Alexandre Lopes do Rosário Ventura
Licenciado em Química Aplicada

Utilization of ionic liquids as solvents and co-catalysts in the production of cyclic carbonates from CO_2

Dissertação para obtenção do Grau de Mestre em Química Bioorgânica

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FACULDADE DE
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RESUMO

A produção de compostos úteis através da fixação química de CO_2 tem atraído imenso interesse por parte da comunidade científica, devido à sua abundância na natureza, não toxicidade e pelo facto de ser barato. Uma das aplicações mais promissoras é a reação de acoplamento CO_2 com epóxidos na produção de carbonatos cíclicos, de elevada importância industrial e com uma ampla variedade de aplicações como solventes verdes, eletrólitos para baterias de lítio e monómeros na produção de polímeros.

Um desafio emergente com a aplicação industrial na produção destes compostos, é a separação e reutilização de catalisadores, nomeadamente complexos acídicos de Lewis, metálicos, homogéneos combinados com um nucleófilo.

O objetivo desta tese passa por investigar a utilização de diferentes líquidos iónicos e solventes eutécticos, capazes de funcionar como solventes e como co-catalisadores assim como possibilitar a separação por extração do produto obtido da mistura reacional. Neste contexto, as condições reacionais foram otimizadas tal como o comportamento de catalisadores e co-catalisadores. Além de diferentes famílias de catiões e aniões, também os solventes eutécticos foram estudados. As reações foram realizadas a alta pressão com os produtos finais a serem analisados por espectroscopia ^{1}HNMR. Um processo extrativo com CO_2 supercrítico foi utilizado para separar os produtos obtidos da mistura reacional. O sistema catalítico foi reutilizado até 3 vezes, sem que existisse perda de atividade.

O ião brometo com a sua respetiva combinação com o catião tetrabutilamónio mostrou ter a melhor atividade catalítica. No entanto, o seu uso como solvente não é viável uma vez que o mesmo é sólido a temperatura ambiente. Como solvente, o cloreto de metiltrioctilamónio mostrou ser o solvente mais promissor provando assim ser uma boa alternativa na reação, pois favorece a cinética da reação e retém o catalisador aquando do processo extrativo com CO_2 supercrítico.

Por fim, um solvente eutéctico tendo como constituinte o TBABr, mostrou ser o melhor solvente eutéctico constituindo assim uma boa alternativa em estudos futuros.

Palavras-chave: Carbonatos cíclicos, Epóxidos, CO_2, Solventes eutécticos, Líquidos Iónicos

ABSTRACT

The production of useful compounds through the chemical fixation of CO_2 has attracted increasing interest from the scientific community, due to its abundance in nature, non-toxicity and low-cost. One of the most promising applications is the direct coupling of CO_2 to epoxides for the production of cyclic carbonates, which holds industrial interest, due to wide range of applications namely as green solvents, electrolytes for lithium batteries and monomers for polymers production.

One technical barrier that needs to be addressed for wide industrial implementation, is the separation and reutilization of catalysts, usually homogeneous Lewis acidic metal-based complexes, combined with a nucleophile.

The aim of this thesis was to investigate the utilization of different ionic liquids and deep eutectic solvents, potentially able to work both as reaction solvent and as co-catalyst, as well as to allow the product separation from the reaction mixture. In this context, reaction conditions were optimized, catalyst and several co-catalysts performances were studied. Different cation and anion families of ionic liquids were also investigated, as well as deep eutectic solvents. Reactions were performed in a high-pressure apparatus and final products analyzed by 1H-NMR spectroscopy. Supercritical CO_2 extraction was applied to separate the product from the reaction mixture. The catalyst system was reused three times, without loss of activity.

The bromide anion and its combination with the tetrabutylammonium cation has shown the best catalytic activity. However, its utilization as a solvent is not viable due to being solid at room temperature. As a solvent, methyltrioctylammonium chloride showed promising results and proved to be a good alternative to perform the reaction, since besides favouring the reaction kinetic, it retains the catalyst allowing the product to be extracted using supercritical CO_2. Moreover, a tetrabutylammonium bromide (TBABr)-based deep eutectic solvent showed the best performance as solvent and co-catalyst and constitutes a good alternative for further studies.

Keywords: Cyclic carbonates, Epoxides, CO_2, Deep eutectic solvents, Ionic liquids.

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GLOSSARY

ALIQUAT 336	Methyltrioctylammonium chloride
$B(CN)_4$	Tetracyanoborate
CO_2	Carbon Dioxide
DES	Deep Eutectic Solvent
EG	Ethylene Glycol
EMim	EthylMethylimidazolium
$EtSO_4$	Ethylsulfate
FDA	Food and Drug Administration
Gly	Glycerol
h	hours
HBD	Hydrogen Bond Donors
IL	Ionic Liquids
K	Kelvin
MPa	MegaPascal
MEK	Methyl-ethyl-ketone
Ntf_2	Bis(trifluoromethylsulfonyl)amide
OTf	Trifluoromethanesulfonate
PPNCl	Bis(triphenylphosphine)iminium chloride
R&D	Research and Development
RTILS	Room Temperature Ionic Liquids
scCO2	Supercritical CO_2
SCF	Supercritical Fluid
TBABr	Tetrabutylammonium Bromide
TBACl	Tetrabutylammonium Chloride
TCA	2,4,6-Trichloroanisole
TOF	Turnover Frequency
TON	Turnover Number
$ZnCl_2$	Zinc Chloride

1. INTRODUCTION

1.1 Green Chemistry and the search for renewable feedstocks

Green Chemistry is a new philosophy that rethinks some of our current chemical processes focusing on the environment as well as on the protection of human health. Their main objective is to eliminate and/or reduce the production and use of dangerous and toxic substances currently used in the industry. The possibility to transform our natural resources as well as create new matter, has been one of the greatest accomplishments in modern chemistry. Yet, it comes with a price. Nowadays, the cities have accumulated waste from chemical transformations as well as by-products dangerous to the environment and human health [1]. Therefore, it became necessary to rethink the use of chemicals and what to do with the possible unwanted products. The first steps towards this environmental change began in the 1970s with the publication of books by Rachel Carson and Barry Commoner in 1971, where they reported the harmful side-effects of some of the chemical products used back then [2]. Their interests were the devastating effects of pollution, as a result of the chemical manufacturing processes for environment, indicating that cleaner, safer, and environmentally friendly approaches are required. In order to reduce the higher levels of pollution, waste prevention instead of waste remediation was a necessary step towards a cleaner production of chemicals. So in 1991, Trost published a first paper about some green chemistry principles and atom economy [3]. The aim was that the materials used in chemical processes would get incorporated into the final product, minimising the formation of waste. Atom economy number became an extremely useful tool for simple evaluation, before any experiments are starts, about the generation of waste in chemical processes.

In 1998, Anastas and Warner proposed a list of principles where the guiding element was “benign by design” [4]. Where the answer for a “greener future” is in changing industrial processes to safer, non-toxic and environmental-friendly methods, like reutilization of catalysts, instead of dealing with the waste produced. The idea is to change the premise and not the solution solely. This list of principles, is considered the steps needed for this change. Recently Sheldon, published a more updated list of the considered principles of Green Chemistry. The author discusses the importance of these principles, when applied to industrial processes, by avoiding waste formation and aiming for high atom economy reactions. An updated list of today’s Green chemistry principles is presented in Table 1.1. [5].

Table 1.1 - List of Green Chemistry principles [5]

1. **It is better to prevent waste than to treat or clean up waste after it is formed.**
2. **Synthetic methods should be designed to maximise the incorporation of all materials used in the process into final product.**
3. **Synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.**
4. **Chemical products should be designed to preserve efficacy of function while reducing toxicity.**
5. **The use of auxiliary substances (e.g. solvents) should be made unnecessary wherever possible, and innocuous when used.**
6. **Energy requirements should be recognised for their environmental and economic impacts and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure.**
7. **A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.**
8. **Unnecessary derivation (e.g. protecting/deprotecting groups) should be avoided whenever possible.**
9. **Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.**
10. **Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.**
11. **Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.**
12. **Substances and the form of a substance used in a chemical process should be chosen so as to minimise the potential for chemical accidents.**

In 2008, Poliakoff *et al*. proposed an updated list of the green engineering principles in order to homogenize green principles debate and communications across chemistry and chemistry engineering lectures [6].

One of the principles in Anastas's list, is the need to replace toxic and volatile organic solvents to safer and greener alternatives such as water, polyethylene glycol based solvents, ionic liquids (IL) and deep eutectic solvents (DES), among others.

Ionic liquids are organic salts possessing a melting point below 373 K and many of them are liquids at room temperature (Room Temperature Ionic Liquids, RTILs). Considered the solvents of the future, these ionic liquids are constituted by ion pairs, cations and anions, providing them unique properties and different applications from the common organic solvents. The number of possible combinations of cations and anions is very large allowing to change their thermal, chemical and electrochemical stability, as well as their high ionic conductivity leading to tuneable physical chemical properties [7]. Figure 1.1 shows some of the cations and anions mostly used.

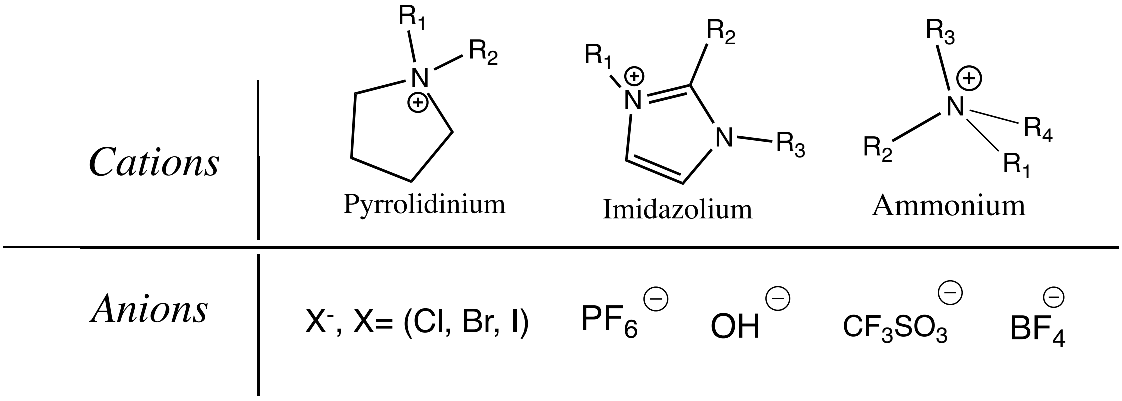


Figure 1.1 - Cations and Anions most commonly used in ILs

In the last decades, several applications of the ILs have been published, for instance, in the separation of azeotropic mixtures and copolymerization of epoxides and CO_2 [8] [9].

Ionic liquids have also been reported for acting as good catalysts in several organic reactions, including Friedel Crafts reaction, Diels-Alder reactions, polymerization and other reactions [10]–[12]. The fields of application of ILs includes organic chemistry and catalysis (as alternative solvents and chiral catalysis), analytical chemistry (for HPLC, GC-MS and NMR as additives), electrochemistry (as electrolytes), pharmaceutical chemistry (as solvent for synthesis of APIs and pharmaceutical drugs based ILs, API-ILs), chemical engineering (selective separations and extraction processes), biochemistry (dissolution and stabilization of proteins) and material science (task-specific ILs as functional materials incorporating luminescent, magnetic, chromogenic and other functionalities) and more recently energy applications (lubricants, fuel cells and batteries).

But the top priority in Green Chemistry agenda, which is holding the attention of various sectors of the society is related with principle number 7. In fact, generalized concerns about the depletion of fossil fuel resources is driving a strong R&D effort on the search of alternative carbon feedstocks. Carbon dioxide (CO_2) which is released in many combustion processes can be a possible source.

Many methods have been developed over the last years for the utilization of CO_2 as chemical feedstock, but only 1% of total CO_2 on earth is actually being used. This is mainly due to its inherent chemical inertness, which has been preventing its widespread utilization as a chemical reactant.

1.2 Carbon dioxide utilization

Carbon dioxide (CO_2) is one of the earth's primary greenhouse gases and it is also the most abundant waste produced by human activities. The greenhouse effects are known as the main cause for global heating which results in climate change and possibly harmful effects for earth's ecosystems, biodiversity and humans worldwide. On the other hand, CO_2 is also non-toxic, non-flammable and generally regarded as safe by the FDA, it is widely used in the food industry, namely in the production of carbonated beverages, baking powder, coffee decaffeination and TCA extraction from cork stoppers. In this latter case, supercritical CO_2 ($scCO_2$) seems to be in fact the only solution to eliminate TCA from cork stoppers, while maintaining fundamental properties of this unique material. The application of CO_2 as a green solvent makes it possible to use CO_2 with no environmental detriment, if it could be withdrawn from the environment, employed in a process and return to the environment clean.

Another strategy is the utilization of CO_2 as C_1 feedstock to produce useful compounds, which has attracted increasing interest from the scientific community. Its non-toxicity, availability, low cost and abundance, make it ideal to produce chemicals with alternative and sustainable carbon resources. The possibility to replace toxic chemicals such as phosgene, isocyanates and carbon monoxide makes carbon dioxide really important from an economic and ecological point of view [13][14].

The use of CO_2 as a carbon feedstock for the chemical industry is not expected to have impact on its mitigation due to the differences between worldwide production of chemicals and CO_2 emissions.

Nevertheless, this strategy can provide access to valuable products from a low-cost and abundant carbon source.

1.2.1 The use of CO_2 as supercritical solvent

Back in the mid 80's, supercritical technology was emerging. It was a technology that was proving to be useful in the industry sector. The first $scCO_2$ applications were the extraction of caffeine from coffee beans, oils from natural products and many others [15].

Supercritical fluids (SCF), are not liquids, gas or solids, they rather stand between liquid and gas gaining different properties and behaviours from these two conventional phases of matter. Scientific community seems to show growing interest in this technology, as over the past decades a significant growth in publications about SCF have been reported [15][16]. When at a certain temperature and pressure, every stable compound can attain the so-called, critical point as illustrated in Figure 1.2.

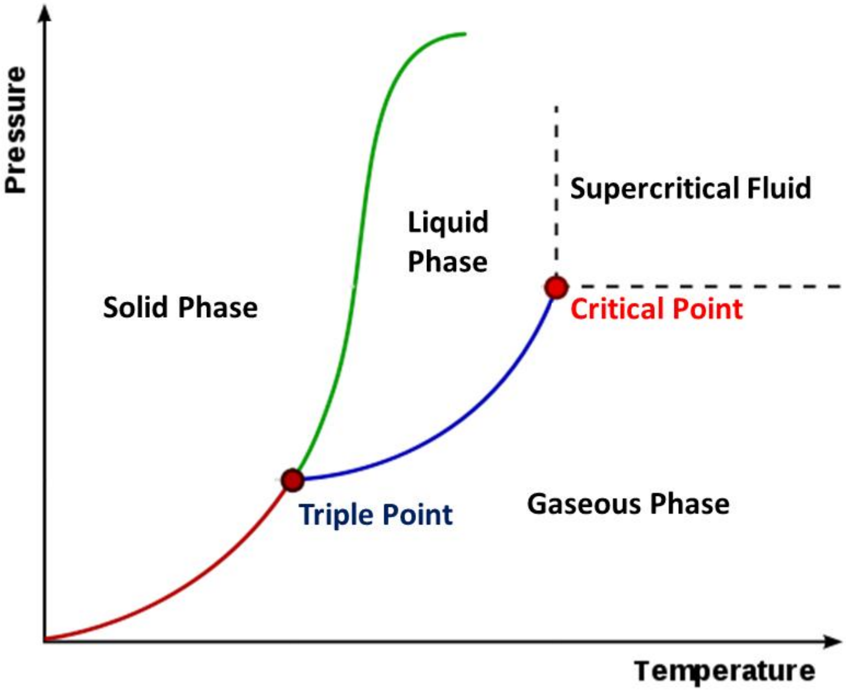


Figure 1.2 – CO_2 phase diagram [17]

Above this point, there is no distinction between liquid-gas phase of the substance. With minor changes on the pressure and temperature, different SCF densities can be obtained. CO_2 has its critical point, temperature and pressure, easily attainable of 304 K and 7,38 MPa. Carbon dioxide behaves like a gas at room temperature but once its pressurized while being heated, it reaches its supercritical state, acquiring unusual proprieties such as high compressibility. In the presence of organic solvents $scCO_2$ expands changing its viscosity, density, polarity and catalyst solubility [18]. Its low toxicity, low price, natural abundancy and being "Green Solvent" make it a useful and promising green solvent, especially as solvent in extraction processes. Currently used in catalysis and oxidation reactions as alternative solvent or efficient extraction methodology [19].

$ScCO_2$ can also be combined with ILs in the implementation of process intensification strategies. One example was published in 2011 by Branco *et al.,* using of chiral ionic liquids in asymmetric dihydroxylation of olefins with supercritical CO_2, as an efficient extraction media [20]. With the combination of ionic liquids and supercritical CO_2 there are numerous advantages since the ionic liquids show no solubility in $scCO_2$ and at the same time $scCO_2$ is soluble in most ILs making possible to extract numerous organic products [20]. Furthermore, the ionic liquid phase containing the catalyst can later be reused in subsequent reaction/extraction cycles, as presented in Figure 1.3. When a mixture of catalysts dissolved in the IL together with products and reactants (P+R) is pressurized with $scCO_2$ an atmosphere of $scCO_2$ separating P+R from catalysts is formed. While the $scCO_2$ is added, it creates an atmosphere in which the P+R are soluble but the mixture with IL and catalyst is immiscible. During decompression CO_2 drags P+R to a trap covered in ice in order to precipitate P+R. The IL, together with the catalysts, remains in the apparatus continuously activating the catalysts until another load of P+R.

Extraction through $scCO_2$ has been recently used in decaffeination, extraction of natural products and dry cleaning [21] [22].

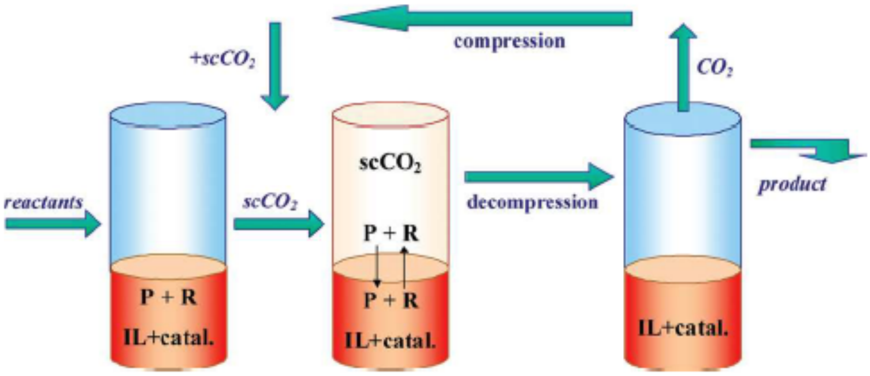


Figure 1.3 - Product recovery using $scCO_2$-IL biphasic system with ionic liquid/phase catalyst recycle [20]

1.3 CO_2 as carbon feedstock

Over the past decade, extensive studies for the development of methodologies to use CO_2 as a chemical reactant have been made. The challenging task to overcome the thermodynamic stability of CO_2 is finally presenting its results. Carbon dioxide is becoming a useful chemical feedstock with different applications [23]. In fact, CO_2 valorisation may reduce world dependence on fossil fuels, providing a secure supply of carbon. With low free energy, carbon dioxide needs to react with high free energy substrates because its utilization and activation is still problematic [23].

Valorisation of CO_2 is currently receiving growing interest from the scientific community, where the search for new applications and reactions continues. Some example reactions are the reduction of CO_2 with H_2 to yield methanol or formic acid and the formation of cyclic or polymeric carbonates, just to name a few [13]. The overall perspective of chemical fixation and utilization of CO_2 can be seen in Figure 1.4 [24].

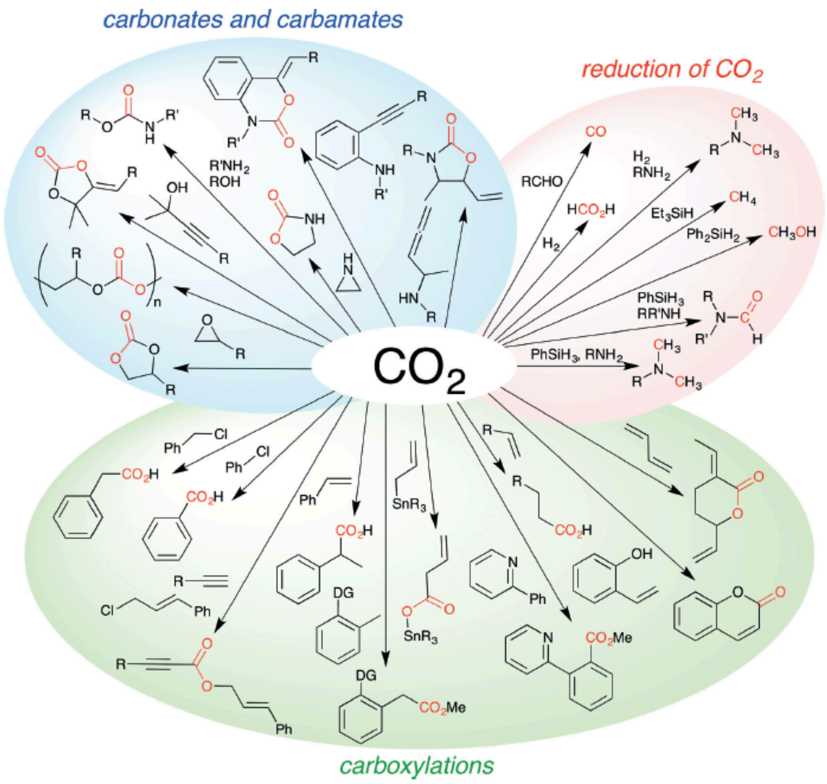


Figure 1.4 - Examples of chemical fixations with CO_2 [24]

In1969, Inoue *et al.,* firstly reported the reaction between CO_2 and epoxides to produce high quality polymers [25]. Polycarbonates, a secondary product, can be derived from fossil fuels or produced via synthetic route. When derived from fossil fuels, it derives from bisphenol A and requires phosgene to react forming the polycarbonate. However, phosgene is toxic and bisphenol A is non-environmental friendly as it derives from fossil fuels and so carbon dioxide is the preferable alternative in these reactions.

Another possible secondary product obtained with the coupling reaction of CO_2 with epoxides are cyclic carbonates (CC), as presented in Figure 1.5. Cyclic carbonates have an important role nowadays in green chemistry as they can be used as green solvents with useful properties such as high boiling point, high polarity and low vapour pressure. They can also be used as electrolytes in *Li*-ion batteries, aprotic polar solvents as well as intermediates in the synthesis of polymeric and fine chemicals [26].

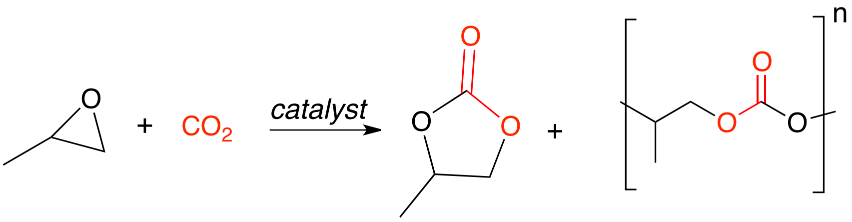


Figure 1.5 - CO_2 addition to propylene oxide

The “greenness” of these alternative reactions with CO_2 fit in “Green Chemistry” philosophy since the use of common volatile organic solvents is avoided. Moreover, most of these reactions have no waste formation with the addition of being atom economically viable with 100% incorporation of CO_2 in the final product.

However, some of these reactions require catalysts and the further sections will closely describe its effect and contribution to the reaction process.

1.4 Catalysis as key technology for CO_2 conversion

Today, the chemical industry production is using processes which are catalytic cycles. The objective is to recycle the catalysts as it bonds to the reactants, allowing these to react to a product, and recycle the catalyst once the reaction is complete. The catalyst is left unaltered and available for the next reaction/cycle [27].

There are two types of catalysis, homogeneous and heterogeneous. The difference relies on whether the reactant and catalyst are in the same phase, liquid or gas, or not [27].

As stated before, in homogeneous catalysis, both the reactant and catalyst are in the same phase, most commonly liquid. Although homogeneous catalysis has a better catalytic activity in terms of catalysts, heterogeneous catalysis allows the reutilization of the same catalysts without loss of activity, in a finite number of cycles. This approach can avoid the waste formation as usually once a catalyst is no longer active it goes to waste causing pollution. The choice of catalyst is very important in homogeneous catalysis, it is possible to choose a preferable product in a reaction by changing ligands around the centre metal, usually a metal ion. Besides metals, catalysts can be Lewis acids (Diels-Alder reaction), porphyrin complexes (epoxidations), enzymatic processes, the usual acid and base reactions and at last, coordination complexes (polyester condensations) [28].

In the case of heterogeneous catalysis, the great majority of catalysts are solid whereas the reactants are most commonly liquids. Two distinguish phases allow purification techniques such as extractions, filtration as well as applications in silica chromatographic columns.

Nowadays, catalysis is considered indispensable in the industry. Fine chemical producers now invest in the use of catalytic conversions in their processes. Homogeneous and heterogeneous catalysts are being used for cycloaddition of CO_2 to epoxides and conversion of petrochemicals [28]. Figure 1.6 shows how a catalyst lowers the substantial energy that molecules must overcome when bonding. In the presence of catalyst, there is a much more complex route, yet more energetically favourable [27].

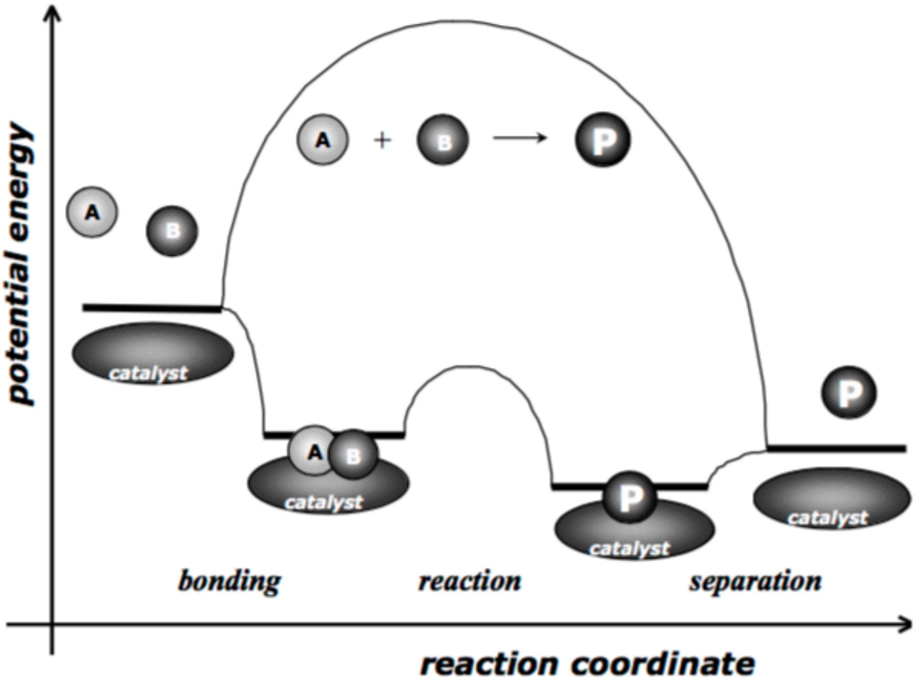


Figure 1.6 - Catalysts effect on reactions

In Figure 1.6, a representation about the catalyst function and its influences in the reaction, by lowering the activation energy needed for A and B to react to produce P. The actual definition for catalyst is: “A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved.”. In order to not get involved, there must be a catalytic cycle which regenerates the catalyst as the reactions occur. The aim is to recycle the catalyst as many times as possible, with high yield catalytic conversions, while remaining active and without formation of by-products. The catalyst needs to be activated for the catalytic cycle to start and once activated it can be present in different intermediate forms. Considering the number of times, a catalyst can cycle through its intermediate phases, we can calculate its turnover number (TON). Turnover number (TON) is calculated using the total number of substrate molecules that a catalyst converts into product molecules. Whereas, turnover frequency (TOF) is calculated with TON but in a certain amount of time [28].

In catalytic systems using $scCO_2$, the synthetic path depends on the catalyst but also on the substrate and reaction conditions [29].

The reaction of CO_2 with epoxides is one of the examples of a possible catalytic system, in this reaction, there can be two products: cyclic carbonates and polycarbonates. Depending on the catalyst, products can choose a preferable synthetic route. Catalysts differ from homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts have being widely used in cycloaddition of CO_2 to epoxides as they are the most active and selective for this reaction [30].

Pescarmona et al. [29] recently used a method to classify homogeneous catalysts, through their number of metal atoms involved in the catalytic cycle: Monometallic pathways, Bimetallic pathways and Non-metallic pathways. This method will be applied in the next chapter when discussing catalysts more deeply. In case of cycloaddition of CO_2 to epoxides, most proposed mechanisms are monometallic, as presented in Figure 1.5. However, there are other applications for these catalysts and how can they relate in reaction. Active homogeneous catalysts can be used with heterogeneous catalysts when coupling CO_2 to epoxides, it requires immobilizing the active homogeneous catalyst on the surface of a support [29][31]. Some of the currently used supports are polymers or silica-based materials [32].

Heterogeneous catalysts have been studied less intensively than homogeneous catalysts as their design flexibility is not as wide as in homogeneous catalysts. Although selectivity and activity of both catalysts can compete, the restricted type of metal complexes used with heterogeneous catalysts cannot match its counterpart. The requirement of a material that is readily reused make its metal complexes limited in terms of design [29][30].

1.4.1 Homogeneous Catalysts

1.4.1.1 Homogeneous Mono-Metallic Pathways

As stated before, most mechanisms for the coupling reaction of epoxides and CO_2 with homogeneous catalysts follow a mono-metallic pathway. Studies have been made to confirm the exact mechanism in these reactions and it came to light that it depends on the substrate and reaction conditions. Another important aspect, is the presence or not of a co-catalyst, acting as a nucleophile to help activating the epoxide or ending chain polymer reactions. These activation step relies on the metal complex as it can activate the CO_2 molecule, the epoxide or both molecules at the same time. This activation of the epoxide is only possible when one of the epoxide’s oxygen atoms interacts with the Lewis acid centre of the metal complex. Then, the presence of the nucleophile ligand, or nucleophile co-catalyst, induces the ring opening from the epoxide by nucleophilic attack. Some metal complexes, also referred as catalysts, can include a ligand that works as a nucleophile [29]. The most assumed mechanism for this reaction is shown in Figure 1.7, where the metal complex is used in a combination with a nucleophile, also referred as co-catalyst.

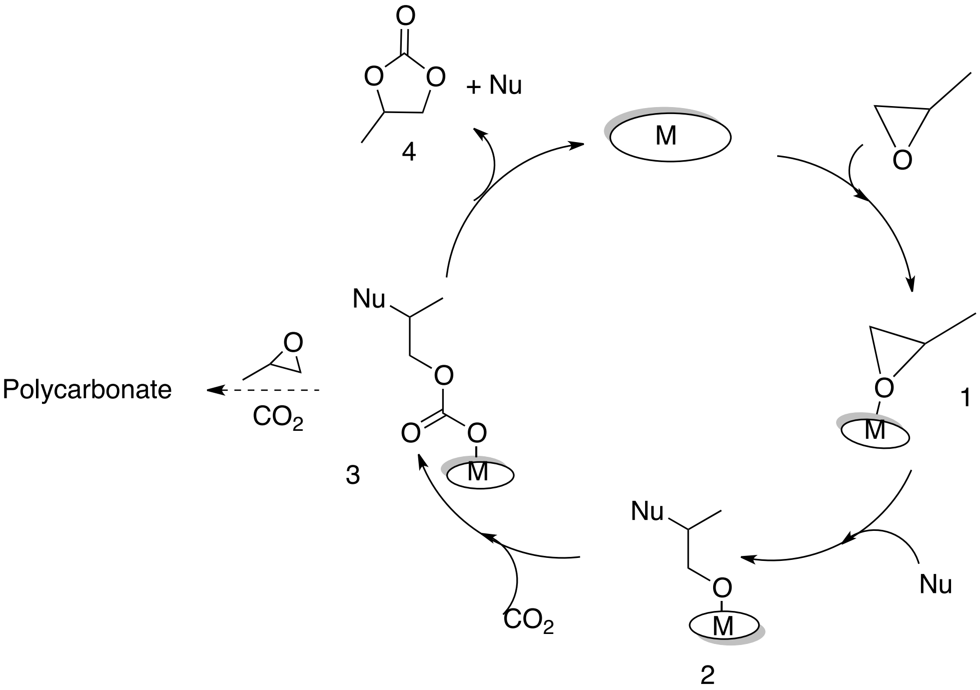


Figure 1.7 - Mono-metallic pathway of CO_2 addition to epoxides [30]

As described before, the first step consists on activating the epoxide by coordination to the Lewis acid metal centre, followed by the nucleophile attack in order to open the epoxide ring and formation of the metal-bound alkoxide (structures 1 and 2). Then, carbon dioxide molecule gets inserted into the metal alkoxide bond resulting in a metal carbonate intermediate (structure 3) which can either evolve towards a cyclic carbonate or propagate by continuous addition of epoxide and CO_2 resulting in polycarbonate.

Another possible mechanism has been proposed for metal salen complexes involving two nucleophiles. Salen complexes are characterised by a planar configuration with a tetradentate coordination of the salen ligand [29].

1.4.1.2 Homogeneous Bi-Metallic Pathways

The most assumed and common mechanism for the addition of CO_2 to epoxides is the mono-metallic mechanism with one metal centre being involved in the reaction. However, Pescarmona describes other metallic mechanisms depending on the number of metal centres involved. In bi-metallic mechanisms two active metallic centres are required, where both metallic centres can be part of the same single complex or the reaction can involve two distinguish mono-metallic complexes.

When considering two separate metal complexes in a bimetallic pathway, the mechanism is inspired in the asymmetric ring opening of epoxides [33]. This intermolecular reaction mechanism is very similar with the mono-metallic, differing on the fact that the ring opening of the epoxide involves the activation of the epoxide, by coordination on the metal of the first complex at the same time as the attack of the nucleophile coordinated to a second metal centre. This bi-metallic initiation is followed by a mono-metallic pathway as described before. For a better understanding, Figure 1.8 shows a plausible mechanism when considering two different metal complexes in addition of CO_2 to epoxides.

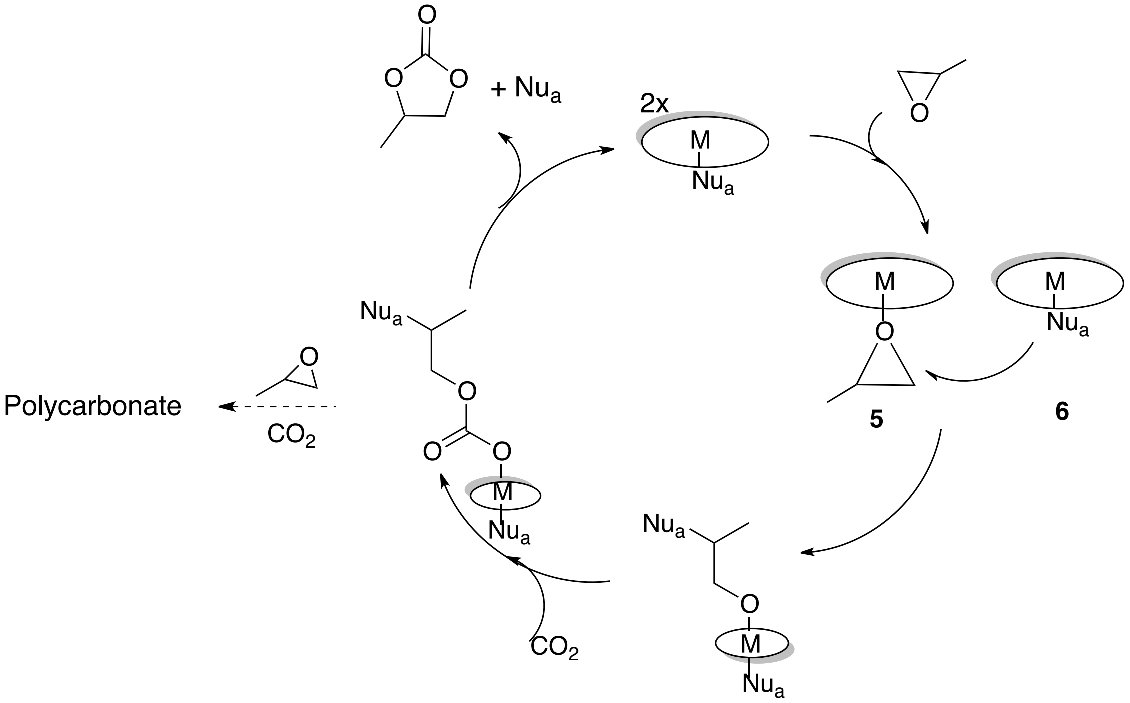


Figure 1.8 - Bi-metallic mechanism for the coupling reaction of CO_2 and epoxide [30]

In contrast with the previous mono-metallic mechanism, some metal complexes can contain two neighbouring metal centres allowing the activation of both CO_2 and epoxide simultaneously. Activating both species promotes the intramolecular nucleophilic attack of the alkoxide to the carbon atom of the activated carbon dioxide molecule. As shown in Figure 1.8, the key steps in this mechanism are the formation of an alkoxide intermediate bonded to one of the metal centres, after the ring opening of the epoxide, and the coordination of carbon dioxide to the second metal centre followed by an intramolecular nucleophilic attack of the alkoxide to the coordinated carbon atom in carbon dioxide.

Accordingly to North et al., this mechanism was proposed to explain the improved catalytic activity of bi-metallic $[Al(salen)]_2O$ complexes compared to monometallic salen complexes [9]. Bi-metallic aluminium (salen) complexes display high catalytic activity for the conversion of terminal epoxides into cyclic carbonates at room temperature.

In 2010, published works were extensively revised by North et al. as well as in 2015 by Martin et al [9] [34]. Salen and salphen metal complexes were studied among the different homogeneous catalytic systems active for cyclic carbonate formation as active catalysts for direct CO_2 coupling with epoxides [34]. These catalysts are characterized by their easy preparation and versatility. The variation in the type of active metal centre and possibility of direct inclusion of a nucleophilic co-catalyst are some of the tuneable features of these catalysts, allowing for large-scale synthesis and potential commercial applications. Kleij's group, in 2012, reported an active mononuclear

Zn(salphen) complex towards CO_2 coupling with terminal epoxides. The metal complex showed high activity due to the constrained geometry imposed by the ligand scaffold which grants increased Lewis acid character to the catalytically active Zn ion [35].

The ideal catalytic system allows the reutilization of catalysts with high yields, conversions together with an extraction method that allows the extraction of products.

1.5 Room Temperature Ionic Liquids as catalysts in the coupling reaction between CO_2 and epoxides

The introduction of ionic liquids (ILs) in catalysis, allows the continuous activation and reutilization of catalysts.

In 2001, Peng and Deng, published the first successful synthesis of cyclic carbonate using RTILs of imidazolium and pyridinium salts [36]. The use of traditional solvents does not always benefit the reaction of CO_2 and epoxides due to the lower solubility of the CO_2 in common solvents. The combination of $scCO_2$ and ILs has already been studied in many phase equilibria systems and it concluded that CO_2 possess high solubility in RTILs however RTILs are not soluble in $scCO_2$. This observation allows the extraction of reaction products without contamination from the IL and a possible reutilization of the catalysts. The advantages of using $scCO_2$ together with the ILs are several. For instance, it can combine homogeneous and heterogeneous catalysis maintaining both its intrinsic characteristics. A selected IL might be immiscible with reactants and products however, it can solubilize the catalyst and make it more active during the reaction [37].

Considering the applications of RTILs to the copolymerization of epoxides and CO_2, Figure 1.9 illustrates a plausible mechanism for the reaction with ILs, where X^- is a common anion and $[cat^+]$ a common cation.

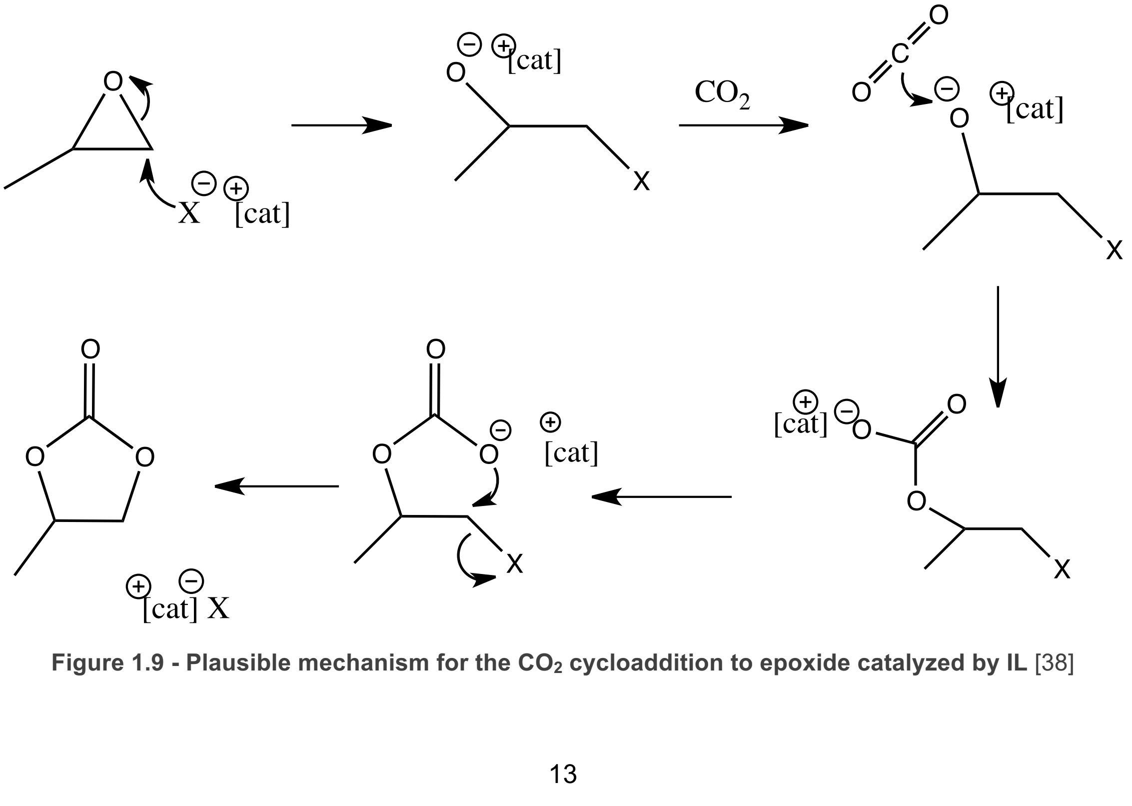


Figure 1.9 - Plausible mechanism for the CO_2 cycloaddition to epoxide catalyzed by IL [38]

In this mechanism, the reaction is initiated with the nucleophilic attack from the anion of the IL to the less hindered carbon atom of the epoxide ring. The attack causes the opening of the epoxide ring and leads to the formation of the oxy-anion between oxygen and [cat$^+$]. The added CO_2 will interact with the oxy-anion producing an alkylcarbonate anion. The last step is the cyclic carbonate formation with an intermolecular cyclic elimination of X^- [38].

1.5.1 DES – Deep Eutectic Solvents

Recently, deep eutectic solvents (DESs) have been described as subclass of ionic liquids sharing many characteristics and properties with ILs. Yet, it is necessary to point out that these are two different types of solvents with different kinds of applications. DES are systems formed from a eutectic mixture of Lewis or Brønsted acids/bases which can contain anionic and/or cationic species; in case of IL, they are formed from systems composed primarily of one type of discrete anion and cation [39]. Although their physical characteristics are similar, the same cannot be said from their chemical properties, resulting in different applications.

The production of DESs involves the simple mixing of the two components, usually with moderate heating. In 2004, Abbott *et al.*, firstly reported the formation of deep eutectic solvents based on mixture between choline chloride and urea (1:2) as an alternative to ionic liquids [40]. They are usually obtained by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between for example a halide ion and the hydrogen-donor moiety is responsible for the decrease in the melting point of the mixture relative to the melting points of the individual components [41].

