# PRODUCTION OF CARBONATE FROM $CO_2$ OR DIOLS

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Thesis to obtain the Master of Science Degree in

## Chemical Engeneering

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# DEDICATION

Dissertation dedicated to my family, in special to my parents João Centeio Lopes and Inês Centeio Lopes, and my siblings for their endless support, love and the enormous effort to my advantage. Also dedicated to my friends and that became my family all these years in this beautiful country.

Special thanks to my supervisors Dr Ana Paula Ribeiro and Professor Luísa Margarida Martins and all the laboratory and office colleagues for their guidance and lessons.

I couldn't do this without all you and your support.

Thank you all!

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## Abstract

$CO_2$ conversion into fine chemicals has attracted attention lately as one of the measures to reduce the global warming effects. Several catalysts and catalytic processes have been developed to convert $CO_2$ into different chemicals.

In this work, we use two approaches to convert $CO_2$ in carbonates. The first one was its direct use to transform styrene oxide and propylene oxide in carbonates and the second approach was the use of urea and diols to produce carbonates and ammonia. The ammonia can be treated with $CO_2$ to produce urea. In both cases, were used four different catalyst, three ferrite and one C-scorpionate, obtained conversions up to 100%. In the second the use of microwaves is a new feature that promotes a decrease in costs, which is a benefit to the process. The green metrics of both processes are calculated to understand the sustainability of the process.

# PRODUCTION OF CARBONATE FROM $CO_2$ OR DIOLS

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## Resumo

A conversão de $CO_2$ em produtos químicos atraiu atenção ultimamente como uma das medidas para reduzir os efeitos do aquecimento global. Vários catalisadores e processos catalíticos foram desenvolvidos para converter $CO_2$ em diferentes produtos químicos.

Neste trabalho, usamos duas abordagens para converter $CO_2$ em carbonatos. O primeiro foi seu uso direto na transformação de óxido de estireno e óxido de propileno em carbonatos e a segunda abordagem foi o uso de ureia e dióis na produção de carbonatos e amónia. A amónia pode ser tratada com $CO_2$ para produzir ureia. Nos dois casos foi usado quatro catalisadores diferentes, três ferrites e um C-scorpionato, obtivendo conversões de até 100%. No segundo, o uso de micro-ondas é um novo recurso que promove uma diminuição nos custos, o que é um benefício para o processo. As métricas de química verde de ambos os processos foram calculadas para entender a sustentabilidade do processo.

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# NOMENCLATURE

| | |
|---:|:---|
| ABS | Acrylonitrile butadiene styrene |
| BPA | Bisphenol A |
| BuBr | 1-bromobutane |
| $Bu_3N$ | Tributylamine |
| CCH | *cis*-1,2-cyclohexanediol |
| DMC | Dimethyl carbonate |
| DPC | Diphenyl carbonate |
| $E_\alpha$ | Activation energy |
| EC | Ethylene carbonate |
| EG | Ethylene glycol |
| EO | Ethylene oxide |
| IPCC | Intergovernmental Panel on Climate Change |
| k | Reaction rate constant |
| MeOH | Methanol |
| MP | 3-mercapto-1,2-propanediol |
| PC | Polycarbonate |
| PET | Polyethylene terephthalate |
| PhOH | Phenol |
| PMMA | Poly(methyl methacrylate) |
| PO | Propylene oxide |
| R | Gas constant |
| SO | Styrene oxide |
| TBABr | Tetrabutylammonium bromide |
| TCH | *trans*-1,2-cyclohexanediol |
| TOF | Turnover frequency |
| TON | Turnover number |
| UN | United Nations |
| $[FeCl_2(Tpm)]$ | Iron(II) C-scorpionate complex |

# Chapter 1

# INTRODUCTION

## 1.1 Global warming, a $CO_2$ problematic

The global warming is caused by greenhouse gases, especially $CO_2$ because of its greenhouse nature and the large amount emitted to the atmosphere, but also by other gases such as methane, nitrous oxide or chlorofluorocarbons, that are present in the atmosphere. Those gases can stay in the atmosphere for years, or even centuries and work as a heat trap, as they absorb sunlight and solar radiation bounced from the earth's surface that is supposed to escape to space, what causes the planet's average temperature to increase. That why it is also known as the greenhouse effect. Global warming is a serious problem with countless possible consequences. Scientists predict social, environmental, economic and health consequences if the actual trends continue. Problems like, melting glaciers, droughts, early snowmelt, extreme weather changing and wildfires that would threaten many species and their natural habitat, and exacerbate the water shortages situation. Rising sea, flooding threatening seaboard cities and an unpredictable number of human life. New pests causing troubles at agricultural and at fisheries level, infectious diseases, air pollution, favourable conditions for pathogens and mosquitoes are other issues to face [1, 2].

There are some controversial around the subject since there are climate change deniers and supporters of the theory-based in a slow down at the rate of increase of the temperature in the last years. Studies involving the comparison of atmospheric samples contained in ice cores evidence that the Earth's climate has changed throughout history, with glacial advance and retreat. Those changes have been related to a small variation of Earth's orbit. Data obtained lately provides evidence that atmospheric $CO_2$ has increased since the Industrial Revolution achieving values never seen before. Studies show that humans activities have major contributions to the actual climate state. Several studies show that over the past 50 years the average global temperature has increased at the fastest rate ever recorded (see Figure **1.1**) and almost every one of the hottest years ever recorded by NASA occurred in this century, and 2016 was the hottest year ever recorded [3]. In May 2013, the daily concentration of $CO_2$ in the atmosphere at Mauna Loa Observatory in Hawaii surpassed 400 parts per million for the first time in human history [4]. With all those studies it is evident that behavior change is needed to revert the current situation, and some measures have been tacked. In December 2015, at the 21st Conference of the Parties (COP21), 195 nations adopted the Paris Agreement. The Intergovernmental

Panel on Climate Change (IPCC) set as a goal to keep the warming under 2ºC above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5ºC above pre-industrial levels [3]. UN report at the end of 2018, set that at 2030 the emissions level needs to be 25% to 55% lower than it was in 2017. Studies indicate that reducing greenhouse emissions won't be enough to avoid severe warming, even if countries manage to reduce emissions to the desired values. The main contributors to polluting the air are fossil fuels and coal-burning plants to produce electricity and heat; other sectors like transportation, industry sector or agriculture and other land usage have a large contribution. In terms of countries, China and the USA are the major contributors, with about 28% and 16% of the global $CO_2$ emissions, respectively. European Union and India are significant contributors [2].



**A World of Agreement: Temperatures are Rising**
Global Temperature Anomaly (°C)

NASA Goddard Institute for Space Studies
Berkeley Earth
Japanese Meteorological Agency
NOAA National Climatic Data Center
Met Office Hadley Centre/Climatic Research Unit
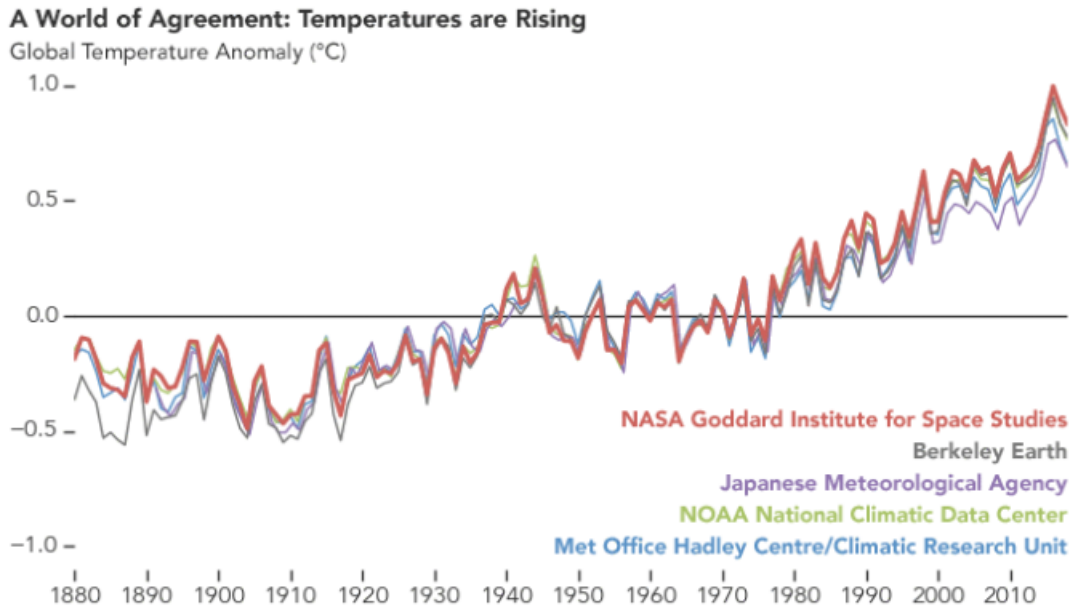
Figure 1.1: Evolution of Earth's average temperature over the years by several entities [3].

There are no magical solutions to solve climate change, but there are a bunch of things that we can do, that together will solve the problem or at least reduce the consequences. It is necessary to raise awareness about the problem, the acts that contribute to its aggravation to be avoided and about the behavior to be adopted to reduce it. Among the measures, there are four considered more important and significantly: i) Reduction of energy consumption by increasing its efficiency; ii) Replacement of fossil fuels with renewable energy sources; iii) $CO_2$ capture and storage; iv) $CO_2$ capture and usage [5]. But other measures can have significant contributions, such as protecting forests, set a price in greenhouse emissions or reduce, reuse and recycle waste [1]. While capture and storage of $CO_2$ is at the moment the most efficient measure to reduce the $CO_2$ of the air, capture, and utilization of $CO_2$ is the most promising not only to reduce the $CO_2$ of the air but also in the production of chemicals with additional value. There are scientists and companies working in alternatives fuels, for example, hydrogen usage, or in batteries to store renewable energy, or capture the $CO_2$ from power plants and other sources to storage underground or use it as starting material to produce more valuable products like gasoline or plastics, others argue on water and toxic waste usage, or nuclear

power should be part of the solutions. Those measures would make a big impact on greenhouse gas emissions since $CO_2$ conversion process to fine chemicals can be part of the solution as carbon feedstock [1, 6].

Focusing on the use of $CO_2$ as the starting material, there have been reported a significant number of successful processes to convert $CO_2$ into different chemicals such as methanol, methylamines, formic acid derivatives, cyclic carbonates, urea, etc [5–9].

## 1.2   Sustainable and green chemistry, $CO_2$ as a starting material

Back in the latte's 1990, with acknowledgment of the climate change problematic, companies worldwide adopted the green chemistry concept, that is based in the following twelve principles [10]:

 I. **Prevention** – prevent waste instead of treating or cleaning up after created.

 II. **Atom Economy** – design methods to maximise the incorporation of all materials into the final product.

 III. **Less Hazardous Synthesis** – design methods to avoid or reduce toxic substances to humans and the environment.

 IV. **Design Benign Chemicals** – design chemicals to preserve the efficacy of function while reducing toxicity.

 V. **Benign Solvents & Auxiliaries** – auxiliary substances made unnecessary (if possible) and innocuous when used.

 VI. **Design for Energy Efficiency** – ambient temperature and pressure preferred. Reduce energy's environment and economic impacts.

 VII. **Use of Renewable Feed stock** – renewable source rather than depleting if technically and economically practicable.

 VIII. **Reduce Derivatives** – avoid/reduce unnecessary privatisation.

 IX. **Catalysis (vs. Stoichiometric)** – catalytic reagents, as selective as possible.

 X. **Design for Degradation** – design products with innocuous degradation.

 XI. **Real-Time Analysis for Pollution Prevention** – Analytically methodologies need to be further developed to allow for real-time, in-process monitoring and control before the formation of hazardous substances.

 XII. **Inherently Benign Chemistry for Accident Prevention** – chose processes that minimise potential accidents.

In 1969, Inoue and co-workers discovered that propylene oxide (PO) polymerises in the presence of $CO_2$ and $ZnEt_2/H_2O$ [11]. After that, a large effort was made all over the world to develop a catalyst and catalytic process that allow the use of $CO_2$ to produce fine chemicals at an industrial level. Many catalysts were found to form only cyclic carbonates, others to form only PC and others both cyclic carbonates and PC but none of those efforts achieved sufficient reproducibility and high turnovers to be implanted at industrial scale. It wasn't until 2002, that Asahi Kasei corp announced the first successfully non-phosgene industrial

process to produce PC from $CO_2$. Later, the company announced five factories producing PC using the Asahi Kasei process, wherein four were already working, in Taiwan, initially with a capacity of 50 kton/year were increased to 150 kton/year, two factories in Korea and one in Russia with 65 kton/year each. The fifth one was predicted to start in 2010 with a capacity to produce 260 kton/year in Saudi Arabia. This new process consists of three process steps to produce the monomer. First to produce ethylene carbonate (EC) from ethylene oxide (EO) and $CO_2$; then to produce dimethyl carbonate (DMC) and ethylene glycol (EG) as a side product from EC and methanol (MeOH); and the last one to produce diphenyl carbonate (DPC) and MeOH as a side product from DMC and Phenol (PhOH). The polymerization step occurs by the reaction between DPC and bisphenol A (BPA). All the side products but EG are recycled. The EG produced is highly pure and it can add value, see Figure **1.2**. Until then, PC ware produced using a process called the "phosgene process" that uses CO as row material. The phosgene process (see Figure **1.3**) has drawbacks like phosgene usage, since it's toxic and corrosive what made the process dangerous and it reflected in the equipment's corrosion and increases process cost, a large amount of solvent usage and wastewater to treat, high toxic CO usage or chlorinate impurities in the final product and risk of chlorinated compounds leakage. Almost all of the phosgene industrial processes were carried out in systems with two immiscible phases, mostly water and a chlorinated organic solvent such as dichloromethane. The sodium salt of BPA dissolved in water reacts in the interface with the phosgene dissolved in the organic phase under strong agitation. Normally the process is carried out in two steps where the first step is the phosgenation of the sodium salt of BPA to produces chloroformates of BPA and the second step is the polycondensation of the chloroformates to produce PC in presence of a catalyst, usually a tertiary amine or a quaternary ammonium salt. The Asahi Kasei corp process not only manages to overcome the weakness of the phosgene process, but it also improves some properties of the PC, allows the reduction of $CO_2$ emission and achieves resource and energy conservation [5, 12–14].
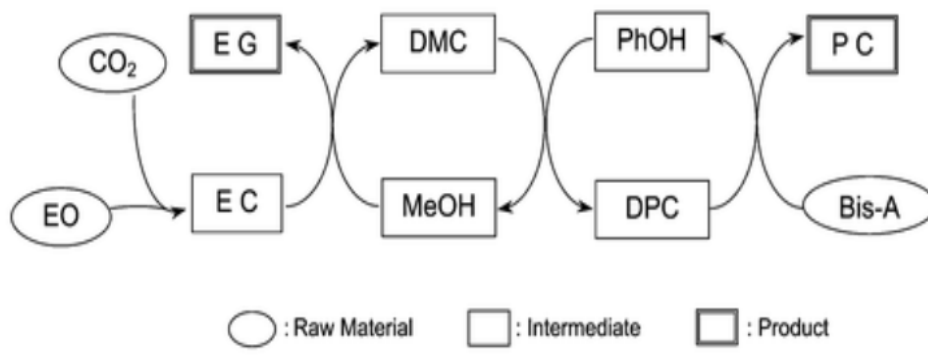


Figure 1.2: Asahi Kasei's phosgene free process for PC production [12].

