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Mechanistic study of C-H activation by iridium complexes

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Mechanistic study of C-H activation by iridium complexes

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List of Abbreviations

ESI	Electron Ionization Source
CRM	Charge Residue Model
IEM	Ion Evaporation Model
QIT	Quadrupole Ion Trap
m/z	mass to charge ratio
MS^n	Tandem mass spectrometry
CID	Collision-Induced Dissociation
DFT	Density Functional Theory
IrPhen	Iridium(III)-1,10-phenanthroline dichloride
DPPP	1,3-Bis(diphenylphosphino)propane
DPPE	1,2-Bis(diphenylphosphino)ethane

Abstract

C-H activation is considered the “holy grail” of chemistry. Selective C-H activation of inactivated C-H bonds is greatly beneficial in many industrial applications and synthesis pathways as it can reduce the number of steps of a particular synthetic method. Remote, selective C-H activation has many applications such as modifying precursors, adding complexity to molecules ,and modifying pre- existing structures in a reduced number of steps. Much work has been done to find a catalyst that can carry out selective C-H activation. Previous work by Swift and Gronert identified an iridium(III) phenanthroline complex that can activate C-H bonds of cyclohexane. Survey studies also showed that this complex can activate C-H bonds in a range of substrates such as alcohols, ethers, esters, amines, and aromatic compounds. The objective of this dissertation is to study the mechanism and regioselectivity of this complex in common precursors, namely 1-butanol, 1-methoxybutane and butyl acetate.

The studies were carried out in the gas phase on a modified mass spectrometer. Selectively deuterated alcohol, ether and ester were either purchased or synthesized to determine the site of activation. The studies showed that the iridium phenanthroline complex can activate the gamma and delta positions in 1-butanol, almost selectively activate (~96% preference) the gamma position in 1-methoxybutane and selectively activate the alpha carbon in butyl acetate. DFT studies showed that the driving force of this selectivity is the formation of either a five or six-membered rings in the transition state.

Since it was observed through DFT calculations that the ligands of the complex influence the transition state, studies were carried out to determine the effect of the ligand on the regioselectivity of the complex. A range of iridium complexes was either purchased or synthesized to study the

impact of sterics, electronic effects, the flexibility of the ligand, the effect of the chelating atom in the neutral ligand and the effect of the anionic ligand. These ligands were used to study the regioselectivity of C-H activation of the model alcohol, ether, and ester. The studies showed that there were only subtle impacts on the regioselectivity of the C-H activation in these substrates. However, the overall reactivities of the complexes were found to be impacted by the nature of the ligand.

In studying ligand effects with the Ir(III) 1,3-bis(diphenylphosphino)propane complex, it was discovered that it had the ability to activate C-H bonds in methoxybutane accompanied by the loss of an alkoxy radical. A survey study was done to determine the scope of the reaction. The studies showed that in order for C-H activation to occur, at least one of the alkyl chains need to have three or more carbons, suggesting that activation was occurring at the gamma or delta site.

Chapter 1 Mass Spectrometry and Gas-phase ion-molecule reactions

1.0 Mass Spectrometry

The first mass spectrometer was invented by J.J. Thompson to measure the mass of charged ions. The mass spectrometer was built using gas-discharge tubes as the source of ions, which were then passed through electric and magnetic fields to be finally detected through the use of a photographic plate.[1,2] Mass spectrometry was initially used in the early 20th century to prove the existence and measure the masses of elemental isotopes. At these early stages, mass spectrometry was also used as a quantitative tool in organic synthesis. However, with increasing understanding of the principle behind this technique, it was used as a tool for elucidating the structure of unknown molecules as well as for mechanistic studies of various processes such as the McLafferty rearrangement.[3–5] In the present, mass spectrometry is a widely used analytical tool in many industries.

1.1 Mass Spectrometers

A mass spectrometer is an analytical instrument that is used to detect the abundance of a particular mass or, more accurately, an m/z of an ion (mass-to-charge ratio).[6] It consists of three main parts. The ionization source, which volatilizes and ionizes the species to be studied, a mass analyzer where the trapping, separation, and manipulation of an ion is performed and a detector where a signal corresponding to the m/z of the ion is detected.

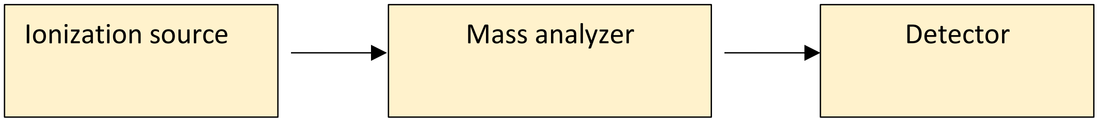


Figure 1 Schematic of a mass spectrometer

1.1.1 Ionization sources

The ionization source transfers the molecules to be analyzed into the gaseous phase in an ionic form. The choice of the ionization source depends on the application. Hard ionization sources such as Electron Ionization (EI) were the first ionization methods to be used. This method results in fragmentation of the ion and requires the sample to be in the gaseous phase before introduction. Soft ionization sources such as ESI (Electrospray ionization), Field Desorption (FD), and Fast Atom Bombardment (FAB) are more likely to produce intact molecular ions. Ionization sources such as Inductively Coupled Plasma (ICP) and Glow Discharge (GD) have been used to produce atomic ions. These ionization sources can be used for quantitative analysis of trace elements and measuring isotope ratios in samples.[7,8] Although many ionization sources are available, only ESI will be described in this chapter.

1.1.1.1 Electrospray ionization (ESI)

ESI was first introduced by Dole in 1968 [9] and later perfected and coupled to MS by Fenn in 1984.[10,11] It is the most widely used technique to analyze samples that are in the liquid phase.[12] In ESI, the sample is usually dissolved in a polar, volatile solvent such as methanol, acetonitrile, or isopropanol.[7] The sample solution is transported through a stainless steel needle which is held at a positive or negative potential relative to the nozzle. The potential gradient between the needle and the nozzle and the repulsion of the ions in the solution against the charged capillary of the needle, forms a Taylor cone which is enriched with either positive or negative ions at the tip. This is the initiation of the electrospray.[13,14]

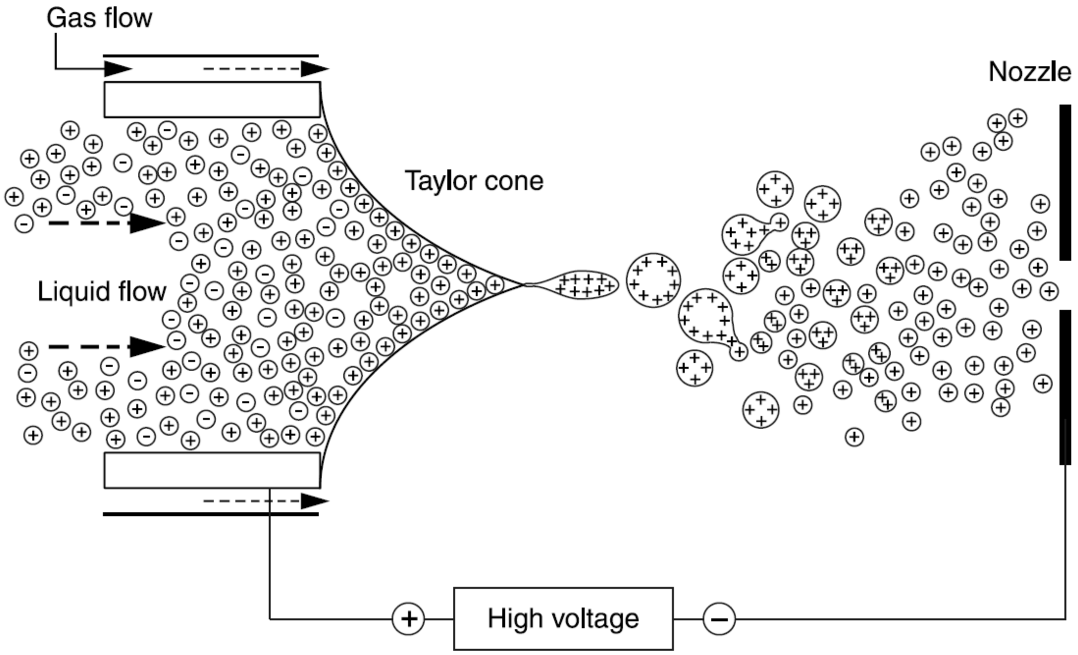


Figure 2 Formation of Taylor cone. Reprinted with permission from John Wiley and Sons. In Mass Spectrometry: Instrumentation, Interpretation, and Applications by Agnieszka Kraj, Ann M. Westman-Brinkmalm, Dominic M. Desiderio, Jerzy Silberring, Nico M. Nibbering, Rolf Ekman. Copyright 2008.

Due to the high electric field, charged droplets are ejected from the tip of the Taylor cone. The droplets reduce in size through evaporation, which can be assisted by the flow of warm nitrogen [8]. The ionization process is seen to occur in three stages; droplet formation, droplet shrinkage, and gas-phase ion formation.[10] The exact mechanism of ion formation is yet to be determined, and two different theories are presented in the literature.

The droplets formed at the tip of the cone will reduce in size through evaporation. Once the radius of the droplets reaches the Rayleigh limit, where the coulombic repulsions of the charges in the droplets overcome the surface tension of the droplet, coulombic fission occurs producing droplets of a smaller size.[14,15]

The Charge Residue Model (CRM), proposes that the gas-phase ions will be produced by the continuous coulombic fission process mentioned above until no evaporation can further occur. This process explains the production of singly and multiply charged ions from a biological sample.[14]

The Ion Evaporation Model (IEM) proposed by Iribarne and Thomson suggests that singly charged gas-phase ions are directly produced from the droplet once it reaches a certain radius (R ~ 10 – 20 nm).[14] The ion evaporation would then continue until it can evaporate no further. The ion-evaporation in this instance would replace the coulombic fission process.

According to the IEM model, the presence of singly and multiply charged ions in the mass spectra can be due to both the IEM and CRM processes. The singly charged ions are produced by the IEM mechanism while the multiply charged ions will be due to the CRM process.[10,14,16]

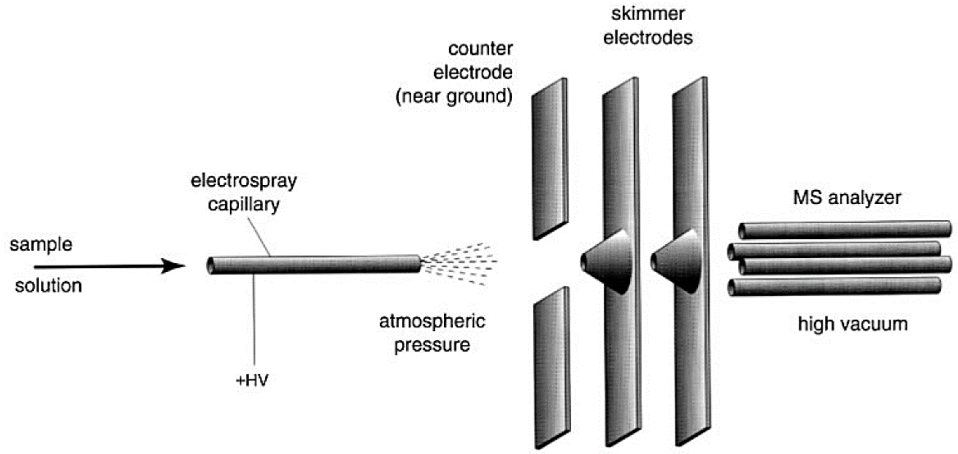


Figure 3 Diagram of ESI interface. Reprinted with permission from John Wiley and Sons. In Journal of Mass spectrometry, Electrospray: Principles and Practice, Simon J. Gaskell. Copyright 1998.

Sample preparation for ESI requires dissolving the analyte in one of the solvents mentioned above at a suitable concentration. The sensitivity of the ESI source is concentration-dependent. The sensitivity is also affected by the experimental conditions of the solution, such as pH, salt concentration, presence of other analytes, and denaturation of the molecules. Formic acid and acetic acid is sometimes added to assist with protonation to increase the sensitivity in the positive mode while ammonia or a volatile amine is added in negative ion mode to assist with de-protonation.[7,14]

ESI is a soft ionization technique that can produce singly or multiply charged ions. Due to the ability to form multiply charged ions, it is a useful technique in analyzing large molecules such as peptides and proteins in mass spectrometers with limited m/z range.[3,12] The soft conditions in this ionization method also makes it the prevalent ionization source for organometallic studies.[17–19] In conclusion, ESI is the most suitable ionization source for large, thermally labile molecules and molecules with low volatility.[10] The ions produced through ESI have been shown to represent the pool of ions present in the solution to a certain degree due to soft ionization conditions. However, electrochemical processes can occur during ESI and create a discrepancy between the oxidation state in sample and what is observed in the gas phase.[14,20]

The ions formed by the ionization source are directed by a series of lenses in an intermediate vacuum region to a small orifice of an endcap electrode into the high vacuum region of the mass analyzer (Figure 3).

1.1.2 Mass analyzers

Mass Analyzers are responsible for separating ions according to their m/z. Analyzers can be scanning or pulsed and trapping or non-trapping (beam instruments). Time-of-flight, Orbitrap, Quadrupole Ion Trap, magnetic sector, and Fourier transform ion cyclotron resonance are a few of the common mass analyzers used at present with each having its own performance parameters.

Mass resolving power, mass accuracy, m/z range, linear dynamic range, precision, efficiency, speed, and compatibility with the ionization source are essential performance parameters in a mass analyzer.[21,22] In this chapter, only ion-trapping mass analyzers will be discussed.

1.1.2.1 Quadrupole Ion trap (QIT)

A QIT or Paul ion trap as it is also known, functions by trapping ions in a potential well. Thus it behaves as both an ion storage and a mass analyzer.[6,23,24] The storing capability is due to the potential well created by the electric field in the ion trap (Figure 4).[26] Each ion is excited by an RF pulse which is applied to the ring electrode, in addition to the AC voltages applied to the endcap electrodes, and then sequentially ejected to the detector in ascending m/z.[6,7,24,25] The trapping potential of the QIT can be used to isolate and store ions of interest[24] to perform further experiments such as collision-induced dissociation (CID), ion-molecule, or ion-ion reactions.

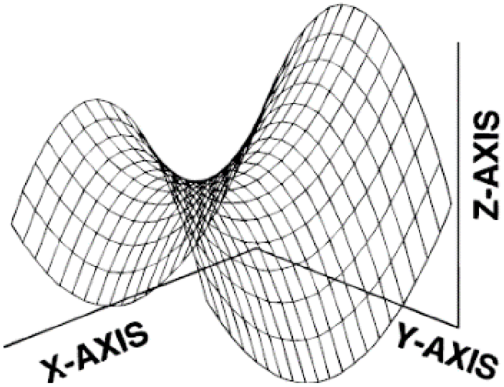


Figure 4 Potential surface of a QIT. Reprinted with permission from John Wiley and Sons. In Journal of Mass Spectrometry, An Introduction to Quadrupole Ion Trap Mass Spectrometry, Raymond E. March. Copyright 1998.

Ions from the ionization source are guided to the cylindrical ion trap as seen in figure 5, through a series of lenses and enter the trap through one of the endcap electrodes.

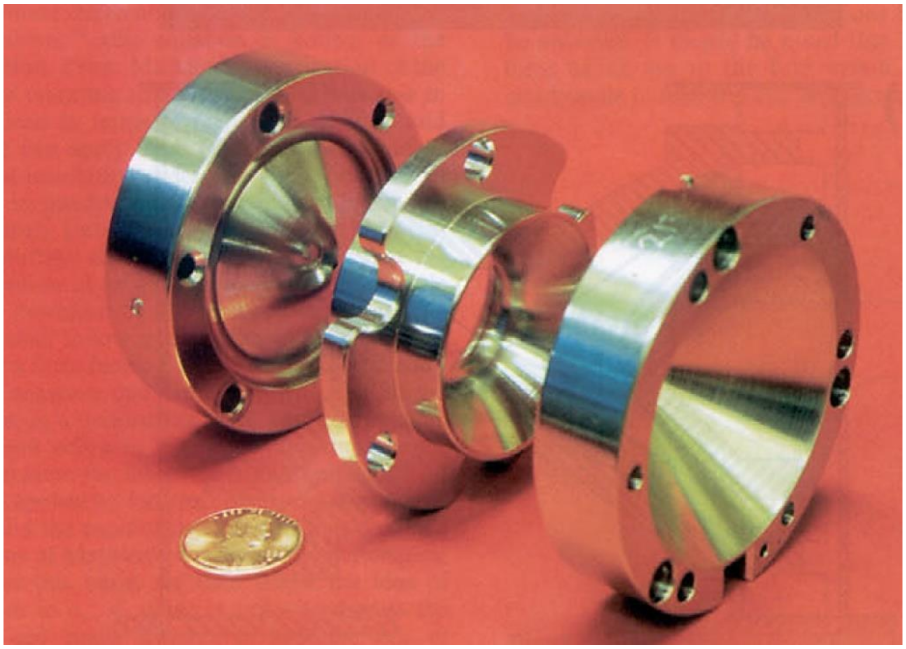


Figure 5 Diagram of the two endcap electrodes and ring electrode in a quadrupole ion trap. Reprinted with permission from John Wiley and Sons. In Journal of Mass Spectrometry, An Introduction to Quadrupole Ion Trap Mass Spectrometry, Raymond E. March. Copyright 1998.

The RF voltage in the ion trap can be held constant or changed depending on the application of the experiment. Once the ions enter the high Rf trapping field, the kinetic energy of the ions would increase. This increased energy is dissipated through collisions with a damping gas. Many instruments operate with a damping gas, which in most cases, is helium, with a pressure of about 1 mtorr.[22,26] The helium gas increases the mass sensitivity and resolution of the trap in addition to cooling and contributing to trapping ions.[27–29] Helium is also used as the target in collision-induced dissociation (CID) in tandem mass spectrometry, as described in section 1.1.2.2.3.

A mass spectrum is obtained in a QIT through a combination of mass selective instability scanning and resonant ejection.[7] In mass selective instability scanning, the RF voltage is ramped up sequentially, making ions unstable. The unstable ions are then ejected through the endcap electrode to the detector.[21] In the resonant ejection, an additional RF voltage is applied to the endcap electrodes. The trapped ions oscillate at different frequencies which are dependent on their m/z. A supplementary RF voltage is applied which corresponds to a frequency near the instability threshold and when the m/z of a specific ion is driven to this frequency by the voltage ramp, it is promptly ejected. [28] A pre-requisite for this method to have acceptable resolution is that all ions be toward the center of the trap. This is done by the helium gas, which removes the excess kinetic energy of the ions through collisions, and reduces the trajectory of the ions to the center of the trap, which results in an increased resolution.[23,25,27] When resonant ejection is combined with the selective instability scan, a higher density of ions will fall into resonance with the supplied RF voltage and be ejected from the trap leading to narrower peaks. Resonant ejection was introduced as a technique to increase the mass range and resolution of a QIT.[22,25,28,28] The ejection of these ions from low m/z to high m/z to the detector generates the mass spectrum.

1.1.2.1.1 Trapping ions in a Quadrupole Ion Trap

In a QIT, an ion of interest is isolated by applying a broad RF pulse, with the frequency of the ion of interest notched out, to the ring electrode of the ion trap.[24,25] All ions except the ions of interest are ejected from the trap.[21,28] This ion can then be fragmented or allowed to react with a second molecule or ion.[22] The products of the fragmentation or reaction can be further isolated and manipulated in the same way.

The motion or trajectory of an ion in a quadrupole field can be mathematically described by the Mathieu equation. This equation describes the stability and instability of ion trajectories in a quadrupole ion trap taking into account the experimental conditions of the ion trap (Equation 1).[29]

$$\frac{d^2u}{d\varepsilon^2} + (a\text{-}2q\cos 2\varepsilon\,)u = 0 \qquad (1)$$

The Mathieu equation is shown above with u describing the dimensions of the ion trap and ε describing the frequency of the RF voltage ($\varepsilon = \frac{\omega t}{2}$). The Mathieu constants "a" and "q" are dependent on the dimensions of the ion trap, frequency of the Rf voltage, and m/z of the ion as shown by equations 2 and 3.

$$a = \frac{8eu}{mz_0^2\omega^2} \qquad (2)$$

$$q = \frac{\text{-}4eV}{mz_0^2\omega^2} \qquad (3)$$

V is the Rf voltage, z_0 is the half-maximum distance between the endcaps, e/m is the reciprocal of the mass to charge ratio of the ion, and ω is the Rf frequency. A stability diagram can be drawn using the Mathieu constants a and q as the coordinates. Ions can be trapped as long as their trajectories are stable in both the r and z directions. R describes the x-y plane while z describes the z-plane.

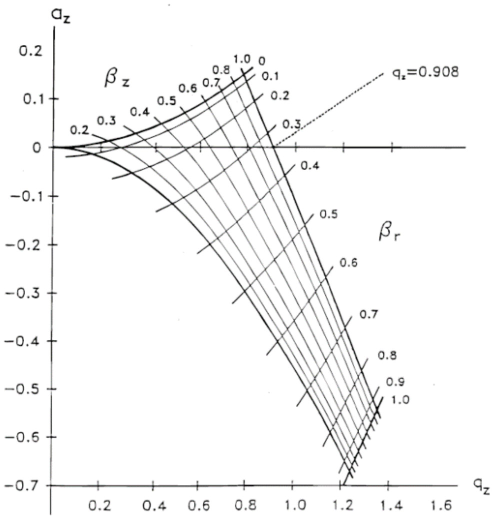


Figure 6 Stability diagram. Reprinted with permission from John Wiley and Sons. In Journal of Mass Spectrometry, An Introduction to Quadrupole Ion Trap Mass Spectrometry, Raymond E. March. Copyright

The stability diagram shown in Figure 6 shows the stable region where the ions can be trapped. β_z is a trapping parameter which is an integer and a complex function of the Mathieu constants a and q. The above diagram shows that for the above β_z value, the q value is 0.908. This will be the lowest cut-off point of the m/z of the ions that can be stored in the ion trap. Ions outside the stability will be neutralized through collision with the quadrupole rods and would not be carried through to the detector.[24,25]

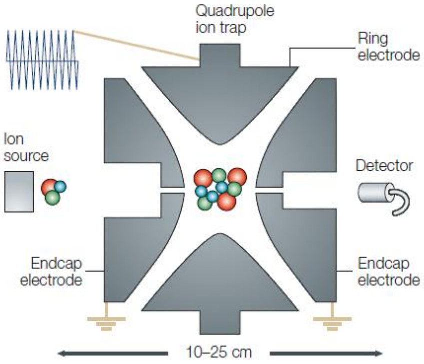


Figure 7 By maintaining stable trajectories ions can be trapped in the ion trap. Reprinted with permission from Springer Nature. In Nature Reviews Drug Discovery, The basics of mass spectrometry in the twenty-first century, Gary L. Glish et al. Copyright 2003.

1.1.2.1.2 Tandem Mass Spectrometry (MS^n)

In tandem mass spectrometry, also known as MS/MS, ions are trapped in the mass analyzer through multiple stages of ion selection so that they can be further studied through fragmentation or reacting with a second ion or molecule.[6,7,22] This is done in a stepwise manner, and the “n” in MS^n corresponds to the number of steps performed to get the final spectra.

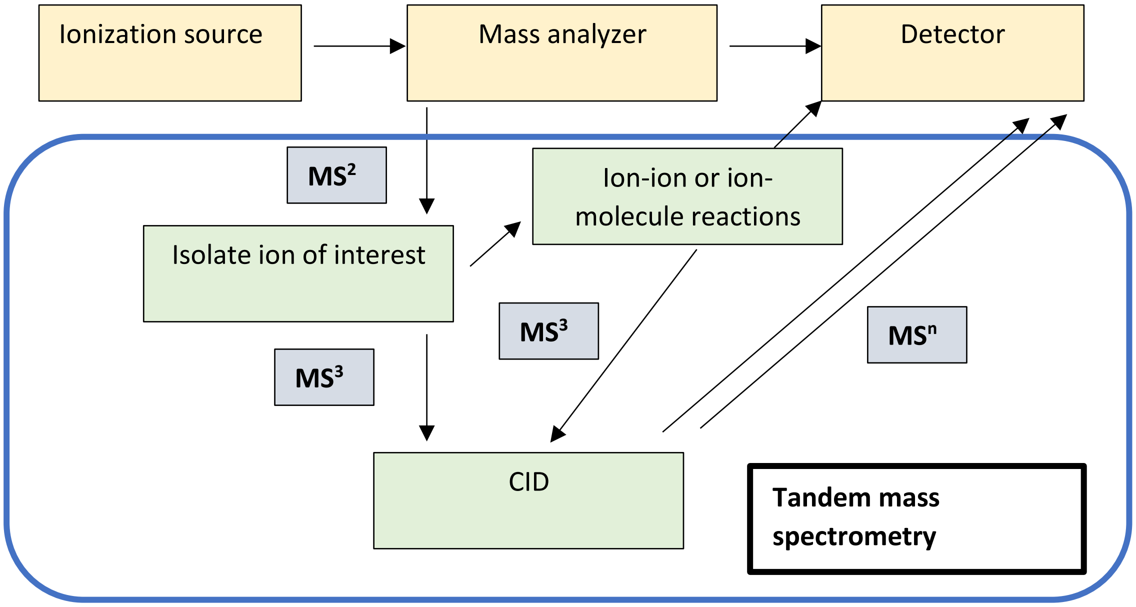


Figure 8 Schematic of a tandem mass spectrometry process

Tandem mass spectrometry can be used to obtain structural information about a molecule or to study bimolecular reactions.[21,22] Tandem mass spectrometry can be either tandem-in-space or tandem-in-time.[7,21,22,25] In tandem-in-space mass spectrometers, isolation, fragmentation, and scanning take place in separate non-trapping mass analyzers. These are generally time-of-flight (TOF) or triple quadrupole analyzers. In tandem-in-time mass spectrometers, the isolation, fragmentation, and separation based on m/z all occur in the same physical device. Therefore, this mode of tandem mass spectrometry is only possible in trapping mass analyzers such as the QIT and FTICR.[7,21] The trapping capability of these analyzers allows ions to be trapped for a prolonged period to perform several ion manipulations. Tandem mass spectrometry allows the study of the relationship between a precursor ion and its product ion.[22]

1.1.2.1.3 Collision Induced Dissociation (CID)

CID is a method of activating an ion to obtain fragmentation. The ion of interest is excited by the application of an RF voltage corresponding to the frequency of motion of the m/z of the specific ion (resonance excitation).[27,31] The excited ion then collides more energetically with the background gas, which in most cases is helium but could also be nitrogen or argon. The kinetic energy from the collisions is converted into vibrational energy of the ion. The increasing internal energy of the ion will eventually lead to fragmentation.[21] The amount of fragmentation can be increased by increasing the collision energy (eV) or changing the buffer gas.[7,30] The CID process can provide information about the structure as well as the origin of ions.[31]

1.1.3 Detectors

Once an ion is ejected from an ion trap, it impinges on a detector, which would result in an output signal.[6] The energy of the impact of the ion striking the detector is converted to an electric current by the detector. The most common detector used in mass spectrometers is an electron multiplier. In an electron multiplier, when an ion strikes the multiplier, a cascade of secondary electrons is emitted. The number of secondary electrons emitted is dependent on the energy/velocity of the incoming ion. These emitted electrons are registered by electronic devices and translated into a mass spectrum by the software of the acquisition system. A detector should have a high conversion efficiency of the energy of the ions into electrons, show a linear response, low noise, and have a short recovery time.[7,32]

1.2 Gas-phase study of ion-molecule reactions

In the past, mass spectrometers were used primarily as a tool for the identification of organic compounds and studying the presence of isotopes.[7] However, advances in trapping or guiding ions in mass spectrometry throughout the years have allowed it to gain popularity as a tool in studying various reactions in the gas phase.[19,33,34] The invention of the QIT and ESI made it possible to explore multiple organometallic, organic, and inorganic gas-phase reactions.[19,35] This ability to study reactions in the gas phase, bridges the gap between condensed-phase and gas-phase work and allows the understanding of various reactions and mechanisms we cannot easily ascertain in the condensed phase. Due to the absence of solvent, solvent-dynamics , and interactions in the gas phase, the reactivity of a certain species is directly related to the structure.[18,31,36]

1.3 Bimolecular reactions in the gas phase

A trapping analyzer such as a QIT or FTICR can be used to study bimolecular reactions in the gas phase. In a QIT, the ion of interest is introduced into the ion trap via the ionization source interface. Once in the ion trap, the ion can be isolated using tandem mass spectrometry. A second reagent can be introduced to the ion trap[37] through various methods which will be discussed in section 1.4, thereby enabling bimolecular reactions. The isolated ion can also react with adventitious molecules found in the ion trap such as O_2, and solvent molecules such as water, methanol etc.[38–40] The product ions from these bimolecular reactions accumulate over time and can then be scanned out to obtain a product mass spectrum. Kinetics of bimolecular reactions can also be obtained in this manner by varying the trapping time. The rate of a reaction is usually expressed as a fraction of the collision-rate of the reaction.[29,37] The ability to carry out bimolecular reactions in the gas-phase opens up mass spectrometry as a technique to study the mechanisms of organic and organometallic reactions, study H/D exchange of biomolecules, intrinsic reactivity of ions, as well as gaining information of the role of solvent and counter-ions of reactions which take place in the condensed-phase.[14,33,34,41]

Gas-phase bimolecular reactions can be either ion-molecule reactions or ion-ion reactions.

1.3.1 Ion-molecule reactions

QITs, FT-ICR, and linear triple quadrupoles are commonly used to study bimolecular ion-molecular reactions in the gas-phase.[22,29,42] In many laboratories, modified commercial mass spectrometers have been utilized to study ion-molecule reactions. This opens up mass spectrometry as a tool for studying organometallic reactions, radical reactions, H/D exchange reactions, identification of functional groups in organic molecules and identifying the functional groups in biomolecules(post-translational modifications).[40]

1.3.1.1 Ion-molecule collision theory

In an ion-molecule reaction, the collision rate of the process is dependent on the polarizability and dipole moment of the neutral molecule, the charge of the ion, and reduced mass. The Langevin model is a simple approach to computing the collision rate, as shown in the equation below,[43] but does not take into account the dipole moment of the neutral molecule. The ion's charge induces a dipole in the neutral molecule. The molecule is then captured due to the attractive interaction force between the ion and molecule as described in equation 4. [36]

$$V_D = \left(\frac{-q\mu_D}{r^2}\right)\cos\theta \qquad (4)$$

V_D is the attractive force potential, μ_D is the induced dipole moment, q is the charge of the ion, r is the distance between the ion and molecule, and θ is the contact angle of the collision. The polarizability of the molecule increases the collisional cross-section which ultimately increases the rate constant.[44]

$$k' = \left(\frac{2\pi q}{\mu^{\frac{1}{2}}}\right)[\alpha^{\frac{1}{2}} + \mu_D \left(\frac{2}{\mu kT}\right)^{\frac{1}{2}} \quad (5)$$

k' is the rate constant for an ion-molecule reaction, μ is the reduced mass, q is the charge of the ion, α is the polarizability, μ_D is the induced dipole moment, and k is the Boltzmann constant.

The attractive force makes the collision cross-section of the reactants larger, thus giving a Langevin collisional rate constant of roughly 1×10^{-9} cm^3 molecule^{-1} s^{-1} for singly charged ions. The collision rate is considered the upper limit for ion-molecule reactions.[45] Su and Bowers later developed a more sophisticated model, average dipole orientation (ADO)[43], which incorporates the dipole moment of the neutral molecule. Computed ADO collision rates are higher than Langevin depending on the magnitude of the dipole moment. Conventional QITs can be used to study reactions with rate constants down to about 1×10^{-13} cm^3 s^{-1}. This lower limit is driven by the viable trapping times of the instruments and problems with chemical impurities when reaction rates become too slow. In special cases, slower reactions can also be studied by modifying the reaction time and reagent pressure accordingly.[29,46]

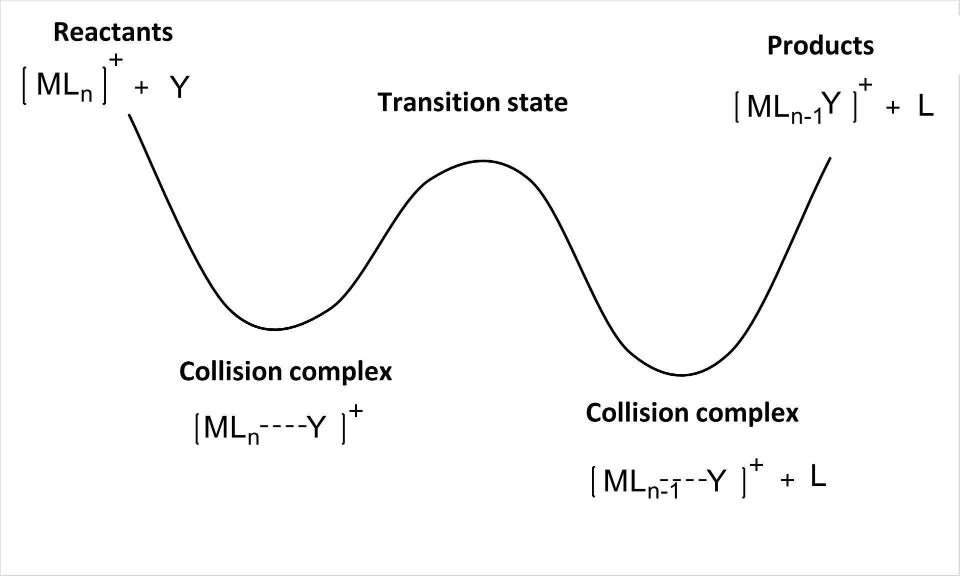


Figure 9 Potential Energy surface of a bimolecular reaction

In an ion-molecule reaction, the reactants experience an attractive ion-neutral electrostatic force, which enhances the collision cross-section, as described above. This leads to the formation of a short-lived ion-neutral collision complex with high internal vibration energy. This energy can be used to drive the reaction over a barrier. If the barrier for the reaction is not significantly higher than the entrance channel (less than 3 kcal/mol), the collision complex can pass over the barrier and the reaction will proceed. If the barrier is significantly higher than the entrance channel, the collision complex of the reactants will either dissociate back to reactants or will eventually dissipate its energy through collisions with the bath gas and be trapped as a non-covalent adduct complex. Thus, the observed rate constant of a gas-phase reaction is correlated to the height of the barrier.[46] The dissipation of energy by collisions with a bath gas is common in QITs but not in ICR instruments and therefore adducts are much more common in QITs.[34]

The interaction of the barriers and ion-molecule attractions described above explain why gas-phase reactions are typically faster than condensed-phase reactions. The presence of an internally excited short-lived collision complex as well as the absence of solvent-shells increases the reactivity of gas-phase processes.[37]

1.4 Methods of introducing a second reagent into the ion trap

When the ion is isolated in the ion trap, neutral reagents can be introduced into the ion trap to react with the isolated ion. The products formed through the ion-molecule reaction will be scanned by the mass analyzer to generate a mass spectrum. There are two popular methods to introduce the second reagent.

The first method is the use of a pulsed valve. Once the ion of interest is isolated, the reagent is then pulsed in. The advantage of this method is that the reagent gas would not be present during the period of ion accumulation in the ion trap. However, this method is not suitable for kinetic studies as the reagent gas dissipates as it is pumped out of the ion trap by the vacuum system and does not have a steady concentration.[47]

The second and most common method is the use of a leak valve to introduce the second reagent. The leak valve is used to introduce a steady flow of the second reagent directly into the ion trap.[48] This method is challenging for kinetics because there is no easy way to determine the concentration of the second reagent in the much higher pressure helium buffer gas. Gronert et al. introduced a modified form of the leak valve introduction where the reagents are first diluted externally with the helium buffer gas. This allows quantitative introduction of the reagent to the ion trap.[29]

The neutral reagent is injected through a septum port at a rate of 30-300 µL/hr to a flow of helium (flow of 1-2 L/min). This ensures rapid volatilization of the reagent as it is carried into the ion trap(Figure 10).

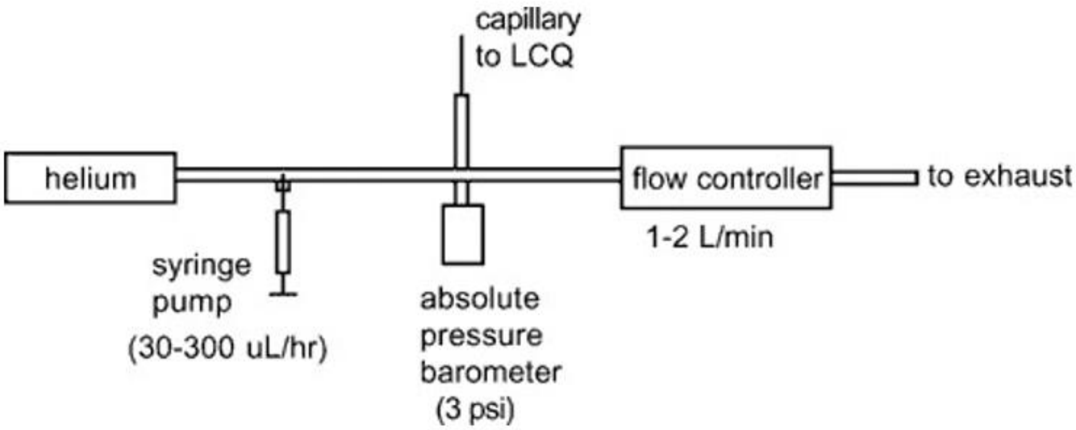


Figure 10 Schematic of the modification by Gronert et al. to introduce a second reagent to the ion trap. Reprinted with permission from John Wiley and Sons. In Mass Spectrometry reviews, Quadrupole ion trap studies of fundamental organic reactions, Scott Gronert. Copyright 2004

The reagent gas partial pressure in the ion trap is $10^{-5} - 10^{-8}$ torr with a helium pressure of 10^{-3} torr. The pressure of the reagent gas can be calculated by using the equation shown below.[49]

$$P_{RX} = 1.75 \times 10^{-3} \times \frac{F_{RX}}{F_{He}} \times \frac{d_{RX}}{MW_{RX}} \times (\frac{MW_{RX}}{MW_{He}})^{1/2} \qquad (6)$$

P_{RX} is the pressure of the neutral reagent, 1.75×10^{-3} is the buffer gas pressure of the ion trap under normal operating conditions, F_{RX} and F_{He} is the flow rate of the neutral reagent and helium gas respectively, d_{RX} is the density of the neutral reagent, MW_{RX} is the molecular weight of the neutral reagent and $(\frac{MW_{RX}}{MW_{He}})^{1/2}$ is the correction term for differential effusion. Since the pressure of the reagent gas can be quantitatively determined, this modification can be used to study the kinetics of ion-molecule reactions.

Lovejoy et al. use a similar method where the reagent gas is prepared in an external chamber. This method can be used to introduce a second ion or modify the ions from the ionization source before introducing it into the ion trap. The external reagent chamber has a continuous flow of helium. The ions from the chamber leave an orifice, which has a diameter of about 0.25 – 0.5 mm. These ions are guided through a series of electrostatic lenses into the ion trap.[50]

1.5 Theoretical studies of gas-phase reactions

Computational modeling has been widely applied to gas phase reactions and with the onset of DFT methods in the early 1990s, it has been possible to investigate reaction mechanisms in relatively large chemical systems.[51]

Theoretical studies have been used to infer the intrinsic reactivity of a compound based on its chemical structure.[18] Theoretical studies are valuable in confirming the experimental data seen in gas-phase reactions. Due to the low-pressure conditions in most mass spectrometers, the reactions observed are a function of the reaction partners (intrinsic reactivity) void of any solvent effects. Theoretical studies can be used to similarly study isolated molecules, thus enabling a direct comparison. The energy of a system is obtained as a function of the molecular geometry. Equilibrium geometries (local minima on the potential energy surface with real vibration frequencies) or transition states (saddle points with one imaginary frequency) are calculated to map out potential energy surfaces. The various models used to compute these energies are accurate, with an average deviation of 8kJ/mol from experimental results.[36,52] A large body of work has been carried out using gas-phase studies in combination with quantum mechanical calculations. This leads to a good correlation between experimental and theoretical work.[53]

1.6 History of organometallic reactions in the gas phase

Many mechanistic studies of organometallic reactions have been carried out in the gas phase.[51] Studies have shown that gas-phase models cannot directly predict the rate constant, turnover numbers, and turnover frequencies of a condensed-phase reaction.[17] However, they help in understanding the intrinsic reactivity of the complex studied as well as the selectivity of the reaction. This aids in designing new complexes with the optimized tuning of reactivity to satisfy the application.[45,51] FAB, FD, and ESI are commonly used ionization sources for organometallic compounds with ESI and FD, producing the least amount of fragmentation. However, the incapability of FD to reproducibly produce ion distributions and intensities limits their use.[54] The ability to produce intact molecular complexes makes ESI the most popular source used for studying organometallic reactions in the gas phase. This requires the complex to form stable ions in the solution, which are then transferred to the gas phase through the ESI process. Neutral complexes can also be studied through ESI by ionizing the complex as part of the ESI process. Protonating the complex, metalation of the complex through the formation of alkali metal adducts, quaternization of complexes containing phosphine and arsine groups, oxidation or reduction of the metal center and displacement of neutral ligands by anionic ligands are the methods used to ionize organometallic complexes prior to ESI. This has allowed ESI with QITs and FT-ICRs to be instrumental in studying intermediates in catalytic cycles in the gas-phase.[19,55]

Transient intermediates of various chemical reactions involving metals have been investigated in the gas-phase,[56] such as the Wittig reaction, Mitsunobu and Staudinger reaction[57], Suzuki coupling of Pd(0) catalyzed reaction of arylboronic acids and aryl halides[58] and C-H activation by Ir(III) complexes.[42] The first application of characterizing ionic transition metal compounds by mass spectrometry was reported by Chat et al. in the study of Ru(II) bipyridyl and 1,10-phenanthroline complexes.[59] Since then organometallic complexes of a wide range of transition metals such as Hg(II), In(III), Au(III), Tl(III)[60], Sn(IV)[61], Ru(III), Fe(II)[62], Ni(II)[63], Pd(II)[64] and Ag(I)[55] have been studied in the gas-phase. This is not only limited to the study of cationic organometallic complexes as studies of anionic metal carbonyl complexes of metals such as Cr(II), Mo(II), Mn(II) and Re(II) have also been successfully completed in the gas phase.[19,65] The study of organometallic catalytic processes has led to the discovery of intermediates of the catalytic cycle, preliminary steps of the cycle and selectivity of catalytic activity, providing useful information of the catalytic processes which can aid in catalytic design.[42,56]

In conclusion, modified mass spectrometers can be used as an analytical tool for the study of bimolecular reactions. This enables the study of organic and organometallic reaction which therefore allows the study of intermediates in a catalytic cycle

Chapter 2 C-H activation

2.0 Introduction to C-H activation

C-H bonds are ubiquitous in nature, and therefore activation of these bonds has been the focus of intense research.[66,67] C-H activation is the cleavage of a C-H bond, which leads to subsequent functionalization of that bond. C-H functionalization can lead to the formation of new carbon-carbon or carbon-heteroatom bonds. [66,68,69] The ability to directly functionalize C-H bonds introduces the C-H bond into the classic library of modifiable functional groups such as alcohols, amines, carbonyls, etc. C-H activation allows one to readily modify precursors, create new strategies for synthesis, and introduce complexity to molecular structures in a reduced number of steps.[69,70] However, activation of C-H bonds has proven to be very challenging due to the apolar nature of the bond as well as the high energy barrier which is generally associated with the activation of a C-H bond.[68,71–73] Enzymes such as cytochrome P-450 and methane monooxygenase naturally activate C-H bonds of alkanes. These complexes have been extensively studied to understand the mechanistic process and aid in catalyst design.[67,70,74]

2.1 Reactivity of C-H bonds

A non-acidic C-H bond has a very low reactivity in part due to the lack of polarity of the bond. A typical C(sp^3) -H bond has a bond dissociation energy(BDE) of 410.8 kJ/mol and a pK_a of about 50 while an alkyl C(sp^2)-H bond has a BDE energy of 397.9 kJ/mol and a pK_a value of about 50.[67,71] The BDE of C-H bonds are inversely related to the stability of the radical formed following the activation of the bond, with C(sp)-H having the highest BDE (552.2 kJ/mol) and C(sp^3) -H having the lowest BDE. The reactivity of C-H activation through electrophilic mechanisms decreases across the series C(sp)-H > C(sp^2)-H > C(sp^3) -H.[66,71,72] The inertness of a C-H bond is attributed to the low-energy of occupied and high energy of unoccupied σ molecular orbitals of C-H bonds. Therefore, no low energy, empty atomic orbitals are available to participate in a chemical reaction.[70] C-H activation can be mediated through metals, metal complexes, acids, and visible light.[71,75,76] Even though C-H bonds are relatively inert, condensed-phase and gas-phase reactions such as photochlorination, auto-oxidation, and combustion reactions have been observed. These processes create free-radical intermediates and have limited selectivity since free-radical reagents only show a modest preference for tertiary bonds over primary and secondary C-H bonds.[67,77]

2.2 Development of C-H activation reactions

The first example of C-H bond activation was reported by Hoffmann in 1883.[71] The reactivity of C-H bonds in this example depended on the formation of highly reactive oxygen and nitrogen-based radicals. The activation was carried out under strongly acidic conditions. However, selectivity could only be obtained by manipulating the proximity of the oxygen or nitrogen radical and the bond to be activated in the unimolecular process.[78]

The first metal-mediated C-H activation was reported by Volhard in 1892 by using mercury(II) chloride.[79] Chatt is the pioneer of modern C-H activation by organometallic complexes, by showing that a ruthenium(0) complex could insert itself into a C-H bond of naphthalene. This was reported in 1965.[80] Since then, many organometallic complexes have been studied to find a complex that can selectively activate C-H bonds of organic substrates.

At the present, various methods are used in synthetic chemistry to complete C-H activation, namely transition metal complexes, single-atom catalysts, visible light activation, and enzymatic C-H activation. However, the challenge still lies in selectively activating C-H bonds which are remote to the functional group.[74]

2.3 Metal-mediated C-H activation

Metal mediated C-H activation of organic substrates allows the formation of metal-carbon (M-C) bonds as well as subsequent functionalization of the activated C-H bond.[67,71,81] Metal mediated C-H activation can occur through a two-step charge transfer process as shown in figure 11. This can proceed through the donation of electrons from the filled C-H orbital to an empty d* orbitals on the metal (forward transfer) and from the d-orbitals of the metal to the empty σ* orbitals of the C-H bond (reverse transfer). Both the forward and reverse charge transfer processes are responsible in weakening the bond, which leads to the breaking of the C-H bond.[71]

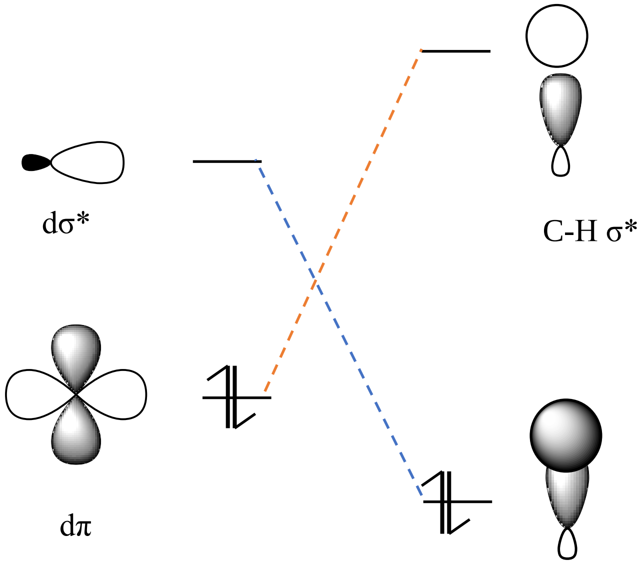


Figure 11 Two-step charge transfer process in metal-mediated C-H activation.

Metal-mediated C-H activation can lead to deprotonation, hydride abstraction, hydrogen atom transfer, insertion into the C-H bond or carbene formation.[82]

De-protonation $\mathrm{R\text{-}H + M \longrightarrow R^{-} + [M\text{-}H]^{+}}$

Hydride abstraction $\mathrm{R\text{-}H + M \longrightarrow R^{+} + [M\text{-}H]^{-}}$

Hydrogen atom transfer $\mathrm{R\text{-}H + M \longrightarrow R^{\bullet} + [M\text{-}H]}$

Insertion into the C-H bond $\mathrm{R\text{-}H + M \longrightarrow R\text{-}M\text{-}H}$

Carbene formation $\mathrm{R\text{-}H_2 + M \longrightarrow M{=}R + H_2}$

Studies have shown that the formation of an M-C bond can be energetically more favorable than a C-H bond (formation of an M-H or H-X bond in the process also plays into this favorability).[71,82] Therefore, C-H activation followed by M-C bond formation can be a thermodynamically favored process and many studies have been carried out to find suitable metal-mediated C-H activation processes.[83] Bare metal atoms, supported metal atoms, and ligated complexes of transition metals have been studied to find a selective catalyst for C-H activation.[76,84,85]

2.4 Mechanisms associated with C-H activation

Metal-mediated C-H activation can be classified as occurring via either an outer-sphere or inner-sphere mechanism.[71]

2.4.1 Outer-sphere mechanism

In the outer-sphere mechanism, the C-H bond is inserted into a ligand of the organometallic complex (e.g., oxygen of M=O complex). This mechanism is commonly seen in alkane oxidation and C-H activation occurring through metal-oxo, metal-carbene, and metal-nitrene species. The metal-carbene or metal-nitrene species is inserted into the C-H bond, usually forming a three-membered transition state which is followed by the dissociation of the rest of the metal complex.[71,86,87]

2.4.2 Inner-sphere mechanism

In the inner-sphere mechanism, the C-H bond is coordinatively bonded to the metal center. Three classes of mechanisms have been identified such as oxidative addition, σ – bond metathesis, and electrophilic activation. The type of inner-sphere mechanism is dependent on the oxidation state of the metal. This affects the charge transfer process occurring in the transition state.[67,71,81,82]

Electron-poor, late transition metals with high oxidation numbers such as Pd(II), Pt(II), Ru(III), and Ir(III) undergo an electrophilic activation. The activation of the C-H bond is usually followed by deprotonation through the participation of an external anion. This de-protonation can also be done intramolecularly through the mediation of a heteroatom ligand on the metal complex such as a halide, alkoxy ion, or carbonate ion and is shown to occur through a concerted mechanism. Electrophilic activation is most often preceded by an agostic interaction. The complexes used for electrophilic activation are relatively tolerant to oxygen and water, and are, therefore, the most intensively studied as catalysts for organic synthesis. [67,69,70,83,88,89]

Low-valent, late transition state metals can undergo C-H activation either through an oxidative addition or σ – bond metathesis pathway depending on the oxidation state of the metal center and the electronic and steric properties of the ligands involved. The oxidative addition mechanism is commonly seen in nucleophilic, electron-rich, d^8 low valent transition metals, with phosphine or nitrogen-based electron donor ligands. The metal should be able to readily access the (n+2) oxidation state. This is a two-step mechanism involving oxidative addition and reductive elimination steps. The complex, in this case, needs to be coordinatively and electronically unsaturated and therefore needs to be generated *in-situ* chemically, thermally, or photochemically.[69,70,70,71,83,90] These reactions are characterized by rapid rates due to their low energy barriers.[67]

The d^0 transition metals cannot undergo oxidative addition. Therefore, the C-H activation for these metals happens via σ – bond metathesis. In this mechanism, no change in oxidation number occurs in the transition state and the activation is thus carried out through a concerted, four-center transition state. A variation of this mechanism is sometimes also seen in metals with d^4 and d^8 configurations.[69–72,83]

2.5 Selectivity and catalyst design

A strong C-H activation catalyst should simultaneously exhibit selectivity, reactivity, and stability.[81] Selectivity is a significant challenge in activation or functionalization of C-H bonds. The functional groups of organic substrates have shown to direct specific C-H bonds for activation through proximity or polarity effects between the C-H bond to be activated and the functional group of the substrate. Site selectivity can be either substrate controlled, or reagent controlled.[71,74] The substrate control makes use of the inherently reactive sites in a substrate such as electron-rich aromatic sites or alpha positions of heteroatom substrates.[91] The most popular method of substrate-controlled selectivity is the introduction of a directing group or heteroatom to the substrate. Classical donor atoms are N, O, P, S, Se, and As. The heteroatom anchors to the metal center and positions a specific bond for selective activation, forming a cyclo-metallated intermediate. A metal-carbon σ – bond intermediate is formed following C-H activation. The directing group assisted C-H activation has been studied using the platinum group transition metals: Ru, Os, Rh, Ir, Pt, and Pd. The co-ordination of the hetero atom changes the electron density at the metal center and sterically controls the activation of a specific C-H bond. [68,89,92]

In reagent control, the reagent needs to be designed to either complement or overcome the inherent selectivity of the substrate. Reagent or catalyst-controlled reactions are governed by external directing forces of the metal complex such as the steric effect. [68,93]

2.6 Organometallic complexes for C-H activation

C-H activation by organometallic complexes has been an intense area of research in the past few decades.[67,94] Ta, Ti, Rh, Ir, Pt, Pd, Re, and Zr are just a few metals that have been studied as catalysts for C-H activation.[69,76,82,83] Organometallic complexes have shown the ability to catalyze C-H functionalization under relatively mild conditions.[86,95–97] The reactivity of the complexes can be tuned by varying the heteroatom donor ligands, chelating ligands, or by employing hydrogen-acceptor complexes. By introducing different ligands and changing the geometry and reactivity, the versatility of the complex can be expanded and be used for a variety of applications.[76,82,98] Closed-shell ligands lower the reactivity of activation compared to the bare metal atom, while open-shell ligands increase the reactivity. Therefore, the reactivity of the metal can be quenched entirely depending on the coordinated ligands. The selectivity is however increased in ligated metal complexes compared to bare metal atoms.[82,99] The true challenge lies in finding a catalyst that can selectively activate the remote C-H bonds in organic substrates.

