Metathesis in Room Temperature Ionic Liquids: A Transformation of Seed Oil-Derived Olefins

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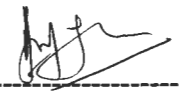
DECLARATION

"I hereby declare that the thesis for the degree of Doctor of Philosophy, at the North-West University hereby submitted, has not previously been submitted by me for the degree at this university, that it is my own work in design and execution and that all material contained herein has been duly acknowledged".



Priya Ann Thomas

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ABSTRACT

One of the most important areas of green chemistry is the application of environmentally friendly solvents in catalysis and synthesis. Conventional organic solvents are a threat to the environment due to their volatile, highly flammable, toxic or carcinogenic nature. The recently emerged room temperature ionic liquids are promising candidates to replace volatile organic solvents due to their interesting properties such as ease of reuse, non volatility and ability to dissolve many kinds of organic and organometallic compounds.

The purpose of the study was to investigate the role of ionic liquids (ILs) for the self-metathesis of seed oil derived olefins. The seed oil derived olefins selected for the studies were methyl oleate and methyl ricinoleate. Self-metathesis of these seed oil-derived olefins was carried out in the presence of ruthenium catalysts (Grubbs first generation catalyst, Grubbs second generation catalyst, Hoveyda Grubbs first generation catalyst and Hoveyda Grubbs second generation catalyst) in room temperature ionic liquids and conventional organic solvents. The ionic liquids used for the study were 1,1-dialkyl and 1,2,3-trialkyl imidazolium type ionic liquids [bmim][X] where X = BF_4^-, PF_6^- and NTf_2^-; [bdmim][X] where X = BF_4^- and PF_6^-. The organic solvents selected for the study were dichloromethane (DCM), 1,2-dichloroethane (DCE), chlorobenzene (PhCl) and toluene (PhMe).

For Grubbs first generation catalyst, the highest activity was observed in [bdmim][BF_4] and the activity of the catalyst increased in the following order: [bdmim][BF_4] > [bdmim][PF_6] > [bmim][BF_4] > [bmim][NTf_2] > [bmim][PF_6]. Studies on the influence of temperature on the activity and selectivity of catalyst proved that the catalytic activity increased with increasing temperature from 20° to 60 °C and thereafter the activity decreased, showing the deactivation of the catalyst at higher temperature. The selectivity was found to decrease with increasing temperature showing the presence of secondary metathesis products at higher temperature. Also, the best catalytic performance was achieved in nitrogen compared to air. The metathesis reaction when performed in conventional organic solvents yielded the highest conversion in DCM and the lowest in PhMe.

Grubbs second generation catalyst exhibited improved conversions and high thermal activity. However, the selectivity towards primary metathesis products was found to be low. For both methyl oleate and methyl ricinoleate metathesis, the highest activity was obtained in [bdmim][BF_4] at all selected temperatures. The higher activity of Grubbs second generation catalyst had been attributed to the stabilization of the metallacycle intermediate by the more bulky and basic N-heterocyclic carbene ligand. For the metathesis in the presence of organic solvents, the highest conversion was observed in DCM and the lowest in PhMe.

For Hoveyda Grubbs first generation catalyst, only a little difference in activity was observed in all the selected [bmim][X] type ILs. When the reaction was carried out in [bdmim][X] type ILs, a slight increase in activity was observed. A similar activity was observed in air and nitrogen atmospheres, showing the stability of the catalyst in the presence of oxygen. Good selectivity (~96%) was obtained up to 40 °C. At 60 °C, selectivity towards primary metathesis products (PMPs) decreased to 82% and at 100 °C, it further decreased to 69%. For the reaction in organic solvents, the catalytic activity was found to increase in the order PhMe < PhCl < DCE < DCM. At 20 °C and 40 °C, the selectivity towards PMPs was 100% in all the selected organic solvents. At higher temperatures, selectivity decreased.

Both substrates methyl oleate and methyl ricinoleate exhibited excellent conversions when the metathesis reaction was carried out using Hoveyda Grubbs second generation catalyst. The highest conversion was obtained in [bdmim][BF_4] at all the selected temperatures. At 20 °C, a conversion of 77% was obtained in [bdmim][BF_4] and it increased to 98% at 100 °C. Under the same reaction conditions, [bmim][BF_4] yielded a conversion of 71% and 97% at 20 and 100 °C, respectively. Good selectivity was achieved at low temperatures of 20 and 40 °C. At 60 °C, a selectivity of 82% was observed which then decreased to 69% at 100 °C.

All the catalysts used in the experiments were soluble in the ILs and the products could be removed from the less dense organic layer by simple decantation, allowing the reuse of catalysts up to three cycles. Grubbs first generation catalyst proved to be stable in three consecutive runs, with the third run showing decreased conversion. Grubbs second generation catalyst exhibited poor recyclability, due to the leaching of the catalyst into the organic layer as was evident from the leaching studies. Hoveyda Grubbs first generation catalyst proved to be the best recyclable catalyst, and could be reused, without loss in activity for the first three cycles. However, Hoveyda Grubbs second generation catalyst exhibited poor recyclability due to the leaching of the catalyst in to the organic layer.

The effects of conventional solvents and ionic liquids on the metathesis of olefins were investigated by means of quantum chemical calculations to establish the factors favouring the metathesis of olefin in ionic liquids. From the results it is evident that the ionic liquids stabilised olefin and the catalyst behave better than the conventional solvents. Ionic liquids also lower the activation energy more than the conventional solvents, leading to faster formation of the alkyledene intermediate.

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LIST OF ABBREVIATIONS

[bdmim] = 1-butyl-2,3-dimethylimidazolium

[bmim] = 1-butyl-3-methylimidazolium

[emim] = 1-ethyl-3-methylimidazolium

ADMP = acyclic diene metathesis polymerization

AR-XPS = angle resolved X-ray photoelectron spectroscopy

Bu = butyl

CM = cross metathesis

Cy = cyclohexyl

DCE = 1,2-dichloroethane

DCM = dichloromethane

ESI-MS = electrospray ionization mass spectrometry

Et = ethyl

EXAFS = extended X-ray absorption fine structure

FAME = fatty acid methyl ester

FCC = fluid catalytic cracking

GC = gas chromatography

ICP-OES = inductively coupled plasma optical emission spectrometry

IL = ionic liquid

IS = internal standard

Mes = 2,4,6-methyl phenyl or mesityl

MO = methyl oleate

MR = methyl ricinoleate

NHC = N-heterocyclic carbene

NMR = nuclear magnetic resonance

OCT = olefin conversion technology

Ph = phenyl

PhCl = chlorobenzene

PhMe = toluene

PMP = primary metathesis product

PVC = poly vinyl chloride

Py = pyridinium

RCM = ring closing metathesis

ROM = ring opening metathesis

ROMP	= ring opening metathesis polymerization
RTIL	= room temperature ionic liquid
S	= solvent
SHOP	= shell higher olefins process
SM	= self metathesis
SMP	= secondary metathesis product
TON	= turn over number
TSIL	= task-specific ionic liquid
VOC	= volatile organic compound

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CHAPTER 1

INTRODUCTION AND AIMS OF THE STUDY

1.1 Background

Over the past decade, olefin metathesis has attracted wide spread attention for the formation of carbon-carbon double bonds. Metathesis is a kind of organic synthesis where carbon compounds from very simple and small molecular weight to very large, complex polymers, macromolecules and even natural products are synthesized. Several metathesis reactions like cross-metathesis (CM), ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMP) have opened path to unsaturated molecules that are impossible to prepare by other means. Homogeneous metathesis is an emerging technology due to its highly selective and active catalyst systems and mild operating conditions required. Olefin metathesis emerged as a powerful tool for organic synthesis due to the discovery of well-defined ruthenium catalysts by Grubbs and co-workers.

Recent developments in olefin metathesis offer new opportunities for converting renewable resources such as vegetable oils and animal fats into a wide range of high-value products. Plant oils and their derivatives have been used by polymer chemists due to their renewable nature, world wide availability, relatively low price, and their rich and growing application possibilities. Fatty acids and esters obtained by the hydrolysis or alcoholysis of triglycerides are valuable renewable building blocks for the synthesis of designed monomers and polymers. Research developed by different groups reveals an increasing interest in the reactivity of their double bonds towards olefin metathesis, which enables the synthesis of a wide variety of monomers.

Room temperature ionic liquids are a new class of compounds that have received wide attention due to their green chemistry. They are considered as potential alternatives to conventional organic solvents. This is due to their high polarity, non-volatility, immiscibility with water and/or organic solvents and many other interesting physicochemical properties. By a judicious combination of cations and anions, it is possible to adjust the solvent properties to the requirement of the reactions. The use of ruthenium-alkylidene catalysts in the chemical industry is restricted by the fact that they are non-recyclable and can be separated from the product only by repeated chromatography. Ionic liquids are known for their ability to recycle homogeneous

catalyst systems. They provide a unique solvent environment to the catalyst system and form biphasic systems with most olefins.

The escalating fuel price and the less availability of fossil organic feedstock, both as energy sources and for the production of chemical raw materials, is a topic of current interest. The increase in world population also demands a high average standard of living, hence it is important to look for alternative feedstocks. Fatty acids or fatty acid esters derived from seed oils are alternative sources of chemicals, since their chemical structures are closely related to those of the hydrocarbons in crude oil [1-3]. Seed oil and their derivatives have recently attracted much attention due to their renewable supply, low cost, versatility and their green chemistry [4].

Natural fats and oils play an important role in the oleochemical industry. About 14% of the world production of fats and oils is used in the oleochemical industry. Long chain vegetable oils, such as soyabean oil, high oleic acid varieties of sunflower seed oil and rapeseed oil (all containing unsaturated C_{18} fatty acids), and palm oil (containing both C_{16} and unsaturated C_{18} chains) are the most important. Short and medium chain vegetable oils, such as coconut and palm kernel oil, are also important sources for the production of cosmetics, soaps, detergents and emulsifiers [4]. Unlike petrochemical products, agricultural products will positively influence the economy and ecology due to their renewable and biodegradable properties [5].

The self and cross metathesis of renewable natural oils with alkenes leads to the production of high value intermediates with applications in the polymer, pharmaceutical and petrochemical industries. The challenge in this field is the length of carbon chain and the lack of functionalities such as hydroxyl and epoxy groups that provide wider industrial applications [6]. However, studies regarding the variation of carbon chain length and the introduction of important functional groups are being reported [7-8]. Olefin metathesis using various kinds of homogeneous and heterogeneous catalysts has become a powerful synthetic tool for the production of value-added products [9-13]. Compared to the other catalytic reactions, metathesis occupies a central role because it shortens many multi-step synthetic schemes and directly leads to polymers.

1.2 Problem statement

Ruthenium-alkylidene complexes are widely used in the metathesis of olefins due to their robustness to air, water and oxygenates as well as their high activity and selectivity. The reactions are performed in a solvent. But a solvent is not always necessary. When a solvent is

advantageous, an environmentally benign solvent such as pentane or heptane is used. The role of a solvent in catalysis is to dissolve and stabilize the substrate, ligand and catalyst without reacting with the catalyst or competing with the substrate for a vacant co-ordination site. However, the ruthenium catalysts are nonrecyclable and can only be removed from the product by repeated chromatography. This poses major problems for their future use in industrial processes. In this context, the role of alternative solvents such as ionic liquids becomes important. Ionic liquids would facilitate the separation of the catalyst from reactants and products, with the catalyst selectively dissolved in the ionic liquid whilst the reactants and products form a separate biphasic layer.

Several studies have aimed at investigating the viability of performing cross metathesis and ring closing metathesis in the most frequently used ionic liquid, [1-butyl-3-methylimidazolium]-type where the anion has been varied. The results proved that the catalysts could be reused without loss of activity. The use of other ionic liquids like [1-butyl-2,3-dimethylimidazolium]-type have also been reported. Grubbs-type catalysts and Hoveyda-type catalysts have been investigated for ring closing metathesis in ionic liquids. Thus ionic liquids have been proven to be suitable solvents for olefin metathesis, especially ring closing metathesis, with similar activities and higher selectivities.

The application of ionic liquids to self and cross metathesis reactions of fatty acid esters remains to be investigated. Very little work has been done on the self and cross metathesis of fatty acid esters with rare yet important functionalities like hydroxyl and epoxy groups. Self and cross metathesis of these compounds would result in monomers, dimers and α-olefins which are of industrial use. The present study therefore aims at investigating self metathesis of vegetable oils in ionic liquids using ruthenium-carbene complexes. The use of ionic liquids as solvents allows for new, innovative and exciting chemistry, with possibly better selectivities and conversions.

1.3 Aims of the study

The study investigated self metathesis of selected vegetable oils (methyl oleate and methyl ricinoleate) in conventional solvents and room temperature ionic liquids using ruthenium carbene complexes (Grubbs-type and Hoveyda-type) as catalysts with a view to achieving the following aims:

- To optimise reaction conditions for self metathesis in ionic liquids.

- To investigate the influence of various solvents on catalyst activity and selectivity.
- To investigate the influence of hydroxyl group on catalyst activity and selectivity.
- To evaluate the recyclability of catalysts in ionic liquids.
- To compare the self metathesis reactions in conventional solvents and room temperature ionic liquids.
- To give further support to the role of ionic liquids and conventional solvents in the metathesis of olefin using Density Functional Theory (DFT) technique (Quantum chemical method).

CHAPTER 2

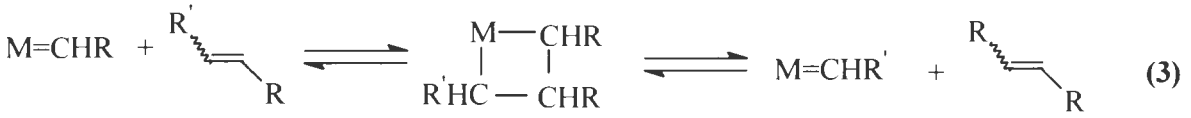
LITERATURE REVIEW

2.1 Olefin metathesis

The word metathesis is derived from the Greek μεταθεσιζ (metathesis) that means transposition. Metathesis involves the exchange of ions to produce the most stable ion pairs (**1**) [14]. It is a catalytic driven reaction in which carbon-carbon double bonds are ruptured and new bonds are formed (**2**) [5]. The process involves the reaction between an olefin and a transition metal alkylidene complex in a [2+2] fashion to generate an unstable metallacyclobutane intermediate. This cyclobutane intermediate then rearranges to form a new metal carbene and an olefin (**3**) [5].

$$A^+B^- + C^+D^- \rightleftharpoons A^+D^- + C^+B^- \qquad \textbf{(1)}$$

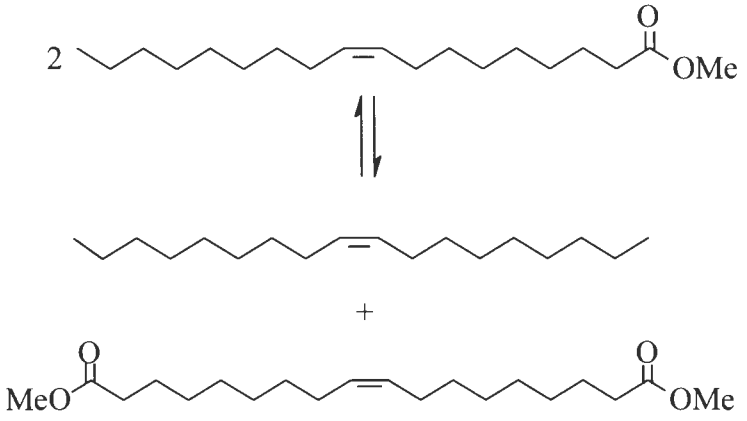
$$2\ RCH{=}CHR' \rightleftharpoons RCH{=}CHR + R'CH{=}CHR' \quad (R \text{ and } R' = \text{alkyl or H}) \qquad \textbf{(2)}$$



(3)

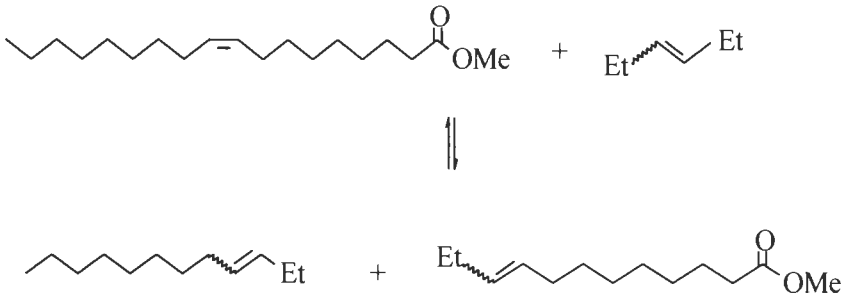
Olefin metathesis was discovered serendipitously by Banks and Bailey (1964), while seeking for an effective heterogeneous catalyst to replace the HF acid catalyst for converting olefins into high-octane gasoline via olefin-isoparaffin alkylation [15]. They reported that propene, when heated with molybdenum in the form of metal, oxide or $[Mo(Co)_6]$, led to the formation of ethylene and 2-butene. This process was commercialized as Philips Triolefin Process. In 1967, Calderon named the reaction as metathesis, while converting 2-pentene into 2-butene and 3-hexene using the catalyst system $WCl_6/EtAlCl_2/EtOH$ [16]. The metathesis reactions are under thermodynamic control, which means they are equilibrated. However, metathesis of a terminal alkene or alkyne displaces the reaction towards the product. The reaction under reduced pressure helps to eliminate volatile olefin and displaces metathesis reaction. Alkene metathesis also leads to the formation of both Z and E isomers. Many metathesis reactions are also under kinetic control. Two main types of metathesis reactions are possible, namely; self metathesis and cross metathesis. Self metathesis takes place between two

identical olefins. For example, the transformation of methyl oleate (methyl 9-octadecenoate), into 9-octadecene and dimethyl 9-octadecenedioate, reaction (**4**) [17,18].



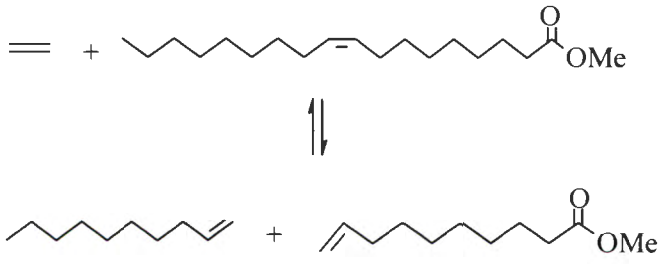
(4)

Cross metathesis takes place between two different acyclic olefins. An example of cross metathesis is the reaction between methyl oleate and 3-hexene leading to 3-dodecene and 9-dodecenoate, reaction (**5**) [4].



(5)

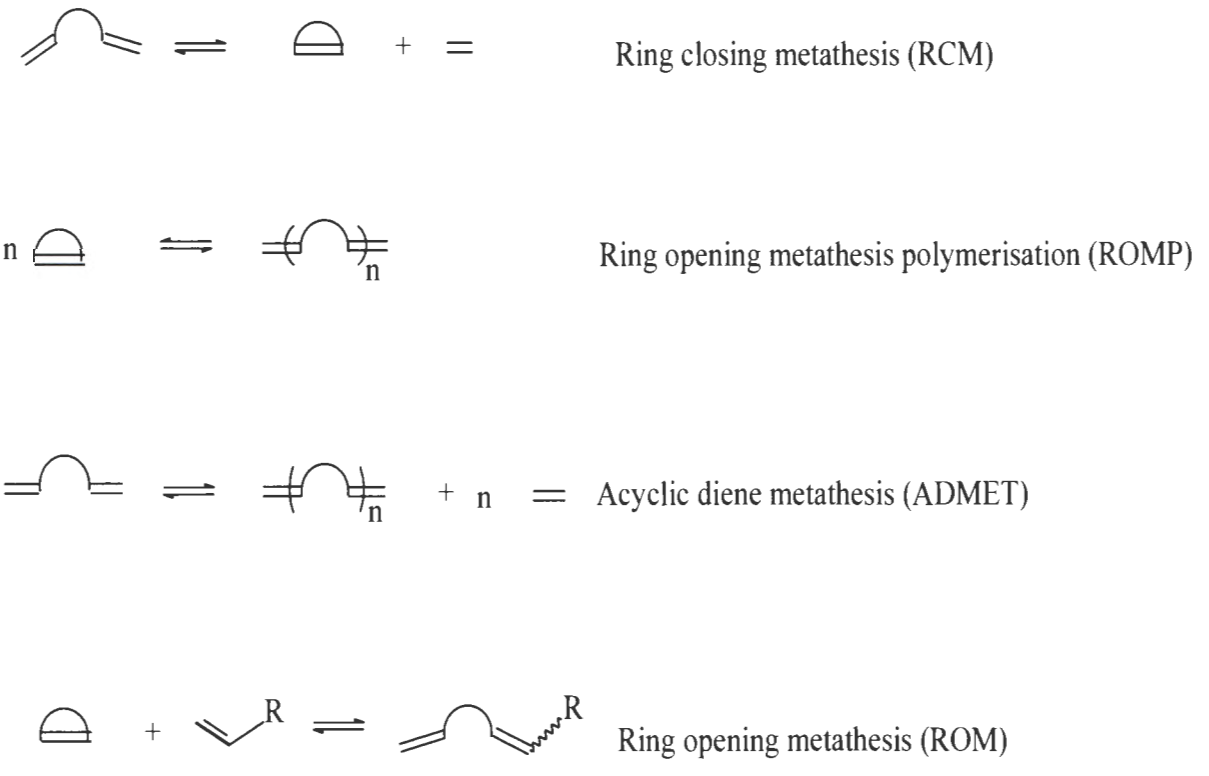
Cross metathesis of unsaturated fatty compounds or other olefins with ethene is known as ethenolysis. Reaction (**6**) shows the ethenolysis of methyl oleate yielding 9-decenoate and 1-decene.



(6)

Ring closing metathesis (RCM) is the most exciting application of olefin metathesis to organic chemistry. In ring closing metathesis, a variety of cyclic olefins and heterocycles are formed from functionalised dienes, diene-ethers, diene-amines, etc. [19]. The ring closing

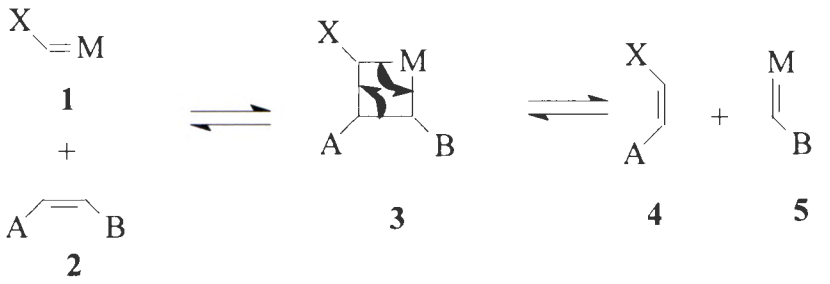
metathesis of a diene could involve two steps. The first step called intermolecular metathesis reaction, results in the formation of a triene. The second step called intramolecular metathesis reaction, yields a cyclic olefin. The triene formed in the first step could react with the starting diene forming a tetraene and so forth. This step growth condensation polymerisation is known as acyclic diene metathesis (ADMET). In ring opening metathesis polymerisation (ROMP), cyclic olefins can be opened and oligomerised and polymerised, especially norbornenes and cyclobutene [20]. The cross metathesis of a cyclic and an acyclic olefin yields polyunsaturated substances. This reaction is called ring opening metathesis (ROM) (**Scheme 1**).



Scheme 1: Various metathesis reactions

2.1.1 Olefin metathesis reaction mechanism

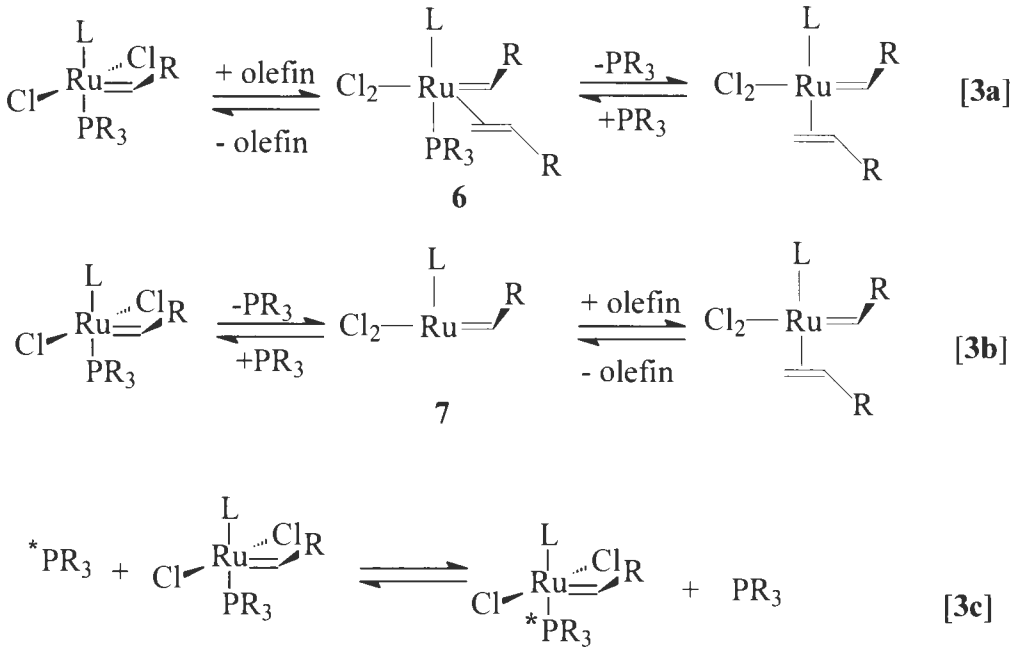
The first catalysed metathesis reactions was reported in 1950s, where propene was transformed into ethylene and 2-butene when it was heated with molybdenum in the form of metal, oxide or $[Mo(CO)_6]$ on alumina. In 1971, Yves Chauvin and Jean-Louis Hérisson proposed a mechanism for the catalysed olefin metathesis involving metal alkylidene and metallacyclobutane intermediates [21]. The mechanism involves the formation of a metal-carbene species, reaction of metal carbene **1** with an olefin **2** resulting in the formation of unstable metallacyclobutane intermediate **3** which then rearranges to form a new olefin **4** and a new metal-carbene species **5** (**Scheme 2**) [22]. Several experiments were done by Chauvin confirming this mechanism [23-25].



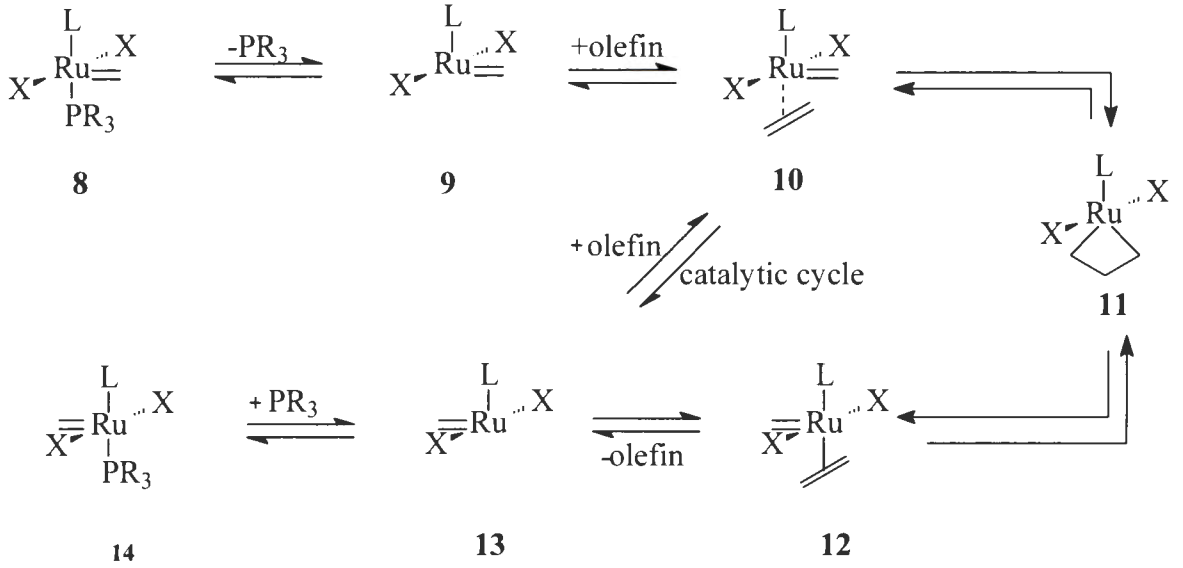
Scheme 2: The metal-carbene mechanism proposed by Chauvin et al.

Experiments done by Katz and co-workers led to the recognition of Chauvin mechanism [26-27]. However, the very first proof for Chauvin mechanism was reported by Schrock and co-workers in 1980 [28]. They reported a tantalum-alkylidene complex, which catalysed the metathesis of *cis*-2-pentene. Grubb's studies on Tebbe's complex [$Cp_2Ti(CH_2)(ClAlMe_2)$] also supported Chauvin mechanism [29]. The titanacyclobutane formed during the reaction was found to be slow metathesis catalysts which helped in understanding all the intermediates in olefin metathesis [30-32].

Sanford *et al.* [33] have reported the mechanism of ruthenium-catalyzed olefin metathesis reactions. They examined the mechanism of the ligand substitution of phosphine with olefinic substrate (**Scheme 3**). The substitution could take place in an associative (Scheme 3a) or a dissociative (**Scheme 3b**) pathway. The associative pathway proceeds by the initial binding of substrate to form the 18-electron transition state intermediate **6** and the dissociative pathway involves the loss of PCy_3 to generate 14-electron intermediate **7**. To distinguish between these possibilities, studies were conducted on the degenerate exchange reaction between free and bound PR_3 (**Scheme 3c**). From early mechanistic studies, an associative exchange was proposed [34]. However, P NMR magnetization transfer (MT) experiments revealed that phosphine substitution proceeds by a dissociatve mechanism [35]. On the basis of above studies, Sanford and group proposed a general mechanism for catalyzed olefin metathesis reactions (**Scheme 4**) [35-36]. In the first step, an intermediate (**9**) is generated from ruthenium alkylidene (**8**) by the loss of one of the ligands. The metal carbene species (**10**) reacts with olefin to form an unstable metallacyclobutane intermediate (**11**). Finally, a new olefin (**14**) is formed by the shift in a direction perpendicular to the initial olefin shift.



Scheme 3: The metal-carbene mechanism proposed by Sanford



Scheme 4: A general mechanism for metal catalysed olefin metathesis

2.1.2 Ligand effects on olefin metathesis reactions

Although olefin metathesis reactions proceed by dissociative pathway, the ligands play an important role in determining the relative rates of the individual steps along the reaction coordinate. It is assumed that formation of 14-electron metallacyclobutane intermediate is the rate determining step [36].

(1) L-Type ligand

It is found that olefin metathesis activity increases by changing the L ligand from a phosphine to N-heterocyclic carbene (NHC) [36]. This is due to the excellent donor activity of NHC ligand. Various studies done by Cavell and co workers [37] proved that NHC's promote and stabilise metal–to-olefin back-bonding to a greater extent than phosphine ligands. This is supported by the observation that the NHC-coordinated complexes show increased affinities for π-acidic olefinic substrates relative to σ-donating phosphine ligands.

(2) Phosphine ligand (PR_3)

The catalyst activity changes by the change in phosphine ligand. It depends on the cone angle and the electron donating ability of phosphine ligand [34]. The rate increases when PCy_3 of the catalyst is replaced by PPh_3, which is expected to be due to the lower basicity of the PPh_3 ligand [35]. But PBn_3 complex initiates at almost the same rate as PCy_3 complex, even though PBn_3 is less basic than PCy_3. The complexities of the steric and electronic changes resulting from phosphine variation are still under investigation.

(3) Halide ligand (X)

When the halide ligands are changed from chloride to iodide, the catalyst initiation increases [36]. This is mainly due to the increase in size of iodide ligand. The larger size of halide increases steric crowding at the ruthenium centre, favouring PR_3 dissociation.

2.2 Homogeneous and heterogeneous catalysts

Various kinds of homogeneous and heterogeneous catalysts have been used for the metathesis of olefins. Transition metal compounds containing ruthenium, molybdenum, tungsten, rhenium, osmium, iridium, tantalum and titanium are found to catalyse olefin metathesis [38-40]. Heterogeneous catalysts consist of a transition metal oxide or chloride supported on a high-surface-area inorganic oxide. They do not contain alkylidine moiety and the initiating metal carbene is formed from the catalyst and olefin. Some examples of heterogeneous catalysts are Re_2O_7/Al_2O_3, MoO_3/SiO_2 and WO_3/SiO_2. These catalysts do not show any activity on the functional groups, but Re_2O_7/Al_2O_3 when promoted with Me_4Sn cocatalyst was found to be active on unsaturated esters.

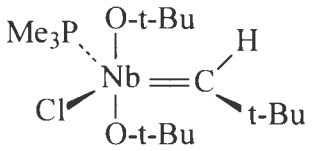
Homogeneous metathesis catalysts consist of a combination of transition metal halide or oxo-halide with alkylating cocatalyst, or a well-defined metal alkylidene complex of a transition metal, such as Ru, Mo, or W. The main problem associated with these classical catalysts is that, functional groups, such as ester can interfere with catalytic activity. They may bind to the active

metal centre or may react directly with the metal centre and destroy the active species. However, these catalysts are sensitive to air and moisture. Their turnover numbers are low and a toxic co-catalyst is required, but they are less expensive and easier to handle than metal-alkylidene catalyst [39,40].

2.2.1 Schrock catalysts

It was believed that metal-alkyl compounds are unstable because of low energy metal-carbon bond. Geoffrey Wilkinson then synthesized stable binary metal-alkyl complexes that did not contain β-hydrogen [10]. Supported by Wilkinson's work, Richard Schrock synthesized the first stable metal-alkylidene complex, $[Ta(CH_2CMe_3)_3(=CHCMe_3)]$, which has the high oxidation state of V. Schrock also synthesized high oxidation state niobium and tantalum-alkylidene complexes, but none of them catalyzed the metathesis of olefins [10].

In 1980, Schrock *et al.* [10] synthesized a tantalum alkylidene complex, $[Ta(=CH–t\text{-}Bu)Cl(PMe_3)(O–t\text{-}Bu)_2]$ **15** which catalysed the metathesis of *cis*-2-pentene. The other members of the family of niobium and tantalum-alkylidene catalysts failed to catalyze the metathesis reaction because of the presence of alkoxide ligands. Later discoveries led to the formation of the most active alkene metathesis catalysts with the general formula $[M(=CHCMe_2Ph)(=N–Ar)(OR_2]$ **16** [10].



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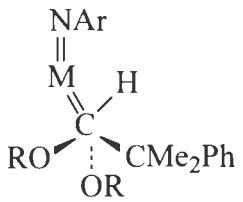


16

Scheme 5: Schrock's catalysts

Schrock's molybdenum catalysts are reactive towards water and air and are intolerant of protons on heteroatoms (carboxylic acids, alcohols, thiols) and some functionalities (aldehydes). However, they can tolerate some other functionalities like sulphur, phosphorus and nitrile [20]. Molybdenum complexes are preferred over tungsten complexes, due to the following reasons:

i) molybdenum complexes are synthesized more easily;
ii) molybdenum is cheaper than tungsten; and
iii) molybdenum is more tolerant of functionalities.

2.2.2 Grubbs catalysts

The first ruthenium carbene complex, $[RuCp\{=C(Me)OMe\}(CO)(PCy_3)][PF_6]$, was synthesized in 1971 by Malcolm Green's group. In 1992, Grubbs reported a well-defined ruthenium-carbene complex, $[RuCl_2(PR_3)(=CH–CH=CPh_2)]$, (R = Ph or Cy) **17** that promoted the ring opening metathesis polymerization of low-strain olefins as well as the catalytic ring closing mechanism of functionalized dienes. In 1995, the new molecularly well-defined catalysts, $[Ru(=CHPh)Cl_2(PR_3)_2]$, R = Ph or Cy, were synthesized and were commercialized with R = Cy, **18**. Ruthenium complex **18** is known as Grubbs first generation catalyst and is found to be stable in air and react with a large variety of functional groups, except for amines, nitriles and basic media.

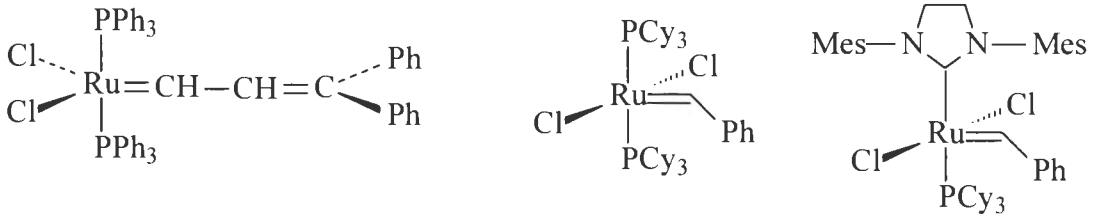
Highly selective CM of vinylsilanes ($H_2C=CHSiR_3$,) with olefins catalysed by **18** was reported by Pietraszuk and coworkers. They studied the CM of vinylsilanes with styrene using catalyst **18** under mild conditions and it was proved to be very effective and selective [41]. It was shown that **18** can effectively catalyse the CM of vinyltrialkoxy- and trisiloxysilanes with substituted styrenes, alkenes, and allyl derivatives [42].

Buchowicz and Mol [18] reported the metathesis of internal linear alkenes, including fatty acid esters using the ruthenium precatalyst **18** in selected organic solvents. The substrates used for the study include trans/cis-4-nonene, trans-4-decene, trans-5-decene, trans/cis-3-heptene, methyl oleate, methyl elaidate and methyl erucate. The reactions were carried out in dichloromethane (DCM), 1,2-dichloroethane (DCE) and 1,2-dichlorobenzene at various temperatures. The best catalytic performance was obtained in DCM and DCE. The reactions proved that catalyst **18** can be used up to a temperature of 70 °C, without any loss in selectivity.

Kawai *et al.* [43] investigated the effect of Grubbs catalyst **18** on the self metathesis of 2-vinylfuran, 2-vinylthiophene and styrene, and cross metathesis between these aromatics and 1-octene. The reaction was carried out at an atmospheric pressure of nitrogen gas or air, at 40°C. The solvent used was toluene and the reactant/catalyst molar ratio was 50/1. Gas chromatography was used to analyse the metathesis product. The results showed that the Grubbs catalyst was inactive for the self metathesis of vinylfuran and vinylthiophene and the activity was lowered in oxygen atmosphere. Cross metathesis result indicated higher catalytic activity for styrene. Under N_2 atmosphere the reaction proceeded at a moderate rate and reached equilibrium at 15 h. But under air, catalytic activity was decreased and equilibrium was reached at 3h, showing that deactivation occurred in presence of oxygen.

Even though Grubbs first generation catalyst is used in organic and polymer chemistry, it is found to be moderately stable in oxygen and high temperature and has low activity towards substituted double bonds. This led to the discovery of second generation Grubbs catalyst. They were prepared by the substitution of a phosphine ligand with an N-heterocyclic ligand, with the general formula $(NHC)(PCy_3)(Cl)_2Ru{=}CHPh$ **19** [10]. This was based on the studies that larger and more basic groups in the catalyst show high activity.

Grubbs second generation catalyst is found to be active in ROMP, RCM and CM reactions. They catalyse the formation of tri- and tetra substituted olefins and functionalised alkenes [36]. When used for the metathesis of methyl oleate at a temperature of 55°C in the absence of a solvent, this catalyst gave a high TON of 440 000 and high selectivity [4]. It was also used for the metathesis of methyl 10-undecenoate and a TON of 11 200 was obtained. Catalyst **19** was also found to effectively catalyse the CM of chloro- and acetoxy- substituted vinylsilanes with various olefins including allyl-, arryl- and silyl-substituted olefins, leading to the formation of unsaturated organosilicon compounds [44].



17 **18** **19**

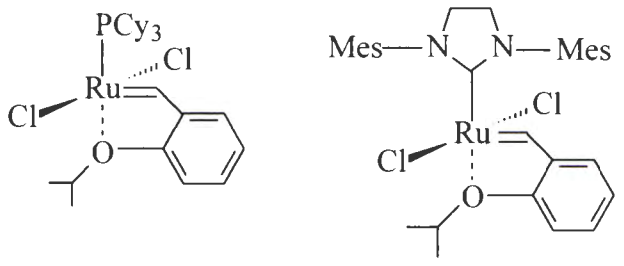
Scheme 6: Grubbs catalysts

2.2.3 Hoveyda-Grubbs catalysts

Following the works of Grubbs, Hoveyda and co-workers reported the synthesis of a new Ru carbene catalyst, derived from Grubbs first generation catalyst [45]. The new Ru carbene complex, now known as Hoveyda-Grubbs first generation catalyst **20**, contains an internal metal oxygen chelate and was obtained by the treatment of $Cl_2Ru(PPh_3)_3$ with (2-isopropoxyphenyl)-diazomethane and PCy_3. Catalyst **20** is found to be an active metathesis catalyst with excellent stability to air and moisture. Another important feature of the catalyst is that it can be recycled in high yield using silica gel column chromatography.

Hoveyda *et al.* [45] reported the effective RCM of five-, six-, seven-, and eight membered carbo- and heterocycles using catalyst **20**. In each case, the catalyst was recovered

chromatographically in high yield and it maintained its catalytic activity in subsequent reactions. Recycling experiments proved that the catalyst can be reused for at least three cycles.



20 **21**

Mes = 2,4,6-methyl phenyl or mesityl
Cy = cyclohexyl

Scheme 7: Hoveyda-Grubbs catalysts

Despite the attractive attributes of catalyst **20**, it was proved to be efficient only with substrates containing terminal alkenes. A new improved version of **20** synthesised is known as Hoveyda-Grubbs second generation catalyst **21** [46]. The new catalyst bearing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and styrenyl ether ligand, was synthesized based on the accelerating effect of a variety of saturated and unsaturated imidazolin-2-ylidene carbine ligands on the activity of Ru based metathesis catalysts [47].

Ru complex **21** was found to effectively catalyse the RCM of several acyclic dienes [46]. 5 mol% of catalyst **21** was used in the synthesis of trisubstituted cyclic alkenes from 1,1-disubstituted and trisubstituted olefins. Catalyst **21** proved to be superior by promoting the RCM reactions that was impossible by catalyst **20**. Like complex **20**, catalyst **21** was recovered with high efficiency after silica gel chromatography and was used in subsequent reactions with equal efficiency.

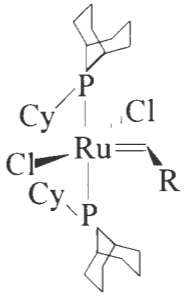
Several reactions have been reported, proving the use of Hoveyda catalyst **21**, in expanding the scope of metal-catalysed olefin metathesis. Cossy *et al.* have reported the CM between á,â-unsaturated aldehydes, esters, allylsilane and functionalized unsaturated alcohols in the presence of catalyst **21** [48]. CM reactions between fluorinated olefins with various functionalised alkenes catalysed by **21** gave higher yields of CM products, predominantly as their *Z* isomer, under mild conditions (45 °C, 3 h) [49]. Attempted tandem enyne RCM-CM between enynes and electron-deficient alkenes has been reported by Grimaud et al [50]. The reaction was carried out in DCM at 40 °C for 12 h using 10 mol% of catalyst **21**, and resulted in a good yield of products.

2.2.4 Phoban catalyst

For industrial applications, catalysts require high turnover numbers (TON) and high selectivities. Grubbs first generation catalyst exhibit poor thermal stability and short lifetimes at low catalyst loadings. Grubbs second generation catalysts show increased activity, but isomerization of olefins results in poor selectivity. Although PCy_3 was determined to be an optimal ligand by Grubbs and coworkers, very little effort has been done on developing ruthenium based catalysts containing two phosphine donor ligands [51].

Forman *et al.* [52] investigated the effectiveness of inexpensive phosphabicyclononane (Phoban) ligands for catalytic metathesis reactions. The ruthenium-carbene complexes **22** and **23** developed by Sasol group are stable in air and moisture and can be stored in an ordinary vial for a long period of time. Complex **23** is stable to column chromatography and maintains its catalytic activity in subsequent metathesis reactions. Both complexes also exhibit improved thermal stability.

Phoban catalysts are found to be efficient in self-metathesis, cross metathesis, ethenolysis, ring closing metathesis, and ring opening metathesis polymerization reactions. A conversion of 98% was obtained by the ring opening metathesis polymerization of cyclooctadiene at 50°C with 0.008 mol% of **23**. The cross metathesis of styrene with 1-dodecene using **23** as the catalyst yielded 87% conversion and the recovered catalyst was used for the self metathesis of methyl oleate yielding 46% conversion [52].



22 (R= C=C(Me)$_2$

23 (R= Ph)

Scheme 8: Phoban derived catalysts developed by Sasol

2.3 Metathesis of vegetable oils

The first self metathesis of unsaturated fatty acids was done by Boelhouwer and co-workers [53]. They transformed methyl oleate (methyl cis-9-octadecenoate) into equimolar amounts of 9-octadecene and dimethyl 9-octadecene-1,18-dioate, in the presence of WCl_6/Me_4Sn catalyst. The equilibrium was reached within 4h at 70°C. These products are useful intermediates in the chemical industry.

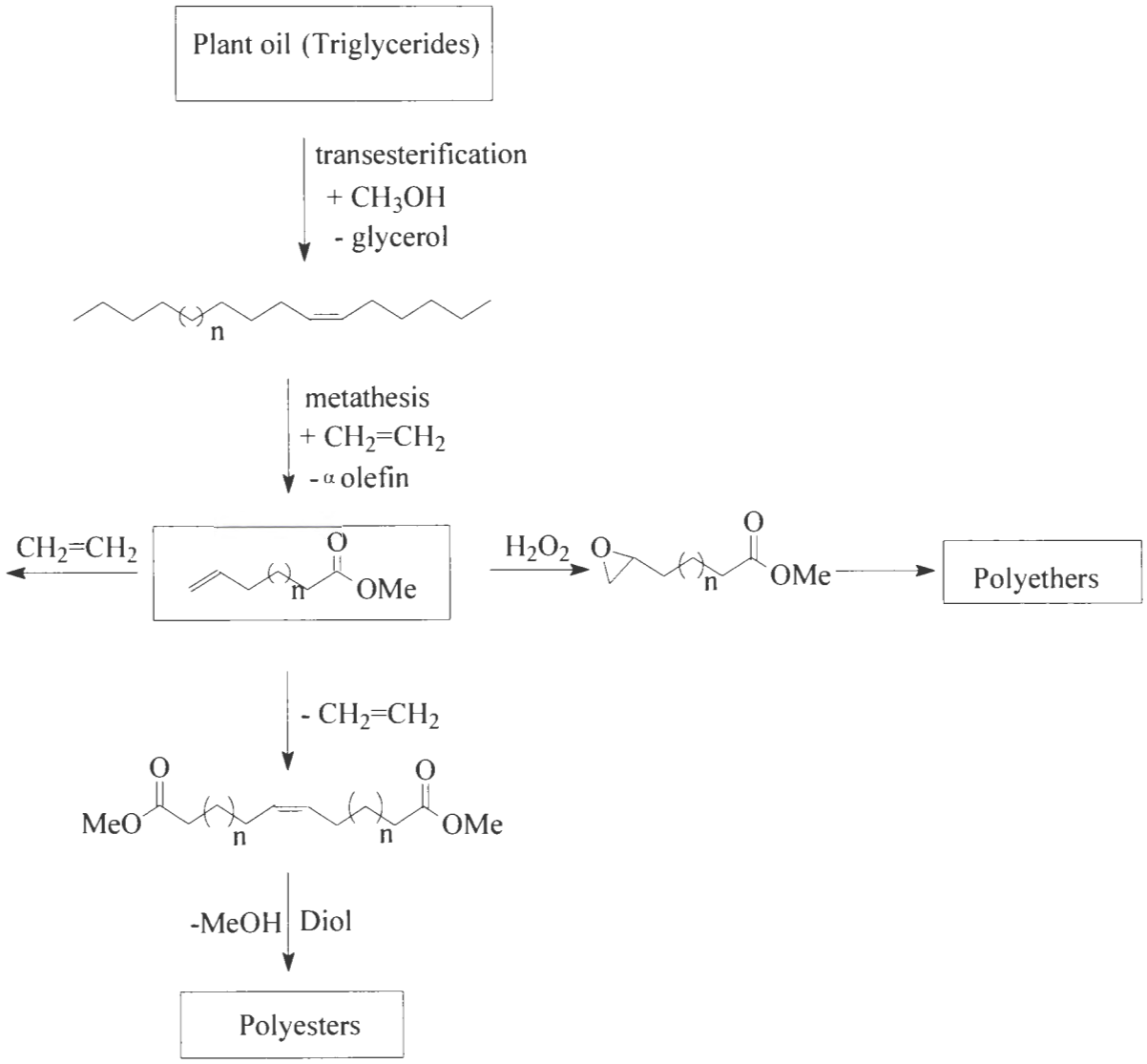
Patel *et al.* [54] obtained methyl 9-undecenoate and 2-undecene, by the cross metathesis of 2-butene with methyl oleate using a series of ruthenium benzylidene catalysts. The experiment was done under an argon atmosphere at a temperature of -5 °C for 2h. The best result was shown by Hoveyda second generation catalyst. Cross metathesis of 2-butene with triolein was carried out under the same reaction conditions. A conversion of 92% and a TON of 92 000 were obtained in 4h reaction time [55]. Patel et al. also investigated the cross metathesis of 2-butene with four vegetable oils (sunflower, canola, linseed and soyabean oil) in the presence of Hoveyda second generation catalyst. TONs of 37 000, 38 000, 23 000 and 24 000 were obtained for canola, sunflower, linseed and soyabean oils, respectively [54].

Marvey *et al.* [56] investigated the metathesis of methyl linoleate, methyl oleate with methyl linoleate and a mixture of fatty esters derived from South African sunflower oil in the presence of a 3 wt.% $Re_2O_7/SiO_2–Al_2O_3/SnBu_4$ catalyst. In the case of methyl linoleate, the substrate conversion of 86.1% was obtained in 2 h reaction time with a selectivity of >95% towards primary metathesis products. The investigation was carried out at different temperatures and the maximum catalyst activity was achieved at a temperature of 20-60°C with the substrate conversion increasing from 86.1 to 86.9%. Lower substrate conversions were obtained at a higher temperatures of 80-100°C. Cross metathesis of methyl oleate and methyl linoleate at 20°C yielded alkenes, monoesters and diesters with a selectivity of >95% towards primary metathesis products. The substrate conversions of 85.6 and 47.6% for methyl linoleate and methyl oleate were obtained in 3h. Metathesis of a mixture of fatty esters also yielded alkenes, monoesters and diesters with the substrate conversions of 81.0 and 45.0% for linoleate and oleate esters, respectively after 3h reaction time. The selectivity towards primary metathesis products was >95%.

Buchowicz *et al.* [18] investigated the metathesis of methyl oleate in the presence of $Ru(=CHPh)Cl_2(PCy_3)_2$ catalyst using dichloromethane and dichloroethane as solvents at 20°C. The selectivity of 96% was obtained towards primary metathesis product, with a conversion of 40% after 4h reaction time. Buchowicz et al. [51] also investigated the metathesis of methyl oleate in the presence of a novel carbene complex $Ru_2(=CHPh)_2$-$(CF_3CO_2)_2(\mu$-$CF_3CO_2)_2(PCy_3)_2(\mu$-$H_2O)$ obtained from $Ru(=CHPh)Cl_2(PCy_3)_2$, in various solvents. The best result was obtained in dichloromethane with 36% conversion at 20°C after 4h reaction time.

Warwel *et al.* [5] synthesised polymers from unsaturated fatty acid methyl esters derived by the transesterification of fats and oils as shown in Scheme 9. Fatty acid esters from high oleic

sunflower oil (oleic acid, 86%), rapeseed oil (oleic acid, 63%), coriander oil (petroselinic acid, 75%), meadowform oil (5-eicosenoic acid, 63%), high euric rapeseed oil (euric acid, 48%) and crambe oil (euric acid, 59%) were ethenolysed using **1** as catalyst.



Scheme 9: Polymers from plant oils

One of the major drawbacks in using ruthenium based catalysts is the high cost of catalyst separation and recovery. During the product purification, isomerization could take place.

2.4 Ionic liquids

The demand for environmentally friendly solvents has led to the development of alternative solvents and technologies. In the previous years, water emerged as a useful reaction medium and has been successfully used in metal catalyzed reactions [57-59]. However, the low miscibility of organic substrates in water has limited its usage in organic reactions. The usage of perfluorinated solvents has been reported for many organic and catalytic reactions [60,61]. The

need for specific ligands to solubilise catalyst in the perfluorinated phase and the decomposition of these solvents at high temperature to toxic compounds has limited its utility. Another type of solvents used in organic and catalytic reactions is supercritical fluids (eg. $ScCO_2$) [62]. Although they are described as green solvents, the critical conditions needed for their use are still limitations.

Ionic liquids (ILs) are a new class of compounds that have received wide attention due to their green chemistry. The terms room temperature ionic liquids (RTIL), molten salt, nonaqueous ionic liquid, liquid organic salt and fused salt have all been used to describe these salts [63]. ILs have been known for a long time, but their use as solvents has recently become significant. ILs such as $[EtNH_3][NO_3]$ was first described in 1914 [64]. In the early 1970s, ILs were initially developed by electrochemists, for use as battery electrolytes [65]. Recently, ILs have found applications such as electrolytes for electrochemical devices and processes, and in homogeneous and heterogeneous catalysis, purification of gases, enzyme catalysis, biological reaction media and removal of metal ions [65].

2.4.1 Properties of ILs

ILs are known as salts that are liquid at room temperature. They are also known as 'designer solvents' as their solvent properties can be tuned for a specific application by varying the anion cation combinations. They have a unique array of physico-chemical properties, which make them superior, compared to the conventional organic solvents [66-72]. The main factors that influence the physical properties of ILs are hydrogen bonding, charge distribution on the anions, polarity and dispersive interactions [73]. Some of their basic properties are listed below.

- ILs have the ability to dissolve many organic, inorganic and organometallic compounds.
- ILs are immiscible with many organic solvents.
- ILs are highly polar.
- ILs consists of loosely coordinating bulky ions.
- ILs do not evaporate since they have very low vapor pressures.
- ILs are thermally stable, approximately up to 300 °C.
- ILs have high thermal conductivity and a large electrochemical window.
- Most ILs have a liquid window of up to 200 °C which enables wide kinetic control.
- ILs are nonaqueous polar alternatives for phase transfer processes.

2.4.1.1 Melting points

ILs are made of positively and negatively charged ions, whereas water and organic solvents are made up of molecules. RTILs are liquid generally up to 200°C. They remain liquid at room temperature because of loosely held ions [74]. ILs consists of bulky and asymmetrical organic cation and evenly shaped smaller anions and their combination lowers the lattice energy and hence the melting point. The melting point of ILs increases with a substitution at C2 position of the imidazolium ring due to aromatic stacking. Addition of other functionalities also increases the melting point due to an increase in the number of interactions between the ions.

2.4.1.2 Vapor pressure

The vapor pressure of the ILs are extremely low and are considered as negligible. Due to their negligible vapor pressure, ILs are introduced as green solvents and they replace the volatile organic compounds (VOC). ILs are therefore not explosive and can be recycled. The non-volatile nature of ILs also help in the easy separation of products by distillation or sublimation [75].

2.4.1.3 Viscosity

ILs are highly viscous at room temperature, and the viscosity decreases with increase in temperature [75]. The viscosity of ILs depends upon the temperature, the tendency to form hydrogen bonds and the strength of van der Waals interactions. An increase in the formation of hydrogen bonds and strong van der Waals force result in an increase in viscosity. It has been shown that the addition of co solvents can decrease the viscosity of ILs [76]. Recent studies have shown that high viscosity of ionic liquids can be reduced by using new bulky counter anions and/or by modifying the cation backbone [77]. For the same cation, viscosity decreases in the order $Cl^- > PF_6^- > BF_4^- \approx NO_3^- > NTf_2^-$.

2.4.1.4 Density

ILs are generally denser than either organic solvents or water, with typical density values ranging from 1 to 1.6 g cm^{-3}. The density of ILs is affected by the anion and cation present. For the same cation, density increases with an increase in the mass of the anion, while for the same anion, density decreases with an increase in the mass of the cation [78]. For the same cation, density increases in the order $[CH_3SO_3]^- \sim [BF_4]^- < [CF_3CO_2]^- < [CF_3SO_3]^- < [C_3F_7CO_2]^- < [N(SO_2CF_3)_2]^-$. For the same anion, density decreases in the order $[beim]^+ > [bmim]^+ > [eeim]^+ > [emim]^+$. It has been reported that an increase in the alkyl chain length on the cation decreases the density preventing close packing of ions [79].

2.4.1.5 Polarity

Solvents are commonly classified based on their polarity. ILs are defined as highly polar solvents since they have the ability to dissolve and stabilize dipolar or charged solutes. Chromatographic and spectroscopic methods have been used to determine the solvent properties of ILs [80]. Efforts have been made to compare the polarities of ILs and conventional solvents. It has been reported by Carmichael and Seddon [81] that 1-alkyl-3-methylimidazolium ILs with anions PF6, BF4, NTf2 and NO3 are in the same polarity region as 2-aminoethanol and lower than alcohols such as methanol, ethanol and butanol. Aki et al. [82] pointed out that [bmim][PF6], [C8mim][PF6], [bmim][NO_3] and [N-bupy][BF_4] are more polar than acetonitrile and less polar than methanol.

2.4.1.6 Toxicity

The early claims that ILs are less toxic and biodegradable, due to their negligible vapor pressure is of less interest. Most of the ILs are water soluble and can affect aquatic environment. The commonly used ILs [bmim][PF_6] and [bmim][BF_4] are known to decompose in the presence of water resulting in the formation of hydrofluoric or phosphoric acids. The studies done by Maginn [83] indicate that [bmim][PF_6] and [bmim][BF_4] are as toxic to *Daphnia magna* (filter feeders at the base of the aquatic food chain) as benzene. Wells and Coombe [84] investigated the level of toxicity of ILs on *Daphnia magna* and the green alga *Pseudokirchneriellasubcapitata.* The results show that alkyl methylimidazolium ILs with C4 side chain constituents exhibit moderate toxicity, whereas C12, C16 and C18 species exhibit high toxicity. Pyridinium, ammonium and phosphonium species with C4 side chain constituents also showed moderate toxicity, whereas C6 and longer side chains showed increasing level of toxicity.

2.4.1.7 Air and moisture stability

Many of ILs are both air and moisture stable and some are hydrophobic, whereas most imidazolium and ammonium salts are hydrophilic. The hydrophobicity of an IL increases with an increase in alkyl chain length [82]. The anions play an important role in determining the water stability of ILs. ILs containing halogen anions exhibit poor stability in water, and release toxic and corrosive species such as HF or HCl [85]. The amount of water absorbed is lowest in PF_6^- and highest in BF_4^- [86]. ILs that are immiscible with water absorb water from the atmosphere. Cammarata et al. pointed that the water molecules absorbed from the air are bonded through hydrogen bonding with $PF6^-$ and $BF4^-$ anions [87].

2.4.1.8 Solvent properties

The main factors affecting the solvent properties of ILs are the ability to act as hydrogen bond donor and/or acceptor and the degree of localization of the charges on the anions [88]. ILs have the ability to solvate both polar and non-polar compounds, allowing the dissolution of organic, inorganic, organometallic compounds, bio-molecules and metal ions. They are immiscible with most of the organic solvents and provide a nonaqueous, polar alternative for two-phase systems [89]. Furthermore, hydrophobic ionic liquids can be used as immiscible polar phases with water. The non-volatile nature of ILs help them to be used in high-vacuum systems. ILs serve as alternative solvents for the chemical reactions where distillation is difficult or practically impossible. Earle et al. [90] pointed out that many ILs especially ILs with NTf_2 anion can be distilled at 200-300 °C and low pressure without decomposition.

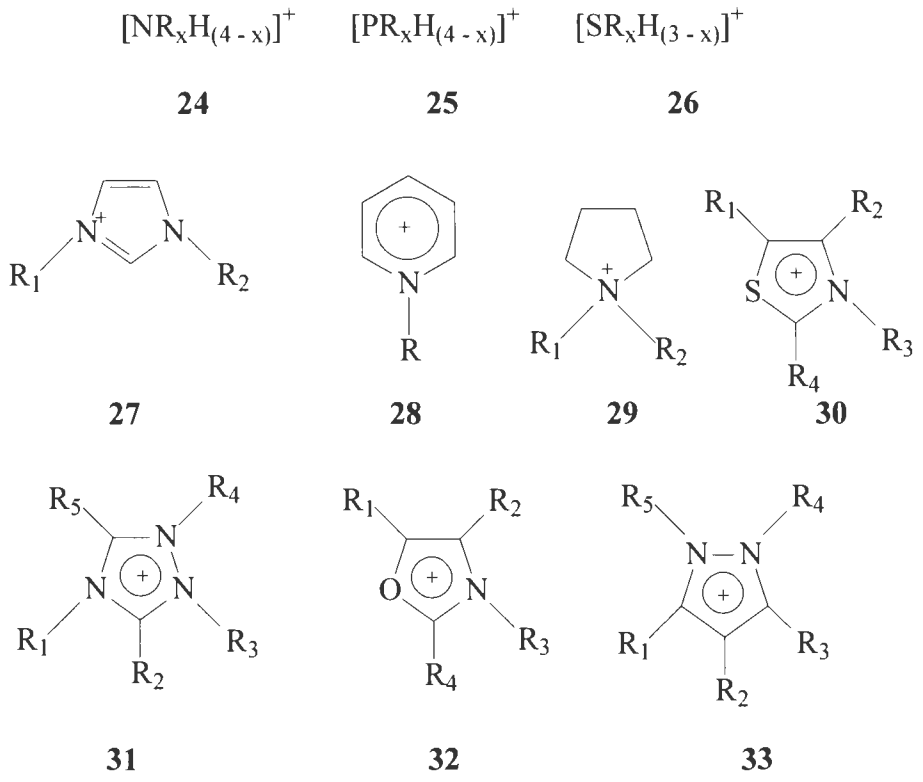
2.5 Structure and synthesis of ILs

2.5.1 Synthesis of ILs

ILs can be prepared with different cation and anion combinations. The physical and chemical properties of ILs can be tuned according to the cation and anion used in the preparation. The properties of ILs are determined by mutual fit of cation and anion, size, geometry and charge distribution. The properties of ILs like acidicity, basicity, water miscibility and immiscibilty, hydrophilic and hydrophobic properties, all result from the composite properties of cations and anions.

2.5.1.1 Cations

The cation of the IL is generally a bulk organic structure with low symmetry. The most popularly used cations are ammonium **24** [91-93], phosphonium **25** [94], sulphonium **26** [95], imidazolium **27** [96-99], pyridinium **28** [100-102], picolnium, pyrrolidinium **29** [103], thiazolium **30** [104], triazolium **31** [105], oxazolium **32** [106] and pyrazolium **33** [107] cations (**Scheme 10**). The most commonly used ILs are the salts based on the *N, N'*-dialkylimidazolium cation **27**. The melting point of ILs decreases with the increase in size and asymmetry of the cation. Also an increase in the branching on the alkyl chain increases the melting point.



Scheme 10: Examples of cations described in ionic liquids

2.5.1.2 Anions

The anions present in the IL determine the hydrophobicity, viscocity, density and solvation of the IL system [108]. There are two different types of IL anions. ILs containing fluorous anions. eg. PF_6^-, BF_4^-, $CF_3SO_3^-$, $(CF_3SO_3)_2N^-$ and ILs containing non-fluorous anions such as $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Au_2Cl_7^-$, $Fe_2Cl_7^-$. The most widely used ILs are the ones with PF_6^- and BF_4^- anions. However, these two anions decompose when heated in the presence of the water and produce HF. Anions such as $CF_3SO_3^-$ and $(CF_3SO_3)_2N^-$ give thermally stable salts [109,110]. In these anions, the fluorine of the anion is bonded to carbon and the C-F bond is inert to hydrolysis.

ILs can be prepared using three different routes (**Scheme 11**) which include:

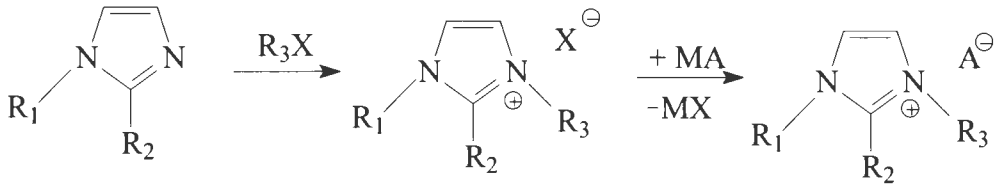
(1) metathetic exchange of anion (Path A). This is the most commonly used method for the synthesis of ILs. The elimination of halide by-product (MX) formed by the metathetic exchange of anions may be difficult by filtration especially for hydrophilic ILs;

(2) acid-base neutralization (Path B) or direct alkylation of alkylimidazole (Path C). In path B, it may be difficult to obtain pure ILs. To obtain a pure IL, the products are dissolved in an organic solvent and treated with activated carbon, and the organic solvent is

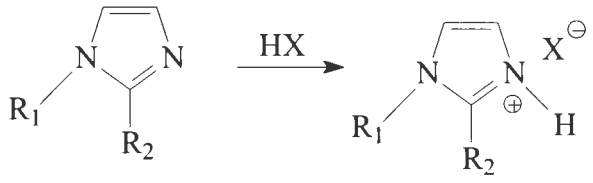
removed under vaccum. Even after the purification method, traces of alkylimidazole or acid may be present in the final ILs. Path C has been described for the preparation of phosphate, sulphate or sulphonate based ILs; and

(3) the carbonate route (Path D). In this method, alkyl halides are replaced by dimethyl carbonate (DMC) and it avoids the presence of halides and other by-products [111]. However this method is limited by the availability of the acid (HX) or ammonium salts.