It inspired many companies to embrace cleaner and more efficient technologies, to achieve a cleaner and healthier environment, to the development of many studies and industrial process that reduce the $CO_2$ release and processes that uses $CO_2$ as raw material, allowing to turn a problematic situation into an economical profit, once $CO_2$ is readily available, non-toxic, non-flammable and a cost-efficient raw material. This alternative method using $CO_2$ is attractive for cyclic compounds such as cyclic carbonates, cyclic carbamates, and cyclic ureas since conventionally they are produced from methods that use toxic and hazardous reagent like phosgene and they have a large range of applications both in organic synthesis and industry.
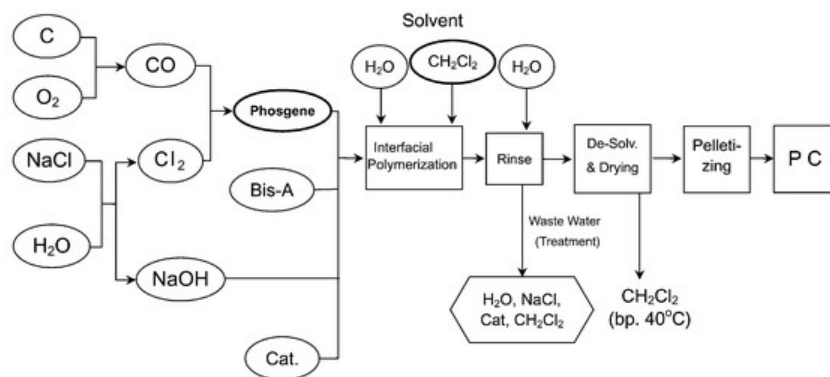
Figure 1.3: Phosgene process for PC production [13].

For instance, cyclic carbonates, in particular, five-membered ones, can be used as a polar aprotic solvent, industrial lubricants, electrolytes in lithium secondary batteries, synthetic building blocks, monomers to product Polycarbonate (PC) and others fine chemicals. They present other characteristics that make them the target of interest, such as high boiling and flashpoints, low toxicities, odour levels, and evaporation rates. They are also soluble in a large range of solvents and biodegradable. Besides they can be produced in different routes that directly, see Figure **1.4**, or indirectly uses $CO_2$. There are reports of methods using $CO_2$ and epoxides [4, 15–17], $CO_2$ and diols [5, 6], $CO_2$ with propargyl alcohols [8], and reaction of urea with diol [4, 18, 19].
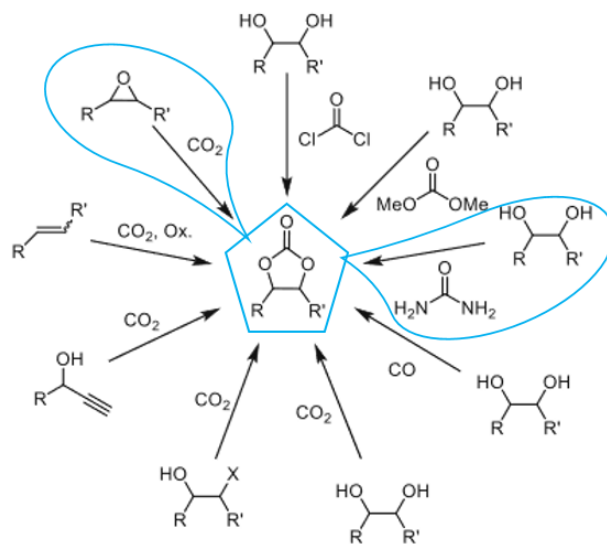


Figure 1.4: Example of different processes to produce a cyclic carbonate, pointing out the ones used in this work [4].

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## 1.3  Brief review in Polycarbonate industries

It's reported that Polycarbonate was invented by Dr Hermann Schnell of Bayer in 1953, no long before chemist Dr Daniel Fox of Germany also invented the same material while developing new wire insulation material [20]. PC, also know by Lexan®, Makrolon®, Makroclear® and so on, was introduced commercially by Bayer in 1958 and later, in 1960 by General Electric Company (GE) of The United States. Then, companies like Teijin Chemicals (1960), Idemitsu Petrochemicals (1960), Mitsubishi Gas Chemical (1961) or later DOW Chemical (1985) start to produce PC all of them using the phosgene process. Nowadays large quantities of PC are produced all over the world with different processes of production and different grades, according to its application. Almost all the PC is produced by Bayer is now know as Covestro, GE is now known as SABIC, Teijin, Idemist, and DOW. It is one of the most used polymers in the plastic industries due to it's physical, chemical and mechanic properties. PC have a large range of applications from biomedical since they are biodegradable and biologically inert, like eyewear plastic lenses, automobile, roof in construction, protection such as bulletproof glass and enclosures inside the bank or protective gear, electronics such as cell phones, personal computers and cameras and so on. Those properties are controlled by the functionalities of the backbones and side groups which can be aromatic, aliphatic or alicyclic. PC is an amorphous thermoplastic that allows design freedom and the possibility of recycling over and over without significant degradation. It's naturally transparent but commercially available in different colours, translucent or not. It's especially used at the applications when impact Resistance or transparency is required, it's also heat resistant that allows it to be used in flame-retardant material. PC shows excellent compatibility with certain polymers. Therefore, it is widely used in blends such as PC/ABS, PC/PET or PC/PMMA. It is reported that in 2016 the global production capacity of PC overcome 5 Mtons and the market was valued at US \$13 billion. Due to increasing demand in different sectors, is expected that the market value keeps growing reaching US \$17 billion and the demand approach 6 Mtons by 2020 [12, 13, 20].

## 1.4  Work's main objectives

The main objective of this work is the chemical fixation of carbon dioxide through catalytic reactions using iron catalysts. The work consists of two different phases, the first one is the direct use of $CO_2$ and epoxides, such as propylene oxide or styrene oxide for the synthesis cyclic carbonates, and the second is the use of diol and urea, that can be produced by $CO_2$ and ammonia, to produce cyclic carbonate. Synthesis by green methods such as microwave will be used. The use of characterisation techniques such as NMR, FT-IR or XDR to characterise catalysts synthesised or the products of reactions is another aspect to consider.

# Chapter 2

# CATALYSTS

## 2.1 Brief introduction

A chemical process to be implemented at the industrial level, the reactions need to be fast and selective, characteristic that most of the reaction with industrial interest hasn't. Here, where catalyst rule takes place since the introduction of catalysts in the process allows the process to take a different path energetically favourable usually by decreasing the activation energy, see Figure **2.1**. This leads to an increase in the reaction velocity allowing to save time and reduce energy usage. It also increases the selectivity and reduces the amount of waste produced in the process by increasing the velocity of the formation of the desired product.
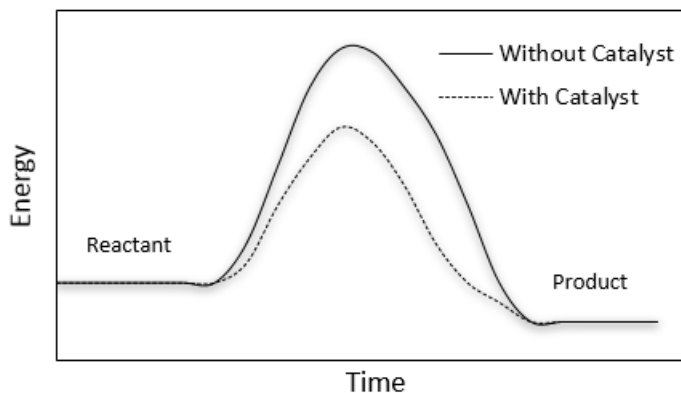


Figure 2.1: Schematic comparison between activation energy of reactions with and without catalyst.

The largest difficulty in $CO_2$ conversion is it's high kinetic and thermodynamic stability because it contains carbon in it's highest oxidation state and to be used as a starting material it requires the input of a large amount of energy. So there are, so far, reduced numbers of successfully developed processes using carbon dioxide as a chemical feedstock at the industrial level. There are two different approaches to convert $CO_2$ into fine chemicals. One is the reductive $CO_2$ conversion that requires a large amount of energy and quite

powerful reducing agents such as $H_2$ and it's used to produce chemicals like methanol or formic acid and so on. The other one is non-reductive and it doesn't involve exchange large quantities of energy since it is either moderately endothermic or exothermic, it conserves the oxidation state of the carbon of $CO_2$ (+4) and it's widely used to produce products like carbonates, polycarbonates, urea, polyurethanes carboxylates, carbamates and so on [5]. To overcome the $CO_2$ kinetic stability, catalyst and catalytic processes have been developed to quickly achieve the reaction equilibrium allowing the reaction to take place under softer conditions. The ideal catalyst must be cheap, effective and environmentally friendly. Both heterogeneous and homogeneous catalysts can be used to convert $CO_2$, but heterogeneous catalysts present advantages in terms of product separation, catalyst recovery, and cost. So there are efforts to replace the homogeneous catalyst by heterogeneous ones and to develop new and more efficient heterogeneous catalysts.

Catalysis is a phenomenon know since the beginning of human history since it is responsible for the fermentation of sugar to produce alcohol or in the bread production process still used today, although it's theory or characteristics weren't known in the beginning. Only later in the 18th century, scientists started to understand the phenomenon and its characteristics. The term catalysis was first used by Jacob Berzelius back in 1836 to describe the rule of leaven in the process to produce alcohol and other compounds that a presence of a small quantity is capable to initiate decomposition and synthesis processes. In 1895, Wilhelm Ostwald defined catalyst as a substance that alters the chemical velocity of a reaction without being consumed itself [21, 22]. Nowadays catalysis is essential to energy conversion, chemical manufacture, and environmental technology. The importance of catalyst used is evidently if you look at the numbers that show us that about 85% of all chemical industries including pharmaceutical industries use catalysts [21]. It is also used in other fields such as environmental pollution control including exhaust converter in vehicles, catalytic reduction processes of nitrogen oxides and catalytic combustion of volatile organic compounds. It is widely used in the biological process known as enzyme. In the economy point of view, although the catalyst sales comprise a significant market, the economic impact of catalysts is amplified by their use. The margin obtained by catalyst usage is, generally, a multiple of the catalysts costs. Studies indicate that catalysts sales overcome 1500 billion US$ per year. From the environmental point of view, the use of catalyst is related to the reduction of energy and raw materials needed. Some products can't be obtained without catalyst usage. It is expected that the importance of catalyst keeps growing shortly as the raw materials diversify and alternative energy sources and use come to play [21, 23].

In this dissertation, a few catalysts are tested. Ones synthesised during this work and others previously synthesised.

## 2.2 Preparation of catalysts

One issue of catalyst usage is its separation from the products at the reaction's end. Magnetic catalysts are an option that may help to overcome this issue leading to an easy separation between catalyst and product. Because of the increasing interest in the implementation of green chemistry principles, iron-based catalysts have been widely employed in organic synthesis in recent years, since some of the characteristics of the iron-based catalysts are low cost and environmentally benign and iron is the most abundant transition metal in our planet [24]. In this dissertation, three iron(II) based magnetic catalyst was prepared and tested for the

different reactions.

Three catalysts were prepared in this dissertation:

I. Nickel ferrite ($NiFe_2O_4$) - From nickel(II) chloride hexahydrate.

II. Copper ferrite ($CuFe_2O_4$) - From copper(II) chloride dihydrate.

III. Manganese ferrite ($MnFe_2O_4$) - From manganese (II) chloride tetrahydrate.

To prepare the catalysts, three solutions were prepared:

I. Solution 1 - 25 mL of solution 0.4 M of iron(III) chloride.

II. Solution 2 - 25 mL of solution 0.2 M of each metal chloride.

III. Solution 3 - solution 3 M of sodium hydroxide.

The solutions 1 and 2 were mixed under agitation and oil bath to guarantee the temperature of 50 °C. Drop by drop the solution 3 was slowly added to the mixture. The addition of solution 3 leads to precipitation. Solution 3 was added until the pH value approaches 12. Then, four/five drops of oleic acid were added, and the mixture was resting in the oil bath with agitation for approximately 1 hour to complete the reaction. The mixture was cooled to room temperature, filtered under vacuum and washed with water and ethanol. The solid was left overnight in the stove to dry.

