



Metallomacrocycles and Metal Organic Frameworks Based on Pyridine Carboxylate Ligands: Synthesis, Characterization and Applications

Guilherme Marques Dias Moreno Rúbio

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Supervisors: Prof. Maria de Fátima Costa Guedes da Silva Dr. Anirban Karmakar

Examination Committee

Chairperson: Prof. Maria Matilde Soares Duarte Marques Supervisor: Prof. Maria de Fátima Costa Guedes da Silva Member of the Committee: Prof. Elisabete Clara Bastos Alegria

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Abstract

This work consisted on the preparation of various molecular complexes, metallomacrocycles and metal organic frameworks (MOFs) using novel carboxylate linkers in the presence of transition metals, and the study of their catalytic and sensing properties.

In this context, we have synthesized three new pro-ligands based on pyridine carboxylates namely, 5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} diisophthalic acid (H₄L1), 3,3'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dicarbonyl)bis(azanediyl)}dibenzoic acid (H₂L2) and 4,4'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H₂L3), and characterized them by ¹H-NMR and FT-IR.

Upon the reaction of the above mentioned pro-ligands with metal salts [like Co(II), Cu(II), Zn(II), Cd(II) and Sm(III)] ten novel compounds have been synthesized. They were characterized by single crystal X-ray diffraction analysis and FT-IR.

Catalytic properties of all compounds have been tested towards Henry reaction and Knoevenagel condensation, and in several they are effective heterogeneous catalyst for the Henry (nitroaldol) reaction (maximum yield=84% in 48h at T=70 °C), and for the Knoevenagel condensation reaction (maximum yield=99%, in 1.5h at T=50 °C). Some of the compounds have also been tested for the catalytic activity towards the microwave-assisted solvent-free peroxidative oxidation of a secondary alcohol (1-phenylethanol) with promising results.

Preliminary studies on the sensing properties of some compounds have also been done, achieving high sensitivity and selectivity towards Fe^{3+} , Fe^{2+} and MnO_{4^-} ions with consequent quenching of luminescence, suggesting that the synthesized MOFs are promising luminescent probes for selectively sensing iron and permanganate ions.

Keywords: MOF; crystalline structure; heterogeneous catalysis; chemical sensor; Henry reaction; Knoevenagel condensation.

Sumário

Este trabalho consistiu na preparação de vários complexos moleculares, metalomacrociclos e redes metalo-orgânicas (MOFs), usando novos ligandos carboxílicos na presença de metais de transição, e o estudo das suas propriedades catalíticas e de deteção.

Neste contexto, foram sintetizados 3 novos pro-ligandos baseados em piridinas carboxílicas, nomeadamente 5,5'-{(piridina-2,6-dicarbonil)bis(azanediyl)} ácido diisoftálico (H₄L1), 3,3'-{(piridina-2,6-dicarbonil)bis(azanediyl)} ácido dibenzóico (H₂L2) e 4,4'-{(piridina-2,6-dicarbonil)bis(azanediyl)} ácido dibenzóico (H₂L3), sendo caracterizados por ¹H-RMN e espectroscopia infravermelha por transformada de Fourier (FT-IR).

Por reação dos supramencionadas pro-ligandos com sais metálicos (Co(II), Cu(II), Zn(II), Cd(II) e Sm(III)) dez novos compostos foram sintetizados e caracterizados por difração de raios-X de cristal único e FT-IR.

As propriedades catalíticas de todos os compostos foram testadas nas reações de Knoevenagel e de Henry e no geral revelaram-se eficazes catalisadores heterogéneos com rendimento máximo de 84% em 48h a T=70 °C no primeiro caso, e de 99% em 1.5h a T=50 °C no segundo.

Nalguns casos testou-se também a actividade catalítica em reações de oxidação peroxidativa de um álcool secundário (1-feniletanol) assistido por micro-ondas e livre de solvente com resultados promissores.

Estudos preliminares relativos às propriedades de deteção química de alguns compostos foram efetuados, obtendo-se elevada sensibilidade aos iões Fe³⁺, Fe²⁺ e MnO4⁻, sendo a luminescência completamente absorvida, sugerindo que os MOFs sintetizados são detetores promissores na deteção seletiva de iões ferro e permanganato.

Palavras-chave: MOF; estrutura cristalina; catálise heterogénea; detetor químico; reação de Henry; condensação de Knoevenagel.

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Abbreviations

DCM	Dichloromethane
DMF	Dimethylformamide
EtOH	Ethanol
FT-IR	Fourier Transfer Infrared Spectroscopy
H ₄ L1	5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} diisophthalic acid
H ₂ L2	3,3'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid
H ₂ L3	4,4'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid
H_2O_2	Hydrogen Peroxide
HPCA	3-hydroxy-4,5,6,7-tetrahydro-isoxazolo[4,5-C] pyridine-4-carboxylic acid
MeCN	Acetonitrile
MeOH	Methanol
MOF	Metal organic framework
NaOH	Sodium hydroxide
NEt ₃	Triethylamine
NMR	Nuclear Magnetic Resonance
RT	Room Temperature
ТВНР	tert-Butyl hydroperoxide
TEMPO	(2,2,6,6-Tetramethyl piperidin-1-yl)oxyl
THF	Tetrahydrofuran
TFA	Trifluoroacetic acid

CHAPTER 1: Introduction

An overview of Metal Organic Frameworks

In the last decades, a new research field built around the concept of metal organic frameworks, had a rapid evolution in terms of its multiple applications. These metal organic frameworks (or MOFs), with their high porosity ¹⁻⁴, are built in mild conditions, using multidentate organic linkers and metal ions or clusters, forming crystalline structures. These are the most recent ones applicable in catalysis, storage, sensing, and many others chemistry fields which we continue to rely in expensive compounds.

There are many synthetic pathways to synthesize metal organic frameworks including traditional synthesis (see Figure 1), hydro or solvothermal, microwave, electrochemical, mechanochemical and sonochemical, among others.

The linker and the metal, when hold together by covalent bonds, form extended 1-D, 2-D or even 3-D infinite network structures (hence the term coordination polymers). MOFs are usually crystalline solids, so that the exact positions of all atoms in the framework can often be identified and correlated with the measured properties.



Figure 1 - Schematic representation of the formation of MOFs with different dimensionalities (1D, 2D and 3D) using a type of traditional synthesis: solvothermal reaction. Adapted from reference 5.

The first reports on these types of compounds date from the late 1950s and early 1960s ^{6–10}. But only in the end of last century Robson and co-workers^{11,12} followed by Kitagawa et al.,^{13,14} Yaghi and co-workers ¹⁵, and Ferey et al.¹⁶ rediscovered and boosted the field (see Figure 2).



Figure 2 - Published Items regarding metal organic frameworks since 1990 until the 3th quarter of 2016. Adapted from <u>webofknowledge.com</u>.

The consequent high surface area (highest surface areas reported to date are over $6,000 \text{ m}^2/\text{g}$) ^{17,18} and the porosity coupled with other properties (see Figure 3) such as structure or coordination of the metal ions/clusters, enables MOFs to be guest-responsive materials with multifunctional abilities.



Figure 3 - Schematic representation of high surface are of MOFs, from reference 19.

Since MOFs have a high compatibility with both organic and inorganic materials, it opens the door to advanced composites with various applications, from (opto)-electronic devices to food packaging materials and membrane separation.^{20,21} Finally, their tuneable adsorption properties and pore size and topology, along with their intrinsic hybrid nature, point MOFs as very promising heterogeneous catalysts.^{22,23}

Metallomacrocycles

The recent interest in the self-assembly of metal organic frameworks are due to their potential properties as novel zeolite-like materials having various applications.

However, the crystal engineering of coordination networks with desired topologies and specific properties remains a difficult challenge, since it depends on a variety of factors that can influence the self-assembly process. In that sense, the existence of metallomacrocycles is a natural improvement to the compound structure. Jingui D., et all, published an article the synthesis of new porous coordination polymers.²⁴ The use of a big ligand, associated with plenty of coordination sites, was the key step to control the growth of two new metallomacrocycles, with very good CO₂ adsorption properties.

Metallomacrocycles are of interest for having internal cavities to accommodate other molecules therefore with applications in gas storage, selective inclusion and separation. In addition, the design of compounds with structures leading to mono- and double-stranded chains is also a great challenge for chemists, because these architectures are aesthetically appealing and exhibit potential applications as molecular magnets.

Crystal structures and space group

In crystallography, crystal structure is the representation of a set of particles (atoms, ions or molecules) that are ordered following a pattern. This occurs from the intrinsic nature of the constituent particles to form symmetric patterns that repeat along the principal directions of three-dimensional space in matter. The smallest group of particles in the material that constitutes the repeating pattern is called the unit cell of the structure. The unit cell completely defines the symmetry and structure of the entire crystal lattice, which is built up by repetitive translation of the unit cell along its principal axes. In that sense, seven crystal systems can be defined, which characterize the crystalline material (see Figure 4).²⁵



Figure 4 - Crystal systems that define a crystal structure. Adapted from reference 25.

Mathematically, the crystal structure can be defined by point groups.²⁶ The crystallographic point group or crystal class is the mathematical group that comprises the symmetry operations that leave at least on point unmoved and the appearance of an unchanged crystal structure. These symmetry operations include reflection, rotation, inversion and improper rotation.

That set of operations, following a specific chart define the crystal class of a crystal structure. There are 32 possible crystal classes, where each one can be classified into one of the seven crystal systems. In addition to the operations of the point group, there are also translational symmetry operations, which is the definition of another characteristic of the crystal: the space group.²⁶

The lengths of the principal axes, or edges, of a unit cell, and the angles between them are the lattice parameters. The consequence of these definitions is that naturally occurs symmetric properties, described by the concept of space groups. All possible symmetric arrangements of particles in space may be described by the set of seven space groups. There are 230 distinct space groups.

Application of MOFs in catalysis

As previously said, the well-defined pores and channels in MOFs enable them to be size- and shapeselective, much like zeolites, although the thermal stability of zeolites is much greater than that of MOFs. Despite this drawback, MOFs are promising materials in catalysis, since they can be used as heterogeneous catalysts.

Catalytically active coordinately unsaturated metal sites can be introduced into MOFs in two ways, either as metal connecting points or as part of the linker. As an example of the first approach, Long and coworkers synthesized a microporous MOF, $Mn_3[(Mn_4Cl)_3BTT_8(CH_3OH)_{10}]_2$ (H₃BTT = 1,3,5benzenetristetrazol-5-yl), which can catalyse the transformation of selected aldehydes and ketones with cyanotrimethylsilane to the corresponding cyanosilylated products in high yield.²⁷ The unsaturated Mn²⁺ ions in the framework act as Lewis acid catalysts, and the MOF framework imposes size selectivity.

An example of incorporating catalytically active metals into linkers is the synthesis of MOFs with metalloporphyrins (see Figure 5). The PIZA-3 (porphyrinic illinois zeolite analogue-3), which is assembled from manganese (II) metalloporphyrins, can affect the catalytic hydroxylation of various linear and cyclic alkanes and the epoxidation of cyclic alkenes.²⁸ Recently, Hupp et al. reported a successful synthesis of MOFs with a variety of metalloporphyrins (containing Al³⁺, Zn²⁺, Pd²⁺, Mn³⁺, and Fe³⁺ ions).²⁸ They are all effective catalysts for the oxidation of alkenes and alkanes.



Figure 5 - Structure of robust porphyrinic materials (**RPM**). Top left: A schematic representation of a generic **RPM** unit cell, based on sheet formation by the tetra-acid ligand (L^1) pillaring by a dipyridyl column (L^2). The grey-black spheres are the paddlewheel-coordinated zinc nodes. Adapted from ref 29.

Much effort has been devoted to the development of homochiral MOFs able to serve as enantioselective catalysts. They can be synthesized from achiral components via self-resolution during crystal growth, or even by enantioselective growth induced by chiral solvents, chiral templates or chiral crystal seeds.³⁰⁻³³ Lin et al. synthesized a series of chiral MOFs from 1,1'-binaphthyl-derived chiral ligands, such as 1,1'-binaphthalene-2,2'-diol (BINOL) and, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), which in fact is the easiest way to develop a chiral MOF. ³⁴⁻³⁶

One of the most interesting reactions, where the application of a MOF based catalyst is relevant is in the Henry (nitroaldol) reaction. This classic carbon–carbon bond formation reaction, discovered in 1895 by the Belgian chemist Louis Henry, is the combination of a nitroalkane and an aldehyde or ketone in the presence of a base to form β -nitroalcohols in two isomeric forms (*syn* and *anti*) (Scheme 1).³⁷ It is, in fact, a useful technique in organic chemistry due to the utility of the corresponding products that can be easily converted in useful synthetic intermediates. The nitroaldol conversions include subsequent dehydration to yield nitroalkenes, oxidation of the secondary alcohol to yield α -nitroketones, or reduction of the nitro group to yield β -aminoalcohols.



