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Oxodiperoxomolybdenum catalyzed olefin epoxidation: the role of Ionic Liquids

ELABORATO FINALE

Presentato da

Cristiana Cesari

Relatore:

Rita Mazzoni

Co-Relatori:

Maria Cristina Cassani

María del Mar Cornejo Argandoña

Gavino Solinas

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Abstract

Ionic Liquids (ILs) constituted by organic cations and inorganic anions are particular salts with a melting point below 100°C. Their physical properties such as melting point and solubility can be tuned by altering the combination of their anions and cations. In the last years the interest in ILs has been centered mostly on their possible use as "green" alternatives to the traditional volatile organic solvents (VOCs) thanks to their low vapour pressure and the efficient ability in catalyst immobilization. In this regard, the subject of the present thesis is the study of the oxodiperoxomolybdenum catalyzed epoxidation of olefins in ILs media with hydrogen peroxide as the oxidant. In particular *N*-functionalized imidazolium salts, such as 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium (**1**), were synthesized with different counterions $[I]^-$, $[PF_6]^-$, $[NO_3]^-$, $[NTf_2]^-$ and $[ClO_4]^-$ and tested as reaction solvents. The counterion exchange with $[Cl]^-$, $[NTf_2]^-$ and $[NO_3]^-$ was also performed in unfuctionalized imidazolium salts such as 3-butyl-1-methylimidazol-3-ium (**3**). All the prepared ILs were tested in catalytic epoxidation of olefins exploiting oxodiperoxomolybdenum complexes $[MoO(O_2)_2(C_4H_6N_2)_2]$ (**4**) and $[MoO(O_2)_2(C_5H_8N_2)_2]$ (**5**) as catalysts. The IL **3[NTf_2]** and the catalysts **5** give rise to the best results leading to the selective formation of the epoxide of *cis*-cyclooctene avoiding hydrolysis side reaction.

A preliminary study on the synthesis of novel NHC oxodiperoxomolybdenum complexes starting from imidazolium salts was also developed.

Sommario

I liquidi ionici (ILs) sono particolari sali costituiti da cationi organici e anioni inorganici con un punto di fusione inferiore a 100°C. Le loro proprietà fisiche, come il punto di fusione e la solubilità, possono essere modulate modificando la combinazione dei loro anioni e cationi. Negli ultimi decenni l'interesse verso i ILs si è focalizzato principalmente, grazie alla loro bassa tensione di vapore e la capacità di immobilizzare efficacemente il catalizzatore, sul loro possibile utilizzo come alternative "green" ai tradizionali solventi organici volatili (VOCs). A questo proposito, lo studio dell'epossidazione di olefine catalizzata da complessi ossodiperosso-molibdeno in mezzi ILs con perossido di idrogeno come ossidante è oggetto della presente tesi. In particolare sono stati sintetizzati sali di imidazolio *N*-funzionalizzati, 1-(2-*t*-Butossicarbonilamino-etil)-3-metilimidazolio (**1**), con diversi controioni quali $[I]^-$, $[PF_6]^-$, $[NO_3]^-$, $[NTf_2]^-$ e $[ClO_4]^-$ e testati come solventi di reazione. Lo scambio del controione con gli anioni $[Cl]^-$, $[NTf_2]^-$ e $[NO_3]^-$ è stato effettuato anche in sali di imidazolio non funzionalizzati come 3-butil-1-metilimidazolio (**3**). Tutti gli ILs preparati sono stati testati nell'epossidazione catalitica di olefine sfruttano i complessi ossodiperossomolibdeno $[MoO(O_2)_2(C_4H_6N_2)_2]$ (**4**) e $[MoO(O_2)_2(C_5H_8N_2)_2]$ (**5**) come catalizzatori. Il liquido ionico **3[NTf_2]** e il catalizzatore **5** danno i migliori risultati portando alla formazione selettiva dell'epossido di *cis*-cicloottene evitando quindi la reazione secondaria di idrolisi.

Si è effettuato inoltre uno studio preliminare sulla sintesi di nuovi complessi ossodiperosso NHC di Molibdeno a partire da sali imidazolio.

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1. INTRODUCTION

This dissertation was developed within a collaboration between the Valerio Zanotti's research group of the Bologna University (Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, with Rita Mazzoni as supervisor) and the Agustin Galindo's research group of Sevilla University (Departamento de Química Inorgánica, Facultad de Química, with María del Mar Cornejo Argandoña as co-supervisor). The research group of Seville has recently devoted a great interest in unconventional solvents as reaction media. In particular their attention was focused on ionic liquids with the aim to implement "Green Chemistry"processes. On the other hand the Bologna group in the latter years have focused its attention to amino/amide functionalized ionic liquids and their use in the preparation of *N*-heterocyclic carbenes (NHCs) metal complexes.

The collaboration was born within the Erasmus project frame and grew with the interest to combine the two different research areas with the aim to improve each other knowledge and investigate the employment of ionic liquids in homogenous catalysis from a new point of view.

1.1. Green chemistry

Waste production in industrial processes is one of the most environmental problems that in the last decades worries the chemistry field. The development of new synthetic methodologies which eliminate or minimize these residues is one of the goals of the "Green Chemistry" concept, also called sustainable chemistry, which is devoted to the utilization of a set of principles that reduce or eliminate the hazardous substances in the design, manufacture and application of chemical products. The ideology of "Green Chemistry" calls for the development of new chemical reactivities and reaction conditions that can potentially provide benefits for chemical syntheses in term of resource efficiency, energy efficiency, product selectivity, operational simplicity, health and environmental safety.[1] All this can be summarized in the twelve principles, that were formalized and extensively promoted since the 1990s by their progenitor, Prof. Paul Anastas, and recently elegantly condensed by Prof. Martyn Poliakoff and co-workers into a mnemonic for easy communication: PRODUCTIVELY (Figure 1).

"Despite their inherent value, all of these principles are very cumbersome to present to a lecture audience. Mnemonics, on the other hand, can provide a very pleasant way to

communicate and learn the principles. As part of an ongoing Anglo–Japanese collaboration, we have felt the need to produce a simpler statement of the principles that can be presented as a single slide, which is understandable to a wide range of audiences including non-native English speakers. After some considerations, we have devised the acronym, 'PRODUCTIVELY', in which we have tried to capture the spirit of each of the twelve principles of green chemistry in just two or three words." [2]

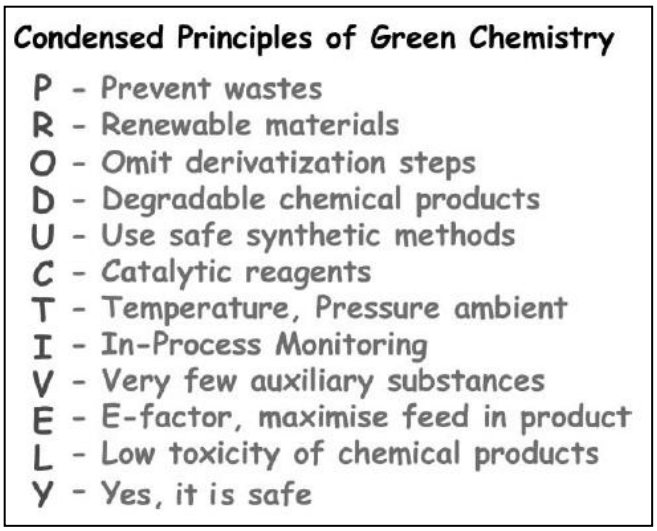


***Figure 1**: condensed of the twelve principles of "Green Chemistry".*

Most of the waste products involves fine chemicals and pharmaceutical industry because these use volatile organic chemicals (VOCs) in large quantities. The environmental impact of the latter is considerable, therefore, the redesign and progressive replacement of the processes with organic solvent by "cleaner" processes are an important objective in the contemporary chemistry. A possible solution to the problem could be the use of unconventional solvents as for example the ionic liquids.

1.2. Ionic Liquids as "Green Solvents"

In the last few decades the study and the investigation of ionic liquids (ILs) application has increased together with the interest in "Green Chemistry". A great interest in this class of compounds has been centered on their possible use as "green" alternatives to the traditional volatile organic solvents. They have promising advantages such as an extremely low vapour pressure (generally negligible), which can match the human requirements of developing greener technologies. This is the reason why ILs are called "green solvents" in many early articles, and indeed the link between ILs and "Green

Chemistry" is mainly related to the characteristic of low volatility. The "greenness" of ILs is also attributable to their non-toxicity, non-explosive and non-flammability that reduces the risk when treating fast, exothermic oxidation and also to their thermal and chemical stability.[3]

The ILs are salts with a melting point below 100°C and many of them are found in liquid state at room temperature, the latter are called RTILs (Room Temperature Ionic Liquids) and this property makes them potentially useful compounds as solvents. In particular the solvents investigated for chemical processes are typically constituted by an organic cations (examples are reported in Figure 2) and inorganic anions (examples are reported in Figure 3).

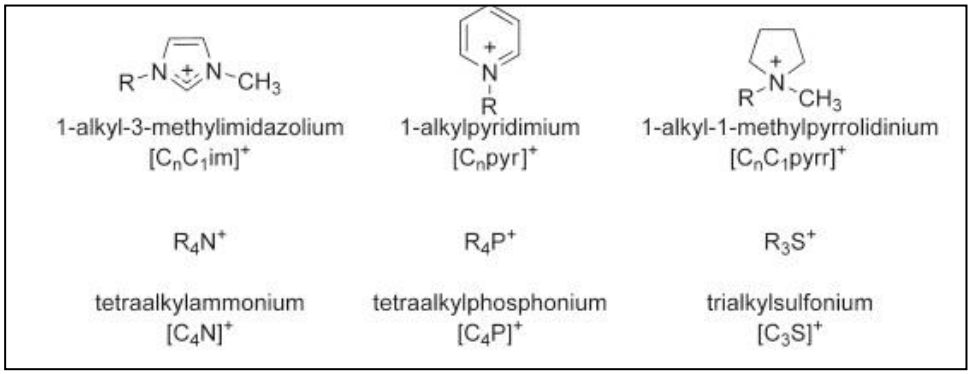


Figure 2: *Some commonly used cations for ionic liquids.*

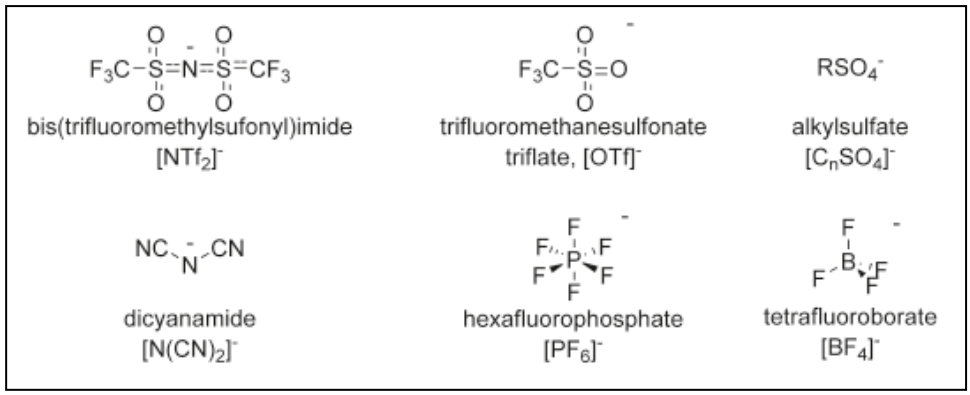


Figure 3: *some commonly used anions for ionic liquids.*

In addition to their "greenness" feature, ILs are often referred as "designable solvents" mainly because their physical properties such as melting point, viscosity, density, solubility and coordination properties, can be tuned according to different reactions or processes by altering the combination of their anions and cations.[4]

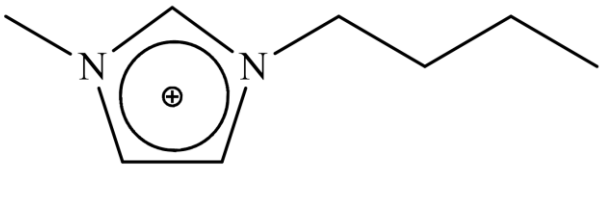
With regard to the catalytic reaction some catalysts proved to improve their catalytic activity in ILs than in traditional solvents, moreover some catalytic reactions which do not work in common organic solvents can be performed in ILs. Another advantage of ILs in catalytic reactions is the efficient immobilization of the catalyst in the ionic liquid phase. The ILs are also able to dissolve many inorganic and organometallic compounds, therefore a large amount of catalysts having polar or ionic character can be immobilized in ILs, it means a easy separation and subsequent reuse of the catalyst.

1.3. The role of the counterion

As mentioned in the previous paragraph, the ionic liquids are particular salts liquid at room temperature and consist in a organic cation and an inorganic anion. The most widely studied ILs are composed of bulky and asymmetrical nitrogen-containing cations (e.g., imidazole, pyrrole, piperidine, and pyridine) in combination with a large variety of anions, ranging from simple halides to more complex organic species.

The ILs properties are controlled by the selection of both, so the change of cation and anion can affect many physical properties as melting point and solubility. In particular the miscibility of ionic liquids in water is a very important parameter because water is ubiquitous and even in little amounts could affect the properties of ILs.

Early investigations about water miscibility found that the behavior of ILs in water varies with the anion, for example in the case of 3-butyl-1-methylimidazolium ($[C_4C_1im]^+$, Figure 4) was demostrated that Cl^-, Br^-, $[OTf]^-$, and $[BF_4]^-$ give ionic liquids that mix with water in all compositions, whereas in the case of $[C(CN)_3]^-$, $[PF_6]^-$ and $[NTf_2]^-$ the ILS lead to a biphasic mixture with water (Figure 4).[5]



Miscible with water	Immiscible with water
$[Cl]^-$, $[Br]^-$, $[OTf]^-$, $[BF_4]^-$	$[C(CN)_3]^-$, $[PF_6]^-$, $[NTf_2]^-$

***Figure 4**: solubility in water of $[C_4C_1im]^+$ with a different counterion.*

For these anions of $[C_4C_1im]^+$ based ILs the octanol-water partition coefficient, K_{ow}, that quantify the hydrophobicity of a compound was measured and resulted to increase in the following order: $[OTf]^- < [BF_4]^- < Br^- < [NO_3]^-$, $Cl^- < [PF_6]^- < [NTf_2]^-$. This suggests that hydrogen bonding to the anion gives a significant contribution to the hydrophilicity of the ionic liquid. On the other hand, it was also observed that cation did not give a significant contribution to the hydrophilicity, in fact, spectroscopic studies did not evidence interations between the water and the cation of the IL.

In presence of an increased amount of water the hydrolysis issue comes up. For water miscible-ionic liquids a self-associate dimeric structure in an "anion-water-water-anion" chain was observed. For ionic liquid that not mix fully with water the dimeric structures forms chain of molecules and percolate through the ionic liquids' structures and cause them to break up into small ionic cluster (Figure 5).

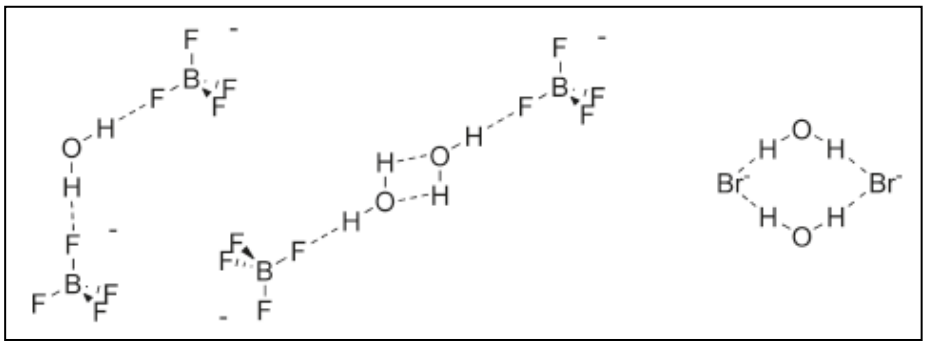


Figure 5*: some observed ionic liquid-water hydrogen-bonded structures:symmetric 2:1 anion-water, anion-water-water-anion chain, and anion-water-anion-water cyclic dimer.*

1.3.1. The hexafluorophosfate problem

Imidazolium-based ILs with hexafluorophosphate anion have been the subject of extensive debates about their eventual decomposition into the toxic hydrofluoridric acid. The hydrolysis of hexafluorophosphate was investigated under several experimental conditions by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The results obtained show that the $[PF_6]$ anion decomposes under acidic conditions or high temperature to give different aggregate ions for example $[F_4PO]^-$ and $[F_2PO_2]^-$. The imidazolium cation remains unchanged but the length of the alkyl chain may increases the possibility of hydrolysis because the anion is less protected and hence more easily hydrolyzable. These observations are very important for the application of ILs with hexafluorophosphate anion as reaction solvents under aqueous and acidic conditions.[6]

1.4. Ionic Liquid for catalytic epoxidation of olefins

Epoxides are important intermediates in many synthesis of fine chemicals, the direct epoxidation of olefins using molecular oxygen in a catalytic mechanism is possible, but it is performed in large scale only for ethylene.[7] Tipically the heavier epoxides are generated from olefins by reaction with a stoichiometric organic oxidant such as *m*-chloroperbenzoic acid (Figure 6).[8]

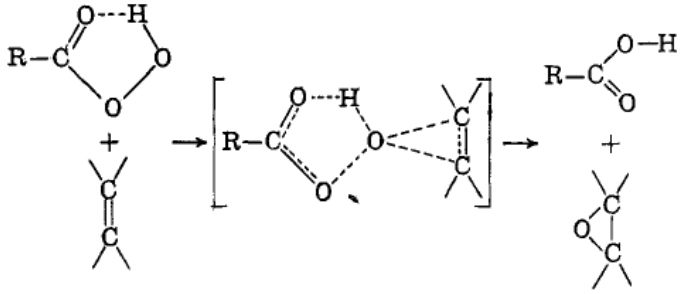


Figure 6: *nonionic mechanism for epoxidation with m-chloroperbenzoic acid, (R =C_6H_4Cl).*

By using metal compounds (e.g. Ti, V, W, Re and Mo) in their highest oxidation state catalytic epoxidation can be achieved with hydroperoxides as oxidants, resulting in more benign waste products and improving atom economy. Among these transition metals, molybdenum (VI) produced some of the more active catalysts studied in this field. In particular the family of the oxodiperoxomolybdenum complexes such as $[MoO(O_2)_2(L)_n]$ (L = two electron donor ligand) results an attractive option for their facile and cheap preparation, chemical simplicity and stability. In Figure 7 the proposed mechanism for oxodiperoxomolydbenum catalyzed olefin epoxidation is described.[9]

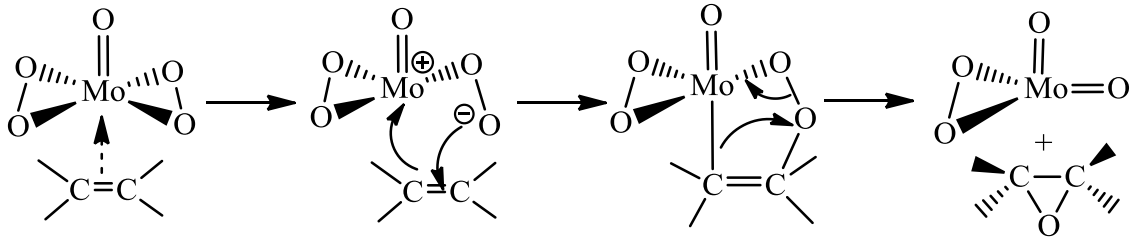
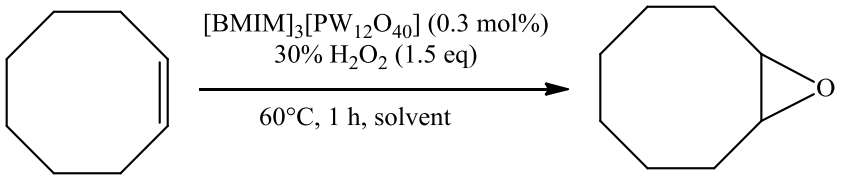


Figure 7: *first study of oxodiperoxomolybdenum complexes catalyst $[MoO(O_2)_2(HMPA)]$ (HMPA: hexamhetylphosphoramine) in olefins oxidation with H_2O_2 as oxidant by Mimoun et al. (1969).*

The epoxidation reaction investigated by Mimoun *et al.* (1969) with $[MoO(O_2)_2(HMPA)]$ (HMPA = hexamhetylphosphoramine) as catalyst and hydrogen peroxide as oxidant employs dichloroethane (DCE) as organic solvents.

In order to obtain "greener" processes, the use of ionic liquids as reaction media in epoxidation was investigated. Molybdenum catalyzed oxidations of organic compounds

in ILs solvents were reported in literature, including processes utilising hydrogen peroxide as the oxidant. In Figure 8 the results obtained in a recent study on the catalytic epoxidation performed by the polyoxometalate catalyst $[BMIM]_3[PW_{12}O_{40}]$ in the presence of H_2O_2 as oxidant and employing ILs compared to the conventional solvent are reported.[10]



Solvents	Yield (%)	Epoxide Selectivity (%)
$[BMIM][PF_6]$	87	99
$[BMIM][N(SO_2CF_3)]$	82	94
$[BMIM][BF_4]$	Trace	12
MeOH	Trace	40
CH_3CN	1	12
CH_2Cl_2	Trace	75

Figure 8: *epoxidation of cyclooctene catalyzed by $[BMIM]_3[PW_{12}O_{40}]$ (BMIM: 1-butyl-3-methyl-imidazolium) in different ILs and organic solvents.*

The use of ILs shown in the latter study sensitively improves both the yield and selectivity. The catalyst behaviour is also affected by the counterion of the imidazolium salt. The ionic liquids are powerful solvents in these reactions due to their ability to solubilize inorganic compounds, insoluble in common organic solvents, immobilizing the catalyst in the IL phase and allowing to recycle it several times as the IL-catalyst system.

Coming back to the molybdenum based catalysts the first oxodiperoxomolybdenum catalyzed [Mo] ([Mo] = acqueous $[Mo(O)(O_2)_2(H_2O)_n]$) epoxidation reaction in ionic liquid media (Figure 9) was recently investigated and published by the Galindo's research group of University of Seville.[11]

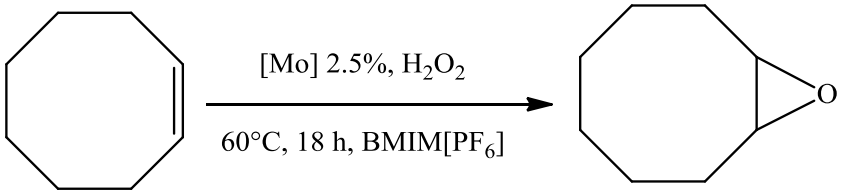


Figure 9: *catalytic epoxidation of cis-cyclooctene by an oxodiperoxomolydenum catalyst with H_2O_2 in 3-butyl-1-methlimidazolium hexafluorophosphate BMIM[PF_6].*

In this study, it was observed that the reaction with H_2O_2 as oxidant gave low selectivity due to complete hydrolysis of the epoxide resulting in a ring opening and a complete conversion to the cyclooctane-1,2-diol (Figure 10).

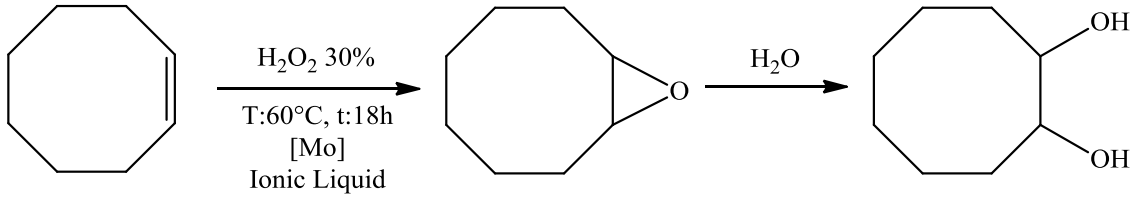


Figure 10: *catalytic oxidation of cis-cyclooctene to the corresponding epoxide followed by hydrolysis to cyclooctane-1,2-diol.*

A large improvement both in rate and selectivity has been registered adding an *N*-donor containing coordinating base species (e.g. pyridines, 2.2'-bipyridines, imidazoles and pyrazoles) that potentially induce both rate and selectivity enhancements in such an oxidation system (Table 1).[11]

Table 1: Comparison of the effect of pyridine additives in the molybdenum catalyzed epoxidation of *cis*-cyclooctene in ionic liquids media.

Base additive [PKa]	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
None	Cl_3CH	17	1	6
	C_4mim-PF_6	29	9	31
	C_8mim-PF_6	38	25	66
	C_{12}mim-PF_6	40	40	100
Pyridine [5.25]	C_8mim-PF_6	29	29	100
	C_{12}mim-PF_6	49	49	100
4-Picoline [5.98]	C_4mim-PF_6	31	18	58
	C_8mim-PF_6	54	54	100
	C_{12}mim-PF_6	46	46	100
4-Picoline-*N*-oxide [1.4]	C_4mim-PF_6	32	23	72
	C_8mim-PF_6	39	39	100
	C_{12}mim-PF_6	48	48	100

Reaction conditions: $[MoO(O_2)_2(H_2O)_n]$ 0.025mmol, base additives 0.10 mmol, H_2O_2aq 30% 3.0 mmol, cis-cyclooctene 1.0 mmol, solvent 2.0 mL, T = 60°C, t = 2h. Extraction with pentane (3x3 mL), yield and conversions calculated by GC.

Examples reported in Table 1 show that, while the activity is not sensitively affected by the presence of the *N*-donor species leading to conversions in the 30%-50% range, the selectivity were markedly improved up to 100%. The latter behavior has been attributed to the fact that the *N*-donor species bind strongly to vacant coordination sites on the metal and block the access of the epoxide to the acidic metal centre. It results in the inhibition of the hydrolysis mechanism and in an increase of selectivity. The *N*-donor bases form with the molydbenum a coordination complex with a poor solubility in common organic solvents, this is a further advantage in the use of ILs as reaction solvents.

1.5. *N*-functionalized Ionic Liquids

Imidazolium salts, previously described for their employment as ILs solvents for catalytic reactions, more generally represent a class of compounds with a great versatility due to their wide range of applications in material science or as *N*-heterocyclic carbene complexes precursors (NHCs).

In particular the attention of the research group of Bologna has been devoted to amino/amide functionalized imidazolium salts with the aim to design and develop transition metal *N*-heterocyclic carbene complexes of gold, silver and rhodium to be mainly employed in catalysis. The use of NHCs as ligands is a result of their capacity to be excellent σ-donors whose steric and electronic properties are easily modulated by varying the substituents on the imidazole ring.[12]

In order to value the influence of *N*-functionalization of NHC lateral chain the group prepared the new amino-Boc protected **1[I]** and amino **2[NO_3]** imidazolium salts (Figure 11) to be employed as ligand precursors.

