The Influence of Dynamic Coordination Spheres in Metal-Based Homogeneous Catalysis

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Abstract

This thesis features two distinct "case studies" that fall under the umbrella of homogeneous catalysis, and where the concept of dynamic coordination sphere could be involved. A combination of laboratory and computational studies has been conducted to attempt to devise metal-based catalysts for these reactions and gain insights into their mechanisms and the role of the dynamic coordination sphere.

Chapter 2 of this thesis focuses on the ring-opening copolymerisation of epoxides and cyclic anhydrides, which results in polyester molecules. The literature provides multiple examples of catalysts based on various metals, but Chapter 2 considers a potential candidate in a novel indium complex, which was found to be active towards ring-opening co-polymerisation in conjunction with a [PPN]Cl co-catalyst, with improved polydispersities observed compared to just the co-catalyst alone. Computational studies were also conducted to examine the propagation cycle of the reaction.

In chapter 3 of this thesis, a series of novel stereogenic-at-metal complexes of ruthenium, rhodium, and iridium is presented. Simple and commercially available 3-amino-1-azacycle ligands were found to effect com-

plete diastereomeric selectivity in the synthesis of these complexes. The complexes can facilitate the transfer hydrogenation of aromatic ketones, but, unfortunately, no stereoselectivity was observed. Nevertheless, this represents an interesting addition to the transfer hydrogenation literature, and these complexes could potentially catalyse the transfer hydrogenation of other unsaturated compounds. Computational studies were also conducted to gain mechanistic insight into the catalytic process, as well as to investigate the diastereoselectivity observed in the synthesis of the complexes.

Acknowledgements

This journey would not have been possible without the invaluable support and contributions of the many people who have stood by me along the way. I am immensely grateful for their confidence in me and in my research.

First and foremost, I would like to express my deepest gratitude to my family for their love, encouragement, and unwavering belief in me. You have been a constant source of strength and have played a vital role in helping me reach this point. To my parents, thank you for the countless sacrifices you have made to allow me to pursue my ambitions and become the person I am today. And to my sister, your steady presence and motivation have meant more to me than you know. I could not have done this without each and every one of you.

I also want to pay tribute to my late grandparents. Thank you for the lifelong love and care you gave me. This thesis is dedicated to you, in the hope of sharing, even in a small way, the joy of reaching this milestone - and with the feeling that you are still very much a part of it.

To my friends (you know who you are), thank you for the much-needed laughter, welcome distractions, and the sense of balance you brought to

my life. You helped carry me through the more difficult moments of this PhD, offering reassurance when I needed it most and reminding me to keep going.

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In loving memory of my grandparents.

Abbreviations

[PPN]Cl Bis(triphenylphosphine)iminium chloride

d.r. Diastereomeric ratio

e.e. Enantiomeric excess

r.t. Room temperature

^{i}Pr Isopropyl

^{t}Bu *Tert*-butyl

Ar Aryl

CA *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride

CHO Cyclohexene oxide

CI Climbing image

Cp* 1,2,3,4,5-Pentamethylcyclopentadienyl

CSD Cambridge Structural Database

Cy Cyclohexyl

DFT Density functional theory

DMAP 4-Dimethylaminopyridine

DMF *N,N*-Dimethylformamide

ECH Epichlorohydrin

ESD Estimated standard deviation

Et Ethyl

GPC Gel permeation chromatography

HPLC High-performance liquid chromatography

HRMS High-resolution mass spectrometry

ICP-MS Inductively coupled plasma mass spectrometry

IUPAC International Union of Pure and Applied Chemistry

MALDI-TOF Matrix-assisted laser desorption/ionisation - time-of-flight

Me Methyl

MS Mass spectrometry

NEB Nudged elastic band

NMR Nuclear magnetic resonance

PA Phthalic anhydride

PDI Polydispersity index

PES Potential energy surface

Ph Phenyl

PPDA 2-Methyl-2-(pyridin-2-yl)-propane-1,3-diamine

PTFE Polytetrafluoroethylene

Py Pyridyl/pyridine

ROCOP Ring-opening copolymerisation

ROP Ring-opening polymerisation

Salen 2,2′-((ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))di-phenolate

Salpy 2,2′-(((2-methyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(azaneylylidene))-bis(methaneylylidene))diphenolate

SC-XRD Single-crystal X-ray diffraction

SO Styrene oxide

TH Transfer hydrogenation

THF Tetrahydrofuran

TOF Turnover frequency

TON Turnover number

TS Transition state

Ts Tosyl (toluenesulfonyl)

VCHO Vinylcyclohexene oxide

XRD X-Ray Diffraction

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CHAPTER 1

Introduction

1.1 Catalysis

1.1.1 Definition of catalysis

Catalysis is the process of increasing the rate of chemical reactions and is achieved by adding a substance known as a catalyst. The International Union of Pure and Applied Chemistry (IUPAC) defines a catalyst as follows:

> *"A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis"*[1]

During the reaction, the catalyst interacts with the other components and provides an alternative energy pathway through the formation of intermediate species or lower energy transition states. The alternative path afforded by the catalyst often features multiple barriers with lower activation energies, compared to the uncatalysed reaction. This allows for milder

conditions to be employed, *e.g.* lower temperature and/or pressure. At the end of the reaction, the catalyst remains unchanged. However, many catalysts often begin as bi-modal pre-catalytic species and can act as initiators (*i.e.* to start the reaction), which then, in turn, generate the active catalytic species which proceed to accelerate it. It is therefore the latter that remains unchanged, whilst regeneration of the pre-catalyst would require an additional step. A generic example that illustrates the basic principle of catalysis is shown in Figure 1.1. However, many pre-catalysts are bimodal as they can both initiate the reaction and then turn into active catalytic species, which proceed to accelerate it.

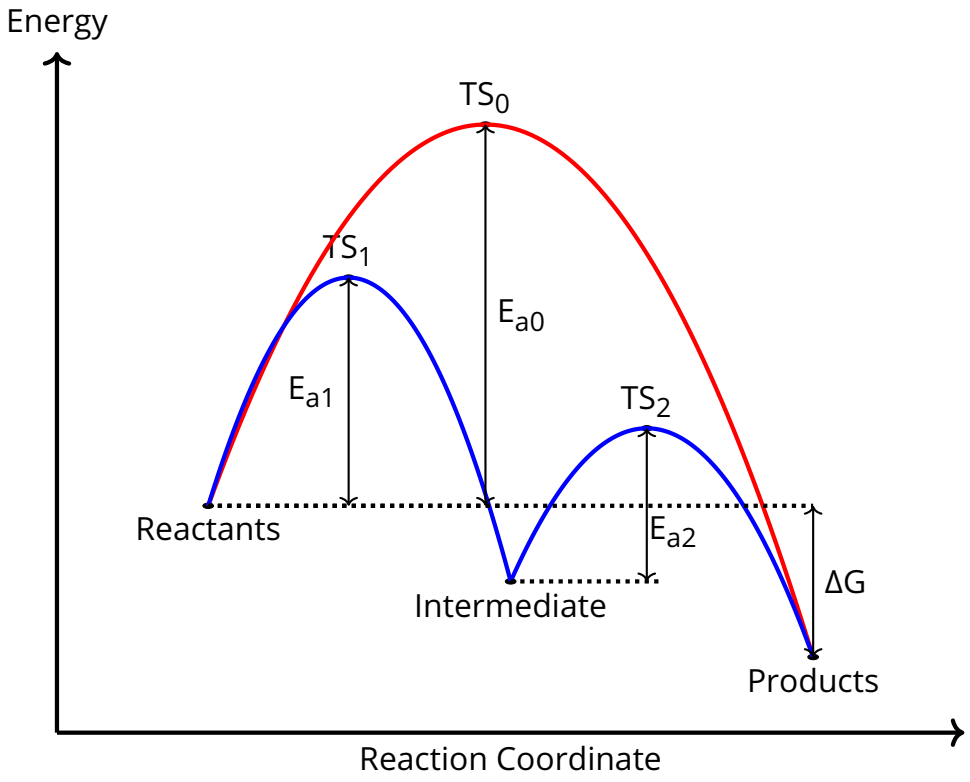


Figure 1.1: Generic example of reaction profiles for catalysed (red) and non-catalysed (blue) reaction. TS and E_a represent the transition states and activation energies for the respective reactions.

Furthermore, due to the way catalysts operate, they do not, and cannot, alter the Gibbs free energy change (ΔG) for a reaction.[2] This is because ΔG is a state function and as such is independent of the reaction path-

way. Consequently, non-spontaneous reactions (*i.e.* thermodynamically unfavourable reactions with $\Delta G > 0$) cannot normally be catalysed, whilst spontaneous reactions (*i.e.* thermodynamically favourable reactions with $\Delta G < 0$) can benefit from significant rate enhancement.[2] This is consistent with the first law of thermodynamics, according to which energy cannot be created or destroyed. Moreover, a catalyst cannot shift the equilibrium position for reactions,[2] as this would constitute a violation of the second law of thermodynamics. Therefore, for reversible reactions, the catalyst will accelerate both the forward and reverse reactions equally and thus can only affect the rate at which equilibrium is reached.

1.1.2 Types of catalysis

Depending on the number of phases involved in the reaction, catalysis falls into two broad categories: homogeneous and heterogeneous catalysis. In the former, the catalyst and the reactants are in the same phase, and thus, only one phase exists. In the latter, the opposite is true, and so the reaction occurs at the interface between the different phases.[1] Both have advantages and disadvantages.

Homogeneous catalysis tends to allow for milder conditions and can feature tunable reaction sites, which can be modified to increase the catalyst's activity and selectivity. Furthermore, as the catalyst is in the same phase as the reactants, this type of catalysis is amenable to spectroscopic monitoring. However, a major drawback of homogeneous catalysis is the separation of the catalyst from the reaction mixture, which is often difficult, and in many cases impossible (*e.g.* polymerisation reactions where the polymer chains grow on the catalyst itself).

On the other hand, heterogeneous catalysis often requires harsher con-

ditions (*e.g.* higher temperature and/or pressure). Furthermore, issues such as mass transfer and aggregation (*e.g.* when nanoparticles are involved) can significantly affect catalytic activity. Nevertheless, the separation of the reactants is often much easier than with homogeneous catalysis and allows for the reaction mixture to be simply filtered (in the case of liquid phase reactions) or a stream of reactants to be passed through a catalyst-packed column. Heterogeneous catalysts are also significantly cheaper than homogeneous catalysts, which can often require expensive and rare metals.

Both categories discussed above can be further divided into subcategories depending on the type of catalyst employed or the type of reaction. Some of these could be included in both homogeneous and heterogeneous catalysis, depending on the phase of the catalyst. For example, **acid/base catalysis** makes use of Brønsted-Lowry or Lewis acids/bases, as well as solid materials like zeolites. **Biocatalysis** employs enzymes, often with narrow and specific substrate requirements,[1] while **organocatalysis** relies on organic compounds such as proline, secondary amines, organophosphines, or thioureas, amongst others.[3] **Photocatalysis** leverages light to induce excitations in light-absorbing molecules, turning them into active catalysts. In **electrocatalysis**, catalysts participate in electrochemical reactions either as one of the electrodes or additives. Catalysis where one of the reaction products itself acts as a catalyst is termed **autocatalysis**.[1] Lastly, biphasic systems represent an intermediate case between homogeneous and heterogeneous catalysis, for example, with liquid-liquid systems, where the catalyst resides on one of the phases and the substrate/reactants in the other.[4]

1.1.3 Measuring catalytic performance

Two of the most commonly used measures of catalyst performance are the turnover number (TON) and the turnover frequency (TOF). These can be calculated as shown in Equation 1.1 and Equation 1.2, respectively.

$$TON = \frac{n_{product}}{n_{catalyst}}$$

Equation 1.1: Turnover number calculation.

$$TOF = \frac{TON}{time}$$

Equation 1.2: Turnover frequency calculation.

The TON represents the number of times the catalyst goes through a cycle to generate an equivalent of product until the catalyst has deactivated or the reaction is stopped. It is expressed as the ratio of moles of product generated to moles of catalyst used (Equation 1.1). Assuming an infinite amount of substrate and infinite reaction time, an ideal catalyst would have a TON of infinity, as it would never be deactivated. As such, the TON measures the robustness and stability of the catalyst. A calculated TON would only be valid within the time frame of the reaction considered. Therefore, it cannot be used to directly compare reactions of different lengths. However, a plot of TON *vs* time would indicate how the catalyst performs throughout the reaction and reveal if any deactivation is taking place. On the other hand, the TOF is defined as *"molecules reacting per active site in unit time"* (Equation 1.1).[1] In 1966, Boudart, in a paper titled *"On the specific activity of platinum catalysts"*,[5] first defined what would later become known as turnover frequency:

"Indeed, the catalytic activity, for a valid comparison, must be referred to the number of exposed surface atoms of a specified kind. Thus, a convenient way to express catalytic activity is by means of a turnover number equal to the number of reactant molecules converted per minute per catalytic site for given reaction conditions."[5]

Another important parameter to consider when evaluating catalytic performance is selectivity. This is relevant when the same catalyst could facilitate different types of reactions that lead to different products. In these cases, a highly selective catalyst would maximise the yield of the desired products compared to any side products. As such, the selectivity of a catalyst would be calculated as the percentage of desired product relative to all products formed, as shown in Equation 1.3.

$$\text{Selectivity} = \frac{n_{\text{desired}}}{\sum n_{\text{products}}} \times 100$$

Equation 1.3: Selectivity calculation.

It should be noted that TON and TOF are intrinsically linked to the conversion of the reaction by virtue of all being a function of the amount of product. However, the selectivity is not necessarily dependent on conversion in all cases. For example, it could stay the same throughout, or it could vary depending on the reaction progress.

Nevertheless, there is no single metric that can define overall catalytic performance. Instead, a combination of metrics can be chosen when screening catalysts that depend on the specific application and are evaluated according to the desired outcome. For example, some relevant parameters for the reactions that will be discussed later in this thesis are as follows:

- In Chapter 2, important parameters are the conversion of cyclic anhyd-

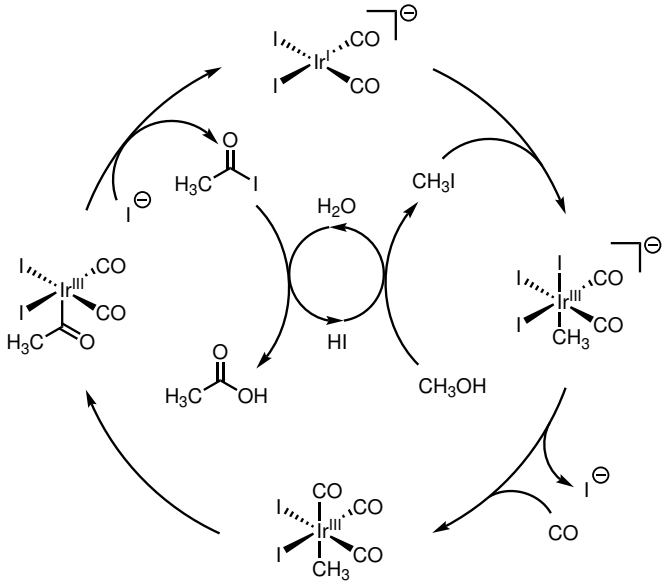
ride and epoxides to polyesters, the selectivity of polyester *vs* polyether by-product, as well as the molecular weight of the resulting polymers.

- In Chapter 3, the conversion of the ketone substrate to an alcohol, as well as the enantioselectivity, are the key parameters considered.

1.1.4 Catalysis in industry

Catalysis is crucial in many industries where processes rely on it for the efficient and selective production of speciality or commodity chemicals. Perhaps one of the most notable examples of an industrial process which employs a homogeneous catalyst is the Cativa^{TM} process,[6] which is used in the production of acetic acid from CH_3OH and CO, using a catalyst based on Ir (catalytic cycle shown in Scheme 1.1). Its predecessor - the Monsanto process[7] - is also a homogeneously catalysed process but employs a catalyst based on Rh. Other important industrial processes using homogeneous catalysts include the Wacker process[8] (for the oxidation of ethylene to acetaldehyde), hydroformylation,[9] and olefin metathesis[10–12] (exchange of alkene fragments), amongst others. On the other hand, many important processes employ heterogeneous catalysts. These include the Haber-Bosch process[13] (for the production of ammonia), the Fischer-Tropsch process[14] (for converting CO and H_2 to hydrocarbons), catalytic cracking (breaking down large hydrocarbons), catalytic reforming, water-gas shift reaction (conversion of CO and water to CO_2 and H_2), etc. Ziegler-Natta catalysts are also a well-known example of olefin polymerisation catalysts used in industry, and both homogeneous and heterogeneous versions exist.[15–20] An overview of some of these processes is shown in Table 1.1.

Furthermore, the use of catalytic processes in industry also has a significant economic and environmental impact. Catalytic processes improve



Scheme 1.1: Catalytic cycle of the Cativa^{TM} process.[21]

Process	Catalyst
Wacker Process[8]	$PdCl_2$, $CuCl_2$
Monsanto Process[7]	*cis*-$[Rh(CO)_2I_2]^-$
Cativa^{TM} Process[6]	*cis*-$[Ir(CO)_2I_2]^-$
Hydroformylation[9]	Co(I) and Rh(I) carbonyl complexes
Olefin metathesis[10–12]	Schrock: Mo(VI), W(VI) supported by alkoxide and imido ligands, Grubbs: Ru(II) carbene complexes
Haber-Bosch Process[13]	Fe-based catalyst with promoters
Fischer-Tropsch Process[14]	Iron or cobalt catalysts
Ziegler-Natta Polymerisation[15,16]	$TiCl_4$ with $AlEt_3$

Table 1.1: Examples of industrially important catalytic processes

energy consumption by allowing reactions to proceed under milder conditions, which in turn lowers operational costs and greenhouse gas emissions. In essence, catalysis allows for more sustainable and cost-effective industrial processes. Moreover, research in catalysis is always ongoing and aims to address challenges such as dependence on rare or expensive metals or to develop catalysts that are more robust and less prone to deactivation.

1.1.5 Catalysis in everyday life

Catalysis also plays an important role in everyday life, often in ways that people do not realise. Below are some examples of catalytic processes that we encounter every day.

In the automobile industry, vehicle exhausts feature catalytic converters, with precious metals (*e.g.* Pt, Pd, or Rh) supported onto a ceramic or metallic surface, that convert harmful gases into less harmful compounds (CO to CO_2, nitrogen oxides (NO_x) into N_2 and H_2O, and unused hydrocarbons from the fuel to CO_2 and H_2O).[22]

In the food industry, some food production processes rely on enzyme catalysts produced by yeast or bacteria. For example, amylase is used in brewing to convert starches to simple sugars, with yeast then releasing enzymes that convert the sugars into alcohol and CO_2. Yeast is also used in baking for the same purpose, with the CO_2 getting trapped into the dough, helping it rise, and giving it texture.[23] Cheese production also uses a complex set of enzymes called rennet, which coagulates the proteins in milk.[24] Many cleaning products, such as laundry or dishwasher detergents, contain enzymes that break down food and dirt.[25]

Furthermore, tens of thousands of enzymatic reactions occur every second in the human body, which are essential to life. Processes such as digestion, energy production, cell repair, and virtually all metabolic processes rely on enzyme catalysts.[26]

1.2 Dynamic coordination sphere

1.2.1 Definition and concept

The way ligands bind to a metal depends on many factors - *e.g.* the denticity and hapticity of the ligand, the nature of the donor atoms, the overall charge of the ligand, as well as the nature and oxidation state of the metal centre. Therefore, as this is a multifactorial interaction, in many cases, the resulting coordination sphere becomes a flexible environment surrounding the metal, which can adapt to changing demands during the catalytic cycle. This is in contrast to cases where the coordination sphere around the metal remains static during catalysis, for example, metallocenes catalysts for polymerisation of olefins, where, after initiation of the catalyst to replace the Metal-Cl with Metal-CH_3 bonds, the ligand environment remains largely unchanged during the catalytic cycle.

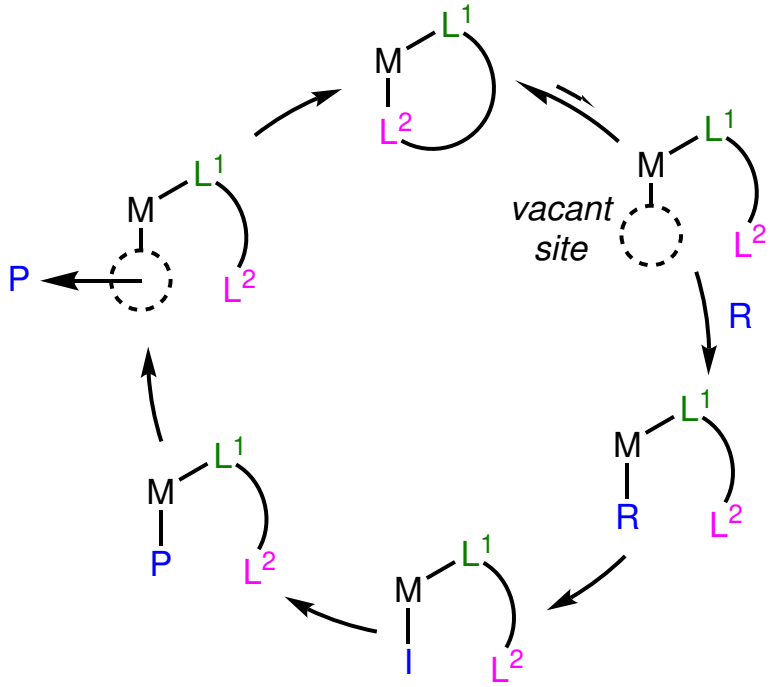
Although exact mentions of the term in the literature are scarce, the concept of "dynamic coordination sphere" is not a new one, and there are many literature examples which leverage dynamic ligand environments for enhanced catalysis. Phenomena such as hemilability, metal-ligand cooperativity, and outer-sphere mechanisms create a flexible and dynamic ligand environment, which plays a crucial role in facilitating and improving catalytic activity. Therefore, these could all be seen as being encompassed under the umbrella of "dynamic coordination sphere".

1.2.2 Role in catalysis

The phenomena discussed above often constitute a critical part of many catalytic reactions, especially in homogeneous catalysis, where all the species involved are in the same phase. The term "Structurally-Responsive Lig-

ands" has recently been used to describe ligands that "exhibit self-tuning denticity, hapticity, or versatile coordination" in response to steric or electronic demands.[27] This type of adaptable and dynamic ligand behaviour can significantly influence catalysis and could also be considered relevant to the concept of dynamic coordination sphere.

Hemilability is generally observed in polydentate ligands where part of the ligand binds strongly to the metal, whilst another part can reversibly dissociate from the metal centre and thereby create a vacant site for substrate coordination or activation.[28] The term was first introduced by Jeffrey and Rauchfuss in 1979.[29] It is a concept that is well-established with regards to transition metals[28], however, literature reports with main-group metals are scarce.[30] The "Salpy" ligand is an example of a ligand that can exhibit hemilabile behaviour, which has been reported by the Ward group in reference to aluminium(III) complexes for isocyanate trimerisation.[31] A generic example of how hemilabile ligands operate is shown in Scheme 1.2.



Scheme 1.2: Generic example of a catalytic process featuring a hemilabile ligand. R, I, and P refer to reactant, intermediate, and product, respectively. Adapted from Chen *et al.* (2023).[32]

Metal-ligand cooperativity occurs when both the ligand and the metal in a complex participate in substrate activation and subsequent transformation and often involves reversible changes within the coordination sphere. This behaviour is often seen in transfer hydrogenation catalysis, where the formal addition of hydrogen occurs *via* metal-hydride species in conjunction with protonation/deprotonation of the ligand.[33] The dynamic behaviour here is exemplified *via* the reversible changes occurring in the coordination sphere, which allows for catalysis that is not accessible through the metal alone. This is closely related to outer sphere mechanisms, where the substrates do not bind directly to the metal centre, but interact with the ligands to effect the catalytic transformation. An example of such a mechanism for the transfer hydrogenation of ketones using Iron(II) PNNP eneamido complexes has been reported by Morris *et al.* .[34,35]

Considering the above, it is therefore important to understand the dynamic changes that occur in the coordination sphere during a catalytic reaction in order to design effective catalysts and elucidate the mechanism through which these operate. This knowledge allows chemists to manipulate the ligand framework and reaction conditions to achieve desired properties and enhance catalytic performance.

1.2.3 Selected literature examples

As mentioned previously, there are only a few direct mentions of "dynamic coordination sphere" in literature reports. Indeed, according to a SciFinder^{n} search,[36] the phrase "dynamic coordination sphere" is first mentioned in the title of a 2004 article by Merkel *et al.* describing the use of iron(III) complexes as models of catechol dioxygenases.[37] However, there are a number of literature reports that utilise the concepts discussed in sec-

tion 1.2.1 to promote or enhance catalytic activity, with selected examples discussed below.

A report by Ward and co-workers explores isocyanate trimerisation reactions (Figure 1.2) by exploiting the dynamic coordination sphere effects in aluminium catalysts. In that report, the inherent lability of complexes of main-group metals is exploited by coupling aluminium with a pyridyl-bis(iminophenolate) ligand, which bears a pendant pyridyl moiety, resulting in a hemi-labile interaction with the aluminium, allowing the association of the isocyanate substrate.[31]

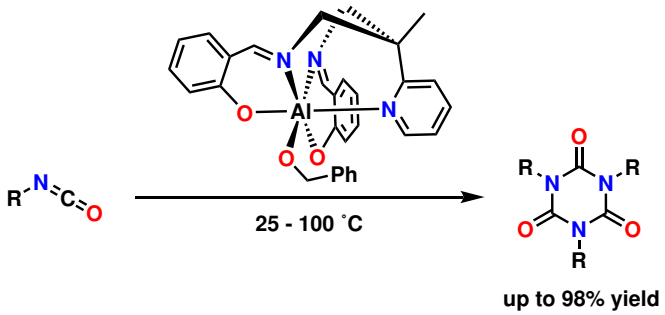


Figure 1.2: Isocyanate trimerisation using an aluminium catalyst reported by Ward and co-workers.[31]

In 2021, Mehrkhodavandi and co-workers reported cationic indium complexes (Figure 1.3) for the ring-opening polymerisation of epoxides and *rac*-lactide.[30] Their results show that the nature of the donor atom on the hemilabile pendant affects both the reactivity and shelf-life of the complexes, which correlated with the affinity of the donor atoms to the indium centre.

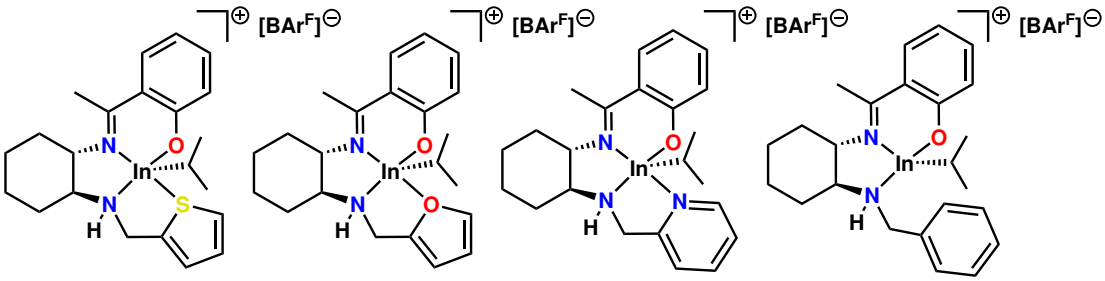


Figure 1.3: Cationic indium complexes reported by Mehrkhodavandi and co-workers[30]

A recent report by Russo *et al.* showcases the selective ring-opening co-polymerisation of cyclohexene oxide and succinic anhydride using Schiff-base aluminium complexes.[38] The report explores different side arms (pyridine, amine, phosphine) and varying substituents on the phenoxy moiety, as shown in Figure 1.4. The authors establish that the electron-withdrawing substituents or strongly nucleophilic side arms result in stable coordination and yield polyesters with polyether sequences in the chain. Conversely, electron-donating groups, coupled with side arms that can reversibly coordinate, yield polyesters with perfectly alternating structures. The importance of the side arm is highlighted by the fact that complexes in which the side arm is permanently de-coordinated resulted in a decrease in selectivity.

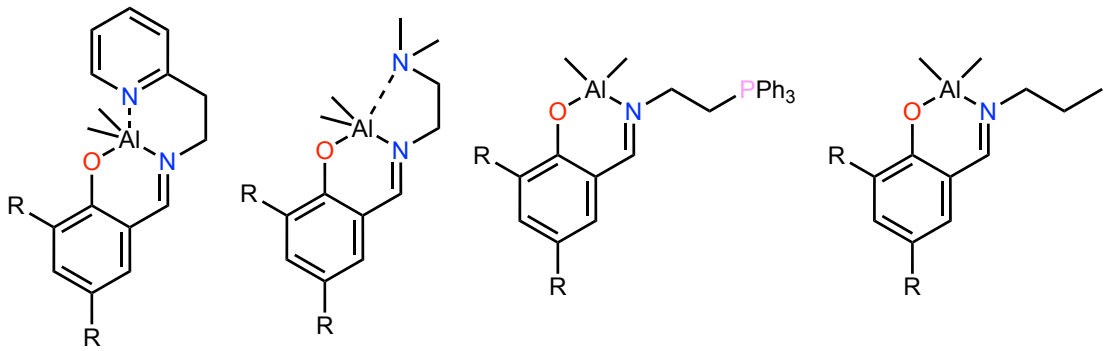


Figure 1.4: Aluminium complexes reported by Ruso *et al.*[38]

1.3 Polymers and polymerisation reactions

1.3.1 Definition and types of polymers

Polymers are large molecules made up of repeat units called monomers, usually bonded together covalently. Polymers can be made up of only a few monomer units or up to millions of monomer units. Due to their versatility, polymers can be classified in different ways based on different criteria

and contexts. At the most basic level, one could classify polymers based on their composition and arrangement of monomers. This gives **homopolymers**, which contain a single repeating unit, **copolymers**, which consist of two monomers, or **terpolymers** consisting of three different monomers. Copolymers can be further divided into different sub-categories, depending on the specific arrangement of the monomer units within the polymer chains. This gives rise to **alternating** copolymers, where the monomer units are arranged in an alternating fashion, **block** copolymers, where blocks of monomers are joined together, **graft** copolymers, which feature polymer chains being "grafted" onto another polymer chain, resulting in a branched polymer, and **random** copolymers, where the monomer units are randomly arranged within the chain. A subset of the latter are **statistical** copolymers, where the monomers are arranged seemingly randomly, but according to an underlying statistical rule, *e.g.* one monomer exhibiting higher reactivity, which causes more of that monomer to be incorporated into the resulting polymer chain. A basic representation of copolymer types is illustrated in Figure 1.5.[39]

Therefore, polymers are a truly versatile class of molecules and can be finely tuned to serve many different purposes, and indeed they do just that, as polymers serve a wide range of industrial applications. In addition, macromolecules vital to life, such as nucleic acids, proteins, and polysaccharides, all fall under the large umbrella of the polymer family.[39]

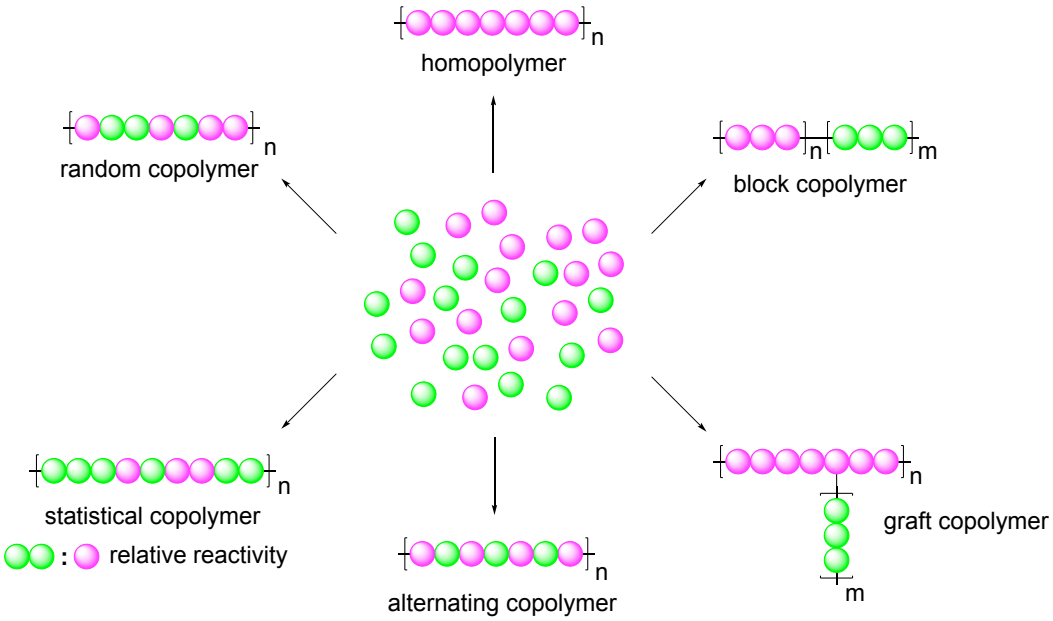


Figure 1.5: Different types of polymers that can be formed from two monomers (homopolymer included for comparison).

1.3.2 Types of polymerisation

Broadly speaking, polymerisation reactions fall into two main categories, based on their mechanism and kinetics. These are step-growth and chain-growth polymerisation.[39] However, a recent report by members of the Subcommittee on Polymer Terminology in the Polymer Division of the International Union of Pure and Applied Chemistry (IUPAC) has raised concerns as to whether the "step-growth" and "chain-growth" nomenclature is appropriate. This is because the *growth* in both mechanisms is through a series of *steps*, and both reactions result in polymer *chains*. The authors have analysed the different terms used across the literature and discussed the advantages and shortcomings of these, with a message to the polymer community in an effort to resolve the issues with the basic terms that we currently use to describe polymer reactions.[40] Nevertheless, as these terms are still in use and relevant within the polymer community, a brief description of these is presented below, with the generic mechanisms of how these operate presented in Figure 1.6.

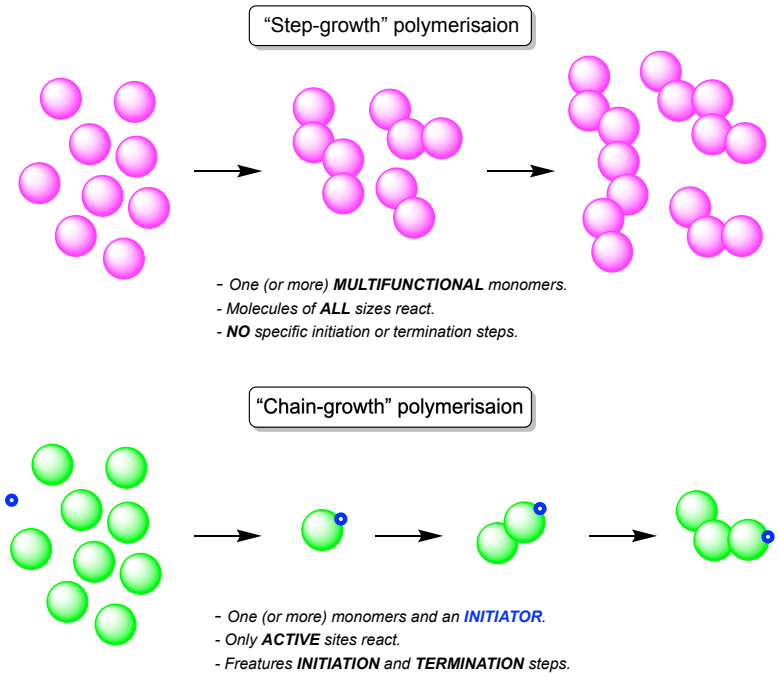
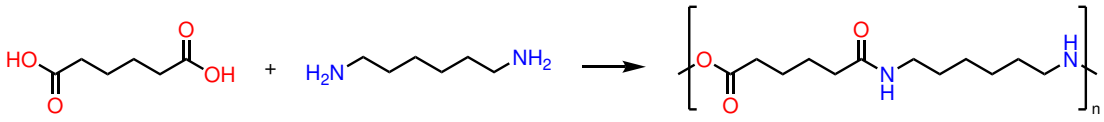


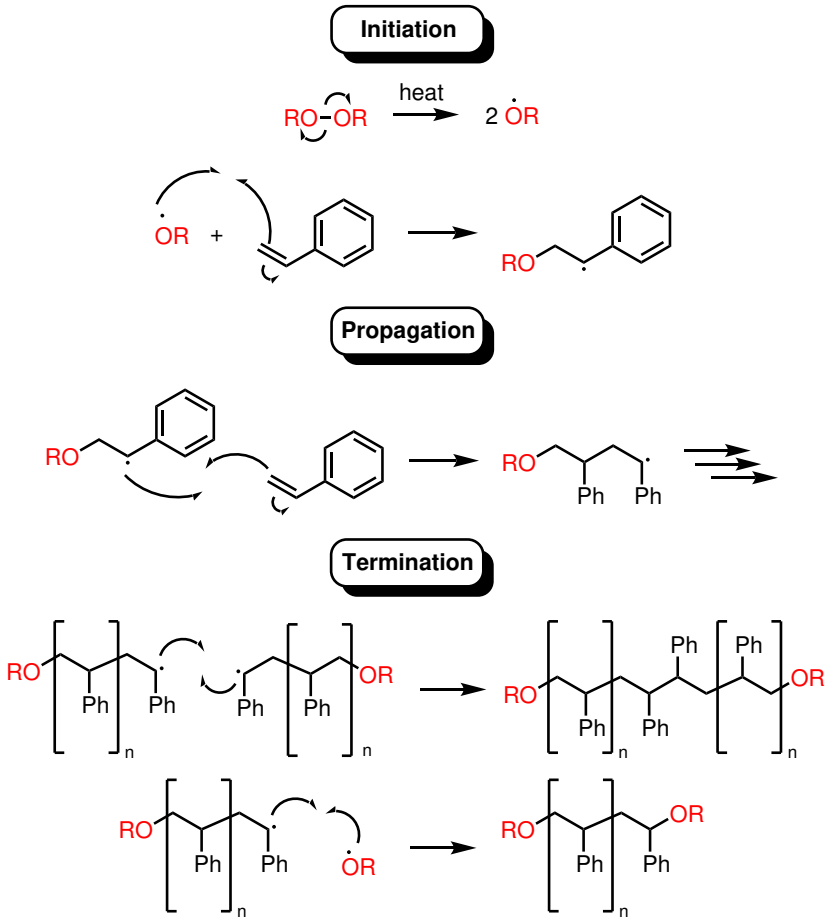
Figure 1.6: Generic representation of "step-growth" *vs* "chain-growth" polymerisation. Adapted from Chan *et al.* (2022).[40]

In step-growth polymerisation, the monomers are multifunctional (have multiple reactive sites) and can react together to form larger, similarly multifunctional units, which can further react with each other. Therefore, no initiator is required. Due to the nature of step-growth polymerisation, monomer concentration decreases rapidly in the initial stages of the reaction and high conversions are required to obtain high molecular weight polymers. Although in theory the molecular weight can double with each step, this is not always the case, and the resulting reaction mixture almost invariably contains a mixture of low and high molecular weight units. An example of this type of polymerisation is the synthesis of nylon 6,6 from 1,6-hexamethylene diamine and adipic acid, as shown in Scheme 1.3.[39,40]



Scheme 1.3: Synthesis of nylon 6,6 from 1,6-hexamethylene diamine and adipic acid

In contrast, chain-growth polymerisation operates quite differently. There is only one reactive site on the growing polymer chain, which is where the next monomer unit is added. Thus, in chain-growth polymerisation, the polymer grows one monomer at a time, and the molecular weight increases linearly compared to step-growth polymerisation. For this reason, chain-growth polymerisation reactions are often more controlled than step-growth polymerisations, due to the inherent limitation in the number of active sites. Another distinct difference is that chain-growth polymerisations require initiators, although these could sometimes be part of bifunctional catalysts. An example of this type of polymerisation is the synthesis of polystyrene, which can be initiated by a peroxide radical to create the active site for further chain growth, as shown in Scheme 1.4.[39,40]



Scheme 1.4: Synthesis of polystyrene initiated by a peroxide radical.

1.3.3 Ring-opening polymerisation

The term ring-opening polymerisation (ROP) represents a type of polymerisation whereby cyclic monomer units are, as the name suggests, ring-opened by the terminus of the growing polymer chain, to form a larger polymer. This type of polymerisation operates under the chain-growth mechanism. Examples of relevant polymers synthesised *via* ROP are the polymerisation products of ethylene oxide (resulting in polyethylene glycol, PEG), lactide (resulting in polylactic acid, PLA), ε-caprolactone (resulting in polycaprolactone, PCL). All of the mentioned are also biodegradable. In all cases, the resulting polymers are comprised of a single repeating monomer unit.

Mechanism	**Chain End**	**Growth**
Anionic ROP	Anionic (nucleophilic)	The nucleophilic anionic chain end attacks the electrophilic site of the monomer, causing ring-opening and chain growth.
Cationic ROP	Cationic (electrophilic)	The cationic chain end attacks a new monomer, opening the ring and transferring the positive charge to the new chain end.
Monomer-Activated ROP	Nucleophilic chain end	The monomer is activated by a catalyst and then attacked by a nucleophilic chain end.
Coordination-Insertion ROP	Chain end coordinated to a metal centre	The monomer coordinates to a metal catalyst and then inserts between the metal and the growing chain end.

Table 1.2: Summary of key features of ring-opening polymerisation mechanisms.[41–44]

For the ROP of lactones, four main mechanisms exist, depending on the catalyst used.[41] These are anionic, cationic, monomer-activated and coordination–insertion mechanisms. These are described below, with a summary shown in Table 1.2. In the anionic mechanism, a nucleophile attacks the carbonyl carbon of the monomer, resulting in an alkoxide growing spe-

cies. A major limitation of this approach is the high level of "back-biting" (intramolecular transesterification) during later stages, resulting in either low molecular weight or cyclic polymers.[41,42] On the other hand, a cationic mechanism operates by the monomer itself attacking a cationic initiator *via* the carbonyl oxygen in an S_N2-type reaction, which results in a partial positive charge on the acyl oxygen and subsequent ring-opening after the adjacent carbon is attacked by another monomer unit.[41,42] This results in a positively-charged chain end. Moving on, in the monomer-activated ROP, the catalyst activates the carbonyl oxygen of the monomer, which is subsequently ring-opened and attacked by the nucleophilic chain end, in contrast to the cationic mechanism, where a new monomer attacks a positively charged chain end.[41,43,44] Lastly, the coordination-insertion is the most common ROP mechanism. In this mechanism, the polymer growth proceeds *via* initial coordination of the monomer to the metal centre of a catalyst, with subsequent insertion of the monomer into the M-O bond, resulting in the polymer chain remaining attached to the catalytic species.[41,42] Industrially, the most commonly employed catalyst for PLA/PCL synthesis is a tin(II) octoate catalyst (structure shown in Figure 1.7), which operates through the coordination-insertion mechanism. The initiation steps of the discussed ROP mechanisms using ε-caprolactone as an example are shown in Scheme 1.5.

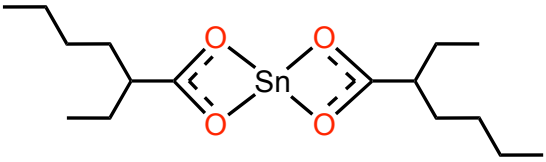
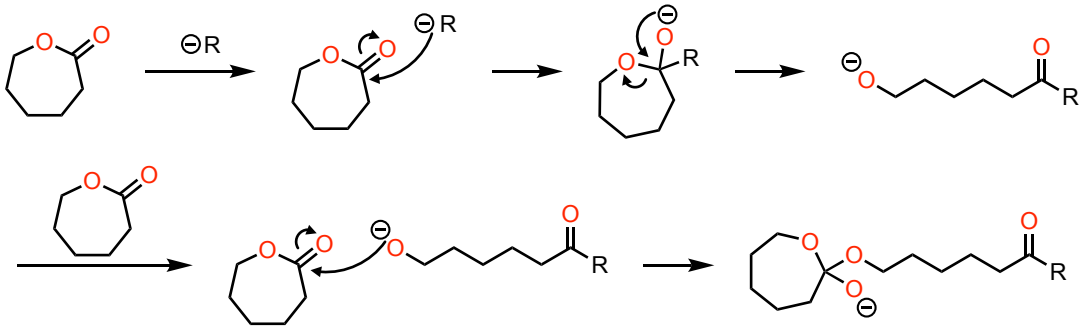
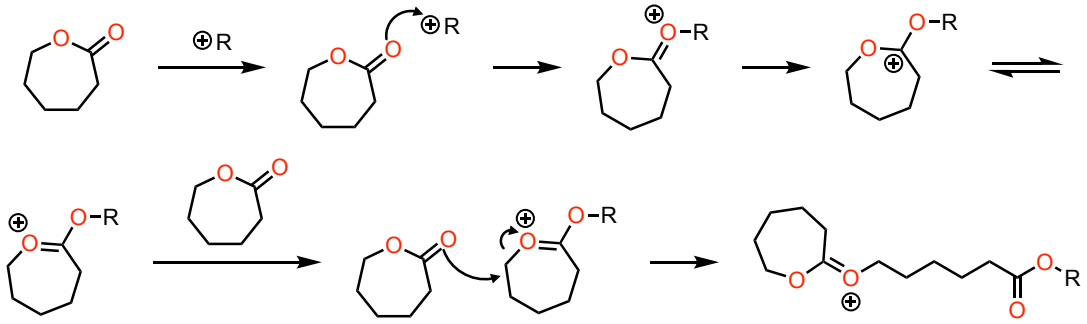


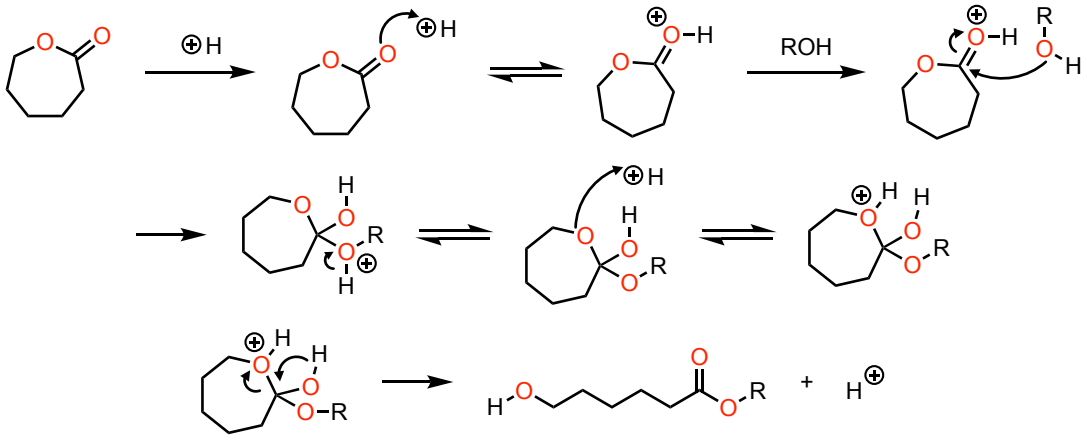
Figure 1.7: Structure of Sn(II) octoate.



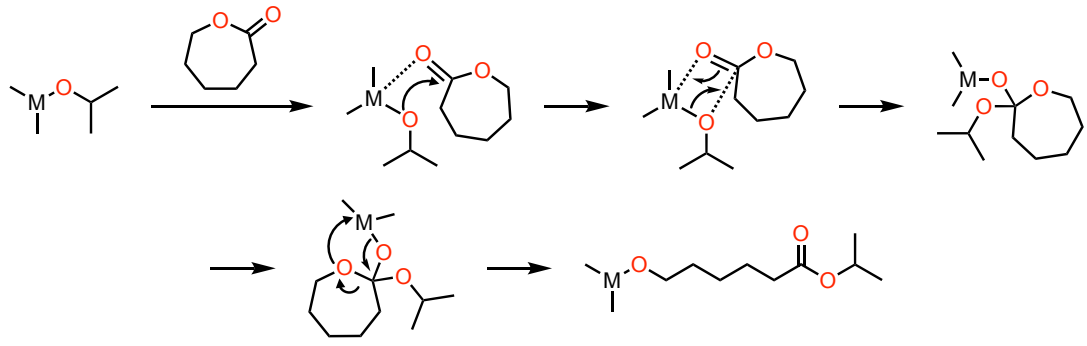
(a) anionic ROP



(b) cationic ROP



(c) monomer-activated ROP

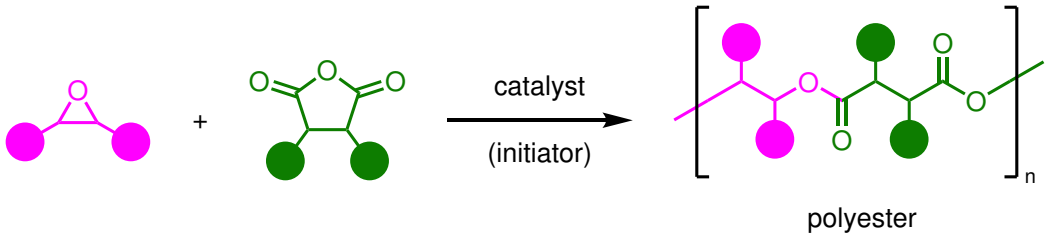


(d) coordination-insertion ROP

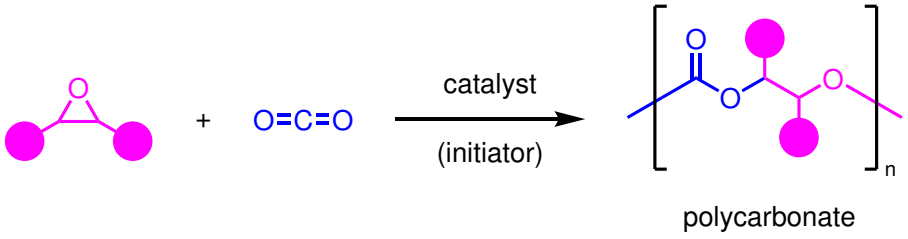
Scheme 1.5: Initiation steps of different ROP mechanisms using ε-caprolactone as an example.[41]

1.3.4 Ring-opening copolymerisation

In contrast to ROP, which featured a single monomer, ring-opening copolymerisation (ROCOP) reactions involve two or more monomers that are ring-opened and appended to the growing polymer chain to create a copolymer. As previously discussed in section 1.3.1 and illustrated in Figure 1.5, these copolymers can be alternating, random, or block-type copolymers. Using two monomers instead of one allows for even further versatility and fine-tuning of the structure and properties of the resulting monomers. ROCOP can occur with different combinations of substrates, with two of the most commonly reported examples being epoxide/carbon dioxide ROCOP and epoxide/anhydride ROCOP, resulting in polycarbonates and polyesters, respectively. Generic schemes of these reactions are shown in Scheme 1.6. Examples of common epoxides and anhydrides reported in the literature, including bio-derived examples, are shown in Scheme 1.7.



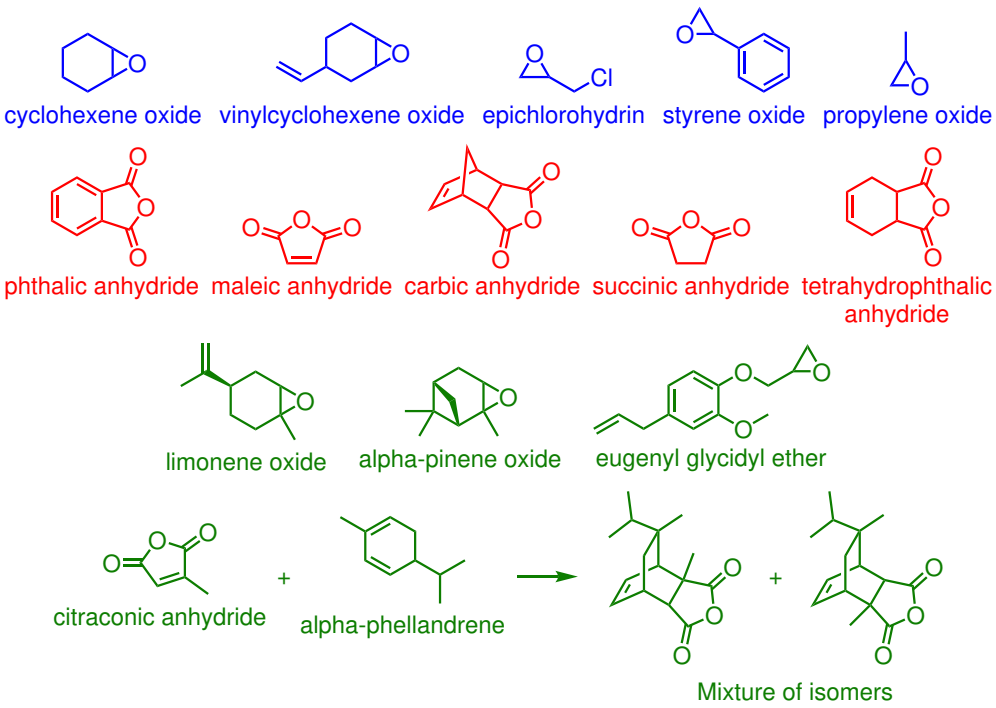
(a) ROCOP of an epoxide and a cyclic anhydride.



(b) ROCOP of an epoxide and carbon dioxide.

Scheme 1.6: Generic example of ring-opening copolymerisation reactions.

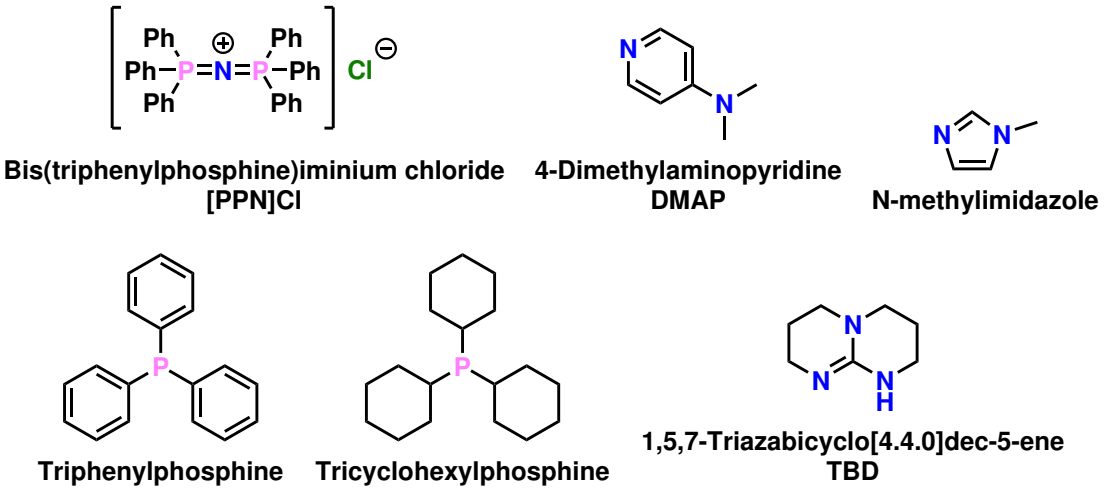
Literature shows that ROCOP of anhydrides and epoxides is generally performed in either neat conditions, where the epoxide serves as a solvent, or in solution with or without a smaller excess of epoxide.[45] The excess



Scheme 1.7: Common monomers reported in the literature for ring-opening copolymerisation reactions, with bio-derived examples shown in green.[45–48]

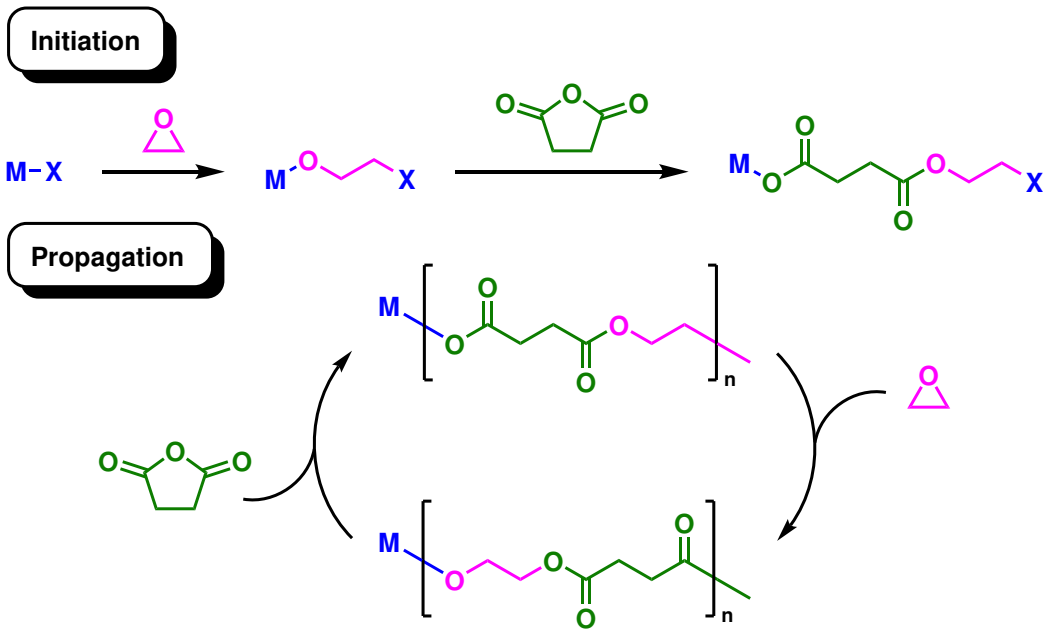
of epoxide is generally utilised to allow for the kinetics to enter a pseudo-zero-order regime.[49] A co-catalyst is added to aid initiation (as will be discussed later), which is often thermodynamically preferred to cleaving the Metal-Ancillary ligand bond (examples of ancillary ligands are Cl, alkoxide, carboxylate).[49] Although studies have noted that the role of the co-catalyst is rather complex, the general understanding is that the co-catalyst is to ring-open the coordinated epoxide species and generate an alkoxide, which then generates a carboxylate upon ring-opening an anhydride moiety.[48] Therefore, the co-catalyst used must be a nucleophile and examples of different co-catalysts reported in the literature are shown in Scheme 1.8, with [PPN]Cl and DMAP being one of the most common examples of co-catalysts.[45,50]

In terms of mechanistic considerations, the intricacies of these will depend on the specific catalyst used. In general, it is widely accepted that the mechanism for ROCOP of anhydrides with cyclic epoxides begins with the initiation of a coordinated epoxide to generate an alkoxide species, which

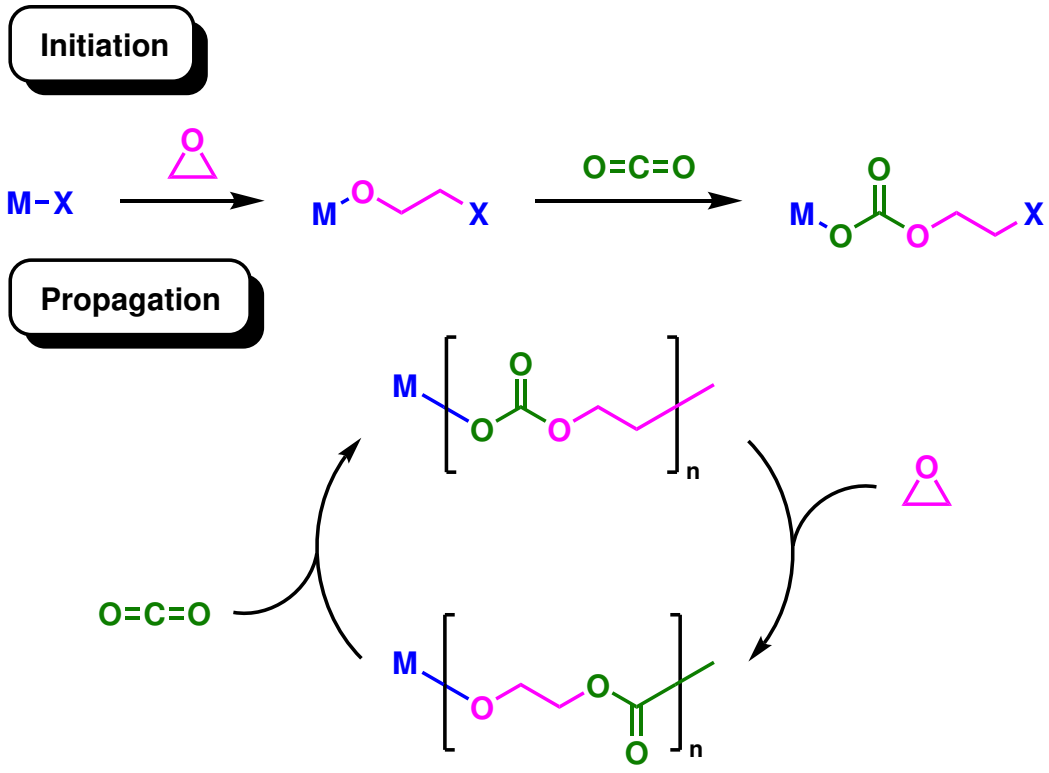


Scheme 1.8: Examples of co-catalysts reported in the literature for the ring-opening co-polymerisation of epoxides and cyclic anhydrides.[45,50]

then enters the propagation cycle, which alternates between alkoxide and carboxylate intermediates. In 2017, Coates and co-workers published one of the most comprehensive analyses of the mechanism for alternating co-polymerisation of epoxides and cyclic anhydrides, which will be further discussed in Chapter 2.[49] The ring-opening co-polymerisation of epoxides with carbon dioxide operates in a similar fashion, alternating between alkoxide and carbonate species. Simplified representations of the elementary steps of the two ROCOP mechanisms are presented in Scheme 1.9.[48,51]



(a) ROCOP of an epoxide and a cyclic anhydride.[48]



(b) ROCOP of an epoxide and carbon dioxide.[51]

Scheme 1.9: Elementary steps of the ring-opening co-polymerisation of epoxides and cyclic anhydrides and co-polymerisation of epoxides and carbon dioxide.

1.4 Transfer hydrogenation

1.4.1 Definition and differences with direct hydrogenation

Hydrogenation is one of the most important transformations in organic chemistry and plays a crucial role in a variety of industries.[33] To achieve this, one can either opt for direct hydrogenation, whereby hydrogen gas is utilised, or transfer hydrogenation.

Transfer hydrogenation reactions are generally described as the formal addition of dihydrogen to another molecule from a source different to gaseous H_2. This process offers many advantages over direct hydrogenation, such as avoiding the use of pressurised hydrogen gas, which requires expensive equipment and is highly flammable. Furthermore, hydrogen donors are readily available, and the catalysts required are often non-sensitive. This leads to a simpler experimental setup and enhanced safety.[33,52]

Many different non-H_2 hydrogen sources have been reported in the literature, with these often depending on the catalyst, substrate, and conditions.[33,52] The most commonly used hydrogen donors are small molecules such as alcohols, which are often used as solvents for the reaction. A typical alcohol used is 2-propanol, which is converted to acetone during the reaction.[33] Other hydrogen donors include formic acid or azeotropic mixtures of formic acid/triethylamine,[53] as well as aqueous formic acid/-formate buffers.[54,55] Sources using formic acid have the advantage of irreversibility as the by-product is gaseous carbon dioxide, which leaves the reaction medium. Hantzsch ester (diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate) is also a common hydrogen donor used in organocatalytic

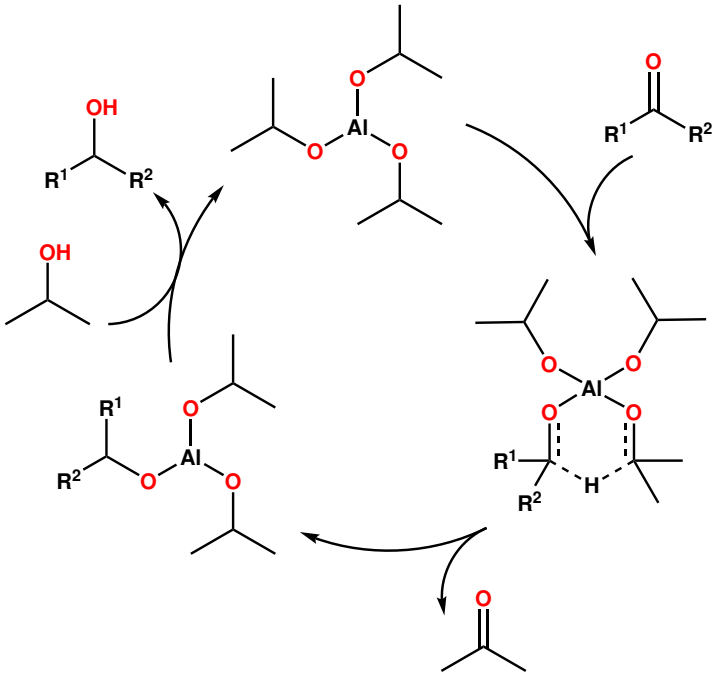
transfer hydrogenation reactions.[56]

1.4.2 History of transfer hydrogenation

In 1925, Meerwein and Schmidt,[57] and Verley,[58] independently reported the reduction of aldehydes to their respective alcohols using a mixture of aluminium ethoxide and ethanol. Ponndorf expanded the scope of the reaction to ketones and upgraded the catalyst to aluminium isopropoxide in isopropanol.[59] This was the first known example of catalytic transfer hydrogenation of carbonyl compounds. This reaction is now known as MPV (Meerwein-Ponndorf-Verley) reduction. The reaction proceeds through initial coordination of the carbonyl substrate to the metal catalyst centre, followed by a pericyclic six-member transition state, whereupon a hydride is transferred from one of the isopropoxy ligands to the carbonyl. Subsequent dissociation of the newly formed carbonyl and displacement of the reduced substrate by a solvent molecule regenerates the catalyst and yields the alcohol product. This mechanism is shown in Scheme 1.10.[60]

The first example of transition-metal catalysed hydrogenation can be attributed to Henbest and co-workers, who demonstrated the transfer hydrogenation of cyclohexanones using iridium-containing compounds such as $HIrCl_2(CH_3SO)_3$ and 2-propanol as the hydrogen source.[61,62]

However, one of the most significant milestones in the field came in the 1960s, when the use of transition metal catalysts for transfer hydrogenation was reported, with Henbest and coworkers showcasing the reduction of cyclohexanones and α,β-unsaturated ketones using 2-propanol.[63] However, perhaps the most significant advancement in the field of transfer hydrogenation came from Noyori and Ikayira in 1995, who reported chiral ruthenium(II) catalysts for the asymmetric transfer hydrogenation of aro-



Scheme 1.10: Mechanism for the MPV reduction reaction.[60]

matic ketones.[64] The [RuCl(η^6-arene)(*N*-arylsulfonyl-DPEN) (DPEN = 1,2-diphenylethylene-1,2-diamine) species reported by the authors effected high enantioselectivity at mild conditions and have become an inspiration for many future reports of derivative complexes which have become known as "Noyori-Ikayira-type" catalysts. The general structure of these catalysts is shown in Figure 1.8. In 2001, Noyori shared the Nobel Prize for Chemistry with Knowles and Sharpless for his pioneering work in the area of asymmetric hydrogenation reactions.[65,66]

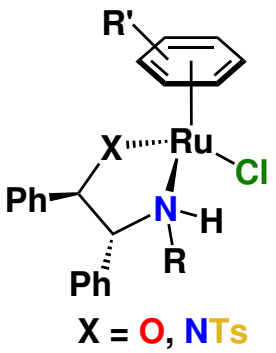


Figure 1.8: Noyori-Ikayira transfer hydrogenation (pre)-catalysts (1995-1996). X = NTs,[53,64,67] O[68].

1.5 Research scope and focus of this work

The objective of this research was to develop metal-based catalysts that could potentially exhibit dynamic coordination sphere effects when employed in catalysis.

- Chapter 2 of this work presents novel indium complexes, which feature a potentially hemilabile pyridyl arm, and examines their effectiveness as catalysts for the ring-opening copolymerisation of epoxides and cyclic anhydrides. The reason behind selecting indium was the lack of reports of indium catalysts for epoxide/anhydride ROCOP, in contrast to multiple reports of similar aluminium catalysts.

- Chapter 3 then presents the ring-size dependent diastereoselective synthesis of novel ruthenium, rhodium, and iridium complexes, featuring simple enantiopure 3-amino-1-azacycle ligands. These complexes successfully facilitate the transfer hydrogenation of aromatic ketones. These were selected due to their simplicity and scarcity of literature reports utilising the readily available enantiopure ligands.

Both chapters also include supporting density functional theory (DFT) studies that provide insight into the respective reaction mechanisms.

CHAPTER 2

Indium-based complexes as catalysts for the ring-opening copolymerisation of epoxides and cyclic anhydrides

2.1 Introduction

2.1.1 Overview of ROCOP literature

The first report for the copolymerisation of cyclic anhydrides and epoxides comes from a 1960 report by Fischer using a benzyldimethylamine catalyst.[69,70] Further such reports also featured the use of tertiary amines as catalysts.[71–73] However, these early works suffered from low molecular weight, low distributions, and selectivity.[45] Later work by Aida and Inoue introduced the first well-controlled alternating copolymerisation of phthalic anhydride and propylene oxide using an aluminium porphyrin catalyst (first complex on Figure 2.1) and a quaternary ammonium salt co-catalyst.[45,74] A

major advancement in the field came from Coates in 2007 with the report of a highly active β-diiminate zinc catalyst (second complex on Figure 2.1), achieving highly alternating, high molecular weight copolymers, with narrow polydispersities.[75] These studies successfully demonstrated that discrete metal complexes are able to effect controlled alternating copolymerisation of a range of anhydrides and epoxides.

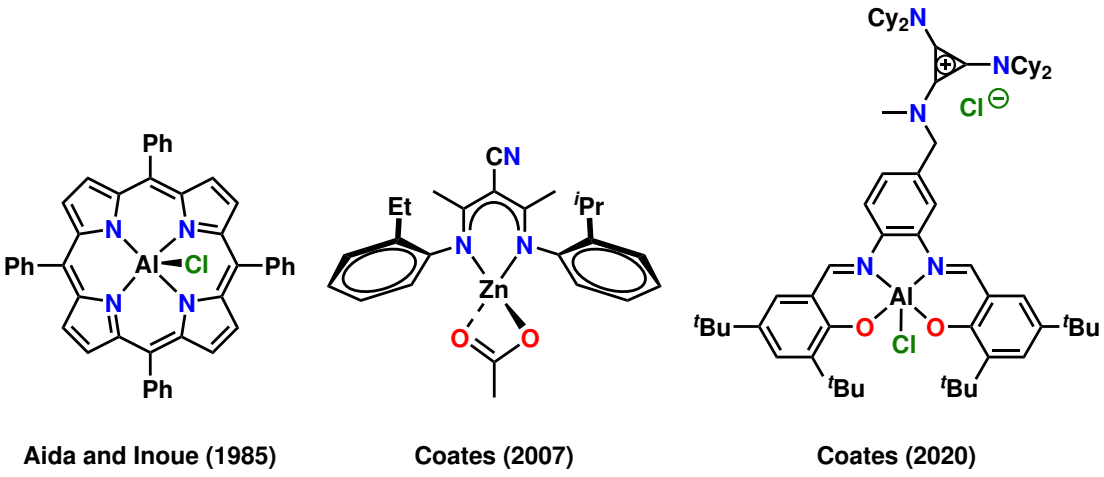


Figure 2.1: Evolution of ROCOP catalysts showing early porphyrin catalyst by Aida and Inoue[74], β-diiminate zinc catalyst[75] and recently reported bifunctional catalyst[76] by Coates and co-workers.

In more recent years, various derivatives of the metal complexes bearing "Salen-type" ligands have become the standard catalysts for the ROCOP of epoxides and cyclic anhydrides. Metals used include main group elements such as aluminium, but transition metals such as cobalt, iron, chromium, and manganese have also been reported.[45] Many of these complexes are often paired with a nucleophilic co-catalyst, such as [PPN]Cl or DMAP, which plays an important role in initiating the reaction. A comprehensive mechanistic study on the reaction was published by Coates and co-workers in 2017 using (Salph)AlCl derivative and [PPN]Cl.[49] Further in 2020, in an important breakthrough, Coates and co-workers reported a bifunctional system with a tethered co-catalyst (third complex on Figure 2.1), which was able to tolerate high amounts of chain-transfer reagents, which would normally lead

to diminished activity in the traditional two-component catalyst/co-catalyst systems.[76] Other advancements in the field also include heterodinuclear systems reported by the Williams group, which can outperform traditional mononuclear complexes (shown in Figure 2.2).[77–81]

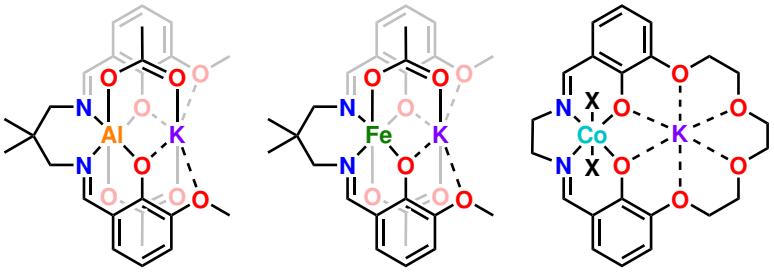


Figure 2.2: Examples of heterodinuclear ROCOP catalysts reported by Williams and co-workers.[77–81]

2.1.2 Indium catalysts in polymerisation

In general, the focus of literature reports using indium-based catalysts for polymerisation seems to be the ring-opening polymerisation of lactide. Reports by Mehrkhodavandi and co-workers constitute a significant portion of the work in the area. Back in 2008, they reported the first indium catalyst enabling the ring-opening polymerisation of *rac*-lactide in the form of a chiral alkoxy-bridged dinuclear indium complex based on an asymmetrically substituted trans-diaminocyclohexane framework (Figure 2.3, left).[82] Further reports by the group include dinuclear indium catalysts supported by a chiral Salen-type ligand (Figure 2.3, middle),[83] air- and moisture-stable dinuclear indium Salan complexes for the ROP of cyclic esters,[84] cationic indium complexes supported by a Salen-type ligand framework (Figure 2.3, right) have been reported for the copolymerisation of epoxides with cyclic ethers and lactide,[85] amongst others.

What appears to be the first example of hemilabile ligand frameworks

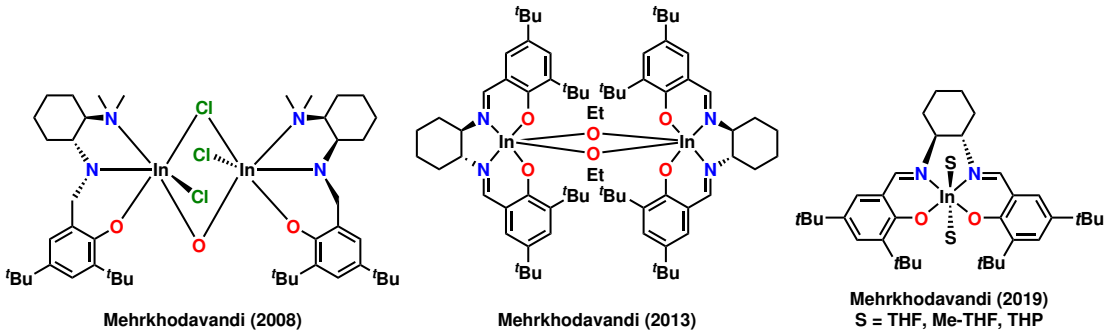


Figure 2.3: Selected indium catalysts reported by Mehrkhodavandi and co-workers.

used with indium is a report from 2001 by Mountford and co-workers using an aminophenolate ligand with a 1,4,7-triazacyclononane hemilabile pendant arm, with the resulting complexes exhibiting no reactivity (Figure 2.4, left).[86] The first example of In-based complexes using hemilabile ligands for polymerisation reactions seems to be a 2020 report by Mehrkhodavandi and co-workers, which was mentioned in Chapter 1.[30] The authors report the use of cationic indium complexes with hemi-Salen type ligands bearing hemilabile thiophenyl, furfuryl or pyridyl pendant groups, which provide stabilisation for the cationic centre (Figure 2.4, middle). The reactivity of these species towards catalysing the ring-opening polymerisation (ROP) of epoxides and lactide is shown in their work. The group later reported another indium complex featuring a PNNO ligand with a hemilabile phosphine donor for the CO_2/epoxide copolymerisation, noting that the pendant phosphine donor arm is dissociated in analogous gallium and aluminium complexes they prepared, but hemilabile in the indium complex (Figure 2.4, right).[87]

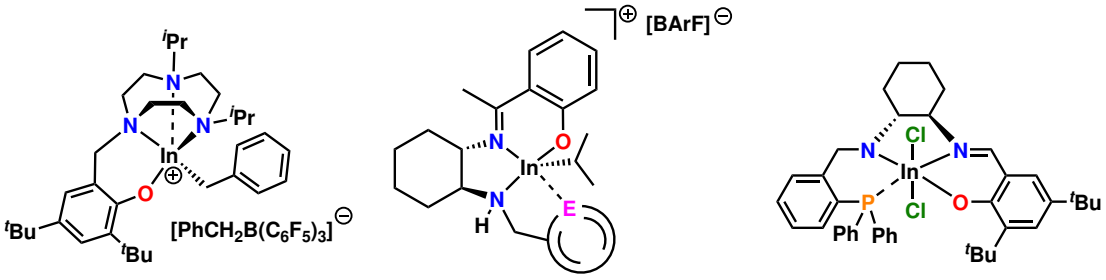


Figure 2.4: Indium complexes with hemilabile ligand frameworks reported by Mountford and co-workers[86] and Mehrkhodavandi and co-workers.[30,87]

2.1.3 The Salpy ligand framework

The so-called "Salen-type ligands" are one of the archetypal ligand frameworks in organometallic chemistry. These ligands are Schiff bases, which means that they feature a carbon doubly bound to a nitrogen. They feature a tetradentate *C2*-symmetric framework and are formally the deprotonated version of the condensation product of salicylic aldehyde (**Sal**) and 1,2-ethylenediamine (**en**). Various derivatives of Salen and similar ligands have been reported in the literature by using amines with different backbones or substituted aromatic aldehydes, thus imparting desired electronic properties.

The "Salpy" ligand is one such modification and can be synthesised from 2-methyl-2-(pyridin-2-yl)propane-1,3-diamine (PPDA) and salicylic aldehyde. The structure of the Salpy ligand, along with some related "Salen-type" ligands, is shown in Figure 2.5. This ligand was first reported by Houser and co-workers, along with some functional derivatives.[88] In contrast to Salen ligand, the Salpy ligand has the potential to be pentadentate as it features a pendant pyridyl group. The authors reported the ligand, amongst other derivatives, and their respective Cu(II) complexes, with a later report exploring the binding preferences of Cu(II) complexes with these ligands.[89] The group has also reported work on using these ligands for mononuclear and

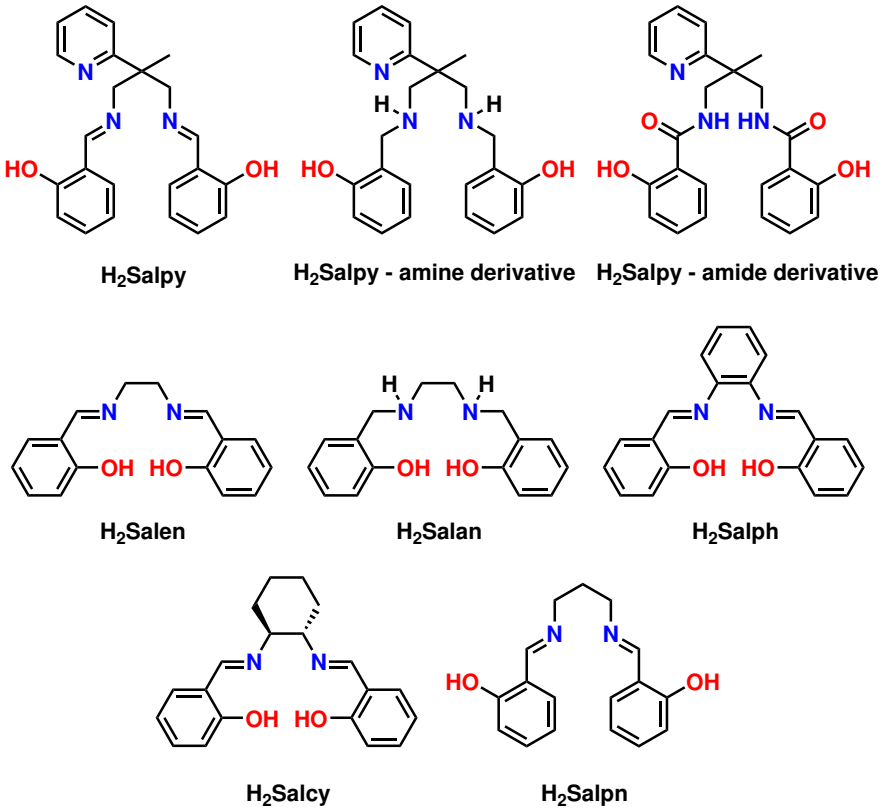


Figure 2.5: Structures of the Salpy and "Salen-type" ligands and select derivatives.

(hydr)oxo-bridged dinuclear iron complexes,[90], with further work published on their redox and acid-based properties.[91]

The PPDA precursor required for the Salpy ligand was first reported by Gade and co-workers, who used it to prepare a series of novel diamidoamine ligands and their respective complexes with titanium and zirconium.[92] Despite first being synthesised more than 25 years ago, PPDA is still vastly under-represented in the literature, likely owing to the laborious multi-stage synthesis required, as shown later in Scheme 2.1. Literature reports that include the use of PPDA seem to be limited to a few research groups - Gade and co-workers[92–95], Houser and co-workers[88–91,96–99], Schrock and co-workers[100–103], Grohmann and co-workers.[104–106], as well as isolated reports by Zabel *et al.*[107], Bahili *et al.*[31], and a patent[108] by Ward and co-workers.

The pendant pyridyl donor on the Salpy ligand could, in certain condi-

tions, exhibit a degree of hemilability by de-coordinating from the metal centre to create an additional vacant site for the binding of substrate species, or, in other cases, coordinate to provide additional stability to intermediate species during the catalytic cycle. Recently, a report by Bahili *et al.* showcased the use of a Salpy-based Al complex for the trimerisation of isocyanates.[31] The catalyst composition for the trimerisation reactions has subsequently been patented.[108] At present, the Salpy ligand and its derivatives still remain vastly under-represented in the literature, with the above reports, as confirmed by a recent structural search using SciFinder^{n}[109], being the only ones mentioning these ligands.

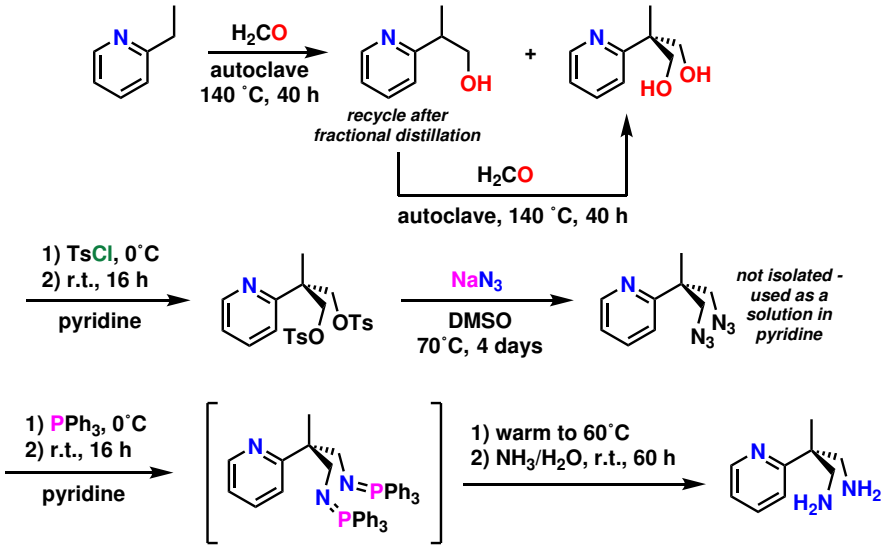
2.1.4 Overview of this chapter

In this chapter, the synthesis of a novel indium (III) based complex bearing a Salpy-type ligand is reported, and the activity of some of these complexes was probed towards the ring-opening copolymerisation of epoxides and cyclic anhydrides. A total of 3 different complexes were synthesised. By varying the substituents in the 3 and 5 positions on the aromatic rings, the *t*-butyl-, chloro-, and bromo-substituted derivatives were prepared and characterised. These add to the scarce number of reports of indium complexes bearing hemilabile ligands. Considering that literature reports on indium complexes mainly focusing on other types of polymerisation and the success of similar aluminium catalysts in the area of copolymerisation catalysis, it was decided that the ring-opening copolymerisation of epoxides and cyclic anhydrides is a suitable reaction to test the catalytic activity of these novel complexes.

2.2 Results and discussion

2.2.1 Synthesis of Indium(III) Salpy complexes

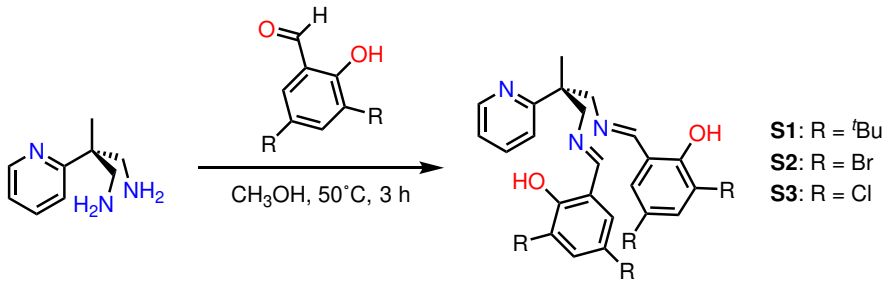
This work began by first synthesising the PPDA precursor required to prepare the Salpy ligands. This was done by using the literature-reported method[92], which involves a multi-step synthesis, as shown in Scheme 2.1. The starting materials - 2-ethylpyridine and aqueous formaldehyde - were placed in an autoclave and heated at 140 °C for 40 hours. This reaction afforded a mixture of mono-hydroxymethylated and bis-hydroxymethylated products. After separation *via* vacuum distillation, the latter is converted to a tosylate, then azide, and finally an amine (PPDA). The mono-hydroxymethylated product can be recycled and used in place of 2-ethylpyridine in further synthetic runs to enhance the yield of bis-hydroxymethylated product in the first step.



Scheme 2.1: Synthesis of 2-methyl-2-(pyridin-2-yl)-propane-1,3-diamine (ppda).

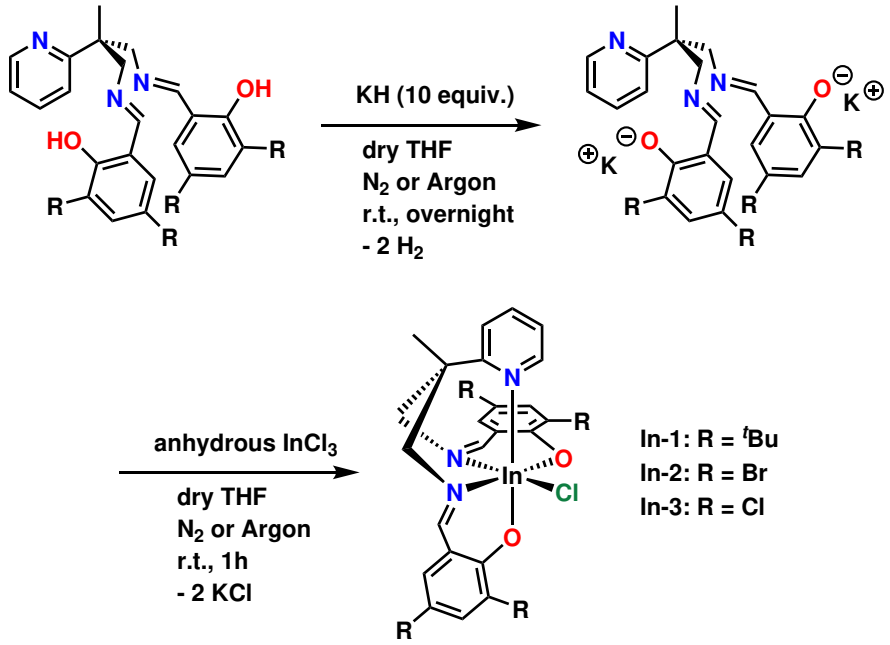
Once the required PPDA precursor was synthesised, the preparation of the Salpy-type ligands was straightforward - PPDA was reacted with the corresponding aldehyde in methanol to afford the corresponding Schiff base pro-ligand (*i.e.* protonated Salpy) in good yields. The reaction is shown in

Scheme 2.2. The Salpy ligands are similar to the common tetradentate Salen-type ligands, in the sense that they feature the N_2O_2 donor set, but they also possess a pyridyl pendant group, as shown previously in Figure 2.5 (top left).



Scheme 2.2: Synthesis of Salpy pro-ligands.

The corresponding Salpy complexes of indium were then prepared in a two-step process as shown in Scheme 2.3. The protonated pro-ligands were treated with anhydrous potassium hydride under an inert atmosphere to generate the corresponding dipotassium salt *in situ*. The reaction solution was then filtered directly onto anhydrous indium(III) chloride using a cannula. Removal of the solvent and addition of dry dichloromethane allows for the potassium chloride by-product to be filtered. Further removal of the solvent and washing with dry pentane affords the corresponding complexes as mononuclear, six-coordinate species. It was found that an excess of potassium hydride produced a cleaner product, likely owing to the elimination of residual water in the solvent. The excess of potassium hydride can then be (*carefully!*) quenched using sequential addition of 2-propanol and water. The resulting complexes feature a potentially hemilabile pyridyl donor, which is expected to dynamically coordinate/de-coordinate in order to accommodate substrates binding to the metal centre, whilst also providing stabilisation when required. The identity of the complexes was confirmed by NMR spectroscopy and high-resolution mass spectrometry (HRMS).



Scheme 2.3: Synthesis of In(Salpy)Cl complexes.

2.2.2 NMR studies of the Salpy ligands and resulting complexes

The pro-ligands and complexes were subjected to analysis by nuclear magnetic resonance (NMR) and mass spectrometry (MS). The NMR spectra of the SalpyH_2 pro-ligands featured signals in line with the same (or derivative) compounds synthesised by previous members of our research group.[110]

A notable feature of the NMR spectra of both the pro-ligands and the respective complexes is the shape of the signals attributed to the two CH_2 groups. The protons of these groups are diastereotopic and are positioned *cis* either to the methyl or the pyridyl group, as illustrated in Figure 2.6. Therefore, these protons are expected to be magnetically inequivalent and to have different chemical shifts in the NMR spectrum. NMR spectra of the ligands recorded in $(CD_3)_3SO$ indeed show two sets of doublets with second-order roofing effect. The spectrum of **S1** was also measured in $CDCl_3$ and features a coalesced 4H singlet for the two CH_2 groups. All the spectra of

the resulting complexes were recorded in $CDCl_3$ and it can be seen that the CH_2 signal presents as a broad apparent quartet for **In-1**, a broad coalesced singlet for **In-2**, and two broad doublets with 0.09 ppm chemical shift difference for **In-3**.

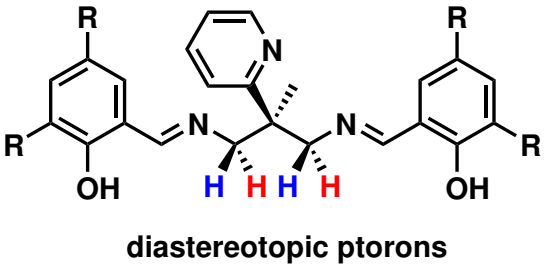


Figure 2.6: Diastereotopic protons in the Salpy ligands. Equivalent protons are shown in the same colour.

As the NMR spectra for **In-2** and **In-3** were recorded in different solvents to the respective pro-ligands, direct comparison with the uncoordinated pro-ligand is only possible for **In-1**, where spectra in $CDCl_3$ are available for both the ligand and complex. For the CH_2 peaks in the spectra of **In-1**, one can observe broadening and partial decoalescence. Furthermore, slight broadening and upfield shift of the signals for the imine protons can also be observed, confirming coordination. Other indicators of coordination are downfield shifts of all pyridyl protons, and most notably to H^6 (*ortho* to the pyridyl nitrogen), which exhibits a 0.61 ppm shift. The signal for H_d (*para* to the imine) does not shift, whilst the signal for H_f (*ortho* to the imine) shifts 0.29 ppm downfield. As expected, phenolic protons were not observed after coordination. Although the two iminophenoxide "arms" are magnetically inequivalent, these gave rise to equivalent signals due to rapid interconversion on the NMR timescale. The shift and shape of the signals of the pyridyl protons indicate that the pyridyl is either coordinated or the hemilabile behaviour is too rapid to detect on the NMR timescale. The ^1H NMR signals of the pro-ligands and complexes are summarised in Table 2.1 and Table 2.2,

respectively, with the atom numbering scheme used to label the NMR signals shown in Figure 2.7.

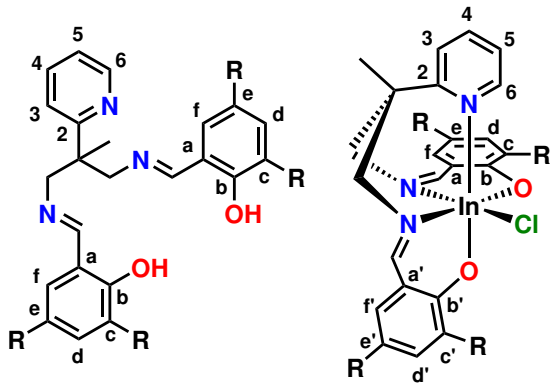


Figure 2.7: Atom numbering scheme for the SalpyH_2 pro-ligands and respective complexes. Only applicable to NMR and not used for SC-XRD labelling.

	S1^a	**S1**^{b}	**S2**^{b}	**S3**^{b}
2×OH	13.53	13.78	14.45	14.38
2×HC=N	8.34	8.52	8.49	8.52
H^6	8.62	8.60	8.63	8.63
H^4	7.64	7.78	7.82	7.82
H^3	7.35*	7.49	7.52	7.52
H^5	7.14	7.23-7.31*	7.32	7.31
2×H^d	7.35*	7.28*	7.78	7.57
2×H^f	7.04	7.21	7.57	7.42
2×CH_2	4.05	4.07, 3.97	4.18, 3.97	4.18, 3.97
CH_3	1.56	1.45	1.45	1.45
2×^{t}Bu	1.42, 1.29	1.34, 1.24	N/A	N/A

Table 2.1: Summary of ^{1}H NMR chemical shifts (ppm) for the **S1**, **S2**, and **S3** pro-ligands. Spectra recorded in ^{a}$CDCl_3$ or ^{b}$(CD_3)_3SO$. *overlapping signals - see experimental section for further details. Numbering scheme shown in Figure 2.7.

	In-1	In-2	In-3
2×HC=N	7.94	7.95	7.97
H^6	9.23	9.17	9.08
H^4	7.86	7.98	7.95
H^3	7.49	7.61	7.59
H^5	7.43	7.56	7.50
2×H^d	7.35	7.71	7.38
2×H^f	6.75	7.10	6.89
2×CH_2	3.92	4.03	4.07, 3.98
CH_3	1.63	1.69	1.68
2×^{t}Bu	1.37, 1.22	N/A	N/A

Table 2.2: Summary of ^{1}H NMR chemical shifts (ppm) for **In-1**, **In-2**, and **In-3** complexes. Spectra recorded in $CDCl_3$. Numbering scheme shown in Figure 2.7.

2.2.3 Measuring conversion and selectivity of ROCOP reactions using ^{1}H NMR

In all cases discussed in this chapter, the conversions were measured using *in situ* nuclear magnetic resonance (NMR) spectroscopy. This was done by withdrawing a small aliquot (approx. 0.1-0.2 cm^3) from the reaction mixture and diluting it with $CDCl_3$, followed by ^{1}H NMR analysis. Phthalic anhydride (PA) is the primary anhydride used in the reactions discussed, and so the conversion was calculated using the relative integrals of the aromatic protons of free PA and polymer-incorporated PA. A representative example of this is shown in Figure 2.8. The equation used to calculate conversion is shown in Equation 2.1.

$$\text{Conversion}(\%) = \frac{I_{\text{PA–poymer}}}{I_{\text{PA}} + I_{\text{PA–poymer}}} \times 100$$

Equation 2.1: Conversion calculation for ROCOP reactions of phthalic anhydride with epoxides. "I" is the relevant ^{1}H NMR integral.

On the other hand, selectivities were measured from the isolated polymer samples in a similar fashion by using the relative integrals of relevant

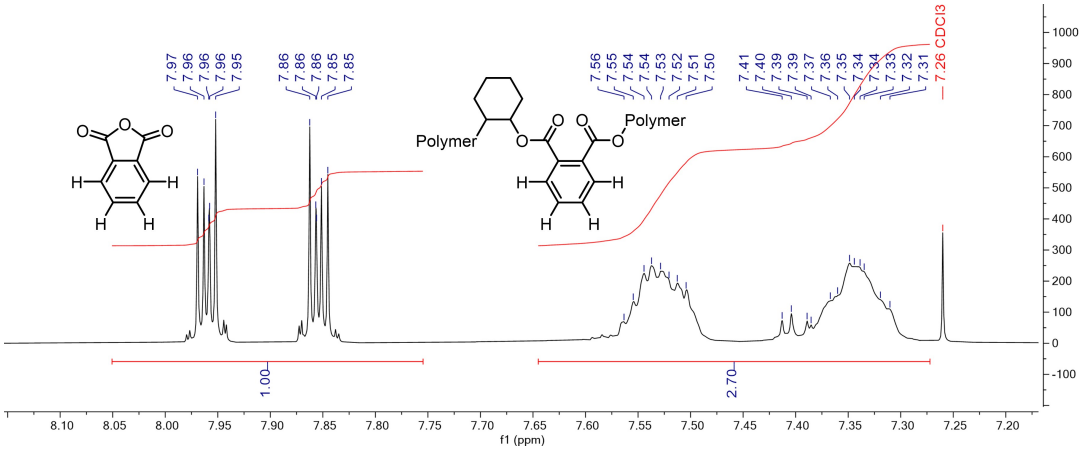


Figure 2.8: A representative example of *in situ* ^{1}H NMR conversion determination of phthalic anhydride containing polymers, using a phthalic anhydride / cyclohexene oxide spectrum as an example.

polyether and polyester signals/regions, which arise from the CH/CH_2 signals of the epoxides used. Literature-reported regions and chemical shifts were used to select the relevant signals/regions to integrate, as shown in Table 2.3.

Epoxide	Polyester	Polyether
CHO[111,112]	≈ 5 ppm (CH)	≈ 3.22-3.64 (CH), 3.46 ppm
VCHO[113]	≈ 5.2-5.4 ppm	≈ 3.5-3.8 ppm
SO[114,115]	≈ 7.5, 6, 4.5 ppm	≈ 7.3, 4.5, 3.68 ppm

Table 2.3: Literature-reported regions and chemical shifts of polyester and polyether related signals of selected epoxides. CHO = cyclohexene oxide, VCHO = 4-vinyl-1-cyclohexene 1,2-epoxide, SO = styrene oxide.

2.2.4 Initial ROCOP investigations using In-1

The **In-1** complex, in combination with [PPN]Cl co-catalyst, was found to be active for the epoxide/anhydride ROCOP at moderate temperatures with excellent conversions and selectivities observed for the initial reactions using phthalic anhydride with selected epoxides. A marked enhancement in both molecular weight and polydispersity of the resulting polyesters was observed when the In-based catalysts were used, compared to just

[PPN]Cl, with the latter yielding broad distributions but relatively low molecular weight polymers. There seems to be no literature reports of In-based complexes being used for the ROCOP of epoxides with cyclic anhydrides, making this the first such example.

Phthalic anhydride (PA) was selected as the anhydride of choice, as there is a clear separation between the PA signals and polymer signals in the crude ^{1}H NMR spectra, thereby allowing for a straightforward calculation of the conversion, as demonstrated in section 2.2.3. ROCOP of PA with several epoxides (cyclohexene oxide (CHO), 4-vinyl-1-cyclohexene 1,2-epoxide (VCHO), styrene oxide (SO) and epichlorohydrin (ECH)) was attempted. The polymers resulting from CHO, VCHO, and SO were successfully isolated as white to off-white powders. However, when ECH was used, isolation of the resulting polymer was not successful due to the apparent low molecular weight, which precluded the formation of an isolable precipitate. In all cases, *in situ* ^{1}H NMR confirmed >95% conversion and ^{1}H NMR of the isolated polymer samples showed >90% selectivity towards polyesters after 2 h at 90 °C with 1:2:400:2000 ratio of indium catalyst : [PPN]Cl : anhydride : epoxide (neat conditions). The excess of epoxide and neat conditions were selected as the epoxide ring-opening has been shown to be the rate-determining step in mechanistic investigations[49] (discussed further in section 2.2.14), thereby allowing for the kinetics to enter into pseudo-zero-order mode.

Attempts to synthesise bio-copolymers using the Diels-Alder adduct of maleic anhydride and α-phellandrene as the anhydride and CHO, VCHO, SO and ECH were unsuccessful as no isolable polymers formed after quenching. Furthermore, attempts to use carbic anhydride yielded ^{1}H NMR spectra with potential polymer signals overlapping, which were difficult to assign. A tentative assignment of the *in situ* ^{1}H NMR spectrum of a reaction between CA and CHO using the conditions mentioned above, revealed integrals ratios

of 0.09:0.15:1.00 at 4.93 – 4.46 ppm (presumed ester CH), 3.37 – 3.07 ppm (presumed ether CH), 3.08 – 2.99 (CHO CH), thereby indicating low selectivity towards alternating polyester product. The respective polymers from the reactions of PA and CA with CHO, VCHO, and SO were isolated and stacked ^{1}H NMR spectra are shown in Figure 2.9. It can be seen that in the case of the PA-containing polymers, there are no visible signals in the expected ether regions (around 3.5 ppm). However, signals in those regions are present when CA was used. Therefore, going forward, the reaction between PA and CHO was chosen as a model reaction for further investigations to gain insight into the influence of the amounts of catalyst and co-catalyst on the reaction, and this combination is indeed an archetypal combination and one of the most widely studied in the ROCOP literature.[45]

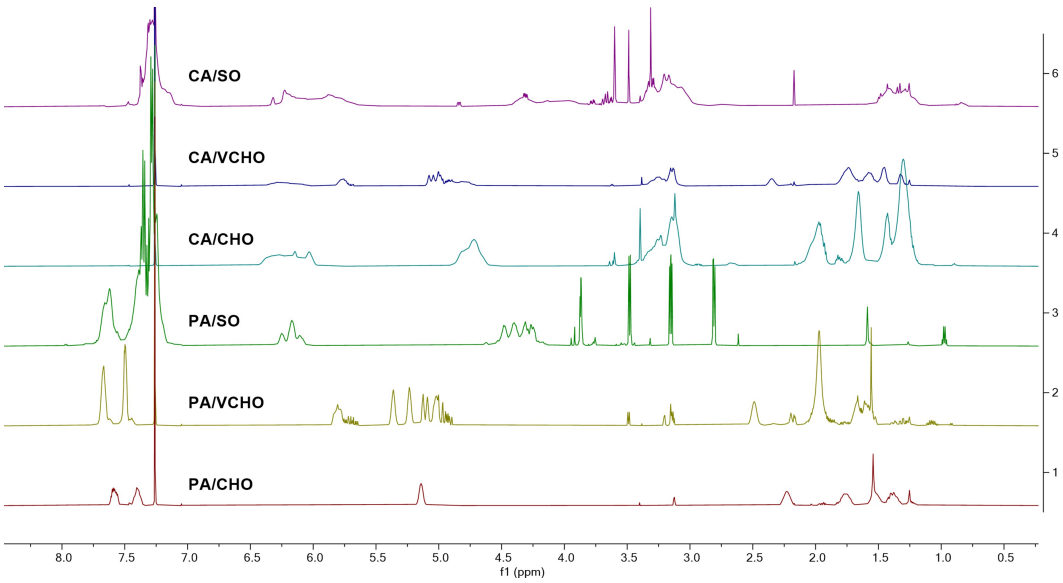


Figure 2.9: Stacked ^{1}H NMR spectra recorded in $CDCl_3$ of various polymers from initial reactions with the **In-1** complex. 2 h at 90°C with 1:2:400:2000 ratio of indium catalyst : [PPN]Cl : anhydride : epoxide

2.2.5 Variation of In-1 and co-catalyst equivalents

Initially, the amount of **In-1** was varied, with 1 or 2 equiv. [PPN]Cl present. Results are shown in Table 2.4 and plotted in Figure 2.10. As can be seen

on the graph, when 2 equiv. of [PPN]Cl are used, the conversion is ≥90% and no information can be gained from the variation of the indium complex equivalent. However, when 1 equivalent of [PPN]Cl is used, there is a linear correlation. At first glance, these data indicate that an increased amount of indium catalyst slows down the reaction rate. However, this trend can be attributed to the decreasing amount of [PPN]Cl relative to the indium catalyst, which can be explained by the proposed mechanism for this reaction reported by Coates and co-workers (discussed later).[49] The mechanism indicates that [PPN]Cl is required to initiate each chain, and thus decreasing the amount of [PPN]Cl available per catalyst would result in fewer active polymer chains. Therefore, the more [PPN]Cl there is, relative to the catalyst, the faster the reaction due to the presence of more initiated polymer chains. It can also be seen that the reaction is generally faster when only the [PPN]Cl catalyst is used. However, this results in polymers with lower molecular weight and higher polydispersity than when used in combination with the indium catalyst, although, as it will be demonstrated laster in section 2.2.7, when the catalyst is included, the amount of [PPN]Cl seems to have little bearing on the resulting molecular weights.

In-1 equiv.	**1 [PPN]Cl / In-1 ratio**	**Conv. (%) / 1 eq. [PPN]Cl**	**2 [PPN]Cl / In-1 ratio**	**Conv. (%) / 2 eq. [PPN]Cl**
0	N/A	80	N/A	100
0.5	2	72	4	100
1	1	68	2	100
2	0.5	51	1	90

Table 2.4: Results from variable **In-1** experiments. Conditions: 2 h at 90 °C , 1 or 2 equiv. [PPN]Cl, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 4.0 μmol.

To further investigate the effect of the co-catalyst on the reaction, the amount of [PPN]Cl was varied against a constant amount of 1 equiv. **In-1** and the % Conversion was plotted *vs* [PPN]Cl equivalents. The reaction was

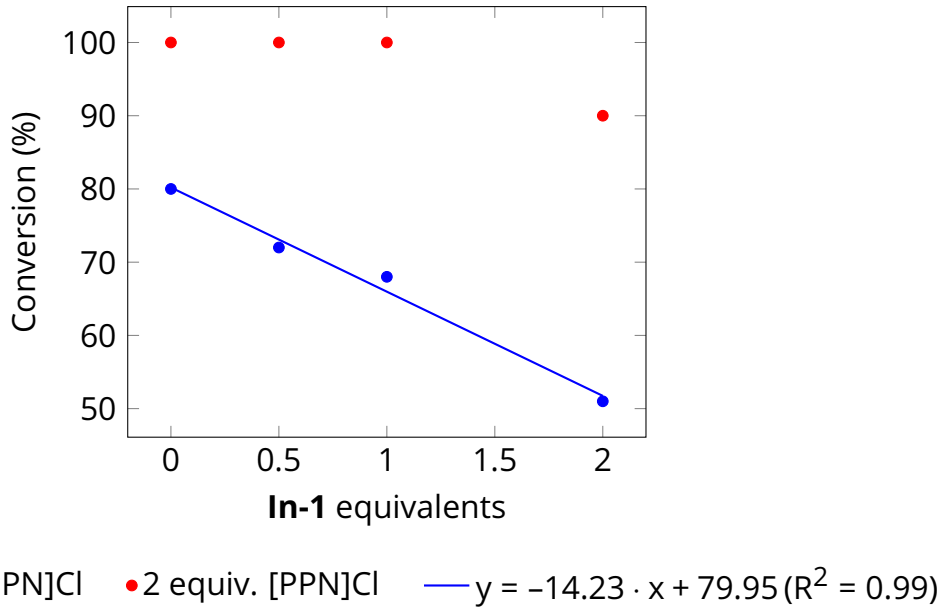


Figure 2.10: Plotted data from variable **In-1** experiments. Conditions: 2 h at 90 °C , 1 or 2 equiv. [PPN]Cl, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 4.0 µmol.

run for 1 h instead of the 2 h used for the reactions from Table 2.4 in order to preclude the reactions from running to full conversions and therefore gather more data. Results are shown in Table 2.5 and plotted in Figure 2.11 and indicate that an increased amount of [PPN]Cl accelerates the reaction in a linear fashion. This is to be expected because, as shown by Coates and co-workers,[49] the ring-opening of the epoxide by an external chloride is the rate-determining step of the reaction. Therefore, as [PPN]Cl is the source of external chloride, increasing its concentration would directly influence the reaction rate, which in turn would affect the conversion. These data are also consistent with the notion mentioned in the previous paragraph that an increase in the [PPN]Cl:[In] ratio results in higher conversions due to more co-catalyst being available to initiate polymer chains. In the case of the reactions from Table 2.5, the ratio of [PPN]Cl:[In] is the same as the [PPN]Cl as only 1 equv. of **In-1** is used.

[PPN]Cl equivalents	Conversion (%)
0.38	14
0.50	26
0.80	34
1.01	53
1.55	64
1.97	82
2.01	91
3.02	100
3.98	100

Table 2.5: Results from the variable [PPN]Cl experiments. Conditions: 1h at 90 °C , 1 equiv. **In-1**, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 4.2 µmol.

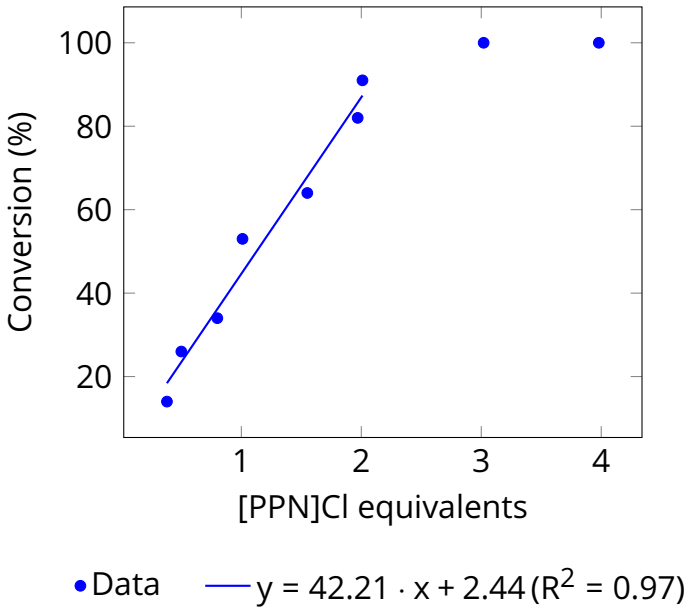


Figure 2.11: Plotted data from variable [PPN]Cl experiments. Conditions: 1h at 90 °C , 1 equiv. **In-1**, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 4.2 µmol. The trendline excludes the data points with 100% conversion (last two).

2.2.6 PA/CHO ROCOP large-scale reaction monitoring

After investigating the influence of different catalyst/co-catalyst equivalents, a large-scale reaction was set up for the ROCOP of PA and CHO in order to investigate the kinetics of the reaction. Aliquots were withdrawn at specified time points using a syringe, which allowed us to monitor how the molecular weight of the polymer changes during the reaction. Part of the aliquots were used for ^{1}H NMR monitoring, and the rest was quenched in methanol, which yielded isolable polymer samples from 75 min onwards (discussed later). As expected, the results indicate pseudo-zero-order kinetics, due to the excess of CHO used (Figure 2.12). The conversion was calculated using the PA(Ar_H polymer)/PA signals of the ^{1}H NMR spectra at different time points. The data from 30 min onwards are presented in Table 2.6 and plotted on Figure 2.12, with initial time points omitted due to inconsistencies in the data at lower conversions.

Time (min)	Conversion (%)
30	15
45	22
60	31
75	41
90	51
105	62
120	73
135	85
150	96
160	99

Table 2.6: Conversions at different time points of a large-scale PA/CHO ROCOP reaction using **In-1** catalyst and [PPN]Cl co-catalyst. Conditions: 90°C , 1 equiv. **In-1**, 2 equiv [PPN]Cl, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 49 µmol.

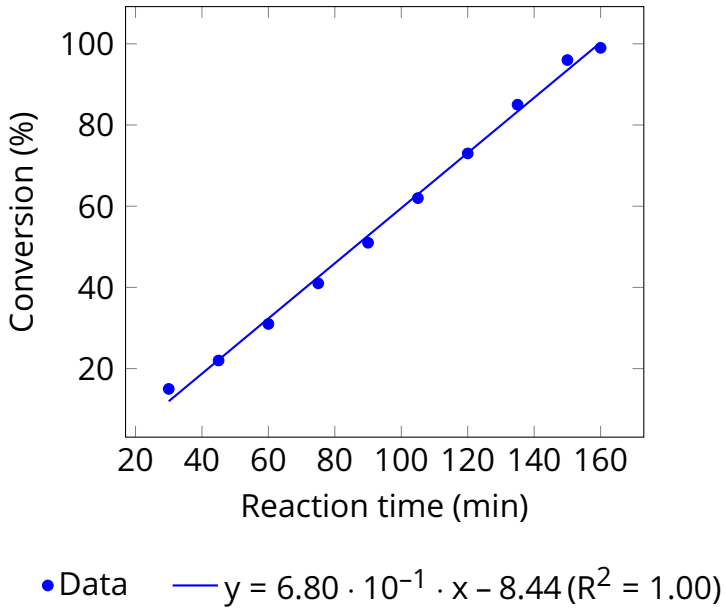


Figure 2.12: Conversion at different time points of a large-scale PA/CHO ROCOP reaction using **In-1** catalyst and [PPN]Cl co-catalyst. Conditions: 90°C , 1 equiv. **In-1**, 2 equiv [PPN]Cl, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 49 µmol. Conversion calculated using the integrals of the aromatic protons of free PA and polymer-PA from ^{1}H NMR spectra of the reaction mixture at different timepoints.

2.2.7 Mass spectrometry results from In-1 ROCOP reactions

The molecular weights of the isolated samples from the reactions discussed in previous sections were determined using MALDI-TOF MS (Matrix-assisted laser desorption/ionisation - time-of-flight mass spectrometry) analysis. More specifically, the samples from the set of experiments where the co-catalyst equivalents were varied (see section 2.2.5) and those isolated from the samples obtained from the large-scale reaction (see section 2.2.6) were used, with data presented in Table 2.7 and Table 2.8, respectively. The data obtained from these experiments allowed for the construction of %Conversion *vs* Molecular weights graph. This yielded a straight line relationship, as shown in Figure 2.13. Furthermore, the relationship observed for the samples from the large-scale reaction (blue line on Figure 2.13) is analogous to that of the %Conversion *vs* Molecular weights for separate re-

actions with different amounts of [PPN]Cl in each (red line on Figure 2.13). The fact that there is an observable relationship of molecular weights *vs* conversion across reactions with different amounts of [PPN]Cl indicates that the amount of [PPN]Cl does not influence the average molecular weights of the resulting polymers. However, the presence of a co-catalyst is crucial for inducing reactivity. Indeed, the data in Figure 2.11 suggests that no conversion would be observed without [PPN]Cl. In addition, as mentioned previously, when [PPN]Cl is used on its own, the resulting polymers exhibit lower molecular weights and a higher polydispersity. These data and those from previous sections therefore indicate that the role of the co-catalyst is more complex than currently understood.

[PPN]Cl eq.	% Conv.	M_n	M_w	PDI
0.80	34	4688	4739	1.011
1.01	53	5940	6059	1.020
1.55	64	6597	6729	1.020
1.97	82	8212	8353	1.017
2.01	91	9054	9141	1.010

Table 2.7: Molecular weight data obtained using MALDI-TOF MS of select samples from the variable [PPN]Cl experiments discussed in section 2.2.5. Conditions: 1h at 90 °C , 1 equiv. **In-1**, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 4.2 µmol.

Time (min)	% Conv.	M_n	M_w	PDI
75	41	4206	4317	1.026
90	51	4988	5102	1.023
105	62	5825	5950	1.021
120	73	6677	6802	1.019
135	85	7403	7584	1.024
150	96	8315	8521	1.025
160	99	8378	8662	1.034

Table 2.8: Molecular weight data obtained using MALDI-TOF MS of select samples from the large-scale PA/CHO polymerisation reaction discussed in section 2.2.6. Conditions: 90°C , 1 equiv. **In-1**, 2 equiv [PPN]Cl, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 49 µmol. Polydisperisty (PDI) is calculated as the ratio of M_w to M_n.

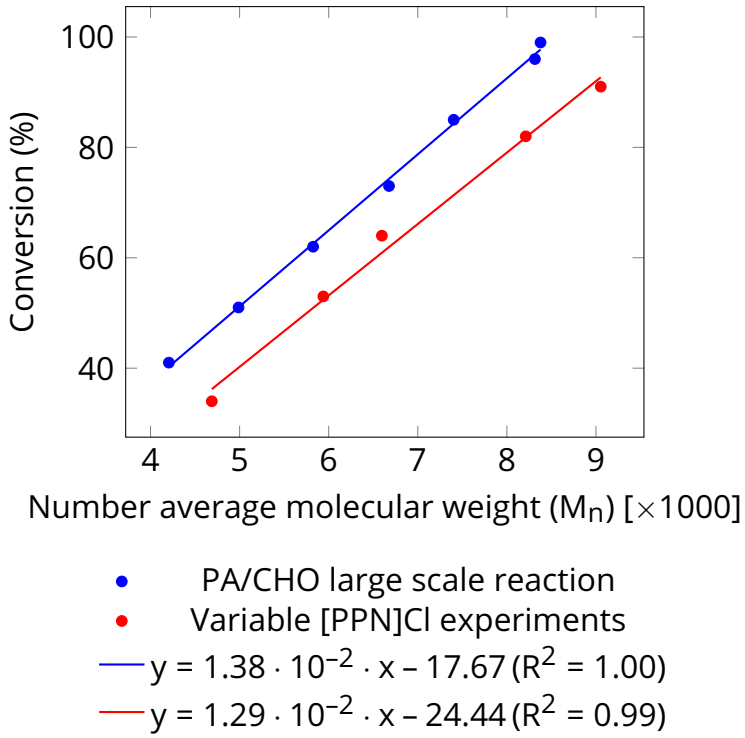


Figure 2.13: Plotted molecular weight data obtained using MALDI-TOF MS of select samples from the large-scale PA/CHO polymerisation reaction discussed in section 2.2.6, conditions: 90°C , 1 equiv. **In-1**, 2 equiv [PPN]Cl, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 49 µmol. (blue) and the variable [PPN]Cl experiments discussed in section 2.2.5, conditions: 1h at 90 °C , 1 equiv. **In-1**, 400 equiv. PA, 2000 equiv. CHO, 1 equiv. = 4.2 µmol. (red).

2.2.8 ROCOP using In-2

After the reactions with the **In-1** discussed above, further experiments were also conducted using the respective dibromo-substituted complex. To that end, reactions were performed using PA with CHO/VCHO/SO at 90°C for 2h using 1:2:400:2000 ratio of indium catalyst : [PPN]Cl : anhydride : epoxide. Reactions with both the presence and absence of the indium complex were performed, with all reactions proceeding to full >95& conversion of the phthalic anhydride as per *in situ* ^{1}H NMR of the reaction mixtures, with >90% polyester selectivity as per ^{1}H NMR of the isolated polymers. ^{1}H NMR spectrum of the resulting PA/CHO copolymer is presented in Figure 2.14, showing the respective ester and polyester signals. In the cases of control reactions, in contrast to previous reactions, 3 equivalents of the [PPN]Cl co-

catalyst were used, with the reasoning being to keep the sum of catalyst and co-catalyst equivalents to 3 (*i.e.* 3 equiv. of [PPN]Cl for the control reactions, and 2 equiv. of [PPN]Cl + 1 equiv. **In-2** otherwise). Next, the respective molecular weights of the resulting polymers were measured using gel permeation chromatography (GPC) and presented in Table 2.9. It can be seen that in all cases, the molecular weights of the resulting polymers were higher in the control reactions, however (with the exception of VCHO), these feature high polydispersities, indicating that the indium complex does provide some level of control. In the case of VCHO, the polydispersities in both reactions are comparable.

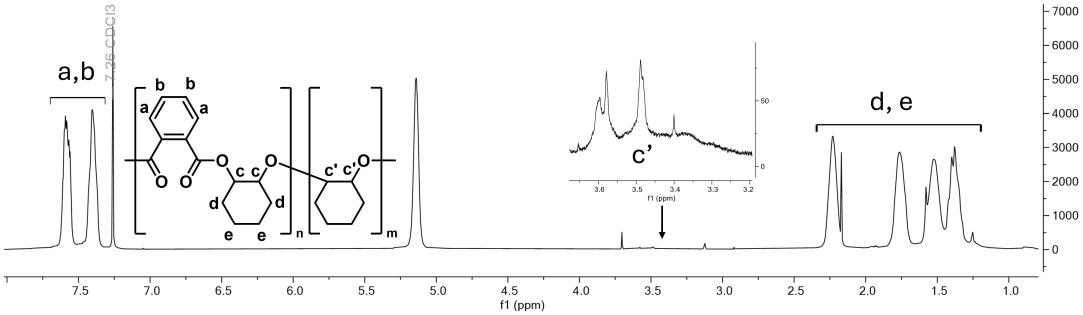


Figure 2.14: ^{1}H NMR spectrum recorded in $CDCl_3$ of an isolated PA/CHO copolymer resulting from the reaction with **In-2** complex, conditions: 2 h at 90°C with 1:2:400:2000 ratio of indium catalyst : [PPN]Cl : anhydride : epoxide.

Anhydride	Epoxide	[In] eq.	[PPN]Cl eq.	% Conv.	M_n	PDI
PA	CHO	1	2	100	16567	1.361
PA	VCHO	1	2	100	25883	1.176
PA	SO	1	2	100	5622	1.131
PA	CHO	0	3	100	23836	1.689
PA	VCHO	0	3	100	32962	1.161
PA	SO	0	3	100	9623	1.435

Table 2.9: Molecular weights and polydispersities of various polymers from reactions with the **In-2** complex. 2 h at 90°C with 1:2:400:2000 ratio of indium catalyst : [PPN]Cl : anhydride : epoxide. Molecular weights were measured using GPC with triple (refractive index, viscometry, light scattering) detection against polystyrene standards. Polydisperisty (PDI) is calculated as the ratio of M_w to M_n.

2.2.9 Co-catalyst screening

Thus far, the [PPN]Cl seemed surprisingly active towards the copolymerisation of the substrates chosen. In order to further investigate whether a different co-catalyst could initiate the reaction with the indium complex, but show lower activity on its own, several bases were screened, which were expected to be able to ring-open the respective epoxides and initiate the reaction, similarly to the chloride from [PPN]Cl acting as a base. The results obtained from these reactions are presented in Table 2.10. It can be seen that DMAP is the only co-catalyst that provided acceptable selectivities. However, in all other cases, the presence of the **In-2** complex seemed to enhance either the selectivity or the conversion. It should be noted here that this comparison was simply an exploratory one, with sublimed DMAP being available, whilst all the other co-catalysts were without further purification.

Co-catalyst	In-2 equiv.	% Conversion	Ester selectivity*
DMAP	1	78	>95
DMAP	0	48	>95
P(*p*-OCH_3Ph)3	1	18	66
P(*p*-OCH_3Ph)3	0	0	N/A
DBU	1	10	3
DBU	0	13	22
DABCO	1	50	58
DABCO	0	50	63

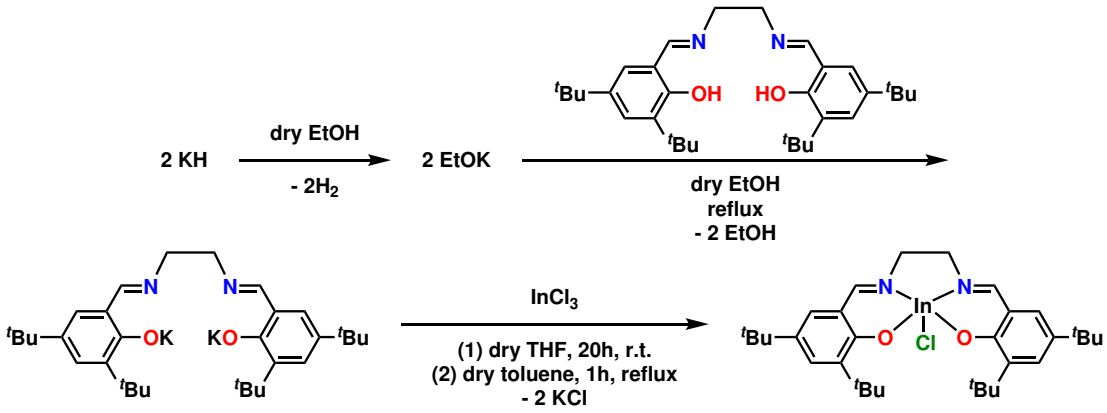
Table 2.10: Exploratory screen of different co-catalysts for the ROCOP of PA and CHO. Reactions performed at 90°C for 2h with 400:2000 PA:CHO ratio and the respective catalyst / co-catalysts ratios. *Selectivities determined *in situ* and are approximate as there was an overlap of other signals around the ether region.

2.2.10 ROCOP using In(3,5-^{t}Bu,^{t}Bu-Salen)Cl

Initially, the more complex Salpy framework was investigated. However, it was recognised that it would have been prudent to evaluate the simpler

Salen framework as well. Although initial synthetic attempts were unsuccessful and resulted in a mixture of pro-ligand and complex, the reaction conditions were ultimately optimised to the successful synthetic procedure shown in Scheme 2.4. Initial tests with PA/CHO and DMAP added as 100 µL standard solution in 1,2-difluorobenzene and stoichiometry of 1:2:400:2000 catalyst : co-cataalyst : anhydride : epoxide at 90 °C for 1 h revealed 72% conversion when both the catalyst and co-catalyst were used, and 85% with DMAP alone.

It was hypothesised that the neat conditions and moderate temperatures employed might be the reason for the higher conversions in the control reactions, where only the co-catalyst was used. This is because the ring-opening of epoxides by nucleophiles is considered a favourable reaction as it relieves ring strain. Combining this with neat conditions, which essentially afford the maximum contraction the epoxide can have, and high temperature, might lead to the undesirable side-reaction where the epoxide is ring-opened without first coordinating to the catalyst. Therefore, some further reactions were performed with PA and CHO / VCHO / SO at 70°C in 1 cm_3 toluene with a target ratio of 1:2:400:400 of anhydride:epoxide:catalyst:co-catalyst. Unfortunately, these revealed negligible conversions after approximately 18 h.



Scheme 2.4: Synthesis of In(3,5-^{t}Bu,^{t}Bu-Salen)Cl

2.2.11 [PPN]Cl ICP-MS investigations

The activity observed for [PPN]Cl control reactions in the absence of metal complexes was surprising and not in line with literature reports, which generally show [PPN]Cl to be less active on its own than in combination with a catalyst. For example, a 2018 report by Shi *et al.* showed only 10% conversion after 40 min at 100°C with CHO : PA : PPNCl ratio of 2500:500:1.[116] In order to further assess the unexpected co-catalyst activity observed in this work, ICP-MS (Inductively coupled plasma – Mass spectrometry) analyses on commercial and recrystallised samples of [PPN]Cl were conducted. Similar to how researchers have observed unexpected reactivity from residual palladium on stirrer bars[117], it was theorised that potential trace metallic impurities could potentially be the reason for the high reactivity observed in control ROCOP reactions where [PPN]Cl is used on its own.

Initial semi-quantitative investigations were mostly unremarkable, with values for transition metals being fractions of ppm, and thus highly unlikely to effect any measurable reactivity. However, it was noted that the presence of ^{43}Ca concentration was measured at around 25 ppm in the commercial [PPN]Cl sample. Although calcium would be an unlikely cause for the observed reactivity, it was decided that further fully quantitative measurements were merited, which revealed 0.872 mg/g Ca concentration in the commercial sample. Next, a five-fold recrystallised sample was prepared by dissolving commercial [PPN]Cl in dry dichloromethane under nitrogen and subsequently precipitating with dry diethyl ether. The final sample was then filtered and dried in vacuo before being subjected to fully quantitative mass spectrometry measurements. These revealed a 0.82 mg/g Ca concentration. This result is comparable to the one obtained from the commercial non-recrystallised sample. With the recrystallised sample at hand, comparison

reactions were performed using the **In-2** as shown in Table 2.11. However, the results between the recrystallised and commercial [PPN]Cl samples are comparable and in line with experiments performed before.

Therefore, it is reasonable to conclude from the above experiments that a clear reason for the high reactivity observed in the control reaction has not fully been established. It is plausible to assume that the reason for such reactivity could be multifactorial and depend on more than just the purity of the [PPN]Cl used. For example, certain impurities in the solvent or reagents, when coupled with [PPN]Cl could in fact be the reason. However, at this stage, it remains unclear.

[In] equiv.	[PPN]Cl equiv.	[PPN]Cl recrystal-lised?	Time (h)	T (°C)	% Conv.
1	1	No	1	90	45
0	1	No	1	90	56
1	1	Yes	1	90	41
0	1	Yes	1	90	54

Table 2.11: Experiments performed with commercial and five-fold recrystallised samples of [PPN]Cl in conjuction with the **In-2** complex.

2.2.12 Final remarks on laboratory studies

Following and in addition to the experiments described above, multiple other experiments were conducted, which included different conditions and attempts to synthesise other indium complexes with the ultimate goal of enhancing the reaction outcomes. For example, an attempt was made to use $In(O_iPr)_3$ and $In(OAc)_3$ instead of $InCl_3$ as a precursor with a 3,5-^{t}Bu-substituted Salen ligand, which would result in an isopropoxide/acetate instead of a chloride auxiliary ligand. However, the ^{1}H NMR spectra of these showed mixtures of free-ligand and more than one other species (likely

bridged dimeric complexes). Some reactions were also conducted using limonene oxide, but these required high temperatures (120-130°C) at which reactivity could simply be attributed to the harsh conditions rather than the catalysts used. Based on the research presented in this chapter, the role of the co-catalyst and the reasons for the high co-catalyst activity observed were not fully understood. Therefore, more research is needed in order to fully understand the role of the catalyst and co-catalyst in order to further optimise the reaction conditions.

2.2.13 Single-crystal X-ray diffraction studies

Crystals of the **In-2** and **In-3** complexes were grown by slow evaporation from a solution in 1,2-difluorobenzene. These were found to be suitable for single-crystal X-ray diffraction (SC-XRD) analysis. Efforts to grow crystals of the **In-1** complexes were, unfortunately, unsuccessful.

Both the **In-2** and **In-3** complexes crystallised in the monoclinic $P2_1/c$ space group and featured a single molecule in the asymmetric unit. In the case of the **In-3**, a disordered 1,2-difluorobenze molecule was also found in the asymmetric unit, whilst in the case of **In-2**, a disordered water molecule was present. The structures are shown in Figure 2.16. A summary of key crystal structure data for both complexes is shown in Table 2.12, with selected bond lengths, valence angles, and torsion angles shown in Table 2.13, Table 2.15, and Table 2.14, respectively.

The possible coordination configurations that the Salpy ligand can adopt upon coordination are limited to β-*cis* and *trans*, with an α-*cis* configuration being impossible due to geometric constraints. These configurations are shown in Figure 2.15. The models of the SC-XRD data show that these complexes adopt the β-*cis* configuration, where one of the iminophenoxide

arms is positioned in the N2-O1-Cl1-N3 plane, whilst the other lies in the N1-O1-O2-N3 plane, with the pendant pyridyl moiety coordinated to the metal. These structures are in line with the SC-XRD structure for [Al(Salpy)CH_3] reported by Bahili *et al.* .[31] Whilst the *trans* configuration is not observed in XRD, it is geometrically feasible and potentially exists in solution. In contrast to the indium complexes discussed herein, the copper(II) complexes reported by Houser and co-workers adopted a square pyramidal geometry with a methanol solvent molecule at the apex and the pyridyl not coordinated.[88]

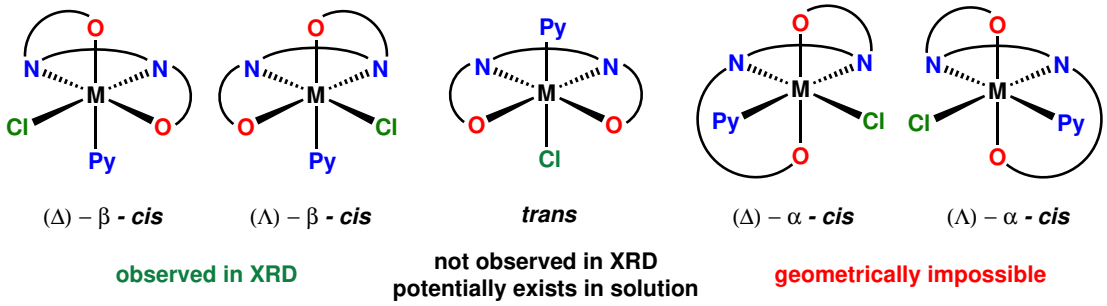
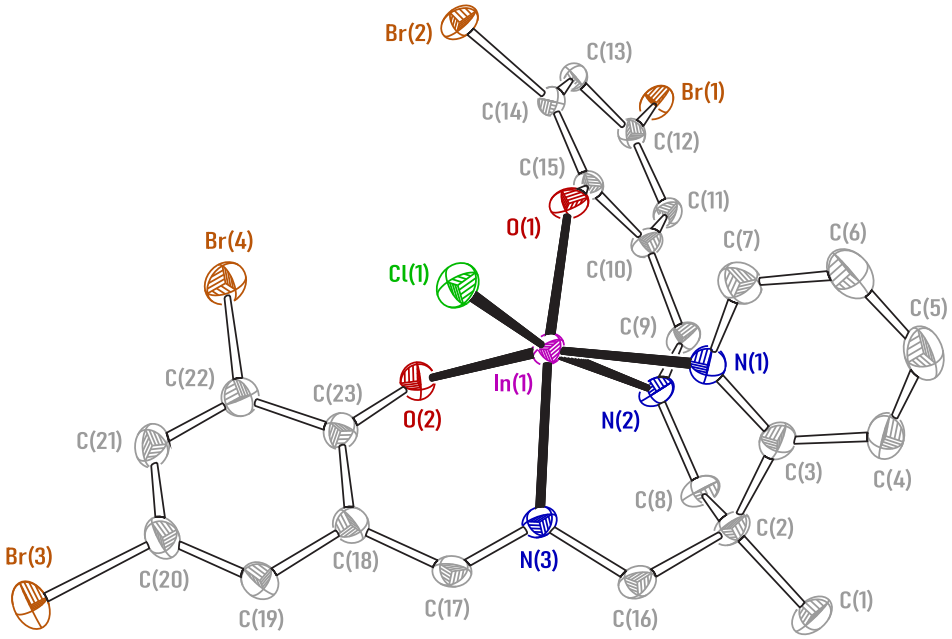


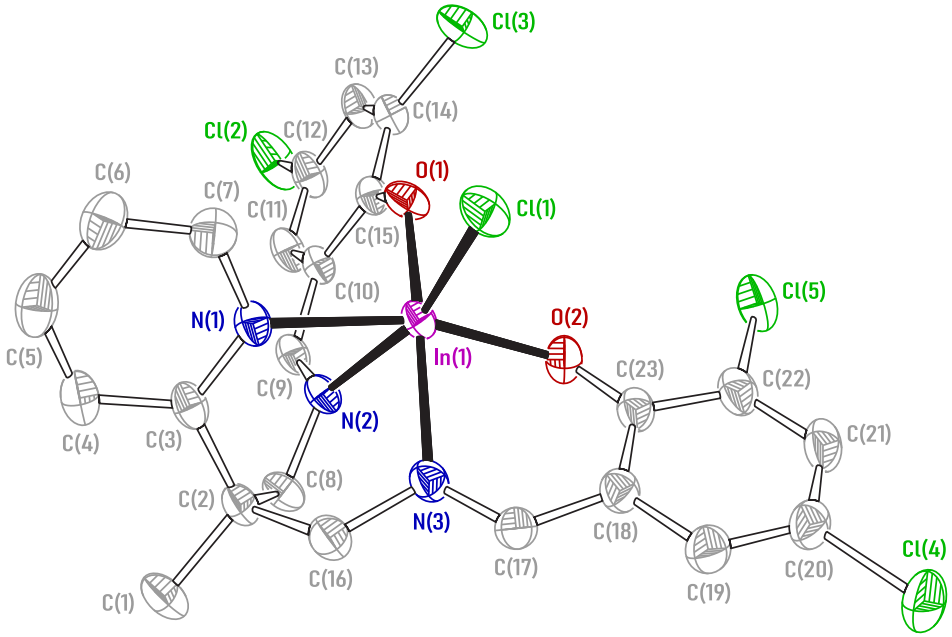
Figure 2.15: Examples of different coordination configurations for Salpy ligands.