Scheme 1 - Nitro-aldol (Henry) reaction between benzaldehyde and nitroethane.

One of the main drawbacks of the Henry reaction is the potential for side reactions throughout the course of the reaction, hence the importance of stereoselectivity provided by well-structured MOFs. Aside from the reversibility of the reaction (retro-Henry) which could prevent the reaction from proceeding, the β -nitro alcohol has the potential to undergo dehydration, and for sterically hindered substrates it is possible that a base catalysed self-condensation (Cannizaro reaction) could occur (Scheme 2).

The application of metal organic frameworks as heterogeneous catalysts has proved to be highly advantageous.³⁸



Scheme 2 - Cannizzaro reaction, where the basic medium promotes the auto-reaction, forming benzyl alcohol and benzoic acid.

Another important organic reaction is the Knoevenagel condensation (Scheme 3). In this case, similarly to the Henry reaction, we have a nucleophilic addition of an active hydrogen compound to a carbonyl group, followed by a dehydration reaction in which occurs the elimination of a water molecule (hence, condensation). The product is often α , β -unsaturated compounds.



Scheme 3 - Knoevenagel condensation reaction where benzaldehyde reacts with malononitrile, forming benzylidenemalononitrile.

In this reaction, the carbonyl group is an aldehyde or a ketone. The catalyst is usually a weakly basic amide.

Limited examples have been reported on the use of metal organic frameworks as catalysts in the Knoevenagel condensation, but those cases have shown already the great possibilities of these compounds (especially when we are trying to find more active and less expensive catalysts).³⁹

Another application of metal organic frameworks is in oxidation reactions. Microwave assisted solvent free peroxidative oxidation of secondary alcohols to the corresponding ketone and oxidation of toluene to benzyl alcohol and benzaldehyde are two of such reactions.

In the first case, a secondary alcohol is converted to a ketone (Scheme 4). The hydrogen from the hydroxyl group is lost along with the hydrogen bonded to the second carbon. The remaining oxygen then forms double bonds with the carbon. This leaves a ketone, as R¹–COR². Ketones cannot normally be further oxidized because this would involve breaking a C–C bond, which requires too much energy.⁴⁰ The reaction can occur using a variety of oxidants, under microwave induction and in the absence of solvent (green reaction).



Scheme 4 - Oxidation of 1-phenylethanol into acetophenone, by a microwave-assisted solvent-free reaction.

The oxidation of toluene (which is a by-product in catalytic reforming and widely used as an industrial feedstock and a solvent) to added value products is very interesting, since both benzyl alcohol and benzaldehyde are used in pharmaceutical industries (Scheme 5).



Scheme 5 - Oxidation reaction of toluene into benzyl alcohol and benzaldehyde.

Ketones are among the most important chemicals, as final products or for further synthesis, e.g. as polymer precursors or substrates in the pharmaceutical industry.⁴¹ Although they can be synthesized by direct oxidation of alkanes⁴² or alkenes,⁴³ these reactions are usually not selective.⁴²

The liquid-phase oxidation of secondary alcohols to ketones appears to be the simplest and the most used synthetic method. However, these reactions are commonly limited to benzylic compounds⁴⁴ and need relatively high catalysts loadings, long reaction time⁴⁴ and/or additives (bases, phase-transfer agents, etc.), as well as oxidants (e.g. manganese salts, chromates)⁴¹ and solvents⁴⁴ that often are expensive and toxic. Moreover, the catalysts used are frequently expensive (based on noble metals), not easy to prepare and not highly active for the oxidation of aliphatic alcohols.

The use of metal organic frameworks in microwave-assisted solvent-free peroxidative oxidation of 1phenylethanol⁴⁵ and the oxidation of toluene under mild conditions ⁴⁶ have already been reported.

Application of MOFs in sensing

The ideal chemical sensor is in theory an inexpensive, portable, foolproof device that responds with perfect and instantaneous selectivity to a target chemical substance. The analyte, that could be present in any desired medium, would promote the sensor to produce a measurable signal output at any required concentration. However, such ideal chemical sensor is far from reality, even with enormous advances in the past decades.

Chemical sensors are complex devices, generally optimized for an application, and although a variety of chemical sensors have successfully been commercialized, improvement is needed. For example, one universal limitation of chemiresistive sensors based on metal oxides, is that they typically must be operated at high temperatures (above 200 °C) to promote reaction of surface-bound oxygen species.⁴⁷ In addition, they typically exhibit cross-sensitivity and significant baseline drift over the life of the sensor. Another important limitation associated with complex sensors is poisoning. For example, H₂ sensors based on reversible, dissociative uptake of H₂ by films of elemental palladium (and concomitant modulation of film resistivity, reflectivity, etc.) are susceptible to poisoning by CO and H₂S. ⁴⁸

Theoretically, MOFs can overcome most of the selectivity challenges that are associated with sensor materials (Figures 6 and 7). Many have proven to be thermally robust, resisting to decomposition at temperatures around 300 °C or higher. ^{49,50}



Figure 6 - Functionalization and signal transduction of metal organic framework (MOF)-based composites for sensing applications. Adapted from reference 51.



Figure 7 - The complementary interaction between a guest analyte and a host binding pocket capable of reporting this binding event converts the receptor into a sensor. The reporter is a dye connected with a receptor.

One important way to detect very low concentrations of an analyte is luminescence quenching.⁵² Luminescence can involve three types of light emission: fluorescence, which is spin-allowed with typical lifetimes about several nanoseconds, phosphorescence, which is spin-forbidden and has lifetimes that can be long as several seconds, and scintillation, which is light emission stimulated by exposure to ionizing radiation and has lifetimes on the order of 1 nanosecond.⁵³

Luminescent metal–organic frameworks (LMOFs) have attracted considerable attention for some time as these can potentially be used in fast and highly selective detection of nitro-explosives and heavy metal ions.

The most common strategy to make LMOFs is to incorporate luminescent metal centres, where the most common choices are lanthanide ions. Although electronic transitions of lanthanide ions are Laporte forbidden, this can be overcome by incorporating a strongly absorbing component called a lumophore into the MOF framework. When stimulated by irradiation, lumophores can transfer energy from their readily accessed triplet excited state to the Ln-emitting states (providing a strong vibronic coupling between the metal and the lumophore). To this phenomenon, it is given the name of Antenna effect.

In the solid state, electronic interactions (such as ligand to ligand charge transfer) can affect luminescence, if lumophores are near. ⁵⁴

Several different detection modes have been proposed as ways to use luminescent MOFs as potential sensors. Some MOFs are highly sensible to Fe(II) and Zn(II) ions (see Figure 8). The technique is based on wavelength shift: the fluorescence emission wavelength shifts depending on the presence and identity of the guest in the MOF.⁵⁵

Another detection mode employs intensity changes, where enhancement or quenching of photoluminescence occurs, depending, e.g., on the solvent.⁵⁶

In other cases, the LMOF can recognize and sense anions and metal ions, which bind to O-H groups and nitrogen atoms in the MOF, respectively.^{57,58} The quenching of LMOFs has also been used in the detection of explosives. Li and co-workers developed a Zn-MOF that incorporates both 4,4'-biphenyldicarboxylate and 1,2-bipyridylethene linkers. The fluorescence of the MOF is quenched significantly by both 2,4-dinitrotoluene (DNT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB).⁵⁹



Figure 8 - Schematic representation fluorescence-based sensing of Fe^{3+} and Zn^{2+} by $[Eu(BTPCA)(H_2O)]\cdot 2DMF\cdot 3H_2O$ ($[H_3BTPCA = 1,1',1''-$ (benzene-1,3,5-triyl)tripiperidine-4-carboxylic acid]). Adapted from reference 60.

CHAPTER 2: Synthesis and characterization of the pro-ligands

The use of rigid multidentate aromatic carboxylate ligands, which provides structural conformation and thermal stability,^{61,62} creates a robust architecture of metal organic frameworks with high versatile binding features.⁶³

Polycarboxylic acids are among the most attractive building blocks (usually in their de-protonated carboxylate form). Some earlier reports relate to the use of dicarboxylate,⁶⁴ tricarboxylate⁶⁵ and tetracarboxylate⁶⁶ ligands, which are inter-bridged by mono- or multi-nuclear metal nodes, leading to stable MOFs with permanent porosity.

In that sense, in a coordination complex the building block offers structural rigidity,⁶⁷ which can place the auxiliary functional groups in a preorganized conformation. Such group could, then, be available to either be involved in self-assembly of the metal organic framework, or even in the coordination of a secondary metal ion, creating a multimetallic complex or framework.⁶⁸⁻⁷⁰



R= -CH₃, -CH₂CH₃, Benzyl

Figure 9 - General examples of amide based carboxylic acid pro-ligands, with structural rigidity associated with reactive amide and carboxylic centres.

In this work, the choice of pyridine based amide carboxylic acid pro-ligands (Figure 9) was not random, but due to the following characteristics: (a) the carboxylic groups can be partially or completely deprotonated by tuning the reaction pH and thus the formation of multidimensional MOFs could be expected; (b) the flexible amide arm of pro-ligands can adopt various conformations, which would further generate diverse architectures; (c) the introduction of an amide functionality can offer additional hydrogen bonding sites as well as a Lewis-basic nature to the frameworks.

The synthesis of 5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} diisophthalic acid (H₄L1) ligand followed a two-step procedure as shown in Scheme 6. The first step (Scheme 6A) is the condensation of the methyl ester of 5-aminoisophthalic acid with 2,6-pyridinedicarboxylic acid chloride in the presence of NEt₃. This produced the methyl ester of compound H₄L1. In the second step (Scheme 6B), the isolated ester was hydrolysed in the presence of NaOH and THF, which lead to the formation of solid product H₄L1 (Figure 10).



Scheme 6 - Reaction scheme in the synthesis of H_4L1 . A: Scheme corresponding to step 1. B: Scheme corresponding to step 2.

Regarding 3,3'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H₂L2) and 4,4'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)} dibenzoic acid (H₂L3), the synthesis followed a three-step procedure, as shown in Schemes 7 and 8 (respectively). In the first step, 3–amino benzoic acid (for H₂L2) or 4-amino benzoic acid (for H₂L3), were esterified (respectively Schemes 7A and 8A) in the presence of methanol and sulfuric acid.

The condensation of the product of the previous reactions (Schemes 7B and 8B, respectively for H_2L2 and H_2L3) with 2,6-pyridinedicarboxylic acid chloride in the presence of NEt₃, produced the respective methyl esters. In the third step (Schemes 7C and 8C) these were hydrolysed in the presence of NaOH and THF, which lead to the formation of solid H_2L2 and H_2L3 (Figure 10).

In the FT-IR spectra of H₄L1, H₂L2 and H₂L3, the characteristic strong bands of the amide groups appear between 3447 and 3466 cm⁻¹. C–O stretching of carboxylate group is observed between 1296 and 1300 cm⁻¹. C=O stretching is observed between 1689 and 1713 cm⁻¹. In the ¹H-NMR spectra, the resonance of the carboxylic hydrogens appears amid 12.89-13.18 ppm and that of the amide hydrogen at 11.19-11.27 ppm.



Scheme 7 – The three-step reaction procedure for the synthesis of H_2L2 .



Scheme 8 - The three-step reaction procedure for the synthesis of H₂L3.



Figure 10 - Synthesized pro-ligands used in the MOFs construction.

CHAPTER 3: Synthesis and characterization of MOFs using H₄L1 pro-ligand

Synthesis of compounds 1, 2 and 3.

The reaction of H₄L1, with cobalt(II) nitrate hexahydrate, zinc(II) nitrate hexahydrate and cadmium(II) nitrate tetrahydrate, under hydrothermal conditions, leads to the formation of compounds $[Co(H_2L1)(MeOH)_4]$.MeOH (1), $[Zn_2(L1)(H_2O)_4]_n$.4n(H₂O) (2) and $[Cd_3(HL1)_2(DMF)_4]_n$. 2n(DMF) (3), respectively. In FT-IR, the C-O bands appear between 1298 cm⁻¹ and 1227 cm⁻¹, which agrees with data collected from H₄L1 ligand (1296 cm⁻¹).