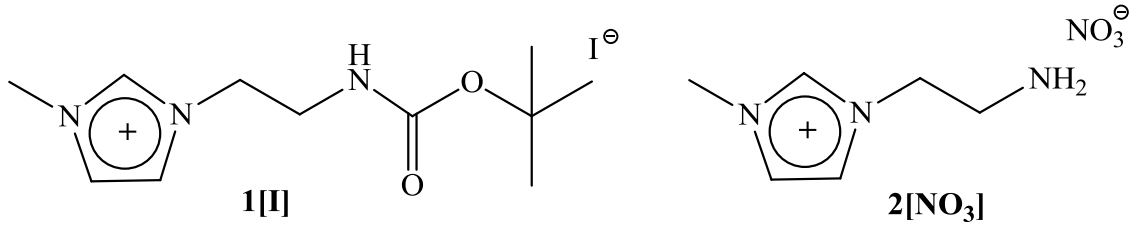


Figure 11: *molecular structures of 1-(2-t-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide (**1[I]**) and 3-(2-aminoethyl)-1-methylimidazolium nitrate (**2[NO_3]**).*

In particular **1[I]** has been then employed toward the synthesis of silver and rhodium complexes (Figure 12).[13,14]

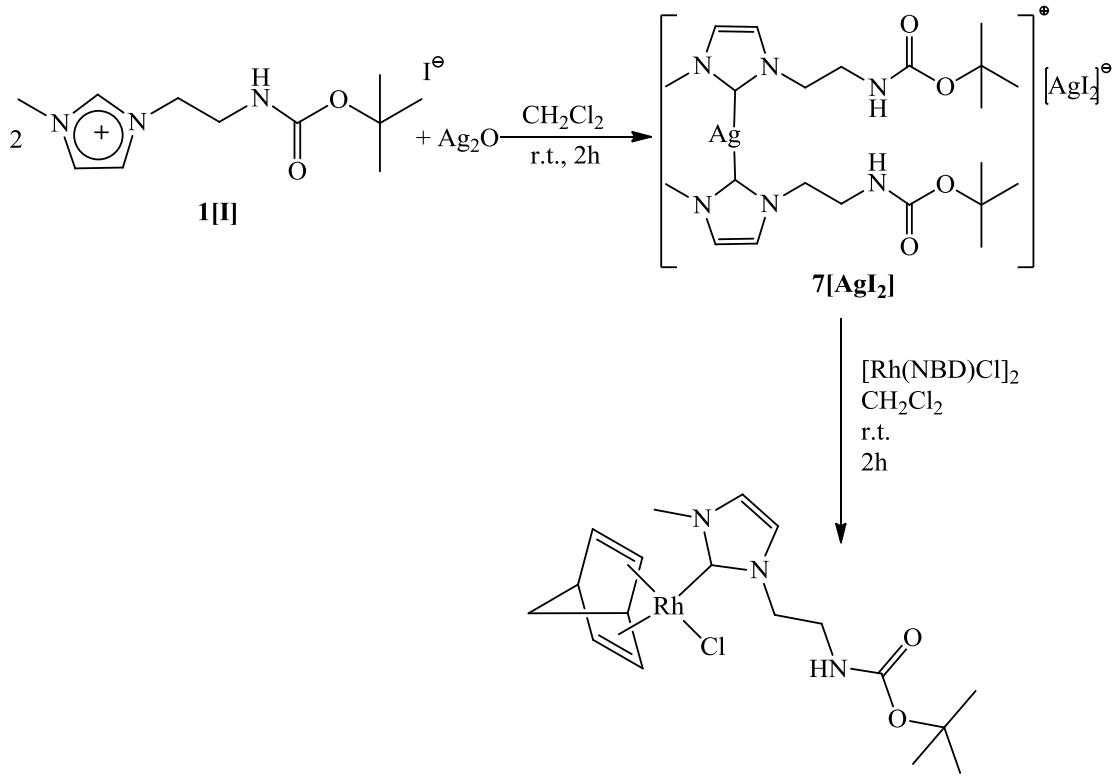


Figure 12: *synthesis of a Rhodium complex by transmetalation of an NHC-Ag complex (**7[AgI$_2$].**)*

While **2[NO$_3$]** showed to play an active role in stabilizing the gold nanoparticles with better electrocatalytic activity than similarly prepared gold nanoparticles stabilized by thiol-functionalized ILs.[15]

Both **1[I]** and **2[NO$_3$]** are ionic liquids at room temperature, hence they are good candidate to be employed as unconventional solvents in catalytic reactions. As previously described the Galindo's group recently demonstrated the active role of nitrogen based donor ligands on the improvement of the selectivity in the epoxidation of *cis*-cyclooctene. Starting from this point it has been supposed that, by employing *N*-functionalized ILs, the nitrogen donor group in the lateral chain of the IL itself could act as ligand, improving the selectivity of the reaction.

Furthermore, a collateral very interesting aspect has to be taken into consideration: few NHC complexes of Molybdenum have been synthesised up to date and the synthesis of new NHC oxodiperoxo complexes of Molybdenum would be of great interest in order to develop new epoxidation catalysts.

The project of the present thesis has been then designed as follow: in the first part of my internship, spent at the University of Bologna, *N*-functionalized imidazolium salts with

several different counterions were prepared and the synthesis of NHC silver complexes was practiced in order to employ them in the preparation of molybdenum complexes. In the second part, spent at the University of Sevilla, the synthesis of ILs (*N*-functionalized and unfuctionalized with different counterions) was continued, the synthesis of molybdenum complexes with different ligands was performed and the study of the catalytic activity of some of them in the prepared ILs was developed.

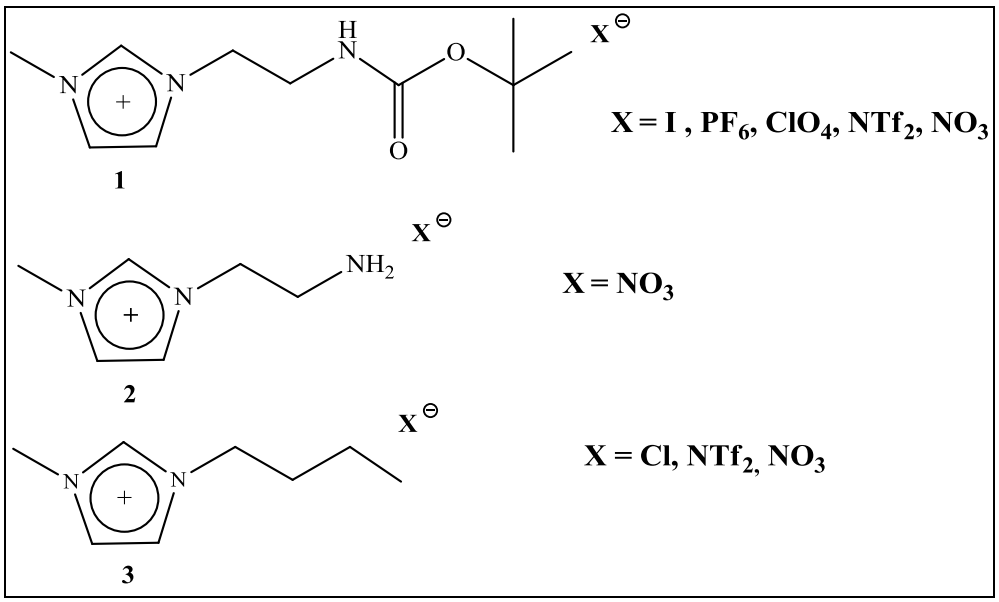
1.6. Goals of the thesis

As outlined in the introduction, the experience on *N*-functionalized imidazolium salts of the research group of Bologna has been exploited to try to improve the catalytic epoxidation of olefins in ionic liquids media investigated in the Seville University. It has been hypotesized that the presence of *N*-donor group in the alkyl chain of the imidazole ring could prevent the epoxide hydrolysis avoiding the ring opening. The expected results could be an increase in the selectivity.

In this regard, catalytic tests of olefins epoxidation with oxodiperoxomolydbenum catalyst and hydrogen peroxide as oxidant in ionic liquids imidazolium functionalizated are part of the present thesis.

The principal goals have concerned:

1. Synthesis and characterization of the Boc-protected 1-(2-aminoethyl)-3-methylimidazolium salts with different counterions (**1[I]**, **1[PF_6]**, **1[NO_3]**, **1[NTf_2]** and **1[ClO_4]**).
2. Synthesis and characterization of 3-(2-aminoethyl)-1-methylimidazolium (**2[NO_3]**), the deprotected form of NHBoc imidazolium salt (**1**).
3. Synthesis and characterization of the unfunctionalized salts, 3-butyl-1-methylimidazolium (**3**), with different counterions (**3[Cl]**, **3[NO_3]** and **3[NTf_2]**)



4. Synthesis of oxodiperoxo Molydenum and Tungsten complexes with *N*-donor bases as ligands the former subsequently used as catalysts in catalytic epoxidation of olefins.
5. Catalytic tests of epoxidation of *cis*-cyclooctene with H_2O_2 30% in IL media testing the efficiency of the functionalized and non-functionalized imidazolium salts as reaction solvents.
6. Preliminary study on the synthesis of novel NHC complexes with Mo(VI) as metal center.

2. RESULTS AND DISCUSSION

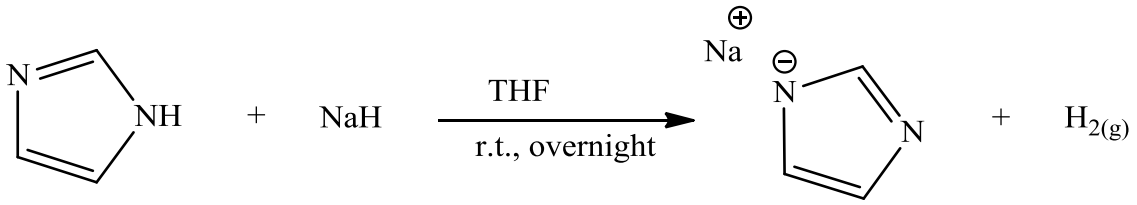
As already mentioned in the description of the goals of the present thesis several functionalized imidazolium salts, 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium (**1**), and non-functionalized, 3-butyl-1-methylimidazolium (**3**), with different counterions were synthesized with the aim to test them as unconventional reaction solvents, ionic liquids, in the catalytic epoxidation of olefins.

2.1. Synthesis of Ionic Liquids

In order to obtain 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide (**1[I]**) the precursor of all the functionalized ionic liquids herein presented, a four steps process is needed as described in the following. These reactions were performed in a large amount adjusting a synthetic procedure developed by the research group of Bologna. [13]

2.1.1. Synthesis of the sodium salt of imidazole

The reduction reaction of the imidazole by sodium hydride was performed under inert and dry atmosphere following a procedure available in literature.[16] The reaction takes place overnight at room temperature in dry THF to obtain the sodium salt of imidazole with a quantitative yield (Scheme 1).

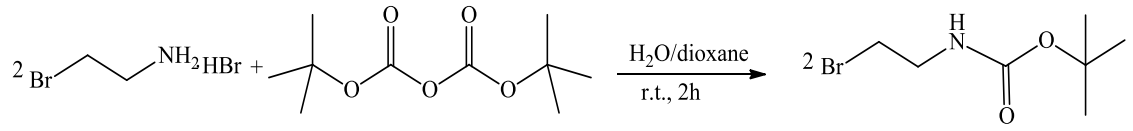


Scheme 1

Some variations on the literature procedure have been done in order to make easier and safer the preparation of large amount of the product. In particular the operations of filtration and separation were effected by cannula and the time of dripping of imidazole in NaH was increased. The white solid obtained was kept in the glove box.

2.1.2. Synthesis of 2-Bromoethylamine-t-butylcarbamate

The protection reaction was performed reacting the 2-bromoethylamine-hydrobromide with di-*tert*-butyldicarbonate (Scheme 2) for 2 hours at room temperature in a 1:1 mixture H_2O/dioxane by following a procedure reported in literature.[16]

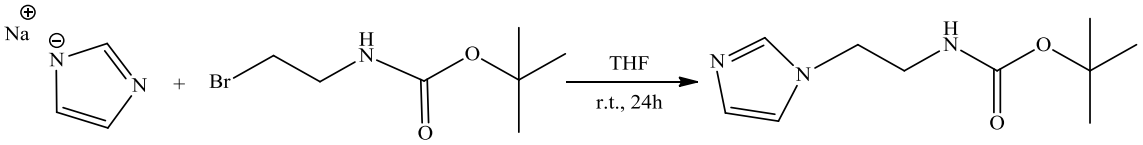


Scheme 2

The reaction gives as product a yellow oil in a yield of 47%.

2.1.3. Synthesis of (2-Imidazol-1-yl-ethyl) *t*-butylcarbamate

After the protection of the amine function, the 2-Bromoethylamine-*t*-butylcarbamate was reacted with the sodium salt of imidazole previously synthesized (Scheme 3).[17]

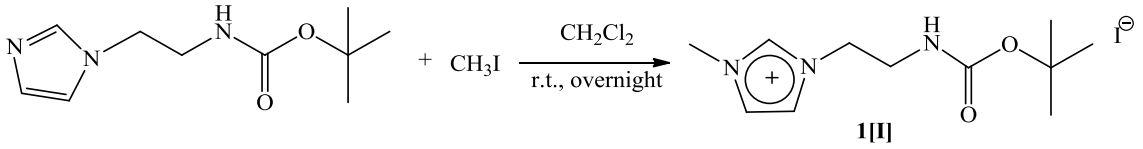


Scheme 3

The product was purified by chromatography on silica gel, eluting with $CH_2Cl_2/CH_3OH/NH_4OH$ (100:5:1), and it was obtained with 55% yield as a yellow oil.

2.1.4. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide (1[I])

The alkylation reaction of the second nitrogen was performed by an excess of methyl iodide stirring overnight in CH_2Cl_2 solution (Scheme 4) following a synthetic method reported in literature.[13]



Scheme 4

The result is a quantitative yield in the corresponding alkylated imidazolium salt with iodide as counterion. The product 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide (**1[I]**) was isolated as a dark yellow viscous liquid, air-stable and soluble in all common organic solvents but completely insoluble in diethyl ether and water. It was fully characterized by NMR and IR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Herein we describe the product characterization which will be useful for the identification of the new imidazolium salts that will be reported in the following. As regards the ^{1}H-NMR spectrum (Figure 13), the acidic proton NCHN was found at 9.92 ppm and the resonance of the imidazole backbone

protons were observed in the aromatic region of the spectra as two singlets, 7.19 and 7.08 ppm (2H). At δ 5.75 ppm was found the broad peak of NH. The signals of CH_2 in the side chain resonate at 4.28 and 3.59 ppm, between them, at chemical shift 3.39 ppm was observed the signal of the methyl bound to the nitrogen of the imidazole ring. Finally at high fields resonates the singlet attributable to the nine protons of the *tert*-butyl group (δ = 1.28 ppm).

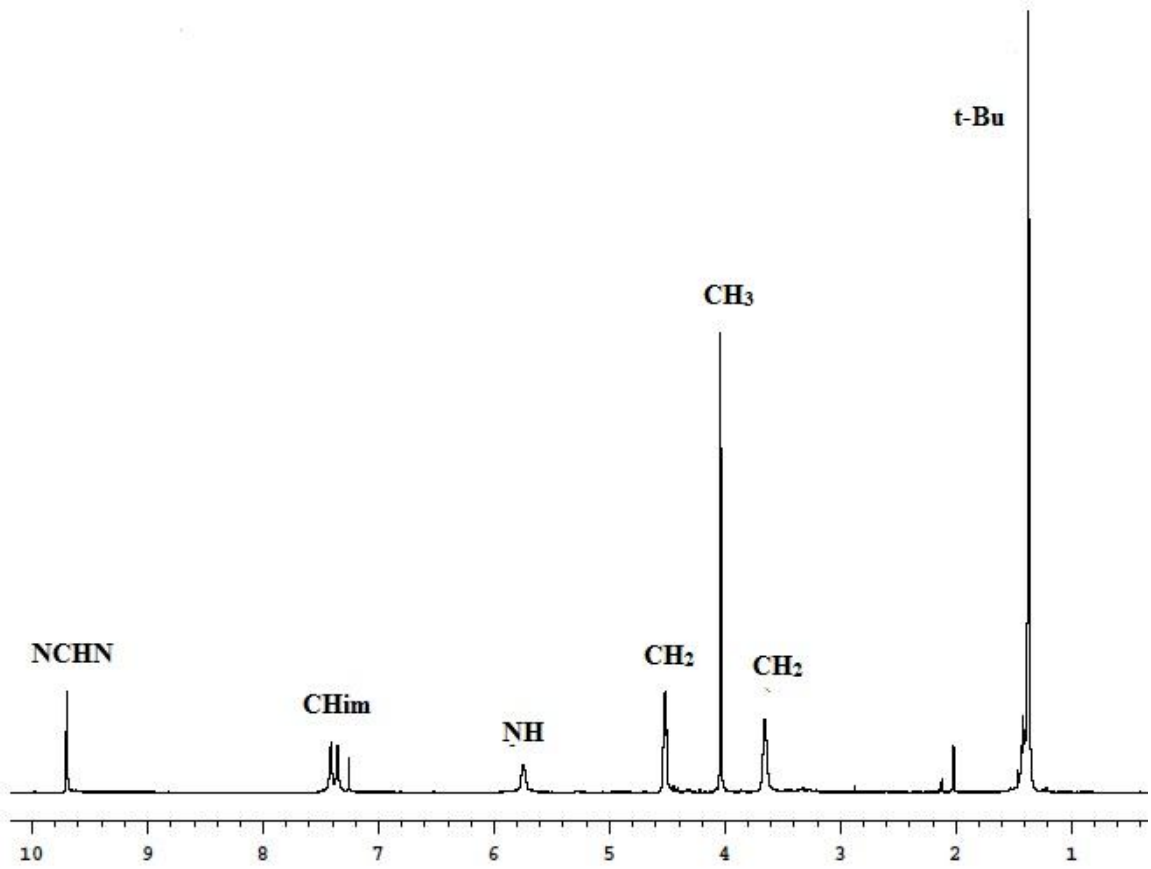


Figure 13: *^{1}H-NMR spectrum of* ***1[I]*** *in $CDCl_3$.*

The presence of the carbonyl of the protective group BOC was determined by ^{13}C-NMR spectrum, where at 156.2 ppm was observed the signal of C=O, and by IR spectrum in CH_2Cl_2, where at 1708 cm^{-1} was noted a band relative to the stretching of the carbonyl. The ESI-MS analysis confirms the nature of the compound with a peak at 226 *m/z* for the positive ion, the molecular ion, and one at 127 *m/z* for the negative ion corresponding to the iodide.

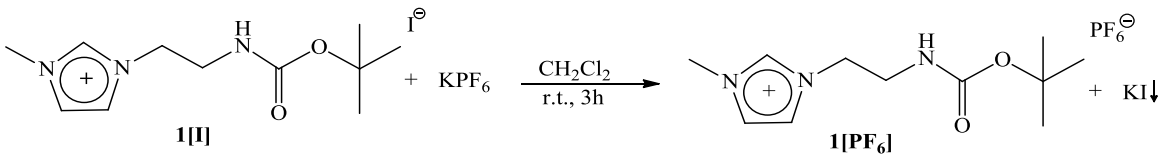
The iodide ion could undergo to oxidation in the presence of oxidating agent such as H_2O_2. Therefore the **1[I]** ionic liquid may not be a good solvent for the catalytic epoxidation of olefins, thus a counterion exchange is necessary.

2.2. Change of the counterion

As explained in the Introduction the counterion plays an important role in the ionic liquids properties particulary in the solubility. Having regard that the iodide may not be used as counterion in epoxidation reactions in ILs due to the oxidant conditions it was decided to perform on **1[I]** a counterion exchange. The anions [PF_6^-], [NO_3^-], [ClO_4^-], [NTf_2^-] were chosen for their unmiscibility with water that helps to avoid the hydrolysis problem.

2.2.1. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium hexafluorophosphate (1[PF_6])

The precursor **1[I]** was reacted with the salt KPF_6 to obtain the exchange of the counterion with a quantitative yield (Scheme 5).



Scheme 5

The product 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium hexafluorophosphate (**1[PF_6]**) was characterized by NMR spectroscopy and ESI-MS analysis. The ^{1}H-NMR spectrum in $CDCl_3$ of **1[PF_6]** shows a shift if compared to the precursor regards the imidazole ring protons (δ 9.92 (NCHN), 7.19 (CH) and 7.08 (CH) for **1[I]**) that shift to 9.54, 7.25 and 7.17 ppm respectively for **1[PF_6]**. The chemical shift relative to methylene groups and CH_3 are comparable with those of the precursor **1[I]**. However the pattern of the ^{1}H-NMR spectrum confirms that the imidazolium cation remain unaltered. The ^{19}F-NMR spectrum (Figure 14) shows the presence of 6 F as a doublet at δ = -72.75 (J_{P-F} = 710Hz) typical of a PF_6 anion.[18] The ESI-MS analysis confirms the product formation, the spectrum shows the molecular ion at 226 *m/z* [$C_{11}H_{20}N_3O_2^+$] for the positive ions and only one peak at 145 *m/z* for the negative ions corresponding to the ion hexafluorophosphate [PF_6^-]. The product appears as a yellow oil with a density of 1.06 g/mL at 25°C, stable in air and with the same solubility behaviour of the precursor **1[I]**.

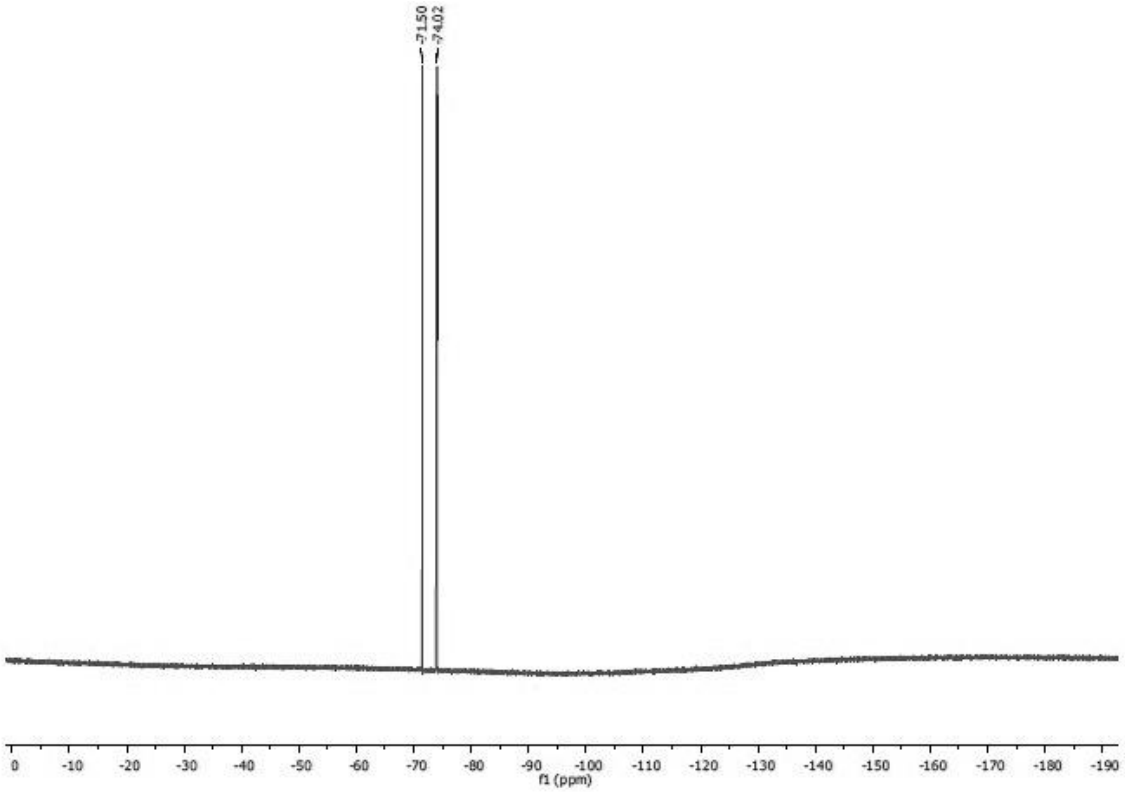


Figure 14: *^{19}F-NMR spectrum of* ***1[PF$_6$]*** *in $CDCl_3$.*

Crystals of **1[PF$_6$]** suitable for single crystal X-ray diffraction were grown by cooling down the reaction product at -20°C. The molecular structure is presented in Figure 15 with crystal data (Table 2), whereas bond distances and angles are reported in the Experimental section. **1[PF$_6$]** crystallizes in the centro symmetric $P2_1$ space group (Z = 8), the bond distances and angles are in line with the values of other known imidazolium salts.[19] The crystal structure was determined in collaboration with Dr. Cristina Femoni of the Department of Physical Chemistry and Inorganic.

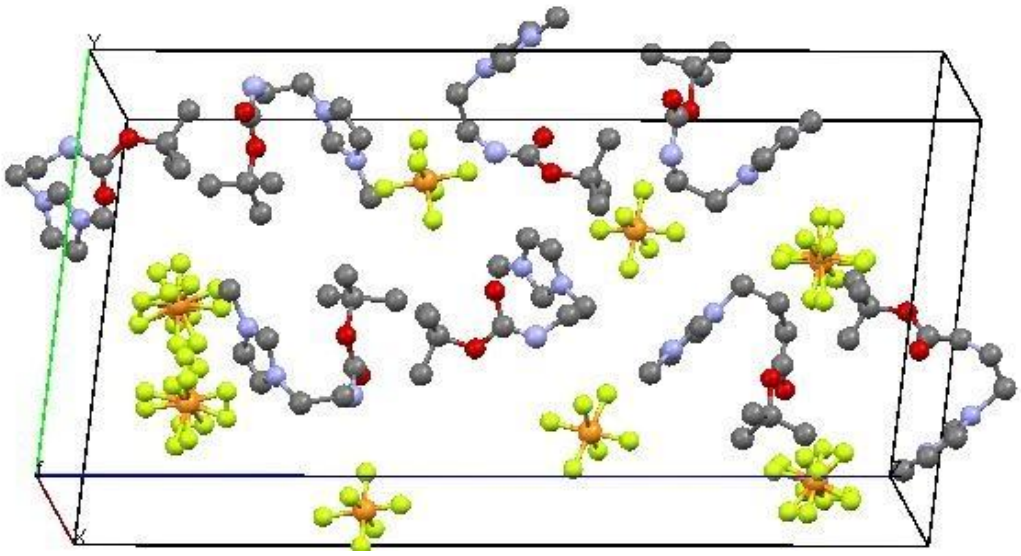


Figure 15: *unit cell of* ***1[PF$_6$]***.

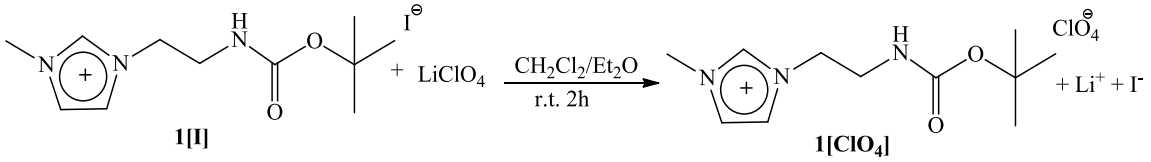
Table 2: crystal data of **1[PF$_6$]**.