In both cases, the complexes adopt a disordered octahedral geometry. The extent of distortion can be compared by calculating the variance of the octahedral angles using Equation 2.2 as reported by Robinson *et al.*[118] In the equation, θ_i represents each of the 12 angles defining an octahedron. The lower the $\sigma^2_{\theta(oct)}$, the closer the geometry to an ideal octahedron. The equation yields 62.49 for **In-2** and 76.79 for **In-3**, indicating less distortion for **In-2**. The similar aluminium complex, [Al(Salpy)CH_3], reported by Bahili *et al.* ,[31,119] features an even less distorted octahedron with $\sigma^2_{\theta(oct)}$ of 40.52, likely owing to the smaller ionic radius of aluminium versus indium.

Upon coordination of the Salpy ligand, 5 rings are formed - 2×[R-N(imine)-In-O(phenoxide)-R], [R-N(imine)-In-N(imine)-R], and 2×[R-N(imine)-In-N(pyridyl)-R]. For the [R-N(imine)-In-O(phenoxide)-R] rings resulting from the coordination of each iminophenoxy arms, it holds true for both com-



(a) In-2



(b) In-3

Figure 2.16: Thermal ellipsoids of **In-2** and **In-3** shown at 30% probability. Hydrogen atoms, as well as residual H_2O molecule (in the case of **In-2**) and 1,2-difluorobenzene solvent molecule (in the case of **In-3**), have been omitted for clarity. The structures were solved and refined by Dr Benjamin Ward. Note that due to the difference in figure sizes, the sizes of the ellipsoids are not comparable between structures.

Parameter	In-2	In-3
Empirical formula	$C_{23}H_{19}N_3O_3ClBr_4In$	$C_{29}H_{21}N_3O_2Cl_5InF_2$
Formula weight/g·mol^{-1}	855.32	773.56
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	8.19970(10)	7.95340(10)
b/Å	19.4701(3)	17.1246(3)
c/Å	16.9281(3)	22.6398(5)
α/°	90	90
β/°	97.378(2)	96.320(2)
γ/°	90	90
V/Å^3	2680.18(7)	3064.77(10)
Z	4	4
T/K	200(2)	150(2)
Radiation	μ(CuKα) = 15.216 mm^{-1}	μ(CuKα) = 10.564 mm^{-1}
ρ_{calc}/g·cm^{-3}	2.120	1.676
Reflections collected	27106 (6.952° ≤ 2Θ ≤ 154.22°)	28433 (7.858° ≤ 2Θ ≤ 153.736°)
Independent reflections	5635 (R_{int} = 0.0530, R_σ = 0.0373)	6393 (R_{int} = 0.0653, R_σ = 0.0390)
Final R_1	0.0351 (I >2σ(I))	0.0502 (I >2σ(I))
Final wR_2	0.0957 (all data)	0.1444 (all data)

Table 2.12: Summary of key crystal structure data for **In-2** and **In-3**. More detailed information is available in the Appendix.

plexes that the [O1-In1-N2-C9-C15-C10] ring is relatively more planar than the [O2-In1-N3-C17-C18-C23] ring. This is evident upon visual inspection of the 3-dimensional geometries and can be quantified by examining the O1-In1-N2-C9 / O1-C15-C10-C9 and O2-In1-N3-C17 / O2-C23-C18-C17 pairs of torsion angles, with the relative difference between the first pair being smaller than that for the second pair. These torsion angles are presented in Table 2.14. This can be attributed to the different geometric demands of the β-*cis* conformation, compared to a *trans* conformation. Furthermore, for both complexes, the remaining 3 newly-formed rings all exhibit a twist-boat-like conformation.

Analysis of key bond lengths between the two compounds showed the

Bond	In-2	In-3
In1-N1	2.297(3)	2.324(3)
In1-O1	2.101(3)	2.077(3)
In1-O2	2.125(3)	2.135(3)
In1-N2	2.255(3)	2.266(3)
In1-N3	2.240(3)	2.244(4)
In1-Cl1	2.4054(10)	2.4155(11)

Table 2.13: Selected bonds lengths measured from the refined SC-XRD structures for **In-2** and **In-3** quoted in Å. More detailed information is available in the Appendix.

Torsion angle	In-2	In-3
O1-In1-N2-C9	-10.3(3)	-1.3(3)
O1-C15-C10-C9	9.4(6)	-1.1(6)
O2-In1-N3-C17	-33.9(3)	28.3(4)
O2-C23-C18-C17	1.1(7)	3.3(8)

Table 2.14: Selected torsion angles measured from the refined SC-XRD structures for **In-2** and **In-3** quoted in degrees.

In1-N1 bond (N1 is the nitrogen of the pendant pyridyl) to be longer in **In-3** compared to **In-2**. It can also be seen that the In1-N1 for either complex is longer than any of the In-N(imine) bonds for either complex. This suggests that the pyridyl is more weakly coordinated than the respective imine nitrogens and suggests a certain degree of hemilability. The In1-O2, In1-N2, and In1-N3 bonds were all shown to be statistically the same between the two complexes, whilst the In1-O1 was determined to be longer in the **In-2** complex, and the In1-Cl1 longer in **In-3**. In both cases, within the same complex, the In1-O1 bonds were shown to be shorter than the In1-O2 bonds. When the In-N(imine) bonds were considered, these were shown to be the equivalent in the **In-2**, whilst in the **In-3**, the In1-N2 bond is marginally longer

$$\sigma^2_{\theta(oct)} = \frac{\sum_{i=1}^{12} (\theta_i - 90°)^2}{11}$$

Equation 2.2: Octahedral angles variance.

Angle	In-2	In-3
O1-In1-Cl1	94.14(8)	93.80(9)
O1-In1-O2	95.34(12)	93.40(14)
O1-In1-N1	98.48(12)	101.82(14)
O1-In1-N2	83.19(11)	83.52(13)
O1-In1-N3	166.43(12)	165.15(13)
O2-In1-Cl1	97.61(9)	95.05(10)
O2-In1-N1	163.24(13)	163.66(14)
O2-In1-N2	95.93(13)	100.79(14)
O2-In1-N3	81.26(13)	81.54(14)
N1-In1-Cl1	90.83(10)	89.87(9)
N2-In1-Cl1	166.39(10)	164.06(10)
N2-In1-N1	76.43(13)	75.39(13)
N3-In1-Cl1	99.32(9)	100.52(10)
N3-In1-N1	83.11(13)	82.25(13)
N3-In1-N2	84.10(12)	83.73(13)

Table 2.15: Selected valence angles measured from the refined SC-XRD structures for **In-2** and **In-3** quoted in degrees. More detailed information is available in the Appendix.

than the In1-N3 bond, with only 0.001 Å between the bond ranges within $\pm$3 estimated standard deviations (ESDs).

In order to compare some of the key bond lengths from **In-2** and **In-3** to literature examples, a search of the Cambridge Structural Database[120] (CSD) was performed (version 5.46 Nov 2024, including Feb 2025 update).[120] A total of 4 searches were performed, as illustrated in Figure 2.17 and bond lengths extracted are presented in Table 2.16. The results show that the In1-N1 bond in **In-2** is in line with the average bond length identified for In-N(Py) from Search 2.1, whilst the same bond in **In-3** is longer than the average. The In-N(imine) bonds for both complexes are also longer than the average bond lengths identified from Search 2.2. For both complexes, the In1-O2 bond is longer than the average, whilst the In1-O1 bond is shorter than the average in the case of **In-3** and in line with the average for **In-2**. In the case of both complexes, the In1-Cl1 bond is shorter than the averages identified from both Search 2.3 and Search 2.4. However, it should be noted

that even though some bonds in **In-2/3** are shorter or longer than the averages identified from the CSD searches, these are still within the minimum and maximum values identified from the searches.

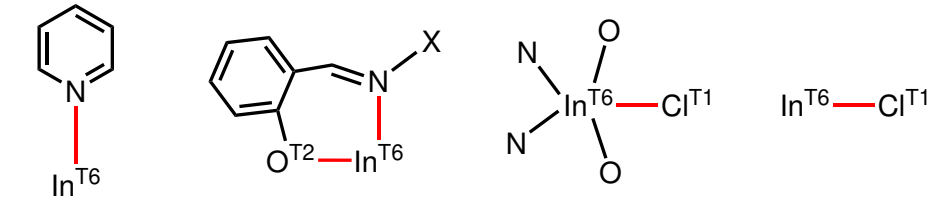


Figure 2.17: Searches of the CSD (version 5.46 Nov 2024, including Feb 2025 updates)[120] for fragments from **In-2/3** complexes. The number after "T" in the superscripts indicates the number of bonded atoms. X represents any atom. Bond lengths of interest are highlighted in red. Results are presented in Table 2.16.

Search (bond)	2.1 (In-N(Py))	2.2 (In-N)	2.2 (In-O)	2.3 (In-Cl)	2.4 (In-Cl)
Hits	271	40	40	52	451
Count	644	106	106	129	1499
Min	2.120	2.107	2.036	2.312	2.001
Max	2.671	2.318	2.188	2.550	2.928
Mean	2.293	2.221	2.098	2.441	2.478

Table 2.16: Bond lengths extracted from the CSD[120] searches from Figure 2.17. "Hits" is the number of unique database identifiers which match the fragments. "Count" is the total number of bonds identified, including multiple bonds from a single hit.

2.2.14 Computational studies

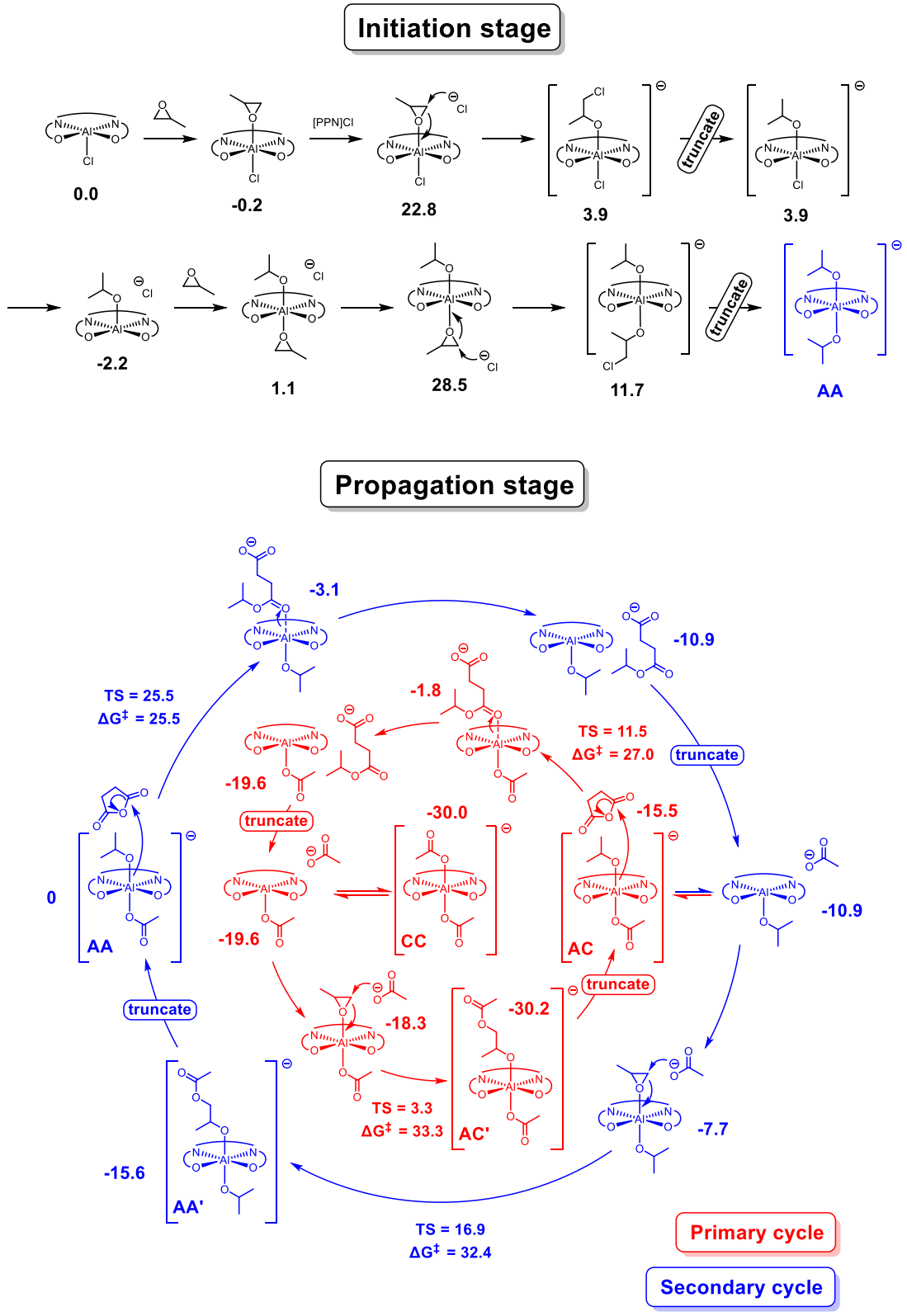
2.2.14.1 Literature reported mechanism

As mentioned in Chapter 1, one of the most comprehensive analyses of the mechanism for alternating copolymerisation of epoxides and cyclic anhydrides has been reported by Coates and co-workers, which is presented in Scheme 2.5. They performed extensive experimental and computational work on the reaction mechanism using (Salph)AlCl derivative and [PPN]Cl. The authors propose an initiation stage culminating in the formation of a

bis-alkoxide species. The propagation stage that follows consists of 2 different cycles connected *via* an alkoxide/carboxylate intermediates, with a proposed bis-carboxylate resting state (species **CC** on Scheme 2.5).[49]

The mechanism begins with the initiation sequence, which consists of the external chlorine from the co-catalyst ring-opening a coordinated epoxide. This adds an additional negative charge on the complex, which allows for decoordination of the chloride ancillary ligand and coordination of a second epoxide, which is then further ring-opened by the decoordenated chloride to result in a bis-alkoxide species (species **AA** on Scheme 2.5). The authors also investigated the possibility of chloride decoordination in the first epoxide ring-opening step, with their calculations revealing a highly endergonic process, which was inconsistent with their experimental results.[49]

The bis-alkoxide species mentioned above then enters a propagation cycle where the anhydride is ring-opened in a concerted fashion by one of the alkoxide moieties to generate a carboxylate. This marks a point in the mechanism where there are two possible pathways to proceed - either the carboxylate decoordinates, allowing for the coordination of an epoxide, which can then be ring-opened by the carboxylate, or another anhydride is ring-opened by the remaining alkoxide. The former requires activation energy of 32.4 kcal/mol to regenerate the bis-alkoxide species, whilst the latter only requires 27 kcal/mol to ultimately proceed to the highly thermodynamically favoured resting state (species **CC** on Scheme 2.5). Therefore, the authors concluded that the primary cycle predicted for the reaction is the one shown in red on Scheme 2.5, with the rate-limiting step deemed to be the epoxide ring-opening.[49]



Scheme 2.5: Calculated mechanism for the ring-opening copolymerisation of epoxides and cyclic anhydrides computed at the SMD(THF)//M06-2X/6-311+G(d,p)//M06-L/6-31+G(d,p) level of theory, reported by Coates and co-workers, with some moieties truncated (replaced with simpler ones) for computational efficiency.[49]

2.2.14.2 DFT investigation using indium(III) Salpy catalyst

As part of the investigations on whether the indium Salpy complexes could be effective catalysts, density functional theory calculations were performed in order to probe the thermodynamic viability of these complexes as catalysts for ROCOP. Structures of related aluminium complexes from in-house calculations performed by Dr Benjamin Ward were taken as a starting point, along with consulting the study and mechanism (Scheme 2.5) by Coates and co-workers discussed above. The DFT calculations were conducted on the carboxylate propagation cycle using the indium(III) Salpy catalyst as a model. This differs from the indium(III) Salpy complexes discussed in the chapter in that the phenoxide aromatic rings of the ligand are not substituted, which allowed for computational efficiency.

Starting with a bis-carboxylate (modelled as bis-acetate), decoordination of one of the moieties leads to a monocarboxylate species, which, after coordination and ring-opening of the epoxide by an external carboxylate, affords a monoalkoxide intermediate. Subsequent coordination of the anhydride in the *cis* position next to the alkoxide allows for a 1,2-migratory insertion to take place, followed by the anhydride ring-opening, which effectively regenerates the carboxylate species, ready to start the cycle again. Although the initiation step has not been investigated separately in this case, it would follow the same pattern as the propagation, with the difference that the starting species would feature a chloride ligand instead of carboxylate, and the external nucleophile for the ring-opening of the epoxide would also be a chloride.

Interestingly, the activation energies reported by Coates and co-workers[49] for the epoxide ring-opening transition states for their Al(Salph)Cl mechanism are higher than the calculations presented here: 32.4 kcal/mol

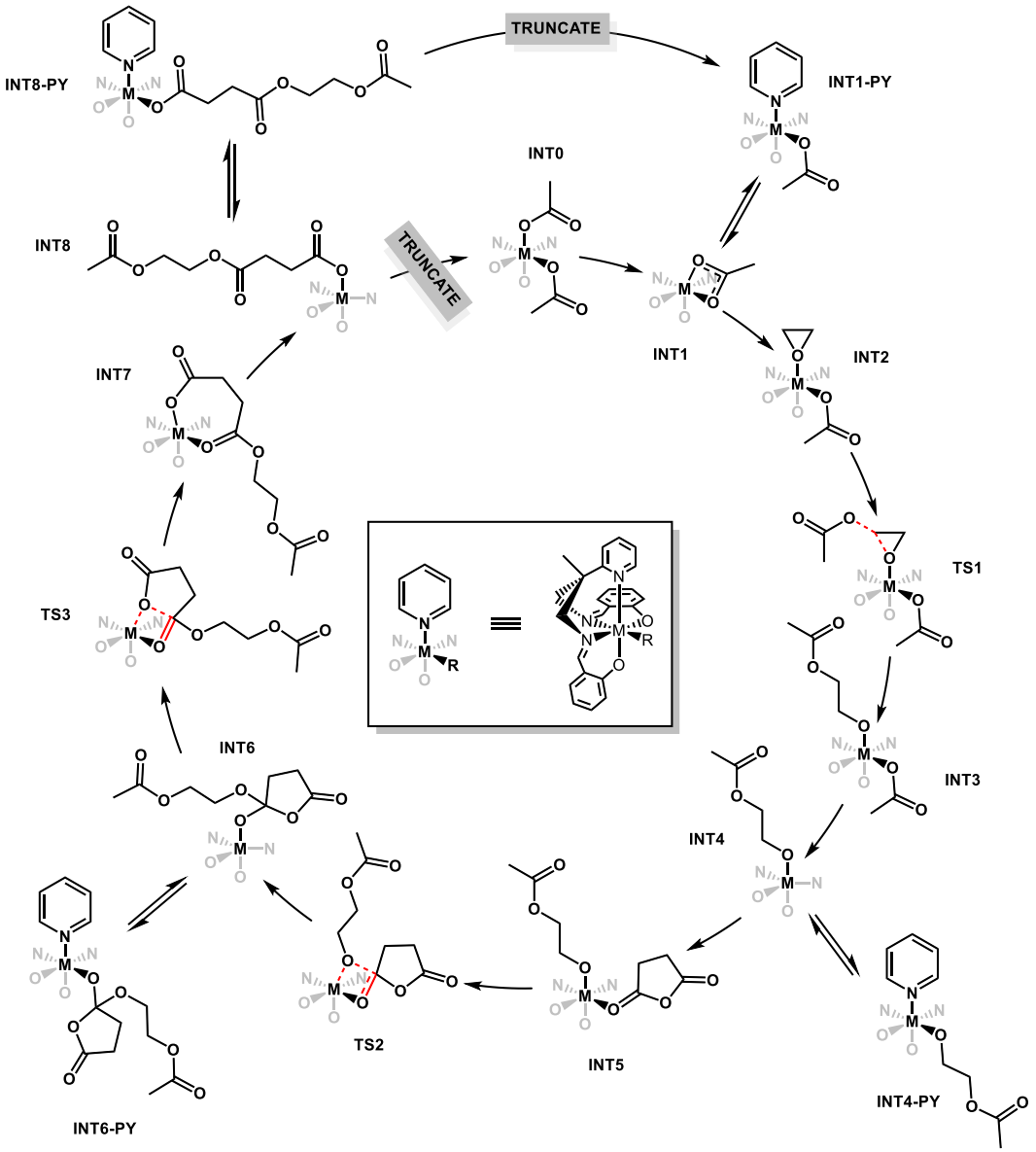
and 33.3 kcal/mol for the alkoxide and carboxylate cycles, respectively,*vs* 19.66 kcal/mol in the case of the indium complex. Furthermore, the anhydride ring-opening transition states for Coates's mechanism[49] also feature notably higher activation barriers than the energies observed here: 25.5 kcal/mol and 27.0 kcal/mol for the alkoxide and carboxylate cycles, respectively,*vs* 4.82 kcal/mol and 5.77 kcal/mol for the 1,2-migratory insertion and subsequent ring-opening, respectively. This suggests that a 2-stage anhydride ring-opening within a *cis* propagating cycle is more thermodynamically favourable than a concerted ring-opening *via* a direct nucleophilic attack of the anhydride carbonyl carbon by the alkoxide ligand seen in the mechanism reported by Coates.[49]

Overall, the mechanism proposed here is thermodynamically favourable, with the epoxide ring-opening transition state having the highest energy activation barrier, and thus being the rate-determining state, similar to Coates' results.[49] Analogous calculations were also performed using gallium and aluminium, in order to gain some insight into how a different group 13 metal might affect the mechanism. The relative energies for the species obtained from these calculations were comparable to their indium counterparts, with a maximum relative energy difference across all species of 9.40 kcal/mol for gallium and 6.94 kcal/mol for aluminium. The difference in the transition state barriers was even less, with a maximum barrier energy difference of 5.85 kcal/mol for gallium and 1.92 kcal/mol for aluminium. These results indicate that the reaction is feasible across all 3 metals and the Salpy complexes of these should, in theory, be able to act as catalysts for the ROCOP of epoxides and cyclic anhydrides. The proposed mechanism for the reaction is shown in Scheme 2.6, with the relevant energies for the species reported in Table 2.17 and the geometries of the transition state structures for the indium mechanism illustrated in Figure 2.18. The mechanism aligns with

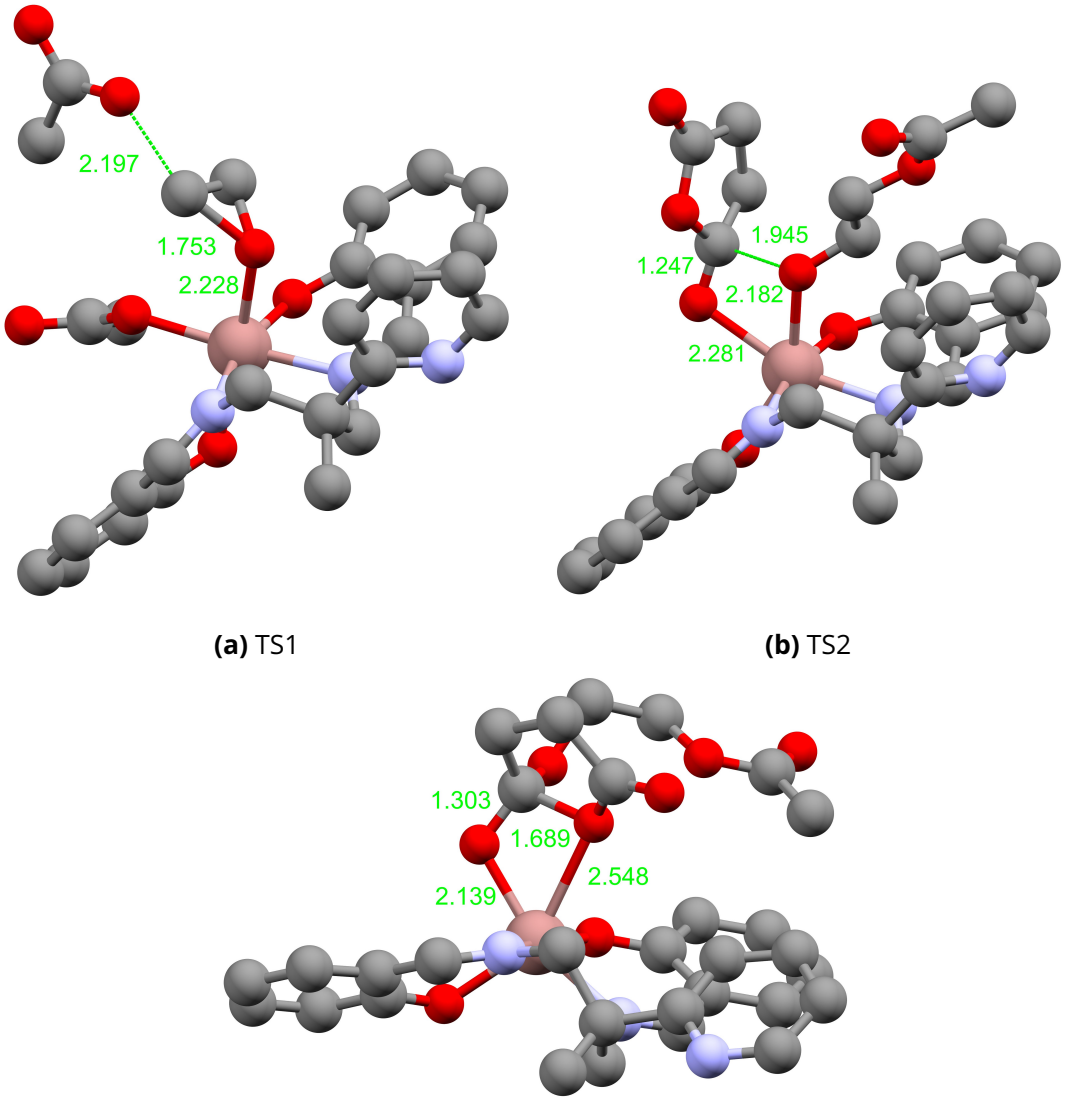
observed experimental results to the extent that catalysis does indeed proceed under the conditions investigated and does show that the indium catalysts discussed are viable catalysts for the reaction. However, as previously discussed, an understanding of the role of co-catalysts is also important and investigating their role computationally should form part of future studies.

Species	M = In	M = Ga	M = Al
INT0	0.00	0.00	0.00
INT1	1.30	-2.42	0.00
INT1-PY	1.47	-2.92	-2.38
INT2	13.13	10.31	11.41
TS1	32.79 (19.66)	30.55 (20.24)	30.66 (19.25)
INT3	-3.12	-4.24	-4.78
INT4	4.01	-5.01	-2.93
INT4-PY	-4.40	-9.25	-8.19
INT5	10.42	1.02	8.17
TS2	15.24 (4.82)	11.70 (10.67)	13.09 (4.92)
INT6	5.90	-0.20	1.92
INT6-PY	7.20	4.48	5.37
TS3	11.67 (4.47)	9.11 (4.63)	11.76 (6.39)
INT7	0.93	-0.46	0.08
INT8	-0.28	-8.08	-5.78
INT8-PY	-7.49	-11.65	-11.10

Table 2.17: Relative Gibbs free energies in kcal/mol for the species from the proposed propagation mechanism for the ring-opening copolymerisation of ethylene oxide and succinic anhydride using M(Salpy)Cl catalyst from Scheme 2.6. Energies for transition state barriers are indicated in brackets. Calculated using Orca 5.0.4[121] at the ωB97M-V[122–125]/def2-QZVPP[126–129]/CPCM(THF)[130,131]//r2SCAN-3c[132–137]/CPCM(THF)[130,131] level of theory with thermochemistry performed at 298.15 K.



Scheme 2.6: Proposed propagation mechanism for the ring-opening copolymerisation of ethylene oxide and succinic anhydride using M(Salpy)Cl catalyst. The acetate ligands in INT0 represent the growing polymer chains, which have been truncated (replaced with simpler moieties) for computational efficiency. The energies are presented in Table 2.17.



(a) TS1 **(b)** TS2

(c) TS3

Figure 2.18: DFT transition state structures with selected bond lengths for the transition states from the proposed propagation mechanism for the ring-opening copolymerisation of ethylene oxide and succinic anhydride using M(Salpy)Cl catalyst from Scheme 2.6. Calculated using Orca 5.0.4[121] at the ωB97M-V[122–125]/def2-QZVPP[126–129]/CPCM(THF)[130,131]//r2SCAN-3c[132–137]/CPCM(THF)[130,131] level of theory with thermochemistry performed at 298.15 K.

2.2.14.3 Differences between the Salpy ligand and the literature reported Salph ligand

A noted difference with the literature mechanism shown in Scheme 2.5 and the mechanism with the indium(III) Salpy catalyst is the different geometry of the Salpy framework, most notably in the orientation the Salpy ligand adopts around the metal centre. In the case of the Salph reported by Coates and co-workers, the ligand adopts a planar coordination environment around the metal centre. On the other hand, the increased flexibility of the Salpy ligand allows for a β-*cis* conformation whereby the two phenoxide moieties are positioned in perpendicular planes around the metal (refer back to Figure 2.15 in section 2.2.13). This difference means that in the case of the Salpy complex, the resulting polymer chains propagate *cis* to one another, rather than *trans* in the case of the Salph ligand. Whilst the mechanism reported by Coates features a concerted anhydride ring-opening, the difference in the complexes used necessitated a two-step process whereby a migratory insertion by the metal-alkoxide into the coordinated anhydride is followed by the anhydride ring-opening to produce a metal-bound carboxylate. This is akin to similar mechanisms reported for the ring-opening polymerisation of lactones,[138], as well as a mechanism reported for ROCOP using a titanium(IV) complex where the catalyst features vacant *cis*-binding sites.[139] The *cis* propagation results in a single-cycle mechanism, in contrast to the dual-cycle proposed by Coates and co-workers.

Furthermore, the Salpy ligand features a pendant pyridyl, which could potentially influence the reaction through both steric and electronic interactions due to its proximity to the active reaction site, compared to the more open environment offered by the Salph ligand.

2.3 Conclusions and outlook

In conclusion, the first example of an In-based catalyst for the ring-opening copolymerisation of epoxides with cyclic anhydrides has been presented, which functions in conjunction with [PPN]Cl co-catalyst. This catalytic system has been shown to be active at moderate temperatures and results in improvement of the observed polydispersities of the produced polymers in comparison to using just a co-catalyst. The role of both the catalyst and co-catalyst was investigated, and their effect on conversion and molecular weight of the resulting polymers was analysed. DFT calculations into the propagation part of the mechanism were conducted, indicating favourable thermodynamics. However, the enhancement provided by these indium complexes was shown to be only in relation to narrower polydispersities of the resulting polymers, and it was evident from this work that the co-catalysts used remain highly active under the conditions explored and effect higher conversions on their own compared to when combined with the indium complexes.

Future work in this field might focus on exploring further complex derivatives. For example, one could imagine that replacing the chloride ligand on the indium metal with an alkyl group might prove effective at initiating the reaction without the need for a co-catalyst. Furthermore, multiple literature examples in the field of polymerisation include cationic indium complexes,[30,140], which could be something to consider for future studies. For example, the chloride ligand could be abstracted and the bulky [BAr^F] counterion introduced, which would produce a cationic indium centre. In addition, heterodinuclear systems[77–81] with Group 13 or transition metals combined with a Group 1 metal have shown high activity due to potential synergistic effects and so this might be another avenue to expore in fur-

ther research by designing heterodinuclear In/Group 1 catalysts. Last but not least, ligands with a tethered co-catalyst coordinated to indium could be another attractive area to consider in future work, as these have been shown to be highly active and able to tolerate chain-transfer agents with aluminium.[76]

CHAPTER 3

Novel complexes of Ruthenium, Rhodium, and Iridium containing cyclic diamine ligands: Activity towards transfer hydrogenation and effects of metal and ring size on coordination

Publication resulting from the work presented in this chapter: V. Y. Vladimirov, M. Charrier-Chardin, B. M. Kariuki, B. D. Ward and P. D. Newman, "Ringing the Changes: Effects of Heterocyclic Ring Size on Stereoselectivity in [(η^5-C_5Me_5)RhCl], [(η^5-C_5Me_5)IrCl] and [Ru(η^6-cymene)Cl] Complexes of Chiral 3-Amino-1-Azacycles", *Molecules*, **2024**, 29, 4659.[141]

3.1 Introduction

3.1.1 Advances in transfer hydrogenation catalysts

As discussed in Chapter 1, transfer hydrogenation is an important process both in organic synthesis and industry and has multiple advantages compared to direct hydrogenation. Noyori and Ikayira's work, mentioned previously, has been the inspiration for the development of many catalytic systems for transfer hydrogenation, with some now commercially available and showing exceptional rates and enantioselectivities. These retain the same features as the original catalyst reported by Noyori and Ikayira - *i.e.* half-sandwich complex, with a diamine ligand and an electron-withdrawing group (*e.g.* a tosyl) on one of the nitrogen atoms, but with modifications aimed at improving catalytic performance.

One such modification, known as "tethering", was introduced by the Wills group in 2004. This introduced a "tether" between the polyhapto aromatic ring and the diamine parts of the complexes. The group reported the synthesis of modified ruthenium dimers, which convert to the respective monomeric tethered ruthenium complexes under the reaction conditions. Their results showed up to quantitative conversions and up to 98% *e.e.* for the reduction of aromatic ketones in formic acid/triethylamine azeotropic mixture at 28°C .[142] Subsequent work by the group saw the development of other complexes with improved catalytic activity, one of which they referred to as "reverse-tethered", indicating the change from tethering the arene to the basic nitrogen instead of the one bearing the tosyl group.[143,144] The length of the tether has also been investigated, with the group reporting that a "4-carbon" tether proved to be the fastest at ketone reduction.[145]

Since those initial reports of tethered complexes, this field has con-

tinued, with further tethered complexes being developed, and tethered versions showing significantly higher activity than their non-tethered counterparts.[146] In 2011, Ikariya and co-workers reported a new generation of "oxo-tethered" catalysts, which have subsequently been commercialised under the name Ts-DENEB®.[147] Some selected examples of tethered catalysts are presented in Figure 3.1.

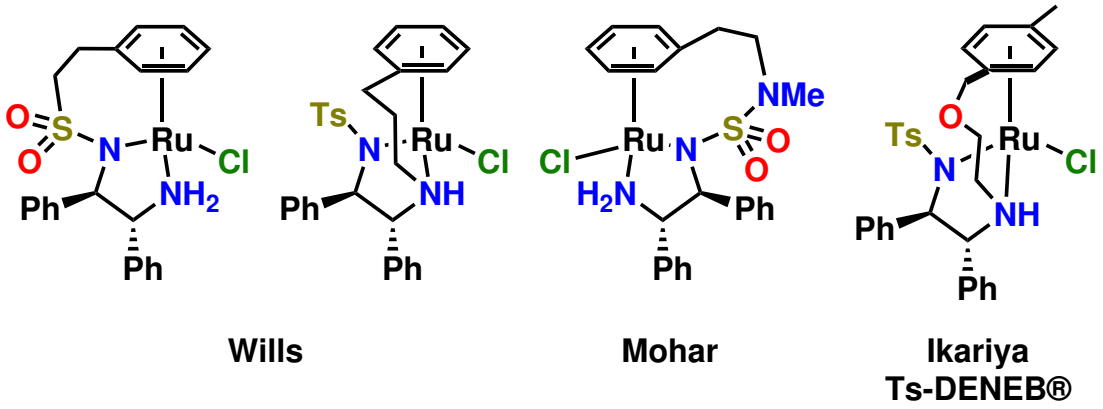


Figure 3.1: Selected examples of "tethered" transfer hydrogenation catalysts. From left to right, complexes reported by Wills and co-workers (first two)[142–144], Mohar and co-workers,[148], and Ts-DENEB® developed by Ikariya and co-workers.[147]

3.1.2 Overview of stereogenic-at-metal complexes

In many chiral complexes, chiral information is held in the coordination sphere by the ligands, which can then direct substrate activation in a way that allows for the process to take place asymmetrically.[149] As the metal centre is often directly involved in catalytic processes, and thus having the metal itself carry the chiral information can be beneficial.[149] When tetrahedral complexes are involved, one could draw clear parallels with chiral carbon atoms, as shown in Figure 3.2. However, some particular challenges that one might expect when dealing with stereogenic-at-metal complexes involve the inherent lability of some metal-ligand bonds, some of which could be broken and re-formed under ambient conditions. Such processes could

inevitably lead to the formation of various isomers, including enantiomers. When the latter are formed, over time, the sample will become racemic, resulting in a diminished performance at asymmetric catalysis.[149]

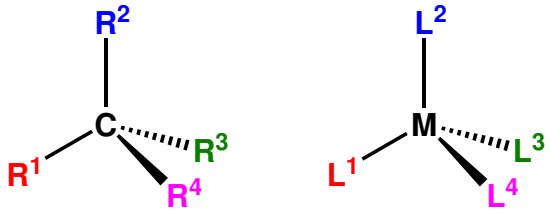


Figure 3.2: Generic comparison of stereogenic carbon and metal.

3.1.3 Importance of stereogenic-at-metal complexes for transfer hydrogenation

It is often desirable to perform the transfer hydrogenation reactions enantioselectively, which necessitates the need for an element in the design of the catalyst that will allow for the desired enantioselectivity to be imparted into the final product. One of the ways this can be achieved is through **stereogenic-at-metal** complexes. Such complexes have been reported as effective catalysts for asymmetric transfer hydrogenation, asymmetric photocatalysis, Lewis acid catalysis, and catalysis involving outer-sphere interactions.[149–161] Selected examples of stereogenic-at-metal complexes developed by Meggers and co-workers are shown in Figure 3.3.

The so-called Noyori-Ikayira catalysts discussed previously are a popular choice for asymmetric transfer hydrogenation reactions. Recently, Hintermair and co-workers demonstrated for the first time the existence of major and minor hydride species formed during asymmetric transfer hydrogenation using Noyori's catalyst (Figure 3.4). The authors used online FlowNMR spectroscopy to detect and quantify their respective kinetics during the reaction and confirmed the thermodynamic preference of one diastereomer

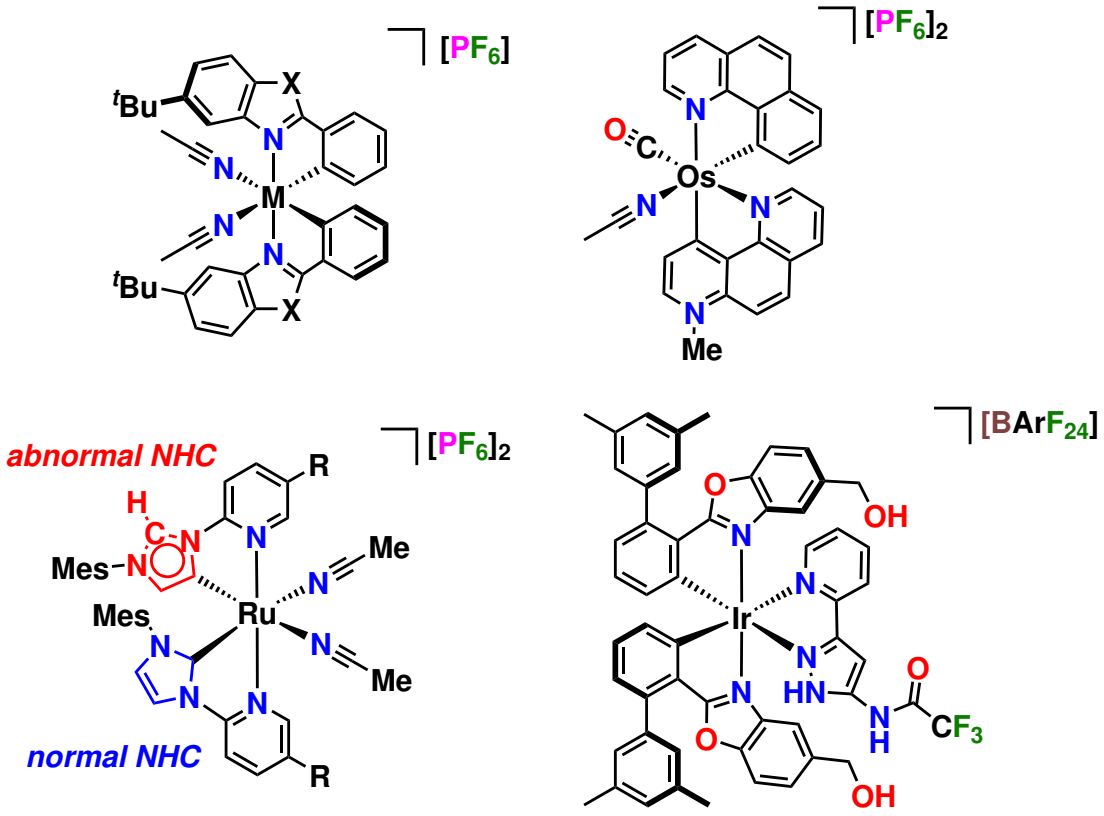
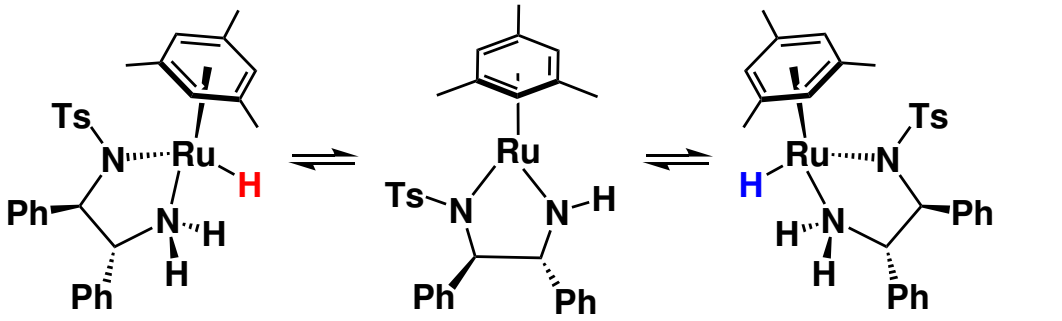


Figure 3.3: Selected examples of stereogenic-at-metal complexes developed by Meggers and co-workers (M=Rh,Ir ; X=O,S ; R=Br,CF_3).[151,155–157,159,160]

over the other using density functional theory. Whilst traditionally the use of chiral ligands has been extensively employed to induce stereoselective catalysis, this study shows that the chirality at the metal can be equally critical. The authors do acknowledge that the major and minor species interconvert during the reaction when 2-propanol is used as a hydrogen source. However, the use of formic acid, which produces a CO_2 by-product,[162] can effectively suppress the interconversion process and prevent a reduction in enantioselectivity. This work effectively demonstrates the chirality of the metal as an additional avenue in rational catalyst design.[163]

Many modifications of the Noyori-Ikayira catalysts have been reported featuring mono-*N*-tosylated diamine ligands, as previously shown in Figure 3.1, solidifying the place of these types of complexes as reliable catalysts for efficient asymmetric transfer hydrogenation. Although less common,

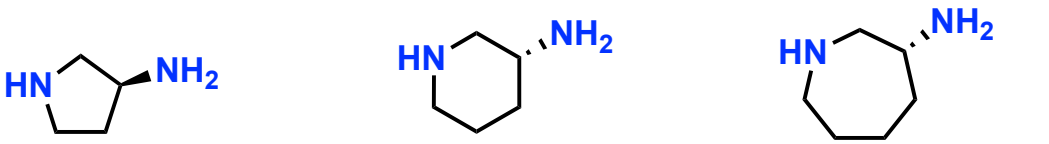


(R,R)S^{Ru}
Major catalyst species (active)
93.2 % *e.e.* (DFT)

(R,R)R^{Ru}
Minor catalyst species (inactive)
36.3% *e.e.* (DFT)

Figure 3.4: Major and minor hydride species formed during asymmetric transfer hydrogenation using Noyori's catalyst as demonstrated by Hintermair and co-workers.[163]

the literature also features examples where the reactions are facilitated even with non-tosylated diamines.[164] Surprisingly, there have been no reports to date featuring the simple 3-amino-1-azacycles shown in Figure 3.5, which are readily available in their enantiopure forms. The resulting complexes of these azacycles will inevitably be stereogenic-at-metal, and with the chiral configuration of the azacycle ligands being pre-ordained, there is a reasonable expectation to observe a level of diastereomeric selectivity upon ligand coordination. The degree of this selectivity would depend on factors such as ring size, steric interactions with the auxiliary polyhapto ligands, and the conformational preferences of the diamine ligands.



(*S*)-pyrrolidin-3-amine
L1

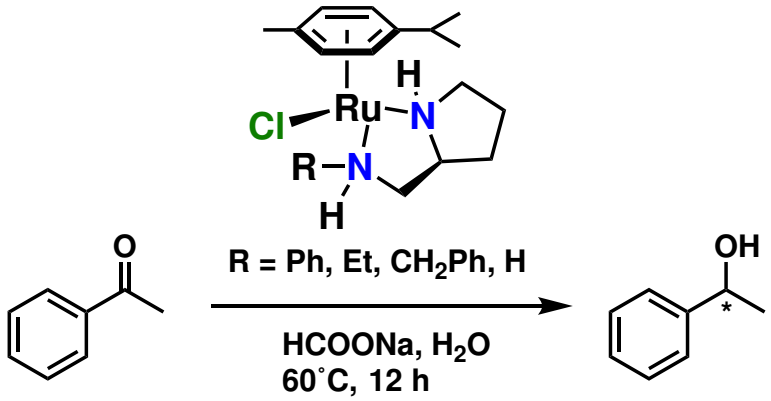
(*R*)-piperidin-3-amine
L2

(*R*)-azepan-3-amine
L3

Figure 3.5: Structures of 3-amino-1-azacycles as potential ligands for stereogenic-at-metal complexes.

The closest example of complexes using ligands similar to those shown in Figure 3.5 seems to be a 2016 report by Kumar and Samuelson of a series

of ruthenium half-sandwich complexes using L-Proline and derivatives as ligands (Scheme 3.1.[55] They report the single-crystal XRD structures of some of their complexes, commenting that these have been isolated as single diastereomers. Their catalysts are able to facilitate transfer hydrogenation in water using sodium formate as a hydrogen source, with a scope encompassing various aromatic ketones. The yields reported range from poor to quantitative, with the complex bearing the *N2*-substituted L-Proline ligand effecting the highest conversion in most cases. The conditions employed in their reactions are mild at 60 °C and 12 h reaction times, however, the 10 mol% catalyst loading employed is high compared to other examples in the literature. Varying enantioselectivities are also reported, with one of the substrate/catalyst combinations showing an *e.e.* of 96%.



Scheme 3.1: Ruthenium half-sandwich complexes using L-Proline-derived ligands reported by Kumar and Samuelson for the transfer hydrogenation of aromatic ketones in water.[55]

3.2 Results and discussion

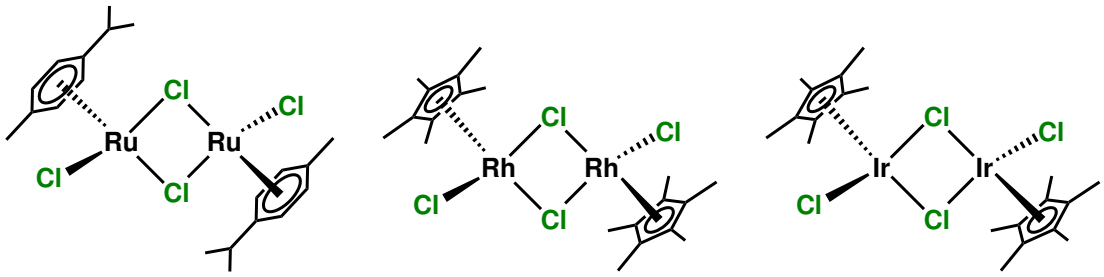
It was surprising that even though the azacycles mentioned above are commercially available, very few transition metal complexes containing these ligands have been reported. This is especially surprising given the vast literature on related chiral diamines. In line with the examples high-

lighted previously, we sought to make half-sandwich Ru(II), Rh(III) and Ir(III) complexes with all three ligands to explore their potential in transfer hydrogenation catalysis. It was expected that these complexes would potentially facilitate asymmetric transfer hydrogenation reactions. Exploring the effects (if any) of azacycle ring expansion was also a topic of interest.

3.2.1 Synthesis of complexes

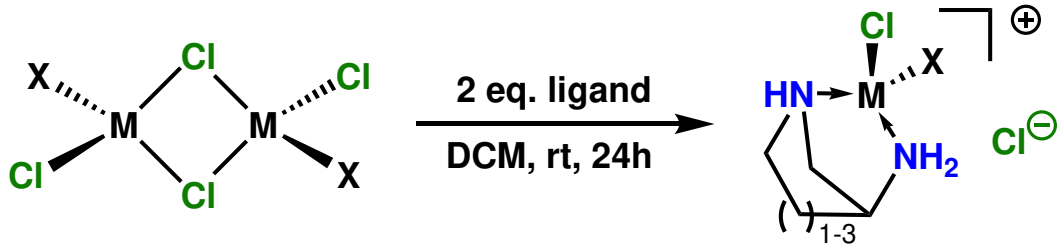
To that end, the enantiopure 3-amino-substituted-N-azacycle ligands were purchased - namely, (*S*)-pyrrolidin-3-amine (**L1**), (*R*)-piperidin-3-amine (L2), and (*R*)-azepan-3-amine (**L3**), as shown in Figure 3.5 above. The corresponding Ru(II), Rh(III), and Ir(III) complexes of those ligands were afforded in a straightforward manner by stirring the corresponding dimeric $[(\text{cycle})MCl_2]_2$ species (cycle = η^6-*p*-cymene for Ru and η^5-1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) for Rh and Ir), shown in Figure 3.6, and the relevant ligand in 1:2 molar ratio, in dichloromethane, at room temperature. This is demonstrated in Scheme 3.2. The reactions with the **Rh Cp* dimer** and the **Ir Cp* dimer** proceed with an observable colour change whereby the solution changed to a lighter colour - red to orange for Rh, and orange to yellow for Ir. This chemical transformation is immediately noticeable. In contrast, when **Ru cymene dimer** was used, there was a slower transition from red to amber, and, upon inspection after 23 hours, a dark brown solution was observed. Photos of the reactions after ligand addition and after 23 hours are shown in Figure 3.7. The resulting complexes were isolated in practically quantitative yields as orange (Rh)/yellow (Ir)/brown (Ru) solids after removal of the volatiles *in vacuo*. In the case of the Ru complexes, these were observed to be somewhat hygroscopic, especially when **L3** was used. All complexes were expected to be and were treated as air

and moisture-stable. This stability was then confirmed when exchanging the chloride for a hexafluorophosphate anion to grow crystals suitable for single-crystal X-ray diffraction (SC-XRD), which involved dissolution in a water/methanol mixture (discussed later in section 3.2.8). The purity of the complexes was assessed by ^{1}H NMR spectroscopy, which did not show detectable levels of the starting materials. Furthermore, high-resolution mass spectrometry (HRMS) revealed the presence of the expected $[M\text{-}Cl]_{+}$ ions. Single-crystal X-ray diffraction (SC-XRD) studies were also performed on crystals grown for the hexafluorophosphate derivatives of **Rh-2**, **Ru-2**, and **Ru-7** (discussed in section 3.2.8).



"Ru cymene dimer" **"Rh Cp* dimer"** **"Ir Cp* dimer"**

Figure 3.6: Metal dimer precursors used in the synthesis of the complexes



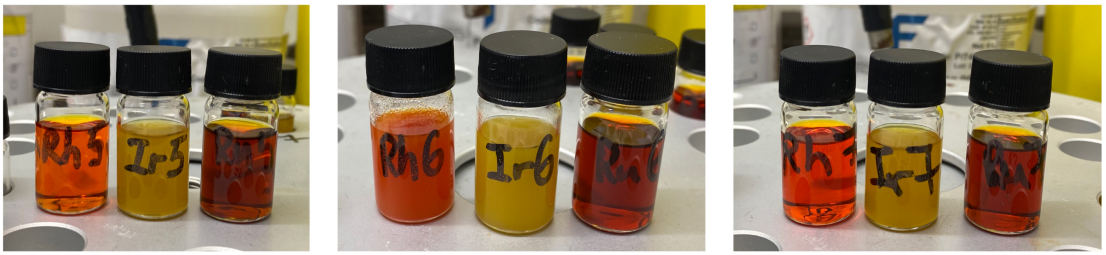
M: Ru(II), Rh(III) or Ir(III)
X: Cp* (Rh, Ir) or p-cymene (Ru)

1: L1 ***2: L2*** ***3: L3***

Ru / L1: **[Ru-1]Cl**	Rh / L1: **[Rh-1]Cl**	Ir / L1: **[Ir-1]Cl**
Ru / L2: **[Ru-2]Cl**	Rh / L2: **[Rh-2]Cl**	Ir / L2: **[Ir-2]Cl**
Ru / L3: **[Ru-3]Cl**	Rh / L3: **[Rh-3]Cl**	Ir / L3: **[Ir-3]Cl**

Scheme 3.2: Synthesis of novel complexes with cyclic diamine ligands

After ligand addition:



After 23 h:

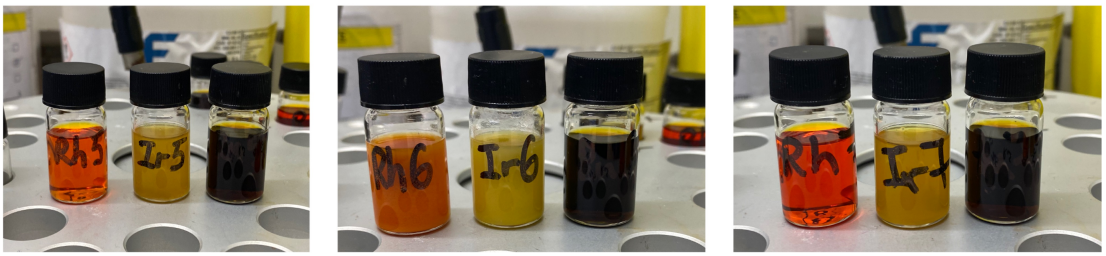


Figure 3.7: Photos of reaction mixtures after ligand addition and after 23 hours. Each photo features three different metal precursors with the same ligand - from left to right: **L1**, **L2**, **L3**. Metal precursors in the vials on each photo from left to right: $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$, $[(\eta^5\text{-}C_5H_5)IrCl_2]_2$, $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$.

Note on atom numbering: For the purposes of the discussion in the subsequent subsections, the following designations are used:

- N1 - the nitrogen atom contained within the ligand's ring.
- C3 - the amino-substituted carbon atom.
- N3 - the amino group at C3.

3.2.2 NMR studies of the complexes

All complexes were subjected to ^{1}H NMR and $^{13}C\{^1H\}$ NMR analysis. As highlighted earlier, the ^{1}H NMR spectra of **[Rh-2]Cl/[Rh-3]Cl**, **[Ru-2]Cl/[Ru-3]Cl**, and **[Ir-2]Cl/[Ir-3]Cl** indicated the presence of a single species which was evident by the presence of a single Cp* signal (in the case of the Rh and Ir) or a single set of signals for the *p*-cymene (in the case of Ru), as well as single set of magnetically inequivalent signals for the diamine ligand. In

the case of the complexes where the **L3** ligand was used, two sets of signals were observed, with approximately 45:55, 65:35, 65:35 *d.r.* (diastereomeric ratio) for Rh, Ir, Ru, respectively. NOESY spectra showed the presence (or lack of) certain through-space interactions between the protons on the pyrrolidine and the Cp* / *p*-cymene. Although complete assignments were not possible for all complexes, selected assigned ^{1}H NMR spectra are presented in Figure 3.8 and Figure 3.9.

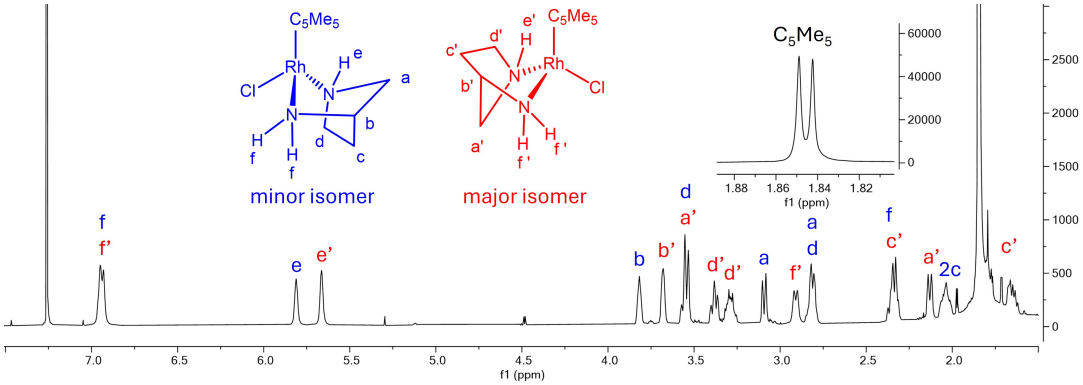


Figure 3.8: Assigned 500 MHz ^{1}H NMR spectra of **Rh-1** recorded in $CDCl_3$.

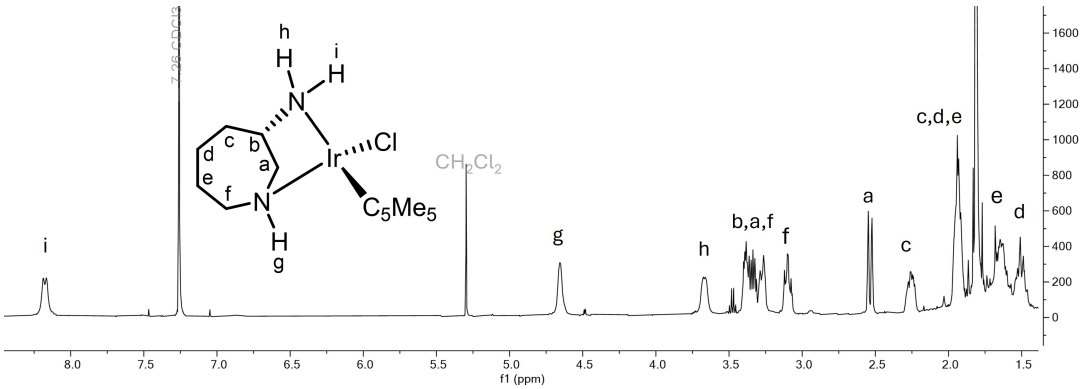


Figure 3.9: Assigned 500 MHz ^{1}H NMR spectra of **Ir-3** recorded in $CDCl_3$.

3.2.3 Diastereomers of resulting complexes and effect of ring size on stereoselectivity

Upon coordination, three chiral centres exist in the cation of each complex - the metal centre, the ring nitrogen atom (N1), and the carbon bearing

the NH_2 group (C3). For bidentate coordination to be possible, both the NH_2 group at the C3 position and the lone pair of the N1 atom must be in axial positions. The chirality at the C3 position is pre-determined due to the use of enantiopure ligands. In addition, as the coordination to the metal centre is what generates the chirality at the N1 position, and coordination happens *via* the lone pair, which must be axial, the chirality at that position is also pre-ordained. Considering the above, the only site at which chirality could differ is the metal centre. The latter's configuration is determined by the orientation in which the ligand is coordinated. Two different ways of coordination can be envisaged, and thus two distinct configurations at the metal centre are possible. Therefore, the resulting two complexes are diastereomers (they could also be considered epimers, as they differ in the absolute configuration of only one of at least two stereocentres[1]). This is illustrated in Figure 3.10, using **[Rh-2]$^+$** as an example.

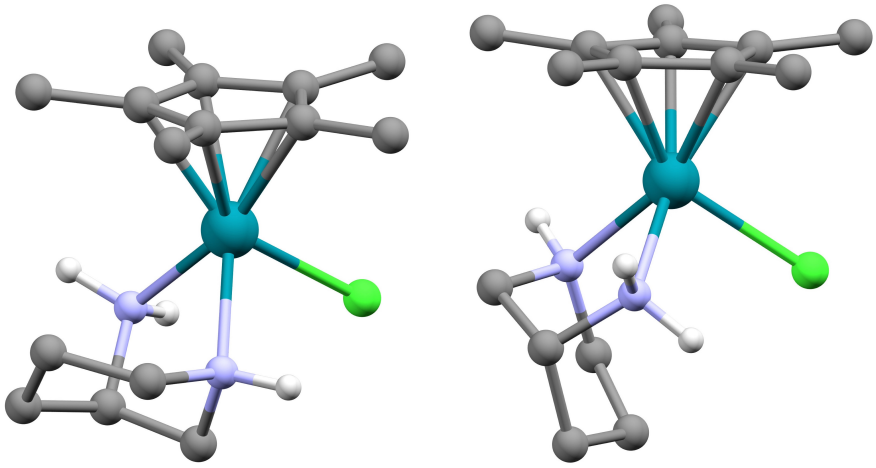


Figure 3.10: The two possible diastereomers of **[Rh-2]$^+$** - R_C,S_N,S_{Rh} (left) and R_C,S_N,R_{Rh} (right). The structures were taken from the results of the calculations described in section 3.2.9.1. Calculated using Orca 5.0.3[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(DCM)[130,131]//r2SCAN-3c[132–137]/CPCM(DCM)[130,131]/298.15 K level of theory.

Based solely on thermodynamic considerations, one could expect that increasing the azacycle ring size of the ligand will induce steric changes in the resulting complex, and potentially lead to one stereoisomer being pre-

ferred. As far as the complexes discussed in this chapter are concerned, the driving force for stereoselective coordination was expected to be from the unfavourable steric interaction between the cyclic polyhapto ligands and the $(CH_2)_n$ backbone of the azacyles, increasing with ring size. However, this does not consider potential kinetic drivers for stereoselection.

As mentioned previously, ^{1}H NMR spectroscopy indicated the formation of a single species for all the complexes with **L2** and **L3**, whilst a diastereomeric mixture of two species was evident for the complexes where **L1** was used, indicating a lack of selectivity. Whilst it's not clear as to whether thermodynamics or kinetics are the driving factor in this case, further density functional theory (DFT) studies (discussed in section 3.2.9.1) and single-crystal X-ray diffraction (SC-XRD) studies (discussed in section 3.2.8) allowed for further insights into the diastereomeric preference.

3.2.4 Investigations on the activity of complexes towards transfer hydrogenation

To test the activity of the complexes towards transfer hydrogenation, a suitable substrate had to be selected. For this purpose, 4-fluoroacetophenone was chosen, due to the presence of a fluorine atom, thus enabling convenient monitoring of the reactions *via* ^{19}F NMR NMR spectroscopy. The effect of the substituent was considered, with literature showing that comparable results can be achieved with both unsubstituted and 4-halogen-substituted acetophenones using ruthenium half-sandwich complexes.[166,167] Initially, the **[Ru-2]Cl** complex was tested. Conditions were partially inspired by literature reports, where 2-propanol is employed as both the solvent and the hydrogen source.[33] The effect of base on the reaction was also evaluated by adding 5 equivalents of potassium

tert-butoxide. The results, presented in Table 3.1, show that the reactions proceed relatively slowly, requiring several days for full conversion at a temperature close to reflux. The presence of base seemed to be crucial for the reaction, with only negligible conversions obtained in its absence.

Catalyst (1 equiv.)	KO^tBu equiv.	Conversion (%)	Time (h)	TOF (s^{-1})
[Ru-2]Cl	5	22	22.75	2.7×10^{-4}
[Ru-2]Cl	None	3	22.75	4×10^{-5}
[Ru-2]Cl*	5	100	120	N/A

Table 3.1: Investigations on the activity of **[Ru-2]Cl** towards the transfer hydrogenation of 4-fluoroacetophenone in 2-propanol. T = 80 °C (* reflux); total volume (including substrate) = 5.1 cm^3; substrate equivalents = 100; substrate concentration = 0.20 $mol{\cdot}dm^{-3}$. Conversion determined by ^{19}F NMR spectroscopy. TOF not relevant for the last entry because no information is available as to the time at which the conversion reached 100%.

3.2.5 Effect of chloride abstraction using silver(I) salts

The effect of silver(I) salts as chloride abstraction agents was investigated, with the initial hypothesis that this would aid the reaction by activating the metal centre for substrate interaction. Two different silver(I) sources were considered – silver hexafluorophosphate, and silver tetrafluoroborate. Addition of either one, with or without the presence of base, did not increase the conversion beyond the 22% previously observed where no chloride abstraction agents were present. Furthermore, a modified version of the catalyst was also considered, whereby the **[Ru-2]Cl** complex was dissolved in acetonitrile, treated with 2 equivalents of silver hexafluorophosphate, left overnight, and then the resulting silver chloride filtered, and the solvent removed, in an attempt to extract both chlorides and potentially yield [Ru(η^6-*p*-cymene)(**L2**)(MeCN)][PF_6]$_2$. However, any such species appeared to be unstable, resulting in gradual darkening from yellow to dark green, poten-

tially indicating decomposition. They also displayed no significant activity as catalysts for transfer hydrogenation. A possible reason for the reduced reactivity when using silver(I) salts could be due to the reaction operating under a different mechanism in these conditions. This is because exchanging both the internal and external chlorides results in the formation of a doubly positively charged metal centre, whilst removing the chlorides using a base results in a neutral species.

Catalyst (1 equiv.)	KO^{t}Bu equiv.	Ag^+ equiv.	Conversion (%)	Time (h)	TOF (s^{-1})
[Ru-2]Cl	5	2 as PF_6^-	3	22.75	4×10^{-5}
[Ru-2]Cl	5	2 as BF_4^-	4	22.75	5×10^{-5}
[Ru-2]Cl	None	2 as PF_6^-	7	22.75	9×10^{-5}
[Ru-2]Cl	None	2 as BF_4^-	8	22.75	1×10^{-4}
[Ru-2]Cl*	5	None	5	22.75	6×10^{-5}
[Ru-2]Cl*	None	None	2	22.75	2×10^{-5}

Table 3.2: Effects of chloride abstraction on the activity of **[Ru-2]Cl** and [Ru(**L2**)(MeCN)][PF_6]$_2$ derivative towards the transfer hydrogenation of 4-fluoroacetophenone in 2-propanol. T = 80 °C; total volume (including substrate) = 5.1 cm^3; substrate equivalents = 100; substrate concentration = 0.20 mol·dm^{-3}; time = 22.75 h. Conversion determined by ^{19}F NMR spectroscopy. Reaction vessels were shielded from light during the reaction. *Modified species used by reacting **[Ru-2]Cl** with $AgPF_6$ and acetonitrile - [Ru(**L2**)(MeCN)][PF_6]$_2$.

3.2.6 Transfer hydrogenation reactions using optimised conditions

Using the results from the previous experiments, the standard conditions were selected as follows: 1/5/100 catalyst/base/substrate ratio, substrate concentration of 0.20 mol·dm^{-3} in 5 cm^3 of 2-propanol at reflux for approximately 68 hours. The lower time was selected (as opposed to the 5 days used before, see last entry from Table 3.1), to allow for any differences in activity to manifest as differences in conversion. The results of

these reactions are presented in Table 3.3 and indicate that all the complexes synthesised perform relatively well for the transfer hydrogenation of 4-fluoroacetophenone. Overall, the iridium complexes perform slightly better than the rest, followed by the ruthenium, and finally the rhodium complexes. Although the differences in conversion are non-negligible, they are relatively minor and could be attributed to experimental errors such as small differences in the purity of the complexes and those from weighing out mg-scale amounts, where small inaccuracies can propagate. The reaction mixtures were tested for the presence of any enantioselectivity of the resulting alcohol. To this end, chiral HPLC was employed, using the Chiralpak IF column with silica-supported amylose stationary phase and hexane/2-propanol mixture as the mobile phase as these conditions have been used before by other researchers in the department. Unfortunately, as shown in Table 3.3, all samples tested were shown to be racemic, with enantiomeric excess values of <2.0 %. An example chiral HPLC chromatogram for the reaction using the **[Ru-2]Cl** complex is shown in Figure 3.11, with peaks at 7.388 min and 8.085 min corresponding to the two enantiomers of 4-fluorophenylmethanol (1.8% *e.e.*, assignment not possible). The chromatograms for the rest of the reactions from 3.3 were visually similar and thus not presented individually.

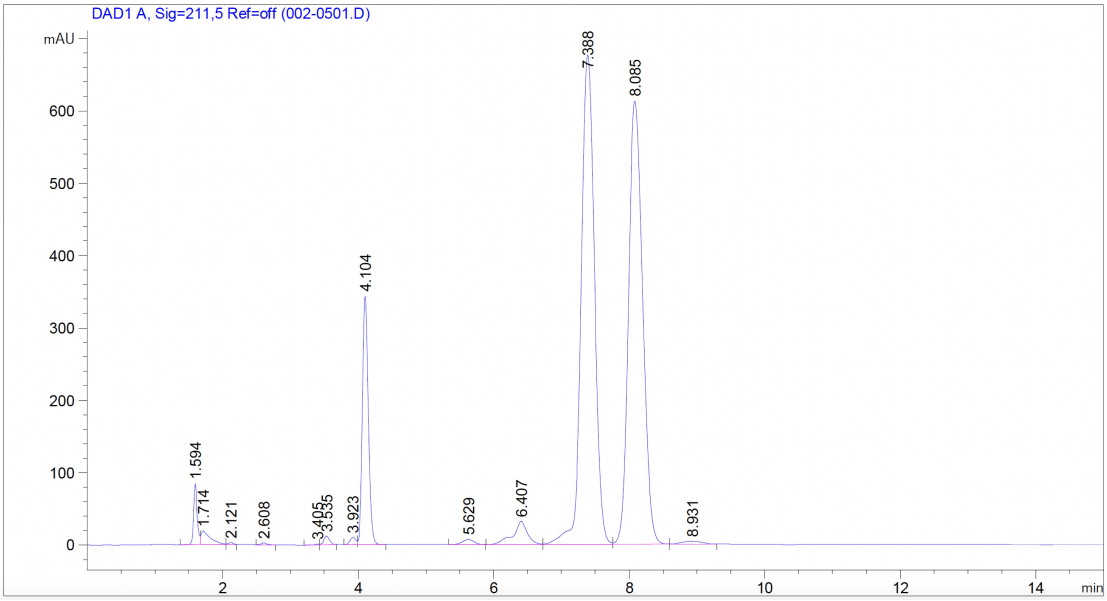


Figure 3.11: Example of a HPLC plot of the 4-fluorophenylmethanol from transfer hydrogenation of 4-fluoroacetophenone by **[Ru-2]Cl**. Chiralpak IF column used with 5.000 µl injection volume eluted with 99:1 Hexane:2-propanol at 2.0 cm^3/min flow rate and detection at 211 nm. The sample was filtered through a 0.2 µm PTFE filter followed by a plug of alumina prior to analysis. The peaks at 7.388 min and 8.085 min are the two enantiomers of 4-fluorophenylmethanol (1.8% *e.e.*, assignment not possible).

Catalyst	Conversion (%)	TOF (s^{-1})	e.e. (%)
[Rh-1]Cl	98	4.0×10^{-4}	1.8
[Rh-2]Cl	89	3.6×10^{-4}	0.5
[Rh-3]Cl	95	3.9×10^{-4}	1.6
[Ir-1]Cl	98	4.0×10^{-4}	0.4
[Ir-2]Cl	97	4.0×10^{-4}	0.2
[Ir-3]Cl	97	4.0×10^{-4}	0.3
[Ru-1]Cl	90	3.7×10^{-4}	0.6
[Ru-2]Cl	90	3.7×10^{-4}	1.8
[Ru-3]Cl	94	3.8×10^{-4}	0.3

Table 3.3: Results for the transfer hydrogenation of 4-fluoroacetophenone in 2-propanol using various catalysts (1 equiv.); T = reflux; KO^{t}Bu equivalents = 5; substrate equivalents = 100; substrate concentration = 0.2 mol·dm^{-3}; total volume (including substrate) = 5.1 cm-3; time = 68 h. Conversion determined by ^{19}F NMR spectroscopy. Enantiomeric excess determined by chiral HPLC: Chiralpak IF column, 5.000 µl injection volume, 99:1 Hexane:2-propanol, 2.0 cm^3/min, 211 nm detection, sample filtered through a 0.2 µm PTFE filter, followed by a plug of alumina prior to analysis.

3.2.7 Other reactions and complexes investigated

So far, only 2-propanol was considered as a hydrogen source. The results indicate that this is feasible, however, it does require reflux conditions for an extended period. To that end, sodium formate and sodium formate/formic acid mixtures were investigated as potential alternatives, whilst also employing milder conditions. Using **[Rh-2]Cl** in 2-propanol with sodium formate as the hydrogen source at 40 °C led to no observable conversion of the 4-fluoroacetophenone in the $^{19}F\{^{1}H\}$ NMR spectrum. Use of 1:1 water:DMF at the same conditions was also attempted, which similarly led to no conversion to the corresponding alcohol. Attempting the reaction in sodium formate / formic acid aqueous mixture at 60 °C for 2h was also unsuccessful. In an attempt to impart stereoselectivity into the transfer hydrogenation reaction, 2 further complexes were investigated. These are shown in Figure 3.12 A number of further reactions were attempted using these complexes.

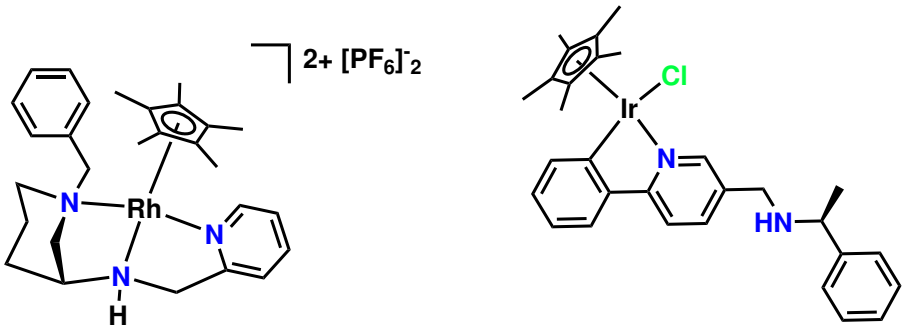
It was anticipated that the **[Rh-4][PF_6]$_2$** complex would not be viable, considering the computational investigations (see later), both due to lack of a vacant coordination site and the only available deprotonation site being constrained within the azacyclic ring. Therefore, in order for catalysis to occur, the pendant pyridyl must decoordinate. It was predicted that this would considerably slow the reaction or halt reactivity altogether. However, one could also imagine the opposite, where the decoordination of the pyridyl is rapid, potentially resulting in faster catalysis. To that end, the reaction was performed at the lower temperature of 50°C , using 1 equiv. of the complex, with 5 equiv. KO^{t}Bu and 100 equiv. (1 mmol) of 4-fluoroacetophenone in 3 cm^3 2-propanol. Upon addition of base, the reaction mixture transitioned from a yellow suspension to a dark brown solution. Approximately 4% con-

version was observed in the ^{19}F NMR spectrum after 2h, 18% after about 19 hours, 26% after 2 days, and 31% after 3 days. This is considerably slower than the reaction rate observed during the investigations with the non-substituted azacycle variants.

Literature reports showed that complexes similar to **Ir-5** have been successfully used in aqueous and buffer solutions.[54] The respective ligand for this complex was already available in the research group, however, initial attempts to synthesise the complex showed this to be impure as per ^{1}H NMR analysis. However, preliminary reactions were conducted to assess its potential utility. An aqueous solution of 3.17 M formic acid / 1.77 M sodium formate was prepared, resulting in a pH 3.5 buffer. This was then used as a solvent/hydrogen donor with the **Ir-5** complex. As seen in Table 3.4, 0.5 equivalents of the complex were sufficient to effect full conversion. Similar reaction with the **[Rh-4][PF_6]$_2$** complex resulted in only 3.8% conversion. Regrettably, after isolating the product from the first reaction shown in the table and subjecting this to chiral HPLC analysis, only 0.6% *e.e.* was observed. Further use of [Cp*Ir(phenylpyridine)Cl], which is essentially a simpler version of the **Ir-5** complex containing unsubstituted phenylpyridine, revealed that it can also afford full conversion under the same conditions. However, stereoselectivity in that case is not expected due to the lack of stereodirecting features.

Ir-5 equiv.	Buffer volume	H_2O added	Conversion(%)
1	2 cm^3	None	100%
0.5	1 cm^3	None	100%
0.5	1 cm^3	1 cm^3	100%

Table 3.4: Investigations on the activity of **Ir-5** towards the transfer hydrogenation of 4-fluoroacetophenone using 3.5 pH formate buffer as solvent / hydrogen donor. T = 60 °C; substrate equivalents = 100. Conversion determined by $^{19}F\{^{1}H\}$ NMR spectroscopy.



[Rh-4][PF$_6$]$_2$ Ir-5

Figure 3.12: Structures of **[Rh-4][PF$_6$]$_2$** and **Ir-5.**

3.2.8 Single-crystal X-ray diffraction studies

In order to elucidate the preferred diastereomers, crystals suitable for single-crystal X-Ray diffraction (SC-XRD) analysis were grown by exchanging the chloride anion from **[Rh-2]Cl**, **[Ru-2]Cl**, **[Ru-3]Cl** for hexafluorophosphate. The hexafluorophosphate salts were generated *in situ* by dissolving a mixture of the respective chloride complex and an excess of sodium hexafluorophosphate in a mixture of methanol and water. This resulted in a substitution of the external chloride counterion by a hexafluorophosphate. The salts of the latter generally exhibit poor solubility in water. Therefore, due to the differences in the volatility of the two solvents, subjecting the samples to slow evaporation resulted in a gradual decrease of the methanol component and yielded crystals of the corresponding hexafluorophosphate salts, which were subjected to single-crystal X-ray diffraction analysis. Using the same approach, crystals of **[Rh-4][PF$_6$]$_2$** were also grown, but the first step of anion exchange was performed at the time of synthesis, with the chloride salt not isolated.

All complexes crystallised in the orthorhombic $P2_12_12_1$ space group. The resulting structures are shown in 3.14 and allowed for the absolute configuration at the metal to be determined as *S*, as per standard Cahn–Ingold–Prelog rules, similar to a carbon stereocentre, as demon-

strated on Figure 3.13. The lowest priority is given to the polyhapto ligand, which only features carbons (Z=6). Highest priority is chlorine (Z=17). The priorities of the two nitrogen-containing substituents are assigned based on the atoms bonded to them, with the ring nitrogen, having two carbons attached, and therefore assigned priority 2, whilst the NH_2 group is assigned priority 3, as it only has one carbon attached. A summary of key crystal structure data parameters is presented in Table 3.6, and selected bond lengths are presented in Table 3.5.

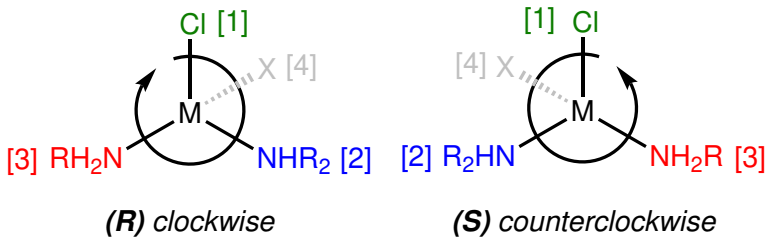
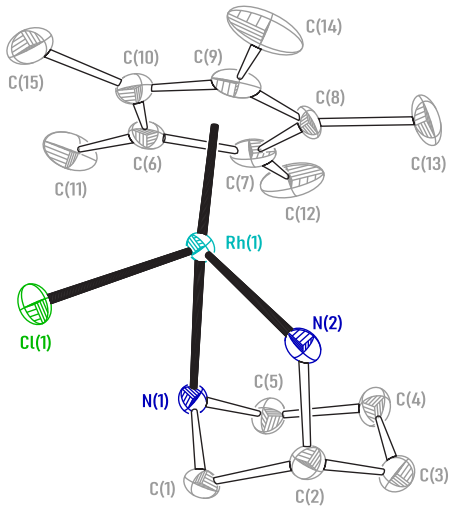


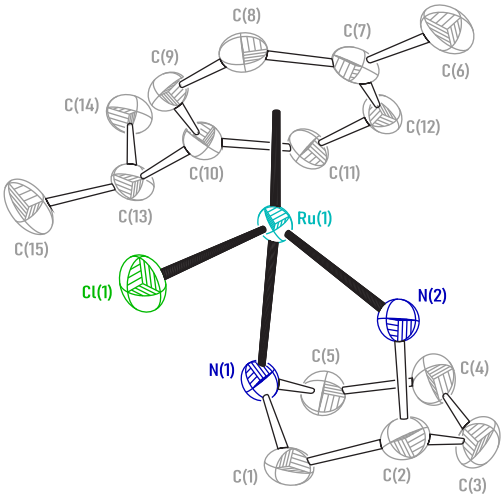
Figure 3.13: Chirality assignment of the metal centre using standard Cahn–Ingold–Prelog rules. The numbers in brackets indicate the priority of the substituent. X = polyhapto ligand (Cp*, or *p*-cymene).

Bond	[Rh-2][PF_6]	[Ru-2][PF_6]	[Ru-3][PF_6]	[Rh-4][PF_6]$_2$
M-(cycle*)	1.794(3)	1.6632(19)	1.685(3)	1.811(3)
M-Cl	2.4352(14)	2.3950(15)	2.4309(18)	N/A
M-N(ring)	2.175(5)	2.173(4)	2.159(7)	2.201(4)
M-N(C3)	2.168(5)	2.144(4)	2.128(6)	2.160(4)
M-Py	N/A	N/A	N/A	2.108(4)

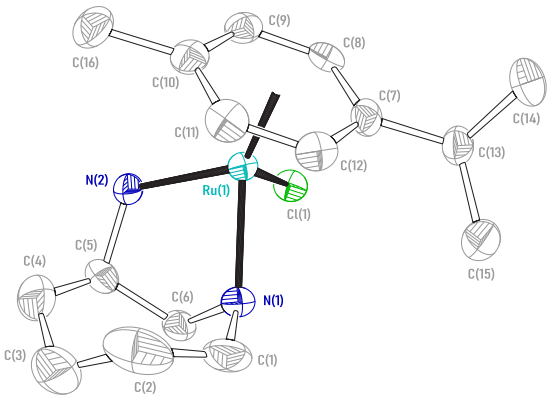
Table 3.5: Selected bond lengths measured from the refined SC-XRD structures of **[Rh-2][PF_6]**, **[Ru-2][PF_6]**, **[Ru-3][PF_6]**, and **[Rh-4][PF_6]$_2$** quoted in Å. *Cycle = η^6-*p*-cymene for Ru and η^5-1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) for Rh, with M-(cycle) distance being the distance from the metal to the centroid of the ring in the respective cycles. More detailed information is available in the Appendix.



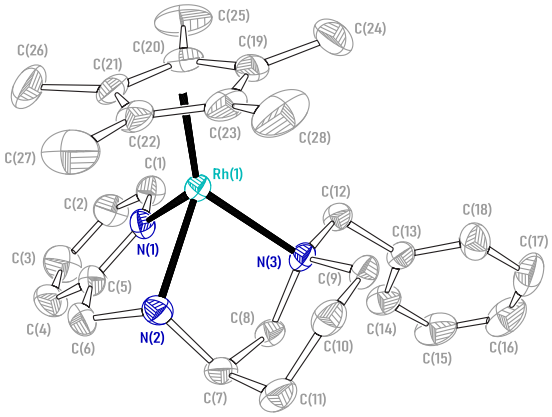
(a) [Rh-2][PF_6]



(b) [Ru-2][PF_6]



(c) [Ru-3][PF_6]



(d) [Rh-4][PF_6]$_2$

Figure 3.14: Thermal ellipsoids of the hexafluorophosphate salts of selected complexes (chloride from original compounds exchanged for PF_6^-), shown at the 30% probability level. PF_6^- anion and hydrogen atoms have been omitted for clarity. The structures for **[Ru-2][PF_6]** and **[Rh-4][PF_6]$_2$** were solved and refined by Dr Benson Kariuki. Note that due to the difference in figure sizes, the sizes of the ellipsoids are not comparable between structures.

Parameter	[Rh-2][PF_6]	[Ru-2][PF_6]	[Ru-3][PF_6]	[Rh-4][PF_6]$_2$
Empirical formula	$C_{15}H_{28}ClF_6N_2PRh$	$C_{15}H_{26}N_2ClRuPF_6$	$C_{16}H_{28}ClF_6N_2PRu$	$C_{28}H_{38}N_3F_{12}P_2Rh$
Formula weight/g·mol^{-1}	518.71	515.87	529.89	809.46
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.5623(2)	10.3999(4)	8.5419(2)	11.4970(3)
b/Å	10.1669(2)	11.5477(5)	11.5358(3)	13.7928(3)
c/Å	22.7249(5)	16.4273(8)	21.8557(7)	21.0676(6)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
V/Å^3	1978.25(7)	1972.84(15)	2153.61(10)	3340.81(15)
Z	4	4	4	4
T/K	180.00(10)	296(2)	298.15	293(2)
Radiation	μ(CuKα) = 9.528 mm^{-1}	μ(MoKα) = 1.067 mm^{-1}	μ(CuKα) = 8.249 mm^{-1}	μ(CuKα) = 5.878 mm^{-1}
ρ_{calc}/g·cm^{-3}	1.742	1.737	1.634	1.609
Reflections collected	7190 (7.78°≤2Θ≤145.692°)	17082 (7.058°≤2Θ≤59.764°)	7960 (8.09°≤2Θ≤145.864°)	12592 (7.662°≤2Θ≤145.81°)
Independent reflections	3841 (R_{int} = 0.0365, R_σ = 0.0400)	4991 (R_{int} = 0.0333, R_σ = 0.0375)	4164 (R_{int} = 0.0351, R_σ = 0.0444)	6497 (R_{int} = 0.0290, R_σ = 0.0401)
Final R_1	0.0345 (I≥2σ(I))	0.0327 (I≥2σ(I))	0.0438 (I≥2σ(I))	0.0312 (I≥2σ(I))
Final wR_2	0.0917 (all data)	0.0665 (all data)	0.1103 (all data)	0.0820 (all data)

Table 3.6: Summary of key crystal structure data for **[Rh-2][PF_6]**, **[Ru-2][PF_6]**, **[Ru-3][PF_6]**, and **[Rh-4][PF_6]$_2$**. More detailed information is available in the Appendix.

[Rh-2][PF_6] crystallised as orange blocks. The azacyclic ring of the ligand was found to be in the chair conformation with the 3-amino group adopting the axial position, as required for bidentate coordination. The hydrogen on the secondary nitrogen of the ring is in the equatorial position with an axially projecting N-Rh bond. It is noteworthy that the $(CH_2)_3$ bridge of the diamine projects towards the methyl groups of the Cp* rather than the chloride ligand as would occur in the other diastereomer (*cf* Figure 3.17).

[Ru-2][PF_6] crystallised as needles. The chair conformation and respective positions of the substituents are as for the Rh complex discussed above. The cymene moiety is positioned in such a way that the carbon bearing the methyl group is roughly above the NH_2 substituent of the ligand, and the one with the isopropyl group is roughly above the ring nitrogen of the azacycle ligand. Looking down the C_2 symmetry axis that goes through the two substituted positions of the aromatic ring, one can observe that the proton of the isopropyl group is positioned in the direction of the ligand, whilst one of the methyl groups is positioned towards the chloride, with the other methyl group pointing away from the plane of the aromatic ring.

[Ru-3][PF_6] crystallised as yellow blocks. In contrast to **[Ru-2][PF_6]**, looking down the C_2 symmetry axis that goes through the two substituted positions of the aromatic ring shows that methyl-substituted carbon of the cymene ligand is roughly positioned above the NH_2 group, whilst one of the carbons ortho to the isopropyl group is positioned roughly above the ring nitrogen atom of the azacycle ligand. Furthermore, another difference from **[Ru-2][PF_6]** is that the proton of the isopropyl group points towards the chloride, with one of the methyl groups pointing towards the ligand, whilst the other methyl group still projects away from the plane of the aromatic ring. The 7-membered azacycle ligand adopts a twist-boat conformation with the 3-amino group similarly axially orientated as seen with the

structures discussed above, with the proton on the ring nitrogen atom still orientated equatorially.

[Rh-4][PF_6]$_2$ crystallised as yellow needles. The conformation of the azacylic ring adopts a chair conformation, in line with that observed for the **[Rh-2][PF_6]** and **[Ru-2][PF_6]** complexes. The benzyl group on the N3 atom projects downwards with the CH_2 group orientated in the same direction as the Rh-N3 bond.

Analysis of the key bond lengths from Table 3.5 shows that in the case of **[Rh-2][PF_6]** and **[Ru-3][PF_6]**, the two M-N bonds are the same length within the respective complexes, whilst in the case of **[Ru-2][PF_6]** and **[Rh-4][PF_6]$_2$**, the M-N(ring) is longer than the M-N(C3-ring position) bond. Between complexes featuring the same metal, the two M-N(ring) bonds are the same between the respective Rh / Ru complexes, and the same holds for the M-N(C3-ring position) bonds. The M-Cl distance is the same between **[Rh-2][PF_6]** and **[Ru-3][PF_6]**, but shorter in **[Ru-2][PF_6]**. When considering the M-cycle distances, the distances from the metal to the centroid of the ring in the respective cycles were compared and reveal that these are the same in the two Rh complexes, but the distance is longer in **[Ru-3][PF_6]** than in **[Ru-2][PF_6]**.

In order to compare some of the key bond lengths from the structure discussed above to literature examples, a search of the Cambridge Structural Database[120] (CSD) was performed (version 5.46 Nov 2024, including Feb 2025 update).[120] A total of 9 searches were performed, as illustrated in Figure 3.15 and bond lengths extracted are presented in Table 3.7. The results reveal that only in the case of **[Rh-4][PF_6]$_2$** is the M-cycle distance in line with the average identified, whilst in the cases of both **[Rh-2][PF_6]** and **[Ru-2][PF_6]** this distance is shorter, and marginal in the case of **[Ru-3][PF_6]** (the maximum distance within 3σ is exactly the same as the average dis-

tance identified from the search). The M-Cl bond is longer than the average for both **[Rh-2][PF$_6$]** and **[Ru-3][PF$_6$]**, but shorter for **[Ru-2][PF$_6$]**. The Rh-Py bond from **[Rh-4][PF$_6$]$_2$** is statistically the same as the average identified from the search. In the case of both **[Rh-2][PF$_6$]** and **[Rh-4][PF$_6$]$_2$**, all the Rh-N bonds (excluding the Rh-Py bond) are longer than the averages from the search. For **[Ru-3][PF$_6$]**, both the Ru-N bonds are the same as the average length from Search 3.8, however, only the Ru-N(ring) bond is in line with the average from Search 3.9, whilst the other Ru-N bond is shorter. When **[Ru-2][PF$_6$]** is considered, the Rh-N(ring) bond is longer than the averages from both Search 3.8 and 3.9, whilst the Rh-N(C3-ring position) bond is in line with the average from Search 3.8 and marginal with respect to the average from Search 3.9 (the maximum distance within 3σ is exactly the same as the average distance identified from the search). It should, however, be noted that although some bonds are either longer or shorter than the averages identified in the CSD searches, all bonds are still in line with the minimum and maximum values identified from the searches.

Search	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9
Hits	3174	1161	57	28	849	4621	2777	207	86
Count	5464	1698	80	25	2327	6312	4395	287	122
Min	1.550	2.296	2.044	2.088	1.885	1.389	2.305	2.009	2.102
Max	1.998	2.533	2.214	2.238	2.341	1.896	2.697	2.303	2.236
Mean	1.810	2.407	2.130	2.140	2.119	1.694	2.413	2.145	2.156

Table 3.7: Bond lengths extracted from the CSD[120] searches from Figure 3.15. "Hits" is the number of unique database identifiers which match the fragments. "Count" is the total number of bonds identified, including multiple bonds from a single hit.

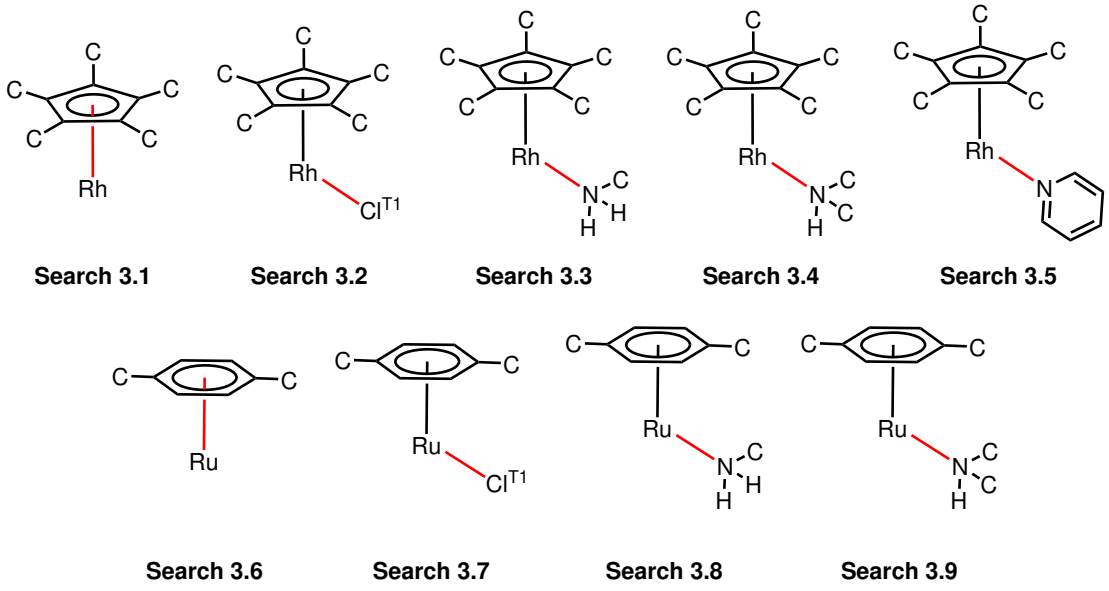


Figure 3.15: Searches of the CSD (version 5.46 Nov 2024, including Feb 2025 updates)[120] for fragments from **[Rh-1]$^+$**, **[Ru-1]$^+$**, **[Ru-2]$^+$**, and **[Rh-4]$^+$**. The number after "T" in the superscripts indicates the number of bonded atoms. X represents any atom. Bond lengths of interest are highlighted in red. The distance between the metal and the centroid of the polyhapto ligand was limited to a maximum of 2 Å in order to filter out intramolecular distances where the ligand is not directly bound to the metal. Any hits relating to the structures deposited to the CSD as part of the publication[141] arising from this work have been excluded. Results are presented in Table 3.7.

3.2.9 Computational studies

3.2.9.1 DFT studies on diastereomer selectivity

To gain some insight into this diastereomeric preference and to be able to quantify it, density functional theory (DFT) studies were performed on the relevant diastereomers, with the results presented in Figure 3.16. The resulting optimised structures for the different Rh, Ir, and Ru complexes are presented in Figure 3.17, Figure 3.18, and Figure 3.19, respectively, with selected distances highlighted.

The following assumptions were made:

- The ligand will adopt the most favourable ring configuration (*i.e.* envelope, chair, and twist-chair for **L1**, **L2**, and **L3**, respectively).
- The 3-NH_2 groups are in the axial positions (necessary for coordina-

tion).

- The proton on the ring nitrogen is in the axial position (necessary for coordination).

The resulting Gibbs free energies indicate a preference for the metal centre configuration, which aligns with that observed from the SC-XRD analysis. This energetic preference holds across the board for all complexes investigated. The energy preference is clear when the **L2** and **L3** ligands are concerned. This is especially true for Ru, where the energy difference is the highest of the three metals. A slight preference is also indicated for the **L1** ligand. However, this is much lower in comparison to **L2** and **L3**. Therefore, these data fully support the experimental observations.

To establish the reason for these preferences, we can examine the distances of the different atoms in the azacycles to other parts of the complex. We can see that the distances between the carbon backbone of the azacycles and the corresponding polyhapto ligands do not give a clear indication of preference for one configuration over the other. However, we can see that shorter C2-Cl distances are preferred for the complexes bearing the 6- and 7-membered azacycle ligands. This could likely be a favourable H-bond-type interaction between one of the protons at the C2 position and the chloride ligand. In addition, one could also consider the reduced number of orbital interactions between the carbon backbone of the azacycle and the chloride ligand.

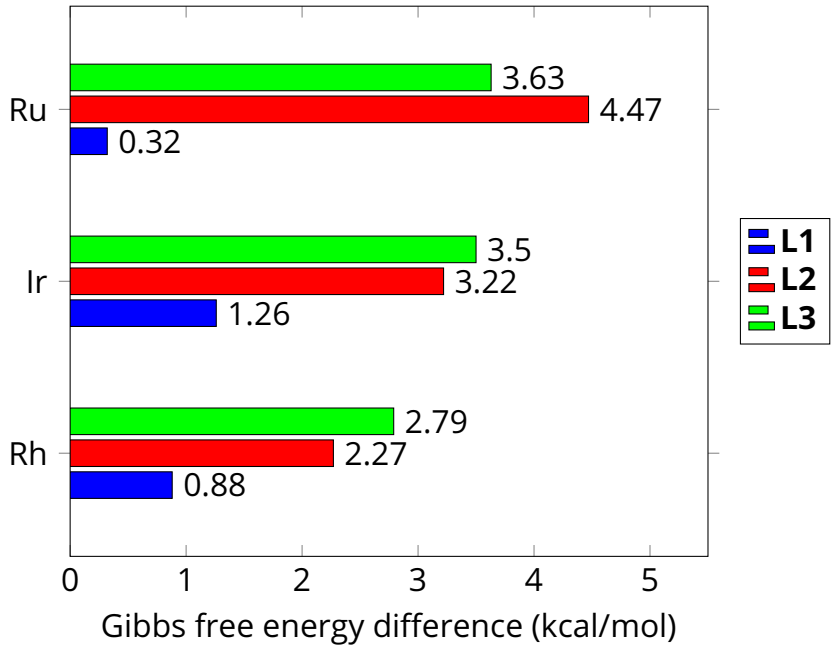
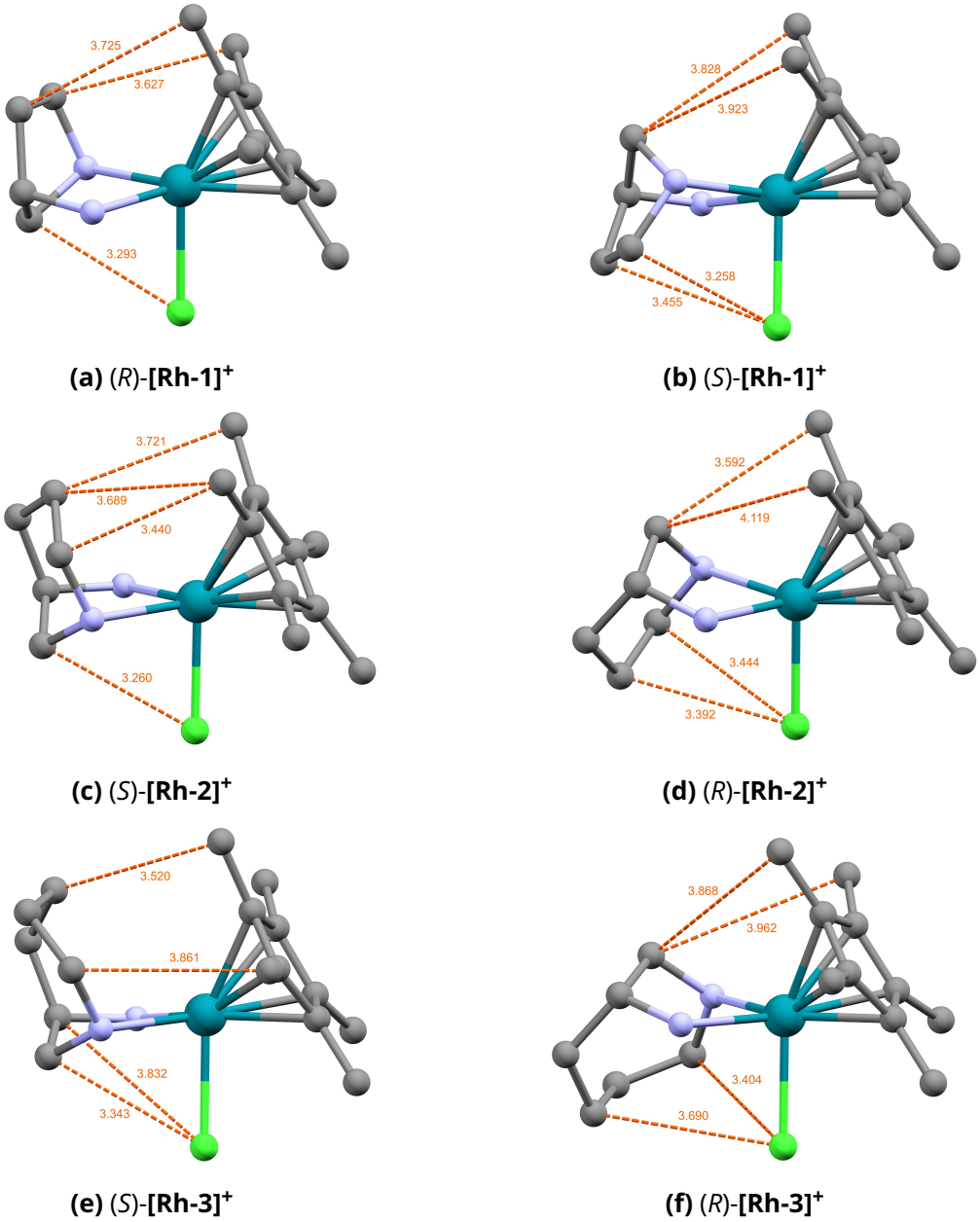


Figure 3.16: Gibbs free energy preference for the metal centre configuration to be the (*S*) for **L2** and **L3**, and (*R*) for **L1**. Calculated using Orca 5.0.3[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(DCM)[130,131]//r2SCAN-3c[132–137]/CPCM(DCM)[130,131]/298.15 K level of theory.

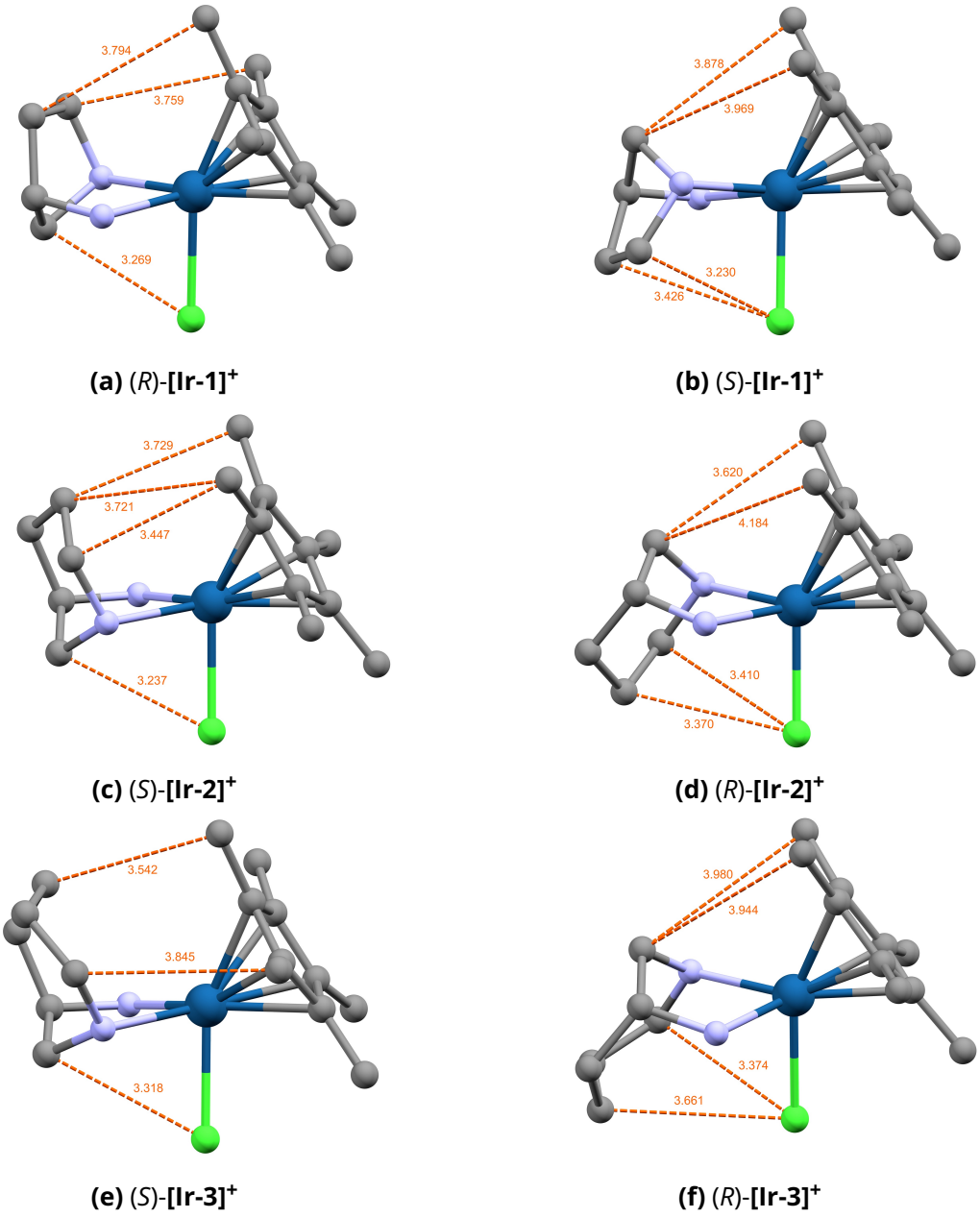


(a) (*R*)-**[Rh-1]$^+$** **(b)** (*S*)-**[Rh-1]$^+$**

(c) (*S*)-**[Rh-2]$^+$** **(d)** (*R*)-**[Rh-2]$^+$**

(e) (*S*)-**[Rh-3]$^+$** **(f)** (*R*)-**[Rh-3]$^+$**

Figure 3.17: Different diastereomers of the cationic part of the Rh complexes (DFT). Calculated using Orca 5.0.3[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(DCM)[130,131]//r2SCAN-3c[132–137]/CPCM(DCM)[130,131]/273.15 K level of theory.

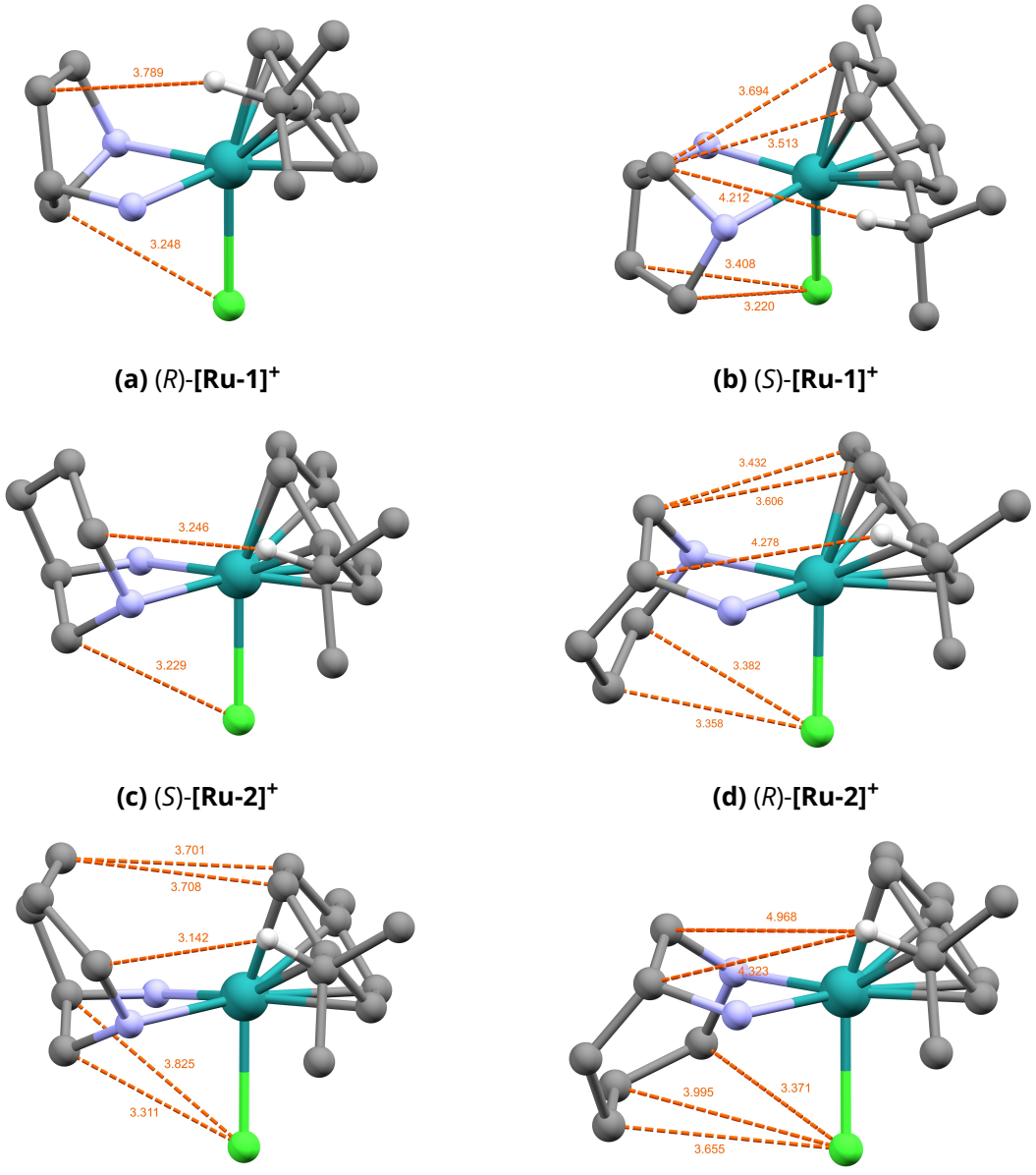


(a) (*R*)-**[Ir-1]**$^+$ **(b)** (*S*)-**[Ir-1]**$^+$

(c) (*S*)-**[Ir-2]**$^+$ **(d)** (*R*)-**[Ir-2]**$^+$

(e) (*S*)-**[Ir-3]**$^+$ **(f)** (*R*)-**[Ir-3]**$^+$

Figure 3.18: Different diastereomers of the cationic part of the Ir complexes (DFT). Calculated using Orca 5.0.3[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(DCM)[130,131]//r2SCAN-3c[132–137]/CPCM(DCM)[130,131]/273.15 K level of theory.



(a) (*R*)-**[Ru-1]$^+$** **(b)** (*S*)-**[Ru-1]$^+$**

(c) (*S*)-**[Ru-2]$^+$** **(d)** (*R*)-**[Ru-2]$^+$**

(e) (*S*)-**[Ru-3]$^+$** **(f)** (*R*)-**[Ru-3]$^+$**

Figure 3.19: Different diastereomers of the cationic part of the Ru complexes (DFT). Calculated using Orca 5.0.3[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(DCM)[130,131]//r2SCAN-3c[132–137]/CPCM(DCM)[130,131]/273.15 K level of theory.

3.2.9.2 DFT studies on the transfer hydrogenation of acetophenone in 2-propanol

DFT studies were performed on the catalytic cycles of both the **[Rh-2]Cl** and **[Ru-2]Cl** complexes, using acetophenone as a substrate. Partial DFT studies were performed for the **[Ir-2]Cl** complex, but the transition state determination was unsuccessful. The proposed mechanism is shown in Figure 3.20, with the relevant energies for the species for the **[Rh-2]Cl** and **[Ru-2]Cl** mechanisms presented in Table 3.8. An initial two-step deprotonation is hereby proposed, whereby each nitrogen atom is deprotonated, which should be feasible in light of the basic conditions used during laboratory experiments. The calculations indicate that there is little discrimination as to which of the atoms is deprotonated first, with a 0.45 and 0.68 kcal/mol preference for the first deprotonation to occur at the NH_2 group first, for Rh and Ru, respectively. The second deprotonation yields a neutral bis-amido species, which represents the active catalytic species. This is followed by the dehydrogenation of 2-propanol to yield acetone and a neutral hydride complex. The latter subsequently hydrogenates the acetophenone substrate to yield 1-phenylethanol and concomitantly regenerates the active catalyst. The mechanism proposed here is an outer-sphere mechanism and features metal-ligand cooperativity, with the substrate being transformed without directly binding to the metal, and with both the metal and ligand taking part in facilitating the hydrogen transfer.

Furthermore, the initial deprotonation of the pre-catalyst generates species akin to the one originally reported by Noyori, containing one amido and one amino moiety within an overall neutral complex.[64] In addition, the proposed bis-amido active catalytic species is also similar to the one isolated by Noyori, as it similarly features two Ru-N bonds of differing lengths.[168] The

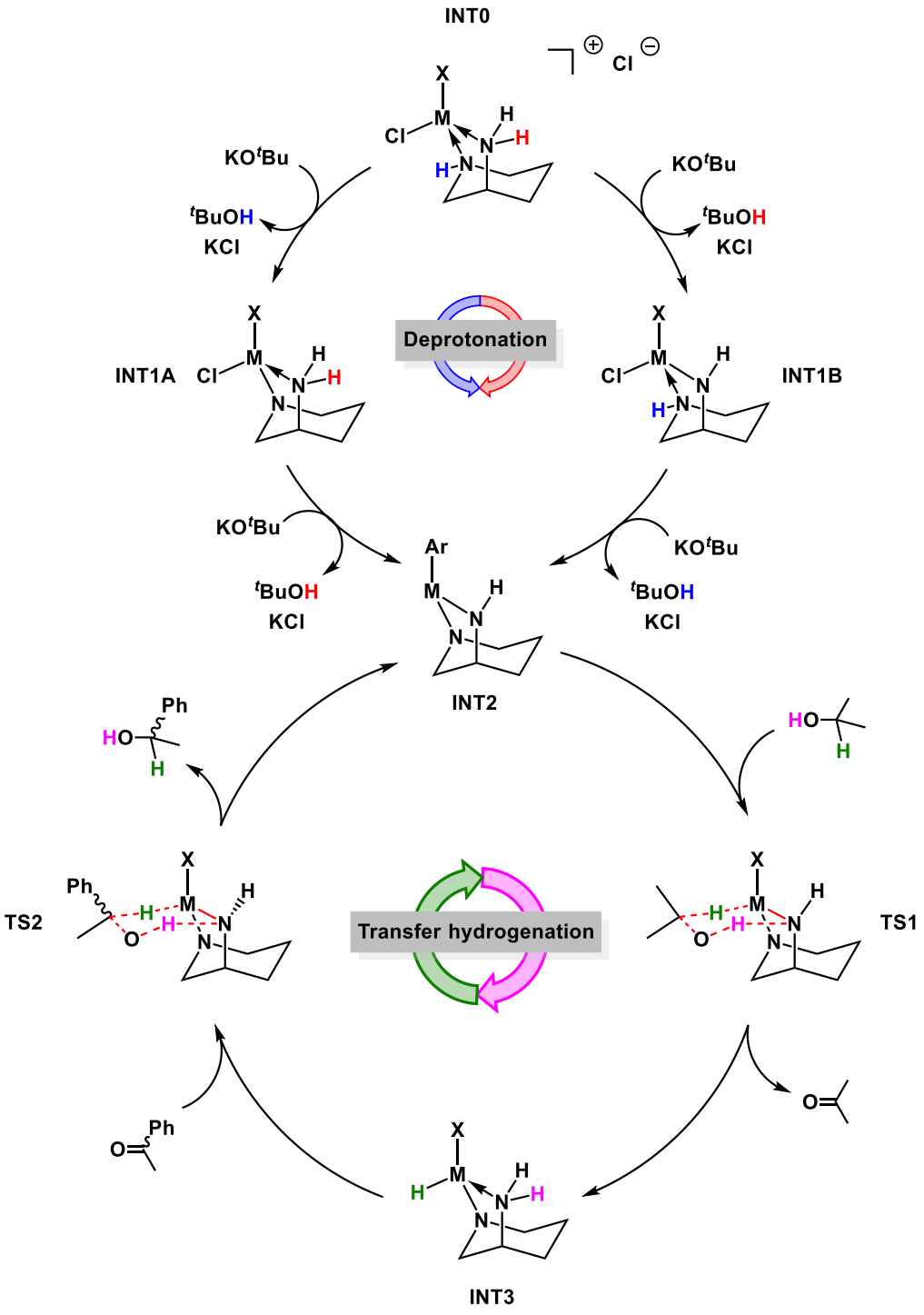


Figure 3.20: Proposed mechanism for the transfer hydrogenation of acetophenone catalysed by the M-2 complexes (M = Rh, Ru, Ir; X = η^6-*p*-cymene) for Ru and η^5-1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) for Rh and Ir). The energies for the **[Rh-2]Cl** and **[Ru-2]Cl** cycles are presented in Table 3.8.

Species	M = Rh	M = Ru
INT0	0.00	0.00
INT1A	-10.03	-10.18
INT1B	-10.48	-10.86
INT2 + 2-propanol	-25.01	-23.20
TS1	-8.99 (16.02)	-10.03 (13.17)
INT3	-37.28	-34.62
TS2 (pro-R)	-10.64 (26.64)	-12.09 (22.53)
TS2 (pro-S)	-8.17 (29.11)	-12.09 (22.53)
INT2 + R-product	-25.93	-24.11
INT2 + S-product	-25.93	-24.11

Table 3.8: Relative Gibbs free energies in kcal/mol for the species from the proposed mechanism for transfer hydrogenation of acetophenone using **[Rh-2]Cl** and **[Ru-2]Cl** catalysts as illustrated in Figure 3.20. Energies for transition state barriers are indicated in brackets. Calculated using Orca 5.0.4[121] at the ωB97M-V[122–125]/def2-QZVPP[126–128,165]/CPCM(ethanol)[130,131]//r2SCAN-3c[132–137]/CPCM(ethanol)[130,131] level of theory with thermochemistry performed at 353.15 K.

data from the calculations show that the Ru-N3 bond (1.926 Å) is shorter than the Ru-N1 bond (2.088 Å), a difference of 0.162 Å. This is similar to Noyori's species, which feature Ru-N bonds of 2.065 Å, and 1.897 Å, a difference of 0.168 Å, with the authors attributing the *"distinct dehydrogenative activity for methanol, ethanol, and 2-propanol"* to the shorter Ru-N distance results.[168] That is why the N3 atom is likely involved in the dehydrogenation/hydrogenation processes, due to the shorter Ru-N3 bond, and the fact that the N1 atom is geometrically constrained within the ring of the ligand.

Overall, the calculated Gibbs free energies and barriers are reasonable for the reaction conditions. In the case of Ru, the transition state barrier is slightly lower for the (*R*) isomer by 2.47 kcal/mol. However, this energy difference does not seem to be translated to experimental results, and it is likely that the reversibility of the reaction, along with the reflux conditions and long reaction time, leads to racemisation of the product.

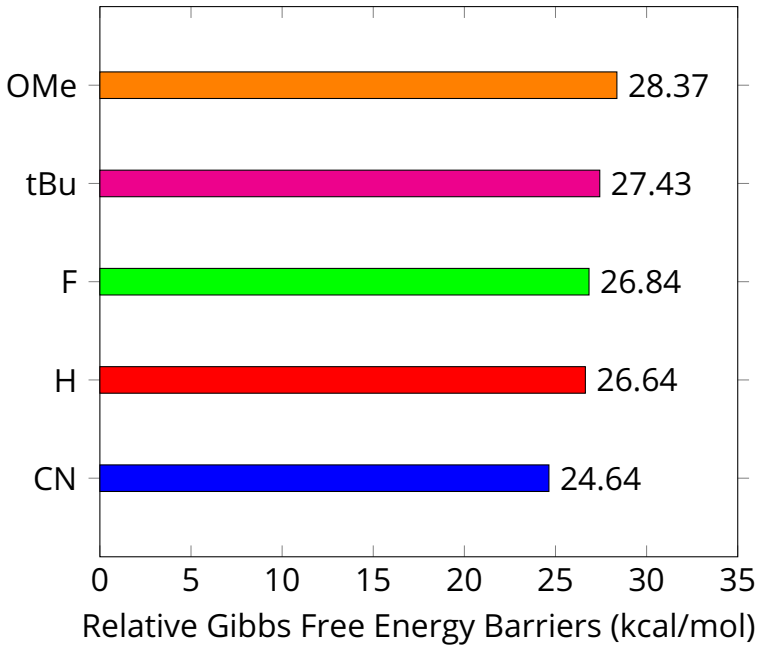


Figure 3.21: Energy barriers for the pro-R transition states for the transfer hydrogenation of unsubstituted and selected 4-substituted acetophenones. Calculated using Orca 5.0.4[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(ethanol)[130,131]//r2SCAN-3c[132–137]/CPCM(ethanol)[130,131]/353.15 K level of theory.

3.2.9.3 DFT studies of substituted acetophenones

The effects of substituents with different electronic effects were also investigated. To model this, the pro-R transition state from the catalytic cycle for **[Rh-2]Cl** was taken and modified to include 4-fluoro, 4-cyano, 4-methoxy, and 4-*tert*-butyl substituents on the acetophenone substrate. These new structures and those of the corresponding substituted acetophenones were then optimised and evaluated at the same level of theory. This allowed us to calculate the transition state energy barriers for the differently-substituted substrates. The 4-position was chosen as it was thought to be sufficiently distant to avoid any steric or through-space effects, with only the relevant inductive/mesomeric effects dominating. Therefore, the effect on the pro-R and pro-S isomers was expected to be similar, and so only the pro-R isomer was evaluated. The results are presented in Figure 3.21, showing a 3.72 kcal/-mol difference between the highest and the lowest energy barrier. Although

this difference is minor compared to the overall magnitude of the transition state barriers, a trend emerges whereby greater electron-donating substituents lead to higher energy transition states.

3.2.9.4 Transition states determination

Locating accurate transition state geometries using DFT is often not a trivial task. This stems from the fact that transition states represent a saddle point on the potential energy surface (PES). During computational investigations of transition states, it is not unusual for multiple transition states of different energies to exist that all connect the desired reactants and products. Moreover, one should note that the PES is multidimensional, with the dimensionality equalling the degrees of freedom. Within the Born-Oppenheimer approximation, when the movement of electrons is disregarded, the nuclear degrees of freedom are usually equal to 3N-6, where N is the number of atoms. The molecules of interest for this chapter have approximately 50-60 atoms, leading to a PES of dimensionality in the hundreds, making it challenging to locate the single transition state with the lowest energy. This especially holds true when one considers the approximations used to speed up calculations. The starting point of any calculation is an adequate input geometry, and this is especially true for transition states, where this initial "guess" must be as close to the saddle point as possible. For this reason, an accurate Hessian matrix is usually calculated as a first step in the transition state optimisation process. This matrix contains the partial second derivatives of the energy functional, and has a single negative eigenvalue at first-order saddle points (*i.e.* transition states). The approach taken to locate transition states relating to this chapter is described below.

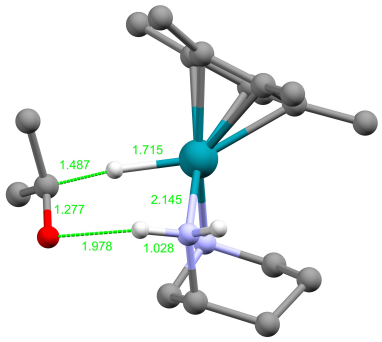
- The substrate/reactant (ketone/alcohol in this case) was added to the

stationary points on both sides. The newly generated structures were then subjected to a Nudged Elastic Band (NEB) calculation,[169–171], and the structure with the highest energy along the path was optimised to a saddle point.

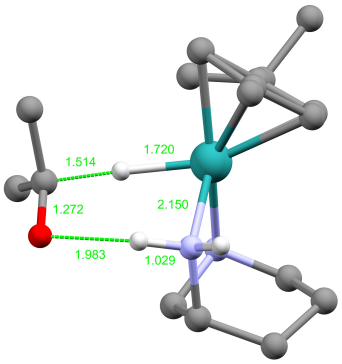
- When optimising the transition state geometry, it was often useful to specify the transition state's active atoms and use a scaling factor on the bond cut-off for those (*e.g.* 1.5) to potentially aid conversion.
- In all cases, an accurate Hessian matrix was calculated for the initial input of the geometry optimisation in order to aid conversion.
- All transitions state structures were confirmed as such by the presence of a single imaginary vibrational frequency (*i.e.* a negative frequency) and visual inspection of the displacement vectors along that frequency.
- For the NEB calculations, 20 images were used, with free end and/or pre-optimisation used in some cases. The number of images was chosen so that it is a multiple of the number of processors being used (which is normally 40).
- In difficult NEB cases, the path was set to re-parametrise at a certain number of iterations (5 or 10) to potentially aid convergence.

The above approach led to the successful determination of 6 transition state structures for the catalytic cycles employing **[Ru-2]Cl** and **[Rh-2]Cl** catalysts. These are shown in Figure 3.22 with selected distances highlighted. There are two bonds being formed (in the case of TS1) and broken (in the case of TS2). In all transition state geometries, the proton is primarily associated with the nitrogen atom, with the N-H bond distances being very close to the hydrogenated complex (*cf.* 1.015 (Rh) and 1.016 (Ru)), which is

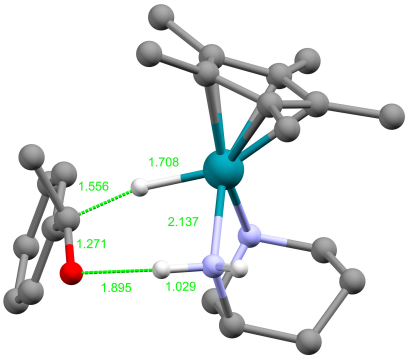
essentially a complete cleavage of the O-H bond of the alcohol (*cf.* 0.966 in 2-propanol). However, the protonation part of the transition state is of little importance as the process would easily be facilitated in the protic environment of the reaction, with a proton transfer likely occurring along the path to the saddle point. The more important step is the C-H bond breakage/-formation, and the calculations indeed located saddle points with imaginary vibrations corresponding to that process along the C-H-M coordinate in all cases. The results show the M-H bond distances at the transition state are closer to those in the ground state hydrogenated complexes (*cf.* 1.578 (Rh) and 1.612 (Ru)) than the C-H distances are to those in the ground state 2-propanol (1.103).



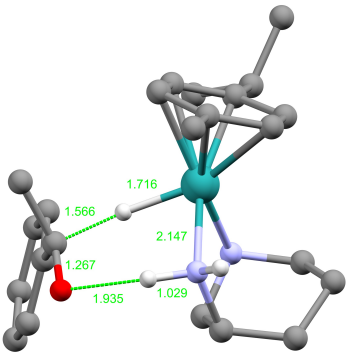
(a) [Rh-2]Cl TS1



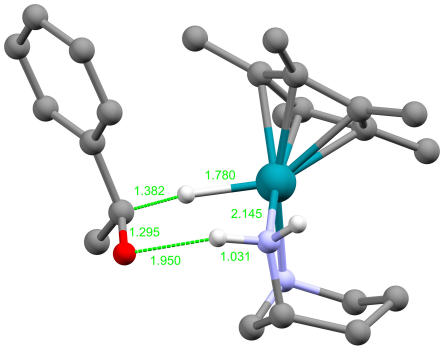
(b) [Ru-2]Cl TS1



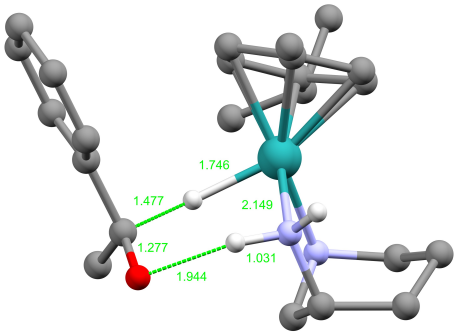
(c) [Rh-2]Cl TS2 pro-*R*



(d) [Ru-2]Cl pro-*R*



(e) [Rh-2]Cl pro-*S*



(f) [Ru-2]Cl pro-*S*

Figure 3.22: DFT transition state structures with selected bond lengths for the transition states from the proposed mechanism for transfer hydrogenation of acetophenone using **[Rh-2]Cl** and **[Ru-2]Cl** catalysts as illustrated in Figure 3.20. Hydrogen atoms (except those bound to nitrogens) have been omitted for clarity. Calculated using Orca 5.0.4[121] at the ωB97M-V[122–125]/def2-QZVPPD[126–128,165]/CPCM(ethanol)[130,131]//r2SCAN-3c[132–137]/CPCM(ethanol)[130,131]/353.15 K level of theory.

3.3 Conclusions and outlook

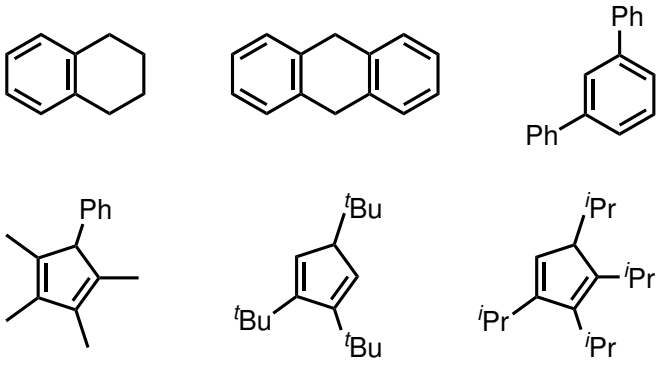


Figure 3.23: Examples of sterically demanding polyhapto ligands that could be used to modify the complexes presented in this chapter.

Nine novel complexes of platinum group metals (Rh, Ru, Ir) with simple and commercially available diamine ligands have been prepared and characterised. Utilising ligands containing a larger ring moiety (6 or 7 *vs* 5) was shown to generate only a single diastereomer upon coordination. This preference is also apparent in the DFT studies performed. All the complexes discussed herein display modest activity towards transfer hydrogenation in initial tests, which is also supported by favourable Gibbs free energies from DFT studies. Although optically pure ligands were employed for the synthesis of the complexes, no discernible enantioselectivity was observed in the resulting alcohol products. Nevertheless, it has been demonstrated that varying azacycle ligand ring size allows for the efficient synthesis of stereogenic-at-metal complexes in essentially quantitative yields and complete selectivity towards a single stereoisomer. Therefore, these represent an interesting and valuable addition to the coordination chemistry literature. Further studies could investigate potential ligand modifications to increase reaction rates and enantioselectivity, as well as look into other substrates or other reaction types. As the DFT studies presented herein show that there is only a small difference in the transition state activation energy barriers

with the current complexes, further modifications, such as the addition of sterically demanding groups to the ligand backbone or opting for polyhapto ligands (examples shown in Figure 3.23, might prove effective at enhancing the stereoselectivity of the reaction. Attempts to isolate certain key intermediates from the catalytic cycle shown in Figure 3.20, such as the neutral bis-amido species (INT2) or the hydride complex (INT3), could also be beneficial in better understanding both the mechanism and reaction demands, which could aid further work in designing better catalysts.

CHAPTER 4

Experimental

4.1 General considerations

4.1.1 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) spectra were recorded on either Bruker Fourier 300, Avance III HD 400 or 500 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) with multiplicities of signals described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sext. = sextet, sept. = septet and m = multiplet, br = broad. All ^{1}H NMR and ^{13}C NMR /^{13}C{^{1}H} NMR spectra are referenced relative to tetramethylsilane (0 ppm) using the respective residual solvent signals (*i.e.* ^{1}H NMR / ^{13}C{^{1}H} NMR : 7.26 (s) / 77.16 (t) ppm for $CDCl_3$). All ^{13}C NMR spectra were recorded as proton decoupled (*i.e.* ^{13}C{^{1}H} NMR). ^{19}F NMR /^{19}F{^{1}H} NMR were recorded without any internal reference. All coupling constants (*J*) are reported as absolute values in units of Hertz (Hz).

4.1.2 Mass spectrometry

Mass spectrometry analyses were performed by Analytical Services, Cardiff University. Instruments used were either Synapt G2-Si (ES^+) or Waters Xevo G2-XS QToF (ESI/ASAP/APCI), or ThermoScientific - Exactive GC (EI/CI).