In conclusion, C-H activation continues to be a hard-sought field of study. More methods of selective activation of C-H bonds would be beneficial for the synthesis of compounds in pharmaceutical and agrochemical industries. The following chapters present studies that were carried out in understanding the mechanism of a potential iridium catalyst that can activate C-H bonds in alcohols, ethers, and esters.

Chapter 3

3.0 Studying the selectivity of C-H activation of alcohols, ethers, and esters using an iridium(III)-1,10-phenanthroline dichloride complex

Iridium complexes play a significant role in many catalyzed reactions. [100] Both Ir(III) as well as Ir(I) organometallic compounds have been used in many synthetic processes such as the synthesis of natural product derivatives as well as C-H functionalization reactions.[56,101,102]

Iridium catalysts have gained popularity in their ability to activate C-H bonds of various substrates. In 1982, Crabtree reported that an Ir(I) complex functionalized a C-H bond of an alkane.[83,103]

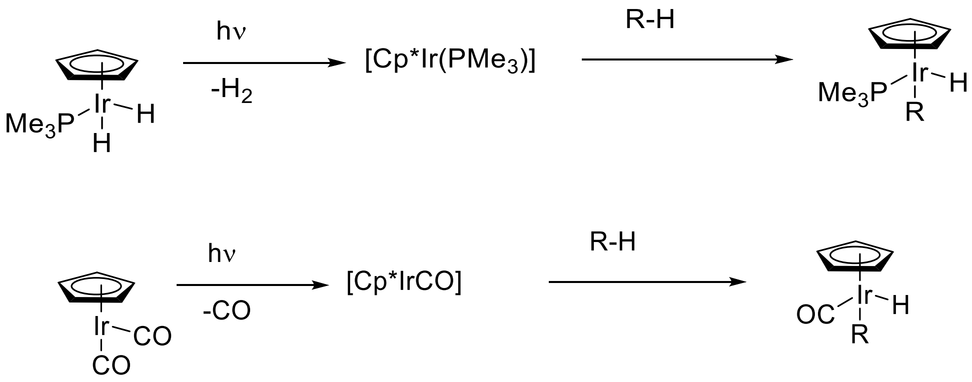


Figure 12 First examples of activation of unactivated C-H bonds by late -transition metals[103]

This was interpreted as an activation of the C-H bond and was one of the first complexes reported to do so.[83,103] In 1993, Berman observed that an Ir(III) methyl cation can undergo C-H functionalization reactions similar to Shilov's catalyst, which was one of the earliest C-H activation catalysts discovered (Figure 12).[83] Since then many iridium complexes have been studied both in the condensed phase as well as the gas phase to further understand the mechanism of metal-mediated C-H activation as shown below in figure 13 .[67,96,104,105]

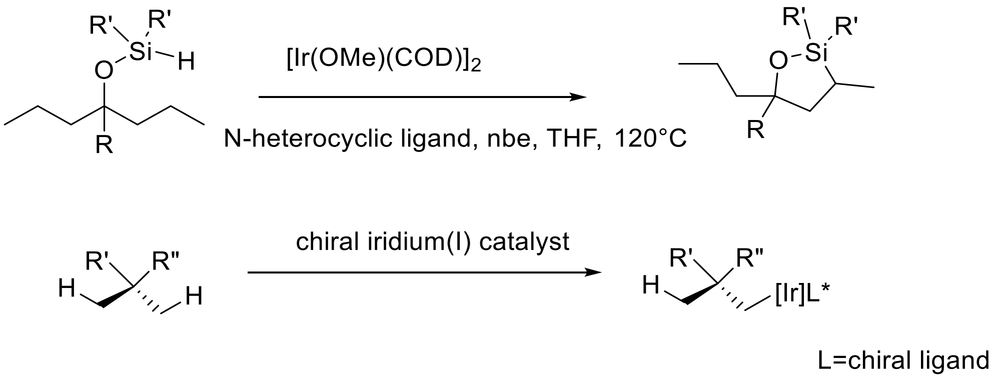


Figure 13 Iridium catalysts used for a) selective remote activation in secondary alcohols, adapted from Iridium-Catalyzed Regioselective Silylation of Secondary Alkyl C–H Bonds for the Synthesis of 1,3-Diols, Bijie Li, Matthias Driess, John F. Hartwig. Copyright 2014, American Chemical Society b) stereoselective C-H activation of secondary alcohols, adapted from Iridium-Catalyzed Asymmetric Borylation of Unactivated Methylene C(sp3)–H Bond, Ronald L. Reyes, Tomohiro Iwai, Satoshi Maeda, et al. Copyright 2019, American Chemical Society.

Homogeneous and heterogeneous iridium complexes have been used for C-H functionalization reactions, with Crabtree's catalyst being considered the industry standard for hydrogen isotope exchange.[84,106] In the recent past iridium pincer complexes have gained popularity as catalysts for C-H activation.[102,107,108] Both PCP and NCN pincer complexes as well as various other pincer complexes have shown selective remote activation of organic substrates. A few of the complexes used so far are shown below.

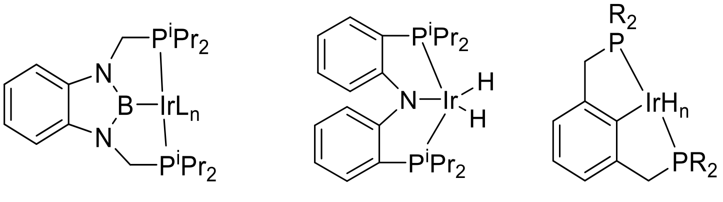


Figure 14 Iridium pincer complexes used in C-H activation[102,104,108]

Studies show that in many instances, a cationic iridium complex is the active species in C-H activation.[109] Cationic iridium(III) octahedral complexes possess filled t_{2g} orbitals and empty e_g orbitals while cationic iridium(I) complexes possess both partially filled s orbitals and d orbitals. These partially filled orbitals will behave as a nucleophile, thus making these complexes more reactive.[110]

Swift and Gronert previously reported that a cationic iridium(III) phenanthroline dichloride complex (Figure 16) can activate secondary C-H bonds in cyclohexane.[111] Although iridium(III) phenanthroline complexes have been studied, this was the first instance that such a complex was shown to activate C-H bonds of inert substrates such as cyclohexane.[97] The C-H activation is identified through the loss of an HCl molecule leading to presumably an Ir-C bond. The cationic iridium(III)-1,10-phenanthroline dichloride complex (here forth referred to as IrPhen) has a valence electron count of only 14, suggesting that it should have high electrophilic reactivity.

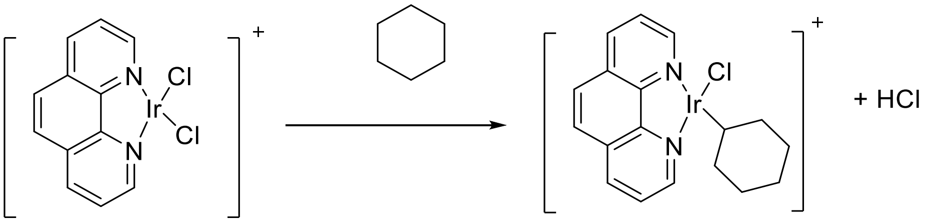


Figure 15 C-H activation of cyclohexane by the IrPhen complex[111]

The activated cyclohexane iridium complex was isolated and subjected to CID. It was observed that the IrPhen complex can perform multiple C-H activations which leads to the formation of benzene from cyclohexane. The IrPhen complex also showed the ability to activate C-H bonds in toluene and ethyl benzene. Kinetic Isotope Effect studies with d_8-toluene showed a value of 2.5 which indicates a hydrogen transfer process. This was further proven using DFT calculations. The DFT calculations showed that the C-H activation occurs through a concerted mechanism in a cyclic transition state. In survey work, this iridium(III) complex was shown to activate C-H bonds in a broad range of substrates such as alcohols, ethers, esters, amines, aromatics, and alkyl halides. The goal of this project is to better understand the mechanism and explore the regioselectivity of this complex with different functional groups.

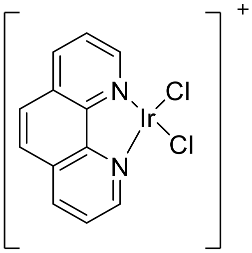


Figure 16 Iridium(III)-1,10-phenanthroline dichloride complex

To build a better understanding of the scope of reactivity and mechanism of action of this complex, reactions were carried out in the gas-phase with alcohols, ethers, and esters. These functional groups are some of the most commonly-used precursors in organic synthesis.[112] Direct functionalization of remote C-H bonds would avoid the requirement of pre-activation of these substrates.[4] As a result, much effort has been put into finding a method that could selectively activate the C-H bonds in these molecules. [66,109,113] The functional groups of alcohols, ethers, and esters can act as an anchor or a directing group to the iridium center.[42,114] This allows the positioning of a specific C-H bond for activation.

3.1 Studying the selectivity of C-H activation in alcohols

Due to the ubiquitous nature of alcohols and the wide variety of transformations available to the hydroxy functional group, extensive research is being done to find methods to selectively activate C-H bonds remote to the functional group.[75,75,81,114] In previous studies by Hartwig et al., C-H functionalization of silyl derivatives of secondary and tertiary alcohols has been achieved using an iridium(III) complex. These studies resulted in activating the primary C-H bonds of the corresponding alcohols. [66,113]

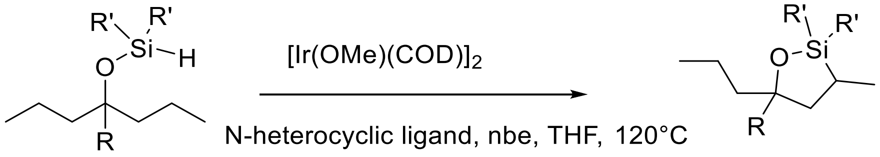


Figure 17 Iridium catalysts used for selective remote activation in secondary alcohols, adapted from Iridium-Catalyzed Regioselective Silylation of Secondary Alkyl C–H Bonds for the Synthesis of 1,3-Diols, Bijie Li, Matthias Driess, John F. Hartwig. Copyright 2014, American Chemical Society

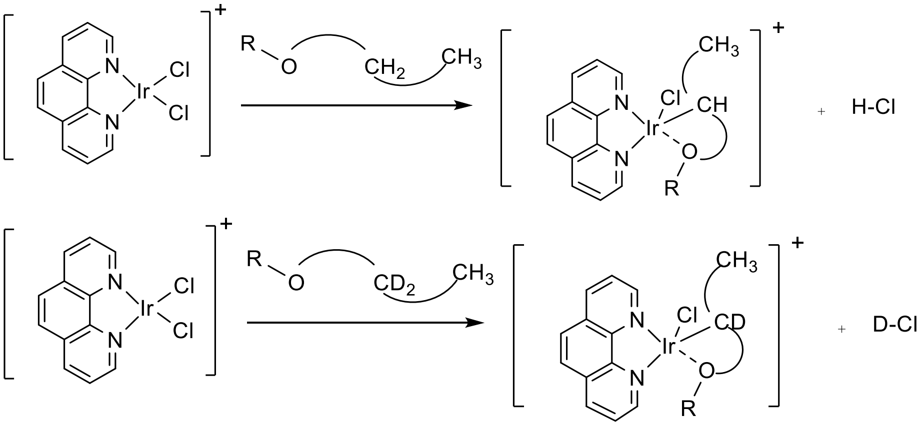
However, most studies showed that the catalysts available so far, activate the alpha C-H bonds of alcohols, hence relying on the direct activation by the hydroxy group.[75,114] To synthesize more complex structures, it would be useful to selectively activate the remote unactivated bonds in organic molecules. Recent studies claiming activation of the bond which is delta to the alcohol functional group in cholesterol by a rhodium complex shows that remote C-H activation and functionalization is possible and can be applied to large complex molecules as well.[66]

3.1.1 Methodology

To study the selectivity of C-H activation in alcohols, reactions were carried out using a modified ThermoFinnigan Deca LCQ mass spectrometer. As previously mentioned in chapter 1, this modification allows the study of bimolecular reactions.

The IrPhen complex was synthesized using a previously established procedure [111] by refluxing 1:1 equivalents of $IrCl_3$ and 1,10-phenanthroline in absolute ethanol. The solution was refluxed for 2 hours and left to cool to room temperature. The solvent was removed under vacuum. The resulting orange solid (IrPhen) was dissolved in methanol to a concentration of 10^{-5}M. The solution was then injected into the mass spectrometer via the ESI source at a flow rate of 5μL/min, capillary voltage of 6kV, and heated capillary temperature of 275^{0}C. The ionized iridium(III) complex was isolated in the ion trap for an activation time of 500-1000 msec to react with the neutral reagent. As per our modification, the neutral reagent was introduced directly into the ion trap via the helium flow.

In the previous studies, the loss of the mass of an HCl molecule indicated C-H activation.[111] Therefore, to study the site of activation, selectively deuterated alcohols were injected without prior dilution at a rate of 30-60μL/hr into the neutral reagent addition manifold in these studies. The loss of a DCl molecule instead of an HCl molecule would indicate the site of activation (Scheme 1). Iridium has two abundant isotopes, 191(37.3%) and 193(62.7%)[115]. In order to prevent any ambiguity regarding the loss of HCl or DCl (confusion with molecules containing the Cl isotopes of 35 and 37), the lowest isotopomer of the iridium complex, which is not the most abundant, was isolated and allowed to react with the neutral reagents. Thus, the iridium complex is isolated at a m/z of 441 considering the lowest isotopes of Ir, C, N, and Cl.



Scheme 1 Loss of HCl vs loss of DCl to study the site of activation

The selectively deuterated alcohols used for this study are shown below. They were all obtained from commercial sources (CDN isotopes).

1,1-d_2 butyl alcohol

1,1,2,2-d_4 butyl alcohol

1,1,2,2,3,3-d_6 butyl alcohol

4,4,4-d_3 butyl alcohol

Figure 18 Selectively deuterated alcohols used

To better understand the mechanism of C-H activation of the IrPhen complex, theoretical studies were also carried out in Gaussian 09 and Gaussian 16 systems using the M06 functional along with the lanl2dz basis set for Ir and 6-311+G** basis set for the other atoms in the complex. The M06 functional was used since it is dispersion corrected and therefore, more appropriate to model small molecules with non-covalent interactions. Intrinsic Reaction Coordinate (IRC) calculations were carried out to verify that the transition state linked the reactants to the products. The zero-point energy calculations were performed using the M06/QZVP basis set while the thermal enthalpy corrections were obtained from the ECP (lanl2dz)/6-311+G** basis set.

3.1.2 Results & discussion

Studies were carried out with ethanol, 1-propanol, 1-butanol, and 1-pentanol. A loss of HCl was seen with all alcohols except ethanol. This indicates that an alkyl chain of either three or more carbons is needed. This hints at the possibility that the activation needs a gamma carbon. To verify this hypothesis, a reaction was also carried out using 2-propanol. In 2-propanol, we saw no loss of

HCl, indicating no activation has taken place. 2-propanol does not have a gamma carbon but rather two beta carbons, which supports this hypothesis.

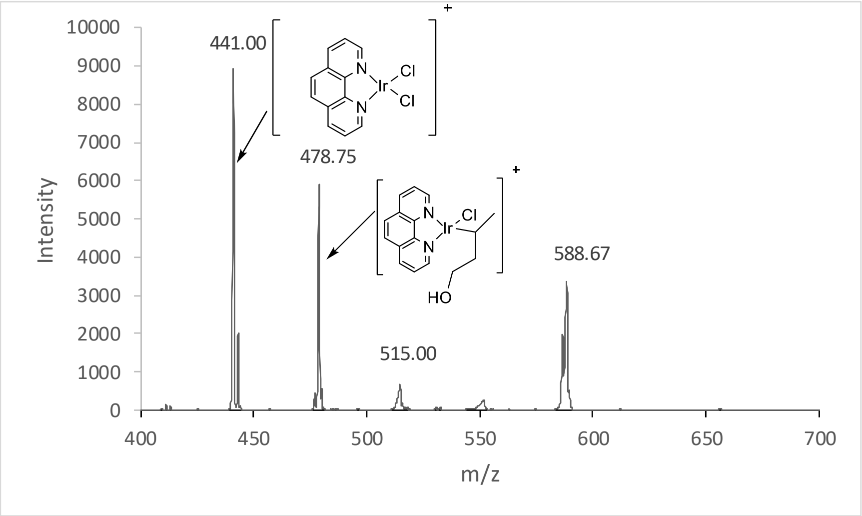
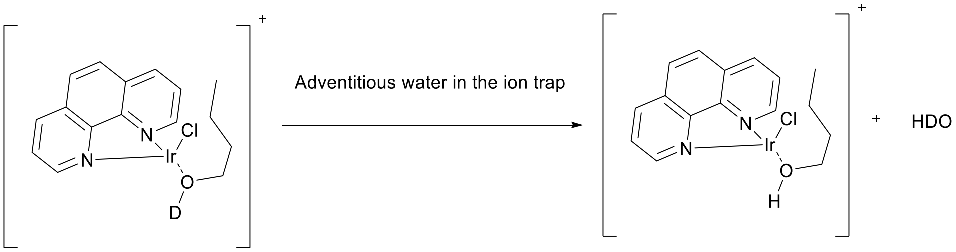


Figure 19 C-H activation of 1-butanol. Peak at 441.00 is the IrPhen complex, peak 478.75 is the C-H activated product bound to the complex through the Ir-C bond, peak 515.00 is the adduct of the 1-butanol molecule and peak 588.67 is an adduct of two 1-butanol molecules. The activation is shown at the gamma carbon but could also occur on the delta carbon.

To determine the position at which C-H activation takes place, studies were carried out with a series of selectively deuterated 1-butanols. Studies carried out with 1-butanol-OD showed a H/D exchange taking place between the acidic deuterium of the iridium-1-butanol complex and the adventitious water present in the ion trap as shown by the equation below. This led to the appearance of DCl loss, but the observed DCl loss is likely all driven by a two-step process of H/D exchange followed by HCl loss. The exchange process was verified by using a series of samples with varying concentrations of 1-butanol-OD in deuterium oxide and comparing the relative intensity of the 1-butanol H/D exchange peak. With high deuterium oxide concentrations, the H/D exchange was suppressed. The mechanism of the H/D exchange is unknown, but potentially involves deprotonation/reprotonation of the alcohol adduct by water.



Scheme 2 H/D exchange of 1-butanol-OD with adventitious water in the ion trap

Studies with 1,1-d_2 1-butanol and 1,1,2,2-d_4 1-butanol show C-H activation rather than C-D activation. This indicates that no activation takes place on either the alpha or beta carbons. A reaction was then carried out with 1,1,2,2,3,3-d_6 1-butanol, which showed the loss of both HCl as well as DCl. The presence of both C-H and C-D activation would indicate that activation is taking place on both the gamma as well as the delta carbon. To confirm this, a reaction was also done with 4,4,4-d_3 1-butanol, which resulted in the loss of both HCl and DCl molecules. This confirmed that the activation does take place on both gamma and delta carbons. The product distribution of C-H vs. C-D activation for each deuterated 1-butanol is shown below.

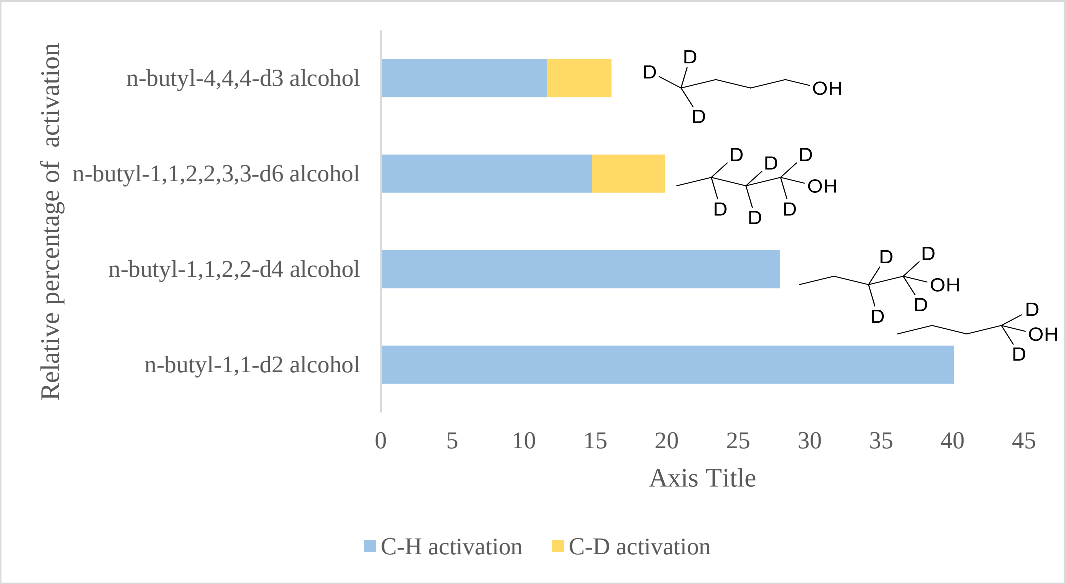


Figure 20 C-H vs C-D activation of 1-butanol

The product distribution we observe for the gamma and delta positions are impacted by kinetic isotope effects (KIE), which alter the intrinsic selectivity. Determining the KIE value would indicate the true product distribution.

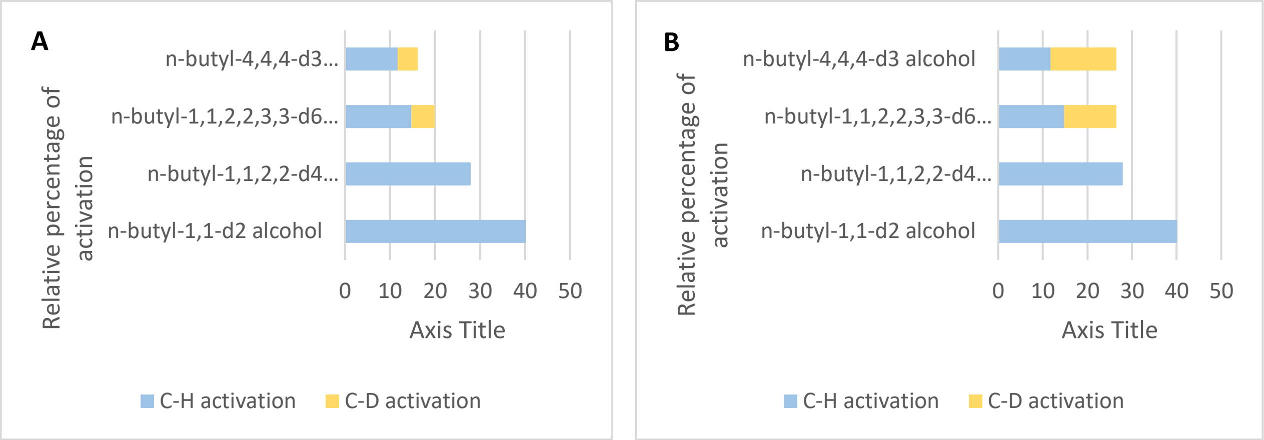


Figure 21 A) production distribution of C-H vs C-D. B) product distribution after taking the isotope effects into account

The KIE studies were carried out by measuring the relative intensity of a C-H and C-D activation for a 50:50 mixture of 1,1,2,2,3,3-d_6 1-butanol and 4,4,4-d_3 1-butanol. The products of C-H and C-D activation in each of these substrates have distinct m/z values and therefore the relative rates of C-H and C-D activation at the gamma and delta carbons can be determined. The results suggest that C-H activation is preferred at the delta carbon by about 54%. The analysis resulted in a KIE value of 2.3 for the gamma position and 3.3 for the delta position, which are consistent with a C-H cleavage in the rate-determining step. These analyses do not consider the impact of vicinal deuteration on the isotope effects. The high relative rate for 1,1-d_2-butanol might suggest that secondary deuterium isotope effects on vicinal carbons may slow the rate, but there is added uncertainty in this measurement because it involves comparing separate experiments rather than a mixture of substrates in a single experiment.

DFT calculations show that C-H activation for the gamma and delta positions are both very exothermic, with the delta product being 1.4 kcal/mol more stable than the gamma product. The enthalpies of the transition states of both the gamma and delta activation are below the entrance channel with the transition state for delta activation being preferred by 3.1 kcal/mol over the transition state for gamma activation. This preference for delta is consistent with the experimental results, but the magnitude of the preference would suggest a greater preference for delta; however, with barriers below the entrance channel, reaction dynamics might also play a role.

Table 1 Calculated enthalpies for activation of the gamma and delta positions in 1-butanol at the 6-311+G** level

Position	Enthalpy of overall reaction (kcal/mol)	Enthalpy of the transition state (kcal/mol)
Gamma position	-33.7	-2.9
Delta position	-35.1	-6.0

The calculations of the transition states showed the formation of a ring structure. The oxygen of the hydroxyl group directs the molecule towards the metal, and positions either the gamma or delta C-H bond in the proximity of the iridium, thus facilitating activation of the bond. The gamma activation forms a five-membered ring while the delta activation forms a six-membered ring, as shown in the structures below.

Ir -C	2.157 Å
C-H	1.704 Å
Ir-Cl	2.48 Å
H-Cl	1.385 Å
Ir-H	1.814 Å
Ir -H-Cl	97°

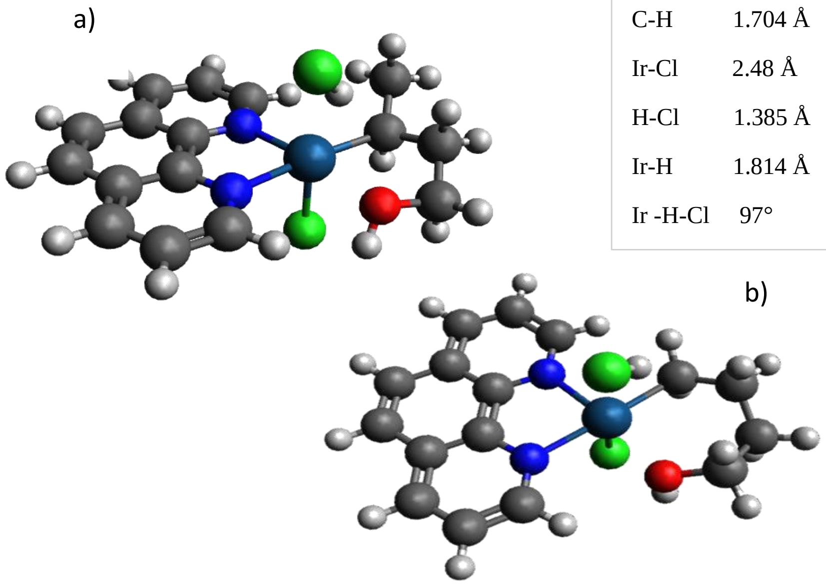


Figure 22 Transition states of a) gamma activation and b) delta activation using the ECP/6-311+G** basis sets. Elements are shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine, and red – oxygen.

The formation of the stable five and six-membered ring structures in the transition state drive the reaction towards either the gamma or delta position. This further explains why no activation is seen on the alpha or beta positions since this would require the formation of three-membered and four-membered ring structures in the transition states. The alpha position offers the weakest of the C-H bonds in 1-butanol. Due to the high strain and undesirable interactions in three and four-membered rings needed in the transition states, the activations of these positions would be energetically unfavorable.

The transition state shows that the C-H activation occurs through a concerted mechanism involving the formation of the Ir-C bond, breaking of the C-H bond, breaking of the Ir-Cl bond as well as the formation of the H-Cl bond. The distance between the Ir and activated hydrogen in the transition state is 1.81Å, and the Ir-H-C angle is 97°. This suggests an agostic interaction existing between the iridium and hydrogen in the complex leading to the transition state. An agostic interaction is a 3-center 2-electron interaction between a metal and a C-H bond. [21] This interaction weakens the inert C-H bond and thus behaves as a metal-mediated polarization, making the C-H bond more reactive.

The 5-membered and 6-membered ring transition structures for the gamma and delta activation are both energetically viable. However, the steric effects due to the proximity of the delta methyl group to the phenanthroline hydrogen in the 5-membered ring transition state could explain why a slightly higher preference is seen for the delta position compared to the gamma.

3.2 Studying the selectivity of C-H activation in ethers

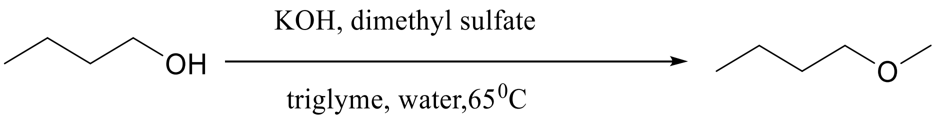
Ethers are molecules with inherently low reactivity[109] and are thus commonly used as protecting groups in synthesis. The direct functionalization of the unactivated C-H bonds in ethers could, therefore, be very useful in designing new ways to modify and introduce complexity to molecules. However, due to their low reactivity, C-H activation of alcohols and ethers did not become a significant field of interest until the 1990s. Radical mediated alkylation, metal carbenoid insertion, and cross dehydrogenative coupling (CDC) reactions are the most common methods of ether functionalization. [117] Most studies carried out thus far have shown activation of the alpha and beta bonds in ethers.[104,109,118,119] This is made possible due to the stabilization of the positive charge on the alpha carbon by the oxygen atom as well as pathways to form 1,2-alkenes.[117,119]

Since the O-H groups of alcohols are commonly protected by methylation during synthesis, a study of the selectivity of remote C-H activation of methyl ethers could lead to novel synthetic strategies.

3.2.1 Methodology

3.2.1.1 Synthesis of selectively deuterated 1-methoxybutane

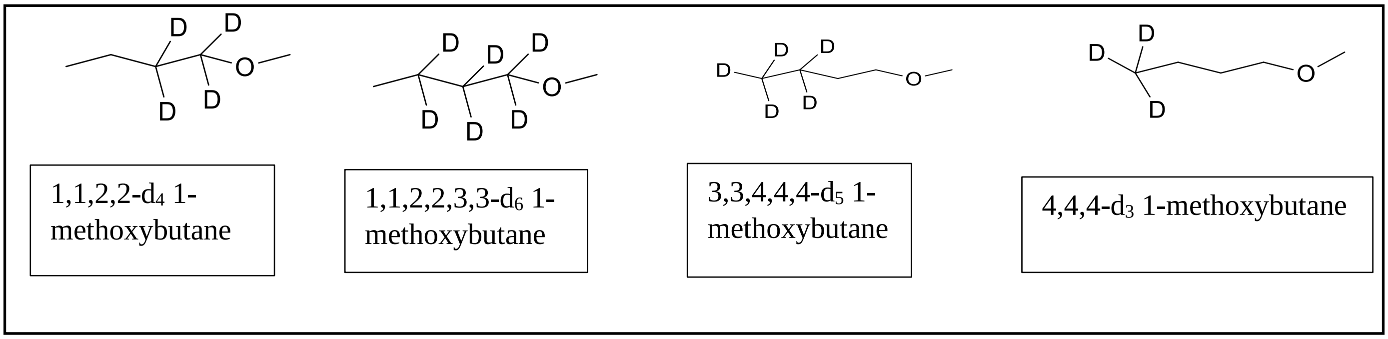
The selectively deuterated 1-methoxybutane molecules were synthesized from the corresponding alcohols following the method by Achet et al. [120]



Scheme 3 Synthesis of selectively deuterated 1-1-methoxybutane

A mixture of the deuterated n-butyl alcohol (960µl, 9.95mmol), triglyme (10.5mL, 0.058mol), and DI water (1670µl, 0.092mol) was heated while stirring for 10 minutes in an oil bath at a temperature of 65^0C. Crushed KOH (2.1g, 0.037mol) was added to the stirred solution. Dimethyl sulfate (996µl, 0.01mol) was introduced to this mixture at a rate of 1.8mL/hr. Once all the dimethyl sulfate was added, the reaction mixture was refluxed for 1.5 hours. The solution was left to cool to room temperature, and the unreacted KOH was filtered out. The filtrate was distilled to obtain the ether at a boiling point of 71^0C.

The following deuterated 1-methoxybutanes were synthesized and used for selectivity studies. The site of activation and KIE were determined using the methodology described in section 3.1.1. DFT calculations were also carried out to further understand the mechanism.



1,1,2,2-d_4 1-methoxybutane

1,1,2,2,3,3-d_6 1-methoxybutane

3,3,4,4,4-d_5 1-methoxybutane

4,4,4-d_3 1-methoxybutane

Figure 23 Selectively deuterated 1-methoxybutane

3.2.2 Results and discussion

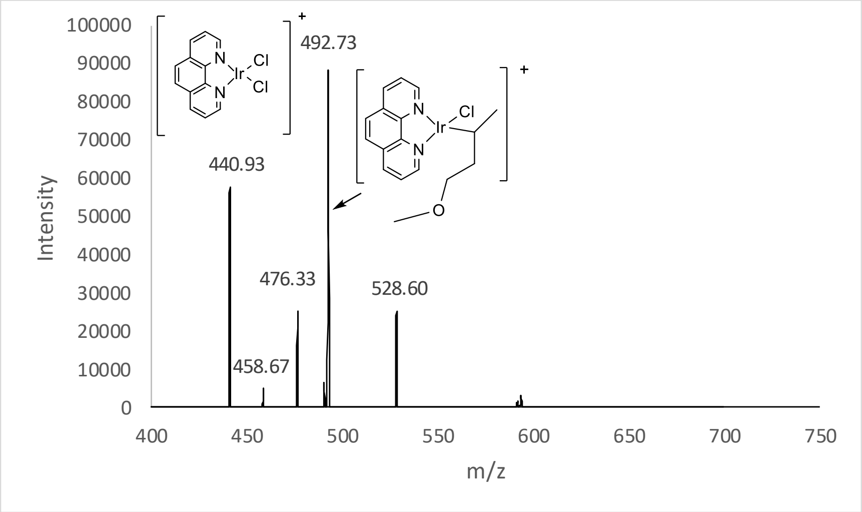


Figure 24 C-H activation of 1-methoxybutane. Peaks at 458.67 and 476.33 are adducts of one and two water molecules respectively. Peak 492.73 is the C-H activated product with loss of HCl and peak 528.6 is the adduct of 1-methoxybutane

Studies were carried out with the synthesized selectively deuterated 1-methoxybutane substrates. The reaction with 1,1,2,2-d_4 -methoxybutane showed no C-D activation, indicating that activation does not happen on the alpha or beta carbons. The reaction with 3,3,4,4,4-d_5-methoxybutane showed a loss of DCl, indicating activation on either gamma or delta activation. To confirm if it was selective activation on either the gamma or delta carbon, studies were also carried out with 4,4,4-d_3-methoxybutane. This did not show any significant C-D activation, which would indicate selective activation on the gamma carbon. To confirm the result, a reaction was also studied with 1,1,2,2,3,3-d_6-methoxybutane. This showed C-D activation as well as a small amount of C-H activation, as seen in the product distributions below. It is important to note that in this experiment the gamma position is at a disadvantage due to the deuterium isotope effect.

More accurate regioselectivities and the KIE values of the gamma and delta positions were determined by considering the relative rates in a mixture of 4,4,4-d_3-methoxybutane and 1,1,2,2,3,3-d_6-methoxybutane. The data indicates that 96% of the activation occurs at the gamma position. The comparison of C-H vs. C-D activation in this experiment led to a KIE value of 2.5 for the gamma position. The KIE for the delta position could not be determined with a high certainty due to the ^{13}C isotopomer of the gamma C-D activation having considerable overlap with the peak for the C-H activation of the delta position.

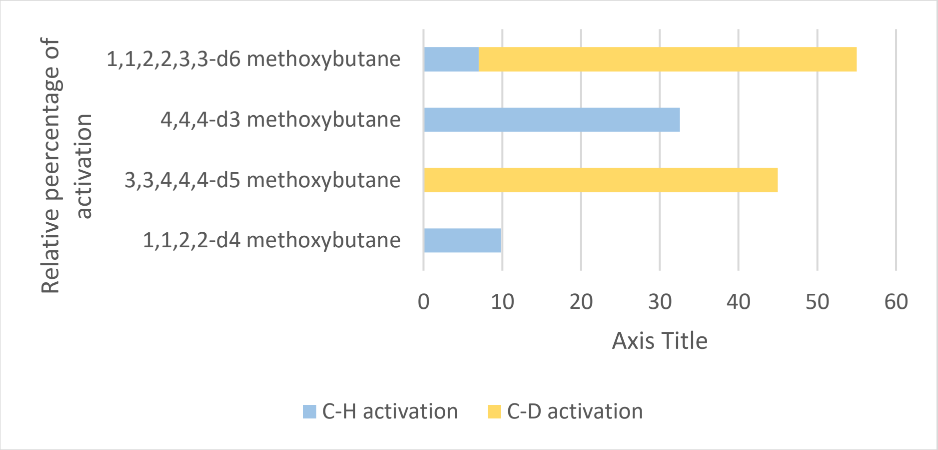


Figure 25 C-H vs C-D activation of 1-methoxybutane

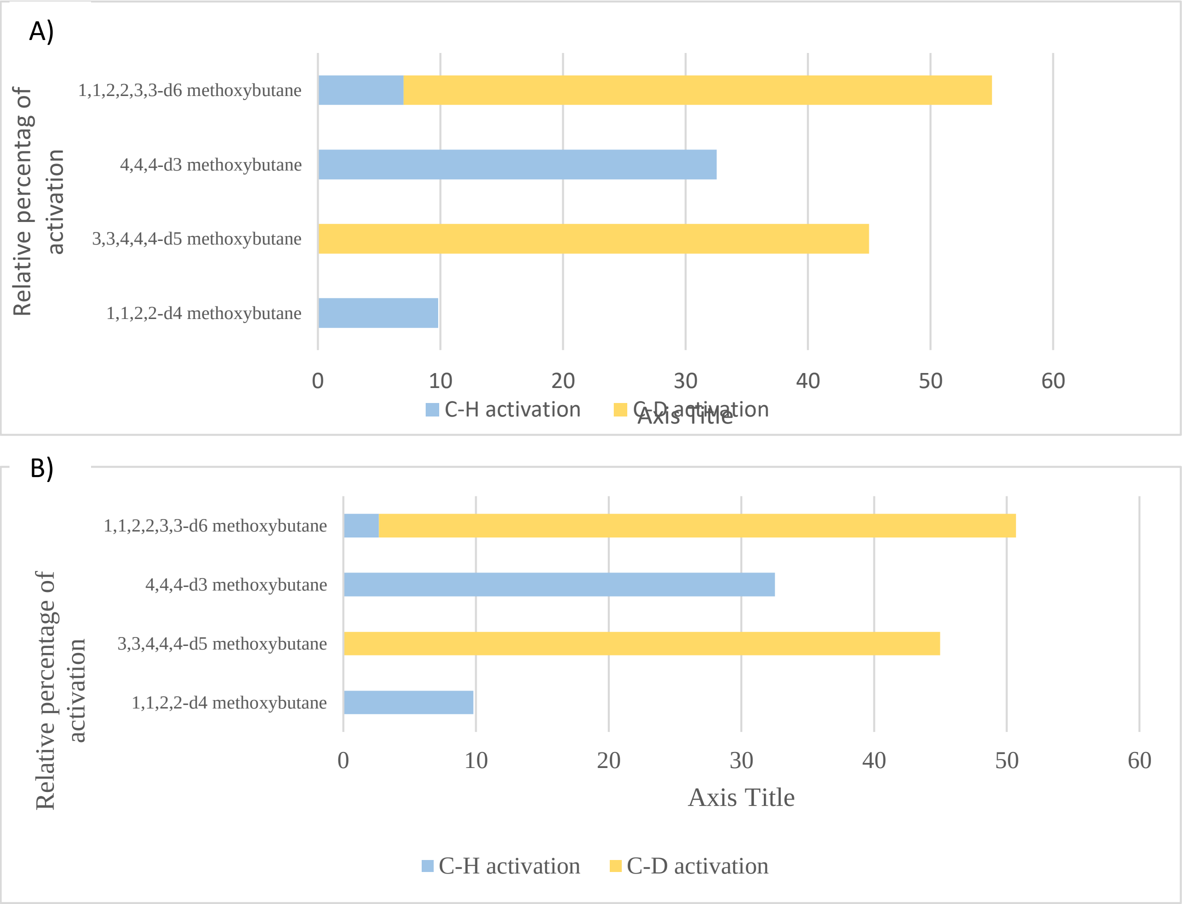


Figure 26 A) production distribution of C-H vs C-D. B) product distribution after taking the isotope effects into account

This would explain why delta activation is only seen when studying 1,1,2,2,3,3-d_6 -methoxybutane and not 4,4,4-d_3-methoxybutane. In the latter, the KIE at the delta position would shift the balance almost completely to gamma activation. The isotope effect on gamma due to the deuteration slows the reaction, making the hydrogen activation on the delta carbon slightly more competitive. Even though slight delta activation is seen, the IrPhen complex shows very good selectivity for the gamma position (96%) in 1-methoxybutane. This is in contrast to what has been observed in many other catalytic complexes so far where either alpha or beta activation of ethers are the most common pathways[24].

DFT calculations were carried out to further explain the nearly selective activation of gamma carbon in 1-methoxybutane. Similar to the alcohols, the reaction enthalpies for both gamma and delta activation show that these are exothermic processes.

Table 2 Calculated enthalpies for activation of the gamma and delta positions in 1-methoxybutane at the 6-311+G** level

Products	**Enthalpy of overall reaction(kcal/mol)**	**Enthalpy of transition state(kcal/mol)**
Activation on the gamma position	-33.5	-26.7
Activation on the delta position	-29.6	-25.7

Therefore, to understand the preference for gamma over delta activation, the transition states were modeled as per section 3.1.1. The structures of the transition state for C-H activation of the gamma and delta positions in 1-methoxybutane are shown below. IRC calculations were done to verify the transition states.

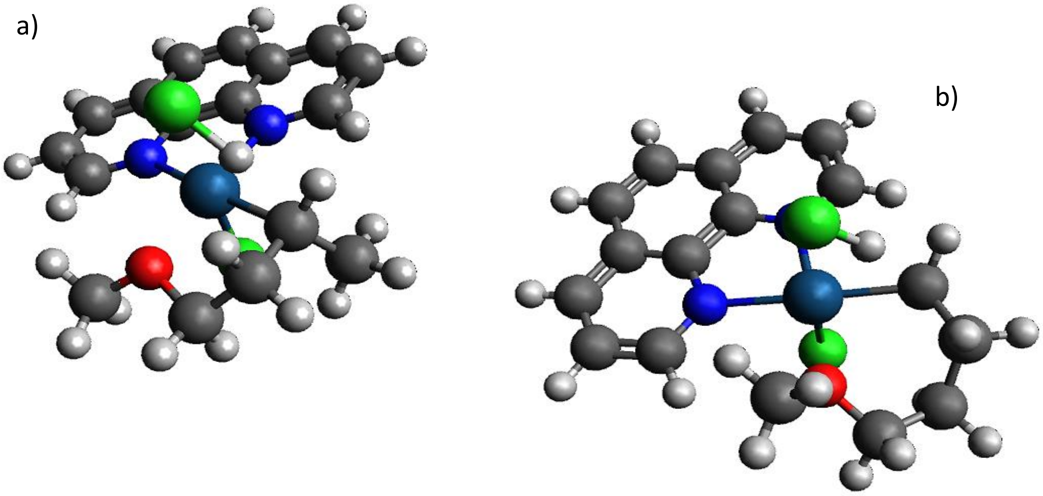


Figure 27 Transition states of a) gamma activation and b) delta activation using the ECP/6-311+G** basis sets. Elements shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine and red – oxygen.

Similar to the transition states of 1-butanol, the 1-methoxybutane, ring structures are formed in the transition states. The gamma activation forms a 5-membered ring while the delta activation forms a 6-membered ring. However, unlike in 1-butanol in which delta activation was preferred, gamma activation is experimentally preferred in 1-methoxybutane. It is also preferred in the computational studies by 1.1 kcal/mol. This can be due to two factors that were seen in theoretical studies. The major factor which encourages gamma activation is the position of the methoxy group. The presence of the methyl group in 1-methoxybutane tilts the preference to form a 5-membered ring. In the 5-membered ring for the gamma activation, the butyl group is in an almost perfect anti-relationship to the methoxy group. The dihedral angle between the methoxy group and the butyl group is 174.6°. The 6-membered ring for delta activation does have somewhat of an anti-configuration as well. However, the dihedral angle, in this case, is only 148.2°. This suggests significant torsional strain. The configuration is not nearly optimum to minimize unfavorable eclipsing interactions. This would make the delta conformation energetically unfavorable compared to the gamma conformation and would explain the preference of gamma over the delta.

The second factor that affects this selectivity is the loss of steric hindrance in the transition state for the activation of the gamma position in 1-methoxybutane. The preference for delta in 1-butanol was due to the steric effects present in the ring of gamma activation by the delta methyl group. In 1-methoxybutane, the delta methyl group is positioned below the plane, away from the H-Cl formation sphere. This would mitigate any steric effects associated with the C-H activation making the activation at the gamma carbon favorable.

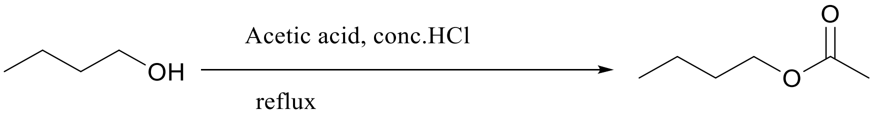
3.3 Selectivity studies of C-H activation with esters

Due to the higher selectivity seen with the ethers, studies were also carried out with esters. The rationale behind this was since replacing the hydroxy group on 1-butanol with a methoxy group increased the selectivity, replacing it with a bulkier group could manipulate the selectivity even further. Esters are biologically and synthetically significant functional groups[121] that are additionally used as protecting groups in organic synthesis[122], and therefore selective activation of these molecules could contribute towards efficient synthetic strategies. Many studies have been carried out with various transition metal systems such as Rh, Pd, and Ir to study the C-H functionalization of aromatic and aliphatic esters. These studies showed activation on alpha, beta, and gamma carbons.[121,123,124] The ester group has a carbonyl oxygen as well as an alkoxy oxygen and therefore, the site of activation is dependent on the binding oxygen of the ester. The binding oxygen would position a particular C-H bond in the proximity of the metal and thus dictates the site of activation.

3.3.1 Methodology

3.3.1.1 Synthesis of deuterated butyl acetate

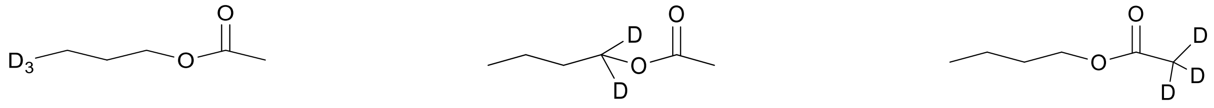
The deuterated esters were synthesized using the Fischer esterification method.



Scheme 4 Synthesis of selectively deuterated butylacetate

Selectively deuterated n-butyl alcohol (610 µL, 6.67 mmol), acetic acid (770 µL, 13.48 mmol) and concentrated HCl (4 mL) were refluxed for 2 hours. The reaction was then cooled to room temperature, and the two layers were separated. The remaining acetic acid was extracted into saturated $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4. The ester was separated from the alcohol through distillation.

The selectivity studies and DFT calculations were performed according to the methodology in 4.1.



4,4,4-d_3 butyl acetate

1,1-d_2 butyl acetate

1,1,1-d_3 butyl acetate

Figure 28 Deuterated butyl acetate molecules which were studied

3.3.2 Results & discussion

To study the site of activation, reactions were carried out with the selectively deuterated butyl acetate. Delta or gamma activation was anticipated due to the similar length of the alkyl chain to 1-butanol and 1-methoxybutane. However, the 4,4,4-d_3 butyl acetate showed only C-H activation indicating that activation does not take place on the delta carbon. Next, studies were carried out with 1,1-d_2 butyl acetate and 1’,1’,1’-d_3 butyl acetate. The reaction with 1,1-d_2 butyl acetate showed C-D activation, while 1,1,1-d_3 butyl acetate showed C-H activation. This indicates that the IrPhen complex can selectively activate the alpha positions of butyl acetate.

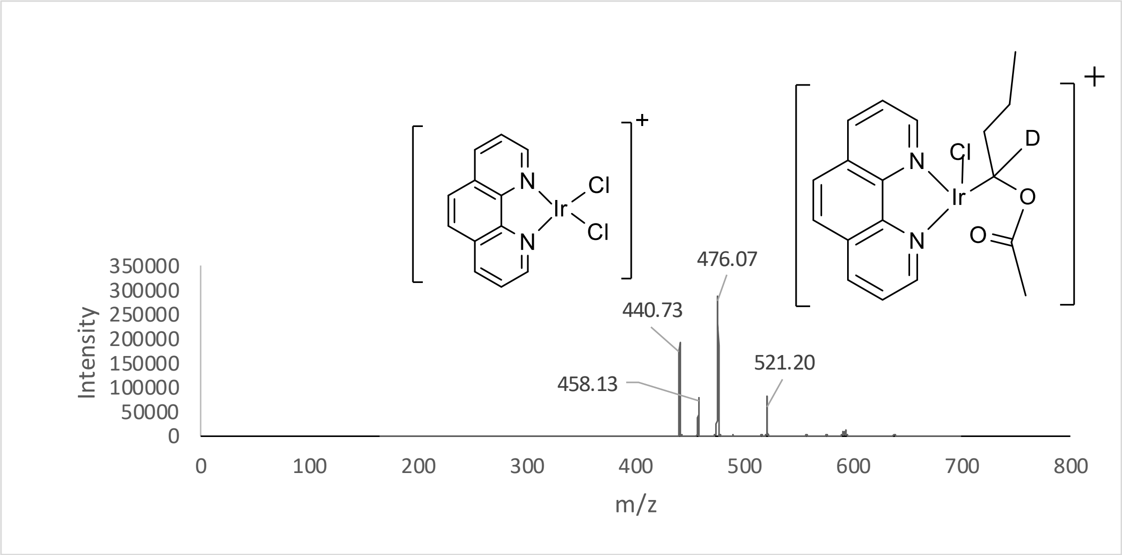


Figure 29 Mass spectrum of the reaction with 1,1-d2 butyl acetate. Peaks at 458.13 and 476.07 are of one and two water molecules, respectively. 521.20 is the C-D activation corresponding to a loss of DCl

Computational modeling showed the formation of the five-membered ring structure involving the carbonyl oxygen in the transition state, enabling activation on the alpha carbon.