Crystal structure analysis of compounds 1, 2 and 3

Complex $[Co(H_2L1)(MeOH)_4]$.MeOH (1) crystallizes in the triclinic P-1 space group, its asymmetric unit containing one Co²⁺ ion, one H₂L1²⁻ anion, four coordinated and one non-coordinated MeOH molecules as depicted in Figure 11A. The compound features a mononuclear Co(II) complex (Figure 11B).

The Co1 centres presents an octahedral environment, the four equatorial sites being occupied by two carboxylate oxygen atoms of the H_2L^{2-} unit [Co1–O1, 2.076(2) Å; Co1–O5, 2.060(2) Å] and two O-atoms from two methanol molecules [Co1–O12, 2.106(3) Å; Co1–O14, 2.135(3) Å]. The axial sites are by the other two MeOH molecules [Co1–O11, 2.079(3) Å; Co1–O13, 2.074(3) Å].

In this compound the organic ligand H₂L²⁻ is almost planar and it coordinates to the metal ion via one of the O-atoms from two carboxylate groups. The two carboxylic acid groups are hydrogen bonded via O3-H3O····O4 (d_{D-A} 2.647(5) Å; <D–H····A 171°), O7-H7····O6 (d_{D-A} 2.607(3) Å; <D–H····A 159°) interactions and expands to 1D hydrogen bonded network (Figure 11C). The structure expands to the second dimension by means of contact interactions involving the methanolic H-atoms as donors and the amide and carboxylate O-atoms as acceptors via O11-H11O····O10 (d_{D-A} 2.773(3) Å; <D–H····A 174°) and O13-H13O····O2 (d_{D-A} 2.687(3) Å; <D–H····A 146°) interactions.



Figure 11 - A: Crystal structure of **1**. B: Schematic representation of **1**. C: Hydrogen bonded packing diagram of complex **1**.

The single crystal X-ray analysis of $[Zn_2(L1)_1(H_2O)_4]_n$. $4n(H_2O)$ (2) reveals that it crystallizes in the monoclinic C2/c space group and is a layer type two dimensional framework constructed from Zn(II) ions and deprotonated L1⁴⁻ ligands.

The asymmetric unit contains a Zn²⁺ ion, half a fully deprotonated ligand (L1⁴⁻) and two coordinated and two non-coordinated water molecules (Figure 12A). The Zn(II) centre has a tetrahedral ($r_4 = 0.91$)⁷¹ geometry, two positions being occupied by two carboxylate oxygens from two L⁴⁻ ligands [Zn1–O1, 1.951(2) Å and Zn1–O4, 1.9875(19) Å] and the other two positions being coordinated by two water molecules [Zn1–O6, 2.008(3) Å and Zn1–O7, 2.003(3) Å] (Figure 12B).

The organic ligand is planar. Each L1⁴⁻ ligand coordinates to four zinc(II) ions and the carboxylate groups coordinates to the metal centres in a monodentate fashion. In **2**, the distance between two neighbouring Zn(II) ions is 8.976 Å.

The 2D polymeric architecture of **2** also has open trigonal channels, which are occupied by the noncoordinated water molecules (Figure 12C).

The non-coordinated water molecules are stabilized by several O-H···O interactions which helps the expansion of the structure to the third dimension. These involve the hydrogens of a non-coordinated water molecule O8 or O9 (as donor) and the carboxylate oxygen O2, O3 and O5 (as acceptor) via O8-H8A····O5 ($d_{D-A} 2.773(3)$ Å; <D–H····A 176°), O8-H8B····O3 ($d_{D-A} 2.889(4)$ Å; <D–H····A 168°) and O9-H9A····O2 ($d_{D-A} 2.786(4)$ Å; <D–H····A 162°) interactions.



Figure 12 - A: The framework **2** with partial atom labelling scheme. B: Schematic representation of **2**. C: Two-dimensional structure of framework **2**.

The single crystal X-ray analysis of $[Cd_3(HL1)_2(DMF)_4]_n.2n(DMF)$ (3) reveals that it crystallizes in a triclinic P-1 space group and is a two dimensional framework. Framework 3 contains three Cd^{2+} ions, two triply deprotonated ligands (HL1³⁻), four coordinated and two non-coordinated dimethylformamide (DMF) molecules (Figure 13A and 13B).

Framework **3** contains two different types of Cd(II) coordination environments [octahedral geometry for Cd1 and distorted pentagonal bipyramidal geometry for Cd2]. The Cd1 cation is coordinated to four of the O-atoms of four distinct HL1³⁻ ligands [Cd1–O1, 2.2702(16) Å and Cd1–O9, 2.2245(16) Å] and further coordinated by the two O-atom of a bridging DMF molecules [Cd1–O11, 2.3332(16) Å].

The coordination sphere around the Cd2 centre is fulfilled by three HL1³⁻ ligands [Cd2–O1, 2.2702(16) Å, Cd2–O2, 2.2674(18) Å, Cd2–O3, 2.4221(17) Å, Cd2–O4, 2.3108(17) Å and Cd2–O10, 2.2376(16) Å], one bridging DMF molecule [Cd2–O11, 2.4430(17) Å] and one monodentate DMF molecule [Cd2–O12, 2.297(2) Å] (Figure 13B). The ligand coordinates simultaneously to five different metal ions, via three of the carboxylate groups which operate in bridging bidentate, syn-syn bridging or chelate fashions. The two crystallographically independent Cd-ions are arranged in trinuclear clusters.

The metal core located on an inversion centre (Cd2) connects to seven carboxylate groups and the one located in a general position (Cd1) coordinates to six different carboxylates. The Cd1····Cd2 and Cd2····Cd2' distances within the tri-nuclear clusters are 3.5146 Å and 7.0291(4) Å, respectively.

Association of its six HL1³⁻ ligands and tri-nuclear Cd(II) cluster results in the formation of 2D singleframework pillared along the crystallographic a-axis (Figures 13C and 13D).





В





Figure 13 - (A) The structure of framework **3** with partial atom labelling scheme. (B) Schematic representation of **3**. (C) and (D) Fragments of the two dimensional structure of framework **3**.

CHAPTER 4: Synthesis and characterization of MOFs using H₂L2 pro-ligand

Synthesis of compounds 4 – 8.

The reaction of H₂L2, with copper(II) nitrate pentahemihydrate, zinc(II) nitrate hexahydrate, cadmium(II) nitrate tetrahydrate and samarium(III) nitrate hexahydrate, under hydrothermal conditions, leads to the formation of compounds $[Cu_4(L2)_2(NO_3)_2(OH)_2(MeOH)_2]$.MeOH (4), $[Cu_2(L2)(DMF)_2]_n$ (5) $[Zn(L2)(H_2O)_2]_n$ (6), $[Cd_2(L2)_2(H_2O)_4]_n$.3nH₂O (7) and $[Sm_3(L2)(DMF)(NO_3)(H_2O)_4]_n$.nDMF (8), respectively. In FT-IR, the C-O stretching appear between 1385 cm⁻¹ and 1160 cm⁻¹, which agrees with data collected from H₂L2 ligand (1297 cm⁻¹).

<u>Crystal structure analysis of compounds 4 – 8.</u>

X-ray crystallography has established that **4** consists of a tetranuclear $[Cu_4(L2)_2(NO_3)_2(OH)_2(MeOH)_2]$.MeOH neutral unit and methanol guest molecule (see Figures 14A and 14B). The asymmetric unit of **4** contains two copper(II) atoms, one L2²⁻ ligand, one bridging nitrate anion, one μ_3 -OH and one coordinated methanol molecule.

There is a $[Cu_4(OH)_2]$ core in **4** with interatomic distances of Cu1···Cu2 = 3.359 Å, Cu1···Cu1' = 2.939 Å, Cu1···Cu2' = 3.319 Å and Cu2···Cu2' = 5.997 Å, all exceeding the sum of the van de Walls radii of Cu atoms (2.80 Å), as in other reported Cu₄ aggregates. The four Cu atoms in the core adopt a parallelogram arrangement and lie in the same plane with a Cu2–Cu1–Cu2' angle of 127.78°. The $[Cu_4(OH)_2]$ cluster can also be viewed as two $[Cu_3(OH)]$ triangles sharing a common Cu1···Cu1' edge.

Between Cu1 and Cu2, there are two bridging nitrate anions which supports the upper and lower planes that consists on the four central copper atoms. Two methanol molecules are coordinated to Cu2 and Cu2' in usual terminal monodentate mode.

The μ_3 -OH group bridges Cu1, Cu2 and Cu1A with a shortest distance of 0.674 Å between O7 and the plane defined by the four Cu atoms. The geometry of Cu1 is a distorted square pyramid, with Cu1–O9 distance of 2.415 Å considerably larger than the other four Cu1-O bond distances (1.909, 1.931, 1.968 and 2.007 Å).

The geometry around Cu2, is also an elongated distorted square pyramid with the oxygen atom from a μ -NO₃ group occupying the axial position (Cu2–O10 = 2.479 Å).

There is methanol water guest molecule in complex **4**, which forms an intermolecular hydrogen bond with the amide oxygen, as evidenced by the O12···O5 distance of 2.759 Å. Furthermore, the –NH groups of the ligand use the protons to form intermolecular hydrogen bonds with methanol oxygen.

All the above, together with other weak interactions such as C-H···O interactions, link the tetranuclear units together to form a 2D structure (Figure 14C).



Figure 14 - (A) Crystal structure of **4** with partial atom labelling scheme. (B) Schematic representation of the complex **4**. (C) Packing diagram of **4**.
The single crystal X-ray analysis of **5** reveals that it crystallizes in the monoclinic P2₁/n space group and is a two-dimensional framework (Figure 15A) constructed by Cu(II) ions and deprotonated $L2^{2-}$ ligands. The asymmetric unit contains a Cu²⁺ ion, one deprotonated ligand ($L2^{2-}$) and the coordinated DMF.

The Cu(II) centre has a square pyramidal ($r_5 = 0.001$)⁷² geometry, the equatorial positions being occupied by four carboxylate oxygen atoms from four L2²⁻ ligands [Cu1–O1, 1.950(3) Å, Cu1–O2, 1.959(3) Å, Cu1–O5, 1.953(3) Å and Cu1–O6, 1.970(3) Å] and the axial positions being engaged with one DMF molecule [Cu1–O7, 2.142(3) Å] (Figure 15B). The carboxylate groups coordinate to two copper(II) ions in a bridging mode.

In this framework, a dinuclear paddlewheel type Cu(II) cluster acts as a secondary building block. The organic ligand is not planar, one of the 3-amino carboxylate units is slightly twisted with respect to pyridyl groups and the C13-C14-N3-C15 torsional angle of 179.8°. In **5**, the distance between two symmetry related copper(II) ions is 2.6247(8) Å. The 2D polymeric architecture of **5** also has open channels with approximate dimension of 8.7 x 8.6 Å² and contains a void space of 19.8% per unit cell per PLATON⁷³ (Figure 15D).



Figure 15 - (A) The framework **5** with partial atom labelling scheme. (B) Schematic representation of **5**. (C) Coordination environment framework **5** around the dinuclear Cu(II) unit. (D) Two dimensional structure of framework.

Single-crystal X-ray diffraction studies reveal that $[Zn(L1)(H_2O)_2]_n$ (6) crystallizes in the monoclinic C2/c space group, and that the asymmetric unit contains one zinc(II) ions, one L2²⁻ ligand, two coordinated water molecules (Figures 16A and 16B).

Compound **6** features a zig-zag type one dimensional polymeric chain, but expands to 3D by means of H-bond interactions. The Zn1 centre presents a distorted tetrahedral environment ($r_4 = 0.92$)⁷¹ and binds to two carboxylate oxygen atoms from two neighbouring L2²⁻ units in a monodentate fashion [Zn1–O1 and Zn1–O6] and to two water molecules [Zn1–O7 and Zn1–O8]. In this framework, the organic ligand is slightly twisted and the dihedral angle between the two carboxylate phenyl rings is 34.6°. The presence of coordinated water molecules prevented the formation of a structure with a higher dimensionality, and a 1D zig-zag chain is formed instead (Figure 16C).

However, the intermolecular organization in the crystal is characterized by hydrogen bonding interactions involving the carboxylate groups as acceptors and the coordinated water molecules as does expanding the structure to the third dimension.



Figure 16 - (A) Coordination scheme in **6** with partial atom labelling scheme. (B) Schematic representation of **6**. (C) One dimensional zig-zag structure of **6**.