4.1.3 High-performance liquid chromatography

High-performance liquid chromatography (HPLC) experiments were performed by Analytical Services, Cardiff University, using a Chiralpak® IF column, 99:1 Hexane:2-propanol eluent at 2 $cm^3 \cdot min^{-1}$ flow rate, and 211 nm detection.

4.1.4 Single crystal X-ray diffraction

4.1.4.1 Data collection and structure refinement

Single-crystal X-ray diffraction data were collected and processed by Dr Benson Kariuki. Data was recorded using an Agilent SuperNova Dual Atlas diffractometer with a mirror monochromator (Mo-Kα radiation source, λ = 0.71073 Å or Cu-Kα radiation source, λ = 1.54184 Å). Sample cooling was achieved using an Oxford Cryosystems cooling apparatus. In some cases, structure solution and refinement were performed by either Dr Benson Kariuki or Dr Benjamin Ward - if this was the case, it is stated when structures are presented within the text. Otherwise, it should be taken that the solution and refinement were performed by the author. Structures were solved using SHELXT[172] and refined using SHELXL[173]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at idealised positions using a riding model. Crystallographic tables

were generated from the corresponding crystallographic information files (CIFs) using the Olex2[174] software and are presented in the Appendix, along with the refinement details. The ORTEP-3 software (version 2023.1)[175] in conjunction with the CorelDRAW Graphics Suite 2021 (version 23.5.0.506) software[176] were used for creating the thermal ellipsoid figures.

4.1.4.2 Data analysis considerations

All parameters reported have been extracted from the corresponding crystallographic information files (CIFs). When bond lengths and angles were discussed for comparison purposes, these were evaluated at the 3σ level by considering the range within 3 times the standard uncertainty (also known as the estimated standard deviation, ESD). For $X(u_X)$, X is the measured value of the parameter of interest and u_X is the uncertainty in the same number of least significant digits. Therefore, at the 3σ level, the true value of X is expected to lie in the range of (X - $3u_X$) to (X + $3u_X$), which represents confidence of approximately 99.7%, assuming a normal distribution. Therefore, values for which the ranges overlap have been interpreted as being the same, whilst values for which the ranges do not overlap have been interpreted as being different.

4.1.5 Computational studies

DFT calculations were performed using the ORCA quantum chemistry software package (version 5.0.4).[121] The relevant structures were subjected to geometry optimisation and confirmed as either stationary points (for ground states) or saddle points (for transition states) via vibrational frequency calculations. For all transition states, an accurate Hessian matrix was calculated for the initial input geometry and the

transition states were confirmed as saddle points by the presence of a single imaginary (i.e. negative) vibrational frequency and by visualising the corresponding vibration using the `orca_pltvib` tool provided with the ORCA software. The conductor-like polarisable continuum model (CPCM) was used to model solvation.[130,131] For the calculation of transition states relating to Chaapter 3, climbing-image nudged elastic band plus zoomed climbing-image nudged elastic band calculation (Zoom-NEB-CI),[169,170] along with the fast inertial relaxation engine (FIRE) optimisation method,[171] as implemented in ORCA, were utilised to obtain an accurate transition state guess prior to eigenvector-following calculations. The geometry optimisation and vibrational frequency calculations were performed at the r^{2}SCAN-3c/CPCM(Solvent)[130–137]/[Temperature] level of theory (step 1), followed by singe-point energy calculations at the ωB97M-V/def2-QZVPPD/CPCM(Solvent)[122–131,165] level of theory, to obtain accurate electronic energies (step 2). To obtain the final Gibbs free energy, the following formula was used: G[1]−E[1]+E[2] where G is the Total Gibbs free energy and E is the electronic energy, with the relevant steps shown in the brackets. The KDIIS algorithm[177] was used for SCF convergence. Other settings should be taken as defined by default in Orca 5.0.4. Examples of the input scripts used are available in the Appendix. The Avogadro software[178] was used for structure visualisation and input geometry preparation. The Mercury software[179] in conjunction with the POV Ray[180] software were used for creating figures of computed geometries.

A publication on best practice DFT protocols by Grimme and co-workers guided the selection of the level of theory employed.[181] The r^{2}SCAN-3c[132] is a composite electronic-structure method that utilises the r^{2}SCAN meta-GGA functional[134,135], refitted D4 dispersion correction[136,137] to calculate the London dispersion interactions, refitted geometrical counterpoise

correction[133] to account for basis set superposition error, and the modified triple-ζ basis set def2-mTZVPP[132]. This method was chosen as the main method for geometry optimisation and thermochemistry due to its efficiency in providing accurate results for organometallic reactions, comparable to much higher levels of theory, as assessed by Grimme and coworkers[132] using the MOR41 benchmark set.[182]

The Gaussian charge scheme with a vdW-type cavity is used by default for the CPCM model in Orca.[131] Additionally, Orca uses the Resolution of Identity (RI-J) for Coulomb integrals (J) by default for meta-GGA functionals, which has been applied to the calculations using the r^{2}SCAN-3c[132–137] method. The RI-J, combined with the Chain of Spheres (COSX) approximation (called RIJCOSX) are also used by default for hybrid functionals and have therefore been automatically applied to the calculations using the ωB97M-V[122–125] functional. These approximations utilise the auxiliary density fitting basis sets, def2-mTZVPP/J[132] and def2/J[128], for r^{2}SCAN-3c and ωB97M-V, respectively. Furthermore, although the KDIIS algorithm[177] was explicitly requested for SCF convergence, ORCA switches this to a trust-region augmented Hessian (TRAH) algorithm[183–186] if convergence problems are detected.

The state of any other settings or parameters that are not mentioned above should be taken to be as defined by default in Orca 5.0.4 unless specified otherwise in the text. Example input scripts are presented in the Appendix.

All calculations were performed remotely using the supercomputing facilities at Cardiff University, operated by Advanced Research Computing at Cardiff (ARCCA) on behalf of the Cardiff Supercomputing Facility and the HPC Wales and Supercomputing Wales (SCW) projects.

4.1.6 Handling of air and moisture sensitive compounds

All experiments involving air/moisture-sensitive compounds were performed using nitrogen dry-boxes and standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents for air/moisture sensitive reactions (except diethyl ether and tetrahydrofuran) were dried by passing through a column of alumina using an MBraun SPS800 solvent purification system and then stored over molecular sieves. Diethyl ether and tetrahydrofuran were first dried over molecular sieves and then refluxed in an argon atmosphere over sodium wire/benzophenone or potassium. Deuterated solvents and epoxides were dried over freshly ground calcium hydride and then degassed by a minimum of three free-pump-thaw cycles, distilled under reduced pressure, and then stored in a nitrogen dry-box.

4.2 Chapter 2

4.2.1 General experimental

All ROCOP reactions and catalyst syntheses were carried out using air- and moisture-sensitive techniques (Schlenk line, Glovebox (MBraun LAB-Star)). Starting materials were purchased from commercial suppliers and used without further purification, with the exception of anhydrides*, which were sublimed under vacuum and kept in a glovebox, and epoxides, which were purified using trap-to-trap distillation and then stored in a glovebox.

*Phthalic anhydride used in reactions was either recrystallised from hot chloroform or a commercially available product purchased from Sigma Aldrich (Phthalic anhydride, anhydrous, free-flowing, Redi-Dri™, ACS reagent $\geq$99%). The performance of both sublimed and this specific commercial product was comparable in terms of conversions obtained.

4.2.2 MALDI sample preparation

A sample of the polymer was dissolved in tetrahydrofuran (HPLC grade) at 10 mg/cm^3. A solution of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) matrix is then prepared at 20 mg/cm^3 in tetrahydrofuran. Aliquots of the two solutions are mixed in a 1:5 (10:50 µL) sample-to-matrix ratio, and sodium acetate (0.5 µL) is added. The mixture is then vortex-mixed and an aliquot (0.5 µL) is deposited onto a MALDI target plate and allowed to air dry. Data was collected in both positive-linear and reflectron modes using a Bruker Autoflex Speed MALDI-ToF mass spectrometer controlled by the FlexControl software, with post-acquisition processing performed using the FlexAnalysis software.

Molecular weights were determined using PolyTools software, which yielded molecular weight distributions for each series found in the sample. For each series, the overall average molecular weight was determined by summing the molecular weights of all series, weighted according to their respective normalised percentage intensities. The normalised percentage intensity was calculated by dividing the percentage intensity of each series by the sum of all intensities, as these did not always sum up to exactly 100%.

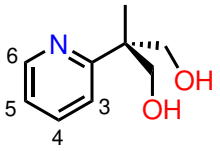
4.2.3 GPC sample preparation

3 mg of the respective polymer were dissolved in 1 cm^3 of tetrahydrofuran and then filtered through 0.2 µm PTFE syringe filter before being subjected to analysis using Agilent 1260 Infinity II fitted with a 5 µm Mixed-D PLgel column and calibrated using polystyrene standards. Detection was achieved using a combination of refractive index, viscometry, and light scattering. The injection volume used was 100.00 µL and the flow rate used was 1.00 cm^3/min.

4.2.4 Procedure for ring opening co-polymerisation of epoxides and cyclic anhydrides

Inside a glovebox, a 7 cm^3 screw-top glass vial was charged with the catalyst, co-catalyst, anhydride, and epoxide, in the required ratios. The reaction is then stirred neat at an elevated temperature using an aluminium heating block. After completion, a small aliquot is withdrawn for *in situ* ^1H NMR studies to determine conversion. Whenever polymers were isolated, this was done by quenching the reaction using an excess of methanol or 2-propanol and shaking to mix well. The resulting copolymer immediately precipitates out of the reaction mixture. The latter is then filtered and washed with methanol. In some cases, small amounts of dichloromethane were used to dissolve the polymer, followed by precipitation in an excess of methanol.

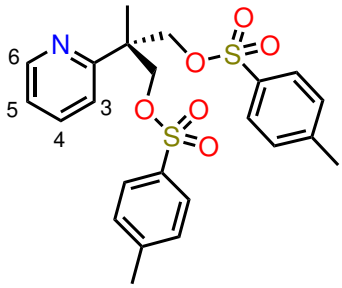
4.2.5 Synthesis of 2-methyl-2-(pyridin-2-yl)propane-1,3-diol



A 250 cm^3 autoclave was charged with 2-ethylpyridine (50 cm^3, 46.85 g, 437 mmol, 1 equiv.) and an aqueous solution of formaldehyde (150 cm^3, 37.8 % w/w, 2.1 mol, 4.6 equiv.). The mixture was mechanically stirred at 140 °C for 40 h. This reaction was repeated 3 times. After cooling down, the water and volatiles were removed using distillation (100 °C for water, ~110 °C for paraformaldehyde, with frequent cleaning of the condenser required to prevent blockage due to build-up of paraformaldehyde residue). Initial vacuum distillation was then used to separate the product of mono-

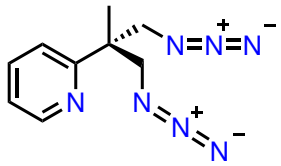
hydroxymethylation (2-(pyridin-2-yl)propan-1-ol, viscous yellow oil, 58.74 g, 33% yield based on 150 cm^3 of 2-ethylpyridine) from the desired product of dihydroxymethylation (the title compound, viscous amber oil, 11.33 g, showing ∼20% contamination with the monohydroxymethylation product, ∼4% yield based on 150 cm^3 of 2-ethylpyridine). The 2-(pyridin-2-yl)propan-1-ol was then used in place of the 2-ethylpyridine and reacted similarly with aqueous solution of formaldehyde (150 cm^3, 37.8 % w/w, 2.1 mol, 4.8 equiv.) to give another mixture of 2-(pyridin-2-yl)propan-1-ol and 2-methyl-2-(pyridin-2-yl)propane-1,3-diol, which was subjected to another fractional vacuum distillation to give the title compound as a viscous amber oil (16.49 g, 7.5% based on 150 cm^3 of 2-ethylpyridine, and 23.0% based on 58.74 g of 2-(pyridin-2-yl)propan-1-ol)) and recover non-reacted 2-(pyridin-2-yl)propan-1-ol (∼37 g, ∼54% recovery). During the second fractional vacuum distillation, a portion of the dihydroxymethylation was allowed to be distilled into the monohydroxymethylation product before the collection of the dihydroxymethylation product commenced, so that the latter could be obtained in high purity. ^{1}H NMR (500 MHz; $CDCl_3$; 297 K) δ 8.49 (1H, ddd, ^3J = 4.9 Hz, ^4J = 1.9 Hz, ^5J = 0.9 Hz, H^6), 7.71 (1H, ddd, ^3J = 8.0 Hz, $^3J'$ = 7.5 Hz, ^4J = 1.9 Hz, H^4), 7.36 (1H, dt, ^3J = 8.1 Hz, $^{4,5}J$ = 1.0 Hz, H^3), 7.19 (1H, ddd, ^3J = 7.5 Hz, $^3J'$ = 4.9 Hz, ^4J = 1.1 Hz, H^5), 3.90-4.40 (2H, br. s, OH), 4.03 (2H, d, ^2J = 11.1 Hz, 2×C<u>H</u>H'), 3.84 (2H, d, ^2J = 11.1 Hz, 2×CH<u>H'</u>), 1.19 (3H, s, CH_3).

4.2.6 Synthesis of 2-methyl-2-(pyridin-2-yl)propane-1,3-diyl bis(4-methylbenzenesulfonate)



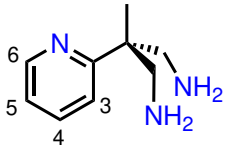
2-methyl-2-(pyridin-2-yl)propane-1,3-diol (16.492 g, 98.63 mmol, 1.0 equiv.) was dissolved in pyridine (130 cm^3) and cooled to 0 °C . Tosyl chloride (47.017 g, 246.63 mmol, 2.5 equiv.) was slowly added in small portions in order to keep the reaction temperature between 5 and 10 °C . After the addition was complete, the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was then poured into a mixture of ice/water (~500 cm^3). The resulting precipitate was filtered, washed with water (100 cm^3), diethyl ether (175 cm^3), and dried on the filter. The title compound was obtained as an off-white solid and used as is without further purification or drying. ^{1}H NMR (500 MHz; $CDCl_3$; 297 K) δ 8.32 (1H, ddd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, ^5J = 1.0 Hz, H^6), 7.65 (4H, m, Ar-H), 7.58 (1H, ddd, ^3J = 8.0 Hz, $^3J'$ = 7.6 Hz, ^4J = 1.9 Hz, H^4), 7.30 (4H, m, Ar-H), 7.16 (1H, dt, ^3J = 8.0 Hz, $^{4,5}J$ = 1.0 Hz, H^3), 7.11 (1H, ddd, ^3J = 7.5 Hz, $^3J'$ = 4.8 Hz, ^4J = 1.0 Hz, H^5), 4.26 (4H, d, *J* 1.4, 2×C<u>H</u>H', 2×CH<u>H</u>'), 2.45 (6H, s, 2×Ar-CH_3), 1.33 (3H, s, CH_3)

4.2.7 Synthesis of 2-(1,3-diazido-2-methylpropan-2-yl)-pyridine



2-methyl-2-(pyridin-2-yl)propane-1,3-diyl bis(4-methylbenzenesulfonate) (25.325 g, 53.25 mmol, 1.0 equiv.) was mixed with sodium azide (10.342, 159.08 mmol, 3.0 equiv.) in DMSO (100 cm^3). The reaction was then stirred at 70 °C for 4 days. After cooling down to room temperature, the reaction mixture was poured into water (100 cm^3) to give a brown suspension. The title product was extracted with diethyl ether (5 $\times$ 50 cm^3). Pyridine (100 cm^3) was then added to the combined ethereal fractions and the ether was removed *in vacuo*. No further purification was carried out due to the hazardous nature of organic azides. The resulting pyridine solution was used as is for the next step of the synthesis, assuming 100% conversion (11.566 g, 53.24 mmol, 0.5324 M).

4.2.8 Synthesis of 2-methyl-2-(pyridin-2-yl)propane-1,3-diamine



Yield: 20%

A solution of 2-(1,3-diazido-2-methylpropan-2-yl)pyridine in pyridine (100 cm^3, 0.5324 M, 53.24 mmol, 1.0 equiv.) was cooled down to 0 °C . A solution

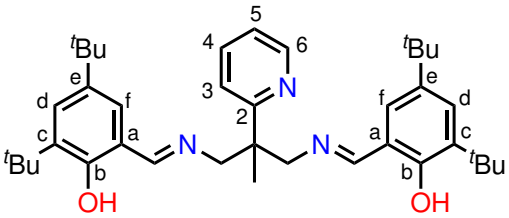
of triphenylphosphine (33.570 g, 127.99 mol, 2.4 equiv.) in pyridine (50 cm^3) was then added dropwise, maintaining a temperature of 0 °C throughout. After the addition was complete, the reaction mixture was left to warm to room temperature and stirred overnight. The solvent was then removed *in vacuo* to give *N,N′*-(2-methyl-2-(pyridin-2-yl)propane-1,3-diyl)bis(1,1,1-triphenylphosphanimine) as an itermediate compound (orange semisolid). The latter was heated gently in order to reduce its viscosity and then poured into an excess of ammonia (10% aqeuous solution, 150-200 cm^3). The reaction mixture was then stirred using a mechanical stirrer for 24 hours at room temperature. The resulting white precipitate of triphenylphosphine oxide was removed by filtration and washed with water (3 $\times$ 100 cm^3). The filtrate and washings were then combined and the solvent was removed *in vacuo*. Vacuum distillation (85-90 °C , full line vacuum) yielded the title compound as a slightly viscous colourless oil (1.774 g). ^{1}H NMR (500 MHz; $CDCl_3$; 298 K) δ 8.59 (1H, ddd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, ^5J = 0.9 Hz, H^6), 7.65 (1H, ddd, ^3J = 8.0 Hz, $^3J'$ = 7.5 Hz, ^4J = 1.9 Hz, H^4), 7.31 (1H, dt, ^3J = 8.0 Hz, $^{4,5}J$ = 1.0 Hz, H^3), 7.12 (1H, ddd, ^3J = 7.5 Hz, $^3J'$ = 4.8 Hz, ^4J = 1.1 Hz, H^5), 3.13 (2H, d, ^2J = 12.9 Hz, 2×C<u>H</u>H'), 2.88 (2H, d, ^2J = 12.9 Hz, 2×CH<u>H</u>'), 1.34 (3H, s, CH_3), 1.27 (4H, br. s, 2×NH_2).

4.2.9 General procedure for the Synthesis of Salpy proligands

2-methyl-2-(pyridin-2-yl)propane-1,3-diamine (1.0 equiv.) and respective aldehyde (2.0 equiv.) were stirred in methanol at 50 °C for 3 hours. The reaction mixture was then allowed to cool down to room temperature and was then further cooled down using an ice bath to give the Shiff base products as yellow precipitates. The latter was filtered, washed with cold methanol

and dried *in vacuo*.

4.2.10 3,5-tBu,tBu-SalpyH$_2$



Yield: 51%

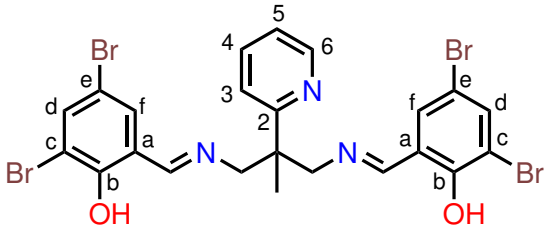
^{1}H NMR (500 MHz, $CDCl_3$, 295 K) δ 13.53 (2H, s, OH), 8.62 (1H, ddd, ^3J = 4.8 Hz, ^4J = 1.9 Hz, ^5J = 0.9 Hz, H^6), 8.34 (2H, s, 2×HC=N), 7.64 (1H, ddd, ^3J = 8.0 Hz, $^3J'$ = 7.5 Hz, ^4J = 1.9 Hz, H^4), 7.35* (1H, dt, ^3J = 8.0 Hz, $^{4,5}J$ = 1.0 Hz, H^3, overlaps with H^d), 7.35* (2H, d, ^4J = 2.5 Hz, 2×H^d, overlaps with H^3), 7.14 (1H, ddd, ^3J = 7.5 Hz, $^3J'$ = 4.8 Hz, ^4J = 1.1 Hz, H^5), 7.04 (2H, d, ^4J = 2.5 Hz, 2×H^f), 4.05 (4H, s, 2×CH_2), 1.56 (3H, s, CH_3), 1.42 (18H, s, 2×C^{c}C(CH_3)$_3$), 1.29 (18H, s, 2×C^{e}C(CH_3)$_3$). * - signals overlap, however, all constituent peaks for each signal are clearly discernable, and so the signals are reported as single values instead of ranges.

^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) δ 13.78 (2H, s, OH), 8.60 (1H, d, ^3J = 4.1 Hz, H^6), 8.52 (2H, s, 2×HC=N), 7.78 (1H, td, ^3J = 7.7 Hz, ^4J = 1.9 Hz, H^4), 7.49 (1H, d, ^3J = 8.0 Hz, H^3), 7.28* (2H, d, 2×H^d, overlaps with H^5), 7.23-7.31* (1H, m, 2×H^5, overlaps with H^d), 7.21 (2H, d, ^4J = 2.4 Hz, 2×H^f), 4.07 (2H, d, ^2J = 12.4 Hz, 2×C<u>H</u>H'), 3.97 (2H, d, ^2J = 12.4 Hz, 2×CH<u>H'</u>), 1.45 (3H, s, CH_3), 1.34 (18H, s, 2×C^{c}C(CH_3)$_3$), 1.24 (18H, s, 2×C^{e}C(CH_3)$_3$). * - signals overlap, however, the peaks for the H^d signal are clearly discernable and thus the signal is reported as a single value, whilst only some of the peaks for the H^5 are visible, so the latter is reported as a range.

$^{13}C\{^{1}H\}$ NMR (126 MHz; $CDCl_3$; 295 K) δ 167.34 (C=N), 163.76, 158.23, 149.11, 140.03, 136.72, 136.51, 127.03, 126.07, 121.63, 121.37, 117.98, 67.02 (CH_2), 46.27 (Py$\underline{C}CH_3$), 35.17 ($\underline{C}(CH_3)_3$), 34.24 ($\underline{C}(CH_3)_3$), 31.62 ($C(\underline{C}H_3)_3$), 29.53 ($C(\underline{C}H_3)_3$), 22.36 (CH_3).

HRMS (ES^+/TOF) *m/z* 598.4378 (calc. 598.4373) $[M\text{-}H]^+$.

4.2.11 3,5-Br,Br-SalpyH$_2$

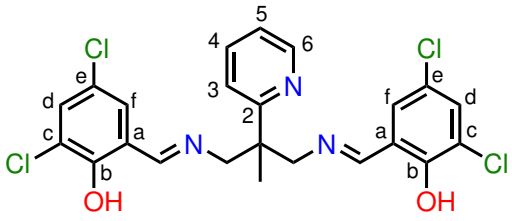


Yield: 78%

^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) δ 14.45 (2H, s, OH), 8.63 (1H, d, ^{3}J = 3.9 Hz, H^6), 8.49 (2H, s, 2×HC=N), 7.82 (1H, td, ^{3}J = 7.8 Hz, ^{4}J = 1.9 Hz, H^4), 7.78 (2H, d, ^{4}J = 2.5 Hz, 2×H^d), 7.57 (2H, d, ^{4}J = 2.5 Hz, 2×H^f), 7.52 (1H, d, ^{3}J = 8.0 Hz, H^3), 7.32 (1H, ddd, ^{3}J = 7.5 Hz, $^{3}J'$ = 4.8 Hz, ^{4}J = 1.1 Hz, H^5) 4.18 (2H, d, ^{2}J = 12.9 Hz, 2×C$\underline{H}$H'), 3.97 (2H, d, ^{2}J = 12.9 Hz, 2×CH$\underline{H}$'), 1.45 (s, 3H).

HRMS (TOF ES+) *m/z* 685.8317 (calc. 685.8289) $[M\text{-}H]^+$.

4.2.12 3,5-Cl,Cl-SalpyH$_2$



Yield: 41%

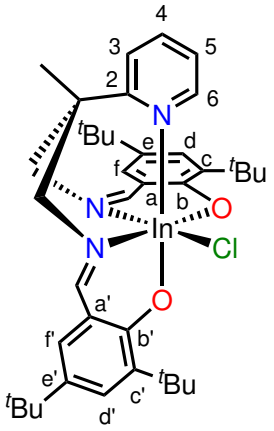
^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) δ 14.38 (2H, s, OH), 8.63 (1H, ddd, ^{3}J = 4.8 Hz, ^{4}J = 1.9 Hz, ^{5}J = 0.9 Hz, H^6), 8.52 (2H, s, 2×HC=N), 7.82 (1H, td,^{3}J = 7.8 Hz, ^{4}J = 1.9 Hz, H^4), 7.57 (2H, d, ^{4}J = 2.6 Hz, 2×H^d), 7.52 (1H, dt, ^{3}J = 8.0 Hz, $^{4,5}J$ = 0.9 Hz, H^3), 7.42 (2H, d, ^{4}J = 2.6 Hz, 2×H^f), 7.31 (1H, ddd, ^{3}J = 7.5 Hz, $^{3}J'$ = 4.8 Hz, ^{4}J = 1.0 Hz, H^5) 4.18 (2H, d, ^{2}J = 13.0 Hz, 2×CHH'), 3.97 (2H, d, ^{2}J = 13.0 Hz, 2×CHH'), 1.45 (s, 3H).

HRMS (TOF ES+) *m/z* 510.0315 (calc. 510.0310) $[M-H]^+$.

4.2.13 General procedure for the synthesis of indium(III) complexes with Salpy ligands

Potassium hydride (10 equiv.) was suspended in a solution of the respective ligand (1.00 equiv.) in dry tetrahydrofuran (10 cm^3). The reaction mixture was then stirred overnight at room temperature. The resulting solution containing the potassium salt of the imine was filtered and transferred onto $InCl_3$(1.00 equiv. = 200 mg) using a cannula. The leftover solids from the first step were washed with dry tetrahydrofuran (10 cm^3) and the wash was also transferred over to the $InCl_3$. This was then stirred at room temperature for 1 hour. The tetrahydrofuran was removed *in vacuo* and dry dichloromethane was added (10 cm^3). The reaction mixture was then filtered to remove the KCl by-product. The dichloromethane was removed *in vacuo*, and the crude product was washed with dry pentane. Removal of all volatiles *in vacuo* gave the respective complexes as yellow solids.

4.2.14 In(3,5-tBu,tBu-Salpy)Cl - In-1



The two iminophenoxide "arms" gave rise to equivalent signals due to rapid interconversion on the NMR timescale.

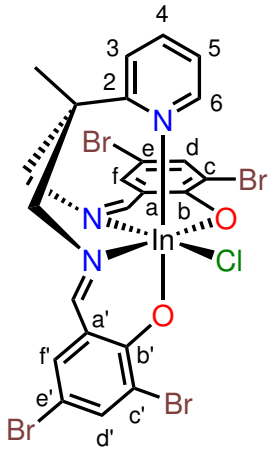
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 9.23 (1H, ddd, ^{3}J = 5.3 Hz, ^{4}J = 1.8 Hz, ^{5}J = 0.6 Hz, H^6), 7.94 (2H, s, 2×HC=N), 7.86 (1H, td, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, H^4), 7.49 (1H, dt, ^{3}J = 8.1 Hz, $^{4,5}J$ = 1.0 Hz, H^3), 7.43 (1H, ddd, ^{3}J = 7.7 Hz, $^{3}J'$ = 5.3 Hz, ^{4}J = 1.1 Hz, H^5), 7.35 (2H, d, ^{4}J = 2.7 Hz, 2×H^d), 6.75 (2H, d, ^{4}J = 2.7 Hz, 2×H^f), 3.92 (4 H, apparent q, J = 13.7, 2×CH_2), 1.63 (3H, s, CH_3), 1.37 (18H, s, 2×$C(CH_3)_3$), 1.22 (18H, s, 2×$C(CH_3)_3$).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) δ

172.04 (C=N), 168.80 (Ar-C(4°)), 162.72 (Ar-C(4°)), 150.58 (C^6), 142.32 (Ar-C(4°)), 139.73 (C^4), 136.06 (Ar-C(4°)), 129.83 (C^d), 128.57 (C^f), 123.97 (C^5), 120.78 (C^3), 117.38 (Ar-C(4°)), 68.76 (CH_2), 42.42 (Py$\underline{C}CH_3$), 35.72 ($C\underline{C}(CH_3)_3$), 33.93 ($C\underline{C}(CH_3)_3$), 31.45 ($C(\underline{C}H_3)_3$), 29.76 ($C(\underline{C}H_3)_3$), 24.36 (CH_3).

HRMS (TOF ASAP+) *m/z* 745.2882 (calc. 745.2865) $[M]^+$.

4.2.15 In(3,5-Br,Br-Salpy)Cl - In-2

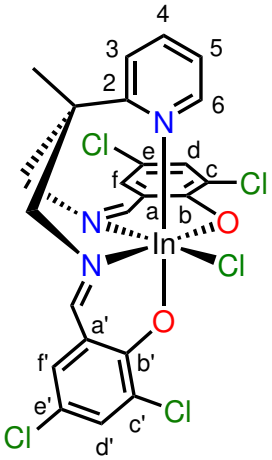


The two iminophenoxide "arms" gave rise to equivalent signals due to rapid interconversion on the NMR timescale.

^{1}H NMR (500 MHz, $CDCl_3$, 295 K) δ 9.17 (1H, ddd, ^{3}J = 5.3 Hz, ^{4}J = 1.9 Hz, ^{5}J = 0.8 Hz, H^{6}), 7.98 (1H, td, ^{3}J = 7.9 Hz, ^{4}J = 1.8 Hz, H^{4}), 7.95 (2H, br s, 2×HC=N), 7.71 (2H, d, ^{4}J = 2.6 Hz, 2×H^{d}), 7.61 (1H, dt, ^{3}J = 8.1 Hz, $^{4,5}J$ = 1.1 Hz, H^{3}), 7.56 (1H, ddd, ^{3}J = 7.7 Hz, $^{3}J'$ = 5.3 Hz, ^{4}J = 1.2 Hz, H^{5}), 7.10 (2H, d, ^{4}J = 2.7 Hz, 2×H^{f}), 4.03 (4 H, br s, 2×CH_2), 1.69 (3H, s, CH_3).

HRMS (TOF ASAP+) *m/z* 836.6765 (calc. 836.6741) $[M]^{+}$.

4.2.16 In(3,5-Cl,Cl-Salpy)Cl - In-3



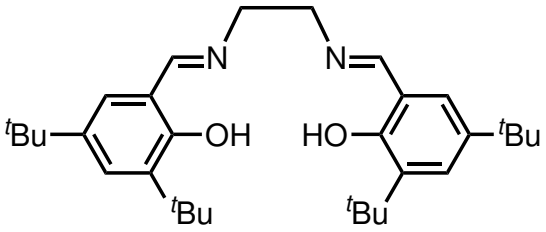
The two iminophenoxide "arms" gave rise to equivalent signals due to rapid interconversion on the NMR timescale.

^{1}H NMR (500 MHz, $CDCl_3$, 295 K) δ 9.08 (1H, dd, ^{3}J = 5.2 Hz, ^{4}J = 1.2 Hz, H^6), 7.97* (2H, br s, 2×HC=N, overlaps with H^4), 7.95* (1H, td, ^{3}J = 7.9 Hz, ^{4}J = 1.8 Hz, H^4, overlaps with HC=N), 7.59 (1H, dt, ^{3}J = 8.1 Hz, $^{4,5}J$ = 1.0 Hz, H^3), 7.50 (1H, ddd, ^{3}J = 7.7 Hz, $^{3}J'$ = 5.3 Hz, ^{4}J = 1.1 Hz, H^5), 7.38 (2H, d, ^{4}J = 2.7 Hz, 2×H^d), 6.89 (2H, d, ^{4}J = 2.7 Hz, 2×H^f), 4.07 (2H, br d, ^{2}J = 14.1 Hz, 2×C<u>H</u>H'), 3.98 (2H, br d, ^{2}J = 13.5 Hz, 2×CH<u>H'</u>), 1.68 (3H, s, CH_3). * - signals overlap, however, all constituent peaks for each signal are clearly discernable, and so the signals are reported as single values instead of ranges.

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) δ 170.70 (C=N), 164.18 (Ar-C), 161.92 (Ar-C), 150.43 (C^6), 140.74 (C^4), 134.19 (C^d), 131.75 (C^f), 128.92 (Ar-C), 124.73 (C^5), 121.57 (C^3), 119.57 (Ar-C), 118.80 (Ar-C), 68.14 (CH_2), 41.78(Py<u>C</u>CH_3), 24.24 (CH_3).

HRMS (TOF ASAP+) *m/z* 658.8774 (calc. 658.8773) $[M]^+$.

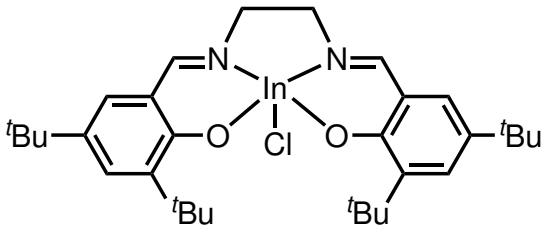
4.2.17 Synthesis of 3,5-^{t}Bu,^{t}Bu-SalenH$_2$



Synthesised according to the literature procedure, with spectral data matching the literature report.[187] ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.64 (s, 2H), 8.39 (s, 2H), 7.36 (d, J = 2.5 Hz, 2H), 7.06 (d, J = 2.4 Hz, 2H), 3.92 (s, 4H), 1.43 (s, 18H), 1.28 (s, 18H).^{1}H NMR (500 MHz, C_6D_6) δ 14.01 (s, 2H), 7.77 (s, 2H), 7.55 (d, J = 2.5 Hz, 2H), 6.97 (d, J = 2.5 Hz, 2H), 3.27 (s, 4H), 1.64 (s, 18H), 1.31

(s, 18H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 167.72, 158.17, 140.20, 136.73, 127.16, 126.19, 117.95, 59.76, 35.16, 34.25, 31.61, 29.56.

4.2.18 Synthesis of In(3,5-^{t}Bu,^{t}Bu-Salen)Cl



Under nitrogen, a Schlenk flask was charged with dry potassium hydride (73.1 mg, 2 equiv.). Dry ethanol (30 cm^3) was added and the mixture was stirred for 5 minutes at room temperature, giving a clear solution. Then, the pro-ligand 3,5-^{t}Bu,^{t}Bu-SalenH_2 (498 mg, 1 equiv.) was added and the resulting yellow suspension was refluxed for 5 minutes, giving a clear bright yellow solution, which yielded a yellow precipitate upon cooling. The solvent was removed *in vacuo* to give a dark yellow/orange solid, to which anhydrous $InCl_3$ (200.5 mg, 1 equiv.) was added. Dry tetrahydrofuran (20 cm^3) was then added to the solids to give an orange suspension, which was stirred for 20 h at room temperature to give a cloudy orange solution. The solvent was removed *in vacuo* to give a dark yellow/orange solid, to which dry toluene (10 cm^3) was added and the mixture was refluxed for 1 h, then filtered through a microfibre glass filter paper to give a bright yellow solution. The solvent was removed *in vacuo* and the resulting yellow solid washed with dry pentane (3 x 15 cm^3) and dried under *in vacuo*. ^{1}H NMR (500 MHz, C_6D_6) δ 7.85 (d, J = 2.6 Hz, 2H), 7.40 (s, 2H), 6.90 (d, J = 2.6 Hz, 2H), 3.15 – 2.99 (m, 2H), 2.48 (dt, J = 8.7, 5.6 Hz, 2H), 1.90 (s, 18H), 1.49 (s, 20H). $^{13}C\{^{1}H\}$ NMR (126 MHz, C6D6) δ 172.40, 168.68, 143.42, 137.72, 130.73, 129.40, 118.06, 53.68, 36.18,

34.18, 31.67, 30.02. Spectral data conforms to the structure and literature-reported data.[187]

4.3 Chapter 3

All reactions and manipulations were performed under ambient atmosphere. Ligands and solvents were purchased from commercial suppliers and used without further purification. The metal precursors [-(η^6-[1-methyl-4-(propan-2-yl)benzene)]$RuCl_2]_2$, [(η^5-(1,2,3,4,5-pentamethylcyclopentadienyl)$RuCl_2]_2$, and [(η^5-(1,2,3,4,5-pentamethylcyclopentadienyl)-$IrCl_2]_2$ used were samples previously synthesised by other group members and were used without further purification.

4.3.1 General procedure for the synthesis of complexes

The relevant metal precursor (100 mg, 1 equiv.) was dissolved in dichloromethane (5 cm^3), followed by the addition of the required amount of ligand (2.1 equiv.) as a solution in dichloromethane. The reaction was stirred at room temperature for 24 hours. The solvent was then removed in vacuo to give the corresponding metal complex. The complexes were then screened as catalysts without further purification.

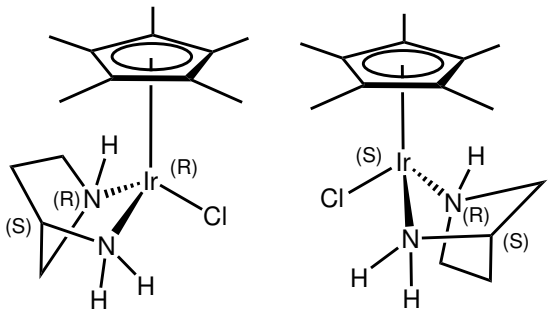
4.3.2 Single crystal XRD sample preparation

To a solution of water/methanol of chloride salts of the respective complexes, an excess of sodium hexafluorophosphate was added. Slow evaporation of the methanol fraction yielded crystals of the respective hexafluorophosphate salts of the complexes, which were suitable for analysis.

4.3.3 General procedure for transfer hydrogenation reactions

A 7 cm^3 glass vial or 10 cm^3 vials were charged with a magnetic stirrer bar. The metal complex, base (if required), and silver salt (if required) were added as standard solutions in 2-propanol. The total volume of the reaction was made up to 5 cm^3 with 2-propanol, and then the required volume of substrate (4-fluoroacetophenone) was added. The reactions were heated at the required temperature and stirred for the respective amounts of time. Small aliquots (0.6-0.7 cm^3) were then withdrawn, filtered through 0.2 μm PTFE filter (if removal of residue was required, *e.g.* if silver salts were used), and analysed by ^{19}F NMR or $^{19}F\{^1H\}$ NMR spectroscopy to determine substrate conversion. The signal of the product was taken to be upfield of the substrate. In cases where enantioselectivity was determined, samples were filtered through 0.2 μm PTFE filter, followed by a plug of alumina, and then analysed by chiral HPLC. In cases where silver salts were added, the reaction vessels were shielded from light during the reaction to preclude potential photodegradation of the silver species.

4.3.4 $S_C,R_N,R/S_{Ir}$ - [(η^5-C_5Me_5)Ir(L1)Cl]Cl

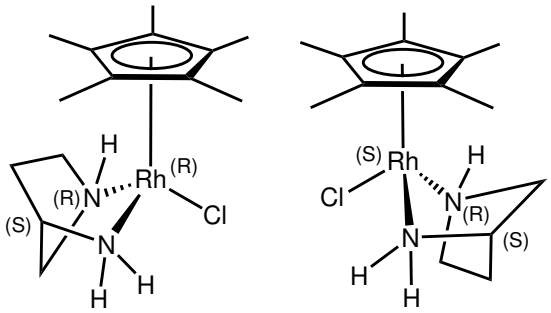


major isomer minor isomer

Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ (major isomer) 7.48 (d, *J* = 10.5 Hz, 1H), 6.38 (s, 1H), 3.86 – 0.53 (m, 8H), 1.82 (s, 15H) ppm; δ (minor isomer) 7.74 (dd, *J* = 9.9, 3.4 Hz, 1H), 6.51 (s, 1H), 3.86 – 0.53 (m, 8H), 1.81 (s, 15H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (major isomer) 86.70 (C), 57.28 (CH_2), 53.54(CH, CH_2), 28.48 (CH_2), 9.55 (CH_3) ppm; δ (minor isomer) 86.60 (C), 64.31 (CH_2), 53.59 (CH), 52.58 (CH_2), 28.57 (CH_2), 9.60 (CH_3) ppm. HRMS (TOF ES+): *m/z* 449.1334 (calc. 449.1335) $[M]^+$.

4.3.5 S_C,R_N,R/S_{Rh} - [(η^5-C_5Me_5)Rh(L1)Cl]Cl



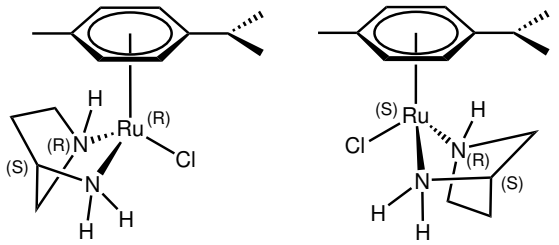
major isomer minor isomer

Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ (major isomer) 6.95 (s br overlapping, 1H), 5.66 (s, 1H), 3.68 (s, 1H), 3.61 - 3.49 (m, overlapping with other isomer, 1H), 3.38 (m, 1H), 3.30 (m, 1H), 2.91 (d, *J* = 10.0 Hz, 1H), 2.41 – 2.29 (m, overlapping with other isomer, 1H), 2.13 (d, *J* = 9.9 Hz, 1H), 1.85 (s, 15H), 1.66 (m, 1H); δ (minor isomer) 6.93 (s br overlapping, 1H), 5.81 (s, 1H), 3.82 (t, *J* = 4.8 Hz, 1H), 3.61-3.49 (m, overlapping with other isomer, 1H), 3.09 (d, *J* = 9.9 Hz, 1H), 2.87 – 2.75 (m, 2H), 2.41 – 2.29 (m, overlapping with other isomer, 1H), 2.09 - 1.99 (m, 2H), 1.84 (s, 15H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (major isomer) 95.31 (d, *J* = 8.1 Hz), 56.64 (CH_2), 52.59(CH / CH_2), 52.46 (CH / CH_2), 28.68 (CH_2), 9.75 (CH_3) ppm; δ (minor isomer) 95.19 (d, *J* = 8.2 Hz), 62.30 (CH_2),

50.77 (CH), 47.43 (CH_2), 29.84 (CH_2), 9.83 (CH_3) ppm. HRMS (TOF ES+) *m/z* 359.0768 (calc. 359.0761) $[M]^+$.

4.3.6 $R_C,S_N,R/S_{Ru}$ - [(η^6-*p*-cymene)Ru(L1)Cl]Cl

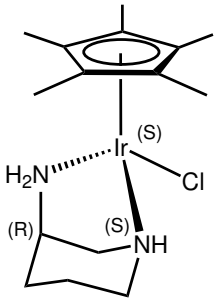


major isomer minor isomer

Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ (major isomer): 8.07 (s br, 1H), 5.99 (d, *J* = 5.8 Hz, 1H), 5.86 – 5.31 (m, 4H), 3.80 – 0.76 (m, 9H), 2.39 (s, 3H), 1.45 – 1.22 (m, 6H) ppm; δ (minor isomer): 8.26 (s br, 1H), 6.48 (d, *J* = 6.0 Hz, 1H), 6.41 (s, 1H), 5.86 – 5.31 (m, 4H), 4.67 (s br, 1H), 3.80 – 0.76 (m, 7H), 2.47 (s, 3H), 1.45 – 1.22 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (incomplete due to weak signals) (126 MHz, $CDCl_3$) δ 81.26, 81.16, 51.65, 30.88, 28.38, 23.75, 23.50, 22.38, 22.27, 18.98, 18.55. HRMS (TOF ES+) *m/z* 357.0679 (calc. 357.0672) $[M]^+$.

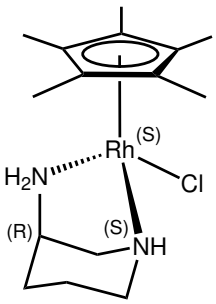
4.3.7 S_C,R_N,S_{Ir} - [(η^5-C_5Me_5)Ir(L2)Cl]Cl



Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 11.5 Hz, 1H), 4.82 (s, 1H), 3.97 (d, *J* = 11.5 Hz, 1H), 3.61 (dd, *J* = 10.9, 5.7 Hz, 1H), 3.25 – 3.16 (m, 2H), 3.07 (tt, *J* = 12.4, 2.7 Hz, 1H), 2.79 (d, *J* = 14.2 Hz, 1H), 2.41 (d, *J* = 11.4 Hz, 1H), 2.19 (m, 1H), 1.80 (s, 15H), 1.74 – 1.43 (m, 2H) ppm. ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$) δ 13C NMR (126 MHz, $CDCl_3$) δ 87.22 (C), 57.29 (CH_2), 52.55 (CH_2), 49.85 (CH), 26.80 (CH_2), 19.77 (CH_2), 9.94 (CH_3) ppm. HMRS (TOF ES+) *m/z* 463.1481 (calc. 463.1492) $[M]^+$.

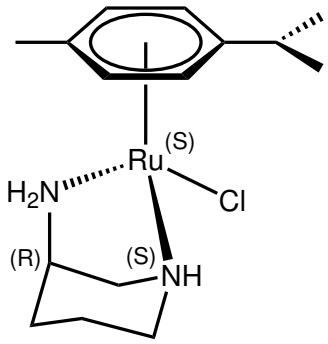
4.3.8 S_C,R_N,S_{Rh} - [(η^5-C_5Me_5)Rh(L2)Cl]Cl



Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 11.0 Hz, 1H), 4.03 (s, 1H), 3.71 (d, *J* = 11.9 Hz, 1H), 3.38 – 3.22 (m, 2H), 3.17 (s br, 1H), 2.96 (t, *J* = 12.4 Hz, 1H), 2.81 (d, *J* = 14.7 Hz, 1H), 2.28 (d, *J* = 11.6 Hz, 1H), 2.20 (m, 1H), 1.84 (s, 15H), 1.80 – 1.69 (m, 1H), 1.43 (t, *J* = 14.1 Hz, 1H). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$) δ 95.80 (d, *J* = 8.3 Hz, C), 56.21 (CH_2), 50.52 (CH_2), 48.75 (CH), 27.15 (CH_2), 19.94 (CH_2), 10.18 (CH_3). HRMS (TOF ES+) *m/z* 373.0919 (calc. 373.0918). HRMS (TOF ES+) $[M]^+$.

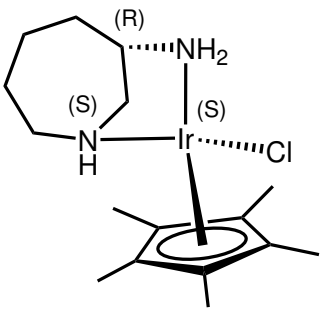
4.3.9 R_C,S_N,S_{Ru} - [(η^6-*p*-cymene)Ru(L2)Cl]Cl



Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 10.4 Hz, 1H), 6.47 (d, *J* = 5.9 Hz, 1H), 5.87 (d, *J* = 5.8 Hz, 1H), 5.30 (d, *J* = 5.7 Hz, 1H), 5.23 (d, *J* = 5.3 Hz, 1H), 4.41 (s, 1H), 3.51 – 3.37 (m, 3H), 3.18 (t, *J* = 11.7 Hz, 1H), 3.08 (s, 1H), 2.97 (s, 1H), 2.85 (d, *J* = 14.3 Hz, 1H), 2.52 (s, 3H), 2.44 – 2.30 (m, 2H), 2.10 (d, *J* = 11.4 Hz, 1H), 1.75 (d, *J* = 15.2 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.31 (d, *J* = 6.9 Hz, 3H).^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$) δ 105.31 (C), 98.63 (C), 84.62 (CH), 83.97 (CH), 82.85 (CH), 82.26 (CH), 55.84 (CH_2), 54.39 (CH_2), 48.74 (CH), 30.60 (CH), 27.16 (CH_2), 23.70 (CH_3), 22.46 (CH_3), 20.00 (CH_2), 19.08 (CH_3). HRMS (TOF ES+) *m/z* 371.0830 (calc. 371.0828) $[M]^+$.

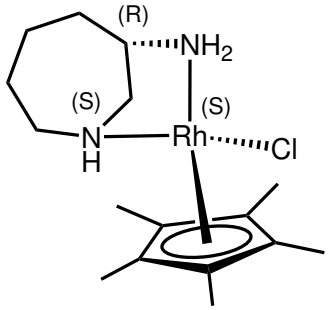
4.3.10 S_C,R_N,S_{Ir} - [(η^5-C_5Me_5)Ir(L3)Cl]Cl



Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 11.7 Hz, 1H), 4.66 (s, 1H), 3.67 (s, 1H), 3.47 – 3.19 (m, 3H), 3.09 (m, 1H), 2.53 (d, *J* = 12.9 Hz, 1H), 2.25 (m, 1H), 1.98 – 1.90 (m, 3H), 1.81 (s, 15H), 1.76 – 1.40 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 87.52, 56.17, 54.77, 53.97, 32.79, 29.05, 22.60, 10.03. HRMS (TOF ES+) *m/z* 477.1640 (calc. 477.1648) $[M]^+$.

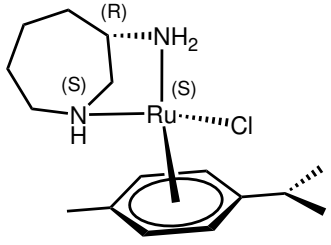
4.3.11 S_C,R_N,S_{Rh} - [(η^5-C_5Me_5)Rh(L3)Cl]Cl



Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 11.1 Hz, 1H), 4.19 (s, 1H), 3.48 (m, 1H), 3.29 (m, 1H), 3.19 (m, 1H), 3.00 (m, 1H), 2.46 (d, *J* = 13.2 Hz, 1H), 2.20 (m, 1H), 1.85 (s, 15H), 2.13 – 1.41 (m, 6H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 95.99 (d, *J* = 8.4 Hz), 54.83, 53.64, 52.07, 33.30, 29.28, 22.53, 10.25. HRMS (TOF ES+) *m/z* 387.1082 (calc. 387.1074) $[M]^+$.

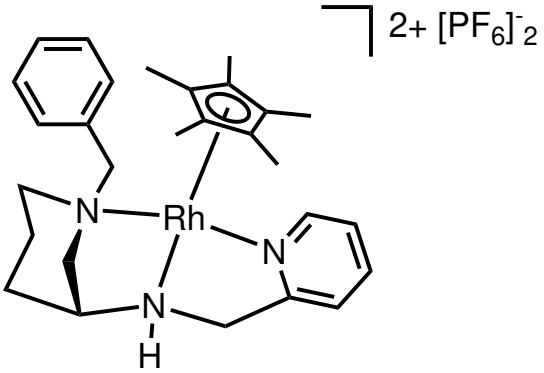
4.3.12 R_C,S_N,S_{Ru} - [(η^6-*p*-cymene)Ru(L3)Cl]Cl



Yield: Quantitative

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 6.11 (d, *J* = 5.9 Hz, 1H), 5.87 (d, *J* = 5.8 Hz, 1H), 5.43 (s, 2H), 4.30 (s, 1H), 3.54 (m, 1H), 3.29 (s, 1H), 3.24 – 3.05 (m, 3H), 2.91 (m, 1H), 2.56 (s, 3H), 2.34 – 1.78 (m, 6H), 1.47 (q, *J* = 12.1 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 108.34, 97.89, 82.63, 82.32 (d, *J* = 5.8 Hz), 80.38, 55.95, 54.34, 53.40, 32.32, 30.90, 29.14, 23.62, 23.02, 21.51, 19.60. HRMS (TOF ES+) *m/z* 385.0990 (calc. 385.0985) $[M]^+$.

4.3.13 [Rh-4][PF_6]$_2$ complex



This complex was synthesised and characterised by Dr Paul Newman in 67& yield *via* the general synthetic procedure detailed in section 4.3.1, with the exception that the required reflux in methanol and the resulting chloride salt was converted to a hexafluorophosphate salt *via* methathesis with excess sodium hexafluorophosphate.

^{1}H NMR (d_6-acetone, 300 MHz): δ 9.14 (d, J 5.5 Hz, 1H), 8.21 (td, J 7.8, 1.4 Hz, 1H), 7.84 (m, 2H), 7.30–7.09 (m, 5H), 6.46 (d, J 4.6 Hz, 1H), 4.90 (dd, J 17.4, 5.7 Hz, 1H), 4.64 (d, J 17.5 Hz, 1H), 4.56 (d, J 13.7 Hz, 1H), 4.25 (d, J 13.3 Hz, 1H), 3.45 (d, J 12.3 Hz, 1H), 3.34 (s br, 1H), 2.59 (m, 1H), 2.14 (m, 1H), 1.75 (s, 15H), 1.38 (m, 1H) ppm. ^{13}C{^{1}H} NMR (d_6-acetone, 75 MHz): δ 161.9 (C), 151.8 (CH), 141.4 (CH), 132.0 (CH), 130.1 (C), 129.2 (CH), 128.4 (CH), 127.9 (CH), 124.6 (CH), 98.8 (d, J 7.9 Hz, C), 65.9 (CH_2), 62.6 (CH), 62.3 (CH_2),

59.5 (CH_2), 55.5 (CH_2), 26.8 (CH_2) 20.4 (CH_2), 8.4 (CH_3) ppm. HRMS (ES): m/z 282.1971 (calc. 282.1970) [L + H]+, 100%.

4.3.14 Attempted synthesis of Ir-6

In a foil-wrapped flask, the ligand (74 mg, 2 equiv.) was dissolved in dichloromethane (30 mL), forming a clear solution. [IrCp*Cl_2]$_2$] (102.2 mg, 1 equiv.) was added to give an orange solution, followed by sodium acetate (70.1 mg, 4 equiv.). The reaction was stirred at r.t. for 22 h to give a cloudy yellow solution, which was filtered through 0.45 µm PTFE filter to give a clear yellow solution. The solvent was then removed *in vacuo*, giving a yellow oil. Dissolving the oil in diethyl ether, sonicating, and removing the solvent in vacuo yielded a sticky yellow/amber solid. The latter was subjected to three cycles of hexane (10 cm^3), sonication (10 min), and filtration, until no solids remained in the flask. The resulting orange solid was washed with hexane (3×5 cm^3). All the solids were then collected from the filter in a new flask by dissolving in dichloromethane (10 cm^3), with further removal of the solvent, subsequent addition of hexane (10 cm^3), brief (1-2 min) sonication, removal of the solvent *in vacuo* and gentle heating (heat gun) under vacuum produced an orange solid (137.80, 38% yield). However, spectroscopic analysis of the product using ^{1}H NMR showed this to be impure, with analysis not possible.

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Appendix

A.4 ORCA input scripts used

Note: Parameters that have not been explicitly defined should be taken as defined by default in ORCA 5.0.4.

A.4.1 DFT calculations from Chapter 2

A.4.1.1 Commands used to run step 1 of the calculations.

```
! r2SCAN-3c cpcm(thf) tightopt freq kdiis defgrid3
```

A.4.1.2 Commands used to run step 2 of the calculations.

```
! wb97m-v def2-qzvpp cpcm(thf) kdiis defgrid3
%method functional hyb_mgga_xc_wb97m_v end
```

A.4.1.3 Modified "%geom" block used for the transition state calculations.

```
%geom
```

```
calc_hess true
TS_Mode {B [atom1] [atom2]} end
end
```

A.4.2 DFT calculations from Chapter 3

A.4.2.1 Commands used to run step 1 of the calculations of the main catalytic cycles.

```
! r2SCAN-3c cpcm(ethanol) verytightopt verytightscf freq kdiis defgrid3
%geom enforcestrictconvergence true end
%freq temp 353.15 end
%scf convcheckmode 0 end
```

A.4.2.2 Commands used to run step 1 of the diastereomer selectivity calculations.

```
! r2SCAN-3c cpcm(ch2cl2) verytightopt verytightscf freq kdiis defgrid3
%geom enforcestrictconvergence true end
%scf convcheckmode 0 end
```

A.4.2.3 caption=Commands used to run step 2 of the calculations of the main catalytic cycles.

```
! wb97m-v def2-qzvppd cpcm(ethanol) verytightscf kdiis defgrid3
%scf convcheckmode 0 end
%method functional hyb_mgga_xc_wb97m_v end
```

A.4.2.4 Commands used to run step 2 of the diastereomer selectivity calculations.

```
! wb97m-v def2-qzvppd cpcm(ch2cl2) verytightscf kdiis defgrid3
%scf convcheckmode 0 end
%method functional hyb_mgga_xc_wb97m_v end
```

A.4.2.5 Modified "%geom" block used for the transition state calculations.

```
%geom
calc_hess true
ts_active_atoms { [list of "active" transition state atoms] } end
ts_active_atoms_factor 1.5
enforcestrictconvergence true
end
```

A.4.2.6 General input script used for the nudged elastic band calculations.

```
! zoom-neb-ci r2SCAN-3c cpcm(ethanol) kdiis %maxcore 4000
%pal nprocs 40 end
%neb
product [product geometry xyz file enclosed in ""]
preopt true
free_end true
nimages 20
reparam 10
opt_method fire
printlevel 4
```

```
end
```

A.5 Energies of species from the density functional calculations.

Explanatory note for the energies presented in the tables below.

- **E_{el}(r^2SCAN-3c)** = Electronic energy from the geometry optimisation step at the r^2SCAN-3c level
- **G(r^2SCAN-3c)** = Total free energy from the frequency calculation step at the r^2SCAN-3c level
- **G_{corr}(r^2SCAN-3c)** = Free energy thermal correction from the calculation at the r^2SCAN-3c level
- **E_{el}(ωB97M-V)** = Electronic energy from the single point calculation of the optimised geometry at the wB97M-V/Def2-QZVPPD level.
- **Final G** = Final free energy

Table A.1: Energies of the species used for the In/Ga/Al(Salpy) ROCOP propagation cycles in E_h. Calculated in Orca 5.0.4 at the ωB97M-V/def2-QZVPP/CPCM(DCM) // r^2SCAN-3c/CPCM(THF)/298.15 K

Compound	E_{el}(r^2SCAN-3c)	G(r^2SCAN-3c)	G_{corr}(r^2SCAN-3c)	E_{el}(ωB97M-V)	Final G
In - INT0	-1850.96563549	-1850.53580280	0.42983269	-1851.31912157	-1850.88928888
In - INT1	-1622.35817113	-1621.97197054	0.38620059	-1622.64469971	-1622.25849912

In - INT1-PY	-1622.35915161	-1621.97185963	0.38729198	-1622.64615913	-1622.25886715
In - INT2	-1776.11941760	-1775.67817738	0.44124022	-1776.44842209	-1776.00718187
In - TS1	-2004.69952946	-2004.21593345	0.48359601	-2005.08816184	-2004.60456583
In - INT3	-2004.75481719	-2004.26721703	0.48760016	-2005.14938387	-2004.66178371
In - INT4	-1776.13676519	-1775.69326438	0.44350081	-1776.46520332	-1776.02170251
In - INT4-PY	-1776.15223166	-1775.70765832	0.44457334	-1776.47924724	-1776.03467390
In - INT5	-2156.63997095	-2156.12423297	0.51573798	-2157.08301873	-2156.56728075
In - TS2	-2156.63704134	-2156.11899545	0.51804589	-2157.07765209	-2156.55960620
In - INT6	-2156.64916471	-2156.12942122	0.51974349	-2157.09423774	-2156.57449425
In - INT6-PY	-2156.65130051	-2156.13066894	0.52063157	-2157.09423660	-2156.57360503
In - TS3	-2156.64275243	-2156.12285246	0.51989997	-2157.08519356	-2156.56529359
In - INT7	-2156.65820080	-2156.13824874	0.51995206	-2157.10235223	-2156.58240017
In - INT8	-2156.65833691	-2156.14147979	0.51685712	-2157.10119036	-2156.58433324
In - INT8-PY	-2156.67247993	-2156.15346613	0.51901380	-2157.11484436	-2156.59583056
Ga - INT0	-3585.63020837	-3585.19680144	0.43340693	-3586.05321243	-3585.61980550
Ga - INT1	-3357.02986496	-3356.63985779	0.39000717	-3357.38495351	-3356.99494633

Ga - INT1-PY	-3357.03230702	-3356.64086510	0.39144192	-3357.38718336	-3356.99574144
Ga - INT2	-3510.78970187	-3510.34400392	0.44569795	-3511.18788305	-3510.74218510
Ga - TS1	-3739.36893051	-3738.88067390	0.48825661	-3739.82689984	-3739.33864322
Ga - INT3	-3739.42182333	-3738.93045179	0.49137155	-3739.88546640	-3739.39409485
Ga - INT4	-3510.81814684	-3510.37085615	0.44729069	-3511.21389366	-3510.76660298
Ga - INT4-PY	-3510.82589256	-3510.37805304	0.44783952	-3511.22119025	-3510.77335073
Ga - INT5	-3891.31967352	-3890.80200478	0.51766874	-3891.83044263	-3891.31277389
Ga - TS2	-3891.30791101	-3890.78672308	0.52118793	-3891.81695277	-3891.29576484
Ga - INT6	-3891.32433294	-3890.80143243	0.52290051	-3891.83762303	-3891.31472252
Ga - INT6-PY	-3891.32076900	-3890.79634245	0.52442655	-3891.83168968	-3891.30726313
Ga - TS3	-3891.31364788	-3890.79023596	0.52341192	-3891.82330145	-3891.29988953
Ga - INT7	-3891.32686692	-3890.80299555	0.52387137	-3891.83900805	-3891.31513668
Ga - INT8	-3891.33799273	-3890.81727148	0.52072125	-3891.84799651	-3891.32727526
Ga - INT8-PY	-3891.34358778	-3890.82253025	0.52105753	-3891.85403732	-3891.33297979
Al - INT0	-1903.29830535	-1902.86097249	0.43733285	-1903.79126052	-1903.35392767
Al - INT1	-1674.69255485	-1674.29904660	0.39350826	-1675.11871428	-1674.72520602

Al - INT1-PY	-1674.69868738	-1674.30400678	0.39468060	-1675.12367647	-1674.72899587
Al - INT2	-1828.45582615	-1828.00614740	0.44967875	-1828.92423560	-1828.47455685
Al - TS1	-2057.03604447	-2056.54432989	0.49171458	-2057.56431653	-2057.07260195
Al - INT3	-2057.09003065	-2056.59561781	0.49441285	-2057.62348085	-2057.12906800
Al - INT4	-1828.48124555	-1828.03085341	0.45039214	-1828.94779721	-1828.49740507
Al - INT4-PY	-1828.49141604	-1828.04026145	0.45115459	-1828.95694678	-1828.50579219
Al - INT5	-2208.97598983	-2208.45377812	0.52221171	-2209.55772332	-2209.03551161
Al - TS2	-2208.97240464	-2208.44799420	0.52441044	-2209.55208268	-2209.02767224
Al - INT6	-2208.98710660	-2208.46190101	0.52520559	-2209.57067375	-2209.04546816
Al - INT6-PY	-2208.98644233	-2208.45883365	0.52760869	-2209.56758708	-2209.03997839
Al - TS3	-2208.97555797	-2208.44912530	0.52643266	-2209.55622180	-2209.02978913
Al - INT7	-2208.99342845	-2208.46623985	0.52718860	-2209.57559088	-2209.04840228
Al - INT8	-2209.00060453	-2208.47674458	0.52385996	-2209.58159220	-2209.05773224
Al - INT8-PY	-2209.00985079	-2208.48573901	0.52411178	-2209.59032410	-2209.06621232
Succinic anhydride	-380.48976296	-380.44150680	0.04825616	-380.60404714	-380.55579098
Ethylene oxide	-153.75939163	-153.72643912	0.03295251	-153.80048133	-153.76752882

Acetate	-228.58256023	-228.56160008	0.02096015	-228.64967895	-228.62871880

Table A.2: Energies of the diastereomers of the Ru/Rh/Ir azacycle complexes in E_h. Calculated in Orca 5.0.3 at the ωB97M-V/def2-QZVPPD/CPCM(DCM) // r^{2}SCAN-3c/CPCM(DCM)/298.15 K

Compound	**E_{el}(r^{2}SCAN-3c)**	**G(r^{2}SCAN-3c)**	**G_{corr}(r^{2}SCAN-3c)**	**E_{el}(ωB97M-V)**	**Final G**
S_C,R_N,R_{Ir} - [(η^5-C_5Me_5)Ir(L1)Cl]$^+$	-1222.45306802	-1222.12479221	0.32827582	-1222.51547629	-1222.18720047
S_C,R_N,S_{Ir} - [(η^5-(Cp*)Ir(L1)Cl]$^+$	-1222.45155404	-1222.12321923	0.32833481	-1222.51352595	-1222.18519115
R_C,S_N,S_{Ir} - [(η^5-(Cp*)Ir(L2)Cl]$^+$	-1261.76068297	-1261.40338997	0.35729300	-1261.82975980	-1261.47246680
R_C,S_N,R_{Ir} - [(η^5-(Cp*)Ir(L2)Cl]$^+$	-1261.75504654	-1261.39856228	0.35648426	-1261.82382420	-1261.46733994
R_C,S_N,S_{Ir} - [(η^5-(Cp*)Ir(L3)Cl]$^+$	-1301.05641190	-1300.67197261	0.38443928	-1301.13288310	-1300.74844381

R_C,S_N,R_{Ir} - [(η^5-(Cp*)Ir(L3)Cl]$^+$	-1301.05101857	-1300.66664674	0.38437183	-1301.12723668	-1300.74286485
S_C,R_N,R_{Ru} - [(η^6-*p*-cymene)Ru(L1)Cl]$^+$	-1212.40896311	-1212.08566044	0.32330267	-1212.47260095	-1212.14929828
S_C,R_N,S_{Ru} - [(η^6-*p*-cymene)Ru(L1)Cl]$^+$	-1212.40860648	-1212.08546394	0.32314254	-1212.47192364	-1212.14878111
R_C,S_N,S_{Ru} - [(η^6-*p*-cymene)Ru(L2)Cl]$^+$	-1251.71882435	-1251.36689640	0.35192795	-1251.78976356	-1251.43783561
R_C,S_N,R_{Ru} – [(η^6-*p*-cymene)Ru(L2)Cl]$^+$	-1251.71171404	-1251.36048218	0.35123186	-1251.78193665	-1251.43070479
R_C,S_N,S_{Ru} - [(η^6-*p*-cymene)Ru(L3)Cl]$^+$	-1291.01301726	-1290.63369460	0.37932266	-1291.09142053	-1290.71209787
R_C,S_N,R_{Ru} - [(η^6-*p*-cymene)Ru(L3)Cl]$^+$	-1291.00722306	-1290.62872335	0.37849971	-1291.08481713	-1290.70631742
S_C,R_N,R_{Rh} - [(η^5-C_5Me_5)Rh(L1)Cl]$^+$	-1228.67644580	-1228.34892547	0.32752033	-1228.72904711	-1228.40152678

S_C,R_N,S_{Rh} - [(η^5-(Cp*)Rh(L1)Cl]$^+$	-1228.67549118	-1228.34782981	0.32766138	-1228.72778765	-1228.40012627
R_C,S_N,S_{Rh} - [(η^5-(Cp*)Rh(L2)Cl]$^+$	-1267.98407667	-1267.62719250	0.35688417	-1268.04313340	-1267.68624923
R_C,S_N,R_{Rh} - [(η^5-(Cp*)Rh(L2)Cl]$^+$	-1267.97920425	-1267.62356129	0.35564296	-1268.03828184	-1267.68263889
R_C,S_N,S_{Rh} - [(η^5-(Cp*)Rh(L3)Cl]$^+$	-1307.27900739	-1306.89494678	0.38406061	-1307.34545108	-1306.96139047
R_C,S_N,R_{Rh} - [(η^5-(Cp*)Rh(L3)Cl]$^+$	-1307.27476341	-1306.89045924	0.38430417	-1307.34124490	-1306.95694073

Table A.3: Energies of the species used for the transfer hydrogenation catalytic cycles in E_h. Calculated in Orca 5.0.4 at the ωB97M-V/def2-QZVPPD/CPCM(Ethanol) // r^{2}SCAN-3c/CPCM(Ethanol)/353.15 K. ACP = acetophenone.

Compound	**E_{el}(r^{2}SCAN-3c)**	**G(r^{2}SCAN-3c)**	**G_{corr}(r^{2}SCAN-3c)**	**E_{el}(ωB97M-V)**	**Final G**
Ru - INT0	-1251.72535202	-1251.38574154	0.33961049	-1251.79638306	-1251.45677258
Ru - INT1A	-1251.22940897	-1250.90615336	0.32325561	-1251.29611299	-1250.97285738

Ru - INT1B	-1251.22915156	-1250.90602513	0.32312644	-1251.29706832	-1250.97394188
Ru - INT2	-790.36486625	-790.05559642	0.30926983	-790.40307966	-790.09380983
Ru - TS1	-984.68855707	-984.28065056	0.40790651	-984.76562330	-984.35771679
Ru - INT3	-791.57317763	-791.24212507	0.33105256	-791.61205107	-791.28099851
Ru - TS2 (R)	-1176.39091862	-1175.93398301	0.45693562	-1176.52279098	-1176.06585536
Ru - TS2 (S)	-1176.39083551	-1175.93413822	0.45669729	-1176.52255831	-1176.06586102
Rh - INT0	-1267.99035274	-1267.64660409	0.34374866	-1268.04943402	-1267.70568536
Rh - INT1A	-1267.49118516	-1267.16409977	0.32708539	-1267.54862788	-1267.22154249
Rh - INT1B	-1267.49114562	-1267.16354675	0.32759887	-1267.54985742	-1267.22225854
Rh - INT2	-806.62819920	-806.31476029	0.31343892	-806.65905810	-806.34561918
Rh - TS1	-1000.94920701	-1000.53699947	0.41220754	-1001.01717911	-1000.60497158
Rh - INT3	-807.83649514	-807.50055967	0.33593547	-807.87008384	-807.53414837
Rh - TS2 (R) ACP	-1192.65137592	-1192.18948453	0.46189139	-1192.77434608	-1192.31245469
Rh - TS2 (R) 4-OCH_3 ACP	-1307.15998636	-1306.66965735	0.49032902	-1307.31443494	-1306.82410593

Rh - TS2 (R) 4-^{t}Bu ACP	-1349.85941917	-1349.29341004	0.56600913	-1350.00969620	-1349.44368707
Rh - TS2 (R) 4-F ACP	-1291.89748733	-1291.44524338	0.45224396	-1292.04786490	-1291.59562094
Rh - TS2 (R) 4-CN ACP	-1284.88566262	-1284.42803649	0.45762613	-1285.04844403	-1284.59081790
Rh - TS2 (S) ACP	-1192.64945319	-1192.18722527	0.46222792	-1192.77074790	-1192.30851998
Acetone	-193.11807988	-193.06935007	0.04872981	-193.16462550	-193.11589570
Acetophenone	-384.81733508	-384.72045550	0.09687959	-384.91763923	-384.82075964
4-OCH_3 ACP	-499.32853825	-499.20350834	0.12502991	-499.46019472	-499.33516480
4-^{t}Bu ACP	-542.02614804	-541.82565900	0.20048904	-542.15374125	-541.95325221
4-F ACP	-484.06357220	-483.97662368	0.08694852	-484.19119357	-484.10424505
4-CN ACP	-477.04742765	-476.95531534	0.09211231	-477.18805292	-477.09594061
Chloride anion	-460.35379340	-460.37208371	-0.01829031	-460.38137116	-460.39966147
2-propanol	-194.31650198	-194.24327836	0.07322362	-194.35810717	-194.28488355
(R)-1-phenylmethanol	-386.01392901	-385.89450012	0.11942889	-386.11063719	-385.99120830

(S)-1-phenylmethanol	-386.01392860	-385.89449894	0.11942966	-386.11063680	-385.99120714
t-butoxide anion	-233.10289129	-233.01792206	0.08496923	-233.15752627	-233.07255704
t-butanol	-233.62331050	-233.52476937	0.09854112	-233.67123216	-233.57269103

Table A.4: Imaginary vibrational modes for the transition states from Chapters 2 and 3. Calculated in Orca 5.0.4 at the ωB97M-V/def2-QZVPP/CPCM(DCM) // r^2SCAN-3c/CPCM(THF)/298.15 K (Chapter 2) ; ωB97M-V/def2-QZVPPD/CPCM(Ethanol) // r^2SCAN-3c/CPCM(Ethanol)/353.15 K (Chapter 3). ACP = acetophenone.

Compound	**Frequency (cm^{-1})**
In - TS1	-442.33
In - TS2	-153.75
In - TS3	-107.71
Ga - TS1	-440.58
Ga - TS2	-173.92
Ga - TS3	-153.80
Al - TS1	-439.30
Al - TS2	-147.80
Al - TS3	-188.02
Ru - TS1	-310.03
Ru - TS2 (R)	-324.08
Ru - TS2 (S)	-247.27
Rh - TS1	-325.40
Rh - TS2 (R) ACP	-392.30
Rh - TS2 (R) 4-OCH_3 ACP	-391.23
Rh - TS2 (R) 4-^{t}Bu ACP	-398.08
Rh - TS2 (R) 4-F ACP	-391.89
Rh - TS2 (R) 4-CN ACP	-345.41
Rh - TS2 (S) ACP	-177.58

A.6 Optimised geometries

A.6.1 Cartesian coordinates for the optimised geometries for the In(Salpy) ROCOP propagation cycle

DFT Cartesian coordinates A.1: In(Salpy) ROCOP propagation cycle - INT0

```
Charge: -1

Multiplicity: 1

Number of atoms: 64


  In -0.76018987331911 0.56555417320251 0.17338656244003

  O -2.41795577470684 0.28793458600971 -1.21043449661657

  O -0.34505555583221 2.47229516446921 -0.68591036148662

  N 3.48963410383343 -2.13053912185173 -1.26848532159228

  N -0.96998844906338 -1.68626548027991 0.28260840039761

  N 0.83461019234910 -0.11157361487572 -1.32239105785572

  C 0.84563804442036 -3.92701140323649 -1.34147596991477

  H -0.22513237816157 -4.01259414568287 -1.56332989917841

  H 1.12591858039874 -4.73702909006754 -0.66077618421422

  H 1.40477256454365 -4.04783886467215 -2.27545934357623

  C 1.14585873807946 -2.55654088586265 -0.70089161276223

  C 2.62655338344045 -2.52856502762086 -0.32343238682722

  C 3.06989594836500 -2.97116069582674 0.92852136477093

  H 2.36788228782892 -3.31926050993404 1.67919807947227

  C 4.42992332758601 -2.97159874712318 1.20828318118874

  H 4.78792621003702 -3.30939416161840 2.17692999193707

  C 5.32089390444200 -2.53489310892521 0.23392370913266

  H 6.39159382290792 -2.51166115413748 0.41178063052269
```

C 4.79872229996066 -2.13144051413077 -0.98798090805813

H 5.46035553633785 -1.79177624006546 -1.78485222556121

C 0.26188023605202 -2.39366335978421 0.58057422293222

H 0.05730934240662 -3.38530464376318 1.01128151704308

H 0.80431168948060 -1.79685079690606 1.31962567911061

C -2.08662745803115 -2.32150002973888 0.17447063245349

H -2.11017845056214 -3.39337852873978 0.42147282115301

C -3.33344765141042 -1.74830203031598 -0.25901651062508

C -4.49145635624080 -2.53241211899626 -0.07085762401573

H -4.38247078257908 -3.49821240240648 0.41966521844347

C -5.73893730322593 -2.10372614005628 -0.47699079622297

C -5.84715137844101 -0.86050378054849 -1.11949161515622

H -6.82182119744954 -0.50681522632639 -1.44808745874656

C -4.73221229415857 -0.07688910217647 -1.34500029296195

C -3.43705191269707 -0.47858666180318 -0.92872777954036

H -6.61768632527380 -2.71800502133991 -0.30864480257224

H -4.81816841952900 0.88187169102302 -1.84973624644977

C 0.81440622509003 -1.49757498181278 -1.78208742156901

H 1.50717495883916 -1.63764064107589 -2.61936350098404

H -0.20092299942528 -1.70703995845318 -2.14164199502455

C 1.79919512481139 0.65560638506189 -1.70168566790971

H 2.60387848461554 0.22377480191673 -2.31149811739969

C 1.93643832896240 2.06001198225627 -1.40315767280053

C 3.19052587101540 2.63927052081349 -1.69416581242968

H 3.97520216077402 1.99142673446628 -2.08147350596078

C 3.44217057990282 3.98170400998836 -1.49392441077410

C 2.40469565521948 4.79624043926492 -1.01454904987181

```
  H 2.58163713747589 5.85736910737557 -0.85432158575359
  C 1.15683343944127 4.26997732382012 -0.74328514937767
  C 0.87237125443092 2.89295085685006 -0.91848980051200
  H 4.41922276814276 4.40066932456064 -1.71278697587027
  H 0.35246189973235 4.90088348392482 -0.37466985190824
  O 0.88676625583678 0.51077928718425 1.60034664134851
  O -2.20925336245537 0.73970125972473 1.76373523660937
  C -3.19949839878125 1.57086412001825 1.90268880795643
  C -3.24236776606294 2.75971482223433 0.96081228897567
  H -2.32218497658072 3.34457736881439 1.06632410209797
  H -3.28018185731436 2.40965686880415 -0.07681883665467
  H -4.10813991764924 3.39049206802734 1.16971809258631
  O -4.06980207102967 1.42091922582352 2.77016703701040
  C 1.16950850509659 1.54049957164208 2.34018572930545
  O 0.48039122257220 2.56189115077963 2.43158668118208
  C 2.47948095261850 1.40812504566841 3.09860631689379
  H 2.55350670231695 0.42346324912784 3.56952851760183
  H 3.30631933403123 1.49086447154167 2.38349032568870
  H 2.57801583658488 2.19445909576053 3.84898046048043
```

DFT Cartesian coordinates A.2: In(Salpy) ROCOP propagation cycle - INT1

```
Charge: 0
Multiplicity: 1
Number of atoms: 57

  In -1.05595363889016 1.06149072985311 0.25631339781745
  O -2.85770558899950 1.11833348747644 -0.84255937271098
  O -0.40214140929076 3.01116168654192 -0.20918796466827
```

N 3.07894936291401 -1.77655710085434 -0.73650595309084

N -1.44837937449761 -1.11848847846249 0.41008440539371

N 0.62846045228391 0.35672621383286 -0.99250317925016

C 0.24985648520628 -3.43503714569571 -1.17628153073359

H -0.80459106898223 -3.38607398913941 -1.47372661738296

H 0.38489805437908 -4.29313615443186 -0.51092347468150

H 0.85544248097937 -3.59400355342875 -2.07494204969254

C 0.66491732004251 -2.13145444498499 -0.46578602250392

C 2.10381394927844 -2.28766896490990 0.02483250848436

C 2.38494290400208 -2.99281714779783 1.20118093343892

H 1.58523826599671 -3.41907018705502 1.79931939114222

C 3.70518068741209 -3.15413383617704 1.59706139522882

H 3.94100802487000 -3.69853796380478 2.50720609617155

C 4.71685732832930 -2.61052966178041 0.81158077679308

H 5.76282367348454 -2.70902938965398 1.08490546498840

C 4.35062313829430 -1.93554510355366 -0.34467880206168

H 5.11012825445153 -1.49891597056410 -0.99281764497546

C -0.27478910053259 -1.90223159645009 0.76425840005793

H -0.56885446356223 -2.87347629348494 1.18565965922824

H 0.27012403460090 -1.34668276216869 1.53656073997226

C -2.60335240441358 -1.67672905892441 0.26044055664113

H -2.69320080255895 -2.74960530345330 0.47932338934321

C -3.80926772652189 -1.02784692491656 -0.17508669705998

C -4.98511987012172 -1.81282680100399 -0.12384532099165

H -4.90639561966354 -2.82706833445276 0.26275884868610

C -6.20626544262097 -1.33014202171981 -0.54127780759015

C -6.27652932113508 -0.02279306083091 -1.04736123353888

```
H -7.23069325632800 0.37483248277825 -1.38465988487890
C -5.14901531924017 0.76984145615748 -1.12661948891596
C -3.88117932015777 0.30888667755120 -0.69790361273903
H -7.09471168273331 -1.95060444250665 -0.48581384455558
H -5.20378925514097 1.77978185001747 -1.52322145107576
C 0.53728273701976 -1.00746620034916 -1.51869349839411
H 1.29377658424702 -1.16806946361866 -2.29343387598198
H -0.45041745955599 -1.10774586937760 -1.98722810217245
C 1.64963094713877 1.08969172623029 -1.29861624715769
H 2.45535136877509 0.62465697891092 -1.87862188357765
C 1.85076200534754 2.47336982192485 -0.96450580950145
C 3.13837524154273 2.98882414072148 -1.24345211112074
H 3.88506704322157 2.30683684676006 -1.64565158220621
C 3.46446923276340 4.30819885511994 -1.01521554056168
C 2.47565059771117 5.16955754983291 -0.51492748619811
H 2.71183884770933 6.21551187954238 -0.33449058419145
C 1.20090729192931 4.70987046057320 -0.25063865802069
C 0.83975074482182 3.35681535994667 -0.45613666778233
H 4.46281298922892 4.67625163855059 -1.22802674164182
H 0.43345828873440 5.37867853146611 0.12897049110070
O 0.09902433946548 1.05016707811894 2.25701233073330
C -0.94031534872926 1.46777351672638 2.85917698002575
O -2.02049129578315 1.66116161360000 2.20785553774820
C -0.89513640349290 1.76798465148280 4.32792095164252
H -0.10405989004036 1.19858126935250 4.81787824860987
H -0.67784433685538 2.83589326736806 4.44679669212364
H -1.86322327633338 1.56840745511503 4.79124354623474
```

DFT Cartesian coordinates A.3: In(Salpy) ROCOP propagation cycle - INT1-PY

```
Charge: 0

Multiplicity: 1

Number of atoms: 57


  In -0.20950706695453 0.04933652482698 0.57612323351401

  O 0.43023311224524 2.02615428301951 1.00533901360665

  O -2.17063100261401 0.65476819863175 -0.01623024561906

  N 1.87326870193231 -0.95080739332741 0.90407228490138

  N 0.86961690978412 0.35268542491897 -1.37960188502188

  N -0.77587129302505 -1.89917327019540 -0.33525069059406

  C 2.27846974719101 -3.07864454111968 -2.17205888862869

  H 3.19540632960968 -2.66091159624766 -2.59631717889080

  H 1.61249013120319 -3.33242813110569 -3.00290114400814

  H 2.52498005897987 -4.00227274549725 -1.63772933939576

  C 1.57211395510334 -2.07714363228187 -1.24923119964505

  C 2.46587304546994 -1.64787395031128 -0.08959644493188

  C 3.81726585881164 -1.97374496140119 0.00052280239693

  H 4.30211848822477 -2.53866842533431 -0.78539375775398

  C 4.54843389493180 -1.58104546085028 1.11660382019209

  H 5.60209117320034 -1.83435256477362 1.19013105572505

  C 3.91943149372635 -0.87390380123729 2.13226860140244

  H 4.45192690219159 -0.55579776115761 3.02207826200358

  C 2.57471516340911 -0.57631189495738 1.98341953960741

  H 2.02569193310692 -0.02517172641815 2.74327252629128

  C 1.17558494447584 -0.85825761550165 -2.13867259229823

  H 1.99356871425277 -0.66071030903504 -2.84452317443154
```

```
H 0.29090694520876 -1.15408468149795 -2.72178647453528
C 1.29911683263280 1.48677794754108 -1.82272767404212
H 1.83540208365058 1.49890518906024 -2.78207939661425
C 1.15521125072696 2.77242603137605 -1.19418556257951
C 1.52438696540485 3.88777977921005 -1.98128968338023
H 1.86285614371203 3.70585270874819 -2.99947488455165
C 1.45714715469535 5.17802737146906 -1.50056863771970
H 1.73682278380330 6.01764568812582 -2.12849718658615
C 1.02819002405239 5.38304970887622 -0.18010045420688
H 0.97205147367897 6.39307427240091 0.21878501184619
C 0.68064254495161 4.31784060400374 0.62670638812656
H 0.35897173146791 4.47616169892992 1.65247164179663
C 0.72959120863698 2.98174683833518 0.16009136218774
C 0.31281572954046 -2.80871875430685 -0.68856025814975
H -0.03845099654253 -3.52110277807022 -1.44689224041988
H 0.61135356543338 -3.38534263473290 0.19855853702149
C -1.99366011942622 -2.28408966404246 -0.53822903435439
H -2.15302097916644 -3.29811399233325 -0.93046059826325
C -3.19259798094981 -1.52658457797203 -0.31142029874928
C -4.40832323924195 -2.24209913731730 -0.41410619706412
H -4.35995195043010 -3.30921437027243 -0.62247742453793
C -5.63192251703384 -1.62979322382485 -0.24833339497683
H -6.55091806362620 -2.20226729015637 -0.32004822953568
C -5.66718197357438 -0.24930642048225 0.00544654726351
H -6.62412599571004 0.25068641761450 0.13467620822079
C -4.50289988432020 0.48798274925961 0.08814599555045
H -4.53116709651954 1.55838242760859 0.27325594447483
```

```
  C -3.22878405049400 -0.11246849857228 -0.06422341772393
  O -0.55822292359316 -0.52297759962513 2.59792553442099
  C -1.24881310387089 0.01968115475701 3.56758898701326
  O -1.26666171799734 -0.47155590481740 4.69863051019208
  C -2.05012821772455 1.26498154415689 3.24651850199650
  H -2.44743364460705 1.70952716344096 4.16039365328385
  H -1.43712122452679 1.99330808501533 2.70661377079765
  H -2.88235195349756 0.99315749744977 2.58732785537654
```

DFT Cartesian coordinates A.4: In(Salpy) ROCOP propagation cycle - INT2

```
Charge: 0
Multiplicity: 1
Number of atoms: 64


  In -0.74824060110291 0.34889607346442 0.18579716629477
  O -2.42243235268661 0.39658674819775 -1.13009929916882
  O -0.05481542000303 2.33792474310763 0.03564765051224
  N 3.44318456971991 -1.75314328888081 -0.78657860518070
  N -1.07042299319935 -1.85532940122890 0.14807572220982
  N 0.85723273050790 -0.17512222071265 -1.26139992453689
  C 1.09283279454153 -3.98743623713949 -1.45934918091063
  H 0.08733133196614 -4.13730623615346 -1.87077900498466
  H 1.31734313092668 -4.81708371126247 -0.78241856366029
  H 1.81512601510612 -4.00553505038845 -2.28217850393680
  C 1.15948174610629 -2.64330184681395 -0.70213970469521
  C 2.56073399056378 -2.50183825751379 -0.11327997112660
  C 2.91750165807118 -3.18519470762335 1.05567643430640
  H 2.19902613769199 -3.81479519117341 1.57286402012470
```

C 4.20893802972402 -3.06030040655144 1.54752280970067

H 4.50256663958108 -3.58193692116470 2.45421333800943

C 5.11789024415322 -2.26046240245114 0.86113964479492

H 6.13639889768100 -2.12855206665902 1.21299346752583

C 4.68758282706577 -1.63740002781098 -0.30241130920868

H 5.37049645025362 -1.01392507682515 -0.87910682468765

C 0.08976136294500 -2.67690283272582 0.45244636311644

H -0.21263596956109 -3.71624942242806 0.64131972244216

H 0.53389776384329 -2.28419132161396 1.37167174420339

C -2.22043456624453 -2.40006003419769 -0.07246159586868

H -2.30858554303061 -3.48791976072522 0.05372707113307

C -3.42324178932666 -1.72233677007882 -0.47616325784272

C -4.61165559601012 -2.48635051885367 -0.43115001355278

H -4.54987374234576 -3.50998633411859 -0.06684894415851

C -5.82810496950868 -1.96887619514610 -0.82289023603320

C -5.87782816725562 -0.65120795660843 -1.30225468516883

H -6.82798901929567 -0.22764201488119 -1.61865998381053

C -4.73379963074265 0.11861774512660 -1.38388604299431

C -3.47217064943792 -0.37748559007152 -0.97891234885663

H -6.72866052602898 -2.57173397659648 -0.76820487758113

H -4.77155728884855 1.13538990289815 -1.76541470787706

C 0.87335620631221 -1.55436153919082 -1.75972942067491

H 1.61342945322455 -1.65080831670909 -2.56172578447813

H -0.11407612549838 -1.76524345340038 -2.19103767406588

C 1.67803724702926 0.67109880940107 -1.79402790123360

H 2.37840679249293 0.29065892440666 -2.54699745563907

C 1.79929791939444 2.07674869039221 -1.52036445799342

```
C 2.85035637037694 2.73985023741548 -2.19823243526380
H 3.48189152741676 2.15159488385397 -2.86084243880869
C 3.08994556431552 4.08736260924772 -2.03958813686085
C 2.25628659183867 4.82388790633304 -1.18373444102580
H 2.42790685673325 5.88884168433032 -1.04716991041693
C 1.21544246383672 4.21600096846101 -0.51093107071838
C 0.94955003624188 2.83232712921589 -0.64669624419978
H 3.90488803925467 4.57021116570859 -2.56879590794712
H 0.56772401254440 4.78605636062013 0.14939380941029
O -1.83342648726663 0.54602483094061 2.00137553900420
C -2.78178320384399 1.37030617747259 2.36610248514171
C -3.08802954152005 2.53282474156731 1.44361190252964
H -2.21394687357084 3.19128750826483 1.39231811526114
H -3.27950490306627 2.17523434585922 0.42629439604252
H -3.94843370133116 3.09616222664485 1.80779539975392
O -3.38967670284579 1.22261523352892 3.42859270699905
O 0.93633458142396 -0.00185241229513 1.83466000941246
C 1.29615094378309 1.05950392211191 2.76113343335853
C 2.28503824586007 0.54344855479182 1.81340130976860
H 1.32188320481553 0.73442657689659 3.79822268449901
H 0.81365482849805 2.01162168738717 2.55193826972845
H 3.03902800471388 -0.16556191396401 2.14908813840366
H 2.52439115301656 1.12592302631173 0.92643751148073
```

DFT Cartesian coordinates A.5: In(Salpy) ROCOP propagation cycle - TS1

```
Charge: -1
Multiplicity: 1
Number of atoms: 71
```

```
In 0.59091970218662 -0.19310379119518 0.67996316898874
O 1.65914194535535 -1.77584528620332 1.67760827888253
O 0.45331518518589 1.12194705624560 2.34232537701649
N -4.42618190193451 -1.27385360748279 -0.21162933120903
N 0.24483849016985 -1.80666555965678 -0.83190958946893
N -1.48648566623474 -0.82530740599821 1.27060590227904
C -2.45719628829878 -3.67352820220567 -1.07433672917264
H -1.54964388492345 -4.25664314903560 -0.87628567399876
H -2.72547822964710 -3.79429449560653 -2.12847064144481
H -3.26935824241728 -4.07707588606042 -0.46034478223468
C -2.21613070113810 -2.18590593159535 -0.74757528233335
C -3.47060771782576 -1.40653391025854 -1.14146499799843
C -3.64384136001476 -0.91797473330607 -2.44170670706968
H -2.87565408907806 -1.05274107288714 -3.19649567028771
C -4.82157398827352 -0.26003425487012 -2.76990583885988
H -4.96931282437425 0.12687445501705 -3.77433394410903
C -5.80285197973650 -0.10499314979787 -1.79668363778225
H -6.73597794098546 0.40825655098700 -2.00730265398025
C -5.55699754187055 -0.63457759301429 -0.53684042645689
H -6.30162003500978 -0.54458820790720 0.25394161403426
C -0.99191725903669 -1.67892755030203 -1.58146640285382
H -0.93947560361079 -2.23390348513594 -2.52928560821744
H -1.12545797249239 -0.61652703785547 -1.81139376100326
C 1.08962669273024 -2.74810761251287 -1.08433134985523
H 0.91255947799147 -3.39517548079506 -1.95563080264394
C 2.26653628097874 -3.03946016902235 -0.30880499640874
```

C 3.20236092391377 -3.92194118602911 -0.89059637132816

H 2.99912079829198 -4.29649615344653 -1.89216108243416

C 4.35451825487123 -4.30200658833495 -0.23372671367940

C 4.58303522025857 -3.81537501675638 1.06235146142356

H 5.48470232113150 -4.10624527554604 1.59626291997483

C 3.67700514090765 -2.97144480762574 1.67495155372805

C 2.49324219083337 -2.54666421362003 1.02359949782621

H 5.06690564624055 -4.96960865284395 -0.70751832311473

H 3.85246400075312 -2.60115752828668 2.68149699194243

C -1.95848407755773 -2.11866455084909 0.77854168585207

H -2.87796589304926 -2.41428689708660 1.29477138473270

H -1.18376359016177 -2.85974139554044 1.01194957326134

C -2.28241427028900 -0.08853156843167 1.97043705363976

H -3.30841038025056 -0.44295130636335 2.13046136753153

C -1.96995619681875 1.18241736736338 2.57312744724763

C -3.07040989537810 1.90006628762507 3.09342105643129

H -4.06114278347090 1.46165298639781 2.98840585792109

C -2.92338231099080 3.12558787541934 3.70969784491480

C -1.63380375302912 3.66172138046885 3.84102965840439

H -1.49585500195867 4.62586667438786 4.32479085003834

C -0.53071516675815 2.97933780715978 3.36620601865786

C -0.64876055917657 1.72448108062218 2.72055626151158

H -3.78733129122512 3.66079180797422 4.09030317890949

H 0.46929253020118 3.39065623198313 3.47552781724813

O 2.39783195979276 0.44468700540108 -0.28670031962832

C 3.60778203715924 0.57293288583899 0.18535896576020

C 3.73798130832015 0.91071879573760 1.65780482678591

```
  H 3.20029362672423 1.84142807018281 1.86849632273946
  H 3.26964408725910 0.12627069169051 2.26256029607009
  H 4.78694029891442 1.01560258522232 1.93984551406373
  O 4.60708958873850 0.45627048705828 -0.53063373211841
  O -0.46612910645448 1.32270790952737 -0.56465539274151
  C 0.27997520342401 2.17503226019707 -1.90258186705365
  C 0.02973192248497 2.67389878870227 -0.56654329628525
  H -0.51215778335164 2.20401260741111 -2.63512243586278
  H 1.18927553169147 1.62586936109009 -2.09688569819416
  H -0.75626743045997 3.42066879585874 -0.43430740464653
  H 0.89415558078677 2.84309758865648 0.08052603771519
  O 1.02230836005962 3.87745350740748 -3.07637982591879
  C 2.22713175823699 4.30879370493939 -3.04118660328146
  O 2.61361005628579 5.34821637100157 -3.62170467774351
  C 3.24282462089911 3.48475320101123 -2.25071629132583
  H 4.21863718601899 3.97432762880295 -2.23085096869407
  H 2.89672660048021 3.32337859490532 -1.22438838446742
  H 3.35318818800570 2.49310431117134 -2.70406756962586
```

DFT Cartesian coordinates A.6: In(Salpy) ROCOP propagation cycle - INT3

```
Charge: -1
Multiplicity: 1
Number of atoms: 71

  In -1.26811449029198 0.60056154588111 0.38627388575437
  O -3.14421353119205 0.39977895486833 -0.72956282609477
  O -1.09810195440997 2.67254822610419 -0.16268018565791
  N 2.65841505675627 -1.35286790008579 -2.12926077816293
```

N -1.39796957603114 -1.65037679734533 0.20035009685189

N -0.06484072559037 0.26293380263569 -1.53439210461490

C 0.19513641035701 -3.51531728740497 -2.03634255121127

H -0.88958738135122 -3.67560522116532 -2.06501473276102

H 0.65869868284322 -4.36826134820407 -1.53112468039620

H 0.56779062280765 -3.47607135599214 -3.06566552634960

C 0.51709424699618 -2.20577337968693 -1.28725411794830

C 2.03513327446861 -2.07690517489385 -1.19024185994426

C 2.74883713362224 -2.74776343344605 -0.18912647283501

H 2.23266393977334 -3.34906408430060 0.55328540248332

C 4.13228291115292 -2.64491799724112 -0.15383714896804

H 4.69962901978364 -3.15675562967601 0.61861205084983

C 4.77578314217169 -1.87567794286933 -1.11828127942951

H 5.85535792977530 -1.76124662248760 -1.12577836682008

C 3.99379134957332 -1.25482398658169 -2.08286266452077

H 4.45740274339222 -0.64860859668277 -2.86107620186200

C -0.09923123474742 -2.29056195741807 0.15334284177913

H -0.15835897269115 -3.34431561440003 0.46412213908620

H 0.54490056125548 -1.75280870727276 0.85827567792980

C -2.48703928821071 -2.33878489887115 0.20932201499275

H -2.42414743242943 -3.43357576773563 0.30320338614216

C -3.81043427956372 -1.78569855026454 0.09041564081503

C -4.89019708134000 -2.64581261829121 0.38113955803061

H -4.66418378541075 -3.65688310072896 0.71587325912977

C -6.20318776745799 -2.23630964038811 0.26491035544865

C -6.46399385525558 -0.93257910834413 -0.18536213111495

H -7.49250490628837 -0.59330743479604 -0.28647060100062

```
C -5.43333929595517 -0.07085193574247 -0.50573016508280
C -4.07127006895830 -0.44916365844920 -0.37902933124529
H -7.01770199118607 -2.91067703856722 0.50923891789476
H -5.63937240645114 0.93594534539330 -0.85973271027102
C -0.10599057533447 -1.07013013039134 -2.13406875290988
H 0.38710123701578 -1.06485171122280 -3.11320477838098
H -1.16207693037356 -1.32558371193408 -2.29016808706709
C 0.62054992364058 1.17764878510437 -2.13260467689772
H 1.19420510254125 0.89449548689991 -3.02503512783372
C 0.73824956648196 2.56250134288000 -1.75184997081739
C 1.74325102296161 3.29719593590074 -2.41965666813230
H 2.35806100557658 2.77287074974472 -3.14930670008294
C 1.96887170817072 4.63495094782277 -2.16742757081932
C 1.15141205454828 5.28830310821123 -1.23198039465112
H 1.30852402944109 6.34382123450946 -1.02138357395552
C 0.14397822895557 4.61056822625000 -0.57512135088142
C -0.10379811873955 3.23068162846897 -0.79800665528447
H 2.75577711663186 5.17191053982448 -2.68738184640766
H -0.49322888187123 5.11885138723968 0.14385125898332
O -2.48539103179505 0.62192607169376 2.18401527357236
C -3.58932745825679 1.23594975647180 2.48130179721467
C -3.88422848032589 2.52559781832273 1.73557161830464
H -3.10411037016851 3.25946391523073 1.96632684463667
H -3.85110040232422 2.35103343502992 0.65567140306239
H -4.85882626378673 2.92655677287248 2.02034219584975
O -4.36380956475236 0.82572329605639 3.35777661946004
O 0.39486299574225 0.53918253149895 1.67594455938349
```

```
  C 2.67817464703478 0.14882334897981 2.15687535775381
  C 1.68602073153485 0.82853448193730 1.22649538364188
  H 1.89201559348106 0.46027251643228 0.20320308550247
  H 1.89550780305072 1.91689878213905 1.21232511875001
  O 4.01135761847067 0.43556065093979 1.64316841283389
  C 5.02804879852936 -0.26701828870768 2.16382540184554
  O 4.89440015289474 -1.10790678944466 3.03373089188373
  C 6.34636001261612 0.13165158896261 1.56424155354985
  H 6.98877585927128 -0.74771692164983 1.48478781471430
  H 6.22218558499918 0.60751303145031 0.59022472002196
  H 6.82995481652828 0.84337520557939 2.24315723599848
  H 2.52032402835298 -0.93524553391477 2.16569929831924
  H 2.59979143934020 0.52918942526202 3.18212151794203
```

DFT Cartesian coordinates A.7: In(Salpy) ROCOP propagation cycle - INT4

```
Charge: 0
Multiplicity: 1
Number of atoms: 64

  In -0.71413902984979 0.42656850753816 0.15775453561206
  O -2.69165681745284 0.52501788705809 -0.54010720856454
  O -0.34183666618606 2.44462899484109 -0.36396483369906
  N 3.57559138379118 -1.60281569829619 -0.47807469689758
  N -1.01528511623441 -1.77715993218058 0.17314667272093
  N 0.96263945982925 -0.08750890574329 -1.17552309952496
  C 1.26517388257570 -3.90047284935979 -1.19083877958351
  H 0.27607585430012 -4.07666312798817 -1.63067776557930
  H 1.46951354086481 -4.69554851481520 -0.46766916829992
```

```
H 2.01582537734291 -3.95387341412141 -1.98638705587887
C 1.30084828648814 -2.52217687262405 -0.49870023693081
C 2.66558765737754 -2.34557046436491 0.16344171830170
C 2.95228872392064 -2.96934477767349 1.38334269062918
H 2.21249181468025 -3.59491331412369 1.87493379345468
C 4.19642030244256 -2.77734478953010 1.96673013918422
H 4.43385081387593 -3.24561867533680 2.91792266364713
C 5.12997194837102 -1.97642314241261 1.31589980096573
H 6.11181427736586 -1.79022135372322 1.74006539131057
C 4.77492606948129 -1.42476963290179 0.09241031893026
H 5.48125871413343 -0.80486393650652 -0.45896313547600
C 0.18055364398047 -2.48827020582506 0.60149237647791
H -0.06542182367933 -3.51499256984049 0.90558618624371
H 0.55512987626925 -1.96059244147196 1.48700399958824
C -2.11556943860412 -2.40933583772303 -0.06162358283772
H -2.12326820753017 -3.50084512330794 0.06457217958436
C -3.36207525097106 -1.82528383085456 -0.47306740342713
C -4.42826796696782 -2.73329804241998 -0.67465012106959
H -4.23569165793581 -3.79131081210574 -0.50831944699657
C -5.68106648165512 -2.31738693264577 -1.06942485761562
C -5.90132748811943 -0.94661520286351 -1.27385130389643
H -6.88300078279986 -0.59745772966282 -1.58463701559879
C -4.88784538545134 -0.02873342547650 -1.08406503910604
C -3.58927547403087 -0.42343168255888 -0.68283647609496
H -6.48118409107904 -3.03508280614522 -1.21792382160774
H -5.05966184759830 1.03238932073085 -1.24128673615867
C 1.07209644764624 -1.48226219916706 -1.61552361734098
```

```
H 1.87930479560473 -1.57807896175698 -2.34939307125509
H 0.13195339105559 -1.74420084226790 -2.11904987011168
C 1.81189003748804 0.77489152892429 -1.64010254719003
H 2.62164124638263 0.39072985913356 -2.27094073642609
C 1.82557073161131 2.19414279853521 -1.43598832993928
C 2.96539830656059 2.87070218396441 -1.93115083389374
H 3.74518834293679 2.27830331758812 -2.40539456307887
C 3.11473118839484 4.23489916071671 -1.81405805420593
C 2.09189058036423 4.97468387869470 -1.19928407748296
H 2.19168616425048 6.05278957450699 -1.09847907064975
C 0.95496557489973 4.35459222358916 -0.72170676214258
C 0.77733775918686 2.95316429066476 -0.81733309746604
H 4.00371967060817 4.72873083269518 -2.19243835318693
H 0.16045974807369 4.92812050619257 -0.25244853109564
O -0.40209015731506 0.54831168523772 2.18494235282026
C 1.92857338464765 0.34248241044236 2.71179381403509
C 0.71104881795897 1.26164720783794 2.67636761425427
H 0.95193257134234 2.15793957084412 2.07739964357851
H 0.49926758369367 1.60531991559148 3.70228861235921
O 3.05112188403112 0.98688472129925 3.37311852120449
C 3.92149793489852 1.66712628046104 2.59908475194073
O 3.81941729914931 1.76987671880519 1.39244438734308
C 5.04336723402796 2.23558271221934 3.41763697367745
H 5.52302063363253 3.04775829848356 2.87052567638944
H 4.68884642779285 2.58053230981837 4.39135887317103
H 5.78085337404346 1.44298817081693 3.59005063465400
H 2.22247470844668 0.04213783557856 1.69960150840602
```

```
  H 1.71338621764102 -0.54637465501452 3.31239746982510
```

DFT Cartesian coordinates A.8: In(Salpy) ROCOP propagation cycle - INT4-PY

```
Charge: 0

Multiplicity: 1

Number of atoms: 64


  In 0.24511542726171 -0.06759675625187 1.03988661502550

  O 0.90449389958560 1.95615891892565 1.28147199513692

  O -1.80683710846787 0.59322863025222 0.97630227873813

  N 2.33851765954410 -1.08003453167123 0.77747320455585

  N 0.78894689901255 0.30843262862968 -1.13682164519338

  N -0.58277873544155 -1.94547884812830 0.13486443362855

  C 1.94683375484069 -3.09582003803224 -2.37084004596687

  H 2.73298440169734 -2.66964733803224 -2.99997248998816

  H 1.09191665031264 -3.32366578766112 -3.01528081063952

  H 2.30949766203088 -4.03502082593878 -1.93989932931787

  C 1.50430055120144 -2.11976066428840 -1.27308267445993

  C 2.66192943894941 -1.73298734172261 -0.35895275832467

  C 3.99295471132429 -2.04582047977537 -0.62677056176034

  H 4.26541957334570 -2.57437969050459 -1.53145251550050

  C 4.98158217132391 -1.68623969286294 0.28326008266532

  H 6.02014886064115 -1.92969350358095 0.07847870929496

  C 4.62860536456767 -1.02361304589329 1.45117329557283

  H 5.36899535307181 -0.73234441164630 2.18847148332740

  C 3.28914961088274 -0.73553525701426 1.65828007516021

  H 2.94270815633086 -0.21748162007066 2.54953984570522

  C 0.92406436607200 -0.86938795051308 -1.99585280516611
```

H 1.56888914440498 -0.63416620144517 -2.85344072911385

H -0.06497927230240 -1.14929043625250 -2.38866575505757

C 0.98626301560986 1.46903260706492 -1.66909263712045

H 1.21620548412853 1.51346344881760 -2.74339771128351

C 0.93934079578439 2.74596882039881 -1.01211269384896

C 1.00052344862434 3.87999852958198 -1.85480774772244

H 1.05596962827267 3.71707206307527 -2.92958955440921

C 0.98233027391661 5.16471135097588 -1.35529824824710

H 1.02074178156767 6.01893681685540 -2.02343471132410

C 0.92083770245528 5.34554584869421 0.03600528221232

H 0.90845210687640 6.35159096933886 0.44882189945269

C 0.88158927526658 4.26342672524494 0.89192236671711

H 0.84399362936526 4.40448949594792 1.96875637992328

C 0.89187440772498 2.92937963826513 0.41097827692636

C 0.40240483374968 -2.85466649262994 -0.44157156108138

H -0.10064276818744 -3.57834517920952 -1.09730795550885

H 0.89151170154007 -3.41860282988346 0.36496907939408

C -1.83579102068058 -2.25041282624863 0.03665225562211

H -2.09440509320734 -3.20716624068511 -0.43897873964789

C -2.96122828982823 -1.48498467541604 0.49585203624836

C -4.21379211966406 -2.14098767966266 0.45313478890987

H -4.24443699551820 -3.16410140939908 0.08336638307028

C -5.37357244412603 -1.53139551912907 0.88002849701534

H -6.32018442898914 -2.06087964993796 0.85034711559009

C -5.30516043749905 -0.21294056740726 1.35872725546891

H -6.20974791389003 0.28224097942199 1.70425838680093

C -4.10610528700854 0.46973721237428 1.39335481841287

```
  H -4.05573583495051 1.49320790122956 1.75530841730893
  C -2.89456726938829 -0.12582094680509 0.95838931084824
  O 0.44666826806860 -0.51713636773324 3.06068127380314
  C -0.57536806347141 -0.07581497020885 3.92107656251962
  H -0.16017464044598 0.12293856443917 4.92423983675581
  H -1.05556789007764 0.86018349390033 3.58302990920631
  C -1.65086180608534 -1.14810337529550 4.02631995901721
  H -1.97435136033050 -1.46465610832396 3.02845395571887
  H -1.29468676558950 -2.02830681708766 4.57417213556350
  O -2.78672394133695 -0.57089507071464 4.72926361850736
  C -3.91194977955714 -1.30632133377832 4.75153010014223
  C -5.04812663759562 -0.55877213087855 5.38544406908133
  H -4.69736918707090 0.11299681898443 6.17155094893286
  H -5.52818773120373 0.04882581162988 4.60916364377837
  H -5.78171917303314 -1.26482724340987 5.77660720372588
  O -3.99070801440521 -2.42746541891772 4.28601589519735
```

DFT Cartesian coordinates A.9: In(Salpy) ROCOP propagation cycle - INT5

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  In -0.77725304163692 0.51775515108757 0.60082029738230
  O -2.59313454759917 0.28163031845556 -0.51561086202728
  O -0.69471261342155 2.56549227811247 0.03119901600279
  N 3.53215674766925 -1.23760892586680 -0.87121125276501
  N -0.86914602340188 -1.71620236515335 0.59908856481211
  N 0.70856385228418 0.15175437820813 -1.01827731673849
```

C 1.25882213497240 -3.62579006790221 -1.17706212125801

H 0.21763875589907 -3.86333722109379 -1.42690660603043

H 1.64755311832020 -4.41322605653518 -0.52445695659214

H 1.84666619445429 -3.61943211502866 -2.10105852902534

C 1.33538353604243 -2.25599363063900 -0.47103432626166

C 2.78723163121761 -2.00642833238172 -0.06700678343678

C 3.32489477209050 -2.61162149773629 1.07537736971288

H 2.71404499176136 -3.25152732003782 1.70554294270150

C 4.65738356916321 -2.39414102854774 1.39649138940667

H 5.08971390685755 -2.85364865615463 2.28086607014713

C 5.42525568838105 -1.57991190119033 0.56972654350536

H 6.47006410082853 -1.37800543176410 0.78455892625844

C 4.81680417096173 -1.03067261793543 -0.55069006246395

H 5.38362856978713 -0.39327600979394 -1.22896115273935

C 0.43764576265179 -2.31105021370951 0.81758193024525

H 0.34681846763926 -3.35243755218233 1.15709280311560

H 0.91360584332977 -1.72879350690058 1.61542848274595

C -1.94200903276931 -2.42846271614831 0.55773539266396

H -1.86954397069743 -3.50834016760140 0.75043802469143

C -3.26045724891447 -1.92094495202670 0.27578156094374

C -4.33955680686098 -2.79944944511173 0.50611917431553

H -4.11922886022983 -3.79048812727398 0.89793925535325

C -5.64781520483049 -2.43155640420277 0.26137415496794

C -5.90284465401763 -1.15860304451268 -0.26593925544940

H -6.92557706582852 -0.85626449358102 -0.47842818220193

C -4.86813923119821 -0.27787384572178 -0.52529711085049

C -3.51945775764610 -0.61085326334701 -0.25285475097618

```
H -6.46208070909648 -3.11992428987449 0.46229741499338
H -5.06585404605195 0.70307318437604 -0.95009652689224
C 0.84537153797530 -1.21992122083112 -1.50938538597452
H 1.52360264721744 -1.24806900429405 -2.36944280879355
H -0.14547853492515 -1.54656652976025 -1.85229684246388
C 1.41699048836290 1.08629704665153 -1.56039960018541
H 2.14918955238387 0.79736878314841 -2.32436267802613
C 1.36834055114739 2.49553295898810 -1.26672510973972
C 2.40839800751635 3.26699312154351 -1.83562415191715
H 3.16298816211409 2.74894623462259 -2.42429571618284
C 2.49417286246335 4.63156281021635 -1.65924811288692
C 1.49961269995042 5.27581606897627 -0.90784284838618
H 1.54570302777217 6.35225659806683 -0.76045891007776
C 0.45637461670332 4.56184292175605 -0.35308275707471
C 0.34719821914900 3.15722540041496 -0.50138150289739
H 3.30955410147804 5.19627631332893 -2.09939253512892
H -0.31720181709150 5.06249387358899 0.22288735269641
O 0.43869156064303 0.63749842343197 2.27770773288440
C 2.61046803965473 0.43299741319281 3.20150457479761
C 1.77283477583722 1.04236384786590 2.08979914800917
H 2.20323175251767 0.70385797698786 1.12891150417963
H 1.87973405302043 2.14326835587280 2.11398322769839
O 3.98908449120463 0.82435220717570 2.95476654854185
C 4.93154024437052 0.20883726213973 3.68870265825578
O 4.68446158114960 -0.63420033028472 4.52997832472049
C 6.30697223953369 0.71347131195627 3.36240271356330
H 7.03100763913229 -0.09252135785622 3.49491507839287
```

```
  H 6.35948762287754 1.11839749390528 2.35032730826880
  H 6.55429513119165 1.51355060561107 4.06979782137424
  H 2.53558186301919 -0.65983147947886 3.18731253506365
  H 2.30188244938585 0.79861409374553 4.18792079884091
  O -2.44776489821644 0.55213959919689 2.38236374460477
  C -3.56875403771752 1.01128807748148 2.33207489593440
  C -4.05021054710000 2.26438376168045 1.67078105866020
  C -5.55782669544341 2.25965095849099 1.90301874012783
  H -3.75139811592305 2.23866335242052 0.61774734380281
  H -3.53562988038955 3.11209509288876 2.13661982642373
  C -5.81855381777355 1.01933780543868 2.71036512856166
  H -5.91962452165277 3.12265673421457 2.47045735959205
  H -6.14444730279906 2.20212509256368 0.98117469575160
  O -6.83376598821410 0.56219044021796 3.13644579844773
  O -4.59417876063608 0.35791777443933 2.95240552228416
```

DFT Cartesian coordinates A.10: In(Salpy) ROCOP propagation cycle - TS2

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  In -1.57241268937666 -0.54842924615339 -0.07831818166046
  O -3.64850728136209 -0.70736105197506 0.28019181139494
  O -1.33259503454990 -2.62240895375832 -0.43344800505670
  N 2.17456434794729 0.39415467088827 2.92626525533143
  N -1.79619479951867 1.49157448073503 0.76306774357613
  N -0.45935848364207 -0.89422568015280 1.81043151369935
  C -0.38049533959152 2.45531204834431 3.64363802477992
```

H -1.47155818572172 2.56194023938221 3.67472780959294

H 0.06059865800092 3.44599756708468 3.49971122236568

H -0.04204472061360 2.06189758572193 4.60810307919073

C 0.02771169121363 1.51061208794819 2.49467404343475

C 1.55262997880853 1.46609346510339 2.42062240469854

C 2.26601915481105 2.54071261774419 1.87541959457786

H 1.74585701251241 3.41077297364359 1.48485134606823

C 3.65211470386425 2.48913938103479 1.84145667191737

H 4.22089659169715 3.31257845272602 1.41918801192884

C 4.29690124470502 1.36722036752189 2.35379814222491

H 5.37921215589985 1.28177794465939 2.34492725321994

C 3.51395892784541 0.35215473309832 2.88611339136326

H 3.97828283723436 -0.54109674329231 3.30344965093707

C -0.52929699409368 2.09291957524577 1.14673417339979

H -0.62623949261850 3.18381135056397 1.23457208585963

H 0.18066365848339 1.87994082736270 0.33996139921918

C -2.90384045930628 2.14864914219663 0.86606721430065

H -2.85675443039930 3.19521206033065 1.19779278503447

C -4.21850388892156 1.64321873230225 0.58718836068328

C -5.27017363075241 2.58758925896336 0.64410882450200

H -5.01665734501216 3.62204615721232 0.86705709531480

C -6.58338265516033 2.23415660503804 0.42309272376800

C -6.88210608450224 0.89076888342357 0.14590593996762

H -7.91293845552736 0.59233441704768 -0.02917581746790

C -5.88523264761140 -0.06261595704978 0.09307904291798

C -4.52558833622575 0.26735448156274 0.30998593691370

H -7.37164800815936 2.97853222700655 0.46704232729965

H -6.11855754482490 -1.10280781286261 -0.11653964449983

C -0.57261205846131 0.13163703800253 2.84982677381930

H -0.10928343495781 -0.21876054804876 3.77867746579942

H -1.64244282555109 0.28284649109762 3.04541145647402

C 0.24337068546920 -1.95327851081669 2.04998378639524

H 0.77997288730373 -2.00294334252671 3.00438662486055

C 0.42394991243840 -3.08906369009775 1.18637102780251

C 1.42626221440621 -4.00408118548645 1.58443419299006

H 1.98729367108003 -3.78455236703720 2.49078436855112

C 1.71161994642407 -5.14069616650728 0.85844612117279

C 0.96389150829819 -5.40579360036002 -0.29898388365867

H 1.17032949672059 -6.29997830592910 -0.88229696309248

C -0.03857469271478 -4.54869719758156 -0.70819528718806

C -0.34545921859755 -3.36507745851158 0.00598816602459

H 2.49308770240248 -5.82110622686987 1.18056894387515

H -0.62536398769546 -4.76043304458220 -1.59797139655126

O 0.16645667054727 0.01329426097865 -1.27159172065998

C 2.46594853732962 0.67978768100956 -1.42676747246932

C 1.48995176738685 -0.42328937219321 -1.04989181501497

H 1.63405200989726 -0.65936597823339 0.01596891061390

H 1.71536310964067 -1.34615049590955 -1.61150403457186

O 3.78427313006241 0.19047231971465 -1.07538198098519

C 4.79611373853620 1.07566579728603 -1.17470102198006

O 4.64329515818659 2.22358570278041 -1.54124078471453

C 6.11039946783458 0.45223869399909 -0.81032763179351

H 6.79012024815528 1.22246862051672 -0.44287458141274

H 5.98628449914091 -0.34113542076827 -0.07076981051484

```
  H 6.54427047803175 0.01187020166212 -1.71568219928301
  H 2.25228426179041 1.59438527904076 -0.86352262615134
  H 2.44106024530635 0.91611372444958 -2.49735672572187
  O -2.03836061610932 -0.10637847438914 -2.26696536582645
  C -0.94274560574165 -0.17904951663546 -2.85783367072609
  C -0.36288302708494 -1.40331920691520 -3.52600039354872
  C 0.73987653171979 -0.84712138003684 -4.41944766650378
  H -1.17497302953582 -1.84808798498660 -4.11310727859489
  H -0.04098577524910 -2.14153152876090 -2.78944059887010
  C 0.46726653826333 0.63554111458980 -4.47040200328789
  H 1.74665845696336 -0.99500564939058 -4.01248562078279
  H 0.74135781997408 -1.24771044358614 -5.43658198427497
  O 0.98687468984383 1.48141443436092 -5.14722245811189
  O -0.53232556698642 0.95975884802383 -3.57904409288515
```

DFT Cartesian coordinates A.11: In(Salpy) ROCOP propagation cycle - INT6

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  In 1.31486927021082 0.09277615456163 0.64068595702902
  O 3.09549635864355 -0.44509071705123 1.61918516297156
  O 1.15063333819747 1.93650846007155 1.64870760330808
  N -3.44140615002248 -1.84773885325778 0.77164317439907
  N 1.21498805642438 -2.04453564499333 0.03165846558453
  N -0.60277020183301 -0.41756589465715 1.59792469006139
  C -1.07076967653329 -4.16043704938587 1.01341536405300
  H -0.06065500910391 -4.40359862426533 1.36411012234419
```

H -1.32041236205242 -4.82479635617260 0.18067904884436

H -1.77478111884663 -4.34937884639213 1.83091809801444

C -1.14304713572189 -2.68691501371247 0.56712576998842

C -2.53033607456089 -2.42828719707590 -0.01929702579692

C -2.83766100660341 -2.82344608836872 -1.32649301908564

H -2.09546931959205 -3.31271436441249 -1.95006686330058

C -4.10882413252428 -2.58012409870648 -1.82749395907746

H -4.36195733450300 -2.87180232657120 -2.84298444132704

C -5.04810113565032 -1.95772676378724 -1.01143647955155

H -6.05240041243347 -1.74257999899422 -1.36334571394268

C -4.66697341782316 -1.62039222662982 0.28011155297977

H -5.37294058825954 -1.13831082811413 0.95533108169889

C -0.06663782303594 -2.43604991489415 -0.53681012899098

H 0.04293784186430 -3.33673040353380 -1.15600644972387

H -0.39985798455268 -1.62184719413599 -1.19297679719498

C 2.20570275873017 -2.87285409302056 0.05571699250602

H 2.06247557347810 -3.86161429835881 -0.40123669850222

C 3.50239085012153 -2.63904102603241 0.62811724585417

C 4.44459509164813 -3.68140606471686 0.46082435549440

H 4.13731689539126 -4.56344169773608 -0.09746014247007

C 5.71937083747636 -3.60668091343314 0.97787258242266

C 6.08639654000818 -2.46161437831693 1.70166602439366

H 7.08711325596409 -2.38484672743173 2.11984589688343

C 5.19371146906439 -1.42609181919891 1.89282347996998

C 3.87990099371648 -1.46798192129219 1.36861565122261

H 6.42385157690172 -4.41898317496583 0.83223743769144

H 5.47783091875069 -0.54078005401805 2.45477699632715

C -0.88431834588110 -1.83734691826252 1.83151859830083

H -1.73729469301531 -1.94684361253320 2.50822527253615

H -0.00238924556491 -2.25820535713178 2.33156971517694

C -1.45151558629822 0.47930234396562 1.98800001068917

H -2.41489054051446 0.13413964352580 2.38147541066571

C -1.26145718858004 1.90343805373870 1.96642431376202

C -2.41645952321659 2.68334926984872 2.20526797777783

H -3.36239828567909 2.16515733539831 2.34356282056526

C -2.37248009126600 4.06010133829023 2.24394764962451

C -1.13529355054716 4.70066845753175 2.07317398087147

H -1.08081324974259 5.78624729784205 2.10569119432779

C 0.02022671423413 3.97230227774245 1.86952201292199

C 0.00578000549476 2.55924771414072 1.80499299065307

H -3.27545724811568 4.63737052259634 2.41387182507926

H 0.97931503276867 4.46816621648346 1.74824473746332

O -0.08110649963197 1.36303257297707 -1.12320571663029

C -2.27393543024008 0.65746395669270 -1.84969529987171

C -1.32728113581620 1.83353193877086 -1.66448147715328

H -1.74044479363914 2.54952981027574 -0.94525230989277

H -1.17028460565676 2.34994743311406 -2.61753400464181

O -3.50487776048182 1.11114086175335 -2.46148581412913

C -4.47276086829473 1.56465906344547 -1.63148482837537

O -4.34211500834705 1.64136091883466 -0.42735498405776

C -5.71432064963684 1.91388281361528 -2.39433791211091

H -6.36032392242458 2.54160222580772 -1.78036312780245

H -5.47103947181140 2.41147317975375 -3.33596720577313

H -6.24387563089056 0.98469206187621 -2.63529577023521

```
 H -2.48689738722005 0.18118620350436 -0.88847604009531
 H -1.85633044285822 -0.07280141448608 -2.54630604263765
 O 2.04562719077602 0.77335608825003 -1.22723418691377
 C 1.06706433767584 1.24840899756176 -1.97407441104974
 C 1.40018914894935 2.51718797917214 -2.78618633247917
 C 0.97640015977222 2.23583677110727 -4.22586960754474
 H 2.47855365516603 2.66690451592830 -2.70888712984225
 H 0.90600251790395 3.38698395126209 -2.34605639575069
 C 0.62494016258394 0.76647411802524 -4.25890143542589
 H 0.09400544381600 2.80277550716720 -4.54369627602305
 H 1.76118189041231 2.42903419548420 -4.96291802702375
 O 0.31939867345889 0.10937613549637 -5.23161736687980
 O 0.67809547941932 0.22998549043405 -3.02819184315387
```

DFT Cartesian coordinates A.12: In(Salpy) ROCOP propagation cycle - INT6-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 75


 In -0.56267187034734 0.75706067063337 -0.38818923475632
 O -1.58557113559542 2.59692192169007 -0.65750931281500
 O 0.84571113446653 1.65611125237169 0.95005722674010
 N -2.21881492793287 -0.56676556970441 -1.42763468630361
 N -2.14456060874962 0.37640400477653 1.19886288037717
 N 0.23385173118189 -1.15786299672695 0.40951158613231
 C -2.71026762802650 -3.37411320225525 1.02459292094855
 H -3.77710162428439 -3.28289210818769 1.24571752569561
 H -2.20074187234962 -3.65538333378570 1.95164068684309
```

H -2.56787756797074 -4.18138824802180 0.29834424064578

C -2.12076197275517 -2.05633143400971 0.50697590306173

C -2.81291121522373 -1.58196818968335 -0.76495712963000

C -3.98187520656721 -2.15320050885363 -1.26289433184536

H -4.45973609384905 -2.97363280495115 -0.74267597953313

C -4.53395870619441 -1.67203877489341 -2.44510418921422

H -5.44472390127306 -2.11481097217360 -2.83786938478394

C -3.90830916615912 -0.62977684131956 -3.11560675597402

H -4.30400077853107 -0.22784379885268 -4.04219513433359

C -2.74875807991759 -0.10365189866857 -2.56888405263130

H -2.21389183540459 0.71228281140777 -3.04748819132182

C -2.29653186213484 -1.00683000176105 1.64656799205686

H -3.28694441486875 -1.14905142176369 2.10006411580301

H -1.54058173524437 -1.22600790532253 2.41512059550924

C -2.94171462089901 1.27043705498478 1.67902436411783

H -3.67319544934745 0.96104237098249 2.43941257038451

C -2.98788053009194 2.66558588361499 1.33013880540403

C -3.81218660784449 3.47640026824054 2.14413631249113

H -4.33003032646483 3.00526525577432 2.97740731690237

C -3.96499933429612 4.82781140066705 1.91788023983617

H -4.59641287315505 5.42906320623994 2.56386858676447

C -3.29330959990206 5.40789745715688 0.83065541089696

H -3.40270009973255 6.47171180861267 0.63349808680303

C -2.49708526765509 4.64506452979713 -0.00006374894395

H -1.98563355135977 5.09275952562671 -0.84783379859131

C -2.31394534595236 3.25557675787264 0.20842358754458

C -0.60937417881542 -2.33037812164390 0.20669164214904

H -0.26735565870726 -3.14627420243212 0.85728331047828

H -0.51473318848056 -2.66989771640361 -0.83422327833510

C 1.33525412500243 -1.28840472250710 1.07395012019652

H 1.61628824869897 -2.29716335706500 1.40686923376304

C 2.26240941754585 -0.25168640522193 1.42774307972546

C 3.51000340567641 -0.68176556292285 1.93731742014690

H 3.68603291517236 -1.75220608182194 2.02753598640874

C 4.50020212484097 0.21015362215937 2.29076909074184

H 5.45746179219447 -0.14288214973600 2.66108147886277

C 4.24602481226039 1.58576557486616 2.16273147323692

H 5.01866196435726 2.30261577173365 2.43031299311204

C 3.02757900661150 2.04377577533248 1.70415499656194

H 2.82925388206875 3.10838102824783 1.61468580657562

C 1.98969331388228 1.15527789133255 1.32563486748053

O 0.19850861945680 0.86978625720529 -2.36902596118630

C 1.47169137900669 0.83088617279029 -2.68888685234957

C 1.75433977757692 1.06028930335811 -4.18849656482606

C 2.73329176162357 -0.02666589142609 -4.61957925978204

H 2.11548185771488 2.07734460379816 -4.36063147271577

H 0.79850129077538 0.94939055327069 -4.70500717305154

H 3.77281995451467 0.32259972320181 -4.66325089126078

H 2.50559864521835 -0.47642971341250 -5.58954610216340

O 2.00366302251052 -0.62041718121204 -2.46595014359524

O 2.19977841253278 1.63373698025059 -1.79248240536469

C 3.60365603951604 1.83530742846417 -1.96896768288525

H 3.83699513320234 2.71684178875195 -1.36383718506085

H 3.85144611315446 2.06730057574950 -3.01267769001133

```
  C 4.44228819925654 0.67268369339606 -1.44255433057725
  H 4.60411876197519 -0.10847181017222 -2.19038379209315
  H 3.95910882694456 0.24423202051886 -0.55849449983272
  O 5.71883075095230 1.25527749880721 -1.07441450883491
  C 6.72449779286888 0.47084102727238 -0.62283293908738
  C 6.52355360787172 -1.01701456645165 -0.62247198401951
  H 5.61687689247963 -1.29567185201052 -0.07682268301437
  H 6.41392782274337 -1.38118190270044 -1.65044136538853
  H 7.39180043481773 -1.48813873703837 -0.16261792972190
  O 7.74614034839112 1.01788577232745 -0.25950695696794
  C 2.65450937101897 -1.07946282917991 -3.53564763985432
  O 3.13329614599990 -2.19810642899128 -3.57700523174065
```

DFT Cartesian coordinates A.13: In(Salpy) ROCOP propagation cycle - TS3

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  In -0.85061897654765 -0.90015293125238 0.71677621202337
  O -2.47446333313820 -1.73965771017658 1.75932059314622
  O 0.86535509412113 -1.31645992010263 1.85215808005623
  N -1.51405599584722 4.87630524392110 -0.36916810073372
  N -2.39924476594150 0.08141617158090 -0.53284879623602
  N -0.62405287775738 1.16912432026066 1.48045780199697
  C -3.53814617173212 3.05030469081838 -0.07372780910428
  H -4.23234026740484 2.21821971246792 0.09178795149485
  H -3.79129597219240 3.53678662337407 -1.01938660723913
  H -3.67731274191171 3.77697889056389 0.73062170640945
```

```
C -2.10248785514845 2.51622714179926 -0.10634757904593
C -1.08944123577538 3.60727974372150 -0.45342947015755
C 0.24201214166843 3.29953907348639 -0.75915509421488
H 0.58357099955061 2.27343122973332 -0.83770864794922
C 1.14363369078056 4.33205072228160 -0.98326507639828
H 2.17952884284206 4.10640131874244 -1.22193464333327
C 0.70046671574640 5.64687901446845 -0.90015055887425
H 1.36935953274455 6.48473761524766 -1.07122947879266
C -0.63690648133981 5.86311566266118 -0.59178990333929
H -1.02793466883980 6.87772826026169 -0.51840459067162
C -2.02940669758553 1.35225926237410 -1.14251762858894
H -2.68855994653257 1.59327676893686 -1.98843967444248
H -1.01356556129030 1.25400720141038 -1.53380901024828
C -3.57239490630709 -0.42790496581476 -0.71590450723489
H -4.23869008481645 0.05582223560268 -1.44322432061731
C -4.11273924114402 -1.57809339890174 -0.04196685394737
C -5.32544845850324 -2.08735933557315 -0.56133582309692
H -5.73833452211021 -1.61722655015360 -1.45163021314674
C -5.98177939599460 -3.14972617656909 0.02181203468055
C -5.43929659189411 -3.72242368563463 1.18224279235394
H -5.94642469863008 -4.55706729308519 1.66017054839896
C -4.26846496154494 -3.23898554201583 1.73236137038623
C -3.55999498890145 -2.16346250615815 1.14858573217871
H -6.90602182656914 -3.52861067014827 -0.40201356422697
H -3.85299240662141 -3.67847055180863 2.63487800690211
C -1.79752338821448 2.02711493830919 1.34327173958522
H -1.70180645321087 2.91344020981712 1.98492806919584
```

H -2.66775263159014 1.45589664227399 1.69230272543669

C 0.44537162358178 1.64607062359151 2.03568963268333

H 0.43757331194575 2.70167779013961 2.33652095620426

C 1.65729660336557 0.93701206063044 2.31811704415217

C 2.73779043897343 1.71882302212224 2.79158839569505

H 2.59153364325560 2.79351319091356 2.88034891894230

C 3.95064447147989 1.15825009842192 3.12482848497102

C 4.10791123290601 -0.23141434997775 3.00375390852509

H 5.06036972258276 -0.69055876985792 3.25622724962164

C 3.06991084587084 -1.02983640129622 2.56676576139878

C 1.81348345581212 -0.48475898380750 2.21331258269774

H 4.76943969871389 1.77825423511919 3.47494340926205

H 3.19026891981513 -2.10620065316489 2.48210282189288

O 1.46159578104966 -3.12616294294542 -0.87824677920164

C 3.82763141613071 -2.63979123940562 -0.96553347228087

C 2.64399709178205 -3.21864658331435 -1.69619397516347

H 2.83447521355910 -4.28115515024219 -1.89058761595691

H 2.52084356453634 -2.70919626947827 -2.65578210141218

O 3.66186065623233 -1.20343971148734 -0.93916096114516

C 4.68177074155096 -0.48370146689070 -0.43167597711020

O 5.71039887564242 -0.98194846653553 -0.01949885635851

C 4.37420799333853 0.98272217083034 -0.48365259710713

H 5.11941557708567 1.53833629893080 0.08505526490880

H 4.38602454619078 1.31248504121638 -1.52858391708013

H 3.37231734533929 1.17411830478906 -0.08760632060212

H 4.75216030328941 -2.89656001496383 -1.49564280228264

H 3.88796286585243 -3.01904710513804 0.06077687612354