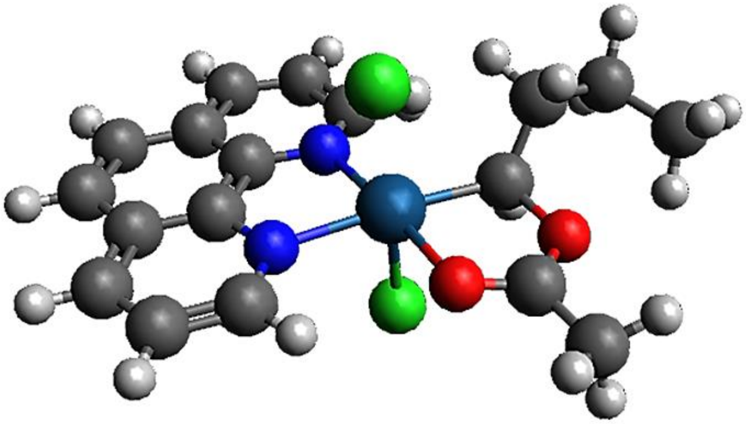
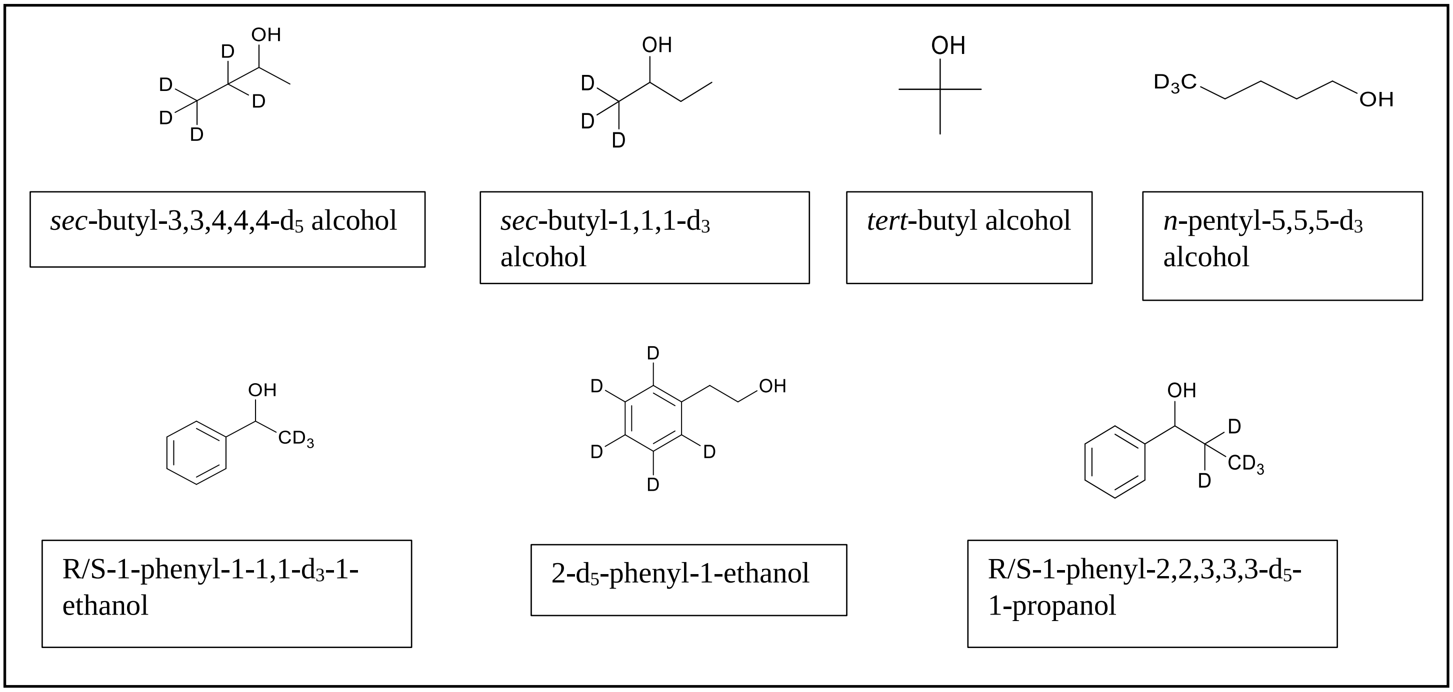


Figure 30 Transition state for alpha activation of butyl acetate using the ECP/6-311+G** basis sets. Elements shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine and red – oxygen.

The transition state shows that the carbonyl oxygen behaves as the directing group rather than the alkoxy oxygen. Binding of the alkoxy oxygen would drive the activation towards the gamma or delta positions, whereas the carbonyl oxygen should drive it towards the alpha and beta positions due to the preference of forming five and six-membered rings. However, we see no activation of the beta carbon. The combination of stabilization of the alpha carbon by the alkoxy oxygen as well as the ability to form a five-membered ring drives the activation selectively towards the alpha carbon.

3.4 Other neutral reagents

In addition to primary alcohols, ethers, and esters, the site of activation was also studied with secondary and tertiary alcohols and 1-phenyl alcohols.



sec-butyl-3,3,4,4,4-d_5 alcohol

sec-butyl-1,1,1-d_3 alcohol

tert-butyl alcohol

n-pentyl-5,5,5-d_3 alcohol

R/S-1-phenyl-1-1,1-d_3-1-ethanol

2-d_5-phenyl-1-ethanol

R/S-1-phenyl-2,2,3,3,3-d_5-1-propanol

Figure 31 Other neutral reagents used for selectivity studies

The reaction studied with *sec*-butyl-3,3,4,4,4-d_5 alcohol showed C-D activation, while *sec*-butyl-1,1,1-d_3 alcohol showed C-H activation. This suggests that the IrPhen complex activates the gamma carbon in this secondary alcohol because if activation occurred at the beta carbon, one would expect some C-H activation in *sec*-butyl-3,3,4,4,4-d_5 alcohol, especially given the expected isotope effect. As shown in the previous studies with the other neutral reagents, the driving force of this activation is the formation of the stable five and six-membered rings. No reaction was seen with *tert*-butyl alcohol since a reaction at the beta carbon would result in a much less stable 4-membered ring in the transition state. The dependence of the stability of the ring in the transition state was further shown with 1-pentanol. Studies carried out with n-pentyl-5,5,5-d_3 alcohol showed only C-H activation. The activation of the omega carbon in pentanol would require the formation of a seven-membered ring. Due to the unfavorable interactions present in a seven-membered ring, the transition state would be high in energy, making the omega activation less likely.

Studies with 1-phenyl-1-ethanol also showed C-H activation. To determine the site of activation, 1-phenyl-2,2,2-d_3-1-ethanol and 2-d_5-phenyl-1-ethanol were studied. Both these reactions showed activation on the aromatic ring. Since the 1-phenylethanol does not possess an alkyl chain with a gamma carbon, no activation of the chain was expected. To see if there is a preference between the aromatic ring vs. an alkyl chain, 1-phenyl-1-d_5-propanol was synthesized following the procedure of Heimark et al.[125] Since the alkyl chain has a gamma carbon present it would compete for activation. The results showed both C-H and C-D activation, indicating activation on both the ring and the alkyl chain. The assumption here is that the ortho hydrogen on the ring is the site of activation because it would lead to a 5-membered ring transition state whereas the meta position would not be feasible because the required ring would not be possible given the anti-juncture imposed by the phenyl ring.

3.5 Summary

The IrPhen complex can selectively activate commonly used precursors in organic syntheses such as alcohols, ethers, and esters. The regioselectivity of the complex was studied using selectively deuterated neutral reagents where the loss of DCl would indicate the site of activation. The results showed that the IrPhen complex activates the gamma and delta bonds in 1-butanol, is highly selective for the gamma bond in 1-methoxybutane, and selectively activates the alpha bond in butyl acetate. Theoretical studies showed that the driving force of this selectivity is the ability of the substrate to form either five-membered or six-membered rings in the transition state. The directing group anchors the substrate to iridium and drives the formation of the ring. This hypothesis of ring driven selectivity was also proven with other substrates such as secondary alcohols and 1-phenyl alcohols.

3.6 Conclusion

The study with various organic substrates such as alcohols, ethers, and esters show that the IrPhen complex can be used as a potential catalyst for C-H activation. Since the selectivity of activation is determined by the positioning of a specific carbon-hydrogen bond by the directing group, the selectivity of this activation can be tuned by tuning the directing group of the substrate. However, the regioselectivity is very sensitive to subtle features in the transition state as evidenced by the differing regioselectivity of 1-butanol and 1-methoxybutane.

Chapter 4

4.0 Studying the ligand effect of the Ir(III) complex on C-H activation

During the past few decades, finding catalysts that can selectively activate C-H bonds has been of great importance.[102,113] Even though many transition metal catalysts are used in the industry, constant work is being done to improve the selectivity, reactivity, and turnover number (TON) of these catalysts. The selectivity and reactivity of catalytic complexes can be tuned using two approaches.[126]

1. Substrate control – Changing the directing group and the proximity of the directing group to the C-H bond in the molecule, to change the selectivity.
2. Catalyst control – Change the environment of the metal to modify the reactivity and selectivity.

The catalyst control approach requires the manipulation of the ligand scaffold to manipulate the reactivity of the ligated metal. Organometallic complexes are formed by the bonding of the empty d-orbitals of the metal with the atomic orbitals of the ligand, affecting the electronic properties of the metal.[127] The catalytic properties of the complex as an entity depends on the metal, and its surrounding ligands.[128] Since the bonding characteristics of each ligand is different, studies have been carried out to determine the ligand effect in C-H activation reactions.[98,113,129,130]

The approach for tuning the metal environment is to modify the catalyst to create a significant electronic or steric bias towards the desired pathway.[126] The studies carried out so far have shown that ligand effects can impact substrate scope, reaction rate, as well as catalyst turnover in the condensed phase.[131] Many theoretical studies, as well as studies in the gas-phase, have been done to explore various ligand effects and to help understand how these affect the reaction mechanism and selectivity.[132,133] Even though the studies carried out in the gas-phase do not directly represent the condensed-phase, in which the complexes are completely saturated by either ligands or solvent molecules, they can give a highly controlled view of the role of the ligand in a mechanism, without the competing effects of solvation dynamics seen in the condensed phase.[36,134] Most importantly, the gas-phase studies can link a specific ligation scheme to reactivity, something that is not always possible in the condensed phase where multiple ligation schemes maybe present in a dynamic equilibrium. Studying the role the ligand plays in the activation of the bonds will help guide the selection of catalysts for a specific purpose as well as the design of new effective catalysts.[130]

The IrPhen complex studied in the first project has two types of ligands which may affect its reactivity.

1. The chelating phenanthroline ligand
2. The anionic chloride ligand

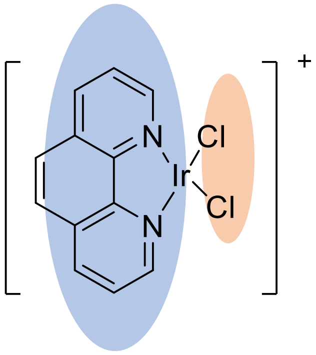


Figure 32 The two types of ligands in the IrPhen complex.1.) Chelating ligand in blue 2.) anionic ligand in orange

The hypothesis is that by changing the ligands of the iridium(III) complex, we can manipulate the selectivity of C-H activation towards our model, deuterium-labeled substrates: 1-butanol, 1-methoxybutane, and butyl acetate. Along with studying the regioselectivity of these reactions with the alcohol, ether, and ester, reactions were also carried out with other neutral reagents to study the scope of reactivity of these new complexes. Studies were done with butylamine, cyclohexylamine, tripropylamine, toluene, ethylbenzene, acetone, bromobutane and bromopropane. These neutral reagents showed C-H activation with the original IrPhen complex studied and therefore were selected for studies with the new iridium(III) complexes. However, none of the newly synthesized iridium complexes demonstrated C-H activation with these substrates.

4.1 Methodology

The regioselectivity and DFT studies were carried out according to the methodology described in section 3.1.1. A series of iridium(III) complexes were synthesized by changing either the chelating phenanthroline ligand or the anionic chloride ligand. The series of complexes studied for this chapter is shown below:

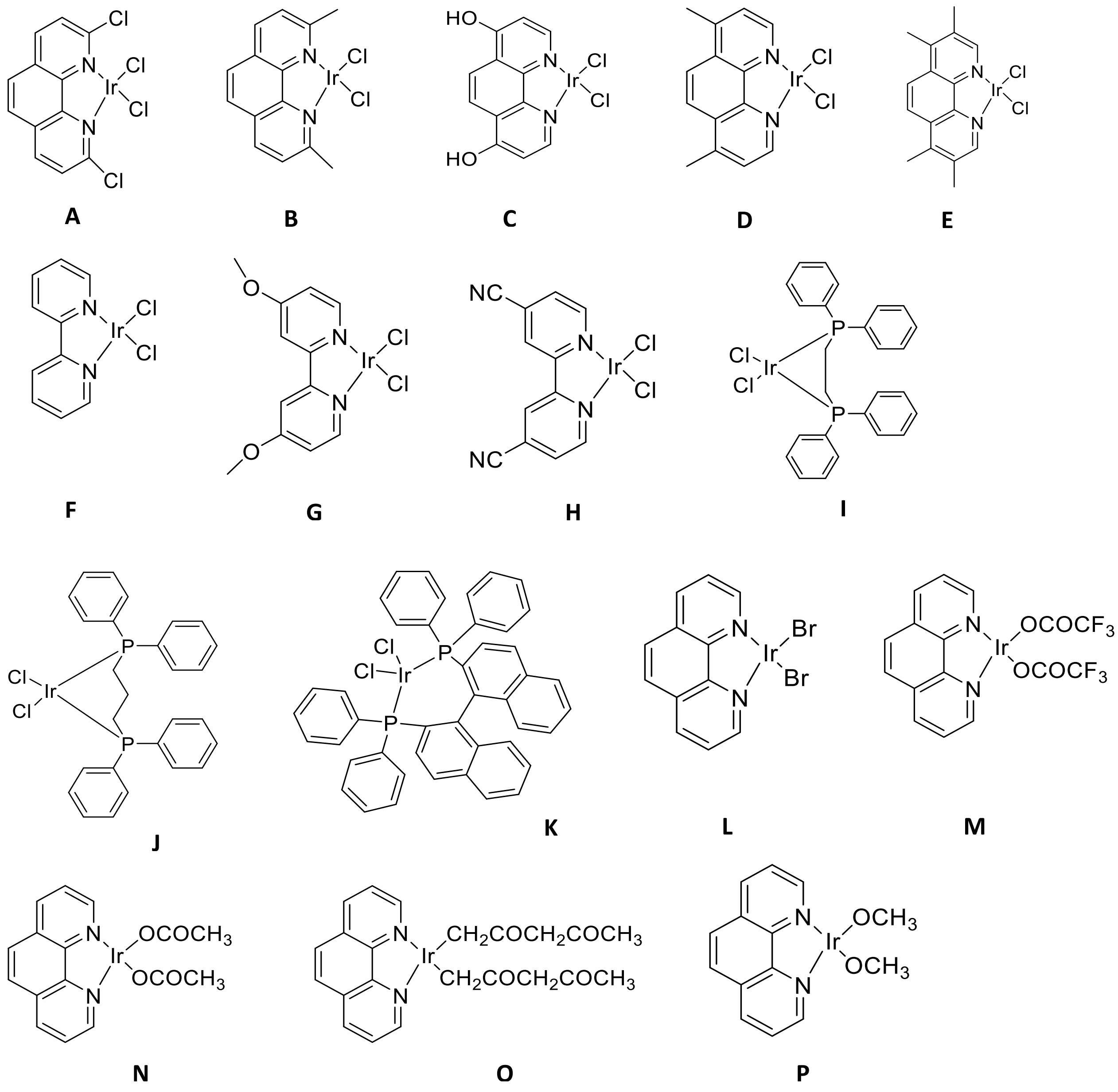
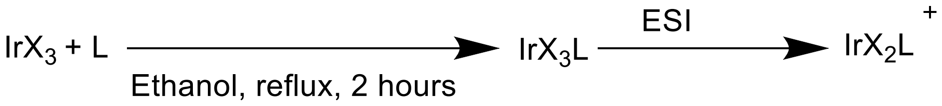


Figure33 Iridium(III) complexes studied to determine the ligand effect on selectivity

4.1.1 Synthesis of iridium(III) complexes

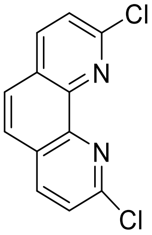
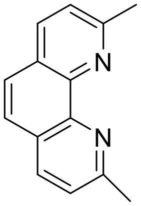
The iridium(III) complexes were synthesized by refluxing equivalent amounts of the iridium(III) salt (1 *10^{-5} mol) with the chelating ligand ((1 *10^{-5} mol) in ethanol (10 mL) for two hours. The solvent was removed under reduced pressure, and the resulting solid was dissolved in methanol and diluted prior to introduction into the ion trap.

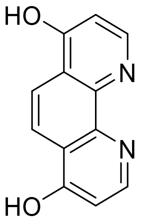
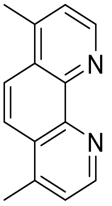
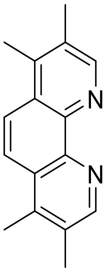
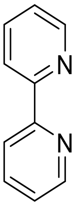
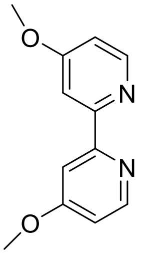
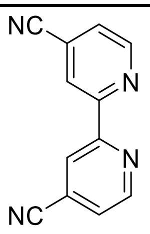


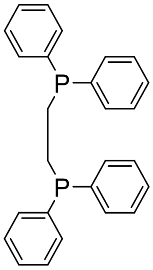
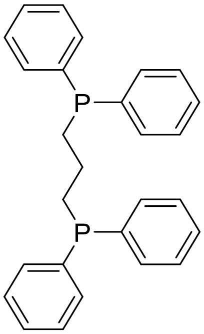
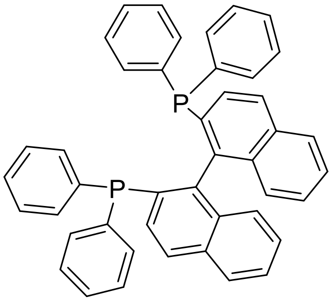
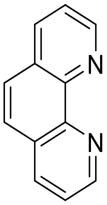
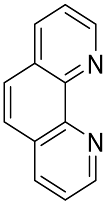
Scheme 3 Synthesis of iridium(III) complexes. L is the chelating ligand and X is the anionic ligand of the iridium salt

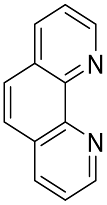
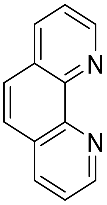
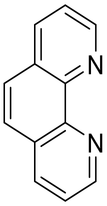
The iridium(III) salt used for complexes A-K was anhydrous iridium(III) chloride. The iridium salts used for complexes M-P were synthesized and then allowed to react with 1,10-phenanthroline as mentioned above. The synthesis of the iridium salts used for L-P is reported in section 4.1.2. The salts and chelating ligands used for the syntheses of complexes A-P are shown in the table below.

Table 3 Combinations of Ir(III) salts and chelating ligands used to synthesize complexes A-P. All complexes were synthesized in 10 mL of ethanol by refluxing for two hours. The salts denoted by the * were synthesized prior to chelation while ** was dehydrated overnight before using for further synthesis

Complex	**IrX_3**	**Chelating ligand**
A	$IrCl_3$	
B	$IrCl_3$	

C	$IrCl_3$	
D	$IrCl_3$	
E	$IrCl_3$	
F	$IrCl_3$	
G	$IrCl_3$	
H	$IrCl_3$	

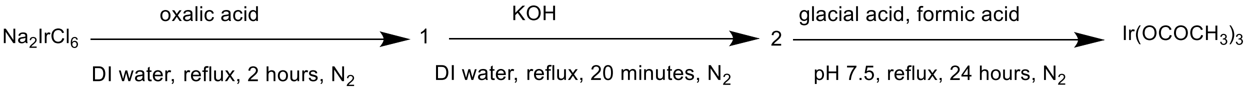
I	$IrCl_3$	
J	$IrCl_3$	
K	$IrCl_3$	
L	$IrBr_3$ **	
M	$Ir(OCOCF_3)_3$ *	

N	$Ir(OCOCH_3)_3$ *	
O	$Ir(CH_2COCH_2COCH_3)_3$	
P	$Ir(OCH_3)_3$ *	

4.1.2 Synthesis of iridium salts

The iridium(III) acetate and iridium(III) trifluoroacetate salts were synthesized according to the method developed by Karch et al. [135]

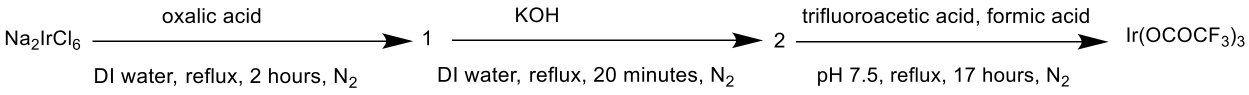
4.1.2.1 Synthesis of iridium(III) acetate



Scheme 4 Synthesis of iridium(III) acetate

Na_2IrCl_6 (123 mg, 0.274 mmol) was dissolved in DI water (3100 µL) under a N_2 atmosphere. A solution of oxalic acid was prepared separately by dissolving oxalic acid (4 mg, 0.004 mmol) in DI water (1000 µL). The oxalic acid solution was then introduced to the Na_2IrCl_6 solution and refluxed for two hours under a N_2 atmosphere. The reduced Ir(III) (**1**) was observed as a brown suspension. To form $Ir(OH)_3$, a 2M KOH solution (1450 µL, 2.58 mmol)was added to the reaction mixture and refluxed for a further 20 minutes. This resulted in a blackish violet suspension (**2**). The mixture was cooled to room temperature, and the pH was adjusted to 7.5 using 50% acetic acid in water. To this solution, glacial acetic acid (1000 µL, 17.4 mmol) and formic acid (500 µL, 10 mmol) were added and refluxed under N_2 atmosphere for 24 hours. The solution was then filtered, and the solvent was removed under reduced pressure. The final iridium(III) acetate was obtained as a bluish-green solid and used without further purification.

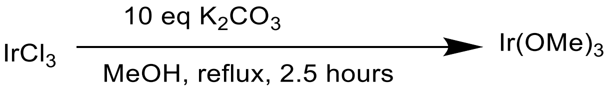
4.1.2.2 Synthesis of iridium(III) trifluoroacetate



Scheme 5 Synthesis of iridium(III) tri(trifluoroacetate)

Na_2IrCl_6 (123 mg, 0.274 mmol) was dissolved in DI water (300 µL) under N_2 atmosphere. A solution of oxalic acid was prepared by dissolving oxalic acid (15.16 mg, 0.168 mmol) in DI water (1000 µL). The oxalic acid solution was introduced to the Na_2IrCl_6 solution and refluxed for two hours under a N_2 atmosphere. The reduced Ir(III) (**1**) was observed as a brown suspension. To form $Ir(OH)_3$, a 4M KOH solution (2000 µL, 9 mmol)was added to the reaction mixture and refluxed for a further 20 minutes. This resulted in a blackish violet suspension (**2**). The mixture was cooled to room temperature and the pH was adjusted to 7.5 using 50% acetic acid in water. To this solution, trifluoroacetic acid (1000 µL, 10mmol) and formic acid (500 µL, 10 mmol) were added and refluxed under N_2 atmosphere for 17 hours. The solution was then filtered, and the solvent was removed under reduced pressure. The final iridium(III) trifluoroacetate was obtained as a yellowish-orange solid and used without further purification.

4.1.2.3 Synthesis of iridium(III) methoxide



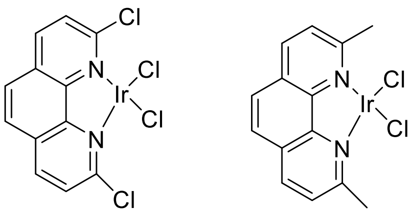
Scheme 6 Synthesis of Ir(III) methoxide salt

$IrCl_3$ (5.72 mg, 0.01 mmol) and 10 molar equivalents of K_2CO_3 (26.48 mg, 0.1 mmol) were refluxed in 10 mL of methanol for two and a half hours. The solid which was formed was filtered and washed with more methanol.

4.2 Results & discussion

4.2.1 Studying the impact of steric effects of ligands on the regioselectivity

The influence of steric effects on the regioselectivity of C-H activation was studied using phenanthroline ligands with substituents in the 2 and 9 positions. The complexes studied were iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride(**A)** and iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride (**B**).



A **B**

Figure 34 Ligands which were used to study the effect of steric influence

These complexes showed no reactivity with any of the model substrates. The feasibility of a reaction is dependent on the exothermicity as well as the activation barrier associated with the transition state. To obtain a better understanding of this lack of reactivity, M06 DFT calculations were carried out using the ECP/6-311+G** basis set. The overall enthalpies of the reactions of these complexes with the three model substrates are given in the table below.

Table 4 Enthalpy values for C-H activation by iridium(III) complexes A & B calculated at the 6-311+G** energy level.

Product	**Enthalpy of C-H activation by A (kcal)**	**Enthalpy of C-H activation by B (kcal)**
1-butanol, gamma C-H	-20.6	-19.0
1-butanol, delta C-H	-20.4	-25.1
1-methoxybutane, gamma C-H	-9.2	-16.1
1-methoxybutane, delta C-H	-15.9	-20.8
butyl acetate, alpha C-H	-13.7	-16.0

The overall reaction enthalpies for the activation of C-H bonds in 1-butanol, 1-methoxybutane, and butyl acetate by complexes **A** and **B** all indicate exothermic reactions, as shown by the enthalpy values above. The barrier for the activation of the delta C-H bond in 1-butanol by complex **A** was calculated to be -21.7 kcal/mol. Nonetheless, the activation barriers which are well below the entrance channel and the exothermic nature of the reaction should result in activation of 1-butanol, 1-methoxybutane, and butyl acetate. However, no C-H activation was seen in the studies which were carried out in the gas phase, although peaks showing adducts of the neutral reagent were present. In order to observe a product of a bimolecular reaction in the ion trap, the rate constant of the reaction needs to be greater 1×10^{-14} cc/molecule/s, but in this case, rapid reactions with adventitious gases in the ion trap would swamp out such a slow reaction.[29] Therefore, even though the reactions are theoretically feasible, the slow kinetic nature of the reaction will prevent any observation of products in these gas-phase studies. If the rate of adduct formation is significantly higher than the rate of activation, the adducts will be the dominant products during the scan. The slower rate of the 2,9-di-substituted phenanthroline complexes can be attributed to the crowded nature of the reaction sphere due to the substituents in the 2 and 9 positions. These substituents conceal the iridium metal, thus hindering the formation of the Ir-C bond. This is evident in the Van der Waals spheres diagram and the transition state of 1-butanol activation of the delta position by 2,9-dichloro-1,10-phenanthroline which are shown below. The transition state is significantly distorted from that seen with IrPhen. As noted in Chapter 3, crowding with the hydrogens at the 2 and 9 positions of phenanthroline was part of the steric factors that drove the regioselectivity so it is not surprising that the methyl and chloro groups at these positions could prove problematic. These results also highlight that these reactions are only observable when the transition state is far below the energy of the reactants. This suggests that there are unfavorable entropic and/or dynamics effects that slow the reaction rate even when the transition state has a very favorable electronic energy relative to the reactants.

These studies indicate that steric bulk at the 2 and 9 position of the phenanthroline can greatly impact the course of the reaction and under the gas phase conditions prevent observable C-H activation reactions. In catalyst design, building bulk at these positions will likely not be productive and other means of altering the regioselectivity would be more promising.

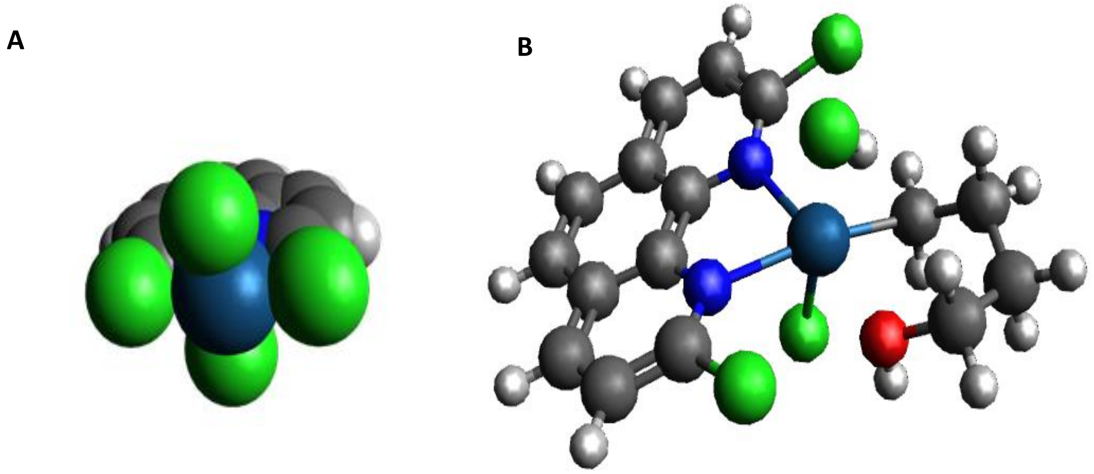
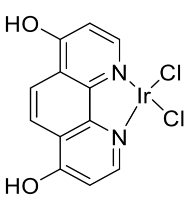


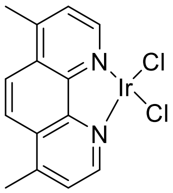
Figure 35 A - Van der Waals sphere display of 2,9-dichloro-1,10-phenanthroline, B - Transition state for delta activation of 1-butanol by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride using the ECP/6-311+G** basis sets. Elements shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine and red – oxygen.

4.2.2 Studying the impact of electronic effects of ligands on the regioselectivity

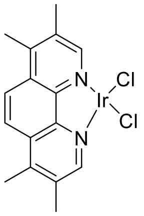
The reactivity of the metal of an organometallic complex can be affected by the overlapping of the molecular orbitals of the ligands. Therefore, substituents on the ligands can alter the electron density of the metal and thereby alter the reactivity of the complex. Phenanthroline ligands with electron-donating substituents were used to study the impact of the electronic effects of the ligand. The following complexes were used for this study and are shown below: iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride (**C**), iridium(III)-4,7-dimethyl-1,10-phenanthroline (**D**) and iridium(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride (**E**). These ligands avoid substituents at the 2 and 9 positions and therefore are free of direct steric effects in the vicinity of the iridium center.



C



D



E

Figure 36 Ligands used to study the impact of electronic effects

Each of these complexes showed C-H activation with the model alcohol, ether, and ester, indicating that the C-H activation process was not extremely dependent on the electronic features of the neutral ligand. The regioselectivity of this activation was studied using the selectively deuterated substrates and the results are shown below alongside the product distribution obtained for the original IrPhen complex for comparison.

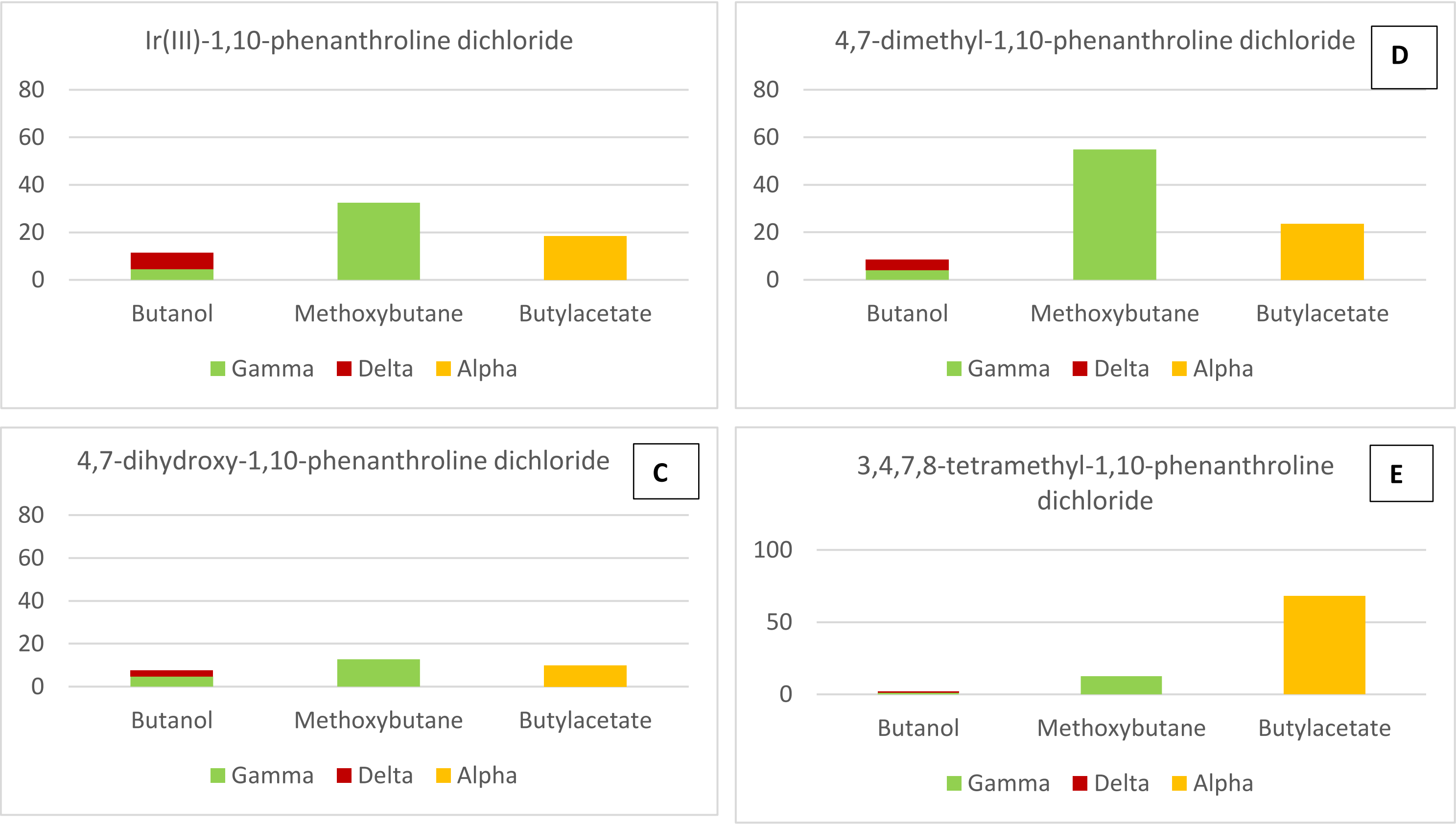


Figure 37 Product distributions of alcohols, ethers and esters with iridium(III) complexes **C, D, and E.** The other products (i.e., missing percentage, are adducts with the substrate or with adventitious species in the ion trap.

The product distributions of complexes **C** and **D** shown above show roughly similar selectivity for the C-H activation of 1-butanol, 1-methoxybutane and butyl acetate as the original IrPhen complex. As seen in the transition state of the delta activation of 1-butanol by the iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride complex, the substituents affecting the electron density of the metal are remote from the reaction sphere and would have little impact on the steric crowding of the transition state. Thus, the regioselectivity of the complex is not greatly affected by the substituents. This explains why we see very subtle changes in the regioselectivity of these complexes despite the large changes in the electron-donating capability of the substituent.

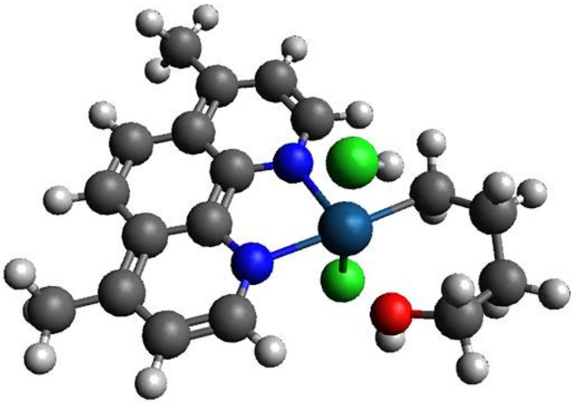


Figure 38 C-H activation of the delta position in 1-butanol by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride using the ECP/6-311+G** basis sets. Elements shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine and red – oxygen.

Table 5 Enthalpies for C-H activation of alcohols, ethers, and esters by **C, D, and E** calculated at the 6-311+G** energy level

Product	**Enthalpy of C-H activation by C (kcal/mol)**	**Enthalpy of C-H activation by D (kcal/mol)**	**Enthalpy of C-H activation by E (kcal/mol)**
1-butanol, gamma C-H	-22.5	-32.9	-24.7
1-butanol, delta C-H	-24.1	-34.2	-26.2

1-methoxybutane, gamma C-H	-26.2	-28.5	-23.3
1-methoxybutane, delta C-H	-18.6	-32.6	-19.1
butyl acetate, alpha C-H	-35.9	- 40.9	-31.3

The reactivities of the different complexes, *i.e.*, **C** vs. **D**, cannot, however, be compared when using our experimental set-up. Due to the relatively high pressure (~1 mtorr of He) in the ion trap, the iridium complexes can form water and methanol adducts with the adventitious water and methanol present. Each complex would have a different affinity towards the water and methanol products and would undergo adduct formation with these products in varying degrees. This is governed by the rate of C-H activation vs. the rate of formation of water or methanol adducts for each complex. These numerous side reactions prohibit the comparison of reaction rates in our system.

Comparisons can be made between each of the substrates with a given complex, but dependent on the assumption that the adventitious gas pressures are constant from experiment to experiment. As a result, those comparisons will have inherent uncertainties. This is acceptable because the major goal of these studies was the regioselectivities, which are obtained in a single experiment for each substrate and are not subject to uncertainty from variations in the pressures of adventitious gases. All complexes show the highest relative reactivity with 1-methoxybutane with the exception of complex **E**, which shows the highest reactivity with butylacetate. The higher electron density on the metal due to the four methyl groups in complex **E** seems to suppress the C-H activation of 1-butanol and 1-methoxybutane. Unlike the gamma and delta position in 1-butanol and 1-

methoxybutane, the alpha position in butylacetate has inherent activation due to the proximity to the oxygen atom. Thus, it might not be as impacted by the electron-rich phenanthroline in complex **E.** Interestingly, this is not as pronounced in complex **C** and that might indicate sigma as well as pi effects from the ligand (i.e., the hydroxy is a pi-donor, but a sigma withdrawing group).

Since all the complexes show similar regioselectivity, only the transition states of the reactions with iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride (**D**) were identified and the activation enthalpies are given in Table 6. We assume a similar trend for the other complexes as well.

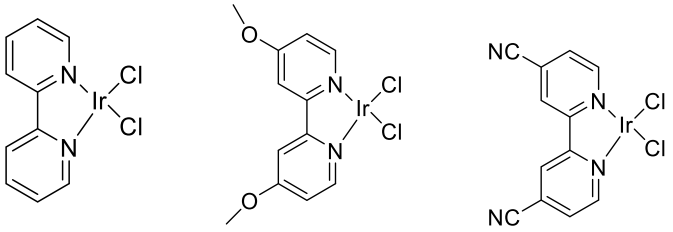
Table 6 Transition state enthalpies for activation by **D** calculated at the 6-311+G** level

Transition state	**Enthalpy of the transition state (Activation barrier) (kcal)**
1-butanol, delta C-H	-29.8
1-butanol, gamma C-H	-27.6
1-methoxybutane, delta C-H	-24.7
1-methoxybutane, gamma C-H	-25.7
butyl acetate, alpha C-H	-24.6

The difference of the transition state values for delta vs gamma are similar to those of the original IrPhen complex, thereby explaining the similar selectivities we see when comparing with IrPhen. In 1-butanol, there is a small preference for the delta C-H bond and in 1-methoxybutane, this switches to a small preference for the gamma C-H bond. This study concludes that electronic effects in the ligand cannot significantly influence the regioselectivity of the reaction. It appears that the inherent regioselectivity is tightly rooted in steric effects. Electronic effects likely impact the rate of the reaction, which could not be effectively evaluated given our experimental conditions.

4.2.3 Studying the impact of the flexibility of ligands on the regioselectivity

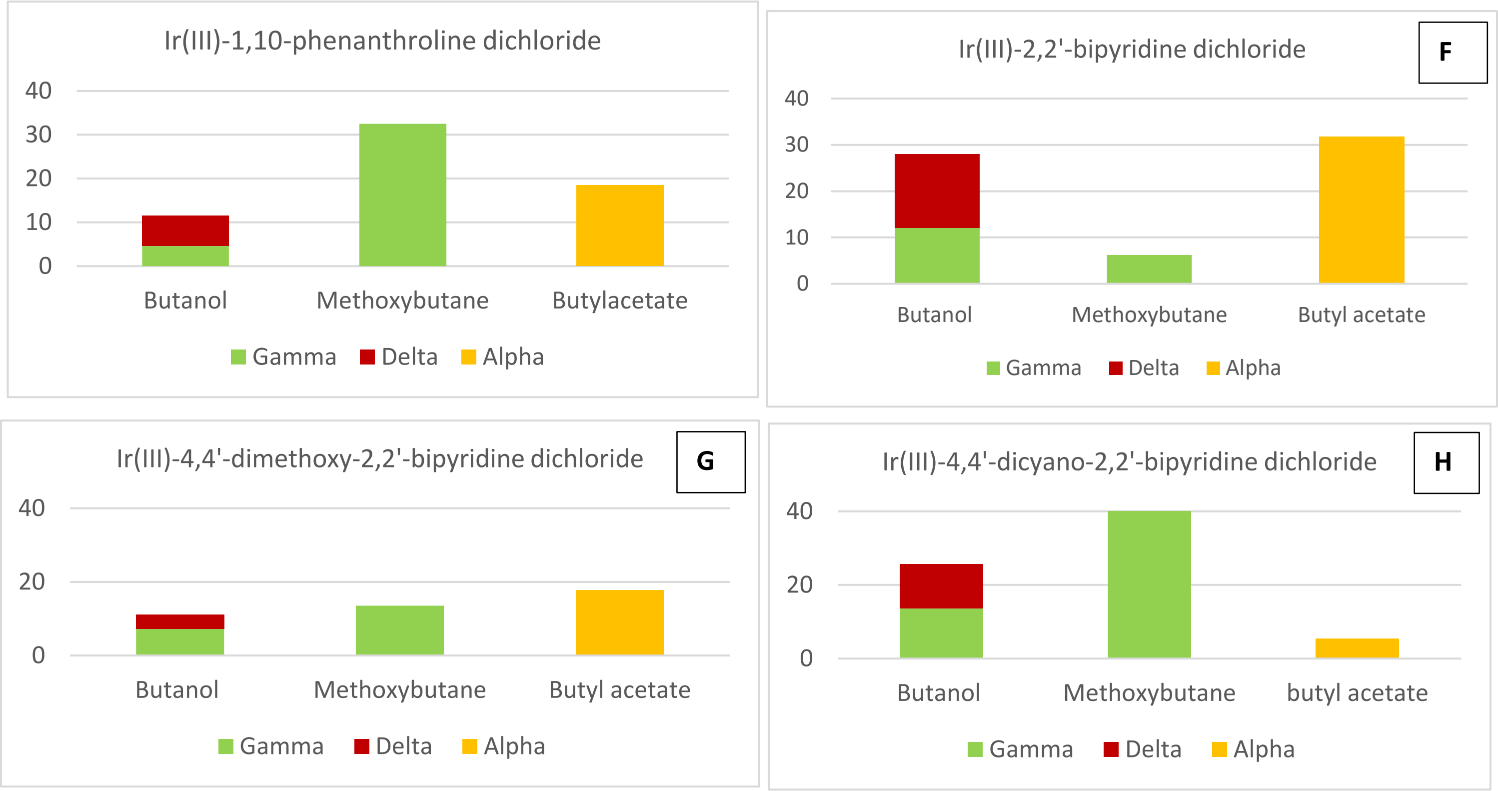
The effect of the flexibility of the chelating ligands was studied by replacing the 1,10-phenanthroline ligand with a more flexible 2,2'-bipyridine ligand. Bipyridine, similar to phenanthroline is a N-heterocyclic ligand which can form stable metal complexes and is stable against substitution.[136] Derivatives of the bipyridine complex were studied to determine if the electronic effects could play a role in concert with factors related to the flexibility of the ligand. Bipyridine(bipy) with electron-donating substituents (**G**) and electron-withdrawing substituents (**H**) were used to study the effect of the electronic properties of the ligand.



F **G** **H**

Figure 39 Complexes used to study the effect of flexibility on regioselectivity of C-H activation

The regioselectivity in the product distributions obtained with the model substrates for the reactions of Complexes F-H are shown in Figure 40 alongside the product distribution of the original IrPhen complex.


Ir(III)-1,10-phenanthroline dichloride

Ir(III)-2,2'-bipyridine dichloride

Ir(III)-4,4'-dimethoxy-2,2'-bipyridine dichloride

Ir(III)-4,4'-dicyano-2,2'-bipyridine dichloride

Figure 40 Product distribution of C-H activation of alcohol, ether and ester with iridium(III) complexes **F, G, & H**

The bipyridine complexes show a similar regioselectivity in C-H activation of 1-butanol, 1-methoxybutane and butyl acetate as the original IrPhen complex. Again, a mix of gamma and delta activation is seen with 1-butanol, almost exclusive gamma activation with 1-methoxybutane, and all alpha activation with butyl acetate. This can be explained by examining the transition state structures of C-H activation of 1-butanol and 1-methoxybutane by complex **F** shown below. The transition states have similar structures as the original IrPhen complex and therefore the bipyridine ring does not affect the basic mechanism or the orientation of the substrates within the steric environment of the metal center. Although the bipyridine allows more flexibility with respect to the orientation of the nitrogens and offers greater ability to shift the position of the sterically relevant C-H bonds on the ligand, it has a surprisingly small impact on the observed regioselectivity.

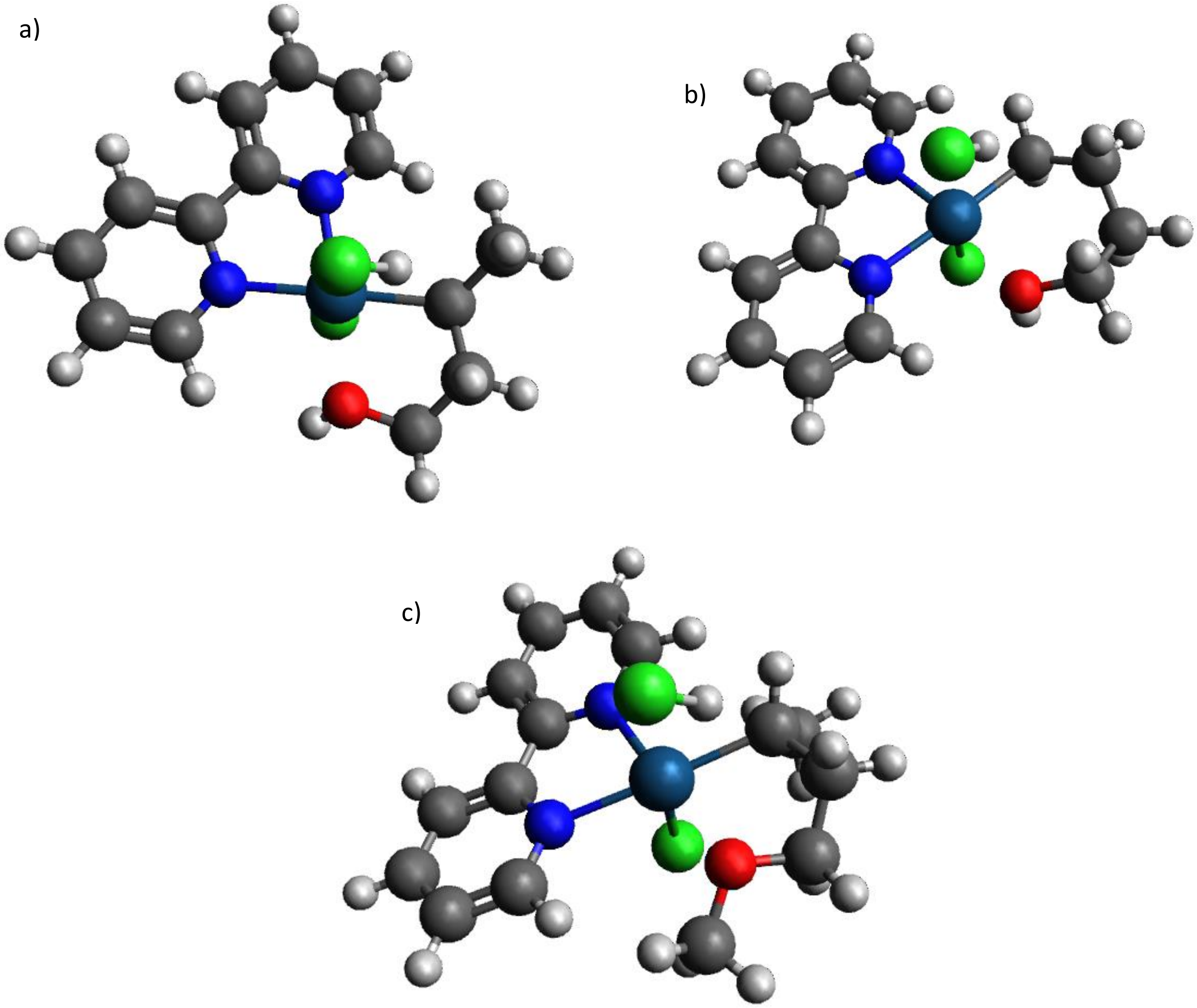


Figure 41 Transition states of a) gamma activation of 1-butanol b) delta activation of 1-butanol and c) gamma activation of 1-methoxybutane by complex **F** using the ECP/6-311+G** basis sets. Elements shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine and red – oxygen.

Table 7 Overall enthalpies of activation for complexes **F**, **G** and **H** at the 6-311+G** energy level

Product	Enthalpy of overall reaction of F (kcal/mol)	Enthalpy of overall reaction of G (kcal/mol)	Enthalpy of overall reaction of H (kcal/mol)
1-butanol, gamma C-H	-25.8	-23.0	-18.2
1-butanol, delta C-H	-23.0	-22.6	-24.7
1-methoxybutane, gamma C-H	-25.6	-16.4	-27.9
1-methoxybutane, delta C-H	-22.1	-17.1	-22.2
butyl acetate, alpha C-H	-33.8	-31.0	-34.9

Table 8 Enthalpies of transition states of **F, G** and **H** at the 6-311+G** energy level

Product	Enthalpy of transition state of F (kcal/mol)	Enthalpy of transition state of G (kcal/mol)	Enthalpy of transition state of H (kcal/mol)
1-butanol, gamma C-H	-20.1	-16.7	-20.2
1-butanol, delta C-H	-23.0	-19.0	-20.5
1-methoxybutane, gamma C-H	-18.6	-16.4	-19.2
1-methoxybutane, delta C-H	-17.5	-13.6	-18.7
butyl acetate, alpha C-H	-27.8	-25.5	-14.4

The computed enthalpies of reaction are all exothermic, as expected, but less so than the reactions with IrPhen by about 5-10 kcal/mol, indicating that the rigidity of the phenanthroline creates a better binding space for the products. This is most dramatic with **G** and suggests that the strong electron-donating group destabilizes the product complex, which is more electron-rich than the reactant complex. Turning to the activation barriers, the preference for delta over gamma activation for 1-butanol is similar in both complexes **F** and **G** (~2-3 kcal/mol) which is similar to the IrPhen complex (~3 kcal/mol). Complex **H,** however, shows no preference for delta over gamma activation in 1-butanol, with both transition states showing a value of ~20 kcal/mol. This is a much smaller difference compared to the IrPhen complex, but the impact in the product distribution is very subtle, with slightly more gamma. There is also slightly more gamma with complex **F**, despite having a similar gamma/delta difference as IrPhen. It is important to note again that these barriers are well below the entrance channel so all pathways have ample energy to cross the barrier, leading to a situation where reaction dynamics may play a role along with barrier heights in the product distributions.

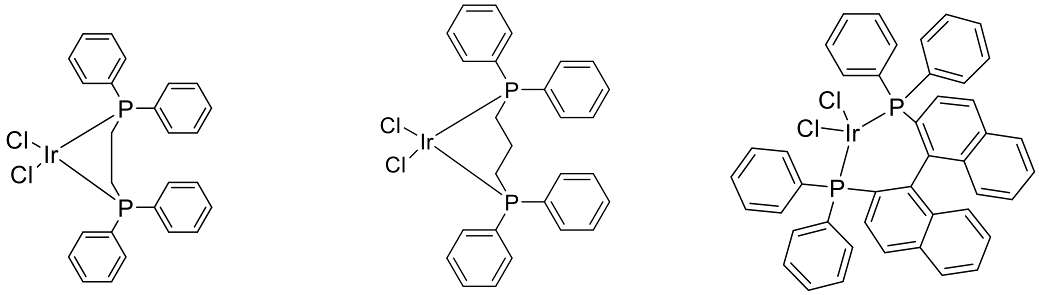
The C-H activation of 1-methoxybutane by complex **F** provides a lower product yield compared to the other complexes, where the reactivity with 1-methoxybutane is generally the highest among the model substrates. This is borne out in the computed barriers. With these complexes, 1-butanol is favored in **F**, more so than in **G** and **H**. It is also noteworthy that **H** has the least favorable transition state with butyl acetate and also gives the lowest C-H activation yield with this substrate. The effect is significant and suggests that the alpha activation of butyl acetate has different electronic demands and can be disadvantaged by strong electron-withdrawing groups on the neutral ligand, suggesting that the alpha C-H activation is more nucleophilic than the gamma and delta C-H activations.