Single-crystal X-ray diffraction studies reveal that complex **7** is a dimeric Cd(II) based metallomacrocyclic complex having formula $[Cd_2(L2)_2(H_2O)_4]_n.3nH_2O$ (Figures 17A and 17B) and it crystallizes in the triclinic P-1 space group. Its asymmetric unit contains one Cd²⁺ ion, one doubly deprotonated L2²⁻ ligand, two coordinated and three non-coordinated H₂O molecules. The Cd(II) centre presents a distorted octahedral environment where the four equatorial sites are occupied by four carboxylate oxygen atoms from two L2²⁻ ligand [Cd1–O1, 2.383(12) Å, Cd1–O2, 2.384(12) Å, Cd1–O5, 2.478(12) Å; Cd1–O6, 2.355(12) Å] and the axial positions are occupied by two O-atoms from water molecules [Cd1–O7, 2.315(18) Å; Cd1–O8, 2.400(18) Å].



Figure 17 - (A) Schematic representation of **7**. (B) Crystal structure of **7**. (C) Hydrogen bonded packing diagram of complex **7**.

In this complex the deprotonated organic ligand (L2²⁻) is planar and coordinates to two Cd(II) ions via chelating bidentate carboxylate groups. In **7**, the distance between two neighbouring Cd(II) ions is 5.469(2) Å.

The amide NH- is involved in hydrogen bonding to the non-coordinated water molecule via N1-H1···O10 $[d_{D-A} 3.02(2) \text{ Å}; <D-H...A 144^{\circ}]$ and N3-H3···O10 $[d_{D-A} 2.93(2) \text{ Å}; <D-H...A 155^{\circ}]$. A few O-H···O interactions are present in this structure which helps its expansion to the second dimension (Figure 17C).

The reaction of H₂L2 with Sm(NO₃)₃.6H₂O in solvothermal condition leads to the formation of the 1D network [Sm(L2)(NO₃)(H₂O)(DMF)]_n.nDMF (**8**) (Figure 18). The asymmetric unit of framework **8** contains one Sm³⁺ ion, one doubly deprotonated L2²⁻ ligand, one nitrate anion, one coordinated DMF, a water molecules and one non-coordinated DMF molecule. The Sm(III) centre has coordination number eight where four of the coordination sites are occupied by four oxygen atoms from syn-anti bridging carboxylate group from four L2²⁻ ligand [Sm1–O1, 2.290(4) Å, Sm1–O2, 2.381(3) Å, Sm1–O5, 2.333(4) Å; Sm1–O6, 2.371(4) Å], two are occupied by a chelating nitrate anion [Sm1–O7, 2.530(5) Å, Sm1–O8, 2.535(4) Å] and the remaining positions are occupied by DMF [Sm1–O11, 2.385(5) Å] and water molecules [Sm1–O10, 2.474(4) Å]. The metal-oxygen bond lengths are within the range of those usually encountered for lanthanide-oxygen assemblies.

In **8** the deprotonated organic ligand (L2²⁻) is almost planar. In the 1D chain, the Sm(III) ions are arranged in a linear fashion The distance between two neighbouring Sm(III) ions is 5.105 Å. The coordinated water and non-coordinated DMF molecules are involved in a hydrogen bonding via O10-H10A···O12 [d_{D-A} 2.681(8) Å; <D–H····A 150°] interaction. Moreover, a few C–H···O interactions are present in this structure.



Figure 18 - (A) The framework **8** with partial atom labelling scheme. (B) Schematic representation of **8**. (C) One dimensional structure of framework **8**.

CHAPTER 5: Synthesis and characterization of MOFs using H₂L3 ligand

Synthesis of compounds 9 and 10.

The reaction of H₂L3, with zinc(II) nitrate hexahydrate under hydrothermal conditions leads to the formation of compounds $[Zn_2(L3)_2(H_2O)_4].2H_2O.3DMF$ (**9**) and $[Zn_5(L3)_4(OH)_2(H_2O)_4]_n$ (**10**), respectively. In FT-IR, the C-O bands appear between 1281 cm⁻¹ and 1180 cm⁻¹, which agrees with data collected from H₂L3 ligand (1300 cm⁻¹).

Crystal structure analysis of compounds 9 and 10

Complex **9** [Zn₂(L3)₂(H₂O)₄].2H₂O.3DMF crystallizes in the triclinic P-1 space group, its asymmetric unit containing one Zn²⁺ ion, one doubly deprotonated L3²⁻ ligand, two coordinated and two non-coordinated H₂O molecules and three non-coordinated DMF molecules. The compound features a dimeric Zn(II) based metallomacrocycle (Figure 19). The Zn1 centre presents a distorted tetrahedral environment (τ_4 = 0.51)⁷¹ with the four sites being occupied by two carboxylate oxygen atoms from two L3²⁻ units [Zn1–O1, 1.965(4) Å; Zn1–O5, 1.962(3) Å] and two O-atoms from two water molecules [Zn1–O12, 2.014(5) Å].

In this complex the deprotonated organic ligand ($L3^{2-}$) is planar and coordinates to two zinc(II) through one of the O-atoms from two carboxylate groups. In **9**, the distance between two neighbouring Zn(II) ions is 5.327 Å.

The structure is stabilized by a few hydrogen bonding interactions involving the non-coordinated water and DMF molecules. These involve the hydrogens of a non-coordinated water molecule O10 and O11 (as donor) and the carboxylate oxygen O6 (as bifurcated donor). The amide NH⁻ is also involved in strong hydrogen bonding with non-coordinated DMF oxygen via N1-H1A···O9 [d_{D-A} 2.888(5) Å; <D–H····A 169°] and N3-H3A···O9 [d_{D-A} 2.993(6) Å; <D–H····A 158°] interactions. Moreover, a few C–H···O interactions are present in this structure which helps its expansion to the uni dimension (Figure 19C).



Figure 19 - (A) Crystal structure of **9**. (B) Schematic representation of **9**. (C) Hydrogen bonded one dimensional packing diagram of complex **9**.

The single crystal X-ray analysis of **10** [Zn₅(L3)₄(OH)₂(H₂O)₄]_n reveals that it is a two-dimensional infinite framework constructed by Zn(II) ions and deprotonated L3²⁻ ligands which crystallize in the triclinic P-1 space group. The asymmetric unit contains 2.5 Zn²⁺ ions, two deprotonated L3²⁻ ligands, one hydroxo and two water molecules (Figure 20). Framework **10** contains three different types of Zn(II) atoms with respect to their coordination environments. The Zn1 and Zn2 have octahedral coordination environments whereas the Zn3 has a tetrahedral geometry (Figure 20C). The Zn1 cation is bound to two of the O-atoms of two distinct L3²⁻ ligands [Zn1–O2, 2.080(4) Å] and further to two μ_3 -bridging hydroxo and two water molecules [Zn1–O13, 2.041(5) Å and Zn1–O14, 2.186(5) Å]. The coordination sphere around the Zn2 centre is fulfil then by the O-atoms from three L3² ligands [Zn2–O1, 2.051(4) Å, Zn2–O5, 2.059(5) Å and Zn2–O11, 2.085(4) Å], one μ_3 -bridging hydroxo [Zn2–O13, 2.095(4) Å], one bridging water [Zn2–O14, 2.222(5) Å] and the remaining site is engaged with a monodentate water molecule [Zn2-O15, 2.070(5) Å]. The tetrahedral coordination scheme around the Zn3 centre is occupied by three O-atoms from three different L3²⁻ ligands [Zn3–O6, 1.995(5) Å, Zn3–O7, 1.937(5) Å and Zn3–O12, 1.958(5) Å] and the remaining site is occupied by a µ3-OH group [Zn3–O13, 2.095(4) Å]. Therefore, two different types of ligands are present in this framework (Fig. 20C): one ligand coordinates to four different metal ions whereas the other coordinates to three metal centres. The Zn-ions are arranged in pentanuclear clusters (Figure 20B).

The minimum Zn1·····Zn2, Zn1·····Zn3 and Zn2····Zn3 distances are 3.1037 Å, 3.5878 Å and 3.183(1) Å, respectively. Association of eight L3²⁻ ligands and penta-nuclear [Zn₅(μ_3 -OH)₂(μ_2 -H₂O)₂] cluster results in the formation of 2D framework polymeric arrays propagating along the *b*-axis (Figures 20D and 20E). This 2D polymeric architecture of **10** also has some open channels with approximate dimension of 10 X 10 Å² (Figure 20D) and a void space of 26.8% per unit cell (PLATON)⁷³ after removing the non-coordinated solvent molecules.









Figure 20 - (A) The structure of **10** with partial atom labelling scheme. (B) Penta-nuclear secondary building block of **10**. (C) Schematic representation of **10**. (D) 2D structure of **10**. (E) 2D structure of **10** (another angle of view).

CHAPTER 6: Catalytic studies

Catalytic Activity in the Henry (nitroaldol) reaction

We have tested the activity of the coordination polymers 1 - 3 and 6 - 10 as heterogeneous catalysts in the Henry (nitroaldol) reaction of various aldehydes with nitroethane. In a typical reaction, a mixture of benzaldehyde (51 µL, 0.50 mmol), nitroethane (200 µL, 2.8 mmol), and catalyst (10.7 mg of 1, 5.73 mg of 2, 28.53 mg of 3, 7.3 mg of 6, 9 mg of 7, 11.7 mg of 8, 22.8 mg of 9, or 20.25 mg of 10, 3 mol% *vs* substrate) was placed in a capped glass vessel, and then 1 ml of H₂O was added into it. The mixture was heated at 70 °C for 48 h and subsequently quenched by centrifugation and extracted with DCM at room temperature. The remaining organic solution was then evaporated under vacuum and the crude product was dissolved in CDCl₃ and analysed by ¹H NMR. The ¹H NMR spectra and the calculation of the yield for products is exemplified in the Appendix by using compound **3** as catalyst (Equations 1-4 and Figure A/7).

By using benzaldehyde as a test substrate, we found that **3** led to the highest product yield, as compared to the other compounds, after the same reaction time and temperature. Consequently, the optimization of the reaction conditions (temperature, reaction time, amount of catalyst, solvent) was carried out in a model nitroethane – benzaldehyde system with **3** as the catalyst (Scheme 9 with typical reaction conditions; Table 1).



Scheme 9 - Henry (nitroaldol) reaction of benzaldehyde with nitroethane in typical conditions.

Under the above typical conditions (3 mol% of solid **3** at 70 °C with water as the best solvent, as indicated below), a conversion of 84% of benzaldehyde into the β -nitroalkanol is reached (entry 6, Table 1) after 48 h. With compounds **1**, **2**, **6**, **7**, **8**, **9**, **10**, yields of 70%, 48%, 69%, 74%, 68%, 68.5% and 60% were obtained, respectively. Hence, our seven compounds activities follow the order of **3**>**7**>**1**>**6**>**9**>**8**>**10**>**2**. The plot of yield versus time for the Henry reaction of benzaldehyde and nitroethane with compound **3** is presented in Figure 21.

A blank reaction was tested with benzaldehyde in the absence of catalyst, at 70 °C in water, and no conversion of aldehyde into β -nitroalkanol was detected, after 48h. The reaction took place after using the free pro-ligands (H₄L1, H₂L2 and H₂L3) instead of catalyst **3**, with a small conversion of the aldehyde into the β -nitroalkanol, after 48h (H₄L1 giving the highest yield 17%). We've also tested the activity of different nitrate salts of cobalt, zinc, cadmium and samarium, obtaining yields of 9-14%.