Formula	$C_{18}H_{20}F_6N_2O_3P$
FW	371.26
T, K	298
cryst syst	monoclin
space group	$P2_1$
a, Å	6.261(3)
b, Å	16.889(7)
c, Å	32.354(13)
α, deg	90.00
β, deg	92.033
γ, deg	90.00
cell volume, Å^3	3419.02
Z	8

The ionic liquid **1[PF$_6$]** in acqueous solution gives hydrolysis problems. In the Introduction (Paragraph 1.3.1) the mechanism of the hydrolysis in ILs was explained: the water forms a dimeric structure with the anion and in presence of a great amount of H_2O chains of molecules which seep in the ILs structure and break them into small ionic cluster influence also the cation behaviour. In our particular case we could observe from the ^{1}H-NMR performed after the addition of water at **1[PF$_6$]** the desappearance of the signal relative to the Boc group which probably corresponds to the deprotection of NH_2 group together with decomposition products.[5]

2.2.2. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium perchlorate (1[ClO_4])

From the reaction between the precursor **1[I]** in CH_2Cl_2 and a solution of salt $LiClO_4$ in Et_2O was performed the anion exchange from iodide to perchlorate (Scheme 6). The reaction mixture was dried, dissolved in distilled water and finally purified from the inorganic salt by an extraction in CH_2Cl_2. It was obtained a yellow oil, with a yield of 76%, identified as 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium perchlorate (**1[ClO_4]**) from IR, NMR and ESI-MS characterizations.



Scheme 6

The ^{1}H-NMR spectrum shows the signals shift of the imidazole ring protons, the acid proton (NCHN) was found at δ 8.83 ppm and the backbone protons of the imidazole ring respectively at 7.31 ppm and 7.26 ppm. The chemical shift relative to methylene groups, CH_3 and t-Bu resonate to 4.36, 3.58 3.96 and 1.39 ppm for **1[ClO_4]**. The counterion exchange was confirmed by ESI-MS analysis that shows, from negative ions, only one peak at 99 *m/z* corresponding to the perchlorate anion. The presence of $[ClO_4]^-$ ion was also identified by IR spectrum (Figure 16), that displays broad peaks at 1097 cm^{-1} and at 1167 cm^{-1}, by comparison with typical IR strecthing of $[ClO_4]$ reported in literature (1090, 1100 cm^{-1}).[20] The stretching of the C=O group of the imidazolium cation was also identified at ν (CO) = 1710 cm^{-1}.

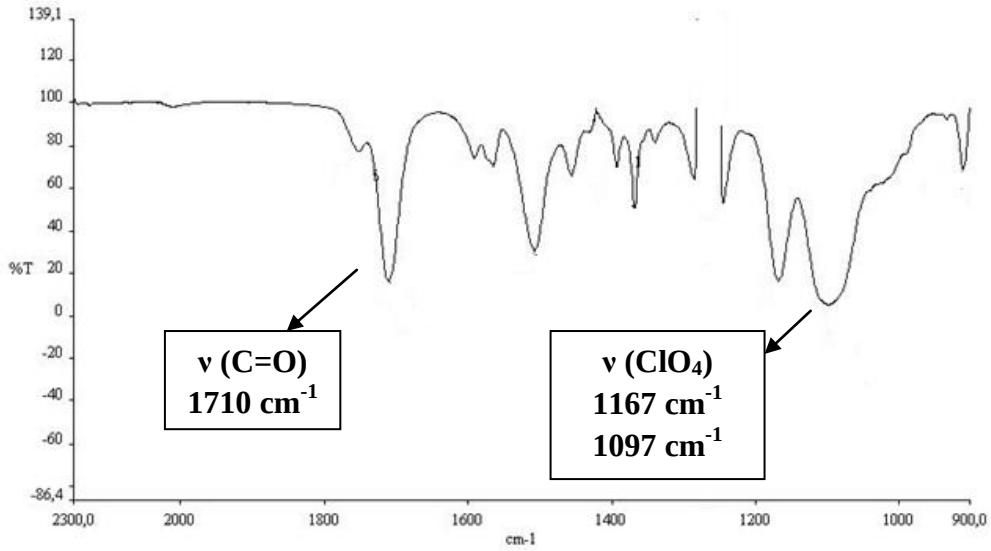
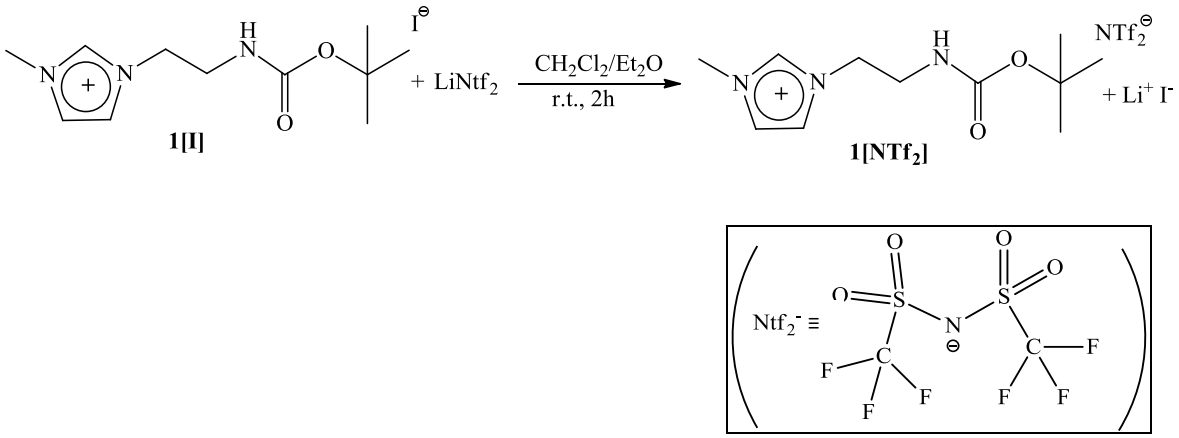


Figure 16: *IR Spectrum of* ***1[ClO_4]*** *in CH_2Cl_2.*

2.2.3. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (1[NTf_2])

The counterion $[NTf_2]^-$ has been choosen assuming that the corresponding ionic liquid would had to be insoluble in water, an important characteristic to avoid hydrolysis problems. In spite of what it was just affirmed, during the internship the partial solubility of **1[NTf_2]** was observed.

A solution of the precursor **1[I]** in CH_2Cl_2 was reacted with the salt $LiNTf_2$ dissolved in Et_2O (Scheme 7) to obtain 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, **1[NTf_2]**, as a thick, yellow oil with a density of 2.30g/mL at 25°C with a yield of 82%. The product was treated and characterized in the same way described for **1[ClO_4]**.



Scheme 7

The ^{1}H-NMR spectrum indicates the shift of the aromatic protons NCHN and the two CH_{im} respectively to δ 8.74, 7.31 and 7.22 ppm. The chemical shift relative to methylene groups, CH_3 and *t*-Bu resonate to 4.31, 3.55 3.93 and 1.38 ppm for **1[NTf_2]**. The ^{19}F-NMR (Figure 17) shows the presence of the counterion as a singlet at -79.1 ppm.

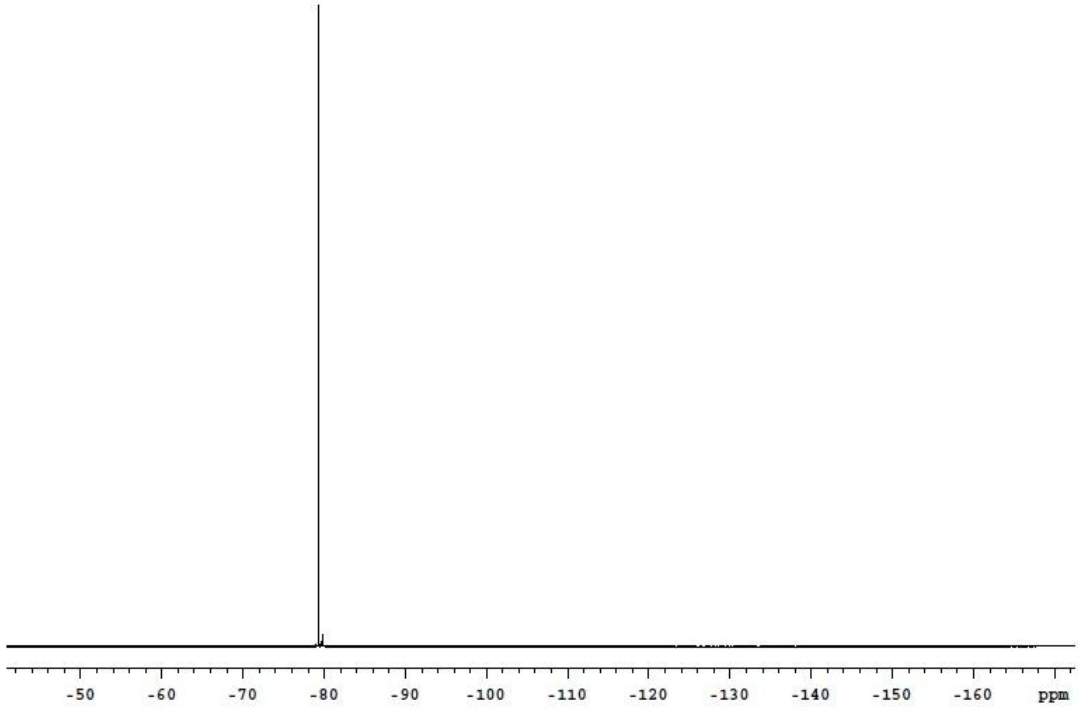


Figure 17: *^{19}F-NMR spectrum of* ***1 [NTf$_2$]****.*

The ESI-MS analysis (Figure 18) confirms the counterion exchange in fact in the spectrum was noted only one peak at 280 *m/z* for the negative ions corresponding to $[C_2F_6NO_4S_2]^-$ and the molecular ion at 226 *m/z* $[C_{11}H_{20}N_3O_2^+]$. In the IR spectrum were observed the peaks of the major functional group of the counterion, R-SO_2-N, SO_2 and CF_3, respectively at 1351, 1191 and 790 cm^{-1},[21] the stretching of the C=O group of the imidazolium cation was also identified at ν (CO) = 1711 cm^{-1}.

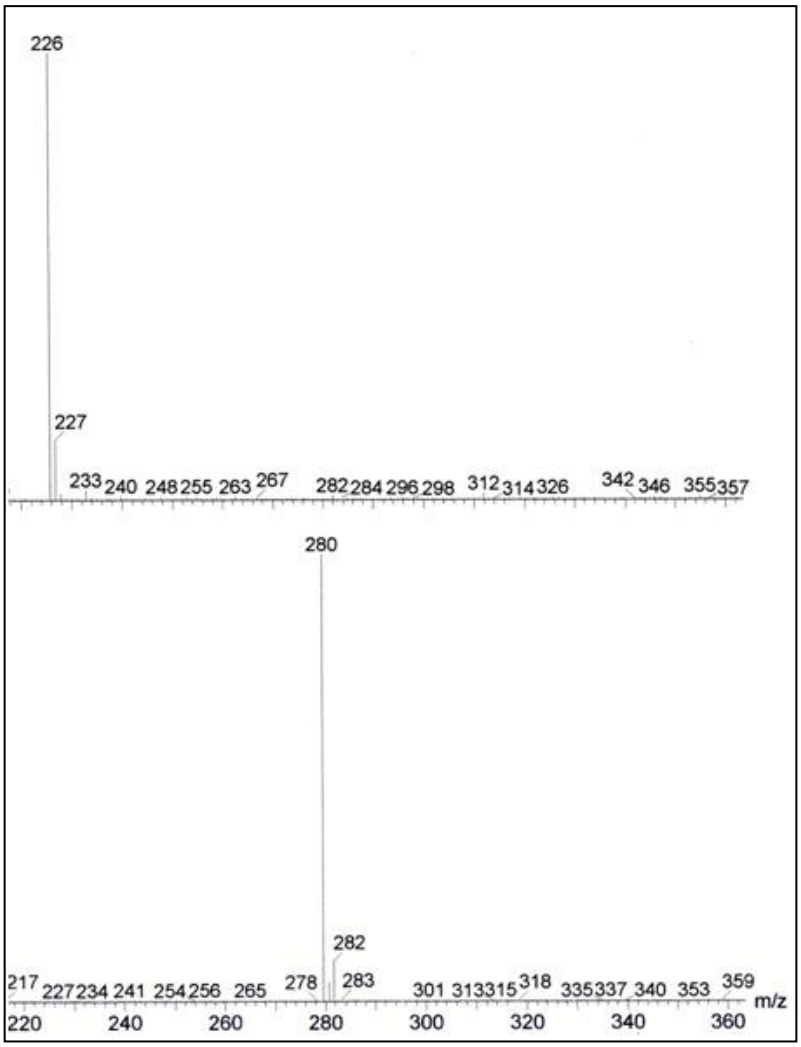
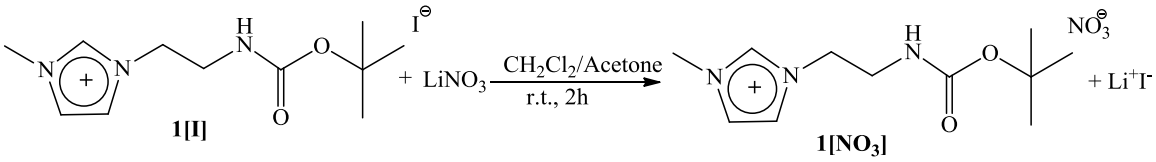


Figure 18: *ESI-MS spectrum of* ***1[NTf$_2$]****, above is shown the peak of the molecular ion and below the negative ion.*

2.2.4. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium nitrate (1[NO_3])

A solution of **1[I]** in CH_2Cl_2 was reacted with a solution of $LiNO_3$ in acetone (Scheme 8) to perform the counterion exchange and obtain the ionic liquid 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium nitrate, **1[NO_3]**, as a thick yellow oil in a quantitative yield. It was used the acetone as a reaction solvent because the salt results not completely soluble neither in dichlorometane nor in diethyl ether. Unfortunately the product was soluble in water, for this reason it was impossible to purify **1[NO_3]** from the inorganic salts by the extraction with CH_2Cl_2/H_2O. The product appears as a yellow oil with a density of 1.14 g/mL at 25°C.



Scheme 8

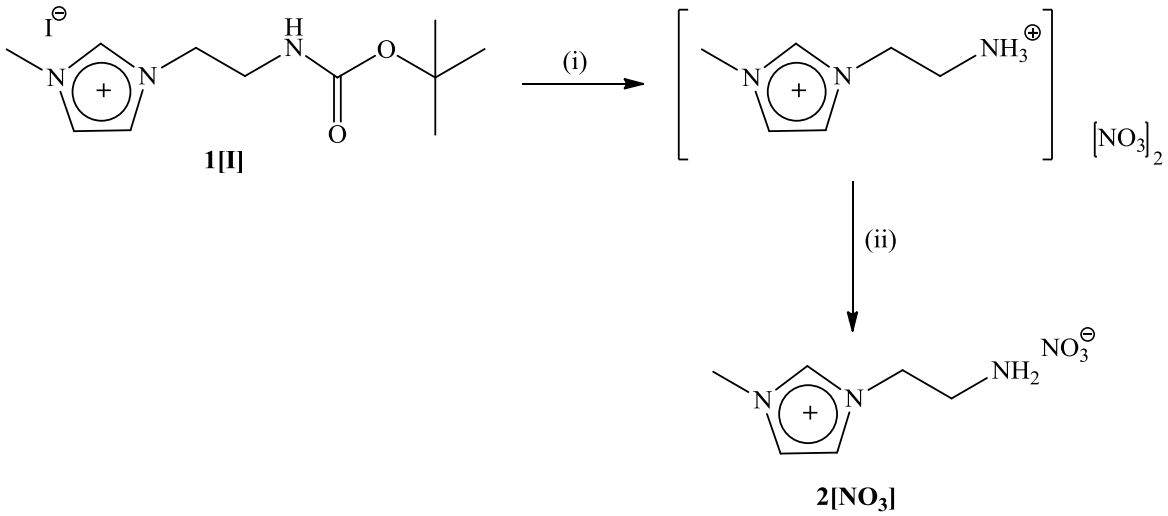
1[NO_3] was characterized by NMR and IR spectroscopy. The NMR analysis was performed in deuterated water for its solubility characteristics. The ^{1}H-NMR spectrum shows a shift of the acid proton (NCHN) to δ 8.61 and the imidazole backbone protons to 7.35 and 7.30 ppm. The peak of NH is not detectable. By IR spectroscopy the presence of the nitrate was observed as a peak at 1368 cm^{-1},[22] the protective group Boc shows a broad peak at 3416 cm^{-1} corresponding to NH and a peak at 1694 cm^{-1} for the carbonyl. The ESI-MS analysis of this product was not developed due to the impossibility to remove the I^- from the reaction mixture, purification of **1[NO_3]** will be matter of further studies.

2.2.5. Synthesis of 3-(2-aminoethyl)-1-methylimidazolium nitrate (2[NO_3])

Once obtained a series of NHBoc functionalized imidazolium salts we also prepared a deprotected form, following a procedure reported in the literature, in order to test the influence of the NH_2 group on catalytic performances.[15]

The precursor, **1[I]**, was deprotected by acid treatment of the amine group (Scheme 9). In the first step a dichloromethane solution of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide was treated with HNO_3 65% at room temperature leading to the insoluble dicationic salt, $[NH_3(CH_2)_2ImMe][NO_3]_2$. On addition of nitric acid the pale yellow solution immediately turns to dark violet due to the concomitant oxidation of the iodide to iodine. After removal of the solvent and iodine under vacuum and washing with acetonitrile, $[NH_3(CH_2)_2ImMe][NO_3]_2$ was obtained as an air-stable white solid. This salt is soluble in DMSO, water and partially soluble in methanol and ethanol. The dicationic species was characterized by NMR and IR spectroscopy. In the ^{1}H-NMR spectrum in DMSO solvent the NCHN resonance was found at δ 9.10 (137.25 in ^{13}C-NMR spectrum), the imidazole backbone protons (CH_{im}) appear as a singlet at 7.73 ppm, whereas the resonance of the ammonium group was found as a broad singlet at δ 8.06 (this resonance was not observed when the spectra was carried out in D_2O). The methylene protons of the side chain give rise to a triplet at 4.40 ppm and a multiplet at

3.35 ppm (corresponding at δ 46.31 for NCH_2 and δ 38.41 for $CH_2NH_3^+$ in the ^{13}C-NMR spectrum).



1[I] **2[NO_3]**

Scheme 9

Subsequent treatment of $[NH_3(CH_2)_2ImMe][NO_3]_2$ in methanol with NaOH led to the formation of 3-(2-aminoethyl)-1-methylimidazolium nitrate, **2[NO_3]**, with a yield of 33%. After evaporation of the solvent, the product can be separated from the saline byproduct by extraction with acetonitrile to afford a pale yellow oil. In the ^{1}H-NMR in DMSO, the NH_2 resonance was not observed whereas the signals corresponding to the ethylamino side chain protons are upfield shifted with respect to $[NH_3(CH_2)_2ImMe][NO_3]_2$, in particular the directly bound amino-methylene protons (CH_2NH_2) are shifted and appear as a triplet at δ 2.89. The ESI-MS analysis indicates the presence of the cation $[NH_2(CH_2)_2ImMe]^+$ with a single peak at *m/z* = 126 and the nitrate anion at 62 *m/z*.

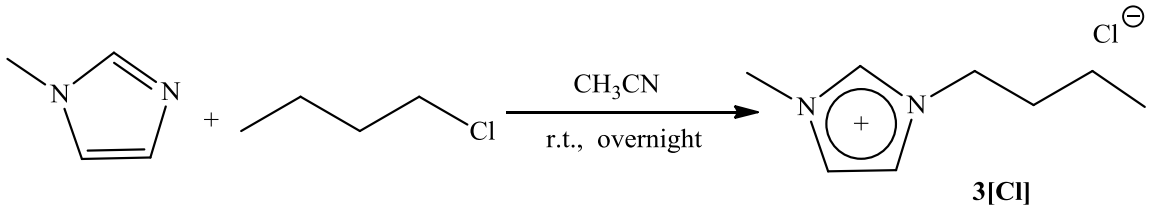
Table 3: Most significant chemical shifts in ^{1}H-NMR spectra of the functionalized imidazolium salts 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium (**1**).

Compounds	NC*H*N δ(ppm)	C*H*im δ(ppm)	NCH_2 δ(ppm)	NCH_3 δ(ppm)
1[I] ($CDCl_3$)	9.92	7.19 7.08	4.28	3.93
1[PF_6] ($CDCl_3$)	9.54	7.25 7.15	4.39	3.92
1[ClO_4] ($CDCl_3$)	8.83	7.31 7.26	4.36	3.96
1[NTf_2] ($CDCl_3$)	8.74	7.31 7.22	4.31	3.93
1[NO_3] (D_2O)	8.61	7.35 7.30	4.12	3.74
2[NO_3] (D_2O)	9.08	7.73 7.71	4.09	3.86

2.3. Non functionalized Ionic Liquids

2.3.1. Synthesis of 3-butyl-1-methylimidazolium chloride (3[Cl])

In a second part of this work a common ionic liquid such as 3-butyl-1-methylimidazolium chloride, **3[Cl]**, has been employed to test the effect of the different counterions. The precursor **3[Cl]** was obtained by reacting 1-methylimidazole with 4-chlorobutane in acetonitrile at room temperature overnight (Scheme 10). After washing with diethyl ether and petroleum ether a white solid with 75% of yield was obtained.

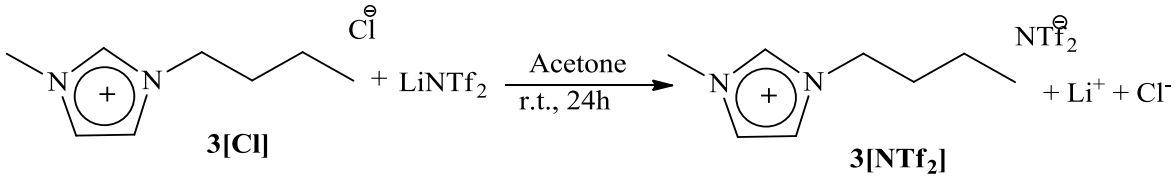


Scheme 10

The ^{1}H-NMR spectrum shows the typical chemical shift of the imidazolium salt. The acidic proton of the imidazole ring was found at δ 8.70 and the resonances of the imidazole backbone were observed as two singlet at 7.46 and 7.42 ppm. The methylene bound to the nitrogen was located at δ 4.18 while the methylenes of the side chain were found at δ 1.79 and 1.32 as multiplets. At 3.88 ppm was found the signal of the three protons of CH_3 and at δ 0.90 resonates the terminal methyl as a triplet.

2.3.2. Synthesis of 3-butyl-1-methylimidazolium bis(trifluoromethylsulfonyl)imide (3[NTf_2])

The counterion exchange from chloride to Bis-(trisfluoromethane)-sulfonimide, $[NTf_2]^-$, was performed by reaction between the precursor **3[Cl]** in acetone and the lithium salt of the corresponding anion at room temperature for 24h (Scheme 11). The product is soluble in CH_2Cl_2 and also partially soluble in water, so the extraction CH_2Cl_2/H_2O to remove the inorganic salts is very difficult. The aqueous phase have to be washed several times to recover all the ionic liquid. Finally a low viscosity, yellow liquid with 87% of yield was obtained.



Scheme 11

The product **3[NTf_2]** was characterized by NMR and IR spectroscopy. The ^{1}H-NMR spectrum shows at chemichal shift 8.65 the signal of NCHN and at δ 7.23 and 7.19 the singlets of the two CH imidazole protons. The signal of methylene were found at 4.09 ppm (NCH_2) as a triplet and the CH_2 of the side chain at respectively 1.73 and 1.31 ppm. The methyl NCH_3 resonates at δ 3.86 while the terminal CH_3 at 0.88 ppm. As regards the ion $[NTf_2]^-$, the ^{19}F-NMR spectrum (Figure 19) shows the presence of the counterion as a singlet at -79.01 ppm. Its presence was also confirmed by the IR spectrum that shows

the peaks of the functional groups R-SO_2-N (1351 cm^{-1}), SO_2 (1191 cm^{-1}) and CF_3 (790 cm^{-1}).[21]

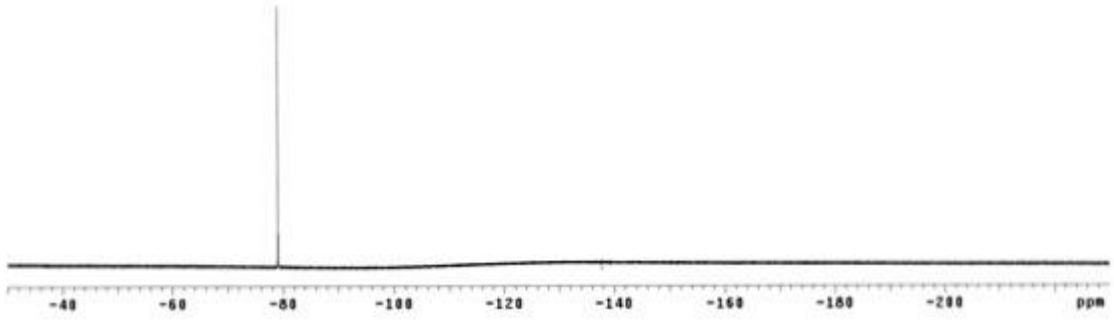
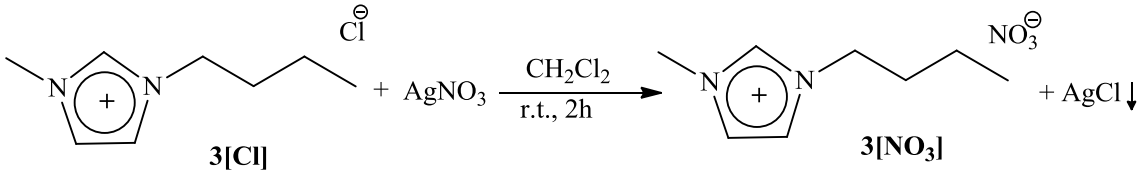


Figure 19: *^{19}F-NMR spectrum of* ***3[NTf$_2$]****.*

2.3.3. Synthesis of 3-butyl-1-methylimidazolium nitrate (3[NO_3])

To the solution of the precursor **3[Cl]** in CH_2Cl_2 a concentrated solution of $AgNO_3$ was added (Scheme 12). The chloride precipitates as AgCl salt and was completely removed by filtration. After purification by actived charcoal, a pale yellow oil was obtained with yield of 85%.