This study with the bipyridine complex and its derivatives enables the exploration of the flexibility of the ligand as well as the electronic effects of the ligand. As seen in section 4.2.2, electronic effects do not significantly affect the regioselectivity of the phenanthroline complexes. This is also true to a significant extent with the bipyridines, but there are modest shifts from delta to gamma across these ligands with very strong electron-donating and withdrawing groups**.** It is interesting that complex **G** with its electron-donating methoxy groups is much less reactive compared to what was seen with complex **F**, which has no substituents, and complex **H**, which has electron-withdrawing cyano groups. The electron-donating methoxy groups on the bipyridine rings increase the electron density of the iridium metal and thereby reduces its reactivity as an electrophilic agent. This is seen in the computed barriers, which are significantly higher for 1-butanol and 1-methoxybutane. In the same manner, the electron-withdrawing cyano groups on the bipyridine lower the electron density of the iridium and thereby increases the electrophilic reactivity. This was most evident with butyl acetate where the reaction was sluggish experimentally and the computed barrier was much higher with complex **H**, despite this being computed as the most exothermic reaction in the set.

This study shows that while the flexibility of the chelating ligand only subtly affects the regioselelctivity of the reaction, strong electronic effects in the substituents do have some effects on the overall reactivity of the complex.

4.2.4 Studying the effect of the chelating atom of ligands on the regioselectivity

Phosphine ligands have been used as scaffolds for many complexes in catalytic processes using organometallic complexes. The electron donation from phosphine ligands can potentially increase the reactivity of the metal, while the bulkiness of some phosphine ligands can control the regioselectivity of a reaction.[137,138] Due to this generally enhanced reactivity of metal complexes with phosphine ligands, they have been studied as potential catalysts for C-H activation.[100,106,130,139] Many bulky phosphine ligands have been studied for C-H activation, with Xanthophos[66] and BINAP[130] ligand complexes showing remote activation of C-H bonds in organic substrates. The hypothesis in this study is that since the chelating atom is directly bound to the metal, it would have an impact on the reactivity of the metal. At the same time, the bulkiness of the phosphine ligands could affect the regioselectivity of the C-H activation of alcohols, ethers, and esters.



I **J** **K**

Figure 42 Phosphine complexes used for the regioselectivity studies of alcohols, ethers and esters

No C-H activation was seen with 1-butanol, 1-methoxybutane, or butyl acetate in either complex **I** or **K**. Complex **J** was also unreactive with the 1-butanol and butyl acetate, but displayed unique reactivity with 1-methoxybutane, specifically a C-O cleavage leading to an alkyl radical expulsion product. Because of this unique reactivity, the reactions of the iridium(III) DPPP dichloride complex (**J**) with 1-methoxybutane will be discussed in Chapter 5. Due to the computational demands of modeling the very large phenylated phosphine ligands, the DFT studies were carried out using the methylated analog of the phosphine complexes. Modeling methyl groups instead of bulkier alkyl groups to reduce the computational requirements has been done in the past in previous computational studies.[77] These methyl groups would still account for the P-C bonds in the original phosphine but reduce the time taken for computational modeling. The enthalpies for the overall reaction for **I** are given in the table below.

Table 9 Overall enthalpies for the C-H activation of alcohol, ethers, and esters by complex **I** at the 6-311+G** energy level

Process	**Enthalpy of the overall reaction (kcal/mol)**
1-butanol, gamma C-H	0.6
1-butanol, delta C-H	-0.1

1-methoxybutane, gamma C-H	-0.2
1-methoxybutane, delta C-H	2.8
Butyl acetate, alpha C-H	-2.1

The relatively endothermic nature of the overall reactions shows that C-H activation by these phosphine complexes is not nearly as energetically favorable as with the IrPhen complex. The impact of these phosphine complexes is twofold as mentioned above: electronic and steric. Even with the relatively small trimethylphosphine ligands, the data shows that steric effects play a major role in the reaction. The methyl groups make the product very crowded as well as the transition state, shown in Figure 43, and this would be exacerbated with bulkier polyphenylphosphine ligands. The low exothermicities are also driven by the greater electron-donating capability of the phosphines compared to the phenanthroline, which stabilize the metal center, making it less reactive.

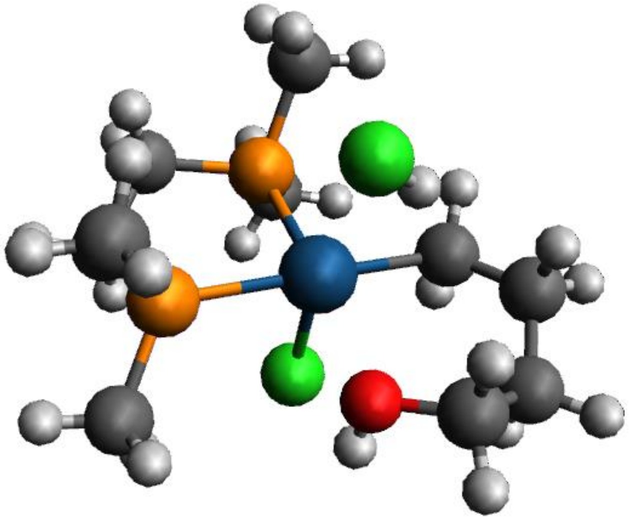
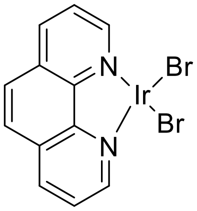


Figure 43 Transition state for delta activation of 1-butanol by the Ir(III)-DPPP complex using the ECP/6-311+G** basis sets. Elements shown by color. Cobalt blue – iridium, blue – nitrogen, dark grey – carbon, light grey – hydrogen, green – chlorine, orange - phosphorous and red – oxygen.

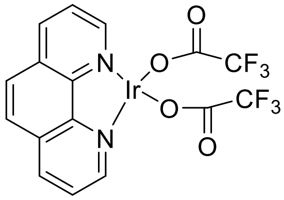
The lack of reactivity with the phosphine ligands aligns with the high calculated enthalpy barrier (4.3 kcal) for the reaction of **I** with 1-butanol. It appears that the bulkiness of the groups, along with the rigidity in this case due to the ethylene spacer group connecting the two phosphine chelators (see Chapter 5 for the enhanced reactivity with the longer spacer) lead to lower reactivity for **I**. In all the phosphines, electronic effects may also contribute to their low reactivity. This study also shows that by changing the chelating atom, the scope of the reaction of the complex can also change, which will be described in more detail in Chapter 5.

4.2.5 Studying the effect on the anionic ligand on the regioselectivity

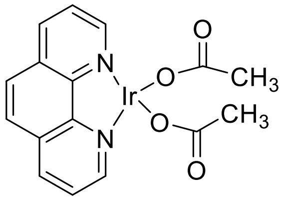
When anionic ligands bind to a metal they can affect the effective electronegativity, spin, ionization potential, polarizability, steric crowding of the metal, which could cause a significant change in the reactivity and regioselectivity of the complex.[140,141] Since the chloride ligand in the IrPhen complex is directly involved in the transition state of C-H activation, studies were carried out to determine the effect of the anionic ligand on the regioselectivity of C-H activation. There may be opportunities to affect reactivity because halogens have a higher electronegativity and poor electron donor capability than other anionic ligands.[140] The complexes used for this study are shown below and include halogen and oxygen-based ligands.



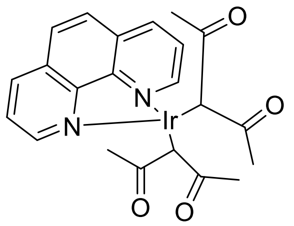
L



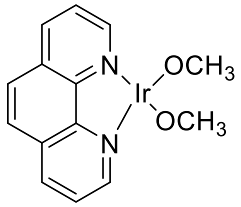
M



N



O



P

Figure 44 Complexes studied to determine the ligand effect on regioselectivity

4.2.5.1 Studying the effect of bromide and methoxide as anionic ligands

The product distribution for the reaction of complex **L** with the model substrates is shown below along with the product distribution of IrPhen for comparison. A fairly similar pattern is seen with the chloride and bromide ligands. Complex **P**, with its methoxide ligands, did show some C-H activation with 1-butanol and 1-methoxybutane, due to the very low efficiency of the reaction the regioselectivity could not be accurately determined using our methodology with deuterated substrates. This low reactivity is in agreement with previous studies where it has been observed that the activity of a catalyst can be inversely correlated with the Lewis basicity of the anionic ligand.[130]

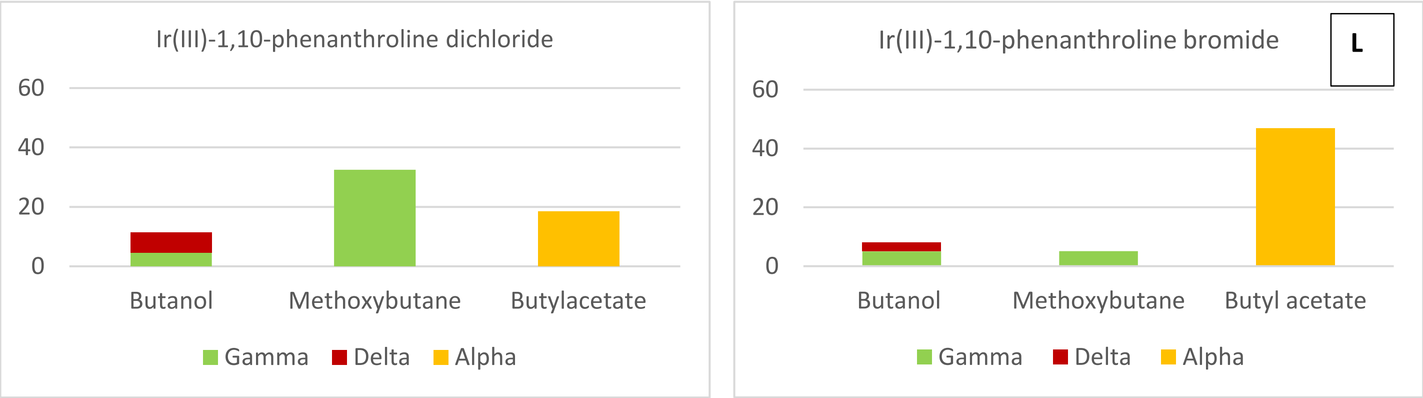


Figure 45 Product distributions showing the regioselectivity of C-H activation of alcohols, ethers and esters by complex **L**

As noted above, complex **L** shows similar regioselectivity in the activation of 1-butanol, 1-methoxybutane, and butyl acetate as the original IrPhen complex. The transition state structures show similar geometries as were observed with the IrPhen complex, which is consistent with the similar regioselectivity. The low reactivity observed experimentally with 1-methoxybutane is consistent with the higher energy of the transition state with complex **L** compared to the other substrates.

Table 10 Enthalpy values for the products and transition states of the reactions with complexes **L** and **P** at the M06 level with the 6-311+G**/LANL2DZ basisi set.

Product	**Overall enthalpy for complex L (kcal/mol)**	**Enthalpy of the transition state for complex L (kcal/mol)**	**Overall enthalpy for complex P (kcal/mol)**
1-butanol, gamma C-H	-17.2	-11.9	-47.3
1-butanol, delta C-H	-25.2	-19.4	-44.6

1-methoxybutane, gamma C-H	-23.1	-16.7	-43.0
1-methoxybutane, delta C-H	-19.6	-14.0	-41.2
butyl acetate, alpha C-H	-28.3	-16.5	-54.0

Although limited C-H activation was observed with complex **P**, the overall exothermicities of the reaction with 1-butanol, 1-methoxybutane, and butyl acetate as well as a transition state are well below the entrance channel for the transition state of the reaction at the delta position of butanol (-21.4 kcal/mol). This suggests that C-H activation should take place. Similar to the dichloro phenanthroline derivative studied in section 4.2.1, the limited amount of reactivity could be due to a very slow reaction rate that cannot be observed in our system because it is swamped out by reactions with adventitious species in the ion trap despite the apparently low barrier to reaction.

4.2.5.2 Studying the effect of trifluoroacetate as an anionic ligand

Complex **M** showed no reaction with the model alcohol, ether, or ester. This can be due to the bidentate nature of the trifluoroacetate ligand. As seen previously in the literature, 16-electron organometallic complexes can have low reactivity,[98] and this could limit their ability to participate in C-H activation.

Using tandem mass spectrometry, we were able to isolate complex **M** and subject it to collision-induced dissociation (CID). The CID process resulted in the loss of a trifluoroacetate ligand, presumably as carbon dioxide and a trifluoromethyl radical. The spectrum showed a peak for this complex stabilized by a water molecule acting as a neutral ligand. The radical loss reduced the Ir(III) complex to an Ir(II) complex (**M’**). The reduction of metals by the decomposition of carboxylate ligands have been shown to be feasible in previous studies by other groups.[142,143] **M'** is formed in a process with a barrier of 21.3 kcal/mol. This value is a reasonable activation barrier for a gas-phase process driven by CID.[144,145]

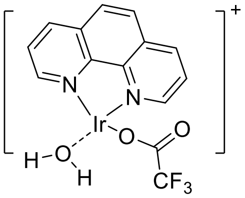


Figure 46 Ir(II)-1,10-phenanthroline trifluoroacetate complex formed through CID (**M'**)

This Ir(II) species was isolated and used to study the regioselectivity of its C-H activation of 1-butanol, 1-methoxybutane and butyl acetate. The product distributions from the studies are shown below.

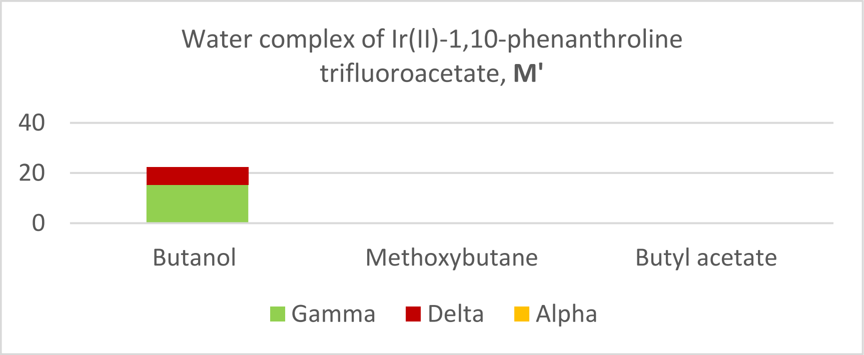


Figure 47 Product distributions showing the regioselectivity of C-H activation of alcohols, ethers and esters by complex **M'**

The activation seen in this study is due to an iridium(II) species which has a significant shift in electronic properties from the Ir(III) species studied throughout this thesis. Moreover, very few iridium(II) complexes have been used for catalytic reactions in the past and no iridium(II) complexes have been reported to our knowledge that have shown the ability to activate C-H bonds at the time of writing this dissertation. The Ir(II) complex readily activates the delta and gamma positions of 1-butanol, but shows either very little or no activation of either 1-methoxybutane or butylacetate.

Table 11 Enthalpy values for complexes **M'**at 6-311+G** level

Process	**Enthalpy of the overall reaction (kcal/mol)**
1-butanol, gamma C-H	-2.9
1-butanol, delta C-H	1.1
1-methoxybutane, gamma C-H	13.4
1-methoxybutane, delta C-H	21.3
Butyl acetate, alpha C-H	12.9

The DFT calculations show very different energetics than the Ir(III) species that have been the focus of the thesis and the reactions are much less favorable. The C-H activation of 1-methoxybutane and butylacetate are endothermic in nature and thereby not feasible. The endothermicity of these reactions can be attributed to the structure of the final activated Ir-C products formed.

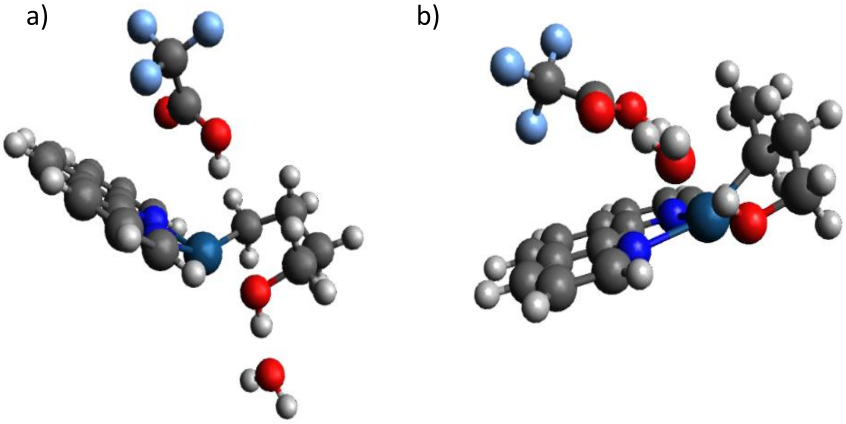


Figure 478 Activated products of the a) delta position in 1-butanol and b) gamma position in 1-butanol by **M'**

Due to the electron density of the fluorine and the oxygen in the trifluoroacetic acid molecule, the iridium complex shifts from its planar configuration to a more distorted structure. This requires energy and can be a major contribution towards the endothermic nature of activation. The 1-butanol activated complexes however, are stabilized through the hydrogen bonding of the hydroxyl hydrogen with the water molecule making the reaction slightly exothermic. The lack of stabilization from hydrogen bonding in 1-methoxybutane and butylacetate makes the activated structure energetically more unfavorable.

Gamma activation of 1-butanol is preferred to the delta activation due to a stronger hydrogen bond (O-H = 1.72 Å delta vs 1.67 Å gamma) as well as the water molecule being closer to the iridium metal in the gamma structure compared to the delta structure. This allows for greater stabilization of the gamma structure.

The study with the trifluoroacetate iridium complex shows that although complexes with this ligand are generally unreactive, gas-phase fragmentation of this complex can lead to a complex containing an iridium(II) center that can be considered as a potential catalyst for remote activation of alcohols.

4.2.5.3 Studying the effect of acetate and acetylacetonate as anionic ligands

Complexes **N** and **O,** both form 16-electron complexes similar to their trifluoroacetate analogue and therefore it is not surprising that they showed no reaction with 1-butanol, 1-methoxybutane or butylacetate. Both the complexes **N** and **O** were subjected to CID, similar to complex **M**. The CID resulted in decarboxylation of **N** but the methyl group remained as a ligand and the complex retained its 16-electron count and Ir(III) center**.** CID of complex **O** resulted in fragmentation of the entire complex. Therefore, the complex still remained relatively saturated and did not undergo a reaction with 1-butanol, 1-methoxybutane and butyl acetate. The lack of water coordination in the acetate complex prevented the system from following the unique pathway seen above for the formation of the Ir(II) species. In its absence, DFT calculations indicate that the formation of Ir(II)-1,10-phenanthroline acetate is an endothermic process (60 kcal/mol) that is outside the normal accessible range by CID (20-45 kcal/mol).

4.3 Summary

This study was carried out to determine the effect of the chelating and anionic ligands of the iridium complex in the C-H activation of 1-butanol, 1-methoxybutane, and butyl acetate. Steric effects were seen to greatly affect the reactivity of the complexes in the 2,9 substituted phenanthrolines. Overall, electronic effects, the flexibility of the ligand, and the nature of the chelating atom all affect the reactivity of the complex, but with very subtle changes in the regioselectivity of the activation. In studying the effect of the anionic ligands, a new Iridium(II) complex was discovered, which could be considered as a potential catalyst for C-H activation of 1-butanol.

4.4 Conclusion

The studies with the different ligands show that even though the reactivity of the reaction can be affected by various chemical characteristics of the ligands, the regioselectivity still remains the same. Various attempts at changing the ligand environment did not yield a significant change in regioselectivity in the C-H bond activations of 1-butanol, 1-methoxybutane and butyl acetate.

Chapter 5

Studying the mechanism of C-O bond cleavage of ethers by an iridium(III)-1,3-bis(diphenylphoshino)propane dichloride complex

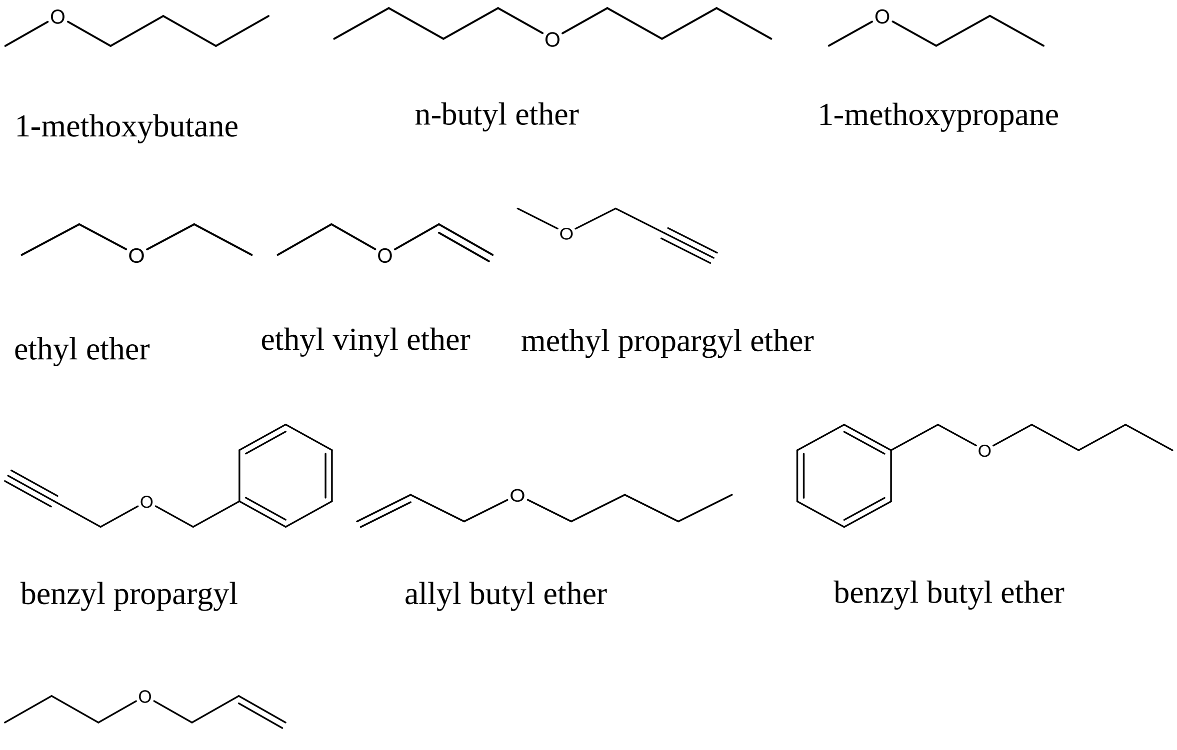
Ir(III)-1,3-bis(diphenylphosphino)propane dichloride (henceforth referred to as IrDPPP) was originally meant to be part of a series used to study the ligand effects on the regioselectivity in Chapter 4, however, it showed a unique pathway in its reaction with methoxybutane. Unlike the other iridium(III) complexes studied in these projects where a loss of HCl accompanied the C-H activation, the IrDPPP complex adds 1-methoxybutane accompanied by the loss of an alkyl radical rather than HCl. This type of reactivity was not seen with any of the other Ir(III) complexes and suggest that the phosphine ligand alters the reaction environment around the Ir(III) center.

The activation of ethers by iridium(III) complexes are quite common, and many gas-phase and theoretical studies have been carried out to understand the mechanism of this activation.[42,110,119] The studies carried out so far show that the C-H activation of ethers can result in either loss of HX, where X is the anionic ligand of the metal complex, dehydrogenation of the ether, or loss of methane or other alkanes or alkenes.[100,119,131,140] These products are formed most commonly through the activation of either the alpha or beta C-H bonds of the ether.[80] The loss of methane is a common product of C-H activation of aliphatic ethers[42,140], although this does compete with the other possible pathways mentioned above. Therefore, many studies have been carried out to study the mechanism of activation and what drives the products that are formed. Most of these studies have been carried out with methyl ethers.[19]

The goal of this project is to study the scope of this reaction with various ethers and to get a better understanding of the mechanism associated with the loss of the alkyl radical. This study will help better understand the scope and utility of the IrDPPP as an ether cleavage agent.

5.1 Methodology

To examine the scope of this reaction, the IrDPPP complex was allowed to react with the series of ethers studied are shown below. All were commercially available except for allyl propyl ether. The same experimental and computational methods from the previous studies were employed here.



1-methoxybutane

n-butyl ether

1-methoxypropane

ethyl ether

ethyl vinyl ether

methyl propargyl ether

benzyl propargyl

allyl butyl ether

benzyl butyl ether

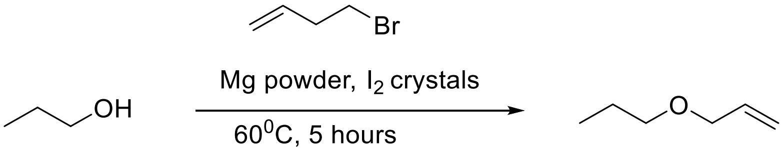
allyl n-propyl ether

Figure 49 Series of ethers studied

To better understand the mechanism of activation, and the products formed, DFT studies were carried out using the M06 functional and ECP (lanl2dz) basis set for iridium and 6-311+G** basis sets for the other atoms. Due to the large size of the IrDPPP complex, the phenyl rings in the DPPP complex were modeled as methyl groups. This was also done in the studies in Chapter 4 and makes the computations practical while still accounting for the presence of P-C bonds of the phosphines.

5.1.1 Synthesis of allyl propyl ether

A mixture of magnesium powder (100mmol, 0.302g), iodine crystals (0.3mmol, 0.04g) and anhydrous propanol (20mmol, 2mL) was added to a round bottom flask. After the bubbling subsided, the reaction was heated to a temperature of 60°C until the iodine color disappeared. The alkoxide was allowed to form. An additional amount of propanol (80mmol, 8mL) was added rapidly, and the mixture was refluxed for five hours. The mixture was cooled, and the unreacted Mg was filtered out. Allyl bromide (0.01mmol, 864µl) was added to the filtrate and refluxed for a further 48 hours. The allyl propyl ether was extracted into xylene. The organic layer was washed and dried with anhydrous Na_2SO_4. The ether distilled out at 87°C.[146] The 1H NMR of the product in $CDCl_3$ is shown in Appendix C as Figure A106.



Scheme 7 Synthesis of allyl propyl ether

5.2 Results & discussion

The reaction of IrDPPP with 1-methoxybutane showed C-H activation through the loss of a methyl radical. The spectrum associated with this reaction is shown in Figure 50 and there is a clean loss of a methyl radical as indicated in the formation of the peak at *m/z* 746, which is the combined mass of the complex and 1-methoxybutane minus 15, the methyl radical.

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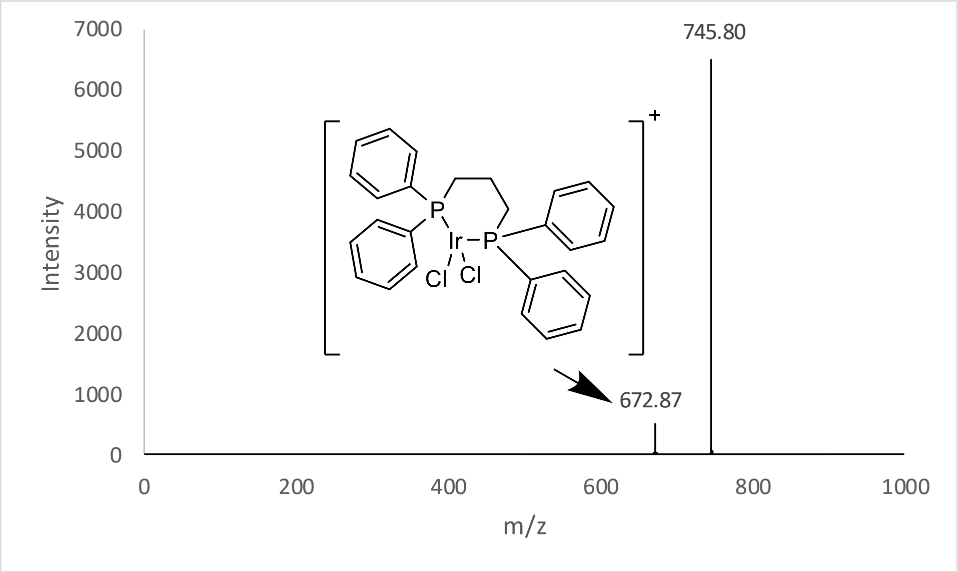
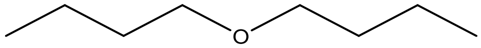
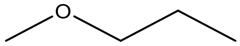
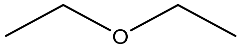
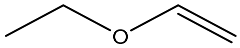
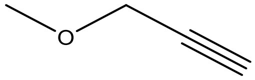
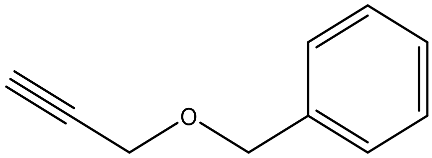
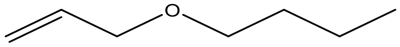
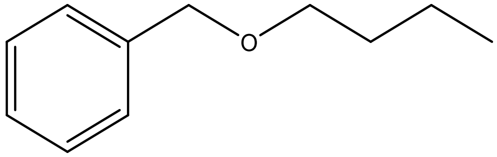
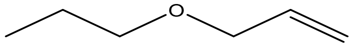


Figure 50 Spectrum showing the reaction of 1-methoxybutane with IrDPPP. Peak 672.8 is the IrDPPP complex while peak 745.8 is methoxybutane-IrDPPP complex with the loss of a methyl radical.

The activation of ethers through the loss of neutral alkanes has been observed in previous work[109], but here we are seeing alkyl radical loss. To determine the scope of this reaction and explore the potential mechanism of it, the IrDPPP complex was allowed to react with the ethers shown in Figure 49. The products that were observed in these reactions are tabulated in Table 12. The scope of the reactions spanned from loss of a radical, to loss of HCl, to no reaction (i.e., only adducts and products of reactions with adventitious gases were observed. The spectra for the reactions are presented in Appendix A3 as Figures A90 - A100.

Table 12 Summary of the results from the ethers studies with IrDPPP

Ether	**Structure**	**Product**
1-Methoxybutane		Loss of methyl radical
Dibutyl ether		Loss of butyl radical
1-Methoxypropane		Loss of methyl radical
Ethyl ether		No reaction
Ethyl vinyl ether		No reaction
Methyl propargyl ether		No reaction
Benzyl propargyl ether		No reaction
Allyl butyl ether		Loss of HCl
Benzyl butyl ether		No reaction
Allyl propyl ether		Loss of allyl radical

The data in Table 12 show that in order for the IrDPPP complex to react and give a distinct product, at least one alkyl chain of the ether needs to consist of three or more carbons. There were no reactions with ethyl ether or ethyl vinyl ether, but when one arm of the ether has at least three carbons, and is aliphatic, reactions occur with the exception of benzyl butyl ether. This species has low volatility and that may have limited the ability to generate products, i.e., the actual pressure of the ether may have been lower than anticipated because of inefficient evaporation in the neutral reagent addition manifold. This requirement could be interpreted as evidence of involvement at the gamma or delta carbon as was observed with the phenanthroline complexes in Chapters 3 and 4. Here though the reaction does not always proceed to C-H activation. In any case, the reactivity pattern is more complicated than the phenanthroline complexes. The substrates 1-methoxypropane, 1-methoxybutane, butyl ether, and allyl propyl ether give radical losses indicating an activation process of the C-O bond. However, allyl butyl ether switches to C-H activation. It is likely that multiple factors are at play to create such an interesting pattern of reactivity. In one case, the agostic interaction with the gamma or delta carbon leads to C-H activation and HCl loss (allyl butyl ether) and in the others, it facilitates the C-O cleavage. The loss of the allyl radical from allyl propyl ether is consistent with the need for an aliphatic gamma carbon to facilitate C-O cleavage through this agostic interaction. A key question is why is this behavior only seen in the IrDPPP complex. In Chapter 4, it was shown that the other phosphine-based ligands did not allow for any reactivity with the model substrates. An obvious issue is the bulkiness of these polyphenylphosphine units that could limit access to the Ir(III) center. DPPP may offer the right balance of flexibility and conformational constraint to allow for limited reactivity. Apparently, the crowding is sufficient to generally prevent C-H activation, but the exothermicity of the addition can drive the C-O cleavage and expulsion of the radical. It is telling that the process is not possible unless the chain is long enough to support the favorable agostic interaction. It is surprising that allyl butyl ether switches to C-H activation. There are two factors that could drive this change. The added carbon compared to allyl propyl either produces a more favorable C-H activation path and the allyl arm positions the substrate more favorably for C-H activation than a methyl (1-methoxybutane) or butyl group (butyl ether). It is also striking that the reactions do not compete and allyl butyl ether gives clean C-H activation and HCl loss. Unfortunately, the size of this system is too large to model the transition states or products with the phenyl groups included and therefore it is not possible to reasonably explore the steric aspects of the reaction with the computational tools that were applied in Chapters 3 and 4.

5.3 Summary

The study to determine the scope of the reaction of IrDPPP with ethers showed that in order for the reaction to occur at least one side chain of the ether needs to have either three or four aliphatic carbons. This indicates that like the phenanthroline complexes, interaction with a gamma or delta carbon is critical to facilitate reactions. With IrDPPP though, the path can go through C-O cleavage and the release of a radical as well as in one example where it can follow the C-H activation pathway. This makes IrDPPP an interesting agent for potentially cleaving ethers in very selective ways, targeting only those ethers that have suitable gamma and delta hydrogens for providing the necessary agostic interaction. The C-H activation can occur either accompanied by a loss of a neutral alkane or loss of an HCl molecule.

Chapter 6

Conclusion

The objective of this thesis was to study the regioselectivity of C-H activation by an IrPhen complex that was discovered previously to be a potent agent for cleaving C-H bonds. A major part of this thesis was the use of deuterium labeling to determine the site of C-H activation in a set of model substrates, namely 1-butanol, 1-methoxybutane and butyl acetate. These were chosen because the butyl change was sufficiently long to allow the full breadth of reactivity to occur at the Ir(III) center and it was possible to obtain the necessary labeled precursors (1-butanols) to prepare substrates that could be used to identify the site of C-H activation. A major goal of the thesis was to explore how features of the IrPhen complex could be manipulated to alter or refine the regioselectivity of its C-H activation processes. To this end, derivatives of the phenanthroline ligand were employed as well as phosphine-based ligands. In addition, the impact of the ionic ligands on the IrPhen complex were explored.

Initially, survey work showed that propanol provided C-H activation, but ethanol did not, highlighting the need for at least three carbons on the alkyl chain. All three of the butyl-based substrates readily showed C-H activation with the IrPhen complex. Since the activation only occurs if the substrate has either three or more carbons the hypothesis tested was that the directing group binds to the iridium and positions a specific carbon-hydrogen bond for activation, likely the gamma or delta carbon in the butyl series. This was tested using selectively deuterated 1-butanol, 1-methoxybutane, and butyl acetate substrates. The study showed that the activation occurs on both the gamma and delta carbons in 1-butanol with a slight preference for the delta position. There is almost exclusive activation on the gamma carbon in 1-methoxybutane. The activation is perfectly selective for the alpha carbon in butyl acetate. The driving force of this selectivity was the transition state structures which are either five or six-membered rings. The preferences are dependent on subtle features in the transition state structure. This validated the hypothesis that the bonding of the oxygen to the iridium leads to a cyclic transition state with a viable configuration for the activation of specific carbon-hydrogen bonds and that this can be manipulated by the nature of the substrate. In the case of 1-methoxybutane, the added methyl group disadvantaged the transition state for delta activation and led to nearly exclusive gamma activation.

Based on the selectivity observed with the IrPhen complex and the participation of the ligands in the sterics of the transition state, the second project was based on the hypothesis that the ligand structure can affect the transition state and thereby alter the regioselectivity of the C-H activation of the model alcohol, ether and ester. This was carried out by creating a library of iridium complexes which would allow for an exploration of the effects of changing the steric demands, electronic properties, flexibility, and chelating atom of the neutral ligand. In addition, the effect of the anionic ligands was explored. The studies showed that although the ligands significantly affect the reactivity of the iridium complex with respect to 1-butanol, 1-methoxybutane and butyl acetate, the regioselectivity of the C-H reactions of these complexes was impacted in relatively subtle ways. However, the project identified a new iridium(II) trifluoroacetate complex that can be a potential agent for the remote C-H activation of butanol.

In studying the effect of the ligands on the regioselectivity of C-H activation, an iridium DPPP complex was identified that can cleave ethers by loss of an alkyl radical and the production of an Ir(IV) alkoxide species. A survey study was carried out to determine the scope of the reaction. The study showed that in order for C-H activation to be seen in our system at least one side chain of the ether needs to have three or more carbons. This would indicate that the gamma and delta carbons are involved, likely through an agostic interaction. In one example, allyl butyl ether, the DPPP complex gave C-H activation instead. It appears that the steric bulk of the ligand is generally suppressing the C-H activation path and forcing it along the C-O cleavage path. Overall, this study showed that the IrDPPP complex could also be a potential agent for the C-O cleavage of ethers and could be a candidate for further studies for suitable applications.

In conclusion, this thesis investigated the mechanism and regioselectivity of C-H activation by iridium complexes. The complexes studied are capable of regioselectivity by remote functional groups. This makes a significant impact on the field since it shows that these species are candidates for selective remote C-H activation catalysts in suitable applications. The Ir(III) species show robust reactivity and were highly functional after various modifications of the phenanthroline ligand. The combination of DFT and gas-phase studies of the C-H activation by the iridium complexes offer a wealth of knowledge that can in the future be translated and transferred to the condensed phase. This will enable further studies and tuning of the iridium complexes for appropriate applications in C-H activation of alcohols, ethers, and esters.

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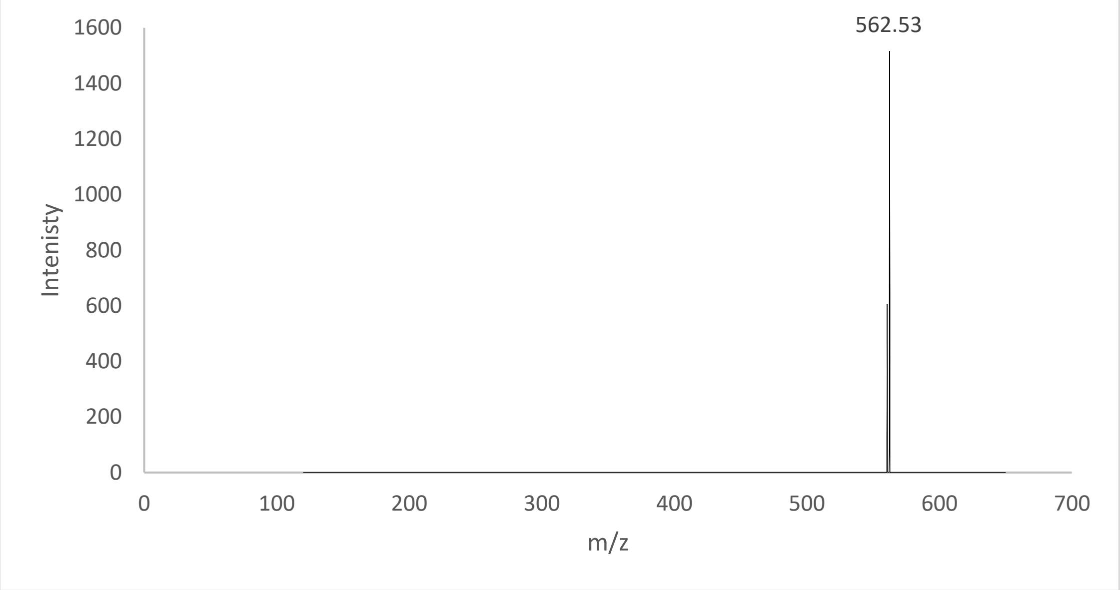
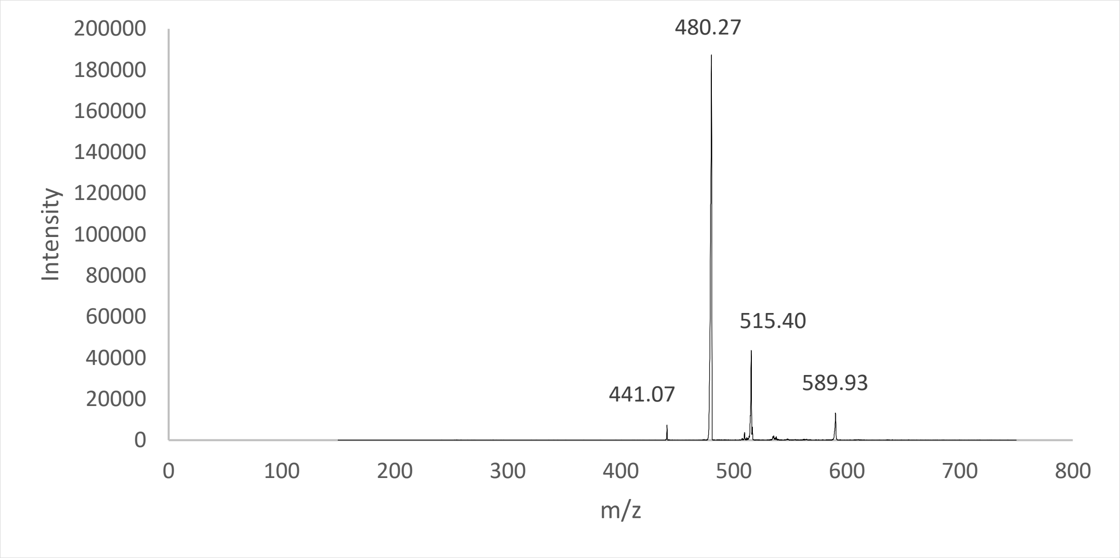
Appendix A – Spectra

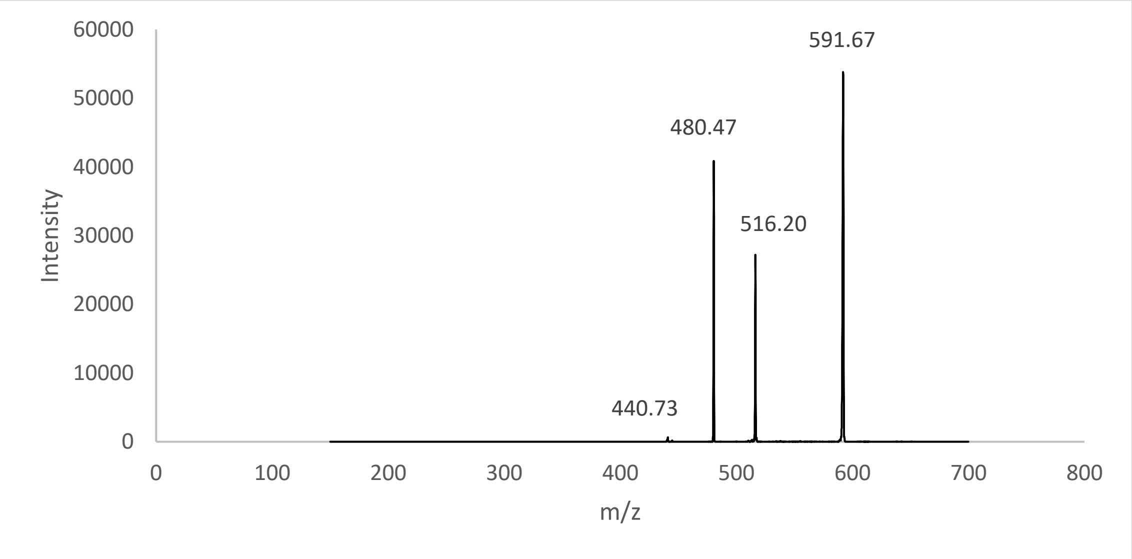
Appendix A1 – Spectra for chapter 3



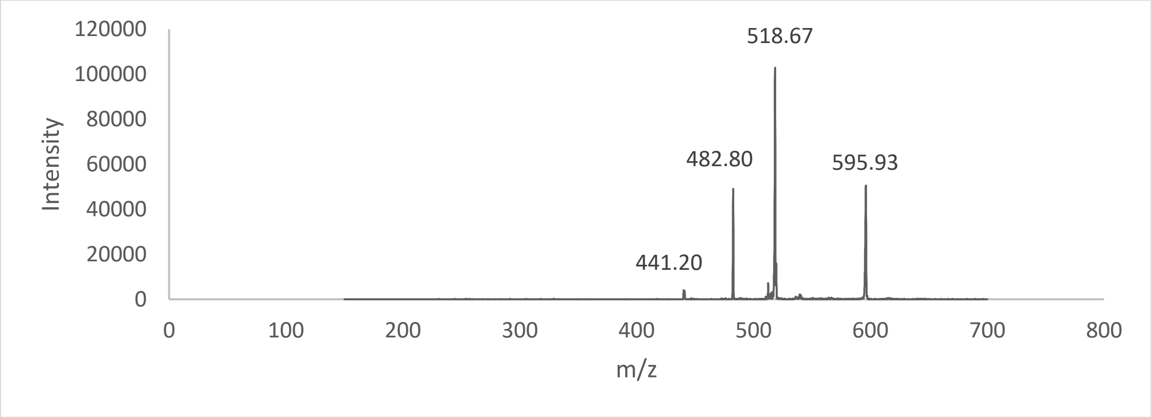
A 1 IrPhen reaction with 2-propanol. The peak at 562.53 is and adduct of two 2-propanol molecules



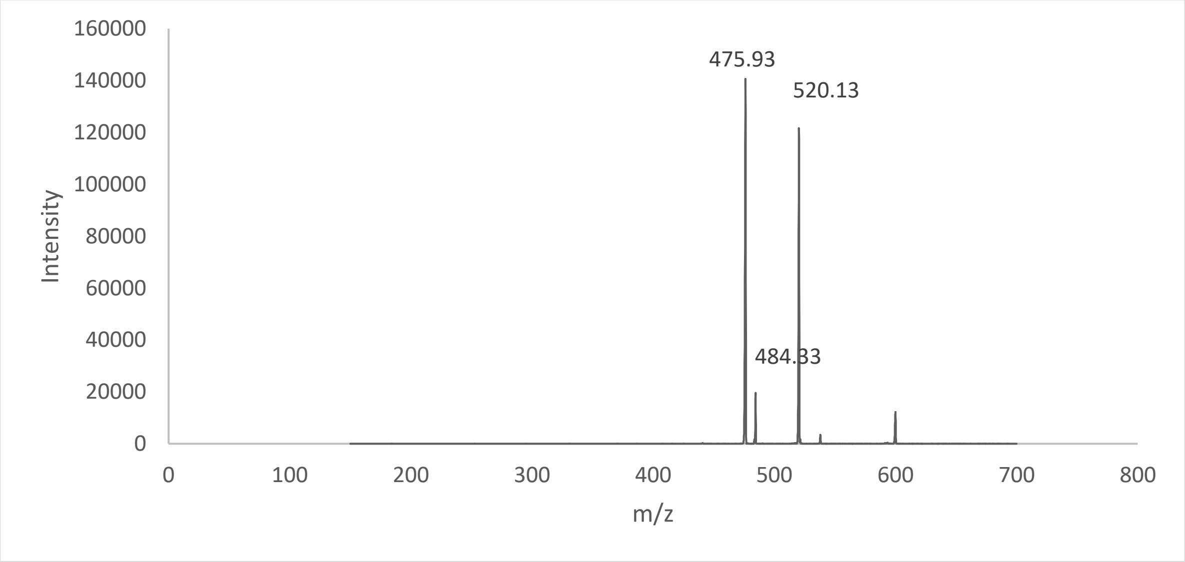
A 2 IrPhen reaction with 1-butanol-OD. The peak at 441.07 is the IrPhen complex, 480.27 is the peak for C-H activation, 515.40 and 589.93 are adducts of one and two 1-butanol molecules respectively



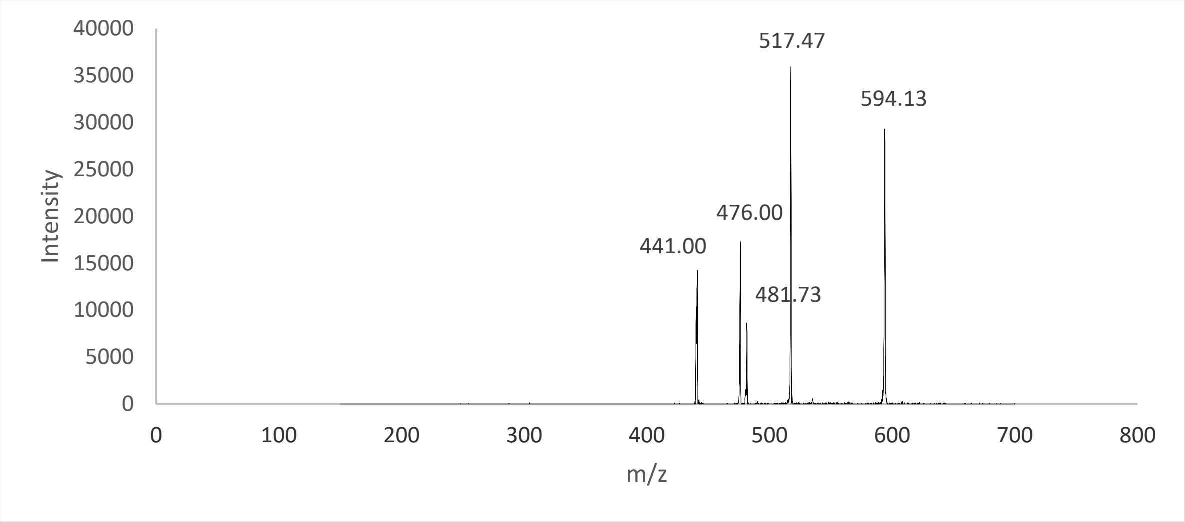
A 3 IrPhen reaction with 1,1,d_2-1-butanol. Peak at 480.47 is C-H activation , 516.20 and 591.67 are adducts of one and two 1-butanol molecules



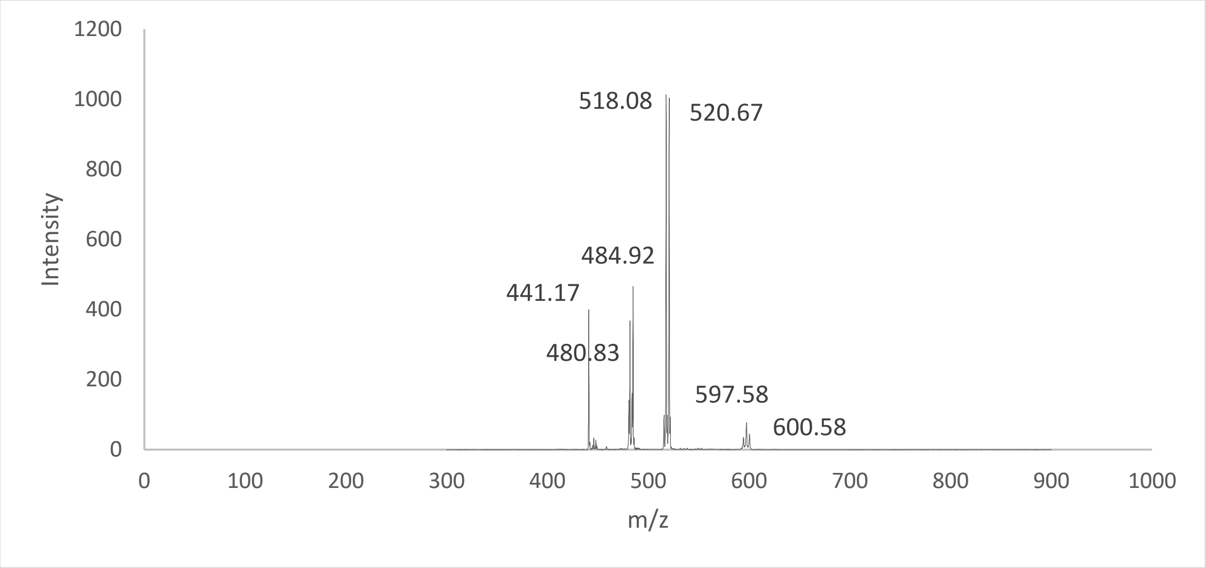
A 4 IrPhen reaction with 1,1,2,2-d_4 1-butanol. Peak 482.80 is C-H activation, peaks 518.67 and 595.93 are adducts of one and two 1-butanol molecules.