After dry, the solids didn't present(or present a small) magnetic behaviour. Thermal treatment was performed, with the catalysts in a muffle for 6 hours at a temperature of 600 °C. After the thermal treatment, all three catalysts present magnetic behaviour.

The other type of catalyst used is the C-scorpionate complexes. The C-scorpionate complexes are molecules composed by three pyrazolates, where one atom of nitrogen of each pyrazolate bonds with the carbon and the other nitrogen atom bonds to the metal in three adjacent vacant positions of the coordination sphere, just like a scorpion that uses two claws and one sting to attack the prey inspiring the name C-scorpionate complex, see Figure **2.2**.
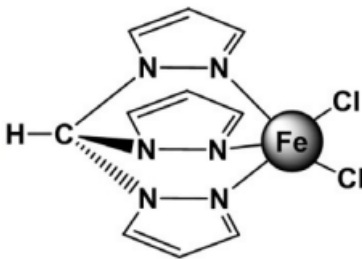


Figure 2.2: Example of a C-scorpionate complex structure, in this case $[FeCl_2(Tpm)]$; Tpm $= HC(pz_3)$; and pz $=$ pyrazolyl [25].

There been reported C-scorpionate complexes prepared using different metals such as iron, nickel, copper, palladium, zinc, rhenium, vanadium, and so on. Different reactions types are performed using those C-scorpionate complexes including cycloaddition, hydrocarboxylation of cyclohexene in the presence of CO,

synthesis of methanol from $CO_2$ and $H_2$ or oxidation of alkanes and alcohols. They reported high activity and selectivity under mild conditions that attracted the attention to test it to these reactions [25–32]. In this work we have used the iron(II) C-scorpionate complex $[FeCl_2(Tpm)]$; Tpm $= HC(pz_3)$; and pz $=$ pyrazolyl.

## 2.3   Catalyst characterization

Catalyst characterisation is very important in the development of catalysts and optimisation of processes. It leads to a better understanding of catalysts and explanation of relations between catalyst properties and catalytic activities. Structure, elemental composition and chemicals properties are important properties that characterise catalyst and several catalyst characterisation techniques have been developed lately with the evolution of computers and others technologies alongside with the need to better understanding of catalysts and the emergence of new catalysts [33, 34].

### 2.3.1   Nickel ferrite

**XRD study**

The powder X-ray pattern recorded for the sample of $NiFe_2O_4$ is shown in Figure **2.3**. It is consistent with the standard pattern cubic spinel structure of bulk $NiFe_2O_4$ JCPDS (Card No. 10-0325). The lattice parameter of $NiFe_2O_4$ is a $= 8.339$ Å. Extra reflections are not detected in the X-ray diffraction pattern.
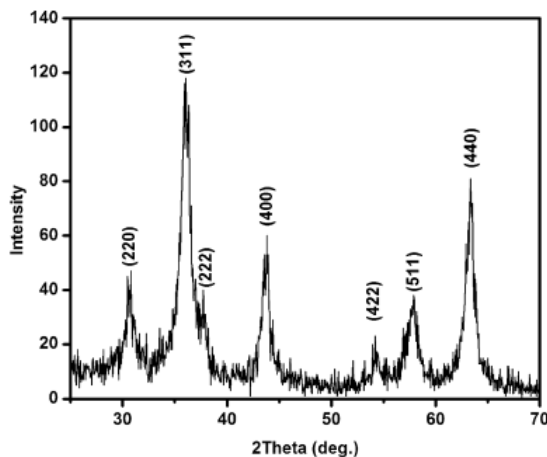


Figure 2.3: Powder XRD pattern of the nickel ferrite sample.

**FT-IR study**

The formation of spinel $NiFe_2O_4$ structure is further supported by FT-IR spectrum shown in Figure **2.4**. The bands at 563 cm$^{-1}$ and 474 cm$^{-1}$ represented tetrahedral and octahedral modes of $NiFe_2O_4$, respectively. The band located at 3399 cm$^{-1}$ can be attributed to the symmetric vibration of –OH groups. The bands with peaks observed at 1045 cm$^{-1}$ can be assigned to O–H bending vibration. The peak at 2333 is ascribed to H–O–H bending vibration of the free or absorbed water.
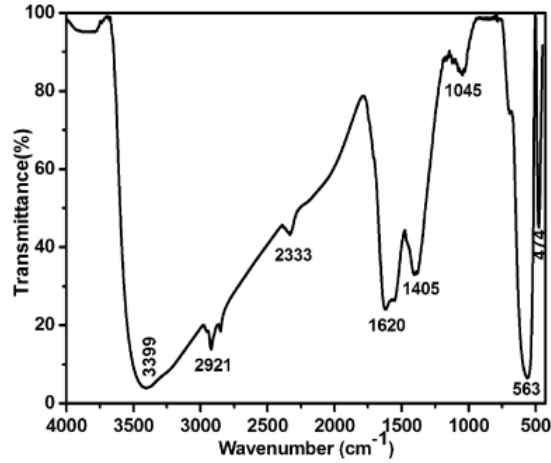
Figure 2.4: FT-IR spectrum of the nickel ferrite sample.

## 2.3.2 Copper ferrite

**XRD study**

Figure **2.5** shows the XRD for $CuFe_2O_4$. The observed reflection peaks found at 18°, 29°, 34°, 35°, 37°, 41°, 43°, 62° and 63° were exactly correlated to the inverse spinel tetragonal copper ferrite structure for the entire obtained product. These reflection peaks corresponded to the reflection planes (101), (112), (103), (211), (202), (004), (220), (224) and (400) respectively. The obtained XRD results are in good agreement with the tetragonal copper ferrite (JCPDS card no. 340425).
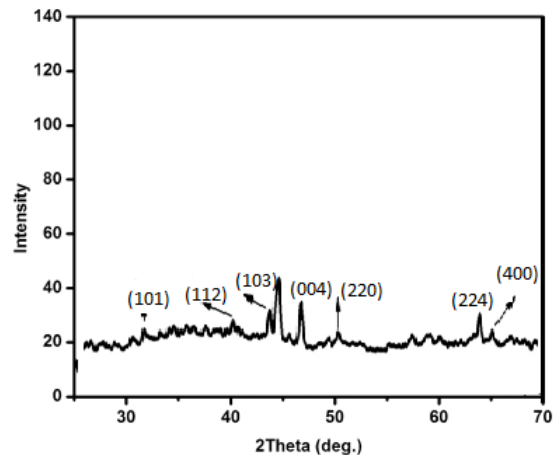


Figure 2.5: Powder XRD pattern of the copper ferrite sample.

**FT-IR study**

In the present study, the observed three phonon modes of Raman peaks located at about 278, 393, and 613 cm$^{-1}$ are corresponding to the characteristic peaks of $CuFe_2O_4$. The first peak located at 278 cm$^{-1}$ could be attributed to the E1g mode of phonon vibration for all the prepared samples. The peaks at about 393 and 613 cm$^{-1}$ for all the samples could be attributed to F2g and A1g mode of phonon vibrations. The band

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observed around 393 cm$^{-1}$ attributed to the metal cation vibration in the octahedral site. The last peak observed at 613 cm$^{-1}$ is assigned to the intrinsic stretching vibration of metal cations at the tetrahedral site. The peaks around 480 and 1300 cm$^{-1}$ present in the sample exactly coincided with the characteristic phonon vibration modes of secondary phase hematite which proved the influence of precursor concentration reflects the structural phenomena of the synthesized product, see Figure **2.6**.
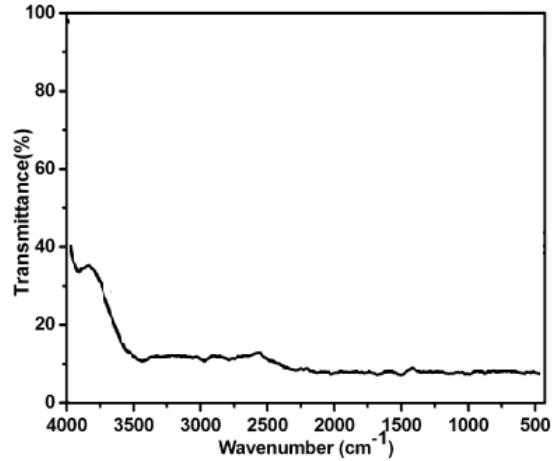


Figure 2.6: FT-IR spectrum of the copper ferrite sample.

### 2.3.3 Manganese ferrite

**XRD study**

The crystal structure and phase purity of the newly synthesized spinel $MnFe_2O_4$ were evaluated by X-ray diffraction (XRD). Figure **2.7** represents the XRD patterns of the sample synthesized. In Figure **2.7** the diffraction peaks show the refection planes (111), (202), (311), (222),(400),(333),(404), (440), (533) and (622) which match well with the standard diffraction values of JCPDS file no 74-2403. All these peaks confirm the cubic spinel lattice of $MnFe_2O_4$.
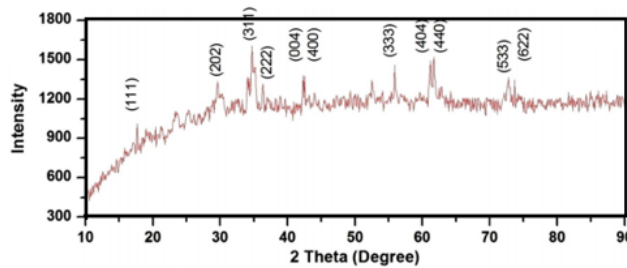


Figure 2.7: Powder XRD pattern of the manganese ferrite sample.

**FT-IR study**

From the FT-IR spectra, it is found that high frequency bands at 875 cm$^{-1}$ is associated to the tetrahedral site while the low frequency band at 629 cm$^{-1}$ is associated to the octahedral site. The sharpness of these

bands is correlated to the high degree of crystallinity of $MnFe_2O_4$ nanostructures. A broad vibration band at 3449 and 3421 cm$^{-1}$ are associated with the O–H stretching vibration of the adsorbed water molecules indicating a higher amount of surface OH. A small band at 1383 cm$^{-1}$ is assigned to the stretching vibrations of the COO group. A band at 1441 and 1449 cm$^{-1}$ are assigned to C–H bending modes. The peaks at 1116 and 1110 cm$^{-1}$ may be due to (C–O–C) symmetric vibration and dehydration of OH group from the polymers. The absence of peaks in the range of 2000–3000 cm$^{-1}$ in the sample confirms the absence of O–H mode, C–O mode and C–H stretching mode, see Figure **2.8**.



Figure 2.8: FT-IR spectrum of the manganese ferrite sample.

# Chapter 3

# CYCLIC CARBONATE FROM EPOXIDE AND CO$_2$

## 3.1 Brief Introduction

Cyclic carbonate and polycarbonate are examples of products used to store $CO_2$ since they were produced, mainly using a process evolving phosgene, a dangerous compound due to its toxicity, and bisphenol A (BPA) usage. This process phosgene free, beside greener is also cheape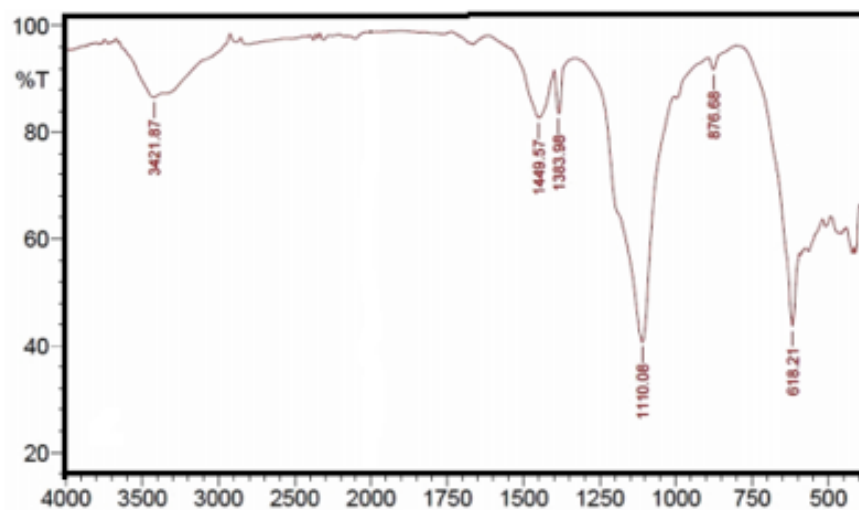r. The process uses epoxide that helps to overcome the thermodynamic stability since they are highly energetic compounds and there is an atom economy since there is no side product been formed, see Figure **3.1**. The drawback of this process is that the epoxides are generally produced by the oxidation of olefins using hazardous hydroperoxide and reactive epoxide is difficult to hand. There are reported a large number and types of catalysts to use in this process, such as alkali metals salts, metal complexes, ionic liquids, metal oxides, zeolites, ammonium salts, phosphines and so on. The direct transformation of $CO_2$ and epoxide to produce cyclic carbonate is one of the most promising routes to use $CO_2$ as a starting material and there are a remarkable number of catalysts developed to perform the reaction with success. Nevertheless, a large number of those catalysts suffer from high costs, low activity, high pressure and temperature required or need of cosolvents usage. So, it's still a challenge to design a highly efficient heterogeneous catalyst to function at low $CO_2$ pressure, low temperature and easily separated catalyst to realise the process [4, 12–14, 16, 17, 35–38].