Abbott & Smith *et al*. recently published their studies on some DESs and their applications, they came up with a general formula that describes DESs [39]:

$$CAT^+X^-z\,Y$$

Equation 1.1 - DESs general formula

Considering CAT^+ is any ammonium, phosphonium or sulfonium cation, and X being a Lewis base, most commonly an halide anion, the complex anionic specie is formed by the X^- and either a Lewis or Brønsted acid Y. Where z is the number of molecules of Y that interact with the anion. Depending on the nature of the complexing agent used, DES can be classified differently.

type	general formula	terms
type I	$Cat^{+}X^{-}zMCl_x$	M = Zn,[1,5,6] Sn,[7] Fe, Al,[8] Ga,[9] In[10]
type II	$Cat^{+}X^{-}zMCl_x \cdot yH_2O$	M = Cr,[11] Co, Cu, Ni, Fe
type III	$Cat^{+}X^{-}zRZ$	Z = $CONH_2$,[12] COOH,[13] OH[14]
type IV	$MCl_x + RZ = MCl_{x-1}^{+} \cdot RZ + MCl_{x+1}^{-}$	M = Al, Zn and Z = $CONH_2$, OH

Figure 1.10 – Different types of DES [39]

Depending on the formation of DES, its applications vary, due to different physicochemical properties. Figure 1.10 shows the how DES were grouped accordingly with their nature of complexing agent [39]. When DES are formed from MCl_x and quaternary ammonium salts, we consider them type I, as they are analogous to the metal halide/imidazolium salt well known systems. Type II DESs, hydrated metal halides and choline chloride, wide the scope of DES as the range of non-hydrated metal halides with low melting point is limited (type I). Type III eutectics are formed between choline chloride and hydrogen bond donors (HBD) [39]. Some of the quaternary ammonium salts and hydrogen bond donors typically used in nowadays research are represented in Figure 1.11.

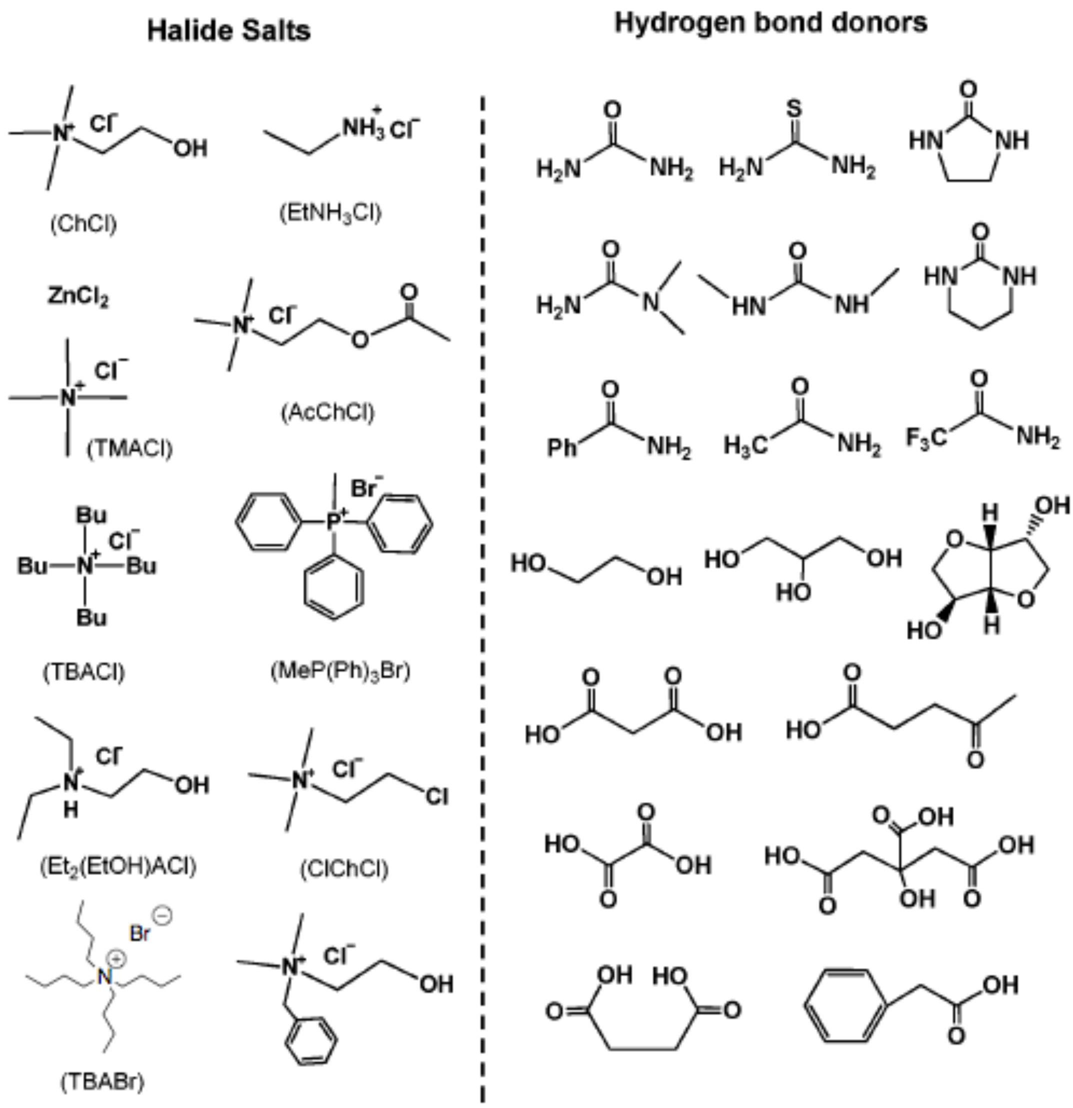


Figure 1.11 - Typical halide salts and HBD structures [41].

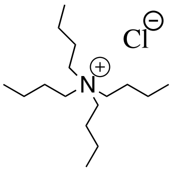
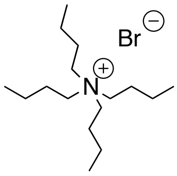
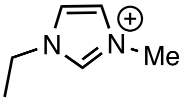
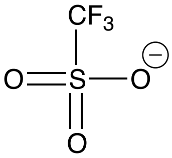
Tetrabutylammonium bromide (TBABr) is currently emerging as one of the most promising ammonium salts and it is a valuable source of bromide and can be used as an IL. It is cheap, environmentally friendly and possess great selectivity [42].

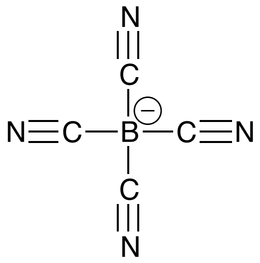
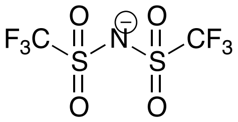
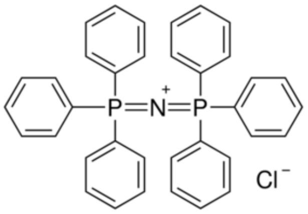
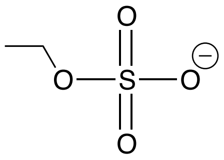
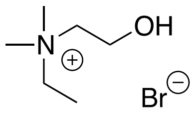
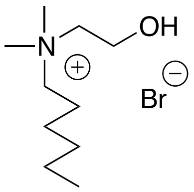
2. MATERIALS AND METHODS

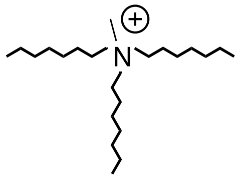
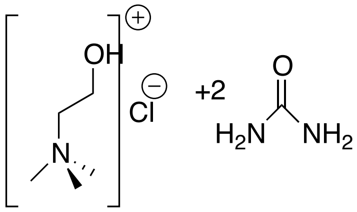
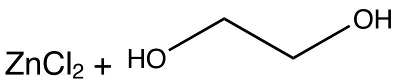
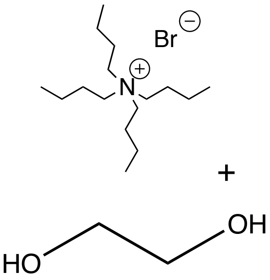
2.1 Materials

All reagents, solvents and chemicals were used as received after being bought or kept in storage without further purification. Carbon dioxide (99,998 mol% purity) was supplied by Air Liquid. Propylene oxide (90% purity) was purchased from Sigma-Aldrich as well as ethyl lactate, methyl-ethyl-ketone. All metal complexes were synthesized by the Coordination Chemistry and Catalysis Research Group from IST-UL. All ionic liquids and DESs were synthesized by Solchemar Lda. Compounds ([N1,1,2,2OH]Br) and ([N1,6,2,2OH]Br) were synthesized in FCT-UNL lab 4.10 by Andreia Forte[43]. The of list of reagents is presented on Table 2.1.

Table 2.1 - List of Ionic liquids and DES used

Name	***Structure***
Tetrabutylammonium Chloride [TBA]Cl	
Tetrabutylammonium Bromide [TBA]Br	
[EthylMethylimidazolium] [EMim$^+$]	
Trifluoromethanesulfonate (Otf)	

Tetracyanoborate ($B(CN)_4$)	
Bis(trifluoromethylsulfonyl)amide (NTf_2)	
Bis(triphenylphosphine)iminium chloride (PPNCl)	
EthylSulfate ($EtSO_4$)	
[N1,1,2,2OH]Br	
[N1,6,2,2OH]Br	

Methyltrioctylammonium Chloride (ALIQUAT 336 – [$N_{1,8,8,8}$]Cl)	
Eutectic mixture Choline: Urea (1:2)	
DES ZnCl2:EG 1:4	
DES [TBA]Br:EG 1:6	

In Figure 2.1, Figure 2.2 and Figure 2.3 are represented the catalysts used during the thesis work. Hence the difference between structures and the number of metal centres in each catalyst.

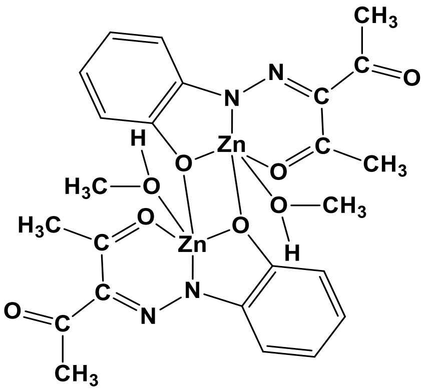


Figure 2.1 - Catalyst ZnR11 MW=631g/mol [44]

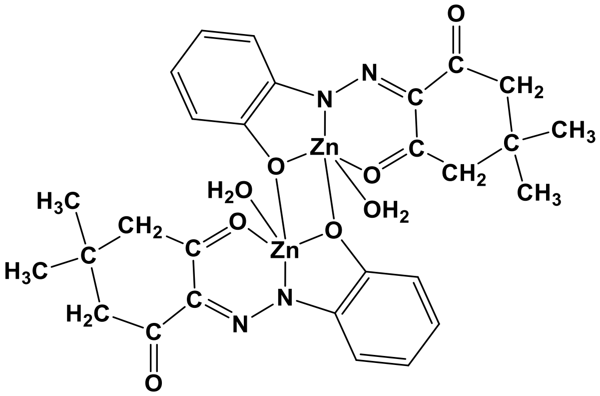


Figure 2.2 - Catalyst ZnR29 MW=683g/mol [44]

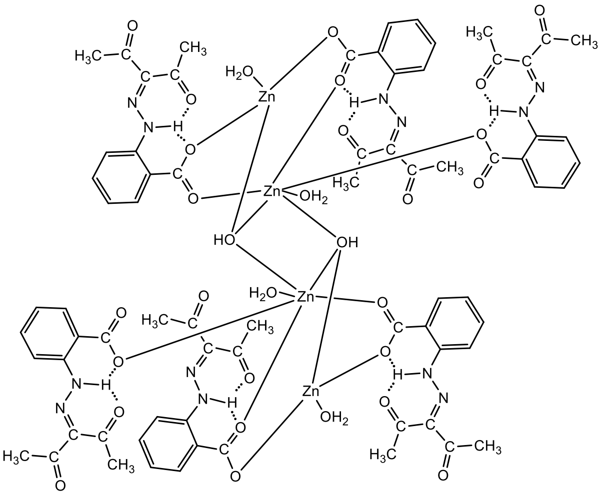


Figure 2.3 - Catalyst ZnR236 MW=1851g/mol [44]

2.2 Experimental Apparatus

All reactions were performed in a high pressure apparatus available at the host laboratory. The experimental apparatus consisted in a stainless steel cylindrical cell with two sapphire windows and an internal volume of approximately 5 cm^3. The sapphire windows allow the visualization of the phases in equilibrium during the reaction. A magnetic bar was used to stir the reaction mixture inside the cell. A thermostated water bath, previously heated, maintained the temperature within ±0,1ºC. The pressure in the cell was measured with a pressure transducer 204 Setra calibrated between 0 MPa and 34.3 MPa (precision: 0,1 %; accuracy: 0.15 % at the lowest pressure). Figure 2.4 shows a representation of the experimental apparatus with the cell underwater.

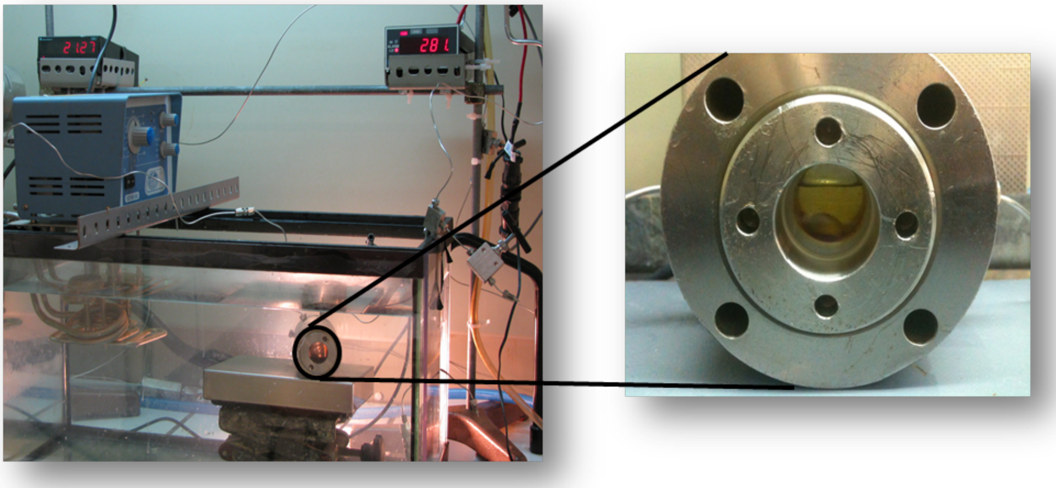


Figure 2.4 - Experimental apparatus with a reaction mixture load

2.3 Methods

2.3.1 General Procedure

The catalyst and co-catalyst were first dissolved in the substrate (14.3 mmol of propylene oxide). The amount of co-catalyst varied between 0.1% to 1% (molar) relatively to the oxide. Whenever used, the volume of solvent added (ionic liquid or PEG), was 1 mL. All mixtures were prepared gravimetrically using analytical balance (Sartorius model R180D) with the precision of ±0.0001 g. The stainless steel cylindrical cell was closed with 2 inner O-rings, 2 sapphire windows, 2 outer O-rings and 2 rings of stainless steel to assure no leaks. The cell was then immersed in the thermostated water bath. Operating a CO_2-compressor, the desired pressure was brought into the cell, as described in detail elsewhere [45].

Temperature and pressure were controlled and a magnetic stirring plate was kept sure to remain active during the reactions. In the end of the reaction, the cell was slowly cooled outside to reduce the pressure inside. Upon reaching around 2 MPa (20 bar), the cell was depressurized to atmospheric pressure. During depressurization, the tube exit was introduced in a glass trap, under a bath of ice in order to collect possible material dragged along with CO_2.

Part of the reaction mixture was collected in the glass trap and the cell opened to collect the remaining. Both contents of the cell and glass trap were mixed and prepared for further analysis as follows. ^{1}H-NMR and ^{13}C-NMR were analysed from the reaction mixture transferred into an NMR tube, to which 0.4 mL of mixture obtained and 0.1 mL of chloroform-d_1 were used. ^{1}H-NMR were recorded on Bruker 500 MHz type (400 MHz). Chloroform-d_1 has a known peak frequency of 7.26 ppm and so other peaks frequencies were compared to it. Integration of the relevant peaks from ^{1}H-NMR for the epoxide propylene oxide and respective carbonate were calculated for formation determination.

2.3.2 ScCO_2 extraction of reaction products

Extraction experiments were performed using the same apparatus with some modifications. Two high-pressure valves were connected directly to the sealing system at the top of the reactor, and further connected to a trap immersed in an ice bath. The two high pressure valves were slowly released and manipulated to control the CO_2 flow and maintain constant the pressure inside the system. Extraction experiments were carried out at 313,2 K and 11,5 MPa during approximately 3 h. The obtained product is pure without contamination from the catalysts.

2.3.3 Synthesis of DES

The original method for preparing DES mixtures, was reported by Abbot *et al.*[40]. For the preparation of DES, two components must be mixed under mild heating and stirring. The salt and hydrogen-bond donor (HBD) were mixed in a round flask with a mechanical stirrer. The mixture was then heated to 343 K for 3 hours, while observing the formation of a colourless liquid representative of DES. Different molar ratio DES based on $ZnCl_2$:EG (1:4), [TBA]Br:EG (1:6) and [TBA]Br:Gly (1:9) were prepared and used.

2.3.3.1 Preparation of $ZnCl_2$:EthyleneGlycol (1:4)[39]

For preparation of DES, were mixed 0.818 mL(14.7 mmol) of ethylene glycol and 0.5g(3.7 mmol) of $ZnCl_2$ by heating at 343 K for 3 hours.

2.3.3.2 Preparation of [Tetrabutylammonium]Bromide:EthyleneGlycol (1:6)[39]

For the preparation of DES, were mixed 0.518 mL(9.3 mmol) of ethylene glycol and 0.5 g (1.55 mmol) of [TBA]Br in a vial with mixing and heating at 343 K for 3 hours.

2.3.3.3 Preparation of [Tetrabutylammonium]Bromide:Glycerol (1:9)[39]

In order to prepare the DES, 1.154 mL(13.9 mmol) of glycerol were added to 0.5 g (1.55 mmol) of [TBA]Br in a vial with mixing and heating at 343 K for 3 hours.

No purification step was needed in the preparation of the Deep Eutectic Solvents.

3. RESULTS AND DISCUSSION

The work presented in this chapter was performed in collaboration with PhD student Ana Inês Paninho and part of it was submitted to the Journal of Supercritical Fluids. The reaction between CO_2 and propylene oxide was selected as a model reaction due to simplicity of analysis and propylene oxide high reactivity. The further section will closely describe how the optimized conditions were determined, the effect of catalysts and co-catalysts and finally the use of ionic liquids and DES.

3.1 Reaction conditions

All product formations were determined by analysis of the reaction solution through ^{1}H-NMR spectroscopy. A ^{1}H-NMR model spectra including the characteristic peaks of the protons from the propylene epoxide and propylene carbonate is presented in Figure 3.1. Propylene oxide and cyclic carbonate both possess six protons (H), considering the following chemical shifts:
Propylene oxide (a) 1.01 (d, 3 h) in the case of methyl group, (b) 2.11 (m,1H) as a single proton from CH; (c) and (d) 2.42 (m,1H) and 2.67 (m, 1H) as two protons from CH_2 of the compound;
Cyclic carbonate (a´) 1.28 (d, 3 h) related to methyl group, (b´) 3,84 (m, 1H) for CH of the cyclic structure and the (c´) and (d´) corresponding to 4.36 (m, 1H) and 4.70 ppm (m,1H) respectively for CH_2 of the compound.
It is clear a significant difference of chemical shifts in the case of CH and CH_2 of both structures allowing to determine the final product conversion of each reaction by NMR.

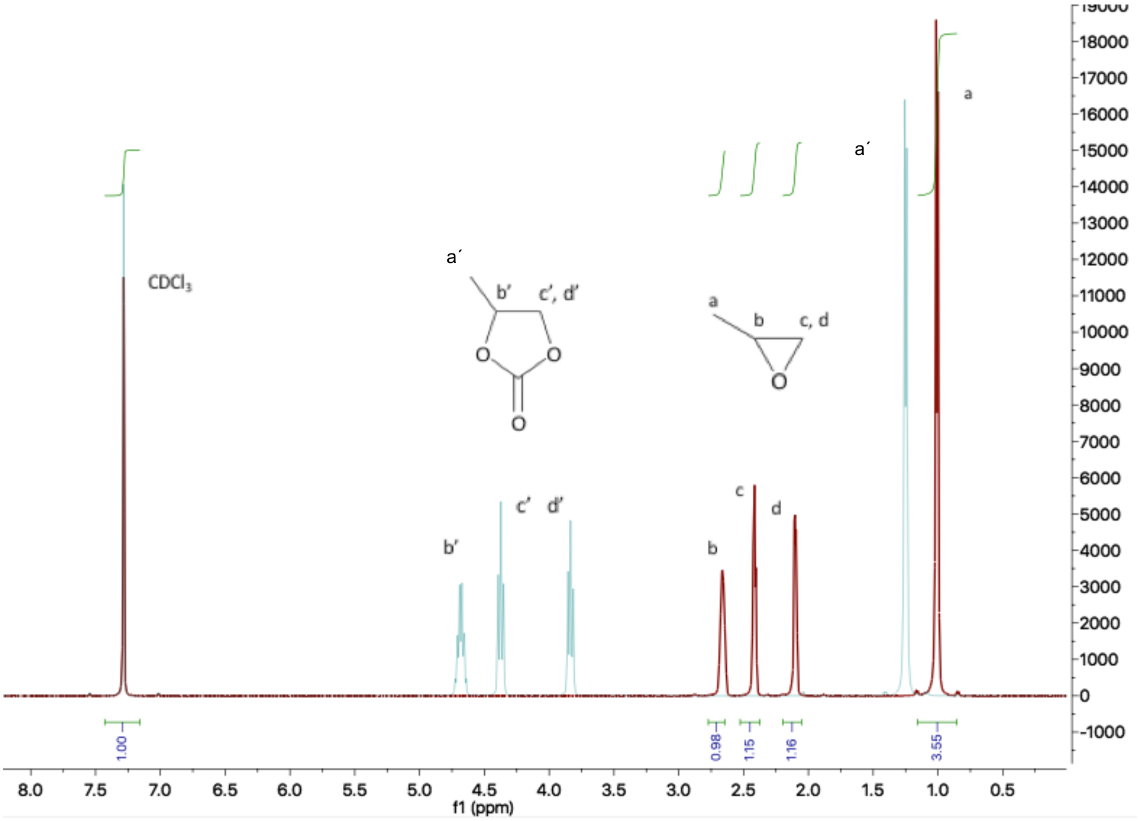


Figure 3.1- ^{1}H-NMR of propylene oxide and cyclic carbonate overlapped

Depending on the selected reaction operatory conditions and type of catalyst employed, the reaction can also produce some quantity of polycarbonates. In the case of carbonates derived from propylene oxide, selectivity towards cyclic or polymeric product can also be determined by ^{1}H-NMR spectroscopy, because chemical shifts do not overlap, as already indicated for the cyclohexene oxide. Another possible product from the coupling reaction of epoxides is the polymer poly(propylene carbonate) with chemical shifts also different from the reagent but difficult to analyse, as presented in Figure 3.2.

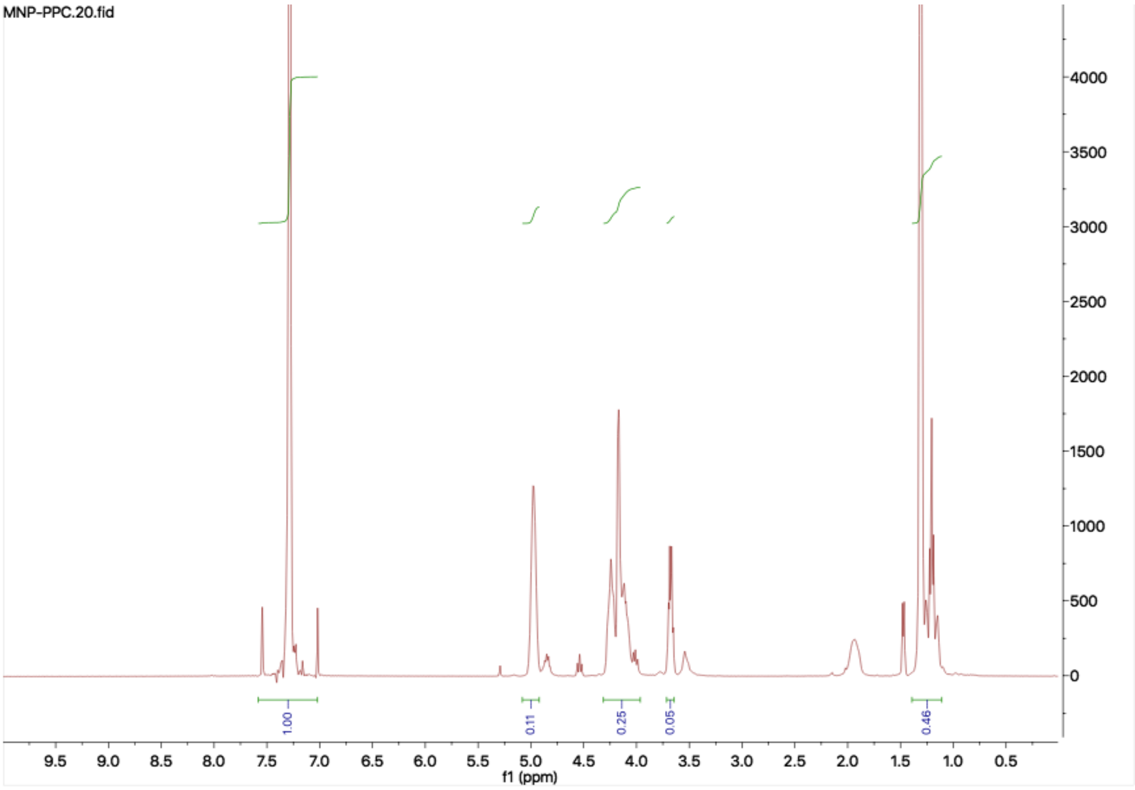


Figure 3.2 - Polymer poly(propylene carbonate) ^{1}H-NMR spectra

3.1.1 Pressure Influence

Following previous studies performed in the host laboratory, a Zn(II) complex of arylhydrazones of *ß*-diketone was used as catalyst in combination with tetrabutylammonium bromide [TBA]Br. An important feature of this type of metal complexes is based on easily preparation and handling. In the present work, propylene oxide was studied and results obtained compared with those previously reported for styrene oxide [44].

For selected model reaction, the temperature was kept stable (333 K or 353 K) and 0.25 mol% of the catalyst ZnR236 was added in all reactions. Table 3.1 and Table 3.2 showed the influence of different pressures. The pressure influence at 333 K was more significant comparing to 353 K as indicated in both tables.

Table 3.1 - Pressure influence at 333 K during 3 h with 0.25 mol% catalyst and 1 mol% [TBA]Br

Pressure (MPa)	**Cyclic carbonate formation (%)**
0.5	52
4	68
8	38
18	31

Table 3.2 - Pressure influence at 353 K during 3 h with 0.25 mol% catalyst and 1 mol% [TBA]Br

Pressure (MPa)	**Cyclic carbonate formation (%)**
0.5	97
4	98
8	97
18	94

Figure 3.3 illustrates the comparable influence of pressure at two different temperatures (333 and 353 K). High formation percentage of cyclic carbonate was obtained in the case of reactions performed at 353 K. Due to higher temperatures, we could not precise the pressure influence (94 to 98% of conversion). However, at 333 K, the results indicated us a strong pressure influences where the highest formation of cyclic carbonates was obtained using 4 MPa (68% of conversion). In order to determine the best reaction conditions, the effect of CO2 pressure for two different temperatures have been studied.

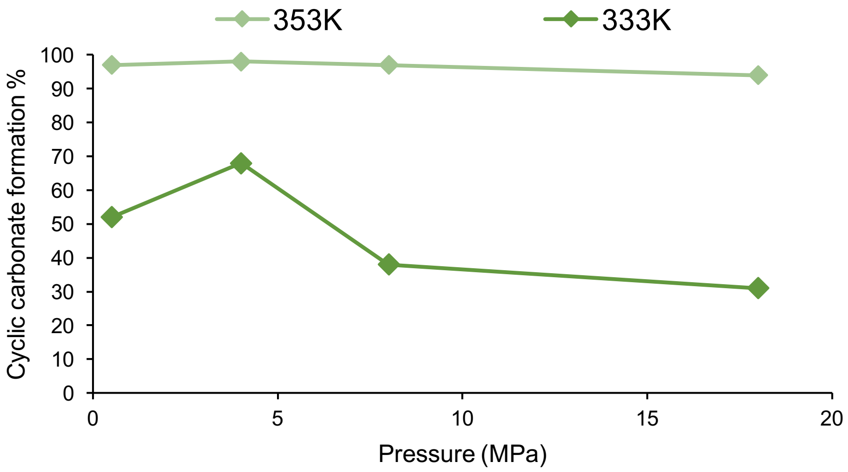


Figure 3.3 - Pressure influence comparison at 333 K and 353 K during 3 h with 0.25 mol% catalyst and 1 mol% [TBA]Br

At 353 K, the cyclic carbonate formation was high. A plausible explanation for the result at 18MPa and 333 K is that using this pressure a fluid expansion can be expected, resulting in lower conversions of cyclic carbonate formation. This drastic volume expansion of the epoxide, is responsible for the precipitation of the catalyst [44]. This change in the catalyst phase can be observed through the reactor sapphire window as seen in Figure 3.4.

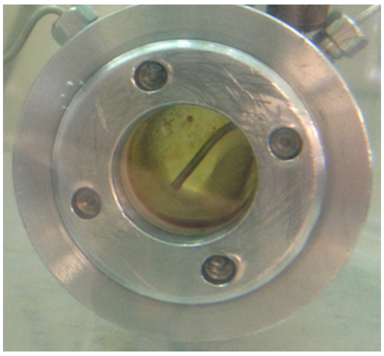


Figure 3.4 - Precipitation of the catalyst phase during CO_2 pressurization

With the expansion of the liquid epoxide due to CO_2 pressurization, a melted [TBA]Br phase in which the metal complex is apparently dissolved is formed. The catalyst is not so active in this melted phase resulting in lower formation of cyclic carbonate.

3.1.2 Temperature Influence

As stated before, along with pressure, temperature is one of the most relevant parameters to achieve high conversions in these reactions. The pressure (4 MPa) was kept stable during the reaction, as well as reaction time (3 h of reaction). For the studies about temperature influence, the catalyst tested was ZnR236 (0.25 mol%) plus [TBA]Br (1 mol%) in all reactions. Different temperatures were studied and it was possible to conclude that, higher the temperature, higher the % of cyclic carbonate formation. Results are presented in Figure 3.5. The apparatus was limited to 353 K as the maximum temperature operable.

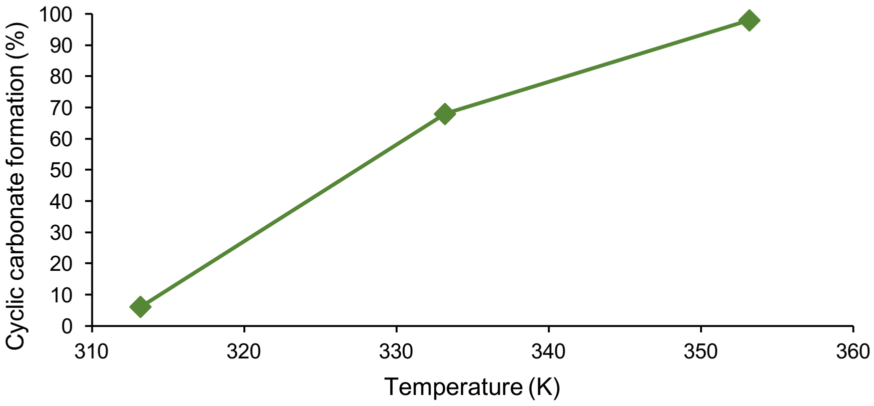


Figure 3.5 - Cyclic carbonate formation relatively to temperature with 0.25 mol% catalyst and 1 mol% of [TBA]Br, 4 MPa, 3 h.

In Figure 3.5, as the temperature rises, the plot shows that the cyclic carbonate formation increases attaining high % of cyclic carbonate formation (98% at 353 K). Furthermore, the activity of the combination of catalyst used was investigated at very mild operatory conditions. Results are presented in Table 3.3. Reactions at 293K showed lower conversion percentages compared to reactions at 323K. Ii seems that higher pressure values allow to achieve higher conversion of desired product (as illustrated in Table 3.3 and Figure 3.6).

Table 3.3 Cyclic carbonate formation comparative study with 0,5 MPa and 4 MPa at 293.2K and 323.2K with 0.25 mol% catalyst and 1 mol% [TBA]Br during 24h

Temperature (K)	Pressure (MPa)	Cyclic carbonate formation (%)
293.2	0,5	24
323.2	0,5	86
293.2	4	72
323.2	4	89

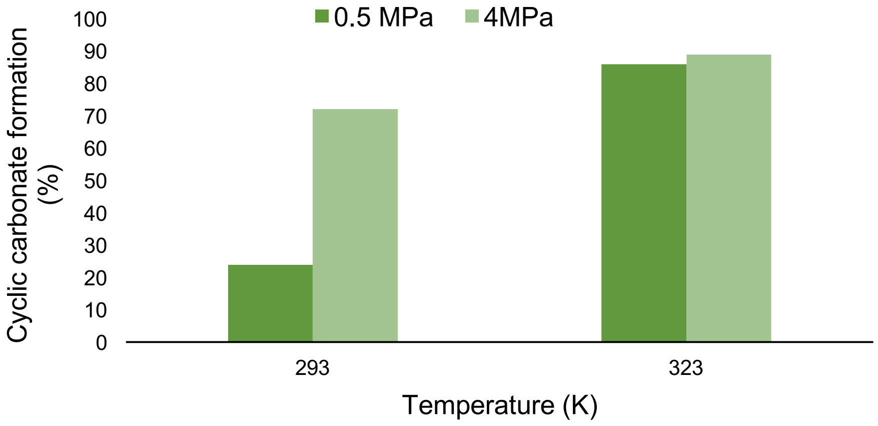


Figure 3.6 - Comparison on the cyclic carbonate formation with 0.05 MPa and 4 MPa at 293K and 323K with 0.25 mol% catalyst and 1 mol% [TBA]Br during 24h

As it can be observed, even at room temperature and very low pressures, the catalyst system is still active with a conversion percentage of 24%. However, by increasing pressure, the conversion percentage increases until 72% at room temperature and 4 MPa as ideal value of the optimized pressure. When temperature is increased to 323K, the conversion yield increases to 86%. Another approach was to study the reaction conversion with 4 MPa at 323K in order to find the optimized conditions. Results showed an increase of 3% from 86% to 89% cyclic carbonate formation at 323K. With all the data collected presented in Table 3.3, we concluded that the catalytic system is active at mild conditions. In order to achieve high % of cyclic carbonate formation, longer reactions times (24 hours) were needed. Since the reaction is sensitive to pressure at lower temperatures, the standard temperature was set to 353.2K in order to avoid longer reaction times.

3.1.3 Effect of the catalyst ZnR236

The amount of catalyst ZnR236 necessary for the reaction was studied. In order to find the optimized amount of catalyst, different molar ratios were studied. The reactions were performed with 1 mol% of [TBA]Br at 353 K with 4 MPa during 3 hours. The results are presented in Table 3.4 and Figure 3.7.

Table 3.4 ZnR236 catalyst mol% study with 1 mol% [TBA]Br at 353 K, 4 MPa during 3 h

ZnR236 (mol%)	[TBA]Br (mol%)	Cyclic carbonate formation (%)
0	1	24
0.05	1	95
0.1	1	99
0.25	1	92

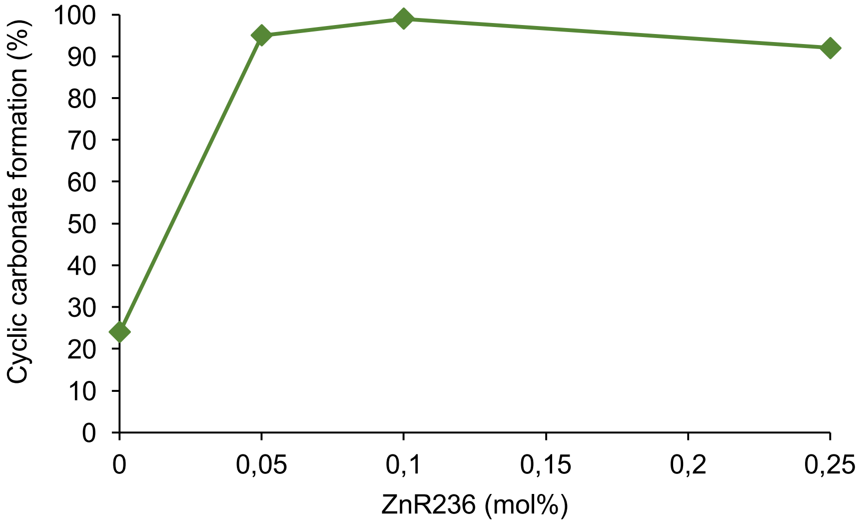


Figure 3.7 - Cyclic carbonate formation relatively to ZnR236 presence with 1 mol% of [TBA]Br at 353 K with 4 MPa during 3 h

Results showed that with 0 mol% of catalyst, there is 24% of cyclic carbonate formation due to the presence of [TBA]Br in the reaction mixture. As described in chapter 1.5, ionic liquids can catalyse the reaction following the mechanism presented in Figure 1.9. The introduction of ZnR236 in the reaction mixture lowers the activation energy barrier necessary for the reaction to occur, as it coordinates with the epoxide. Catalyst molar ratio showed great importance in the coupling reaction, as Table 3.4 shows, where from 0% to 0.05% the cyclic carbonate formation increased from 24% to 95%, indicating that with higher molar ratio of catalyst in the reaction mixture, higher the formation of cyclic carbonate formation. With the increasing molar ratio from the catalyst, the amount of active sites in metal complexes increase. Therefore, there are more active sites to complex with the epoxide which results in a lower activation barrier, resulting in higher percentages of cyclic carbonate formation.

3.1.4 Effect of the co-catalyst Tetrabutylammonium bromide, [TBA]Br

The effect of the co-catalysts was also studied. In order to find the optimum molar ratio between catalyst and co-catalyst, different mol% of co-catalyst were used. The data collected is presented in Table 3.5, where the variance of the molar ratio of the co-catalyst is showed, in Figure 3.8, a plot to a better understanding of the data.

Table 3.5 - TBABr influence at 353 K, 4 MPa during 3 h with 0.05mol% of ZnR236 catalyst

ZnR236 (mol%)	[TBA]Br (mol%)	Cyclic carbonate formation (%)
0.05	0	0
0.05	0.2	73
0.05	0.3	79
0.05	0.4	92
0.05	1	93

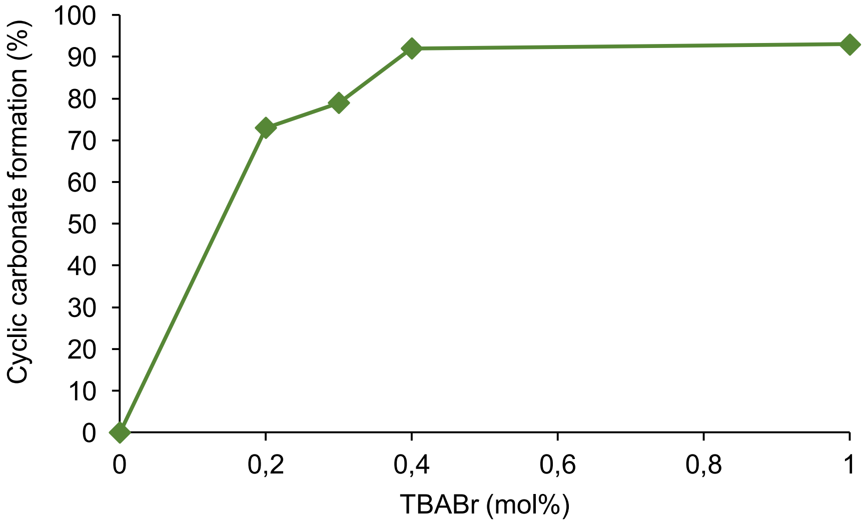
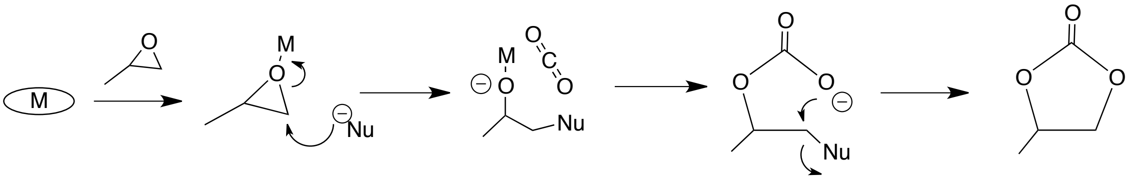


Figure 3.8 – [TBA]Br influence at 353 K, 4 MPa during 3 h with 0.05 mol% of ZnR236 catalyst

The plot shows how tetrabutylammonium bromide, [TBA]Br, affects the carbonate conversion, with higher molar ratio of [TBA]Br in the reaction, a higher cyclic carbonate formation percentage is obtained. With 0.4% of [TBA]Br the reaction reached 92% cyclic carbonate formation and so with 1% we were sure [TBA]Br percentage was optimized. No coupling reaction was observed in the absence of [TBA]Br, making inevitable how important the presence of [TBA]Br is in the reaction.



M = Metal complex

Figure 3.9 - Effect of the nucleophile

Bromide is a good nucleophile and a good leaving group favouring the cyclic carbonate formation. Figure 3.9 shows the mechanism for the coupling reaction and the importance of the nucleophile in the reaction, in this case, bromide. The coordinated complex formed between epoxide and metal complex facilitates the nucleophilic attack of bromide to the tense and rigid 3-member epoxide ring. Tetrabutylammonium presence during the ring closing step promotes bromide as leaving group therefore enhancing the formation of organic cyclic carbonates.

3.2 Catalysts

After finding the optimized reaction conditions, the catalyst performance and effect was studied. In the present work, the type of catalysts are mainly arylhydrazones of *ß*-diketones (AHBDs) which are versatile compounds, easily modified. AHBDs can be easily prepared [41] [42]. As discussed before, metal centres, ligands, homo, hetero catalysts/catalysis have all a significant importance in the reaction yield and conversion.

3.2.1 Different metal complexes

The first condition studied was the use of different catalyst with different metal ions and metal centres. One important factor studied in these reactions was the steric hindrance of the catalyst when coordinating with the epoxide. The complex formed between the epoxide and the Lewis acid highly facilitates the nucleophilic ring opening of the epoxide [48]. Different metal ions will have different behaviours when coordinating with the epoxide.