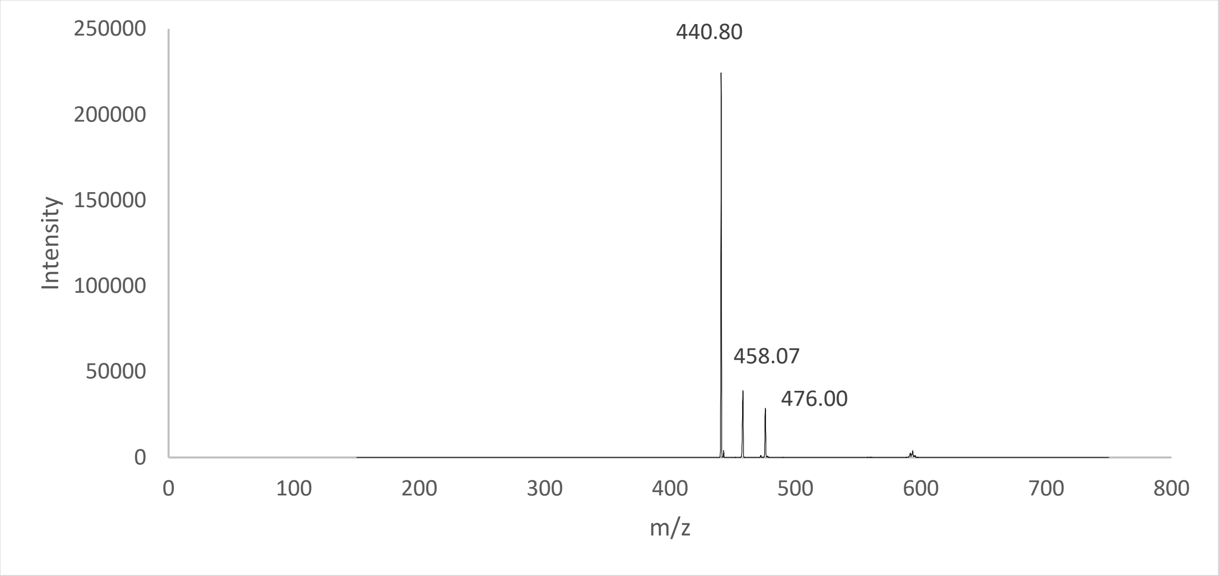
A 5 IrPhen reaction with 1,1,2,2,3,3-d_6 1-butanol. Peak 484.33 is C-H activation, peaks 520.13 and 476.93 are 1-butanol and two water molecule adducts respectively.



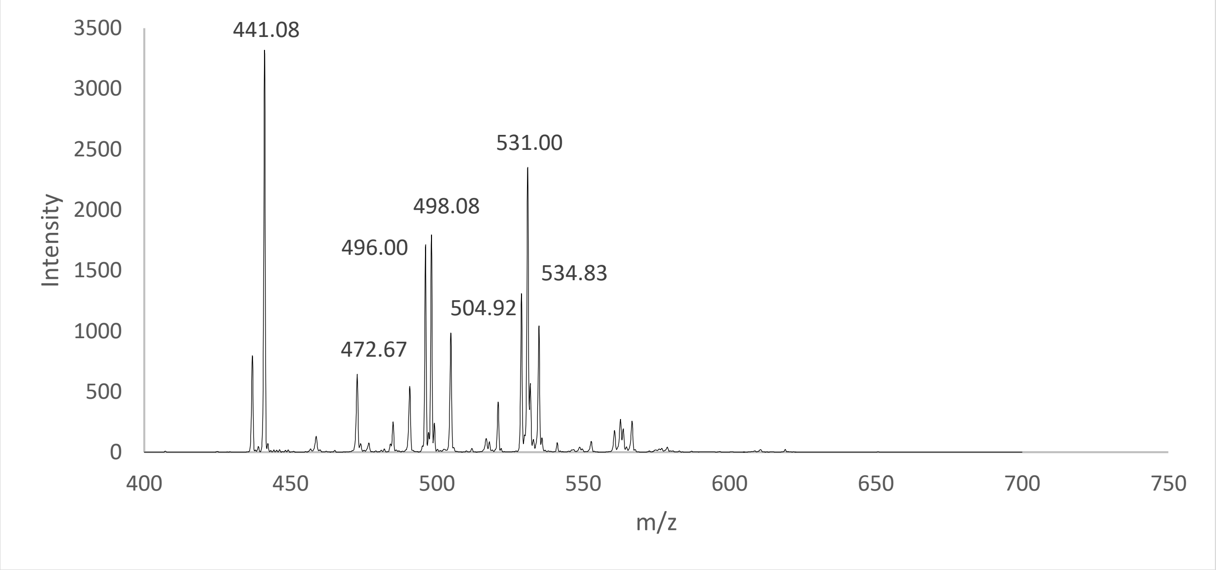
A 6 IrPhen reaction with 4,4,4-d_3 1-butanol. Peak 481.67 is C-H activation, peaks 517.53 and 593.73 are one and two 1-butanol molecule adducts.



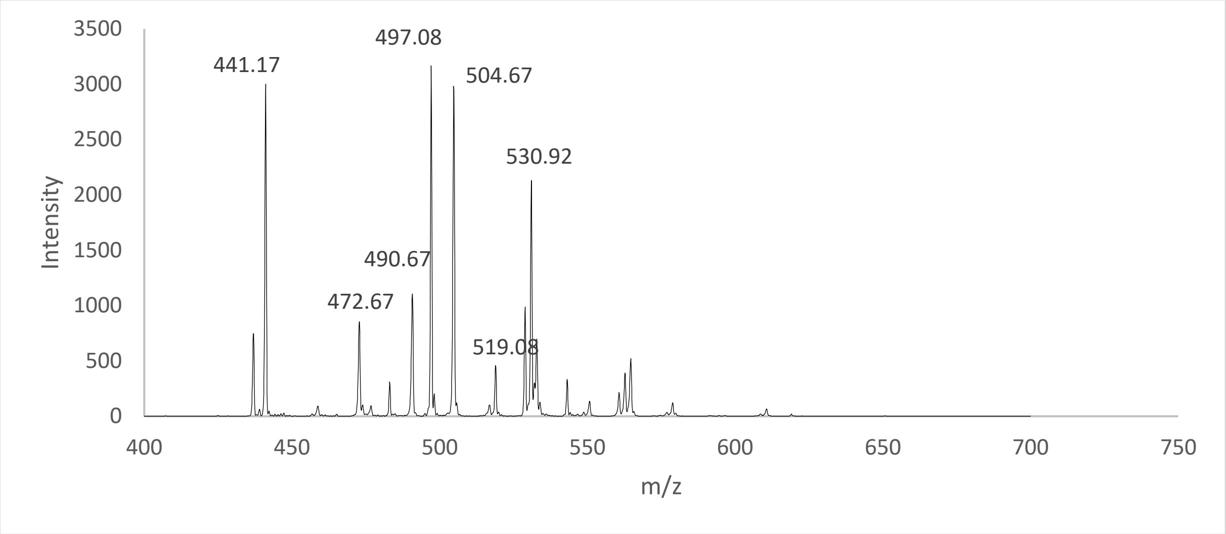
A 7 IrPhen with a 50:50 mixture of 1,1,2,2,3,3-d_6 1-butanol and 4,4,4-d_3 1-butanol. Peaks 481, 518 and 597 are C-H activation, and adducts of one and two 1-butanol molecules with 1,1,2,2,3,3-d6 1-butanol. Peaks 484, 521 and 601 are C-H activation and adducts of one and two 1-butanol molecules respectively



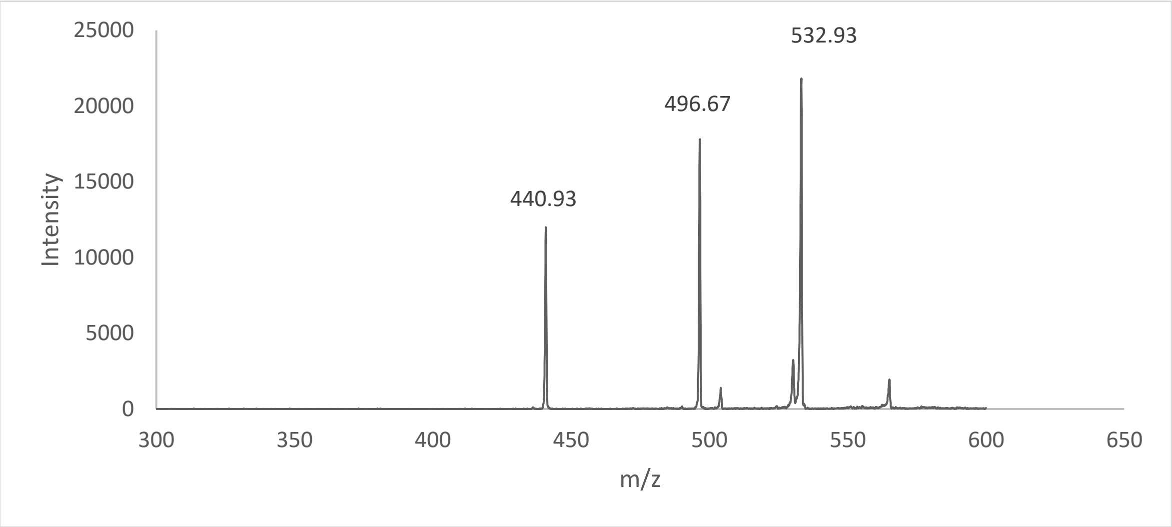
A 8 IrPhen with CCl4. The peak at 440.80 is the IrPhen complex, 458.07 and 476.00 are adducts of one and two water molecules



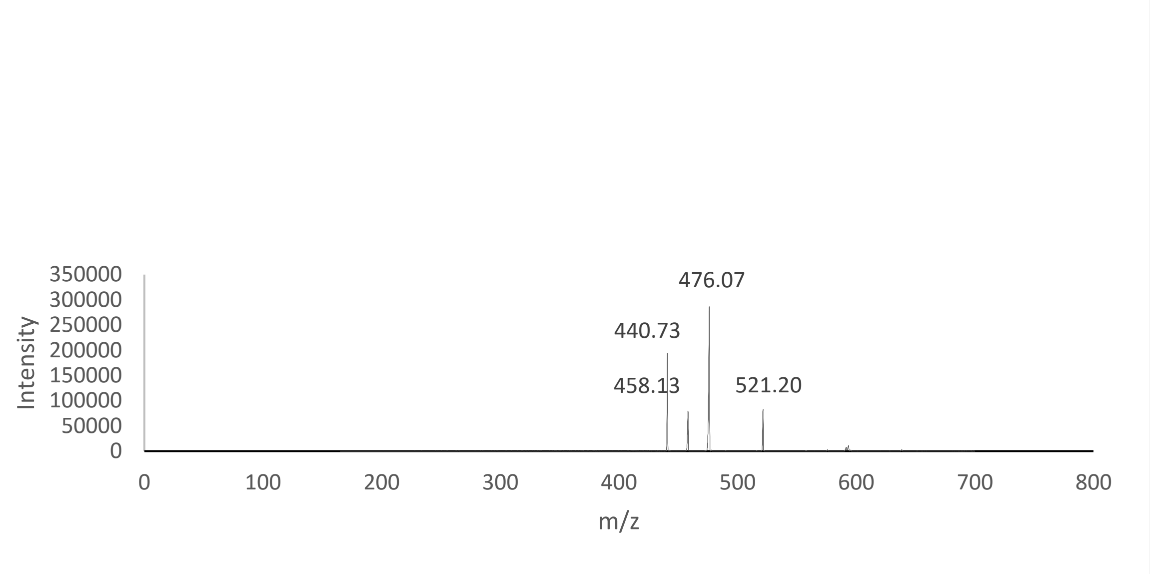
A 9 IrPhen with a 50:50 mixture of 1,1,2,2,3,3-d_6 1-methoxybutane and 4,4,4-d_3 1-methoxybutane. 441.08 is the IrPhen complex, 472.67 is a methanol adduct, 496.00 is the C-H activation of 4,4,4-d_3 1-methoxybutane, 498.08 is the C-D activation of 1,1,2,2,3,3-d_6 1-methoxybutane, 504.92 is an adduct of two methanol adducts and peaks 531.00 and 534.83 are adducts of 4,4,4-d_3 1-methoxybutane and 1,1,2,2,3,3-d_6 1-methoxybutane molecules respectively



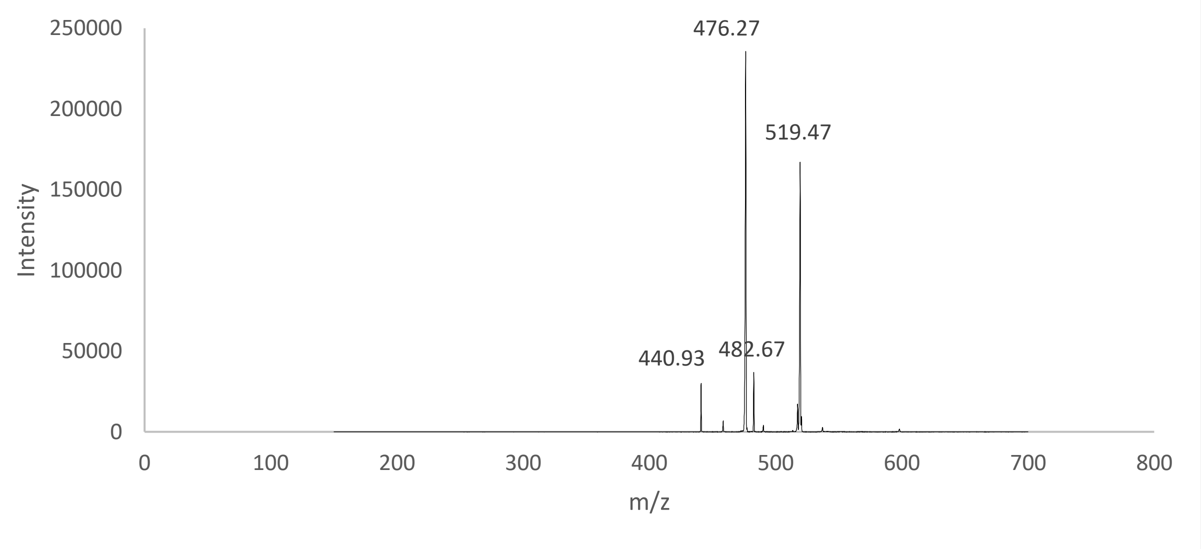
A 10 IrPhen with 1,1,2,2-d$_4$ 1-methoxybutane. 441.17 is the IrPhen complex, 472.67 is a methanol adduct, 490.67 is an adduct of one water and methanol molecules, 497.08 is the peak for C-H activation , 504.67 is an adduct of two methanol molecules, 510.08 and 530.92 are adducts of two methanol molecules with one water molecule and a 1-methoxybutane molecule respectively.



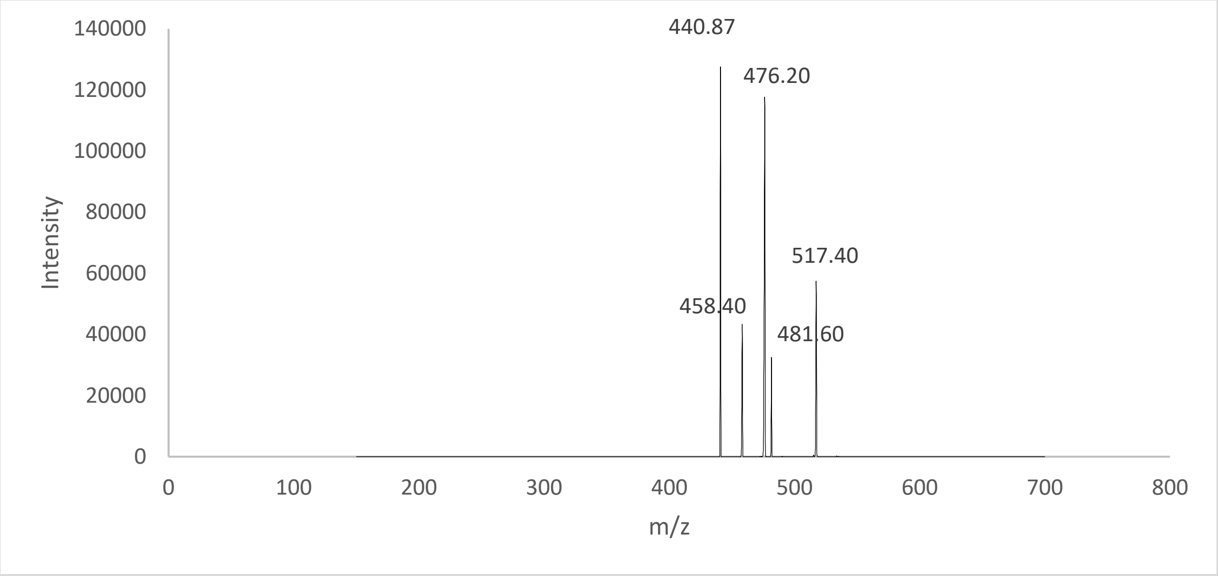
A 11 IrPhen with 3,3,4,4,4-d$_5$ 1-methoxybutane.The peak at 440.93 is the iridium(III) phenanthroline complex, 496.67 is the peak for C-D activation and 532.93 is a 1-methoxybutane adduct



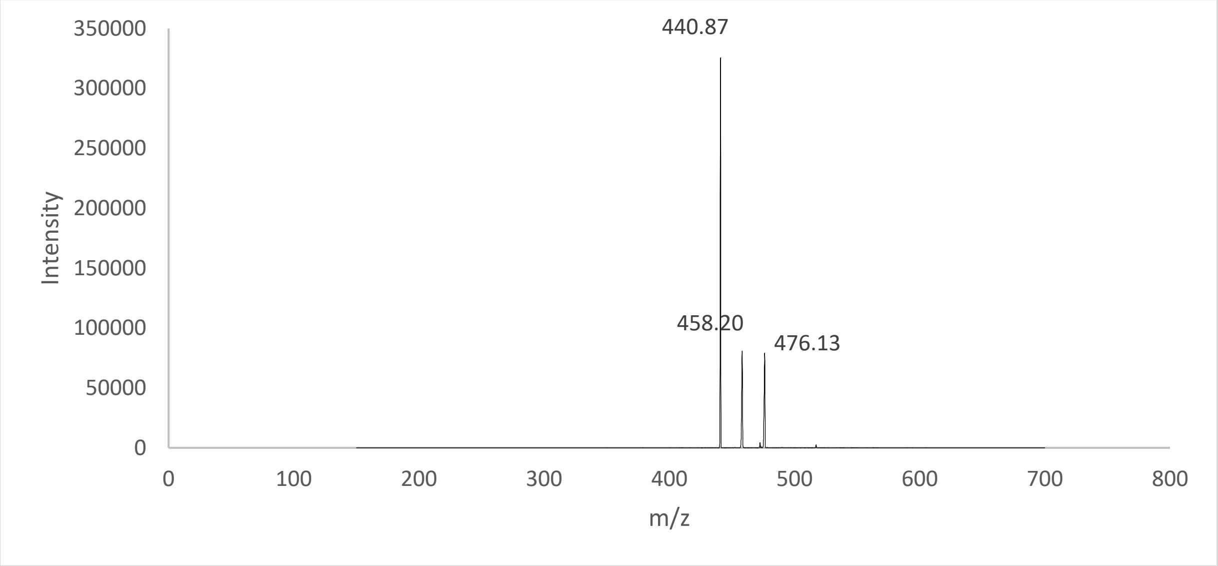
A 12 IrPhen with 1,1-d$_2$ butyl acetate. Peak at 440.73 is the iridium complex, 458.13 and 476.07 are adducts of one and two water molecules and 521.20 is the peak for C-D activation



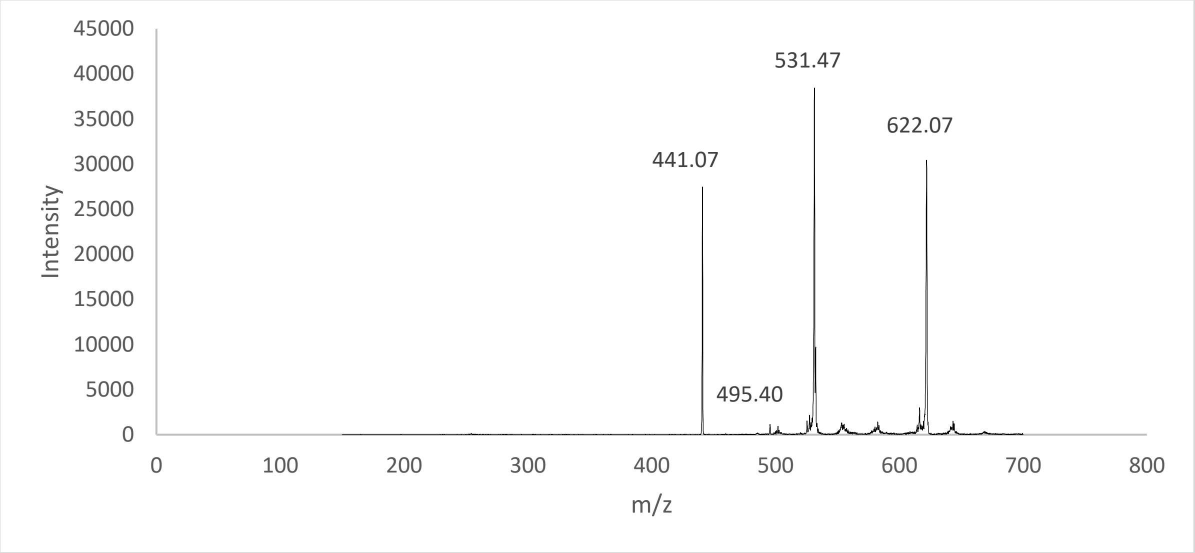
A 13 IrPhen with sec-3,3,4,4,4-d$_5$ 1-butanol. Peak at 440.93 is the iridium complex, 476.27 is and adduct of two water molecules, 482.67 is the peak for C-D activation and 519.47 is an adduct of a 1-butanol molecule.



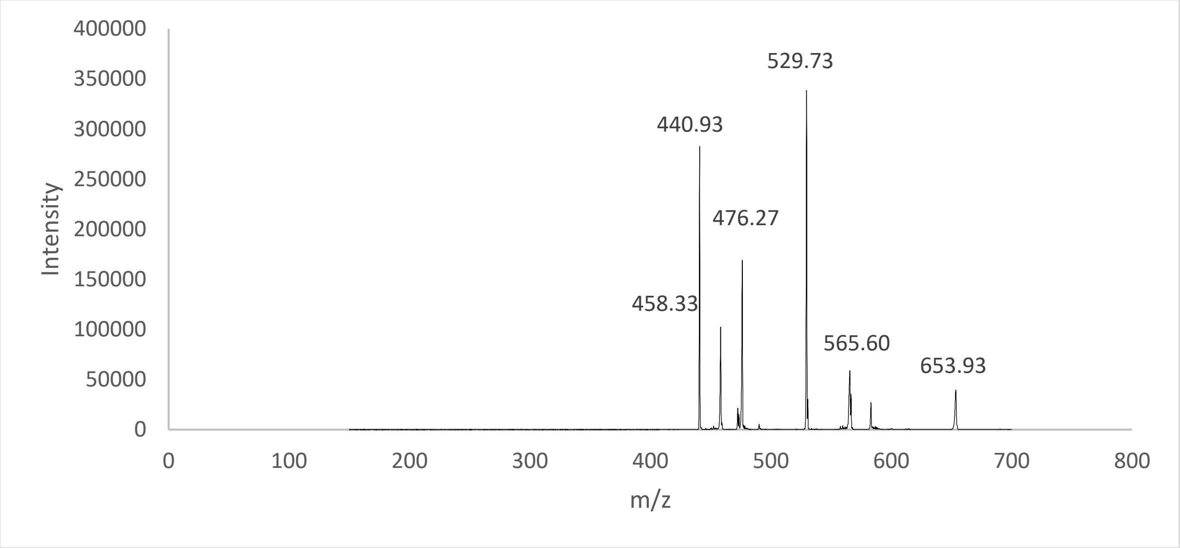
A 14 IrPhen with sec-2,2,2-d_3 1-butanol. Peak at 440.87 is the iridium complex, 458.40 and 476.20 are adducts of one and two water molecules respectively, 481.60 is the peak for C-H activation and 517.40 is a 1-butanol adduct.



A 15 IrPhen with tert-1-butanol. Peak at 440.87 is the iridium complex, 458.40 and 476.20 are adducts of one and two water molecules respectively.

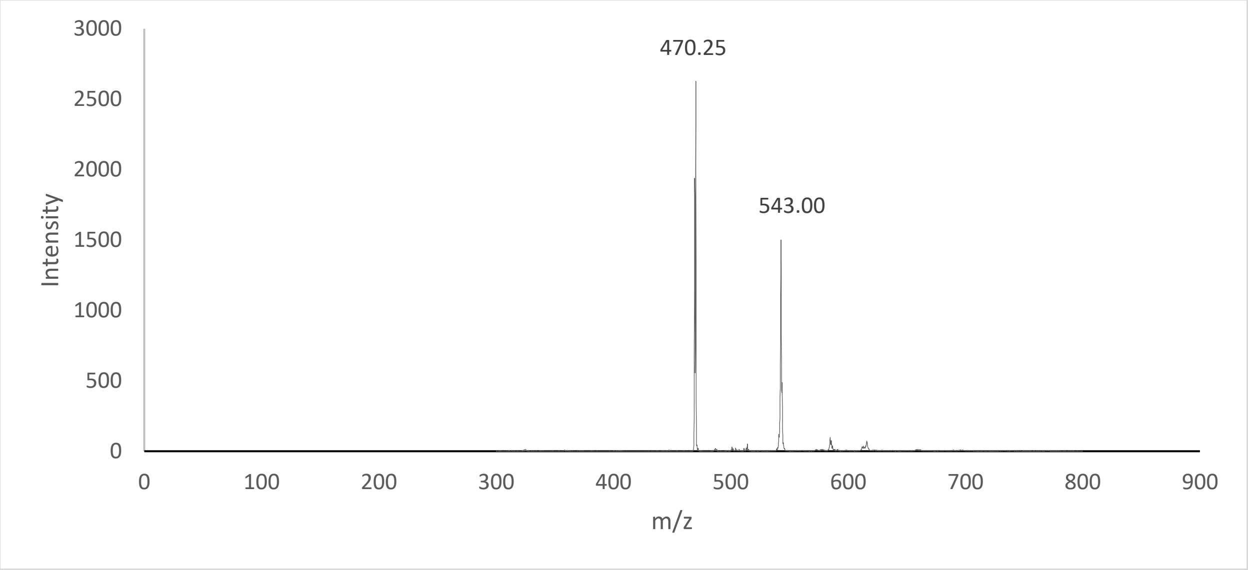


A 16 IrPhen with 5,5,5-d3 pentanol. The peak at 441.07 is the iridium complex, 495.50 is the peak for C-H activation, 521.47 and 622.07 are adducts of one and two neutral reagent molecules respectively.

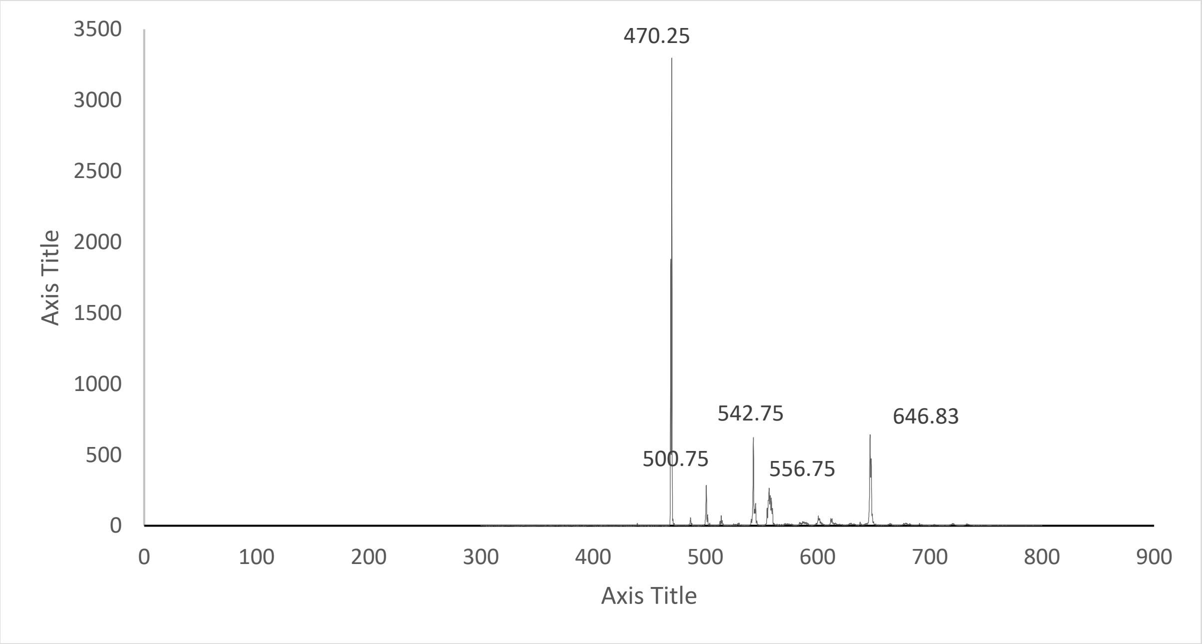


A 17 IrPhen with 1-phenyl-1,1,1-d_3 ethanol. The peak at 441.07 is the iridium complex, 459.33 and 476.27 are adducts of one and two water molecules respectively, 565.50 is the phenyl ethanol adduct, 529.73 and 653.93 are the C-H activation peaks from one and two phenyl ethanol molecules respectively.

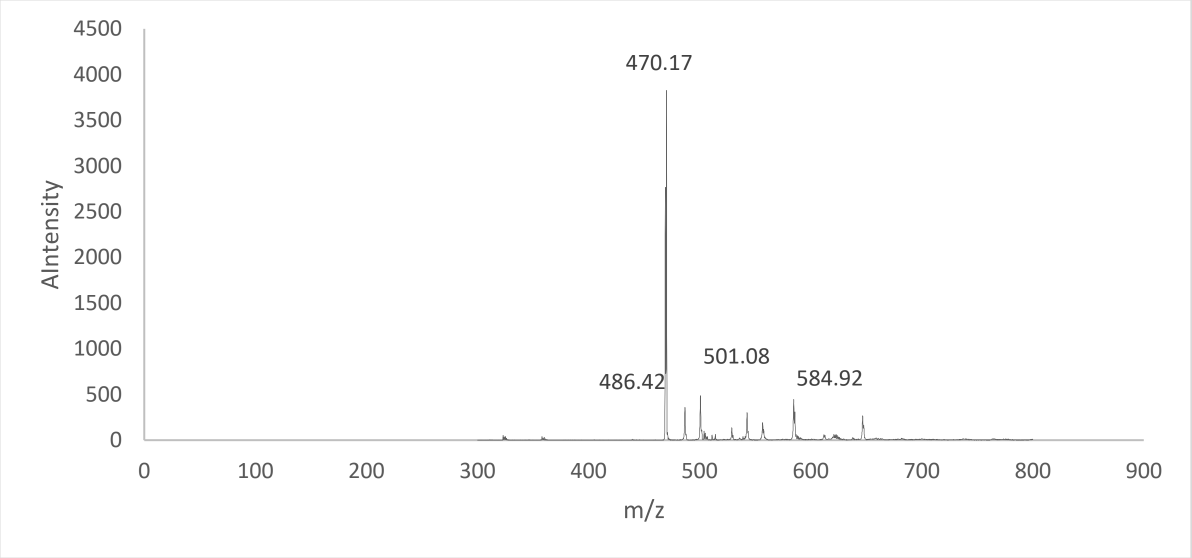
Appendix A2 – Spectra for chapter 4



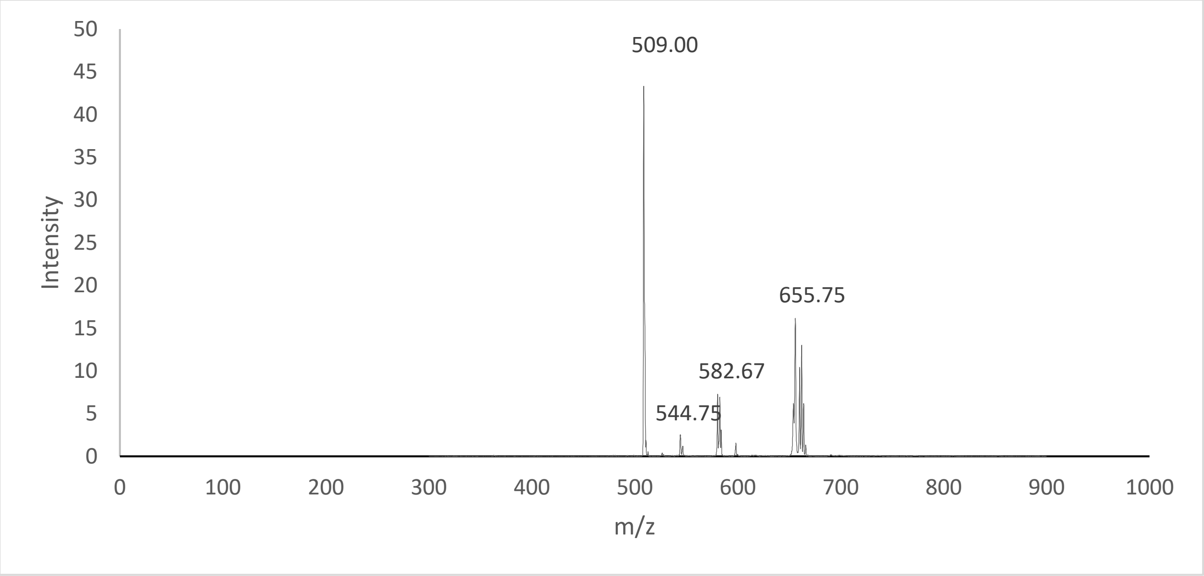
A 18 Ir(III)-2,9-dimethyl-1,10-phenanthroline with 1-butanol. The peak at 543.00 is a 1-butanol adduct and 470.25 is the iridium complex.



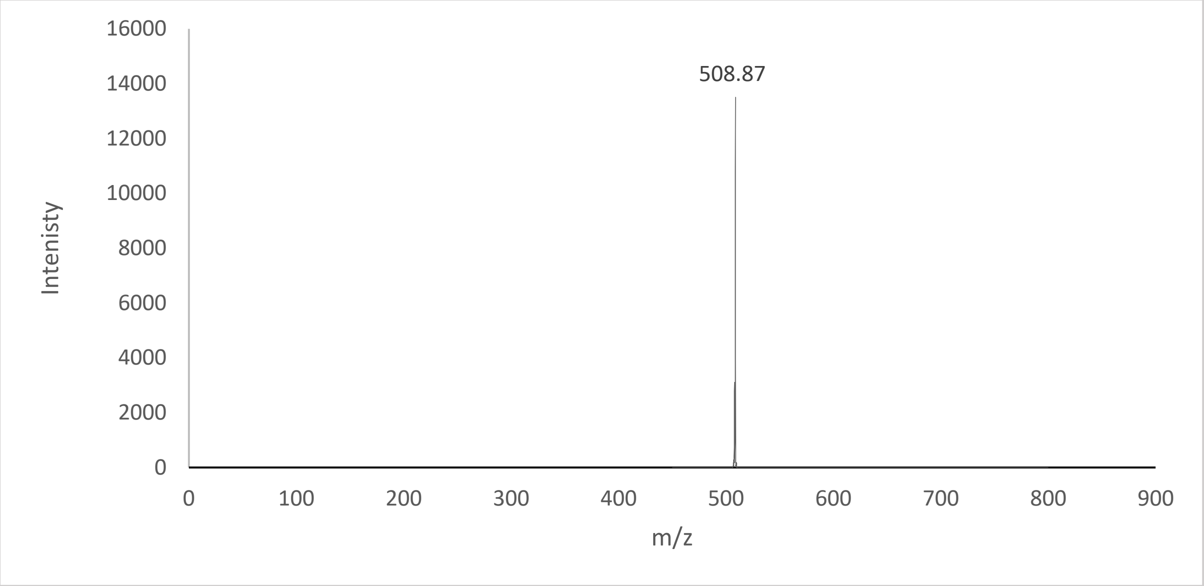
A 19 Ir(III)-2,9-dimethyl-1,10-phenanthroline with 1-methoxybutane. The peak at 500.75, 556.75 and 646.83 are adducts of one methanol molecule, one 1-methoxybutane molecule and two 1-methoxybutane molecules respectively, 542.75 is a 1-butanol adduct and 470.25 is the iridium complex.



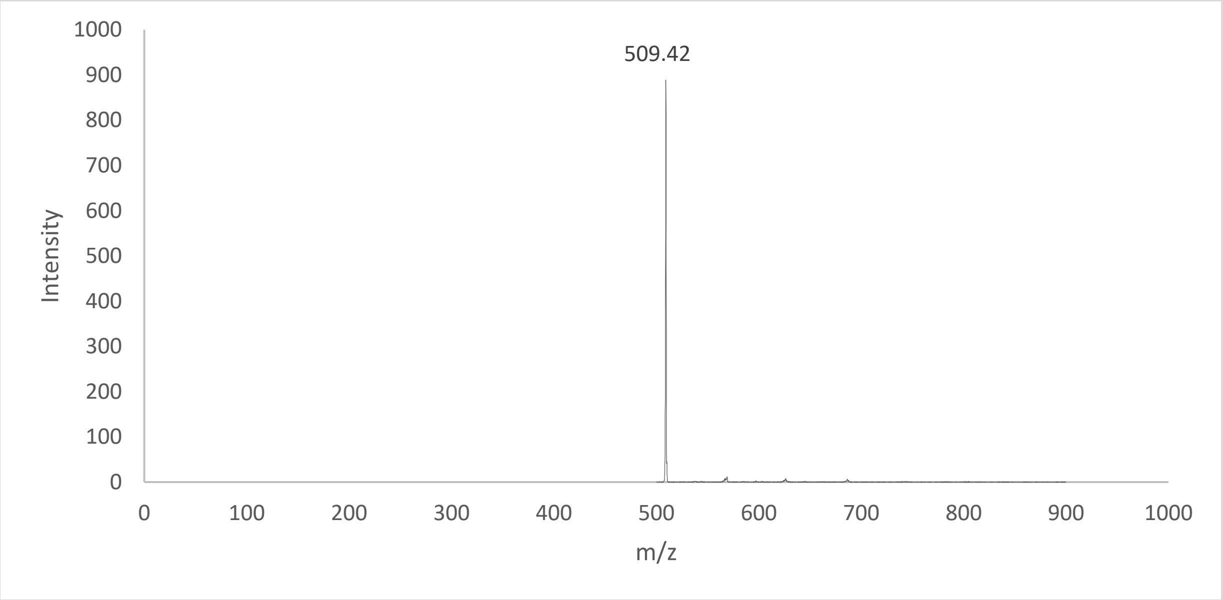
A 20 Ir(III)-2,9-dimethyl-1,10-phenanthroline with butylacetate. The peak at 486.42, 501.08 and 584.92 are adducts of one water molecule, one methanol molecule and one butyl acetate molecule respectively, 470.17 is the iridium complex.



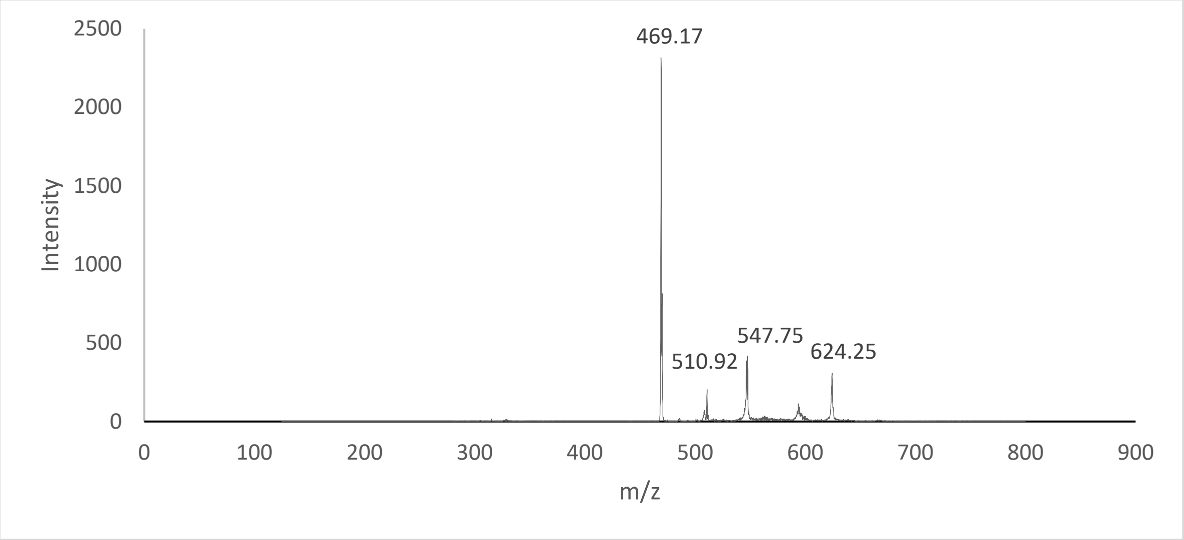
A 21 Ir(III)-2,9-dichloro-1,10-phenanthroline with 1-butanol. The peak at 544.75 is an adduct of two water molecules, 582.67 and 655.75 are adducts of one and two 1-butanol molecules respectively and 509.00 is the iridium complex.



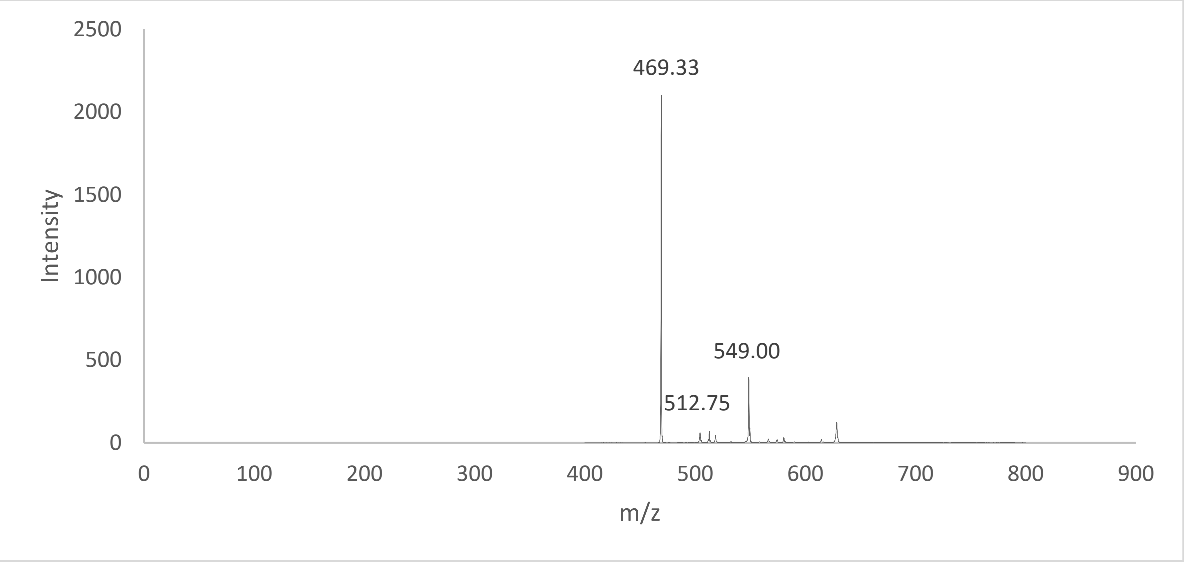
A 22 Ir(III)-2,9-dichloro-1,10-phenanthroline with 1-methoxybutane. The peak at 508.87 is the iridium complex.



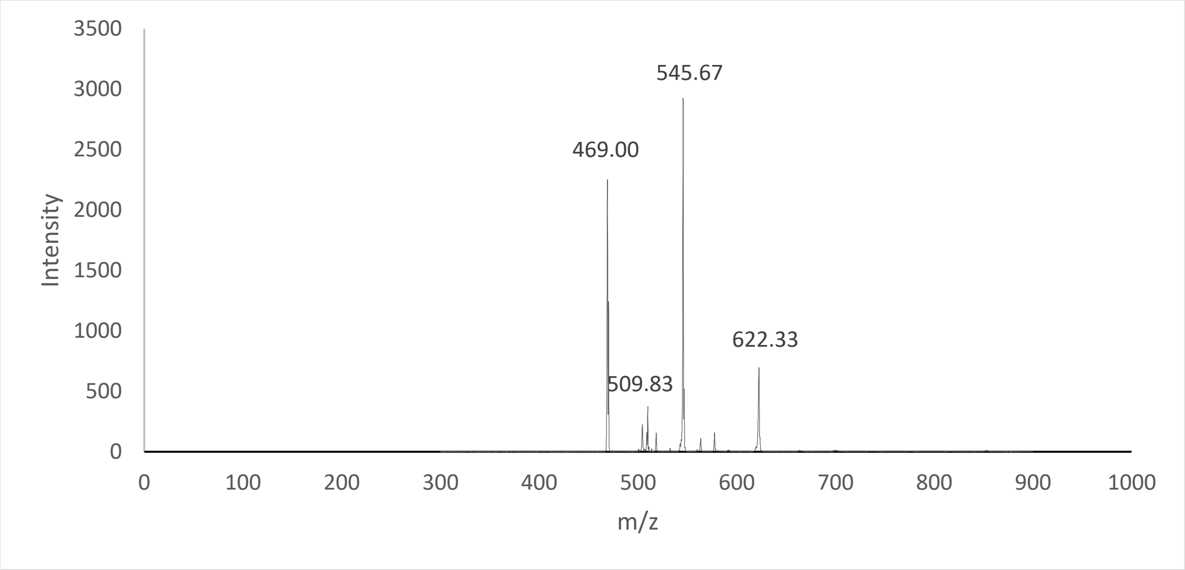
A 23 Ir(III)-2,9-dichloro-1,10-phenanthroline with 1-methoxybutane. The peak at 509.42 is the iridium complex.



