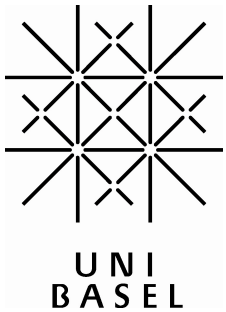

NEW SILVER COMPLEXES WITH LIGANDS BASED ON 4-SUBSTITUTED-3,6-DIPYRIDIN-2-YLPYRIDAZINES

Inauguraldissertation

Zur
Erlangung der Würde eines Doktors der Philosophie
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Auf Antrag von

Prof. Dr. Edwin CONSTABLE
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Basel, den 19. September 2006

Prof. Dr. Hans-Jakob WIRZ

à mes parents, Paulette et Raymond

à Frédérique

Summary

Chapter I gives a brief introduction to supramolecular chemistry, silver chemistry, pyridazine chemistry.

Chapter II discusses the general procedure used for this work. It introduces the Sonogashira reaction used to prepare the ethynyl precursors, and the inverse electron demand Diels Alder reaction used to synthesise all the ligands presented in this work.

Chapter III describes the synthesis and the characterisation of phenyl substituted pyridazines and their silver complexes. This chapter presents the crystal structure of ligand **8**.

Chapter IV discusses the synthesis and characterisation of the halogenated pyridazine and their silver complexes. It also discusses the crystal structure of ligand **15** and complexes **15sc**, **18sc** and **20sc**.

Chapter V describes the synthesis of diverse pyridazines. These ligands have methoxy, cyano, tert-butyl phenyl substituents. It also shows the crystal structure of ligand **34** and complexes **30sc**, **39sc**, **42sc**, **43sc** and **49sc**.

Chapter VI discusses the synthesis and characterisation of pyridazine substituted with alkyl chains. The crystal structure of complex **53sc** is presented.

Chapter VII gives the conclusion to this work and a general overview of the ligands and complexes synthesised in this thesis.

ACKNOWLEDGEMENTS

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One of these results has been published:

"*Self-assembly of a novel pentanuclear centred-tetrahedral silver species*"
E. C. Constable, C. E. Housecroft, M. Neuburger, S. Reymann, S. Schaffner, *Chem. Commun.*, **2004**, 1056-1057.

CONTENTS

ABBREVIATIONS

General

NaOH	sodium hydroxide
$MgSO_4$	magnesium sulfate
$Na_2S_2O_3$	sodium thiosulfate
MeCN	acetonitrile
DCM	dichloromethane
DMSO	dimethylsulfoxide
$CDCl_3$	deuterated chloroform
CD_3CN	deuterated acetonitrile
EtOAc	ethyl acetate
NaCl	sodium chloride
$NaNO_2$	sodium nitrite
$SiMe_3$	trimethylsilyl
THF	tetrahydrofurane
Bpy	Bipyridine

Analysis

STM	scanning tunnelling microscopy
TLC	thin layer chromatography
ESI/MS	electrospray ionisation mass spectrometry
FAB/MS	fast atom bombardment mass spectrometry
^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance

^{1}H NMR

J	coupling constant
δ	chemical shift
d	doublet
dd	doublet of doublets
dt	doublet of triplets
m	multiplet
s	singlet

CHAPTER I

INTRODUCTION

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INTRODUCTION

I.1 Supramolecular chemistry

The importance of supramolecular chemistry was recognized by the 1987 Nobel Prize for chemistry which was awarded to Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen in recognition of their work in this area.

Supramolecular chemistry refers to the area of chemistry which focuses on the non-covalent bonding interactions in molecules[1]. Traditional organic synthesis involves the making and breaking of covalent bonds to construct a desired molecule. In contrast, supramolecular chemistry utilizes weaker and reversible non-covalent interactions, such as hydrogen bonding, metal coordination, van der Waals forces, π-π interactions and/or electrostatic effects to assemble molecules. Important concepts that are demonstrated by supramolecular chemistry include molecular recognition and self-assembly.

Supramolecular chemistry processes have been applied to the development of new materials and the topic is often pursued to develop new functions that cannot be exhibited by a single molecule. These functions include magnetic properties, light responsiveness, catalytic activity, self-healing polymers, chemical sensors, etc. Supramolecular chemistry is also important to the development of new pharmaceutical therapies by understanding the interactions at a drug binding site.

I.2 Molecular recognition

Molecular recognition involves selection and binding of substrates by a given receptor molecule similar to the "lock and key" concept devised by Emil Fisher[2]. The binding sites can distinguish the shape, size, bonding and electronic properties of the substrate[3]. This process occurs through non-covalent chemical bonds including hydrogen bonding, hydrophobic interactions, ionic interactions, or other interactions between two molecules[4-6].

For example, molecular recognition can be used for the development of specific molecular diagnostics and sensor materials. Chawala et al.[7] report the role of hydrogen bonding in shaping the cavity of azocalixarenes and showed the role of ionic recognition through the azo quinoidal form (Figure 1.1).

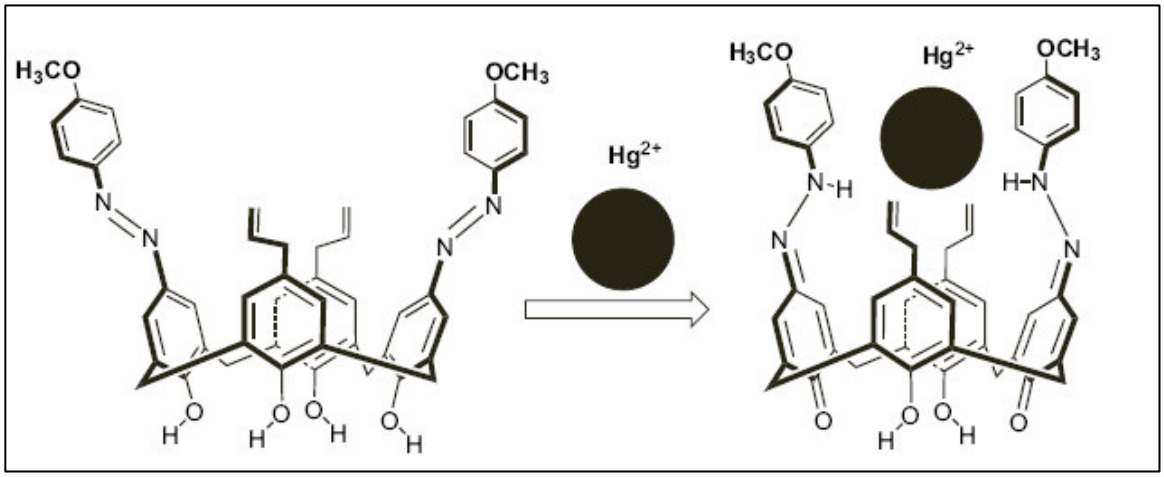

Figure 1.1: Example of ionic recognition through the azo quinoidal form of a derivatized calixarene.

I.3 Self-assembly

Self-assembly is a process generating supramolecular entities from molecular components capable of mutual interactions[8-10]. In that sense, self-assembly may be regarded as a branch of supramolecular synthesis. Self-assembly is a very powerful strategy for the generation of structural and functional complexity. Indeed, in the living world, both structural and functional features of biological assemblies are

mainly generated through self-assembly processes. The best example is deoxyribonucleic acid (DNA) which forms a double helix from two complementary oligonucleotides[11] (Figure 1.2). Hosseini's group[12] has reported the hydrogen bonded network formed between the dicationic tecton (bisamidinium) and hexacyanometallate complex anion, presented in Figure 1.3.

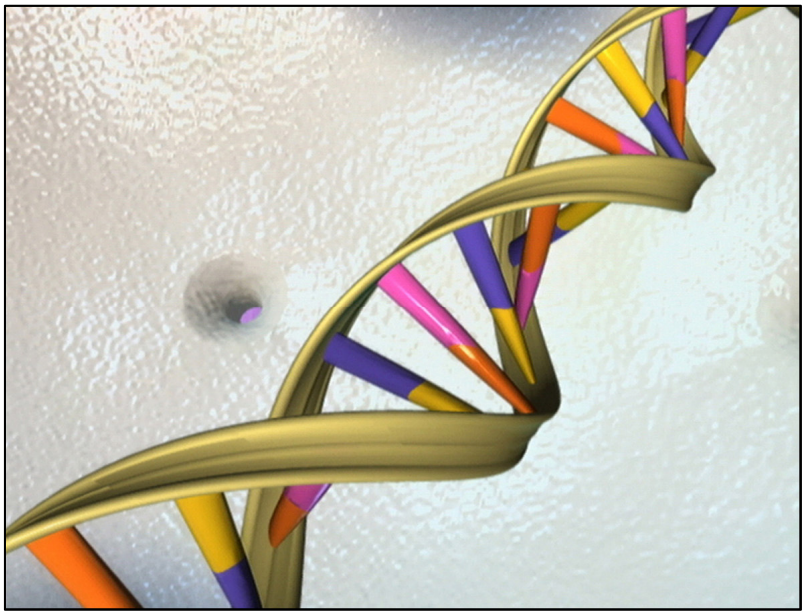

Figure 1.2: Diagram showing a part of the double helix of DNA.

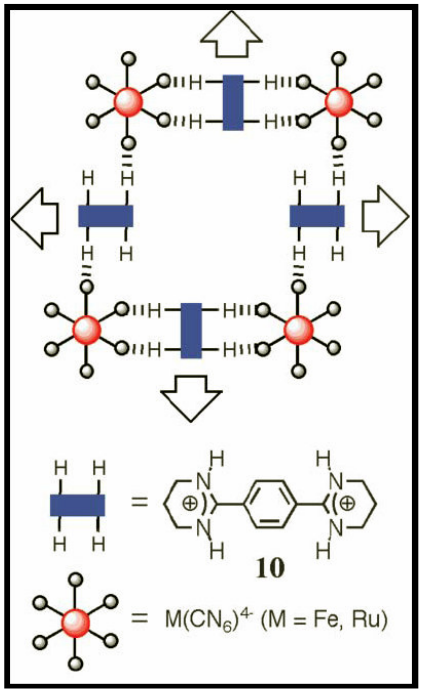

Figure 1.3: A schematic representation of the 2-D hydrogen bonded network formed between the dicationic tecton **10** and hexacyanometallate complex anion.

I.4 Metallosupramolecular chemistry

Metallosupramolecular chemistry has become a main research area in supramolecular chemistry. Constable has defined metallosupramolecular chemistry as follows: "*Metallosupramolecular chemistry is concerned with the use of metal ions to control the assembly of appropriate molecular components containing metal-binding domains*".[13]

The principle of the formation of metallosupramolecules depends mainly on the number and orientation of the coordination sites of ligands and the coordination number and geometry of the metal ions. A variety of metallosupramolecular architectures, including rods[14], helices[15-18], knots[19-21], catenanes[22,23], rotaxanes[24-27], grids[28-31], cages[32-34] and dendrimers[35,36] have been formed spontaneously by the self-assembly of labile metal ions with multidendate ligands.
In the following discussion, examples of a few self-assembly structures are presented.

Supramolecular helices

There has been considerable interest in helical supramolecular architectures, particularly helices from coordination compounds. Field and Venkataraman[15] report an ortho-substituted phenyl amine (Figure 1.4) that can form an hydrogen bonded supramolecular helix. They showed that the conformation of the intermolecular hydrogen-bonding, and thus the supramolecular structure, can be controlled through an internal hydrogen bond (Figure 1.5)

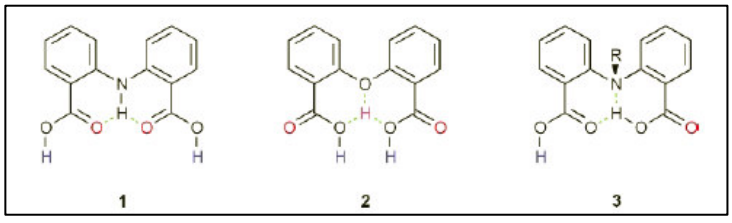

Figure 1.4: Compounds used for the preparation of the supramolecular helices.

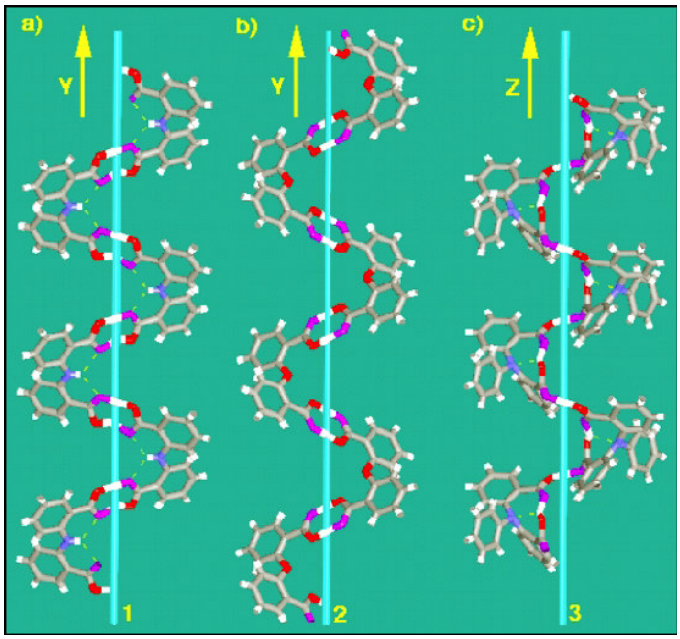

Figure 1.5: The supramolecular structures from a) **1**, b) **2**, c) **3** (R=phenyl) from single crystal X-ray diffraction.

Supramolecular catenanes

A catenane is a mechanically interlocked molecular architecture consisting of two or more interlocked macrocycles. These compounds are very interesting from a photophysical and photochemical viewpoint because of the properties which originate from the electronic interactions of the various subunits. Catenanes that exhibit coordination ability (catenands) can give rise to metal complexes (catenates) where the photochemical and the photophysical properties are profoundly affected by the nature of the coordinated metal[23].

Reports[22] present the use of long biphenylethene-4,4'-dicarboxylate (bpea) and chelating 1,10-phenanthroline (phen) as mixed ligands. Wang et al. have isolated a new species [Zn(bpea)(phen)] (**1**), containing polymeric chains that are assembled via molecular recognition into an intriguing 3D polycatenated array featuring an uneven "density of catenation" (Figure 1.6)[22].

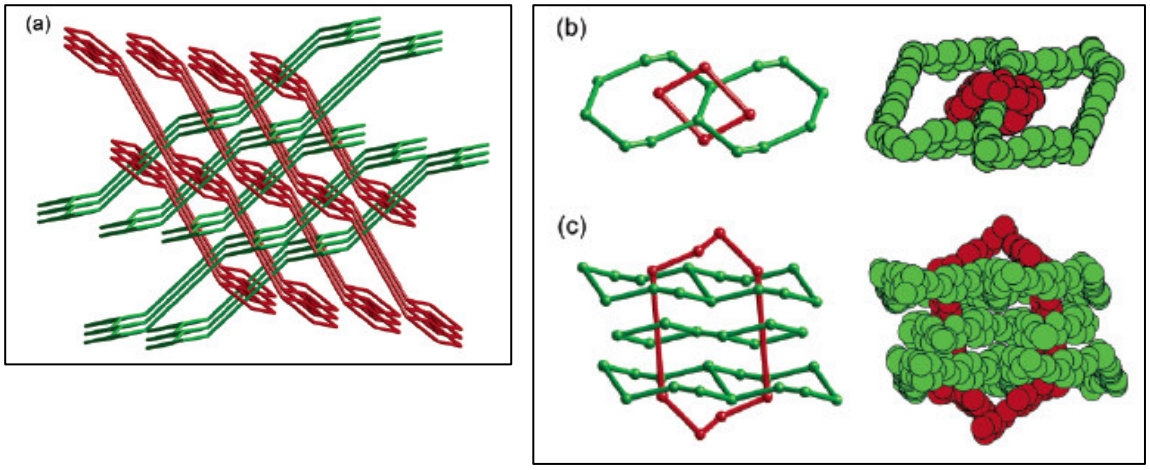

Figure 1.6: Schematic view of the polycatenation in **1** (a) and the schematic and space-filling presentations of the two kinds of windows in one layer unevenly catenated by those from other independent layers (b and c). Two sets of layers are shown in red and green.

Supramolecular rotaxanes

A rotaxane is a mechanically-interlocked molecular architecture consisting of a dumbbell-shaped molecule that is threaded through a macrocycle or ring-like molecule. Rotaxanes are usually based on the movement of the macrocycle along the dumbbell. The macrocycle can rotate around the axis or slide from one coordination site to another and these systems can therefore be used as molecular switches.

Sauvage has reported a rotaxane incorporating two different ligand domains. The system can be switched from a four coordinated Cu(I) to a five coordinated Cu(II) and vice versa by oxidising or reducing the metal[37] (Figure 1.7).

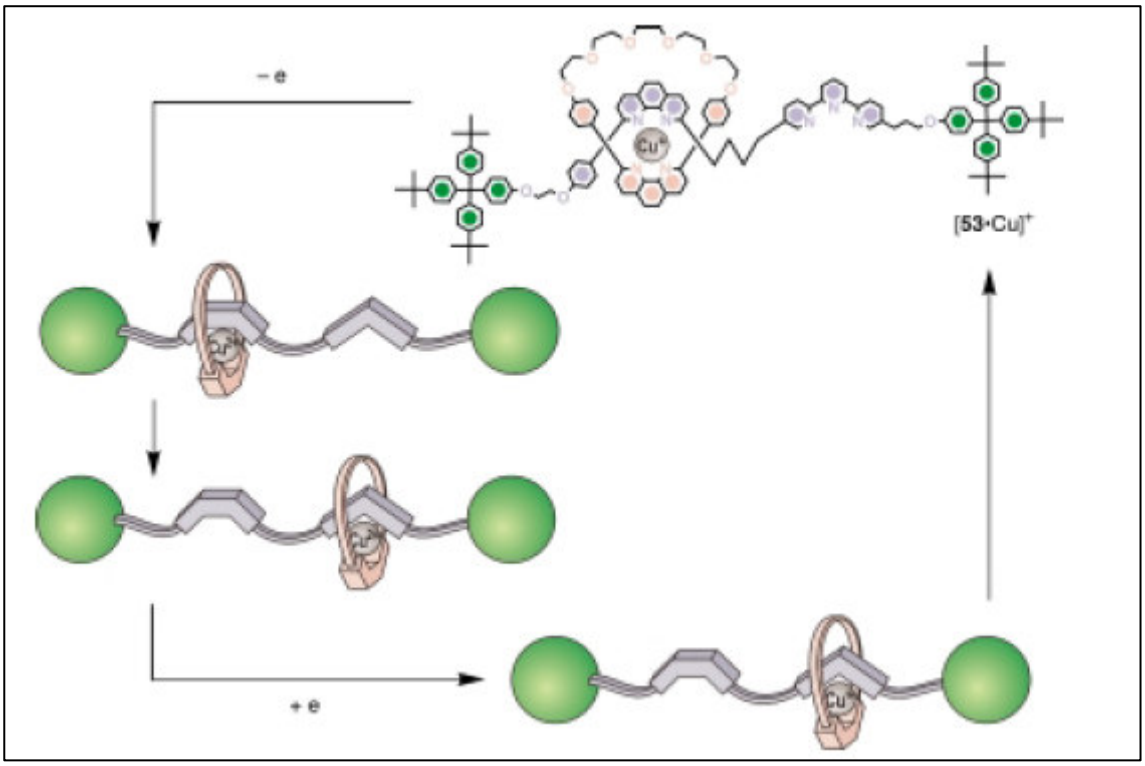

Figure 1.7: Representation of the molecular motion processes of the rotaxanes by oxidising or reducing the metal centre.

Supramolecular grids

Supramolecular grids are entities based on multidendate ligands and metal ions. The grid type complexes are generally based on metal-ligand coordination.

Barboiu et al.[31] used 2-iminopyridine groups to have access to bifunctional bipyridine-type ligands, which generate grid-type compounds in the presence of tetrahedral metal ions (Cu(I) and Ag(I)). Metal-ion binding imposes a cisoid arrangement of pyridine nitrogens, as is common in very numerous complexes of bipyridine (bipy). This is presented in Figure 1.8.

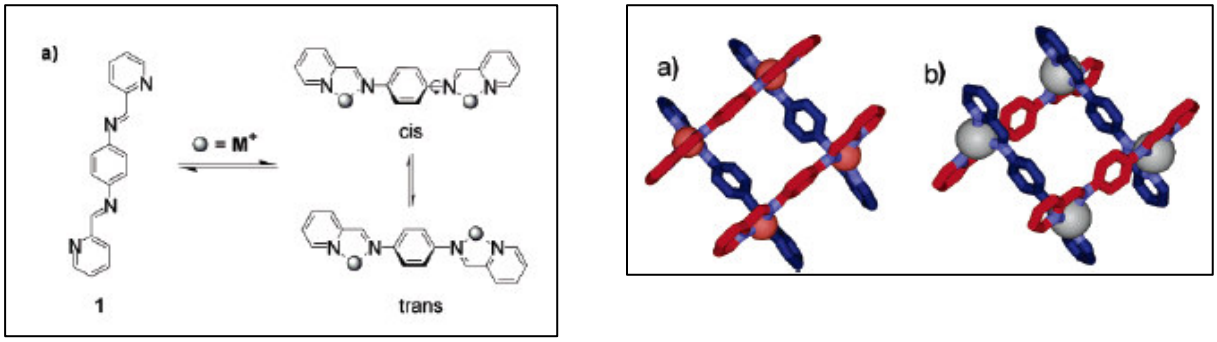

Figure 1.8: Crystal structure of the grid complexes (stick representation), Cu^+, red-brown spheres; Ag^+, grey spheres.

Osborn's group[29] presented a grid like structure based on the coordination of Cu(I) and 3,6-dipyridin-2-ylpyridazine (dppn). This ligand presents two chelating sites based on nitrogen atoms and is almost planar. This leads to a grid like Cu(I) complex where π-π interactions between two ligands may play a role of the formation of a supramolecular grid. Figure 1.9 shows the ligand and its grid like structure when coordinating the metal ion (Cu(I)).

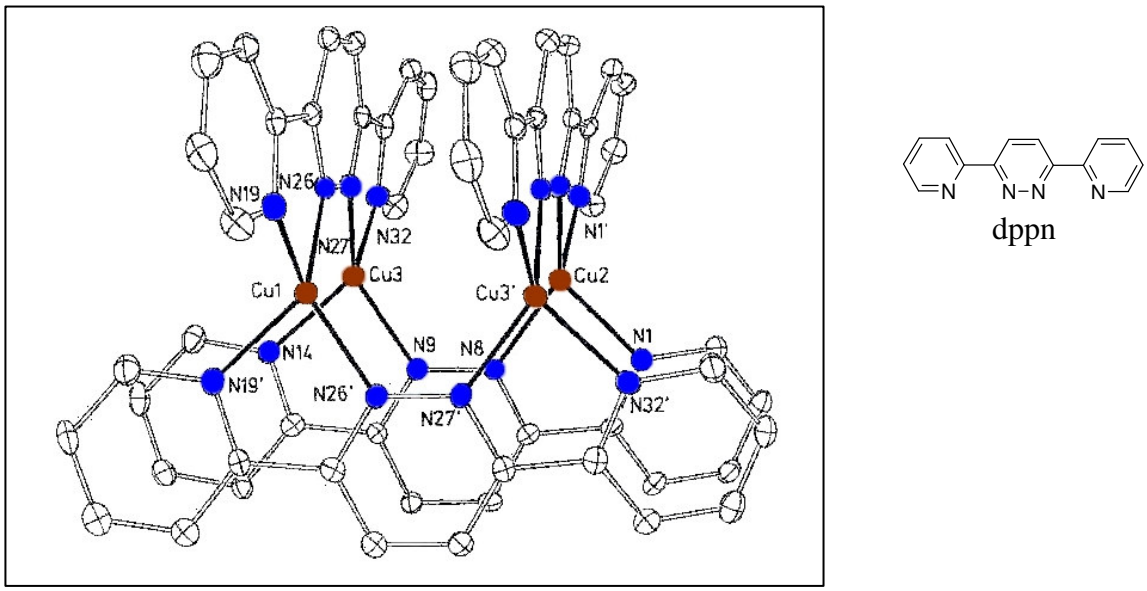

Figure 1.9: Grid like structure of $[Cu_4(dppn)_4](CF_3SO_3)_4$ presented by Osborn.

I.5 Silver(I) chemistry

Silver(I) coordination chemistry has attracted many research groups[38-41]. The silver ion is of great interest in the synthesis of coordination complexes. This is probably due to the flexibility of its coordination sphere and the ease with which it varies its coordination number (from 2 to 4, rarely 5 or 6). Coordination complexes of silver are known to be alterable via several methods: typically by changes in ligand geometry, rigidity or functionality and/or by modifications to the counter-ion or solvent system[42,43].

Many silver coordination architectures are readily obtained through slight variations in ligand and/or anion and include discrete, small molecules, supramolecular arrays, and 1-, 2-, and 3-dimensional network[44-46].

Silver is often used to prepare coordination polymers[47,48] or associated with N-donor ligands to form chelating systems[49,50].

Silver coordination polymers

Silver based coordination polymers have received great attention lately[51,52]. This is owed to the rich chemistry that is available to this versatile metal[53].

A report has shown the use of aliphatic N-donor ligands for ligand directed strategy in the assembly of discrete clusters. They investigated 1D chains, 2D layers, 3D networks. They showed that this family of amine (*cis-cis*-1,3,5-triaminocyclohexane, *cis-trans*-1,3,5-triaminocyclohexane, *cis*-1,3-diaminocyclohexane, *cis*-3,5-diaminopiperidine) form a diverse set of coordination polymers with silver salts Ag(I)[54].
Figure 1.10 presents the chain formation of silver perchlorate and *cis*-1,3-diaminocyclohexane.

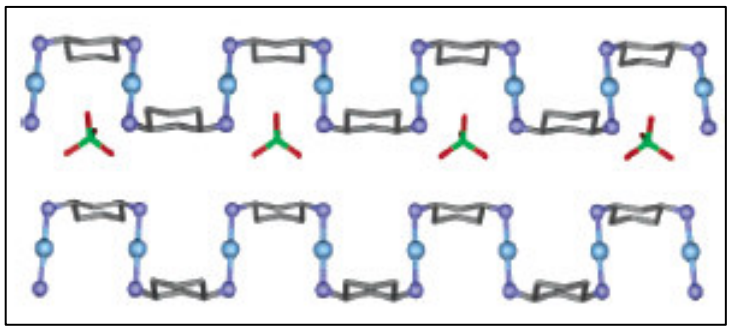

Figure 1.10: The chain formation of silver perchlorate and *cis*-1,3-diaminocyclohexane

Pickering et al. also introduced the macrocyclic formation of the coordination polymer based on silver nitrate and *cis-cis*-1,3,5-triaminocyclohexane. In that case the asymmetric unit is composed of one ligand (*cis-cis*-1,3,5-triaminocyclohexane), one silver(I) ion and one nitrate couterion. Here, each Ag(I) has a trigonal planar coordination sphere with three *cis* amines of different ligands, forming an infinite tubular channel. The macrocyclic tube formation and the packing of the coordination polymer are shown in Figure 1.11.

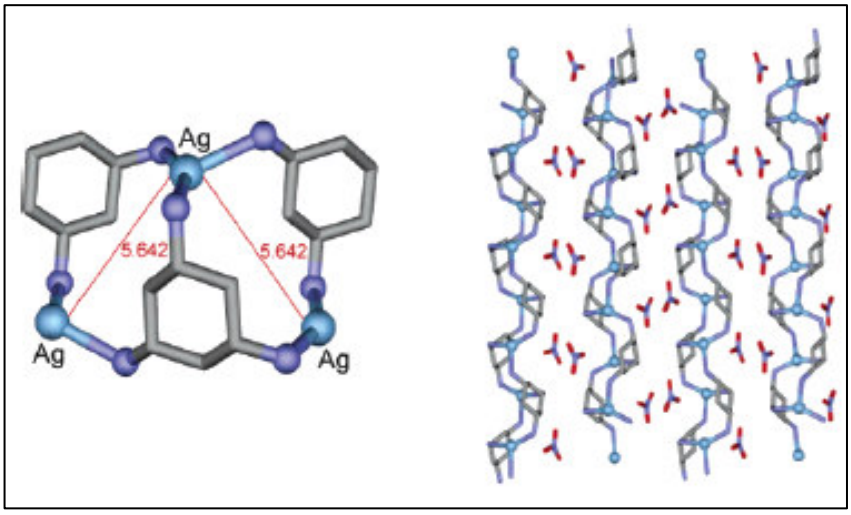

Figure 1.11: Macrocyclic tube formation and the packing of the coordination polymer based on silver nitrate and *cis-cis*-1,3,5-triaminocyclohexane.

Zubieta et al.[55] published the synthesis of a silver coordination polymer prepared with 2,4'-bipyridine as the N-donor ligand. They realised that the crystal structure of that compound consists of a one – dimensional sinusoidal chain. Here, the Ag(I) sites exhibit a "T"-shaped geometry. The silver centre is coordinated to two nitrogen donor from two 2,4'-bipyridine groups and to a sulfate counter ion. This is presented in Figure 1.12.

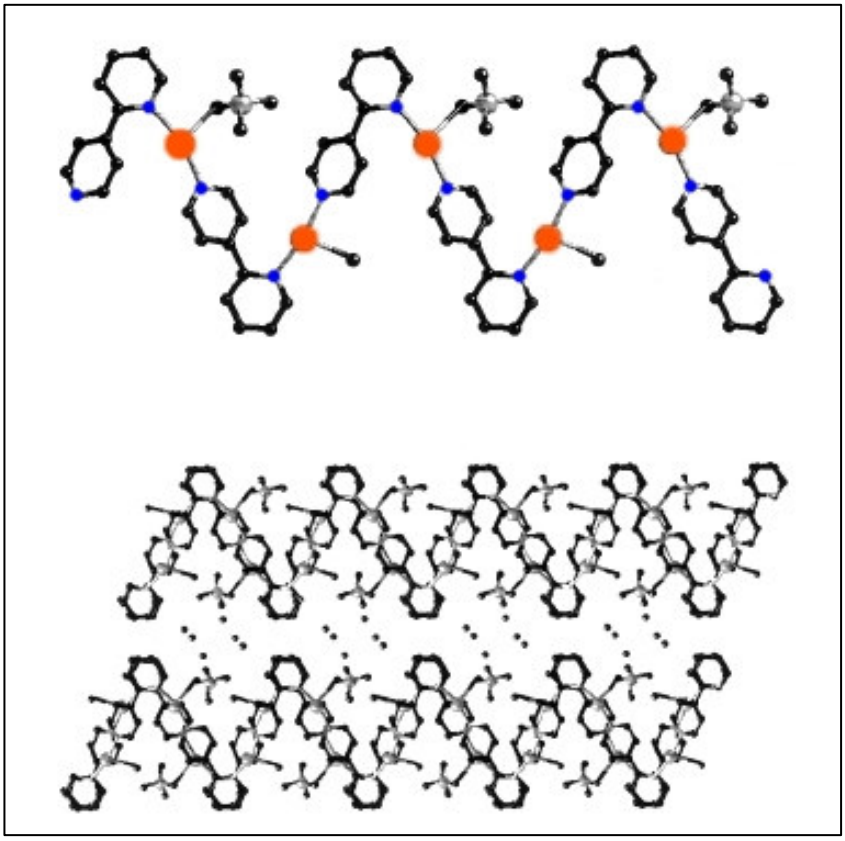

Figure 1.12: A view of the one-dimensional chain of $[Ag_2(2,4'\text{-bpy})_2(SO_4)(H_2O)] \cdot 5H_2O$ and a view parallel to the chain axis and parallel to the crystallographic *b* axis

The chains exhibit two distinct silver sites: the first exhibits an essentially 'T' shaped Ag(I) center, bonded to two nitrogen donors from two 2,4'-bpy groups and one oxygen of the sulfate ligand, with an additional secondary Ag···O (sulfate) interaction. The second silver is also 'T'-shaped but through coordination to two pyridyl nitrogen donors and an aqua ligand.

An interesting paper[56] presents the synthesis of eight new silver coordination polymers based on 4,4'-(3,3'-(1,3,4-oxadiazole-2,5-diyl)bis(3,1-phenylene))bis(ethyne-2,1-diyl)dibenzonitrile (L11). They used five different silver salts and different solvent system to prepare the eight new silver coordination polymers. Figure 1.13 summarises the conditions of the complexes sythesis.

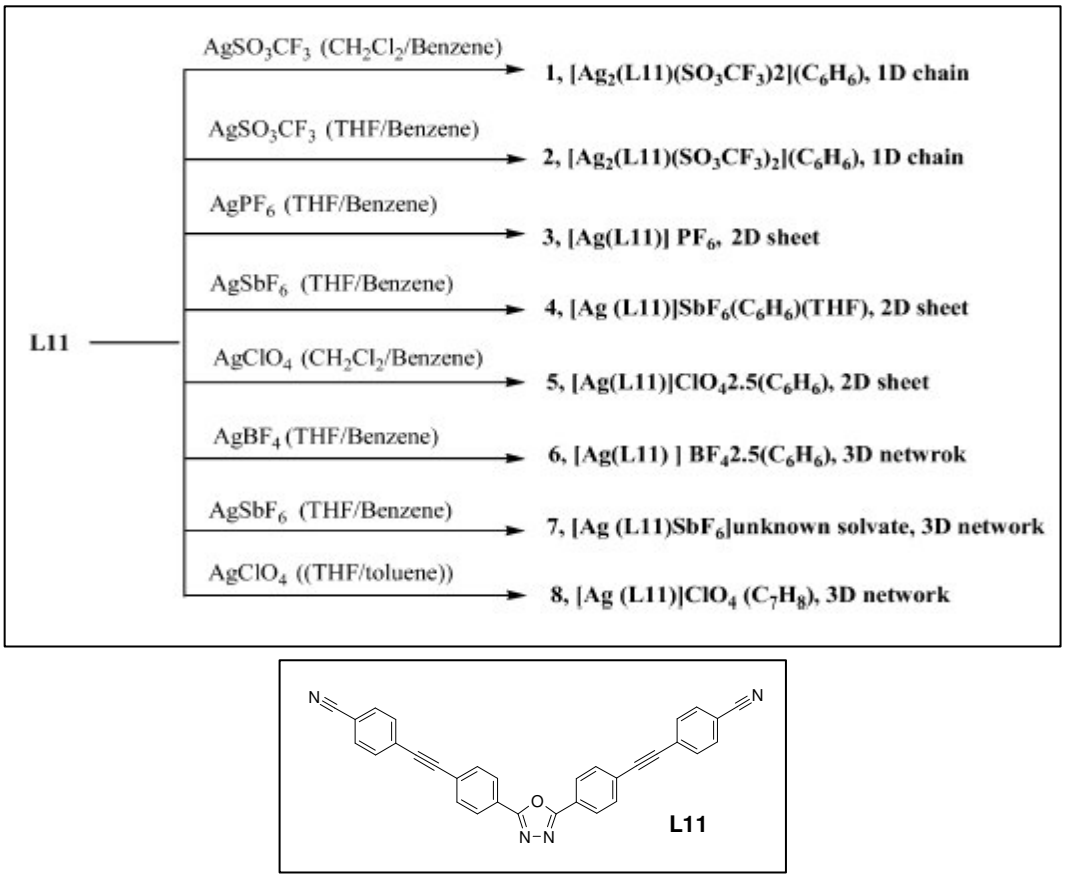

Figure 1.13: Synthesis of the silver coordination polymers **1** to **8** and schematic drawing of ligand **L11**.

They showed that in this Ag(I)-**L11** system, the conformation of **L11** is versatile and depends greatly on the counterion and solvent system used in the formation of the complexes: (a) in one-dimensional structures **1** and **2**, the ligand displays conformation II with the central oxadiazole and its two adjacent phenyl rings being coplanar; (b) in two-dimensional compounds **3**-**5**, L11 takes either conformation I or II but with the central oxadiazole and two neighbouring phenyl rings being nonplanar; and (c) in three-dimensional compounds **6**-**8**, **L11** chooses an intermediate conformation between I and III, with the two long cyanophenylacetylene arms lying in

different planes. Figure 1.14 presents the eight silver coordination polymers based on ligand **L11**.

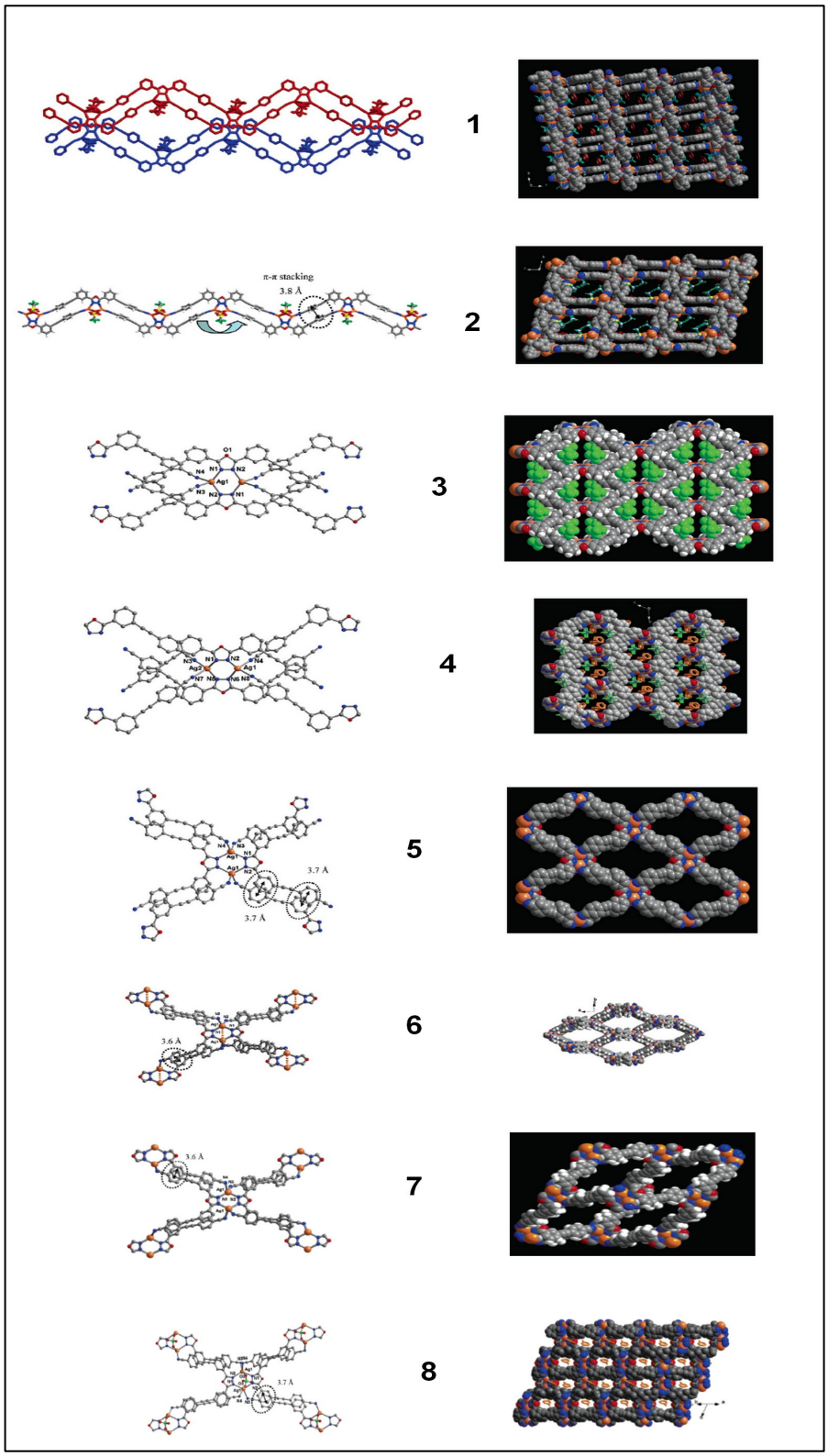

Figure 1.14: The eight silver coordination polymers based on ligand **L11**.

Silver complexes based on chelating ligands

Ligands containing multiple binding sites are considered as multidentate ligands and offer the possibility to make several bonds to one metal centre. Bidentate ligands, like 2,2'-bipyridines, are called chelating ligands. In that case, two adjacent nitrogen atoms can coordinate one metal centre[43,57].

The case of bipyridine is very interesting. A recent report presented a "sandwich-shaped" silver(I) metallomacrocycle (based on 4-(2-pyridyl)pyrimidine (pprd)) encapsulating a XF_6^{2-} (X= Si, Ge, Sn) anion[58] (Figure 1.15).

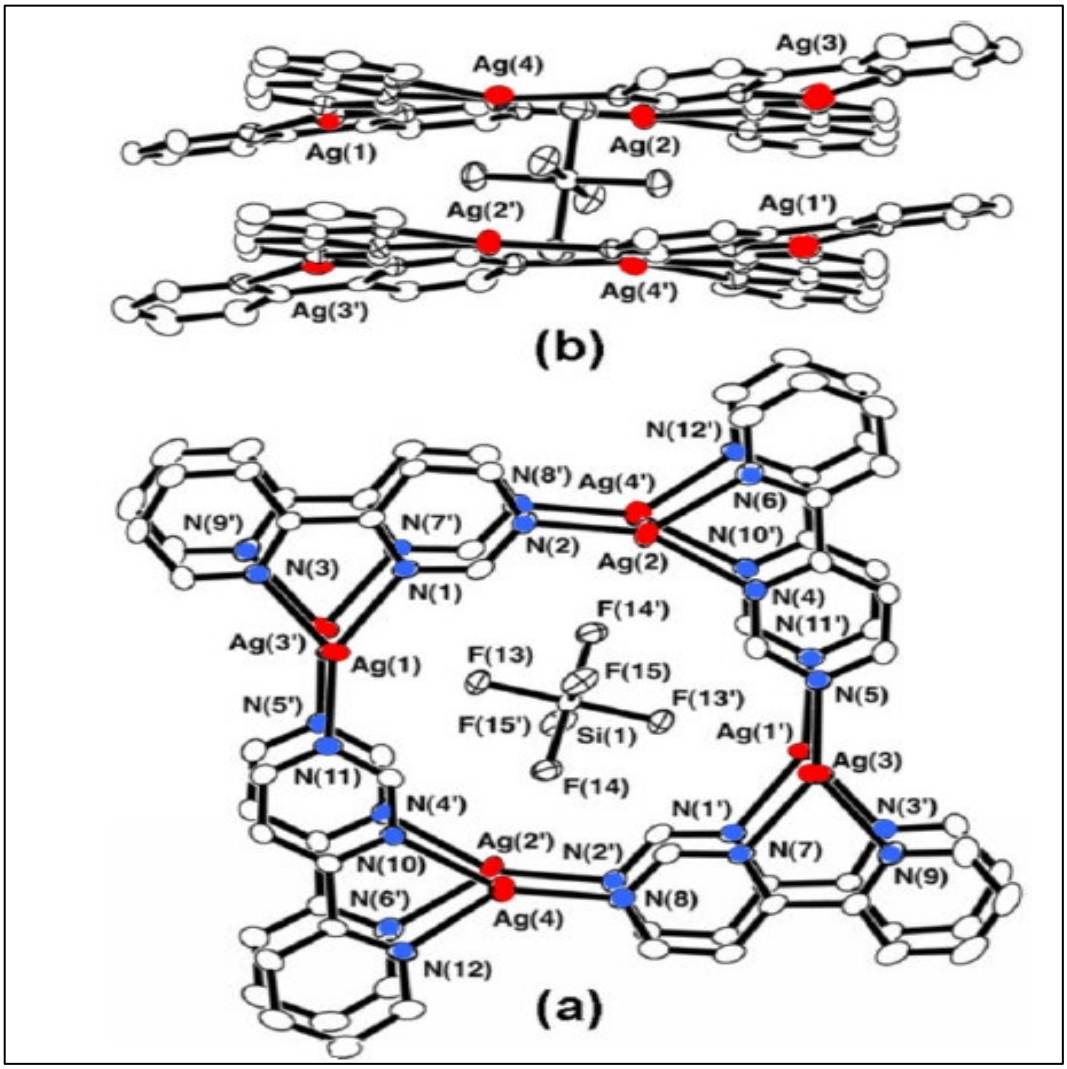

Figure 1.15: (a) Top view and (b) side view of $\{[Ag_4(pprd)_4]_2(SiF_6)\}(BF_4)_6\ 8MeNO_2\}$. The six BF_4^- anions and the eight solvated MeNO2 molecules are omitted for clarity.

The 4-(2-pyridyl)pyrimidine (pprd) ligand has two coordination sites, one is a simple chelating site analogous to 2,2'-bipyridine and the other is an *exo* N-donor site for bridging. Since the two coordination sites are oriented ca. 90° to each other, the pprd ligand is expected to produce both finite metallomacrocyclic compounds and infinite polymeric compounds. Four silver atoms are joined by the four pprd ligands in a "head-to-tail" fashion to afford a square $[Ag4(pprd)4]^{4+}$ metallomacrocycle. It is to be noted that the SiF_6^{2-} anion is encapsulated in the central vacant space between the two $[Ag4(pprd)4]^{4+}$ metallomacrocycles, resulting in the formation of a sandwich-shaped structure.

Recently, in our group, silver complexes based on 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (**A**), 3,6-bis(2-pyridyl)pyridazine (**B**) and 4-phenyl-3,6-bis(2-pyridyl)pyridazine (**C**) have been synthesised[59,60] (Figure 1.16).

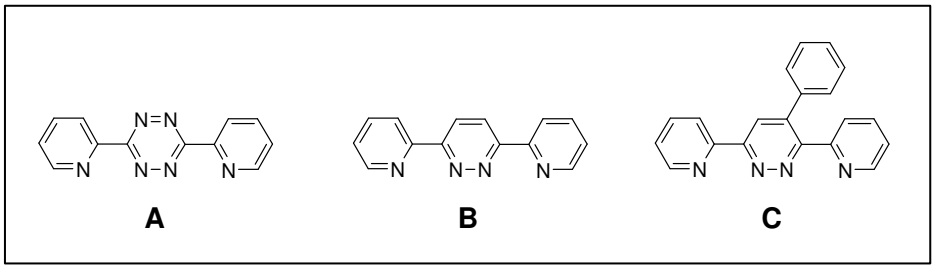

Figure 1.16: Schematic representation of ligands **A**, **B** and **C**.

The investigations of these complexes were based on a previous paper published by Osborn[61], where a tetranuclear 2x2 grid was prepared with the spontaneous self-assembly of a copper(I) salt with 3,6-bis(2-pyridyl)pyridazine (**B**). Much of the successful metal-directed chemistry utilised in the synthesis of topological novel species is based upon the assumption the coordination behaviour of silver(I) and copper(I) is similar. They showed that the behaviour of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (**A**) with silver(I) does not parallel that 3,6-bis(2-pyridyl)pyridazine (**B**) with copper(I) and that instead of a tetranuclear complex with a tetrahedral geometry about the metal, a dinuclear chelating species with near planar silver centres were obtained. Figure 1.17 shows the three silver(I) species, obtained by Constable, with the chelating ligands **A**, **B** and **C**.

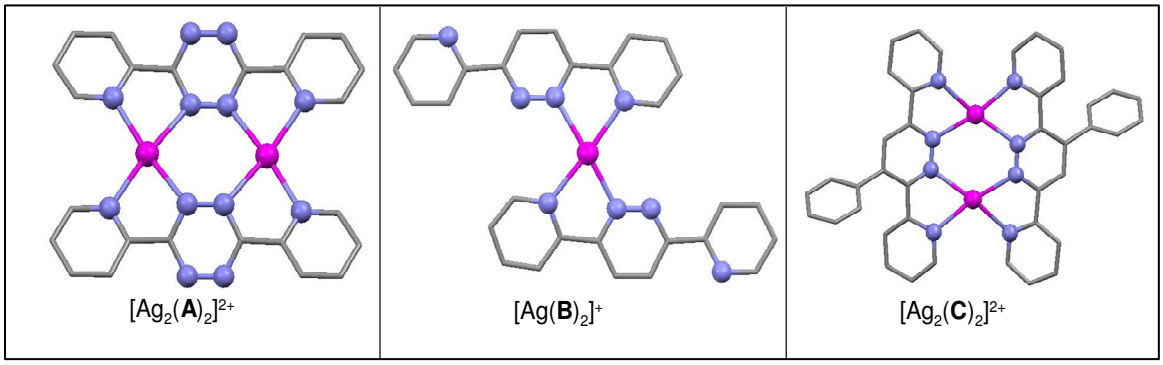

Figure 1.17: Silver complexes of ligands **A**, **B** and **C**.

Ligand **A** appeared to be responsible for imposing the extremely unusual near-planar geometry upon the silver centre. They also showed that the coordination behaviour of silver(I) with 3,6-bis(2-pyridyl)pyridazine (**B**) presents a rich structural diversity and that, in contrast to the corresponding behaviour of copper(I), no grid-like structure were obtained. In the reaction with the phenyl-substituted ligand (**C**), a single isomer is obtained in the solid state and no strong packing interactions (which might favour this isomer) were observed.

I.6 Tetrazine chemistry

First synthesised by Hantsch and Lehmann, in 1900, 1,2,4,5-tetrazine is probably the best-known tetrazine isomer[62]. Interest in the physical and spectroscopic properties of 1,2,4,5-tetrazine and in the high reactivity of tetrazines as dienes in (4+2) cycloaddition reactions is still increasing. Figure 1.18 shows the structure of the 1,2,4,5-tetrazine molecule.

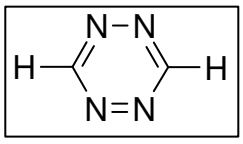

Figure 1.18: 1,2,4,5-Tetrazine.

Compounds containing the 1,2,4,5-tetrazine skeleton are used as pharmaceuticals. For example, 3-amino-6-aryl-1,2,4,5-tetrazine showed modest antimalarial

activities[63], some hexahydro-s-tetrazines proved to have useful analgesic and antiflammatory activity. For a series of tetrahydro-s-tetrazines the antibacterial and antifungal have been evaluated[64], and a special 1,4-dihydro-s-tetrazine derivative has pronounced antiviral activity[62].

We attached particular attention to 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine and the substituted 3,6-bis(2-pyridyl)pyridazine (synthesized by an inverse electron demand Diels-Alder reaction) and their metal complexes[65-71]. These ligands have been used to study the coordination behaviour of different metals such as copper[72], iridium[73], palladium[74]. Our group prepared a polymeric sodium complex of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine[75]. Bu et al. presented a one-dimensional chain based on the diprotonated salt of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine[76].

The next few pages will introduce some complexes, obtained with 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine or substituted 3,6-bis(2-pyridyl)pyridazines and various metal centres such as ruthenium(II), copper(I), nickel(II) or zinc(II).

Published in 2006 by Thomas[77] et al., the preparation of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine ruthenium based complexes show interesting crystal structures. They used [([n]aneS$_4$)Ru] metal centres. In fact, they prepared dinuclear ruthenium complexes bridged by 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine. Figure 1.19 presents these three dinuclear ruthenium complexes.

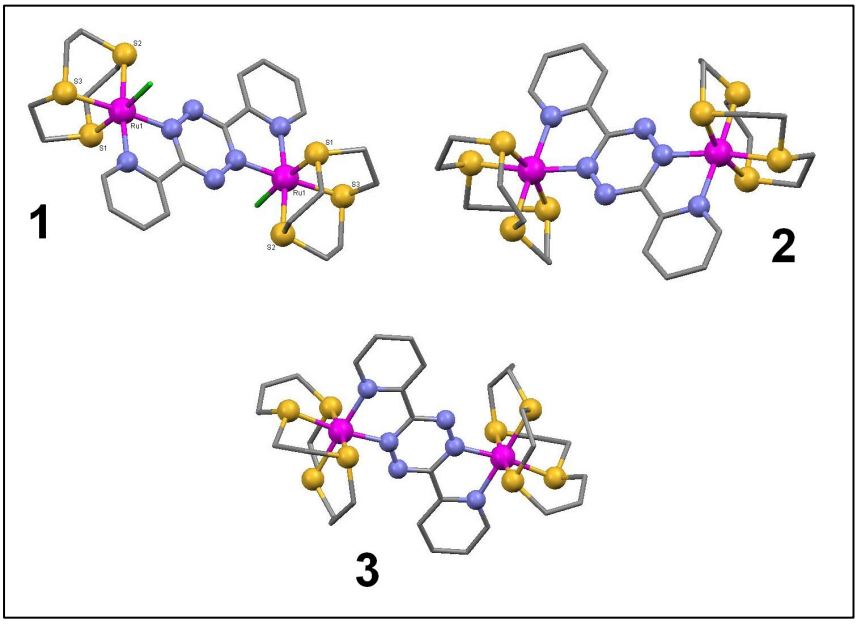

Figure 1.19: Diagram of the structures of the three ruthenium complexes.

These ruthenium, 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine based coordination complexes show interesting photochemical properties. A comparison of the electrochemistry of the three complexes reveals that the first oxidation of the [RuII([n]aneS4)]-based systems, is a ligand-based couple. This indicates that the formation of the radical anion form of the bridging ligand is stabilized by coordination to the metal centre.

A report from Hoogenboom[78] describes the polymerisation of L-lactide utilizing a novel supramolecular initiating system, based on the 3,6-bis(2'-pyridyl)pyridazine ligand. For this purpose they synthesized and polymerized a hydroxyl-functionalized 3,6-bis(2'-pyridyl)pyridazine. The resulting macroligands were assembled into grid like complexes with copper(I) (Figure 1.20)

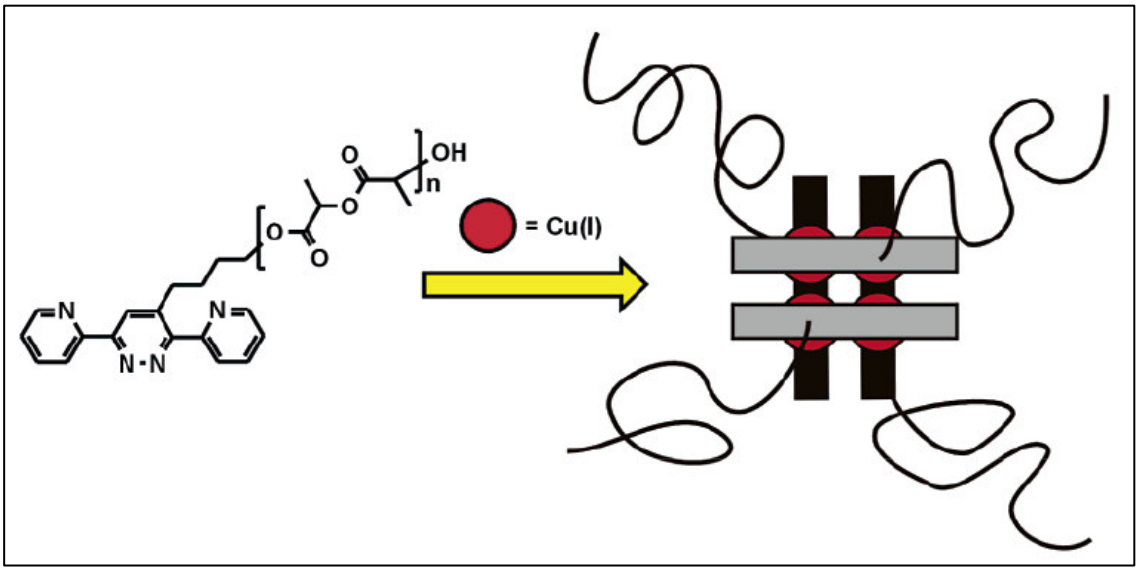

Figure 1.20: Schematic representation of the formation of polymeric gridlike complexes from the macroligands.

They showed that this coper(I) complex has a grid-like structure. In fact, this species exhibits UV-vis spectroscopy absorption bands at 295 and 440 nm. These absorption bands were also described for similar unfunctionalized grid-like complexes.

Another report[79] introduced the preparation and characterisation of a tetranuclear nickel(II) complex with 3,6-bis(2'-pyridyl)pyridazine as a ligand. $[Ni_4(\mu\text{-}OH)_2(\mu\text{-}dppn)_4(\mu\text{-}H_2O)_2](Cl)(ClO_4)_5$, (ddpn= 3,6-bis(2'-pyridyl)pyridazine). The tetranuclear nickel complex is schown in Figure 1.21.

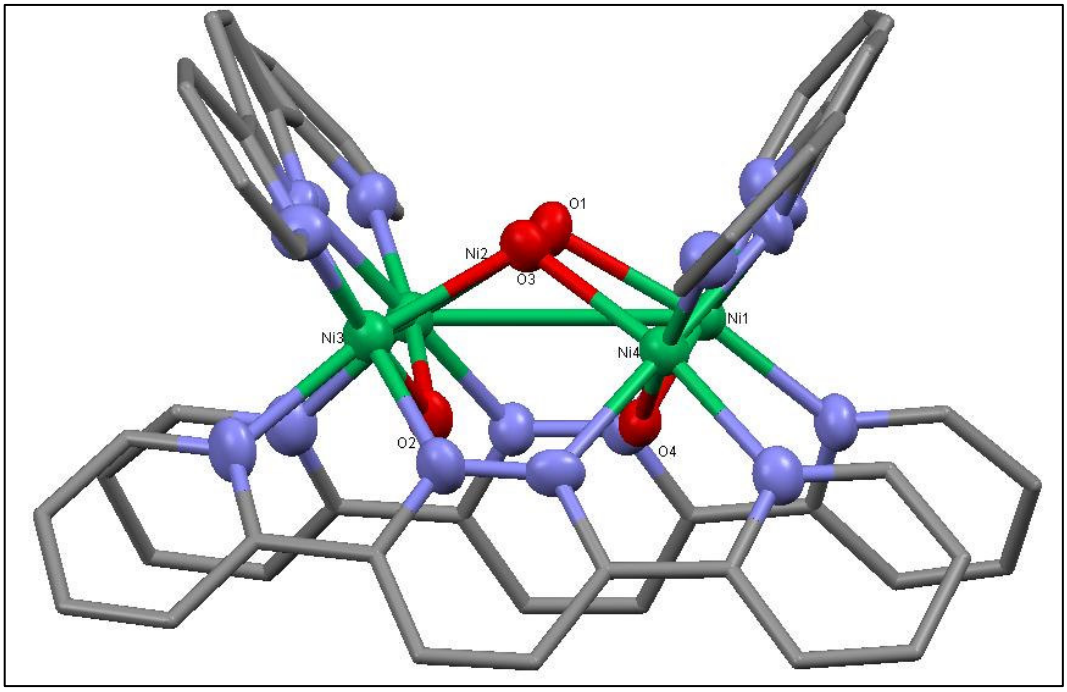

Figure 1.21: Side view of the tetranuclear $[Ni_4(\mu\text{-}OH)_2(\mu\text{-}dppn)_4(\mu\text{-}H_2O)_2](Cl)(ClO_4)_5$ cation.

The pair of nickel atoms that are connected by the (μ-dppn) ligand are joined through the hydroxyl group and water molecule bridges to form the tetranuclear core. Within this tetranuclear unit, one nickel atom is six-coordinate with distorted octahedral geometry and an N_4O_2 donor set from two equivalent dppn ligands and two oxygen atoms of the bridging hydroxyl and water molecule.

The last example presents another tetranuclear coordination complex based on the complexation of zinc and 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine[80] (dptz). The ligand used for this coordination becomes a bridging ligand. Although the two pyridyl groups of dptz can rotate around the C–C bonds between the pyridine rings and tetrazine ring, upon coordinating to metal ions the three aromatic rings can become almost coplanar to bridge two metal centres. The dptz ligand would serve as a rigid multitopic spacer ligand and a thermodynamically stable assembly could be formed

by the use of the Zn(II). Figure 1.22 shows the molecular structure of the tetranuclear Zn(II) complex. Figure 1.23 shows the space filling diagram of that complex.

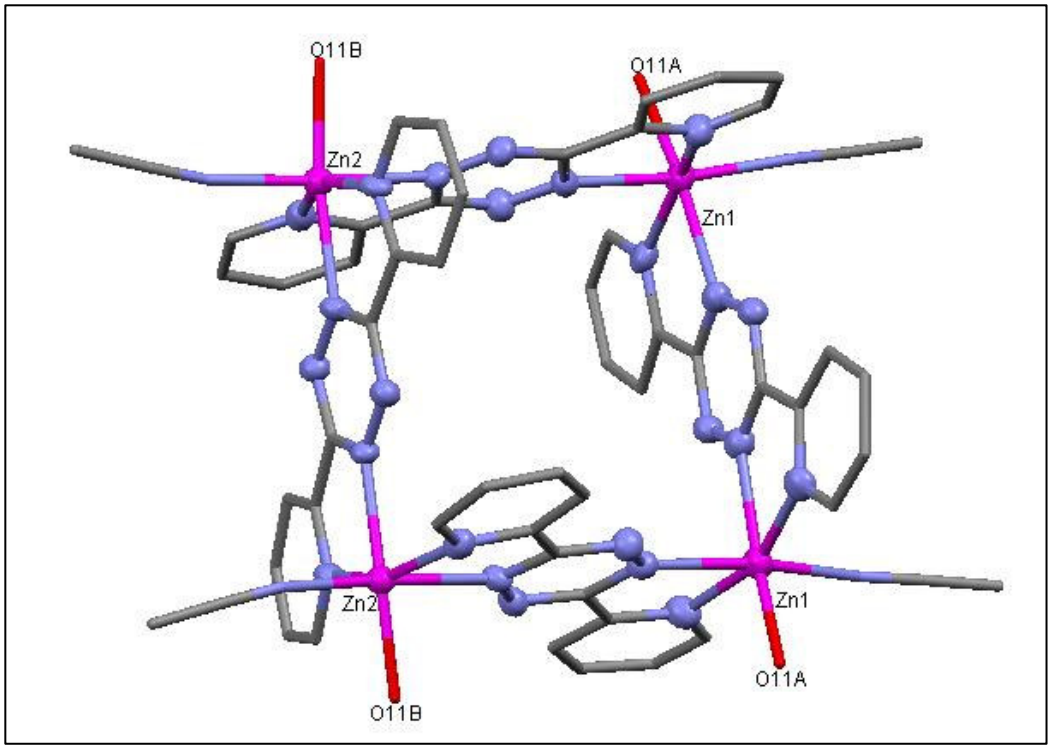

Figure 1.22: The molecular structure of the tetranuclear Zn(II) complex.

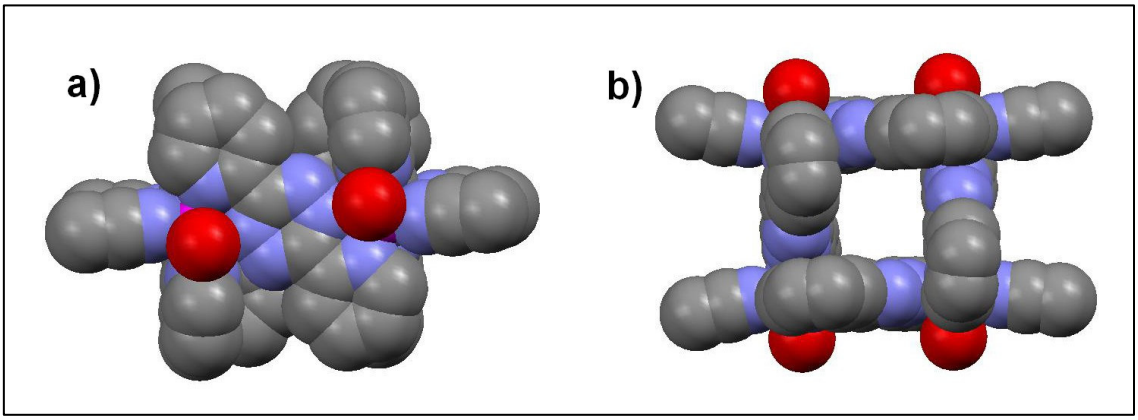

Figure 1.23: Space-filling diagrams showing (a) a side-view and (b) a top-view of the box cavity of the tetranuclear Zn(II) complex.

Literature examples show diverse structures features for complexes involving 1,2,4,5-tetrazine based ligands. For these reasons, we embarked on a study of related ligands and their silver complexes.

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CHAPTER II

General procedure

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GENERAL PROCEDURE

II.1 Introduction

The synthesis of 3,6-dipyridin-2-ylpyridazine substituted ligands is generally a two step synthesis involving 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine and an alkyne compound. The first step is to prepare the alkyne compound with the Sonogashira[1] reaction. The second step consists in an inverse electron demand Diels-Alder[2] reaction. Here the alkyne compound and the 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine react together to give the desired ligand. As all the ligands have been prepared with this two step reaction, a general approach to these main reactions will be given in this chapter.

II.2 The Sonogashira reaction

II.2.1 General approach

The Sonogashira reaction was the main method of preparing all the precursors (except for those we bought) used to synthesise the target ligands. The Sonogashira reaction is a palladium catalysed coupling of terminal alkynes to aromatic bromides or iodides in amine solvent. It is probably the most frequently used carbon-carbon bond forming processes in organic chemistry[3,4].

This coupling is a powerful method to form a carbon-carbon single bond between an sp and sp^2 hybridised carbon centre.

This protocol is based on the discovery of CuI-transmetallation in amines[5] and on a combination of three catalytic cycles (A, B, B', Figure 2.1). This reaction follows the normal oxidative addition, reductive elimination process common to the Pd-catalysed carbon-carbon bond forming reactions. We must say that the exact mechanism is not known. In particular the structure of the catalytically active species and the role of the CuI catalyst remain obscure.The mechanism is described in Figure 2.1.

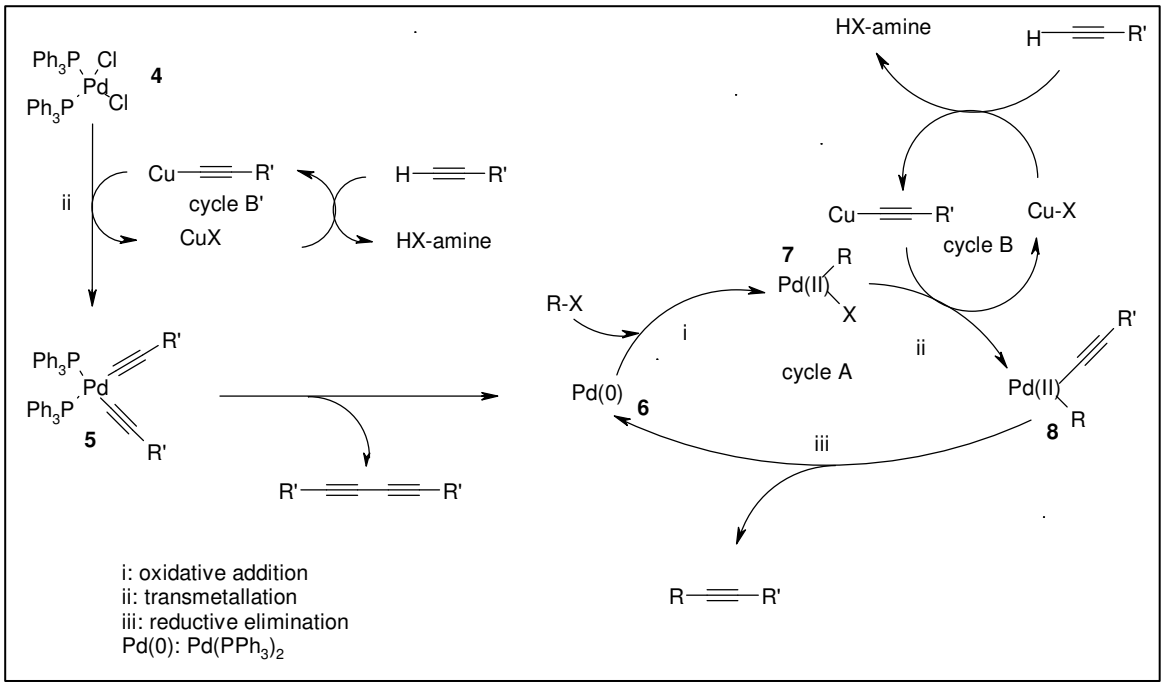


Figure 2.1: Pd-catalysed cross-coupling reaction of halogenated organic substrates with terminal alkynes.

The process may be considered to involve Pd(0) species (6) (neutral $Pd(0)(PPh_3)_2$ or anionic $[Pd(0)(PPh_3)_2X]^-$) which is generated from the Pd(II) pre-catalyst (4) and gives the Pd(II) intermediate (7) by the oxidative addition of sp^2 carbon halide. Subsequent reaction with a terminal alkyne, possibly via a transient copper acetylide species (cycle B), leads to the alkynylpalladium(II) derivatives (8). This then leads to the required coupled products and regenerates the active palladium species (6). There is no evidence for the acceleration of the reductive elimination step by Cu(I) (step iii, from (8) to (6)), although some destabilisation of cis-alkenylacetylide (8) via coordination of Cu(I) to the acetylide ligand is expected[6].

II.2.2 Experimental conditions for the Sonogashira reaction

The Sonogashira reaction is a reliable method for the synthesis of conjugated alkynes by coupling vinyl halide, aryl iodides, bromides or triflates with the terminal alkynes. This synthesis needs a careful choice of substrate and a large amount of

palladium and copper catalyst. Side reactions are often observed if less reactive halide compounds are chosen.

The organic solvents used for this synthesis are toluene, dimethylformamide or tetrahydrofuran. We also need an amine such as diethyl-, triethyl-, or isopropylamine. We decided to use distilled, dried and degassed triethylamine as a solvent. Bis(triphenylphosphine)palladium dichloride and copper(I) chloride were used as catalyst and dissolved in the triethylamine. The reacting halide component and the ethynyl component were added to the suspension. The reaction mixture was then heated under argon at 40-60°C for a range of time varying between 6 to 20 hours. The general scheme of the reaction is presented in Figure 2.2. We obtain a protected intermediate (purified by chromatographic work-up). The deprotection needs the presence of a base. We used an aqueous sodium hydroxide solution (1M).

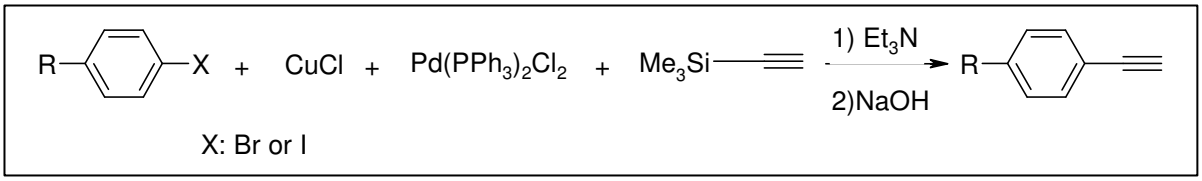


Figure 2.2: General reaction scheme for the Sonogashira reaction.

The palladium catalyst was easily synthesised in a 5 g amount in good yield. This reaction was carried out according to the Cookson[7] method.

The Sonogashira reaction is generally very efficient and with some reactive compounds it can be carried out without heating. This method has been developed by many research groups[8-12] and it is possible to run the reaction without the copper(I) chloride catalyst[13-15]. The main reason for removing the copper(I) chloride is to stop undesired complexation between copper and N-donor-functionalities (if present in the reaction mixture) such as 2,2'-bipyridine or 2,2':6',2''-terpyridine.

II.3 Inverse electron demand Diels Alder reaction

II.3.1 General approach

Ligands containing multiple binding sites are of interest for the construction of structural and reactivity models of certain metallobiomolecules as well as

polyelectronic systems[16]. In this work we decided to focus our interest on highly functionalized pyridazines (such as 3,6-bis(2-pyridyl)-4-phenylpyridazine[17]). Examples of pyridazine molecules synthesised in this thesis are shown in Figure 2.3.

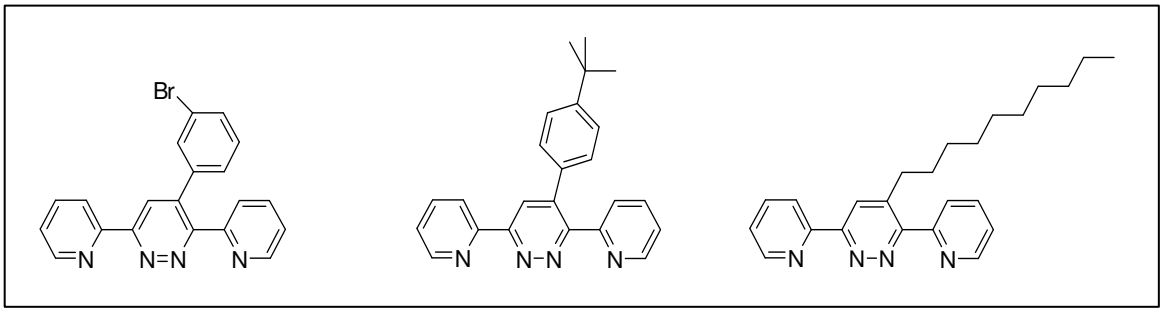


Figure 2.3: Examples of some functionalized pyridazines synthesised in this work.

These compounds can act as metal-coordinating ligands for copper(I)[18], silver(I)[19] and nickel(II)[20] ions, resulting in grid-like metal complexes (Figure 2.4). The introduction of functional groups could allow the incorporation of the ligands and the corresponding metal complexes into larger assemblies and polymers.

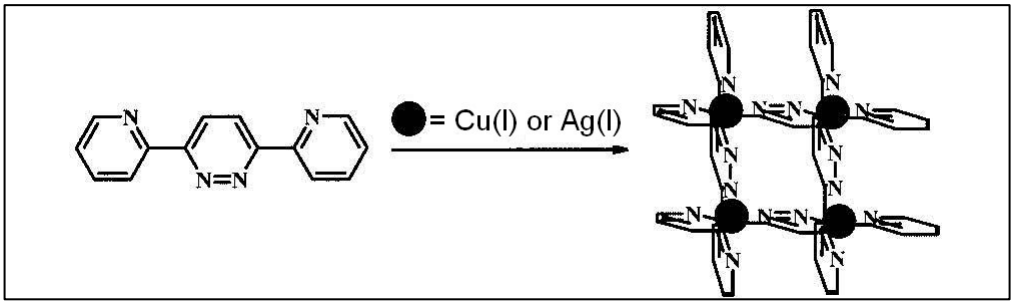


Figure 2.4: Self-assembly of 3,6-di(2-pyridyl)pyridazine into a grid like metal complex with copper(I) or silver(I) ions.

Functionalized pyridazine ligands are easily accessible via an inverse electron demand Diels Alder reaction between 1,2,4,5-tetrazines and a wide range of alkynes, whereby the 1,2,4,5-tetrazine acts as the electron deficient diene. The synthesis of 3,6-dipyridin-2-ylpyridazine and its utilisation in inverse type Diels Alder reaction was first described by Butte and Case[17]. By coupling two 2-cyanopyridines with hydrazine hydrate, 3,6-di(2-pyridyl) dihydrotetrazine was obtained. Oxidation of this dihydrotetrazine resulted in the fully-conjugated 3,6-di(2-pyridyl)tetrazine.

Carboni and Lindsey[21] showed that dienophiles, containing electron-releasing substituents, were found to facilitate the reaction while electron-attracting groups exhibited a retarding effect. Figure 2.5 shows a representation of the inverse electron demand Diels Alder reaction.

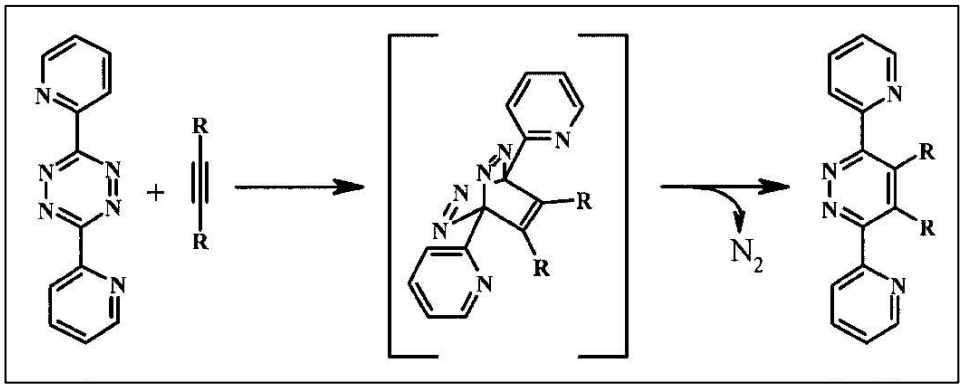


Figure 2.5: Schematic representation of the investigated inverse electron demand Diels-Alder reaction between 3,6-di(2-pyridyl)-1,2,4,5-tetrazine and alkynes.

This cycloaddition is generally slow, but as described before it depends on the nature of the dienophile. For electron withdrawing substituents in the 3- or 6- positions, the reactivity is particularly high, and 1,2,4,5-tetrazine (Figure 2.6) was found to be the second case of Diels Alder reactions with inverse electron demand, as proven by the kinetic measurements of Sauer et al.[22].

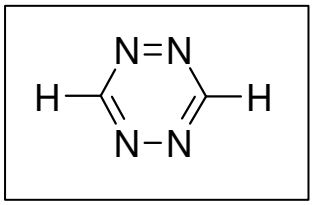


Figure 2.6: Schematic representation of 1,2,4,5 tetrazine.

[4+2]-Cycloaddition of 1,2,4,5-tetrazines are LUMO - HOMO controlled reactions[23]. Donor substituents raise the HOMO energy of the dienophile and by decreasing the LUMO - HOMO gap, increase the rate constant of the cycloaddition step. In principle, any exchange of hydrogen in the dienophile for a larger substituent has an impeding steric effect. So, the substitution of hydrogen by a substituent in the dienophile component, depending on its electron-donating power, can lead to an increase or

decrease of the dienophile's reactivity. This effect is the main explanation for the different reaction times of each ligands synthesised in this work.

In the course of the [4+2]-cycloaddition of tetrazine, the colour (purple) of the diene component disappears. It is easy to monitor the reactions by the disappearance of the typical n→π* absorption[24] of tetrazines. For a large number of dienophiles, 1,2,4,5-tetrazine can be used as an electron poor diene in inverse-type Diels Alder reactions to yield a wide variety of pyridazine derivatives, not easily accessible by other synthetic methods. The results obtained by Sauer[23], using 1,2,4,5-tetrazine as the diene can be applied to other tetrazines.

Following this idea we used 3,6-di(2-pyridyl)-1,2,4,5-tetrazine as an electron poor diene in inverse-type Diels-Alder reaction with many different alkynes. Some examples are given in figure 2.7.

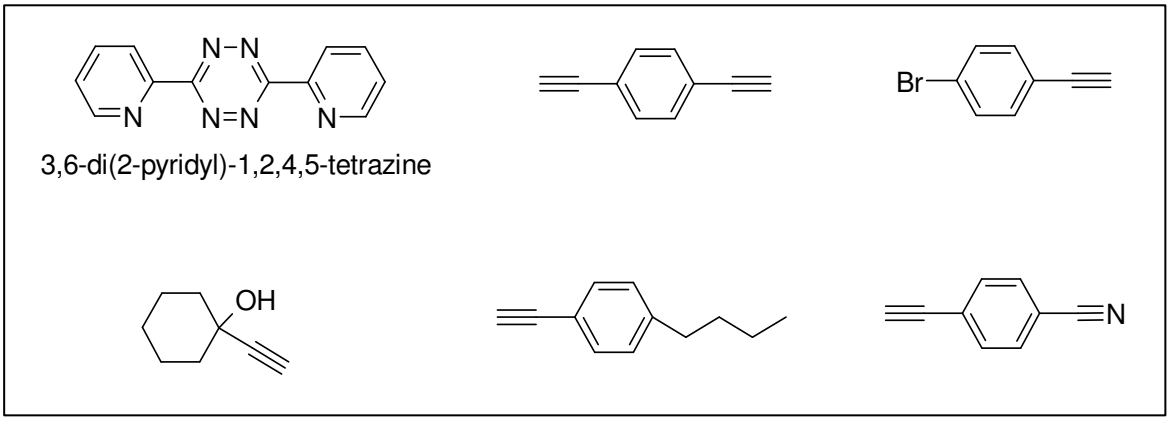


Figure 2.7: 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine and some alkynes used for the inverse-type Diels Alder reaction.

II.3.2 Experimental conditions of the inverse-type Diels Alder reaction

II.3.2.1 Experimental conditions for the 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine synthesis.

3,6-Di(2-pyridyl)-1,2,4,5-tetrazine was obtained by using the Butte and Case[17] synthesis. The compound was prepared by the action of hydrazine on 2-cyanopyridine to give the orange, dihydro compound followed by oxidation with nitric

acid and purification by chromatographic work up. Figure 2.8 shows the general synthesis of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine.