Table 3.6 - Comparison between different metal ions at 333 K, 4 MPa during 3 h with 0.4 mol% [TBA]Br

Catalyst	Catalyst (mol%)	Co-Catalyst (mol%)	Cyclic carbonate formation (mol%)
Only [TBA]Br	0	0.4	2
CuR11	0.1	0.4	20
ZnR29	0.1	0.4	27
ZnR236	0.05	0.4	48
ZnR11	0.1	0.4	41

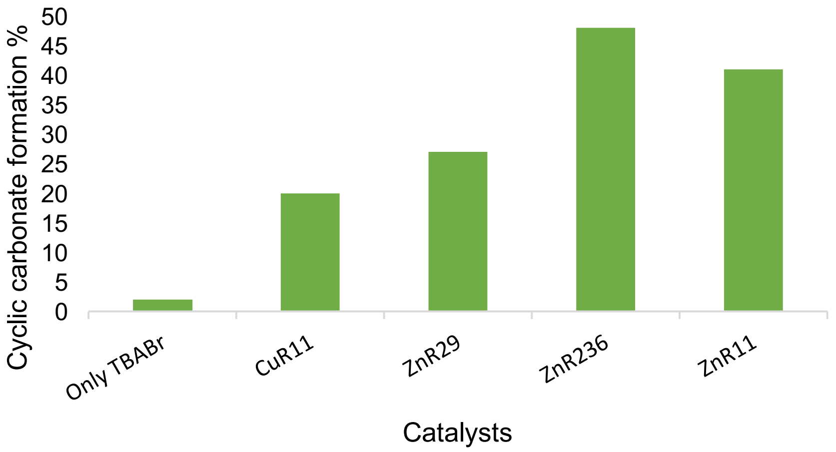


Figure 3.10 - Catalysts comparative study, all reactions were performed at 333 K and 4 MPa during 3 h with 0.4 mol% of co-catalyst (TBABr)

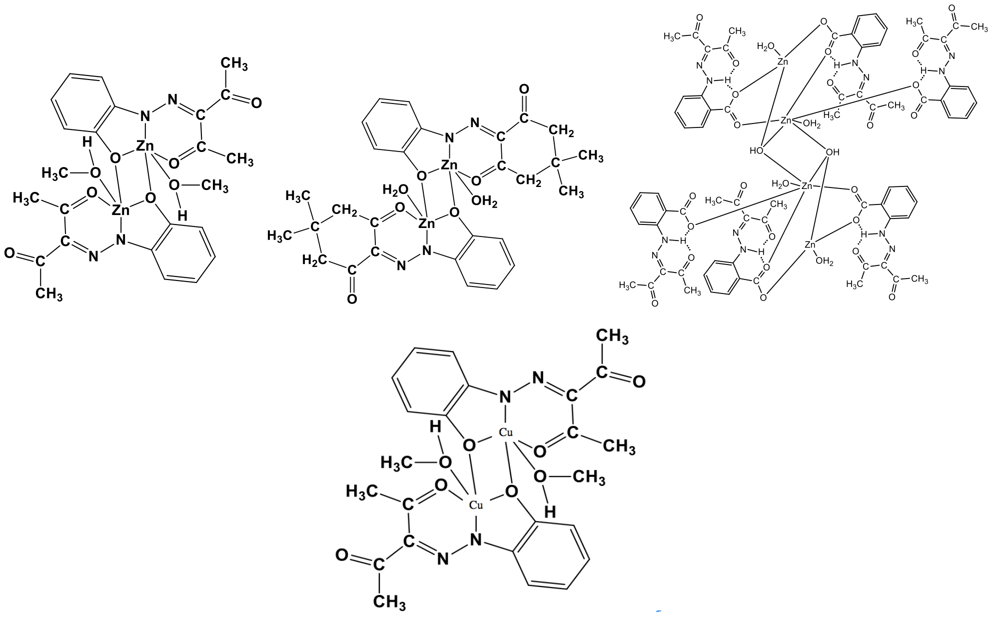


Figure 3.11 - Different catalysts studied ZnR11,29 and 236 and CuR11 [44]

The main difference between ZincR11, R29 and R236 are the number of metal centres available in the complex, as presented in Figure 3.11, both ZnR11 and ZnR29 have two metal centres whereas ZnR236 has four metal centres. This was taken into consideration when calculating each catalysts mol% on the reaction since the reaction is very sensitive to proportion between components of the catalytic mixture. The proportion between co-catalyst and metal complexes highly affects the reaction yield and conversion and so it was kept the same ratio between all metal complexes and [TBA]Br. Results are shown in Figure 3.10. ZnR236 doubles the number of active metal centres when comparing with ZnR11 and ZnR29 metal complexes, enhancing the activity towards the formation of cyclic carbonate. The existence of four different active sites in the metal complex ZnR236, greatly enhances the results like Figure 3.10 shows. When comparing ZnR11 and ZnR29, which have 2 active sites in metal complex, their structures are very similar differing only in the groups complexed with Zn. A less steric hindrance complex enhances the results as well as groups that active the epoxide facilitating the attack from the nucleophile.

3.3 Ionic liquids as solvents and co-Catalysts

3.3.1 Effect of ILs as co-catalyst and solvents in the reaction

The effect of different co-catalysts was studied using 0.05 mol% of ZNR236 and 0.4 mol% of co-catalyst, as presented in Table 3.6. All reactions were performed at 333 K and 3 h. 333 K was selected as the temperature at which 68% of carbonate formation was attained using [TBA]Br as co-catalyst (see Table 3.1). The choice of these conditions allows to observe both positive and negative effects of changing the co-catalyst. The presence of the co-catalyst is very important for the opening of the epoxide ring step since the co-catalyst will act as a nucleophile and will affect the formation of cyclic carbonate *versus* poly(propylene carbonate).

Ionic liquids were firstly introduced in the reaction as co-catalysts. They were investigated in order to study their activity in comparison with [TBA]Br.

3.3.1.1 Comparing different anions: Chloride *versus* Bromide

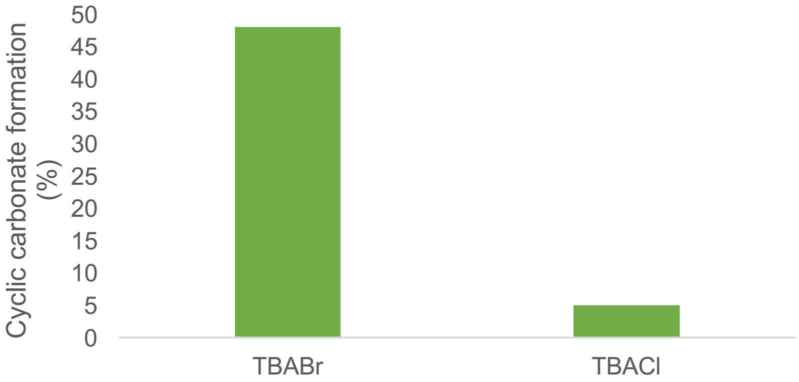


Figure 3.12 - Study on the effect of the anion in the coupling reaction between propylene oxide and CO_2 using 0.05% ZnR236 and 0.4% of co-catalyst at 333 K, 4 MPa and 3 h

The effect of the anion bromide and chloride was compared as shown in Figure 3.12. Tetrabutylammonium bromide showed superior results, with 48% of cyclic carbonate formation whereas, tetrabutylammonium chloride showed results of 4%. The main difference in these two species is mainly the nucleophilicity of the anions and the leaving group capability of both species, bromide and chloride. Literature reports that the bulkiness of the tetrahedral ammonium ion forces the halide ion away from the cation, resulting in less electrostatic interaction between anion and cation which increases the nucleophilicity of the anion [38]. This explains the results obtained in the reaction, with [TBA]Br showing enhanced results when compared with [TBA]Cl. Being bulkier than chloride, when pushed away from the cation, bromide quickly reacts as a nucleophile by attacking the epoxide ring. Besides being a better attack nucleophile, bromide is also a better leaving group than chloride, leading to the formation of cyclic carbonate.

3.3.1.2 Comparing different cations: Tetrabutylammonium *versus* Ethyl-Methyl-imidazolium

Table 3.7 – Cation interference as co-catalyst in the coupling reaction with 0.05% of ZnR236 and 0.4% of co-catalyst, at 333 K, 4 MPa, 3 h

[TBA]Br (mol%)	[EMIm]Br (mol%)	Cyclic carbonate formation (%)
0.4	-	48
-	0.4	4

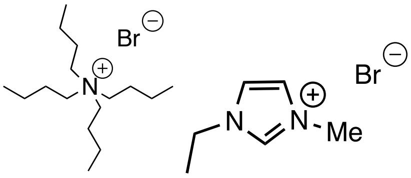


Figure 3.13 – [TBA]Br and [EMIm]Br structures

When studying the cation behaviour between [TBA] and [EMIm], the main difference is the stabilization of charge. When analysing [TBA] cation, it is bulky and so, as stated before, bromide is pushed away from the centre being more available for a possible attack on the epoxide. On the other hand, [EMIm] allows the stabilization of charge due to the ionic bonding between species. The strength of ionic bond between the planar five-member ring imidazolium and bromide is stronger than the interaction between [TBA] and bromide, so the halide ion is not as available as it is in [TBA], leading to a worse nucleophilic attack to the epoxide. In Table 3.7, [TBA] showed 48% of cyclic carbonate formation, confirming the hypothesises that the bulkiness and charge stabilization do influence the cyclic carbonate formation percentage.

3.3.1.3 Effect of non-halogenated anions

Table 3.8 – Anion interference as co-catalyst in the coupling reaction with 0.05 mol% of ZnR236 at 333 K with 4 MPa during 3 h

[EMIm]Br (mol%)	[EMIm]Ntf$_2$ (mol%)	[EMIm]B(CN)$_4$ (mol%)	[EMIm]EtSO$_4$ (mol%)	Cyclic Carbonate Formation (%)
0.4	-	-	-	4
-	0.4	-	-	0
-	-	0.4	-	0
-	-	-	0.4	0

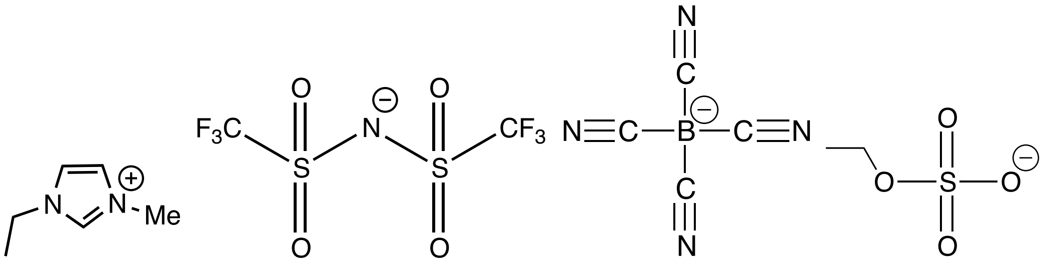


Figure 3.14 – [EMIm] structure and its correspondent anions Ntf_2, $B(CN)_4$ and $EtSO_4$ structures

The ion bromide showed its importance again when studying the anion interference in the cyclic carbonate formation. Table 3.8 shows that [EMim]Br had with the highest percentage inside the [EMim] group, with 4% cyclic carbonate formation. Bromide's bulkiness and nucleophilicity are two factor to take in consideration when analysing the other anion species. In some cases, groups are very large making it hard for the negative charge to be available, in order to attack the epoxide ring. Other possible explanation is the electronegativity of the anion studied, some groups are not as electronegative as bromide and so the negative charge is not strong enough to open the epoxide ring. Besides, the existence of ionic bonds in most species is not favourable in the epoxide ring opening as the negative charge is not as available, resulting in lower conversions.

3.3.1.4 Effect of different ammonium-based cations

Table 3.9 – Anion chloride interference as co-catalyst in the coupling reaction with 0.05mol% of ZnR236 at 333 K with 4 MPa during 3 h

Choline Cl (mol%)	ALIQUAT Cl (mol%)	PPNCl (mol%)	[TBA]Cl (mol%)	Cyclic carbonate formation (%)
0.4	-	-	-	0
-	0.4	-	-	0
-	-	0.4	-	6
-	-	-	0.4	5

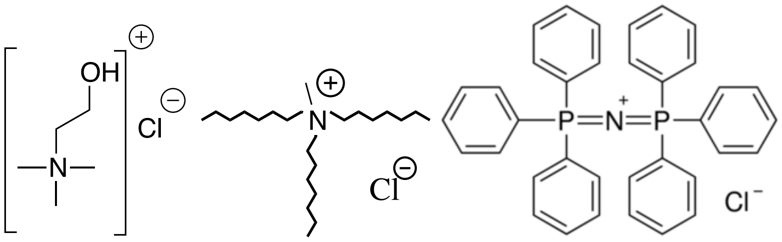


Figure 3.15 – Choline Cl, ALIQUAT Cl and PPNCl structures

Another approach was to use different cations while using chloride as the anion in the species used. Chloride is one chemical element very similar to bromide, both being used as nucleophiles in many reactions. However, as seen in Table 3.9 the chloride species used showed lower % of cyclic carbonate formation. The availability of the anion chloride is different in each structure. When considering bis(triphenyphosphine)iminium chloride (PPNCl), the bulkiness of the structure keeps the chloride away from the centre of the structure which makes chloride more available in this structure when compared with methytrioctylammonium chloride (ALIQUAT Cl). However when comparing [TBA] and [PPN] effect on the coupling reaction, both have ~5% of cyclic carbonate formation, indicating that [TBA] also pushed chloride away from the centre of the structure.

3.3.1.5 Effect of hydroxyl-functionalized ammonium salts

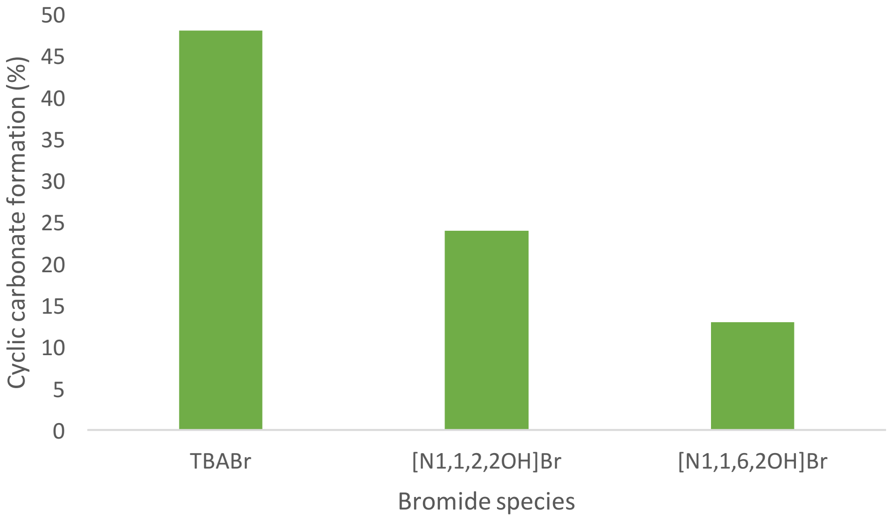


Figure 3.16 - Bromide species influence on cyclic carbonate formation with 0.05mol% of ZnR236 and 0.4mol% of co-catalyst at 333 K with 4 MPa during 3 h

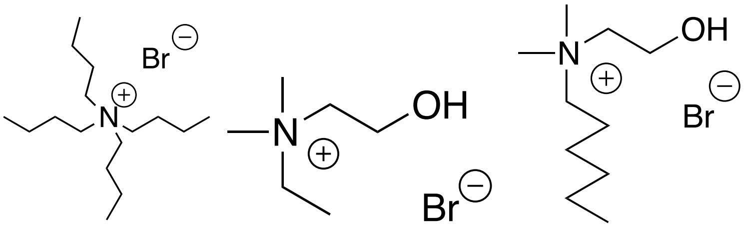


Figure 3.17 – [TBA]Br, [N1,1,2,2OH]Br and [N1,1,6,2OH]Br structures

Accordingly to Figure 3.16, both bromide containing species when compared to [TBA]Br showed lower conversions, 24% and 13% for [N1,1,2,2OH]Br and [N1,1,6,2OH]Br, respectively. Bromide effect is clearly evident when comparing with the groups studied before, sustaining the hypothesis that it is in fact the best nucleophile between chloride and bromide. The difference between both bromide species is the existence of a six carbon chain in [N1,1,6,2OH]Br where [N1,1,2,2OH]Br only has a chain with two carbons. [N1,1,2,2OH]Br better results can be explained by the steric hindrance that exists in the [N1,1,6,2OH]Br structure, making it hard to move around and making the nucleophile bromide not as available as it is in the [N1,1,2,2OH]Br structure. According to the literature, longer alkyl chains showed enhanced results when compared to short alkyl chains, however, in this case, due to propylene oxide simplicity over the studied epoxide in the literature (cyclohexene oxide), the same conclusion cannot be applied as the epoxide ring studied is far more complex than propylene oxide [49]. The introduction of hydroxyl groups, OH in both species, as described in literature, enhances the catalytic activity [50]. The presence of hydroxyl groups in catalysts or reaction media behaves like the Lewis acid catalyst, by having a cooperation function in the ring opening step of the epoxide. However, in this case, it did not enhance the results when compared with [TBA]Br, due to the ammonium being substituted with less bulky chains. The negative charge is not as available as it is in [TBA]Br structure, in [N1,1,2,2OH]Br and [N1,1,6,2OH]Br structures the bromide anion is closer to the cation due to the non-existence of the butyl alkyl chains showing lower results.

3.3.1.6 Utilization of ILs as reaction solvents

Another approach was to use ionic liquids as solvents. Ionic liquids as alternative green solvents, allow a better dissolution of the catalyst and co-catalyst. Besides dissolution, some ionic liquids also allow the extraction of the product obtained through $scCO_2$, keeping the remaining catalyst active through its ionic stabilization.

Table 3.10 - Effect of ILs as solvents in the cyclic carbonate formation with 0.25 mol% ZnR236 and 1 mol% [TBA]Br at 333 K with 4 MPa during 3 h

Ionic Liquid (1 mL)	Cyclic carbonate formation (%)
[EMIm] $B(CN)_4$	11
[EMIm] $EtSO_4$	17
[EMIm] Otf	9
[BMIm] Otf	13
[BMIm] Ntf_2	7

Some ILs previously used as co-catalysts were re-tested as alternative solvents in the coupling reaction of epoxides with CO_2. The possibility to better dissolve catalysts and co-catalyst together with the use of a IL as solvents greatly enhances the results as presented in Table 3.10 when compared with ILs used in Table 3.8 as co-catalysts. The delocalization of the negative charge through the anion and cation species affects the percentage of cyclic carbonate formed as it conditioners the availability of the charge during the ring-opening step. [BMIm] Ntf_2 was used instead of [EMIm] Ntf_2 in order to understand how the alkyl chain would affect the cyclic carbonate formation. With a bulkier group in the imidazolium group, the Ntf_2 negative charge is pushed away from the cation facilitating the attack on the epoxide ring. The same thing was also observed when [EMIm] Otf and [BMIm] Otf were studied. With 13% cyclic carbonate formation, the bulkier substituted imidazolium showed enhanced results when compared with a shorter alkyl chain substituted imidazolium, with 9% confirming the hypothesis that a bulkier group pushes away the negative charge. Due to showing the most promising results, [EMIm] $EtSO_4$ was picked for comparison with some commercially available green solvents in order to understand its behaviour. Results are presented in Figure 3.18.

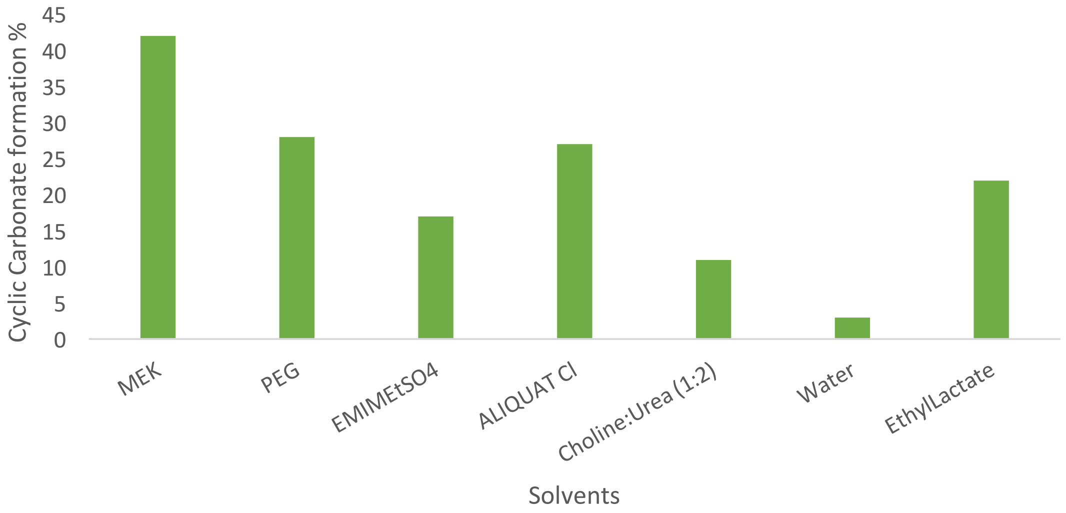


Figure 3.18 - Ionic liquids as solvents with 0.25 mol% of ZnR236 and 1 mol% [TBA]Br were used at 333 K with 4 MPa during 3 h

Results showed that MEK (methyl-ethyl-ketone), was the most successful alternative solvent in the coupling reaction with CO_2. Accordingly to the literature, MEK is mostly used as solvent for CO_2 dissolution method of solid substrates [51]. Some literature also reports MEK as a carbonyl solvent with high conversions in this epoxide substrate [52]. Although it showed good results and it is considered green, it is also very volatile and unable to hold the catalyst making it impossible to extract the product without catalyst contamination. Considered an organic solvent, MEK was used only for comparison since it presents good comparison results and it is soluble in $CO_{2.}$ The two solvents that showed the most promising results were Polyethylene Glycol (PEG) and methyltrioctylammonium chloride (ALIQUAT Cl) with 28% and 27%, respectively. Literature reports PEG as a competitor to ILs when used as a benign alternative for the catalyst-bearing phase in biphasic catalysis with $scCO_2$ [53]. The eutectic mixture used, choline: urea (1:2), showed promising results, 11% cyclic carbonate formation. However due to the presence of bromide when used as co-catalyst ([TBA]Br), chloride competes with bromide when attacking the epoxide as a nucleophile, resulting in lower conversion. In the case of [EMIm] $EtSO_{4,}$ that had been previously used as a co-catalyst, it showed much better results when used as solvent, with 17%. The electronic stabilization from the [EMIm] group when used as a solvent, greatly enhances the results when compared to the same stabilization as a co-catalyst. Ethyl lactate, considered a green solvent, was also considered promising with 22% cyclic carbonate formation. Most of the solvents used were not considered green enough when compared with ALIQUAT Cl and so, it was used in the reactions that followed.

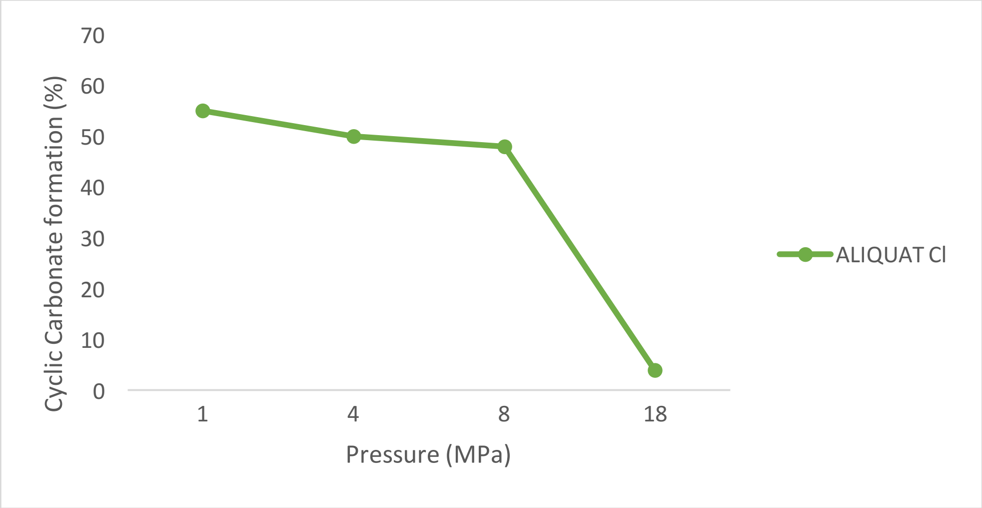


Figure 3.19 - ALIQUAT Cl pressure influence on cyclic carbonate formation with 0.25 mol% of ZnR236 and 1 mol% of [TBA]Br at 333 K during 3 h

Considered greener, ALIQUAT Cl was picked for a pressure influence study in order to understand its full potential, results are presented in Figure 3.19. The plot shows that from 1MPa to 8MPa ALIQUAT Cl has an average of 50% cyclic carbonate formation. However, at 18MPa, due to its expansion it drops to 4%. This can be explained by the expansion in the reaction mixture, that is 1:1. With the volume expansion molecules are not as available as before and so the yield drops. Other plausible explanation is the competition between bromide and chloride as nucleophiles. The presence of both nucleophiles in the reaction mixture makes both ions compete as nucleophiles and as leaving groups, where bromide clearly enhances results whereas chloride is not so reactive.

3.3.2 Extraction

The use of solvents in the coupling reaction of epoxides allows the extraction of product without catalyst contamination. Besides that, the use of an ionic liquid or DES as a solvent keeps the catalyst active enhancing the number of cycles that a catalyst can work efficiently.

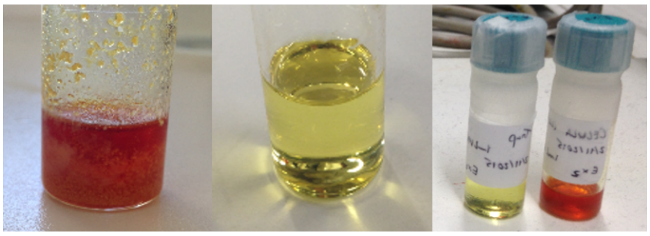
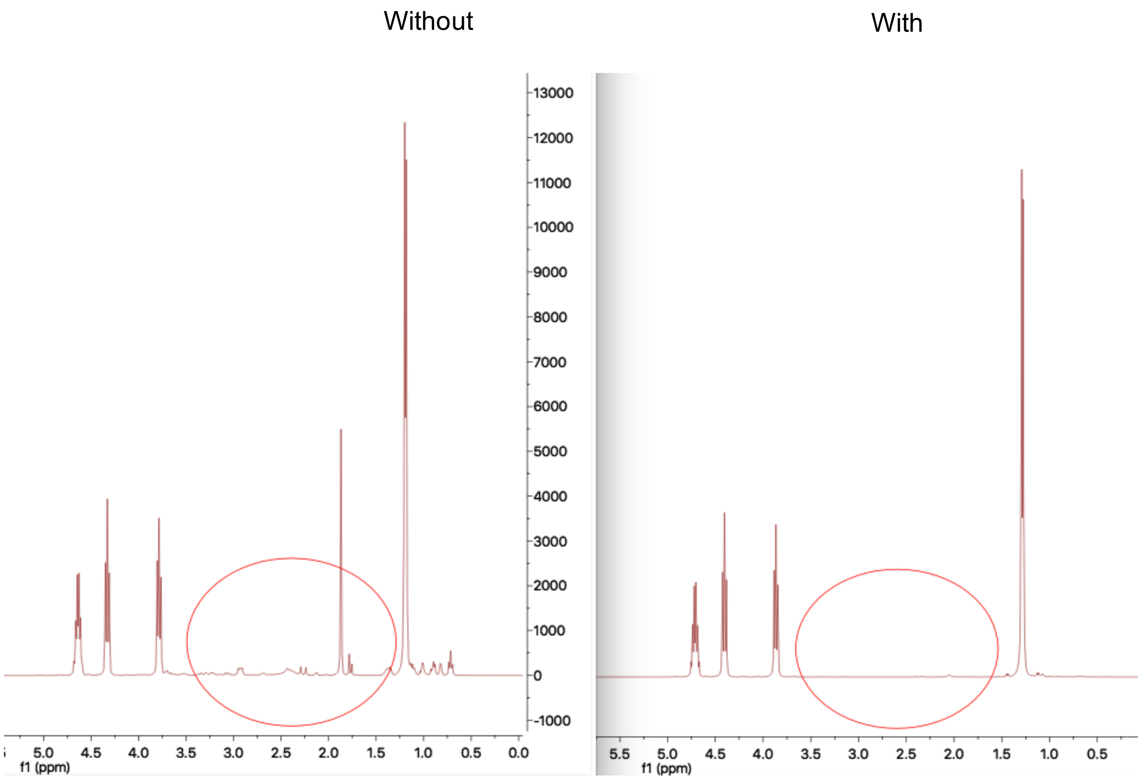


Figure 3.20 - Product obtained with and without extraction with $scCO_2$

In Figure 3.20 we can clearly confirm that the extraction was successful just by looking at both liquid colours. The orange colour present on the left vial of Figure 3.20 indicates the presence of catalyst ZnR236 whereas in the middle picture, we can confirm that there is no contamination from the catalyst (no orange colour). Due to not being soluble in CO_2, the catalyst remains in the cell while the obtained product is dragged into a trap covered in ice. The use of this solvents together with the use of supercritical carbon dioxide ($scCO_2$) makes it possible to extract and reutilize catalysts in reactions. Through ^{1}H-NMR analysis we can confirm the extraction of the product was successful, as presented in Figure 3.21. The spectra obtained after extraction is much cleaner, without peak signals from the presence of catalyst, and easier to integrate. The area marked by a red circle elucidates the main difference between spectra with and without catalyst. During the time that catalysts remain in the cell together with IL or DES, it remains active through ionic stabilization for a new catalytic cycle.



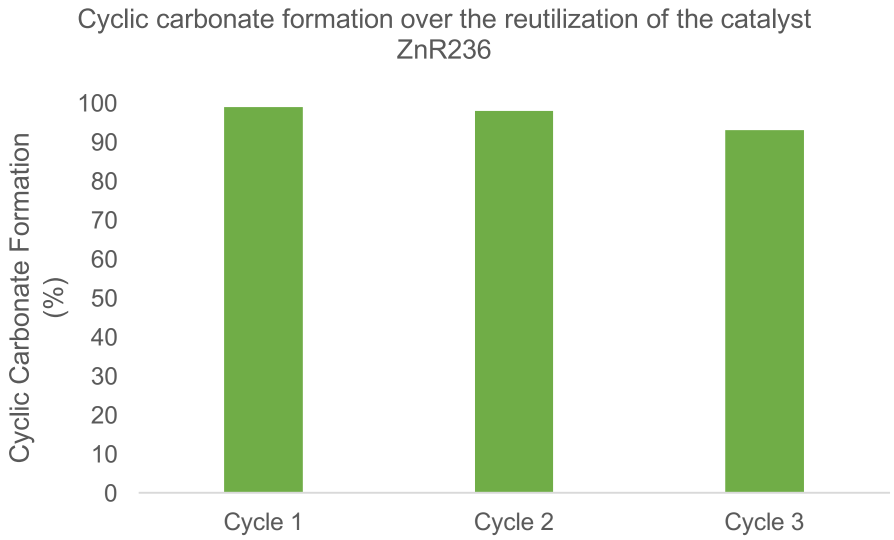
Without

With

Figure 3.21 – ^{1}H-NMR spectra without and with extraction respectively

Due to their unique properties such as viscosity and density, ILs allow the combination between the advantages of both homogeneous and heterogeneous catalysts, one selected IL may dissolve the catalyst however it may also be immiscible with the reactants and products [54].

While aiming for the extraction opportunity, reutilization of the catalyst was studied. After performing the extraction, with the catalyst inside the cell, propylene oxide was added. Results are presented in Figure 3.22.



Cyclic carbonate formation over the reutilization of the catalyst ZnR236

Figure 3.22 - Cyclic carbonate formation over the reutilization of the catalyst ZnR236

3.4 DES

After finding that the presence of [TBA]Br is highly required in the reaction, a new approach was studied. The insertion of [TBA]Br in the solvent should increase the availability of the ion bromide in the reaction's key step, epoxide opening. Results are presented in Figure 3.23. A final approach was to use $ZnCl_2$ dissolved in ethylene glycol, creating an innovative catalytic system involving the catalyst. The catalyst is available as a solvent instead of being dissolved in the propylene oxide. Results are presented in Figure 3.24.

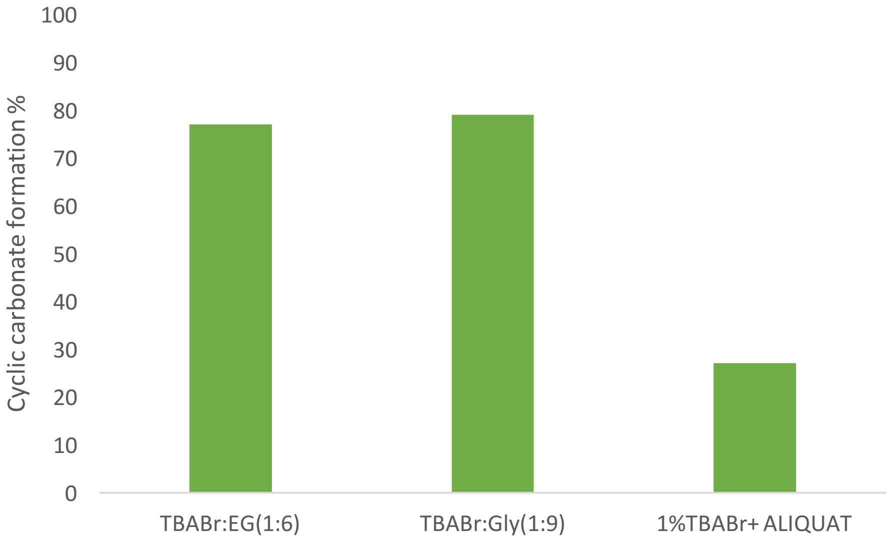


Figure 3.23 - DES comparison study using 0.25 mol% of ZnR236 and 1 mL of DES at 333 K, 4 MPa, 3 h.

Results show that the insertion of [TBA]Br in DES in order to behave like a solvent, resulted in an enhanced result. Proving that bromide in [TBA]Br is more available when mixed as a solvent than when added as a co-catalyst. Both DES with [TBA]Br showed results of 78% cyclic carbonate formation. When comparing with the results of [TBA]Br solved in ALIQUAT, due to the expansion in ALIQUAT, [TBA]Br is not as available as it is in other DES and so the formation % of cyclic carbonate lowers considerably. Another plausible explanation is the competition between nucleophiles, bromide and chloride. The existence of chloride in ALIQUAT competes with bromide from [TBA]Br when it comes to the epoxide ring-opening step, where [TBA]Br is a more favourable nucleophile and leaving group, making the mixture ALIQUAT Cl + [TBA]Br not to work as expected with 27% of cyclic carbonate formation. Literature reports studies on the [TBA]Br-based DESs physical properties such as viscosity, ionic conductivity and density [42].

3.5 DES utilization as a catalytic system

A final approach was to use the metal complex as part of DES in the coupling reaction together with co-catalyst [TBA]Br. The metal catalyst chosen was $ZnCl_2$ together with Ethylene glycol while having [TBA]Br as co-catalyst. Results are presented in Figure 3.24.

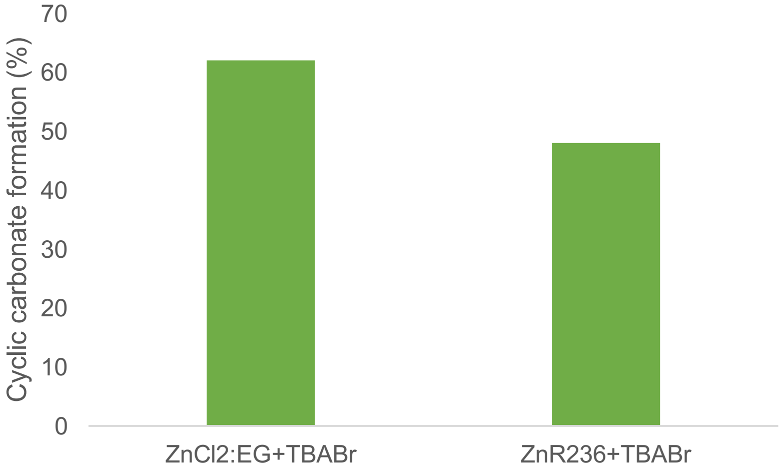


Figure 3.24 – DES utilization as a catalytic system at 333 K, 4 MPa during 3 h with 0.05 mol% of catalyst and 0.4 mol% of [TBA]Br

The use of $ZnCl_2$ together with EG allows for the dissolution of $ZnCl_2$ in ethylene glycol making the catalyst dissolved in EG. EG also allows for the dissolution of [TBA]Br in reactional mixture enhancing the results when compared with the use of ZnR236 and [TBA]Br. These enhanced results are explained with the availability of each species in the reaction, because catalyst and co-catalyst are dissolved in EG before being added with propylene oxide. The fact that chloride is complexed with zinc, acting as a catalyst, it is also available as a nucleophile although not as available as bromide in [TBA]Br, which facilitates the attack from the nucleophile bromide.

4. CONCLUSIONS

In this work, different ionic and deep eutectic liquids, were tested as co-catalysts and solvents for the production of cyclic carbonates, via direct coupling of CO_2 to epoxides.

The reaction conditions were optimized and different anions and cations were explored. The bromide anion and its combination with the tetrabutylammonium cation presented the best catalytic activity. Its utilization as a solvent is however limited, by high melting temperature.

Alternatively, methyltrioctylammonium chloride showed good results, since besides favouring the reaction kinetic, it retained the catalyst inside the reactor, allowing the product to be extracted using supercritical CO_2. The use of an ionic liquid as solvent in the reaction allowed to obtain a pure product (free of solvents) avoiding the need for complex separation steps.

Propylene carbonate extraction was performed using supercritical CO_2 extraction step at 313.2 K and 11.5 MPa. The catalyst system was reused three times, without loss of activity and with good reproducibility.

Furthermore, in order to investigate a solvent bearing the bromide anion, a tetrabutylammonium bromide ([TBA]Br)-based deep eutectic solvent was explored for the first time. [TBA]Br:Glycerol presented superior results, which constitutes a good alternative for further studies. The insertion of a catalyst/co-catalyst in the IL/DES structure (solvent structure), clearly enhances carbonate formation and opens the possibility of developing a metal-free process.

Considering the wide industrial implementation of the process, the results presented in this work allow for future utilization of complex substrates, namely with solubility limitations, such as naturally-derived limonene and pinene oxide.

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6. APPENDIXES

Table 6.1 - Reaction Index

Date	*Epoxide (mL)*	*Sample*	*Catalyst*	*Temperature (°C)*	*Pressure (bar)*	*Time (h)*	*Conversion %*
30/09/2015	O-prop (1)	**VE 1**	1% TBABr	40	40	3	-
12/10/2015	O-prop (1)	**VE 2**	1% TBABr + 0,25% Zn236	80	40	3	92
13/10/2015	O-prop (1)	**VE 3**	1% TBABr + 0,25% Zn236	80	40	3	92
14/10/2015	O-prop (1)	**VE 4**	1% TBABr + 0,25% Zn236	80	40	3	93
26/10/2015	O-prop (1)	**VE 5**	1% TBABr + 0,25% Zn236	40	40	24	99
27/10/2015	O-prop **(5)**	**VE 6**	5% TBABr + 1,25% Zn236	40	40	24	98
11/11/2015	O-prop (1)	**VE 7**	Reutilization (**EX 3**)	40	40	24	99
16/11/2015	O-prop (1)	**VE 8**	Reutilization (**EX 3**)	40	40	24	98
24/11/2015	O-prop (1)	**VE 9**	1% TBABr+ 0,05% Zn236	80	40	3	93
25/11/2015	O-prop (1)	**VE 10**	0,2% TBABr+ 0,05% Zn236	80	40	3	72
26/11/2015	O-prop (1)	**VE 11**	0,3% TBABr + 0,05% Zn236	80	40	3	79
30/11/2015	O-prop (1)	**VE 12**	1% TBABr+ 0,1% Zn236	80	40	3	99
9/12/2015	O-prop (1)	**VE 13**	0,4% TBABr+ 0,05% Zn236	80	40	3	90
18/12/2015	O-prop (1)	**VE 14**	0,4% TBABr + 0,05% Zn236	60	40	3	48

Date	***Epoxide (mL)***	***Sample***	***Catalyst***	***Temperature (°C)***	***Pressure (bar)***	***Time (h)***	***Conversion %***
18/12/2015	O-prop (1)	**VE 15**	0,4%TBABr + 0,05% Zn236	80	40	3	72
21/12/2015	O-prop (1)	**VE 16**	0,1% TBABr + 0,1% Zn236	80	40	24	Poli (0%)
5/1/2016	O-prop (1)	**VE 17**	0,1%Zn236+1% EMIMNtf$_2$	60	40	3	2
6/1/2016	O-prop (1)	**VE 18**	0,05%Zn236+0,4% EMIMNtf$_2$	60	40	3	0
11/1/2016	O-prop (1)	**VE 19**	0,05%Zn236+0,4% EMIMNtf$_2$	60	40	24	0
14/1/2016	O-prop (1)	**VE 20**	0,05%Zn236+0,4% EMIMBr	60	40	3	4
15/1/2016	O-prop (1)	**VE 21**	0,05%Zn236+0,4% EMIMEtSO$_4$	60	40	3	0
19/1/2016	O-prop (1)	**VE 22**	0,05%Zn236+0,4% EMIMB(CN)$_4$	60	40	3	0
1/2/2016	O-prop (1)	**VE 23**	**0,05%Zn236+0,4% TBABr** + PPG (**1**)	60	40	3	6
2/2/2016	O-prop (1)	**VE 24**	**0,05%Zn236+0,4% TBABr** + PEG (**1**)	60	40	3	9
4/2/2016	O-prop (1)	**VE 25**	0,05%Zn236+0,4% PPNCl	60	40	3	6
10/2/2016	O-prop (1)	**VE 26**	**0,05%Zn236+ 0,4% TBABr**+ EMIMEtSO$_4$ **(1)**	60	40	3	1
12/2/2016	O-prop (1)	**VE 27**	0,25%Zn236+1% TBABr + PEG (**1**)	60	40	3	27
16/2/2016	O-prop (1)	**VE 28**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	60	40	3	27
18/2/2016	O-prop (1)	**VE 29**	**0,2%Li[FeCl$_2$(TPMS)]+** 0,4%TBABr	60	40	3	8
18/2/2016	O-prop (1)	**VE 30**	**0,2%FeCl$_2$(TPM)+** 0,4%TBABr	60	40	3	18
19/2/2016	O-prop (1)	**VE 31**	0,25%Zn236+ 1%TBABr +EMIMEtSO$_4$(**1**)	60	40	3	17

Date	***Epoxide (mL)***	***Sample***	***Catalyst***	***Temperature (^oC)***	***Pressure (bar)***	***Time (h)***	***Conversion %***
24/2/2016	O-prop (1)	**VE 32**	0,25%Zn236+ 1%TBABr	60	40	3	68
25/2/2016	O-prop (1)	**VE 33**	0,05%Zn236+ 0,4%TBACl	60	40	3	5
26/2/2016	O-prop (1)	**VE 34**	0,05%Zn236+ 0,4%TBABr	60	40	3	44
1/3/2016	O-prop (1)	**VE 36**	0,05%Zn236+ 0,4%CholineCl	60	40	3	0 (wrong)
2/3/2016	O-prop (1)	**VE 37**	0,2%$FeCl_2$(TPM)	60	40	24	0
4/3/2016	O-prop (1)	**VE 38**	0,25%Zn236+ 1%TBABr+MEK(**1**)	60	40	3	42
7/3/2016	O-prop (1)	**VE 39**	0,25%Zn236+ 1%TBABr	Room T	5	24	24
9/3/2016	O-prop (1)	**VE 40**	0,05%Zn236	80	40	3	0
16/3/2016	O-prop (1)	**VE 41**	0,25%Zn236+ 1%TBABr	50	5	24	87
18/3/2016	O-prop (1)	**VE 42**	**0,1%Zn11**+ 0,4%TBABr	60	40	3	41
18/3/2016	O-prop (1)	**VE 43**	0,25%Zn236+ 1%TBABr	60	180	3	31
22/3/2016	O-prop (1)	**VE 44**	0,1%CuR11 + 0,4%TBABr	60	40	3	20
29/3/2016	O-prop (1)	**VE 45**	0,25%Zn236+ 1%TBABr + H_2O(**1**)	60	40	3	3
31/3/2016	O-prop (1)	**VE 46**	0,25%Zn236+ 1%TBABr	60	5	3	69
31/3/2016	O-prop (1)	**VE 47**	0,25%Zn236+ 1%TBABr+ EthylLactate(**1**)	60	40	3	22
1/4/2016	O-prop (1)	**VE 48**	0,25%Zn236+ 1%TBABr+ Choline:Urea(1:2)(**1**)	60	40	3	11
4/4/2016	O-prop (1)	**VE 49**	0,05%Zn236+ 0,4%CholineCl	60	40	3	0

Date	***Epoxide (mL)***	***Sample***	***Catalyst***	***Temperature (°C)***	***Pressure (bar)***	***Time (h)***	***Conversion %***
13/4/2016	O-prop (1)	**VE 50**	0,25%Zn236+ 1%TBABr+ BMIMOTf(**1**)	60	40	3	13
21/4/2016	O-prop (1)	**VE 51**	0,25%Zn236+ 1%TBABr+ BMIMNTf$_2$(**1**)	60	40	3	7
22/4/2016	O-prop (1)	**VE 52**	0,25%Zn236+ 1%TBABr+ EMIMOTf(**1**)	60	40	3	9
22/4/2016	O-prop (1)	**VE 53**	0,25%Zn236+ 1%TBABr	60	88	3	38
26/4/2016	O-prop (1)	**VE 54**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	60	80	3	48
27/4/2016	O-prop (1)	**VE 55**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	80	40	3	50
2/5/2016	O-prop (1)	**VE 56**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	60	180	3	4
28/4/2016	O-prop (1)	**VE 57**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	60	5	3	50
28/4/2016	O-prop (1)	**VE 58**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	60	40	24	72
30/5/2016	O-prop (1)	**VE 59**	0,25%Zn236+1% TBABr + ALIQUAT Cl (**1**)	40	40	3	14
4/5/2016	O-prop (1)	**VE 60**	0,25%Zn236+0,4% ALIQUAT Cl	60	40	3	0
18/5/2016	O-prop (1)	**VE 61**	0,05%Zn236+0,4% ALIQUAT Cl	60	40	3	0
19/5/2016	O-prop (1)	**VE 62**	0,25%Zn236+1% TBABr + EMIMB(CN)$_4$ (**1**)	60	40	3	11

2/6/2016	O-prop (1)	**VE 63**	0,25%Zn236+ 1%TBABr+ ALIQUAT Cl (**1**)	60	10	3	55
30/6/2016	O-prop (1)	**VE 64**	0,05%ZnTPyP+ 0,4%TBABr	60	40	3	25
13/7/2016	O-prop (1)	**VE 65**	0,05%ZnTDCPP+ 0,4%TBABr	60	40	3	14
13/7/2016	O-prop (1)	**VE 66**	0,05%Zn236+ 0,4%Andreia37	60	40	3	24
18/7/2016	O-prop (1)	**VE 67**	0,05%Zn236+ 0,4%Andreia43	60	40	3	13
18/7/2016	O-prop (1)	**VE 68**	0,05%Zn236+ 0,4%DES2	60	40	3	12
19/7/2016	O-prop (1)	**VE 69**	0,2%$ZnCl_2$:EG+ 0,4%TBABr	60	40	3	62
19/7/2016	O-prop (1)	**VE 70**	0,25%Zn236+ 1mL DES2	60	40	3	77
21/7/2016	O-prop (1)	**VE 71**	0,25%Zn236+ 1mL DES3	60	40	3	79
21/10/2016	O-prop (1)	**VE 72**	0,2% $ZnCl_2$:EG(1:4)	60	40	3	0
24/11/2016	O-prop (1)	**VE 73**	ALIQUAT (1mL)	60	40	3	13
24/11/2016	CHO (1)	**VE 74**	ALIQUAT (1mL)	80	40	3	Inês

*Compressor problems.