```
O -0.66149530342708 -2.63908047390796 -0.51395401687309
C 0.32465282567147 -2.51296402073251 -1.35615544541535
C 0.00645248327748 -2.67115188513516 -2.85305058209477
C 0.50343890101038 -1.42760206349700 -3.59297387919517
H -1.07983197478258 -2.75537004692752 -2.92468514424951
H 0.44203318573514 -3.59809848923487 -3.23666331893555
C 0.80278587291245 -0.37499930801452 -2.54679933484980
H 1.41471392176257 -1.59947399675459 -4.17734547493437
H -0.23667225526359 -1.01990144043299 -4.28844304441141
O 1.11117532278397 0.78138951026578 -2.77973902618513
O 0.68306216802080 -0.86333397054830 -1.31734407683890
```

DFT Cartesian coordinates A.14: In(Salpy) ROCOP propagation cycle - INT7

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

In -0.79081549701839 -0.65887042226179 0.56344770027458
O -2.41451149041434 -1.60042935184736 1.54384999701757
O 0.76771670512700 -1.19444015300754 1.87199894878496
N -1.56443041052350 5.12151428632688 -0.11294594456151
N -2.39365583719035 0.33140510655769 -0.60397542015054
N -0.66611681525381 1.33489472255942 1.52958908134458
C -3.58054117379794 3.26450533823836 0.04261027143990
H -4.26752264534358 2.41655289602917 0.14755403171426
H -3.82952074544532 3.80676662081883 -0.87346726629719
H -3.73558163693968 3.93801107113578 0.88932799198804
C -2.13922052752665 2.74582120695548 -0.00959165964187
```

```
C -1.13348350158818 3.86331171878033 -0.28541343318829
C 0.19850048340842 3.58221359631848 -0.61400860701820
H 0.54361518923063 2.56419979605976 -0.76425268792632
C 1.09419288908243 4.63273984402663 -0.76842945117433
H 2.13060298284403 4.42917831013165 -1.02406813611389
C 0.64551681668512 5.93670982632331 -0.59361512641570
H 1.31028356780774 6.78752445800356 -0.70763864505170
C -0.69212275433125 6.12527427616432 -0.26851965095684
H -1.08728872287600 7.13075583222742 -0.12451972043139
C -2.05057835186002 1.65081821217410 -1.12085633738082
H -2.72189685415089 1.93794016341143 -1.94252257645431
H -1.03662169418182 1.59515862791489 -1.52420734557713
C -3.55020708344997 -0.19678712794684 -0.83517427091253
H -4.22802375472439 0.31805978428361 -1.52992230572017
C -4.04881545794154 -1.41101601830582 -0.24949165061930
C -5.23413127312898 -1.93967137563143 -0.80919710890478
H -5.66835465201616 -1.42943740590221 -1.66679668884867
C -5.83717020673657 -3.07132048934152 -0.30319877120676
C -5.26633209607427 -3.69761949889186 0.81574670899213
H -5.73165227135503 -4.58856276156519 1.23051547108004
C -4.12148452582377 -3.19721479652354 1.40428480281169
C -3.46972148379914 -2.04626927607899 0.90229129991141
H -6.74173707344898 -3.46494509820884 -0.75521346495420
H -3.68565443225372 -3.67797584985188 2.27570351054580
C -1.84132566060193 2.18853753683081 1.42045558891467
H -1.76264845113694 3.04732790722007 2.10146780062449
H -2.70979778852902 1.59243018757628 1.73041524080449
```

```
C 0.41443698144294 1.78450882743852 2.07926583323532
H 0.42713922431930 2.82732010266854 2.42347198092761
C 1.62834317582117 1.04489329802320 2.29774852809629
C 2.74828009211260 1.80191270626423 2.71172450383919
H 2.63024453679540 2.87963903632871 2.80716497978589
C 3.96649219691714 1.21655026952180 2.98419273350565
C 4.08712042290154 -0.17603720725845 2.86737165858775
H 5.04009323527389 -0.65560469505371 3.07679924352471
C 3.01058943890714 -0.95176949624370 2.48415337569302
C 1.75118238931481 -0.38168495423289 2.18476716313961
H 4.81430975601602 1.82122038047604 3.28945153787625
H 3.10305630527450 -2.03115961974670 2.39723609674421
O 1.33550085817712 -3.63892031921070 -0.81871052658006
C 3.71115435054717 -3.36288701930152 -0.99519031212256
C 2.49011554362505 -3.96192095015883 -1.64174021701809
H 2.57186577748012 -5.05280383190633 -1.63681047985034
H 2.36017998496710 -3.61570335721939 -2.66818798289555
O 3.57201795616017 -1.92877478065604 -1.07306855169371
C 4.57398772106896 -1.19356274793935 -0.53711408993175
O 5.55883201745213 -1.69342491601506 -0.03435424110828
C 4.29763344296731 0.27073669468419 -0.68148935557797
H 5.03853161033895 0.84183916013465 -0.12271706723575
H 4.34193240305129 0.54216701528292 -1.74225658105511
H 3.28835776252919 0.50008437748986 -0.32575135070848
H 4.60866251006418 -3.68888233014343 -1.53372407558910
H 3.79289254938233 -3.66882357599971 0.05348384422929
O -0.58900561618139 -2.73510764572602 -0.39147505052034
```

```
  C 0.30179464857266 -2.92362780656146 -1.23176443261792
  C 0.15836590588216 -2.44151086571918 -2.64873252123366
  C 1.04005717789168 -1.25404860676942 -3.07007550438924
  H -0.89386427506498 -2.16282072921667 -2.75327278332466
  H 0.34369791369856 -3.28152147080217 -3.32959841801612
  C 0.94413433357054 -0.00583782606611 -2.19883003690065
  H 2.10139841195755 -1.52543933343536 -3.07879663543004
  H 0.77729619459323 -0.98379532656230 -4.09665520740986
  O 1.18501136316273 1.09066927471293 -2.71306872303809
  O 0.69869793428650 -0.17996343178463 -0.93967951167964
```

DFT Cartesian coordinates A.15: In(Salpy) ROCOP propagation cycle - INT8

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  In 0.96956020689104 1.30607841506307 -1.34502126686274
  O -0.75660191046238 2.19195933942568 -2.09426458209002
  O 2.24308761217271 2.92487587840327 -1.72407109280459
  N 3.32585660096029 -3.95431216161844 -1.76177036555067
  N -0.18513484837267 -0.58410829299584 -1.24642328150164
  N 2.41431008924355 0.08098543524685 -2.44038489251582
  C 0.81313418835065 -3.36205322712309 -2.68939685032390
  H -0.15361444350973 -2.96714704259101 -3.02321194996708
  H 0.63627694739304 -4.23361107507742 -2.05384474742627
  H 1.37502889156846 -3.68948908893419 -3.56749849410728
  C 1.56005574700412 -2.27065630842852 -1.91232952600902
  C 2.85927216818151 -2.78830277132872 -1.29392229838191
```

C 3.57328355186695 -2.03969934329871 -0.34922035465102

H 3.20040481319813 -1.09063300463591 0.02344146251308

C 4.79064173526881 -2.51901763652552 0.11748730608738

H 5.35633573297857 -1.94779624844249 0.84816526621734

C 5.26766045299177 -3.73309535959139 -0.36259819291077

H 6.21145760038420 -4.14736529208054 -0.02174723733061

C 4.49722995549696 -4.40968163510237 -1.29974520772049

H 4.83346544155578 -5.36440335563424 -1.70348925317248

C 0.60624544432090 -1.72953663222394 -0.80330553631476

H -0.04630872871606 -2.54928222705554 -0.47324862295775

H 1.17728740628682 -1.40257137387024 0.07181832611862

C -1.46238550355672 -0.68564794780064 -1.41249614124383

H -1.93084327578894 -1.66103907745340 -1.22530133136450

C -2.36148617324782 0.36408523506495 -1.80593153856730

C -3.72571691552125 -0.00375712410032 -1.88439516146554

H -3.99391081656881 -1.03005581925795 -1.64408047450322

C -4.70520560665176 0.89349489234844 -2.24829862624894

C -4.33565316079823 2.21432374630728 -2.53962785858448

H -5.09545908119103 2.93887835800830 -2.82158981551795

C -3.01513406743023 2.61340102788259 -2.47107350982605

C -1.98716986699155 1.71473596644815 -2.11236593050765

H -5.74399541048419 0.58397205582641 -2.29946530301427

H -2.72861897240867 3.63699768096762 -2.69431345240129

C 1.93742325316240 -1.19163157821860 -2.97226155681671

H 2.69080284601992 -1.62994433747447 -3.64036944542373

H 1.03978460214993 -0.98485019964138 -3.56976899350779

C 3.65876250285071 0.41519789023968 -2.58721097936306

```
H 4.32775150802390 -0.31345052196855 -3.06256628227599
C 4.26756820326595 1.65601850577122 -2.20688346875855
C 5.67856042270628 1.70789369034273 -2.31257700203391
H 6.20170342251061 0.80853232335008 -2.63091498900678
C 6.38947419827421 2.85018938933762 -2.01989651482462
C 5.68732212444005 4.00144304487867 -1.62906546764528
H 6.23261994816572 4.91361965647516 -1.39973219510865
C 4.31022540641589 3.99655741255786 -1.53244285146251
C 3.55260619474661 2.83553372368456 -1.80818381172630
H 7.47151161496176 2.86325722940241 -2.09878120652685
H 3.76721134249467 4.88946843199967 -1.23615638907054
O -4.20612338247051 0.07794317193375 2.34162991951027
C -6.22287094387929 0.48988290730281 1.00429076615734
C -5.59672352811284 0.49155679453393 2.37862440294283
H -6.08356039152546 -0.23170457496536 3.03616257227907
H -5.67460830547146 1.49510411566643 2.80980328913440
O -6.18387075306954 -0.82887673494851 0.40256619037510
C -7.15396498826508 -1.69666363348866 0.76869308246479
O -8.04973921819678 -1.41521206073787 1.53847609730831
C -6.95514191483743 -3.03288983028927 0.11852966519656
H -7.88463663060634 -3.60159867899715 0.15403723986128
H -6.60687774537359 -2.92211909864763 -0.91099432285499
H -6.18466229022640 -3.57790203008953 0.67605385060260
H -5.66485690951737 1.12672792774243 0.31566412441105
H -7.25850322435200 0.83744531011145 1.07773757853460
O -3.60191456257365 2.14003993115345 1.63473691511428
C -3.30418482820779 1.01160154257595 1.96903729684850
```

```
C -1.90512539088721 0.46283234932136 2.05557328375345
C -0.86451060972125 1.42920989472299 1.51069732408865
H -1.87579674174521 -0.49781420552643 1.52599401559633
H -1.69862163091499 0.22848529498648 3.10685421378808
C 0.55777152406969 0.90004143702203 1.65795110928865
H -1.09587606981551 1.69393436616295 0.47392679611997
H -0.90214526279974 2.37286092149886 2.07097609544624
O 0.88408013826819 0.26596800973024 2.65808999230230
O 1.41578026562881 1.20678622666653 0.71422019018917
```

DFT Cartesian coordinates A.16: In(Salpy) ROCOP propagation cycle - INT8-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

 In -0.90463585789014 1.25793052772642 -0.54201678642838
 O -2.45670102217149 2.61321426585201 -1.03275356592657
 O 0.20173164658938 2.81469324678980 0.42414499203922
 N -1.99120114393860 -0.65266579040241 -1.35403011423574
 N -2.29247613121686 0.62483722348725 1.13497688933129
 N 0.46087489218155 -0.12950638996406 0.52706641358327
 C -1.59917857546884 -3.09541463015865 1.47643598635212
 H -2.64052204202811 -3.33228834205190 1.70984169636594
 H -1.04463367028895 -3.06687034198862 2.41967833408621
 H -1.18372942741684 -3.89924061489689 0.85958300154406
 C -1.46803692743365 -1.73819376191724 0.77399934782611
 C -2.24571084682201 -1.69672955421626 -0.53570943568970
 C -3.16037621755570 -2.67551895326871 -0.91650775997253
```

H -3.36518893069582 -3.51983974964489 -0.27061443734696

C -3.80820435081872 -2.57345591800216 -2.14286307606320

H -4.52125267831043 -3.33541757425315 -2.44401984724173

C -3.52955945228567 -1.49747424270595 -2.97433042770379

H -4.00796459233746 -1.38365790824466 -3.94112822501866

C -2.61256595209008 -0.55444903300676 -2.53914168883744

H -2.35061636949768 0.30858888660944 -3.14508213620295

C -2.01186305323517 -0.66547042713227 1.76484085110622

H -2.92228871763937 -1.05917632222893 2.23641727468804

H -1.25751453994853 -0.53161937109304 2.55438768653411

C -3.33548383416485 1.28349902832846 1.51729972737114

H -3.94013821366670 0.86765013337562 2.33568567504956

C -3.81443881258416 2.53044481058947 0.98498325171338

C -4.85507804594351 3.15293382288175 1.71328362911142

H -5.20133177820202 2.67078848682252 2.62549872640501

C -5.42427072013445 4.34085761099584 1.30738709150868

H -6.21460659459955 4.80313948861424 1.88975384068669

C -4.96727394899380 4.93565980103609 0.12094117044787

H -5.40625667946723 5.87103091667093 -0.21794636441230

C -3.96938615813786 4.34697120141198 -0.62955390055458

H -3.62368323517901 4.80218896821557 -1.55357268739150

C -3.35792126940282 3.13129705446417 -0.23614720784602

C 0.05938693454433 -1.53175955517629 0.48265278078541

H 0.63292217176980 -2.10194841139498 1.22557584033567

H 0.28626855811095 -1.94431401401079 -0.50909362668070

C 1.37825594909278 0.21925204035046 1.37330686151906

H 1.87052619185266 -0.58135434034676 1.94194562387201

```
C 1.84644944987919 1.53996864683519 1.67524213232271
C 2.93737347072524 1.61247299579412 2.57558997285005
H 3.34598000043536 0.68110288336136 2.96315459972883
C 3.48856555544749 2.81423595901166 2.96003355102330
H 4.32569690770529 2.84375703927517 3.65059551062872
C 2.94645686073096 4.00197060735913 2.43974105099377
H 3.37812763997513 4.95953392016463 2.72116230076864
C 1.86699570889325 3.97460131390733 1.58136000622418
H 1.43866528804212 4.89454909056604 1.19324799512323
C 1.25914119719927 2.75575181244176 1.18543424600227
O -0.18640048386649 1.38065304950111 -2.54720834986991
C 0.95356447129077 1.70342316997500 -3.08918799896311
O 1.15592578604645 1.62190172372064 -4.30081537646049
C 2.03458507924138 2.19984121545750 -2.14057536467970
H 2.18520360283015 1.44027245412497 -1.36226657907641
H 1.64746549507001 3.08906406267317 -1.62808536197267
C 3.36400019280108 2.51763312337947 -2.83287284182372
H 3.22494112987685 3.29581526521564 -3.58604443685905
H 3.75694452138294 1.61836997729331 -3.31657930337293
C 4.33276055059283 3.01707019759064 -1.79692724334073
O 4.58191375779270 4.18353126043622 -1.56466925136230
O 4.85500270945588 1.99369639233906 -1.08880188879910
C 5.65517220811227 2.36057401286574 0.06479777876069
H 6.57599130153773 2.84679748636422 -0.27060175967608
H 5.08595285178761 3.06532744402802 0.67875306498009
C 5.92051285045417 1.06488843776447 0.80882716814591
H 4.98981961208563 0.50129891090375 0.92747826402156
```

```
  H 6.61014315688575 0.42622961616490 0.24081196303171
  C 6.50783409871351 1.24314514291941 2.18527099733200
  O 6.45939861571223 0.40286476487562 3.06100747961001
  O 7.11121432829032 2.43462273863507 2.32777105222886
  C 7.71312675845133 2.68893784249123 3.62175860362837
  H 8.49320880447263 1.95116213053950 3.82553611334953
  H 8.13793723342283 3.68975991158794 3.55023487465619
  H 6.95096273395057 2.64774313232006 4.40424162613577
```

A.6.2 Cartesian coordinates for the optimised geometries for the Ga(Salpy) ROCOP propagation cycle

DFT Cartesian coordinates A.17: Ga(Salpy) ROCOP propagation cycle - INT0

```
Charge: -1
Multiplicity: 1
Number of atoms: 64

  Ga -0.68597337153309 0.43910156551104 0.13868168865519
  O -2.17319465319213 0.33306289571139 -1.17373125311587
  O -0.38206434597326 2.28307500982481 -0.37929196499043
  N 3.45330956040467 -1.83501430348818 -1.01671318033323
  N -0.96005001834468 -1.62567647233587 0.36576674282173
  N 0.73469148026188 -0.15635791692360 -1.28394481069641
  C 0.96251625075315 -3.96290226043264 -1.17643728265633
  H -0.09034519465683 -4.12299852868677 -1.43865259079519
  H 1.26067639156719 -4.73033950562287 -0.45538023623332
  H 1.56977082224591 -4.08134398038808 -2.08051354244685
```

C 1.14833299960577 -2.55473465151270 -0.57379696585361

C 2.60881576616502 -2.41306715330446 -0.15356188709736

C 3.05532994503723 -2.93610413261051 1.06675888549065

H 2.36600126210450 -3.43237658676081 1.74334556165217

C 4.39502136237608 -2.82062638763736 1.40751110031025

H 4.75560062808764 -3.21694091655930 2.35279483022898

C 5.26467182320841 -2.18965813674527 0.52292700259444

H 6.31883279805808 -2.06800193669995 0.75220926671794

C 4.74478025645385 -1.72389196060970 -0.67676801812982

H 5.39222074426291 -1.23705476177984 -1.40611173917691

C 0.21523627235019 -2.41689415475879 0.68122003545642

H -0.07278125771829 -3.41638883803474 1.03736251201895

H 0.75270578112027 -1.89650182965275 1.47649270415857

C -2.10813744933574 -2.20495867567439 0.26123942288511

H -2.19082179133702 -3.26550656552700 0.53643268062378

C -3.30332429153606 -1.57752700710565 -0.22699549735437

C -4.52267074677467 -2.26680947718978 -0.07201572839323

H -4.51693139920452 -3.20870273548079 0.47372710081679

C -5.70471167070467 -1.76998500642152 -0.58440679769433

C -5.67493967358776 -0.56586985407680 -1.30565460558693

H -6.59670732798028 -0.16568981027534 -1.72178758899551

C -4.49204312665020 0.12264466049916 -1.49747214368998

C -3.26876798686110 -0.34454457282562 -0.95762131690839

H -6.63819492005143 -2.30496472207800 -0.44187386081679

H -4.47209782734995 1.05368966638042 -2.05758107327545

C 0.76702334217583 -1.55739621876148 -1.69553174737240

H 1.46313217104952 -1.69563512608303 -2.53036612738247

```
H -0.23766858958026 -1.82654299043958 -2.04492317035399
C 1.64050543144202 0.63542039895092 -1.75121281284352
H 2.40296329829976 0.22062761441412 -2.42049936881692
C 1.75901661365093 2.03866173534663 -1.46651000662632
C 2.91928336352727 2.69254334337120 -1.93312632417208
H 3.66965745204675 2.09798237989520 -2.45162827001397
C 3.11858309468005 4.04483835363016 -1.74163477168891
C 2.12367824155433 4.78619932587279 -1.08312032032335
H 2.26309336610622 5.85341501333817 -0.92619792773999
C 0.96728954470711 4.18237496108430 -0.63007316079488
C 0.74268223058098 2.79326817807022 -0.79777907336392
H 4.02276851686474 4.52779453372690 -2.09830422447849
H 0.19785565483356 4.75651580476170 -0.12102948528791
O 0.83804509925466 0.35759698668625 1.41348226240615
O -1.94812293569972 0.71459648495047 1.62052618907073
C -3.04622057547293 1.38555088984784 1.79167469090919
C -3.25843306494386 2.62202031128355 0.93981020646125
H -2.53914244570190 3.38728093592618 1.25323584492035
H -3.05386230164115 2.40833672267940 -0.11177146011328
H -4.27346438918852 3.00358268909480 1.06629943458359
O -3.88067112190379 1.07051866831746 2.65219237378269
C 1.35798566296318 1.23501232682274 2.21562008472011
O 0.84460519897939 2.30097467276523 2.56801310330609
C 2.73498246671862 0.82566811617532 2.72087621627702
H 2.67286158576254 -0.14952058319737 3.21585666828252
H 3.41418714302998 0.70971631466788 1.86832770658386
H 3.13862885463359 1.56645720007428 3.41363601987823
```

DFT Cartesian coordinates A.18: Ga(Salpy) ROCOP propagation cycle - INT1

```
Charge: 0

Multiplicity: 1

Number of atoms: 57


  Ga -1.00464163005521 0.93558350966742 0.16194414400306

  O -2.54900036741210 1.00913067272625 -0.95753028760520

  O -0.54877591584311 2.77176203239508 -0.19174110369675

  N 3.06443812950733 -1.89680847997489 -0.88385835446491

  N -1.35642543702748 -1.05562840923813 0.50126883118018

  N 0.54304889192502 0.30687530080284 -0.97077170875307

  C 0.19164643122166 -3.47936063482570 -1.06642547489338

  H -0.88002458095613 -3.42775053347661 -1.29331226352502

  H 0.36481092917664 -4.31860851596972 -0.38585969164698

  H 0.73308556187190 -3.67117346626687 -1.99915490718756

  C 0.66571171953321 -2.16014630671695 -0.42794200624697

  C 2.13088582239559 -2.32203401613242 -0.02385013682590

  C 2.47397680897800 -2.95408362326730 1.17711027164137

  H 1.70664074965758 -3.31231305686091 1.85658169590072

  C 3.81374156352158 -3.13125227477621 1.49287158656999

  H 4.09730663624117 -3.61959091709188 2.42101756872751

  C 4.78271928511646 -2.67605484736463 0.60430532845638

  H 5.84207507441165 -2.78983042671626 0.81222017162095

  C 4.35539588865282 -2.06981412531905 -0.56904757212645

  H 5.07960025429769 -1.70343586533962 -1.29624742126391

  C -0.19293517136504 -1.86017665605052 0.84248358792724

  H -0.49889946322693 -2.80247281494291 1.31643118667144
```

```
H 0.40509398832028 -1.28843049433700 1.55905873326108
C -2.52880881623737 -1.59293967249498 0.42631769760297
H -2.64873897556104 -2.63997018490526 0.73299313461236
C -3.70254022786570 -0.92741248125302 -0.05982637563355
C -4.93558328095242 -1.60221206583932 0.07224137011398
H -4.94591893248284 -2.55944283385124 0.58969198786400
C -6.10501420505901 -1.07563160765386 -0.43430563051017
C -6.05491716022513 0.14886249844132 -1.11863768891922
H -6.96757629342713 0.57283899115086 -1.53027474288048
C -4.86223424997279 0.82769922550747 -1.28135106034994
C -3.65337914043302 0.32453224637665 -0.75273314272598
H -7.04591221400236 -1.60302732018204 -0.31584761630790
H -4.82467272429326 1.77335965960084 -1.81454358912089
C 0.48064561043837 -1.05919073251730 -1.49684444973568
H 1.22653620880058 -1.20034661976739 -2.28413189327846
H -0.51365871491070 -1.19011573007167 -1.94108641937925
C 1.58939698976376 1.03280159214398 -1.21214895286681
H 2.42075812584032 0.57294905977880 -1.75700318823483
C 1.75064592591128 2.40605157567428 -0.84128049820897
C 3.02166761628207 2.98710915224159 -1.04697845222864
H 3.82231261223764 2.35327248923942 -1.42319498709523
C 3.25821438080714 4.31841000165234 -0.77861614624994
C 2.19747777710576 5.11481879250738 -0.31628332828628
H 2.36807871596879 6.16832099957282 -0.10802443251785
C 0.93648089834466 4.58478416376716 -0.12391850407716
C 0.67060047635055 3.21790984554892 -0.36760403174782
H 4.24310244838646 4.74738563486579 -0.93180497056353
```

```
 H 0.11590288574406 5.20412831873780 0.22723822691424
 O 0.11462512329514 1.03874011115032 1.99727033722179
 C -0.95231223741104 1.40548264514391 2.58392417292999
 O -2.02575230343237 1.47922280724878 1.89968613326188
 C -0.94739025445840 1.77976032988897 4.03334581908278
 H -0.13279479986625 1.28134265604268 4.56115690192046
 H -0.79118435460685 2.86282093485004 4.10173155947731
 H -1.90953207902147 1.54829946647993 4.49429058219304
```

DFT Cartesian coordinates A.19: Ga(Salpy) ROCOP propagation cycle - INT1-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 57

 Ga -0.06342463118449 -0.04769486543223 0.38666673553235
 O 0.56089462030461 1.70090739611072 0.93910380184949
 O -1.77408981278969 0.68520210670510 -0.19609063240984
 N 1.83006011910997 -0.93762468448929 0.84478396054502
 N 0.89862771636767 0.25447599273299 -1.42713347728124
 N -0.64554100187371 -1.86482260067402 -0.38132915015423
 C 2.42365743701930 -3.14491541314370 -2.14230064792489
 H 3.36448363615965 -2.73221487217595 -2.51717820192020
 H 1.80603109454147 -3.40939201766289 -3.00653335419275
 H 2.63816656264237 -4.06197761220430 -1.58358698938748
 C 1.66982564010701 -2.13239163326738 -1.27542465950202
 C 2.48398203351319 -1.68622496437731 -0.06936638832889
 C 3.80957987501564 -2.05369400200669 0.14736022658925
 H 4.33870568130086 -2.65671937103913 -0.57965303432852
```

C 4.45230686107970 -1.65209104835549 1.31279335916009

H 5.48584745524490 -1.93641180002529 1.48803735976149

C 3.75920869092853 -0.89538722391567 2.24865111444280

H 4.22139333051307 -0.56925547025167 3.17410141907557

C 2.44570902135062 -0.55537877103765 1.97280997571862

H 1.85269571716163 0.04058581935388 2.66053946614012

C 1.30327868918089 -0.92808522444591 -2.18636457689989

H 2.16338023928935 -0.68833424808612 -2.82496022824504

H 0.47747341710223 -1.24899941793244 -2.83925318540034

C 1.14361842847555 1.42363067836649 -1.91806036179640

H 1.59377006823714 1.49398695850745 -2.91716733691459

C 0.89352777573371 2.66823699316817 -1.24978553866064

C 1.01795351727077 3.85371095972939 -2.00502831970627

H 1.24372394824861 3.76801963086925 -3.06627796356849

C 0.85314018954459 5.09695000130836 -1.42975820685426

H 0.93977741127182 5.99866457202489 -2.02727024954815

C 0.58454767949738 5.17584288118924 -0.05400061245879

H 0.45899412031778 6.14926918521424 0.41410753598472

C 0.48249805155244 4.03558718682524 0.72025856283438

H 0.28464576990045 4.09850721987079 1.78678338617667

C 0.62571386049884 2.74780365805359 0.15450111265795

C 0.38252692605844 -2.83161785843831 -0.76461487332382

H -0.00160783836407 -3.48269839816616 -1.56086404706730

H 0.63910377217526 -3.46693003476139 0.09562158103764

C -1.88507884428612 -2.22341707613935 -0.46333501033711

H -2.11213771012332 -3.25288547393787 -0.76966189479973

C -3.01611131519126 -1.38247930306747 -0.20541266371665

```
C -4.28701707561444 -1.99446322158263 -0.14967579136616
H -4.34420709191791 -3.07656559282828 -0.24963173473872
C -5.43574510851760 -1.25416099129049 0.03621153377709
H -6.40413651326285 -1.74066048858442 0.09140797883151
C -5.33262318440719 0.14234307986747 0.14110108798685
H -6.23122881936900 0.73830804766342 0.28149433088378
C -4.10687162915413 0.77572163274562 0.06562675103211
H -4.02983844945773 1.85701104298915 0.13994518417714
C -2.91060154667801 0.04121591334825 -0.10180285493267
O -0.62300178612462 -0.61056492900359 2.16766298735369
C -1.44639319465466 -0.14691133590157 3.06917756899028
O -1.88143587718099 -0.86612863436253 3.97375423758353
C -1.81020329008307 1.32376412284897 3.02342034019717
H -2.71901805713501 1.50231684549455 3.60137309955485
H -0.98833289891309 1.88912624452467 3.47858567258788
H -1.92120368043247 1.68491040907528 1.99964161530305
```

DFT Cartesian coordinates A.20: Ga(Salpy) ROCOP propagation cycle - INT2

```
Charge: 0
Multiplicity: 1
Number of atoms: 64

Ga -0.63614605449635 0.20549115453403 0.16966734257933
O -2.07455809976987 0.45511340029639 -1.08705664403902
O -0.06040402590752 2.04075777554895 0.19990410916084
N 3.42843282805480 -1.74208263494883 -0.70485911038958
N -1.01490926284306 -1.80921023317645 0.22479993639865
N 0.79884631829801 -0.26214873853759 -1.21206519657301
```

```
C 1.17297548306740 -4.06513829494635 -1.32098240454847
H 0.18903917428313 -4.25569748512120 -1.76572096637736
H 1.39338382700048 -4.86791368894049 -0.61091731903860
H 1.92826428598406 -4.08649998503244 -2.11368655992294
C 1.17372011028804 -2.69749069383747 -0.60336691332345
C 2.56530026973872 -2.49329051716936 -0.00968447697666
C 2.94185770733532 -3.13991814038684 1.17359434796979
H 2.23988791943521 -3.77298780739959 1.70875296952326
C 4.23239320228060 -2.97585763815835 1.65574827529146
H 4.54118395256749 -3.46893673637864 2.57331935258859
C 5.12184413842984 -2.17479377303501 0.94501116080491
H 6.13920686941383 -2.01382898124013 1.28795260672395
C 4.67262618728168 -1.58854564475717 -0.23027056421849
H 5.33905953142695 -0.96404851752094 -0.82481904511963
C 0.07372212953075 -2.73039913041992 0.52092213032431
H -0.31666362708624 -3.75102990466464 0.62520309580659
H 0.51047353694338 -2.43175489591842 1.47617414612835
C -2.19780040678491 -2.27691991200862 -0.00477847241658
H -2.36604001630980 -3.35229920405583 0.13480156113883
C -3.32590660436859 -1.51932919009285 -0.46768543385626
C -4.58000867737694 -2.16763214331622 -0.47820504735900
H -4.64400763388784 -3.17295400456140 -0.06650243270909
C -5.70568080873891 -1.55645234569784 -0.98982699890862
C -5.58648551336711 -0.27156397962068 -1.54211575427422
H -6.46306656530396 0.21858430362384 -1.95876813802832
C -4.36976949409308 0.38316477437539 -1.56865325691759
C -3.20689942720235 -0.20567858196356 -1.02368920087813
```

H -6.66421274578259 -2.06492115546605 -0.97824551282424

H -4.27761722210933 1.37655048643119 -1.99895589149014

C 0.85986122726771 -1.64852504455627 -1.68896935709715

H 1.60763834867815 -1.73393400064763 -2.48412554724279

H -0.11736503505612 -1.89841839381313 -2.12291827199688

C 1.55057661824506 0.60625600490083 -1.80873516975683

H 2.22307655100544 0.24755726880097 -2.59591308241853

C 1.59612968298068 2.01600090861447 -1.55733370576952

C 2.49940907738480 2.77817859005867 -2.33152244597555

H 3.10930443888959 2.26013644021718 -3.06893391200043

C 2.61655735338897 4.14247012854974 -2.17019185191856

C 1.81443080439260 4.78236854578066 -1.21164981064780

H 1.89540226390833 5.85784598649438 -1.07395629055586

C 0.92084153843353 4.06831863655168 -0.43681228633268

C 0.78402242403086 2.66911881110945 -0.58030654841644

H 3.31539523308180 4.71258958807337 -2.77347637440342

H 0.30183008283780 4.56329324202546 0.30632108987347

O -1.61835879349120 0.38964607963776 1.82767909326914

C -2.34174706235157 1.33960331453892 2.36051478071800

C -3.06180527817203 2.28852364901563 1.42583770452510

H -2.39221823842056 2.65412494705060 0.64402835761231

H -3.87160919519882 1.74016815038785 0.92998111488790

H -3.48842547847306 3.12208681338175 1.98627509851824

O -2.48584305170560 1.42953544180295 3.58267239169380

O 1.01431617592588 -0.17826755116712 1.67108908429521

C 1.27175038496478 0.75982872476141 2.74691886322525

C 2.29525304313591 0.50191425707817 1.73284160801428

```
  H 1.34770200259338 0.28729225323014 3.72334159023714
  H 0.68805550249770 1.67441487470275 2.68514385175242
  H 3.12607361493022 -0.16352048558690 1.95810559495779
  H 2.45670447836454 1.23505488256940 0.94609873670292
```

DFT Cartesian coordinates A.21: Ga(Salpy) ROCOP propagation cycle - TS1

```
Charge: -1
Multiplicity: 1
Number of atoms: 71

  Ga 0.51352790232600 -0.22614099698633 0.61129228484171
  O 1.42989445556627 -1.62883610362921 1.62897502781142
  O 0.54089614195297 1.01023042064169 2.10456639609035
  N -4.37450192390480 -1.27684341969469 -0.23288839141953
  N 0.26433107644467 -1.62934943969230 -0.89048466268415
  N -1.39053850718992 -0.82718424701075 1.17782688855864
  C -2.35634276957353 -3.62503029195229 -1.21673131573920
  H -1.42678819664319 -4.18331942768705 -1.05217591190108
  H -2.63661372779830 -3.71855700308149 -2.27055203070145
  H -3.14480648279037 -4.07752877313088 -0.60558091065085
  C -2.16048532893673 -2.14332815087195 -0.84002449962969
  C -3.44449753269102 -1.39280945765881 -1.18978544259458
  C -3.66482850742837 -0.91172951936861 -2.48605423218700
  H -2.91380253942544 -1.03366469260327 -3.26046524775785
  C -4.86459527576618 -0.28004372875622 -2.78249921718939
  H -5.04961760564944 0.10023683841962 -3.78328918057915
  C -5.82063294540220 -0.14251773366787 -1.78128456823919
  H -6.77017997478637 0.35006329988984 -1.96637323950213
```

C -5.52758304713693 -0.66194870162534 -0.52761330923985

H -6.25078157507050 -0.58426991040846 0.28405885143333

C -0.96331106795519 -1.55881426736477 -1.66320895439053

H -0.86319802776215 -2.10747576851173 -2.61021430109412

H -1.15533396579103 -0.50702153695900 -1.88745083582465

C 1.12994974975239 -2.55683046894028 -1.12961463103706

H 0.99975775543571 -3.18453179674030 -2.02161332114609

C 2.24704995945636 -2.86597759905611 -0.28256444367270

C 3.23281553699282 -3.74024602994865 -0.78388264125205

H 3.14554467209544 -4.07870739123407 -1.81463955869053

C 4.29209635588107 -4.15880212005640 -0.00413719371612

C 4.36159729698400 -3.72768075966466 1.32965467817125

H 5.18571053829913 -4.05588946149990 1.95872680205479

C 3.39820926986860 -2.89055172834547 1.86051169540740

C 2.32018461041271 -2.41661809078561 1.07720213651737

H 5.05164991960164 -4.81862713164126 -0.41084653681870

H 3.45399420142859 -2.55932341600070 2.89390125357261

C -1.87131856270104 -2.11471737237477 0.67996935848871

H -2.77693935454622 -2.42096410826924 1.21313849001649

H -1.08850026912725 -2.85588179024400 0.88246183189504

C -2.17867579079555 -0.11003046700093 1.90786656488807

H -3.19563665938895 -0.47503728953089 2.09226217664792

C -1.83812555332913 1.14467408198200 2.51741391829731

C -2.88415848276325 1.87128031816874 3.12469580947054

H -3.89236275870241 1.46475363344137 3.06775026909814

C -2.65591196151489 3.06984978433122 3.76994492180962

C -1.34199814863211 3.55898694212717 3.84038032075631

```
H -1.14431328510131 4.49987241456963 4.34866331093661
C -0.29077688573072 2.86243200488758 3.27544707268903
C -0.49740692782966 1.64011764530608 2.59275191912003
H -3.47508462974226 3.62056731537246 4.22099195850488
H 0.72683652919278 3.23916638277074 3.33549449593944
O 2.18638397412463 0.36488876355178 -0.23449361598757
C 3.42117341575896 0.49235593352720 0.16066811794806
C 3.66199726710229 0.81378496297678 1.62143082998435
H 3.28426468538411 1.82221841324237 1.82473604055878
H 3.10195578230386 0.13116085274241 2.26516462061494
H 4.72816345287486 0.77068401350396 1.85086292672655
O 4.36981653697585 0.40621541797859 -0.62786663196182
O -0.45382905615667 1.19793635587584 -0.50346081870903
C 0.22110015950225 1.99113942214639 -1.91637699092226
C 0.08967849281031 2.52582265144950 -0.57589621104826
H -0.62339643697242 2.03229121989092 -2.58776180954660
H 1.08815006163632 1.39571064188185 -2.15960324167671
H -0.65742053524437 3.30429264518646 -0.40421084782789
H 1.00435015376214 2.66832461148854 0.00123281826620
O 0.96094852290486 3.56147632797607 -3.25689519421024
C 2.11401800236633 4.10961469208651 -3.16872705485492
O 2.52724028749792 4.99578275402783 -3.95052214592457
C 3.02120343758315 3.67198063308451 -2.01885159509375
H 4.05077119998353 3.99280574608373 -2.19287172647063
H 2.66702255289768 4.13898410740592 -1.09197563021512
H 2.99401034281973 2.58912894397901 -1.86655569500890
```

DFT Cartesian coordinates A.22: Ga(Salpy) ROCOP propagation cycle - INT3

```
Charge: -1

Multiplicity: 1

Number of atoms: 71


  Ga -1.13198784030341 0.41067820259661 0.34951059956942

  O -2.84223876617496 0.47481741978446 -0.70311684878069

  O -0.94243002696736 2.35310691356052 0.12853654529527

  N 2.63482149493126 -1.39710647578776 -2.02707601304284

  N -1.37956294350611 -1.66965082424142 0.24152912216747

  N -0.09576976460931 0.13344914512551 -1.46612976935149

  C 0.22318012009159 -3.63306312671203 -2.01164905415490

  H -0.85762369516523 -3.80935517518267 -2.07340795781901

  H 0.68385762731024 -4.48339132025848 -1.49930106783356

  H 0.62698578271245 -3.57975966057481 -3.02870864475628

  C 0.50154126120372 -2.32524053963699 -1.24205004572005

  C 2.01406143558162 -2.16348029330350 -1.12043049126128

  C 2.72767309098581 -2.84855419898080 -0.12941079848879

  H 2.21276862497553 -3.48939695964819 0.58039859814066

  C 4.10582728849350 -2.70420884471360 -0.05877221339058

  H 4.67242676388498 -3.22259556009460 0.70969483072339

  C 4.74509574994541 -1.88241552308206 -0.98201856958149

  H 5.82012736587502 -1.73137434555876 -0.95874009019989

  C 3.96544467973496 -1.26055653511492 -1.94803618876036

  H 4.42713186201210 -0.61922846520276 -2.69881804442047

  C -0.14797497671424 -2.43361309303456 0.18509774757246

  H -0.32660692687462 -3.49067287450037 0.42985505152397

  H 0.52699538025877 -1.99652158515737 0.92563044560988
```

C -2.51921335235756 -2.27207455630232 0.23104522889384

H -2.54376462636209 -3.36748894862149 0.32163288949337

C -3.78410501687168 -1.61200108055017 0.06601425185436

C -4.95615225104215 -2.35911265773697 0.29648473565162

H -4.85314194459510 -3.37957286500874 0.66175240045808

C -6.21104219388126 -1.82513776266910 0.07889943394402

C -6.31006343157611 -0.51585746256728 -0.41848705415516

H -7.29110398648879 -0.08362895326008 -0.60274268104392

C -5.18052092927584 0.23611105951406 -0.67908316700438

C -3.87865239536420 -0.26982752918850 -0.43502057779474

H -7.10388641358785 -2.40936424267224 0.27761140813557

H -5.26126737327398 1.24917797643398 -1.06420946498490

C -0.13088443064332 -1.19303335879286 -2.08135886878912

H 0.36280577463187 -1.17193803130598 -3.05964321278874

H -1.18453239819888 -1.45471954995525 -2.24373995265195

C 0.52397498897834 1.06832863662420 -2.10516716352458

H 1.04129787678542 0.80712562690813 -3.03703268285942

C 0.61018628478867 2.45024304531442 -1.72356730904706

C 1.44882193963324 3.27487748166475 -2.50407216960931

H 1.99393363287685 2.81672372673241 -3.32766905069641

C 1.59307516370096 4.62305793784766 -2.24685256874149

C 0.86622882920754 5.18658478715710 -1.18478825098554

H 0.96298746830469 6.24847687472233 -0.96969748104283

C 0.02680061225514 4.41413220942711 -0.40762560916147

C -0.13021125744829 3.02166575617604 -0.63687809053221

H 2.24915063710440 5.23673869536468 -2.85582966083082

H -0.53646312662098 4.85199651870501 0.41228863152512

```
  O -2.20605852179967 0.44185380719745 2.02660355299574
  C -3.30098480821673 1.00403252375444 2.42933138858346
  C -3.66731488913500 2.35051613102795 1.83139932746466
  H -2.98886638836924 3.10676441093699 2.24359130113476
  H -3.52413088855938 2.34759306762871 0.74912266352535
  H -4.69512027040528 2.61631698157732 2.08703860475587
  O -4.01367664104197 0.50876427485537 3.31679863345198
  O 0.41970265137523 0.22384229856913 1.45234361732927
  C 2.69219606859039 0.13340477391884 2.06782032781024
  C 1.67131860211123 0.73187940598193 1.11298452620899
  H 1.98911527574218 0.46965773740851 0.08584317579745
  H 1.71690471834211 1.83739004094658 1.18077660688571
  O 4.00780675718685 0.57088024752290 1.61875273462403
  C 5.07112281740126 -0.05949983423705 2.13813526663847
  O 4.99467935438843 -0.94777555002143 2.96704263563492
  C 6.35818212487603 0.48848928069169 1.59037922895562
  H 7.13366226155911 -0.27730173165706 1.64182920454336
  H 6.23564511559693 0.84782892188320 0.56663639001835
  H 6.66611191453075 1.33535847532086 2.21467311886065
  H 2.64694560216078 -0.96017465200927 2.03758265438980
  H 2.53575747530518 0.46982977446054 3.09946393363858
```

DFT Cartesian coordinates A.23: Ga(Salpy) ROCOP propagation cycle - INT4

```
Charge: 0
Multiplicity: 1
Number of atoms: 64

  Ga -0.59667699000970 0.28153259404066 0.05157621305689
```

O -2.36871477735743 0.52962316820029 -0.57629445103799

O -0.30840533979665 2.17143549811050 -0.28881654796006

N 3.57266360258879 -1.70448967104803 -0.56887567434650

N -0.95514138603823 -1.75276931704468 0.18984979193798

N 0.91401326102756 -0.19927228933495 -1.18288999606444

C 1.21109430412785 -4.00817037206428 -1.15770975654877

H 0.20389565375793 -4.18043003292429 -1.55588532941664

H 1.43041911261141 -4.78706168697274 -0.42137737946219

H 1.93097836387410 -4.09450866032743 -1.97864746489483

C 1.29219973887245 -2.61335264359301 -0.50648225698572

C 2.67947856011442 -2.43789105175485 0.10546628323751

C 2.99969129261594 -3.05363837843301 1.32118886619142

H 2.26944719925772 -3.66869016244310 1.83985558728359

C 4.26270173431898 -2.86691057035530 1.86348127687890

H 4.52721347789379 -3.33013312896425 2.80999435554180

C 5.18051278681119 -2.07641019809910 1.17781107506629

H 6.17635042156706 -1.89383240776503 1.56956828875464

C 4.79046938035709 -1.52945054562114 -0.03686285788654

H 5.48255946183711 -0.91663881053627 -0.61371138420509

C 0.20980352450919 -2.51170608322655 0.62161919273446

H -0.08156529095141 -3.51791104320059 0.95142949671740

H 0.62409592350264 -1.97779767225963 1.48313111452510

C -2.08679622891603 -2.34868340264308 0.01866456625563

H -2.14803716488982 -3.42809542204426 0.20858382747915

C -3.29670453866885 -1.70695838207086 -0.40336711949230

C -4.44571284700486 -2.51385797957934 -0.54916771471973

H -4.35914986173432 -3.57663704843348 -0.33185911383311

C -5.65245722728150 -1.98483952204131 -0.95672172323094

C -5.73052882769896 -0.61044458054837 -1.22915214926205

H -6.67459779618384 -0.17805651706345 -1.55132110110474

C -4.62496968121571 0.20800431296443 -1.09375778541917

C -3.37846424696076 -0.30846540676615 -0.67841672376240

H -6.52615854326608 -2.61922265789308 -1.06468314446213

H -4.68670108420897 1.27203492583859 -1.30331626109587

C 1.02827560555981 -1.59372757017029 -1.63039766929208

H 1.82124347096295 -1.67887742880494 -2.37955001976925

H 0.08156193105097 -1.86752880562547 -2.11325616031732

C 1.78977651974388 0.64989497917312 -1.63659337277325

H 2.59185178126884 0.25456580621098 -2.26686153192134

C 1.81688752198395 2.05682711200976 -1.40988668198081

C 2.92871228763248 2.77265409435610 -1.90956909569315

H 3.71429408135410 2.21637555848616 -2.41695764758669

C 3.03474695930076 4.13650943499921 -1.75145721876061

C 2.00158022020041 4.82554338642380 -1.09188645022263

H 2.07392507190118 5.90268254209829 -0.96150402686615

C 0.89212303960212 4.16165388299832 -0.60802913883926

C 0.76352266160124 2.75909519049758 -0.74557678308380

H 3.89888184505648 4.67228550470382 -2.13032109431323

H 0.09257796209709 4.69718248866498 -0.10391193870626

O -0.29537181001284 0.33425837893861 1.87849766125320

C 1.98520202380146 0.32093035609339 2.60624928014029

C 0.70008375884573 1.13293701591829 2.47224403008002

H 0.91262279089353 2.05262386289955 1.90190319539336

H 0.37112540615949 1.44173970748036 3.47763922731837

```
  O 2.98779900721330 1.07728730723537 3.33810215333958
  C 3.86140378716629 1.81257710968764 2.62004132908908
  O 3.89742110156094 1.82999387719991 1.40523421200617
  C 4.76070029713402 2.61272619900568 3.51625757453038
  H 5.66743531566377 2.88742269261104 2.97625797217286
  H 4.23282238704898 3.52921394861246 3.80425086049728
  H 5.00307636235826 2.06466073641702 4.42923656996913
  H 2.37687619876202 0.04094630614987 1.62220922819800
  H 1.81003644662653 -0.57875852837335 3.20373153566851
```

DFT Cartesian coordinates A.24: Ga(Salpy) ROCOP propagation cycle - INT4-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 64

  Ga 0.17631033029143 -0.25777044853843 0.63391919579719
  O 0.81056558522113 1.50660341308101 1.20365472913078
  O -1.62956061875112 0.46628983821116 0.33925990973846
  N 2.15198384671102 -1.12144185707335 0.65386408888082
  N 0.82904348803875 0.25315472717082 -1.29155114453382
  N -0.47625920219607 -2.01599972987756 -0.25315567192155
  C 2.29247620411912 -2.99677907517194 -2.60173867928299
  H 3.14899133952584 -2.51210056912043 -3.07877952537752
  H 1.54655315303768 -3.19711043308107 -3.37748259980331
  H 2.61702709000380 -3.95635044135392 -2.18560761984743
  C 1.67007618992033 -2.10749328458587 -1.52149766920827
  C 2.66317119968788 -1.75046786050143 -0.42520053954041
  C 4.01591176174544 -2.08005928837652 -0.46763332107229
```

H 4.43203492644574 -2.58896599158481 -1.32796950890250

C 4.83394377976963 -1.76165102302616 0.61071658363064

H 5.88971407147245 -2.01583019457517 0.58425895484208

C 4.28750854877676 -1.12656798910636 1.71848420779782

H 4.89041158825159 -0.86882943333533 2.58262050992018

C 2.93647417673149 -0.82144911882498 1.69818492592385

H 2.44244018580877 -0.32519571240735 2.52877053492315

C 1.13121125832943 -0.83276122685552 -2.22491746409972

H 1.86889555917500 -0.49601190852942 -2.96512174299339

H 0.21747586204092 -1.11905451564540 -2.76770818149836

C 0.94388285384886 1.46755515282653 -1.71648926010791

H 1.21214653951053 1.63417398757538 -2.76867029623330

C 0.77085944118256 2.64786349877198 -0.92096476548833

C 0.74171171522896 3.89038487353806 -1.58956088055783

H 0.79828848994219 3.89330584743186 -2.67661908303061

C 0.63691003928033 5.08025527736531 -0.89897531110744

H 0.60375089729885 6.02670048148911 -1.42890928807590

C 0.58570762209631 5.04543989470635 0.50424805914094

H 0.50893051367059 5.97577739009279 1.06217275511126

C 0.63650948885895 3.84792884911313 1.19128833824043

H 0.60482557803844 3.82416605071453 2.27728407762190

C 0.72543679736284 2.61007158479222 0.50988335018065

C 0.49729348653550 -2.90151378900597 -0.88837692742730

H 0.00690375962268 -3.48867469800063 -1.67647894168938

H 0.90281407394733 -3.60600221234239 -0.14737043449526

C -1.70433244070902 -2.40997016897184 -0.17567597594660

H -1.96011944184737 -3.41087208787673 -0.54872250204543

```
C -2.79186079769948 -1.64486746587240 0.36192050487934
C -4.00341186092682 -2.32158738395203 0.61803975824652
H -4.04915213416831 -3.39131108001505 0.42267060546885
C -5.10391462739993 -1.66296624569067 1.12670720897318
H -6.02075584086549 -2.20221262442129 1.34155914053286
C -5.01961339962161 -0.27978719148752 1.35546207915565
H -5.88114802601385 0.25210770115358 1.75247349605978
C -3.85989568419868 0.42004489754529 1.08205380179872
H -3.79749345404589 1.49075051593572 1.25708935319716
C -2.70472596070160 -0.23310285113794 0.59039543580966
O -0.05442594365223 -0.88340341759542 2.40192067817717
C -0.81887261901762 -0.14349296630918 3.31643559446679
H -0.19474459143016 0.23230652301778 4.14878127174375
H -1.30129479411372 0.73790431586895 2.86021224741984
C -1.90932665584349 -1.04408302923822 3.87666580073872
H -2.51693350503528 -1.45939171336218 3.06620588180498
H -1.49089076006180 -1.86808555010085 4.46680838975208
O -2.75326370213845 -0.22450414035210 4.73583508881204
C -3.90026841262550 -0.78082784720271 5.15854616308937
C -4.73414637592893 0.19641329510416 5.93561127963406
H -4.11189874160706 0.90087709469580 6.49121617749734
H -5.34085300528563 0.76882702482395 5.22409014811444
H -5.40397713364917 -0.34246470349290 6.60689234896640
O -4.22505171199479 -1.92689096702641 4.90997465906791
```

DFT Cartesian coordinates A.25: Ga(Salpy) ROCOP propagation cycle - INT5

```
Charge: 0
Multiplicity: 1
```

```
Number of atoms: 75


 Ga -0.64821417764367 0.61282659058753 -0.05586962625676
 O -2.50695111260975 0.88183615383876 -0.29563239867291
 O -0.43976519045691 2.46228104903559 -0.62175888651037
 N 3.45021958970293 -1.23288277853431 -0.73209390476310
 N -1.00895478393735 -1.39920537673945 0.28877539434994
 N 0.72047229534895 0.01750263192394 -1.39315159276594
 C 1.29289780221673 -3.72980073854118 -0.91903589640651
 H 0.30822435692272 -4.03752777976237 -1.29039566629836
 H 1.57472528538263 -4.39153316678897 -0.09453193364712
 H 2.02570387206123 -3.84771804093742 -1.72423388770343
 C 1.24378078070904 -2.26455118938684 -0.43779800131910
 C 2.62875405081220 -1.89495022235251 0.09175339423085
 C 3.03653565702213 -2.29467366589642 1.36987307127118
 H 2.37154022630092 -2.86337184228522 2.01376748381879
 C 4.31085010673516 -1.96526087717414 1.81020738589671
 H 4.64173269854054 -2.26401968841930 2.80090486757908
 C 5.15146509348395 -1.24730800001075 0.96513106013897
 H 6.15246909411901 -0.95970783228767 1.27157584517694
 C 4.67692282196863 -0.91455230424821 -0.29641030439511
 H 5.30757721967734 -0.36705360634444 -0.99646580955914
 C 0.17527807367311 -2.14324053487054 0.70327037603579
 H -0.10771514345618 -3.14227743583050 1.05955454284707
 H 0.59809753734381 -1.58782191096810 1.54608400224837
 C -2.15351647262871 -1.99552067734413 0.25485931631712
 H -2.20064893786154 -3.06223772093111 0.50662161733941
```

C -3.39988897754763 -1.36369050073965 -0.06437601920283

C -4.55411365428895 -2.17522063689082 -0.08865963149876

H -4.43916173801670 -3.23889139878685 0.10852946147272

C -5.80175962573430 -1.64558596355811 -0.34200977156339

C -5.91874716152008 -0.26657310570410 -0.56746701391922

H -6.89717210253231 0.16792969481546 -0.75571844051485

C -4.80803019213172 0.55669548500923 -0.54646785349942

C -3.51954572343590 0.03723842417503 -0.30374015896741

H -6.68004357164237 -2.28251606478659 -0.35405545538024

H -4.89990955358525 1.62589478899328 -0.71571913060024

C 0.85667728665135 -1.41932060082770 -1.66683453442633

H 1.60098919572241 -1.57587605413442 -2.45380989599716

H -0.10696596791809 -1.78937291365549 -2.03842502244045

C 1.54641005019686 0.82244231186426 -1.99742195465359

H 2.30025736238467 0.37084847815853 -2.64831116392374

C 1.58066587943352 2.24454888381896 -1.90687813017476

C 2.63929149522880 2.91103464045977 -2.56736171456243

H 3.38292339734196 2.30996120758901 -3.08689991382826

C 2.74074579702129 4.28424627303335 -2.55558417957737

C 1.75619102509585 5.03234143879530 -1.88490935513773

H 1.82417409176322 6.11754063241058 -1.87282457792668

C 0.70148556097719 4.41662638152094 -1.24226963261148

C 0.58023556718046 3.00641567917569 -1.22499050610781

H 3.56187048540579 4.78309285606317 -3.05978399138242

H -0.06001617117004 4.99727740173174 -0.72933872544805

O 0.04937485359317 0.83104207852675 1.64930805961294

C 1.96412812747458 0.87469845041045 3.04368185043487

```
C 1.35109991933041 1.36872579443825 1.74553921817180
H 2.00892136781869 1.03991310442398 0.91906429650520
H 1.34324976268741 2.47254138658587 1.73049434998877
O 3.34814804082226 1.31398708939901 3.04602180836043
C 4.14956821821852 0.77293578379092 3.98126938139780
O 3.76493614167260 -0.02621592854648 4.81300000707455
C 5.55177833229102 1.29762280193447 3.88050052488666
H 6.25236988630471 0.52384780035607 4.19959285660269
H 5.78427162145991 1.63795562465163 2.86997661364023
H 5.64984965495547 2.14882845846596 4.56417819899109
H 1.93072952874157 -0.21875143850811 3.09200505843729
H 1.44922396789065 1.28570021613774 3.92005404741016
O -3.50265193486973 -2.18317291712674 3.32604340787565
C -3.74726744452343 -1.01528436116174 3.20940717573722
C -2.83717502708081 0.17466461215906 3.31530570321016
C -3.71302952877407 1.36819953663153 2.94868709735970
H -1.96451085139297 0.03962069402525 2.66884222897945
H -2.46414018457329 0.21770122080969 4.34490038458400
C -5.10048399448926 0.79928690172634 2.83012844503555
H -3.71816276955660 2.17092159938270 3.69086152064372
H -3.44180872318545 1.81110308363768 1.98317403513701
O -6.14887488486289 1.35188642350584 2.66020170352608
O -5.04858757825952 -0.58907638991892 2.95908888931623
```

DFT Cartesian coordinates A.26: Ga(Salpy) ROCOP propagation cycle - TS2

```
Charge: 0
Multiplicity: 1
Number of atoms: 75
```

Ga -1.41247246790540 -0.46330842442734 0.01315877624310

O -3.24673759625264 -0.81011603761578 0.48015873287048

O -1.18882475209293 -2.31581377066449 -0.50922991545735

N 2.20265157694872 0.44327811872191 2.82872335621862

N -1.66914197160555 1.47337613694780 0.64442281602943

N -0.44452869158929 -0.78094034239068 1.76297991879473

C -0.33489540722925 2.59210932221514 3.54661788059319

H -1.42507086927712 2.71006900664718 3.55895162621664

H 0.11719397601637 3.57522102643282 3.38679224478723

H -0.01374948778324 2.21787009678350 4.52473224312672

C 0.07787088343364 1.61680067968961 2.42597918849440

C 1.60141230435249 1.54775509165258 2.37126398516841

C 2.33398321062699 2.63405370167931 1.87631573557445

H 1.82642018302921 3.52749366671620 1.52266589338015

C 3.71831871235661 2.55892182033993 1.83782351523095

H 4.30251648330152 3.38876372272546 1.45067622409204

C 4.34243015736882 1.40266285082580 2.29789881171215

H 5.42299097485608 1.29718693536993 2.28177133010758

C 3.54174545743067 0.37978501573802 2.78647259908921

H 3.99006526150000 -0.53926518141329 3.16329633858311

C -0.45899277698028 2.16566405980921 1.05495243584545

H -0.63823793157706 3.24609144459054 1.13551699525988

H 0.28896715427165 1.99793120240463 0.27529172778949

C -2.80814360370781 2.08340299971309 0.67279240570705

H -2.82486042737370 3.15303219871945 0.91828693571340

C -4.07623601215013 1.46281792029583 0.42999706741284

```
C -5.20985875247643 2.29950080078824 0.34510157110029
H -5.06157715881207 3.37577099671135 0.40771344486802
C -6.47791335596309 1.78145097218401 0.18534294278472
C -6.63782542643441 0.38754197628968 0.13107514622451
H -7.63263191300940 -0.03505261119633 0.01236434527070
C -5.55130911279911 -0.46070599683996 0.22811297567149
C -4.23850385136611 0.04227039438369 0.37041169729060
H -7.33865772415750 2.43824247499124 0.11268743514801
H -5.67747245931542 -1.53905250538597 0.18975488672426
C -0.55129696809147 0.25712405816197 2.79344630754220
H -0.10294924017693 -0.09550940050028 3.72816971323255
H -1.61982930242128 0.42747793505990 2.97891655406637
C 0.19173537939245 -1.87091985074616 2.05931034940531
H 0.67218744231999 -1.93045528763385 3.04124923245273
C 0.34027555249168 -3.02269705956715 1.22304944690263
C 1.19888255662090 -4.04525809481644 1.68614689346808
H 1.71127606996759 -3.89568285171853 2.63451875781792
C 1.39863203230807 -5.20342713273957 0.96609229879561
C 0.71264395969489 -5.37181370408464 -0.24845817618123
H 0.85568040750191 -6.28298279338110 -0.82444248353351
C -0.14632857692469 -4.40107963084000 -0.72435544384078
C -0.35722810938290 -3.19417280468565 -0.01542395034966
H 2.06739543660322 -5.97504621885095 1.33316612609798
H -0.68261915425917 -4.53686231727438 -1.65955424583999
O 0.16196682567686 0.08334517225838 -1.10199654995929
C 2.49166383385652 0.60203628519893 -1.33758230498466
C 1.46001295769151 -0.45568852004622 -0.97787869703496
```

```
H 1.63963614230153 -0.76623696627871 0.06197157887682
H 1.59306949710222 -1.35314835028427 -1.60561605471326
O 3.78571181374322 0.01587289432911 -1.04988045966886
C 4.84928266970978 0.83826078898785 -1.15037985372529
O 4.76105309706362 2.00369953348200 -1.48079068666714
C 6.12726385973708 0.12097780052614 -0.83251134233584
H 6.89328463200979 0.84478149372320 -0.55204138484311
H 5.98070548600574 -0.61549515953817 -0.03933367693800
H 6.45973611525152 -0.41167938411152 -1.73100694261805
H 2.35472889370920 1.50001162796145 -0.72623503155326
H 2.45138447752045 0.89126156502266 -2.39441984794893
O -2.07411153218948 0.03678512629413 -1.94861013109820
C -1.02938645705113 0.03230030188023 -2.62761484448361
C -0.50307312062324 -1.10835149345407 -3.46411266172803
C 0.53733862631421 -0.45710798653604 -4.36693718043437
H -1.35887272510751 -1.48566432914833 -4.03620064888391
H -0.13921329527491 -1.92228050562503 -2.83622816083438
C 0.27204708946858 1.02200011858362 -4.23553643832252
H 1.56878764481810 -0.65070091420374 -4.05154633771209
H 0.46401327078023 -0.74268546954637 -5.41968656273964
O 0.75330760808698 1.93788078992803 -4.84689161011764
O -0.66671948188001 1.24432097078127 -3.25263886323398
```

DFT Cartesian coordinates A.27: Ga(Salpy) ROCOP propagation cycle - INT6

```
Charge: 0
Multiplicity: 1
Number of atoms: 75
```

```
Ga 1.29430051702199 -0.28436907894181 0.41212592068092
O 2.94718723603707 -0.37337715757872 1.31531895380812
O 1.17313085892205 1.59273841109652 0.85710677251614
N -3.30485221895154 -2.16800462966449 0.65873765391926
N 1.36029568852649 -2.30597047829504 0.06130883681605
N -0.43568416904452 -0.64671042618586 1.35756259403153
C -0.98974399988802 -4.40430419092459 1.06096431037681
H -0.00265895171653 -4.65643181582243 1.46680584571307
H -1.23047074226999 -5.11297817347505 0.26275248301147
H -1.73170003183322 -4.51474893927111 1.85899872295958
C -0.99113795308148 -2.96254388335114 0.51700584287303
C -2.35266312942504 -2.69503271556982 -0.12253671241029
C -2.60960786362427 -3.06166974715270 -1.44784885164119
H -1.83414326705289 -3.50552873830578 -2.06457128452439
C -3.88084537509824 -2.86554831295865 -1.97131162859094
H -4.09819579642260 -3.14503232009417 -2.99850463600808
C -4.86468135630445 -2.30718069335981 -1.16299893059769
H -5.87003673612711 -2.12908912193544 -1.53190323288058
C -4.52597824900123 -1.97805509942000 0.14294048463482
H -5.26573335118312 -1.53632546695162 0.80887386593510
C 0.13816288834960 -2.80878561130173 -0.54781710258795
H 0.31482745569012 -3.76704165373303 -1.05401445492309
H -0.16509242971943 -2.07372055462677 -1.30345835648019
C 2.37843802311047 -3.07623102736046 0.24216547606116
H 2.31974669142450 -4.11893945405388 -0.09543584604249
C 3.60554147464715 -2.67130627289216 0.86472455196876
C 4.62213013430124 -3.64296393778680 0.98622760242885
```

```
H 4.43135614492342 -4.63858819863859 0.59117634841364
C 5.82930805679851 -3.35489922481309 1.58794710670947
C 6.04279155933923 -2.06265388256635 2.08999156453557
H 6.98842501610210 -1.81938228422290 2.56797950340550
C 5.06860217006460 -1.08715745587460 1.98618718645477
C 3.82700993639256 -1.35512523813169 1.37297485232463
H 6.59983076913853 -4.11418876776648 1.67253761930153
H 5.23552576652595 -0.08625198188646 2.37366683207198
C -0.73256332558935 -2.03700229619033 1.72329239240676
H -1.59599753557959 -2.07245300501380 2.39297562473343
H 0.13546739950703 -2.42777866318765 2.26804863896123
C -1.30379975269044 0.26901143387246 1.66817630129664
H -2.24298415885126 -0.05854217869120 2.12596118664868
C -1.15426002895113 1.67486842683880 1.47434497933655
C -2.28269137491761 2.48888309398799 1.72209107184720
H -3.21126683573515 2.00629509387766 2.02042551267893
C -2.22602140294482 3.85787485059982 1.57645988978177
C -1.00537810562294 4.45087353508053 1.20987634601977
H -0.94423985057948 5.53132502937879 1.10443600364562
C 0.12324495711142 3.68715735733778 0.98486384752352
C 0.08355945958678 2.27678499229460 1.08853050312381
H -3.10395524355354 4.46986109709455 1.75580534816037
H 1.06713534775864 4.14935643210532 0.70952867362868
O -0.59818631637422 0.70011388708230 -1.59123541198667
C -2.92281473238006 1.08600393636602 -1.58638334158478
C -1.58680291298775 1.61247382579529 -2.07219850758473
H -1.42175760584722 2.61969041226869 -1.66194459680935
```

```
 H -1.57905190699834 1.66387314188589 -3.16948470782329
 O -3.87933998674598 2.13764400528878 -1.85886750245875
 C -4.99903292850264 2.16143789246770 -1.10503245609227
 O -5.25305134684495 1.33293827327750 -0.25459589204571
 C -5.84945625504815 3.34868182794260 -1.44463846035556
 H -6.83793765624477 3.23340129440285 -1.00021059250852
 H -5.37347948214832 4.24877630513113 -1.03942745602609
 H -5.92621826345030 3.47457912426266 -2.52755238293115
 H -2.89230665575483 0.87774613239182 -0.51436855799421
 H -3.22235950075208 0.17609314631941 -2.11857220887622
 O 1.49457304163556 -0.03211496259419 -1.44784441335433
 C 0.70808431017077 0.80110539326880 -2.13008592942588
 C 1.24322488396690 2.23920124171761 -2.31261332661742
 C 1.03229864302053 2.57994806199582 -3.78359243396887
 H 2.30637097052411 2.20836716504563 -2.06497316906446
 H 0.75783358265323 2.93133558857938 -1.62233083967125
 C 0.78591287263511 1.24712978662233 -4.45177034245660
 H 0.15511261352413 3.21297419392473 -3.96231882876092
 H 1.88675959961575 3.07190924602834 -4.25597216706386
 O 0.72427805576829 1.01925628810996 -5.64107936210495
 O 0.61871266104486 0.27631771685039 -3.53440332649197
```

DFT Cartesian coordinates A.28: Ga(Salpy) ROCOP propagation cycle - INT6-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

 Ga -0.67612082882437 0.54256478648442 -0.33536549261423
```

O -1.52244583366341 2.24527304137979 -0.71614932507283

O 0.59490779451039 1.46737385957457 0.81261607971588

N -2.26911895089616 -0.52222196296273 -1.38136576862424

N -2.07895301409590 0.24765145161366 1.19246248757263

N 0.09097598924685 -1.25043706592006 0.29722841001235

C -2.87387937860123 -3.45214537672484 0.88844485337073

H -3.93577211326730 -3.32730283697189 1.11857855071080

H -2.37273626370761 -3.80000244982067 1.79731659292973

H -2.76826992850081 -4.22798382811298 0.12274597448743

C -2.23590514732175 -2.13794766413609 0.43200350575494

C -2.90218273793029 -1.56674424055871 -0.80818562582562

C -4.06887609396622 -2.07966462131806 -1.36926674256965

H -4.57438518522801 -2.92146661377598 -0.91285886442909

C -4.57809417805815 -1.51031440178534 -2.53063581543932

H -5.48679287469260 -1.90478344397022 -2.97617953746332

C -3.91056755922445 -0.44083982275646 -3.11343562511926

H -4.27152839572960 0.02894327646273 -4.02210237649773

C -2.75759668224697 0.02560853062200 -2.50341525592305

H -2.19640445483347 0.86233025636079 -2.90729324395680

C -2.34060466134911 -1.12917875398950 1.61069117091558

H -3.34077867122245 -1.20548574648352 2.05692488534992

H -1.60685434381064 -1.43051925039722 2.37312592586591

C -2.73469230619398 1.20429034273162 1.75857955117196

H -3.42168054902721 0.96081693016394 2.58034675864011

C -2.66133129129876 2.59012351575481 1.39178274086447

C -3.28950850478563 3.52099831084115 2.24687864691286

H -3.75159443847238 3.15067795062271 3.16006248021235

C -3.32055285933658 4.86866346342778 1.95347893686592

H -3.79817744410581 5.57123235162608 2.62867336704643

C -2.73292726491778 5.31307269436210 0.75840375320439

H -2.75390636439148 6.37147177726005 0.50963110792396

C -2.13046789864004 4.42622807160273 -0.11302794325257

H -1.68338230459843 4.77118400673127 -1.04128861505939

C -2.06784781279722 3.04114647297896 0.16869763157087

C -0.74183634559312 -2.43096531018188 0.09774694242754

H -0.38869915253586 -3.24854968186211 0.73964114953977

H -0.66838025763169 -2.76465199137830 -0.94691374346448

C 1.21690757154519 -1.39154133357727 0.91779725802184

H 1.52939933639488 -2.40645898626099 1.19534414154555

C 2.11018504568299 -0.34141312423858 1.30128466934439

C 3.36626874502443 -0.71538778348983 1.82738192292418

H 3.60691972356787 -1.77532894512643 1.88606830289150

C 4.28272963880952 0.22711091765630 2.24624264879957

H 5.24947000268855 -0.07502826957795 2.63629172981891

C 3.94059704323487 1.58767374890729 2.16310386781612

H 4.65481179090249 2.34115421301263 2.48663283620094

C 2.71078792263685 1.98609244330530 1.67774568828611

H 2.44668144593185 3.03833286002593 1.61802196633937

C 1.75424232450481 1.04292433792632 1.23012986037038

O 0.16088626704731 0.53321366119789 -2.08902837635298

C 1.40392214544629 0.62994602780500 -2.49006094694514

C 1.56203236404400 0.73854686259122 -4.02384220279446

C 2.63950071511900 -0.26052014205504 -4.43044908206866

H 1.78379867428426 1.76955037740484 -4.31141165736782

```
  H 0.59674808286630 0.46655053781704 -4.45629630057366
  H 3.62073789932317 0.20442944882447 -4.59023703057541
  H 2.40498904692477 -0.83118317453412 -5.33293740164355
  O 2.14498888183251 -0.71924549798108 -2.17948946274599
  O 2.07834455928462 1.60798713835589 -1.74221734542199
  C 3.44318902525183 1.91776343052893 -2.02439994413923
  H 3.61865138837373 2.87749265004193 -1.52828061440565
  H 3.61436056355029 2.05877950597268 -3.09960018811389
  C 4.41817227475120 0.90048195073573 -1.43095569437734
  H 4.67802655029333 0.10318354366898 -2.13245473614901
  H 3.98687857908978 0.46837329674840 -0.52270883684079
  O 5.61532518284030 1.65088191632819 -1.09619710932390
  C 6.71296884480328 1.01225001615439 -0.62972057198751
  C 6.69538565545668 -0.48802912117894 -0.56907152652753
  H 5.82282132503032 -0.85561669611539 -0.02063367998111
  H 6.64523072995687 -0.90303552688359 -1.58238008131977
  H 7.60989493486358 -0.82961297961667 -0.08498962109393
  O 7.66413142580117 1.69255076826904 -0.30119244581716
  C 2.77134818375867 -1.19894351544807 -3.25098246295356
  O 3.38763441682164 -2.25037058468907 -3.23108510059375
```

DFT Cartesian coordinates A.29: Ga(Salpy) ROCOP propagation cycle - TS3

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  Ga -0.95949230972526 -0.76175632273643 0.74355981354262
  O -2.35862666723329 -1.53232050742832 1.75709202645187
```

```
O 0.48327264220249 -1.32171171984649 1.86247139446774
N -1.91719915950172 4.91805283317559 -0.44121740078080
N -2.30602331082242 0.07424082411035 -0.54821523736044
N -0.68460316839868 1.13916626420522 1.39011312096332
C -3.69190842786810 2.86784972062426 -0.11159285602263
H -4.28689998490995 1.96301304775176 0.05548656980125
H -3.99902065604163 3.32400714961337 -1.05633358740703
H -3.91384577175920 3.57247795862256 0.69408990063407
C -2.20447203193316 2.50618961507944 -0.13834662894973
C -1.33237419859388 3.71225153469027 -0.49050890304756
C 0.03034585680409 3.57059111580136 -0.77657891428007
H 0.50519719406036 2.59673478148353 -0.82804769419908
C 0.79488661971198 4.70510630975931 -1.01735916675313
H 1.85370898806104 4.60796578543131 -1.24185590942327
C 0.18678882728343 5.95415040740165 -0.97027114804227
H 0.74484716444715 6.86678675925061 -1.15575657917873
C -1.17071832235580 6.00386760808018 -0.67895228428285
H -1.68929488932906 6.96135268145284 -0.63312855024643
C -1.97974773605348 1.35503636363400 -1.16149897701969
H -2.59831777995327 1.53961102699035 -2.05030959884515
H -0.93413525560667 1.32412904446152 -1.47680841471109
C -3.44783309731759 -0.48686223624556 -0.77785106527650
H -4.09196148551608 -0.06461874345768 -1.55917950306262
C -3.97055457497844 -1.61220869827823 -0.05719052464554
C -5.14614747201524 -2.21326242228886 -0.55706410802379
H -5.55074691509067 -1.84757127608307 -1.49866756967604
C -5.77679196646307 -3.23722711054574 0.11781920491168
```

C -5.24904064252081 -3.66457488153743 1.34568403886126

H -5.74097164890711 -4.46415116540476 1.89400872476083

C -4.11201742832567 -3.08323542542426 1.87519885175222

C -3.42956851893691 -2.05578063917951 1.19176902656126

H -6.67354828079276 -3.69551838547948 -0.28619627971108

H -3.70682307670923 -3.41207206864173 2.82784343189444

C -1.83828259393268 2.03340217549377 1.30488058337648

H -1.68622938414901 2.91715585845834 1.93721623125728

H -2.70018016813758 1.48369031046823 1.70378895089658

C 0.43975014652129 1.59212381263350 1.85499138352117

H 0.50658662052813 2.65756856679703 2.10490699411239

C 1.60325747314352 0.80294725576428 2.10400621186059

C 2.79697850579381 1.47430584996363 2.44975231266672

H 2.79801497881666 2.56259155405122 2.44274581251129

C 3.93960779241175 0.77939415164895 2.78167528720522

C 3.89901970656604 -0.62467486090726 2.80288432913949

H 4.79330242470573 -1.18312579432692 3.06727295772866

C 2.74148264109528 -1.31201435995639 2.49301345656987

C 1.56370736764443 -0.62667663993202 2.12315150545422

H 4.85506565657248 1.30633321222079 3.03030251217570

H 2.70921305062634 -2.39749652184396 2.51812476422943

O 1.31410111226906 -3.03323724436358 -0.73767702951096

C 3.73099910102127 -2.88754908627268 -0.88004412223236

C 2.46801308847951 -3.38663926997031 -1.52965992925608

H 2.50231691252207 -4.48177545052885 -1.55414361509246

H 2.39068543769858 -3.02206821452102 -2.55558503710098

O 3.78458807448034 -1.45226033464880 -1.04660407709051

```
C 4.86702702910062 -0.83389425549111 -0.52752659093652
O 5.76896150833627 -1.43152526033546 0.02510102321398
C 4.80581055962490 0.64526871622653 -0.75404640320239
H 5.54891076120754 1.14276749288286 -0.13090046396478
H 5.01957741524460 0.85036068712931 -1.80933867339301
H 3.80225835197488 1.02440880438636 -0.54462967519321
H 4.59895702931376 -3.34942095726269 -1.36544833615874
H 3.74947597737450 -3.13166533319702 0.18765258160326
O -0.73489461249087 -2.30620036319073 -0.44376407780964
C 0.30614724965838 -2.25394571360749 -1.20609191791161
C 0.11350901018115 -2.09907918212621 -2.71580923130426
C 0.97846056743047 -0.94773493867022 -3.22696284651623
H -0.94435012145134 -1.86116708802081 -2.85175628515664
H 0.30864599261784 -3.04893491351291 -3.22454440162155
C 1.20561041087043 -0.00653235127924 -2.05707330073225
H 1.96004494155279 -1.26698331162981 -3.59629432765900
H 0.50233580826770 -0.39718781933309 -4.04346390844862
O 1.66251429263414 1.12582133031677 -2.17440147856829
O 0.85363736896382 -0.54505974255496 -0.91490637231922
```

DFT Cartesian coordinates A.30: Ga(Salpy) ROCOP propagation cycle - INT7

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

Ga -0.72873781096047 -0.49931339106823 0.51048369712475
O -2.13344403831800 -1.32136405183859 1.54904740167936
O 0.64830604028813 -1.15185786547287 1.67534136614788
```

```
N -1.72075539302190 5.10965441877585 -0.26176686981984
N -2.16787178796723 0.27645290936414 -0.70555704208217
N -0.67096236310674 1.31342479391846 1.40674873622937
C -3.60772373941778 3.11964440020653 -0.16314649567687
H -4.23993740768886 2.22706640546971 -0.08874033365417
H -3.85274637289021 3.64816090309181 -1.08821458825088
H -3.84491616165174 3.77656555807733 0.67767209228138
C -2.13478761705635 2.69961264152855 -0.15058925098709
C -1.19495393225412 3.88202846855467 -0.38279002566780
C 0.17045700754248 3.68800786427880 -0.62588543555404
H 0.59307967480080 2.69389481705040 -0.73277874198614
C 1.00025509415413 4.79512077748089 -0.74806369910770
H 2.06169946610747 4.65953865014942 -0.93750590586891
C 0.45383981379410 6.06782086791611 -0.62758323058856
H 1.06470177242012 6.96066124887225 -0.71972705713879
C -0.91054367228028 6.16874295707138 -0.38610963698164
H -1.38124676753273 7.14668420889943 -0.28651007788799
C -1.91845312135954 1.60740091527168 -1.24795856172170
H -2.59249181377589 1.81869693732509 -2.08910260283147
H -0.89407836501629 1.64061137141507 -1.62096561057935
C -3.29821048392805 -0.31402214221487 -0.92958912712076
H -3.97627882791990 0.11890186170930 -1.67590446992236
C -3.76041758395250 -1.47697162277774 -0.23336074071739
C -4.91301195034673 -2.12793527700015 -0.72318559752540
H -5.34946814145983 -1.77350388164746 -1.65502050292328
C -5.48157204711487 -3.18751802627392 -0.04824565421688
C -4.91406461988931 -3.59929753050598 1.16876207909076
```

H -5.35865884191514 -4.42761069413765 1.71515449891409

C -3.80021691352008 -2.96821760660193 1.68887943351480

C -3.17748048406827 -1.90011580137173 1.00551609591397

H -6.36116605656180 -3.68629375568243 -0.44207718269147

H -3.36578159774583 -3.28599250372955 2.63248829001367

C -1.85848984880995 2.14869414717327 1.28566208367997

H -1.80619194259116 3.00265633953150 1.97392891714021

H -2.71925180985242 1.53296836443900 1.57734291261343

C 0.37948607982450 1.76219523095836 2.01608645649466

H 0.36654007118453 2.79266788857901 2.39150424935191

C 1.57154396045943 1.00724117965534 2.26792966285493

C 2.68510775038327 1.70475211581910 2.78539101694527

H 2.60330557644048 2.78249244697047 2.91286898415093

C 3.85335026558287 1.05370118153592 3.12194036038638

C 3.92044128888382 -0.34026686970022 2.96974428161497

H 4.83366145633989 -0.86763895420988 3.23471000970163

C 2.84461452672647 -1.05688054206045 2.48267528858352

C 1.64360455614731 -0.41452942954148 2.10546604329895

H 4.70336945857291 1.60746760037215 3.50722049033134

H 2.89739280321508 -2.13601466290348 2.36537964838147

O 1.08590121540586 -3.58279570454339 -0.97933247640982

C 3.47245008116383 -3.49386716369043 -1.14492603029568

C 2.20663394148502 -3.92901149424903 -1.83616722802339

H 2.19743304084096 -5.01896360258460 -1.92797465302126

H 2.10699820625570 -3.48354531336483 -2.82732798942399

O 3.46473628821689 -2.05026322937167 -1.10559027761593

C 4.50568964002688 -1.46162616933732 -0.46963781811278

```
  O 5.40369984283799 -2.09644049402043 0.04383573411630
  C 4.39589807199730 0.02984862780249 -0.52406839159392
  H 5.14903639366679 0.47652583344517 0.12452759876360
  H 4.55028062251464 0.36267985147666 -1.55650499227018
  H 3.39345647558858 0.34909366452098 -0.22419045486354
  H 4.34198035653080 -3.85205601702503 -1.70842980421356
  H 3.51861813763502 -3.89107284911037 -0.12541435369624
  O -0.67841205418033 -2.45745995753897 -0.41771096024514
  C 0.15107496639864 -2.70019029868487 -1.30014332812438
  C 0.04071082406904 -2.09637759878567 -2.67236265233553
  C 1.02979162595386 -0.96984866921425 -3.00475133563518
  H -0.97994640701672 -1.70910277858197 -2.73318137737507
  H 0.13662445242778 -2.89048903730737 -3.42255076032590
  C 1.11383825937027 0.17804048947434 -2.00617320071812
  H 2.05260597544250 -1.34802869217312 -3.10585143188336
  H 0.75877174378161 -0.55432564095537 -3.98010057245575
  O 1.63713008923172 1.23250938819244 -2.38039474316543
  O 0.70415306146159 -0.02841800709580 -0.79714415601273
```

DFT Cartesian coordinates A.31: Ga(Salpy) ROCOP propagation cycle - INT8

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  Ga 0.93870891962629 1.08798437541493 -1.38147759622211
  O -0.56458798865128 1.97342294468186 -2.07895322403902
  O 1.95817075221436 2.69537327946694 -1.64361021715277
  N 3.42258018637478 -3.93944788990011 -1.85805195810521
```

N -0.14166687609810 -0.66127711124522 -1.21325609911273

N 2.27579312579898 0.03483268656471 -2.41330390125119

C 0.83662467271323 -3.47093098491906 -2.66141951809553

H -0.15585693662087 -3.11450276562022 -2.96119455243841

H 0.71571203222024 -4.34759835675541 -2.01939673999640

H 1.37999402454110 -3.77766977818030 -3.55842817515930

C 1.56767731000209 -2.35059776713478 -1.91223365442830

C 2.90812034257535 -2.81417034349805 -1.34213011826186

C 3.60763639168051 -2.05649375305471 -0.39387618087877

H 3.19432832741731 -1.14029392325211 0.01680171578046

C 4.86188512511766 -2.48295773960415 0.02460966696617

H 5.41713578946601 -1.90328135998952 0.75667808463544

C 5.38857692680433 -3.65504418537026 -0.50473812460045

H 6.36223658251394 -4.02789668861800 -0.20219239145984

C 4.62852113904327 -4.34466609082415 -1.44125102686644

H 5.00320364072193 -5.26803096301380 -1.88240506471766

C 0.63564307208966 -1.82204474883198 -0.78155171849019

H -0.02918362766051 -2.63387957139335 -0.45934603761401

H 1.21757785176396 -1.51395535572320 0.09118449819333

C -1.41914069396779 -0.77060179858139 -1.37888230919287

H -1.89210684540072 -1.74000807466322 -1.17861141746046

C -2.29095761647802 0.28699448156224 -1.79454611141797

C -3.66935268944838 -0.00705914486069 -1.87779581682653

H -4.00062512968398 -1.00907041074796 -1.61503128054470

C -4.58426769476698 0.94410623989090 -2.27608063548943

C -4.12804659809469 2.23001055128230 -2.60023339296462

H -4.83884263382330 2.99124027210116 -2.91147918796904

```
C -2.78470150111590 2.55076005592194 -2.52821659452697
C -1.83087478384898 1.59619676512992 -2.12601744293286
H -5.64074131340333 0.70246445965429 -2.33204405571820
H -2.43217604704645 3.54778196602516 -2.77524568508320
C 1.85714061202256 -1.24801240332230 -2.97252056476144
H 2.61966498370256 -1.62724120139295 -3.66413025263644
H 0.93659505172504 -1.07998004483657 -3.54547184134283
C 3.52366114663880 0.39132799501215 -2.51856750992338
H 4.21605979949124 -0.31196165370766 -2.99471042545580
C 4.07718826935372 1.63300089468006 -2.09059870033252
C 5.48251384044210 1.77970714668381 -2.15635699965734
H 6.07626030419809 0.92635950805114 -2.47761161457668
C 6.09438277448103 2.96618059975662 -1.81993669448952
C 5.29637736978422 4.05630463916058 -1.42995954472823
H 5.76932500649224 5.00000788966146 -1.16951466755900
C 3.92069681741749 3.95452350253606 -1.37322088497471
C 3.26635612875862 2.74237589089712 -1.68753969119700
H 7.17409618814065 3.06363150537546 -1.86408718343059
H 3.30680879109828 4.80017638343191 -1.07700644927721
O -4.15051478738387 0.14772603793330 2.33040842737153
C -6.15740862034937 0.60846536537072 0.99597591956952
C -5.52840517550404 0.60160210130646 2.36924296279138
H -6.03405794148942 -0.10306098681660 3.03267633202424
H -5.57633652973276 1.60973861036153 2.79393153044431
O -6.15662738182690 -0.71489416828145 0.40310343429765
C -7.14830748032475 -1.55359774512820 0.77921016168679
O -8.03352148335257 -1.24213475561089 1.54958833608502
```

```
  C -6.98714935269847 -2.89982774902148 0.13941054848088
  H -7.93103487283895 -3.44370608545013 0.18325993980289
  H -6.64028618514678 -2.80670380957639 -0.89232940111104
  H -6.22889982701092 -3.46015974682815 0.69851671285109
  H -5.58284472522587 1.22464674321367 0.30205590382824
  H -7.18266734450247 0.98558744152677 1.06885764087716
  O -3.48997734306147 2.18857228633578 1.61257485267077
  C -3.22390381726917 1.05238272072980 1.94712563443744
  C -1.84142908919781 0.46038838265834 2.01831320887000
  C -0.78548229850585 1.38345991287930 1.42683159176554
  H -1.85453814075696 -0.51166961392911 1.50967865682629
  H -1.62147578758773 0.24181035780545 3.07028011426351
  C 0.61051262615073 0.78092027302665 1.48652171537661
  H -1.05534253180071 1.67064255186842 0.40713845359321
  H -0.74485224150064 2.31896693405755 2.00013383650475
  O 0.98580253541284 0.16352036764184 2.47794569380515
  O 1.40462347518162 1.00523465002522 0.46350708067148
```

DFT Cartesian coordinates A.32: Ga(Salpy) ROCOP propagation cycle - INT8-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  Ga -0.68785542314367 0.08904880729375 -0.01557756459818
  O -1.10824762547384 1.80909939640997 -0.80203456637052
  O 0.56922168557046 0.91734042436147 1.22437253415785
  N -2.18444767454319 -0.88101345079583 -1.21755283544852
  N -2.33147308838300 0.32560571146345 1.22449364578491
```

N -0.38647552161733 -1.69890030977709 0.93198627358150

C -3.83838241406149 -3.15615745753891 1.27547216090869

H -4.87034061356934 -2.79658975350102 1.23368466302164

H -3.61311926149254 -3.40580428552084 2.31714268311415

H -3.75962778386735 -4.07200163688838 0.68044740588044

C -2.85102856831112 -2.09262262565068 0.78690974407469

C -3.12297202166840 -1.66693803877168 -0.64828099181301

C -4.22803117801701 -2.08509062492134 -1.38511015335783

H -4.98227276739201 -2.71836270796811 -0.93512700797126

C -4.35440613470513 -1.69481319756253 -2.71346616923576

H -5.21293457511908 -2.01839972036212 -3.29481942422490

C -3.37108593954262 -0.89974335200587 -3.28764588618507

H -3.42671491226876 -0.58200814209983 -4.32323419049188

C -2.30000009607809 -0.51075088012143 -2.50095827628673

H -1.50145439394715 0.11292585196484 -2.89193458197417

C -2.95493002938275 -0.88433513932514 1.75881437148346

H -4.01280135469787 -0.69495871970441 1.98217635050930

H -2.45834538233098 -1.17238256306874 2.69781682896758

C -2.81020252451009 1.47775015569884 1.55757066523462

H -3.63913829048823 1.51887881112511 2.27662549493858

C -2.35082671404649 2.73895524232685 1.04863329789210

C -2.81562432869275 3.91050331069550 1.68263126491778

H -3.46508808607984 3.80546783010051 2.54962813932466

C -2.45479712794838 5.16499833617207 1.23460696863868

H -2.81000003584782 6.05617770295405 1.74182369366667

C -1.62933255319514 5.26937802077963 0.10414723236977

H -1.34003660196274 6.25143307544727 -0.26220366196942

C -1.17980713478523 4.14227985818705 -0.55824677313457

H -0.54930230388591 4.22506808530051 -1.43958592627501

C -1.52052547020175 2.84572586366444 -0.11218130589039

C -1.43109367783558 -2.71965550218939 0.84824722091871

H -1.37554740207256 -3.37563053708947 1.72674018859374

H -1.27823501227959 -3.33945981932450 -0.04694116426511

C 0.69668361301017 -1.98139778115161 1.58093837562352

H 0.81214299803003 -2.99637044385487 1.98273970456584

C 1.76871751762770 -1.07404642299366 1.86230055770709

C 2.94388631706068 -1.60992738008947 2.43366666475364

H 3.00797880490623 -2.68816148558939 2.56631635186238

C 3.99288574537951 -0.80132382425108 2.81649297380221

H 4.89320384907196 -1.22892636280879 3.24546802338951

C 3.86962459359426 0.58908237192662 2.65853291070427

H 4.68482057332956 1.23757901763769 2.97101832042265

C 2.72692264718750 1.14924691454143 2.12107338431175

H 2.63158516848731 2.22562053246010 2.00326552250607

C 1.64267302846386 0.34295542293425 1.69908925596817

O 0.57024612829452 -0.37398775348987 -1.43712572262744

C 1.37543444559016 0.33858523978643 -2.17689506326112

O 1.65528419800185 0.02597646793334 -3.33563088482944

C 2.01588113020106 1.55011442332364 -1.51898349509631

H 2.70528714782943 1.17334178350610 -0.75244927669623

H 1.24173153621199 2.10926270984198 -0.98484264752712

C 2.75971674903523 2.45722741996048 -2.50401874697335

H 2.08681626153879 2.79662449941180 -3.29495389405434

H 3.59344535739747 1.91433192618512 -2.96018622281370

```
  C 3.27357500215444 3.66795652630704 -1.77449190106968
  O 2.80967141529840 4.78937184389866 -1.84676813081872
  O 4.30857477852868 3.34925332147155 -0.96889542525782
  C 4.81863975887601 4.41634821062506 -0.12805725637920
  H 5.21384028762637 5.21678988290096 -0.76035827207996
  H 3.99909295280753 4.81839158144628 0.47630351057521
  C 5.89326167804944 3.77783781945876 0.73048465356853
  H 5.48661686310090 2.91477640595556 1.26867371302404
  H 6.70794783861315 3.39669304980441 0.10098074292493
  C 6.52231776227510 4.68527388608991 1.75704029096621
  O 7.24906644049036 4.29527820231872 2.64818402705311
  O 6.20137294639665 5.97533744086189 1.56665073557791
  C 6.78188611254411 6.91710801089566 2.50433002318906
  H 7.87260734830758 6.88145751315169 2.44566699010578
  H 6.41108300819769 7.89447988118526 2.19699259005103
  H 6.45776033435856 6.68282112865008 3.52137726834425
```

A.6.3 Cartesian coordinates for the optimised geometries for the Al(Salpy) ROCOP propagation cycle

DFT Cartesian coordinates A.33: Al(Salpy) ROCOP propagation cycle - INT0

```
Charge: -1
Multiplicity: 1
Number of atoms: 64

  Al -0.68527337725353 0.45053207860198 0.19025571137864
  O -2.06752911045927 0.32803692261300 -1.09991573821523
```

O -0.37672497799705 2.21785537773698 -0.27203325883845

N 3.43732831789662 -1.81976691918971 -0.96982965838807

N -0.94193721528394 -1.57486489251930 0.45078096377493

N 0.71151765020307 -0.14071513685052 -1.20428345626941

C 0.91140689899578 -3.94818788547660 -1.10545787699999

H -0.14965034719848 -4.09263813908591 -1.34260580228900

H 1.21463706857003 -4.71941114170089 -0.39057953585871

H 1.49453564590347 -4.07788661325779 -2.02391924817061

C 1.13282821982321 -2.54182262406408 -0.51144738862279

C 2.60183484941481 -2.42398270909784 -0.11627575095279

C 3.06184919576164 -2.99219724105406 1.07889834910037

H 2.37637199362288 -3.50507051510414 1.74730086799158

C 4.40688091967480 -2.89925732547909 1.40370664115343

H 4.77833178263889 -3.33117892923727 2.32898695277792

C 5.26842737874396 -2.24347903386301 0.52890874089207

H 6.32688301294080 -2.13825677704358 0.74631039743806

C 4.73462422006244 -1.73024216848094 -0.64486537140808

H 5.37503199876349 -1.22111398727454 -1.36515710287941

C 0.22688542261689 -2.38200117613759 0.76087900935092

H -0.07016867656426 -3.37509505858718 1.12677299622661

H 0.78597793352092 -1.86562336064336 1.54313419683254

C -2.08367169492461 -2.16687565184465 0.33190727364740

H -2.16664468380890 -3.22584053739917 0.61083784589051

C -3.26470645565964 -1.55024522909683 -0.20128254793614

C -4.49244459339049 -2.23161082451007 -0.09648306185081

H -4.52200929080205 -3.16117798324919 0.46929228126149

C -5.64025120584520 -1.74007406592988 -0.68752000334199

C -5.56139978598096 -0.55649704185326 -1.43842169205920

H -6.45550919780500 -0.16454693732266 -1.91785026960668

C -4.36506925184447 0.12203100071693 -1.58179966801847

C -3.18238881662440 -0.33517913573069 -0.95377471735416

H -6.58442931601334 -2.26541582262262 -0.58478768053824

H -4.30775303466000 1.03736250786877 -2.16490992965150

C 0.74439764068763 -1.54053422487847 -1.62601353728160

H 1.43446770440836 -1.67611420725582 -2.46629598183870

H -0.26288995556562 -1.80765255167912 -1.96958795396228

C 1.60592560909351 0.64753738398528 -1.70119369200381

H 2.35312394457165 0.23306501571211 -2.38715754964050

C 1.71850765178725 2.05367405416139 -1.42940202192782

C 2.84520445668924 2.73468084422929 -1.93352831375885

H 3.59656754519509 2.15957640521849 -2.47232406925336

C 3.00891967917155 4.09409094079037 -1.75267216637429

C 2.01190089776034 4.80964217284526 -1.06903154459704

H 2.12471088238922 5.88150737271934 -0.92274539611990

C 0.88656501244624 4.17568322536254 -0.57835820070738

C 0.70349941104759 2.77974799055286 -0.73132137394138

H 3.88735268469856 4.60245828954645 -2.13746226885736

H 0.11616774618158 4.73027911593473 -0.04924977590039

O 0.75475587392592 0.38150823611483 1.41814319657602

O -1.91858573168087 0.74996584141211 1.56841595259335

C -3.02861333647507 1.38437885643475 1.77724608197050

C -3.29282568963791 2.62093005277419 0.93871540349587

H -2.59932248829837 3.40849585292541 1.25546362824184

H -3.08692283989047 2.42413363190756 -0.11583476212221

```
H -4.31961946543418 2.96552816304202 1.07590582640305
O -3.83386505974258 1.04233136127472 2.65472431293998
C 1.38962888014075 1.21136562329840 2.18376093150400
O 0.94606902901324 2.27378985278550 2.63126227931651
C 2.80245405191168 0.75468301987495 2.51628220149449
H 2.77214875863202 -0.24118288754423 2.97178320283719
H 3.37906494412333 0.66351849710370 1.58795817859359
H 3.29942068581220 1.45534904752017 3.18974494385375
```

DFT Cartesian coordinates A.34: Al(Salpy) ROCOP propagation cycle - INT1

```
Charge: 0
Multiplicity: 1
Number of atoms: 57

Al -0.99460639952798 0.94604062078917 0.22645840911121
O -2.42955705409331 0.97282260963144 -0.90027062230193
O -0.54906037574501 2.69603384458457 -0.11214682045813
N 3.03531429695391 -1.91799908670630 -0.91273468631874
N -1.33055953977233 -1.01129727568406 0.57988317235238
N 0.50531924279742 0.31289932694999 -0.90736856239784
C 0.14776454741929 -3.47079169140992 -1.00777732233388
H -0.92921897430006 -3.41285551966252 -1.20617532552864
H 0.33387588705443 -4.31001669346563 -0.33046784193065
H 0.66218259798224 -3.66791168853156 -1.95466440909003
C 0.64729261956950 -2.15318666048574 -0.38624294288926
C 2.12184548475304 -2.32582288350366 -0.02302487229665
C 2.49251012953231 -2.95237527758187 1.17273108997567
H 1.74063268250486 -3.29719317286371 1.87607295103751
```

C 3.83865842458142 -3.14178759098789 1.45202403496022

H 4.14321911823415 -3.62614005847395 2.37561659762834

C 4.78686907051502 -2.70390984235855 0.53278067138202

H 5.85045649947356 -2.82750648879648 0.71148095569078

C 4.33274414826858 -2.10243371622288 -0.63295470695447

H 5.03995797115223 -1.74987435485804 -1.38338395993175

C -0.17487671900392 -1.83889539920026 0.90472407271487

H -0.48869850441397 -2.77611801682562 1.38334221466191

H 0.44929903145709 -1.28032533896134 1.60770847961728

C -2.49783431540085 -1.56194358016980 0.49522738243365

H -2.61721250105266 -2.60813492265144 0.80335056924164

C -3.66123035366446 -0.90455790738253 -0.02513951952273

C -4.90539475427494 -1.56040600032339 0.07435667712730

H -4.95173339406617 -2.50404582205726 0.61445281402072

C -6.04383912986180 -1.02794290469439 -0.49573783093540

C -5.94503179285538 0.17510474389719 -1.21190948178120

H -6.83309195069389 0.59950437341217 -1.67383028245996

C -4.73528943833642 0.83223803682821 -1.34496033755935

C -3.56301683560703 0.32549827763891 -0.74663145446060

H -6.99800896583417 -1.53653075328721 -0.40338009908681

H -4.66055201777438 1.76077661299589 -1.90389330061077

C 0.43767980197152 -1.05022408436351 -1.44740186440384

H 1.16755098472683 -1.18551648046555 -2.25046691732009

H -0.56510522286147 -1.18059588351535 -1.87190892206096

C 1.55286983502228 1.02733849074335 -1.18300409230510

H 2.36480143189204 0.56490138582989 -1.75380541200474

C 1.72611272612762 2.40150321764401 -0.82062289030406

```
C 2.97899776580163 3.00291556788179 -1.06338172194665
H 3.78210426778586 2.38406212128474 -1.45893537100839
C 3.19298845665279 4.34124272374823 -0.80542848821314
C 2.12815169374660 5.11776057439885 -0.31963914740940
H 2.28288861485412 6.17561670123225 -0.12135176351568
C 0.88211671163125 4.56386713931366 -0.09204433411475
C 0.64433970890345 3.19100022331201 -0.32106252756640
H 4.16409781043907 4.79087686862148 -0.98546946591019
H 0.05824664910506 5.16873891417436 0.27645036918584
O 0.09551992504957 1.01211134305585 1.94971296672462
C -0.96527485257366 1.37469254561084 2.55565500425332
O -2.02849544792738 1.44783599236689 1.85415181955685
C -0.95999246295008 1.73566076982218 4.00423258801650
H -0.14691191827131 1.22934215250006 4.52695108995258
H -0.79979877872879 2.81764229763254 4.08206447133224
H -1.92401643636732 1.50331161958988 4.46078889595472
```

DFT Cartesian coordinates A.35: Al(Salpy) ROCOP propagation cycle - INT1-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 57

Al -0.06679457590348 -0.05554816213173 0.38309781595449
O 0.53694685878421 1.61560557970815 0.89804053245873
O -1.69807636079739 0.63191948838706 -0.17490086958531
N 1.80062099573800 -0.89745336582920 0.82188723788349
N 0.83526090700283 0.22523417092416 -1.41579411580174
N -0.62773848769764 -1.86075742768458 -0.33830273444896
```

C 2.42235552409590 -3.14757889788048 -2.12703513539258

H 3.35285644155015 -2.72453597551852 -2.51639714991930

H 1.80122870541368 -3.43461084082320 -2.98156579580521

H 2.65764904911879 -4.05347817955518 -1.55849570577189

C 1.66073663625549 -2.13678096467180 -1.26768136813058

C 2.46901088004474 -1.65827807524380 -0.07286415503142

C 3.79582826484711 -2.01483801403646 0.15341728980067

H 4.32951178613785 -2.62516073473702 -0.56409354034890

C 4.43191065682421 -1.59335181410546 1.31485321251923

H 5.46647568082288 -1.86809856388420 1.49921649161320

C 3.72726416233577 -0.82913068300331 2.23593937363811

H 4.18091331759293 -0.48783165130049 3.16011451159355

C 2.41380470885347 -0.50047879139527 1.94839750166480

H 1.81708390364796 0.10203597017914 2.62648508551913

C 1.25735782779905 -0.94974531997141 -2.18162415186529

H 2.10366972775428 -0.69387506516523 -2.83191468761274

H 0.43028016847503 -1.29144827171787 -2.82216479889425

C 1.06425915600174 1.39101958258942 -1.92640710476097

H 1.49424462246394 1.45620008612070 -2.93414263030857

C 0.83183261014683 2.63649678473093 -1.25462092685169

C 0.94944762750658 3.83203551017297 -1.99214369036427

H 1.14185004227322 3.76486459905922 -3.06131909494463

C 0.82025046639645 5.06507068484928 -1.38452643392460

H 0.89949578960418 5.97848789456466 -1.96513091442479

C 0.60020948941416 5.11899351759497 0.00110367986731

H 0.50603665865488 6.08461949271547 0.49215558998438

C 0.50714866872787 3.96467547346221 0.75707796366445

```
H 0.34622094693642 4.00946340431657 1.83073364990130
C 0.60655105087954 2.69017539285785 0.15633866262638
C 0.38952765280155 -2.83815460729197 -0.72862832953747
H -0.00602615522944 -3.49881110314701 -1.51116412931524
H 0.66238133978940 -3.46192465508837 0.13504913728590
C -1.86531932225570 -2.22855601717295 -0.42775461312280
H -2.08889796100161 -3.25972735693901 -0.72910363659893
C -2.99734214404358 -1.38252750801849 -0.19450970625481
C -4.27986382670028 -1.96786414780419 -0.16110107224229
H -4.35915687292821 -3.05017505861846 -0.24228355586019
C -5.41517883715799 -1.19570906107218 -0.02142000423022
H -6.39627697251709 -1.65778175967594 0.01813358831664
C -5.28273563913493 0.20020246844812 0.05464315902975
H -6.17148595524642 0.81845462654843 0.15573407720990
C -4.04104317096580 0.80605244460275 -0.00091378748056
H -3.94150434397123 1.88687627583834 0.05114057250446
C -2.86169643455582 0.03734739724672 -0.11300064792720
O -0.59959817874513 -0.57999955825615 2.08137468723364
C -1.37673829163909 -0.15996981746822 3.03977197999308
O -1.74605049259004 -0.90519951684748 3.95199851937776
C -1.77696962525612 1.30228593697495 3.03887853750588
H -2.65278265475585 1.45252633225405 3.67297488177093
H -0.94221906717993 1.88294622854652 3.44896980564248
H -1.95772695441831 1.67079162336296 2.02747694219775
```

DFT Cartesian coordinates A.36: Al(Salpy) ROCOP propagation cycle - INT2

```
Charge: 0
Multiplicity: 1
```

```
Number of atoms: 64


  Al -0.59897867419970 0.20066431705892 0.22258883976614
  O -1.95657192310014 0.43705656223372 -1.00205730620675
  O -0.05075426105865 1.95552605563011 0.20639040002521
  N 3.42431749537430 -1.74106474260419 -0.70398754380218
  N -0.98796636206783 -1.78227839807167 0.27439880633393
  N 0.77334725816325 -0.27718996006274 -1.18272597892579
  C 1.17885889027340 -4.07957157911984 -1.27888386569036
  H 0.19446008627491 -4.27828550439144 -1.71884283492634
  H 1.40561334544252 -4.87617992727963 -0.56372253686162
  H 1.93165895459275 -4.10308732276926 -2.07398318818315
  C 1.17513647486677 -2.70638096252307 -0.57201731552221
  C 2.57121483949580 -2.49035536886559 0.00598760625506
  C 2.96310547618464 -3.12514264428711 1.19088984912519
  H 2.27047325686131 -3.75888832213630 1.73716807683469
  C 4.25674412507177 -2.94867893746198 1.66043369956289
  H 4.57673834596737 -3.43213419359104 2.57930313890109
  C 5.13456650575009 -2.14753285504367 0.93547592168805
  H 6.15363409815950 -1.97656244855831 1.26835151109545
  C 4.67159567132131 -1.57571557319089 -0.24172799404133
  H 5.32930331823391 -0.95338346812455 -0.84817011326272
  C 0.08130666648015 -2.73498546763033 0.55696648661499
  H -0.33077542087439 -3.74847745218864 0.64310031867194
  H 0.52671021364279 -2.46572745818855 1.51667198890486
  C -2.17239448755136 -2.24892240396072 0.04172915619528
  H -2.35018805085388 -3.32260126501489 0.17974204115733
```

C -3.28547554457364 -1.48278322479372 -0.44045806144866

C -4.55156901694875 -2.10207741716167 -0.48863621265922

H -4.65529867084602 -3.10255438214535 -0.07307277526036

C -5.64149578027221 -1.46449318467119 -1.04588051418796

C -5.46858779154508 -0.18892568914185 -1.60610243058836

H -6.31711392093715 0.31802462438676 -2.05918366794769

C -4.23496526804248 0.43563489412795 -1.59602004715972

C -3.11286832978201 -0.17854682807814 -0.99856502853886

H -6.61356663750993 -1.94651624636947 -1.06487531956136

H -4.10216059824622 1.42195666968603 -2.03219650497035

C 0.84262246893020 -1.66587768045772 -1.65883518959688

H 1.58245678556957 -1.75099159553919 -2.46153394219521

H -0.13731785893750 -1.92552561901015 -2.08083873048058

C 1.50512590421828 0.58290822291461 -1.81683992061801

H 2.15427517734328 0.22118430320696 -2.62189851915525

C 1.54871098228848 1.99592850850056 -1.57924746681341

C 2.41519030061479 2.77443785623250 -2.37508963865592

H 3.01344920677605 2.27202637771529 -3.13272696095429

C 2.51018577293025 4.14107581521097 -2.20693385705493

C 1.72457840737651 4.76010110958882 -1.22175751036261

H 1.79037408663946 5.83615308348690 -1.08034487995909

C 0.86595277951725 4.02559364426242 -0.42459978699135

C 0.75321729373678 2.62670997453773 -0.57714342893790

H 3.18035972381943 4.72868676654510 -2.82589436429944

H 0.25987700756694 4.50533032577791 0.33909599030095

O -1.59506175962873 0.39246355060257 1.76750463166410

C -2.33212044861002 1.29447340584110 2.35347043146217

```
  C -3.04734964430889 2.28998950668247 1.46433612652935
  H -2.36247037491929 2.70426152216370 0.72016697629206
  H -3.83953215116744 1.76518190058291 0.91740921437784
  H -3.49391032914922 3.08536688783832 2.06333874572698
  O -2.48580218150257 1.31677207307482 3.57770135296905
  O 0.94753406970230 -0.18067366920852 1.59431262135361
  C 1.22849575208250 0.69530142555439 2.71943210547708
  C 2.24295401946302 0.47354358569731 1.68803180400126
  H 1.29594588653547 0.16622574718954 3.66657149407090
  H 0.66047615247718 1.62114544598130 2.70757465691131
  H 3.05864157259980 -0.22145802379925 1.87303452693971
  H 2.41408711428898 1.24384565312890 0.94061491661143
```

DFT Cartesian coordinates A.37: Al(Salpy) ROCOP propagation cycle - TS1

```
Charge: -1
Multiplicity: 1
Number of atoms: 71

  Al 0.52066432679027 -0.18553790122409 0.59179020404770
  O 1.35416936104746 -1.54477068314765 1.57208851632786
  O 0.53244457815482 0.99252593148313 2.02165496049410
  N -4.35349555567590 -1.28541590971255 -0.24362394249275
  N 0.27866279857991 -1.54299077045710 -0.90799932174602
  N -1.35037113276016 -0.80013397792622 1.13946119978304
  C -2.29792762167438 -3.59723054905479 -1.26115127632508
  H -1.35668554160594 -4.13848927304619 -1.10636257918947
  H -2.58193485693347 -3.68706021224638 -2.31436850119908
  H -3.07379615439829 -4.07116669186717 -0.64993688503573
```

C -2.12953739549304 -2.11594695449006 -0.87090392298633

C -3.42993951346982 -1.38857978744498 -1.20811508965827

C -3.66944712614664 -0.91416911301440 -2.50368614540557

H -2.92246245140255 -1.02575357223493 -3.28367439953993

C -4.88189334029368 -0.30346441171918 -2.79164428044101

H -5.08186895437235 0.07100639820996 -3.79177127054199

C -5.83162163274903 -0.17931144924693 -1.78249324664007

H -6.79090861170198 0.29669775665061 -1.96066900633038

C -5.51916299797019 -0.69038308437030 -0.53016184172105

H -6.23666543563458 -0.62257066336884 0.28745475444606

C -0.94751883148959 -1.49711782771546 -1.69032382022133

H -0.83084611330157 -2.04066904859480 -2.63822792822563

H -1.16770991057561 -0.45132888604969 -1.91186669137066

C 1.13422448681445 -2.48221075898084 -1.14604389241912

H 1.00696603839403 -3.10728885211403 -2.03969716037400

C 2.22671484321617 -2.81431511388886 -0.27649276743774

C 3.20996193268942 -3.71210416522546 -0.73593202730535

H 3.16129180127629 -4.04856861515901 -1.76989286710805

C 4.22035569765483 -4.15711402305856 0.09374459676378

C 4.23607766549318 -3.73158459157636 1.43109054652022

H 5.02009154938801 -4.08359302774394 2.09742639383118

C 3.26973628979977 -2.87121867873458 1.91985345245033

C 2.24908389127392 -2.36623944150045 1.08328725520993

H 4.98230067695351 -4.83507011996279 -0.27726762396072

H 3.28422619990133 -2.54463576629220 2.95620232103565

C -1.82898947914591 -2.09266399800936 0.64574036368770

H -2.72749620430629 -2.40822697241422 1.18539026156709

```
H -1.03874948530464 -2.82813073699620 0.83937527241860
C -2.14451827421078 -0.11682526052732 1.89708629568500
H -3.14913847108081 -0.50644230350592 2.09648433383280
C -1.81205899366422 1.12937515885627 2.52762098638710
C -2.83933093928122 1.83587248218864 3.18483586588755
H -3.84964631533728 1.43232521250508 3.14628153995411
C -2.58657494706529 3.01490896069455 3.85841229988642
C -1.26920355224720 3.49771401346397 3.90653651642859
H -1.05462969638924 4.42161026761526 4.43859781005527
C -0.23521041574565 2.81660313113055 3.29112395545808
C -0.47036546283308 1.61970317913014 2.57567390786283
H -3.38976790383564 3.55482868308511 4.34962629035989
H 0.78504256728967 3.18870296078445 3.33461638654388
O 2.13574561828011 0.37225019425536 -0.17067816034087
C 3.38119934368107 0.51534144019951 0.17373114634515
C 3.66644184493153 0.83266473007719 1.62781265020851
H 3.29495871293698 1.84074198760283 1.84443128846233
H 3.12373923190430 0.14888678948197 2.28502764059986
H 4.73876412087511 0.78962606601512 1.82634581415016
O 4.30366794274357 0.44446061511021 -0.64620022199150
O -0.40262842731112 1.16298204397376 -0.48238865970385
C 0.22934391813037 1.94768146305779 -1.91131220080596
C 0.09990602044388 2.50514052201529 -0.58005371908028
H -0.62221861421252 1.95859287000991 -2.57491899618880
H 1.11007795461042 1.37374978415234 -2.15659318012232
H -0.66865299399095 3.26300282123642 -0.41334892408659
H 1.01606910145691 2.68216648347291 -0.01553557915746
```

```
O 0.91606029635967 3.51471826293744 -3.29206103076930
C 2.06948874895447 4.06704201724158 -3.24971765527678
O 2.46695703337262 4.92055745259059 -4.07482882217562
C 2.99897869258358 3.67620763106504 -2.10058807480188
H 4.01742151084903 4.02365501211687 -2.28817949791040
H 2.63786633021385 4.14404836714657 -1.17694203485458
H 3.00627222656618 2.59493250306539 -1.93315158174924
```

DFT Cartesian coordinates A.38: Al(Salpy) ROCOP propagation cycle - INT3

```
Charge: -1
Multiplicity: 1
Number of atoms: 71

Al -1.10987479898304 0.37740682942065 0.33595791407347
O -2.74734970329139 0.47361698865344 -0.65638143582948
O -0.89461079463906 2.22717213193151 0.15576935148123
N 2.62224326166092 -1.38522824258865 -1.97127546597113
N -1.37728940762121 -1.66800598877606 0.25116578223331
N -0.12464319595546 0.09547361608653 -1.45888415533779
C 0.23560030382994 -3.66861372691989 -2.01275439895553
H -0.84267647738422 -3.85175572314764 -2.09471621546447
H 0.69207895536195 -4.51796216931802 -1.49502295373709
H 0.65796250260167 -3.60956610299158 -3.02204832151387
C 0.49102387177814 -2.36080078304828 -1.23402239963633
C 2.00053483721531 -2.18745365083870 -1.09741258291489
C 2.71271176901738 -2.90353837941144 -0.12702240238137
H 2.19638429104986 -3.57369277087317 0.55433559227929
C 4.08850957963707 -2.75005906813973 -0.03879237108451
```

H 4.65343427409888 -3.29105590123574 0.71515627158558

C 4.72802485478101 -1.88794398413841 -0.92476583289893

H 5.80123264203717 -1.72699526486028 -0.88536237257232

C 3.95106020326129 -1.23958993987123 -1.87510087496639

H 4.41321429657823 -0.56745584473325 -2.59821852096537

C -0.17562163681618 -2.48316331254743 0.18423672528388

H -0.40504858918599 -3.53806319881979 0.39253387406878

H 0.51161462685521 -2.10062801686130 0.94138189735592

C -2.52664091081394 -2.25466980633338 0.23881862224664

H -2.57141789313038 -3.34945177480748 0.32075330518272

C -3.77823435800540 -1.57209516998743 0.06787880565094

C -4.97396357760961 -2.28734759938595 0.26885603095822

H -4.90943406073549 -3.31038901372312 0.63575586445744

C -6.20662196346911 -1.71604617741716 0.01680284763250

C -6.25439269230576 -0.40636300284162 -0.48695300930354

H -7.21760092759753 0.05207470608019 -0.69960219625412

C -5.09720382206661 0.31353166332103 -0.71985747774392

C -3.82102212702965 -0.22998318533706 -0.43258822675666

H -7.12159502542702 -2.27283211350693 0.19259129575353

H -5.13897847891681 1.32680003151694 -1.11086548093993

C -0.14521770728702 -1.23316884773760 -2.07470788538045

H 0.35218131596579 -1.21012760344289 -3.05124804112326

H -1.19605254014985 -1.50371625830658 -2.24232711278520

C 0.48734328161221 1.02460784116719 -2.11568265020483

H 0.99620260168343 0.76059947333728 -3.05089427527871

C 0.56253754406225 2.41051974732489 -1.74529633871404

C 1.34790273087719 3.26172446517520 -2.54871826489179

H 1.87324470686222 2.82732231743997 -3.39776867136078

C 1.46210594161412 4.61213460427385 -2.28086156722847

C 0.76347303106554 5.14354786618347 -1.18412782770068

H 0.83909022809973 6.20571132455094 -0.96199983067454

C -0.02130175663812 4.33950338279918 -0.38029332008466

C -0.14556993411703 2.94762701704847 -0.62330544553204

H 2.07504468957958 5.25170265942970 -2.90802314077363

H -0.56134060642141 4.75267687326047 0.46774533737826

O -2.09507872039069 0.42296890377776 1.95337732857678

C -3.15266457708475 0.98074071427796 2.44646864226623

C -3.54638481337282 2.34209646311945 1.90148573247372

H -2.81890794316416 3.08164873396942 2.25575610750520

H -3.49942785642097 2.34857004511500 0.81059922948982

H -4.54258406373151 2.62168173129341 2.25014187452369

O -3.80978451749330 0.47107712073930 3.36737696817247

O 0.43433718920752 0.13951473031672 1.29324559190909

C 2.68310636742506 0.11135720326988 2.00700699427251

C 1.66604579648780 0.73303384666059 1.06159042406023

H 2.03736126926911 0.57714254167740 0.02932403792032

H 1.64983194337465 1.83036602770248 1.22135489952827

O 3.99469027590799 0.61814736528947 1.62341813868339

C 5.06385115388829 -0.00029286381171 2.14451991920215

O 4.99478178218772 -0.92833258680597 2.92949360528786

C 6.34591242405353 0.61480252702987 1.65960732227278

H 7.15201154703565 -0.11727691522182 1.72599851638498

H 6.24629388593000 0.98982290067015 0.63881773667957

H 6.59136111873360 1.46205727098360 2.31042406765009

```
  H 2.67678949034485 -0.97868501509449 1.90722235391410
  H 2.48840489222358 0.37656833798850 3.05293205856573
```

DFT Cartesian coordinates A.39: Al(Salpy) ROCOP propagation cycle - INT4

```
Charge: 0
Multiplicity: 1
Number of atoms: 64

  Al -0.58781823823940 0.27462578724757 0.02253784796761
  O -2.27882116848428 0.50584501210537 -0.56629445917739
  O -0.26651247487492 2.06283729914326 -0.30177601774562
  N 3.54523255665955 -1.68839367003795 -0.56717228646435
  N -0.95410311054293 -1.71932273699292 0.19050692940363
  N 0.87389356428308 -0.23805486257546 -1.20159616830272
  C 1.21030552616870 -4.04278779961317 -1.10397165853222
  H 0.20629102719709 -4.23386258110397 -1.50149798178336
  H 1.43253523747377 -4.80058917731017 -0.34669462719719
  H 1.93449488773161 -4.14501256905586 -1.91938396010934
  C 1.27713296833535 -2.63065730612023 -0.48998733114832
  C 2.66294142836442 -2.42626697894419 0.11638494920763
  C 2.99277065184748 -3.02146127256337 1.33994042918947
  H 2.27163535968880 -3.64157165852784 1.86548022526675
  C 4.25138310129620 -2.80617925419459 1.88137700123181
  H 4.52270323747778 -3.25272227704706 2.83397341666584
  C 5.15607864657909 -2.00757019932130 1.18732039320883
  H 6.14765732145788 -1.80182738522693 1.57843590565936
  C 4.75881598098202 -1.48429168594074 -0.03535387576171
  H 5.44128069198570 -0.86780960907396 -0.61981279851679
```

C 0.19304982929082 -2.50527222130484 0.63346033486123

H -0.12313645736595 -3.50478867249653 0.95997909642451

H 0.61256590664530 -1.97976789711007 1.49622979849000

C -2.08564973663882 -2.31929821766039 0.01928521219050

H -2.15263459364369 -3.39593382341802 0.21915317731473

C -3.28809053513816 -1.67395120256964 -0.41741400988006

C -4.45215064989437 -2.45284321700896 -0.57513062012721

H -4.39732950717357 -3.51742551759140 -0.35632430096175

C -5.63849891101678 -1.88755381906502 -0.99815333343493

C -5.67550904853579 -0.51201112842932 -1.27183604790922

H -6.60401166083972 -0.05525981528962 -1.60524070653678

C -4.54910574822801 0.27812043465590 -1.12422280705836

C -3.32819361014774 -0.27759878373727 -0.69353721985633

H -6.52895423629210 -2.49632098282653 -1.11698565244391

H -4.57945140221785 1.34336993343793 -1.33485192578902

C 0.99731387490713 -1.64019716787948 -1.63387613187117

H 1.78619382945192 -1.73359391701637 -2.38641214317987

H 0.05044599131346 -1.93203962383882 -2.10525911032880

C 1.76295512046511 0.58696257958398 -1.68119688609132

H 2.54771207657599 0.17457120065466 -2.32101906998316

C 1.81857911483826 1.99279837253189 -1.46009934024855

C 2.91956537609853 2.71027402707955 -1.97627001169631

H 3.69424231745954 2.16097633005411 -2.50753803791434

C 3.02477205075308 4.07325302985362 -1.80171948817015

C 2.00522685292469 4.75244611045737 -1.11123772944834

H 2.08055856437077 5.82791415938654 -0.96964258297826

C 0.90549157934069 4.08268203667986 -0.61045075444806

```
  C 0.78165623930700 2.68372664967224 -0.76559825579565
  H 3.87927868765089 4.61673063022904 -2.19145889452725
  H 0.11707372091634 4.61149580989809 -0.08224457045111
  O -0.23213021122668 0.30436972298430 1.75235994132174
  C 1.99898559307843 0.33690561245538 2.58982357895276
  C 0.69196765911463 1.10873696974509 2.43430422558336
  H 0.89835754708286 2.05905084177735 1.91263730641018
  H 0.30880580349782 1.36209180822115 3.43624855054152
  O 2.95599122220607 1.10523507572357 3.36807524857378
  C 3.82190968688305 1.88744017023249 2.69199303598370
  O 3.85902903028517 1.96999927659028 1.47989534606366
  C 4.74717751640426 2.60409495650541 3.63169630863482
  H 5.24544414259497 3.41978465121476 3.10743709968688
  H 4.20562046077754 2.97947875079995 4.50327541920376
  H 5.50225683316965 1.89461548638724 3.98891380128626
  H 2.42485787349947 0.09496346364581 1.61002924832795
  H 1.83786461206854 -0.58315915806166 3.15950696821659
```

DFT Cartesian coordinates A.40: Al(Salpy) ROCOP propagation cycle - INT4-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 64

  Al 0.13978234470907 -0.24945545940229 0.60003474762316
  O 0.75062137832563 1.42974697552994 1.13732555502283
  O -1.57660660853097 0.42569335828049 0.29118186164644
  N 2.08290281888821 -1.05521795201312 0.64680045140794
  N 0.76784715711669 0.22478526741466 -1.29976377312601
```

N -0.46804905402982 -2.00816708902436 -0.23057100144909

C 2.31216118202992 -3.00543608072119 -2.56037251767378

H 3.16371430814398 -2.51235646947711 -3.03807355594052

H 1.57738841038330 -3.23443945097337 -3.33889908266703

H 2.65146993637103 -3.95103542201168 -2.12448680472446

C 1.66277351761334 -2.10976828562336 -1.50370904601755

C 2.62886429941504 -1.70912125334883 -0.40131198408066

C 3.98373057544144 -2.03179587002253 -0.40593480559151

H 4.42017515552913 -2.55878952002007 -1.24508233925124

C 4.77546117088188 -1.68317892455455 0.68194591691265

H 5.83306294423006 -1.93112940812851 0.68656629958006

C 4.19740696748592 -1.02629655651591 1.76071441887286

H 4.77691529234394 -0.74486927411978 2.63339355887683

C 2.84604353173653 -0.72989760505089 1.70158852565588

H 2.33256824305735 -0.21682266718007 2.50926805320166

C 1.09497181109596 -0.86086831821441 -2.22671237743644

H 1.82389246705773 -0.51620887385381 -2.97168438158739

H 0.18746560888386 -1.17558619309309 -2.76407212630870

C 0.89557874054318 1.43395841119891 -1.73924076900225

H 1.17260283551151 1.59110856623080 -2.78999912948792

C 0.73866918328040 2.61801819420558 -0.94641166436702

C 0.73683059748180 3.86877128570019 -1.59673090148030

H 0.78489117535634 3.88831306898533 -2.68406574414020

C 0.67064762711155 5.04879874906290 -0.88297110873926

H 0.65719151440463 6.00535293640154 -1.39541204669315

C 0.63502004644800 4.99145812147320 0.51982542542902

H 0.59062843804545 5.91432134586120 1.09340836062332

```
C 0.66122558241510 3.78134075850376 1.18787805804251
H 0.64120489133911 3.74047406090596 2.27371823782079
C 0.70317171435761 2.55707456478268 0.48160443181292
C 0.50264919248648 -2.90548129816005 -0.85689211868560
H 0.01313963887339 -3.50738662578080 -1.63422008713414
H 0.91541851982741 -3.59488033049617 -0.10574479496031
C -1.69462933544048 -2.41286649965073 -0.16922809405535
H -1.94068448699551 -3.41834009267173 -0.53485117037474
C -2.79143442563216 -1.63965171315605 0.33528517201800
C -4.01727346233718 -2.29064071229697 0.58081881811525
H -4.07802562202819 -3.36440472238941 0.41367276062919
C -5.11625840746448 -1.59628661094619 1.04615407636484
H -6.04773392225824 -2.11193604547239 1.25615700574911
C -5.01263769136471 -0.20854212553564 1.23487774240435
H -5.87401624568904 0.34910471600984 1.59500618446006
C -3.83462410662231 0.46477636791503 0.96769787142687
H -3.75765743052503 1.53914531112092 1.11193703712541
C -2.68301899336393 -0.22716945903980 0.52923197337259
O -0.11589730969454 -0.85735948199015 2.28368877891966
C -0.83153597166686 -0.15137779743674 3.25345784736602
H -0.17457532571979 0.19090841962179 4.07584928269301
H -1.32500361404580 0.75101034549287 2.84911207829096
C -1.90858052877199 -1.06086164559657 3.82565207903648
H -2.56311895924528 -1.42836700200679 3.02902708714307
H -1.47417007790144 -1.91827949698415 4.35368450163068
O -2.69367273007336 -0.27231069077888 4.76584193343936
C -3.83750475672070 -0.82279994066059 5.20438727335766
```

```
  C -4.60616139998891 0.12431710536687 6.07997899880389

  H -3.93892687943844 0.77627872103138 6.64730219332643

  H -5.22981012059042 0.75552361330535 5.43617818872785

  H -5.25839562062091 -0.43901559379796 6.74853309952116

  O -4.20808573146145 -1.94088170620449 4.89865553852373
```

DFT Cartesian coordinates A.41: Al(Salpy) ROCOP propagation cycle - INT5

```
Charge: 0

Multiplicity: 1

Number of atoms: 75


  Al -0.71504331604364 0.22787177297598 0.57738539084014

  O -2.25338435706016 0.18697587658113 -0.51362884630569

  O -0.68178740590802 2.07316484283054 0.41047715759906

  N 3.43070260054849 -1.23195572822442 -0.77304442044426

  N -0.87709920146875 -1.79900689674303 0.65406238092587

  N 0.55101047643699 -0.03138649992854 -0.93559762212977

  C 1.32451460728740 -3.76723107163795 -1.14132369959958

  H 0.30739074250915 -4.05798301854184 -1.43052785975707

  H 1.73118206737145 -4.54025152596410 -0.48224833518767

  H 1.94524261141169 -3.71891524520670 -2.04262014830659

  C 1.30008915717970 -2.40244637733920 -0.42073118941228

  C 2.72959266800785 -2.07023765674412 0.00034130289416

  C 3.29974314298437 -2.68161521046765 1.12356179042074

  H 2.72694615544386 -3.38413072693944 1.72235545537052

  C 4.60997570110997 -2.38409514947967 1.46933313701735

  H 5.06438022794877 -2.84358073148145 2.34253005761945

  C 5.32655802451106 -1.48655395530140 0.68333638834653
```

H 6.35094382815305 -1.21633723005580 0.92135350815608

C 4.69473162123472 -0.94786828924354 -0.42918798219755

H 5.22424281138533 -0.25284274984957 -1.08063588190654

C 0.37443842770600 -2.52214166269636 0.84606288011980

H 0.17745361195973 -3.58157934198765 1.05796634434982

H 0.87307477305463 -2.06705275206906 1.70396778789026

C -1.97065944582643 -2.47538048560491 0.52768548521553

H -1.94852703562455 -3.56165382901839 0.68265945624571

C -3.23173717597003 -1.90428135497767 0.14945925300526

C -4.39138106069187 -2.69850388856223 0.22793690242820

H -4.30626347036645 -3.70113832962060 0.64257128608630

C -5.61556106765867 -2.22412611399834 -0.20284303879071

C -5.68665014969570 -0.93918459042749 -0.76095574434419

H -6.64195219199949 -0.55976400466342 -1.11565104989492

C -4.55896234998682 -0.14439934192176 -0.87534956259322

C -3.30174495136704 -0.59089759799885 -0.40973830566546

H -6.50567526679069 -2.83981106507250 -0.12393336983120

H -4.61650927325738 0.84574161170452 -1.32026008485054

C 0.75651087502100 -1.38885816238562 -1.45045982393767

H 1.43493241713200 -1.36924290217225 -2.31001561247157

H -0.21574417213971 -1.76170618353461 -1.79913455948355

C 1.19519441468932 0.93033542522691 -1.51561812362220

H 1.89188814769195 0.67973368777959 -2.32290469445641

C 1.07775452215101 2.32701936379857 -1.20836723330517

C 1.91994998393353 3.22030766120082 -1.90353361464278

H 2.62628215627711 2.80828938266643 -2.62181175550503

C 1.86432354587717 4.58258104422193 -1.68904765285697

```
C 0.93614265984096 5.08409334254661 -0.76214167948876
H 0.87859372024015 6.15554858717272 -0.58532159599124
C 0.09147387995876 4.23877196369838 -0.06841005830411
C 0.13524534481509 2.83766894826683 -0.26040281912757
H 2.52245496984606 5.25522328294896 -2.22945738142553
H -0.62572737204870 4.62927229861719 0.64873083115762
O 0.50326868052517 0.17052442061318 1.91322402433610
C 2.54322114780932 0.35807917044608 3.09128337095734
C 1.70798748138986 0.87117065761368 1.92935398602544
H 2.29937113772296 0.72554837931978 1.00499842289223
H 1.56079938780851 1.96302406480668 2.03934695360428
O 3.85881402137303 0.96730623426300 2.97290074702535
C 4.83825540776907 0.44751685067316 3.73076821434407
O 4.67126882693212 -0.47053013825077 4.51148194641926
C 6.14171782678335 1.15846443453609 3.50818887757308
H 6.96866859541360 0.50347905521156 3.78559921189749
H 6.24104176225259 1.49094725758962 2.47266232797091
H 6.16805115679604 2.04476792103105 4.15265819051085
H 2.64294526041744 -0.73048495598411 3.03490096821363
H 2.10714707195713 0.62713384042324 4.06073630307896
O -2.11901089369176 0.33073021873999 2.13894704724840
C -3.11152499586422 1.01423447461605 2.28970716311522
C -3.53163855503888 2.27219925129656 1.60038253935803
C -4.94749996383085 2.51919575295881 2.11057563347182
H -3.43278447205976 2.14520923835826 0.52033684300208
H -2.82304868744582 3.05574074249194 1.89242688639686
C -5.13705210530856 1.51594850769369 3.21092272558892
```

```
  H -5.12142121380376 3.52455989681495 2.50234301737092
  H -5.71083774123583 2.32158443787498 1.34887545710732
  O -6.02769587305688 1.35470443476807 3.98588574388550
  O -4.01959389342816 0.64750642971745 3.23562034875328
```

DFT Cartesian coordinates A.42: Al(Salpy) ROCOP propagation cycle - TS2

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  Al -1.36800802014713 -0.44797641091909 -0.06030760785594
  O -3.10116566953592 -0.79779000837654 0.47085679263021
  O -1.12234756209813 -2.21859950669762 -0.54439953939236
  N 2.19142297566909 0.47181353696211 2.74803451904217
  N -1.63716669780438 1.46648618913075 0.55357360306747
  N -0.46049011360016 -0.74346614531683 1.69404355242614
  C -0.36390593329638 2.63523245717892 3.47314922315771
  H -1.45441045180843 2.75057001475953 3.46879346380612
  H 0.08722761779263 3.61940802741677 3.31763010945546
  H -0.05707173826891 2.26526052457565 4.45760290414300
  C 0.06723723119212 1.65619524343399 2.36267824741992
  C 1.59077247557638 1.59131659569829 2.32824541251452
  C 2.32462566543747 2.69726318817478 1.87947722299013
  H 1.81605278019028 3.60077347589307 1.55387406591809
  C 3.70891977646615 2.62606772623162 1.84545538976650
  H 4.29394956555775 3.47026411125811 1.49193975021684
  C 4.33257405980581 1.45361278820810 2.26387617294633
  H 5.41335484800879 1.34976883308543 2.24738228775105
```

C 3.53119089776610 0.41245769259340 2.71030491482829

H 3.97933203737264 -0.51934294777186 3.05475798208570

C -0.45234791327008 2.19609477169022 0.98140442994273

H -0.66406272032495 3.27045303301378 1.06416205955646

H 0.31513356886342 2.05156789307574 0.21775172661855

C -2.78428130279808 2.06239726943988 0.60351893433285

H -2.81743198926179 3.13123794604940 0.84939263871495

C -4.04430034756586 1.41154901158770 0.39942467553440

C -5.21087323257020 2.20042320552775 0.33668200927147

H -5.10621254119048 3.28334393578669 0.36509894425710

C -6.46113787019931 1.62335886769778 0.24147532437830

C -6.56377420412280 0.22305755191358 0.23703169825852

H -7.54418988881225 -0.24268600937021 0.17205801912207

C -5.43948600305544 -0.57815835958184 0.31737381649318

C -4.14718910870106 -0.01359759583025 0.38588070192509

H -7.35197452105814 2.24039998588337 0.18331080954602

H -5.52200617751870 -1.66153288492123 0.31880220042096

C -0.56836841581627 0.29897682750227 2.72393457164591

H -0.12957322128647 -0.05175893718715 3.66423694698542

H -1.63780997778767 0.47351044163041 2.90080862003661

C 0.14283573108739 -1.83961458950817 2.03670977407054

H 0.58833336317583 -1.89548485930477 3.03515242896067

C 0.28827755308533 -3.01050947523157 1.22609481233217

C 1.08073692472544 -4.06586968745924 1.72559833112955

H 1.56117841385664 -3.93786708528132 2.69374786661573

C 1.25413521263606 -5.23403271106717 1.01216984070965

C 0.61044021311798 -5.37276480496754 -0.22876164901572

H 0.73437284291672 -6.29135956676607 -0.79736331445126

C -0.18326408749970 -4.36404651479018 -0.74108322944436

C -0.36371957198706 -3.15059001743299 -0.03786085178260

H 1.87112566977364 -6.03575411515283 1.40475516363940

H -0.68660325194952 -4.47736484762412 -1.69747149073725

O 0.19500084769862 0.08840539322777 -1.03184597110105

C 2.52965115671581 0.57141125745783 -1.25764419957575

C 1.47847786001790 -0.47750781651488 -0.93011264619212

H 1.66098275205796 -0.83445698476704 0.09442255412204

H 1.59556741666440 -1.35145768903811 -1.59464206533896

O 3.81518392102812 -0.05778394334311 -1.02795630068808

C 4.89696655122618 0.73969519001566 -1.12985524336699

O 4.83222506390368 1.91591228236001 -1.42626320351111

C 6.16045554978426 -0.01941164075181 -0.85332994730039

H 6.97921754475257 0.67960411417100 -0.68156084975569

H 6.03386276657837 -0.68371109518929 0.00528995565598

H 6.39748102749364 -0.64146232014444 -1.72379447734069

H 2.42998395345248 1.44091064076623 -0.59985268181541

H 2.47297870063382 0.91446219611871 -2.29766503032718

O -2.04166272966104 0.03138651549117 -1.88147278996040

C -1.02915233358410 0.08166095263803 -2.60803366191987

C -0.47843759253823 -1.01842525997746 -3.47399281862056

C 0.54744329211997 -0.31397045828466 -4.35302522252807

H -1.32644187863547 -1.39697471632922 -4.05782200342878

H -0.09853702669597 -1.84290272473267 -2.87001192446909

C 0.25541295215166 1.15225799461589 -4.16423433266058

H 1.58233731851571 -0.50080851415030 -4.04534470888751

```
  H 0.47710600486085 -0.55969063553265 -5.41595299960355
  O 0.71647080121209 2.10592487136322 -4.72530205872220
  O -0.70163081049173 1.31223832568966 -3.17200164864853
```