Table 1: Optimization of the parameters of the Henry nitroaldol reaction between benzaldehyde and nitroethane ^a									
Entry	Catalyst	Time (h)	Amount of Catalyst (mol%)	T (℃)	Solvent	Yield (%) ^b	Selectivity (syn/anti) ^c	TONd	
1	3	1	3.0	70	H₂O	34	68·32	11	
2	3	3	3.0	70	H ₂ O	55	69·31	18	
3	3	6	3.0	70	H ₂ O	65	70:30	22	
4	3	12	3.0	70	H ₂ O	73	69:31	24	
5	3	24	3.0	70	H ₂ O	76	68:32	25	
6	3	48	3.0	70	H ₂ O	84	70:30	28	
•	,		Different a	mounts of c	atalyst 3	0.			
7	3	48	1.0	70	H ₂ O	80	79:21	80	
8	3	48	5.0	70	H ₂ O	85	80:20	17	
			Diffe	erent Solven	ts				
9	3	48	3.0	70	THF	64	76:24	21	
10	3	48	3.0	70	MeOH	77	84:16	26	
	Different Temperatures								
12	3	48	3.0	30	H ₂ O	7	84:16	2	
13	3	48	3.0	50	H ₂ O	67	82:18	22	
14	3	48	3.0	100	H ₂ O	46	73:27	15	
			Oth	ner catalysts	6				
15	1	48	3.0	70	H ₂ O	70	70:30	23	
16	2	48	3.0	70	H ₂ O	48	77:23	16	
19	6	48	3.0	70	H ₂ O	69	71:29	23	
20	7	48	3.0	70	H ₂ O	74	81:19	25	
21	8	48	3.0	70	H ₂ O	68	80:20	23	
22	9	48	3.0	70	H ₂ O	69	71:29	23	
23	10	48	3.0	70	H ₂ O	60	78:22	20	
			Blai	nk Reaction	S				
24	Blank	48	-	70	H ₂ O	-	-	-	
25	Zn(NO3)2.6H2O	48	3.0	70	H ₂ O	14	78:22	5	
26	Cd(NO ₃) ₂ .4H ₂ O	48	3.0	70	H ₂ O	11	73:27	4	
27	Co(NO ₃) ₂ .6H ₂ O	48	3.0	70	H ₂ O	9	72:28	3	
28	Sm(NO3)3.6H2O	48	3.0	70	H ₂ O	12	76:24	4	
29	H ₄ L1	48	3.0	70	H ₂ O	17	77:23	6	
30	H ₂ L2	48	3.0	70	H ₂ O	14	76:24	5	
31	H ₂ L3	48	3.0	70	H ₂ O	16	78:22	5	
^a Reaction and wat	^a Reaction conditions: 3.0 mol% of catalyst, benzaldehyde (52 μL, 0.5 mmol), nitroethane (0.2 mL, 2.67 mmol) and water (1.0 mL). ^b Number of moles of β-nitroalkanol per 100 moles of aldehyde. ^c Calculated by ¹ H NMR. ^d Number of moles of β-nitroalkanol per mole of catalyst.								



Figure 21 - Plot of yield vs time for the reaction of benzaldehyde and nitroethane with water as solvent and at $T = 70 \text{ }^{\circ}\text{C}$, in the presence of catalyst **3**.

We also have tested the activity of compound **3** in the reactions of a variety of para-substituted aromatic aldehydes, cinnamaldehyde and acetaldehyde with nitroethane, and obtained the corresponding β -nitroalkanols with yields ranging from 21 up to 99 % (see table 2). The nature of the substrates is an important factor. Indeed, aryl aldehydes bearing electron-withdrawing groups (nitro, chloro and hydroxy) exhibit higher reactivity (Table 2, entries 1, 3 and 5) as compared to those having electron-donating moieties, which may be related to an increase of the electrophilicity of the substrate in the former case. We have also concluded that can exist a cause-effect relationship between the rigidity and the addition type. It seems that the increase of the substrate rigidity is linked to the occurrence of *anti*-addition (comparing entries 1 and 2 with entry 7 of table 2).

We also concluded that a decrease in solvent polarity as also an effect in the substrate diffusion along the catalyst porous channels to the active site, where the reaction occurs. That fact could explain the catalyst increasing reactivity but simultaneously the stereoselectivity decrease, which is probably why the use of less polar solvents (THF and MeOH, respectively entries 9 and 10, table 1) affects the stereoselectivity and the reaction yield.

Comparing the obtained values for this heterogeneous catalyst with homogeneous counterparts, we see that although already published results are slightly better,^{74,75} it is important to notice that usually homogeneous catalysts have higher contact with the reactional mixture (since are in the same phase), but disadvantages regarding a final separation.

Analysing also the turnover number in terms of moles of the active sites we conclude that, for the number of active sites it possesses, the inactivity of the catalyst occurs in less cycles than for other catalysts such as, e.g., compound **10**. In the figure 22, is proposed the catalytic cycle for the Henry reaction catalysed by **3**.

	Table 2: Henry reaction of various aldehydes and nitroethane with catalyst 3 ^a								
Entry	Aldehyde	Yield(%) ^b	Selectivity ^c (<i>syn/anti</i>)	TON ^d					
1	02N-СНО	95	75:25	32					
2	н ₃ со—Сно	21	77:23	7					
3	СІ— СНО	70	81:19	23					
4	н ₃ с-Сно	54	82:18	18					
5	но-Сно	66	76:14	22					
6	СНО	63	81:19	21					
7	Acetaldehyde	99	88:12	33					
^a Reaction conditions unless stated otherwise: 3.0 mol% of catalyst 3 , aldehyde (0.5 mmol), nitroethane (0.2									
mL, 2.6	mL, 2.6 mmol) and water (1.0 mL). ^b Number of moles of β -nitroalkanol per 100 moles of aldehyde.								
^c Calculated by ¹ H NMR. ^d Number of moles of β -nitroalkanol per mole of catalyst									



Figure 22 - Proposed catalytic cycle for the formation of the β -nitroalkanol in Henry reaction catalysed by **3**.

Catalytic Activity in the Knoevenagel Condensation reaction

We have also tested the activity of the coordination polymers 1 - 3 and 6 - 10 as heterogeneous catalysts in the Knoevenagel condensation reaction with various aldehydes. In a typical reaction, a mixture of benzaldehyde (51 µL, 0.50 mmol), malononitrile (66 mg, 1 mmol), and catalyst (10.7 mg of 1, 5.73 mg of 2, 28.53 mg of 3, 7.3 mg of 6, 9 mg of 7, 11.7 mg of 8, 22.8 mg of 9, or 20.25 mg of 10, 3 mol% *vs* substrate) was placed in a capped glass vessel, and then 1 ml of THF was added. The mixture was heated at 50 °C for 1.5 h and subsequently quenched by centrifugation at room temperature. The solvent was then evaporated under vacuum and the crude product was dissolved in CDCl₃ and analysed by ¹H NMR. The ¹H NMR spectra and the calculation of the yield for compound 9 are presented in Appendix (see Figure A/8).

By using benzaldehyde as a test compound, we found that 9 led to the highest product yield, as compared to the other compounds after the same reaction time and temperature. Consequently, the optimization of the reaction conditions (temperature, reaction time, amount of catalyst, solvent) was carried out in a model malononitrile – benzaldehyde system with 9 as the catalyst (Scheme 10 with typical reaction conditions; Table 3).



Scheme 10 – Knoevenagel condensation reaction of benzaldehyde with malononitrile in typical conditions.

Under the above typical conditions (3 mol % of solid **9** at 50 °C with THF as the best solvent, as indicated below), a conversion of 99% of benzaldehyde into α , β -unsaturated ketone is reached (entry 4, Table 3) after 1.5 h. With compounds **1**, **2**, **3**, **6**, **7**, **8**, **10**, yields of 65%, 87%, 80%, 91%, 84%, 73% and 94% were obtained, respectively. Hence, our seven compounds activities follow the order of **9**>**10**>**6**>**2**>**7**>**3**>**8**>**1**. The plot of yield versus time for the Henry reaction of benzaldehyde and malononitrile with compound **9** is presented in Figure 23.

A blank reaction was tested with benzaldehyde in the absence of catalyst, at 50 °C in THF, and no conversion of aldehyde into α , β -unsaturated ketone was detected, after 1.5 h. The reaction also didn't take place after using the free pro-ligands (H₄L1, H₂L2 and H₂L3) instead of catalyst **9**. We've also checked the reaction with the different nitrate salts (cobalt, zinc, cadmium and samarium), obtaining respectively yields on the order of 26-31%.

Table 3: Optimization of the parameters of the Knoevenagel condensation reaction between benzaldehyde and malononitrile ^a										
Entry	Catalyst	Time (h)	Amount of Catalyst (mol%)	T (℃)	Solvent	Yield (%) ^b	TON°			
1	9	0.3	3.0	50	THF	53	18			
2	9	0.6	3.0	50	THF	72	24			
3	9	1.0	3.0	50	THF	84	28			
4	9	1.5	3.0	50	THF	99	33			
Different amounts of catalyst 9										
5	9	1.5	1.0	50	THF	97	97			
6	9	1.5	5.0	50	THF	>99	20			
			Different so	olvents						
7	9	1.5	3.0	50	CH₃CN	93	31			
8	9	1.5	3.0	50	MeOH	92	31			
	Different temperature									
9 9 1.5 3.0 RT THF 38 11										
	Other catalysts									
10	1	1.5	3.0	50	THF	65	22			
11	2	1.5	3.0	50	THF	87	29			
12	3	1.5	3.0	50	THF	80	27			
13	6	1.5	3.0	50	THF	91	30			
14	7	1.5	3.0	50	THF	84	28			
15	8	1.5	3.0	50	THF	73	24			
16 10		1.5	3.0	50	THF	94	31			
			Blank Rea	ictions						
17	Blank	1.5	-	50	THF	24	0			
18	Zn(NO3)2.6H2O	1.5	3.0	50	THF	31	10			
19	Cd(NO ₃) ₂ .4H ₂ O	1.5	3.0	50	THF	29	10			
20	Co(NO ₃) ₂ .6H ₂ O	1.5	3.0	50	THF	26	9			
21	Sm(NO3)3.6H2O	1.5	3.0	50	THF	30	10			
22	H4L1	1.5	3.0	50	THF	No reaction	0			
23	H₂L2	1.5	3.0	50	THF	No reaction	0			
24	H ₂ L3	1.5	3.0	50	THF	No reaction	0			
aRe malono	^a Reaction conditions unless stated otherwise: 3.0 mol% of catalyst, solvent (THF) 1 mL, malononitrile (66 mg, 1.0 mmol) and benzaldehyde (52 μL, 0.5 mmol). ^b Calculated by ¹ H NMR. ^c Number of moles of product per mole of catalyst.									



Figure 23 - Plot of yield vs time for the Knoevenagel condensation reaction of benzaldehyde and malononitrile with THF as solvent and $T = 50 \, {}^{\circ}$ C, in the presence of catalyst **9**.

We have also performed the Knoevenagel condensation reaction of various aldehydes (aromatic and aliphatic) with malononitrile catalysed by compound **9**, producing the corresponding α , β -unsaturated ketone with yields ranging from 32 up to >99 % (see table 4).

The aldehydes containing electron-withdrawing groups exhibit higher reactivity (Table 4, entries 1, 3 and 5) as compared to those having electron-donating moieties, which may be related to an increase of the electrophilicity of the substrate in the former case.

Already published works using homogeneous catalysts usually have better results⁷⁶ but in this case compound **9** showed in comparison (since its heterogeneous and so, theoretically, less active) very good results.

In an ultimate analysis, if we compare the nuclearity of compound **9** with compound **10** we realize that, even with the highest yield, if we analyse the turnover number in terms of moles of product per moles of active sites (moles of the metal centre) for compound **9** this property is slightly smaller. In figure 24 it is represented the proposed catalytic cycle for the Knoevenagel condensation reaction catalysed by compound **9**.

Table 4: Knoevenagel condensation reaction of various aldehydes with malononitrile with									
	catalyst 9 ª								
Entry	Compound	Yield ^b (%)	TON ^c						
1	O ₂ N-CHO	>99	33						
2	н₃со-√сно	32	11						
3	СІ—	98	33						
4	н ₃ с-Сно	51	17						
5	но-Сно	48	16						
6	CHO	50	17						
7	7 Acetaldehyde 92 31								
^a Reaction conditions: 3.0 mol% of catalyst 9 , solvent (THF) 1 mL, malononitrile (66 mg, 1.0									
mmol) and benzaldehyde (52 $\mu L,$ 0.5 mmol). $^{b}\text{Calculated}$ by ^{1}H NMR. $^{c}\text{Number}$ of moles of									
product per mole of catalyst.									



Figure 24 - Proposed catalytic cycle for the Knoevenagel condensation reaction catalysed by $\mathbf{9}$ (X = O or N of a coordinated group).

Catalytic Activity in the microwave-assisted solvent-free peroxidative

oxidation of secondary alcohols to the corresponding ketone

We have tested the catalytic activity of the coordination polymers **4** and **5** as heterogeneous catalysts in microwave-assisted solvent-free peroxidative oxidation carried out under mild conditions, using *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant (Scheme 11).

In a typical reaction, a mixture of 1-phenylethanol, *t*-BuOOH (aq. 70%, 2 eq) as the oxidizing agent and catalyst (6.8 mg of **4** or 10.8 mg of **5**, 20 µmol) was placed in a capped glass vessel, and no solvent was added into it.