Below are the ^{1}H-NMR spectra of the reactions presented in Table 6.1.

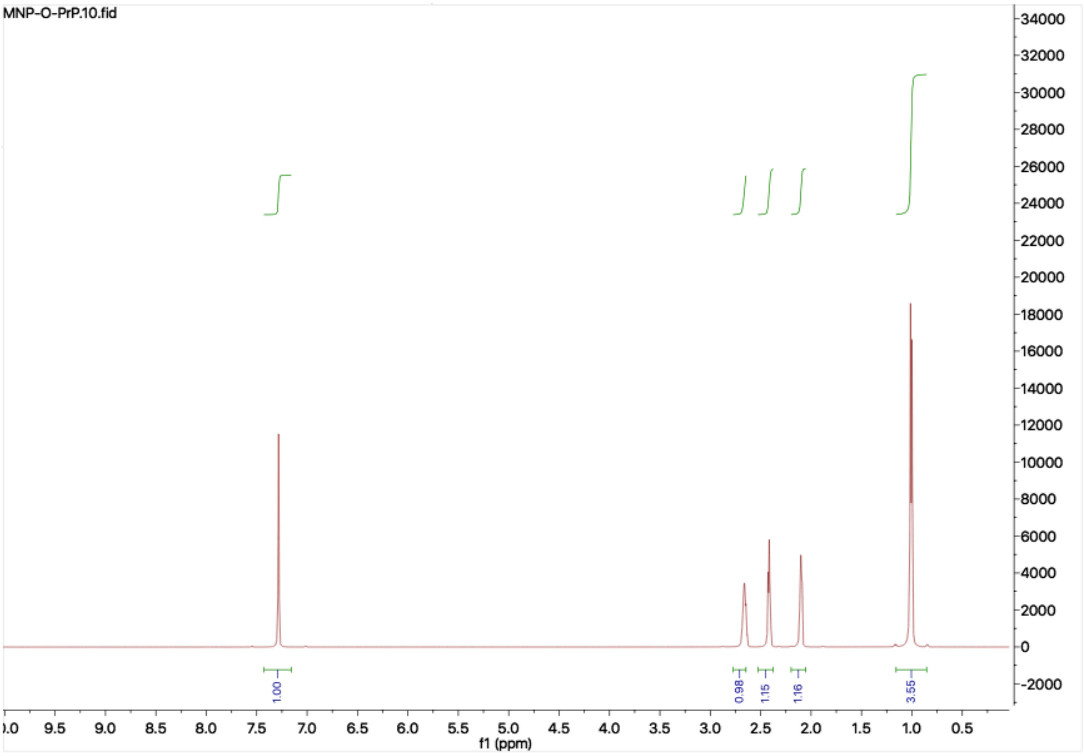

Figure 6.1 - Propylene oxide HNMR spectra

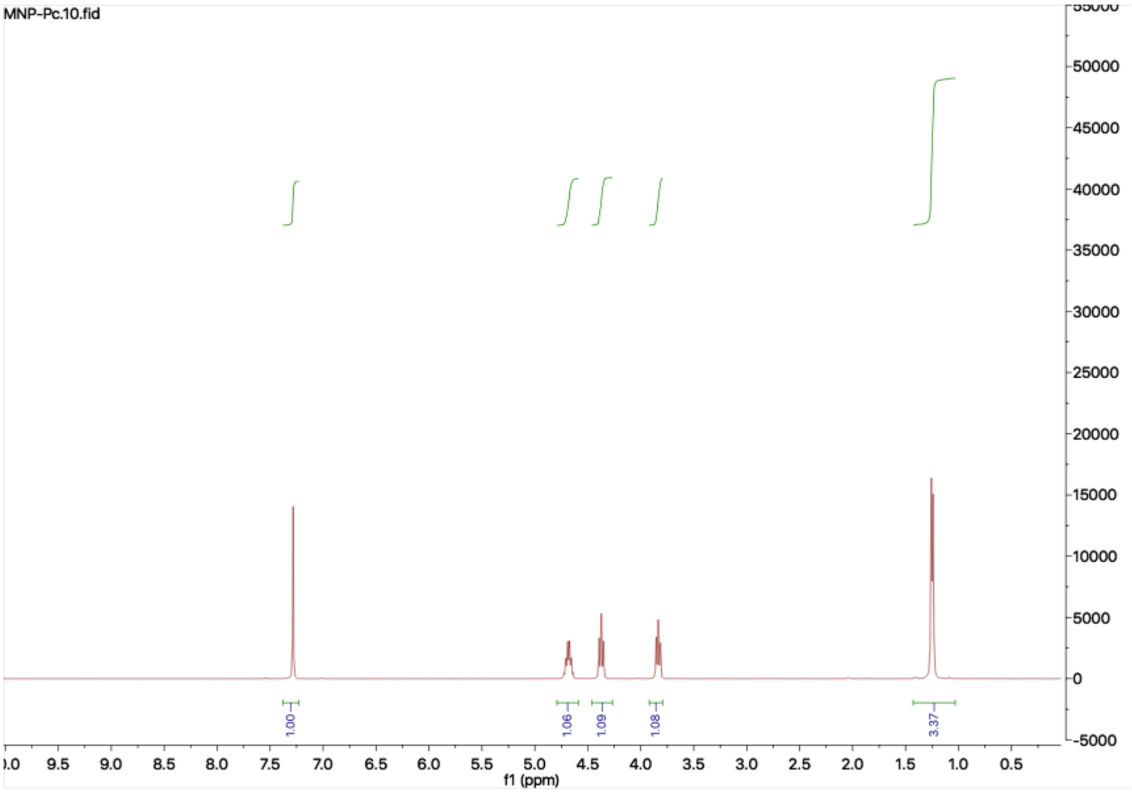

Figure 6.2 - Cyclic carbonate HNMR spectra

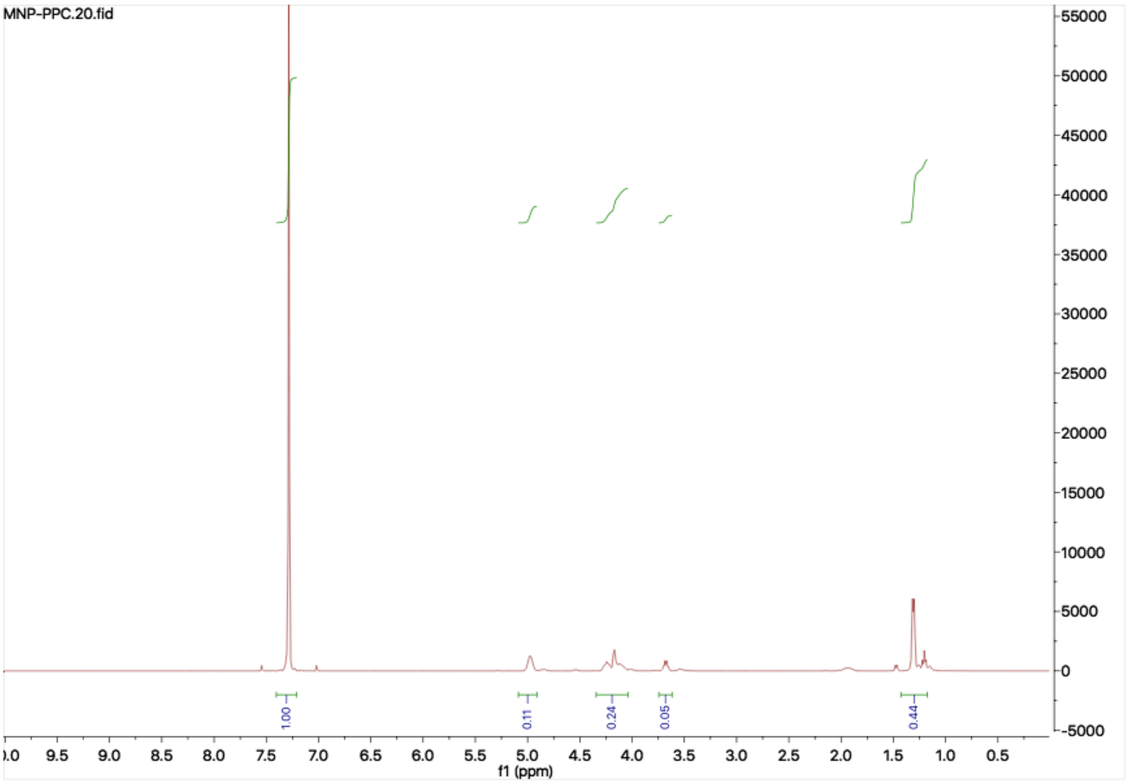

Figure 6.3 - Poly(propylene carbonate) HNMR spectra

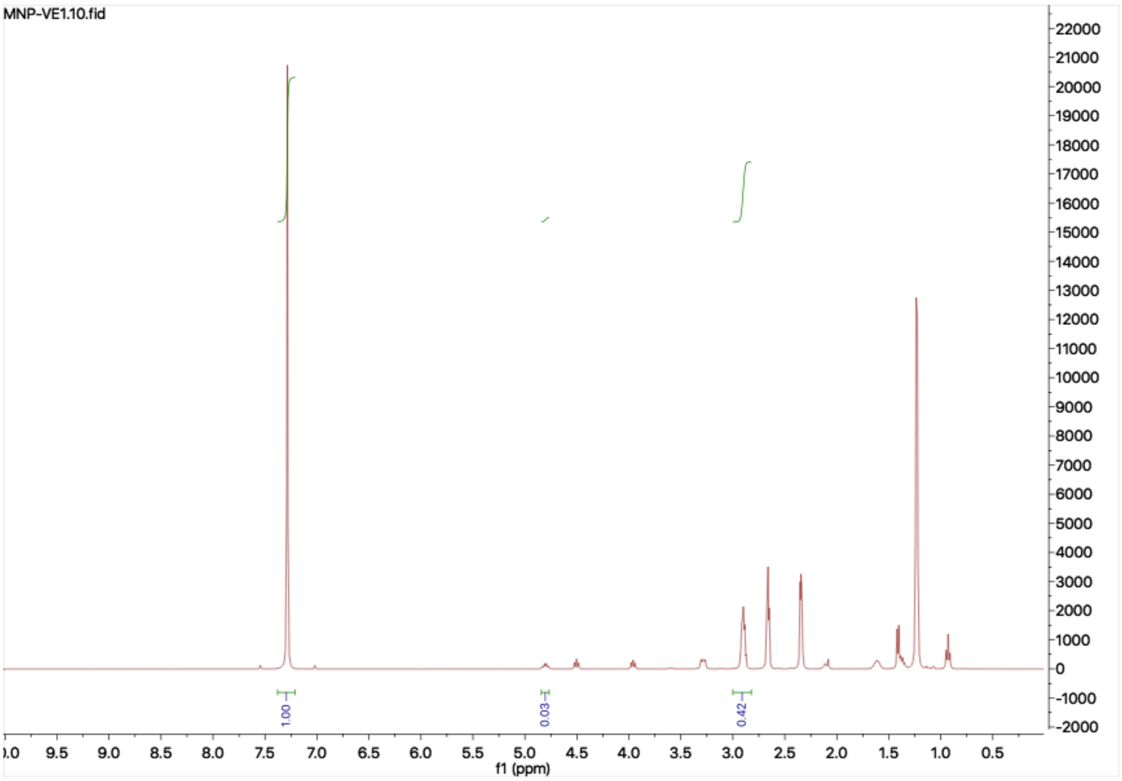

Figure 6.4 - VE 1 HNMR spectra

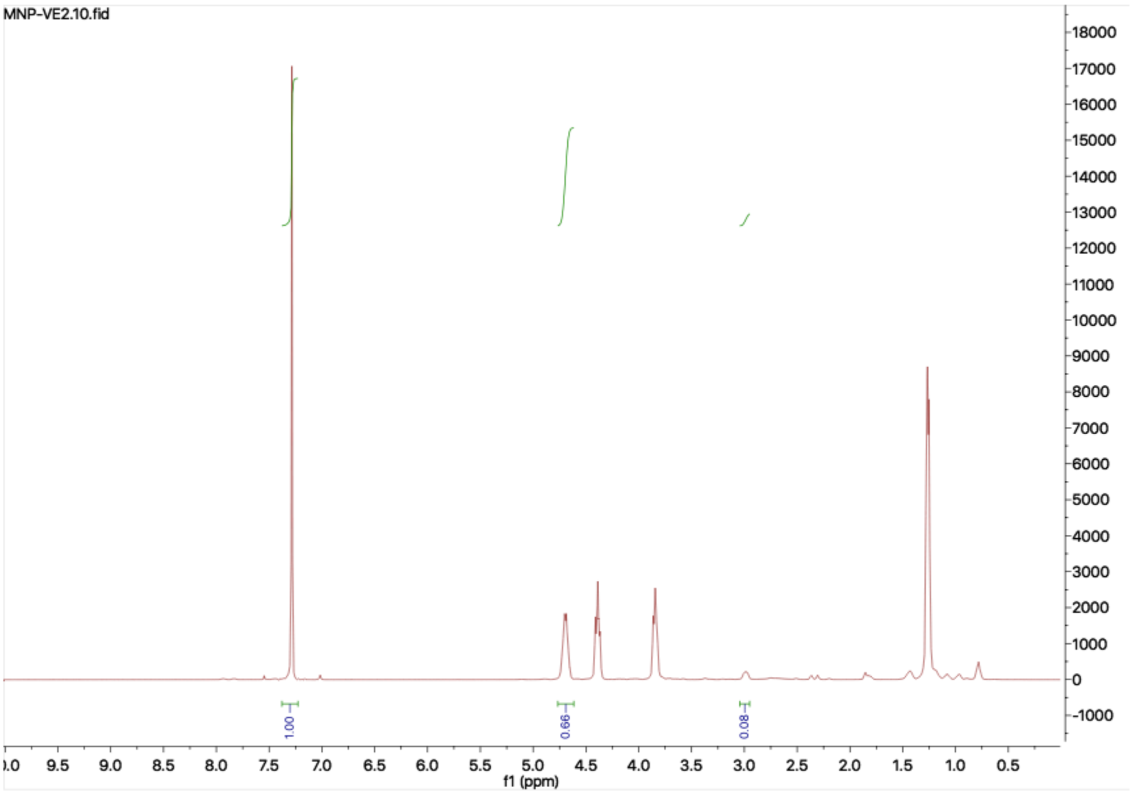

Figure 6.5 - VE 2 HNMR spectra

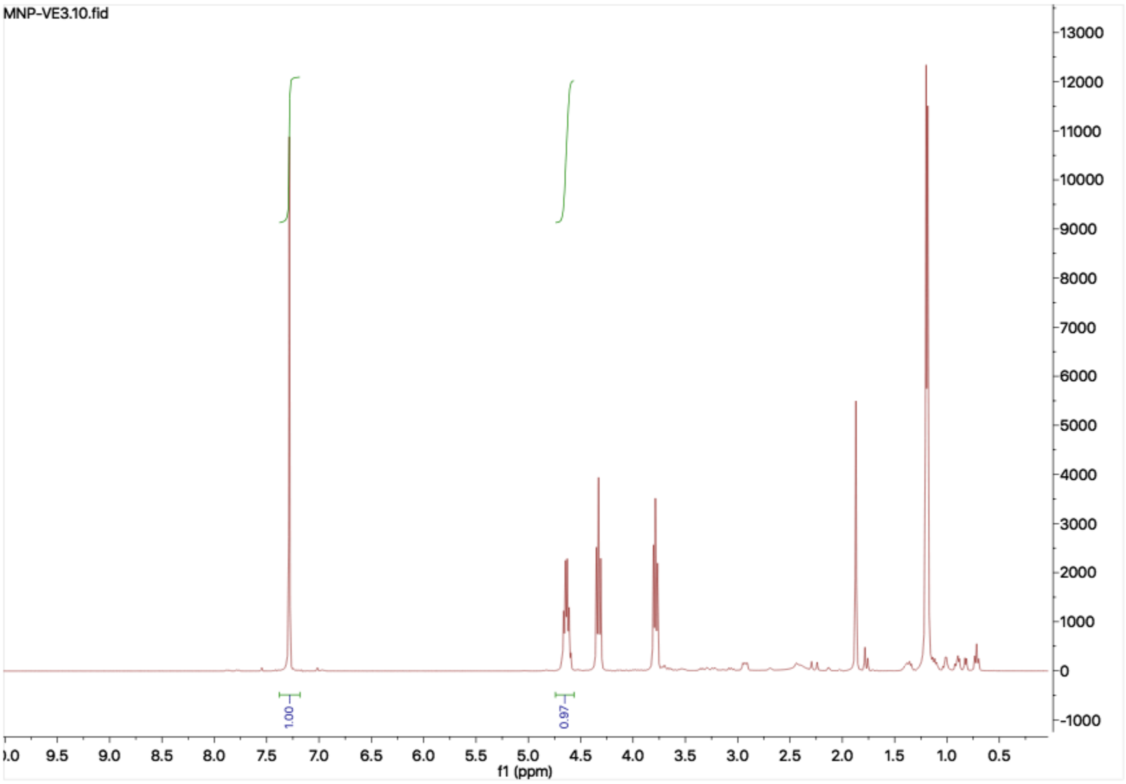

Figure 6.6 - VE 3 HNMR spectra

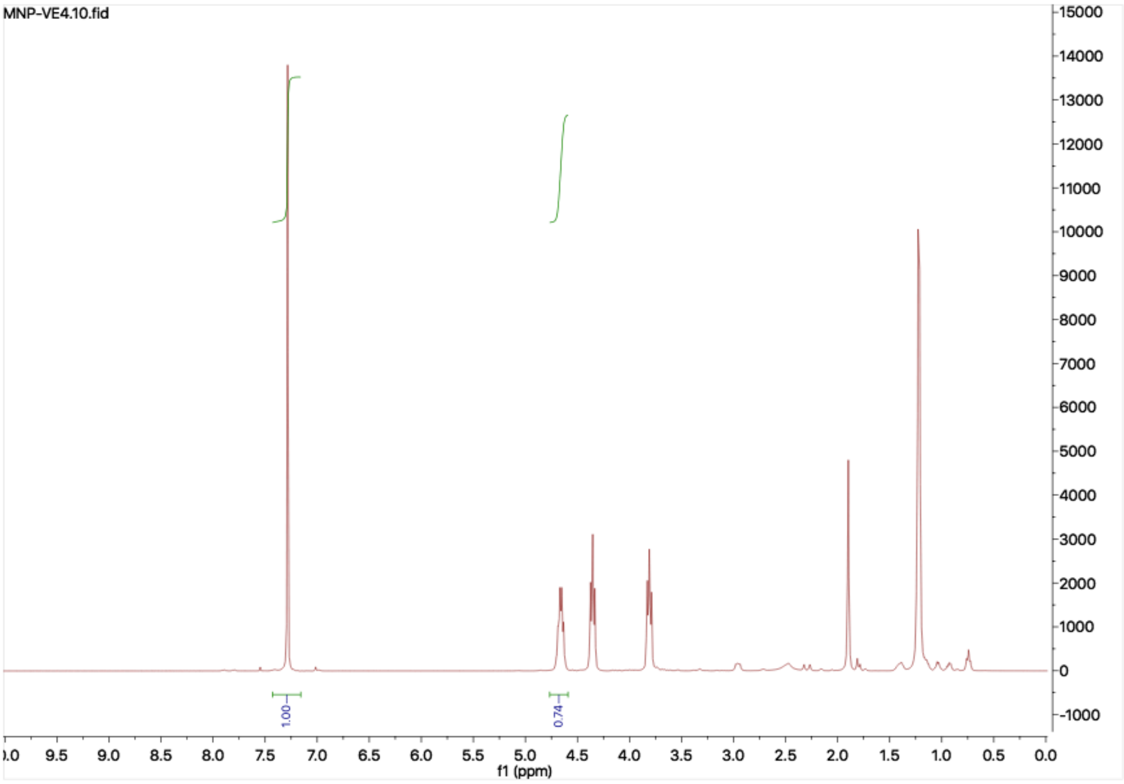

Figure 6.7 - VE 4 HNMR spectra

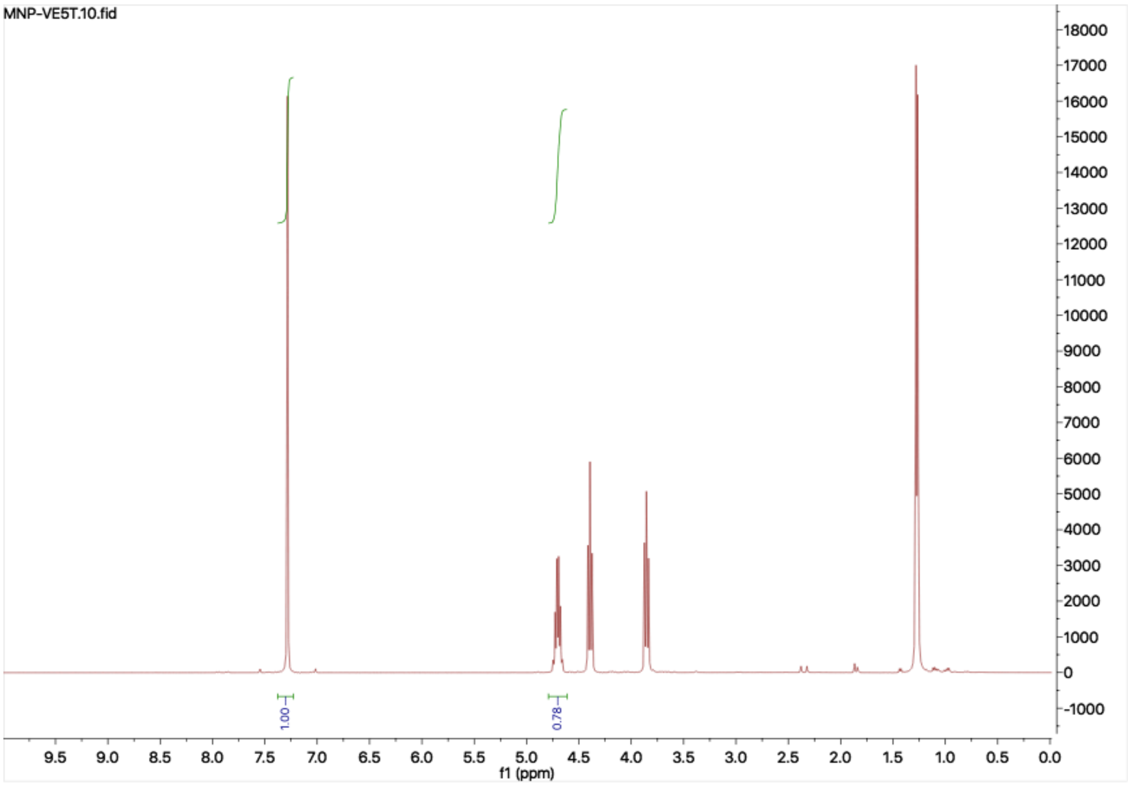

Figure 6.8 - VE 5 HNMR spectra

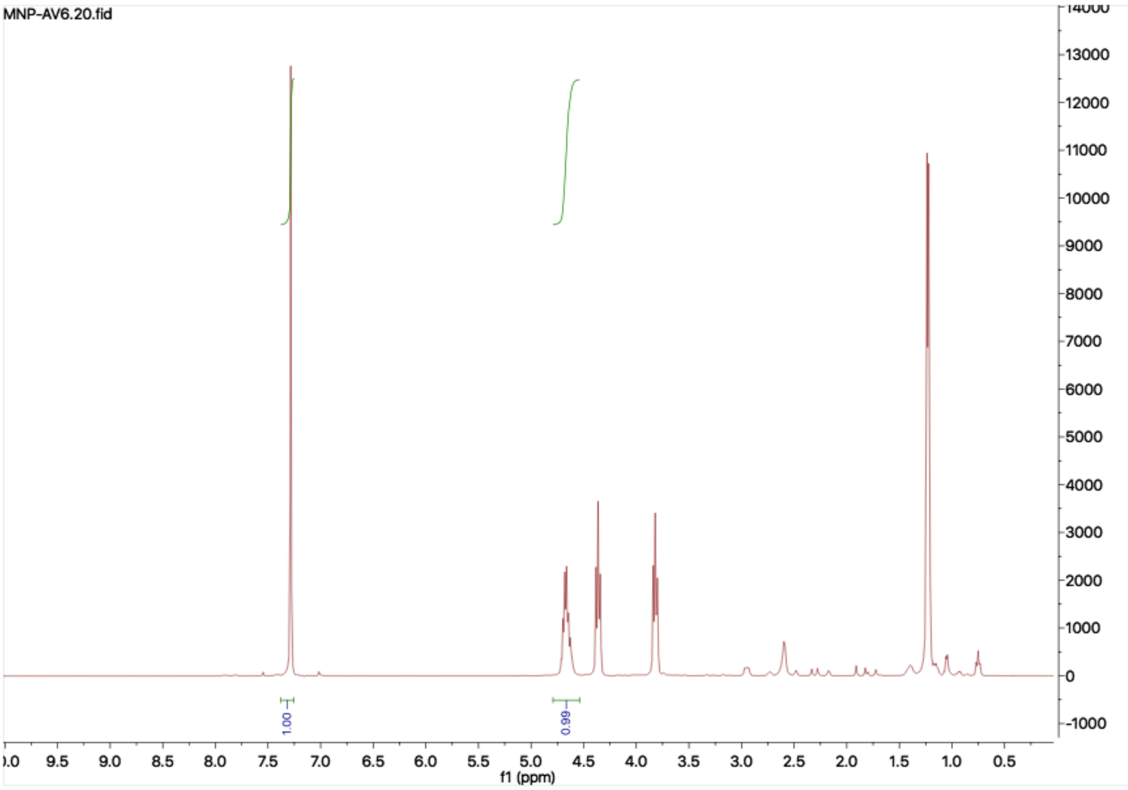

Figure 6.9 - VE 6 HNMR spectra

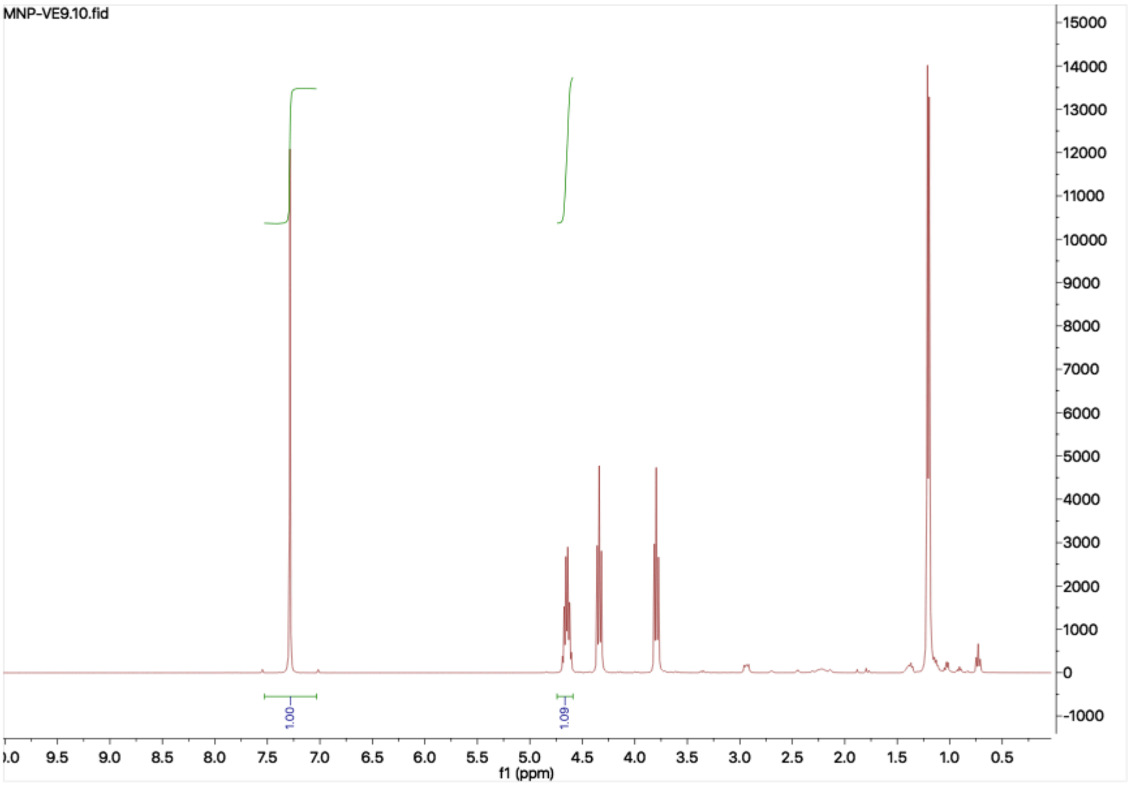

Figure 6.10 - VE 9 HNMR spectra

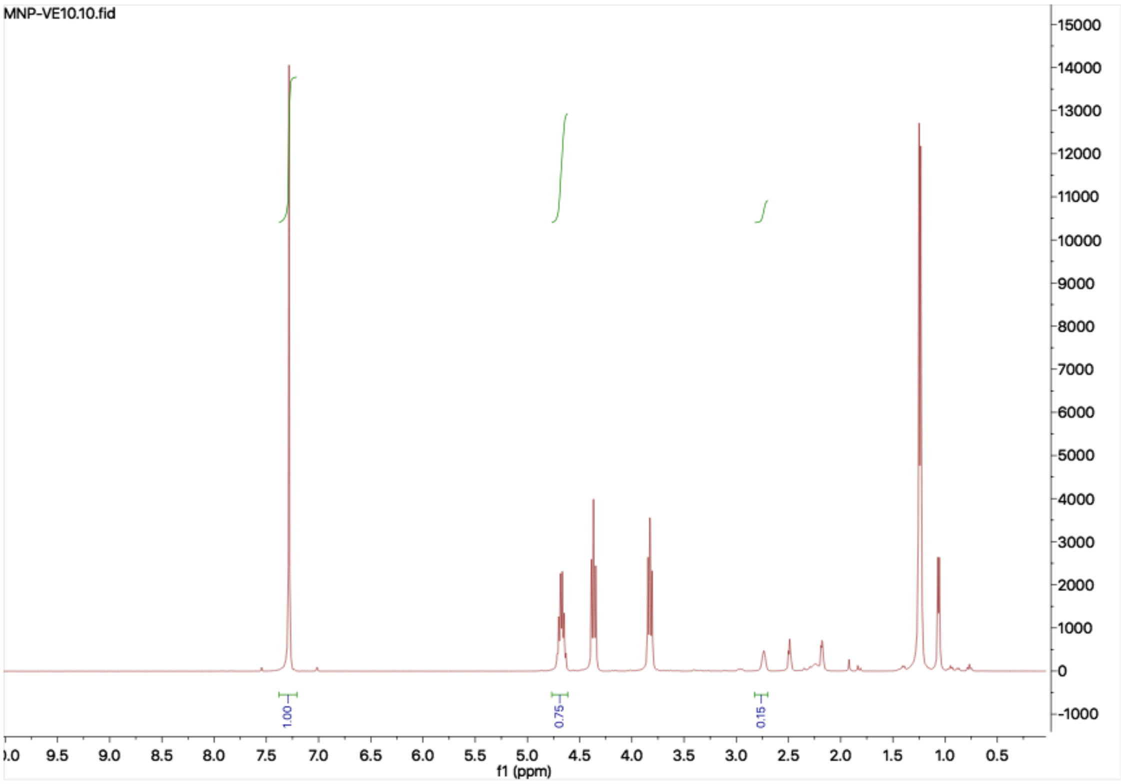

Figure 6.11 - VE 10 HNMR spectra

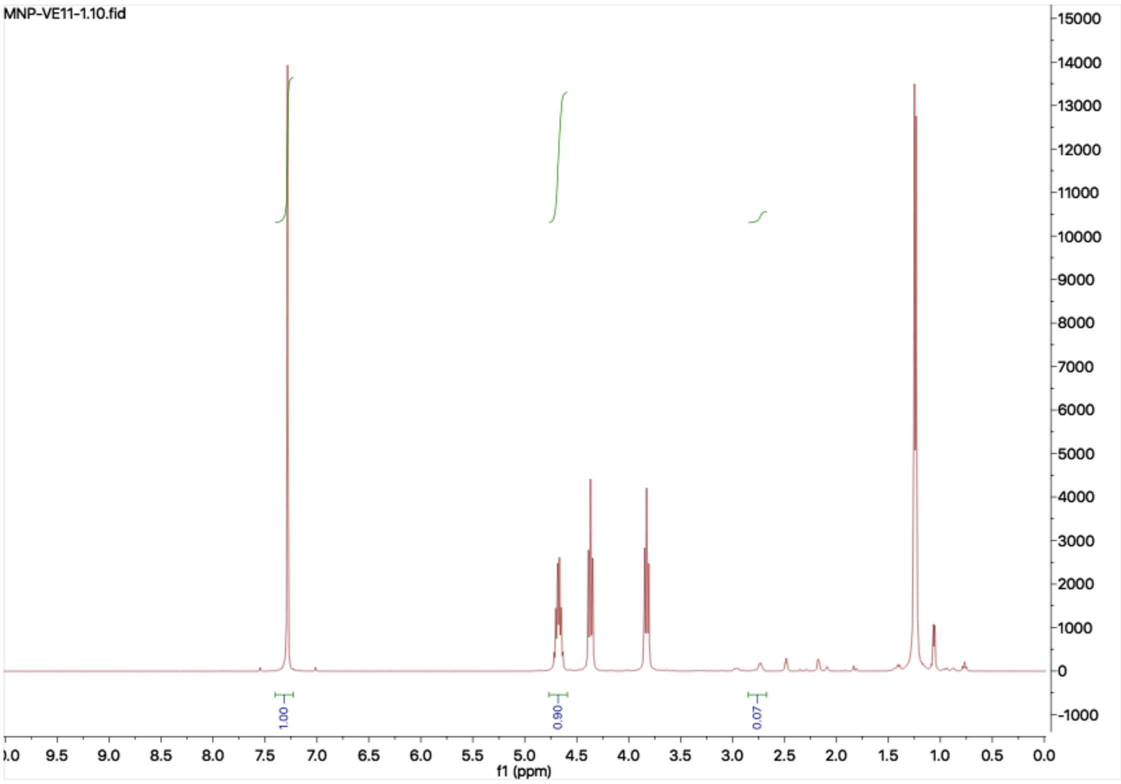

Figure 6.12 - VE 11 HNMR spectra

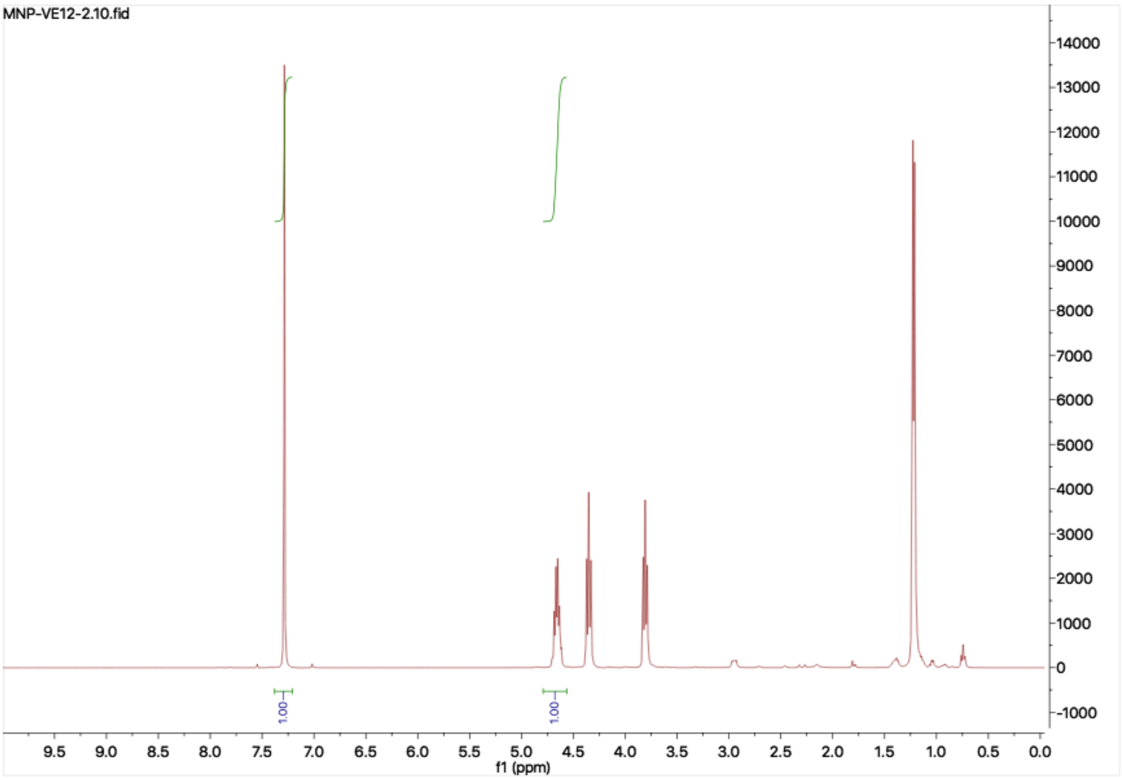

Figure 6.13 - VE 12 HNMR spectra

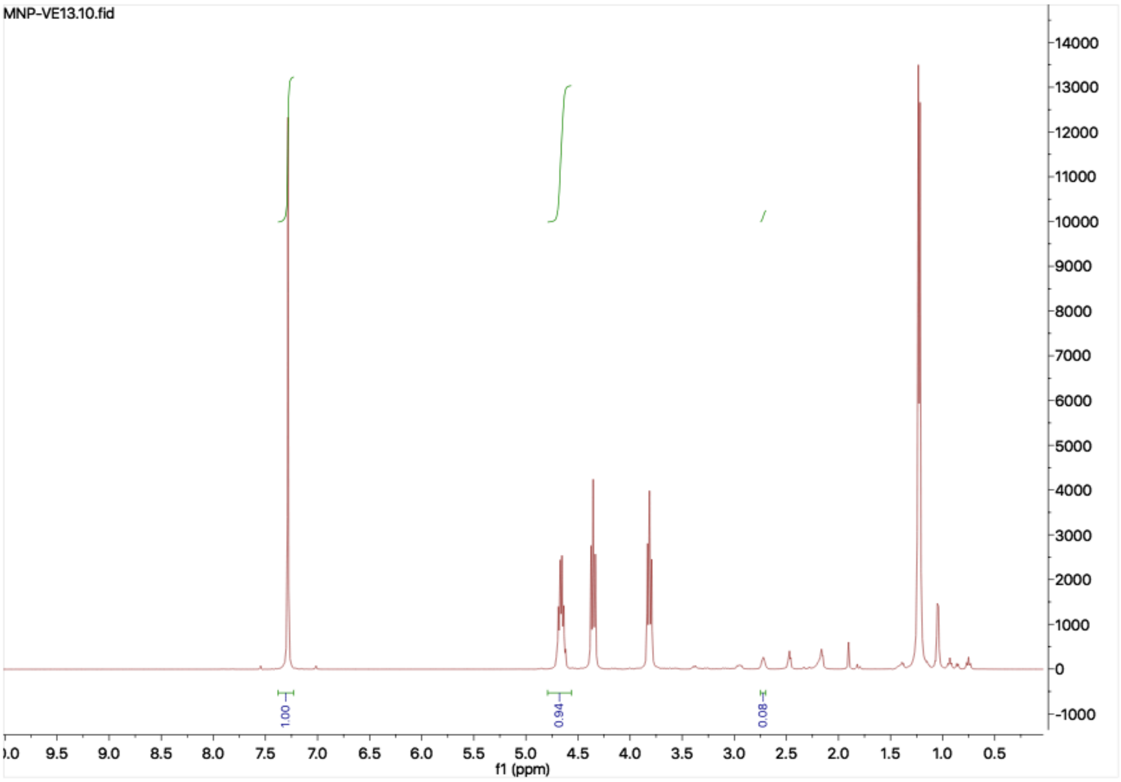

Figure 6.14 - VE 13 HNMR spectra