3[Cl] **3[NO_3]**

Scheme 12

The ^{1}H-NMR analysis was performed in deuterated water because the ionic liquid synthesized results more soluble in water than in organic solvents. The chemical shift of the molecular ion are very similar to the precursor **3[Cl]**, the protons in the ring imidazole were found respectively at δ 8.67 7.43, 7.39 ppm. The presence of the nitrate as counterion was confirmed by IR spectroscopy, from the spectrum (Figure 20) a broad peak at 1349 cm^{-1} corresponding to [NO_3^-] was observed.[22]

It is hypotesized that the nitrate ion makes the imidazole salt more soluble in aqueous solvent.

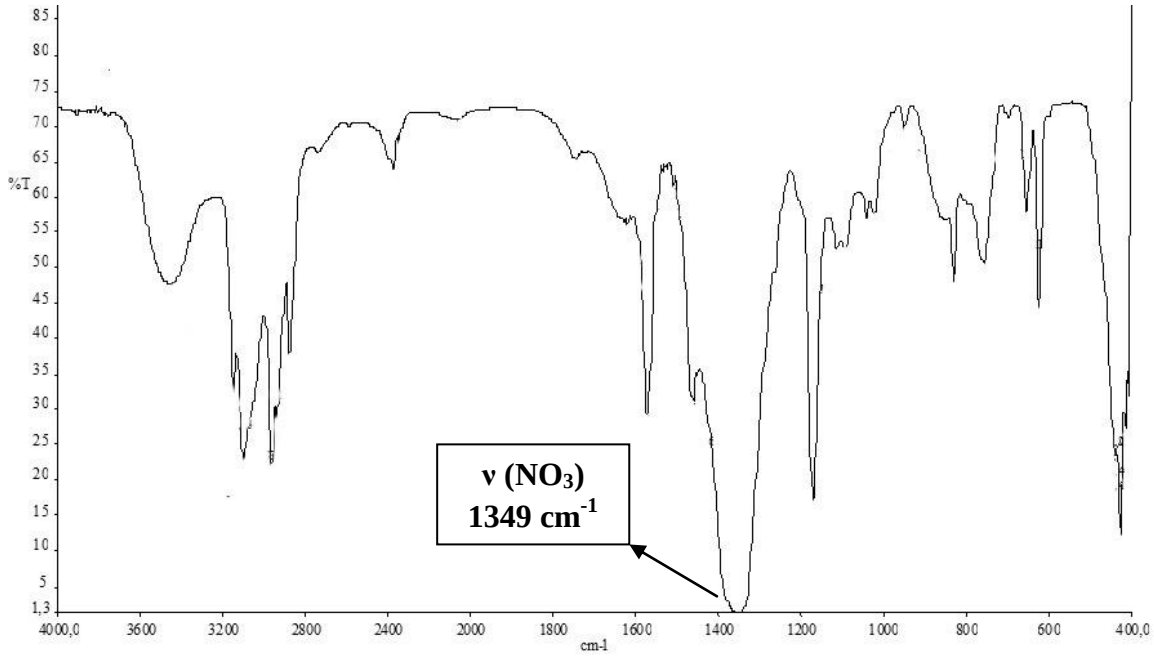


Figure 20: *IR Spectrum of* ***3[NO3]*** *in NaCl.*

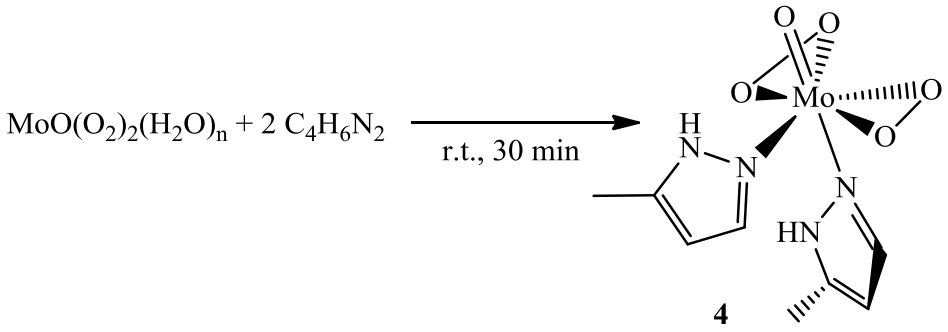
2.4. Oxodiperoxomolybdenum Complexes

Hereafter the two oxodiperoxo Molybdenum complexes, and the precursors, that were tested as catalyst in the catalytic epoxidation of olefins are listed. The synthesis procedure of these complexes has been developed by the Seville group. The synthesis of an oxodiperoxo Tungsten complex was also investigated with the aim to test it as a catalyst for the same reaction.

2.4.1. Synthesis of $[Mo(O)(O_2)_2(H_2O)_n]$ solution in acqueous hydrogen peroxide

The solution of $[Mo(O)(O_2)_2(H_2O)_n]$ was obtained by mixing MoO_3 with 30% acqueous hydrogen peroxide and stirring for 48h at 55°C. The solution was moved to a volumetric flask and diluted with distilled water to give a known concentration of the $[Mo(O)(O_2)_2(H_2O)_n]$ solution that is the precursor of the molybdenum catalysts used in catalytic epoxidation.[7]

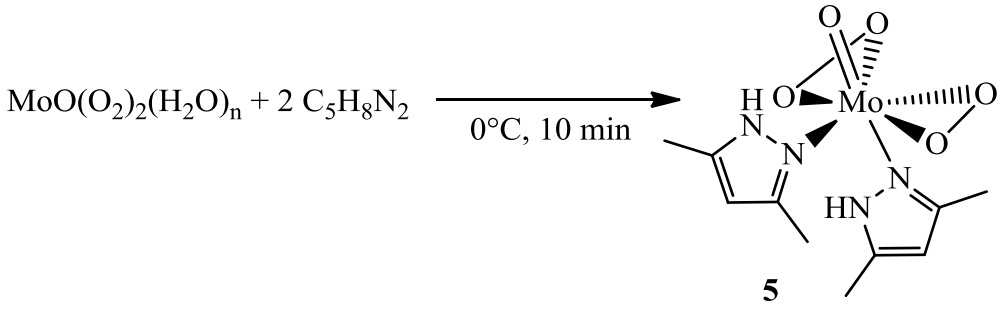
2.4.2. Synthesis of [Mo(O)(O$_2$)$_2$(C$_4$H$_6$N$_2$)$_2$] complex (4)



Scheme 13

The product complex **4** was obtained, following a procedure reported in literature,[7] by mixing a [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] solution with 4 equivalent of 3-methylpyrazole (Scheme 13). After 30min under stirring, the product **4** was observed as a yellow precipitate. After the filtration the solution remained was placed in a crystallizer and for slow evaporation of the solvent yellow crystals were isolated (yield: 70%) and analyzed by elemental analysis which confirmed the formation of the pure product **4**. The IR data agree with the presence of two pyrazole ligands, one oxo and two peroxo groups in the metal coordination sphere (Mo=O and O-O at 3146, 951 and 873 cm^{-1} respectively) showing also the peaks relative to the stretching of aromatic CH. The ^{1}H-NMR spectrum shows the chemical shift of the two CH pyrazole as singlets at δ 7.58 and 6.28, and the methyl signal at 2.35 ppm.

2.4.3. Synthesis of [Mo(O)(O$_2$)$_2$(C$_5$H$_8$N$_2$)$_2$] complex (5)

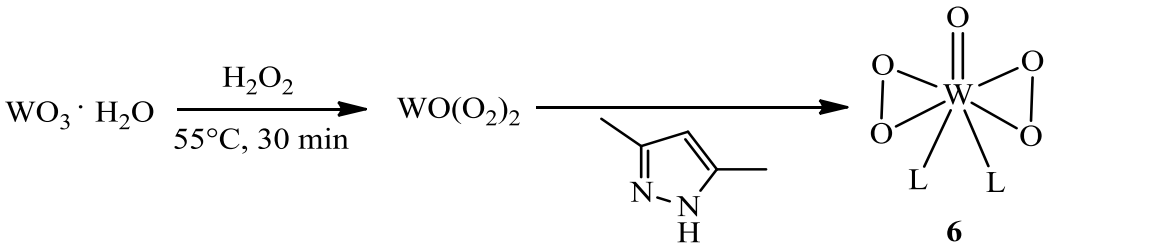


Scheme 14

To the [Mo(O)(O$_2$)$_2$(H$_2$O)$_n$] solution 2 equivalent of 3,5-di methylpyrazole were added at low temperature (Scheme 14) to give immediatly a powdery yellow solid, **5**, characterized by IR and NMR spectroscopy. The ^{1}H-NMR spectrum shows the characteristic peak of the CH pyrazole at δ 5.81 and the singlet of the two methyls at 2.22

ppm, while the IR spectrum confirms the presence of the oxodiperoxomolybdenum moiety by the band at 956 cm^{-1} of Mo=O and the frequency of peroxo groups at 860 cm^{-1}.

2.4.4. Synthesis of $[W(O)(O_2)_2(C_5H_8N_2)_2]$ complex (6)



(L: 3-5,dimethylpirazole)

Scheme 15

In the last time of the internship we attempted to synthesized an oxodiperoxo tungsten complex with two dimethylpyrazole as ligands with the intent to obtain a complex with the same structure of **5** to test as catalyst in the catalytic epoxidation of olefin. A commercial tungstic acid powder was mixed with an aqueous solution of H_2O_2 (30%) for 30min at 55°C, to the yellow solution was added 3,5-dimethylpyrazole as solid to give a colourless solution (Scheme 15). After the solvent removal under vacuum a white solid, **6**, was obtained and characterized by NMR and IR spectroscopy. In the IR spectrum, according to the literature, the intense bands at 980 and 886 cm^{-1} can be assigned respectively to ν(W=O) and ν(O-O).[23] The ^{1}H-NMR spectrum (Figure 21) confirms the presence of the 3,5-dimethylpyrazole with a singlet of CH pyrazole at δ 6.29 and the signal of the methyls at 2.36 ppm. The solid is insoluble in some organic solvents as methanol, acetone, DMSO and presents a low solubility in water. An attempt was made to crystallize the product by dissolving it in distilled water with the help of heat, the solution was placed in a crystallizer in order to obtain the crystals for slow evaporation of the solvent. Until now good crystals for X-Ray analysis were not obtained. The study of this reaction is still at a preliminary level and requests more attention in the future work.

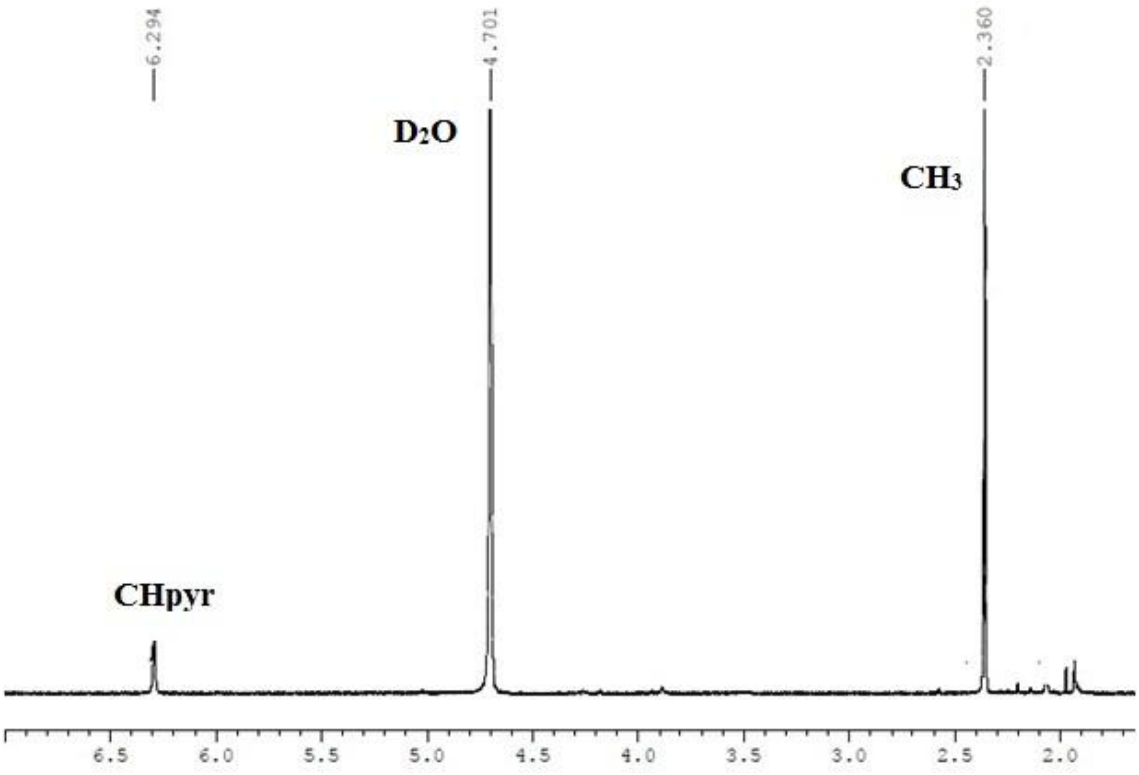


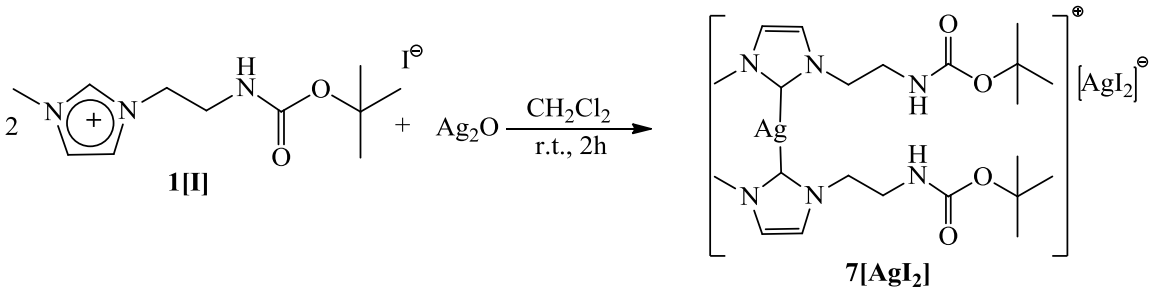
Figure 21: *^{1}H-NMR spectrum of [W(O)(O$_2$)$_2$(C$_5$H$_8$N$_2$)$_2$] complex (**6**) in D$_2$O.*

2.5. *N*-Heterocyclic Carbene-molybdenum (VI) Complexes

As outlined in the Introduction, NHCs have attracted considerable attention as a new class of ligands over the past decade for their stability and catalytic properties, but not much is known about the NHC with molybdenum and in this regards literature is poor. In this session two synthesis attempts of NHC oxodiperoxo molybdenum complexes, with the aim to apply in future in catalytic reactions are listed.

The more frequent synthetic routes for the preparation of NHC complexes are basically two: obtain the carbene by deprotonation of the corresponding salt, or, if the carbenes are highly reactive, use NHC silver complexes, that are stable, as transmetallating agents.

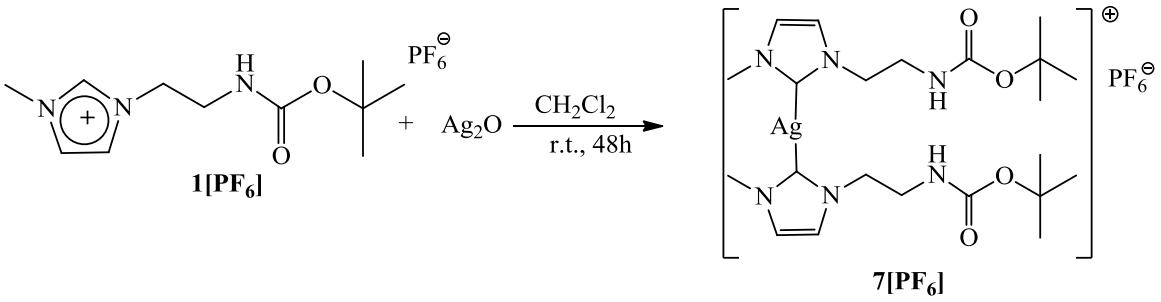
2.5.1. Synthesis of (1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver iodide (7[AgI_2])



Scheme 16

The imidazolium salt **1[I]** was treated with a slurry of Ag_2O, following a procedure reported in literature,[13] in CH_2Cl_2 in a 2:1 molar ratio and stirred at room temperature for 2h in the dark and under nitrogen (Scheme 16). The resulting gray suspension was filtered and the volatiles removed under reduced pressure to afford in quantitative yields the silver complex (1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver iodide, **7[AgI_2]**, as a white solid that was analyzed by IR and NMR spectroscopy. In the ^{1}H-NMR spectrum in $CDCl_3$ the complete disappearance of the high frequency peak for the imidazolium proton was coupled with the appearance in the ^{13}C-NMR spectrum of a singlet at δ 184.9 assigned to a Ag-$C_{carbene}$ carbon. The chemical shift of CH_{im} fall at 121.7 and 121.4 ppm, perfectly in keeping with the values reported in literature. In the IR spectrum in THF the carbonyl stretching frequency (ν_{CO}) of the carbamate group appeared at 1716 cm^{-1}.

2.5.2. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver hexafluorophosphate (7[PF_6])

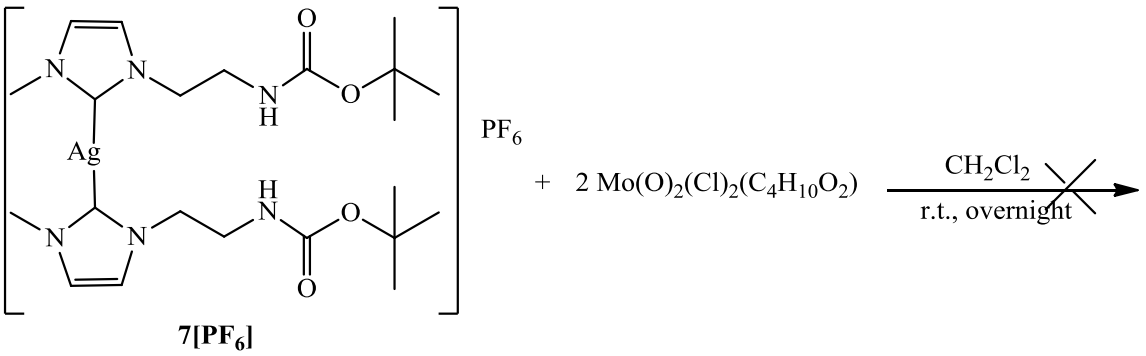


1[PF_6] **7[PF_6]**

Scheme 17

The use of the silver base Ag_2O has been found a very advantageous method in order to trap the carbene molecule. The reaction occurs between **1[PF_6]** and an excess of Ag_2O in a homogeneous solution of CH_2Cl_2 in a 1:1 molar ratio (Scheme 17). After 48h under stirring, the solvent was removed under vacuum to give the complete formation of the biscarbene salt 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver hexafluorophosphate, **7[PF_6]** as a white solid. Although the reaction requires a longer time (48h) if compared with the synthesis reported in literature (24h),[12] the new method avoid the use of a biphasic dichloromethane/water reaction mixture as well as the basic PTC as phase transfer catalyst. The reaction results longer but easier to be performed and worked up. The product formation was confirmed by NMR spectroscopy. In the ^{1}H-NMR spectrum only one signals set attributed to the silver complex was observed; the two peaks of imidazolium ring at δ 7.07 and 6.98, the methyl signal at 3.85 ppm, the singlet of *t*-Bu at δ 1.39 and the signals of the methylene groups at 4.26 and 3.52 ppm.

2.5.3. Reaction of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver (7[PF_6]) with dichloro(1,2-dimethoxiethane) diperoxo molybdenum



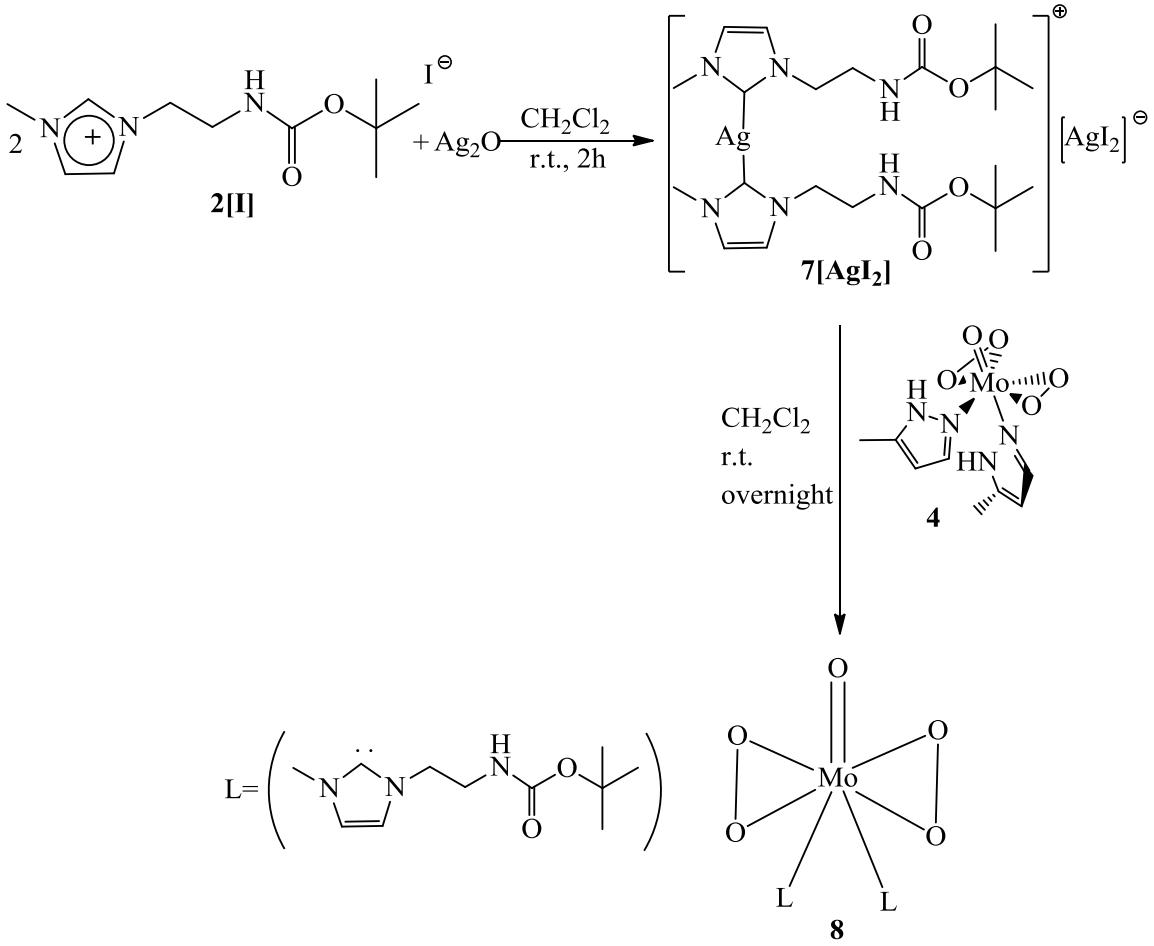
7[PF_6]

Scheme 18

The silver hexafluorophosphate complex **7[PF_6]** was reacted with dichloro(1,2-dimethoxiethane) diperoxo molybdenum, available in the Galindo's laboratory, in CH_2Cl_2 solution and was stirred overnight under nitrogen atmosphere (Scheme 18). From the formed precipitate different unidentified products were observed but not the required complex. The transmetalation reaction with [$Mo(O)_2(Cl)_2(C_4H_{10}O_2)$] as molydbenum complex precursor does not take place.

In order to obtain the NHC molybdenum complex with functionalized NHC as ligand, a change of the molydbenum precursor was attempted. For the transmetallation reaction it was tested the [$Mo(O)(O_2)_2(C_4H_6N_2)_2$] (**4**) complex, which synthetic procedure and characterization was previously reported.

2.5.4. Synthesis of oxo-diperoxo bis(1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium) molydbenum complex (8)



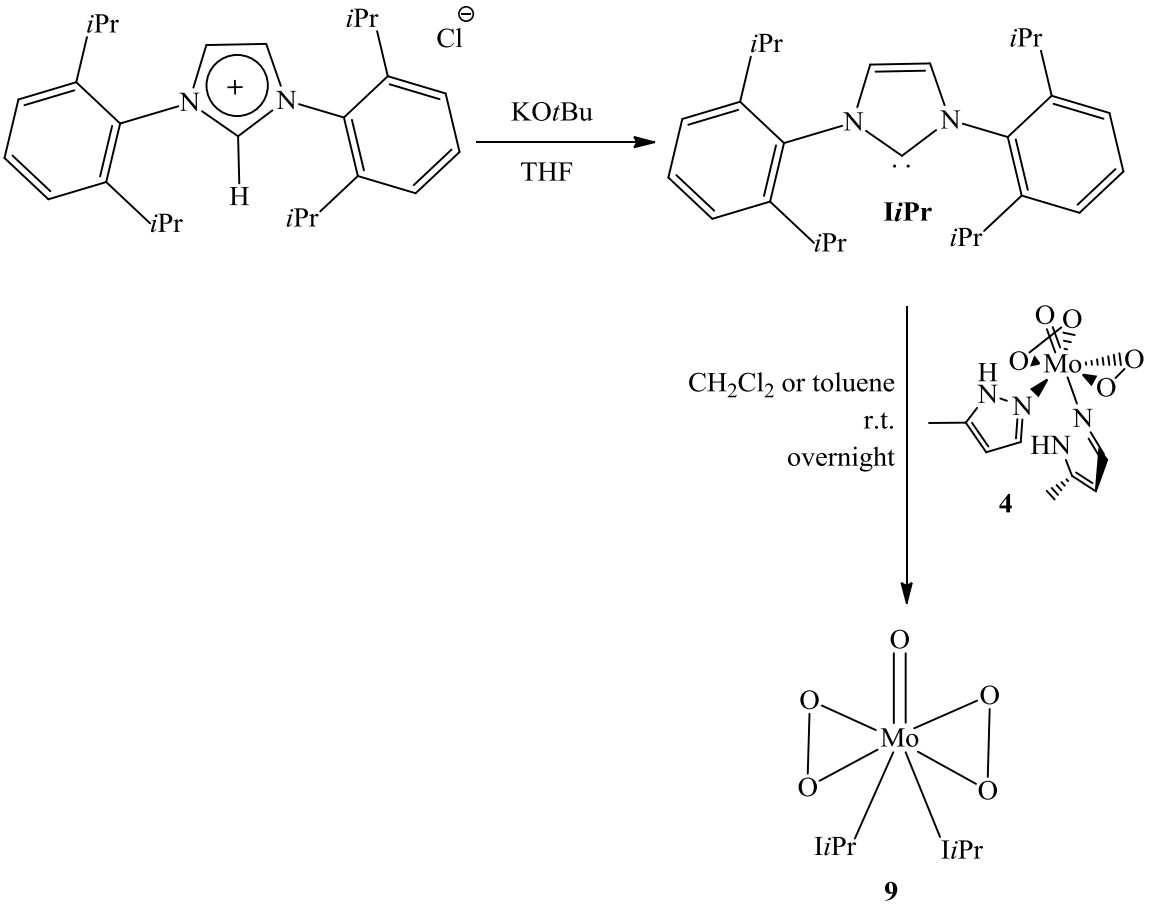
Scheme 19

In order to obtain a NHC molybdenum complex with the functionalized imidazolium salt as ligands the silver complex, **7[AgI_2]**, was prepared as previously described and reacted *in situ* with a solution of [$Mo(O)(O_2)_2(C_4H_6N_2)_2$] (**4**) in CH_2Cl_2 (Scheme 19). The mixture was stirred overnight. At the end of the reaction the solution was filtered and dried under vacuum to give a yellow solid that was characterized by NMR and IR spectroscopy. The ^{1}H-NMR shows three set of signals, between 6.7-7.3 ppm were observed six signals relative to CH imidazole and also the tipical region of CH_2 shows six signals as multiplets. In the methyl zone appear three singlet (δ = 3.93, 3.74, 3.75) for the NCH_3 and three singlet for *t*-Bu (1.33, 1.29, 1.28 ppm). The major set displays the typical chemical shift of an imidazolium salt of the type **1** in particular at δ 9.88 the signal of the acid proton NCHN was observed. Another set of signals can be attributed to the unreacted silver complex (**7[AgI_2]**) and the last one, the less intense, maybe belong to

the derived molybdenum complex. The spectrum shows also the signal of the 3-methylpyrazole as a singlet at 2.34 ppm and a multiplet at δ 6.06 and 7.48.