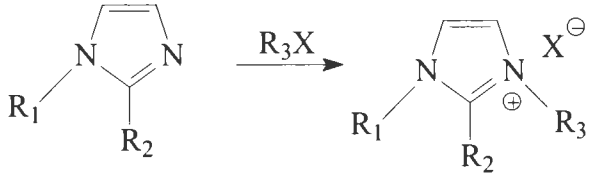
Path A:



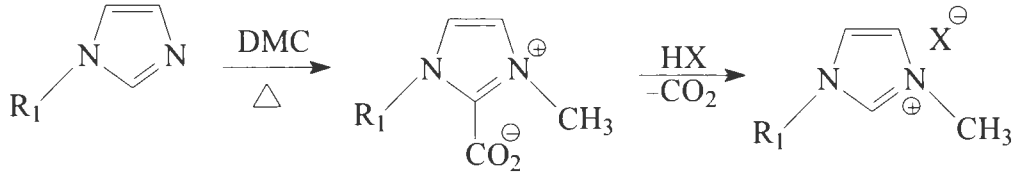
Path B:



Path C:



Path D:



Scheme 11: General route for ionic liquid's synthesis [112]

Liquid imidazolium salts are prepared by anion exchange from imidazolium halide precursors, which involve long reaction times. Olivier-Bourbigou *et al.* [112] described the synthesis of 1-alkyl-3-methyl imidazolium bromides in short reaction time giving high yields without purification. The synthesis of [bmim][BF_4] by a rapid one-pot solvent-free synthesis in a

batch-mode reactor using a microwave irradiation has been reported [113]. The synthesis of ILs using microwave or ultrasounds has also been described [114]. The methods for the synthesis of ILs have been decscribed in various articles [115-119].

2.5.2 Structure of ionic liquids

A simplified picture of ILs is that it contains coulombic interactions, like in a molten salt. However, some of the experimental results regarding ILs cannot be explained using this type of electrostatic interactions. It is therefore proposed that molecular interactions such as hydrogen bonding, π-π stacking and other dispersive forces such as van der Waals interactions are also present in ILs. Hardacre and coworkers [120] reported the relationship between the crystal and liquid structure of ILs. The liquid structure of ILs are investigated using techniques like neutron diffraction, X-ray scattering, EXAFS, NMR, etc. It has been proposed that the high probability of finding the anion, such as Cl^-, is close to the C2 of the imidazolium ring. Also, the larger anions such as $[PF_6]^-$ or $[NTf_2]^-$ can be located over the centre of the imidazolium ring. The symmetrical chloride anion with highly charged density forms a regular network compared to $[NTf_2]^-$. $[NTf_2]^-$ is highly disordered and can display different conformations with possible small cluster formation [121].

It has been reported that the hydrogen bonding depends on the nature of the anions. The [bmim] cation forms a stronger hydrogen bond than the phosphonium cation with the chloride anion [122]. Based on the ESI-MS studies to determine the strength of cation-anion interactions, two classes of ILs have been proposed. One class is the tightly associated anion to [bmim] cation such as $[CF3COO]^-$, $[Br]^-$, $[BF_4]^-$ and $[N(CN)_2]^-$. The other one is the ILs in which the anion is loosely interacting with [bmim] cation such as $[OTf]^-$, $[PF_6]^-$ and $[NTf_2]^-$. Among the ILs investigated, $[NTf_2]^-$ was found to be least interacting [123]. The ionic strength of interaction for different [bmim] cation-anion pair is found to be in the order $[Cl]^- > [BF_4]^- > [NTf_2]^-$. For the [emim] cation, the intermolecular energies follow the trend $[CF_3CO_2]^- > [BF_4]^- > [CF_3SO_3]^- > [NTf_2]^- \sim [PF_6]^-$.

2.6 Purification of ionic liquids

The physical and chemical properties of ILs and their catalytic activity can be affected by the presence of small amounts of impurities. Impurities arise from the incomplete synthesis of ILs and include volatiles, alkylating agents, inorganic halides, protic impurities, organic amines and/or water. Koenig *et al.* [124] described melt-crystallization for ultra-purification of ILs. The coloured impurities present in ILs are probably due to oxidation products, thermal degradation impurities from the starting materials, or traces of compounds from the starting

material. Decolourisation of ILs has been reported using activated charcoal [125], or by treating the ILs with silica [126] or alumina [127]. To remove the acid impurities, acid neutralization by a column was reported by Lungwitz and Spange [128]. Recently, X-ray photoelectron spectroscopy (AR-XPS) has been described as a suitable method to determine low level impurities [129].

2.7 Application of ionic liquids

Due to the unique physio-chemical properties, ILs have found various applications in reaction and synthesis media. The various areas where ILs found useful are [130]:

- solvents for organic, organometallic synthesis and catalysis;
- electrolytes in electrochemistry;
- stationary phases for chromatography;
- matrices for mass spectrometry;
- supports for the immobilization of enzymes;
- separation technologies;
- liquid crystals;
- templates for synthesis of nano-materials and materials for tissue preservation;
- preparation of polymer-gel catalytic membranes; and
- generation of high conductivity materials.

The major applications of ILs are discussed in detail below.

2.7.1 Replacement of solvents

The search for alternative solvents has become high priority recently due to the introduction of cleaner technologies. A majority of common solvents that are used today have potential health hazards. Environmentally friendly ILs have already replaced hazardous VOCs in liquid-liquid extractions where hydrophobic molecules such as derivatives of benzene will partition to the IL phase. The research done by Huddleston *et al.* [131] showed that [bmim][PF_6] could be used to extract aromatic compounds from water. Fadeev and Meagher [132] showed that two imidazolium ILs with $[PF_6]^-$ anion could be used for the extraction of butanol from aqueous fermentation broths. ILs have also been used for the extraction of alcohols from alcohols/alkane mixtures [133] and also for the extraction of aromatics from aromatic/alkane mixtures [134]. Reports on the binary temperature-composition curves of ILs with alcohols, alkanes, aromatics and water; ternary temperature-composition curves of ILs with alcohols and water; solubilities of some organics and water in ILs all support the solvent properties of ILs [135-137].

2.7.2 Purification of gases

Various works have been published regarding the solubility of gases in ILs [138-140]. The idea of purification of gases using ILs emerged from these experimental studies. Anthony and coworkers [141] have reported the solubility of nine different gases up to 13 bar. The solubilities of carbon dioxide, carbon monoxide, ethylene, methane, ethane, argon, oxygen, hydrogen and nitrogen were investigated in [bmim][[PF_6]. Among the gases selected, the highest solubility and strongest interactions with [bmim][PF_6], was exhibited by carbon dioxide followed by ethylene and ethane. The relatively high solubility of CO_2 in IL was attributed to its large quadrapole moment.

Camper and coworkers [138] investigated the solubility of carbon dioxide and ethylene in different ILs: [bmim][PF6], [emim][NTf_2], [emim][CF_3SO_3], [emem][dca] and [thtdp][Cl]. They explained the solubility of carbon dioxide and ethylene, at low pressures, using the regular solution theory. At high pressures, regular solution theory was found to be limited and this limitation was explained by the dominant entropic effects.

2.7.3 Catalysis

The application of ILs as solvents for transition metal catalysis is a topic of current interest and several reactions are under investigation. The first transition metal catalyzed reaction in ILs was carried out in different ILs: 1-butylpyridiniumchloride; [BuPy]Cl and tetrabutylphosphonium chloride; [Bu_4P]Cl. Various nickel complexes were used as catalysts and were found to catalyse the dimerization of alkenes [142,143]. In metal catalysed reactions, ILs assist in the activation of the catalyst, help to improve the stability of the catalyst, immobilization of solid catalyst, recycling and also favours product removal and influence the selectivity of reaction [144]. Some of the transition metal catalysed reactions where ILs are used are olefin hydroformylation [145-150], carbonylation [151], Heck reaction [152-157], hydrogenation of olefins and diolefins [157-160], olefin metathesis [161-163] and olefin polymerization [163,164].

2.7.4 Biological reactions media

It has been reported that IL biphasic systems can be used to separate many biologically important materials such as carbohydrates and organic acids [165,166]. ILs assist in the dissolution of carbohydrates, their recovery from solution, or their transformation into derivatives like ethers and esters [167,168]. Research done by Gutovski and group [169] revealed that ILs with the anions [PF_6] and [BF_4] exhibited poor ability to dissolve carbohydrates. Later, Zhao and group [170] also eliminated [NTf_2] and [$N(CN)_2$] anions for

poor dissolution of carbohydrates. It was found that good dissolution of ILs is possible with halide based ILs, especially with chloride anion. The reason for this has been reported as the small size and strong electronegativity of the chloride ion [171]. ILs containing formate, acetate and phosphate anions were also reported as good anions for the dissolution of carbohydrates [170,172]. The cation of the ILs are also involved in the dissolution process. It has been found that for the same anion, increasing the alkyl chain on the dialkyl imidazolium cation decreases the solubilisation, whereas, introduction of certain functional groups such as allyl group enhances the dissolution process. The studies done by Pfruender et al. [173] showed that water immiscible ILs; [bmim][PF_6], [bmim][NTf_2] and [oma][NTf_2] (methyl trioctylammonium bistrifluoromethanesulphonylimide) do not disturb microbial cells and can be used as substrate reservoirs and *in situ* product extracting agents for biphasic whole cell biocatalytic processes.

2.7.5 Removing of metal ions

Dai *et al.* [174] reported the use of ILs as extraction solvents for the separation of metal ions. They used strontium nitrate as the metal compound and the presence of ILs resulted in improving the ability of crown ethers to remove metal ions from aqueous solutions. The work done by Visser et al. [175,176] explains the use of ILs to remove cadmium and mercury from contaminated water. They prepared a series of hydrophobic task-specific ionic liquids by appending different functional groups: thioether, urea and thiourea, to immidazolium cations. Synthesised TSIL cations were combined with PF_6^- anion and used alone or in a mixture with [bmim][PF_6]. The result revealed increased distribution ratios for thiourea and urea derivatised cations. The other works reported in the literature include the extraction of Na^+ and Cs^+ using [$C_n$mim][PF_6] [3]; Li^+, K^+ and Rb^+ using [$C_n$mim][PF_6] [4]; Na^+, K^+ and Cs^+ using [$C_n$mim][NTF_2] [5,6]; Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} using [$C_n$mim][PF_6] [177].

2.7.6 Electrochemical devices

ILs are characterized by large window of electrochemical stability, high conductivities, wide liquid range and higher thermal stability. These properties make them suitable for use in electrochemical devices including batteries, supercapacitors, fuel cells, photovoltaic cells, electroplating and many more [178]. ILs have also been proven to be good electrolytes for lithium rechargeable batteries.

2.8 Challenges of ionic liquids

The main challenges faced in the use of ILs are high cost and lack of physical property and toxicity data. ILs are significantly more expensive than organic solvents. The cost of the IL depends on the composition of cations and anions and the scale of production. The reason for the

high cost of ILs can be attributed to the expensive cleaning methods due to their non volatile nature and low melting points. Also, the desired IL quality (halide, water and amine content) may also affect the price. There are a number of commercial suppliers of ILs such as Solvent innovation, Cytec, Sigma-Aldrich, Merck, Acros-Organics, etc. (Table 1).

Table 1: Some of the major suppliers of ionic liquids **[179]**

Supplier	Website
Merck KGaA/EMD Chemicals	http://ildb.merck.de/ionicliquids/en/startpage.htm
BASF	http://www.basionics.com
Cytec	http://www.cytec.com/
SACHEM	http://www.sacheminc.com/products-and-services/ionic-liquids.html
DuPont	http://www.dupont.com/fluorointermediates/pdf/k15303.pdf
Scionix	http://www.scionix.co.uk
Solvent Innovation	http://www.solvent-innovation.com/index_overview.htm
IoLiTec	http://www.iolitec.de/ionic_e.htm
Accelergy	http://www.accelergy.com/
ACROS	http://www.acros.com/_Rainbow/pdf/AO_IonicLiqui_Eur_def.pdf
Sigma-Aldrich	http://www.sigmaaldrich.com/catalog/search/TablePage/16255866
Kanto Chemical Co.	http://www.kanto.co.jp/english/
Nippon Gohsei	http://www.nichigo.co.jp/english/pro/chemical.html
Solchemar	http://www.solchemar.com/
Chemada	http://www.chemada.com/cat0.htm

A rough estimate of the cost of cations and anions used in the preparation of ILs [179] is shown in table 2. From the table, it is clear that anions such as $[BF_4]^-$ and $[PF_6]^-$ used in combination with dialkylimidazolium cations are quite expensive. The reason for this is that the sources for these anions ($Na[BF_4]$, $H[PF_6]$) and cations (1-methylimidazole) are not cheap.

Table 2: Rough estimation of cost of cations and anions used in the preparation of ILs **[180].**

Cheap	Expensive
Cations:	
$[HNR_3]^+$, alkylmethylimidazolium	$[NR_4]^+$
$[HPR_3]^+$, $[PR_4]^+$	dialkylimidazolium
	Alkylpyridinium
Anions	
$[Cl]^-$, $[AlCl_4]^-$	$[PF_6]^-$
$[MeSO_4]$	$[BF_4]^-$
[acetate]	$[CF_3SO_3]^-$, $[SbF_6]^-$
$[NO_3]^-$	$[(CF_3SO_2)_2N]^-$

The non availability of toxicity and biodegradability data are other challenges for the application of ILs. These data are needed for the industrial scale use of ILs. Incomplete physico-chemical data also pose problems for the future use of ILs. The data that are available today are mainly on physical properties such as viscosity, density and phase transitions. Until recently, very few microscopic physical properties are available which are needed for the synthesis of new ILs.

The recycling process of ILs that are available today involves the washing of ILs with water or VOCs which is a threat to the environment. However, the adoption of supercritical extraction technologies and membrane separation processes has helped in the recycling of ILs. Still, some solid impurities are found to be adsorbed on the ILs, which need to be eliminated using new technologies.

The high viscosities of ILs also pose problems for their large scale application. The viscosities of ILs are higher than those of conventional organic solvents and similar to those of oils. The high viscosities may lead to a decrease in the rate of many organic reactions. Increasing the temperature and changing the anion-cation combimations can lower the viscosity of ILs.

2.9 Olefin metathesis in ionic liquids

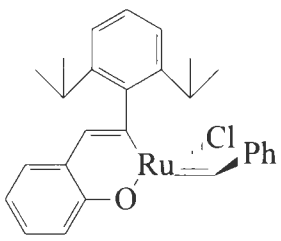
2.9.1 Applications of untagged olefin metathesis catalysts

Chauvin and Olivier-Bourbigou were the first to report on olefin metathesis in RTIL [181]. They studied the self-metathesis of 2-pentene using $W(OAr)_2Cl_4$ (ArOH = 2,6-diphenylphenol or 2,4,6-trimethylphenol) dissolved in [bmim]Cl-$AlCl_3$-$EtAlCl_2$ ionic liquid (**Scheme 12**). Efficient catalyst separation and recycling through a decantation of the hydrocarbon layer were reported.

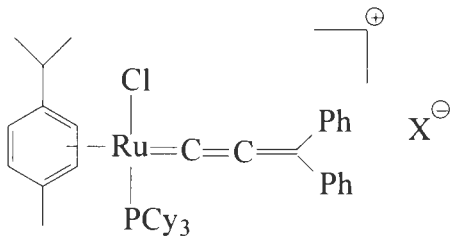
2-pentene 2-butene (25%) 3-hexene (25%)

Scheme 12: First example of olefin metathesis in ionic liquids

Bayer [182] investigated the application of Grubbs catalyst 1 and 2, shiff-base bearing catalyst **34**, and the cationic allenylidene **35** (X = OTf) (**Scheme 13**) in imidazole and pyridinium based ILs. Catalyst **34** was found to be more successful in the RCM of several dienes both in pure ILs and in a two phase system composed of anhydrous hexane and an IL.



34

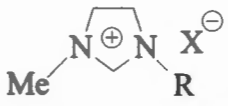


35

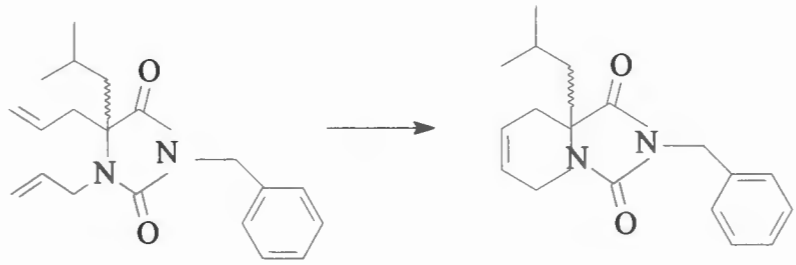
Scheme 13: Untagged olefin metathesis catalysts used by Bayer [182]

Buijsman *et al.* [183] investigated the effect of ionic liquids (**36a – e**) in ring closing metathesis reaction of substrate **37** in the presence of Grubbs catalysts (**Scheme 14**). The studies indicated that [bmim][PF_6] is the best solvent. A conversion of 98% and ruthenium contamination of 3.2μg per mg of product were obtained at a temperature of 50°C after 20 h.

The low ruthenium content proved that the catalyst remains present in the ionic liquid. The catalyst was found to be stable up to three runs. This work can be considered as the first systematic study on the application of ILs as a solvent for olefin metathesis.



36a R=butyl, X=BF_4
36b R=butyl, X=PF_6
36c R=octyl, X=BF_4
36d R=octyl, X=PF_6
36e R=octyl, X=SbF_6

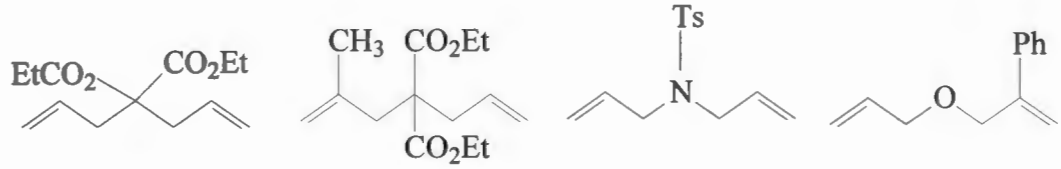


37 **38**

Scheme 14: Bicyclic hydantoin 38 synthesis performed by Buijsman *et al.* [183]

Microwave accelerated RCM using Grubbs second generation catalyst in [bmim][BF_4] has been reported by Mayo and co workers [184]. In all the substrates tested (**Scheme 15**), the reactions were completed in 15 s with 100% conversion. The enhancement in catalytic activity was explained by the fact that microwave energy produces non-thermal effects, which was supported by a study conducted in DCM (a microwave-transparent solvent).

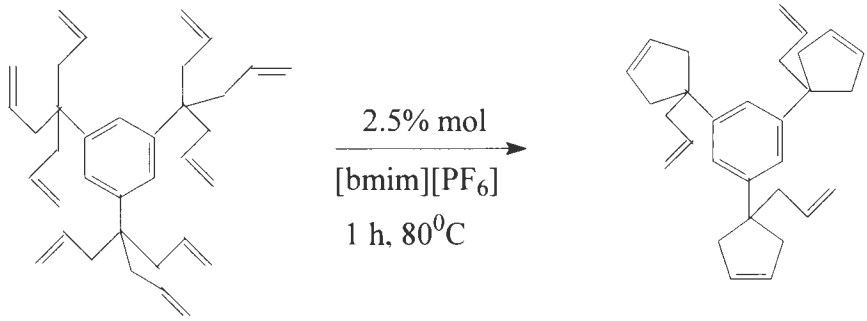
Astruc and coworkers have reported the RCM reaction of polyolefin **43** to form polycyclic cycloptenylaryl derivative **44** (**Scheme 16**). The reaction was carried out using first generation Grubbs catalyst in [bmim][PF6] at 80 °C and a conversion of 75% was obtained after extraction with ether [185].



39 **40** **41** **42**

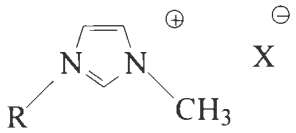
Scheme 15: Representative RCM structures metathesised by Mayo *et al.* [184]

Williams and co-workers [186] investigated the self-metathesis of 1-octene using several ILs (**Scheme 17**). Among the Ru alkylidene catalysts tested, the second generation Hoveyda-Grubbs catalyst exhibited good activity and selectivity. Leaching studies done by ICP OES analysis shows that less than 2 % of the Hoveyda-Grubbs catalyst leached into the organic layer. Among the 1,3 disubstituted ILs, [bmim][BF_4] performed the best. The results obtained show that alkyl chains of short length enhanced the catalytic activity, while longer ones inhibited it. Recycling studies proved that catalytic activity can be retained through two catalyst cycles.



43 **44**

Scheme 16: Formation of polycyclic cyclopentenylaryl derivative by RCM



R = C_2H_5, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}

X = BF_4, PF_6, NTf_2

Scheme 17: Imidazolium type ILs used by Williams *et al.* [186]

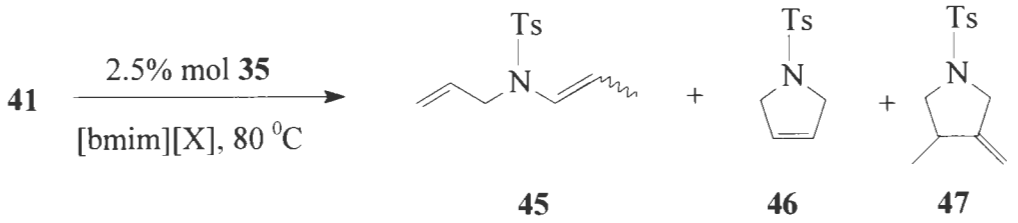
In 2006, Tang and co-workers reported the self-cross-metathesis of styrene derivatives in DCM, [bmim][BF_4] and [bmim][PF_6] using Grubbs second generation catalyst [187]. A slightly higher conversion (85%) was obtained in [bmim][PF_6] compared to the reaction in DCM (81%). The studies also reveal that ILs containing the catalyst could be recovered and reused for at least four cycles with a little drop in activity.

Ethenolysis of methyl oleate in RTILs has been reported by Thurier *et al.* [188]. Among the catalysts tested, Hoveyda-Grubbs first generation catalyst exhibited a better efficiency and selectivity than the other catalysts. A conversion of 91% was obtained for the ethenolysis of methyl oleate in toluene. After 3.5 h of reaction time, methyl oleate yielded 88% of decene and 89% of methyl-9-decenoate. The reaction carried out in [bmim][NTf_2] gave 79% conversion , whereas in [bdmim][NTf_2] a conversion of 83% was obtained. Recycling studies proved that the first generation Hoveyda catalyst could be reused for three consecutive runs without loss of activity.

2.9.2 Application of charged olefin metathesis catalysts

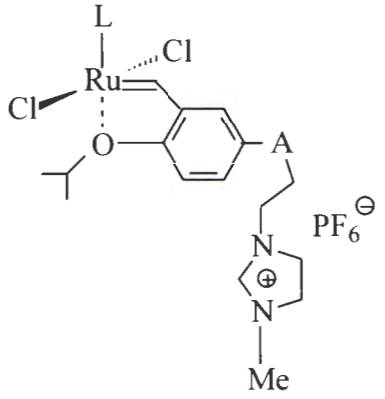
The problem associated with non-charged catalysts is the leaching of the catalyst or its decomposition product into the organic phase. This results in the gradual loss in activity of the catalyst containing IL. This can be overcome by the use of charged catalyst systems. The application of charged catalyst systems helps to improve the immobilization of the catalyst by increasing the catalyst affinity to the IL.

Dixneuf and co-workers were the first to report on the metathesis reaction in ILs in the presence of ruthenium allenylidene salts [189]. They studied the RCM of a diallylamide in [bmim][X] type ILs and biphasic media containing one ionic salt and an organic phase. Catalyst **35** where X = PF_6, BF_4 and OTf was used for the conversion of **41** in different ILs. The reaction led to the transformation of **41** and the formation of *N*-tosyldihydropyrrole **45** together with the cycloisomerisation and isomerisation byproducts **46** and **47** (Scheme 18). The reaction carried out in [bmim][BF_4]-toluene resulted in a conversion of 96% after 5.25 h at 80 °C, whereas, the same reaction carried out in [bmim][BF_4] gave only 40% conversion after 5.5 h of reaction time. Catalyst **35** was also used in the ROMP of norbornene in [bdmim][PF_6] and [bdmim][PF_6]-toluene biphasic mixture [190]. The reaction was found to be effective for up to six catalytic cycles in [bdmim][PF_6]-toluene medium.



Scheme 18: RCM of 41 in ILs with 35 as catalyst.

Maudit and co-workers have reported the synthesis of imidazolium tagged Ru catalyst **48.** For the RCM of diallyltosilamine **41**, Grubbs first generation catalyst, Hoveyda second generation catalyst and imidazolium tagged catalyst **48** were used in [bmim][PF_6] medium. Catalyst **48** was found to be active even after 10 cycles (Scheme 19). However, in RCM of some oxygen containing substrates, its recyclability was limited to only three or four cycles [191].

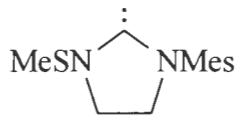


48, A = CH_2, L = PCy_3

49, A = CH_2, L = SIMes

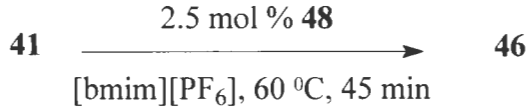
50, A = OCH_2CH_2, L = PCy_3

51, A = OCH_2CH_2, L = SIMes



(SIMes)

Scheme 19: Imidazolium tagged Ru catalysts

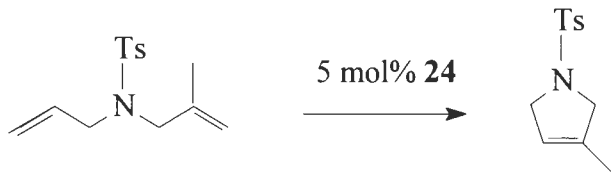


Scheme 20: RCM of 41 with 48 as catalyst

A more improved catalyst **49**, known as 'the second generation IL catalyst' was prepared by Mauduit and co-workers [192]. RCM of **52** was done using catalyst **49** in the presence of [bmim][PF_6]. They obtained high conversions up to three cycles and thereafter the conversion decreased rapidly at 60 °C (**Scheme 21**). But at a lower temperature of 40 °C, poor recyclability was observed. When the reaction was repeated using less viscous IL, [bmim][NTf_2], increased reactivity and good recyclability of the catalyst were observed. However, due to the partial miscibility of toluene (extraction solvent) in [bmim][NTf_2], product extraction was found to be difficult. This problem was solved by conducting the metathesis reaction under biphasic conditions. Excellent results were obtained in 25/75 [bmim][PF_6]-toluene medium at 25 °C. A conversion of 98% was obtained and the catalyst was found to be active for up to 8 cycles. Leaching studies done using ICP-MS spectroscopic analysis revealed extremely low Ru contamination of products (1 to 22 ppm) even at high catalyst loading (5 mol%). The reaction was found to be successful for other diene substrates (**Scheme 22**).

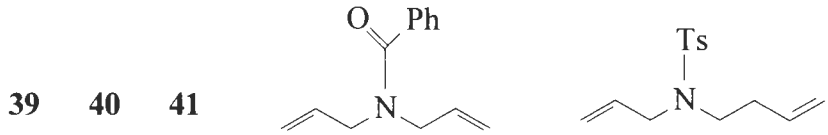
Mauduit and coworkers also studied the scope of second generation IL catalyst **49** in the CM reaction of electron deficient olefins (**Scheme 23**) [193]. CM reaction between olefin **56** and methyl acrylate **57** was carried out in a [bmim][PF_6]/toluene (20/80) mixture at room temperature with 5 mol% of catalyst **49**. The reaction resulted in a 80% yield of product in the first two cycles and thereafter the yield decreased. The decrease in reactivity was attributed to the difficulty in re-anchoring of the catalytic species to the cationic imidazolium-tagged ligand

due to the large excess of methyl acrylate. The addition of 1,7-octadiene as additive gave good isolated yields up to the third run and thereafter it decreased.



52 **53**

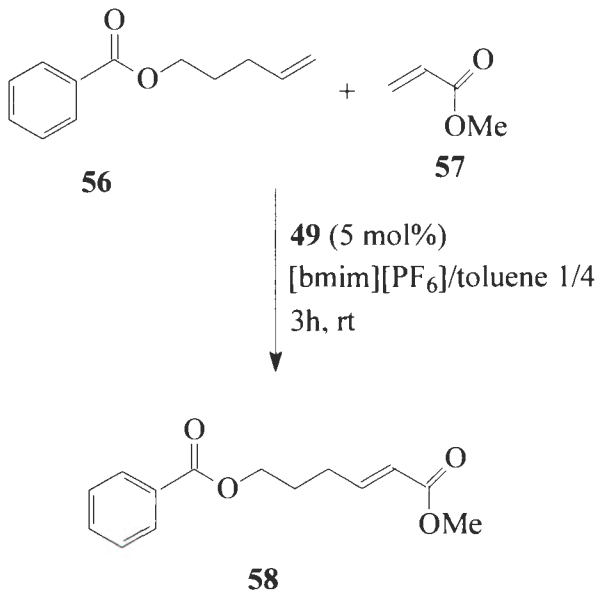
Scheme 21: RCM of trisubstituted diene with catalyst 49 [192]



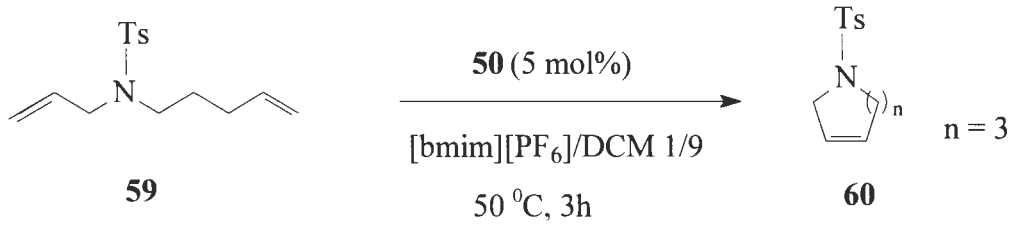
54 **55**

Scheme 22: Additional substrates studied by Mauduit [193]

The first generation catalyst **50** developed by Yao and Zhang exhibited excellent activity compared to Maudit's catalyst. Catalyst **50** was used in the RCM of olefin **58** and remained active for ten cycles (**Scheme 24**). The reactions were carried out in [bmim][PF_6]/DCM mixture at 50 °C. The complex **50** was proved to be useful in the RCM of several dienes, leading to the formation of cyclic compounds with di- and trisubstituted olefins.

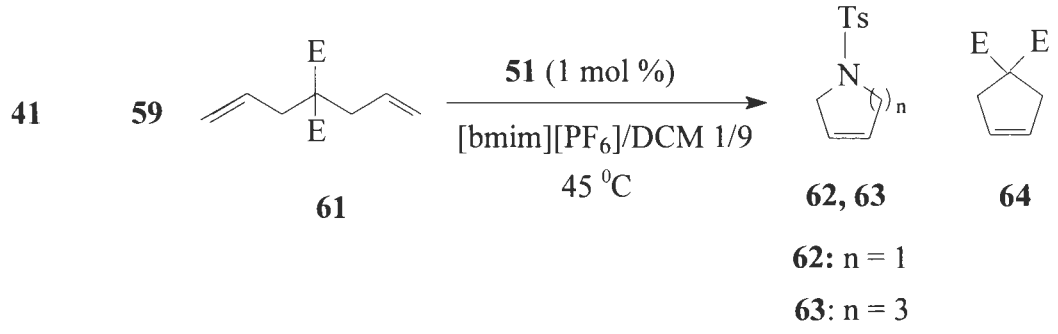


Scheme 23: CM reaction between olefin 56 and methyl acrylate 57 [193]



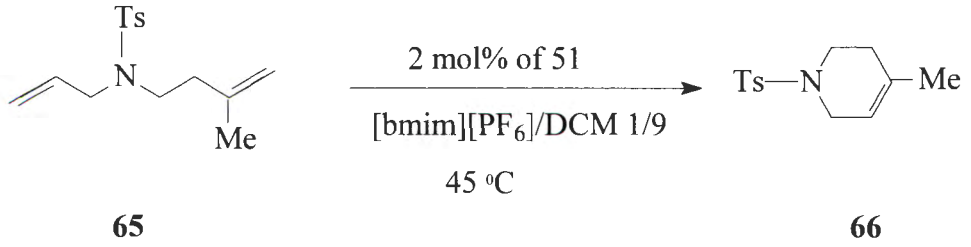
Scheme 24: RCM reaction using Yao's first generation catalyst 50

The development of second generation IL catalyst **51** by Yao and Sheets proved to be useful in the RCM of several di-, tri- and tetrasubstituted diene and enyne substrates [194]. Catalyst **51** was initially tested for the RCM of dienes **61-63**. The reactions were performed in [bmim][PF_6]/DCM (1/9) mixture at 45 °C (**Scheme 25**). In all the three dienes tested, catalyst **51** was found to be active even after 10 runs.

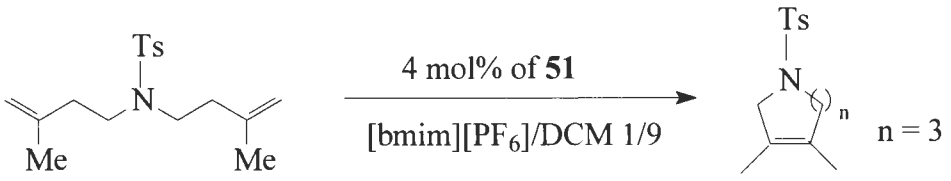


Scheme 25: RCM of disubstituted dienes using Yao's second generation catalyst 51

After the successful RCM reaction in dienes, catalyst **51** was evaluated for the RCM of tri- and tetrasubstituted olefins. The trisubstituted olefin **65** underwent RCM to cyclic olefin **66** in 2 hours reaction time (**Scheme 26**). A conversion of 96% was obtained in the first run. Both the catalyst and IL were recycled and reused for six runs and a conversion of 90% was obtained in the last run. RCM of tetrasubstituted diene **67** in the presence of 4 mol% of catalyst **51** resulted in 79% conversion at 45 °C in 16 h (**Scheme 27**). The recovered catalyst was used in the second run and a similar activity was observed.



Scheme 26: RCM of trisubstituted diene using Yao's second generation catalyst 51

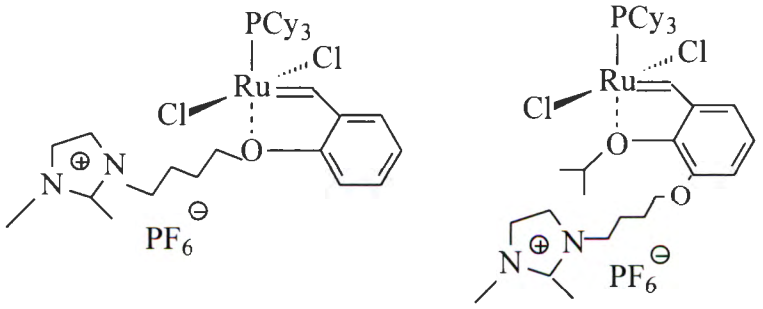


67 **68**

Scheme 27: RCM of tetrasubstituted diene using Yao's second generation catalyst 51

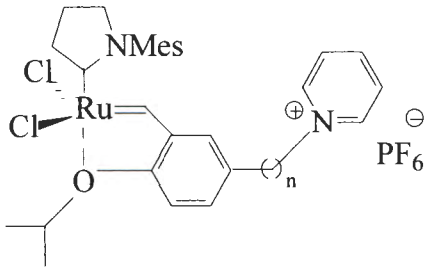
Dixneuf *et al.* reported the synthesis of two Hoveyda-type catalyst, **69** and **70**, containing an ionic tag [195]. However, these catalysts exhibit poor recyclability. This could be due to the destabilisation of the catalyst caused either by the replacement of the isopropyl ether fragment with the n-alkyl ether chain in **69** or by the presence of the additional ortho-substituent in **70** [196] (**Scheme 28**). Dixneuf *et al.* investigated the ethenolysis of methyl oleate in [bdmim][NTf_2] using **69** and **70**. The reactions were performed in [bdmim][NTf_2] at 20 °C using 5 mol% of catalysts. For the first run, catalyst **70** displayed a high conversion (89%) compared to catalyst **69** (38%). Unfortunately, it was found to be poorly recyclable.

Mauduit and co-workers reported the synthesis of new pyridinium containing Ru catalysts **71-73** [197,198] (**Scheme 29**). RCM of diethyl 2-allyl-2-methallylmalonate using catalyst **71** led to 84% of conversion after 6 h with 1 mol% of DCM at room temperature. The recyclability of catalyst **71** was also evaluated by performing RCM of 2-allyl-2-methallyltosylamine using 5 mol% of catalyst in two different ILs: [bmim][PF_6] and [bmPy][BF_4] with toluene as co-solvent (**Scheme 30**). The activated pyridinium catalyst exhibited good activity in the first two cycles and the activity decreased thereafter. Non-activated pyridinium catalyst **72** showed good recyclability up to six cycles. Catalyst **73** was also found to exhibit increased activity and recyclability >98% up to 6 cycles.



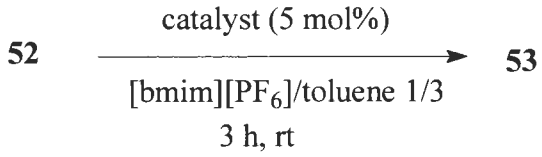
69 **70**

Scheme 28: Hoveyda-type catalysts containing ionic tag developed by Dixneuf



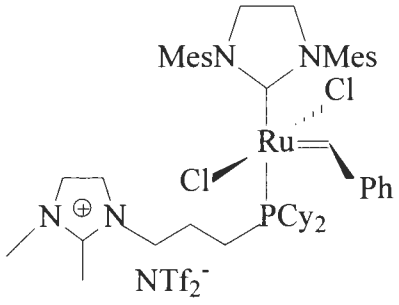
71, n = 0
72, n = 3
73, n = 1

Scheme 29: Pyridinium tagged catalysts developed by Mauduit



Scheme 30: Pyridinium tagged catalysts' [71-73] performance in RCM of 52

In 2008, an ionophillic phosphine-based Ru complex **74** was synthesised by Consorti and co workers [199] (**Scheme 31**). The catalyst was found to be active in the RCM of 1, 7 octadiene in [bmim][PF_6]/toluene media even after 8 cycles. Very low levels of Ru by-products in the organic phase were detected after each recycling (down to 2ppm when 0.25 mol% of catalyst was loaded).



74

Scheme 31: Ionophilic phosphine based Ru complex 74

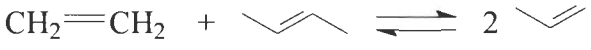
2.10 Applications of olefin metathesis

2.10.1 Hydrocarbon industries

Olefin metathesis has opened up new industrial routes for the synthesis of petrochemicals, oleochemicals, polymers and specialty chemicals. The most important industrial application of olefin metathesis is the production of propene using olefin conversion technology (OCT) and Shell higher olefins process (SHOP). Propene is mainly obtained from naphtha steam crackers (65%) and from gasoline-making from fluid catalytic cracking (FCC) units at refineries.

A small amount is being produced by dehydrogenation of propane and by coal gasification via Fischer-Tropsch chemistry. There is a strong global demand for propene, since it is used in the preparation of polypropylene, acrylonitrile, oxoalcohol, 1-butanol and acrylic acid.

An alternative route for the production of propene is the application of metathesis reaction for the conversion of ethene and 2-butene, known as reverse Philips triolefin process (Scheme 32). This reverse process is now offered by ABB Lummus Global, Houston (USA), for license as olefins conversion technology (OCT). The reaction is carried out using WO_3/SiO_2 (metathesis catalyst) and MgO (isomerisation catalyst) at >260 °C and 30-35 bar [200]. Another route for the production of propene is Meta-4, and was a joint development by the Institut du Pétrole (IFP) and the Chinese Petroleum Corporation (Taiwan). The process involves the reaction of ethene and 2-butene in the presence of a Re_2O_7/Al_2O_3 catalyst at 35 °C and 60 bar [201].



Scheme 32: Reverse triolefin process

The Shell higher olefins process is used for producing linear higher olefins from ethene. This process takes place in three stages. In the first step, ethene is oligomerised in the presence of a nickel-phosphine catalyst to produce a mixture of linear even-numbered α-olefins in the range C_4 to C_{40}.The products are separated using distillation and fractionation. In the second step, the lighter ($<C_6$) and heavier ($<C_{18}$) olefins undergo double bond isomerisation over a solid potassium metal catalyst to give a mixture of internal alkenes. In the final step, internal olefins are subjected to CM in the presence of an alumina-supported molybdate catalyst. The final products consist of 10-15% of the desired C_{11}-C_{14} linear internal olefins, which can be converted into detergent alcohols by a hydroformylation process [202,203].

2.10.2 Polymer industries

Immediately after the discovery of olefin metathesis, polymerisation of cyclopentene to polypentenamer was reported [204]. Trans-polypentenamer has properties close to those of natural rubber, while the cis form is similar to some special rubbers [205]. In the polymer field, ROMP of cycloalkenes lead to the formation of polymers like polyoctenamerpolynorbornene, polydicyclopentadiene and hydrogenated polymers. Polymers are also synthesised from unsaturated fatty acid methyl esters (FAMEs) obtained by the transesterification of fats and oils with methanol. Ethenolysis of FAMEs yield α-olefins, functionalised polyolefins, polyesters,

polyethers and sugar tensides. α-olefins are used in the formation of detergent alcohols, plasticizer alcohols, poly(α-olefins), epoxides, alkyl aromatics, personal care products, flavors and fragrances. Oleochemical internal epoxides obtained from FAMEs find application as PVC stabilisers, plasticizers and intermediates for the production of polyols. Ethenolysis of 2,4,4-trimethyl-2-pentene yield neohexene, a starting material for polycyclic musks such as Tonalide®[5].

2.10.3 Pharmaceutical Industries

Metathesis has found applications in pharmaceuticals used in the treatment of major diseases such as bacterial infections, hepatitis C, Alzheimer's disease, cancer, Down's syndrome, arthritis, osteoporosis, inflammation, fibrosis, HIV/AIDS, migraine, etc. [206]. Using RCM, Fuerstner and Thiel synthesised a seven membered azepin compound called balanol, which is used as anticancer agents and in controlling inflammation, cardiovascular disorders, central nervous system dysfunction, and even HIV infection [207]. The production of insect pheromones, which are known as environmentally friendly pest-control agents, has also been reported [208]. Recently, olefin metathesis has also been applied in the synthesis of steroids. Biologically active compounds such as vitamin D and hormone analogues, steroid dimmers and macromolecules have been prepared using commercially available first and second generation Grubbs and Hoveyda ruthenium complexes [209].

2.11 Conclusions

With the discovery of molybdenum and ruthenium complexes, olefin metathesis became one of the most powerful and attractive tools for the formation of carbon-carbon double bonds widely used in organic synthesis. The importance of olefin metathesis has been recognised by the award of Nobel Prize in Chemistry for 2005 jointly to Yves Chauvin, Robert. H. Grubbs and Richard. R. Schrock. Compared to the molybdenum Schrock' catalysts, most of the available ruthenium catalysts can be handled in air and are compatible with functionalised substrates, including carbonyl, hydroxyl or carboxylic acid groups. The synthesis of a large number of compounds via olefin metathesis is due to the numerous types of metathesis transformations, such as cross metathesis, ring closing metathesis, ring opening metathesis and many others.

The introduction of room temperature ionic liquids to the transition metal catalysed reactions instead of conventional organic solvents, has made the process more compatible to the environment and is found to be economical due to their unique physical and chemical properties such as non-volatility, excellent thermal stability, the ease of recovery and good ability to dissolve many organometallic compounds. In most of the publications reported, the use of ionic

liquids in metathesis has led to significant enhancement in the reactivity, yield and reaction rate. Another advantage of using ionic liquids is the ease of recovering and reusing the catalyst and the ionic liquids without much drop in activity.

Recent developments in olefin metathesis have shown promise of a great future for the "green" metathesis in ionic liquids both in scientific research and in industrial and pharmaceutical applications. In spite of all these developments, many critical areas in catalytic olefin metathesis remain to be modified. One area relates to the development of more robust and active catalysts that can be easily prepared. The preparation of catalysts that can control olefin stereochemistry remains as a challenge. Although many of the metathesis reactions yield the desired products, the high catalyst loadings required for an efficient and cost effective process is also under question.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Methyl oleate (≥99%) and methyl ricinoleate (>99%) were obtained from Sigma-Aldrich and were treated with activated alumina and stored under N_2 atmosphere at a subzero temperature. The ionic liquids used were 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide ([bmim][NTf_2]), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bdmim][PF_6]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bdmim][BF_4]), and are all reagent grade chemicals from Sigma-Aldrich. The organic solvents used in the study were dichloromethane, 1,2-dichloroethane, chlorobenzene and toluene all from Sigma-Aldrich. Ethyl vinyl ether was purchased from Fluka. Nonadecane purchased from Fluka was used as the internal standard (**IS**). Ruthenium catalysts were stored under N_2 and used as purchased from Sigma-Aldrich.

3.2 Apparatus

All the reactions were performed under a N_2 atmosphere in a glass reactor fitted with a thermometer and a rubber septum. The hot plate stirrer and oil or water bath were used for controlling the temperature. The thermometer positioned in the oil/water bath was used to monitor the reaction temperature. The reagents were introduced using a syringe inserted through the septum. A needle inserted through the septum and connected to a N_2 supply was used to ensure a slow and steady N_2 gas. The reaction mixture was stirred by means of a magnetic stirrer bar. Sampling was done using a syringe through the septum, and aliquots were transferred to 2 mL vials. The reaction was terminated by quenching on the addition of two drops of ethyl vinyl ether. The quenched sample was diluted with a solvent and analyzed using gas chromatography (GC). The experimental set up for the metathesis reactions is shown in figure 1.

3.3 Chemical methods

3.3.1 General metathesis experiments

The glass reaction flask closed with a rubber septum was purged with N_2 to remove oxygen and other impurities. The reaction flask was charged with solvent and catalyst. The mixture was stirred vigorously to afford complete dissolution of the catalyst. The substrate containing the internal standard was then introduced. The resulting solution was vigorously stirred using a stirrer bar and a motor stirrer. Samples were taken at regular intervals and

quenched by adding two drops of ethyl vinyl ether. The reaction was monitored for four hours. The quenched sample was diluted with a solvent and analyzed by GC.

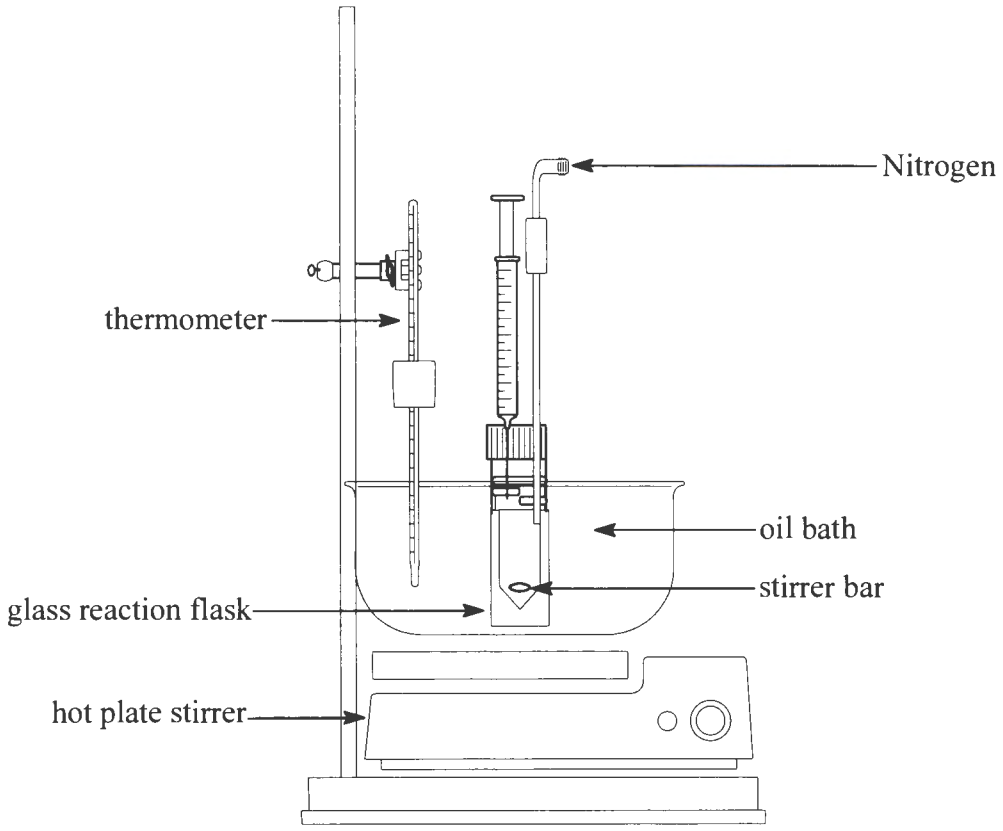


Figure 1: Experimental set-up for the metathesis experiments

3.3.1.1 Metathesis in ionic liquids

The selected IL (1 mL), followed by a known amount of catalyst was added to the reaction flask and purged with N_2. In all the reactions, substrate/catalyst molar ratio used was 100:1. The following amounts of catalysts were added to the respective reactions:

Grubbs first generation catalyst – 12.4 mg, 0.015 mmol;

Grubbs second generation catalyst – 12.4 mg, 0.014 mmol;

Hoveyda Grubbs first generation catalyst – 12.4 mg, 0.015 mmol; and

Hoveyda Grubbs second generation catalyst – 12.4 mg, 0.015 mmol.

The reaction mixture was stirred at the desired reaction temperature to ensure the complete dissolution of the catalyst. The substrate (0.5 mL) to which 0.05 g of internal standard had been added was injected into the reaction mixture. The reaction mixtures were all biphasic. Samples were taken at 5, 10, 15, 20, 30, 60, 120, 240 minutes from the top organic layer and quenched with ethyl vinyl ether.

3.3.1.2 Metathesis in organic solvents

A weighed amount of catalyst was dissolved in 2 mL of the selected organic solvent and poured into the glass reaction flask. The substrate (0.5 mL) to which 0.05 g of internal standard had been added was injected into the reaction mixture. The reactions were all homogeneous. Samples were taken at 5, 10, 15, 20, 30, 60, 120, 240, 300 minutes and immediately quenched with a few drops of ethyl vinyl ether. In all the reactions, the substrate/catalyst molar ratio used was 100:1. The following amounts of catalysts were added to the respective reactions.

Grubbs first generation catalyst – 12.4 mg, 0.015 mmol

Grubbs second generation catalyst – 12.4 mg, 0.014 mmol

Hoveyda-Grubbs first generation catalyst – 12.4 mg, 0.015 mmol

Hoveyda-Grubbs second generation catalyst – 12.4 mg, 0.015 mmol

3.3.2 Recycling experiments

The selected IL (1 mL), followed by a known amount of catalyst was added to the reaction flask and purged with N_2. The substrate (0.5 mL) to which 0.05 g of internal standard has been added was injected into the reaction mixture. Sampling was done for a period of four hours at regular intervals. The progress of the reaction was monitored using GC. After extraction of reaction products with heptane (2 × 3 mL), the glass reactor was loaded with fresh substrate (0.5 mL) and was introduced for a new run. The reaction was monitored for four hours and was analyzed using GC. A third loading of substrate (0.5 mL) was carried out and the reaction monitored for four hours.

3.3.3 Leaching studies

Leaching of the catalyst into the organic layer was followed using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. The top organic layer was removed from the biphasic layer and was filtered through a plug of silica gel in order to remove IL traces. The samples were prepared by weighing 5 mg of the crude compound and then adding 15 mL of 0.12 M hydrochloric acid. The analyses were performed on a PE Instrument Elan 6000 inductive coupled plasma optical emission spectrometer using ^{99}Ru and ^{101}Ru standard. All samples were diluted 10 times in ultra pure water. The Ru level was determined by comparison with a standard Ru sample (10 μg/mL).

3.3.4 Density Functional Theory (DFT) investigation

Geometry optimisations were done using the Density Functional Theory (DFT) method with the B3LYP functional and utilising the LanL2DZ basis set. DFT/B3LYP is considered

adequate for providing information related to molecular reactivity [210]. The solvent effect was taken into account by utilising the Polarisable continuum model incorporated in the Gaussian program [211, 212]. The dielectric constant for the ionic liquids [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] are 12.2, 11.8 and 14.0, respectively and were obtained from the studies by Ho *et al.* [213].

The solvent effect was calculated using the equation

$$G_{solution} = G_{vacuo} + \Delta G_{solv}$$

where $\Delta G_{solv} = (E_{sol} + G_{nes}) - E_{vacuo}$

E_{sol} and E_{vacuo} are the electronic energy of the solute in solution and *in vacuo*, respectively and G_{nes} is the non-electrostatic contributions to the solvation free energy.

The activation energy of the forward reaction was estimated using the equation

$$E_{act} = G_{inter\text{-}1} - (G_{react\text{-}1} + G_{react\text{-}2})$$

where E_{act} is the activation energies for the forward and reverse reactions,

$G_{inter\text{-}1}$ is the free energy of the alkyledene intermediate,

$G_{react\text{-}1}$ is the free energy of the reactant 1 (olefin),

$G_{react\text{-}2}$ is the free energy of reactant 2 (the active catalyst),

$G_{prod\text{-}1}$ is the free energy of the product 1 (styrene), and

$G_{pod\text{-}2}$ is the free energy of the second product (the generated active catalyst).

The reaction enthalpy was calculated using the equation

$$\Delta_r H = \Sigma\, H(\text{products}) - \Sigma\, H(\text{reactants})$$

The nucleophilicity values were estimated as the inverse of the electrophilicity index value, with the electrophilicity index value being estimated from [214].

$$\omega = \frac{\chi^2}{2\eta}$$

where $\chi \cong -\frac{1}{2}(E_{HOMO} + E_{LUMO})$ and $\eta \cong -\frac{1}{2}(E_{HOMO} - E_{LUMO})$

3.4 GC analysis

The progress of the reaction was monitored using gas chromatography (GC). Chromatograms were obtained using Varian Star 3400 *CX* GC equipped with a DB-624 capillary column (J&W Scientific, 30 m × 0.53 mm x 3μm) and a flame ionization detector (FID). The oven temperature was held at 200 °C and then increased to 270 °C at a rate of 20 °C min^{-1}. The injector temperature was set at 270 °C and the detector temperature at 300 °C with N_2 (300kPa) as carrier gas. The GC injector type was isothermal. A 0.2 μL of the reaction sample was injected through the injector port of the GC into the capillary column, and then the results were shown on the recorder. The GC method run time was 5 min. The results obtained from the GC included a gas chromatogram and a sheet of peak areas for each product.

The substrate conversions were calculated from the peak areas of the GC analyses using the following equation:

$$Conversion\ (\%) = \frac{n_0 - n_t}{n_0} \times 100$$

where n_0 = number of moles of substrate at the beginning of the reaction, and

n_t = number of moles of substrate after time *t*.

Selectivity towards primary metathesis products was calculated using the equation:

$$Selectivity\ (\%) = \frac{Yield\ of\ PMPs}{\sum Yield\ of\ products} \times 100$$

Turn over number (TON) was calculated using the equation:

$$TON = Substrate{:}\,Catalyst\ ratio\ \times substrate\ conversion$$

CHAPTER 4

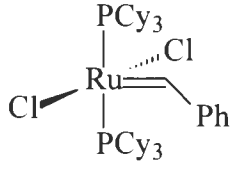
RESULTS AND DISCUSSION

4.1 Introduction

Metathesis of unsaturated fatty acid esters in the presence of various ruthenium carbene complexes was investigated. The chapter is divided into six sections. In the first section describes the results obtained from Grubbs first generation catalyst are presented, the second section deals with the results from Grubbs second generation catalyst, followed by the results with Hoveyda Grubbs first generation catalyst and then the results obtained with Hoveyda Grubbs second generation catalyst. The recycling of different catalysts in various ionic liquids is described in the fifth section. In the last section the density functional theory (DFT) method is utilised to understand the preference of ionic liquids as solvents for the metathesis of olefin.

The unsaturated fatty acid esters used for the study were methyl oleate and methyl ricinoleate. Metathesis of the above mentioned substrates was carried out in the presence of room temperature ionic liquids. The ionic liquids selected for the study were 1,1 dialkyl imidazolium type ([bmim][X]) and 1,2,3 trialkyl imidazolium type ([bdmim][X]) combined with different anions. In particular, the influence on the catalytic activity by the anion (X) and other reaction parameters was examined. The study further evaluates the metathesis activity in ILs against the activity in conventional organic solvents. ***Parts of the work have already been published in International Journal of Molecular Sciences 2009, 10(11), 5020-5030 and 2011, 12(6), 3989-3997.***

4.2 Metathesis of unsaturated fatty acid esters using Grubbs first generation catalyst [18]



18

4.2.1 Metathesis of methyl oleate in [bmim][X] type ILs

Methyl oleate was used as a substrate ester to optimize Grubbs first generation catalyst **18**. [bmim]X] type ILs were tested for their suitability as reaction media. The anions selected for the study were hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-) and bis (trifluoromethyl sulphonyl)imide (NTf_2^-). Some of the properties of [bmim][PF_6], [bmim][BF_4] and

[bmim][NTf_2] are shown in Table 3. PF_6^- and BF_4^- anions are neutral, weakly coordinating and form highly viscous imidazolium ILs while PF_6^- and NTf_2^- form hydrophobic ILs with NTf_2^- forming a less viscous imidazolium IL. When mixed with methyl oleate, all the ILs formed a biphasic system.

Table 3: Polarity (E_T^N), solubility and viscosity of [bmim][X] ILs [215]

X	E_T^N	Solubility in H_2O	Viscosity (cP)(25 °C)
PF_6	0.667	Insoluble	207
BF_4	0.673	Soluble	233
NTf_2	0.642	Insoluble	52

The reactions were carried out at temperatures ranging from 20-100 °C. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.5 mL of methyl oleate followed by the addition of 12.3 mg of Grubbs catalyst. The chromatogram resulting from the metathesis of methyl oleate with nonadecane as internal standard is shown in Figure 2. Two primary metathesis products (PMPs) were obtained in the metathesis of methyl oleate (**75**), namely; octadec-9-ene (**76**) and dimethyl octadec-9-ene-1,18-dioate (**77**), as illustrated in **Scheme 33**.

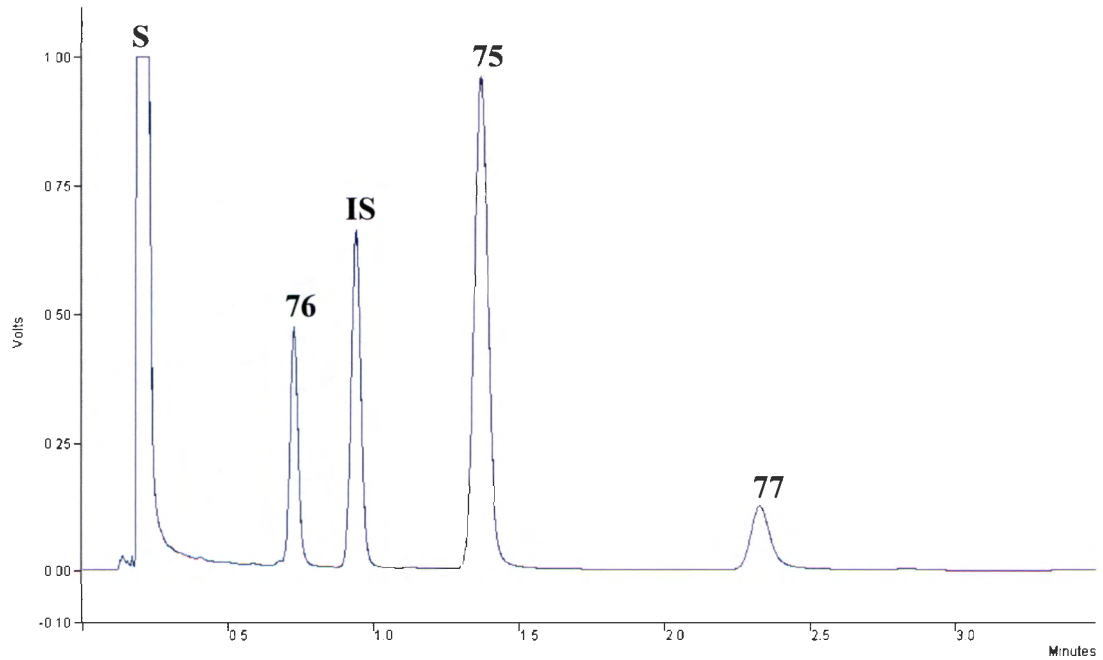


Figure 2: A Typical gas chromatogram resulting from the metathesis of methyl oleate. (*S is solvent peak while IS is that of the internal standard)*

Scheme 33: Primary metathesis products from self-metathesis of methyl oleate

$2\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$

75

$\rightleftharpoons$

$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3$

76

+

$CH_3COO(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$

77

4.2.1.1 Influence of the solvent

The activity and selectivity of **18** at 20 °C after 4 h reaction time is shown in Table 4. The highest conversion was observed in [bmim][BF_4] with a conversion of 54% and the lowest in [bmim][PF_6] with a conversion of 50 %. Excellent selectivities of 100% were obtained in all the runs. At 20 °C there was no trace of secondary metathesis products in all the selected solvents.

Table 4: Activity of **18** for the SM of MO in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)	TON
[bmim][PF_6]	50	100	50
[bmim][BF_4]	54	100	54
[bmim][NTf_2]	51	100	51

4.2.1.2 Influence of the anions of IL

Anions play a significant role in determining the properties of ILs. For example, [bmim][PF_6] is immiscible with water, whereas, [bmim][BF_4] is soluble in water. Furthermore, the anions determine viscocity, density, hydrophobicity and solvation of ILs. The influence of anion on the catalytic activity of **18** at 20 °C after 4 h reaction time is shown in Figure 3. The metathesis activity showed a decreasing trend with the catalyst, according to the solvent/anion order $BF_4^- > NTf_2^- \sim PF_6^-$.

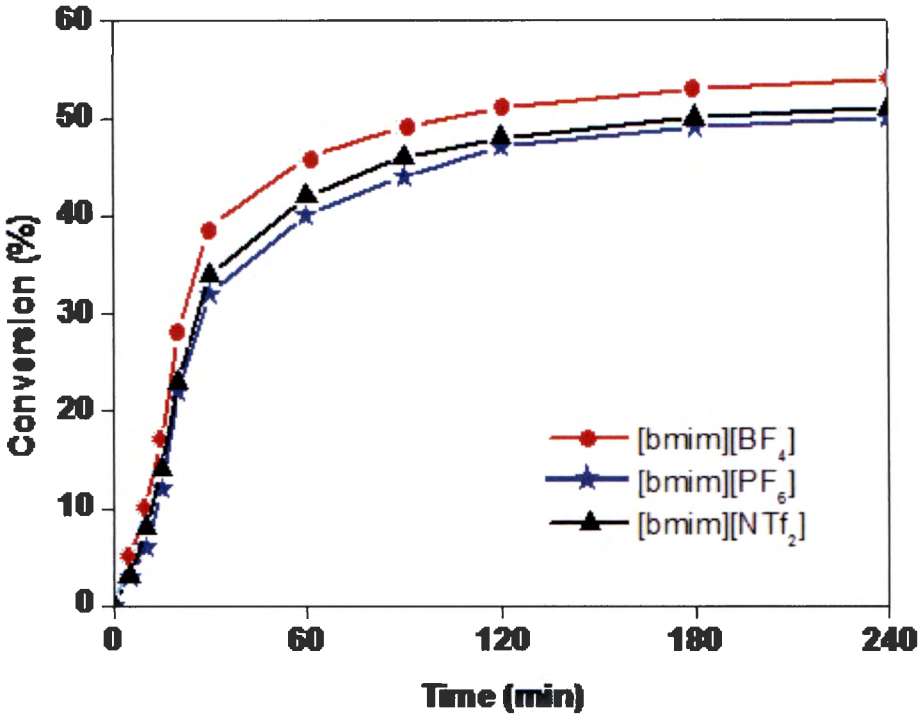


Figure 3: Influence of the anions of [bmim][X] type ILs on the activity of **18** at 20 °C.

4.2.1.3 Influence of reaction temperature

The activity of **18** in ILs at different reaction temperature is summarized in Table 5-7. Increasing the reaction temperature from 20-100 °C resulted in a rate enhancement with optimum reaction temperature reached at almost 80 °C with [bmim][PF_6]. Excellent selectivity (>98%) was achieved at moderate reaction temperatures (≤60 °C) but decreased at higher temperatures with the formation of secondary metathesis products (SMPs) shown in Scheme 34 [4]. The SMPs arising from the metathesis of methyl oleate at higher temperature are 8-heptadecene (**80**), dimethyl -9-nonadenedioate (**81**), 9-nondecene (**82**), dimethyl -8-heptadenedioate (**83**), 10-decadecene (**84**) and dimethyl -8- hexadecenedioate (**85**). A typical chromatogram resulting from the metathesis of methyl oleate at higher temperature is presented in Figure 4. The formation of SMPs at high reaction temperatures was evidence of double bond isomerization occurring.