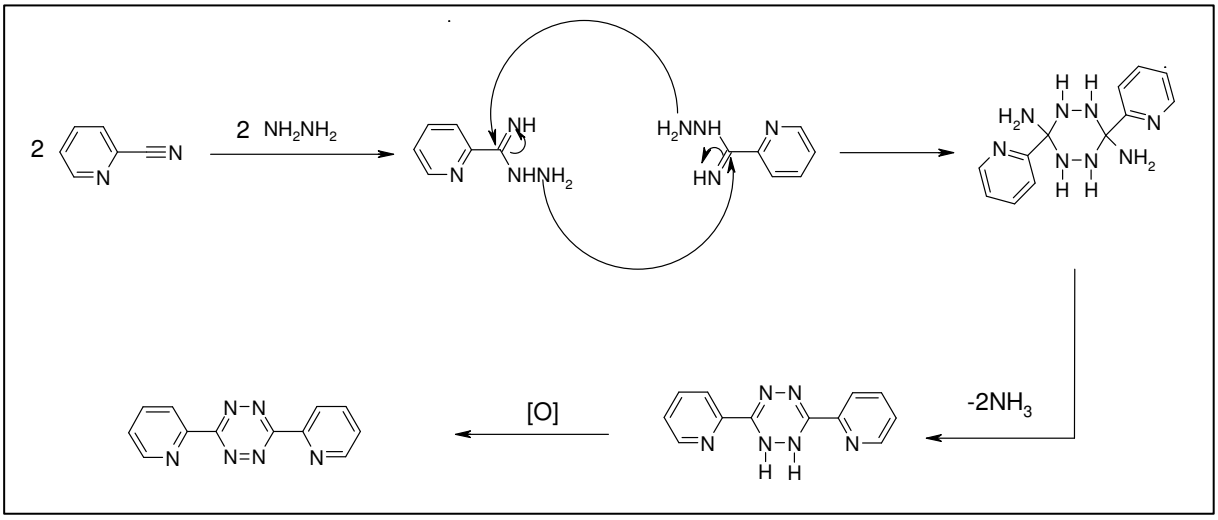


Figure 2.8: Synthetic method to form 3,6-di(2-pyridyl)-1,2,4,5-tetrazine.

II.3.2.2 Experimental conditions of the inverse-type Diels-Alder reaction

The ligand synthesis was achieved by using the 3,6-di(2-pyridyl)-1,2,4,5-tetrazine and the substituted alkyne corresponding to the target molecule. The two compounds were placed under reflux. Several attempts with different organic solvents were made. We tried dimethyl sulfoxide, dimethylformamide, diphenyl ether and toluene. Finally we choose toluene, which had an advantage in respect of its boiling point compared to the three other solvents. Evaporation and purification were much easier with toluene. The reflux time varied from 24 hours to 15 days. The typically purple colour of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine was very useful to determine the reaction times. In fact, the colour of the refluxing solution changed from purple to orange, yellow or brown (depending on the alkyne), when the end of the reaction was reached. We only needed to confirm the presence of the desired ligand with a rapid TLC plate.

In some cases it was impossible to obtain the target ligand with this procedure. We decided to increase the temperature (up to 170°C) and try the reaction without any solvent. Sometimes this strategy enabled us to synthesise the ligand.

The new compounds were then purified by chromatographic work-up (in almost every synthesis) or recrystallisation. The ligands were dried under high vacuum and analysed (^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis) to confirm that the reactions were successful. Figure 2.9 presents schematic examples of some ligand syntheses.

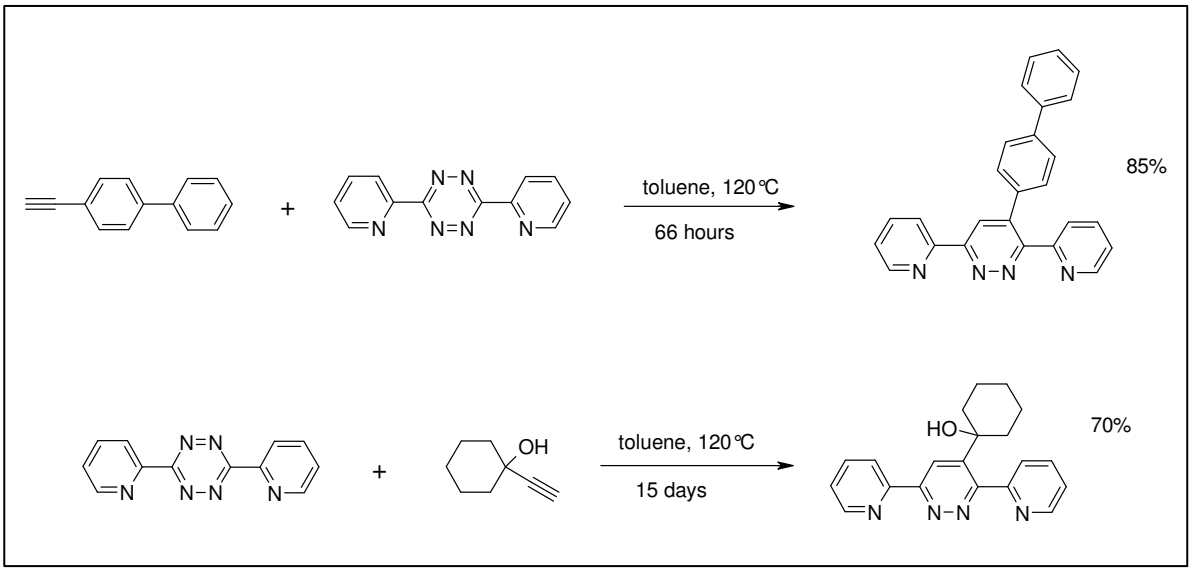


Figure 2.9: Examples of some ligand syntheses.

II.4 Conclusion

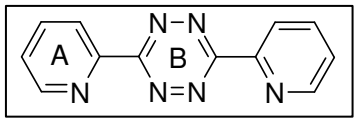
This chapter outlines a general approach for the two main reactions, used to synthesise the N-donor ligands. Some other syntheses have been done and will be discussed in the appropriate chapters.

To prepare the target ligand we typically used the Sonogashira reaction followed by an inverse electron demand Diels Alder reaction. The first step is a palladium catalysed coupling of terminal alkynes to aromatic bromides or iodides in an amine solvent and the second step is a [4+2] cycloaddition involving an electron poor diene compound (3,6-di(2-pyridyl)-1,2,4,5-tetrazine) and dienophiles (alkynes with different electron donating power).

Specific notes, yields and comments will be given for each ligand in the coming chapters.

II.5 Experimental part

Synthesis of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (1)



2-Cyanopyridine (15.0 g; 144 mmol) and hydrazine (19.3 g; 60.3 mmol) were refluxed for 6 hours in 100 ml of ethanol. The resulting orange precipitate was filtered and recrystallised from ethanol. The orange precipitate was dried under high vacuum and dissolved in 70 ml of acetic acid. Concentrated nitric acid (12 ml) was added dropwise with cooling. The solution was stirred at room temperature for 2 hours. Then 100 ml of water was added and the mixture was made alkaline by the addition of sodium hydrogen carbonate (excess). The solution was stirred overnight at room temperature, and then filtered. The product was extracted with chloroform and purified by chromatographic work-up (alumina, dichloromethane/MeOH/EtOAc (1:1:1), the second band was collected) to give a purple powder (5.8 g, 24 mmol, 34%, $C_{12}H_8N_8$, 236.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.96 (d, J=4.7 Hz, 2H, H_{6A}), 8.73 (d, J=7.9 Hz, 2H, H_{3A}), 7.99 (td, J=7.8, 1.6 Hz, 2H, H_{4A}), 7.56 (dd, J=7.6, 4.8 Hz, 2H, H_{5A}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 163.9, 151.0, 150.1, 137.5, 126.6, 124.5.
MS (ES) *m/z* $[Na+L+MeCN]^+$ 300, $[Na+L+MeCN_2]^+$ 340, $[L]^+$ 535.
Elem. Anal. ($C_{12}H_8N_6$) [%] calc. C 61.0, H 3.4, N 35.6; found C 60.6, H 3.4, N 35.1.

Synthesis of bis(triphenylphosphine)palladium dichloride (2)

Under argon, palladium dichloride (2.51 g, 14.1 mmol) was suspended in chloroform (100mL) and triphenylphosphine (9.62 g, 36.7 mmol) was added. The mixture was stirred at room temperature for 1 hour and triphenylphosphine (4.80 g, 18.3 mmol) was added and then refluxed for 10 min at 60°C. The solvent was removed and the residue was recrystallised from hexane to give yellow crystals of $[PdCl_2(PPh_3)_2]$ (5.9 g, 8.4 mmol, 60%, $C_{36}H_{30}Cl_2P_2Pd$, 701.9 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.70 (m, 12H, C_6H_5), 7.38 (m, 18H, C_6H_5).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 143.9, 133.6, 130.5, 129.8, 126.7, 128.0.

Elem. Anal. ($C_{36}H_{30}Cl_2P_2Pd$) [%] calc. C 61.6, H 4.3, found C 62.5, H 4.4.

II.6 Bibliography

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CHAPTER III

Phenyl substituted pyridazines

CHAPTER III

PHENYL SUBSTITUTED PYRIDAZINES

III.1 Introduction

Introducing phenyl substituents on N-donor ligands, such as 2,2'-bipyridine[1,2,3] and terpyridines, has attracted a lot of research interest. The phenyl group can be used to prepare rigid linear bridging ligands composed of two 2,2':6',2''-terpyridines[4].
In this chapter, we focus our interest on phenyl substituted pyridazine. We used the phenyl group as a substituent and as a linker. An example, in our research group, has been published[5]. It has been shown that the phenyl group can be used as a rigid linker between two or three terpyridines and can form co-ordination polymers and oligomers.

This chapter describes the synthesis and the characterisation of the six ligands **3**, **4**, **6**, **8**, **10**, and **13** shown in Figure 3.1 and their silver complexes **3sc**, **4sc**, **6sc**, **8sc**, **10sc**, and **13sc**. It also introduces the synthesis of the ethynyl precursors **5**, **7**, **9**, **11**, and **12** (Figure 3.2).

To simplify the comprehension of the numbering and permit readers to see the relationship between the ligand and its corresponding silver complex, we decided to assign the same number to a ligand and its silver complex. The difference lies in the abbreviation that follows the number assigned to the silver complex. This abbreviation is "**sc**" and stands for "silver complex".

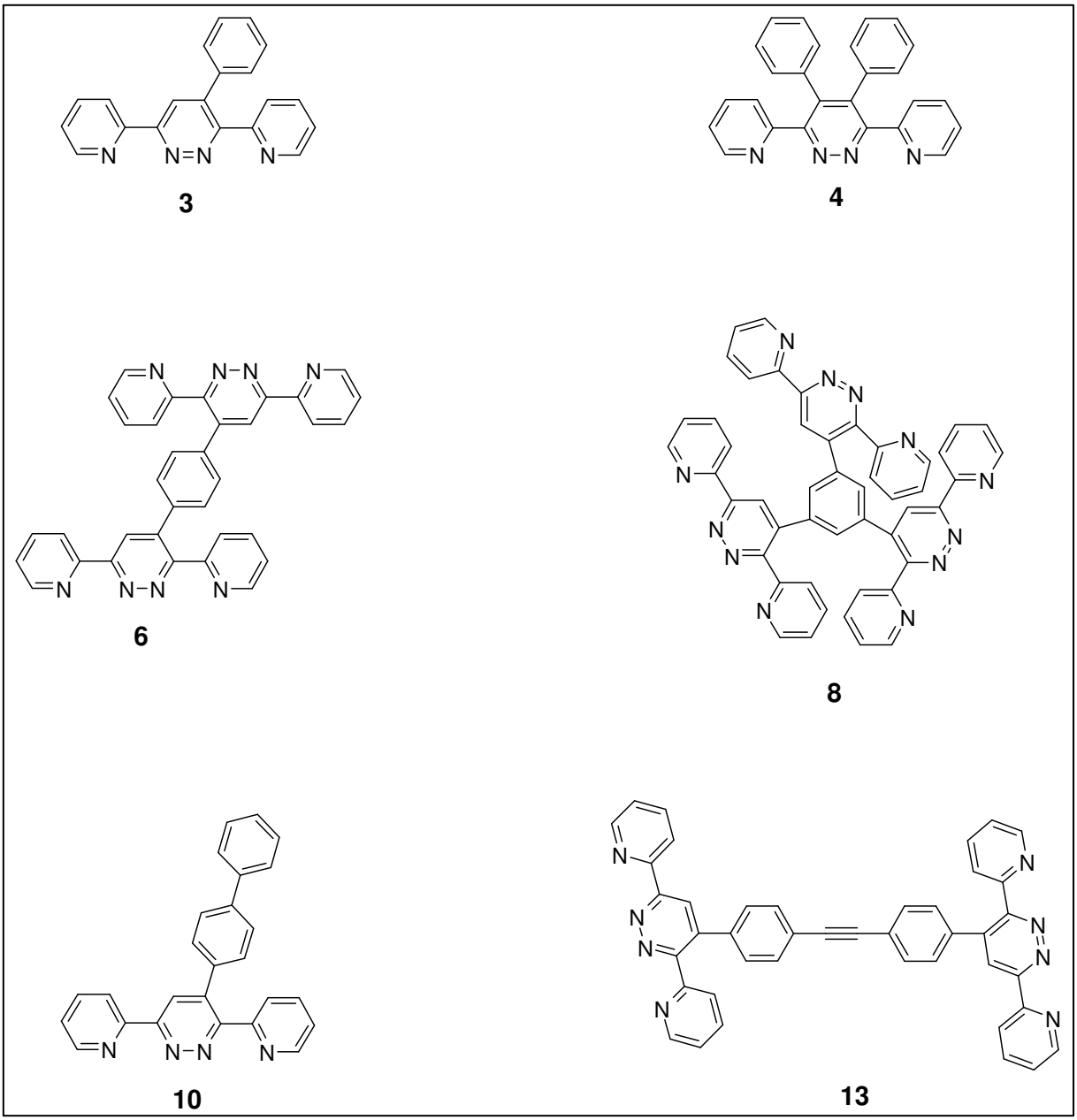


Figure 3.1: Phenyl substituted pyridazine ligands presented in this chapter.

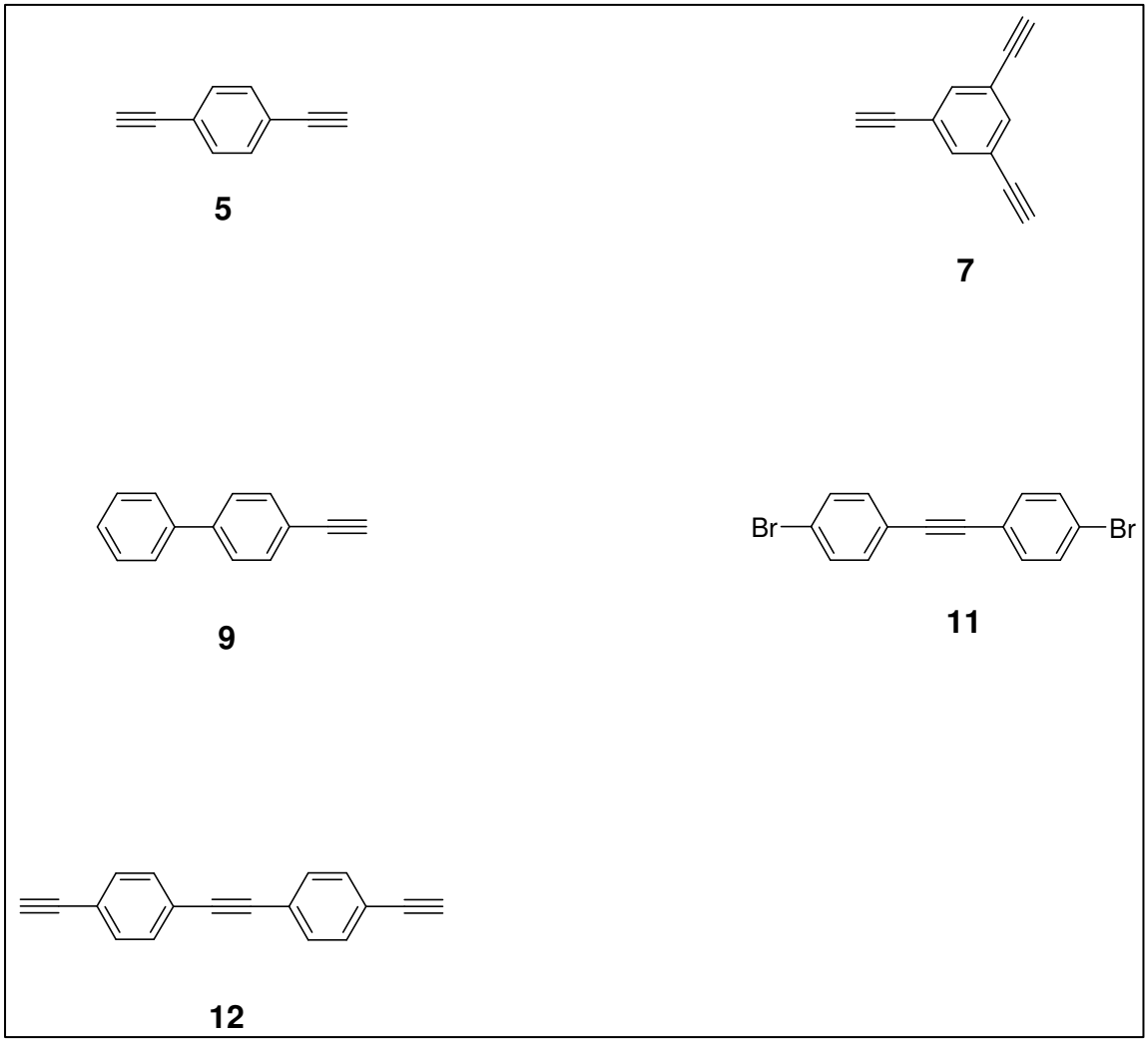


Figure 3.2: Ethynyl precursors described in this chapter.

III.2 Synthesis of the ethynyl precursors

III.2.1 Synthetic method

According to the procedure presented in chapter II, we prepared five ethynyl precursors. We used the basic Sonogashira reaction[6], where the halogenated phenyl compound was mixed with trimethylsilylacetylene, copper(I) chloride and bis(triphenylphosphine)palladium dichloride in triethylamine. This solution was refluxed under nitrogen for several hours to give the protected ethynyl precursors. The deprotection was easily achieved with the use of a strong base. In our case, a solution of 1M sodium hydroxide was the most appropriate. Figure 3.3 describes the general synthetic method.

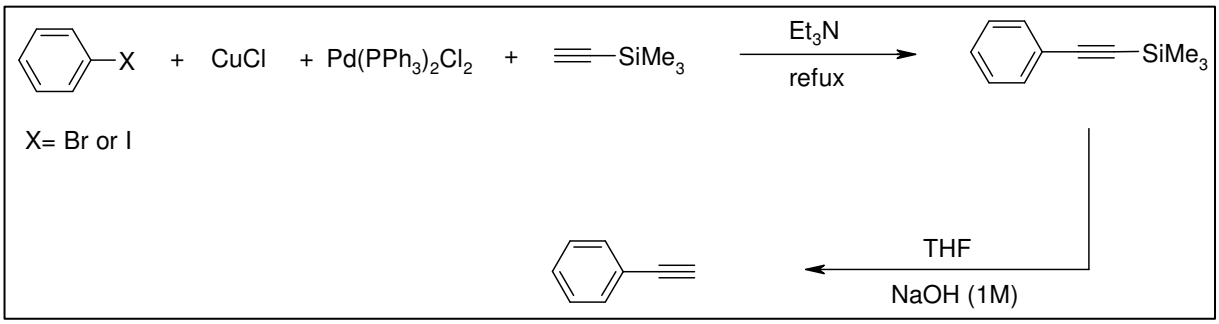


Figure 3.3: General synthetic method for the family of ethynyl precursors described in this chapter.

Copper(I) chloride and bis(triphenylphosphine)palladium dichloride were used in a catalytic amount[7] varying from 5 to 10% in regard of the amount of the halogenated compounds shown in Figure 3.4.

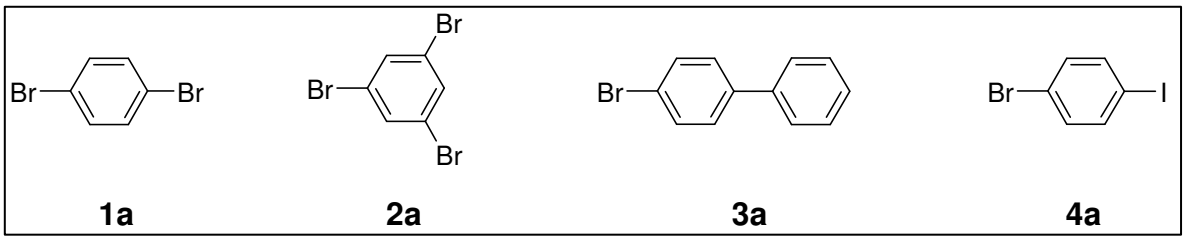


Figure 3.4: Halogenated compounds used for the synthesis of the ethynyl precursors.

For each ethynyl precursor presented in here, the reactant ratio, time and yield are listed in the Table 3.1. Purification methods and synthetic details are discussed in the experimental section at the end of this chapter.

Precursor	**Halogenated compound**	**Reaction ratio** (halogenated / tms acetylene)	**Reaction temperature** (°C)	**Reaction time** (hr)	**Yield** (%)
5	**1a**	1 to 3	40	19	39
7	**2a**	1 to 4	40	18	50
9	**3a**	1 to 2	40	18	75
11	**4a**	acetylene	50	12	60
12	**11**	1 to 3	60	6	53

Table 3.1: Reaction conditions of the synthesis of the ethynyl precursors **5**, **7**, **9** and **12**.

All the ethynyl precursors have been synthesised by following the Sonogashira method. Compounds **5**, **7**, **9**, were synthesised without isolation and characterisation of the protected intermediate. In fact, the purification of the intermediate is a chromatographic work-up with hexane, as an eluent, over alumina. This method enables us to obtain the pure intermediate without traces of the catalysts or the trimethylsilylacetylene. We always collected the major compound. This intermediate was deprotected and isolated as a pure compound. Compound **12** resulted from a two step synthesis[8] with **11** as an intermediate. The synthetic procedure is described in Figure 3.5.

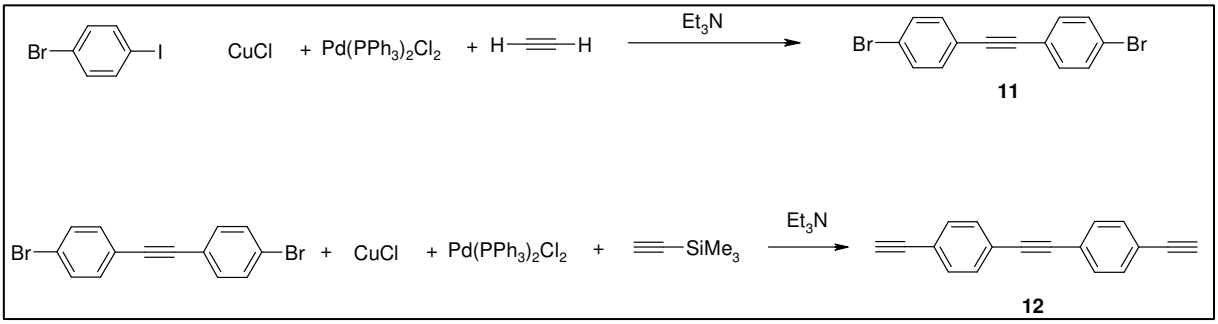


Figure 3.5: Synthetic procedure for compounds **11** and **12**.

For the synthesis of the ethynyl precursors, it was necessary to add an excess of trimethylsilylacetylene to the reaction mixture. But, this excess leads to a coupling reaction[9] between to trimethylsilylacetylene molecules. Nevertheless, this side product was not really a problem to us, because it was easy to remove from the crude products by the chromatographic work-up.

This method was the most appropriate to form the carbon-carbon bond[10] and to access to the desired ethynyl precursors.

III.2.2 Characterisation of the ethynyl precursors

All the ethynyl precursors have been characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

^{1}H NMR spectroscopy

^{1}H NMR spectroscopic characterisation was always the first analysis to be carried out. In the case of the "phenyl-ethynyl" compounds, we focused our interest on the presence of the ethynyl and aromatic signals[7], and on the absence of a signal for the $SiMe_3$ group, present in the protected compound. Table 3.2 shows the ^{1}H NMR signals of the precursors.

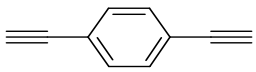
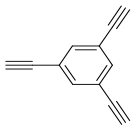
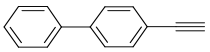
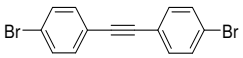
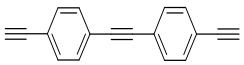
	Ethynyl precursor	**Aromatic signals** (δ/ppm)	**Ethynyl signals** (δ/ppm)
	**5**	7.47	3.18
	**7**	7.56	3.10
	**9**	7.55	3.15
	**11**	7.48-7.37	none
	**12**	7.47	3.18

Table 3.2: ^{1}H NMR characterisation of the precursors **5**, **7**, **9**, **11** and **12** (see figure 3.6).

The ^{1}H NMR spectrum of each ethynyl precursor could be assigned by the chemical shifts and the relative integrals.

As expected[11] the different aromatic signals are at around δ 7.5 ppm and the ethynyl signals are near to δ 3.2 ppm. We can notice that almost all the aromatic signals are singlets. This phenomenon is due to the symmetry of the molecules **5**, **7** and **12** where all the aromatic protons appear to be equivalent. Compound **9** shows a multiplet integrating for 9 protons and the halogenated precursor **11** shows a doublet of doublets. Figure 3.6 shows the ^{1}H NMR spectrum of the five ethynyl compounds.

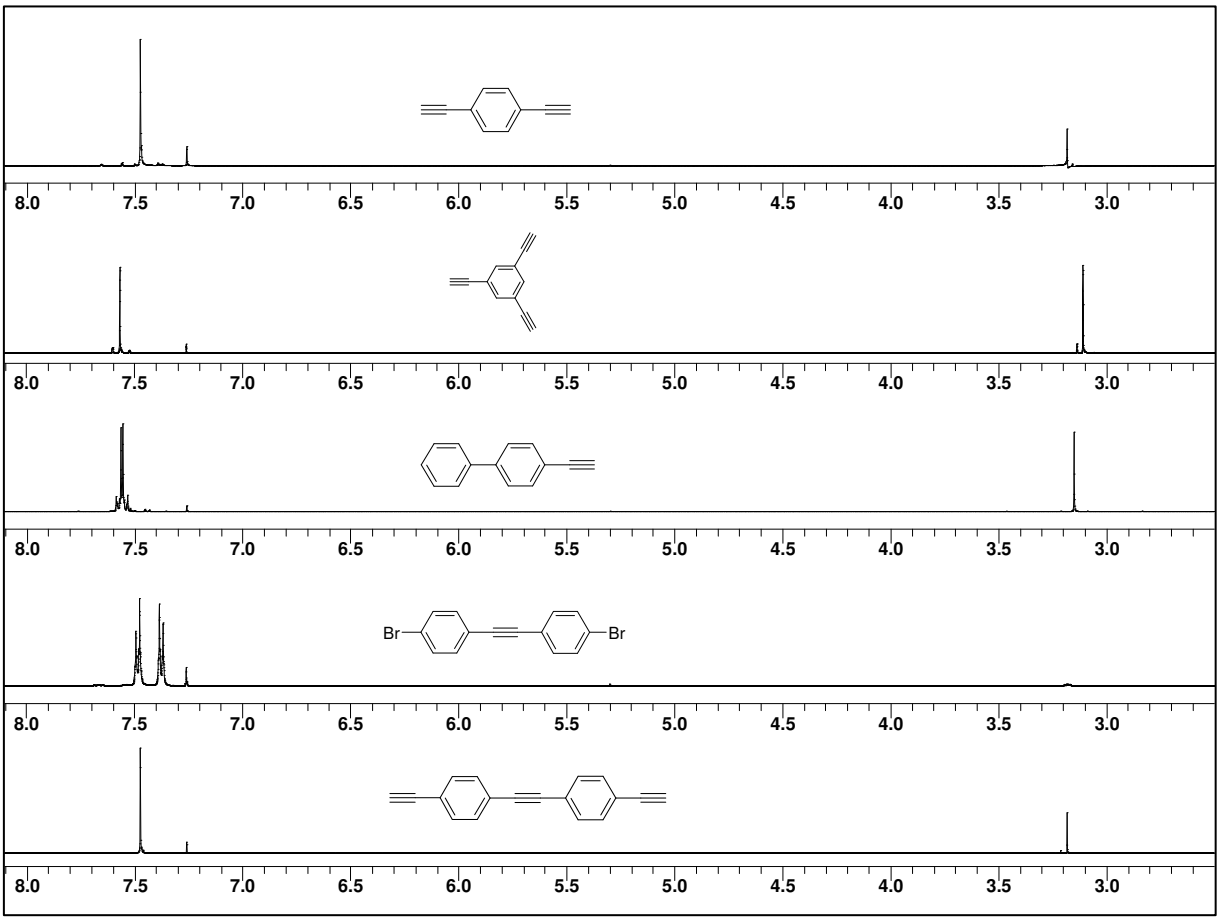


Figure 3.6: ^{1}H NMR spectra of the ethynyl compounds **5**, **7**, **9**, **11** and **12** in $CDCl_3$ solution.

Mass spectrometric characterisation

Most of the ethynyl precursors (**5**, **7**, **9** and **11**) have been characterised by fast atom bombardment spectrometry. All the ethynyl precursors have one or two peaks corresponding to the *m/z* of the precursor or to the *m/z* of the precursor with an ion of sodium. Figure 3.7 shows an example of a mass spectrum of one of the alkyne derivatives.

The mass spectrometry characterisation of each ethynyl precursor is given in the experimental part.

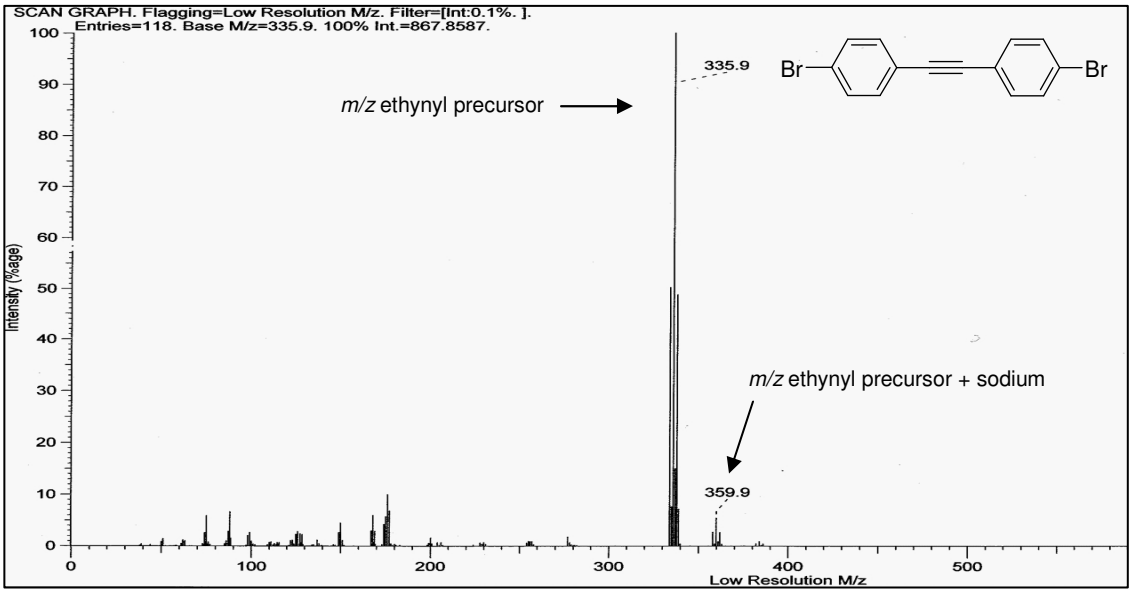


Figure 3.7: Mass (FAB) spectrum of 1,2-bis(4-bromophenyl)ethyne (**11**).

After purification and characterisation, the ethynyl precursors were used to synthesise the target ligands. The phenyl substituted ligand synthesis and characterisation will be discussed in the third part of this chapter.

III.3 Synthesis of the phenyl substituted pyridazine

III.3.1 Synthetic method

We decided to base the synthesis of the phenyl substituted pyridazines on the method presented in chapter II[12]. These ligands are easily accessible via an inverse electron demand Diels Alder reaction between 1,2,4,5-tetrazines and a wide range of alkynes, whereby the 1,2,4,5-tetrazine acts as the electron deficient diene[13].

To carry out the synthesis of the phenyl substituted pyridazines, we used 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (**1**) that has been dissolved in toluene with the ethynyl precursors and placed under reflux. By using this method we synthesized four different ligands (**3**, **6**, **8** and **10**). We were obliged to modify the procedure for the synthesis of the ligands **4** and **13**. They were not accessible by refluxing a toluene solution of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (**1**) and the corresponding ethynyl precursor. It appeared that the temperature was too low to synthesise the ligands. There was not enough energy to proceed to the inverse electron demand Diels Alder reaction. Several attempts, with several solvent systems were carried out, but always resulted in a very low yield. Thus, we decided to do the synthesis of ligands **4** and **13** without solvent at 170°C. This method has been adopted for the synthesis of all the disubstituted pyridazines presented in this work. Reactant ratio, time, solvent and yields are listed in Table 3.3.

Ligand	**Reaction ratio** (tetrazine / ethynyl)	**Reaction temperature** (°C)	**Solvent**	**Reaction time**	**Yield** (%)
3	1 to 1.2	120	toluene	24 hrs	55
4	1 to 1.4	170	none	66 hrs	78
6	2.1 to 1	120	toluene	14 days	90
8	3 to 1	120	toluene	6 days	69
10	1 to 1.8	120	toluene	66 hrs	85
13	4 to 1	170	none	18 hrs	80

Table 3.3: Reaction conditions for the synthesis of the ligands **3**, **4**, **6**, **8**, **10** and **13**.

All the inverse electron-demand Diels Alder reactions presented in this chapter were easy to carry out and there was no need to use a nitrogen or argon atmosphere or freshly distilled toluene. We were obliged to find the optimal conditions (temperature, time, and reactant ratio) and after various unsuccessful attempts we learnt by experience how to carry out successful syntheses.

It was really useful to us to repeat the synthesis of 4-phenyl-3,6-dipyridin-2-ylpyridazine (**3**) presented by Butte and Case[12]. This was the first synthesis, of a substituted pyridazine, made for this work, it enabled us to set all the reaction conditions, see the characteristic colour changing (from purple to yellow), showing the end of the reaction, and compare and assign all the NMR signals of that ligand **3**. Compounds **6**, **8** and **10**, have been successfully synthesized by using the same method as the one described by Butte and Case. They were obtained as powders (respectively pink, pale pink and violet) with relatively good yields. For compounds **4** and **13**, it was impossible to follow the reaction by looking at the colour. At 170°C, we almost reached the melting points and the mixture colour was brown. We then decided to monitor the progress of the reaction by TLC.

All the ligands have been purified by chromatographic work up, except for compound **3** which was recrystallised from ethanol.

III.3.2 Characterisation of the phenyl substituted pyridazines

Every compound has been characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

^{1}H NMR spectroscopy

^{1}H NMR spectroscopy of compounds **3**, **4**, **6**, **8**, **10** and **13** were run in deuterated chloroform and could be assigned by the chemical shifts, relatives integrals, and the coupling patterns.

The ^{1}H NMR spectra of the compounds **3**, **6** and **8** and the assignments are shown in Figure 3.8.

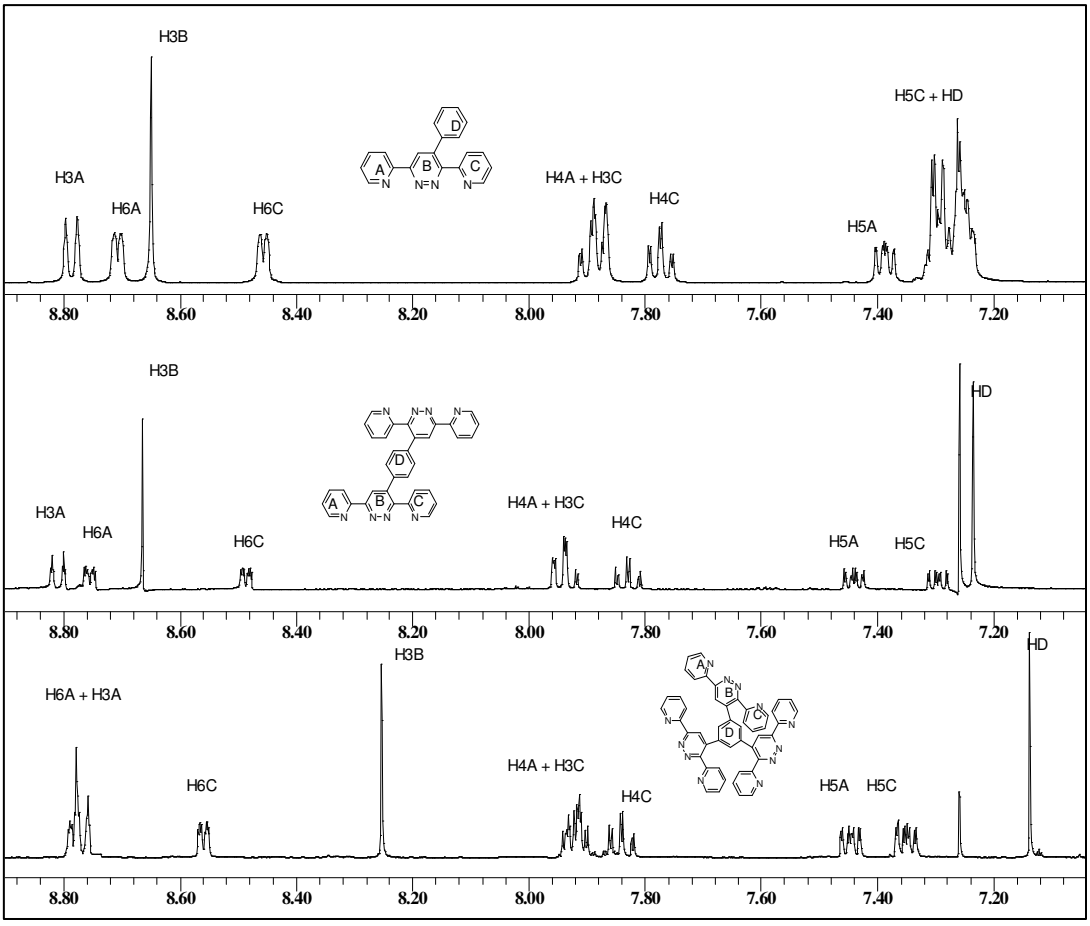


Figure 3.8: The ^{1}H NMR spectra and assignments of ligands **3**, **6** and **8** in $CDCl_3$ solution.

The ^{1}H NMR spectrum of each ligand (**3**, **6** and **8**) shows the typical signals for mono-substituted dipyridin-2-ylpyridazine[14].

The asymmetry of the dipyridin-2-ylpyridazine part of the molecule (due to the substituent) result in a set of nine different NMR signals instead of the four signals present in the spectrum of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**1**). Each ^{1}H NMR spectrum shows four doublets (H_{3A}, H_{3C}, H_{6A}, H_{6C}), two triplets of doublets (H_{4A}, H_{4C}), two doublets of doublets (H_{5A}, H_{5C}) and the typical singlet[14] (H_{3B}). All these signals are in the same region, between δ 7 and 9 ppm. We can also notice an overlapping of some signals. In compound **3** the protons signals H_{4A} and H_{3C} overlap at δ 7.8 ppm. This case is also present in the ^{1}H NMR spectra of compound **8**. For that ligand there is an other overlapping, the proton signals of H_{6A} and H_{3A} are in the same region (δ 8.8 ppm).

The protons of the substituent ring are also assigned by the coupling patterns and relative integrals. For ligand **3**, the five protons signal is a multiplet and also overlaps with the H_{5C} proton signal. The signals of the phenyl substituent from the compounds **6** and **8** are as expected[5]. They both present a singlet integrating respectively for 4 and 3 protons.

The ^{1}H NMR spectra of the compounds **4**, **10** and **13** and the assignments are shown in Figure 3.9.

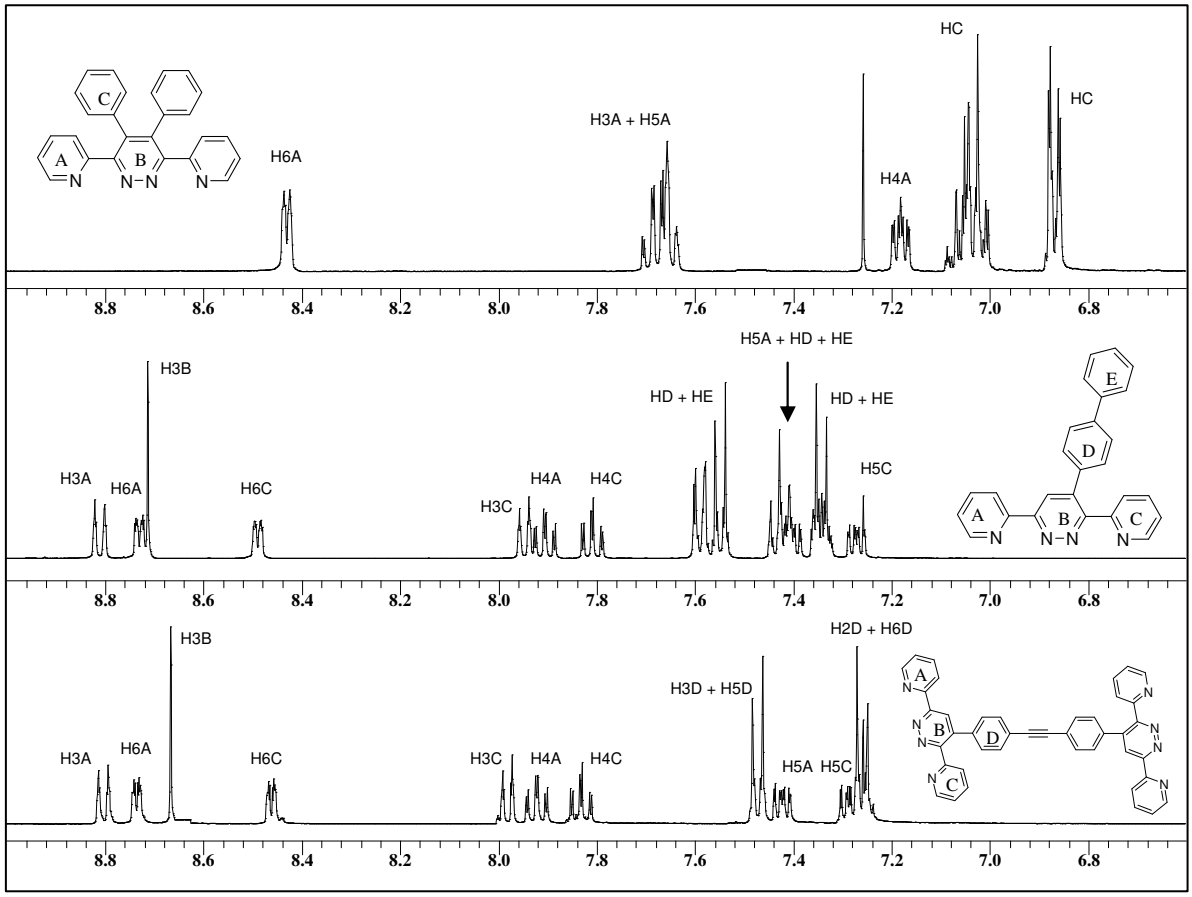


Figure 3.9: The ^{1}H NMR spectra and assignments of ligands **4**, **10** and **13** in $CDCl_3$ solution.

The ^{1}H NMR spectrum of compound **4** shows five signals. The symmetry of the ligand simplifies the spectrum. That spectrum is composed of five signals: three of them are corresponding to the pyridyl rings protons (H_{6A}, H_{3A}+H_{5A} (overlapped) and H_{4A}) and the two others are the phenyl ring signals integrating for 3 and 2 protons. ^{1}H NMR spectra of compounds **10** and **13** are similar to the spectra of ligands **3**, **6** and **8**. They present nine different NMR signals with the typical H_{3B} signal and the substituent signals (biphenyl and bi-substituted phenyl).

All the ^{1}H NMR spectroscopic data for the ligands presented in this chapter are summarized in the Table 3.4.

Ligand	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring
3 (δ/ppm)	8.80 d	7.91 td	7.41 dd	8.72 d	8.66 s	7.89 d	7.79 td	7.29 m	8.47 d	7.29 m
4 (δ/ppm)	7.68 m	7.18 td	7.68 m	8.43 d	∘	∘	∘	∘	∘	7.00-6.87 m
6 (δ/ppm)	8.81 d	7.94 m	7.44 dd	8.75 d	8.66 s	7.94 m	7.78 td	7.30 dd	8.48 d	7.23 s
8 (δ/ppm)	8.77 m	7.90 m	7.44 dd	8.77 m	8.25 s	7.90 m	7.86 td	7.35 dd	8.56 d	7.14 s
10 (δ/ppm)	8.81 d	7.90 td	7.41 m	8.73 d	8.71 s	7.95 d	7.81 td	7.28 dd	8.49 d	7.56-7.41 m
13 (δ/ppm)	8.80 d	7.92 td	7.42 dd	8.74 d	8.66 s	7.98 d	7.83 td	7.29 td	8.46 d	7.47-7.26 d

Table 3.4: The ^{1}H NMR spectroscopic characterisation of ligands **3**, **4**, **6**, **8**, **10** and **13**.

We can see that all the mono-substituted ligands present the same chemical shift for the same proton. In fact, the H_{3A} proton is around δ 8.8 ppm for each ligand, the H_{4A} proton is around δ 7.9 ppm, and the H_{5A} proton is around δ 7.4 ppm. It means that we have the same chemical effect, due to the substituent, for each mono-substituted compound. This effect is not depending from the number of phenyl substituent ring: compound **10** has nearly the same chemical shifts as compound **3**. This effect is also not depending on the number of the pyridazines attached on the phenyl ring: compounds **3**, **6** and **8** have almost the same chemical shifts.

Mass spectrometry

Mass spectrometry of ligands **3**, **4**, **6**, **8** and **10** was run with the electrospray ionisation technique. For all the spectra, except the one from compound **10**, we can see the $[L]^+$ peak. The other peaks correspond to *m/z* of the ligand with a solvent molecule and a sodium or potassium ion. All *m/z* are perfectly consistent with the calculated mass. Mass spectrometry of compound **13** was performed with MALDI mass spectrometry and shows a peak corresponding to *m/z* of the free ligand.

Figure 3.10 shows the mass spectra of compound **4** and **10**.

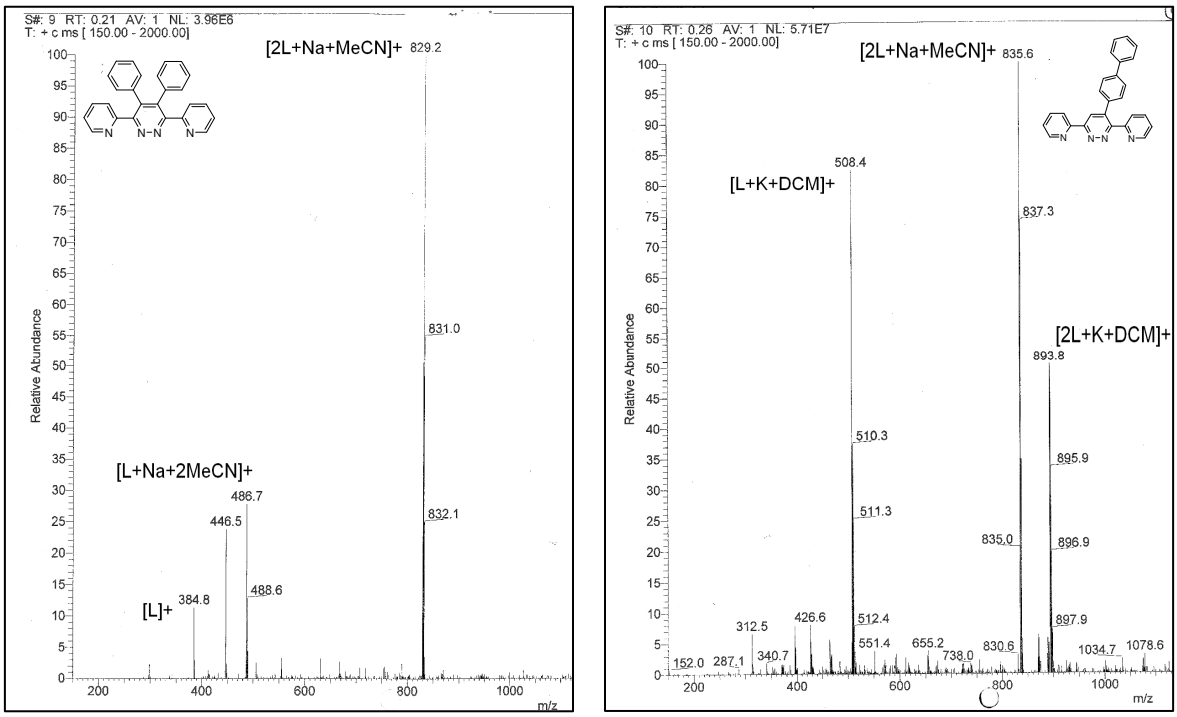


Figure 3.10: Mass spectra of the ligand **4** and **10**.

Table 3.5 summarises the calculated and detected *m/z* values for each ligand.

Ligand	**3**		**4**		**6**		**8**		**10**		**13**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L]^+$	310.4	309	386.4	385	542.6	543	774.8	775	°	°	641.7	643
$[Na+L+MeCN]^+$, $2H_2O$	410.4	411	°	°	°	°	°	°	°	°	°	°
$[Na+2L+MeCN]^+$, $2H_2O$	677.4	678	°	°	°	°	°	°	°	°	°	°
$[Na+L+MeCN]^+$	°	°	477.4	477	°	°	°	°	°	°	°	°
$[Na+L+2MeCN]^+$	°	°	487.4	487	°	°	°	°	°	°	°	°
$[Na+2L+MeCN]^+$	°	°	829.4	829	1044.6	1045	°	°	834.4	835	°	°
$[K+L+2MeCN]^+$	°	°	°	°	664.6	664	°	°	°	°	°	°
$[K+2L+2MeCN]^+$	°	°	°	°	1201.6	1202	°	°	°	°	°	°
$[K+L+DCM]^+$	°	°	°	°	°	°	°	°	507.4	508	°	°
$[K+2L+DCM]^+$	°	°	°	°	°	°	°	°	892.4	893	°	°

Table 3.5: Calculated and detected *m/z* values for the ligands **3**, **4**, **6**, **8**, **10** and **13**.

Single crystal structure for ligand **8**

A crystal of the compound **8** suitable for single X-ray diffraction was grown from a chloroform solution. Details of the structure solution are given in Appendix 1. Figure 3.11 shows the molecular structure of **8**.

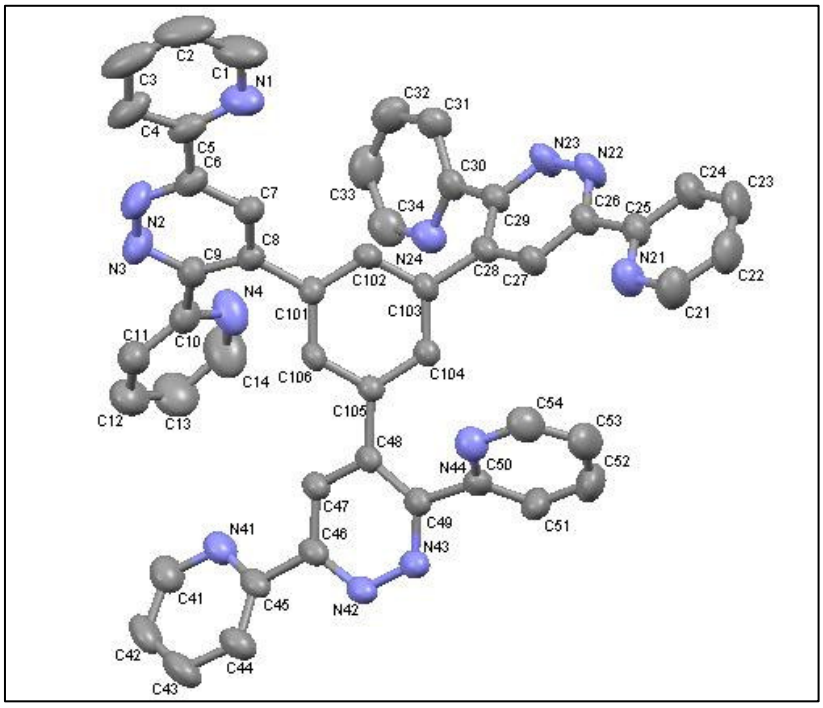


Figure 3.11: The molecular structure of ligand **8** with the labelling scheme.

Compound **8** has three dipyridin-2-ylpyridazine groups attached to the phenyl ring. Each dipyridin-2-ylpyridazine is composed of three heterocyclic rings called A, B and C as mentioned in chapter II. π-π stacking interactions are observed between two pyridyl rings from two different molecules (Figure 3.12). The π-π stacking interaction[15,16], with a distance from 3.52 Å, takes place between the pyridyl ring A from one ligand **8** and pyridyl ring A from an other ligand **8**. The two molecules are related by a centre of symmetry.

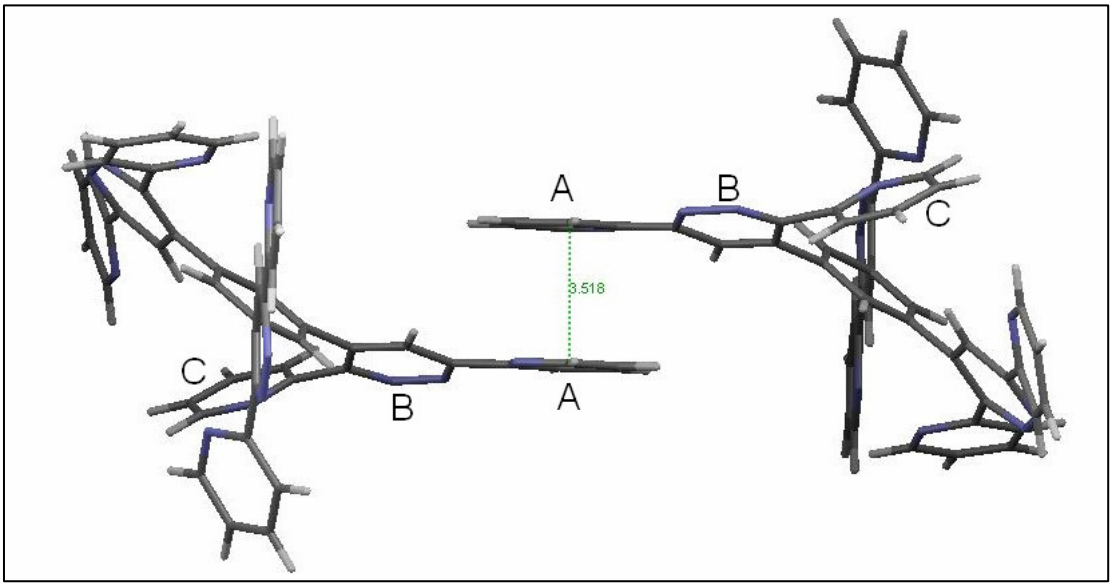


Figure 3.12: The arrangement of two molecules and the π-π stacking interaction in the crystal structure of compound **8**.

We noticed that this ligand does not superimpose with its mirror image and is therefore chiral. Figure 3.13 shows a simplified drawing of ligand **8** and its mirror image.

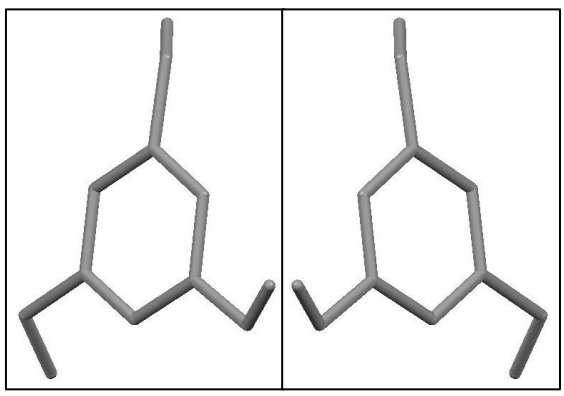


Figure 3.13: Simplified representation of ligand **8** and its mirror image.

The pyridyl rings A, B and C are not coplanar. The torsion angles from C-C-C-N are varying between 4.0° and 47.5°. Table 3.6 summarises the C-C-C-N torsion angles present, between the pyridyl rings, in ligand **8**.

	Torsion angles (C-C-C-N)		
C4-C5-C6-N2	15.44°	40.68°	C11-C10-C9-N3
C51-C50-C49-N43	47.50°	31.06°	C44-C45-C46-N42
C24-C25-C26-N22	4.02°	41.88	C31-C30-C29-N23

Table 3.6: C-C-C-N torsion angles present in ligand **8**.

III.4 Synthesis of the silver complexes

III.4.1 Synthetic method

The silver(I) centre in each complex possesses d^{10} electronic configuration. The complexes are mainly square planar[17]. We considered that the introduction of a range of different substituents on the four position of the pyridazine would force the adjacent 3-(2'-pyridyl) ring out of the plane leading to structures with a non planar shape.

Unfortunately, it was impossible to grow crystals from the five new silver(I) complexes synthesised and presented in this chapter.

All the ligands synthesised in this chapter have been used to prepare their silver complexes **3sc**, **4sc**, **6sc**, **8sc**, **10sc** and **13sc**. The reaction of the ligands with the silver salt in acetonitrile proceeded smoothly to give a yellow-orange solution from witch the complex was obtained.

Table 3.7 summarises the experimental conditions for the synthesis of the species **3sc**, **4sc**, **6sc**, **8sc**, **10sc** and **13sc**.

Silver complex	**Reaction ratio** (ligand / silver)	**Silver salt**	**Yield** (%)
3sc	1 to 1	$AgCF_3SO_3$	88
4sc	1 to 1	$AgBF_4$	86
6sc	1 to 1	$AgCF_3SO_3$	91
8sc	1 to 3	$AgBF_4$	77
10sc	1 to 1	$AgBF_4$	92
13sc	1 to 2	$AgBF_4$	88

Table 3.7: Experimental method for the synthesis of the silver complexes **3sc**, **4sc**, **6sc**, **8sc**, **10sc** and **13sc**.

All the silver complexes were prepared by mixing the silver salt and the ligand in acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes. They were easily accessible and it was not necessary to proceed to a chromatographic work up or recrystalisation. All the silver complexes are insoluble in chloroform, slightly soluble in acetonitrile, and soluble in dimethylsulfoxide. However, it was not always possible to obtain ^{13}C NMR spectroscopic data (except for **10sc**).

III.4.2 Characterisation of the silver complexes

The complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. Because of the low solubility of some of these silver complexes, it was sometimes impossible to obtain a well resolved ^{1}H NMR or ^{13}C NMR spectrum. Compounds **3sc**, **4sc**, **6sc**, **8sc** were not soluble enough in DMSO to obtain the carbon NMR spectrum. Complex **8sc** was not soluble enough in DMSO to obtain the proton NMR spectrum. They were all characterised by mass spectrometry.

^{1}H NMR spectroscopy

^{1}H NMR spectroscopy of complexes **3sc**, **4sc**, **6sc**, **8sc**, **10sc** and **13sc** have been run in deuterated dimethylsulfoxide and could be assigned by the chemical shifts, relatives integrals and the coupling patterns.

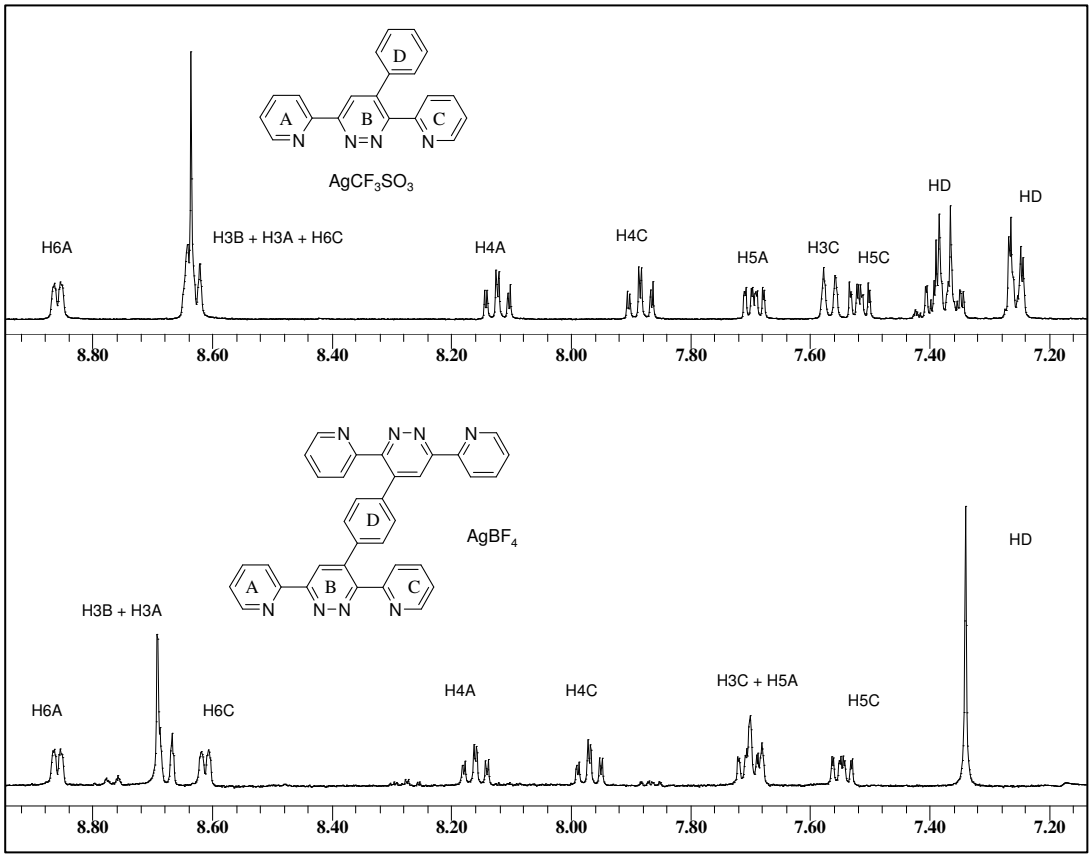


Figure 3.14: ^{1}H NMR spectra of silver complexes **3sc** and **6sc**.

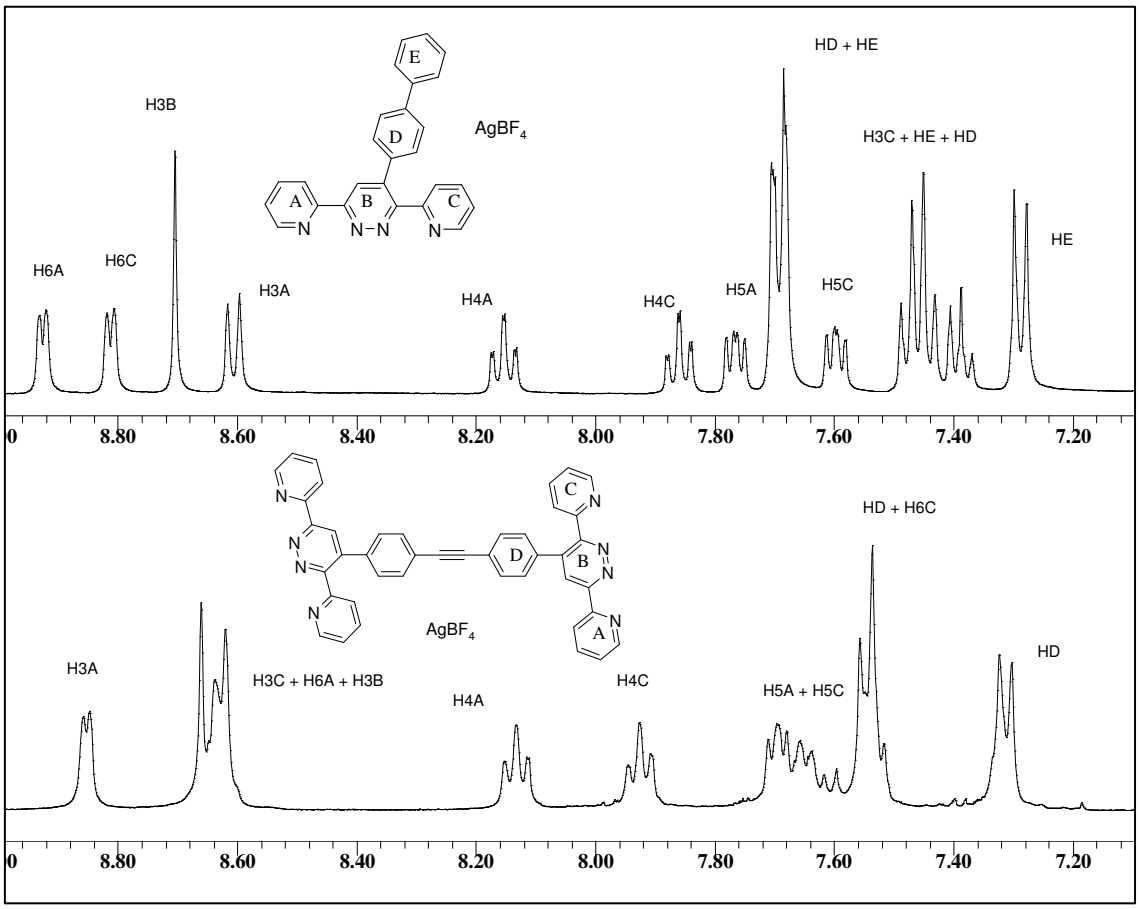


Figure 3.15: ^{1}H NMR spectra of silver complexes **10sc** and **13sc**.

^{1}H NMR spectra of the silver complexes **3sc**, **6sc**, **10sc** and **13sc** and the assignments are shown in figures 3.14 and 3.15.

^{1}H NMR spectrum of 3,6-bis(2′-pyridyl)- 3,4-diphenyl pyridazine silver complex (**4sc**) is presented in Figure 3.16.

All the ^{1}H NMR spectra show the same signals as those present in the ^{1}H NMR spectrum of their respective ligand. For the mono substituted pyridazine silver complexes **3sc**, **6sc**, **10sc** and **13sc** we can see the signal (singlet) of the H_{3B} proton. This signal is typically shifted to high field, which is characteristic for a one to one silver complexation[18].

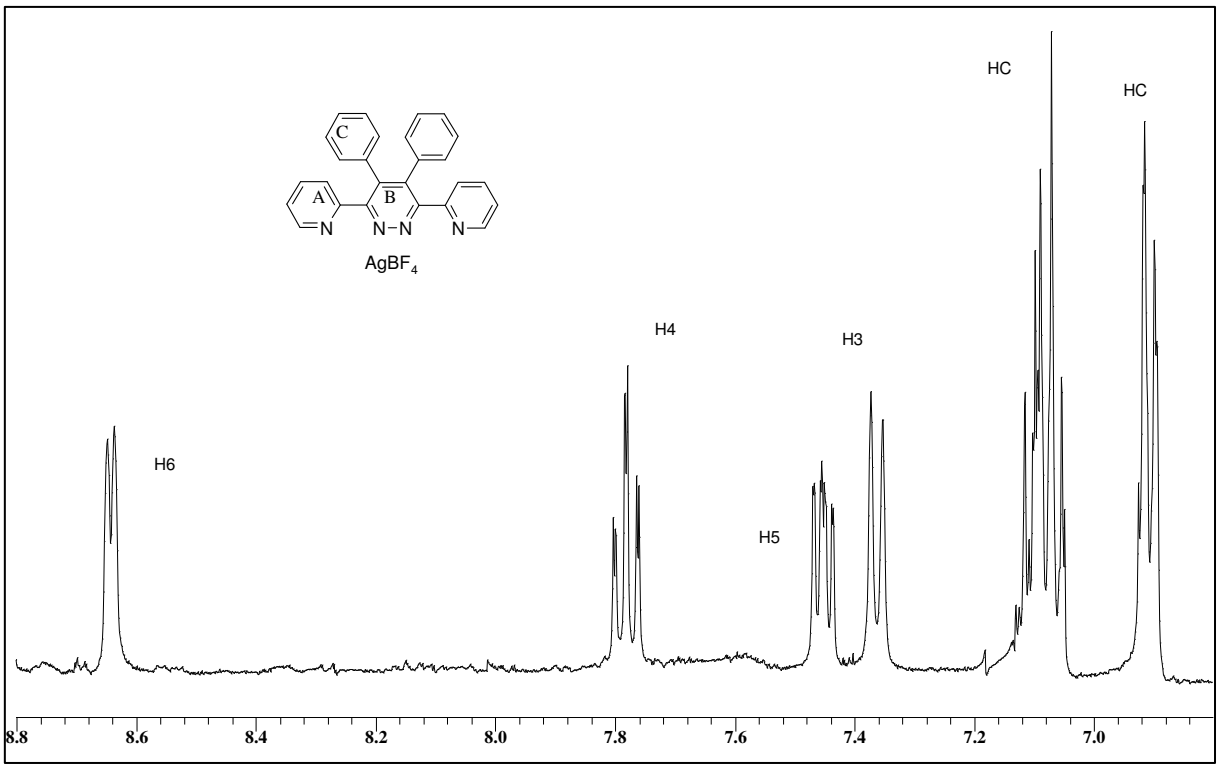


Figure 3.16: ^{1}H NMR spectrum of 3,6-bis(2′-pyridyl)- 3,4-diphenyl pyridazine silver complex (**4sc**).

The spectra of all the silver complexes exhibited a single ligand environment. No species other than the free ligands and the silver complexes were detected by ^{1}H NMR spectroscopy.

The complexation of the ligand and the silver species induces some overlapping signals. In the silver complex **13sc** three signals (H_{3C}, H_{6A} and H_{3B}) have almost the same chemical shift (δ 8.62 ppm). This case also appears in the ^{1} H NMR spectrum of 4-phenyl-3,6-dipyridin-2-ylpyridazine silver complex (**3sc**). It is important to notice that the protons H_{3B}, H_{6A+6C} and H_{3A+3C} are the most affected by the silver complexation, with their signals being shifted to higher field. This effect is due to the short distance between the affected proton and the N-Ag bond.

The species **4sc** shows sharp signals. There is no H_{3B} signal because both 3B and 4B positions are substituted by phenyl groups. All the proton signals are present. The overlapping of the signals from the protons H_{3A} and H_{5A} present in the ^{1}H NMR of the free ligand disappears in the ^{1}H NMR of the silver complex and shows the different shifts (high and low field) that are induced by the silver complexation.

Table 3.8 summarises the ^{1}H NMR spectroscopic data for the silver complexes presented in this chapter.

Silver Complex	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring
3sc (δ/ppm)	8.65 m	8.14 td	7.72 dd	8.87 d	8.65 m	7.58 d	7.90 fd	7.54 dd	8.65 m	7.39-7.27 m
4sc (δ/ppm)	7.38 d	7.80 td	7.47 dd	8.66 d	∘	∘	∘	∘	∘	7.10-6.92 m
6sc (δ/ppm)	8.69 m	8.18 t	7.72 m	8.88 d	8.69 m	7.72 m	8.00 td	7.56 dd	8.18 d	7.36 s
8sc (δ/ppm)	∘	∘	∘	∘	∘	∘	∘	∘	∘	∘
10sc (δ/ppm)	8.62 d	8.17 td	7.78 dd	8.94 d	8.72 s	7.44 m	7.88 td	7.61 dd	8.83 d	7.56-7.41 m
13sc (δ/ppm)	8.87 d	8.15 td	7.67 m	865 m	8.65 m	8.65 m	7.94 td	7.67 m	7.57 m	7.57 m - 7.33 d

Table 3.8: The ^{1}H NMR spectroscopic characterisation of silver complexes **3sc**, **4sc**, **6sc**, **8sc**, **10sc** and **13sc**.

The ^{1}H NMR characterisation of the different silver complexes synthesised in this chapter was successful, except for 1,3,5-tris(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzene silver complex (**8sc**) which could not be characterised by ^{1}H or ^{13}C NMR spectroscopy. There was no doubt about the ligand (fully characterised and X-ray structure) but the nature of the complex was hard to determine.
All the silver complexes could be characterised by mass spectrometry.

Mass spectrometry

Mass spectrometry of all the silver complexes was run with electro spray ionisation technique. The species have been dissolved in acetonitrile.
The mass spectrometry of the complexes **3sc**, **4sc** and **6sc** show the expected[19] $[AgL]^{+}$ peak. Beside this peak we could see the ligand peak (**6sc**), the $[Ag(L)MeCN]^{+}$ and $[AgL_2]^{+}$ peaks (**3sc**, **4sc**) and the $[NaL_2MeCN]^{+}$ peak for the complex **3sc**.
As the 1,3,5-tris(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzene silver complex (**8sc**) could not be characterised by NMR spectroscopy because of its low solubility in acetonitrile, we decided to run the mass spectrometry in acetonitrile. For the electrospray technique, we do not need a lot of compound in the solution (less than 0.1mg per mL) and the low solubility of the complex was not a problem in this case.

We obtained an electrospray spectrum that exhibited two peaks. These peaks were assigned to the ligand peak (*m/z*= 775) and to the $[AgL_2MeCN]^+$ peak (*m/z*=1033). 3,6-Bis(2′-pyridyl)-4-biphenylpyridazine (**10sc**) and 1,2-bis(4-phenyl-3,6-dipyridin-2-ylpyridazine)ethyne silver complex (**13sc**) both show the same peaks assigned to the ligand and to the species $[AgL]^+$.

Table 3.9 summarises the calculated and the detected *m/z* values for each silver complex and Figure 3.17 shows representative mass spectra (**3sc** and **10sc**).

silver complex	**3sc**		**4sc**		**6sc**		**8sc**		**10sc**		**13sc**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L]^+$	°	°	°	°	542	543	774	775	386	387	643	643
$[Ag+L+MeCN]^+$	459	458	535	534	°	°	°	°	°	°	°	°
[Na+2L+MeCN]	683	683	°	°	°	°	°	°	°	°	°	°
$[Ag+L]^+$	418	417	494	495	650	652	°	°	492	493	751	753
$[Ag+2L]^+$	628	727	880	881	°	°	°	°	°	°	°	°
$[Ag+2L+MeCN]^+$	°	°	°	°	°	°	1031	1033	°	°	°	°

Table 3.9: Calculated and detected *m/z* values for the species **3sc**, **4sc**, **6sc**, **8sc**, **10sc** and **13sc**.

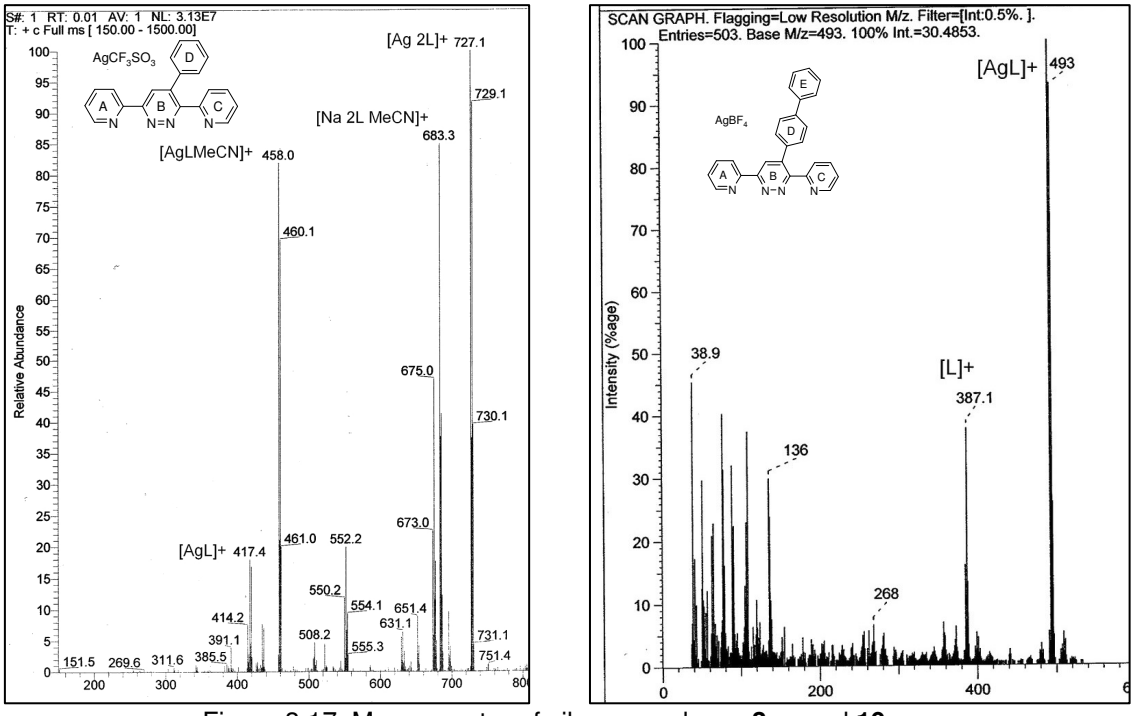


Figure 3.17: Mass spectra of silver complexes **3sc** and **10sc**.

Structural proposal

Many attempts, to obtain single crystals suitable for X-Ray analysis, were unsuccessful. We tried different solvent systems, different technique (slow diffusion and slow evaporation). It was impossible to determine the structure of the complexes prepared in this chapter.

But, with a closer look at the mass spectrometry and the result obtained by Christopher B. Smith in our group[17] (he presented the silver complexes of 3,6-di(2-pyridyl)pyridazine and 4-phenyl-3,6-dipyridin-2-ylpyridazine (**3**)) we can try to predict the possible structures of the phenyl substituted pyridazine silver complexes. In fact, most of the complexes show $[AgL]^+$ and/or $[AgL_2]^+$ peaks in their mass spectrum. This would mean that one ligand is coordinated with one silver ion, or that two ligands are coordinated with one silver ion. The geometry of the complexes is likely to be square planar. Figure 3.18 shows a drawing of the possible structures.

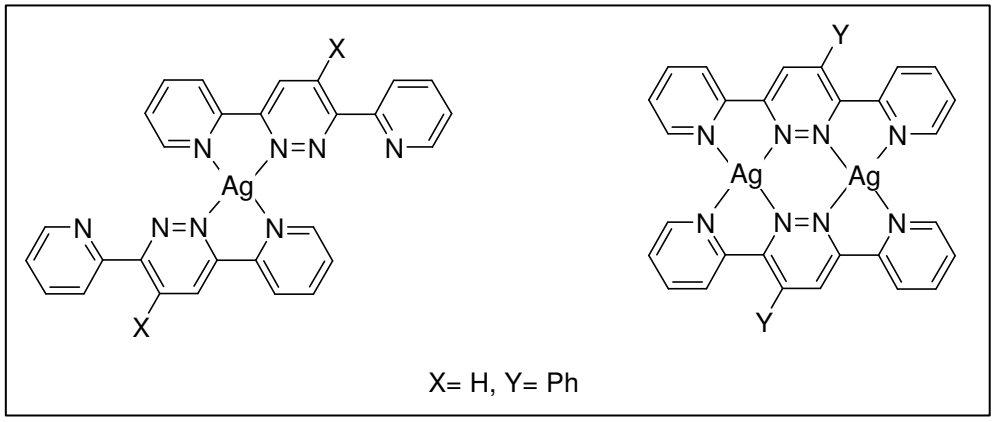


Figure 3.18: Drawing of the possible crystal structures from the silver complexes presented in this chapter.

The crystal structure of compound **3sc** was obtained by C. B. Smith and is showed in figure 3.19. This crystal structure shows a dinuclear $[Ag_2L_2]^{2+}$ cation.

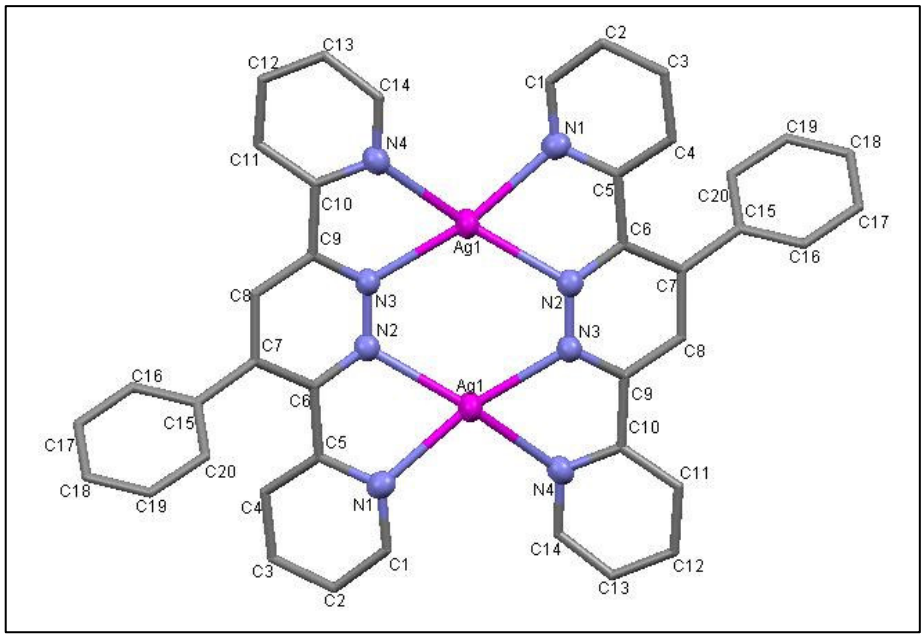


Figure 3.17: Crystal structure from complex **3sc** synthesised by Christopher B. Smith[17].