DFT Cartesian coordinates A.43: Al(Salpy) ROCOP propagation cycle - INT6

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  Al 1.31086161760554 -0.29139025455977 0.41221499769160
  O 2.89957893707335 -0.39601804593079 1.24297629783363
  O 1.16840511263694 1.49013054155857 0.84189521453487
  N -3.25867083561736 -2.13533205487783 0.69351443187586
  N 1.37452053499306 -2.27230458725394 0.03907424326008
  N -0.36897224476901 -0.67853298234214 1.36912784309182
  C -0.95218257367535 -4.42660596341624 1.01533210137261
  H 0.04071047696693 -4.69006257333796 1.39919297192750
  H -1.20602737211374 -5.11469366683305 0.20320845321736
  H -1.68168180213961 -4.55712915632068 1.82193036012398
  C -0.95974000432168 -2.97153637831710 0.50958840247021
  C -2.33021564485145 -2.68374440584202 -0.10101252178336
  C -2.61642044480640 -3.05046286650474 -1.42059005688773
  H -1.85845956458501 -3.51110459841858 -2.04707630335443
  C -3.89156830342519 -2.83160511155767 -1.92426080476712
  H -4.13148007194058 -3.11076271722552 -2.94650208876336
  C -4.85080725704142 -2.24991742157845 -1.10222010640077
  H -5.85807571956215 -2.05233590519450 -1.45563884475450
  C -4.48421283461471 -1.92254109829412 0.19638094871860
```

```
H -5.20430084767811 -1.46372090945672 0.87262110025652
C 0.15217507382096 -2.78617864975451 -0.56806730290430
H 0.33758719614359 -3.73442733265796 -1.08925093535097
H -0.16987713724955 -2.04577915590543 -1.30923647547973
C 2.38403049395220 -3.05875349404159 0.20880094186341
H 2.31747146308981 -4.09736817757658 -0.13787703672095
C 3.61218651996044 -2.66417794585453 0.83565852697621
C 4.63532736196737 -3.62395985604990 0.97071134458259
H 4.46170975638054 -4.62469037850865 0.58057100908030
C 5.83261911071604 -3.31243614031095 1.58362304780727
C 6.02410970792279 -2.01452771446261 2.07882163090743
H 6.96212622924321 -1.75683516921686 2.56409629494862
C 5.03796425816500 -1.05055488326274 1.96001828728903
C 3.81101416331003 -1.34515303687657 1.33608400058975
H 6.61339929781610 -4.05965005052287 1.68169690503434
H 5.18802207471707 -0.04495363326824 2.34240172360156
C -0.67303899517558 -2.07344303697494 1.72739631299918
H -1.52408118329052 -2.11320703039041 2.41241268716464
H 0.20107830476948 -2.47994918987480 2.25018817703601
C -1.24094910018111 0.21947595059566 1.73006601918382
H -2.16072072604216 -0.12471257706949 2.21257790341511
C -1.10594942931526 1.62859313886521 1.56241149593322
C -2.20707060021001 2.45300029033609 1.87977829245283
H -3.12956169723213 1.98153381243813 2.21327618568035
C -2.12722538857588 3.82400487477803 1.75722753211575
C -0.91406061522452 4.40102717711032 1.34291499468604
H -0.83841480254908 5.48212908286867 1.25537797735560
```

C 0.18959168983377 3.62243607612355 1.04905043644604

C 0.12121640633962 2.21392525757586 1.13134836131476

H -2.98225820218334 4.45049453642125 1.98942224372611

H 1.12819242506909 4.07296944270202 0.73855334965044

O -0.66924699027978 0.73079965664856 -1.57139979145029

C -2.97070611068809 1.18849534256464 -1.54509270427388

C -1.63680384729802 1.63083563824840 -2.11145205537594

H -1.42960151358955 2.66520648543014 -1.79953795182468

H -1.65749722481577 1.58167855501953 -3.20920770798424

O -3.92488418796726 2.19963686412614 -1.94722760060485

C -5.10069651664947 2.21503589604599 -1.28510091290388

O -5.38724892234670 1.41755409194040 -0.41512276882404

C -5.96711004247347 3.34920137479427 -1.74421815136299

H -6.99951501734621 3.16794409175252 -1.44466083021151

H -5.61475170789308 4.27042871153675 -1.26611403130695

H -5.89589562839320 3.48662327798501 -2.82555758514208

H -2.92777317333986 1.12978716696813 -0.45434613374892

H -3.27769249742782 0.21485524436211 -1.94394197049594

O 1.39260098880439 -0.04823319071328 -1.36853328293838

C 0.64731632626014 0.78744010629405 -2.08683996022506

C 1.22000919462811 2.20700093426899 -2.28928011604021

C 1.01854554565582 2.52939784666736 -3.76554179670713

H 2.28222676907406 2.15313636908766 -2.04111021821661

H 0.75086819775683 2.91988956751237 -1.60879542628143

C 0.76212143563799 1.18887945613500 -4.41500109433602

H 0.14678979737138 3.16658929729893 -3.95641579510629

H 1.87866357245788 3.00777578966719 -4.24135668946670

```
  O 0.71130431655554 0.94260742040779 -5.60127388494855
  O 0.57210242218426 0.23627197441949 -3.48368211127122
```

DFT Cartesian coordinates A.44: Al(Salpy) ROCOP propagation cycle - INT6-PY

```
Charge: 0
Multiplicity: 1
Number of atoms: 75

  Al -0.68534143376563 0.50166578341017 -0.29436022911695
  O -1.47406566735826 2.13576669985502 -0.67419538985788
  O 0.53873037771072 1.34050225747096 0.81110984551549
  N -2.23894324568437 -0.50553591061135 -1.33995089128424
  N -2.05748304712127 0.23208910896726 1.20301957933067
  N 0.03782966312300 -1.28752411563257 0.30937397482285
  C -2.97101801136492 -3.43974136777281 0.88810506552630
  H -4.03257432008591 -3.28410274008851 1.10129514612653
  H -2.49496006306145 -3.80454510743501 1.80386303265949
  H -2.87577190307722 -4.21679935822260 0.12225031373589
  C -2.28809402673835 -2.14439603691867 0.44689491546150
  C -2.91054679000314 -1.54558887033330 -0.80066678254840
  C -4.06365984074359 -2.03938508790864 -1.40491422045924
  H -4.59563795802626 -2.87587369839090 -0.96938876549707
  C -4.52330716945192 -1.45917979728950 -2.58089946082800
  H -5.42122400933274 -1.83793636583321 -3.06065750810942
  C -3.81672709824934 -0.39920426272875 -3.13430976504062
  H -4.13500537733831 0.07884866706536 -4.05450694545119
  C -2.68121213722472 0.04823689882992 -2.48022782753986
  H -2.09477615014961 0.87738342668111 -2.86246981661636
```

C -2.36750588217173 -1.13597018494459 1.62505239664013

H -3.37173875243420 -1.17984711524242 2.06589036786909

H -1.64734806836762 -1.46031763314888 2.39098107357716

C -2.69347752567719 1.19798393840046 1.77976029495226

H -3.37937984927561 0.96706743014340 2.60524938006686

C -2.60288367833033 2.57897667076443 1.40228620159935

C -3.21527667802720 3.53988551507453 2.23270677125105

H -3.67609820277294 3.20419804633739 3.15988935366822

C -3.23259789217733 4.87778518196096 1.89298964703603

H -3.69671699885110 5.60867978180945 2.54729602511087

C -2.65080230812397 5.27571332548333 0.67877945214494

H -2.66403442487930 6.32557027758925 0.39569356159503

C -2.06413047196902 4.35474981557991 -0.16925577872910

H -1.62110736885068 4.66452551696124 -1.11186865927433

C -2.01153104204294 2.98238414949216 0.16412643839512

C -0.80188959589771 -2.46929209884266 0.12760317300403

H -0.46504554184638 -3.27725011061199 0.78998978933437

H -0.72651198961242 -2.82656783857272 -0.90931928857810

C 1.17923247670577 -1.46045364994686 0.89510862597348

H 1.48795099652257 -2.48273048337917 1.14694985171644

C 2.08567396784481 -0.42313374664959 1.28252751406695

C 3.34676378198494 -0.78935416361488 1.79645635983621

H 3.60635413593887 -1.84585133878890 1.83321974486577

C 4.24381680552188 0.16322111740836 2.23812760391009

H 5.21599101833435 -0.12806669065296 2.62300558971033

C 3.87458198172158 1.51818122096191 2.18929834879112

H 4.57331916244733 2.27651449052962 2.53460729204620

```
C 2.63733743333363 1.90613556887545 1.71092371686398
H 2.35296219906358 2.95428380813539 1.67619418842372
C 1.70706553930278 0.95269309396677 1.23706012402319
O 0.19547193398072 0.45579560075279 -1.91650619328847
C 1.40391925375569 0.59652008159469 -2.39399731967659
C 1.47453904952081 0.69700531314917 -3.93607472464590
C 2.55862562250361 -0.27156134326852 -4.39508450696696
H 1.64899598971382 1.73186219912566 -4.24194968347907
H 0.49595403483365 0.39259815530428 -4.31349653612865
H 3.51193011748686 0.22253136043840 -4.62195178777820
H 2.28906794075277 -0.86451651551404 -5.27314912252134
O 2.21135471880831 -0.71557713566120 -2.11365212112102
O 2.07911821045155 1.61329831542435 -1.69701878636564
C 3.42430228965879 1.94538625124025 -2.03843839981470
H 3.59351730151311 2.92721369647284 -1.58504533402496
H 3.55642132119466 2.04970177953647 -3.12341386267165
C 4.44182325426172 0.97277510904910 -1.44086630187115
H 4.69823213958344 0.15659175816698 -2.12126175715397
H 4.04884725012578 0.56489066231204 -0.50417191805344
O 5.63167009795600 1.76148256272953 -1.17267492250290
C 6.76059864228718 1.16385075915414 -0.72682434649892
C 6.77168413903405 -0.33156194857994 -0.59131631512653
H 5.92745253183541 -0.68429017113365 0.00911836061655
H 6.68886795266429 -0.79853949924659 -1.57951081642858
H 7.71039680486560 -0.63414961410044 -0.12806047719201
O 7.71236094677068 1.87441159810847 -0.47266536689875
C 2.79495663924637 -1.18610413372386 -3.21373577202881
```

```
  O 3.45270679772402 -2.21200885952336 -3.21494541909827
```

DFT Cartesian coordinates A.45: Al(Salpy) ROCOP propagation cycle - TS3

```
Charge: 0

Multiplicity: 1

Number of atoms: 75


  Al -0.92305608916922 -0.79089713449789 0.70048378386362
  O -2.27702531057674 -1.45829784363075 1.69208715970026
  O 0.45984241657175 -1.30112848792448 1.77560933198730
  N -1.94974170153270 4.89159393762866 -0.45537893164860
  N -2.23192974902176 0.04416064914335 -0.58514612469003
  N -0.67176054486078 1.08480565316960 1.33082879891739
  C -3.68532472999315 2.80694819854025 -0.16041870324808
  H -4.26649203377642 1.89109986833227 -0.00563283882704
  H -3.99187157335436 3.26560895566623 -1.10420645638036
  H -3.92694936564780 3.50082943378619 0.64897724100684
  C -2.19188141908471 2.47176403048306 -0.17430180845280
  C -1.33962994291918 3.69826147535964 -0.50319865214349
  C 0.03006010427653 3.58755496115793 -0.77015328567538
  H 0.52476411338223 2.62379012410079 -0.81834149587818
  C 0.77424744284007 4.73909868787551 -0.99247029570143
  H 1.83817448595984 4.66578545146629 -1.20131406417071
  C 0.13946530473027 5.97497264610735 -0.94724218527104
  H 0.68096224157910 6.90018165995104 -1.11900122451173
  C -1.22277672996412 5.99429129977385 -0.67566382597080
  H -1.76202078693176 6.94040677307802 -0.63178224210200
  C -1.93083589957200 1.33260003215415 -1.20160395559730
```

H -2.54755958481826 1.50418201385320 -2.09413431182072

H -0.88311381034542 1.33284827934631 -1.50883139765916

C -3.38200495768144 -0.50357580162784 -0.81504978352184

H -4.02259917521052 -0.08388952160724 -1.60012536880481

C -3.91889183354927 -1.60581687987483 -0.06932406650578

C -5.10639556124233 -2.20997906274149 -0.53115597408487

H -5.51846416334888 -1.88035475853879 -1.48282844248723

C -5.74008090340077 -3.19545626877130 0.19810287477090

C -5.20425607684599 -3.57295560701778 1.43857797864879

H -5.70107321692940 -4.33992895767292 2.02753951719534

C -4.05382840721561 -2.98278841030253 1.93087813616480

C -3.36909568995587 -2.00040406831557 1.18967604920956

H -6.64704045194106 -3.66093097015935 -0.17385496943724

H -3.64283351767470 -3.27269348851875 2.89370603314047

C -1.82963143214987 1.98105366972055 1.26271220160198

H -1.68222719510393 2.85513641314661 1.90929439528108

H -2.68985345966224 1.42181761334856 1.65126633922137

C 0.43673581702510 1.55777026982901 1.81914228602932

H 0.48289402286173 2.62005942709278 2.08484872768526

C 1.60447145826207 0.78084652534917 2.08303213248514

C 2.79125679345323 1.43974444637996 2.46786244997657

H 2.80340902754817 2.52801782224081 2.47153857857323

C 3.91619117082066 0.72670071608393 2.82461902672833

C 3.85912493244652 -0.67710251057982 2.83337171139388

H 4.74012161534133 -1.24660559995684 3.11817990325560

C 2.70287420741730 -1.35115772485474 2.48738887876762

C 1.54839074322224 -0.64594672640185 2.08763147290452

```
H 4.83105175622117 1.23979181150679 3.10293823151127
H 2.65850766764765 -2.43642624308623 2.50385962194442
O 1.29929558456597 -3.02097332749812 -0.76272406629491
C 3.71598146649988 -2.88351292907145 -0.91001960112201
C 2.44814220447741 -3.36295220682579 -1.56548460651041
H 2.47821557668469 -4.45743886727368 -1.61448586266829
H 2.37035860695886 -2.97644121094897 -2.58364201569110
O 3.77565217783146 -1.44505777196848 -1.04736476951455
C 4.85794564224066 -0.84178586962991 -0.50996177619723
O 5.75372729973983 -1.45444604174713 0.03601228891440
C 4.80442842632858 0.64188177643228 -0.70682489728108
H 5.56023468100920 1.12185221170921 -0.08528220654695
H 5.00134513946796 0.86719761096456 -1.76114900577572
H 3.80708257076309 1.02291578733284 -0.47261321164602
H 4.58084441361676 -3.33864952518172 -1.40719271913776
H 3.73603879210749 -3.14937075597048 0.15242712771553
O -0.73401415678320 -2.26279726751587 -0.42779316812271
C 0.30116494465691 -2.20865205081809 -1.20852117548972
C 0.08083481910174 -2.06437082320685 -2.71794665461318
C 0.93947533822528 -0.90945411738077 -3.23155001237913
H -0.97917047375503 -1.82865592639961 -2.83985116001025
H 0.27334255434496 -3.01350356509822 -3.22761755881153
C 1.20159283347398 -0.00040712269756 -2.04666880780153
H 1.90809248039682 -1.22532296657758 -3.63609952831218
H 0.44536629740446 -0.33292647633121 -4.01897194991907
O 1.68009407687772 1.12180155542147 -2.12795488026478
O 0.84262869563786 -0.56331689930972 -0.90871223989401
```

DFT Cartesian coordinates A.46: Al(Salpy) ROCOP propagation cycle - INT7

```
Charge: 0

Multiplicity: 1

Number of atoms: 75


  Al -0.67208702587382 -0.48170344525779 0.43498464624577

  O -2.01005315999042 -1.23493896674639 1.47329014363956

  O 0.65995352890080 -1.07672686239192 1.55911482086993

  N -1.80902039700531 5.10308957163793 -0.27113131642460

  N -2.12444970160236 0.26719527958286 -0.74701644105659

  N -0.68119007094075 1.29617116599284 1.34431828902237

  C -3.65485456047358 3.07485724619043 -0.18952818771196

  H -4.26922515170778 2.16892592507447 -0.12781376139312

  H -3.91191370122104 3.61224337580740 -1.10625339179668

  H -3.90398780724379 3.71429254165790 0.66142277758175

  C -2.17409782248803 2.68303897846002 -0.18405547990496

  C -1.25858341426956 3.88683063197492 -0.39847448571673

  C 0.11172064076968 3.72215028442334 -0.63668279853806

  H 0.55443222656864 2.73691696460416 -0.74225024597853

  C 0.92004279416106 4.84592357495456 -0.74753716059186

  H 1.98495866827001 4.73242851841260 -0.93211961235996

  C 0.34773840711448 6.10688940294547 -0.62136365566487

  H 0.94103534657185 7.01235755156120 -0.70480430267585

  C -1.01917437365249 6.17891644315830 -0.38476650508076

  H -1.50950367639394 7.14667681107304 -0.28016891878748

  C -1.93774987040847 1.60815131058535 -1.29496819184754

  H -2.63942119630753 1.79791212093454 -2.11840948800811
```

H -0.92499073460848 1.68522910256435 -1.69101438371588

C -3.25295598245531 -0.33510167423017 -0.95351360582683

H -3.95171312563655 0.08290012810357 -1.68896493523153

C -3.69051985837477 -1.48956065944289 -0.22654228253290

C -4.84857563457580 -2.16864054576047 -0.65698568485306

H -5.31336212420075 -1.86111086201693 -1.59184669719444

C -5.38907570984048 -3.19991428393099 0.08376768412024

C -4.78922340005882 -3.54602183144349 1.30569382348137

H -5.21441819214869 -4.34919880709768 1.90276514779534

C -3.66849019128108 -2.88142534394829 1.76834265461719

C -3.07113712354012 -1.84903907069719 1.01282887028626

H -6.27352464363913 -3.72496115057034 -0.26239416771073

H -3.20971865807805 -3.14855287329078 2.71627967540852

C -1.88686114462290 2.11098054985586 1.24126741046444

H -1.85394850184491 2.95355618671266 1.94487225053175

H -2.73449383257496 1.47189846086225 1.51980366110202

C 0.34064539830844 1.77267983094039 1.98245675081989

H 0.28751331255568 2.79306858365551 2.38081100520543

C 1.54937322707184 1.04817916849923 2.24776266027481

C 2.63601799588561 1.74549048540204 2.81575573221194

H 2.54137256222386 2.81987952806395 2.96184784141902

C 3.79673210914917 1.09360564551342 3.18082545166353

C 3.87641730362575 -0.29798313289937 3.01174156537122

H 4.78188515467938 -0.82427717400750 3.30453378006181

C 2.82319999625810 -1.01381939271451 2.47484286129766

C 1.63849168763866 -0.36714141513487 2.05794480991917

H 4.62959529509686 1.64476792179149 3.60548360589084

H 2.88614113419220 -2.09107455406834 2.34439252580836

O 0.97252688089435 -3.59529733497153 -1.09908442050432

C 3.36155071183384 -3.64352643412690 -1.19309091078488

C 2.09604254570628 -3.98018599217867 -1.93850121931499

H 2.02213924234849 -5.06301424217997 -2.06938579401131

H 2.05296633920622 -3.49237073464971 -2.91394804934881

O 3.43553215897638 -2.20344236970686 -1.10555100604816

C 4.50367876146152 -1.69742508941170 -0.44115473880439

O 5.34212742219849 -2.40140444979295 0.08156220850834

C 4.50796865665771 -0.20172787383649 -0.48449767969776

H 5.25862969730536 0.18223535235351 0.20584723461644

H 4.74392351762250 0.12237772021985 -1.50443762316384

H 3.52062592239322 0.19515077142567 -0.23396903316803

H 4.22642828786498 -4.03254947732081 -1.74308045734388

H 3.35195038938046 -4.07633188867433 -0.18737818870550

O -0.62218659355893 -2.28107978226357 -0.46817366837699

C 0.15600435440245 -2.59585323908262 -1.37721079877141

C 0.10007977890746 -1.93474142141566 -2.72394223585017

C 1.14534051471080 -0.83580985180556 -2.97098181931693

H -0.90076165660210 -1.49918352103892 -2.78890992877780

H 0.18392784853753 -2.69444242038410 -3.50915769243021

C 1.21426742662082 0.28097627171301 -1.93653105939654

H 2.15638635092373 -1.25033248180170 -3.03831723593437

H 0.93443872260682 -0.38019515533841 -3.94355083685703

O 1.85700098624644 1.29509567951221 -2.22415293266976

O 0.64046573137278 0.10006671941006 -0.79494685835482

DFT Cartesian coordinates A.47: Al(Salpy) ROCOP propagation cycle - INT8

```
Charge: 0

Multiplicity: 1

Number of atoms: 75


  Al 0.95570175946228 1.11982943288372 -1.36560606333705

  O -0.48759267816671 1.92726406158709 -2.05268604381616

  O 1.95813307454520 2.62519907760581 -1.64288913762780

  N 3.37570290934682 -3.95438266902376 -1.84488712445278

  N -0.10526375816901 -0.59939448748425 -1.16205503374193

  N 2.24875636446492 0.04689839659745 -2.36937379269126

  C 0.77641466897164 -3.44559322183956 -2.57161420536444

  H -0.21805909724624 -3.07419411973376 -2.84542333433469

  H 0.65923214648616 -4.31409412111738 -1.91778881719782

  H 1.28649423964036 -3.77036709719283 -3.48178896427721

  C 1.55014406601206 -2.33183522714891 -1.85735564548533

  C 2.89689438058431 -2.81681558693943 -1.32098767050551

  C 3.63723195747092 -2.06994561724915 -0.39528507809439

  H 3.25423006501308 -1.14431477306705 0.02237483293142

  C 4.89342790290793 -2.51974906933722 -0.00832171069085

  H 5.47938100096699 -1.94852747657646 0.70625509173223

  C 5.38257093621394 -3.70419034434968 -0.54599109044632

  H 6.35626373438596 -4.09528507483021 -0.26753693208821

  C 4.58402336627051 -4.38195220205417 -1.45881862979452

  H 4.92820420263808 -5.31439690492914 -1.90576175536257

  C 0.66430013606485 -1.76217540265614 -0.71258093975281

  H -0.00222534957218 -2.55396870242412 -0.34716079967018

  H 1.27672640471880 -1.43810566764882 0.13243502376531
```

C -1.38360003420269 -0.72744504974708 -1.31912871513326

H -1.85184801183660 -1.69255420455427 -1.09127141943069

C -2.25640591951150 0.31755332865997 -1.76275773079371

C -3.63720137363495 0.04627743801336 -1.84508420782116

H -3.99174429093364 -0.94124806379784 -1.55895815090988

C -4.52750593908746 1.01002347136507 -2.27281001684603

C -4.04107207675986 2.27598310606333 -2.62914593252378

H -4.73420368740829 3.04293971107230 -2.96509773734934

C -2.69023035244114 2.57113244372631 -2.55837393558937

C -1.76660251234943 1.60538477800065 -2.12160691517382

H -5.58924351497842 0.79211175135539 -2.32900020060497

H -2.31504366578232 3.55358729418923 -2.82953224430953

C 1.82596880213607 -1.23908594621219 -2.92839762366596

H 2.57864841720641 -1.61989271250903 -3.62960400236257

H 0.89811520499723 -1.07279740851877 -3.48966931635543

C 3.50366774809566 0.37745230145337 -2.50686364754880

H 4.17634678603827 -0.33916764247309 -2.99028756277887

C 4.07852589178662 1.61756437848090 -2.10782366448236

C 5.47892132102497 1.77752515299016 -2.20454523917710

H 6.07852534068539 0.92641221294939 -2.52077766774184

C 6.07701296498136 2.98096616679796 -1.90176582391038

C 5.27007392595424 4.06746058726054 -1.51947021053479

H 5.73510542851977 5.02236138045603 -1.28723771685941

C 3.89600350926307 3.94974649625621 -1.43575729902014

C 3.26092490223985 2.72036417210248 -1.71174833325823

H 7.15411943958842 3.09479938623515 -1.96687461784904

H 3.27569214565998 4.79304083779550 -1.14623770571669

```
O -4.16434564391949 0.08641482818490 2.34793017302145
C -6.16253873632990 0.56150438177283 1.00715440803126
C -5.55143426905912 0.51158618817250 2.38776976424213
H -6.05161752362832 -0.22893860616262 3.01533451469990
H -5.62458392694282 1.50053739468512 2.85195976994439
O -6.14266112944874 -0.74039491822090 0.36857517153618
C -7.13353087835369 -1.59862469717552 0.70062203626730
O -8.03163961343123 -1.32050937193709 1.46880965263591
C -6.95367109585691 -2.92031493621111 0.01628237042049
H -7.89510124742049 -3.47015569368707 0.02415852024157
H -6.58931971932680 -2.78888564276147 -1.00519373139252
H -6.20233632521705 -3.49641860247072 0.56866331712025
H -5.58401264178085 1.20645064375585 0.34314987803550
H -7.19189555350165 0.92738767724812 1.07861407441817
O -3.53885616717969 2.17112093493100 1.73258321419195
C -3.25247859377059 1.02615976207110 2.01644885656127
C -1.85836743935897 0.46025499187629 2.07058327943603
C -0.82830080514263 1.41206995241924 1.47783325534246
H -1.85639712314354 -0.50649440900515 1.55238748750827
H -1.62620007017333 0.23557505585869 3.11879572806844
C 0.57047716193769 0.81601348220519 1.45781770944750
H -1.12944509037572 1.72990711913745 0.47605421585693
H -0.77339130286360 2.32766443115425 2.08117795687906
O 0.99105466898735 0.14847479156635 2.39574480519858
O 1.30695018303844 1.10321667210975 0.40841903033761
```

DFT Cartesian coordinates A.48: Al(Salpy) ROCOP propagation cycle - INT8-PY

```
Charge: 0
```

```
Multiplicity: 1

Number of atoms: 75


  Al -0.68895951559030 0.08759165470244 0.03221844433449

  O -1.08470372718134 1.75757991497053 -0.65704984468105

  O 0.49762134223887 0.81366505447819 1.26142833580142

  N -2.16294538323910 -0.79477085939734 -1.18256739147201

  N -2.28401606075988 0.25986930338186 1.27360953170783

  N -0.39030363122639 -1.72355769252532 0.86262518753359

  C -3.83756840943311 -3.20053307708479 1.17190271434321

  H -4.86681376831904 -2.83121760583178 1.14710867434798

  H -3.61429017754830 -3.50171368700717 2.20038425296806

  H -3.76590595843992 -4.08793382017917 0.53430011797102

  C -2.84253625157667 -2.12361391137638 0.73538888918767

  C -3.10368968029095 -1.62051311002473 -0.67419358194829

  C -4.19347230377037 -2.01400756140688 -1.44632039510431

  H -4.94523756181649 -2.67737527400432 -1.03751436455976

  C -4.30629918408690 -1.56040567131193 -2.75504729727512

  H -5.15226916738010 -1.86341826112638 -3.36522829959807

  C -3.32228888539365 -0.72789795793710 -3.27227603908343

  H -3.36438422107751 -0.35957502821077 -4.29157734321183

  C -2.26828549643036 -0.36694762362928 -2.45077860261529

  H -1.47436336733198 0.28551128067934 -2.80102630849032

  C -2.92194053051181 -0.96359377419702 1.76358380593253

  H -3.97471647267171 -0.77089066763717 2.00647990717833

  H -2.41903320034144 -1.30060240447103 2.68263545482724

  C -2.77944141546273 1.39345193955884 1.64921711056793
```

H -3.60811425362490 1.40031060798646 2.36882553782587

C -2.34515461987550 2.67396955445062 1.16952296459394

C -2.83496638990835 3.83222378809253 1.80622239602146

H -3.47719484052414 3.71326562723755 2.67683554969798

C -2.50756389774737 5.09387544029601 1.35054924274576

H -2.87993876408650 5.97824213892665 1.85743913228063

C -1.69642034550562 5.21509739172107 0.21138222945118

H -1.43838288589399 6.20346047459682 -0.16131646643943

C -1.22313784619172 4.09781117834112 -0.45261926559697

H -0.60459475151429 4.19384325785214 -1.34112073670233

C -1.52299774872828 2.79702925330083 0.00686186352904

C -1.42643366095314 -2.75295318214720 0.75681737505840

H -1.35990535632144 -3.43910796709709 1.61115311661527

H -1.28173337627829 -3.33981586698796 -0.16176736119294

C 0.70333568370315 -2.04609533217984 1.47668306710948

H 0.82997532908135 -3.08132801931851 1.81763193975913

C 1.76846937028506 -1.14498063173739 1.79937760285777

C 2.96291342327713 -1.67509060179383 2.33084056670612

H 3.06617660700018 -2.75640993924449 2.39762668416563

C 3.98469881014170 -0.85088039990218 2.75590044879954

H 4.90490189327663 -1.26948426039022 3.15035304533956

C 3.80810812493234 0.54126592983132 2.68916756096488

H 4.60248311577058 1.19923507348465 3.03412269813089

C 2.63953994520849 1.09158263805391 2.19736487223359

H 2.49972059941603 2.16825307729058 2.15013631827842

C 1.59291337955282 0.27097310739847 1.72059400134839

O 0.52924088386090 -0.31153567657546 -1.30954758926595

```
C 1.36623419940356 0.33438306607471 -2.07019882456547
O 1.63847748195509 -0.03336927593088 -3.21481061043437
C 2.05300849998653 1.54384509340571 -1.45394415537205
H 2.75123492946596 1.16109399508219 -0.69912766256416
H 1.30859115473601 2.13096871681983 -0.90718110494618
C 2.78421253276065 2.39957215831945 -2.48340902028901
H 2.09951645740576 2.75219264129086 -3.25926257065174
H 3.55356099620902 1.80102336101869 -2.98893995500348
C 3.47349347137226 3.61030667473300 -1.91251181549168
O 3.51617596978641 4.70198052599506 -2.44597257726377
O 4.08417351315908 3.34316323393336 -0.73975717098180
C 4.83236337944312 4.43802540571781 -0.14758742259245
H 5.62122581012601 4.74715331944769 -0.84038961631123
H 4.16019595767186 5.28491236439725 0.01847411953666
C 5.39579632584961 3.89376651288624 1.15045436958042
H 4.58176340506099 3.58366982301155 1.81704372044470
H 6.00027435016057 2.99856452372829 0.96221914848320
C 6.25616704533674 4.85129102074429 1.93586719742675
O 6.83284899483023 4.55162267677007 2.96153971156016
O 6.30785065951725 6.07239829521647 1.37986271793443
C 7.11064527791413 7.05461234829422 2.08282817283754
H 8.14974251340299 6.72056666604020 2.13763214942740
H 7.02982069309566 7.96723109492161 1.49309893679300
H 6.71753098063884 7.20916793618294 3.09073250946593
```

A.6.4 Cartesian coordinates for the optimised geometries for the Rh(L2) cycle

DFT Cartesian coordinates A.49: Rh - INT0

```
Charge: 1

Multiplicity: 1

Number of atoms: 46


  C -2.40965286946630 1.89867974147964 -0.52766679805816

  C -3.17215199464251 0.73001940962776 0.10628624362632

  C -2.62836895642776 -0.62184899723611 -0.33652423432351

  H -4.23501424397667 0.79091538226025 -0.15206473111419

  H -3.10380621893873 0.79995195252809 1.19451389659639

  N -1.15188045379474 -0.65980384845164 -0.14462000339525

  H -3.07905566210919 -1.43768026156927 0.23249978749589

  H -2.84509414552635 -0.79402744747650 -1.40180517039882

  C -0.52890873320467 0.34805562985579 -1.04911079798897

  C -0.89284296341150 1.70878302153869 -0.48323912028791

  H -0.92217664908301 0.23928234511450 -2.06919229090335

  H 0.55122866321111 0.19598189287267 -1.06386336487612

  N -0.36526040392879 1.73927906433616 0.91860375374678

  H -0.40859741024246 2.50020536630680 -1.06997565499256

  H -2.68940335699791 2.84267649729672 -0.04404744359361

  H -2.68250386516622 1.98880459617648 -1.58651965796720

  Rh -0.45316804607851 -0.20290169620651 1.88502894485554

  H -0.83565750896203 2.46300274966299 1.45812239557301

  H -0.80415079572911 -1.58560290763415 -0.38512801632941

  H 0.62265313099678 1.98564078768900 0.89852672746292
```

```
Cl 1.80235694465942 -0.62801618880504 1.01882205217956
C -1.97929043303848 -1.15788828800741 3.17217691929058
C -1.79998418411590 0.20854488772582 3.56736159608731
C -0.41486128513086 0.37510508364858 3.97114102962106
C -2.85368951862163 1.24660696354121 3.74222120978117
C 0.23168461774844 -0.89292404236797 3.85081542070960
C -0.71159308650919 -1.83640027160525 3.29092030602830
C -0.46651582366948 -3.28781578681148 3.06124482805370
C -3.26878359601589 -1.81398732752335 2.83230462924638
C 0.17080079090183 1.62721038034044 4.52484220417549
C 1.61860311326615 -1.20590008547624 4.27644774962455
H -0.27742377278458 2.51079652164297 4.06202883630242
H 1.25203132864914 1.66414332648488 4.37370118333858
H -0.02299294689412 1.68161975671615 5.60397152685945
H -3.80805702814349 0.94593719481818 3.30659686045699
H -2.55474043970152 2.20746827380260 3.31153011029962
H -3.01058185700836 1.40861732302973 4.81650895422817
H -3.69843789493412 -2.21720946036463 3.75935074528842
H -3.12961260868447 -2.65265742069536 2.14656429582309
H -3.99546586479179 -1.11770302669290 2.40868865898479
H -1.11214151945415 -3.67807829815027 2.27062895964724
H -0.67390159851556 -3.85569698911977 3.97764155535922
H 0.57283975768993 -3.47232862251848 2.77928727336783
H 2.05319993084217 -2.01134221726449 3.68279628199420
H 1.58636480190499 -1.53093209391339 5.32531521223153
H 2.26976465583039 -0.33199287060590 4.21295713589256
```

DFT Cartesian coordinates A.50: Rh - INT1A

```
Charge: 0

Multiplicity: 1

Number of atoms: 45


  C -2.48774125955697 1.79289893735541 -0.62478578419853

  C -3.18551959017493 0.61198614146145 0.05941997238245

  C -2.48959733966483 -0.71927621685459 -0.26503583819760

  H -4.24178556006750 0.57510164126424 -0.23961722213435

  H -3.16366672295744 0.76316839508405 1.14295443176561

  N -1.03615907500194 -0.69328986343037 -0.06709175780056

  H -2.92990886032744 -1.52608846685408 0.32954320375662

  H -2.68846114356694 -0.96727953652185 -1.32548320292929

  C -0.50145652197414 0.32471898499143 -0.97962104523867

  C -0.96545891817774 1.70558852643215 -0.51850531284679

  H -0.86236521411751 0.14609056193563 -2.00746078949673

  H 0.59159682404006 0.28218589719934 -0.99331332317206

  N -0.50701876731288 1.81801873306118 0.90132307941236

  H -0.50578118636707 2.50796625017595 -1.11458510959176

  H -2.84916780636449 2.74656801930135 -0.21584486720264

  H -2.72802379555644 1.79594649724708 -1.69636056658561

  Rh -0.46449984275123 -0.13256994449793 1.86660933227587

  H -1.06121264006423 2.50388727566465 1.40864503300038

  H 0.45825079459161 2.14091565942533 0.92191620820027

  Cl 1.97587509504797 -0.22493940717887 1.11828375136222

  C -1.98424355530659 -1.08782252885327 3.13964866521642

  C -1.74587921734347 0.26086295089161 3.57888201524642

  C -0.37072158102330 0.35935290761205 4.03237469124727
```

```
C -2.76844910637831 1.32888535278691 3.76851095262838
C 0.23094952645307 -0.91126434782745 3.84466834655530
C -0.73733206643469 -1.80111869365423 3.22809952697167
C -0.53055630007471 -3.25106453445697 2.94361261972674
C -3.31545967193393 -1.69440806749821 2.85807492384698
C 0.24815080604867 1.57084195141429 4.64589745843421
C 1.60616953639068 -1.30386347663140 4.25140039378830
H -0.14632751442081 2.48623179705136 4.19469295700820
H 1.33403593756046 1.57041525188023 4.52118836426228
H 0.03308283984212 1.61368042567524 5.72184511629975
H -3.69639474458000 1.11190068982597 3.23616391303634
H -2.39947158146444 2.30791956354500 3.44704265730523
H -3.00611770086730 1.40940097858444 4.83762880203586
H -3.77171750435887 -1.98982349525579 3.81285635254686
H -3.23000147077133 -2.59315348658762 2.24356865878322
H -4.00027122910575 -0.99735942159822 2.36960305721145
H -1.18505309684635 -3.59161008371344 2.13667397825505
H -0.74851442707931 -3.85750270727061 3.83313178024690
H 0.50294245448452 -3.45081021464592 2.64833541868399
H 2.03896009003288 -2.03039526481976 3.56094500989516
H 1.55929626675511 -1.76780328702033 5.24625814935700
H 2.27499484074580 -0.44290034469540 4.30866599864969
```

DFT Cartesian coordinates A.51: Rh - INT1B

```
Charge: 0
Multiplicity: 1
Number of atoms: 45
```

C -2.38877602236452 1.94935869735773 -0.49023663981495

C -3.19064826833718 0.77947376836623 0.09015268567557

C -2.66073798757896 -0.57028313684474 -0.37777131644916

H -4.24947246847425 0.86315810146211 -0.18278642586819

H -3.13307126469778 0.81413304328144 1.18019991789174

N -1.19078202758715 -0.63761419980582 -0.16485850836896

H -3.13452457215167 -1.39194570742816 0.16591261399147

H -2.86663550939592 -0.71325675417882 -1.45058233913324

C -0.53447548674552 0.38881058789919 -1.02503832466901

C -0.86794671473366 1.72139783353852 -0.38049959858920

H -0.91728301774234 0.32256696896067 -2.05433024311574

H 0.54145992117462 0.20808978086605 -1.02140397596905

N -0.32483989029337 1.67153387771860 0.98821803342252

H -0.36628438819012 2.52296077401787 -0.95317577543089

H -2.66478797375676 2.88133689343066 0.02067792776641

H -2.63877599534180 2.08095198286800 -1.55326961292187

Rh -0.48841143821626 -0.20521466472966 1.85806699749823

H -0.87536776359027 2.31632712535542 1.55549447441477

H -0.85314053136715 -1.56249730893934 -0.42133225291206

Cl 1.80429443392820 -0.95602727278201 0.89549737601162

C -1.95457889467998 -1.19315432934882 3.16125415736637

C -1.79642904395754 0.20240448401951 3.52394896452282

C -0.42447543199925 0.38698511974698 3.93359829233892

C -2.87647089140069 1.21634470338927 3.70303039793328

C 0.23384518804631 -0.88443793928587 3.83093724873188

C -0.70640125320831 -1.86576618979563 3.35521175252582

C -0.44785214578287 -3.32551663004781 3.18625942117676

```
  C -3.24067054264626 -1.85403619155633 2.80616809238025
  C 0.15784358752837 1.65026664071919 4.46940086441807
  C 1.63429542442616 -1.15813915648432 4.24862771295261
  H -0.30232851046406 2.52603739700132 4.00257373969699
  H 1.23612984934461 1.69743244110643 4.29685068643717
  H -0.01350835743725 1.72090440473601 5.55164446960587
  H -3.81805164309289 0.90254857250097 3.24798242559096
  H -2.59466455505713 2.18847608388278 3.28582369630625
  H -3.05799429544644 1.36174529614646 4.77602381877389
  H -3.70128884130256 -2.24506104002386 3.72339812468812
  H -3.08890925224945 -2.69809791030288 2.12870703617599
  H -3.95085763439713 -1.15915880964803 2.35247452594599
  H -1.10707802846126 -3.76066266937736 2.43023262399689
  H -0.61977058867214 -3.86323745605069 4.12829154114691
  H 0.58552578024401 -3.51165140897046 2.88147620941452
  H 2.05438090086499 -2.01527960163375 3.72067861472668
  H 1.64084257920539 -1.37806996856065 5.32510001987268
  H 2.28180356605731 -0.29518623257642 4.07846054984417
```

DFT Cartesian coordinates A.52: Rh - INT2

```
Charge: 0
Multiplicity: 1
Number of atoms: 43

  C -2.49382788836691 1.45700905234260 -0.96158155863440
  C -3.07605347144515 0.16409088459564 -0.37562958475653
  C -2.04661579601953 -0.98143954663489 -0.39512051570360
  H -3.98118875772610 -0.12847260419091 -0.92628839631819
```

H -3.37474069777332 0.34236512677635 0.66505134820904

N -0.71119918525227 -0.62562862412328 0.11399463592830

H -2.43866088043421 -1.83193274105041 0.17932885709108

H -1.93476946403648 -1.32988827877413 -1.44130729103177

C -0.21142793301271 0.48277416603451 -0.72243637976137

C -1.06454769210822 1.70777738335607 -0.43735680670280

H -0.25014661997162 0.21121792553426 -1.79317351347462

H 0.83652803259573 0.69274215319667 -0.46229225009803

N -1.02547181792771 1.83205621515207 1.02592797819838

H -0.65571012453342 2.61475518758586 -0.91691791104642

H -3.14296248097037 2.31190799621555 -0.72733383346210

H -2.44188382384029 1.38459005578234 -2.05772150263558

Rh -0.88121258543105 0.18148088469098 2.03393737490363

C -2.15416696707248 -0.91498632360628 3.36948182272377

C -1.80686018599280 0.34607985534586 4.02499860879497

C -0.40325495010385 0.36596388879666 4.19028708970759

C -2.78790983492633 1.38239007881782 4.45974252056551

C 0.13619460552385 -0.88707105423603 3.65778991373173

C -0.95037071704306 -1.68987902672619 3.21359650547026

C -0.86430793997040 -3.06935923983904 2.65322190187953

C -3.54232728227572 -1.38577418995466 3.10559744108056

C 0.41943988459322 1.44144603842880 4.81468039725052

C 1.57506855486330 -1.27455728944149 3.69405980536203

H -0.11822241240653 2.39206848156140 4.84518919033457

H 1.35370856732241 1.59388331833426 4.26587507818695

H 0.68463254638370 1.16899963436704 5.84487092129396

H -3.59980127860308 1.48712336105226 3.73399106258919

```
  H -2.31143368610960 2.35831269671798 4.58085821625988
  H -3.23839856684378 1.10526855302271 5.42198469562597
  H -3.94274152064156 -1.88012609152123 4.00166812193826
  H -3.57391226156130 -2.10741128716214 2.28550720944356
  H -4.20762140273472 -0.55375804056108 2.86062221575720
  H -1.65547263616650 -3.25114383937920 1.92106128817876
  H -0.96929933061069 -3.81578682877822 3.45102639894593
  H 0.09646122039561 -3.23913850116485 2.16003362629191
  H 1.80204055653286 -2.04047935309851 2.94848132144344
  H 1.83387984951472 -1.67945511635733 4.68219863562328
  H 2.22382538115293 -0.41329547102846 3.51155247219449
  H -1.47438900696643 2.67840050992065 1.36421288862096
```

DFT Cartesian coordinates A.53: Rh - TS1

```
Charge: 0
Multiplicity: 1
Number of atoms: 55

  C -1.55523918957370 1.32037323090244 -3.06586192088034
  C -2.18370049981740 0.06256716001897 -2.46050132749469
  C -1.19224890018741 -1.11366463367713 -2.45662154082652
  H -3.09355937282045 -0.21091800664645 -3.01215102205072
  H -2.48359742078624 0.27728000647031 -1.43010818687522
  N 0.13828123452842 -0.80114225511894 -1.91498964883484
  H -1.62177820433924 -1.95846418064696 -1.90570374564082
  H -1.06284249941083 -1.45691773695515 -3.50229879346462
  C 0.69039901636854 0.27912236288544 -2.73678311844248
  C -0.14023134398202 1.54653502513498 -2.54020138644954
```

H 0.67624169630663 0.00034784400814 -3.80633178193407

H 1.72673890646601 0.48075430806978 -2.45686400962071

N -0.13156220485663 1.79140006058416 -1.06223141001532

H 0.31355901634482 2.41001570904776 -3.04974788055102

H -2.18517667766281 2.20036952176628 -2.87488922453377

H -1.47750201980656 1.21573347379594 -4.15652616525210

Rh -0.00483445518890 -0.04502066629581 0.03863167334862

H -0.90424384108402 2.39316296753461 -0.78651971300784

H 0.75026549071172 2.27219626489657 -0.84336518429641

H 1.66034976999164 0.34560346533739 -0.08797890349494

C -1.85809857712388 -0.94488464691280 0.95416047653182

C -1.51285861346720 0.26663841108697 1.65246554746220

C -0.23451854041525 0.10575746173576 2.27160266241994

C -2.39076164886251 1.46587064806639 1.78398951614017

C 0.25975917859576 -1.19806190688768 1.88943387375718

C -0.73532635235212 -1.83971365611174 1.08002983944877

C -0.67781083145504 -3.25129456261675 0.60025440521305

C -3.21797682890692 -1.30951488141731 0.45833041792057

C 0.36255754389179 1.04168757497521 3.27087360399689

C 1.50281213431714 -1.86003719911603 2.38326557982731

H 0.28569339046910 2.08520417379628 2.95060570292434

H 1.41572563427063 0.82193062011705 3.45292995116593

H -0.16595931339609 0.95257854474611 4.22979988728148

H -2.99777709177550 1.61644786427495 0.88615914620983

H -1.80232975055699 2.37075007831874 1.95898708390069

H -3.07705708951303 1.34422240572758 2.63249712709230

H -3.73875925609838 -1.89397635485330 1.22966979268320

```
  H -3.18571689667361 -1.92373740778911 -0.44521655878318
  H -3.82685082599461 -0.42627623264717 0.25108103781905
  H -1.32775806465027 -3.41024332361828 -0.26369579227124
  H -1.00874526774090 -3.93369979404725 1.39481166585225
  H 0.33983952265817 -3.53686036800014 0.31997060152555
  H 1.94902199891449 -2.49701607908046 1.61493038322494
  H 1.26448851343493 -2.49716100497431 3.24590710217388
  H 2.25262763416153 -1.13554506500865 2.70594719568373
  C 3.78084964813155 -0.03960644484981 -0.69670398690384
  C 3.13207829028603 1.50070782600434 1.23547783159234
  C 2.91579663706964 1.13076425398680 -0.22708749269759
  O 2.71176526542299 2.09848654875006 -1.03431760326360
  H 2.37182273536548 2.21262597950087 1.56472729092052
  H 4.11470260412558 1.98793994334545 1.30408328880099
  H 3.13527057116078 0.63178546145183 1.89635041528549
  H 3.50419250006131 -0.35875831216541 -1.70455947025887
  H 3.71626296451898 -0.89293175359836 -0.01446467109141
  H 4.82371968092488 0.30658727669784 -0.72125256126736
```

DFT Cartesian coordinates A.54: Rh - INT3

```
Charge: 0
Multiplicity: 1
Number of atoms: 45

  C -2.43141076668337 1.74645696421999 -0.69539830722540
  C -3.11352626149696 0.58736570448498 0.03844716698212
  C -2.40736516029300 -0.74148349758061 -0.27595043089643
  H -4.17419957059711 0.53545572518815 -0.24396609099335
```

H -3.07670866971322 0.76327242756066 1.12077718383148

N -0.95101282517550 -0.72449228914243 -0.09386199954732

H -2.84060606902412 -1.54297788713410 0.33434165053748

H -2.62418716286091 -0.99874685638410 -1.33339162858039

C -0.41214517845709 0.30241595018699 -0.98727683586291

C -0.90939498423891 1.68492095443112 -0.55892472104328

H -0.72875935867514 0.12203460409258 -2.03255488330631

H 0.68670121393681 0.28152571831438 -0.96102855705835

N -0.50388638975991 1.83404075385133 0.87567631345108

H -0.45167231774140 2.48879997979737 -1.15547479492336

H -2.80967443164477 2.71521170953963 -0.34042084565531

H -2.65987494100765 1.68979279816275 -1.76855023285481

Rh -0.43122903221218 -0.08940548830305 1.85941007415682

H -1.12190474719135 2.48685793603250 1.35388026293338

H 0.42710594291576 2.23585354912580 0.92606741476813

H 1.03158622451732 -0.18820079099828 1.27568292850547

C -2.02867564394071 -1.06818889016742 3.24356752200578

C -1.78875954537709 0.23737848160283 3.71482133118157

C -0.37231439170663 0.36640212399353 4.02764916287366

C -2.79657602589196 1.31842100337421 3.92680787011761

C 0.24494050733246 -0.89463242213314 3.76706002531413

C -0.75541037924169 -1.77173647200478 3.19849312201790

C -0.58545800774785 -3.22378276012016 2.88739231700034

C -3.35926285337334 -1.67820243293732 2.94764342547600

C 0.25090250113132 1.55893955000166 4.67932329262621

C 1.64969252769502 -1.27808104701044 4.10613706870850

H -0.15987530025584 2.49067224447829 4.27707554547585

```
  H 1.33374339727680 1.57578506270078 4.52889693478357
  H 0.06367801933195 1.55971857535808 5.76232453997040
  H -3.75192157406199 1.07913498360684 3.45294864946460
  H -2.44634424397812 2.27727405190140 3.52715733972633
  H -2.98120070949704 1.46727516460199 4.99905811483669
  H -3.81781924514450 -2.04332211702009 3.87685813208296
  H -3.26783630741040 -2.53447536653087 2.27484474428272
  H -4.05352585152054 -0.96214897288113 2.49835832979640
  H -1.20692549381457 -3.52277316002083 2.03751108957661
  H -0.87318191882741 -3.84911014085804 3.74434483811164
  H 0.45363536430831 -3.45540052742528 2.63863020804820
  H 2.03648937916047 -2.03220496684688 3.41627392961382
  H 1.68995421521953 -1.69933936327700 5.11972078201182
  H 2.32042606573660 -0.41548056783191 4.07606801767777
```

DFT Cartesian coordinates A.55: Rh - TS2 (R) Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 62

  C -2.38682782163275 1.47333435992662 -2.56624661466973
  C -2.87583407569129 0.12469525624002 -2.03275686048413
  C -1.78842185369592 -0.95786272720878 -2.15000392739946
  H -3.78143140201509 -0.19083395247436 -2.56860561223216
  H -3.14942704313775 0.24044108241111 -0.97981315129601
  N -0.46474139496488 -0.56434167390930 -1.64353296963999
  H -2.11866982515610 -1.86942459752856 -1.63818616741996
  H -1.67957784227105 -1.22092642711524 -3.22078510743172
```

C -0.04940569109246 0.61975459898955 -2.40006579230122

C -0.97796337108180 1.78732076489106 -2.07029309060675

H -0.08914715269482 0.42243943977074 -3.48693533658737

H 0.98084974174294 0.88220991962030 -2.14986645109121

N -0.93495159035961 1.91240194758807 -0.57771936339489

H -0.62249474327417 2.72640828725185 -2.52036892498197

H -3.08413425848029 2.27632420957362 -2.28937809329357

H -2.34325879244588 1.45367043852685 -3.66354319157211

Rh -0.56657169769832 0.02818572528256 0.36170055931386

H -1.75907747262961 2.39616156823553 -0.22816915252341

H -0.10415980572086 2.47196209192960 -0.34125676349690

H 1.04443248068322 0.56567480993196 0.17789502150695

C -2.30922751775929 -1.03663232209331 1.31867887639598

C -1.95694252295448 0.12539899423407 2.09897525768428

C -0.63317687337076 -0.03588804778253 2.60762868140966

C -2.86797531554730 1.26837852979251 2.39829402441844

C -0.12266266467505 -1.28159591292700 2.07748968789944

C -1.15156570860520 -1.89146464740197 1.28901146074767

C -1.07037820245424 -3.25161116138212 0.67970590308608

C -3.68586328964295 -1.40940715047517 0.87882633988045

C 0.01709835510477 0.83188660152693 3.63412162894657

C 1.16061469624316 -1.94348332868602 2.45134185506552

H -0.13605833203071 1.89546922828935 3.42713992073447

H 1.09170559754432 0.64869300459335 3.69177056511443

H -0.40819211259711 0.62506806470997 4.62575161247497

H -3.53542750155259 1.47733666062055 1.55660383755232

H -2.30300412258224 2.17644332115478 2.62573000309262

```
H -3.49553683764015 1.03722929315085 3.26914351553488
H -4.13947567658667 -2.07271674943385 1.62853907310937
H -3.69007618469824 -1.94612372272728 -0.07362944905775
H -4.33312651394636 -0.53433125946327 0.78234386834127
H -1.86225840403117 -3.41196176839749 -0.05533074808821
H -1.17610154828995 -4.02014575043420 1.45692420001062
H -0.10712747728655 -3.41132565867449 0.18580384466323
H 1.53439888093747 -2.57801114371212 1.64338381779918
H 0.99941924943172 -2.58614610555033 3.32792747746720
H 1.93576590475851 -1.22050084038494 2.71372647732666
C 3.05488708700980 0.67064506322248 -0.90027984653455
C 2.68410636221221 1.57006806341873 1.46335560268504
C 2.22885256208590 1.56014451686553 0.00919911128856
O 1.77874578545078 2.65132081781885 -0.46257497693518
C 4.13490393735710 -1.43572108667249 -1.41901583619691
C 4.66305289423357 -0.88776934711650 -2.58856649166913
C 4.38673010723137 0.43905576171936 -2.91180216176816
C 3.58504550647799 1.21135440891704 -2.07515173018435
C 3.34049294305606 -0.66071510117053 -0.58106024393174
H 2.91718947255276 -1.10064713308045 0.31757935169623
H 3.36067690179653 2.24477149262930 -2.32278971699667
H 4.79657757362257 0.87457468702999 -3.81946950484973
H 4.33935105079687 -2.47200662978742 -1.16291031282636
H 5.28408259120481 -1.49292120565595 -3.24340953924689
H 1.95720664169614 2.11255549550662 2.07021503165294
H 3.64064164921571 2.10953812466016 1.49580416169933
H 2.84344466784738 0.57359882121579 1.87890636011001
```

DFT Cartesian coordinates A.56: Rh TS2 (R) 4-OCH_3 Acetophenone

```
Charge: 0

Multiplicity: 1

Number of atoms: 66


  C -2.37560019262943 1.46473122291207 -2.57713806188908

  C -2.86992238706009 0.12054695067961 -2.03755326023976

  C -1.78663139357314 -0.96675113708104 -2.14857468729796

  H -3.77646746859262 -0.19432491554834 -2.57222580213083

  H -3.14343035226034 0.24290964221621 -0.98546075764974

  N -0.46154186371310 -0.57623036751327 -1.64325411385976

  H -2.12081724761785 -1.87458984388285 -1.63279013624797

  H -1.67792494693129 -1.23545624032307 -3.21796269395012

  C -0.04104838468632 0.60256038390314 -2.40596231313935

  C -0.96540517060961 1.77495840383688 -2.08297850525321

  H -0.08000308751836 0.39897036235602 -3.49169177685537

  H 0.98989362137298 0.86209781750079 -2.15580662449531

  N -0.91881042840924 1.90785676831087 -0.59151720005437

  H -0.60586986360702 2.70998808062054 -2.53851839390632

  H -3.06966188222415 2.27167709559136 -2.30359323143572

  H -2.33240875395793 1.44018018979578 -3.67437696501018

  Rh -0.56303239440070 0.02733586621030 0.35858984019377

  H -1.73542243529024 2.40477418588286 -0.24294411064178

  H -0.07620684227620 2.45662278634403 -0.36232599051408

  H 1.06253030867923 0.57262702660417 0.17105363922262

  C -2.30752140471973 -1.02532415921667 1.31484942788966

  C -1.95151728182864 0.13714771709463 2.09422578606521
```

```
C -0.63065147781467 -0.03012609987585 2.60671470414341
C -2.85843067837493 1.28442889127402 2.38920060805238
C -0.12459097908215 -1.27922834748648 2.07961857645983
C -1.15443548905928 -1.88666884656926 1.29118903079698
C -1.07792090498804 -3.24895713772109 0.68602533911707
C -3.68596417021900 -1.39339494339650 0.87683338030307
C 0.01968043796631 0.83477171807364 3.63555215963641
C 1.15550629578141 -1.94574315652374 2.45589925329611
H -0.12594704333472 1.89910447796432 3.42711758736439
H 1.09270548525101 0.64496082136869 3.69965001081320
H -0.41293490965332 0.63110441179111 4.62466848723834
H -3.52069188820590 1.49644222320953 1.54417675841332
H -2.29022319480868 2.18977782333333 2.61928330791478
H -3.49137925939900 1.05618187067926 3.25692610313068
H -4.14228196985546 -2.04983364911205 1.63095865555617
H -3.69321370809003 -1.93592672162200 -0.07222063101094
H -4.32890339008304 -0.51571147842763 0.77557929304602
H -1.87445468599359 -3.41125105578755 -0.04349227419411
H -1.17919319403848 -4.01469898468126 1.46654320275411
H -0.11783326148424 -3.41094323747826 0.18664832327080
H 1.52803771508194 -2.58191240452136 1.64865583480173
H 0.99016559064233 -2.58758340394528 3.33234000752990
H 1.93297967406293 -1.22576100594977 2.71936734431833
C 3.05662325670211 0.64844270602592 -0.89363444481848
C 2.67732015902711 1.55236128363133 1.46305768635870
C 2.21818873545729 1.52903190222117 0.00775815920320
O 1.77898736659389 2.63057972328091 -0.46761910043160
```

```
  C 4.15943368461153 -1.45387835897574 -1.39589100481240
  C 4.67702821045645 -0.90991880195419 -2.57998280573941
  C 4.38429148760921 0.41300858956256 -2.92061091918375
  C 3.57536802839987 1.17241088641798 -2.07659741271686
  C 3.36460589971844 -0.67950940055475 -0.56894330050745
  H 2.95648975185550 -1.12210651345193 0.33553365252784
  H 3.34050108174980 2.19963499363070 -2.34020369406206
  H 4.77439898772654 0.86059073924473 -3.82777335534386
  H 4.38780552282271 -2.48642246373259 -1.14655023772640
  O 5.44952841837547 -1.74839308471095 -3.32692319623047
  H 1.94673752530774 2.09233521983606 2.06788929874078
  H 3.62949023857835 2.09925449553245 1.49099755590892
  H 2.84397733102498 0.55976000152410 1.88569479976600
  C 5.98785720607624 -1.23818320880758 -4.55356191058075
  H 6.55887516076161 -2.05878718798507 -4.98996263615434
  H 6.65226433006638 -0.38531642302193 -4.36815581569184
  H 5.18718247463119 -0.93984469860300 -5.24131045005812
```

DFT Cartesian coordinates A.57: Rh TS2 (R)TS2 (R) 4-^{t}Bu Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 74

  C -2.38080001329973 1.48045333964750 -2.56894154088816
  C -2.87166738901342 0.13172583879063 -2.03749882608551
  C -1.78539974332857 -0.95196845136155 -2.15476967595941
  H -3.77717323016780 -0.18231771993638 -2.57439462134167
  H -3.14593202545136 0.24684679568102 -0.98472956041582
```

N -0.46155323832886 -0.56079430662546 -1.64669379490676

H -2.11735104589859 -1.86372615173632 -1.64444183740750

H -1.67569158149194 -1.21395364640319 -3.22571718972125

C -0.04420808748620 0.62373352818773 -2.40192570424471

C -0.97181291730647 1.79179352825996 -2.07197863944944

H -0.08270565563333 0.42701388696829 -3.48895056193804

H 0.98594706978956 0.88462791499777 -2.15030078866458

N -0.92790900550302 1.91555558613808 -0.57946644926319

H -0.61469336825454 2.73071794526509 -2.52123114114067

H -3.07728376467116 2.28387803123813 -2.29123333442239

H -2.33676280936076 1.46232866535612 -3.66625892204899

Rh -0.56480228262965 0.03027846597015 0.35879608091916

H -1.74876572197861 2.40412578881716 -0.22899509499634

H -0.09158260118680 2.46946268850758 -0.34440825414791

H 1.05318720183548 0.57424108553901 0.17748017798767

C -2.30791481807781 -1.03304393858906 1.31077455650195

C -1.95438387675108 0.12610476725554 2.09561631001936

C -0.63209785743834 -0.03972234192335 2.60554849361506

C -2.86403254110743 1.26945949615686 2.39749053757875

C -0.12306503066500 -1.28461837175019 2.07151629040623

C -1.15219500474064 -1.89055256367579 1.28068680196405

C -1.07243186711552 -3.24912168435689 0.66764742170276

C -3.68527966685844 -1.40201034966423 0.87009793102618

C 0.01782796782319 0.82265983341379 3.63673178267752

C 1.15926970750502 -1.94950905292787 2.44311962239929

H -0.13299980113699 1.88735872237739 3.43393567647702

H 1.09191196506950 0.63721078316746 3.69610618568309

H -0.41029665881399 0.61236860608858 4.62641307512005

H -3.52870961460340 1.48330282907189 1.55482838501122

H -2.29798238145246 2.17544346757504 2.63040207199226

H -3.49449692934316 1.03562595166739 3.26552876667002

H -4.14047030380394 -2.06459494069807 1.61950436293944

H -3.69064143193242 -1.93819671918575 -0.08260850386262

H -4.33038416808805 -0.52529699803325 0.77416786311010

H -1.86808522611095 -3.40879795233539 -0.06341334052128

H -1.17274413399029 -4.01962528317175 1.44360033129619

H -0.11162829754725 -3.40626021017129 0.16809276277932

H 1.53389340501606 -2.57886443928699 1.63150932694328

H 0.99635548438052 -2.59771253212920 3.31531135343096

H 1.93432588962766 -1.22855127046749 2.71115268394009

C 3.05346738031265 0.66711655801321 -0.89140721240753

C 2.67855793005350 1.56551479927996 1.47023479597584

C 2.22184410712141 1.55148862563104 0.01538522545928

O 1.77632596801233 2.64834003575445 -0.45619755698888

C 4.15190650664824 -1.43015248548941 -1.40932806363784

C 4.67945133948994 -0.91106341406218 -2.60308342358982

C 4.37306166901578 0.41679981492143 -2.91260645969474

C 3.57190546370966 1.19096166041656 -2.07430249478296

C 3.35984621761402 -0.65965736320352 -0.57096261324628

H 2.95394077857809 -1.10328837639689 0.33417659323112

H 3.34185688055693 2.21953691114674 -2.33750055804116

H 4.75724976496978 0.87052746370642 -3.82021911735558

H 4.35818203154821 -2.45966400395093 -1.12840775272648

C 5.54777313696875 -1.79683459447696 -3.49839096611571

```
  H 1.94963112279826 2.10543338001803 2.07705244304835
  H 3.63273442740076 2.10895920231793 1.50186759792161
  H 2.84175846883390 0.57015144988042 1.88730311443423
  C 6.02007988437272 -1.06636278530895 -4.76107291594021
  C 4.73681385086136 -3.03431923977478 -3.93032406548321
  C 6.79021239637379 -2.25323092410590 -2.70887488585092
  H 3.84048055475138 -2.73459211718230 -4.48511852707599
  H 4.42258353998570 -3.63176894807228 -3.06885392092674
  H 5.34734298814938 -3.67222515119122 -4.58008409595998
  H 7.38187095288596 -1.38886838604281 -2.38669704683614
  H 7.42244298838326 -2.88772258651831 -3.34104847544030
  H 6.51337534509027 -2.82921205542780 -1.82023597730662
  H 5.17624655701418 -0.74038650538586 -5.37924910820576
  H 6.63329226645429 -1.74646588108021 -5.36189127065742
  H 6.63144088156629 -0.19033370512451 -4.51776433256485
```

DFT Cartesian coordinates A.58: Rh TS2 (R) 4-F Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 62

  C -2.38639531517284 1.47348462151625 -2.56672328369722
  C -2.87334153216046 0.12386959606337 -2.03386826282891
  C -1.78425056846638 -0.95699018705730 -2.15114485011167
  H -3.77827429011238 -0.19292337929854 -2.57007354441715
  H -3.14745768172931 0.23890092303296 -0.98100682168317
  N -0.46122711305601 -0.56165744208954 -1.64417584776167
  H -2.11322663532959 -1.86919603215142 -1.63967660835364
```

H -1.67467906873197 -1.21954632876685 -3.22196594301814

C -0.04780432814829 0.62351920281788 -2.40004836201197

C -0.97821159007842 1.78953786006573 -2.07024544049361

H -0.08649998802314 0.42659128303229 -3.48699986604518

H 0.98173936235744 0.88779421440322 -2.14924291754952

N -0.93575645732250 1.91421651274814 -0.57754317738414

H -0.62406603881344 2.72930412052607 -2.51991249292344

H -3.08507911069530 2.27523751226009 -2.28979616899102

H -2.34237971031566 1.45431984641264 -3.66400597956868

Rh -0.56509307886181 0.02968046742555 0.36145449044592

H -1.76072221379112 2.39656529811645 -0.22802018136985

H -0.10647308304964 2.47523547073008 -0.34060080141244

H 1.04485266026025 0.56953016373198 0.17905915580047

C -2.30766489594365 -1.03664886004410 1.31719330508459

C -1.95564929008330 0.12467319197376 2.09882596317621

C -0.63193755136405 -0.03683822365939 2.60731039194614

C -2.86710307522416 1.26696716009778 2.39937369962547

C -0.12106996927036 -1.28179683038480 2.07561885359743

C -1.14991112689404 -1.89118510575568 1.28669714360379

C -1.06825026357409 -3.25080976151142 0.67627033261465

C -3.68426626347902 -1.40924468213463 0.87710027532028

C 0.01809491094276 0.82978926746609 3.63492097989488

C 1.16222414985269 -1.94400635536210 2.44882429625431

H -0.13600643725492 1.89356776672009 3.42972177671543

H 1.09285770524078 0.64733523190647 3.69199235343303

H -0.40672384434701 0.62100338171996 4.62633558667818

H -3.53418072296300 1.47700160295053 1.55765468524132

H -2.30251925513615 2.17483037085394 2.62853271603845

H -3.49508357991450 1.03424339866334 3.26949884104427

H -4.13784219530773 -2.07289512121431 1.62652885219105

H -3.68841051627961 -1.94551793155220 -0.07560064303369

H -4.33155797546836 -0.53414687368188 0.78102815795255

H -1.86265566920491 -3.41242652266867 -0.05573060092259

H -1.16932397296101 -4.01990552106016 1.45353569054343

H -0.10657717508767 -3.40833348921819 0.17857457734565

H 1.53555949951947 -2.57840855143932 1.64050940894654

H 1.00124355387769 -2.58715408681587 3.32508325468665

H 1.93750128239310 -1.22128847583868 2.71172022987646

C 3.05630046151500 0.67018998314887 -0.89712235689041

C 2.68271494343488 1.57464691670290 1.46425198712360

C 2.23085464957611 1.56150233644649 0.00931046096966

O 1.78414317000916 2.65161627629147 -0.46757284362756

C 4.13078418084824 -1.44648803629428 -1.40671468899854

C 4.63358672953555 -0.87327669758143 -2.56448606861152

C 4.37888489372961 0.43969027360700 -2.92078220854327

C 3.58092009141041 1.20629806633849 -2.07624781273072

C 3.34204015510058 -0.66028518558978 -0.57486695241324

H 2.92424272516589 -1.09989744832332 0.32590406818738

H 3.35722293119662 2.23825108683347 -2.32873185879017

H 4.79622017377115 0.84823503005789 -3.83610479170144

H 4.34976272254459 -2.48340367210244 -1.17110389960472

F 5.40686884272623 -1.63406481466875 -3.38348912225783

H 1.95325718720189 2.11676165559618 2.06830322166807

H 3.63826291208666 2.11572198625056 1.49791126169872

```
  H 2.84251168931907 0.57934353975703 1.88249838004250
```

DFT Cartesian coordinates A.59: Rh TS2 (R) 4-CN Acetophenone

```
Charge: 0

Multiplicity: 1

Number of atoms: 63


  C -2.37699401323538 1.47958034390483 -2.56448430409636

  C -2.86088774083219 0.12485562297086 -2.04134084969416

  C -1.76775006670858 -0.95184042007435 -2.16084739086147

  H -3.76271013029445 -0.19152857292714 -2.58281261479688

  H -3.13934522411428 0.23214253658619 -0.98866440182203

  N -0.44999368646539 -0.55041300754035 -1.64584777012974

  H -2.09422659088688 -1.86766247223730 -1.65432608182341

  H -1.65245147342352 -1.20873545780582 -3.23219838011355

  C -0.03708118168922 0.63751579150051 -2.39586644955778

  C -0.97143302266670 1.79966686065069 -2.06274532707700

  H -0.07201991892105 0.44560823537011 -3.48359610647430

  H 0.99067851645542 0.90420502836594 -2.14038814043539

  N -0.93446307073248 1.91757123475895 -0.56902036794085

  H -0.61979993813479 2.74262703661590 -2.50720308080081

  H -3.07966816031387 2.27684425474938 -2.28493511774789

  H -2.32975386170036 1.46705488202992 -3.66166797830650

  Rh -0.55862308969391 0.02724280992427 0.35918223130645

  H -1.76682047700780 2.38746710879818 -0.21986378914627

  H -0.11702209319635 2.48883083230022 -0.32373740528727

  H 1.04027531607080 0.55892156143112 0.19343116689892

  C -2.30192989126031 -1.04957092351324 1.31232978367882
```

C -1.95693834334315 0.11469211164338 2.09210195986053

C -0.63273244446533 -0.03937119032199 2.60317411375870

C -2.87432144147220 1.25287906180456 2.38976867752434

C -0.11520802466745 -1.28216227740081 2.07421031806896

C -1.13946508876764 -1.89702659348006 1.28236973174284

C -1.04996313011276 -3.25610954251807 0.67204040521065

C -3.67462379823905 -1.42815693690709 0.86584394696823

C 0.01280772442639 0.83397094174639 3.62787376812074

C 1.17013402907694 -1.93802355166505 2.45091815512882

H -0.14645209432811 1.89615771375632 3.41845319970270

H 1.08848917155788 0.65692169439025 3.68540647002852

H -0.41063355025845 0.62696551669191 4.62018737344994

H -3.54250827539966 1.45761692996463 1.54765239865826

H -2.31451242629061 2.16407893954164 2.61733363068874

H -3.50096926356791 1.01846332029785 3.26035767524637

H -4.12710179302746 -2.09697516305055 1.61129257793382

H -3.67199187710772 -1.96147395375417 -0.08855513406208

H -4.32642238684432 -0.55640355496061 0.77029747938236

H -1.83599797313660 -3.41782210061035 -0.06895837897558

H -1.15931200955488 -4.02572401237540 1.44766713347465

H -0.08261942006459 -3.41253150466747 0.18523823242290

H 1.54979374914653 -2.56970012743205 1.64339277988215

H 1.00894773343599 -2.58318364550004 3.32558946200580

H 1.94036866546520 -1.21151418330056 2.71844033478688

C 3.05942370684889 0.68268266839960 -0.88760675100646

C 2.70200059416795 1.59720320320184 1.47504558273166

C 2.26005853045126 1.59432041574001 0.01975864404625

```
  O 1.80771006064547 2.67292461881782 -0.46144032275329
  C 4.09258032857897 -1.44841150387758 -1.39156061264383
  C 4.60524541833466 -0.91046031150986 -2.58393697802514
  C 4.34416727360947 0.42508944599992 -2.92501915211622
  C 3.57331963598331 1.20637261723814 -2.07949608663754
  C 3.33189350512147 -0.64972061779933 -0.55583372151050
  H 2.92145101356038 -1.07470369341011 0.35458200442092
  H 3.35835377779435 2.23943594030690 -2.33382894448444
  H 4.74649085777980 0.83601648071259 -3.84578183794227
  H 4.29281034478065 -2.48425659695271 -1.13635022581446
  C 5.39002643461480 -1.72232968319101 -3.44659342620084
  H 1.97286424989219 2.14377926519554 2.07516382128740
  H 3.66116279067429 2.13149951232486 1.51684620736735
  H 2.85184860222602 0.60008176521790 1.89178309945639
  N 6.03143494122627 -2.38452470416601 -4.15053523695674
```

DFT Cartesian coordinates A.60: Rh - TS2 (S) Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 62

  C -2.36548817315122 2.55456062618804 -2.13512588394393
  C -3.22241731441773 1.41236660418537 -1.57619547104376
  C -2.80971299113443 0.05229317307516 -2.16296520972216
  H -4.28476763714309 1.60809244933187 -1.77646556561533
  H -3.10169507366916 1.37534901591810 -0.48970554889019
  N -1.36374949877647 -0.20414671765867 -2.11315232709794
  H -3.34662975839050 -0.75284790944243 -1.65157141870179
```

H -3.12878119749413 0.01821805047066 -3.22258766868910

C -0.72852978266728 0.83792888655939 -2.92807802340281

C -0.88645213643257 2.18535135869931 -2.23042622656024

H -1.19196500474239 0.88309695738453 -3.92943724135442

H 0.33557675277567 0.63444303391151 -3.05958875457057

N -0.25908284340029 1.97955641271054 -0.88831041912988

H -0.34184798909455 2.98042787556883 -2.76304821393709

H -2.49829012179827 3.46615838960443 -1.53584358532305

H -2.69192844159574 2.79706790712899 -3.15546065263740

Rh -0.60438655445039 -0.01142909081554 -0.17011920509612

H -0.52855305821491 2.71228813262518 -0.23625396272296

H 0.76174809305752 2.01923135954341 -1.03027348018405

H 1.02614775258373 -0.20878531700441 -0.85706844831022

C -2.25430154837215 -0.88127450663778 1.08670083592041

C -1.73959256671086 0.29556203423255 1.71932509218298

C -0.34968016478250 0.06913519217856 2.05182607140474

C -2.51727738245284 1.49199543253680 2.15307988051336

C -0.00871350094069 -1.23406634852339 1.59096174353331

C -1.16413817293665 -1.80954072165488 0.93418562976779

C -1.26628774612664 -3.20246584891705 0.40692095055286

C -3.69265973981401 -1.18239421827626 0.83536685046656

C 0.48503204822973 0.99994054509623 2.86701677211205

C 1.27042409994632 -1.95485549854729 1.82937268994202

H 0.36270993193938 2.03735545239144 2.53862537049096

H 1.54488762966501 0.74762191185707 2.80242518786461

H 0.18716003936477 0.95273313381602 3.92317599634806

H -3.50890684753108 1.52598753988058 1.69710365969431

H -1.99033367443912 2.42170123950645 1.91431972418547

H -2.64935030866454 1.46575753368688 3.24308389250101

H -4.14684869846884 -1.52459015356183 1.77561192610852

H -3.81797367569104 -1.98254285961596 0.10271232268916

H -4.25612925492898 -0.30796008414681 0.50089302977347

H -1.97886286622328 -3.26031500256910 -0.42101808086420

H -1.60617689347764 -3.89368605746345 1.19029032600446

H -0.29802615801990 -3.55839415587193 0.04465305593632

H 1.56969846973283 -2.54750254601357 0.96105127513779

H 1.13881248847448 -2.64593243032695 2.67341192489233

H 2.08611318912931 -1.27139746528487 2.07015476583947

H 3.22649387113017 -1.23428212203798 -2.90238066434257

C 2.24308637668412 -1.15896563528212 -2.42023371618097

C 4.15839990769308 0.80631717192028 1.75810854284205

C 4.95250677445744 -0.32883388623100 1.93119825063718

C 3.28541053438787 0.88924438884626 0.68041900893451

C 3.16931272188392 -0.16065196063476 -0.23595446039258

C 4.85724916716797 -1.37371482929356 1.01756817017056

C 2.25553452315740 0.02226250478511 -1.44389639193282

C 3.96897978747881 -1.29243372956162 -0.05525411294435

O 2.27786912511569 1.21248028007014 -1.95335661766917

H 2.01961501385405 -2.10827777671447 -1.92316498443094

H 4.22238412356382 1.62800037200111 2.46719383684352

H 5.64051593545447 -0.39364956034988 2.76982081868864

H 2.67407887447853 1.77687743498698 0.54019658914958

H 5.47487002583402 -2.26016721022825 1.13731256110248

H 3.90999991781882 -2.12391810526902 -0.75014793133115

```
  H 1.49491960109499 -0.99038065276298 -3.19700248520877
```

A.6.5 Cartesian coordinates for the optimised geometries for the Ru(L2) cycle

DFT Cartesian coordinates A.61: Ru - INT0

```
Charge: 1

Multiplicity: 1

Number of atoms: 45


  Ru 6.75725535136339 4.82516975512763 11.34920492377226

  Cl 7.63286458655363 6.65459730947355 12.72340391414523

  N 5.54648155750041 6.33532195818023 10.39873489054227

  H 4.62603233169665 5.99238109379813 10.13196606024084

  H 5.39478286114091 7.04589326561009 11.11361668209509

  N 8.06447012657122 5.57532850767456 9.77200447148419

  H 9.01818093577173 5.54963031330097 10.12851196867314

  C 7.35792936518547 3.42532320872289 12.94074683275028

  H 8.10122300158767 3.63878491092810 13.70034440158000

  C 7.75060644231232 2.86215637524559 11.71159188519175

  C 6.00882712604557 3.84123791028755 13.17280575488538

  H 5.76618061128441 4.35513577476526 14.09737925558502

  C 5.41440400895742 3.14726068240654 10.91613118808052

  H 4.68955623298381 3.09202440729276 10.10893736165096

  C 9.16007507732424 2.39846757863262 11.43148791661810

  H 9.33825729432480 2.54689169529553 10.35759227580253

  C 6.74443933829870 2.73341285594315 10.69465402740950
```

H 7.02596687917729 2.35017117726624 9.71807189128645

C 5.02243261253800 3.71173101285473 12.17595430066564

C 7.69075876111198 6.99552414100724 9.50669560436604

H 8.25266889115384 7.38319031027357 8.64670111311285

H 7.92182180367249 7.59701709061359 10.38606564280521

C 9.24287876684603 0.88962070138447 11.71672604017537

H 9.06198298237946 0.69400089860982 12.77989050947211

H 10.23944634624849 0.51519740898360 11.46158719015301

H 8.50422883944242 0.33094870846680 11.13255811213944

C 3.61954706514159 4.18037638497240 12.40266733983974

H 3.58664075315403 4.98279377271214 13.14376384303149

H 3.01870694251549 3.34314847077714 12.77827188733168

H 3.15848286570114 4.52474357633039 11.47273688731692

C 6.59672259869736 4.81129831634353 7.91959784961526

H 5.98411513567796 4.11803623894924 8.50105386067020

H 6.62966906834486 4.41904103728034 6.89733704822460

C 8.01622797175856 4.82991742928227 8.47583531443881

H 8.39182430134977 3.81635822102066 8.63684935310559

H 8.69660696597661 5.33126996206398 7.77179558456557

C 6.20479825383501 6.97819607812376 9.21020831337262

H 5.82526751207370 8.00197267388513 9.10323575762792

C 10.22893108062405 3.16668501548204 12.20735655875676

H 10.12446894444183 4.24854746059750 12.07003061113270

H 11.22079561581454 2.86860480992213 11.85445871912116

H 10.18164403632471 2.94820660764344 13.27971970925491

C 5.94476770264876 6.19949779961053 7.92113444873216

H 6.35825127099132 6.80579177310554 7.10581402093489

```
  H 4.86687978345573 6.11229531975231 7.73876867824284
```

DFT Cartesian coordinates A.62: Ru - INT1A

```
Charge: 0

Multiplicity: 1

Number of atoms: 44


  Ru 6.76501118935632 4.82860792429055 11.31892770608815
  Cl 7.52979898188631 6.76798734811806 12.80474703619282
  N 5.52691019929603 6.32603125691990 10.34594751795583
  H 4.62008146587504 5.96488155292032 10.05961337294248
  H 5.35247176725617 7.02933888261962 11.06205197616837
  N 8.04938474016187 5.51419515691618 9.83458169996158
  C 7.36174500750274 3.45299759977808 12.93566836050509
  H 8.11338030402486 3.67394516575528 13.68533221193493
  C 7.75209892311579 2.88774562807823 11.70033405187479
  C 6.00905141535674 3.82019572947557 13.20837876022451
  H 5.77461408186327 4.31457650617978 14.14550835312462
  C 5.40962377742971 3.19054343875876 10.93546521222896
  H 4.67635634598023 3.14875943489742 10.13402006236502
  C 9.16240565398519 2.43243195191877 11.40942293466304
  H 9.34211018760045 2.62127251265618 10.34196173566559
  C 6.73667080222964 2.75746540317740 10.69398277574980
  H 6.99979020784392 2.36805102878862 9.71547678696225
  C 5.02300666283454 3.72701209486548 12.21125258146677
  C 7.70490243071357 6.90955596815640 9.53969224645794
  H 8.30182613639422 7.28674667283102 8.69221565086500
  H 7.91075432669590 7.54340957868277 10.40637754461786
```

```
C 9.26108654745598 0.91664775435372 11.64411012285383
H 9.07869963679252 0.68314144281532 12.69974917624215
H 10.26089420998584 0.55539382244405 11.38036547175730
H 8.52754510893775 0.37127811857611 11.04085825442348
C 3.61611243481724 4.18375391786886 12.45221225553516
H 3.57674201158352 4.93752070757336 13.24303055945260
H 2.99648605073347 3.33245931090476 12.76039891024761
H 3.17197364000366 4.59835416783679 11.54224881597634
C 6.59144028522640 4.79023753610766 7.90870659695102
H 5.93348576117147 4.11657048925253 8.46691662441886
H 6.65275187281000 4.39648188410967 6.88532392243724
C 7.98602647562078 4.78715198016424 8.55798572615167
H 8.33178647461768 3.75581917863580 8.69166480157600
H 8.69847063948613 5.26197137690736 7.85769709757693
C 6.22236361801949 6.96712066982166 9.18365173479938
H 5.86305432637866 8.00069371949157 9.07498829244061
C 10.22938422712454 3.18013059059243 12.20853615088069
H 10.12187420464695 4.26450257842923 12.09906404640840
H 11.22376658572027 2.89420846733941 11.85133448645664
H 10.17926614518788 2.93199596513813 13.27470428024128
C 5.97899871302964 6.19736079500899 7.88559702709787
H 6.44107744004387 6.78872988178926 7.08400041307471
H 4.90456898320337 6.14778480905442 7.66173665498424
```

DFT Cartesian coordinates A.63: Ru - INT1B

```
Charge: 0
Multiplicity: 1
Number of atoms: 44
```

Ru 6.73681956699006 4.82349189961086 11.30908087266437

Cl 7.86783774599553 6.64880028668813 12.77720867701717

N 5.56117875153495 6.27642163009908 10.44880035960825

H 4.67392691791338 5.87040768234532 10.15542402690892

N 8.05451787171461 5.57873420016748 9.74541133100642

H 9.00805611837474 5.55869518287046 10.10188034202746

C 7.35034188544293 3.40171943835414 12.95543312997879

H 8.08028823047702 3.59633218346022 13.73219540110125

C 7.75240868008822 2.84489402612303 11.73084828744319

C 6.00811269850846 3.86557075566835 13.14754972984619

H 5.76392974040300 4.39533558736318 14.06351865164567

C 5.42324681314025 3.17523694995334 10.89088438199737

H 4.70924729164774 3.11634836089242 10.07427047924213

C 9.16231722517617 2.37381922105562 11.45698067055469

H 9.34034935407958 2.51807107489707 10.38176127914233

C 6.76634964902304 2.75902310884031 10.69174327329534

H 7.06434102733912 2.39032731321008 9.71376835701927

C 5.01931357524700 3.73298436326934 12.14966207605421

C 7.64452249445582 6.99418715317149 9.51303942773708

H 8.18732511564448 7.41103899329575 8.65242827358581

H 7.87319415613711 7.57402078202217 10.40773402406905

C 9.25853020011214 0.86831648303640 11.75071446463829

H 9.08481602308173 0.67846224259707 12.81641144799332

H 10.25463893286103 0.49332342511926 11.49245413673623

H 8.51731684567201 0.30247913972937 11.17635130338678

C 3.62089660019075 4.22250658553622 12.36455108567257

```
  H 3.59678299945460 5.02441696494456 13.10739001492074
  H 2.99178958647362 3.40104975847814 12.72873471391923
  H 3.17990330090257 4.58782308301495 11.43254344772491
  C 6.59061197334185 4.82218821800031 7.88978572567620
  H 5.99709084275600 4.11181372931843 8.47049766813153
  H 6.62502306993492 4.44284173862365 6.86152673080188
  C 8.01291463014026 4.85497382983865 8.44120445201619
  H 8.40384179349228 3.84332713521170 8.58621799647407
  H 8.68235970108539 5.37488785322182 7.73830354335111
  C 6.15085858611385 6.92673746232963 9.26506942895660
  H 5.76024351079614 7.95520047532022 9.16442035212074
  C 10.23030342972830 3.15388288167597 12.22310498433795
  H 10.12095393912226 4.23278103354102 12.06771390529808
  H 11.22522280334775 2.85225223705411 11.88051507574198
  H 10.17805027176501 2.95477233892708 13.29925980482263
  C 5.91429704002654 6.19834139938161 7.92736132468936
  H 6.31150284789148 6.83186441346539 7.12100851090935
  H 4.83726616237588 6.08817737827628 7.74518682973464
```

DFT Cartesian coordinates A.64: Ru - INT2

```
Charge: 0
Multiplicity: 1
Number of atoms: 42

  Ru 7.04410418878267 4.25046085307965 10.66915774561618
  N 7.34818108292192 6.14882715530867 10.77816404806169
  H 7.08581465330820 6.75146942749914 11.55387304246659
  N 7.24713976265417 4.65341657897160 8.63062218826951
```

C 7.08786532551883 3.45665881081285 12.77173957503503

H 7.48630475792547 3.96317716328571 13.64426066781899

C 7.95553338203434 2.70280984987965 11.91992115934685

C 5.76782860689495 3.72250883608451 12.36257022613352

H 5.14864487344682 4.40140608159472 12.94324726092747

C 6.06661281035422 2.26349563721757 10.40553768914159

H 5.69798512210109 1.86464344831888 9.46467567593352

C 9.41632240221208 2.50676949197434 12.26141656121698

H 9.91357676911040 2.17663282472410 11.33925466202205

C 7.40593669910710 2.03938294970069 10.78035536603321

H 8.06131729731893 1.46407768648592 10.13377819532632

C 5.23858666913688 3.15212868382112 11.15068973448711

C 8.09618282776414 5.85839192948048 8.56375780438511

H 8.14555418946980 6.24990381988979 7.53164149235682

H 9.11915926703545 5.60425063499751 8.87993128605586

C 9.54215493065774 1.38394254920244 13.30370895086940

H 9.05596229384115 1.67700662845174 14.24167885934463

H 10.59712016233121 1.17948502152995 13.51544268445974

H 9.07483050181340 0.45906558268781 12.94959087643596

C 3.82130914143010 3.41581995041035 10.74150716291135

H 3.48348774572091 4.39282409122398 11.09773818333148

H 3.16399489231025 2.65265074764971 11.17827264317262

H 3.70845411281011 3.37493051871430 9.65465950732341

C 5.21642126762018 6.17192260023111 8.69260760223171

H 4.81313894546743 5.81838320513050 9.64891844716999

H 4.36044593058780 6.48934096555158 8.08042005916028

C 5.95529653940317 5.00176446401031 8.01440068081876

```
  H 5.30579933600286 4.11512787991943 8.00880801411434
  H 6.13588027647573 5.27128307389055 6.95499888818114
  C 7.50650733235802 6.88617881906791 9.51242283955314
  H 8.17367728870034 7.75345676687928 9.65329810062547
  C 10.10924862502176 3.78272355721480 12.74353403398800
  H 9.97155761423056 4.59729438122001 12.02397158057540
  H 11.18207341636743 3.59943756012987 12.86351893585348
  H 9.72068157164497 4.11069435421476 13.71388109858192
  C 6.15010691110538 7.36209862701368 8.95503347690899
  H 6.34555146549579 7.90516402366764 8.01933525619017
  H 5.67783901150561 8.07369276886103 9.64612773756326
```

DFT Cartesian coordinates A.65: Ru - TS1

```
Charge: 0
Multiplicity: 1
Number of atoms: 54

  Ru -0.40994924891155 -0.09515712441026 0.07297187293605
  N -1.63843482788211 1.43262838809536 -0.81026931462959
  H -2.60003428741477 1.15402589363600 -0.99004816296842
  N 0.84169155324167 0.54276614830294 -1.48291787913632
  C 0.20973380985927 -1.32371547498081 1.77865876178346
  H 0.92352698958763 -1.02554417540882 2.53950958827580
  C 0.66764166797291 -1.95442376553421 0.59442498250015
  C -1.16954084583700 -1.01850399139464 1.97885041461826
  H -1.47986544979384 -0.49797260948987 2.87772278577643
  C -1.66741463254314 -1.92275662423750 -0.24028692196940
  H -2.37876595536322 -2.11586544904026 -1.03827264844425
```

C 2.11193093512403 -2.33136875548535 0.35924728810793

H 2.29571301339805 -2.20342111275221 -0.71761274777609

C -0.31491358085687 -2.26876521526308 -0.40381098627246

H 0.00643084892738 -2.72837832185807 -1.33417834286648

C -2.10598975981150 -1.24267861610156 0.94657218231710

C 0.48485352322664 1.93119635170164 -1.78256325884137

H 1.63628995106459 -4.45413570259880 0.13323695869633

H 3.34649441655926 -4.12112152475348 0.47614603972342

C 2.31937537608427 -3.81467275537964 0.70259470380301

H 2.13762821814335 -3.98589303355898 1.77042378613100

H -3.97584318058626 -0.55740800379327 0.13388305014858

H -4.13120839611340 -1.66946987632510 1.49757004589911

C -3.54107468737974 -0.83469146996800 1.09915790812342

H -3.63793492118272 0.00950572819884 1.78773161186722

H -0.76726686041010 -0.63488178869130 -4.30193980627552

H -1.37064501098048 -0.87471560799669 -2.66378652173776

C -0.75388842299010 -0.21849114855882 -3.28531670456773

H 1.34609909242149 0.23764396152965 -3.49692956388487

H 1.02965924345965 -1.24475108705480 -2.59586222838148

C 0.68220857270418 -0.21363746237751 -2.73415038617529

H 3.05360205490452 -1.62300709258186 2.19604131463873

H -1.36114331034837 3.03923979854260 -2.17639467127825

C -1.01549692999968 2.00221735759489 -2.04760344061639

H 4.12812497161543 -1.69050056090289 0.79593625918278

C 3.10822914368987 -1.45250933924195 1.11474843402146

H 2.92376085406047 -0.39038084825758 0.92209936387703

H -2.44891441074678 1.14430375592485 -3.43668398474804

```
 H -0.95928626563366 1.75706955534022 -4.15045210249739
 C -1.35980827841346 1.19224587713930 -3.29762642354533
 H 1.03322309379926 2.29951933289645 -2.66808075904401
 H 0.73195049575760 2.58209713889727 -0.94011714678885
 H 0.18081888288506 1.29319281241506 0.89917570026458
 H -1.65057384539348 2.18213008233771 -0.10561333073571
 C 1.68532658248007 2.79676527139832 1.62666704092925
 C -0.38356639529549 2.13601118800044 2.96768058705621
 C 0.16710262766473 2.61855782630822 1.63026047882190
 O -0.54507366738148 3.43396832548736 0.96317632690874
 H -1.44554379096850 1.89483614076188 2.87788214538260
 H -0.27600232837519 2.96661175680974 3.67922186592678
 H 0.16098740135531 1.27343185073135 3.36109542204267
 H 2.06253876293887 2.98720071601419 0.61911272448883
 H 2.19884310300211 1.92837418020630 2.04996346148789
 H 1.91439410468518 3.67327909972682 2.24875422744428
```

DFT Cartesian coordinates A.66: Ru - INT3

```
Charge: 0
Multiplicity: 1
Number of atoms: 44

 Ru 6.77846095139638 4.82283604592278 11.30906195322014
 H 7.44491203438631 6.06831111276258 12.08621174160287
 N 5.56952405031011 6.38741861078219 10.41248537178517
 H 4.65491473126983 6.05407279265458 10.11671494466265
 H 5.39548328033536 7.07952098457862 11.13503340891843
 N 8.08055353253721 5.49534884057378 9.78436258064402
```

C 7.36613895629513 3.51250317562950 12.95018296536261

H 8.10667107058575 3.74669212994970 13.70711032659096

C 7.76987802571624 2.89765679111092 11.73674426704182

C 6.00655318542545 3.88930048133320 13.17498934962667

H 5.73002653446327 4.40706195482144 14.08807297063842

C 5.42275988677470 2.99249100284845 10.96087241699897

H 4.68420404356903 2.82701751009983 10.18100950598674

C 9.18904914540597 2.44927260998307 11.46698428408632

H 9.37360875688290 2.62733378840627 10.39717082512126

C 6.75099138937179 2.60999176556379 10.76076277650157

H 7.03699688864181 2.14022522794863 9.82300535347240

C 5.04867743153922 3.71837479638608 12.14603852664186

C 7.76351474877860 6.90530547531149 9.56007796797206

H 8.33677197513637 7.31385563188402 8.70579041698633

H 8.02011106674803 7.49535315135797 10.45074545090916

C 9.30929412054578 0.93855509254170 11.72276294768799

H 9.12541214906913 0.71765001813990 12.78116075360735

H 10.31417679571984 0.58355460946588 11.46842605217462

H 8.58477557761779 0.37400961688873 11.12610470283108

C 3.63366306207324 4.18686507380448 12.32482831084580

H 3.58248497022489 5.02217251377892 13.02893482410478

H 3.00946219846103 3.37318801629573 12.71575594531524

H 3.19926232378173 4.50237351017257 11.37091429213662

C 6.46447790691673 4.88182594948322 7.93516037653065

H 5.80333311262370 4.25146227820804 8.54083241182099

H 6.43765460735072 4.48589721318871 6.91038821479368

C 7.89163827446289 4.80009376020761 8.50367459744115

```
  H 8.18536463708891 3.74780392307135 8.60975719522851
  H 8.58197704684178 5.24452974321609 7.75777474866190
  C 6.27148666475254 7.04329379619717 9.25974280100447
  H 5.95476060855940 8.09521795423065 9.19239416269455
  C 10.24647330747915 3.21574458750504 12.26049439476472
  H 10.13395699133080 4.29726388224527 12.13253239299172
  H 11.24613903090634 2.92950584296857 11.91771329526494
  H 10.18788907283293 2.98557876576792 13.33052628522374
  C 5.95044148163660 6.32682949337155 7.94674443903605
  H 6.43906777681862 6.89965948308245 7.14656873190570
  H 4.87062659733535 6.35987099625918 7.74497071916243
```

DFT Cartesian coordinates A.67: Ru - TS2 (R) Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 61

  Ru -0.81524533060941 -0.54714916818117 -0.01388379315628
  N -2.15844897382422 0.91079619158924 -0.83783770657594
  H -3.09360776036191 0.55788728306551 -1.02673507325796
  N 0.35861315242997 0.20326800349010 -1.57074256565585
  C -0.01191301131278 -1.82870464476529 1.58131193589651
  H 0.76368619795974 -1.55106400963837 2.28724837893730
  C 0.33951133869905 -2.40894879511042 0.33915621550374
  C -1.37366013174755 -1.55281684855806 1.91505118576699
  H -1.60595073104700 -1.07180908856774 2.85848713827290
  C -2.05960699148797 -2.37539005956369 -0.28023943003330
  H -2.83647367107142 -2.53709207544363 -1.02299589979235
```

C 1.75785755958165 -2.77699570355818 -0.03162091862356

H 1.84485704150924 -2.63832588976420 -1.11861221028414

C -0.72446249387658 -2.70053988866739 -0.58082227299109

H -0.48391756870622 -3.11975071256211 -1.55368452745164

C -2.40269616703480 -1.76715994300141 0.97464679049433

C -0.08187618900566 1.57741161180553 -1.81815136448880

H 0.42727560766560 2.00559540424862 -2.70023843461899

H 0.15379491795645 2.21145957352738 -0.95873101689060

C 1.99019310951801 -4.26521423987662 0.27496098522972

H 1.90864381747136 -4.44751344450375 1.35321773509807

H 2.99064828354521 -4.57099861301228 -0.05002638608318

H 1.25474316544653 -4.89678157732891 -0.23480082855688

C -3.82458975714899 -1.40011930222073 1.27938232427165

H -3.87153343844362 -0.59617200821352 2.01945910321079

H -4.36245191663442 -2.26718950505022 1.68278727335604

H -4.35082793502156 -1.07955832917943 0.37496961133052

C -1.22642274144089 -0.59377940682941 -3.36436693040291

H -1.79676819077130 -1.29544788448165 -2.74705195593724

H -1.23784415274652 -0.98727787858668 -4.39004685179511

C 0.21833570841421 -0.52675276533681 -2.83948563564391

H 0.62037594144397 -1.54169166572235 -2.73433520829775

H 0.84269846300688 -0.02121504740224 -3.60149035452824

C -1.58876474909619 1.56782733282372 -2.05716830912540

H -1.99830319132248 2.58583899725909 -2.14070161281373

C 2.82214377013169 -1.91016057830855 0.63916748910044

H 2.64210309452644 -0.84689929392452 0.45229516715044

H 3.81018795403867 -2.16719869054520 0.24357969155924

```
H 2.85005765316240 -2.07223903726948 1.72283643604708
C -1.90289024517167 0.78362754284395 -3.33141116756546
H -1.53837718193914 1.39349938117654 -4.16913198231062
H -2.98932896030361 0.68447204481399 -3.46380762277897
H -2.23176898258215 1.62962449306309 -0.10532651023699
H -0.29946694774678 0.85260390289948 0.83351291613271
C 1.01619602103332 2.61683653226444 1.35947253907858
C -0.70237319644349 1.62428136166267 2.98105815717740
C -0.42461614600172 2.21151718883010 1.60190428245006
O -1.34426080056053 2.89435843582677 1.05937451270352
C 3.40044300501702 2.21159962891972 1.51383757717310
C 3.65862038496669 3.45881153024001 0.94401358193422
C 2.59497793649870 4.28359936928466 0.58381766239716
C 1.28295481357297 3.86353378553124 0.78696138587901
C 2.08986934616684 1.79680639101035 1.72271988603391
H 1.89885423385390 0.81578714901631 2.14917261086658
H 0.44804912135446 4.49856790760506 0.50525593881518
H 2.78750845254625 5.25807359472596 0.14245745124354
H 4.22388823760125 1.55859716403477 1.79142740793944
H 4.68273601530832 3.78348544984233 0.78118370063951
H -1.73015377357268 1.25647325541954 3.01850681165813
H -0.59572876421260 2.44198826624843 3.70686185015531
H -0.01549425318096 0.82372732210537 3.26335083639381
```

DFT Cartesian coordinates A.68: Ru - TS2 (S) Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 61
```

Ru -0.22500331822034 -0.24942340648585 -0.50237703151502

N -1.42480519209374 1.27641285694126 -1.42523054417263

H -2.38470616049828 1.00122873068023 -1.61865806996169

N 1.05233016055984 0.35542228612716 -2.03672944944553

C 0.35884696315703 -1.45806099302697 1.23293518949798

H 1.06687801594294 -1.15255007875309 1.99605219755754

C 0.82031474867778 -2.11471696582407 0.06471103278354

C -1.01627309239934 -1.12803869344065 1.41507222023991

H -1.31970733591726 -0.57369949286815 2.29642512628796

C -1.50445037217326 -2.04667508275814 -0.79809564247446

H -2.20927544870650 -2.23336136452026 -1.60350631508759

C 2.26216646968781 -2.51401876727990 -0.14648038657848

H 2.46322758350568 -2.40047786050560 -1.22179585238163

C -0.15459104343523 -2.42029532325266 -0.94333344163411

H 0.16881924102364 -2.89397666081504 -1.86585864950118

C -1.94768307991072 -1.35501385710131 0.38042346691505

C 0.71982943674357 1.74448851048073 -2.36015560449137

H 1.29158126153534 2.09632399863417 -3.23700854325955

H 0.95652079878723 2.40181808091442 -1.51981643053949

C 2.44360210962422 -3.99602528166498 0.21653854546416

H 2.24276370801886 -4.15240021498814 1.28321253368162

H 3.46987623272701 -4.31871578579962 0.00985118854989

H 1.76080856923641 -4.63248118274670 -0.35646420707098

C -3.37645643160360 -0.92088115113249 0.51595058092223

H -3.46057560335807 -0.06168560781877 1.18778609198708

H -3.98186801365354 -1.73723306460334 0.92926210497843

H -3.80228640001234 -0.65623218081289 -0.45682840547838

C -0.50460238813552 -0.41358293395936 -3.86350924550773

H -1.13881893487129 -1.05871468009958 -3.24776826001430

H -0.50020676121312 -0.84095861097617 -4.87553601588448

C 0.91974132922496 -0.41464711598840 -3.28252319202414

H 1.25495221036305 -1.44669638822271 -3.12374233910437

H 1.60474273325795 0.02259895471882 -4.03415066552014

C -0.77410872853016 1.82493125881931 -2.65727615129000

H -1.10737580940592 2.86319739693879 -2.80573414533629

C 3.25884551659486 -1.64036317148721 0.61486769469120

H 3.09168778341670 -0.57770734382681 0.40924614449480

H 4.28003024205123 -1.89487498906109 0.31352640928083

H 3.18607774664197 -1.79912810713153 1.69689889209806

C -1.09921229689478 1.00166954505517 -3.90379178396584

H -0.67812096659819 1.55311425860254 -4.75535075157406

H -2.18566363656870 0.95957403801909 -4.06349591923459

C -0.30334110358262 1.96742189874721 2.33389299055297

C -1.66958499645566 2.16506930543864 2.55438102373000

C -2.27426967165776 1.72343629482084 3.72649502605282

H -3.33941794422035 1.87979851179718 3.87734455564152

C -1.51758784764517 1.08297004799949 4.70747329682603

H -1.98750537150113 0.73751935096128 5.62430335281757

C -0.15232880359070 0.89376408360825 4.50382498120034

H 0.44824792329741 0.40103446141017 5.26402859265348

H -2.25218081481542 2.66559045366421 1.78667862998502

C 0.45047544558132 1.33281904031727 3.32667663945801

H 1.51425158532511 1.16618445105093 3.18803206227175

```
  C 0.30515678129359 2.46999643450672 1.03332003240811
  H 0.35139564455182 1.16659213277899 0.34041606023123
  O -0.39992566423906 3.28003618679641 0.34218992543042
  C 1.81857156558070 2.69788567121373 1.06008375056774
  H 2.38563990146304 1.81478918233459 1.36410846146390
  H 2.02903755643928 3.50991847277837 1.76884016787828
  H 2.15812036947807 3.00963990924239 0.07032888204681
  H -1.44260640188064 2.03739055155311 -0.72996080759823
```

A.6.6 Cartesian coordinates for the diastereomers for the Ir complexes

DFT Cartesian coordinates A.69: S_C, R_N, R_{Ir} - $[\eta^5\text{-}C_5Me_5Ir(L1)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 43

  Ir -0.55736737872828 -0.59254898890000 1.92013328097574
  Cl 1.28991111776805 -1.76152162433729 0.79581722907884
  C -1.93086968290285 -1.44685739992125 3.37618838080496
  C -1.89754620960219 -0.00346694319927 3.54060944833524
  C -0.53480943107609 0.35122782720604 3.89710033138893
  C -3.09445366172316 0.88256217130015 3.59897688115624
  C 0.25665799910850 -0.84249560057359 3.92783925942397
  C -0.61727257539842 -1.96790883385342 3.60946836656678
  C -0.21788769036322 -3.40176753903009 3.62250763293623
  C -3.14898987447155 -2.24510024084920 3.06641089161081
```

```
C -0.04409737188567 1.71403724295047 4.24552128725721
C 1.68840641376137 -0.94667747675463 4.32190276196460
H -0.68480924496807 2.49927402143790 3.84000941806987
H 0.97664648339559 1.87559054745413 3.89013868127308
H -0.03968052898244 1.82174821611607 5.33752149785254
H -3.86058998527533 0.57319475766453 2.88409015091712
H -2.84510152262627 1.92837716635417 3.40830687661837
H -3.53501612560688 0.82825261887804 4.60306412384098
H -3.64750461686261 -2.52103032482790 4.00412110969452
H -2.90165971137784 -3.16581070678715 2.53287615320013
H -3.86330128636952 -1.67238665625006 2.46886330749833
H -0.86484927231088 -4.00373638959292 2.98034121498523
H -0.29325057967822 -3.79258137818788 4.64518203270557
H 0.81343918670059 -3.52710378149776 3.28584101474984
H 2.19353965628911 -1.74043437768156 3.76690025148602
H 1.75724108290208 -1.18191210047664 5.39165729032451
H 2.22091304285595 -0.00940080047713 4.14553827894455
C -2.36136407646020 1.40342677978798 -0.08671423365903
C -1.23657582322050 2.11217812975318 0.70266723756947
N -0.11003923943298 1.12882950328994 0.63253319404669
C -1.64820675149083 0.22874444998645 -0.78472036122597
C -0.19733887040899 0.68009024960313 -0.78917708962092
N -1.69011091103609 -0.97659428915723 0.09983489715392
H -2.04769423892508 -0.00180389925211 -1.77678279869230
H 0.52419924815202 -0.10769556863008 -1.00586357074727
H -0.05115408374415 1.52935442139697 -1.46920163794953
H 0.78684485484810 1.55570153097340 0.85121962322281
```

```
  H -2.79783216774031 2.07422605186545 -0.83034637564900
  H -3.16674978048921 1.05065575837481 0.56395044262287
  H -1.49171216785495 2.33491528988232 1.73676762178090
  H -0.93162067960269 3.04160766290724 0.20468504120548
  H -1.26369743999408 -1.76956566945867 -0.37936796099646
  H -2.65450610517174 -1.23173380748653 0.29978881727792
```

DFT Cartesian coordinates A.70: S_C,R_N,S_{Ir} - $[\eta^5\text{-}C_5Me_5Ir(L1)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 43

  Ir -0.44778447882508 -0.47252044477039 2.00261381766287
  Cl 1.70991957846639 -1.05424064457025 0.99843605540042
  C -1.92644453749560 -1.31943991996217 3.34482904411344
  C -1.78926914422343 0.09303355333350 3.60909822840666
  C -0.41265616477846 0.32366989414612 4.03554427131123
  C -2.87677263477361 1.11142211309022 3.62524121677112
  C 0.27250192072916 -0.93142956054402 4.02752249866900
  C -0.65016406345074 -1.95983735208938 3.57022987926486
  C -0.36176509559138 -3.42100413708535 3.51118771112463
  C -3.18108343375579 -2.00681764049917 2.93272051644268
  C 0.13723578023660 1.63375572800403 4.48255075621657
  C 1.67639750328336 -1.16924522942144 4.45640943272136
  H -0.30228399034159 2.46322459910308 3.92195331532791
  H 1.22263665297141 1.67293806765701 4.36923853408526
  H -0.10071414778286 1.78688632071679 5.54284156086219
  H -3.72764104309041 0.80528509265001 3.01251434535545
```

H -2.52225314581327 2.08225469922890 3.26711622762541

H -3.23538843941693 1.24807537213737 4.65342457960248

H -3.74157952348059 -2.30137141458438 3.82857228144826

H -2.97184998955611 -2.91363087022779 2.35943839537314

H -3.82449596741332 -1.35262468415099 2.33790771836816

H -1.01848943159385 -3.92930130792342 2.80135049781732

H -0.51303584834081 -3.87475552884722 4.49892016715058

H 0.67248387214750 -3.60536411100161 3.21051413031034

H 2.13322583758806 -1.98291630592006 3.89017929112380

H 1.67930751782041 -1.44633401551462 5.51841457303979

H 2.29188005382809 -0.27571869654469 4.33468020297523

C -0.28823332286493 0.29143200528593 -1.43820216512589

C -0.75892686842334 -1.13652732367809 -1.08238044649520

N -1.55851272803923 -0.92796568968886 0.16675070307034

C -1.06460150897755 1.20326944320282 -0.46947142128350

C -2.27645108733379 0.34999710120875 -0.13005612634183

N -0.30712519491032 1.36340869029024 0.81200609171128

H -1.31280656959399 2.17919596103484 -0.89702114605978

H -2.84932520800824 0.69627835195048 0.73347065015246

H -2.93636182550927 0.23589612027018 -1.00074333677185

H -2.20180862333947 -1.69935439093764 0.32432929234382

H -0.55461941889051 0.54402938822757 -2.46735503150246

H 0.79241320141908 0.40712937458670 -1.32488042343757

H 0.05681357049673 -1.83474185735619 -0.89886129054420

H -1.42378279176510 -1.53907145849088 -1.85647309306694

H -0.69321133919369 2.14049159308222 1.34433342950412

H 0.66792207758653 1.58803911460188 0.62077506527687

DFT Cartesian coordinates A.71: R_C,S_N,S_{Ir} - $[\eta^5\text{-}C_5Me_5Ir(L2)Cl]^+$

```
Charge: 1

Multiplicity: 1

Number of atoms: 46


  Ir -0.42054624362992 -0.41223684892304 1.95167193453949

  Cl 1.81768431663300 -0.92086763272282 1.07725823614648

  C -1.98071892053547 -1.20687661982658 3.29150070228884

  C -1.75462256261931 0.18262811805668 3.58517552285334

  C -0.36406205374675 0.32809143185585 3.99437777694990

  C -2.77296670287157 1.26752553067667 3.67258392915150

  C 0.23780756442287 -0.97164712042634 3.97056143219761

  C -0.73714650092750 -1.92623090735794 3.48329123109783

  C -0.55007191321742 -3.40249077832664 3.39197595669592

  C -3.29507264984748 -1.84067663604218 3.00026215965286

  C 0.26246699762340 1.59365772890450 4.47012195796178

  C 1.62118118785326 -1.29621113955890 4.40642761015787

  H -0.14333600623817 2.45887637413092 3.93869613104046

  H 1.34597484200134 1.57940300939304 4.33238962579678

  H 0.05709033111214 1.73142666014358 5.53924340774024

  H -3.71863730620700 0.98634475937183 3.20592323982573

  H -2.41746717524208 2.19553270880560 3.21448739904676

  H -2.97202192677774 1.48056698377449 4.73063372571896

  H -3.74992748173550 -2.13361285723238 3.95575576503820

  H -3.18520589163517 -2.74624033242425 2.39954004265810

  H -3.98772654254098 -1.16069559755035 2.49984803878375

  H -1.20192847127844 -3.83782628105756 2.63056285693042
```

```
H -0.78878799288412 -3.87573883983664 4.35305628010211
H 0.48295009731782 -3.65335809293556 3.13948156108573
H 2.02219557446685 -2.15761520208899 3.87030147767943
H 1.59520552707350 -1.53911507173597 5.47677157238483
H 2.29854101472245 -0.45189998569724 4.26518431727193
C -2.32109665136586 1.52442225953033 -0.66586467246957
C -3.11139216193434 0.42576062286038 0.05518648762964
C -2.58638671206832 -0.96928409329110 -0.25808694093186
H -4.16892239966950 0.48020895669499 -0.22550092270976
H -3.05717172865386 0.58885178173940 1.13411225919859
N -1.10751722809711 -1.01157115788049 -0.05763789990387
H -2.79936346933631 -1.23850000446019 -1.30301164680241
H -3.04886461127776 -1.72108020190230 0.38460134992541
C -0.80858025933185 1.30766894856010 -0.60414279934910
H -2.58321333026635 2.50924954604530 -0.26043947523751
H -2.58847807871618 1.53710084158825 -1.72981049787019
C -0.47444610386638 -0.10087509768243 -1.05661679386406
N -0.27321331764362 1.43507600513243 0.79317013761688
H -0.30584864371351 2.04045256779719 -1.24744017368641
H 0.60180373829374 -0.27657663864133 -1.07037995053424
H -0.88495108162792 -0.29222799877644 -2.05644417799317
H -0.77546310002290 -1.95976081309666 -0.22054554552825
H 0.71930789385864 1.66044770297698 0.74497368721014
H -0.72407386585255 2.21181341143585 1.27231368450277
```

DFT Cartesian coordinates A.72: R_C,S_N,R_{Ir} - [η^5-C_5Me_5Ir(L2)Cl]$^+$

```
Charge: 1
Multiplicity: 1
```

```
Number of atoms: 46


  Ir -0.45229646575517 -0.42108429598164 1.98691696192176
  Cl 1.76226241045657 -0.81248553288424 1.04076829103024
  C -1.94918028295551 -1.21219015430693 3.34587727039985
  C -1.72495866671259 0.17376987497770 3.65275035581114
  C -0.32476935740637 0.33090760032589 4.02608725073348
  C -2.75478341991024 1.24700983160057 3.72680005714273
  C 0.28116896243578 -0.97204011971904 3.98924654888045
  C -0.69602176470731 -1.93072599601966 3.53320855393516
  C -0.50534409297366 -3.40549006062845 3.43015929468959
  C -3.25483027233841 -1.82899368880438 2.98179984365214
  C 0.30494764159611 1.59207957983369 4.51038400990305
  C 1.68009370769675 -1.28409161965096 4.38278746905557
  H -0.11979687943234 2.46496476062542 4.00732924986505
  H 1.38387714571186 1.58854368131863 4.34058886928221
  H 0.13014857069442 1.70790713072924 5.58764552923711
  H -3.65962147753220 0.98655081562878 3.17421578805523
  H -2.37684545610108 2.20423644436127 3.35552314946806
  H -3.03473437509479 1.39582865564010 4.77746818081159
  H -3.78417923775214 -2.12084305041119 3.89761890675544
  H -3.11947288088174 -2.73130409497440 2.37982124021271
  H -3.89238335876233 -1.13228540425740 2.43159650225906
  H -1.15277121102223 -3.83713415163112 2.66268147537099
  H -0.75010704455758 -3.88503236707605 4.38650002000600
  H 0.52922515439598 -3.65354458404591 3.18226266082672
  H 2.06738230313341 -2.15074541738559 3.84489413900067
```

```
 H 1.69335759348124 -1.51147525720902 5.45665635961253
 H 2.34674732197600 -0.43821907316974 4.20519720765364
 C -1.11195467831848 0.23275279280622 -1.91977641381202
 C 0.22731563327857 0.82636569829131 -1.47220240117898
 C 0.09704998539721 1.82951135018691 -0.32791723537687
 H 0.70716982612375 1.33709843597593 -2.31424310761737
 H 0.90120460878190 0.02333598229407 -1.16700669527058
 N -0.83583163151744 1.36089971194320 0.74970308592034
 H -0.30031949876010 2.78452131090953 -0.70240299438854
 H 1.07305664663488 2.01459147771821 0.12984773561141
 C -1.97073909409324 -0.16195331614183 -0.72101561895538
 H -0.94284943467481 -0.63166109555678 -2.57277833041299
 H -1.68831428863305 0.96490304161388 -2.49852909157324
 C -2.17085121384510 1.06201116250066 0.15863795955984
 N -1.29027473646465 -1.21474912637544 0.12484486907394
 H -2.93921476607844 -0.54780256620684 -1.05732930373355
 H -2.88125395030222 0.87038009662009 0.96656554810324
 H -2.53362852521125 1.90772081794737 -0.44230310064578
 H -0.93452260762824 2.13007837286453 1.40818087399689
 H -1.95614981521819 -1.94667475948176 0.35508582194382
 H -0.54838702715346 -1.66559289479481 -0.40932678681652
```

DFT Cartesian coordinates A.73: R_C,S_N,S_{Ir} - [η^5-C_5Me_5Ir(L3)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 49

 Ir -0.58091995675554 -0.68026450061606 1.81641148449770
```

```
Cl 0.97641574280587 -2.29843829657528 0.79822929719210
C -2.00440560001121 -1.43319623092498 3.31784830629094
C -2.02567091890830 0.02293484892706 3.32332465465258
C -0.69550909412563 0.47197957323054 3.65705784889354
C -3.25656745243128 0.86177778106535 3.28120753121261
C 0.14661673590138 -0.68437331448970 3.85961097270558
C -0.68627068757267 -1.85889800986775 3.66872841699970
C -0.25058103703774 -3.26784833887819 3.85975725625727
C -3.18835940004584 -2.32310286080873 3.14896798230375
C -0.27370763545470 1.89018152771597 3.82386806332517
C 1.56568440043425 -0.68505343842643 4.31461348703048
H -0.84596021420521 2.56129550597568 3.17810574417265
H 0.79029419059379 2.01946426964049 3.60935727458717
H -0.44324324616027 2.19770373097588 4.86330905656744
H -3.95208275117716 0.55007580760689 2.49776214722693
H -3.02846659899197 1.91994679292253 3.14182899387062
H -3.77940503163508 0.75643791366501 4.24086376143134
H -3.59125907476726 -2.57868961609676 4.13739762689619
H -2.92352975268565 -3.25499131586889 2.64368916576883
H -3.98765732558706 -1.83640768339789 2.58631987874966
H -0.81805128134677 -3.95364730757646 3.22706666795664
H -0.42260497032842 -3.54769626825046 4.90725682151528
H 0.81141067821152 -3.39320531589120 3.64244642151669
H 2.10784970685830 -1.54427811453257 3.91259359870391
H 1.60942129240410 -0.73843083487486 5.40975059425076
H 2.08501723540837 0.22344740236191 4.00028208904991
H -3.53344140988148 -1.07536811427067 -0.96449262984460
```

```
 H -3.49196949961942 -0.69563879158421 0.75690592425321
 C -3.04096986735015 -0.45100489427388 -0.20651527610640
 H -4.31127981201991 1.23389236420113 -0.24676166660686
 C -3.28119549684954 1.01844471807489 -0.55473354756273
 H -1.58997765720733 -1.87651805551357 -0.24984331779667
 N -1.60430279308535 -0.86615042511291 -0.12168104296425
 H -3.26174942537525 1.14834126363966 -1.64425929964781
 C -2.33170483169742 2.04519371344855 0.07302717793830
 H -2.11497242721303 1.78425534831665 1.11293463467426
 C -0.74799372459081 -0.29310883936404 -1.20573656093131
 H -1.33381474726588 -0.13168615036722 -2.11819012053534
 H -2.83658333430474 3.01798342761910 0.09372048077572
 H 0.03051954884895 -1.02798330713711 -1.42501930597855
 C -1.02841924416422 2.21491814776265 -0.70854856985104
 C -0.09997514734654 1.00544379144166 -0.74427681944095
 H -1.26975901776011 2.46356770265045 -1.75024115203730
 N 0.50122152464689 0.74373294525269 0.60818772811452
 H 0.63618306304441 1.62670862669824 1.09635365740424
 H -0.46428766373460 3.06966096897661 -0.31096179220417
 H 0.71830190217443 1.23394976368909 -1.44054216640775
 H 1.42805210736144 0.33757208884113 0.48490852112979
```

DFT Cartesian coordinates A.74: R_C,S_N,R_{Ir} - $[\eta^5\text{-}C_5Me_5Ir(L3)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 49

 Ir -0.30651317280291 -0.35467981921570 2.04160754021388
```

```
Cl 2.03068761823598 -0.16955679070348 1.34615720577288
C -1.95040516364357 -1.07492642802085 3.25467093497326
C -1.63279279809871 0.27789567985092 3.64283054486460
C -0.26452316344204 0.31971448361328 4.11007025241533
C -2.57248236020622 1.43211912937689 3.60626137823362
C 0.24689849535987 -1.03949458853193 4.05673178762897
C -0.77041706609589 -1.89136232365694 3.52095077491109
C -0.69148694106019 -3.36987323487532 3.35556552273473
C -3.27838793903325 -1.59193921766753 2.81940127871326
C 0.44233505946491 1.49453137553662 4.69494509810327
C 1.59044773703713 -1.47093918657348 4.52664982115924
H 0.06669937662089 2.43273947076190 4.27973717363996
H 1.51637963243631 1.44325502782308 4.50052917783858
H 0.29605821040457 1.52153299913047 5.78225787792641
H -3.30270811769982 1.33746209029628 2.79727530816223
H -2.04278769457815 2.38277644030513 3.50095848021094
H -3.12971230211824 1.46904998236912 4.55052456323561
H -3.80879733876554 -2.01919971350015 3.67992068301353
H -3.17306005438796 -2.38049082384207 2.06881890235051
H -3.90127682467186 -0.79815010866841 2.40107510775336
H -1.31602688809648 -3.71496028186296 2.52742923895862
H -1.05421900000613 -3.85849610757150 4.26880359094731
H 0.33434826585584 -3.70049384800384 3.17915052883952
H 1.93822798744876 -2.35889146710568 3.99498503879039
H 1.52865591114024 -1.71331518978629 5.59538357260968
H 2.33099547024609 -0.67945233776711 4.39920714407314
H -0.36047755604890 3.16063441538735 0.07767340629983
```

```
H 0.96600903589795 2.04925989307456 0.46072509809108
C 0.01053084867246 2.13759293448522 -0.06077882313842
H 1.01485619491489 2.59418467969289 -1.83883254746157
C 0.21650388355105 1.89804681107740 -1.55265836401221
H -1.48910206793654 1.81853709287539 1.26822211506374
N -0.96048959042055 1.21520462632332 0.64521084023436
H -0.66888375541010 2.21109840457561 -2.12135003640357
C 0.61898868415735 0.47932219413774 -1.96875137172800
H 1.35776460334740 0.08379246288423 -1.26136121349018
C -1.96944729437802 0.54558765326057 -0.22619369381321
H -2.34851894983232 1.22488030277346 -0.99934301345993
H 1.12107083050620 0.52955410866656 -2.94214181126063
H -2.80834389368608 0.27838432567310 0.42474591853527
C -0.56683131836179 -0.47568958300395 -2.11749211284124
C -1.39370202459698 -0.71967882274075 -0.85762697970445
H -1.25242157709313 -0.07590633987513 -2.87643804297200
N -0.59530118471145 -1.45435817623471 0.19368552258258
H 0.32789325736813 -1.68373122254792 -0.17318434830985
H -0.21841070153562 -1.44649857574244 -2.49438734781246
H -2.24181384236303 -1.35788799810037 -1.13400138869665
H -1.04477052158445 -2.34174439835260 0.40093966622344
```

A.6.7 Cartesian coordinates for the diastereomers for the Rh complexes

DFT Cartesian coordinates A.75: S_C,R_N,R_{Rh} - [η^5-C_5Me_5Rh(L1)Cl]$^+$

```
Charge: 1
```

```
Multiplicity: 1

Number of atoms: 43


  Rh -0.56424508347230 -0.62541150110204 1.90149846830991

  Cl 1.21211479694881 -1.92155479251254 0.82345986858357

  C -1.92607245476419 -1.48037894251841 3.36718454878647

  C -1.91688901534859 -0.03463099158465 3.50226060499753

  C -0.57280389338603 0.35154635302769 3.86529544588140

  C -3.12734794923934 0.83340953008206 3.49996802536904

  C 0.24292514518328 -0.82216259739886 3.90676935642114

  C -0.60976410663124 -1.96688444551862 3.61781691309709

  C -0.18603449968719 -3.39083410388003 3.66232281697767

  C -3.12514635000610 -2.31048584772475 3.07247555951229

  C -0.10016912069093 1.72415517956838 4.19720565852898

  C 1.67555694324797 -0.88500828066684 4.30206637798461

  H -0.83811689953711 2.48781958553953 3.94738439260807

  H 0.84074246083818 1.95942944660629 3.69096575404026

  H 0.08605169901930 1.78158444644131 5.27701675082835

  H -3.88042883533020 0.46975279373014 2.79680432877726

  H -2.89444108679735 1.87117608321309 3.25216743852574

  H -3.57885648929095 0.82735098025477 4.50081941344865

  H -3.61943383216913 -2.57740818657813 4.01553416568388

  H -2.85633068133381 -3.23763082791236 2.56108513903106

  H -3.85290250141038 -1.76895785146187 2.46286061601664

  H -0.79973302039470 -4.01496341114311 3.00883282543905

  H -0.29470743833761 -3.76489427735952 4.68886433397893

  H 0.85893448052820 -3.50277200802922 3.36739476943505
```

```
 H 2.19959167057062 -1.67643989425365 3.76127356474043
 H 1.75158357537321 -1.09957315205526 5.37609731748801
 H 2.18341797113743 0.06318264541689 4.11038001663408
 C -2.25804853333729 1.48629717461414 -0.06281067855028
 C -1.08896764377849 2.11590184637102 0.72986600096325
 N -0.02454753837782 1.07084256694800 0.64673413583583
 C -1.62705942153127 0.26625634040024 -0.76239234629995
 C -0.14854351210197 0.61927704662110 -0.76877431432357
 N -1.75643386953645 -0.93257880193953 0.11558217029497
 H -2.04032837468899 0.07338924376572 -1.75773975307984
 H 0.51626363926688 -0.21879430915927 -0.97991198515843
 H 0.05370416417194 1.44977807696782 -1.45888802288740
 H 0.89880161811124 1.43980449230583 0.86097156305929
 H -2.73567131396255 -1.11576411535346 0.32198125158946
 H -1.38682983533881 -1.75565783559349 -0.35872731354690
 H -2.64544495627057 2.18742639672527 -0.80564569770460
 H -3.08871962776416 1.18964860610455 0.58401447243711
 H -1.32626382421708 2.34620172870203 1.76727392342742
 H -0.73382645566432 3.03242561033980 0.24049212281803
```

DFT Cartesian coordinates A.76: S_C,R_N,S_{Rh} - [η^5-C_5Me_5Rh(L1)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 43

 Rh -0.42332948610642 -0.47244286156733 1.99442560039292
 Cl 1.74523269488202 -1.09587693594065 1.06290551529457
 C -1.91917637404489 -1.30801262801887 3.32841276533351
```

C -1.77286750040071 0.09942165675820 3.58756912425197

C -0.40275510903115 0.32396497244259 4.02231242175530

C -2.85118044659214 1.12638473302522 3.58800196694927

C 0.27258936678132 -0.93186931382820 4.02537755989275

C -0.65039952404560 -1.95014585240280 3.55677684588880

C -0.36204689222526 -3.40925813941246 3.47843443782271

C -3.17412419702309 -1.98701217511597 2.90914258905427

C 0.15314694128702 1.63161085437551 4.46462597961441

C 1.66473207049202 -1.17886081103510 4.47962276717825

H -0.28510122748139 2.46298231339288 3.90590177119275

H 1.23872004412849 1.66566464782674 4.35060409231245

H -0.08142627723039 1.78763362069610 5.52562206955047

H -3.71352666619162 0.81264955039430 2.99590479358600

H -2.49402887020746 2.08717100766308 3.20580324020076

H -3.19435202351934 1.29091166563209 4.61763869644471

H -3.74470689854913 -2.26911630625746 3.80312987552171

H -2.96931310548971 -2.90150705527925 2.34683992660541

H -3.80940081819786 -1.33224576225790 2.30618533260178

H -1.01847533409989 -3.90977333134149 2.76285253396805

H -0.51436663578790 -3.87500500252787 4.46071403878007

H 0.67324721672182 -3.58886782101154 3.17861317606697

H 2.12374366401771 -2.00397927722799 3.93252766576784

H 1.64352078517725 -1.44375279071646 5.54513666756425

H 2.29120688873598 -0.29242539200268 4.36254178997359

C -0.24639584643175 0.27490002745157 -1.40473823952466

C -0.72871320644476 -1.15081872823516 -1.05606051621196

N -1.54073422027992 -0.94151822914943 0.18092355709227

```
 C -1.03112909804070 1.19230112824665 -0.44720100944782
 C -2.24578832891935 0.34074313228915 -0.10955972973882
 N -0.28247863382585 1.36621618259755 0.83320279546754
 H -1.28165585778562 2.16205314649221 -0.88903349111445
 H -2.81605114063645 0.69053160617461 0.75468251614717
 H -2.91103696088956 0.23794149613875 -0.97851237877012
 H -2.18650166453252 -1.71158098012596 0.33591724958800
 H 0.69255526887483 1.59580987915763 0.65069973104294
 H -0.67913282986236 2.13938885231059 1.36330324607579
 H -0.49387647215624 0.52786122112342 -2.43848926302856
 H 0.83291207603029 0.38461069312802 -1.27312158589352
 H 0.08238558267185 -1.85277312155740 -0.86372102107095
 H -1.38300095377146 -1.54904987230483 -1.84229510417857
```

DFT Cartesian coordinates A.77: R_C,S_N,S_{Rh} - $[\eta^5\text{-}C_5Me_5Rh(L2)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 46

 Rh -0.40397078689019 -0.39976460333590 1.94677148257804
 Cl 1.85200133024487 -0.91171190620248 1.15361787408772
 C -1.97963582839760 -1.18969314112866 3.28626816624362
 C -1.74299470764005 0.19216593476271 3.58095827485366
 C -0.35408762891420 0.32961559814967 3.98274627970381
 C -2.75159420816027 1.28493921699221 3.66132790898268
 C 0.23665761459027 -0.97205151289826 3.96531476183739
 C -0.74158488315050 -1.91186787556021 3.46667342160514
 C -0.55733256437138 -3.38528419770582 3.34470162049779
```

```
C -3.29629013480748 -1.81417948143924 2.99214259587966
C 0.28420379249799 1.59181606368403 4.44878641632394
C 1.60562315353125 -1.31066219547641 4.42713942581338
H -0.12302396819733 2.45872870306207 3.92119307918560
H 1.36634762872520 1.57035343329234 4.30087417373246
H 0.09141930603824 1.73306461220602 5.52015062084978
H -3.70539934267012 1.00362112898891 3.21189161749772
H -2.39497255419182 2.20485438944548 3.18775770826100
H -2.93437902155214 1.51649982018124 4.71868779280114
H -3.75702956024664 -2.09934793101822 3.94762169791575
H -3.19161150037359 -2.72444345976512 2.39788043406992
H -3.98358237413242 -1.13180683100236 2.48765898535041
H -1.20811332151081 -3.80398457078157 2.57305461483287
H -0.80141222108052 -3.87750281895304 4.29514466329446
H 0.47656691224027 -3.63330136765091 3.09323660566758
H 2.00912790193667 -2.17788275034735 3.90276738232725
H 1.55177939714243 -1.55144036595733 5.49765446699672
H 2.29484560949868 -0.47350851510815 4.30278425005552
C -2.29673382921165 1.51334546905330 -0.66354348468810
C -3.08232685703865 0.41325406556600 0.05882103856653
C -2.55242249309499 -0.97847316312696 -0.26131354649286
H -4.14140750541653 0.46604268844190 -0.21633052950161
H -3.02412462131668 0.57479816832973 1.13824897052346
N -1.07907195748387 -1.01845696784512 -0.04844171009520
H -2.76051674090389 -1.23723089676290 -1.31074416468133
H -3.02076664770310 -1.73720183322529 0.36945925813868
C -0.78315523780188 1.30939216548011 -0.58328578107664
```

```
  H -2.57049131810617 2.49901200332563 -0.26768606214709
  H -2.55593806495238 1.51496360617091 -1.72961203362638
  C -0.43143869214466 -0.09920494968897 -1.02659985589152
  N -0.27183324186770 1.45275024003946 0.81755456964145
  H -0.28147920413963 2.04139754649422 -1.22963630420079
  H 0.64650749653099 -0.26640058109558 -1.01397947422523
  H -0.81409329480212 -0.28878374820168 -2.03886690265106
  H -0.73923146158357 -1.96490531317603 -0.20496009322754
  H 0.72205498243610 1.67352599847644 0.79010021208924
  H -0.73243935155833 2.23108012531120 1.28472957230079
```

DFT Cartesian coordinates A.78: R_C,S_N,R_{Rh} - $[\eta^5\text{-}C_5Me_5Rh(L2)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 46

  Rh -0.42269434051569 -0.41214541631542 1.97907308642595
  Cl 1.82249266878521 -0.78966766288182 1.12844604252874
  C -1.94361021937328 -1.18438879797465 3.32789854783582
  C -1.70262395304797 0.19194452300682 3.63988530814224
  C -0.30654327650930 0.33096458077750 4.01353437908059
  C -2.71624856823223 1.27920721726615 3.70478912448450
  C 0.28091855528536 -0.97818804085282 3.98689555027361
  C -0.70252387625221 -1.91512947687344 3.51394880735104
  C -0.52558232025338 -3.38815946226017 3.38093881431305
  C -3.25386163983418 -1.78557621778428 2.95961497873340
  C 0.34276335896332 1.58548839373178 4.48637639524195
  C 1.66300745213616 -1.31229373873027 4.41158254615624
```

H -0.07834495567013 2.46215502024245 3.98682830657438

H 1.41986113244966 1.56807204086331 4.30540366013748

H 0.18230325456472 1.70658131136091 5.56558297567760

H -3.63293779667807 1.02109675608379 3.17134635297030

H -2.33227830804467 2.22723116489207 3.31629811810705

H -2.97846944268645 1.44978672699604 4.75705007402705

H -3.78838028631121 -2.06831213151929 3.87572774105668

H -3.12910533532689 -2.69269076412753 2.36284613871063

H -3.88493044974997 -1.08378695298478 2.40852472978389

H -1.16377400355186 -3.79629463840805 2.59298461074883

H -0.79455205241142 -3.88604132822155 4.32157681677676

H 0.51118843500446 -3.64229728219405 3.14917060377272

H 2.05137700865423 -2.18341867569717 3.88202627643077

H 1.64306222178751 -1.54399839598833 5.48513354651400

H 2.34668166295392 -0.47562285890242 4.25792927003630

C -1.05305337643194 0.20523141495118 -1.89670256540122

C 0.27551947547819 0.80872062637988 -1.43246466180630

C 0.11310088332246 1.83087947456925 -0.31006651728109

H 0.77317969826205 1.30460826331916 -2.27311351611999

H 0.94382362099233 0.01369454046476 -1.09448522260275

N -0.82193272888914 1.36199771883443 0.76014260356229

H -0.29432557586589 2.77212825253363 -0.71029402892815

H 1.08001638452745 2.04234459696766 0.15618146976193

C -1.92567112810911 -0.19276691491799 -0.70843719498750

H -0.87023138474200 -0.66037171988655 -2.54457757731418

H -1.62490557896907 0.93282332946693 -2.48585844089439

C -2.14574277741854 1.03179975649452 0.16738677727468

```
 N -1.25419372328542 -1.24023589531599 0.14240998812763
 H -2.88939580364890 -0.57848953593622 -1.06022038843529
 H -2.85658168749244 0.82881633119250 0.97242977643536
 H -2.52875010861416 1.86714719198652 -0.43690985538733
 H -0.93396783209898 2.13034952045932 1.41753565263199
 H -1.92171718372816 -1.96736341746531 0.38289848145090
 H -0.50942609942431 -1.69808942760245 -0.38026758197828
```

DFT Cartesian coordinates A.79: R_C,S_N,S_{Rh} - $[\eta^5\text{-}C_5Me_5Rh(L3)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 49