Table 5: Activity of **18** in [bmim][PF_6] for the SM of MO at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	50	100	50
40	57	100	57
60	60	99	60
80	62	92	62
100	63	92	63

Table 6: Activity of **18** in [bmim][BF_4] for the SM of MO at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	54	100	54
40	60	100	60
60	61	99	61
80	64	92	64
100	65	92	65

Table 7: Activity of **18** in [bmim][NTf_2] for the SM of MO at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	51	100	51
40	56	100	56
60	59	99	59
80	61	92	61
100	63	92	63

Scheme 34: Secondary metathesis products resulting from the metathesis of methyl oleate

$C_9=C_8COOMe$
75
⇅
$C_{10}=C_7COOMe$
78
+
$C_8=C_9COOMe$
79
⇅
Self-metathesis of 79
80 + 81
Cross-metathesis of 75 with 78
82 + 83
Cross-metathesis of 75 with 79
84 + 85

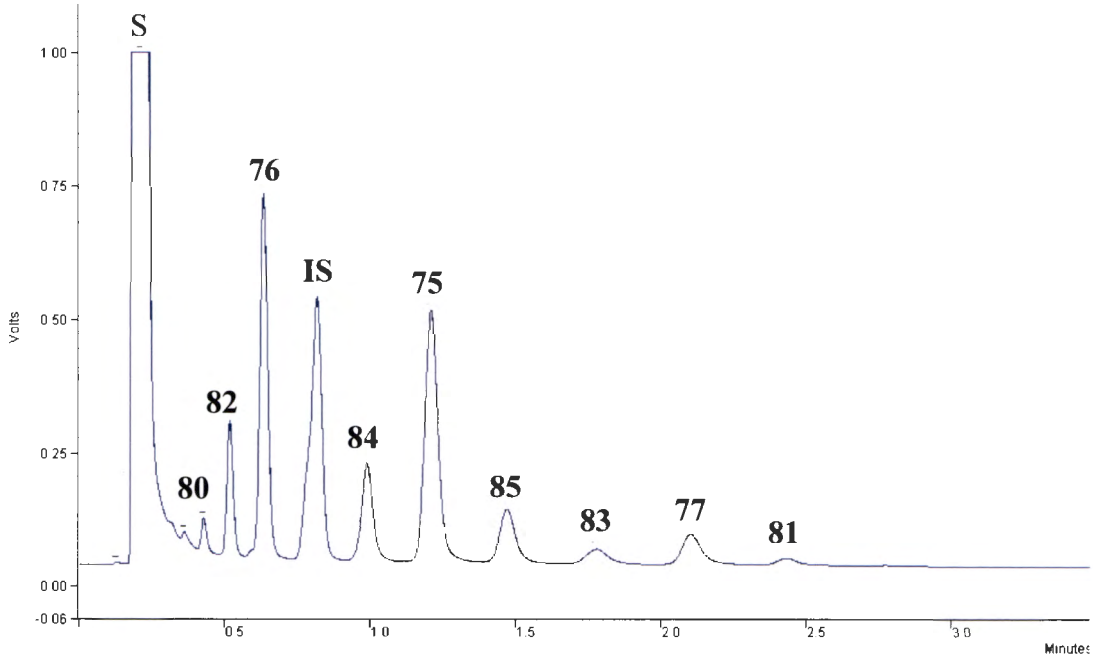


Figure 4: A typical gas chromatogram resulting from the metathesis of methyl oleate at higher reaction temperature

The activity of **18** in [bmim][X] type ILs at 40 °C, 60 °C, 80 °C and 100 °C, after 4 hour reaction time is shown in Figure 5-8. As seen in the figure, only a small difference in catalytic activity was observed at all the temperatures studied. At all the selected temperatures, a slightly higher activity was observed in $[bmim][BF_4]$. At higher temperatures of 80 and 100 °C, the

substrate conversion was found to slightly decrease, an indication of catalyst deactivation. It has been proved by several experimental studies that the catalyst decomposition sometimes leads to unwanted side reactions, such as olefin isomerizations [216-219].

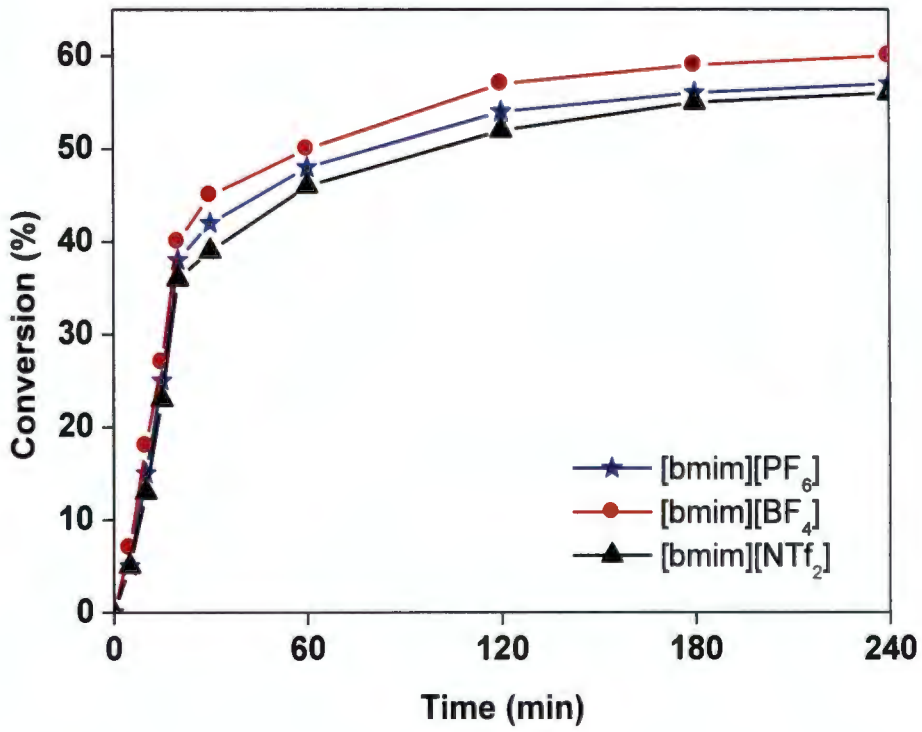


Figure 5: Conversion of MO in [bmim][X] type ILs using **18** at 40 °C

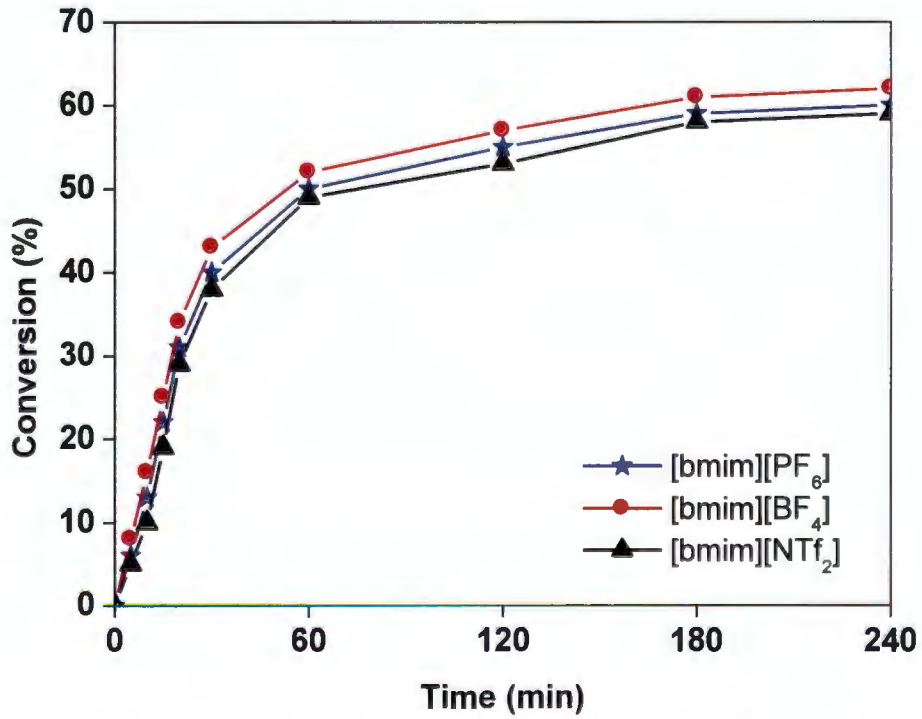


Figure 6: Conversion of MO in [bmim][X] type ILs using **18** at 60 °C

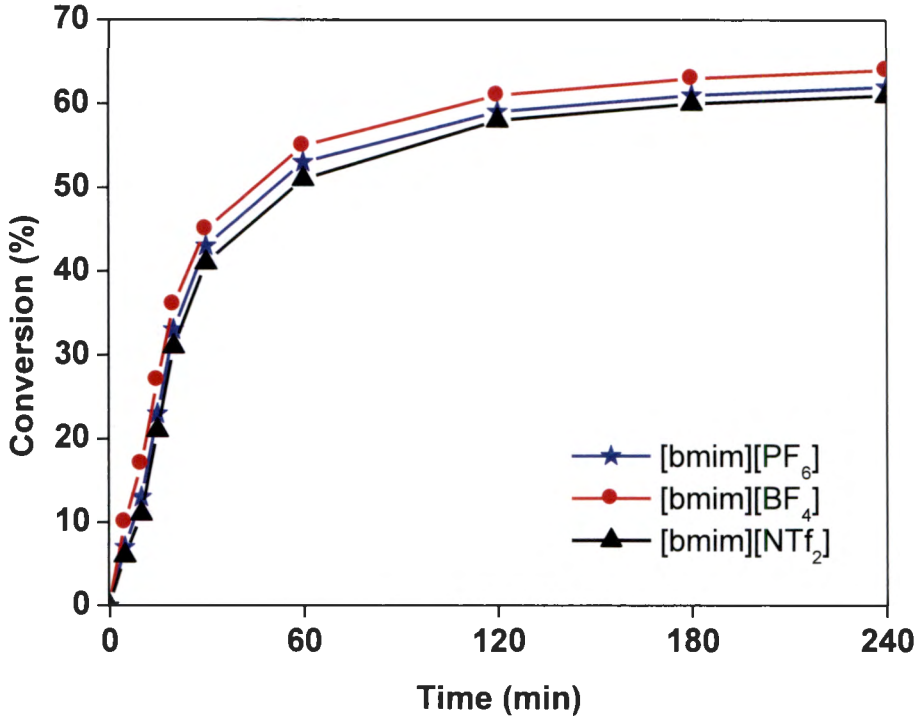


Figure 7: Conversion of MO in [bmim][X] type ILs using **18** at 80 °C

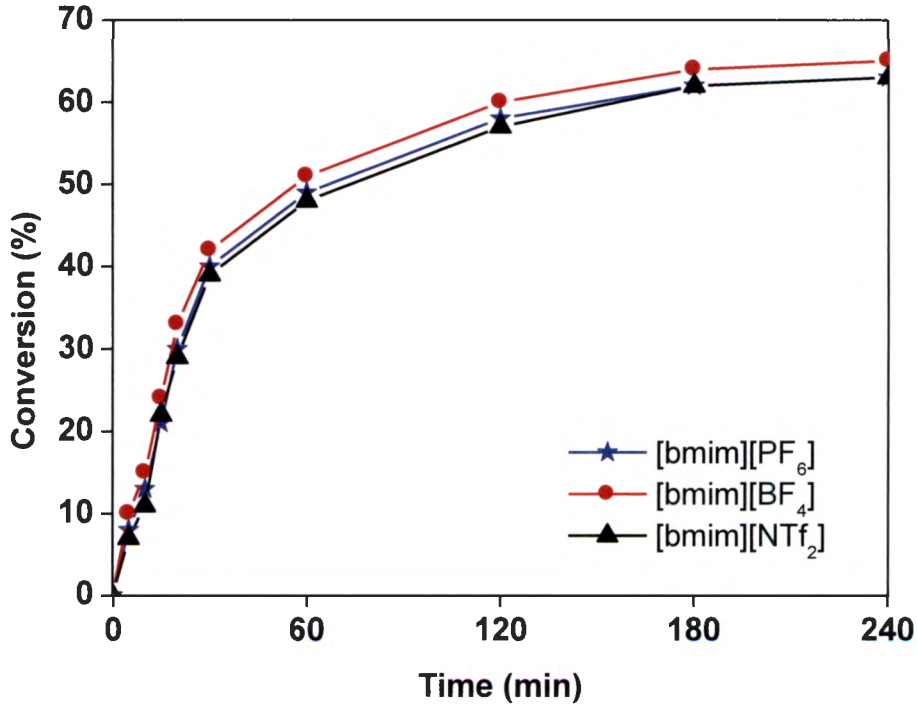


Figure 8: Conversion of MO in [bmim][X] type ILs using **18** at 100 °C

The oleate conversions as a function of reaction temperatures (20 to 100 °C) for the metathesis of methyl oleate in the presence of Grubbs catalyst **18** is shown in Figure 9. The activity of the catalyst increased with increasing temperature from 20° – 60 °C with oleate conversions increasing from 54 to 62% in [bmim][BF_4]. At higher temperatures of 80° to 100 °C, the substrate conversion remained almost steady. It has been proved by Buchowiz and Mol[18] that, for the metathesis of 4-nonene, the ruthenium catalyst, **18**, can withstand temperatures only up to 70 °C. A similar pattern was also obtained by Marvey et al. [56] for the metathesis of methyl linoleate in the presence of 3wt% ReO_7/SiO_2-$Al_2O_3/SnBu_4$ catalyst system.

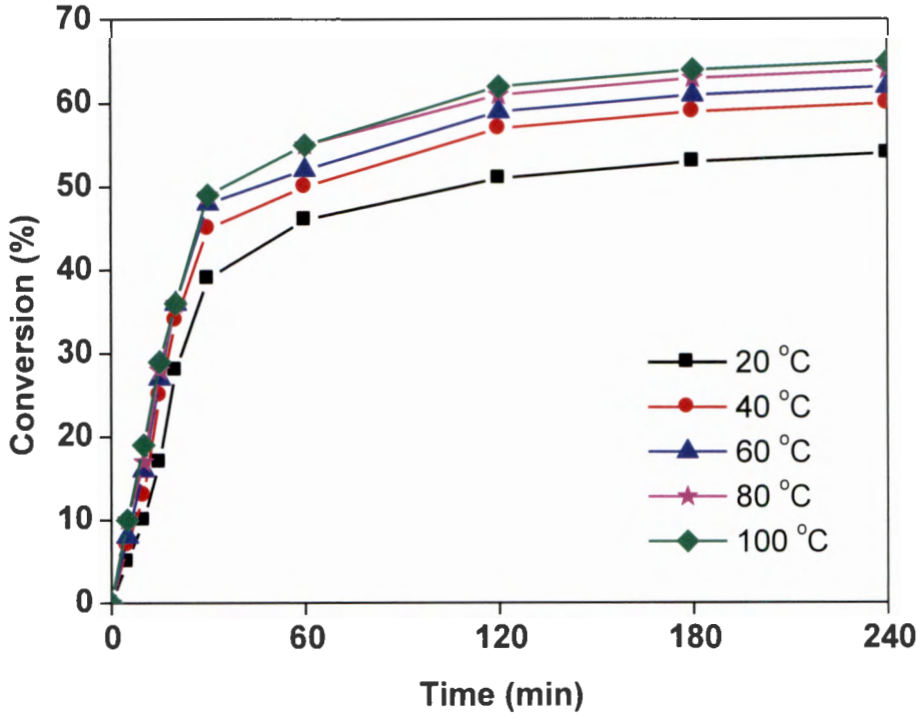


Figure 9: Influence of temperature on the activity of **18** in [bmim][BF_4] from 20 to 100 °C

4.2.1.4 Influence of the reaction atmosphere

The influence of the reaction atmosphere on the activity of Grubbs catalyst **18** was investigated using methyl oleate in [bmim][BF_4] at different temperatures. The experiment was conducted in two different reaction atmospheres, air and N_2, at the substrate/catalyst molar ratio 100:1. The activity of **18** at different temperatures in air using [bmim][BF_4] as a solvent is shown in Table 8.

Table 8: Activity of **18** for the SM of MO in air using [bmim][BF_4]

Temp (°C)	Conv (%)	Selec (%)	TON
20	52	100	52
40	58	100	58
60	60	99	60
80	62	92	62
100	63	92	63

Figures 10 to 14 reveal that the conversion of MO under N_2 is higher than under air, after 4 h reaction time. However, the activity under air was found to be higher in the first hour of reaction and thereafter it decreased. From the results, it can be concluded that Grubbs catalyst **18** is active under both atmospheres.

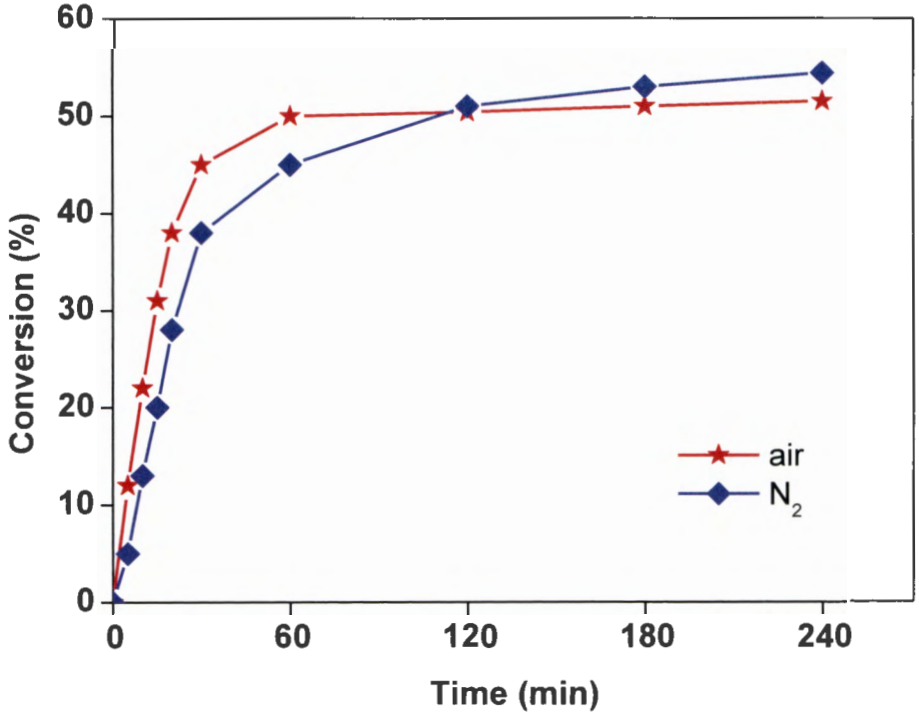


Figure 10: Conversion of MO in [bmim][BF_4] using **18** at 20 °C under air and N_2

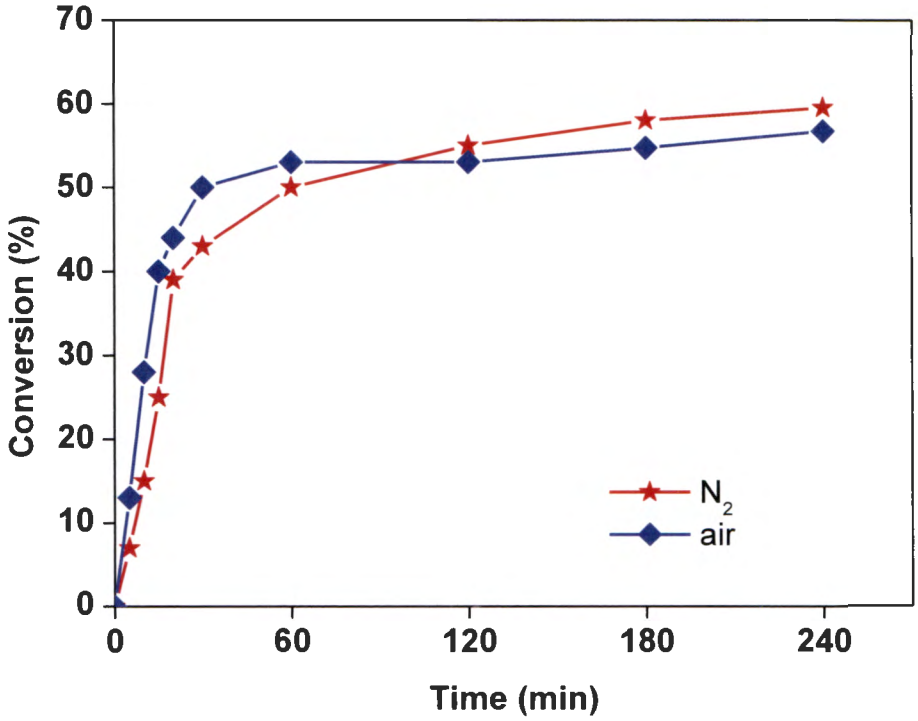


Figure 11: Conversion of MO in [bmim][BF_4] using **18** at 40 °C under air and N

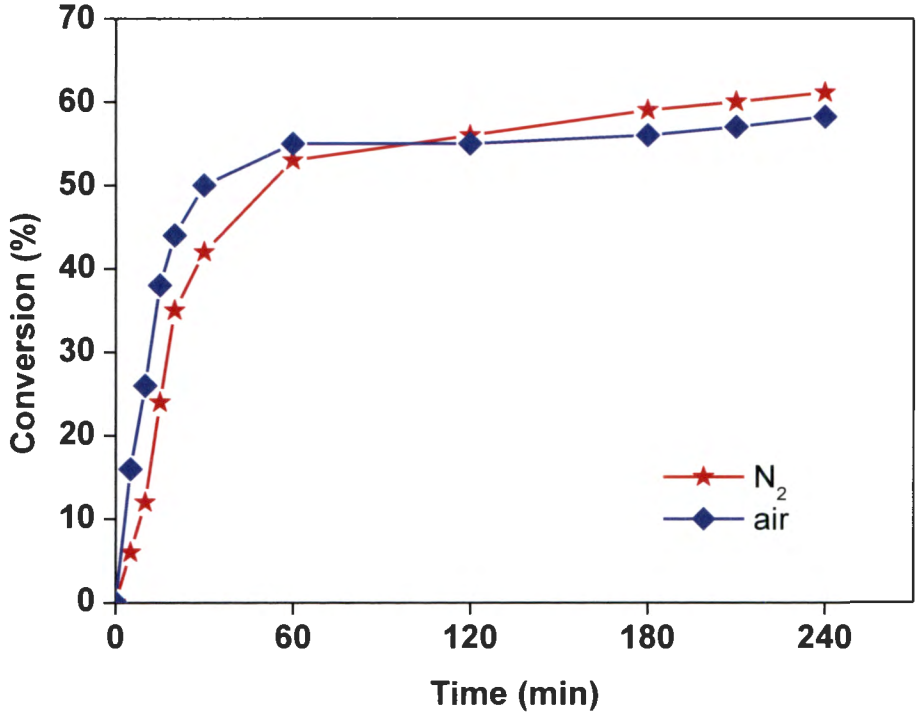


Figure 12: Conversion of MO in [bmim][BF_4] using **18** at 60 °C under air and N_2

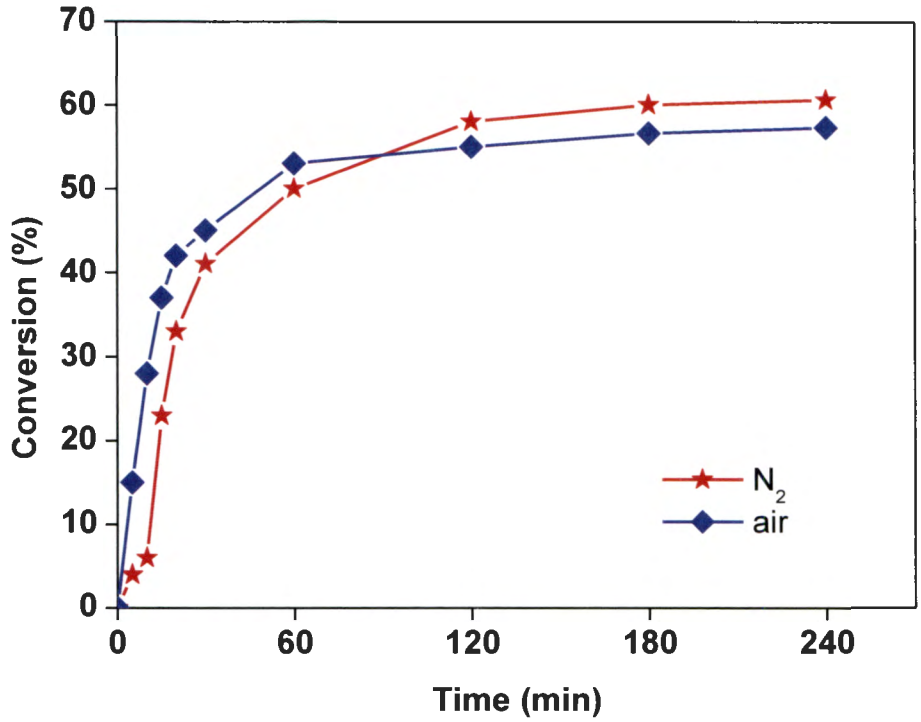


Figure 13: Conversion of MO in [bmim][BF_4] using **18** at 80 °C under air and N_2

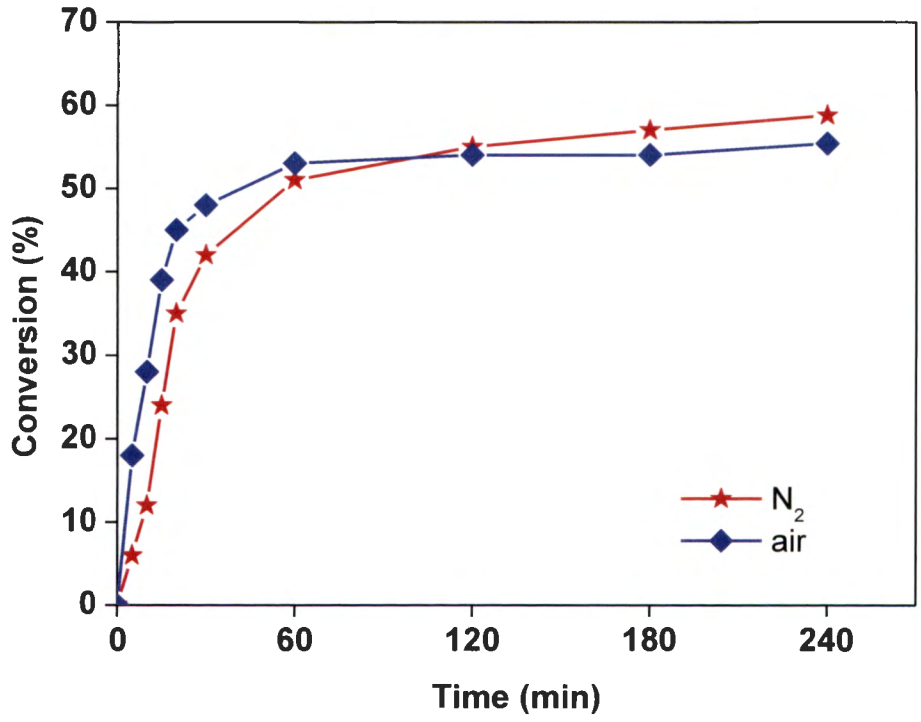


Figure 14: Conversion of MO in [bmim][BF_4] using **18** at 100 °C under air and N_2

4.2.2 Metathesis of methyl oleate in [bdmim][X] type ILs

Self-metathesis of methyl oleate was carried out in [bdmim][X] type ILs. The ILs selected for the study were [bdmim][PF_6] and [bdmim][BF_4]. The reactions were carried out at temperatures ranging from 20-100 °C. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.5 mL of methyl oleate followed by the addition of 12.3 mg of Grubbs catalyst.

The activity of **18** in [bdmim][X] type ILs at different reaction temperature is summarized in Tables 9 and 10. At all the selected temperatures, the highest conversion was observed in [bdmim][BF_4]. At 20 °C, a conversion of 55% was observed, which then increased upto 60% at 60 °C and thereafter it decreased, showing the deactivation of catalyst. Excellent selectivities were obtained at temperature up to 60 °C and thereafter it decreased showing the presence of SMPs.

Table 9: Activity of **18** for the SM of MO in [bdmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	52	100	52
40	55	100	55
60	60	99	61
80	57	92	57
100	53	92	53

Table 10: Activity of **18** for the SM of MO in [bdmim][BF_4] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	55	100	55
40	57	100	57
60	62	99	62
80	59	92	59
100	55	92	55

The conversion of MO in [bmim][X] and [bdmim][X] type ILs at different reaction temperature is shown in Figures 15-19. At 20 °C and 60 °C, the highest conversion was observed in [bdmim][BF_4], whereas at other temperatures, the reaction in [bmim][BF_4] excelled.

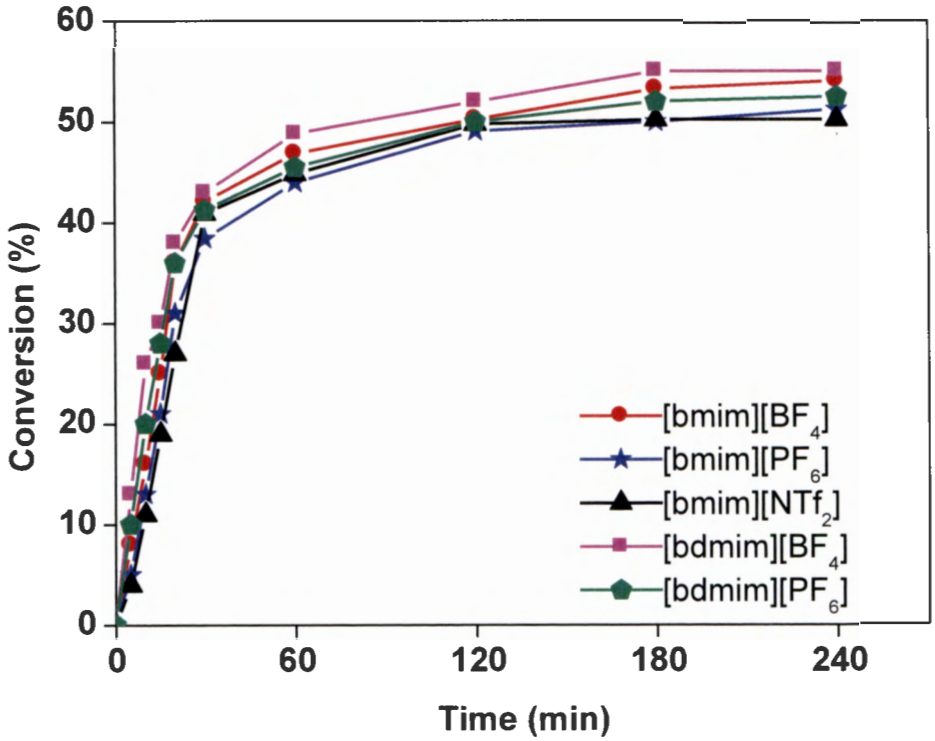


Figure 15: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **18** at 20 °C

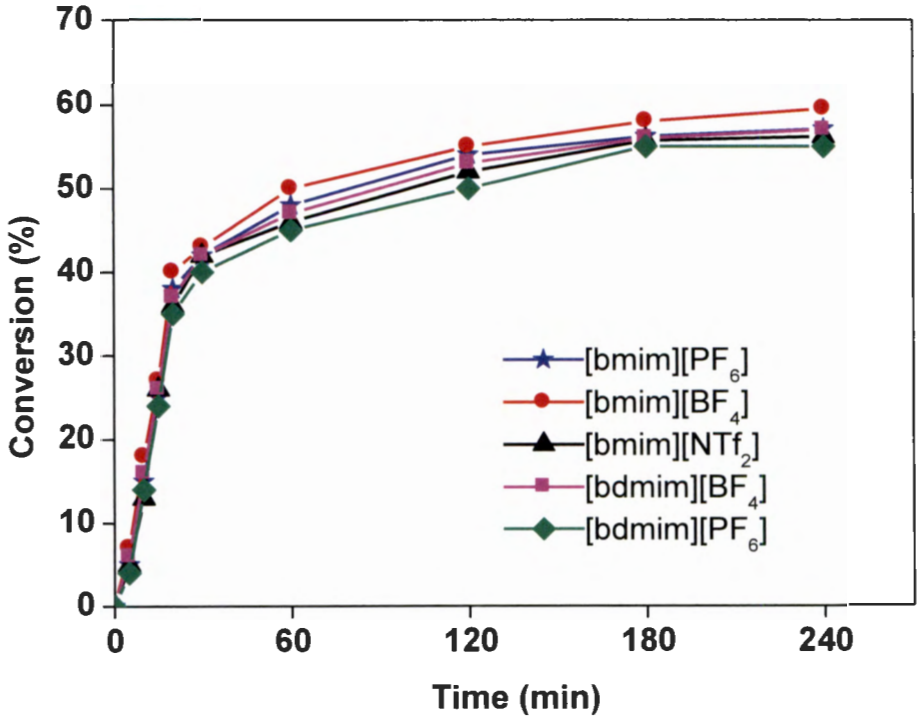


Figure 16: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **18** at 40 °C

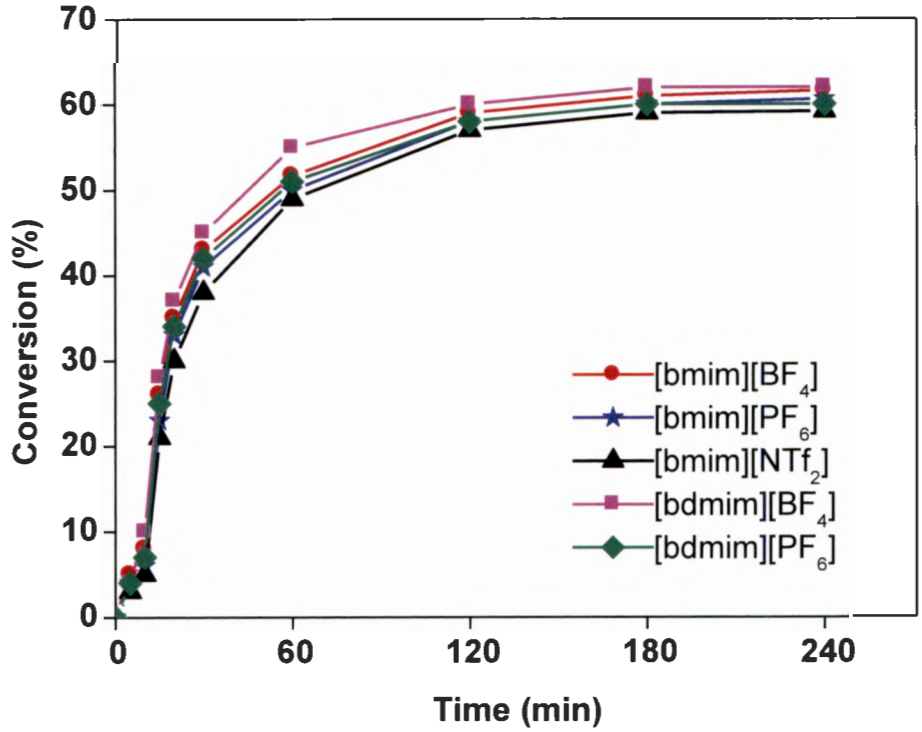


Figure 17: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **18** at 60 °C

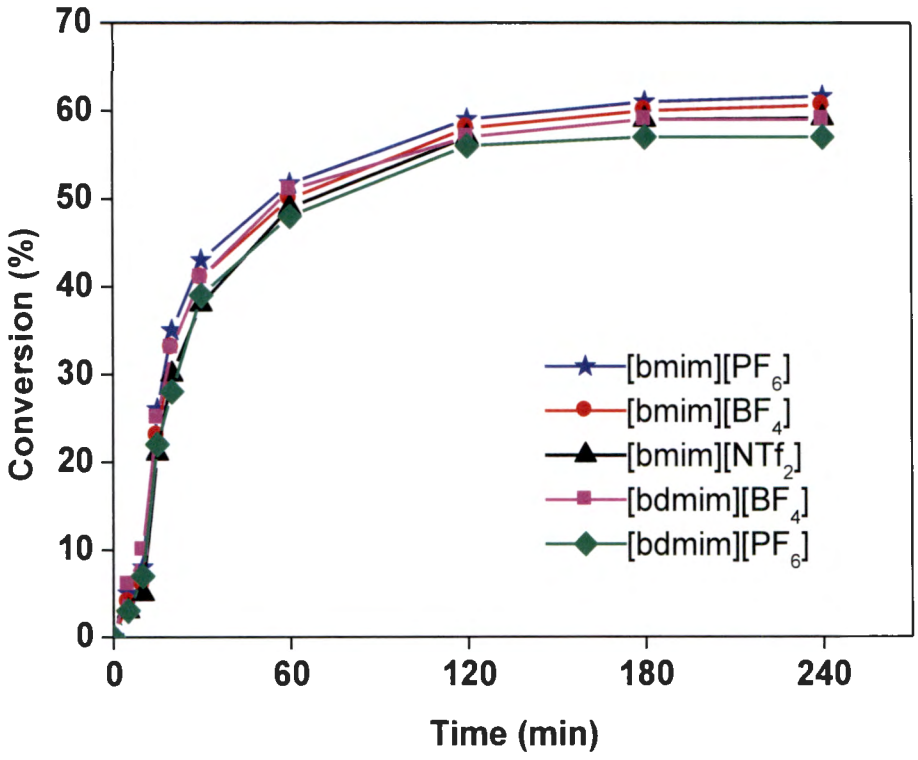


Figure 18: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **18** at 80 °C

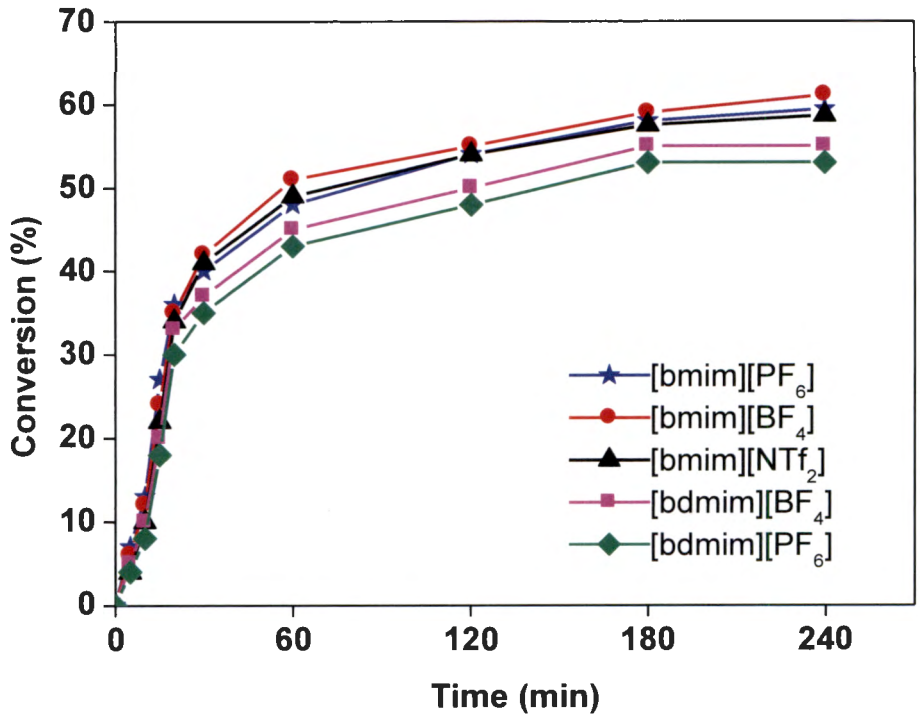


Figure 19: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **18** at 100 °C

4.2.3 Metathesis of methyl ricinoleate (MR) in [bmim][X] and [bdmim][X] type ILs

The self-metathesis of methyl ricinoleate was carried out in the presence of Grubbs catalyst **18** at 20 °C using [bmim][X] and [bdmim][X] type ILs. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.2 mL of substrate followed by the addition of 0.59 mg of Grubbs catalyst. A typical chromatogram resulting from the metathesis of methyl ricinoleate is shown in Figure 20. The primary metathesis products obtained from the metathesis of methyl ricinoleate are 9-octadecene-7,12-diol and dimethyl 9-octadecenedioate (**Scheme 35**).

The activity of **18** in [bmim][X] type ILs is summarized in table 11. At 20 °C, a conversion of 45% was obtained for the reaction in [bmim][BF_4], whereas the reaction in [bmim][PF_6] gave only a conversion of 41%. The activity of $RuCl_2(PCy_3)_2$(=CHPh) dereased in the order [bmim][PF_6] > [bmim][BF_4] > [bmim][NTf_2]. Excellent selectivity (99%) was obtained, showing the absence of secondary metathesis products. The activity of **18** in [bmim][X] type ILs at 20 °C is shown in Figure 21.

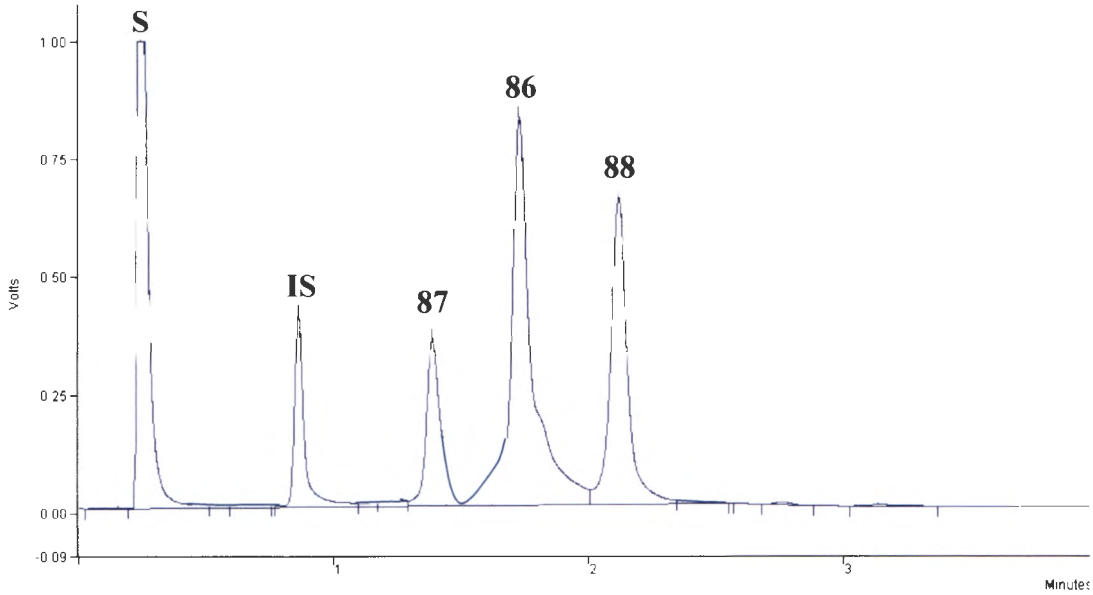
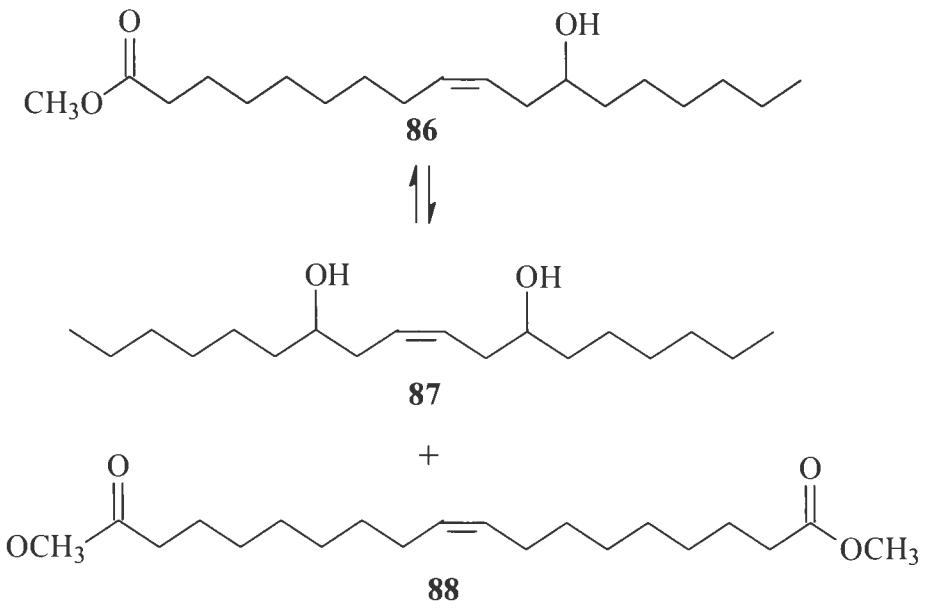


Figure 20: Chromatogram resulting from the metathesis of methyl ricinoleate.



Scheme 35: Primary metathesis products from self-metathesis of methyl ricinoleate

Table 11: Activity of **18** for the SM of MR in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bmim][PF_6]	41	100
[bmim][BF_4]	45	100
[bmim][NTf_2]	38	100

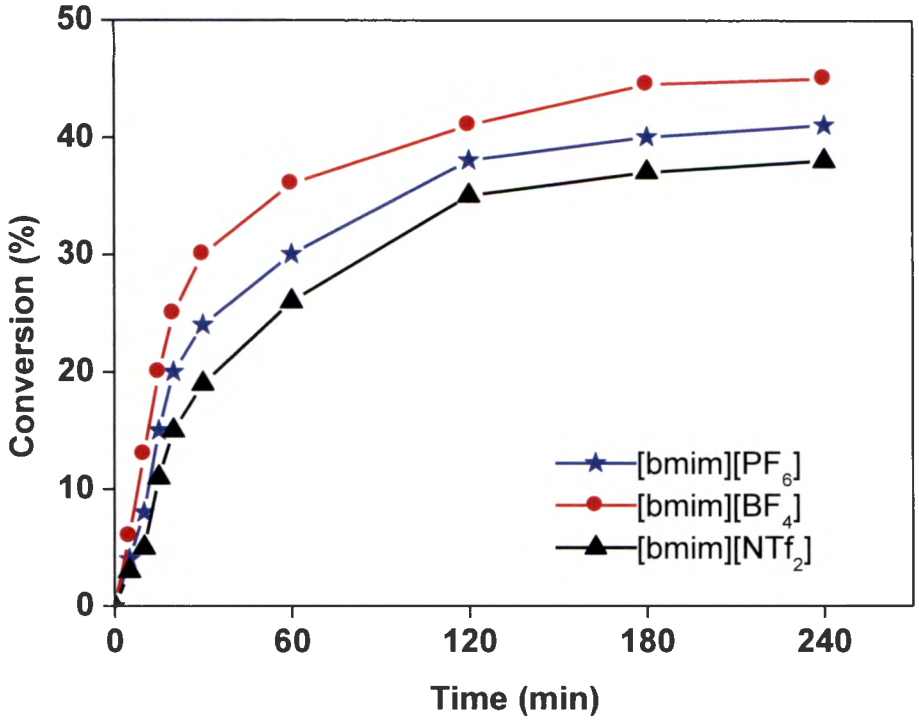


Figure 21: Conversion of MR in [bmim][X] type ILs using **18** at 20 °C

Table 12: Activity of **18** for the SM of MR in [bdmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bdmim][PF_6]	43	100
[bdmim][BF_4]	49	100

The SM of methyl ricinoleate was also carried out in [bdmim][X] type ILs at 20 °C. The activity of **18** for the conversion of methyl ricinoleate in [bdmim][X] type ILs at 20 °C is shown in Table 12. A conversion of 49 % was obtained in [bdmim][BF_4], whereas a conversion of 43 % was obtained in [bdmim][PF_6]. The activity of **9** in [bdmim][X] type ILs is compared in Figure 22. The highest conversion was obtained in [bdmim][BF_4]. The influence of cations of the ILs on the activity of **18** for the SM of methyl ricinoleate at 20 °C is compared in Figure 23. It is clear from the figure that [bdmim] cations excelled [bmim] cations in the reaction.

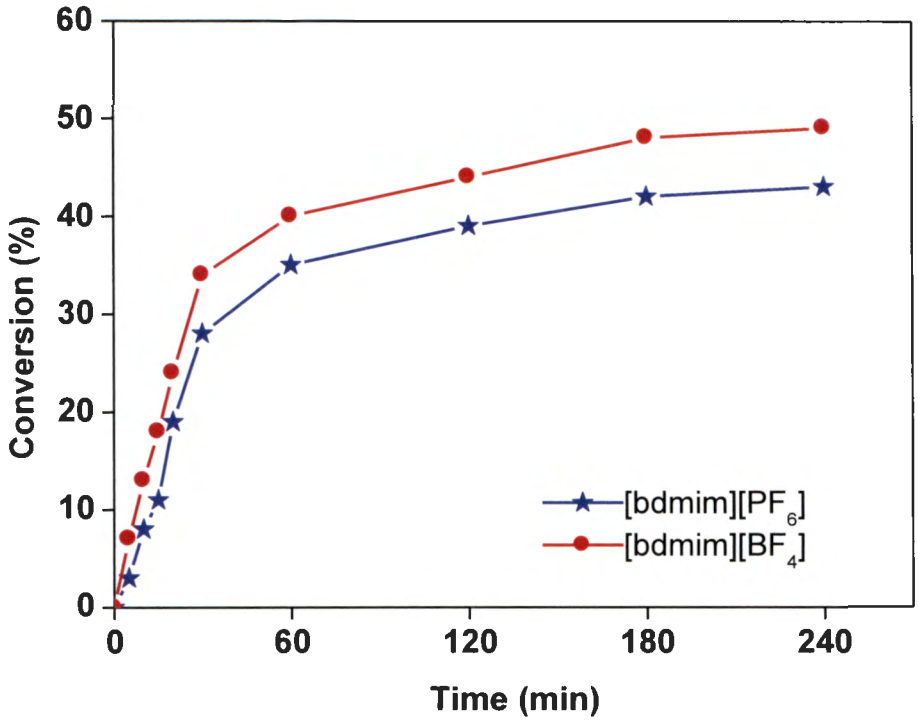


Figure 22: Conversion of MR in [bdmim][X] type ILs using **18** at 20 °C

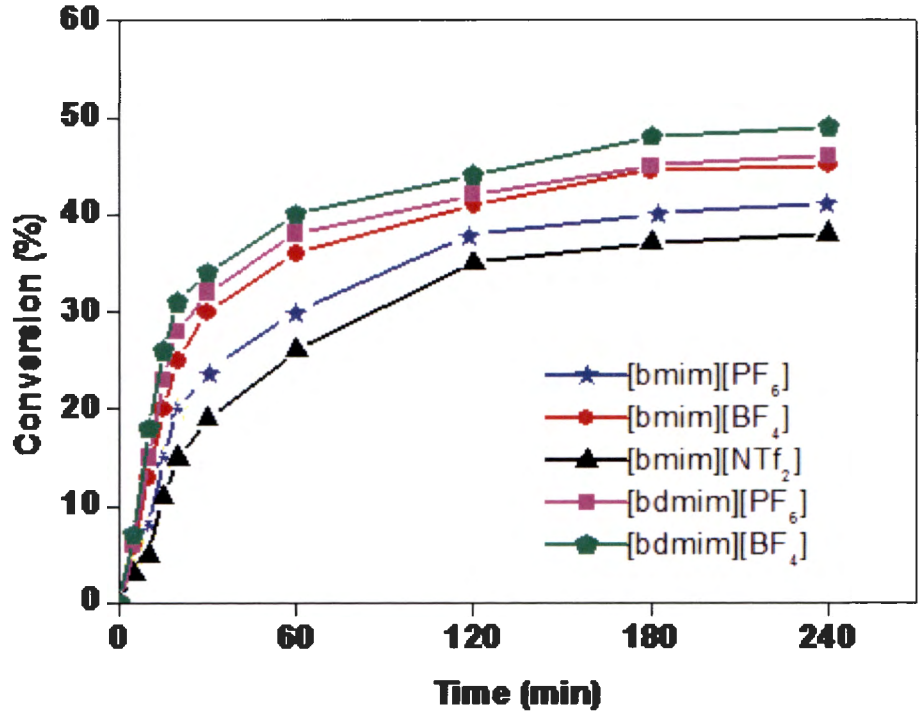


Figure 23: Conversion of MR in [bmim] and [bdmim][X] type ILs using **18** at 20 °C

4.2.4 Metathesis of methyl oleate in organic solvents

The self-metathesis of methyl oleate was carried out using Grubbs catalyst **18** in conventional organic solvents. The organic solvents selected for the study are dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **18** in selected organic solvents at 20, 40, 60, 80 and 100 °C, respectively is shown in Table 13 to 16. At all the selected temperatures, the best catalytic performance was observed in DCM and the lowest in PhMe. The activity of **18** was found to increase in the order PhMe < PhCl < DCE ~ DCM, in accordance with an increase in solvent polarity. Selectivity towards PMPs was 100% in all the selected organic solvents. The conversion of methyl oleate in organic solvents at different temperatures is shown in Figure 24 to 28. Metathesis in DCM and DCE exhibited similar substrate conversion. MO conversion of 50 and 48 was observed in DCM and DCE respectively. These results are in agreement with those obtained by Buchowicz and Mol [18] and Marvey *et al.* [6].

Table 13: Activity of **18** for the SM of MO in DCM at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	50	100
40	52	100
60	59	98
80	58	91
100	55	91

Table 14: Activity of **18** for the SM of MO in DCE at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	48	100
40	50	100
60	57	98
80	55	91
100	50	91

Table 15: Activity of **18** for the SM of MO in PhCl at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	45	100
40	48	100
60	53	98
80	50	91
100	47	91

Table 16: Activity of **18** for the SM of MO in PhMe at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	43	100
40	46	100
60	50	98
80	47	91
100	45	91

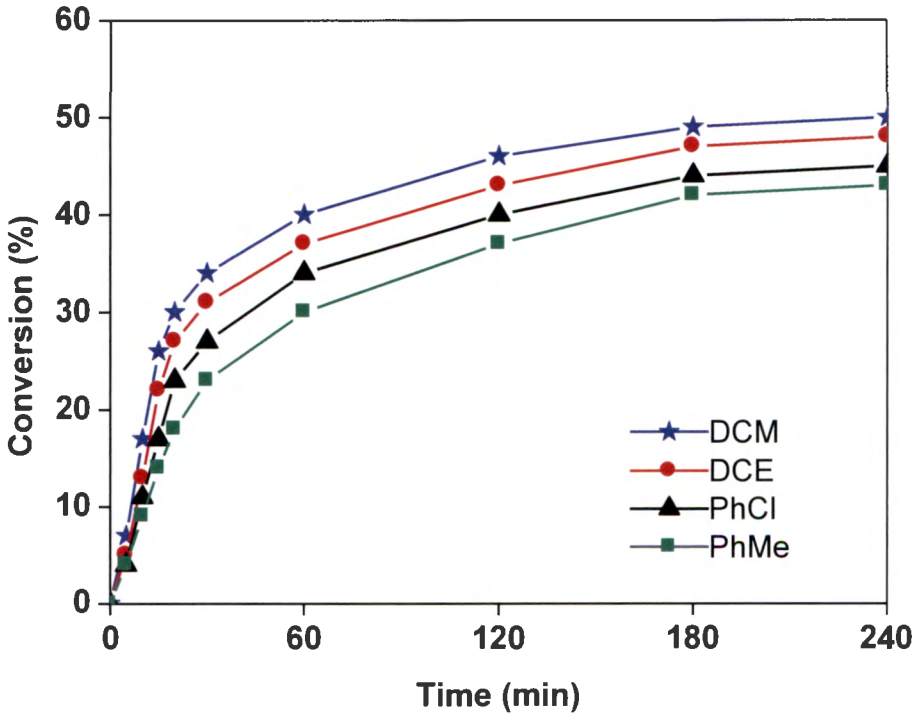


Figure 24: Conversion of MO in organic solvents using **18** at 20 °C

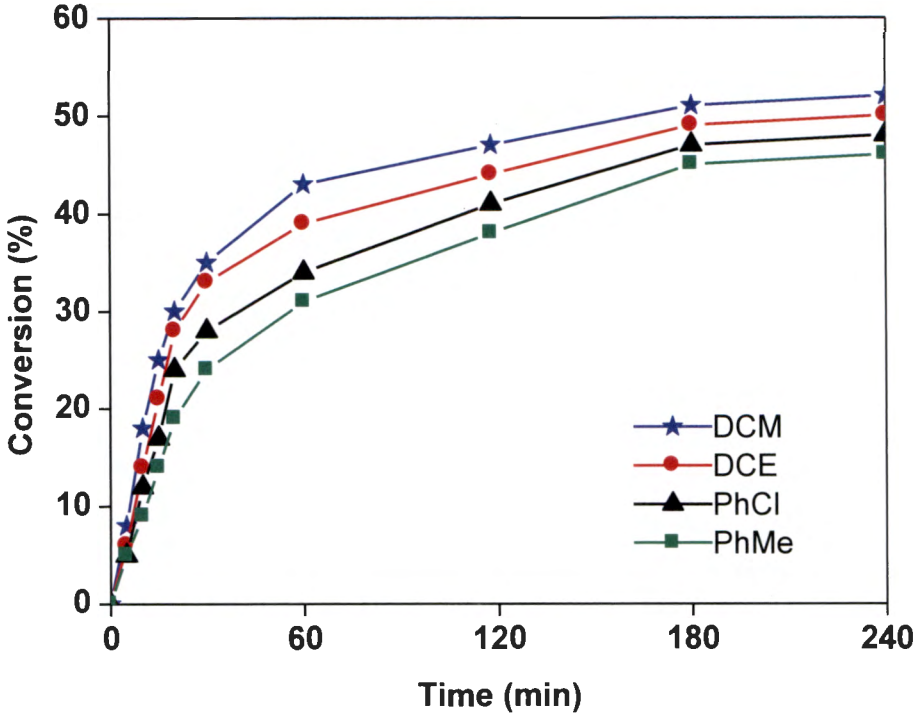


Figure 25: Conversion of MO in organic solvents using **18** at 40 °C

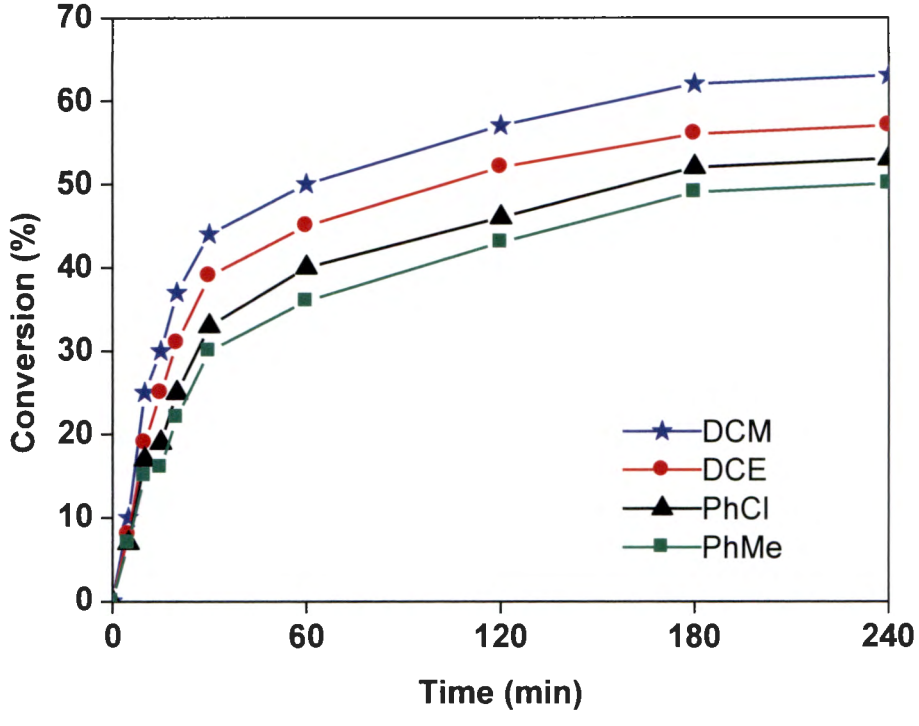


Figure 26: Conversion of MO in organic solvents using **18** at 60 °C

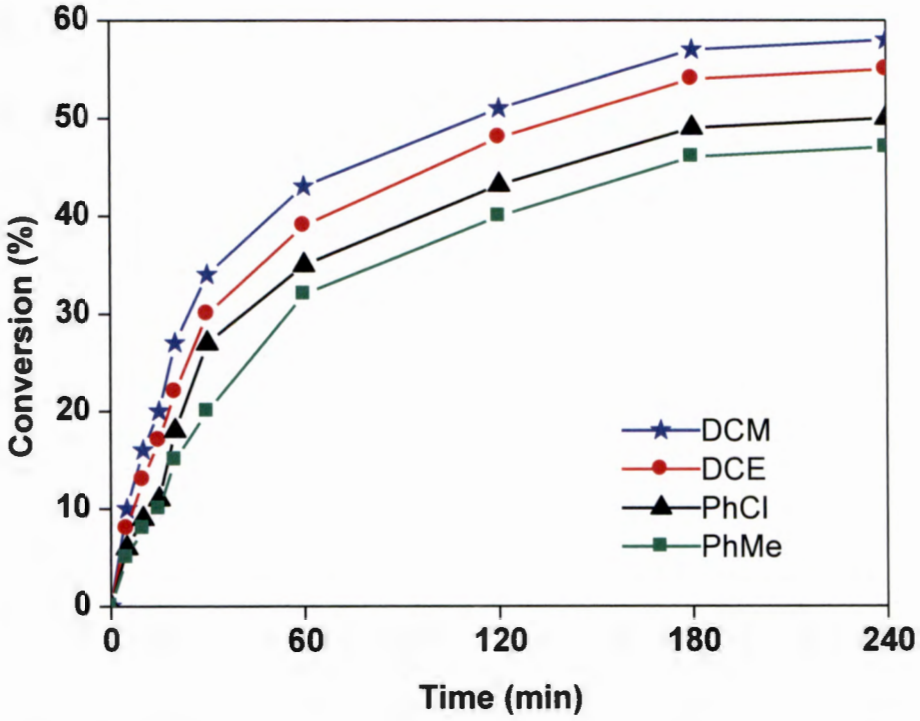


Figure 27: Conversion of MO in organic solvents using **18** at 80 °C

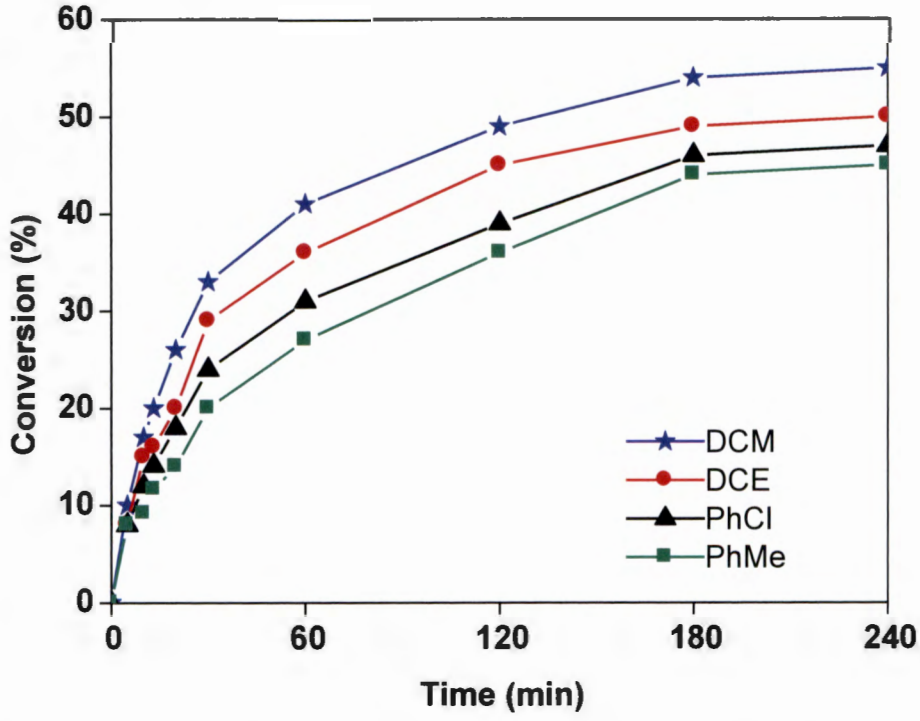


Figure 28: Conversion of MO in organic solvents using **18** at 100 °C

In Figures 29 to 33 a comparison of the activity of **18** in selected ILs and organic solvents at different temperatures is made. It is clear from the figures that a significant rate enhancement occurred in ILs when compared to the organic solvents.