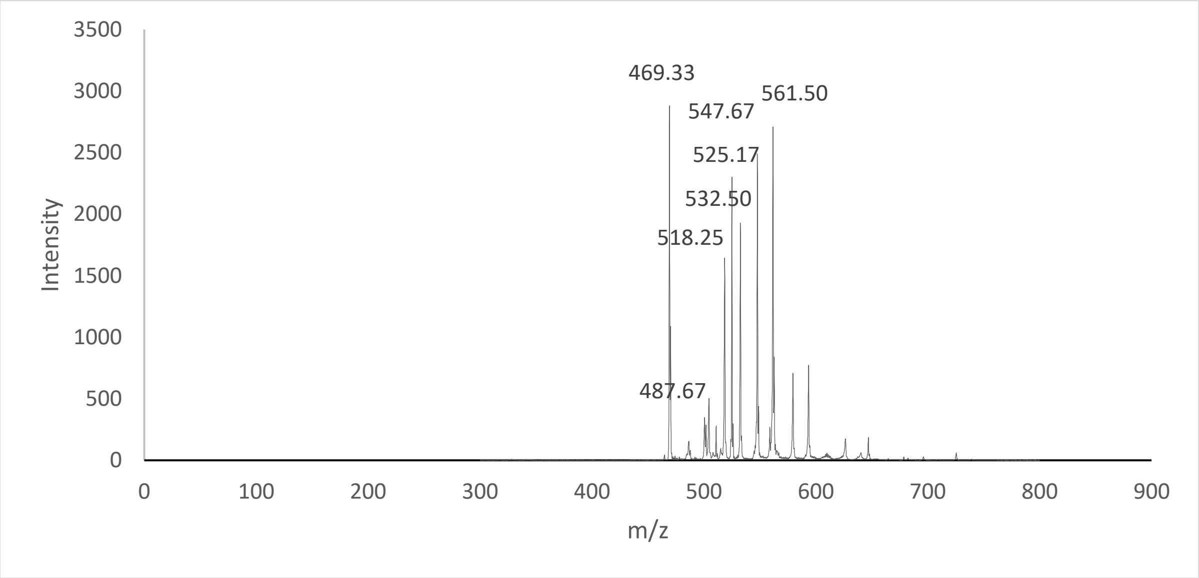
A 24 Ir(III)-4,7-dimethyl-1,10-phenanthroline dichloride with 1,1,2,2-d_4 1-butanol. Peak at 469.17 is the iridium phenantholine complex, 510.92 is the peak for C-H activation, 547.75 and 624.25 are adducts of one and two 1-butanol molecules respectively



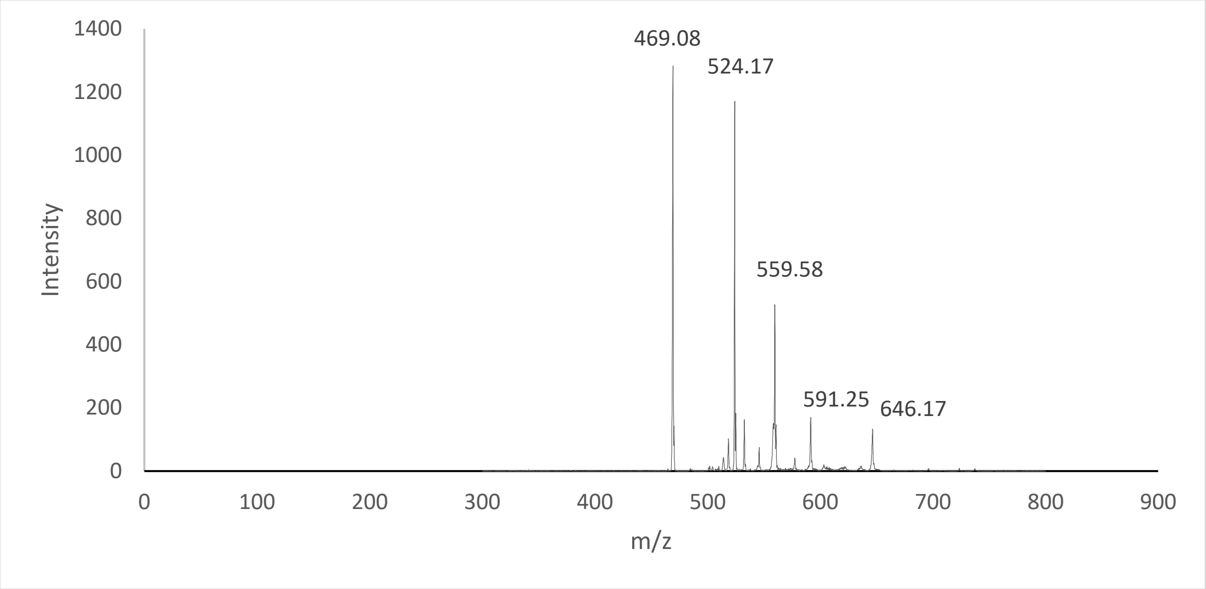
A 25 Ir(III)-4,7-dimethyl-1,10-phenanthroline dichloride with 1,1,2,2,3,3-d_6 1-butanol. Peak at 469.33 is the iridium phenantholine complex, 512.75 is the peak for C-H activation and 549.00 is the 1-butanol adduct



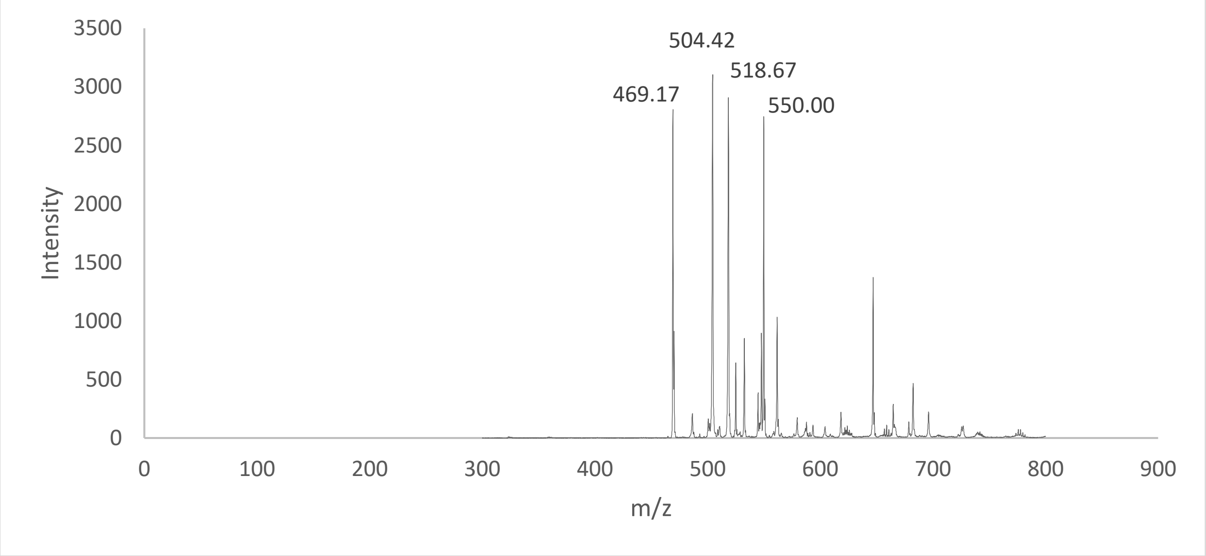
A 26 Ir(III)-4,7-dimethyl-1,10-phenanthroline dichloride with 4,4,4-d_3 1-butanol. Peak at 469.00 is the iridium phenanthroline complex, 509.83 is the peak for C-H activation, 545.67 and 622.33 are adducts of one and two 1-butanol molecules



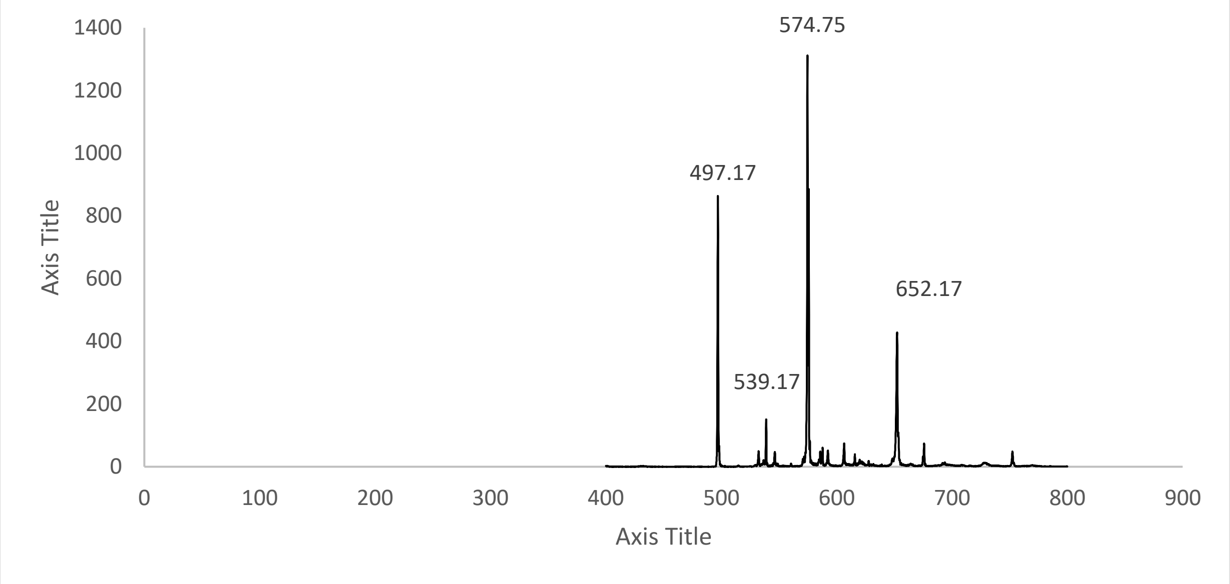
A 27 Ir(III)-4,7-dimethyl-1,10-phenanthroline dichloride with 3,3,4,4,4-d_5 1-methoxybutane. Peak at 469.33 is the iridium phenanthroline complex, 487.67 is a water adduct, 518.25, 532.50 and 547.67 are adducts of two, three and five oxygen atoms respectively, 525.17 is the peak for C-D activation and 561.50 is the 1-methoxybutane adduct



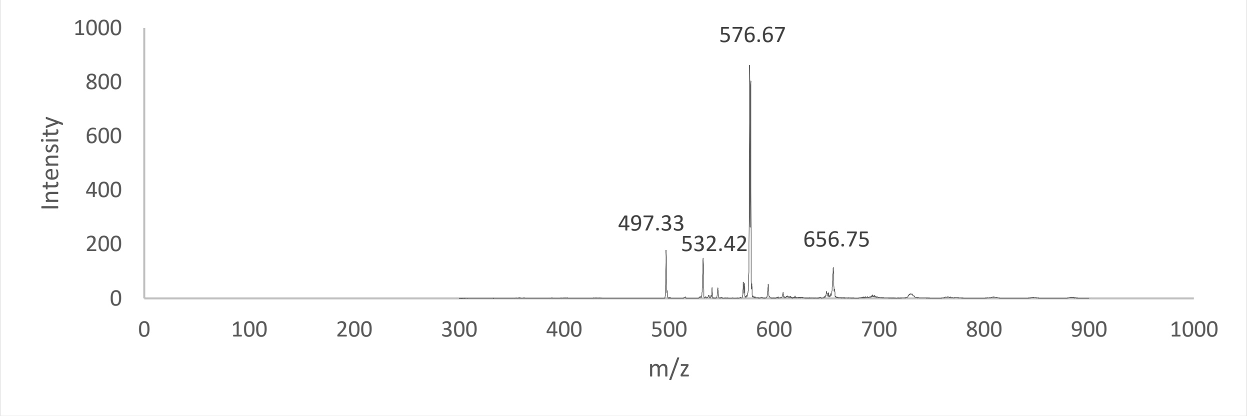
A 28 Ir(III)-4,7-dimethyl-1,10-phenanthroline dichloride with 4,4,4-d_3 1-methoxybutane. Peak at 469.08 is the iridium phenanthroline complex, 524.17 is the peak for C-H activation, 559.58 and 646.17 are adducts of one and two 1-methoxybutane molecules and 591.25 is and adduct for one 1-methoxybutane and one oxygen molecule



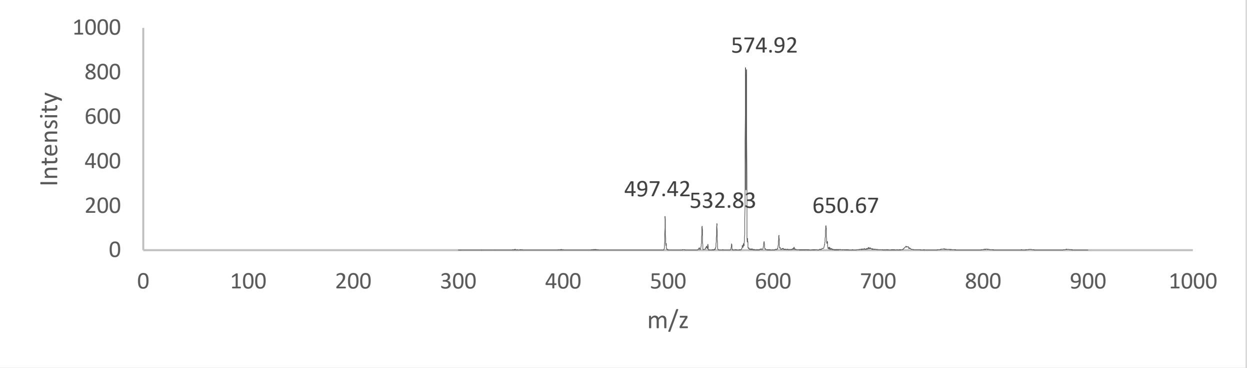
A 29 Ir(III)-4,7-dimethyl-1,10-phenanthroline dichloride with 1,1-d_2 butyl acetate. Peak at 469.17 is the iridium phenanthroline complex, 504.42 and 518.67 are adducts of two water molecules and one oxygen molecule respectively and 550.00 is the peak for C-D activation



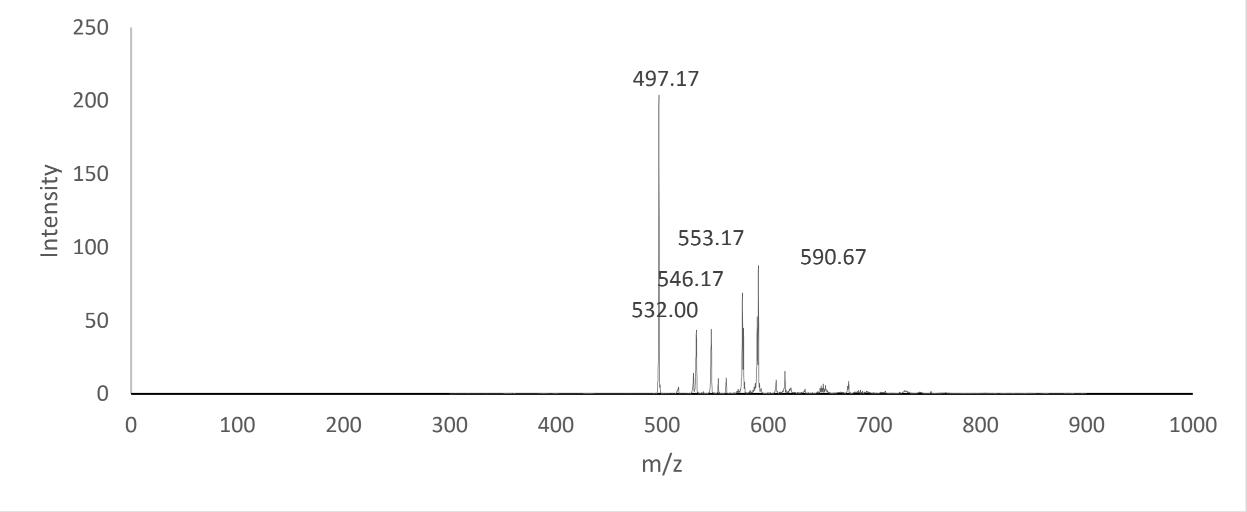
A 30 Ir(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride with 1,1,2,2-d_4 1-butanol. Peak at 497.17 is the iridium phenanthroline complex, 539.17 is the peak for C-H activation, 574.75 and 652.17 are adducts of one and two 1-butanol molecules respectively



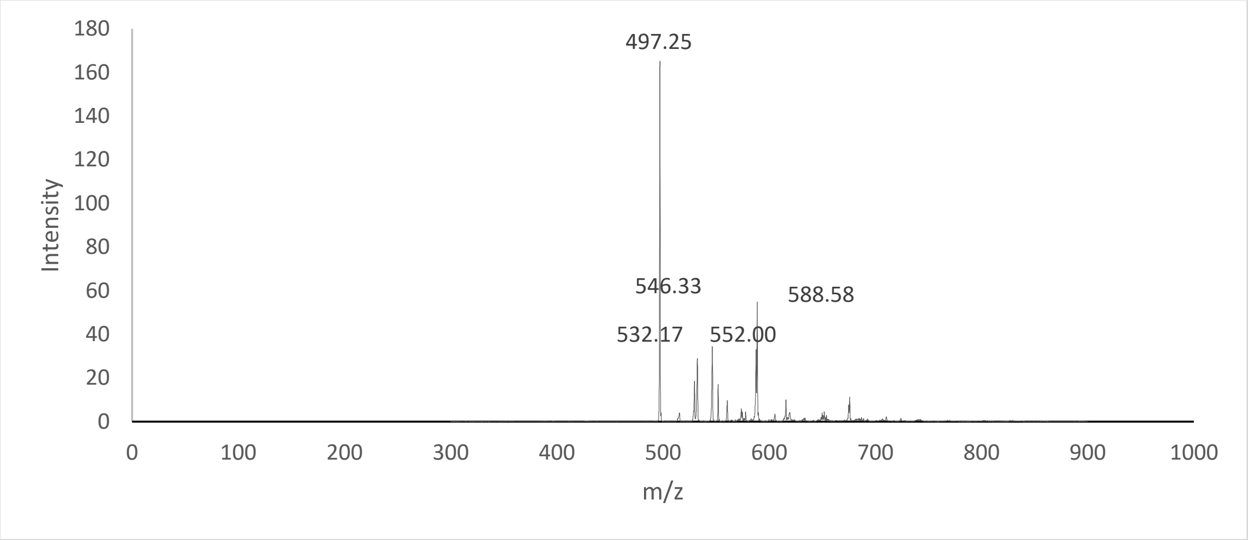
A 31 Ir(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride with 1,1,2,2,3,3-d_6 1-butanol. Peak at 497.33 is the iridium phenanthroline complex, 532.42 is an adduct of two water molecules, 576.67 and 656.75 are adducts of one and two 1-butanol molecules



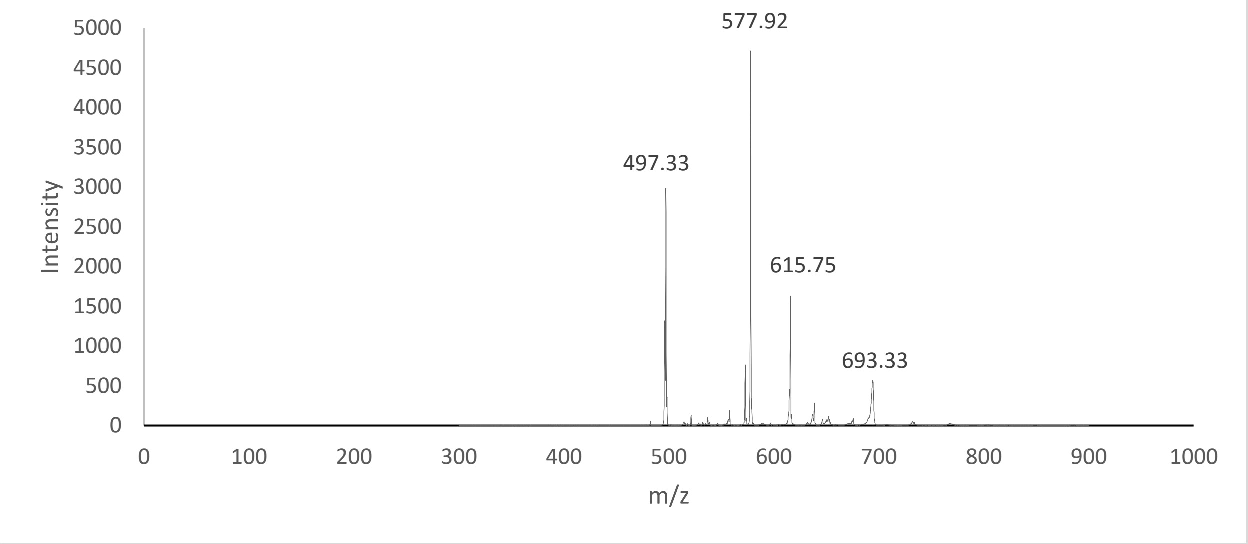
A 32 Ir(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride with 4,4,4-d$_3$ 1-butanol. Peak at 497.42 is the iridium phenanthroline complex, 532.83 is an adduct of two water molecules, 574.92 and 650.67 are adducts of one and two 1-butanol molecules



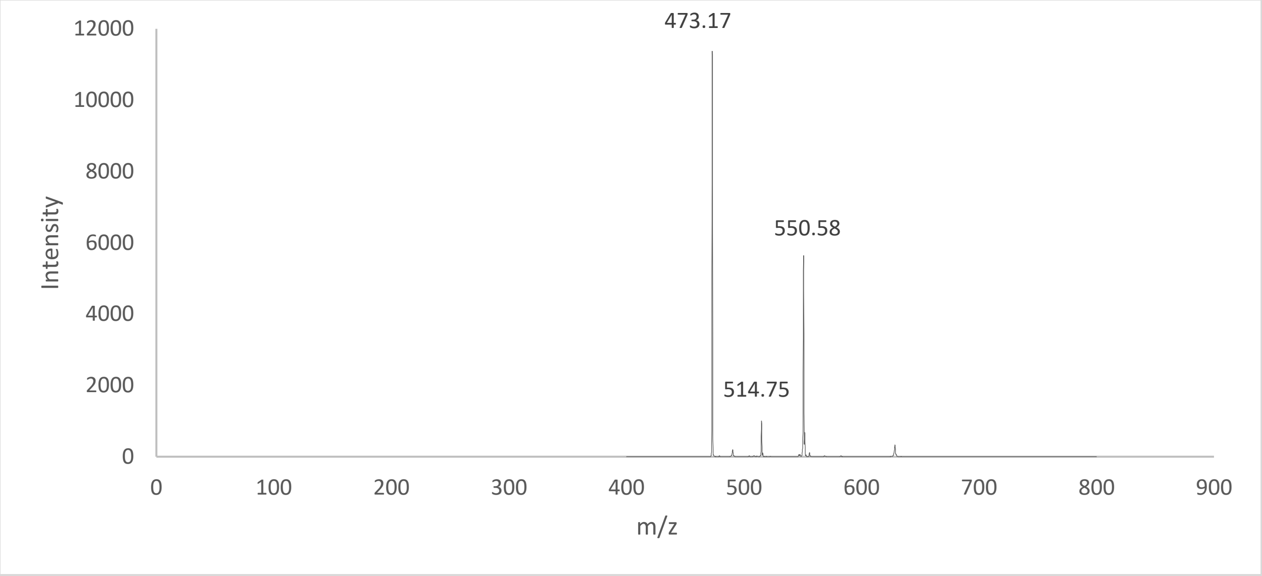
A 33 Ir(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride with 3,3,4,4,4-d$_5$ 1-methoxybutane. Peak at 497.17 is the iridium phenanthroline complex, 532.00 is an adduct of two water molecules, 546.17 is an adduct of three oxygen atoms, 553.17 is the peak for C-D activation and 590.67 is a 1-methoxybutane adduct



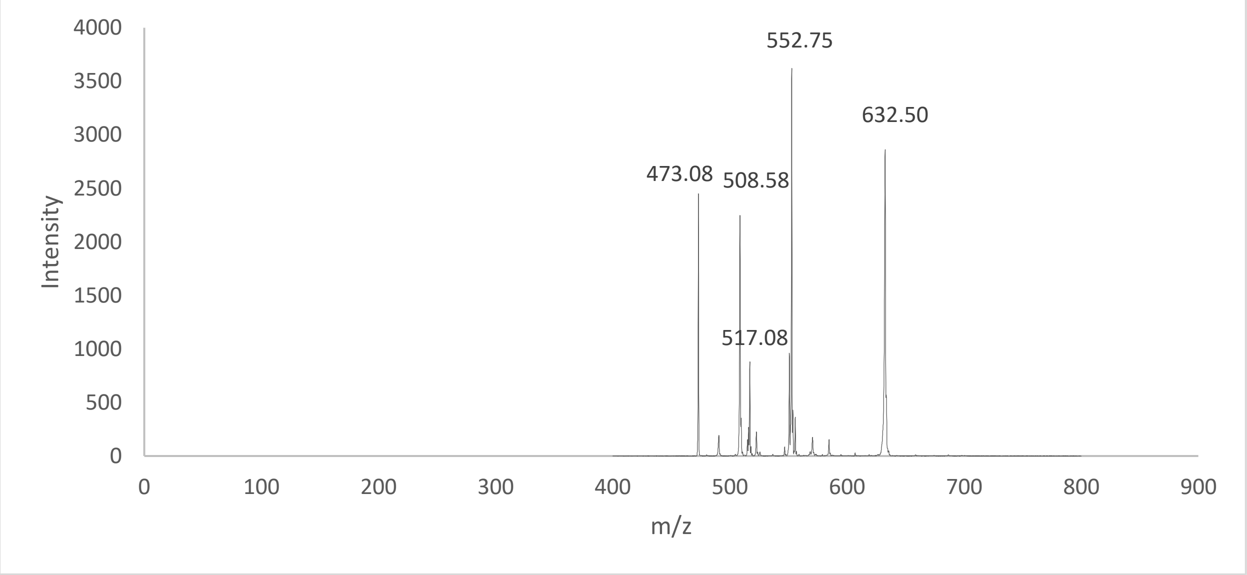
A 34 Ir(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride with 4,4,4-d_3 1-methoxybutane. Peak at 497.25 is the iridium phenanthroline complex, 532.17 is an adduct of two water molecules, 546.33 is an adduct of three oxygen atoms, 552.00 is the peak for C-H activation and 588.58 is a 1-methoxybutane adduct



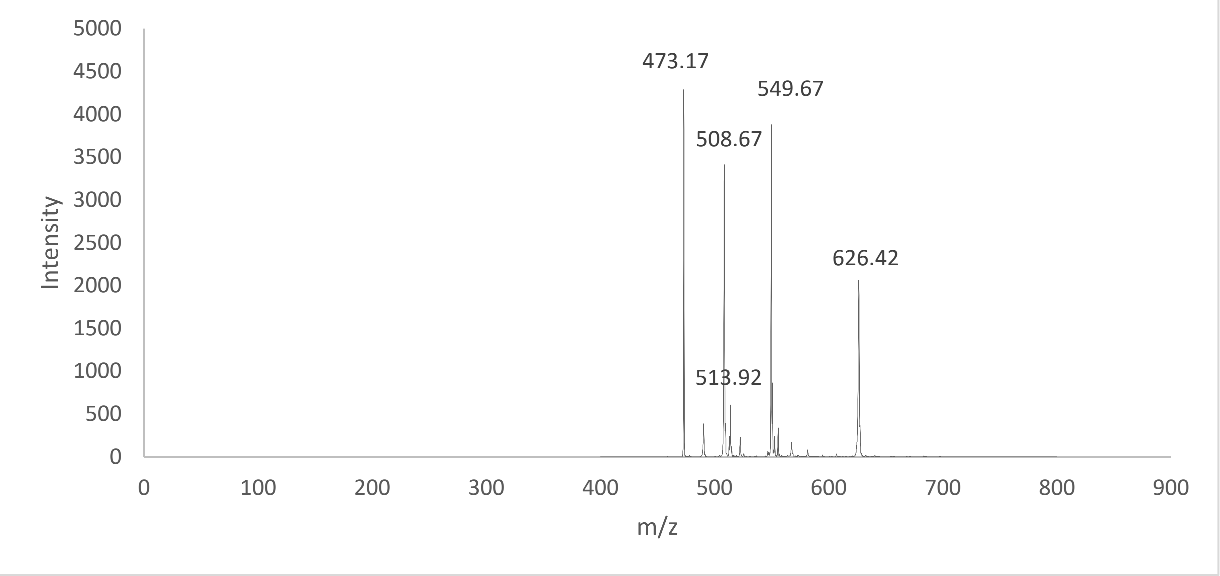
A 35 Ir(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride with 1,1-d_2 butyl acetate. Peak at 497.33 is the iridium phenanthroline complex, 577.92 is the peak for C-D activation, 693.33 is C-D activation from the second butyl acetate molecule and 615.75 is the butyl acetate adduct



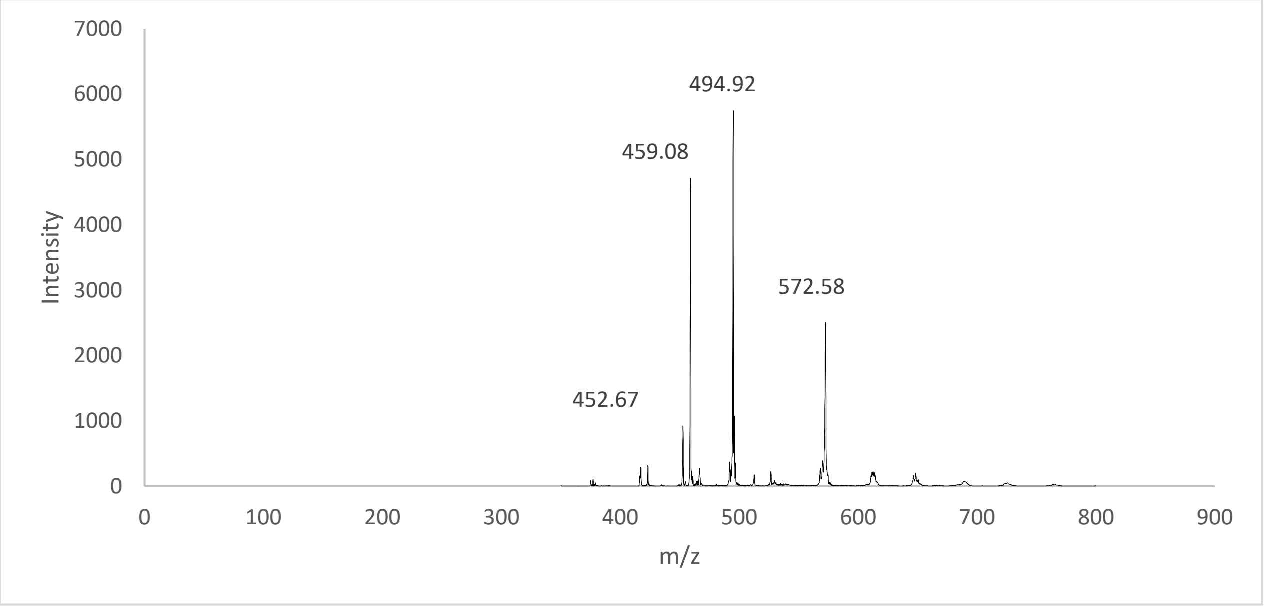
A 36 Ir(III)-4,7-dihydroxy-1,10-phenanthroline dichloride with 1,1-d_2 1-butanol. Peak at 473.17 is the iridium phenanthroline complex, 514.75 is the peak for C-H activation and 550.58 is the 1-butanol adduct



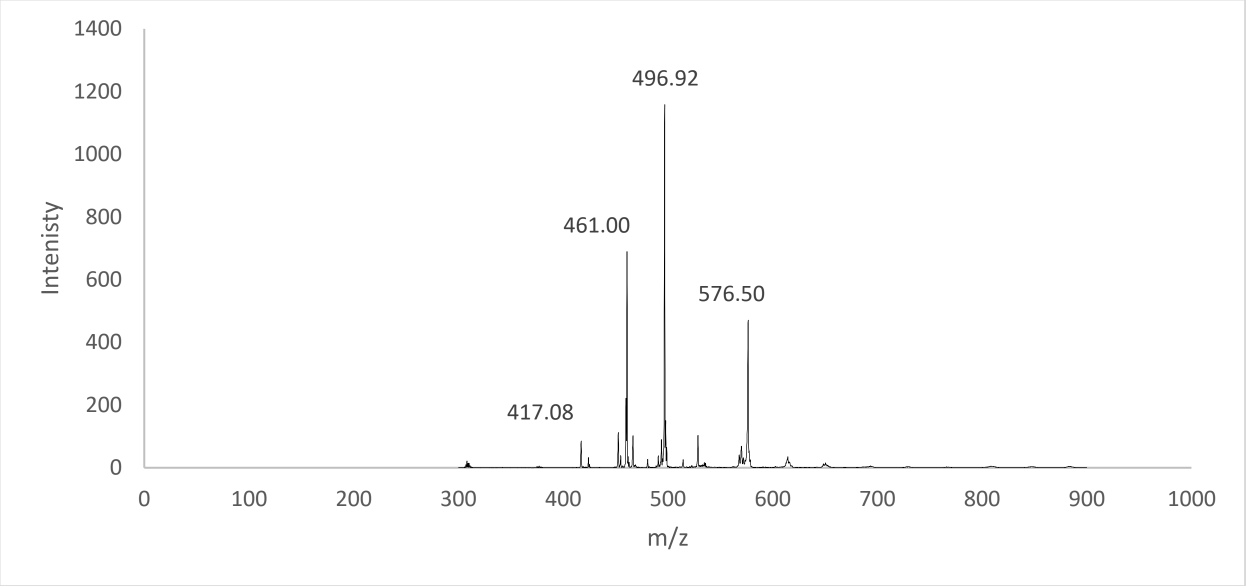
A 37 Ir(III)-4,7-dihydroxy-1,10-phenanthroline dichloride with 1,1,2,2,3,3-d_6 1-butanol. Peak at 473.08 is the iridium phenanthroline complex, 508.58 is an adduct of two water molecules, 517.08 is the peak for C-H activation, 552.75 and 632.50 are adducts of one and two 1-butanol molecules respectively.



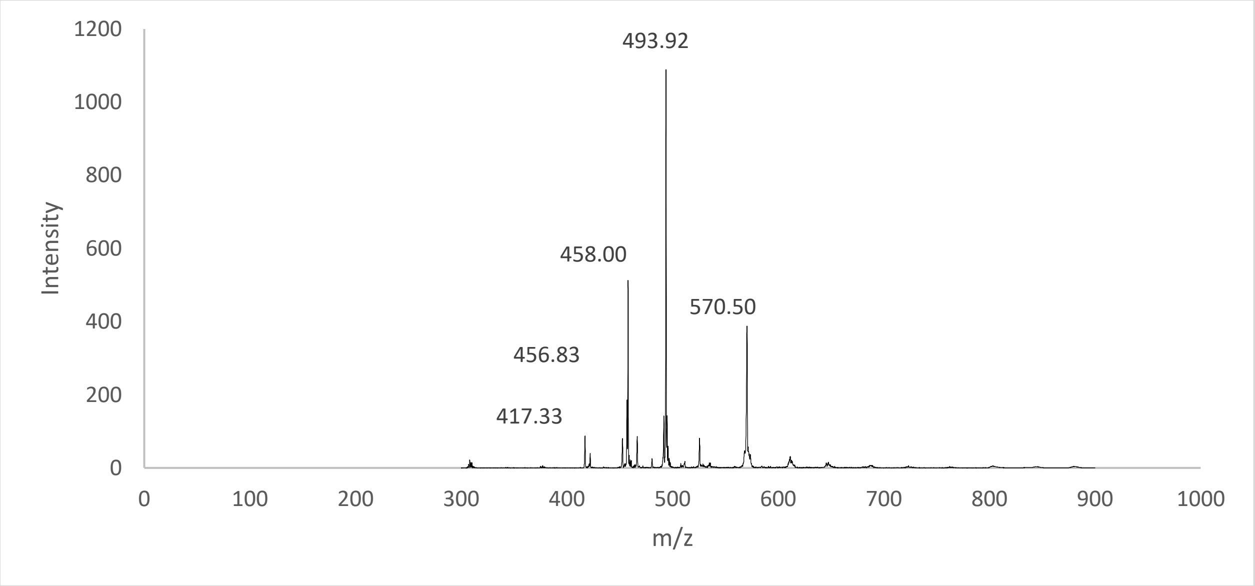
A 38 Ir(III)-4,7-dihydroxy-1,10-phenanthroline dichloride with 4,4,4-d_3 1-butanol. Peak at 473.17 is the iridium phenanthroline complex, 508.67 is an adduct of two water molecules, 513.92 is the peak for C-H activation, 549.67 and 626.42 are adducts of one and two 1-butanol molecules respectively



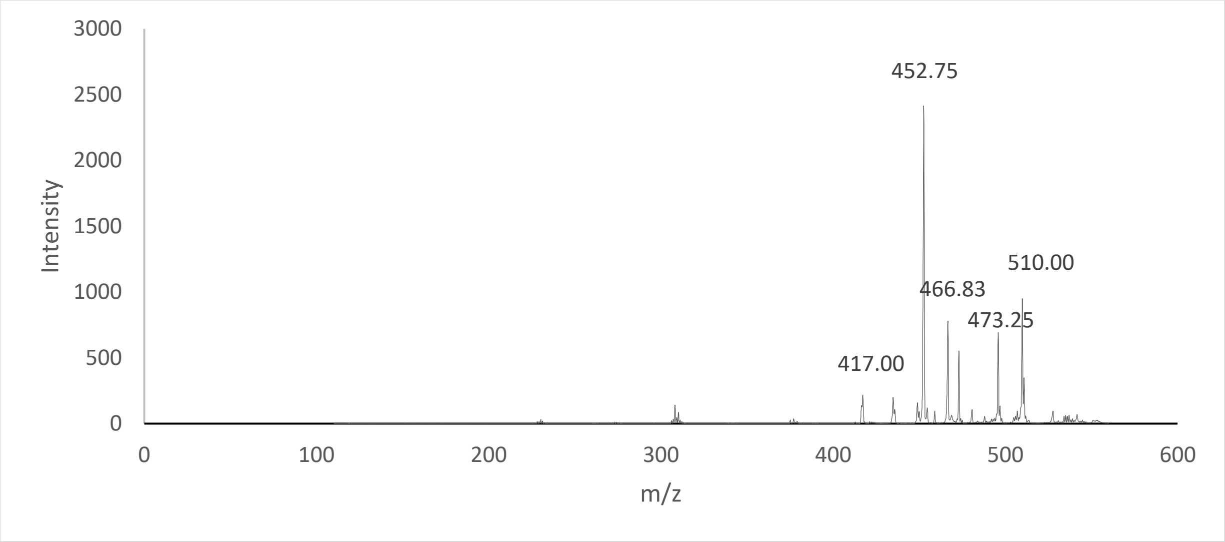
A 39 Ir(III)-4,4'-bipyridine dichloride with 1,1,2,2-d_4 1-butanol. Peak at 452.67 is an adduct of two water molecules, 459.08 C-H activation, 494.92 and 572.58 are adducts of one and two 1-butanol molecules respectively



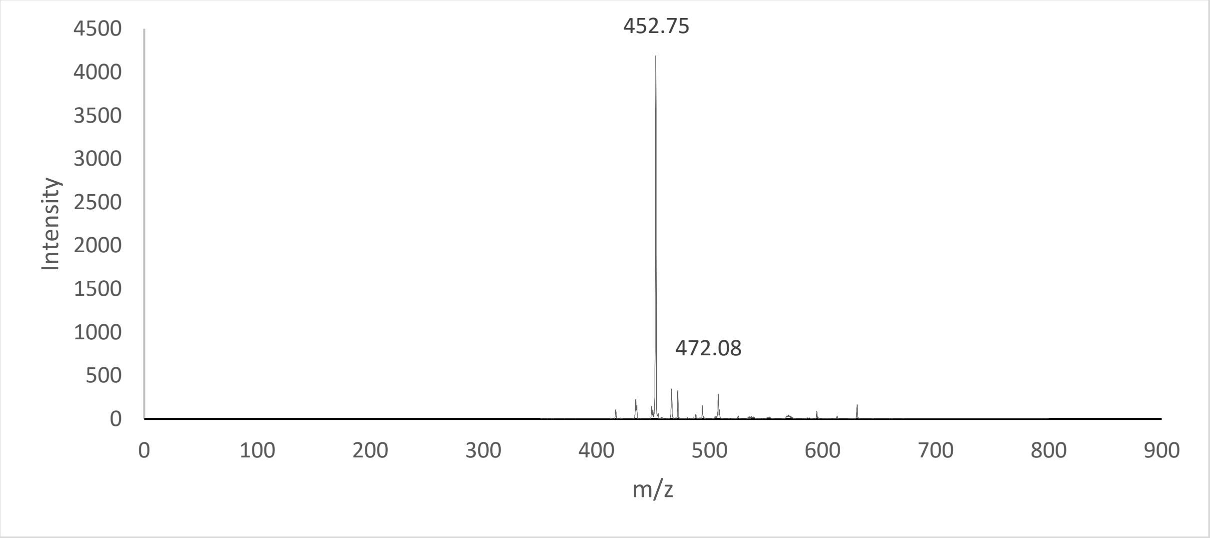
A 40 Ir(III)-4,4'-bipyridine dichloride with 1,1,2,2,3,3-d_6 1-butanol. Peak at 417.08 is the iridium bipyridine complex, 461 is the peak for C-H activation,496.92 and 576.50 are the peaks for adducts of one and two 1-butanol molecules respectively



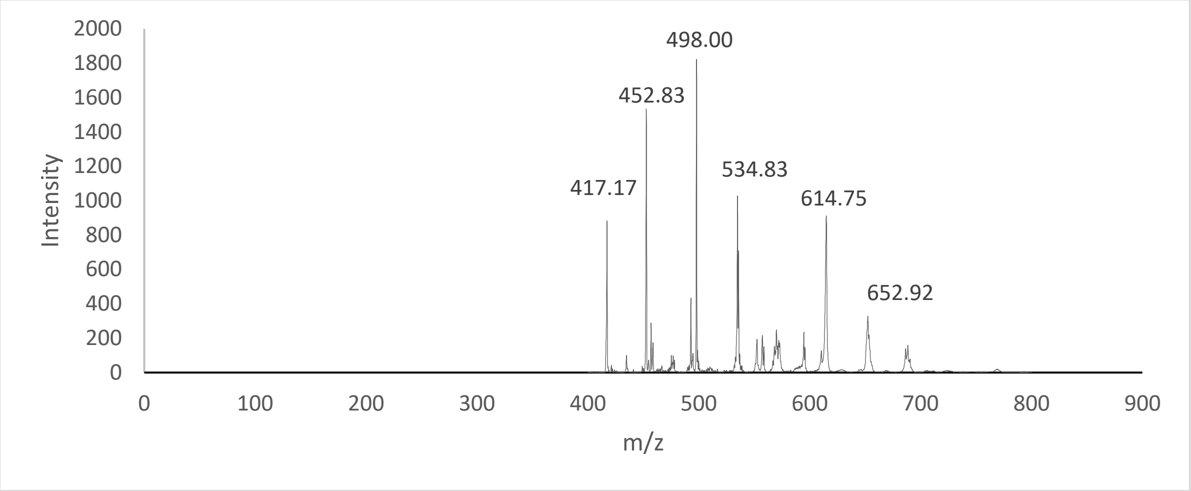
A 41 Ir(III)-4,4'-bipyridine dichloride with 4,4,4-d_3 1-butanol. Peak at 417.08 is the iridium bipyridine complex, 461 is the peak for C-H activation,496.92 and 576.50 are the peaks for adducts of one and two 1-butanol molecules respectively



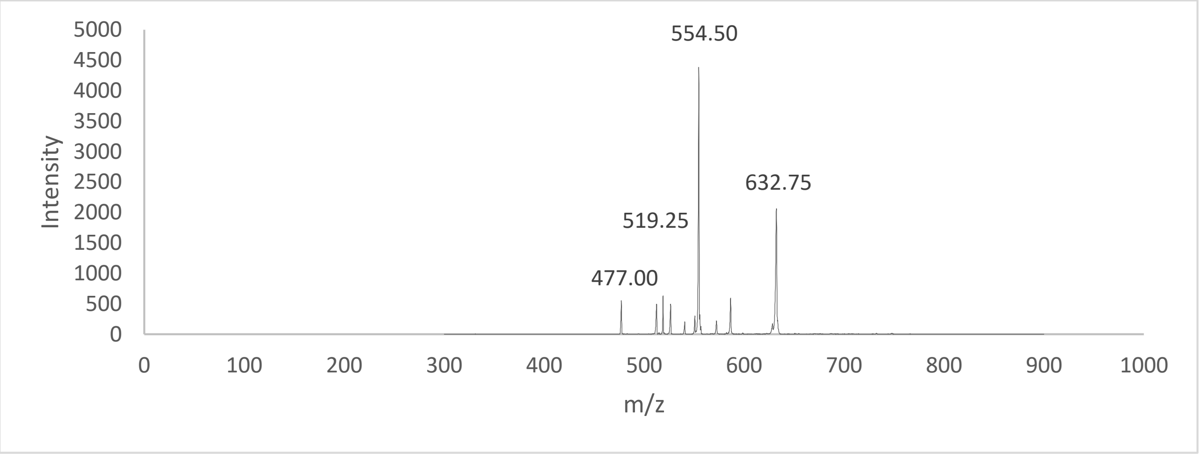
A 42 Ir(III)-4,4'-bipyridine dichloride with 3,3,4,4,4-d_5 1-methoxybutane. Peak at 417.00 is the iridium bipyridine complex, 452.75 is the adduct of two water molecules, 466.83 is an adduct of one MeOH adduct and one water molecules, 473.25 is the peak for C-D activation and 510.00 is the adduct of a 1-methoxybutane molecule



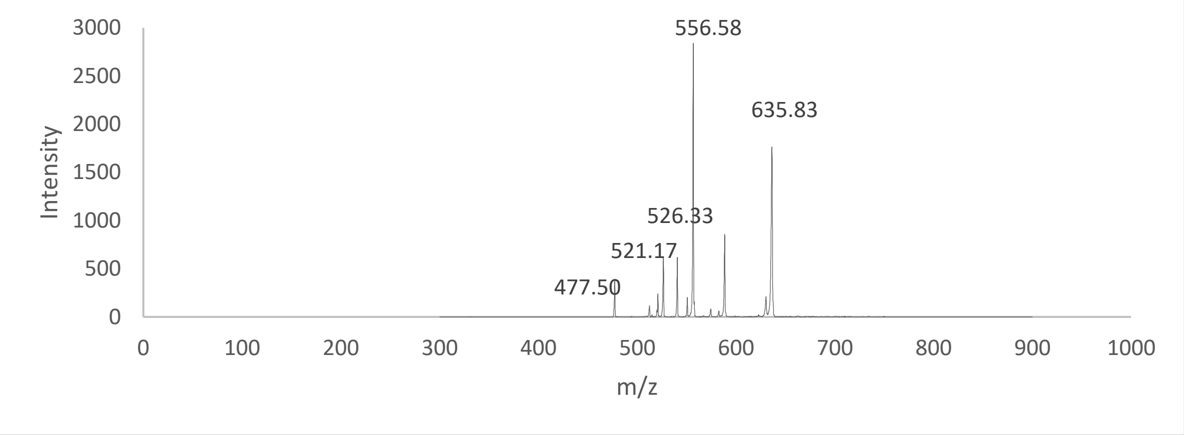
A 43 Ir(III)-4,4'-bipyridine dichloride with 4,4,4-d_3 1-methoxybutane. The peak at 452.75 is the adduct of two water molecules and 472.08 is the peak for C-H activation



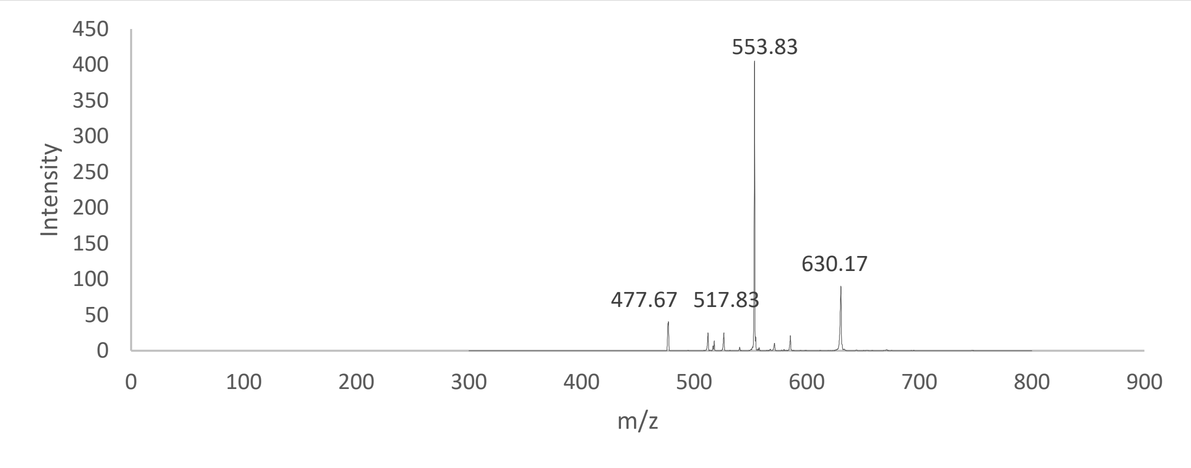
A 44 Ir(III)-4,4'-bipyridine dichloride with 1,1-d_2 butyl acetate. The peak at 417.17 is the iridium bipyridine complex, 452.83 is the adduct of two water molecules, 498.00 is peak for C-D activation, 534.83 is a butyl acetate adduct, 614.75 is C-D activation from the second butyl acetate molecule and 652.92 is an adduct of two butyl acetate molecules



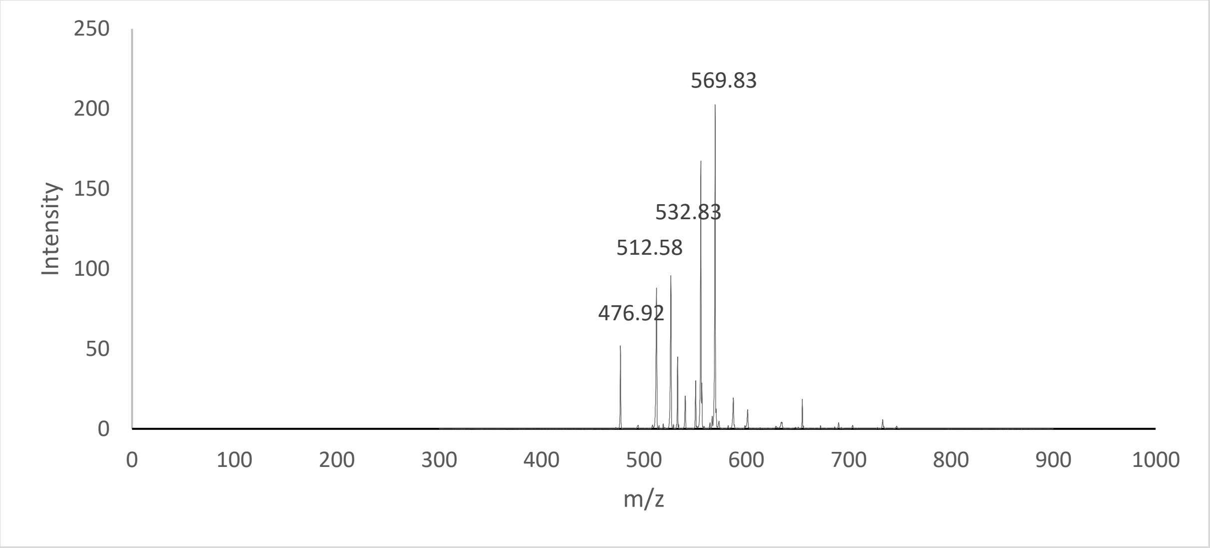
A 45 Ir(III)-2,2'-dimethoxy-4,4'-bipyridine dichloride with 1,1,2,2-d_4 1-butanol. The peak at 477.00 is the iridium bipyridine complex, 519.25 is the peak for C-H activation, 554.50 and 632.75 are the peaks for one and two 1-butanol molecules respectively



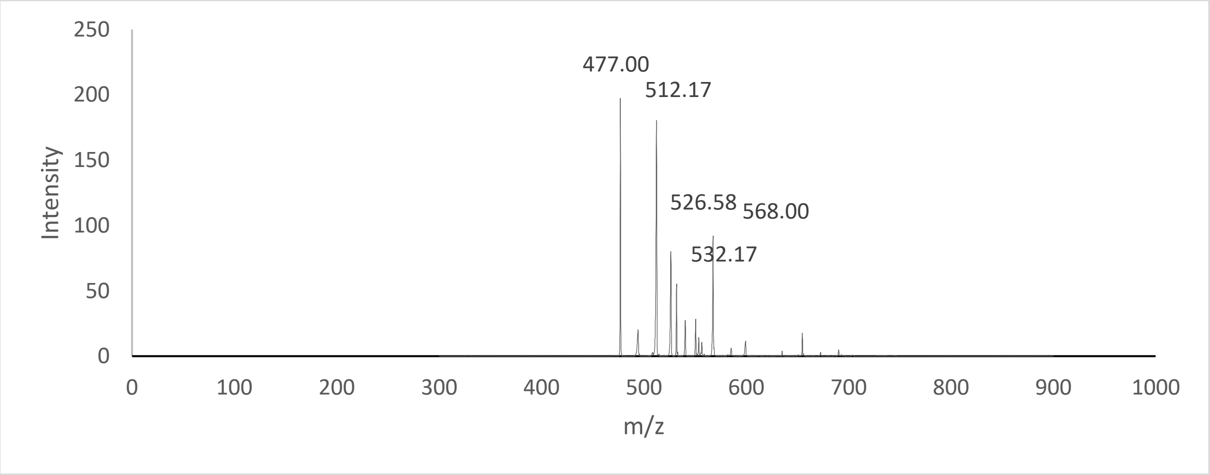
A 46 Ir(III)-2,2’-dimethoxy-4,4’-bipyridine dichloride with 1,1,2,2,3,3-d_6 1-butanol. The peak at 477.50 is the iridium bipyridine complex, 521.17 is the peak for C-H activation, 526.33 is a water and MeOH adduct and 556.58 and 635.83 are one and two 1-butanol molecules respectively



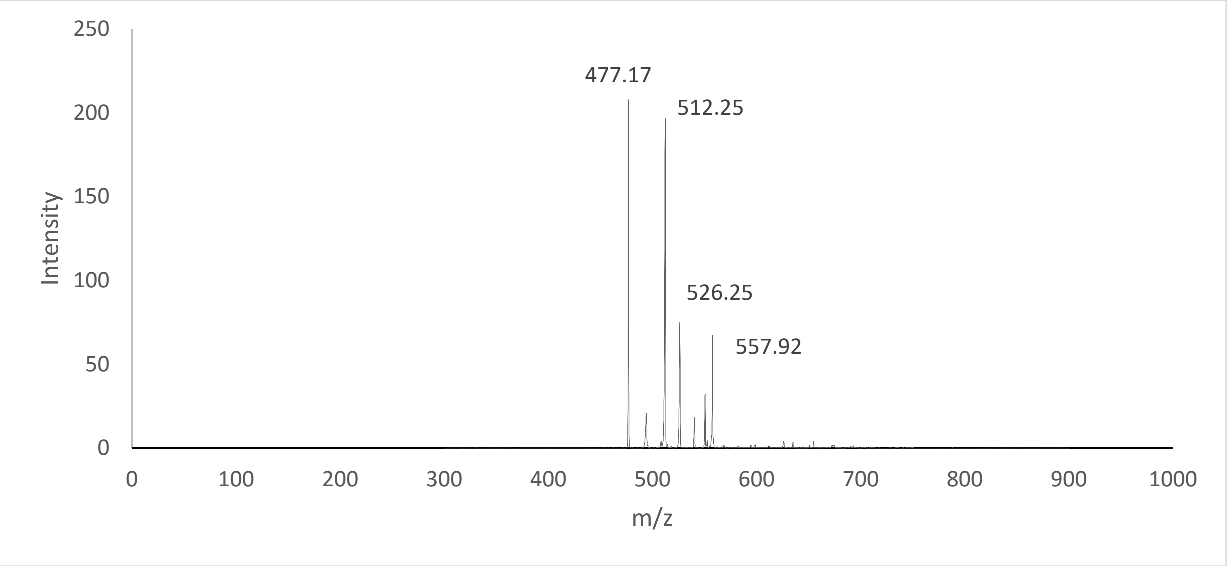
A 47 Ir(III)-2,2’-dimethoxy-4,4’-bipyridine dichloride with 4,4,4-d_3 1-butanol. The peak at 477.67 is the iridium bipyridine complex, 517.83 is the peak for C-H activation, 553.83 and 630.17 are adducts of one and two 1-butanol molecules respectively



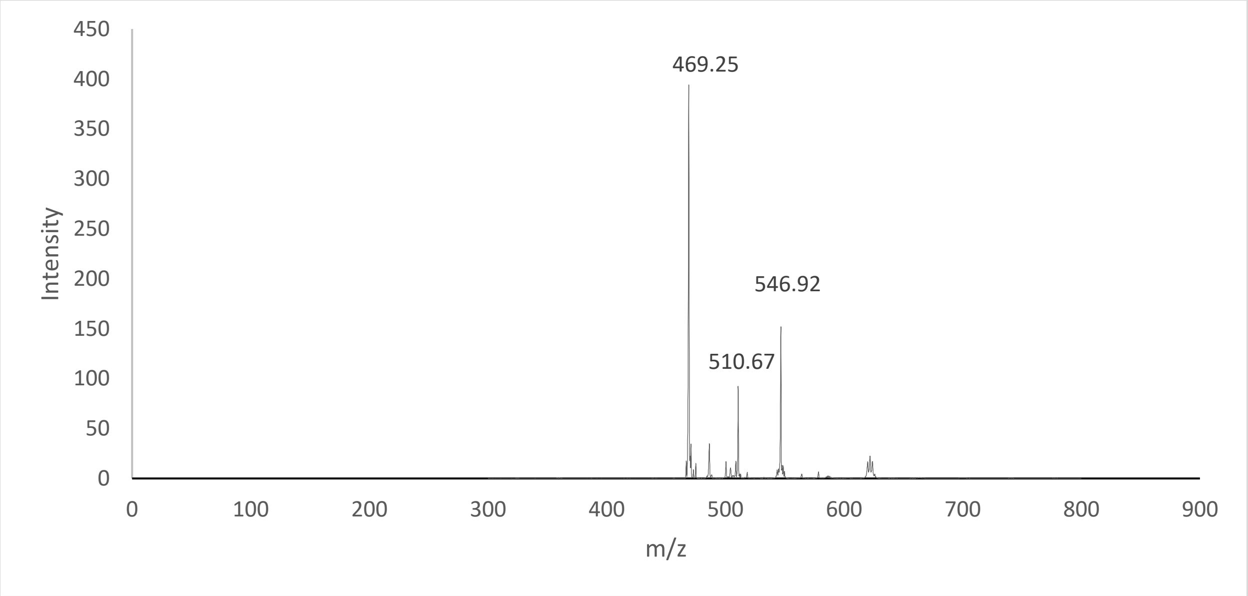
A 48 Ir(III)-2,2'-dimethoxy-4,4'-bipyridine dichloride with 3,3,4,4,4-d_5 1-methoxybutane. The peak at 476.92 is the iridium bipyridine complex, 512.58 is the adduct of two water molecules, 532.83 is the peak for C-D activation and 569.83 is the 1-methoxybutane adduct