The two ligands are arranged in a trans configuration about the dinuclear silver core. We can also see that the phenyl substituents are twisted with respect to the pyridazine that they are bounded to with a torsion angle of 58°. There are no π-stacking or short C···H interactions involving the heterocyclic or phenyl rings of the ligand. The terminal pyridine rings are significantly out of the plane of the pyridazine (angle: 28.7° and 35.5°). This twisting is reminiscent of the distortion from ideal square planar geometry. This distortion has a consequence for the coordination geometry and the sum of bond angles about the silver is 688.5°, which is best described as a flattened tetrahedron.

These square planar or almost square planar geometries were the most frequently encountered during all this work. But sometimes, we were faced with different and unexpected geometries. This will be described in the coming chapters.

III.5 Conclusion

In this chapter we described the synthesis of the ethynyl precursors **5**, **7**, **9**, **11** and **12** that have been prepared with the Sonogashira reaction.

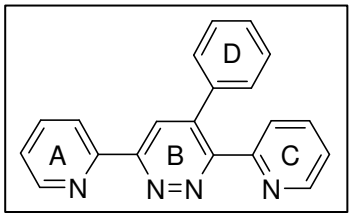
We also showed the methodology to access to mono- and di-substituted pyridazine, based on an inverse electron demand Diels-Alder reaction that enabled us to prepare the ligands **3**, **4**, **6**, **8**, **10** and **13**. All these ligands were characterised by NMR, mass spectrometry and elemental analysis. We also obtained a single X-ray crystal structure for the ligand **8**.

Five new silver complexes (**4sc**, **6sc**, **8sc**, **10sc** and **13sc**) were prepared and characterised by NMR, mass spectrometry (apart from some cases, discussed in the chapter).

Unfortunately, it was impossible to obtain suitable crystal from the silver complexes to do single X-ray diffraction.

III.6 Experimental part

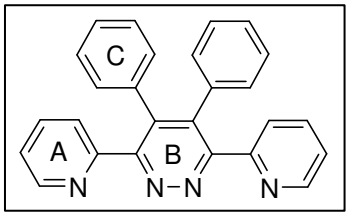
Synthesis of 4-phenyl-3,6-dipyridin-2-ylpyridazine (3)



Phenylethyne (330 mg, 3.24 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (660 mg, 2.80 mmol) were dissolved in 25 ml of toluene and refluxed for 24 hours. The solvent was removed by evaporation and the solid residue was recrystallised from ethanol to give a beige powder (480 mg, 1.54 mmol, 55.0%, $C_{20}H_{14}N_4$, 310.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.80 (d, J=7.9 Hz, 1H, H_{3A}), 8.72 (d, J=4.8 Hz, 1H, H_{6A}), 8.66 (s, 1H, H_{3B}), 8.47 (d, J=5.0 Hz, 1H, H_{6C}), 7,91 (td, J=7.6, 1.6 Hz, 1H, H_{4A}), 7.89 (d, J=7.7 Hz, 1H, H_{3C}), 7.79 (td, J=7.7, 1.6 Hz, 1H, H_{4C}), 7.41 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.29 (m, 6H, H_{5C} and H_D).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.3, 157.7, 155.7, 153.3, 149.4, 149.0, 140.5, 137.2, 136.9, 136.6, 128.9, 128.4, 125.7, 124.9, 124.8, 123.4, 121.9, 3 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 309, $[Na+L+MeCN+2H_2O]^+$ 411, $[Na+2L+2H_2O]^+$ 678.
Elem. Anal. ($C_{20}H_{14}N_8$) [%] calc. C 77.4, H 4.6, N 18.0, found C 77.0, H 4.7, N 17.8.

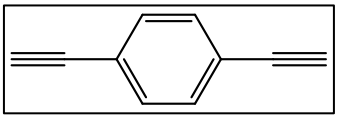
Synthesis of 3,6-bis(2′-pyridyl)- 4,5-diphenyl pyridazine (4)



Diphenylethyne (214 mg, 1.20 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (200 mg, 0.85 mmol) were heated without solvent at 170°C for 66 hours. The product was purified by chromatographic work-up (alumina, $CHCl_3$, the third band was collected) to give a red powder (258 mg, 0.66 mmol, 77.6%, $C_{26}H_{18}N_4$, 386.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.43 (d, J=4.4 Hz, 2H, H_{6A}), 7.68 (m, 4H, H_{3A+5A}), 7,18 (td, J=7.0, 1.6 Hz, 2H, H_{4A}), 7.0 (m, 6H, H_C), 6.87 (m, 4H, H_C).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.9, 156.1, 148.8, 139.2, 136.1, 134.7, 130.1, 127.5, 127.2, 125.0, 122.8, 2 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 385, $[L+Na+MeCN]^+$ 477, $[L+Na+2MeCN]^+$ 487, $[2L+Na+MeCN]^+$ 829.
Elem. Anal. ($C_{26}H_{18}N_4$) [%] calc. C 80.8, H 4.7, N 14.5, found C 79.4, H 4.6, N 14.2.

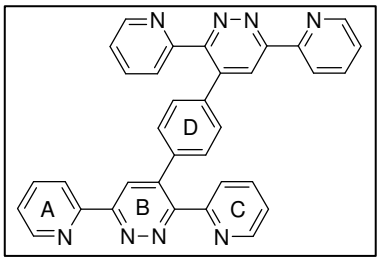
Synthesis of 1,4-diethynylbenzene (5)



Under argon and exclusion of moisture, 1,4 dibromobenzene (1.0 g, 4.2 mmol), CuCl (84 mg, 0.85 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.59 g, 0.85 mmol) were suspended in dry, argon degassed, triethylamine (50 ml). Then trimethylsilylacetylene (1.8 ml, 13 mmol) was added and the mixture stirred at 40°C for 19 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina/hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (75 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange powder (170 mg, 1.35 mmol, 32.1%, $C_{10}H_6$, 126.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.47 (s, 4H, C_6H_4), 3.18 (s, 2H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 132.1, 122.1, 83.2, 79.1.
MS (ES) *m/z* $[L+Na]^+$ 349.

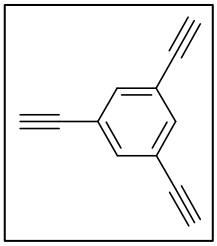
Synthesis of 1,4-bis(3,6-bis(2′-pyridyl)pyridazine-4yl)benzene (6)



1,4 Diethynylbenzene (**5**) (0.04 g, 0.3 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.15 g, 0.64 mmol) were dissolved in toluene (50 ml). The mixture was heated under reflux at 120°C for 14 days. The solvent was removed by evaporation and the product purified by chromatographic work-up (silica, dichloromethane/MeOH (98:2), the first band was collected), to give a pale pink powder (0.15 g, 0.27 mmol, 90%, $C_{34}H_{22}N_8$, 542.6 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.81 (d, J=8.0 Hz, 2H, H_{3A}), 8.75 (d, J=5.5 Hz, 2H, H_{6A}), 8.66 (s, 2H, H_{3B}), 8.48 (d, J=5.5 Hz, 2H, H_{6C}), 7,94 (m, 4H, H_{4A} + H_{3C}), 7.78 (td, J=7.5, 1.6 Hz, 2H, H_{4C}), 7.44 (dd, J=7.6, 4.8 Hz, 2H, H_{5A}), 7.30 (dd, J=7.6, 4.8 Hz, 2H, H_{5C}), 7.23 (s, 4H, H_D).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 169.2, 164.1, 158.2, 150.5, 149.4, 149.0, 139.8, 137.3, 137.1, 136.6, 131.7, 129.0, 124.9, 123.4, 121.9, 2 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 543, $[L+K+2MeCN]^+$ 664, $[2L+Na+MeCN]^+$ 1045, $[2L+K+2MeCN]^+$ 1202.
Elem. Anal. ($C_{34}H_{22}N_8$) [%] calc. C 75.3, H 4.1, N 20.6, found C 73.2, H 4.2, N 20.7.

Synthesis of 1,3,5-triethynylbenzene (7)

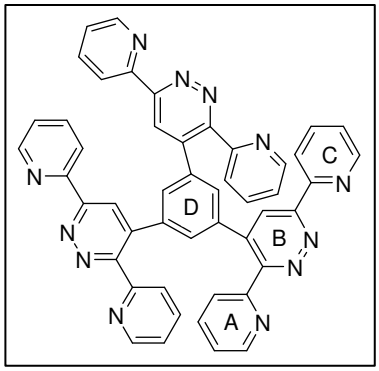


Under argon and exclusion of moisture, 1,3,5 tribromobenzene (1.5 g, 4.8 mmol), CuCl (0.10 g, 0.95 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.66 g, 0.95 mmol) were suspended in dry, argon degassed, triethylamine (75 ml). Then trimethylsilylacetylene (2.6 ml, 19 mmol) was added and the mixture stirred at 40°C

for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina/hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (75 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown powder (367 mg, 2.44 mmol, 50.8%, $C_{12}H_6$, 150.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.56 (s, 3H, C_6H_3), 3.10 (s, 3H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 135.6, 135.1, 134.1, 122.8, 81.5, 81.0, 79.2, 78.6.
MS (ES) *m/z* $[L]^+$ 150.

Synthesis of 1,3,5-tris(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzene (8)

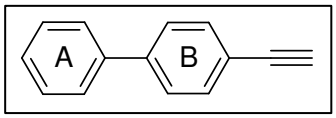


1,3,5-Triethynylbenzene (**7**) (0.15 g, 0.99 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (700 mg, 2.97 mmol) were dissolved in toluene (50 ml). The mixture was heated under reflux at 120°C for 6 days. The solvent was removed by evaporation and the product purified by chromatographic work-up (silica, dichloromethane/MeOH (9:1), the second band was collected), to give a pink powder (0.54 g, 0.69 mmol, 69%, $C_{48}H_{30}N_{12}$, 774.8 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.77 (m, 6H, H_{6A}+H_{3A}), 8.56 (d, J=5.0 Hz, 3H, H_{6C}), 8.25 (s, 3H, H_{3B}), 7.90 (m, 6H, H_{4A}+H_{3C}), 7.86 (td, J=7.5, 1.6 Hz, 3H, H_{4C}), 7.44 (dd, J=7.6, 4.8 Hz, 3H, H_{5A}), 7.35 (dd, J=7.6, 4.8 Hz, 3H, H_{5C}), 7.14 (s, 3H, H_D).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.9, 157.7, 155.2, 153.1, 149.2, 148.9, 139.3, 137.4, 137.4,137.1, 136.6, 129.4, 125.4, 124.9, 124.4, 123.8, 121.8.
MS (ES) *m/z* $[L]^+$ 775.
Elem. Anal. ($C_{48}H_{30}N_{12}$) [%] calc. C 74.4, H 4.1, N 21.7, found C 70.4, H 4.2, N 21.5.

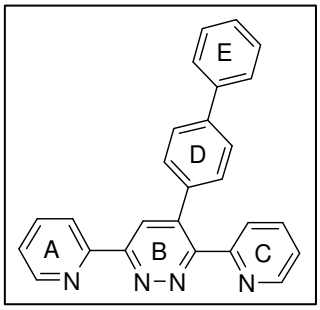
Synthesis of 4-ethynylbiphenyl (9)



Under argon and exclusion of moisture, 4-bromobiphenyl (2.0 g, 8.6 mmol), CuCl (60 mg, 0.61 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.44 g, 0.61 mmol) were suspended in dry, argon degassed, triethylamine (75 ml). Then trimethylsilylacetylene (2.3 ml, 17 mmol) was added and the mixture stirred at 40°C for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina/hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (50 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a beige powder (1.16 g, 6.51 mmol, 75.7%, $C_{14}H_{10}$, 178.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.55 (m, 9H, H_{A+B}), 3.15 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 140.5, 132.6, 131.9, 128.6, 126.8, 126.8, 126.7, 121.4, 83.3, 78.1.
MS (ES) *m/z* $[L]^+$ 178.
Elem. Anal. ($C_{14}H_{10}$) [%] calc. C 94.3, H 5.7, found C 93.3, H 6.1.

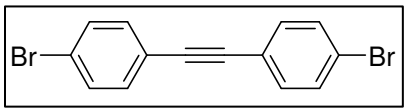
Synthesis of 3,6-bis(2′-pyridyl)- 4-biphenylpyridazine (10)



4-Ethynyl-biphenyl (**9**) (400 mg, 2.25 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (300 mg, 1.27 mmol) were dissolved in toluene (70 ml). The mixture was heated under reflux at 120°C for 66 hours. The solvent was removed by evaporation and the product purified by chromatographic work-up (alumina, hexane/EtOAc (1:1), the second band was collected), to give a violet powder (0.42 g, 1.1 mmol, 85%, $C_{26}H_{18}N_4$, 386.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.81 (d, J=8.0 Hz, 1H, H_{3A}), 8.73 (d, J=5.6 Hz, 1H, H_{6A}), 8.71 (s, 1H, H_{3B}), 8.49 (d, J=5.0 Hz, 1H, H_{6C}), 7.95 (d, J=7.5 Hz, 1H, H_{3C}), 7.90 (td, J= 7.5, 1.6 Hz, 1H, H_{4A}), 7.81 (td, J= 7.5, 1.6 Hz, 1H, H_{4C}), 7.56 (m, 4H, H_{D+E}), 7.41 (m, 3H, H_{5A} + H_{D+E}), 7.34 (m, 3H, H_{D+E}), 7.28 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.2, 157.6, 155.8, 153.3, 149.4, 149.0, 141.0, 140.1, 140.0, 137.1, 136.5, 135.7, 129.3, 128.7, 127.6, 127.0, 126.9, 125.4, 124.8, 124.7, 123.3, 121.8, 4 carbon signals unresolved.
MS (ES) *m/z* $[L+K+DCM]^+$ 508, $[2L+Na+MeCN]^+$ 835, $[2L+K+DCM]^+$ 893.
Elem. Anal. ($C_{26}H_{18}N_4$) [%] calc. C 80.8, H 4.7, N 14.5 found, C 80.8, H 4.7, N 14.3.

Synthesis of 1,2-bis(4-bromophenyl)ethyne (11)

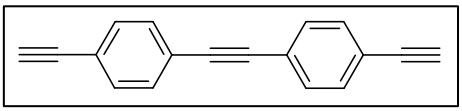


Under argon, 1-iodo-4-bromobenzene (10 g, 35 mmol), CuCl (36 mg, 0.36 mmol) and $PdCl_2(PPh_3)_2$ (**3**) (0.13 g, 0.36 mmol) were dissolved in dry, argon degassed, triethylamine (100ml). Acetylene gas was bubbled through the solution for 5 hours. The solution was refluxed at 50°C for 12 hours. The solvent was removed and the residue extracted with hexane (180 ml). The solution was filtered and the solvent

removed from the filtrate by evaporation. The compound was recrystallised from hexane to give a pale brown powder (3.6 g, 11 mmol, 60%, $C_{14}H_8Br_2$, 336.0 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.48 (d, J=6.8 Hz, 4H, C_6H_4), 7.37 (d, J=6.8 Hz, 4H, C_6H_4).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 132.9, 131.6, 122.7, 121.8, 89.4.
MS (ES) *m/z* $[L]^+$ 336, $[LNa]^+$ 359.
Elem. Anal. ($C_{14}H_8Br_2$) [%] calc. C 50.0, H 2.4, found, C 50.2, H 2.6.

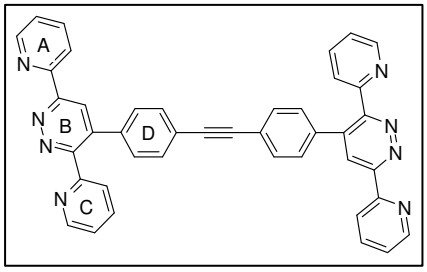
Synthesis of 1,2-bis(4-ethynylphenyl)ethyne (12)



Under argon and exclusion of moisture, 1,2-bis(4-bromophenyl)ethyne (**11**) (1.5 g, 4.5 mmol), CuCl (105 mg, 1.05 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (750 mg, 1.05 mmol) were suspended in dry, argon degassed triethylamine (110 ml). Then trimethylsilylacetylene (2.1 ml, 15 mmol) was added and the mixture stirred at 60°C for 6 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane/dichloromethane (95:5) the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a beige powder (0.54 g, 2.4 mmol, 53%, $C_{18}H_{10}$, 226.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.47 (s, 8H, C_6H_4-C_6H_4), 3.18 (s, 2H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 132.1, 131.5, 123.3, 122.1, 90.7, 83.2, 79.0
MS (maldi) *m/z* $[L]^+$ 226.
Elem. Anal. ($C_{18}H_{10}$) [%] calc. C 95.5, H 4.5, found, C 92.9, H 4.6.

Synthesis of 1,2-bis(4-phenyl-3,6-dipyridin-2-ylpyridazine)ethyne (13)



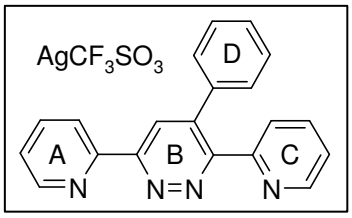
1,2-Bis(4-ethynylphenyl)ethyne (**12**) (0.15 g, 0.66 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (625 mg, 2.65 mmol) were heated without solvent at 170°C for 18 hours. The product was purified by chromatographic work-up (silica, dichloromethane/MEOH (9:1), the second band was collected) to give a pale brown powder (0.34 g, 0.53 mmol, 80%, $C_{42}H_{26}N_8$, 641.7 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.80 (d, J=7.5 Hz, 2H, H_{3A}), 8.74 (d, J=4.5 Hz, 2H, H_{6A}), 8.66 (s, 2H, H_{3B}), 8.46 (d, J=5.0 Hz, 2H, H_{6C}), 7.98 (d, J=7.5 Hz, 2H, H_{3C}), 7.92 (td, J=7.5, 1.6 Hz, 2H, H_{4A}), 7.83 (td, J=7.5, 1.6 Hz, 2H, H_{4C}), 7.47 (d, J=8.6 Hz, 4H, H_{3D+5D}), 7.42 (dd, J=7.6, 4.8 Hz, 2H, H_{5A}), 7.29 (dd, J=7.6, 4.8 Hz, 2H, H_{5C}), 7.26 (d, J=8.6 Hz, 4H, H_{2D+6D}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.0, 157.7, 155.5, 153.2, 149.4, 149.0, 139.8, 137.2, 137.1, 136.7, 131.6, 128.9, 125.4, 124.9, 124.8, 123.5, 123.1, 121.8, 90.2, 2 carbon signals unresolved.
MS (maldi) *m/z* $[L]^+$ 643.
Elem. Anal. ($C_{42}H_{26}N_8$) [%] calc. C 78.5, H 4.1, N 17.4, found C 76.6, H 4.4, N 16.0.

Silver complexes

All the silver complexes have been prepared by using the same procedure. One equivalent of silver tetrafluoroborate or silver trifluoromethane sulfonate was mixed with one equivalent of the diazine ligand in 15 ml of acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes.

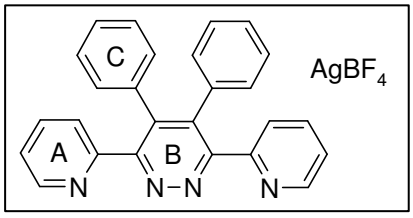
Synthesis of 4-phenyl-3,6-dipyridin-2-ylpyridazine silver complex (3sc)



4-Phenyl-3,6-dipyridin-2-ylpyridazine (**3**) (50 mg, 0.16 mmol) and silver trifluoromethanesulfonate (41 mg, 0.16 mmol) were used to prepare the silver complex (79 mg, 0.14 mmol, 88%, $C_{20}H_{14}N_4AgCF_3SO_3$, 567.3 g/mol).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.87 (d, J=4.0 Hz, 1H, H_{6A}), 8.65 (m, 3H, $H_{3B+3A+6C}$), 8.14 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.90 (td, J=8.4, 1.6 Hz, 1H, H_{4C}), 7.72 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.58 (d, J=8.0 Hz, 1H, H_{3C}), 7.54 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.39 (m, 3H, H_D), 7.27 (m, 2H, H_D).
^{13}C NMR the product was not enough soluble in DMSO to record the ^{13}C NMR spectrum.
MS (ES) *m/z* $[Ag+L]^+$ 417, $[Ag+L+MeCN]^+$ 458, $[Na+2L+MeCN]^+$ 683, $[Ag+2L]^+$ 727.
Elem. Anal. ($C_{20}H_{14}N_4AgCF_3SO_32H_2O$) [%] calc. C 41.8, H 3.0, N 9.3, found, C 41.7, H 2.7, N 9.2.

Synthesis of 3,6-bis(2′-pyridyl)- 3,4-diphenyl pyridazine silver complex (4sc)

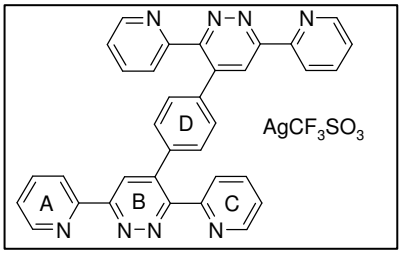


3,6-Bis(2′-pyridyl)-3,4-diphenyl pyridazine (**4**) (50 mg, 0.09 mmol) and silver tetrafluoroborate (18 mg, 0.09 mmol) were used to prepare the silver complex (43 mg, 0.074 mmol, 86%, $C_{26}H_{18}N_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.66 (d, J=4.8 Hz, 2H, H_6), 7.80 (td, J=6.0, 1.6 Hz, 2H, H_4), 7.47 (dd, J=7.6, 5.2 Hz, 2H, H_5), 7.38 (d, J=8.0 Hz, 2H, H_3), 7.10 (m, 3H, H_C), 6.92 (m, 2H, H_C).
^{13}C NMR the product was not enough soluble in DMSO to record the ^{13}C NMR spectrum.

MS (ES) *m/z* $[Ag+L]^+$ 495, $[Ag+L+MeCN]^+$ 534, $[Ag+2L]^+$ 881.

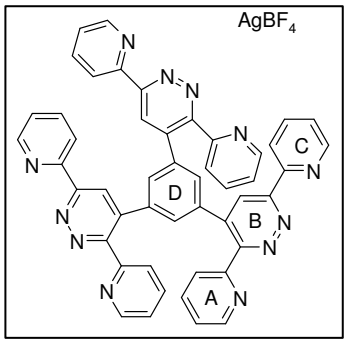
Synthesis of 1,4-bis(3,6-bis(2′-pyridyl)pyridazine) benzene silver complex (6sc)



1,4-Bis(3,6-bis(2′-pyridyl)pyridazine) benzene (**6**) (60 mg, 0.11 mmol) and silver trifluoromethanesulfonate (56 mg, 0.22 mmol) were used to prepare the silver complex (79 mg, 0.10 mmol, 91%, $C_{34}H_{22}N_8AgCF_3SO_3$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.88 (d, J=4.0 Hz, 2H, H_{6A}), 8.69 (m, 4H, H_{3B+3A}), 8.63 (d, J=4.8 Hz, 2H, H_{6C}), 8.18 (t, J=8.0Hz, 2H, H_{4A}), 8.00 (td, J=8.0, 1.6 Hz, 2H, H_{4C}), 7.72 (m, 4H, H_{3C+5A}), 7.56 (dd, J=7.6, 5.2 Hz, 2H, H_{5C}), 7.36 (s, 4H, H_D).
^{13}C NMR the product was not enough soluble in DMSO to record the ^{13}C NMR spectrum.
MS (ES) *m/z* $[L]^+$ 543, $[Ag+L]^+$ 652.

Synthesis of 1,3,5-tris(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzene silver complex (8sc).



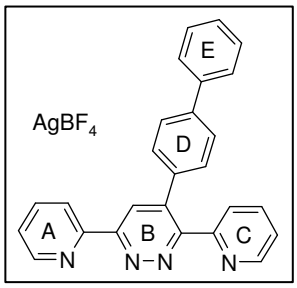
1,3,5-tris(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzene (**8**) (95 mg, 0.13 mmol) and silver tetrafluoroborate (76 mg, 0.39 mmol) were used to prepare the silver complex (98 mg, 0.10 mmol, 77%, $C_{48}H_{30}N_{12}Ag_3B_3F_{12}$).

^{1}H NMR the product was not enough soluble in DMSO to record the ^{1}H NMR spectrum.

^{13}C NMR the product was not enough soluble in DMSO to record the ^{13}C NMR spectrum.

MS (ES) *m/z* $[L]^+$ 775, $[Ag+2L+MeCN]^+$ 1033.

Synthesis of 3,6-bis(2′-pyridyl)- 4-biphenylpyridazine silver complex(10sc)



3,6-Bis(2′-pyridyl)- 4-biphenylpyridazine (**10**) (50 mg, 0.13 mmol) and silver tetrafluoroborate (25 mg, 0.13 mmol) were used to prepare the silver complex (68 mg, 0.12 mmol, 92%, $C_{26}H_{18}N_4AgBF_4$).

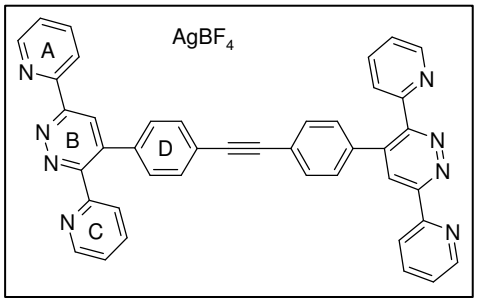
^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.94 (d, J=4.0 Hz, 1H, H_{6A}), 8.83 (d, J+4.4 Hz, 1H, H_{6C}), 8.72 (s, 1H, H_{3B}), 8.62 (d, J=8.0 Hz, 1H, H_{3A}), 8.17 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.88 (td, J=8.0, 1.6 Hz, 1H, H_{4C}), 7.78 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.71 (m, 4H, H_{D+E}), 7.61 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.44 (m, 4H, H_{3C+E+D}), 7.30 (d, J=7.8 Hz, 2H, H_E).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.7, 155.4, 152.9, 150.6, 150.5, 150.1, 140.8, 140.7, 138.7, 138.6, 137.5, 134.0, 129.7, 128.9, 128.0, 127.2, 126.7, 126.6, 126.4, 126.1, 125.0, 123.4, 4 carbon signals unresolved.

MS (ES) *m/z* $[L]^+$ 387, $[Ag+L]^+$ 493.

Elem. Anal. ($C_{26}H_{18}N_4AgBF_4$) [%] calc. C 53.7, H 3.12, N 9.64, found, C 57.6, H 3.4, N 10.3.

Synthesis of 1,2-bis(4-phenyl-3,6-dipyridin-2-ylpyridazine)ethyne silver complex (13sc)



1,2-Bis(4-phenyl-3,6-dipyridin-2-ylpyridazine)ethyne (**13**) (50 mg, 0.08 mmol) and silver tetrafluoroborate (31 mg, 0.16 mmol) to prepare the silver complex (59 mg, 0.07 mmol, 88%, $C_{42}H_{26}N_8AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.87 (d, J=4.0 Hz, 1H, H_{3A}), 8.65 (m, 3H, $H_{3C+6A+3B}$), 8.15 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.94 (td, J=8.0, 1.6 Hz, 1H, H_{4C}), 7.67 (m, 2H, H_{5A+5C}), 7.57 (m, 3H, H_{D+6C}), 7.33 (d, J=8.4 Hz, 2H, H_D).
^{13}C NMR the product was not enough soluble in DMSO to record the ^{13}C NMR spectrum.
MS (ES) *m/z* $[L]^+$ 643, $[Ag+L]^+$ 753.
Elem. Anal. ($C_{42}H_{26}N_8AgBF_4$) [%] calc. C 60.2, H 3.1, N 13.4, found, C 60.5, H 3.6, N 12.7.

III.7 Bibliography

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CHAPTER IV

Halogenated pyridazines

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HALOGENATED PYRIDAZINES

IV.1 Introduction

In order to see the effect of the substituents on the 4-position of the tetrazine, we turned our attention to halogenated substituents. In fact the halogenated substituents offer the opportunity to introduce electron withdrawing substituents[1, 2, 3, 4] onto the pyridazine ligands. They have been used to prepare macrocycles[5] or polymers[6] based on halo-substituted terpyridines and ruthenium.

To prepare the halogenated ligands, we used bromo, iodo, and fluoro substituted phenyl acetylenes. They reacted with 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) to give the desired ligands. This chapter presents all the halogenated precursors synthesized (**14**, **17**, **19**, **23**, **25** and **27** shown in Figure 4.1) and their respective pyridazines (**15**, **18**, **20**, **24**, **26** and **28** shown in Figure 4.2). They have all been characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.
The target molecules were the silver complexes (**15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**).
So, we will talk about the synthesis of the ethynyl precursors, the desired ligands and finally about the silver complexes.

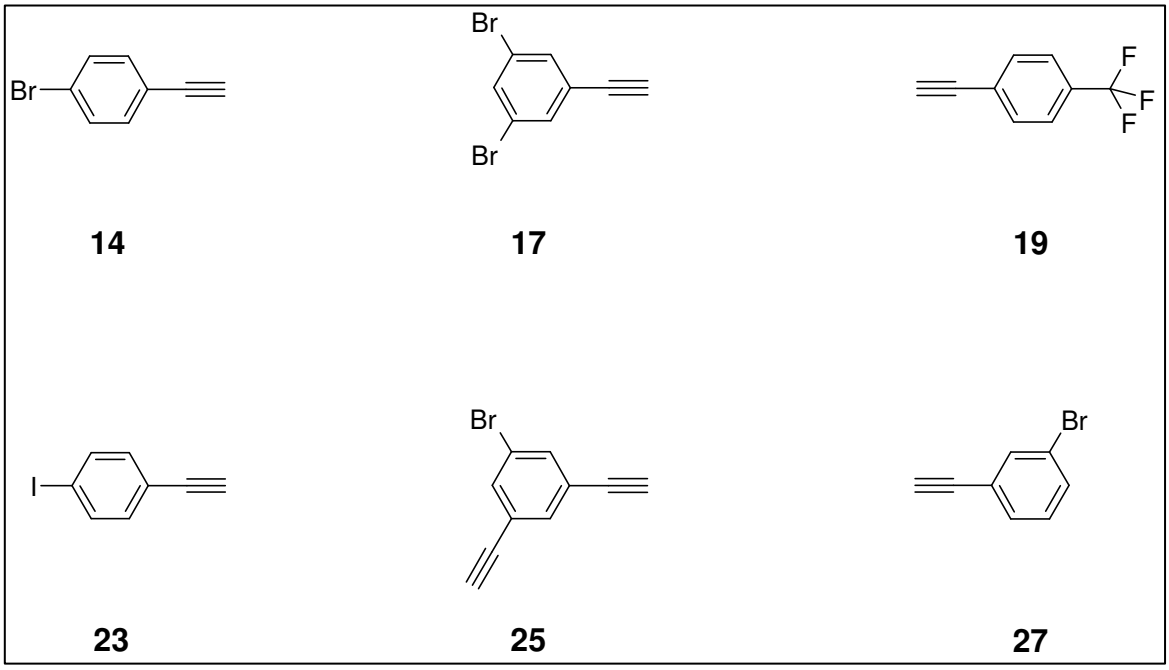


Figure 4.1: Ethynyl precursors described in this chapter.

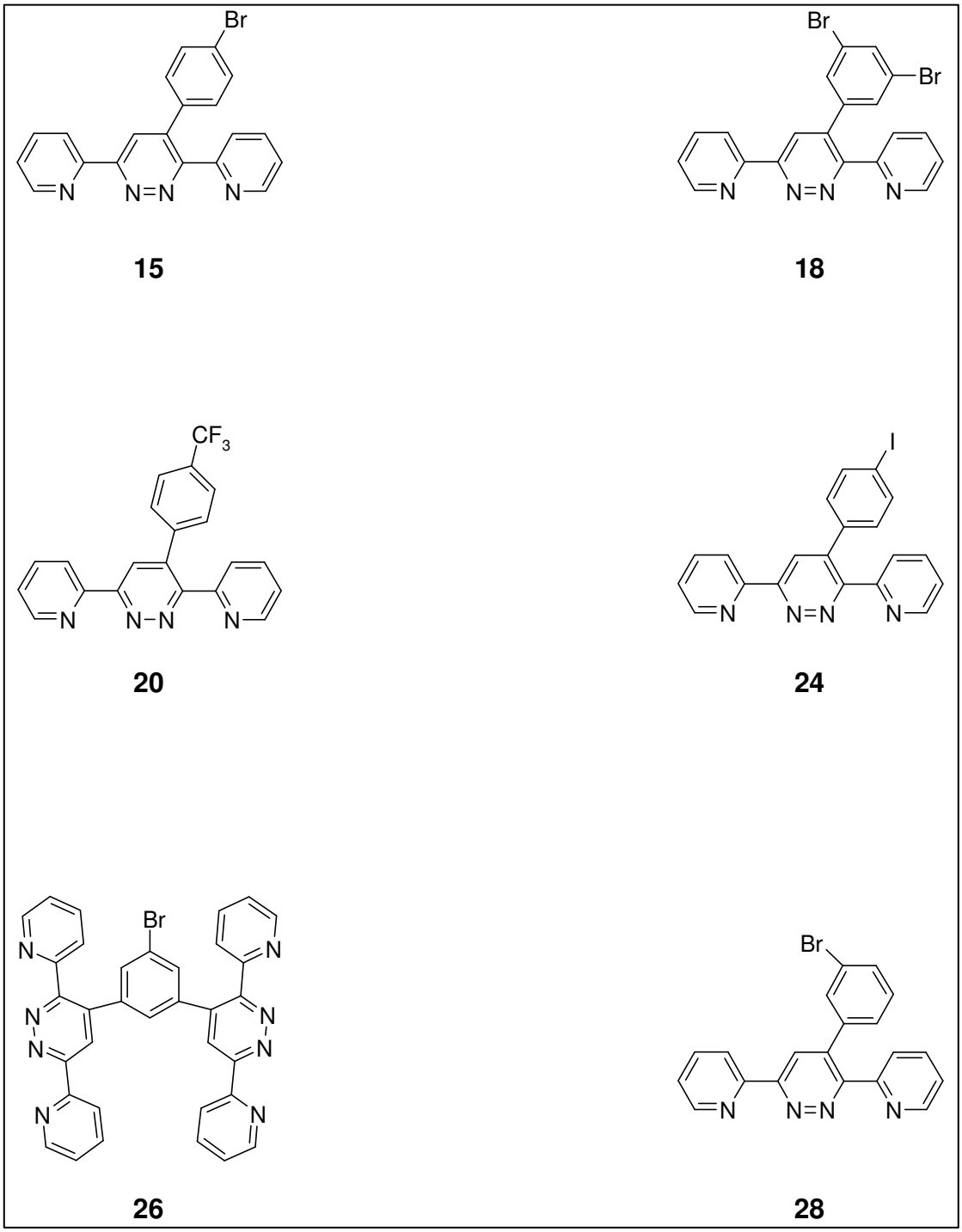


Figure 4.2: Halogenated pyridazines presented in this chapter.

IV.2 Synthesis of the ethynyl precursors

IV.2.1 Synthetic method

To prepare these compounds, we used the Sonogashira[7] reaction as described in the chapter II. To obtain the desired ethynyl precursor we needed an halogenated phenyl compound. These compounds were mixed with trimethylsilylacetylene, copper(I) chloride and bis(triphenylphosphine)palladium dichloride in triethylamine. This solution was refluxed under nitrogen to give the protected ethynyl precursor. This intermediate was dissolved in tetrahydrofuran and a solution of 1M sodium hydroxide was added. The target molecule was extracted and purified by chromatographic work-up over alumina.

The problem of this reaction is that the trimethylsilylacetylene reacts with the halogenated compounds. We were obliged to use di-halogenated compounds containing an iodinated part. In fact, the Sonogashira reaction works much better with an iodo compound than with a bromo compound[8]. For compounds **14**, **19** and **27**, we used commercial iodo compounds, and they were directly accessible with the Sonogashira reaction. Compounds **17**, **23** and **25** are obtained via a multiple step synthesis. Figure 4.3 shows the synthetic method adopted for the synthesis of compounds **14**, **19** and **27**. Figure 4.4 shows the multiple step synthesis for the preparation of compounds **17**, **23** and **25**.

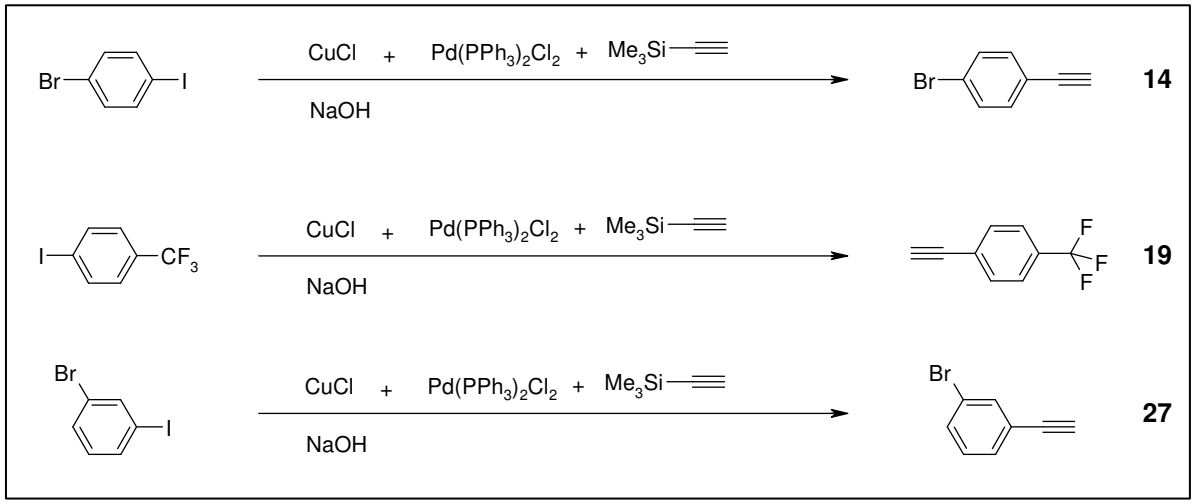


Figure 4.3: Synthetic method for the synthesis of compounds **14**, **19** and **27**.

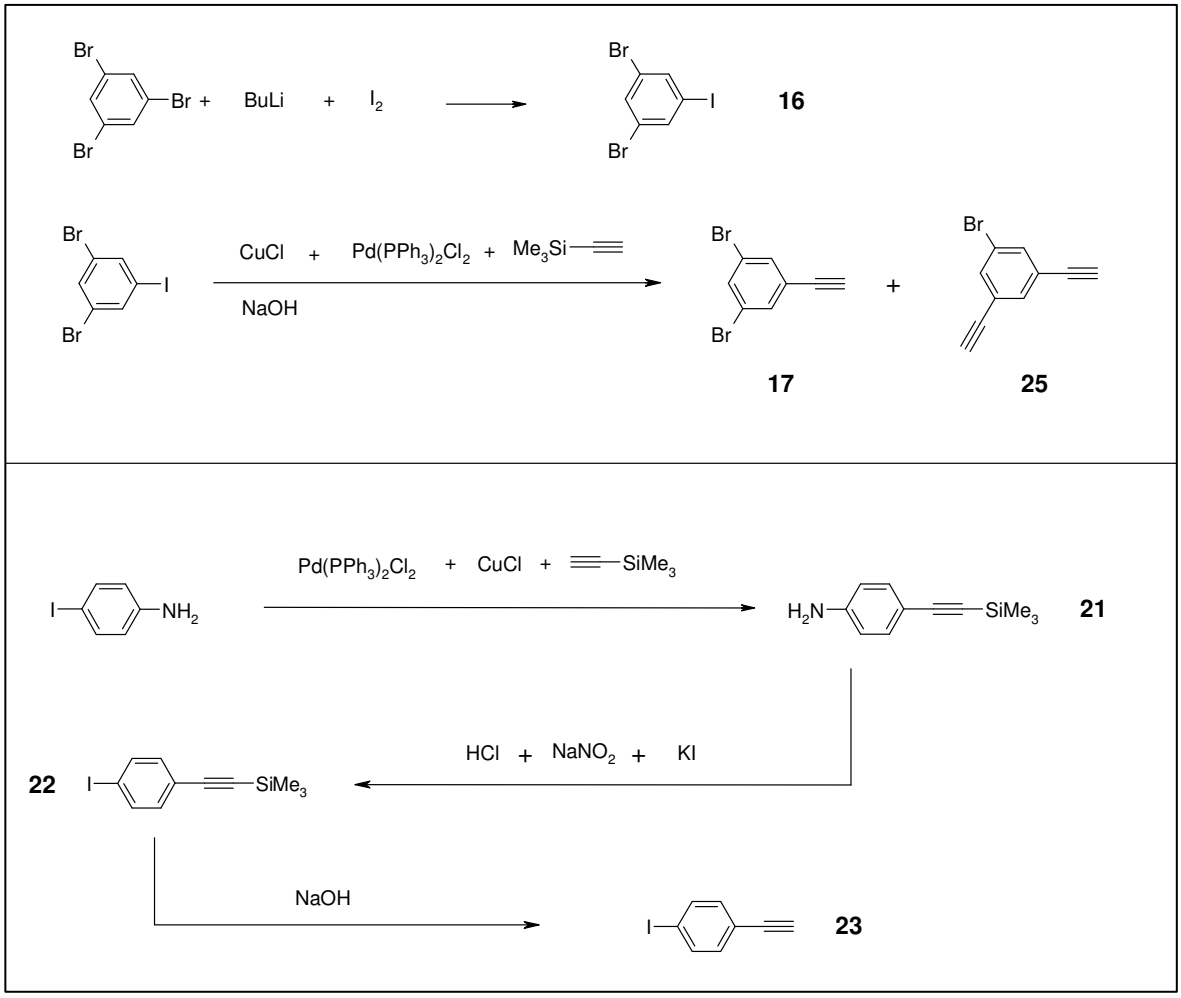


Figure 4.4: Multiple step synthesis for the preparation of compounds **17**, **23** and **25**.

The preparation of 1-iodo-3,5-dibromobenzene (**16)** starting from 1,3,5-tribromobenzene is easily accessible by using butyllithium and iodine[9], and results with an acceptable yield of product (65%). This compound needs to be purified by recrystalisation from hexane. We then proceeded to the Sonogashira reaction to synthesize 1,3-dibromo-5-ethynylbenzene (**17**). At the end of the reaction after deprotection, we noticed the presence of second spot on the TLC plate and we decided to investigate this using ^{1}H NMR spectroscopy characterization. We found that this side product was 1-bromo-3,5-diethynylbenzene (**25**). This compound was obtained with a low yield, near to 6%, but we had enough material to proceed to a full characterization.

To synthesize compound **23** we needed three steps. In fact, it was not possible to use 1,4-diiodobenzene and to proceed directly to the Sonogashira reaction. Trimethylsilylacetylene would have reacted with both iodo groups present in the

starting material. This would also happen, if we had decreased the amount of trimethylsilylacetylene added in the reaction. We decided to synthesize 4-((trimethylsilyl)ethynyl)aniline (**21**) by reacting 4-iodoaniline with trimethylsilylacetylene, copper(I) chloride and bis(triphenylphosphine)palladium dichloride (**2**). Compound **21** was mixed with hydrochloric acid, sodium nitrite and potassium iodide to obtain 4-((trimethylsilyl)ethynyl)iodobenzene (**22**). Finally, compound **22** was deprotected with an aqueous solution of sodium hydroxide to obtain 1-ethynyl-4-iodobenzene[10] (**23**). Figure 4.5 shows the compounds used to prepare the ethynyl compounds.

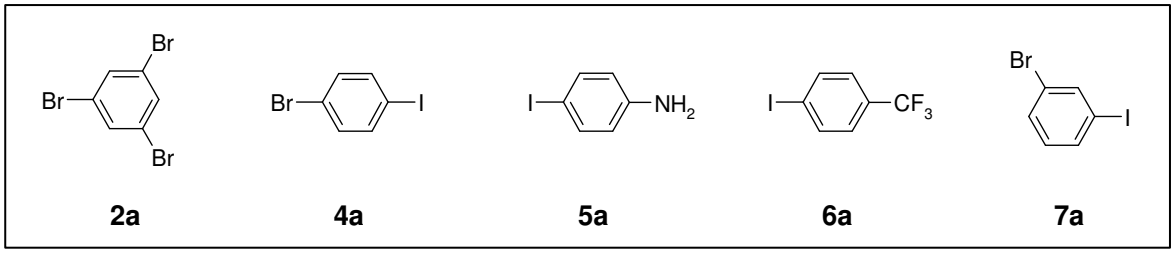


Figure 4.5: Compounds used to prepare the ethynyl compounds.

For each ethynyl precursor presented here, the reactant ratio, time and yield are listed in the Table 4.1. Purification methods and synthetic details are discussed in the experimental section at the end of this chapter.

Precursor	**Halogenated compound**	**Reaction ratio** (halogenated / tms acetylene)	**Reaction temperature** (°C)	**Reaction time** (hr)	**Yield** (%)
14	**4a**	1/1.3	40	18	73
17	**16**	1/1.3	60	20	97
19	**6a**	1/1.9	60	20	17
23	**22**	°	°	°	85
25	**16**	1/1.4	60	18	6
27	**7a**	1/1.1	40	18	48

Table 4.1: Reaction conditions for the synthesis of the ethynyl precursors **14**, **17**, **19**, **23**, **25** and **27**.

Compounds **14**, **17**, **23** and **27** were obtained, after purification, with relative good yields and could be used for the synthesis of the pyridazine ligands.
We made several attempts to synthesis compounds **19** and **25**. Each time the yields were very low and we did a last attempt with a lot of starting materials in order to obtain these ethynyl precursors in sufficient quantity, so that we could proceed to the ligand synthesis.

IV.2.2 Characterisation of the ethynyl precursors

All the ethynyl precursors have been characterized by ^{1}H NMR spectroscopy. ^{13}C NMR spectroscopy could only be obtained for compounds **14**, **17**, **23**, **25** and **27**. Compounds **14**, **17** and **25** were characterized by mass spectrometry.
The general procedure and characterization of intermediates **16**, **21** and **22** are discussed at the end of this chapter in the experimental section.

^{1}H NMR spectroscopy

We first focused our interest in the ^{1}H NMR spectroscopic characterization. The halogenated phenyl ethynyl compounds synthesized in this chapter should have the characteristic signals for the ethynyl and phenyl groups[11]. It was also important to see the absence of the $SiMe_3$ signals. This would show that the deprotection had been carried out successfully. Table 4.2 summarises the ^{1}H NMR signals of the precursors.

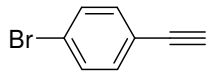
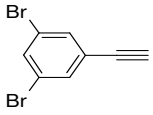
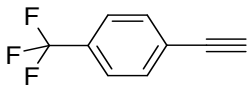
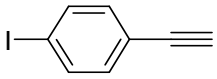
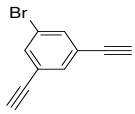
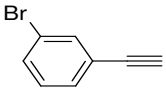
	Ethynyl precursor	Phenyl signals (δ/ppm)	Ethynyl signals (δ/ppm)
	**14**	7.46-7.35 (d-d)	3.12 (s)
	**17**	7.65-7.55 (t-d)	3.16 (s)
	**19**	7.58 (s)	3.19 (s)
	**23**	7.66-7.21 (d-d)	3.14 (s)
	**25**	7.60-7.52 (d-t)	3.13 (s)
	**27**	7.65-7.48-7.41-7.18 (t-d-d-t)	3.13 (s)

Table 4.2: ^{1}H NMR characterisation of the precursors **14**, **17**, **19**, **23**, **25** and **27**.

The ^{1}H NMR spectrum of each ethynyl precursor could be assigned by the chemical shifts and the relative integrals. As expected[12], the different phenyl signals are at around δ 7.5, 7.6 ppm and the ethynyl signals are near to δ 3.1 ppm. The ^{1}H NMR spectra of compounds **14** and **23** show two doublets. Each signal integrated for two protons. They also show one singlet for the ethynyl signal. The ^{1}H NMR spectrum of the ethynyl precursor **17** shows a triplet and a doublet for the phenyl protons and one singlet for the ethynyl signal. The ^{1}H NMR spectrum of compound **19** shows an unexpected singlet for the phenyl protons and a singlet for the ethynyl proton. Because of the symmetry of compound **25**, we can see a doublet and a triplet signal for the phenyl protons on the ^{1}H NMR spectrum. As expected, we also see the ethynyl proton signal. The ^{1}H NMR spectrum of **27** shows four different signals for the phenyl protons. This molecule is unsymmetrical and exhibits a triplet, doublet, doublet and triplet signals. We can also notice the presence of the ethynyl signal. In

every ethynyl precursor synthesised in this chapter, there is no $SiMe_3$ signal on the ^1H NMR spectra. Figure 4.6 shows the ^1H NMR spectra of the ethynyl precursors **23** and **27**.

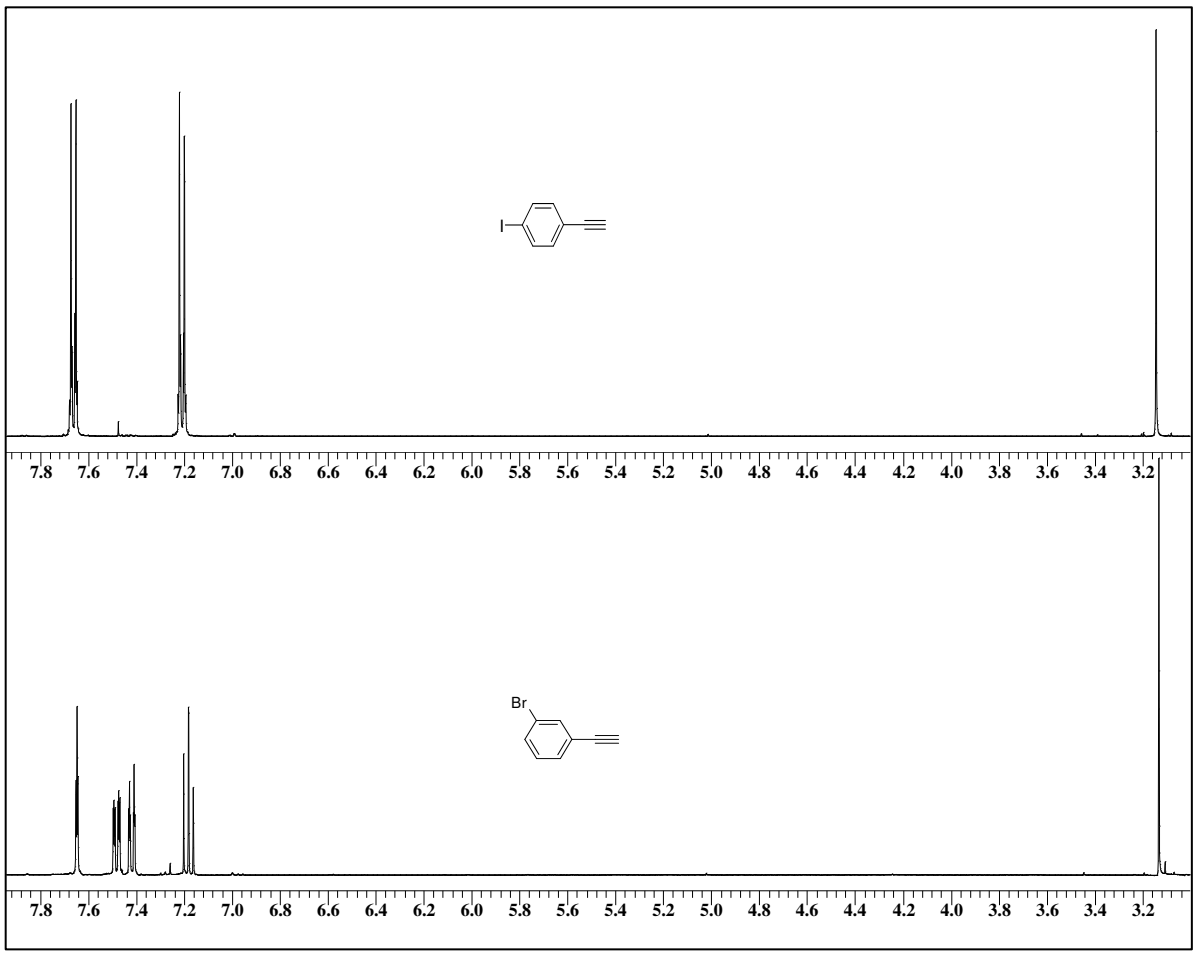


Figure 4.6: ^1H NMR spectra of the ethynyl precursors **23** and **27** in $CDCl_3$ solution.

Mass spectrometric characterisation

We were only able to obtain mass spectra for 1-bromo-4-ethynylbenzene (**14**), 1,3-dibromo-5-ethynylbenzene (**17**) and 1-bromo-3,5-diethynylbenzene (**25**). Compound **14** was characterised with the fast atom bombardment technique and its mass spectrum shows only one peak corresponding to the $[L]^+$ peak. The two other compounds (**17** and **25**) were characterised with the electrospray technique. The spectra of this two ethynyl precursors show $[L]^+$ and $[L\text{-}Br]^+$ peaks. The mass

spectrum of 1,3-dibromo-5-ethynylbenzene (**17**) shows an additional peak corresponding to $[L\text{-}2Br]^+$. Table 4.3 summarises the different mass peaks detected for **14**, **17** and **25**.

Ligand	**14**		**17**		**25**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L]^+$	180.9	181	259.9	260	203.9	204
$[L\text{-}Br]^+$	°	°	180	179	124	125
$[L\text{-}2Br]^+$	°	°	100.1	100	°	°

Table 4.3: Calculated and detected m/z values for **14**, **17** and **25**.

All *m/z* values are perfectly consistent with the calculated mass values. We were not able to obtain mass spectra for 1-ethynyl-4-(trifluoromethyl)benzene (**19**), 1-ethynyl-4-iodobenzene (**23**) and 1-bromo-3-ethynylbenzene (**27**). They were not soluble enough in the different solvents we tried. ^{1}H NMR spectroscopic characterisation of these three compounds was sufficient to establish their identity, and we decided to carry on with the synthesis of their respective ligands. This will be discussed later on in this chapter. Two examples of mass spectra are presented in Figure 4.7 (ethynyl precursors **17** and **25**).

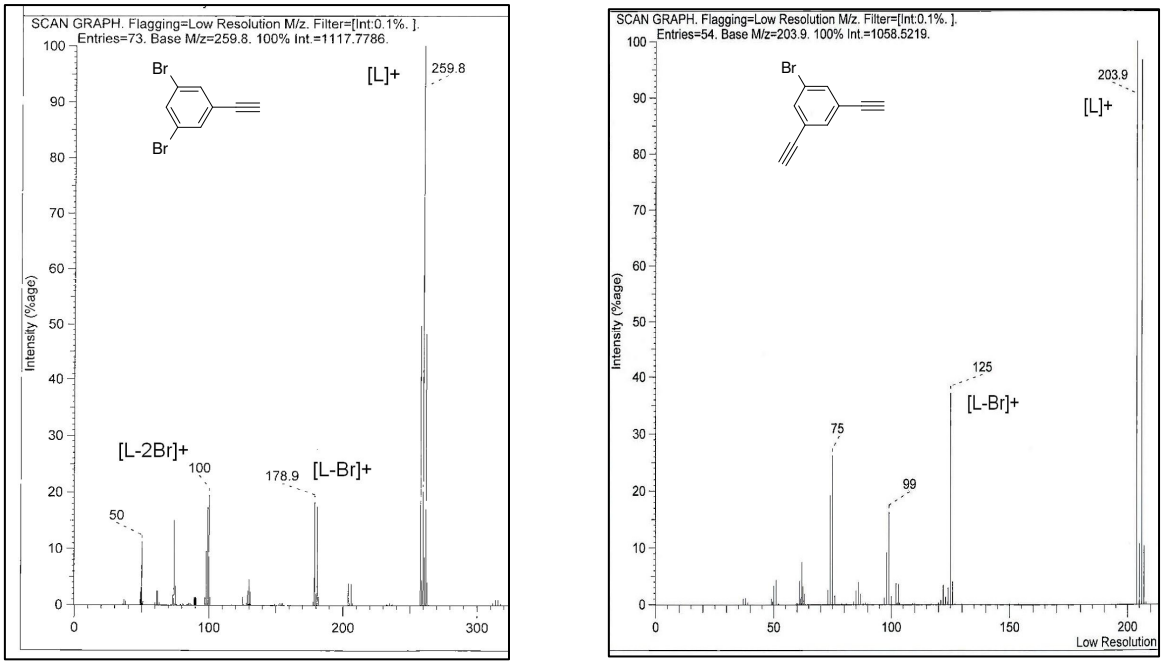


Figure 4.7: Mass spectra of the ethynyl precursors **17** and **25**.

IV.3 Synthesis of the halogenated pyridazine

IV.3.1 Synthetic method

This part of the chapter introduces the synthesis and the characterisation of six new substituted pyridazine ligands. These compounds are 4-(4-bromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**15**), 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**18**), 3,6-di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine (**20**), 4-(4-iodophenyl)-3,6-di(pyridin-2-yl)pyridazine (**24**), 4,4'-(5-bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) (**26**) and 4-(3-bromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**28**).

The synthesis of these new N-donor ligands follows the procedure presented in chapter II. They were obtained via an inverse electron demand Diels Alder[13, 14] reaction between 1,2,4,5-tetrazine and the ethynyl precursors presented in the first part of this chapter. To carry out these reactions, we used 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) dissolved in toluene with the ethynyl precursor. This mixture was then placed under reflux. All the compounds presented in this part of the chapter were prepared with this method. Reactant ratio, time, solvent and yields are listed in the table 4.4.

Ligand	**Reaction ratio** (tetrazine / ethynyl)	**Reaction temperature** (°C)	**Solvent**	**Reaction time**	**Yield** (%)
15	1 to 1	120	toluene	11 days	91
18	1 to 1	120	toluene	6 days	58
20	1 to 1	120	toluene	4 days	74
24	1 to 1	120	toluene	74 hrs	92
26	2.2 to 1	120	toluene	14 days	87
28	1 to 1	120	toluene	9 days	83

Table 4.4: Reaction conditions for the synthesis of the ligands **15**, **18**, **20**, **24**, **26**, **28**.

The reaction times are really long for all the syntheses except for the synthesis of the iodophenyl substituted pyridazine **24**. These different reaction times are based on the disappearance of the purple colour of the 1,2,4,5-tetrazine. We never stopped the reactions until the purple colour has entirely disappeared. This factor sometimes

gives us really long reaction times but always with good yields. The inverse electron demand Diels-Alder reaction is not so fast but is a really good working reaction. All the ligands introduced in this chapter were purified by chromatographic work-up.

IV.3.2 Characterisation of the halogenated pyridazines

All the compounds were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analyses.

^{1}H NMR spectroscopy

^{1}H NMR spectra of ligands **18**, **24**, **26** and **28** were run in deuterated chloroform. ^{1}H NMR spectra of compounds **15** and **20** were run in deuterated acetonitrile and dimethylsulfoxide respectively. The spectra could be assigned by the chemical shifts, relatives integrals and the coupling patterns of the signals without the need of COSY experiments.

The ^{1}H NMR spectra of the compounds **15** and **18** and the assignments are shown in Figure 4.8.

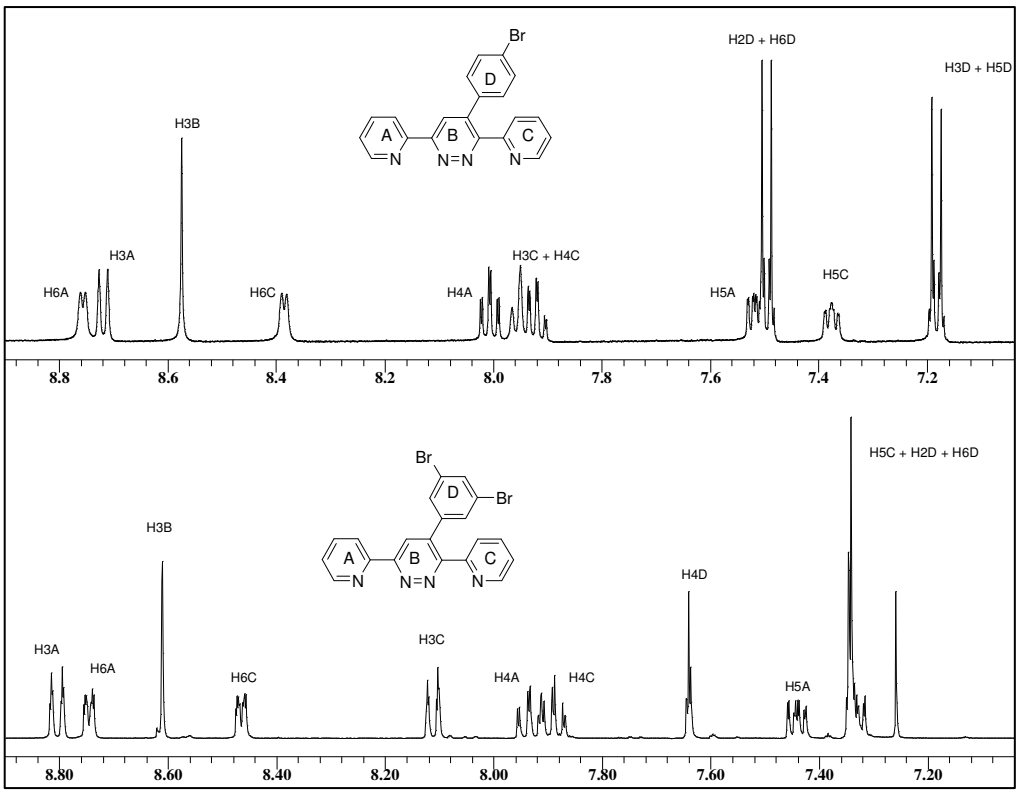


Figure 4.8: The ^{1}H NMR spectra and assignments of ligands **15** and **18**.

The ^{1}H NMR spectra of the compounds **20** and **24** and the assignments are shown in Figure 4.9 and compounds **26** and **28** in Figure 4.10.

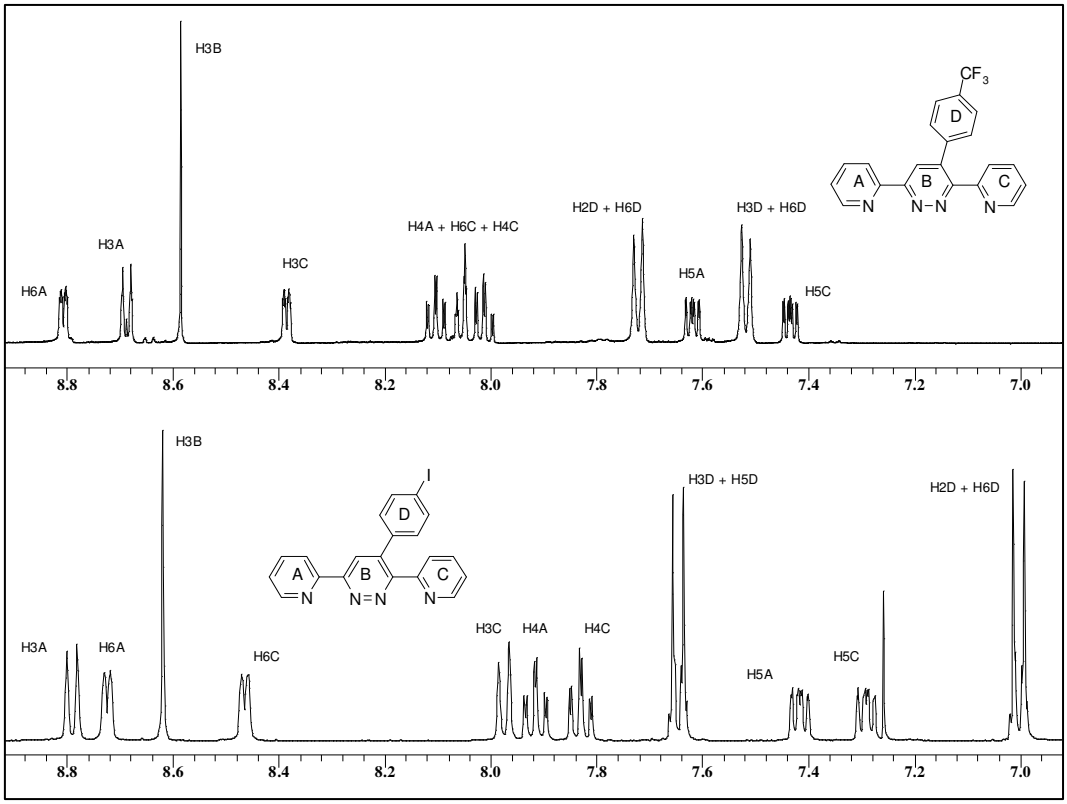


Figure 4.9: The ^{1}H NMR spectra and assignments of ligands **20** and **24.**

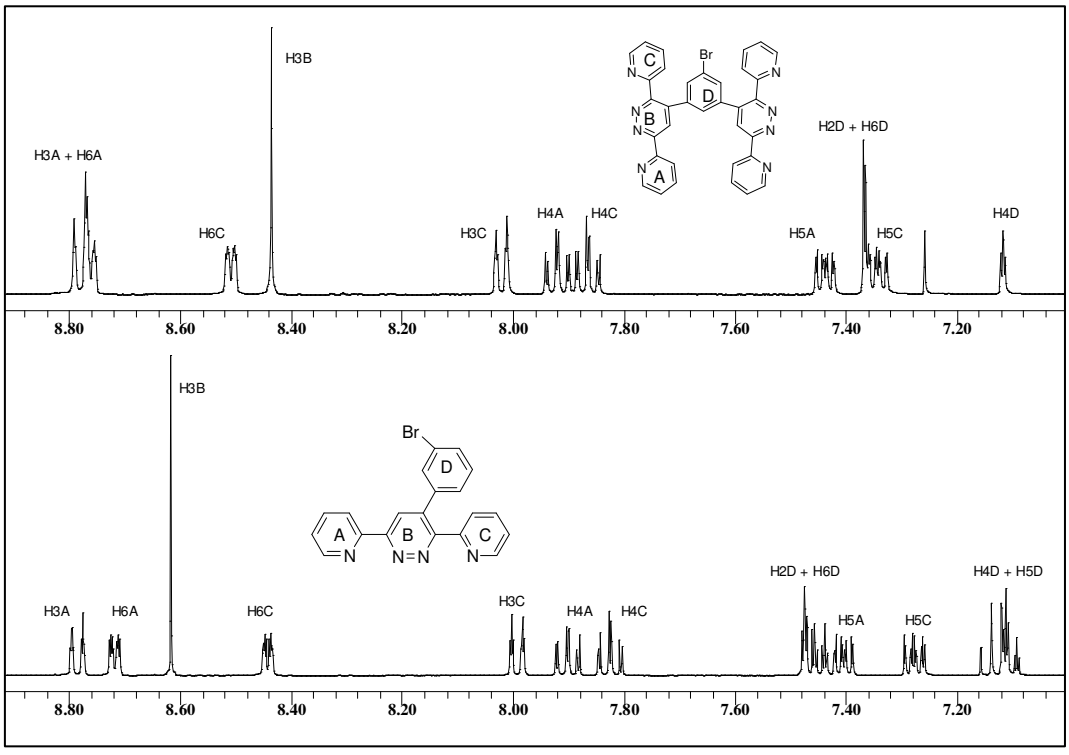


Figure 4.10: The ^{1}H NMR spectra and assignments of ligands **26** and **28**.

The ^{1}H NMR spectra of ligands **15**, **18**, **20**, **24**, **26** and **28** present well defined and sharp peaks. As for the non symmetrical compounds shown in chapter III, the spectra present a set of nine NMR signals. Each ^{1}H NMR spectrum shows four doublets (H_{3A}, H_{3C}, H_{6A}, H_{6C}), two triplets of doublets (H_{4A}, H_{4C}), two doublets of doublets (H_{5A}, H_{5C}) and the typical singlet (H_{3B})[15]. These signals are in the same ^{1}H NMR region between δ 7 and δ 9 ppm.

Each ligand has an halogenated phenyl group, and the protons of this group are present in the same ^{1}H NMR region as the other aromatic rings. The proton signals of the phenyl group are two doublets (**15**, **26** and **28**), a triplet and a doublet (**18** and **20**) or a triplet, doublet and multiplet (**28**). These signals sometimes overlap with the dipyridin-2-ylpyridazine signals. We will discuss this later on.

The ^{1}H NMR spectrum of 4-(4-bromophenyl)-3,6(di-pyridin-2-yl)pyridazine (**15**) shows four doublets (H_{3A}, H_{3C}, H_{6A}, H_{6C}), two triplets of doublets (H_{4A}, H_{4C}), two doublets of doublets (H_{5A}, H_{5C}) and a singlet (H_{3B}). In this molecule, the signals of the protons H_{5A} and H_{2D+6D} overlap. This case is also present in the ^{1}H NMR spectrum of 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**18**), except that in that compound it is the signals of the proton H_{5C} that overlap with the signal of the phenyl group. The ^{1}H NMR spectra of 3,6-di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine (**20**) and 4-(4-iodophenyl)-3,6-di(pyridin-2-yl)pyridazine (**24**) show nine, well defined and separated, NMR signals. These spectra also present the two doublets of the protons of the phenyl group. The two last ligands introduced in this chapter, (4,4'-(5-bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) (**26**) and 4-(3-bromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**28**) also show well defined ^{1}H NMR spectra. Compound **26** has eight NMR signals. One of these signals results from the overlapping of two signals corresponding of the protons H_{3A} and H_{6A}. We also notice that the ^{1}H NMR of the H_{3B} signal is slightly shifted to highfield compared to compound **28** which should have approximately the same spectrum for the 3,6-di(pyridin-2-yl)pyridazine protons . This is due to the halogen atom (bromine) placed at the same position on the phenyl ring as in compound **28**. The phenyl ^{1}H NMR signals are not overlapping with another signal in these two last ^{1}H NMR spectra.

All the ^{1}H NMR spectroscopic data for the ligands presented in this chapter are summarized in Table 4.5.

Ligand	Solvent	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring
15 (δ/ppm)	CD_3CN	8.72 d	8.00 td	7.52 dd	8.76 d	8.56 s	7.96 d	7.92 td	7.38 dd	8.39 d	7.49-7.18 d
18 (δ/ppm)	$CDCl_3$	8.80 d	7.93 td	7.44 dd	8.75 d	8.61 s	8.11 d	7.89 td	7.34 m	8.46 d	7.64 t-7.34 m
20 (δ/ppm)	DMSO-d_6	8.69 d	8.10 td	7.61 dd	8.81 d	8.58 s	8.38 d	8.01 td	7.44 dd	8.46 d	7.72-7.52 d
24 (δ/ppm)	$CDCl_3$	8.79 d	7.92 td	7.41 dd	8.72 d	8.62 s	7.97 d	7.83 td	7.29 dd	8.56 d	7.64-7.00 d
26 (δ/ppm)	$CDCl_3$	8.77 m	7.92 td	7.44 dd	8.77 m	8.43 s	8.02 d	7.87 td	7.34 dd	8.51 d	7.36 d-7.11 t
28 (δ/ppm)	$CDCl_3$	8.78 d	7.90 td	7.40 dd	8.72 d	8.62 s	7.99 d	7.82 td	7.28 td	8.44 d	7.48 t-7.45 d-7.12m

Table 4.5: The ^{1}H NMR spectroscopic characterisation of ligands **15**, **18**, **20**, **24**, **26** and **28**.

We can notice that the ligands, the ^{1}H NMR spectra of which were run in deuterated chloroform,have similar chemical shifts for corresponding protons. However, there is an exception to this statement. The chemical shifts of the protons from ring A from compounds **18**, **24**, **26** and **28** are the same. This is not true for the protons from ring B and C. Their chemical shifts are approximately in the same NMR region but are not as accurately reproduced as the chemical shifts from the A ring protons in going from one compound to another. That would mean that the substituent mostly affects the protons from ring B and C, and present different chemical shifts for the different substituents. Of course, it was not possible to include compounds **15** and **20** in this remark. Their ^{1}H NMR spectra were not run in the same deuterated solvent as ligands **18**, **24**, **26** and **28**.

Mass spectrometry

Mass spectra of ligands **15**, **18**, **20**, **24**, **26** and **28** were obtained with the electrospray technique. For all the spectra except the one from compounds **26** and **28**, we can see the $[L]^+$ peak. The other peaks correspond to *m/z* values of the ligand with a solvent molecule and a sodium or potassium ion. All *m/z* values are perfectly consistent with the calculated mass values.

Figure 4.11 shows the mass spectra of compounds **15** and **28**.

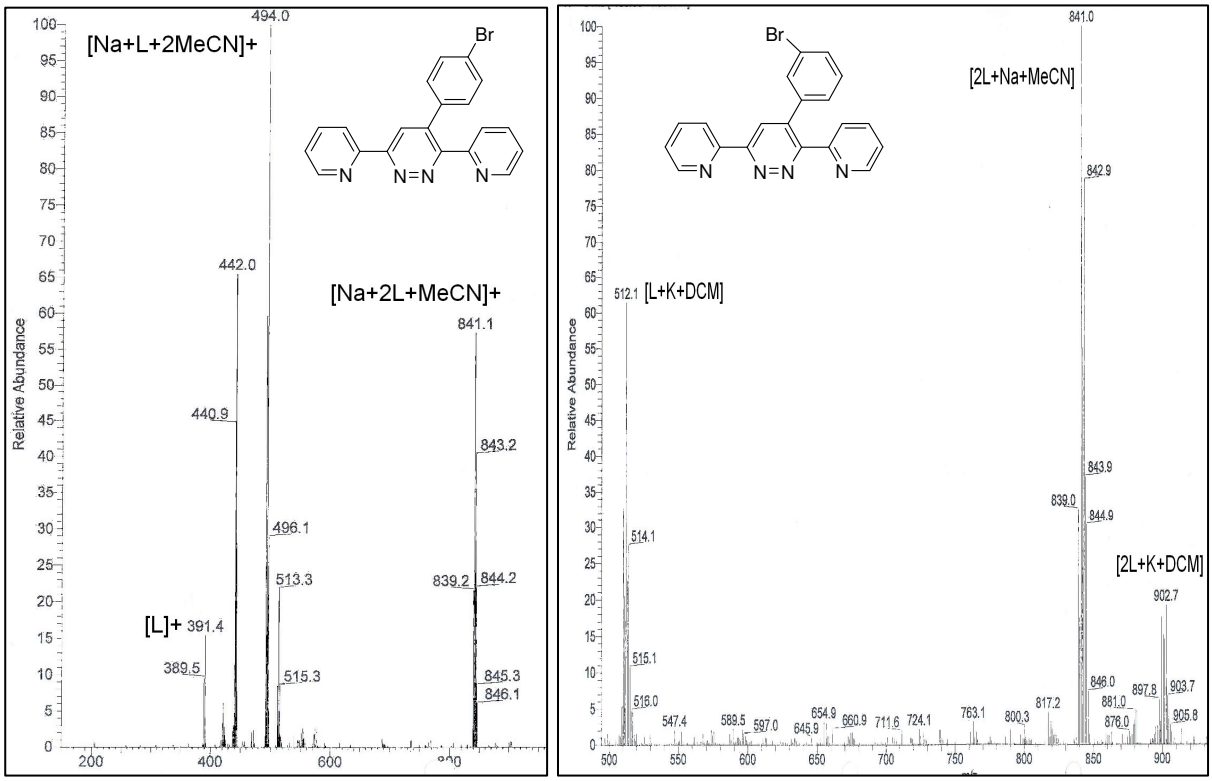


Figure 4.11: Mass spectra of the ligand **15** and **28**.

All the *m/z* (calculated and detected) values, from each ligand synthesised in this chapter, are listed in Table 4.6.

Ligand	15		18		20		24		26		28	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
[L]$^+$	389	391	°	°	378	379	436	437	°	°	°	°
[Na+L+2MeCN]$^+$	492	494	°	°	°	°	°	°	°	°	°	°
[Na+2L+MeCN]$^+$	840	841	°	°	°	°	934	935	1306	1307	840	841
[Na+L+MeCN]$^+$	°	°	°	°	441	442	498	499	°	°	°	°
[K+L+DCM]$^+$	°	°	592	593	°	°	°	°	743	744	511	512
[K+2L+DCM]$^+$	°	°	°	°	°	°	°	°	1366	1366	902	903
[Na+2L+K]$^+$	°	°	998	999	°	°	°	°	°	°	°	°

Table 4.6: Calculated and detected *m/z* values for the ligands **15**, **18**, **20**, **24**, **26** and **28**.

Single crystal structure for ligand **15**

A crystal of the compound **15** suitable for single X-ray diffraction was grown from a chloroform solution. Details of the structure solution are given in Appendix 2. Figure 4.12 shows the molecular structure of **15**.

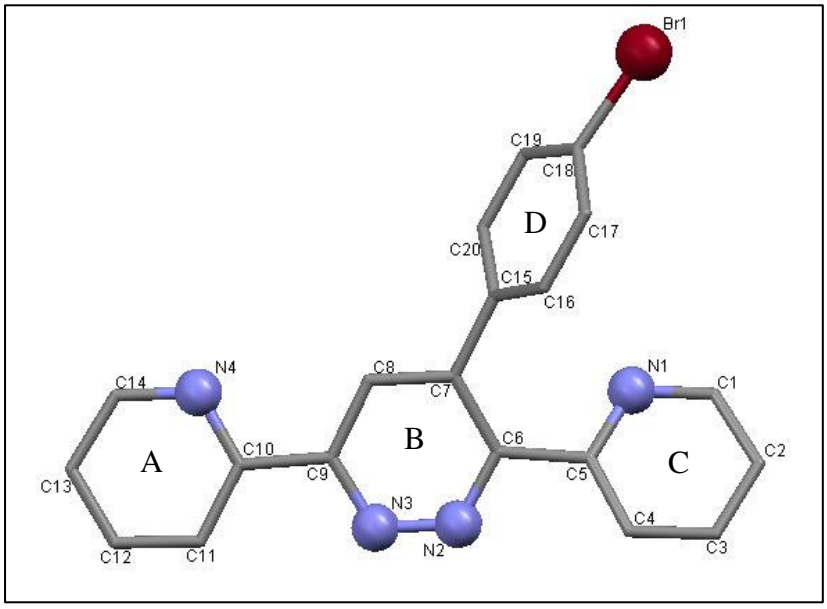


Figure 4.12: The molecular structure of ligand **15** with the labelling scheme.

Compound **15** shows two different torsion angles between rings A, B and C. In fact, the torsion angle between ring A and ring B is 4.1° (C11-C10-C9-N3). These two rings are almost co-planar. The torsion angle between the ring B and C is 27.4° (C4-C5-C6-N2). This effect is due to the presence of the substituent (bromophenyl ring D) that forces the twist of ring C. It is also interesting to notice that ring B and ring D are not co-planar; the torsion angle between these two rings is 120° (C8-C7-C15-C16). Compound **15** does not present hydrogen bonds or π-π stacking interactions with another molecule in the unit cell. The N atoms are arranged in a *trans*, *trans*-conformation. The packing shows two repetitive orientations. There are two different channels. In one of them the bromophenyl ring is oriented to the upper side of the cell axis c. In the second channel the bromophenyl ring is oriented to bottom of the cell axis c. This is presented in Figure 4.13.