The study of this synthesis is still at a preliminary level, nevertheless the presence of one unidentified set of signal with the typical pattern of NHC as ligand indicate the possibility to obtain the product. Further studies are needed (variation of stoichiometry and reaction conditions) in order to isolate and characterize the product.

2.5.5. Synthesis of oxo-diperoxo (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)molydbenum complex (9)



Scheme 20

The synthesis of NHC molybdenum complex was also attempted with a different imidazolium salt as ligand precursor. Unlike previous procedure in this case the carbene was obtained for deprotonation of the relative salt because the 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, available in the Galindo's laboratory, has a steric hyndrance by phenyls and isopropyl groups that allows to stabilize the carbene.

The carbene formation was performed by reaction with KO*t*Bu in dry THF. After 30min under stirring the formed carbene was extracted with toluene. In the first attempt the reaction between the carbene and the precursor molybdenum **4** complex was effected in CH_2Cl_2 solution (Scheme 20). After a night under stirring and solvent removal a brown pale solid was obtained and analyzed by NMR spectroscopy. In the ^{1}H-NMR spectrum (CD_2Cl_2) the characteristic peak of the imidazole proton at high field (δ 9.22) was observed that states the certain presence of the free imidazolium salt. The aromatic region shows a lot of peaks difficult to be attributed, one set sure belong to the ligand and it was hypothesized that the others are of the complex. The typical signals of isopropyl were observed as a multiplet (attributable to the CH) at δ 2.40 for the salt and at δ 2.88 fot the complex, and two doublets at 1.19 and 1.11 ppm for the free ligand and at 1.18 and 1.14 ppm for the complex (attributable to the CH_3). This could support the hypothesis of formation of the product [$MoO(O_2)_2$ (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)] (**9**) though in lower amount than the imidazolium salt. The IR spectrum shows only the tipical peaks of the 1,3-bis(2,6-diisopropylphenyl)imidazolium salt. Successively it was decided to repeat the reaction with toluene as solvent and with a molar ratio 1:1; at the end of the reaction, performed with the same procedure, the solvent was removed under vacuum and the solid dissolved in dry acetonitrile. Precipitation from the solution of little yellow crystals was observed. The crystals were characterized by NMR (Figure 22) and IR spectroscopy (Figure 23) and compared with the spectrum of the imidazolium salt and the precursor molybdenum complex **4**.

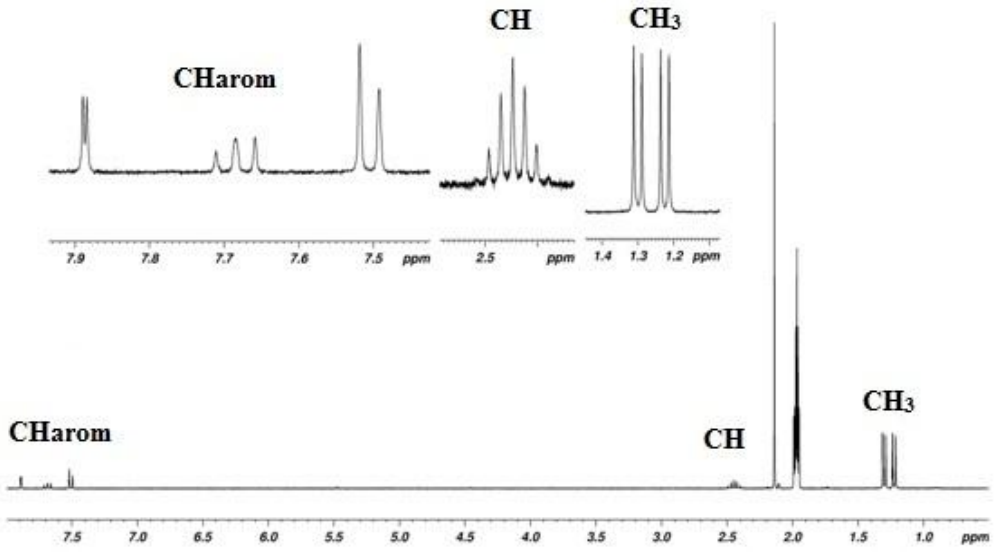


Figure 22: *^{1}H-NMR of **9** in CD_3CN.*

The ^{1}H-NMR spectrum (Figure 22) shows only one set of signals attributable to the complex **9**, the characteristic signals of the isopropyl group were observed at δ 2.45 as a septet (CH) and at 1.3 and 1.23 ppm as a two doublets (CH_3). The chemical shifts of the aromatic protons appear between 7.90 and 7.40 ppm.

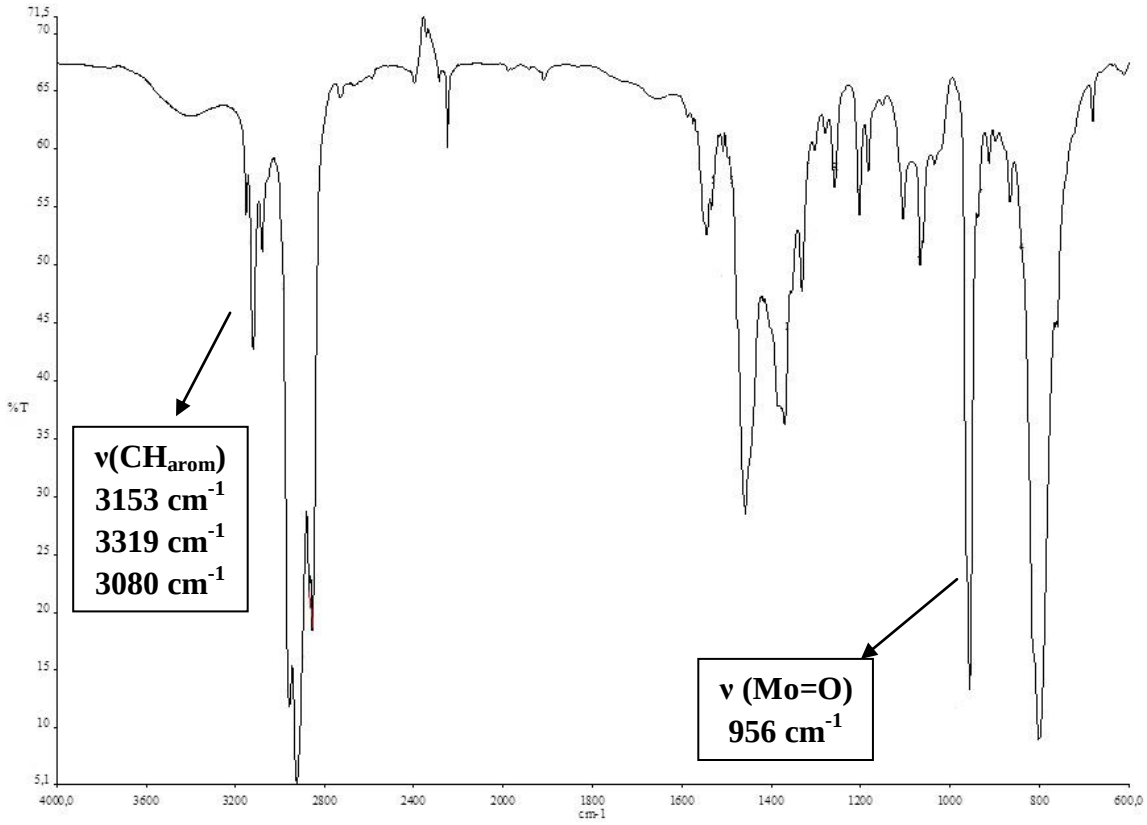


Figure 23: *IR Spectrum of the* ***9*** *in NaCl, nujol.*

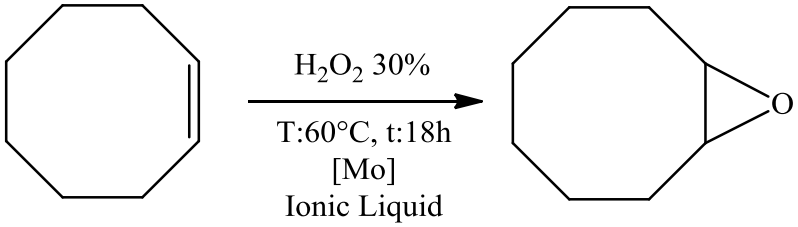
The IR spectrum (Figure 23) in the aromatic region shows at 3153, 3120 and 3080 cm^{-1} the CH peaks of the ligand (*cf.* imidazolium salt: 3154, 3123, 3062 cm^{-1}) and at 956 cm^{-1} the frequency of Mo=O (*cf.* $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$: 951 cm^{-1}).

The preliminary results reported allows to hypotize that the Mo-NHC complex can be formed either with a transmetallation reaction or by the deprotonation of imidazolium salt. Further investigation will be developed in order to optimize the reaction procedure and characterization.

2.6. Epoxidation reaction

As previously underlined, one of the principal scope of this thesis was to employ the imidazolium salts **1**, **2** and **3** described in the previous paragraph as "green" solvent for the olefin epoxidation catalysed by molybdenum complexes. The tests were repeated with two oxodiperoxomolybdenum complexes as catalysts: $[MoO(O_2)_2(C_4H_6N_2)_2]$ (**4**) (already formed or formed *in situ* from $[MoO(O_2)_2(H_2O)_n]$ as catalytic precursor) and $[MoO(O_2)_2(C_5H_8N_2)_2]$ (**5**). The research group has focused its attention on these molybdenum complexes because are cheaper than the other metallic compounds. The olefinic substrate and the oxidant are the same in all tests, the first one is the *cis*-cyclooctene that is an olefin type for the oxidation reactions because is the alkene with greater tendency for the epoxidation.[11] As oxidant was chosen hydrogen peroxide in aqueous solution at 30% because has an high active oxygen content and the waste produced is only plain water, moreover the use of this one is more simple and safe than the use of molecular oxygen. The use of ionic liquids as reaction solvents has several advantages than the conventional solvents, the more important are the non-volatility and the capacity of immobilizing the catalyst in the ionic liquid with the aim of recover and reuse it. Different ionic liquids have been tested for each catalytic tests to observe the effect of water miscibility on the tendency of hydrolysis. The hydrolysis of the epoxy product is one of the main problems of this reaction, in fact this is a side reaction of the oxidation that causes the opening of the ring and the subsequent formation of cyclooctane-1,2-diol (see Introduction, Paragraph 1.4).

2.6.1. Catalytic epoxidation of *cis*-cyclooctene in ionic liquid with $[Mo(O)(O_2)_2(H_2O)_n]$ as a catalytic precursor



Scheme 21

The Scheme 21 shows the operative condition of the catalytic epoxidation of *cis*-cyclooctene.

Hereafter in the Table 4 are shown the results of the catalytic reaction with $[MoO(O_2)_2(H_2O)_n]$ as catalytic precursor that by adding two equivalents of 3,5-dimethylpyrazole gives rise to the catalyst *in situ*. The molar ratio substrate/catalyst is 40:1. The percentage yield indicates the amount of cyclooctene oxide formed with respect to the initial cyclooctene, the conversion refers to the percentage of cyclooctene reacted and the selectivity represents the percentage of olefin converted to the epoxide. The concentration of the analytes and hence the yield, conversion and selectivity, were calculated according to the peaks area obtained by GC analyses of the reagent (*cis*-cyclooctene) and the product (oxide of *cis*-cyclooctene) comparing to the peak area of internal standard, dodecane, that was added in a known amount (for further details see the Experimental)

Table 4: Reaction Conditions: T: 60°C, t: 18h, ionic liquid: 2mL, 3,5-dimethylpyrazole: 4mg, *cis*-cyclooctene: 137µL, $[MoO(O_2)_2(H_2O)_n]$: 120µL, H_2O_2 30%: 340µL. Molar ratio substrate/catalyst 40:1.

Ionic liquid	Yield (%)	Conversion (%)	Selectivity (%)
3[PF_6]	74.8	95.5	78.3
3[NTf_2]	26.3	>99	26.3
3[NO_3]	8.6	72.2	12.0
1[NTf_2]	11.8	11.8	100
1[NO_3]	0	27.9	0
1[I]	0	21.7	0
2[NO_3]	0	23.9	0

IL **3[PF_6]** has been employed as the reference experiment, since it demonstrated to be the best unconventional solvent in the catalytic epoxidation in previous studies developed by the Seville group.[11] Under the reaction conditions employed the new ionic liquids (entries 2-7 in Table 3) unfortunately never works better that the reference **3[PF_6]** neither by changing the counterion (**3[NTf_2]** and **3[NO_3]**) nor by adding an *N*-functionalization on the cation (**1[I], 1[NTf_2]**, **1[NO_3]** and **2[NO_3]**).

The more promising results have been obtained employing $[NTf_2]^-$ as the counterion. In the case of the *N*-functionalized **1[NTf_2]** although the conversion is low (11.8%), the selectivity is total. Quite surprisingly in the case of the unsubstituted **3[NTf_2]**, the

reaction works the other way around leading to the complete conversion with a low selectivity (26.3%). These results are not easy to be rationalized, anyway, if compared with the reference experiment, clearly show an influence of $[NTf_2]^-$ and/or of the NHBoc function on the catalytic behaviour of the complex when formed *in situ*. Performing the reaction in **1[NO_3]**, **2[NO_3]** and **3[NO_3]** a detectable amount of cyclooctene oxide has been registered only in the case of **3[NO_3]**. That means that, whatever the substituent on the ligand, $[NO_3]^-$ as the counterion has a very detrimental effect. In all the cases before the begin of the reaction, when was added hydrogen peroxide, a color change from yellow to red was observed probably due to the H_2O_2 decomposition. Since $[NO_3]^-$ was the only counterion in our hands in the case of deprotected IL **2[NO_3]**, we did not employ this IL in the following experiments. With regard to the other ILs prepared **1[PF_6]** has never been employed in these experiments due to the fact that in the presence of water hydrolysis of $[PF_6]^-$ occurs subsequently leading to the partial deprotection of the NHBoc group avoiding the control on the structure of the IL under biphasic conditions. On the other hand IL **1[I]** has been also tested, after the addition of the reagents the solution became suddenly brown confirming that the redox properties of this particular counterion negatively affect the reaction behaviour as expected. Apart of the counterion destiny, which anyway in this case affect the composition of the solution, the conversion is really low and no product has been obtained. This is the reason why this IL has never been tested in the following experiments.

In all the cases in which a low selectivity is observed the low yield in cyclooctene oxide is probably attributable to ring opening by hydrolysis of the epoxide, giving cyclooctane-1,2-diol as product as described in the previous paragraph (for more details see the Introduction).

2.6.2. Catalytic epoxidation of *cis*-cyclooctene in ionic liquid with [$Mo(O)(O_2)_2(C_4H_6N_2)_2$] (4) as the catalyst

The catalytic tests have been repeated with the preformed $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ (**4**) as catalyst. Complex **4** has been synthesized as described in Experimental section (Paragraph 4.14.2) as an orange cristalline solid and dissolved in the reaction flask containing the ionic liquid and the olefinic substrate. The molar ratio between the olefin and the catalyst is 40:1. Even in this case the results have been referred to the behaviour of the same catalytic reaction in **3[PF_6]** as solvent discussed in a precedent study of the Seville group.

Table 5: Reaction Conditions: T: 60°C, t:4h, $[MoO(O_2)_2(C_4H_6N_2)_2]$ (**4**): 9mg, ionic liquid: 2mL, H_2O_2 30%: 340µL, *cis*-cyclooctene: 137µL, molar ratio substrate/catalyst 40:1.

Ionic liquid	Yield (%)	Conversion (%)	Selectivity (%)
3[PF_6]	43.0	53.0	81.1
3[NTf_2]	55.0	80.0	68.7
3[NO_3]	6.8	30.9	21.9
1[NTf_2]	18.4	39.3	46.7

From the Table 5 can be observed that, even though the conversion results lower in the case of **3[PF_6]** and **3[NTf_2]** with respect to the ones obtained with the catalyst *in situ*, the selectivity is increased in both the ILs and sensitively in the case of the ionic liquid **3[NTf_2]** (26.3% *in situ* to 68.7% preformed) which behaviour, under these conditions, is quite similar to the reference. **3[NO_3]** and **1[NTf_2]** gave poor results both in term of conversions and selectivity confirming the detrimental effect of $[NO_3]^-$ as counterion and the negative effect of the NHBoc substituent on the cation.

2.6.2.1. Recovery and reuse of the catalyst solution

In order to test the catalytic efficiency of the **3[NTf_2]** as a reaction solvent, at the end of the reaction this one was recycled and reused in subsequent cycles. In Figure 24 are depicted the subsequent steps of the recycling.

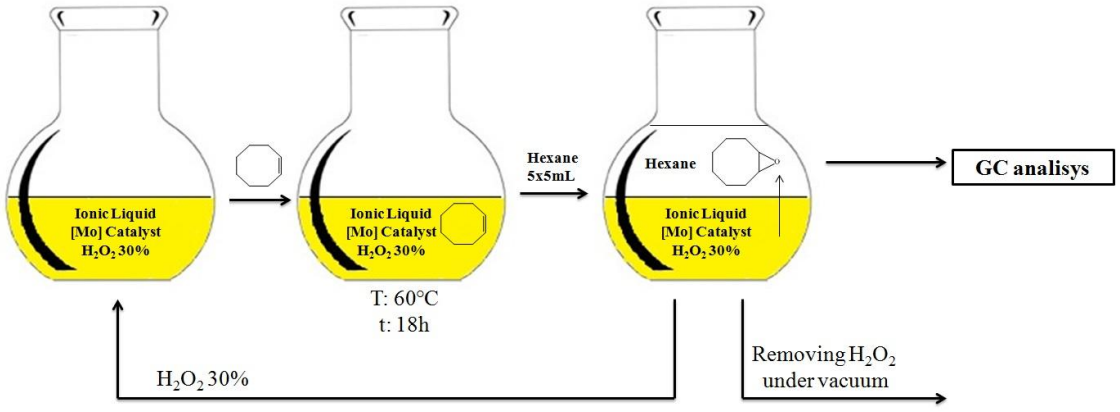


Figure 24: *recycling [Mo]-IL system. Reaction Conditions: ionic liquid (2mL), cis-cyclooctene (1mmol), [Mo]catalyst (0.025mmol), H_2O_2 30% (3mmol).*

As mentioned in the Introduction (Paragraph 1.3) the major advantage of the use of the ionic liquids as reaction solvents is the efficient immobilization of the catalyst in the ionic liquid phase, which means that, after product extraction, the reaction medium and the catalyst can be recycled several times. Recycling the system could lead, also, to have a better turnover number (TON) and atom economy (AE).[24] In our particular case after the extraction with hexane, the remaining mixture (IL with the catalyst inside) was heated at 60°C under vacuum for one hour to remove all the volatiles and the H_2O_2 30% residual. The mixture is now ready for another run; the fresh olefinic substrate *cis*-cyclooctene and the oxidant H_2O_2 were added to the recycled system and heated at 60°C for 4 hours (Figure 24).

Table 6: Recycling of the catalyst $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ (**4**) and the ionic liquid. (Reaction Conditions: T: 60°C, t:4h, H_2O_2 30%: 340µL, *cis*-cyclooctene: 137µL).

Ionic Liquid	Run	Yield (%)	Conversion (%)	Selectivity (%)
3[NTf_2]	1	55	80	68.7
	2	58.7	67.4	87.1
	3	37.6	46.5	80.8
1[NTf_2]	1	18.4	39.3	46.7
	2	10.8	36.6	29.4
	3	0	12.8	0

In the Table 6 the values of yield, conversion, and selectivity for subsequent epoxidation on the same system [Mo]-IL to test their recyclability are listed. It can be noted that, as previously stated, **3[NTf_2]** works better then **1[NTf_2]**. The conversion and yield values are not very high and decrease quickly during the successive runs but it can be observed how the yield in **3[NTf_2]** tests decreases more slowly than the conversion resulting in an increase in selectivity. Accordingly, though yields and conversions are relatively low, this increase in selectivity affirms how **3[NTf_2]** could be a good reaction solvent due to its effective recyclability that allows to reuse the same [Mo] catalyst more times.

2.6.3. Catalytic epoxidation of *cis*-cyclooctene in ionic liquid with [$Mo(O)(O_2)_2(C_5H_8N_2)_2$] (5) as a catalyst

All previous catalytic tests were effected in the same conditions also with [$Mo(O)(O_2)_2(C_5H_8N_2)_2$] (**5**) as catalyst for comparing the results and prove the better performances. The catalyst already formed like a yellow powdery solid (its synthesis was reported in the Experimental section, Paragraph 4.14.2) was charged in the reactor, containing the IL and the olefinic substrate, at last H_2O_2 30% was added and the mixture was heated at 60°C under stirring for 18 hours. The molar ratio substrate/catalyst is 40:1. Even in this case the results were referred to the behaviour of the same catalytic reaction in **3[PF_6]** as solvent.

Table 7: Reaction Conditions: T: 60°C, t:18h, ionic liquid: 2mL, [$MoO(O_2)_2(C_5H_8N_2)_2$] (**5**): 9mg, *cis*-cyclooctene: 137µL, H_2O_2 30%: 340µL .

Ionic liquid	Yield (%)	Conversion (%)	Selectivity (%)
3[PF_6]	97.4	97.4	100
3[NTf_2]	97.2	97.2	100
3 [NO_3]	3.3	26.3	12.5
1[NTf_2]	3.2	19.8	16.2

From Table 7 we can notice that the tests with **3[NO_3]** and **1[NTf_2]** as solvents result with a very low conversion (3.3 % and 3.2% respectively), in agreement to the results of the previous tests, with the catalyst formed *in situ* and the [$MoO(O_2)_2(C_4H_6N_2)_2$] (**4**) catalyst (6.8% and 18.4% respectively). We can affirm that these ILs do not work very well in catalytic epoxidation of olefins likely due to the negative effect of $[NO_3]^-$ as counterion and the adverse effect of the NHBoc substituent on the cation.

As established above, **3[NTf_2]** gives the best results also in this catalytic test, its yield and conversion (97.2%) are comparable with those of **3[PF_6]** (97.4%), moreover it shows total selectivity towards the epoxide formation.

As expected, the system with the catalyst [$MoO(O_2)_2(C_5H_8N_2)_2$] (**5**) charged already formed carry out best results than the previous test with the same catalyst formed *in situ* (for **3[NTf_2]** 26.3% *in situ* to 97.2% preformed and for **3[PF_6]** 74.8% *in situ* to 97.4% preformed).

The recyclability of the system **3[NTf_2]** and **3[PF_6]** ILs in subsequent runs was tested with the same procedure described in the Figure 24.

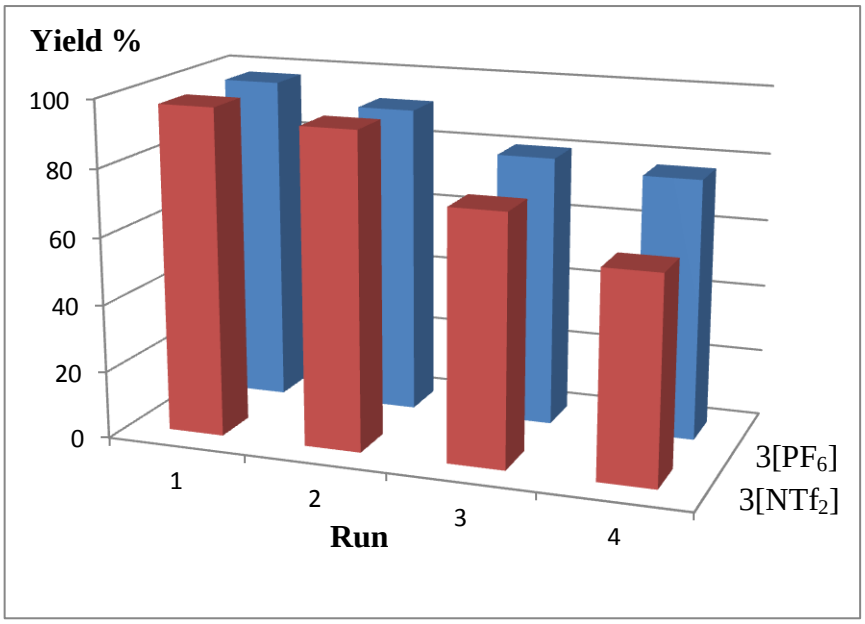
Table 8: Recycling of the catalyst [$MoO(O_2)_2(C_5H_8N_2)_2$] (**5**) and the ionic liquid (Reaction Conditions: T: 60°C, t:18h, *cis*-cyclooctene: 137µL, H_2O_2 30%: 340µL).

Ionic Liquid	Run	Yield (%)	Conversion (%)	Selectivity (%)
3[PF_6]	1	97.4	97.4	100
	2	91.7	97.6	93.9
	3	78.1	78.1	100
	4	77.2	80.4	96
3[NTf_2]	1	97.2	97.2	100
	2	93.6	95.3	98.3
	3	74	80.2	92.3
	4	60.6	60.6	100

From the Table 8 it is observed how both systems have good recyclability; in the first two runs the conversion and the yield are virtually unchanged (yield: 97.4% to 91.7% for **3[PF_6]** and 97.2% to 93.6% for **3[NTf_2]**) while in the subsequent runs begin to descrease (fourth run: 77.2% and 60.6%).

The Graphic 1 shows better the decreasing of the yield in the susbequent runs for both ILs, **3[PF_6]** and **3[NTf_2]** .

Graphic 1: Yield versus runs for the ionic liquids **3[PF_6]** and **3[NTf_2]**.



Established the recyclability behavior of the system, the most important observation to point out in the latter catalytic test is about the full selectivity that remains unchanged in all the runs.