## 3.2 General Procedure

The catalysts test was performed under the following conditions: 1.75 mmol of the substrate, $5.25 * 10^{-2}$ mmol of co-catalyst tetrabutylammonium bromide (TBABr) 98.0 % pure and the desired amount of catalyst was mixed in the reactor. The $CO_2$ was introduced in the reactor until the pressure of 4 MPa. The reactor is plunged in the oil bath with magnetic stirring and temperature set at the desired value for five hours. All the samples were analyzed by NMR using Chloroform-d as a deuterated solvent, to identify and quantify the
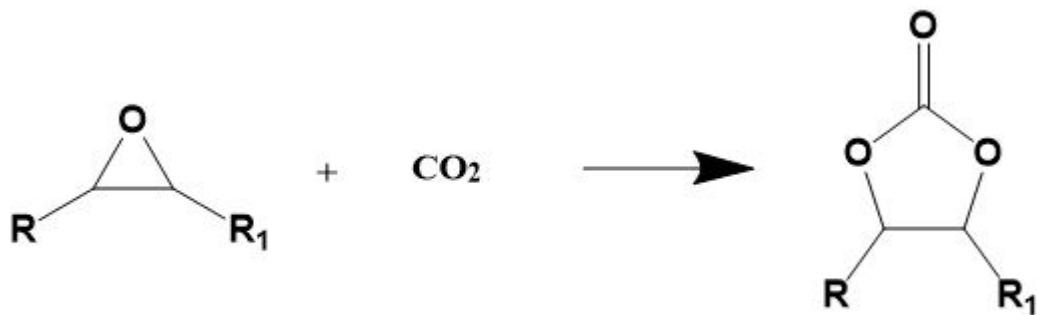
Figure 3.1: Scheme of cyclic carbonate production from epoxide and $CO_2$.

products.

## 3.3 Results and discussion

To test those catalysts in this process, two substrates were used, styrene oxide (SO) 97.0 % pure and propylene oxide (PO) 99.5 % pure both purchased from Acros Organics and used without further purification, see Figure **3.2**. These two are widely used in this reaction process with different catalysts and presenting very high yields with some catalysts.



(a) SO  (b) PO
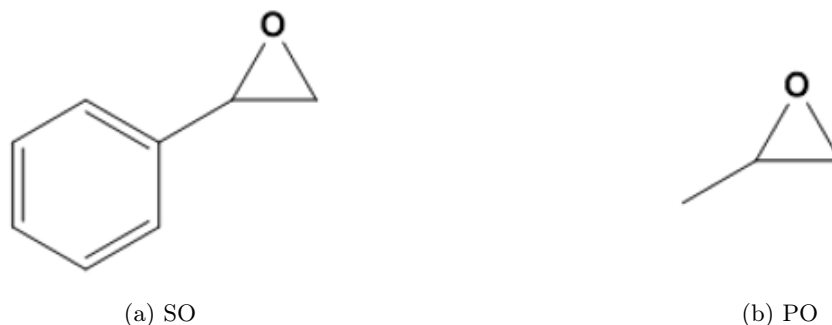
Figure 3.2: Substrates used in the reactions with $CO_2$ at different conditions.

Different results were observed, and the yields of each reaction at different conditions presented in the following Table **3.1**. The catalyst turnover number (TON) and turnover frequency (TOF) was calculated by the equations **3.1** and **3.2**, respectively.

$$TON = \frac{Yield(\%) * mol\ of\ reactant}{100 * mol\ of\ catalyst} \tag{3.1}$$

$$TOF = \frac{TON}{reactoin\ time} \tag{3.2}$$

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Table 3.1: Reaction of $CO_2$ with epoxide and $8.75 * 10^{-3}$ mmol of catalyst at temperature of 40 °C.

| Entry | Epoxide | Catalyst | Yields (%) | TON | TOF(h$^{-1}$) |
|---|---|---|---|---|---|
| 1 | | $NiFe_2O_4$ | 9.9 | 19.5 | 3.9 |
| 2 | SO | $CuFe_2O_4$ | 3.8 | 7.7 | 1.5 |
| 3 | | $MnFe_2O_4$ | 3.8 | 7.4 | 1.5 |
| 4 | | $[FeCl_2(Tpm)]$ | 19.4 | 38.5 | 7.7 |
| 5 | | $NiFe_2O_4$ | 7.4 | 14.6 | 2.9 |
| 6 | PO | $CuFe_2O_4$ | 0.1 | 0.2 | 0.0 |
| 7 | | $MnFe_2O_4$ | 9.1 | 18.3 | 3.7 |
| 8 | | $[FeCl_2(Tpm)]$ | 13.0 | 25.9 | 5.2 |

Reaction conditions: Epoxide (1.75 mmol); TBABr ($5.25 * 10^{-2}$ mmol); Pressure 4 MPa; Reaction time (5 h).

Catalysts are very important parameters in a chemical process, as it is reported previously in this dissertation. Temperature is another parameter very important in a chemical process once the reactions happen when the molecules/particles collide with enough energy to overcome the activation energy and the increase of temperature results in a faster movement of the particles what increases the frequency of collisions and the amount of energy generated. The temperature affects the reaction rate constant exponentially according to the Arrhenius equation, see Equation **3.3**, and the reaction rate is proportional to the reaction rate constant. So it is important to test the effects of those parameters in the reaction. First was studied the effects of catalyst concentration by increasing twice the amount of catalyst while maintaining the temperature constant, and the results presented, see Table **3.2**. Then the temperature effect also by increasing twice the temperature value while maintaining the amount of catalyst equal to the initial values of Table **3.1**. The results are presented in Table **3.3**.

$$k = A * exp(\frac{-E_\alpha}{RT})$$  (3.3)

Where k stands for reaction rate constant, $E_\alpha$ is the activation energy of the reaction, R is the perfect gases constant and T is the temperature in Kelvin (K).

Table 3.2: Reaction of $CO_2$ with epoxide and $1.75 * 10^{-2}$ mmol of catalyst at temperature of 40 °C.

| Entry | Epoxide | Catalyst | Yields (%) | TON | TOF(h$^{-1}$) |
|---|---|---|---|---|---|
| 1 | | $NiFe_2O_4$ | 6.5 | 6.4 | 1.3 |
| 2 | SO | $CuFe_2O_4$ | 2.9 | 2.8 | 0.6 |
| 3 | | $MnFe_2O_4$ | 5.7 | 5.6 | 1.1 |
| 4 | | $[FeCl_2(Tpm)]$ | 5.7 | 5.5 | 1.1 |
| 5 | | $NiFe_2O_4$ | 13.0 | 12.8 | 2.6 |
| 6 | PO | $CuFe_2O_4$ | 18.7 | 18.2 | 3.6 |
| 7 | | $MnFe_2O_4$ | 15.3 | 15.4 | 3.1 |
| 8 | | $[FeCl_2(Tpm)]$ | 23.7 | 23.1 | 4.6 |

Reaction conditions: Epoxide (1.75 mmol); TBABr ($5.25 * 10^{-2}$ mmol); Pressure 4 MPa; Reaction time (5 h).

From the Table **3.1** it can be observed that the higher yields are obtained from the reaction with SO in the presence of C-scorpionate iron(II) complex, Table **3.1 entry 4**. From the Table **3.2** the higher yields is

observed at the reaction with PO with $[FeCl_2(Tpm)]$ catalyst, Table **3.2 entry 8**. It can be observed that for the reactions with PO the yields, as expected, increase from with the increase of catalyst concentration. Nevertheless, for the reactions with SO the yields decrease. This behaviour must be related to the fact of PO is more reactive than SO.

Table 3.3: Reaction of $CO_2$ with epoxide and $8.75 * 10^{-3}$ mmol of catalyst at temperature of 80 °C, during five hours.

| Entry | Epoxide | Catalyst | Yields (%) | TON | TOF($h^{-1}$) |
|-------|---------|----------|------------|------|---------------|
| 1 | | $NiFe_2O_4$ | 49.2 | 92.6 | 18.5 |
| 2 | SO | $CuFe_2O_4$ | 67.5 | 128.5 | 25.7 |
| 3 | | $MnFe_2O_4$ | 54.8 | 110.5 | 22.1 |
| 4 | | $[FeCl_2(Tpm)]$ | 78.6 | 156.4 | 31.3 |
| 5 | | $NiFe_2O_4$ | 18.0 | 35.5 | 7.1 |
| 6 | PO | $CuFe_2O_4$ | 23.7 | 45.0 | 9.0 |
| 7 | | $MnFe_2O_4$ | 28.1 | 51.5 | 10.3 |
| 8 | | $[FeCl_2(Tpm)]$ | 67.5 | 125.9 | 25.2 |

Reaction conditions: Epoxide (1.75 mmol); TBABr ($5.25 * 10^{-2}$ mmol); Pressure 4 MPa; Reaction time (5 h).

From the Table **3.3** it is observed that the higher hield is from the reaction with SO in presence of $[FeCl_2(Tpm)]$ catalyst, Table **3.3 entry 4**. The yields of all the reactions increased in comparison with the Table **3.1**, as it was expected since the temperature increased.



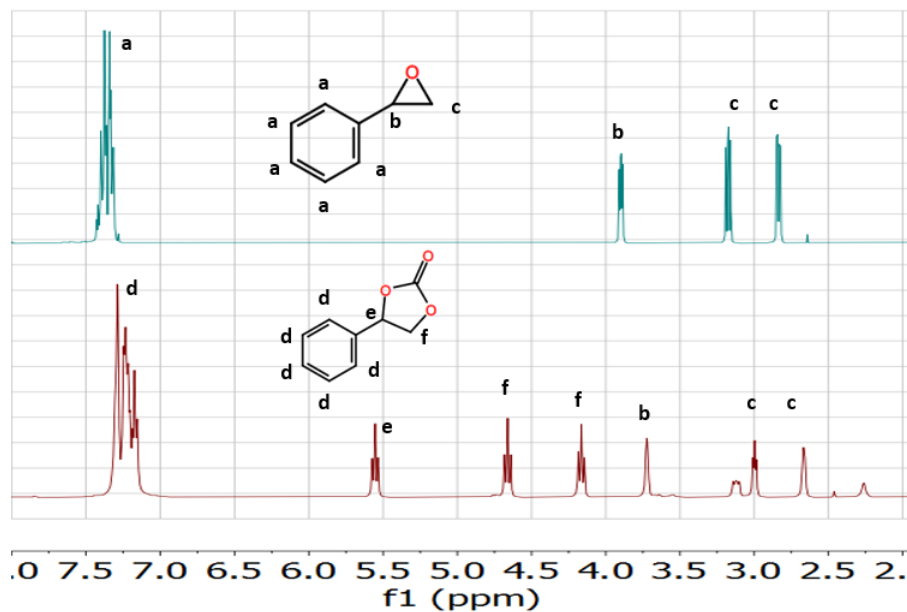Figure 3.3: Comparison between $^1H$ NMR spectrum of the substrate SO and one sample.

To identify and quantify the products of the reactions was used $^1H$ NMR spectrum. To do so, it's necessary to identify peaks corresponding to reactants used and assign the peaks corresponding to expected products. From the Figure **3.4** the peak were attributed to the reactant, SO, and one of the samples to exemplify.

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SO: $^1H$ NMR $\delta$ 2.84ppm (t, 1H, $CH_2$), $\delta$ 3.18ppm (t, 1H, $CH_2$), $\delta$ 3.90ppm (t, 1H, $CH$), $\delta$ 7.37ppm (M, 5H, $C_5H_5$). Sample: $^1H$ NMR $\delta$ 4.16ppm (t, 1H, $CH_2$), $\delta$ 4.66ppm (t, 1H, $CH_2$), $\delta$ 5.55ppm (t, 1H, $CH$), $\delta$ 3.25ppm (m, 5H, $C_5H_5$).
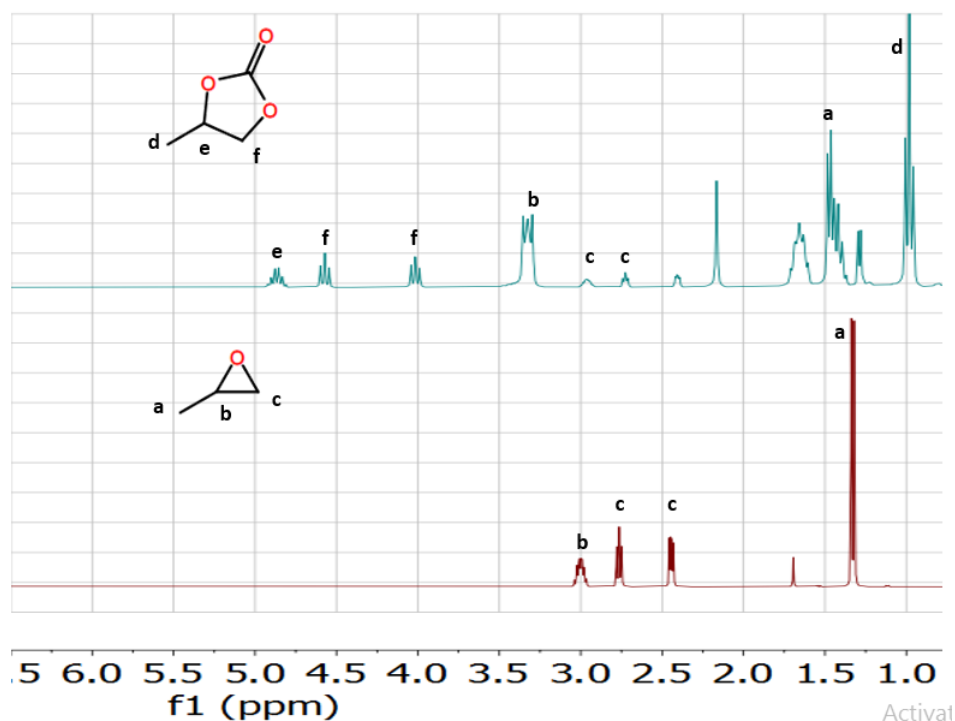


Figure 3.4: Comparison between $^1H$ NMR spectrum of the substrate PO and one sample.