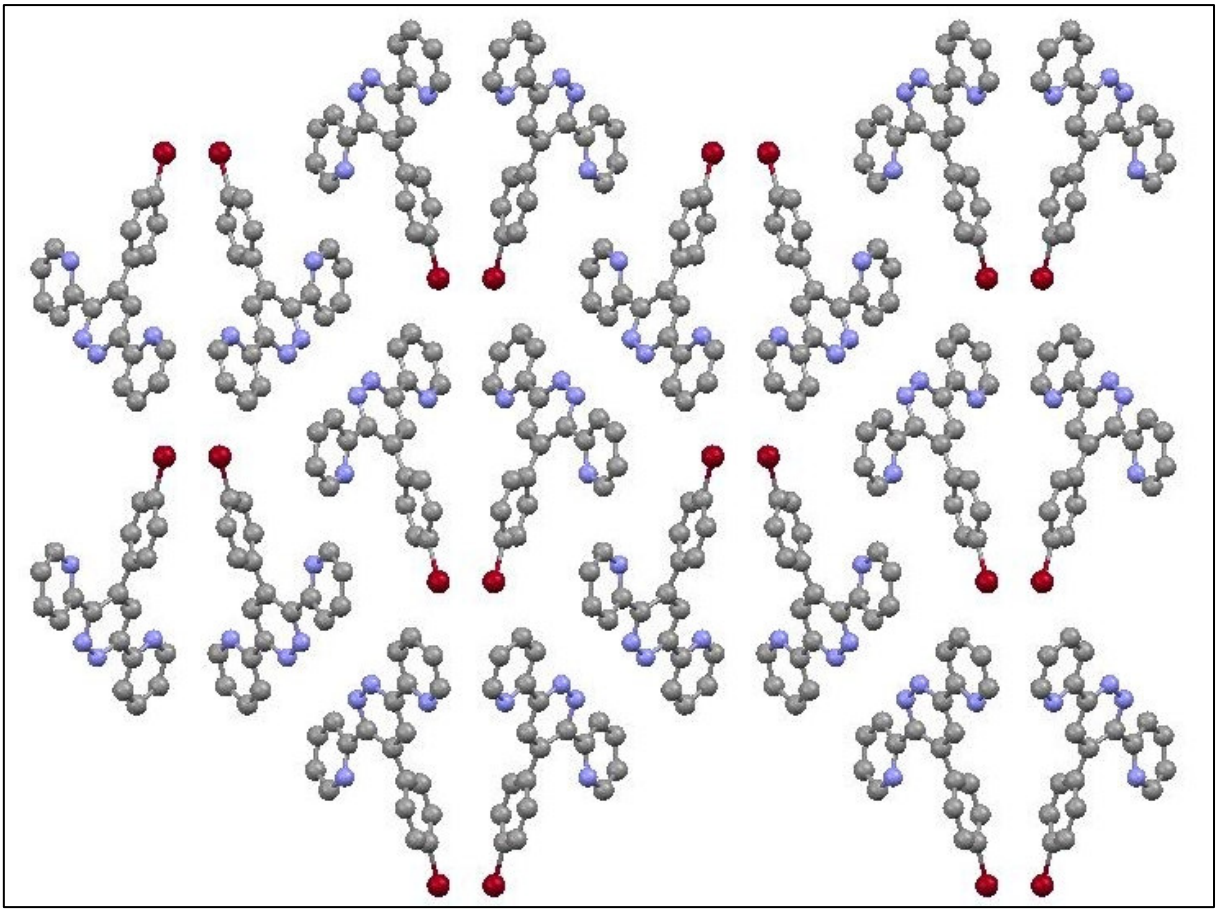


Figure 4.13: The packing diagram showing the orientation of the bromine atoms in the crystal structure of **15**.

IV.4 Synthesis of the silver complexes

IV.4.1 Synthetic method

As discussed in chapter III, the silver(I) complexes of bipyridine ligands are mainly square planar[16]. Our attempts to grow single crystals of the complexes described in chapter III were unsuccessful. All these complexes contained phenyl-substituted pyridazines. In the current chapter, ligands are halo-substituted, and we hoped that steric factors might play a part in forcing the coordination geometry at the silver(I) centres to be non planar.

The ligands synthesised in this chapter have been used to prepare their silver complexes **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**. The reaction of the ligands with the silver salt in acetonitrile proceeded smoothly to give a yellow-orange solution from which the complex was obtained.

Table 4.7 summarises the experimental conditions for the synthesis of the species **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**.

Silver complex	**Reaction ratio** (ligand / silver)	**Silver salt**	**Yield** (%)
15sc	1 to 1	$AgCF_3SO_3$	88
18sc	1 to 1	$AgCF_3SO_3$	85
20sc	1 to 1	$AgBF_4$	73
24sc	1 to 1	$AgBF_4$	90
26sc	1 to 2	$AgBF_4$	67
28sc	1 to 1	$AgBF_4$	72

Table 4.7: Experimental conditions for the synthesis of the silver complexes **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**.

All the silver complexes were prepared by mixing the silver salt and the ligand in acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes. They were easily accessible and it was not necessary to proceed to a chromatographic work up or recrystallisation. All the silver complexes are insoluble in chloroform, slightly soluble in acetonitrile, and soluble in dimethylsulfoxide.

IV.4.2 Characterisation of the silver complexes

The complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. ^{1}H and ^{13}C NMR spectra of compound **15sc** were run in deuterated acetonitrile. ^{1}H and ^{13}C NMR spectra of the five other complexes were run in deuterated DMSO. They were all characterised by mass spectrometry except compound **26sc**.

^{1}H NMR spectroscopy

All the complexes were characterised by ^{1}H NMR spectroscopy. Figure 4.14 shows the ^{1}H NMR spectra of 4-(4-bromophenyl)-3,6(di-pyridin-2yl)pyridazine silver complex (**15sc**) and 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**18sc**).

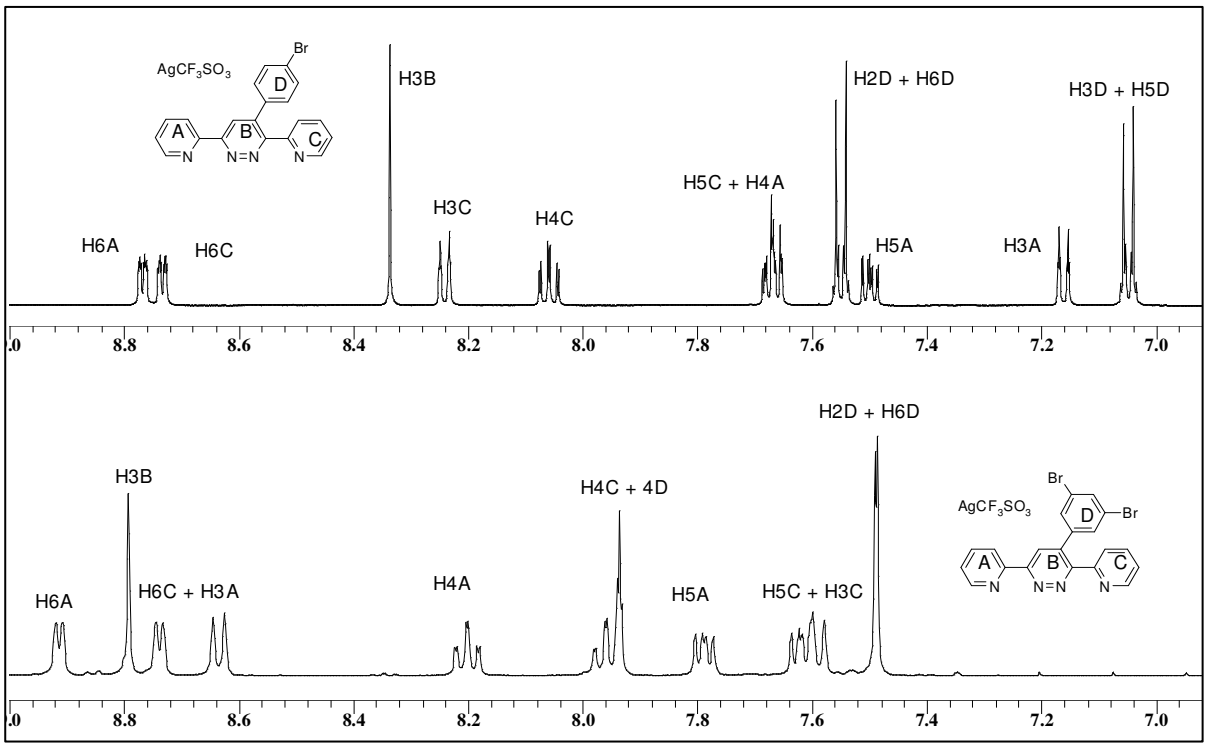


Figure 4.14: ^{1}H NMR spectra of silver complexes **15sc** and **18sc**.

The next figure presents the ^{1}H NMR spectra of 3,6-di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine silver complex (**20sc**) and 4-(4-iodophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**24sc**) (Figure 4.15).

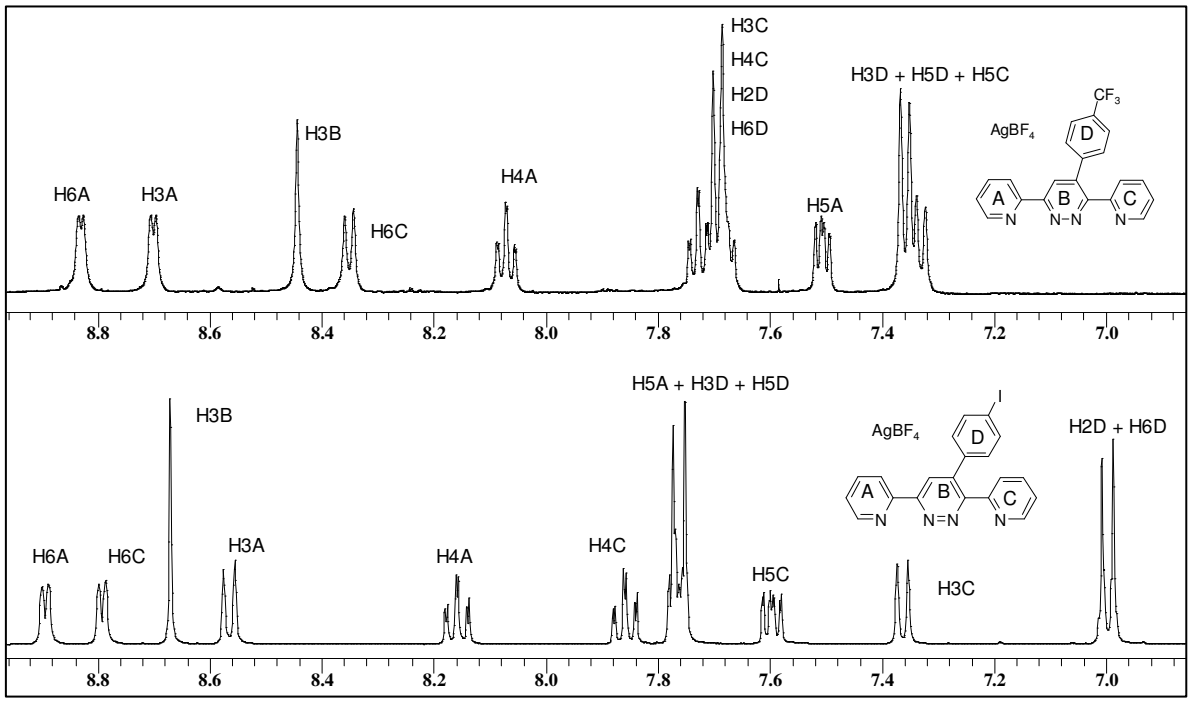


Figure 4.15: ^{1}H NMR spectra of silver complexes **20sc** and **24sc**.

Figure 4.16 shows the ^{1}H NMR spectra of 4,4'-(5-bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) silver complex (**26sc**) and 4-(3-bromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**28sc**).

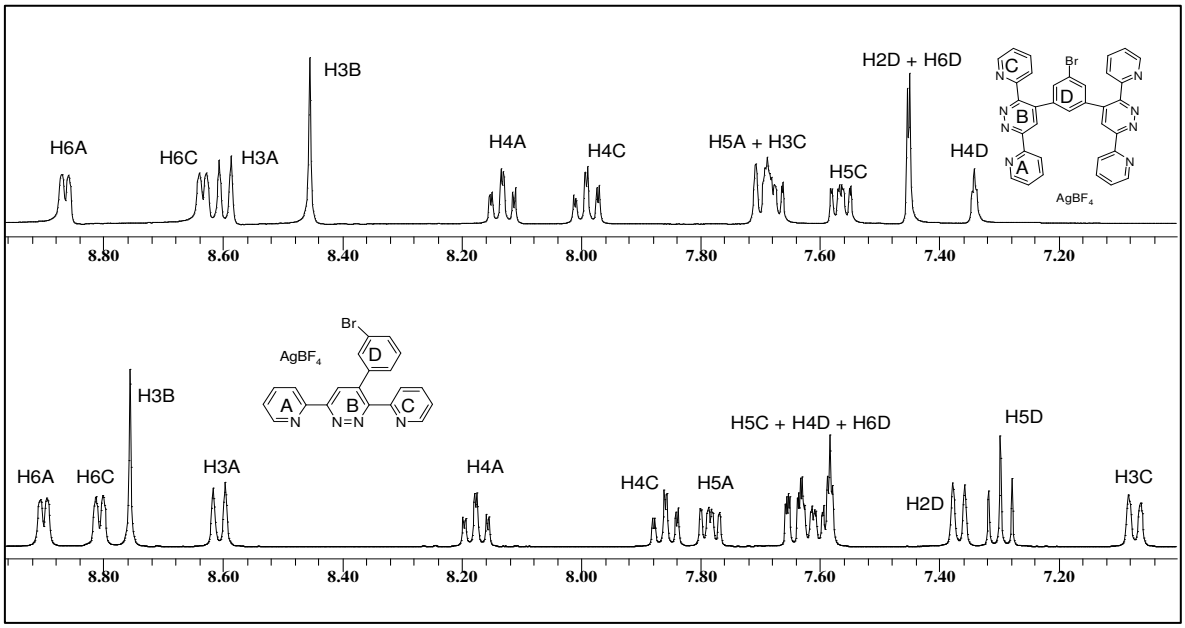


Figure 4.16: ^{1}H NMR spectra of silver complexes **26sc** and **28sc**.

The ^{1}H NMR spectra of complexes **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc** could be assigned by the chemical shifts, relatives integrals and the coupling patterns of the signals.

All the ^{1}H NMR spectra show the same signals as those present in the ^{1}H NMR spectrum of their respective ligand. For the mono substituted pyridazine silver complexes **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc** we can see the signal (singlet) of the H_{3B} proton.

The spectra of all the silver complexes exhibited a single ligand environment. No species other than the free ligands and the silver complexes were detected by ^{1}H NMR spectroscopy. The complexation of the ligand and the silver species induces some overlapping signals. In the spectrum of 4-(4-bromophenyl)-3,6-di-pyridin-2yl-pyridazine silver complex (**15sc**) two signals have the same chemical shift. The signals of the protons H_{5C} and H_{4A} are overlapping in the same NMR region (δ 7.70 ppm). This case also appears in the ^{1}H NMR spectrum of 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**18sc**) for the signals of the H_{4C} and H_{4D} protons. These complexes show the same spectra as the one presented in chapter III. In fact, the protons H_{3B}, H_{6A} and H_{6C} are mostly affected by the silver complexation. Again, this effect is due to the short distance between the affected proton and the Ag-N bond.

A closer look at all the ^{1}H NMR spectra, shows that all the spectra present an overlapping of two, three or four signals. We found overlapping of signals around δ 7.6 to 7.7 ppm. For species **20sc** this effect concerns the protons H_{3C}, H_{4C},H_{2D} and H_{6D}, for the silver complex **24sc**, the protons H_{5A}, H_{3D} and H_{5D}, for compound **26sc**, the protons H_{5A} and H_{3C} are concerned. The last silver complex (**28sc**) shows an overlapping of signals of protons H_{5C}, H_{4D} and H_{6D}.

It is important to notice that all the ^{1}H NMR spectra of the silver(I) complexes have sharp signals and that there is no signal missing. We also noticed that the H_{3C} proton signal is shifted to the higher field. This is the case for all the silver complex spectra presented in this chapter. This is probably due to the short distance between the H_{3C} proton and the Ag-N bond and to the presence of the substituent that is really close to that proton.

Table 4.8 summarises the ^{1}H NMR spectroscopic data for the silver complexes presented in this chapter.

Complex	Solvent	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring
15sc (δ/ppm)	CD_3CN	7.14 d	7.65 m	7.47 dd	8.75 d	8.32 s	8.23 dt	8.04 td	7.65 m	8.72 d	7.53-7.03 d
18sc (δ/ppm)	DMSO	8.74 d	8.20 td	7.79 dd	8.91 d	8.79 s	7.60 m	7.96 m	7.60 m	8.74 d	7.96 m-7.49 d
20sc (δ/ppm)	DMSO	8.68 d	8.10 td	7.62 dd	8.81 d	8.58 s	8.05 d	8.01 td	7.43 dd	8.38 d	7.72-7.52 d
24sc (δ/ppm)	DMSO	8.58 d	8.17 td	7.79 m	8.91 d	8.68 s	7.38 d	7.88 td	7.62 dd	8.81 d	7.79 m-7.01 d
26sc (δ/ppm)	DMSO	8.61 d	8.15 td	7.70 m	8.88 m	8.47 s	7.70 m	8.01 td	7.58 dd	8.65 d	7.47 d-7.36 s
28sc (δ/ppm)	DMSO	8.62 d	8.19 td	7.80 dd	8.92 d	8.77 s	7.10 d	7.87 td	7.63 m	8.82 d	7.63 m-7.38 d-7.31 t

Table 4.8: The ^{1}H NMR spectroscopic characterisation of silver complexes **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**.

The ^{1}H NMR characterisation of the different silver complexes synthesised in this chapter was successful. We could also characterise all the complexes by ^{13}C NMR spectroscopy. Details on this ^{13}C NMR characterisation are given in the experimental part at the end of this chapter.

Mass spectrometry

Mass spectra of all the silver complexes were run with the electrospray ionisation technique. The species were dissolved in acetonitrile. We were not able to obtain a mass spectrum of 4,4'-(5-bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) silver complex (**26sc**). This silver(I) complex was not soluble enough in acetonitrile to obtain a suitable spectrum. The mass spectra of complexes **15sc**, **18sc** and **24sc** showed an $[AgL_2]^+$ peak. The mass spectrum of complex **15sc** shows three peaks corresponding to $[AgLMeCN]^+$, $[Ag_2LCF_3SO_3]^+$ as well as the $[AgL_2]^+$ peak. The mass spectrum of 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**18sc**) has two peaks ($[AgL]^+$ and $[AgL_2]^+$).

All the calculated and detected *m/z* values are summarised in Table 4.9. Figure 4.17 shows a representative mass spectrum (**28sc**).

silver complex	**15sc**		**18sc**		**20sc**		**24sc**		**26sc**		**28sc**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L]^+$	°	°	°	°	379	378	436	436	°	°	°	°
$[Ag+L+MeCN]^+$	537	538	°	°	°	°	584	585	°	°	°	°
$[Ag+L]^+$	°	°	575	575	485	487	°	°	°	°	497	497
$[Ag+2L]^+$	887	887	1047	1048	°	°	980	980	°	°	884	885
$[Ag+2L+MeCN]^+$	°	°	°	°	°	°	°	°	°	°	°	°
$[2Ag+2L+2MeCN]^+$	°	°	°	°	°	°	934	935	°	°	1082	1081
$[2Ag+L+CF_3SO_3]^+$	752	753	°	°	°	°	°	°	°	°	°	°

Table 4.9: Calculated and detected *m/z* values for the species **15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**.

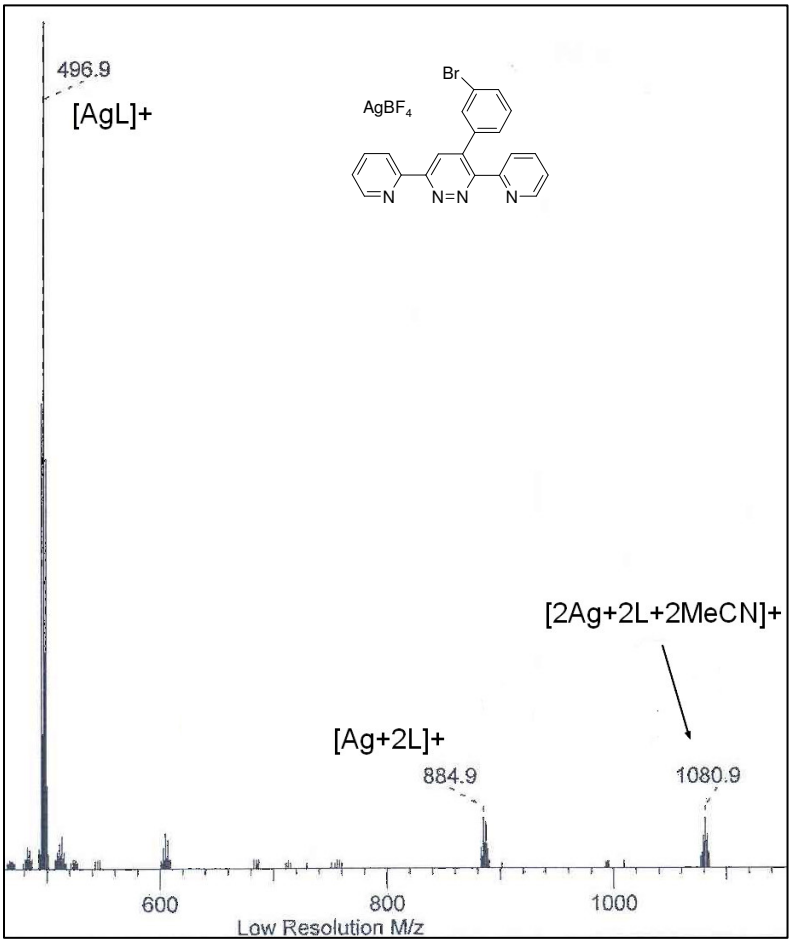


Figure 4.17: Mass spectrum of silver complex **28sc**.

Single crystal structure for silver complex **15sc**

Crystals of **15sc** are colourless plates. **15sc** crystallizes in the triclinic space group P-1. A dinuclear $[Ag_2(\mathbf{15})_2]^{2+}$ cation is observed. One N atom of the pyridyl ring and one N atom of the pyridazine ring coordinate a silver atom. One silver centre, (coordinating ring A and B from each ligand) exhibits four normal Ag-N contacts (2.360(3), 2.363(3), 2.363(3), and 2.374(4)Å). The other silver atom centre (coordinating ring B and C from each ligand) has four Ag-N contacts (2.395(4), 2.411(3), 2.513(3), and 2.330(4)Å) and one silver-triflate contact (2.683(3)Å). The distance between Ag-O is too long to be considered as a bond, but there is an interaction between the silver and the oxygen. The two ligands are arranged in a *cis* configuration around the dinuclear silver core (Figure 4.18).

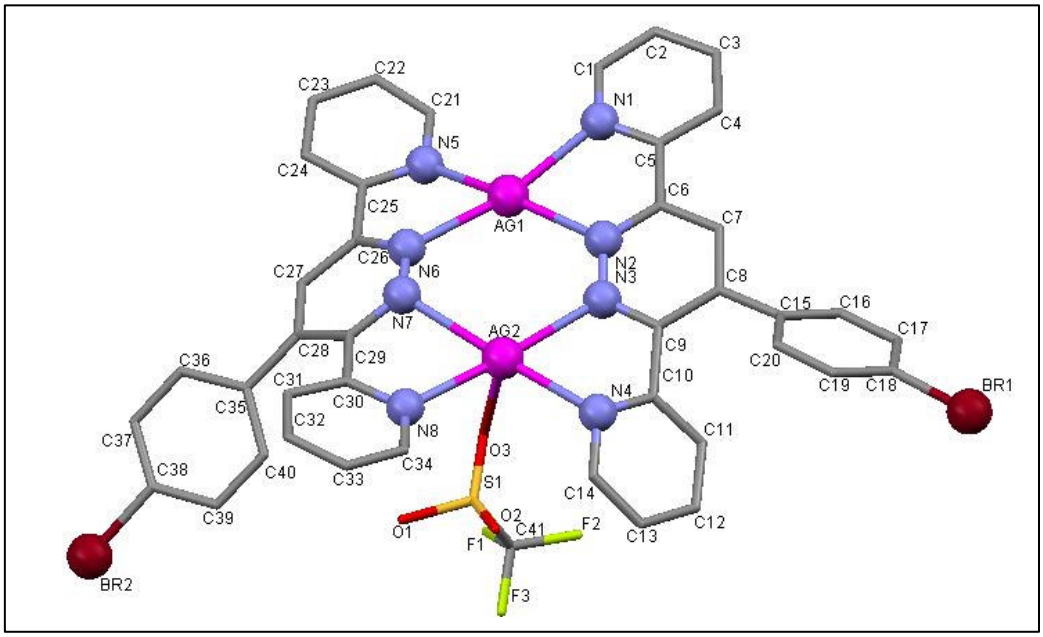


Figure 4.18: The molecular structure of **15sc** with the labelling scheme.

The bromo-phenyl substituents are twisted with respect to the pyridazine that they are bounded to, with a torsion angle of 48° (C7-C8-C15-C16). The terminal pyridine rings are also significantly out of the plane of the pyridazine with torsion angles of 6, 27, 39 and 43° (Figure 4.19).

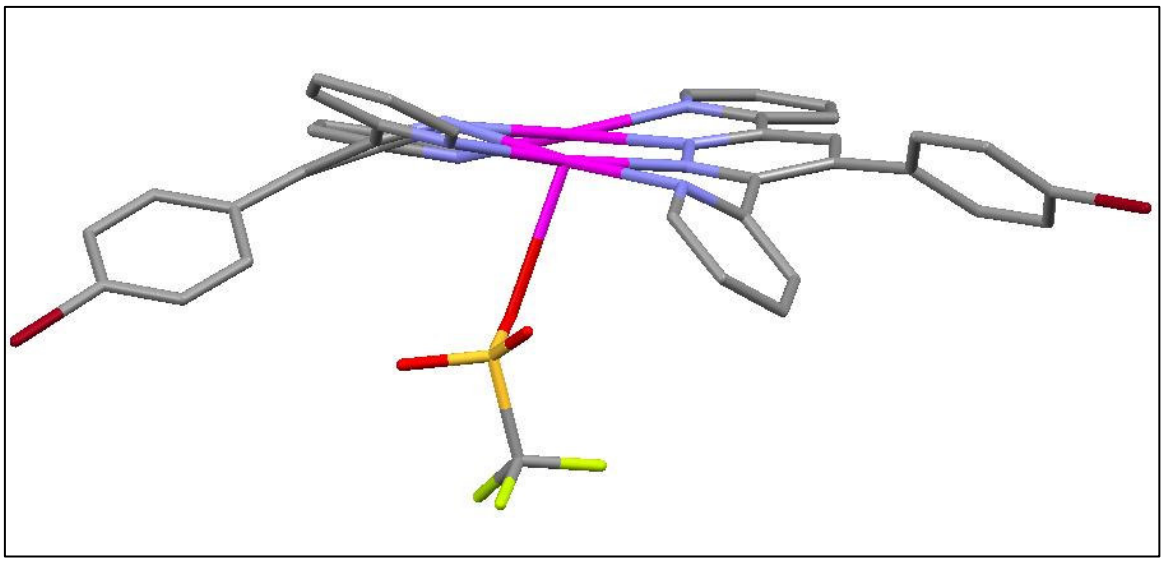


Figure 4.19: The molecular structure of **15sc**, non planar rings.

The silver-silver distance is 4.027(4)Å, and the N-Ag-N angles are between 69 and 71°. The Ag-O distance is 2.693(3)Å. The important bonds and angles are listed in Table 4.10. Details of the structure solution are given in Appendix 3.

Distances Å		
Ag1	N1	2.374(4)
Ag1	N2	2.363(3)
Ag1	N5	2.360(3)
Ag1	N6	2.363(3)
Ag2	N3	2.411(3)
Ag2	N4	2.395(4)
Ag2	N7	2.513(3)
Ag2	N8	2.330(4)
Ag2	O3	2.693(3)
Ag1	Ag2	4.027(4)

Angles deg(°)			
N1	Ag1	N2	70.09 (12)
N1	Ag1	N5	108.13 (12)
N2	Ag1	N5	166.15 (12)
N1	Ag1	N6	165.26 (13)
N2	Ag1	N6	114.18 (11)
N5	Ag1	N6	71.19 (12)
N3	Ag2	N4	71.23 (12)
N3	Ag2	N7	109.02 (11)
N4	Ag2	N7	174.91 (13)
N3	Ag2	N8	174.62 (13)
N4	Ag2	N8	109.41 (12)
N7	Ag2	N8	69.85 (12)

Table 4.10: Important bond distances and angles present in **15sc**.

The packing shows an alternating orientation of the $[Ag_2(\mathbf{15})_2]^{2+}$ species. The silver atom linked to a triflate is alternatively placed on an up or down position. Consequently the substituent has the same alternating arrangement (Figure 4.20).

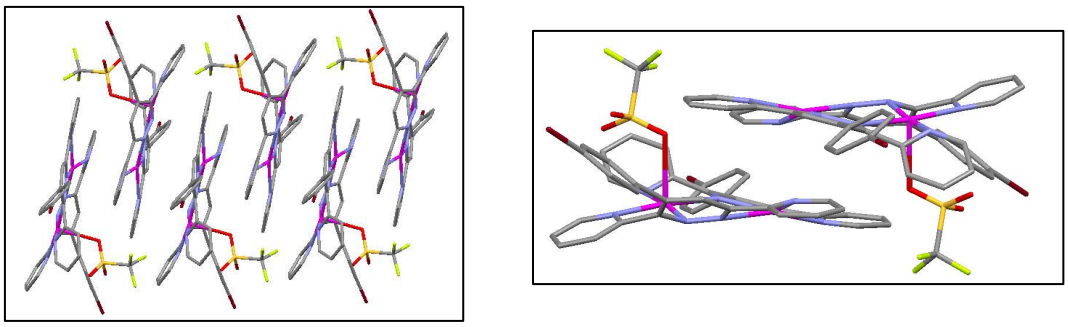


Figure 4.20: Arrangement of the $[Ag_2(\mathbf{15})_2]^{2+}$ ions and the triflate anions.

The first picture in Figure 4.20 shows a layer composed of $[Ag_2(\mathbf{15})_2]^{2+}$ species. Each layer is separated by the triflate anion (Figure 4.21). There are no π-stacking interactions or hydrogen bonds involving the heterocyclic or substituent rings of the ligand.

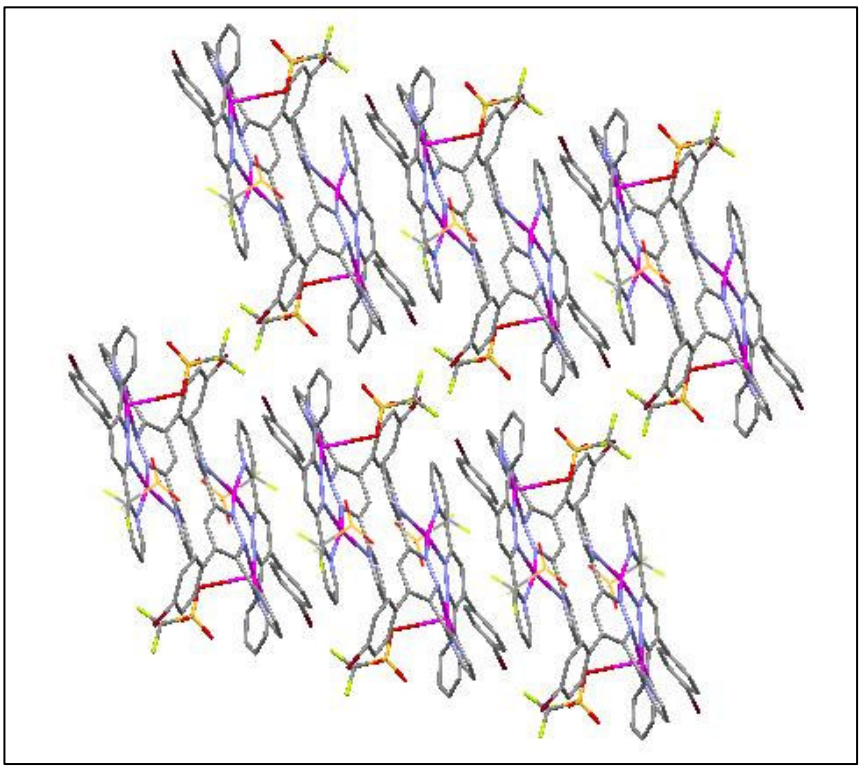


Figure 4.21: Layer motif in **15sc**.

Single crystal structure for silver complex **18sc**

Crystals of **18sc** are yellow plates. **18sc** crystallizes in the monoclinic space group $P2_1/a$. A dinuclear $[Ag_2(\mathbf{18})_2]^{2+}$ cation is observed. One nitrogen atom of the pyridyl ring and one nitrogen atom of the pyridazine coordinate a silver atom. The two silver centres are equivalent. The **18sc** possesses a centre of symmetry and the two ligands are arranged in a *trans* configuration around the dinuclear silver core. The unit cell has two ligands, two silvers, one tetrafluoroborate and one acetonitrile. The molecular structure of **18sc** with labelling scheme is given in Figure 4.22.

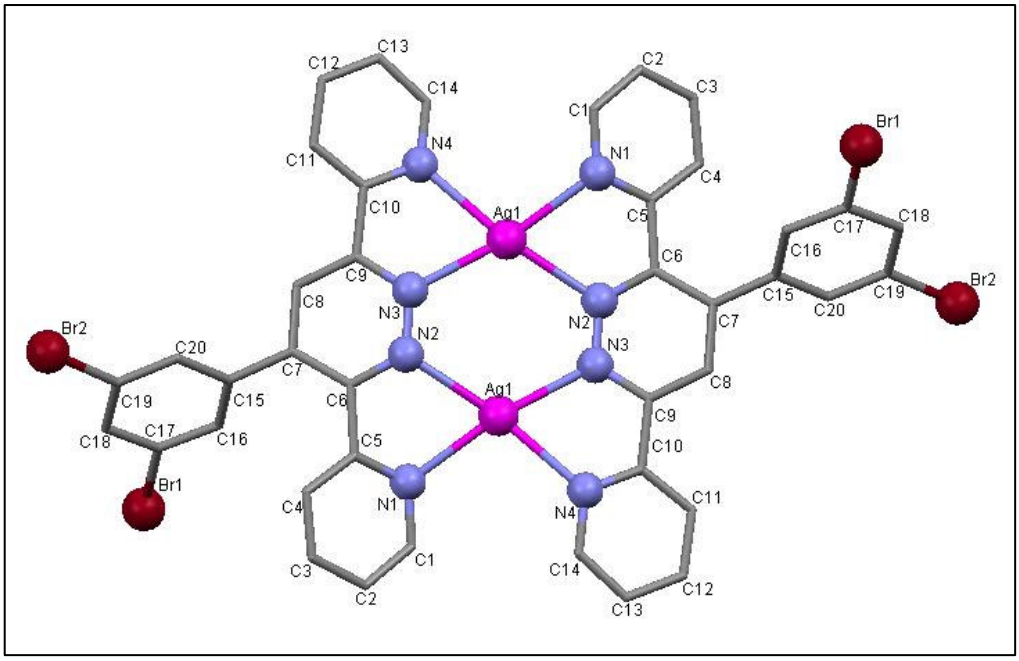


Figure 4.22: The molecular structure of **18sc** with the labelling scheme.

The silver centre Ag_1 (coordinating ring A and B from one ligand to ring C and B from the other ligand) and, because of the symmetry, the silver centre Ag_2 (coordinating ring C and B from one ligand to ring A and B from the other ligand) have four normal Ag-N contacts (2.355(3), 2.370(3), 2.313(3) and 2.430(3)Å)[17].

The dibromo-phenyl substituents are twisted with respect to the pyridazine that they are bounded to, with a torsion angle of 51° (C8-C7-C15-C16). The terminal pyridine rings are also significantly out of the plane of the pyridazine with torsion angles of 27.21° and 34.63° (Figure 4.23).

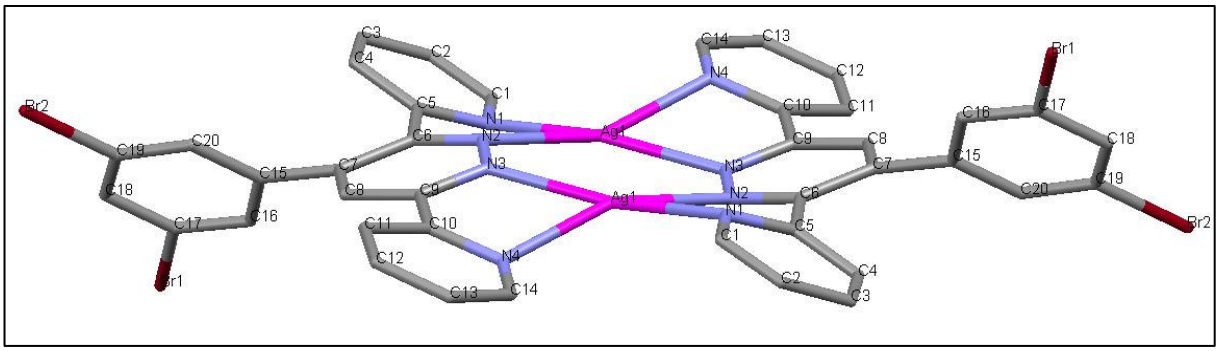


Figure 4.23: The molecular structure of **18sc**, non planar rings.

The silver-silver distance is 3.691(3)Å, and the N-Ag-N angles are 70.43(11)° and 70.64(11)°. The important bonds and angles are listed in Table 4.11. Details of the structure solution are given in Appendix 4.

Distances Å		
Ag1	N4	2.430(3)
Ag1	N3	2.313(3)
Ag1	N1	2.355(3)
Ag1	N2	2.370(3)

Angles deg(°)			
N4	Ag1	N3	70.64(11)
N4	Ag1	N1	103.54(11)
N3	Ag1	N1	165.38(11)
N4	Ag1	N2	158.26(11)
N3	Ag1	N2	119.90(11)
N1	Ag1	N2	70.43(11)

Table 4.11: Important bond distances and angles present in **18sc**.

The packing shows five $[Ag_2(\mathbf{18})_2]^{2+}$ species. They are alternately placed in the “up to down” and “down to up” orientation. In fact, two parallel $[Ag_2(\mathbf{18})_2]^{2+}$ species are oriented from “up to down”, then one $[Ag_2(\mathbf{18})_2]^{2+}$ specie is oriented from “down to up”, and again two $[Ag_2(\mathbf{18})_2]^{2+}$ are oriented from “up to down” (Figure 4.24). This kind of chain is repetitive and parallel. Between all the $[Ag_2(\mathbf{18})_2]^{2+}$ species that are oriented from “down to up” there is a space filled with two tetrafluoroborate anions.

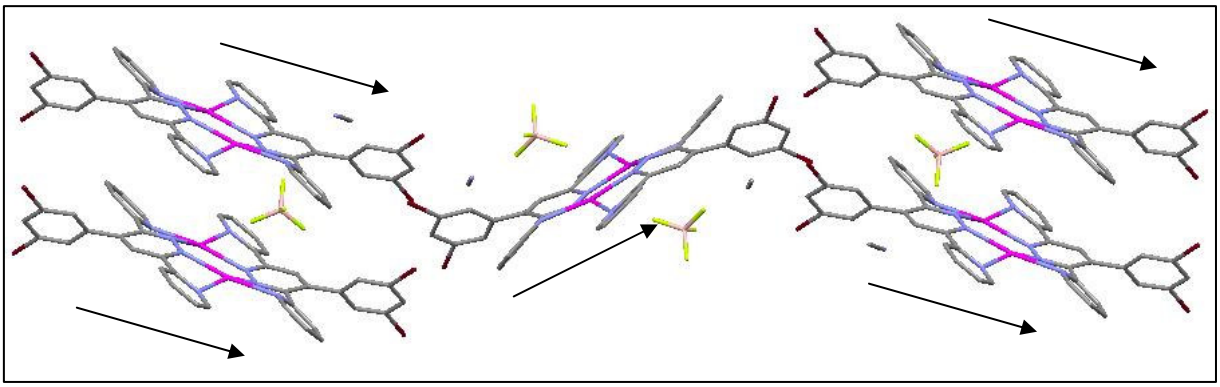


Figure 4.24: Arrangement of the $[Ag_2(\mathbf{18})_2]^{2+}$ species in the crystal structure of **18sc**.

Figure 4.25 shows different views of the packing of **18sc**. We can see the different orientations of the layers and the presence of the tetrafluoroborate anion occupying the space between some layers.

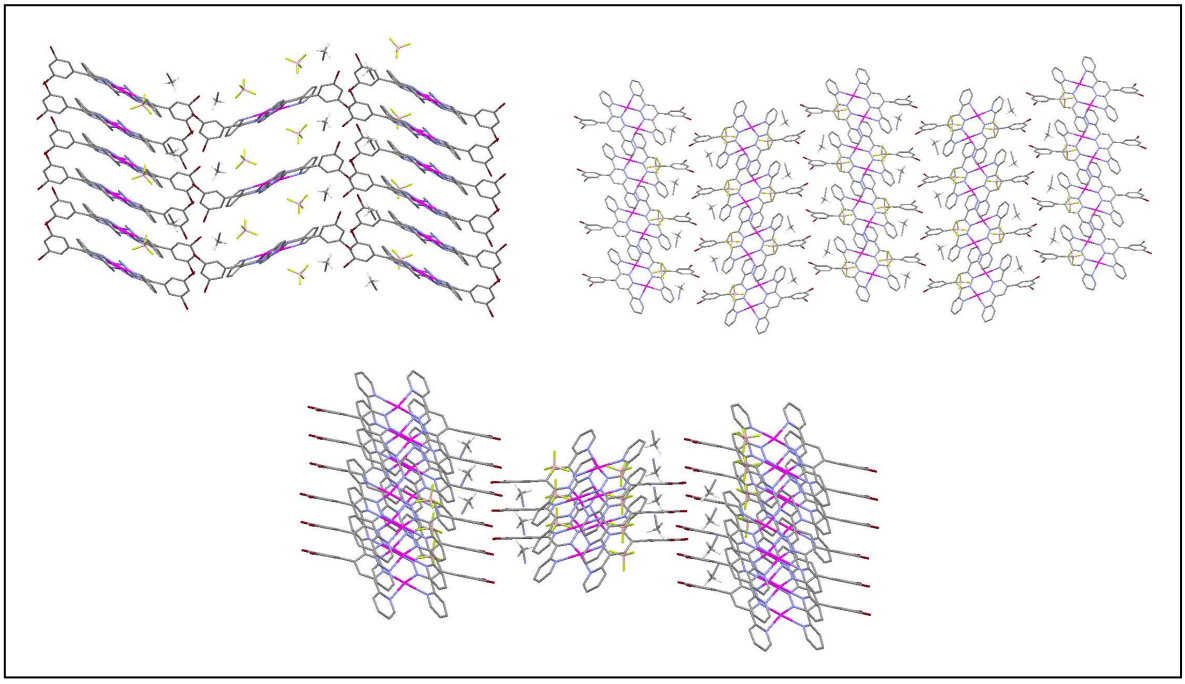


Figure 4.25: Layer motifs in **18sc**.

Single crystal structure for silver complex **20sc**

Crystals of **20sc** are pale red plates. **20sc** crystallizes in the monoclinic space group C2/c. This third structure also shows a dinuclear $[Ag_2(\mathbf{20})_2]^{2+}$ cation. One nitrogen atom of the pyridyl ring and one nitrogen atom of the pyridazine coordinate a silver atom. The two silver centres are equivalent. **20sc** possesses a centre of symmetry and the two ligands are arranged in a *trans* configuration around the dinuclear silver core.

The unit cell contains two ligands, two silvers, one tetrafluoroborate and 1/3 acetonitrile. The molecular structure of **20sc** with labelling scheme is given in Figure 4.26.

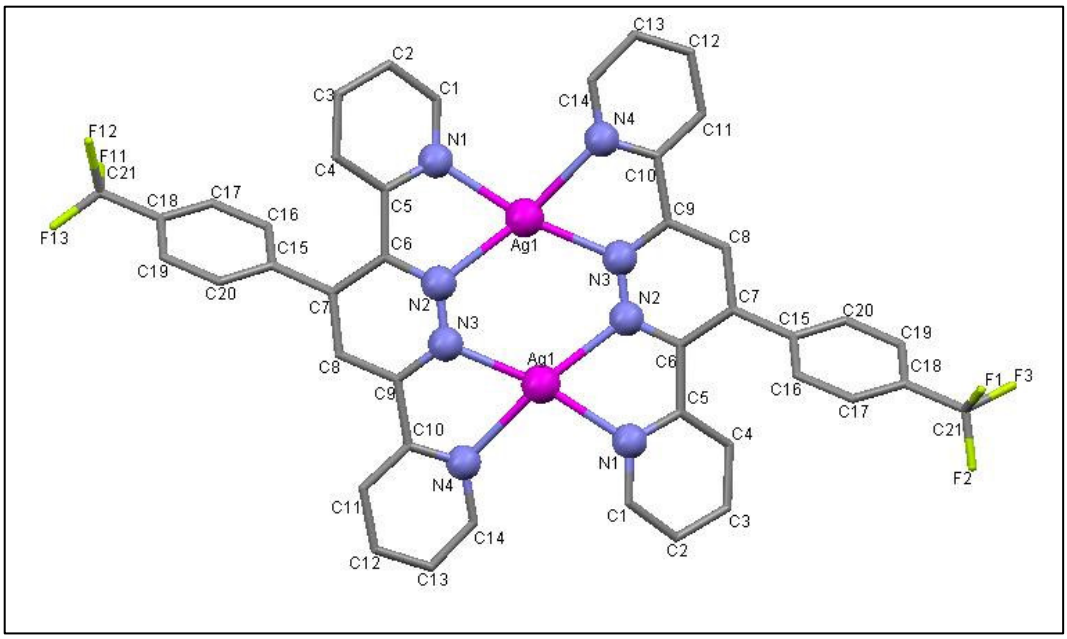


Figure 4.26: The molecular structure of **20sc** with the labelling scheme.

The silver centre Ag_1 (coordinating ring A and B from one ligand to ring C and B from the other ligand) and, because of the symmetry, the silver centre Ag_2 (coordinating ring C and B from one ligand to ring A and B from the other ligand has four normal Ag-N contacts (2.311(2), 2.3838(17), 2.2721(18) and 2.476(2)Å)[18].

The CF_3-phenyl substituents are twisted with respect to the pyridazine that they are bounded to, with a torsion angle of 58° (C8-C7-C15-C16). The terminal pyridine rings are also significantly out of the plane of the pyridazine with torsion angles of 28.59° and 35.63° (Figure 4.27). We can notice that the pyridyl ring (ring C) adjacent to the

substituent has a larger torsion angle than the other pyridyl ring (ring A). This larger torsion angle is due to the steric effect induced by the substituent.

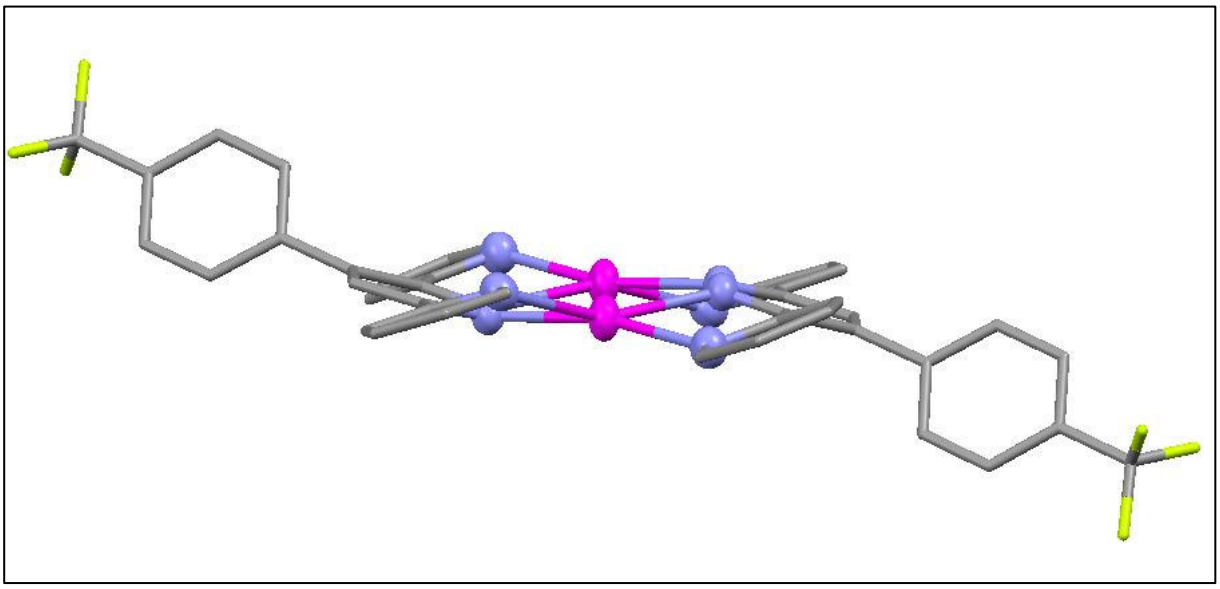


Figure 4.27: The molecular structure of **20sc**, non planar rings.

The silver-silver distance is 3.6439(4)Å, and the N-Ag-N angles are 70.66(6)° and 71.09(7)°. The important bonds and angles are listed in Table 4.12. Details of the structure solution are given in Appendix 5.

Distance		**Å**
Ag1	N4	2.476(2)
Ag1	N3	2.2721(18)
Ag1	Ag1	3.6439(4)
Ag1	N1	2.311(2)
Ag1	N2	2.3838(17)
Ag1	F4	2.809(2)

Angles			**deg(°)**
N4	Ag1	N3	70.66(6)
N4	Ag1	Ag1	128.26(5)
N3	Ag1	Ag1	61.84(4)
N4	Ag1	N1	102.57(7)
N3	Ag1	N1	165.36(7)
Ag1	Ag1	N1	128.24(5)
N4	Ag1	N2	155.66(6)
N3	Ag1	N2	120.42(6)
Ag1	Ag1	N2	58.64(4)
N1	Ag1	N2	71.09(7)

Table 4.12: Important bond distances and angles present in **20sc**.

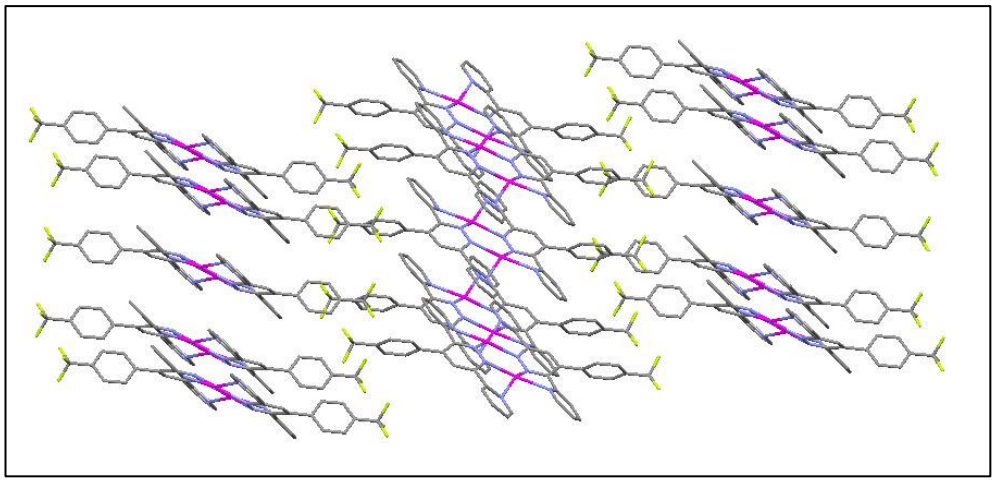


Figure 4.28: Arrangement of the $[Ag_2(\mathbf{20})_2]^{2+}$ cations in the crystal structure of **20sc**.

The packing shows 15 $[Ag_2(\mathbf{20})_2]^{2+}$ species. They are not coplanar. Five $[Ag_2(\mathbf{20})_2]^{2+}$ species are parallel, the next five $[Ag_2(\mathbf{20})_2]^{2+}$ ions are parallel. This two groups of five $[Ag_2(\mathbf{20})_2]^{2+}$ ions are not in the same plan, they are twisted in regard to each others. The third group of five $[Ag_2(\mathbf{20})_2]^{2+}$ ions is parallel to the first group. The packing shows a repetitive scheme (Figure 4.28).

The three crystal structure obtained in this chapter show $[Ag_2(L)_2]^{2+}$ species. **15sc** presents a *cis* arrangement of the substituents around the silver centers. Silver complexes **18sc** and **20sc** present a *trans* arrangement of the substituent around the silver centers. This effect is probably due to the contre-anion but we could not obtain a crystal structure of the silver complex composed of ligand **15** and silver tetrafluoroborate to proove this statement.

The mass spectrometry showed that the solution species of **15sc**, **18sc** and **20sc** are composed of one silver and one ligand or one silver and two ligands. This is different from the x-ray analysis that always showed a crystal structure composed of two silvers and two ligands.

We also noticed that the withdrawing substituents have an influence on the Ag-N bond lengths. In fact, in complexes **28sc** and **20sc** the shortest bond length, between a silver atom and a nitrogen atom is, in both cases, the Ag-N3 distance. The N3 atom

is placed on ring B, that is directly related to the halogenated substituent. This case is not true for **15sc**, the shortest Ag-N distance is Ag-N8. The N8 atom belongs to the external pyridil ring C. Here the steric effects are responsible for that short distance.

IV.5 Conclusion

In this chapter we described the synthesis of the ethynyl precursors **14**, **17**, **19**, **23**, **25** and **27** that have been prepared with the Sonogashira reaction.

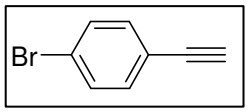
We also showed the methodology to access to mono-substituted pyridazines, based on a retro Diels-Alder reaction that enabled us to prepare the ligands **15**, **18**, **20**, **24**, **26** and **28**. All these ligands were characterised by NMR spectroscopy, mass spectrometry and elemental analysis. We also obtained a single X-ray crystal structure for the ligand **15**.

Six new silver complexes (**15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**) were prepared and characterised by NMR, mass spectrometry (apart from some cases, discussed in the chapter).

We obtained suitable crystals for silver complexes **15sc**, **18sc** and **20sc** to carry out single X-ray diffraction analysis. All the crystal structures showed a dinuclear $[Ag_2(L)_2]^+$ cation with an arrangement of the ligands in a *cis* (4-(4-bromophenyl)-3,6(di-pyridin-2yl)pyridazine silver complex (**15sc**)) or a *trans* (4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**18sc**) and 3,6-di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine silver complex (**20sc**)) conformation. None of these crystal structures showed a grid like structure[19], π-stacking or hydrogen bonding interactions.

IV.6 Experimental part

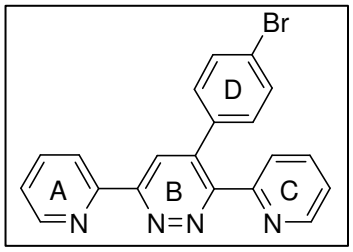
Synthesis of 1-bromo-4-ethynylbenzene (14)



Under argon and exclusion of moisture, 1-bromo-4-iodobenzene (1.0 g, 3.4 mmol), CuCl (66 mg, 0.66 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.43 g, 0.66 mmol) were suspended in dry, argon degassed, triethylamine (50 ml). Then trimethylsilylacetylene (0.60 ml, 4.3 mmol) was added and the mixture stirred at 40°C for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown powder (0.45 g, 2.5 mmol, 73%, C_8H_5Br, 181.0 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz,) δ/ppm: 7.46 (d, J=8.1 Hz, 2H, H_{4+6}), 7.35 (d, J=8.6 Hz, 2H, H_{3+5}), 3.12 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 133.5, 131.6, 123.1, 121.0, 82.5, 78.3.
MS (FAB) *m/z* $[L]^+$ 181.

Synthesis of 4-(4-bromophenyl)-3,6(di-pyridin-2-yl)pyridazine (15)

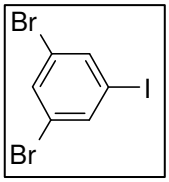


A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.26 g, 1.1 mmol) and 1-bromo-4-ethynylbenzene (**14**) (0.21 g, 1.1 mmol) in toluene (50 ml) was refluxed for 11 days at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, EtOAc, The third band was

collected). The product was obtained as an orange powder (0.39 g, 1.0 mmol, 91%, $C_{20}H_{13}BrN_4$, 389.3 g/mol).

^{1}H NMR (CD_3CN, 500 MHz) δ/ppm: 8.76 (d, J=4.5 Hz, 1H, H_{6A}), 8.72 (d, J=8.0 Hz, 1H, H_{3A}), 8.56 (s, 1H, H_{3B}), 8.39 (d, J=4.5 Hz, 1H, H_{6C}), 8.00 (td, J=7.9, 1.6 Hz, 1H, H_{4A}), 7.96 (d, J=8.0 Hz, 1H, H_{3C}), 7.92 (td, J=7.8, 1.6 Hz, 1H, H_{4C}), 7.52 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.49 (d, J=8.5 Hz, 2H, H_{2D+6D}), 7.38 (dd, J=7.3, 4.4 Hz, 1H, H_{5C}), 7.18 (d, J=8.5 Hz, 2H, H_{3D+5D}).
^{13}C NMR (CD_3CN, 125 MHz) δ/ppm: 158.4, 157.8, 155.7, 153.1, 149.7, 148.6, 139.1, 137.4, 136,7, 136.5, 131.4, 130.7, 125.1, 124.9, 123.6, 122.2, 121.3, 117.3, 2 carbon signals unresolved.
MS (ESI) m/z: $[L]^+$ 391, $[Na+L+2MeCN]^+$ 494, $[Na+2L+MeCN]^+$ 841.

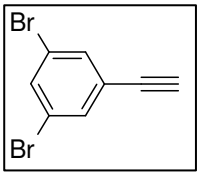
Synthesis of 1,3-dibromo-5-iodobenzene (16)



Under argon and exclusion of moisture 1,3,5-tribromobenzene (5.0 g, 16 mmol) was dissolved in dry diethyl ether. The solution was cooled down at -90°C. BuLi (10 ml, 1.60 M in hexane, 16 mmol) was slowly added (half an hour). The mixture was stirred at -90°C for one hour. A solution of I_2 (4.2 g, 17 mmol) in diethyl ether was added. The mixture was stirred until the temperature reached 20°C. The organic phase was washed with a 5% aqueous solution of Na_2SO_3 and with a saturated aqueous solution of NaCl. The compound was recrystallised from hexane to give a brown powder (3.8 g, 10 mmol, 65%, $C_6H_3Br_2I$, 361.7 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.44 (d, J=1.6 Hz, 2H, H_{4+6}), 7.28 (t, J=1.6 Hz, 1H, H_2).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 138.4, 133.6, 123.3, 94.4.
MS (ESI) m/z: $[L]^+$ 362, $[(L-I)]^+$ 235, $[(L-I-Br)]^+$ 154, $[(L-I-2xBr)]^+$ 74.
Elem. Anal. ($C_6H_3Br_2I$) [%] calc. C 19.9, H 0.8, found, C 20.0, H 0.9.

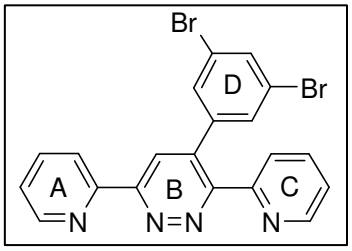
Synthesis of 1,3-dibromo-5-ethynylbenzene (17)



Under argon and exclusion of moisture, 1,3-dibromo-5-iodobenzene (**16**) (0.50 g, 1.4 mmol), CuCl (30 mg, 0.30 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.20 g, 0.30 mmol) were suspended in dry, argon degassed triethylamine (50 ml). Then trimethylsilylacetylene (0.25 ml, 1.8 mmol) was added and the mixture stirred at 60°C for 20 hours. The solvent was removed and the residue extracted with hexane (120 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane/dichloromethane (9:1), the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown powder (0.35 g, 1.4 mmol, 97%, $C_8H_4Br_2$, 259.9 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7. 65 (t, J=2.0 Hz, 1H, H_2), 7.55 (d, J=2.0 Hz, 2H, H_{4+6}), 3.16 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 134.6, 133.5, 125.4, 122.5, 80.5, 79.8.
MS (ESI) m/z: $[L]^+$ 260, $[(L\text{-}Br)]^+$ 179, $[(L\text{-}2xBr)]^+$ 100.

Synthesis of 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine (18)

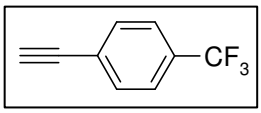


A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.18 g, 0.77 mmol) and 1,3-dibromo-5-ethynylbenzene (**17**) (0.21 g, 0.77 mmol) in toluene (50 ml) was refluxed for 6 days at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, EtOAc/hexane (3:1),

the third band was collected). The product was obtained as a beige powder (0.21 g, 0.45 mmol, 58%, $C_{20}H_{12}Br_2N_4$, 465.9 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.80 (d, J=8.0 Hz, 1H, H_{3A}), 8.75 (d, J=5.5 Hz, 1H, H_{6A}), 8.61 (s, 1H, H_{3B}), 8.46 (d, J=4.5 Hz, 1H, H_{6C}), 8.11 (d, J=7.6 Hz, 1H, H_{3C}), 7.93 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.89 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.64 (t, J=1.5 Hz, 1H, H_{4D}), 7.44 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.34 (m, 3H, H_{5C} and H_{2D+6D}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.8, 157.5, 154.7, 152.8, 149.4, 148.8, 140.7, 137.8, 137.3, 136.9, 133.8, 130.5, 125.5, 125.1, 124.8, 123.8, 122.7, 121.9, 2 carbon signals unresolved.
MS (ESI) m/z: $[L+K+DCM]^+$ 593, $[2L+Na+K]^+$ 999.
Elem. Anal. ($C_{20}H_{12}Br_2N_4$) [%] calc. C 51.3, H 2.6, N 12.0, found, C 51.7, H 2.7, N 12.0.

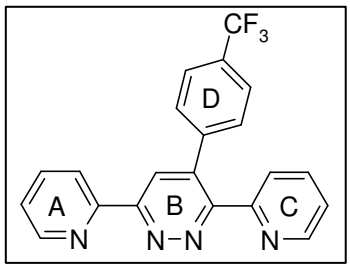
Synthesis of 1-ethynyl-4-(trifluoromethyl)benzene (19)



Under argon and exclusion of moisture, 1-iodo-4-(trifluoromethyl)benzene (2.0 g, 7.4 mmol), CuCl (72 mg, 0.74 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.52 g, 0.74 mmol) were suspended in dry, argon degassed, triethylamine (130 ml). Then trimethylsilylacetylene (2.0 ml, 14 mmol) was added and the mixture stirred at 60°C for 20 hours. The solvent was removed and the residue extracted with hexane (120 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange oil (210 mg, 1.23 mmol, 16.6%, $C_9H_5F_3$, 170.1 g/mol).

^{1}H NMR ($CDCl_3$, 250 MHz) δ/ppm: 7.58 (s, 4H, C_6H_4), 3.19 (s, 1H, ethynyl).
^{13}C NMR not soluble enough in $CDCl_3$ to record the carbon NMR spectrum.

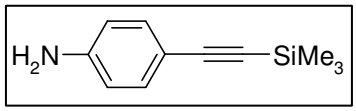
Synthesis of 3,6-di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine (20)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.13 g, 0.53 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (**19**) (90 mg, 0.53 mmol) in toluene (50 ml) was refluxed for 4 days at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, EtOAc/hexane (1:1), the second band was collected). The product was obtained as a deep red powder (0.15 g, 0.39 mmol, 74%, $C_{21}H_{13}F_3N_4$, 378.1 g/mol).

^{1}H NMR (DMSO, 500 MHz) δ/ppm: 8.81 (d, J=5.5 Hz, 1H, H_{6A}), 8.69 (d, J=8.0 Hz, 1H, H_{3A}), 8.58 (s, 1H, H_{3B}), 8.38 (d, J=7.6 Hz, 1H, H_{3C}), 8.10 (td, J=7.6, 1.6 Hz, 1H, H_{4A}), 8.05 (d, J=5.5 Hz, 1H, H_{6C}), 8.01 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.72 (d, J=8.5 Hz, 2H, H_{2D+6D}), 7.61 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.52 (d, J=8.5 Hz, 2H, H_{3D+5D}), 7.44 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}).
^{13}C NMR (DMSO, 125 MHz) δ/ppm: 158.0, 157.4, 154.8, 152.4, 149.9, 148.7, 141.2, 138.6, 137.8, 137.2, 129.6, 128.7, 128.5, 125.5, 125.3, 125.2, 125.2, 125.1, 124.8, 124.0, 121.3.
MS (ESI) m/z: $[L]^+$ 379, $[L+Na+MeCN]^+$ 442.
Elem. Anal. ($C_{21}H_{13}F_3N_4$) [%] calc. C 66.7, H 3.5, N 14.8, found, C 65.9, H 3.5, N 14.7.

Synthesis of 4-((trimethylsilyl)ethynyl)aniline (21)

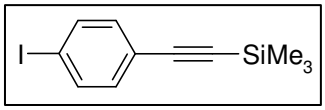


Under argon and exclusion of moisture, 4-iodoaniline (10 g, 46 mmol), CuCl (90 mg, 0.91 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.64 g, 0.91 mmol) were suspended in dry, argon degassed, triethylamine (200 ml). Then trimethylsilylacetylene (7.6 ml, 55 mmol) was added and the mixture stirred at 60°C for 20 hours. The solvent was removed and the residue extracted with hexane (300 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by

chromatographic work-up (alumina, hexane/dichloromethane (4:1) the second band was collected). The product was dissolved in THF (150 ml) and an aqueous solution of 1M NaOH was added (200 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange powder (5.11 g, 27.0 mmol, 59.1%, $C_{11}H_{15}NSi$, 189.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.27 (d, J=2.8 Hz, 2H, H_{2+6}), 6.57 (d, J=2.8 Hz, 2H, H_{3+4}), 3.49 (s, 2H, NH_2), 0.22 (s, 9H, Me_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 146.7, 133.3, 114.5, 112.5, 105.9, 91.4, 0.1.
MS (FAB) m/z: $[L]^+$ 189, $[(L\text{-}CH_3)]^+$ 174, $[(L\text{-}3CH_3)]^+$ 144.

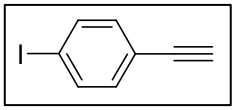
Synthesis of 4-((trimethylsilyl)ethynyl)iodobenzene (22)



Under argon 4-((trimethylsilyl)ethynyl)aniline (**21**) (1.3 g, 6.9 mmol) was suspended in water (50 ml). Concentrated hydrochloric acid (2.5 ml) was added and the brown solution cooled to 0°C. A solution of sodium nitrite (0.49 g, 7.2 mmol) in 10 ml water was slowly added. The mixture was stirred at 0°C for one hour. A catalytic amount of copper(I) iodide (125 mg) was added before the slow addition of potassium iodide (2.9 g, 18 mmol). The mixture was stirred at 0°C for 6 hours. From time to time, tetrahydrofuran (total 50 ml) was added to increase the solubility. Water (50 ml) and diethyl ether (80 ml) were added under vigorous stirring and the two layers separated. The aqueous layer was extracted with diethyl ether and the combined organic phases washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the dark residue purified by chromatographic work-up (alumina, hexane, the second band was collected) to give a white solid (1.1 g, 3.6 mmol, 52%, $C_{11}H_{13}ISi$, 300.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.63 (d, J=2.8 Hz, 2H, H_{2+6}), 7.18 (d, J=2.8 Hz, 2H, H_{3+4}), 0.24 (s, 9H, Me_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 137.3, 133.4, 122.6, 103.9, 95.9, 94.4, -0.1.
MS (EI) m/z: $[L]^+$ 300, $[(L\text{-}CH_3)]^+$ 285, $[(L\text{-}CH_3I)]^+$ 158, $[(L\text{-}2CH_3I)]^+$ 143.

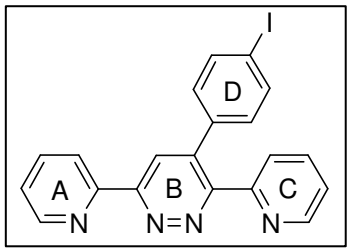
Synthesis of 1-ethynyl-4-iodobenzene (23)



4-((Trimethylsilyl)ethynyl)iodobenzene (**22**) (1.0 g, 3.4 mmol) was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange powder (0.66 g, 2.9 mmol, 85%, C_8H_5I, 227.9 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.66 (d, J=8.8 Hz, 2H, H_{3+5}), 7.21 (d, J=8.8 Hz, 2H, H_{2+6}), 3.14 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 137.4, 133.5, 121.5, 94.8, 82.6, 78.6.

Synthesis of 4-(4-iodophenyl)-3,6-di(pyridin-2-yl)pyridazine (24)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (414 mg, 1.75 mmol) and 1-ethynyl-4-iodobenzene (**23**) (400 mg, 1.75 mmol) in toluene (120 ml) was refluxed for 74 hours at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, EtOAc/hexane (1:1), the second band was collected). The product was obtained as a pink solid (0.70 g, 1.6 mmol, 92%, $C_{20}H_{13}IN_4$, 436.0 g/mol).

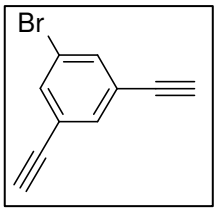
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.79 (d, J=8.0 Hz, 1H, H_{3A}), 8.72 (d, J=4.4 Hz, 1H, H_{6A}), 8.62 (s, 1H, H_{3B}), 8.46 (d, J=4.4 Hz, 1H, H_{6C}), 7.97 (d, J=8.0 Hz, 1H, H_{3C}), 7.92 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.83 (td, J=8.0, 1.6 Hz, 1H,H_{4C}), 7.64 (d, J=8.8 Hz, 2H, H_{3D+5D}), 7.41 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.29 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 7.00 (d, J=8.4 Hz, 2H, H_{2D+6D}).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.9, 157.7, 155.4, 153.1, 149.4, 149.0, 139.5, 137.5, 137.2, 136.7, 136.6, 130.5, 125.3, 124.9, 124.8, 123.5, 121.8, 94.7, 2 carbon signals unresolved.

MS (ESI) m/z: $[L]^+$ 437, $[L+Na+MeCN]^+$ 499, $[2L+Na+MeCN]^+$ 935.

Elem. Anal. ($C_{20}H_{13}IN_4$) [%] calc. C 55.1, H 3.0, N 12.8, found, C 55.0, H 3.0, N 12.6.

Synthesis of 1-bromo-3,5-diethynylbenzene (25)



Under argon and exclusion of moisture, 1,3-dibromo-5-iodobenzene (**16**) (4.2 g, 12 mmol), CuCl (115 mg, 1.16 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (823 mg, 1.16 mmol) were suspended in dry, argon degassed, triethylamine (120 ml). Then trimethylsilylacetylene (2.3 ml, 17 mmol) was added and the mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (120 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed and the product was purified by chromatographic work-up (alumina, hexane) to give an orange powder (side product from the synthesis of 1,3-dibromo-5-ethynylbenzene (**17**)) (0.14 g, 0.68 mmol, 5.7%, $C_{10}H_5Br$, 204.0 g/mol).

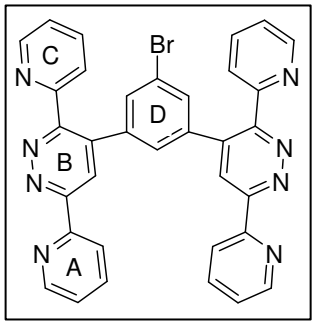
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.60 (d, J=1.6 Hz, 2H, H_{2+6}), 7.52 (t, J=1.2 Hz, 1H, H_4), 3.13 (s, 2H, ethynyl).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 135.1, 134.1, 124.1, 122.6, 81.0, 79.2.

MS (EI) m/z: $[L]^+$ 204, $[(L-Br)]^+$ 125.

Elem. Anal. ($C_{10}H_5Br$) [%] calc. C 58.6, H 2.5, found, C 58.9, H 3.3.

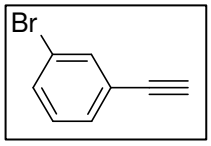
Synthesis of 4,4'-(5-bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) (26)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.16 g, 0.68 mmol) and 1-bromo-3,5-diethynylbenzene (**25**) (64 mg, 0.31 mmol) in toluene (60 ml) was refluxed for 14 days at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, EtOAc/hexane (2:1), the second band was collected). The product was obtained as a deep pink solid (0.16 g, 0.26 mmol, 87%, $C_{34}H_{21}BrN_8$, 621.5 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.77 (m, 4H, H_{3A+6A}), 8.51 (d, J=5.0 Hz, 2H, H_{6C}), 8.43 (s, 2H, H_{3B}), 8.02 (d, J=8.0 Hz, 2H, H_{3C}), 7.92 (td, J=7.6, 1.6 Hz, 2H, H_{4A}), 7.87 (td, J=7.6, 1.6 Hz, 2H, H_{4C}), 7.44 (dd, J=7.6, 4.8 Hz, 2H, H_{5A}), 7.36 (d, J=1.6 Hz, 2H, H_{2D+6D}), 7.34 (dd, J=7.6, 4.8 Hz, 2H, H_{5C}), 7.11 (t, J=2.0 Hz, 1H, H_{4D}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.8, 157.7, 154.9, 152.9, 149.3, 148.9, 139.1, 138.4, 137.2, 136.8, 131.5, 128.1, 125.4, 124.9, 124.8, 123.8, 122.0, 121.8.
MS (ESI) m/z: $[L+K+DCM]^+$ 744, $[2L+Na+MeCN]^+$ 1307, $[2L+K+DCM]^+$ 1366.
Elem. Anal. ($C_{34}H_{21}BrN_8$) [%] calc. C 65.7, H 3.4, N 18.0, found, C 65.2, H 3.7, N 17.1.

Synthesis of 1-bromo-3-ethynylbenzene (27)

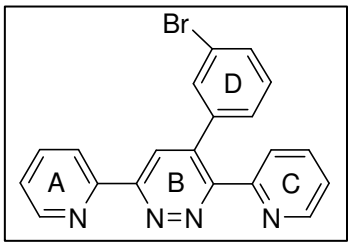


Under argon and exclusion of moisture, 1-bromo-3-iodobenzene (2.0 g, 7.1 mmol), CuCl (70 mg, 0.71 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.50 g, 0.71 mmol) were suspended in dry, argon degassed, triethylamine (80 ml). Then trimethylsilylacetylene (1.3 ml, 7.9 mmol) was added and the mixture stirred at 40°C for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by

chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown powder (0.62 g, 3.4 mmol, 48%, C_8H_5Br, 181.0 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.65 (t, J=1.7 Hz, 1H, H_2), 7.48 (d, J=8.0 Hz, 1H, H_4), 7.41 (d, J=7.6 Hz, 1H, H_6), 7.18 (t, J=7.6 Hz, 1H, H_5), 3.13 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 134.8, 131.9, 130.6, 129.7, 124.1, 122.0, 81.9, 78.6.

Synthesis of 4-(3-bromophenyl)-3,6-di(pyridin-2-yl)pyridazine (28)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.46 g, 1.9 mmol) and 1-ethynyl-3-bromobenzene (**27**) (0.35 g, 1.9 mmol) in toluene (60 ml) was refluxed for 9 days at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, chloroform, the third band was collected). The product was obtained as a beige powder (0.61 g, 1.6 mmol, 83%, $C_{20}H_{13}BrN_4$, 389.2 g/mol).

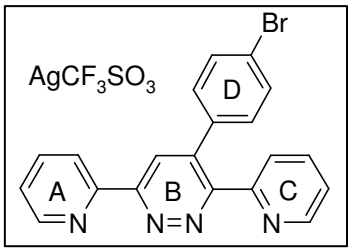
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.78 (d, J=7.5 Hz, 1H, H_{3A}), 8.72 (d, J=4.5 Hz, 1H, H_{6A}), 8.62 (s, 1H, H_{3B}), 8.44 (d, J=4.0 Hz, 1H, H_{6C}), 7.99 (d, J=8.0 Hz, 1H, H_{3C}), 7.90 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.82 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.48 (t, J=1.5 Hz, 1H, H_{2D}), 7.45 (d, J=7.5 Hz, 1H, H_{6D}), 7.40 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.28 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 7.12 (m, 2H, H_{4D+5D}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.9, 157.7, 155.2, 153.0, 149.4, 148.8, 139.1,139.0, 137.2, 136.7, 131.6, 131.3, 129.7, 127.5, 125.5, 124.8, 124.7, 123.5, 122.4, 121.8.

MS (ESI) m/z: $[L+K+DCM]^+$ 512, $[2L+Na+MeCN]^+$ 841, $[2L+K+DCM]^+$ 903.
Elem. Anal. ($C_{20}H_{13}BrN_4$) [%] calc. C 61.7, H 3.4, N 14.4, found, C 61.8, H 3.4, N 14.2.

Silver complexes

All the silver complexes were prepared by using the same procedure. One equivalent of silver tetrafluoroborate or silver trifluoromethane sulfonate was mixed with one equivalent of the diazine ligand in 15 ml of acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes.

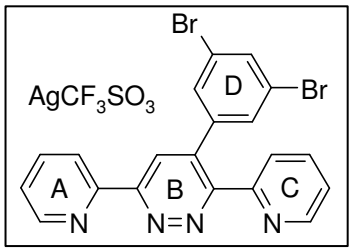
Synthesis of 4-(4-bromophenyl)-3,6-di(pyridin-2yl)pyridazine silver complex (15sc)



4-(4-Bromobenzene)-3,6-di(pyridin-2-yl)pyridazine (**15**) (30 mg, 0.08 mmol) and silver trifluoromethanesulfonate (21 mg, 0.08 mmol) were used to prepare the silver complex (46 mg, 0.07 mmol, 88%, $C_{20}H_{13}BrN_4AgCF_3SO_3$).

^{1}H NMR (CD_3CN, 500 MHz) δ/ppm: 8.75 (d, J=5.0 Hz, 1H, H_{6A}), 8.72 (d, J=5.0 Hz, 1H, H_{6C}), 8.32 (s, 1H, H_{3B}), 8.23 (dt, J=8.2, 0.9 Hz, 1H, H_{3C}), 8.04 (td, J=7.8, 1.6 Hz, 1H, H_{4C}), 7.65 (m, 2H, H_{5C+4A}), 7.53 (d, J=8.8 Hz, 2H, H_{2D+6D}), 7.47 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.14 (d, J=7.8 Hz, 1H, H_{3A}), 7.03 (d, J=8.5 Hz, 2H, H_{3D+5D}).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.4, 155.1, 152.2, 150.8, 149.6, 140.3, 138.9, 137.6, 134.1, 131.7, 131.1, 127.6, 126.6, 126.2, 125.2, 123.7, 123.3, 117.9, 1.1, 2 carbon signals unresolved.
MS (ES) *m/z* $[Ag+L+MeCN]^+$ 538, $[2Ag+L+CF_3SO_3]^+$ 753, $[Ag+2L]^+$ 887.
Elem. Anal. ($C_{20}H_{13}BrN_4AgBF_4$ + CH_3CN) [%] calc. C 42.3, H 2.6, N 11.2, found, C 43.4, H 2.7, N 10.0.

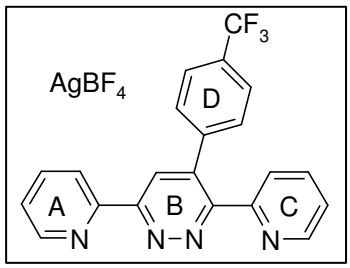
Synthesis of 4-(3,5-dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (18sc)



4-(3,5-Dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**18**) (60 mg, 0.13 mmol) and silver trifluoromethane sulfonate (25 mg, 0.13 mmol) were used to prepare the silver complex (72 mg, 0.11 mmol, 85%, $C_{20}H_{12}Br_2N_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.91 (d, J=4.0 Hz, 1H, H_{6A}), 8.79 (s, 1H, H_{3B}), 8.74 (d, J=4.4 Hz, 1H, H_{6C}), 8.63 (d, J=8.0 Hz, 1H, H_{3A}), 8.20 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.96 (m, 2H, H_{4C+4D}), 7.79 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.60 (m, 2H, H_{5C+3C}), 7.49 (d, J=1.6 Hz, 2H, H_{2D+6D}).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.5, 155.3, 152.3, 150.8, 150.4, 149.7, 139.0, 138.9, 138.3, 137.7, 133.9, 130.9, 127.7, 126.6, 126.1, 125.1, 123.6, 122.4, 2 carbon signals unresolved.
MS (ES) *m/z* $[Ag+L]^+$ 575, $[Ag+2L]^+$ 1048.
Elem. Anal. ($C_{20}H_{12}Br_2N_4AgBF_4$) [%] calc. C 35.3, H 2.1, N 8.2, found, C 35.6, H 2.1, N 8.3.

Synthesis of 3,6-di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine silver complex (20sc)



3,6-Di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine (**20**) (40 mg, 0.11 mmol) and silver tetrafluoroborate (20 mg, 0.11 mmol) were used to prepare the silver complex (46 mg, 0.08 mmol, 73%, $C_{21}H_{13}F_3N_4AgBF_4$).