The complete formation of the epoxide and its no conversion to the diol means that the hydrolysis was inhibited (for more details about the hydrolysis problem in the ILs employed see the Introduction, Paragraph 1.3.1). We can now affirm that the catalyst $[MoO(O_2)_2(C_5H_8N_2)_2]$ (**5**) with the ILs **3[PF_6]** and **3[NTf_2]** give rise to a very selective catalytic systems in the epoxidation of olefins. Further studies should be made on this catalytic system to test the reproducibility of these results.

3. CONCLUSIONS

In the present thesis work different *N*-functionalized (**1[I]**, **1[PF_6]**, **1[ClO_4]**, **1[NTf_2]**, **1[NO_3]**, **2[NO_3]**) and non-functionalized imidazolium salts (**3[Cl]**, **3[NTf2]**, **3[NO3]**) have been synthesised and characterized in order to be tested as "green" ILs solvents in the catalytic epoxidation of olefins employing oxodiperoxomolybdenum complexes as catalysts and H_2O_2 30% as benign oxidant.

Two different *N*-functional groups have been inserted in the imidazolium salt cation structure: NHBoc in the case of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium (**1**) and NH_2 for the 3-butyl-1-methylimidazolium (**3**). Several counterions has been also employed $[I]^-$, $[PF_6]^-$, $[NO_3]^-$, $[ClO_4]^-$, $[NTf_2]^-$ in order to value their influence on catalytic activity.

Crystals structure of the imidazolium salt 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methyl-imidazolium hexafluorophosphate (**1[PF_6]**) was determined on a suitable crystal obtained by cooling the oily product at -20°C. (Figure 15).

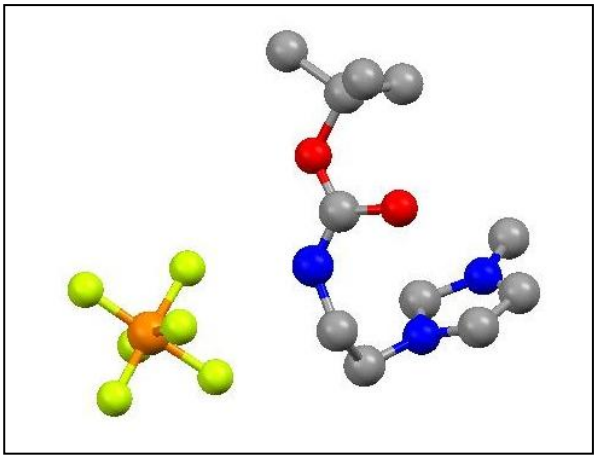


Figure 15: *X-ray structure of* ***1[PF_6]****. Hydrogen atoms have been omitted for clarity.*

The ionic liquids synthesized were tested in olefin epoxidation catalyzed by oxodiperoxomolybdenum complexes $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ (**4**) and $[Mo(O)(O_2)_2(C_5H_8N_2)_2]$ (**5**) (preformed and formed *in situ*). The **1[NTf_2]**, **1[NO_3]**, **1[I]**, **2[NO_3]** and **3[NO_3]** gave poor results both in term of conversions and selectivity due to the detrimental effect of $[NO_3]^-$ and I^- as counterion and the negative effect of the NHBoc substituent on the cation perhaps for its poor tendency to coordinate the molybdenum.

3[NTf_2] ionic liquid resulted a good and selective solvent for catalytic epoxidation giving conversions comparable to the reference IL **3[PF_6]**. **3[NTf_2]** and **3[PF_6]** were recycled in subsequent cycles leading to an effective recyclability that allows to reuse the same [Mo] catalyst more times as summarized in Table 8.

Table 8: Recycling of the catalyst [$MoO(O_2)_2(C_5H_8N_2)_2$] (**5**) and the ionic liquid, molar ratio substrate/catalyst 40:1 (Reaction Conditions: T: 60°C, t:18h, *cis*-cyclooctene: 137µL, H_2O_2 30%: 340µL).

Ionic Liquid	Run	Yield (%)	Conversion (%)	Selectivity (%)
3[PF_6]	1	97.4	97.4	100
	2	91.7	97.6	93.9
	3	80.3	78.1	100
	4	77.2	80.4	96
3[NTf_2]	1	97.2	97.2	100
	2	93.6	95.3	98.3
	3	74	80.2	92.3
	4	60.9	60.6	100

From these results we can affirm that the $[NTf_2]^-$ ion is a good counterion giving a total selectivity in the epoxide and avoiding the hydrolysis problems despite its partial solubility in water.

Based on this assumption, further investigations could be focused on other unreactive counterions such as $[OTf]^-$ which, according to the literature, has a good hydrofilicity resulting in ionic liquids miscible with water (more details in the Introduction, Paragraph 1.3).

It was also synthesized an oxodiperoxo tungsten complex with two dimethylpyrazole as ligands (**6**) which will be tested as catalyst in the catalytic epoxidation of olefin in a future work.

The final part of the internship was focused on the preliminary study of the NHC oxodiperoxo molybdenum complexes in particular the syntheses of the oxo-diperoxo bis(1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium)molydbenum complex (**8**) and the oxo-diperoxo (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)molydbenum

complex (**9**). The complexes **8** and **9** were characterized by IR and NMR analysis and now we are attempting to crystallize them to obtain the X-Ray structure. Further investigation are needed to optimize the reaction procedure (variation of stoichiometry and reaction conditions) in order to isolate and fully characterize the complexes **8** and **9**.

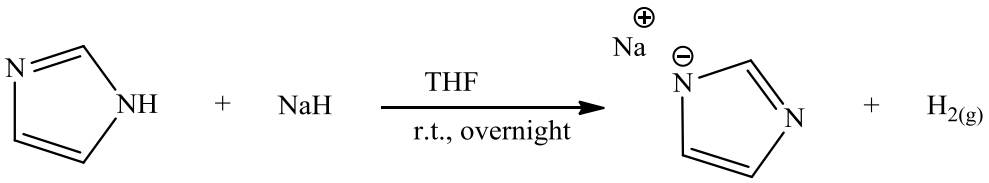
4. EXPERIMENTAL

4.1. Materials and General Procedure

All reactions were carried out under argon using standard Schlenk techniques. The solvents dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were degassed and distilled on appropriate drying agent (Na on benzophenone for THF and CaH_2 for CH_2Cl_2) and kept on molecular sieves in a inert atmosphere. The other solvents employed: dioxane, methanol (MeOH), hexane and diethyl ether (Et_2O) were used without further purification. The deuterated solvents, used after being dried on appropriate drying agents and degassed, were stored in ampoules under argon on 4Å molecular sieves. Reagents: imidazole, 2-bromoethylamine-hydrobromide, di-*tert*-butyldicarbonate, sodium hydroxide, ammonium hydroxide, methyl iodide, potassium hexaflurophosphate, lithium perchlorate, lithium bis(trifluoromethan)-sulfonimide, lithium nitrate, silver nitrate, silver(I) oxide, 1-methylimidazole, 4-chlorobutan-1-ylium, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, 3-methylpyrazole, 3,5-dimethylpyrazole, tunstic acid, molybdenum (VI) oxide were used as purchased from Sigma Aldrich. NaH (60% dispersion in mineral oil Sigma Aldrich) was washed several times with petroleum ether and the resulting white powder stored under argon. KO*t*Bu (99.99%, Sigma Aldrich) was stored under argon.

All reactions were followed, and the products characterized through IR and NMR spectroscopy. The IR spectra were recorded with a FT-IR Perkin-Elmer Spectrum 2000 spectrometer using a NaCl cell (thickness 1mm) for liquids coumpounds and KBr or NaCl pellets (neat or nujol) for solids and oils. The accuracy on the wave number is ± 1 cm^{-1}. The NMR spectra were recorded using Varian Inova 300 (^1H, 300.1; ^{13}C, 75.5 MHz), Varian MercuryPlus VX 400 (^1H, 399.9; ^{13}C, 100.6 MHz), Varian Inova 600 (^1H, 599.7; ^{13}C, 150.8 MHz) instruments. The spectra were referenced internally to residual solvent resonances, and unless otherwise stated, they were recorded at 298 K for characterization purposes. All chemical shift values are reported in ppm (δ scale), using, as an internal standard, the residual proton resonance of the non-deuterated: $CDCl_3$ (7.26, 77.0) D_2O (4.80). ESI-MS analyses were performed by direct injection of methanol solutions of the metal complexes using a Waters ZQ 4000 mass spectrometer. Elemental analyses were performed on a Thermo-Quest Flash 1112 Series EA instrument.

4.2. Synthesis of sodium salt of imidazolium[16]



The reaction is performed under nitrogen atmosphere. In a 250mL flask NaH (3.80g, 0.158mol) (we usually employ NaH 60% in mineral oil, previously washed three times with petroleum ether in order to enhance NaH activity, and kept under nitrogen) and dry THF (20mL) was added. Subsequently imidazole (11.73g, 0.1726mol), dissolved in THF (50mL), was added dropwise in 30min. The reaction mixture was stirred at room temperature overnight. At the end of the reaction the mixture was filtered and washed with dry THF. The residual solvent removed under vacuum leading to a white solid with a quantitative yield.

The product is kept under inert atmosphere.

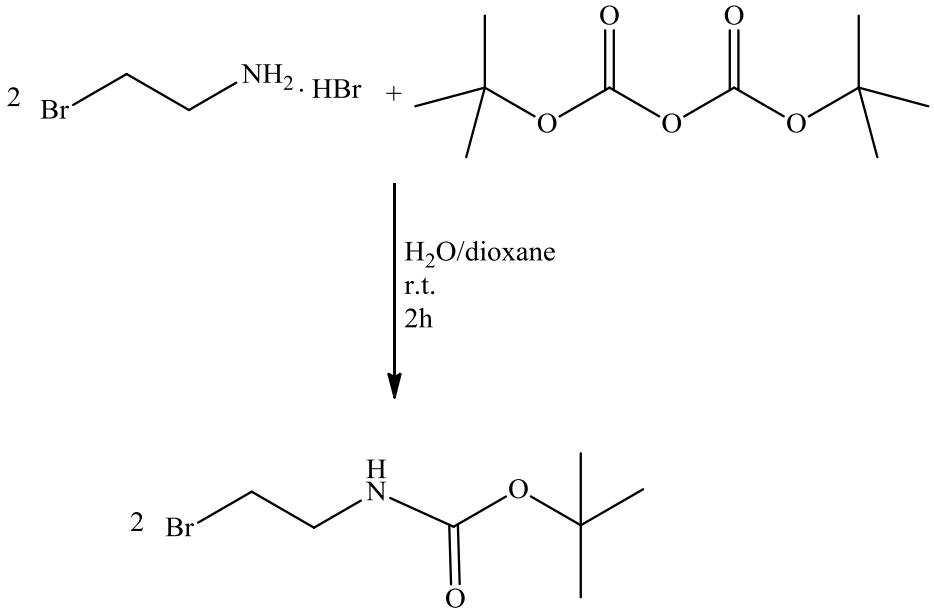
This reaction was performed also in larger quantities attempting a small scale-up, in a 1L flask was added 32.0g (1.35mol) of NaH in dry THF (170mL) and 100g (1.47mol, 1.09eq.) of imidazole in dry THF (420mL), the dripping has lasted 2 hours while the reaction time was the same.

^{1}H-NMR (D_2O)

δ(ppm): 7.64 (s, 1H);

7.00 (s, 2H).

4.3. Synthesis of 2-Bromoethylamine-*t*-butylcarbamate[16]



In a 1L three necked flask 12.30g (0.06mol) of 2-bromoethylamine-hydrobromide were dissolved in 60mL of a 1:1 di H_2O/dioxane mixture. The solution was cooled in an ice bath. Other two solutions (NaOH 1M in 60mL of water, 0.06mol) and (6.54g of di-*tert*-butyldicarbonate in 70mL of dioxane, 0.03mol) were prepared and separately added in two dropping funnel. NaOH solution was dropped in 15min while the di-*tert*-butyldicarbonate solution in 30min. Then the ice bath was removed and the mixture stirred for 2h at room temperature. Then the solution was extracted with CH_2Cl_2 (200mL) and the aqueous phase washed once more with 100mL of CH_2Cl_2. The organic phase was washed with citric acid 5% (2x100mL) and sodium chloride 10% (2x100mL). CH_2Cl_2 was dried with sodium sulphate, the solution filtered and the solvent removed under vacuum. 3.16g of a yellow oil was obtained and identified as 2-Bromoethylamine-*t*-butylcarbamate (Y = 47%).

This reaction was was then carried with five times the amount of the above procedure. In these condition the dripping times double and the reaction lasts 3 hours. After the filtration by cannula and the purification was obtained the product in the same yield.

^{1}H-NMR ($CDCl_3$)

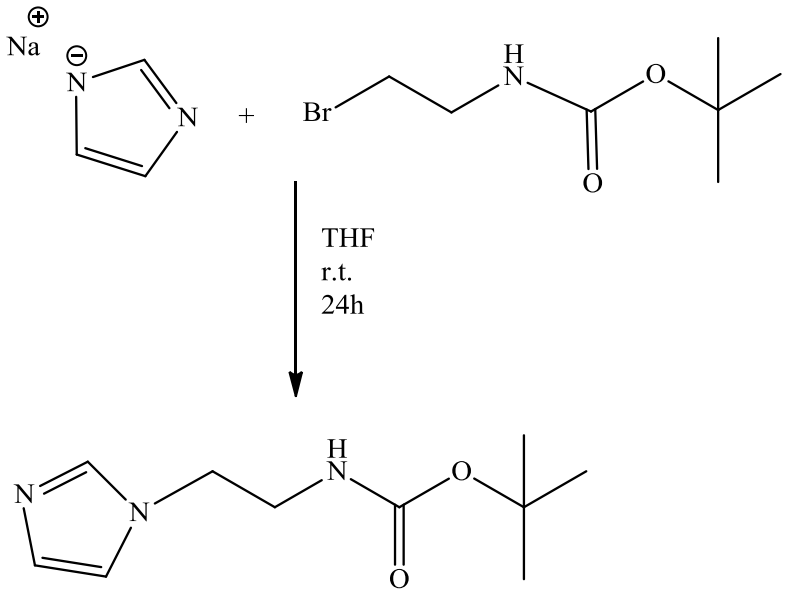
δ(ppm): 4.95 (s, NH);

3.69 (s, 8H, dioxane);

3.52 (m, 2H),

3.44 (m, 2H)

4.4. Synthesis of (2-Imidazol-1-yl-ethyl) *t*-butylcarbamate [17]



In a 1L flask, to a suspension of imidazolium salt 31.25g (0.28mol, 2eq) in dry THF (300mL) kept under inert atmosphere, was added with a cannula 2-Bromoethylamine-*t*-butylcarbamate (31.44g, 0.14mol) already dissolved in dry THF (200mL). The reaction mixture was stirred at room temperature for 24 hours. The crude reaction was filtered on celite and washed with dry THF, then the solvent was removed under vacuum. The yellow oil thus obtained was dissolved in CH_2Cl_2 and purified by column chromatography on silica. At first eluted with CH_2Cl_2, then with a mixture of CH_2Cl_2/CH_3OH (100:5) and finally with a mixture of $CH_2Cl_2/CH_3OH/NH_4OH$ (100:5:1). 12.27g of a yellow oil was isolated and identified as (2-Imidazol-1-yl-ethyl) *t*-butylcarbamate. (Y = 55%,).

^{1}H-NMR ($CDCl_3$)

δ(ppm): 7.50 (s, 1H, NCHN);

7.05 (s, 1H, CH_{im}), 6.90 (s, 1H, CH_{im});

4.90 (br s, 1H, NH);

4.07 (t, 2H, NCH_2, J = 5.6Hz);

3.42 (m, 2H, C*H*$_2$NH);

1.42 (s, 9H, CH_3).

^{13}C-NMR ($CDCl_3$)

δ(ppm): 155.8 (C=O);

137.1 (NCHN);

129.2 (CH_{im}), 118.8 (CH_{im});

79.6 (Cq, t-Bu);

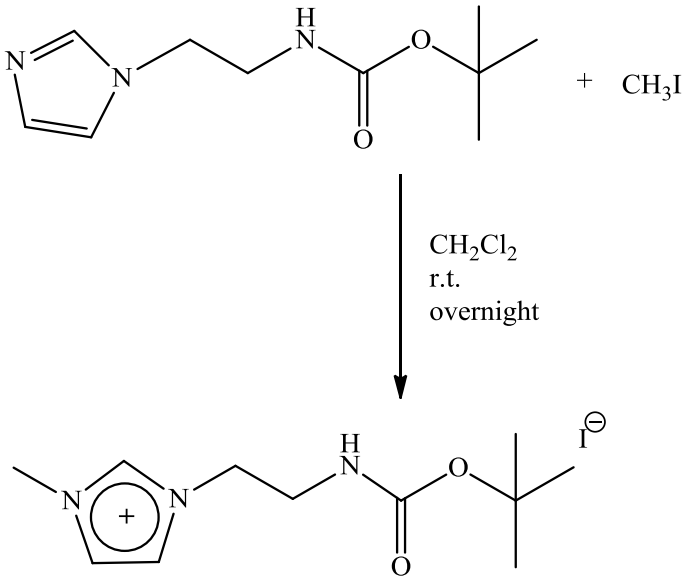
46.4 (NCH_2);

41.3 (CH_2NH);

28.1 (CH_3).

IR (THF) ν (CO): 1714 cm^{-1}

4.5. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide (1[I])[13]



1[I]

In a 250mL flask, kept under inert atmosphere, 5.30g (0.024mol) of (2-Imidazol-1-yl-ethyl) *t*-butylcarbamate was dissolved in 10mL of dry CH_2Cl_2, subsequently an excess of CH_3I (5mL, 0.080mol, 3eq.) was added. The reaction mixture was stirred at room temperature overnight. The product was washed with Et_2O (3x10mL) and, after having removed the washing water, the residual solvent and methyl iodide in excess were removed under vacuum. 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide, **1[I]**, was obtained with a quantitative yield.

Experimental

^{1}H -NMR ($CDCl_3$)

δ(ppm): 9.92 (s, 1H, NCHN);

7.19 (s, 1H, CH_{im}), 7.08 (s, 1H, CH_{im});

5.75 (br s, 1H, NH);

4.28 (t, 2H, NCH_2, J = 5.6Hz);

3.93 (s, 3H, NCH_3);

3.59 (m, 2H, CH_2NHBoc);

1.28 (s, 9H, CH_3).

^{13}C -NMR ($CDCl_3$)

δ(ppm): 156.2 (C=O);

137.0 (CH, NCHN);

123.1 (2CH, CH_{im});

79.9 (Cq, t-Bu);

46.7 (NCH_2);

40.2 (CH_2NH);

37.2 (NCH_3);

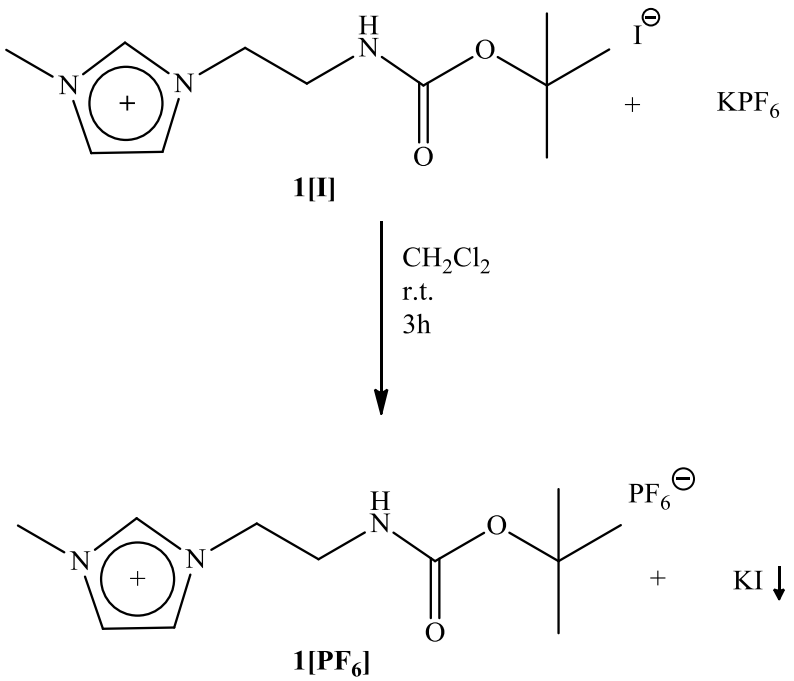
28.6 (CH_3, t-Bu).

IR (CH_2Cl_2) ν (CO): 1708 cm^{-1}

(NaCl) ν (CO): 1703 cm^{-1}

ESI-MS (MeOH, *m/z*): 226 (100) $[M]^+$, 127 (100) $[M]^-$.

4.6. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium hexaflurophosphate (1[PF_6])



1[PF_6]

To a solution of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium iodide, **1[I]**, (4.42g, 0.012mol) in CH_2Cl_2 (20mL) 2.54g (0.013mol, 1.1eq) of KPF_6 solid was added. The reaction mixture was stirred for 3h, at the end of the reaction, the reaction mixture was filtered on a celite pad and the solvent was removed under vacuum.

A yellow oil identified as 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium hexafluorofosfate, **1 [PF_6]** was obtained in quantitative yield.

The density was estimated as 1.06g/mL at 25°C.

^{1}H -NMR ($CDCl_3$)

δ(ppm): 9.54 (s, 1H, NCHN);

7.25 (s, 1H, CH_{im}), 7.17 (s, 1H, CH_{im});

5.62 (br s, 1H, NH);

4.39 (t, 2H, NCH_2, J = 5.6Hz);

3.92 (s, 3H, NCH_3);

3.56 (m, 2H, C*H*$_2$NHBoc);

1.28 (s, 9H, CH_3);

Experimental

^{13}C-NMR ($CDCl_3$)

δ(ppm): 156.40 (C=O);

137.23 (CH, NCHN);

123.02 (2CH, CH_{im});

49.78 (NCH_2);

40.20 (CH_2NH);

37.01 (NCH_3);

28.28 (CH_3).

^{19}F-NMR ($CDCl_3$)

δ(ppm): -72.75 (d, 6F, J = 710 Hz)

ESI-MS (MeOH, *m/z*): 226 (100) $[M]^+$, 145 (100) $[M]^-$.

X-RAY STRUCTURE

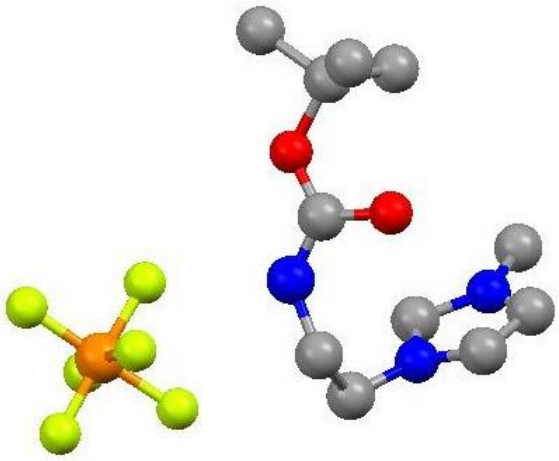


Figure 25: *X-ray structure of 1-(2-t-Butoxycarbonylamino-ethyl)-3-methylimidazolium hexafluorophosphate ,* ***1 [PF_6]****. Hydrogen atoms have been omitted for clarity.*

Table 9: Bond lengths (Å) and angles (°) for **1[PF_6]**.

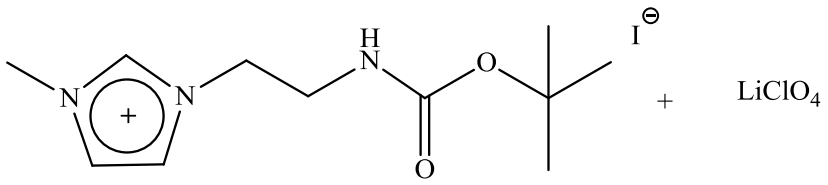
Bond Lenghts

C41-N42	1.49(3)	C50-O52	1.31(2)
N42-C43	1.38(2)	O52-C53	1.48(2)
N42-C46	1.33(3)	C53-C54	1.61(3)
C43-N44	1.24(2)	C53-C55	1.37(5)
N44-C45	1.40(2)	C53-C56	1.54(4)
N44-C47	1.42(2)	P2-F21	1.73(1)
C45-C46	1.39(3)	P2-F22	1.624(9)
C47-C48	1.61(3)	P2-F23	1.65(1)
C48-N49	1.43(2)	P2-F24	1.571(9)
N49-C50	1.26(2)	P2-F25	1.58(1)
C50-O51	1.33(2)	P2-F26	1.56(1)

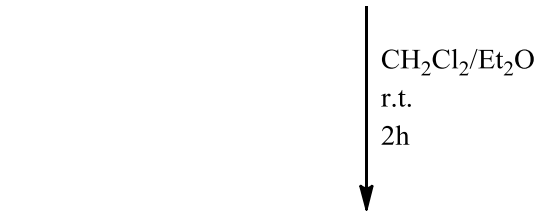
Angles

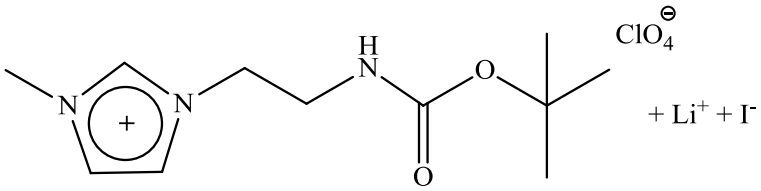
C41-N42-C43	126(2)	C54-C53-C55	115(2)
C41-N42-C46	124(2)	C54-C53-C56	105(2)
C43-N42-C46	110(2)	C55-C53-C56	115(2)
N42-C43-N44	105(2)	F21-P2-F22	81.4(6)
C43-N44-C45	114(2)	F21-P2-F23	168.3(7)
C43-N44-C47	123(1)	F21-P2-F24	99.1(6)
C45-N44-47	120(1)	F21-P2-F25	90.6(7)
N44-C45-C46	102(2)	F21-P2-F26	88.3(7)
N42-C46-C45	108(2)	F22-P2-F23	87.2(5)
N44-C47-C48	115(1)	F22-P2-F24	178.9(6)
C47-C48-N49	113(1)	F22-P2-F25	91.1(6)
C48-N49-C50	129(2)	F22-P2-F26	86.6(5)
N49-C50-O51	121(2)	F23-P2-F24	92.3(6)
N49-C50-O51	122(2)	F23-P2-F25	87.3(6)
O51-C50-O52	116(2)	F23-P2-F26	93.4(6)
C50-O52-C53	120(1)	F24-P2-F25	87.9(6)
O52-C53-C54	103(2)	F24-P2-F26	94.4(6)
O52-C53-C55	123(2)	F25-P2-F26	177.6(6)
O52-C53-C56	93(2)		

4.7. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium perchlorate (1[ClO_4])



1[I]





1[ClO_4]

In a 50mL flask 0.22g (62mmol) of **1[I]** was dissolved in CH_2Cl_2 (20mL), to this a solution of $LiClO_4$ (0.33g, 5eq, 3.12mmol) was added in Et_2O (15mL). The reaction mixture was stirred for 2h. At the end of the reaction the product was filtered and, after removing the solvent under reduced pressure, was dissolved in H_2O. The product can be separated from salts by extraction in CH_2Cl_2, the organic phase was dried with sodium sulphate anhydrous and filtered on filter paper. Removed the solvent, a yellow oil with a yield of 76% was obtained.