The peaks were also assign to the other substrate used in this process, see Figure **3.4**.
PO: $^1H$ NMR $\delta$ 1.33ppm (d, 3H, $CH_3$), $\delta$ 2.45ppm (t, 1H, $CH_2$), $\delta$ 2.77ppm (t, 1H, $CH_2$), $\delta$ 3.00ppm (m, 1H, $CH$). Sample: $^1H$ NMR $\delta$ 0.98ppm (T, 3H, $CH_3$), $\delta$ 4.02ppm (t, 1H, $CH_2$), $\delta$ 4.57ppm (t, 1H, $CH_2$), $\delta$ 4.88ppm (m, 1H, $CH$).

## 3.4    Mechanism proposed

The reactions mechanism in presence of bimetallic catalyst and TBABr as co-catalyst is reported, see Figure **3.5**. North et al reported the important role of TBABr in the reaction, first in the ring-opening and then in the activation of $CO_2$ by decomposition into tributylamine ($Bu_3N$) and 1-bromobutane (BuBr) [37]. The first step of the reaction is the coordination of the metal of the salt **9a** to the oxygen atom leading to the activation of the epoxide to ring-opening from the bromide from TBABr forming the intermediate **11**. Then the $Bu_3N$ reacts with $CO_2$ to form a carbonate salt to coordinate to the other aluminium of the intermediate **11** to form the intermediate **12**. Then the oxygen form the epoxide attacks the carbonyl from the urea releasing $Bu_3N$ to a new cycle and forming the intermediate **13**. The last step is the ring-closure forming the cyclic carbonate and regenerates both the catalyst **9a** and the co-catalyst TBABr [4, 35, 37, 39]. The mechanism of the reaction used in this work should be similar to the one presented here since both use the same co-catalyst

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with an important role in the reaction process. The difference is the catalysts. The catalysts used in this work are not bimetallic unlike the one used in the mechanism presented. Two different catalysts close to each other should participate in the reaction instead of one bimetallic catalyst.
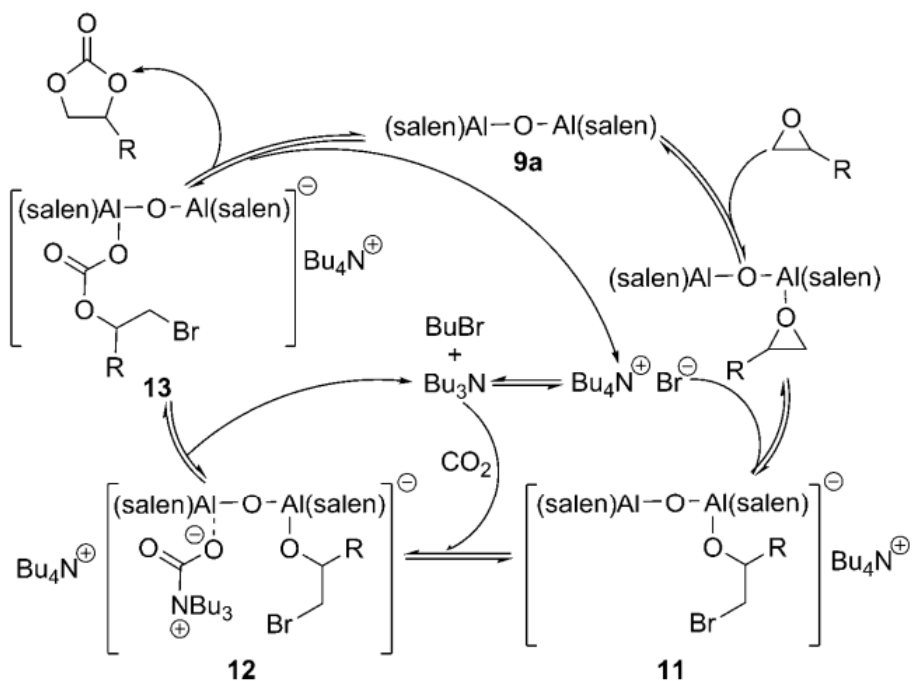


Figure 3.5: Reaction mechanism with bimetallic aluminium salt catalyst and TBABr as co-catalyst [39].

# Chapter 4

# CYCLIC CARBONATE FROM UREA AND 1,2-DIOLS

## 4.1 Brief Introduction

Nowadays cyclic carbonate is mostly produced using epoxide and $CO_2$. This process has some issues related to the toxicity of some epoxides, the difficulties to hand them, high pressure or high temperature required, low conversion and yields in some cases. In an attempt to overcome those issues and achieve a process more eco-friendly to convert $CO_2$ into value-added compounds, an alternative process was developed. In 1991, Su and Speranza were the first ones to announce this alternative process [40]. Although low conversion and decomposition of urea were reported, it was the beginning of the search for a new catalyst to perform this reaction more efficiently. The new procedure uses as a starting material urea and 1,2-diols and produces cyclic carbonate and ammonia as a side product. Although this process does not use direct $CO_2$ as raw material it produces ammonia as a side product and the ammonia produced can be treated with $CO_2$ to produce the initial starting material, urea, see Figure **4.1**. This process has the advantages of using urea and diols that are cheap and readily available compounds, also diols are generally bioavailable from a renewable resource, the ammonia produced is easily separable from the product, very low risk of explosions or poisons. Since then, there were reported catalysts to successfully perform this reaction with remarkable results [18, 19, 41–43].

## 4.2 General Procedure

To prepare this reaction, 0.5 mmol of urea, 0.5 mmol of the substrate and the intended amount of catalyst was mixed in the reactor with 1 mL of solvent (toluene). The reactor was plunged in an oil bath at 150 °C with magnetic stirring for six hours.
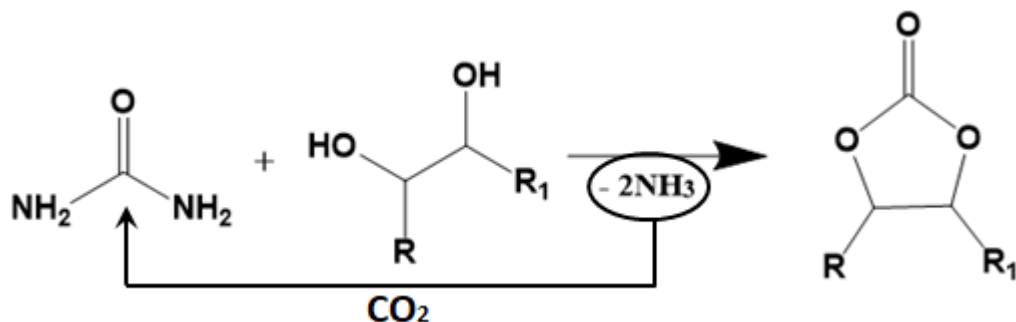
Figure 4.1: Scheme of cyclic carbonate production from urea and 1,2-diol.

## 4.3 Results and discussion

In this process was used three substrates, 3-mercapto-1,2-propanediol (MP) 95.0 % pure purchased from Aldrich Chemical co, *cis*-1,2-cyclohexanediol (CCH) 98.0 % pure and *trans*-1,2-cyclohexanediol (TCH) 99.0 % pure both purchased from Tokyo Chemical Industry Co, see Figure **4.2**. Those substrate were used without further purification and the results of the reactions are presented in the Table **4.1**.
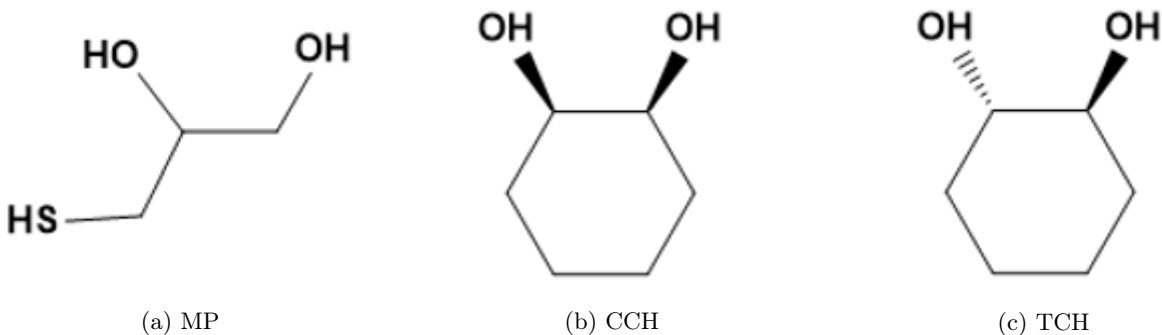


(a) MP         (b) CCH         (c) TCH

Figure 4.2: Substrates used in the reactions with urea at different conditions.

From the Table **4.1** is observed that the best yield is obtained for the reaction to CCH in presence of $CuFe_2O_4$ as a catalyst **4.1 entry 6**.

To identify and quantify the products obtained was used NMR. The peaks of products and reactants were assign, see Figures **4.3** and **4.4**.
MP: $^1H$ NMR $\delta$ 1.58ppm (t, 1H, $SH$), $\delta$ 2.68ppm (m, 2H, $CH_2$), $\delta$ 3.59ppm (m, 2H, $CH_2$), $\delta$ 3.83ppm (m, 1H, $CH$).
CCH and TCH: $^1H$ NMR $\delta$ 1.34ppm (m, 4H, $CH_2$), $\delta$ 1.63ppm (m, 2H, $CH_2$), $\delta$ 1.77ppm (m, 2H, $CH_2$), $\delta$ 3.80ppm (m, 2H, $CH$).

Table 4.1: Reaction of urea, diol and 0.02 mmol of catalyst at temperature of 150 °C.

| Entry | Diol | Catalyst | Yields (%) | TON | TOF (h$^{-1}$) |
|-------|------|----------|------------|-----|----------------|
| 1 | | $NiFe_2O_4$ | 1.2 | 0.3 | 0.1 |
| 2 | MP | $CuFe_2O_4$ | 2.9 | 0.7 | 0.1 |
| 3 | | $MnFe_2O_4$ | 1.3 | 0.3 | 0.1 |
| 4 | | $[FeCl_2(Tpm)]$ | 5.1 | 1.2 | 0.2 |
| 5 | | $NiFe_2O_4$ | 9.1 | 2.2 | 0.4 |
| 6 | CCH | $CuFe_2O_4$ | 30.1 | 7.5 | 1.2 |
| 7 | | $MnFe_2O_4$ | 9.9 | 2.5 | 0.4 |
| 8 | | $[FeCl_2(Tpm)]$ | 14.5 | 3.5 | 0.6 |
| 9 | | $NiFe_2O_4$ | 25.4 | 6.3 | 1.0 |
| 10 | TCH | $CuFe_2O_4$ | 10.7 | 2.7 | 0.4 |
| 11 | | $MnFe_2O_4$ | 3.6 | 0.9 | 0.1 |
| 12 | | $[FeCl_2(Tpm)]$ | 13.8 | 3.3 | 0.6 |

Reaction conditions: Urea (0.05 mmol); Diol (0.05 mmol); Pressure 1 atm; Reaction time (5 h)
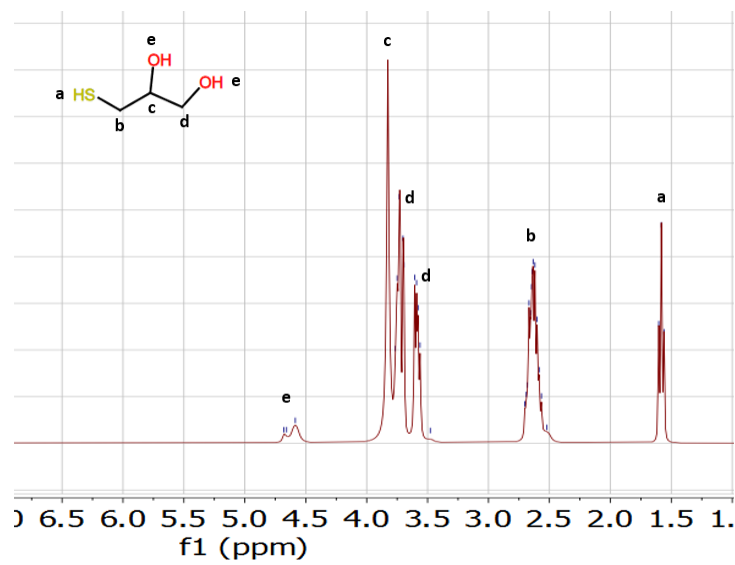


Figure 4.3: $^1H$ NMR spectrum of the substrate MP, with the peaks assigned.