 Rh -0.57389664759024 -0.70087054100672 1.80443764428787
 Cl 0.95602991735716 -2.37395058742299 0.86156442345114
 C -1.99386842895309 -1.43617886532996 3.31271789817517
 C -2.02477512881993 0.01448990952469 3.30941251040208
 C -0.70312883397679 0.47756397768016 3.63218489067911
 C -3.26067706596714 0.84262908112395 3.24509280704528
 C 0.14667003342173 -0.66809480499020 3.83647840102996
 C -0.67695866138827 -1.84891519255554 3.67227223099580
 C -0.24155992841559 -3.25002361362896 3.89969994470511
 C -3.16854357011379 -2.33563251362472 3.13851720285598
 C -0.29094575689277 1.89877655792129 3.78589913846276
 C 1.57174905296616 -0.65223359704472 4.26890487037898
 H -0.86778353812991 2.56368314321129 3.13798569385703
 H 0.77266739783682 2.03409062459650 3.57376840648052
 H -0.46278912237057 2.21191362323300 4.82374345235462
```

H -3.93310279780487 0.53660410646248 2.43933667853115

H -3.03970247506020 1.90516151800995 3.13103786090916

H -3.80934349837144 0.71421879022760 4.18760708735805

H -3.56802069835891 -2.60554666859313 4.12485935552723

H -2.89385369301745 -3.26125618594640 2.62642956489642

H -3.97333555798898 -1.85216650809861 2.58099072471711

H -0.78330564750661 -3.94977886973363 3.25969886742146

H -0.45454546473879 -3.51218210411993 4.94490750347040

H 0.82837245507686 -3.37451009521903 3.72752178667173

H 2.11272026664185 -1.51502899318972 3.87306607631937

H 1.63227255527892 -0.68802810696432 5.36426862196166

H 2.08037682906778 0.25501628716723 3.93404255144678

H -3.51286182205532 -1.06860416190338 -1.00570864735898

H -3.50321896423694 -0.70965789759471 0.71902091728186

C -3.02706072470618 -0.45781976326617 -0.23154696438955

H -4.27320043161625 1.24907282568012 -0.26702083195441

C -3.24434313024890 1.01821270598660 -0.56768519729936

H -1.58822045234406 -1.89610538710891 -0.22729564370560

N -1.59988924034546 -0.88324892858591 -0.12092129538342

H -3.21204983146707 1.15744645405723 -1.65571531465717

C -2.28140346391762 2.02182807642810 0.07683265195352

H -2.07231391576221 1.74418423606693 1.11410766996353

C -0.71515860675377 -0.32958041581993 -1.18917229255220

H -1.27782078812316 -0.16573078534493 -2.11672338025296

H -2.77141902544168 3.00181934640783 0.11081780602791

H 0.05787421935800 -1.07653244685150 -1.38730416799444

C -0.97261969795199 2.18170517894682 -0.69770445790412

```
 C -0.05442230650147 0.96389493063838 -0.72769254156113
 H -1.20694762175160 2.43467525051933 -1.73991804584791
 N 0.53830868596745 0.70492829937841 0.62472219839777
 H 1.45163688497175 0.26681217706394 0.51505217437065
 H -0.40341943855564 3.03085196245975 -0.29520324137764
 H 0.76509050894537 1.18372293600714 -1.42671651283702
 H 0.69278717035508 1.58723503514531 1.10828892268841
```

DFT Cartesian coordinates A.80: R_C,S_N,R_{Rh} - $[\eta^5\text{-}C_5Me_5Rh(L3)Cl]^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 49

 Rh -0.27770001867768 -0.34220499556430 2.03871278610314
 Cl 2.07483549115067 -0.16034074168919 1.42877370979340
 C -1.94002836936875 -1.03988271643654 3.23276974790735
 C -1.61179347616977 0.30069347933154 3.63720630732662
 C -0.25013438299611 0.31982705780908 4.10515075194665
 C -2.53487027846469 1.46631125512529 3.60179448538588
 C 0.24279490563959 -1.04363204679405 4.05414129860423
 C -0.77879663725128 -1.87322206415152 3.50319237586506
 C -0.71620777346863 -3.34909175005147 3.31953564912602
 C -3.26706943922921 -1.53605702157145 2.77335695897674
 C 0.47721776404586 1.48541823548538 4.68061874545735
 C 1.56801356368383 -1.49928337499479 4.54662748431035
 H 0.11087098382190 2.42857434499446 4.26845162100723
 H 1.54914596377377 1.41765329802163 4.47996327281663
 H 0.33934633377630 1.51555465169894 5.76920736839589
```

H -3.26425312203169 1.38662324744747 2.79040255615876

H -1.99398479867704 2.41186561353946 3.50932230049915

H -3.09744873681728 1.50199375666163 4.54342862297944

H -3.79467421335038 -2.00412952168144 3.61441365728927

H -3.16315760294602 -2.29163279957087 1.98902362156715

H -3.89339294672148 -0.72546181047238 2.39497468342966

H -1.35683688073311 -3.68034366259493 2.49797912003958

H -1.07086513977918 -3.84460993720214 4.23261195202129

H 0.30434291697512 -3.68799428362128 3.12781566952639

H 1.91324932265546 -2.38838147085500 4.01515757385405

H 1.47750560251762 -1.75233934845991 5.61140323515204

H 2.32341706148588 -0.71836257086144 4.44577429026199

H -0.32869151884068 3.16877375178797 0.09656661164571

H 0.99183988450361 2.05589325686746 0.49590138051709

C 0.03980882619617 2.14322014932349 -0.03378189440215

H 1.05860944199390 2.59314364681640 -1.80668050509342

C 0.26029083205813 1.89641246023052 -1.52211607474513

H -1.46440991574020 1.82350006668152 1.29005343387310

N -0.93457971737894 1.22501684060857 0.66342603415216

H -0.62193613237766 2.20177694571303 -2.10007233018726

C 0.66966014443469 0.47520019191918 -1.92294116320851

H 1.39565932808758 0.08365002953934 -1.19974724927269

C -1.93443574882708 0.54232844457004 -0.20360387446235

H -2.32389595101542 1.21329122030183 -0.98005184627642

H 1.18830069446153 0.51852646611001 -2.88797898236034

H -2.77166391626406 0.26994468557924 0.44779757291961

C -0.51576352951217 -0.47806707739520 -2.08472118886257

```
  C -1.35352610092442 -0.72351417765012 -0.83195048863031
  H -1.19288122706099 -0.07571114447083 -2.84995731321933
  N -0.56728721217761 -1.46089295441409 0.22054293078040
  H -1.02002640854016 -2.34590770010869 0.43105720783500
  H -0.16530045785017 -1.44907489019418 -2.45921977732232
  H -2.20217973721383 -1.35672811872688 -1.11983643046373
  H 0.36025232914417 -1.69112691663076 -0.13260589901799
```

A.6.8 Cartesian coordinates for the diastereomers for the Ru complexes

DFT Cartesian coordinates A.81: S_C,R_N,R_{Ru} - [η^6-(*p*-cymene)Ru(L1)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 42


  Ru 6.69087280044121 4.82991553704497 11.36596309919183
  Cl 6.68510618941340 6.88928118477191 12.67174167683419
  C 7.40476554653503 3.42552280371435 12.92700708041695
  H 8.18815647607731 3.61202351188000 13.65123272322167
  C 7.71410852914436 2.88856567544083 11.64801400890688
  C 6.07922800707887 3.83728326296529 13.22118411740174
  H 5.89340697683486 4.36114472928376 14.15409753539332
  C 5.34486841801587 3.15813979550720 11.01798130461982
  H 4.57175753191390 3.12069482817837 10.25492407074523
  C 9.10985406347846 2.45166152450429 11.27062810224142
  H 9.25395367507794 2.70889251835683 10.21091063090636
```

C 6.66030070653839 2.73699448046880 10.69568078728069

H 6.88309121962627 2.36062686965724 9.70162034729632

C 5.01475065095762 3.70066832894446 12.29382350838596

C 9.17476192601610 0.91755094320564 11.38506305991463

H 8.99844836296350 0.60693650973691 12.42093336264448

H 10.16715577228448 0.56703692645519 11.08475862840788

H 8.42894439641930 0.43429961476416 10.74651072838081

C 3.62519551927704 4.15382144918268 12.61926450260972

H 3.64342295444244 4.98175090367219 13.33277561049437

H 3.05947362771243 3.32966586097841 13.07012490830858

H 3.09567428571452 4.47217281758355 11.71709761932303

C 10.21987361620568 3.09761318114776 12.10019718157231

H 10.13954769680046 4.18945598592883 12.13400225959426

H 11.19162353513880 2.84074530948351 11.66865332306094

H 10.20847333660945 2.72648149194325 13.13055562515402

C 7.40976691558768 5.26286958903369 8.10617475183545

C 5.90414949051800 5.18221475030649 8.44669213880073

N 5.80887159184953 5.95672036152873 9.72762024351792

C 7.95165281128795 6.33542835547245 9.07021328706704

C 6.70134360315460 7.11683437870098 9.43143830204760

N 8.39538048605033 5.68242998474849 10.33967430803690

H 8.75446864582895 6.94413633645404 8.64331734622289

H 6.80735147119486 7.77319389604728 10.29461918731953

H 6.32430109311820 7.68032541457515 8.56778572931843

H 4.85401574555209 6.24546450206731 9.92856533377655

H 9.12476179184888 5.00315786743971 10.13554113224314

H 8.80390294164863 6.38165956871037 10.96010228769957

```
  H 7.55908112420611 5.57708097386787 7.07063279563985
  H 7.92008183346449 4.30482611166336 8.24550901948408
  H 5.52889931047213 4.16733695463344 8.56648159945542
  H 5.30242532349920 5.69052490994986 7.68259673522646
```

DFT Cartesian coordinates A.82: S_C,R_N,S_{Ru} - [η^6-(*p*-cymene)Ru(L1)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 42

  Ru 6.73348843843182 4.72152462979752 11.33410989512358
  Cl 7.50091176890554 6.61504844456464 12.66215509269052
  C 7.31980931950434 3.34248547768857 12.94161272037053
  H 8.05731111130109 3.56154306105082 13.70548343263377
  C 7.72405786921682 2.77823047665793 11.71530338897752
  C 5.96659372960428 3.75279532567391 13.16214341020120
  H 5.71377862069864 4.26556462074243 14.08452659254852
  C 5.39558491985095 3.05944584313729 10.89618774364570
  H 4.68519611258731 3.01520682130119 10.07492113150912
  C 9.14519447889421 2.34372391492032 11.44428860769132
  H 9.28768547244354 2.37839278550498 10.35473550256979
  C 6.72770950255793 2.64254908730753 10.68799959065002
  H 7.02641990470983 2.28712302859692 9.70463358816476
  C 4.98950278724822 3.62162539620474 12.15549866408456
  C 9.30442982221088 0.88091431985780 11.88956707388086
  H 9.16941550097277 0.79791274410886 12.97399576699500
  H 10.30682437808658 0.52002511642927 11.63821825980187
  H 8.57061540797699 0.23207617237906 11.40021546742694
```

```
C 3.58323741590874 4.08634589455443 12.36976514810664
H 3.53819859158370 4.86956601315924 13.13018604686019
H 2.97522630919417 3.24034845057627 12.71284571618736
H 3.13688357191550 4.45512730983646 11.44188497064454
C 10.19757919212435 3.24144736296466 12.09571566705852
H 10.04339203055974 4.29347297713480 11.83088583288833
H 11.19395199044598 2.94106270227001 11.75759909773893
H 10.18146808252587 3.15493174894644 13.18726302160422
C 7.44548634621923 7.55403588649219 9.38624902484675
C 8.62692279213410 6.59354227186972 9.64566561416074
N 7.97843403429836 5.24438849258554 9.62372067838469
C 6.27187322747765 6.62518187028285 9.02593944151533
C 6.98861936998785 5.38801285743097 8.51213051717954
N 5.55300749035152 6.18588918920011 10.26365959790246
H 5.57283477746674 7.06798648246946 8.31003814728233
H 6.35574958495600 4.50195484736307 8.42007437198981
H 7.49544342206105 5.58867257989291 7.55828083217528
H 8.66130299422057 4.51651008604397 9.42732903590742
H 5.36673286806041 6.98656451108495 10.86596100597711
H 4.65132914407362 5.79126935002256 10.00453794538513
H 7.65815160672053 8.21315818843151 8.54104067415803
H 7.22032465692697 8.17428631476920 10.25691888492248
H 9.12787182754856 6.75898824061970 10.59887344292253
H 9.36060952803665 6.63968910607491 8.83115935523545
```

DFT Cartesian coordinates A.83: R_C,S_N,S_{Ru} - [η^6-(*p*-cymene)Ru(L2)Cl]$^+$

```
Charge: 1
Multiplicity: 1
```

```
Number of atoms: 45

 Ru 6.75453418937274 4.75974262758555 11.31152511543602
 Cl 7.59970103881249 6.62294613598264 12.64760650194960
 C 7.34279590413674 3.40708928790998 12.94582467024201
 H 8.07234545870776 3.64908278845537 13.71017253292016
 C 7.76025468971427 2.81746357905851 11.73724785738619
 C 5.98666710397707 3.81577266718152 13.14658663808929
 H 5.72544335556250 4.35189308351458 14.05322352607527
 C 5.43357496774898 3.05660808324546 10.89981865635773
 H 4.72109172958593 2.97067609034796 10.08433113670139
 C 9.17940899042461 2.36462078714487 11.49033132275424
 H 9.37136501761988 2.48581526028953 10.41517696085405
 C 6.77088201609833 2.65155568578884 10.70917565768590
 H 7.07128169827209 2.24667638518587 9.74702964515339
 C 5.01761841624648 3.65160045413908 12.13764042637702
 C 9.27766421889093 0.86551413599509 11.81851484686509
 H 9.08339833910703 0.69700908210915 12.88387521443405
 H 10.28267543067072 0.49739178125522 11.58895318527859
 H 8.55536192343628 0.28048795387611 11.23977841140297
 C 3.60768924380167 4.11486903992086 12.32970261834949
 H 3.55721607935970 4.93921110424540 13.04532942265440
 H 3.00772025139512 3.28491427864168 12.72230621734749
 H 3.15689704753653 4.42666790234892 11.38331937923200
 C 10.22648092933166 3.16833241163327 12.26012610304537
 H 10.10708313969877 4.24505697604621 12.09683125921054
 H 11.22738069579431 2.87758382995977 11.92742917716238
```

```
  H 10.16922817990852 2.97494970385048 13.33672653120155
  C 5.97592285121809 6.05096547111200 7.84531413221654
  C 6.63887062801249 4.66828409232238 7.88282552118920
  C 8.05171150801037 4.71099892298121 8.45492514850286
  H 6.68616555295234 4.25321884601939 6.87019711502310
  H 6.02565416463020 3.98347938979339 8.47368021278704
  N 8.07767537389572 5.48574851431398 9.73403583742822
  H 8.73663608104156 5.20089715968161 7.74713836904009
  H 8.43277278349375 3.70421069487227 8.64359952293314
  C 6.21544085653977 6.86245762801978 9.11816028826438
  H 4.90101656952681 5.95093867462324 7.65194788292381
  H 6.39333583084615 6.64119839879349 7.02026372459691
  C 7.69766382858659 6.89687087007189 9.43181955594991
  N 5.54727601023100 6.24503318367528 10.31468672385744
  H 5.83135216332853 7.88105296900478 8.98106325073897
  H 7.91441465101295 7.51988110314224 10.29980694171206
  H 8.26699831393646 7.26888165885372 8.56973500761531
  H 9.02615307209809 5.47562531284962 10.10486566356506
  H 4.62858940030571 5.89696698237420 10.04874855326074
  H 5.39237030512188 6.97027901178337 11.01425353422844
```

DFT Cartesian coordinates A.84: R_C,S_N,R_{Ru} – [η^6-(*p*-cymene)Ru(L2)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 45

  Ru 6.73337439122670 4.71519710598904 11.31630504846678
  Cl 7.45539033524879 6.62105114223988 12.64512390848195
```

C 7.34679768623978 3.36055370518506 12.95001399004710

H 8.08693273161593 3.59214811641552 13.70689307805819

C 7.74416034537319 2.78604807758049 11.72626772385556

C 5.99425719625890 3.77149503689871 13.16535077573308

H 5.74612967282404 4.30521767569767 14.07735084567092

C 5.41111150267965 3.02725126358816 10.92624628013893

H 4.69097392612157 2.96076823348776 10.11410660166706

C 9.16316915429579 2.34839007110360 11.45403206910421

H 9.32529523040803 2.43457183964691 10.37003037188791

C 6.74485088441914 2.62240058905767 10.70534623839568

H 7.03638927556828 2.24438496820648 9.72866235963799

C 5.00496181371662 3.60417899779571 12.17763924966179

C 9.28681363746973 0.85945073645722 11.82061694071569

H 9.12399774051171 0.71878851134697 12.89506329712325

H 10.28965550064850 0.49752018463704 11.57288127041754

H 8.55589079936325 0.25130878669865 11.27783182458626

C 3.59120807614706 4.04133487577541 12.40426284017429

H 3.54173648546063 4.84569768675535 13.14204478281527

H 3.00863846603245 3.19287715908284 12.78344400965518

H 3.11726515287890 4.37293654031341 11.47591339252905

C 10.21982101202570 3.18537184478332 12.17441972708061

H 10.08317022697799 4.25621637835115 11.98713687686000

H 11.21514561855539 2.89744008094012 11.82318842135694

H 10.19247696588916 3.01970707156360 13.25654879758481

C 7.62210323283591 7.38165791812691 8.47303575095196

C 6.90822786403280 8.04568506979312 9.65416018574348

C 5.54850844801087 7.42738009710305 9.97089269123298

```
  H 6.75250236410780 9.10949432574422 9.44383614948052
  H 7.54048749732159 7.99105617339135 10.54233406195052
  N 5.56521252235501 5.92693338352704 9.93359319640340
  H 4.80097665889638 7.75443602857112 9.23285967433003
  H 5.21137747186391 7.73463301654546 10.96498831820819
  C 7.52189059281427 5.86064658845632 8.54946690080327
  H 8.67210395214853 7.69591407931751 8.44122668834886
  H 7.16721296725699 7.68396216794335 7.52188309638574
  C 6.05564637862969 5.46893722338555 8.60202985808516
  N 8.16593824405671 5.32273810403502 9.80785812623898
  H 8.00655643042396 5.40388250445041 7.67956757135451
  H 5.91689850139380 4.38779477788562 8.52271347324037
  H 5.49802871995078 5.95733281862744 7.79035440834804
  H 4.59902325976567 5.62492426398591 10.03803603756776
  H 8.78798304611146 6.02370017875529 10.21012292961893
  H 8.75533802006655 4.53147460075733 9.56428016000059
```

DFT Cartesian coordinates A.85: R_C,S_N,S_{Ru} - [η^6-(*p*-cymene)Ru(L3)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 48

  Ru 6.70605603951296 4.78609384725017 11.30807362515575
  Cl 7.57817133276971 6.61639288498105 12.67803699192070
  C 7.32277599117189 3.36324820564088 12.87994649971857
  H 8.05700754297445 3.56888791911784 13.65093734193487
  C 7.73251614182104 2.81483882756104 11.64994246100476
  C 5.96816670791154 3.75881046512030 13.10720601635455
```

H 5.70943123128284 4.25595897269073 14.03650980542217

C 5.40137865358353 3.08668432855726 10.83450045735370

H 4.68217420213062 3.02844456770825 10.02272211994933

C 9.14126804860169 2.32403283691086 11.41364871184162

H 9.30940321212801 2.32117270826648 10.32887703821704

C 6.74108724719135 2.70245803310633 10.61747511818464

H 7.03628220012703 2.34551208873533 9.63447381141246

C 4.99191589614640 3.62359479627334 12.09978015503313

C 9.23092535896807 0.86732213799836 11.89965601313300

H 9.07287942330402 0.81779351503869 12.98305071983921

H 10.22205645502004 0.45960911518730 11.67647652689388

H 8.47982313582239 0.23690582689712 11.41251821304912

C 3.57992105857937 4.06552951839719 12.32460792494032

H 3.53192683459392 4.88269855321504 13.04880953187382

H 3.00166416223125 3.22328632700677 12.72346538054252

H 3.10234589952737 4.37673653845000 11.39137216939754

C 10.21794959316022 3.19034962994267 12.06704984088661

H 10.12092948765393 4.24139956165775 11.77506163404781

H 11.20706019526818 2.83745988640038 11.75968614005393

H 10.17414122075782 3.13239040180355 13.15974384467861

C 8.51232404473730 4.84800146363538 8.63996279163164

N 8.02229630426507 5.66232435978019 9.79928081818774

C 7.48642660110389 6.99852217132643 9.38998263077774

C 5.97934949043647 6.92214975244785 9.21656003731546

H 7.97259367816451 7.34855277656879 8.47204268293403

H 7.72251531671479 7.70360544738865 10.19106972828298

C 7.61944315830935 4.87757212554042 7.40000951693580

```
  H 8.63360430002514 3.82397205226198 8.99682093900791
  H 9.51050070314757 5.21593754294133 8.36500512079825
  C 6.10849703328263 4.82884407800757 7.64694985306962
  H 7.92033408149463 4.01627016259523 6.79205395527024
  H 7.84741486421305 5.76473669522655 6.79568645502821
  C 5.50043960146264 6.19947011870276 7.95898409715806
  H 5.87162229257949 4.10763123826500 8.43364714182580
  H 5.62119492665328 4.46060089454563 6.73656773398166
  H 4.40577156245891 6.11764751640998 8.00620251396933
  H 5.71915265943733 6.86859937337239 7.11645859812949
  H 5.59345089609467 7.95010705986629 9.16799903943303
  N 5.44118304907659 6.28730543843992 10.46604311774464
  H 8.83966111189370 5.85182909162805 10.37746587305890
  H 4.49508160782740 5.95403926512360 10.29378565951174
  H 5.36886544438157 7.00144988201113 11.19072360310741
```

DFT Cartesian coordinates A.86: R_C,S_N,R_{Ru} - [η^6-(*p*-cymene)Ru(L3)Cl]$^+$

```
Charge: 1
Multiplicity: 1
Number of atoms: 48

  Ru 6.75653804505606 4.71973767674768 11.35683555847977
  Cl 7.58319700212251 6.57803487062766 12.69233679551040
  C 7.33374387289622 3.31983056576532 12.96081317121287
  H 8.05740649361274 3.53079409265595 13.73965034472083
  C 7.76065581302228 2.78041006503563 11.73100228699777
  C 5.97522970708295 3.72127222095948 13.16230016416846
  H 5.70444225312742 4.22214772794234 14.08642098093566
```

C 5.44340610196697 3.04265349003330 10.88681217297251

H 4.74236844207673 2.99837863815924 10.05666766941315

C 9.18595094753027 2.35151710658804 11.47722631180078

H 9.37055495271044 2.46981473181628 10.39983659884264

C 6.78419225883855 2.65226903302556 10.68262557795244

H 7.09757556319338 2.30888310113110 9.69999590856169

C 5.01031746955799 3.58123840040549 12.14668269628243

C 9.30584235905060 0.85343236248277 11.80479823566771

H 9.12214995164461 0.68285221962567 12.87158023202792

H 10.31394206103991 0.49940499411800 11.56708387914933

H 8.58672442114476 0.25939060144533 11.23140763831523

C 3.59190527672605 4.01422796503272 12.35374582680985

H 3.52723755555213 4.80142066361495 13.10874095650681

H 3.00193996680225 3.15733192568489 12.70105993548353

H 3.13485832661068 4.36673344775723 11.42442545299566

C 10.22541799260449 3.17079457754912 12.24141708168738

H 10.09173770308849 4.24560425558066 12.07619871513428

H 11.22869124307857 2.89145445271652 11.90610500501236

H 10.17384665389892 2.97948112400005 13.31846257701720

C 5.24238601678362 7.44995299052389 10.42935025329678

N 5.54338732829518 6.00906332629694 10.07814841315382

C 6.06957477689177 5.77201919792894 8.70263633490942

C 7.57671445201831 5.99388262558909 8.65343288148719

H 5.55912739549654 6.39917756428623 7.96154683754450

H 5.84899441904115 4.72669690851679 8.46268281650022

C 5.95307866344467 8.51724064599093 9.60374415892599

H 5.49024439762124 7.57755953273560 11.48561374309023

```
H 4.16007463008034 7.58898779069777 10.31577537974570
C 7.48139056660089 8.42931704771175 9.54214606954107
H 5.66907586983086 9.46745245619921 10.07312690706604
H 5.54473872141371 8.55486340906672 8.58535333250161
C 7.99876690575284 7.45136733362616 8.48582340754096
H 7.87604919739158 8.18279544601173 10.53503808156518
H 7.87882661450215 9.41983479358868 9.29095340678784
H 9.09557513611529 7.49039180805004 8.44748896197133
H 7.64218936410738 7.77323165177160 7.49836287183849
H 7.95967526108118 5.43589434959353 7.79029287986644
N 8.17943823883751 5.37926395081373 9.89522272702686
H 4.64372108276275 5.53812168091414 10.10893221640026
H 8.77505692421085 6.06373212365461 10.36143227016201
H 8.79071160368362 4.61414305593057 9.62372427541862
```

A.6.9 Cartesian coordinates of auxiliary molecules used in the catalytic cycles

A.6.9.1 For the ROCOP propagation cycles from Chapter 2

DFT Cartesian coordinates A.87: Acetate

```
Charge: -1
Multiplicity: 1
Number of atoms: 7

O -0.20933429672224 0.25668518766749 0.20326187604894
C -1.31871862821066 -0.27294470485220 -0.08201242747661
O -2.46061663171184 0.22438394174897 0.12770847904828
```

```
  C -1.29586841733670 -1.66500960124409 -0.74075721013105
  H -0.27984078101690 -1.99261847697026 -0.97758603818310
  H -1.89853043319735 -1.65694042594480 -1.65544701986057
  H -1.75420081180431 -2.39355592040511 -0.06187765944589
```

DFT Cartesian coordinates A.88: Ethylene oxide

```
Charge: 0
Multiplicity: 1
Number of atoms: 7

  O -1.21932175274382 0.93375271392927 -0.01246446617350
  C -1.90117615416299 -0.33214239408043 -0.08398786922138
  C -0.43897678688983 -0.27379893308415 -0.08561807849032
  H -2.42947886433297 -0.51582909256635 -1.01915772325454
  H -2.42329668028390 -0.62322634398267 0.82707835095246
  H 0.10022702205627 -0.41482728330756 -1.02196246007790
  H 0.10669321635724 -0.52223866690811 0.82428224626517
```

DFT Cartesian coordinates A.89: Succinic anhydride

```
Charge: 0
Multiplicity: 1
Number of atoms: 11

  O -0.03520013386825 -0.47034656523213 -0.40147025182534
  C 0.08140813066102 -1.54953440594087 -1.27559937708591
  O 1.15823555873825 -1.99490306692224 -1.54869373362832
  C -1.37093465967848 -0.11458288525284 -0.22416289085599
  O -1.66571131799729 0.79530988247682 0.49534725615908
```

```
  C -1.28515064549193 -1.97622373782351 -1.73908293870526
  C -2.24993891931616 -1.02119488913525 -1.04273803808191
  H -1.43065652285057 -3.02594304266341 -1.46618480227764
  H -1.31488037188279 -1.91516554082338 -2.83126942261821
  H -2.95512204731074 -1.51937348398647 -0.37048705635603
  H -2.83493907100305 -0.40495226469674 -1.73224874472445
```

A.6.9.2 For the transfer hydrogenation cycles from Chapter 3

DFT Cartesian coordinates A.90: Acetone

```
Charge: 0
Multiplicity: 1
Number of atoms: 10

  C -1.53199231257785 0.56981829310391 -0.09250308063316
  C -0.24704675195897 1.35297897959610 -0.14227297014728
  C 1.01492523653642 0.58800866062902 0.15630514588980
  H 1.02158453766429 0.32671616929075 1.22220296129708
  H 1.89810511427305 1.18562626199849 -0.07613511221832
  H 1.03237575554958 -0.35665886365916 -0.39802896990451
  O -0.22936686951558 2.54553793381170 -0.41044024457336
  H -2.39636350733920 1.23407484019427 -0.14539087393208
  H -1.57306920968972 -0.04425038785431 0.81373598656934
  H -1.55228199294203 -0.12363188711079 -0.94292284234749
```

DFT Cartesian coordinates A.91: Acetophenone

```
Charge: 0
Multiplicity: 1
```

```
Number of atoms: 17


  C -1.55710436670092 0.57658062478363 -0.07390027752903
  C -0.26058318186238 1.31366051887342 -0.13829939975134
  C 1.01542495077064 0.56316447623699 0.14017555152716
  H 0.99337691071387 0.12559340307229 1.14468158758951
  H 1.86286754612631 1.24455801483211 0.05548287268424
  H 1.13664932888719 -0.26434649337636 -0.56803730322220
  O -0.23740610277282 2.50910440993894 -0.41298754409040
  C -1.61799947389096 -0.78944437418136 0.23219457091965
  C -2.84520927339767 -1.44255205626640 0.28409706881249
  C -4.02134105390643 -0.74015461565452 0.03164487131357
  C -3.96945096265192 0.62048144948707 -0.27440467324502
  C -2.74654888532243 1.27407207103211 -0.32684886948577
  H -0.71079917860477 -1.35101241339174 0.43131988181537
  H -2.88362869797878 -2.50159565687579 0.52228728582421
  H -4.97907050064264 -1.25171315105014 0.07302112388758
  H -4.88635155784710 1.16871384995094 -0.47153061437385
  H -2.69447550091919 2.33225994258885 -0.56375613267617
```

DFT Cartesian coordinates A.92: 4-OCH_3 Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 21


  C -1.56894377756751 0.56828182137775 -0.07237315655226
  C -0.29093422589240 1.31371239394740 -0.13952605025255
  C 0.99528458347773 0.57397276305198 0.13489121502669
```

```
  H 0.98325048833630 0.13694804415897 1.13978837272357
  H 1.83554807849941 1.26400594601562 0.04714884058395
  H 1.12428916648261 -0.25196183146471 -0.57373316656418
  O -0.27215054193550 2.51333477168908 -0.41303437909993
  C -1.62537684309575 -0.80257029560195 0.23546693569323
  C -2.83454950025888 -1.46846825242891 0.29165000695620
  C -4.02875704549544 -0.77668368366548 0.03982627270817
  C -3.99385603459595 0.59072696451908 -0.26976200481425
  C -2.77170537292553 1.24203992701083 -0.32153915117655
  H -0.71588284771816 -1.36071144125779 0.43426787347924
  H -2.88053157370308 -2.52705016799744 0.52933974359894
  O -5.16024127117875 -1.51338909194992 0.11891247450822
  H -4.90366711010127 1.14532261947563 -0.46792261502396
  H -2.73880982929806 2.30071570731516 -0.56056807473571
  C -6.41467348734444 -0.85681983357987 -0.13067849632323
  H -7.17612398669432 -1.62847031770933 -0.01455089039585
  H -6.44795856359512 -0.45351116661219 -1.14917963286629
  H -6.58648030539587 -0.05445487629390 0.59585588252654
```

DFT Cartesian coordinates A.93: 4-^{t}Bu Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 29

  C -1.55622221572806 0.57969116514076 -0.06708476875359
  C -0.26601189591920 1.31653929752842 -0.14999632283330
  C 1.01414127482608 0.56924039598618 0.12349686361207
  H 1.00207609226615 0.14081411845568 1.13211358774930
```

```
H 1.86046063285783 1.25027983737264 0.02484203925323
H 1.12978447443981 -0.26467705033782 -0.57808945498627
O -0.24366567940112 2.51098423802206 -0.43536956475863
C -1.62097463121374 -0.78415177579798 0.25169310068855
C -2.84356610796778 -1.43471587355241 0.32054489666764
C -4.04879566003778 -0.75889843913057 0.07637957142370
C -3.97436678400199 0.60324046068164 -0.24217296911659
C -2.75328610645522 1.26012620918478 -0.31268730166308
H -0.71482726136508 -1.34867471162641 0.44863317157351
H -2.85580695509500 -2.49157526665958 0.57073486717440
C -5.37302497709634 -1.51641135715999 0.16454997224766
H -4.87803155707274 1.16914829735822 -0.43970677983430
H -2.71682165575508 2.31661536177834 -0.56105286320685
C -6.58162534075966 -0.61973828402742 -0.12868671253523
C -5.52958686462390 -2.09453033493201 1.58511601709487
C -5.36302570909415 -2.66984040401152 -0.85831120853102
H -5.52623250847180 -1.29260903248318 2.33181197920448
H -4.72420878821783 -2.79432578337077 1.82844247608395
H -6.48112883273005 -2.63295990078713 1.66139178659785
H -5.24261238625469 -2.28308405866587 -1.87639252612101
H -6.31128809589696 -3.21689669868092 -0.80661493365476
H -4.55217137067407 -3.37786915818716 -0.66132611471754
H -6.65628183033806 0.20651393474317 0.58680236792032
H -7.49665275921418 -1.21583127116185 -0.04881400092564
H -6.54084650100538 -0.20242391567931 -1.14080717565374
```

DFT Cartesian coordinates A.94: 4-F Acetophenone

```
Charge: 0
```

```
Multiplicity: 1
Number of atoms: 17


  C -1.55982629705154 0.57336967583271 -0.06550140586610
  C -0.26683819054629 1.30907692658887 -0.14858781707566
  C 1.01181214541940 0.56098101862948 0.12420861651014
  H 1.00028636307302 0.13300926527239 1.13307483729455
  H 1.85796403878423 1.24194931998382 0.02503277083166
  H 1.12702821385057 -0.27259830209947 -0.57789565998614
  O -0.24754550705944 2.50241919825478 -0.43382403730965
  C -1.61926912517737 -0.79052887551510 0.25226032882793
  C -2.83948109174610 -1.45095131619059 0.32387132040700
  C -3.99168402748290 -0.72371629695311 0.07274844315845
  C -3.97849457647455 0.62713792663632 -0.24561172300053
  C -2.75226068707414 1.26908518079663 -0.31251135388720
  H -0.71254438045366 -1.35356818153657 0.44739344490525
  H -2.90261132612146 -2.50632047030554 0.56863312784438
  F -5.18321964048131 -1.35798466697943 0.14047124321875
  H -4.90992506781217 1.15166625115183 -0.43374247264697
  H -2.70467084364627 2.32509334643298 -0.55856966322586
```

DFT Cartesian coordinates A.95: 4-CN Acetophenone

```
Charge: 0
Multiplicity: 1
Number of atoms: 18


  C -1.56228659010708 0.56861743738407 -0.06811005670325
  C -0.26076909368076 1.30928481825619 -0.15360404627563
```

```
 C 1.01425613945813 0.56514605775671 0.12813260400983
 H 0.99471967704284 0.13812759285791 1.13744176984266
 H 1.86078555245743 1.24590246406392 0.03254325884812
 H 1.13197831002459 -0.27012250111930 -0.57189664873719
 O -0.25355045511496 2.49735597105096 -0.44768942755584
 C -1.61766900630921 -0.79417058793681 0.24787504113855
 C -2.83710622424917 -1.45029233299898 0.32107025602485
 C -4.01695240797197 -0.73585556151249 0.07592908379116
 C -3.97412303183265 0.63046176835793 -0.24272022977655
 C -2.74992073956155 1.27019120655316 -0.31238047359684
 H -0.71035739653957 -1.35693663712535 0.43953185547193
 H -2.88342859594179 -2.50627988283575 0.56589018089561
 C -5.27306536162844 -1.40249545949033 0.15196440238891
 H -4.89579640042724 1.17155370111676 -0.43021435696659
 H -2.69834391333744 2.32613692817147 -0.55684751180849
 N -6.29575046228112 -1.94326498255007 0.21406429900875
```

DFT Cartesian coordinates A.96: 2-propanol

```
Charge: 0
Multiplicity: 1
Number of atoms: 12

 C -1.51999571980329 0.57808178124363 -0.14972459719060
 C -0.24689279376904 1.38471442673423 -0.36600395383720
 C 0.98766388737156 0.65714068271998 0.13347882331871
 H 0.89266212658003 0.44096163785107 1.20388769592907
 H 1.88571544342009 1.26317397446944 -0.02257982138617
 H 1.11118709802697 -0.28962485867774 -0.40126147456882
```

```
  O -0.30458335829621 2.63783070798463 0.35022914503694
  H -2.39986588732839 1.13957729357344 -0.48421379437296
  H -1.64157181451450 0.33826725531309 0.91287119560791
  H -1.48086331871660 -0.35886432150384 -0.71619839891992
  H -1.08435431972799 3.11587444954812 0.04086490157735
  H -0.13075134324261 1.59462697074393 -1.44236972119432
```

DFT Cartesian coordinates A.97: t-butanol

```
Charge: 0
Multiplicity: 1
Number of atoms: 15

  C -1.52852205755637 0.54172440334506 -0.03683192582792
  C -0.25554297012650 1.35438986685988 -0.27332278975786
  C 0.96780155512004 0.61434174864473 0.25223924111430
  H 0.85759046904933 0.40442277395963 1.32138330654655
  H 1.87104031205140 1.21559019057778 0.10418509178905
  H 1.09198344283934 -0.33529668834416 -0.27709275841808
  O -0.31878265588499 2.58288871015349 0.49503657491954
  H -2.40879699331934 1.10137218071748 -0.37507004793564
  H -1.64508447840637 0.31760407181284 1.02869889931376
  H -1.49326174435977 -0.40317498106701 -0.58984810653185
  H -1.08466964641831 3.08100380254060 0.18038712883296
  C -0.09506626159727 1.69055865895719 -1.75585241092952
  H -0.02099853987068 0.77613381601837 -2.35446515881495
  H 0.81006721206140 2.28573800795656 -1.91608382085456
  H -0.95863764358191 2.26300343786753 -2.11507322344577
```

DFT Cartesian coordinates A.98: (R)-1-phenylmethanol

```
Charge: 0

Multiplicity: 1

Number of atoms: 19


  C -1.66083823211438 -0.43583472536195 -0.14797928131020

  C -2.30983001733907 -0.32097806178567 1.22352358816825

  O -2.31374315943675 0.52773966458251 -0.99465444687969

  C -0.16549115980521 -0.20234091324805 -0.08494729613914

  C 0.34667256632393 1.08269731150035 0.12025404706936

  C 0.72169764363134 -1.27223243918031 -0.21186440138057

  C 1.72023726116090 1.28970940362365 0.20158137307961

  H -0.33657305444455 1.92312704108798 0.21230117993384

  C 2.09811888276386 -1.06769494262219 -0.12623024055263

  H 2.10684271813305 2.29307530564907 0.35995906875161

  C 2.60077557794614 0.21446871205357 0.07974020638877

  H 3.67328937077535 0.37760014837654 0.14156398462440

  H 0.33160269023250 -2.27386990089012 -0.38133105313396

  H 2.77755211689465 -1.90967705991220 -0.22867305964634

  H -1.87229917041357 -1.05268971439192 1.90907636616559

  H -2.14945068929053 0.68164884306791 1.63459016580911

  H -3.38624245166384 -0.50685961299795 1.15056157746256

  H -1.88977364890378 0.48836765685037 -1.86189622654440

  H -1.83477724445003 -1.44964671640157 -0.54312555186615
```

DFT Cartesian coordinates A.99: (S)-1-phenylmethanol

```
Charge: 0

Multiplicity: 1
```

```
Number of atoms: 19


  C 1.66092797592296 -0.43566575938987 -0.14874260078096
  O 2.31361200913190 0.52891717385026 -0.99445178526416
  C 0.16558350198137 -0.20231077448177 -0.08517361806669
  C -0.72160330207448 -1.27201611885786 -0.21364673977716
  C -0.34658068637229 1.08240964797916 0.12202304857936
  C -2.09802241527100 -1.06762635040368 -0.12759590182638
  H -0.33150893746923 -2.27339037869233 -0.38466285075842
  C -1.72013919582606 1.28928032011661 0.20377696435399
  H -2.77745233906952 -1.90946118343801 -0.23126324141729
  C -2.60067618268630 0.21421599858461 0.08036760317296
  H -3.67318662959174 0.37724195356295 0.14252671296142
  H 0.33665704489516 1.92271067057759 0.21529400437289
  H -2.10674460332225 2.29239935575620 0.36371179823075
  H 1.88945625424286 0.49051686263167 -1.86164631772372
  C 2.31019573127205 -0.32235944276773 1.22275667999326
  H 1.87283780688299 -1.05488133217848 1.90755453495608
  H 2.14986636556859 0.67978331802173 1.63501889001343
  H 3.38660043117881 -0.50811277066115 1.14935818499645
  H 1.83483717060617 -1.44901119020990 -0.54509536601583
```

DFT Cartesian coordinates A.100: t-butoxide anion

```
Charge: -1
Multiplicity: 1
Number of atoms: 14


  C -1.51831318412010 0.54838651492235 -0.03337728482611
```

```
C -0.25581853165154 1.43210353737745 -0.22122659135187
C 0.96986408312385 0.60076885260567 0.24416948450090
H 0.87721940358976 0.37212467363689 1.31367857657814
H 1.88646729103884 1.18785212762763 0.10296907894536
H 1.08300661258160 -0.34824254689240 -0.30040896367013
O -0.36319414237407 2.60882436335486 0.47595008650212
H -2.40484079598676 1.10439544246084 -0.36481529047789
H -1.64803192052872 0.31372996777938 1.03104305202571
H -1.47732350789349 -0.39870454636659 -0.59093579029850
C -0.09116414663050 1.68890721554268 -1.74413305984254
H -0.01634081633993 0.76602827202617 -2.33772541741081
H 0.81375298956556 2.28444500271408 -1.92112954323467
H -0.94971333437449 2.26523112321098 -2.11244833743967
```

A.7 X-ray crystallographic data

A.7.1 In-3

Note: Structure solved and refined by Dr Benjamin Ward.

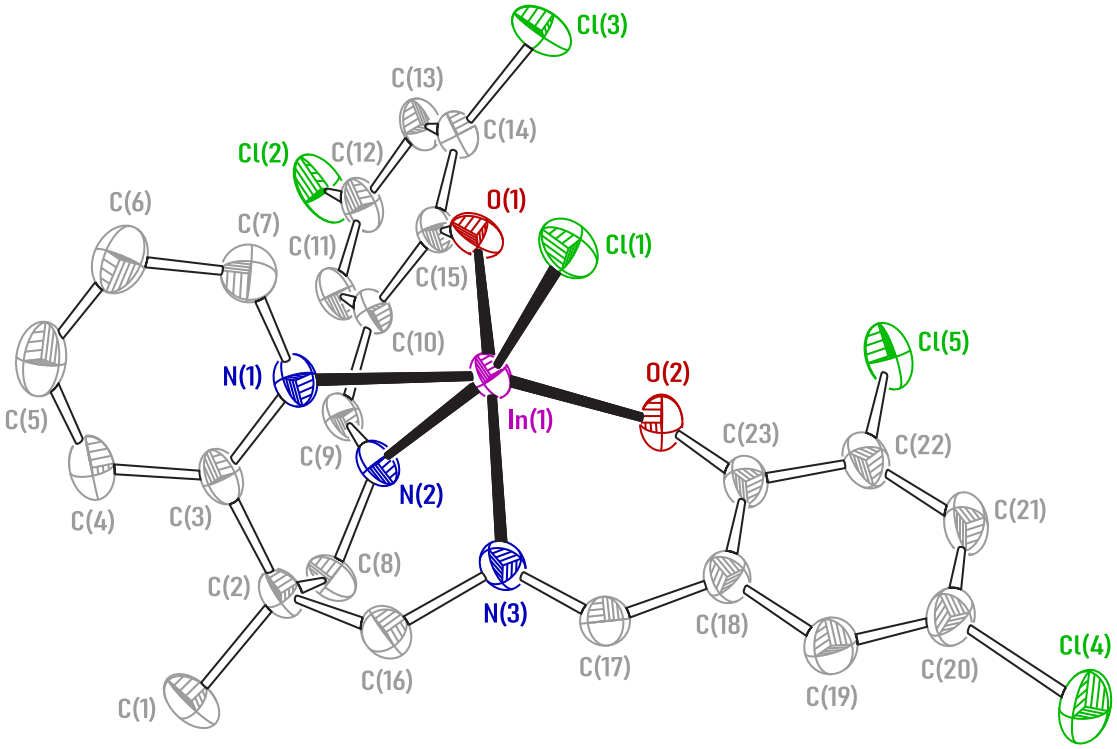


Figure A.1: Thermal ellipsoids of **In-3** shown at 30% probability. Hydrogen atoms and 1,2-difluorobenzene solvent omitted for clarity.

A.7.1.1 Refinement model description

1. Restrained distances

C24-C25 = C25-C26 = C26-C27 = C27-C28 = C28-C29 = C29-C24 1.39 with sigma of 0.02

2. U_{iso}/U_{aniso} restraints and constraints

C24 ≈ C25 ≈ C26 ≈ C27 ≈ C28 ≈ C29 ≈ F1 ≈ F2: within 2Å with sigma of 0.04 and sigma for terminal atoms of 0.08 within 2Å

U_{anis}(C24) ≈ U_{eq}, U_{anis}(C25) ≈ U_{eq}, U_{anis}(C26) ≈ U_{eq}, U_{anis}(C27) ≈ U_{eq}, U_{anis}(C28) ≈ U_{eq}, U_{anis}(C29) ≈ U_{eq}, U_{anis}(F1) ≈ U_{eq}, U_{anis}(F2) ≈ U_{eq}: with sigma of 0.01 and sigma for terminal atoms of 0.02

3.a Secondary CH_2 refined with riding coordinates:

C8(H8A,H8AB), C16(H16A,H16B)

3.b Aromatic/amide H refined with riding coordinates:

C4(H4), C5(H5), C6(H6), C7(H7), C9(H9), C11(H11), C13(H13), C17(H17),

C19(H19), C21(H21), C25(H25), C26(H26), C27(H27), C28(H28)

3.c Idealised Me refined as rotating group:

C1(H1A,H1B,H1C)

A.7.1.2 Crystallographic tables

Table A.5: Crystal data and structure refinement for **In-3**.

Identification code	**In-3**
Empirical formula	$C_{29}H_{21}N_3O_2Cl_5InF_2$
Formula weight	773.56
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.95340(10)
b/Å	17.1246(3)
c/Å	22.6398(5)
α/°	90
β/°	96.320(2)
γ/°	90
Volume/Å^3	3064.77(10)
Z	4
ρ_{calc} / g/cm^3	1.676
μ/mm^{-1}	10.564
F(000)	1536
Crystal size/mm^3	0.253×0.2×0.034
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.858 to 153.736
Index ranges	$-7 \leq h \leq 9$, $-21 \leq k \leq 21$, $-28 \leq l \leq 27$

Reflections collected	28433
Independent reflections	6393 [R_{int} = 0.0653, R_σ = 0.0390]
Data/restraints/parameters	6393/102/380
Goodness-of-fit on F^2	1.034
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0502, wR_2 = 0.1338
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.1444
Largest diff. peak/hole / e $Å^{-3}$	1.34/-0.97

Table A.6: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **In-3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	$\mathbf{U_{eq}}$
In1	6996.6(3)	6567.7(2)	2948.8(2)	41.81(12)
Cl1	9542.0(14)	7205.1(8)	2706.8(6)	64.1(3)
Cl2	1096.0(18)	4118.0(12)	908.9(10)	99.7(7)
Cl3	7427.4(18)	5223.4(9)	1085.7(7)	73.1(4)
Cl4	13400(2)	5509.5(14)	5431.1(8)	101.3(6)
Cl5	10718.6(19)	4316.4(9)	3337.9(8)	79.4(4)
F1	5038(16)	7531(7)	984(7)	276(6)
F2	4687(12)	6469(5)	260(4)	186(3)
O1	6549(4)	6020(2)	2127.7(14)	53.5(7)
O2	8272(4)	5578.3(19)	3360.6(16)	57.1(8)
N1	5515(4)	7730(2)	2779.3(17)	46.2(7)
N2	4265(4)	6246(2)	3025.0(17)	44.6(7)
N3	6990(5)	6932(2)	3900.3(16)	47.8(8)
C1	2679(7)	7808(3)	4002(3)	64.4(13)
C2	4030(5)	7459(3)	3645(2)	47.5(9)
C3	4213(5)	7911(2)	3078(2)	46.4(9)

C4	3135(7)	8532(3)	2885(3)	59.1(12)
C5	3488(8)	8973(3)	2407(3)	68.8(15)
C6	4862(7)	8803(3)	2121(3)	66.5(14)
C7	5850(7)	8169(3)	2312(2)	59.9(11)
C8	3536(6)	6592(3)	3531(2)	51.0(10)
C9	3276(5)	5897(2)	2635(2)	46.2(9)
C10	3693(5)	5524(2)	2098(2)	44.8(8)
C11	2403(6)	5074(3)	1791(2)	56.0(11)
C12	2684(6)	4683(3)	1289(3)	60.8(12)
C13	4234(6)	4740(3)	1058(2)	58.2(11)
C14	5485(6)	5186(3)	1351(2)	49.8(9)
C15	5287(5)	5603(2)	1883.0(19)	42.8(8)
C16	5735(6)	7514(3)	4049(2)	54.8(10)
C17	8107(6)	6725(3)	4321(2)	51.9(10)
C18	9402(6)	6144(3)	4288(2)	52.7(10)
C19	10659(6)	6115(4)	4781(2)	63.4(12)
C20	11887(6)	5548(4)	4816(3)	67.4(14)
C21	11910(6)	4997(4)	4374(3)	67.3(14)
C22	10680(6)	5016(3)	3887(3)	59.6(12)
C23	9395(6)	5593(3)	3819(2)	50.6(9)
C24	3410(17)	7239(7)	909(6)	137(4)
C25	2064(18)	7439(7)	1202(6)	145(4)
C26	553(17)	7077(7)	1053(5)	141(4)
C27	501(16)	6494(6)	619(5)	126(3)
C28	1888(15)	6286(6)	364(5)	123(3)
C29	3292(15)	6662(6)	518(4)	112(3)

Table A.7: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **In-3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In1	29.70(17)	45.71(18)	50.51(18)	-3.28(10)	6.55(11)	0.38(9)
Cl1	34.9(5)	78.8(8)	80.2(8)	-6.7(6)	13.3(5)	-13.1(5)
Cl2	46.3(7)	109.4(12)	140.4(15)	-68.2(12)	-2.8(8)	-7.1(7)
Cl3	55.7(7)	87.7(9)	80.5(8)	-20.9(7)	28.4(6)	-9.3(6)
Cl4	52.5(8)	158.6(18)	87.4(10)	16.3(11)	-16.0(7)	12.0(9)
Cl5	59.3(8)	69.1(8)	109.5(11)	-8.0(7)	7.7(7)	16.9(6)
F1	215(10)	275(11)	317(12)	-68(10)	-60(9)	-14(9)
F2	189(7)	240(8)	132(5)	79(5)	32(5)	60(6)
O1	41.8(16)	65.4(19)	55.5(16)	-14.9(14)	15.3(13)	-9.5(14)
O2	50.4(18)	53.2(17)	65.1(19)	-3.3(14)	-5.0(15)	9.5(14)
N1	35.1(17)	43.3(17)	60(2)	0.4(15)	5.8(14)	1.0(13)
N2	30.7(16)	46.9(17)	58.0(19)	-3.8(15)	12.9(14)	-2.4(13)
N3	37.7(18)	55(2)	50.7(18)	-7.8(15)	3.8(14)	2.4(15)
C1	46(3)	75(3)	75(3)	-22(3)	19(2)	5(2)
C2	35(2)	51(2)	57(2)	-8.4(18)	8.5(17)	4.9(17)
C3	29.4(18)	44.0(19)	65(2)	-10.5(18)	1.5(16)	-0.2(15)
C4	47(3)	50(2)	77(3)	-13(2)	-7(2)	8.8(19)
C5	66(3)	46(2)	89(4)	-6(2)	-20(3)	4(2)
C6	65(3)	51(3)	80(3)	13(2)	-7(3)	-8(2)
C7	52(3)	57(3)	71(3)	6(2)	9(2)	-8(2)
C8	41(2)	55(2)	60(2)	-6.8(18)	18.5(19)	-4.3(17)
C9	30.8(19)	45(2)	64(2)	-1.2(17)	10.8(17)	-0.1(15)
C10	35(2)	42.7(19)	57(2)	-2.1(17)	8.8(17)	2.8(16)
C11	32(2)	53(2)	83(3)	-8(2)	9(2)	-2.3(18)

C12	42(2)	57(3)	83(3)	-20(2)	0(2)	1(2)
C13	48(3)	56(3)	70(3)	-17(2)	0(2)	6(2)
C14	42(2)	49(2)	59(2)	-4.2(18)	7.1(18)	3.4(17)
C15	35.4(19)	39.5(18)	54(2)	-0.6(16)	5.3(16)	-0.8(15)
C16	46(2)	62(3)	57(2)	-12(2)	4.3(19)	4(2)
C17	42(2)	66(3)	48(2)	-0.4(19)	3.6(17)	-2(2)
C18	38(2)	63(3)	58(2)	7(2)	6.5(18)	-0.7(19)
C19	47(3)	82(3)	61(3)	5(2)	2(2)	-3(2)
C20	36(2)	100(4)	66(3)	22(3)	2(2)	-3(2)
C21	36(2)	77(3)	89(4)	26(3)	8(2)	4(2)
C22	43(2)	58(3)	80(3)	12(2)	15(2)	2(2)
C23	39(2)	51(2)	62(2)	8.4(19)	7.2(18)	1.2(18)
C24	122(6)	138(7)	143(7)	2(6)	-28(6)	-11(6)
C25	166(8)	135(7)	128(6)	-40(6)	-10(6)	7(6)
C26	149(7)	158(7)	119(6)	0(6)	29(6)	14(6)
C27	145(7)	129(6)	107(6)	13(5)	28(5)	-48(5)
C28	145(7)	109(5)	115(6)	29(5)	23(6)	-25(5)
C29	135(7)	120(6)	84(4)	32(4)	18(5)	20(5)

Table A.8: Bond Lengths for **In-3**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In1	Cl1	2.4155(11)	C3	C4	1.406(6)
In1	O1	2.077(3)	C4	C5	1.373(9)
In1	O2	2.135(3)	C5	C6	1.362(9)
In1	N1	2.324(3)	C6	C7	1.381(8)
In1	N2	2.266(3)	C9	C10	1.445(6)
In1	N3	2.244(4)	C10	C11	1.404(6)

Cl2	C12	1.741(5)	C10	C15	1.413(6)
Cl3	C14	1.720(5)	C11	C12	1.359(7)
Cl4	C20	1.738(5)	C12	C13	1.394(8)
Cl5	C22	1.729(6)	C13	C14	1.368(7)
F1	C24	1.381(15)	C14	C15	1.424(6)
F2	C29	1.350(12)	C17	C18	1.442(7)
O1	C15	1.305(5)	C18	C19	1.416(7)
O2	C23	1.294(6)	C18	C23	1.418(7)
N1	C3	1.333(6)	C19	C20	1.373(8)
N1	C7	1.348(6)	C20	C21	1.378(9)
N2	C8	1.464(6)	C21	C22	1.392(8)
N2	C9	1.265(6)	C22	C23	1.417(7)
N3	C16	1.475(6)	C24	C25	1.364(13)
N3	C17	1.279(6)	C24	C29	1.323(12)
C1	C2	1.536(6)	C25	C26	1.362(13)
C2	C3	1.520(7)	C26	C27	1.397(12)
C2	C8	1.549(6)	C27	C28	1.348(12)
C2	C16	1.554(6)	C28	C29	1.302(12)

Table A.9: Bond Angles for **In-3**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O1	In1	Cl1	93.80(9)	C11	C10	C9	115.8(4)
O1	In1	O2	93.40(14)	C11	C10	C15	121.1(4)
O1	In1	N1	101.82(14)	C15	C10	C9	123.0(4)
O1	In1	N2	83.52(13)	C12	C11	C10	120.3(4)
O1	In1	N3	165.15(13)	C11	C12	Cl2	120.7(4)
O2	In1	Cl1	95.05(10)	C11	C12	C13	120.9(5)

O2	In1	N1	163.66(14)	C13	C12	Cl2	118.5(4)
O2	In1	N2	100.79(14)	C14	C13	C12	118.9(5)
O2	In1	N3	81.54(14)	C13	C14	Cl3	119.0(4)
N1	In1	Cl1	89.87(9)	C13	C14	C15	123.3(4)
N2	In1	Cl1	164.06(10)	C15	C14	Cl3	117.7(3)
N2	In1	N1	75.39(13)	O1	C15	C10	125.7(4)
N3	In1	Cl1	100.52(10)	O1	C15	C14	118.8(4)
N3	In1	N1	82.25(13)	C10	C15	C14	115.4(4)
N3	In1	N2	83.73(13)	N3	C16	C2	113.1(4)
C15	O1	In1	132.5(3)	N3	C17	C18	126.5(4)
C23	O2	In1	126.0(3)	C19	C18	C17	115.4(5)
C3	N1	In1	121.5(3)	C19	C18	C23	120.8(5)
C3	N1	C7	120.0(4)	C23	C18	C17	123.7(4)
C7	N1	In1	117.8(3)	C20	C19	C18	120.4(6)
C8	N2	In1	115.2(3)	C19	C20	Cl4	119.9(5)
C9	N2	In1	126.1(3)	C19	C20	C21	120.6(5)
C9	N2	C8	117.8(4)	C21	C20	Cl4	119.5(4)
C16	N3	In1	118.7(3)	C20	C21	C22	119.7(5)
C17	N3	In1	124.3(3)	C21	C22	Cl5	119.1(4)
C17	N3	C16	116.7(4)	C21	C22	C23	122.5(5)
C1	C2	C8	106.4(4)	C23	C22	Cl5	118.4(4)
C1	C2	C16	106.3(4)	O2	C23	C18	124.0(4)
C3	C2	C1	112.6(4)	O2	C23	C22	119.9(5)
C3	C2	C8	113.2(4)	C22	C23	C18	116.1(5)
C3	C2	C16	107.9(4)	C25	C24	F1	128.5(13)
C8	C2	C16	110.2(4)	C29	C24	F1	110.5(13)
N1	C3	C2	117.5(4)	C29	C24	C25	120.8(12)

N1	C3	C4	120.0(5)	C26	C25	C24	118.9(11)
C4	C3	C2	122.4(4)	C25	C26	C27	117.2(11)
C5	C4	C3	119.3(5)	C28	C27	C26	121.8(12)
C6	C5	C4	120.1(5)	C29	C28	C27	118.2(12)
C5	C6	C7	118.5(5)	C24	C29	F2	118.1(12)
N1	C7	C6	122.0(5)	C28	C29	F2	119.0(11)
N2	C8	C2	113.8(4)	C28	C29	C24	122.9(12)
N2	C9	C10	127.8(4)				

Table A.10: Hydrogen Atom Coordinates ($Å^2 \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **In-3**.

Atom	***x***	***y***	***z***	$\mathbf{U_{eq}}$
H1A	1585.27	7814.06	3756.76	97
H1B	2999.2	8342.67	4121.36	97
H1C	2592.51	7490.04	4357.76	97
H4	2171.82	8646.38	3083.75	71
H5	2773.97	9397.91	2276.46	83
H6	5134.86	9112.57	1796.83	80
H7	6792.97	8038.45	2108.14	72
H8A	3910.95	6286.05	3892.1	61
H8AB	2288.16	6553.75	3459.88	61
H9	2120.23	5877.64	2704.81	55
H11	1329.04	5041.23	1936.44	67
H13	4417.03	4473.35	702.36	70
H16A	6212.25	8043.88	4012.53	66
H16B	5519.98	7440.42	4467.73	66
H17	8079.26	6980.56	4692.52	62
H19	10652.19	6489.94	5090.18	76

H21	12761.96	4605.51	4401.43	81
H25	2179.45	7825.2	1505.21	174
H26	-424.95	7213.83	1235.98	169
H27	-541	6237.87	500.41	151
H28	1842.9	5875.5	80.45	147

A.7.2 In-2

Note: Structure solved and refined by Dr Benjamin Ward.

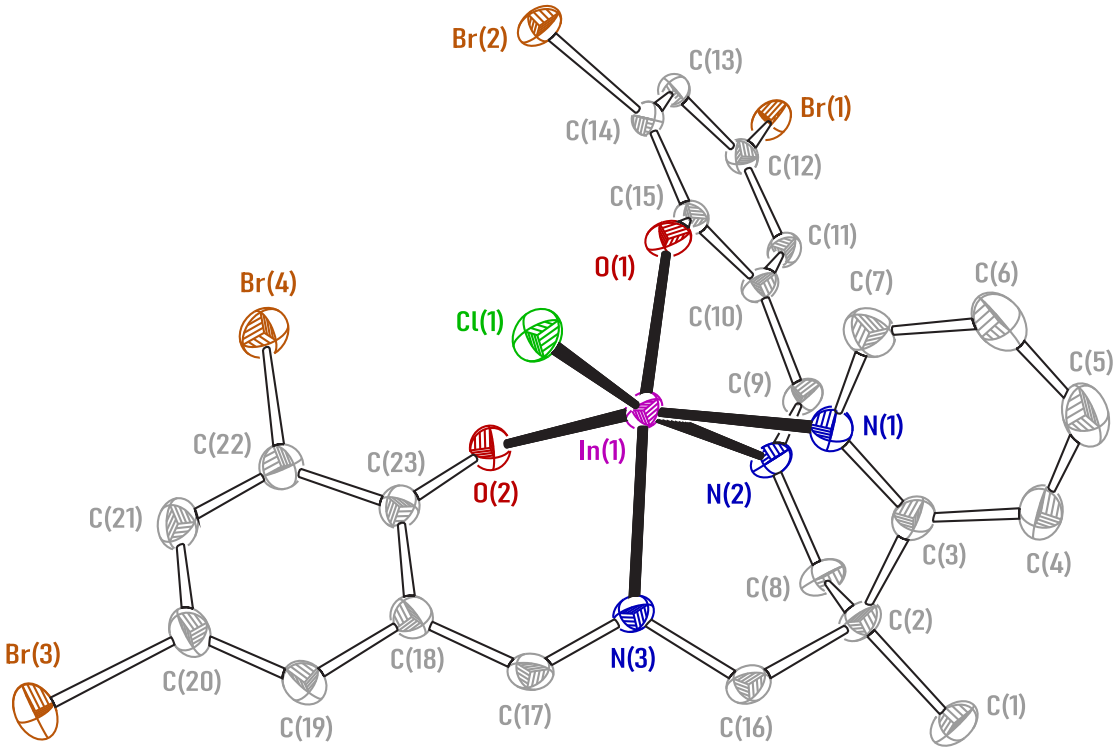


Figure A.2: Thermal ellipsoids of **In-2** shown at 30% probability. Hydrogen atoms and residual water molecule omitted for clarity.

A.7.2.1 Refinement model description

1. Restrained distances

O3-H1O = O3-H2O = O3A-H3O = O3A-H4O 0.84 with sigma of 0.02

H1O-H2O = H3O-H4O 1.333 with sigma of 0.04

2. U_{iso}/U_{aniso} restraints and constraints

O3 ≈ O3A: within 2Å with sigma of 0.04 and sigma for terminal atoms of 0.08 within 2Å

U_{anis}(O3) ≈ U_{eq}, U_{anis}(O3A) ≈ U_{eq}: with sigma of 0.1 and sigma for terminal atoms of 0.2

3. Others

Fixed Sof: O3(0.5) H2O(0.5) H1O(0.5) O3A(0.5) H3O(0.5) H4O(0.5)

4.a Secondary CH_2 refined with riding coordinates:

C8(H8A,H8AB), C16(H16A,H16B)

4.b Aromatic/amide H refined with riding coordinates:

C4(H4), C5(H5), C6(H6), C7(H7), C9(H9), C11(H11), C13(H13), C17(H17), C19(H19), C21(H21)

4.c Idealised Me refined as rotating group:

C1(H1A,H1B,H1C)

A.7.2.2 Crystallographic tables

Table A.11: Crystal data and structure refinement for **In-2**.

Identification code	**In-2**
Empirical formula	$C_{23}H_{19}N_3O_3ClBr_4In$
Formula weight	855.32
Temperature/K	200(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.19970(10)
b/Å	19.4701(3)
c/Å	16.9281(3)
α/°	90

β/°	97.378(2)
γ/°	90
Volume/Å^3	2680.18(7)
Z	4
ρ_{calc} / g/cm^3	2.12
μ/mm^{-1}	15.216
F(000)	1632
Crystal size/mm^3	0.198×0.104×0.017
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.952 to 154.22
Index ranges	-10 ≤ h ≤ 9, -24 ≤ k ≤ 24, -18 ≤ l ≤ 21
Reflections collected	27106
Independent reflections	5635 [R_{int} = 0.0530, R_σ = 0.0373]
Data/restraints/parameters	5635/24/338
Goodness-of-fit on F^2	1.026
Final R indexes [I≥2σ (I)]	R_1 = 0.0351, wR_2 = 0.0899
Final R indexes [all data]	R_1 = 0.0402, wR_2 = 0.0957
Largest diff. peak/hole / e Å^{-3}	1.30/-1.03

Table A.12: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **In-2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U_{eq}**
In1	3578.8(3)	7361.6(2)	3268.3(2)	29.86(9)
BR_1	7844.5(5)	4701.7(2)	988.5(3)	40.72(12)
Br2	1588.4(5)	5902.6(2)	1052.6(3)	39.82(11)
Br3	-1989.6(9)	6720.8(5)	6201.0(4)	74.4(2)
Br4	393.5(7)	5340.8(3)	3654.3(4)	54.35(14)

Cl1	844.3(12)	7821.8(6)	2982.6(7)	45.9(2)
O1	3526(3)	6886.0(15)	2151.2(17)	35.2(6)
O2	2966(4)	6461.3(15)	3875.7(19)	40.4(6)
O3	5640(30)	5549(11)	4414(18)	80(5)
O3A	5390(50)	5550(20)	4660(20)	120(11)
N1	4690(5)	8396.3(18)	2964(2)	37.1(7)
N2	6295(4)	7140.4(18)	3356(2)	33.8(7)
N3	4199(4)	7734.9(18)	4523(2)	32.9(7)
C1	8308(6)	8621(3)	4561(3)	48.5(11)
C2	6783(5)	8252(2)	4119(3)	37.1(9)
C3	6152(5)	8615(2)	3341(3)	39.3(9)
C4	6944(7)	9169(3)	3033(3)	52.1(12)
C5	6208(8)	9506(3)	2363(4)	60.8(15)
C6	4708(8)	9293(3)	1997(3)	58.4(14)
C7	3984(7)	8725(3)	2311(3)	47.1(10)
C8	7340(5)	7502(2)	3998(3)	38.5(9)
C9	7015(5)	6767(2)	2892(2)	33.4(8)
C10	6197(5)	6346.0(19)	2243(2)	30.7(7)
C11	7184(5)	5850.1(19)	1937(2)	31.1(7)
C12	6504(5)	5388.8(19)	1374(2)	30.0(7)
C13	4838(5)	5408.0(19)	1096(2)	29.5(7)
C14	3881(4)	5900.9(19)	1387(2)	28.1(7)
C15	4501(5)	6402.2(18)	1953(2)	27.4(7)
C16	5462(5)	8271(2)	4696(2)	36.2(8)
C17	3393(5)	7544(2)	5085(2)	37.4(8)
C18	2099(5)	7036(2)	5015(3)	38.9(9)
C19	967(6)	7069(3)	5581(3)	42.8(9)

C20	-311(6)	6618(3)	5524(3)	49.6(11)
C21	-507(6)	6102(3)	4955(3)	49.5(11)
C22	627(6)	6052(2)	4422(3)	42.7(9)
C23	1940(5)	6524(2)	4412(3)	37.1(8)

Table A.13: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **In-2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
In1	22.90(13)	33.46(14)	33.53(14)	-8.48(9)	4.75(9)	-0.55(8)
BR_1	33.3(2)	35.7(2)	53.6(3)	-16.83(17)	7.00(18)	3.58(15)
Br2	25.8(2)	47.4(2)	44.7(2)	-12.46(18)	-1.33(16)	0.74(15)
Br3	59.9(4)	119.1(6)	48.7(3)	1.5(3)	24.6(3)	-25.2(4)
Br4	61.2(3)	37.5(2)	63.4(3)	-3.1(2)	4.2(2)	-8.9(2)
Cl1	26.6(4)	54.5(6)	56.7(6)	-6.9(5)	5.3(4)	6.4(4)
O1	29.6(13)	41.2(14)	34.0(13)	-12.3(11)	1.0(11)	7.0(11)
O2	41.7(16)	35.4(14)	45.4(16)	-3.5(12)	10.9(13)	-1.4(12)
O3	53(8)	62(6)	127(18)	15(8)	14(9)	3(5)
O3A	73(14)	139(15)	150(20)	49(15)	20(12)	17(10)
N1	37.3(18)	34.4(16)	40.7(18)	-6.1(14)	10.0(14)	-1.1(13)
N2	25.1(15)	38.4(17)	36.9(16)	-13.4(14)	-0.1(12)	-1.0(12)
N3	27.4(15)	37.9(16)	33.4(16)	-11.2(13)	4.0(12)	-2.0(13)
C1	32(2)	56(3)	58(3)	-24(2)	6.6(19)	-10.4(19)
C2	28.2(18)	38.4(19)	45(2)	-18.5(17)	6.2(16)	-4.6(15)
C3	38(2)	38(2)	44(2)	-17.3(17)	14.8(17)	-5.3(16)
C4	56(3)	46(2)	60(3)	-18(2)	29(2)	-14(2)
C5	81(4)	46(3)	64(3)	-7(2)	40(3)	-11(3)
C6	82(4)	48(3)	49(3)	3(2)	25(3)	1(3)

C7	54(3)	47(2)	42(2)	-3.8(19)	12(2)	2(2)
C8	27.5(19)	44(2)	43(2)	-18.7(18)	-0.4(16)	0.4(16)
C9	25.2(17)	34.7(18)	40(2)	-12.9(16)	2.9(15)	1.8(14)
C10	28.9(18)	29.5(16)	33.2(18)	-7.1(14)	1.8(14)	-0.3(13)
C11	26.6(17)	32.6(17)	34.4(18)	-5.3(14)	5.0(14)	-1.3(14)
C12	32.1(18)	28.1(16)	31.2(17)	-2.4(13)	9.1(14)	0.1(13)
C13	33.2(18)	28.1(16)	27.6(16)	-2.4(13)	4.8(14)	-5.5(13)
C14	24.1(16)	31.7(17)	28.6(16)	0.1(13)	4.2(13)	-1.5(13)
C15	27.9(17)	28.6(16)	26.1(16)	-1.9(13)	5.2(13)	1.5(13)
C16	31.6(19)	39.7(19)	37.5(19)	-13.4(16)	4.8(15)	-0.8(15)
C17	38(2)	44(2)	30.4(18)	-9.8(16)	4.8(16)	2.1(17)
C18	38(2)	43(2)	37(2)	0.2(17)	6.6(16)	0.3(17)
C19	44(2)	52(2)	33(2)	4.0(18)	7.7(17)	-2.4(19)
C20	44(2)	66(3)	40(2)	12(2)	11.2(19)	-6(2)
C21	46(3)	50(2)	52(3)	15(2)	6(2)	-13(2)
C22	48(2)	35(2)	44(2)	5.9(17)	3.7(19)	-3.2(17)
C23	35(2)	35.2(19)	40(2)	2.7(16)	3.8(16)	-0.6(15)

Table A.14: Bond Lengths for **In-2**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In1	Cl1	2.4054(10)	C2	C8	1.553(6)
In1	O1	2.101(3)	C2	C16	1.549(5)
In1	O2	2.125(3)	C3	C4	1.395(7)
In1	N1	2.297(4)	C4	C5	1.380(9)
In1	N2	2.255(3)	C5	C6	1.369(10)
In1	N3	2.240(3)	C6	C7	1.393(7)
BR_1	C12	1.899(4)	C9	C10	1.463(5)

Br2	C14	1.893(4)	C10	C11	1.401(5)
Br3	C20	1.911(5)	C10	C15	1.418(5)
Br4	C22	1.892(5)	C11	C12	1.374(5)
O1	C15	1.307(5)	C12	C13	1.388(6)
O2	C23	1.321(5)	C13	C14	1.371(5)
N1	C3	1.353(6)	C14	C15	1.415(5)
N1	C7	1.342(7)	C17	C18	1.444(6)
N2	C8	1.472(5)	C18	C19	1.418(6)
N2	C9	1.270(5)	C18	C23	1.419(6)
N3	C16	1.474(5)	C19	C20	1.361(7)
N3	C17	1.281(6)	C20	C21	1.386(8)
C1	C2	1.549(6)	C21	C22	1.380(7)
C2	C3	1.525(7)	C22	C23	1.417(6)

Table A.15: Bond Angles for **In-2**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O1	In1	Cl1	94.14(8)	C6	C5	C4	120.0(5)
O1	In1	O2	95.34(12)	C5	C6	C7	118.0(6)
O1	In1	N1	98.48(12)	N1	C7	C6	122.3(5)
O1	In1	N2	83.19(11)	N2	C8	C2	113.2(4)
O1	In1	N3	166.43(12)	N2	C9	C10	125.5(4)
O2	In1	Cl1	97.61(9)	C11	C10	C9	115.7(3)
O2	In1	N1	163.24(13)	C11	C10	C15	120.8(3)
O2	In1	N2	95.93(13)	C15	C10	C9	123.4(3)
O2	In1	N3	81.26(13)	C12	C11	C10	120.3(4)
N1	In1	Cl1	90.83(10)	C11	C12	BR_1	119.8(3)
N2	In1	Cl1	166.39(10)	C11	C12	C13	120.8(3)

N2	In1	N1	76.43(13)	C13	C12	BR_1	119.4(3)
N3	In1	Cl1	99.32(9)	C14	C13	C12	118.7(3)
N3	In1	N1	83.11(13)	C13	C14	Br2	119.1(3)
N3	In1	N2	84.10(12)	C13	C14	C15	123.7(3)
C15	O1	In1	127.3(2)	C15	C14	Br2	117.3(3)
C23	O2	In1	117.9(3)	O1	C15	C10	124.9(3)
C3	N1	In1	121.5(3)	O1	C15	C14	119.5(3)
C7	N1	In1	117.5(3)	C14	C15	C10	115.6(3)
C7	N1	C3	120.1(4)	N3	C16	C2	112.8(3)
C8	N2	In1	115.7(2)	N3	C17	C18	125.6(4)
C9	N2	In1	127.0(3)	C19	C18	C17	116.8(4)
C9	N2	C8	117.2(3)	C19	C18	C23	120.6(4)
C16	N3	In1	119.2(3)	C23	C18	C17	122.5(4)
C17	N3	In1	122.2(3)	C20	C19	C18	119.2(5)
C17	N3	C16	118.3(3)	C19	C20	Br3	119.8(4)
C1	C2	C8	105.5(4)	C19	C20	C21	122.4(4)
C1	C2	C16	105.7(3)	C21	C20	Br3	117.7(4)
C3	C2	C1	111.5(4)	C22	C21	C20	118.5(4)
C3	C2	C8	113.2(3)	C21	C22	Br4	118.9(4)
C3	C2	C16	110.3(3)	C21	C22	C23	122.6(5)
C16	C2	C8	110.3(4)	C23	C22	Br4	118.5(4)
N1	C3	C2	116.4(4)	O2	C23	C18	123.5(4)
N1	C3	C4	119.6(5)	O2	C23	C22	120.0(4)
C4	C3	C2	124.0(4)	C22	C23	C18	116.5(4)
C5	C4	C3	120.0(5)				

Table A.16: Hydrogen Bonds for **In-2**. *1-X,1-Y,1-Z

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3	H1O	O2	0.84(2)	2.26(15)	2.88(3)	130(16)
O3A	H3O	O3A*	0.85(2)	1.78(17)	2.56(7)	154(31)
O3A	H4O	O2	0.85(2)	2.4(3)	2.86(4)	112(24)

Table A.17: Hydrogen Atom Coordinates ($Å^2 \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **In-2**.

Atom	*x*	*y*	*z*	U_{eq}
H2O	6300(200)	5330(90)	4170(110)	120
H1O	5400(200)	5890(70)	4120(100)	120
H3O	5200(400)	5130(40)	4700(200)	180
H4O	4600(300)	5760(120)	4850(170)	180
H1A	9186.12	8631.17	4219.4	73
H1B	8691.15	8372.21	5053.76	73
H1C	8012.94	9091.47	4690.32	73
H4	7989.35	9314.53	3283.83	63
H5	6743.49	9886.35	2155.75	73
H6	4176.58	9525.93	1541.41	70
H7	2955.46	8565.33	2055.18	57
H8A	8486.31	7505.69	3872.43	46
H8AB	7325.79	7245.2	4501.68	46
H9	8182.6	6761.53	2972.28	40
H11	8328.27	5832.64	2119.33	37
H13	4368.48	5085.68	710.55	35
H16A	6006.63	8212.27	5248.85	43
H16B	4922.42	8727.23	4660.72	43
H17	3669.62	7754	5590.29	45
H19	1099.45	7401.69	5994.15	51

H21	-1402.51	5789.91	4933.11	59

Table A.18: Atomic Occupancy for **In-2**.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O3	0.5	H2O	0.5	H1O	0.5
O3A	0.5	H3O	0.5	H4O	0.5

A.7.3 [Rh-2][PF_6]

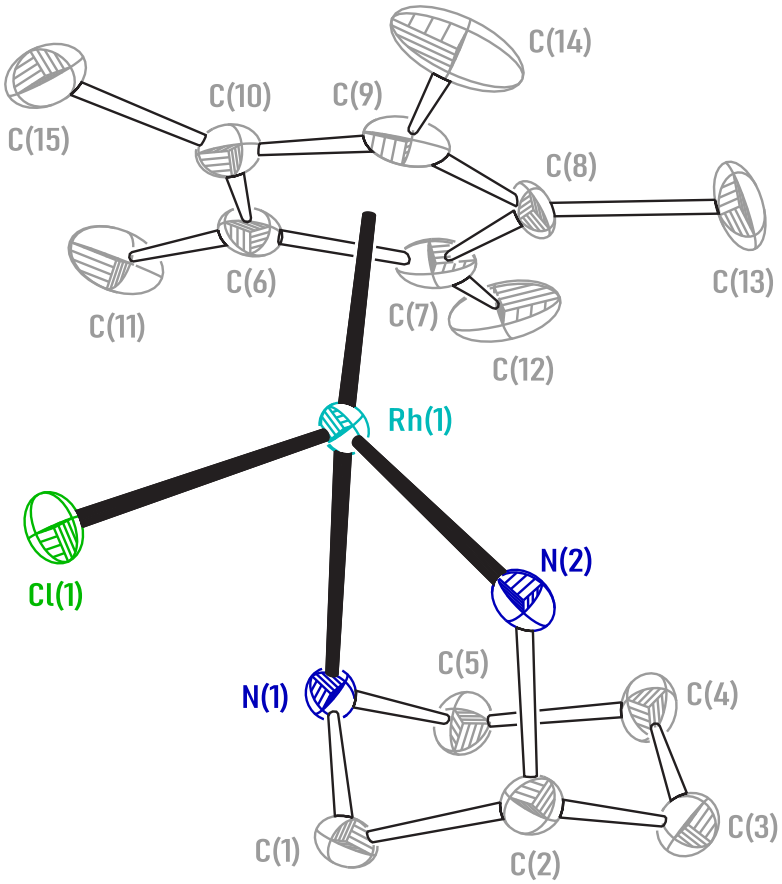


Figure A.3: Thermal ellipsoids of **[Rh-2][PF_6]** shown at 30% probability. Hydrogen atoms and PF_6^- anion omitted for clarity.

A.7.3.1 Refinement model description

1. Restrained distances

F6-F1 ≈ F6-F2 ≈ F6-F4 ≈ F6-F3 ≈ F1-F2 ≈ F1-F4 ≈ F1-F5 ≈ F2-F3 ≈ F2-F5 ≈

F4-F3 ≈ F4-F5 ≈ F3-F5 ≈ F6A-F1A ≈ F6A-F2A ≈ F6A-F4A ≈ F6A-F3A ≈ F1A-F2A ≈ F1A-F4A F1A-F5A ≈ F2A-F3A ≈ F2A-F5A ≈ F4A-F3A ≈ F4A-F5A ≈ F3A-F5A with sigma of 0.04

P1-F1 ≈ P1-F3 ≈ P1-F3 ≈ P1-F4 ≈ P1-F5 ≈ P1-F6 ≈ P1A-F1A ≈ P1A-F2A ≈ P1A-F3A P1A-F4A ≈ P1A-F5A ≈ P1A-F6A with sigma of 0.02

2. Rigid body (RIGU) restrains

P1A, F5A, F1A, F3A, F2A, F4A, F6A with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

P1, F5, F1, F3, F2, F4, F6 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

3. Others

Sof(P1A)=Sof(F1A)=Sof(F6A)=Sof(F4A)=Sof(F2A)=Sof(F5A)=Sof(F3A)=1-FVAR(1)

Sof(P1)=Sof(F1)=Sof(F2)=Sof(F3)=Sof(F4)=Sof(F5)=Sof(F6)=FVAR(1)

4.a Ternary CH refined with riding coordinates:

N1(H1), C2(H2)

4.b Secondary CH_2 refined with riding coordinates:

N2(H2A,H2B), C4(H4A,H4B), C1(H1A,H1B), C5(H5A,H5B), C3(H3A,H3B)

4.c Idealised Me refined as rotating group:

C12(H12A,H12B,H12C), C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C11(H11A,H11B,H11C), C15(H15A,H15B,H15C)

A.7.3.2 Crystallographic tables

Table A.19: Crystal data and structure refinement for **[Rh-2][PF_6]**.

Identification code	**[Rh-2][PF_6]**
Empirical formula	$C_{15}H_{28}ClF_6N_2PRh$
Formula weight	518.71

Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.5623(2)
b/Å	10.1669(2)
c/Å	22.7249(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1978.25(7)
Z	4
ρ_{calc} / g/cm^3	1.742
μ/mm^{-1}	9.528
F(000)	1048
Crystal size/mm^3	0.436×0.273×0.056
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.78 to 145.692
Index ranges	$-8 \leq h \leq 10$, $-6 \leq k \leq 12$, $-27 \leq l \leq 27$
Reflections collected	7190
Independent reflections	3841 [R_{int} = 0.0365, R_σ = 0.0400]
Data/restraints/parameters	3841/457/305
Goodness-of-fit on F^2	1.053
Final R indexes [I≥2σ (I)]	R_1 = 0.0345, wR_2 = 0.0897
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0917
Largest diff. peak/hole / e Å^{-3}	0.85/-0.63
Flack parameter	-0.024(10)

Table A.20: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Rh-2][PF$_6$]**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U_{eq}**
Rh1	5215.9(5)	8142.3(4)	5927.1(2)	21.79(15)
Cl1	5367.9(17)	6755.1(14)	5055.4(6)	32.0(3)
N2	6925(6)	9460(6)	5543(2)	30.0(11)
N1	3777(6)	9420(5)	5384(2)	28.1(11)
C9	6465(8)	7179(8)	6620(3)	39.4(18)
C8	5839(9)	8357(7)	6846(3)	35.2(15)
C4	4477(8)	11433(6)	5921(3)	40.7(15)
C6	3804(8)	7029(8)	6534(3)	36.4(16)
C1	4765(9)	9823(6)	4876(3)	34.4(14)
C10	5209(12)	6352(6)	6453(3)	42.0(17)
C5	3146(8)	10604(6)	5675(3)	37.3(15)
C3	5745(9)	11699(7)	5469(3)	41.9(16)
C7	4185(9)	8296(7)	6799(3)	39.0(16)
C12	3011(13)	9228(10)	7052(4)	74(3)
C2	6214(8)	10445(7)	5136(3)	34.2(14)
C13	6753(15)	9448(11)	7136(4)	84(4)
C14	8175(10)	6818(14)	6610(4)	77(3)
C11	2176(10)	6525(12)	6430(4)	73(3)
C15	5355(17)	4972(7)	6237(4)	79(4)
P1	9855(10)	2516(8)	6631(3)	29.7(15)
F1	8380(12)	3202(13)	6350(5)	86(4)
F2	9508(17)	1252(11)	6239(5)	64(3)
F3	11441(11)	1939(11)	6880(4)	63(3)
F4	10154(15)	3782(10)	7018(5)	66(3)

F5	10880(13)	3086(11)	6101(4)	75(3)
F6	8944(16)	1957(12)	7170(5)	86(4)
P1A	9699(17)	2381(15)	6630(7)	46(4)
F1A	7881(13)	2369(14)	6676(7)	63(4)
F6A	9750(30)	1740(20)	7244(8)	102(6)
F4A	9730(30)	3851(16)	6825(11)	95(7)
F2A	9740(30)	900(14)	6421(9)	71(5)
F5A	9660(30)	2820(20)	5977(7)	121(6)
F3A	11538(16)	2449(19)	6597(9)	78(5)

Table A.21: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Rh-2][PF_6]**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Rh1	18.3(2)	26.3(2)	20.8(2)	-1.72(15)	0.25(15)	-0.31(15)
Cl1	29.1(6)	37.7(7)	29.1(6)	-10.4(6)	2.1(5)	2.1(7)
N2	24(2)	41(3)	24(2)	-1(2)	-1(2)	-1(2)
N1	25(2)	27(2)	32(3)	1(2)	-8(2)	-1(2)
C9	31(3)	60(5)	28(3)	17(3)	1(3)	9(3)
C8	51(4)	38(4)	16(3)	-2(3)	-9(3)	-19(3)
C4	44(4)	29(3)	49(4)	-7(3)	-5(4)	2(3)
C6	34(3)	46(4)	30(3)	14(3)	-6(3)	-11(3)
C1	38(3)	39(3)	26(3)	6(2)	-8(3)	-3(3)
C10	64(5)	31(3)	31(3)	6(2)	-5(4)	1(4)
C5	34(3)	30(3)	48(4)	-1(3)	-3(3)	5(3)
C3	42(4)	35(3)	49(4)	8(3)	-10(3)	-7(3)
C7	47(4)	47(4)	22(3)	10(3)	18(3)	17(3)
C12	92(8)	74(6)	58(5)	31(5)	47(6)	39(6)

C2	30(3)	39(3)	33(3)	7(3)	0(3)	-10(3)
C13	126(10)	89(7)	35(4)	0(5)	-26(5)	-69(7)
C14	33(4)	152(10)	46(5)	19(6)	-3(4)	29(6)
C11	41(5)	118(9)	58(5)	38(6)	-13(4)	-38(5)
C15	159(12)	33(3)	45(4)	3(3)	-15(7)	16(6)
P1	37(3)	27(2)	25(2)	-1.7(15)	0.6(19)	5.2(19)
F1	66(6)	102(7)	88(7)	-23(6)	-29(5)	42(6)
F2	72(7)	60(5)	62(6)	-32(5)	0(5)	8(5)
F3	71(5)	71(6)	48(5)	-2(4)	-12(4)	33(5)
F4	62(6)	54(5)	81(6)	-34(4)	-21(5)	17(4)
F5	82(6)	86(6)	57(5)	27(5)	16(4)	4(5)
F6	102(8)	84(6)	72(6)	-6(5)	48(6)	-13(6)
P1A	40(5)	49(6)	49(6)	-3(4)	3(4)	6(4)
F1A	39(6)	60(8)	92(10)	-17(7)	-2(5)	6(5)
F6A	89(12)	138(12)	79(8)	25(7)	-20(7)	-10(10)
F4A	74(12)	52(7)	158(16)	-22(8)	10(11)	2(7)
F2A	55(9)	56(7)	102(12)	-5(6)	7(9)	1(6)
F5A	129(14)	152(13)	82(8)	36(8)	3(8)	-9(11)
F3A	48(6)	87(11)	98(12)	-32(9)	14(6)	-4(6)

Table A.22: Bond Lengths for **[Rh-2][PF_6]**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rh1	Cl1	2.4352(14)	C6	C7	1.460(11)
Rh1	N2	2.167(5)	C6	C11	1.504(10)
Rh1	N1	2.175(5)	C1	C2	1.513(9)
Rh1	C9	2.140(7)	C10	C15	1.492(10)
Rh1	C8	2.167(6)	C3	C2	1.536(10)

Rh1	C6	2.155(7)	C7	C12	1.495(10)
Rh1	C10	2.178(6)	P1	F1	1.578(10)
Rh1	C7	2.176(6)	P1	F2	1.592(11)
N2	C2	1.493(8)	P1	F3	1.584(10)
N1	C1	1.489(8)	P1	F4	1.579(9)
N1	C5	1.476(8)	P1	F5	1.599(10)
C9	C8	1.410(10)	P1	F6	1.560(10)
C9	C10	1.416(12)	P1A	F1A	1.561(14)
C9	C14	1.510(10)	P1A	F6A	1.540(16)
C8	C7	1.421(10)	P1A	F4A	1.559(15)
C8	C13	1.509(10)	P1A	F2A	1.579(16)
C4	C5	1.524(9)	P1A	F5A	1.552(15)
C4	C3	1.519(11)	P1A	F3A	1.578(15)
C6	C10	1.398(12)			

Table A.23: Bond Angles for **[Rh-2][PF_6]**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Rh1	Cl1	89.66(15)	C11	C6	Rh1	126.7(5)
N2	Rh1	N1	77.6(2)	N1	C1	C2	106.1(5)
N2	Rh1	C10	137.7(3)	C9	C10	Rh1	69.4(4)
N2	Rh1	C7	126.6(3)	C9	C10	C15	125.6(10)
N1	Rh1	Cl1	85.09(14)	C6	C10	Rh1	70.3(4)
N1	Rh1	C10	144.0(3)	C6	C10	C9	109.0(6)
N1	Rh1	C7	104.2(2)	C6	C10	C15	125.3(10)
C9	Rh1	Cl1	107.9(2)	C15	C10	Rh1	127.2(5)
C9	Rh1	N2	104.0(2)	N1	C5	C4	110.0(5)
C9	Rh1	N1	166.9(2)	C4	C3	C2	111.9(5)

C9	Rh1	C8	38.2(3)	C8	C7	Rh1	70.6(4)
C9	Rh1	C6	64.5(2)	C8	C7	C6	107.0(6)
C9	Rh1	C10	38.3(3)	C8	C7	C12	127.8(9)
C9	Rh1	C7	64.2(3)	C6	C7	Rh1	69.6(4)
C8	Rh1	Cl1	146.0(2)	C6	C7	C12	124.6(8)
C8	Rh1	N2	99.2(2)	C12	C7	Rh1	131.9(5)
C8	Rh1	N1	128.8(2)	N2	C2	C1	107.2(5)
C8	Rh1	C10	63.6(2)	N2	C2	C3	111.0(5)
C8	Rh1	C7	38.2(3)	C1	C2	C3	109.0(6)
C6	Rh1	Cl1	104.3(2)	F1	P1	F2	88.9(7)
C6	Rh1	N2	164.0(2)	F1	P1	F3	174.2(9)
C6	Rh1	N1	111.1(2)	F1	P1	F4	89.7(7)
C6	Rh1	C8	64.8(2)	F1	P1	F5	88.6(7)
C6	Rh1	C10	37.6(3)	F2	P1	F5	88.5(7)
C6	Rh1	C7	39.4(3)	F3	P1	F2	93.5(7)
C10	Rh1	Cl1	87.87(18)	F3	P1	F5	86.2(6)
C7	Rh1	Cl1	143.6(2)	F4	P1	F2	178.5(8)
C7	Rh1	C10	63.8(3)	F4	P1	F3	87.9(7)
C2	N2	Rh1	112.9(4)	F4	P1	F5	92.0(7)
C1	N1	Rh1	106.4(4)	F6	P1	F1	94.5(8)
C5	N1	Rh1	116.1(4)	F6	P1	F2	92.9(8)
C5	N1	C1	109.3(5)	F6	P1	F3	90.7(7)
C8	C9	Rh1	71.9(4)	F6	P1	F4	86.6(7)
C8	C9	C10	108.3(6)	F6	P1	F5	176.7(9)
C8	C9	C14	125.5(9)	F1A	P1A	F2A	91.9(11)
C10	C9	Rh1	72.3(4)	F1A	P1A	F3A	177.7(14)
C10	C9	C14	126.0(9)	F6A	P1A	F1A	88.1(11)

C14	C9	Rh1	125.8(6)	F6A	P1A	F4A	98.6(14)
C9	C8	Rh1	69.9(4)	F6A	P1A	F2A	82.4(12)
C9	C8	C7	108.3(6)	F6A	P1A	F5A	171.8(15)
C9	C8	C13	125.9(9)	F6A	P1A	F3A	91.9(12)
C7	C8	Rh1	71.2(4)	F4A	P1A	F1A	90.4(12)
C7	C8	C13	125.6(9)	F4A	P1A	F2A	177.5(15)
C13	C8	Rh1	128.5(5)	F4A	P1A	F3A	87.4(12)
C3	C4	C5	112.6(6)	F5A	P1A	F1A	92.5(12)
C10	C6	Rh1	72.1(4)	F5A	P1A	F4A	89.6(13)
C10	C6	C7	107.2(6)	F5A	P1A	F2A	89.4(12)
C10	C6	C11	127.6(8)	F5A	P1A	F3A	87.9(12)
C7	C6	Rh1	71.1(4)	F3A	P1A	F2A	90.4(12)
C7	C6	C11	124.9(8)				

Table A.24: Hydrogen Atom Coordinates ($Å^2 \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Rh-2][PF_6]**.

Atom	***x***	***y***	***z***	**U_{eq}**
H2A	7422.12	9881.93	5830.2	36
H2B	7627.25	8987.65	5346.01	36
H1	2897.81	8902.91	5233.06	34
H4A	4060.65	12264.87	6059.49	49
H4B	4932.54	10981.76	6255.7	49
H1A	4213.33	10448.68	4629.71	41
H1B	5040.92	9063.99	4638.61	41
H5A	2450.75	10345.66	5991.26	45
H5B	2551.55	11117.81	5393.6	45
H3A	6655.79	12058.04	5665.81	50
H3B	5374.64	12350.1	5189.95	50

H12A	3364.99	10115.46	6996.85	112
H12B	2888.2	9055.99	7464.76	112
H12C	2027.3	9110.53	6856.42	112
H2	6953.97	10663.57	4821.53	41
H13A	7767.94	9508.7	6958.91	125
H13B	6863.79	9263.1	7548.62	125
H13C	6209.45	10266.17	7086.33	125
H14A	8363.95	6200.58	6298.45	116
H14B	8458.68	6427.81	6979.83	116
H14C	8788.92	7594.41	6546.23	116
H11A	1529.61	7229.3	6288.13	109
H11B	1754.11	6193.06	6791.93	109
H11C	2203.56	5832.87	6142.89	109
H15A	4611.44	4824.16	5928	119
H15B	5156.97	4373.53	6554.89	119
H15C	6391.95	4831.83	6088.7	119

Table A.25: Atomic Occupancy for **[Rh-2][PF_6]**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
P1	0.610(13)	F1	0.610(13)	F2	0.610(13)
F3	0.610(13)	F4	0.610(13)	F5	0.610(13)
F6	0.610(13)	P1A	0.390(13)	F1A	0.390(13)
F6A	0.390(13)	F4A	0.390(13)	F2A	0.390(13)
F5A	0.390(13)	F3A	0.390(13)		

A.7.4 [Ru-2][PF_6]

Note: Structure solved and refined by Dr Benson Kariuki.

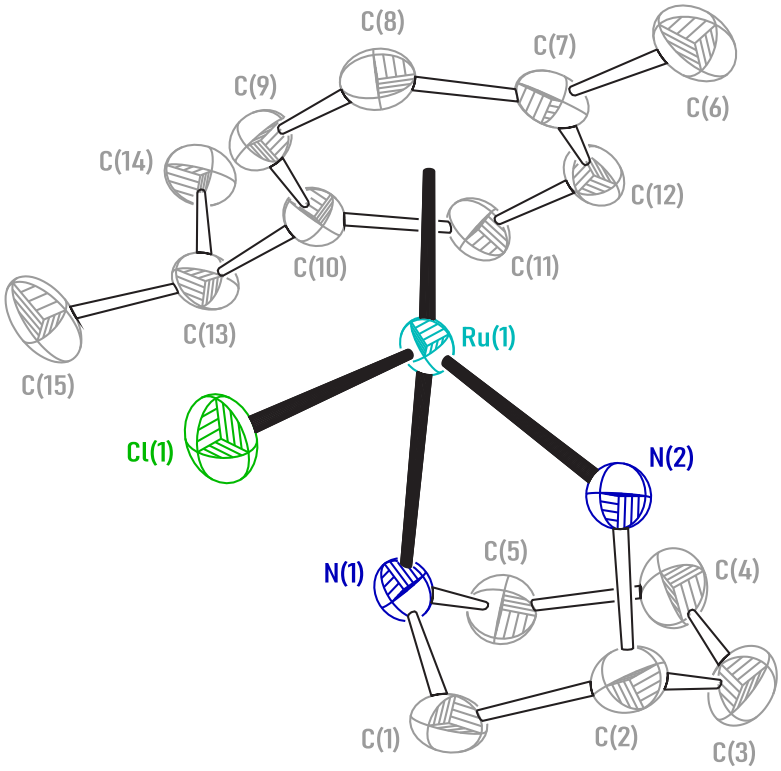


Figure A.4: Thermal ellipsoids of **[Ru-2][PF_6]** shown at 30% probability. Hydrogen atoms and PF_6^- anion omitted for clarity.

A.7.4.1 Refinement model description

1. U_{iso}/U_{aniso} restraints and constraints

P1 ≈ F1 ≈ F2 ≈ F3 ≈ F4 ≈ F5 ≈ F6 ≈ P1A ≈ F1A ≈ F2A ≈ F3A ≈ F4A ≈ F5A ≈ F6A: within 2Å with sigma of 0.01 and sigma for terminal atoms of 0.02 within 2Å

U_{anis}(P1) ≈ U_{eq}, U_{anis}(F1) ≈ U_{eq}, U_{anis}(F2) ≈ U_{eq}, U_{anis}(F3) ≈ U_{eq}, U_{anis}(F4) ≈ U_{eq}, U_{anis}(F5) ≈ U_{eq}, U_{anis}(F6) ≈ U_{eq}, U_{anis}(P1A) ≈ U_{eq}, U_{anis}(F1A) ≈ U_{eq}, U_{anis}(F2A) ≈ U_{eq}, U_{anis}(F3A) ≈ U_{eq}, U_{anis}(F4A) ≈ U_{eq}, U_{anis}(F5A) ≈ U_{eq}, U_{anis}(F6A) ≈ U_{eq}: with sigma of 0.01 and sigma for terminal atoms of 0.02

2. Same fragment restrains

P1, F1, F2, F3, F4, F5, F6 sigma for 1-2: 0.01, 1-3: 0.04 as in P1A, F1A, F2A, F3A, F4A, F5A, F6A

3. Others

Sof(P1A)=Sof(F1A)=Sof(F2A)=Sof(F3A)=Sof(F4A)=Sof(F5A)=Sof(F6A)=1-FVAR(1)

Sof(P1)=Sof(F1)=Sof(F2)=Sof(F3)=Sof(F4)=Sof(F5)=Sof(F6)=FVAR(1)

4.a Ternary CH refined with riding coordinates:

C2(H2), C13(H13), N1(H1)

4.b Secondary CH_2 refined with riding coordinates:

C1(H1A,H1B), C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B), N2(H2A,H2B)

4.c Aromatic/amide H refined with riding coordinates:

C8(H8), C9(H9), C11(H11), C12(H12)

4.d Idealised Me refined as rotating group:

C6(H6A,H6B,H6C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)

A.7.4.2 Crystallographic tables

Table A.26: Crystal data and structure refinement for **[Ru-2][PF_6]**.

Identification code	**[Ru-2][PF_6]**
Empirical formula	$C_{15}H_{26}N_2ClRuPF_6$
Formula weight	515.87
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.3999(4)
b/Å	11.5477(5)
c/Å	16.4273(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1972.84(15)

Z	4
ρ_{calc} / g/cm^3	1.737
μ/mm^{-1}	1.067
F(000)	1040
Crystal size/mm^3	0.54×0.15×0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.058 to 59.764
Index ranges	$-13 \leq h \leq 14$, $-15 \leq k \leq 15$, $-20 \leq l \leq 22$
Reflections collected	17082
Independent reflections	4991 [R_{int} = 0.0333, R_σ = 0.0375]
Data/restraints/parameters	4991/357/302
Goodness-of-fit on F^2	1.042
Final R indexes [I≥2σ (I)]	R_1 = 0.0327, wR_2 = 0.0611
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.0665
Largest diff. peak/hole / e Å^{-3}	0.50/-0.37
Flack parameter	-0.044(16)

Table A.27: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **[Ru-2][PF$_6$]**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U_{eq}**
C1	7432(5)	5998(5)	5792(4)	64.6(16)
C2	6010(5)	6024(6)	5606(4)	67.4(17)
C3	5726(6)	5363(7)	4830(4)	86(2)
C4	6305(5)	4151(7)	4836(3)	76.3(17)
C5	7654(5)	4113(7)	5161(3)	63.7(14)
C6	3493(5)	3716(4)	7531(4)	62.7(14)
C7	4836(4)	3236(4)	7415(3)	46.2(11)

C8	5765(4)	3352(4)	8014(3)	47.1(11)
C9	7051(5)	2981(4)	7881(3)	47.5(12)
C10	7436(4)	2500(4)	7139(3)	43.0(11)
C11	6464(5)	2358(4)	6541(3)	45.9(10)
C12	5200(4)	2715(4)	6677(3)	46.2(12)
C13	8825(4)	2158(4)	6955(4)	51.8(12)
C14	8968(4)	854(5)	7020(3)	59.2(13)
C15	9796(5)	2787(5)	7485(5)	80(2)
N1	7745(3)	4769(4)	5945(3)	51.1(10)
N2	5371(4)	5480(3)	6329(2)	48.5(10)
Cl1	7289.5(13)	5715.5(12)	7731.6(9)	62.3(4)
Ru1	6489.3(3)	4159.2(3)	6911.8(2)	35.13(9)
P1	1581(2)	5300(2)	5281.7(14)	50.1(5)
F1	797(5)	4550(5)	5901(4)	102.9(18)
F2	2595(4)	4292(5)	5130(4)	93.1(15)
F3	2462(4)	5750(6)	5991(3)	94.7(16)
F4	2364(5)	6089(5)	4673(4)	110.2(19)
F5	581(5)	6290(4)	5417(4)	106.3(18)
F6	730(5)	4830(6)	4563(3)	111.5(19)
P1A	1489(14)	5229(14)	5294(10)	82(4)
F1A	650(20)	5360(30)	6074(12)	93(6)
F2A	2588(18)	4500(20)	5719(17)	97(6)
F3A	2260(20)	6357(17)	5515(17)	98(6)
F4A	2270(20)	5160(20)	4478(12)	90(5)
F5A	436(19)	5960(20)	4848(16)	96(6)
F6A	728(18)	4087(17)	5083(16)	82(5)

Table A.28: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Ru-2][PF_6]**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	50(3)	67(4)	77(4)	28(3)	6(3)	-10(3)
C2	53(3)	73(4)	77(4)	32(3)	3(3)	4(3)
C3	56(3)	139(7)	61(4)	41(4)	-2(3)	5(4)
C4	65(3)	130(5)	34(2)	0(4)	1(2)	-12(5)
C5	52(3)	92(4)	47(3)	5(3)	14(2)	2(4)
C6	42(2)	59(3)	87(4)	7(3)	15(3)	3(3)
C7	40(2)	37(2)	61(3)	3(2)	13(2)	-5(2)
C8	55(3)	46(3)	41(3)	1(2)	10(2)	1(2)
C9	48(2)	52(3)	42(3)	10(2)	-3(2)	2(2)
C10	39(2)	34(2)	56(3)	2(2)	3.0(19)	3.9(19)
C11	44(2)	41(2)	54(3)	-11(2)	5(2)	-6(2)
C12	41(2)	42(2)	56(3)	-1(2)	-2(2)	-11(2)
C13	39(2)	44(2)	73(3)	10(3)	8(2)	4.2(18)
C14	50(2)	51(3)	77(4)	4(3)	14(2)	9(2)
C15	39(3)	59(4)	143(6)	-4(4)	-7(3)	1(3)
N1	31.3(19)	67(3)	55(3)	11(2)	1.6(17)	-2.8(19)
N2	37.2(19)	50(2)	58(3)	10.7(19)	-0.8(18)	2.9(18)
Cl1	62.3(7)	50.3(7)	74.2(9)	-12.3(7)	-15.4(6)	-7.6(7)
Ru1	29.19(14)	36.92(16)	39.27(17)	-0.86(16)	-0.44(14)	-1.01(15)
P1	36.9(9)	67.5(11)	45.8(10)	-4.7(9)	-1.4(9)	5.0(9)
F1	76(3)	116(4)	117(4)	36(3)	16(3)	-17(3)
F2	75(3)	89(3)	116(4)	-24(3)	4(3)	27(3)
F3	72(2)	131(4)	81(3)	-33(3)	-19(2)	-10(3)
F4	105(3)	113(4)	112(4)	40(3)	33(3)	6(3)

F5	83(3)	102(4)	134(5)	-15(3)	10(3)	44(3)
F6	98(3)	155(5)	82(3)	-39(3)	-31(3)	12(4)
P1A	63(6)	101(6)	81(6)	-11(6)	2(6)	-1(6)
F1A	74(9)	122(11)	84(10)	-17(10)	12(9)	-7(10)
F2A	81(9)	107(10)	101(10)	19(10)	-18(9)	9(9)
F3A	97(10)	94(10)	103(10)	-8(10)	-6(10)	-16(9)
F4A	86(9)	106(10)	77(9)	-5(9)	17(9)	3(10)
F5A	81(10)	112(11)	94(11)	12(11)	-20(10)	11(10)
F6A	73(9)	80(9)	92(10)	-17(9)	-1(9)	-1(9)

Table A.29: Bond Lengths for **[Ru-2][PF_6]**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.511(7)	C11	Ru1	2.167(4)
C1	N1	1.477(7)	C12	Ru1	2.174(4)
C2	C3	1.514(9)	C13	C14	1.517(7)
C2	N2	1.499(6)	C13	C15	1.518(7)
C3	C4	1.524(9)	N1	Ru1	2.173(4)
C4	C5	1.502(7)	N2	Ru1	2.144(4)
C5	N1	1.496(7)	Cl1	Ru1	2.3950(13)
C6	C7	1.515(6)	P1	F1	1.565(5)
C7	C8	1.385(7)	P1	F2	1.590(5)
C7	C12	1.404(7)	P1	F3	1.571(4)
C7	Ru1	2.186(4)	P1	F4	1.579(5)
C8	C9	1.421(6)	P1	F5	1.561(4)
C8	Ru1	2.171(5)	P1	F6	1.573(5)
C9	C10	1.399(7)	P1A	F1A	1.559(12)
C9	Ru1	2.175(5)	P1A	F2A	1.582(12)

C10	C11	1.419(6)	P1A	F3A	1.572(12)
C10	C13	1.527(6)	P1A	F4A	1.571(12)
C10	Ru1	2.187(4)	P1A	F5A	1.563(12)
C11	C12	1.396(6)	P1A	F6A	1.576(12)

Table A.30: Bond Angles for **[Ru-2][PF_6]**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	105.6(5)	C11	Ru1	C9	66.97(19)
C1	C2	C3	110.6(5)	C11	Ru1	C10	38.05(17)
N2	C2	C1	105.4(4)	C11	Ru1	C12	37.51(17)
N2	C2	C3	111.6(5)	C11	Ru1	N1	96.49(17)
C2	C3	C4	112.3(5)	C11	Ru1	Cl1	151.93(13)
C5	C4	C3	113.5(6)	C12	Ru1	C7	37.58(18)
N1	C5	C4	110.5(4)	C12	Ru1	C9	79.39(19)
C6	C7	Ru1	126.5(3)	C12	Ru1	C10	68.66(17)
C8	C7	C6	121.2(5)	C12	Ru1	Cl1	152.80(13)
C8	C7	C12	117.8(4)	N1	Ru1	C7	155.10(18)
C8	C7	Ru1	70.9(3)	N1	Ru1	C9	125.21(16)
C12	C7	C6	120.9(5)	N1	Ru1	C10	97.93(16)
C12	C7	Ru1	70.8(3)	N1	Ru1	C12	119.32(17)
C7	C8	C9	121.3(5)	N1	Ru1	Cl1	87.65(12)
C7	C8	Ru1	72.0(3)	N2	Ru1	C7	95.13(17)
C9	C8	Ru1	71.1(3)	N2	Ru1	C8	119.33(16)
C8	C9	Ru1	70.8(3)	N2	Ru1	C9	156.65(16)
C10	C9	C8	121.5(5)	N2	Ru1	C10	160.74(16)
C10	C9	Ru1	71.8(3)	N2	Ru1	C11	123.40(17)
C9	C10	C11	116.4(4)	N2	Ru1	C12	97.58(17)

C9	C10	C13	123.1(4)	N2	Ru1	N1	76.63(15)
C9	C10	Ru1	70.8(3)	N2	Ru1	Cl1	84.59(12)
C11	C10	C13	120.5(4)	F1	P1	F2	92.4(3)
C11	C10	Ru1	70.2(3)	F1	P1	F3	90.3(3)
C13	C10	Ru1	128.2(3)	F1	P1	F4	178.4(4)
C10	C11	Ru1	71.7(2)	F1	P1	F6	90.2(3)
C12	C11	C10	121.8(4)	F3	P1	F2	88.4(3)
C12	C11	Ru1	71.5(3)	F3	P1	F4	88.8(3)
C7	C12	Ru1	71.6(3)	F3	P1	F6	178.5(3)
C11	C12	C7	121.2(4)	F4	P1	F2	88.9(3)
C11	C12	Ru1	71.0(2)	F5	P1	F1	88.0(3)
C14	C13	C10	109.6(4)	F5	P1	F2	179.2(4)
C14	C13	C15	111.7(4)	F5	P1	F3	92.3(3)
C15	C13	C10	113.1(4)	F5	P1	F4	90.7(3)
C1	N1	C5	109.0(4)	F5	P1	F6	89.1(3)
C1	N1	Ru1	107.7(3)	F6	P1	F2	90.1(3)
C5	N1	Ru1	115.3(3)	F6	P1	F4	90.7(4)
C2	N2	Ru1	114.3(3)	F1A	P1A	F2A	95.4(12)
C7	Ru1	C10	82.08(17)	F1A	P1A	F3A	90.9(12)
C7	Ru1	Cl1	115.28(14)	F1A	P1A	F4A	176.0(14)
C8	Ru1	C7	37.07(19)	F1A	P1A	F5A	86.6(11)
C8	Ru1	C9	38.18(16)	F1A	P1A	F6A	88.8(11)
C8	Ru1	C10	68.76(17)	F3A	P1A	F2A	88.2(11)
C8	Ru1	C12	66.68(18)	F3A	P1A	F6A	179.0(14)
C8	Ru1	N1	163.14(16)	F4A	P1A	F2A	88.6(11)
C8	Ru1	Cl1	88.52(13)	F4A	P1A	F3A	88.5(11)
C9	Ru1	C7	68.24(19)	F4A	P1A	F6A	91.8(12)

C9	Ru1	C10	37.42(17)	F5A	P1A	F2A	178.0(13)
C9	Ru1	Cl1	87.95(14)	F5A	P1A	F3A	91.2(12)
C10	Ru1	Cl1	113.90(13)	F5A	P1A	F4A	89.4(11)
C11	Ru1	C7	68.18(18)	F5A	P1A	F6A	89.8(11)
C11	Ru1	C8	79.51(18)	F6A	P1A	F2A	90.9(11)

Table A.31: Hydrogen Atom Coordinates ($Å^2 \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Ru-2][PF$_6$]**.

Atom	***x***	***y***	***z***	**U_{eq}**
H1A	7923.92	6292.16	5334.64	77
H1B	7623.01	6465.15	6267.61	77
H2	5722.5	6827.94	5548.63	81
H3A	6066.57	5790.53	4370.15	103
H3B	4801.6	5304.12	4761.24	103
H4A	5766.53	3649.78	5165.56	92
H4B	6302.6	3848.84	4285.35	92
H5A	7907.08	3314.64	5250.33	76
H5B	8237.61	4448.6	4765.75	76
H6A	2948.71	3126.38	7757.78	94
H6B	3154.81	3958.91	7015.36	94
H6C	3524.63	4365.63	7895.21	94
H8	5542.57	3678.44	8511.46	56
H9	7650.45	3060.37	8297.83	57
H11	6674.09	2018.65	6045.24	55
H12	4586.77	2606.64	6272.18	55
H13	9000.72	2371.71	6388.74	62
H14A	8728.09	607.86	7557.61	89
H14B	9845.53	642.53	6917.58	89

H14C	8420.06	486.2	6627.36	89
H15A	9619.01	3602.91	7475.56	121
H15B	10646.7	2649.42	7280.24	121
H15C	9735.27	2506.74	8033.7	121
H1	8634.4	4725.16	6138.79	61
H2A	4626.49	5174.29	6170.4	58
H2B	5197.24	6031.29	6691.14	58

Table A.32: Atomic Occupancy for **[Ru-2][PF_6]**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
P1	0.845(5)	F1	0.845(5)	F2	0.845(5)
F3	0.845(5)	F4	0.845(5)	F5	0.845(5)
F6	0.845(5)	P1A	0.155(5)	F1A	0.155(5)
F2A	0.155(5)	F3A	0.155(5)	F4A	0.155(5)
F5A	0.155(5)	F6A	0.155(5)		

A.7.5 [Rh-4][PF_6]$_2$

Note: Structure solved and refined by Dr Benson Kariuki.

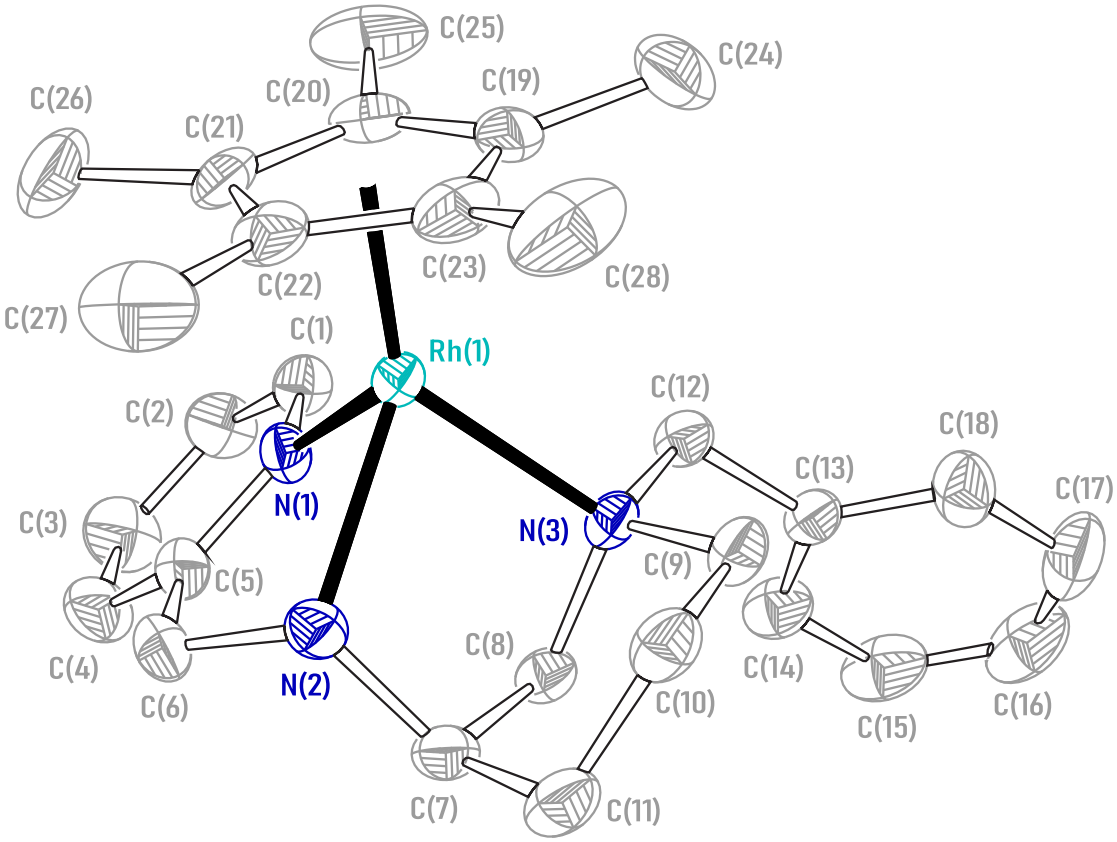


Figure A.5: Thermal ellipsoids of **[Rh-4][PF_6]$_2$** shown at 30% probability. Hydrogen atoms and PF_6^- anions omitted for clarity.

A.7.5.1 Refinement model description

1. U_{iso}/U_{aniso} restraints and constraints

P1 ≈ F1 ≈ F2 ≈ F3 ≈ F4 ≈ F5 ≈ F6 ≈ P1A ≈ F1A ≈ F2A ≈ F3A ≈ F4A ≈ F5A ≈ F6A: within 2Å with sigma of 0.01 and sigma for terminal atoms of 0.02 within 2Å

P2 ≈ F7 ≈ F8 ≈ F9 ≈ F10 ≈ F11 ≈ F12 ≈ P2A ≈ F7A ≈ F8A ≈ F9A ≈ F10A ≈ F11A ≈ F12A: within 2Å with sigma of 0.01 and sigma for terminal atoms of 0.02 within 2Å

U_{anis}(P1) ≈ U_{eq}, U_{anis}(F1) ≈ U_{eq}, U_{anis}(F2) ≈ U_{eq}, U_{anis}(F3) ≈ U_{eq}, U_{anis}(F4) ≈ U_{eq}, U_{anis}(F5) ≈ U_{eq}, U_{anis}(F6) ≈ U_{eq}, U_{anis}(P1A) ≈ U_{eq}, U_{anis}(F1A) ≈ U_{eq}, U_{anis}(F2A) ≈ U_{eq}, U_{anis}(F3A) ≈ U_{eq}, U_{anis}(F4A) ≈ U_{eq}, U_{anis}(F5A) ≈ U_{eq}, U_{anis}(F6A) ≈ U_{eq}: with sigma of 0.01 and sigma for terminal atoms of 0.02

U_{anis}(P2) ≈ U_{eq}, U_{anis}(F7) ≈ U_{eq}, U_{anis}(F8) ≈ U_{eq}, U_{anis}(F9) ≈ U_{eq}, U_{anis}(F10) ≈ U_{eq}, U_{anis}(F11) ≈ U_{eq}, U_{anis}(F12) ≈ U_{eq}, U_{anis}(P2A) ≈ U_{eq}, U_{anis}(F7A) ≈ U_{eq}, U_{anis}(F8A) ≈ U_{eq}, U_{anis}(F9A) ≈ U_{eq}, U_{anis}(F10A) ≈ U_{eq}, U_{anis}(F11A) ≈ U_{eq}, U_{anis}(F12A) ≈ U_{eq}: with sigma of 0.01 and sigma for terminal atoms of 0.02

2. Same fragment restrains

P1, F1, F2, F3, F4, F5, F6 sigma for 1-2: 0.01, 1-3: 0.04 as in P2A, F7A, F8A, F9A, F10A, F11A, F12A

P1, F1, F2, F3, F4, F5, F6 sigma for 1-2: 0.01, 1-3: 0.04 as in P2, F7, F8, F9, F10, F11, F12

P1, F1, F2, F3, F4, F5, F6 sigma for 1-2: 0.01, 1-3: 0.04 as in P1A, F1A, F2A, F3A, F4A, F5A, F6A

3. Others

Sof(P1A)=Sof(F1A)=Sof(F2A)=Sof(F3A)=Sof(F4A)=Sof(F5A)=Sof(F6A)=1-FVAR(1)

Sof(P1)=Sof(F1)=Sof(F2)=Sof(F3)=Sof(F4)=Sof(F5)=Sof(F6)=FVAR(1)

Sof(P2A)=Sof(F7A)=Sof(F8A)=Sof(F9A)=Sof(F10A)=Sof(F11A)=Sof(F12A)=1-FVAR(2)

Sof(P2)=Sof(F7)=Sof(F8)=Sof(F9)=Sof(F10)=Sof(F11)=Sof(F12)=FVAR(2)

4.a Ternary CH refined with riding coordinates:

C7(H7), N2(H2A)

4.b Secondary CH_2 refined with riding coordinates: C6(H6A,H6B), C8(H8A,H8B), C9(H9A,H9B), C10(H10A,H10B), C11(H11A,H11B), C12(H12A,H12B)

4.c Aromatic/amide H refined with riding coordinates: C1(H1), C2(H2), C3(H3), C4(H4), C14(H14), C15(H15), C16(H16), C17(H17), C18(H18)

4.d Idealised Me refined as rotating group: C24(H24A,H24B,H24C), C25(H25A,H25B,H25C), C26(H26A,H26B,H26C), C27(H27A,H27B, H27C),

C28(H28A,H28B,H28C)

A.7.5.2 Crystallographic tables

Table A.33: Crystal data and structure refinement for **[Rh-4][PF_6]$_2$**.

Identification code	**[Rh-4][PF_6]$_2$**
Empirical formula	$C_{28}H_{38}N_3F_{12}P_2Rh$
Formula weight	809.46
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.4970(3)
b/Å	13.7928(3)
c/Å	21.0676(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3340.81(15)
Z	4
ρ_{calc} / g/cm^3	1.609
μ/mm^{-1}	5.878
F(000)	1640
Crystal size/mm^3	0.17×0.09×0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.662 to 145.81
Index ranges	$-11 \leq h \leq 14$, $-16 \leq k \leq 16$, $-26 \leq l \leq 25$
Reflections collected	12592
Independent reflections	6497 [R_{int} = 0.0290, R_σ = 0.0401]

Data/restraints/parameters	6497/750/549
Goodness-of-fit on F^2	1.024
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0312, wR_2 = 0.0784
Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0820
Largest diff. peak/hole / e Å^{-3}	0.40/-0.40
Flack parameter	-0.008(5)

Table A.34: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **[Rh-4][PF$_6$]$_2$**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U_{eq}**
C1	9660(4)	5565(4)	4380(3)	47.9(11)
C2	10316(5)	5497(6)	4917(3)	65.3(16)
C3	9834(6)	5104(7)	5454(3)	80(2)
C4	8696(6)	4776(6)	5441(3)	67.6(17)
C5	8078(5)	4858(4)	4888(3)	48.3(12)
C6	6855(5)	4494(4)	4820(3)	52.2(14)
C7	5773(4)	5972(4)	4488(3)	48.3(12)
C8	6665(4)	6748(3)	4334(2)	43.3(10)
C9	5939(4)	6907(4)	3267(3)	47.9(11)
C10	4909(4)	6256(4)	3411(3)	53.2(13)
C11	4672(5)	6185(4)	4120(3)	56.9(14)
C12	7985(4)	7309(3)	3493(3)	43.2(10)
C13	7814(4)	8385(3)	3583(3)	44.9(11)
C14	8117(5)	8802(4)	4160(3)	61.2(15)
C15	8034(7)	9787(5)	4249(5)	83(2)
C16	7666(8)	10371(5)	3768(6)	95(3)
C17	7354(7)	9978(5)	3195(5)	92(3)

C18	7438(7)	8969(4)	3101(3)	64.7(14)
C19	8005(6)	5078(4)	2530(3)	55.6(14)
C20	8863(5)	4617(4)	2896(3)	53.7(13)
C21	8348(5)	3819(4)	3225(3)	51.7(13)
C22	7168(5)	3783(4)	3045(3)	53.8(14)
C23	6933(5)	4572(5)	2624(3)	57.8(15)
C24	8207(11)	5865(6)	2076(3)	101(3)
C25	10134(6)	4838(8)	2882(5)	100(3)
C26	8968(8)	3094(5)	3637(5)	91(3)
C27	6324(8)	3014(6)	3254(5)	101(3)
C28	5847(8)	4695(8)	2246(4)	103(3)
N1	8548(4)	5235(3)	4360(2)	42.0(9)
N2	6252(4)	5003(3)	4297(2)	43.5(10)
N3	6984(3)	6656(3)	3654(2)	38.5(8)
Rh1	7507.9(3)	5130.9(2)	3538.8(2)	34.31(11)
P1	8358(10)	2712(8)	1308(5)	52(2)
F1	7431(14)	2717(13)	1865(7)	71(4)
F2	9334(11)	2327(16)	1766(7)	87(4)
F3	9264(16)	2705(16)	739(8)	73(5)
F4	7397(15)	3067(13)	831(9)	100(4)
F5	8011(14)	1628(9)	1143(9)	71(4)
F6	8680(17)	3788(10)	1464(10)	91(4)
P1A	8326(8)	2794(6)	1279(4)	51.5(18)
F1A	7222(12)	2930(11)	1720(7)	83(4)
F2A	9172(11)	2813(14)	1864(5)	101(4)
F3A	9421(11)	2647(11)	830(7)	71(3)
F4A	7492(10)	2775(10)	687(5)	80(3)

F5A	8210(13)	1652(6)	1342(8)	79(3)
F6A	8414(12)	3921(6)	1199(8)	91(3)
P2	3090(6)	3237(5)	4039(4)	71.0(16)
F7	3666(10)	3944(6)	3529(5)	116(3)
F8	2440(12)	4113(8)	4354(7)	125(4)
F9	2626(13)	2520(8)	4550(6)	140(4)
F10	3747(9)	2388(7)	3689(6)	95(3)
F11	4194(11)	3470(10)	4471(6)	127(4)
F12	2039(8)	3041(9)	3582(6)	127(4)
P2A	3011(9)	3128(7)	4141(5)	78(2)
F7A	4089(11)	3819(9)	4259(8)	104(4)
F8A	2108(14)	3954(11)	4272(10)	134(6)
F9A	1990(10)	2363(9)	4081(7)	106(4)
F10A	3907(13)	2292(10)	4008(9)	118(5)
F11A	3049(15)	2854(12)	4872(5)	138(5)
F12A	2994(16)	3367(14)	3421(6)	144(5)

Table A.35: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Rh-4][PF_6]$_2$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	38(2)	53(3)	53(3)	1(2)	-6(2)	1(2)
C2	47(3)	89(5)	59(4)	1(3)	-9(3)	2(3)
C3	68(4)	115(6)	56(4)	8(4)	-22(3)	9(4)
C4	66(3)	92(5)	45(3)	16(3)	-1(3)	14(3)
C5	51(3)	47(3)	47(3)	9(2)	1(2)	6(2)
C6	57(3)	49(3)	51(3)	15(3)	7(2)	-2(2)
C7	44(3)	49(3)	51(3)	-3(2)	13(2)	2(2)

C8	45(2)	38(2)	47(3)	-8(2)	3(2)	3.3(19)
C9	41(2)	43(2)	60(3)	3(2)	-4(2)	8.3(19)
C10	37(2)	52(3)	71(4)	0(3)	-3(2)	6(2)
C11	39(2)	48(3)	83(4)	-4(3)	10(3)	4(2)
C12	40(2)	37(2)	53(3)	-3(2)	5(2)	-1.9(17)
C13	39(2)	35(2)	60(3)	1(2)	8.7(19)	-1.1(15)
C14	61(3)	51(3)	71(4)	-13(3)	6(3)	-4(3)
C15	84(4)	53(4)	113(7)	-31(4)	22(4)	-12(3)
C16	79(5)	40(3)	165(9)	-8(4)	22(6)	-3(3)
C17	61(4)	64(4)	153(8)	48(5)	16(5)	13(4)
C18	58(3)	56(3)	81(4)	20(3)	3(4)	-7(4)
C19	85(4)	44(3)	38(3)	-9(2)	15(2)	4(3)
C20	49(3)	60(3)	53(3)	-21(3)	16(2)	0(2)
C21	57(3)	39(3)	59(3)	-11(2)	3(3)	17(2)
C22	62(3)	37(2)	63(3)	-17(2)	12(2)	-5(2)
C23	60(3)	66(4)	47(3)	-29(3)	-13(3)	14(3)
C24	190(10)	67(4)	46(4)	2(3)	28(5)	7(5)
C25	55(4)	131(7)	114(6)	-51(6)	33(4)	-17(4)
C26	112(6)	61(4)	100(6)	2(4)	-9(5)	44(4)
C27	104(6)	74(5)	125(8)	-39(5)	41(6)	-47(5)
C28	99(6)	124(7)	87(5)	-51(6)	-41(5)	48(6)
N1	41(2)	43(2)	41(2)	9.2(19)	-2.9(17)	0.6(17)
N2	40.1(19)	44(2)	47(2)	2(2)	6.9(17)	-3.6(17)
N3	38.2(17)	28.3(16)	49(2)	-1.7(16)	0.7(16)	3.6(14)
Rh1	34.60(15)	30.42(15)	37.90(16)	-1.13(10)	-0.06(19)	1.46(16)
P1	44(4)	46(3)	65(4)	-14(3)	6(3)	1(3)
F1	71(6)	66(7)	75(7)	-16(5)	24(7)	-8(7)

F2	67(6)	117(9)	78(7)	8(7)	-4(5)	9(6)
F3	76(9)	80(8)	64(7)	18(6)	19(6)	10(7)
F4	96(7)	102(8)	103(9)	-4(7)	-17(7)	38(7)
F5	55(5)	64(6)	94(9)	-25(6)	10(6)	-12(4)
F6	113(9)	58(6)	103(9)	-34(6)	20(7)	-25(6)
P1A	53(3)	49(3)	52(3)	-5(2)	5(2)	0(2)
F1A	86(6)	81(6)	83(6)	-5(5)	33(5)	15(5)
F2A	92(6)	136(9)	74(5)	-14(6)	-27(5)	-4(6)
F3A	51(4)	72(6)	90(7)	-9(6)	16(5)	9(4)
F4A	68(4)	106(6)	66(4)	-9(4)	-9(5)	-10(6)
F5A	102(7)	50(4)	86(7)	0(4)	15(5)	4(4)
F6A	106(6)	50(4)	117(8)	-1(5)	9(6)	0(4)
P2	63(2)	60(3)	90(3)	-17(2)	0(2)	-13.1(19)
F7	143(8)	81(5)	123(7)	7(5)	39(6)	-16(5)
F8	98(7)	111(6)	168(8)	-62(6)	11(8)	2(7)
F9	154(8)	118(6)	149(8)	41(6)	35(8)	-35(7)
F10	90(5)	74(5)	121(8)	-21(5)	12(6)	-12(4)
F11	122(7)	126(9)	134(8)	8(7)	-31(6)	-19(7)
F12	94(6)	133(7)	153(8)	-24(7)	-33(6)	12(5)
P2A	82(4)	64(4)	87(4)	-7(3)	1(3)	-4(3)
F7A	85(6)	69(6)	159(10)	-7(7)	9(7)	-39(5)
F8A	103(9)	121(9)	180(11)	-38(9)	-9(9)	30(8)
F9A	100(7)	107(7)	112(8)	-48(7)	3(6)	-35(6)
F10A	121(8)	85(7)	149(10)	-1(8)	7(9)	13(7)
F11A	162(10)	145(10)	107(9)	6(8)	-23(8)	-41(8)
F12A	167(10)	158(10)	106(8)	29(8)	-1(8)	-22(9)

Table A.36: Bond Lengths for **[Rh-4][PF_6]$_2$**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.364(8)	C22	C23	1.428(10)
C1	N1	1.358(6)	C22	C27	1.504(9)
C2	C3	1.371(10)	C22	Rh1	2.165(5)
C3	C4	1.385(10)	C23	C28	1.491(9)
C4	C5	1.369(8)	C23	Rh1	2.178(5)
C5	C6	1.500(8)	N1	Rh1	2.108(4)
C5	N1	1.343(7)	N2	Rh1	2.161(4)
C6	N2	1.480(7)	N3	Rh1	2.202(3)
C7	C8	1.516(7)	P1	F1	1.584(8)
C7	C11	1.513(8)	P1	F2	1.573(9)
C7	N2	1.500(7)	P1	F3	1.589(8)
C8	N3	1.483(7)	P1	F4	1.572(9)
C9	C10	1.517(7)	P1	F5	1.587(9)
C9	N3	1.493(6)	P1	F6	1.564(9)
C10	C11	1.522(9)	P1A	F1A	1.584(7)
C12	C13	1.509(6)	P1A	F2A	1.571(8)
C12	N3	1.501(6)	P1A	F3A	1.589(7)
C13	C14	1.389(9)	P1A	F4A	1.574(7)
C13	C18	1.366(8)	P1A	F5A	1.586(7)
C14	C15	1.374(9)	P1A	F6A	1.568(8)
C15	C16	1.361(14)	P2	F7	1.596(8)
C16	C17	1.370(14)	P2	F8	1.567(8)
C17	C18	1.408(10)	P2	F9	1.556(8)
C19	C20	1.404(9)	P2	F10	1.576(8)
C19	C23	1.430(9)	P2	F11	1.593(9)

C19	C24	1.466(9)	P2	F12	1.569(9)
C19	Rh1	2.201(5)	P2A	F7A	1.584(9)
C20	C21	1.428(9)	P2A	F8A	1.566(9)
C20	C25	1.493(9)	P2A	F9A	1.582(9)
C20	Rh1	2.182(5)	P2A	F10A	1.572(9)
C21	C22	1.409(9)	P2A	F11A	1.586(10)
C21	C26	1.504(9)	P2A	F12A	1.552(10)
C21	Rh1	2.156(5)			

Table A.37: Bond Angles for **[Rh-4][PF_6]$_2$**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	121.5(6)	C22	Rh1	C23	38.4(3)
C1	C2	C3	119.3(6)	C22	Rh1	N3	145.5(2)
C2	C3	C4	119.7(6)	C23	Rh1	C19	38.1(2)
C5	C4	C3	118.7(6)	C23	Rh1	C20	63.4(2)
C4	C5	C6	122.7(6)	C23	Rh1	N3	110.7(2)
N1	C5	C4	121.9(5)	N1	Rh1	C19	130.3(2)
N1	C5	C6	115.3(5)	N1	Rh1	C20	97.2(2)
N2	C6	C5	110.6(4)	N1	Rh1	C21	93.1(2)
C11	C7	C8	108.7(5)	N1	Rh1	C22	123.7(2)
N2	C7	C8	108.9(4)	N1	Rh1	C23	157.2(2)
N2	C7	C11	110.0(5)	N1	Rh1	N2	77.18(16)
N3	C8	C7	108.2(4)	N1	Rh1	N3	89.98(17)
N3	C9	C10	112.4(4)	N2	Rh1	C19	152.2(2)
C9	C10	C11	112.0(5)	N2	Rh1	C20	155.4(2)
C7	C11	C10	111.4(4)	N2	Rh1	C22	99.5(2)
N3	C12	C13	117.5(4)	N2	Rh1	C23	115.0(2)

C14	C13	C12	119.0(5)	N2	Rh1	N3	79.23(16)
C18	C13	C12	121.8(5)	F1	P1	F3	178.7(9)
C18	C13	C14	119.0(5)	F1	P1	F5	89.9(7)
C15	C14	C13	120.7(7)	F2	P1	F1	91.6(8)
C16	C15	C14	120.4(8)	F2	P1	F3	89.6(8)
C15	C16	C17	120.2(6)	F2	P1	F5	89.7(8)
C16	C17	C18	119.8(7)	F4	P1	F1	90.0(8)
C13	C18	C17	120.0(7)	F4	P1	F2	177.8(9)
C20	C19	C23	107.9(5)	F4	P1	F3	88.8(8)
C20	C19	C24	125.7(7)	F4	P1	F5	88.7(8)
C20	C19	Rh1	70.6(3)	F5	P1	F3	89.6(8)
C23	C19	C24	126.0(7)	F6	P1	F1	90.0(7)
C23	C19	Rh1	70.0(3)	F6	P1	F2	91.3(8)
C24	C19	Rh1	130.3(4)	F6	P1	F3	90.5(8)
C19	C20	C21	108.9(5)	F6	P1	F4	90.3(8)
C19	C20	C25	125.7(7)	F6	P1	F5	179.0(10)
C19	C20	Rh1	72.0(3)	F1A	P1A	F3A	179.1(8)
C21	C20	C25	125.0(7)	F1A	P1A	F5A	90.1(6)
C21	C20	Rh1	69.8(3)	F2A	P1A	F1A	91.9(7)
C25	C20	Rh1	130.2(5)	F2A	P1A	F3A	88.8(7)
C20	C21	C26	126.5(7)	F2A	P1A	F4A	179.3(7)
C20	C21	Rh1	71.8(3)	F2A	P1A	F5A	90.2(7)
C22	C21	C20	107.2(5)	F4A	P1A	F1A	88.8(6)
C22	C21	C26	126.1(7)	F4A	P1A	F3A	90.5(6)
C22	C21	Rh1	71.3(3)	F4A	P1A	F5A	90.0(6)
C26	C21	Rh1	126.4(5)	F5A	P1A	F3A	89.4(6)
C21	C22	C23	108.8(5)	F6A	P1A	F1A	89.8(6)

C21	C22	C27	124.5(7)	F6A	P1A	F2A	91.6(7)
C21	C22	Rh1	70.6(3)	F6A	P1A	F3A	90.6(6)
C23	C22	C27	126.6(7)	F6A	P1A	F4A	88.3(6)
C23	C22	Rh1	71.3(3)	F6A	P1A	F5A	178.2(8)
C27	C22	Rh1	125.5(5)	F8	P2	F7	90.7(7)
C19	C23	C28	126.3(7)	F8	P2	F10	177.0(8)
C19	C23	Rh1	71.8(3)	F8	P2	F11	89.1(7)
C22	C23	C19	107.1(5)	F8	P2	F12	91.4(7)
C22	C23	C28	125.2(8)	F9	P2	F7	175.6(8)
C22	C23	Rh1	70.3(3)	F9	P2	F8	91.9(7)
C28	C23	Rh1	133.3(5)	F9	P2	F10	90.9(7)
C1	N1	Rh1	125.6(4)	F9	P2	F11	90.4(8)
C5	N1	C1	118.9(5)	F9	P2	F12	92.9(8)
C5	N1	Rh1	115.2(3)	F10	P2	F7	86.6(6)
C6	N2	C7	113.3(5)	F10	P2	F11	92.0(7)
C6	N2	Rh1	106.0(3)	F11	P2	F7	86.1(7)
C7	N2	Rh1	111.7(3)	F12	P2	F7	90.7(7)
C8	N3	C9	108.0(4)	F12	P2	F10	87.3(6)
C8	N3	C12	110.9(4)	F12	P2	F11	176.7(9)
C8	N3	Rh1	104.8(3)	F7A	P2A	F11A	88.2(8)
C9	N3	C12	110.7(4)	F8A	P2A	F7A	93.1(8)
C9	N3	Rh1	112.4(3)	F8A	P2A	F9A	90.4(8)
C12	N3	Rh1	109.8(3)	F8A	P2A	F10A	179.5(10)
C19	Rh1	N3	102.10(19)	F8A	P2A	F11A	91.2(9)
C20	Rh1	C19	37.4(2)	F9A	P2A	F7A	173.7(10)
C20	Rh1	N3	125.1(2)	F9A	P2A	F11A	86.5(8)
C21	Rh1	C19	63.9(2)	F10A	P2A	F7A	87.5(8)

C21	Rh1	C20	38.4(2)	F10A	P2A	F9A	89.0(8)
C21	Rh1	C22	38.1(3)	F10A	P2A	F11A	88.8(9)
C21	Rh1	C23	64.3(2)	F12A	P2A	F7A	92.0(9)
C21	Rh1	N2	117.3(2)	F12A	P2A	F8A	90.5(9)
C21	Rh1	N3	163.5(2)	F12A	P2A	F9A	93.2(9)
C22	Rh1	C19	63.6(2)	F12A	P2A	F10A	89.5(9)
C22	Rh1	C20	63.4(2)	F12A	P2A	F11A	178.3(10)

Table A.38: Hydrogen Atom Coordinates ($Å^2 \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Rh-4][PF$_6$]$_2$**.