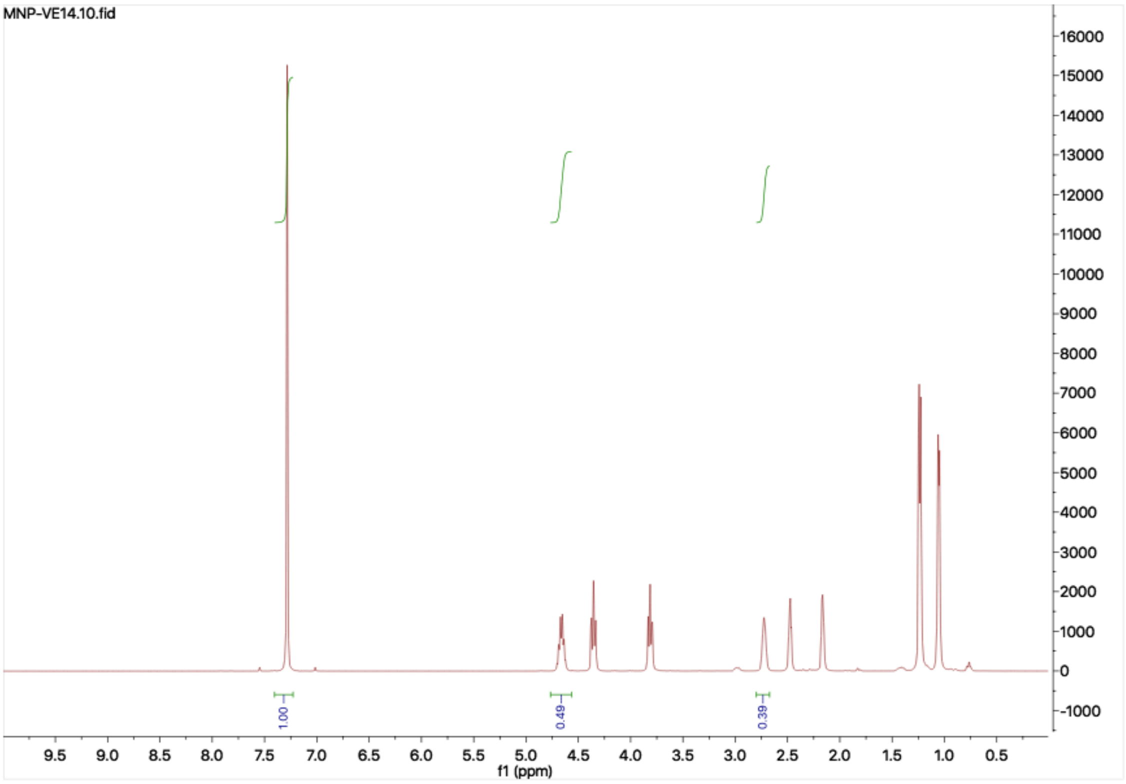

Figure 6.15 - VE 14 HNMR spectra

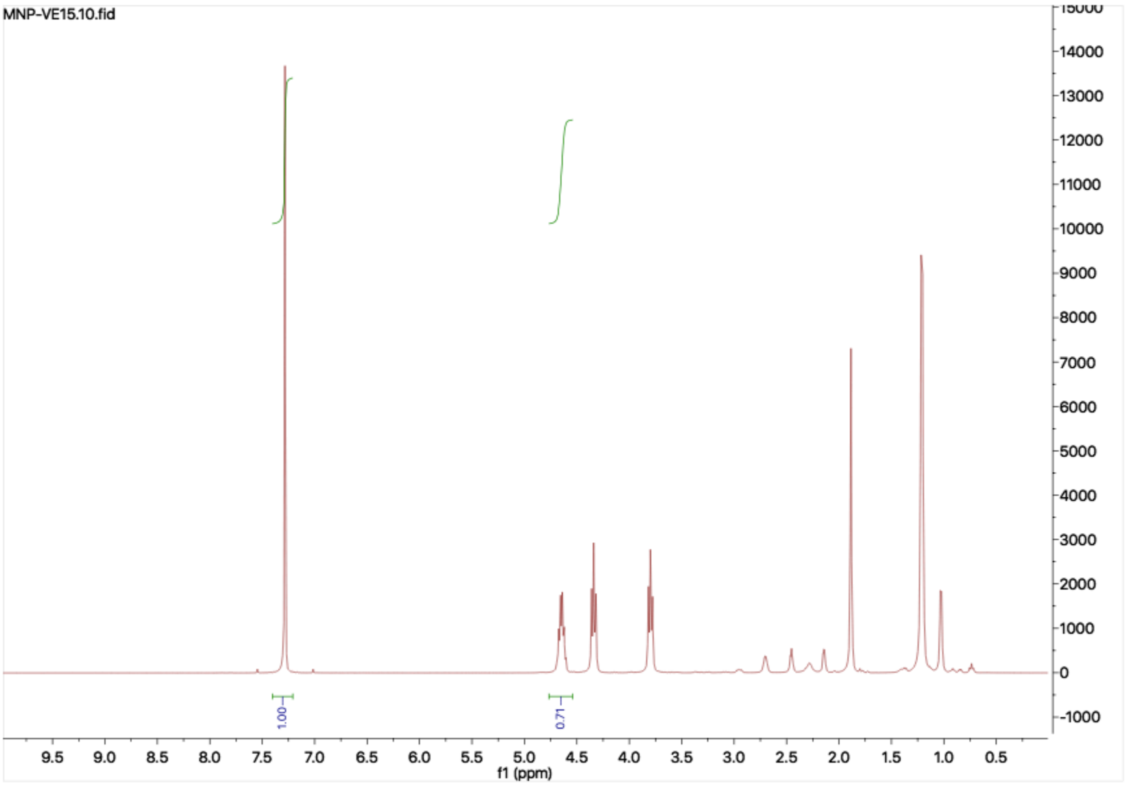

Figure 6.16 - VE 15 HNMR spectra

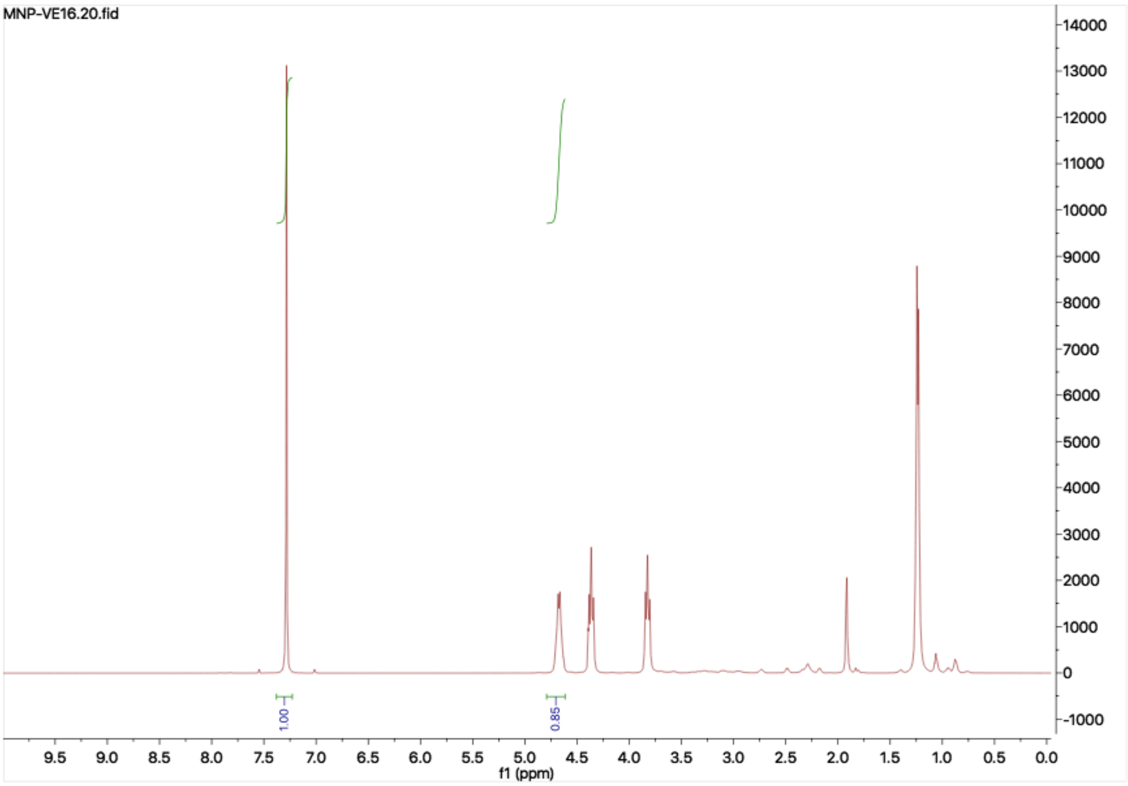

Figure 6.17 - VE 16 HNMR spectra

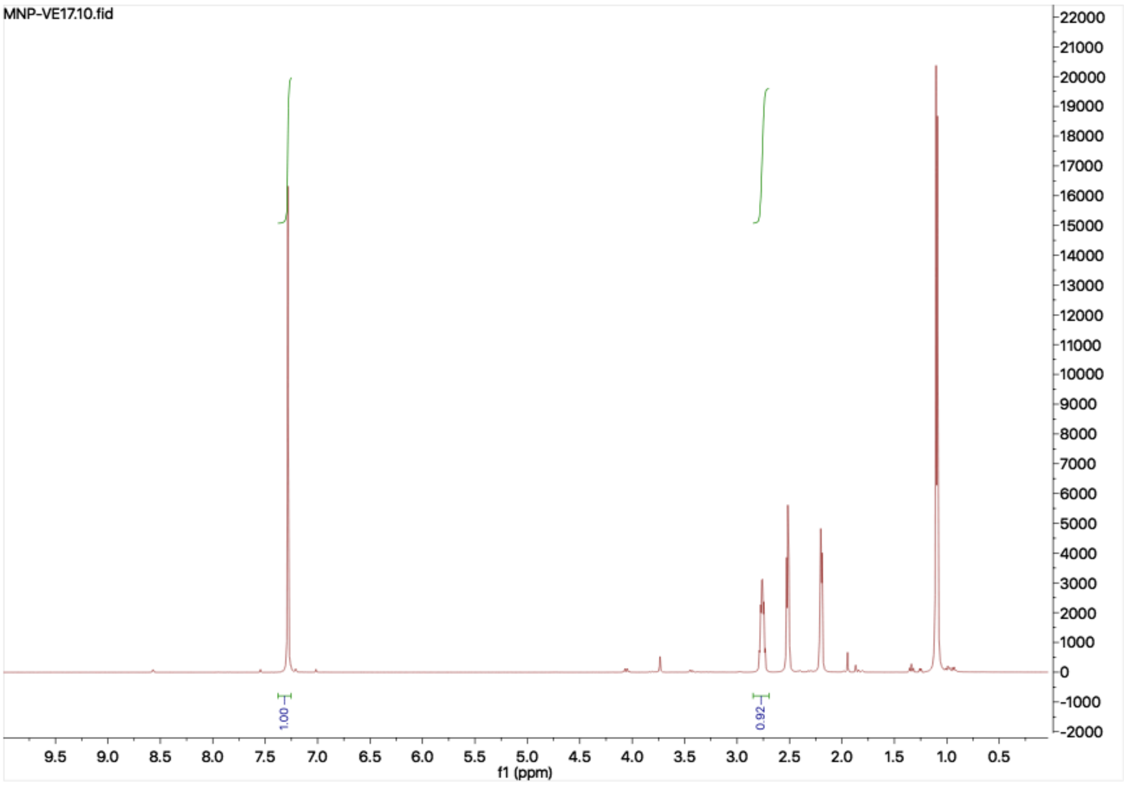

Figure 6.18 - VE 17 HNMR spectra

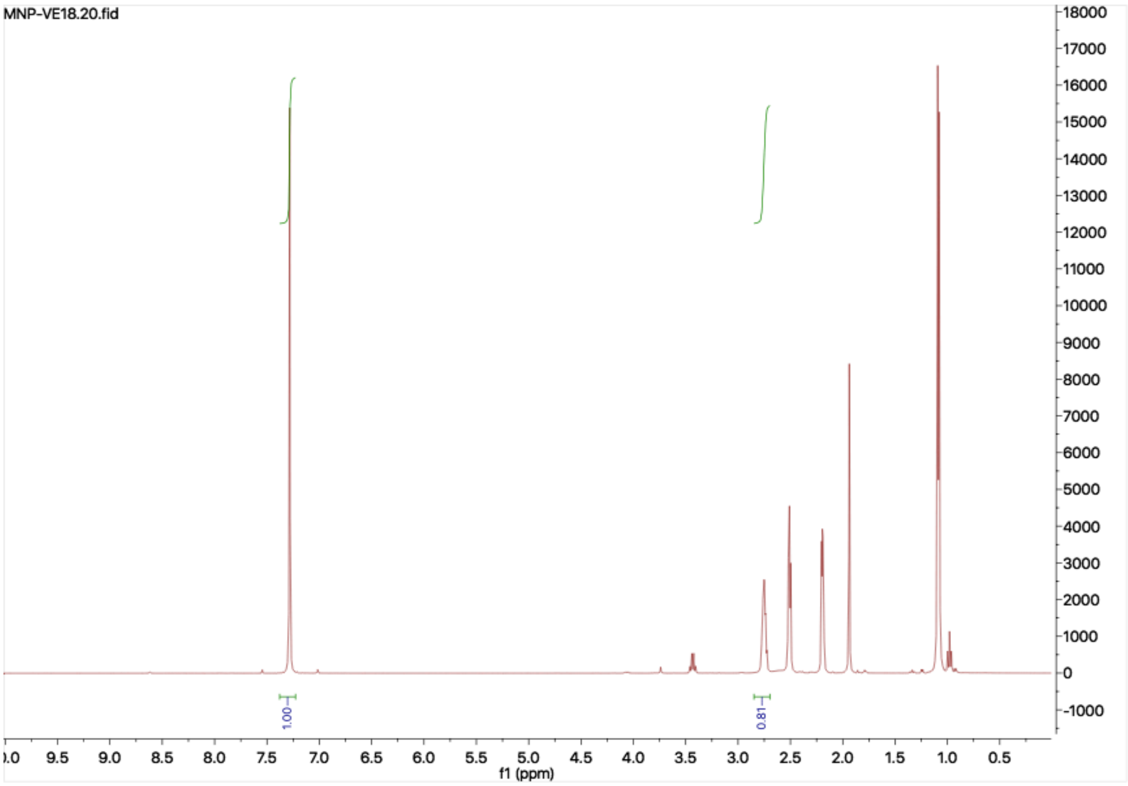

Figure 6.19 - VE 18 HNMR spectra

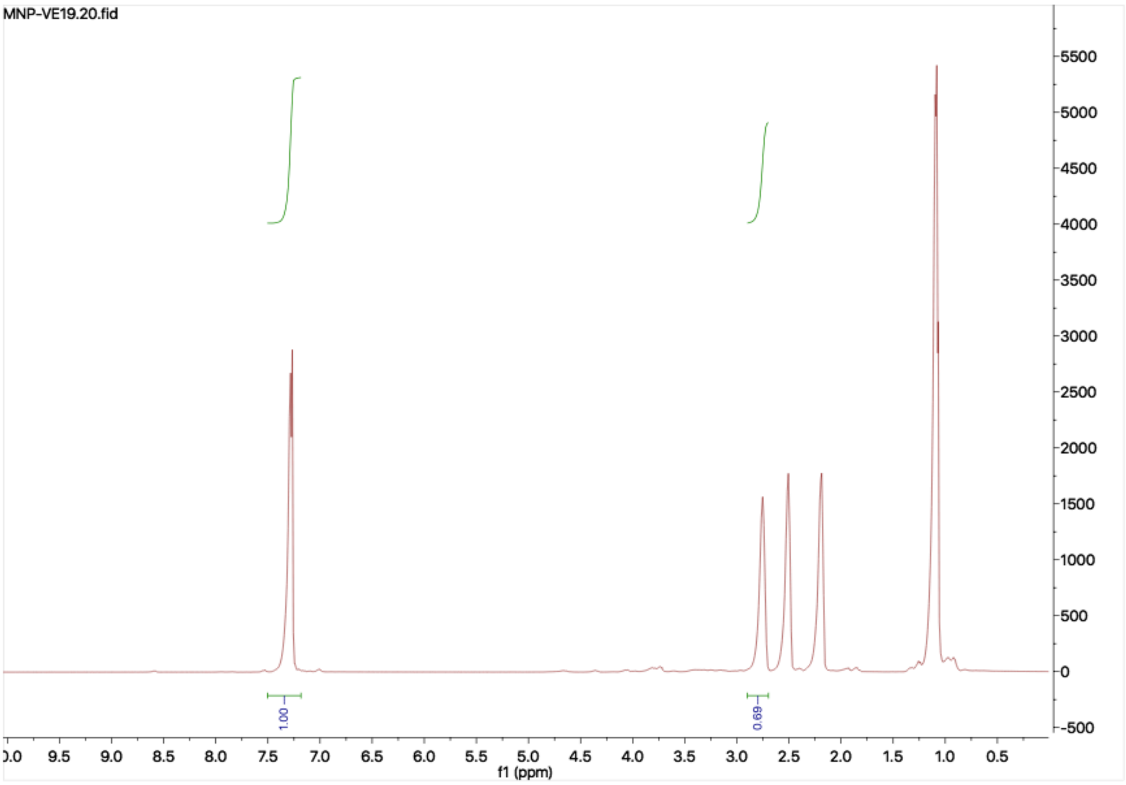

Figure 6.20 - VE 19 HNMR spectra

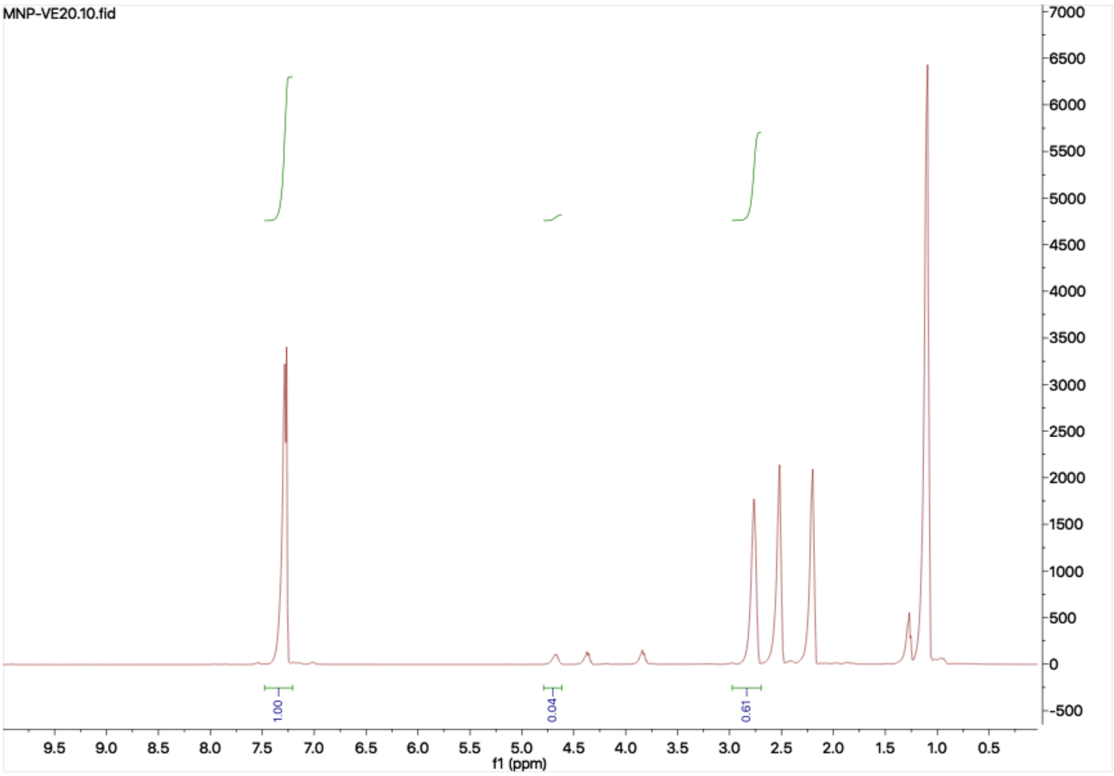

Figure 6.21 - VE 20 HNMR spectra

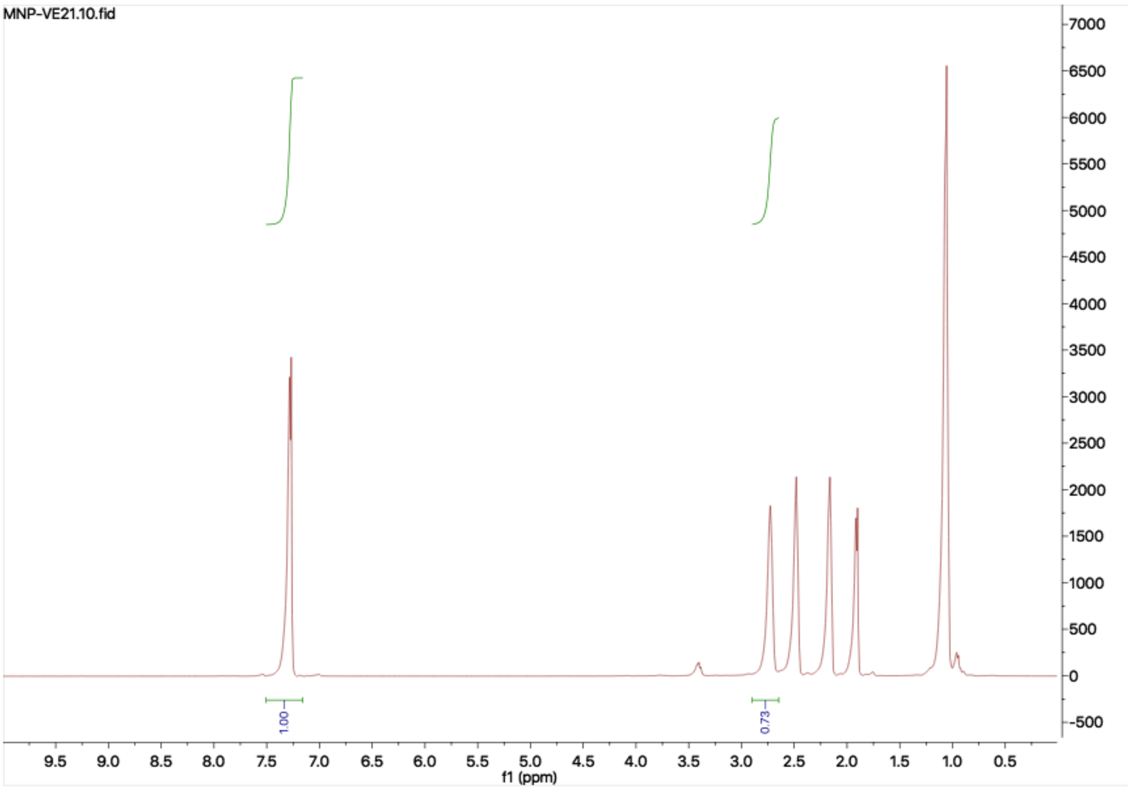

Figure 6.22 - VE 21 HNMR spectra

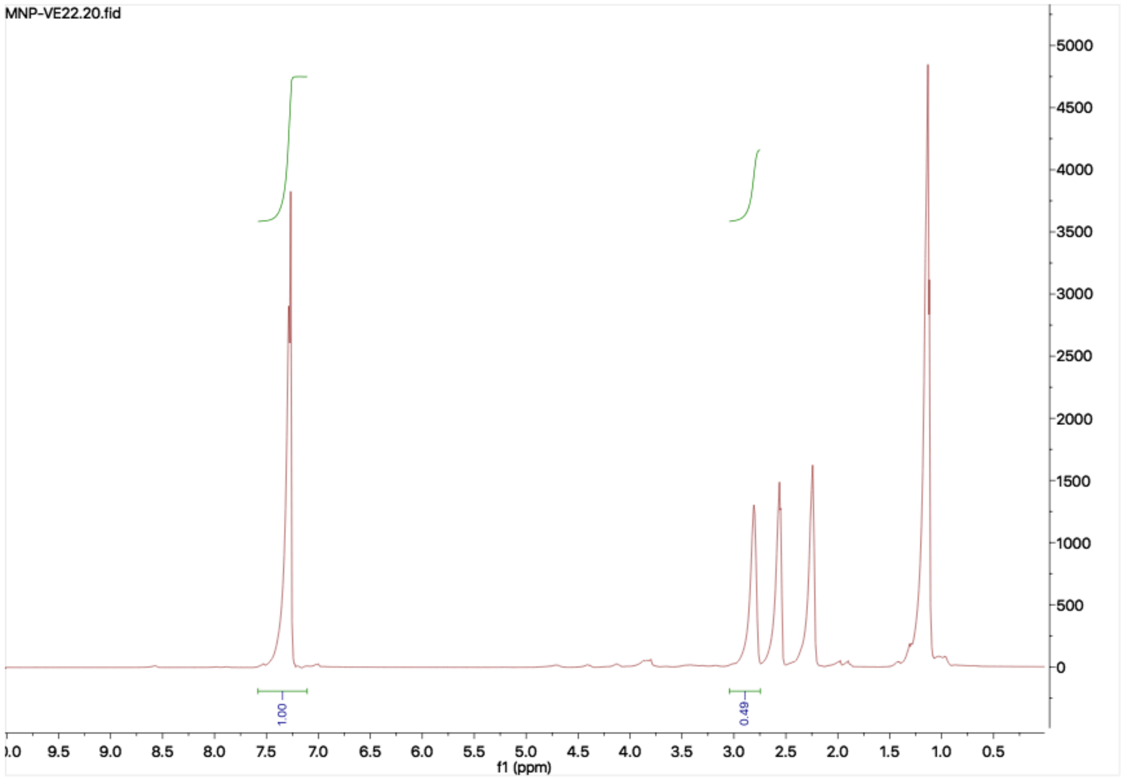

Figure 6.23 - VE 22 HNMR spectra

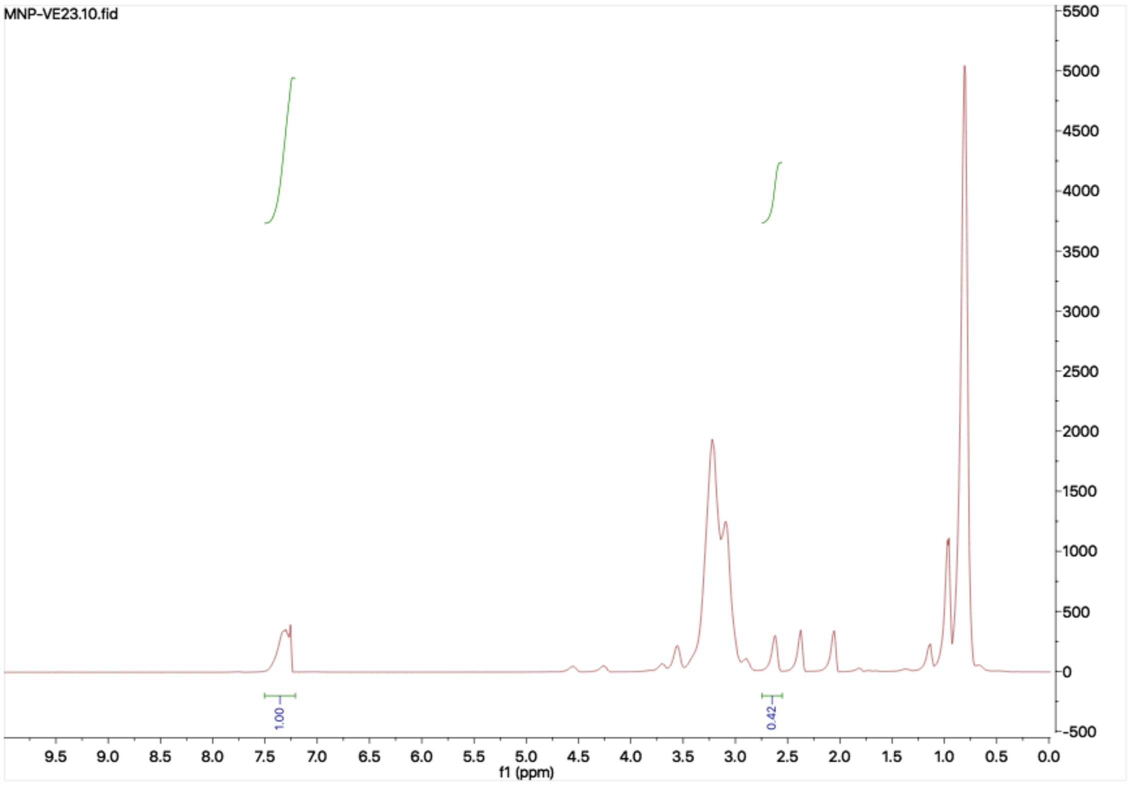

Figure 6.24 - VE 23 HNMR spectra

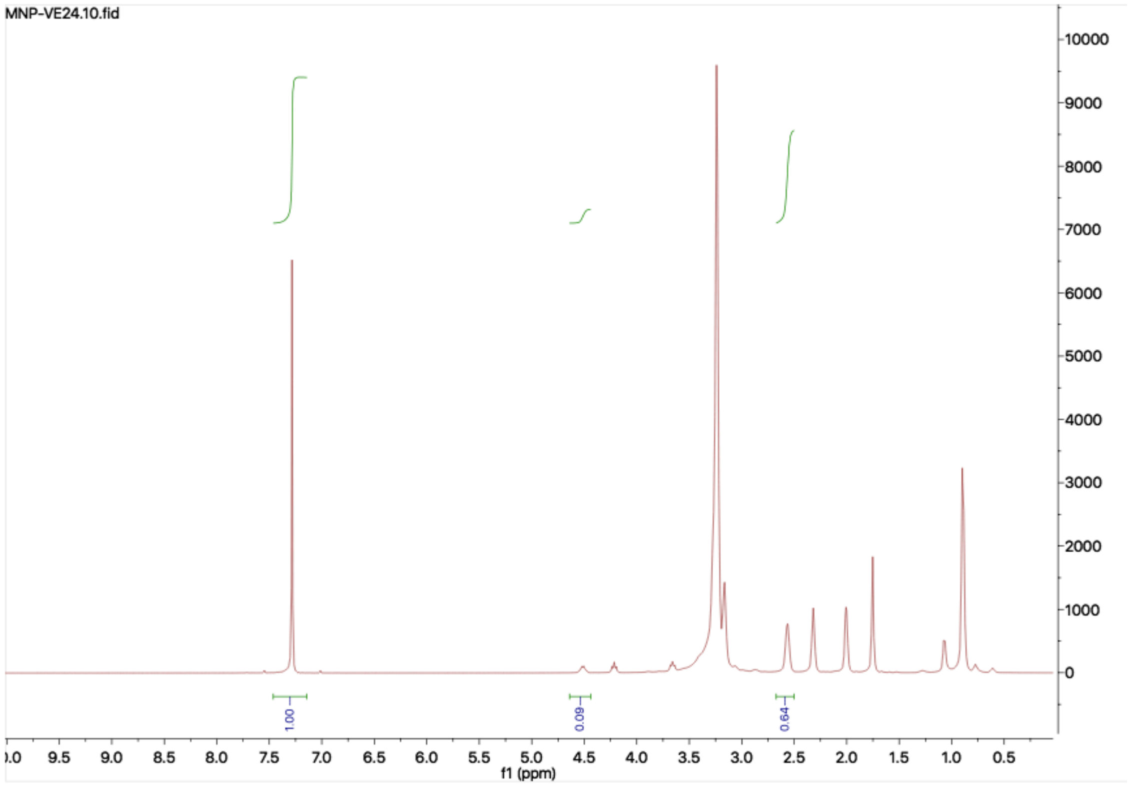

Figure 6.25 - VE 24 HNMR spectra

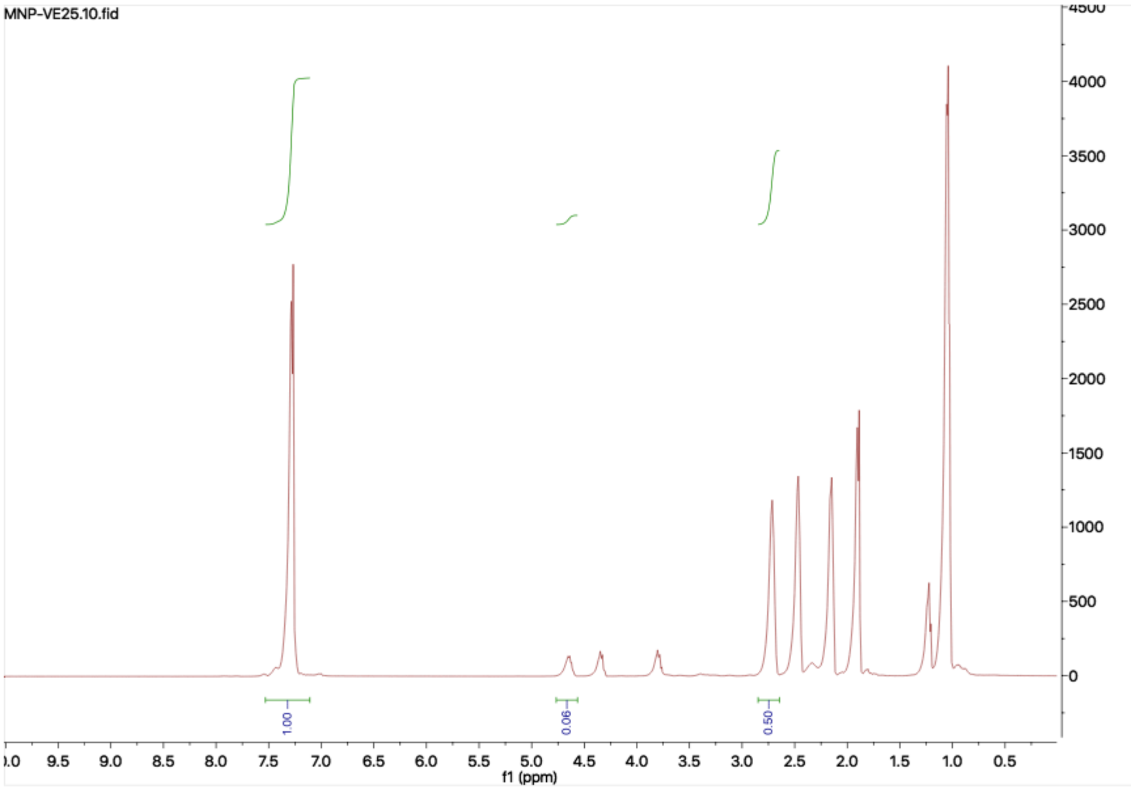

Figure 6.26 - VE 25 HNMR spectra

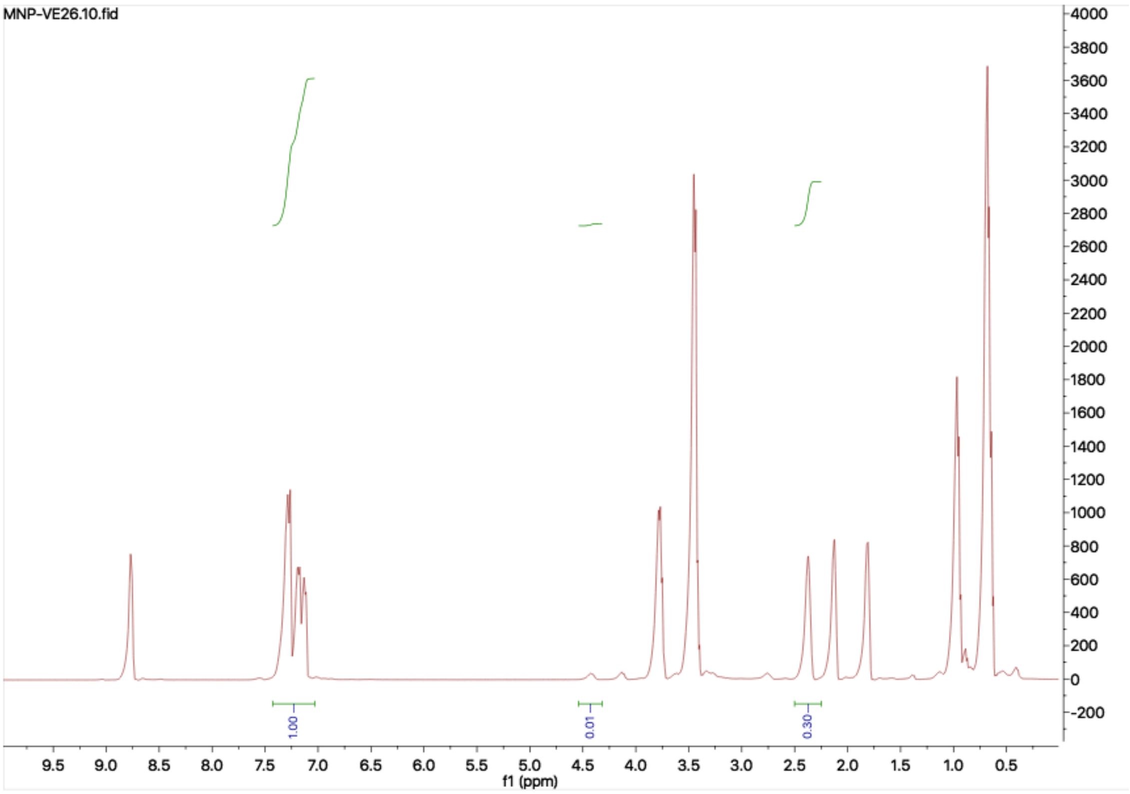

Figure 6.27 - VE 26 HNMR spectra

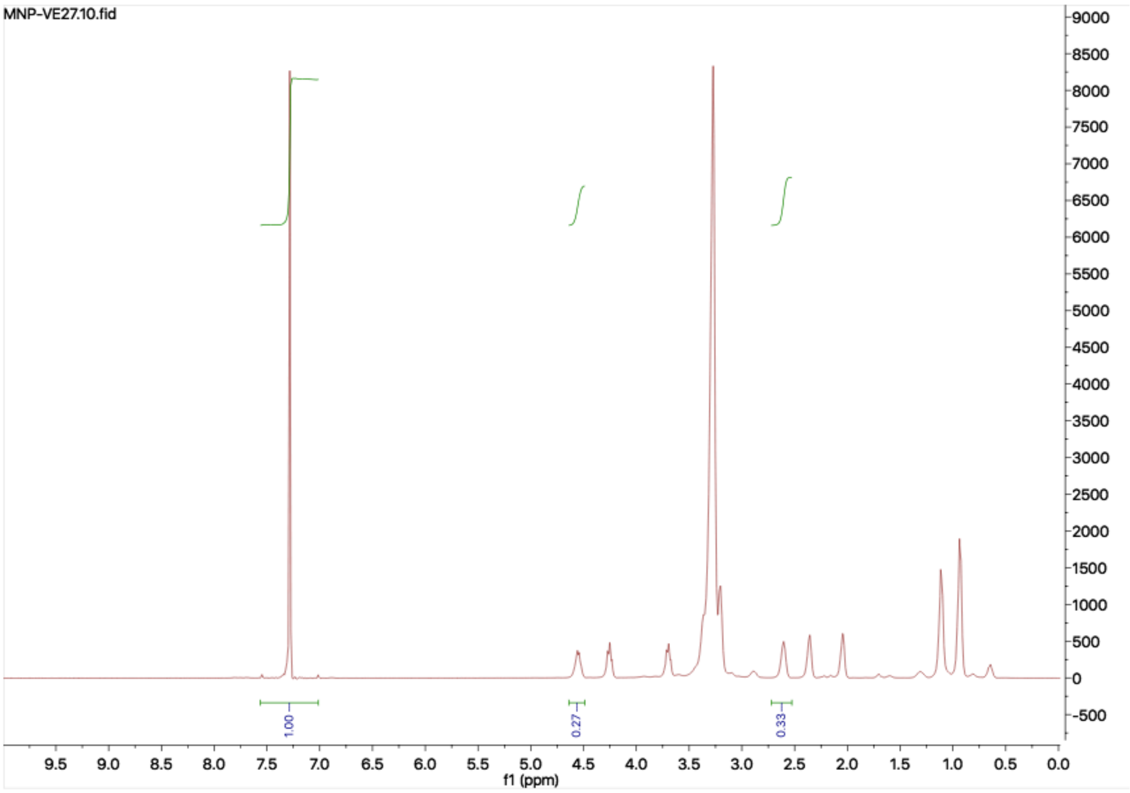

Figure 6.28 - VE 27 HNMR spectra

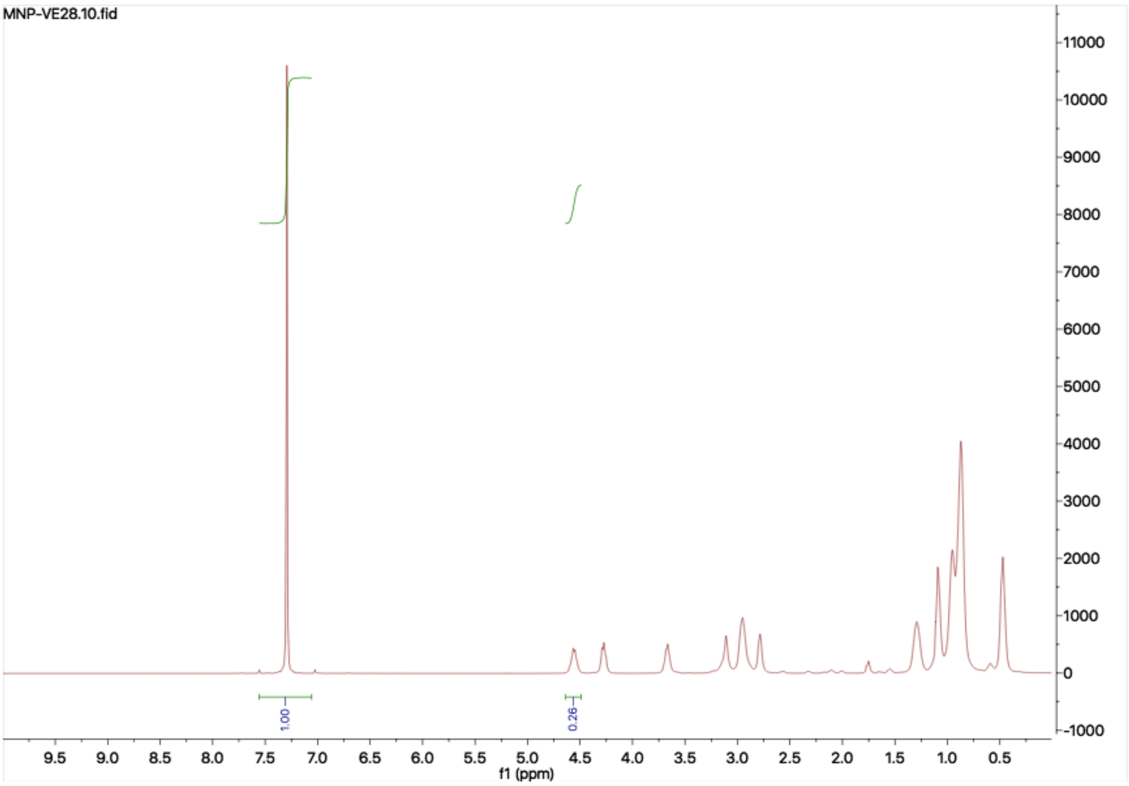

Figure 6.29 - VE 28 HNMR spectra

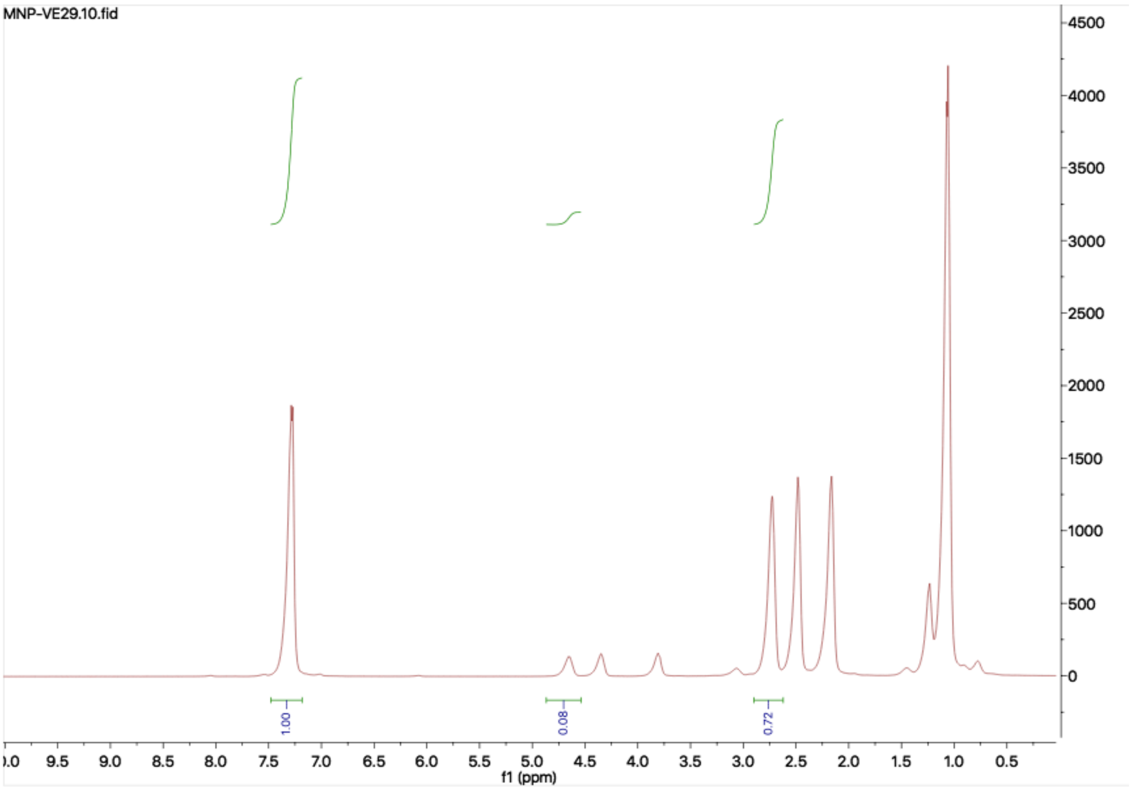