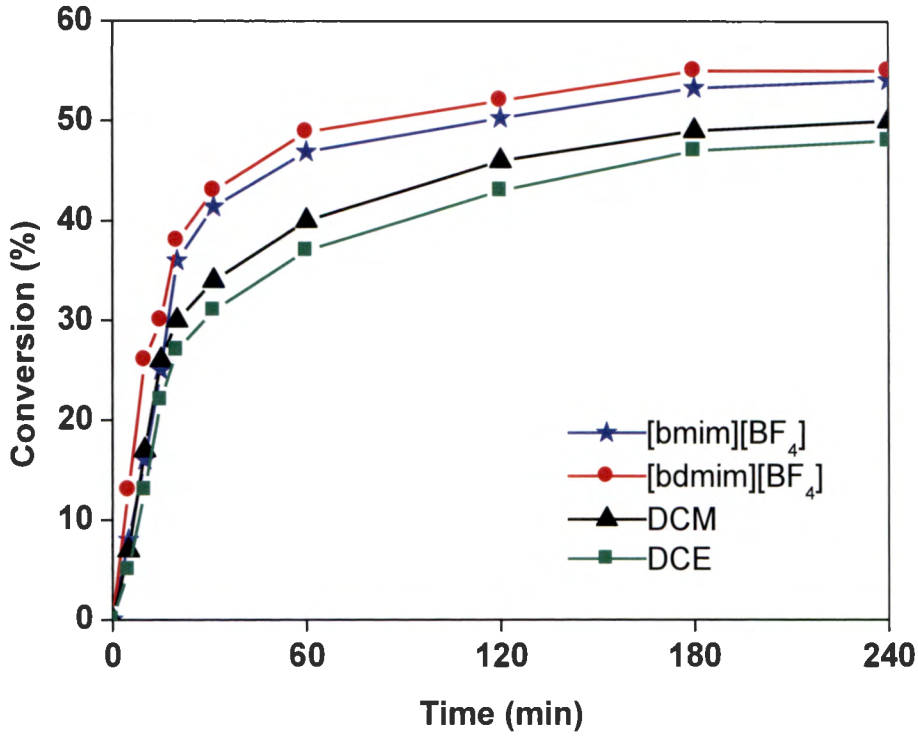


Figure 29: Conversion of MO in selected ILs and organic solvents using **18** at 20 °C

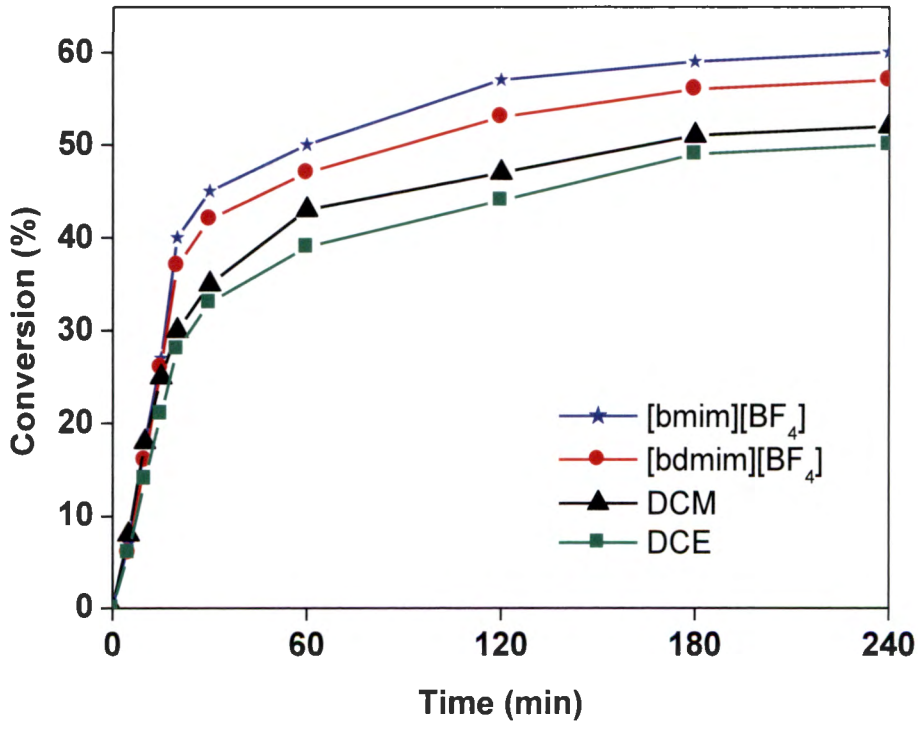


Figure 30: Conversion of MO in selected ILs and organic solvents using **18** at 40 °C

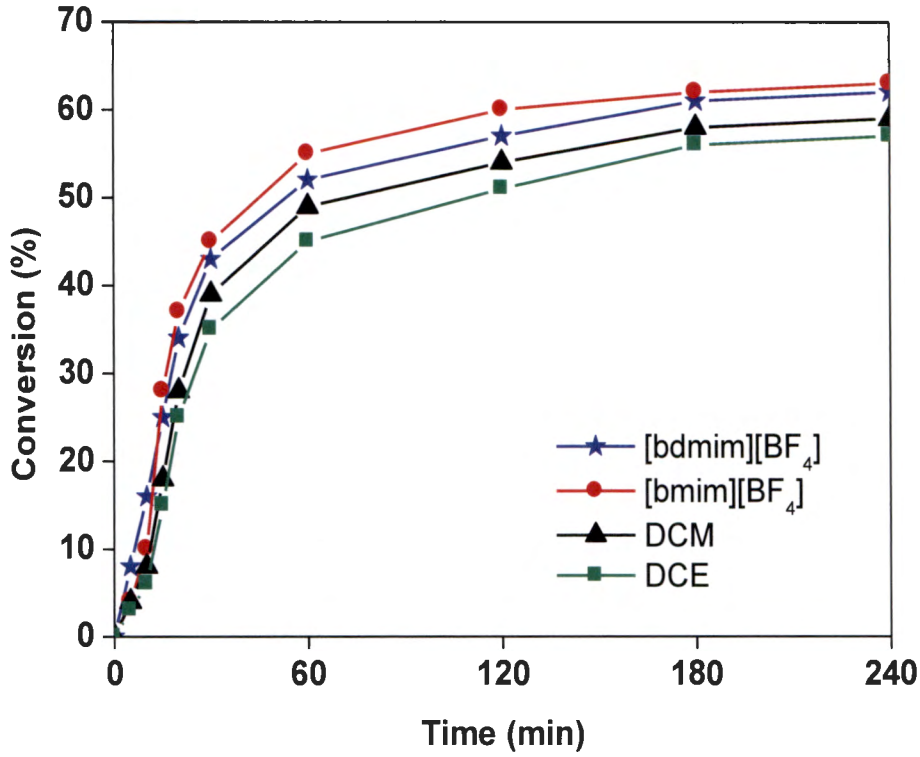


Figure 31: Conversion of MO in selected ILs and organic solvents using **18** at 60 °C

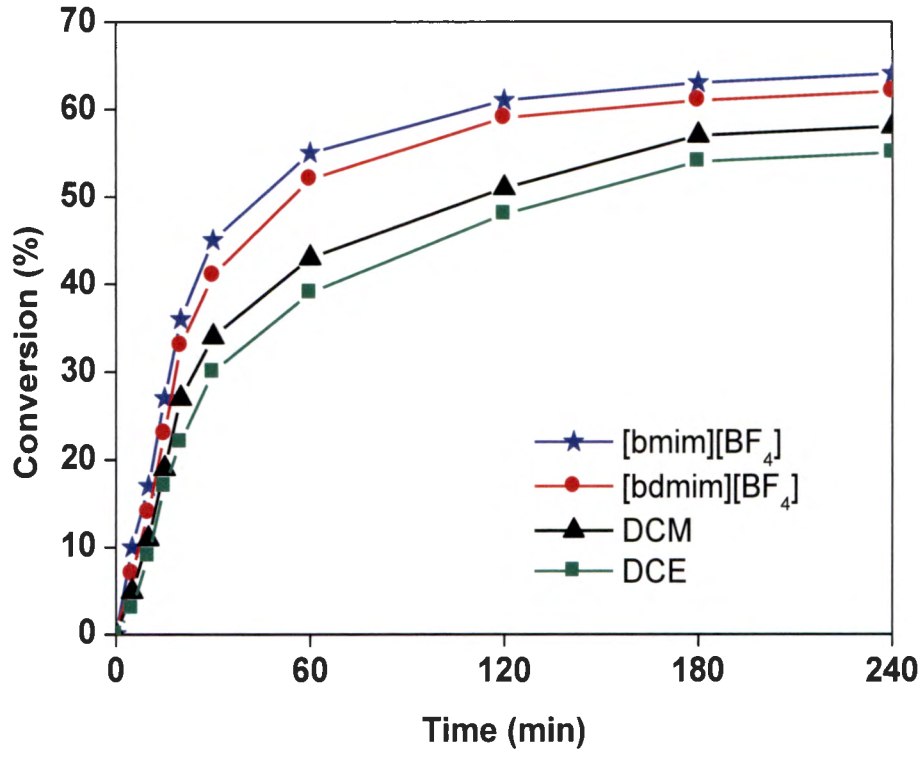


Figure 32: Conversion of MO in selected ILs and organic solvents using **18** at 80 °C

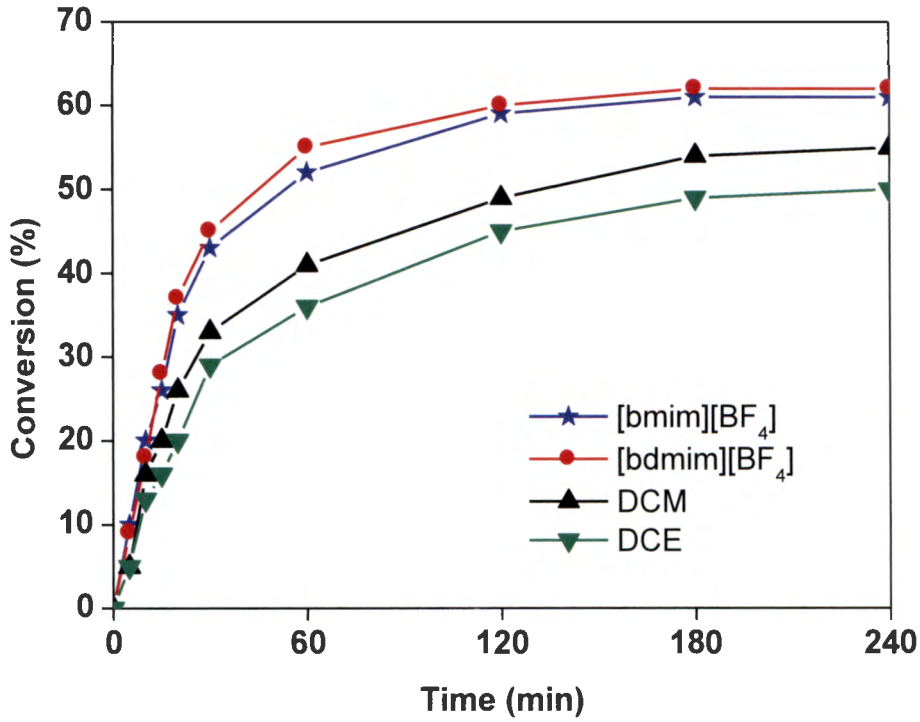


Figure 33: Conversion of MO in selected ILs and organic solvents using **18** at 100 °C

4.2.5 Metathesis of methyl ricinoleate (MR) in organic solvents

The SM of methyl ricinoleate using Grubbs catalyst **18** was carried out in four different organic solvents, namely; dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **18** in selected organic solvents at 20 °C is shown in Table 17. Grubbs catalyst **18** showed highest activity in DCM with a substrate conversion of 36% and the lowest in PhMe with a conversion of 31%. The activity of **18** was found to be in the order DCM > DCE > PhCl > PhMe. Excellent selectivity of 99 % was observed at a temperature of 20 °C, showing the absence of SMPs.

Table 17: Activity of **18** for the SM of MR in organic solvents at 20 °C after 4 h reaction time

Solvent	Conv (%)	Selec (%)
DCM	36	99
DCE	35	99
PhCl	33	99
PhMe	31	99

The conversion of MR in organic solvents in the presence of **9** at 20 °C is shown in Figure 34 while in Figure 35 a comparison of the activity of **18** in selected organic solvents and

[bdmim][X] ILs at 20 °C is made. It is clear from the figure that a significant rate enhancement occurred in [bdmim][X] ILs compared to organic solvents.

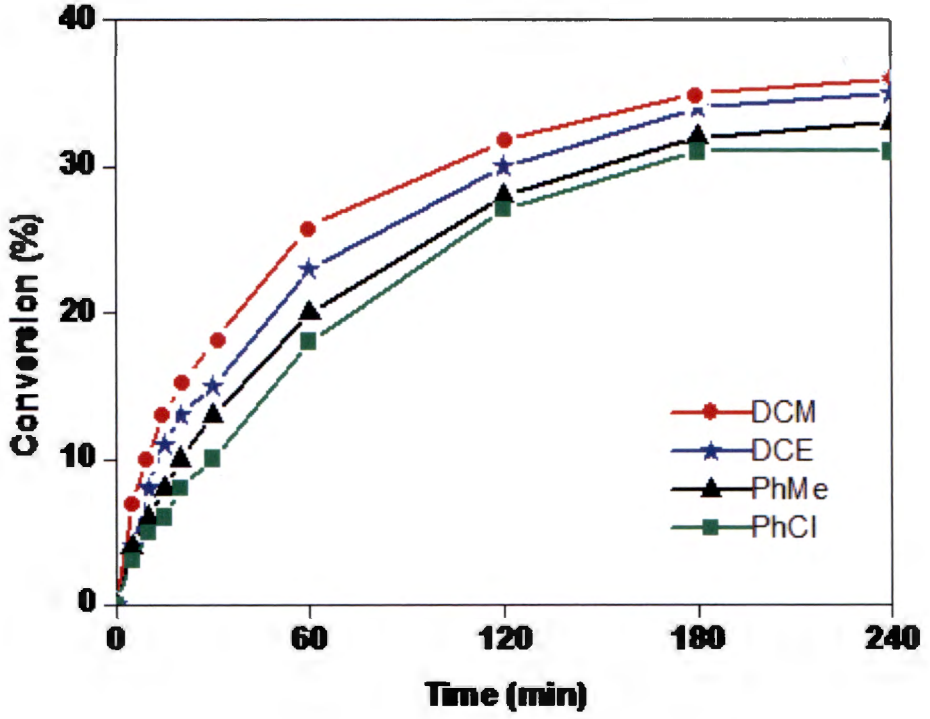


Figure 34: Conversion of MR in organic solvents using **18** at 20 °C

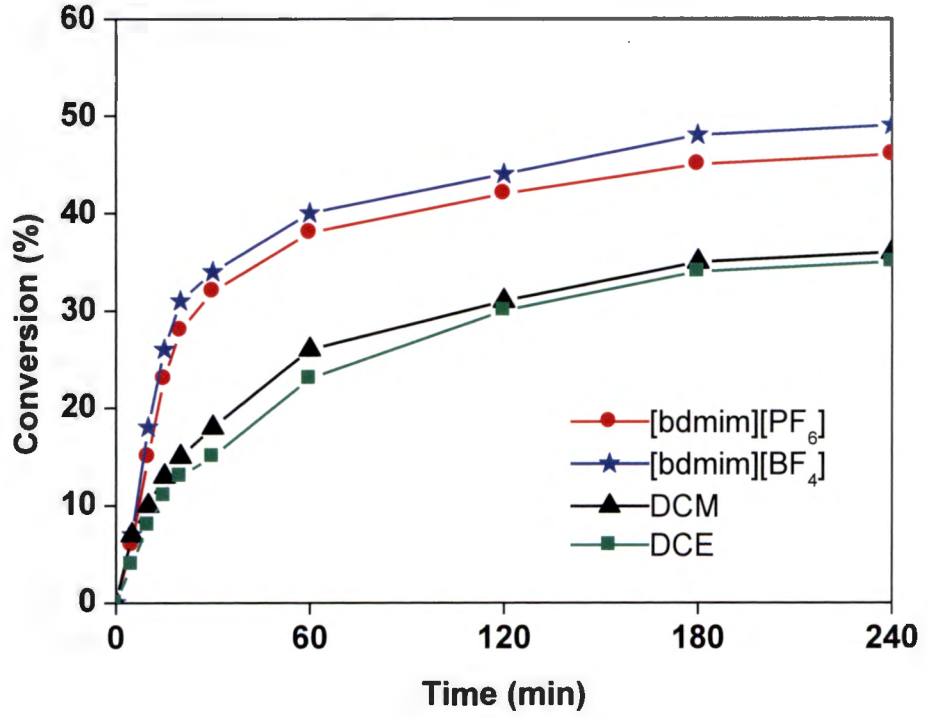
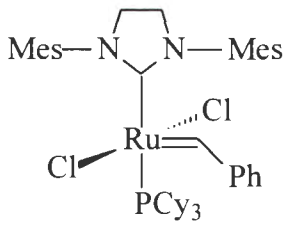


Figure 35: Conversion of MR in selected organic solvents and ILs using **18** at 20 °C

4.3 Metathesis of unsaturated fatty acid esters using Grubbs second generation catalyst 19



19

4.3.1 Metathesis of methyl oleate in [bmim][X] type ILs

The reactivity of methyl oleate in [bmim][X] type ILs was investigated in the presence of Grubbs catalyst **19**. The substrate/catalyst molar ratio used was 100:1. The reactions were carried out at different temperatures ranging from 20 °C to 100 °C. The ILs selected for the study were [bmim][PF_6], [bmim][BF_4] and [bmim][NTf_2]. In all the reactions, 1 mL of the particular solvent was added to 0.5 mL of substrate followed by the addition of 12.3 mg of Grubbs catalyst.

4.3.1.1 Influence of the solvent

The influence of [bmim][X] ILs in the metathesis of methyl oleate was investigated in the presence of catalyst **19** at different temperatures. The activity of **19** for the SM of methyl oleate in [bmim][X] type ILs is shown in Table 18. The highest activity was observed in [bmim][NTf_2] with a substrate conversion of 61% and the lowest in [bmim][PF_6] with a conversion of 53%. A 100 % selectivity was obtained in all the runs showing the absence of SMPs.

Table 18: Activity of **19** for the SM of MO in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)	TON
[bmim][PF_6]	53	100	53
[bmim][BF_4]	59	100	59
[bmim][NTf_2]	61	100	61

4.3.1.2 Influence of the anions of IL

The influence of anions of IL on the metathesis of methyl oleate using **19** has been studied. The influence of anion on the catalytic activity of **19** is shown in Figure 36. Metathesis activity increased in the order $NTf_2^- > BF_4^- > PF_6^-$.

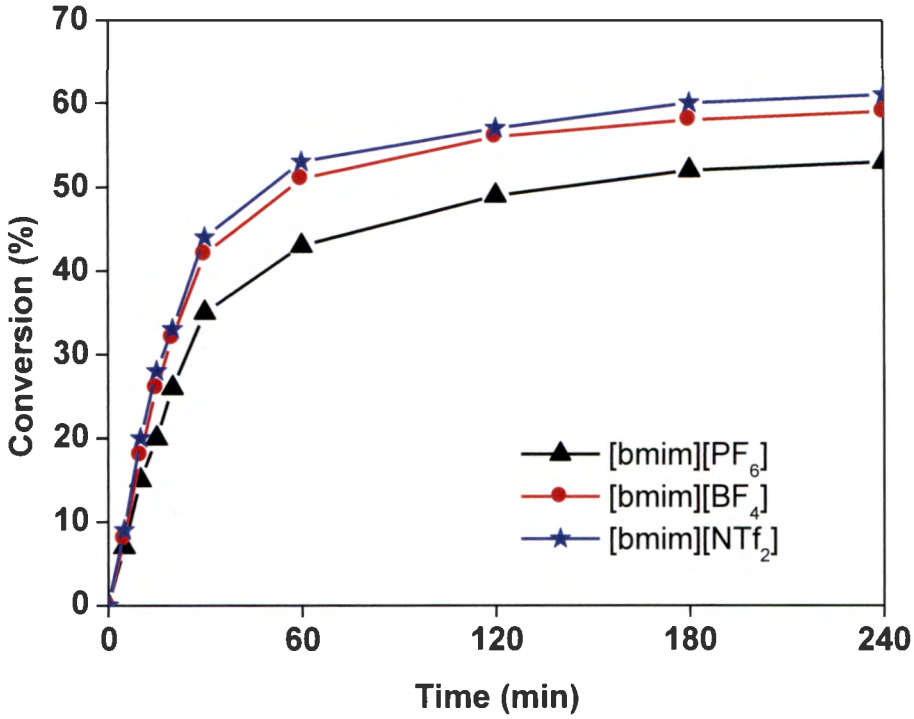


Figure 36: Influence of the anions of [bmim][X] type ILs on the activity of **19** at 20 °C.

4.3.1.3 Influence of reaction temperature

The influence of reaction temperature on the activity of **19** for the SM of methyl oleate was investigated. A summary of the activity of **19** in [bmim][X] type ILs at different reaction temperature is given in Table 19 to 21. At 20 °C, the highest conversion of 61% was observed in [bmim][NTf_2] followed by the reaction in [bmim][BF4] (59%). At all other temperatures (40, 60, 80 and 100 °C), the highest conversion occurred in [bmim][BF_4]. The conversion of methyl oleate in [bmim][X] type ILs at 40 °C, 60 °C, 80 °C and 100 °C, after 4 hour reaction time is shown in Figures 37 to 40.

Table 19: Activity of **19** for the SM of MO in [bmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	53	100	53
40	65	96	65
60	72	82	75
80	79	76	79
100	81	69	81

Table 20: Activity of **19** for the SM of MO in [bmim][BF_4] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	59	100	59
40	69	96	69
60	78	82	78
80	83	76	83
100	85	69	85

Table 21: Activity of **19** for the SM of MO in [bmim][NTf_2] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	61	100	61
40	67	96	67
60	75	82	73
80	80	76	80
100	82	69	82

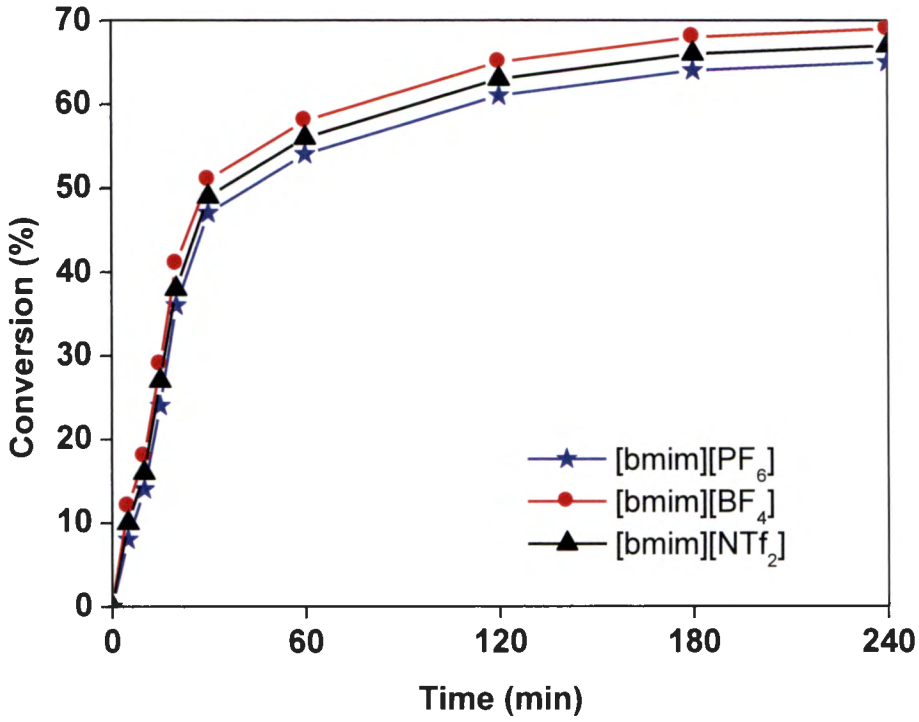


Figure 37: Conversion of MO in [bmim][X] type ILs using **19** at 40 °C

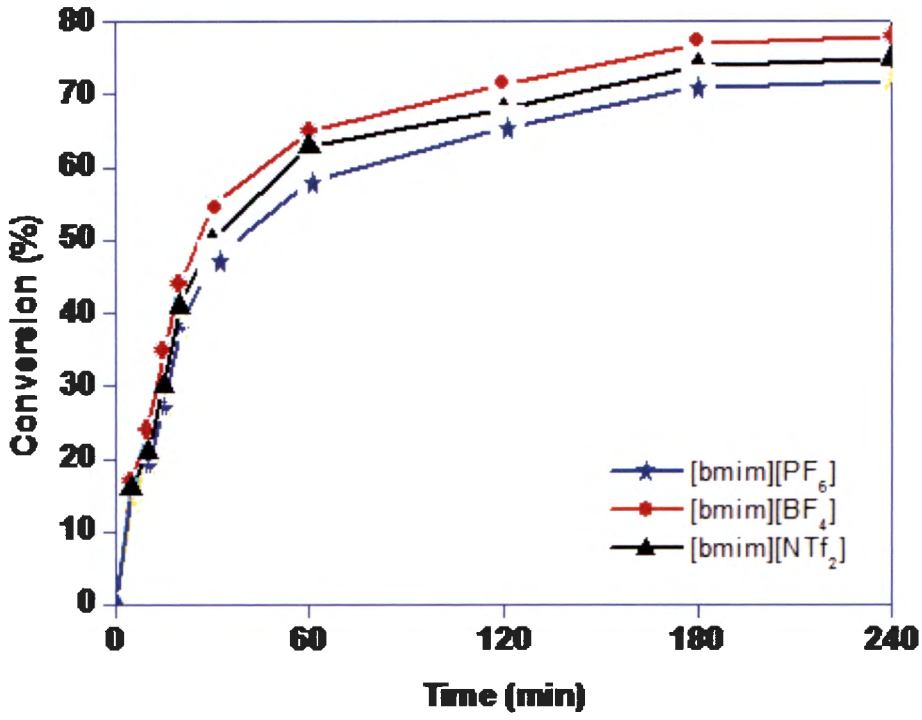


Figure 38: Conversion of MO in [bmim][X] type ILs using **19** at 60 °C

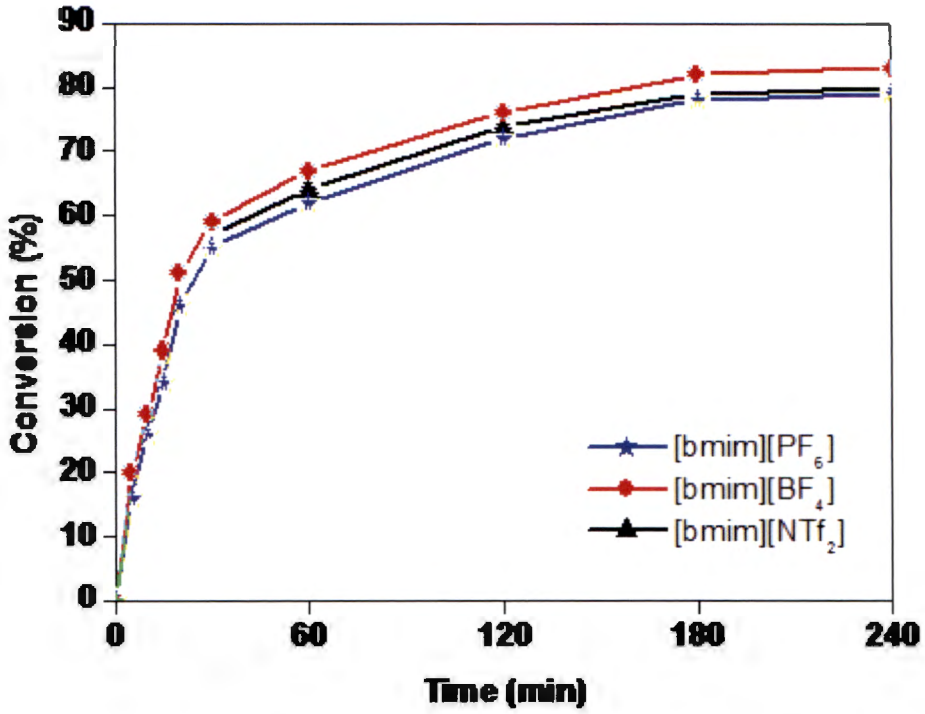


Figure 39: Conversion of MO in [bmim][X] type ILs using **19** at 80 °C

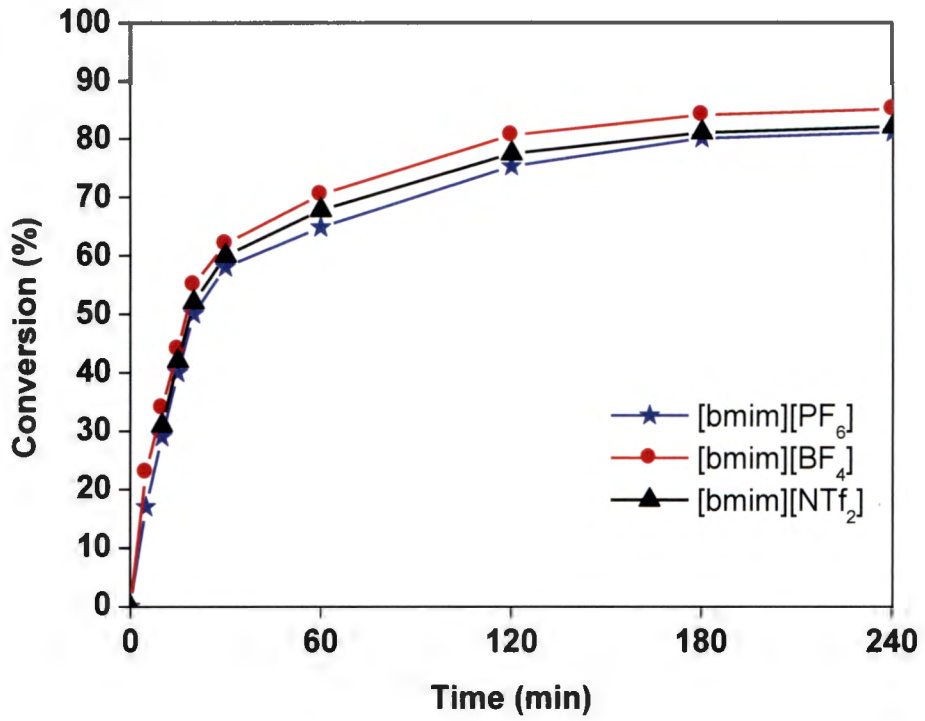


Figure 40: Conversion of MO in [bmim][X] type ILs using **19** at 100 °C

Oleate conversions as a function of reaction temperatures (20 to 100 °C) for the metathesis of methyl oleate in the presence of **19** are shown in Figure 41. The activity of the catalyst increased

with increasing the temperature from 20 – 100 °C with oleate conversions increasing from 59 to 85%. The results reveal that catalyst **19** can withstand higher temperature of 100 °C. But as the temperature increased, the selectivity towards PMPs decreased from 100 to 69%.

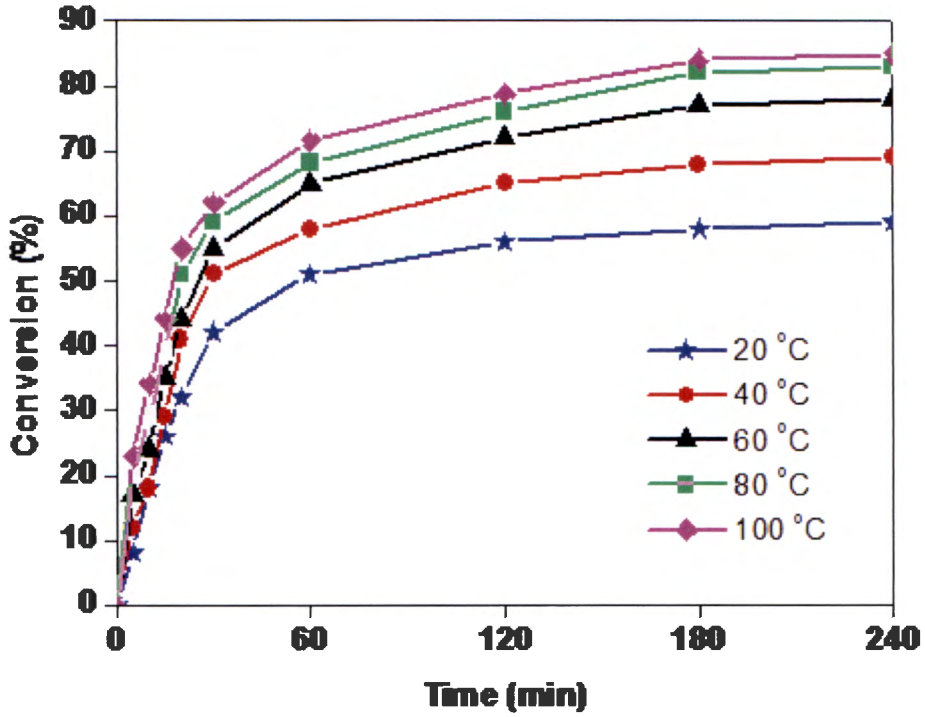


Figure 41: Influence of temperature on the activity of **19** in [bmim][BF_4] from 20 to 100 °C

4.3.1.4 Influence of reaction atmosphere

The influence of reaction atmosphere on the activity of Grubbs catalyst **19** was investigated using methyl oleate in [bmim][BF_4] at different temperatures. The experiment was conducted in two different reaction atmospheres, air and N_2, at the substrate/catalyst molar ratio 100:1. The activity of **19** at different temperatures under air using [bmim][BF_4] as a solvent is shown in Table 22. Substrate conversions as a function of reaction time under N_2 and air atmospheres at 20, 40, 60, 80 and 100 °C are shown in Fihures 42 - 46. It is clear from the figures that **19** has very little difference in substrate conversion in air and nitrogen atmospheres. At all the selected temperatures, the activity of **19** was found to be same in air and N_2 atmospheres. This proves the statement that Grubbs second generation catalyst is stable under air atmosphere.

Table 22: Activity of **19** for the SM of MO in [bmim][BF_4] in air after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	58	100	58
40	68	96	68
60	77	82	77
80	82	76	82
100	84	69	84

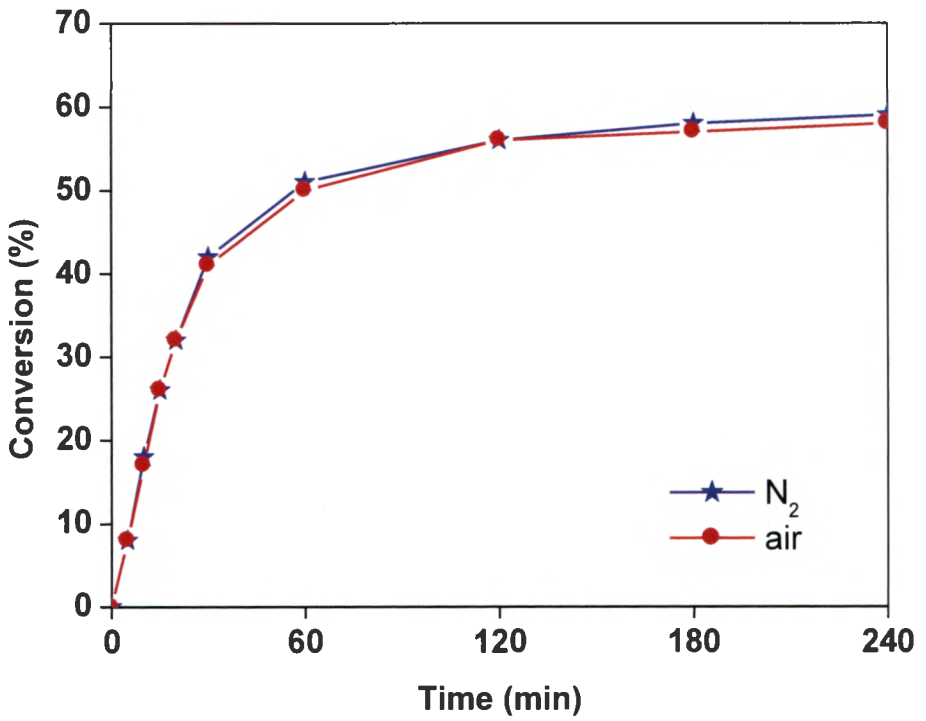


Figure 42: Conversion of MO in [bmim][BF_4] using **19** at 20 °C in air and N_2

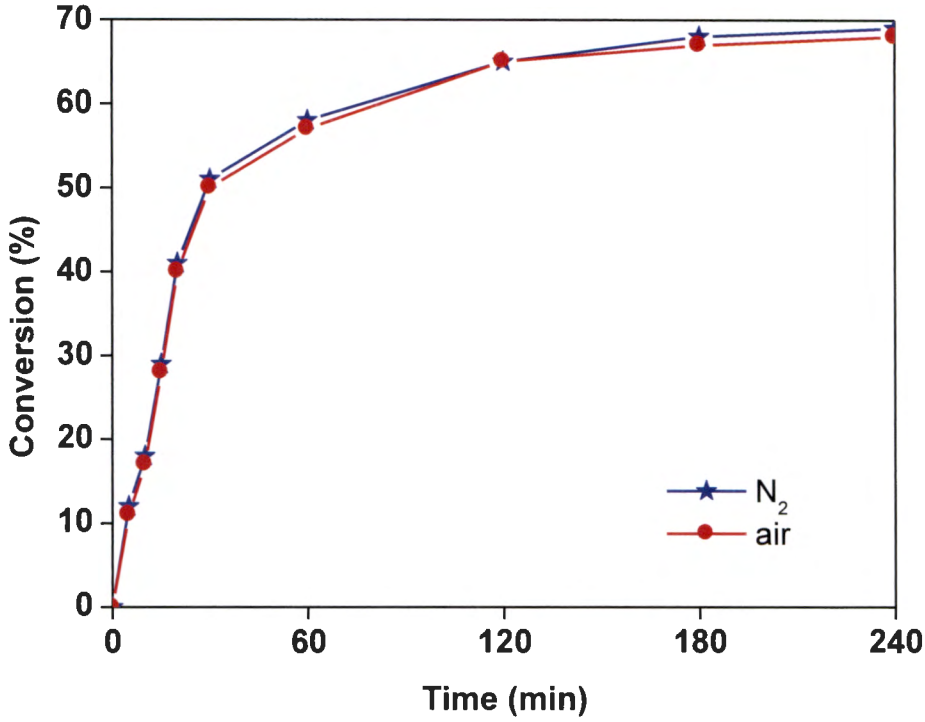


Figure 43: Conversion of MO in [bmim][BF_4] using **19** at 40 °C in air and N_2

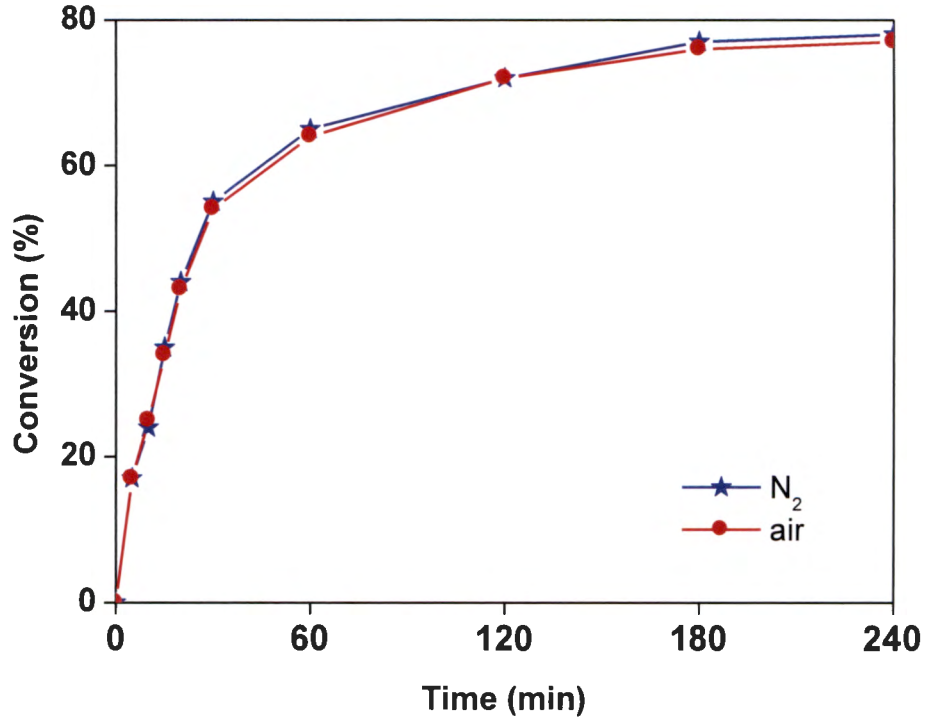


Figure 44: Conversion of MO in [bmim][BF_4] using **19** at 60 °C under air and N_2

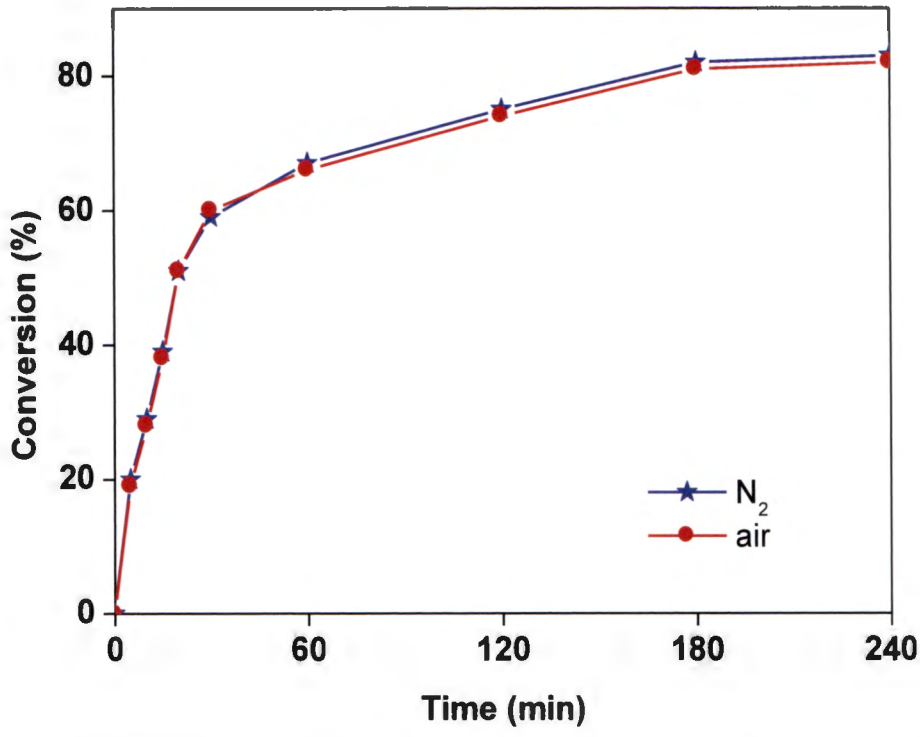


Figure 45: Conversion of MO in [bmim][BF_4] using **19** at 80 °C under air and N_2

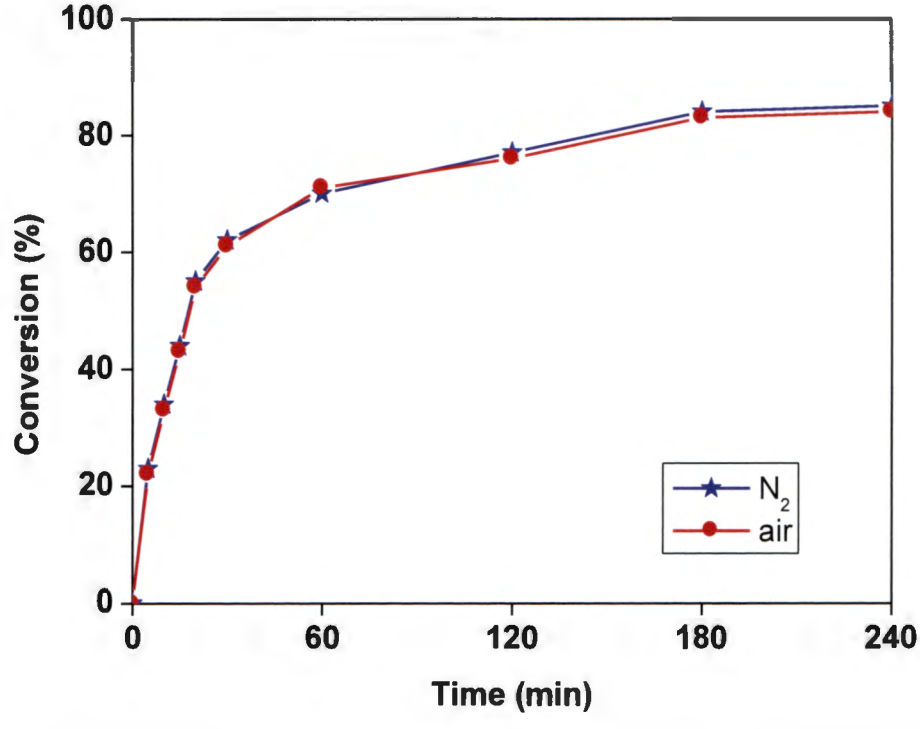


Figure 46: Conversion of MO in [bmim][BF_4] using **19** at 100 °C under air and N_2

4.3.2 Metathesis of methyl oleate in [bdmim][X] type ILs

The metathesis of methyl oleate was investigated in the presence of Grubbs catalyst **19** in [bdmim][X] type ILs. The ILs selected for the study were [bdmim][PF_6] and [bdmim][BF_4]. The reactions were carried out at temperatures ranging from 20-100 °C. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.5 mL of methyl oleate followed by the addition of 12.3 mg of Grubbs catalyst.

A summary of the activity of **19** in [bdmim][X] type ILs at different reaction temperature is presented in Tables 23 and 24. At all the selected temperatures, the highest conversion was observed in [bdmim][BF_4]. At 20 °C, a conversion of 62% was obtained in [bdmim][BF_4], whereas the reaction in [bdmim][PF_6] gave only a conversion of 55%. Methyl oleate conversion increased with increasing temperature and reached 90% at 100 °C in [bdmim][BF_4]. However, the selectivity towards PMPs was very poor even at moderate temperatures.

Table 23: Activity of **19** for the SM of MO in [bdmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	55	100	55
40	71	96	71
60	80	82	80
80	85	76	85
100	87	69	87

Table 24: Activity of **19** for the SM of MO in [bdmim][BF_4] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	62	100	62
40	73	96	71
60	83	82	83
80	87	76	86
100	90	69	89

The activity of [bmim][X] and [bdmim][X] type ILs at different reaction temperature are shown in Figures 47 to 51. At all selected temperatures, the highest conversion was obtained in [bdmim][BF_4]. Poor conversion in [bmim] type ILs compared to [bdmim] type ILs may be due to the carbene formation of the catalyst. [bdmim] type ILs can prevent the carbene formation of catalyst, which is believed to be formed by the deprotonation of imidazolium cation or from the oxidative addition of imidazolium to Ru centre [188].

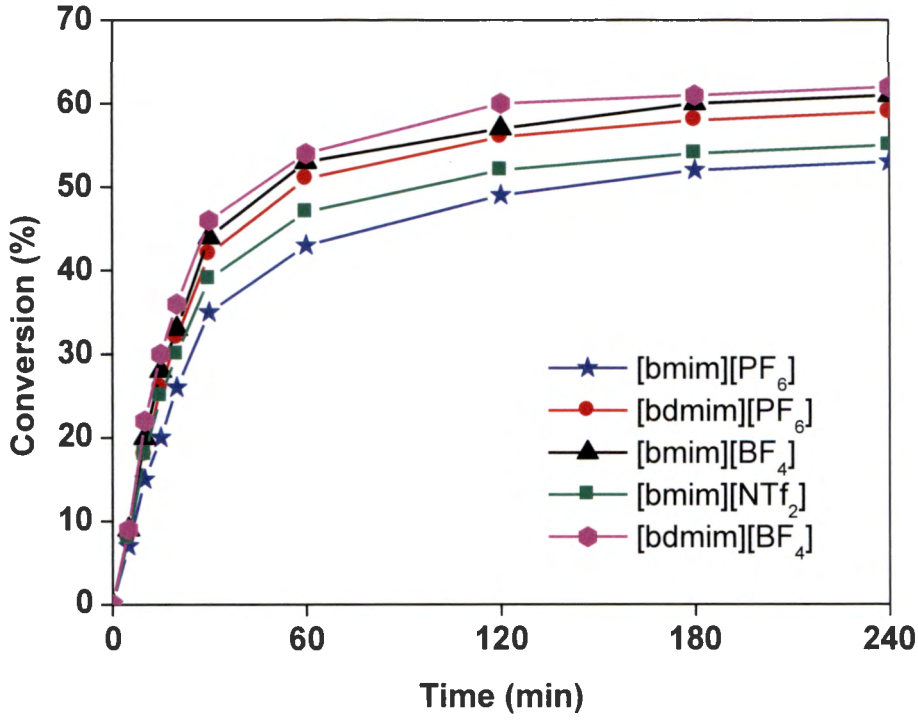


Figure 47: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **19** at 20 °C

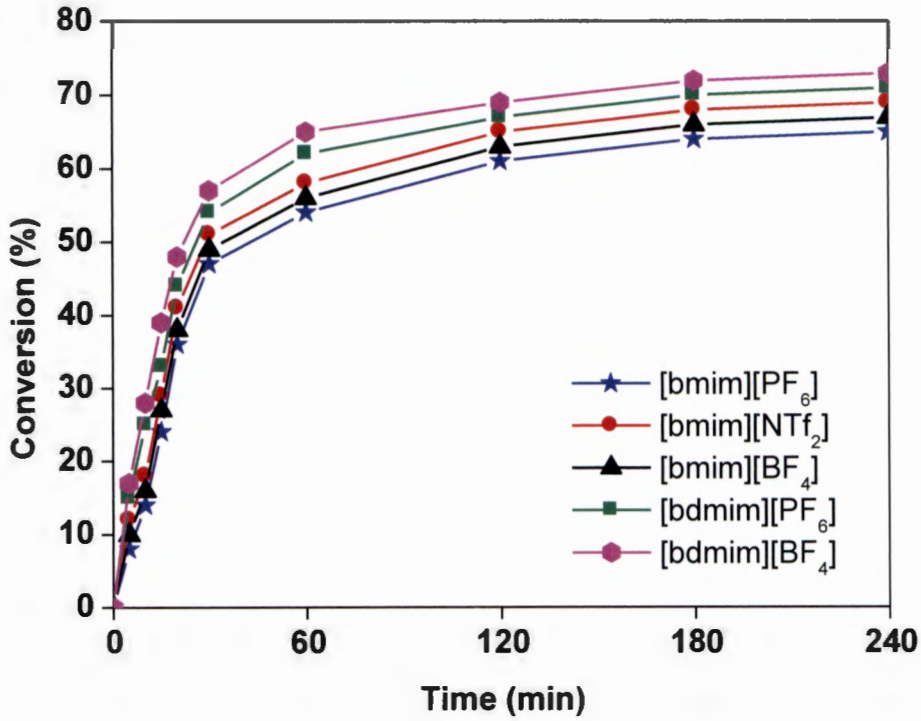


Figure 48: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **19** at 40 °C

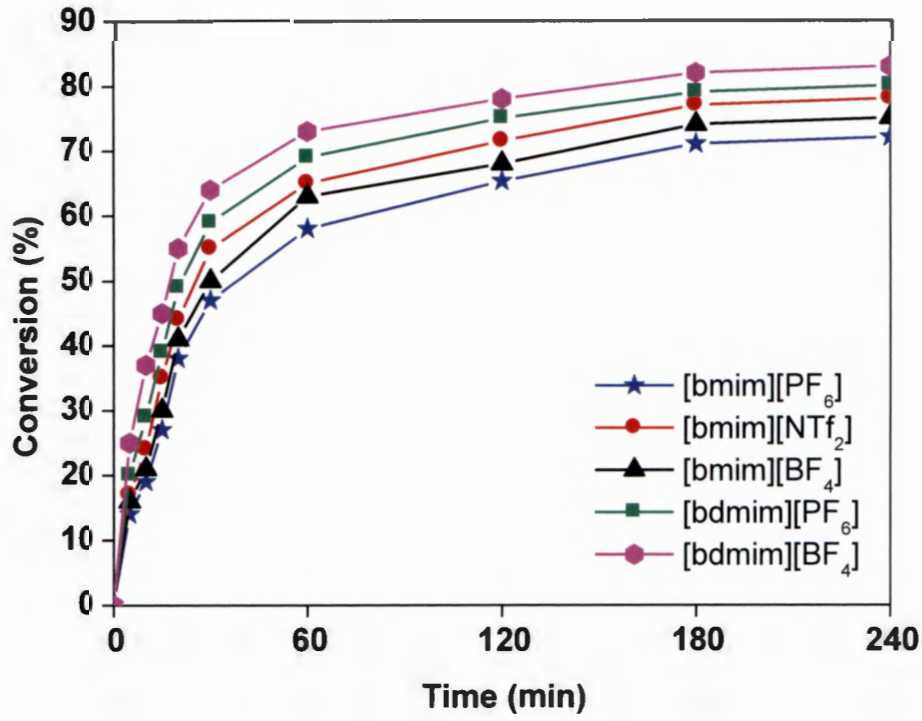


Figure 49: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **19** at 60 °C

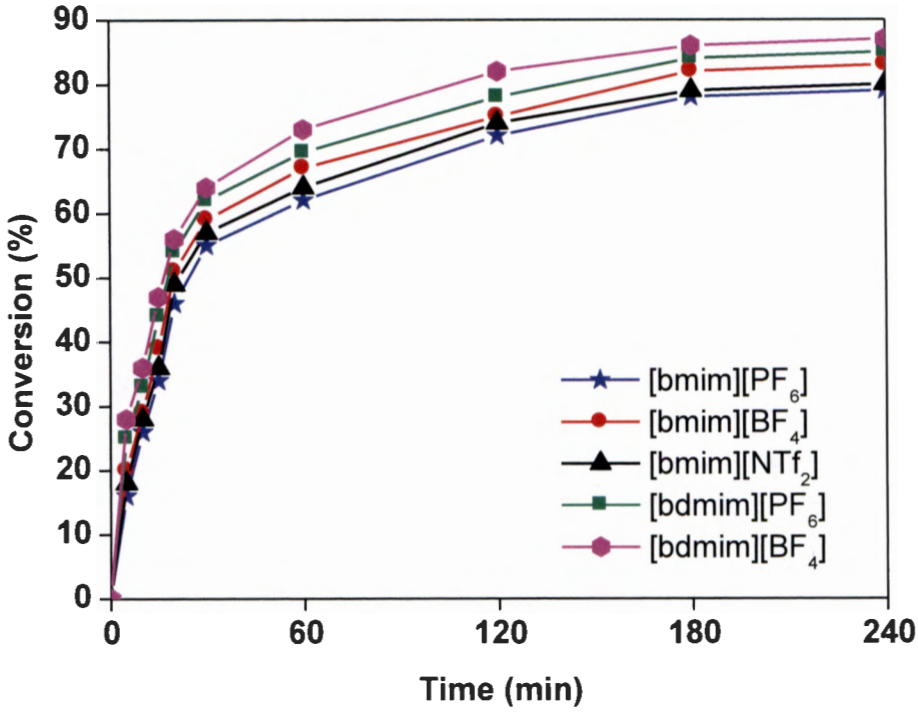


Figure 50: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **19** at 80 °C

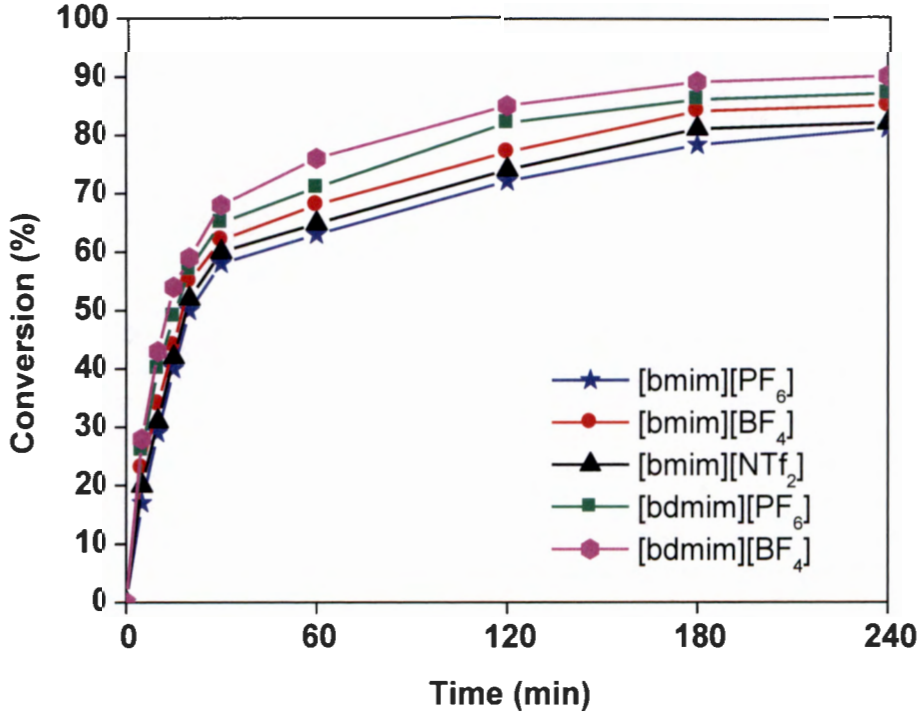


Figure 51: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **19** at 100 °C

4.3.3 Metathesis of methyl ricinoleate in [bmim][X] and [bdmim][X] type ILs

The self-metathesis of methyl ricinoleate was carried out in the presence of **19** at 20 °C using [bmim][X] and [bdmim][X] type ILs. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.2 mL of substrate followed by the addition of 0.59 mg of Grubbs catalyst.

The activity of **19** in [bmim][X] type ILs is summarised in Table 25. The reaction on [bmim][BF_4] gave the highest conversion of 51% and the lowest in [bmim][NTf_2] (46%). The activity of **10** was found to increase in the order [bmim][PF_6] > [bmim][BF_4] > [bmim][NTf_2]. Excellent selectivity (99%) was obtained, showing the absence of secondary metathesis products. The conversion of methyl ricinoleate in [bmim][X] type ILs at 60 °C is shown in Figure 52.

Table 25: Activity of **19** for the SM of MR in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bmim][PF_6]	48	100
[bmim][BF_4]	51	100
[bmim][NTf_2]	46	100

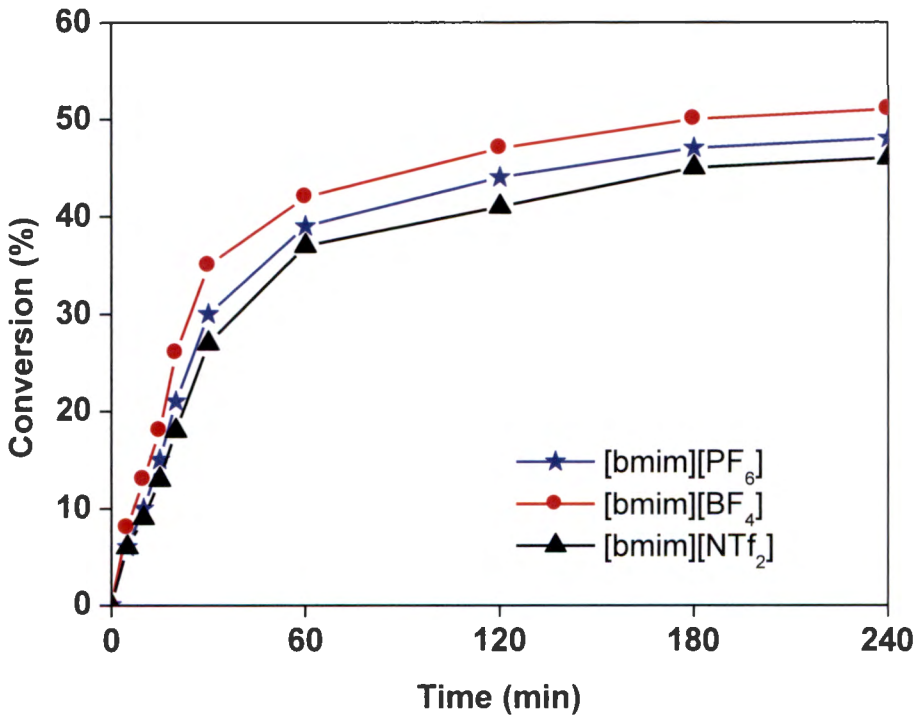


Figure 52: Conversion of MR in [bmim][X] type ILs using **19** at 20 °C

The SM of methyl ricinoleate was also carried out in [bdmim][X] type ILs at 20 °C. The activity of **19** for the conversion of methyl ricinoleate in [bdmim][X] type ILs at 20 °C is shown in Table 26. A conversion of 53 % was obtained in [bdmim][BF_4], whereas a conversion of 50 % was obtained in [bdmim][PF_6]. Excellent selectivity of 99 % was obtained in all the cases. Substrate conversion using **19** in [bdmim][X] type ILs is shown in Figure 53 whereas the influence of cations of the ILs on the activity of **19** for the SM of methyl ricinoleate at 20 °C is given in Figure 54.

Table 26: Activity of **19** for the SM of MR in [bdmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bdmim][PF_6]	50	100
[bdmim][BF_4]	53	100

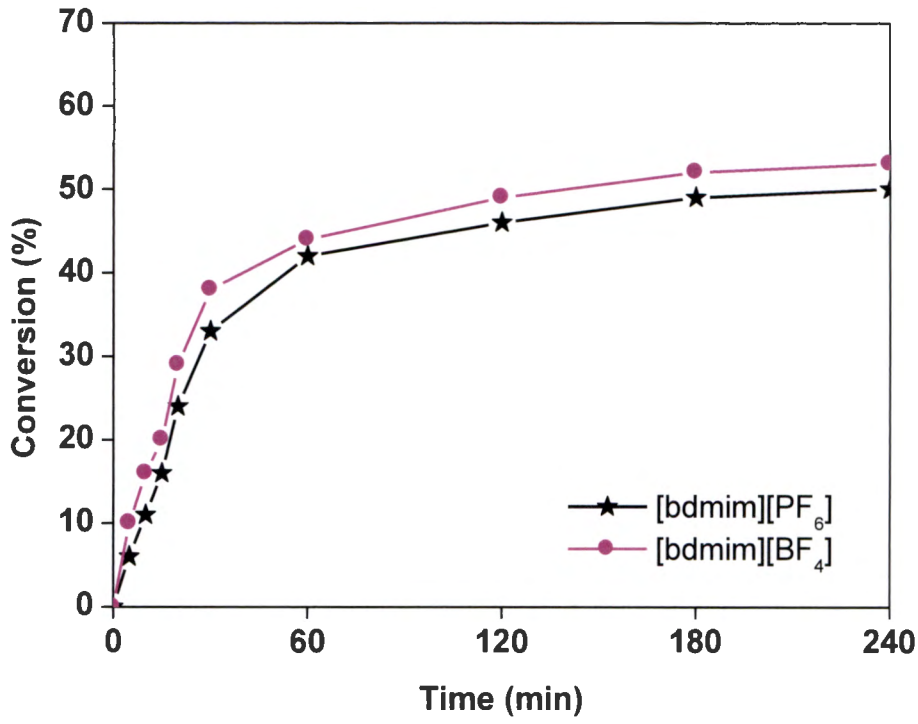


Figure 53: Conversion of MR in [bdmim][X] type ILs using **19** at 20 °C

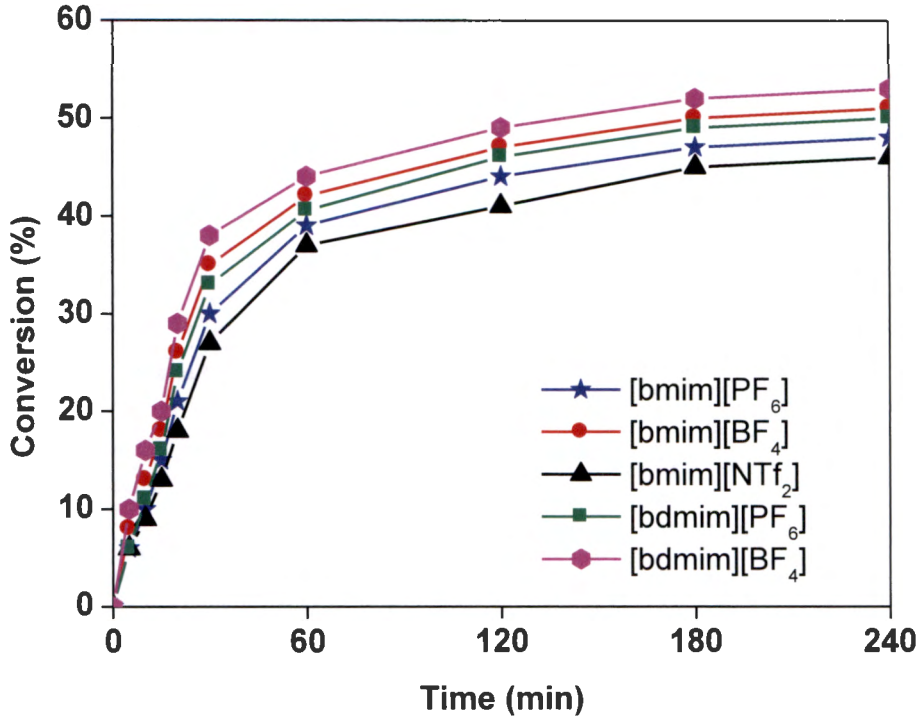


Figure 54: Conversion of MR in [bmim] and [bdmim][X] type ILs using **19** at 20 °C

4.3.4 Metathesis of methyl oleate in organic solvents

The SM of methyl oleate was carried out using **19** in conventional organic solvents. The organic solvents selected for the study were dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **19** in selected organic solvents at different temperatures is presented in Tables 27 to 31. At all the selected temperatures, the best catalytic performance occurred in DCM and the lowest in PhMe. At 20 °C, the reaction in DCM gave a conversion of 56%, whereas the reaction in PhMe gave a conversion of only 50%. The activity of **19** was found to increase in the order PhMe < PhCl < DCE < DCM. The conversion of methyl ricinoleate in organic solvents at different temperatures is shown in Figures 55 to 59.