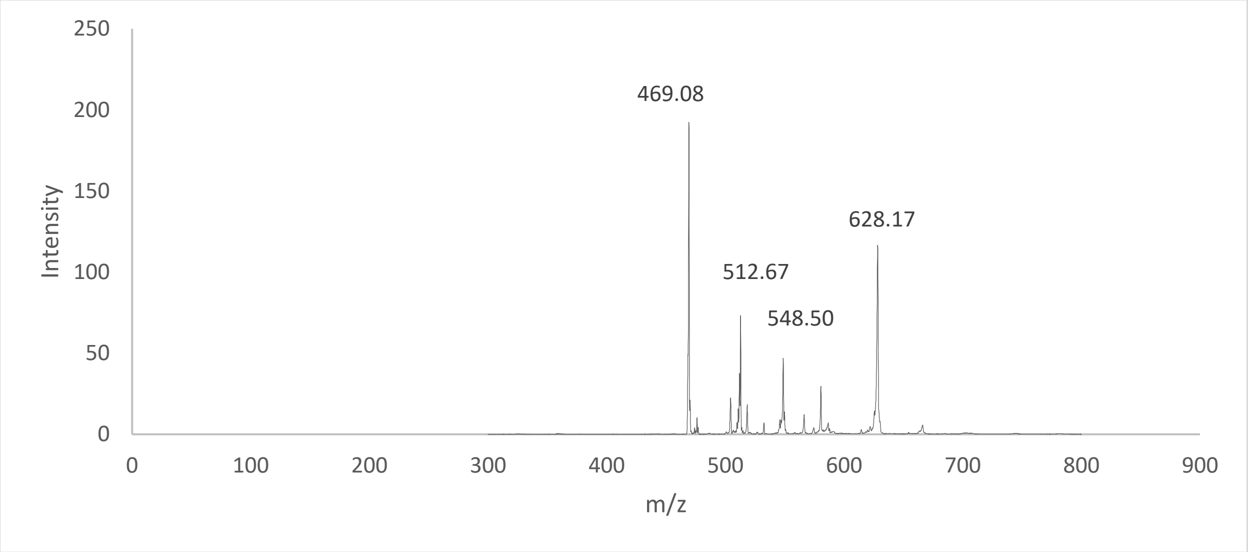
A 49 Ir(III)-2,2'-dimethoxy-4,4'-bipyridine dichloride with 4,4,4-d_3 1-methoxybutane. The peak at 477.00 is the iridium bipyridine complex, 512.17 is the adduct of two water molecules, 532.17 is the peak for C-H activation and 568.00 is the 1-methoxybutane adduct



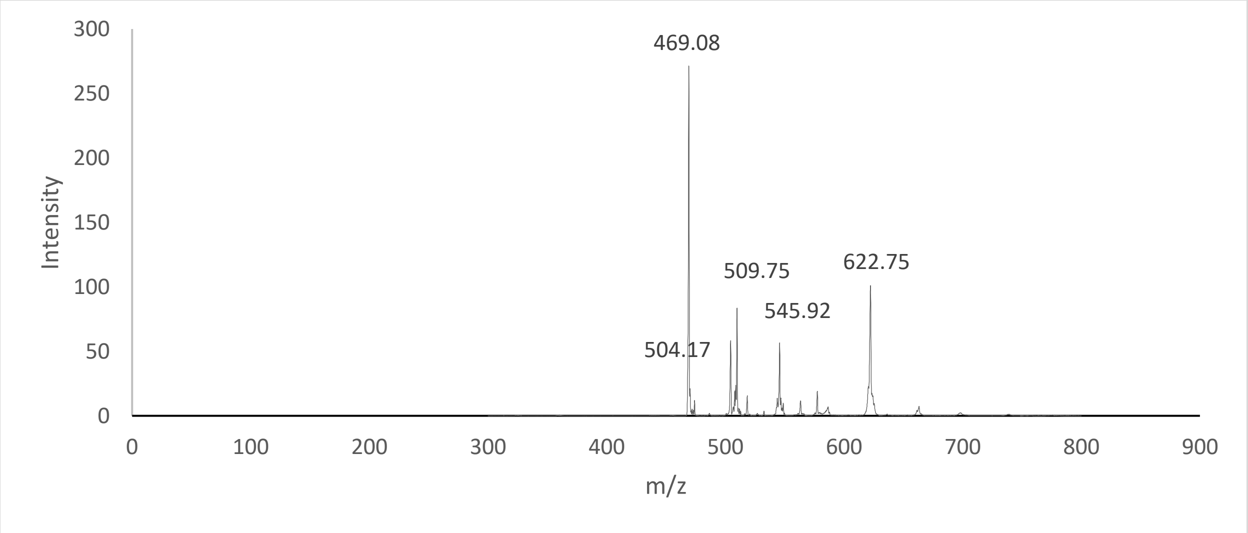
A 50 Ir(III)-2,2'-dimethoxy-4,4'-bipyridine dichloride with 1,1-d_2 butyl acetate. The peak at 477.17 is the iridium bipyridine complex, 512.25 is the adduct of two water molecules, 526.25 is and adduct of water and methanol and 557.92 is the peak for C-D activation



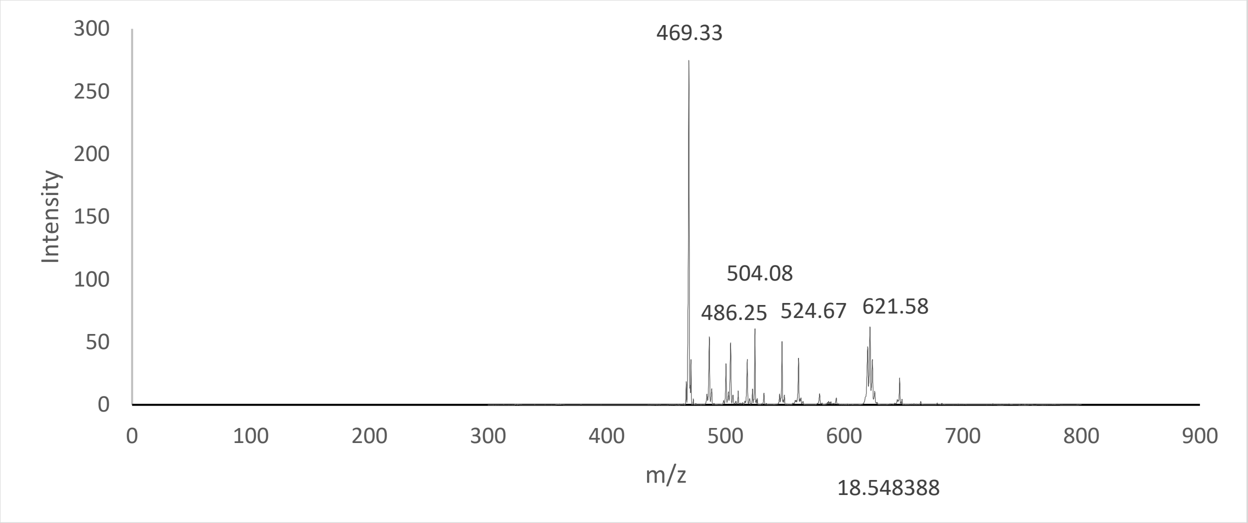
A 51 Ir(III)-2,2'-dicyano-4,4'-bipyridine dichloride with 1,1,2,2-d_4 1-butanol. The peak at 469.25 is the iridium bipyridine complex, 510.67 is the peak for C-H activation and 546.92 is a 1-butanol adduct



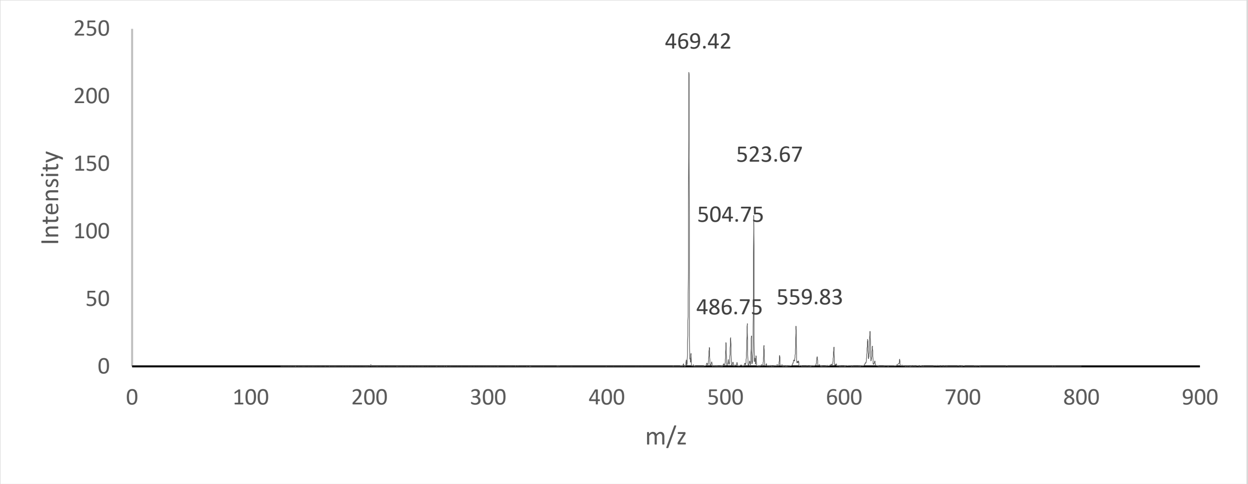
A 52 Ir(III)-2,2'-dicyano-4,4'-bipyridine dichloride with 1,1,2,2,3,3-d_6 1-butanol. The peak at 469.08 is the iridium bipyridine complex, 512.67 is the peak for C-H activation, 548.50 and 628.17 are adducts of one and two 1-butanol molecules respectively



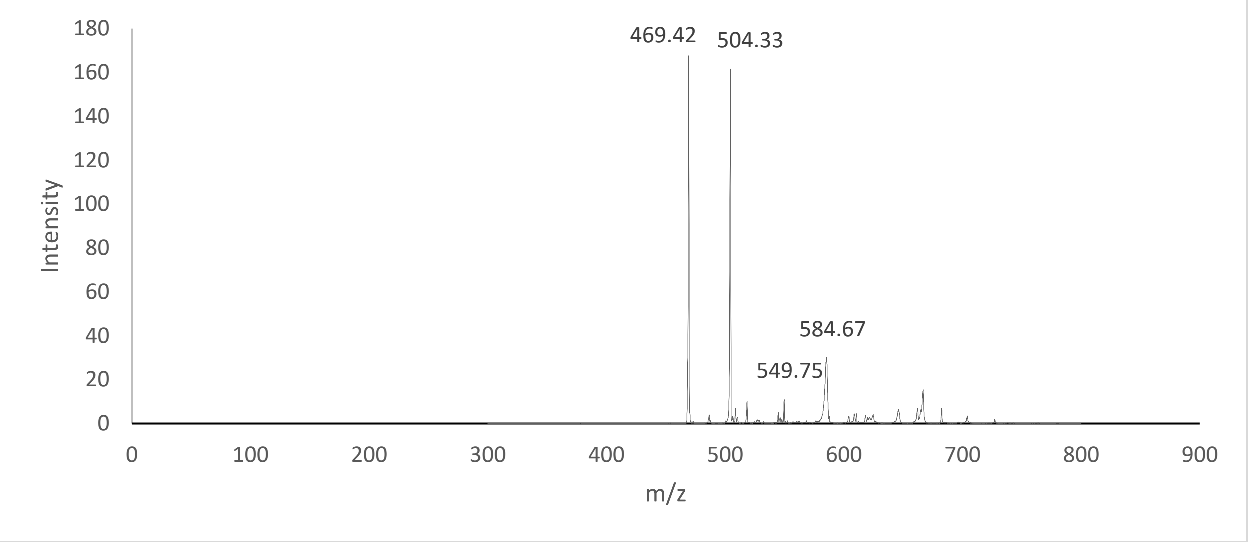
A 53 Ir(III)-2,2'-dicyano-4,4'-bipyridine dichloride with 4,4,4-d_3 1-butanol. The peak at 469.08 is the iridium bipyridine complex, 504.17 is a water adduct, 509.75 is the peak for C-H activation, peaks 545.92 and 622.75 are one and two 1-butanol molecules respectively



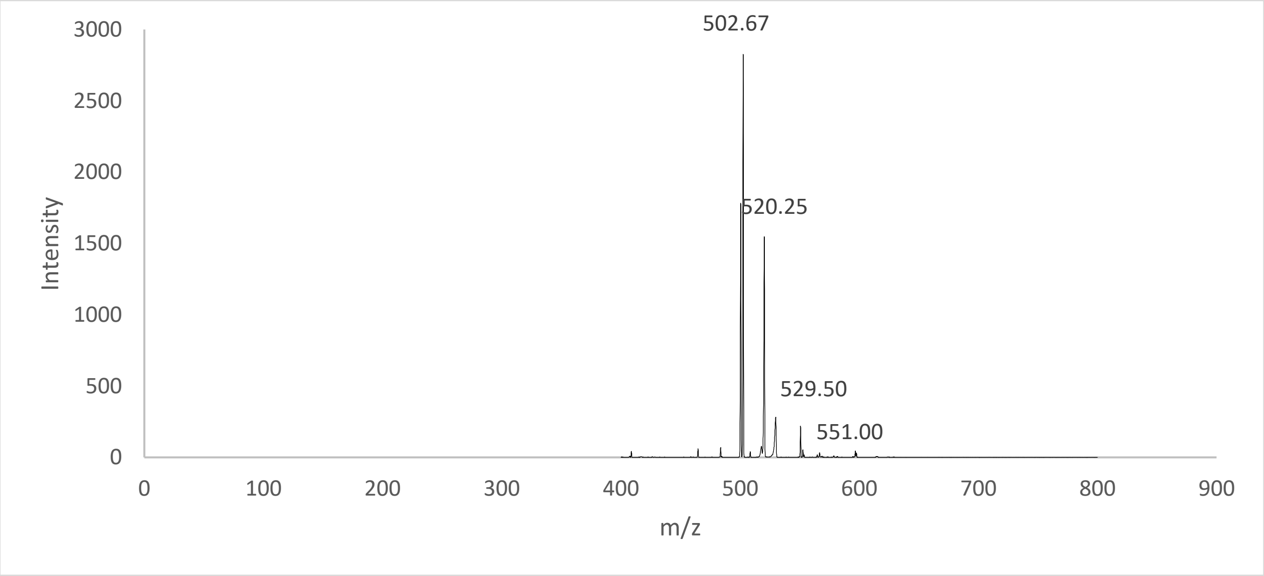
A 54 Ir(III)-2,2'-dicyano-4,4'-bipyridine dichloride with 3,3,4,4,4-d_5 1-methoxybutane. The peak at 469.33 is the iridium bipyridine complex, 486.25 and 504.08 are adducts of one and two water molecules respectively, 524.67 is the peak for C-D activation and peak 621.58 is C-D activation from a second 1-methoxybutane molecule



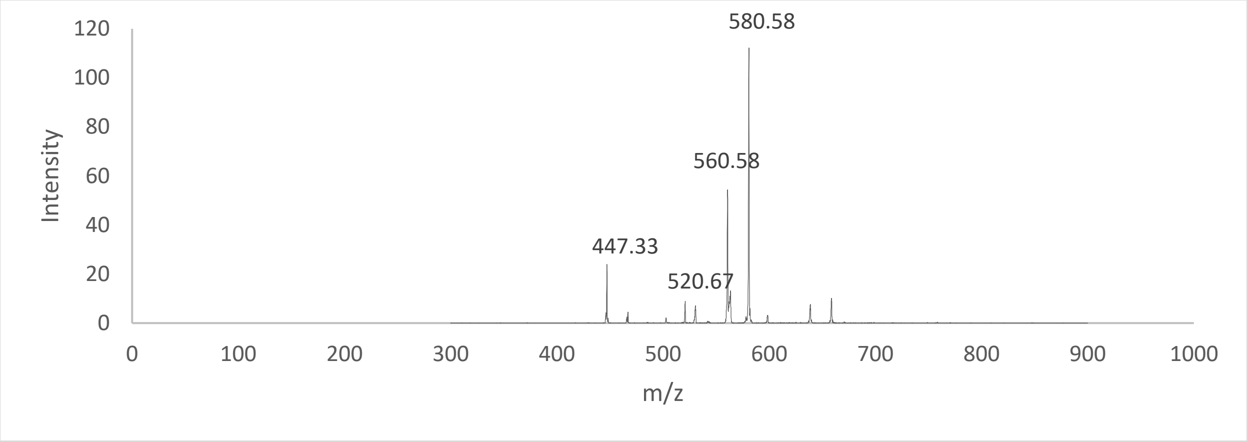
A 55 Ir(III)-2,2'-dicyano-4,4'-bipyridine dichloride with 4,4,4-d_3 1-methoxybutane. The peak at 469.42 is the iridium bipyridine complex, 486.75 and 504.75 are adducts of one and two water molecules respectively, 523.67 is the peak for C-H activation and peak 559.83 is a 1-methoxybutane adduct



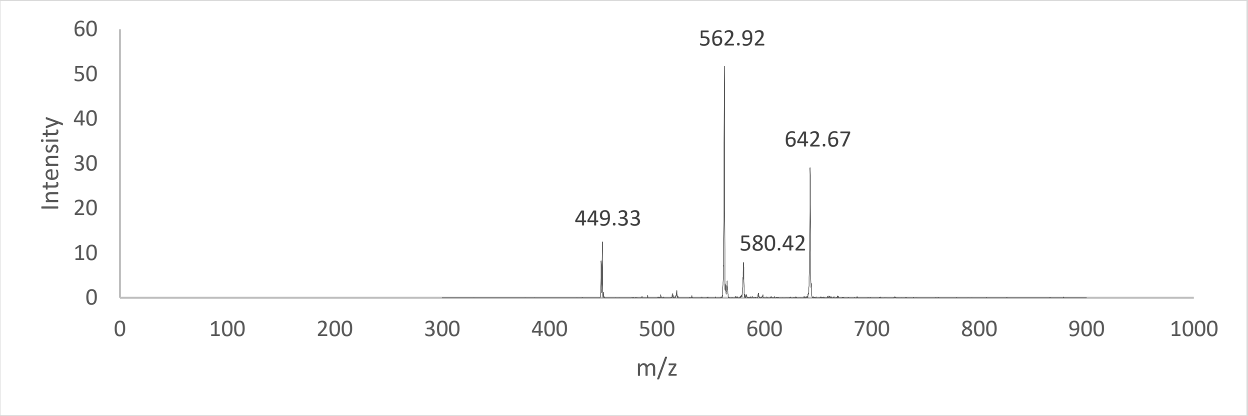
A 56 Ir(III)-2,2'-dicyano-4,4'-bipyridine dichloride with 1,1-d_2 butyl acetate. The peak at 469.42 is the iridium bipyridine complex, 504.33 is an adduct of two water molecules, 549.75 is the peak for C-D activation and 584.67 is a butyl acetate adduct



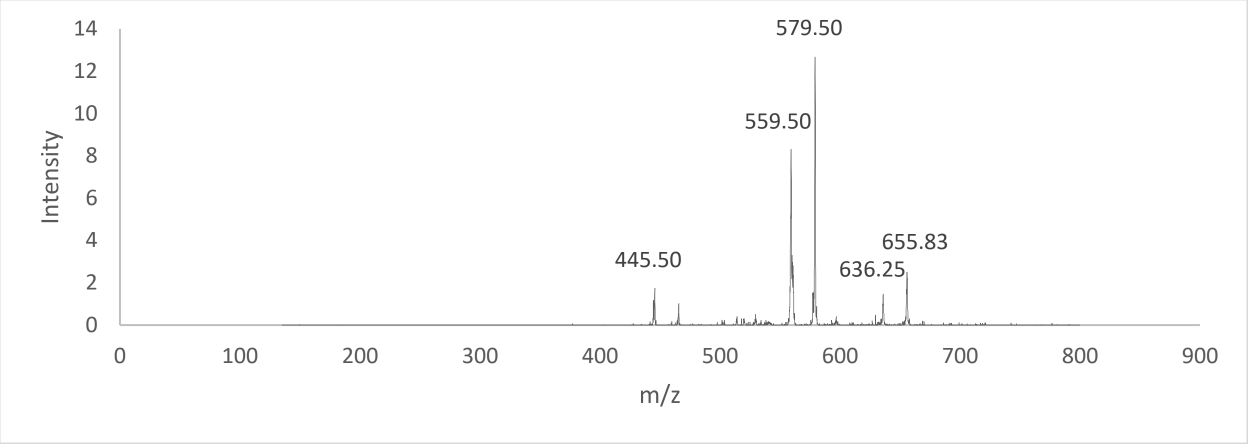
A 57 CID of the 597 peak (peak for Ir(III)-1,10-phenanthroline di(trifluoroacetate). Peak at 502.67 is the water adduct of Ir(II)-1,10-phenanthroline trifluoroacetate, 520.25 is an adduct of two water molecules of the mono trifluoroacetate complex, 529.50 and 551.00 is the loss of a CF_3 radical and decarboxylation from the di(trifluoroacetate) complex respectively



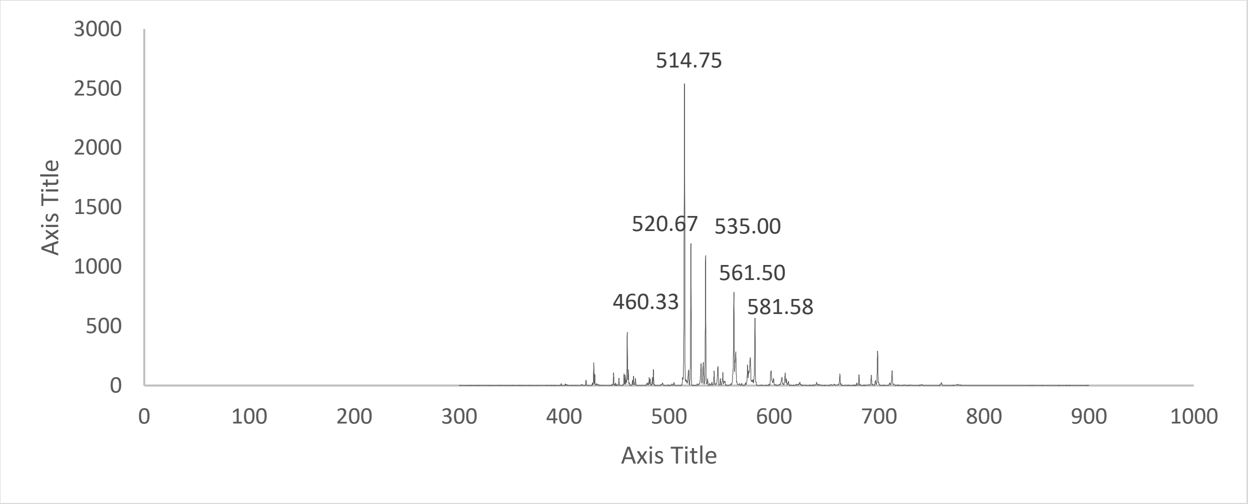
A 58 Ir(II)-1,10-phenanthroline trifluoroacetate with 1,1,2,2-d_4 1-butanol. The peak at 447.33 is the peak for C-H activation, 520.67 is the water adduct of the iridium complex, 560.58 is the 1-butanol adduct of the monotrifluoroacetate iridium complex and 580.58 is an adduct of one 1-butanol and one water molecules of the iridium complex



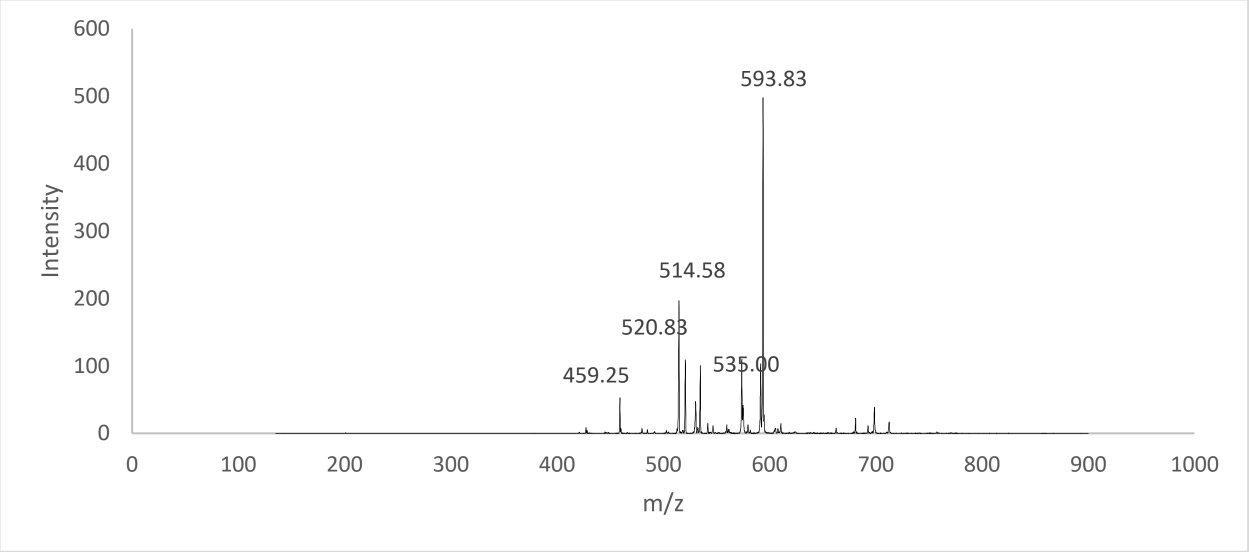
A 59 Ir(II)-1,10-phenanthroline trifluoroacetate with 1,1,2,2,3,3-d_6 1-butanol. The peak at 449.33 is the peak for C-H activation, 562.92 is a 1-butanol adduct, 580.42 is an adduct of one 1-butanol molecule and water molecule and 642.67 is an adduct of two 1-butanol molecules



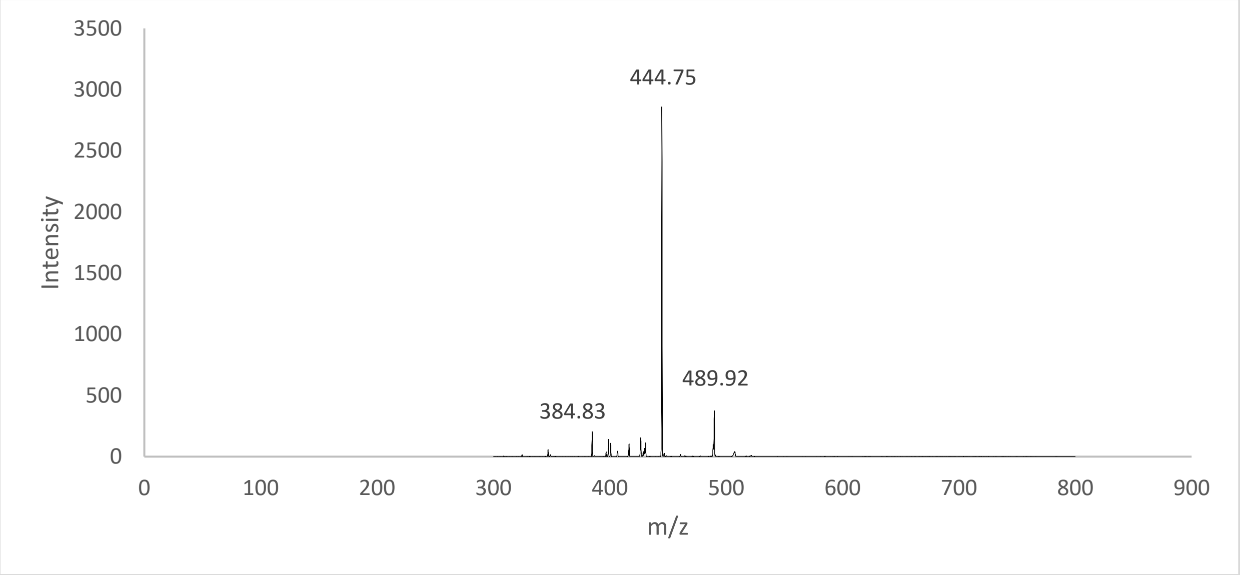
A 60 Ir(II)-1,10-phenanthroline trifluoroacetate with 4,4,4-d_3 1-butanol. The peak at 445.50 is the peak for C-H activation, 559.50 and 636.25 are adducts of one and two 1-butanol molecules respectively, 579.50 and 655.83 are adducts of a water molecule and one and two 1-butanol molecules respectively



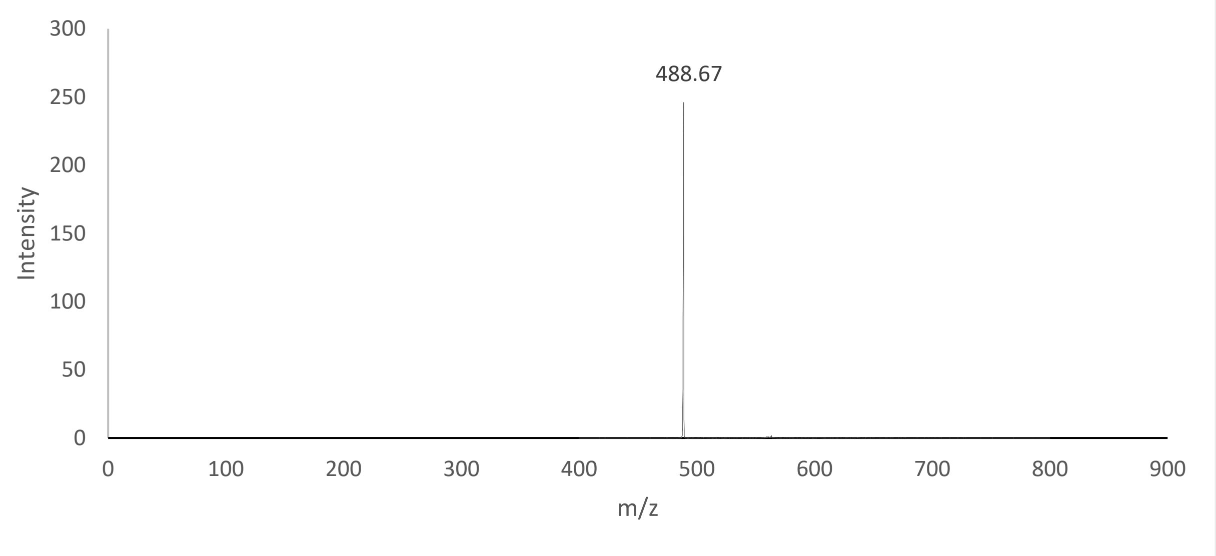
A 61 Ir(II)-1,10-phenanthroline trifluoroacetate with 3,3,4,4,4-d_5 1-methoxybutane. The peak at 460.33 is the peak for C-D activation, 514.75 is a methanol adduct, 520.67 and 535.00 are adducts of two water molecules and a water and methanol molecule respectively and peaks 561.50 and 581.58 are adducts of one water molecule with two methanol molecules and two methanol and additional water molecules respectively



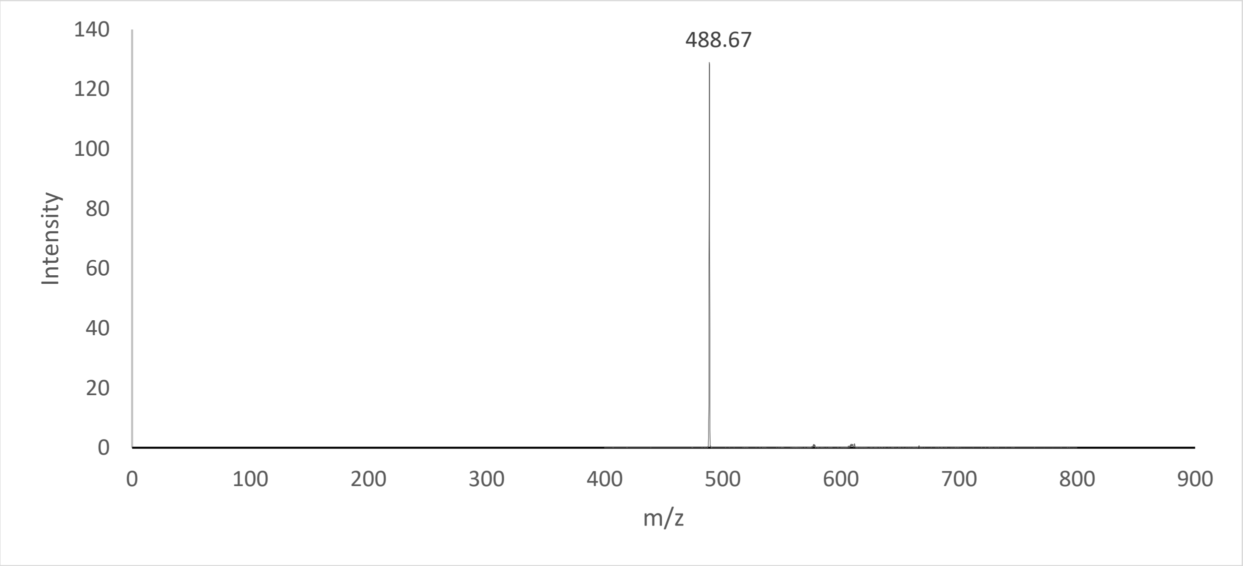
A 62 Ir(II)-1,10-phenanthroline trifluoroacetate with 4,4,4-d_3 1-methoxybutane. The peak at 459.25 is the peak for C-D activation, 514.58 is a methanol adduct, 520.83 and 535.00 are adducts of two water molecules and a water and methanol molecule respectively and 593.83 is a 1-methoxybutane adduct



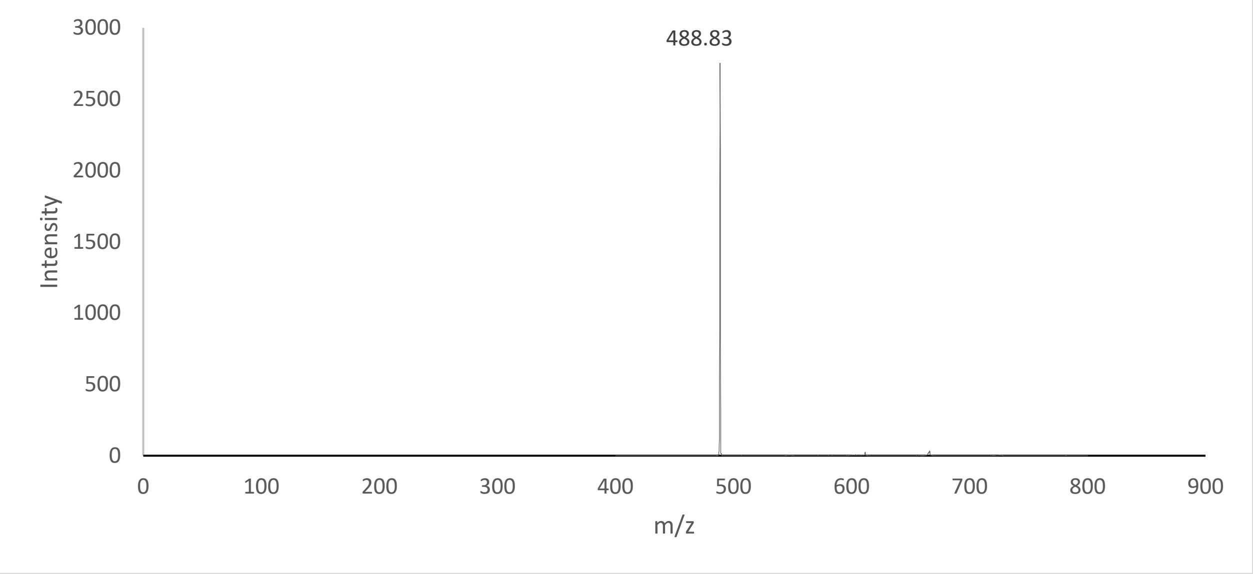
A 63 CID of the 489.92 peak (peak for iridum(III)-1,10-phenanthroline diacetate). Peak at 444.75 is decarboxylation of the iridium complex



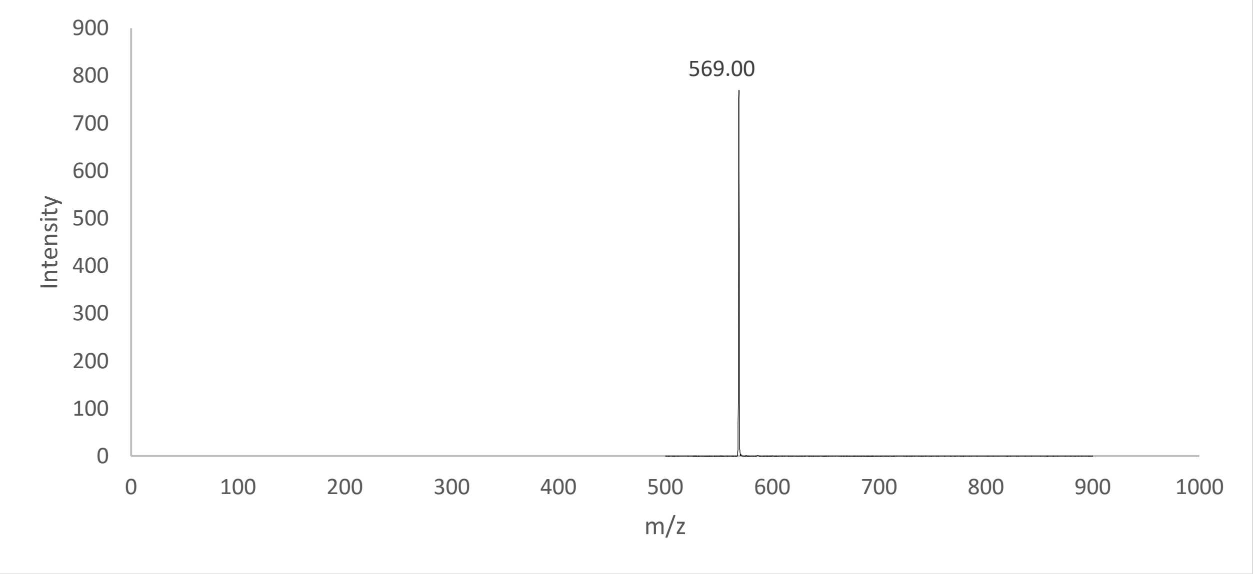
A 64 Ir(II)-1,10-phenanthroline diacetate with 1-butanol. The peak at 488.67 is the peak for the iridium diacetate complex



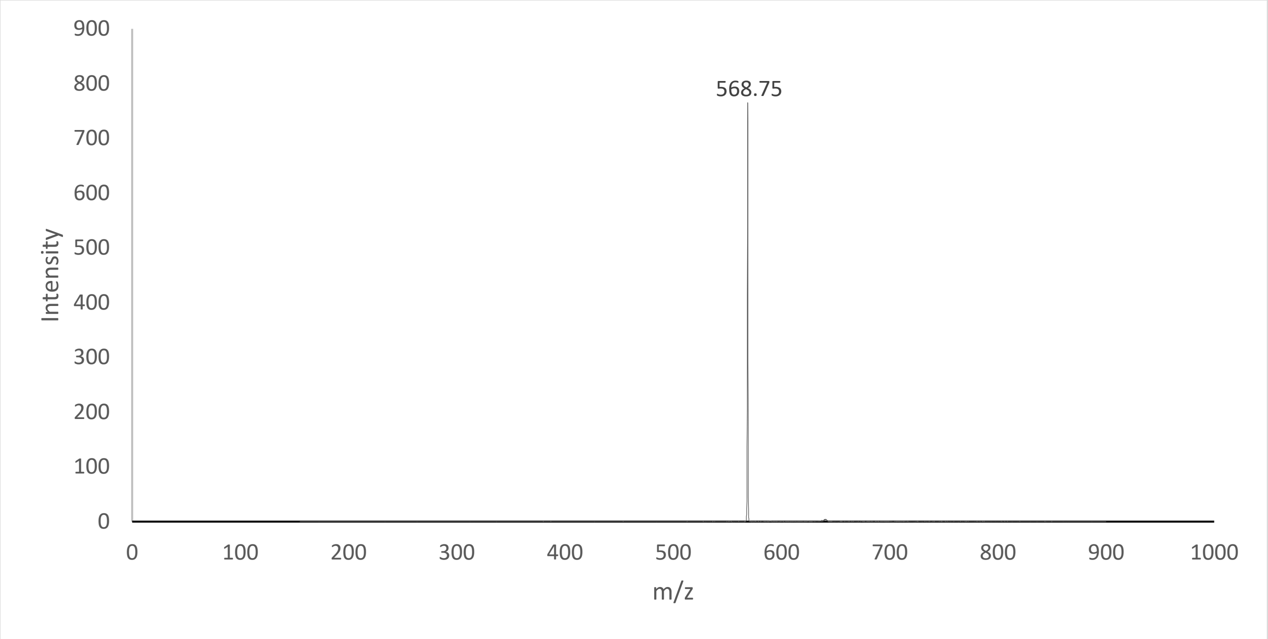
A 65 Ir(II)-1,10-phenanthroline diacetate with 1-methoxybutane. The peak at 488.67 is the peak for the iridium diacetate complex



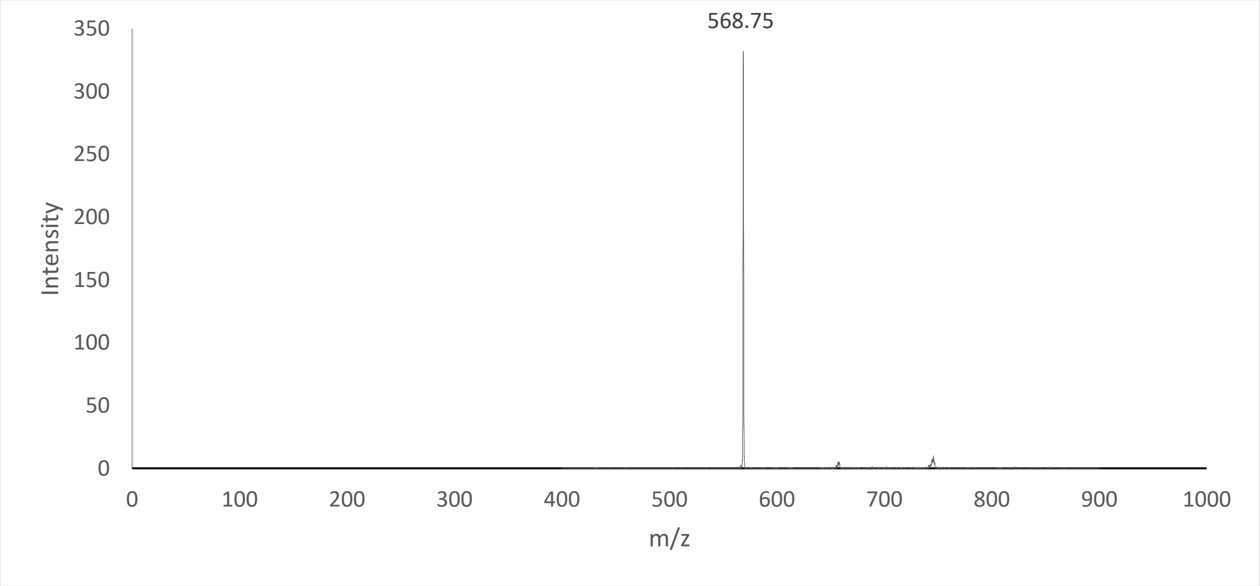
A 66 Ir(II)-1,10-phenanthroline diacetate with butyl acetate. The peak at 488.83 is the peak for the iridium diacetate complex



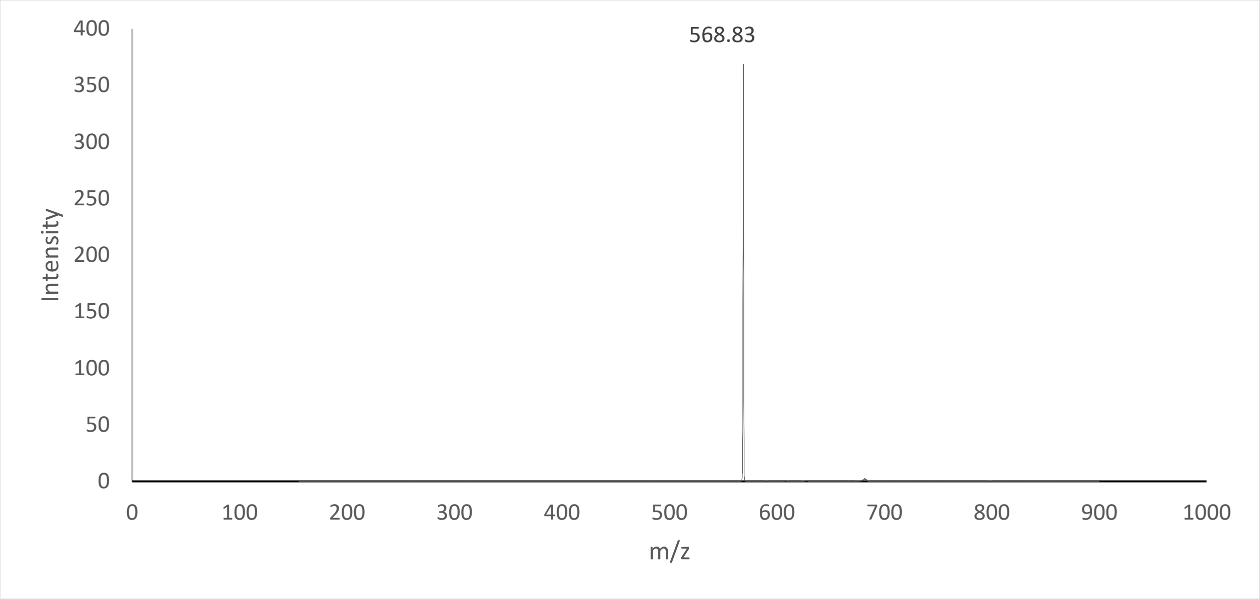
A 67 Peak for iridium(III)-1,10-phenanthroline di(acetylacetonate)



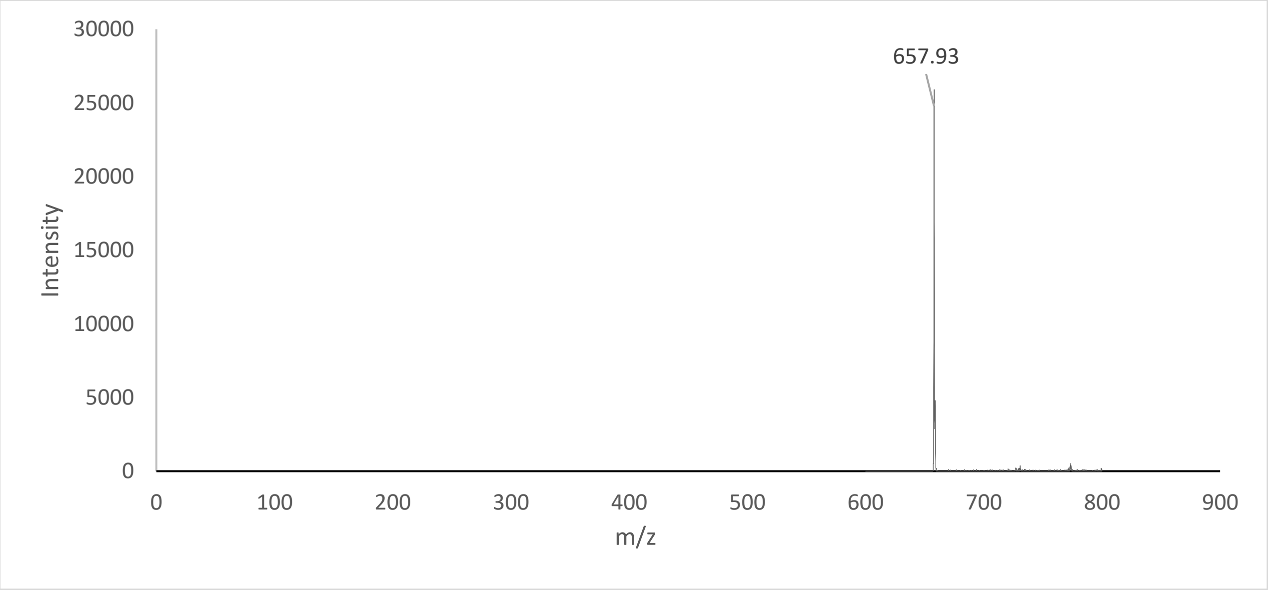
A 68 Ir(III)-1,10-phenanthroline di(acetylacetonate) with 1-butanol. The peak at 568.75 is the peak for the iridium acetylacetonate complex



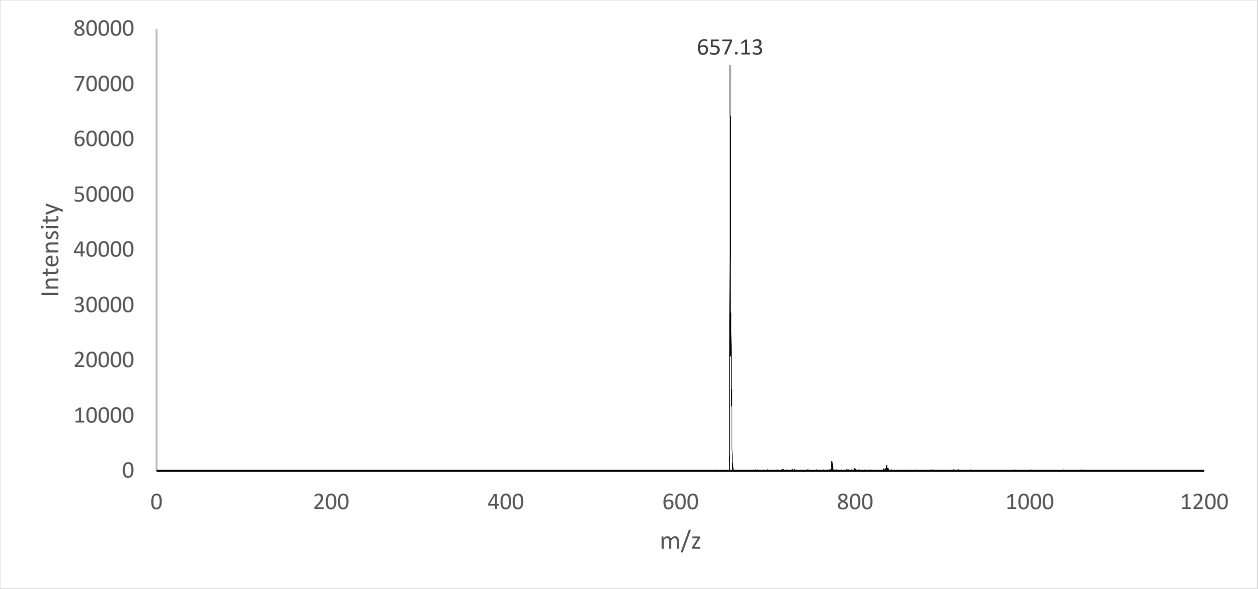
A 69 Ir(III)-1,10-phenanthroline di(acetylacetonate) with 1-methoxybutane. The peak at 568.75 is the peak for the iridium acetylacetonate complex



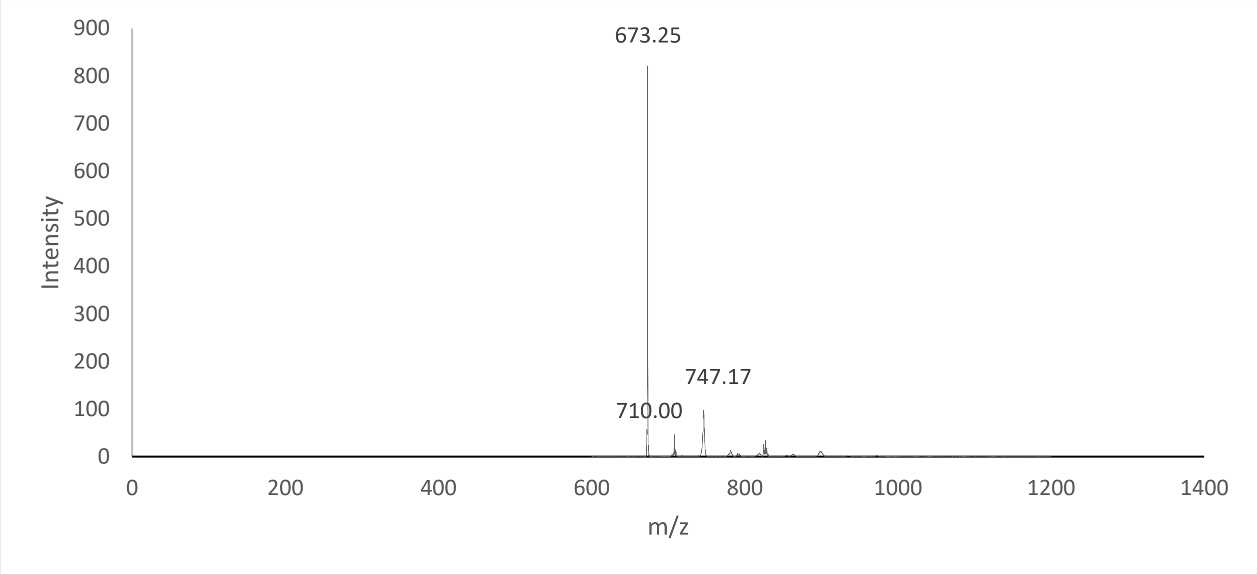
A 70 Ir(III)-1,10-phenanthroline di(acetylacetonate) with 1-methoxybutane. The peak at 568.75 is the peak for the iridium acetylacetonate complex