Atom	***x***	***y***	***z***	**U_{eq}**
H1	9982.4	5843.71	4018.18	58
H2	11081.57	5714.77	4919.63	78
H3	10269.36	5058.62	5825.22	96
H4	8357.95	4504.61	5801.16	81
H6A	6866.53	3802.76	4734.87	63
H6B	6436.59	4597.55	5214.25	63
H7	5607.47	5975.54	4943.82	58
H8A	6341.79	7385.65	4415.59	52
H8B	7349.14	6665.4	4598.01	52
H9A	6132.75	6852.47	2819.98	58
H9B	5723.67	7575.66	3349.11	58
H10A	5060.09	5612.95	3244.08	64
H10B	4223.69	6508.8	3199.44	64
H11A	4339.94	6790.3	4268.9	68
H11B	4109.59	5674.07	4197.9	68
H12A	8189.19	7197.98	3052.38	52
H12B	8646.16	7112.23	3748.12	52

H14	8379.23	8411.16	4490.08	73
H15	8229.44	10056.02	4639.07	100
H16	7626.87	11037.76	3828.2	114
H17	7086.91	10375.57	2869.99	111
H18	7237.46	8701.17	2711.44	78
H24A	8840.25	6261.05	2220.94	151
H24B	7517.12	6254.17	2041.16	151
H24C	8394.7	5596.38	1668.47	151
H25A	10472.86	4563.69	2506.06	150
H25B	10501.27	4565.61	3250.01	150
H25C	10245.32	5528.12	2879.72	150
H26A	8414.88	2771.12	3904.7	137
H26B	9532.29	3422.34	3894.95	137
H26C	9353.78	2625.07	3373.63	137
H27A	5544.02	3252.59	3210.39	152
H27B	6468.75	2852.23	3690.33	152
H27C	6421.75	2447.06	2995.58	152
H28A	5868.19	4270.96	1884.99	155
H28B	5788.33	5354.79	2104.79	155
H28C	5186.5	4538.59	2505.16	155
H2A	5607.32	4596.06	4149.94	52

Table A.39: Atomic Occupancy for **[Rh-4][PF_6]$_2$**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
P1	0.43(3)	F1	0.43(3)	F2	0.43(3)
F3	0.43(3)	F4	0.43(3)	F5	0.43(3)
F6	0.43(3)	P1A	0.57(3)	F1A	0.57(3)

F2A	0.57(3)	F3A	0.57(3)	F4A	0.57(3)
F5A	0.57(3)	F6A	0.57(3)	P2	0.566(9)
F7	0.566(9)	F8	0.566(9)	F9	0.566(9)
F10	0.566(9)	F11	0.566(9)	F12	0.566(9)
P2A	0.434(9)	F7A	0.434(9)	F8A	0.434(9)
F9A	0.434(9)	F10A	0.434(9)	F11A	0.434(9)
F12A	0.434(9)				

A.7.6 [Ru-3][PF_6]

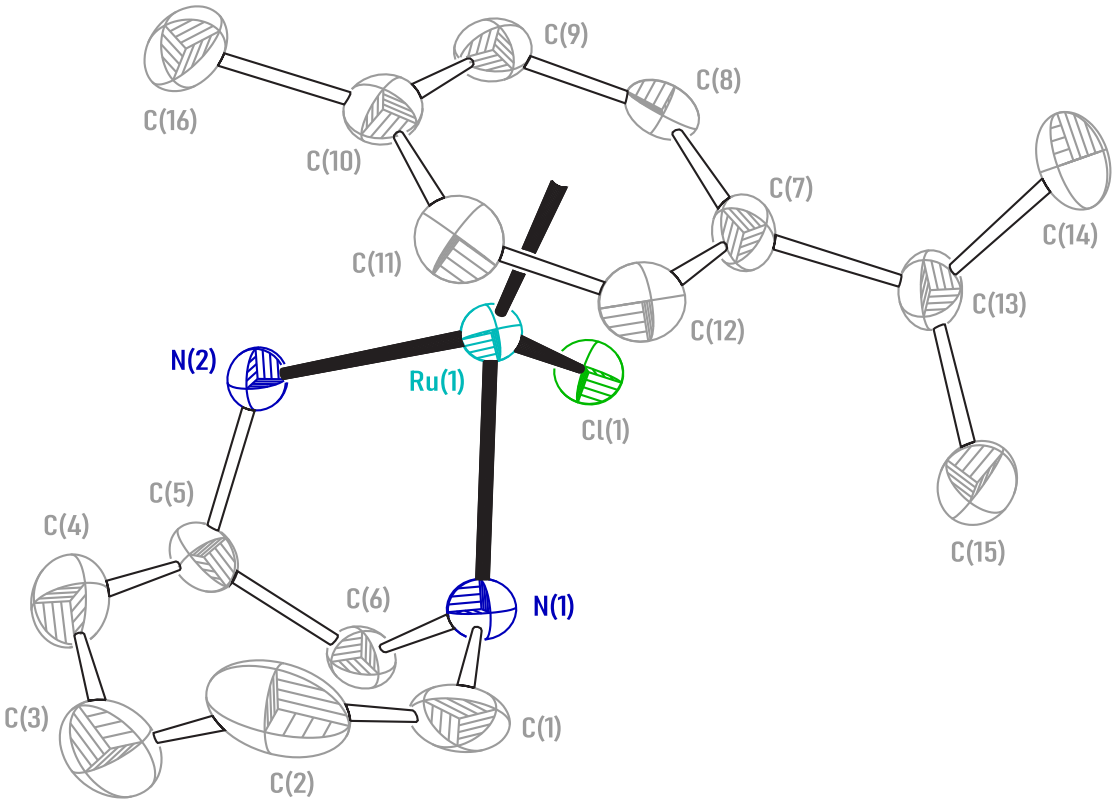


Figure A.6: Thermal ellipsoids of **[Ru-3][PF_6]** shown at 30% probability. Hydrogen atoms and PF_6^- anion omitted for clarity.

A.7.6.1 Refinement model description

1. Restrained distances

F6-F1 ≈ F6-F2 ≈ F6-F4 ≈ F6-F3 ≈ F1-F2 ≈ F1-F4 ≈ F1-F5 ≈ F2-F3 ≈ F2-F5 ≈

F4-F3 ≈ F4-F5 ≈ F3-F5 ≈ F6A-F1A ≈ F6A-F2A ≈ F6A-F4A ≈ F6A-F3A ≈ F1A-F2A ≈ F1A-F4A F1A-F5A ≈ F2A-F3A ≈ F2A-F5A ≈ F4A-F3A ≈ F4A-F5A ≈ F3A-F5A with sigma of 0.04

P1-F1 ≈ P1-F3 ≈ P1-F3 ≈ P1-F4 ≈ P1-F5 ≈ P1-F6 ≈ P1A-F1A ≈ P1A-F2A ≈ P1A-F3A P1A-F4A ≈ P1A-F5A ≈ P1A-F6A with sigma of 0.02

2. U_{iso}/U_{aniso} restraints and constraints

U_{anis}(C4) ≈ U_{eq}: with sigma of 0.01 and sigma for terminal atoms of 0.02

3. Rigid body (RIGU) restrains

P1A, F5A, F1A, F3A, F2A, F4A, F6A with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

P1, F5, F1, F3, F2, F4, F6 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

4. Others

Sof(P1A)=Sof(F5A)=Sof(F3A)=Sof(F4A)=Sof(F2A)=Sof(F1A)=Sof(F6A)=1-FVAR(1)

Sof(P1)=Sof(F1)=Sof(F2)=Sof(F4)=Sof(F3)=Sof(F6)=Sof(F5)=FVAR(1)

5.a Ternary CH refined with riding coordinates:

N1(H1), C5(H5), C13(H13)

5.b Secondary CH_2 refined with riding coordinates:

N2(H2A,H2B), C6(H6A,H6B), C4(H4A,H4B), C3(H3A,H3B), C1(H1A,H1B), C2(H2C,H2D)

5.c Aromatic/amide H refined with riding coordinates:

C12(H12), C8(H8), C9(H9), C11(H11)

5.d Idealised Me refined as rotating group:

C15(H15A,H15B,H15C), C16(H16A,H16B,H16C), C14(H14A,H14B,H14C)

A.7.6.2 Crystallographic tables

Table A.40: Crystal data and structure refinement for **[Ru-3][PF_6]**.

Identification code	**[Ru-3][PF_6]**
Empirical formula	$C_{16}H_{28}ClF_6N_2PRu$
Formula weight	529.89
Temperature/K	298.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.5419(2)
b/Å	11.5358(3)
c/Å	21.8557(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2153.61(10)
Z	4
ρ_{calc} / g/cm^3	1.634
μ/mm^{-1}	8.249
F(000)	1072
Crystal size/mm^3	0.291×0.11×0.056
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.09 to 145.864
Index ranges	$-10 \leq h \leq 10$, $-8 \leq k \leq 13$, $-18 \leq l \leq 26$
Reflections collected	7960
Independent reflections	4164 [R_{int} = 0.0351, R_σ = 0.0444]
Data/restraints/parameters	4164/463/312
Goodness-of-fit on F^2	1.078
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.1057

Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1103
Largest diff. peak/hole / e Å^{-3}	1.44/-0.51
Flack parameter	-0.028(9)

Table A.41: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **[Ru-3][PF$_6$]**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U_{eq}**
Ru1	5616.0(5)	6034.0(4)	4394.3(2)	37.22(17)
Cl1	6025(2)	7379.1(16)	5235.4(9)	51.5(4)
P1	8330(30)	1650(19)	3284(8)	82(6)
N1	7580(8)	6911(6)	3979(3)	54.1(16)
N2	4481(8)	7471(5)	3975(3)	50.3(14)
C7	6394(10)	4463(6)	4891(4)	50.5(18)
C12	6547(10)	4288(6)	4248(4)	53(2)
C8	4918(10)	4806(6)	5108(4)	49.0(18)
C9	3637(10)	4981(6)	4717(4)	52.6(19)
C10	3795(10)	4812(6)	4077(4)	52.0(19)
C6	7146(11)	8154(8)	3869(4)	57(2)
C11	5277(11)	4460(7)	3856(4)	56(2)
F1	8320(40)	1290(20)	2590(10)	115(9)
C15	9358(12)	4472(10)	5059(6)	82(3)
F2	9140(40)	480(20)	3458(14)	118(9)
C5	5527(13)	8228(8)	3585(4)	63(2)
C16	2441(12)	5049(9)	3648(5)	72(3)
F4	7460(30)	2804(18)	3116(11)	91(7)
F3	8340(30)	1960(20)	3981(7)	94(7)
C4	5374(15)	7896(15)	2922(5)	102(4)

C13	7727(10)	4271(7)	5339(4)	57(2)
C3	6827(18)	7437(16)	2594(5)	110(5)
C1	8381(13)	6403(10)	3451(5)	78(3)
C2	7500(20)	6335(13)	2871(6)	118(6)
F6	6730(30)	980(30)	3348(17)	149(9)
C14	7658(15)	3023(9)	5581(7)	103(4)
F5	9940(30)	2250(30)	3184(13)	126(9)
P1A	8159(10)	1566(8)	3251(4)	72(2)
F5A	8623(19)	1844(12)	2576(5)	117(5)
F3A	9486(19)	628(14)	3269(8)	142(6)
F4A	9188(19)	2502(13)	3555(9)	151(6)
F2A	7023(18)	611(11)	2943(7)	134(5)
F1A	6737(16)	2417(12)	3242(7)	108(4)
F6A	7587(17)	1088(17)	3890(6)	136(5)

Table A.42: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Ru-3][PF_6]**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ru1	36.6(2)	35.1(2)	40.0(3)	-2.2(2)	1.8(2)	-0.3(2)
Cl1	59.9(11)	46.2(8)	48.6(9)	-9.4(7)	1.6(8)	-5.1(8)
P1	118(12)	74(8)	55(9)	-10(6)	7(7)	16(7)
N1	45(3)	64(4)	54(4)	10(3)	0(3)	-10(3)
N2	44(3)	49(3)	58(4)	11(3)	-6(3)	-1(3)
C7	55(4)	35(3)	62(5)	5(3)	-9(4)	6(3)
C12	57(5)	36(3)	67(5)	-13(3)	9(4)	6(3)
C8	60(4)	38(3)	49(4)	7(3)	11(4)	-7(3)
C9	47(4)	37(4)	74(6)	0(3)	4(4)	-4(3)

C10	55(4)	35(3)	66(5)	-5(3)	-5(4)	-9(3)
C6	59(5)	61(4)	53(4)	10(4)	-6(4)	-22(4)
C11	75(6)	44(4)	50(4)	-20(3)	1(4)	-3(4)
F1	159(19)	103(16)	83(10)	-19(9)	1(10)	15(13)
C15	59(5)	78(6)	108(8)	22(6)	-15(6)	-5(6)
F2	166(18)	100(11)	89(15)	-1(9)	10(13)	33(11)
C5	66(5)	62(5)	62(5)	22(4)	2(5)	0(5)
C16	62(5)	71(6)	83(7)	-5(5)	-22(5)	-14(5)
F4	123(16)	80(10)	71(11)	-12(8)	-10(11)	19(10)
F3	130(16)	94(12)	58(9)	0(7)	1(8)	42(11)
C4	79(7)	164(10)	64(6)	14(6)	-12(5)	-5(7)
C13	56(5)	50(4)	66(5)	8(4)	-11(4)	7(3)
C3	116(11)	160(14)	55(6)	4(8)	11(7)	-16(11)
C1	66(6)	92(7)	76(6)	11(5)	38(5)	4(5)
C2	152(14)	124(12)	77(8)	-33(8)	54(9)	-35(10)
F6	145(14)	146(16)	156(19)	-9(13)	13(11)	-9(11)
C14	89(7)	73(6)	148(12)	55(8)	-11(9)	15(6)
F5	129(13)	129(15)	119(16)	-12(11)	13(10)	3(10)
P1A	80(4)	69(4)	68(5)	8(3)	6(3)	24(3)
F5A	163(11)	91(8)	98(7)	17(6)	33(7)	8(8)
F3A	144(10)	143(10)	140(12)	41(8)	44(8)	75(8)
F4A	127(10)	139(9)	186(14)	-38(9)	-24(9)	11(8)
F2A	162(10)	119(8)	120(9)	-13(7)	2(8)	-13(7)
F1A	107(8)	110(8)	106(9)	-29(6)	-21(7)	45(7)
F6A	120(9)	204(13)	85(7)	33(7)	5(6)	23(9)

Table A.43: Bond Lengths for **[Ru-3][PF_6]**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	Cl1	2.4309(18)	C7	C13	1.518(11)
Ru1	N1	2.159(7)	C12	C11	1.397(12)
Ru1	N2	2.128(6)	C8	C9	1.404(12)
Ru1	C7	2.214(7)	C9	C10	1.417(12)
Ru1	C12	2.188(7)	C10	C11	1.414(12)
Ru1	C8	2.190(7)	C10	C16	1.515(13)
Ru1	C9	2.198(8)	C6	C5	1.519(13)
Ru1	C10	2.210(8)	C15	C13	1.540(14)
Ru1	C11	2.183(7)	C5	C4	1.504(14)
P1	F1	1.572(17)	C4	C3	1.527(19)
P1	F2	1.56(3)	C13	C14	1.534(13)
P1	F4	1.565(18)	C3	C2	1.52(2)
P1	F3	1.563(16)	C1	C2	1.47(2)
P1	F6	1.576(18)	P1A	F5A	1.561(12)
P1	F5	1.556(18)	P1A	F3A	1.567(13)
N1	C6	1.501(11)	P1A	F4A	1.543(13)
N1	C1	1.464(12)	P1A	F2A	1.616(13)
N2	C5	1.513(11)	P1A	F1A	1.561(10)
C7	C12	1.424(12)	P1A	F6A	1.579(12)
C7	C8	1.404(12)			

Table A.44: Bond Angles for **[Ru-3][PF_6]**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ru1	Cl1	84.7(2)	C1	N1	C6	111.8(7)
N1	Ru1	C7	110.9(3)	C5	N2	Ru1	115.0(5)
N1	Ru1	C12	95.0(3)	C12	C7	Ru1	70.1(4)

N1	Ru1	C8	144.5(3)	C12	C7	C13	123.2(8)
N1	Ru1	C9	172.5(3)	C8	C7	Ru1	70.5(4)
N1	Ru1	C10	135.5(3)	C8	C7	C12	117.1(8)
N1	Ru1	C11	105.4(3)	C8	C7	C13	119.7(8)
N2	Ru1	Cl1	83.92(19)	C13	C7	Ru1	131.3(6)
N2	Ru1	N1	78.9(3)	C7	C12	Ru1	72.1(4)
N2	Ru1	C7	170.2(3)	C11	C12	Ru1	71.1(4)
N2	Ru1	C12	145.0(3)	C11	C12	C7	120.9(8)
N2	Ru1	C8	133.4(3)	C7	C8	Ru1	72.4(5)
N2	Ru1	C9	102.6(3)	C9	C8	Ru1	71.6(4)
N2	Ru1	C10	92.4(3)	C9	C8	C7	122.3(7)
N2	Ru1	C11	110.8(3)	C8	C9	Ru1	71.0(4)
C7	Ru1	Cl1	96.3(2)	C8	C9	C10	120.4(8)
C12	Ru1	Cl1	130.2(2)	C10	C9	Ru1	71.7(5)
C12	Ru1	C7	37.7(3)	C9	C10	Ru1	70.8(5)
C12	Ru1	C8	66.9(3)	C9	C10	C16	120.9(9)
C12	Ru1	C9	79.5(3)	C11	C10	Ru1	70.2(4)
C12	Ru1	C10	67.9(3)	C11	C10	C9	117.5(8)
C8	Ru1	Cl1	85.0(2)	C11	C10	C16	121.6(8)
C8	Ru1	C7	37.2(3)	C16	C10	Ru1	128.0(6)
C8	Ru1	C9	37.3(3)	N1	C6	C5	110.1(7)
C8	Ru1	C10	67.6(3)	C12	C11	Ru1	71.6(4)
C9	Ru1	Cl1	102.8(2)	C12	C11	C10	121.7(8)
C9	Ru1	C7	67.8(3)	C10	C11	Ru1	72.3(4)
C9	Ru1	C10	37.5(3)	N2	C5	C6	105.9(6)
C10	Ru1	Cl1	138.2(2)	C4	C5	N2	110.2(9)
C10	Ru1	C7	80.9(3)	C4	C5	C6	117.3(9)

C11	Ru1	Cl1	163.3(2)	C5	C4	C3	118.0(10)
C11	Ru1	C7	67.9(3)	C7	C13	C15	113.6(8)
C11	Ru1	C12	37.3(3)	C7	C13	C14	109.3(8)
C11	Ru1	C8	79.0(3)	C14	C13	C15	108.2(8)
C11	Ru1	C9	67.1(3)	C2	C3	C4	114.3(12)
C11	Ru1	C10	37.6(3)	N1	C1	C2	117.4(10)
F1	P1	F6	87.3(15)	C1	C2	C3	119.4(12)
F2	P1	F1	90.6(15)	F5A	P1A	F3A	89.0(8)
F2	P1	F4	178.4(18)	F5A	P1A	F2A	84.1(8)
F2	P1	F3	87.3(15)	F5A	P1A	F1A	93.2(8)
F2	P1	F6	86.8(16)	F5A	P1A	F6A	170.5(11)
F4	P1	F1	89.7(15)	F3A	P1A	F2A	88.5(10)
F4	P1	F6	91.6(16)	F3A	P1A	F6A	87.7(8)
F3	P1	F1	177.8(19)	F4A	P1A	F5A	96.8(10)
F3	P1	F4	92.3(14)	F4A	P1A	F3A	93.4(10)
F3	P1	F6	91.8(15)	F4A	P1A	F2A	177.9(10)
F5	P1	F1	89.2(15)	F4A	P1A	F1A	90.5(8)
F5	P1	F2	91.4(16)	F4A	P1A	F6A	92.3(10)
F5	P1	F4	90.1(16)	F1A	P1A	F3A	175.2(11)
F5	P1	F3	91.6(15)	F1A	P1A	F2A	87.5(8)
F5	P1	F6	176.1(18)	F1A	P1A	F6A	89.5(8)
C6	N1	Ru1	108.8(5)	F6A	P1A	F2A	86.8(9)
C1	N1	Ru1	120.5(6)				

Table A.45: Hydrogen Atom Coordinates ($Å^2 \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **[Ru-3][PF_6]**.

Atom	***x***	***y***	***z***	$\mathbf{U_{eq}}$
H1	8377.66	6939.16	4300.76	65

H2A	3703.94	7205.34	3742.56	60
H2B	4057.45	7907.8	4266.87	60
H12	7505.68	4057.05	4088.02	64
H8	4785.23	4921.42	5526.04	59
H9	2677.52	5208.85	4877.84	63
H6A	7906.53	8509.13	3598.05	69
H6B	7157.56	8573.65	4253.66	69
H11	5409.19	4340.3	3438.41	68
H15A	9526.41	3930.08	4731.82	122
H15B	10143.82	4362.27	5367.61	122
H15C	9422.09	5247.81	4902.36	122
H5	5162.67	9029.33	3627.01	76
H16A	1799.54	5656.21	3814.15	108
H16B	1825.56	4358.44	3601.56	108
H16C	2838	5284.1	3256.3	108
H4A	5007.08	8571.29	2699.43	123
H4B	4563.6	7309.74	2891.02	123
H13	7592.41	4803.01	5684.35	69
H3A	6562.12	7287.72	2169.7	132
H3B	7626.61	8034.14	2599.66	132
H1A	8703.17	5623.68	3560.67	93
H1B	9325.49	6848.05	3376.87	93
H2C	6642.25	5799.16	2932.98	141
H2D	8189.96	5990.45	2568.46	141
H14A	6758.36	2934.55	5839.38	155
H14B	8589.4	2859.66	5810.92	155
H14C	7584.57	2494.65	5242.46	155

Table A.46: Atomic Occupancy for **[Ru-3][PF_6]**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
P1	0.314(17)	F1	0.314(17)	F2	0.314(17)
F4	0.314(17)	F3	0.314(17)	F6	0.314(17)
F5	0.314(17)	P1A	0.686(17)	F5A	0.686(17)
F3A	0.686(17)	F4A	0.686(17)	F2A	0.686(17)
F1A	0.686(17)	F6A	0.686(17)		

A.8 Selected NMR spectra

Figure A.7: ^{1}H NMR spectrum of 3,5-tBu,tbu-SalpyH_2 recorded at 500 MHz in $CDCl_3$

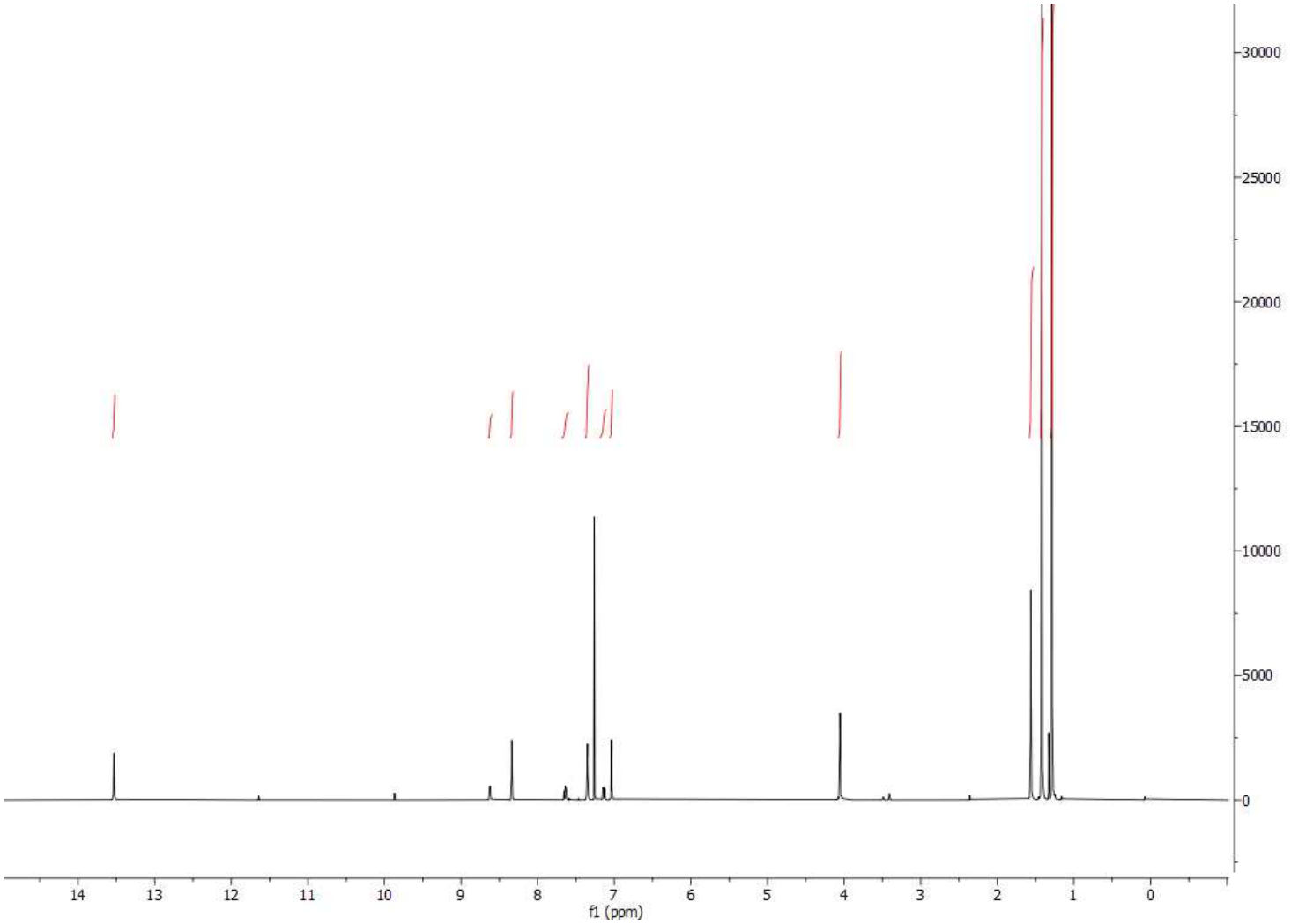


Figure A.8: $^{13}C\{^{1}H\}$ NMR spectrum of 3,5-tBu,tbu-SalpyH_2 recorded at 125 MHz in $CDCl_3$

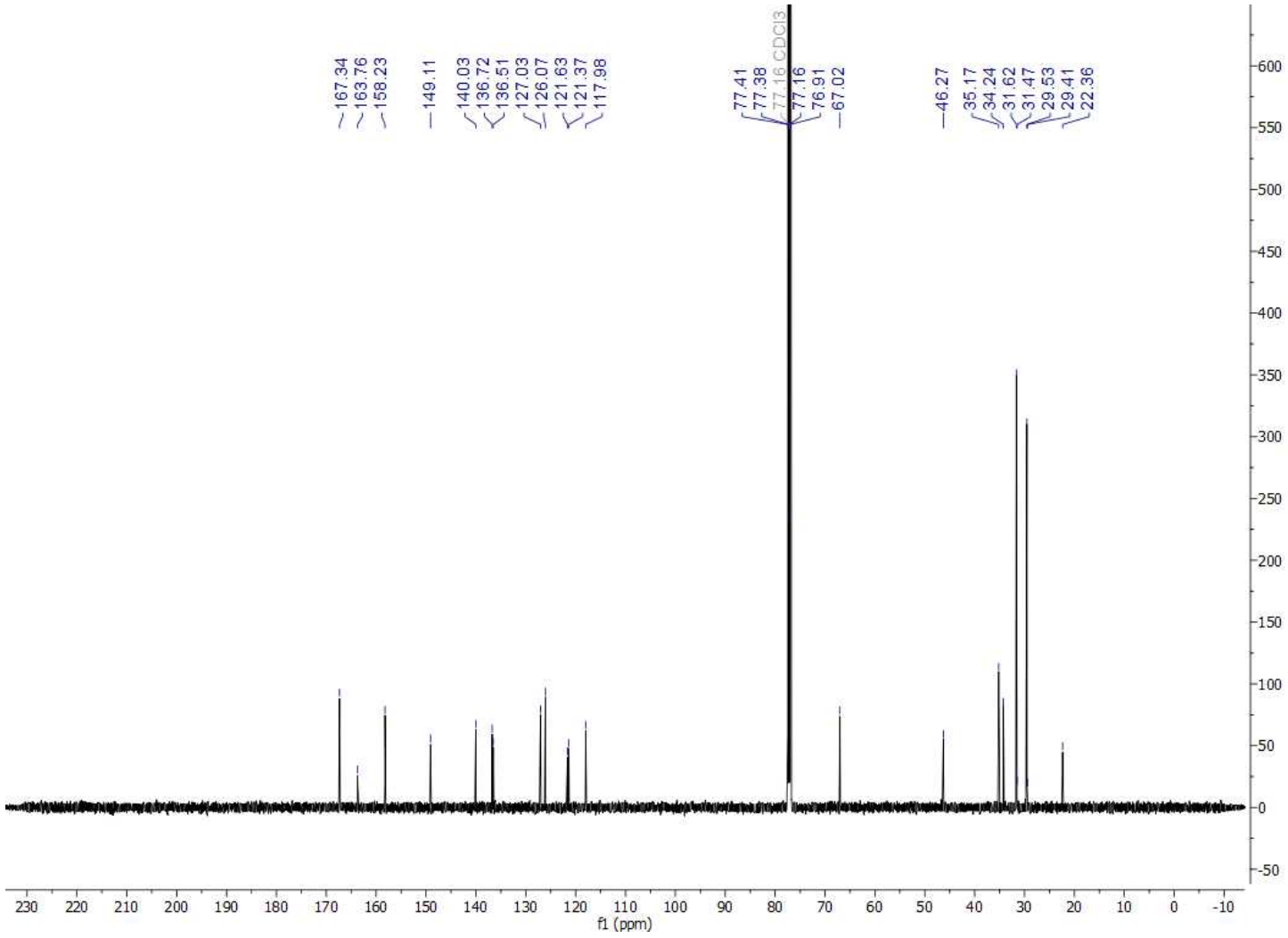


Figure A.9: ^{1}H NMR spectrum of 3,5-Br,Br-SalpyH_2 recorded at 500 MHz in DMSO-d^{6}

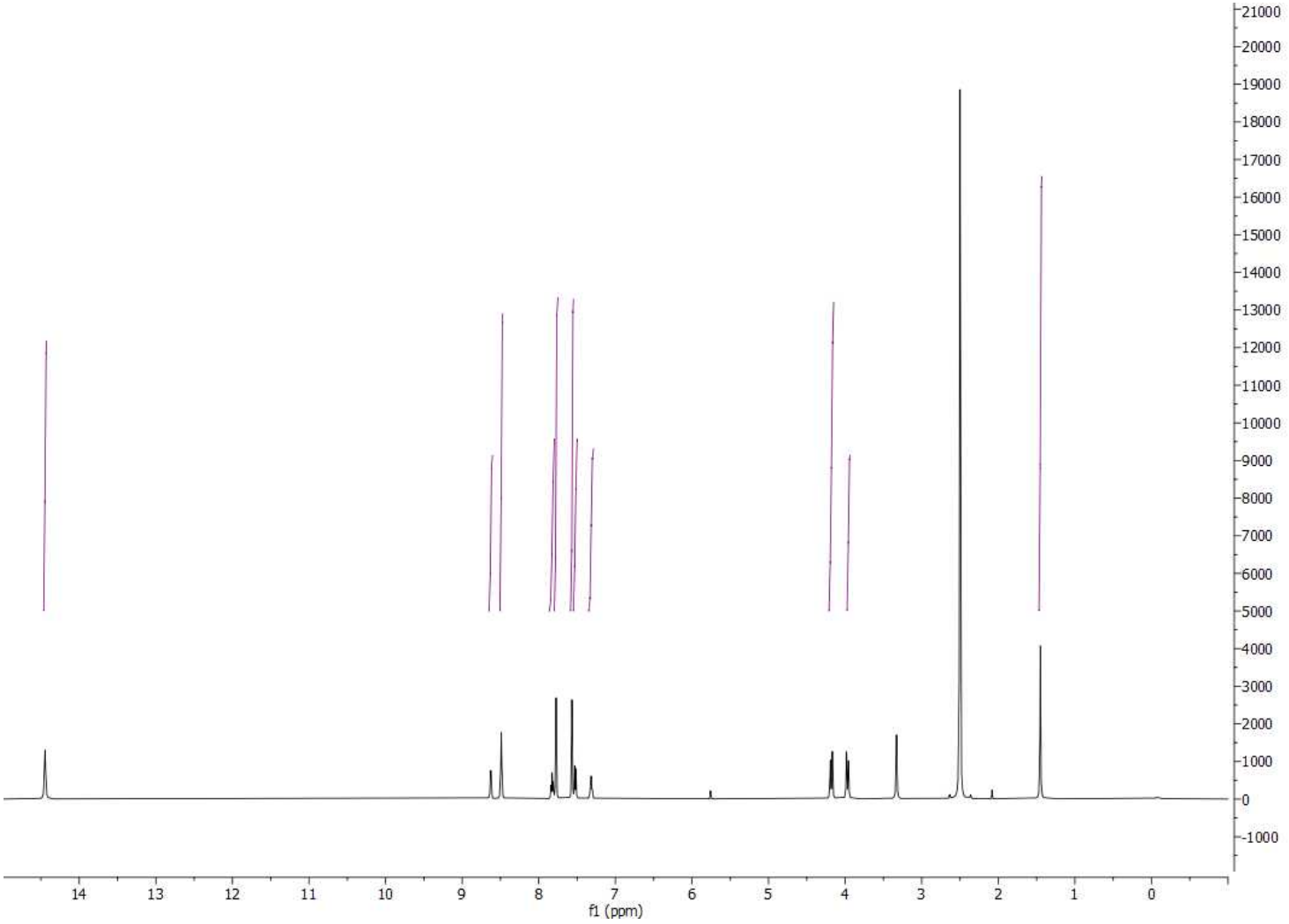


Figure A.10: ^{1}H NMR spectrum of 3,5-Cl,Cl-SalpyH_2 recorded at 500 MHz in DMSO-d^{6}

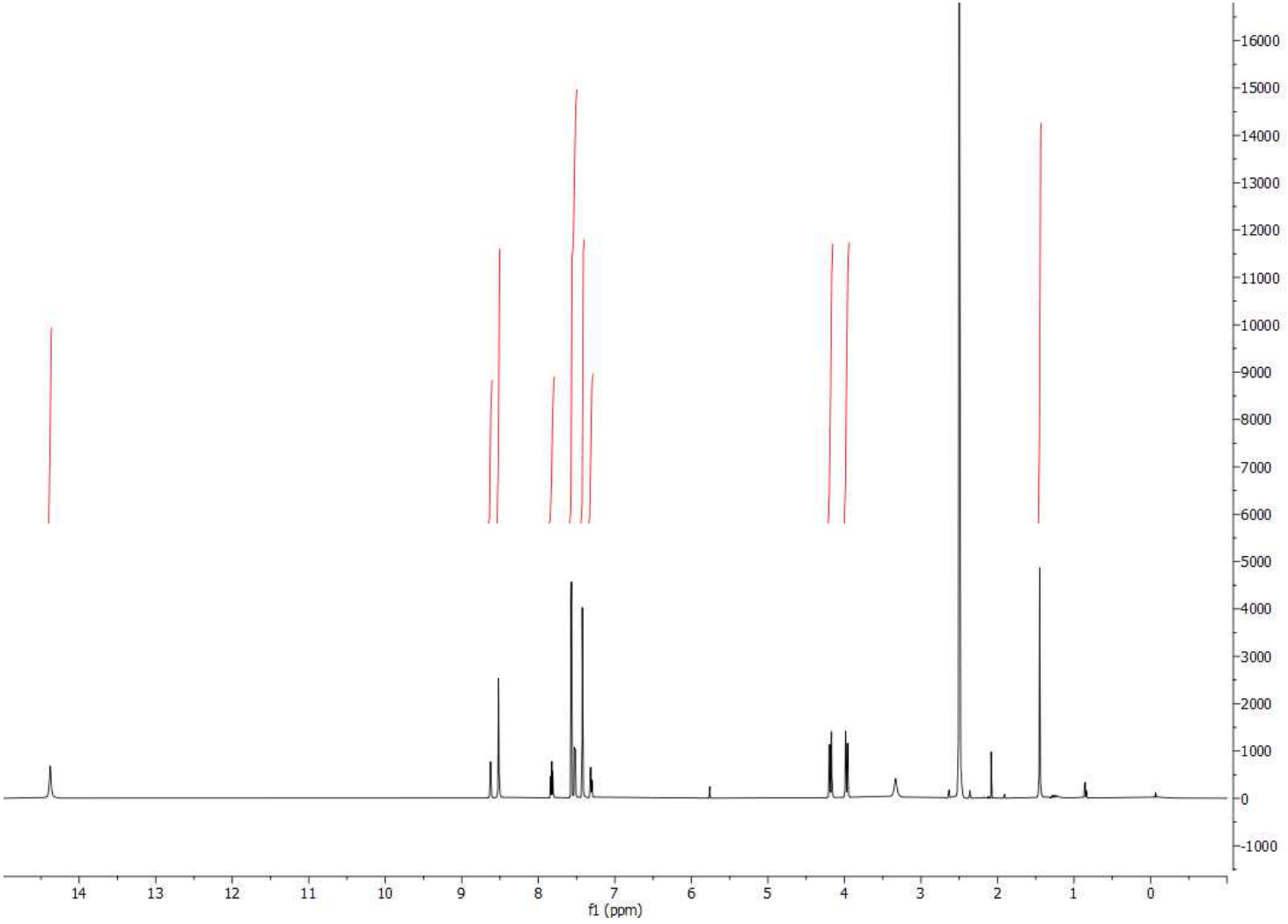


Figure A.11: ^{1}H NMR spectrum of **In-1** recorded at 500 MHz in $CDCl_3$

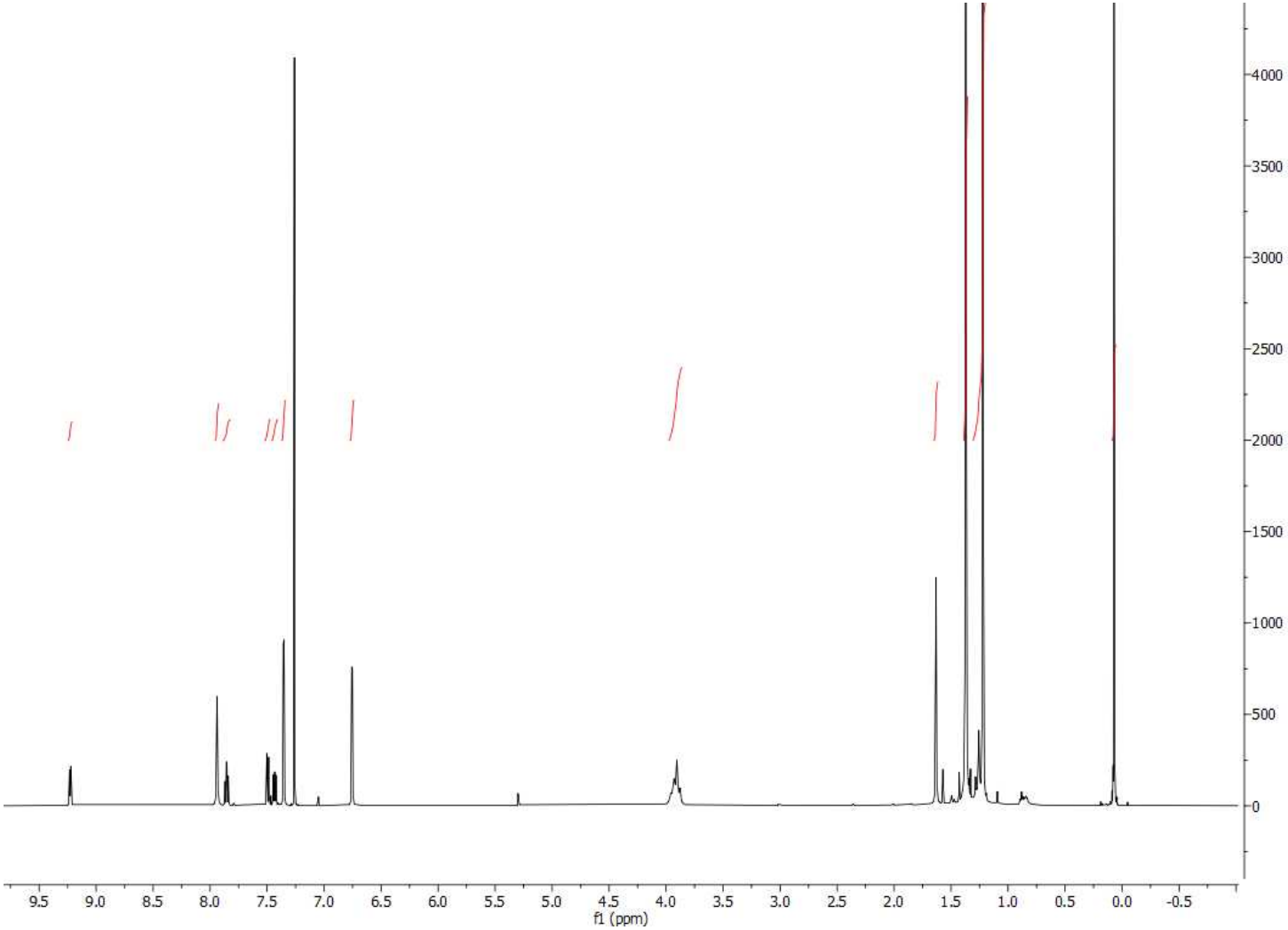


Figure A.12: ^{13}C NMR spectrum of **In-1** recorded at 125 MHz in $CDCl_3$

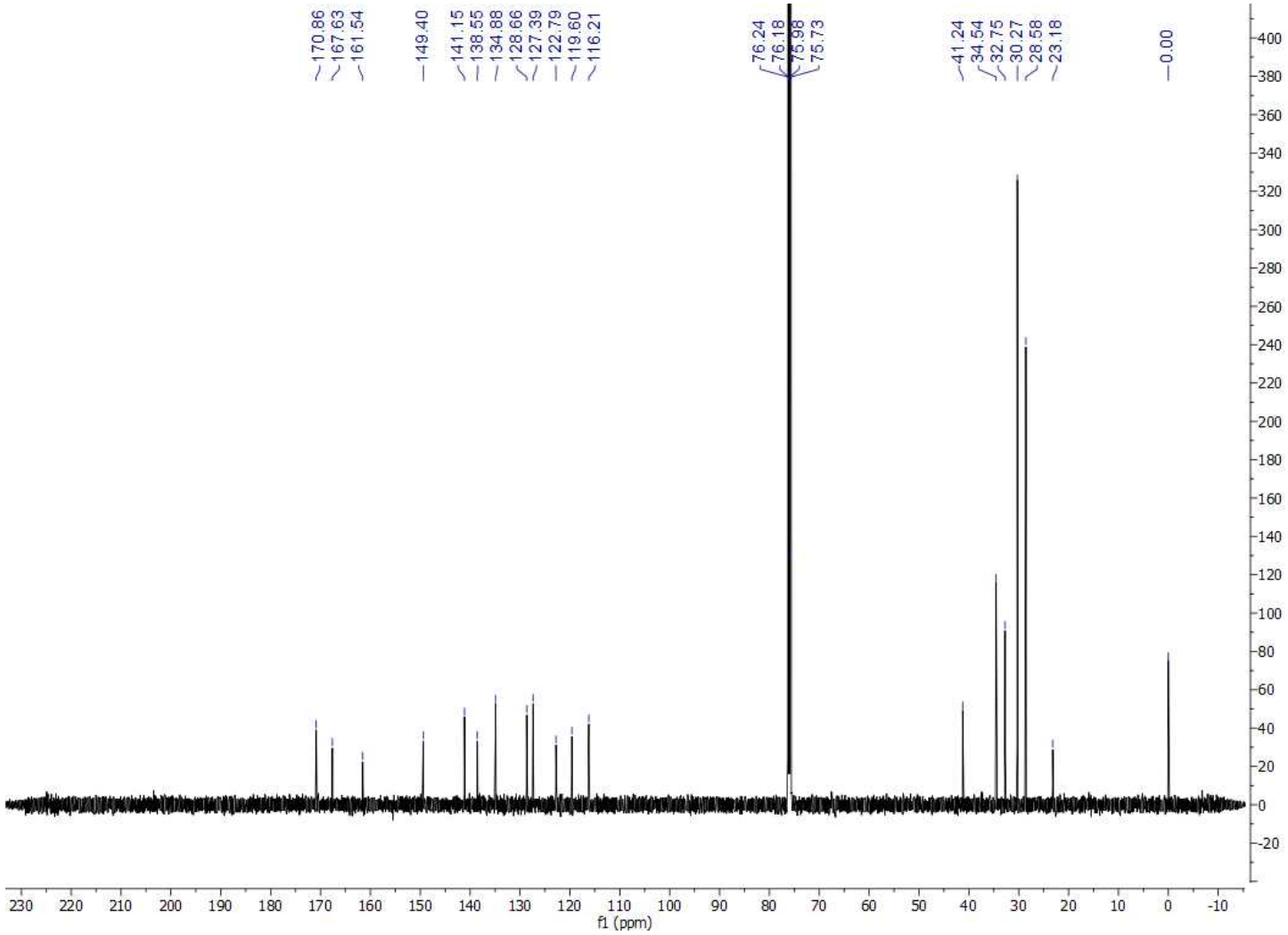


Figure A.13: $^{1}H,^{1}H$ COSY NMR spectrum of **In-1** recorded in $CDCl_3$

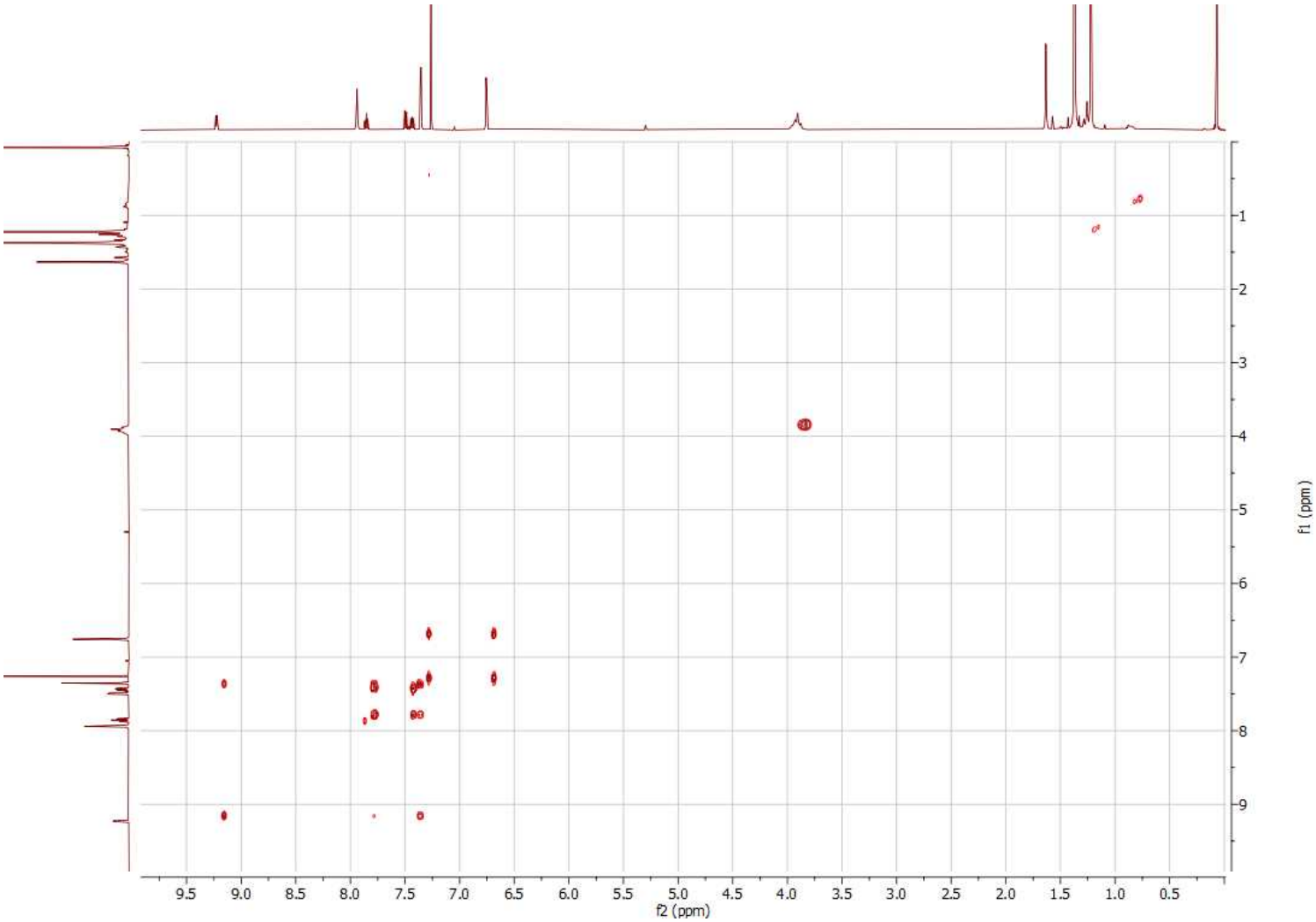


Figure A.14: $^{1}H,^{13}C$ HSQC NMR spectrum of **In-1** recorded in $CDCl_3$

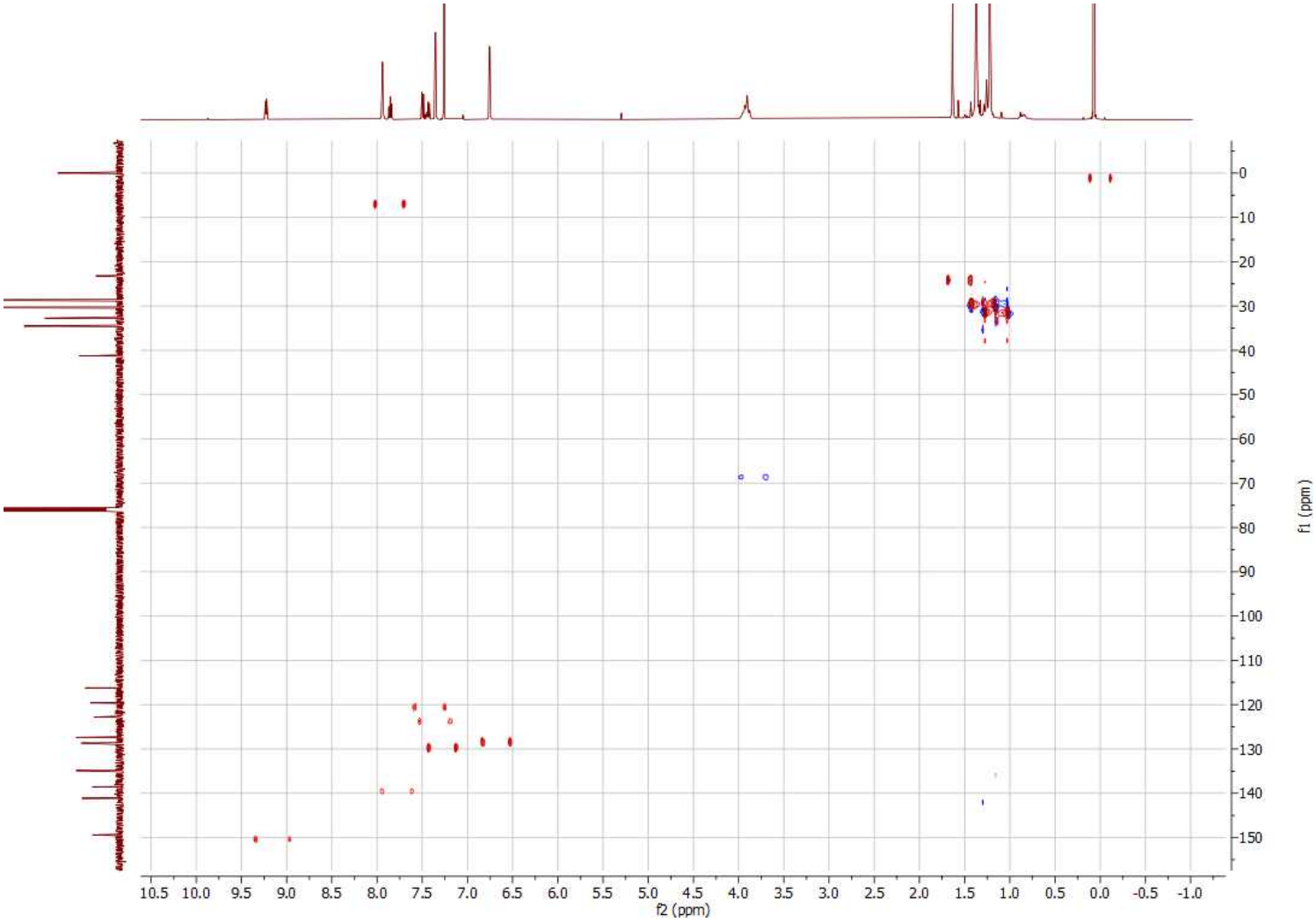


Figure A.15: $^{1}H,^{13}C$ HMBC NMR spectrum of **In-1** recorded in $CDCl_3$

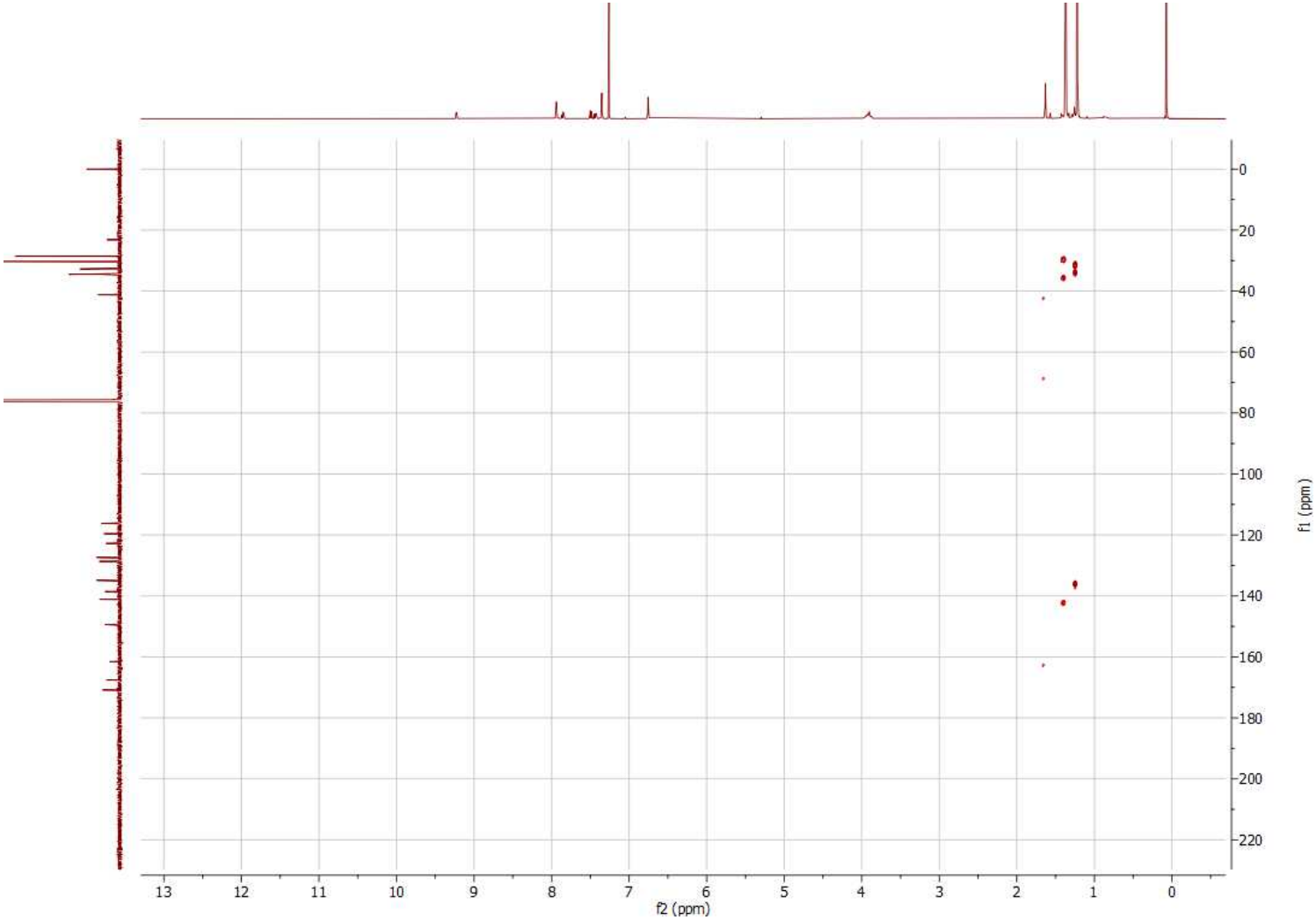


Figure A.16: ^{1}H NMR spectrum of **In-2** recorded at 500 MHz in $CDCl_3$

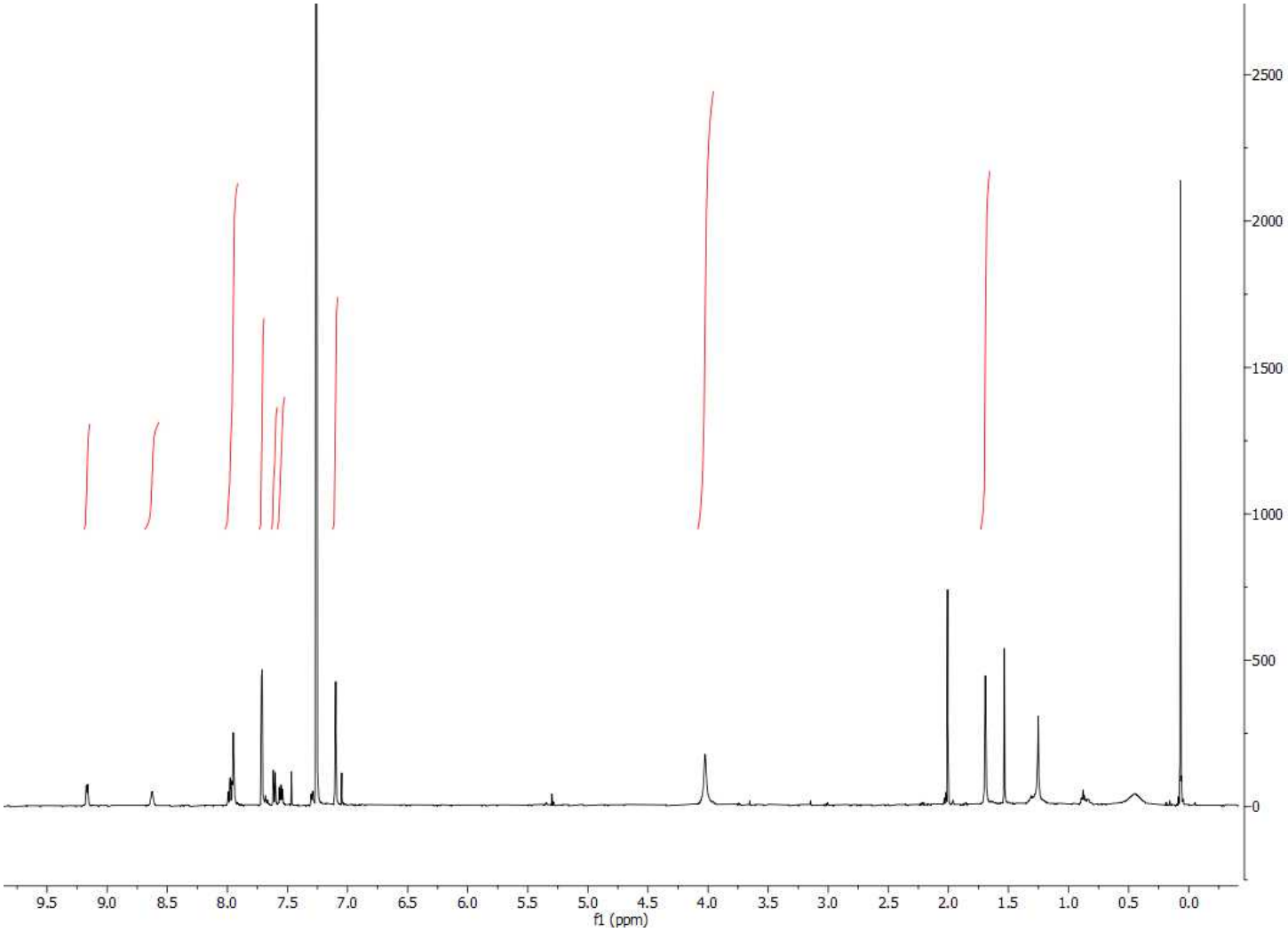


Figure A.17: ^{1}H NMR spectrum of **In-3** recorded at 500 MHz in $CDCl_3$

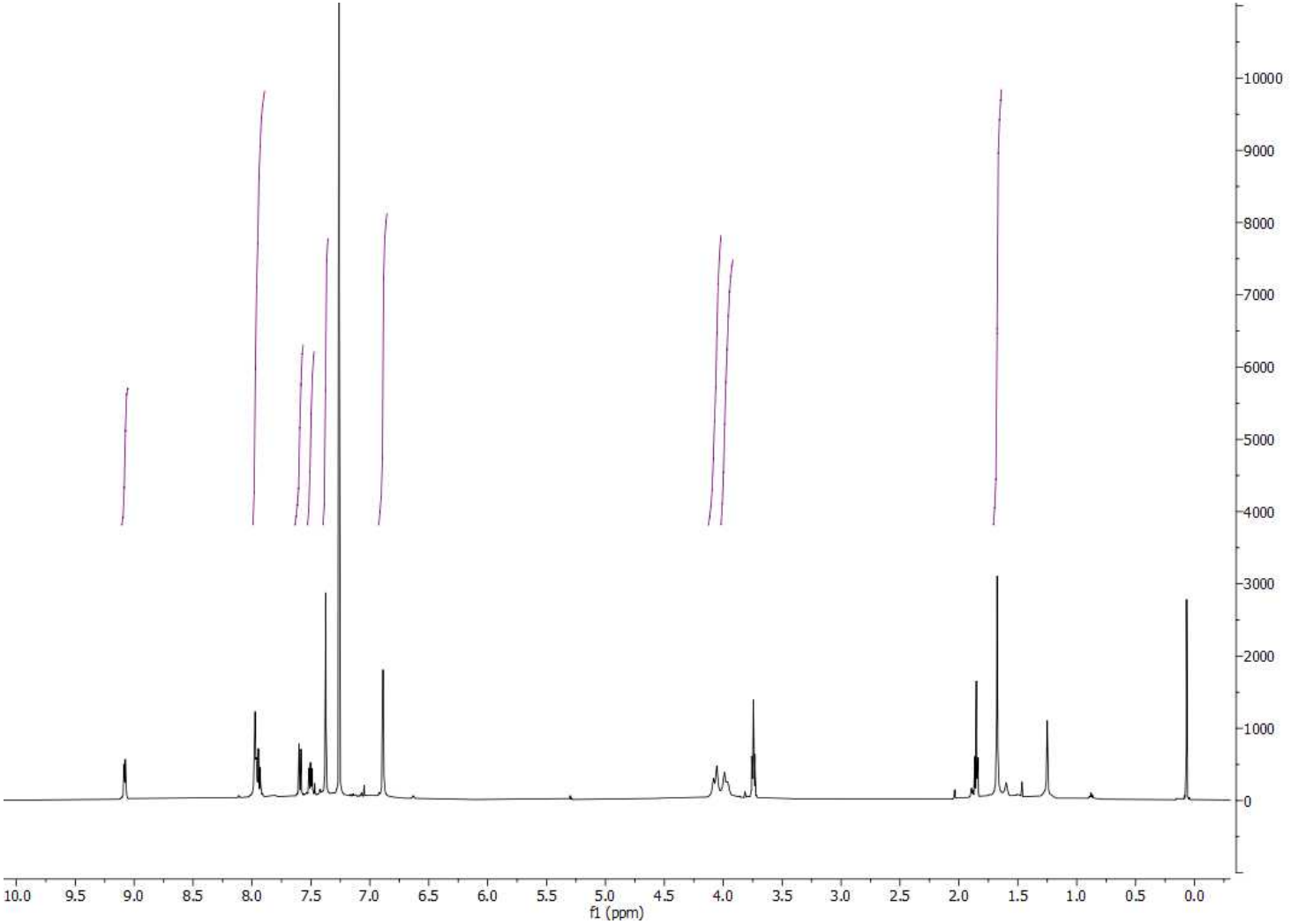


Figure A.18: ^{13}C NMR spectrum of **In-3** recorded at 125 MHz in $CDCl_3$

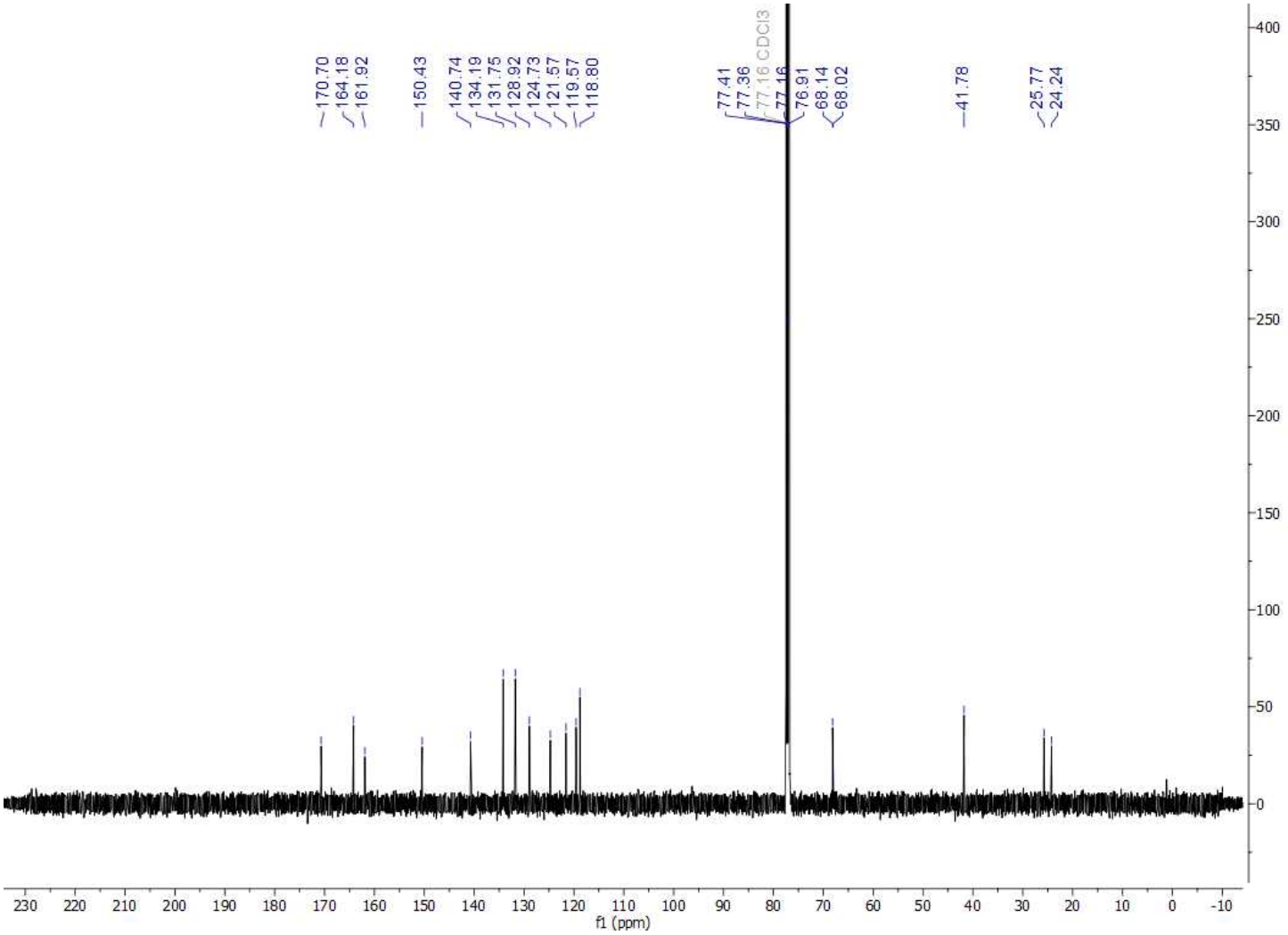


Figure A.19: $^{1}H,^{1}H$ COSY NMR spectrum of **In-3** recorded in $CDCl_3$

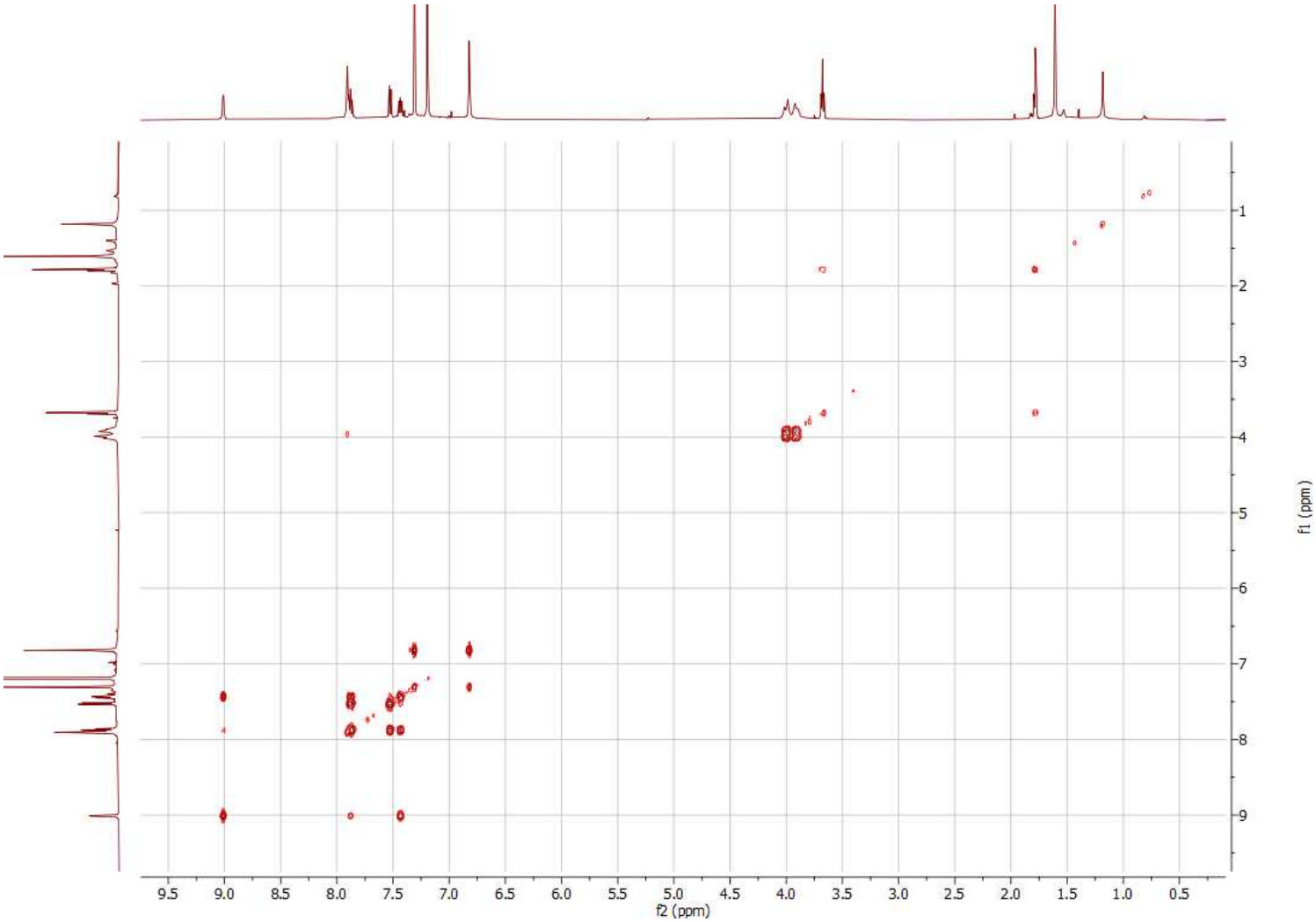


Figure A.20: $^{1}H,^{13}C$ HSQC NMR spectrum of **In-3** recorded in $CDCl_3$

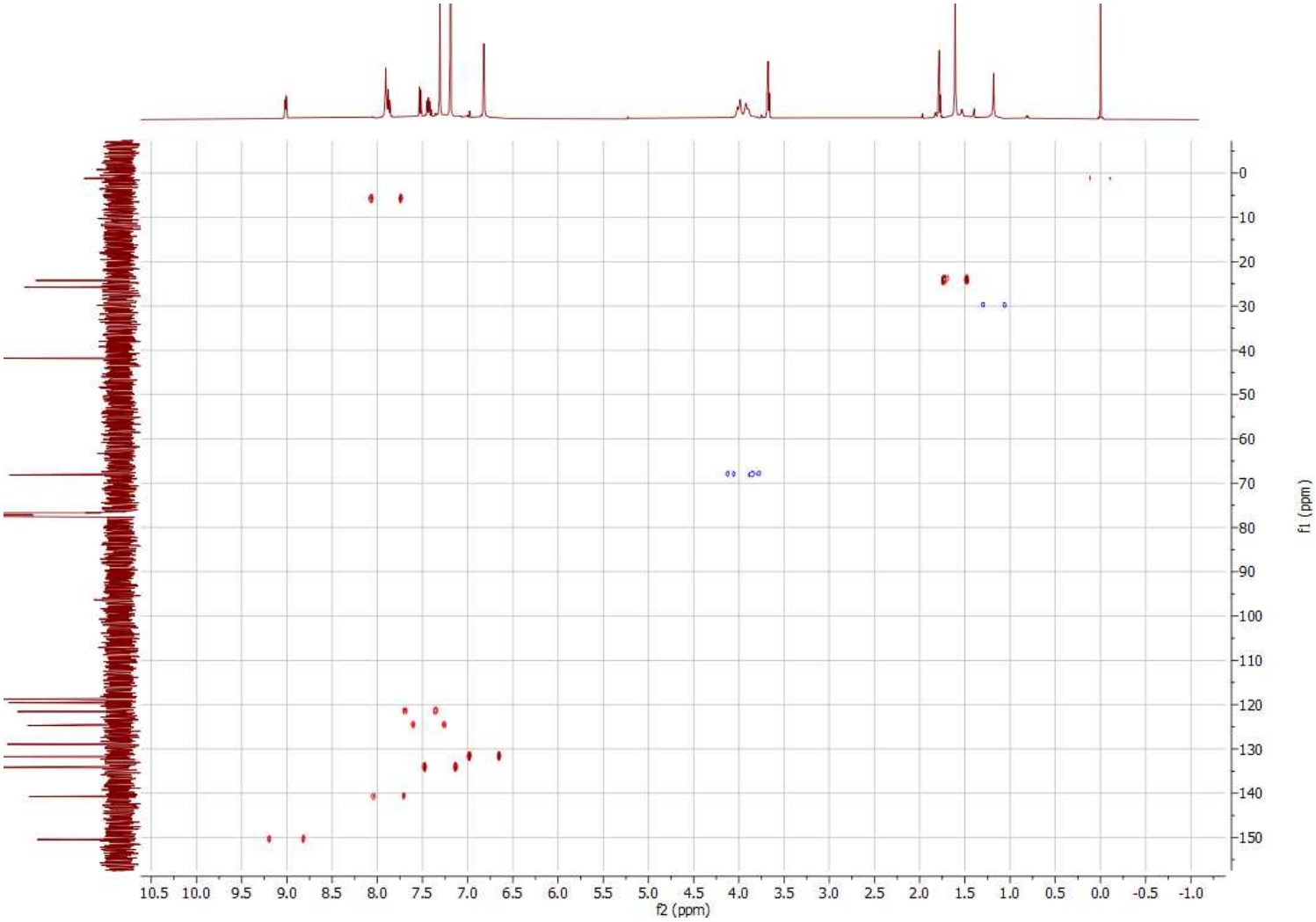


Figure A.21: $^{1}H,^{13}C$ HMBC NMR spectrum of **In-3** recorded in $CDCl_3$

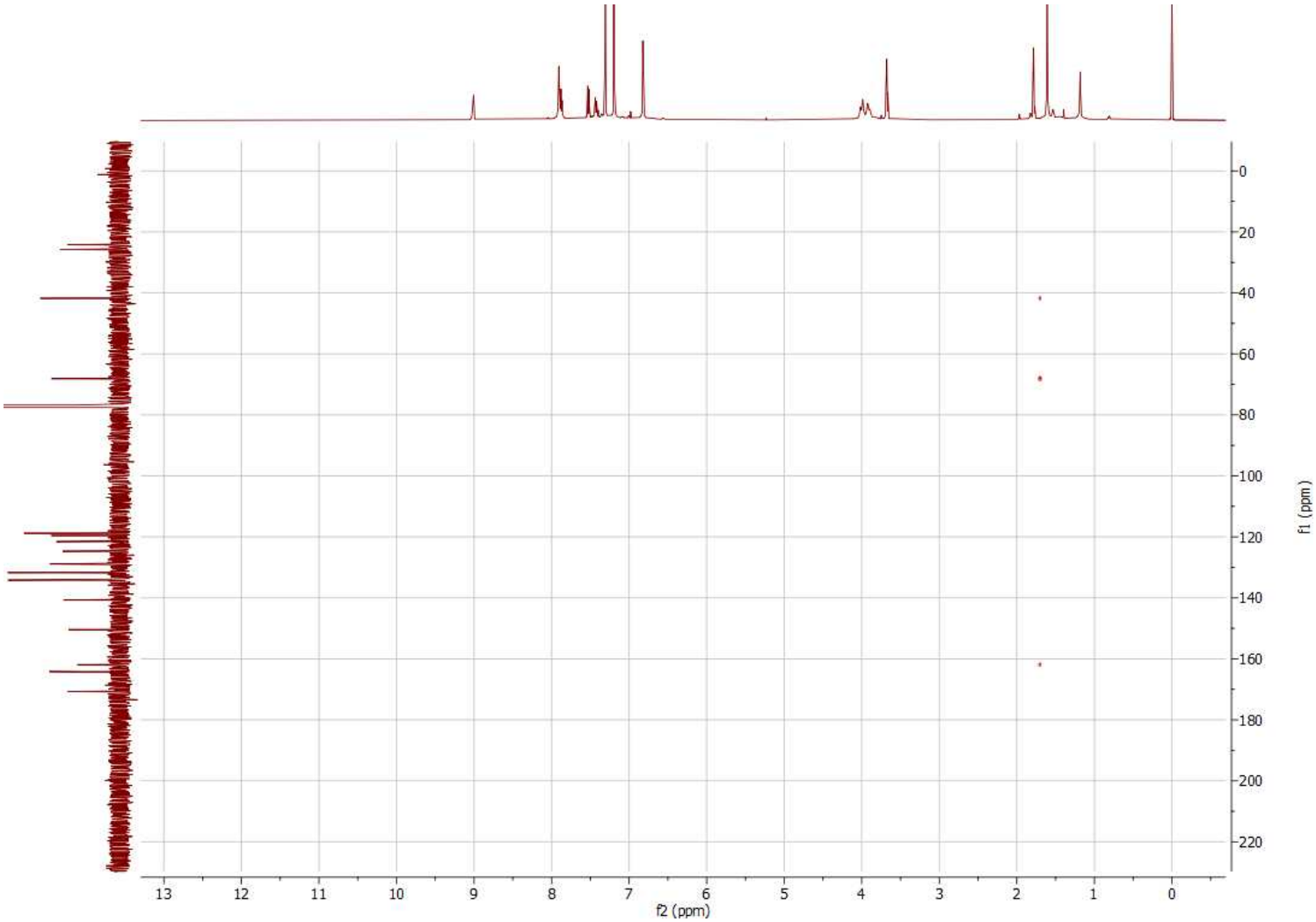


Figure A.22: ^{1}H NMR spectrum of Ir-1 recorded at 500 MHz in $CDCl_3$

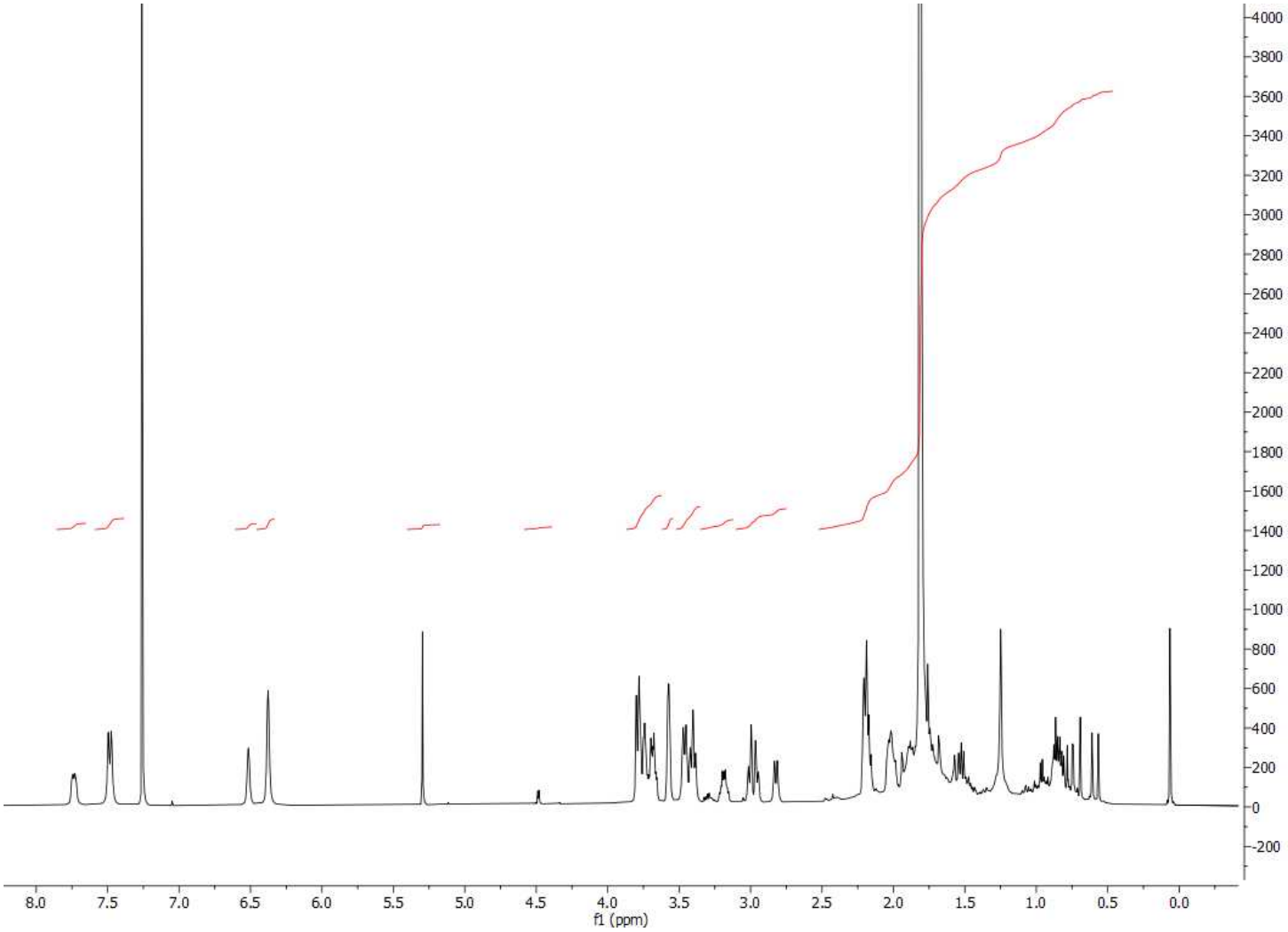


Figure A.23: $^{13}C\{^{1}H\}$ NMR spectrum of Ir-1 recorded at 125 MHz in $CDCl_3$

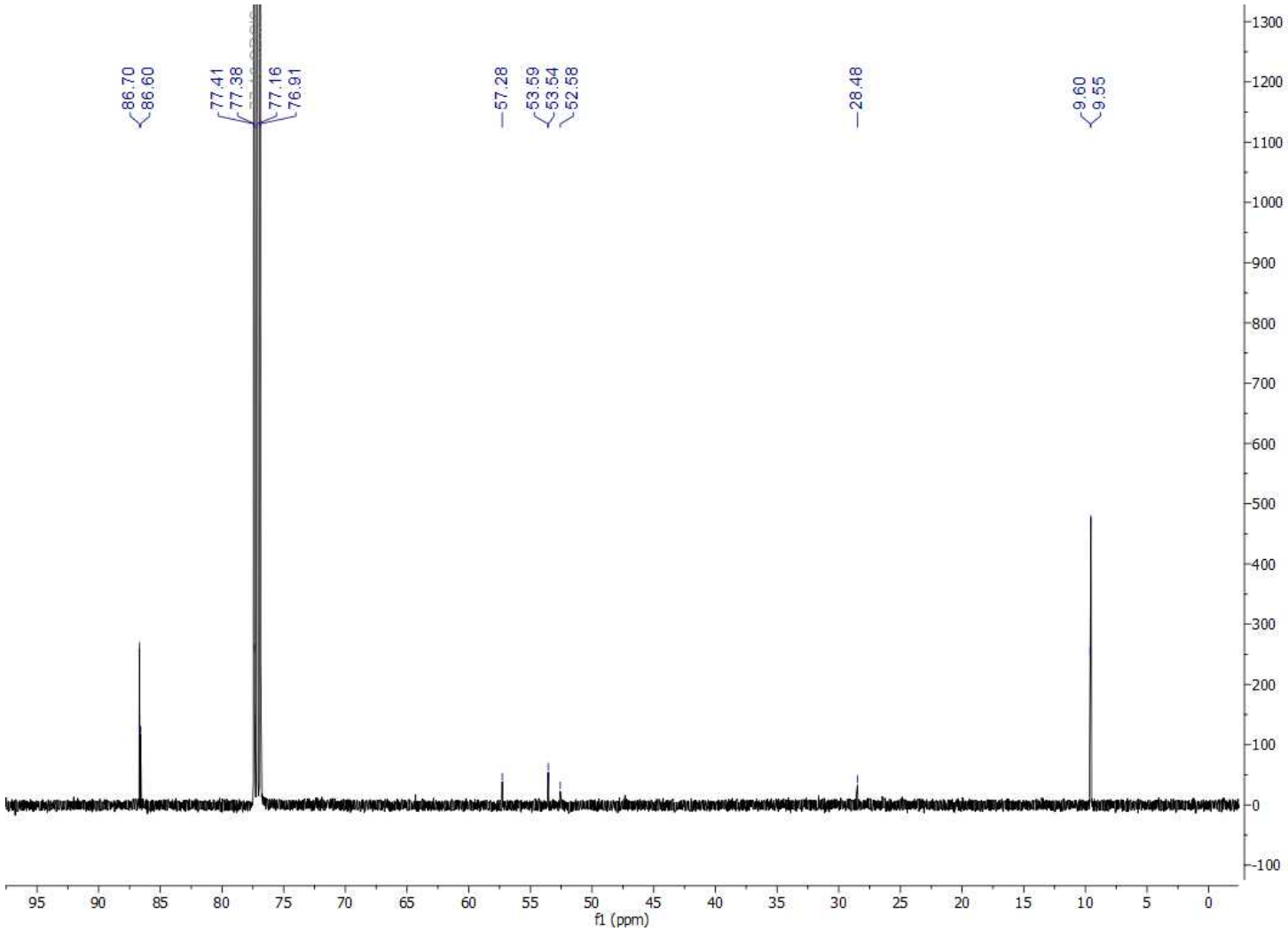


Figure A.24: $^{1}H,^{1}H$ COSY NMR spectrum of Ir-1 in $CDCl_3$

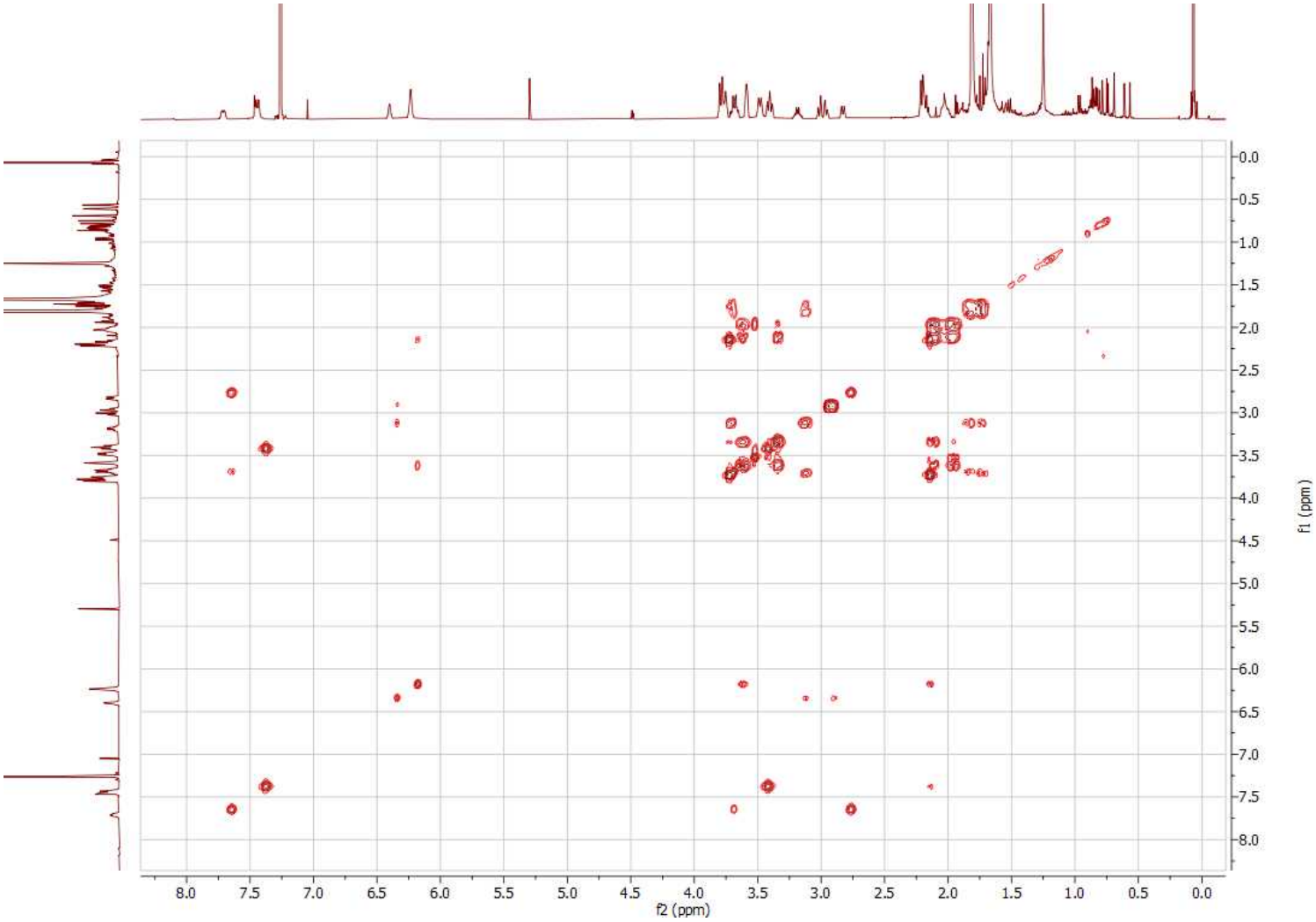


Figure A.25: $^{1}H,^{13}C$ HSQC NMR spectrum of Ir-1 in $CDCl_3$

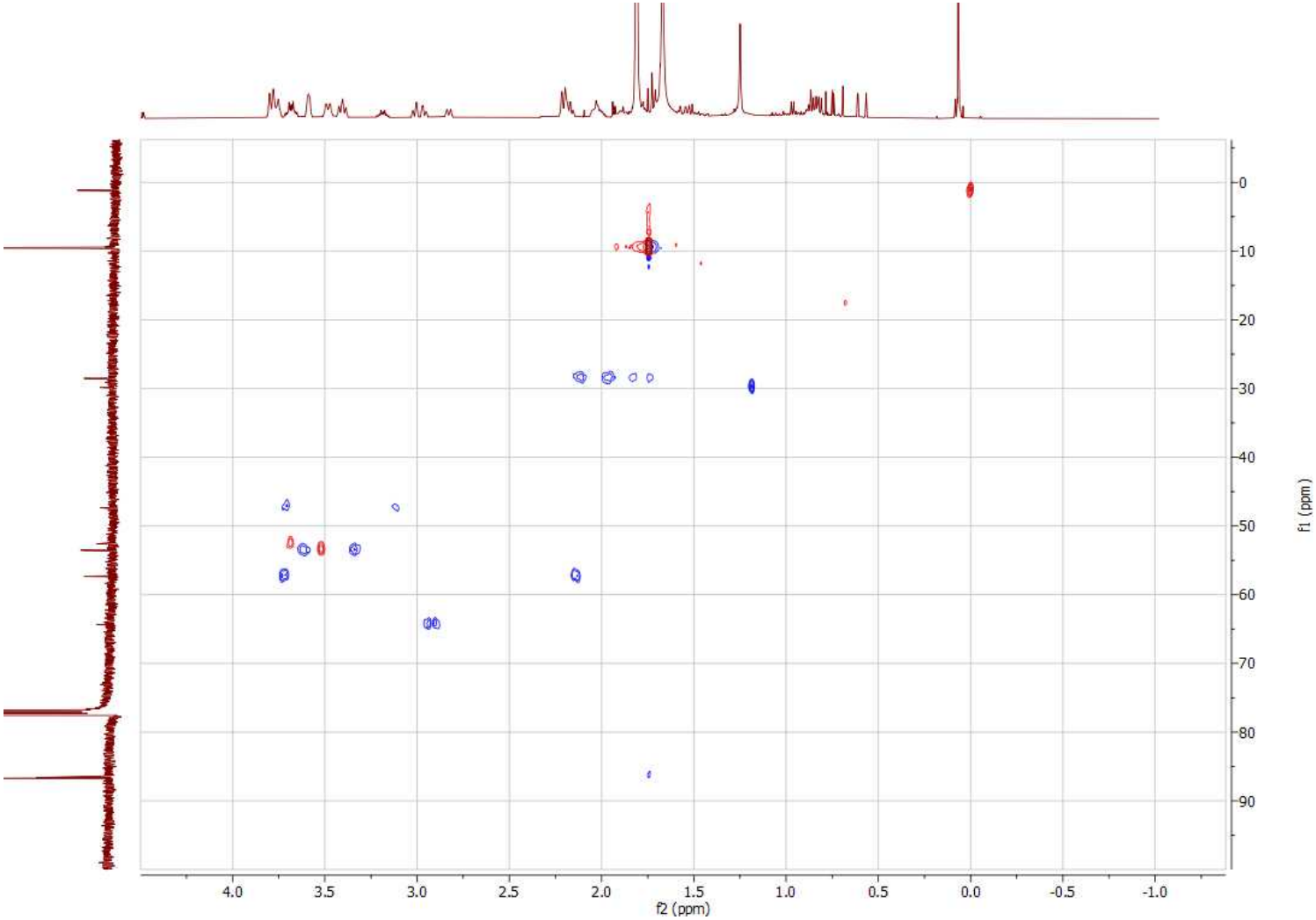


Figure A.26: $^{1}H,^{1}H$ NOESY NMR spectrum of Ir-1 in $CDCl_3$

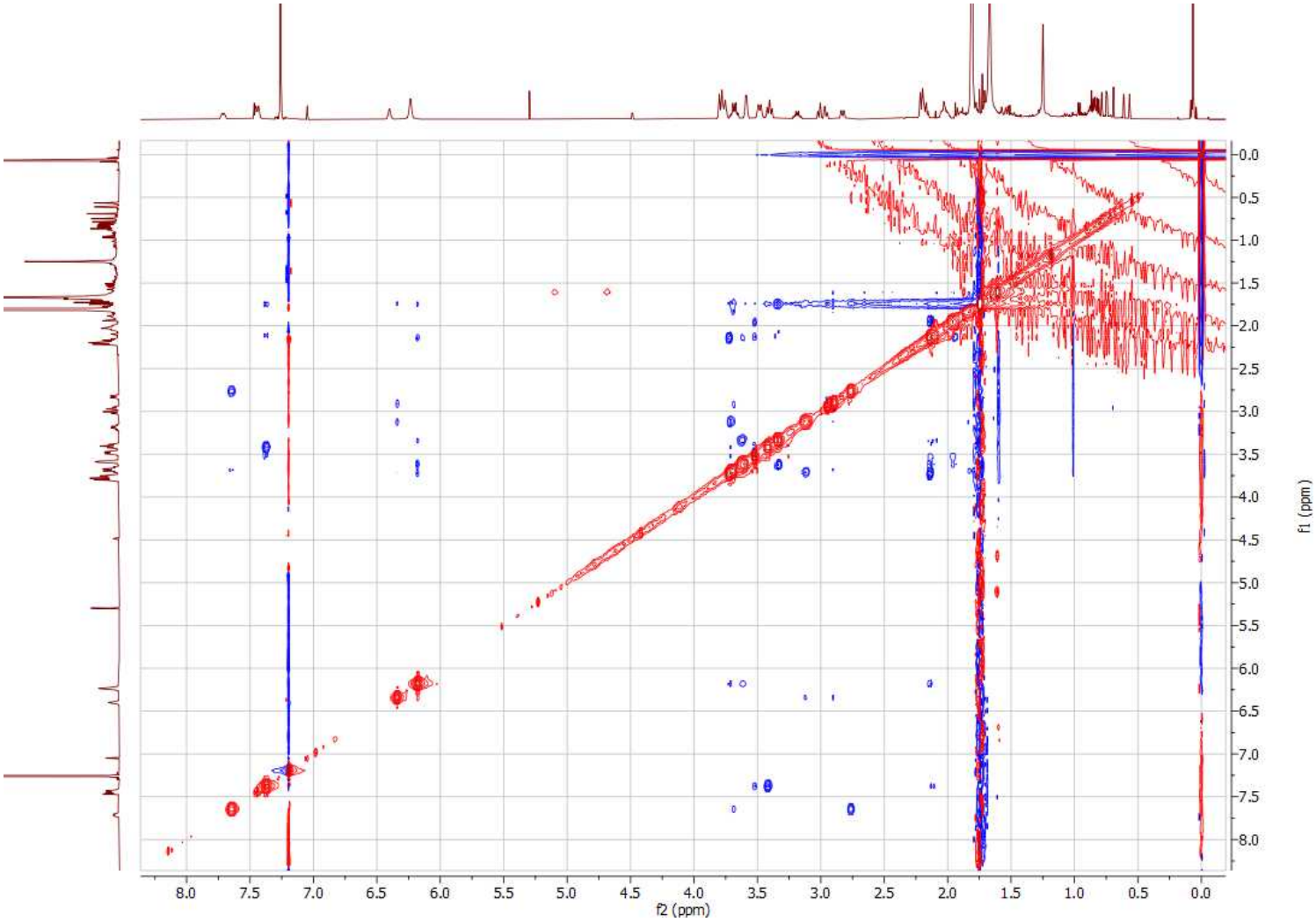


Figure A.27: ^{1}H NMR spectrum of Ir-2 recorded at 500 MHz in $CDCl_3$

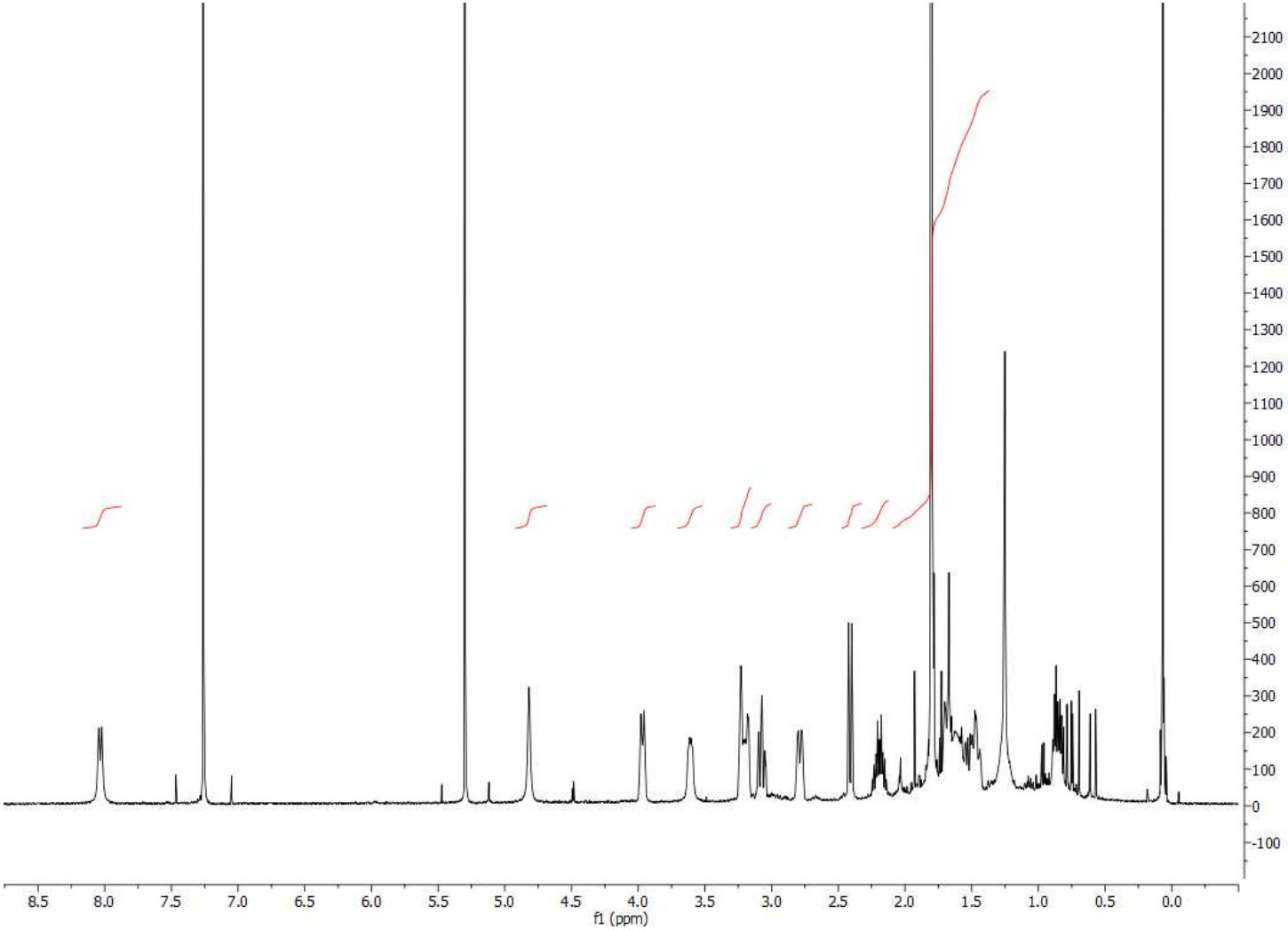


Figure A.28: $^{13}C\{^{1}H\}$ NMR spectrum of Ir-2 recorded at 125 MHz in $CDCl_3$

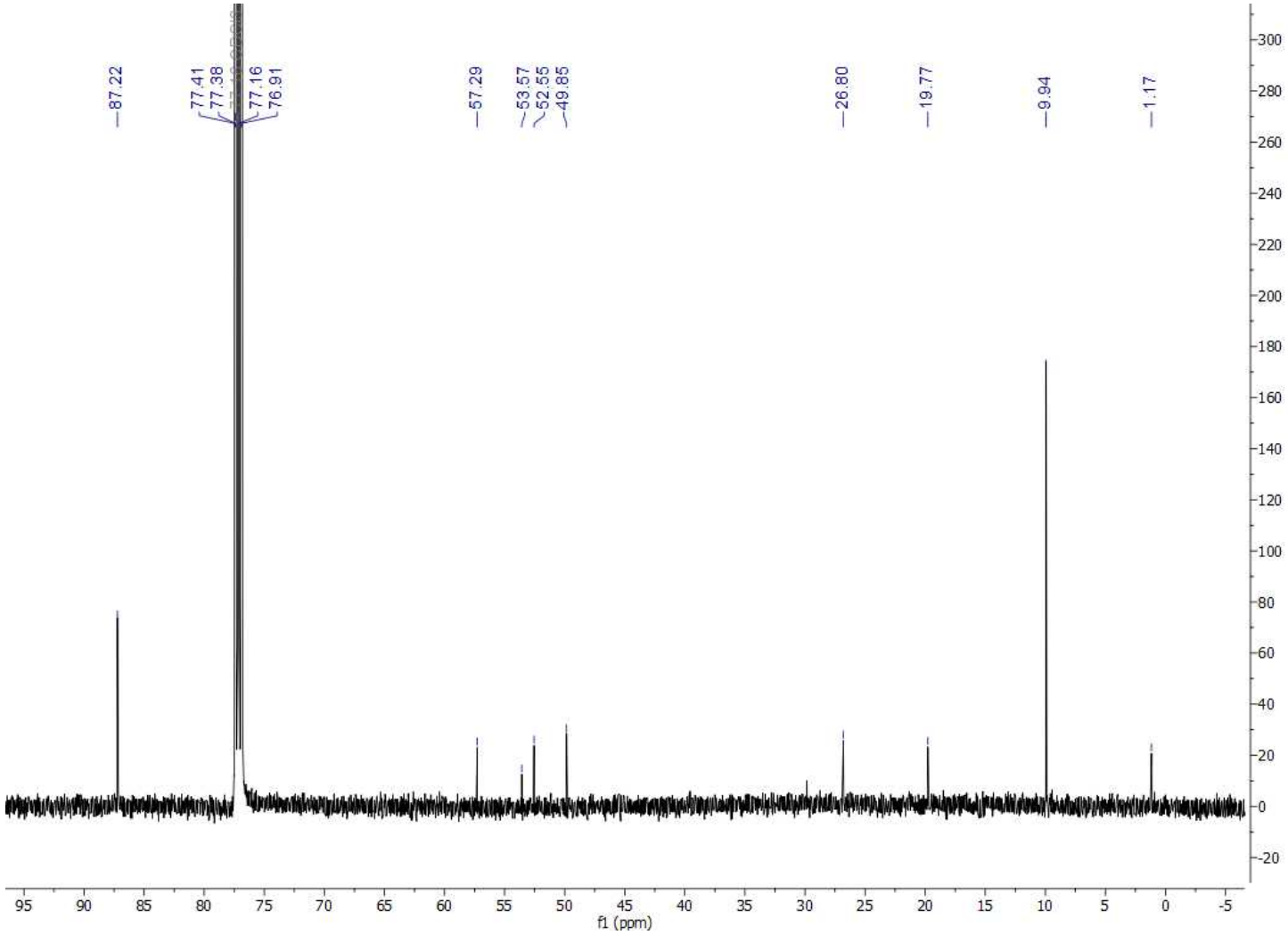


Figure A.29: ^{1}H NMR spectrum of Ir-3 recorded at 500 MHz in $CDCl_3$

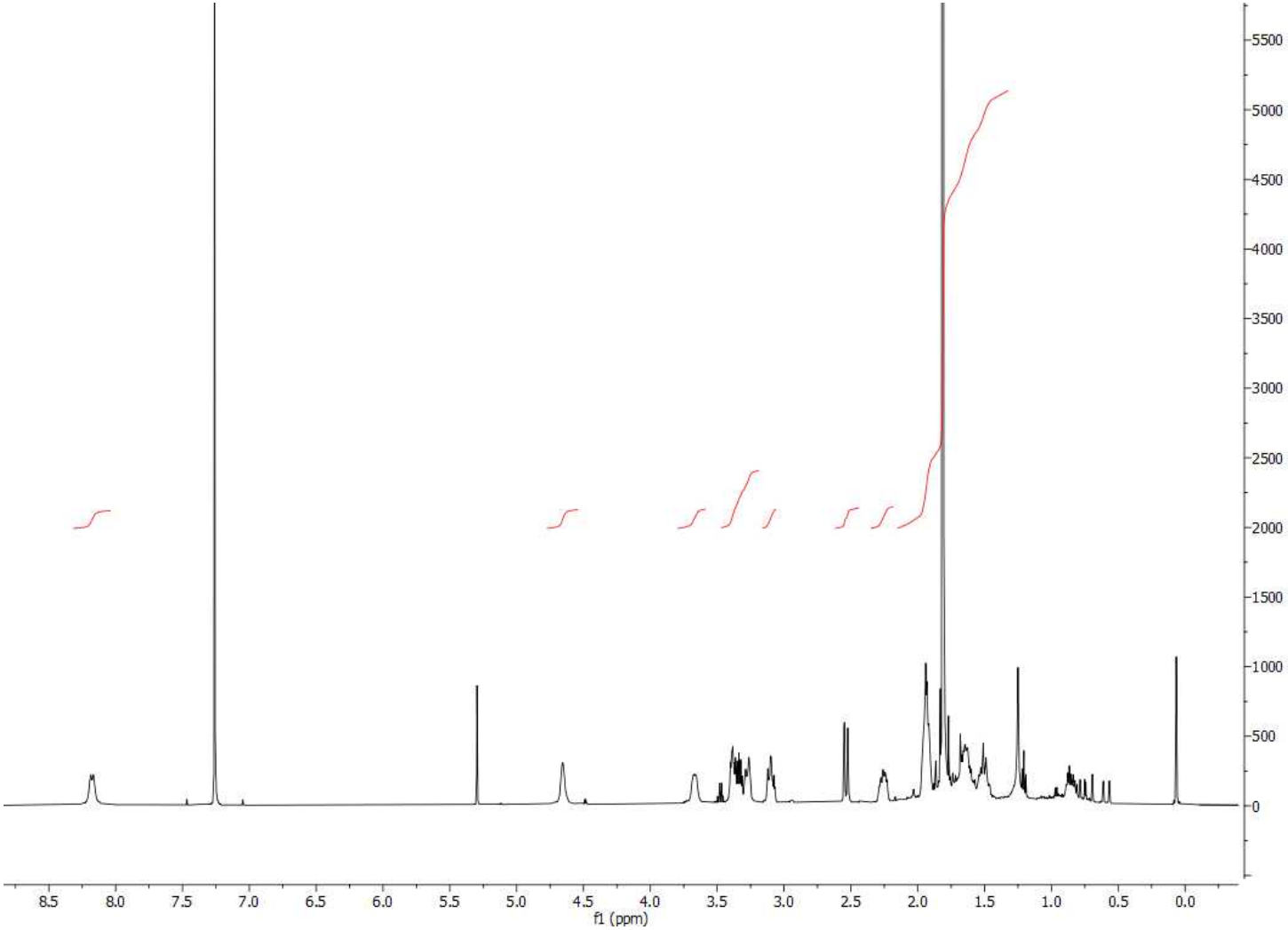


Figure A.30: $^{13}C\{^{1}H\}$ NMR spectrum of Ir-3 recorded at 125 MHz in $CDCl_3$

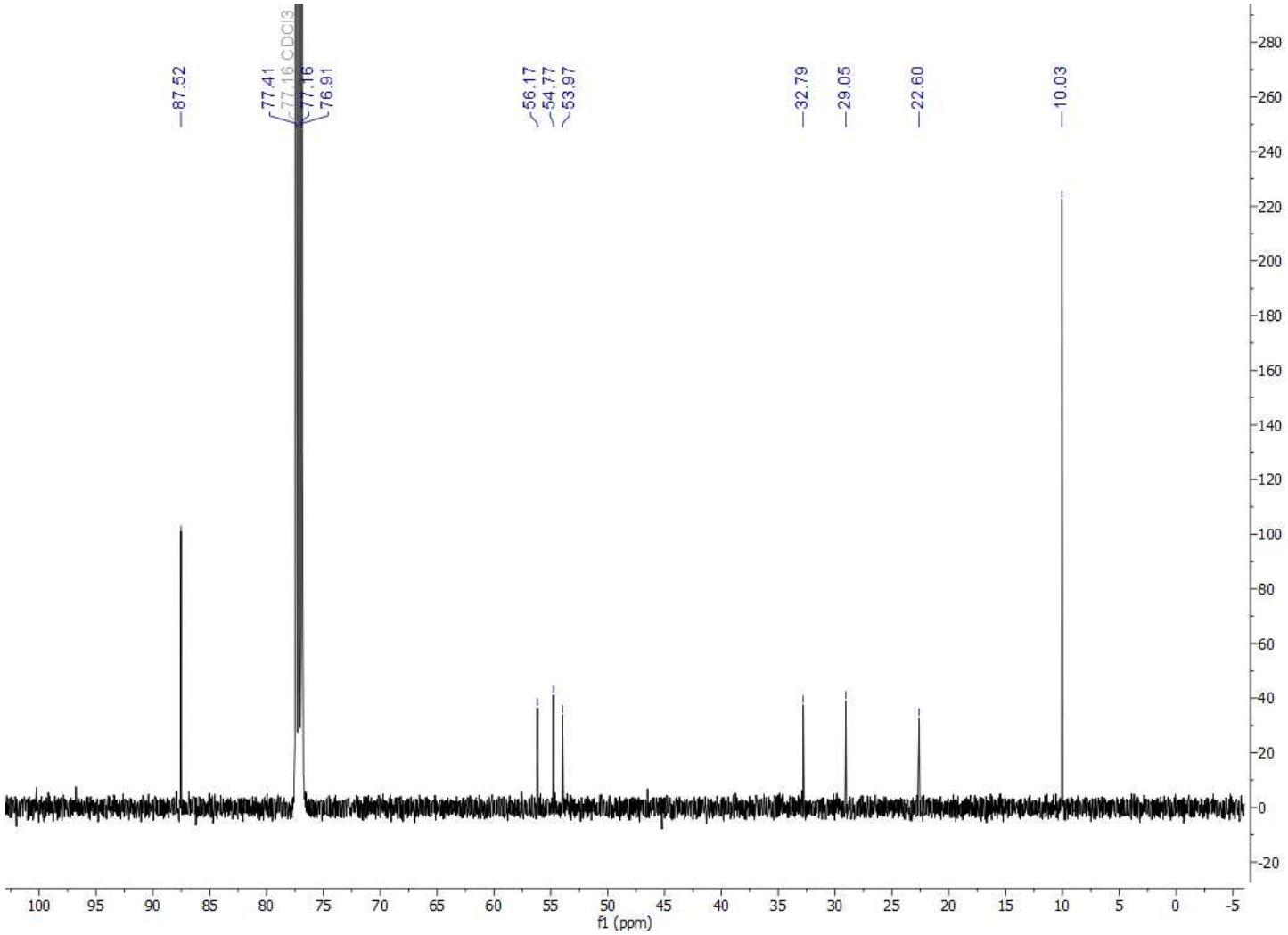


Figure A.31: $^{1}H,^{1}H$ COSY NMR spectrum of Ir-3 in $CDCl_3$

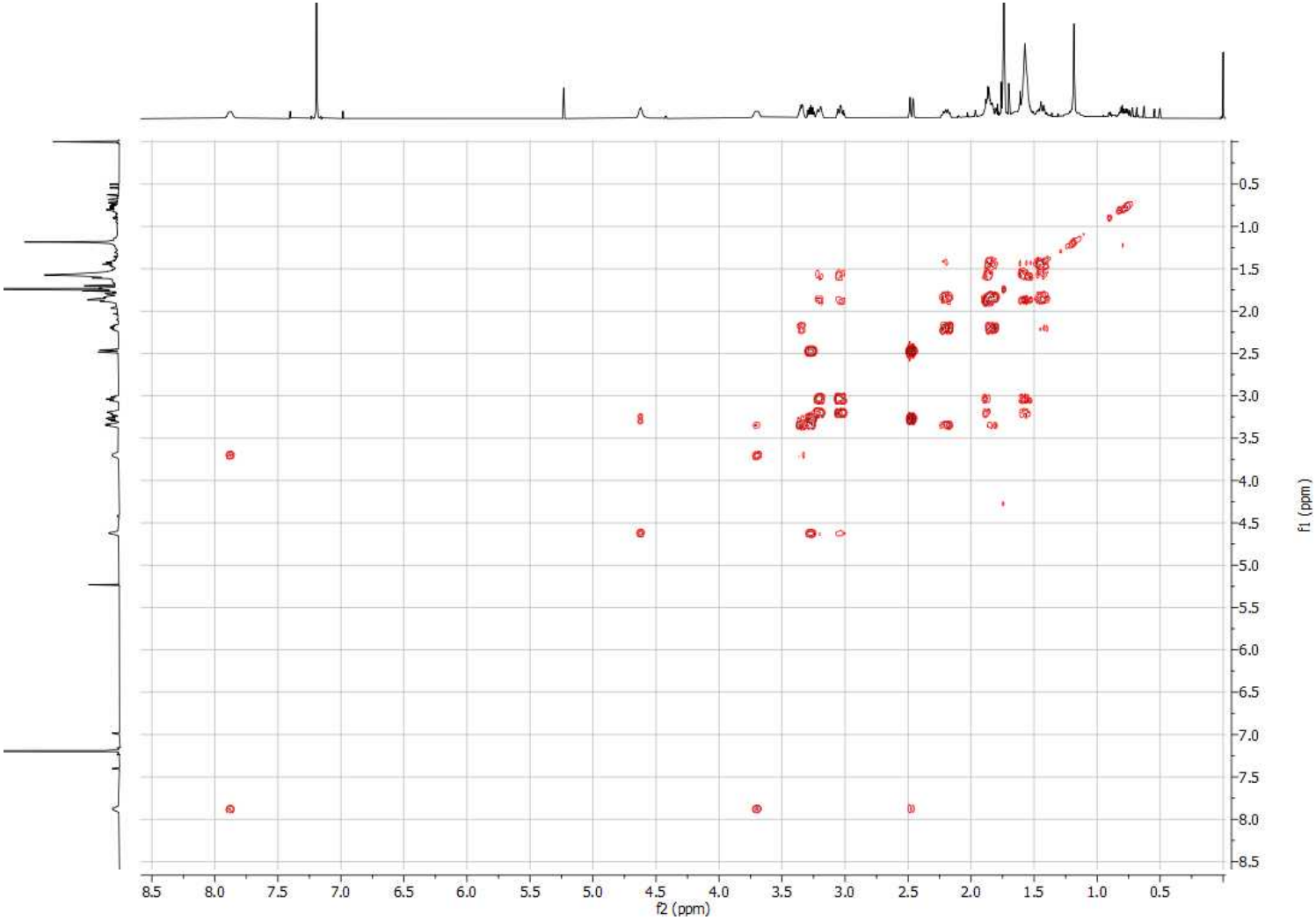


Figure A.32: $^{1}H,^{13}C$ HSQC NMR spectrum of Ir-3 in $CDCl_3$

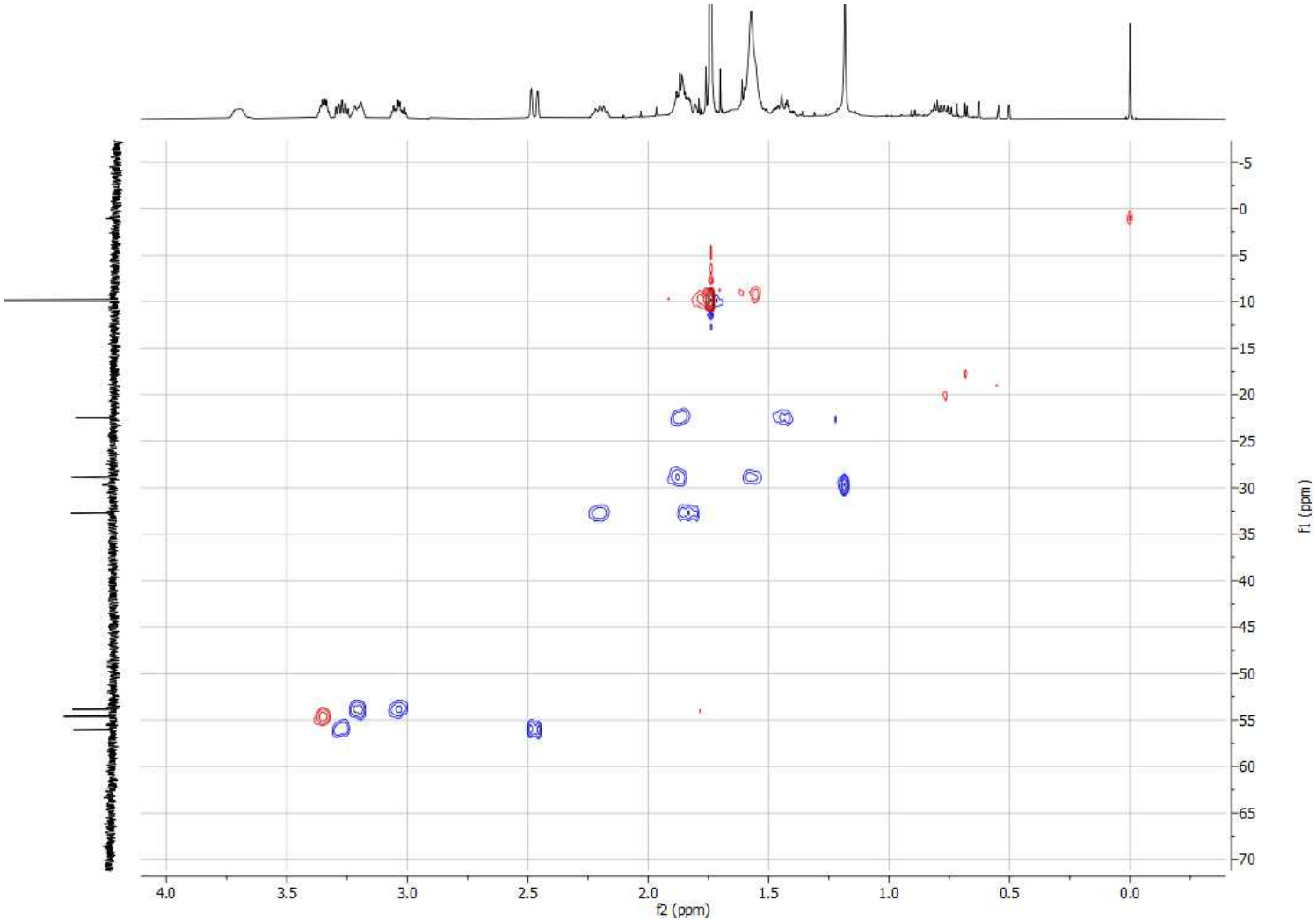


Figure A.33: $^{1}H,^{1}H$ NOESY NMR spectrum of Ir-3 in $CDCl_3$

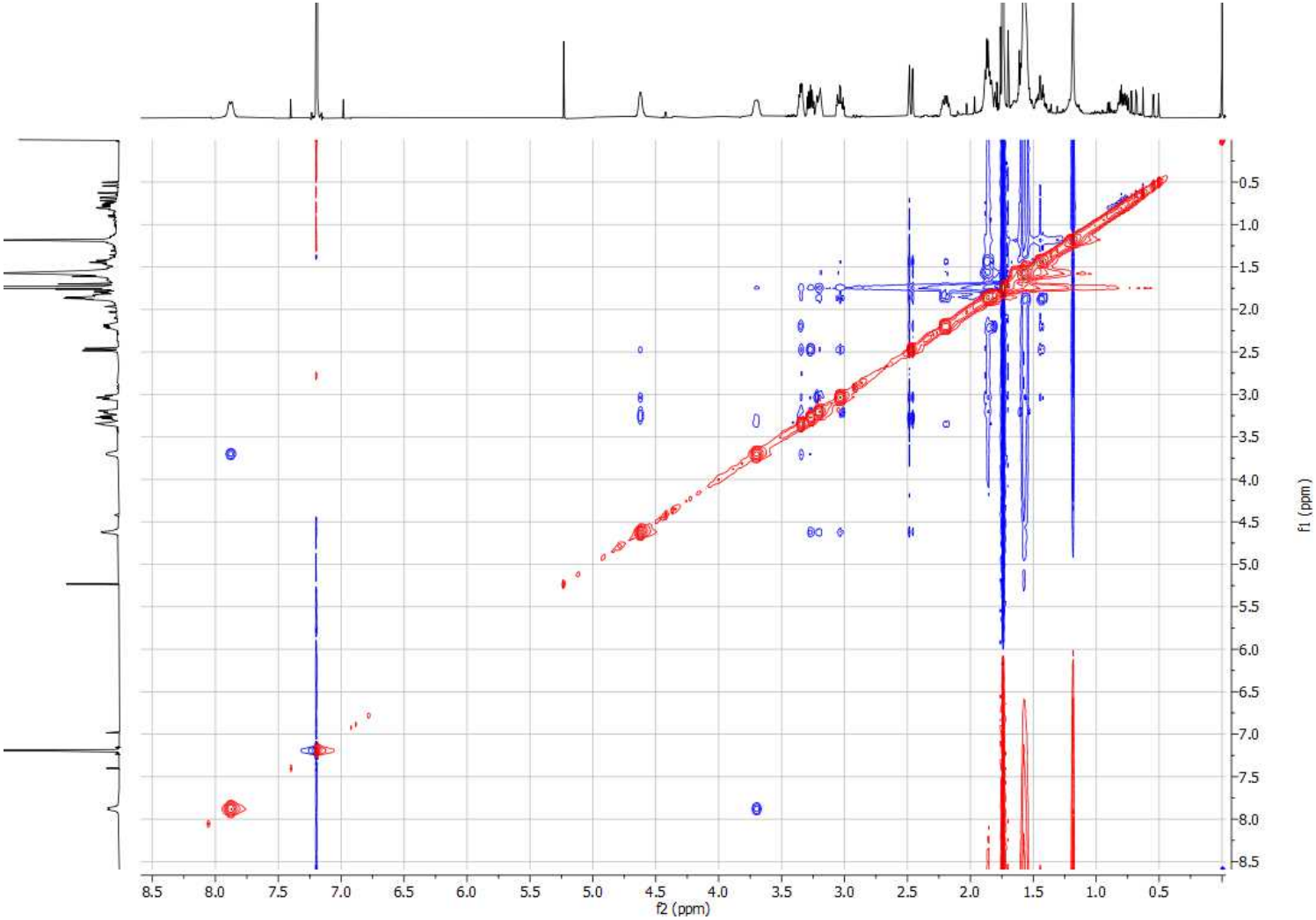


Figure A.34: ^{1}H NMR spectrum of Rh-1 recorded at 500 MHz in $CDCl_3$

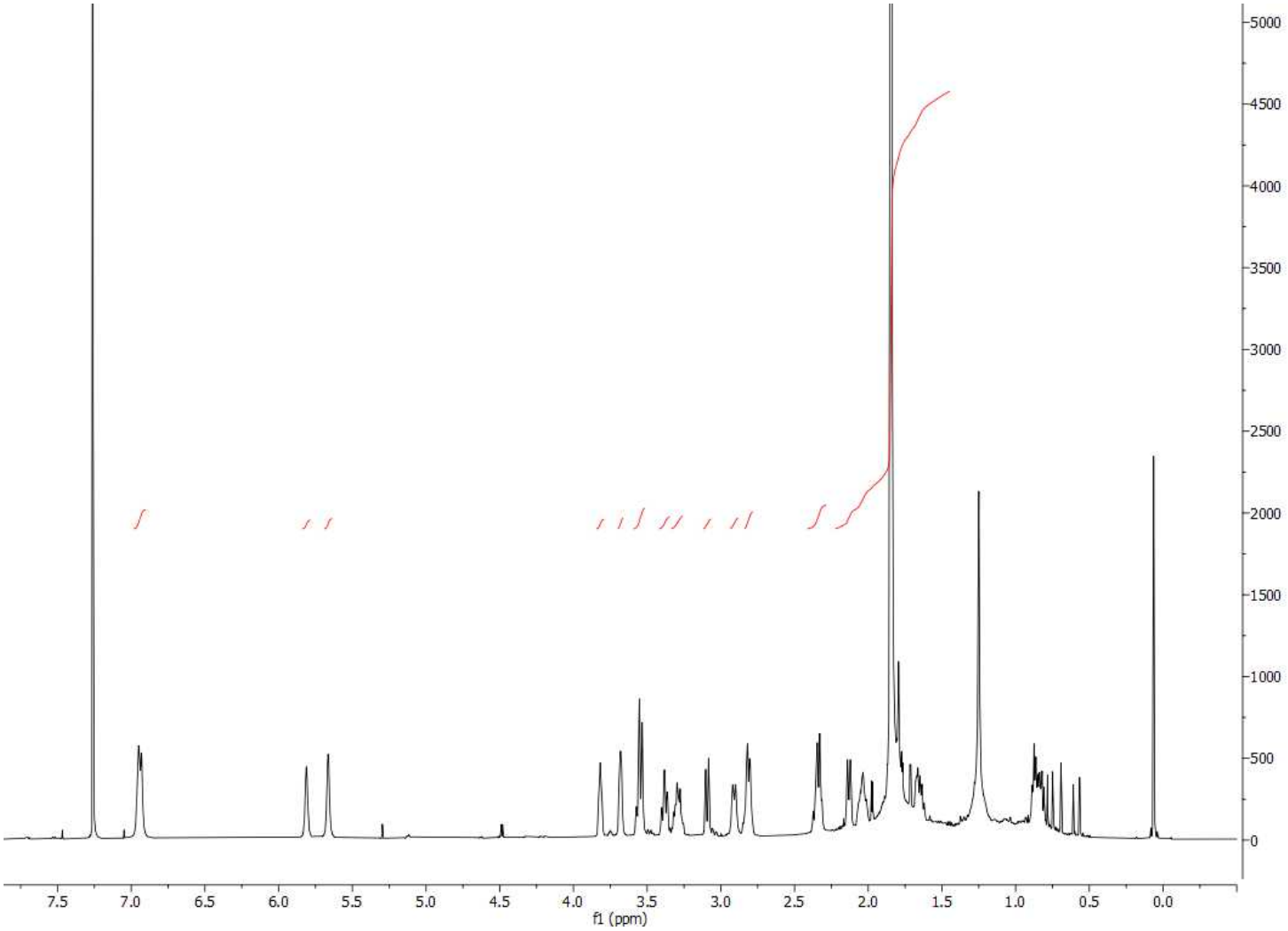


Figure A.35: $^{13}C\{^{1}H\}$ NMR spectrum of Rh-1 recorded at 125 MHz in $CDCl_3$