Table 27: Activity of **19** for the SM of MO in DCM at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	56	100
40	65	100
60	74	98
80	79	91
100	82	91

Table 28: Activity of **19** for the SM of MO in DCE at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	54	100
40	62	100
60	70	98
80	76	91
100	80	91

Table 29: Activity of **19** for the SM of MO in PhMe at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	50	100
40	58	100
60	65	98
80	72	91
100	76	91

Table 30: Activity of **19** for the SM of MO in PhCl at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	52	100
40	60	100
60	67	98
80	73	91
100	78	91

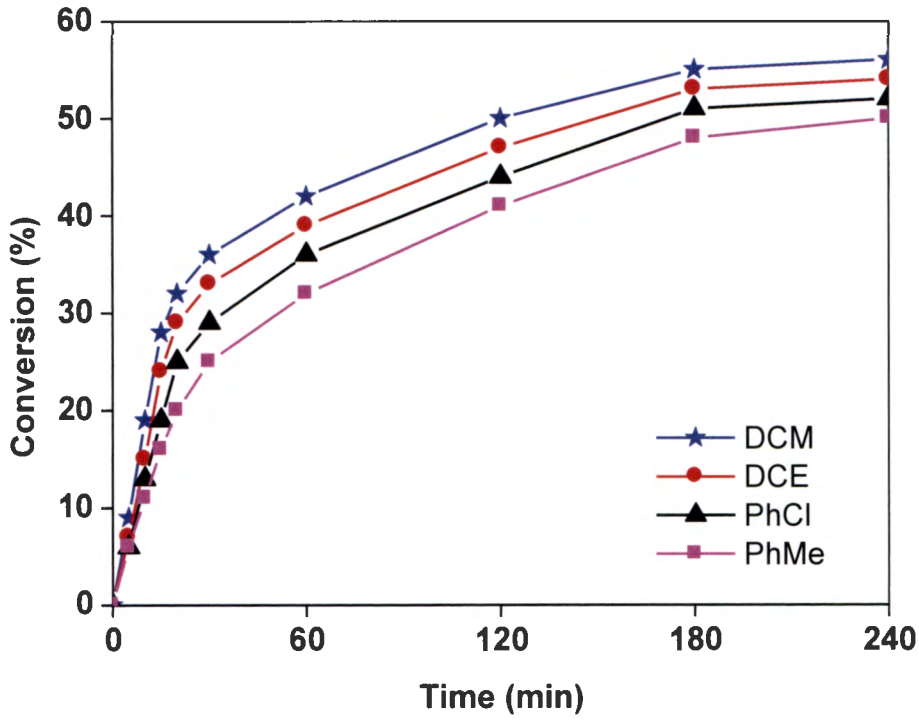


Figure 55: Conversion of MO in organic solvents using **19** at 20°C

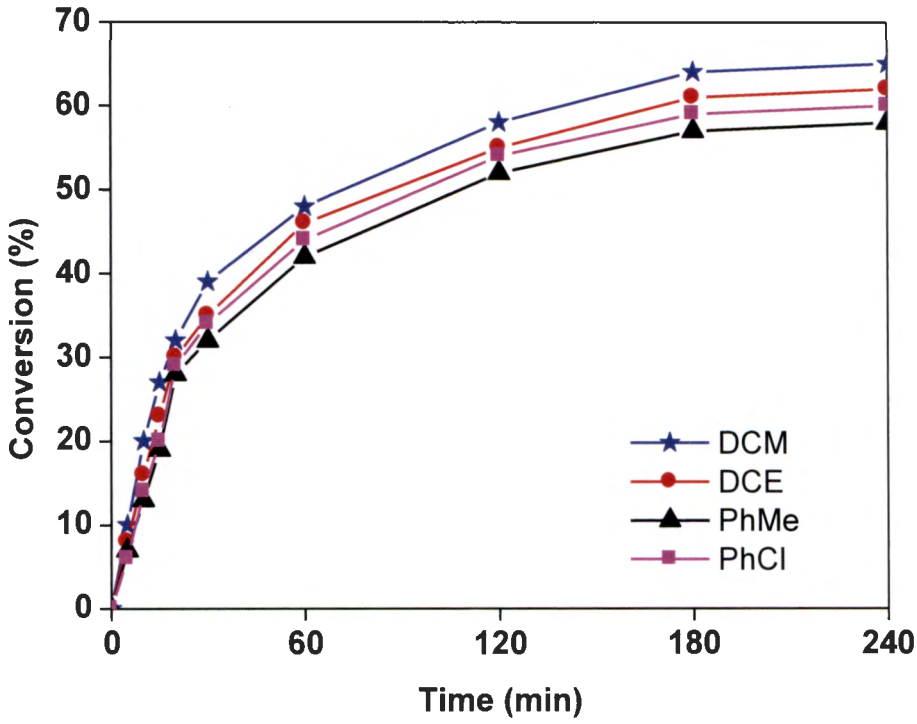


Figure 56: Conversion of MO in organic solvents using **19** at 40°C

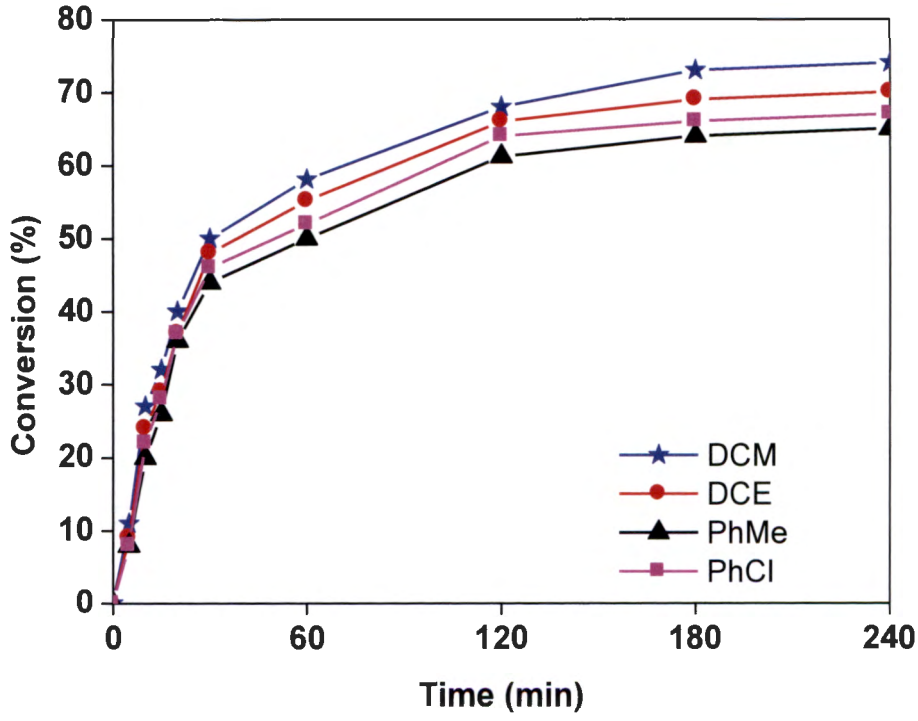


Figure 57: Conversion of MO in organic solvents using **19** at 60°C

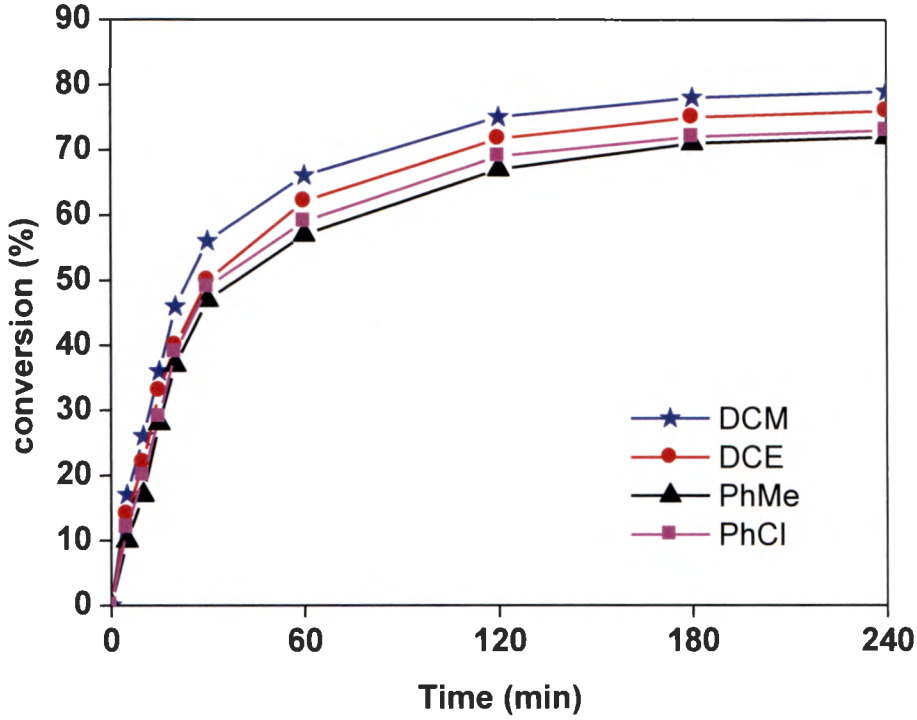


Figure 58: Conversion of MO in organic solvents using **19** at 80°C

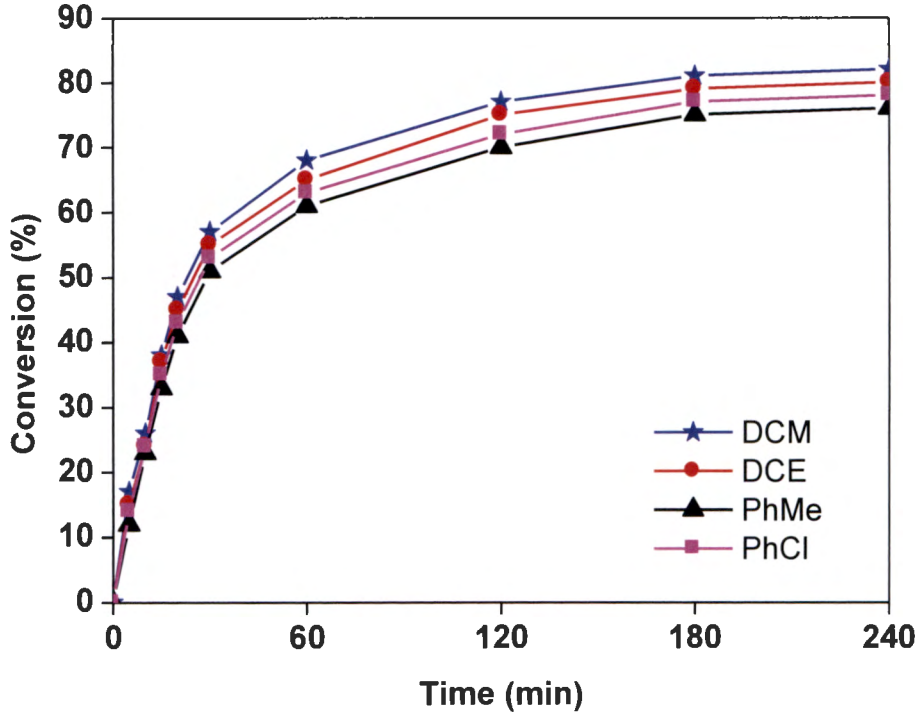


Figure 59: Conversion of MO in organic solvents using **19** at 100°C

A comparison of the activity of **19** in selected ILs and organic solvents at different temperatures is given in Figures 60 to 64. It is clear from the figures that a significant rate

enhancement occurred in ILs when compared to the organic solvents. The high activity in ILs may be due to the weak coordination ability, which depends on the nature of the anion as applied to the catalytic complex [224].

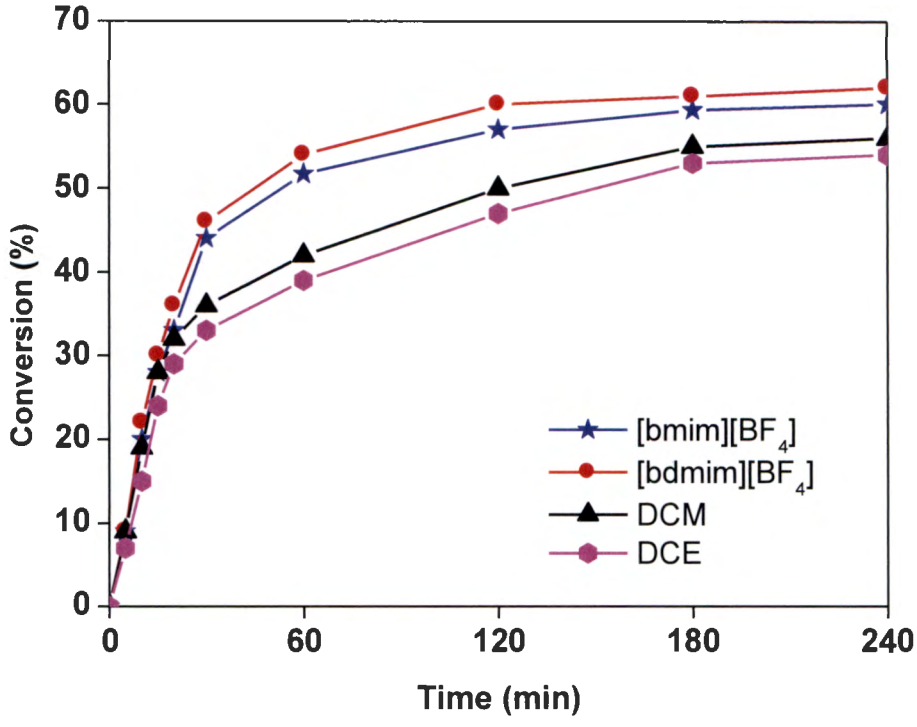


Figure 60: Conversion of MO in selected ILs and organic solvents using **19** at 20°C

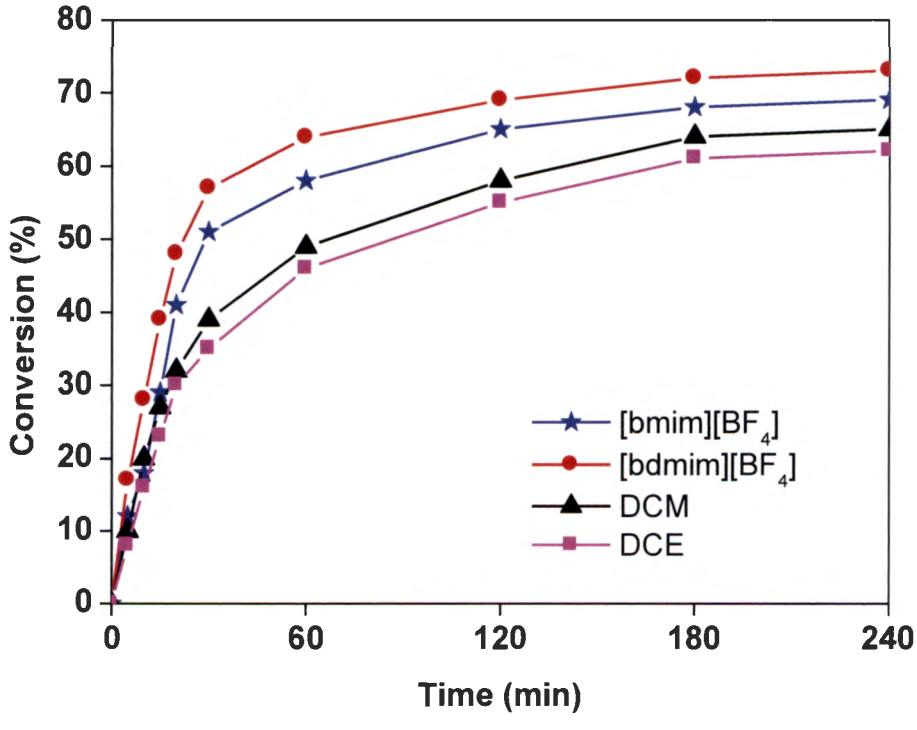


Figure 61: Conversion of MO in selected ILs and organic solvents using **19** at 40°C

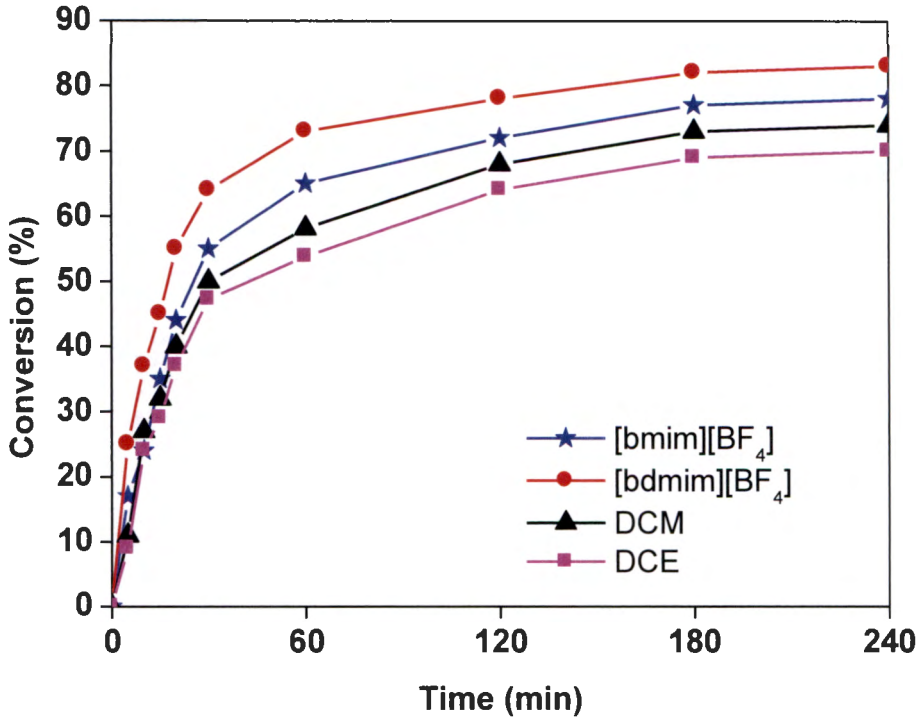


Figure 62: Conversion of MO in selected ILs and organic solvents using **19** at 60°C

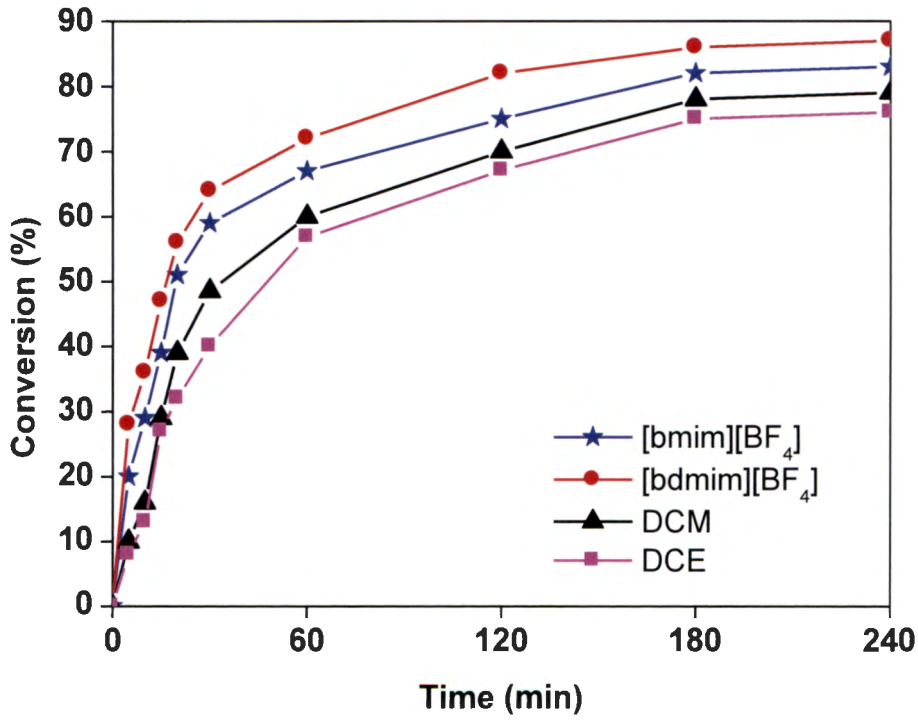


Figure 63: Conversion of MO in selected ILs and organic solvents using **19** at 80°C

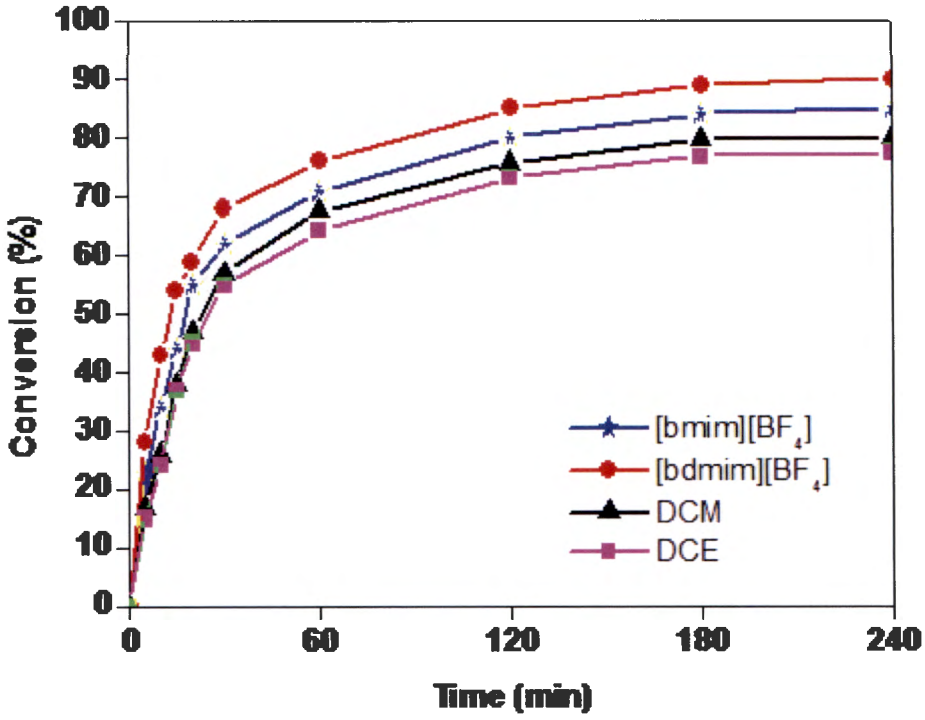


Figure 64: Conversion of MO in selected ILs and organic solvents using **19** at 100°C

4.3.5 Metathesis of methyl ricinoleate in organic solvents

The SM of methyl ricinoleate using Grubbs catalyst **19** was carried out in four different organic solvents, namely, dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **19** in organic solvents at 20 °C is shown in Table 31. Catalyst 10 showed highest activity in DCM with a substrate conversion of 36% and the lowest in PhMe with a conversion of 31%. The catalytic activity was found to be in the order DCM > DCE > PhCl > PhMe. Very good selectivity of 99 % was observed at a temperature of 20 °C, showing the absence of SMPs.

Table 31: Activity of **19** for the SM of MR in organic solvents at 20 °C after 4 h reaction time

Solvent	Conv (%)	Selec (%)
DCM	44	100
DCE	43	100
PhCl	40	100
PhMe	38	100

The conversion of MR in organic solvents in the presence of **19** at 20 °C is shown in Figure 65. A comparison of the activity of **19** in selected organic solvents and [bdmim][X] ILs at

20 °C is given in Figure 66. It is clear from the figure that a significant rate enhancement occurred in ILs compared to organic solvents, which can be attributed to the weak coordination ability of ILs [224].

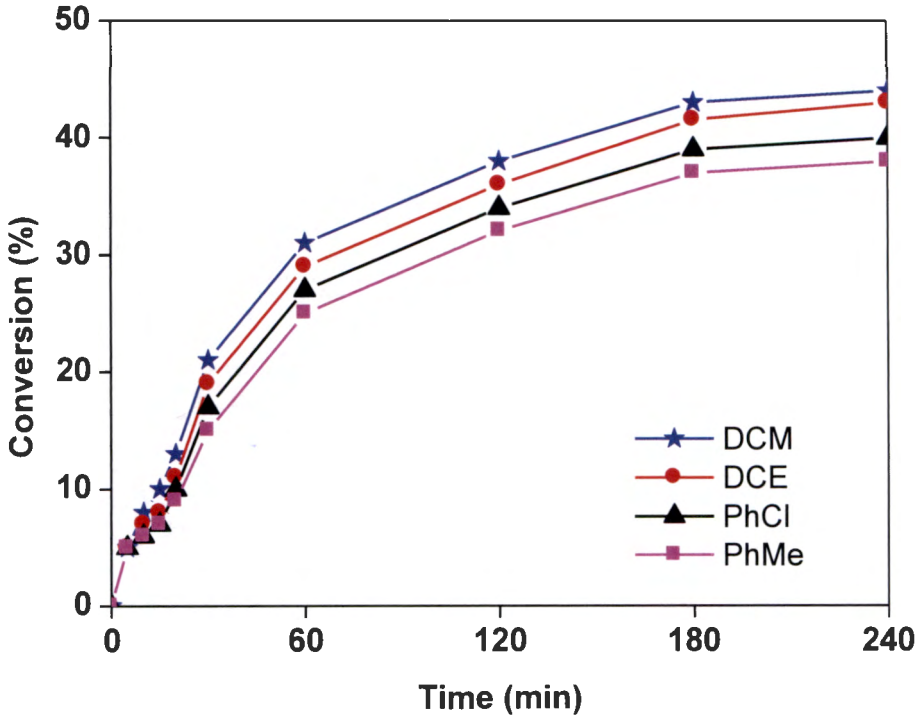


Figure 65: Conversion of MR in organic solvents using **19** at 20 °C

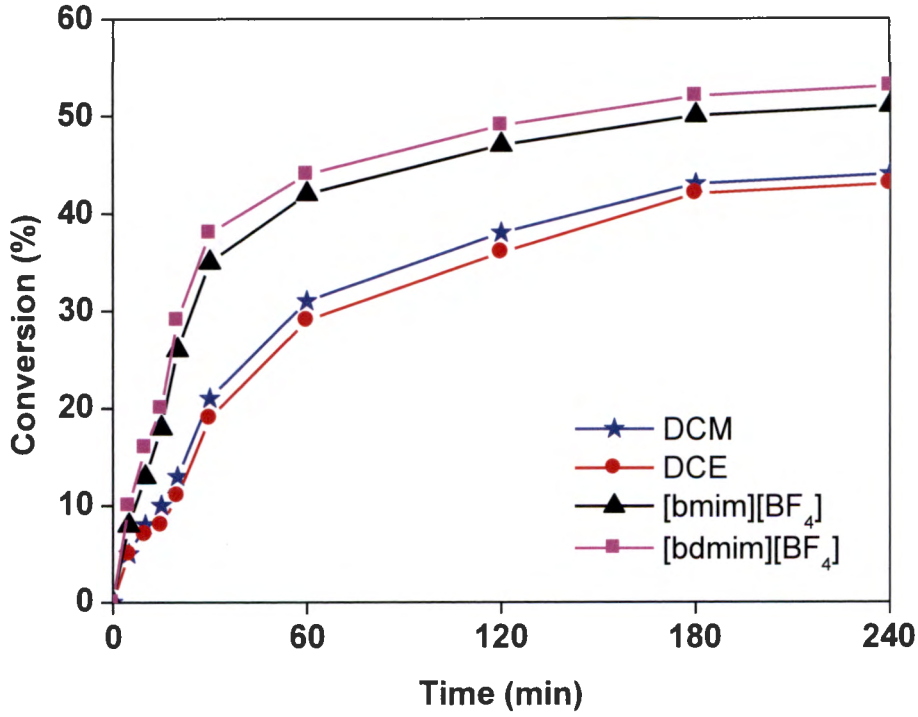
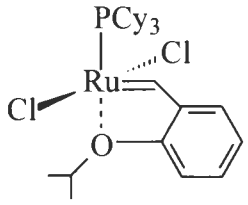


Figure 66: Conversion of MR in selected organic solvents and ILs using **19** at 20 °C

4.4 Metathesis of unsaturated fatty acid esters using Hoveyda-Grubbs first generation catalyst 20



20

4.4.1 Metathesis of methyl oleate in [bmim][X] type ILs

The reactivity of methyl oleate was investigated in the presence of Hoveyda Grubbs catalyst **20**. The substrate/catalyst molar ratio used was 100:1. The reactions were carried out at 20, 40, 60, 80 and 100 °C in RTILs ([bmim][PF_6], [bmim][BF_4] and [bmim][NTf_2]). In all the reactions, 1mL of the particular solvent was added to 0.5 mL of substrate followed by the addition of 12.3 mg of Grubbs catalyst.

4.4.1.1 Influence of the solvent

The influence of [bmim][X] type ILs on methyl oleate was investigated in the presence of **20** at different temperatures. The activity of **20** for the SM of methyl oleate in [bmim][X] type ILs is shown in Table 32. Similar conversions were obtained in all the three ILs. Conversion of 54%, 53% and 52% were obtained for the reaction in [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2], respectively. Excellent selectivity of 100% was obtained in all the runs showing the absence of SMPs.

Table 32: Activity of **20** for the SM of MO in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)	TON
[bmim][PF_6]	52	100	52
[bmim][BF_4]	54	100	54
[bmim][NTf_2]	53	100	53

4.4.1.2 Influence of the anions of IL

The effect of varying the anion counterpart in [bmim][X] type ILs on the metathesis of methyl oleate using **20** was also studied. The influence of anions on the catalytic activity of **20** is shown in Figure 67. Similar activities were obtained for all the three ILs.

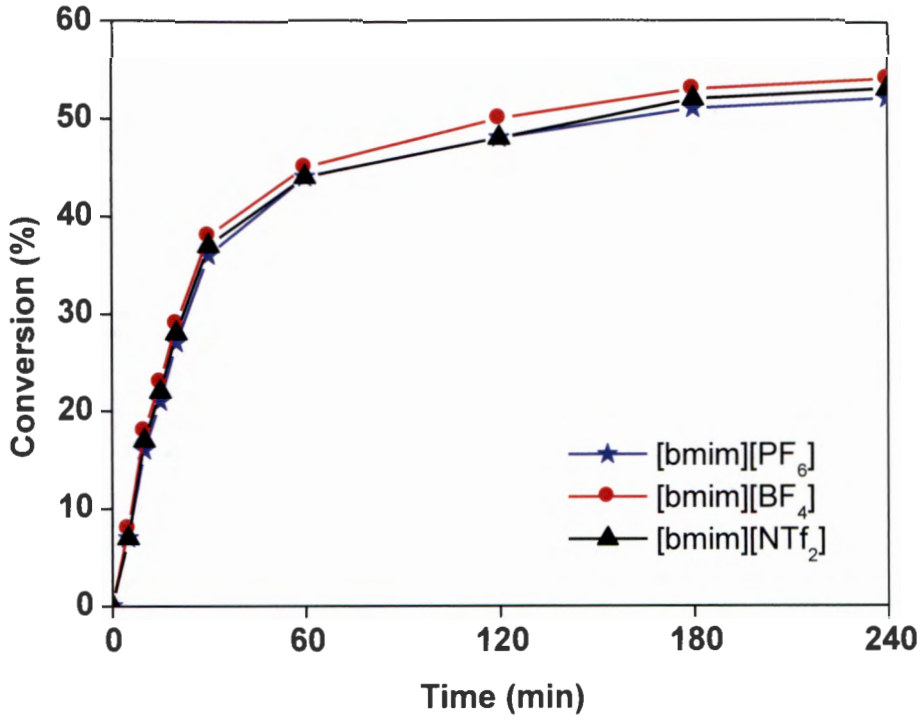


Figure 67: Influence of the anions of [bmim][X] type ILs on the activity of **20** at 20 °C.

4.4.1.3 Influence of reaction temperature

The influence of reaction temperature on the activity of **20** for the SM of methyl oleate was investigated. A summary of the activity of **20** in [bmim][X] type ILs at different reaction temperature is given in Table 33 to 37. Similar conversions were obtained in all the three ILs at the selected temperatures. At 20 °C, substrate conversion of 52%, 54% and 53% were obtained in [bmim][PF_6], [bmim][BF_4] and [bmim][NTf_2], respectively. At 100 °C, the reaction in [bmim][BF_4] yielded a conversion of 62%, while the reaction in [bmim][NTf_2] gave a conversion of 61%, followed by the reaction in [bmim][PF_6] with a conversion of 60%. The conversion of methyl oleate in [bmim][X] type ILs at 40 °C, 60 °C, 80 °C and 100 °C, after 4 hour reaction time is shown in Figures 68 to 71.

Table 33: Activity of **20** for the SM of MO in [bmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	52	100	52
40	55	100	55
60	57	97	57
80	59	92	59
100	63	87	63

Table 34: Activity of **20** for the SM of MO in [bmim][BF_4] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	54	100	54
40	56	100	56
60	59	97	59
80	62	92	62
100	67	87	67

Table 35: Activity of **20** for the SM of MO in [bmim][NTf_2] at different temperatuires after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	53	100	54
40	54	100	56
60	59	97	59
80	61	92	62
100	65	87	67

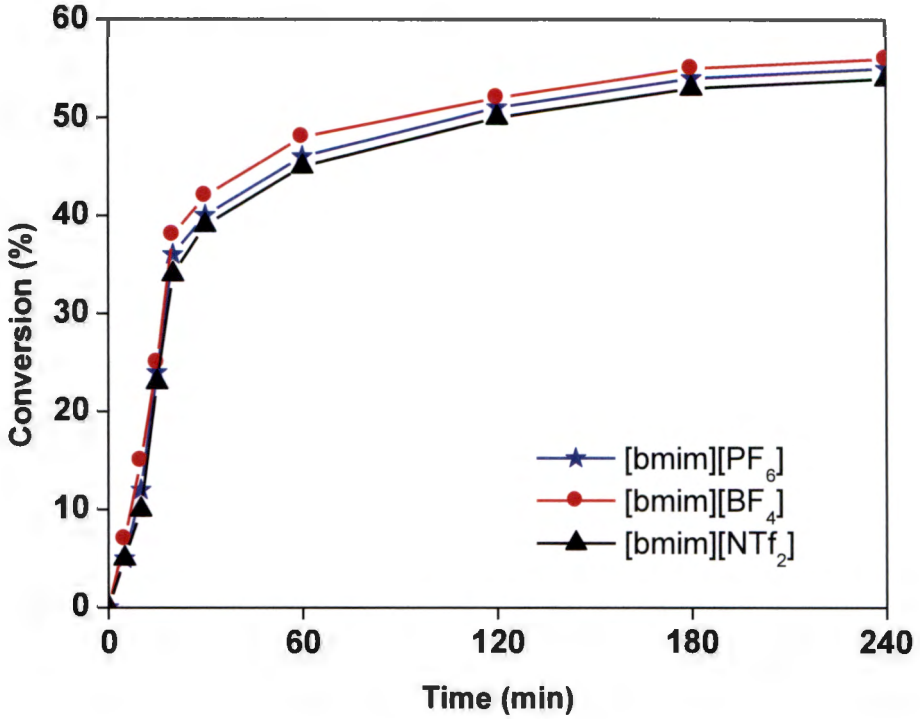


Figure 68: Conversion of MO in [bmim][X] type ILs using **20** at 40 °C

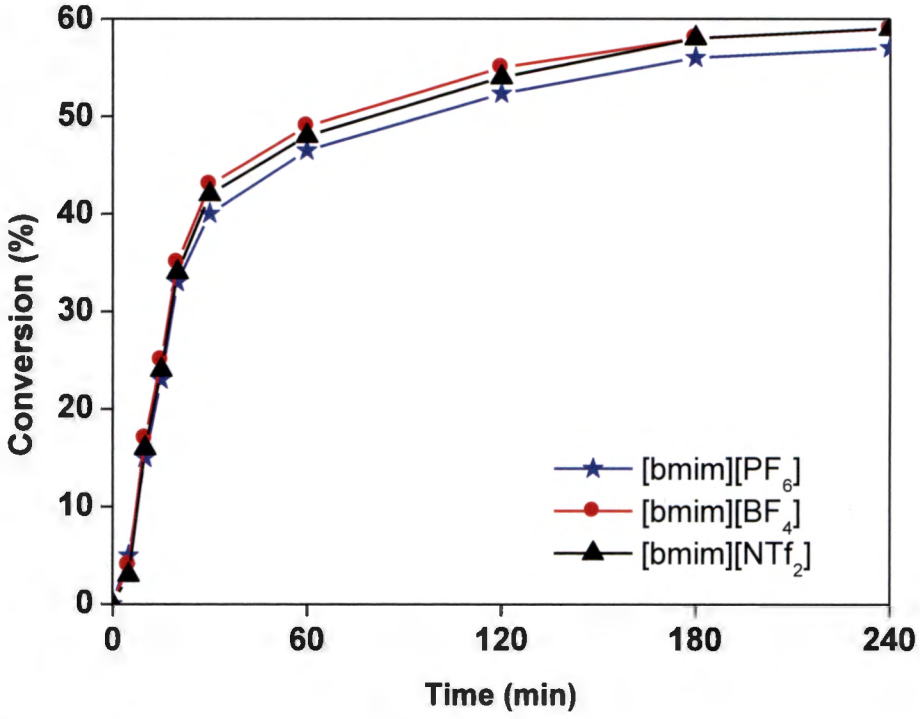


Figure 69: Conversion of MO in [bmim][X] type ILs using **20** at 60 °C

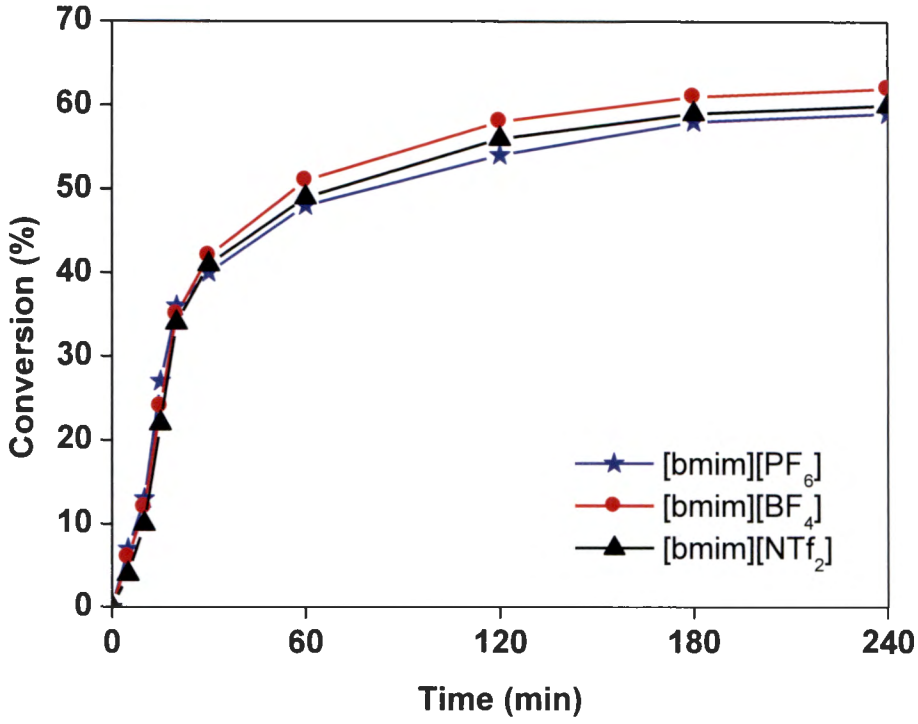


Figure 70: Conversion of MO in [bmim][X] type ILs using **20** at 80 °C

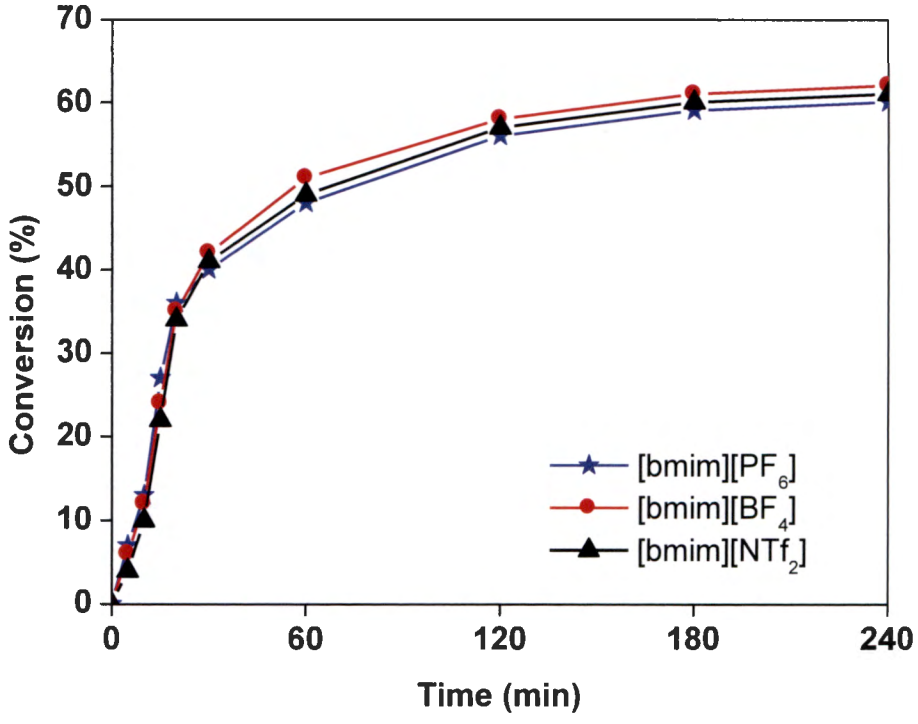


Figure 71: Conversion of MO in [bmim][X] type ILs using **20** at 100 °C

Oleate conversions as a function of reaction temperatures (20 to 100 °C) for the metathesis of methyl oleate in the presence of **20** are shown in Figure 72. The activity of the

catalyst increased with increasing emperature from 20 – 100 °C with oleate conversions increasing from 54 to 67%. The results reveal that catalyst **20** can withstand higher temperature of 100 °C. But as the temperature increased, the selectivity towards PMPs decreased from 100 to 69% due to the formation of SMPs at higher temperatures.

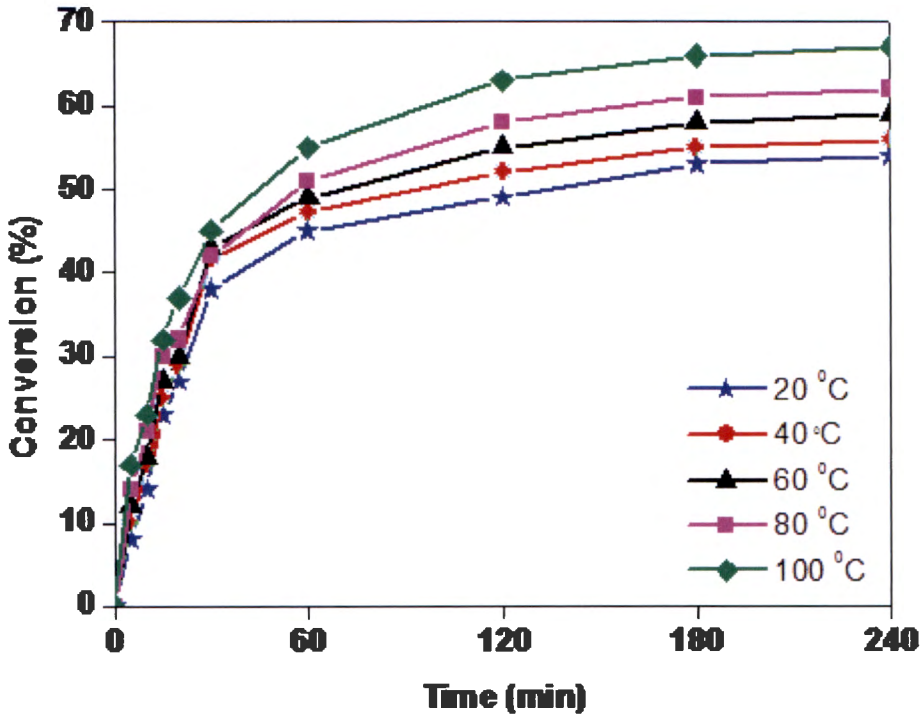


Figure 72: Influence of temperature on the activity of **20** in [bmim][BF_4] from 20 to 100 °C

4.4.1.4 Influence of reaction atmosphere

The influence of reaction atmosphere on the activity of **20** was investigated using methyl oleate in [bmim][BF_4] at different temperatures. The experiment was conducted in two different reaction atmospheres, air and N_2, at the substrate/catalyst molar ratio 100:1. The activity of **20** at different temperatures under air using [bmim][BF_4] as a solvent is shown in Table 36. Substrate conversion as a function of reaction time under N_2 and air atmospheres at different temperatures ranging from 20 to 100 °C are shown in Figures 73 to 77. It is clear from the figures that **20** has very little difference in substrate conversion in air and nitrogen atmospheres. At all the selected temperatures, the activity of **20** was found to be same in air and N_2 atmospheres. This proves the statement that Grubbs second generation catalyst is stable under air atmosphere.

Table 36: Activity of **20** for the SM of MO in [bmim][BF_4] under air after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	53	100	53
40	55	100	55
60	58	97	58
80	61	92	61
100	61	87	61

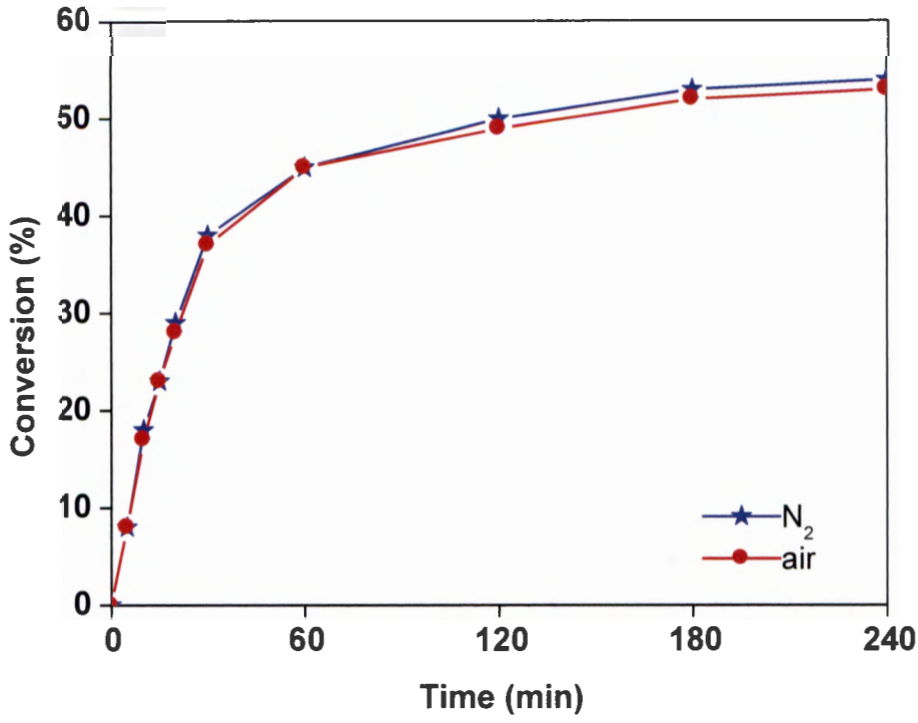


Figure 73: Conversion of MO in [bmim][BF_4] using **20** at 20 °C in air and N_2 atmospheres

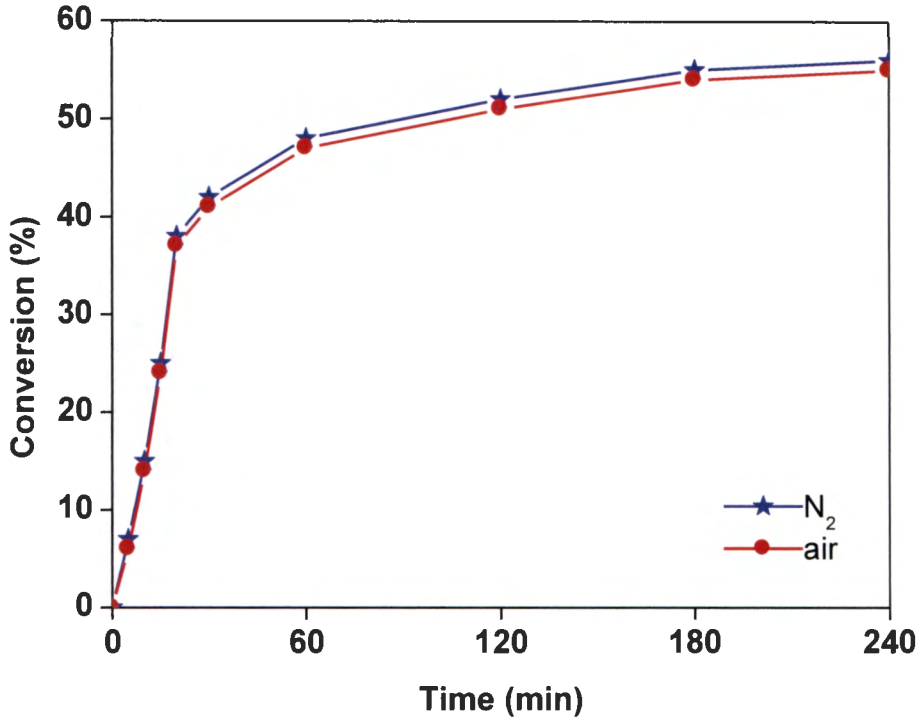


Figure 74: Conversion of MO in [bmim][BF_4] using **20** at 40 °C in air and N_2 atmospheres

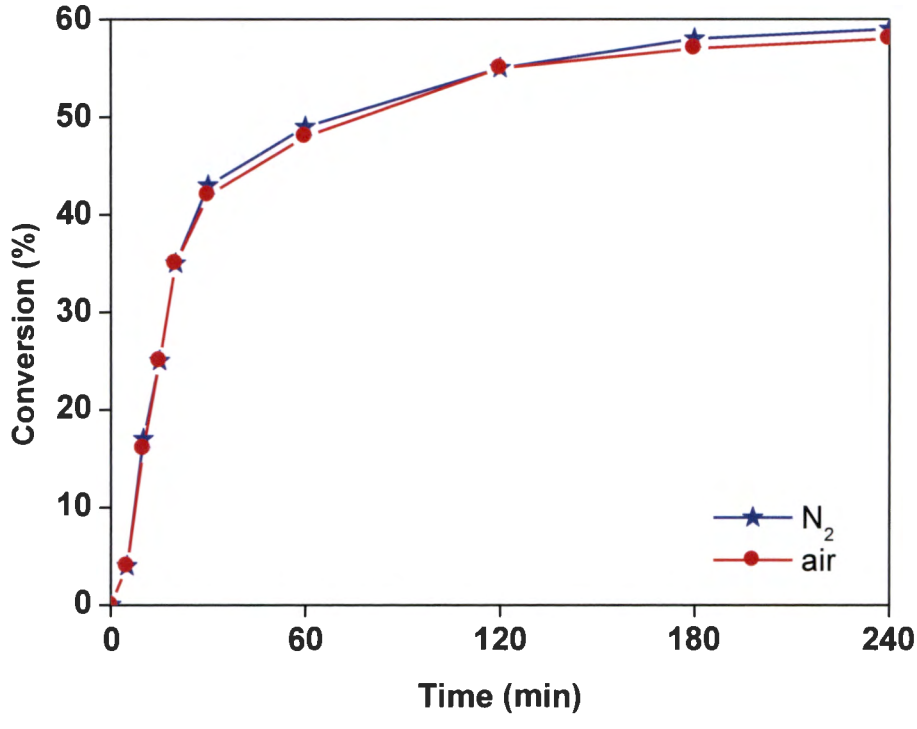


Figure 75: Conversion of MO in [bmim][BF_4] using **20** at 60 °C in air and N_2 atmospheres

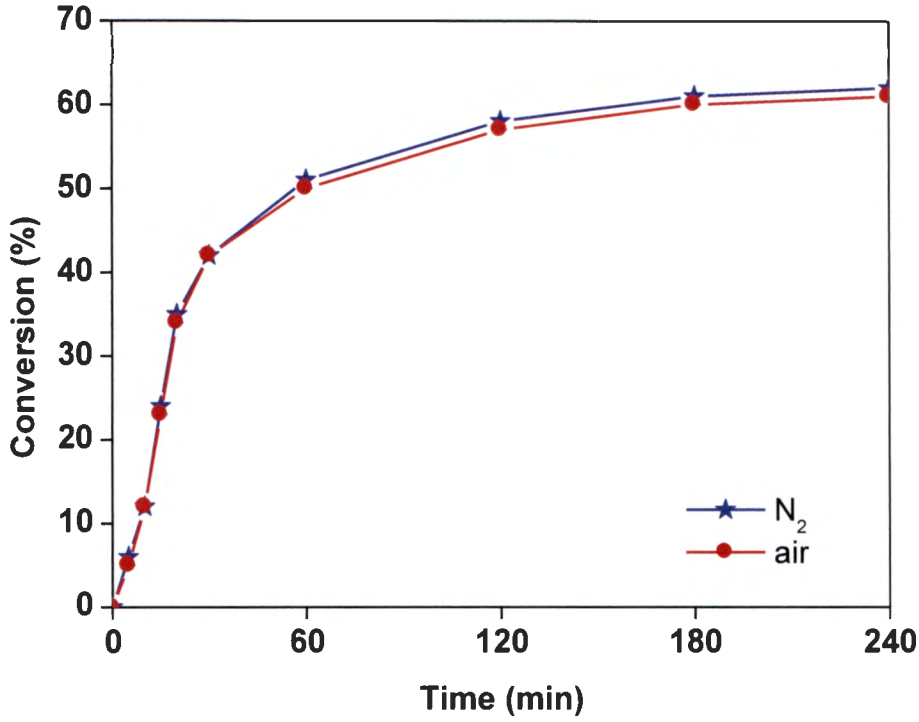


Figure 76: Conversion of MO in [bmim][BF_4] using **20** at 80 °C in air and N_2 atmospheres

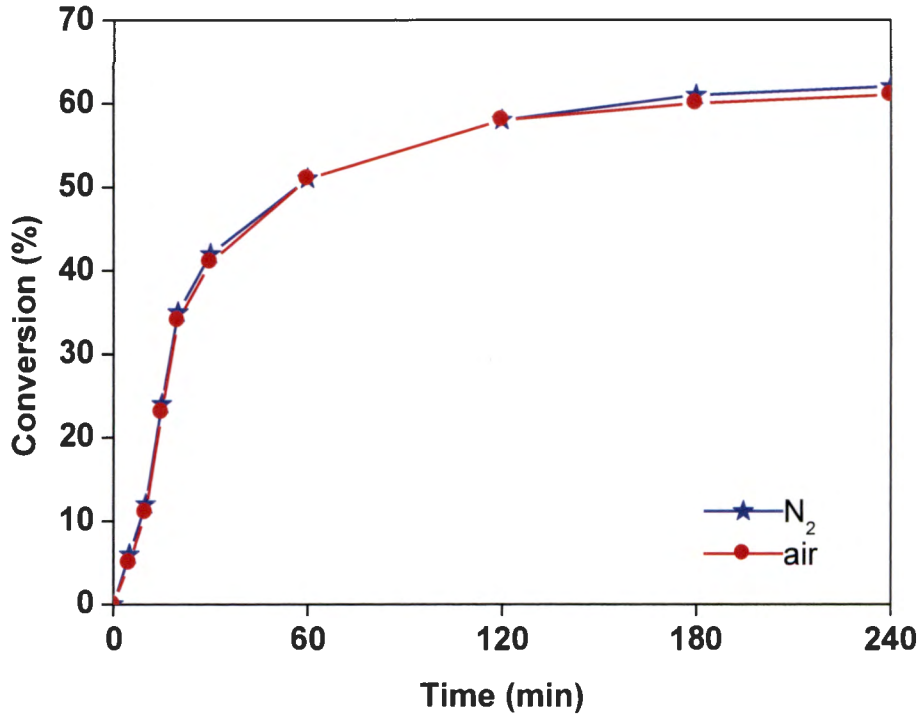


Figure 77: Conversion of MO in [bmim][BF_4] using **20** at 100 °C in air and N_2 atmospheres

4.4.2 Metathesis of methyl oleate in [bdmim][X] type ILs

The metathesis of methyl oleate was investigated in [bdmim][X] type ILs using Hoveyda Grubbs catalyst **20**. The ILs selected for the study were [bdmim][PF_6] and [bdmim][BF_4]. The reactions were carried out at temperatures ranging from 20-100 °C. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.5 mL of methyl oleate followed by the addition of 12.3 mg of Grubbs catalyst.

Table 37 and 38 are the summaries of the activity of **20** in [bdmim][X] type ILs at different reaction temperatures. At all the selected temperatures, the highest conversion was observed in [bdmim][BF_4]. A conversion of 56% was obtained at 20 °C, which then increased on increasing the temperature and gave a conversion of 67% at 100 °C. At moderate temperature ($\leq$ 60 °C), very good selectivity was obtained. However, at temperatures above 60 °C, poor selectivity was obtained.

Table 37: Activity of **20** for the SM of MO in [bdmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	54	100	55
40	57	100	68
60	60	97	76
80	64	92	84
100	66	87	88

Table 38: Activity of **20** for the SM of MO in [bdmim][BF_4] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	56	100	62
40	58	100	71
60	63	97	83
80	65	92	86
100	67	87	89

The activity of [bmim][X] and [bdmim][X] type ILs at different reaction temperature are shown in Figures 78 to 82. At all the selected temperatures, the highest substrate conversion occurred in [bdmim][BF_4].

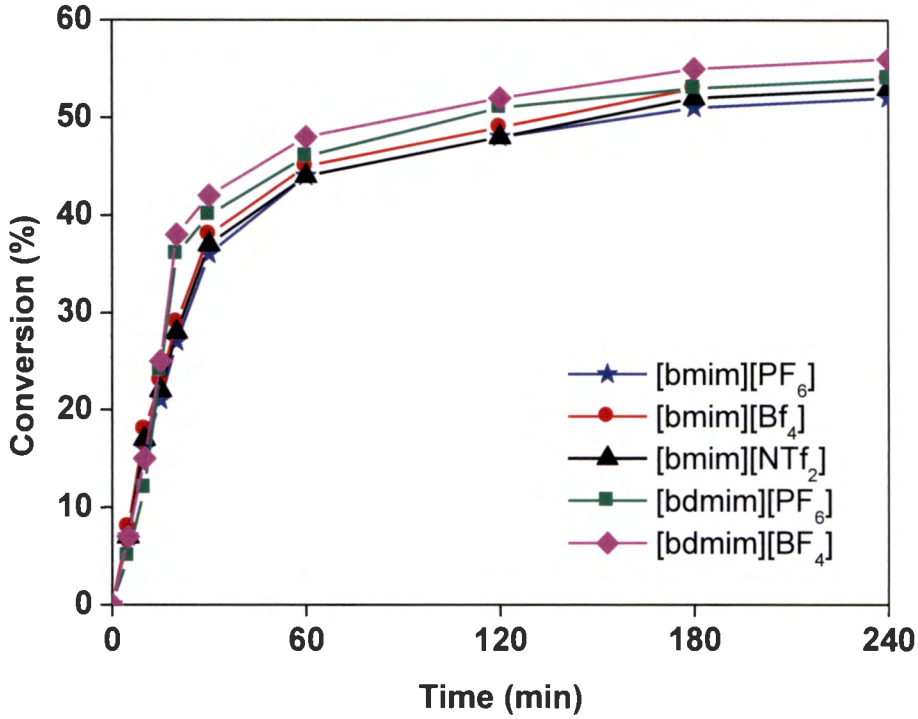


Figure 78: Conversion of MO in [bmim][X] and [bdmim][X] type ILs at using **20** at 20 °C

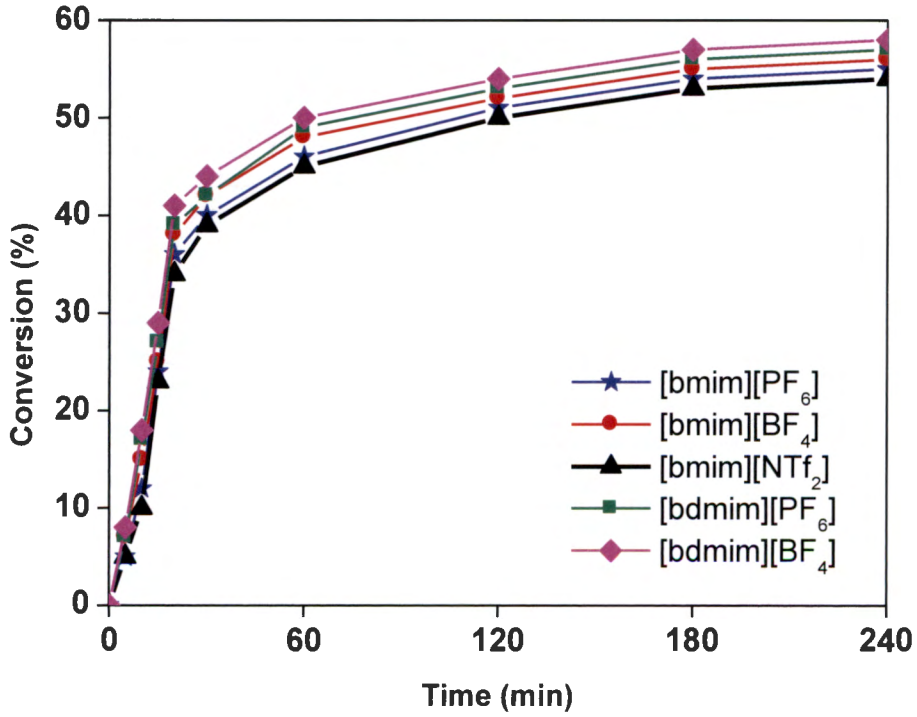


Figure 79: Conversion of MO in [bmim][X] and [bdmim][X] type ILs at using **20** at 40 °C

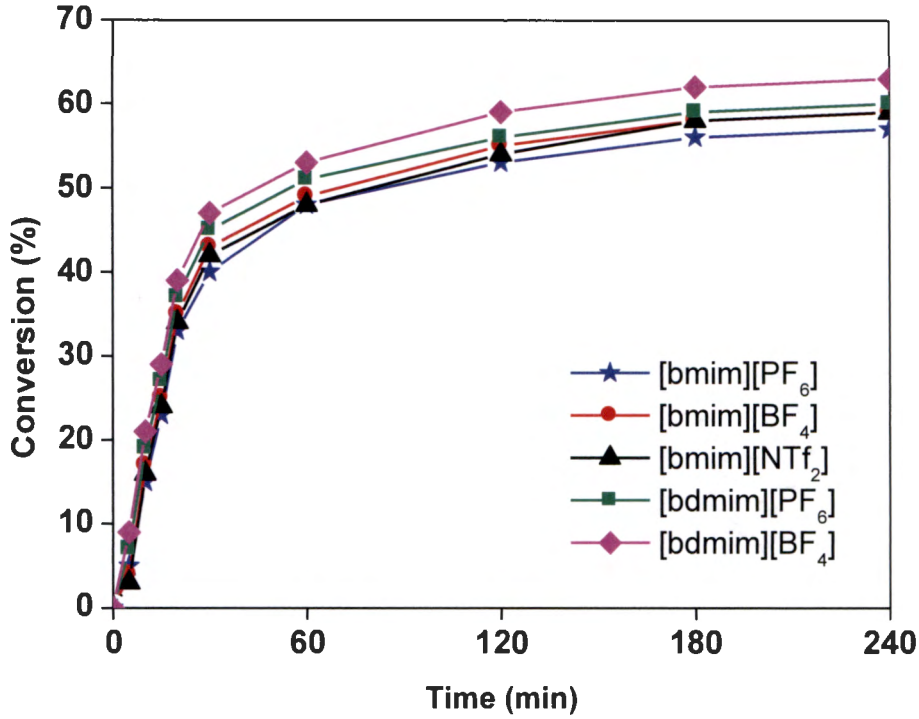


Figure 80: Conversion of MO in [bmim][X] and [bdmim][X] type ILs at using **20** at 60 °C

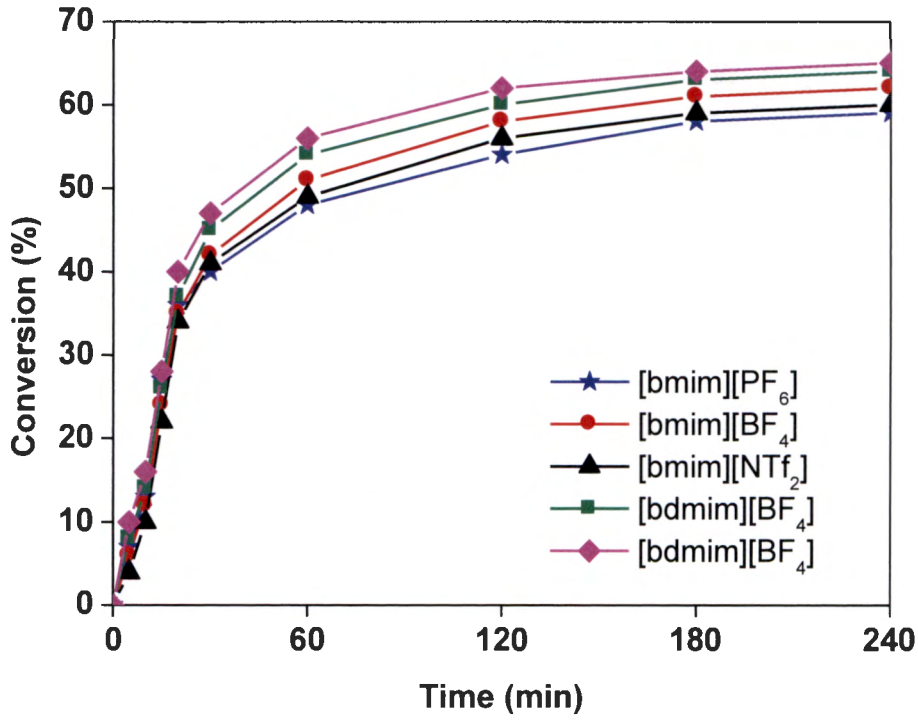


Figure 81: Conversion of MO in [bmim][X] and [bdmim][X] type ILs at using **20** at 80 °C

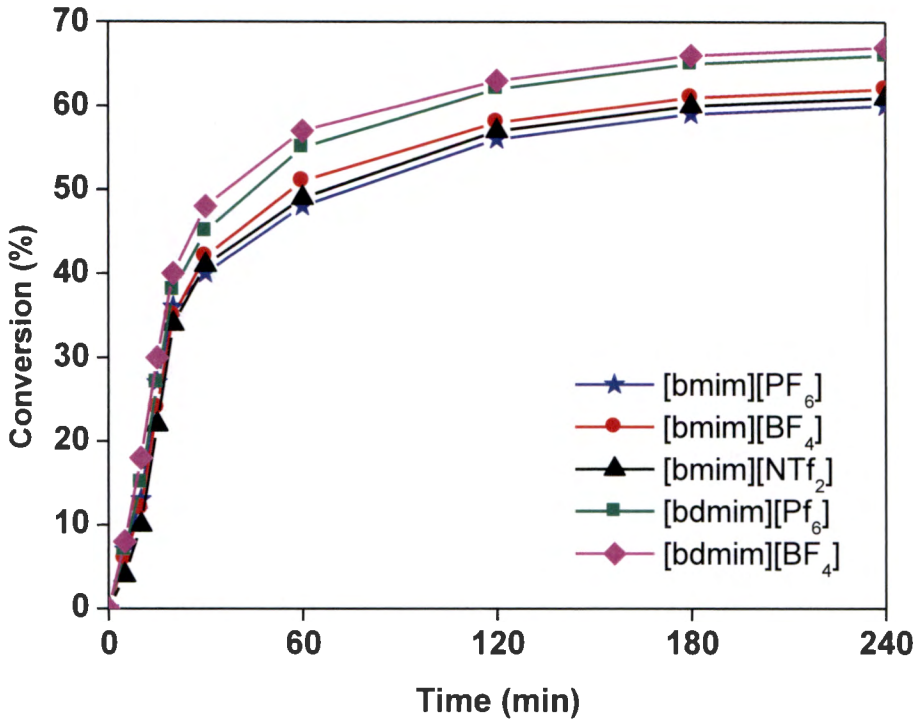


Figure 82: Conversion of MO in [bmim][X] and [bdmim][X] type ILs at using **20** at 100 °C

4.4.3 Metathesis of methyl ricinoleate in [bmim][X] and [bdmim][X] type ILs

The self-metathesis of methyl ricinoleate was carried out in the presence of catalyst **20** at 20 °C using [bmim][X] and [bdmim][X] type ILs. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.2 mL of substrate followed by the addition of 0.59 mg of Grubbs catalyst.