## 4.4 Reaction under Microwave Irradiation

### 4.4.1 Brief Introduction

The microwave chemistry is the science of applying microwave irradiation to a chemical reaction. It is a breakthrough in organic synthetic chemistry and an alternative to conventional heating for introducing energy into reactions. Microwave heating uses the ability of some compounds to transform electromagnetic energy into heat and it's been used in a large number of chemical reactions including alkylation, oxidation, reduction, Knoevenagel condensation, hydrolysis, esterification, decarboxylation, Mannich reaction and so on. It is also used in other fields such as material synthesis, biomedical process, nanotechnology and so on. In 1986, Gedye and Giguere Majetich groups find out that microwave irradiation usage results in significant
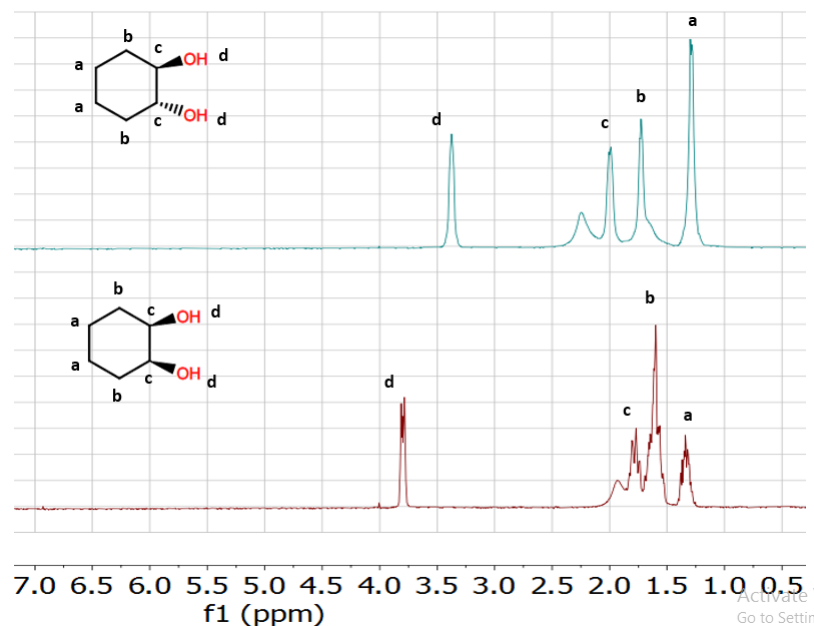
Figure 4.4: $^1H$ NMR spectrum of the substrates CCH and TCH, with the peaks assigned.

rate enhancements in organic chemical reactions. Since then the use of microwave irradiation received great attention both in academia and in industry. Over 6000 articles have been published after the first one with exponential growth over the last twenty years. Reactions that in classical conditions require long reaction time, high temperatures or Lewis acid catalyst, that lead to decomposition partial or total of some sensitive compounds, has been tested under microwave reaction overcoming those issues. There are often reported activation and amazing rate accelerations, high yields and selectivity at milder conditions than conventional conditions related to the reduction of side products, lower energy consumption in comparison with conventional reactions, greater reproducibility and cleaner routes by reducing or eliminating the solvent usage. The short time reaction time associated with the microwave irradiation avoids decomposition of products and reactants and prevents undesired polymerization and cycloreversion. Those changes have been related to the transition's state hardness, where the harder state been favourable under microwave irradiation [44–49].

### 4.4.2 General Procedure

To prepare this process, 0.5 mmol of urea, 0.5 mmol of substrate and catalyst were mixed in the microwave tube reactor G10 with 1 mL of solvent (toluene). Then the tube was taken to the microwave synthesis reactor, monowave 300 from Anton Paar in the following conditions. The temperature was set at 180 °C with the power of 50 W, with a magnetic stirring velocity at 600 rpm for four hours.

### 4.4.3 Results and discussion

The same three substrates used before in this reaction without the microwave irradiation was used here. At first, it was used the same amount of catalyst that was used in the first experience without microwave

irradiation and results presented, see Table **4.2**. The catalyst effects were studied by decreasing twice the amount of catalyst used initially, and the results are presented in Table **4.3**.

Table 4.2: Reaction of urea and diols under microwave irradiation, 0.02 mmol of catalyst at temperature of 180 °C.

| Entry | Diol | Catalyst | Yields (%) | TON | TOF($h^{-1}$) |
|-------|------|----------|-----------|-----|---------------|
| 1 |  | $NiFe_2O_4$ | 0.5 | 0.1 | 0.0 |
| 2 | MP | $CuFe_2O_4$ | 0.7 | 0.2 | 0.0 |
| 3 |  | $MnFe_2O_4$ | 0.9 | 0.2 | 0.1 |
| 4 |  | $[FeCl_2(Tpm)]$ | 1.1 | 0.3 | 0.1 |
| 5 |  | $NiFe_2O_4$ | 0.7 | 0.2 | 0.0 |
| 6 | CCH | $CuFe_2O_4$ | 0.9 | 0.2 | 0.1 |
| 7 |  | $MnFe_2O_4$ | 0.8 | 0.2 | 0.0 |
| 8 |  | $[FeCl_2(Tpm)]$ | 1.0 | 0.2 | 0.1 |
| 9 |  | $NiFe_2O_4$ | 0.7 | 0.2 | 0.0 |
| 10 | TCH | $CuFe_2O_4$ | 0.9 | 0.2 | 0.1 |
| 11 |  | $MnFe_2O_4$ | 0.9 | 0.2 | 0.1 |
| 12 |  | $[FeCl_2(Tpm)]$ | 1.1 | 0.3 | 0.1 |

Reaction conditions: Urea (0.05 mmol); Diol (0.05 mmol); Pressure 1 atm; Reaction time (4 h).

Table 4.3: Reaction of urea and diols under microwave irradiation, 0.01 mmol of catalyst at temperature of 180 °C for four hours.

| Entry | Diol | Catalyst | Yields (%) | TON | TOF($h^{-1}$) |
|-------|------|----------|-----------|-----|---------------|
| 1 |  | $NiFe_2O_4$ | 0.2 | 0.1 | 0.0 |
| 2 | MP | $CuFe_2O_4$ | 0.3 | 0.1 | 0.0 |
| 3 |  | $MnFe_2O_4$ | 0.0 | 0.0 | 0.0 |
| 4 |  | $[FeCl_2(Tpm)]$ | 0.8 | 0.4 | 0.1 |
| 5 |  | $NiFe_2O_4$ | 0.4 | 0.2 | 0.0 |
| 6 | CCH | $CuFe_2O_4$ | 0.4 | 0.2 | 0.0 |
| 7 |  | $MnFe_2O_4$ | 0.3 | 0.2 | 0.0 |
| 8 |  | $[FeCl_2(Tpm)]$ | 0.9 | 0.4 | 0.1 |
| 9 |  | $NiFe_2O_4$ | 0.4 | 0.2 | 0.0 |
| 10 | TCH | $CuFe_2O_4$ | 0.4 | 0.2 | 0.1 |
| 11 |  | $MnFe_2O_4$ | 0.3 | 0.2 | 0.0 |
| 12 |  | $[FeCl_2(Tpm)]$ | 0.9 | 0.4 | 0.1 |

Reaction conditions: Urea (0.05 mmol); Diol (0.05 mmol); Pressure 1 atm; Reaction time (4 h).

From the Tables **4.2** and **4.3** unlike it was expected the yields decrease in comparison with Table **4.1**. Urea decomposition, as it has been reported in the literature, catalyst deactivation or side reaction are some aspects that may underlie this behaviour. Comparing entry to entry the values of the Tables **4.2** and **4.3**, it is observed that the values decrease as expected, since the catalyst concentration decreases.

## 4.5 Mechanism proposed

The mechanism of the reaction in the presence of iron catalyst was proposed in the literature, see Figure **4.5**. The first step is the activation of the carbonyl group of urea by coordination to the metal through the oxygen atom, intermediate **I**. Then one of the hydroxy groups of the diol attacks the carbonyl carbon of urea to generate the intermediate **II**. The following step is a proton exchange between the oxygen atom and one of the ammonia atom from the urea followed by an intramolecular substitution reaction with the oxygen atom of the other hydroxyl group bonding to carbon and the first ammonia been free, the five-membered cyclic carbonate (intermediate **IV**) is formed. The final step is the release of the second ammonia and the restore of the catalyst. To support the mechanism proposed, an additional experiment was performed such as $^{13}C$-labelled urea usage to confirm the carbonyl group origin or intermediate isolation [18]. The mechanism of the reaction performed in this work should be similar to this due to semblance between the systems.
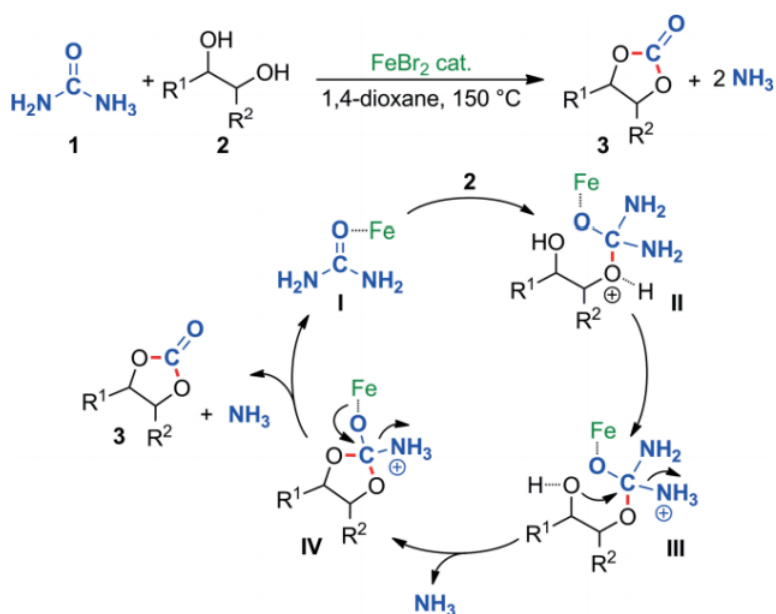


Figure 4.5: Reaction mechanism catalysed by iron bromide [18].

# Chapter 5

# GREEN METRICS

Green chemistry metrics measure aspects of a chemical process relating to the principles of green chemistry. These metrics quantifies the efficiency or environmental performance of chemical processes, and allow changes in performance to be measured. The motivation for using these metrics is the expectation that quantifying technical and environmental improvements can make the benefits of new technologies more tangible and understandable and more likely to be used at industrial level. Numerous metrics have been formulated over time, such as: i) Carbon efficiency that measures how much carbon from the reagents ends up in the useful products [50]; ii) Environmental (E) factor was the first metrics developed and it relate the waste produced to the desired product, still one of the most popular and flexible metric [50, 51]; iii) The Eco-Scale gives a score from 0 to 100 and takes into account cost, safety, technical set-up, energy and purification aspects [51]. In this work, two metrics were calculated, the Effective mass yield and the Atom economy.

## 5.1   Effective mass yield

Hudlicky et al. [52] proposed a metric known as effective mass yield that is defined 'as the percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis.' Or, stated mathematically: This metric attempts to define yield in terms of what proportion of the final mass, i.e., the mass of the product, that is made from non-toxic materials. The introduction of reagent and reactant toxicity is an extremely important consideration that is frequently absent from discussions about yield.

$$Effective\ mass\ yield = \frac{Mass\ of\ products}{Mass\ of\ non\ benign\ reagents} \tag{5.1}$$

Values for effective mass yield are showed in Table **5.1**.

The values are higher for the more efficient reaction, which means that the processes are more green than harmful for the environment.

Table 5.1: Effective mass yield for the reactions studied in this thesis.

| Reagents | Product | Effective mass yield |
|---|---|---|
| 3-mercapto-1,2-propanediol + urea | 3-mercapto-1,2-propylene carbonate | 1.3 |
| *cis*-1,2-ciclohexandiol + urea | 1,2-cyclohexylene carbonate | 0.7 |
| *trans*-1,2-ciclohexandiol + urea | 1,2-cyclohexylene carbonate | 0.7 |
| styrene oxide + $CO_2$ | styrene carbonate | 1.0 |
| propylene oxide + $CO_2$ | propylene carbonate | 1.8 |

## 5.2   Atom economy

When developing chemical processes, chemists for obvious reasons focus mainly on maximizing selectivity and yield. In recent years, another variable some chemists have been considering is the atom economy. This term, first introduced by Barry Trost, [53] was an attempt to prompt synthetic organic chemists to pursue 'greener chemistry'. Simply stated, the atom economy is a calculation of how much of the reactants remain in the final product. The final product in this context applies to a single chemical transformation, a series of chemical transformations in a single stage of a multistage synthetic route, or the entire route to a final product. The method for calculating the atom economy is kept deliberately simple by making certain key assumptions, ignoring reaction yield and molar excesses of reactants. It also does not account for solvents and reagents.

$$Atom\ economy = \frac{Molecular\ weight\ of\ products}{Molecular\ weight\ of\ reagents} \tag{5.2}$$

The calculation considers only the reactants used and ignores the intermediates that are made in one stage and consumed in the next. Because of this, it is not possible to multiply the atom economy of each stage to give an overall process atom economy.

The atom economy for the cyclic carbonate of $CO_2$ and epoxides and the cyclic carbonate from urea and 1,2-diols reactions are presented in Table **5.2**. All results have to be between 0 and 1, and it is important that some of the metrics are close to the maximum value. It is an indication that both the methods follow a green chemistry approach.

Table 5.2: Atom Economy for the reactions studied in this thesis.

| Reagents | Product | Atom economy |
|---|---|---|
| 3-mercapto-1,2-propanediol + urea | 3-mercapto-1,2-propylene carbonate | 0.7 |
| *cis*-1,2-ciclohexandiol + urea | 1,2-cyclohexylene carbonate | 0.8 |
| *trans*-1,2-ciclohexandiol + urea | 1,2-cyclohexylene carbonate | 0.8 |
| styrene oxide + $CO_2$ | styrene carbonate | 1.0 |
| propylene oxide + $CO_2$ | propylene carbonate | 1.0 |

# Chapter 6

# CONCLUSIONS AND FUTURE WORK

Both methods are very simple to use and complex equipment is not needed. In the first method, it is a little more difficult, since the $CO_2$ usage is required which due to the pressure imposed on the system requires little more care. In the second method, the microwave synthesis reactor is the most complex equipment, it is, however, easy to use.