Typical conditions consisted of 1 h reaction time, at 80 °C and under low-power (between 10 and 25 W) microwave irradiation. At the end, to the reaction mixture was added 10 mL of Et₂O and 90 μ L of cycloheptanone, and a 0.4 μ L was taken and injected in the gas chromatography. Yield calculations are present in the Appendix (Equation 5 – 8 and Figures A/9 and A/10).

Acetophenone is the only product detected in the assayed conditions. The results of these tests, in terms of yield and of turnover number (TON, moles of product/mol of catalyst), are summarized in Table 5.



Scheme 11 - Peroxidative oxidation reaction of 1-phenylethanol into acetophenone in microwave (MW) solvent-free conditions.

Under typical reaction conditions (80 °C and 1h reaction time) acetophenone yields up to 8% (TON = 75) for catalyst **4** (entry 1) and 11% (TON = 95) for catalyst **5** (entry 10), in the absence of any additive were obtained.

With the aim to increase the yields of the reaction in solvent-free MW-assisted peroxidative oxidation of the above-mentioned substrate, the influence of 2,2,6,6-tetramethylpiperidyl-1-oxyl radical (TEMPO) was investigated.⁷⁷

However, contrary to what was previously observed, we found that the addition of TEMPO has an inhibition effect on the yield of reaction (entry 5 and entry 14, respectively using catalyst **4** and **5**).

We also found that increasing the amount of catalyst does not increase the yield of reaction but, by the contrary, decreases it.

The temperature has an important effect on the catalytic system, since changing the temperature from 80 °C to 120 °C (comparison between entries 1 and 4, for complex 4, and between entries 10 and 13, for compound 5) results in a yield increase from 8% to 43%, in the case of 4, and from 11% to 42%, in the case of 5. Further conditions will be investigated in the future, to analyse the influence of the additives in the deactivation of the catalyst, and what would be the ideal reaction temperature.

Comparing with already published works using homogeneous catalysts for this reaction,⁷⁸ we see that both compounds have modest but interesting results.

Tabl	l e 5: Optimiz oxio	zation of the pa dation of 1-phe	arameter enylethar	s for the microwave- nol under mild condit	assisted (N	/W) solvent-free p atalyst 4 and 5 ª.	eroxidative
Entry	Catalyst	Additive (µmol)	Time (h)	Time Amount of (h) Catalyst (µmol)		Acetophenone Yield (%) ^b	TON ^c
1		-	1		80	8	75
2		-	0.5		80	5	53
3		-	3		80	17	173
4		-	1	20	120	43	425
5	4	TEMPO (50 µmol)	1		80	4	45
6		TEMPO (50 µmol)	O 1 ol) 1		120	36	361
7		-	1	40	120	33	334
8		-	1	80	120	23	233
9		HPCA (50 µmol)		20	120	36	358
Entry	Catalyst	Additive	Time	Amount of	T (°C)	Acetophenone	TON℃
Lindy	Outaryot	(µmol)	(h)	(h) Catalyst (µmol)		Yield (%) ^b	TOIL
10		-	1		80	11	95
11		-	0.5		80	8	82
12		-	3		80	10	111
13		-	1	20	120	42	420
14	5	TEMPO (50 µmol)	1		80	6	56
15	5	TEMPO (50 µmol)	1		120	36	363
16		-	1	40	120	31	308
17		-	1	80	120	28	283
18		HPCA (50 µmol)	1	20	120	18	183
· ·					- (10.0		

^aTypical reaction conditions: 0.4 mol% of catalyst **4** (6.8 mg) or **5** (10.8 mg), 1-phenylethanol (0.600 ml; 5 mmol), TBHP (aq. 70%) (0.688ml; 10 mmol). ^bNumber of moles of acetophenone per 100 moles of 1-phenylethanol. ^cNumber of moles of acetophenone per mole of catalyst.

Catalytic Activity in the oxidation of toluene to benzyl alcohol and

<u>benzaldehyde</u>

The substrate toluene was used as model substrate to investigate the catalytic performance of the Cu(II) complex **4** and compound **5** in the peroxidative oxidation of toluene, using hydrogen peroxide (H_2O_2) as oxidant (Scheme 12).

In a typical reaction, a mixture of toluene, H_2O_2 (30 v/v) as the oxidizing agent and catalyst (6.8 mg of **4** and 10.8 mg of **5**, 20 µmol) was placed in a capped glass vessel, and MeCN was added, and the system left under stir for 24 h, at 50 °C. At the end, to the reaction mixture was added 5 mL of MeCN and 300 µL of benzaldehyde, and a 0.4 µL was taken and injected in the gas chromatography. Benzyl alcohol and benzaldehyde are the only products detected in the assayed conditions. The results of these tests, in terms of yield and of turnover number (TON, moles of product/mol of catalyst), are summarized in Table 6.



Scheme 12 - Oxidation reaction of toluene into benzyl alcohol and benzaldehyde under mild conditions.

Under typical reaction conditions (50 °C and 24 h) benzaldehyde yields are very modest (maximum of 5% yield, TON = 27, for catalyst **4**, entry 1, and 6%, TON = 30, for catalyst **5**, entry 6). With the aim to increase the activity of **4** and **5** in the oxidation of toluene the influence of additives was investigated. In the case of catalyst **4**, there is an increase of 2% with the addition of HNO₃ or TFA (respectively entries 3 and 5) with an increase of TON to 33 and 36 respectively. In the case of catalyst **5**, the use of additives had an opposite effect (a decrease of 2% in the yield).

Further conditions will be investigated in the future, to analyse the influence of additives and of temperatures in the reaction yields and, furthermore, why in the case of oxidation of toluene, the catalytic activity is so low.

	Table 6-A: Peroxidative oxidation of toluene under mild conditions with catalysts 4. ^a										
Entry	Catalyst	Additive (µmol)	Time (h)	Amount of Catalyst (µmol)	7 (℃)	Solvent	Benzaldehyde Yield (%) ^b	Benzyl Alcohol Yield (%) ^c	Selectivity towards Benzaldehyde ^d	TON⁰	
1	4	-					5	0	1.00	27	
2	4	HPCA (0.125 mmol)						0	0	-	0
3	4	HNO ₃ (0.125 mmol)	24	20	50	MeCN	7	0	1.00	33	
4	4	TEMPO (0.125 mmol)					0	2	0.00	10	
5	4	TFA (0.0262 μmol)					7	0	1.00	36	
^a Typi	^a Typical reaction conditions: $0.4 \text{ mol}\%$ of catalyst 4 (6.8 mg) tolyana (0.610 ml : 5.7 mmol) $H_{2}O_{2}$ (1.02 ml : 33.3 mmol)										

^a Typical reaction conditions: 0.4 mol% of catalyst **4** (6.8 mg), toluene (0.610 mL; 5.7 mmol), H₂O₂ (1.02 mL; 33.3 mmol) and acetonitrile (3.0 mL). ^b Number of moles of benzaldehyde per 100 moles of toluene. ^cNumber of moles of benzyl alcohol per 100 moles of toluene. ^d Selectivity of the reaction towards Benzaldehyde. ^eSum of number of moles of selected products (benzaldehyde and benzyl alcohol) per mole of catalyst.

Table 6-B: Peroxidative oxidation of toluene under mild conditions with catalysts 5. ^a										
Entry	Catalyst	Additive (µmol)	Time (h)	Amount of Catalyst (µmol)	7 (℃)	Solvent	Benzaldehyde Yield (%) ^b	Benzyl Alcohol Yield (%) ^c	Selectivity towards Benzaldehyde ^d	TON ^e
6	5	-			50	MeCN	6	0	1.00	30
7	5	HPCA (0.125 mmol)					0	0	-	0
8	5	HNO₃ (0.125 mmol)	24	20			4	6	0.39	47
9	5	TEMPO (0.125 mmol)					0	0	-	0
10	5	ΤFA (0.0262 μmol)					4	0	1.00	22

^a Typical reaction conditions: 0.4 mol% of catalyst 5 (10.8 mg), toluene (0.610 mL; 5.7 mmol), H₂O₂ (1.02 mL; 33.3 mmol) and acetonitrile (3.0 mL). ^b Number of moles of benzaldehyde per 100 moles of toluene. ^cNumber of moles of benzyl alcohol per 100 moles of toluene. ^d Selectivity of the reaction towards Benzaldehyde. ^eSum of number of moles of selected products (benzaldehyde and benzyl alcohol) per mole of catalyst.

CHAPTER 7: Sensing studies

The investigation of the sensing properties of compounds **2** and **3** was undertaken following a simple procedure developed for the analysis of the quenching interactions of a compound with different ion solutions of known.

Typical conditions consisted in the preparation of different ion solutions with 10^{-2} M concentration of different cations and anions (see Figure 25 and 27). Those solutions were then added to a glass vessel, followed by the addition of 3 mg of compound (**2** or **3**). After stirring for 1h, all the samples were kept at room temperature for 48 h. Afterwards we have measured the fluorescence intensity of all samples in a Spectrofluorimeter by using a quartz cell.

Compound **2** exhibited an emission peak at 438 nm upon excitation at 310 nm. This emission band can be assigned to ligand-centred emission, because similar emission was observed at 445 nm for H₄L1. The luminescent property of **2** led us to investigate its potential application in the detection of common metal ions. The luminescence spectra of **2** dispersed in the water solutions containing different metal ions (3 mL, 10^{-2} mol.dm⁻³) were studied (Figure 26), and compared and we found that only Fe(II), Fe(III) and MnO₄⁻ ions can bring essentially complete quenching to the system. Ions like Br⁻, BF₄⁻ and Co(II) also showed good quenching abilities for compound **2** (although not total quenching as in the previous cases). This result demonstrates that **2** can be highly effective and a selective luminescent sensor for Fe(II), Fe(III) and MnO₄⁻ ions.



Figure 25 - Excitation and emission intensities in the fluorescence spectra of compound **2** for some ion aqueous solutions with 10^2 M concentration, with emission peak at 438 nm upon excitation at 310 nm.



Figure 26 - Emission spectra of **2** towards different metal ions in water solution (of 10^{-2} M concentration), with an emission peak wavelength of 438 nm.

In compound **3**, the emission peak appeared at 450 nm upon excitation at 310 nm. Also, as the previous case, this emission band can be assigned to ligand-centred emission. The luminescence spectra of compound **3** dispersed in the ionic aqueous solutions, was quenched by Fe(II), Fe(III) and MnO₄⁻ ions (Figure 28). Br⁻, BF₄⁻, Co(II), I⁻ and Cu(II) also showed good quenching properties towards compound **3**. This result demonstrates that **3** also can also be highly effective and selective luminescent sensors for Fe(II), Fe(III) and MnO₄⁻ ions.



Figure 27 - Excitation and emission intensities in the fluorescence spectra of compound **3** for some ion aqueous solution with 10^{-2} M concentration, with emission peak at 450 nm upon excitation at 310 nm.



Figure 28 - Emission spectra of **3** towards different metal ions in water solution (of 10^{-2} M concentration), with an emission peak wavelength of 450 nm.

CHAPTER 8: Experimental Section

The synthetic work was performed in air. All the chemicals were obtained from commercial sources and used as received. The ¹H NMR spectra was recorded at room temperature on a Bruker Avance II + 300 (UltraShieldMagnet) spectrometer operating at 300 MHz for proton. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. ¹H abbreviations: s = singlet, d = doublet, t = triplet, q = quartet. The FT-IR (4000-400 cm⁻¹) were recorded on a Bruker Vertex 70 instrument in KBr pellets. Abbreviations: s = strong, m = medium, w = weak, bs = broad and strong, mb = medium and broad. X-ray quality single crystals of the compounds were immersed in cryo-oil, mounted in a nylon loop and measured at room temperature (**1-10**). Intensity data were collected using a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromatic Mo-K α (λ 0.71069) radiation. The products of the catalysed oxidation reactions were analysed by gas chromatography, by using a Fisons Trio 2000 Gas Chromatography/Mass Spectrometer. The fluorescence spectra were recorded on a Spectrofluorimeter Perkin Elmer LS55 Perkin Elmer Lambda 35, where samples were placed in a 3 mL quartz cell.

Synthesis of 5,5'-[(pyridine-2,6-dicarbonyl)bis(azanediyl)] diisophthalic acid (H₄L1)

Preparation of two different solutions, one with the methyl ester of 5-aminoisophthalic acid (MW = 194 g.mol⁻¹; m = 388 mg) with 20ml of dichloromethane (DCM), and another of 2,6-Pyridinedicarboxylic acid chloride (MW = 204 g.mol⁻¹; m = 204 mg) with 5ml DCM.