A summary the activity of **20** in [bmim][X] type ILs is presented in Table 39. The highest activity was observed in [bmim][BF_4] with a substrate conversion of 47%. [bmim][PF_6] exhibited a substrate conversion of 44%, followed by [bmim][NTf_2] with a conversion of 42 %. The activity of **20** decreased in the order [bmim][PF_6] > [bmim][BF_4] > [bmim][NTf_2]. Excellent selectivity (99%) was obtained, showing the absence of secondary metathesis products. The conversion of methyl ricinoleate in [bmim][X] type ILs at 20 °C is presented in Figure 83.

Table 39: Activity of **20** for the SM of MR in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bmim][PF_6]	44	100
[bmim][BF_4]	47	100
[bmim][NTf_2]	42	100

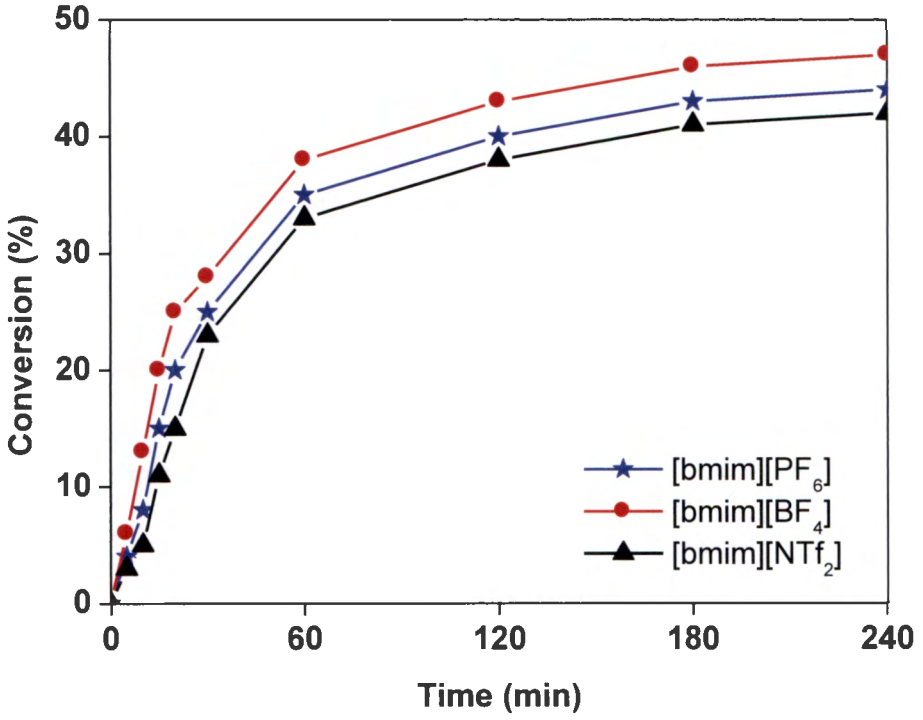


Figure 83: Conversion of MR in [bmim][X] type ILs using **20** at 20 °C

The SM of methyl ricinoleate was also carried out in [bdmim][X] type ILs at 20 °C. Table 40 shows the activity of **20** for the conversion of methyl ricinoleate in [bdmim][X] type ILs at 20 °C. A conversion of 51 % was obtained in [bdmim][BF_4], whereas a conversion of 46 % was obtained in [bdmim][PF_6]. A comparison of the activity of **20** in [bdmim][X] type ILs. Figure 85 compares the influence of cations of the ILs on the activity of **20** for the SM of methyl ricinoleate at 20 °C is given in Figure 85. It is clear from the figure that [bdmim] cations excelled [bmim] cations in the reaction.

Table 40: Activity of **20** for the SM of MR in [bdmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bdmim][PF_6]	46	100
[bdmim][BF_4]	51	100

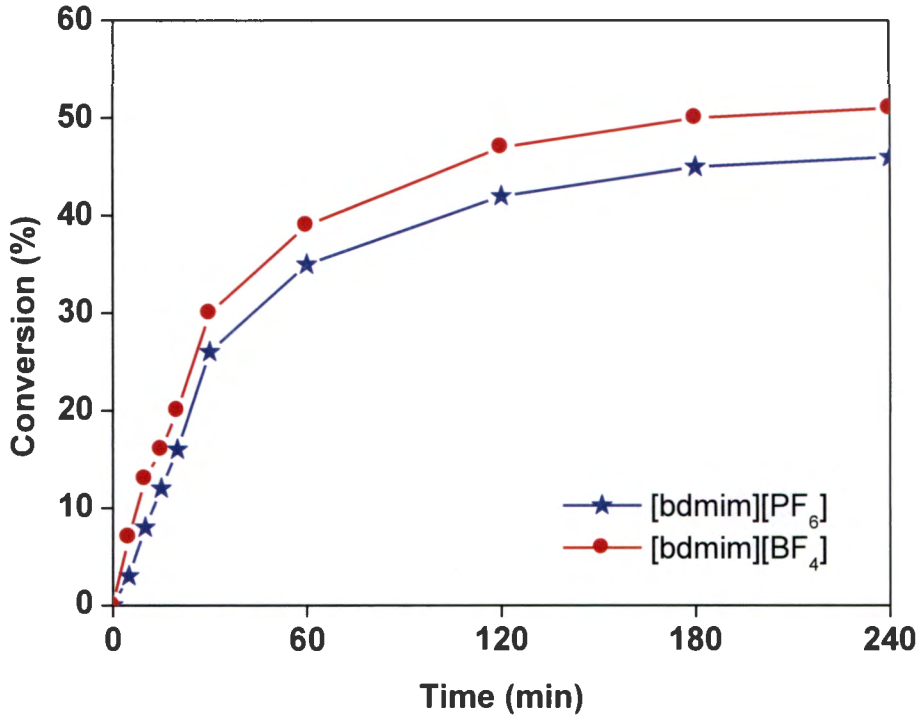


Figure 84: Conversion of MR in [bdmim][X] type ILs using **20** at 20 °C

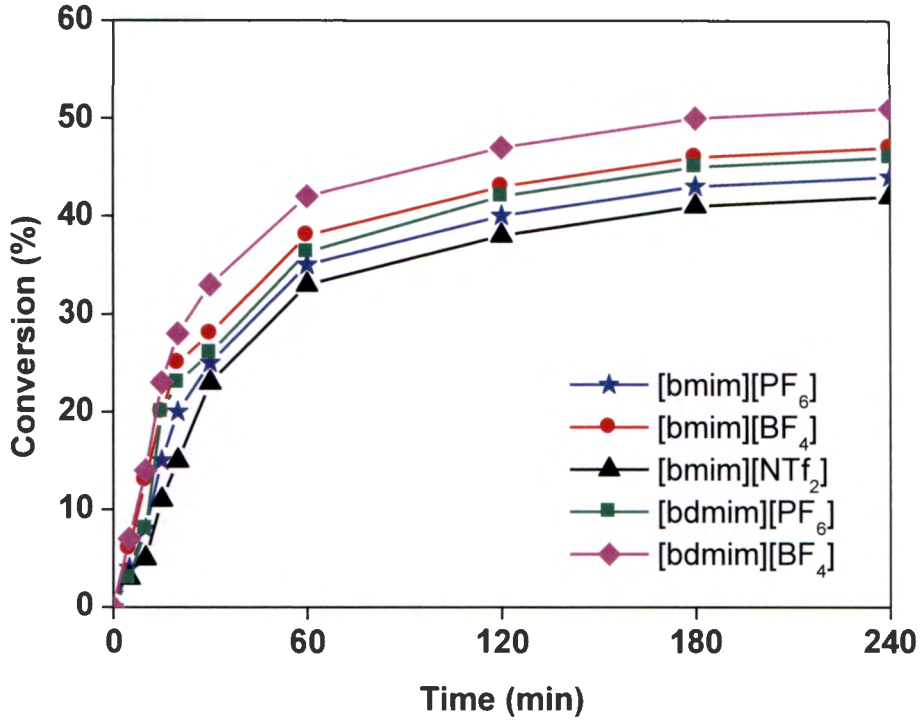


Figure 85: Conversion of MR in [bmim] and [bdmim][X] type ILs using **20** at 20 °C

4.4.4 Metathesis of methyl oleate in organic solvents

The SM of methyl oleate was carried out using **20** in conventional organic solvents. The organic solvents selected for the study were dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **20** in selected organic solvents at 20, 40, 60, 80 and 100 °C, respectively are shown in Tables 41 to 45. At all the selected temperatures, the best catalytic performance occurred in DCM and the lowest in PhMe. The activity of **20** was found to increase in the order PhMe < PhCl < DCE < DCM. At 20 °C and 40 °C, the selectivity towards PMPs was 100% in all the selected organic solvents. At higher temperatures, selectivity decreased. Figure 86 to 90 represent the conversion of methyl ricinoleate in organic solvents at different temperatures.

Table 41: Activity of **20** for the SM of MO in DCM at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	51	100
40	54	100
60	58	97
80	60	92
100	62	87

Table 42: Activity of **20** for the SM of MO in DCE at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	50	100
40	53	100
60	55	98
80	57	91
100	59	91

Table 43: Activity of **20** for the SM of MO in PhCl at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	46	100
40	49	100
60	52	98
80	54	91
100	57	91

Table 44: Activity of **20** for the SM of MO in PhMe at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	44	100
40	47	100
60	51	98
80	53	91
100	55	91

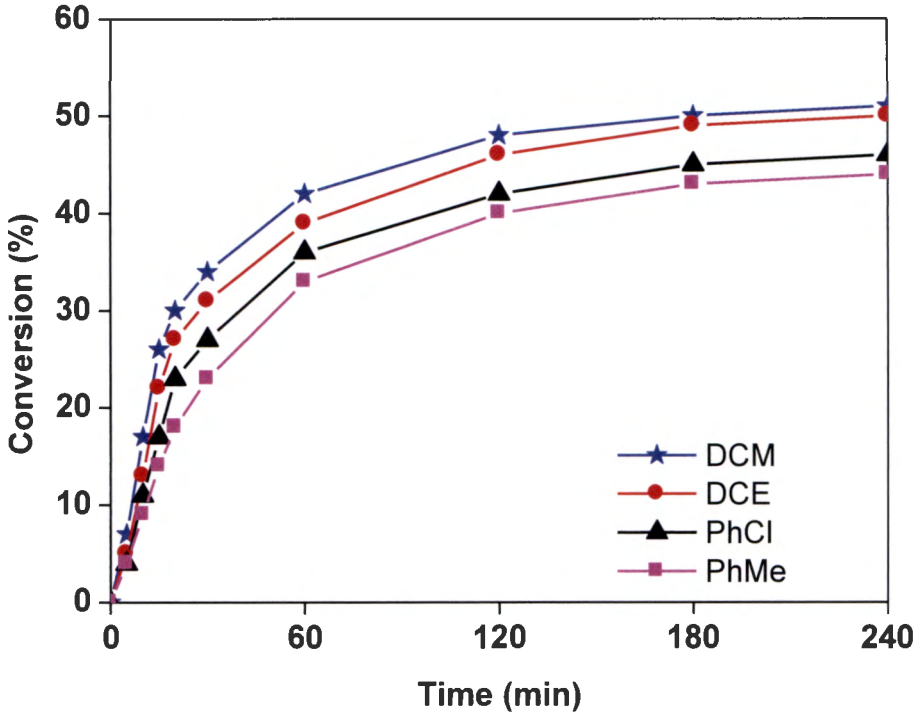


Figure 86: Conversion of MO in organic solvents using **20** at 20°C

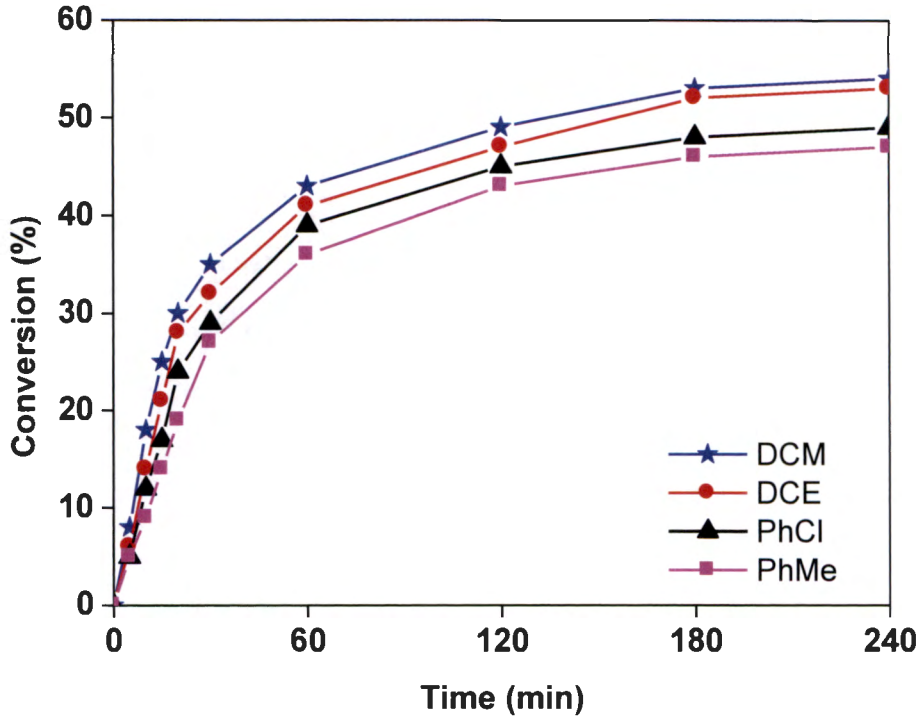


Figure 87: Conversion of MO in organic solvents using **20** at 40°C

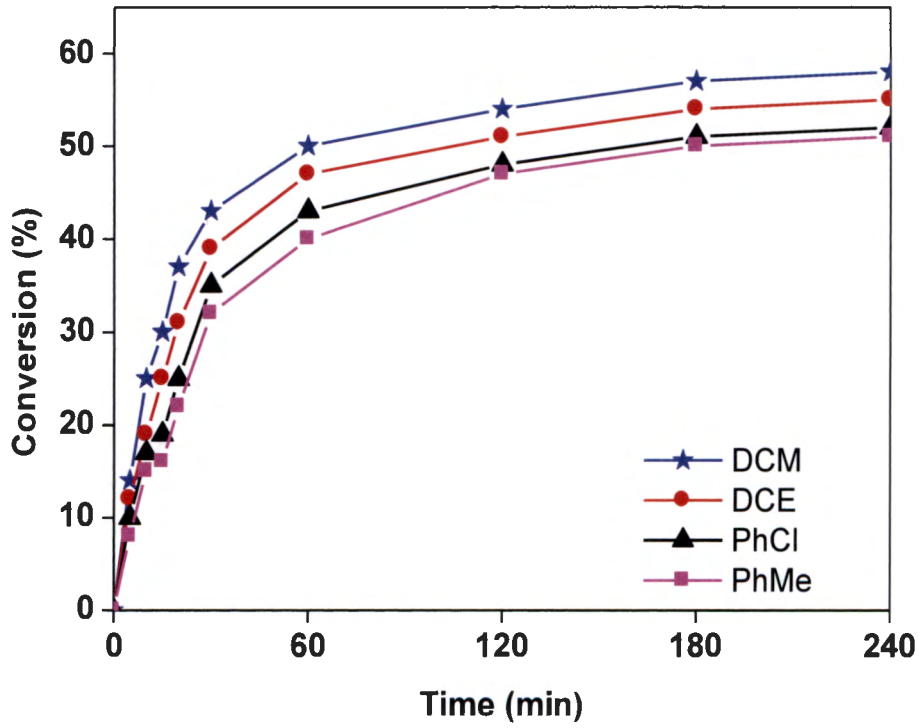


Figure 88: Conversion of MO in organic solvents using **20** at 60°C

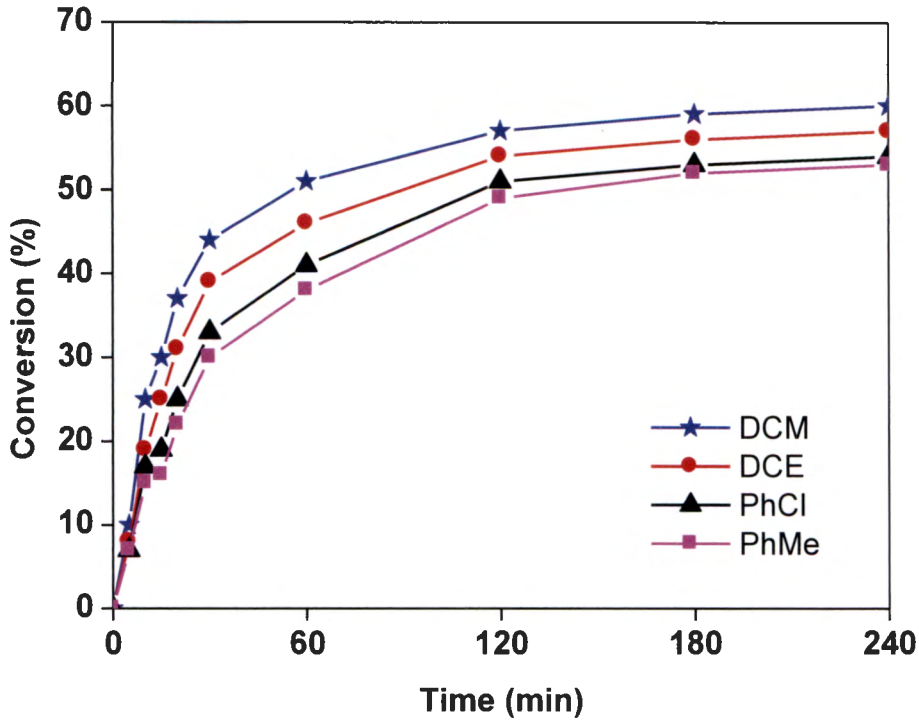


Figure 89: Conversion of MO in organic solvents using **20** at 80°C

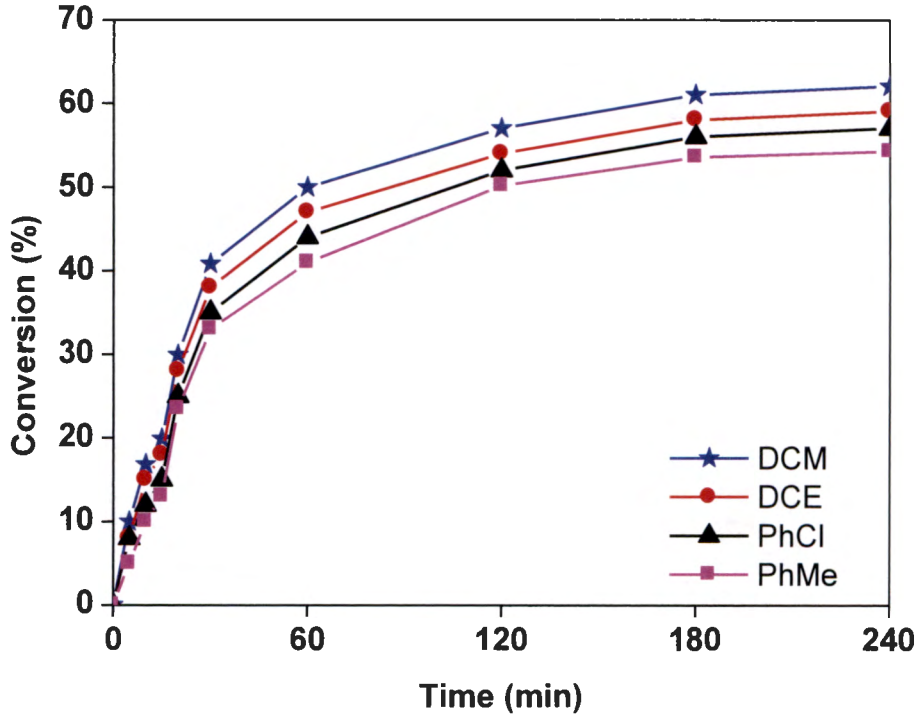


Figure 90: Conversion of MO in organic solvents using **20** at 100°C

A comparison of the activity of **20** in selected ILs and organic solvents at different temperatures is given in Figures 91 to 95. It is clear from the figures that a significant rate enhancement occurred in ILs as opposed to the organic solvents.

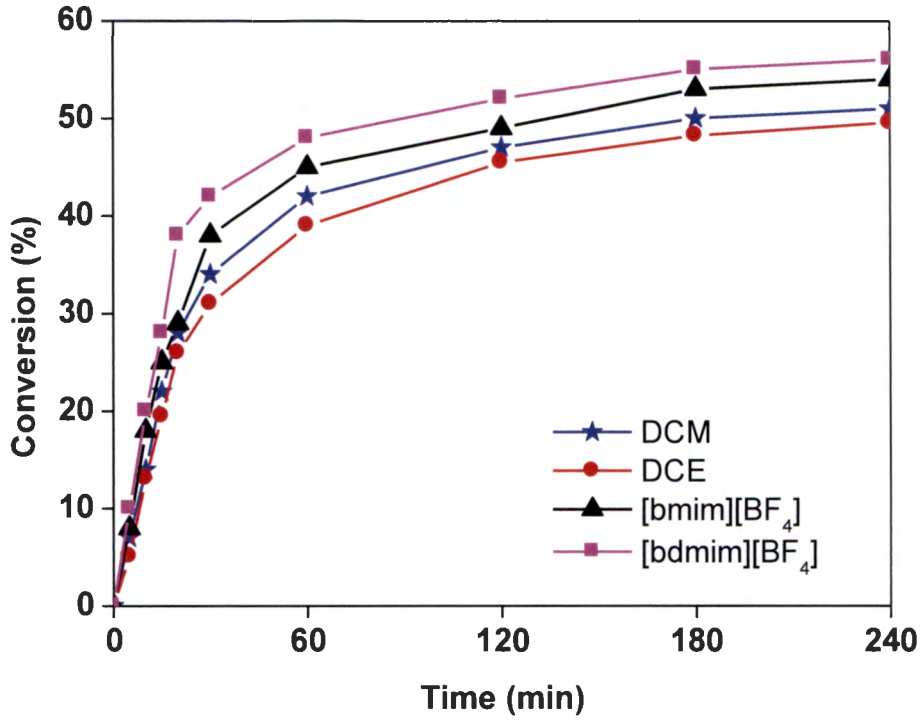


Figure 91: Conversion of MO in selected ILs and organic solvents using **20** at 20°C

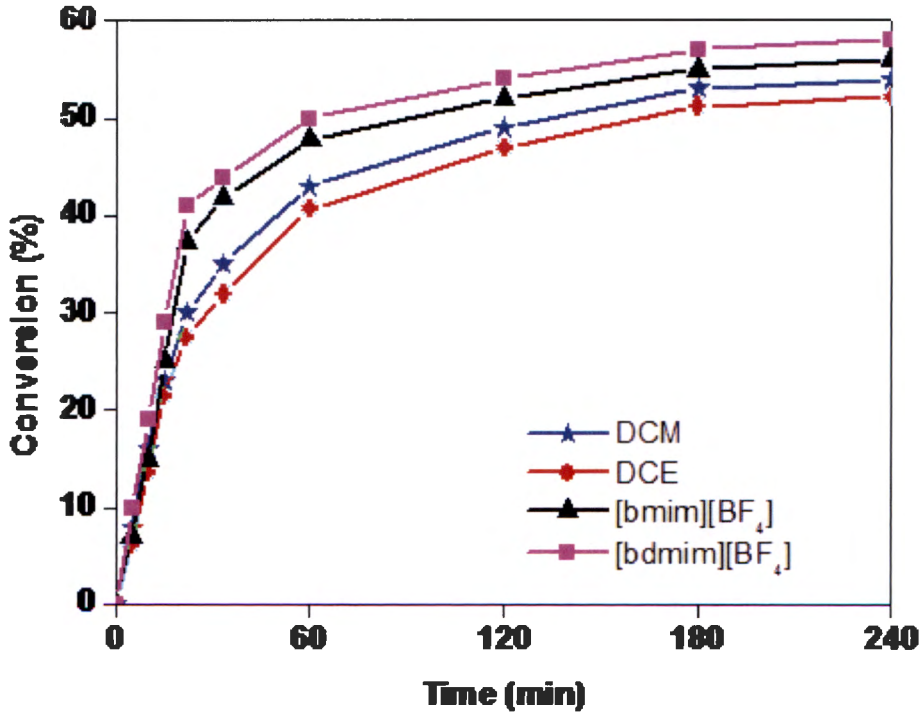


Figure 92: Conversion of MO in selected ILs and organic solvents using **20** at 40°C

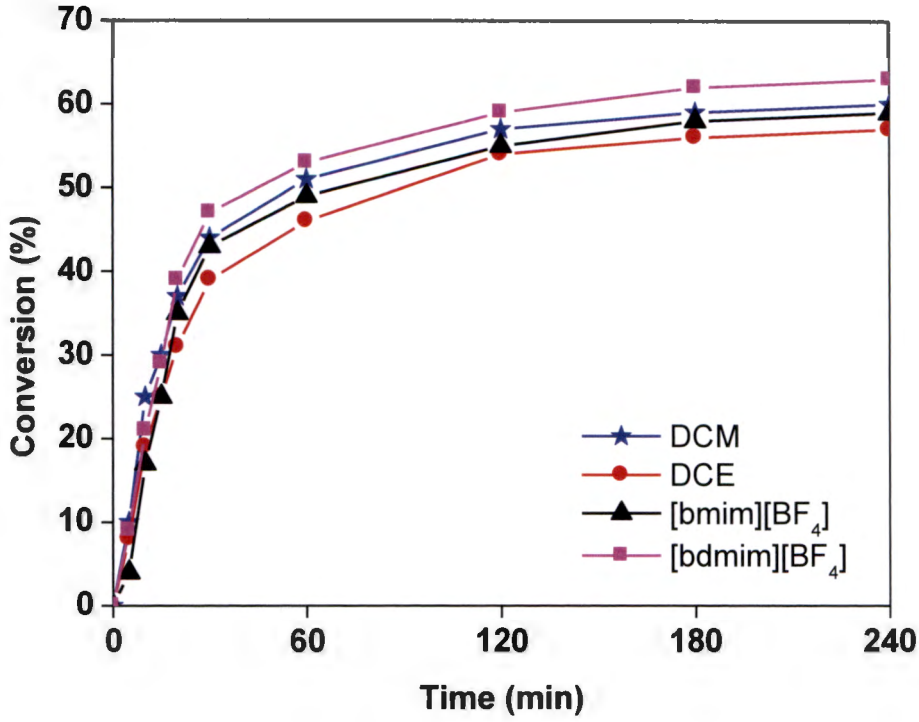


Figure 93: Conversion of MO in selected ILs and organic solvents using **20** at 60°C

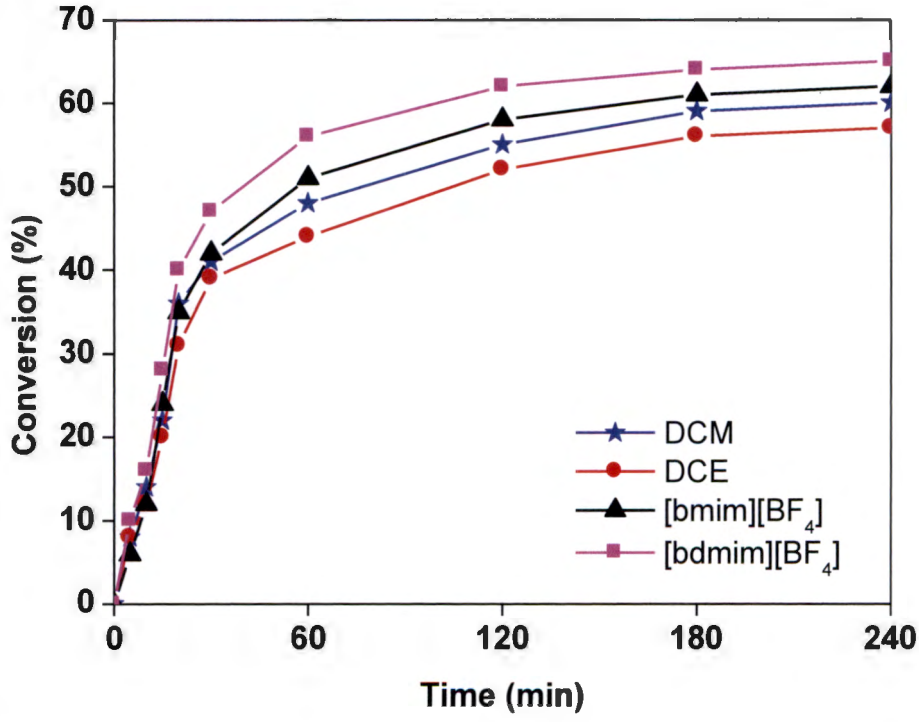


Figure 94: Conversion of MO in selected ILs and organic solvents using **20** at 80°C

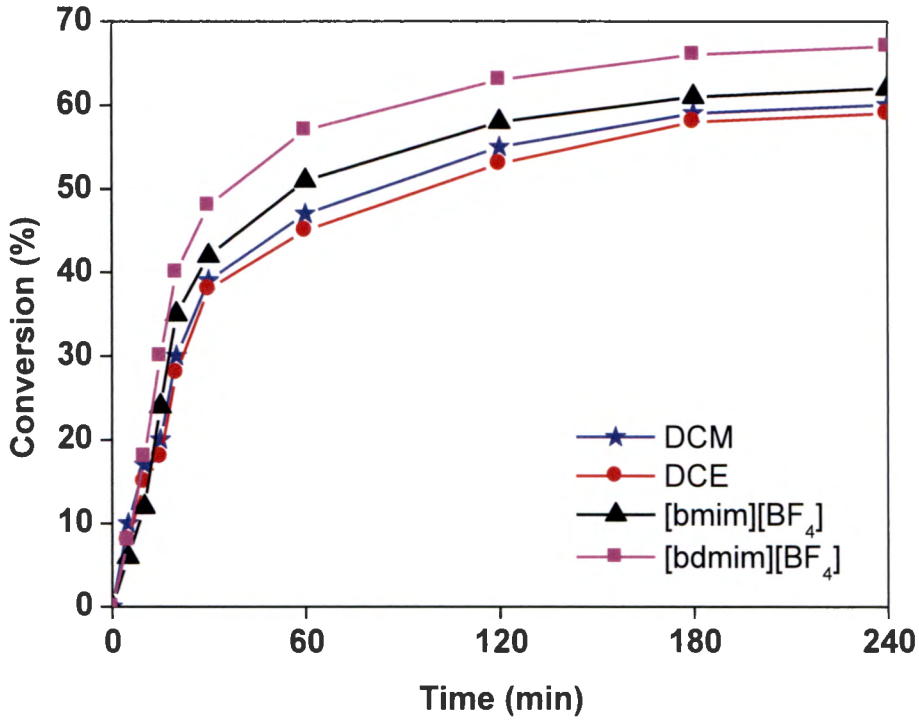


Figure 95: Conversion of MO in selected ILs and organic solvents using **20** at 100°C

4.4.5 Metathesis of methyl ricinoleate in organic solvents

The SM of methyl ricinoleate using **20** was carried out in four different organic solvents, namely; dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **20** in selected organic solvents at 20 °C is given in Table 45. The highest activity was obtained in DCM (36%) and the lowest in PhMe (31%). The activity of **20** was found to be in the order DCM > DCE > PhCl > PhMe. Very good selectivity of 99 % was observed at a temperature of 20 °C, showing the absence of SMPs.

Table 45: Activity of **20** for the SM of MR in organic solvents at 20 °C after 4 h reaction time

Solvent	Conv (%)	Selec (%)
DCM	40	100
DCE	38	100
PhCl	37	100
PhMe	35	100

The conversion of MR in organic solvents in presence of catalyst **20** at 20 °C is shown in Figure 96 while the conversion of methyl ricinoleate in presence of **20** in selected organic

solvents and ILs at 20 °C is presented in Figure 97. It is clear from the figure that a significant rate enhancement occurred in ILs compared to organic solvents.

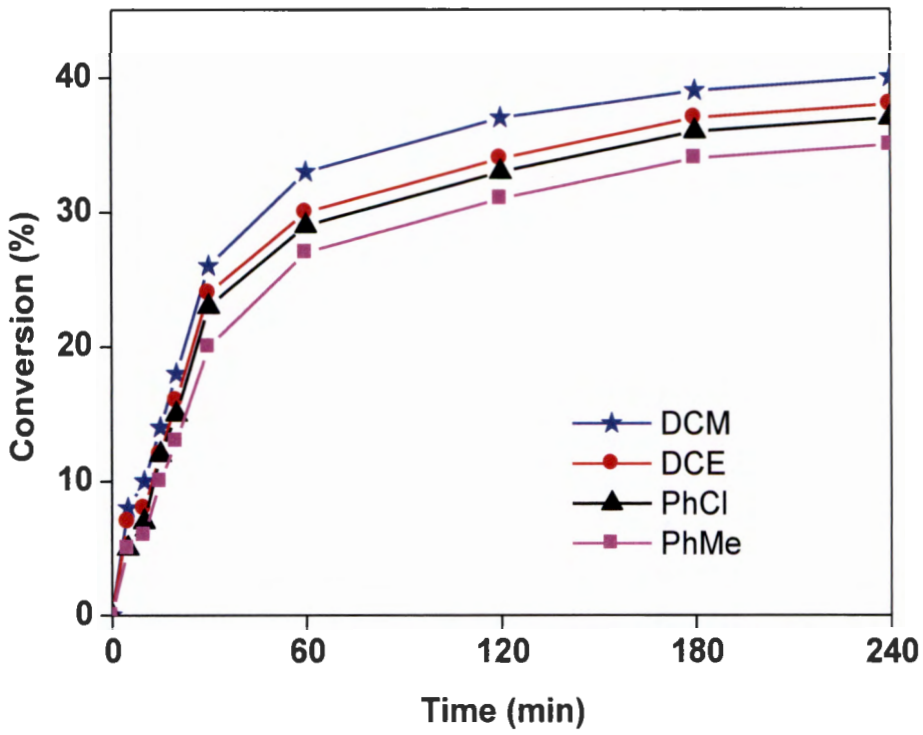


Figure 96: Conversion of MR in organic solvents using **20** at 20 °C

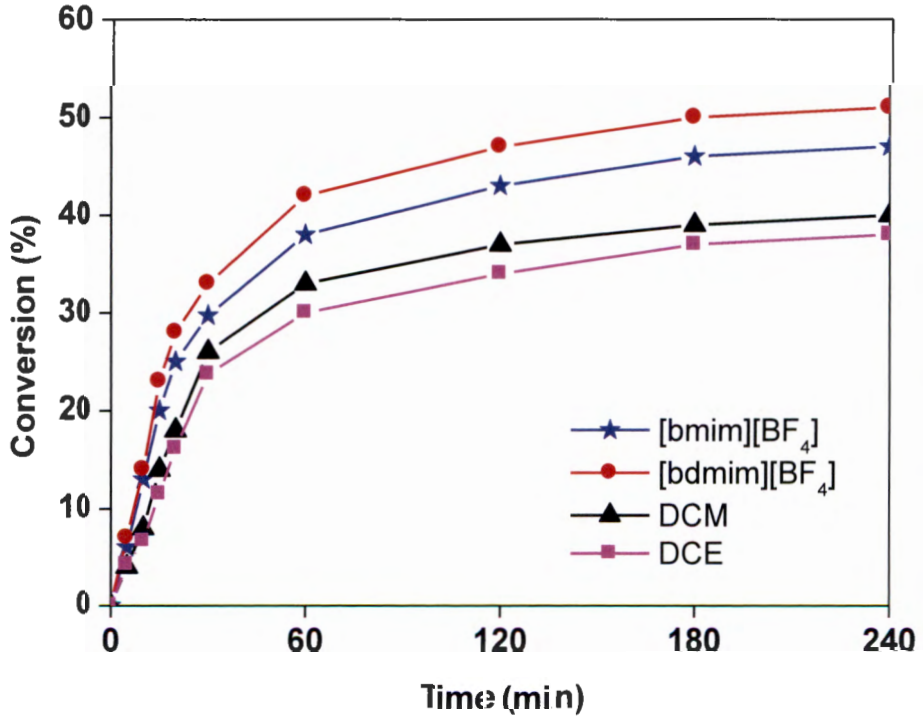
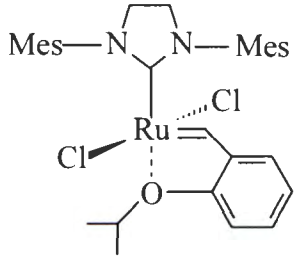


Figure 97: Conversion of MR in organic solvents and ILs using **20** at 20 °C

4.5 Metathesis of unsaturated fatty acid esters using Hoveyda-Grubbs second generation catalyst 21



21

4.5.1 Metathesis of methyl oleate in [bmim][X] type ILs

The SM of methyl oleate was investigated in presence of Hoveyda Grubbs second generation catalyst **21**. The substrate/catalyst molar ratio used was 100:1. The reactions were carried out at different temperatures ranging from 20 °C to 100 °C in RTILs ([bmim][PF_6], [bmim][BF_4] and [bmim][NTf_2]). In all the reactions, 1mL of the particular solvent was added to 0.5 mL of substrate followed by the addition of 12.3 mg of Grubbs catalyst.

4.5.1.1 Influence of the solvent

The influence of [bmim][X] type ILs on methyl oleate metathesis was investigated in presence of **21** at different temperatures. The activity of **21** for the SM of methyl oleate in [bmim][X] type ILs is shown in Table 46. A conversion of 71% was obtained in [bmim][BF**4**], whereas the reaction in [bmim][PF_6] gave a conversion of 67%. 100 % selectivity was obtained in all the runs showing the absence of SMPs.

Table 46: Activity of **21** for the SM of MO in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)	TON
[bmim][PF_6]	67	100	53
[bmim][BF_4]	71	100	59
[bmim][NTf_2]	64	100	61

4.5.1.2 Influence of the anions of IL

The effect of varying the anion counterpart in [bmim][X] type ILs on the metathesis of methyl oleate using catalyst **21** has been studied. Figure 98 shows the influence of anion on the

catalytic activity of **21**. The trend in metathesis activity decreased in the order BF_4^- > PF_6^- > NTf_2^-.

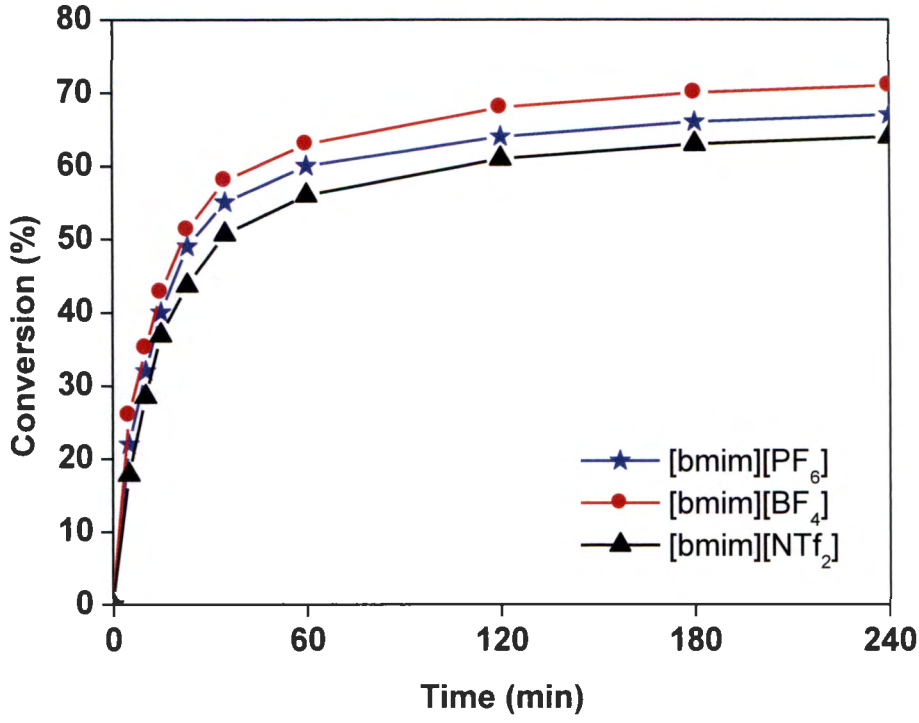


Figure 98: Influence of the anions of [bmim][X] type ILs on the activity of **21** at 20 °C.

4.5.1.3 Influence of reaction temperature

The influence of reaction temperature on the activity of **21** for the SM of methyl oleate was investigated. A summary of the activity of **21** in [bmim][X] type ILs at different reaction temperature is given in Tables 47 to 49. The catalytic activity increased with increasing temperature. However, the selectivity towards PMPs was very low, at high temperatures (≥ 60 °C). The conversion of methyl oleate in [bmim][X] type ILs at 40 °C, 60 °C, 80 °C and 100 °C, after 4 hour reaction time is shown in Figures 99 to 102.

Table 47: Activity of **21** for the SM of MO in [bmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	67	100	53
40	76	96	65
60	82	82	75
80	90	76	79
100	92	69	81

Table 48: Activity of **21** for the SM of MO in [bmim][BF_4] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	71	100	59
40	79	96	69
60	87	82	78
80	85	76	83
100	97	69	85

Table 49: Activity of **21** for the SM of MO in [bmim][NTf_2] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	64	100	61
40	74	96	67
60	85	82	73
80	92	76	80
100	94	69	82

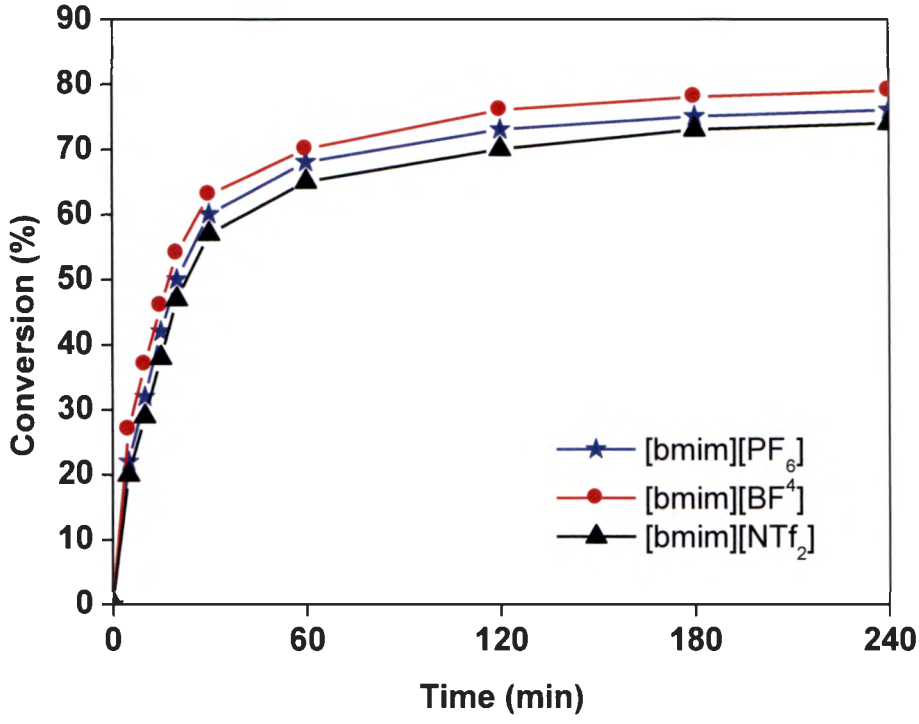


Figure 99: Conversion of MO in [bmim][X] type ILs using **21** at 40 °C

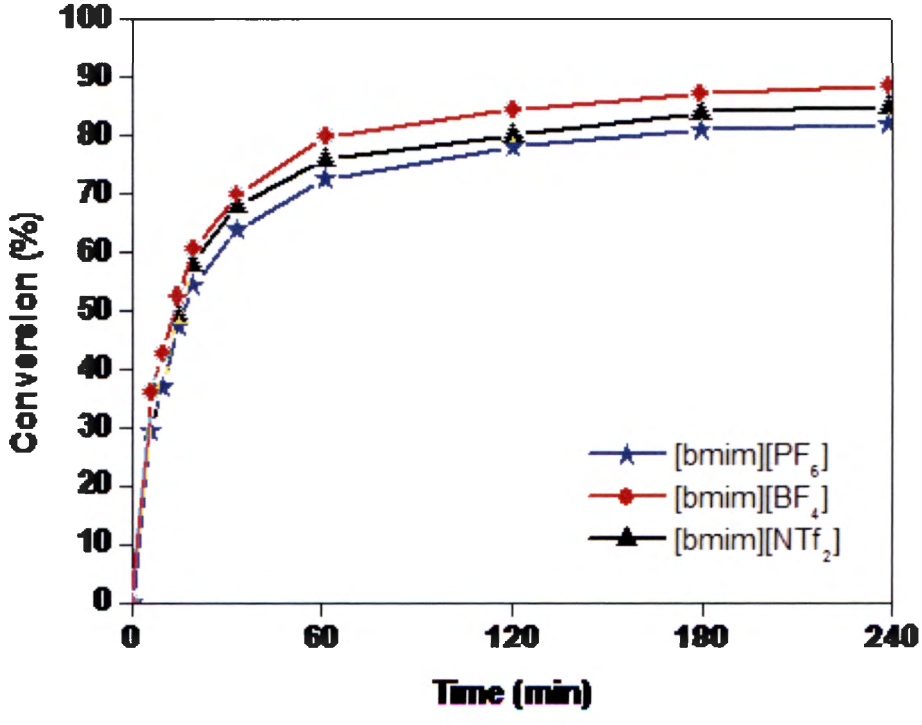


Figure 100: Conversion of MO in [bmim][X] type ILs using **21** at 60 °C

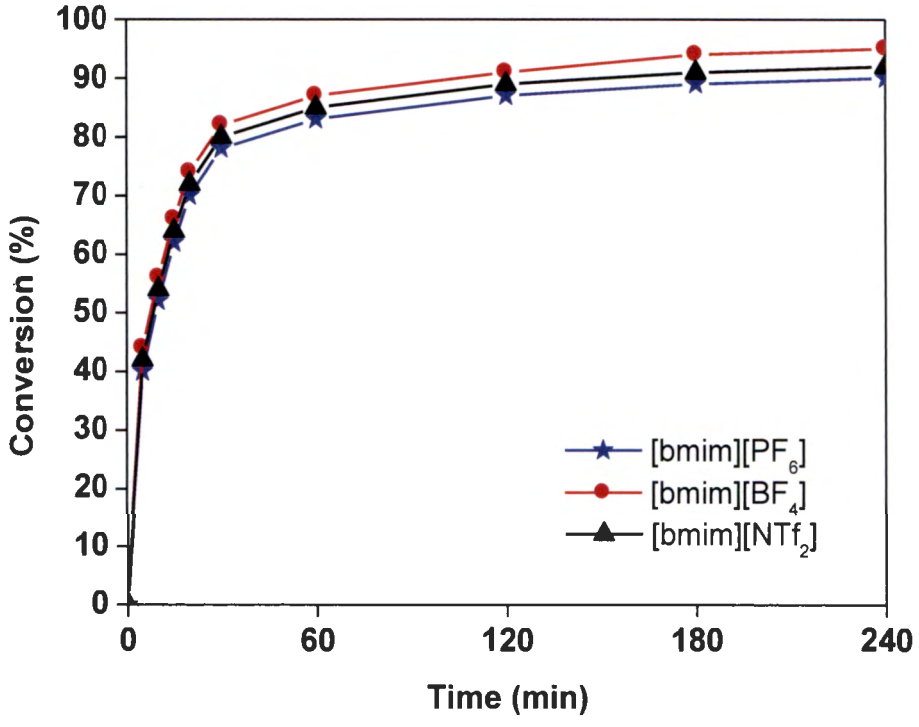


Figure 101: Conversion of MO in [bmim][X] type ILs using **21** at 80 °C

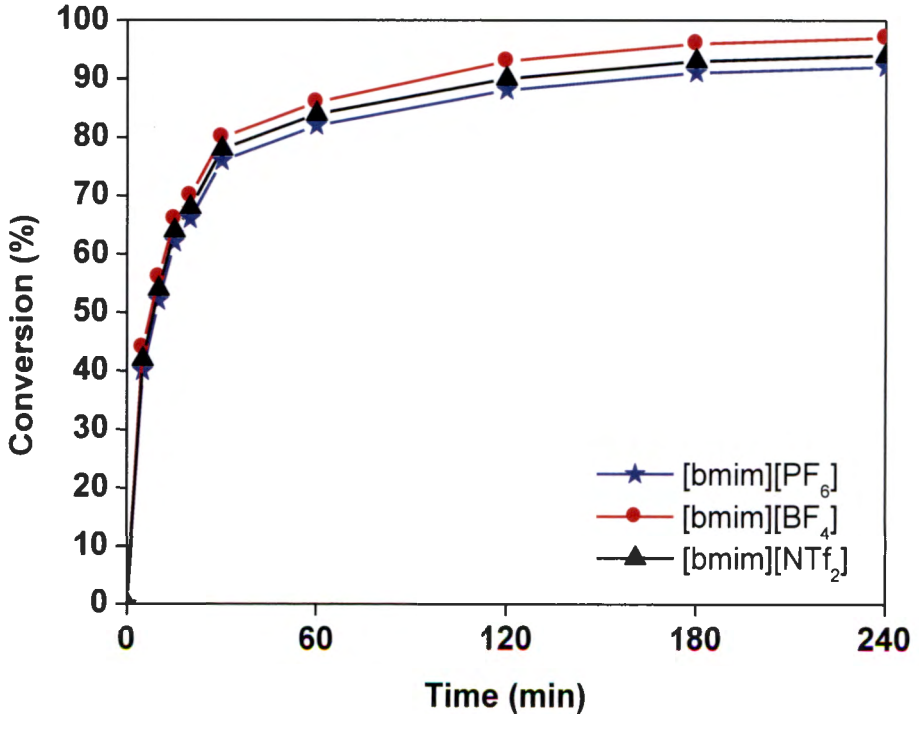


Figure 102: Conversion of MO in [bmim][X] type ILs using **21** at 100 °C

Oleate conversions as a function of reaction temperatures (20 to 100 °C) for the metathesis of methyl oleate in the presence of **21** are shown in Figure 103. The activity of the catalyst increased with increasing the temperature from 20 – 100 °C with oleate conversions increasing from 71 to 97%. The results reveal that Hoveyda Grubbs catalyst **21** can withstand higher temperature of 100 °C. But as the temperature increased, the selectivity towards PMPs decreased from 100 to 69%.

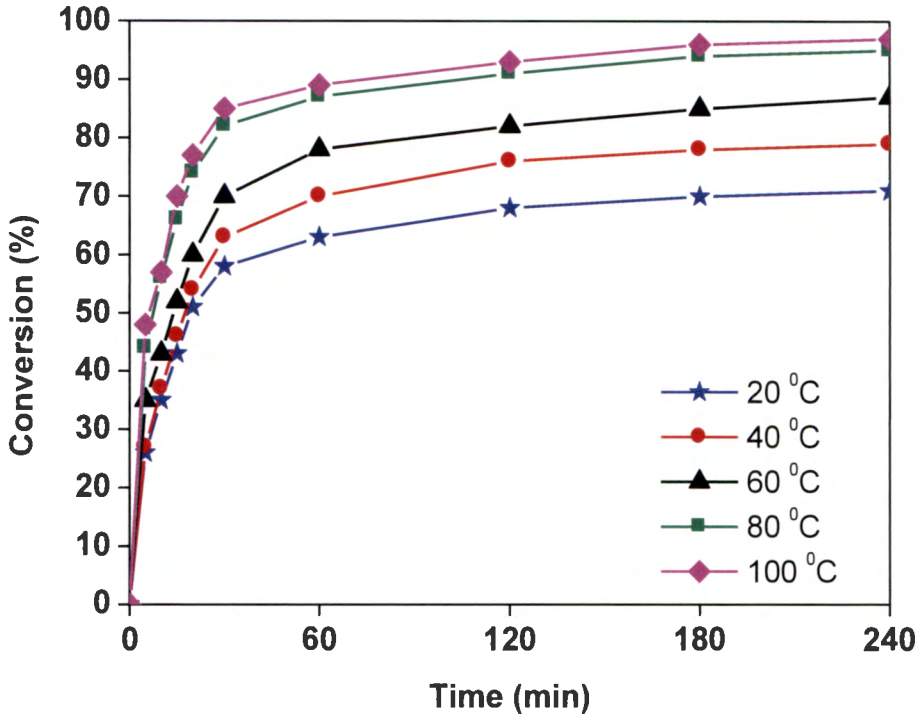


Figure 103: Influence of temperature on the activity of **21** in [bmim][BF_4] from 20 to 100 °C

4.5.1.4 Influence of reaction atmosphere

The influence of reaction atmosphere on the activity of **21** was investigated using methyl oleate in [bmim][BF_4] at different temperatures. The experiment was conducted in two different reaction atmospheres, air and N_2, at the substrate/catalyst molar ratio of 100:1. The activity of **21** at different temperatures under air using [bmim][BF_4] as a solvent is shown in Table 50 while Figures 104 to 108 represent the substrate conversion as a function of reaction time under N_2 and air atmospheres at 20, 40, 60, 80 and 100 °C. It is clear from the figures that **21** has very little difference in substrate conversion in air and nitrogen atmospheres. At all the selected temperatures, the activity of **21** was found to be same in air and N_2 atmospheres. This proves the statement that Hoveyda-Grubbs second generation catalyst is stable under air atmosphere.

Table 50: Activity of **21** for the SM of MO in [bmim][BF_4] under air after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	70	100	58
40	78	96	68
60	86	82	77
80	94	76	82
100	96	69	84

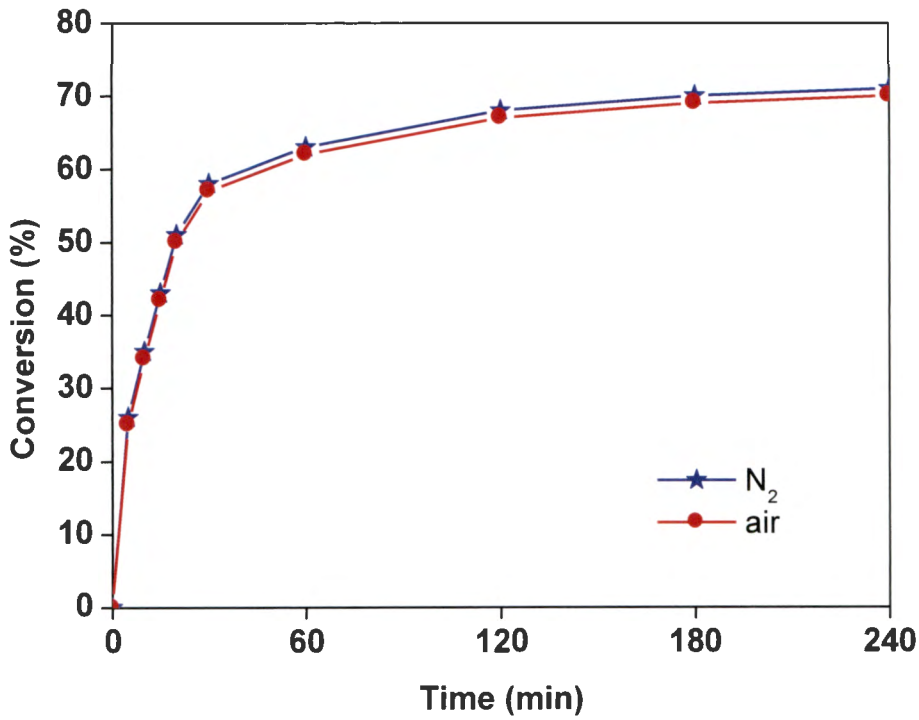


Figure 104: Conversion of MO in [bmim][BF_4] using **21** at 20 °C in air and N_2 atmospheres

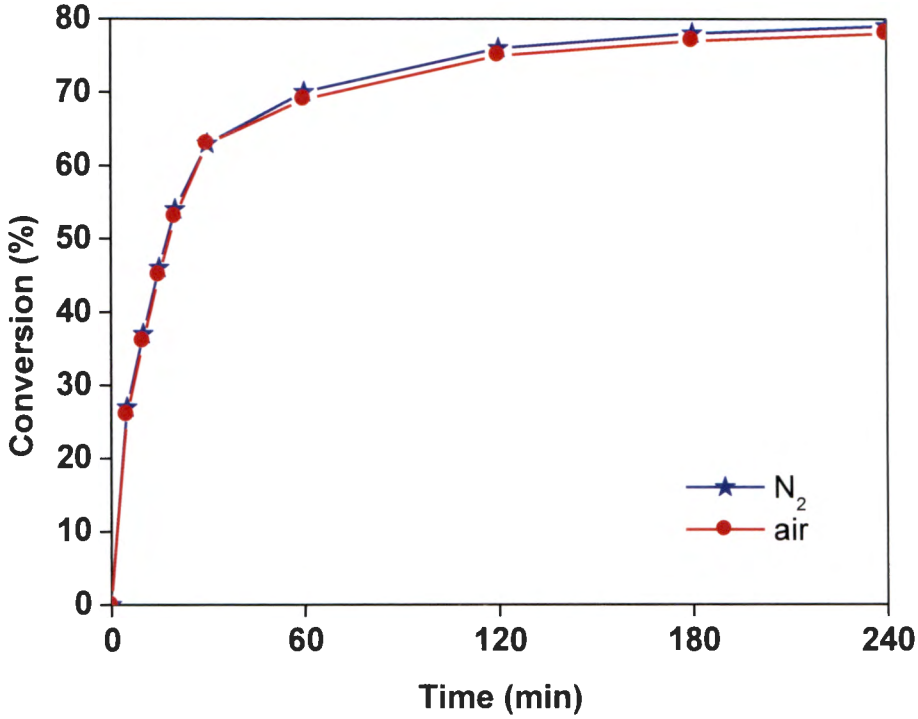


Figure 105: Conversion of MO in [bmim][BF_4] using **21** at 40 °C in air and N_2 atmospheres

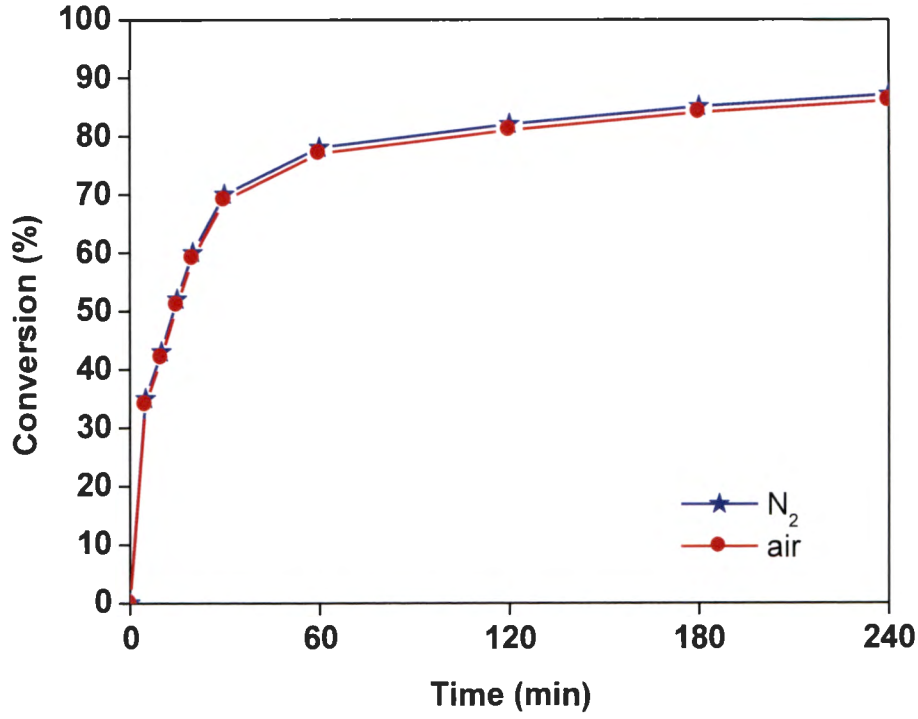


Figure 106: Conversion of MO in [bmim][BF_4] using **21** at 60 °C in air and N_2 atmospheres

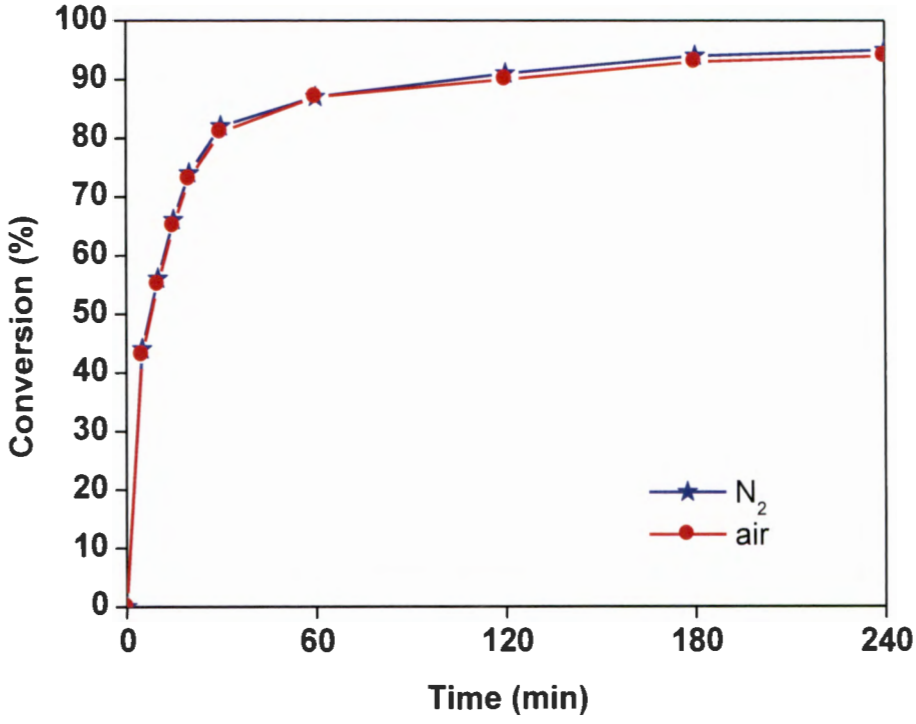


Figure 107: Conversion of MO in [bmim][BF_4] using **21** at 80 °C in air and N_2 atmospheres

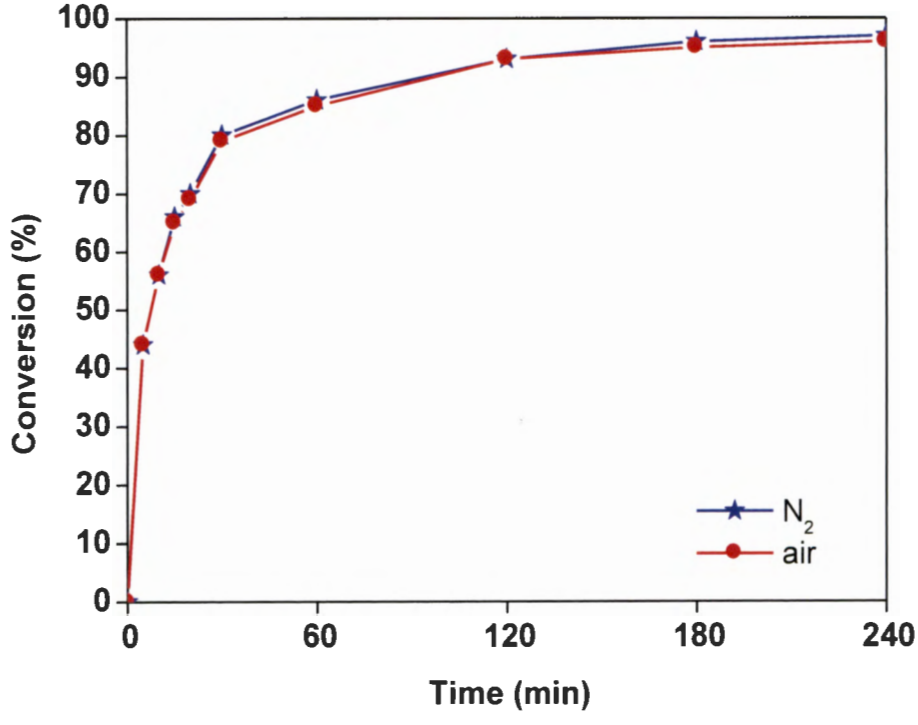


Figure 108: Conversion of MO in [bmim][BF_4] using **21** at 100 °C in air and N_2 atmospheres

4.5.2 Metathesis of methyl oleate in [bdmim][X] type ILs

The metathesis of methyl oleate was investigated in the presence of **21** in [bdmim][X] type ILs. The ILs selected for the study are [bdmim][PF_6] and [bdmim][BF_4]. The reactions

were carried out at temperatures ranging from 20-100 °C. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.5 mL of methyl oleate followed by the addition of 12.3 mg of Grubbs catalyst.