It is been reported process in similar conditions with those performed in this work. For instance, Castro et al (2016) reported reactions of PO and SO with $CO_2$ and TBABr as co-catalyst in presence of several catalysts with yields up to 72% and 84% respectively [17]. Clegg et al (2010) reported reactions of SO with $CO_2$ in the presence of metal salts catalyst and presented yields up to 57% [39]. In comparison with the best yields obtained in this work, it is observed that $[FeCl_2(Tpm)]$ is a very promising catalyst to convert $CO_2$ with epoxide. Related to the second process used, Peña et al (2016) reported reactions using iron bromide ($FeBr_2$) as a catalyst to perform the transformation of urea and CCH with yields of 75% [18]. Others reported reactions of urea with different substrates and catalyst with yield up to 100% [19, 43]. Concerning the reactions under microwave irradiation, Zhang et al (2018) reported yields up to 93.7% in the transformation of glycerol and urea to form cyclic carbonate [49]. It is observed that the catalyst used presented values way too low in comparison with others works developed and the use of microwave irradiation didn't presented the expected effect in this reaction.

It is part of the future work to test other substrates, catalysts and solvents as well as to determine ideal conditions for the realisation of reactions such as temperature and concentration of different species in order to achieve higher yields, specially when microwave is used. Studying reaction kinetics, understanding the mechanism and catalyst recovery are other important matter to consider.

Exploration of a variety of metrics has revealed the following:
First, pursuing a metric such as yield, a ubiquitous metric chemists utilise to evaluate reaction efficiency, will not by itself drive a business towards sustainable practices. However, from an economic standpoint, the yield remains a very good metric, especially for high value added materials such as pharmaceuticals; Second, atom economy may be useful as an organising concept or in combination with other metrics, but at this time it is not considered to be useful as a stand-alone metric.

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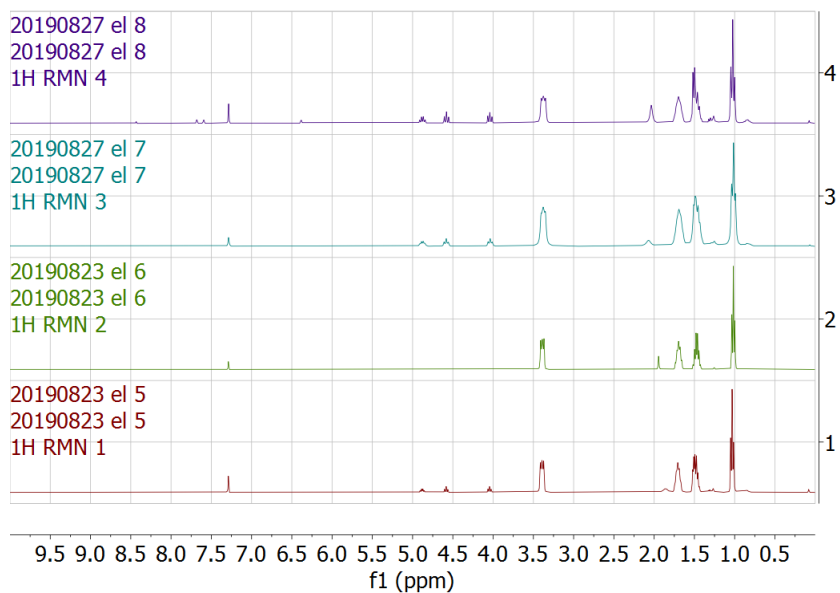
# APPENDIX

## Annex A

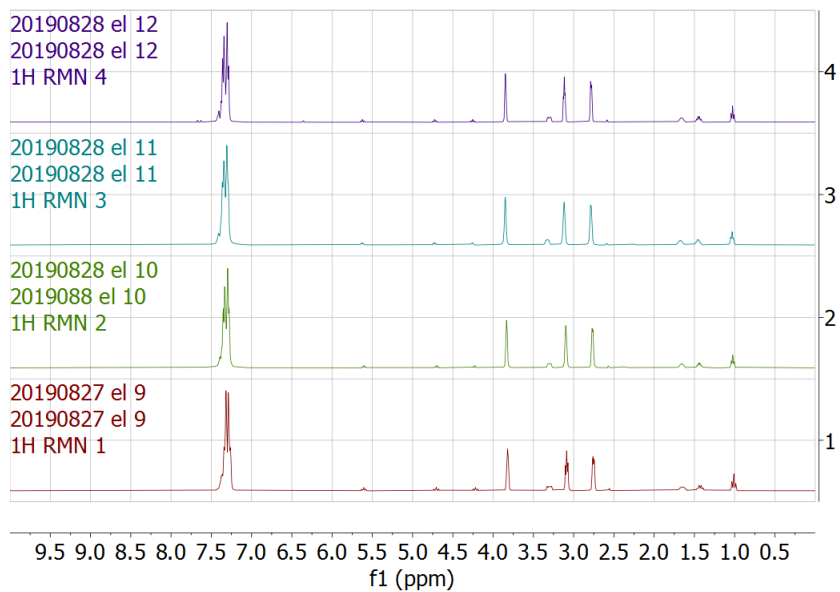**A1** - $^{1}H$ NMR from reactions of $CO_2$ and SO in the conditions of **Table 3.1**:
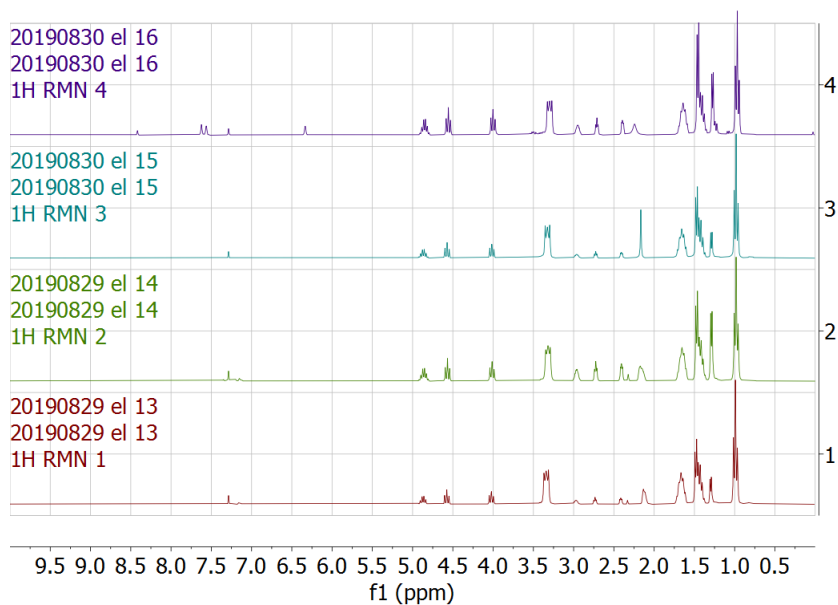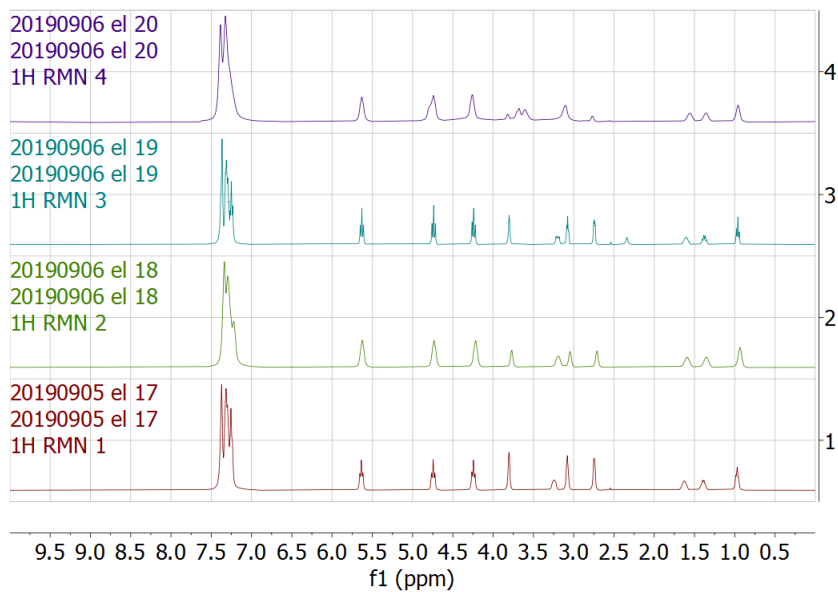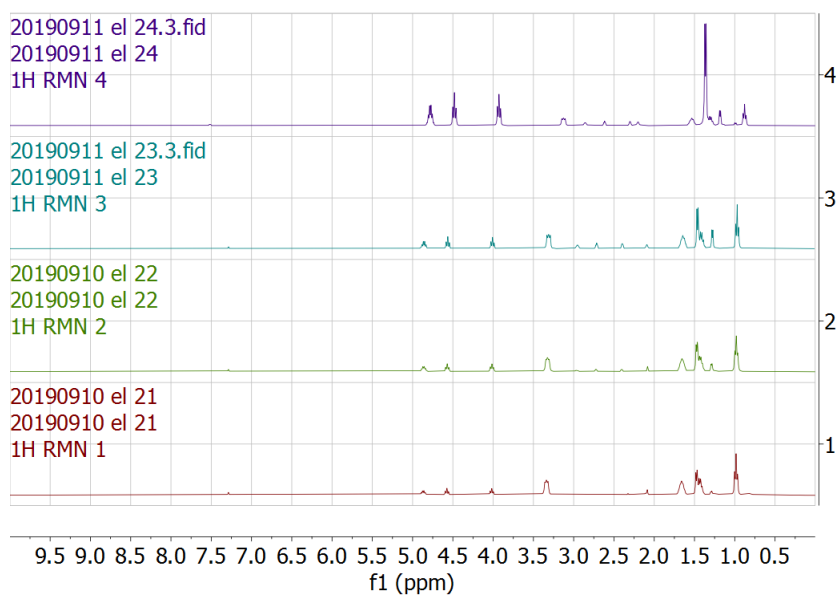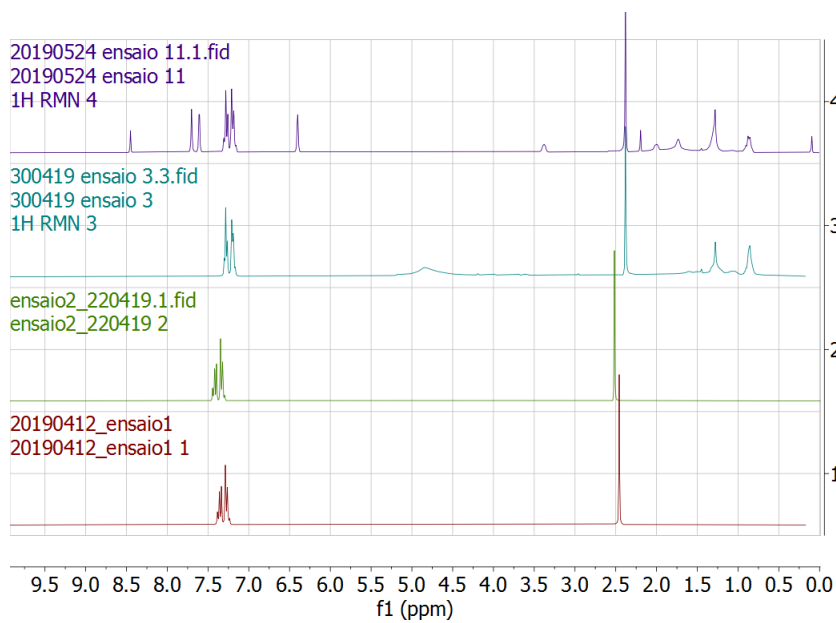1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$.
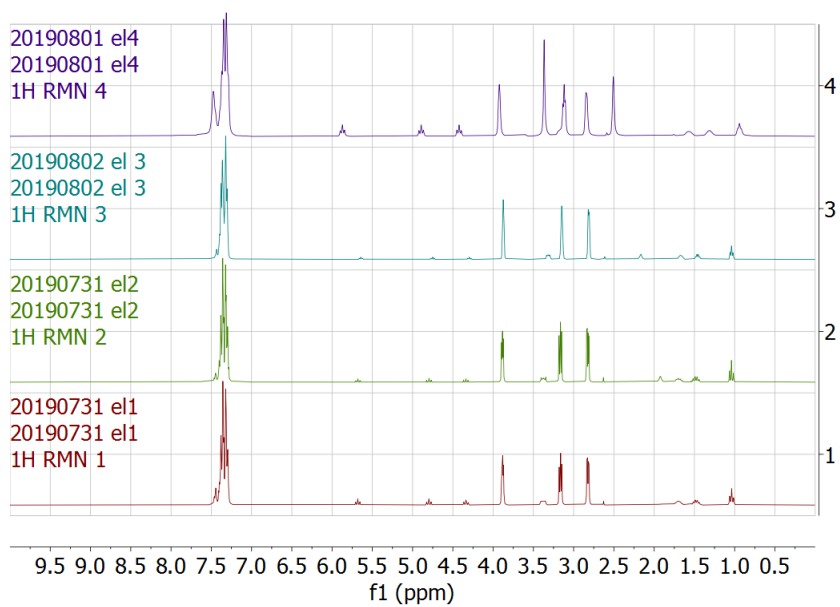
**A2** - $^1H$ NMR from reactions of $CO_2$ and PO in the conditions of **Table 3.1**: 1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$.