^{1}H -NMR ($CDCl_3$)

δ(ppm): 8.83 (s, 1H, NCHN);

7.31 (s, 1H, CH_{im}), 7.26 (s, 1H, CH_{im});

5.46 (br s, 1H, NH);

4.36 (t, 2H, NCH_2, J = 5.4Hz);

3.96 (s, 3H, NCH_3);

3.58 (m, 2H, C*H*$_2$NHBoc);

1.39 (s, 9H, CH_3).

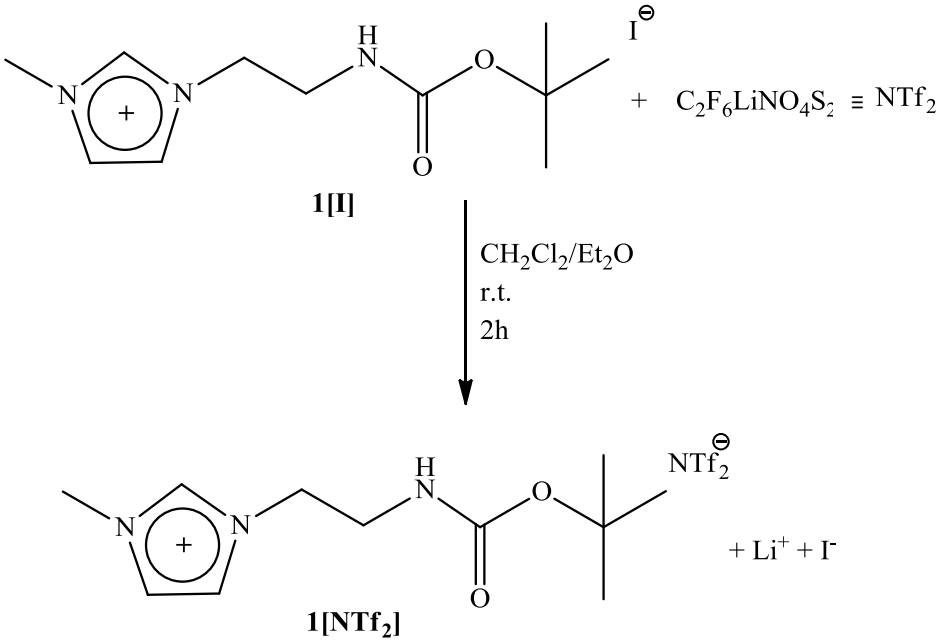
ESI-MS (MeOH, *m/z*): 226 (100) $[M]^+$, 99 (100) $[M]^-$.

IR (CH_2Cl_2) ν (ClO_4): 1097 cm^{-1}

ν (ClO_4): 1167 cm^{-1}

ν (C=O): 1710 cm^{-1}

4.8. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (1[NTf_2])



To a solution of **1[I]** (5.27g, 0.015mol) in CH_2Cl_2 (35mL) 7.01g (0.024mol, 1.6eq) of $C_2F_6LiNO_4S_2$ dissolved in 25mL of Et_2O was added. The reaction mixture was stirred for 2h. At the end of the reaction the solvent was removed under reduced pressure and then the product was dissolved in H_2O and extracted with CH_2Cl_2. The organic phase was dried with sodium sulphate anhydrous and filtered on filter paper. After removing the solvent 6.22g of a yellow oil identified as -(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium bis(trifluoromethane) sulfinimide ,**1[NTf_2]**, were obtained. Yield: 82%.

The density was estimated as 2.30g/mL at 25°C.

^{1}H -NMR ($CDCl_3$)

δ(ppm): 8.74 (s, 1H, NCHN);

7.31 (s, 1H, CH_{im}), 7.22 (s, 1H, CH_{im});

5.29 (br s, 1H, NH);

4.31 (t, 2H, NCH_2, J = 5.6Hz);

3.93 (s, 3H, NCH_3);

3.55 (m, 2H, CH_2NHBoc);

1.38 (s, 9H, CH_3).

^{19}F-NMR ($CDCl_3$)

δ(ppm): -79.10 (s, 6F)

ESI-MS (MeOH, *m/z*): 226 (100) $[M]^+$, 280 (100) $[M]^-$.

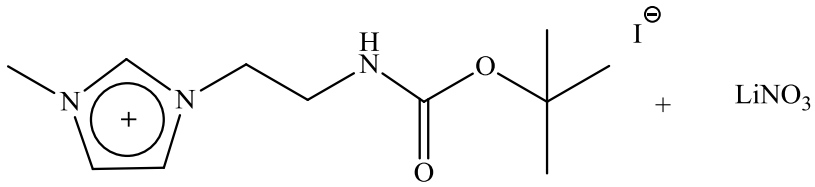
IR (NaCl) ν (CO): 1711 cm^{-1}

ν ($R-SO_2-N$): 1351 cm^{-1}

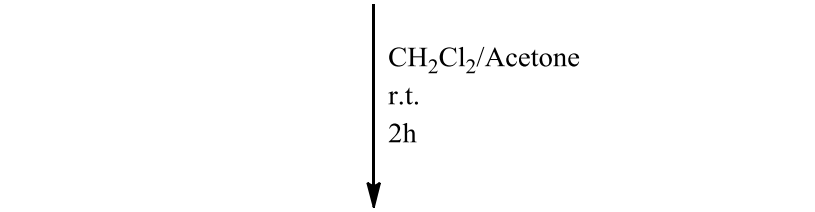
ν (SO_2): 1191 cm^{-1}

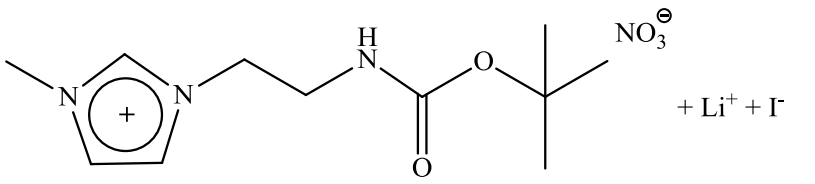
ν (CF_3): 790 cm^{-1}

4.9. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazolium nitrate (1[NO_3])



1[I]





1[NO_3]

In a 100mL flask was dissolved 3.67g (10.4mmol) of **1[I]** in CH_2Cl_2 (30mL), to this a solution of $LiNO_3$ (1.43g, 2eq, 20.7mmol) in acetone (15mL) was added. The reaction mixture was stirred for 2h. Unlike to the previous procedure the extraction CH_2Cl_2/H_2O was not made because this ionic liquid results soluble in water. At the end of the reaction the product was filtered and the solvent removed under reduced pressure, a yellow oil with a quantitative yield was obtained, **1[NO_3]**. The density was estimated as 1.14g/mL at 25°C.

^{1}H -NMR (D_2O)

δ(ppm): 8.61 (s, 1H, NCHN);

7.35 (s, 1H, CH_{im}), 7.30 (s, 1H, CH_{im});

4.12 (t, 2H, NCH_2, J = 5.6Hz);

3.74 (s, 3H, NCH_3);

3.35 (m, 2H, C*H*$_2$NHBoc);

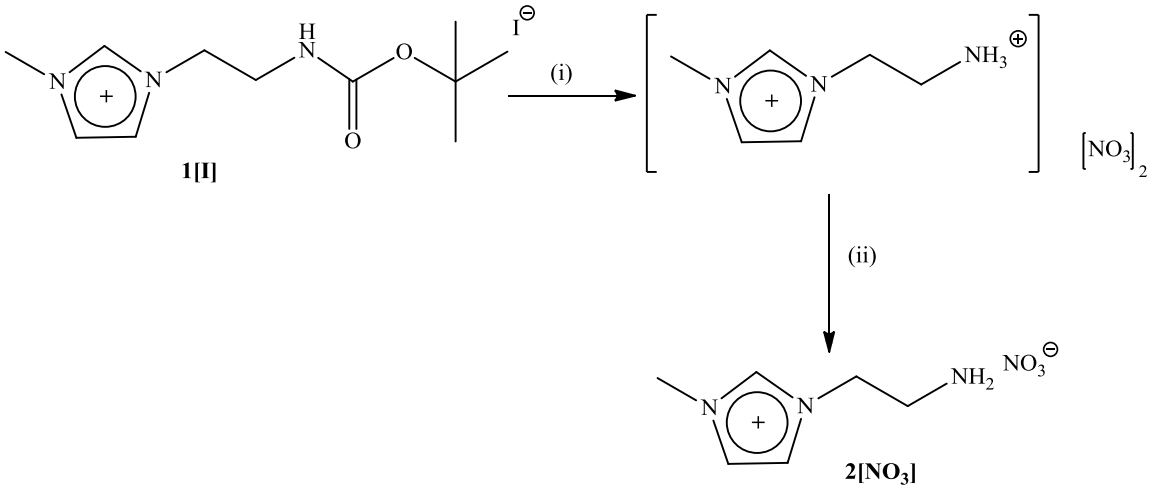
1.21 (s, 9H, CH_3).

IR (NaCl) ν (NH): 3413 cm^{-1}

ν (CO): 1694 cm^{-1}

ν (NO_3): 1368 cm^{-1}

4.10. Synthesis of 3-(2-aminoethyl)-1-methylimidazolium nitrate (2[NO_3])[15]



1[I] **2[NO_3]**

Experimental

i) Synthesis of 3-(2-ammonioethyl)-1-methylimidazolium nitrate

To a solution of **1[I]** (3.19g, 9.0mmol) dissolved in CH_2Cl_2 (30mL), 3mL of HNO_3 (65 wt.%) was added dropwise. The reaction mixture rapidly turned to dark violet due to the oxidation of the iodide to iodine with the concomitant formation of an insoluble product. After stirring the reaction for 1 h, the solvent was removed under reduced pressure and then kept under vacuum until all the iodine has sublimed. The resulting pale yellow viscous material was first washed with CH_2Cl_2 (3x5mL) and then with acetonitrile (2x5mL) to yield 3-(2-ammonioethyl)-1-methylimidazolium nitrate as a white solid.

^{1}H -NMR (DMSO)

δ(ppm): 9.10 (s, 1H, NCHN);

8.06 (br s, 3H, NH_3);

7.73 (s, 2H, CH_{im});

4.40 (t, 2H, NCH_2, J = 5.8Hz);

3.84 (s, 3H, NCH_3);

3.35 (m, 2H, $CH_2NH_3^+$).

^{13}C-NMR (DMSO)

δ(ppm): 137.25 (CH, NCHN);

123.69 (CH, CH_{im}), 122.28 (CH, CH_{im});

46.31 (NCH_2);

38.41 (CH_2NH_3);

35.52 (NCH_3).

^{1}H -NMR (D_2O)

δ(ppm): 8.91 (s, 1H, NCHN);

7.62 (s, 1H, CH_{im}), 7.56 (s, 1H, CH_{im});

4.63 (t, 2H, NCH_2, J = 6.2Hz);

3.96 (s, 3H, NCH_3);

3.60 (m, 2H, CH_2NH_3);

IR (KBr) ν (NH): 3424 cm^{-1}

ν (CH): 3149, 3109, 3047, 2987, 2924 cm^{-1}

ν (NO_3): 1383 cm^{-1}

*ii) Synthesis of 3-(2-aminoethyl)-1-methylimidazolium nitrate (**2[NO_3]**)*

To a suspension of $[NH_3(CH_2)_2ImMe][NO_3]_2$ (3.19g, 9mmol) in CH_3OH (35mL), 0.36g (9mmol) of solid NaOH was added at room temperature. After stirring the reaction for 3h the solvent was completely removed under reduced pressure and kept under vacuum at 70°C for 1h. On addition of acetonitrile (30mL) a white solid separated from the pale yellow solution. The suspension was filtered on a celite pad, the solvent was removed from the filtrate and then the yellow oil, identified as $[NH_2(CH_2)_2ImMe][NO_3]$,**2[NO_3]**, was kept for 2h at 70°C under vacuum (0.57g, Y: 33%).

The density has been estimated as 1.14g/mL.

^{1}H -NMR (DMSO)

δ(ppm): 9.08 (s, 1H, NCHN);

7.73 (s, 1H, CH_{im}), 7.71 (s, 1H, CH_{im});

4.09 (t, 2H, NCH_2, J = 5.8Hz);

3.86 (s, 3H, NCH_3);

3.35 (m, 2H, CH_2NH_2);

2.89 (t, 2H, NCH_2).

^{13}C-NMR (DMSO)

δ(ppm): 137.1 (CH, NCHN);

123.6 (CH, CH_{im}), 122.5 (CH, CH_{im});

51.9 (NCH_2);

41.3 (CH_2NH_2);

35.7 (NCH_3).

^{1}H -NMR (D_2O)

δ(ppm): 7.45 (d, 1H, CH_{im}, J = 1.9Hz);

7.41 (d, 1H, CH_{im}, J = 1.9Hz);

4.21 (t, 2H, NCH_2);

3.86 (s, 3H, NCH_3);

3.03 (t, 2H, NCH_2, J = 5.8Hz);

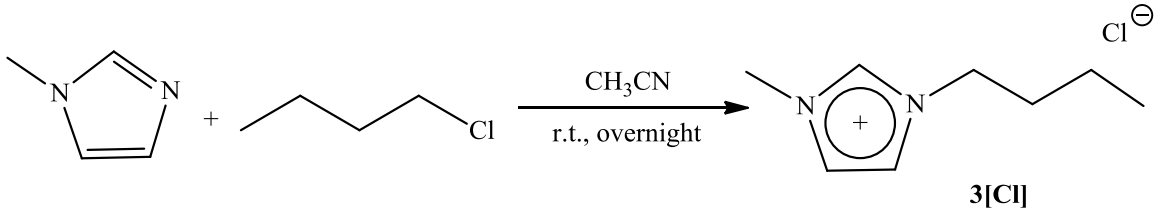
IR (NaCl) ν (NH): 3365 cm^{-1}

ν (CH): 3147, 3110, 2953 cm^{-1}

ν (NO_3): 1352 cm^{-1}

ESI-MS (MeOH, *m/z*): 126 (100) $[M]^+$, 62 (100) $[M]^-$.

4.11. Synthesis of 3-butyl-1-methylimidazolium chloride (3[Cl])



3[Cl]

To a solution of 1-methylimidazole (3mmol, 0.24mL) in 3mL of acetonitrile, 0.36mL (3mmol) of 1-chlorobutane was added. The reaction mixture was stirred at room temperature overnight. At the end of the reaction the solvent was removed under vacuum. The solid formed was washed with 3x5mL of diethyl ether and 3x5mL of petroleum ether, then the product was dried giving a white solid identified as 3-butyl-1-methylimidazolium chloride, **3[Cl]**. Yield: 75%

^{1}H -NMR (D_2O)

δ(ppm): 8.70 (s, 1H, NCHN);

7.46 (s, 1H, CH_{im}), 7.42 (s, 1H, CH_{im});

4.18 (t, 2H, NCH_2, J = 7.5 Hz);

3.88 (s, 3H, NCH_3);

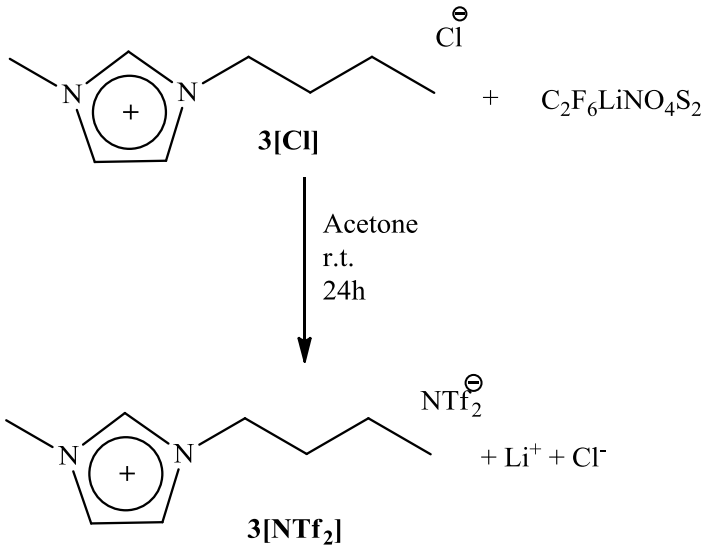
1.79 (m, 2H, CH_2);

1.32 (m, 2H, CH_2);

0.90 (t, 3H, CH_3, J = 7.5 Hz);

IR (NaCl, nujol, cm^{-1}): 3399, 3067, 2960, 2740, 2120, 1636, 1571, 1466, 1431, 1381, 1337, 1170, 1116, 1019, 950, 873 755, 655, 625

4.12. Synthesis of 3-butyl-1-methylimidazol-3-ium bis(trifluoromethylsulfonyl)- imide (3[NTf_2])



In a 100mL flask 4.36g (25mmol) of **3[Cl]** was dissolved in acetone (30mL) and then 10.76g (37.5mmol, 1.5eq) of $C_2F_6LiNO_4S_2$ solid was added. The reaction mixture was stirred for 24h. At the end of the reaction the solvent was removed under reduced pressure and then the product was dissolved in H_2O and extracted with CH_2Cl_2. After removing the solvent from the organic phase 9.01g of a yellow oil identified as 3-butyl-1-methylimidazol-3-ium ,**3[NTf_2]**, were obtained. Yield: 87 %.

^{1}H -NMR (D_2O)

δ(ppm): 8.65 (s, 1H, NCHN);

7.23 (s, 1H, CH_{im}), 7.19 (s, 1H, CH_{im});

4.09 (t, 2H, NCH_2, J = 7.5 Hz);

3.86 (s, 3H, NCH_3);

1.75 (m, 2H, CH_2);

1.31 (m, 2H, CH_2);

0.88 (t, 3H, CH_3, J = 7.5 Hz);

IR (NaCl) ν (R-SO_2-N): 1351 cm^{-1}

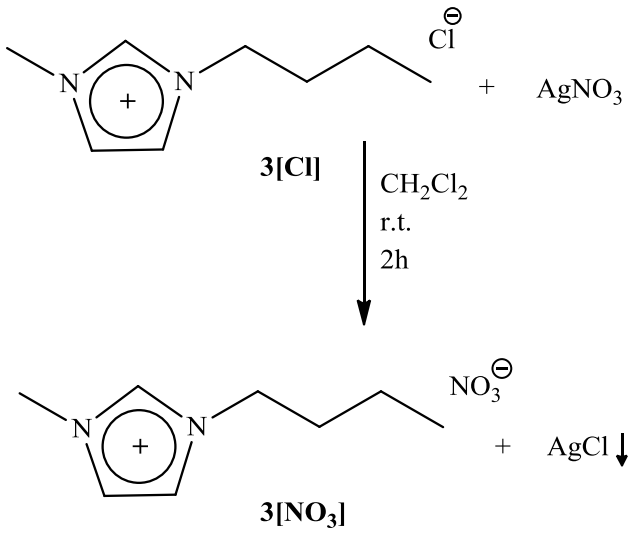
ν (SO_2): 1191 cm^{-1}

ν (CF_3): 790 cm^{-1}

^{19}F-NMR ($CDCl_3$)

δ(ppm): -79.01 (s, 6F)

4.13. Synthesis of 3-butyl-1-methylimidazol-3-ium nitrate (3[NO_3])[25]



To a solution of **3[Cl]** (4.48g, 0.026mol) in CH_2Cl_2 (50mL) an excess of a concentrated solution of $AgNO_3$ was added to remove the chloride that precipitates as AgCl. After 2h the formation of a white solid was observed and it was removed by filtration.The solvent was removed under reduced pressure and the resultant oil was stirred with activated charcoal for 12h. Then the product was filtered on filter paper and a pale yellow oil was obtained. Yield: 85%.

^{1}H -NMR (D_2O)

δ(ppm): 8.67 (s, 1H, NCHN);

7.43 (s, 1H, CH_{im}), 7.39 (s, 1H, CH_{im});

4.14 (t, 2H, NCH_2, J = 7.2 Hz);

3.85 (s, 3H, NCH_3);

1.76 (m, 2H, CH_2);

1.26 (m, 2H, CH_2);

1.22 (t, 3H, CH_3, J = 7.2 Hz);

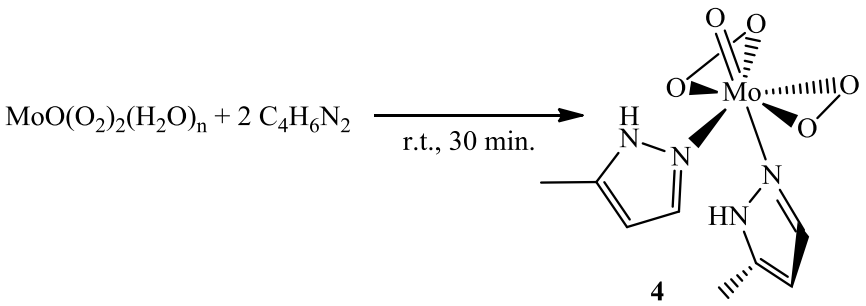
IR (NaCl) ν (NO_3): 1349 cm^{-1}

4.14. Oxodiperoxomolybdenum Complexes

4.14.1. Synthesis of $[Mo(O)(O_2)_2(H_2O)_n]$ solution in acqueous hydrogen peroxide[7]

In a 250mL Erlenmeyer flask a suspension of 1.5g (10.4mmol) of MoO_3 dissolved in 12mL of 30% acqueous hydrogen peroxide was heated at 55°C under stirring. At the beginning a pale green suspension with a little foam over was observed but after 1h turned to a orange solution with some solid at the bottom, then other 12mL of H_2O_2 30% were added and it kept under stirring for 48h for a complete dissolution. At the end of the reaction the dissolution was cooled in a ice bath, moved to a 50mL volumetric flask containing some drops of H_2O_2 30% and made up to volume with distilled water. The resulting solution consists of several molybdenum species in equilibrium but will hereon be referred simply as aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ with concentration 0.208M.

4.14.2. Synthesis of $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ complex (4)[7]



4

In a 50mL flask 15mL (3.45mmol) of the solution $[Mo(O)(O_2)_2(H_2O)_n]$ 0.208M and 1132μL (13.8mmol) of 3-methylpyrazole ($C_4H_6N_2$) were placed. The reaction mixture was stirred for 30min at room temperature, at the end of this a yellow solution with a yellow solid on the bottom was observed. Then, the solution was filtered and the solid washed with acetone and diethyl ether, the solid was preserved and the solution was moved to a crystallizer. After 24h was observed a yellow cristalline solid identificates as $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ complex, **4**. Yield: 70%.

Anal. calc. for $C_8H_{12}MoN_4O_5$: C, 28.25; H, 3.56; N, 16.47

Found: C, 28.39; H, 3.94; N, 16.13 %

^{1}H -NMR (CD_3OD)

δ(ppm): 7.58 (s, 1H, CH_{pyr});

6.20 (s, 1H, CH_{pyr});

2.35 (s, 3H, CH_3).

IR (KBr) ν(CH_{arom}): 3146 cm^{-1}

ν (C-N): 1280 cm^{-1}

ν (Mo=O): 950 cm^{-1}

ν (O-O): 874 cm^{-1}

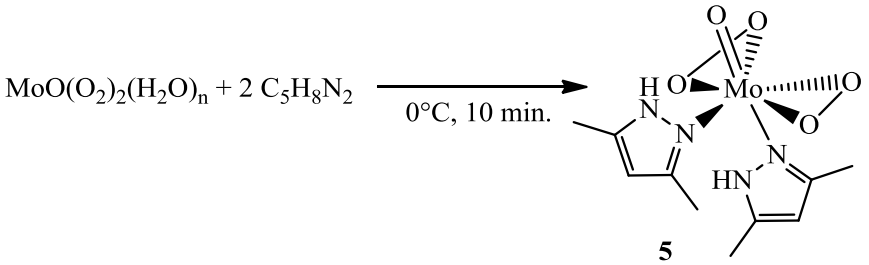
IR (NaCl, nujol) ν (CH_{arom}): 3146 cm^{-1}

ν (C-N): 1280 cm^{-1}

ν (Mo=O): 951 cm^{-1}

ν (O-O): 873 cm^{-1}

4.14.3. Synthesis of [$Mo(O)(O_2)_2(C_5H_8N_2)_2$] complex (5)



5

In a schlenk tube containing 33mL (6.86mmol) of the solution [$Mo(O)(O_2)_2(H_2O)_n$] 0.208M, 1.32g (13.7mmol, 2eq.) of 3,5-di methylpyrazole was added. The reaction mixture was stirred for 10min in a bath ice. The product, immediatly, precipitates from the solution. After the filtration 1.37g of a yellow powdery solid identificate as [$Mo(O)(O_2)_2(C_5H_8N_2)_2$], **5**, was isolated. Yield: 54%. All the operations were conducted under inert atmosphere of nitrogen because the product decomposes slowly to a brown solid.

^{1}H -NMR ($CDCl_3$)

δ(ppm): 5.81 (s, 1H, CH_{pyr});

2.22 (s, 6H, CH_3)

^{1}H -NMR (D_2O)

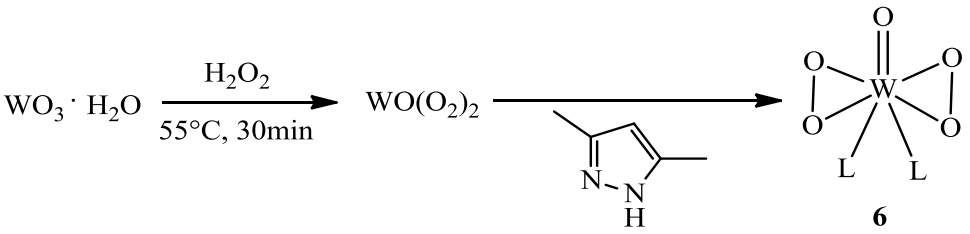
δ(ppm): 6.03 (s, 1H, CH_{pyr});

2.21 (s, 6H, CH_3)

IR (NaCl, nujol) ν (Mo=O): 956 cm^{-1}

ν (O-O): 860 cm^{-1}

4.14.4. Synthesis of [$W(O)(O_2)_2(C_5H_8N_2)_2$] complex (6)



6

(L: 3,5-dimethylpirazole)

In a 100mL flask 2.88g (11.55mmol) of tungstic acid was dissolved in a 35mL of hydrogen peroxide in aqueous solution at 30% . The reaction mixture was stirred for 30 minutes at 55°C thus obtaining a turbid pale yellow solution that was filtered and cooled in a ice bath.[26] At this solution 2.22g (23.1mmol, 2eq.) of 3,5-dimethylpyrazole was added, immediately the formation of a solid from the yellow solution was observed. After few minutes under stirring the precipitate was completely dissolved. The solution rest overnight was clear and colourless. The solvent was evaporated under vacuum to obtain a white solid, **6**, with a yield of 68%.