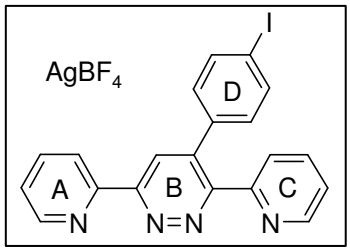
^{1}H NMR (DMSO, 500 MHz) δ/ppm: 8.81 (d, J=3.6 Hz, 1H, H_{6A}), 8.68 (d, J=7.8 Hz, 1H, H_{3A}), 8.58 (s, 1H, H_{3B}), 8.38 (d, J=4.0 Hz, 1H, H_{6C}), 8.10 (td, J=6.0, 1.6 Hz, 1H, H_{4A}), 8.05 (d, J=7.4 Hz, 1H, H_{3C}), 8.01 (td, J=6.0, 1.6 Hz, 1H, H_{4C}), 7.72 (d, J=6.4 Hz,

1H, H_{2D+6D}), 7.62 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.52 (d, J=6.4 Hz, 2H, H_{3D+5D}), 7.43 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}).

^{13}C NMR (DMSO, 125 MHz) δ/ppm: 157.9, 157.3, 154.7, 152.3, 149.8, 148.6, 141.1, 138.5, 137.7, 137.1, 129.5, 128.7, 128.4, 125.4, 125.3, 125.2, 125.1, 124.8, 124.0, 122.9, 121.2.

MS (ES) *m/z* $[L]^+$ 378, $[Ag+L]^+$ 487, $[2Ag+L]^+$ 595.

Synthesis of 4-(4-iodophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (24sc)



4-(4-Iodophenyl)-3,6-di(pyridin-2-yl)pyridazine (**24**) (90 mg, 0.21 mmol) and silver tetrafluoroborate (39 mg, 0.21 mmol) were used to prepare the silver complex (0.12 g, 0.19 mmol, 90%, $C_{20}H_{13}IN_4AgBF_4$).

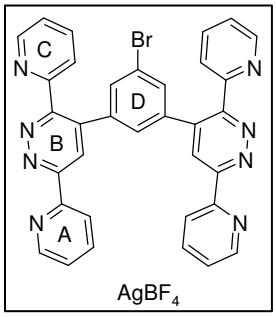
^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.91 (d, J=4.0 Hz, 1H, H_{6A}), 8.81 (d, J=4.4 Hz, 1H, H_{6C}), 8.68 (s, 1H, H_{3B}), 8.58 (d, J=8.4 Hz, 1H, H_{3A}), 8.17 (td, J=7.8, 1.6 Hz, 1H, H_{4A}), 7.88 (td, J=7.8, 1.6 Hz, 1H, H_{4C}), 7.79 (m, 3H, $H_{5A+3D+5D}$), 7.62 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.38 (d, J=8.0 Hz, 1H, H_{3C}), 7.01 (d, J=8.0 Hz, 2H, H_{2D+6D}).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.5, 155.2, 152.3, 150.8, 150.7, 149.6, 140.4, 138.9, 137.7, 137.5, 134.4, 131.0, 127.5, 126.6, 126.2, 125.2, 123.7, 98.83, 2 carbon signals unresolved.

MS (ES) *m/z* $[L]^+$ 436, $[Ag+L+MeCN]^+$ 585, $[Ag+2L+2MeCN-I]^+$ 935, $[Ag+2L]^+$ 980.

Elem. Anal. ($C_{20}H_{13}IN_4AgBF_4$) [%] calc. C 38.1, H 2.1, N 8.9, found, C 38.0, H 2.2, N 8.8.

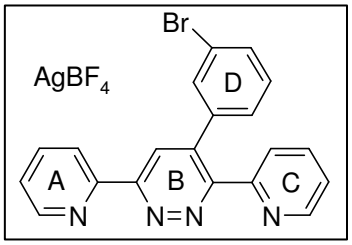
Synthesis of 4,4'-(5-bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) silver complex (26sc)



4,4'-(5-Bromo-1,3-phenyl)bis(3,6-di(pyridin-2-yl)pyridazine) (**26**) (35 mg, 0.06 mmol) and silver tetrafluoroborate (22 mg, 0.12 mmol) were used to prepare the silver complex (84 mg, 0.08 mmol, 67%, $C_{34}H_{21}BrN_8Ag_2B_2F_8$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.88 (d, J=4.0 Hz, 2H, H_{6A}), 8.65 (d, J=4.4 Hz, 2H, H_{6C}), 8.61 (d, J=8.0 Hz, 2H, H_{3A}), 8.47 (s, 2H, H_{3B}), 8.15 (td, J=7.6, 1.6 Hz, 2H, H_{4A}), 8.01 (td, J=7.6, 1.6 Hz, 2H, H_{4C}), 7.70 (m, 4H, H_{5A+3C}), 7.58 (dd, J=7.6, 5.2 Hz, 2H, H_{5C}), 7.47 (d, J=1.6 Hz, 2H, H_{2D+6D}), 7.36 (s, 1H, H_{4D}).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 167.3, 162.5, 157.6, 156.3, 153.2, 150.8, 149.7, 138.5, 138.4, 138.2, 137.4, 131.8, 126.4, 126.1, 125.5, 122.5, 115.4.
Elem. Anal. ($C_{34}H_{21}BrN_8Ag_2B_2F_8$ + H_2O) [%] calc. C 39.7, H 2.3, N 10.9, found, C 40.0, H 2.5, N 10.9.

Synthesis of 4-(3-bromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (28sc)



4-(3-Bromophenyl)-3,6-di(pyridin-2-yl)pyridazine (**28**) (70 mg, 0.18 mmol) and silver tetrafluoroborate (35 mg, 0.18 mmol) were used to prepare the silver complex (77 mg, 0.13 mmol, 72%, $C_{20}H_{13}BrN_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.92 (d, J=4.4 Hz, 1H, H_{6A}), 8.82 (d, J=4.4 Hz, 1H, H_{6C}), 8.77 (s, 1H, H_{3B}), 8.62 (d, J=8.4 Hz, 1H, H_{3A}), 8.19 (td, J=7.6, 1.6 Hz, 1H, H_{4A}), 7.87 (td, J=7.6, 1.2 Hz, 1H, H_{4C}), 7.80 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.63 (m, 3H,

$H_{5C+4D+6D}$), 7.38 (d, J=8.0 Hz, 1H, H_{2D}), 7.31 (t, J=8.0 Hz, 1H, H_{5D}), 7.10 (d, J=8.4 Hz,1H, H_{3C}).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.5, 155.0, 152.1, 150.9, 150.8, 149.4, 139.9, 137.7, 132.2, 131.7, 130.6, 128.2, 128.0, 126.8, 125.3, 123.9, 122.0, 3 carbon signals unresolved.

MS (ES) *m/z* $[Ag+L]^+$ 497, $[Ag+2L]^+$ 885, $[2Ag+2L+2MeCN]^+$ 1081.

Elem. Anal. ($C_{20}H_{13}BrN_4AgBF_4$) [%] calc. C 41.1, H 2.2, N 9.6, found, C 41.2, H 2.3, N 9.6.

IV.7 Bibliography

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CHAPTER V

Diverse pyridazines

CHAPTER V

DIVERSE PYRIDAZINES

V.1 Introduction

In this chapter, we focused on the effect of different substituents. We did not focus our interest on a general chemical family as we did in the two previous chapters. We used electron withdrawing or donating groups such as methoxy[1], cyano[2], methyl[3,4] or ^{t}butyl[5,6]-substituted phenyl substituents. We tried to find out the relationship between the substituent and the adopted structure by each silver complex. The different substituents introduced in this chapter have also been used by different research groups to prepare substituted terpyridine[7,8] or bipyridine[9, 10] metal complexes.

To prepare these different ligands, we used methoxy, acetophenone, cyano, methyl, dimethoxy, ^{t}butyl-substituted phenyl acetylenes and trimethylsilylacetylene. We reacted all the ethynyl precursors with 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) to give the target ligands.

This chapter presents the synthesis and characterisation of all the ethynyl precursors (**29**, **31**, **33**, **35**, **38** and **41** shown in Figure 5.1) used to prepare the N-donor ligands (**30**, **32**, **34**, **36**, **39**, **42**, **43** and **44** shown in Figure 5.2). They have all been characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.
We then synthesised and characterised all the silver complexes (**30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**).

So, we will talk about the synthesis of the ethynyl precursors, the desired ligands and finally about the silver complexes.

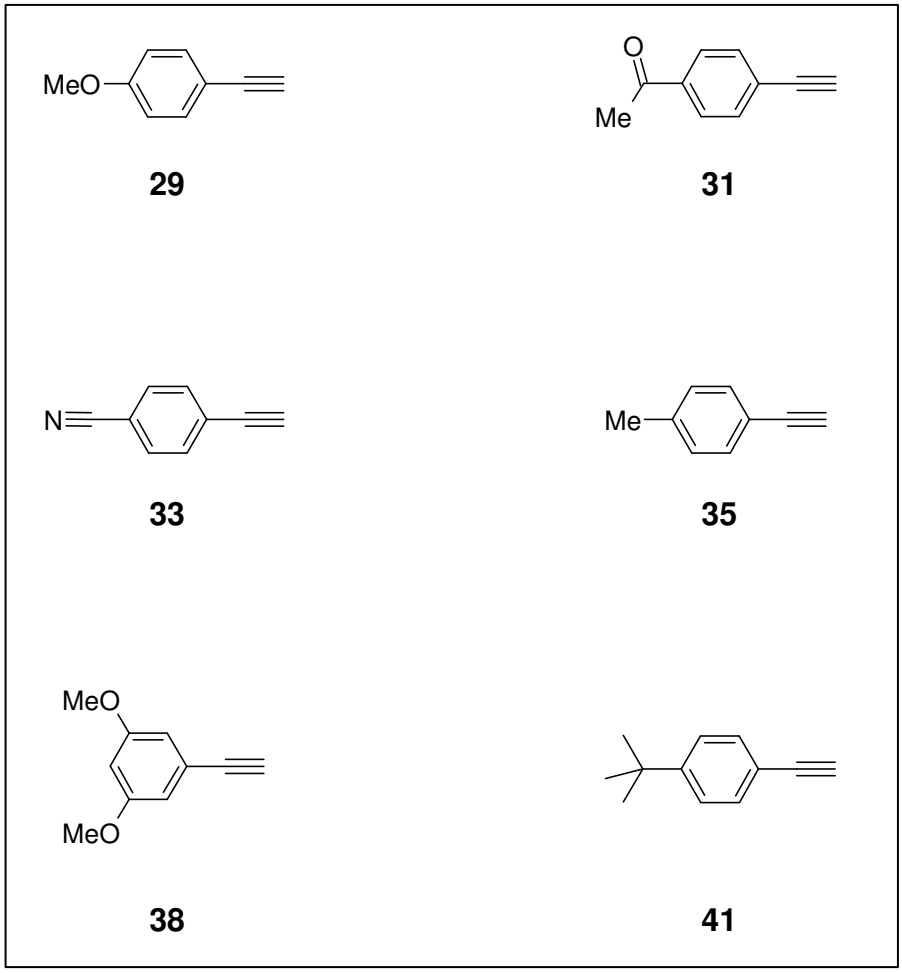


Figure 5.1: Ethynyl precursors described in this chapter.

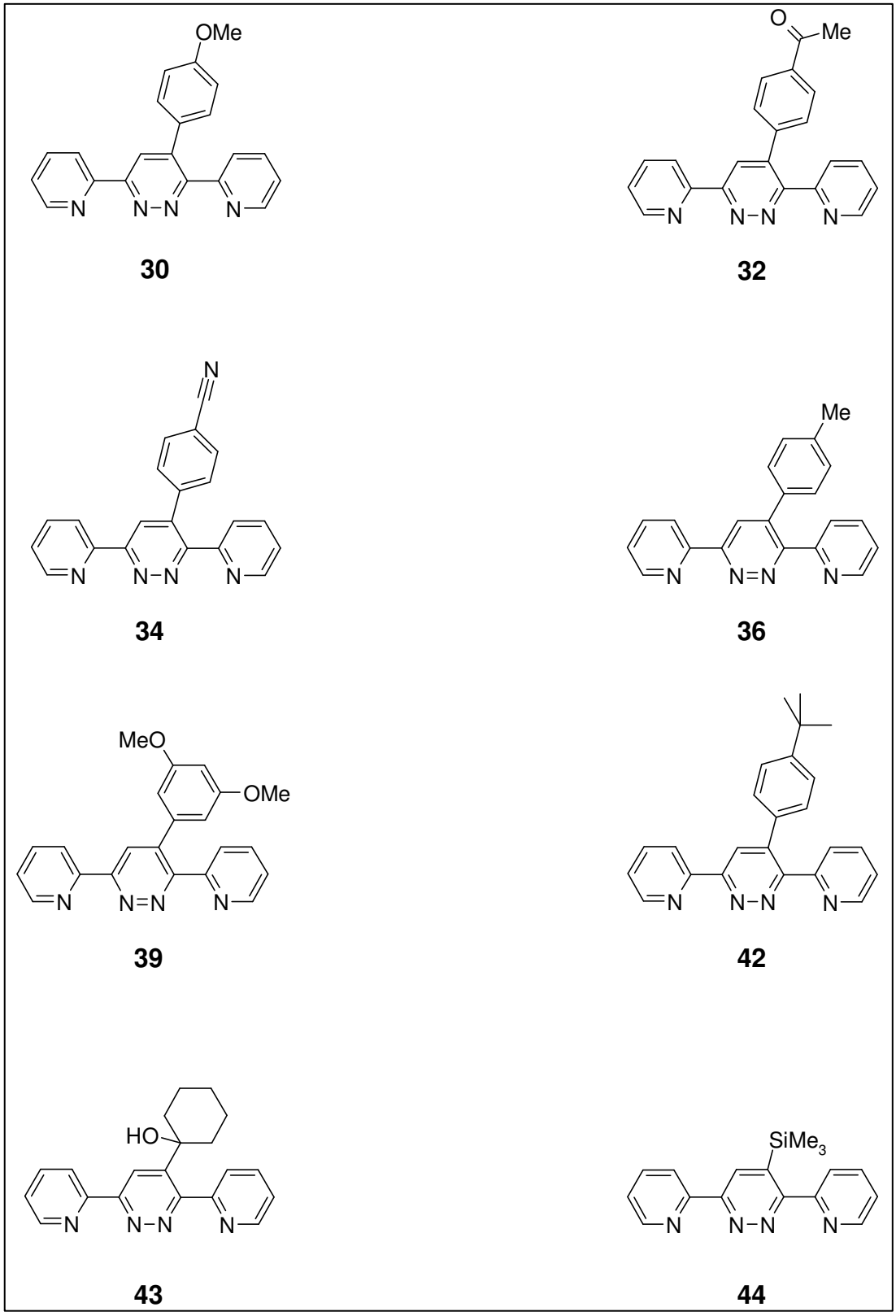


Figure 5.2: Diverse pyridazine ligands presented in this chapter.

V.2 Synthesis of the ethynyl precursors

V.2.1 Synthetic method

We prepared all these ethynyl compounds using the Sonogashira[11] reaction. We followed the procedure introduced in chapter II. The starting compounds of this reaction are halogenated molecules. The halogenated compounds were mixed with trimethylsilylacetylene, copper(I) chloride and bis(triphenylphosphine)palladium dichloride in triethylamine. The solution was refluxed under nitrogen to give the protected ethynyl precursor. The intermediate compound was purified by chromatographic work-up and then dissolved in tetrahydrofuran and an aqueous solution of 1M sodium hydroxide was added. The target molecule was extracted and purified by chromatographic work up over alumina.

Compounds **29**, **31**, **33** and **35** were prepared with commercial iodo or bromo precursors. They were directly accessible with the procedure described above. The synthetic method to prepare compounds **29**, **31**, **33** and **35** is shown in Figure 5.3.

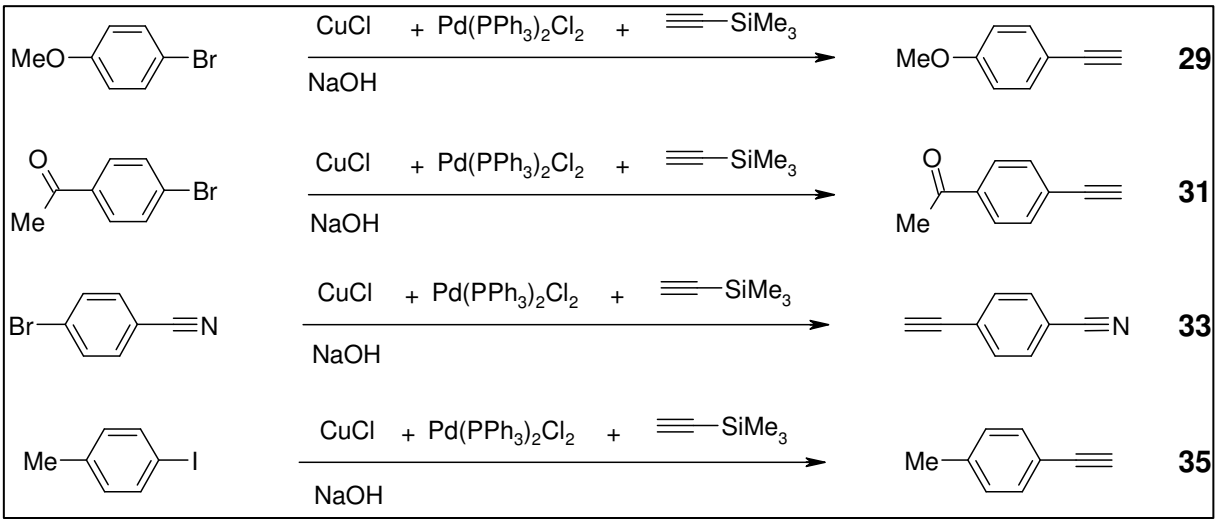


Figure 5.3: Synthetic method for the synthesis of compounds **29**, **31**, **33** and **35**.

Figure 5.4 shows the multiple step synthesis for the preparation of compounds **38** and **41**.

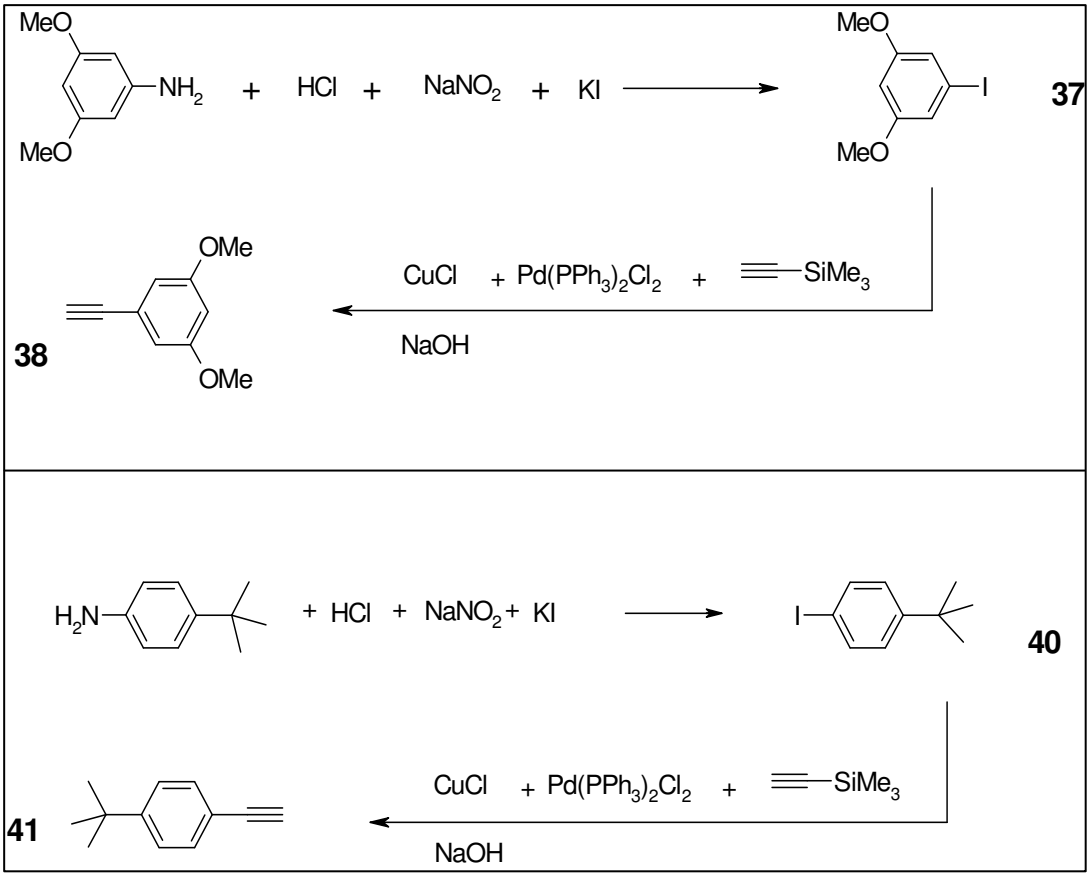


Figure 5.4: Multiple step synthesis for the preparation of compounds **38** and **41**.

The preparation of compound **38** needs 1-iodo-3,5-dimethoxybenzene (**37**) as an intermediate. We synthesised **37** starting from 3,5-dimethoxyaniline that was mixed with $NaNO_2$, hydrochloridric acid and potassium iodide. 1-Iodo-3,5-Dimethoxybenzene (**37**) was purified by chromatographic work-up over alumina and used in the Sonogashira[11] reaction to obtain 1-ethynyl-3,5-dimethoxybenzene (**38**). We repeated the same procedure to prepare 1-tert-butyl-4-ethynylbenzene (**41**). In that case the synthesized intermediate is 1-tert-butyl-4-iodobenzene (**40**).

Figure 5.5 shows the halogenated compounds (bought or prepared) used to prepare the ethynyl compounds.

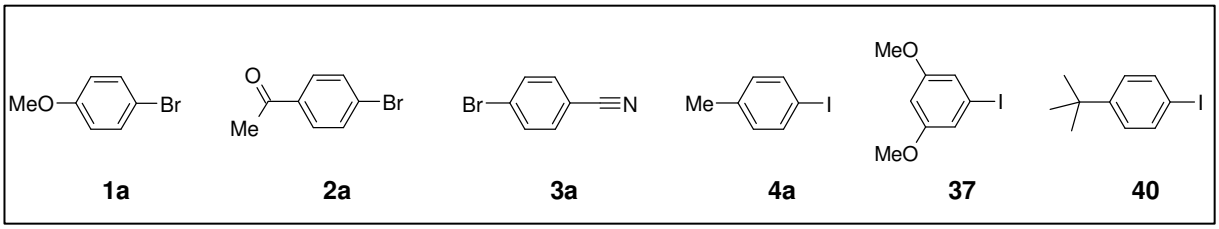


Figure 5.5: Compounds used to prepare the ethynyl compounds.

For each ethynyl precursor presented here, the reactant ratio, time and yield are listed in the Table 5.1. Purification methods and synthetic details are discussed in the experimental section at the end of this chapter.

Precursor	**Halogenated compound**	**Reaction ratio** (halogenated / tms acetylene)	**Reaction temperature** (°C)	**Reaction time** (hr)	**Yield** (%)
29	**1a**	1.1/1	60	14	57
31	**2a**	1/1.5	60	14	76
33	**3a**	1/1.7	65	14	91
35	**4a**	1/1.4	60	4	39
38	**37**	1/1.6	60	18	76
41	**40**	1/1.7	60	18	27

Table 5.1: Reaction conditions for the synthesis of the ethynyl precursors **29**, **31**, **33**, **35**, **38** and **41**.

Compounds **29**, **31**, **33**, **35**, **38** and **41** were obtained, after purification, in relatively good yields and could be used for the synthesis of the pyridazine ligands.

V.2.2 Characterisation of the ethynyl precursors

All the ethynyl precursors have been characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. Compounds **29**, **31**, **33** and **38** were characterized by mass spectrometry.

The general procedure and characterization of intermediates **37** and **40** are discussed at the end of this chapter in the experimental section.

^{1}H NMR spectroscopy

We first focused our interest in the ^{1}H NMR spectroscopic characterisation. The halogenated phenylethynyl compounds synthesized in this chapter should have the characteristic ethynyl signal and the phenyl signals[12]. It was also important to see the absence of the $SiMe_3$ signals. This would show that the deprotection had been carried out successfully. Table 5.2 summarises ^{1}H NMR signals of the precursors.

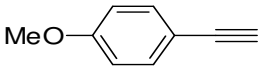
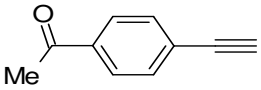
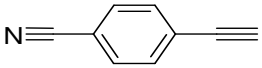
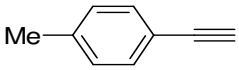
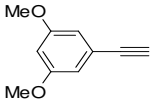
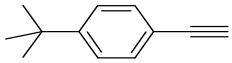
	Ethynyl precursor	Phenyl signals (δ/ppm)	Ethynyl signals (δ/ppm)	Other signals (δ/ppm)
	**29**	744-8.65(d-d)	3.01 (s)	3.81 (s)
	**31**	7.89-7.55 (d-d)	3.24 (s)	2.47 (s)
	**33**	7.61-7.56 (d-d)	3.32 (s)	°
	**35**	7.45-7.16 (d-d)	3.09 (s)	2.39 (s)
	**38**	6.65-6.47 (d-t)	3.04 (s)	3.78 (s)
	**41**	7.45-7.36 (d-d)	3.04 (s)	1.33 (s)

Table 5.2: ^{1}H NMR characterisation of the precursors **29**, **31**, **33**, **35**, **38** and **41**.

The ^{1}H NMR spectrum of each ethynyl precursor could be assigned by the chemical shifts and the relative integrals. As expected[12], the different phenyl signals are at around δ 7.5, 7.6 ppm and the ethynyl signals are near to δ 3.1 ppm. There is only one exception.

The ^{1}H NMR spectra of all but one of the ethynyl compounds show two doublets in the aromatic region. Each signal integrates for two protons. There is also one singlet for the ethynyl group signal. The ^{1}H NMR spectrum of ethynyl precursor **38** presents a triplet and a doublet for the phenyl protons and one singlet for the ethynyl signal.

Compounds **29**, **31**, **35** and **38** present an additional signal corresponding to the methoxy or methyl group. In each case, this ^{1}H NMR signal is a singlet with an integral corresponding to three protons. Compound **38** has two methoxy groups and this additional ^{1}H NMR signal integrates for six protons. The ^{t}butyl group of 1-tert-butyl-4-ethynylbenzene (**41**) has a ^{1}H NMR signal integrating for nine protons (δ/ppm 1.33).

In every ethynyl precursors synthesised in this chapter, there is no $SiMe_3$ signal in the ^1H NMR spectrum. Figure 5.6 presents the ^1H NMR spectra of the ethynyl precursors **31** and **33**.

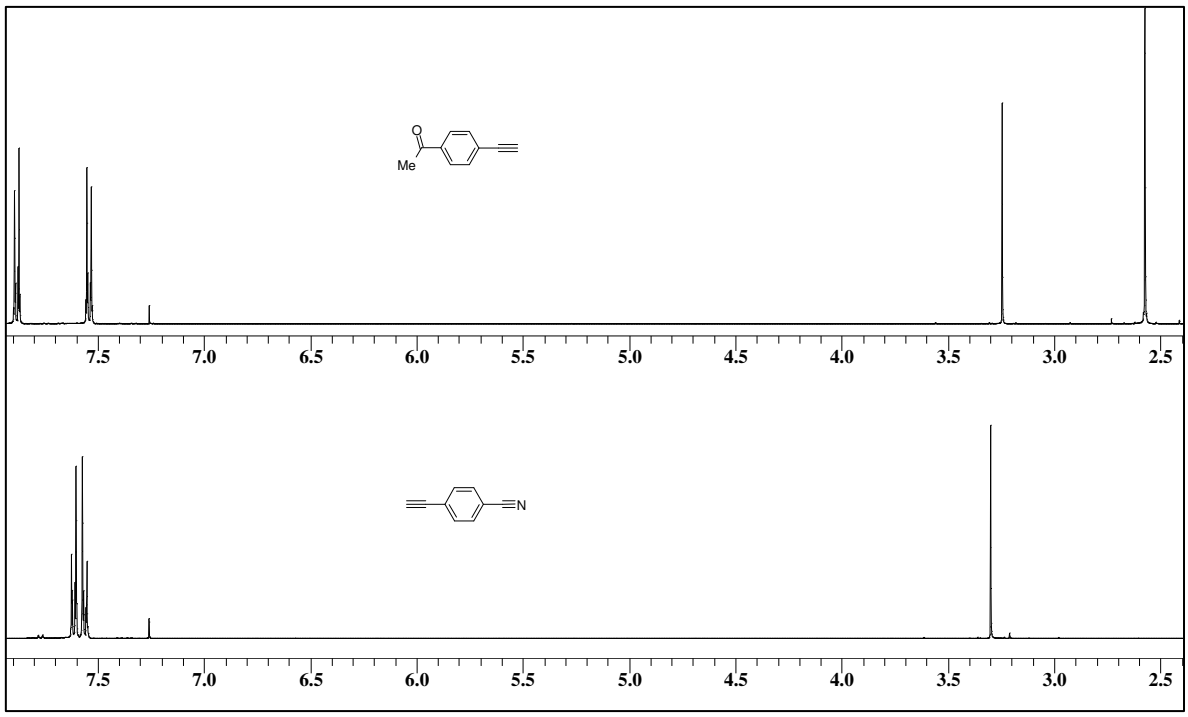


Figure 5.6: ^1H NMR spectra of the ethynyl precursors **31** and **33**.

Mass spectrometric characterisation

We were only able to obtain mass spectra for 1-ethynyl-4-methoxybenzene (**29**), 1-(4-ethynylphenyl)ethanone (**31**), 4-ethynylbenzonitrile (**33**) and 1-ethynyl-3,5-dimethoxybenzene (**38**). Compound **29** was characterised with the MALDI technique and its mass spectrum shows two peaks corresponding to $[L]^+$ and $[L+K]^+$. The three other compounds were characterised with the electrospray technique. They all present the $[L]^+$ peak. Ethynyl precursor **29** shows two other peaks corresponding to $[L\text{-}COMe]^+$ and $[L\text{-}Me]^+$. Compound **38** shows two other peaks. One corresponds to the loss of two methoxy groups and the second to the loss of one methoxy group.
Table 5.3 summarises the different mass peaks detected for **29**, **31**, **33** and **38**.

Ligand	29		31		33		38	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
[L]$^+$	132	132	144	144	127	127	162	162
[L-C0Me]$^+$	°	°	100	101	°	°	°	°
[L-Me]$^+$	°	°	129	129	°	°	°	°
[L+K]$^+$	170	171	°	°	°	°	°	°
[L-2OMe]$^+$	°	°	°	°	°	°	101	102
[L-OMe]$^+$	°	°	°	°	°	°	133	133

Table 5.3: Calculated and detected m/z values for **29**, **31**, **33** and **38**.

All m/z are perfectly consistent with the calculated mass. Two examples of mass spectra are presented in Figure 5.7.

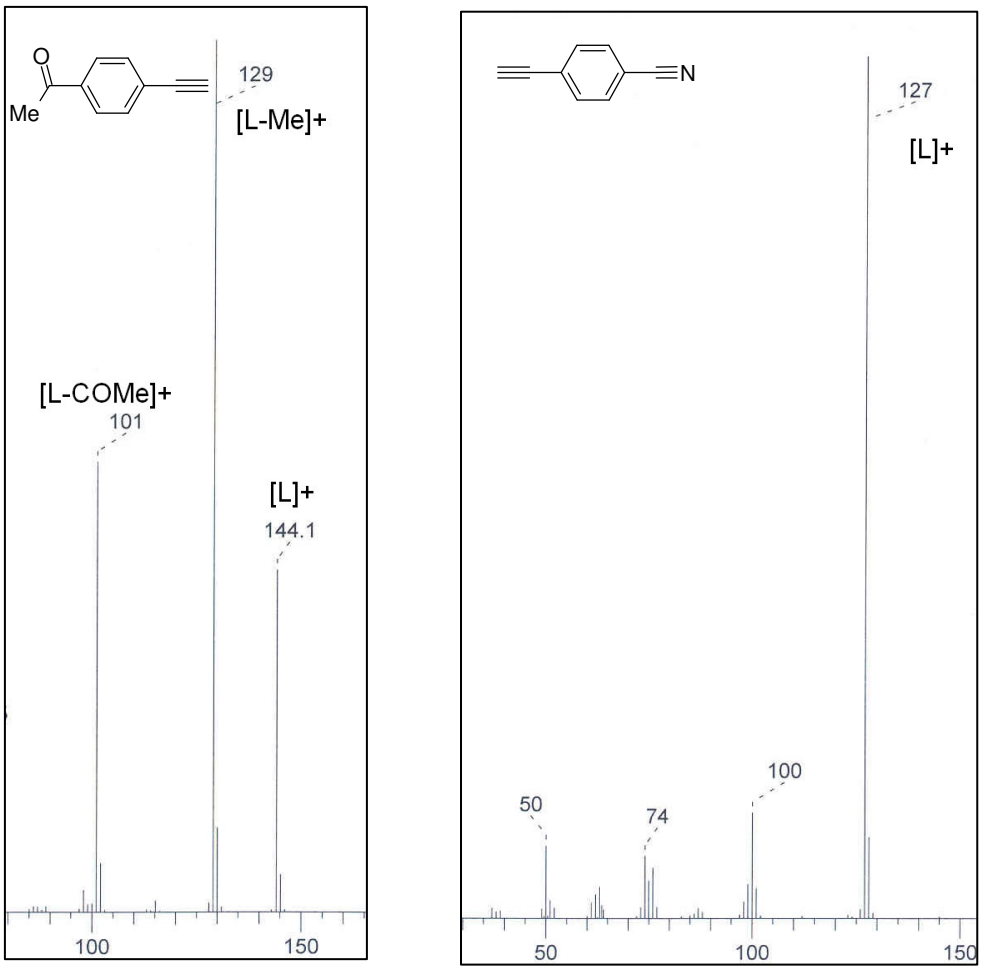


Figure 5.7: Mass spectra of the ethynyl precursors **31** and **33**.

V.3 Synthesis of diverse substituted pyridazine

V.3.1 Synthetic method

This part of the chapter introduces the synthesis and the characterisation of eight new substituted pyridazine ligands. The synthesised compounds are 4-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**30**), 1-(4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)phenyl)ethanone (**32**), 4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzonitrile (**34**), 3,6-di(pyridin-2-yl)-4-tolylpyridazine (**36**), 4-(3,5-dimethoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**39**), 4-(4-tert-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**42**), 1-(3,6-di(pyridin-2-yl)pyridazin-4-yl)cyclohexan-1-ol (**43**) and 3,6-di(pyridin-2-yl)-4-(trimethylsilyl)pyridazine (**44**).

The synthesis of these new N-donor ligands follows the procedure presented in chapter II. They were obtained via an inverse electron demand Diels Alder reaction[13] between 1,2,4,5-tetrazine and the ethynyl precursors presented in the first part of this chapter. To carry out these reactions, we used 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) dissolved in toluene with the ethynyl precursor. This mixture was then placed under reflux. All the compounds presented in this part of the chapter were prepared with this method. Reactant ratio, time, solvent and yields are listed in the table 5.4.

Ligand	**Reaction ratio** (tetrazine / ethynyl)	**Reaction temperature** (°C)	**Solvent**	**Reaction time**	**Yield** (%)
30	1 to 1	120	toluene	70 hours	70
32	1 to 1	120	toluene	72 hours	75
34	1 to 1.1	120	toluene	6 days	88
36	1 to 1	120	toluene	6 days	91
39	1 to 1	120	toluene	7 days	88
42	1 to 1.4	120	toluene	42 hours	87
43	1 to 1.2	120	toluene	15 days	71
44	1 to 1.3	120	toluene	60 hours	50

Table 5.4: Reaction conditions for the synthesis of the ligands **30**, **32**, **34**, **36**, **39**, **42**, **43** and **44**.

The reaction times are long and range between 42 and 72 hours to 6 days to 15 days. We always followed the progress of the reactions by TLC plates and judged whether the reaction was completed by the disappearance of the purple colour. These long reaction times are not really an advantage, but all the retro Diels-Alder reactions ended up with good yields. All the ligands introduced in this chapter were purified by chromatographic work-up.

V.3.2 Characterisation of the halogenated pyridazines

All the compounds were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analyses.

^{1}H NMR spectroscopy

^{1}H NMR spectroscopy of ligands **30**, **32**, **34**, **36**, **39**, **42**, **43** and **44** were run in deuterated chloroform. The spectra could be assigned by the chemical shifts, relatives integrals and the coupling patterns.

The ^{1}H NMR spectra of the compounds **30** and **32** and the assignments are shown in Figure 5.8.

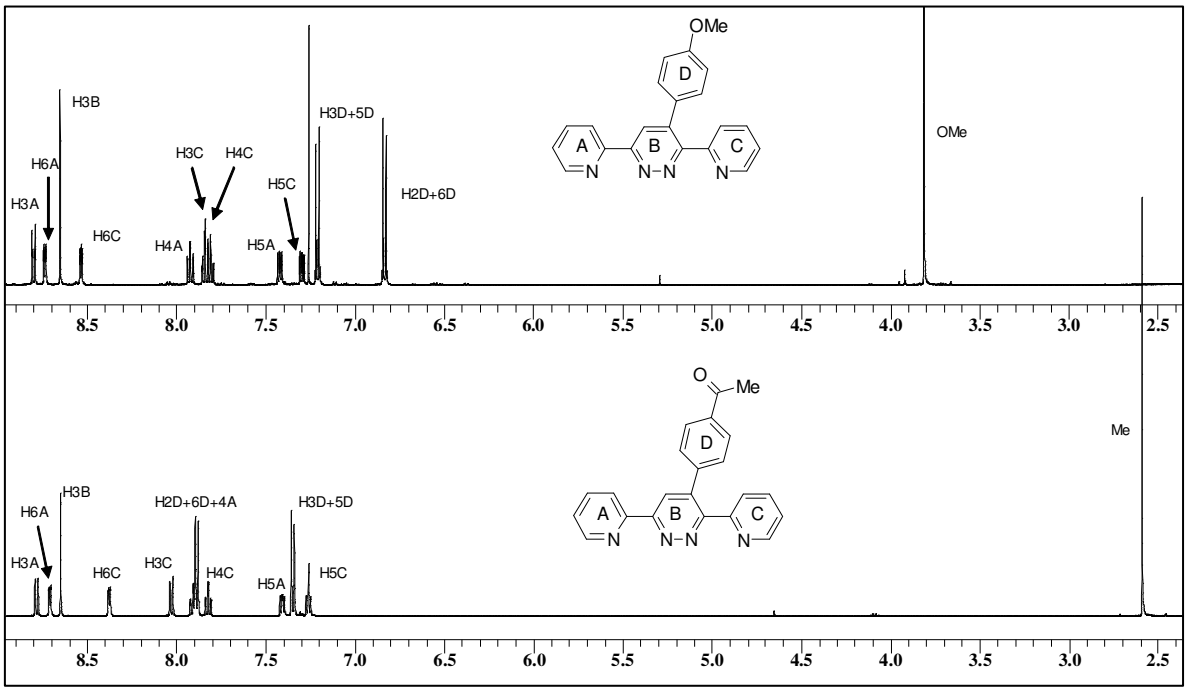


Figure 5.8: The ^{1}H NMR spectra and assignments of ligands **30** and **32**.

The ^{1}H NMR spectra of the compounds **34** and **36** and the assignments are shown in Figure 5.9, and compounds **39** and **42** in Figure 5.10.

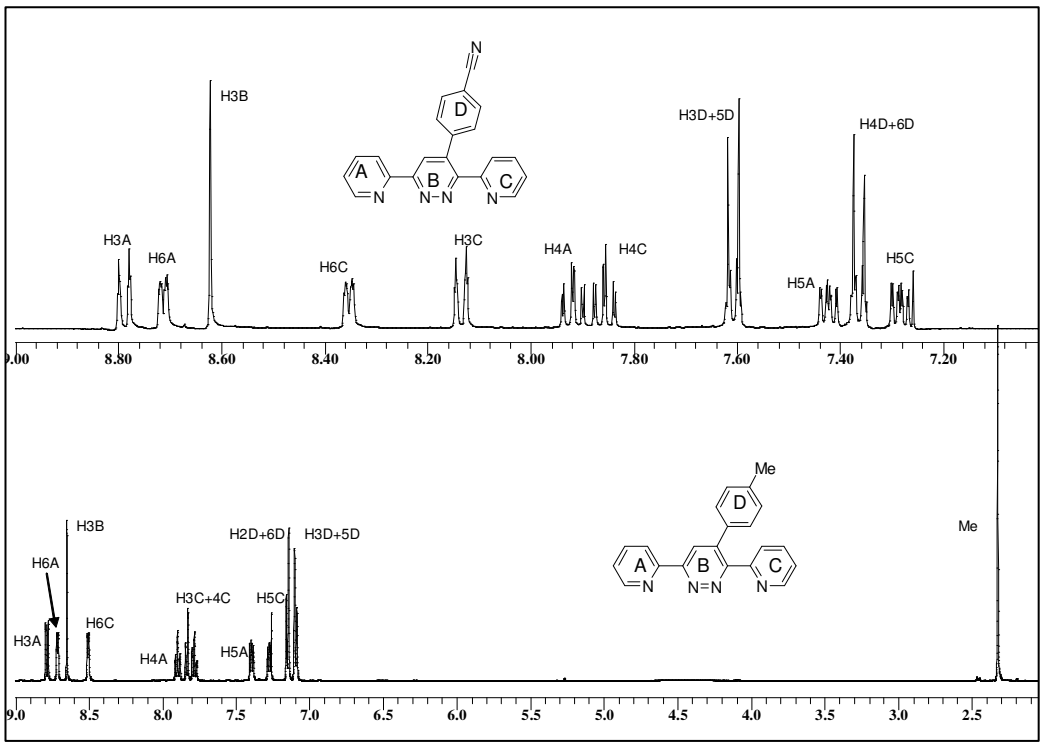


Figure 5.9: The ^{1}H NMR spectra and assignments of ligands **34** and **36**.

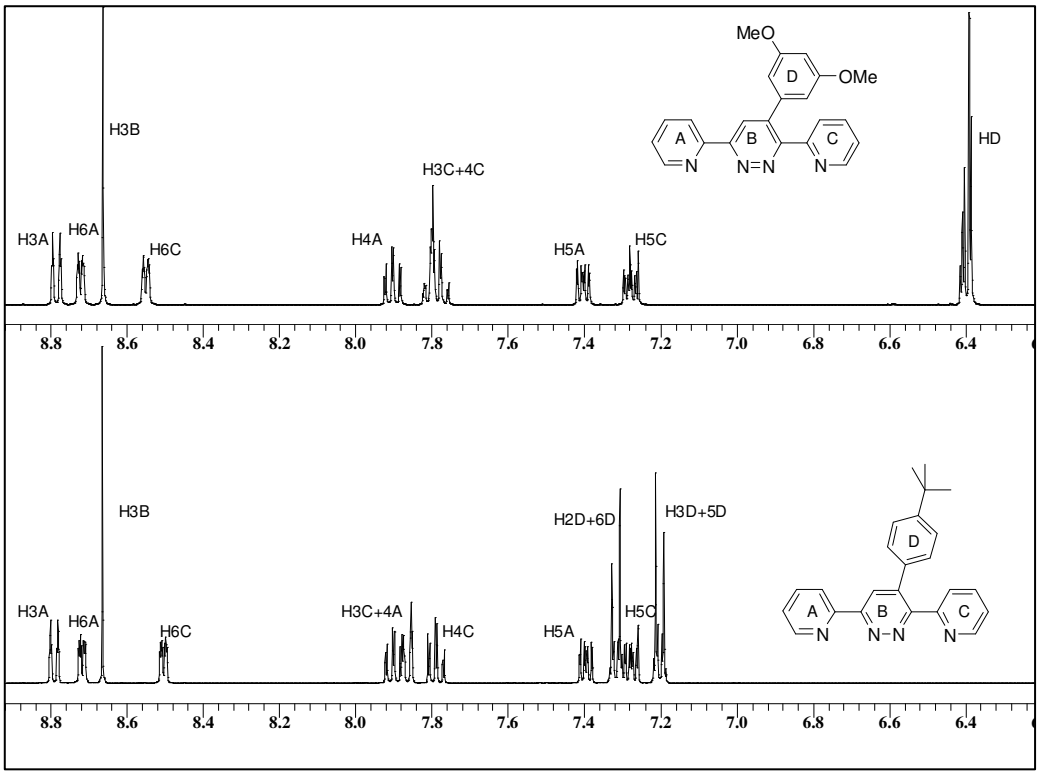


Figure 5.10: The ^{1}H NMR spectra and assignments of ligands **39** and **42** without the substituent signals (methoxy and tert-butyl).

The ^{1}H NMR spectra of the compounds **43** and **44** and the assignments are shown in Figure 5.11.

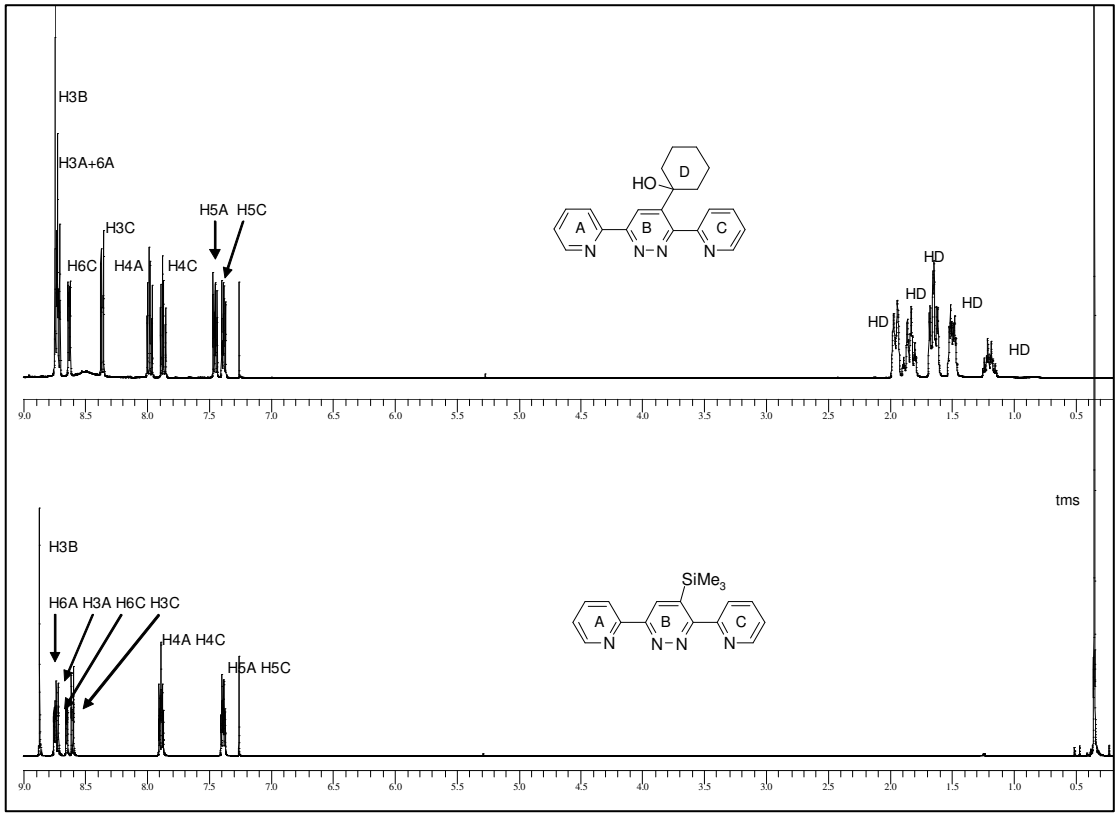


Figure 5.11: The ^{1}H NMR spectra and assignments of ligands **43** and **44**.

The ^{1}H NMR spectra of ligands **30**, **32**, **34**, **36**, **39**, **42**, **43** and **44** present well defined and sharp signals. As for the non symmetrical compounds shown in chapter III and IV, the spectra present a set of nine NMR signals. Each ^{1}H NMR spectrum shows four doublets (H_{3A}, H_{3C}, H_{6A}, H_{6C}), two triplets of doublets (H_{4A}, H_{4C}), two doublets of doublets (H_{5A}, H_{5C}) and the typical singlet (H_{3B})[14]. These signals are in the same ^{1}H NMR region between δ 7 and 9 ppm.

The ligands have different substituents. Compounds **30**, **32**, **34**, **36**, **39** and **42** each contains phenyl group, substituted in the 3,5- or 4-positions. The proton signals of the phenyl group are two doublets (**30**, **32**, **34**, **36** and **42**) or a triplet and a doublet (**39**). Compound **43** has a cyclohexanol as a substituent and the proton signals of that group are composed of five signals in the ^{1}H NMR region between δ 1 and δ 2 ppm. The last ligand (**44**) has a trimethylsilyl substituent and the proton signal of that group is a singlet placed at δ 0.3 ppm.

The ^{1}H NMR spectra of compounds **30**, **32**, **34**, **36**, **39** and **42** show four doublets (H_{3A}, H_{3C}, H_{6A}, H_{6C}), two triplets of doublets (H_{4A}, H_{4C}), two doublets of doublets (H_{5A}, H_{5C}) and a singlet (H_{3B}).

The ^{1}H NMR spectrum of compounds **30** shows well defined signals and no overlapping signals. The ^{1}H NMR signal of the methoxy group is a singlet integrating for three protons (δ 3.8 ppm). The ^{1}H NMR spectrum of compounds **32** shows nine well defined and separated signals. The ^{1}H NMR signal of the phenyl's substituent is a singlet integrating for three protons. The ^{1}H NMR spectrum of compounds **34** shows also nine well defined and separated signals. The ^{1}H NMR spectrum of compounds **36** shows all the expected signals[14]. In that compound, the signals of protons H_{3C} and H_{4C} overlap. The ^{1}H NMR signal of the phenyl's substituent is a singlet integrating for three protons (methyl group).

The ^{1}H NMR spectrum of compounds **39** shows all the expected signals[14]. In this compound, the signals of protons H_{3C} and H_{4C} overlap. The ^{1}H NMR signal of the phenyl's substituent is a singlet integrating for six protons (two methyl groups).

Similar case is also present in the ^{1}H NMR spectrum of **42**. In this ligand, the signals of protons H_{3C} and H_{4A} overlap. The ^{1}H NMR signal of the ^{t}butyl group is a singlet and is integrating for nine protons (δ 1.30 ppm).

The two last ligands have a different substituent (not phenyl group). The ^{1}H NMR spectra show all the proton signals. For these two compounds the ^{1}H NMR signal of the proton H_{3B} is shifted to the low field, in regard of the six other ligands. This is due to the cyclohexanol substituent for **43** and to the trimethylsilyl group for **44**. The ^{1}H NMR spectra also show some signals that overlap. The ^{1}H NMR signals of protons H_{3A} and H_{6A} for **43** and **44** overlap.

We can see that in the ligand containing phenyl groups, the ^{1}H NMR signals of the protons from the phenyl group do not overlap with other ^{1}H NMR signals.

All the ^{1}H NMR spectroscopic data for the ligands presented in this chapter are summarized in Table 5.5.

Ligand	Solvent	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring	Others
30 (δ/ppm)	$CDCl_3$	8.80 d	7.92 td	7.42 dd	8.74 d	8.65 s	7.85 d	7.82 td	7.30 dd	8.54 d	7.21-6.84 d	3.81 s
32 (δ/ppm)	$CDCl_3$	8.78 d	7.90 m	7.41 dd	8.71 d	8.65 s	8.02 d	7.82 td	7.27 m	8.38 d	7.90 m-7.35 d	2.59 s
34 (δ/ppm)	$CDCl_3$	8.79 d	7.92 td	7.42 dd	8.71 d	8.62 s	8.13 d	7.86 td	7.28 dd	8.35 d	7.61-7.36 d	°
36 (δ/ppm)	$CDCl_3$	8.82 d	7.95 td	7.45 dd	8.75 d	8.70 s	7.84 m	7.84 m	7.33 m	8.55 d	7.21-7.09 d	2.36 s
39 (δ/ppm)	$CDCl_3$	8.78 m	7.90 td	7.40 dd	8.71 m	8.66 s	7.80 m	7.80 m	7.28 dd	8.55 d	6.39 m	3.64 s
42 (δ/ppm)	$CDCl_3$	8.79 d	7.88 m	7.39 dd	8.72 d	8.66 s	7.88 m	7.90 td	7.91 dd	8.50 d	7.32-7.19 d	1.30 s
43 (δ/ppm)	$CDCl_3$	8.72 m	7.98 td	7.45 dd	8.72 m	8.74 s	8.36 d	7.87 td	7.38 dd	8.63 d	1.96 d-1.85 m-1.64 m-1.21 m	8.51 d
44 (δ/ppm)	$CDCl_3$	8.73 d	7.90 td	7.40 dd	8.75 d	8.87 s	8.61 d	7.88 td	7.38 dd	8.66 d	°	0.35 s

Table 5.5: The ^{1}H NMR spectroscopic data for the ligands presented in this chapter.

We can notice that for the ligands, the ^{1}H NMR spectra have similar chemical shifts for corresponding protons. As we said in chapter IV, the chemical shifts of the protons from ring A from compounds **30**, **32**, **34**, **36**, **39**, **42**, **43** and **44** are the same. This is not true for the protons from ring B and C. Their chemical shifts are approximately in the same NMR region but are not as accurately reproduced as the chemical shifts from the A ring protons in going from one compound to another. That would mean that the substituent mostly affects the protons in rings B and C, and present quite diagnostic chemical shifts for the different substituents.

Mass spectrometry

Mass spectra of ligands **32**, **34**, **36**, **39**, **42**, **43** and **44** were obtained using the electrospray technique. The mass spectrum of compound **30** was obtained using the MALDI technique. This ligand's mass spectrum shows $[L]^+$ and $[Na+L_2+MeCN]^+$ peaks. The mass spectra of compounds **32** and **34** show two peaks corresponding to $[Na+L+MeCN_2]^+$ and $[Na+L_2+MeCN]^+$. The mass spectrum of **36** shows only one peak ($[L]^+$). The other ligands mass spectra show peaks corresponding to *m/z* values

of the ligand with a solvent molecule and a sodium or potassium ion. All *m/z* values are perfectly consistent with the calculated mass values. Figure 5.12 shows the mass spectra of compounds **39** and **42**.

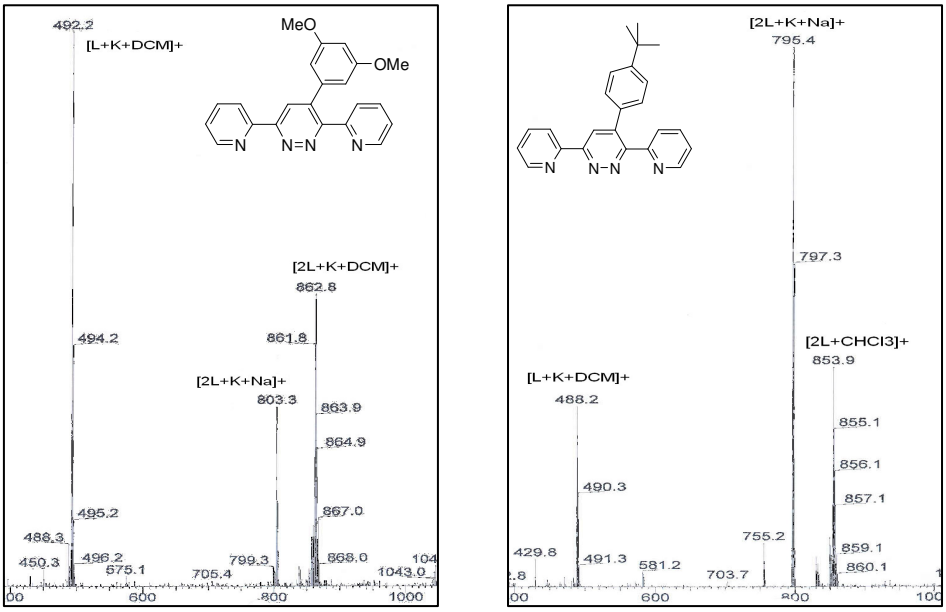


Figure 5.12: Mass spectra of the ligands **39** and **42**.

All the *m/z* (calculated and detected) values, from each ligand synthesised in this chapter, are listed in Table 5.6.

Ligand	**30**		**32**		**34**		**36**		**39**		**42**		**43**		**44**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L]^+$	340	342	◦	◦	◦	◦	324	323	◦	◦	◦	◦	◦	◦	◦	◦
$[Na+L+2MeCN]^+$	◦	◦	457	456	439	439	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦
$[Na+2L+MeCN]^+$	743	744	766	767	733	733	◦	◦	◦	◦	◦	◦	727	727	675	675
$[Na+L+MeCN]^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦
$[K+L+DCM]^+$	◦	◦	◦	◦	◦	◦	◦	◦	491	492	486	488	◦	◦	◦	◦
$[K+2L+DCM]^+$	◦	◦	◦	◦	◦	◦	◦	◦	864	863	◦	◦	◦	◦	◦	◦
$[Na+2L+K]^+$	◦	◦	◦	◦	◦	◦	◦	◦	802	803	727	727	◦	◦	◦	◦
$[L+CHCl_3]^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	454	454	◦	◦
$[2L+CHCl_3]^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	853	854	785	787	◦	◦

Table 5.6: Calculated and detected *m/z* values for the ligands**30**, **32**, **34**, **36**, **39**, **42**, **43** and **44**.

Single crystal structure of ligand **34**

A crystal of compound **34** suitable for single X-ray diffraction was grown from a chloroform solution. Details of the structure solution are given in Appendix 6. Figure 5.13 shows the molecular structure of **34**.

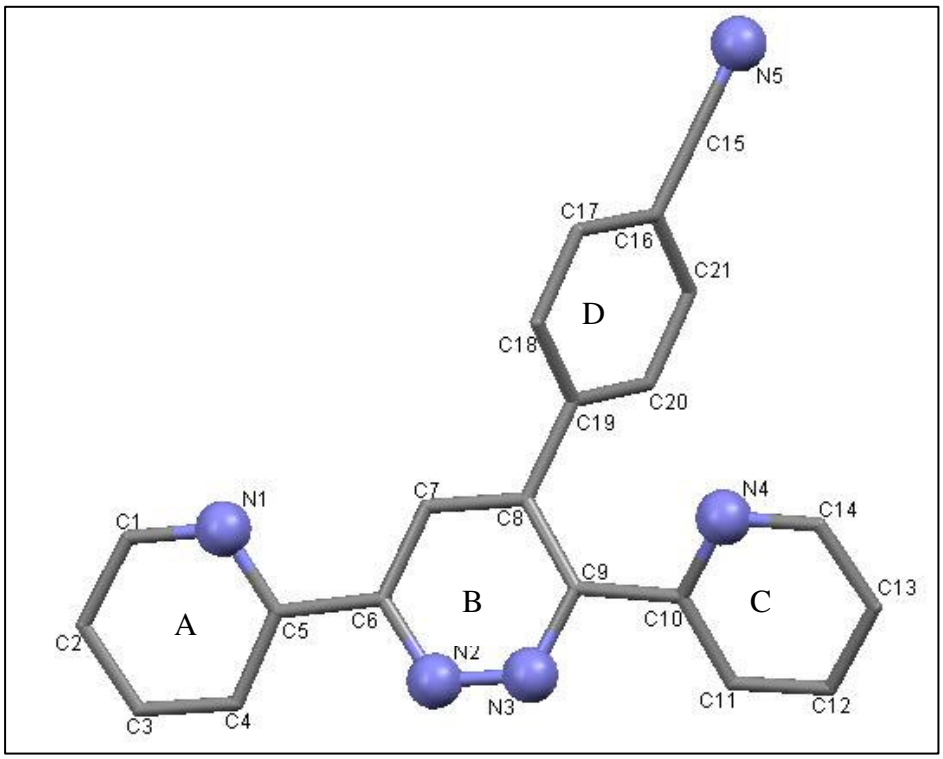


Figure 5.13: The molecular structure of ligand **34** with the atom labelling scheme.

Compound **34** shows two different torsion angles between rings A, B and C. In fact, the torsion angle between ring A and ring B is 9.66° (C7-C6-C5-N1). These two rings are almost co-planar. The torsion angle between rings B and C is 24.29° (C8-C9-C10-N4). This effect is due to the presence of the substituent (cyanophenyl ring D) that forces the twist of ring C. It is also interesting to notice that ring B and ring D are not co-planar. The torsion angle between these two rings is 54.55° (C7-C8-C19-C18). Compound **34** does not present hydrogen bonds or π-π stacking interactions with another molecule in the unit cell. The N atoms in adjacent rings are arranged in a *trans*, *trans*-conformation.

The packing shows alternating orientations that repeat through the lattice. The arrangement of **34** in the crystal shows optimal space filling and the substituent is oriented to the upper side for one molecule and to the bottom side for the other molecule. This is presented in Figure 5.14.

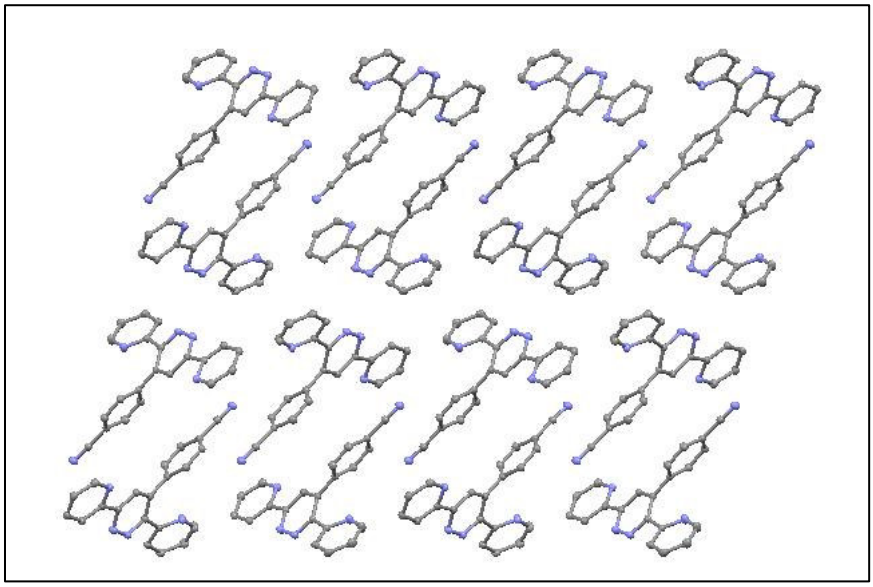


Figure 5.14: The packing diagram showing the orientation of the ligand in the crystal structure of **34**.

V.4 Synthesis of the silver complexes

V.4.1 Synthetic method

The ligands synthesised in this chapter have diverse substituents. We hoped that this diversity would lead to silver(I) complexes with differing structures. We also thought that steric factors might play a part in forcing the coordination geometry at the silver(I) centres to be non-planar. We hoped especially that sterically demanding groups like trimethylsilyl or ^{t}butylphenyl would lead to non planar silver(I)centres.

The ligands synthesised in this chapter have been used to prepare the silver complexes **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**. The reaction of the ligands with silver tetrafluoroborate in acetonitrile proceeded smoothly to give a yellow-orange solution from which the complex was obtained.

Table 5.7 summarises the experimental conditions for the synthesis of the species **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**.

Silver complex	**Reaction ratio** (ligand / silver)	**Silver salt**	**Yield** (%)
30sc	1 to 1	$AgBF_4$	81
32sc	1 to 1	$AgBF_4$	85
34sc	1 to 1	$AgBF_4$	92
36sc	1 to 1	$AgBF_4$	82
39sc	1 to 1	$AgBF_4$	75
42sc	1 to 1	$AgBF_4$	89
43sc	1 to 1	$AgBF_4$	81
44sc	1 to 1	$AgBF_4$	88

Table 5.7: Experimental conditions for the synthesis of the silver complexes **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**.

All the silver complexes were prepared by mixing silver tetrafluoroborate and the ligand in acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes. They were easily accessible and it was not necessary to proceed to a chromatographic work up.

V.4.2 Characterisation of the silver complexes

The complexes were characterised by ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. ^1H NMR and ^{13}C NMR spectra of compounds **36sc** and **44sc** were run in deuterated acetonitrile. ^1H NMR and ^{13}C NMR spectra of the five other complexes were run in deuterated DMSO. All the complexes were characterised by mass spectrometry.

^1H NMR spectroscopy

All the complexes were characterised by ^1H NMR spectroscopy. Figure 5.15 shows the ^1H NMR spectra of 4-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (**30sc**) and 1-(4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)phenyl)ethanone silver complex (**32sc**).

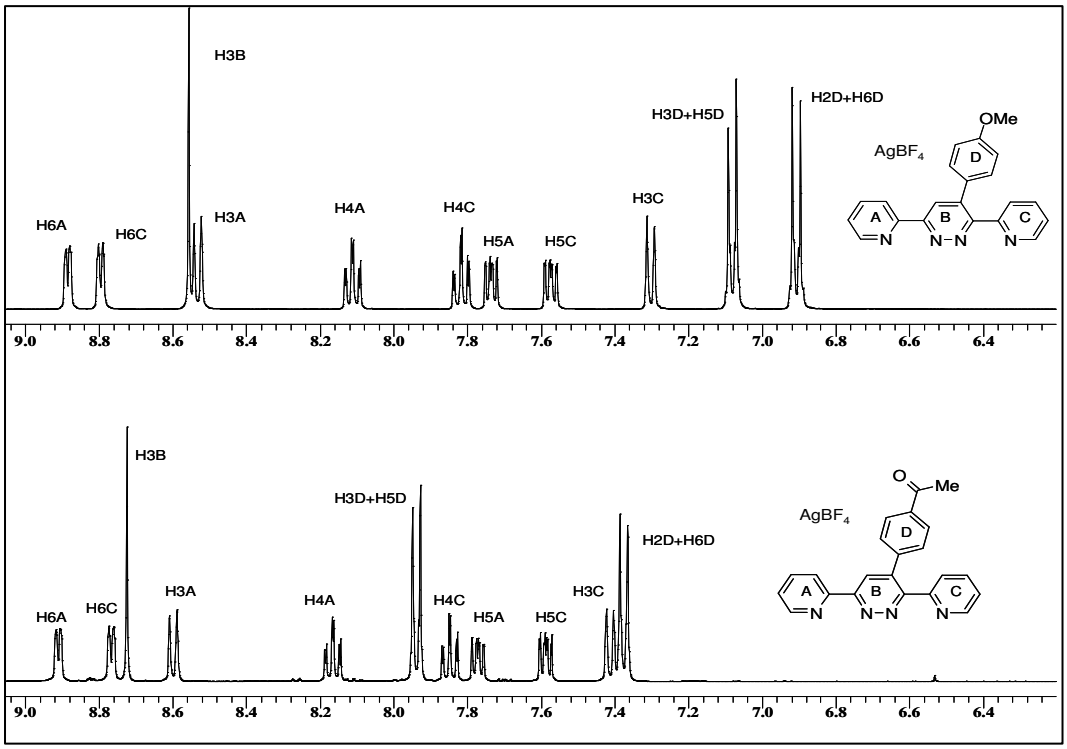


Figure 5.15: ^{1}H NMR spectra of silver complexes **30sc** and **32sc** (methyl signals not shown).

The next figure presents the ^{1}H NMR spectra of 4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzonitrile silver complex (**34sc**) and 3,6-di(pyridin-2-yl)-4-tolylpyridazine silver complex (**36sc**).

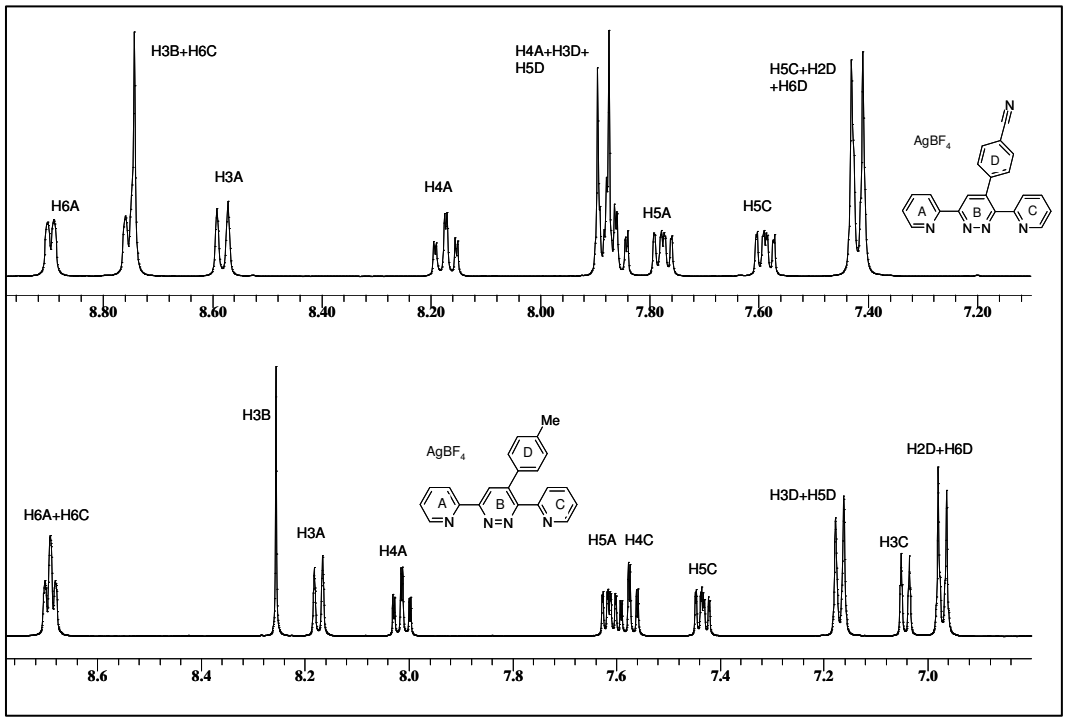


Figure 5.15: ^{1}H NMR spectra of silver complexes **34sc** and **36sc** (methyl signal not shown).

Figure 5.17 shows the ^{1}H NMR spectra of **39sc** and **42sc**. Figure 5.18 shows the ^{1}H NMR spectra of **43sc** and **44sc**.

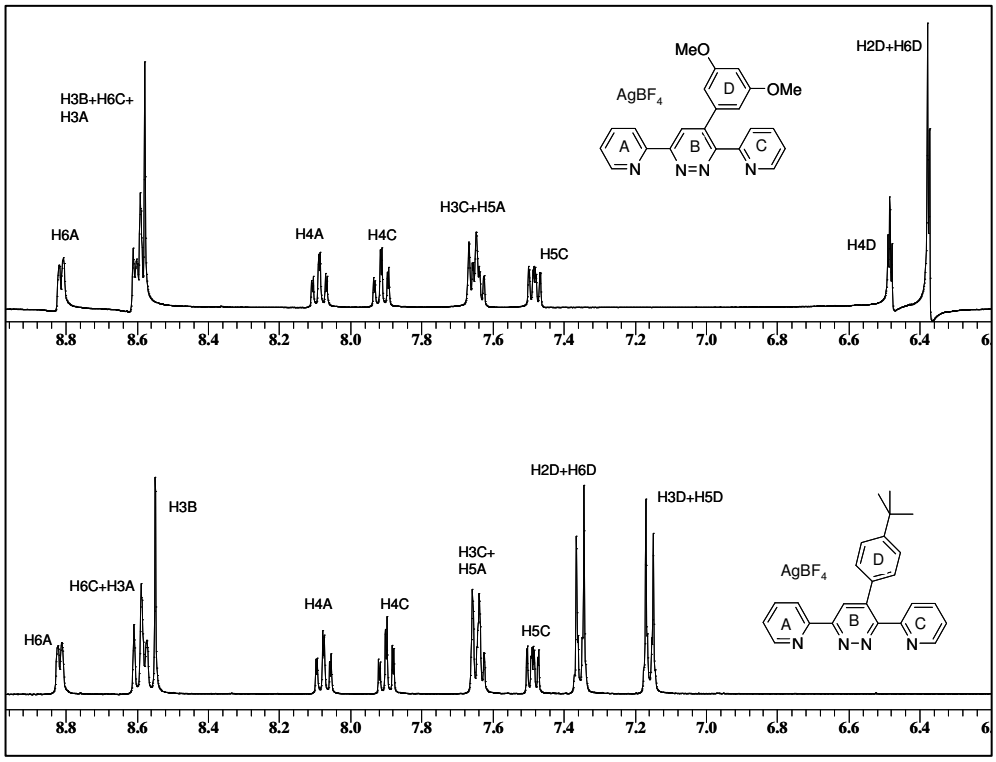


Figure 5.17: ^{1}H NMR spectra of silver complexes **39sc** and **42sc** (methyl and ^{T}butyl signals not shown).

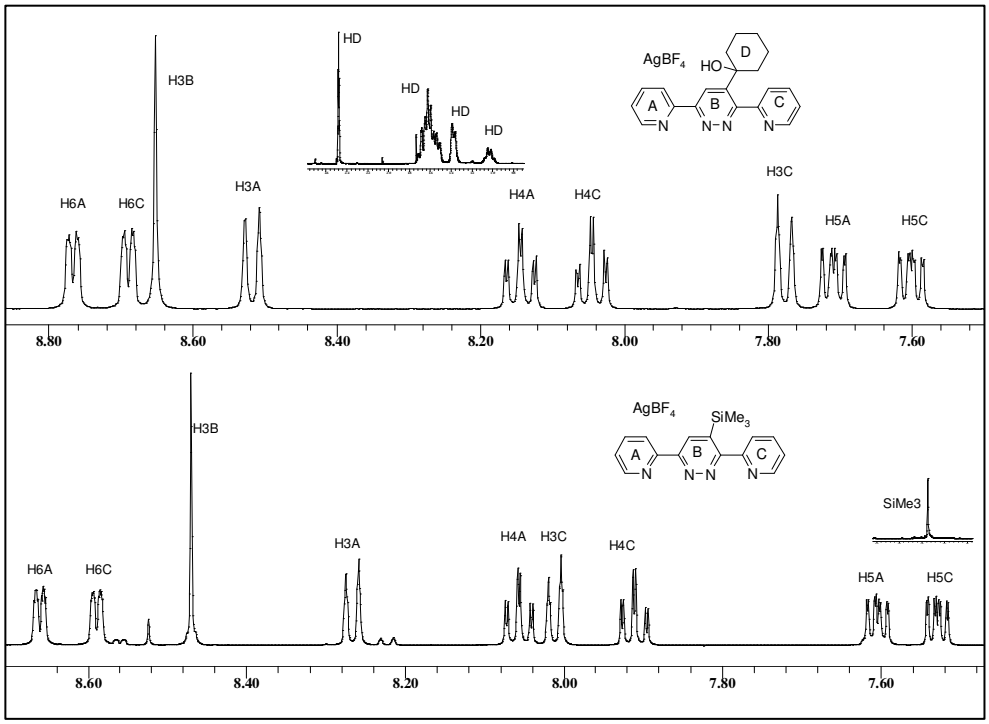


Figure 5.18: ^{1}H NMR spectra of silver complexes **43sc** and **44sc**.

The ^{1}H NMR spectra of complexes **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc** could be assigned by the chemical shifts, relatives integrals and the coupling patterns of the signals.

All the ^{1}H NMR spectra show the same signals as those present in the ^{1}H NMR spectrum of their respective ligand. For the mono substituted pyridazine silver complexes **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc and 44sc**, we can see the signal (singlet) of the H_{3B} proton.

The ^{1}H NMR spectra of 3,6-di(pyridin-2-yl)-4-tolylpyridazine silver complex (**36sc**) and 3,6-di(pyridin-2-yl)-4-(trimethylsilyl)pyridazine silver complex (**44sc**) were run in deuterated acetonitrile. They both present a single ligand environment. No species other than the free ligands and the silver complexes were detected by ^{1}H NMR spectroscopy. The complexation of the ligand and the silver species induces some overlapping signals for **36sc**. The signals of the protons H_{6A} and H_{6C} overlap. The ^{1}H NMR spectrum of complex **44sc** presents well defined and sharp signals. In both spectra the ^{1}H NMR signal of proton H_{3C} is shifted to higher fields. This proton is affected by the silver complexation. This effect is due to the short distance between the affected proton and the Ag-N bond.

The six other ^{1}H NMR spectra (**30sc**, **32sc**, **34sc**, **39sc**, **42sc** and **43sc**) were run in deuterated dimethylsulfoxide. **30sc**, **32sc** and **43sc** have well defined, sharp and separated ^{1}H NMR signals. The ^{1}H NMR spectra show the same signals as those present in the ^{1}H NMR spectrum of their respective ligand. Again, the protons H_{3B} and H_{3C} are mostly affected by the silver complexation. The ^{1}H NMR signal of proton H_{3C} is typically shifted to high field, which is characteristic for a one to one silver complexation[15].

The three last ^{1}H NMR spectra (**34sc**, **39sc** and **42sc**) show all the expected signals[15]. A closer look, at all the ^{1}H NMR spectra, shows that they present an overlapping of two or three signals. For species **34sc**, this effect concerns protons H_{3B} and H_{6C}, and H_{3A}, H_{3D} and H_{5D}; for the silver complex **39sc**, the protons H_{5A} and H_{3C} and the protons H_{3B}, H_{6C} and H_{3A}. The last silver complex (**42sc**) shows an overlapping of signals of protons H_{6C} and H_{3A} and the signals of protons H_{3C} and H_{5A} overlap.

It is important to notice that all the ^{1}H NMR spectra of the silver(I) complexes have sharp signals and that there is no signal missing.

Table 5.8 summarises the ^{1}H NMR spectroscopic data for the silver complexes presented in this chapter.

Complex	Solvent	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring	Others
30sc (δ/ppm)	DMSO	8.55 d	8.13 td	7.75 dd	8.90 d	8.57 s	7.32 d	7.83 td	7.59 dd	8.81 d	7.11-6.92 d	3.77 s
32sc (δ/ppm)	DMSO	8.51 d	8.08 td	7.69 dd	8.82 d	8.64 s	7.33 d	7.76 td	7.50 m	8.68 d	7.85-7.29 d	2.60 s
34sc (δ/ppm)	DMSO	8.60 d	8.19 td	7.79 dd	8.91 d	8.77 m	8.13 d	7.88 m	7.60 dd	8.77 m	7.88 m-7.44 d	∘
36sc (δ/ppm)	CD_3CN	8.17 d	8.01 td	7.60 dd	8.69 m	8.25 s	7.04 m	7.57 m	7.43 m	8.69 m	7.17-6.97 d	2.33 s
39sc (δ/ppm)	DMSO	8.60 m	8.10 td	7.66 m	8.83 d	8.60 m	7.66 m	7.93 td	7.50 dd	8.60 m	6.50 t-6.39 d	3.62 s
42sc (δ/ppm)	DMSO	8.61 m	8.09 td	7.65 m	8.83 d	8.56 s	7.65 m	7.92 td	7.50 dd	8.61 m	7.37-7.17 d	1.26 s
43sc (δ/ppm)	DMSO	8.72 m	8.16 td	7.73 dd	8.78 d	8.67 s	7.79 d	8.06 td	7.62 dd	8.71 d	1.64 m-1.41 m-1.05 m	8.51 d
44sc (δ/ppm)	CD_3CN	8.26 d	7.06 td	7.61 dd	8.66 d	8.47 s	8.01 d	7.91 td	7.53 dd	8.59 d	∘	0.19 s

Table 5.8: The ^{1}H NMR spectroscopic characterisation of silver complexes **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**.

Mass spectrometry

Mass spectra of all but one of the silver complexes were run using the electro-spray ionisation technique. That of complex **30sc** was run using the MALDI technique. The species were dissolved in acetonitrile. The mass spectra of complexes **30sc**, **34sc** and **36sc** showed $[L]^+$, $[AgL]^+$ and $[AgL_2]^+$ peaks. The mass spectra of **34sc** and **36sc** also present an additional peak corresponding to the $[Ag_2L_2BF_4]^+$ species. The mass spectrum of complex **32sc** shows $[AgLMeCN]^+$ and $[AgL(MeCN)_3]^+$ peaks. The mass spectra of **39sc**, **42sc**, **43sc** and **44sc** show different peaks and the major one corresponds to the $[AgL_2]^+$ peak.

All the calculated and detected *m/z* values are summarised in the Table 5.9.

silver complex	**30sc**		**32sc**		**34sc**		**36sc**		**39sc**		**42sc**		**43sc**		**44sc**	
	m/z cal.	*m/z* det.	*m/z* cal.	*m/z* det.	*m/z* cal.	*m/z* det.	*m/z* cal.	*m/z* det.	*m/z* cal.	*m/z* det.	*m/z* cal.	*m/z* det.	*m/z* cal.	*m/z* det.	*m/z* cal.	*m/z* det.
[L]$^+$	340	340	◦	◦	336	336	325	325	372	372	◦	◦	◦	◦	◦	◦
[AgLMeCN]$^+$	◦	◦	498	499	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	454	454
[AgL]$^+$	448	448	◦	◦	442	442	432	431	◦	◦	◦	◦	439	439	◦	◦
[Ag2L]$^+$	787	788	◦	◦	776	777	756	755	850	849	842	841	773	772	720	719
[AgL3MeCN]$^+$	◦	◦	585	585	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦
[2Ag2LBF4]$^+$	◦	◦	◦	◦	973	973	952	951	◦	◦	◦	◦	967	967	914	914
[Na2LMeCN]$^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	795	796	◦	◦	◦	◦
[3Ag2L2BF4]$^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	1109	1110
[3Ag3L2BF4]$^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	1417	1416
[3Ag2L3BF4]$^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	1610	1609
[5Ag3L4BF4]$^+$	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	◦	1805	1804

Table 5.9: Calculated and detected *m/z* values for the species **30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**.