Figure 6.30 - VE 29 HNMR spectra

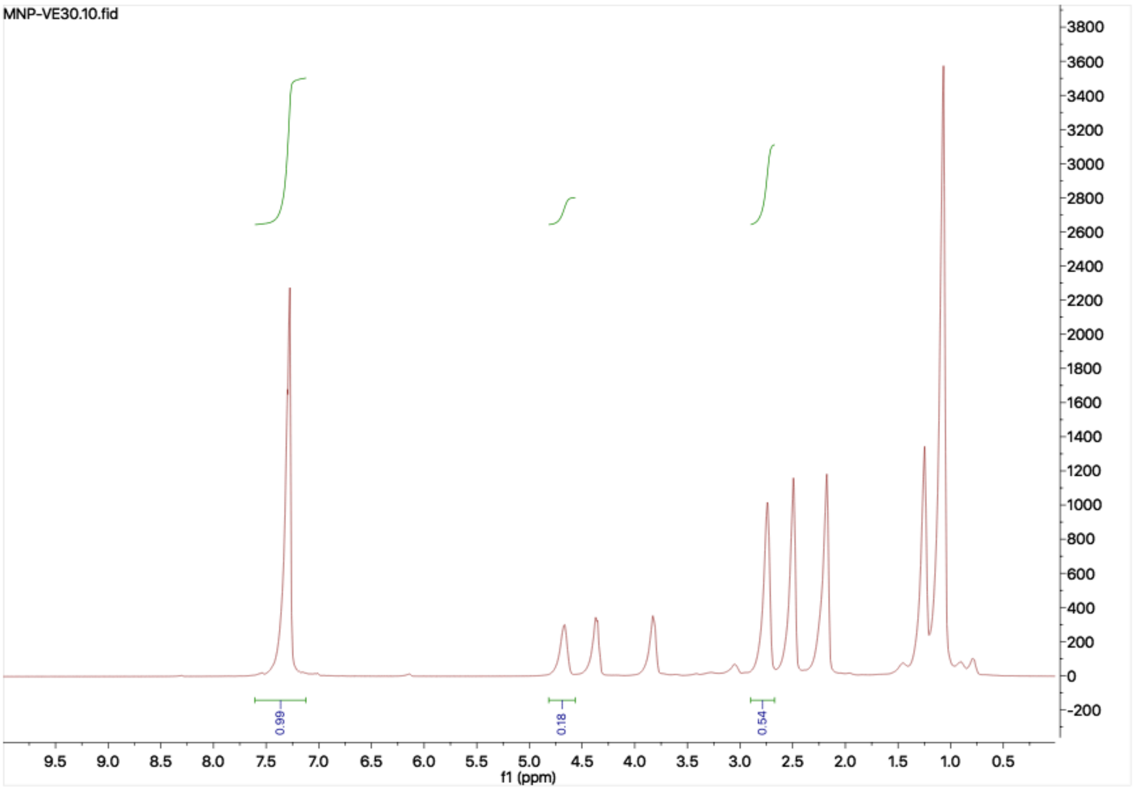

Figure 6.31 - VE 30 HNMR spectra

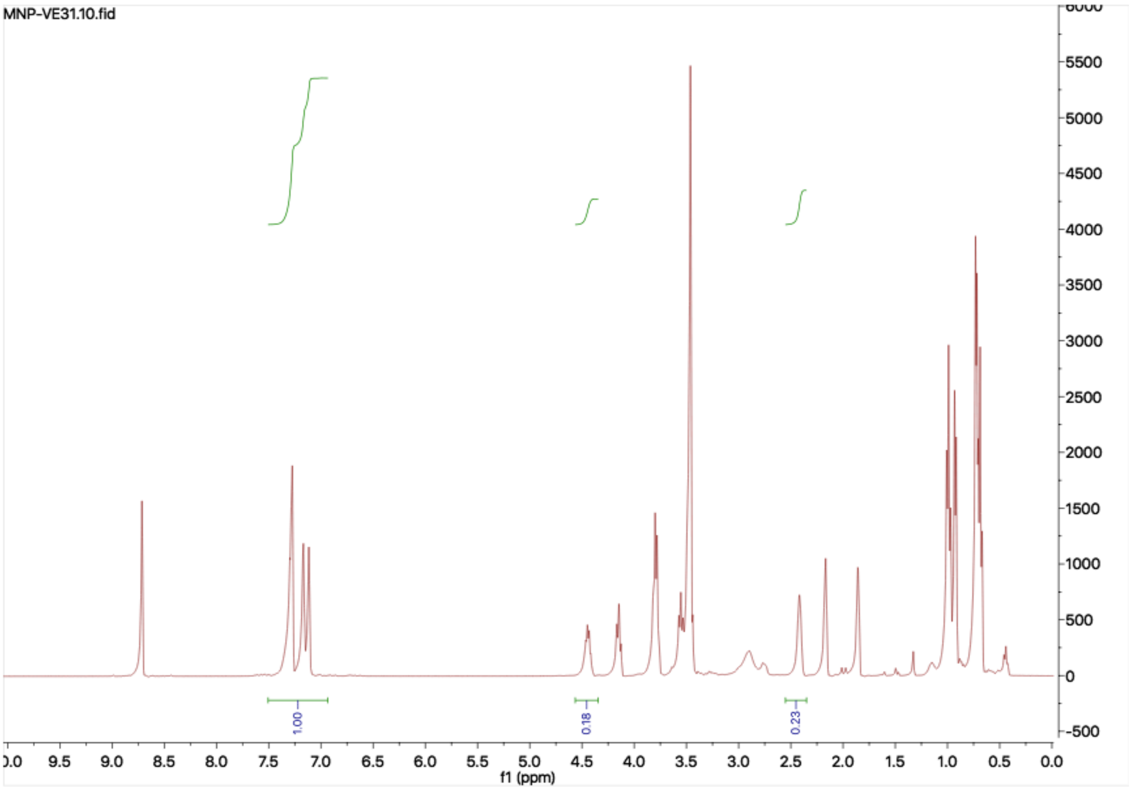

Figure 6.32 - VE 31 HNMR spectra

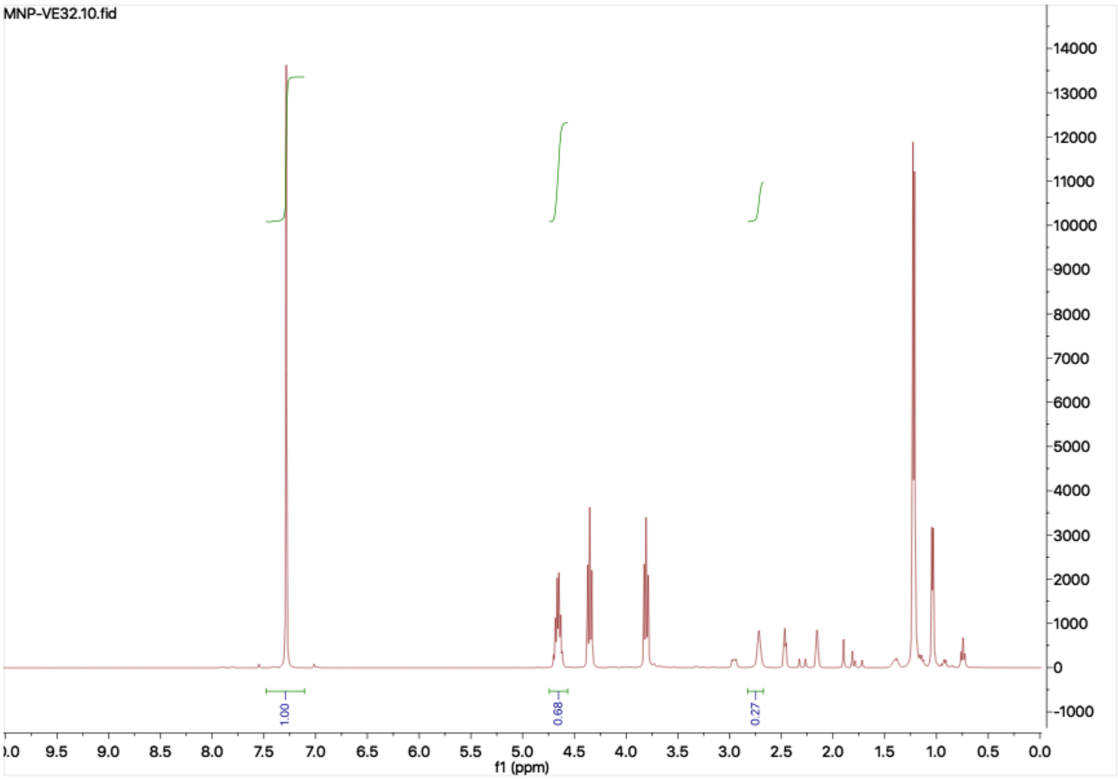

Figure 6.33 - VE 32 HNMR spectra

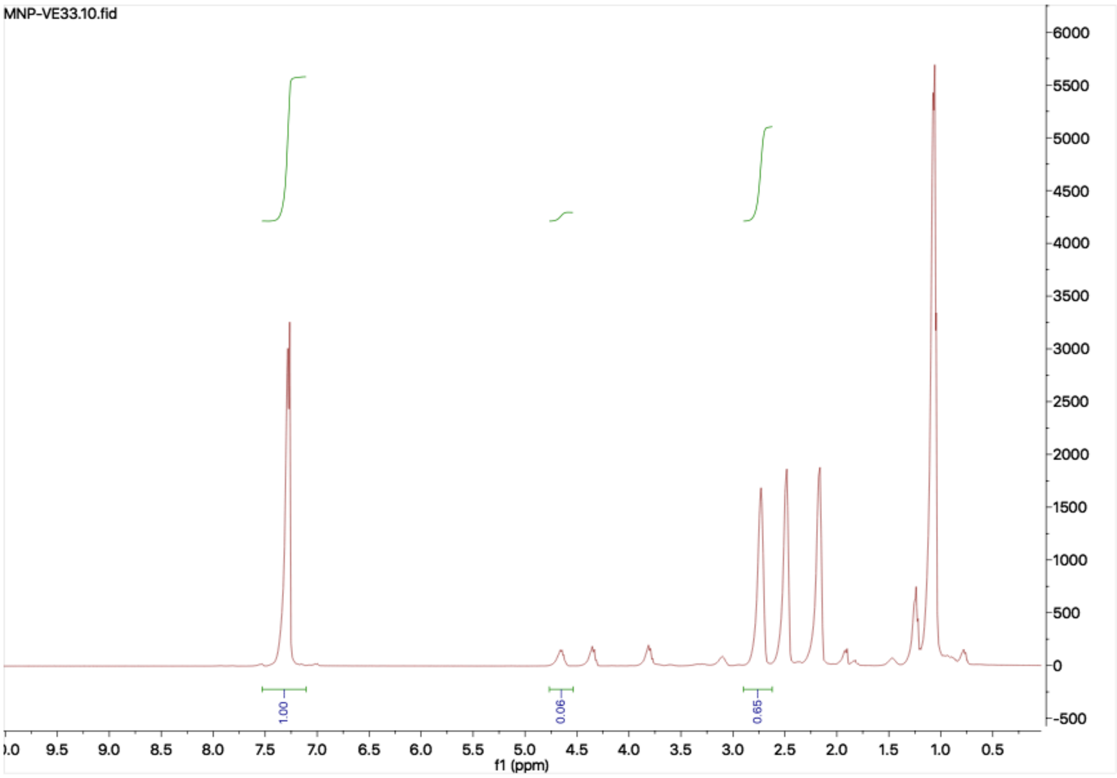

Figure 6.34 - VE 33 HNMR spectra

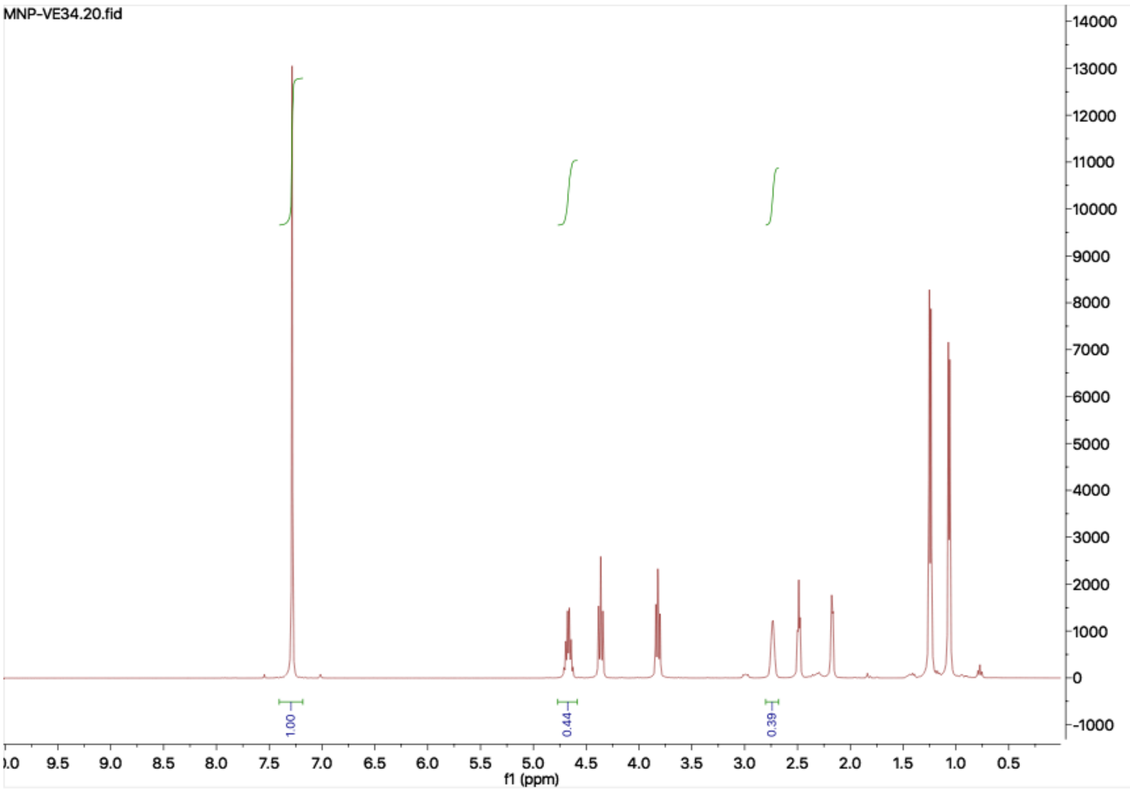

Figure 6.35 - VE 34 HNMR spectra

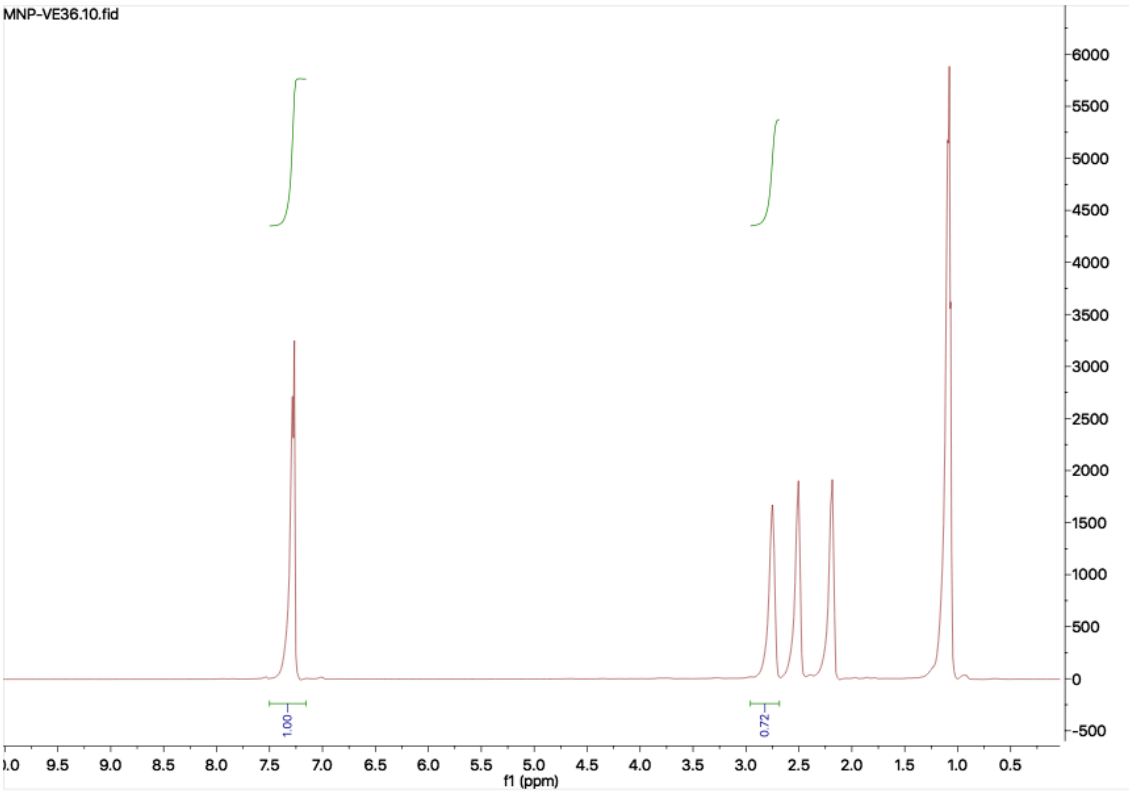

Figure 6.36 - VE 36 HNMR spectra

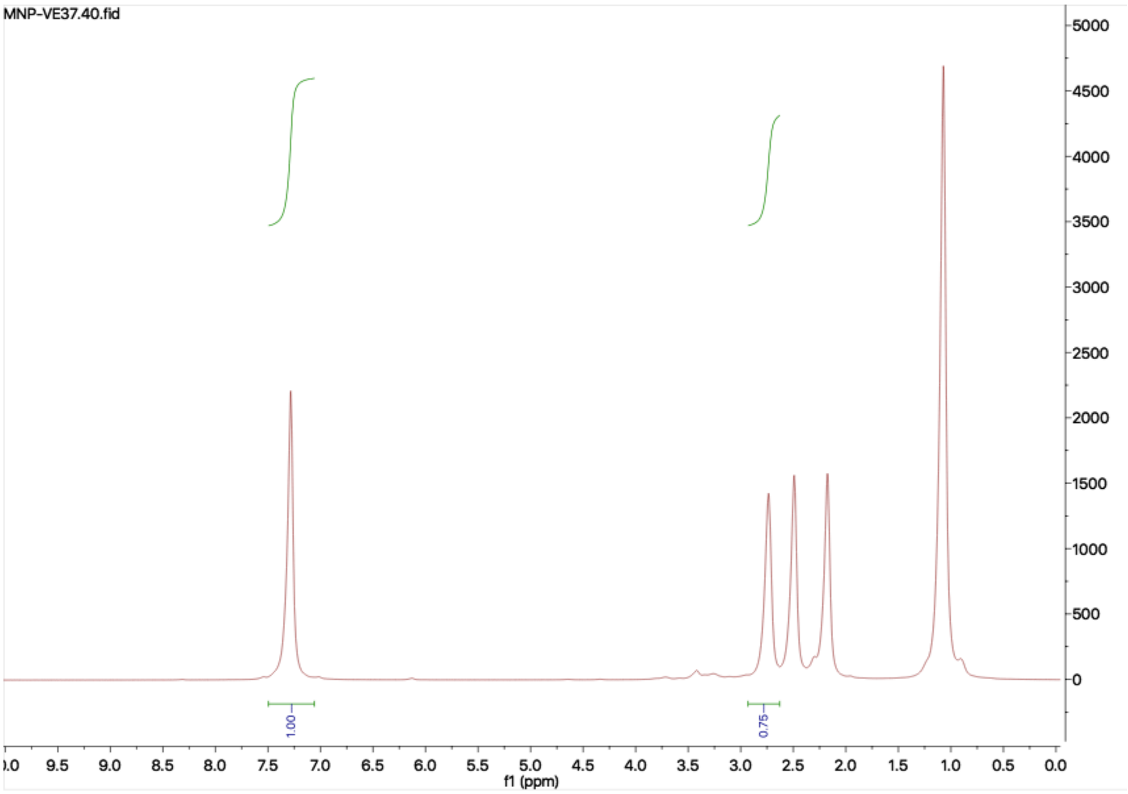

Figure 6.37 - VE 37 HNMR spectra

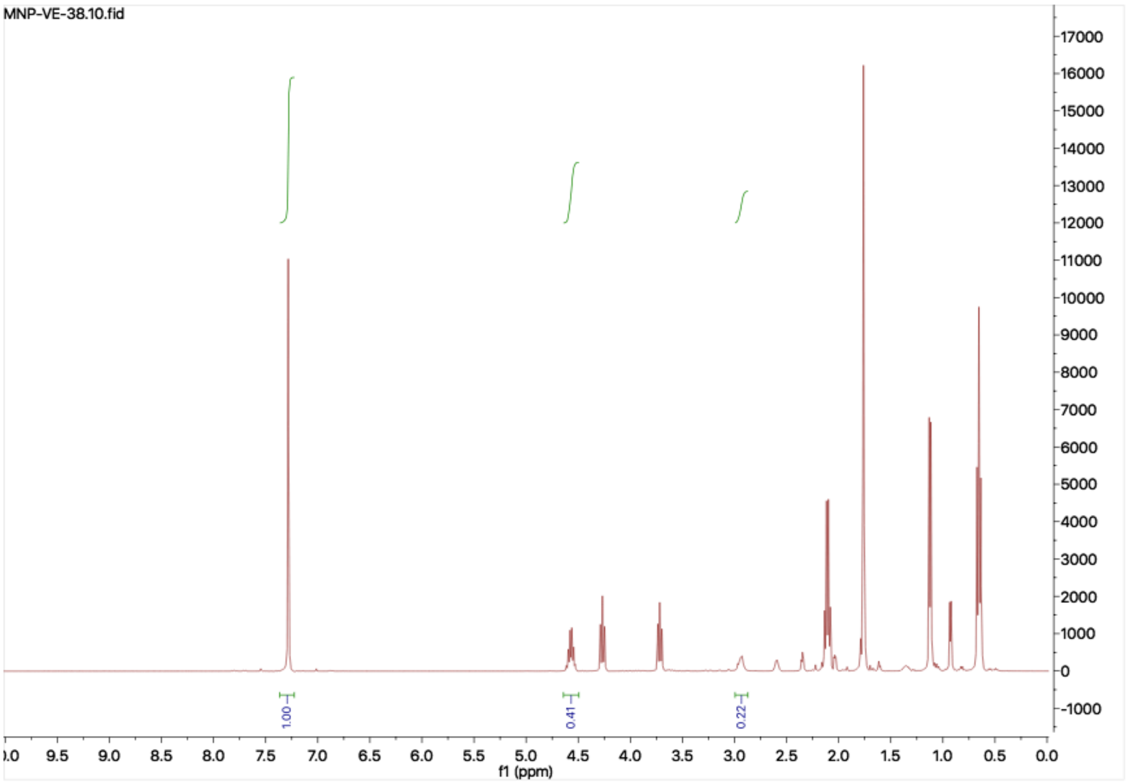

Figure 6.38 - VE 38 HNMR spectra

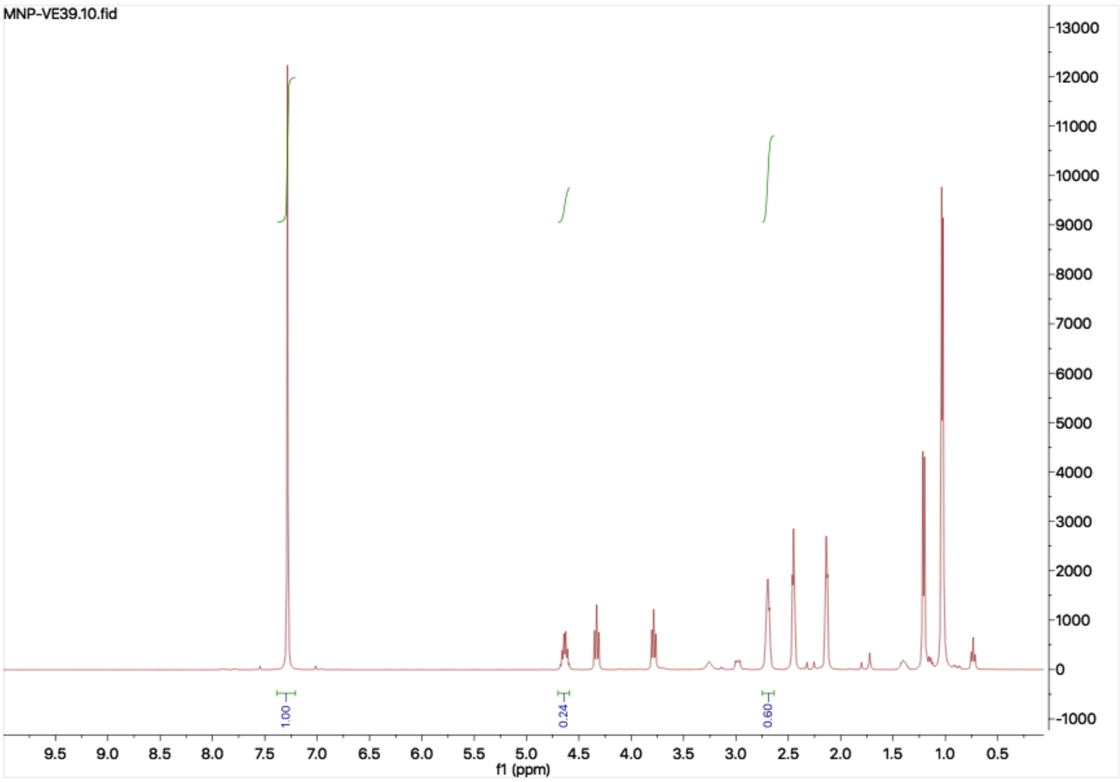

Figure 6.39 - VE 39 HNMR spectra

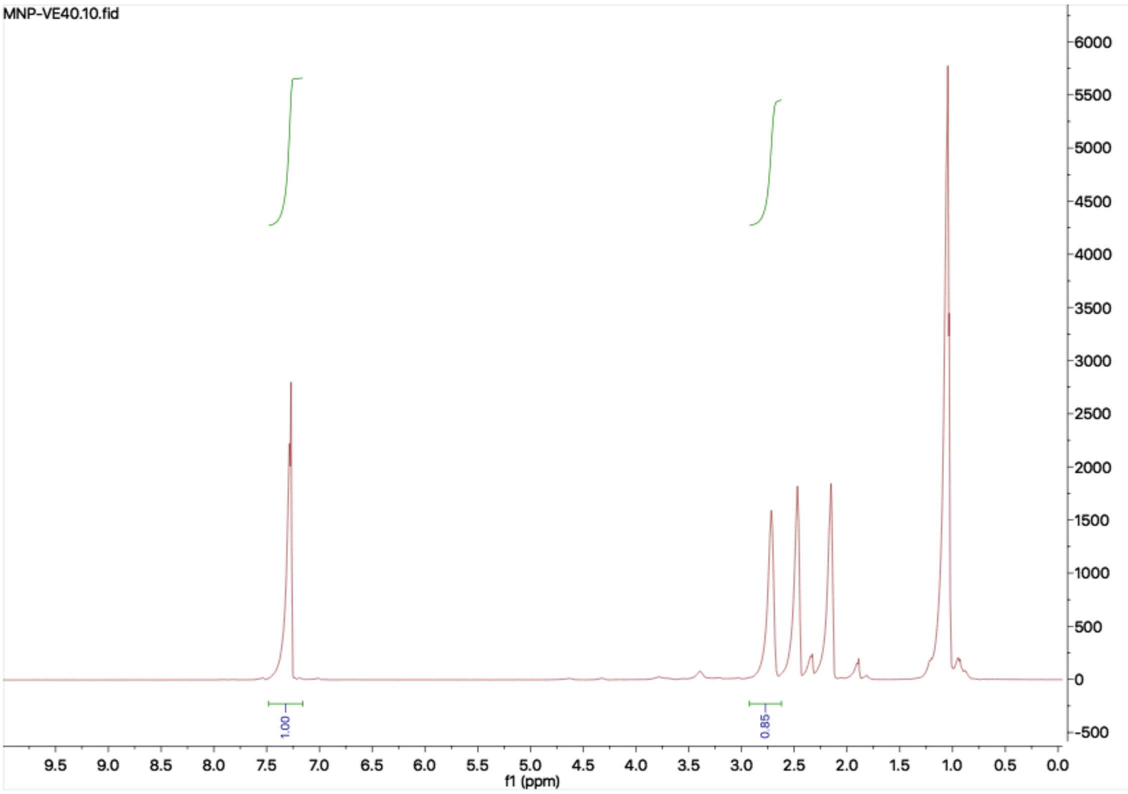

Figure 6.40 - VE 40 HNMR spectra

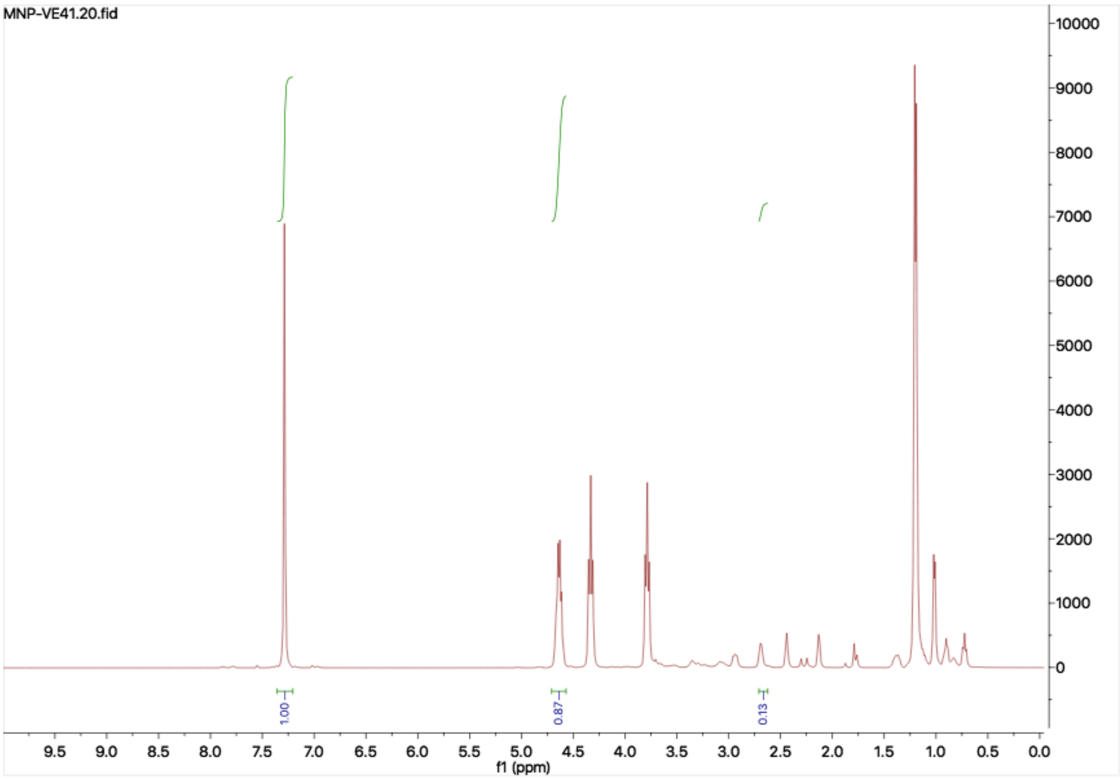

Figure 6.41 - VE 41 HNMR spectra

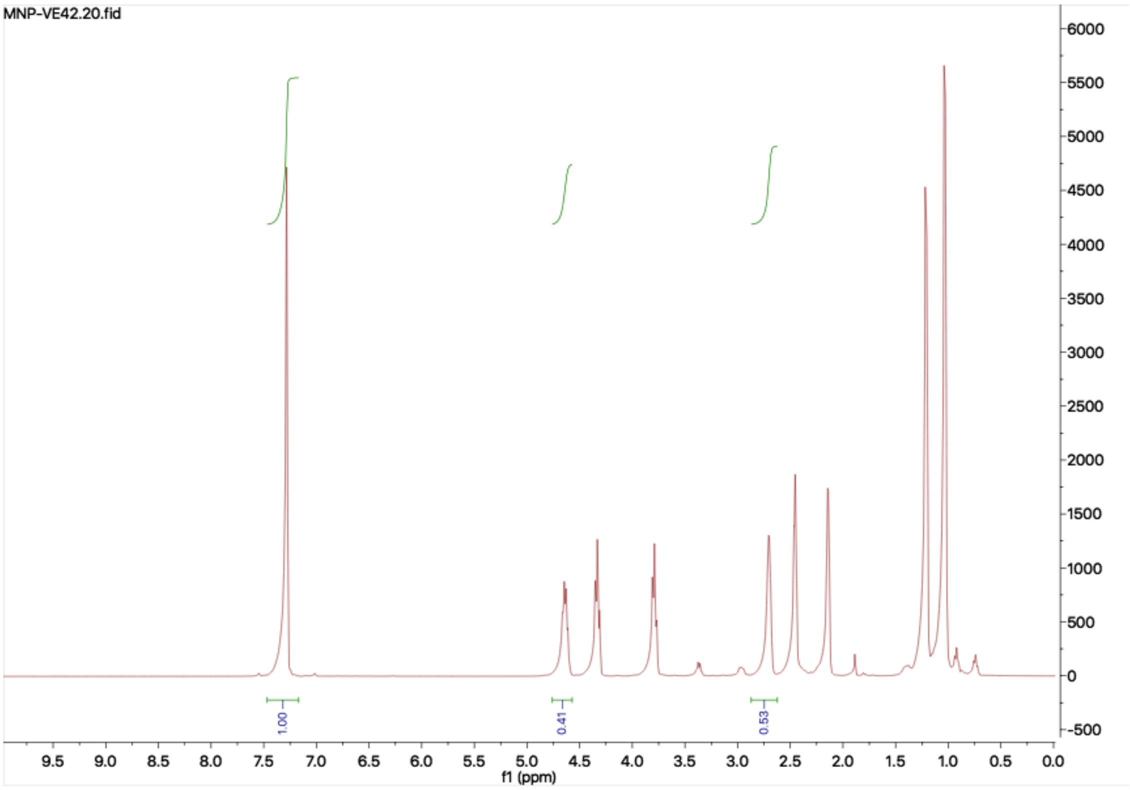

Figure 6.42 - VE 42 HNMR spectra

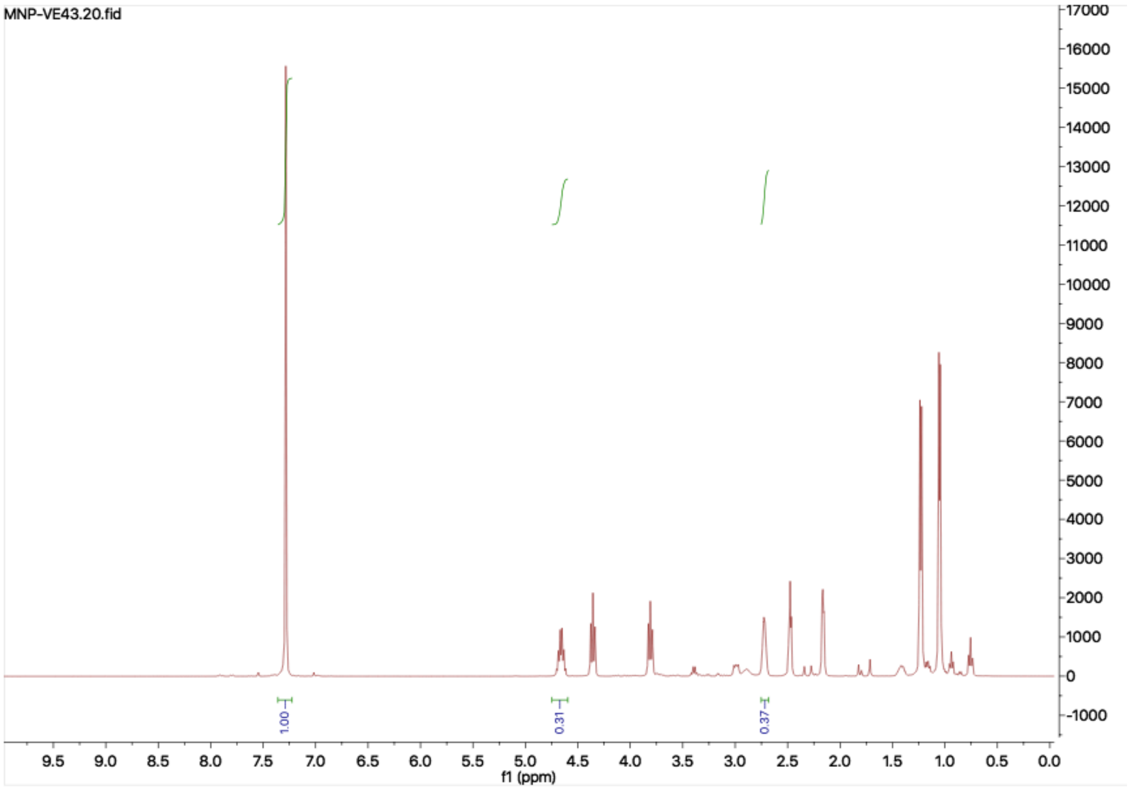

Figure 6.43 - VE 43 HNMR spectra

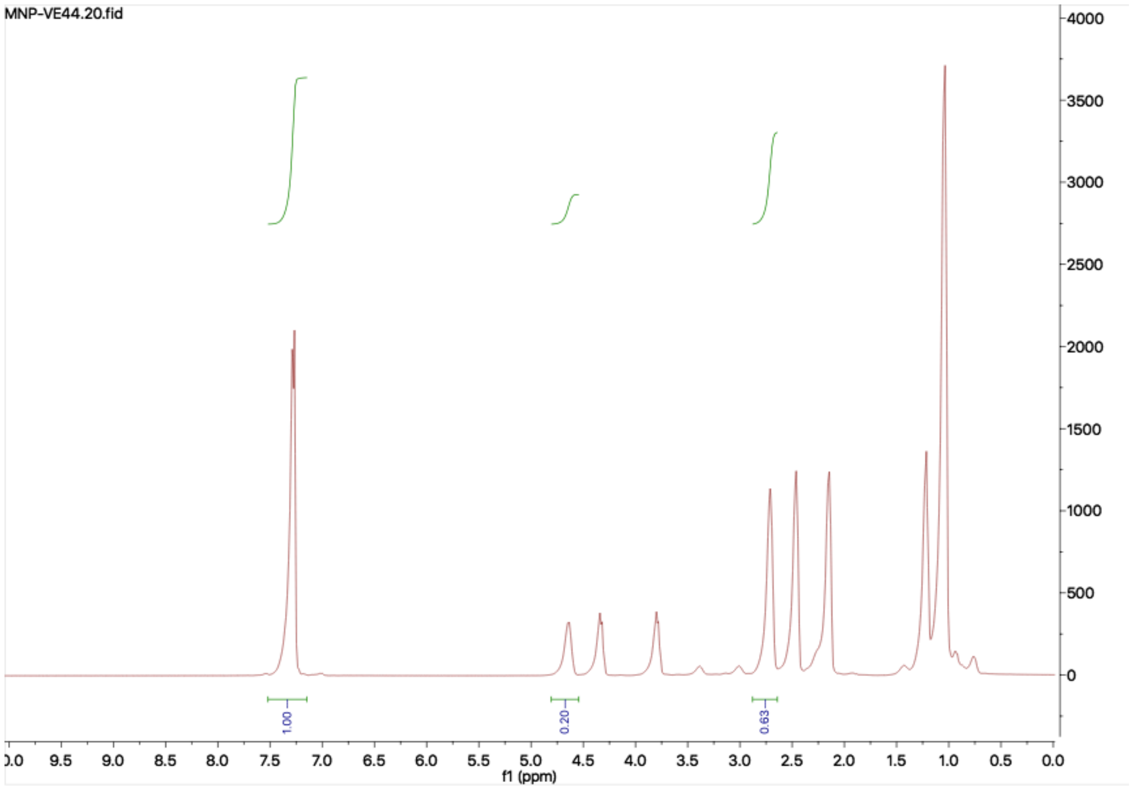

Figure 6.44 - VE 44 HNMR spectra

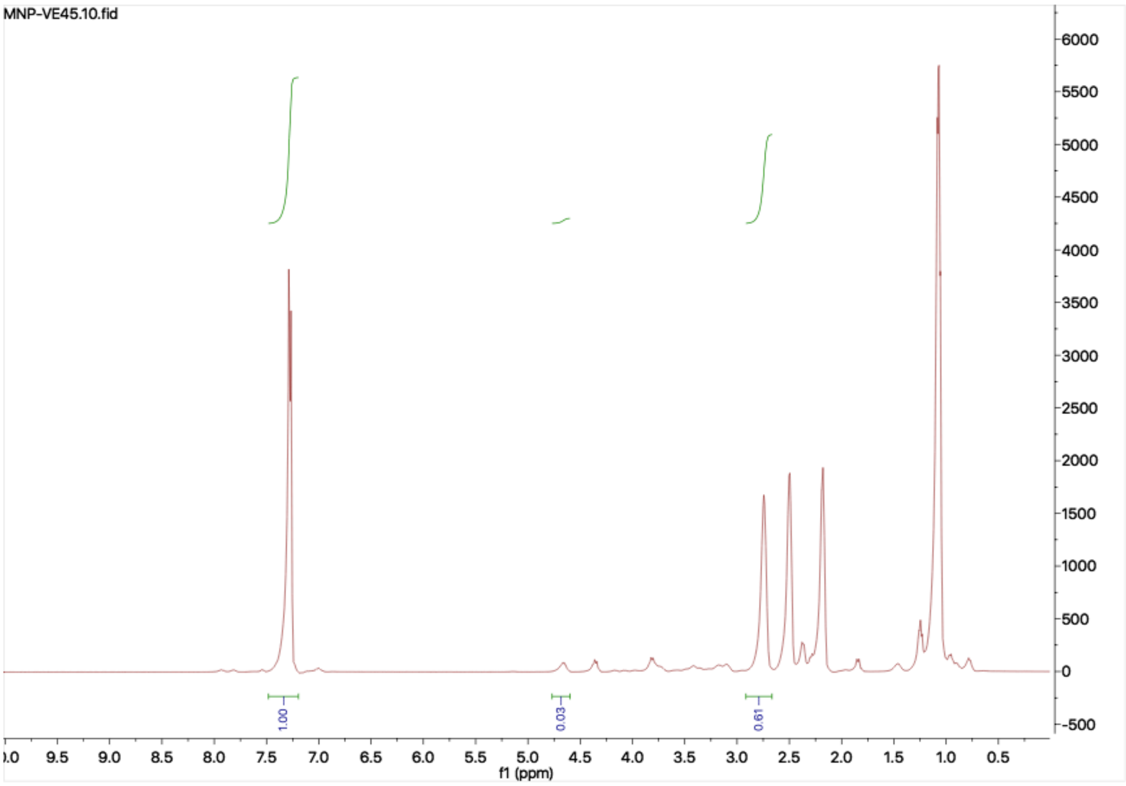

Figure 6.45 - VE 45 HNMR spectra