After stirring until dissolution of the methyl ester of 5-aminoisophthalic acid solution, addition of 600 μ L of trimethylamine drop wise followed by addition of the second solution, and stir overnight at room temperature (RT). The mixture was taken to dryness, then addition of water and filtration.

After drying the precipitate (which is the ester of the ligand), the product was hydrolysed as follows.

Addition of 30 ml of tetrahydrofuran (THF) to the dried precipitate, and stir until complete dissolution. Preparation of a sodium hydroxide solution (MW = 40 g.mol⁻¹; m = 50 mg) with 10 ml of water. Addition drop wise the NaOH aqueous solution drop wise to the ester solution while stirring, reflux for 1 hour and then stir at RT overnight.

After reaction completion, total evaporation of THF. Addition of HCl drop wise until reaction mixture becomes acidic. Filtration of the formed precipitate.

1H-NMR (DMSO-d6): 12.89 (2H, bs, -COOH), 11.21 (2H, s, -NH), 8.74 (2H, s, Ar-H), 8.67 (4H, s, Ar-H), 8.20-8.31 (3H, m, Ar-H). FT-IR (KBr, selected peaks)[cm-1]: 3466 (bs), 1713 (s), 1649 (m), 1550 (s), 1453 (s), 1385 (w), 1296 (s), 1227 (m), 1147 (m), 1083 (m), 1000 (m), 908 (w), 844 (w), 758 (s), 667 (s), 601 (m).

Synthesis of 3,3'-[(pyridine-2,6-dicarbonyl)bis(azanediyl)] dibenzoic acid

<u>(H₂L2)</u>

The first step is the formation of methyl ester of 3-amino benzoic acid. The remaining steps are made in the same way as in the synthesis of H_4L1 , changed only for each ligand the different methyl ester produced.

Addition to 2g of 3-amino benzoic acid (MW = 121 g.mol⁻¹) of 20 ml methanol (MeOH), and stir until complete dissolution. Addition to the reaction mixture of 8 ml sulfuric acid (H_2SO_4), drop wise, and reflux overnight.

After completion, evaporation of the remaining MeOH from the reaction mixture. Addition of sodium bicarbonate (NaHCO₃) until the mixture becomes completely neutral. Addition of sufficient DCM (around 40 ml) to the reaction mixture, to proceed to liquid – liquid extraction. Since the ester must be solubilized in the organic solution, addition of 1 - 2 g of sodium sulphate (Na₂SO₄) to absorb the remaining water. Remove the solid by filtration, until obtain a clear organic solution.

Extraction of DCM by evaporation, until dryness. Collect the methyl ester of 3-amino benzoic acid.

The second step is like the synthesis of H_4L1 , using methyl ester of 3-amino benzoic acid in place of methyl ester of 5-aminoisophthalic acid.

1H-NMR (DMSO-d6): 13.18 (2H, bs, -COOH), 11.19 (2H, s, -NH), 8.56 (2H, s, Ar-H), 8.45 (2H, d, Ar-H), 8.18-8.35 (3H, m, Ar-H), 7.79 (2H, d, Ar-H), 7.60 (2H, t, Ar-H). FT-IR (KBr, selected peaks)[cm-1]: 3462 (bs), 1701 (s), 1661 (s), 1591 (s), 1553 (m), 1487 (w), 1441 (s), 1297 (s), 1230 (m), 1141 (m), 1082 (m), 946 (m), 815 (m), 758 (s), 739 (s), 679 (s), 564 (w).

Synthesis of 4,4'-[(pyridine-2,6-dicarbonyl)bis(azanediyl)] dibenzoic acid (H₂L3)

This ligand was synthesized similarly to ligand H₂L2, using 4-amino benzoic acid in place of 3-amino benzoic acid.

1H-NMR (DMSO-d6): 13.14 (2H, bs, -COOH), 11.27 (2H, s, -NH), 8.43 (2H, d, Ar-H), 8.34 (1H, d, Ar-H), 8.05 (8H, m, Ar-H). FT-IR (KBr, selected peaks)[cm-1]: 3447 (bs), 1689 (s), 1609 (s), 1537 (s), 1410 (s), 1320 (s), 1300 (s), 1242 (s), 1179 (s), 1120 (m), 1085 (m), 1000 (m), 932 (m), 854 (s), 770 (s), 748 (s), 714 (m), 552 (m).

Synthesis of compounds 1 – 10.

Compound 1

A solution of H₄L1 (12.3 mg; 0.025mmol) with cobalt(II) nitrate hexahydrate (14.6mg; 0.050 mmol), in a 2ml solution of MeOH was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **1**.

FT-IR (KBr, selected peaks)[cm-1]: 3490 (mb), 1572 (m), 1384 (m), 1298 (w), 1003 (w), 759 (w), 722 (w). MW (based on X-ray analysis) considering C₂₈H₃₃CoN₃O₁₅: 710.50 g.mol⁻¹.

Compound 2

A solution of H₄L1 (12.3 mg; 0.025mmol) with zinc(II) nitrate hexahydrate (14.9mg; 0.050 mmol), in a 2ml solution of DMF with ammonium hydroxide (NH4OH) was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **2**.

FT-IR (KBr, selected peaks)[cm-1]: 3436(bs), 2361(w), 1558(s), 1384(s), 1227(m), 1151(w), 1105(w), 1081(w), 906(w), 765(w), 726(w), 670(w), 604(w), 457(w). MW (based on X-ray analysis) considering C₂₃H₂₇N₃O₁₈Zn₂: 764.21 g.mol⁻¹.

Compound 3

A solution of H₄L1 (12.3 mg; 0.025mmol) with cadmium(II) nitrate tetrahydrate (15.4mg; 0.050 mmol), in a 2ml solution of DMF with sodium azide (NaN₃) was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **3**.

FT-IR (KBr, selected peaks)[cm-1]: 3854(w), 3587(m), 3519(m), 2361(w), 2070(s), 1735(m), 1679(w), 1650(w), 1624(m), 1552(m), 1435(m), 1252(m), 1078(m), 753(m). MW (based on X-ray analysis) considering $C_{70}H_{80}Cd_3N_{14}O_{28}$: 1902.68 g.mol⁻¹.

Compound 4

A solution of H_2L2 (10.1 mg; 0.025mmol) with copper(II) nitrate pentahemihydrate (11.6mg; 0.050 mmol), in a 2ml solution of DMF and MeOH (1:2) was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small blue crystals of **4**.

FT-IR (KBr, selected peaks)[cm-1]: 3466 (bs), 2361 (w), 1682 (m), 1612 (m), 1560 (s), 1491 (w), 1403 (s), 1385 (s), 1245 (m), 1152 (w), 1074 (w), 1002 (w), 902 (w), 808 (w), 770 (m), 681 (m), 601 (w), 492 (w). MW (based on X-ray analysis) considering C_{11.50}H₁₀CuN₂O₆: 335.75 g.mol⁻¹.

Compound 5

A solution of H₂L2 (10.1 mg; 0.025mmol) with copper(II) nitrate pentahemihydrate (11.6mg; 0.050 mmol), in a 2ml solution of DMF was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small blue crystals of **5**.

FT-IR (KBr, selected peaks)[cm-1]: 3433(bs), 2360(w), 1668(s), 1585(s), 1385(s), 1079(w), 768(m), 679(m), 502(m), 431(w). MW (based on X-ray analysis) considering C₂₄H₂₀CuN₄O₇: 539.98 g.mol⁻¹.

Compound 6

A solution of H₂L2 (10.1 mg; 0.025mmol) with zinc(II) nitrate hexahydrate (14.9mg; 0.050 mmol), in a 2ml solution of DMF and MeOH (1:2) with ammonium hydroxide (NH4OH) was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **6**. FT-IR (KBr, selected peaks)[cm-1]: 3372 (s), 3298 (bs), 3188 (s), 2362 (w), 1680 (s), 1665 (s), 1612 (s), 1579 (s), 1476 (m), 1440 (s), 1372 (s), 1321 (m), 1261 (s), 1145 (m), 1080 (m), 1001 (m), 944 (m), 822 (s), 769 (s), 748 (s), 675 (s), 595 (w), 538 (w), 426 (w). MW (based on X-ray analysis) considering $C_{30}H_{20}N_3O_{10}Zn_2$: 713.23 g.mol⁻¹.

Compound 7

A solution of H₂L2 (10.1 mg; 0.025mmol) with cadmium(II) nitrate hexahydrate (15.4mg; 0.050 mmol), in a 2ml solution of DMF and dioxane (1:2) with ammonium hydroxide (NH₄OH) was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **7**. FT-IR (KBr, selected peaks)[cm-1]: 3446 (b), 1574 (mb), 1384 (mb), 767 (w). MW (based on X-ray analysis) considering $C_{42}H_{34}Cd_2N_6O_{22}$: 1199.55 g.mol⁻¹.

Compound 8

A solution of H₂L2 (10.1 mg; 0.025mmol) with samarium(III) nitrate hexahydrate (22.2mg; 0.050 mmol), in a 2ml solution of DMF and 0.5ml of Water was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **8**.

FT-IR (KBr, selected peaks)[cm-1]: 3853(w), 3347(mb), 1670(m), 1540(s), 1407(s), 1160(w), 1079(m), 1003(w), 890(w), 773(m), 754(m), 673(m), 574(w), 435(w). MW (based on X-ray analysis) considering $C_{27}H_{29}N_6O_{12}Sm$: 779.91 g.mol⁻¹.

Compound 9

A solution of H₂L3 (10.1 mg; 0.025mmol) with zinc(II) nitrate hexahydrate (14.9mg; 0.050 mmol), in a 2ml solution of DMF was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **9**.

FT-IR (KBr, selected peaks)[cm-1]: 3429 (bs), 2361 (w), 1606 (mb), 1540 (w), 1384 (s), 1180 (w), 1000 (w), 783(w), 669 (w). MW (based on X-ray analysis) considering C₆₀H₈₄N₁₂O₂₆Zn₂: 1520.13 g.mol⁻¹.

Compound 10

A solution of H₂L3 (10.1 mg; 0.025mmol) with zinc(II) nitrate hexahydrate (14.9mg; 0.050 mmol), in a 2ml solution of DMF with ammonium hydroxide (NH₄OH) was prepared and then transferred and sealed in an 8ml glass vessel and heated (solvothermal reactor) at 70°C for 48h. Subsequent cooling of that solution to room temperature afforded small colourless crystals of **10**.

FT-IR (KBr, selected peaks)[cm-1]: 3358 (bs), 1589 (s), 1397 (m), 1352 (m), 1281 (m), 1027 (m), 768 (m). MW (based on X-ray analysis) considering C₂₇H_{31.50}N₅O_{10.50}Zn_{1.25}: 675.78 g.mol⁻¹.

Henry Reaction

The Henry (nitroaldol) reaction of benzaldehyde with nitroethane was carried out in a 5 mL glass vessel. To the glass vessel, a mixture of benzaldehyde (52 μ L, 0.5 mmol), nitroethane (0.2 mL, 2.6 mmol), water (1.0 mL) and 3.0 mol% of catalyst was added and sealed.

The glass vessel was then placed in an oil bath at a designated temperature (in typical conditions, T = 70 °C), and the system was left under stirring for 48h. Finally, 1 mL of DCM was added to extract the raw product. A 1 mL sample of the organic part was centrifuged, and the DCM was evaporated under vacuum, leaving the reaction product. To this sample, 500 µL of CDCl₃ was added, and the sample was analysed by NMR.

Knoevenagel Condensation

The **Knoevenagel condensation reaction of benzaldehyde with malononitrile** was carried out in a 5 mL glass vessel. To the glass vessel, a mixture of benzaldehyde (52 µL, 0.5 mmol), malononitrile (66 mg, 1 mmol), THF (1.0 mL) and 3.0 mol% of catalyst was added and sealed.

The glass vessel was then placed in an oil bath at a designated temperature (in typical conditions, T = 50 °C), and the system was left under stirring for 1.5h. Finally, 1 mL sample was centrifuged, and the THF was evaporated under vacuum, leaving the raw product. To this sample, 500 μ L of CDCl₃ was added, and the sample was analysed by NMR.

Microwave-assisted solvent-free peroxidative oxidation of 1-phenylethanol

The **microwave-assisted (MW) solvent-free peroxidative oxidation of 1-phenylethanol** was carried out in a focused Anton Paar Monowave 300 reactor using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector.