We can notice that the data are consistent with each complex involving the $[AgL_2]^+$ cation or the $[Ag_2L_2BF_4]^+$ cation. This would mean that one ligand is coordinated with one silver ion, or that two ligands are coordinated with one silver ion.
The mass spectrum of compound **44sc** shows peaks of multinuclear species.

Figure 5.19 shows representative mass spectra (**34sc** and **36sc**).

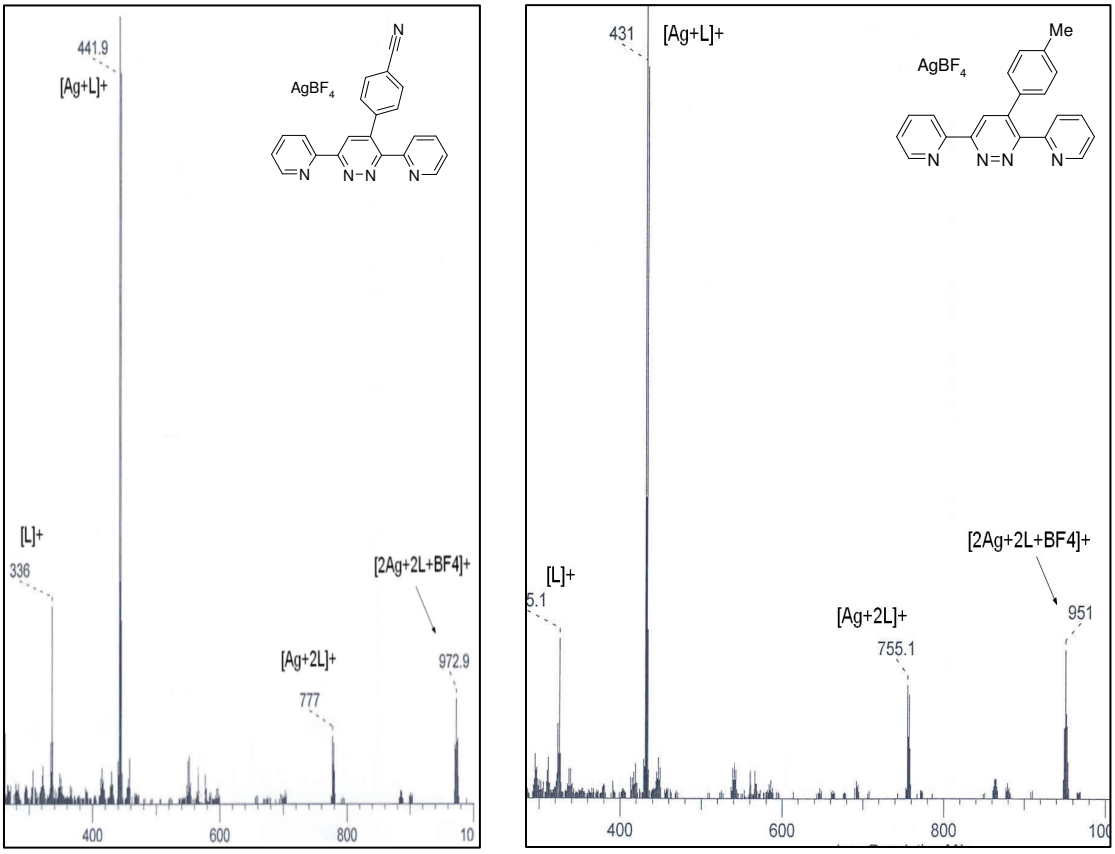


Figure 5.19: Mass spectra of silver complex **34sc** and **36sc**.

Single crystal structure for silver complex **30sc**

Crystals of **30sc** are colourless plates. **30sc** crystallizes in the monoclinic space group C2/c. The system is polymeric with a repeat unit of $[Ag_3(\mathbf{30})_2]^{3+}$. The cation possesses a centre of symmetry. One ligand coordinates to three silver centres. Ring A (N1) and B (one of the two nitrogen N2) acts like a bipyridine and coordinates to a silver cation (Ag2). The second nitrogen of ring B (N4) is linked to a silver cation (Ag2). The last pyridyl ring (ring C) is strongly twisted and its nitrogen atom (N3) coordinates to a silver cation (Ag1). The two ligands are arranged in a *trans* configuration around the dinuclear silver core.

The molecular structure of **30sc** with labelling scheme is given in Figure 5.20.

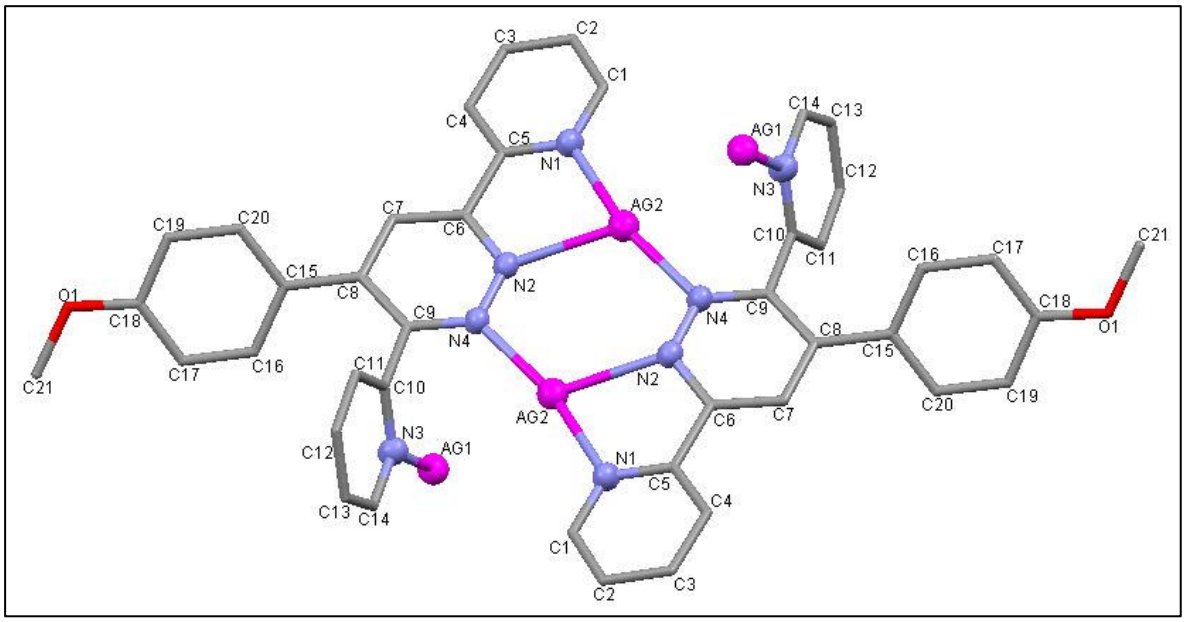


Figure 5.20: The molecular structure of **30sc** with the labelling scheme.

The silver centre Ag_2 has three normal Ag-N contacts[16] (2.207(2), 2.407(2) and 2.166(2)Å). The other silver atom centre (coordinating ring C from one ligand and ring C from a second ligand) has one Ag-N contact (2.130(4)Å).

The methoxy-phenyl substituent is twisted with respect to the pyridazine that it is bounded to, with a torsion angle of 39.05° (C7-C8-C15-C16). The terminal pyridine rings are also significantly out of the plane of the pyridazine with torsion angles of 20.34° (N1-C5-C6-N2) and 70.07° (N4-C9-C10-N3) (Figure 5.21).

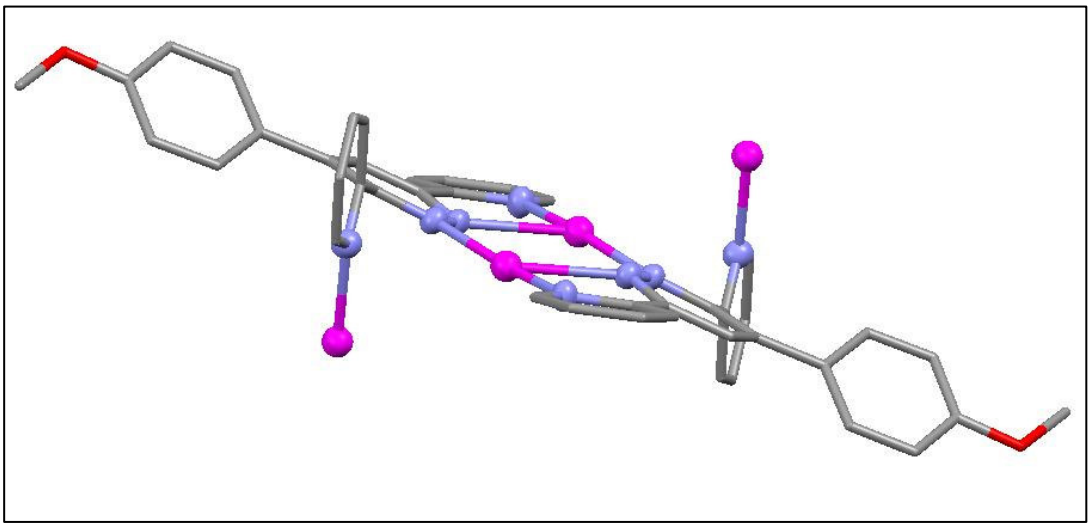


Figure 5.21: The molecular structure of **30sc**, non planar rings.

The silver-silver distance is 3.587(2)Å, and the N-Ag-N angles are between 71 and 176°. The important bond distances and angles are listed in Table 5.10. Details of the structure solution are given in Appendix 7.

Bond distance Å		
Ag1	Ag2	3.5362(2)
Ag1	Ag2	3.5362(2)
Ag1	N3	2.130(2)
Ag1	N3	2.130(2)
Ag2	N1	2.207(2)
Ag2	N2	2.407(2)
Ag2	N4	2.166(2)

Angles deg(°)			
Ag2	Ag1	Ag2	179.912(14)
Ag2	Ag1	N3	64.45(6)
Ag2	Ag1	N3	115.55(6)
Ag2	Ag1	N3	115.55(6)
Ag2	Ag1	N3	64.45(6)
N3	Ag1	N3	176.38(12)
Ag1	Ag2	N1	110.48(6)
Ag1	Ag2	N2	148.88(5)
N1	Ag2	N2	71.78(7)
Ag1	Ag2	N4	65.42(6)
N1	Ag2	N4	164.89(8)
N2	Ag2	N4	119.73(7)
Ag2	N1	C1	122.50(17)
Ag2	N1	C5	119.04(16)

Table 5.10: Important bond distances and angles present in **30sc**.

The packing shows a polymer with the repeat unit of the $[Ag_3(\mathbf{30})_2]^{3+}$ cation. These units are linked by a silver cation (Ag1). This silver cation coordinates the nitrogen atom (N3) from the pyridil ring C. In that structure we can see that the substituent induces a large torsion angle for the pyridyl ring C and enables to the $[Ag_3(\mathbf{30})_2]^{3+}$ species to be linked together to form a polymer. Part of the polymeric chain is presented in Figure 5.22.

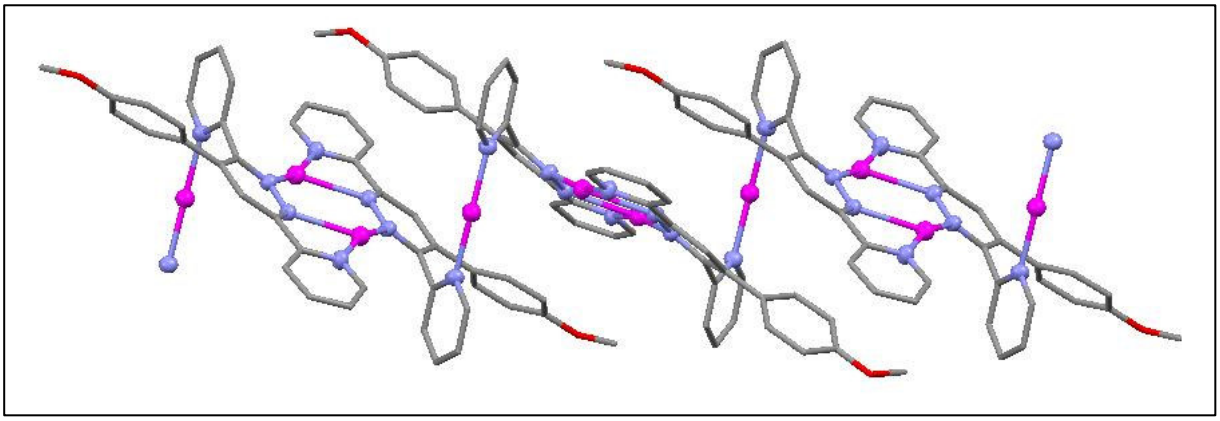


Figure 5.22: Polymer of the $[Ag_3(\mathbf{30})_2]^{3+}$ species.

These polymers form layers that are placed one over the other. They have the same orientation (Figure 5.23). There are no π-stacking interactions or hydrogen bonds involving the heterocyclic or substituent rings of the ligand.

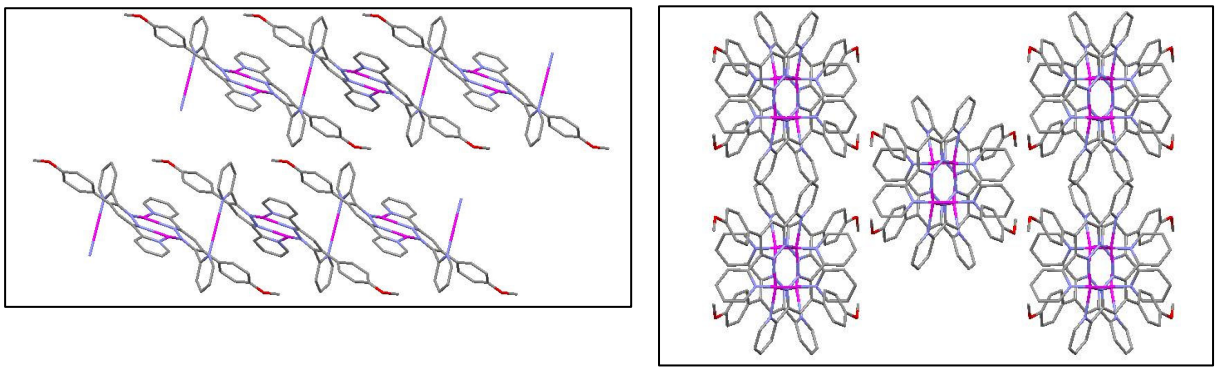


Figure 5.23: Arrangement of the $[Ag_3(\mathbf{30})_2]^{3+}$ ions (cell axes b and c).

Single crystal structure for silver complex **34sc**

Crystals of **34sc** are yellow plates. **34sc** crystallizes in the monoclinic space group $P2_1/c$. A dinuclear $[Ag_2(\mathbf{34})_2]^{2+}$ cation is observed. The **34sc** possesses a centre of symmetry and the two ligands are arranged in a *trans* configuration around the dinuclear silver core. The unit cell has one ligand, one silver and one tetrafluoroborate.

Each silver cation is coordinated to three nitrogens. The silver cation is coordinated to two nitrogen atoms (ring A and B) from one ligand and to one nitrogen atom from the second ligand (ring C).

The silver centre exhibits three Ag-N contacts[17] (2.505(2), 2.236(2) and 2.213(2)Å). The silver centre is bound to N1, N3 and N4. The last nitrogen shows an interaction with the silver centre, but this cannot be considered as a bond because distance Ag-N2 of 2.738(2)Å is too long. The molecular structure of **34sc** and labelling scheme are presented in Figure 5.24.

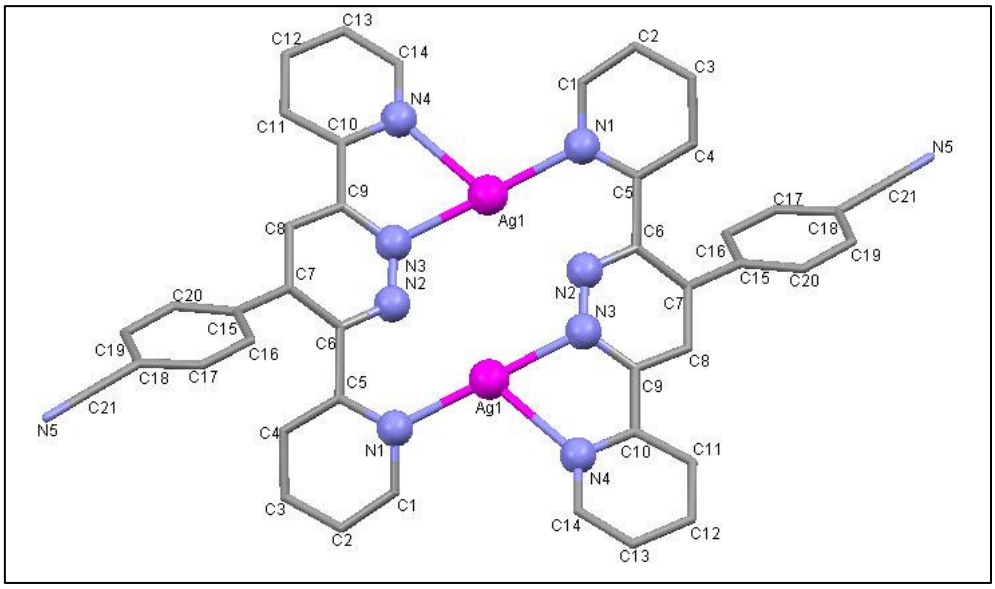


Figure 5.24: The molecular structure of **34sc** with the labelling scheme.

The cyano-phenyl substituents are twisted with respect to the pyridazine that they are bound to, with a torsion angle of 27.84° (C8-C7-C15-16). The terminal pyridine rings are also significantly out of the plane of the pyridazine with torsion angles of 38.96° (N1-C5-C6-N2) and 19.14° (N3-C9-C10-N4) (Figure 5.25).

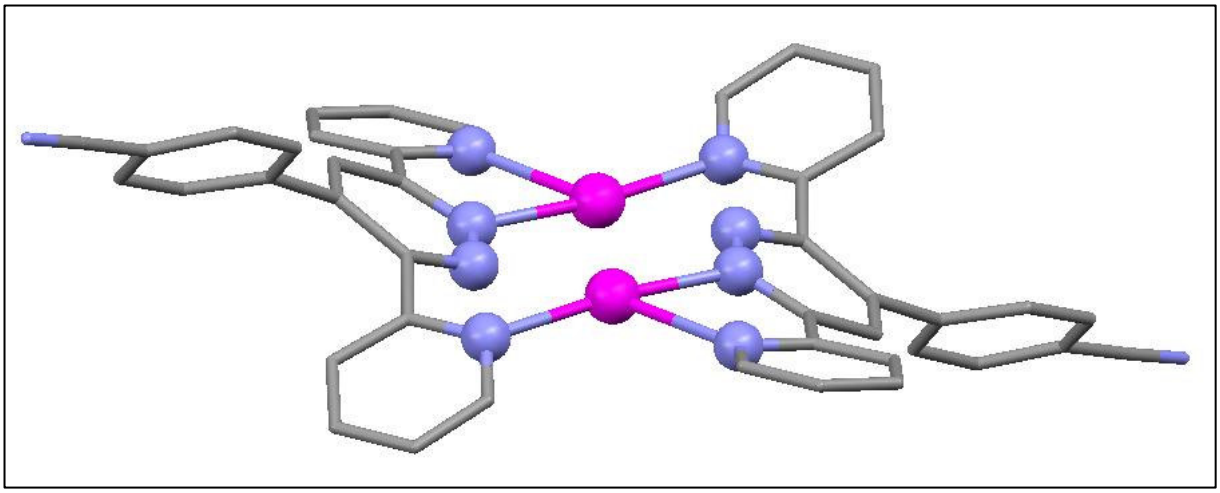


Figure 5.25: The molecular structure of **34sc**, showing the non-planarity of the rings.

The silver-silver distance is 4.206(3)Å, and the N-Ag-N angles are 67.35(7)° and 171.93(8)°. The important bonds and angles are listed in Table 5.11. Details of the structure solution are given in Appendix 8.

Bonds		**Å**
Ag1	N4	2.505(2)
Ag1	N3	2.236(2)
Ag1	N1	2.213(2)
Ag1	N2	2.738(2)

Angles			**Deg(°)**
N4	Ag1	N3	70.45(8)
N4	Ag1	N1	111.23(8)
N3	Ag1	N1	171.93(8)
N4	Ag1	N2	172.01(7)
N3	Ag1	N2	109.83(8)
N1	Ag1	N2	67.35(7)

Table 5.11: Important bond distances and angles present in **34sc**.

The packing shows an alternating arrangement of the $[Ag_2(\mathbf{34})_2]^{2+}$ species. In fact, they present offset rows forming a layer. This repetitive arrangement is also present in the different layers from the packing. Figure 5.26 shows different views of the packing of **34sc**.

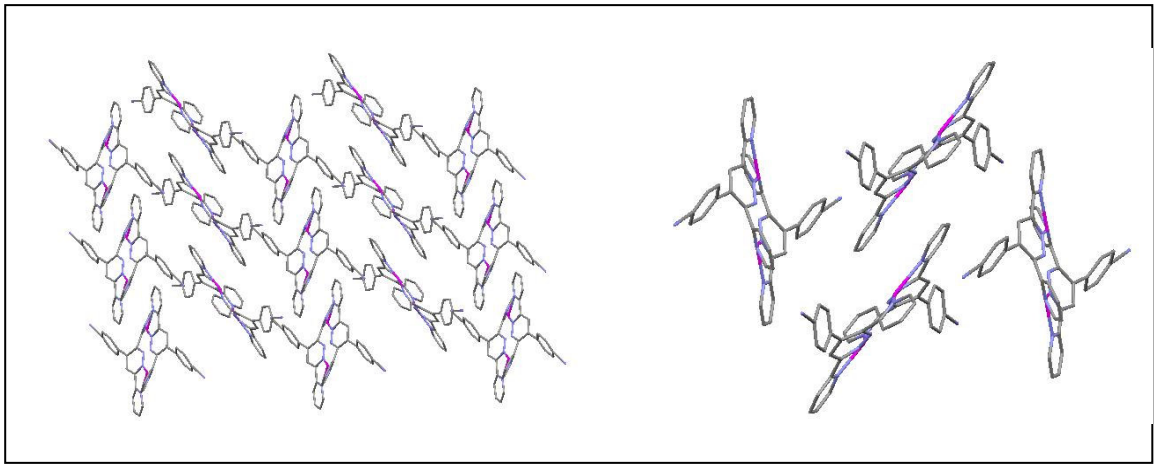


Figure 5.26: Layer motifs in **34sc**.

There are no π-stacking interactions or hydrogen bonds involving the heterocyclic or substituent rings of the ligand.

Single crystal structure for silver complex **39sc**

Crystals of **39sc** are pale yellow prisms. **39sc** crystallizes in the monoclinic space group $C2_1/c$. A mononuclear $[Ag(\mathbf{39})_2]^+$ cation is observed. The **39sc** complex possesses a centre of symmetry and the two ligands are arranged in a *trans* configuration around the mononuclear silver core. The asymmetric unit has two ligands, one silver and one tetrafluoroborate ion.

The silver cation is coordinated to two nitrogen atoms. The coordination sites are the nitrogen from ring B and ring C (N1 and N2). The symmetry of the structure induces that the silver is than coordinated to the nitrogen from ring B and ring C from the second ligand. The two other nitrogen (N3 and N4) are not coordinated to the silver centre. The silver centre has two normal Ag-N contacts[18] (2.3737(19) and 2.304(2) Å).

The molecular structure of **39sc** with labelling scheme is given in Figure 5.27.

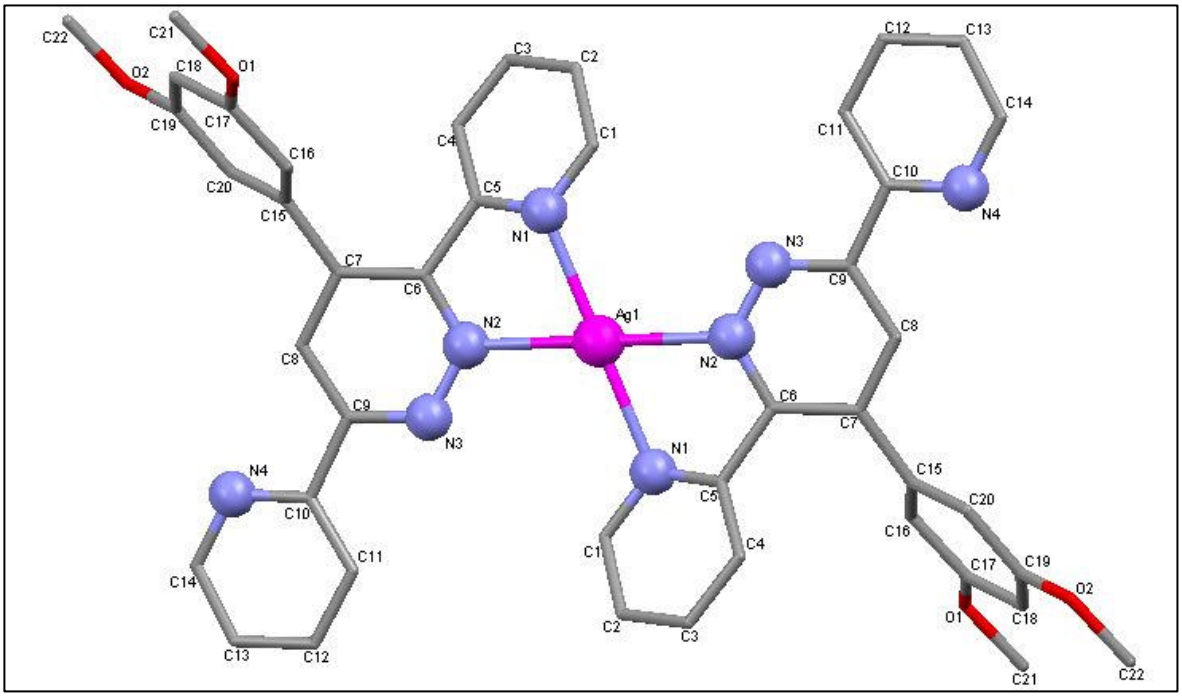


Figure 5.27: The molecular structure of **39sc** with the labelling scheme.

The dimethoxy-phenyl substituent is twisted with respect to the pyridazine that it is bound to, with a torsion angle of 116.20° (C8-C7-C15-16). The terminal pyridine rings

are also significantly out of the plane of the pyridazine with torsion angles of 32.73° (N3-C9-C10-C11) and 8.75° (N1-C5-C6-N2) (Figure 5.28).

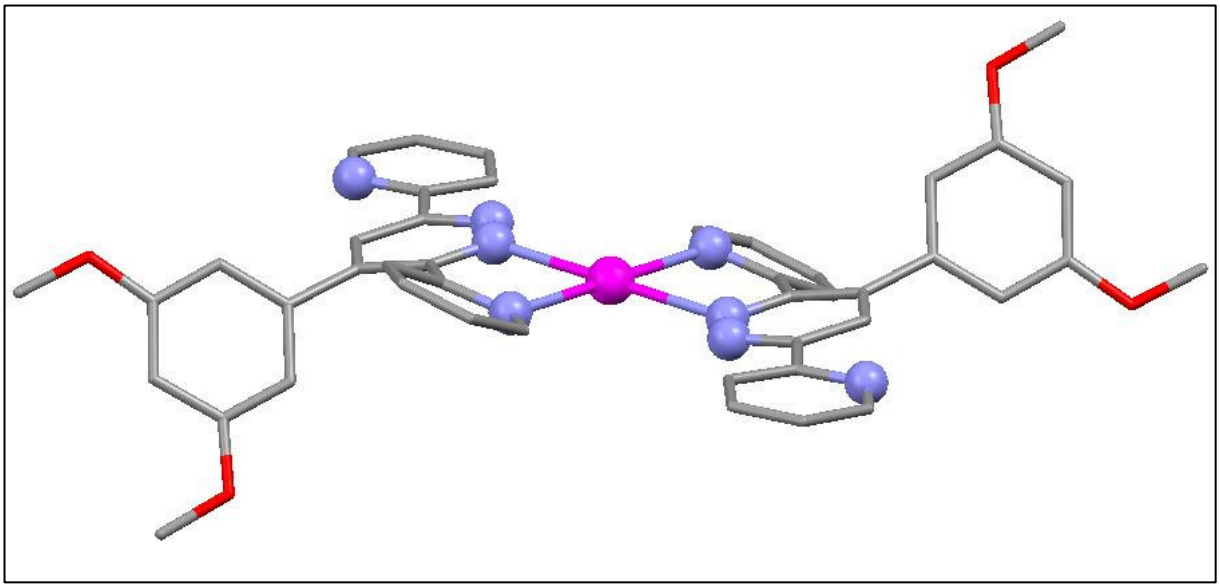


Figure 5.28: The molecular structure of **39sc**, showing the non-planarity of the rings.

The structure confirms a mononuclear complex and there are no Ag-Ag contacts. The N-Ag-N angle is 71.23°. The important bonds and angles are listed in Table 5.12. Details of the structure solution are given in Appendix 9.

Bond		**Å**
Ag1	N2	2.3737(19)
Ag1	N1	2.304(2)

Angles			**Deg(°)**
N2	Ag1	N1	71.23(7)
N2	Ag1	N1	108.77(7)
N1	Ag1	N1	179.995

Table 5.12: Important bond distances and angles present in **39sc**.

The packing shows four $[Ag(\mathbf{39})_2]^+$ cations. They are alternately placed in the “up to down” and “down to up” orientation (Figure 5.29).

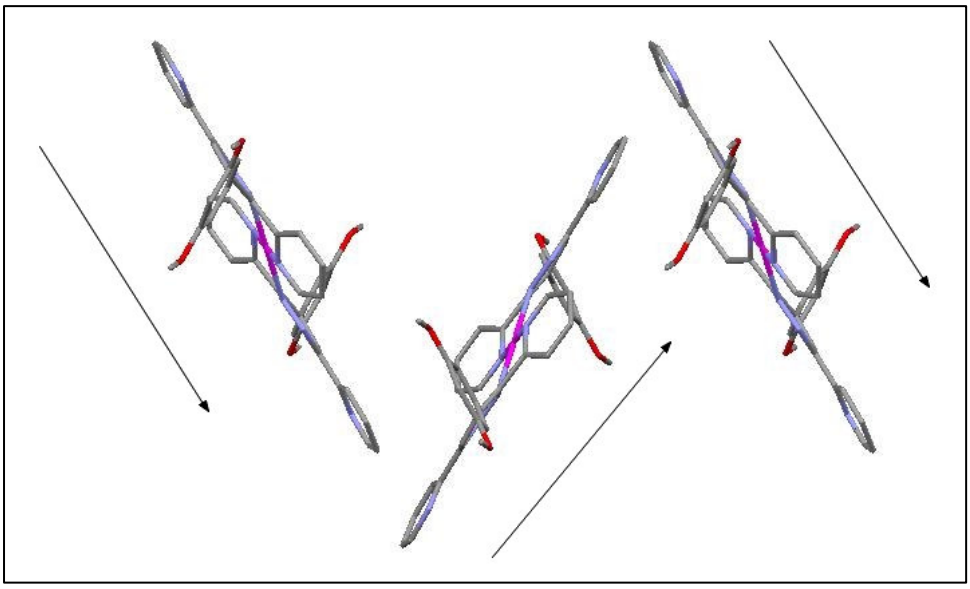


Figure 5.29: Arrangement of the $[Ag(\mathbf{39})_2]^+$ cations in the crystal structure of **39sc**.

Single crystal structure for silver complex **42sc**

42sc crystallizes in the monoclinic space group C2/a. A dinuclear $[Ag_2(\mathbf{42})_4]^{2+}$ cation is observed. The **42sc** possesses a centre of symmetry and two ligands are arranged in a *cis* configuration around the mononuclear silver core. The asymmetric unit has four ligands, two silver atoms, one tetrafluoroborate and one diethyl ether molecule. The molecular structure of **42sc** with labelling scheme is given in Figure 5.30.

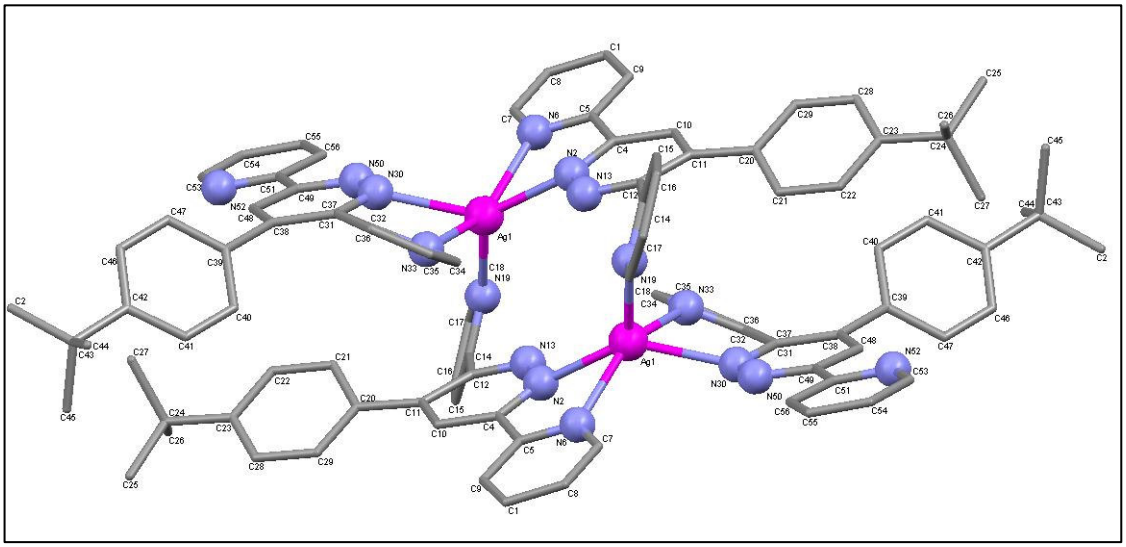


Figure 5.30: The molecular structure of **42sc** with the labelling scheme.

Each silver centre is five coordinated. Two ligands present two N-donors to one silver ion and one ligand present one N-donor to the other silver ion. The second ligand presents two N-donors to one silver ion and two N-donors are left free.

The ^{t}butyl-phenyl substituents are twisted with respect to the pyridazine that they are bounded to, with a torsion angle of 51.09° (C48-C38-C39-C47) and 24.18° (C10-C11-C20-C29). The terminal pyridine rings are also significantly out of the plane of the pyridazine with torsion angles of 35.22° (N33-C32-C31-N30), 176.09° (N50-C49-C51-N52), 3.69° (N2-C4-C5-N6) and 57.03° (N13-C12-C14-N19) (Figure 5.31).

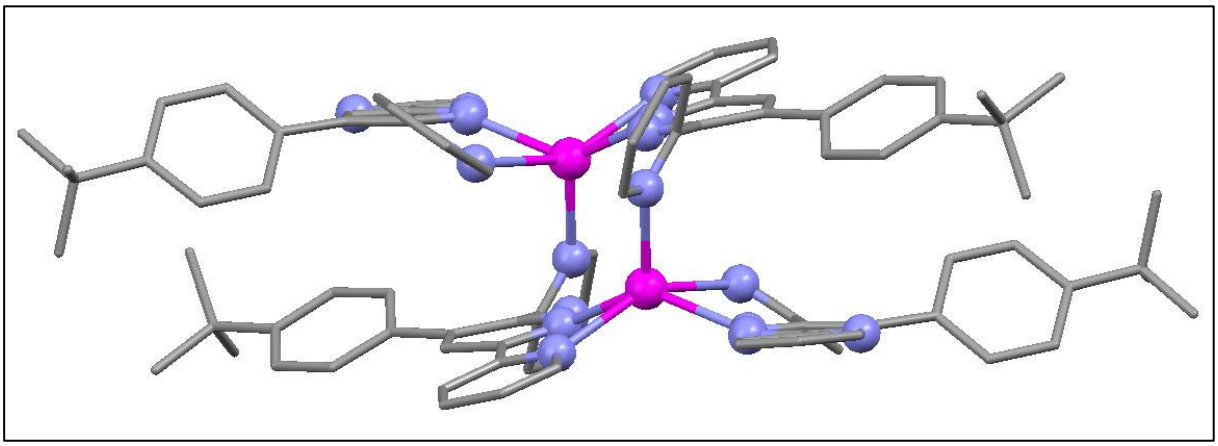


Figure 5.31: The molecular structure of **42sc**, non planar rings.

The silver centre has five Ag-N contacts[19] (2.369(2), 2.3301(19), 2.471(2), 2.3705(19) and 2.4575(19)Å). The five nitrogens are almost arranged like a square pyramid around the silver centre (Figure 5.32).

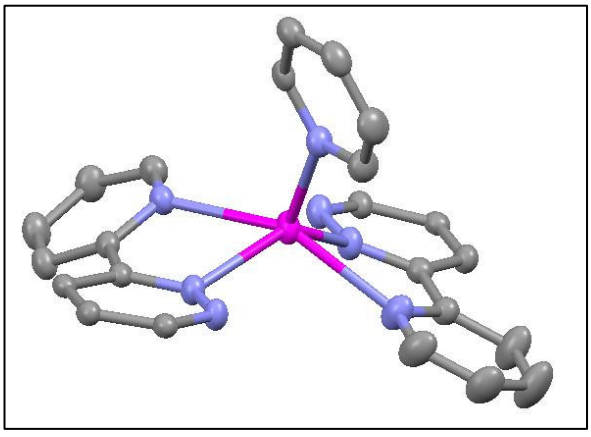


Figure 5.32: Arrangement of the nitrogens around the silver centre.

The silver-silver distance is too long to be considered bounding (5.025Å), and the N-Ag-N angles are between 57° and 150°. The important bonds and angles are listed in Table 5.13. Details of the structure solution are given in Appendix 10.

Bond		**Å**
Ag1	N19	2.369(2)
Ag1	N2	2.3301(19)
Ag1	N6	2.471(2)
Ag1	N30	2.3705(19)
Ag1	N33	2.4575(19)

Angle			**Deg(°)**
N19	Ag1	N2	126.90(7)
N19	Ag1	N6	99.10(7)
N2	Ag1	N6	67.39(7)
N19	Ag1	N30	95.26(7)
N2	Ag1	N30	137.41(7)
N6	Ag1	N30	103.88(7)
N19	Ag1	N33	110.06(7)
N2	Ag1	N33	98.36(7)
N6	Ag1	N33	150.17(8)
N30	Ag1	N33	68.13(6)

Table 5.13: Important bond distances and angles present in **42sc**.

The packing shows different layers composed of $[Ag_2(\mathbf{42})_4]^{2+}$ species. Each layer present an alternating orientation of the $[Ag_2(\mathbf{42})_4]^{2+}$ species. They are placed in the "down to up" and "up to down" orientation. The layers follow the same orientation as one another (Figure 5.33).

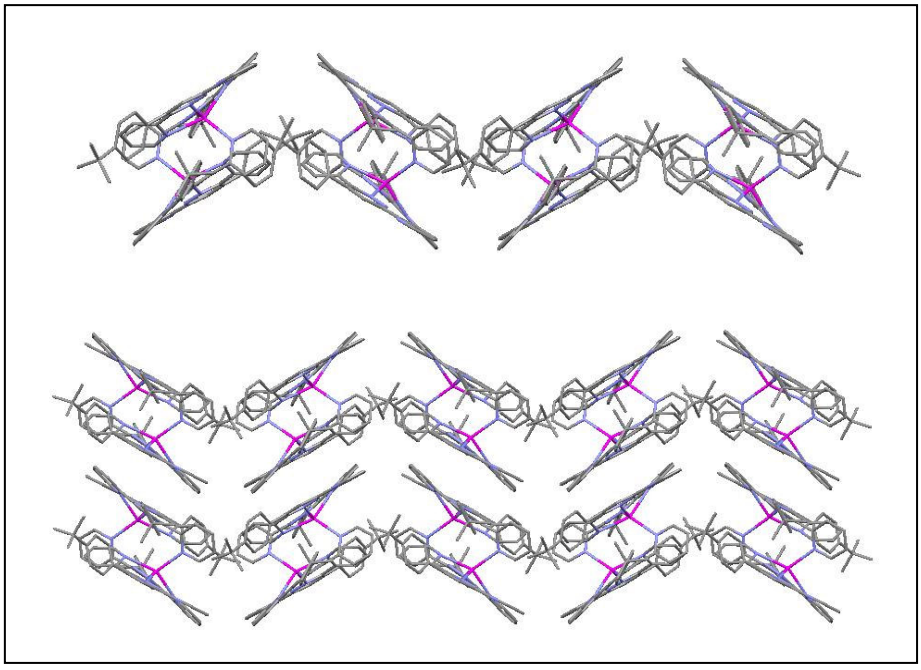


Figure 5.33: Layer motifs in **42sc**.

Single crystal structure for silver complex **44sc**[19]

44sc crystallizes in the monoclinic space group P2/n. A pentanuclear $[Ag_5(\mathbf{44})_4]^{5+}$ cation is observed. This structure is best described as a tetrahedron of four silver atoms with a fifth silver at the centre. Details of the structure solution are given in Appendix 11, along with the atomic coordinates. The molecular structure of **44sc** with labelling scheme is given in Figure 5.34.

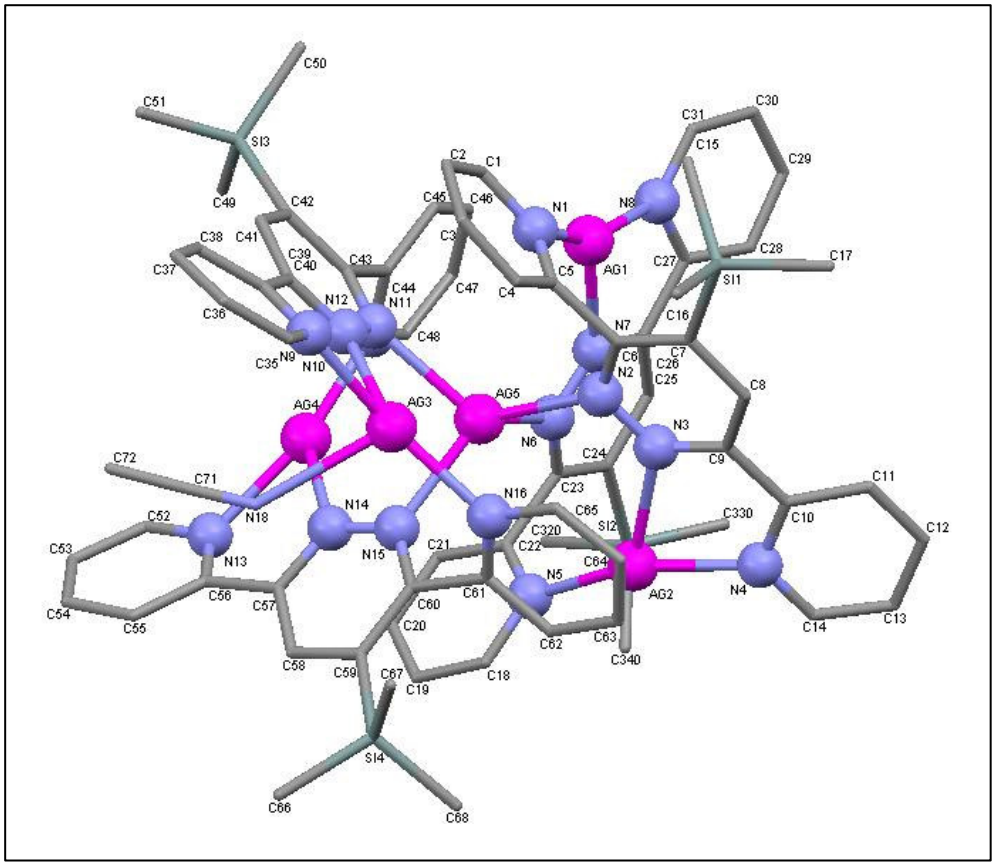


Figure 5.34: The molecular structure of **44sc** with the labelling scheme.

The central silver Ag5 is in a distorted tetrahedral N4 environment provided by the four pyridazine N2 donors. The Ag5–N contacts are 2.347(4) and 2.364(4) Å and the N–Ag5–N angles are 88.64(15)-122.23(15)°. The remaining four silver centres each show one short bond to a nitrogen in a ring C (2.176(4)–2.219(4) Å), one longer bond to a nitrogen in a ring A (2.220(5)-2.321(4) Å) and longer contacts to a chelating N1 of a ring B (2.380(4)–2.419(4) Å), together with a contact to the fluorine of a tetrafluoroborate anion (Ag…F, 2.847–3.248 Å). The coordination geometry is best described as two-coordinate linear (N–Ag–N, 155.80(16)–157.55(19)° for the two shortest Ag–N bonds) with an additional interaction with the chelating B1 donor. Each

ligand binds the central silver atom and then acts as a bidentate donor and a monodentate donor to two further silver atoms of the outer Ag4 tetrahedron. The torsion angles between the B and C rings lie between 65.7° and 74.4°. However, instead of simply forming a [4 + 4] metallomacrocycle, an additional silver atom is bound to account for the four uncoordinated N2 atoms of the B ring that would otherwise result. The relationship between the four ligands and the silver core is shown in Figure 5.35.

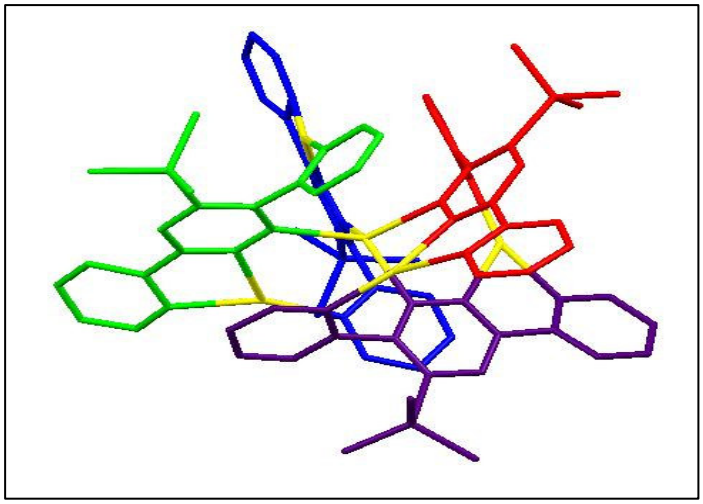


Figure 5.35: A graphical representation of the cation $[Ag_5(\mathbf{44})_4]^{5+}$.

We note that the four silicon atoms and five silver atoms describe a metal-centred pair of stellated tetrahedra (Figure 5.36).

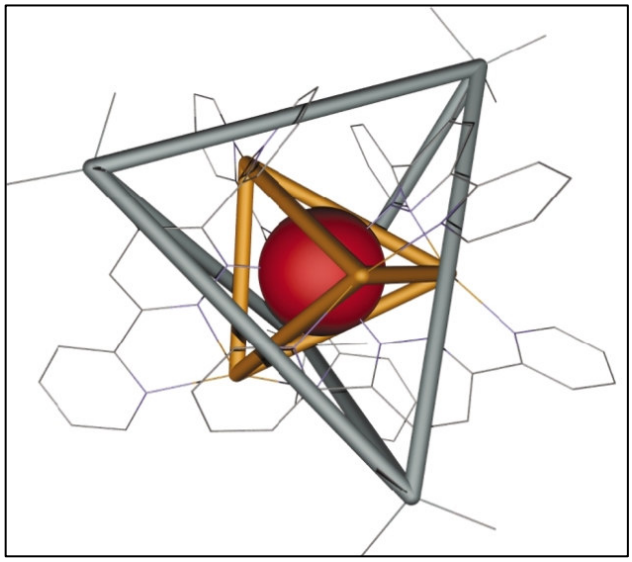


Figure 5.36: The relationship between the Ag_4 and Si_4 tetrahedra and the central Ag^+ centre.

V.5 Conclusion

In this chapter we described the synthesis of the ethynyl precursors **29**, **31**, **33**, **35**, **38** and **41** that have been prepared with the Sonogashira reaction.

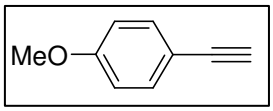
We also showed the methodology to access to mono-substituted pyridazines, based on a retro Diels-Alder reaction that enabled us to prepare the ligands **30**, **32**, **34**, **36**, **39**, **42**, **43** and **44**. All these ligands were characterised by NMR spectroscopy, mass spectrometry and elemental analysis. We also obtained a single X-ray crystal structure for the ligand **34**.

Eight new silver complexes (**30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**) were prepared and characterised by NMR, mass spectrometry (apart from some cases, discussed in the chapter).

We obtained suitable crystals for silver complexes **30sc**, **34sc 39sc**, **42sc** and **44sc** to carry out single X-ray diffraction analysis. Some of the crystal structures showed a dinuclear $[Ag_2(L)_2]^{2+}$ cation with an arrangement of the ligands in a *trans* conformation (**30sc** and **34sc**). The crystal structure of complex **39sc** showed an $[Ag\ (L)_2]^{+}$ cation. Crystal structure of complexes **42sc** and **44sc** showed unexpected $[Ag_2(L)_4]^{2+}$ and $[Ag_5(L)_4]^{5+}$ cations. The steric environment of the ^{t}butyl phenyl or trimethylsilyl substituents leads to these multinuclear silver structures by forcing the pyridyl ring C of the ligand to be significantly out of the plane of the ligand. None of these crystal structures showed a grid like structure[20], π-stacking or hydrogen bonding interactions.

V.6 Experimental part

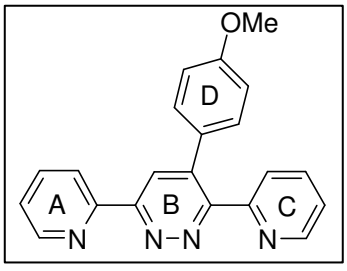
Synthesis of 1-ethynyl-4-methoxybenzene (29)



Under argon and exclusion of moisture, 4-iodoanisole (3.0 g, 19 mmol), CuCl (0.28 g, 2.8 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (1.8 g, 2.8 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (2.3 ml, 17 mmol) was added and the mixture stirred at 60°C overnight. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange powder (1.4 g, 11 mmol, 57%, C_9H_8O, 132.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.44 (d, J=8.6 Hz, 2H, H_{3+5}), 6.85 (d, J=9.0 Hz, 2H, H_{4+6}), 3.81 (s, 3H, CH3), 3.01 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.8, 133.5, 114.1, 113.8, 83.6, 75.7, 55.2.
MS (MALDI) m/z: $[L]^+$ 132, $[L+K]^+$ 171.

Synthesis of 4-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (30)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.60 g, 2.5 mmol) and 1-methoxy-4-ethynylbenzene (**29**) (0.33 g, 2.5 mmol) were dissolved in toluene (50 ml). The solution was refluxed for 70 hours. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina,

chloroform, the third band was collected). The product was obtained as a beige powder (591 mg, 1.73 mmol, 69.5%, $C_{21}H_{16}N_4O$, 340.4 g/mol).

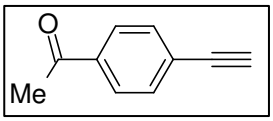
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.80 (d, J=7.9 Hz, 1H, H_{3A}), 8.74 (d, J=4.8 Hz, 1H, H_{6A}), 8.65 (s, 1H, H_{3B}), 8.54 (d, J=4.8 Hz, 1H, H_{6C}), 7.92 (td, J=7.7, 1.6 Hz, 1H, H_{4A}), 7.85 (d, J=7.6 Hz, 1H, H_{3C}), 7.81 (td, J=7.4, 1.6 Hz, 1H, H_{4C}), 7.42 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.30 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 7.21 (d, J=8.8 Hz, 2H, H_{3D+5D}), 6.84 (d, J=8.9 Hz, 2H, H_{2D+6D}), 3.81 (s, 3H, OCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.8, 158.3, 157.6, 156.0, 153.4, 149.3, 149.0, 140.1, 137.3, 136.7, 130.4, 128.8, 125.2, 124.9, 124.8, 123.3, 121.9, 114.0, 55.3, 2 carbon signals unresolved.

MS (MALDI) m/z: $[L]^+$ 342, $[Na+2L+MeCN]^+$ 744.

Elem. Anal. ($C_{21}H_{16}N_4O$) [%] calc. C 74.1, H 4.7, N 16.5, found, C 73.7, H 4.8, N 16.5.

Synthesis of 1-(4-ethynylphenyl)ethanone (31)



Under argon and exclusion of moisture, 4-bromoacetophenone (2.0 g, 10 mmol), CuCl (0.22 g, 2.2 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (1.5 g, 2.1 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (2.1 ml, 15 mmol) was added and the mixture stirred at 60°C overnight. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane/dichloromethane (25:1), the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (100 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange powder (1.1 g, 7.6 mmol, 76%, $C_{10}H_8O$, 144.2 g/mol).

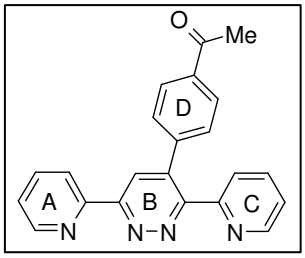
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.89 (d, J=8.5 Hz, 2H, H_{2+6}), 7.55 (d, J=8.5 Hz, 2H, H_{3+5}), 3.24 (s, 1H, ethynyl), 2.47 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 197.1, 136.6, 132.2, 128.0, 126.8, 82.6, 80.3, 26.5.

MS (ESI) m/z: $[(L\text{-}COCH_3)]^+$ 101, $[(L\text{-}CH_3)]^+$ 129, $[L]^+$ 144.

Elem. Anal. ($C_{10}H_8O$) [%] calc. C 83.3, H 5.6, found, C 83.3, H 5.7.

Synthesis of 1-(4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)phenyl)ethanone (32)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.50 g, 2.1 mmol) and 1-(4-ethynylphenyl)ethanone (**31**) (0.31 g, 2.2 mmol) were dissolved in toluene (80 ml). The solution was refluxed for 72 hours. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, dichloromethane/EtOAc (5:1), the second band was collected). The product was obtained as a beige solid (0.58 g, 1.6 mmol, 75%, $C_{22}H_{16}N_4O$, 352.4 g/mol).

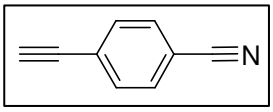
^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 8.78 (d, J=8.0 Hz, 1H, H_{3A}), 8.71 (d, J=4.7 Hz, 1H, H_{6A}), 8.65 (s, 1H, H_{3B}), 8.38 (d, J=4.7 Hz, 1H, H_{6C}), 8.02 (d, J=7.8 Hz, 1H, H_{3C}), 7.90 (m, 3H, $H_{2D+6D+4A}$), 7.82 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.41 (dd, J=7.5, 4.4 Hz, 1H, H_{5A}), 7.35 (d, J=8.1 Hz, 2H, H_{3D+5D}), 7.27 (dd, J=7.5, 4.4 Hz, 1H, H_{5C}), 2.59 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz) δ/ppm: 197.6, 158.0, 157.8, 155.3, 153.1, 149.6, 149.0, 142.1, 139.6, 137.4, 136.9, 136.6, 129.2, 128.4, 125.7, 125.1, 124.9, 123.7, 122.0, 26.7, 2 carbon signals unresolved.

MS (EI) m/z: $[Na+L+2MeCN]^+$ 456, $[Na+2L+MeCN]^+$ 767.

Elem. Anal. ($C_{22}H_{16}N_4O$) [%] calc. C 75.0, H 4.6, N 15.9, found, C 75.2, H 4.7, N 15.7.

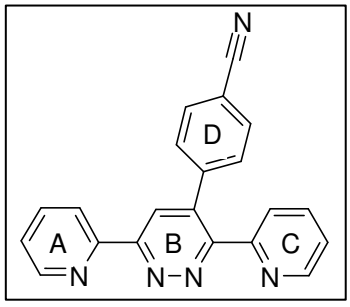
Synthesis of 4-ethynylbenzonitrile (33)



Under argon and exclusion of moisture, 4-bromonitrobenzene (2.0 g, 11 mmol), CuCl (0.16 g, 1.6 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.40 g, 0.57 mmol) were suspended in dry, argon degassed, triethylamine (120 ml). Then trimethylsilylacetylene (2.6 ml, 19 mmol) was added and the mixture stirred at 65°C overnight. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (5O ml) and an aqueous solution of 1M NaOH added (75 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown powder (1.3 g, 10 mmol, 91%, C_9H_5N, 127.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.61 (d, J=8.4 Hz, 2H, H_{2D+6D}), 7.56 (d, J=8.4 Hz, 2H, H_{3D+5D}), 1.26 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 132.6, 131.9, 126.9, 118.2, 112.2, 81.8, 81.5.
MS (EI) m/z: $[L]^+$ 127.
Elem. Anal. (C_9H_5N, 0.2 H_2O) [%] calc. C 82.7, H 4.1, N 10.6, found C 82.8, H 4.2, N 10.5.

Synthesis of 4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzonitrile (34)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.83 g, 3.5 mmol) and 4-ethynylbenzonitrile (**33**) (0.50 g, 3.9 mmol) were dissolved in toluene (140 ml). The solution was refluxed for 6 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:1), the second band was collected). The product was obtained as a pale yellow powder (1.03 g, 3.07 mmol, 87.7%, $C_{21}H_{13}N_5$, 335.4 g/mol).

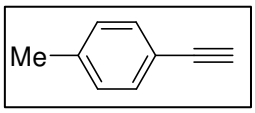
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.79 (d, J=8.0 Hz, 1H, H_{3A}), 8.71 (d, J=4.8 Hz, 1H, H_{6A}), 8.62 (s, 1H, H_{3B}), 8.35 (d, J=4.4 Hz, 1H, H_{6C}), 8.13 (d, J=8.0 Hz, 1H, H_{3C}), 7.92 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.86 (td, J=8.0, 1.6 Hz, 1H, H_{4C}), 7.61 (d, J=8.4 Hz, 2H, H_{3D+5D}), 7.42 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.36 (d, J=8.4 Hz, 2H, H_{4D+6D}), 7.28 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.7, 157.5, 154.7, 152.7, 149.4, 148.7, 142.3, 138.7, 137.2, 136.9, 132.0, 129.4, 125.5, 125.0, 124.7, 123.8, 121.8, 118.4, 111.9, 2 carbon signals unresolved.

MS (EI) m/z: $[Na+L+2MeCN]^+$ 439, $[Na+2L+MeCN]^+$ 733.

Elem. Anal. ($C_{21}H_{13}N_5$) [%] calc. C 75.2, H 3.9, N 20.9, found, C 75.0, H 4.0, N 20.7.

Synthesis of 1-ethynyl-4-methylbenzene (35)

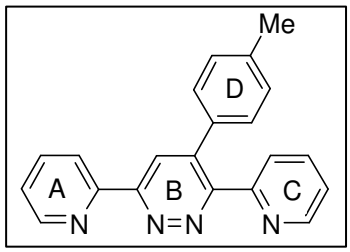


Under argon and exclusion of moisture, 4-iodotoluene (3.0 g, 14 mmol), CuCl (70 mg, 0.85 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.60 g, 0.85 mmol) were suspended in dry, argon degassed, triethylamine (120 ml). Then trimethylsilylacetylene (2.6 ml, 19 mmol) was added and the mixture stirred at 60°C for 4 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane/dichloromethane (99:1), the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (150 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a yellow powder (0.62 g, 5.3 mmol, 39%, C_9H_7, 116.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.45 (d, J=8.0 Hz, 2H, H_{2+6}), 7.16 (d, J=8.0 Hz, 2H, H_{3+5}), 3.09 (s, 1H, ethynyl), 2.39 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 138.8, 131.9, 128.9, 118.9, 83.7, 76.4, 21.3.

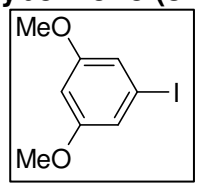
Synthesis of 3,6-di(pyridin-2-yl)-4-tolylpyridazine (36)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.78 g, 3.3 mmol) and 1-ethynyl-4-methylbenzene (**35**) (0.39 g, 3.4 mmol) were dissolved in toluene (90 ml). The solution was refluxed for 6 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:2), the second band was collected). The product was obtained as an orange powder (0.97 g, 3.0 mmol, 91%, $C_{21}H_{16}N_4$, 324.1 g/mol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 8.82 (d, J=7.8 Hz, 1H, H_{3A}), 8.75 (d, J=4.5 Hz, 1H, H_{6A}), 8.70 (s, 1H, H_{3B}), 8.55 (d, J=4.5 Hz, 1H, H_{6C}), 7.95 (td, J=7.8, 1.6 Hz, 1H, H_{4A}), 7.84 (m, 2H, H_{3C+4C}), 7.45 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.33 (m, 1H, H_{5C}), 7.21 (d, J=6.8 Hz, 2H, H_{2D+6D}), 7.09 (d, J=6.8 Hz, 2H, H_{3D+5D}), 2.36 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 125 MHz) δ/ppm: 158.3, 157.6, 155.8, 153.3, 149.3, 148.9, 140.4, 138.5, 137.3, 136.7, 133.7, 129.2, 128.9, 125.5, 125.0, 124.8, 123.4, 121.9, 21.2, 2 carbon signals unresolved.
MS (EI) m/z: $[L]^+$ 323.
Elem. Anal. ($C_{21}H_{16}N_4$) [%] calc. C 77.8, H 5.0, 17.3, found C 77.1, H 5.0, N 17.0.

Synthesis of 1-iodo-3,5-dimethoxybenzene (37)



Under argon 3,5-dimethoxyaniline (5.0 g, 32 mmol) was suspended in water (150 ml). Concentrated hydrochloric acid (2.5 ml) was added and the brown solution cooled to 0°C. A solution of sodium nitrite (2.3 g, 34 mmol) in 30ml water was slowly added. The mixture was stirred at 0°C for one hour. A catalytic amount of copper(I) iodide (125 mg) was added before the slow addition of potassium iodide (14 g, 88 mmol). The mixture was stirred at 0°C for 6 hours. From time to time, tetrahydrofuran (total 90 ml) was added to increase the solubility. Water (50 ml) and diethyl ether (80 ml)

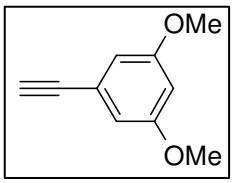
were added under vigorous stirring and the two layers separated. The aqueous layer was extracted with diethyl ether and the combined organic phases washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the dark residue purified by chromatographic work-up (alumina, chloroform, the third band was collected) to give a yellow solid (2.7 g, 10 mmol, 31%, $C_8H_9IO_2$, 264.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 6.86 (d, J=2.0 Hz, 2H, H_{2+6}), 6.40 (t, J=2.0 Hz, 1H, H_4), 3.76 (s, 6H, $(OCH_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 161.0, 115.7, 100.6, 99.0, 55.4.

MS (EI) m/z: $[L]^+$ 264.

Synthesis of 1-ethynyl-3,5-dimethoxybenzene (38)



Under argon and exclusion of moisture, 1-iodo-3,5-dimethoxybenzene (**37**) (1.0 g, 3.8 mmol), CuCl (40 mg, 0.38 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.27 g, 0.38 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (0.8 ml, 6 mmol) was added and the mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane/dichloromethane (9:1), the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (150 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown powder (0.47 g, 2.9 mmol, 76%, $C_{10}H_{10}O_2$, 162.2 g/mol).

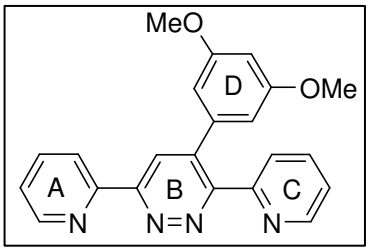
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 6.65 (d, J=2.0 Hz, 2H, H_{2+6}), 6.47 (t, J=2.0 Hz, 1H, H_4), 3.78 (s, 6H, $(OCH_3)_2$), 3.04 (s, 1H, ethynyl).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 160.4, 123.3, 109.9, 102.2, 85.5, 76.7, 55.3.

MS (EI) m/z: $[L\text{-}2OCH_3]^+$ 102, $[L\text{-}OCH_3]^+$ 133, $[L]^+$ 162.

Elem. Anal. ($C_{10}H_{10}O_2$) [%] calc. C 74.1, H 6.2, found, C 73.6, H 6.4.

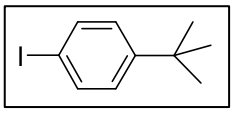
Synthesis of 4-(3,5-dimethoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (39)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.26 g, 1.1 mmol) and 1-ethynyl-3,5-dimethoxybenzene (**38**) (0.20 g, 1.2 mmol) were dissolved in toluene (35 ml). The solution was refluxed for 7 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:2), the second band was collected). The product was obtained as a pale orange powder (0.36 g, 0.97 mmol, 88%, $C_{22}H_{18}N_4O_2$, 370.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.78 (d, J=8.4 Hz, 1H, H_{3A}), 8.71 (d, J=5.0 Hz, 1H, H_{6A}), 8.66 (s, 1H, H_{3B}), 8.55 (d, J=5.0 Hz, 1H, H_{6C}), 7.90 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.80 (m, 2H, H_{3C+4C}), 7.40 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.28 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 6.39 (m, 3H, H_D), 3.64 (s, 6H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 160.6, 158.3, 157.7, 155.8, 153.3, 149.3, 149.1, 140.3, 138.6, 137.1, 136.4, 125.2, 124.7, 123.2, 121.8, 107.0, 100.9, 55.3, 4 carbon signals unresolved.
MS (EI) m/z: $[L+K+DCM]^+$ 492, $[2L+K+Na]^+$ 803, $[2L+K+DCM]^+$ 863.
Elem. Anal. ($C_{22}H_{18}N_4O_2$) [%]: calc. C 71.3, H 4.9, N 15.1, found, C 71.3, H 4.9, N, 15.0.

Synthesis of 1-tert-butyl-4-iodobenzene (40)

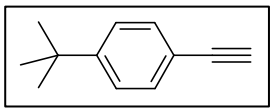


Under argon 4-tert-butylaniline (3.0 g, 20 mmol) was suspended in water (150 ml). Concentrated hydrochloric acid (4.6 ml) was added and the brown solution cooled to 0°C. A solution of sodium nitrite (1.4 g, 20 mmol) in 20 ml water was slowly added. The mixture was stirred at 0°C for one hour. A catalytic amount of copper(I) iodide (115 mg) was added before the slow addition of potassium iodide (9.0 g, 55 mmol).

The mixture was stirred at 0°C for 6 hours. From time to time, tetrahydrofuran (total 70 ml) was added to increase the solubility. Water (50 ml) and diethyl ether (80 ml) were added under vigorous stirring and the two layers separated. The aqueous layer was extracted with diethyl ether and the combined organic phases washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the dark residue purified by chromatographic work-up (alumina, chloroform, the third band was collected) to give a red oil (4.6 g, 18 mmol, 90%, $C_{10}H_{13}I$, 260.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.61 (d, J=8.4 Hz, 2H, H_{3+5}), 7.14 (d, J=8.8 Hz, 2H, H_{2+6}), 1.30 (s, 9H, t-butyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 150.8, 137.0, 90.6, 127.5, 34.5, 31.1.
MS (EI) m/z: $[L\text{-}3CH_3]^+$ 217, $[L\text{-}CH_3]^+$ 245, $[L]^+$ 260.
Elem. Anal. ($C_{22}H_{18}N_4O_2$ + CH_3CN) [%]: calc. C 47.9, H 5.4, found, C 47.8, H 5.3.

Synthesis of 1-tert-butyl-4-ethynylbenzene (41)

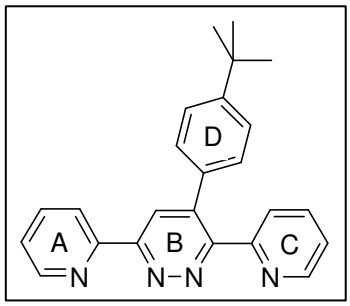


Under argon and exclusion of moisture, 1-tert-butyl-4-iodobenzene (**40**) (2.0 g, 7.7 mmol), CuCl (80 mg, 0.77 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.54 g, 0.77 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (1.8 ml, 13 mmol) was added and the mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (120 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange oil (0.33 g, 2.1 mmol, 27%, $C_{12}H_{14}$, 158.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.45 (d, J=8.4 Hz, 2H, H_{3+5}), 7.36 (d, J=8.8 Hz, 2H, H_{2+6}), 3.04 (s, 1H, ethynyl), 1.33 (s, 9H, t-butyl).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 152.0, 131.8, 125.2, 119.0, 83.78, 76.4, 34.7, 31.1.

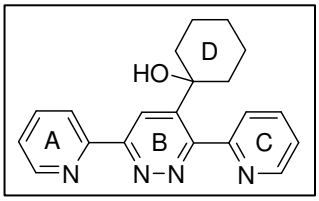
Synthesis of 4-(4-tert-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (42)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.20 g, 1.3 mmol) and 1-tert-butyl-4-ethynylbenzene (**41**) (0.28 g, 1.8 mmol) were dissolved in toluene (30 ml). The solution was refluxed for 42 hours. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (2:1), the second band was collected). The product was obtained as a beige powder (0.42 g, 1.1 mmol, 87%, $C_{24}H_{22}N_4$, 366.5 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.79 (d, J=7.8 Hz, 1H, H_{3A}), 8.72 (d, J=4.8 Hz, 1H, H_{6A}), 8.66 (s, 1H, H_{3B}), 8.50 (d, J=4.8 Hz, 1H, H_{6C}), 7.88 (m, 2H, H_{3C+4A}), 7.90 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.39 (dd, J=6.8, 4.4 Hz, 1H, H_{5A}), 7.32 (d, J=9.2 Hz, 2H, H_{2D+6D}), 7.91 (dd, J=6.8, 4.4 Hz, 1H, H_{5C}), 7.19 (d, J=8.8 Hz, 2H, H_{3D+5D}), 1.30 (s, 9H, t-butyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.3, 157.6, 156.0, 153.4, 151.6, 149.4, 149.0, 140.3, 137.1, 136.4, 133.7, 128.6, 125.5, 125.3, 124.8, 124.6, 123.2, 121.8, 34.6, 31.2, 2 carbon signals unresolved.
MS (EI) m/z: $[L+K+DCM]^+$ 488, $[2L+K+Na]^+$ 795, $[2L+CHCl_3]^+$ 854.
Elem. Anal. ($C_{22}H_{18}N_4O_2$) [%]: calc. C 78.7, H 6.1, N 15.3, found, C 78.5, H 6.2, N 15.1.

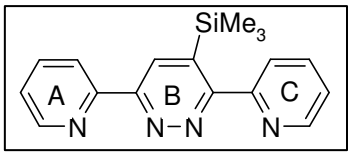
Synthesis of 1-(3,6-di(pyridin-2-yl)pyridazin-4-yl)cyclohexan-1-ol (43)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.30 g, 1.3 mmol) and 1-ethynyl-cyclohexan-1-ol (0.19 g, 1.5 mmol) were dissolved in toluene (70 ml). The solution was refluxed for 15 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:1), the second band was collected). The product was obtained as a pale pink powder (0.30 g, 0.90 mmol, 71%, $C_{20}H_{20}N_4O$, 332.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.74 (s, 1H, H_{3B}), 8.72 (m, 2H, H_{3A+6A}), 8.63 (d, J=5.0 Hz, 1H, H_{6C}), 8.36 (d, J=7.6 Hz, 1H, H_{3C}), 7.98 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.87 (td, J=7.6, 1.6 Hz, 1H, H_{4C}), 7.45 (dd, J=7.6, 4.8 Hz, 1h, H_{5A}), 7.38 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 1.96 (d, J=12.1 Hz, 2H, CH_{2D}), 1.85 (m, 2H, CH_{2D}), 1.64 (m, 3H, CH_D+CH_{2D}), 1.21 (m, 1H, CH_D).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.0, 157.6, 157.3, 153.2, 149.5, 147.7, 146.6, 138.2, 137.0, 126.4, 124.7, 124.2, 121.8, 121.7, 70.8, 36.2, 25.6, 21.8, 2 carbon signals unresolved.
MS (EI) m/z: $[L+CHCl_3]^+$ 454, $[Na+2L+MeCN]^+$ 727, $[2L+CHCl_3]^+$ 787.
Elem. Anal. ($C_{20}H_{20}N_4O$) [%] calc. C 72.1, H 6.4, N 16.8, found, C 71.9, H 6.1, N 16.7.

Synthesis of 3,6-di(pyridin-2-yl)-4-(trimethylsilyl)pyridazine (44)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (1.0 g, 4.2 mmol) and trimethylsilylacetylene (0.75 ml, 5.4 mmol) in toluene (50 ml) was refluxed for 60 hours. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (alumina, EtOAc/hexane (1:2), the second band was collected). The product was obtained as a yellow powder (0.64 g, 2.1 mmol, 50%, $C_{17}H_{18}N_4Si$, 306.4 g/mol).

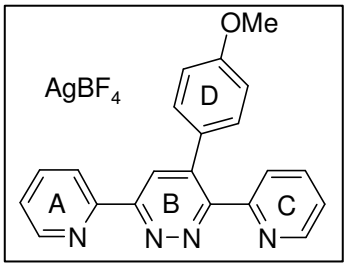
^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.87 (s, 1H, H_{3B}), 8.75 (d, J=4.8 Hz, 1H, H_{6A}), , 8.73 (d, J=7.9 Hz, 1H, H_{3A}), 8.66 (d, J=4.8Hz, 1H, H_{6C}), 8.61 (d, J=8.0 Hz, 1H, H_{3C}), 7.90 (td, J=8.1, 1.6 Hz, 1H, H_{4A}), 7.88 (td, J=8.1, 1.6 Hz, 1H, H_{4C}), 7.40 (dd, J=7.5, 4.4 Hz, 1H, H_{5A}), 7.38 (dd, J=7.5, 4.4 Hz, 1H, H_{5C}), 0.35 (s, 9H, Si $(CH_3)_3$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 162.0, 156.3, 155.5, 153.9, 149.4, 147.4, 139.9, 137.2, 137.0, 132.4, 124.5, 124.2, 122.8, 121.8, 1.1, 2 carbon signals unresolved.
MS (ESI) m/z: $[Na+2L+MeCN]^+$ 675.
Elem. Anal. ($C_{17}H_{18}N_4Si$) [%] calc. C 66.6, H 5.9, N 18.3; found, C 67.0, H 6.0, N 18.2.

Silver complexes

All the silver complexes were prepared by using the same procedure. One equivalent of silver tetrafluoroborate or silver trifluoromethane sulfonate was mixed with one equivalent of the diazine ligand in 15 ml of acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes.

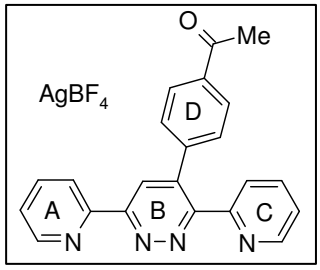
Synthesis of 4-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (30sc)



4-(4-Methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**30**) (32 mg, 0.16 mmol) and silver tetrafluoroborate (55 mg, 0.16 mmol) were used to prepare the silver complex (68 mg, 0.13 mmol, 81%, $C_{21}H_{16}N_4OAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.90 (d, J=4.8 Hz, 1H, H_{6A}), 8.81 (d, J=4.8 Hz, 1H, H_{6C}), 8.57 (s, 1H, H_{3B}), 8.55 (d, J=8.0 Hz, 1H, H_{3A}), 8.13 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.83 (td, J=8.0, 1.6 Hz, 1H, H_{4C}), 7.75 (dd, J=6.8, 4.8 Hz, 1H, H_{5A}), 7.59 (dd, J=8.0, 4.8 Hz, 1H, H_{5C}), 7.32 (d, J=8.0 Hz, 1H, H_{3C}), 7.11 (dt, J=9.2, 2.0 Hz, 2H, H_{3D+5D}), 6.92 (dt, J=9.2, 2.0 Hz, 2H, H_{2D+6D}), 3.77 (s, 3H, O-CH_3).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 160.2, 157.5, 155.2, 153.1, 150.5, 150.4, 150.1, 140.7, 138.6, 137.4, 130.6, 126.8, 126.7, 126.3, 125.9, 124.9, 123.4, 114.2, 55.2, 2 carbon signals unresolved.
MS (MALDI) *m/z* $[L]^+$ 340, $[Ag+L]^+$ 448, $[Ag+2L]^+$ 788.

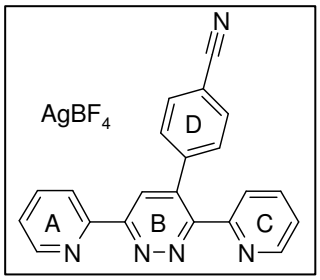
Synthesis of 1-(4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)phenyl)ethanone silver complex (32sc)



1-(4-(3,6-Di(pyridin-2-yl)pyridazin-4-yl)phenyl)ethanone (**32**) (70 mg, 0.20 mmol) and silver tetrafluoroborate (38 mg, 0.20 mmol) to prepare the silver complex (92 mg, 0.17 mmol, 85%, $C_{22}H_{16}N_4OAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.82 (d, J=4.0 Hz, 1H, H_{6A}), 8.68 (d, J=4.4 Hz, 1H, H_{6C}), 8.64 (s, 1H, H_{3B}), 8.51 (d, J=8.0 Hz, 1H, H_{3A}), 8.08 (td, J=8.0, 2.0 Hz, 1H, H_{4A}), 7.85 (d, J=8.8 Hz, 2H, H_{3D+5D}), 7.76 (td, J=7.8, 1.6 Hz, 1H, H_{4C}), 7.69 (dd, J=6.8, 4.4 Hz, 1H, H_{5A}), 7.50 (dd, J=6.8, 4.0 Hz, 1H, H_{5C}), 7.33 (d, J=7.6 Hz, 1H, H_{3C}), 7.29 (d, J=8.0 Hz, 2H, H_{2D+6D}), 2.60 (s, 3H, CH_3).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 197.4, 157.6, 155.4, 152.4, 150.8, 150.6, 149.8, 140.3, 139.6, 138.9, 137.6, 136.9, 129.5, 128.4, 127.6, 126.6, 126.1, 125.1, 123.5, 2 carbon signals unresolved.
MS (ES) *m/z* $[Ag+L+MeCN]^+$ 499, $[Ag+L+3MeCN]^+$ 585.
Elem. Anal. ($C_{22}H_{16}N_4OAgBF_4$ + $0.5H_2O$) [%] calc. C 47.5, H 3.1, N 10.1, found, C 47.7, H 3.3, N 10.0.

Synthesis of 4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzonitrile silver complex (34sc)



4-(3,6-Di(pyridin-2-yl)pyridazin-4-yl)benzonitrile (**34**) (80 mg, 0.24 mmol) and silver tetrafluoroborate (46 mg, 0.24 mmol) were used to prepare the silver complex (0.12 g, 0.22 mmol, 92%, $C_{21}H_{13}N_5AgBF_4$).

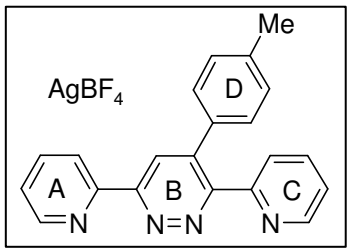
^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.91 (d, J=4.0 Hz, 1H, H_{6A}), 8.77 (m, 2H, H_{3B+6C}), 8.60 (d, J=8.0 Hz, 1H, H_{3A}), 8.19 (td, J=8.0, 2.0 Hz, 1H, H_{4A}), 7.88 (m, 3H, $H_{4C+3D+5D}$), 7.79 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.60 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.44 (d, J=8.0 Hz, 2H, H_{2D+6D}), 7.44 (d, J=8.0 Hz, 2H, H_{3C})

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.4, 155.3, 152.1, 150.8, 150.6, 149.6, 139.9, 139.8, 138.9, 137.7, 132.5, 130.1, 127.8, 126.7, 126.2, 125.3, 123.7, 118.2, 111.9, 2 carbon signals unresolved.

MS (ES) *m/z* $[L]^+$ 336, $[Ag+L]^+$ 442, $[Ag+2L]^+$ 777, $[2Ag+2L+BF_4]^+$ 973.

Elem. Anal. ($C_{42}H_{26}N_{10}Ag_2BF_4$ + $3H_2O$) [%] calc. C 49.1, H 3.1, N 13.6, found, C 49.1, H 2.9, N 13.6.