The activity of **21** in [bdmim][X] type ILs at different reaction temperature is summarized in Tables 51 and 52. At all the selected temperatures, the highest conversion was observed in [bdmim][BF_4]. At 20 °C, the reaction in [bdmim][BF_4] exhibited a conversion of 77% which then increased to 98% at 100 °C. At higher temperatures ($\geq$60 °C), SMPs were formed as is evident from the figures on selectivity.

Table 51: Activity of **21** for the SM of MO in [bdmim][PF_6] at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)	TON
20	74	100	55
40	81	96	68
60	90	82	76
80	93	76	84
100	95	69	88

Table 52: Activity of **21** for the SM of MO in [bdmim][BF_4] at different temperatures after 4 h reaction time.

Temp (°C)	Conv (%)	Selec (%)	TON
20	77	100	62
40	85	96	71
60	92	82	83
80	96	76	86
100	98	69	89

The activity of [bmim][X] and [bdmim][X] type ILs at different reaction temperatures is hown in Figures 109 to 113. At all the selected temperatures, the highest conversion was observed in [bdmim][BF_4], followed by [bdmim][PF_6].

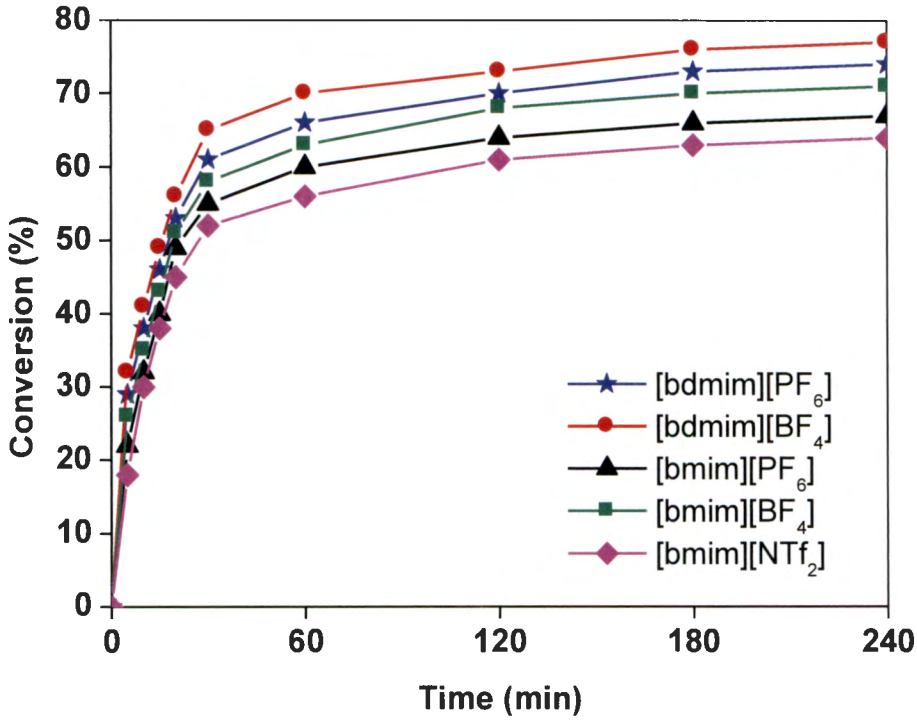


Figure 109: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **21** at 20 °C

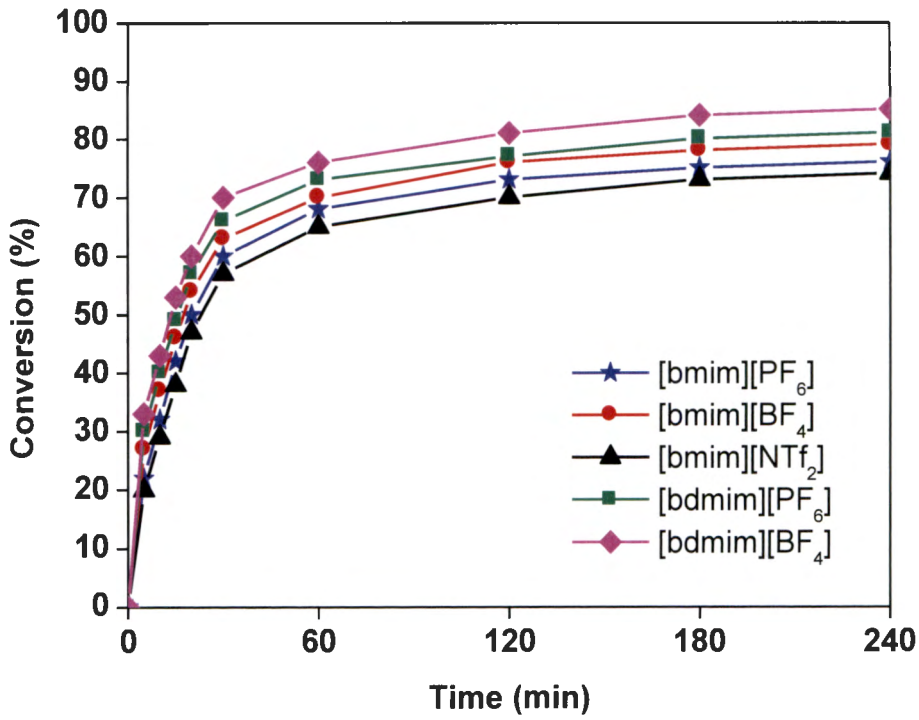


Figure 110: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **21** at 40 °C

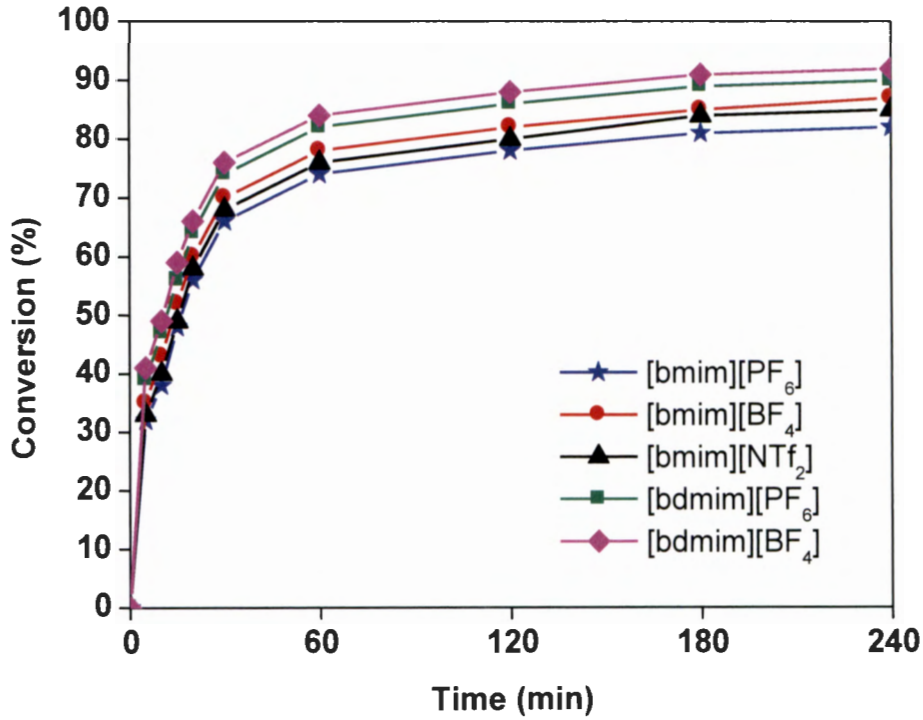


Figure 111: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **21** at 60 °C

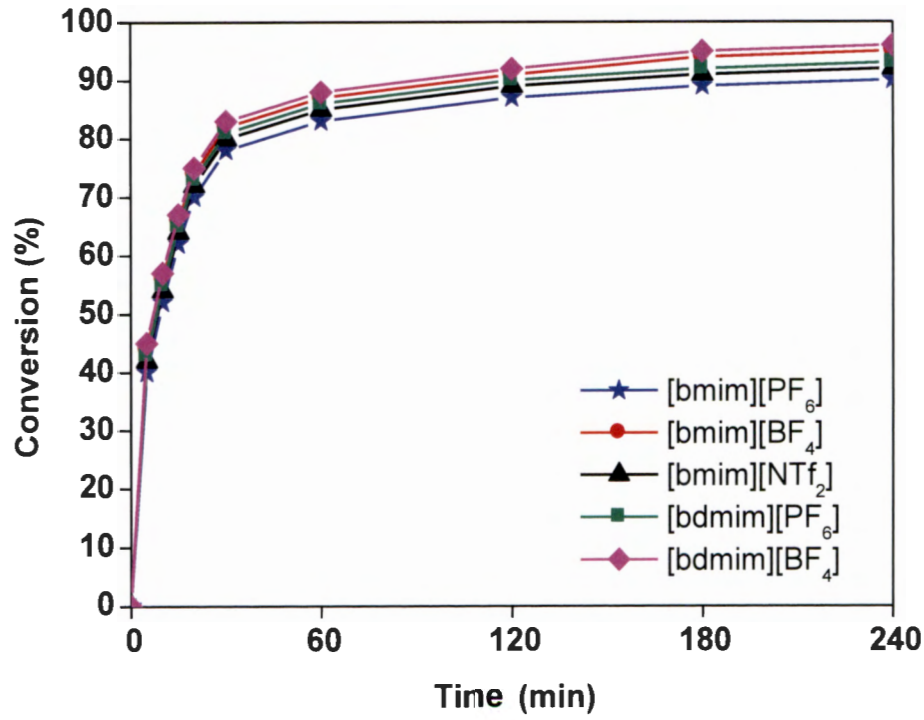


Figure 112: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **21** at 80 °C

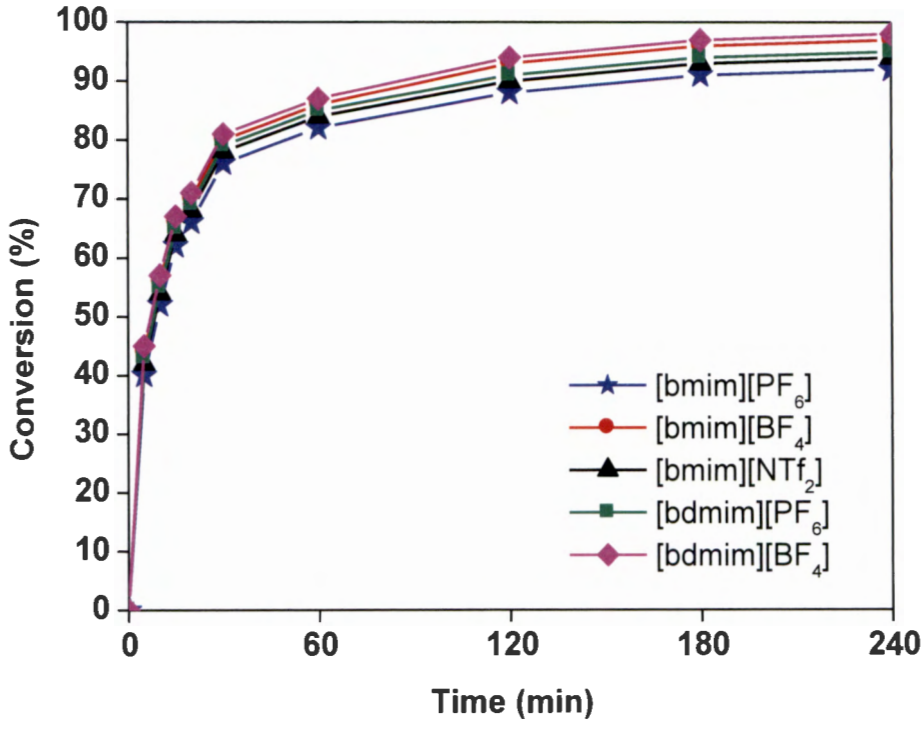


Figure 113: Conversion of MO in [bmim][X] and [bdmim][X] type ILs using **21** at 100 °C

4.5.3 Metathesis of methyl ricinoleate in [bmim][X] and [bdmim][X] type ILs

The self-metathesis of methyl ricinoleate was carried out in the presence of Hoveyda Grubbs catalyst **21** at 20 °C using [bmim][X] and [bdmim][X] type ILs. The substrate/catalyst molar ratio used was 100:1. In all the reactions, 1mL of the particular solvent was added to 0.2 mL of substrate followed by the addition of 0.59 mg of Grubbs catalyst.

A summary of the activity of **21** in [bmim][X] type ILs is given in Table 53. Substrate conversions of 55%, 51% and 49% were observed in [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] respectively. The activity of **21** decreased in the order [bmim][BF_4] > [bmim][PF_6] > [bmim][NTf_2]. Excellent selectivity (99%) was obtained, showing the absence of secondary metathesis products. The conversion of methyl ricinoleate in [bmim][X] type ILs at 20 °C is shown in Figure 114.

Table 53: Activity of **21** for the SM of MR in [bmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bmim][PF_6]	51	100
[bmim][BF_4]	55	100
[bmim][NTf_2]	49	100

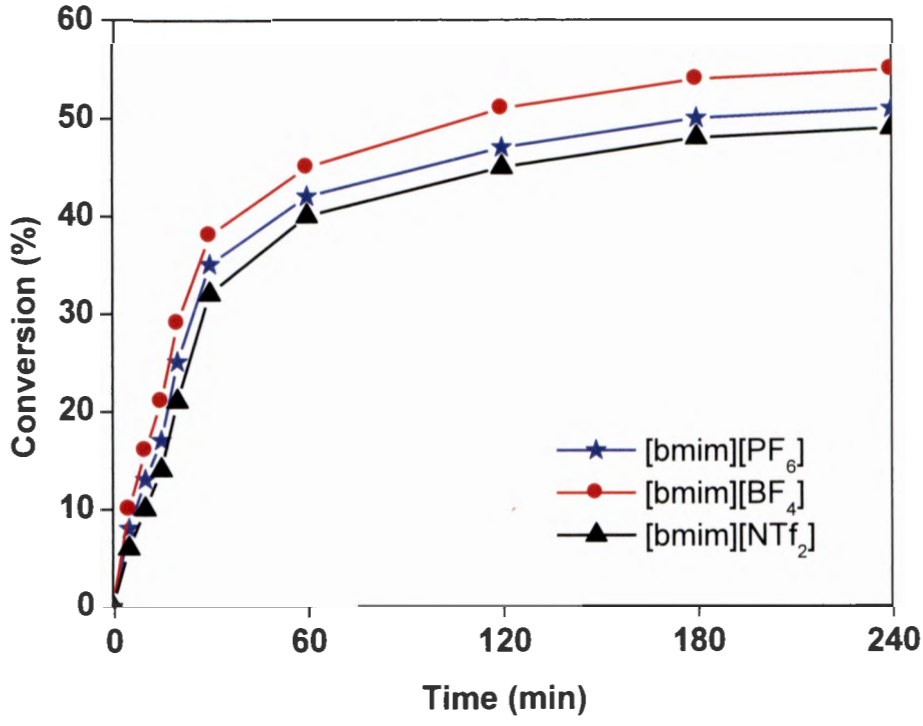


Figure 114: Conversion of MR in [bmim][X] type ILs using **21** at 20 °C

The SM of methyl ricinoleate was also carried out in [bdmim][X] type ILs at 20 °C. The activity of **21** for the conversion of methyl ricinoleate in [bdmim][X] type ILs at 20 °C is shown in Table 54. A conversion of 57% was obtained in [bdmim][BF_4], whereas a conversion of 53% was obtained in [bdmim][PF_6]. A comparison of the activity of **21** in [bdmim][X] type ILs is given in Figure 115. Also, a comparison of the influence of cations of the ILs on the activity of **21** for the SM of methyl ricinoleate at 20 °C is given in Figure 116. It is clear from the figure that [bdmim] cations excelled [bmim] cations in the reaction.

Table 54: Activity of **21** for the SM of MR in [bdmim][X] type ILs at 20 °C after 4 h reaction time

RTIL	Conv (%)	Selec (%)
[bdmim][PF_6]	53	100
[bdmim][BF_4]	57	100

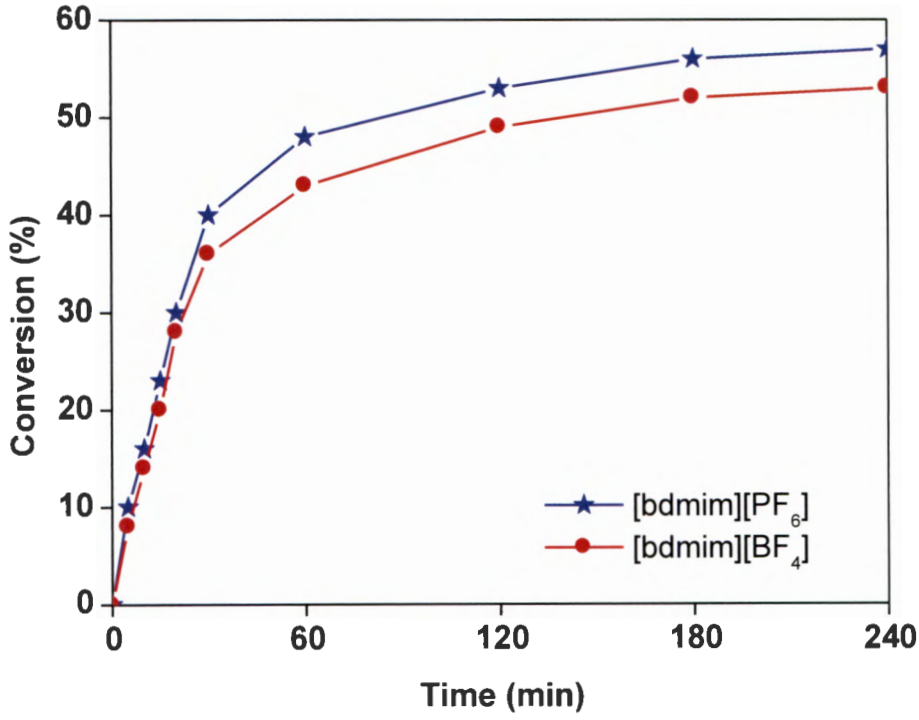


Figure 115: Conversion of MR in [bdmim][X] type ILs using **21** at 20 °C

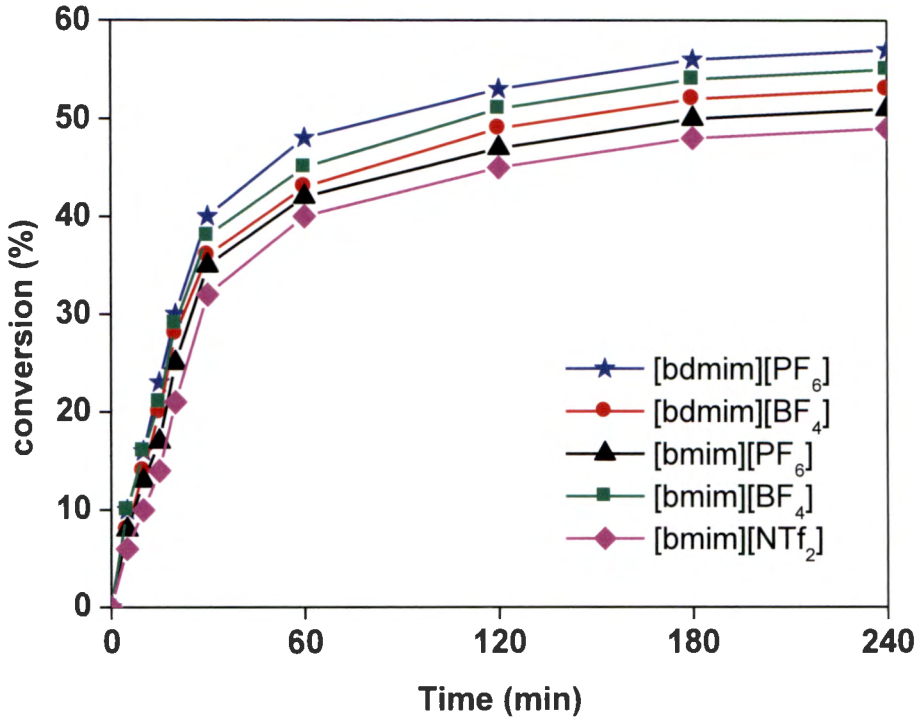


Figure 116: Conversion of MR in [bmim] and [bdmim][X] type ILs using **21** at 20 °C

4.5.4 Metathesis of methyl oleate in organic solvents

The SM of methyl oleate was carried out using **21** in conventional organic solvents. The organic solvents selected for the study were dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). Tables 55 to 58 represent the activity of **21** in selected organic solvents at 20, 40, 60, 80 and 100 °C, respectively. At all the selected temperatures, the best catalytic performance occurred in DCM and the lowest in PhMe. The activity of **21** was found to increase in the order PhMe < PhCl < DCE < DCM. Good selectivities were obtained at moderate temperatures (≥ 40 °C), afterwards, poor selectivities were obtained which shows the presence of SMPs. The conversions of methyl ricinoleate in organic solvents at different temperatures are shown in Figures 117 to 121.

Table 55: Activity of **21** for the SM of MO in DCM at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	62	100
40	68	96
60	74	82
80	82	76
100	86	69

Table 56: Activity of **21** for the SM of MO in DCE at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	60	100
40	66	100
60	72	98
80	80	91
100	84	91

Table 57: Activity of **21** for the SM of MO in PhMe at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	53	100
40	61	100
60	67	98
80	74	91
100	78	91

Table 58: Activity of **21** for the SM of MO in PhCl at different temperatures after 4 h reaction time

Temp (°C)	Conv (%)	Selec (%)
20	57	100
40	64	100
60	69	98
80	76	91
100	80	91

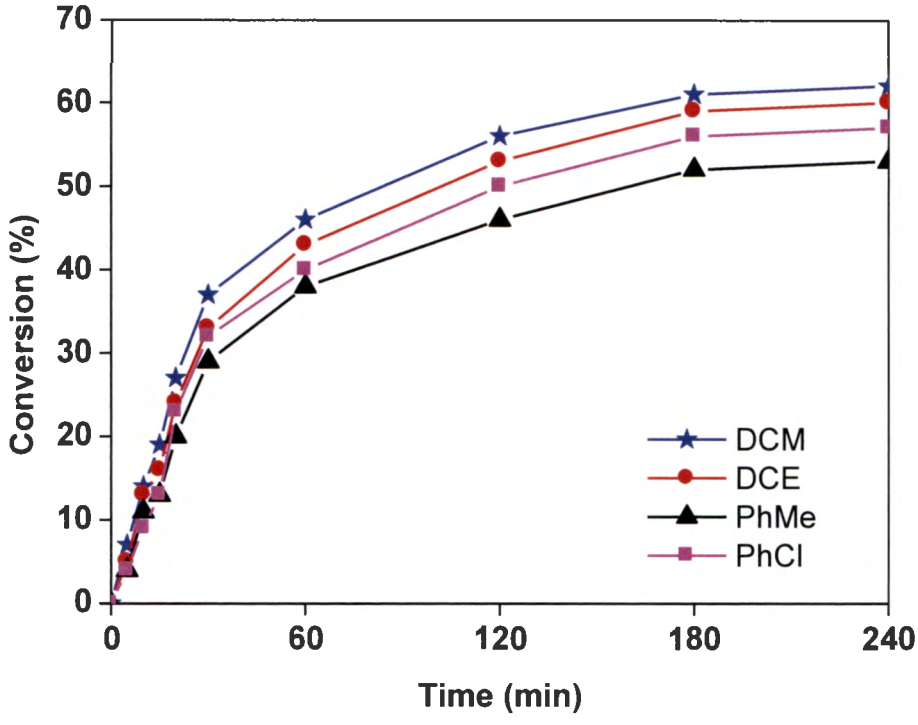


Figure 117: Conversion of MO in organic solvents using **21** at 20°C

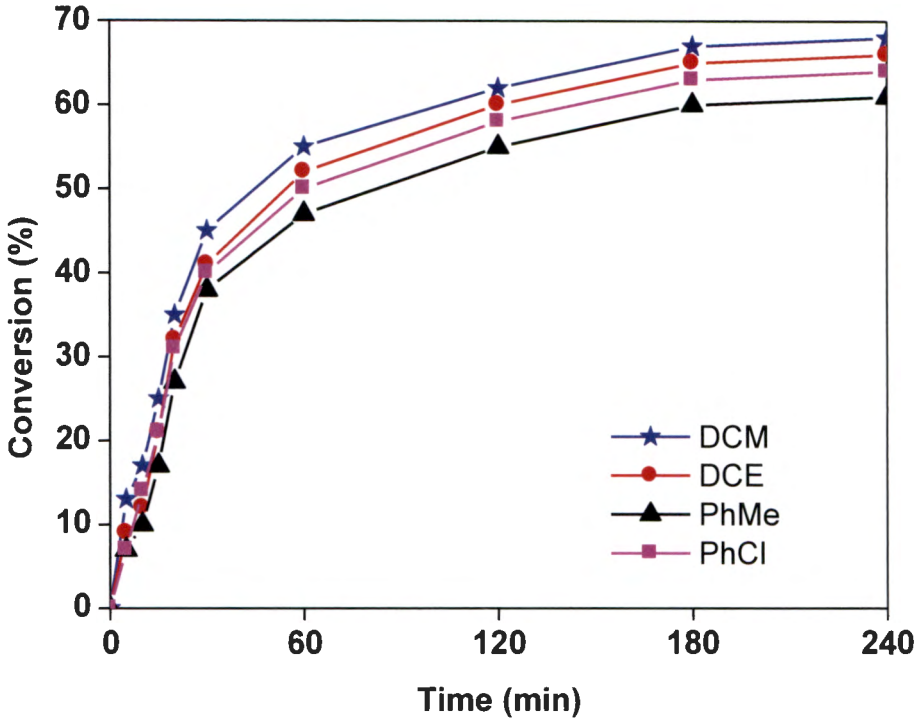


Figure 118: Conversion of MO in organic solvents using **21** at 40°C

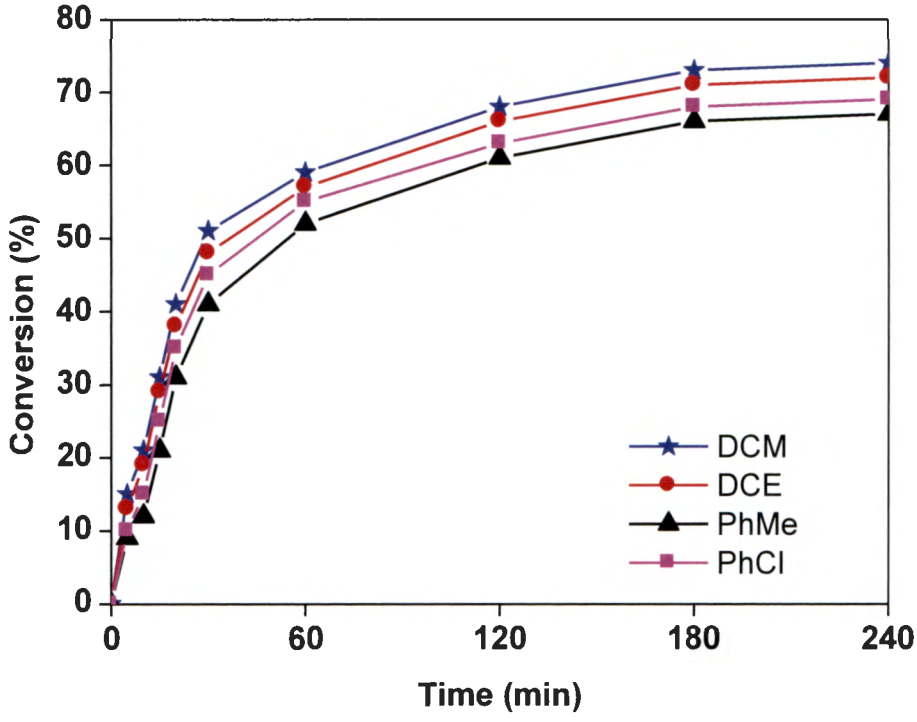


Figure 119: Conversion of MO in organic solvents using **21** at 60°C

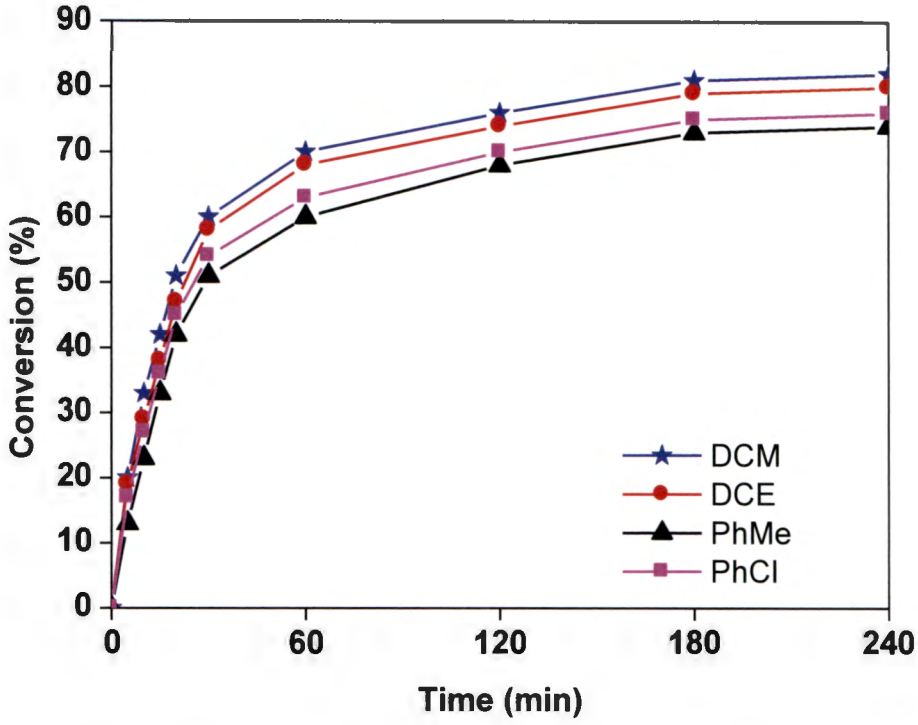


Figure 120: Conversion of MO in organic solvents using **21** at 80°C

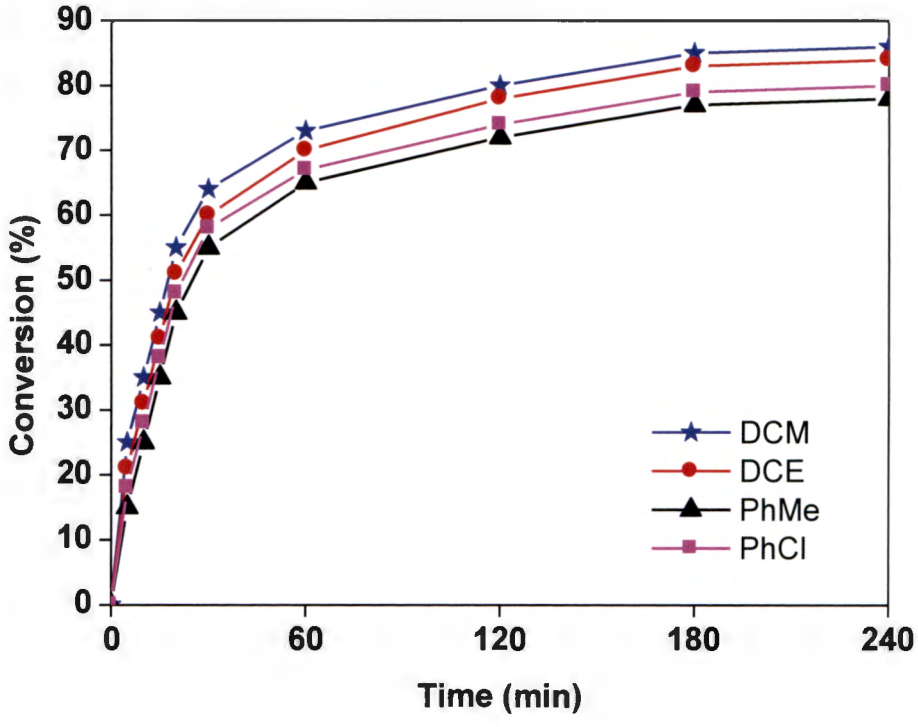


Figure 121: Conversion of MO in organic solvents using **21** at 100°C

A comparison of the activity of **21** in selected ILs and organic solvents at different temperatures is given in Figures 122 to 126. It is clear from the figures that a significant rate enhancement occurred in ILs as opposed to the organic solvents.

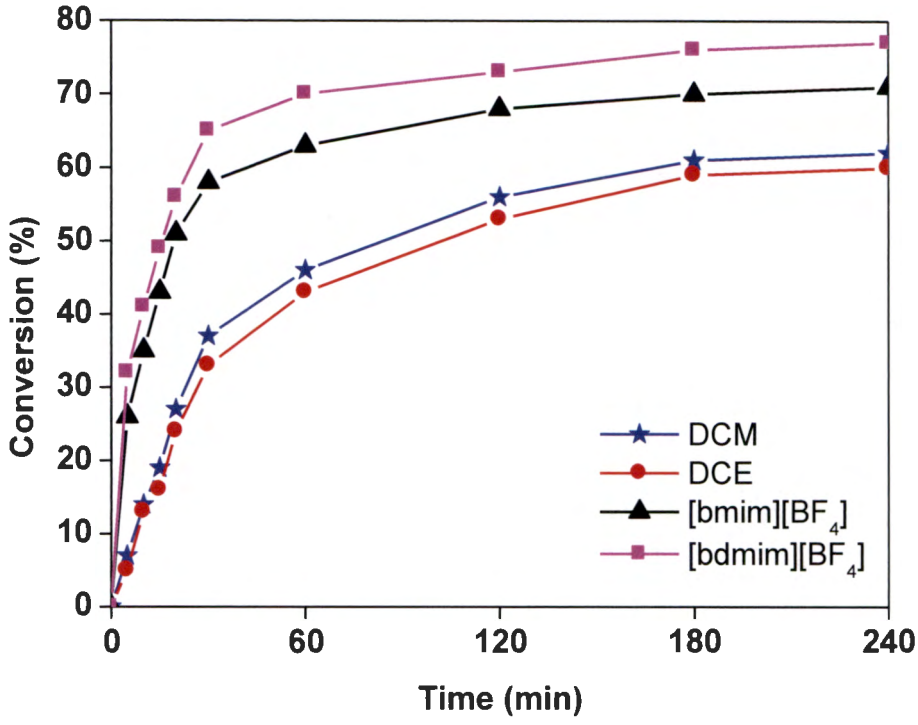


Figure 122: Conversion of MO in selected ILs and organic solvents using **21** at 20°C

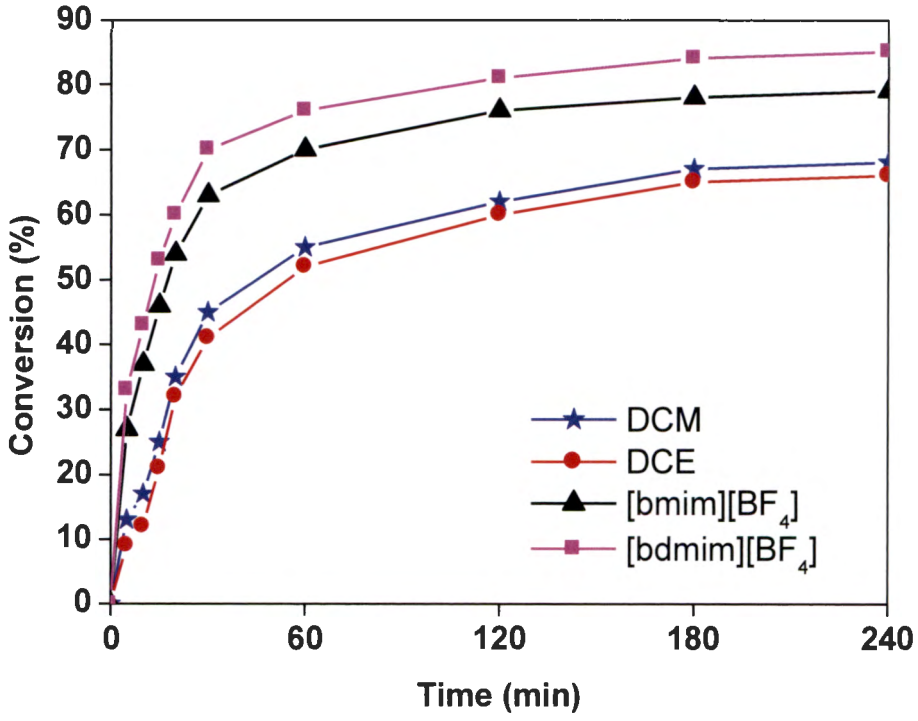


Figure 123: Conversion of MO in selected ILs and organic solvents using **21** at 40°C

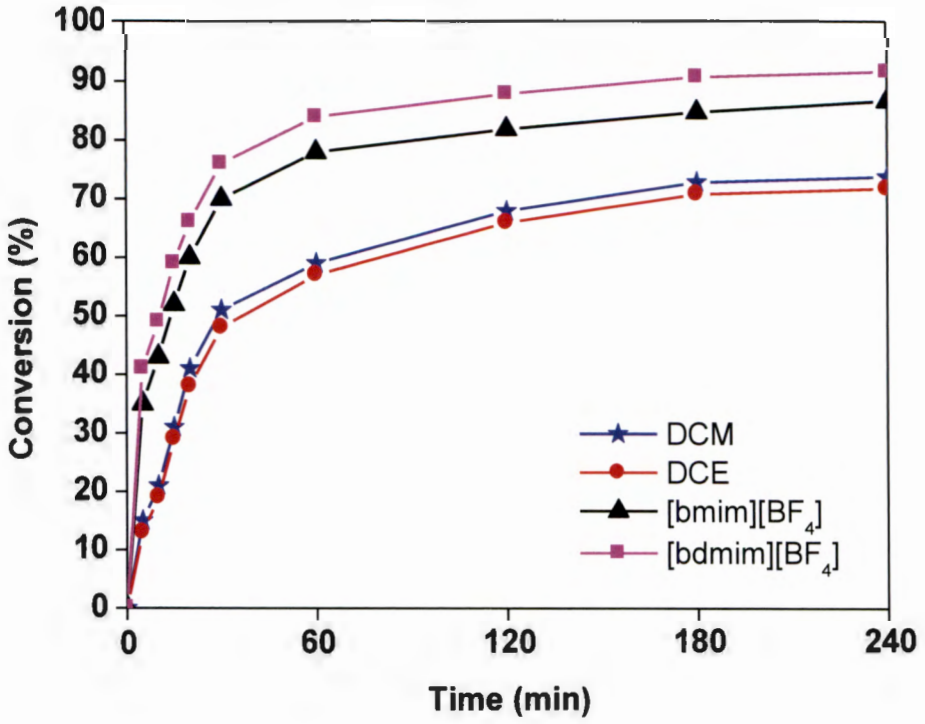


Figure 124: Conversion of MO in selected ILs and organic solvents using **21** at 60°C

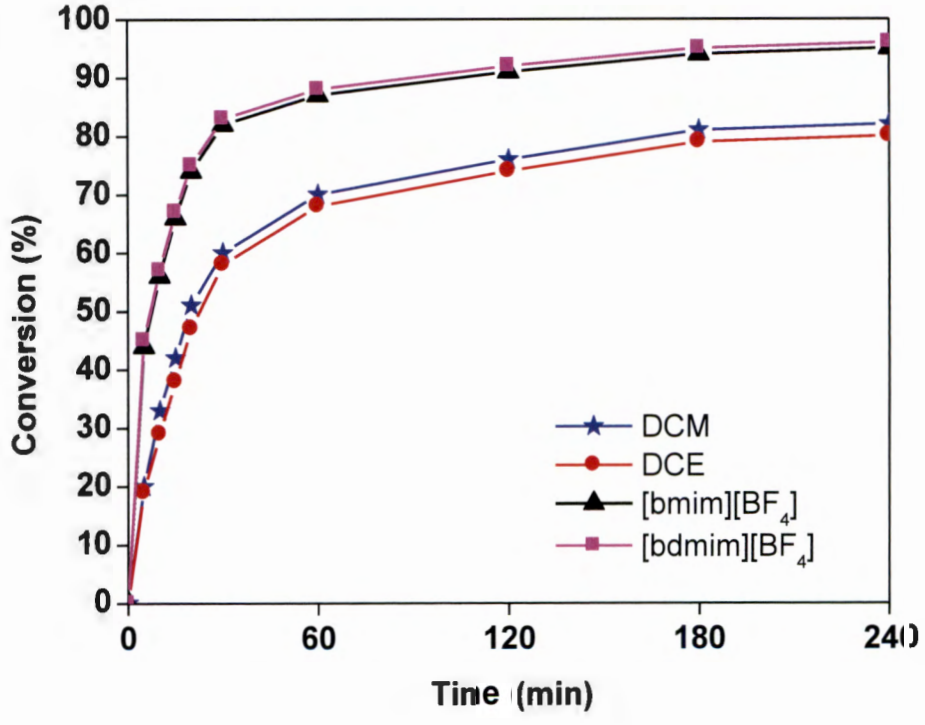


Figure 125: Conversion of MO in selected ILs and organic solvents using **21** at 80°C

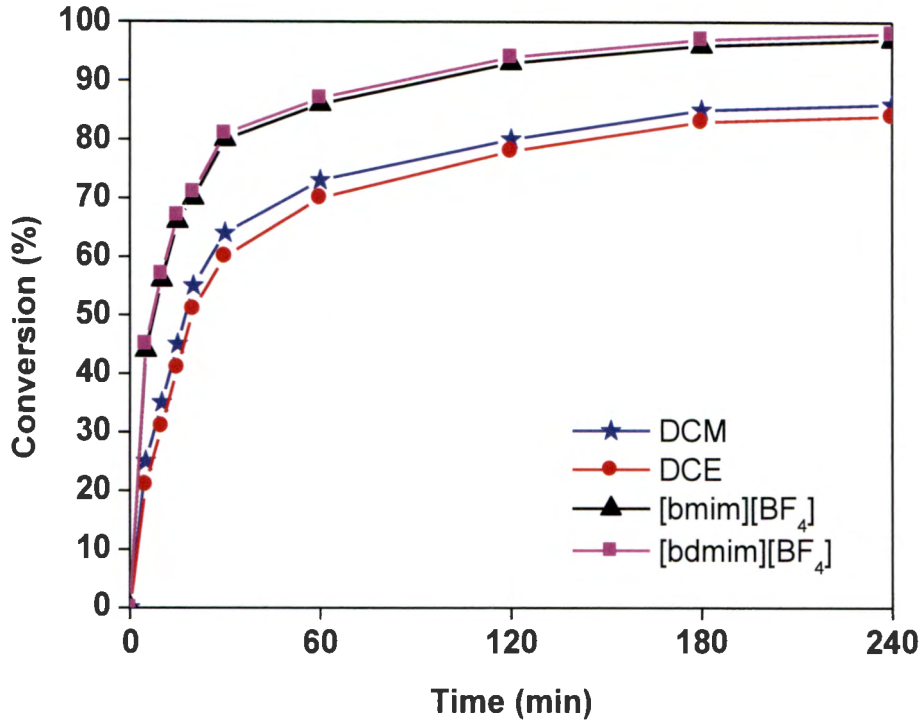


Figure 126: Conversion of MO in selected ILs and organic solvents using **21** at 100°C

4.5.5 Metathesis of methyl ricinoleate in organic solvents

The SM of methyl ricinoleate using **21** was carried out in four different organic solvents, namely; dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). The activity of **21** in selected organic solvents at 20 °C is shown in Table 59. Catalyst **21** showed highest activity in DCM with a substrate conversion of 54% and the lowest in PhMe with a conversion of 44%. The catalytic activity of **21** was found to be in the order DCM > DCE > PhCl > PhMe. A very good selectivity of 99 % was observed at a temperature of 20 °C, showing the absence of SMPs.

Table 59: Activity of **21** for the SM of MR in organic solvents at 20 °C after 4 h reaction time

Solvent	Conv (%)	Selec (%)
DCM	54	99
DCE	51	99
PhMe	44	99
PhCl	48	99

The conversion of MR in organic solvents in presence of **21** at 20 °C is shown in Figure 127 while a comparison of the activity of **21** in selected organic solvents and [bdmim][X] ILs at 20 °C is given in Figure 128. It is clear from the figure that a significant rate enhancement occurred in [bdmim][X] ILs compared to organic solvents.

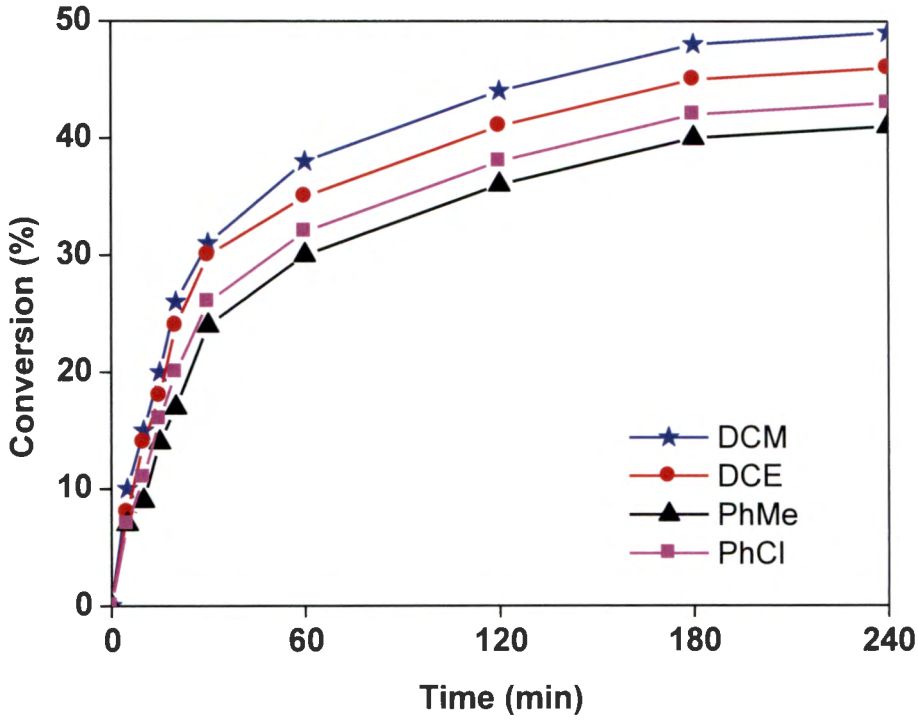


Figure 127: Conversion of MR in organic solvents using **21** at 20 °C

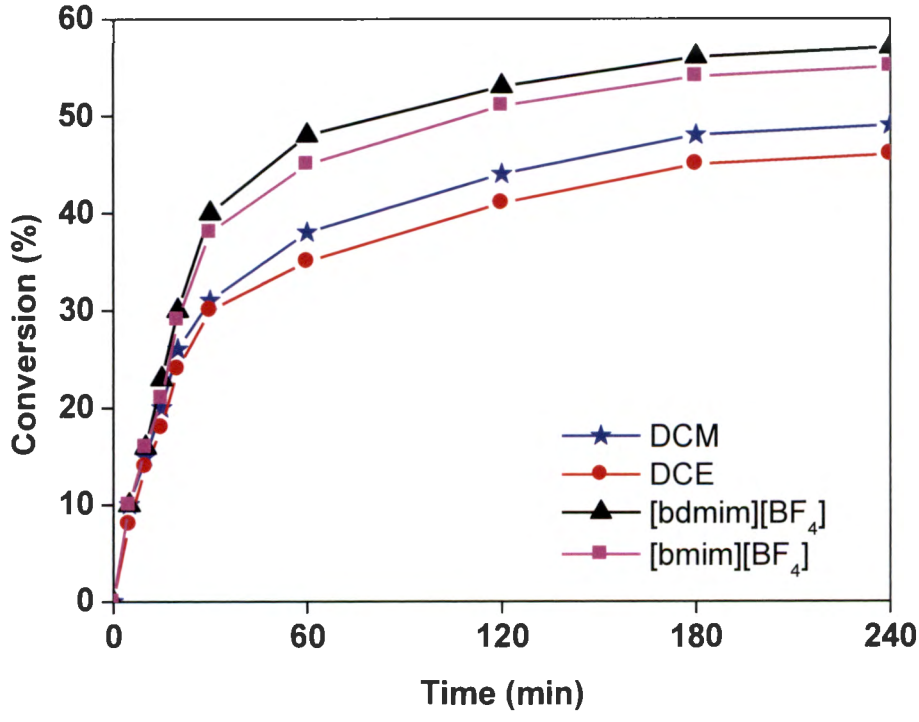


Figure 128: Conversion of MR in organic solvents and ILs using **21** at 20 °C

4.6 Catalyst Recycling in Ionic Liquids

The increased use of large quantities of organic solvents as liquid media for chemical reactions and extractions is a major challenge in today's chemical industry. As solvents, ionic liquids are more advantageous than conventional organic solvents, which make them recyclable and environmentally friendly. The successful introduction of RTILs to some transition metal catalyzed chemical reactions instead of organic solvents, has made the process more compatible to the environment and economical due to their unique physical and chemical properties. Most work reported in the literature are based on the recycling of RTILs in RCM and ROMP [190, 192-194, 220, 221]. Very few publications concerning self-cross metathesis in RTILs have been reported [187, 188].

4.6.1 Recycling of Grubbs first generation catalyst in ILs

To study recyclability, Ru catalysts in different ILs were subjected to consecutive runs. The metathesis reaction was carried out in ILs, and after extraction of reaction products with heptane (2 x 3 mL), the glass reactor was loaded with fresh methyl oleate and introduced for a new run. The recycling of Grubbs first generation catalyst in different ILs is shown in Table 60. Grubbs first generation catalyst proved to be stable in three consecutive runs, with the third run resulting in a decreased conversion. For the first two runs, conversions of 57% and 56% were obtained in [bmim][BF_4], whereas for the third run, the conversion of methyl oleate decreased to 42%. The same trend in activity was observed for the reaction in [bdmim][BF_4], with the third run showing a decrease in conversion.

Table 60: Recycling of Grubbs first generation catalyst in ILs at 40 °C

RTILs	Conv (%)	Selec (%)
[bmim][BF_4]	1st run: 57	99
	2nd run: 56	99
	3rd run: 42	98
[bdmim][BF_4]	1st run: 58	99
	2nd run: 56	99
	3rd run: 45	98

4.6.2 Recycling of Grubbs second generation catalyst in ILs

Recycling of Grubbs second generation catalyst was done in different RTILs. The recycling of the catalyst in RTILs for the conversion of methyl oleate at 40 °C is shown in Table 61. The activity of the catalyst was found to decrease in the subsequent runs. For the first run,

conversions of 67% and 72 % was obtained in [bmim][BF_4] and [bdmim][BF_4], respectively. In the next two runs, the activity of the catalyst was found to decrease, whereas an increased conversion of the substrate was observed in the third cycle compared to first generation catalyst. This result is in agreement with that obtained by Tang *et al.* [187]. They reported that ILs containing Grubbs second generation catalyst can be recovered and reused for at least four cycles with only a little drop in activity. The gradually lowering yields were caused by the decomposition of catalyst and by extraction of the catalyst into the organic layer [187].

Table 61: Recycling of Grubbs second generation catalyst in ILs at 40 °C

RTILs	Conv (%)	Selec (%)
[bmim][BF_4]	1st run: 67	99
	2nd run: 50	97
	3rd run: 45	97
[bdmim][BF_4]	1st run: 72	99
	2nd run: 60	97
	3rd run: 58	97

4.6.3 Recycling of Hoveyda-Grubbs first generation catalyst in ILs

The recycling of Hoveyda-Grubbs first generation catalyst for three cycles is shown in Table 62. The catalyst was found to be active for the first two runs, whereas for the third run the activity was found to decrease slightly. From the results, it can be concluded that Hoveyda-Grubbs first generation catalyst can be reused for at least three runs without much loss in activity.

Table 62: Recycling of Hoveyda-Grubbs first generation catalyst in ILs at 40 °C

RTILs	Conv (%)	Selec (%)
[bmim][BF_4]	1st run: 56	99
	2nd run: 56	99
	3rd run: 49	99
	4th run: 22	99
[bdmim][BF_4]	1st run: 58	99
	2nd run: 58	99
	3rd run: 53	99
	4th run: 30	99

4.6.4 Recycling of Hoveyda-Grubbs second generation catalyst in RTILs

To study the recyclability of Hoveyda-Grubbs second generation catalyst in RTILs, the reaction was carried out in [bmim][BF_4] and [bdmim][BF_4]. The substrate used was methyl oleate and the reaction was carried out at a temoerature of 40 °C. The activity of catalyst for the first three cycles is shown in Table 63. For the first run, activities of 74% and 85% were obtained for the reaction in [bmim][BF_4] and [bdmim][BF_4], respectively. In spite of the good activity in the first run, the second generation Hoveyda-Grubbs catalyst exhibited low catalytic activity during the second run. The poor recyclability of Hoveyda-Grubbs second generation catalyst is also confirmed by Thurier *et al.* [188]. The significant decrease in substrate conversion in subsequent runs was further proved by the leaching studies.

Table 63: Recycling of Hoveyda-Grubbs second generation catalyst in ILs at 40 °C

RTILs	Conv (%)	Selec (%)
[bmim][BF_4]	1st run: 74	99
	2nd run: 40	95
	3rd run: 15	95
[bdmim][BF_4]	1st run: 85	99
	2nd run: 54	95
	3rd run: 23	95

4.7 Leaching of the catalysts

Leaching of the Ru catalysts into the organic layer was carried out using ICP-OES analysis. The samples were prepared by weighing 5 mg of the crude compound (which was filtered to remove IL traces) and then adding 10 mL of 0.12 M hydrochloric acid. All the samples were diluted 10 times in ultra pure water. The Ru level was determined by comparison with a standard Ru sample in mg/L.

The amount of catalyst leached into the organic layer after first run is shown in Table 64. As seen from the table, only minute traces of Grubbs first generation catalyst (0.9817 mg/L) leached into the organic layer. This explains the reason for the good recycling effects shown by catalyst **18**, which exhibited very good substrate conversion in all the three runs. In the case of catalyst **19**, a considerable amount of the catalyst was present in the organic layer. Ru content of 4.7060 mg/L was leached into the organic layer. For catalyst **19**, the substrate conversion

decreased in the second run, due to the leaching of the catalyst from the IL layer to the organic layer.

Catalyst **20** was found to be the best recycling catalyst. Very good conversions were exhibited in the first three runs. This can be explained by the leaching data shown in Table 64. The amount of catalyst **20** that was leached into the organic layer was found to be only 0.7305 mg/L. For Hoveyda Grubbs second generation catalyst **21**, a significant amount (7.2507 mg/L) of the catalyst was leached into the organic layer. This is evident from the recycling studies done on the catalyst. The catalyst yielded poor recycling data in the second run. Most of the leaching studies reported in literature are with charged catalyst systems. Buijsman and co-workers reported that catalyst **19** could be recycled three times but with significant Ru residual contaminations within the final product were detected [183].

Table 64: Ru content present in the organic layer

Catalyst	Amount of Ru (mg/L)
18	0.9817
19	4.7060
20	0.7305
21	7.2507

4.8 DFT investigation of the role of ILs and conventional solvents in the metathesis of olefin

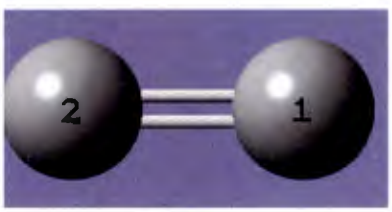
Due to the high computational demand in studying large molecules, the study considers only ethylene, the simplest olefin, is considered with a view to explaining the preference of ionic liquids as solvents for the metathesis of olefins. Moreover, only the Grubbs' first generation catalyst is considered and only the alkyledene intermediate is taken into consideration. The products of the metathesis are styrene and an active catalyst that could be used in the second circle of metathesis. To have a better understanding of the effects of the solvents, efforts were made to obtain the solvent effects (ΔG_{solv}) on olefin in order to establish their varying influence on the stabilisation of olefin. Information from the solvent effect (ΔG_{solv}) provides indication of the stabilisation extent of the solvent. Moreover, the activation energy, the equilibrium constant and the reaction rates in all the different media selected were determined in order to have an understanding of the effect of the solvent on these quantities. The solvents that result in lower

values of reaction rate are better than solvent that results in higher reaction rates. Also solvents that results in high yield are better than solvents that results in low yields.

The three ionic liquids chosen include [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] and the four conventional solvents chosen include dichloromethane (DCM) 1,2 dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). To determine the activation energy, the equilibrium constant and the reaction rate, optimisation calculations were performed in all the solvents followed by the calculations of the harmonic frequencies to obtain the free energy *in vacuo* and in different solvents.

4.8.1 Results *in vacuo*

The optimised geometries of the reactants, the intermediate (i.e., the metal alkyledene) and the products are shown in Figures 129 to 131. Table 65 reveals the most interesting geometry parameters of the alkyledene intermediate. The shortest bond length corresponds to the C69-C72 while the longest bond length corresponds to the Ru-P bond. A comparison of the energy of the alkyledene (-1184.9684559) and the sum of the energy of the active catalyst (-1106.3794335 au) and olefin (-78.5782089 au) indicate that the alkylede is 6.786 kcal/mol more stable than the sum of the isolated active catalyst and the olefin molecules.



Ethene

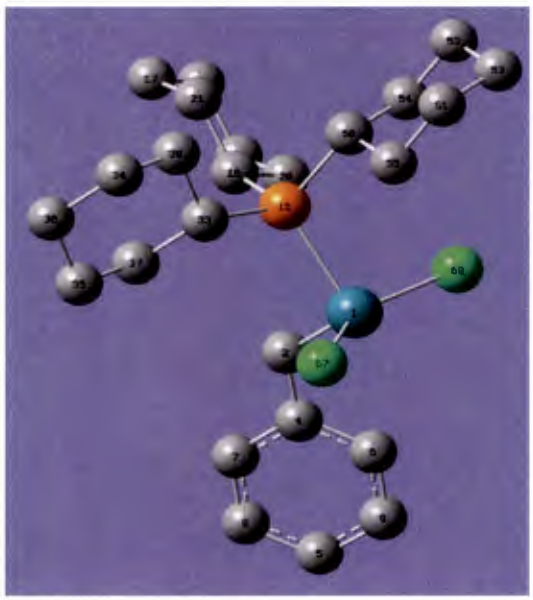

active catalyst

Figure 129: The optimised geometries of the reactant molecules (ethene and the active catalyst). *The blue atom is the ruthenium metal, the green atoms are the chlorine atoms, the orange atom is phosphorus and the grey atoms are the carbon atoms. The hydrogen atoms are not shown for simplicity sake.*

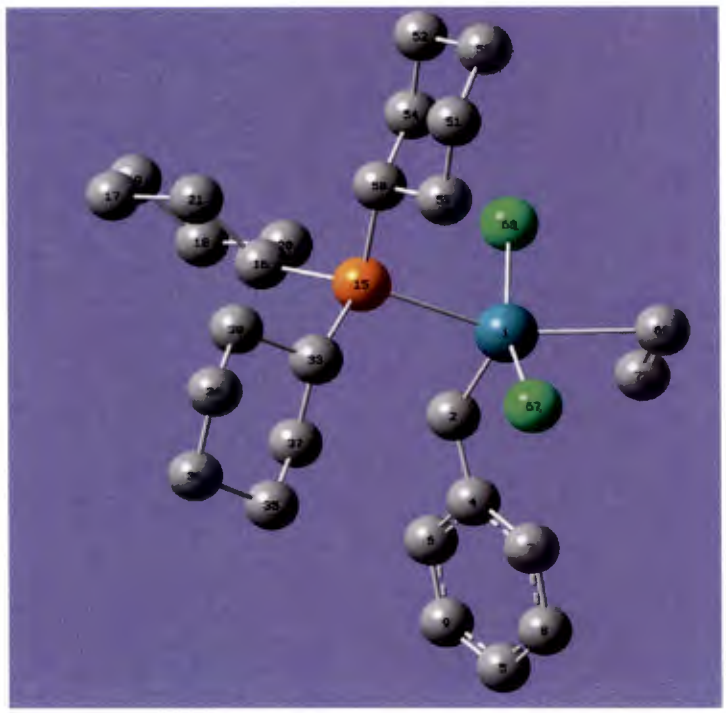
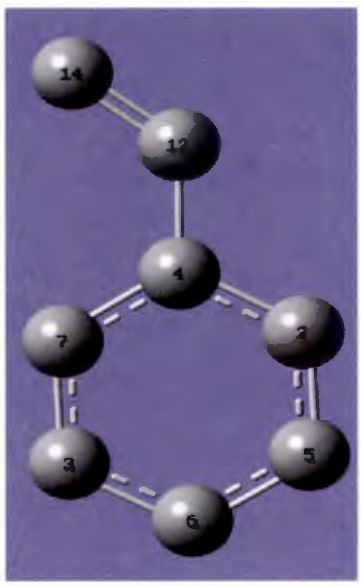
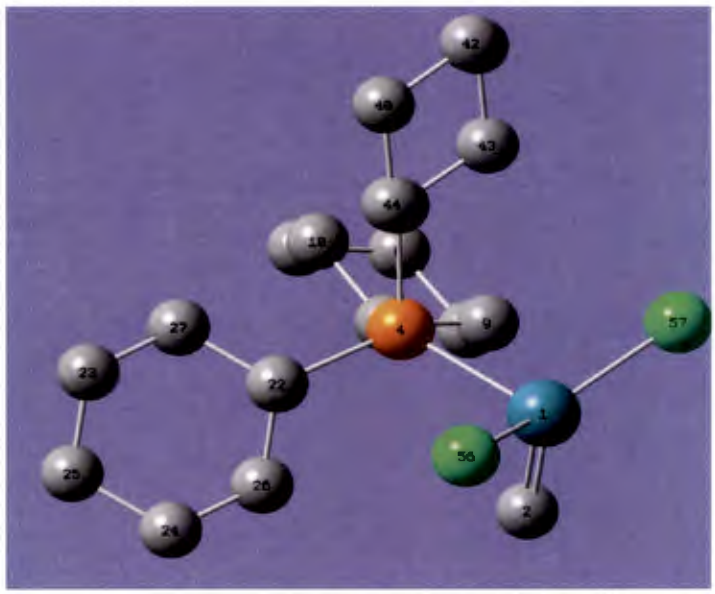


Figure 130: The optimised geometry of metal-alkyldene intermediate. *The blue atom is the ruthenium metal, the green atoms are the chlorine atoms, the orange atom is phosphorus and the grey atoms are the carbon atoms. The hydrogen atoms are not shown for simplicity sake.*



Styrene



the new active catalyst

Figure 131: The optimised geometries of the product (styrene) and the new active catalyst. *The blue atom is the ruthenium metal, the green atoms are the chlorine atoms, the orange atom is phosphorus and the grey atoms are the carbon atoms. The hydrogen atoms are not shown for simplicity sake.*

Table 65: Selected geometric parameters of the alkyledene intermediate. *The numbering of the atoms is with respect to the numbering shown in Figure 130 for the alkyledene intermediate.*

Bond	Bond length (Å)	Bond angle	Bond angle
Ru-C2	1.871	C2RuP	92.5
Ru-P	2.514	C2RuCl67	33.4
Ru-Cl68	2.482	C2RuCl68	33.4
Ru-Cl67	2.472	C2RuC69	27.8
Ru-C69	2.372	PRuC69	14.8
C69-C72	1.379		

4.8.2 The bulk solvent effects

The solvent effects together with their components, the non-electrostatic ($G_{non\text{-}el}$) and electrostatic (G_{ele}) due to the different solvents on substrate (olefin, ethane) and the catalyst are shown in Table 66. For the purpose of illustrating the effects of the solvent on olefin metathseis, this work has been restricted to the determination of the metal-alkyledene intermediate and the styrene product.

The solvent effect is given by [242]:

$$\Delta G_{solv} = G_{el} + G_{cav} + G_{dis} + G_{rep}$$

where G_{cav}, G_{dis} and G_{rep} are the non-electrostatic contributions (cavitation, dispersion and repulsion contributions, respectively). Together G_{cav}, G_{dis} and G_{rep} are known as the non-electrostatic contributions to the solvent effect ($G_{non\text{-}el}$).

The results reveal that the olefin is strongly stabilised by non-electrostatic interactions, e.g., dispersion interactions. Moreover, non-electrostatic interactions are more predominant in the ionic liquids than in conventional solvents, which suggest that ionic liquids have greater tendency to stabilise olefin than conventional solvents. This result implies that olefin metathesis would preferentially occur in ionic liquids than in conventional solvents.

Table 66: Comparison of the solvent effect on the substrate and on the catalyst.