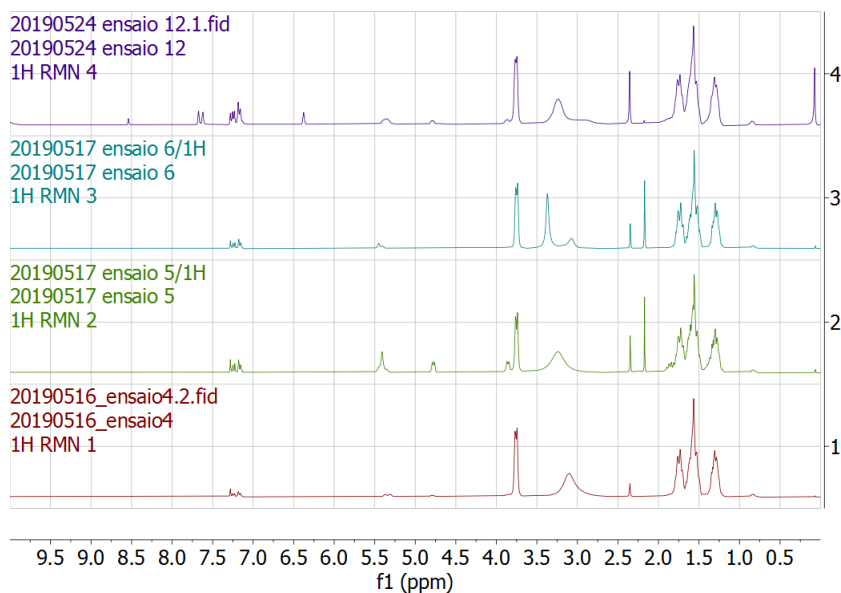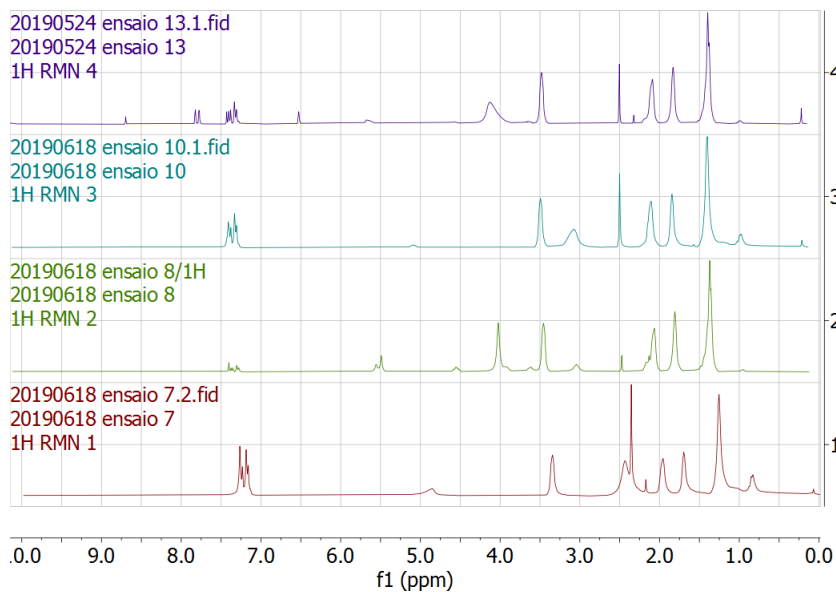**A3** - $^1H$ NMR from reactions of $CO_2$ and SO in the conditions of **Table 3.2**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$.

**A4** - $^1H$ NMR from reactions of $CO_2$ and PO in the conditions of **Table 3.2**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-[$FeCl_2(Tpm)$].



**A5** - $^1H$ NMR from reactions of $CO_2$ and SO in the conditions of **Table 3.3**:
1-$NiFe_2O_4$;  2-$CuFe_2O_4$;  3-$MnFe_2O_4$  4-[$FeCl_2(Tpm)$].

**A6** - $^1H$ NMR from reactions of $CO_2$ and PO in the conditions of **Table 3.3**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$.



# Annex B

**B1** - $^1H$ NMR from reactions of urea and MP in the conditions of **Table 4.1**:
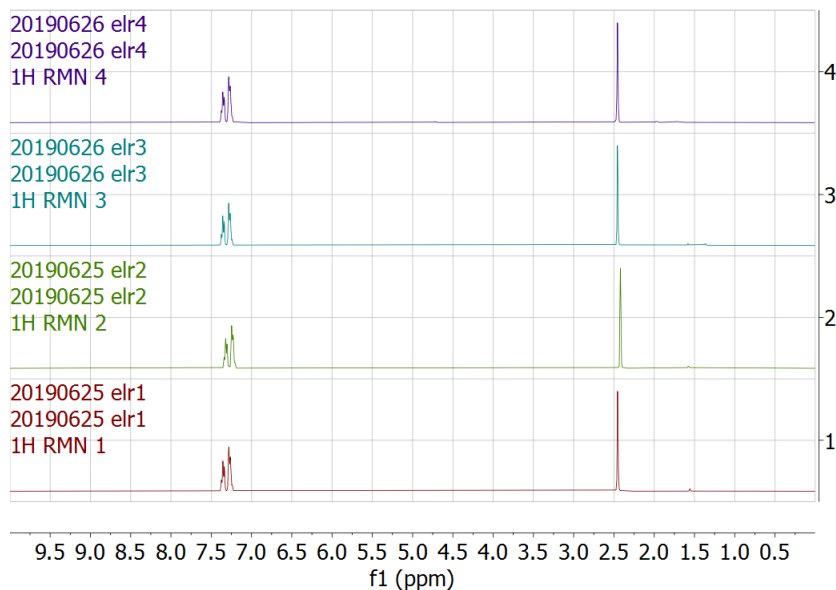1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$

**B2** - $^1H$ NMR from reactions of urea and CCH in the conditions of **Table 4.1**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$



**B3** - $^1H$ NMR from reactions of urea and TCH in the conditions of **Table 4.1**:
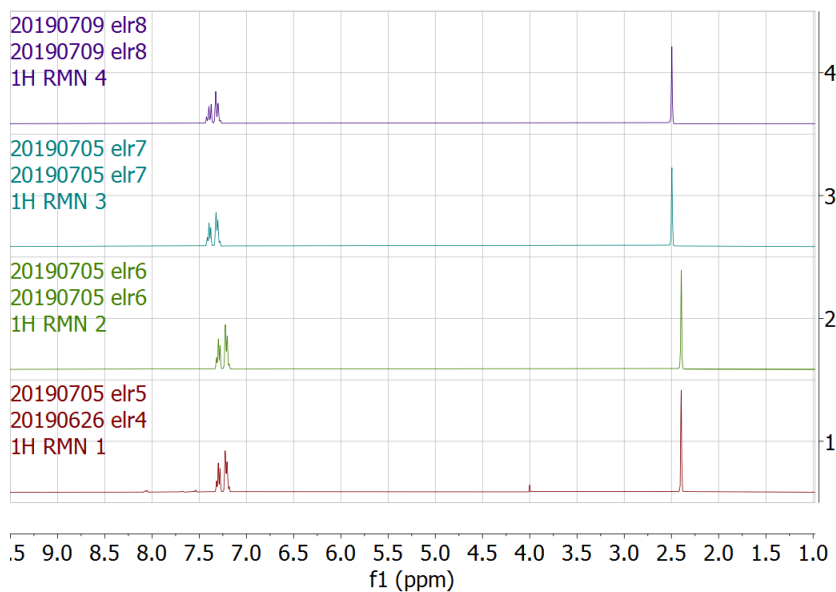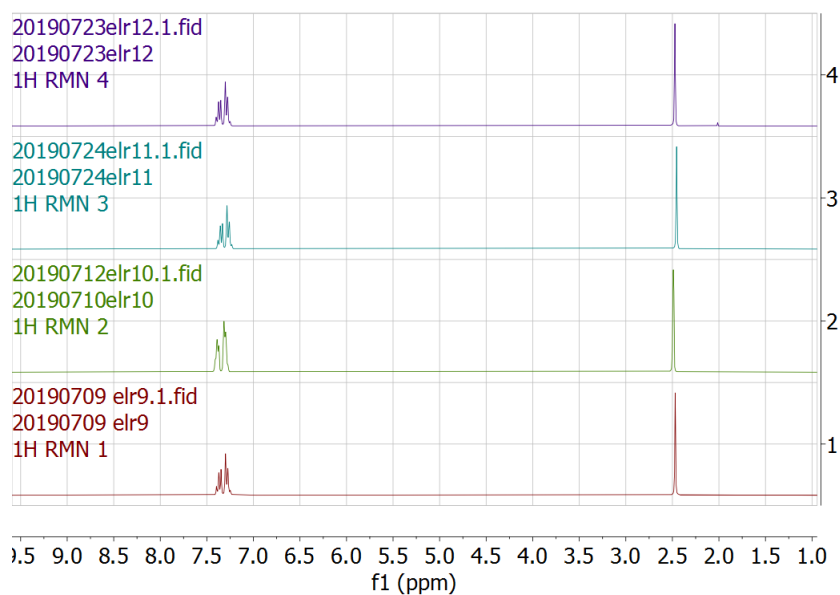1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$

# Annex C

**C1** - $^1H$ NMR from reactions of urea and MP in the conditions of **Table 4.2**:
$1\text{-}NiFe_2O_4$; $2\text{-}CuFe_2O_4$; $3\text{-}MnFe_2O_4$ $4\text{-}[FeCl_2(Tpm)]$



**C2** - $^1H$ NMR from reactions of urea and CCH in the conditions of **Table 4.2**:
$1\text{-}NiFe_2O_4$; $2\text{-}CuFe_2O_4$; $3\text{-}MnFe_2O_4$ $4\text{-}[FeCl_2(Tpm)]$

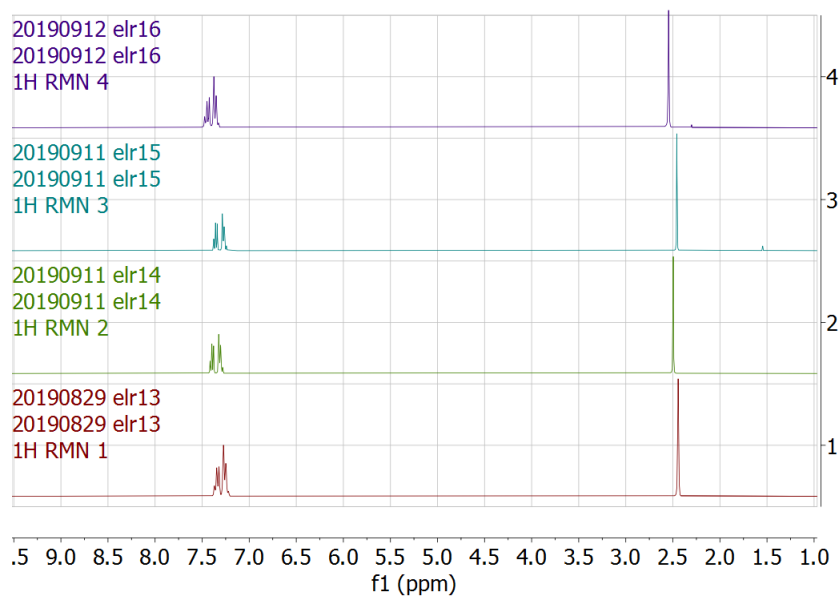**C3** - $^1H$ NMR from reactions of urea and TCH in the conditions of **Table 4.2**:
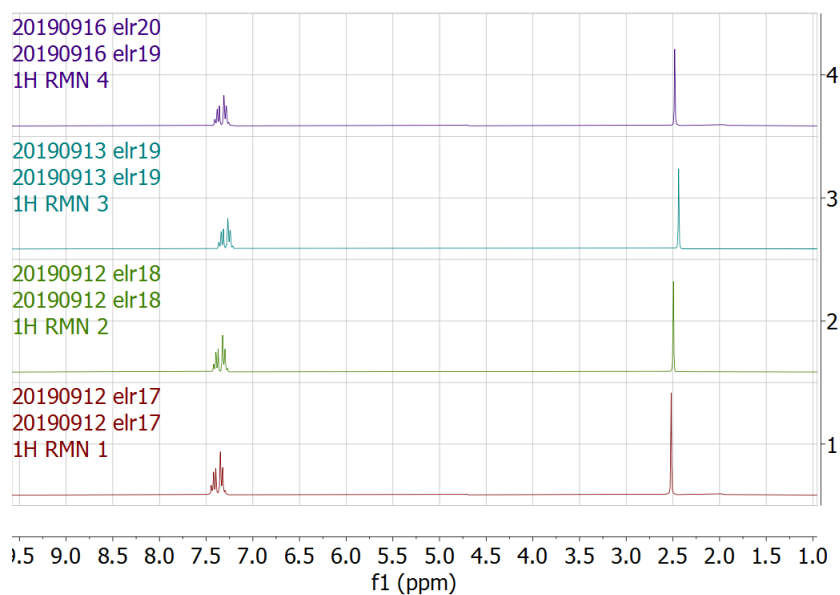1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$



**C4** - $^1H$ NMR from reactions of urea and MP in the conditions of **Table 4.3**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$

**C5** - $^1H$ NMR from reactions of urea and CCH in the conditions of **Table 4.3**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$



**C6** - $^1H$ NMR from reactions of urea and TCH in the conditions of **Table 4.3**:
1-$NiFe_2O_4$; 2-$CuFe_2O_4$; 3-$MnFe_2O_4$ 4-$[FeCl_2(Tpm)]$