^{1}H -NMR (D_2O)

δ(ppm): 6.29 (s, 1H, CH_{pyr}),

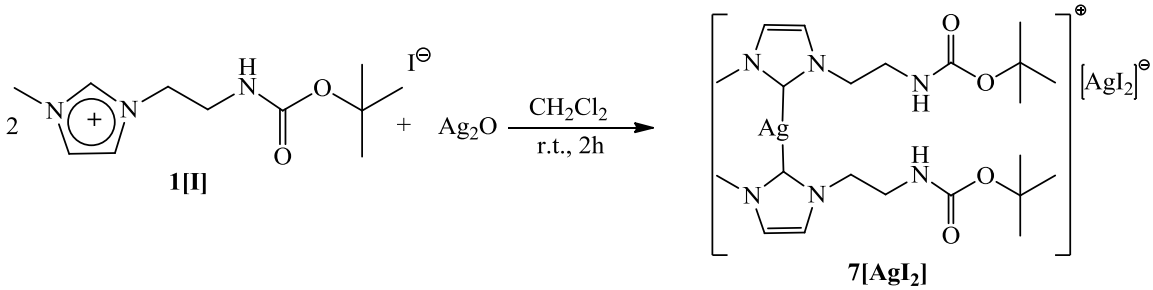
2.36 (6H, CH_3)

IR (KBr) ν (W=O): 980 cm^{-1}

ν (O-O): 886 cm^{-1}

4.15. *N*-Heterocyclic Carbene-molybdenum (VI) Complexes

4.15.1. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver iodide (7[AgI_2])[13]



1[I] **7[AgI_2]**

To a solution of **1[I]** 0.467g (1.32mmol), kept under inert atmosphere and without light, in CH_2Cl_2 (ca. 10mL) stirred in a Schlenck, Ag_2O 0.158g (0.68mmol) was added. The suspension was stirred for 2h, filtered and the solvent removed under vacuum to give 0.63g of a white solid identificated as (1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-ylidene silver iodide, **7[AgI_2]**, in quantitative yield.

^{1}H -NMR ($CDCl_3$)

δ(ppm): 7.00 (s, 1H, CH_{im}), 6.91 (s, 1H, CH_{im});

4.34 (t, 2H, NCH_2);

3.89 (s, 3H, NCH_3);

3.56 (m, 2H, CH_2NHBoc);

1.40 (s, 9H, CH_3).

^{13}C -NMR ($CDCl_3$)

δ(ppm): 184.9 (C-Ag);

157.0 (C=O);

121.7 (CH_{im}), 121.4 (CH_{im});

79.8 (Cq, t-Bu);

50.9 (NCH_2);

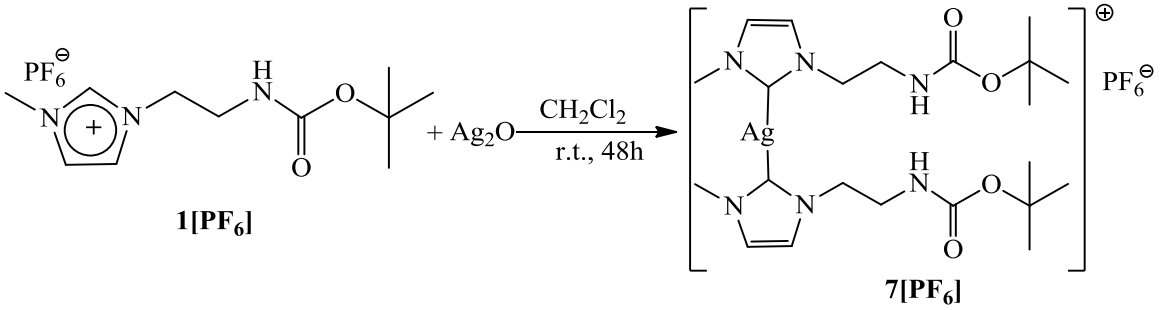
41.4 (CH_2NH);

39.0 (NCH_3);

28.4 (CH_3, t-Bu).

IR (THF) ν (CO): 1716cm^{-1}

4.15.2. Synthesis of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver hexafluorophosphate (7[PF_6])



1[PF_6] **7[PF_6]**

A mixture of 0.50g (1.35mmol) of **1[PF_6]** in 10mL of CH_2Cl_2 and 0.156g (0.68mmol) of Ag_2O was stirred under inert atmosphere and without light for 24h. After this time the conversion of the reagent was not complete, by ^{1}H-NMR spectrum the ratio product:reagent was 1:4, so one equivalent of Ag_2O (0.156g, 0.68mmol) and CH_2Cl_2 (ca. 10mL) was added to the solution and stirred overnight. At the end of the reaction the solvent was removed under vacuum to obtain a white solid identificated as (1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-ylidene silver hexafluorophosphate, **7[PF_6]**, with a quantitative yield.

^{1}H -NMR ($CDCl_3$)

δ(ppm): 7.07 (s, 1H, CH_{im}), 6.98 (s, 1H, CH_{im});

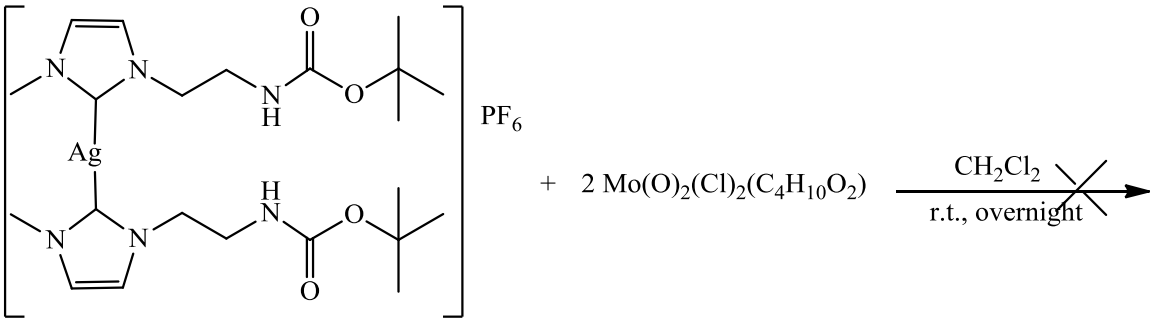
4.26 (t, 2H, NCH_2);

3.85 (s, 3H, NCH_3);

3.52 (m, 2H, C*H*$_2$NHBoc);

1.39 (s, 9H, CH_3).

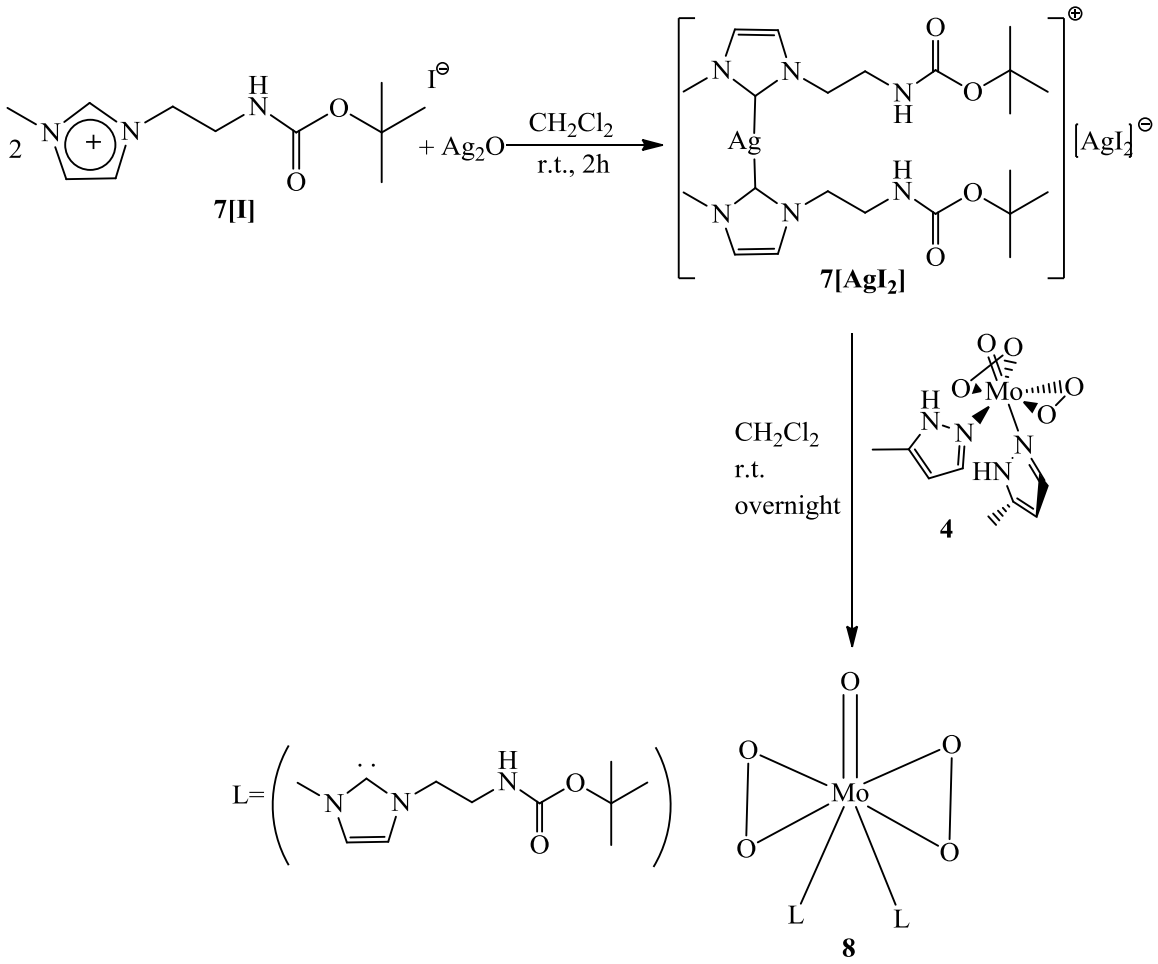
4.15.3. Reaction of 1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methylimidazol-2-ylidene silver with (7[PF_6]) dichloro (1,2-dimethoxiethane) diperoxo molybdenum



7[PF_6]

In a 100mL flask kept under inert atmosphere 0.156g (0.68mmol) of **7[PF_6]** were dissolved in 15mL of CH_2Cl_2 and then 0.39g (1.35mmol) of dichloro(1,2-dimethoxiethane) diperoxo molybdenum in CH_2Cl_2 (ca.20mL) was added. The mixture was stirred at room temperature overnight. The product formation was not observed.

4.15.4. Synthesis of $[MoO(O_2)_2$ (1-(2-*t*-Butoxycarbonylamino-ethyl)-3-methyl-imidazol-2-ylidene)$_2]$ (8)



In a 250mL flask, under inert atmosphere and without light, 0.48g (1.35mmol) of **1[I]** was put in 15mL of CH_2Cl_2 and then 0.16g (67.4mmol) of Ag_2O was added. The reaction mixture was stirred for 2 hours at room temperature to give the product **7[I]**.[12] At the end of the reaction a solution of **4** (0.17g, 67.4mmol) in CH_2Cl_2 (40mL) was added to the reaction mixture. After stirring overnight a white solid was separated from the pale yellow solution. The suspension was filtered and the solvent removed from the filtrate. The waxy yellow solid was washed with petroleum ether and was obtained a dry yellow solid product, **8** or a mixture of **1[I]**, **7[AgI$_2$]** and the product **8**.

Experimental

^{1}H -NMR (CD_2Cl_2)

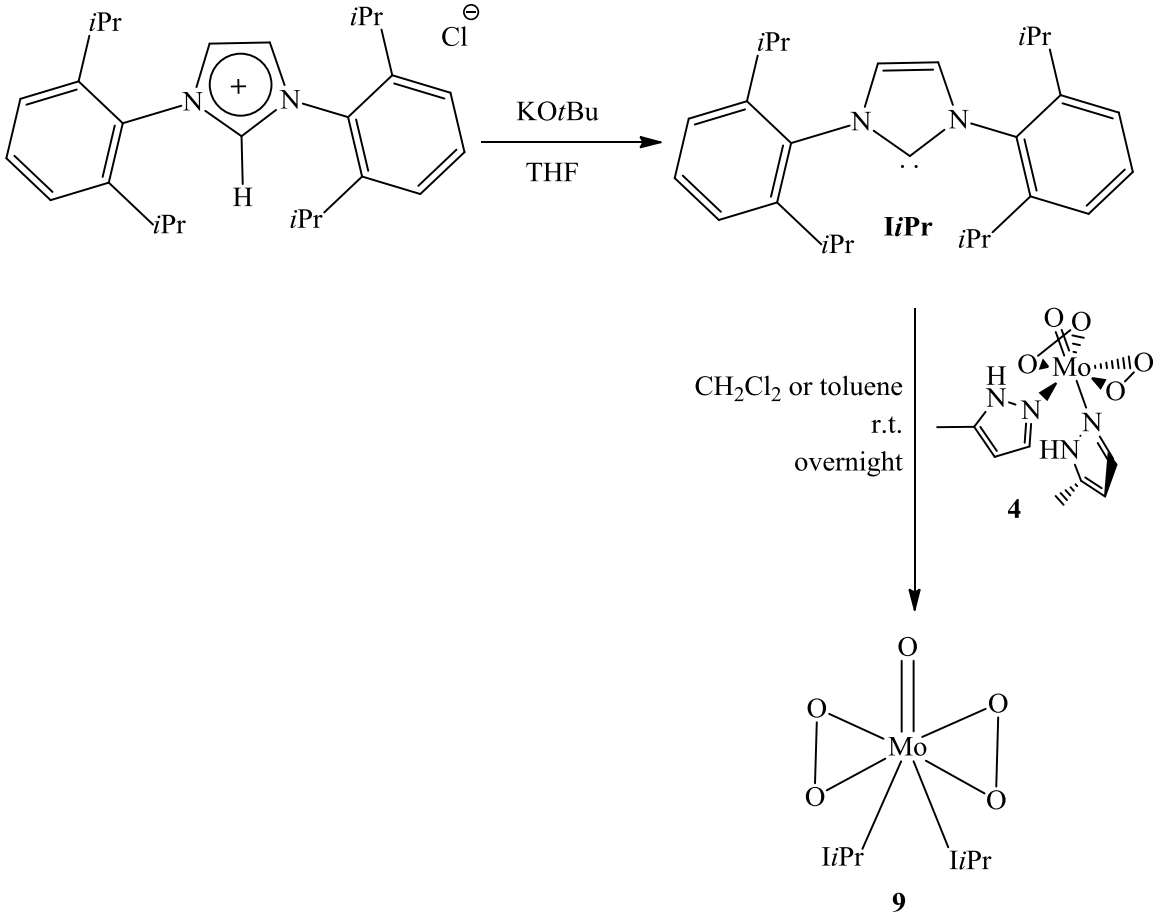
δ(ppm): 7.17 (s, 1H, CH_{im}), 6.93 (s, 1H, CH_{im});
4.32 (t, 2H, NCH_2);
3.74 (s, 3H, NCH_3);
3.24 (m, 2H, C*H*$_2$NHBoc);
1.33 (s, 18H, CH_3);

^{13}C-NMR ($CDCl_3$)

δ(ppm): 181.28 (C-Carbene);
156.85 (C=O);
139.92 (CH, NCHN);
122.55 (CH_{im});
49.59 (NCH_2);
40.90 (CH_2NH);
36.72 (NCH_3);
28.47 (CH_3).

IR (KBr) ν (NH): 3384 cm^{-1}
ν (C=O): 1700 cm^{-1}

4.15.5. Synthesis of $[MoO(O_2)_2$ (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)] (9)



a)

In a 100mL reaction flask under inert atmosphere, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.55g, 1.30mmol) and KO*t*Bu (0.18g,1.64mmol, 1.26eq.) were suspended, in 15mL of dry THF and stirred for 30min. The solvent was removed under vacuum to yield a yellow-orange solid, to this solid 5mL of toluene was added which dissolved most of the material, the solid residue is the excess KO*t*Bu and the unreacted starting material. The mixture was filtered and dried *in vacuo* to yield I/*i*Pr as a flocculent white solid. This solid was dissolved in the minimum amount of CH_2Cl_2 and then was added a solution of **4** (0.17g, 63mmol) in dry CH_2Cl_2 (40mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum and washed with pentane to obtain a pale brown solid containing mixture of products: the unreacted imidazolium salt and trace of **9**.

IR (KBr, cm^{-1}): 3422, 3153, 2965, 2929, 2871, 2374, 1653, 1534, 1458, 1388, 1365, 1331, 1260, 1205, 1182, 1102, 1061, 887, 808, 760, 684, 539, 441

b)

In a 100mL reaction flask under inert atmosphere, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.55g, 1.30mmol) and KO*t*Bu (0.18g,1.64mmol, 1.26eq.) were suspended, in 15mL of dry THF and stirred for 30min. The solvent was removed under vacuum to yield a yellow-orange solid, to this solid 30mL of toluene was added which dissolved most of the material, the solid residue is the excess KO*t*Bu and the unreacted starting material. The mixture was filtered and moved to a clean reaction flask, then 0.44g (1.3mmol) of **4** was added as a yellow crystalline solid. The reaction mixture was stirred overnight at room temperature. At the end of the reaction an orange solid was observed at the bottom of the flask. The solution was removed by cannula, the solid was dried under vacuum and dissolved in dry acetonitrile. From the solution the precipitation of little yellow crystals of **9** was observed.

^{1}H -NMR (CD_3CN)

δ(ppm): 7.88--7.49 (CH_{arom});
2.45 (sept, 1H, CH, J = 6.9Hz);
1.3 (d, 3H, CH_3, J = 6.9Hz);
1.23 (d, 3H, CH_3, J = 6.9Hz).

IR (NaCl, nujol) ν (CH_{arom}): 3153 cm^{-1},3119 cm^{-1},3080 cm^{-1}
ν (Mo=O): 956 cm^{-1}

4.16. General procedure of catalytic olefin epoxidation

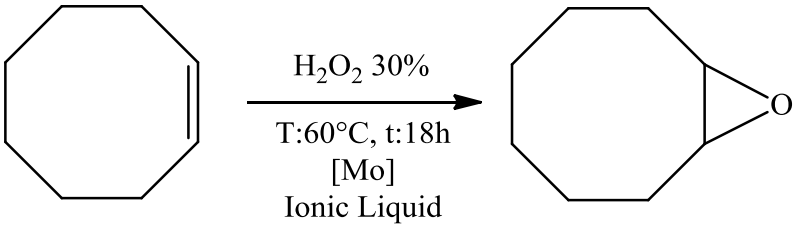
All tests were performed in glass ampoules of 50mL equipped with a Young valve and cointaining a stirrer. The component were charged into the ampoule in order: the solvent, the nitrogen ligand, the olefinic substrate, the catalyst/precursor of molybdenum and the oxidant in the specified amounts. Then, the vial was sealed and heated to the specified temperature, maintaining costant stirring in a thermostatted oil bath for the duration of the reaction. When the reaction was completed, the reactor was cooled in an ice bath for 5min to avoid the possibility of losing a significant amount of volatile products. The products was extracted with diethyl ether (3x5mL) or hexane (5x5mL) and then analyzed by gas chromatography (GC). The solution extracted with diethyl ether was dried with $MgSO_4$ to remove the water in. Once prepared the solution in the extraction solvent in a 25mL volumetric flask with a standard compound, a litte amount of this solution was moved to a vial and analyzed by GC using an appropriate program for the corresponding analytes (the Galaxy Workstation software).

In these tests the ionic liquids were used as reaction solvents, due to their high viscosity they should be added with a syringe. As catalysts were used oxodiperoxomolybdenum complexes, $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ (**4**) and $[Mo(O)(O_2)_2(C_5H_8N_2)_2]$ (**5**) or catalyst complex was formed *in situ* by the reaction of a precursor (aqueous solution of $[Mo(O)(O_2)_2(H_2O)_n]$) with the *N*-donor base additive (3,5-dimethylpyrazole); as oxidant was used hydrogen peroxide in aqueous solution at 30%.

4.16.1. Recycling the [Mo]-IL mixture

In some tests the ionic liquid and the catalyst were reused in subsequent catalytic cycles. Recycling the system could lead to several advantages such as a better turnover number (TON) and atom economy (AE). In these experiments, after the extraction of the product, all the oxidant residues, byproducts and solvents were removed, before to add again the oxidant and the fresh substrate. The oxidant hydrogen peroxide was removed easily under vacuum at 60°C for one hour.

4.16.2. Catalytic epoxidation of *cis*-cyclooctene in ionic liquid with $[Mo(O)(O_2)_2(H_2O)_n]$ as a catalytic precursor



The reactor (a 50mL ampoule equipped with a Young valve and containing a stirrer) was charged with the compounds in the following order:

- Reaction solvent: ionic liquid → 2.0 mL
- *N*-donor base additive: 3,5-dimethylpyrazole → 4.0 mg (0.05 mmol, 2.0 eq.)
- Olefin Substrate: *cis*-cyclooctene → 137 µL (1.0 mmol)
- Catalyst: $[MoO(O_2)_2(H_2O)_n]$ → 140 µL (0.025 mmol)
- Oxidant: H_2O_2 30% → 340 µL (3.0 mmol)

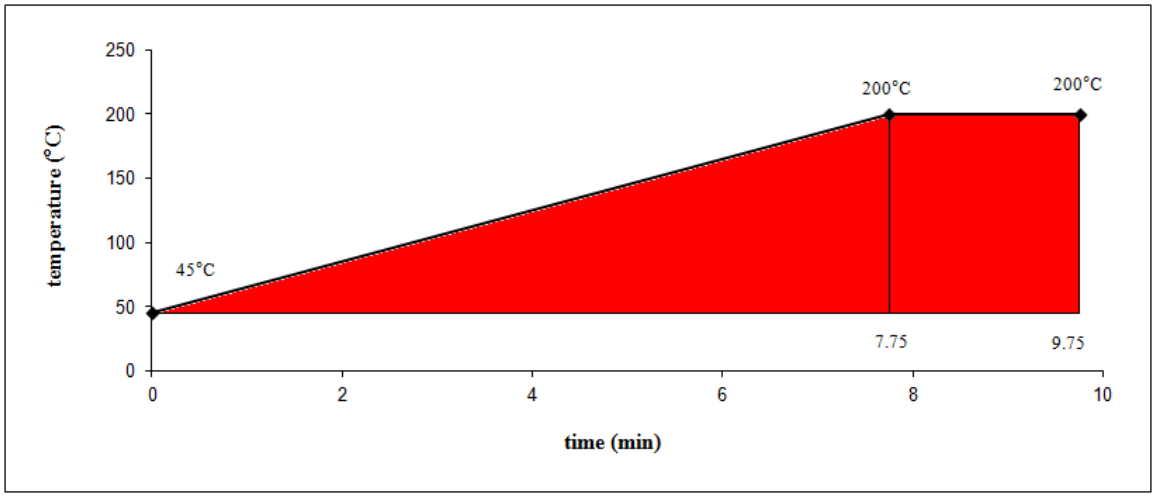
Here the catalyst was formed *in situ* from the catalytic precursor and the *N*-donor base. The mixture was stirred for 18h at 60°C. At the end of the reaction the ampoule was cooled at 0°C and after the product was extracted with apolar solvents like diethyl ether and hexane. Initially the extraction was performed with diethyl ether (3x5mL), and dried with $MgSO_4$ to remove the water in. Subsequently hexane (5x5mL) was used as extraction solvent because some ionic liquids synthesized have a counterion (NTf_2, NO_3) which makes them partially soluble in diethyl ether. However the extraction with hexane has the disadvantage to be long and laborious because the product transfer from the liquid ionic to the solvent is very slow. The organic layer was placed in a 25mL volumetric flask and the standard compound (50µL of dodecane) was added, then it was analyzed by GC using an appropriate method.

Hereafter the parameters and the temperature range (Graphic 2) used in the method for analyze the *cis*-cyclooctene oxidation are shown:

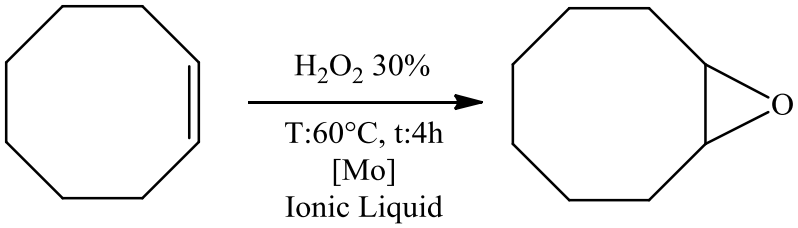
- Injection volume: 0.6µL
- Analytes: *cis*-cyclooctene (t: 4.6min) / oxide of *cis*-cyclooctene (t: 6.3min)
- Standard compound: dodecane (t: 5.8min)
- Column flow: 1mL/min

Rate (°C/min)	T (°C)	t (min)	Total (min)
Initial	45	0.00	0.00
20	200	2.00	9.75

Graphic 2: Temperature ramp versus time for *cis*-cyclooctene.



4.16.3. Catalytic epoxidation of *cis*-cyclooctene in ionic liquid with $[Mo(O)(O_2)_2(C_4H_6N_2)_2]$ (4) as a catalyst



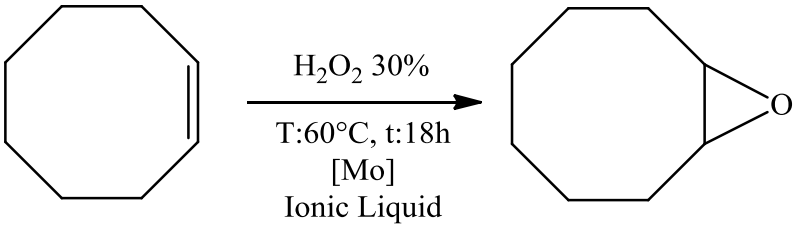
The reactor was charged with the compounds in the following order:

- Catalyst: $[MoO(O_2)_2(C_4H_6N_2)_2]$ (**4**) → 9.0 mg (0.025 mmol)
- Reaction solvent: ionic liquid → 2.0 mL
- Oxidant: H_2O_2 30% → 340 µL (3.0 mmol)
- Olefin Substrate: *cis*-cyclooctene → 137 µL (1.0 mmol)

The mixture was stirred for 4h at 60°C. Then it was cooled and extracted with hexane in the same procedure described in the previous paragraph. Also here the standard compound was dodecane.

The analyse method was the same of the Graphic 2.

4.16.4. Catalytic epoxidation of *cis*-cyclooctene in ionic liquid with [**Mo(O)(O$_2$)$_2$(C$_5$H$_8$N$_2$)$_2$**] **(5) as a catalyst**



- Reaction solvent: ionic liquid → 2.0 mL
- Catalyst: [MoO(O$_2$)$_2$(C$_5$H$_8$N$_2$)$_2$] (**5**) → 9.0 mg (0.025 mmol)
- Olefin Substrate: *cis*-cyclooctene → 137 µL (1.0 mmol)
- Oxidant: H$_2$O$_2$ 30% → 340 µL (3.0 mmol)

The whole procedure is the same as described above, the only one difference is that here the catalyst was charged already formed. The GC analysis use the same method (Graphic 2).

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