Synthesis of 3,6-di(pyridin-2-yl)-4-tolylpyridazine silver complex (36sc)



3,6-di(pyridin-2-yl)-4-p-tolylpyridazine (**36**) (70 mg, 0.22 mmol) and silver tetrafluoroborate (42 mg, 0.22 mmol) were used to prepare the silver complex (92 mg, 0.18 mmol, 82%, $C_{21}H_{16}N_4AgBF_4$).

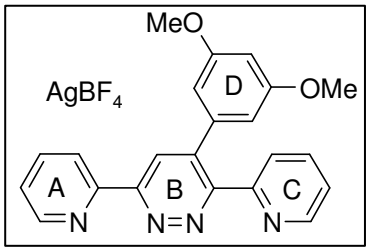
^{1}H NMR (CD_3CN, 500 MHz) δ/ppm: 8.69 (m, 2H, H_{6A+6C}), 8.25 (s, 1H, H_{3B}), 8.17 (d, J=6.4 Hz, 1H, H_{3A}), 8.01 (td, J=6.4, 1.2 Hz, 1H, H_{4A}), 7.60 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.57 (td, J=6.4, 1.2 Hz, 1H, H_{4C}), 7.43 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.17 (d, J=6.0 Hz, 2H, H_{3D+5D}), 7.04 (d, J=6.4 Hz, 1H, H_{3C}), 6.97 (d, J=6.4 Hz, 2H, H_{2D+6D}), 2.33 (s, 3H, Me).

^{13}C NMR (CD_3CN, 125 MHz) δ/ppm: 159.0, 156.1, 153.4, 152.2, 152.1, 150.4, 143.4, 141.5, 140.1, 138.5, 132.4, 130.6, 130.1, 129.0, 127.7, 127.5, 126.4, 124.8, 21.2, 2 carbon signals unresolved.

MS (ES) *m/z* $[L]^+$ 325, $[Ag+L]^+$ 431, $[Ag+2L]^+$ 755, $[2Ag+2L+BF_4]^+$ 951.

Elem. Anal. ($C_{21}H_{16}N_4AgBF_4$ + $0.5H_2O$) [%] calc. C 47.8, H 3.2, N 10.6, found, C 47.8, H 3.4, N 10.5.

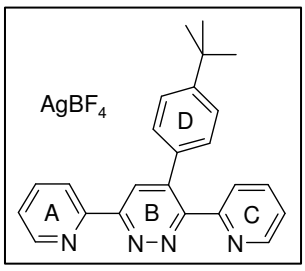
Synthesis of 4-(3,5-Dimethoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (39sc)



4-(3,5-Dimethoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**39**) (60 mg, 0.16 mmol) and silver tetrafluoroborate (32 mg, 0.16 mmol) were used to prepare the silver complex (69 mg, 0.12 mmol, 75%, $C_{22}H_{18}N_4O_2AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.83 (d, J=4.8 Hz, 1H, H_{6A}), 8.60 (m, 3H, $H_{3B+6C+3A}$), 8.10 (td, J=7.8, 1.6 Hz, 1H, H_{4A}), 7.93 (td, J=7.8, 1.6 Hz, 1H, H_{4C}), 7.66 (m, 2H, H_{3C+5A}), 7.50 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 6.50 (t, J=2.4 Hz, 1H, H_{4D}), 6.39 (d, J=2.8 Hz, 2H, H_{2D+6D}), 3.62 (s, 6H, OMe).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 160.3, 158.2, 156.6, 154.5, 151.6, 149.4, 140.1, 138.1, 137.7, 137.1, 125.7, 125.6, 125.2, 124.1, 122.1, 107.0, 100.7, 55.2, 3 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 372, $[Ag+2L]^+$ 849.
Elem. Anal. ($C_{66}H_{54}N_{12}O_6Ag + H_2O$) [%] calc. C 64.1, H 4.6, N 13.6, found, C 64.0, H 4.6, N 13.6.

Synthesis of 4-(4-tert-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (42sc)



4-(4-tert-Butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**42**) (70 mg, 0.19 mmol) and silver tetrafluoroborate (37 mg, 0.19 mmol) were used to prepare the silver complex (93 mg, 0.17 mmol, 89%, $C_{24}H_{22}N_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.83 (d, J=4.0 Hz, 1H, H_{6A}), 8.61 (m, 2H, H_{6C+3A}), 8.56 (s, 1H, H_{3B}), 8.09 (td, J=7.6, 5.2 Hz, 1H, H_{4A}), 7.92 (td, J=7.6, 2.4 Hz, 1H, H_{4C}),

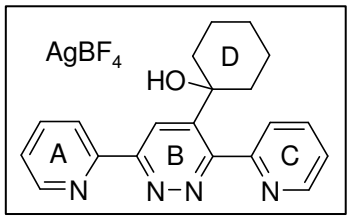
7.65 (m, 2H, H_{3C+5A}), 7.50 (dd, J=7.2, 2.0 Hz, 1H, H_{5C}), 7.37 (d, J=8.4 Hz, 2H, H_{2D+6D}), 7.17 (d, J=8.4 Hz, 2H, H_{3D+5D}), 1.26 (s, 9H, ^{t}bu).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 154.5, 151.5, 150.1, 149.4, 140.0, 138.0, 137.1, 132.8, 128.6, 125.7, 125.3, 125.2, 124.2, 121.9, 34.3, 30.8, 8 carbon signals unresolved.

MS (ES) *m/z* $[Na+2L+MeCN]^+$ 796, $[Ag+2L]^+$ 841.

Elem. Anal. ($C_{48}H_{44}N_8Ag + 2H_2O$) [%] calc. C 65.8, H 5.5, N 12.8, found, C 65.4, H 5.4, N 12.8.

Synthesis of 1-(3,6-di(pyridin-2-yl)pyridazin-4-yl)cyclohexan-1-ol silver tetrafluoroborate (43sc)



1-(3,6-Di(pyridin-2-yl)pyridazin-4-yl)cyclohexan-1-ol (**43**) (70 mg, 0.21 mmol) and silver tetrafluoroborate (41 mg, 0.21 mmol) were used to prepare the silver complex (92 mg, 0.17 mmol, 81%, $C_{20}H_{20}N_4OAgBF_4$).

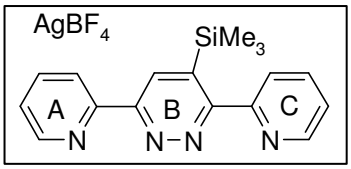
^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.78 (d, J=4.0 Hz, 1H, H_{6A}), 8.71 (d, J=5.2 Hz, 1H, H_{6C}), 8.67 (s, 1H, H_{3B}), 8.16 (td, J=7.2, 1.6 Hz, 1H, H_{4A}), 8.06 (td, J=7.2, 1.6 Hz, 1H, H_{4C}), 7.79 (d, J=8.4 Hz, 1H, H_{3C}), 7.73 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.62 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 1.64 (m, 7H, H_D), 1.41 (m, 2H, H_D), 1.05 (m, 1H, H_D).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 159.6, 157.4, 155.0, 154.4, 150.7, 150.2, 148.5, 138.9, 137.7, 126.3, 125.6, 124.2, 123.5, 122.9, 71.7, 36.4, 24.5, 21.0, 2 carbon signals unresolved.

MS (ES) *m/z* $[Ag+L]^+$ 439, $[Ag+2L]^+$ 772, $[2Ag+2L+BF_4]^+$ 967.

Elem. Anal. ($C_{20}H_{20}N_4OAgBF_4$) [%] calc. C 45.6, H 3.8, N 10.6, found, C 40.8, H 3.8, N 10.6.

Synthesis of 3,6-di(pyridin-2-yl)-4-(trimethylsilyl)pyridazine silver complex (44sc)



3,6-Di(pyridin-2-yl)-4-(trimethylsilyl)pyridazine (**44**) (25 mg, 0.08 mmol) and silver tetrafluoroborate (16 mg, 0.08 mmol) were used to prepare the silver complex (35 mg, 0.07 mmol, 88%, $C_{17}H_{18}N_4SiAgBF_4$).

^{1}H NMR (CD_3CN, 500 MHz) δ/ppm: 8.66 (d, J=4.3 Hz, 1H, H_{6A}), 8.59 (d, J=4.8 Hz, 1H, H_{6C}), 8.47 (s, 1H, H_{3B}), 8.26 (d, J=8.0 Hz, 1H, H_{3A}), 8.06 (td, J=7.8, 1.7 Hz, 1H, H_{4A}), 8.01 (d, J=7.8 Hz, 1H, H_{3C}), 7.91 (td, J=7.7, 1.7 Hz, 1H, H_{4C}), 7.61 (dd, J=7.6, 4.9 Hz, 1H, H_{5A}), 7.53 (dd, J=7.6, 4.9 Hz, 1H, H_{5C}), 0.19 (s, 9H, $Si(CH_3)_3$).
^{13}C NMR (CD_3CN, 125 MHz) δ/ppm: 164.8, 156.2, 154.6, 152.1, 151.3, 150.3, 143.7, 140.2, 139.1, 135.0, 127.6, 126.5, 124.7, 124.5, 0.3, 2 carbon signals unresolved.
MS (ES) *m/z* $[Ag+L+MeCN]^+$ 454, $[Ag+2L]^+$ 719, $[2Ag+2L+BF_4]^+$ 914, $[3Ag+2L+2BF_4]^+$ 1109, $[3Ag+3L+2BF_4]^+$ 1416, $[4Ag+2L+3BF_4]^+$ 1609, $[5Ag+3L+4BF_4]^+$ 1804.
Elem. Anal. ($C_{17}H_{18}N_4SiAgBF_4$+ $C_{17}H_{18}N_4SiAg$) [%] calc. C 44.6, H 4.0, N 12.2, found, C 44.3, H 4.1, N 12.3

V.7 Bibliography

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CHAPTER VI

PYRIDAZINES WITH PENDANT ALKYL CHAINS

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PYRIDAZINES WITH PENDANT ALKYL CHAINS

VI.1 Introduction

In order to further investigate the effect of the substituents on the 4-position of the tetrazine, we decided to focus our interest on substituents based on alkyl chains[1,2]. These substituents have also been used by other research groups to prepare complexes based on bipyridine and ruthenium[3] or cobalt[4]. These complexes were used to do STM measurements[5].
We prepared these pyridazine ligands and complexes and used then for STM measurements, but the different attempts to obtain STM images were unsuccessful. However we obtained a single crystal structure from decyl-substituted pyridazine silver complex.

To prepare these ligands, we used butyl, octyl or decyl substituted phenyl acetylenes and dodecyne. They reacted with 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) to give the desired ligands. This chapter presents all the alkyl chain precursors synthesized (**45**, **48** and **51** shown in Figure 6.1) and their respective pyridazines (**46**, **49**, **52**, and ligand **53** shown in Figure 6.2). They have all been characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.
The target molecules were the silver complexes (**45sc**, **48sc**, **51sc** and **53sc**).
So, we will talk about the synthesis of the ethynyl precursors, the desired ligands and, finally, about the silver complexes.

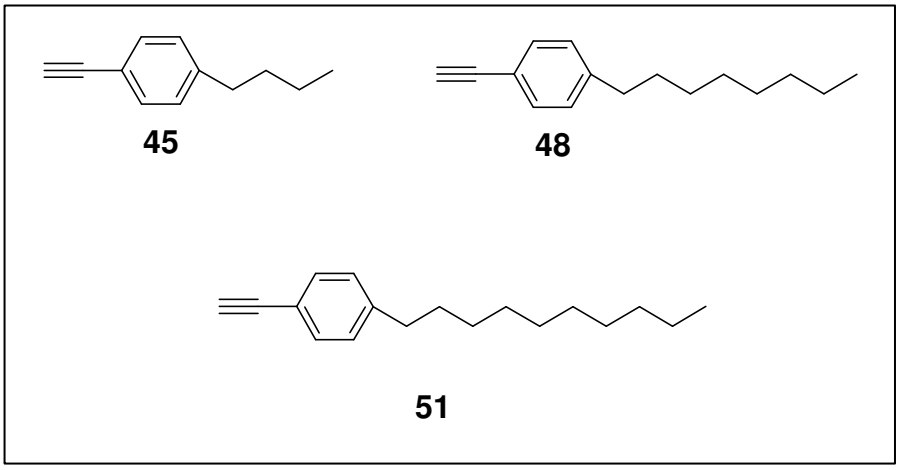


Figure 6.1: Ethynyl precursors described in this chapter.

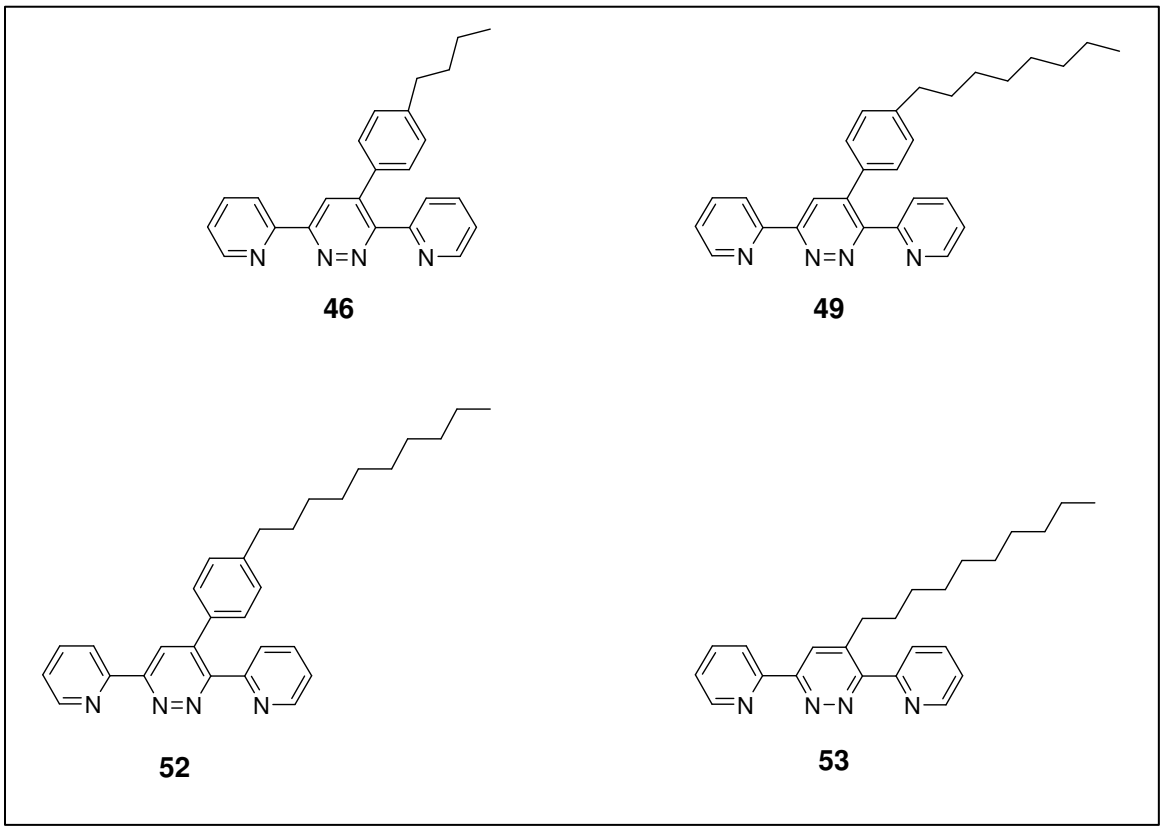


Figure 6.2: Alkylated pyridazines presented in this work.

VI.2 Synthesis of the ethynyl precursors

VI.2.1 Synthetic method

To prepare these compounds, we used the Sonogashira[6] reaction as described in the chapter II. To obtain the desired ethynyl precursor we needed a halogenated phenyl compound. These compounds were mixed with trimethylsilylacetylene, copper(I) chloride and bis(triphenylphosphine)palladium dichloride in triethylamine. This solution was refluxed under nitrogen to give the protected ethynyl precursor. This intermediate was dissolved in tetrahydrofuran and a solution of 1M sodium hydroxide was added. The target molecule was extracted and purified by chromatographic work-up over alumina.

We always used iodo phenyl compounds. Ethynyl precursor **45** was prepared with the commercial 1-butyl-4-iodobenzene (A). To prepare compound **48** and **51** we needed to synthesise the halogenated compounds 1-iodo-4-octylbenzene (**47**) and 1-iodo-4-decylbenzene (**50**). We synthesised **47** and **50** starting from 4-octylaniline and 4-decylaniline that was mixed with $NaNO_2$, hydrochloric acid and potassium iodide. More details of these syntheses are given in the experimental part at the end of this chapter.

Figure 6.3 shows the general synthetic method adopted for the synthesis of compounds **48** and **51**.

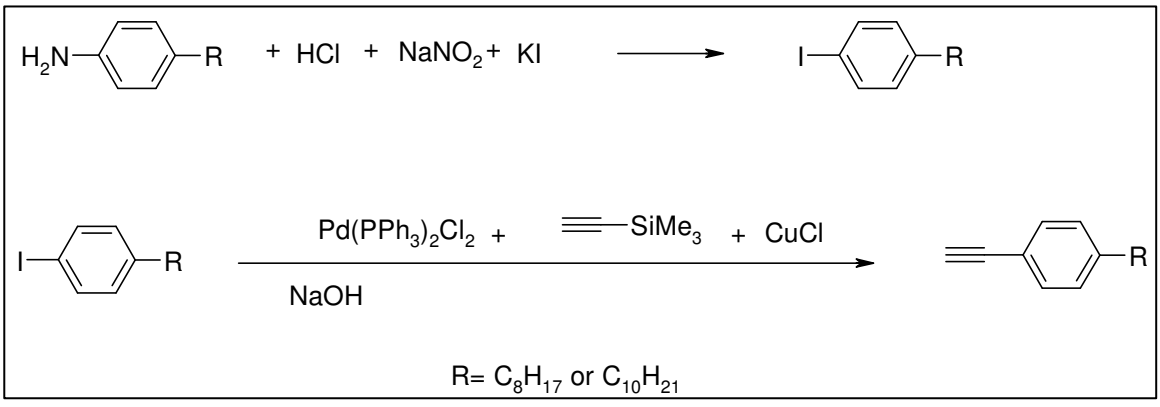


Figure 6.3: Synthetic methods for the synthesis of compounds **48** and **51**.

The preparation of 1-butyl-4-ethynylbenzene (**45**) follows the literature and examples given in chapter II. We mixed 1-butyl-4-iodobenzene with trimethylsilylacetylene, copper(I) chloride and bis(triphenylphosphine)palladium dichloride in triethylamine. This solution was refluxed under nitrogen to give the protected ethynyl precursor. This intermediate was dissolved in tetrahydrofuran and a solution of 1M sodium hydroxide was added. 1-Butyl-4-ethynylbenzene (**45**) was extracted and purified by chromatographic work-up over alumina.

The last ethynyl compound used in this chapter was dodecyne. This compound is available commercially and was used directly, to synthesise 4-decyl-3,6-di(pyridin-2-yl)pyridazine (**53**), without any further purification. More details of that reaction will be given in the second part of this chapter.

Figure 6.4 shows the compounds used to prepare the ethynyl compounds.

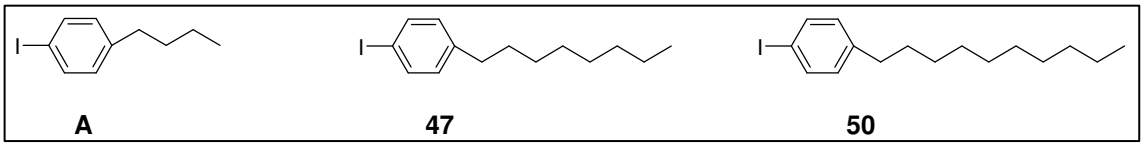


Figure 6.4: Compounds used to prepare the ethynyl compounds.

For each ethynyl precursor presented here, the reactant ratio, time and yield are listed in the Table 6.1. Purification methods and synthetic details are discussed in the experimental section at the end of this chapter.

Precursor	**Halogenated compound**	**Reaction ratio** (halogenated / tms acetylene)	**Reaction temperature** (°C)	**Reaction time** (hr)	**Yield** (%)
45	**A**	1/2.1	60	18	90
48	**47**	1/1.8	60	18	88
51	**50**	1/1.7	60	18	93

Table 6.1: Reaction conditions for the synthesis of the ethynyl precursors **45**, **48** and **51**.

Compounds **45, 48** and **51** were obtained, after purification, with good yields and could be used for the synthesis of the pyridazine ligands.

VI.2.2 Characterisation of the ethynyl precursors

All the ethynyl precursors have been characterized by ^{1}H NMR spectroscopy. ^{13}C NMR spectroscopy could only be obtained for compounds **45, 48** and **51.** Compounds **45, 48** and **51** were characterized by mass spectrometry.
The general procedure and characterization of intermediates **47** and **56** are discussed at the end of this chapter in the experimental section.

^{1}H NMR spectroscopy

We first focused our interest in the ^{1}H NMR spectroscopic characterization. The ethynyl compounds synthesized in this chapter should have the characteristic signals for the ethynyl and phenyl groups[7]. It was also important to see the absence of the $SiMe_3$ signals. This would show that the deprotection had been carried out successfully. We also focused our interest on the ^{1}H NMR signals of the protons from the alkyl chain. Table 6.2 summarises the ^{1}H NMR signals of the precursors.

Ethynyl precursor	Phenyl signals (δ/ppm)	Ethynyl signals (δ/ppm)	Alkyl chain
45	740-7.13 (d-d)	3.02 (s)	2.60t- 1.54m- 1.34m- 0.94t
48	7.42-7.14 (t-d)	3.04 (s)	2.61t- 1.62m- 1.29m- 0.91t
51	7.42-7.14 (t-d)	3.04 (s)	2.61t- 1.61m- 1.30m- 0.90t

Table 6.2: ^{1}H NMR characterisation of the precursors **45**, **48** and **51**.

The ^{1}H NMR spectrum of each ethynyl precursor could be assigned by the chemical shifts and the relative integrals. As expected[7], the different phenyl signals are at around δ 7.5, 7.6 ppm and the ethynyl signals are near to δ 3.1 ppm. The ^{1}H NMR signals of the protons from the alkyl chain are between δ 0.9 and 2.6 ppm. We can

notice that the spectra have the same diagnostic pattern of signals and that all the signals are placed in the same region. Figure 6.5 shows the ^{1}H NMR spectra of the ethynyl precursors **48** and **51**

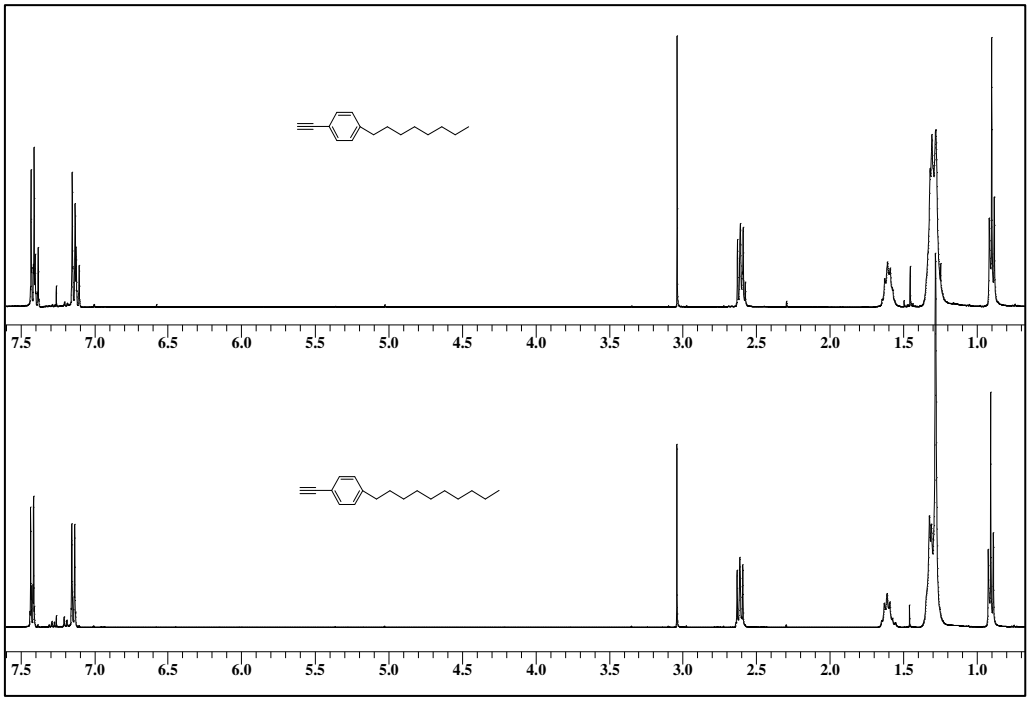


Figure 6.5: ^{1}H NMR spectra of the ethynyl precursors **48** and **51**.

Mass spectrometric characterisation

We obtained mass spectra for 1-butyl-4-ethynylbenzene (**45**), 1-ethynyl-4-octylbenzene (**48**) and 1-decyl-4-ethynylbenzene (**51**). They were all characterised with the electrospray technique. These compounds show simple mass spectra with two peaks. In each case the peaks could be assigned to the "phenyl-ethynyl-CH_2" *m/z* value and to the "L" *m/z* value. Table 6.3 summarises the different mass peaks detected for **45**, **48** and **51**.

Ligand	**45**		**48**		**51**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L]^+$	158	158	214	214	242	242
$[ethynyl\text{-}phenyl\text{-}CH_2]^+$	114	115	114	115	114	115

Table 6.3: Calculated and detected *m/z* values for **45**, **48** and **51**.

All *m/z* values are perfectly consistent with the calculated mass values. Two examples of mass spectra are presented in Figure 6.6 (ethynyl precursors **48** and **51**).

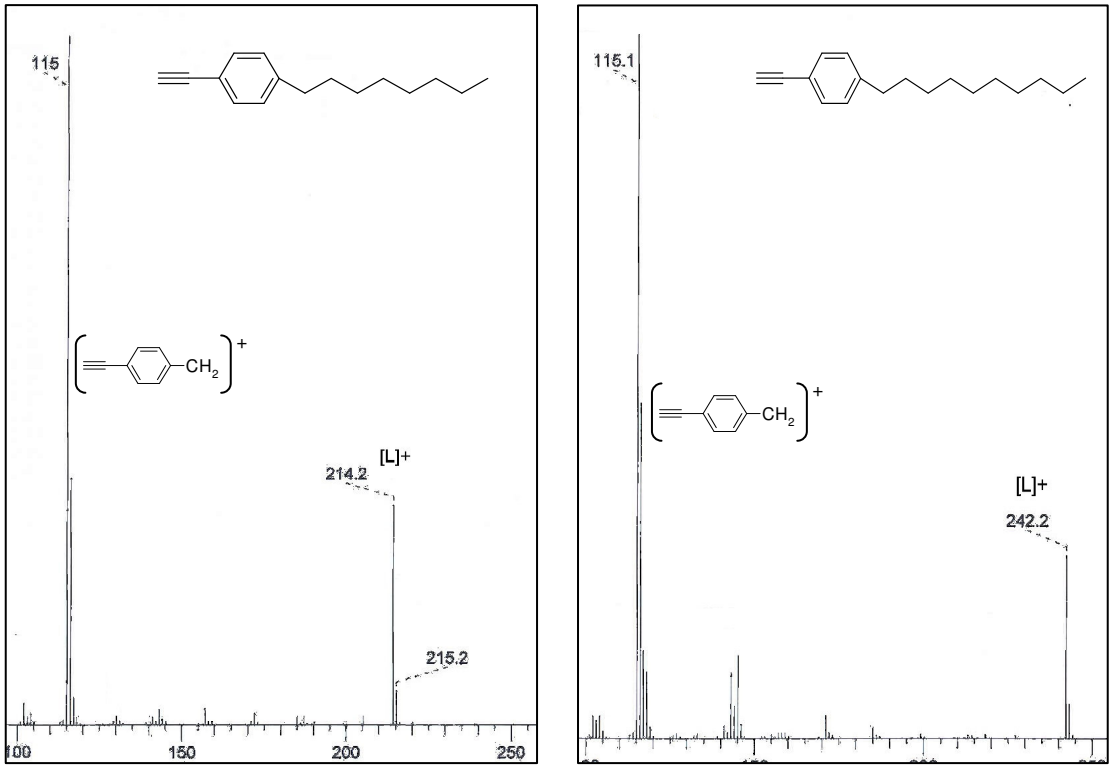


Figure 6.6: Mass spectra of the ethynyl precursors **48** and **51**.

VI.3 Synthesis of pyridazine with pendant alkyl chains

VI.3.1 Synthetic method

As presented in the other chapters the synthesis of substituted pyridazine with alkyl chains is based on the method presented in chapter II[8]. These ligands are easily accessible via an inverse electron demand Diels Alder reaction between 1,2,4,5-tetrazines and a wide range of alkynes, whereby the 1,2,4,5-tetrazine acts as the electron deficient diene[9].

The procedure to synthesise the N-donor pyridazine ligands is the same as the procedures presented in the past chapters. 3,6-Bis(2'-pyridyl)-1,2,4,5-tetrazine (**1**)

was dissolved in toluene with the ethynyl precursors and placed under reflux. By using this method we synthesized four different ligands (**46**, **49**, **52** and **53**).
Reactant ratio, time, solvent and yields are listed in Table 6.4.

Ligand	**Reaction ratio** (tetrazine / ethynyl)	**Reaction temperature** (°C)	**Solvent**	**Reaction time**	**Yield** (%)
46	1 to 1.2	120	toluene	88 hrs	78
49	1 to 1.3	120	toluene	7 days	93
52	1 to 1.1	120	toluene	3 days	90
53	1 to 1.6	120	toluene	50 hrs	68

Table 6.4: Reaction conditions for the synthesis of the ligands **46**, **49**, **52** and **53**.

All the inverse electron-demand Diels Alder reactions presented in this chapter were easy to carry out and there was no need to use a nitrogen or argon atmosphere or freshly distilled toluene. These reactions had various reaction times based on the disappearance of the characteristic purple colour of the 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine (**1**). They all had relatively good yields (between 68% and 90%).
The four ligands were purified by chromatographic work-up over alumina.

VI.3.2 Characterisation of alkylated pyridazines

Every compound has been characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analyses.

^{1}H NMR spectroscopy

^{1}H NMR spectroscopy of compound **46** and **49** were run in deuterated chloroform, **52** and **53** were run deuterated DMSO, and could be assigned by the chemical shifts, relatives integrals, and the coupling patterns.

The ^{1}H NMR spectra of the compounds **46** and **49** and the assignments are shown in Figure 6.7.

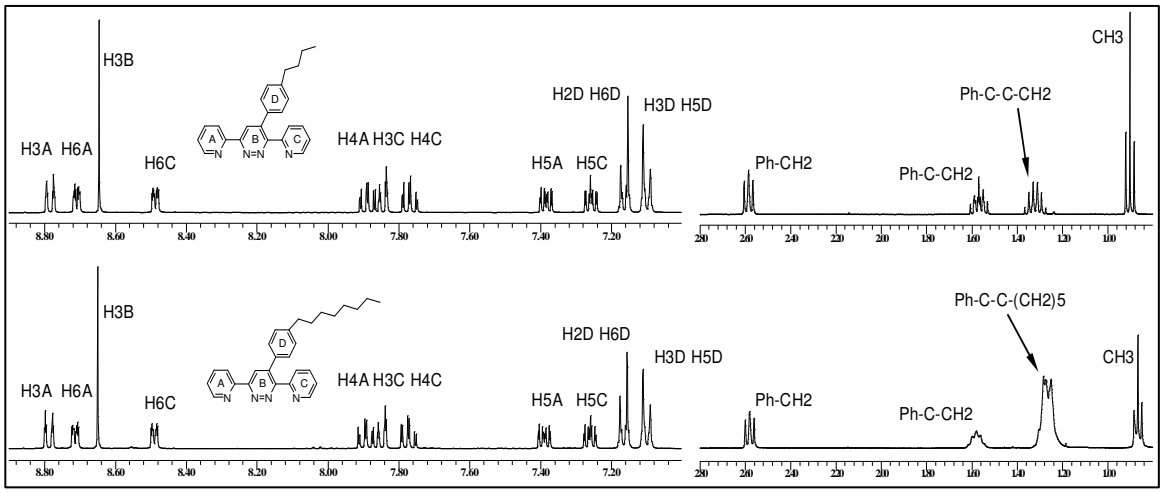


Figure 6.7: The ^{1}H NMR spectra and assignments of ligands **46** and **49** run in deuterated chloroform.

The ^{1}H NMR spectra of the compounds **52** and **53** and the assignments are shown in Figure 6.8.

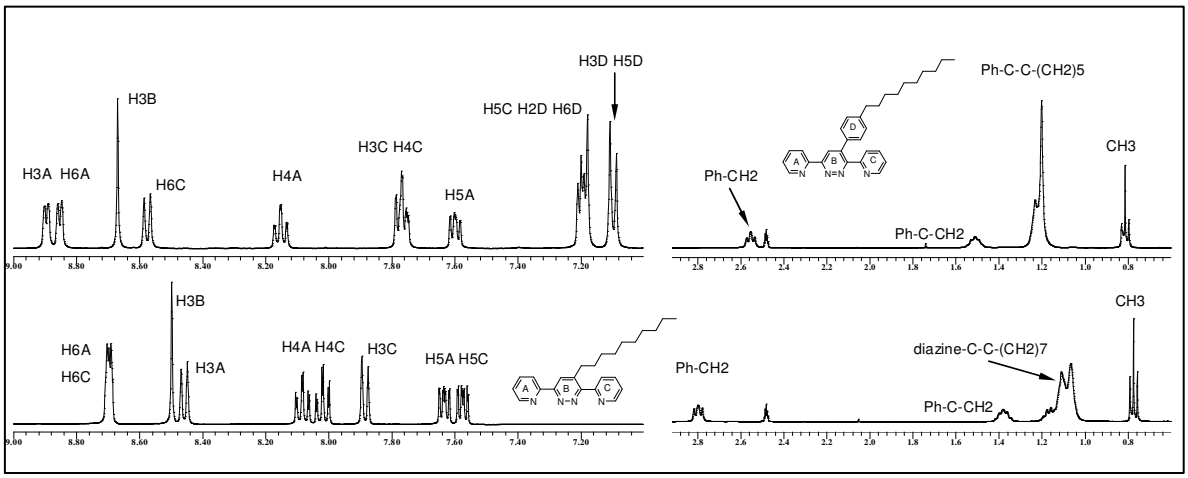


Figure 6.8: The ^{1}H NMR spectra and assignments of ligands **52** and **53** run in deuterated DMSO.

We can see that the compounds show sharp and well defined ^{1}H NMR spectra. The non symmetry of the dipyridin-2-ylpyridazine part of the molecule (due to the substituent) result in a set of nine different NMR signals instead of the four signals present in the spectrum of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**). Each ^{1}H NMR spectrum shows four doublets (H_{3A}, H_{3C}, H_{6A}, H_{6C}), two triplets of doublets (H_{4A}, H_{4C}), two doublets of doublets (H_{5A}, H_{5C}) and the typical singlet[10] (H_{3B}). All these signals are in the same region, between δ 7 and 9 ppm. We can also notice an overlapping of some signals. In compound **53** the protons signals H_{6A} and H_{6C} overlap at δ 8.6 ppm.

The protons of the substituent ring are also assigned by the coupling patterns and relative integrals. The signals of the phenyl substituent from the compounds **46**, **49** and **52** are as expected[10]. They present two doublets, both, integrating respectively for 2 protons.

The ^{1}H NMR signals of the alkyl chain always show the same shapes. In fact, there are a triplet, two multiplets and a triplet. All the ^{1}H NMR spectroscopic data for the ligands presented in this chapter are summarized in the Table 6.5.

Ligand	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring	Others
46 (δ/ppm)	8.78 d	7.89 td	7.38 dd	8.71 d	8.46 s	7.84 d	7.77 td	7.25 m	8.48 d	7.16-7.10 d	2.58t- 1.57m- 1.32m- 0.90t
49 (δ/ppm)	8.78 d	7.89 td	7.39 dd	8.71 d	8.65 s	7.85 d	7.77 td	7.26 m	8.49 d	7.16-7.10 d	2.58t- 1.56m- 1.27m- 0.86t
52 (δ/ppm)	8.80 d	7.92 td	7.42 dd	8.74 d	8.67 s	7.85 d	7.80 td	7.29 m	8.51 d	7.18-7.11 d	2.59t- 1.59m- 1.28m- 0.88t
53 (δ/ppm)	8.72 d	7.87 td	7.38 dd	8.72 m	8.49 s	8.08 d	7.87 td	7.38 dd	8.72 m	ₒ	3.06t- 1.58m- 1.24m- 0.85t

Table 6.5: The ^{1}H NMR spectroscopic characterisation of ligands **46**, **49**, **52** and **53**.

We can see that all the phenyl mono-substituted ligands have the same chemical shift for the same proton. In fact, the H_{3A} proton is around δ 8.8 ppm for each ligand, the H_{4A} proton is around δ 7.9 ppm, and the H_{5A} proton is around δ 7.4 ppm.

It means that we have the same chemical effect, due to the substituent, for each mono-substituted compound. This effect does not depend on the length of the alkyl chain.

Mass spectrometry

Mass spectra of ligands **46**, **49**, **52** and **53** were recorded with the electrospray ionisation technique. For all the spectra we can see the $[L+K+DCM]^+$ peak and the $[2L+K+DCM]^+$ peak. All the mass spectra have an additional peak corresponding to $[2L+Na+MeCN]^+$ for **46**, **49** and **52**. Ligand **53** has a third mass peak where the *m/z* value correspond to $[2L+Na+K]^+$. All *m/z* are perfectly consistent with the calculated mass.

Figure 6.9 shows the mass spectra of compound **49** and **52**.

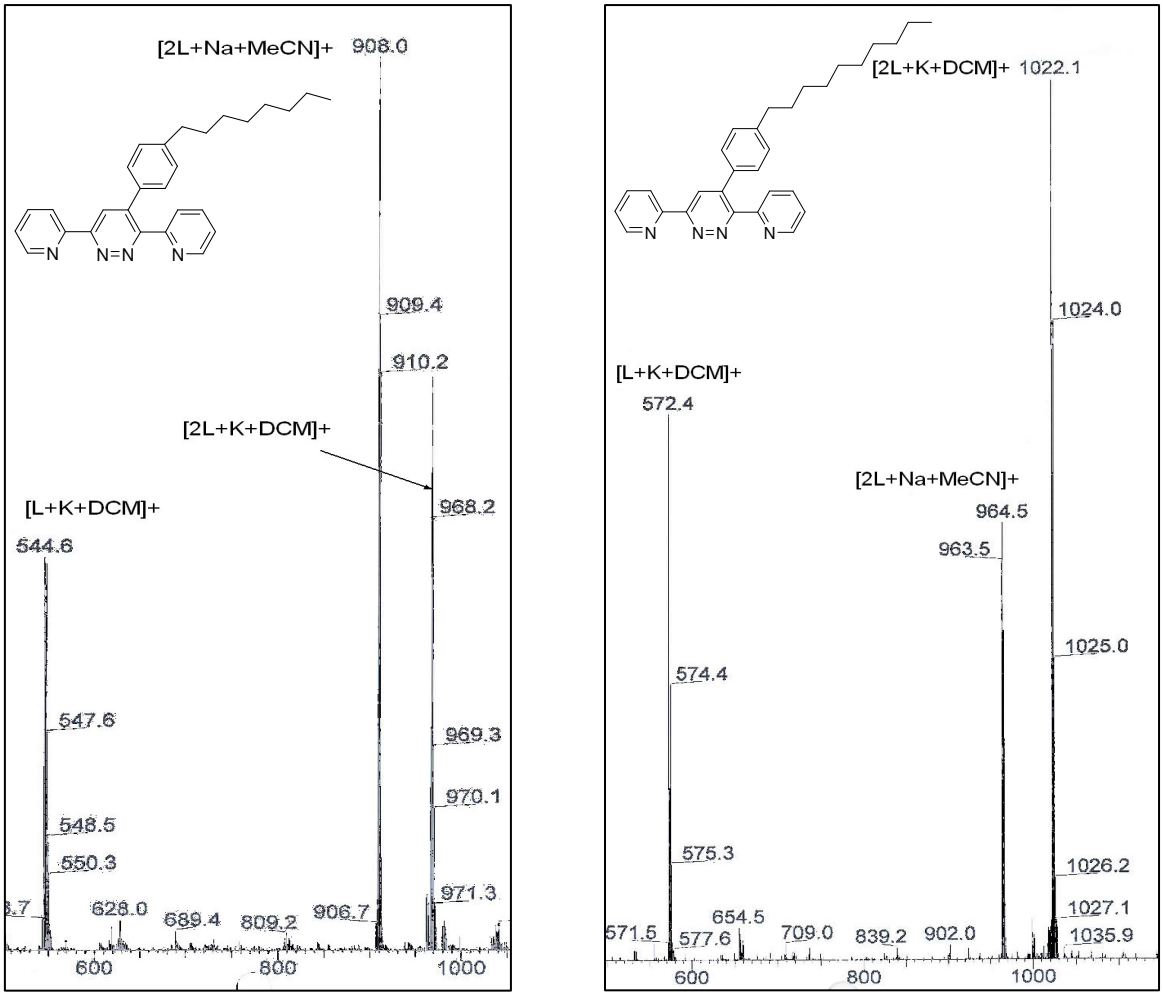


Figure 6.9: Mass spectra of the ligand **49** and **52**.

All the *m/z* values for each ligand are summarised in Table 6.6.

Ligand	**46**		**48**		**52**		**53**	
	m/z calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.	*m/z* calc.	*m/z* det.
$[L+Na+K]^+$	°	°	°	°	°	°	811	811
$[Na+2L+MeCN]^+$	796	795	908	908	965	964	°	°
$[K+L+DCM]^+$	487	488	543	544	571	572	495	496
$[K+2L+DCM]^+$	855	855	910	910	1020	1022	868	869

Table 6.6: Calculated and detected *m/z* values for the ligands **46**, **48**, **52** and **53**.

VI.4 Synthesis of the silver complexes

VI.4.1 Synthetic method

The ligands synthesised in this chapter have long alkyl chains. In these cases we did not think that the substituents will induce steric effects leading to non square planar silver(I)centres. The past chapters of this work showed us that almost all the complexes, of which we had a crystal structure, showed a $[Ag_2(L)_2]^+$ cation.

The ligands synthesised in this chapter have been used to prepare their silver complexes **46sc**, **49sc**, **52sc** and **53sc**. The reaction of the ligands with the silver salt in acetonitrile proceeded smoothly to give a yellow-orange or brown solution from which the complex was isolated as $[BF_4]^+$ salts.
Table 6.7 summarises the experimental conditions for the synthesis of the species **46sc**, **49sc**, **52sc** and **53sc**.

Silver complex	**Reaction ratio** (ligand / silver)	**Silver salt**	**Yield** (%)
46sc	1 to 1	$AgBF_4$	84
49sc	1 to 1	$AgBF_4$	88
52sc	1 to 1	$AgBF_4$	78
53sc	1 to 1	$AgBF_4$	88

Table 6.7: Experimental method for the synthesis of the silver complexes **46sc, 49sc, 52sc and 53sc.**

All the silver complexes were prepared by mixing silver tetrafluoroborate and the ligand in acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes. They were easily accessible and it was not necessary to proceed to a chromatographic work up or recrystallisation. All the silver complexes are insoluble in chloroform, slightly soluble in acetonitrile, and soluble in dimethylsulfoxide.
The silver complexes were easily accessible and there was no need to proceed to purification. Column chromatography or recrystallisations were not necessary.

VI.4.2 Characterisation of the silver complexes

The complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry.
All the ^{1}H and ^{13}C NMR spectra of the silver complexes were run in deuterated dimethylsulfoxide. It appeared to be the best solvent for NMR characterisation of the complexes.
46sc, **49sc**, **52sc** and **53sc** were also characterised by mass spectrometry. All the details are given in the experimental section at the end of this chapter.

[1]H NMR spectroscopy

[1]H NMR spectroscopy of complexes **46sc**, **49sc**, **52sc** and **53sc** were run in deuterated dimethylsulfoxide and could be assigned by the chemical shifts, relative integrals and the coupling patterns. [1]H NMR spectra of the silver complexes **46sc**, **49sc**, **52sc** and **53sc** and the assignments are shown in figures 6.10 and 6.11.

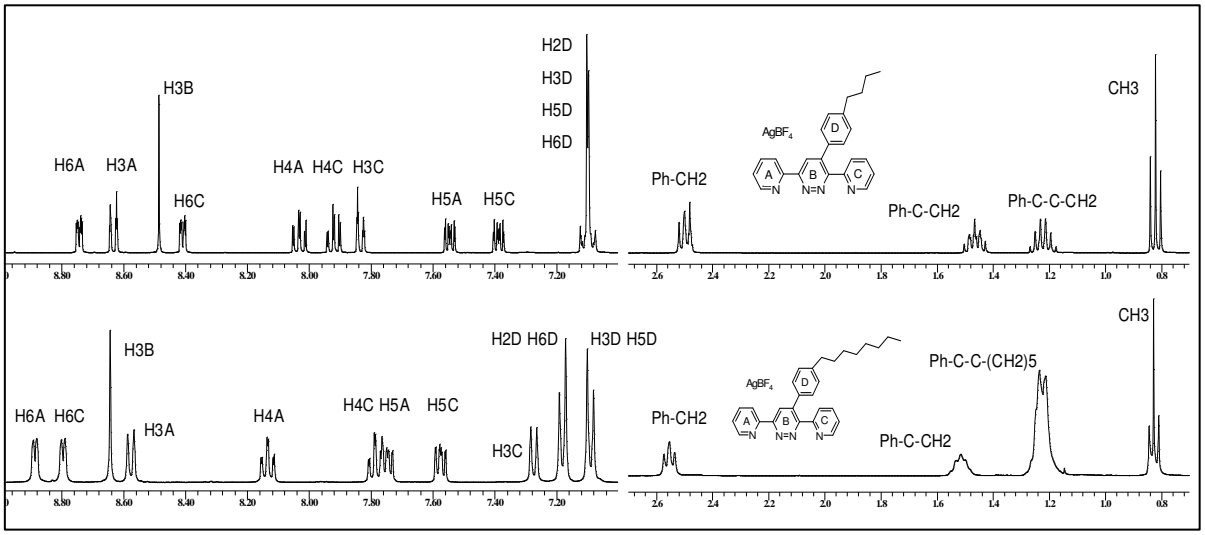


Figure 6.10: [1]H NMR spectra of silver complexes **46sc** and **49sc**.

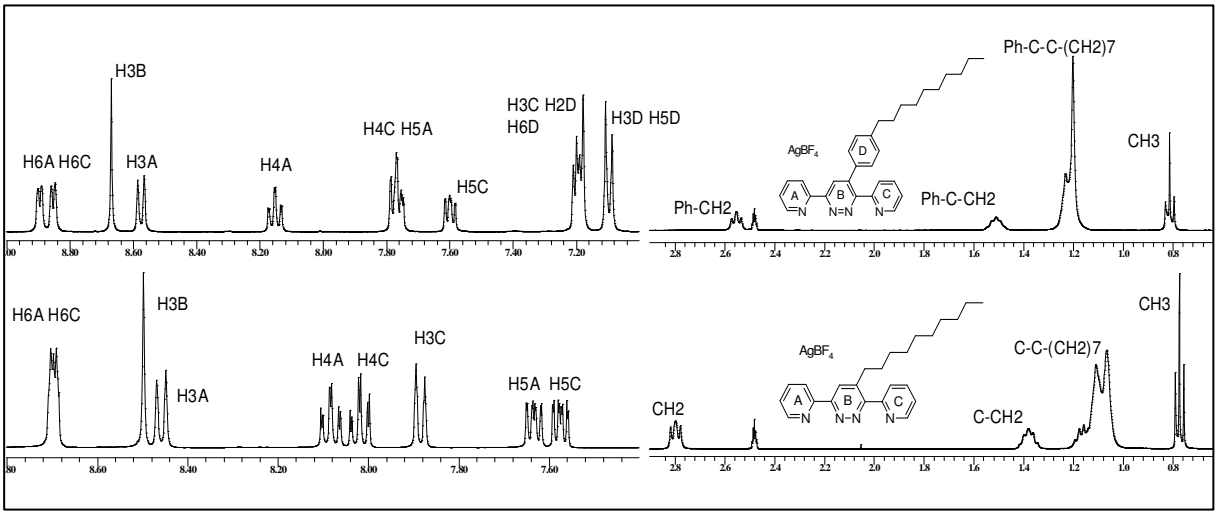


Figure 6.11: [1]H NMR spectra of silver complexes **52sc** and **53sc**.

All the [1]H NMR spectra show the same signals as those present in the [1]H NMR spectrum of their respective ligand. The spectrum of each of the alkyl chain substituted pyridazine silver complexes **46sc**, **49sc**, **52sc** and **53sc** exhibits a signal

(singlet) for the H_{3B} proton. This signal is typically shifted to higher field with respect to the free ligand, which is characteristic for a silver complexation[11]. The spectra of all the silver complexes exhibited a single ligand environment. No species other than the free ligands and the silver complexes were detected by ^{1}H NMR spectroscopy.

The complexation of the ligand and the silver species induces some overlapping of signals. In the silver complex **46sc** the phenyl proton signals have the same chemical shift (δ 7.10 ppm). Overlapping also appears in the ^{1} H NMR spectrum of **49sc**, and the signals of protons H_{4C} and H_{5A} overlap. Complex **52sc** has three signals that overlap (H_{3C}, H_{2D} and H_{6D}). The last spectrum shows the overlapping of the signals of protons H_{6A} and H_{6C}. It is important to notice that the protons H_{3B}, H_{6A+6C} and H_{3A+3C} are the most affected by the silver complexation, with their signals being shifted to higher field. This effect is due to the short distance between the affected proton and the N-Ag bond.

Table 6.8 summarises the ^{1}H NMR spectroscopic data for the silver complexes presented in this chapter.

Complex	H3A	H4A	H5A	H6A	H3B	H3C	H4C	H5C	H6C	Phenyl Ring	Others
46sc (δ/ppm)	8.65 d	8.05 td	7.56 dd	8.76 d	8.50 s	7.84 d	7.95 td	7.41 m	8.43 d	7.12m	2.51m- 1.48m- 1.24m- 0.84t
49sc (δ/ppm)	8.59 d	8.15 td	7.80 m	8.90 d	8.66 s	7.29 d	7.80 m	7.59 dd	8.81 d	7.19-7.10 d	2.57t- 1.53m- 1.24m- 0.85t
52sc (δ/ppm)	8.59 d	8.17 td	7.88 m	8.91 d	8.69 s	7.21 m	7.88 m	7.62 dd	8.87 d	7.21m- 7.11 d	2.57t- 1.53m- 1.23m- 0.83t
53sc (δ/ppm)	8.47 d	8.10 td	7.65 dd	8.71 m	8.52 s	7.90 d	8.03 td	7.59 dd	8.71 m	°	2.82t- 1.40m- 1.13m- 0.79t

Table 6.8: The ^{1} H NMR spectroscopic characterisation of silver complexes **46sc**, **49sc**, **52sc** and **53sc**.

For the free ligands, we saw that protons in the same region but in different ligands, came at the same chemical shifts in the ^{1}H NMR spectrum. However this is not true in the silver complexes. There is an effect due to the complexation but this effect on the ^{1}H NMR spectra is not the same for the different complexes. We could think it will be the same effect for the three complexes. In fact the only difference between these three complexes is the length of their alkyl chain. We have seen that for the free

ligands this length has no influence on their respective ^{1}H NMR spectra. However the complexes exhibit significantly different ^{1}H NMR spectra.

Mass spectrometry

All the silver complexes were characterised by mass spectrometry. Mass spectrometry of complexes **46sc**, **49sc** and **52sc** were recorded using the electrospray ionisation technique. For these three spectra, we can see the $[L]^+$ peak, the $[Ag+L]^+$ peak, the $[Ag+L+MeCN]^+$ peak, the $[Ag+2L]^+$ peak and the $[2Ag+2L+BF_4]^+$ peak. The last complex (**53sc**) shows four peaks ($[L]^+$, $[Ag+L+MeCN]^+$, $[Ag+2L]^+$ and $[2Ag+2L+BF_4]^+$).

Table 6.9 summarises the calculated and the detected *m/z* values for each silver complex, and Figure 6.12 shows representative mass spectra (**46sc** and **49sc**).

silver complex	**46sc**		**49sc**		**52sc**		**53sc**	
	m/z cal	*m/z* det	*m/z* cal	*m/z* det	*m/z* cal	*m/z* det	*m/z* cal	*m/z* det
$[L]^+$	366	367	422	423	450	451	374	375
$[AgLMeCN]^+$	°	°	°	°	°	°	521	522
$[AgL]^+$	472	473	528	529	556	557	°	°
$[Ag2L]^+$	840	841	952	953	1008	1009	856	857
$[AgL3MeCN]^+$	599	600	656	657	682	683	°	°
$[2Ag2LBF4]^+$	1034	1035	1146	1147	1202	1203	1050	1051

Table 6.9: Calculated and detected *m/z* values for the species **46sc**, **49sc**, **52sc** and **53sc**.

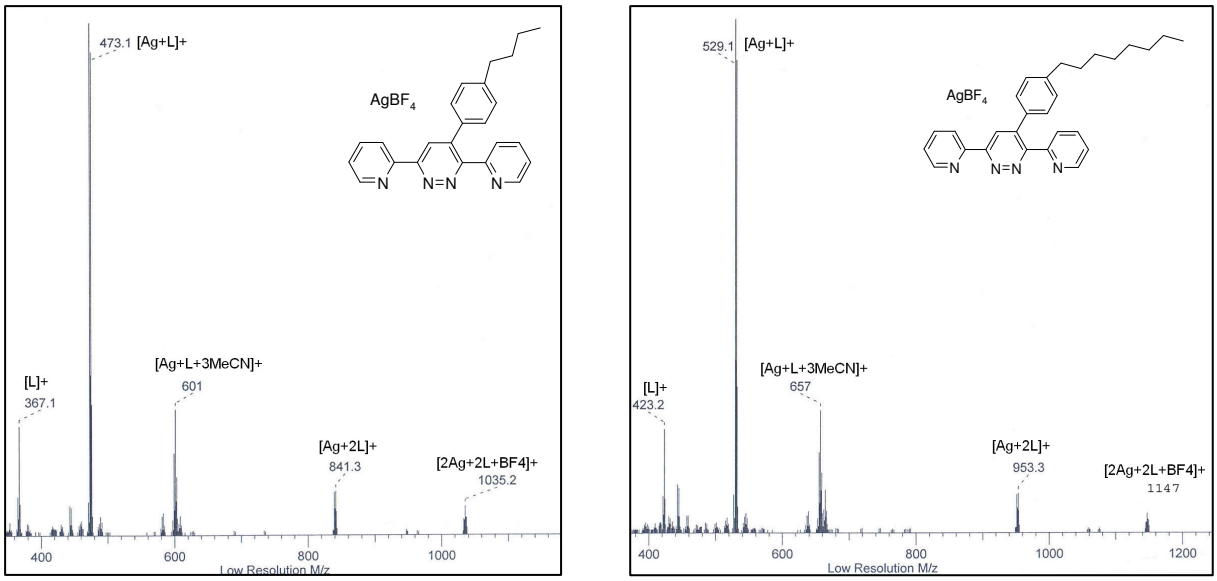


Figure 6.12: Mass spectra of silver complexes **46sc** and **49sc**.

Single crystal structure for silver complex **53sc**

Crystals of **53sc** are colourless plates. **53sc** crystallizes in the triclinic space group P-1. Two crystallographically independant (but structurally similar) $[Ag(\mathbf{53})_2]^+$ cations are observed. Two ligands coordinate to each silver ion. The difference between two independant complex ion lies in the bond angles and in the torsion angles. Each ligand has two N-donor sites that coordinate a silver ion, and two other N-donor sites remain uncoordinated. This case appears in the two different $[Ag(\mathbf{53})_2]^+$ species. Each species exhibits four normal Ag-N contacts[12] (species A: 2.333(3), 2.378(3), 2.375(3), 2.347(3)Å, species B: 2.268(3), 2.419(4), 2.297(3), 2.420(3)Å). In each species, the two ligands are arranged in a *trans* configuration around the silver core (Figure 6.13).

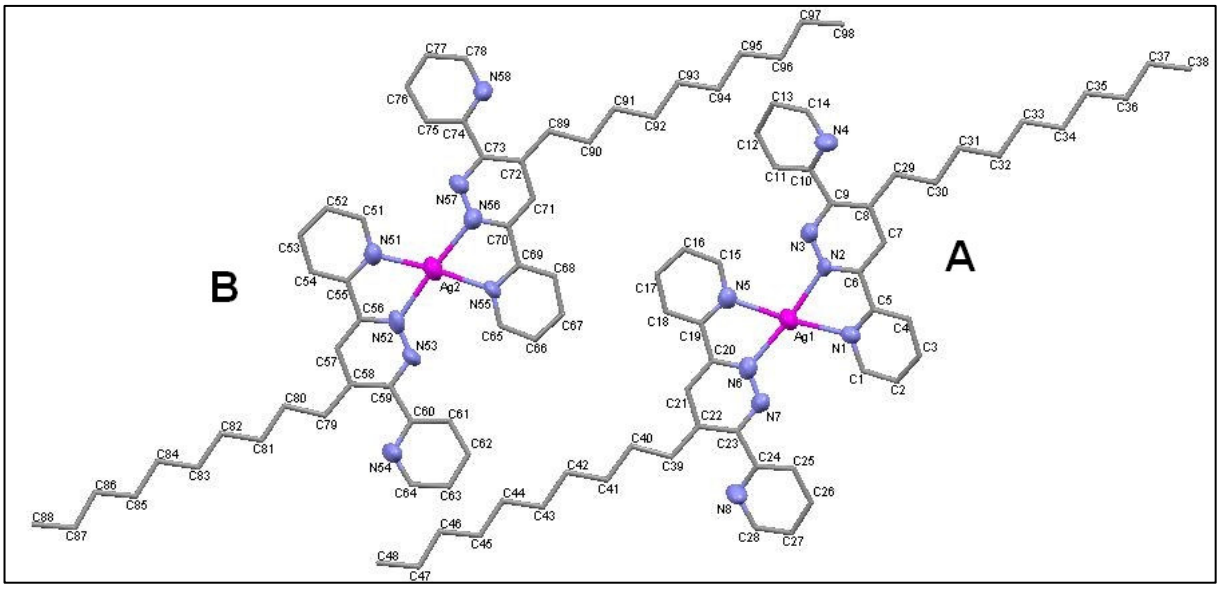


Figure 6.13: The molecular structure of (the two species) **53sc** with the labelling scheme.

The decyl chain substituents are twisted with respect to the pyridazine unit to which they are bound, with a torsion angle of 0.48° and 4.51° (species A) and 0.03° and 1.91 (species B). The terminal pyridine rings are also significantly out of the plane of the pyridazine unit with torsion angles between 2.92° and 28.71° (Figure 6.14).

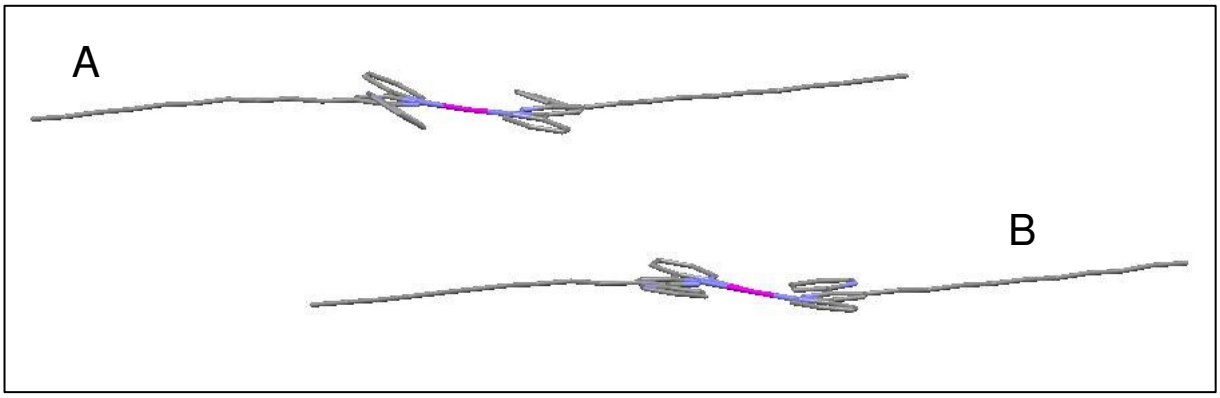


Figure 6.14: The molecular structure of **53sc**, non planar rings.

The silver-silver distance (between specie A and B) is 14.5Å (i. e. far too long to be a bounding interaction), and the N-Ag-N angles are between 69.1 and 69.9°. The important bonds, angles and torsion angles are listed in Table 6.10. Details of the structure solution are given in Appendix 12.

Bond		Å
Ag1	N1	2.333(3)
Ag1	N2	2.378(3)
Ag1	N5	2.375(3)
Ag1	N6	2.347(3)
Ag2	Ag2	3.5375(15)
Ag2	N51	2.268(3)
Ag2	N52	2.419(4)
Ag2	N55	2.297(3)
Ag2	N56	2.420(3)

Angles			Deg(°)
N1	Ag1	N2	69.74(15)
N1	Ag1	N5	173.28(17)
N2	Ag1	N5	104.11(15)
N1	Ag1	N6	116.34(15)
N2	Ag1	N6	173.03(14)
N5	Ag1	N6	69.65(15)
N51	Ag2	N52	69.12(16)
N51	Ag2	N55	174.00(15)
N52	Ag2	N55	106.21(16)
N51	Ag2	N56	114.69(16)
N52	Ag2	N56	175.94(13)
N55	Ag2	N56	69.89(15)

Torsion angles specie A				Deg(°)
N55	C19	C20	N6	17.42
N7	C23	C24	C25	21.60
C11	C10	C9	N3	28.71
N2	C6	C5	N1	16.50

Torsion angles specie B				Deg(°)
N51	C55	C56	N52	9.15
N53	C59	C60	C61	2.92
C75	C74	C73	N57	3.22
N56	C70	C69	N55	13.62

Table 6.10: Important bond distances, angles and torsion angles present in **53sc**.

The packing shows four $[Ag(\mathbf{53})_2]^+$ species. They are almost coplanar. There is an alternating placement of the species. One B, then two A and finally one B species. The two A species are really close together, one over the other. There is certainly an interaction between the two A species, but the distance between two pyridyl rings (ring A from species A and ring A from species B : 3.7Å) indicates only weak π-π interactions (Figure 6.15).

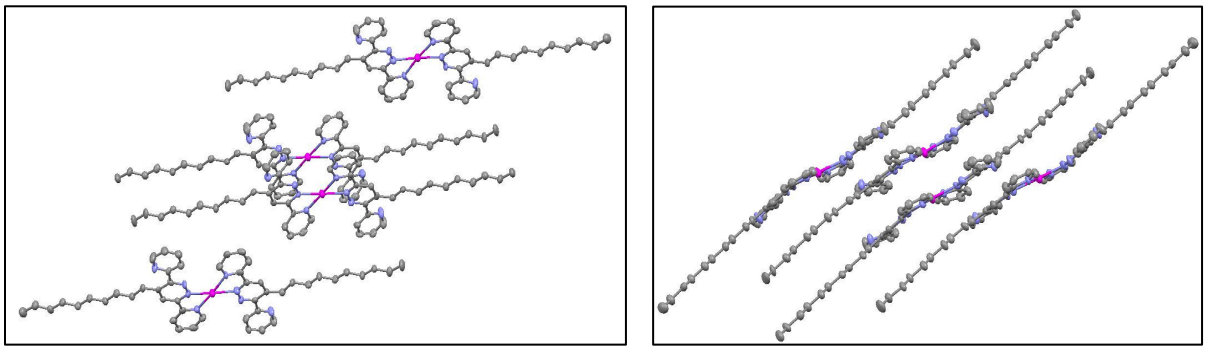


Figure 6.15: Arrangement of the $[Ag(\mathbf{53})_2]^+$ cations in the crystal structure of **53sc**.

VI.5 Conclusion

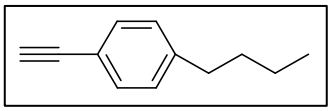
In this chapter we described the synthesis of the ethynyl precursors **45, 48** and **51** that have been prepared with the Sonogashira reaction.

We also showed the methodology to access to mono-substituted pyridazines, based on a retro Diels-Alder reaction that enabled us to prepare the ligands **46**, **49**, **52** and **53**. These ligands were characterised by NMR spectroscopy, mass spectrometry and elemental analysis. Four new silver complexes (**46sc**, **49sc**, **52sc** and **53sc**) were prepared and characterised by NMR spectroscopy, and mass spectrometry.

We obtained suitable crystals for silver complex **53sc** to carry out single X-ray diffraction analysis. The crystal structures showed two $[Ag(L)_2]^+$ cation in the asymmetric unit with an arrangement of the ligands in a *trans* conformation around the silver centre. This crystal structures did not show a grid like structure[13], or hydrogen bonding interactions.

VI.6 Experimental part

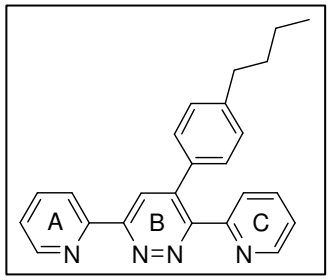
Synthesis of 1-butyl-4-ethynylbenzene (45)



Under argon and exclusion of moisture, 1-butyl-4-iodobenzene (2.0 g, 7.7 mmol), CuCl (76 mg, 0.77 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.55 g, 0.77 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (1.4 ml, 10 mmol) was added and the mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (120 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown oil (1.1 g, 6.9 mmol, 90%, $C_{12}H_{14}$, 158.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.40 (d, J=8.4 Hz, 2H, H_{2+6}), 7.13 (d, J=8.0 Hz, 2H, H_{3+5}), 3.02 (s, 1H, ethynyl), 2.60 (t, J=8.0 Hz, 2H, Ph-CH_2), 1.54 (m, 2H, Ph-C-CH_2), 1.34 (m, 2H, Ph-C-C-CH_2), 0.94 (t, J=7.8 Hz, 3H, Ph-C-C-C-CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 143.9, 131.9, 128.3, 119.1, 83.8, 35.5, 33.3, 29.6, 22.2, 13.9.
MS (EI) m/z: $[L\text{-}(CH_2\text{-}CH_2CH_3)]^+$ 115, $[L\text{-}(CH_2CH_3)]^+$ 128, $[L]^+$ 158.

Synthesis of 4-(4-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (46)

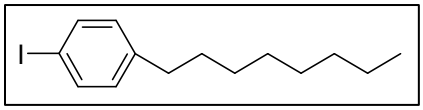


3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.52 g, 2.2 mmol) and 1-butyl-4-ethynylbenzene (**45**) (0.40 g, 2.5 mmol) were dissolved in toluene (120 ml). The

solution was refluxed for 88 hours. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:1), the second band was collected). The product was obtained as brown oil (0.62 g, 1.7 mmol, 78%, $C_{24}H_{22}N_4$, 366.5 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.78 (d, J=7.6 Hz, 1H, H_{3A}), 8.71 (d, J=5.0 Hz, 1H, H_{6A}), 8.46 (s, 1H, H_{3B}), 8.48 (d, J=5.0 Hz, 1H, H_{6C}), 7.89 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.84 (d, J=7.6 Hz, 1H, H_{3C}), 7.77 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.38 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.25 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 7.16 (d, J=8.5 Hz, 2H, H_{2D+6D}), 7.10 (d, J=8.1 Hz, 2H, H_{3D+5D}), 2.58 (t, J=7.5 Hz, 2H, Ph-CH_2), 1.57 (m, 2H, Ph-C-CH_2), 1.32 (m, 2H, Ph-C-C-CH_2), 0.90 (t, J=7.1 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.3, 157.6, 155.9, 153.4, 149.3, 148.9, 143.3, 140.4, 137.0, 136.4, 133.9, 128.7, 128.4, 125.4, 124.8, 123.2, 121.7, 35.2, 33.2, 22.2, 13.8, 3 carbon signals unresolved.
MS (ESI) m/z: $[L+K+DCM]^+$ 488, $[2L+Na+MeCN]^+$ 795, $[2L+K+DCM]^+$ 855.
Elem. Anal. ($C_{24}H_{22}N_4$) [%]: calc. C 78.7, H 6.1, N 15.3, found C 77.7, H 6.2, 15.1.

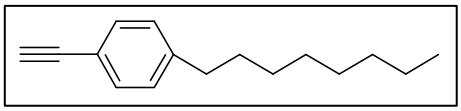
Synthesis of 1-iodo-4-octylbenzene (47)



Under argon, 4-octylaniline (1.0 g, 4.9 mmol) was suspended in water (150 ml). Concentrated hydrochloric acid (1.8 ml) was added and the brown solution cooled to 0°C. A solution of sodium nitrite (0.80 g, 12 mmol) in 20 ml water was slowly added. The mixture was stirred at 0°C for one hour. A catalytic amount of copper(I) iodide (115 mg) was added before the slow addition of potassium iodide (4.0 g, 25 mmol). The mixture was stirred at 0°C for 6 hours. From time to time, tetrahydrofuran (total 70 ml) was added to increase the solubility. Water (50 ml) and diethyl ether (80 ml) were added under vigorous stirring and the two layers separated. The aqueous layer was extracted with diethyl ether and the combined organic phases washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the dark residue purified by chromatographic work-up (alumina, hexane, the second band was collected) to give an orange oil (1.5 g, 4.7 mmol, 96%, $C_{14}H_{21}I$, 316.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.59 (d, J=7.6 Hz, 2H, H_{2+6}), 6.93 (d, J=8.0 Hz, 2H, H_{3+5}), 2.53 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.58 (t, J=7.6 Hz, 2H, Ph-C-CH_2), 1.27 (m, 10 H, Ph-C-C-$(CH_2)_5$), 0.89 (t, J=7.1 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 142.4, 137.1, 130.5, 90.4, 76.9, 35.4, 31.8, 31.2, 29.2, 22.6, 14.0, 1 carbon signal unresolved.
MS (ESI) m/z: $[L\text{-}(CH_2)_6CH_3]^+$ 216, $[L]^+$ 316.

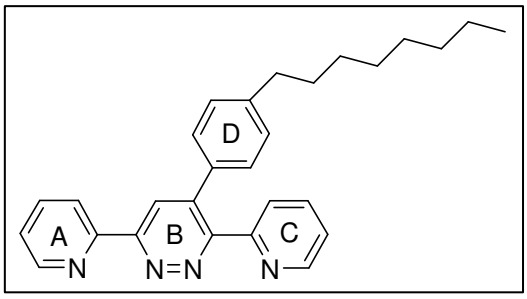
Synthesis of 1-ethynyl-4-octylbenzene (48)



Under argon and exclusion of moisture, 1-iodo-4-octylbenzene (**47**) (1.0 g, 3.2 mmol), CuCl (32 mg, 0.32 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.23 g, 0.32 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (0.9 ml, 6 mmol) was added and the mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (100 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (120 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange oil (0.60 g, 2.8 mmol, 88%, $C_{16}H_{22}$, 214.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.42 (d, J=8.0 Hz, 2H, H_{2+6}), 7.14 (d, J=8.0 Hz, 2H, H_{3+5}), 3.04 (s, 1H, ethynyl), 2.61 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.61 (m, 2H, Ph-C-CH_2), 1.30 (m, 10H, Ph-C-C-$(CH_2)_5$), 0.90 (t, J=7.5 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 144.2, 132.3, 128.6, 120.5, 84.1, 36.2, 32.1, 31.5, 29.7, 29.6, 22.9, 14.4, 2 carbon signals unresolved.
MS (ESI) m/z: $[L\text{-}(CH_2)_6CH_3]^+$ 115, $[L]^+$ 214.

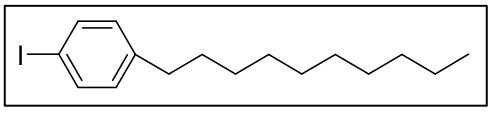
Synthesis of 4-(4-octylphenyl)-3,6-di(pyridin-2-yl)pyridazine (49)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.35 g, 1.5 mmol) and 1-ethynyl-4-octylbenzene (**48**) (0.40 g, 1.9 mmol) were dissolved in toluene (75 ml). The solution was refluxed for 7 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (3:2), the second band was collected). The product was obtained as a brown oil (0.60 g, 1.4 mmol, 93%, $C_{28}H_{30}N_4$, 422.6 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.78 (d, J=8.1 Hz, 1H, H_{3A}), 8.71 (d, J=4.5 Hz, 1H, H_{6A}), 8.65 (s, 1H, H_{3B}), 8.49 (d, J=4.5 Hz, 1H, H_{6C}), 7.89 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.85 (d, J=8.1 Hz, 1H, H_{3C}), 7.77 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.39 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.26 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 7.16 (d, J=8.0 Hz, 2H, H_{2D+6D}), 7.10 (d, J=8.0 Hz, 2H, H_{3D+5D}), 2.58 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.58 (m, 2H, Ph-C-CH_2), 1.27 (m, 10H, Ph-C-C-$(CH_2)_5$), 0.86 (t, J=7.5 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.3, 157.6, 155.9, 153.4, 149.3, 148.9, 143.4, 140.4, 137.1, 136.4, 133.9, 128.7, 128.4, 125.4, 124.8, 124.6, 123.2, 121.8, 35.5, 31.7, 31.1, 29.3, 22.6, 14.0, 4 carbon signals unresolved.
MS (ESI) m/z: $[L+K+DCM]^+$ 544, $[2L+Na+MeCN]^+$ 908, $[2L+K+DCM]^+$ 910.
Elem. Anal. ($C_{28}H_{30}N_4$ + 0.2 H_2O) [%]: calc. C 78.8, H 7.1, N 13.1, found, C 78.7, H 7.3, N 13.1.

Synthesis of 1-decyl-4-iodobenzene (50)

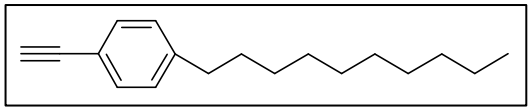


Under argon, 4-decylaniline (2.0 g, 8.6 mmol) was suspended in water (150 ml). Concentrated hydrochloric acid (3.6 ml) was added and the brown solution cooled to 0°C. A solution of sodium nitrite (1.6 g, 23 mmol) in 30 ml water was slowly added. The mixture was stirred at 0°C for one hour. A catalytic amount of copper(I) iodide

(145 mg) was added before the slow addition of potassium iodide (8.0 g, 49 mmol). The mixture was stirred at 0°C for 6 hours. From time to time, tetrahydrofuran (total 70 ml) was added to increase the solubility. Water (50 ml) and diethyl ether (80 ml) were added under vigorous stirring and the two layers separated. The aqueous layer was extracted with diethyl ether and the combined organic phases washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the dark residue purified by chromatographic work-up (alumina, hexane, the first band was collected) to give a brown oil (2.9 g, 8.4 mmol, 98%, $C_{16}H_{25}I$, 344.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.59 (d, J=8.0 Hz, 2H, H_{2+6}), 6.93 (d, J=8.4 Hz, 2H, H_{3+5}), 2.53 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.58 (m, 2H, Ph-C-CH_2), 1.28 (m, 14H, Ph-C-C-$(CH_2)_7$), 0.90 (t, J=7.5 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 142.4, 137.2, 130.5, 128.3, 128.1, 125.5, 90.5, 35.4, 31.8, 31.2, 29.6, 29.1, 22.6, 14.1.
MS (ESI) m/z: $[L\text{-}(CH_2)_8CH_3]^+$ 216, $[L]^+$ 344.
Elem. Anal. ($C_{16}H_{25}I$) [%]: calc. C 55.8, H 7.3, found, C 57.5, H 7.4.

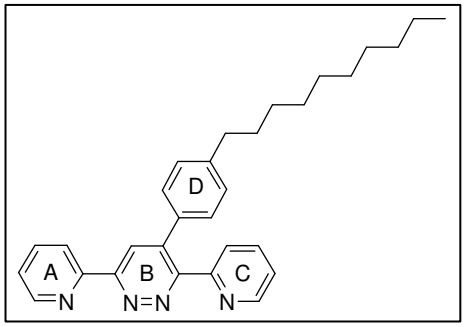
Synthesis of 1-decyl-4-ethynylbenzene (51)



Under argon and exclusion of moisture, 1-iodo-4-octylbenzene (**50**) (2.0 g, 5.8 mmol), CuCl (57 mg, 0.58 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.41 g, 0.58 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (1.25 ml, 9.03 mmol) was added and the mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (100 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The product was dissolved in THF (100 ml) and an aqueous solution of 1M NaOH added (120 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a beige powder (1.3 g, 5.4 mmol, 93%, $C_{18}H_{26}$, 242.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.42 (d, J=8.0 Hz, 2H, H_{2+6}), 7.14 (d, J=8.0 Hz, 2H, H_{3+5}), 3.04 (s, 1H, ethynyl), 2.61 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.62 (m, 2H, Ph-C-CH_2), 1.29 (m, 14H, Ph-C-C-$(CH_2)_7$), 0.91 (t, J=7.5 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 144.2, 132.2, 128.6, 125.8, 119.5, 84.1, 76.4, 36.2, 32.2, 31.5, 29.8, 29.6, 29.4, 29.3, 22.9, 14.4.
MS (ESI) m/z: $[L\text{-}(CH_2)_8CH_3]^+$ 115, $[L]^+$ 242.
Elem. Anal. ($C_{18}H_{26}$) [%]: calc. C 89.2, H 10.8, found, 89.1, 10.8.

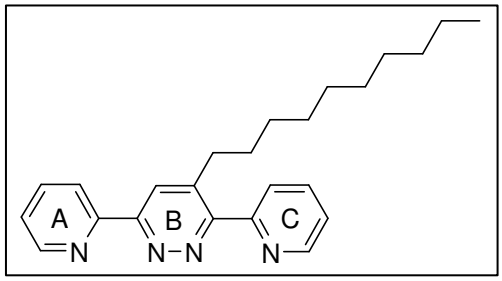
Synthesis of 4-(4-decylphenyl)-3,6-di(pyridin-2-yl)pyridazine (52)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.71 g, 3.0 mmol) and 1-decyl-4-ethynylbenzene (**51**) (0.80 g, 3.3 mmol) were dissolved in toluene (70 ml). The solution was refluxed for 3 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:1), the second band was collected). The product was obtained as a beige solid (1.2 g, 2.7 mmol, 90%, $C_{30}H_{34}N_4$, 450.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.80 (d, J=8.1 Hz, 1H, H_{3A}), 8.74 (d, J=4.5 Hz, 1H, H_{6A}), 8.67 (s, 1H, H_{3B}), 8.51 (d, J=4.5 Hz, 1H, H_{6C}), 7.92 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.85 (d, J=8.1 Hz, 1H, H_{3C}), 7.80 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.42 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.29 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}), 7.18 (d, J=8.0 Hz, 2H, H_{2D+6D}), 7.11 (d, J=8.0 Hz, 2H, H_{3D+5D}), 2.59 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.59 (m, 2H, Ph-C-CH_2), 1.28 (m, 14H, Ph-C-C-$(CH_2)_5$), 0.88 (t, J=7.5 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.6, 150.7, 149.3, 145.2, 137.3, 136.6, 134.5, 128.8, 128.5, 125.5, 125.3, 124.9, 124.7, 123.3, 123.2, 121.9, 117.5, 114.4, 35.6, 31.8, 31.2, 29.6, 29.4, 29.2, 22.7, 14.1, 4 carbon signals unresolved.
MS (ESI) m/z: $[L+K+DCM]^+$ 572, $[2L+Na+MeCN]^+$ 964, $[2L+K+DCM]^+$ 1022.
Elem. Anal. ($C_{30}H_{34}N_4$) [%]: calc. C 80.0, H 7.6, N 12.4, found, C 80.0, H, 7.6, N 12.4.

Synthesis of 4-decyl-3,6-di(pyridin-2-yl)pyridazine (53)



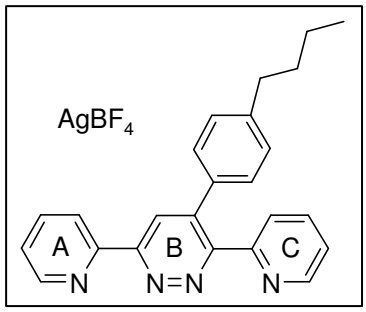
3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.94 g, 4.0 mmol) and dodecyne (1.0 g, 6.0 mmol) were dissolved in toluene (70 ml). The solution was refluxed for 50 hours. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (4:1), the second band was collected). The product was obtained as a yellow oil (1.0 g, 2.7 mmol, 68%, $C_{24}H_{30}N_4$, 374.5 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.72 (m, 3H, $H_{3A+6A+6C}$), 8.49 (s, 1H, H_{3B}), 8.08 (d, J=7.6 Hz, 1H, H_{3C}), 7.87 (m, 2H, H_{4A+4C}), 7.38 (m, 2H, H_{5A+5C}), 3.06 (t, J=7.6 Hz, 2H, diazine-CH_2), 1.58 (m, 2H, diazine-C-CH_2), 1.24 (m, 14H, diazine-C-C-$(CH_2)_7$), 0.85 (t, J=7.2 Hz, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.1, 157.1, 156.4, 153.6, 149.3, 148.4, 142.8, 137.1, 136.7, 125.5, 124.7, 124.5, 123.4, 121.7, 32.2, 31.8, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 22.6, 14.0.
MS (ESI) m/z: $[L+K+DCM]^+$ 496, $[2L+Na+K]^+$ 811, $[2L+DCM+K]^+$ 869.
Elem. Anal. ($C_{24}H_{30}N_4$) [%]: calc. C 77.0, H 8.1, N 15.0, found, C 76.6, H 8.1, N 14.8.