Solvent	solvent effect (ΔG_{solv})		
	ΔG_{solv}	G_{ele}	$G_{non\text{-}ele}$
Dichloromethane	1.74	-1.11	2.85
1,2 dichloroethane	2.13	-1.14	3.27
Chlorobenzene	2.65	-0.97	3.62
Toluene	2.30	-0.59	2.88
[bmim][BF_4]	3.71	-1.17	4.88
[bmim][PF_6]	3.72	-1.16	4.88
[bmim] [NTf_2]	3.68	-1.19	3.68

4.8.3 The role of the catalyst and the nucleophilicity of the solvent

Nucleophilicity gives information on the tendency of a molecule to donate electrons to the electron deficient centre of another molecule. It is understood that before the catalyst interacts with the substrate, it first undergoes a decomposition reaction forming an electrophile and is then considered active. It is at this stage that solvents have a strong influence on the catalyst. In the active form, the catalyst has a strong preference to react with more nucleophilic species. Therefore the solvent with greater nucleophilic character tends to bind strongly onto the catalyst, which makes the solvent less effective in olefin metathesis. Therefore understanding the nucleophilic character of the solvent provides information on the preferred solvent for the olefin metathesis.

The quantum parameters relevant for the estimation of the nucleophilic nature of the solvents are given in Table 67. The nucleophilic values (N_{nu}) of each solvent is given in the last column of Table 67. Since the ω value is the only relevant parameter for discussing the behaviour of the solvents towards the reactants, other parameters listed in Table 67 are hereby not discussed in detail. The order of nucleophilicity is such that DCM < DCE < PhCl < PhMe. This means that DCM has the least tendency to provide electrons to the cation and therefore, among the conventional solvents, would form the weakest bond with the cation. In contrast, PhMe has the highest tendency to donate electrons to the cation and therefore, among the conventional solvents, would form the strongest bond with the cation. Overall the order of reactivity in these solvents is such that PhMe < PhCl < DCE < DCM which agrees well with the experimental observations.

Among the ionic liquids, [bmim][BF_4] has the highest nucleophilicity while [bmim][NTf_2] has the lowest. However, overall, all ionic liquids have lower nucleophilicity than the conventional solvents, suggesting that ionic liquids have the least tendency to donate electrons to the active catalyst. Therefore ionic liquids would have weaker interactions with olefin than conventional solvents.

Table 67: Molecular properties of the ionic liquids [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] and conventional solvents DCM, DCE, PhCl and PhMe calculated at B3LYP/6-31+G(d,p) *in vacuo*.

Solvent	Quantum chemical properties[a]						
	E_{HOMO}	E_{LUMO} (eV)	ΔE (eV)	η	σ	ω	N_{nu}
DCM	-8.422	-0.45	-7.972	3.986	0.251	2.468	0.405
DCE	-8.351	-0.185	-8.166	4.083	0.245	2.231	0.448
PhCl	-6.715	-0.366	-6.349	3.175	0.315	1.974	0.506
PhMe	-6.412	0.112	-6.524	3.262	0.307	1.521	0.657
[BMIM] BF_4	-7.818	-0.837	-6.981	3.491	0.287	2.683	0.373
[BMIM] PF_6	-8.463	-1.556	-6.907	3.453	0.290	3.633	0.275
[BMIM] NTf_2	-7.659	-1.721	-5.937	2.969	0.337	3.704	0.27

[a] ω is the Electrophilicity index, N_{nu} is the nucleophilicity index, E_{HOMO} is the energy of the highest occupied molecular orbital (eV), E_{LUMO} is the energy of the lowest unoccupied molecular orbital (eV), ΔE (eV) is the energy difference between the HOMO and the LUMO, η is the global hardness and σ is the global softness values.

4.9 Transition state theory

To better understand the factors involved in olefin metathesis, it is important to understand the theory explaining the reaction mechanism. One of such theories that is often used is the transition state theory. This theory considers that the reaction between one, two or more reactants, reaches the product state by passing over an activated complex. This activated complex is called a transition state. In the transition state theory, a potential surface is often assumed to connect the reactants, the transition state and the product. The transition state is the highest point (the maximum) on the potential surface and the rate of the reaction is related to the height of the barrier between the reactants and the transition state.

Table 68: Activation energy E_{act} (kcal/mol) estimated from the free energies (kcal/mol) of the reactant and the intermediate. DFT/LanL2DZ calculations in different media.

Medium	Forward reaction			
	$G_{inter-1}$	$G_{react-1}$	$G_{react-2}$	E_{act-A}
Vacuum	-743211.284	-49290.255	-693928.788	7.759
Dichloromethane	-743558.604	-49306.791	-694245.479	-6.333
1,2 dichloroethane	-743556.381	-49306.405	-694242.993	-6.983
Chlorobenzene	-743552.51	-49305.885	-694238.879	-7.745
Toluene	-743553.207	-49306.234	-694238.551	-8.422
[bmim]BF4	-743548.897	-49304.826	-694240.358	-3.713
[bmim]PF6	-743548.823	-49304.82	-694240.24	-3.763
[bmim] NTf_2	-743549.182	-49304.849	-694240.811	-3.521

4.9.1 The activation energy

Activation energy (ΔE_{act}) represents the energy change for a reaction in which a ground state is transformed into a transition state. It is also defined as the energy barrier for a reaction. A smaller value of ΔE_{act} for a reaction corresponds to a faster formation of the transition state. Solvent molecules influence the activation energy of reactions; a solvent with lower activation energy would lead to faster formation of the intermediate. In the current work, the activation energy in different solvents was estimated following the procedure discussed in the computational detail section. The results for the ΔE_{act} corresponding to the forward reaction are reported in Table 68. The results reveal that the presence of the solvent changes the activation energy. The lowest activation energy was obtained with ionic liquids. It was lower in DCM and DCE than in PhCl and PhMe. These results imply that ionic liquids give quicker formation of the intermediate.

4.9.2 Equilibrium constant

The free energy change of the reaction in each medium may also be utilized to estimate the equilibrium constant for the process. Considering that the reactions were performed at room temperature, the equilibrium constant, K_{eq}, may be estimated from the equation

$\Delta G° = - RT\ln K_{eq}$

which when rearranged can be written as

$$\ln K_{eq} = \frac{-\Delta G^0}{RT} \text{ or } K_{eq} = e^{\frac{-\Delta G^0}{RT}}$$

where R = 8.314 J mol^{-1} K^{-1} or 0.008314 kJ mol^{-1} K^{-1} and T is the temperature on the Kelvin scale.

The calculated equilibrium constant values are reported in Table 69. The results reveal that in all the solvents, $K_{eq} >> 0$ indicating that the presence of a solvent favours the formation of products. The highest yields corresponding to the largest value of K_{eq}, appear to correspond to reactions conducted in conventional solvents.

Table 69: The equilibrium constant and the rate constant for the metathesis of olefin in different media

Medium	K_{eq}	k_{TST} (s^{-1})
Vacuum	4.43×10^{-4}	5.69×10^{-10}
Dichloromethane	2.54×10^{6}	2.59×10^{-10}
1,2 dichloroethane	6.59×10^{6}	3.48×10^{-10}
Chlorobenzene	7.16×10^{6}	9.16×10^{-10}
Toluene	3.25×10^{6}	1.06×10^{-9}
[bmim]BF4	2.06×10^{6}	3.12×10^{-10}
[bmim]PF6	2.06×10^{6}	3.24×10^{-10}
[bmim] NTf_2	2.04×10^{6}	2.71×10^{-10}

4.9.3 Reaction rate

The transition state theory is also used to estimate the rate constant for a reaction from the following equation:

$$k_{TST} = (k_B T/h) \exp(-\Delta G^{\ddagger\circ}/RT)$$

where k_B and h are Boltzmann's and Planck's constants, respectively and $\Delta G^{\ddagger\circ}$ is the change in the standard Gibbs free energy between the transition state and reactants species (including the respective zero-point energies). The calculated reaction rate constants in different solvents are also reported in Table 69. The calculated reaction rate constants in different solvents are also reported in Table 69. The results reveal that the reaction rate in different solvents follows the order toluene > chlorobenzene > vacuo > 1,2-chloroethene > $[bmim]PF_6$ > $[bmim]BF_4$ > $[bmim]NTf_2$ > dichloromethane. These results imply that the metathesis reaction is favoured in organic solvents, which is in contrast to the trends observed from experimental data.

CHAPTER 5

CONCLUSIONS

5.1 Metathesis reactions using Grubbs first generation catalyst

The efficacy of [bmim][X] and [bdmim][X] type ILs as reaction media in fatty acid ester metathesis was evaluated and the effects of anion, reaction temperature, solvent polarity, viscosity and ligand-anion interaction on the reaction have been addressed. For the first generation Grubbs catalyst, the highest activity was found in [bdmim][BF_4] with a methyl oleate conversion of 55%, TON of 55 and selectivity of 100% at 20 °C. The activity of the catalyst was found to increase in the order [bdmim][BF_4] > [bdmim][PF_6] > [bmim][BF_4] > [bmim][NTf_2] > [bmim][PF_6]. Studies on the influence of temperature on the activity and selectivity of catalyst proved that the catalytic activity increased with increasing temperature from 20 to 60 °C and thereafter the activity decreased, showing the deactivation of the catalyst at higher temperature. The selectivity was found to decrease with increasing temperature showing the presence of secondary metathesis products at higher temperature. Deactivation of the catalyst was observed when the reaction atmosphere was changed from N_2 to air. However, in the first hour of the reactions the activity under air was found to be higher and thereafter it decreased.

When methyl ricinoleate was used as the substrate ester, the highest conversion was observed in [bdmim][BF_4] (49%) and the lowest in [bmim][NTf_2] (39%) at 20 °C. A selectivity of 99% was obtained showing the absence of SMPs. The activity of the catalyst was found to increase in the order [bdmim][BF_4] > [bmim][BF_4] > [bdmim][PF_6] > [bmim][PF_6] > [bmim][NTf_2].

Investigation of metathesis reaction in the presence of conventional organic solvents yielded the highest conversion in DCM (50%) and the lowest in PhMe (43%) for methyl oleate as the substrate ester. Excellent selectivity of 100% was obtained at moderate temperatures up to 60 °C and thereafter, the selectivity decreased as in the case of RTILs. The activity of the catalyst was found to increase with an increase in temperature up to 60 °C and thereafter deactivation occurred. For the SM of methyl ricinoleate, a highest conversion of 36% was observed in DCM and the lowest in PhMe (31%). The reaction when compared to that in RTILs, reveal that a significant rate enhancement was observed in RTILs, showing the superiority of RTILs as reaction media.

5.2 Metathesis reactions using Grubbs second generation catalyst

The activity of second generation Grubbs catalyst was investigated for the SM of methyl oleate and methyl ricinoleate in RTILs and organic solvents. At 20 °C, the highest conversion was observed in [bdmim][BF_4] with a conversion of 61% and the lowest in [bmim][PF_6] (53%). On increasing the temperature from 20 to 100 °C, the activity of the catalyst was also found to increase with increasing TON. At 100 °C, the conversion of methyl oleate in [bdmim][BF_4] reached to 90% after 4 h reaction time. While excellent selectivity was achieved at a moderate reaction temperature, a loss in selectivity occured at higher reaction temperatures with the formation of SMPs. At 20 °C, excellent selectivity of 100% was obtained which was found to decrease from a temperature of 60 °C. At 60 °C, the selectivity obtained was 82% while at 100 °C, it further fell down to 69%. Only a very little difference in substrate conversion was observed under N_2 and air atmospheres. A conversion of 59% was obtained under N_2, whereas in presence of air, the conversion was 58%. This shows that the Grubbs second generation catalyst is active in both atmospheres.

For methyl ricinoleate metathesis, the highest activity was observed in [bdmim][BF_4] with a conversion of 53% at 20 °C after 4 h reaction time. The trend in metathesis activity decreased in the order [bdmim][BF_4] > [bdmim][PF_6] > [bmim][BF_4] > [bmim][PF_6] > [bmim][NTf_2]. There was no trace of SMPs at 20 °C and the selectivity towards PMPs was found to be 99%.

For the metathesis in the presence of organic solvents, the highest conversion was observed in DCM with methyl oleate conversion of 56% at 20 °C. The catalytic activity and TON increased with an increase in temperature. At 100 °C, a conversion of 82% was obtained. Beyond 60 °C, presence of SMPs was observed. At 60 °C, the selectivity towards PMPs was 98% which then decreased to 91% at 100 °C. The activity of the catalyst was found to decrease in the order DCM > DCE > PhCl > PhMe. For methyl ricinoleate metathesis, the highest conversion of 44% was observed in DCM and the lowest in PhMe with 38%. Excellent selectivity of 99% was obtained at the selected temperature of 20 °C[98].

5.3 Metathesis reactions using Hoveyda-Grubbs first generation catalyst

For the metathesis of methyl oleate with Hoveyda Grubbs first generation catalyst, not much difference in activity was observed in the selected [bmim][X] type ILs. At 20 °C, the reaction in [bmim][BF_4] yielded 54% conversion, [bmim][NTf_2] yielded 53% and [bmim][PF_6] yielded a conversion of 52%. The catalytic activity increased with increasing temperature.

However, similar conversions were observed in all the runs at a particular temperature. A good selectivity (~96%) was obtained up to 40 °C. At 60 °C, selectivity towards PMPs decreased to 82% and at 100 °C, it further decreased to 69%. When the reaction was carried out in [bdmim][X] type ILs, a slight increase in substrate conversion was observed with the reaction in [bdmim][BF_4] showing a conversion of 56% at 20 °C. The catalyst was found to be stable in oxygen atmosphere exhibiting a conversion of 53% in [bmim][BF_4] at 20 °C. A similar conversion of 54% was observed in N_2 atmosphere in [bmim][BF_4] reaction medium.

For the metathesis of methyl ricinoleate in [bmim][X] type ILs, the highest substrate conversion was observed in [bmim][BF_4] (47%). At 20 °C, a conversion of 44% and 42% were obtained in [bmim][PF_6] and [bmim][NTf_2] respectively. Comparing the reaction in [bmim][X] type and [bdmim][X] type ILs, the highest conversion was observed in [bdmim][BF_4]. The reaction yielded a conversion of 51%. Excellent selectivity (99%) towards PMPs was observed in all the runs.

The investigation of metathesis reaction of methyl oleate and methyl ricinoleate using Hoveyda Grubbs first generation catalyst was carried out in presence of selected organic solvents at 20, 40, 60, 80 and 100 °C. At all the selected temperatures, the best catalytic performance occurred in DCM and the lowest in PhMe. DCM yielded a conversion of 51% at 20 °C, which then increased with increasing temperature and reached 62% at 100 °C. For methyl ricinoleate, metathesis in DCM yielded the highest conversion of 40% at 20 °C and excellent selectivity of 99% was obtained in all the selected organic solvents. The catalytic activity was found to increase in the order DCM > DCE > PhCl > PhMe.

5.4 Metathesis reactions using Hoveyda-Grubbs second generation catalyst

The effect of varying the anion counterpart in [bmim][X] type ILs on the metathesis of methyl oleate using Hoveyda Grubbs second generation catalyst was studied. The results reveal that the reaction in [bmim][BF_4] excelled the reaction in other two solvents. [bmim][BF_4] yielded a conversion of 71% whereas the reaction in [bmim][NTf_2] gave only a conversion of 64%. The trend in metathesis activity increased in the order BF_4^- > PF_6^- > NTf_2^-. To investigate the influence of reaction temperature on the activity of the catalyst for the SM of methyl oleate, the reaction was carried out at different temperatures ranging from 20 to 100 °C in [bmim] and [bdmim][X] type ILs. The substrate conversion increased with increase in temperature. The highest conversion was obtained in [bdmim][BF_4] at all the selected temperatures. At 20 °C, a conversion of 77% was obtained in [bdmim][BF_4] whereas it increased to 98% at 100 °C. Under the same reaction conditions, [bmim][BF_4] yielded a conversion of 71% and 97% at 20 and 100

°C, respectively. Good selectivity was achieved at low temperatures of 20 and 40 °C. At 60 °C, a selectivity of 82% was observed which then decreased to 69% at 100 °C. From these results, it is clear that at higher reaction temperatures, a considerable amount of SMPs were formed. Under air atmosphere, a similar activity was observed for the reaction in [bmim][BF_4] at all selected temperatures. It can therefore be concluded that Hoveyda Grubbs second generation catalyst is stable in oxygen atmosphere.

The catalytic activity on Hoveyda Grubbs second generation catalyst was investigated for the SM of methyl ricinoleate in [bmim] and [bdmim][X] type ILs at 20 °C. A substrate conversion of 55%, 51% and 49% was obtained for the reaction in [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] respectively. The highest conversion occurred in [bdmim][BF_4] (57%) and the lowest in [bmim][NTf_2] (49%). In all the runs, excellent selectivity of 99% was obtained showing the absence of SMPs.

The catalytic activity of Hoveyda-Grubbs second generation catalyst was also investigated in the presence of organic solvents. At 20 °C, the highest methyl oleate conversion occurred in DCM (62%). The activity increased with increasing temperature. For the SM of methyl oleate in DCM, conversions of 68%, 74%, 82% and 86% were obtained for the reaction at 40, 60, 80 and 100 °C, respectively. Excellent selectivity was obtained at moderate temperature (>~ 98%) and after 60 °C, selectivity was found to decrease. At 80 °C, selectivity reached 91%. For methyl ricinoleate metathesis, a conversion of 54% was obtained in DCM with 99% selectivity at 20 °C. A conversion of 51% was obtained in DCE, followed by 48% in PhCl and finally the lowest in PhMe with a conversion of 44% [223].

5.5 Catalyst recycling and leaching studies in ILs

Recycling of Ru catalysts was evaluated for the SM of methyl oleate in [bmim] and [bdmim][BF_4] ILs at 40 °C. Grubbs first generation catalyst proved to be stable in three consecutive runs, with the third run resulting in a decreased conversion. For the first run in [bdmim][BF_4], a conversion of 57% was obtained whereas for the second run a conversion of 56% was obtained. Grubbs second generation catalyst showed an increased conversion in the third cycle when compared with the first generation catalyst. For the first run in [bdmim][BF_4], a conversion of 72% was obtained. In the 2^{nd} run, the activity considerably decreased to 60% and for the 3^{rd} cycle a conversion of 58% was obtained, which is higher than for the 3^{rd} run using Grubbs first generation catalyst (45%).

Comparing the first and second generation Hoveyda-Grubbs catalysts, the best result was obtained with Hoveyda Grubbs first generation catalyst. For first generation catalyst a conversion of 58% was obtained in the first two runs in [bdmim][BF_4], and for the 3rd run, a conversion of 53% was obtained. The results prove that Hoveyda Grubbs first generation catalyst can be reused for three runs without loss of activity. In the case of Hoveyda Grubbs second generation catalyst, the catalytic activity decreased from 74% to 40% in the 2nd run. For the 3rd run the catalytic activity was observed to be very poor (15%). In spite of good activity in the first run, the second generation Hoveyda-Grubbs catalyst showed low catalytic activity during the second run.

Compared to the first generation Grubbs catalyst, the second generation catalyst shows improved activity and thermal stability, though at the expense of low selectivities. The higher activity of Grubbs second generation catalyst had been attributed to the stabilization of the metallacycle intermediate by the more bulky and basic N-heterocyclic carbene ligand [33, 35]. Isopropoxy benzylidene derivatives, pioneered by Hoveyda, exhibit high activity and possess excellent functional group tolerance. Excellent air stability, ease of storage and handling constitute additional advantages. The reason for the high activity of the Hoveyda-Grubbs second generation catalyst can be attributed to the absence of phosphine ligand. It has been proved that phosphine ligand suppresses the catalyst activity in Ru-catalyzed olefin metathesis [35]. The presence of free phosphine in solution can inhibit coordination of olefins to the transition metal centre by re-association with the active Ru complex. With the non-phosphine Ru complex **20**, activation occurs through the loss of O→Ru chelation. The styrenyl ether ligand competes less effectively with olefin substrates for Ru chelation [47].

5.6 DFT investigation

Results from quantum chemical calculations reveal that the ionic liquids stabilised olefin and the catalyst better than the conventional solvents. Ionic liquids also lowered the activation energy more than the conventional solvents, leading to faster formation of the alkyledene intermediate. The equilibrium constant is higher for conventional solvents than for ionic liquids which suggest that conventional solvents have greater tendency to produce high yield than ionic liquid solvents.

The discrepancy in the values may be related to the incomplete consideration of the characteristics of the ionic liquids in the computation procedures. For the calculations in ionic liquids solvents, it is important to specify the 3-rank symmetric tensor representing the dielectric

constant and the ionic strength in mol/dm^3 Å^2 [222]. However, these values were not available yet, instead the calculations were performed only by specifying the dielectric constant for each ionic liquid. The dielectric constants were obtained from the work by Huang *et al.* [219].

5.7 Summary and outlook

Olefin metathesis still stimulates researchers because of its ease of use and versatility and the reduction in steps required to synthesize complex molecules. Grubbs first generation Ru catalyst possesses a remarkable application profile combining satisfactory activity with an excellent tolerance for the functional groups. Unfortunately, its life time in the reaction medium is limited. Compared to the first generation catalyst, the second generation catalyst show improved activity and thermal stability, though at the expense of low selectivities. The higher activity of Grubbs second generation catalyst had been attributed to the stabilization of the metallacycle intermediate by the more bulky and basic N-heterocyclic carbene ligand [33, 35].

Isopropoxy benzylidene derivatives, pioneered by Hoveyda, exhibit high activity and possess excellent functional group tolerance. Excellent air stability, ease of storage and handling constitute additional advantages. The reason for the high activity of the Hoveyda-Grubbs second generation catalyst can be attributed to the absence of phosphine ligand. It has been proved that phosphine ligand suppresses the catalyst activity in Ru-catalyzed olefin metathesis [35]. The presence of free phosphine in solution can inhibit coordination of olefins to the transition metal centre by re-association with the active Ru complex. With the non-phosphine Ru complex **20**, activation occurs through the loss of O→Ru chelation. The styrenyl ether ligand competes less effectively with olefin substrates for Ru chelation [47].

The use of ILs in catalysis appears favorable as providing for sufficient simplicity of product isolation and catalyst regeneration. All the catalysts used in the experiments were soluble in ILs and the products could be removed from the less dense organic layer by simple decantation, allowing the reuse of catalysts up to three cycles. Development of these methods is expected to give easy access to effective catalyst separation, and is currently under vigorous study. The best catalytic performance was achieved in [bdmim][X] type ILs compared to [bmim][X] type ILs. [bdmim] type ILs can prevent the carbene formation of catalyst, which is believed to be formed by the deprotonation of imidazolium cation or from the oxidative addition of imidazolium to Ru centre [188].

Catalytic olefin metathesis is a ground-breaking advance that has cleared the route to many difficult chemical syntheses, and is likely to continue to do so. The major disadvantages of

the Ru catalysts are their poor recyclability and the difficulty of removing the Ru waste from the products. However, by the introduction of ILs as solvents, these catalysts are prevented from being tied up in unproductive degenerate metathesis reactions, since it remains in the IL layer. High conversions can therefore be achieved, and the catalyst can be reused and recycled. To overcome the problem of leaching of the catalyst into the organic phase, charged catalyst systems have been successfully employed. These charged catalysts improve the immobilization of the catalyst by increasing catalyst affinity to the ionic liquid.

The metathesis of fatty acid derivatives from plant oils has the potential to produce value-added chemicals. New generation catalysts with improved properties that allow for the improved conversions and selectivities will be economically very interesting, especially if the oil price continues to soar. The remaining challenge will be the development of more active catalytic systems that can be applied to a variety of metathesis reactions. It will also be crucial to develop catalysts that have a large functional group tolerance and allow for the direct reaction with substrates containing -CN, $-NH_2$ and other functional groups at low catalyst loadings. Another challenge lies in obtaining highly pure oils or fatty acid derivatives. Therefore efficient, simple and cost-effective pre-treatment strategies will have to be developed.

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APPENDIX 1

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C18:1 Methyl Ester Metathesis in [bmim][X] Type Ionic Liquids;

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Article

C18:1 Methyl Ester Metathesis in [bmim][X] Type Ionic Liquids

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Abstract: The efficacy of [bmim][X] ionic liquids (ILs) (X = PF_6^-, BF_4^- and NTf_2^-) as reaction media for methyl oleate metathesis was compared with that of conventional organic solvents (PhCl, PhMe, DCM and DCE) using the well-defined first and second generation Grubbs precatalysts, $RuCl_2(PCy_3)(L)(=CHPh)$ (L = PCy_3 or H_2IMes). Best catalytic performance, with excellent selectivity (>98%) at moderate reaction temperatures, was achieved in [bmim][X] ILs compared to conventional solvents. The effects of anion, reaction temperature, solvent polarity, solvent viscosity, and ligand-anion interaction on the reaction are also addressed.

Keywords: metathesis; methyl oleate; [bmim][X]; $RuCl_2(PCy_3)(L)(=CHPh)$

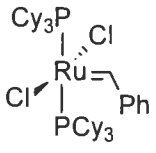
1. Introduction

Room temperature ionic liquids (RTILs) have recently attracted considerable attention as potential alternatives to conventional organic solvents due to several of their unique physicochemical properties such as high polarity, non-volatility, non-flamability and immiscibility with water and/or organic solvents [1–6]. RTILs also provide excellent solvent media in many homogeneously catalyzed reactions such as olefin hydrogenation, hydroformylation, oligomerization and Pd mediated carbon-carbon coupling reactions and allow for simple recycling and reuse of transition metal catalysts [7–9]. The discovery of the well-defined ruthenium catalysts by Grubbs and coworkers has also advanced olefin metathesis as a powerful tool in organic synthesis [10,11]. However, the use of these catalysts in

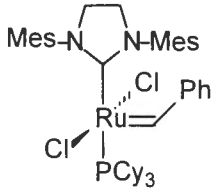
chemical industry is restricted by the fact that they are non-recyclable and their separation from the product stream still poses a serious challenge. Furthermore, most of the work on RTILs reported in the literature is based on ring closing metathesis (RCM) [12–17] and ring opening metathesis (ROM) [18]. Self- metathesis (SM) and cross-metathesis (CM) reactions in RTILs remain almost unexplored and very few works have been published [19–21].

The present study aims to investigate the self-metathesis of methyl oleate in [bmim][X] type ionic liquids using the well-defined first and second generation Grubbs precatalysts, $RuCl_2(PCy_3)_2(=CHPh)$ (**1**) and $RuCl_2(PCy_3)(H_2IMes)(=CHPh)$ (**2**) (Scheme 1). In particular, the influence on the catalytic activity by the anion (X) and other reaction parameters was examined. The study further evaluates the metathesis activity in [bmim][X] ILs against the activity in conventional organic solvents (PhCl, PhMe, DCM and DCE).

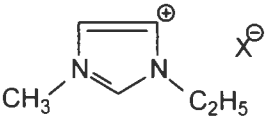
Scheme 1. Grubbs precatalysts and imidazolium ILs.



1



2



3a $X=PF_6$
3b $X=BF_4$
3c $X=NTf_2$

Mes = 2,4,6-methyl phenyl or mesityl
Cy = cyclohexyl

Fatty acid esters derived from seed oils are an alternative source of chemicals, since their chemical structures are closely related to those of the hydrocarbons in crude oil. Seed oil and their derivatives have recently attracted much attention due to their renewable supply, low cost, versatility and their green chemistry. Fatty acid monoesters, like methyl oleate, are usually derived from transesterification of seed oil with lower alcohols, yielding glycerol as the by-product [22]. Self and cross metathesis of fatty acid esters would result in the formation of monomers, dimers and α-olefins with interesting applications in polymer, pharmaceutical and petrochemical industries [23,24].

2. Results and Discussion

2.1. Self-Metathesis in [bmim][X] Type Ionic Liquids

The self-metathesis of methyl oleate in [bmim][X] type RTILs was carried out in presence of Grubbs precatalysts **1** and **2**. Different anions (X = hexafluorophosphate (PF_6^-), tetraflouroborate (BF_4^-) and bis (trifluoromethylsulphonyl)imide (NTf_2^-)) in conjunction with a common cation, 1-butyl-3-methylimidazolium (bmim) were tested for their suitability as reaction media. Table 1 presents some of the properties of [bmim][PF_6], [bmim][BF_4] and [bmim][NTf_2]. PF_6^- and BF_4^- anions are neutral, weakly coordinating and form highly viscous imidazolium ILs while PF_6^- and NTf_2^- form hydrophobic ILs with NTf_2^- forming a less viscous imidazolium IL [25]. When mixed with methyl

oleate all the ILs formed a biphasic system. Two primary metathesis products (PMPs) were obtained in the metathesis of methyl oleate (**A**), namely, octadec-9-ene (**B**) and dimethyl octadec-9-ene-1,18-dioate (**C**), as illustrated in Scheme 2 [26].

Table 1. Polarity (E_T^N), solubility and viscosity of [bmim][X] ILs [25].

X	E_T^N	Solubility in H_2O	Viscosity (cP)(25 °C)
PF_6	0.667	Insoluble	207
BF_4	0.673	Soluble	233
NTf_2	0.642	Insoluble	52

Scheme 2. Primary metathesis products from self-metathesis of methyl oleate.

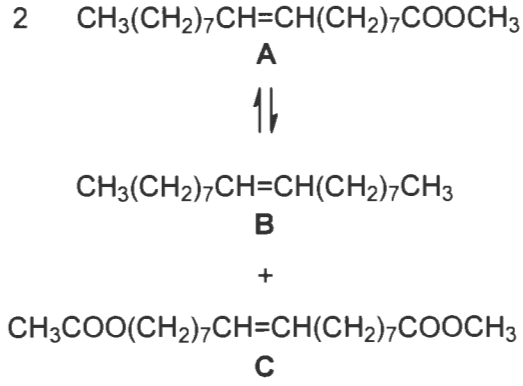
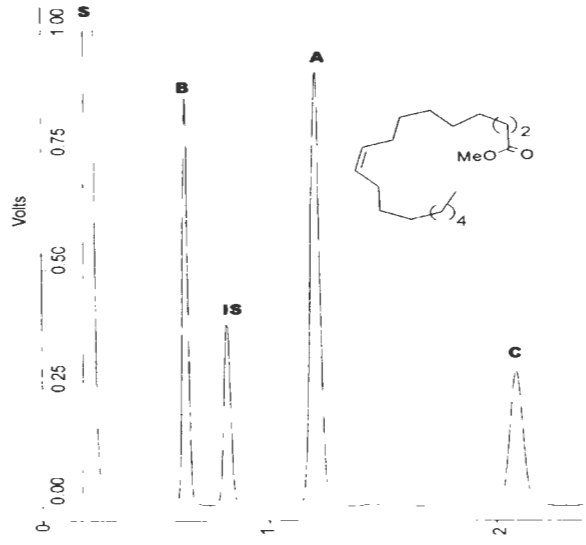


Figure 1 shows a typical gas chromatogram resulting from the metathesis of methyl oleate with nonadecane as internal standard (**IS**).

Figure 1. Typical gas chromatogram resulting from the metathesis of methyl oleate.



2.1.1. Influence of RTIL Anion [X]

Anions play a significant role in determining the properties of ILs. For example, [bmim][PF_6] is immiscible with water, whereas, [bmim][BF_4] is soluble in water. Furthermore, the anions determine viscosity, density, hydrophobicity and solvation of ILs [27]. The effect of varying the anion counterpart in [bmim][X] type RTILs on the metathesis of methyl oleate using Grubbs catalysts has been studied. Figure 2 shows the influence of anion on the catalytic activity of **1**. The metathesis activity showed a decreasing trend with catalyst **1** according to the solvent/anion order $BF_4^- > NTf_2^- \sim PF_6^-$. For catalyst **2** the trend in metathesis activity decreased in the order $NTf_2^- \sim BF_4^- > PF_6^-$ as illustrated in Figure 3.

Figure 2. Influence of [bmim][X] type ILs on the activity of **1** at 20 °C.

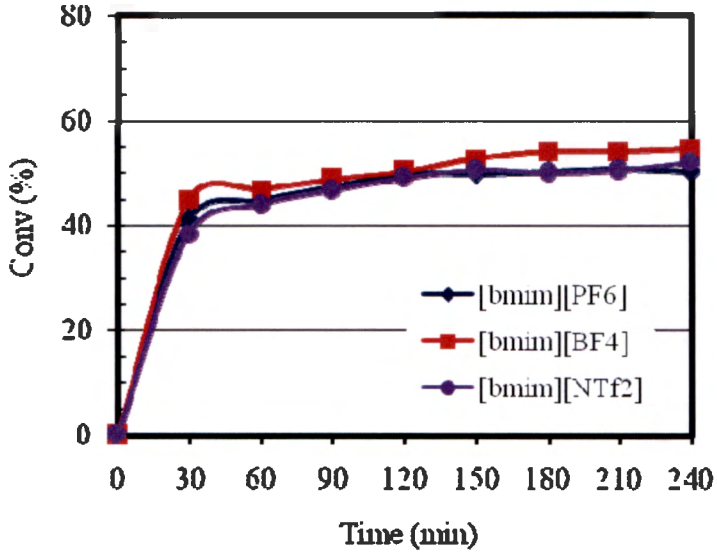
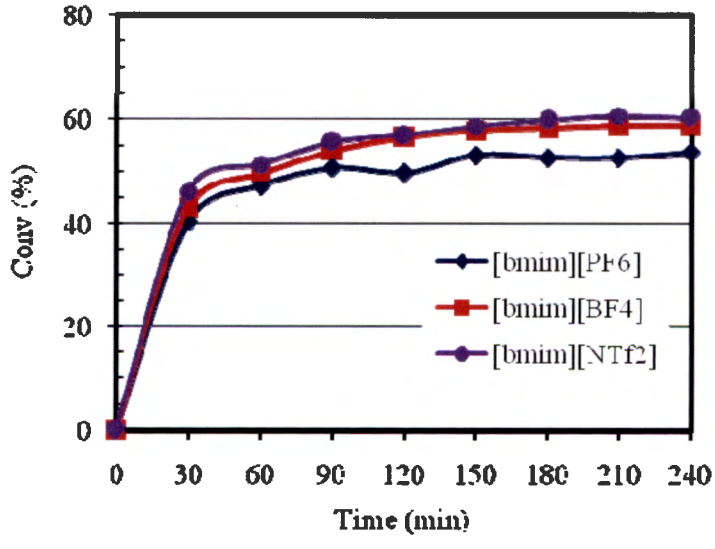


Figure 3. Influence of [bmim][X] type ILs on the activity of **2** at 20 °C.



Clearly only a small difference in catalytic activity occurred in different ILs for both **1** and **2**. The effect on solvent efficacy and the catalytic activity upon changing the ligand L on the catalyst was evident from a change in the activity trend as PCy_3 replaced H_2IMes. However, no simple correlation could be deduced between solvent polarity and catalytic activity like it was the case for conventional organic solvents [26]. On the other hand it could be that the coordination ability of the anion to the catalyst was important in determining the activity pattern as observed [28].

2.1.2. Influence of Reaction Temperature

Table 2 summarizes the activity of **1** and **2** in **3a–3c** at different reaction temperatures in a closed system. Increasing the reaction temperature from 20–100 °C resulted in a rate enhancement with optimum reaction temperature reached at almost 80 °C in **3a**. Excellent selectivity (>98%) was achieved at moderate reaction temperatures (≤60 °C) but decreased at higher temperatures with the formation of secondary metathesis products (SMPs) (F to J) shown in Scheme 3 [23]. The formation of SMPs at high reaction temperatures was evidence of double bond isomerization (A to D and E) occurring.

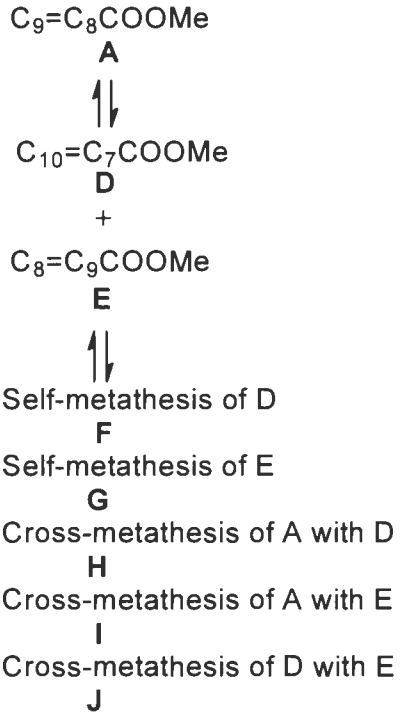
Table 2. Activity of **1** and **2** in **3a–3c** after 4 hour reaction time.

RTIL	Catalyst	Temp. (°C)	Conv (%)	Selec[a] (%)	TON
3a	**1**	20	50.1	100	50.1
	2		52.9	100	52.8
	1	40	57.1	100	57.1
	2		64.9	90	64.9
	1	60	59.4	99	59.4
	2		74.9	81	74.9
	1	80	61.6	92	61.6
	2		79.0	60	79.0
	1	100	62.0	92	62.0
	2		79.1	47	79.1
3b	**1**	20	54.4	100	54.4
	2		58.8	100	58.8
	1	60	61.1	95	61.1
	2		78.2	87	78.2
3c	**1**	20	51.2	100	51.2
	2		60.5	99	60.5
	1	60	60.5	99	60.5
	2		72.7	72	72.7
3a*	**1**	60	23.0	88	2300
	2		62.0	85	6200

MO/Ru ratio = 100, [a] selectivity towards PMPs. *MO/Ru molar ratio = 10,000.

At 60 °C, the best catalytic performance occurred in **3b** with **2** generally displaying superior activity than **1** in all the runs. However, **2** suffered a significant loss in selectivity at temperatures >60 °C compared to **1**, with the result that comparatively higher yields of SMPs were obtained. A radical change in the activity trend from NTf_2^- > BF_4^- > PF_6^- at 20 °C to BF_4^- > PF_6^- > NTf_2^- at 60 °C in the case of **2** was quite remarkable, especially for NTf_2^- which showed more sensitivity towards a change in reaction temperature. It appears in this instance, given the inverse relationship that exists between temperature and viscosity of ILs [25], that the lowering in the viscosity of [bmim][NTf_2] through an increase in reaction temperature might have compromised its solvent efficacy and performance. Such an effect was, however, not so much pronounced for BF_4^- and PF_6^- whose viscosities at elevated temperatures remained relatively high to that of NTf_2^- given their extreme high viscosities at room temperature. If this was to be true for NTf_2^-, then BF_4^- and PF_6^- would be seen as more suited for high temperature reactions and NTf_2^- for reactions at low temperatures.

Scheme 3. SMPs resulting from the metathesis of methyl oleate.



For MO/Ru molar ratio of 10,000, TONs of 2,300 and 6,200 were obtained at 60 °C in **3a** for **1** and **2**, respectively. The difference in TONs could be attributed to the short lifetime and poor thermal stability of **1** compared to **2** [29,30]. In spite of significantly enhanced activity of **2** relative to **1**, catalyst **2** displayed poor selectivity, especially at high reaction temperatures. High selectivities and TONs are some of the important indicators if the process is to find industrial application.

2.2. [bmim][X] ILs vs. Conventional Organic Solvents

Self-metathesis of MO in organic solvents was carried out in presence of **1** and **2** and the results are summarized in Table 3. The solvents used for this study were DCM, DCE, PhMe and PhCl. The best

catalytic performance among the conventional solvents occurred in DCM and the lowest in PhMe. The activity of **1** and **2** were found to increase in the order PhMe < PhCl < DCE ~ DCM in accordance to an increase in solvent polarity. Selectivity towards PMPs was 100% in all the organic solvents. These results are in agreement with the work done by Buchowicz and Mol [31] and Marvey *et al.* [26].

Table 3. Activity of **1** and **2** in conventional organic solvents.

Entry	Solvent	Catalyst	Conv (%)	Selec (%)
1	PhCl	**1**	47.1	100
		2	50.6	100
2	PhMe	**1**	45.0	100
		2	48.0	100
3	DCM	**1**	49.0	100
		2	51.3	100
4	DCE	**1**	48.9	100
		2	50.7	100

MO/Ru ratio 100, 20 °C, 4 h.

Compared to [bmim][X] ILs, the conventional organic solvents were less efficient in that relatively lower methyl oleate conversions were obtained for both **1** and **2**. Figures 4 and 5 compare the activities of **1** and **2**, respectively, in [bmim][BF_4], DCM and DCE.

From the results obtained, it is clear that a significant rate enhancement occurred in [bmim][BF_4] as opposed to the best of the conventional solvents, namely, DCM and DCE. A further substantial rate enhancement occurred in [bmim][BF_4] at a higher reaction temperature (60 °C). Therefore, [bmim][X] ILs provide excellent reaction media for methyl oleate metathesis and can be used as convenient substitutes for conventional organic solvents due to their "green" characteristics and possibilities for easy product separation and catalyst recycling [9].

Figure 4. Activity of **1** in [bmim][BF_4], DCM and DCE at 20 °C.

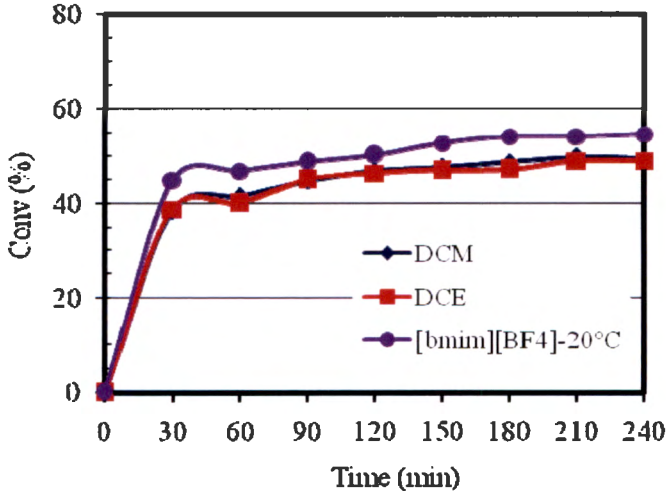
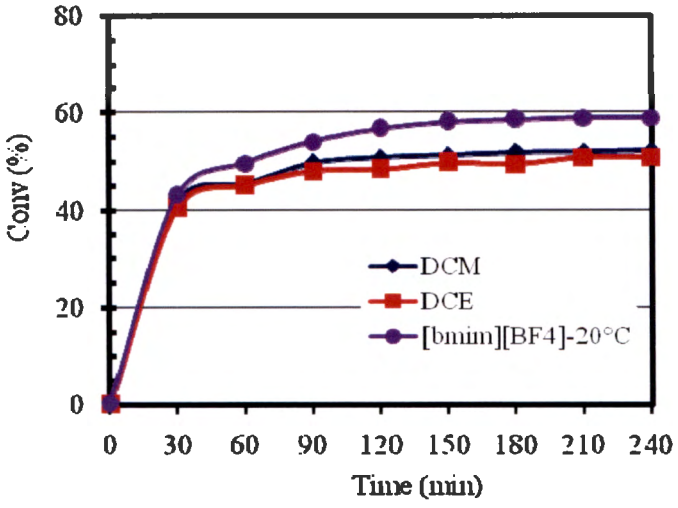


Figure 5. Activity of **2** in [bmim][BF_4], DCM and DCE at 20 °C.



3. Experimental Section

3.1. Materials and Apparatus

Chlorobenzene (PhCl), dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium bis (trifluoromethylsulphonyl)imide ([bmim][NTf_2]) were all reagent grade from Sigma-Aldrich. Methyl oleate (≥99%) was obtained from Sigma-Aldrich and was treated with activated alumina and stored under N_2 at a subzero temperature. Ethyl vinyl ether was purchased from Fluka. Nonadecane purchased from Fluka was used as the internal standard (**IS**). Grubbs precatalysts **1** and **2** were stored under N_2 and used as purchased from Sigma-Aldrich. Chromatograms were obtained using Varian Star 3400 *CX* GC equipped with a DB-624 capillary column (J&W Scientific, 30 m × 0.53 mm) and a flame ionization detector (FID). The oven temperature was held at 200 °C and then increased to 270 °C at a rate of 20 °C min^{-1}. The injector temperature was set at 270 °C and the detector temperature at 300 °C with N_2 as carrier gas.

3.2. Metathesis Experiments

All the reactions were performed under a N_2 atmosphere in a glass reactor fitted with a thermometer and a rubber septum. For the reaction in organic solvents, 12.4 mg of **1** (0.015 mmol) or **2** (0.014 mmol) was dissolved in 2.0 mL of organic solvent followed by 0.1 g of internal standard and 0.5 mL substrate. For the reaction in RTILs, 0.5 mL of the substrate was added to 1 mL of ionic liquid and stirred for 10 min to attain the reaction temperature. An internal standard (0.05 g) was added followed by the addition of 12.4 mg of **1** or **2**. Both catalysts were soluble in ILs with the substrate forming a biphasic mixture with ILs. Samples were withdrawn by a syringe at regular time intervals for up to 5 hours. The reaction was terminated by immediately quenching with a few drops of ethyl vinyl ether [31]. The quenched sample was diluted with solvent (**S**) and analyzed by GC. The following formulas were used in the calculations:

$$Conversion(\%) = \frac{n_0 - n_t}{n_0} \times 100$$

where n_0 = number of moles of substrate at the beginning of the reaction. n_t = number of moles of substrate after time *t*.

$$Selectivity(\%) = \frac{yield\ of\ PMPs}{\sum yield\ of\ products} \times 100$$

TON = MO/Ru ratio x substrate conversion; TON is the number of moles of substrate that a mole of catalyst can convert before becoming inactivated.

4. Conclusions

The efficacy of [bmim][X] ILs as reaction media in methyl oleate metathesis was evaluated and the effects of anion, reaction temperature, solvent polarity, viscosity and ligand-anion interaction on the reaction have been addressed. The nature of the anion in [bmim][X] ILs proved to have a slight influence on catalytic performance, suggesting that only a small degree in rate enhancement could be expected from the variation of the anion. The results obtained further indicate that reaction temperature has a significant effect on solvent efficacy with anions displaying varied sensitivities upon a change in ligand L and reaction temperature. While excellent selectivity is achieved at a moderate reaction temperature, a loss in selectivity occurs at higher reaction temperatures with the formation of SMPs and is more pronounced for L = H_2IMes. Indeed [bmim][X] ILs outperformed conventional solvents as reaction media for the ruthenium-catalysed self-metathesis of fatty acid methyl esters and have demonstrated their potential as excellent substitutes to these solvents with an added advantage that they meet greener character requirements and allow for easy catalyst separation and recycling.

Acknowledgements

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APPENDIX 2

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Metathesis of Fatty Acid Ester Derivatives in 1,1-Dialkyl and 1,2,3-Trialkyl Imidazolium Type Ionic Liquids

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Article

Metathesis of Fatty Acid Ester Derivatives in 1,1-Dialkyl and 1,2,3-Trialkyl Imidazolium Type Ionic Liquids

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Abstract: The self-metathesis of methyl oleate and methyl ricinoleate was carried out in the presence of ruthenium alkylidene catalysts **1–4** in [bmim] and [bdmim][*X*] type ionic liquids (RTILs) (*X* = PF_6^-, BF_4^- and NTf_2^-) using the gas chromatographic technique. Best catalytic performance was obtained in [bdmim][X] type ionic liquids when compared with [bmim][*X*] type ionic liquids. Catalyst recycling studies were also carried out in the room temperature ionic liquids (RTILs) with catalysts **1–4** in order to explore their possible industrial application.

Keywords: self-metathesis; methyl oleate; methyl ricinoleate; [bmim][*X*]; [bdmim][*X*]

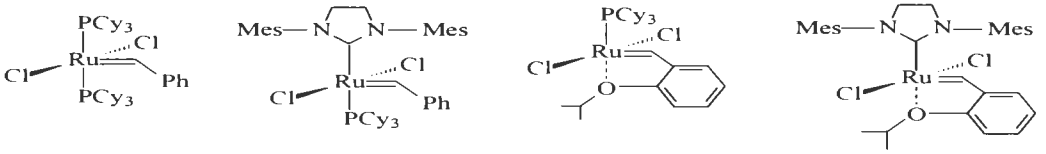
1. Introduction

Room temperature ionic liquids (RTILs) have been receiving considerable attention as innovative solvents for metal catalyzed organic reactions [1–6]. Most ionic liquids are based on ammonium, imidazolium, phosphonium, pyridinium, sulphonium, picolinium, pyrrolidinium, thiazolium, oxazolium, and pyrazolium cations. The important properties of ionic liquids, such as affinity to water and miscibility with other solvents, can be adjusted by the proper choice of alkyl substituents and counter anion. The most commonly used ionic liquids in olefin metathesis are 1,3-dialkylimidazolium

and 1,2,3-trialkylimidazolium salts. Buijsman and co-workers [3] were the first group that reported the application of ionic liquids as a medium for olefin metathesis. They studied ring closing metathesis (RCM) of several substrates using Grubbs first and second generation catalysts in RTILs, and [bmim][PF_6] was found to be the optimal solvent for the reactions. The activity and recyclability of Grubbs second generation catalyst in the self-cross-metathesis of some terminal olefins in RTILs has also been reported by Tang and co-workers [7]. Self-metathesis of 1-octene in 1,3-dialkylimidazolium and 1,2,3-trialkylimidazolium type ionic liquids have been reported by Williams and co-workers [8]. The results from the study showed that ionic liquids with shorter alkyl chain length enhanced the catalytic activity while the longer ones inhibited it. To overcome the problem associated with the leaching of products into the substrate, many charged catalyst systems have been employed [9–14].

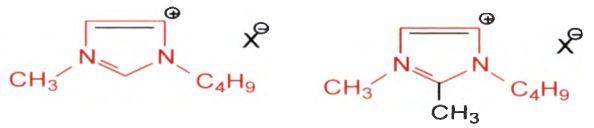
The present work is an extension of our previous one which highlighted the self-metathesis reaction of methyl oleate in [bmim][*X*] type ionic liquids [15]. In this study, we report the self-metathesis of methyl oleate and methyl ricinoleate using the catalysts [**1**–**4**] in [bmim][*X*] and [bdmim][*X*] type ionic liquids (Scheme 1). The study also compares the metathesis activity in [bdmim] and [bmim] type ionic liquids. Catalyst recycling was also carried out in ionic liquids with the catalysts **1**–**4**.

Scheme 1. Ruthenium catalysts and imidazolium ionic salts.



1 **2** **3** **4**

Mes = 2,4,6-methyl phenyl or mesityl
Cy = cyclohexyl



5a X=PF_6
5b X=BF_4
5c X=NTf_2

6a X=PF_6
6b X=BF_4

2. Results and Discussion

2.1. Self-Metathesis of Methyl Oleate

The self-metathesis of methyl oleate was carried out in the presence of ruthenium alkylidene catalysts **1**–**4** at 40 °C. The Hoveyda-Grubbs catalysts **3** and **4** were evaluated in 1-butyl 3-methylimidazolium (bmim) and 1-butyl 2,3-dimethylimidazolium (bdmim) based ionic liquids with different anions (PF_6^-, BF_4^- and NTf_2^-) (Scheme 1). Figure 1 shows the activity of **3** in [bmim] and [bdmim] type ionic liquids. For catalyst **3**, similar conversions were observed in [bmim] and [bdmim] type ionic liquids (ILs). As there was not much difference in the catalytic activity, the benefit of selecting a particular IL (among PF_6^-, BF_4^- and NTf_2^-) was found to be of less importance. For catalyst **4**, the highest activity was found in [bdmim][BF_4] with a conversion of 85% (Figure 2).

Comparing the cations of the ionic liquids, the C2-methylated imidazolium cation [bdmim] led to a slightly better conversion. The benefit of using [bdmim] cation in the ethenolysis of methyl oleate has been previously reported by Thurier *et al.* [16].

Figure 1. Activity of **3** for the self-metathesis of methyl oleate in different ILs.

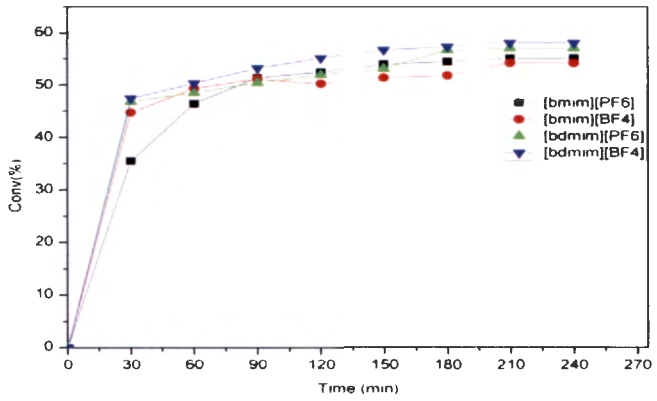
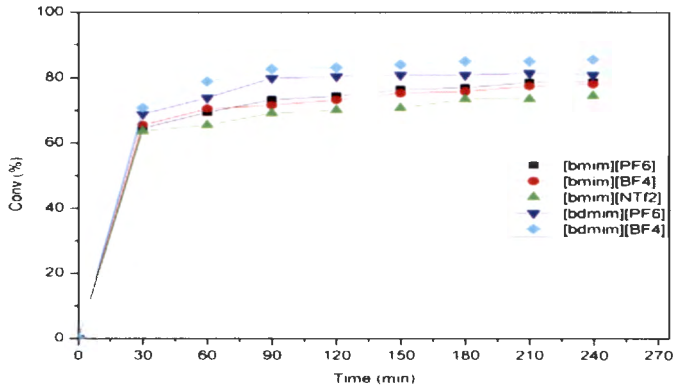


Figure 2. Activity of **4** for the self-metathesis of methyl oleate in different ILs.



To study the effect of temperature on metathesis activity, the reactions were conducted at temperatures 40 °C and 60 °C. The results are summarized in Table 1. An increase in substrate conversion was observed with increase in temperature. At both the temperatures, the highest substrate conversion was seen with catalyst **4**. Generally for all the runs, Hoveyda-Grubbs catalyst **4** exhibited good activity, although isomerization and formation of secondary metathesis products [17] seems to be a drawback. Hoveyda-Grubbs catalyst **3** and **4** showed good solubility in ionic liquid compared to Grubbs catalyst **1** and **2**. The reason for the high activity of the Hoveyda-Grubbs second generation catalyst can be attributed to the absence of phosphine ligand. It has been proved that phosphine ligand suppresses the catalyst activity in Ru-catalyzed olefin metathesis [18]. The presence of free phosphine in solution can inhibit coordination of olefins to the transition metal centre by re-association with the active Ru complex. With the non-phosphine Ru complex (catalyst **4**), activation occurs through the loss of O→Ru chelation. The styrenyl ether ligand completes less effectively with olefin substrates for Ru chelation [19]. [bdmim] type ILs can prevent the carbene formation of catalyst, which is believed to be formed by the deprotonation of imidazolium cation or from the oxidative addition of imidazolium to Ru centre [20].

Table 1. Activity of **3** and **4** for the self-metathesis of methyl oleate in [bmim] and [bdmim][*X*] type ionic liquids.

RTIL	Catalyst	Temperature (°C)	Conversion (%)	Selectivity [a] (%)
5a	1	40	57	99
	2		65	97
	3		55	99
	4		78	96
	1	60	59	99
	2		75	94
	3		57	98
	4		87	93
5b	1	40	58	99
	2		67	96
	3		56	99
	4		79	96
	1	60	61	99
	2		78	94
	3		59	97
	4		87	95
5c	1	40	57	99
	2		64	96
	3		54	99
	4		74	97
	1	60	60	99
	2		73	96
	3		59	99
	4		85	95
6a	3	40	57	99
	4		81	98
	3	60	60	97
	4		90	95
6b	3	40	58	99
	4		85	99
	3	60	60	97
	4	40	92	95

0.5 mL of MO (MO/Ru ratio = 100), 1 mL of IL, reaction time = 4 h; [a] selectivity towards PMPs.

2.2. Self-Metathesis of Methyl Ricinoleate

The self-metathesis of methyl ricinoleate was carried out in the presence of catalysts **1** and **2** in [bmim][X] type ILs. Table 2 summarizes the activity of catalysts **1–4** for the self-metathesis of methyl ricinoleate. For catalyst **1**, the highest activity was shown in **5a** with a substrate conversion of 45% and the activity was found to be in the order $PF_6 > BF_4 > NTf_2$ (Figure 3). For catalyst **2**, the same trend was followed, with the reaction in **5a** yielding the highest conversion of 58% (Figure 4). The primary

metathesis products (PMP) obtained from the metathesis of methyl ricinoleate (**A**) were 9-octadecene-7,12-diol (**B**) and dimethyl 9-octadecenedioate (**C**), as illustrated in Scheme 2 [21].

Table 2. Activity of **1** and **2** for the self-metathesis of methyl ricinoleate.

RTIL	Catalyst	Temperature (°C)	Conversion (%)	Selectivity [a] (%)
5a	**1**	60	45	99
	2		58	99
5b	**1**	60	41	99
	2		56	99
5c	**1**	60	38	99
	2	60	55	99

0.2 mL of MR (MR/Ru ratio = 100), 0.5 mL of IL, reaction time = 4 h; [a] selectivity towards PMPs.

Figure 3. Activity of 1 for the self-metathesis of methyl ricinoleate in different ionic liquids.

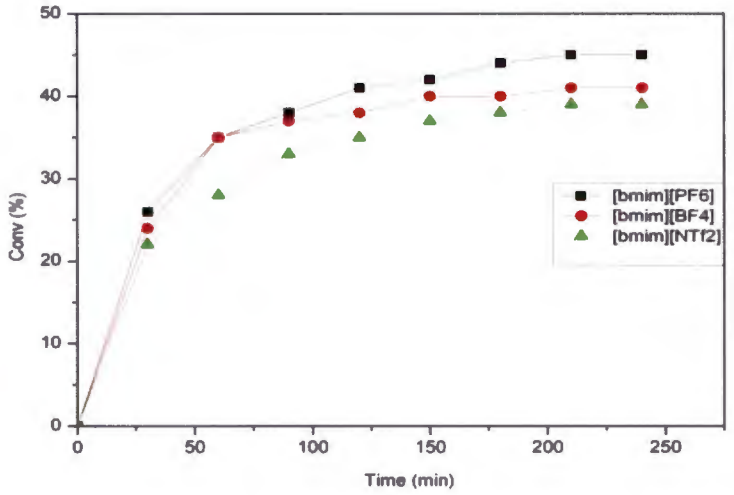
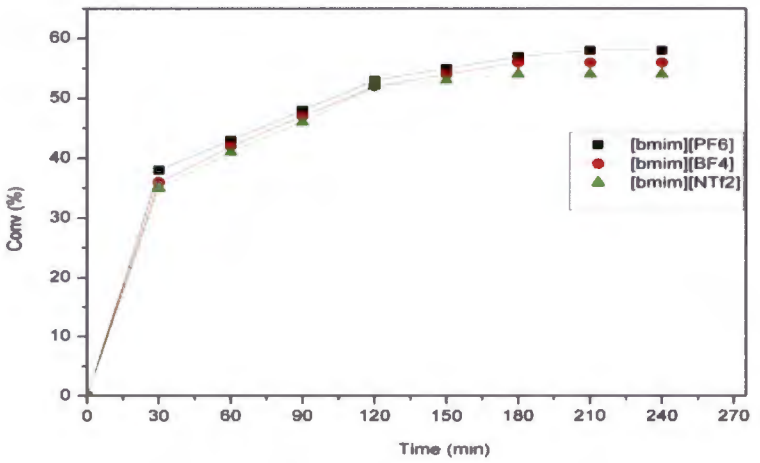
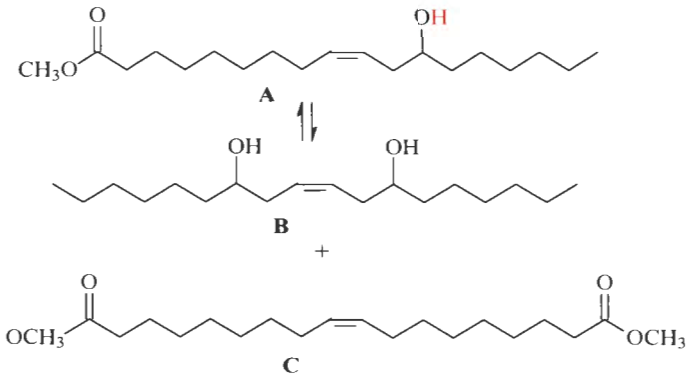


Figure 4. Activity of 2 for the self-metathesis of methyl ricinoleate in different ionic liquids.



Scheme 2. Primary metathesis products from self-metathesis of methyl ricinoleate.



2.3. Catalyst Recycling in Ionic Liquids

As solvents, ionic liquids are more advantageous than conventional organic solvents, which make them recyclable and environmentally friendly. It has been reported that the ionic liquids could be reused for at least three runs [3,16,22,23]. In a typical experiment, metathesis reaction was carried out in ionic liquids, and, after extraction of reaction products with heptane (2 × 3 mL), the glass reactor was loaded with fresh methyl oleate and was introduced for a new run.

To study the recyclability, Ru catalysts **1**–**4**, in different ionic liquids, were subjected to consecutive runs (Table 3). Grubbs catalyst **1** proved to be stable in three consecutive runs, with the third run resulting in a decreased conversion. Grubbs catalyst **2** showed an increased conversion in the third cycle when compared with catalyst **1**. Comparing the Hoveyda-Grubbs catalysts **3** and **4**, the best result was obtained with catalyst **3**. The results prove that catalyst **3** can be reused for three runs without loss of activity. In spite of good activity in the first run, the second generation Hoveyda-Grubbs catalyst **4** showed low catalytic activity during the second run.

Table 3. Recycling of catalysts in [bmim][BF_4] [a] and [bdmim][BF_4] [a,b].

Catalyst	Conversion (%)	Selectivity (%)
1	1st run: 57 (58)	99
	2nd run: 56 (56)	99
	3rd run: 42 (45)	98
2	1st run: 67 (72)	99
	2nd run:50 (60)	97
	3rd run:45 (57)	97
3	1st run: 56 (58)	99
	2nd run: 56 (58)	99
	3rd run: 49 (53)	99
	4th run: 22 (30)	99
4	1st run: 74 (85)	99
	2nd run: 40 (54)	95
	3rd run: 15 (23)	95

[a] All reactions were performed at 40 °C for 4 hours, substrate/Ru = 100; [b] values in bracket are for [bdmim][BF_4].

3. Experimental Section

3.1. Materials and Apparatus

1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide ([bmim][NTf_2]), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bdmim][PF_6]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bdmim][BF_4]), were all reagent grade chemicals from Sigma-Aldrich. Methyl oleate (≥99%) and methyl ricinoleate (>99%) were obtained from Sigma-Aldrich and were treated with activated alumina and stored under N_2 atmosphere at a subzero temperature. Ethyl vinyl ether was purchased from Fluka. Nonadecane purchased from Fluka was used as the internal standard (**IS**). Ruthenium catalysts **1–4** were stored under N_2 and used as purchased from Sigma-Aldrich. Chromatograms were obtained using Varian Star 3400 *CX* GC equipped with a DB-624 capillary column (J&W Scientific, 30 m × 0.53 mm) and a flame ionization detector (FID). The oven temperature was held at 200 °C and then increased to 270 °C at a rate of 20 °C min^{-1}. The injector temperature was set at 270 °C and the detector temperature at 300 °C with N_2 as carrier gas.

3.2. Metathesis Experiments

All the reactions were performed under a N_2 atmosphere in a glass reactor fitted with a thermometer and a rubber septum. For the reaction in RTILs, 0.5 mL of the substrate was added to 1 mL of ionic liquid and stirred for 10 min to attain the reaction temperature. An internal standard (0.05 g) was added followed by the addition of 12.4 mg of catalyst. All the catalysts were soluble in ILs with the substrate forming a biphasic mixture with ILs. Samples were withdrawn by a syringe at regular time intervals for up to 4 hours. The reaction was terminated by immediately quenching with a few drops of ethyl vinyl ether [22]. The quenched sample was diluted with solvent and analyzed by GC.

4. Conclusions

For the self-metathesis of methyl oleate, Hoveyda-Grubbs catalyst **4** provided the best result with enhanced activity. Similar conversions were observed in all the three [bmim][*X*] type ionic liquids selected. However, when compared with [bdmim][*X*] type ionic liquids, higher activity was observed, which shows the superiority of [bdmim][*X*] type ionic liquids as reaction media. Furthermore, it was found that Hoveyda-Grubbs catalyst **3** could be reused for three consecutive runs without loss of activity. Overall, the use of ionic liquids in the metathesis reaction opens a route for the use of vegetable oil as a renewable source of raw materials for the chemical industry.

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APPENDIX 3

Paper presented at the International Science and Technology Conference, Vaal University of Technology, Vanderbijilpark, South Africa in Oct 2009.

Metathesis of methyl oleate in room temperature ionic liquid: A comparison with conventional organic solvents

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Abstract:

Room temperature ionic liquids are a new class of compounds that have received wide attention due to their green chemistry. Recent studies have aimed at investigating the viability of performing ring-closing metathesisin commercial room temperature ionic liquid, 1-butyl-3-methyl imidazoliumhexafluorophosphate, [bmim][PF_6] **3**. In this paper, we compare the self-metathesis of methyl oleate using the well-defined first and second generation Grubbs precatalysts, $RuCl_2(PCy_3)_2$(=CHPh) **1** and $RuCl_2(PCy_3)(H_2IMes)$(=CHPh) **2** , in [bmim][PF_6] and selected conventional organic solvents (PhCl, PhMe, DCM and DCE). The results obtained show higher activity in [bmim][PF_6] compared to PhCl and PhMe but similar activity and selectivity in DCM and DCE. [bmim][PF_6] is, therefore, an excellent substitute to organic solvents with an added advantage that it meets greener character requirements and offer easy separation of reaction products.

Key words: Metathesis, methyl oleate, RTILs, Grubbs catalysts

APPENDIX 4

Paper presented at the New Zealand Institute of Chemistry Conference, University of Waikato, Hamilton, NewZealand in Nov 2011.

Metathesis in eco-friendly solvents: A transformation of seed oil-derived olefins

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Abstract

The self-metathesis of methyl oleate and methyl ricinoleate catalyzed by the first and second generation Hoveyda-Grubbs catalyst was investigated in room temperature ionic liquids and dimethyl carbonate (a non-toxic organic solvent). The study showed that the ionic liquid has a significant effect on the activity of catalysts. The reaction carried out in dimethyl carbonate, performed equally well as in dichloromethane or other aromatic solvents. The results demonstrated that room temperature ionic liquids and dimethyl carbonate can be used as a substitute to environmentally unfriendly organic solvents.