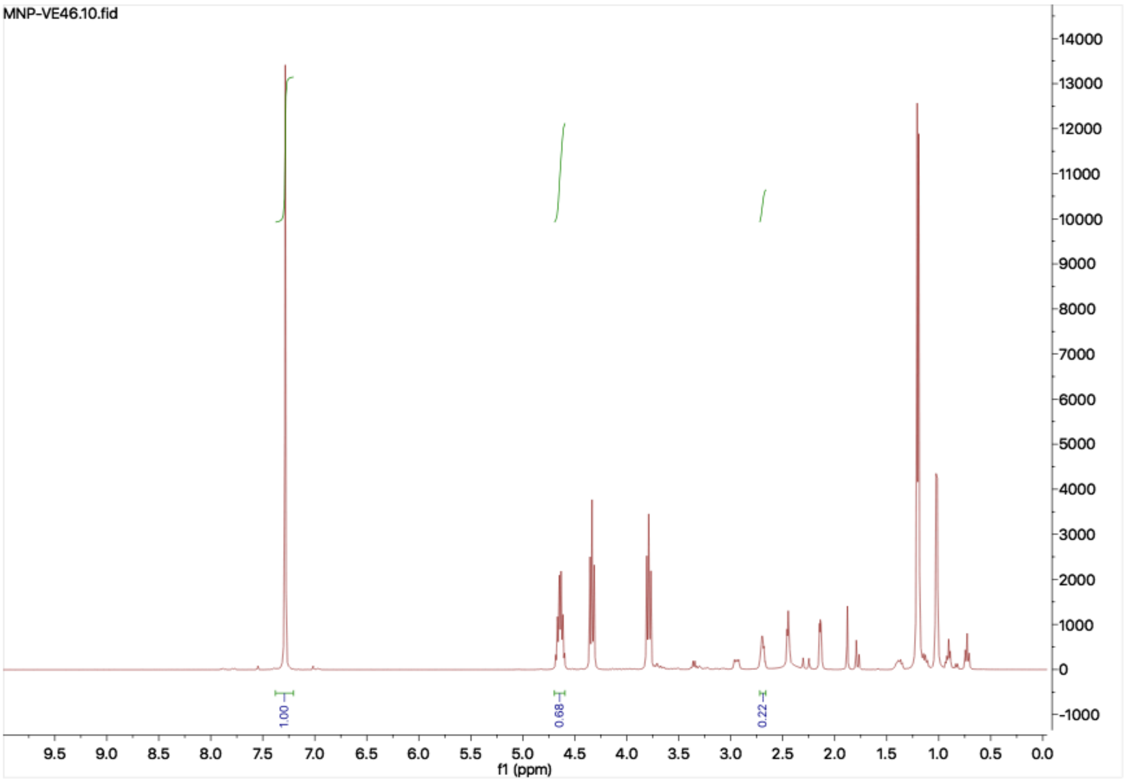

Figure 6.46 - VE 46 HNMR spectra

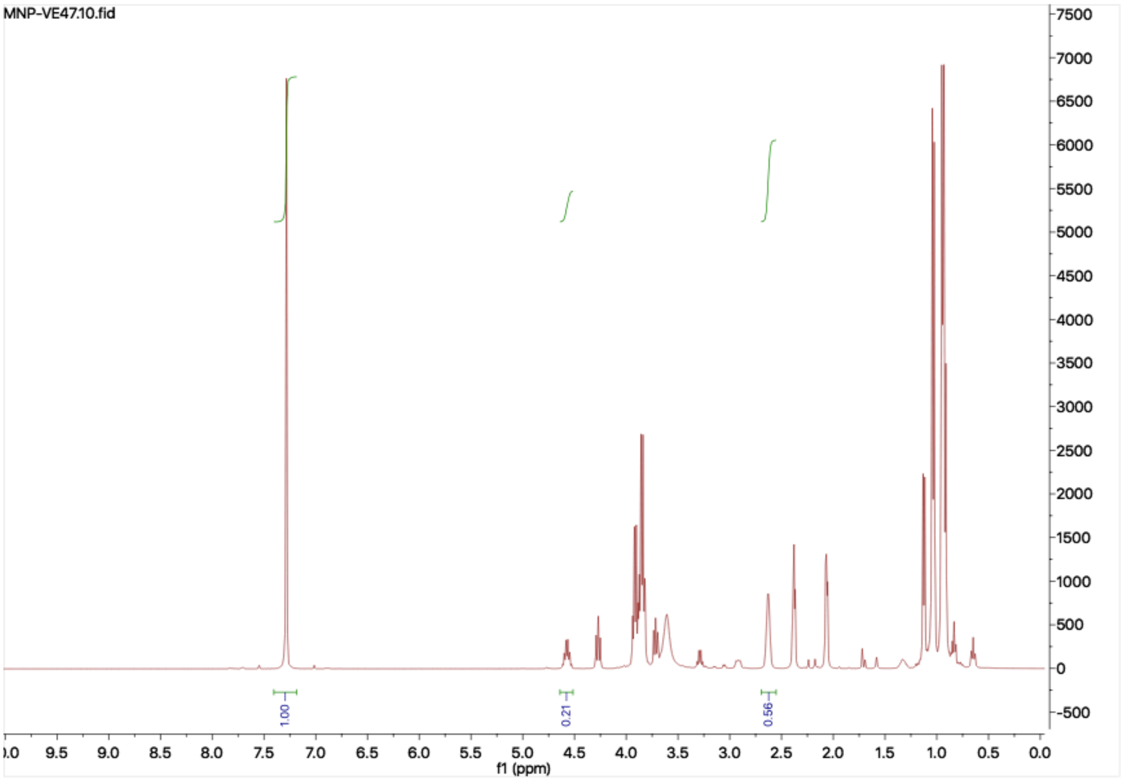

Figure 6.47 - VE 47 HNMR spectra

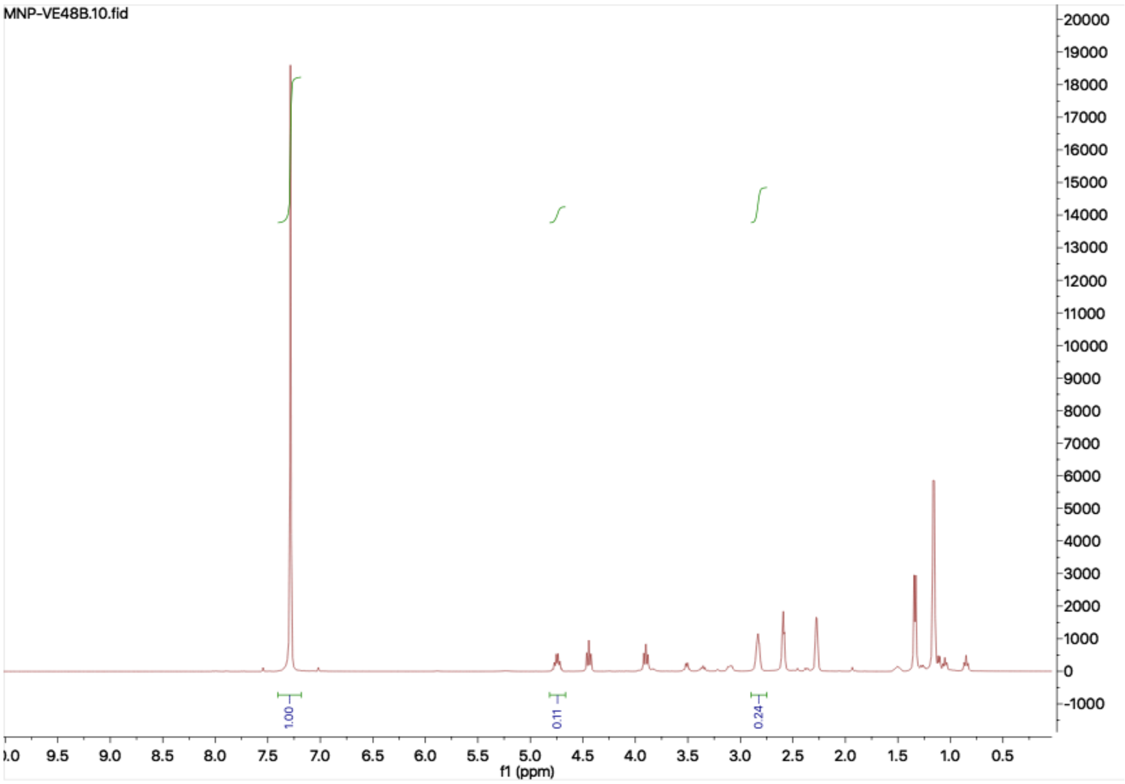

Figure 6.48 - VE 48 HNMR spectra

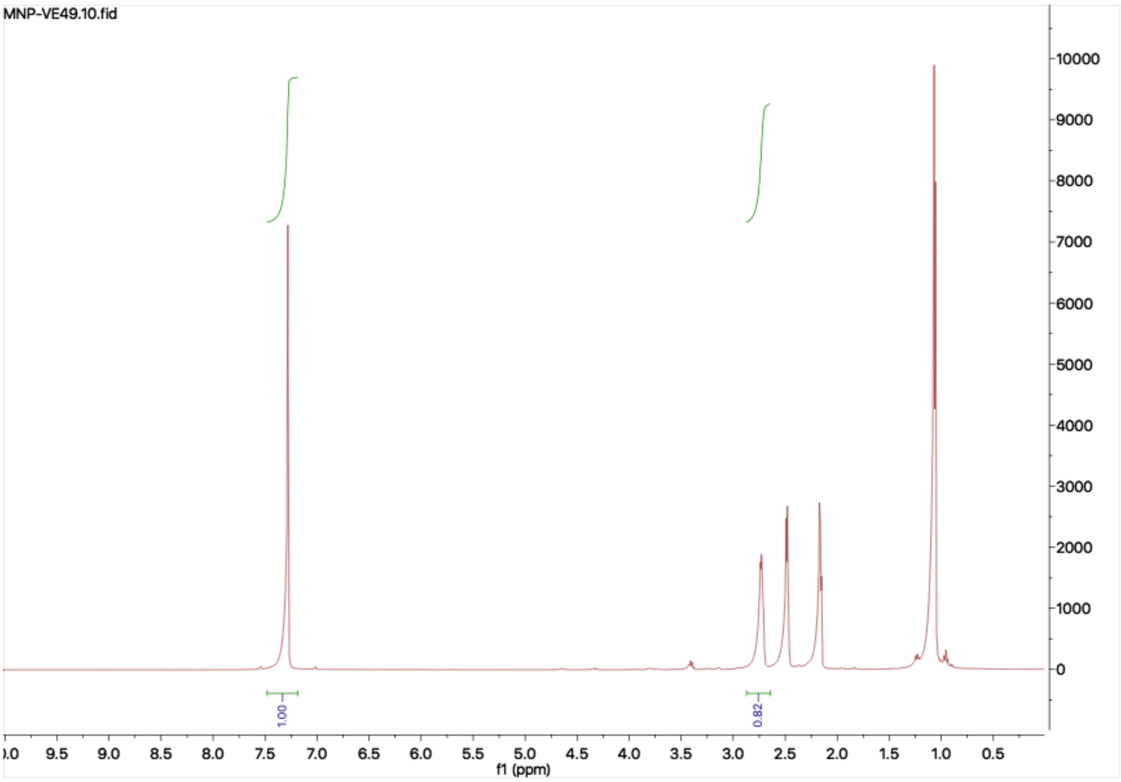

Figure 6.49 - VE 49 HNMR spectra

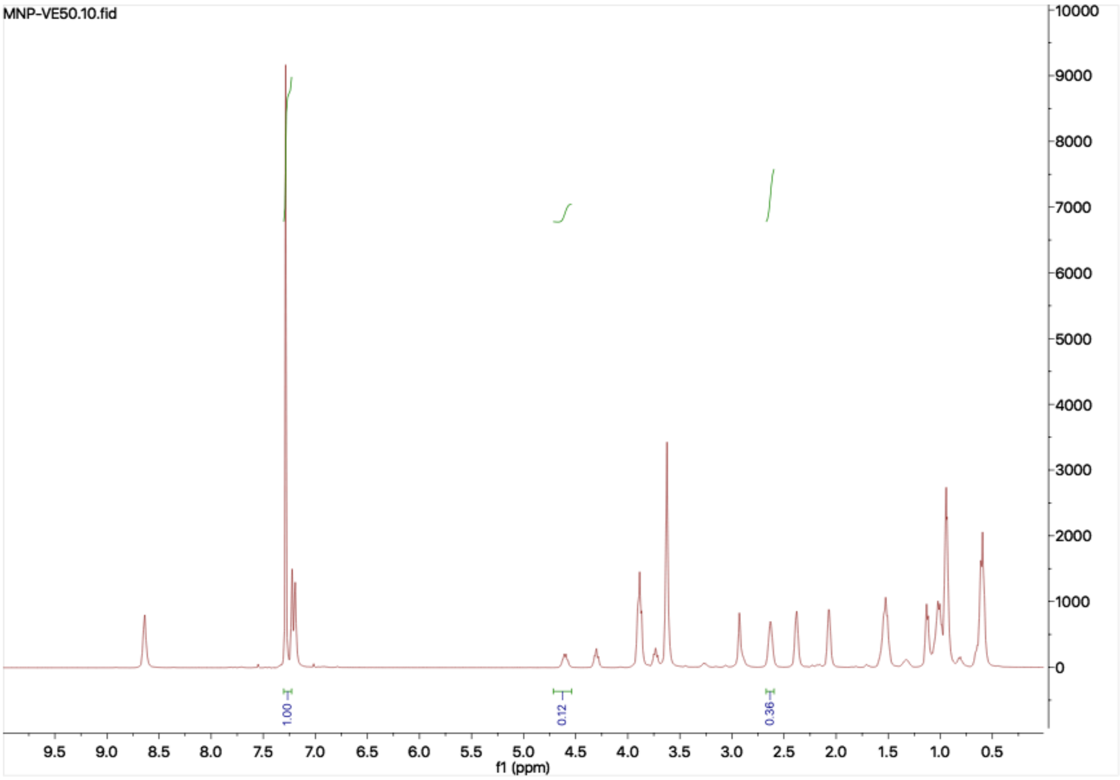

Figure 6.50 - VE 50 HNMR spectra

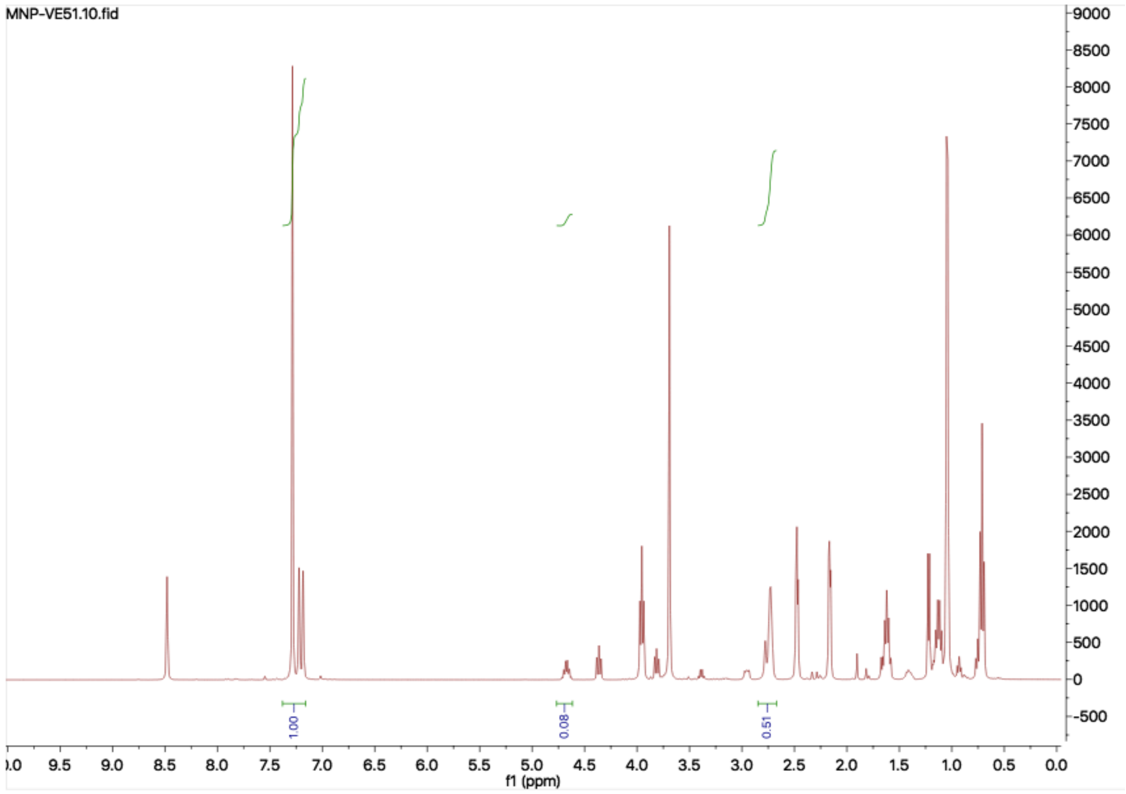

Figure 6.51 - VE 51 HNMR spectra

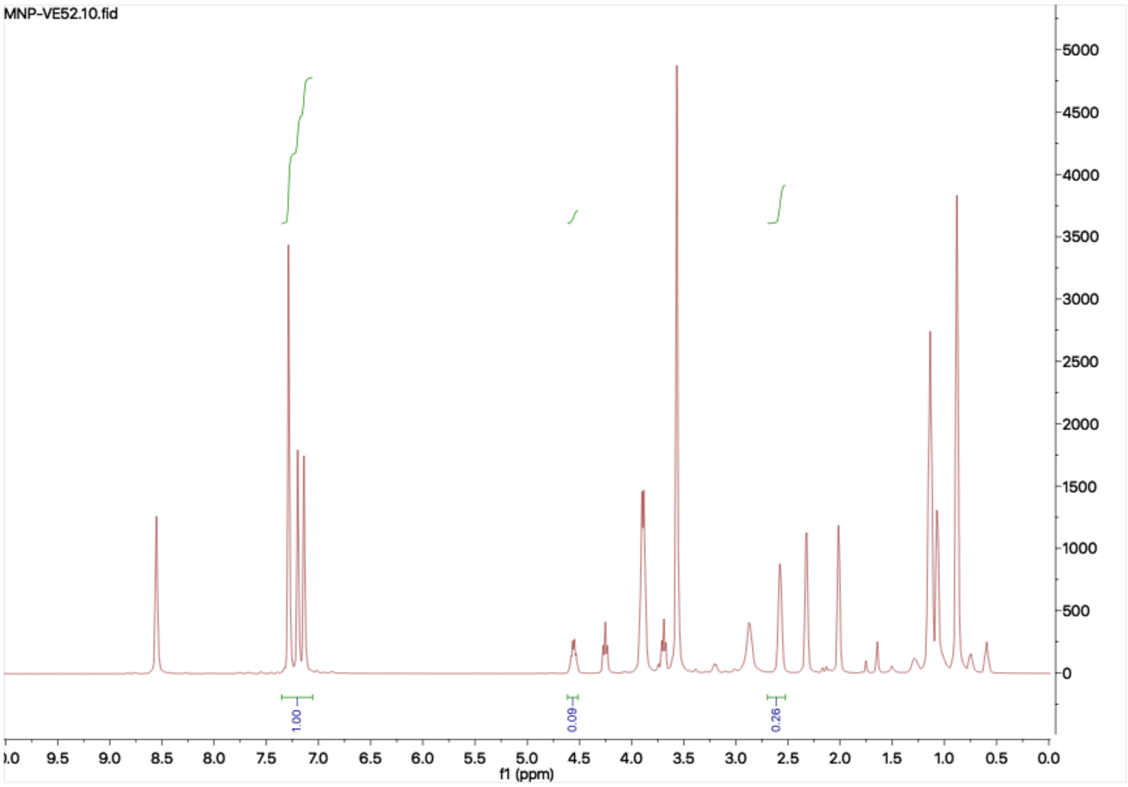

Figure 6.52 - VE 52 HNMR spectra

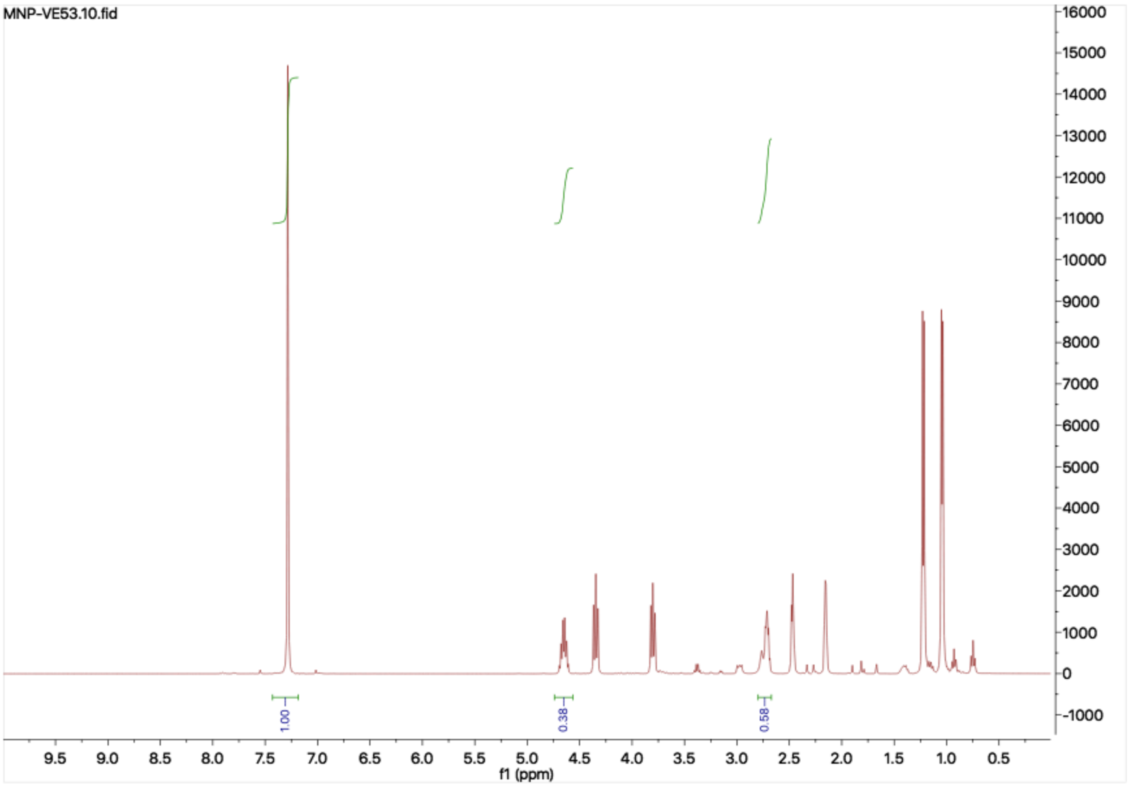

Figure 6.53 - VE 53 HNMR spectra

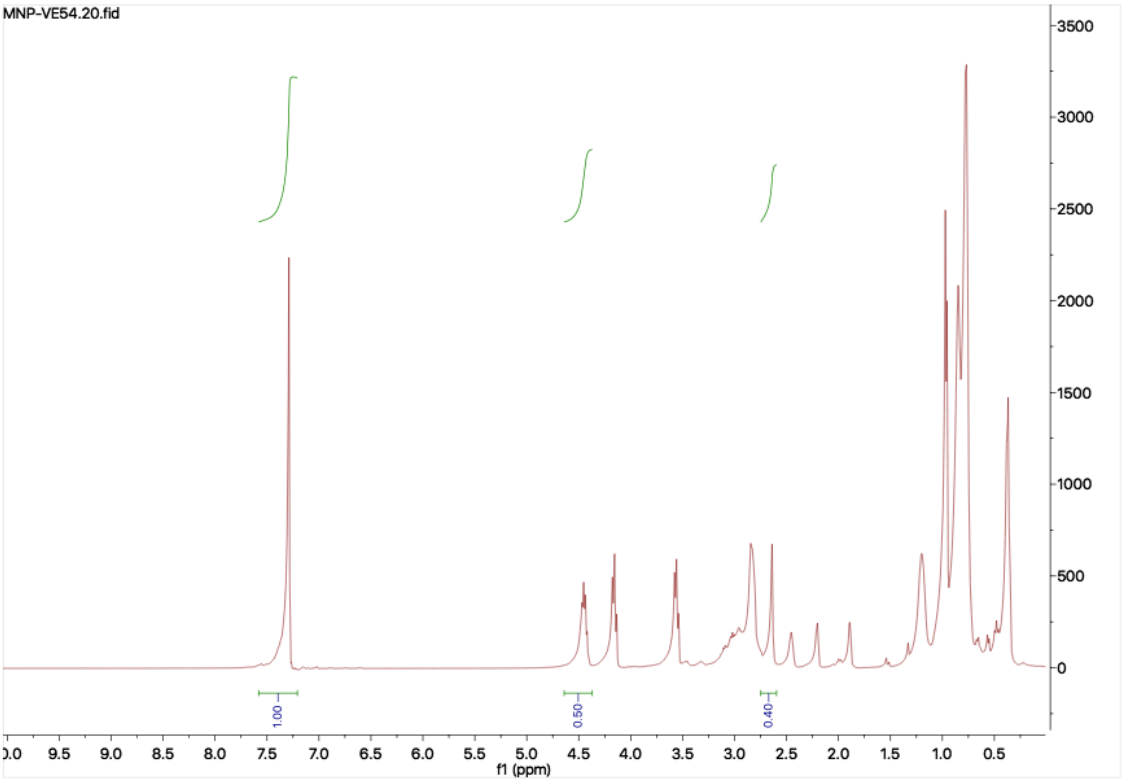

Figure 6.54 - VE 54 HNMR spectra

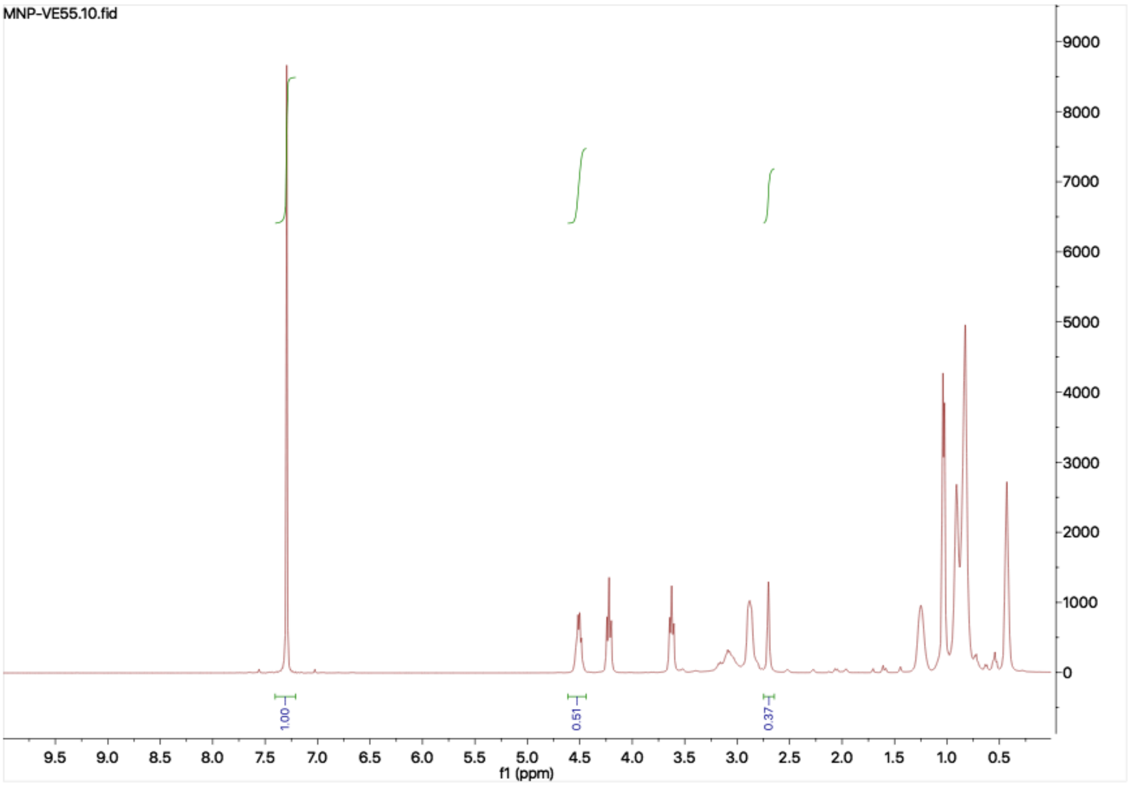

Figure 6.55 - VE 55 HNMR spectra

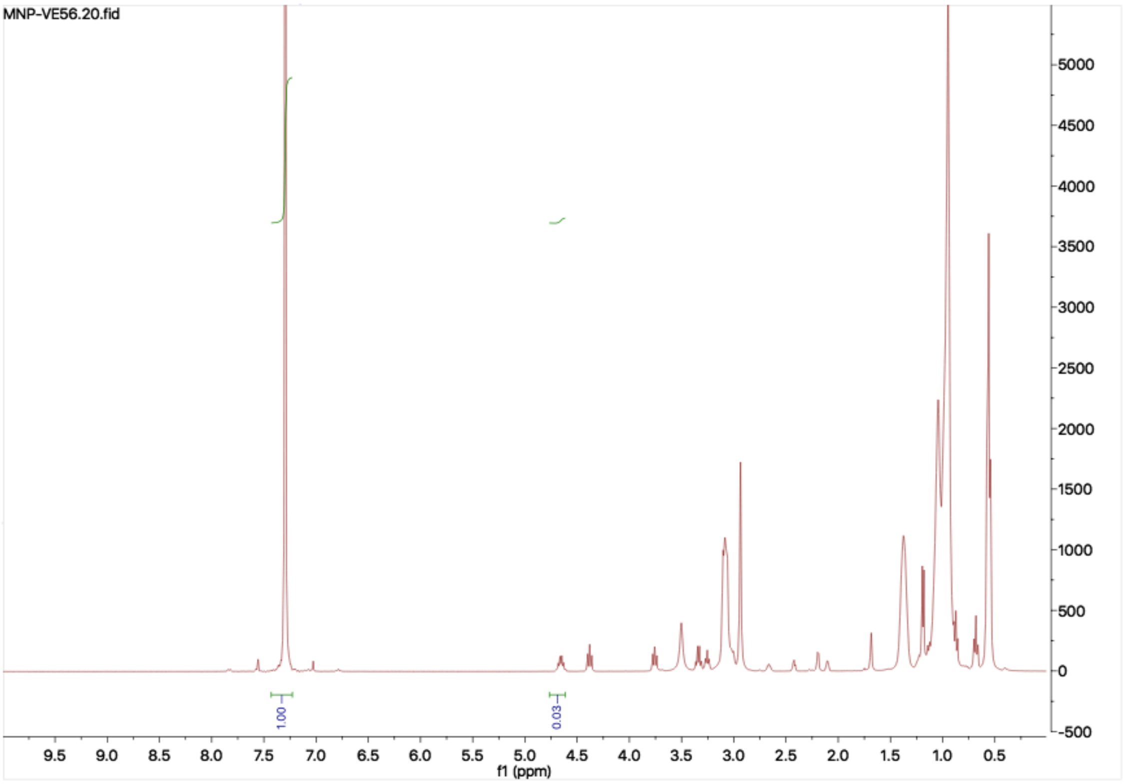

Figure 6.56 - VE 56 HNMR spectra

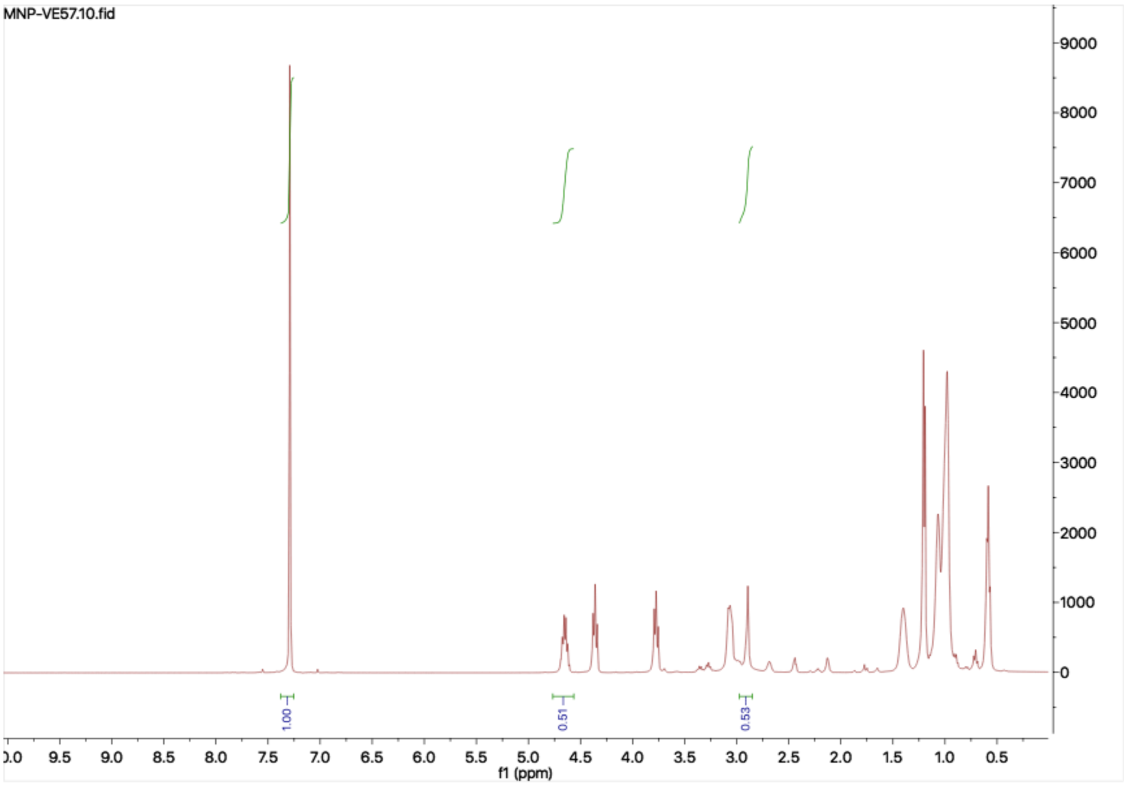

Figure 6.57 - VE 57 HNMR spectra

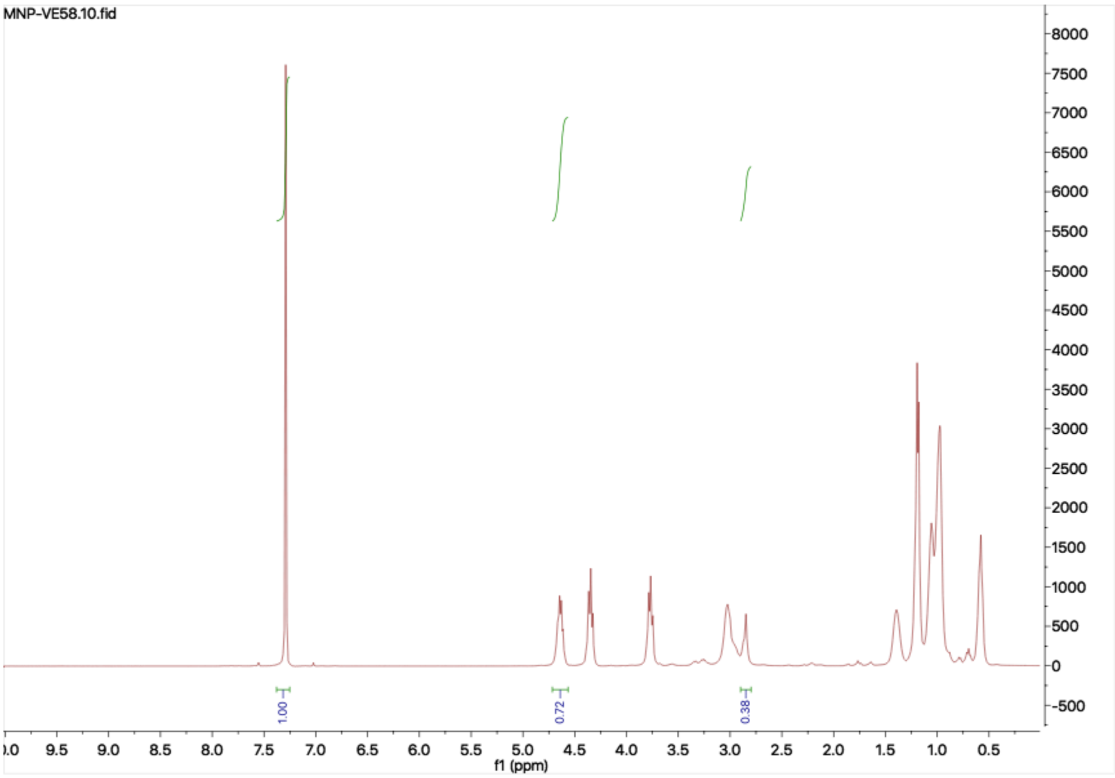

Figure 6.58 - VE 58 HNMR spectra

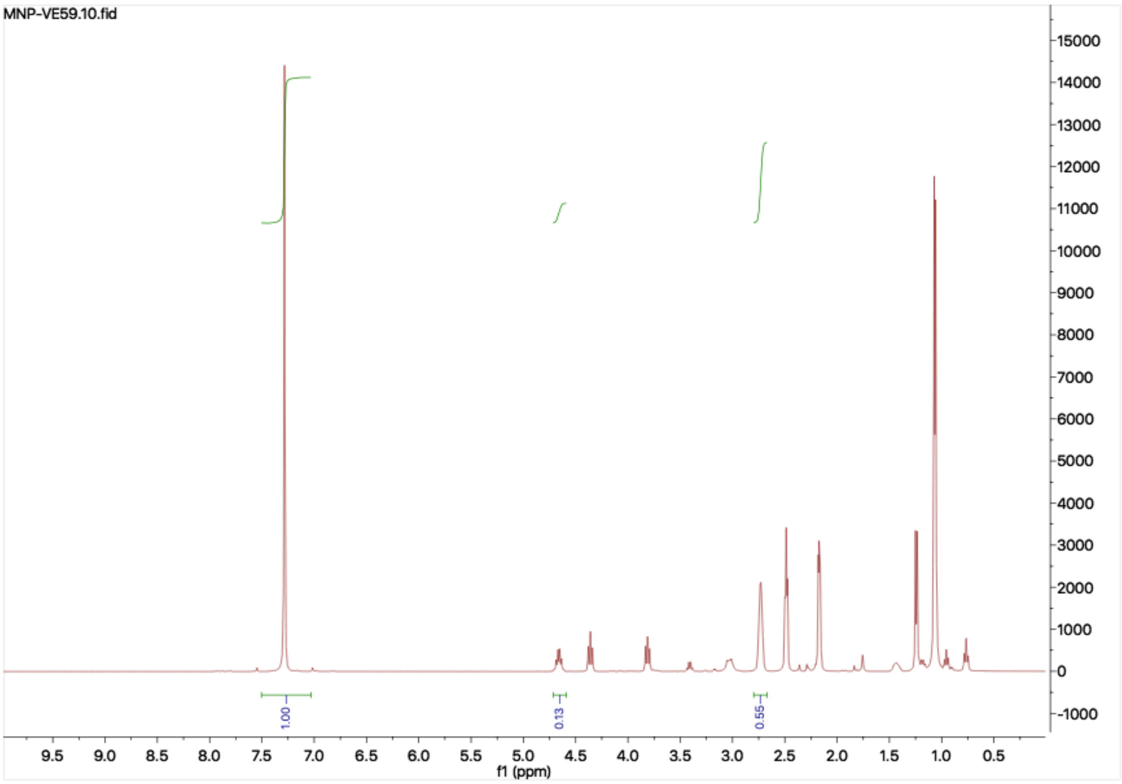

Figure 6.59 - VE 59 HNMR spectra

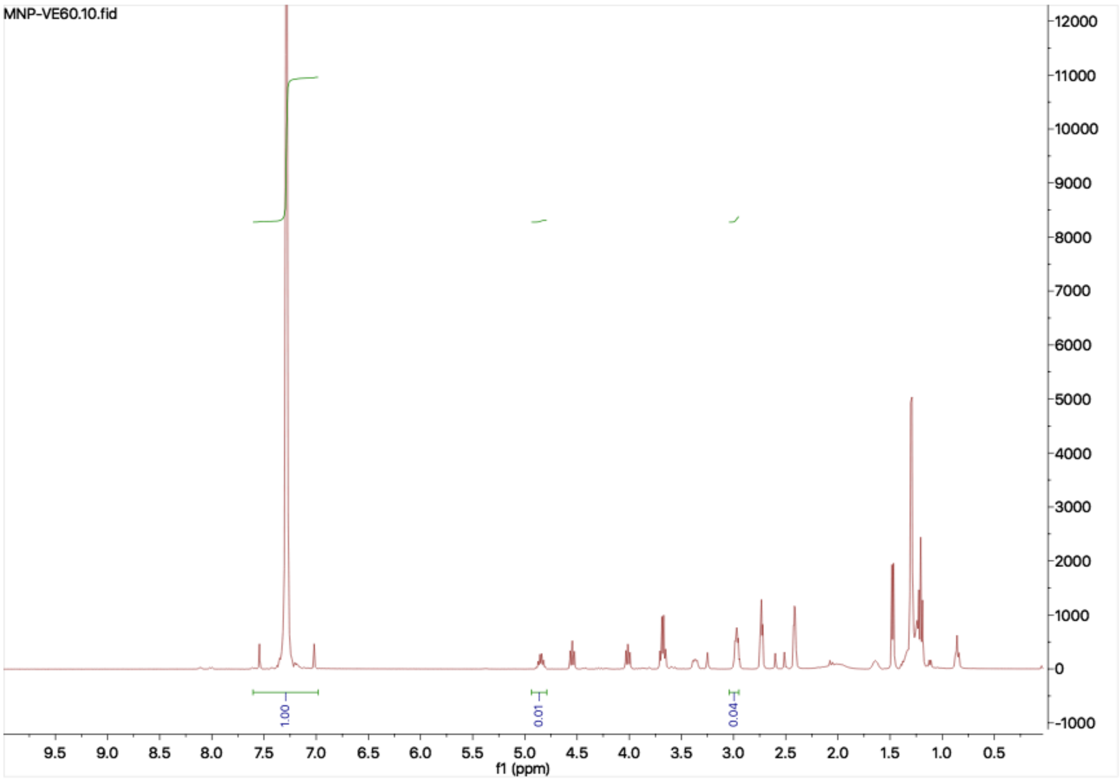

Figure 6.60 - VE 60 HNMR spectra

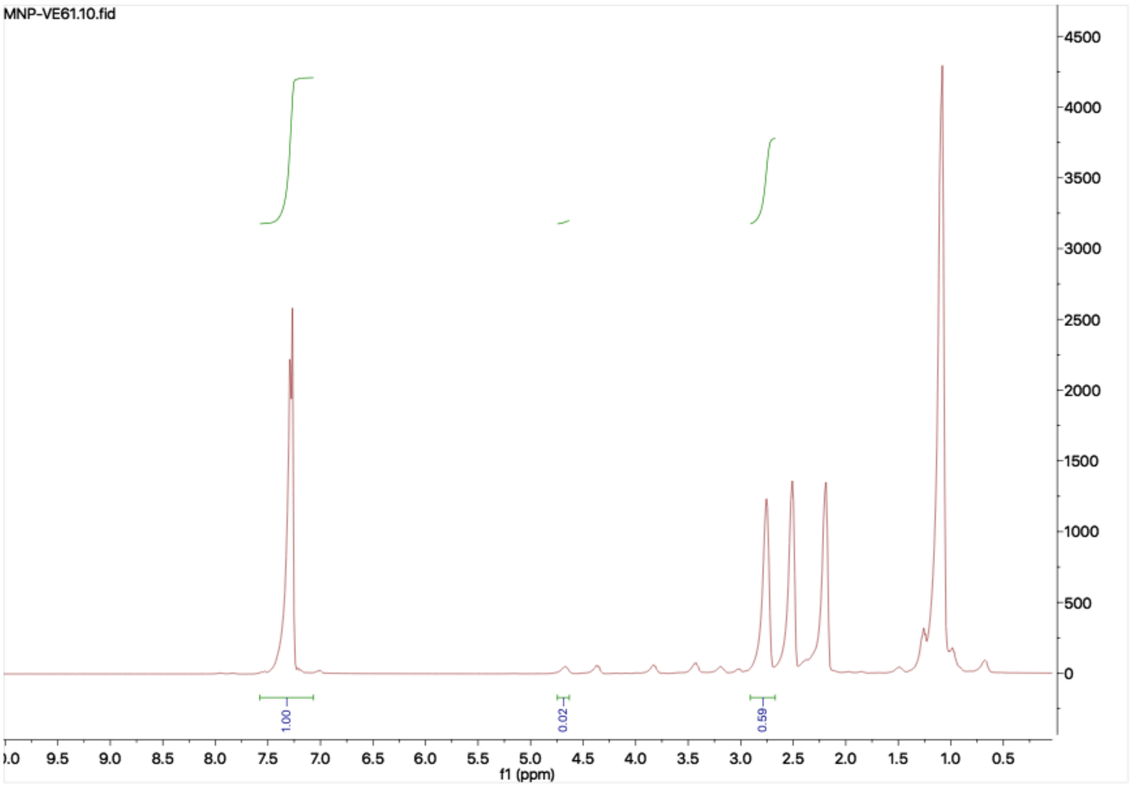