Silver complexes

All the silver complexes were prepared by using the same procedure. One equivalent of silver tetrafluoroborate or silver trifluoromethane sulfonate was mixed with one equivalent of the diazine ligand in 15 ml of acetonitrile. The mixture was sonicated for five minutes and then stirred under reflux for a further fifteen minutes. The solvent was evaporated to give the silver complexes.

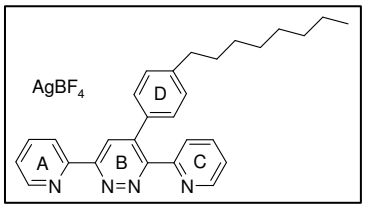
Synthesis of 4-(4-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (46sc)



4-(4-Butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**46**) (70 mg, 0.19 mmol) and silver tetrafluoroborate (37 mg, 0.19 mmol) were used to prepare the silver complex (88 mg, 0.16 mmol, 84%, $C_{24}H_{22}N_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.76 (d, J=4.0 Hz, 1H, H_{6A}), 8.65 (d, J=8.0 Hz, 1H, H_{3A}), 8.50 (s, 1H, H_{3B}), 8.43 (d, J=4.0 Hz, 1H, H_{6C}), 8.05 (td, J=7.6, 1.6 Hz, 1H, H_{4A}), 7.95 (td, J=7.6, 1.6 Hz, 1H, H_{4C}), 7.82 (d, J=8.0 Hz, 1H, H_{3C}), 7.56 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.41 (dd, J=7.8, 5.2 Hz, 1H, H_{5C}), 7.12 (m, 4H, $H_{2D+3D+5D+6D}$), 2.51 (m, 2H, Ph-CH_2), 1.48 (m, 2H, Ph-C-CH_2), 1.24 (m, 2H, Ph-C-C-CH_2), 0.84 (t, J=7.2 Hz, 3H, CH_3).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 158.3, 157.2, 155.6, 152.5, 149.7, 148.6, 142.8, 139.6, 137.6, 136.8, 133.6, 128.5, 128.2, 125.2, 124.6, 123.6, 121.1, 34.3, 32.7, 21.6, 13.6, 3 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 367, $[Ag+L]^+$ 473, $[Ag+L+3MeCN]^+$ 600, $[Ag+2L]^+$ 841, $[2Ag+2L+BF_4]^+$ 1035.
Elem. Anal. ($C_{24}H_{22}N_4AgBF_4$ + 0.5 CH_3CN) [%] calc. C 51.6, H 4.0, N 10.8, found, C 51.8, H 4.3, N 10.3.

Synthesis of 4-(4-octylphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (49sc)



4-(4-Octylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**49**) (70 mg, 0.17 mmol) and silver tetrafluoroborate (32 mg, 0.17 mmol) were used to prepare the silver complex (91 mg, 0.15 mmol, 88%, $C_{28}H_{30}N_4AgBF_4$).

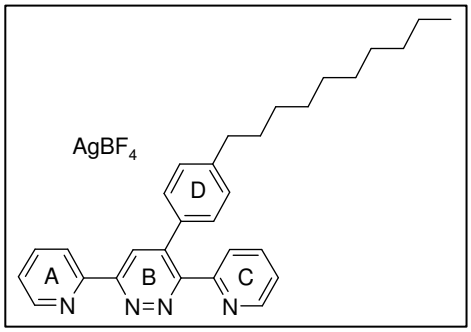
^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.90 (d, J=4.4 Hz, 1H, H_{6A}), 8.81 (d, J=5.2 Hz, 1H, H_{6C}), 8.66 (s, 1H, H_{3B}), 8.59 (d, J=8.0 Hz, 1H, H_{3A}), 8.15 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.80 (m, 2H, H_{4C+5A}), 7.59 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.29 (d, J=8.0 Hz, 1H, H_{3C}), 7.19 (d, J=8.4 Hz, 2H, H_{2D+6D}), 7.10 (d, J=8.0 Hz, 2H, H_{3D+5D}), 2.57 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.53 (m, 2H, Ph-C-CH_2), 1.24 (m, 10H, Ph-C-C-$(CH_2)_5$), 0.85 (t, J=7.2 Hz, 3H, CH_3).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.7, 155.2, 152.7, 150.7, 150.6, 149.8, 144.1, 141.3, 138.8, 137.4, 132.2, 129.0, 128.7, 127.4, 126.5, 126.2, 125.1, 123.6, 34.7, 31.2, 28.7, 28.6, 28.5, 22.0, 13.9, 3 carbon signals unresolved.

MS (ES) *m/z* $[L]^+$ 423, $[Ag+L]^+$ 529, $[Ag+L+3MeCN]^+$ 657, $[Ag+2L]^+$ 953, $[2Ag+L+BF_4]^+$ 1147.

Elem. Anal. ($C_{28}H_{30}N_4AgBF_4$) [%] calc. C 54.5, H 4.9, N 9.1, found, C 54.2, H 4.9, N 9.4.

Synthesis of 4-(4-decylphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (52sc)

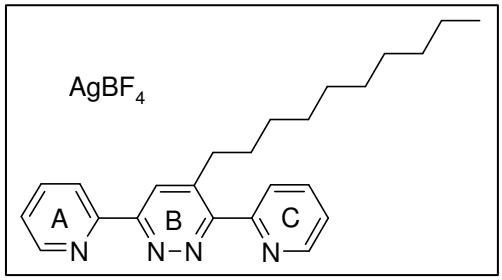


4-(4-Decylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**52**) (80 mg, 0.18 mmol) and silver tetrafluoroborate (35 mg, 0.18 mmol) were used to prepare the silver complex (87 mg, 0.14 mmol, 78%, $C_{30}H_{34}N_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.91 (d, J=4.4 Hz, 1H, H_{6A}), 8.87 (d, J=4.8 Hz, 1H, H_{6C}), 8.69 (s, 1H, H_{3B}), 8.59 (d, J=8.0 Hz, 1H, H_{3A}), 8.17 (t, J=7.6 Hz, 1H, H_{4A}), 7.88 (m, 2H, H_{4C+5A}), 7.62 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.21 (m, 3H, $H_{3C+2D+6D}$), 7.11 (d, J=8.4 Hz, 2H, H_{3D+5D}), 2.57 (t, J=7.6 Hz, 2H, Ph-CH_2), 1.53 (m, 2H, Ph-C-CH_2), 1.23 (m, 14H, Ph-C-C-$(CH_2)_7$), 0.83 (t, J=7.4 Hz, 3H, CH_3).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.6, 154.9, 152.3, 150.9, 149.4, 144.3, 141.6, 139.0, 137.5, 131.9, 129.1, 128.7, 127.8, 126.7, 126.3, 125.3, 123.9, 34.7, 31.2, 30.6, 28.9, 28.9, 28.7, 28.6, 28.5, 22.0, 13.8, 3 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 451, $[Ag+L]^+$ 557, $[Ag+L+3MeCN]^+$ 683, $[Ag+2L]^+$ 1009, $[2Ag+L+BF_4]^+$ 1203.
Elem. Anal. ($C_{30}H_{34}N_4AgBF_4$ + H_2O) [%] calc. C 54.3, H 5.5, N 8.5, found, C 53.9, H 5.3, N 8.5.

Synthesis of 4-decyl-3,6-di(pyridin-2-yl)pyridazine silver complex (53sc)



4-Decyl-3,6-di(pyridin-2-yl)pyridazine (**53**) (60 mg, 0.16 mmol) and silver tetrafluoroborate (31 mg, 0.16 mmol) were used to prepare the silver complex (77 mg, 0.14 mmol, 88%, $C_{24}H_{30}N_4AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.71 (m, 2H, H_{6A+6C}), 8.52 (s, 1H, H_{3B}), 8.47 (d, J=8.0 Hz, 1H, H_{3A}), 8.10 (td, J=7.6, 2.0 Hz, 1H, H_{4A}), 8.03 (td, J=7.6, 1.6 Hz, 1H, H_{4C}), 7.90 (d, J=7.6 Hz, 1H, H_{3C}), 7.65 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.59 (dd, J=7.6, 1.6 Hz, 1H, H_{5C}), 2.82 (t, J=6.0 Hz, 2H, CH_2), 1.40 (m, 2H, C-CH_2), 1.13 (m, 14H, C-C-$(CH_2)_7$), 0.79 (t, J=6.8 Hz, 3H, CH_3).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 159.3, 155.1, 154.0, 150.5, 150.3, 149.6, 143.3, 138.5, 137.7, 126.6, 125.9, 124.7, 124.6, 122.6, 31.2, 31.1, 28.8, 28.6, 28.5, 28.4, 28.3, 22.0, 13.8, 1 carbon signal unresolved.
MS (ES) *m/z* $[L]^+$ 375, $[Ag+L+MeCN]^+$ 522, $[Ag+2L]^+$ 857, $[2Ag+L+BF_4]^+$ 1051.
Elem. Anal. ($C_{72}H_{90}N_{12}Ag_2BF_4$) [%] calc. C 60.6, H 6.4, N 11.8, found, C 60.7, H 6.3, N 11.9.

VI.7 Bibliography

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CHAPTER VII

Conclusion

CHAPTER VII

CONCLUSION

This work introduces the synthesis of new substituted pyridazines ligands and their silver(I) complexes. We focussed our attention on the diversity of the ligands and silver complexes prepared.

We synthesised four different family of ligands. First we prepared phenyl substituted pyridazines (**4**, **6**, **8**, **10**, and **13**) and the silver complexes (**4sc**, **6sc**, **8sc**, **10sc**, and **13sc**). Then we prepared halogenated pyridazines (**14**, **17**, **19**, **23**, **25** and **27**) and the corresponding silver complexes (**15sc**, **18sc**, **20sc**, **24sc**, **26sc** and **28sc**). We also focussed our attention on pyridazines substituted with electron-withdrawing or donating groups (**29**, **31**, **33**, **35**, **38** and **41**) and their silver complexes (**30sc**, **32sc**, **34sc**, **36sc**, **39sc**, **42sc**, **43sc** and **44sc**). The last chapter of this work presents pyridazines with alkyl chains (**46**, **49**, **52**, and **53**) and the respective silver complexes (**45sc**, **48sc**, **52sc** and **53sc**).

The aim of this project was to study the silver complexes and their crystal structure. We wanted to find the relationship between the different substituted pyridazine silver complexes and their crystal structure. We obtained three crystal structure of free ligands (**8**, **15** and **34**) and nine crystal structure of silver complexes (**15sc**, **18sc**, **20sc**, **30sc**, **34sc**, **39sc**, **42sc**, **44sc** and **53sc**). The crystal structures of the ligands are presented in Figure 7.1. Those of the silver complexes are shown in Figure 7.2.
We saw that the electronic effect, steric effects and the nature of the counter-anion influence the shape of the crystal structure. It is hard to determine which effect is predominant for the formation of the structure of the complexes. The most important effect is the steric factor of the substituent. This forces the outher ring (C) to be significantly out of the plan and enables other structures (polymers or multi-nuclear silver core).

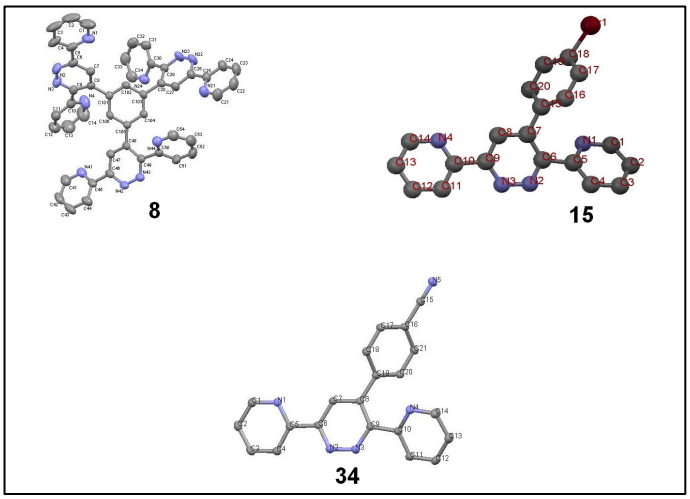


Figure 7.1: Crystal structure of ligands **8**, **15** and **34**.

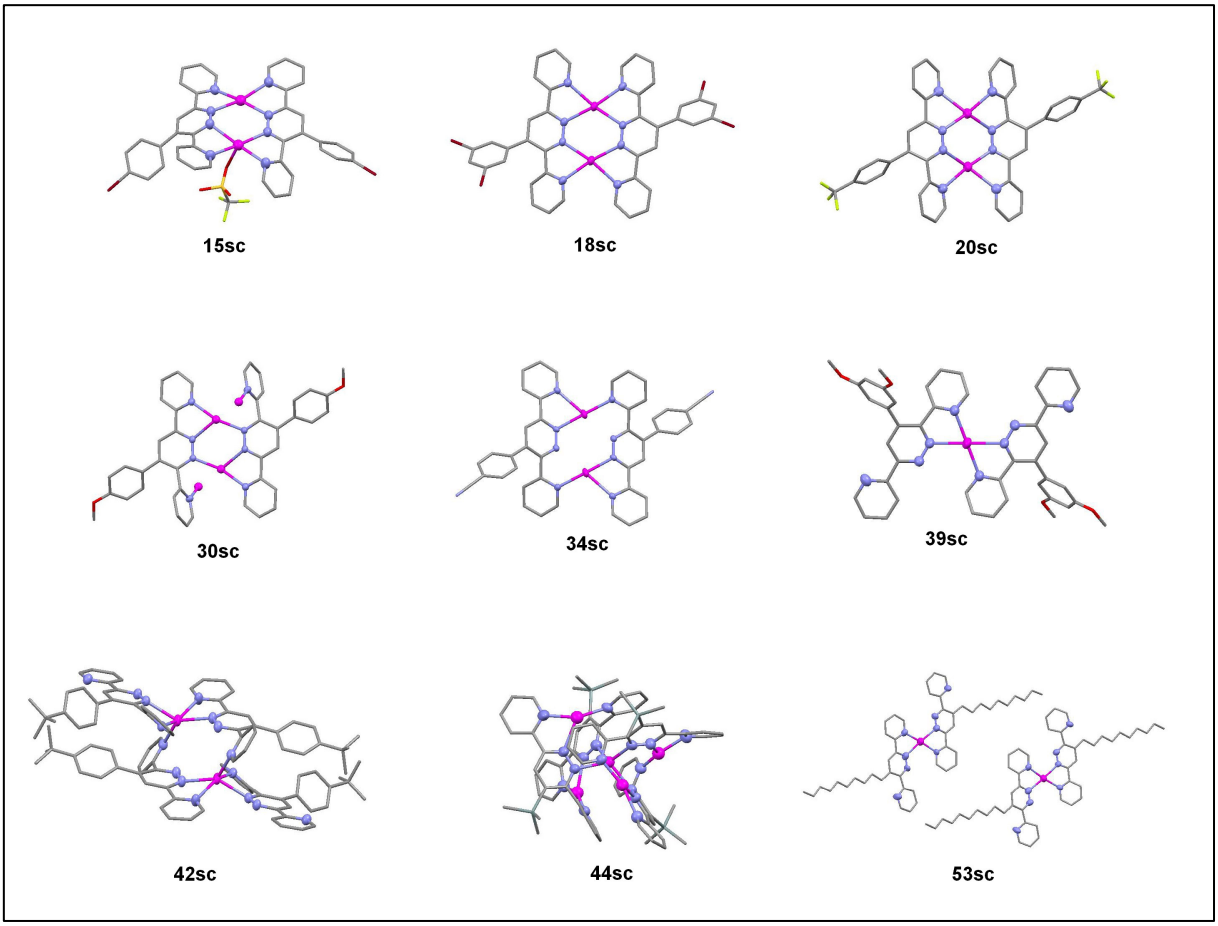


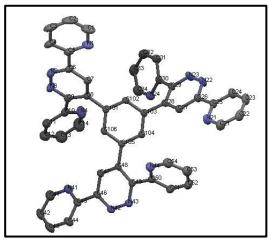
Figure 7.2: Crystal structure of silver complexes **15sc**, **18sc**, **20sc**, **30sc**, **34sc**, **39sc**, **42sc**, **44sc** and **53s**

APPENDICES

Appendix 1

X-ray characterisation

1,3,5-Tris(3,6-di(pyridin-2-yl)pyridazin-4-yl)benzene $C_{49}\ H_{31.5}\ N_{12.5}\ O_{0.25}$ **(8)**



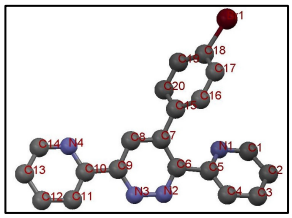
General parameters

empirical formula		$C_{49}\ H_{31.5}\ N_{12.5}\ O_{0.25}$
formula weight		799.37
temperature (K)		173
wavelength (Å)		0.71073
cryst system		triclinic
space group		P -1
unit cell dimensions (Å)	a	12.3401
	b	13.3823
	c	13.6639
[deg]	α	73.983
	β	77.345
	γ	79.120
crystal size (mm)		0.10x0.10x0.10
volume ($Å^3$)		2096.3
Z		2
density (calc) (gcm^{-3})		1.266
crystal colour		colorless
crystal description		block
abs coefficient (mm^{-1})		0.080
F (000)		830
theta range for data collection (deg)		3.06 to 28.50
index ranges	h	-16 to 16
	k	-17 to 17
	l	-18 to 18
reflections collected		10593
reflections for refinement		6433
parameters		578
goodness of fit on F^2		1.0723
R1 (all data)		0.0594
wR2 (all data)		0.0605
R1 (ref)		0.0496
wR2 (ref)		0.0564

Appendix 2

X-ray characterisation

4-(4-Bromobenzen)-3,6-di-pyridin-2-ylpyridazine $C_{20}H_{13}BrN_4$ (15)



General parameters

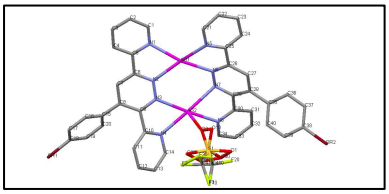
empirical formula		$C_{20}H_{13}BrN_4$
formula weight		389.25
temperature (K)		123
wavelength (Å)		0.71073
cryst system		orthorombic
space group		Pcab
unit cell dimensions (Å)	a	6.2688(3)
	b	21.845(3)
	c	24.209(3)
[deg]	α	90
	β	90
	γ	90
crystal size (mm)		0.14x0.17x0.40
volume ($Å^3$)		3315.4(5)
Z		8
density (calc) (gcm^{-3})		1.560
crystal colour		Colorless
crystal description		plate
abs coefficient (mm^{-1})		2.489
F (000)		1568
theta range for data collection (deg)		3.26 to 29.99
index ranges	h	-8 to 8
	k	-30 to 30
	l	-34 to 31
reflections collected		69540
reflections for refinement		4828
parameters		279
goodness of fit on F^2		1.1129
R1 (all data)		0.0500
wR2 (all data)		0.0341
R1 (ref)		0.0248
wR2 (ref)		0.0259

Appendix 3

X-ray characterisation

4-(4-Bromobenzene)-3,6-di(pyridin-2yl)pyridazine silver complex

$C_{42}H_{26}Ag_2Br_2F_6N_8O_6S_2$ **(15sc)**



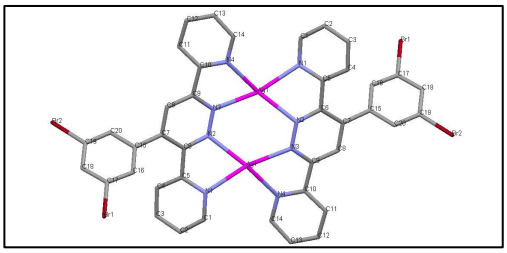
empirical formula		$C_{42}H_{26}Ag_2Br_2F_6N_8O_6S_2$
formula weight		1292.38
temperature (K)		173
wavelength (Å)		0.71073
cryst system		triclinic
space group		P-1
unit cell dimensions (Å)	a	9.8179(2)
	b	14.3098(2)
	c	15.8176(2)
[deg]	α	81.2132
	β	78.5495
	γ	83.9300
crystal size (mm)		0.10x0.10x0.20
volume ($Å^3$)		2145.9(1)
Z		4
density (calc) (gcm^{-3})		2.000
crystal colour		colorless
crystal description		plate
abs coefficient (mm^{-1})		2.959
F (000)		1259.219
theta range for data collection (deg)		5.20 to 27.44
index ranges	h	-12 to 12
	k	-18 to 18
	l	-20 to 20
reflections collected		19368
reflections for refinement		9795
parameters		677
goodness of fit on F^2		1.1055
R1 (all data)		x
wR2 (all data)		x
R1 (ref)		0.0397
wR2 (ref)		0.0475

Appendix 4

X-ray characterisation

4-(3,5-Dibromophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex

$C_{22}H_{15}AgBBr_2F_4N_5$ **(18sc)**



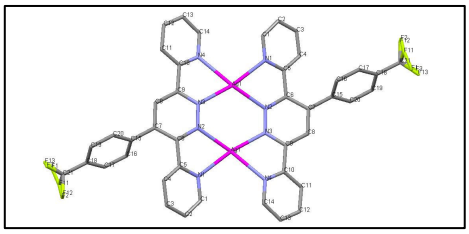
empirical formula		$C_{22}H_{15}AgBBr_2F_4N_5$
formula weight		703.87
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		P 1 21/a 1
unit cell dimensions (Å)	a	8.1005(9)
	b	34.509(4)
	c	8.4695(8)
[deg]	α	90
	β	97.13
	γ	90
crystal size (mm)		0.06x0.28x0.32
volume ($Å^3$)		2349.3(4)
Z		4
density (calc) (gcm^{-3})		1.990
crystal colour		yellow
crystal description		plate
abs coefficient (mm^{-1})		4.313
F (000)		1360
theta range for data collection (deg)		3.002 to 29.506
index ranges	h	-11 to 10
	k	-47 to 47
	l	-11 to 11
reflections collected		57426
reflections for refinement		6410
parameters		376
goodness of fit on F^2		1.0355
R1 (all data)		0.072
wR2 (all data)		0.0696
R1 (ref)		0.0405
wR2 (ref)		0.0454

Appendix 5

X-ray characterisation

3,6-Di(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine silver complex

$C_{47.20}H_{33.80}Ag_2B_2F_{14}N_{10.60}$ **(20sc)**

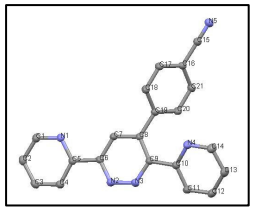


empirical formula		$C_{47.20}H_{33.80}Ag_2B_2F_{14}N_{10.60}$
formula weight		1252.79
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		C 1 2/c 1
unit cell dimensions (Å)	a	12.7058(5)
	b	10.9051(4)
	c	35.4146(13)
[deg]	α	90
	β	93.1367
	γ	90
crystal size (mm)		0.12x0.22x0.29
volume ($Å^3$)		4899.6(3)
Z		4
density (calc) (gcm^{-3})		1.698
crystal colour		pale red
crystal description		plate
abs coefficient (mm^{-1})		0.900
F (000)		2484.800
theta range for data collection (deg)		3.059 to 26.967
index ranges	h	-16 to16
	k	-12 to 14
	l	-46 to 46
reflections collected		65828
reflections for refinement		5587
parameters		416
goodness of fit on F^2		1.0634
R1 (all data)		0.0448
wR2 (all data)		0.0360
R1 (ref)		0.0329
wR2 (ref)		0.0325

Appendix 6

X-ray characterisation

4-(3,6-Di(pyridin-2-yl)pyridazin-4-yl)benzonitrile $C_{21}H_{13}N_5$ (34)



General parameters

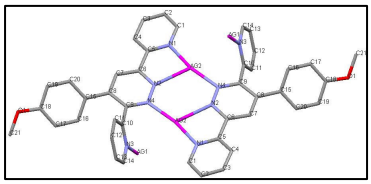
empirical formula		$C_{21}H_{13}N_5$
formula weight		335.37
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		P 1 21/c 1
unit cell dimensions (Å)	a	14.5427(3)
	b	6.48220(10)
	c	17.9287(4)
[deg]	α	90
	β	105.9912(12)
	γ	90
crystal size (mm)		0.18x0.22x0.30
volume ($Å^3$)		1624.71(6)
Z		4
density (calc) (gcm^{-3})		1.371
crystal colour		colorless
crystal description		plate
abs coefficient (mm^{-1})		0.086
F (000)		696
theta range for data collection (deg)		2.914 to 27.478
index ranges	h	-18 to 18
	k	-8 to 8
	l	-23 to 23
reflections collected		7452
reflections for refinement		3724
parameters		235
goodness of fit on F^2		1.0975
R1 (all data)		0.0821
wR2 (all data)		0.1082
R1 (ref)		0.0398
wR2 (ref)		0.0432

Appendix 7

X-ray characterisation

4-(4-Methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex

$C_{21}H_{16}Ag_{1.5}B_{1.5}F_6N_40$ **(30sc)**



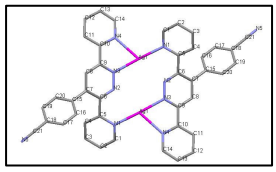
General parameters

empirical formula		$C_{21}H_{16}Ag_{1.5}B_{1.5}F_6N_40$
formula weight		632.39
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		C 1 2/c 1
unit cell dimensions (Å)	a	25.405(3)
	b	11.560(3)
	c	17.609(3)
[deg]	α	90
	β	122.06
	γ	90
crystal size (mm)		0.06x0.13x0.22
volume ($Å^3$)		4392.3(2)
Z		8
density (calc) (gcm^{-3})		1.917
crystal colour		colorless
crystal description		plate
abs coefficient (mm^{-1})		1.428
F (000)		2468.147
theta range for data collection (deg)		5.05 to 29.99
index ranges	h	-35 to 35
	k	-16 to 16
	l	-24 to 24
reflections collected		123897
reflections for refinement		6381
parameters		344
goodness of fit on F^2		°
R1 (all data)		0.0210
wR2 (all data)		°
R1 (ref)		0.0219
wR2 (ref)		1.2050

Appendix 8

X-ray characterisation

4-(3,6-Di(pyridin-2-yl)pyridazin-4-yl)benzonitrile silver complex $C_{21}H_{13}AgBF_4N_5$ **(34sc)**



General parameters

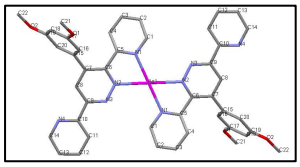
empirical formula		$C_{21}H_{13}AgBF_4N_5$
formula weight		530.04
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		P2/c
unit cell dimensions (Å)	a	10.0117(9)
	b	9.8350(10)
	c	19.4852(11)
[deg]	α	90
	β	95.780(6)
	γ	90
crystal size (mm)		O.10x0.12x0.20
volume ($Å^3$)		1908.9(3)
Z		4
density (calc) (gcm^{-3})		1.844
crystal colour		yellow
crystal description		plate
abs coefficient (mm^{-1})		1.115
F (000)		1.048
theta range for data collection (deg)		3.024 to 27.522
index ranges	h	-10 to 13
	k	-12 to 12
	l	-25 to 25
reflections collected		38527
reflections for refinement		4383
parameters		289
goodness of fit on F^2		1.0510
R1 (all data)		0.0419
wR2 (all data)		0.0337
R1 (ref)		0.0361
wR2 (ref)		0.0327

Appendix 9

X-ray characterisation

4-(3,5-Dimethoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex

$C_{44}H_{36}AgBF_4N_8O_4$ **(39sc)**



General parameters

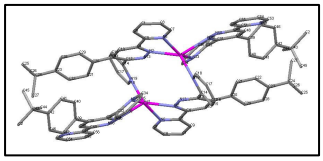
empirical formula		$C_{44}H_{36}AgBF_4N_8O_4$
formula weight		935.49
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		C 2/c
unit cell dimensions (Å)	a	34.9234(15)
	b	6.6039(8)
	c	20.7468(12)
[deg]	α	90
	β	123.924(13)
	γ	90
crystal size (mm)		0.05x0.12x0.24
volume ($Å^3$)		3970.4(8)
Z		4
density (calc) (gcm^{-3})		1.565
crystal colour		pale yellow
crystal description		prism
abs coefficient (mm^{-1})		0.583
F (000)		1904
theta range for data collection (deg)		1.405 to 23.905
index ranges	h	-43 to 44
	k	0 to 8
	l	-26 to 26
reflections collected		15371
reflections for refinement		4209
parameters		300
goodness of fit on F^2		1.1935
R1 (all data)		0.0410
wR2 (all data)		0.0437
R1 (ref)		0.0380
wR2 (ref)		0.0410

Appendix 10

X-ray characterisation

4-(4-Tert-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex

$C_{50}H_{49}AgBF_4N_8O_{0.5}$ **(42sc)**



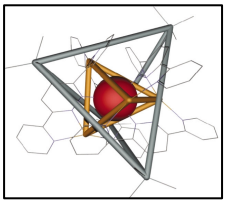
General parameters

empirical formula		$C_{50}H_{49}AgBF_4N_8O_{0.5}$
formula weight		964.66
temperature (K)		293
wavelength (Å)		0.71073
cryst system		monoclinic
space group		P 2/a
unit cell dimensions (Å)	a	21.788
	b	9.171
	c	22.625
[deg]	α	90
	β	90.62
	γ	90
crystal size (mm)		°
volume ($Å^3$)		4520.61
Z		4
density (calc) (gcm^{-3})		1.417
crystal colour		°
crystal description		°
abs coefficient (mm^{-1})		0.509
F (000)		1988
theta range for data collection (deg)		1.800 to 26.869
index ranges	h	-27 to 27
	k	-11 to 11
	l	-28 to 25
reflections collected		34780
reflections for refinement		11539
parameters		582
goodness of fit on F^2		0.9936
R1 (all data)		0.0416
wR2 (all data)		0.0447
R1 (ref)		0.0312
wR2 (ref)		0.0407

Appendix 11

X-ray characterisation

3,6-Di(pyridin-2-yl)-4-(trimethylsilyl)pyridazine silver complex (44sc)



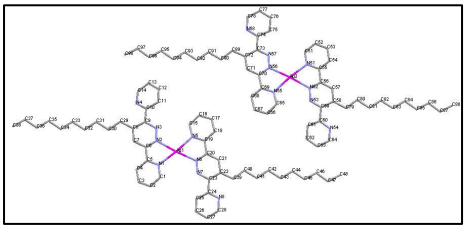
General parameters

empirical formula		$C_{78}H_{89.5}Ag_5B_5F_{20}N_{19.5}O_1Si_4$
formula weight		2401.90
temperature (K)		173
wavelength (Å)		0.71073
cryst system		monoclinic
space group		P 2/n
unit cell dimensions (Å)	a	25.1896(3)
	b	15.2357(2)
	c	27.9532(3)
[deg]	α	90
	β	106.6790(7)
	γ	90
crystal size (mm)		0.16x0.18x0.20
volume ($Å^3$)		10276.6
Z		4
density (calc) (gcm^{-3})		1.552
crystal colour		yellow
crystal description		block
abs coefficient (mm^{-1})		1.069
F (000)		4773.353
theta range for data collection (deg)		5.00 to 27.44
index ranges	h	-32 to 32
	k	-19 to 19
	l	-36 to 36
reflections collected		12698
reflections for refinement		1315
parameters		1315
goodness of fit on F^2		1.0127
R1 (all data)		◦
wR2 (all data)		◦
R1 (ref)		0.0496
wR2 (ref)		0.0510

Appendix 12

X-ray characterisation

4-Decyl-3,6-di(pyridin-2-yl)pyridazine silver complex $C_{48}H_{60}AgBF_4N_8$ 53sc

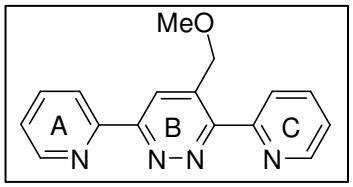


General parameters

empirical formula		$C_{48}H_{60}AgBF_4N_8$
formula weight		943.73
temperature (K)		173
wavelength (Å)		0.71073
cryst system		triclinic
space group		P-1
unit cell dimensions (Å)	a	8.1443(7)
	b	24.5845(17)
	c	25.8037(17)
[deg]	α	115.007(4)
	β	98.246(4)
	γ	97.300(4)
crystal size (mm)		0.10x0.10x0.50
volume ($Å^3$)		4531.2(6)
Z		4
density (calc) (gcm^{-3})		1.383
crystal colour		yellow
crystal description		plate
abs coefficient (mm^{-1})		0.505
F (000)		1968
theta range for data collection (deg)		1.556 to 25.429
index ranges	h	-9 to 9
	k	-29 to 29
	l	-30 to 30
reflections collected		14192
reflections for refinement		10378
parameters		955
goodness of fit on F^2		1.1274
R1 (all data)		0.1274
wR2 (all data)		0.1529
R1 (ref)		0.0879
wR2 (ref)		0.0975

Compounds synthesised but not discussed in this work

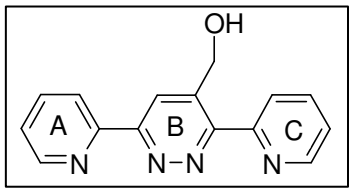
Synthesis of 4-(methoxymethyl)-3,6-di(pyridin-2-yl)pyridazine (54)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (500 mg, 2.11 mmol) and 3-methoxyprop-1-yne (280 mg, 3.99 mmol) in toluene (80 ml) was refluxed for 24 hours at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by recrystallisation from ethanol. The product was obtained as a beige powder (0.46 g, 1.7 mmol, 81%, $C_{16}H_{14}N_4O$, 278.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.92 (m, 1H, H_{3A}), 8.76 (m, 2H, H_{6A+3B}), 8.71 (d, J=4.6 Hz, 1H, H_{6C}), 8.43 (d, J=8.0 Hz, 1H, H_{3C}), 7.90 (m, 2H, H_{4A+4C}), 7.39 (m, 2H, H_{5A+5C}), 5.02 (s, 2H, CH_2), 3.54 (s, 3H, OCH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 155.8, 153.7, 149.5, 148.4, 139.8, 137.0, 136.8, 124.4, 124.3, 123.7, 122.8, 121.7, 70.8, 58.9, 2 carbon signals unresolved.
MS (ESI) m/z: $[(L\text{-}CH_3)+Na+MeCN]^+$ 328, $[2(L\text{-}CH_3)+2Na+MeCN]^+$ 615.
Elem. Anal. ($C_{16}H_{14}N_4O$) [%] calc. C 69.0, H 5.0, N 20.1, found, C 68.3, H 5.2, N 19.8.

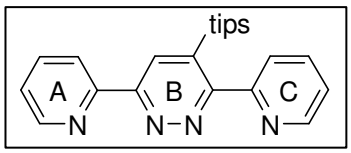
Synthesis of (3,6-di(pyridin-2-yl)pyridazin-4-yl)methanol (55)



A solution of 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.30 g, 2.1 mmol) and 1-hydroxyprop-2-yne (0.13 g, 2.5 mmol) in toluene (30 ml) was refluxed for 46 hours at 120°C. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, EtOAc, the third band was collected). The product was obtained as a purple powder (0.20 g, 0.76 mmol, 36%, $C_{15}H_{12}N_4O$, 264.3 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.72 (m, 2H, H_{3A+6A}), 8.68 (d, J=5.0 Hz, 1H, H_{6C}), 8.61 (s, 1H, H_{3B}), 8.57 (d, J=8.0 Hz, 1H, H_{3C}), 7.97 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.87 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.46 (dd, J=7.5, 4.4 Hz, 1H, H_{5A}), 7.38 (dd, J=7.5, 4.4 Hz, 1H, H_{5C}), 4.72 (s, 2H, CH_2).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.1, 158.0, 155.1, 152.9, 149.4, 148.0, 139.8, 137.9, 137.1, 125.8, 124.9, 124.8, 124.4, 121.6, 63.3.
MS (ESI) m/z: $[L+Na+2MeCN]^+$ 369, $[2L+Na+MeCN]^+$ 591.
Elem. Anal. ($C_{15}H_{12}N_4O$) [%] calc. C 68.2, H 4.6, N 21.2, found, C 67.8, H 4.6, N 21.0.

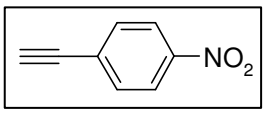
Synthesis of 3,6-di(pyridin-2-yl)-4-(triisopropylsilyl)pyridazine (56)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.69 g, 2.9 mmol) and triisopropylsilylacetylene (0.53 g, 2.9 mmol) were dissolved in toluene (100 ml). The solution was refluxed for 10 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/dichloromethane/EtOAc (1:1:1), the third band was collected). The product was obtained as a white solid (135 mg, 0.346 mmol, 11.7%, $C_{23}H_{30}N_4Si$, 390.6 g/mol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 9.01 (s, 1H, H_{3B}), 8.76 (m, 2H, H_{6A+3A}), 8.65 (d, J=4.7 Hz, 1H, H_{6C}), 8.38 (d, J=7.8 Hz, 1H, H_{3C}), 7.88 (m, 2H, H_{4A+4C}), 7.39 (m, 2H, H_{5A+5C}), 1.50 (q, J=7.5 Hz, 3H, CH (TIPS)), 1.07 (d, J=7.5 Hz, 18H, CH_3 (TIPS)).
^{13}C NMR ($CDCl_3$, 125 MHz) δ/ppm: 163.9, 157.2, 155.3, 153.6, 149.5, 147.9, 137.1, 136.7, 133.9, 124.5, 124.0, 123.8, 121.7, 19.2, 13.0, 2 carbon signals unresolved.
MS (ESI) m/z: $[L-(CH(CH_3)_2)]^+$ 347, $[2Na+2(L-TIPS)]^+$ 512, $[Na+2L+MeCN]^+$ 843.

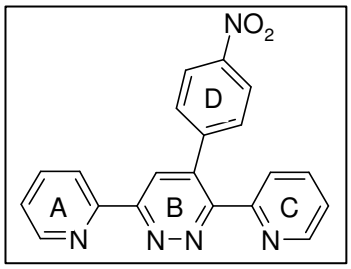
Synthesis of 1-ethynyl-4-nitrobenzene (57)



Under argon and exclusion of moisture, 4-bromonitrobenzene (2.0 g, 9.9 mmol), CuCl (0.15 g, 1.5 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (1.0 g, 1.4 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). Then trimethylsilylacetylene (2.9 ml, 21 mmol) was added and the mixture stirred at 75°C overnight. The solvent was removed and the residue extracted with hexane (150 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane/dichloromethane (33:1), the second band was collected). The product was dissolved in THF (50 ml) and an aqueous solution of 1M NaOH added (75 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give an orange powder (1.1 g, 7.6 mmol, 77%, $C_8H_5NO_2$, 144.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.19 (d, J=8.8 Hz, 2H, H_{2+6}), 7.63 (d, J=8.8 Hz, 2H, H_{3+5}), 3.36 (s, 1H, ethynyl);
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 147.5, 132.9, 128.8, 123.5, 82.3, 81.5.
MS (EI) m/z: $[L\text{-}NO_2]^+$ 101, $[L\text{-}O_2]^+$ 117, $[L]^+$ 147.
Elem. Anal. ($C_8H_5O_2$) [%] calc. C 65.3, H 3.4, N 9.5, found, C 64.7, H 3.7, N 9.1.

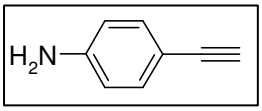
Synthesis of 4-(4-nitrophenyl)-3,6-di(pyridin-2-yl)pyridazine (58)



3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.40 g, 1.7 mmol) and 1-ethynyl-4-nitrobenzene (**57**) (0.30 g, 2.1 mmol) were dissolved in toluene (80 ml). The solution was refluxed for 5 days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:2), the second band was collected). The product was obtained as a brown powder (0.51 g, 1.4 mmol, 83%, $C_{20}H_{13}N_5O_2$, 355.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.77 (d, J=8.1 Hz, 1H, H_{3A}), 8.70 (d, J=4.1 Hz, 1H, H_{6A}), 8.63 (s, 1H, H_{3B}), 8.32 (d, J=5.0 Hz, 1H, H_{6C}), 8.15 (m, 3H, $H_{3'}$ + H_{2D+6D}), 7.90 (td, 1H, J=7.5, 1.6 Hz, H_{4A}), 7.85 (td, J=7.5, 1.6 Hz, 1H, H_{4C}), 7.41 (m, 3H, H_{5A} + H_{3D+5D}), 7.27 (dd, J=7.6, 4.8 Hz, 1H, H_{5C}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 157.7, 157.4, 154.6, 152.7, 149.4, 148.7, 147.4, 144.2, 138.4, 137.3, 136.9, 129.6, 125.5, 125.0, 124.6, 123.8, 123.4, 121.8, 2 carbon signals unresolved.
MS (EI) m/z: $[L]^+$ 356, $[Na+L+CHCl_3]^+$ 477, $[Na+2L+2MeCN]^+$ 773.

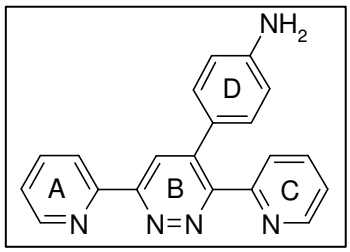
Synthesis of 4-ethynylaniline (59)



4-Trimethylsilylethynylaniline (**21**) (1.3 g, 6.7 mmol) was dissolved in THF (75 ml) and an aqueous solution of 1M NaOH added (150 ml). The mixture was stirred at room temperature overnight and then diluted with water until a precipitate was formed. The compound was extracted with dichloromethane and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give a brown black powder (0.77 g, 6.6 mmol, 98%, C_8H_7N, 117.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.29 (d, J=8.4 Hz, 2H, H_{3+5}), 6.58 (d, J=8.4 Hz, 2H, H_{2+6}), 3.82 (bs, 2H, NH_2), 2.97 (s, 1H, ethynyl).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 146.9, 133.3, 114.5, 111.1, 84.3, 74.8.
MS (EI) m/z: $[L]^+$ 117.
Elem. Anal. ($C_{21}H_{13}N_5$) [%] calc. C 82.0, H 6.0, N 12.0, found, C 82.0, H 6.2, N 11.8.

Synthesis of 4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)aniline (60)

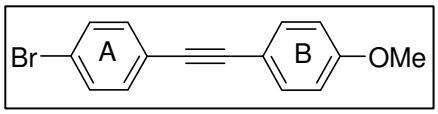


3,6-Bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.81 g, 3.4 mmol) and 4-ethynylaniline (**59**) (0.40 g, 3.4 mmol) were dissolved in toluene (120 ml). The solution was refluxed for 5

days. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatographic work-up (alumina, chloroform, the third band was collected). The product was obtained as a dark brown powder (0.99 g, 3.0 mmol, 88%, $C_{20}H_{15}N_5$, 325.4 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.76 (d, J=7.5 Hz, 1H, H_{3A}), 8.72 (d, J=5.5 Hz, 1H, H_{6A}), 8.59 (s, 1H, H_{3B}), 8.55 (d, J=5.5 Hz, 1H, H_{3C}), 7.88 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.77 (m, 2H, H_{4C+6C}), 7.38 (dd, J=7.6, 4.8 Hz, 1H, H_{5A}), 7.26 (m, 1H, H_{5C}), 7.04 (d, J=8.5 Hz, 2H, H_{3D+5D}), 6.56 (d, J=8.5 Hz, 2H, H_{2D+6D}).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 158.3, 157.5, 156.4, 153.6, 149.3, 149.1, 147.0, 140.3, 137.1, 136.4, 130.3, 126.0, 124.8, 124.7, 124.6, 123.1, 121.8, 114.8, 2 carbon signals unresolved.
MS (EI) m/z: $[L]^+$ 326, $[L+K+2MeCN]^+$ 447, $[2L+Na+MeCN]^+$ 713, $[2L+K+2MeCN]^+$ 773.

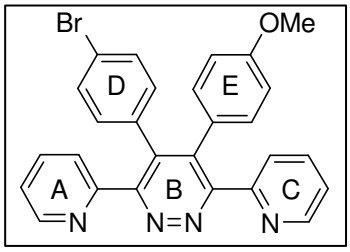
Synthesis of 1-bromo-4-(4-methoxyphenylethynyl)benzene (61)



Under argon and exclusion of moisture, 1-iodo-4-bromobenzene (1.0 g, 3.5 mmol), 1-ethynyl-4-methoxybenzene (**29**) (0.50 g, 3.8 mmol), CuCl (37 mg, 0.38 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.27 g, 0.38 mmol) were suspended in dry, argon degassed, triethylamine (100 ml). The mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (100 ml). The solution was filtered and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The solvent was removed to give a beige solid (0.82 g, 2.9 mmol, 83%, $C_{15}H_{11}BrO$, 287.2 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.46 (m, 4H, $H_{3+5+10+14}$), 7.36 (d, J=8.8 Hz, 2H, H_{2+6}), 6.88 (d, J=8.6 Hz, 2H, H_{11+13}), 3.83 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.7, 133.0, 132.8, 131.5, 122.5, 122.0, 114.9, 114.0, 90.5, 87.0, 55.3.
MS (ESI) m/z: $[L-CH_3]^+$ 273, $[L]^+$ 287.
Elem. Anal. ($C_{15}H_{11}BrO$) [%]: calc. C 62.7, H 3.9, found, C 62.7, H 3.9.

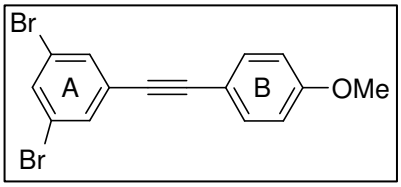
Synthesis of 4-(4-bromophenyl)-5-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (62)



1-bromo-4-((4-methoxyphenyl)ethynyl)benzene (**61**) (0.30 g, 1.1 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.25 g, 1.1 mmol) were heated without solvent at 170°C for 5 days. The product was purified by chromatographic work-up (alumina, hexane/EtOAc (1:1)) and then purified again by chromatographic work-up (alumina, $CHCl_3$, the third band was collected) to give a violet powder (0.23 g, 0.47 mmol, 45%, $C_{27}H_{19}N_4BrO$, 494.1 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.46 (d, J=4.5 Hz, 1H, H_{6A}), 8.40 (d, J=8.0 Hz, 1H, H_{3A}), 7.72 (m, 2H, H_{6C+4A}), 7.67 (td, J=4.5, 1.6 Hz, 1H, H_{4C}), 7.60 (d, J=8.1 Hz, 1H, H_{3C}), 7.19 (m, 4H, $H_{5A+5C+2D+6D}$), 6.74 (m, 4H, $H_{3D+5D+2E+6E}$), 6.58 (d, J=8.4 Hz, 2H, H_{3E+5E}), 3.69 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.2, 158.8, 158.5, 156.1, 155.8, 148.9, 148.7, 138.8, 138.1, 136.3, 136.2, 134.0, 131.7, 131.4, 130.8, 126.3, 124.9, 123.0, 122.8, 121.5, 113.3, 55.0, 5 carbon signals unresolved.
MS (ESI) m/z: $[L+K+DCM]^+$ 618, $[2L+DCM+K]^+$ 1113.
Elem. Anal. ($C_{27}H_{19}N_4BrO$) [%]: calc. C 65.5, H 3.9, N 11.31, found, C 64.8, H 4.00, N 11.1.

Synthesis of 1,3-dibromo-5-((4-methoxyphenyl)ethynyl)benzene (63)

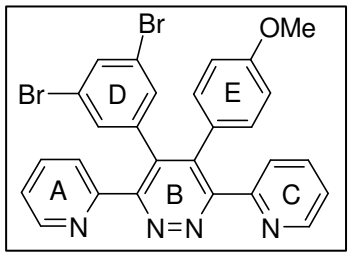


Under argon and exclusion of moisture, 4-iodoanisole (0.54 g, 2.3 mmol), 1-ethynyl-3,5-dibromobenzene (**17**) (0.60 g, 2.3 mmol), CuCl (23 mg, 0.23 mmol), and $PdCl_2(PPh_3)_2$ (**3**) (0.17 g, 0.23 mmol) were suspended in dry, argon degassed, triethylamine (60 ml). The mixture stirred at 60°C for 18 hours. The solvent was removed and the residue extracted with hexane (100 ml). The solution was filtered

and the solvent removed from the filtrate by evaporation. The residue was purified by chromatographic work-up (alumina, hexane, the second band was collected). The solvent was removed to give a beige solid (0.56 g, 1.5 mmol, 65%, $C_{15}H_{10}Br_2O$, 363.9 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 7.69 (t, J=8.0 Hz, 1H, H_2), 7.59 (d, J=7.8 Hz, 2H, H_{4+6}), 7.44 (d, J=8.4 Hz, 2H, H_{10+14}), 6.88 (d, J=8.8 Hz, 2H, H_{11+13}), 3.83 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 141.2, 135.3, 133.8, 133.2, 132.7, 124.7, 122.7, 122.5, 114.1, 75.5, 55.3.
MS (ESI) m/z: $[L]^+$ 365.
Elem. Anal. ($C_{15}H_{11}Br_2O$) [%]: calc. C 49.2, H 2.8, found, C 49.3, H 2.9.

Synthesis of 4-(3,5-dibromophenyl)-5-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (64)

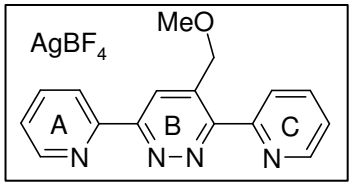


1,3-Dibromo-5-(4-methoxyphenylethynyl)benzene (**63**) (0.20 g, 0.55 mmol) and 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**1**) (0.13 g, 0.55 mmol) were heated without solvent at 170°C for 10 days. The product was purified by chromatographic work-up (alumina, EtOAc, the third band was collected) to give a beige powder (0.23 g, 0.40 mmol, 73%, $C_{27}H_{19}N_4Br_2O$, 572.0 g/mol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ/ppm: 8.45 (d, J=4.7 Hz, 1H, H_{6A}), 8.40 (d, J=4.7 Hz, 1H, H_{6C}), 7.87 (d, J=8.0 Hz, 1H, H_{3A}), 7.77 (td, J=7.5, 1.6 Hz, 1H, H_{4A}), 7.67 (td, J=7.5 Hz, 1H, H_{4C}), 7.60 (d, J=8.0 Hz, 1H, H_{3C}), 7.37 (t, J=8.0 Hz, 1H, H_{2D}), 7.20 (m, 2H, H_{5A+5C}), 6.98 (d, J=7.5 Hz, 2H, H_{4D+6D}), 6.76 (d, J=8.4 Hz, 2H, H_{2E+6E}), 6.61 (d, J=8.8 Hz, 2H, H_{3E+5E}), 3.69 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 100 MHz) δ/ppm: 159.1, 158.9, 157.8, 155.7, 155.1, 148.9, 148.6, 139.0, 138.6, 136.5, 136.1, 132.7, 131.8, 131.2, 125.8, 124.9, 123.2, 122.9, 121.7, 113.3, 55.0, 6 carbon signals unresolved.
MS (ESI) m/z: $[L+K+DCM]^+$ 696, $[2L+MeCN+Na]^+$ 1213, $[2L+CHCl_3]^+$ 1269.

Elem. Anal. ($C_{27}H_{19}N_4Br_2O$) [%]: calc. C 56.4, H 3.3, N 9.7, found, C 56.5, H 3.2, N 9.7.

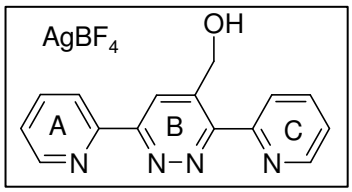
Synthesis of 4-(methoxymethyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (54sc)



4-(Methoxymethyl)-3,6-di(pyridin-2-yl)pyridazine (**54**) (60 mg, 0.22 mmol) and silver tetrafluoroborate (42 mg, 0.22 mmol) were used to prepare the silver complex (61 mg, 0.13 mmol, 60%, $C_{16}H_{14}N_4OAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.84 (d, J=4.8 Hz, 1H, H_{6A}), 8.78 (d, J=4.4 Hz, 1H, H_{6C}), 8.59 (d, J=7.6 Hz, 1H, H_{3A}), 8.23 (d, J=8.0 Hz, 1H, H_{3C}), 8.11 (m, 2H, H_{4A+4C}), 7.67 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.61 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 4.90 (s, 2H, CH_2).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 156.5, 152.3, 151.4, 150.2, 149.1, 139.7, 138.3, 137.6, 125.7, 124.6, 124.3, 122.7, 122.0, 69.6, 58.4, 1 carbon signal unresolved.
MS (ES) *m/z* $[Ag+L]^+$ 387, $[Ag+L+MeCN]^+$ 428, $[Na+2L+MeCN]^+$ 619, $[Ag+2L]^+$ 663.

Synthesis of (3,6-di(pyridin-2-yl)pyridazin-4-yl)methanol silver complex (55sc)

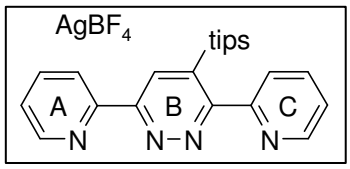


(3,6-Di(pyridin-2-yl)pyridazin-4-yl)methanol (**55**) (50 mg, 0.19 mmol) and silver tetrafluoroborate (37 mg, 0.19 mmol) were used to prepare the silver complex (71 mg, 0.15 mmol, 79%, $C_{15}H_{12}N_4OAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.76 (m, 3H, $H_{3B+3A+6A}$), 8.46 (d, J=7.8 Hz, 1H, H_{3C}), 8.11 (m, 3H, $H_{4A+4C+6C}$), 7.67 (dd, J=7.6, 5.2 Hz, 1H, H_{5A}), 7.62 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 4.83 (d, J=4.4 Hz, 2H, CH_2).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 156.9, 155.3, 152.8, 150.6, 150.3, 149.9, 138.8, 137.9, 126.3, 125.1, 124.8, 124.0, 122.7, 59.5, 1 carbon signal unresolved.
MS (ES) *m/z* $[Ag+L]^+$ 371, $[Ag+2L]^+$ 635, $[2Ag+L+BF_4]^+$ 831.
Elem. Anal. ($C_{15}H_{12}N_4OAgBF_4$) [%] calc. C 39.3, H 2.6, N 12.2, found, C 39.3, H 2.7, N 12.2.

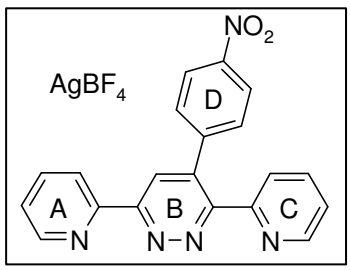
Synthesis of 3,6-di(pyridin-2-yl)-4-(triisopropylsilyl)pyridazine silver complex (56sc)



3,6-Di(pyridin-2-yl)-4-(triisopropylsilyl)pyridazine (**56**) (40 mg, 0.10 mmol) and silver tetrafluoroborate (20 mg, 0.10 mmol) were used to prepare the silver complex (46 mg, 0.08 mmol, 80%, $C_{23}H_{30}N_4SiAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.83 (m, 2H, H_{3B+6A}), 8.71 (d, J=6.0 Hz, 1H, H_{6C}), 8.61 (d, J=8.0 Hz, 1H, H_{3A}), 8.22 (d, J=7.8 Hz, 1H, H_{3C}), 8.11 (td, J=8.0, 2.4 Hz, 1H, H_{4A}), 8.05 (td, J=7.2, 1.8 Hz, 1H, H_{4C}), 7.62 (m, 2H, H_{5A+5C}), 1.01 (m, 21H, TIPS).
^{13}C NMR the product was not enough soluble in CD_3CN or DMSO to record the ^{13}C NMR spectrum.
MS (ES) *m/z* $[L-(CH(CH_3)_2)]^+$ 347, $[Ag+L-(CH(CH_3)_2)+MeCN]^+$ 494, $[Ag+L+MeCN]^+$ 537, $[Ag+2(L-(CH(CH_3)_2))+MeCN]^+$ 843, $[Ag+2L]^+$ 887.

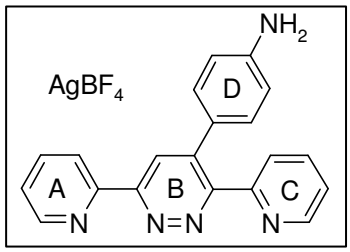
Synthesis of 4-(4-nitrophenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (58sc)



4-(4-Nitrophenyl)-3,6-di(pyridin-2-yl)pyridazine (**58**) (70 mg, 0.20 mmol) and silver tetrafluoroborate (38 mg, 0.20 mmol) were used to prepare the silver complex (93 mg, 0.17 mmol, 85%, $C_{20}H_{13}N_5O_2AgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.91 (d, J=4.0 Hz, 1H, H_{6A}), 8.77 (s, 1H, H_{3B}), 8.70 (d, J=4.0 Hz, 1H, H_{6C}), 8.62 (d, J=8.0 Hz, 1H, H_{3A}), 8.25 (d, J=8.8 Hz, 2H, H_{2D+6D}), 8.18 (td, J=7.8, 2.0 Hz, 1H, H_{4A}), 7.91 (td, J=7.8, 2.0 Hz, 1H, H_{4C}), 7.77 (dd, J=6.0, 4.8 Hz, 1H, H_{5A}), 7.57 (m, 4H, $H_{3C+5C+3D+5D}$).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 157.5, 155.6, 152.4, 150.7, 150.3, 150.0, 147.6, 142.2, 139.3, 138.8, 137.7, 130.6, 127.5, 126.6, 125.1, 123.6, 123.3, 2 carbon signals unresolved.
MS (ES) *m/z* $[Ag+L]^+$ 462, $[Ag+2L]^+$ 817, $[2Ag+2L+BF_4]^+$ 1013.
Elem. Anal. ($C_{20}H_{13}N_5O_2AgBF_4$) [%] calc. C 43.7, H 2.4, N 12.7, found, C 43.8, H 2.8, N 12.7.

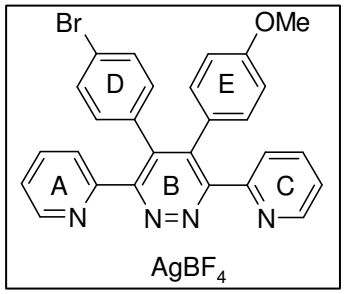
Synthesis of 4-(3,6-di(pyridin-2-yl)pyridazin-4-yl)aniline silver complex (60sc)



4-(3,6-Di(pyridin-2-yl)pyridazin-4-yl)benzenamine (**60**) (80 mg, 0.25 mmol) and silver tetrafluoroborate (48 mg, 0.25 mmol) were used to prepare the silver complex (99 mg, 0.19 mmol, 76%, $C_{20}H_{15}N_5AgBF_4$).

^{1}H NMR (CD_3CN, 500 MHz) δ/ppm: 8.64 (d, J=3.6 Hz, 1H, H_{6A}), 8.61 (d, J=3.6 Hz, 1H, H_{6C}), 8.12 (m, 2H, H_{3B+3A}), 7.98 (td, J=6.0, 1.6 Hz, 1H, H_{4A}), 7.60 (m, 2H, H_{4C+5A}), 7.40 (dd, J=7.6, 5.2 Hz, 1H, H_{5C}), 7.12 (d, J=6.4 Hz, 1H, H_{3C}), 6.79 (d, J=6.8 Hz, 2H, H_{3D+5D}), 6.54 (d, J=6.4 Hz, 2H, H_{2D+6D}), 4.64 (bs, 2H, NH_2).
^{13}C NMR (CD_3CN, 125 MHz) δ/ppm: 158.6, 155.8, 154.0, 152.0, 151.9, 151.3, 150.6, 143.6, 139.9, 138.4, 131.6, 127.8, 127.5, 127.2, 126.2, 124.6, 122.4, 115.0, 2 carbon signals unresolved.
MS (ES) *m/z* $[L]^+$ 326, $[2Ag+L+BF_4+2MeCN]^+$ 711.
Elem. Anal. ($C_{20}H_{15}N_5AgBF_4 + H_2O$) [%] calc. C 44.6, H 3.2, N 13.0, found, C 44.9, H 3.2, N 13.1.

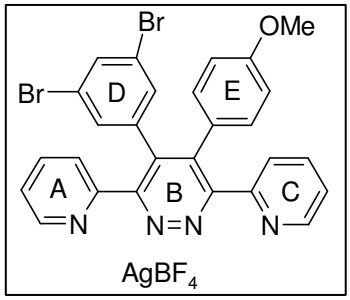
Synthesis of 4-(4-bromophenyl)-5-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (62sc)



4-(4-Bromophenyl)-5-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**62**) (60 mg, 0.12 mmol) and silver tetrafluoroborate (24 mg, 0.12 mmol) were used to prepare the silver complex (69 mg, 0.10 mmol, 83%, $C_{27}H_{19}N_4BrOAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.86 (d, J=4.0 Hz, 1H, H_{6A}), 8.82 (d, J=4.4 Hz, 1H, H_{6C}), 7.86 (m, 2H, H_{4A+4C}), 7.60 (m, 2H, H_{5A+5C}), 7.39 (d, J=8.4 Hz, 2H, H_{2E+6E}), 7.26 (d, J=7.6 Hz, 1H, H_{3A}), 7.16 (d, J=8.0 Hz, 1H, H_{3C}), 6.82 (d, J=8.4 Hz, 2H, H_{3E+5E}), 6.75 (d, J=3.6 Hz, 4H, $H_{2D+3D+5D+6D}$), 3.66 (s, 3H, CH_3).
^{13}C NMR (DMSO, 100 MHz) δ/ppm: 159.0, 152.7, 150.8, 139.5, 137.5, 132.8, 131.9,, 131.2, 131.0, 126.1, 124.8, 121.8, 113.7, 55.0, 13 carbon signals unresolved (the sample was only poorly soluble in DMSO).
MS (ES) *m/z* $[Ag+L]^+$ 603, $[Ag+L+3MeCN]^+$ 728.

Synthesis of 4-(3,5-dibromophenyl)-5-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine silver complex (64sc)



4-(3,5-Dibromophenyl)-5-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**64**) (70 mg, 0.12 mmol) and silver tetrafluoroborate (24 mg, 0.12 mmol) were used to prepare the silver complex (81 mg, 0.11 mmol, 92%, $C_{27}H_{19}N_4Br_2OAgBF_4$).

^{1}H NMR (DMSO, 400 MHz) δ/ppm: 8.77 (d, J=4.8 Hz, 1H, H_{6A}), 8.61 (d, J=4.4 Hz, 1H, H_{6C}), 7.95 (td, J=8.0, 1.6 Hz, 1H, H_{4A}), 7.82 (d, J=8.0, 1.6 Hz, 1H, H_{4C}), 7.66 (s, 1H, H_{4D}), 7.54 (m, 3H, $H_{5A+5C+3A}$), 7.23 (d, J=8.0 Hz, 1H, H_{3C}), 7.16 (d, J=1.6 Hz, 2H, H_{2D+6D}), 6.80 (d, J=8.8 Hz, 2H, H_{2E+6E}), 6.70 (d, J=8.8 Hz, 2H, H_{3E+5E}), 3.66 (s, 3H, CH_3).

^{13}C NMR (DMSO, 100 MHz) δ/ppm: 159.0, 158.0, 153.2, 153.1, 150.5, 149.8, 139.9, 137.9, 137.5, 137.4, 137.3, 132.8, 131.7, 131.2, 125.9, 125.7, 124.8, 124.5, 121.6, 113.5, 55.0, 5 carbon signals unresolved.

MS (ES) *m/z* $[L]^+$ 573, $[Ag+L]^+$ 681, $[Ag+2L]^+$ 1255,$[2Ag+2L+BF_4]^+$ 1451.

Elem. Anal. ($C_{27}H_{19}N_4Br_2OAgBF_4$ + 0.5 CH_3CN) [%] calc. C 42.6, H 2.5, N 8.0, found, C 43.0, H 2.4, N 7.7.

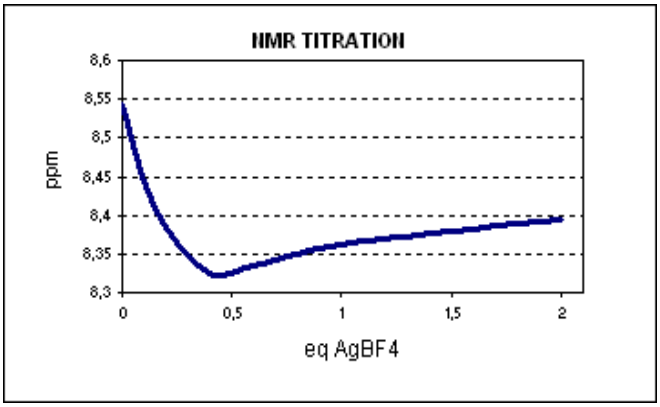
NMR TITRATION

4-(4-bromophenyl)-3,6(di-pyridin-2-yl)pyridazine (**15**) with AgBF4

eq AgBF4	shift ppm
0	8,544
0,1	8,444
0,2	8,385
0,3	8,348
0,4	8,326
0,5	8,326
0,6	8,334
0,8	8,349
0,9	8,356
1	8,361
1,1	8,367
1,2	8,369
1,4	8,376
1,6	8,383
1,8	8,389
2	8,395

9 mg Ligand in 0.3 mL CD3CN

0.1 eq is 0.0023 mmol of AgBF4 and 0.025 mL CD3CN



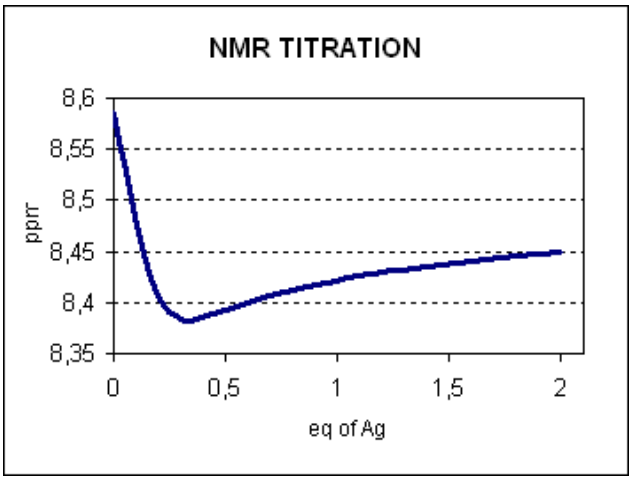
NMR TITRATION

4-phenyl-3,6-dipyridin-2-ylpyridazine (**3**) with AgBF4

eq AgBF4	Shift ppm	NMR file
0	8,586	632
0,1	8,476	633
0,2	8,407	634
0,3	8,383	635
0,4	8,385	636
0,5	8,393	637
0,6	8,4	638
0,7	8,407	639
0,8	8,412	640
0,9	8,417	641
1	8,421	642
1,1	8,427	643
1,2	8,429	644
1,4	8,435	645
1,6	8,44	646
1,8	8,445	648
2	8,45	649

3.4 mg Ligand in 0.3 mL CD3CN

0.1 eq is 0.0010 mmol of AgBF4 and 0.02mL CD3CN



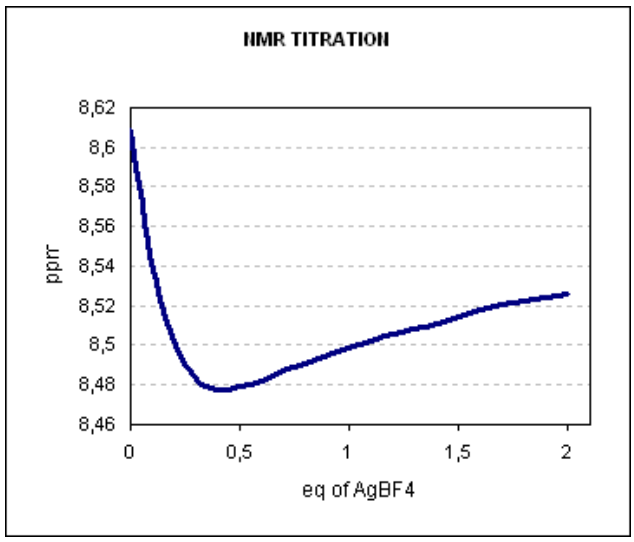
NMR TITRATION

4-(4-nitrophenyl)-3,6-di(pyridin-2-yl)pyridazine (**58**) with AgBF4

4 mg Ligand in 0.3 mL CD3CN

0.1 eq is 0.0011 mmol of AgBF4 and 0.02 mL CD3CN

eq AgBF4	shift ppm	NMR file
0	8,609	650
0,1	8,538	651
0,2	8,502	652
0,3	8,483	653
0,4	8,478	654
0,5	8,479	655
0,6	8,482	656
0,7	8,487	657
0,8	8,491	658
0,9	8,495	659
1	8,499	662
1,1	8,502	663
1,2	8,506	664
1,4	8,511	665
1,6	8,518	666
1,8	8,522	667
2	8,526	668



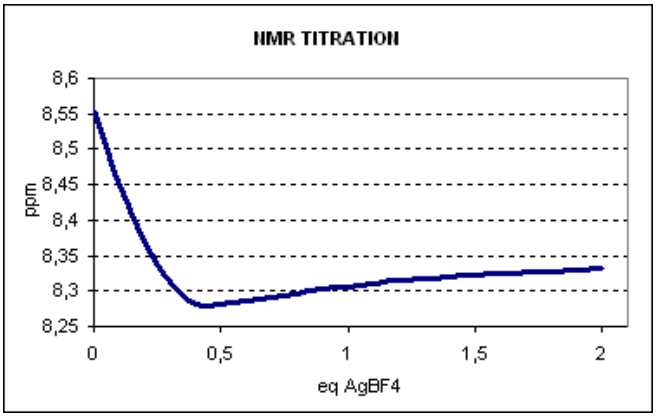
NMR TITRATION

4-(4-methoxyphenyl)-3,6-di(pyridin-2-yl)pyridazine (**30**) with AgBF4

eq AgBF4	shift ppm	NMR file
0	8,554	572
0,1	8,447	573
0,2	8,371	574
0,3	8,312	575
0,4	8,281	576
0,5	8,281	577
0,6	8,285	578
0,7	8,292	579
0,8	8,297	580
0,9	8,302	581
1	8,306	582
1,1	8,31	583
1,2	8,314	584
1,6	8,324	589
1,8	8,328	590
2	8,332	591

7 mg Ligand in 0.3 mL of CD3CN

0.1 eq is 0.0020 mmol of AgBF4 and 0.025 mL CD3CN



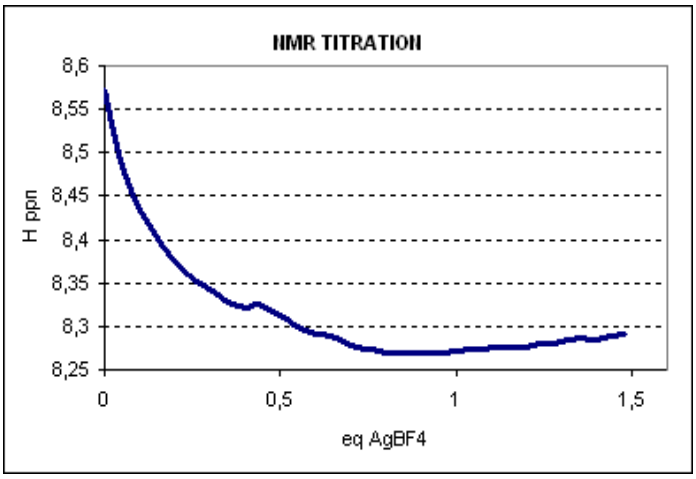
NMR TITRATION

4-(4-tert-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**42**) with AgBF4 (single H_{3B} signal)

16 mg of Ligand in 0.3 mL CD3CN

0.04 eq is 0.00175 mmol AgBF4 and 12.5µL CD3CN

NMR file	eq AgBF4	H shift
1032	0	8,571
1033	0,04	8,499
1034	0,08	8,452
1035	0,12	8,421
1036	0,16	8,395
1037	0,2	8,376
1038	0,24	8,359
1039	0,28	8,348
1040	0,32	8,336
1044	0,36	8,326
1045	0,4	8,321
1046	0,44	8,326
1047	0,48	8,317
1048	0,52	8,309
1049	0,56	8,298
1050	0,6	8,292
1051	0,64	8,288
1052	0,68	8,282
1053	0,72	8,277
1054	0,76	8,273
1055	0,8	8,27
1056	0,84	8,269
1057	0,88	8,269
1058	0,92	8,269
1059	0,96	8,27
1060	1	8,272
1061	1,04	8,273
1062	1,08	8,274
1063	1,12	8,276
1064	1,16	8,276
1065	1,2	8,277
1067	1,24	8,28
1068	1,28	8,281
1069	1,32	8,284
1070	1,36	8,286
1071	1,4	8,285
1073	1,44	8,288
1074	1,48	8,292



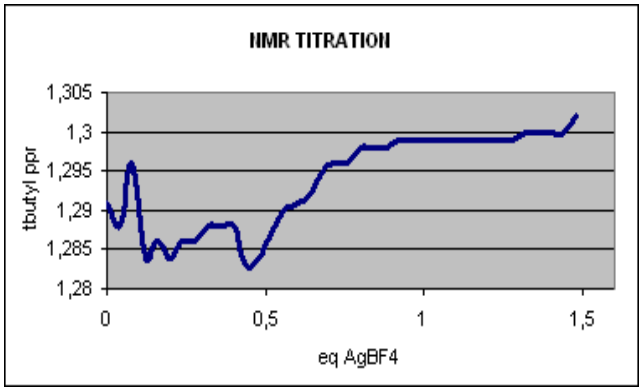
NMR TITRATION

4-(4-tert-butylphenyl)-3,6-di(pyridin-2-yl)pyridazine (**42**) with AgBF4 (tert-butyl signals)

NMR file	eq AgBF4	terbut shift
1032	0	1,291
1033	0,04	1,288
1034	0,08	1,296
1035	0,12	1,284
1036	0,16	1,286
1037	0,2	1,284
1038	0,24	1,286
1039	0,28	1,286
1040	0,32	1,288
1044	0,36	1,288
1045	0,4	1,288
1046	0,44	1,283
1047	0,48	1,284
1048	0,52	1,287
1049	0,56	1,29
1050	0,6	1,291
1051	0,64	1,292
1052	0,68	1,295
1053	0,72	1,296
1054	0,76	1,296
1055	0,8	1,298
1056	0,84	1,298
1057	0,88	1,298
1058	0,92	1,299
1059	0,96	1,299
1060	1	1,299
1061	1,04	1,299
1062	1,08	1,299
1063	1,12	1,299
1064	1,16	1,299
1065	1,2	1,299
1067	1,24	1,299
1068	1,28	1,299
1069	1,32	1,3
1070	1,36	1,3
1071	1,4	1,3
1073	1,44	1,3
1074	1,48	1,302

16 mg of Ligand in 0.3 mL CD3CN

0.04 eq is 0.00175 mmol AgBF4 and 12.5µL CD3CN



Curriculum Vitae

PERSONNAL INFORMATIONS

Name	Sébastien Reymann
Nationality	French
Date of birth	10th August 1976 (Haguenau-France)
Gender	male
E-mail	reymann_s@yahoo.fr

DIPLOMA

2002-2006 **PhD in Inorganic Chemistry**
University of Basel (Switzerland)
"*New silver complexes with ligands based on 4-substituted-3,6-dipyridin-2-ylpyridazines*"

2001-2002 **DEA in Transition Metals Chemistry and Molecular Engineering**
University Louis Pasteur (Strasbourg-France)

2000-2001 **Maîtrise in Chemistry**
University Louis Pasteur (Strasbourg-France)

1998-2000 **Licence in chemistry**
University Louis Pasteur (Strasbourg-France)

1996-1998 **DEUG in chemistry** (diplôme d'etudes universitaires general)
University Louis Pasteur (Strasbourg-France)

1995-1996 **DUT in chemistry** (diplôme universitaire de technologie)
Institut Universitaire de Technologie Robert Schuman (Strasbourg-France)

PROFESSIONAL

2002-2006 **Studies towards PhD**
University of Basel
"*New silver complexes with ligands based on 4-substituted-3,6-dipyridin-2-ylpyridazines*"
Assistant in Lab Classes
Supervisor: Prof. Dr. Edwin C. Constable

2001-2002	**Preparation of a diploma in chemistry** (8 months) University Louis Pasteur (Strasbourg-France) "*Synthesis of organic-inorganic hybrids. Association of zirconium and titanium oxalates with bisamidinium*" Supervisor: Prof. Dr. Mir Wais Hosseini
2000-2001	**Preparation of a diploma in chemistry** (4 months) CNRS, Institut Charles Sadron (Strasbourg-France) "*Copollymer stars based on polyoxyde d'ethylene et de polystyrene*" Supervisor: Prof. Dr. Pierre Lutz
1995-1996	**Training Period** (2 months) Lilly France (Strasbourg-France) "*Quality controls of in and out coming compounds*"

PUBLICATION, PRESENTATION

"*Self-assembly of a novel pentanuclear centred-tetrahedral silver species*"
E. C. Constable, C. E. Housecroft, M. Neuburger, S. Reymann, S. Schaffner, *Chem. Commun.*, **2004**, 1056-1057

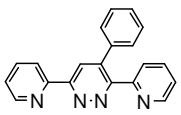
Posters at the meetings of the Swiss Chemical Society in 2004 and 2005

SKILLS

Languages	Fluent, both written and spoken English Fluent spoken German, written German
Computer software	Structural analysis (Chem3D, Mercury) Word processing (word, excel) NMR spectrum analysis (WinNMR, Mestrec)

MISCELLANEOUS

Photography, Music (playing guitar), Cinema, Nature



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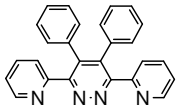

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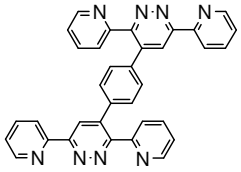

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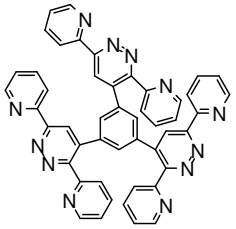

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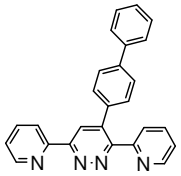

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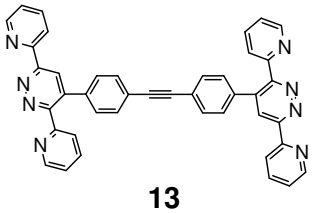

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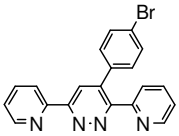

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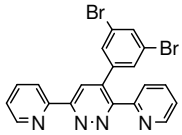

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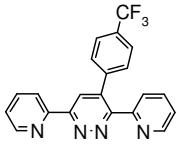

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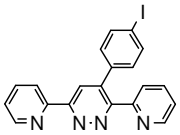

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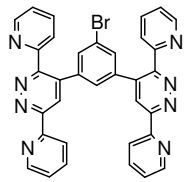

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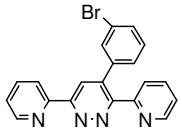

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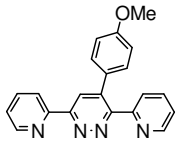

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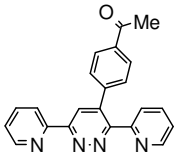

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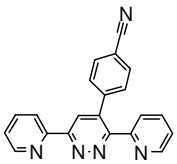

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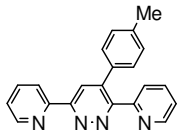

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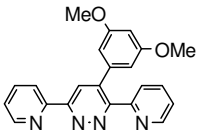

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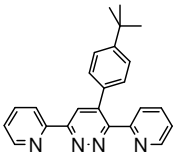

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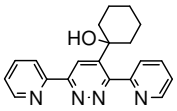

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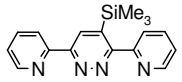

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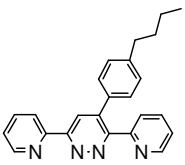

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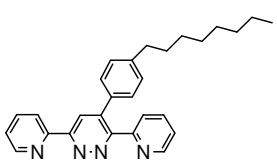

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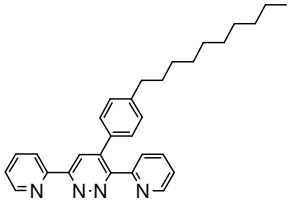

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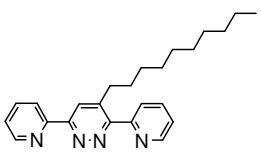

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