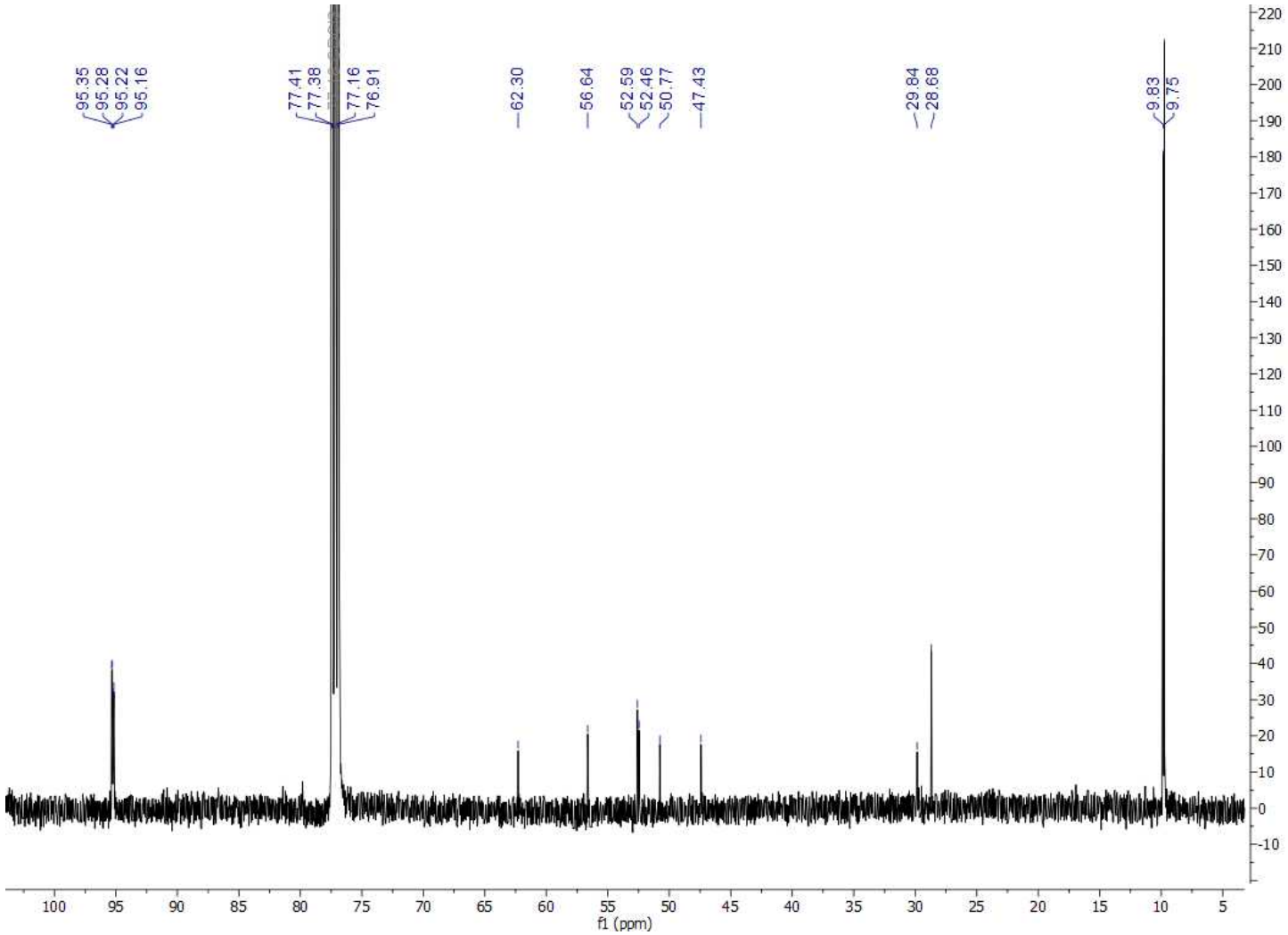


Figure A.36: $^{1}H,^{1}H$ COSY NMR spectrum of Rh-1 in $CDCl_3$

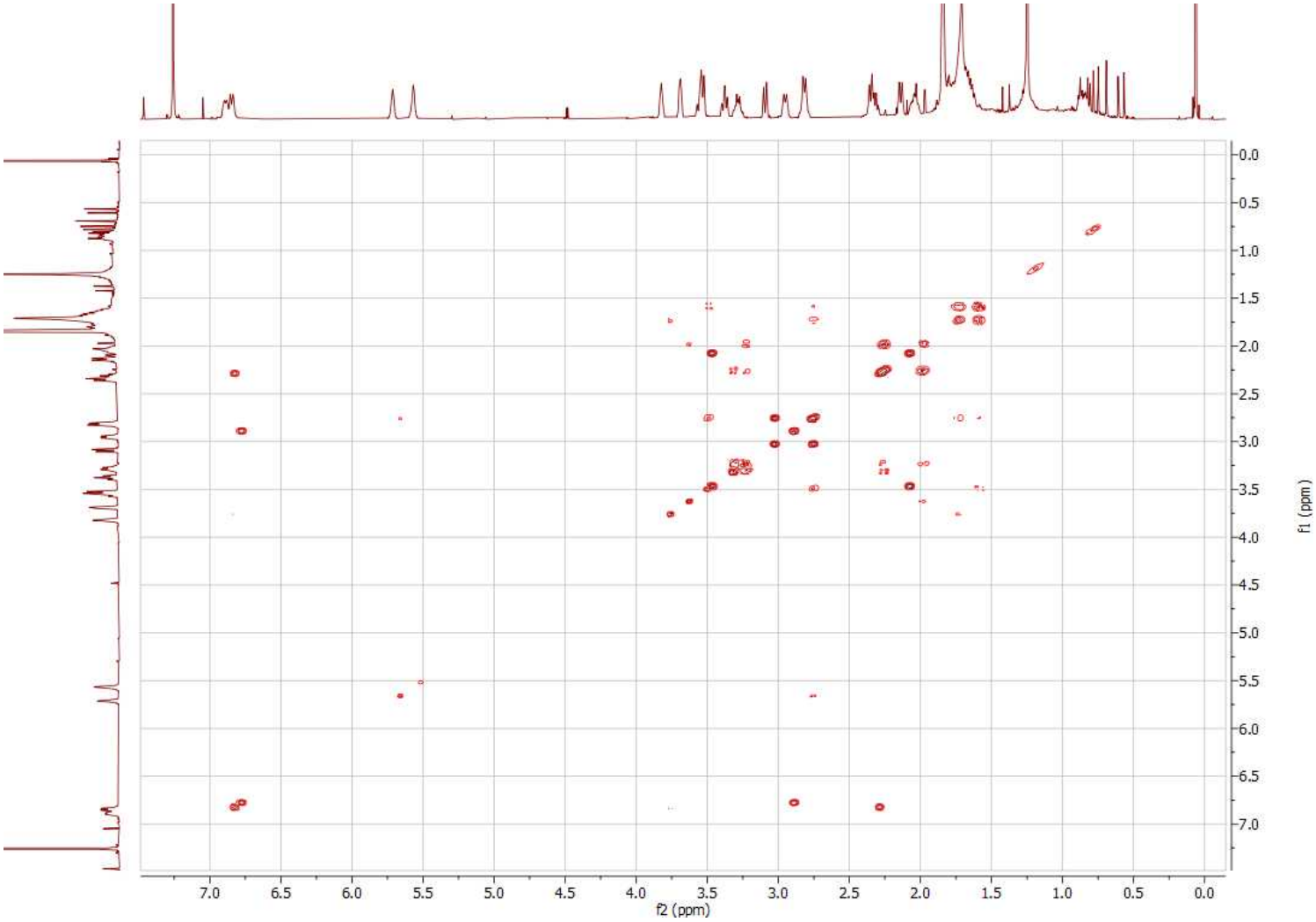


Figure A.37: $^{1}H,^{13}C$ HSQC NMR spectrum of Rh-1 in $CDCl_3$

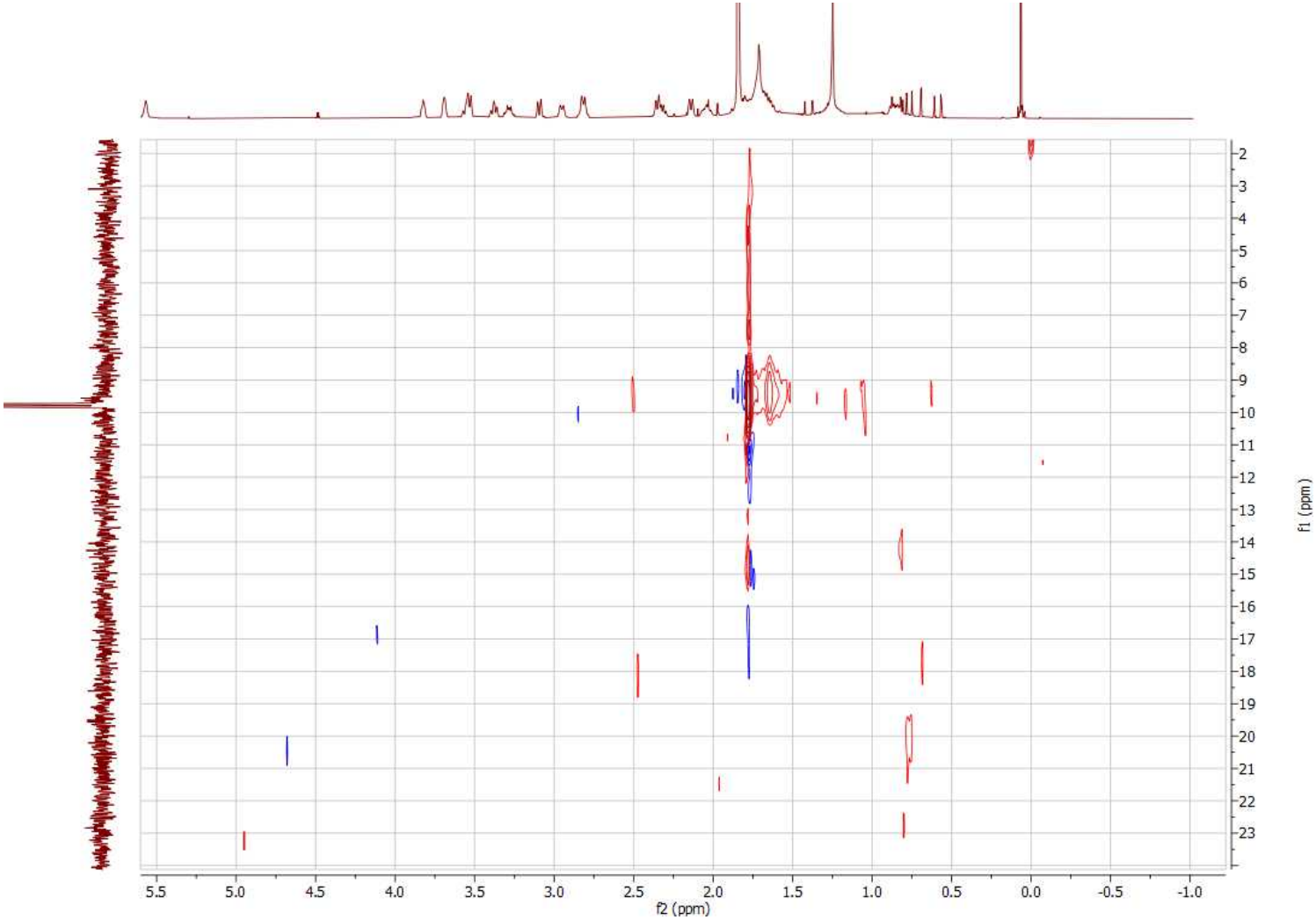


Figure A.38: $^{1}H,^{1}H$ NOESY NMR spectrum of Rh-1 in $CDCl_3$

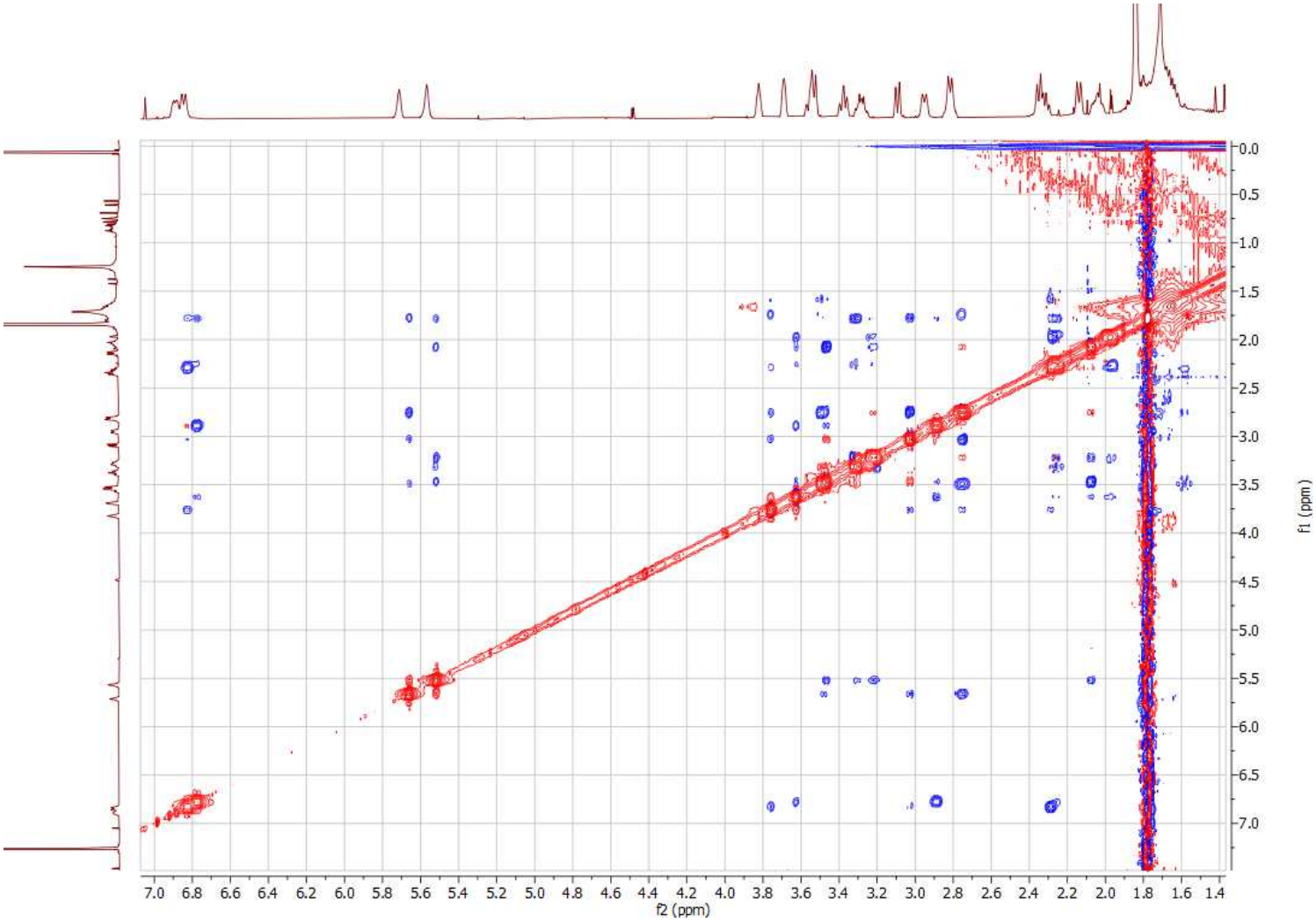


Figure A.39: ^{1}H NMR spectrum of Rh-2 recorded at 500 MHz in $CDCl_3$

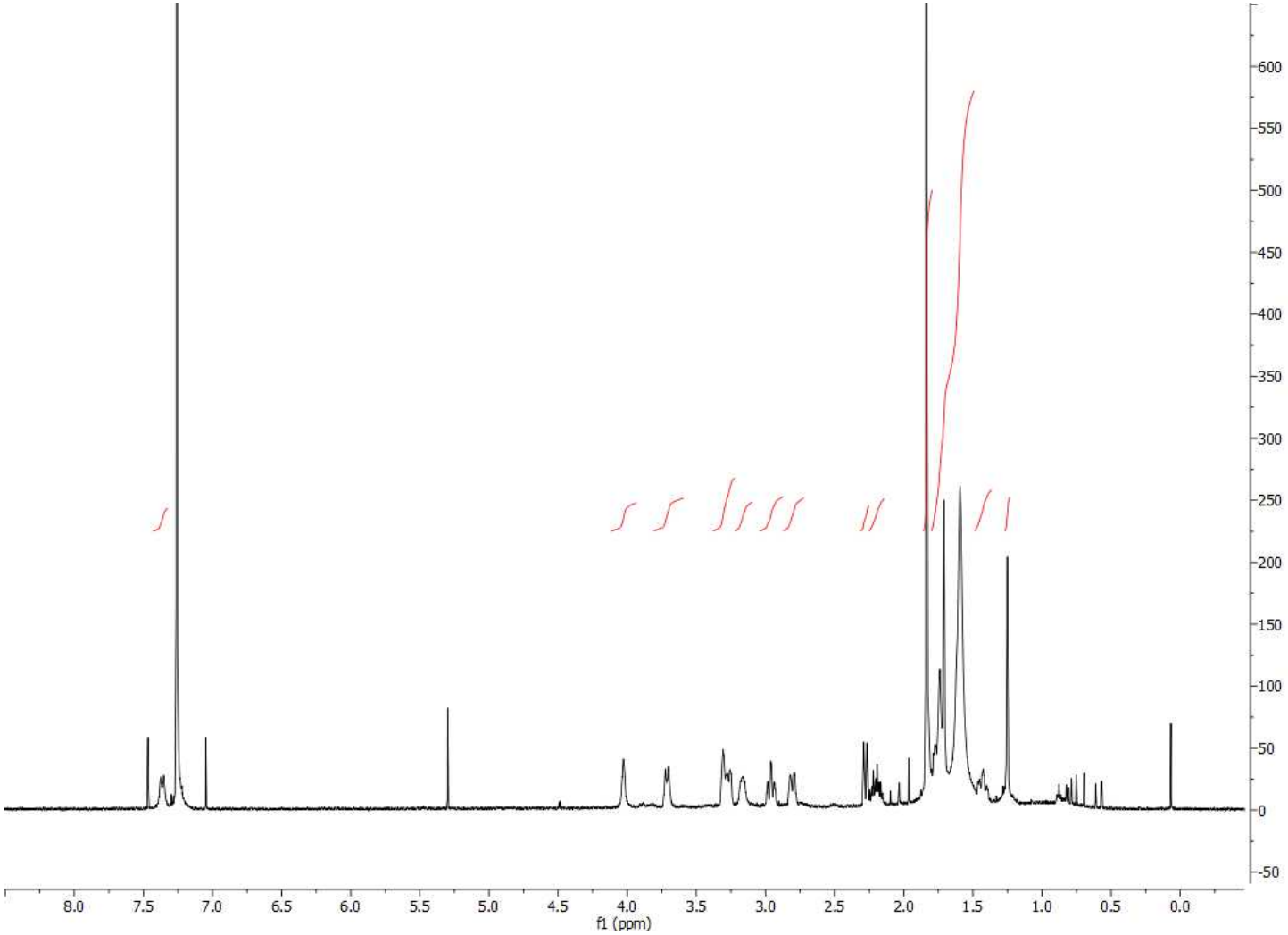


Figure A.40: $^{13}C\{^{1}H\}$ NMR spectrum of Rh-2 recorded at 125 MHz in $CDCl_3$

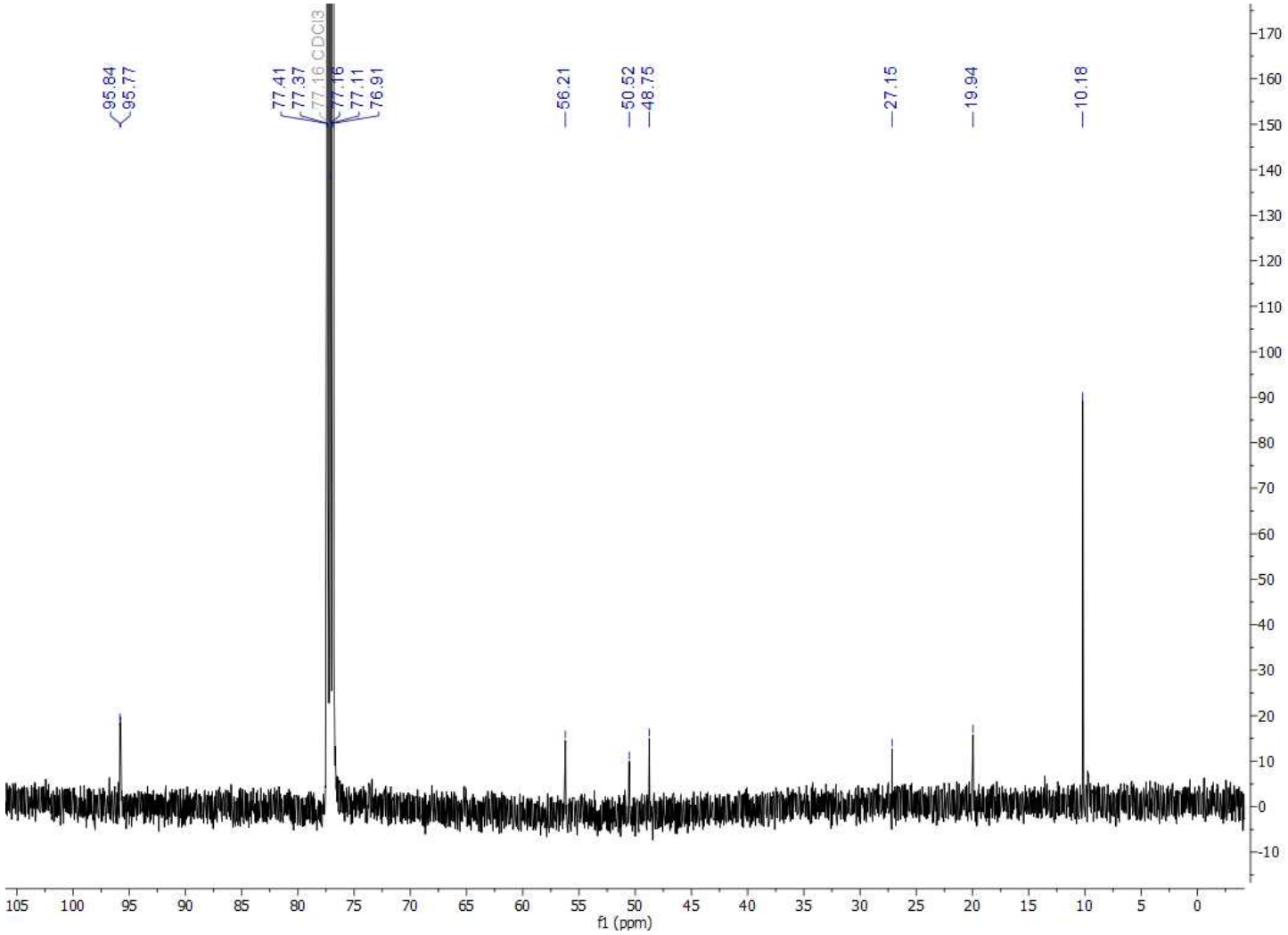


Figure A.41: ^{1}H NMR spectrum of Rh-3 recorded at 500 MHz in $CDCl_3$

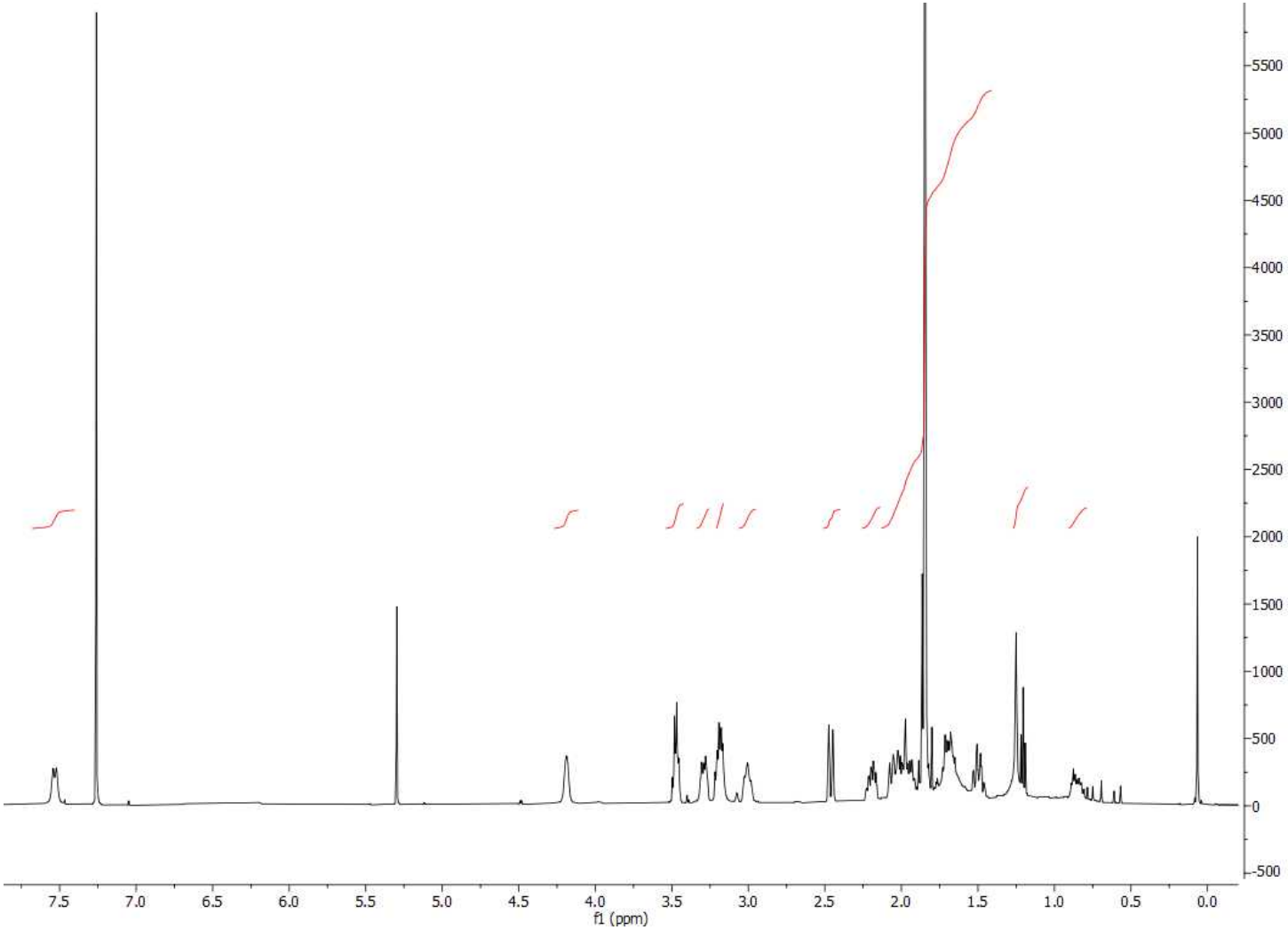


Figure A.42: $^{13}C\{^{1}H\}$ NMR spectrum of Rh-3 recorded at 125 MHz in $CDCl_3$

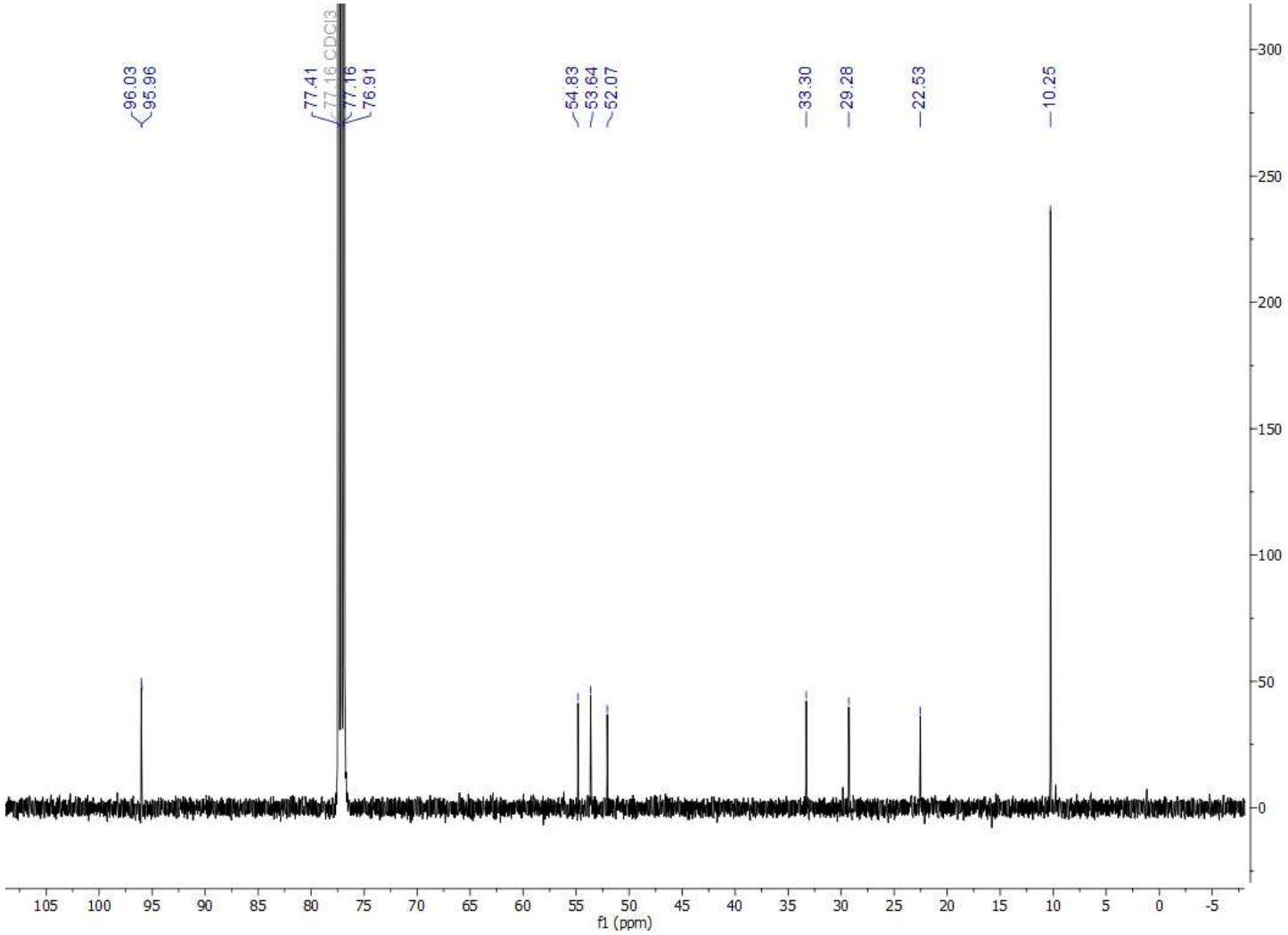


Figure A.43: ^{1}H NMR spectrum of Ru-1 recorded at 500 MHz in $CDCl_3$

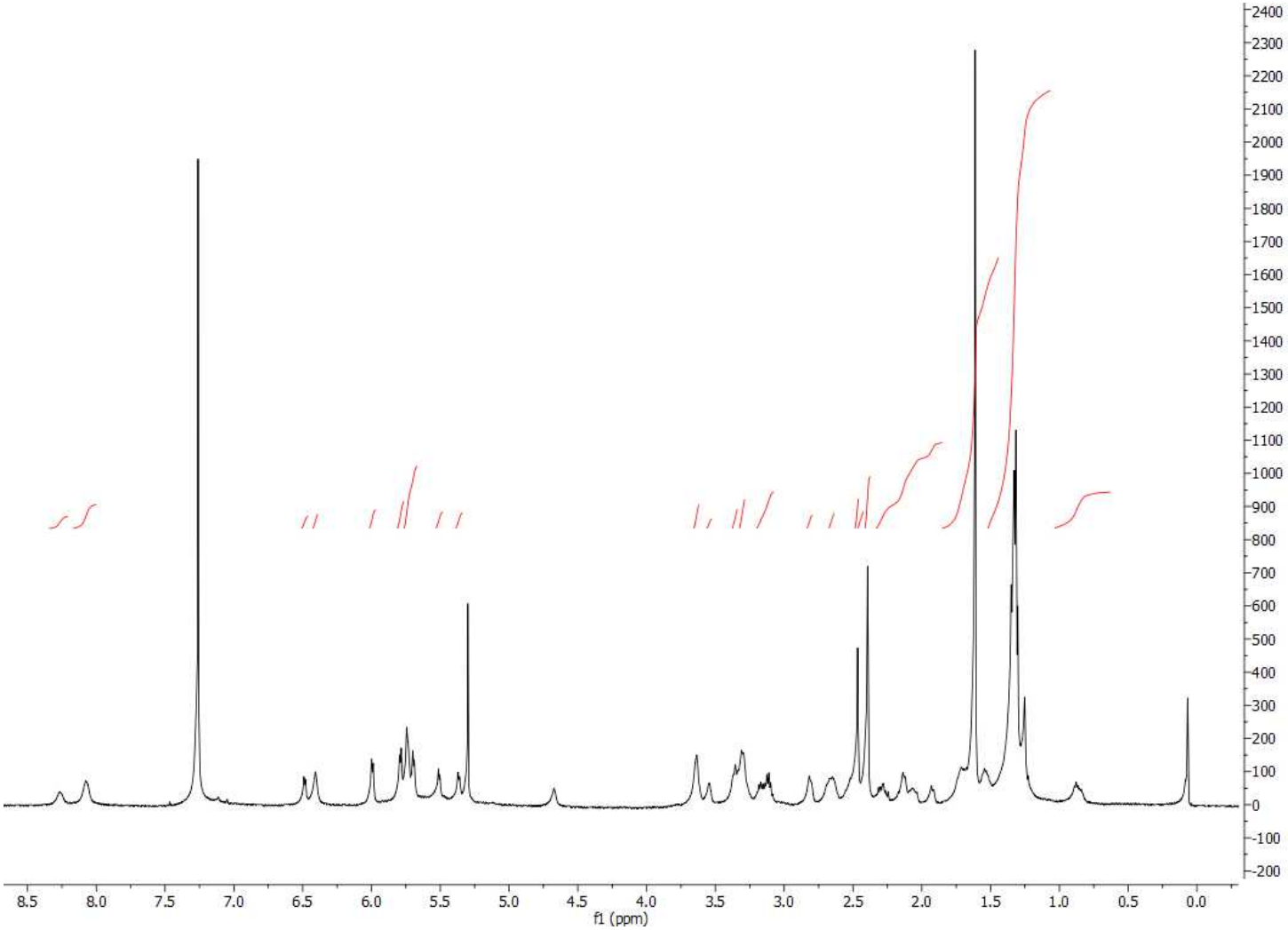


Figure A.44: $^{13}C\{^{1}H\}$ NMR spectrum of Ru-1 recorded at 125 MHz in $CDCl_3$

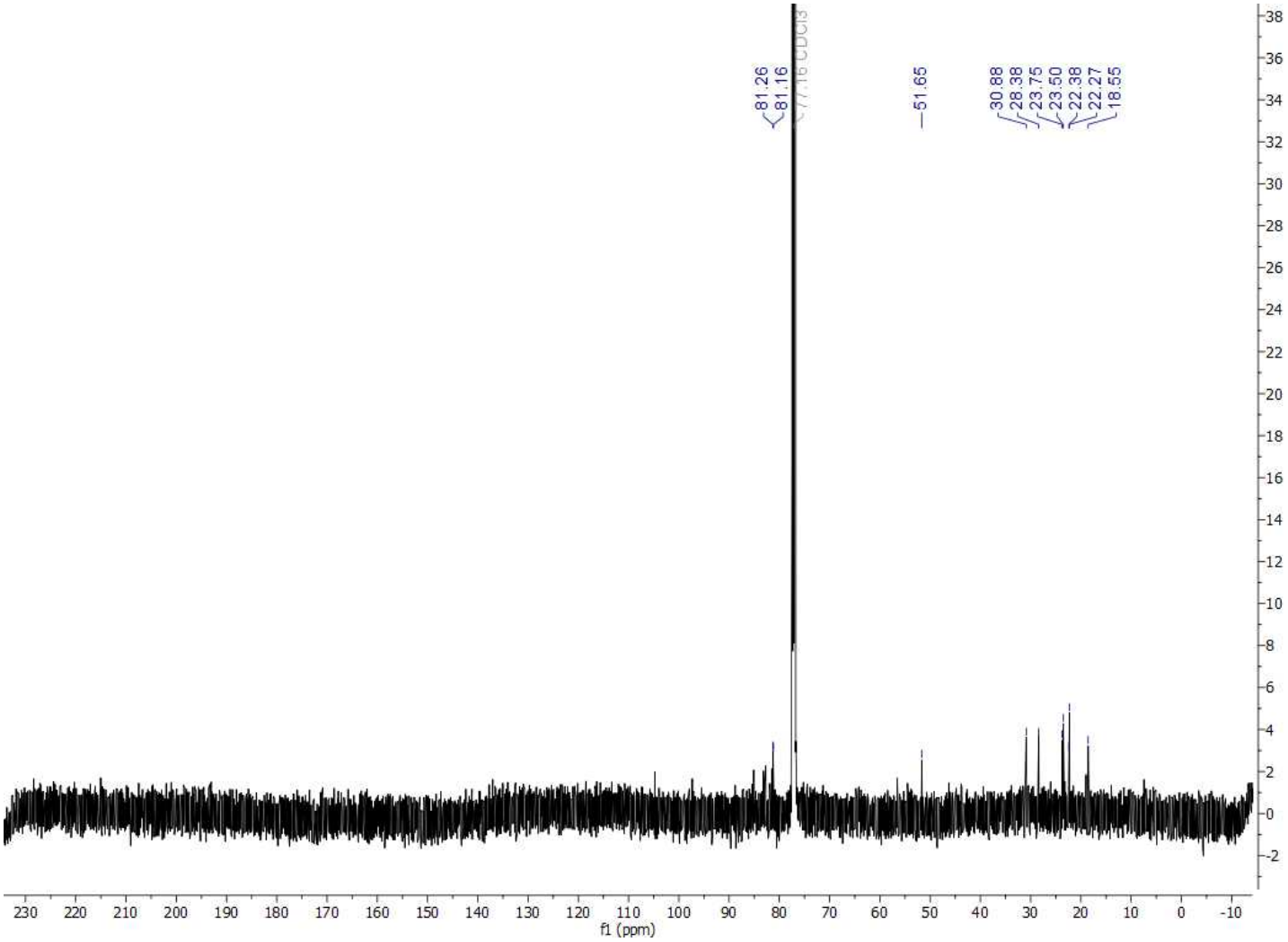


Figure A.45: ^{1}H NMR spectrum of Ru-2 recorded at 500 MHz in $CDCl_3$

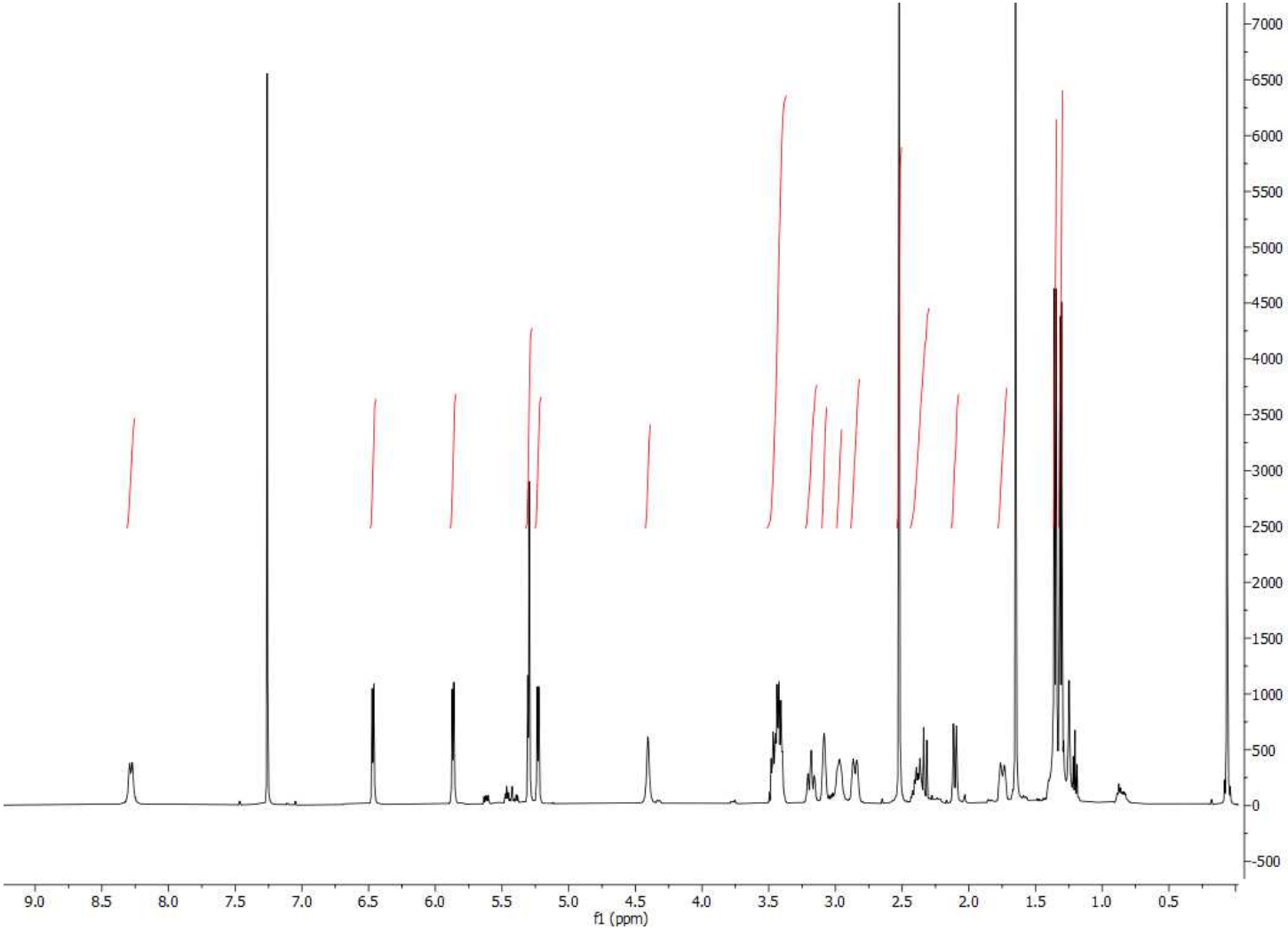


Figure A.46: $^{13}C\{^{1}H\}$ NMR spectrum of Ru-2 recorded at 125 MHz in $CDCl_3$

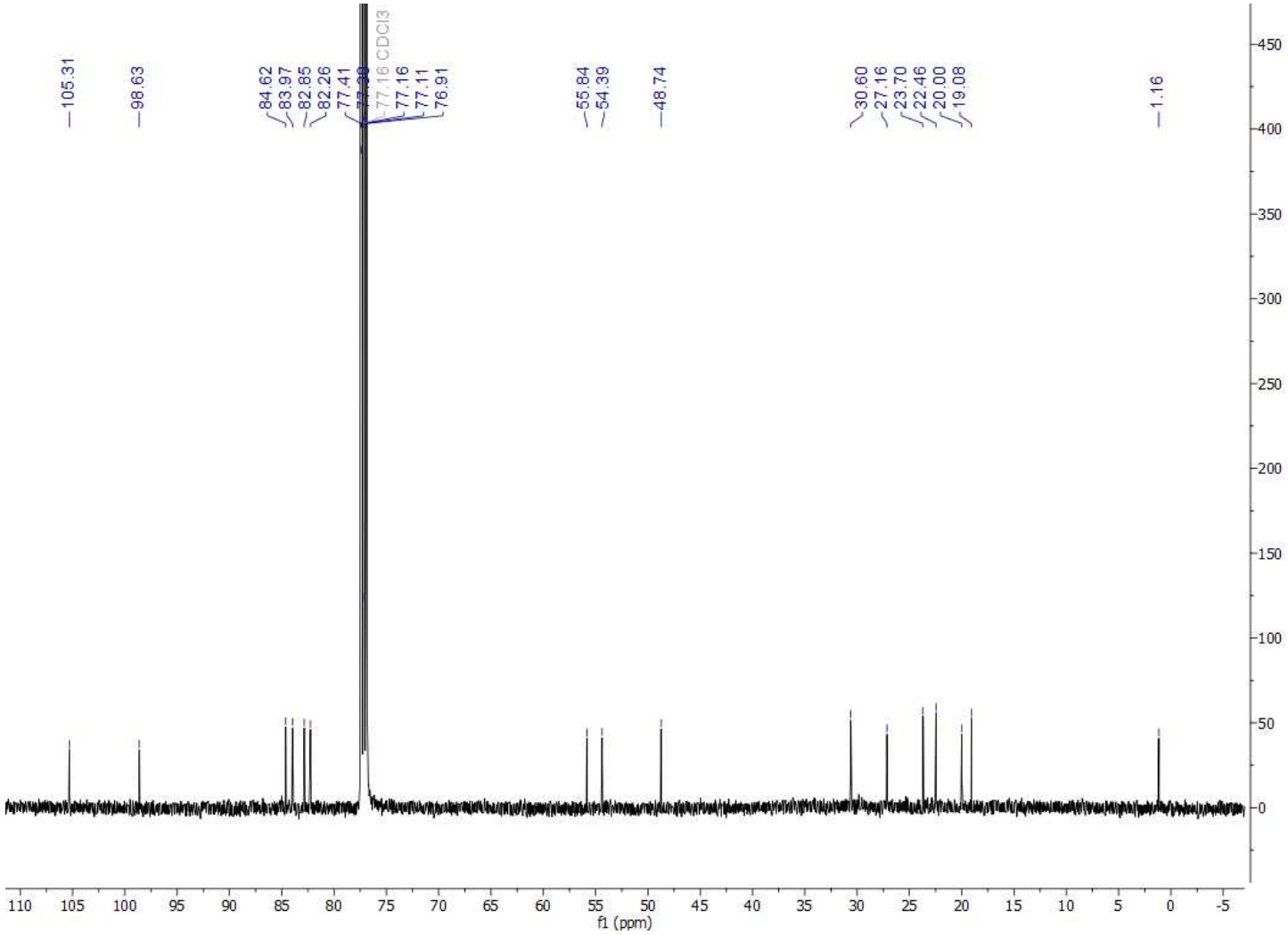


Figure A.47: ^{1}H NMR spectrum of Ru-3 recorded at 500 MHz in $CDCl_3$

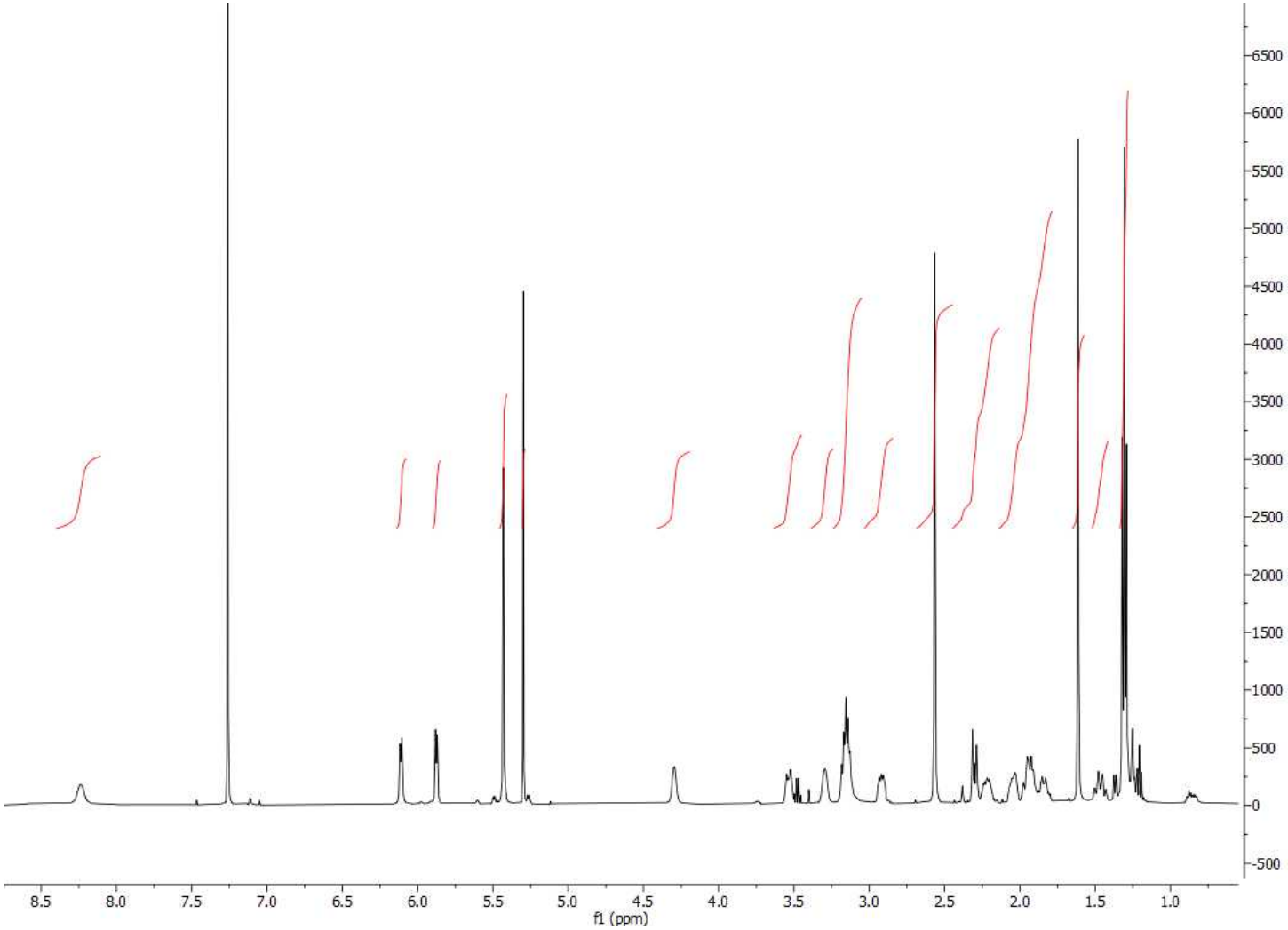


Figure A.48: $^{13}C\{^{1}H\}$ NMR spectrum of Ru-3 recorded at 125 MHz in $CDCl_3$

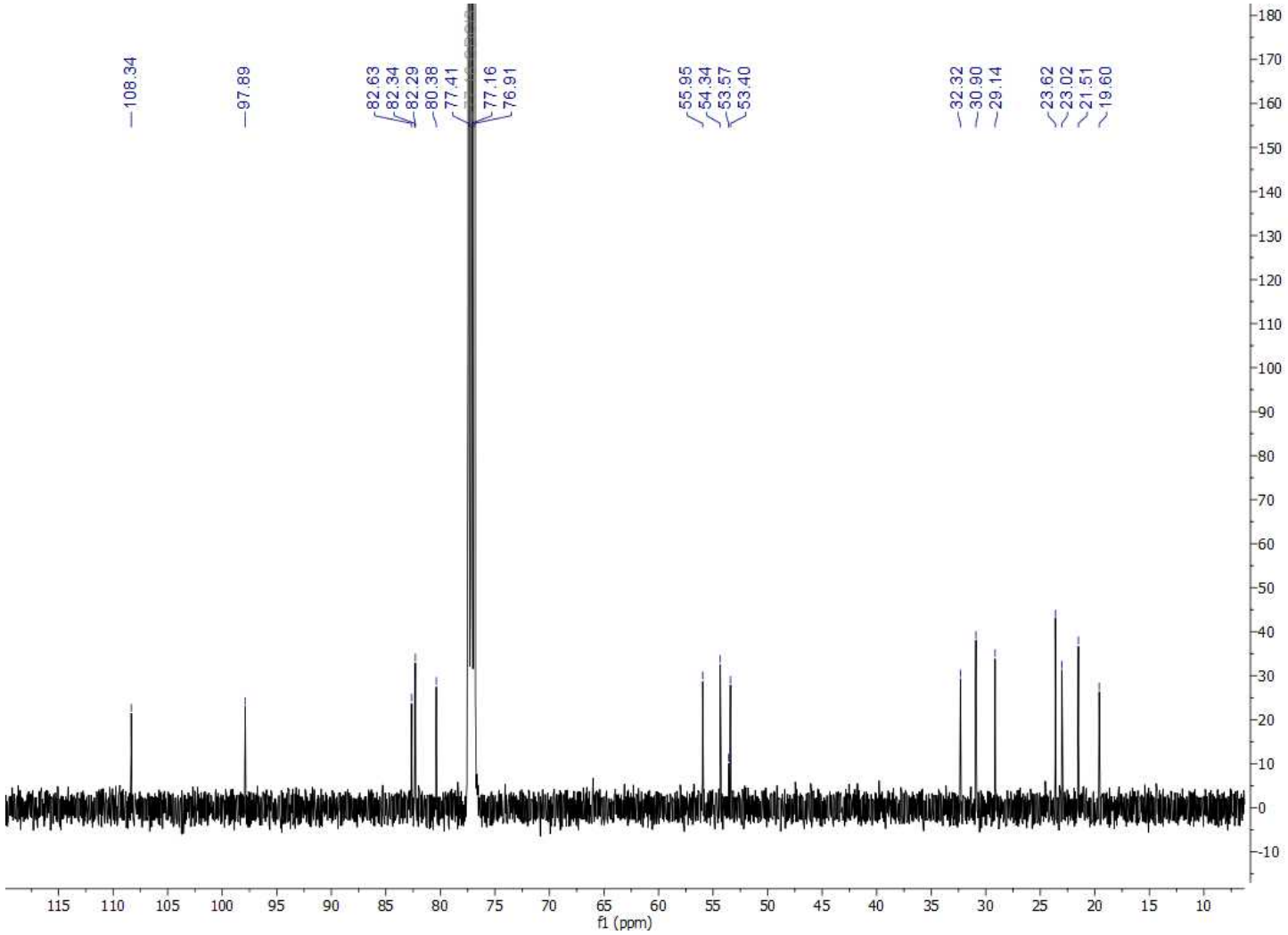


Figure A.49: $^{1}H,^{1}H$ COSY NMR spectrum of Ru-3 in $CDCl_3$

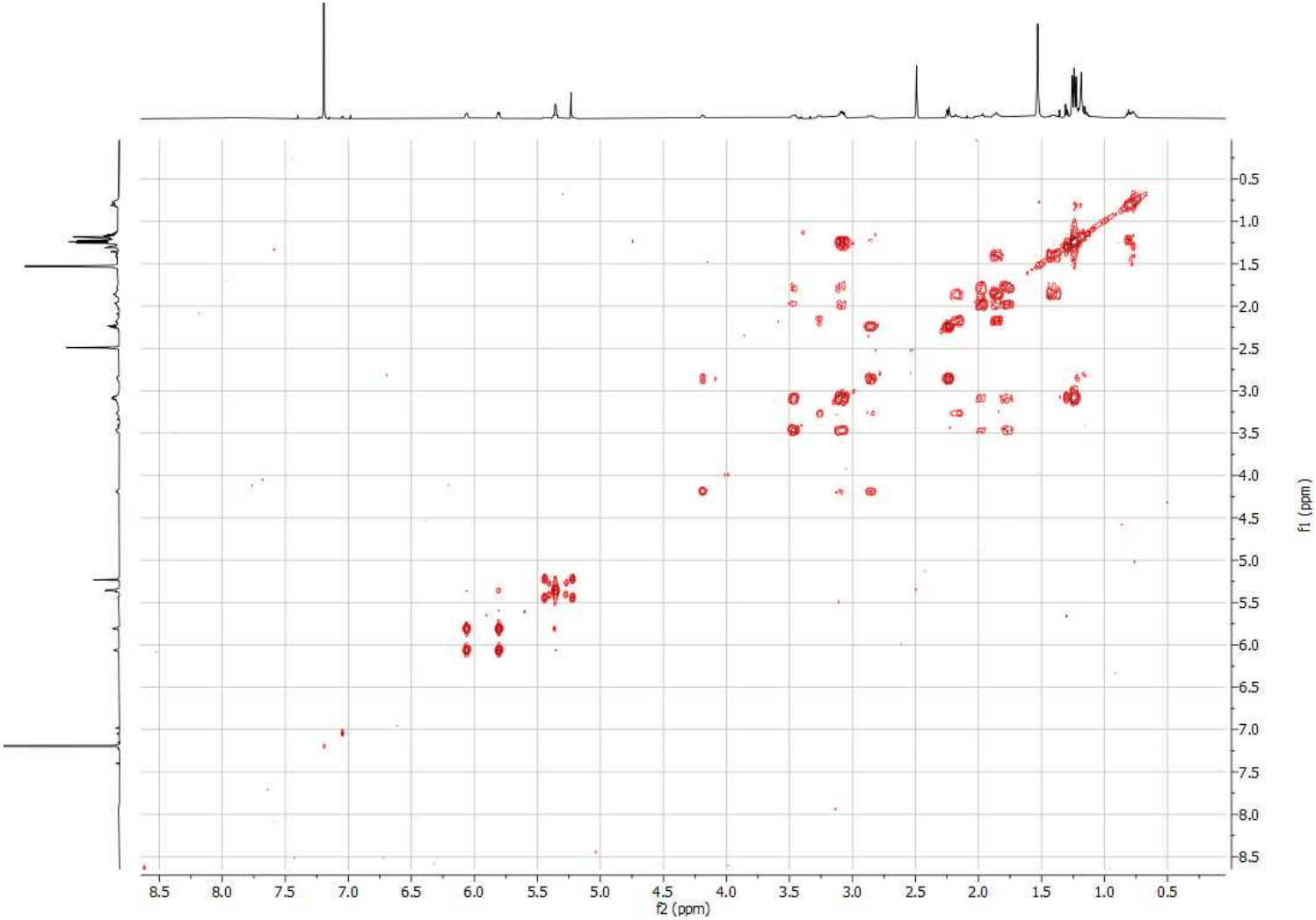


Figure A.50: $^{1}H,^{13}C$ HSQC NMR spectrum of Ru-3 in $CDCl_3$

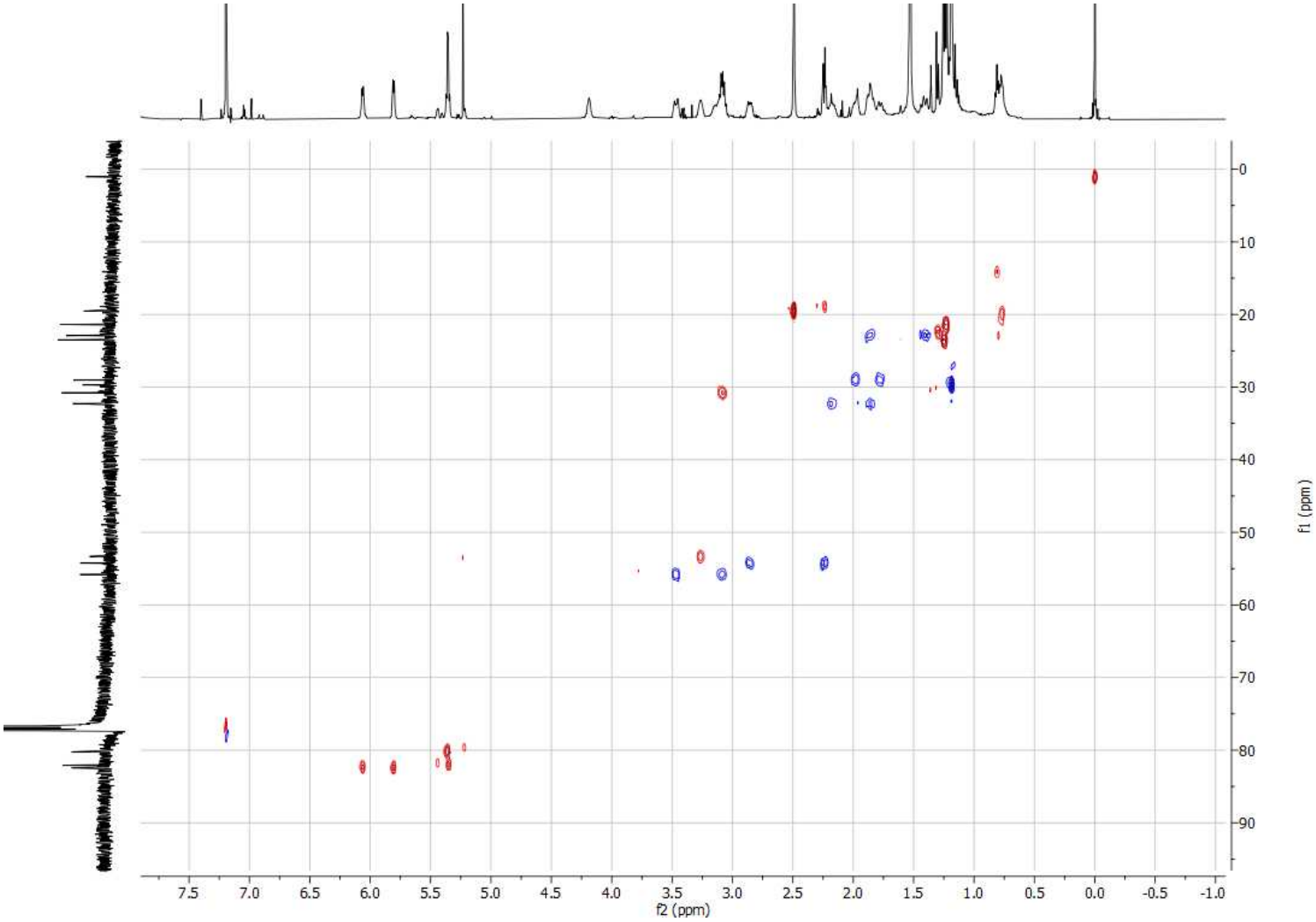


Figure A.51: $^{1}H,^{13}C$ HMBC NMR spectrum of Ru-3 in $CDCl_3$

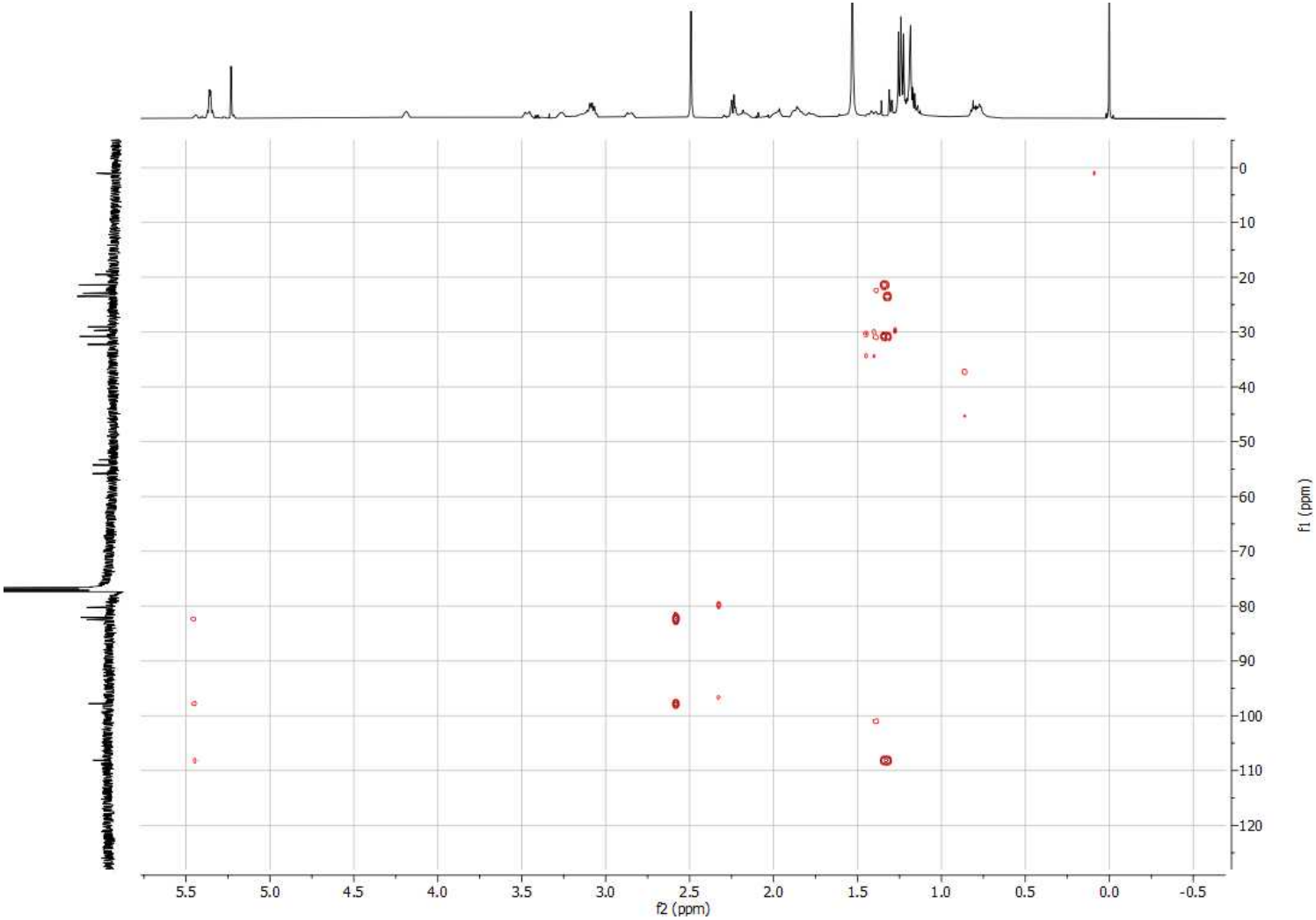
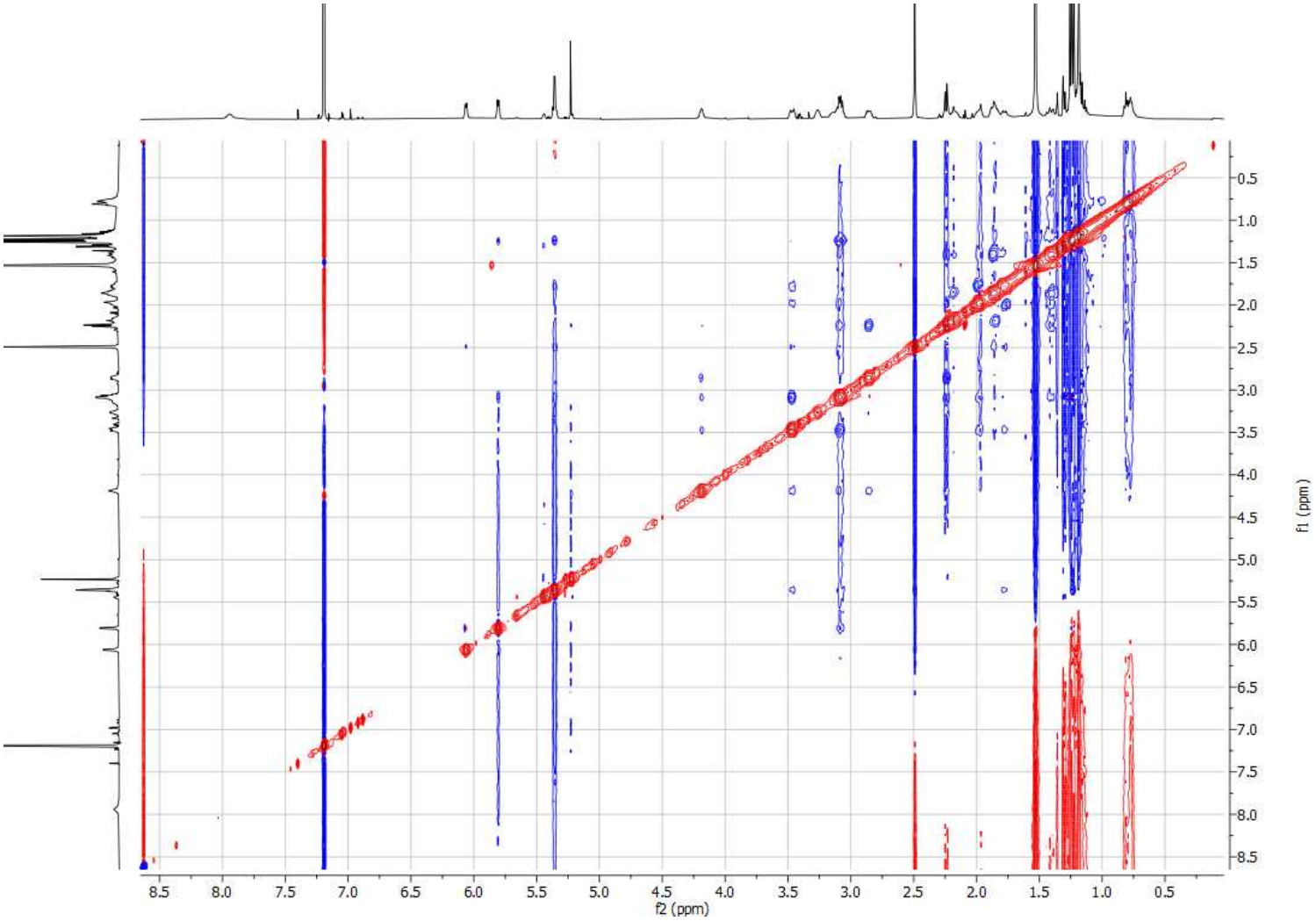


Figure A.52: $^{1}H,^{1}H$ NOESY NMR spectrum of Ru-3 in $CDCl_3$



A.9 Selected mass spectrometry data

Figure A.53: HRMS of 3,5-tBu,tBu-SalpyH_2

Figure A.54: HRMS elemental composition report of 3,5-tBu,tBu-SalpyH$_2$

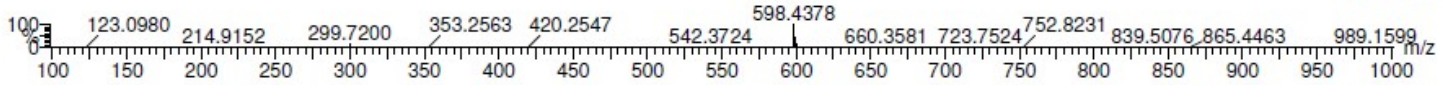
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-39 H: 0-56 N: 0-3 O: 0-2

18-Mar-2020
PDN_MS30246_ESP 70 (0.663) Cm (70-(1:7+160))

VYVtBuLp

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
4.83e+006



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
598.4378	598.4373	0.5	0.8	13.5	758.4	n/a	n/a	C39 H56 N3 O2

Figure A.55: HRMS of 3,5-Br,Br-SalpyH_2

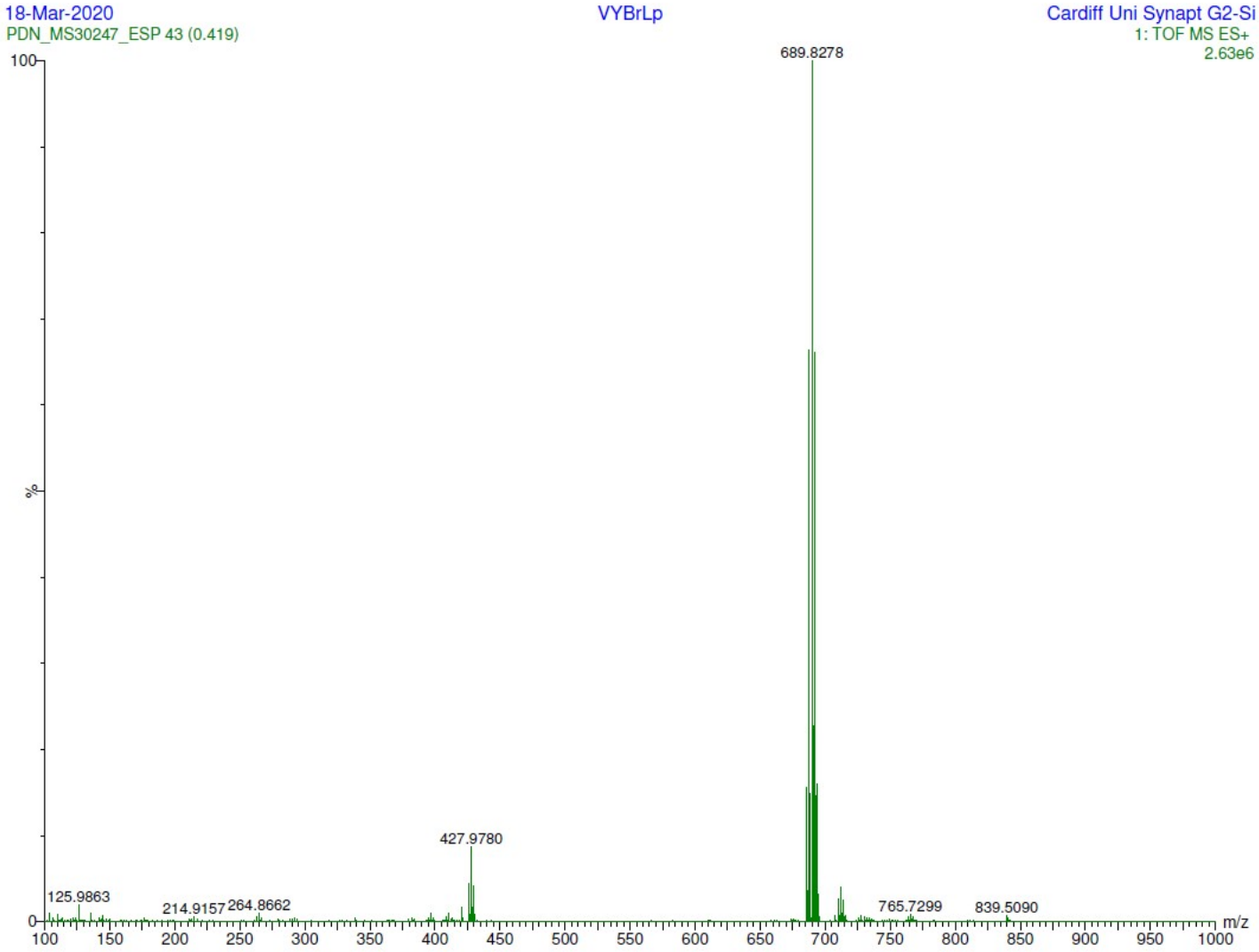
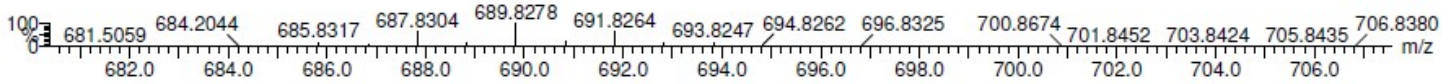


Figure A.56: HRMS elemental composition report of 3,5-Br,Br-SalpyH$_2$

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
64 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-230 N: 0-3 O: 0-2 Br: 0-4

18-Mar-2020 VYBrLp Cardiff Uni Synapt G2-Si
PDN_MS30247_ESP 43 (0.419) 1: TOF MS ES+
2.63e+006



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
685.8317	685.8289	2.8	4.1	13.5	623.6	n/a	n/a	C23 H20 N3 O2 Br4

Figure A.57: HRMS of 3,5-Cl,Cl-SalpyH$_2$

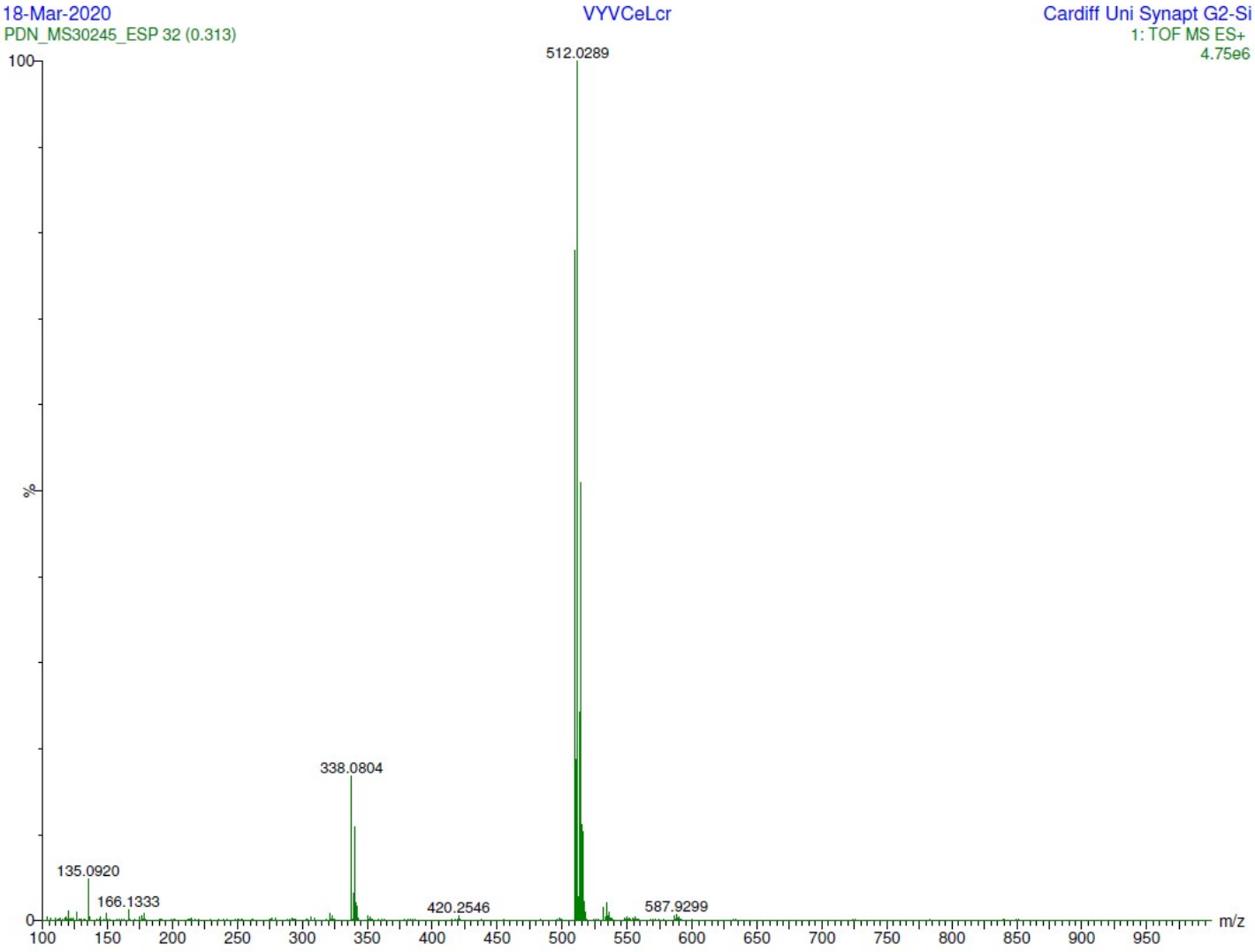


Figure A.58: HRMS elemental composition report of 3,5-Cl,Cl-SalpyH$_2$

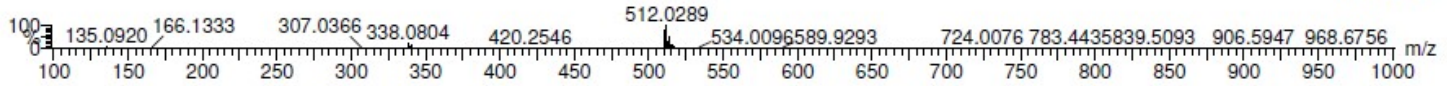
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
64 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-230 N: 0-3 O: 0-2 Cl: 0-4

18-Mar-2020
PDN_MS30245_ESP 32 (0.313)

VYVCeLcr

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
4.75e+006



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
510.0315	510.0310	0.5	1.0	13.5	921.7	n/a	n/a	C23 H20 N3 O2 Cl4

Figure A.59: HRMS of **In-1**

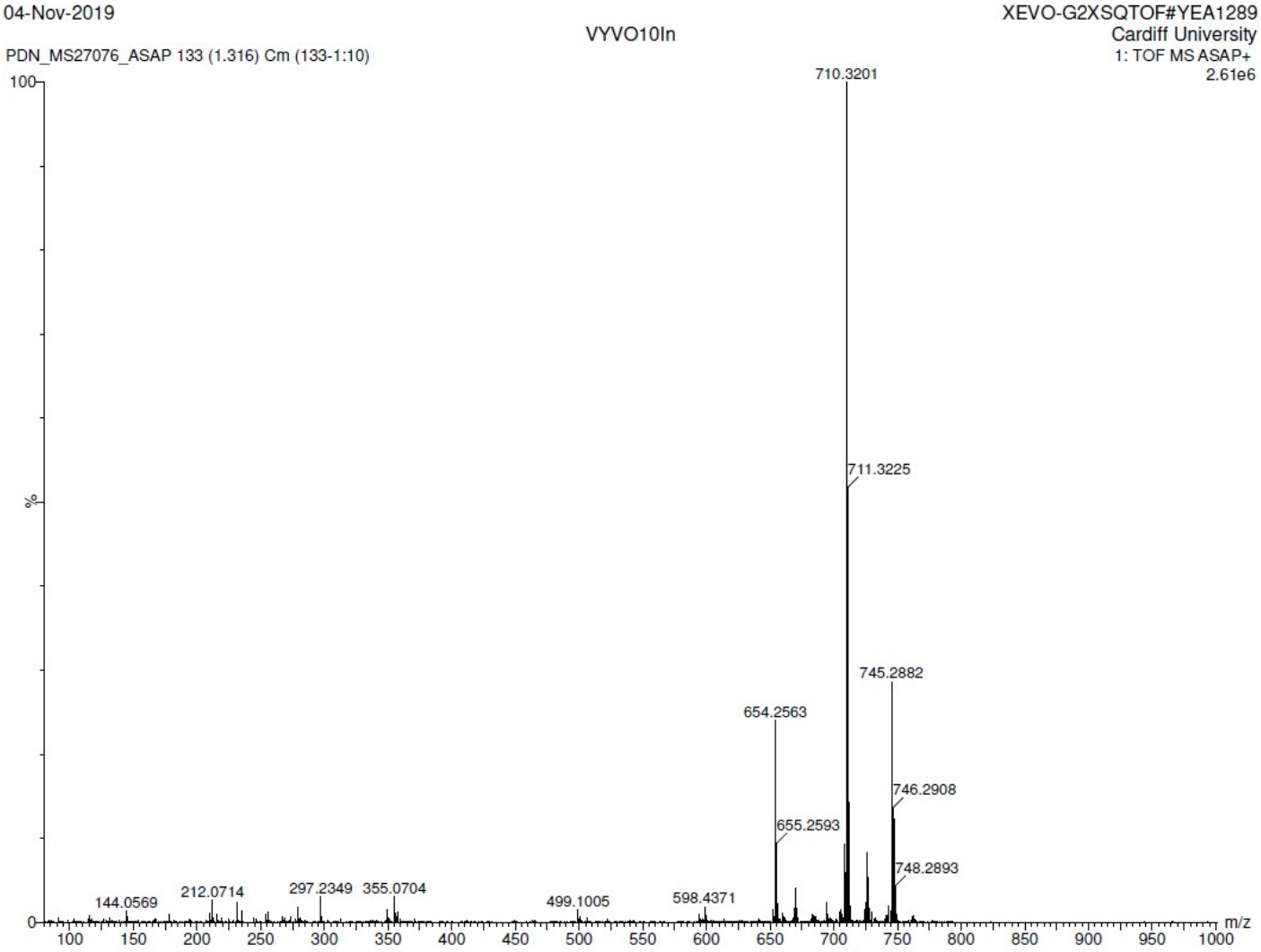


Figure A.60: HRMS elemental composition report of **In-1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 200.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
42 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-39 H: 0-53 N: 0-3 O: 0-2 Cl: 0-1 115In: 0-1

Minimum:				-1.5				
Maximum:		5.0	5.0	200.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
745.2882	745.2865	1.7	2.3	15.0	426.8	n/a	n/a	C39 H53 N3 O2 Cl 115In

Figure A.61: HRMS of **In-2**

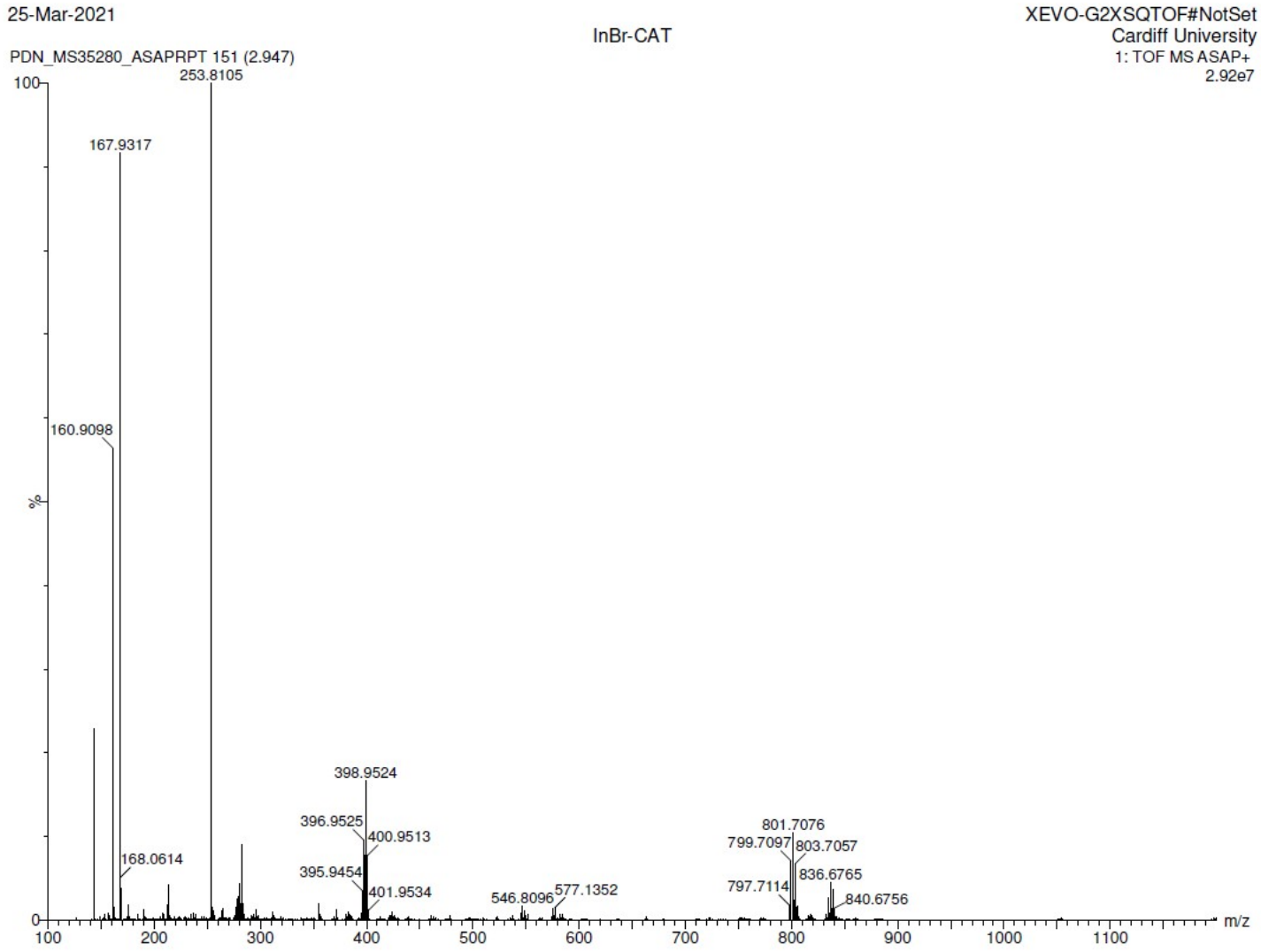


Figure A.62: HRMS elemental composition report of **In-2**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
1297 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-18 N: 0-3 O: 0-2 35Cl: 0-1 79Br: 0-4 81Br: 0-4 115In: 0-1

Minimum:				-1.5				
Maximum:		5.0	5.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
836.6765	836.6741	2.4	2.9	15.0	543.9	n/a	n/a	C23 H17 N3 O2 35Cl 79Br2 81Br2 115In

Figure A.63: HRMS of **In-3**

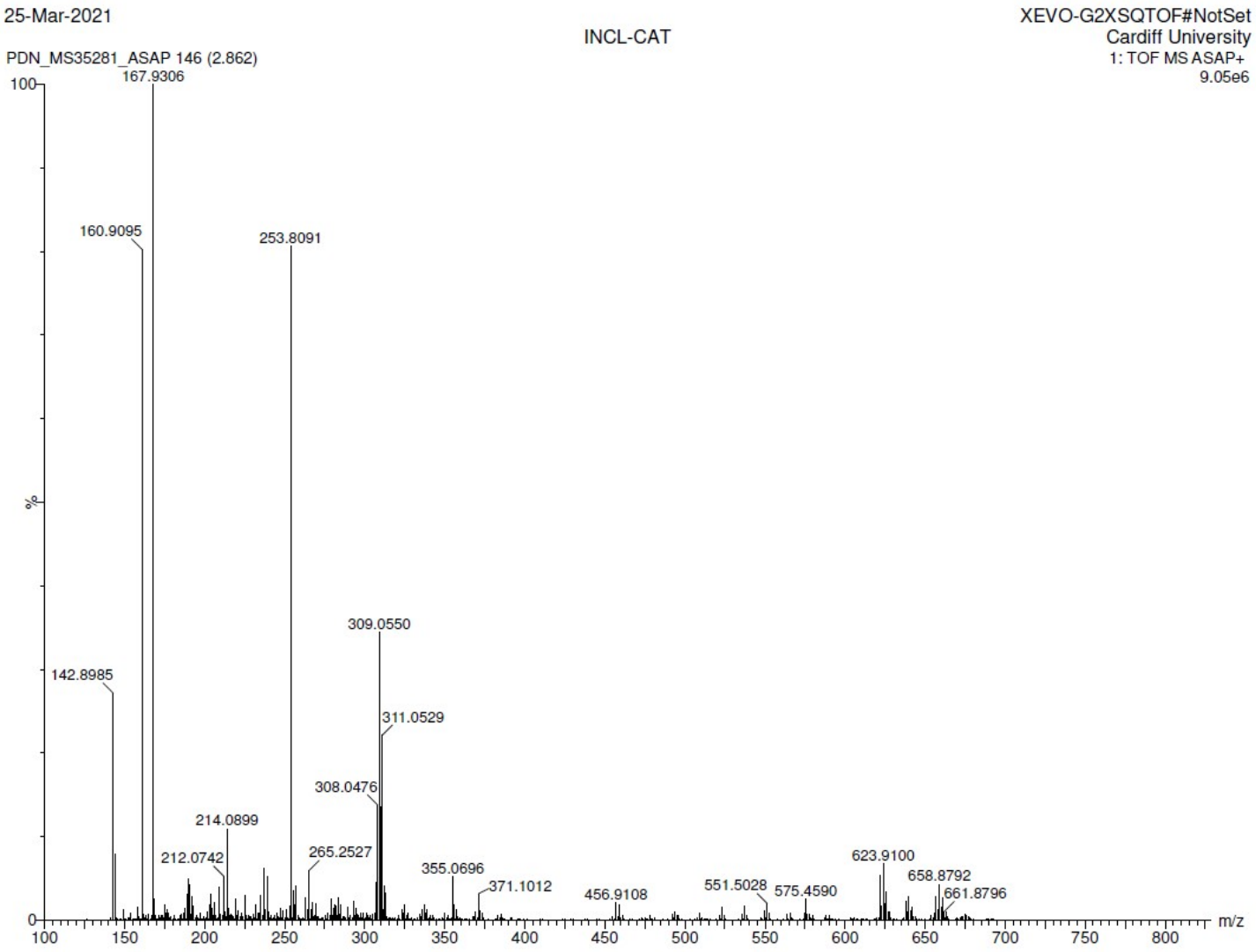


Figure A.64: HRMS elemental composition report of **In-3**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
233 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-17 N: 0-3 O: 0-2 115In: 0-1 35Cl: 0-4 37Cl: 0-1

Minimum:				-1.5				
Maximum:		5.0	5.0	100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
658.8774	658.8773	0.1	0.2	15.0	89.7	n/a	n/a	C23 H17 N3 O2 115In 35Cl4 37Cl

Figure A.65: HRMS of Ru-1

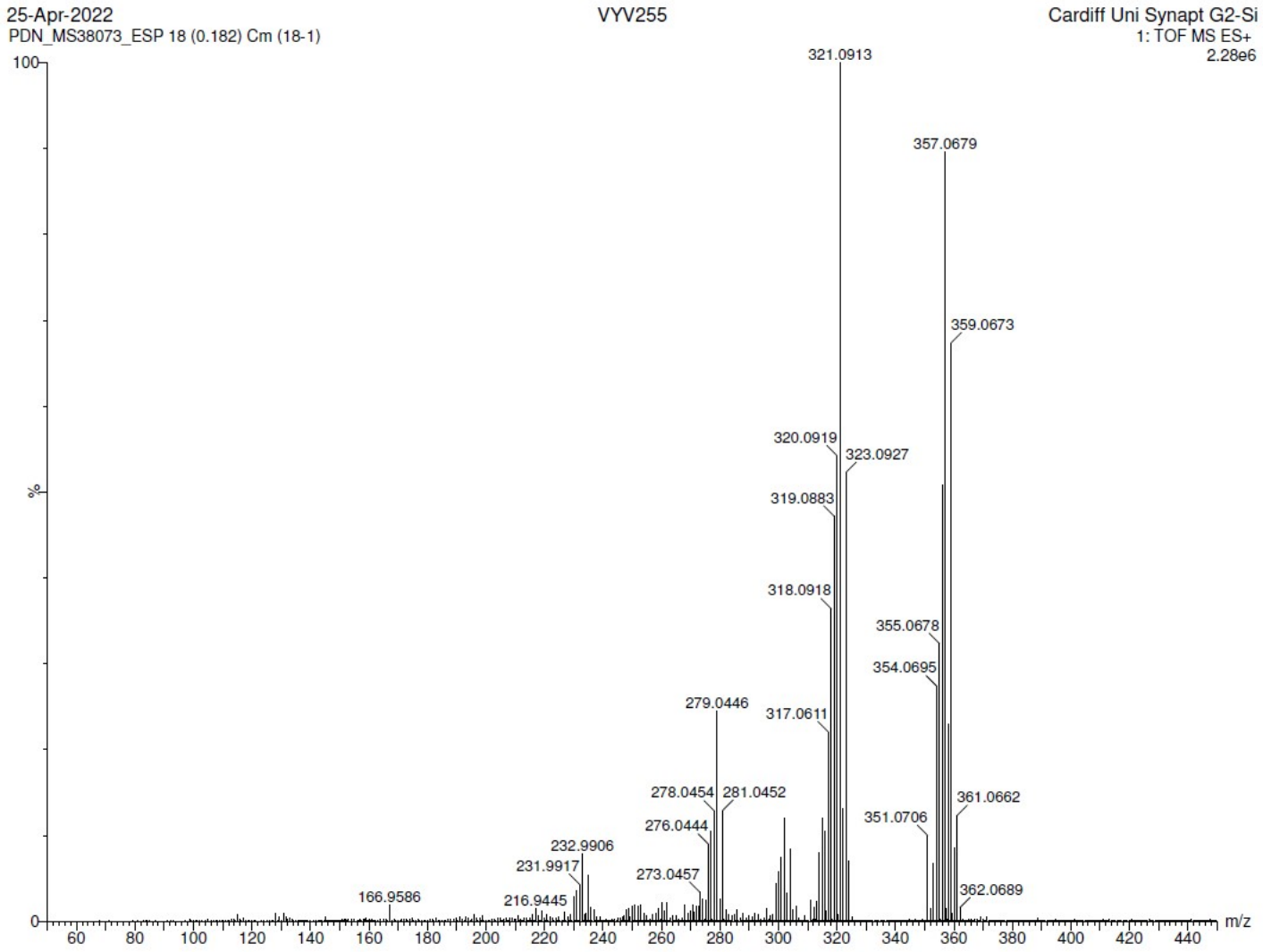
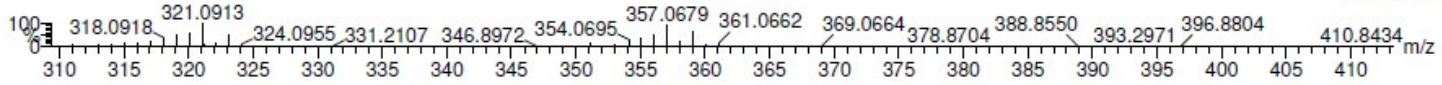


Figure A.66: HRMS elemental composition report of Ru-1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-14 H: 0-24 N: 0-2 Cl: 0-1 102Ru: 0-1

25-Apr-2022 VYV255 Cardiff Uni Synapt G2-Si
PDN_MS38073_ESP 18 (0.182) 1: TOF MS ES+
2.28e+006



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
357.0679	357.0672	0.7	2.0	3.5	978.8	n/a	n/a	C14 H24 N2 Cl 102Ru

Figure A.67: HRMS of Ru-2

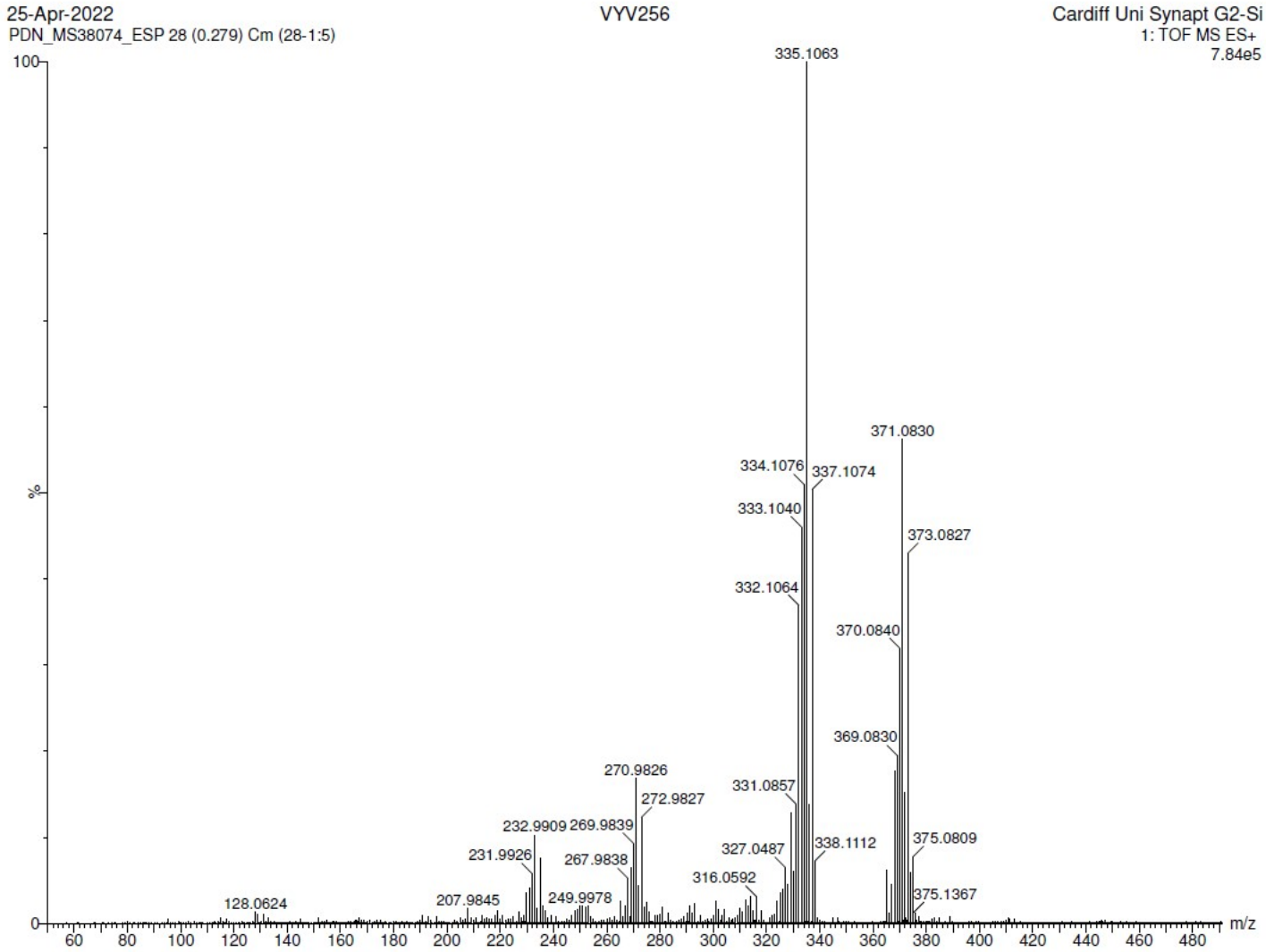


Figure A.68: HRMS elemental composition report of Ru-2

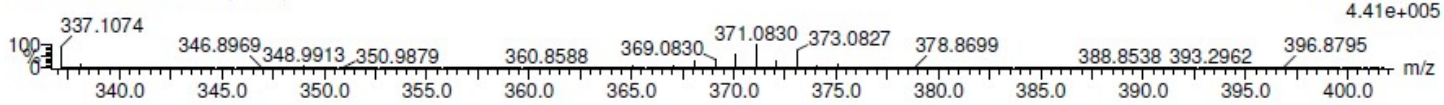
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-15 H: 0-26 N: 0-2 Cl: 0-1 102Ru: 0-1

25-Apr-2022
PDN_MS38074_ESP 28 (0.279)

VYV256

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
4.41e+005



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
371.0830	371.0828	0.2	0.5	3.5	936.5	n/a	n/a	C15 H26 N2 Cl 102Ru

Figure A.69: HRMS of Ru-3

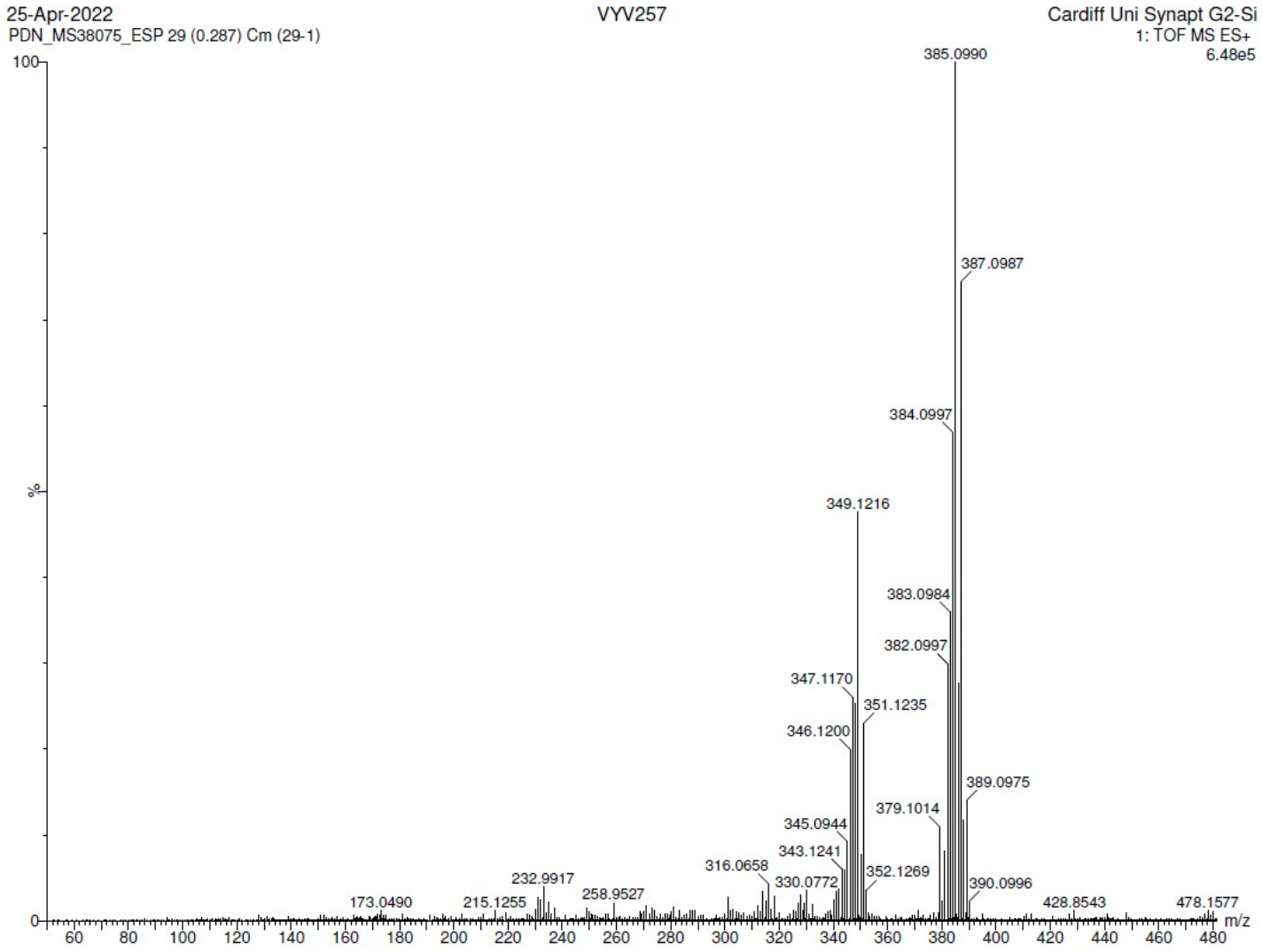


Figure A.70: HRMS elemental composition report of Ru-3

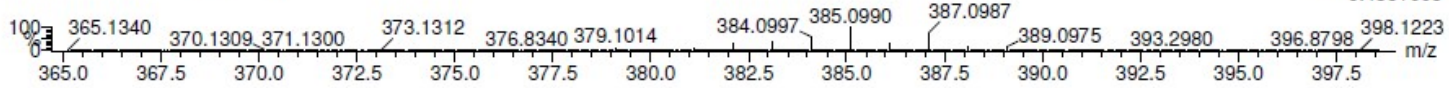
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-28 N: 0-2 Cl: 0-1 102Ru: 0-1

25-Apr-2022
PDN_MS38075_ESP 29 (0.287)

VYV257

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
6.48e+005



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
385.0990	385.0985	0.5	1.3	3.5	872.2	n/a	n/a	C16 H28 N2 Cl 102Ru

Figure A.71: HRMS of Rh-1

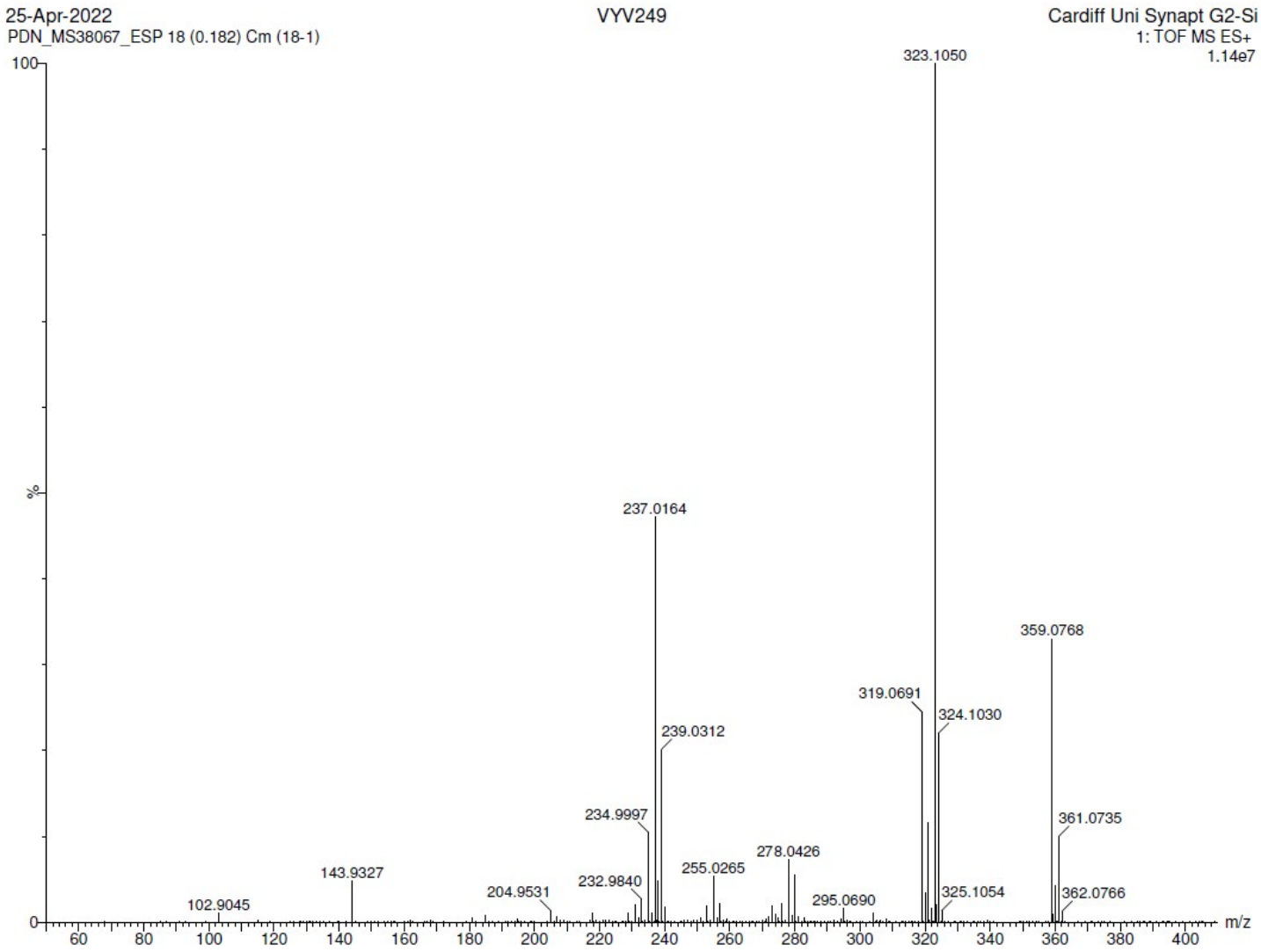


Figure A.72: HRMS elemental composition report of Rh-1

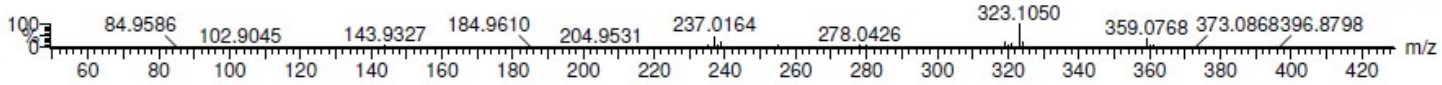
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-14 H: 0-25 N: 0-2 Cl: 0-1 103Rh: 0-1

25-Apr-2022
PDN_MS38067_ESP 18 (0.182)

VYV249

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
1.14e+007



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
359.0768	359.0761	0.7	1.9	3.0	962.9	n/a	n/a	C14 H25 N2 Cl 103Rh

Figure A.73: HRMS of Rh-2

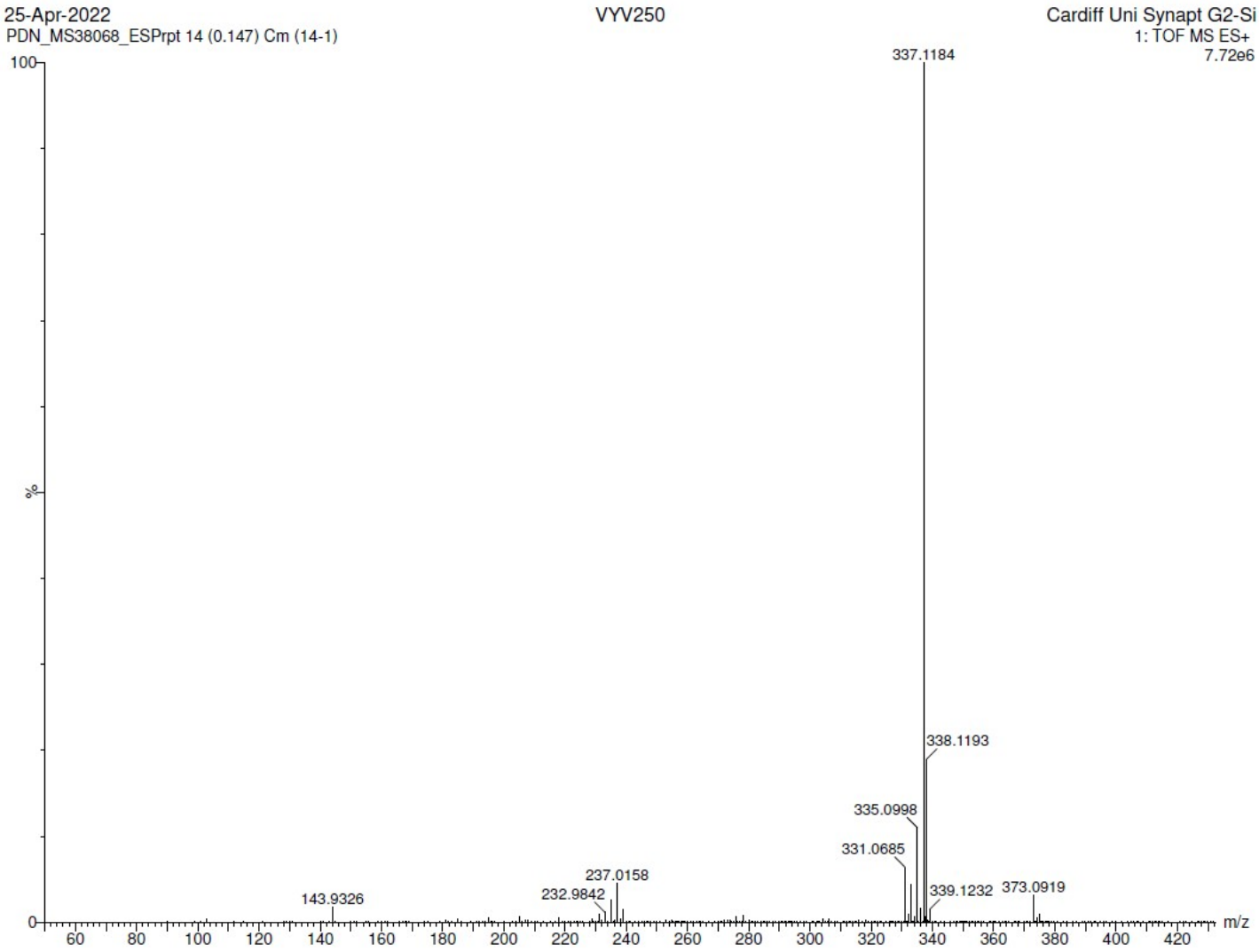


Figure A.74: HRMS elemental composition report of Rh-2

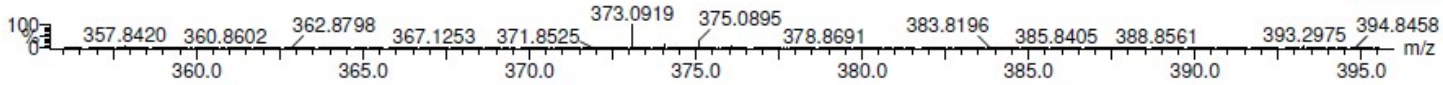
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-15 H: 0-27 N: 0-2 Cl: 0-1 103Rh: 0-1

25-Apr-2022
PDN_MS38068_ESPrpt 14 (0.147)

VYV250

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
2.41e+005



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
373.0919	373.0918	0.1	0.3	3.0	743.4	n/a	n/a	C15 H27 N2 Cl 103Rh

Figure A.75: HRMS of Rh-3

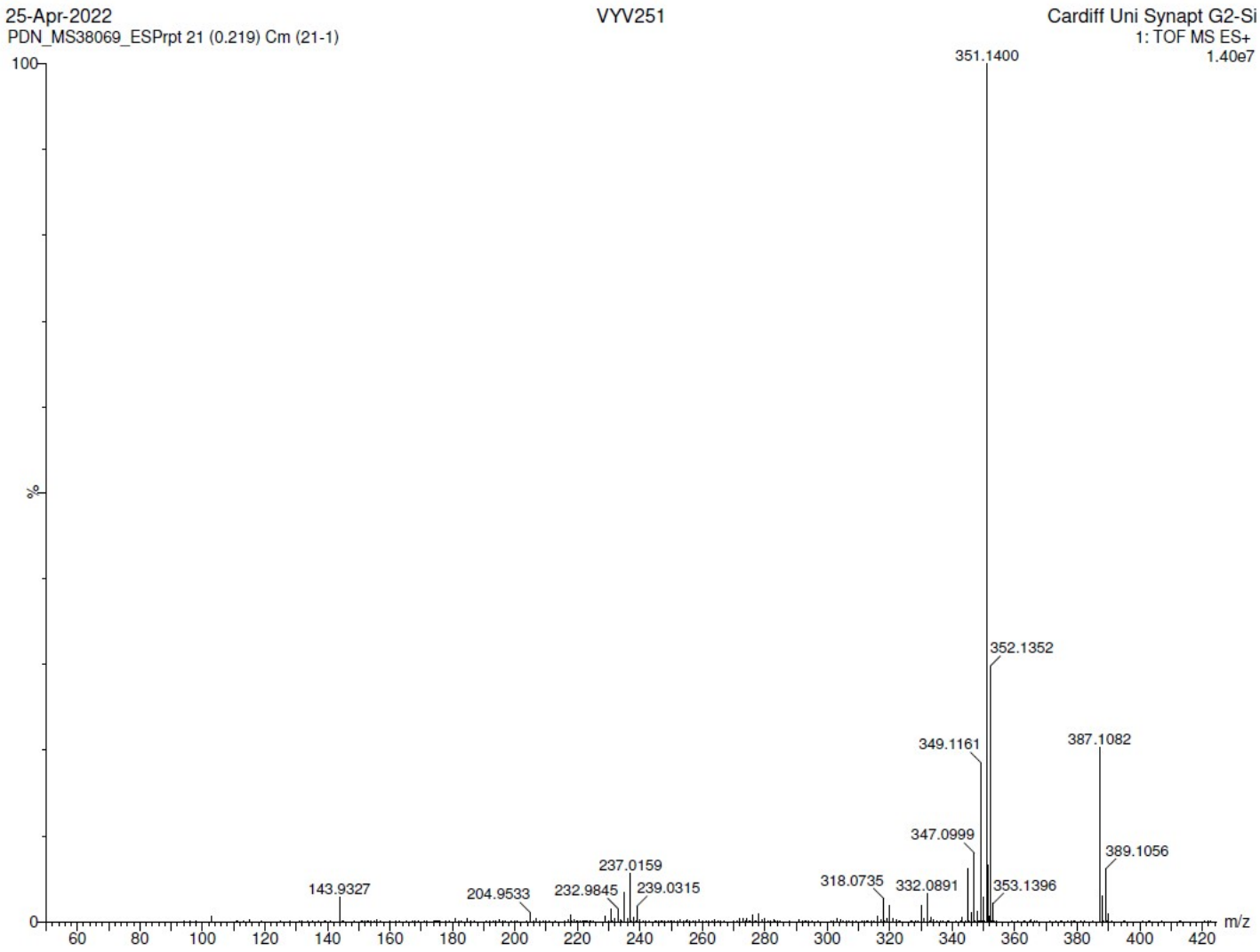


Figure A.76: HRMS elemental composition report of Rh-3

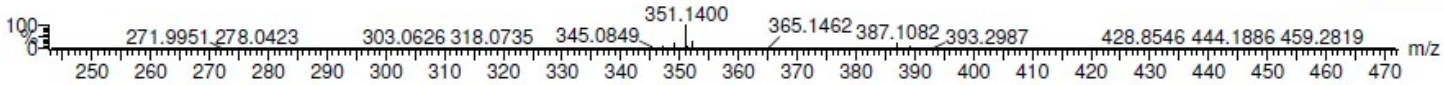
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-29 N: 0-2 Cl: 0-1 103Rh: 0-1

25-Apr-2022
PDN_MS38069_ESPrpt 21 (0.219)

VYV251

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
1.40e+007



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
387.1082	387.1074	0.8	2.1	3.0	950.4	n/a	n/a	C16 H29 N2 Cl 103Rh

Figure A.77: HRMS of Ir-1

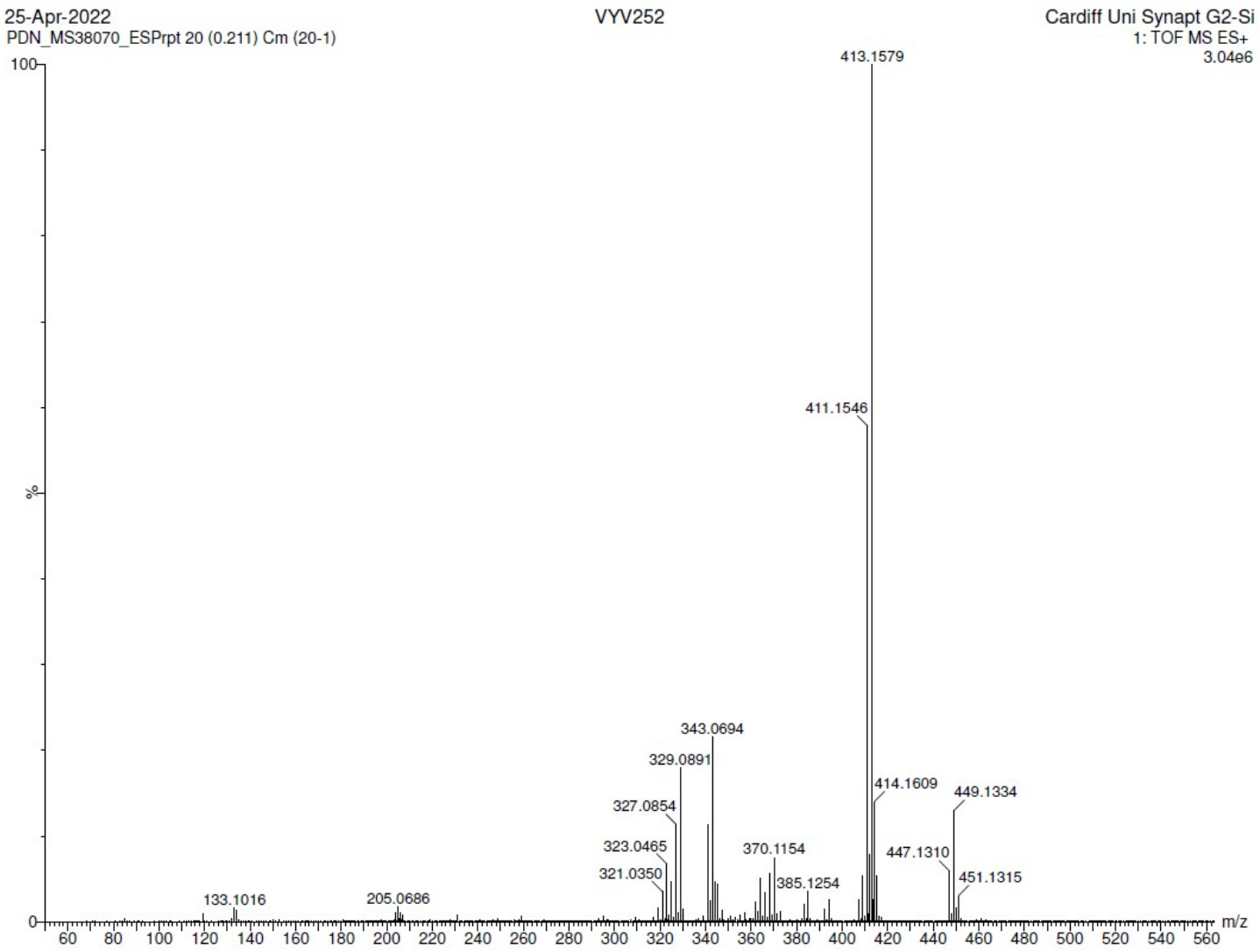


Figure A.78: HRMS elemental composition report of Ir-1

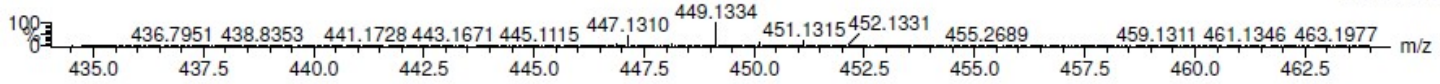
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-14 H: 0-25 N: 0-2 Cl: 0-1 193Ir: 0-1

25-Apr-2022
PDN_MS38070_ESPrpt 20 (0.211)

VYV252

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
3.94e+005



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
449.1334	449.1335	-0.1	-0.2	4.0	801.9	n/a	n/a	C14 H25 N2 Cl 193Ir

Figure A.79: HRMS of Ir-2

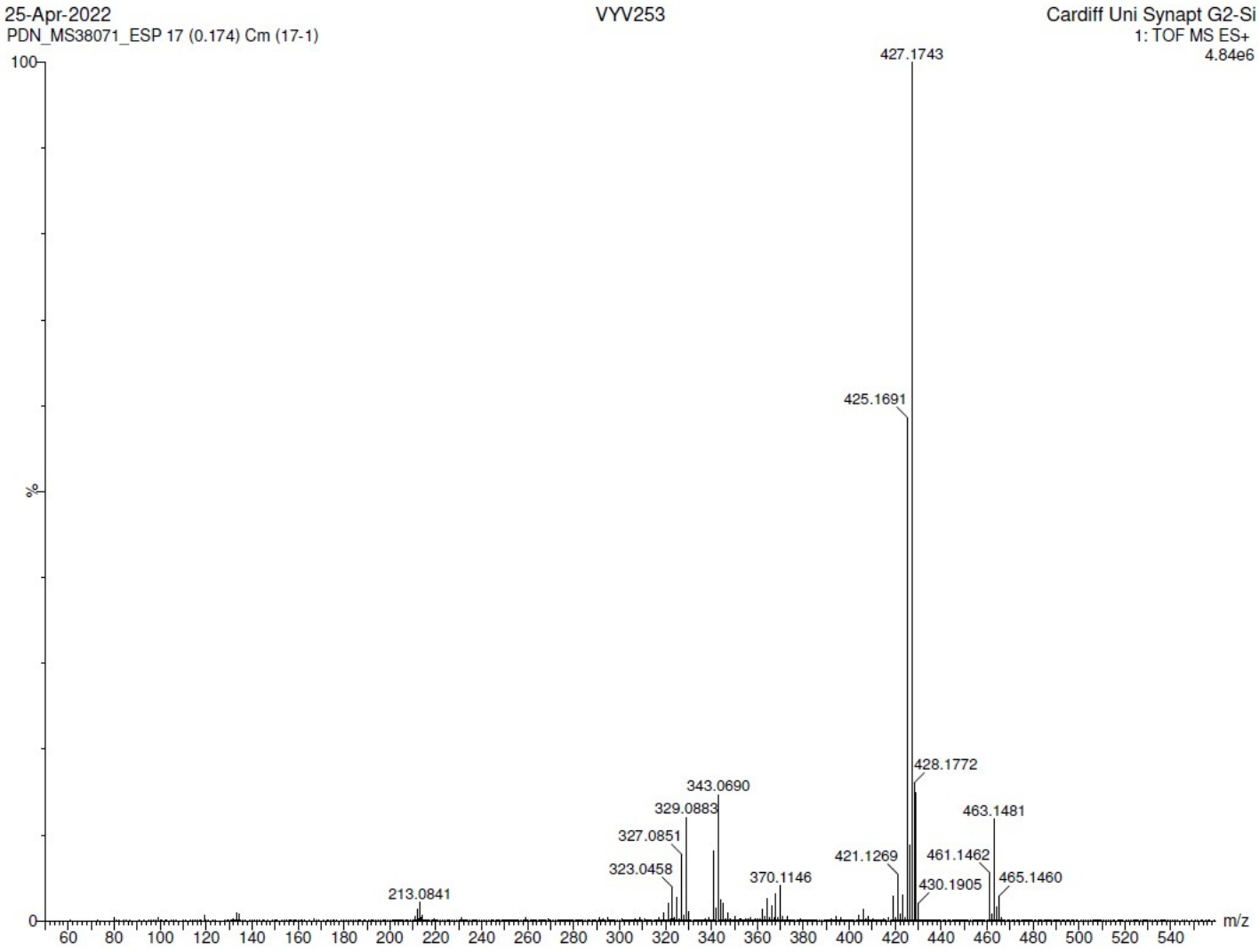


Figure A.80: HRMS elemental composition report of Ir-2

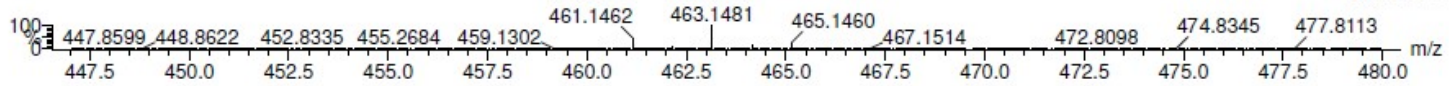
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-15 H: 0-27 N: 0-2 Cl: 0-1 193Ir: 0-1

25-Apr-2022
PDN_MS38071_ESP 17 (0.174)

VYV253

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
5.73e+005



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
463.1481	463.1492	-1.1	-2.4	4.0	722.0	n/a	n/a	C15 H27 N2 Cl 193Ir

Figure A.81: HRMS of Ir-3

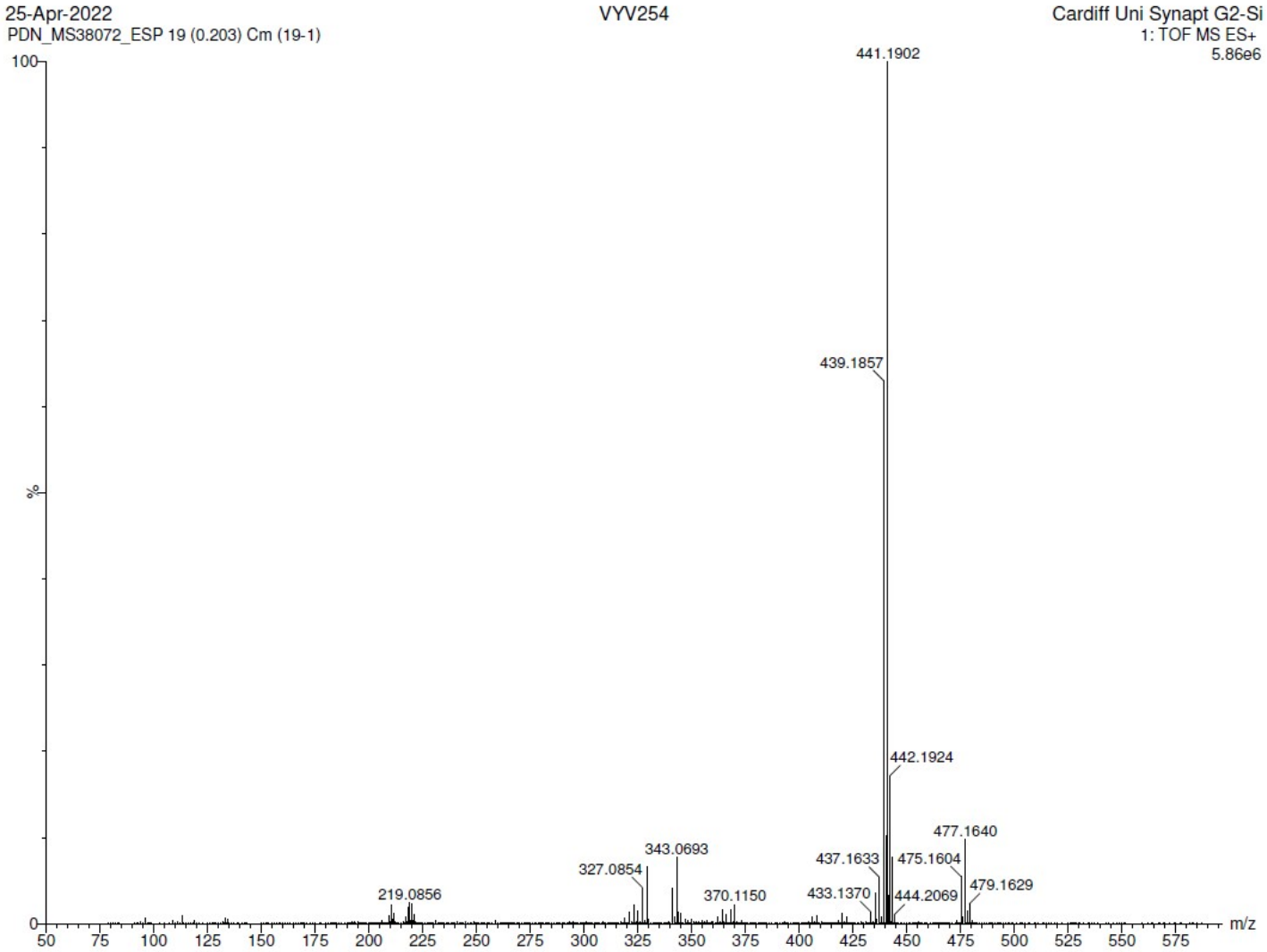


Figure A.82: HRMS elemental composition report of Ir-3

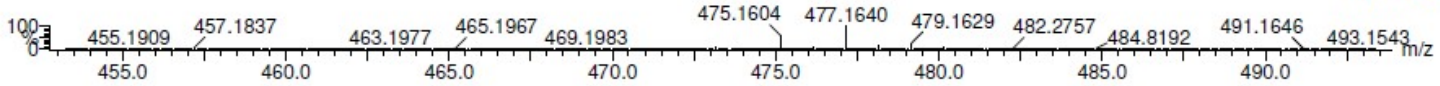
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 0-29 N: 0-2 Cl: 0-1 193Ir: 0-1

25-Apr-2022
PDN_MS38072_ESP 19 (0.203)

VYV254

Cardiff Uni Synapt G2-Si
1: TOF MS ES+
5.74e+005



Minimum:				-1.5				
Maximum:		20.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
477.1640	477.1648	-0.8	-1.7	4.0	745.4	n/a	n/a	C16 H29 N2 Cl 193Ir