In a Pyrex tube a mixture of 10 µmol of catalyst (generally 0.4 mol% of the substrate), 5 mmol of alcohol (1-phenylethanol) and t-BuOOH (10 mmol, 70%) were added and the cylindrical Pyrex tube was sealed. The Pyrex tube was then placed in the microwave reactor and the system was left under stirring and under irradiation (10-25 W), at 80 or 120 °C for 1h. Finally, 300 µL of benzaldehyde (internal standard) and 5 mL of MeCN (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (1 µL) from the upper organic layer was analysed by GC using the internal standard method. Blank experiments, in the absence of any catalyst, were performed under the studied reaction conditions and no significant conversion was observed.

Oxidation of toluene to benzaldehyde under mild conditions

The **oxidation of toluene** was carried out in a 5 mL vessel, using a magnetic stirrer and a thermopar to define with precision the reaction temperature. The reaction mixture [toluene (0.610 ml, 5.7 mmol), 0.4% mol of catalyst (respectively 6.8 mg of **4** and 10.8 mg of **5**), acetonitrile (3 ml) and hydrogen peroxide H_2O_2 (1.02 ml; 33.3 mmol)] were added in a 6ml glass vessel, and sealed.

The glass vessel was then placed in the stirrer and the system was left under stirring and under heating at 50 °C for 24 h. Finally, 90 μ L of cycloheptanone (internal standard) and 10 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added.

The obtained mixture was stirred for 10 min and then a sample (1 μ L) from the upper organic layer was analysed by GC using the internal standard method. Blank experiments were performed and confirmed that no product of toluene oxidation was obtained unless the metal catalyst was used.

Sensing studies

The samples were prepared using the following procedure: 3 mg of compound were dispersed in 3 mL of ionic solution (with 10⁻² mol.dm⁻³ concentration) in a 10 mL glass tube. Then, the samples stay stirring for 1 h, and then placed in a cool dry place for 48h. Afterwards, the solutions were placed in a quartz cell and the fluorescence intensities were measured in the Spectrofluorimeter.

Conclusions

In a first analysis, the choice of the pro-ligands for the architectural structure of metal organic frameworks considers some generic ideas on possible interactions between amide and carboxylic groups with the metal ions. In that sense, three new pro-ligands based on pyridine carboxylates have been synthesized and characterized: H_4L1 , H_2L2 and H_2L3 .

Although it is guessable the possible locations for N-H.....Metal or O-H.....Metal coordination sites, metal organic frameworks have shown some amazing possibilities. The interactions not only in some specific sites, but with all the structure, allows to construct some amazing architectures. It allowed the discovery of 10 new compounds, with very interesting properties in the field of catalysis and in the field of sensing. Compound **1** and **4** features a mononuclear and a tetranuclear complex, respectively. Compound **7** and **9** features a metallomacrocycle type structure. The remaining compounds are 1-dimensional (**8** and **6**) or 2-dimensional (**2**, **3**, **5** and **10**) metal organic frameworks.

The catalytic properties of all the compounds have been studied, and we found out that compound **3** act as effective heterogeneous catalyst for the Henry (nitroaldol) reaction (Yield=84%, in 48h at T=70 °C), whereas compound **9** act as effective heterogeneous catalyst for the Knoevenagel condensation reaction (Yield=99%, in 1.5h at T=50 °C) and compound **4** act as a modest heterogeneous catalyst, for microwave-assisted solvent-free peroxidative oxidation of 1-phenyl ethanol (Yield=43%, in 1h at T=120 °C).

Sensing properties of **2** and **3** have also been tested. These have high sensitivity and selectivity for Fe^{3+} , Fe^{2+} and MnO_{4^-} ions and the luminescence is completely quenched, which suggests that the synthesized MOFs are promising luminescent probe for selectively sensing iron and permanganate ions. We see conditions to analyse in more detail the sensing properties of these compounds in the detection of nitro-explosives, drugs and contaminants in industrial wastes.

Further Prospects

As a continuation of my work, the first objective is to analyse other conditions for the synthesis of the catalysts, to increase their purity and crystallinity.

With that set up, I intend to proceed with other conditions in the catalytic studies, for example try Henry and Knoevenagel reactions in solvent free conditions, using microwave-assisted reactions.

In other hand, it is also intended to improve catalytic conditions in oxidation reactions, specially the oxidation of toluene which showed the more modest results. The influence of the solvents, the compound purity and crystallinity, and the use of other additives will be subject of analyzation.

Also, I will proceed with the sensing studies for all the compounds, and including other kind of compounds (not only other ions but also has been said previously nitro-explosives).

Finally, as these types of pro-ligands show I resonance due to the phenyl rings, we will use other proligands with these kinds of structures.

In the future, I would like to use this experience to further deep my knowledge in metal organic frameworks, crystal structure analysis and catalytic/sensing properties, to pursue the PhD.
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Appendix



Figure A/ 1 - FT-IR of the H₄L1 ligand.



Figure A/2 - ^{1}H NMR for H₄L1 ligand.



Figure A/3 - FT-IR of the H_2L2 ligand.



Figure A/ 4 - ^{1}H NMR for H₂L2 ligand.



Figure A/ 5 - FT-IR of the H_2L3 ligand.



Figure A/ 6 - ^{1}H NMR for H₂L3 ligand.

Total amount of compounds (T) = \sum Integrated Areas of compounds Total amount of compounds (T) = \int Benzaldehyde + \int Syn addition + \int Anti addition

Equation 1 - Calculation of the sum of integrated areas, related to the different compounds in study: the reactant and the products.

% Unreacted Belzaldehyde (%UnB) =
$$\frac{1}{T} \times 100\%$$

% Converted Benzaldehyde (%C) = 100% – % Unreacted Benzaldehyde

Equation 2 - Calculation of the converted benzaldehyde (and the unconverted benzaldehyde) to calculate the yield and selectivity of the reaction for the Anti and the Syn additions.

$$Yield_{Compound}(\%) = \frac{1}{T} \times \int Area \ of \ the \ compound \ \times 100\%$$

Equation 3 - Yield of the compound is the percentage of the reactant which produce a specific compound.

$$Selectivity = \frac{1}{\sum Yield_{Compound}(\%)} \times Yield_{Compound}(\%) \times 100\%$$

Equation 4 - The selectivity shows the percentage of the selectivity of the reaction towards a specific product.

For entry 6 of the table 1 (Henry reaction, with catalyst **3** (3.0 mol), at 70 °C, with water as solvent), we have the following calculations:

$$T = 1 + 3.69 + 1.55 = 6.24$$
 % $UnB = \frac{1}{6.24} \times 100\% = 16.0\%$ % $C = 100.0\% - 16.0\% = 84.0\%$

$$Yield(\%) = \begin{cases} \frac{1}{6.24} \times \int Syn \ addition \times 100\% = \frac{1}{6.24} \times 3.69 \times 100\% = 59.2\% \\ \frac{1}{6.24} \times \int Syn \ addition \times 100\% = \frac{1}{6.24} \times 1.55 \times 100\% = 24.8\% \end{cases}$$

$$Selectivity = \begin{cases} \frac{1}{\sum Yield(\%)} \times Yield_{Syn \ addition}(\%) \times 100\% = \frac{1 \times 59.2\% \times 100\%}{84\%} = 70.5\% \\ \frac{1}{\sum Yield(\%)} \times Yield_{Anti \ addition}(\%) \times 100\% = \frac{1 \times 24.8\% \times 100\%}{84\%} = 29.5\% \end{cases}$$



Figure A/7 - Example of integration in the ¹H-NMR spectrum for the determination of Henry reaction products (Table 1, entry 6).

Calculation of the product yield in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalysed by 9

$$\begin{cases} T = \int Benzaldehyde + \int 2 - benzylidenemalononitrile = 1 + 77.4 = 78.4\\ Yield (\%) = \frac{\int 2 - benzylidenemalononitrile}{T} \times 100\% = \frac{77.4}{78.4} \times 100\% = 98.7\% \end{cases}$$



Figure A/8 - Example of integration in the ¹H-NMR spectrum for the determination of Knoevenagel condensation reaction of benzaldehyde with malononitrile (Table 3, entry 4).

Calculation of the yield and conversion for compound 4 in the peroxidative oxidation of 1phenylethanol reaction

$$R_{Unreacted Substrate} = \frac{\int Unreacted Substrate}{\int Standard}$$

$$R_{Product} = \frac{\int Product}{\int Standard}$$

Equation 5 - Calculation of the R ration, for the Unreacted Substrate and for the Product.

$$Compound(mmol) = \frac{R}{C} \times \sum Volumes = \frac{R}{C} \times V_{substrate} + V_{Oxidant} + V_{benzaldehyde}$$

Equation 6 - Calculation of the number of moles for a specific compound, considering the R ratio and the calibration coefficient C (see Figure A/9).

$$Yield (\%) = \frac{Product (mmol)}{Substrate (mmol)} \times 100\%$$

Equation 7 - Yield of the oxidation reaction of 1-phenylethanol to acetophenone.

 $Conversion~(\%) = \frac{Initial~Substrate~(mmol) - Unreacted~Substrate~(mmol)}{Initial~Substrate~(mmol)} \times 100\%$

Equation 8 - Conversion of the substrate (1-phenylethanol) in the oxidation reaction.



Figure A/9 - Calibration curve for Acetophenone concentration calculation. The coefficient used is the equation slope. In this case C = 3.1007.



Figure A/ 10 - Example of intensity measurement dependent of retention time in gas chromatography for the determination of the products in microwave-assisted free-solvent peroxidative reaction of 1-phenylethanol (Table 5, entry 1).

$$R_{Unreacted Substrate} = \frac{202998.45}{105745.90} = 1.92$$
$$R_{Product} = \frac{37483.80}{105745.90} = 0.35$$

$$C_{Product} = 3.1007$$

 $C_{Substrate} = 3.2437$

$$\begin{cases} Unreacted Substrate (mmol) = \frac{R}{C} \times \sum Volumes = \frac{1.92}{3.2437} \times 6.6 = 3.90\\ Product (mmol) = \frac{R}{C} \times \sum Volumes = \frac{0.35}{3.1007} \times 6.6 = 0.80 \end{cases}$$

$$\begin{cases} Conversion (\%) = \frac{10 - 3.90}{10} \times 100\% = 61\% \\ Yield (\%) = \frac{0.80}{10} \times 100\% = 8\% \end{cases}$$

Table A1: Crystal data and structure refinement details for compounds 1-10										
Identification name	1	2	3	4	5	6	7	8	9	10
Formulae	C ₂₈ H ₃₃ Co	$C_{23} \; H_{27} \; N_3$	$C_{70} H_{80} Cd_3$	$C_{11.50} \; H_{10}$	$C_{24}H_{20}Cu$	$C_{30} H_{20} N_3$	$\rm C_{42}H_{34}Cd_{2}$	$C_{27}H_{29}N_6$	$\rm C_{60}H_{84}N_{12}$	$C_{27}H_{31.50}N_5$
	$N_3 O_{15}$	O ₁₈ Zn ₂	$N_{14} O_{28}$	$Cu\;N_2\;O_6$	$N_4 O_7$	$O_{10} Zn_2$	$N_6 O_{22}$	O ₁₂ Sm	$O_{26} Zn_2$	O _{10.50} Zn _{1.25}
Molecular weight /g.mol ⁻¹	710.50	764.21	1902.68	335.75	539.98	713.23	1199.55	779.91	1520.13	675.78
Crystal system	Triclinic	monoclinic	Triclinic	Triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	P-1	C 2/c	P-1	P-1	P 21/n	C 2/c	P -1	P-1	P -1	P -1
Temperature /K	296	296	296	296	296	296	296	296	296	296
Wavelength /Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a /Å	8.298	17.894	10.105	8.8368	9.1237	12.632	9.354	10.164	7.034	15.627
b/Å	11.705	15.289	12.392	9.9857	15.718	12.081	10.820	11.064	16.582	15.654
c /Å	16.879	10.815	15.806	16.3956	19.921	27.668	15.308	15.948	18.425	19.192
α/°	74.29	90	102.70	91.165	90	90	84.045	82.519	81.687	111.05
β/°	86.584	90.742	92.042	103.967	93.27	100.797	73.498	75.47	89.129	99.873
γ/°	81.848	90	91.628	92.411	90	90	64.959	63.7	85.846	106.17
V/ Å ³	1562,00	2958.2	1928.26	1402.06	2852	4147.4	1345.6	1556	2120.8	4010.5
Z	2	4	1	4	4	8	1	2	1	4
Density /g.cm ⁻³	1.511	1.716	1.639	1.591	1.258	2.284	1.480	1.665	1.190	1.119