Figure 6.61 - VE 61 HNMR spectra

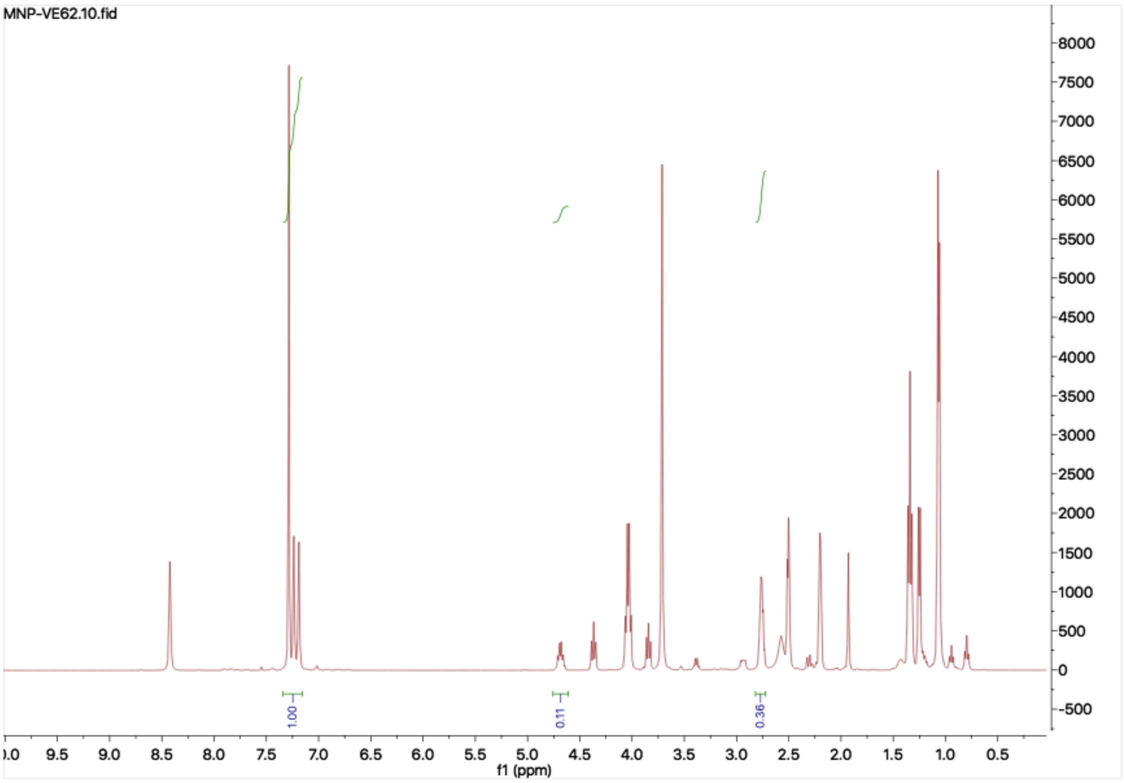

Figure 6.62 - VE 62 HNMR spectra

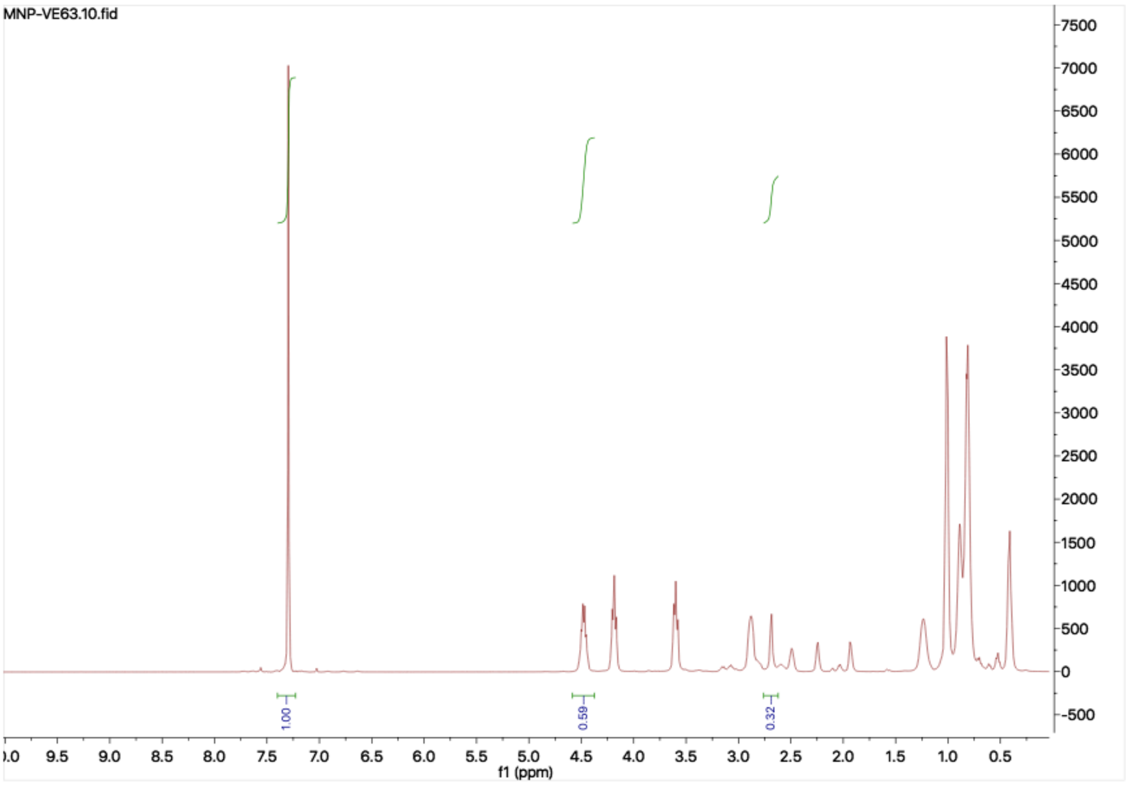

Figure 6.63 - VE 63 HNMR spectra

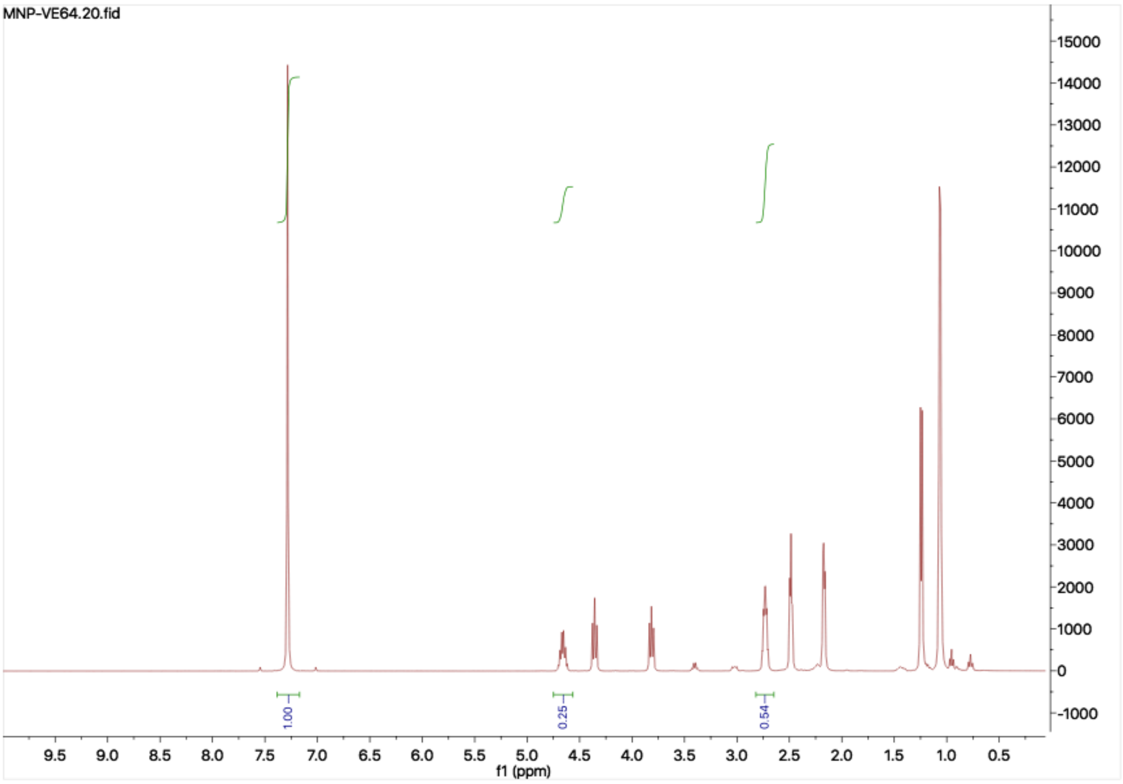

Figure 6.64 - VE 64 HNMR spectra

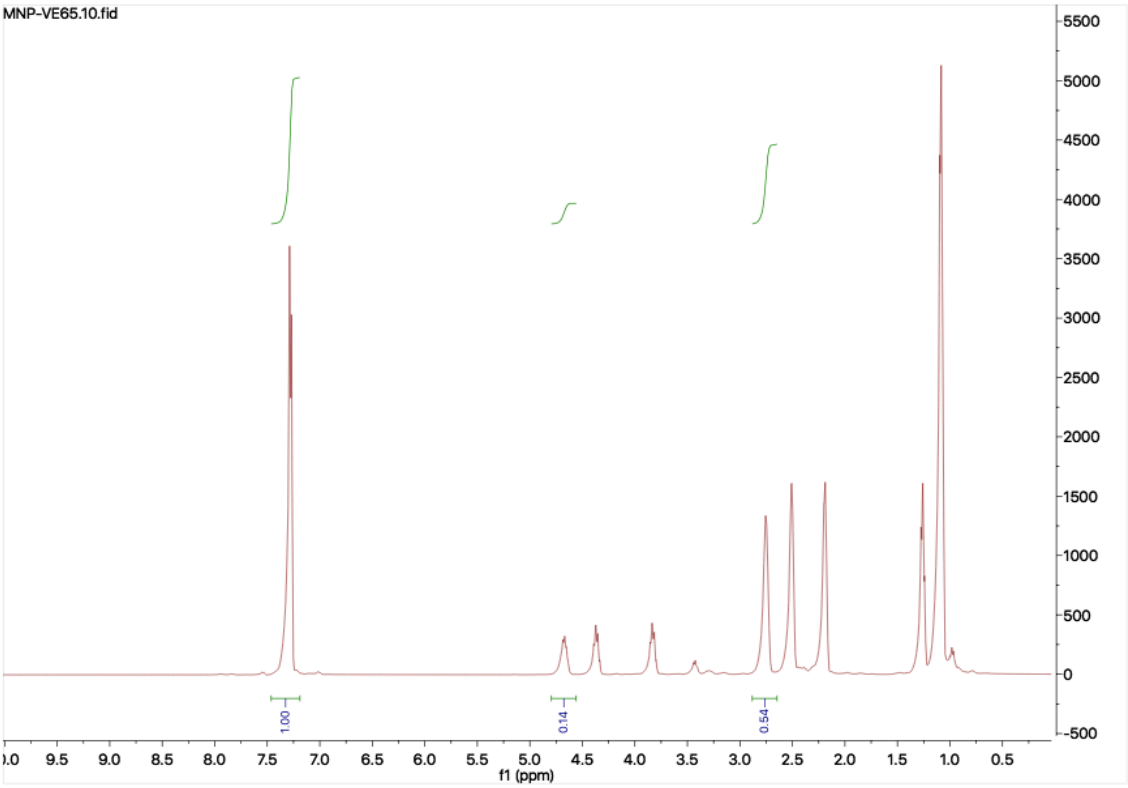

Figure 6.65 - VE 65 HNMR spectra

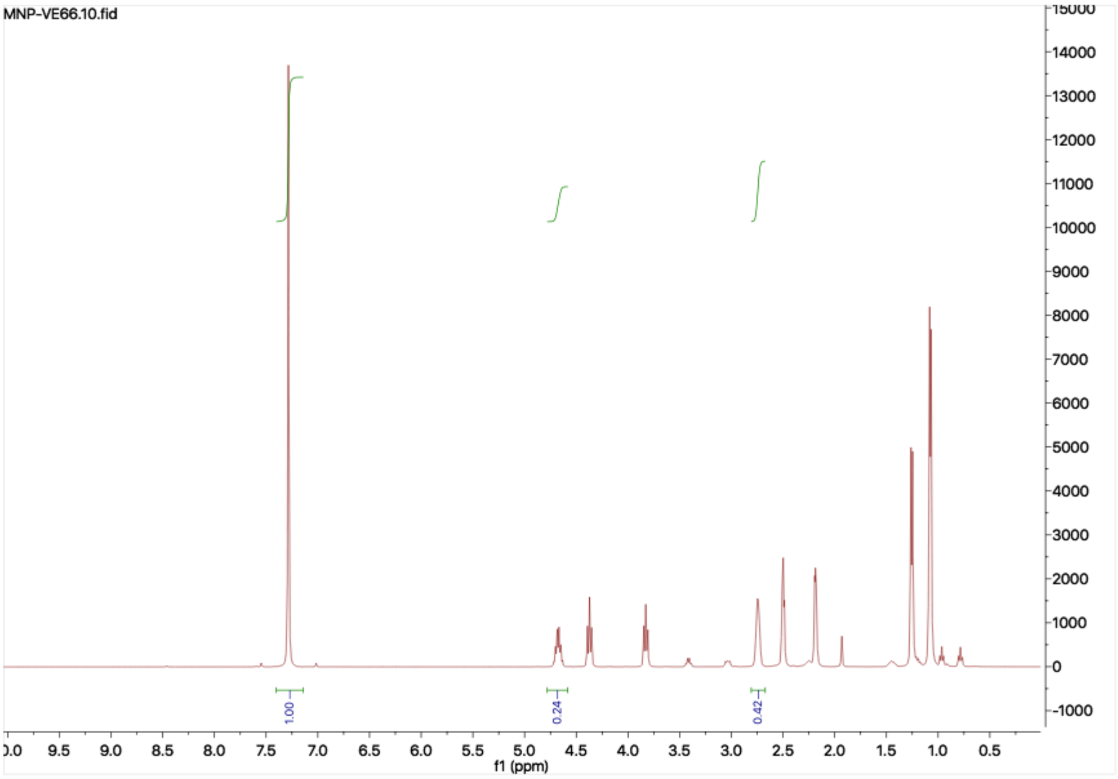

Figure 6.66 - VE 66 HNMR spectra

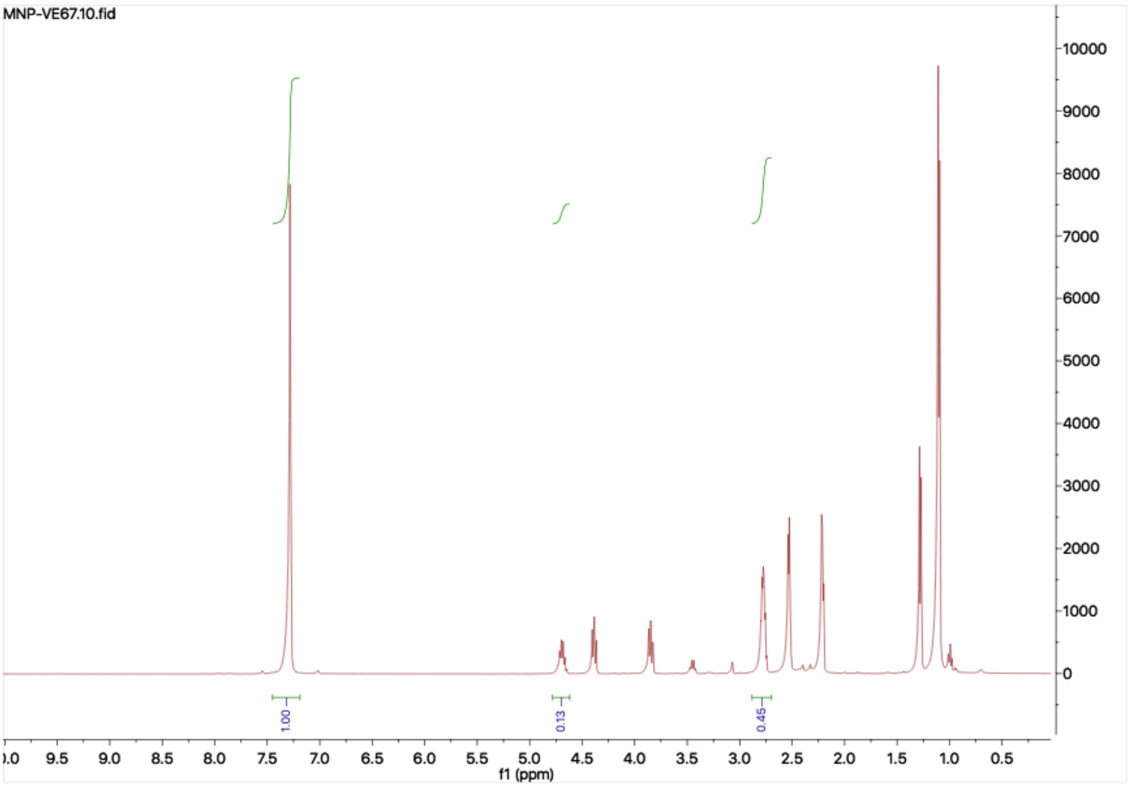

Figure 6.67 - VE 67 HNMR spectra

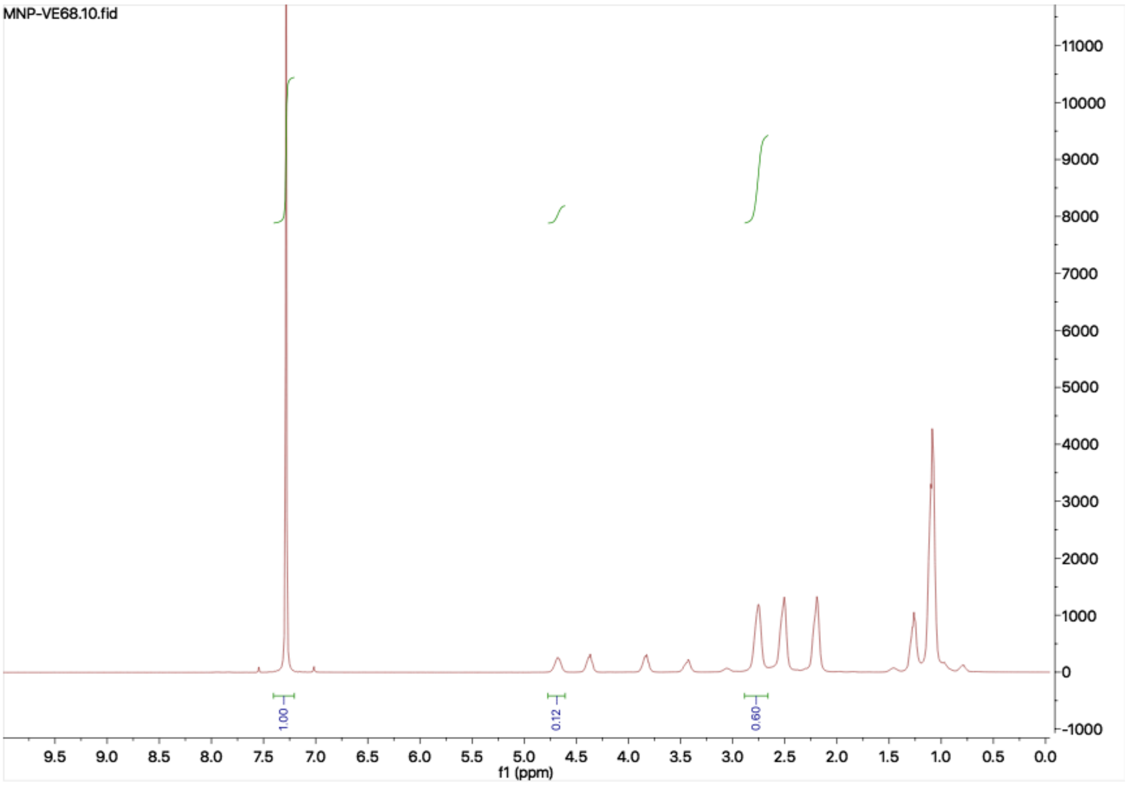

Figure 6.68 - VE 68 HNMR spectra

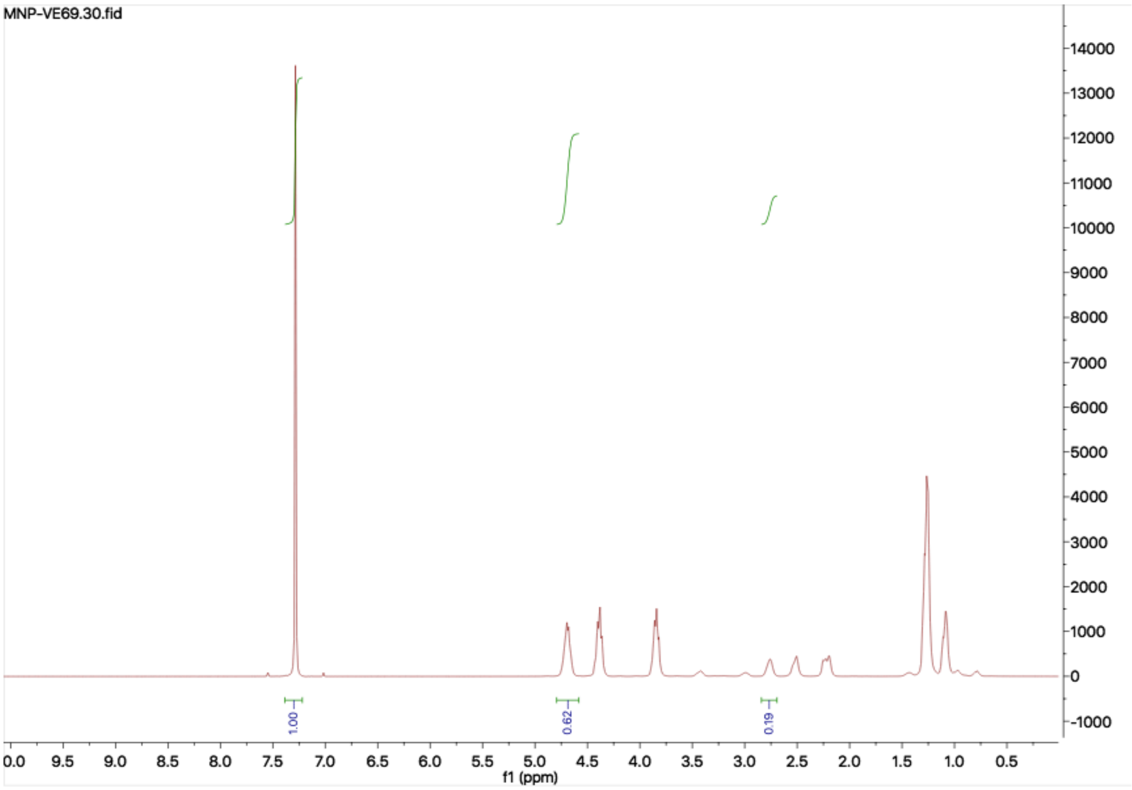

Figure 6.69 - VE 69 HNMR spectra

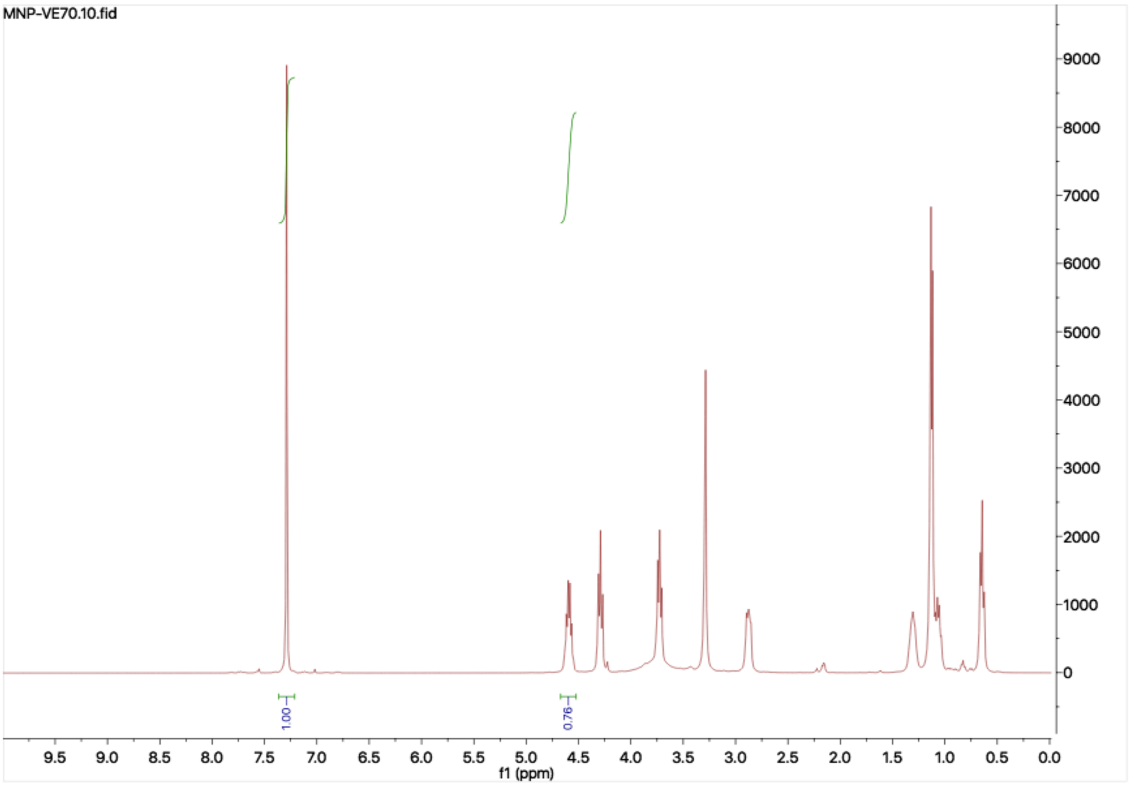

Figure 6.70 - VE 70 HNMR spectra

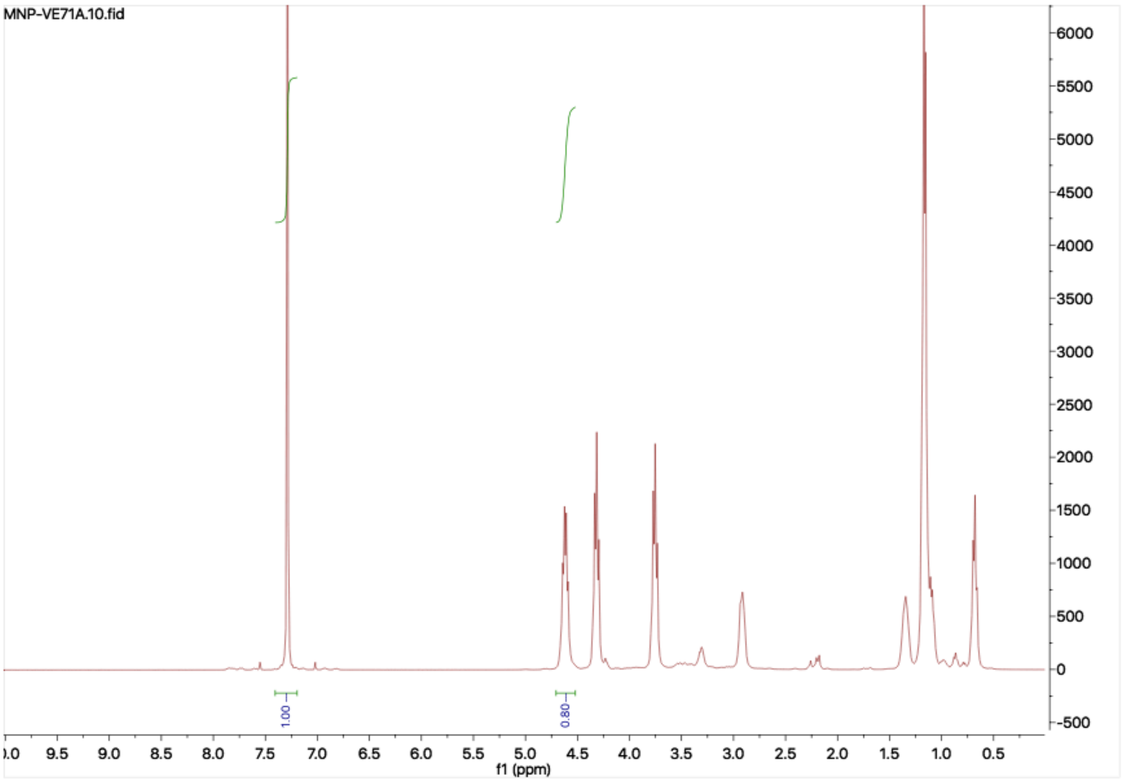

Figure 6.71 - VE 71 HNMR spectra

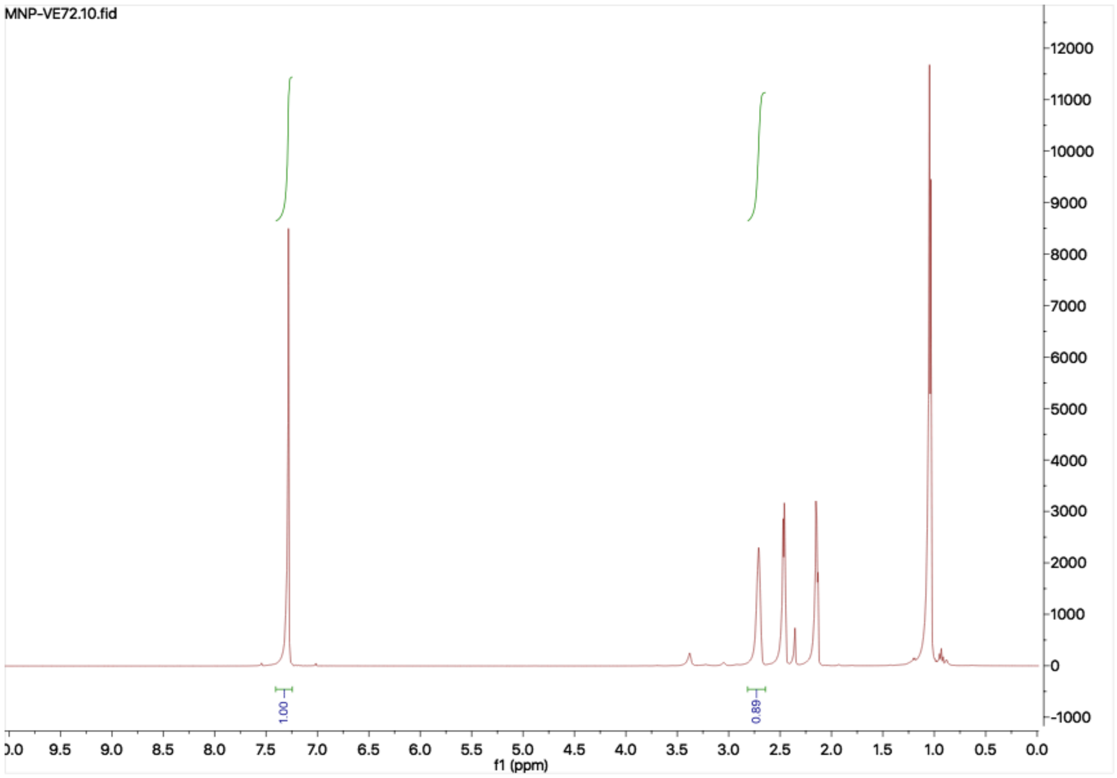

Figure 6.72 - VE 72 HNMR spectra

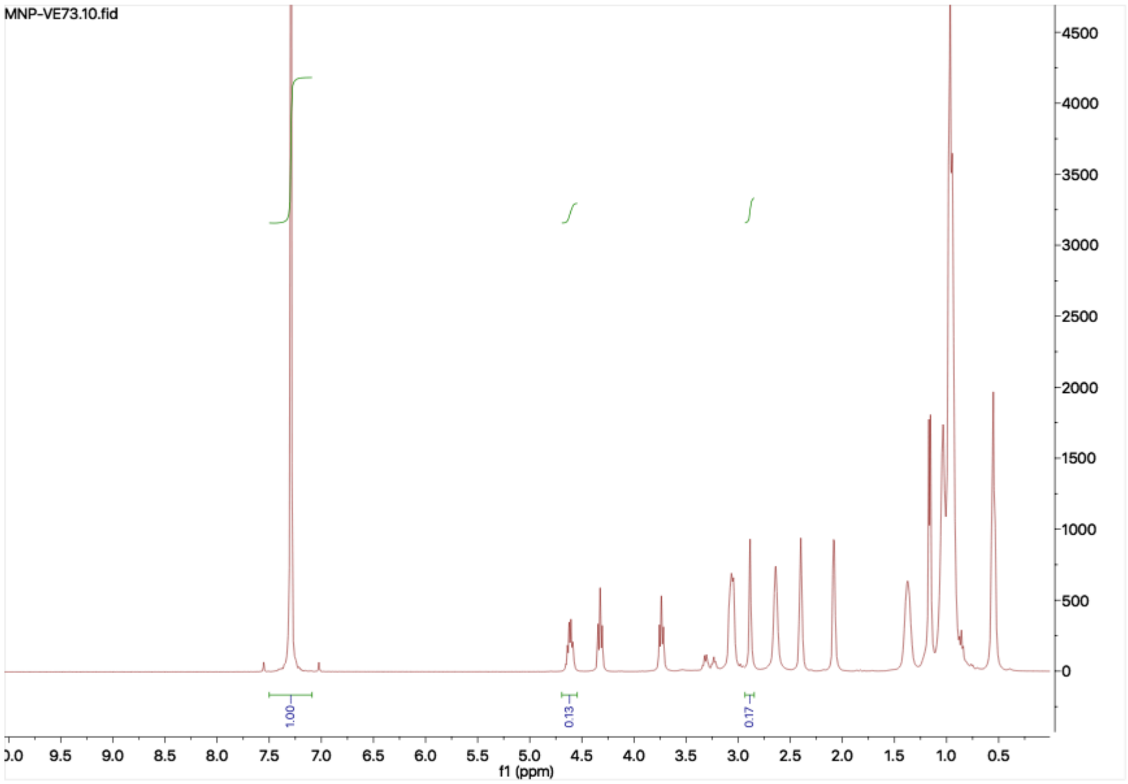

Figure 6.73 - VE 73 HNMR spectra

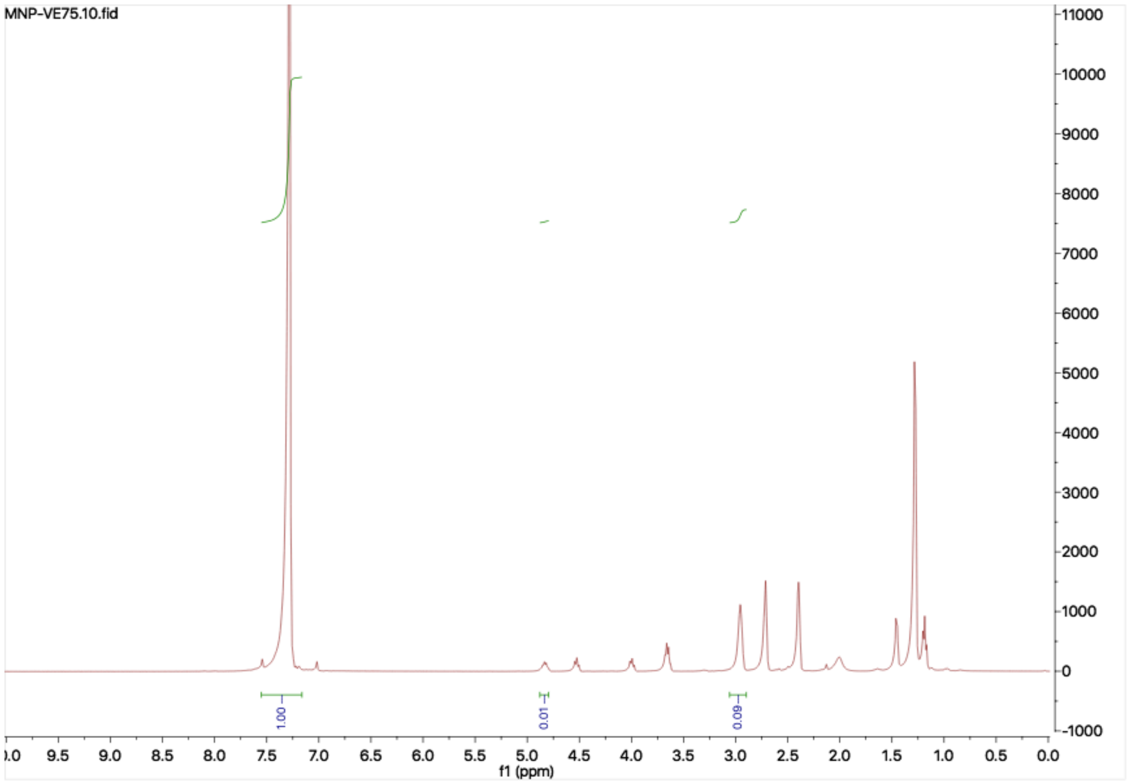

Figure 6.74 - VE 75 HNMR spectra

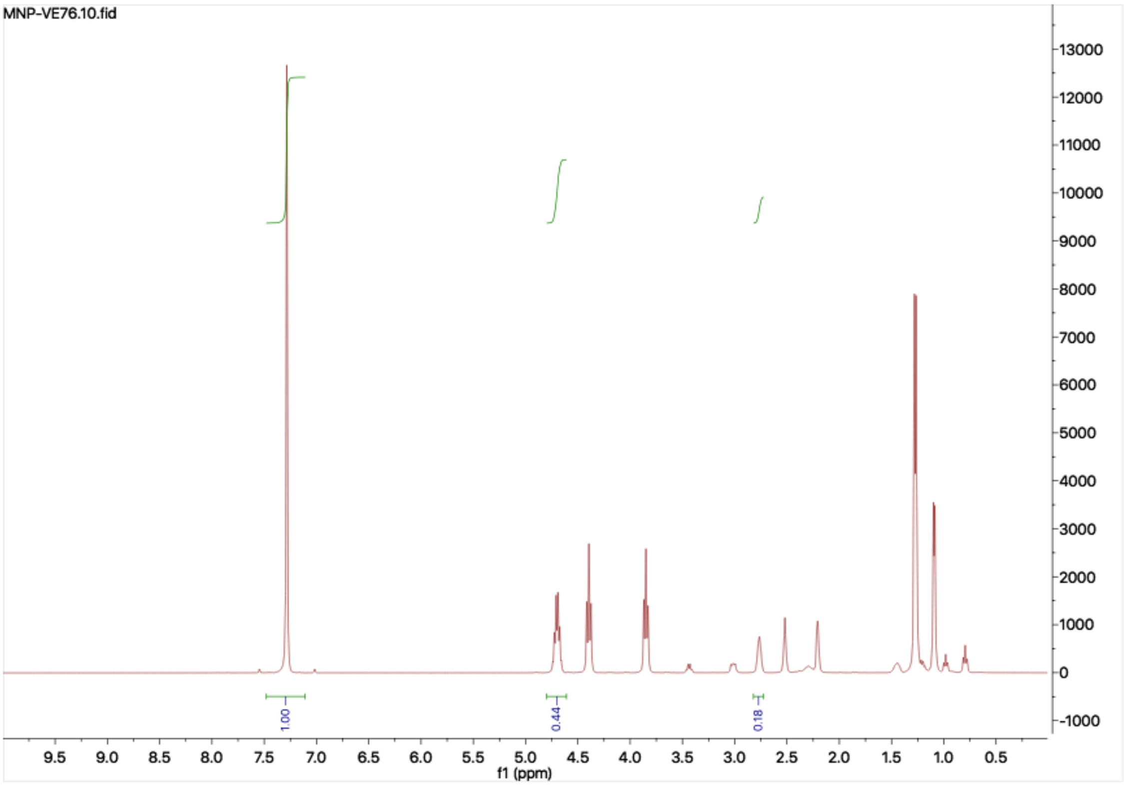

Figure 6.75 - VE 76 HNMR spectra

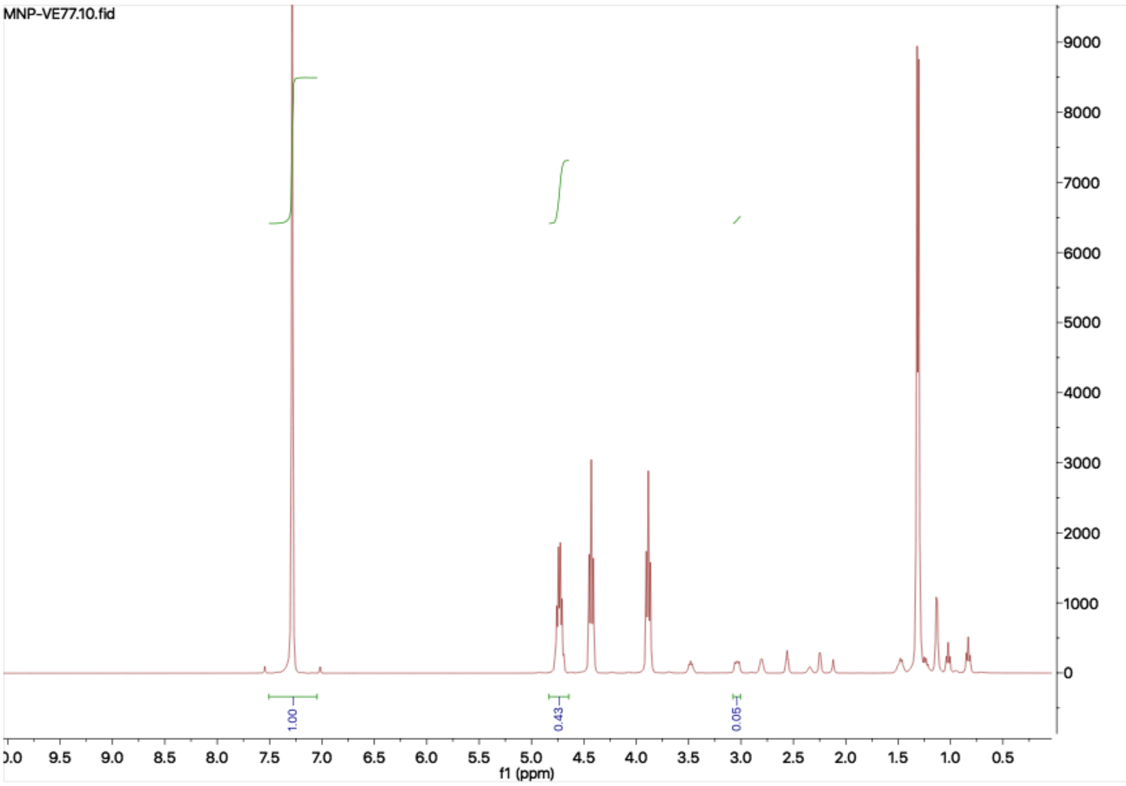

Figure 6.76 - VE 77 HNMR spectra