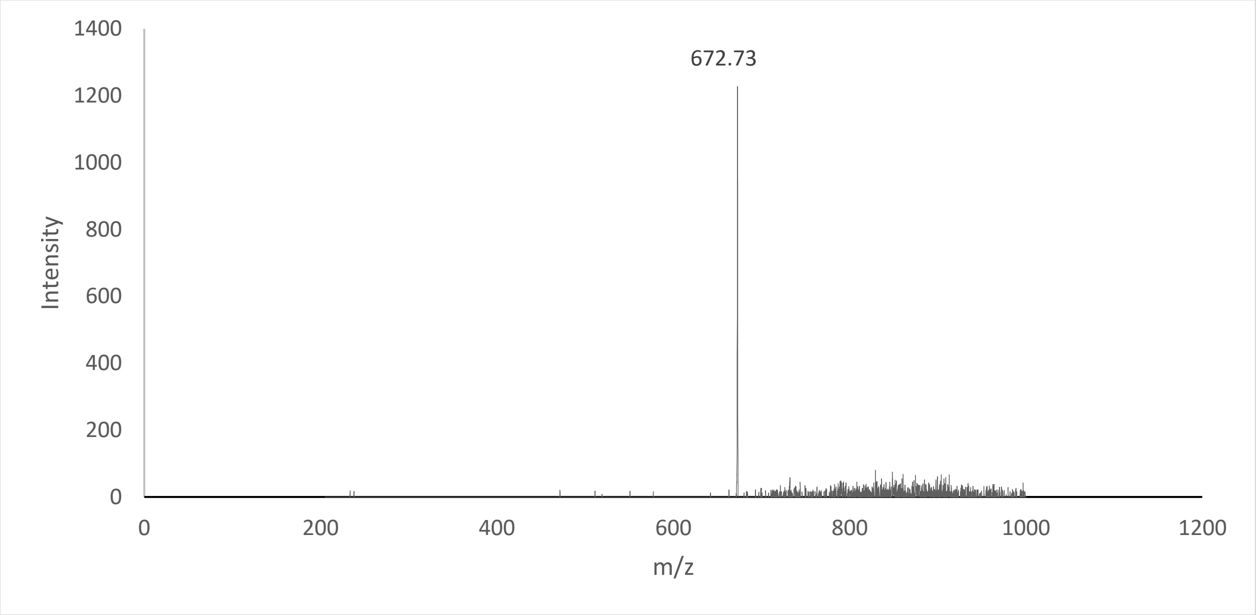
A 71 Ir(III)-DPPE dichloride with 1-butanol. The peak at 657.93 is the peak for the iridium complex



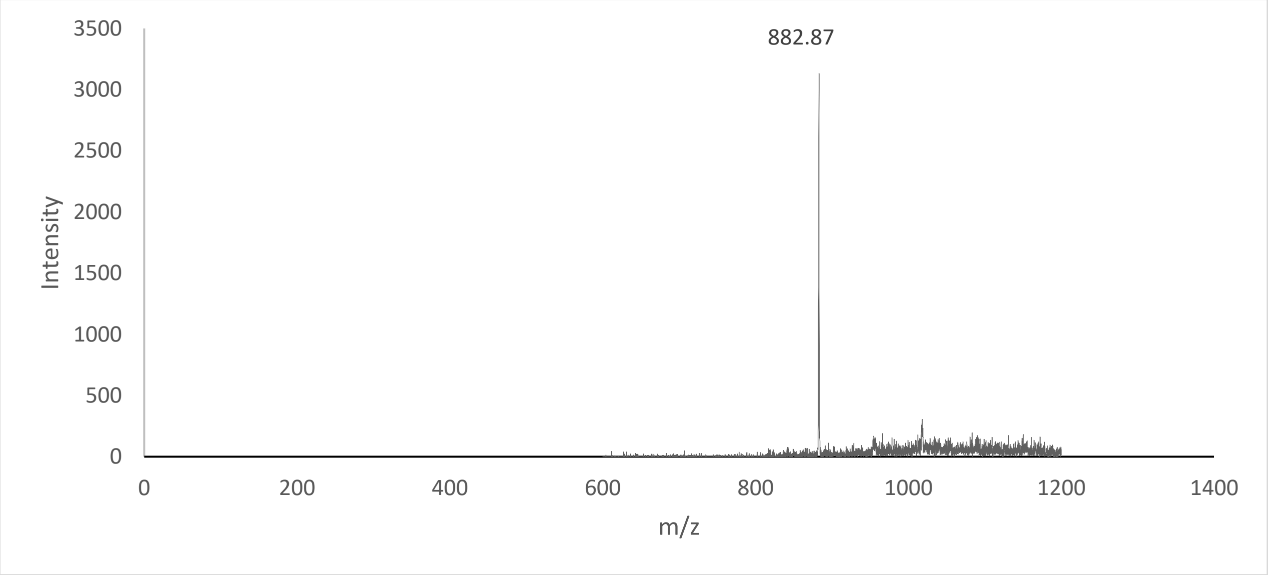
A 72 Ir(III)-DPPE dichloride with butyl acetate. The peak at 657.13 is the peak for the iridium complex



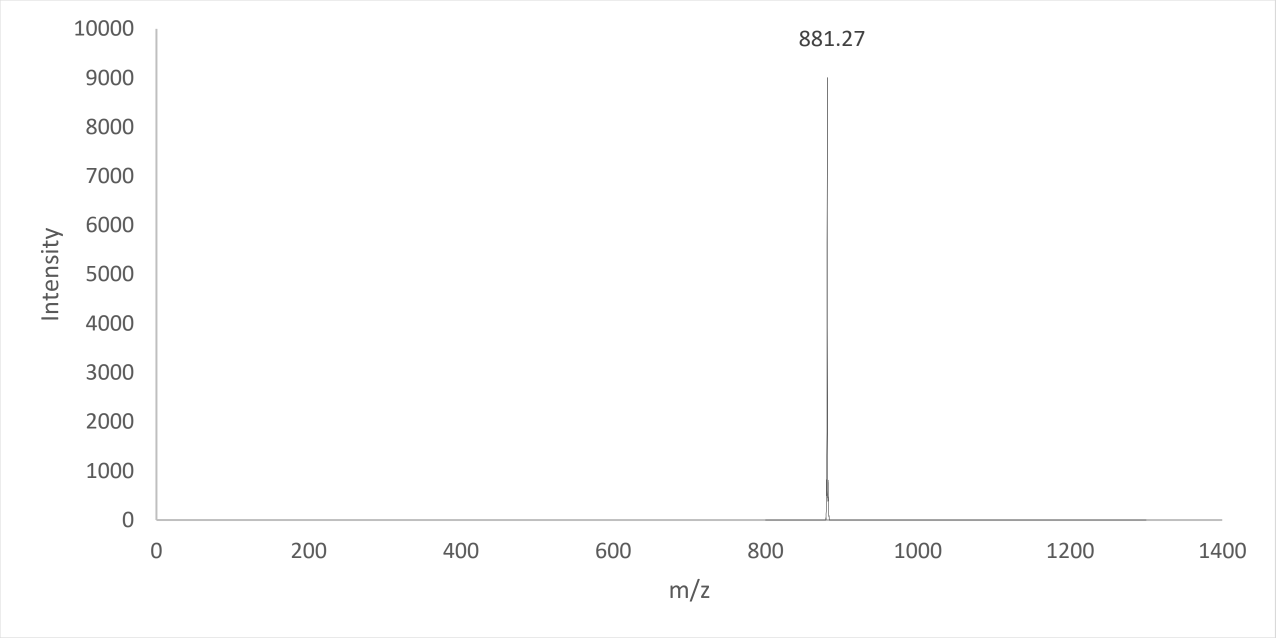
A 73 Ir(III)-DPPP dichloride with 1-butanol. The peak at 673.25 is the peak for the iridium complex. Peaks at 710.00 and 747.17 are adducts of two water molecules and a 1-butanol molecule respectively



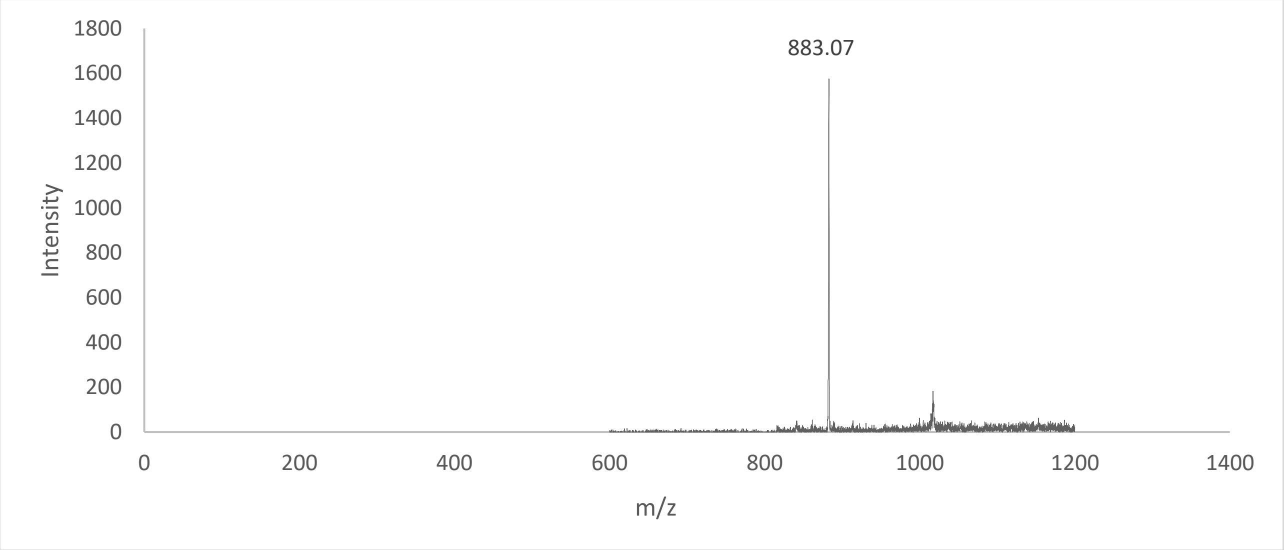
A 74 Ir(III)-DPPP dichloride with butyl acetate. The peak at 672.73 is the iridium complex



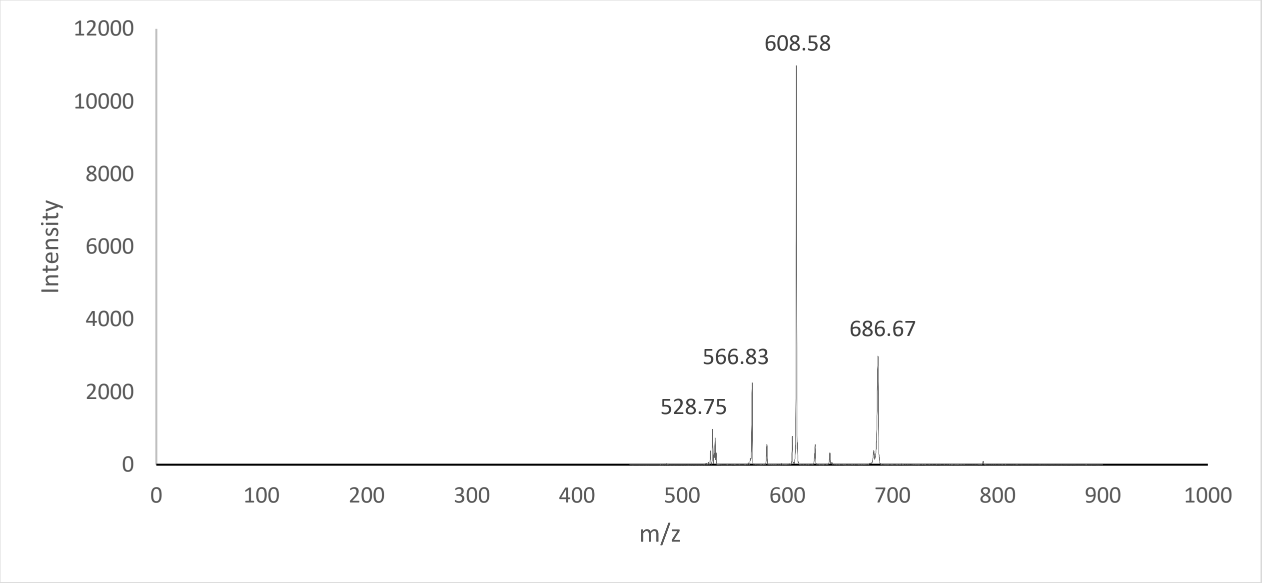
A 75 Ir(III)-BINAP dichloride with 1-butanol. The peak at 882.87 is the iridium complex



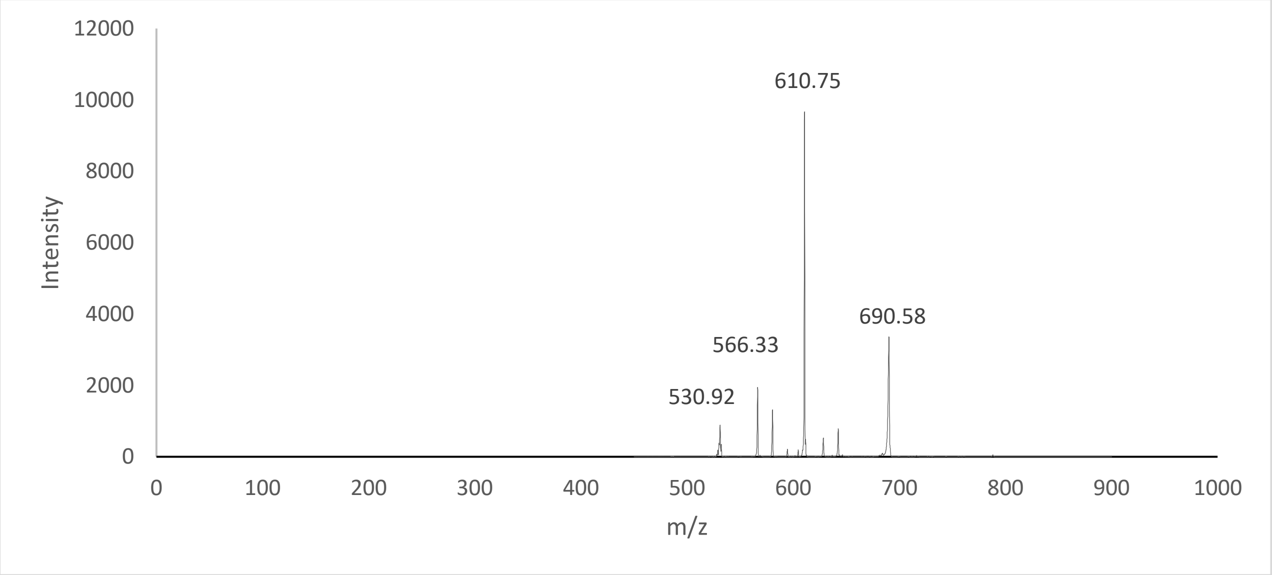
A 76 Ir(III)-BINAP dichloride with 1-methoxybutane. The peak at 881.27 is the iridium complex



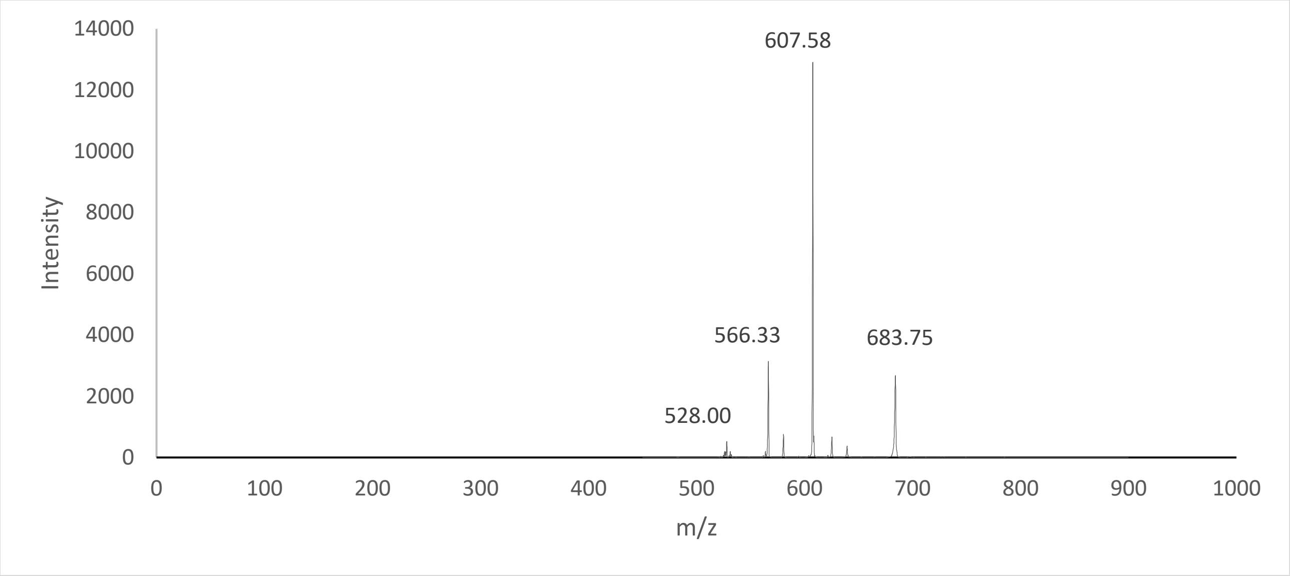
A 77 Ir(III)-BINAP dichloride with butyl acetate. The peak at 883.07 is the iridium complex



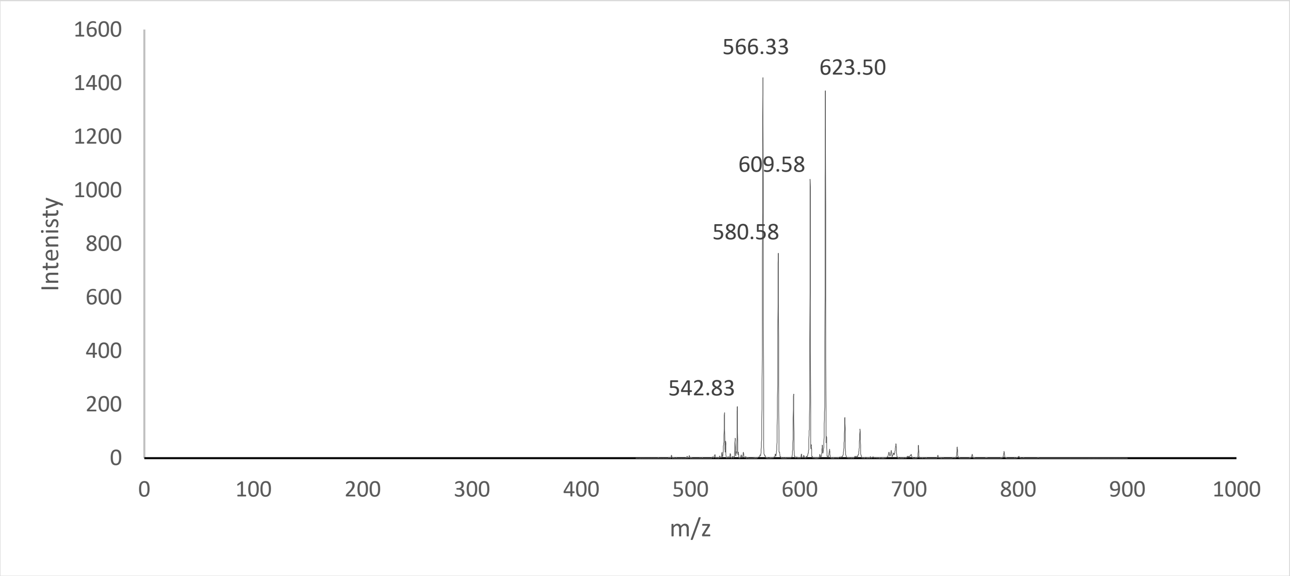
A 78 Ir(III)-1,10-phenanthroline dibromide with 1,1,2,2-d_4 1-butanol. The peak at 528.75 is the peak for C-H activation, 566.83 is the adduct of two oxygen molecules, peaks 608.58 and 686.67 are adducts of one and two 1-butanol molecules respectively



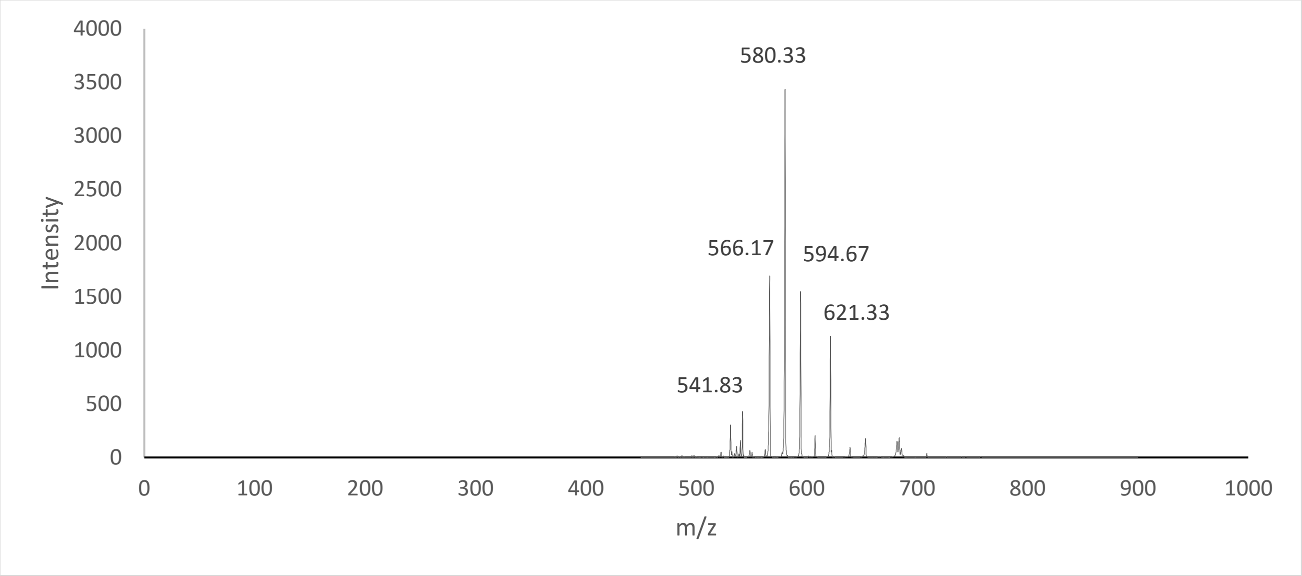
A 79 Ir(III)-1,10-phenanthroline dibromide with 1,1,2,2,3,3-d_6 1-butanol. The peak at 530.92 is the peak for C-H activation, 566.33 is the adduct of two oxygen molecules, peaks 610.75 and 690.58 are adducts of one and two 1-butanol molecules respectively



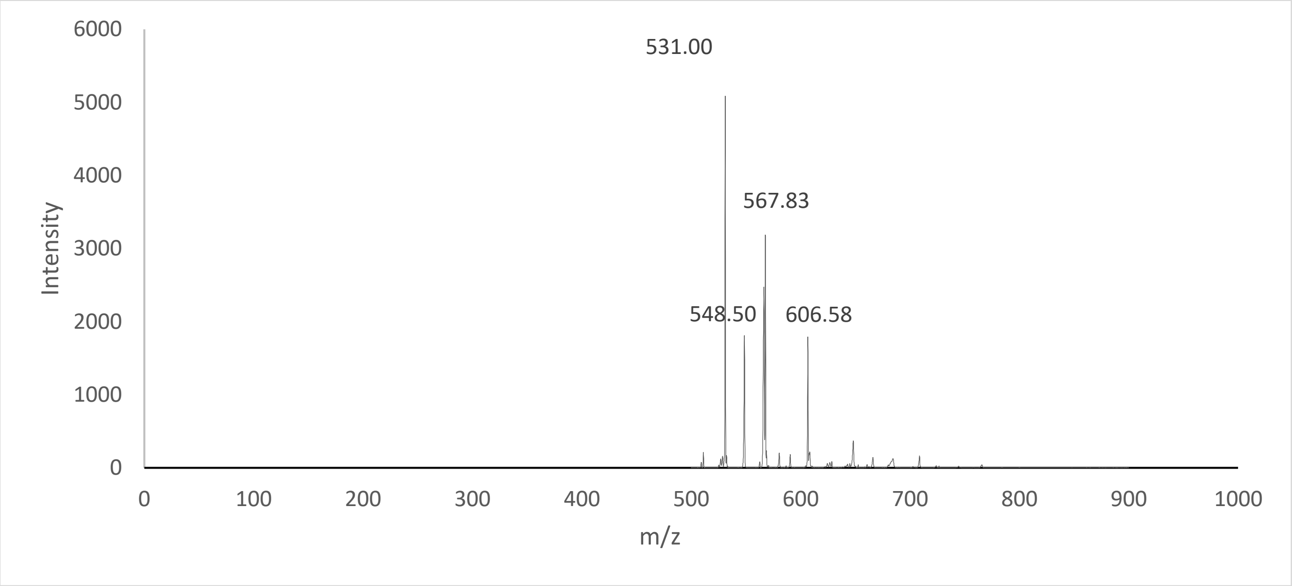
A 80 Ir(III)-1,10-phenanthroline dibromide with 4,4,4-d_3 1-butanol. The peak at 528.00 is the peak for C-H activation, 566.33 is the adduct of two oxygen molecules, peaks 607.58 and 683.75 are adducts of one and two 1-butanol molecules respectively



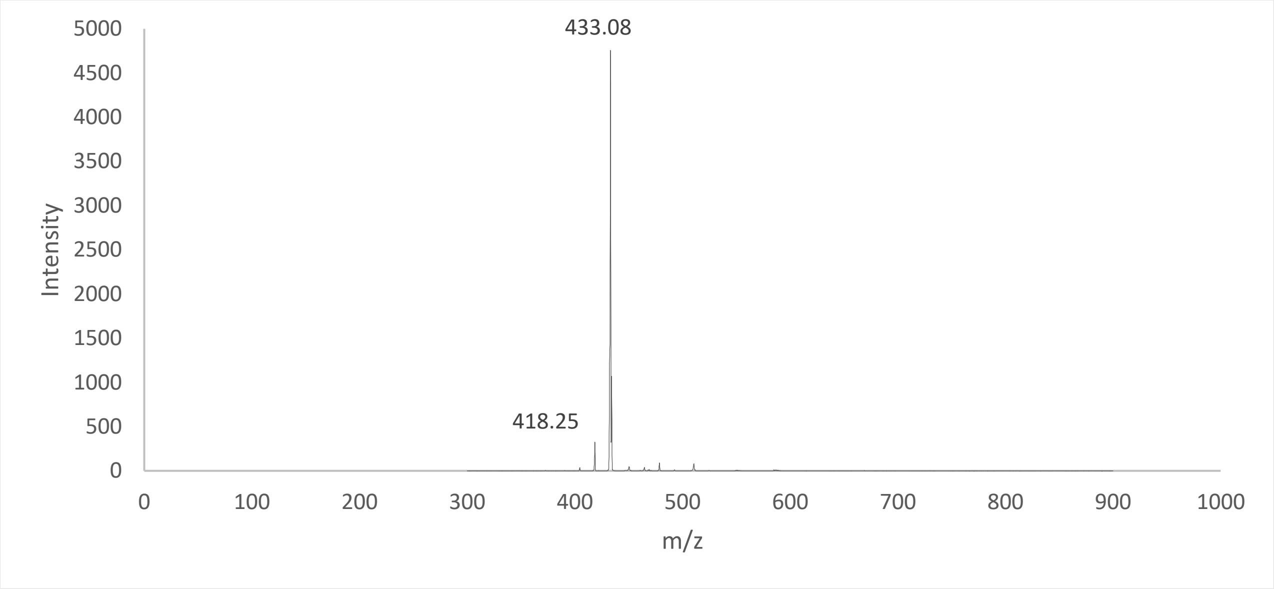
A 81 Ir(III)-1,10-phenanthroline dibromide with 3,3,4,4,4-d_5 1-methoxybutane. The peak at 542.83 is the peak for C-D activation, 566.33 is the adduct of two oxygen molecules, 580.58 and 609.58 are adducts of a methanol molecule with a water molecule and five oxygen atoms respectively, 623.50 is a 1-methoxybutane adduct



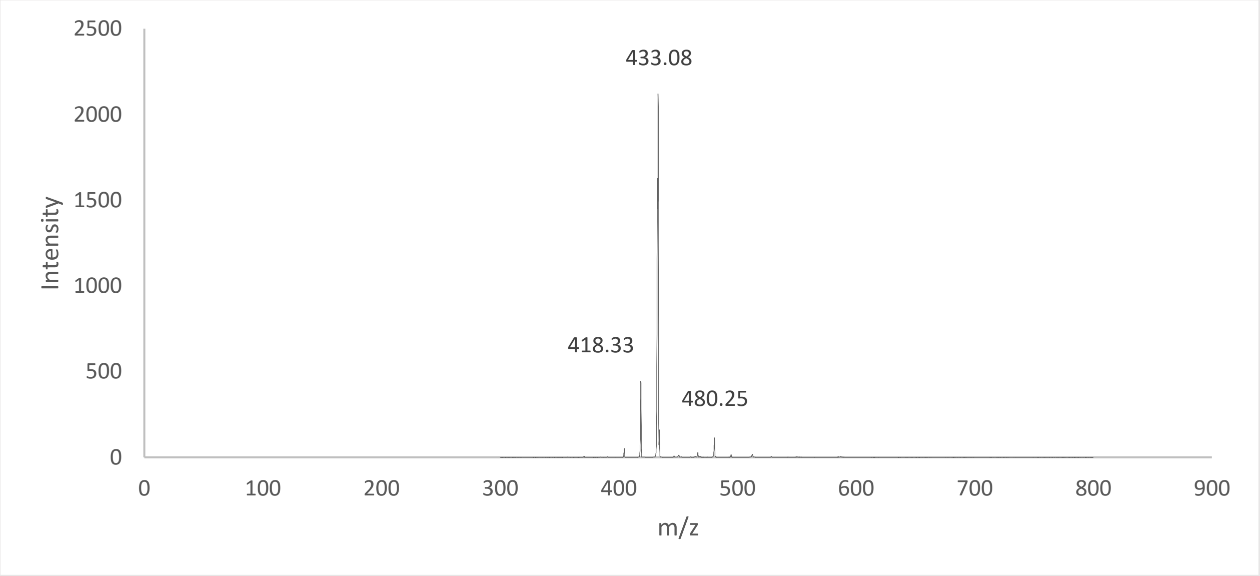
A 82 Ir(III)-1,10-phenanthroline dibromide with 4,4,4-d_3 1-methoxybutane. The peak at 541.83 is the peak for C-H activation, 566.17 is the adduct of two oxygen molecules, 580.33 and 594.58 are adducts of a methanol molecule with a water molecule and two methanol molecules respectively, 621.33 is a 1-methoxybutane adduct



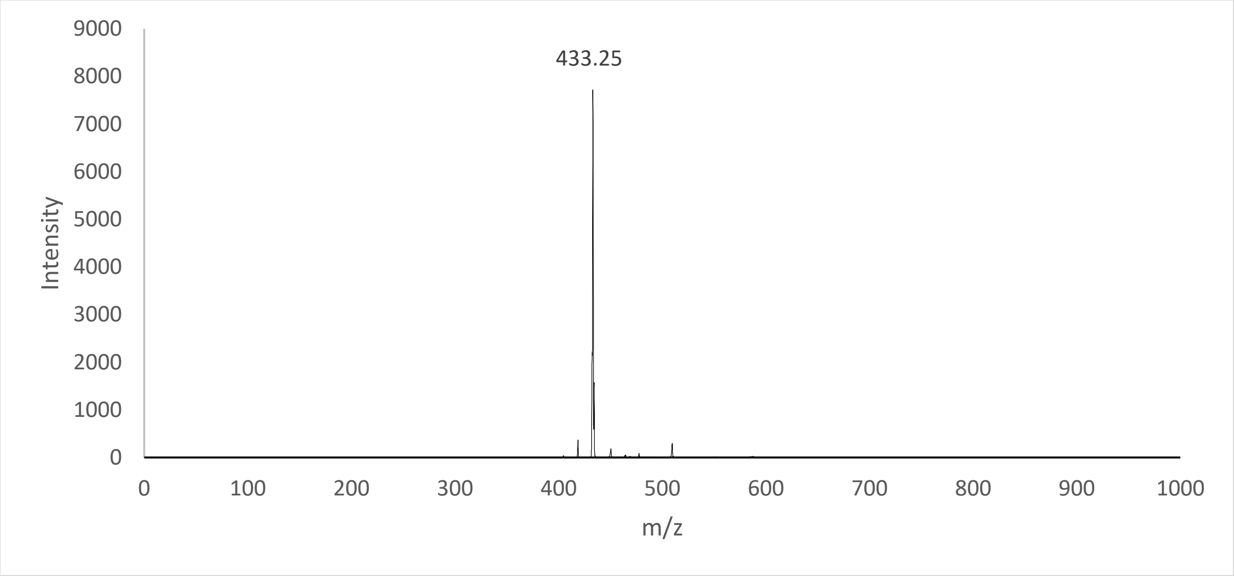
A 83 Ir(III)-1,10-phenanthroline dibromide with 1,1-d_2 butyl acetate. The peak at 548.50 and 531.00 are adducts of a water molecule and 1-butanol molecule (artifact) respectively, 567.83 is the peak for C-D activation and 606.58 is the adduct of a butyl acetate molecule



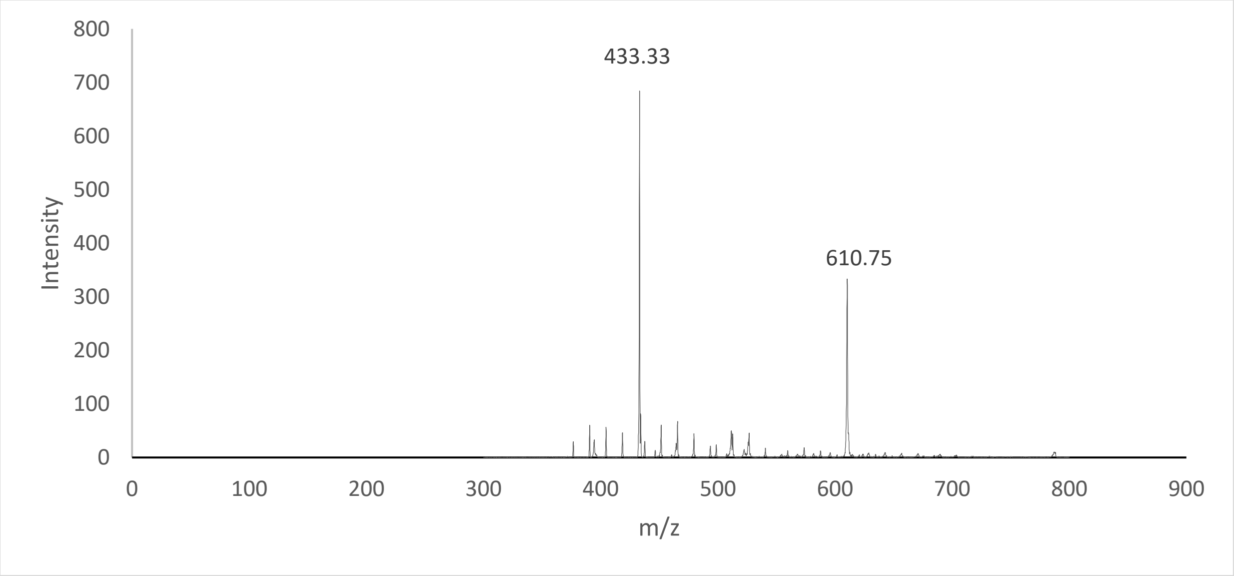
A 84 Ir(III)-1,10-phenanthroline dimethoxide with 1,1,2,2-d_4 1-butanol. The peak at 433.08 is the iridium complex and 418.25 is the loss of a methyl radical from the iridium complex



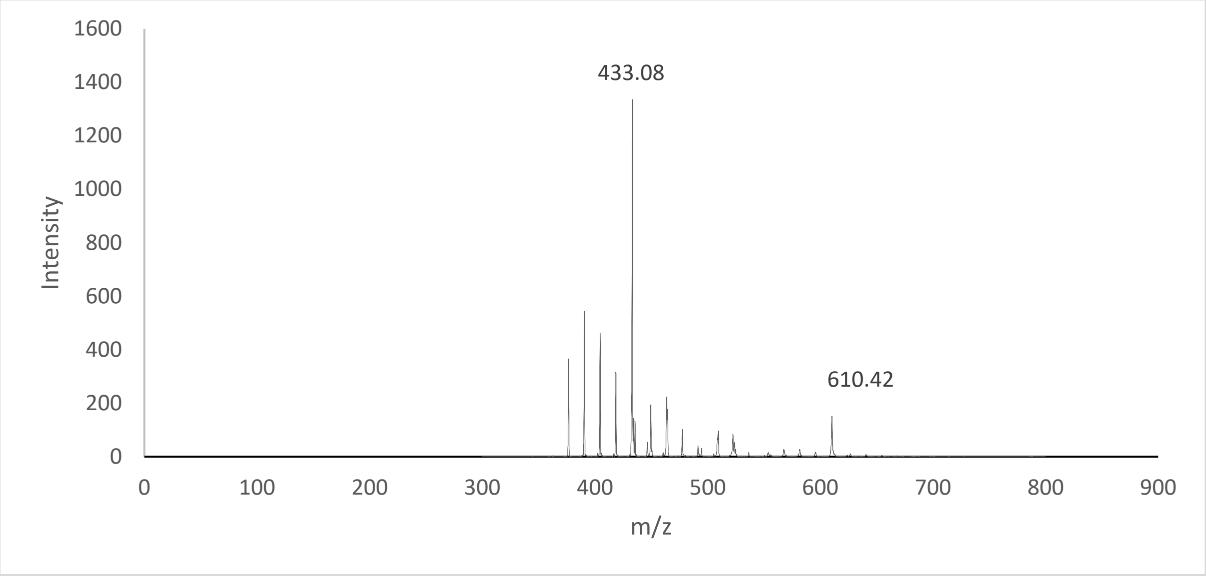
A 85 Ir(III)-1,10-phenanthroline dimethoxide with 1,1,2,2,3,3-d_6 1-butanol. The peak at 433.08 is the iridium complex, 418.33 is the loss of a methyl radical from the iridium complex and 480.25 is the peak for C-D activation



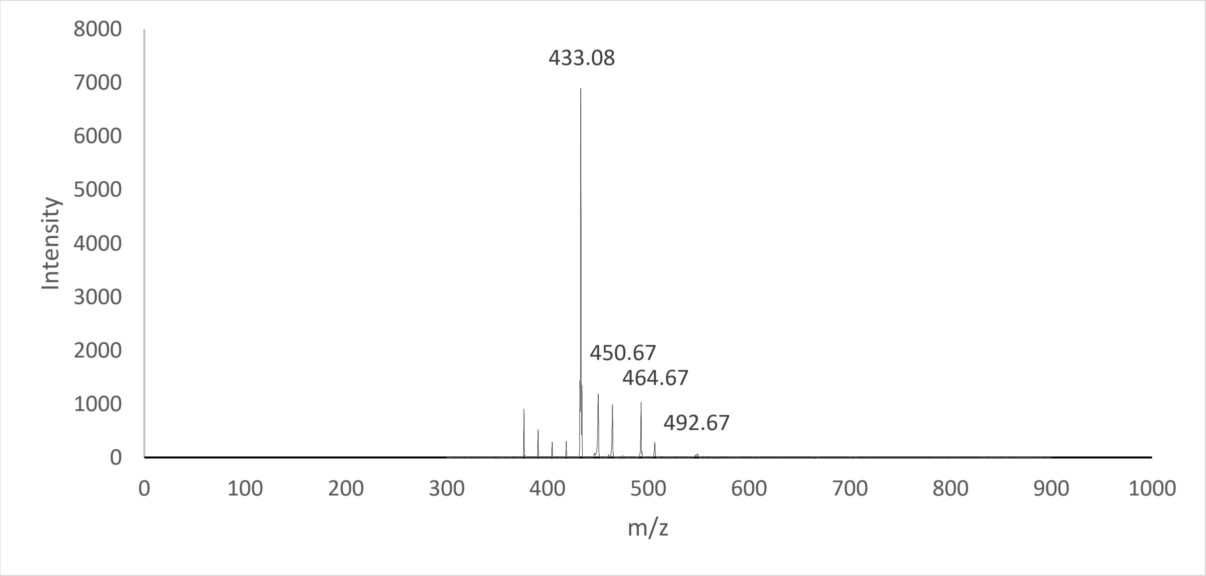
A 86 Ir(III)-1,10-phenanthroline dimethoxide with 4,4,4-d_3 1-butanol. The peak at 433.25 is the iridium complex



A 87 Ir(III)-1,10-phenanthroline dimethoxide with 3,3,4,4,4-d_5 1-methoxybutane. The peak at 433.33 is the iridium complex and 610.75 is a 1-methoxybutane adduct

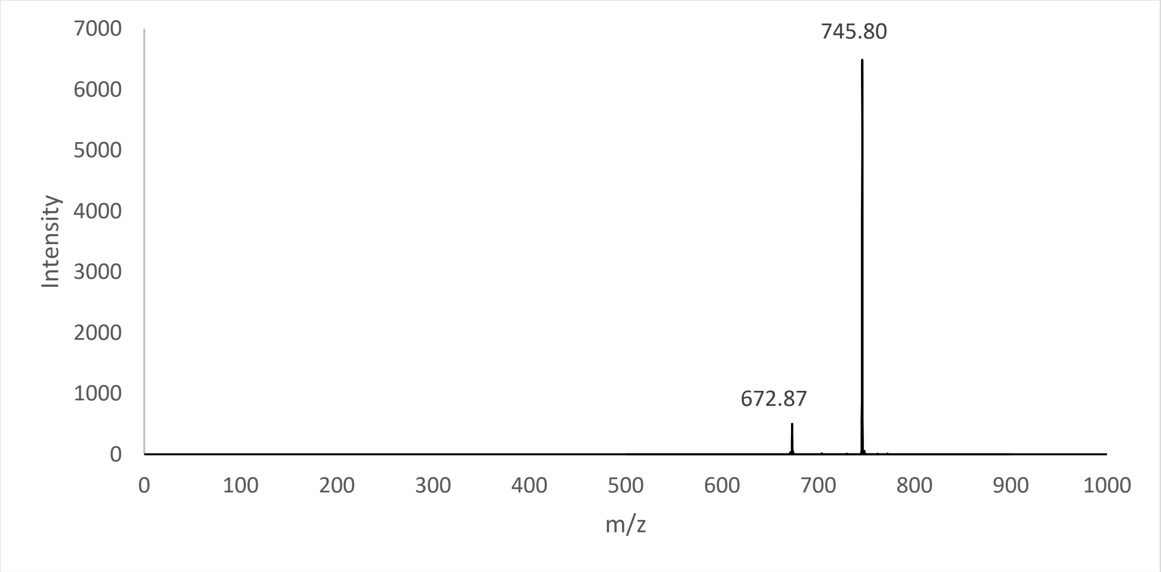


A 88 Ir(III)-1,10-phenanthroline dimethoxide with 4,4,4-d_3 1-methoxybutane. The peak at 433.08 is the iridium complex and 610.42 is a 1-methoxybutane adduct

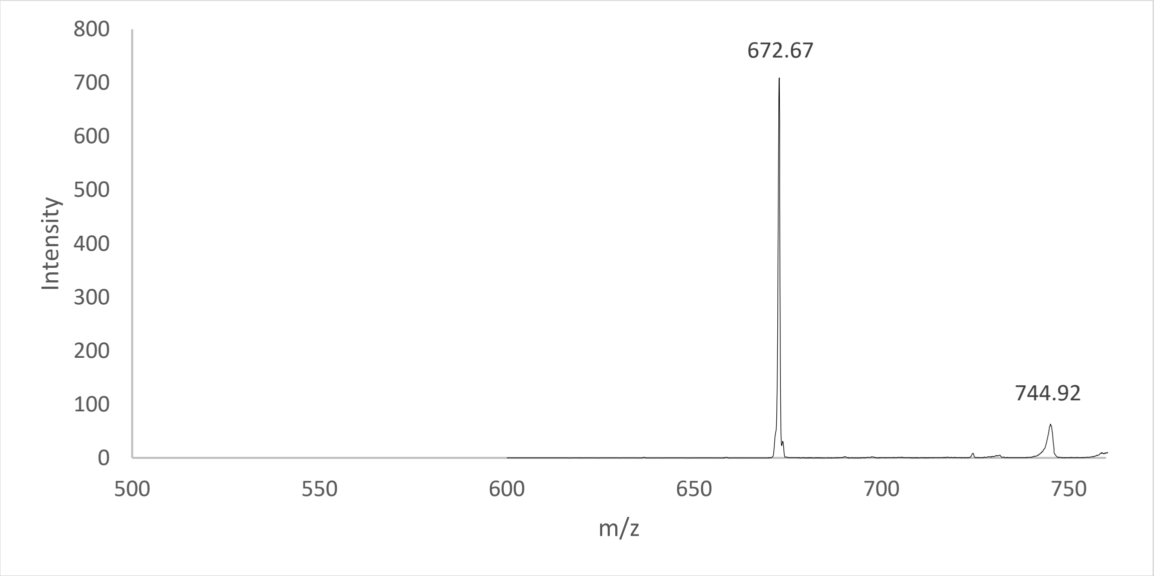


A 89 Ir(III)-1,10-phenanthroline dimethoxide with 1,1-d_2 butyl acetate. The peak at 433.08 is the iridium complex, peaks 450.67, 464.67 and 492.67 are adducts of one water molecule, one methanol molecule and two methanol molecules respectively

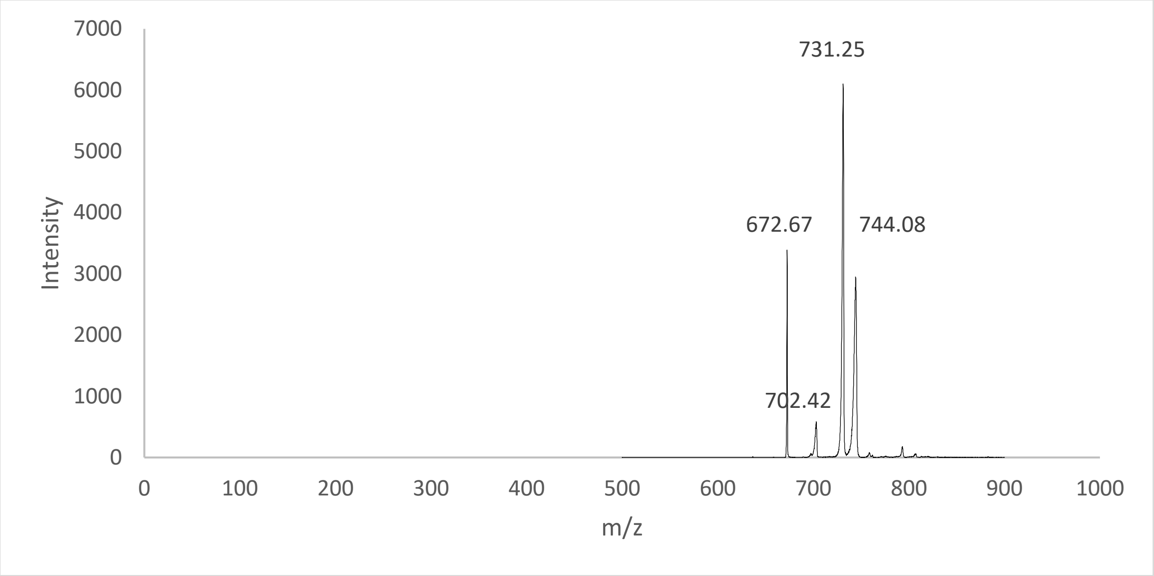
Appendix A3 – Spectra for chapter 5



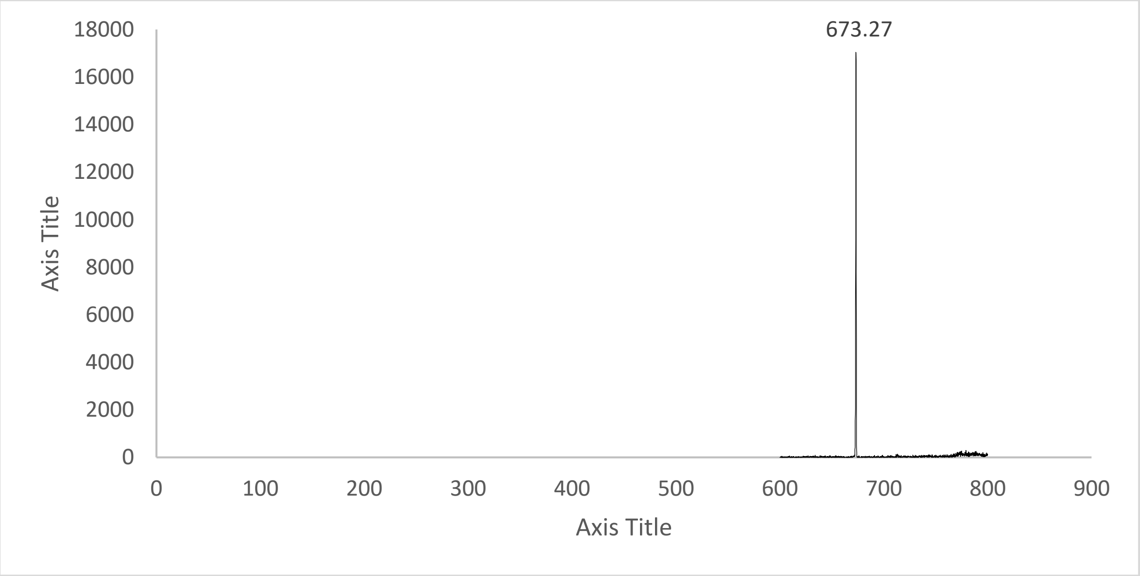
A 90 Ir(III) DPPP dichloride with 1-methoxybutane. The peak at 745.80 is due to loss of methyl radical and 672.87 is the iridium complex.



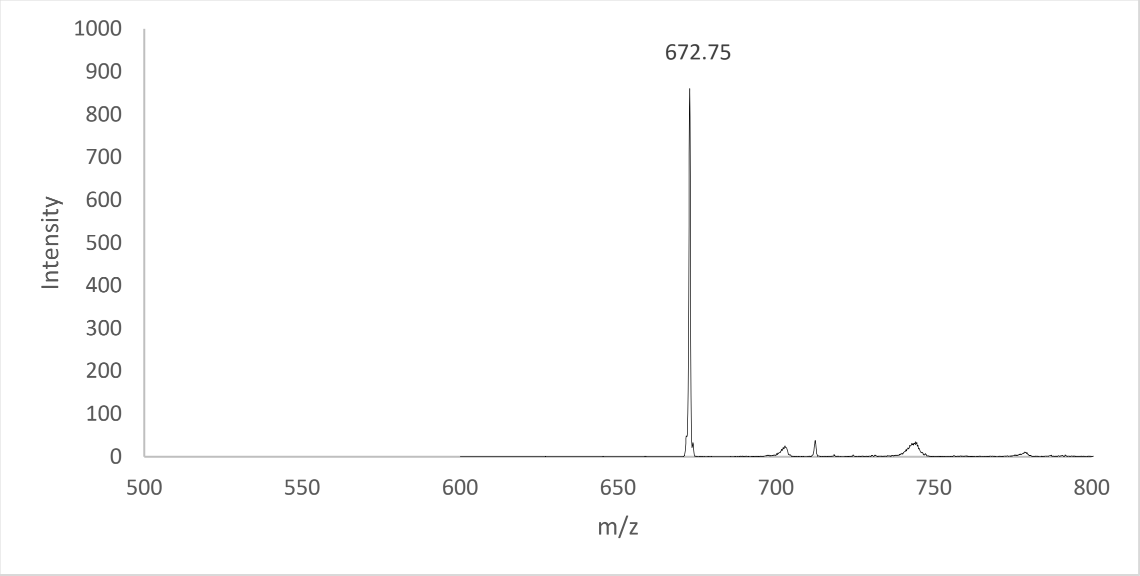
A 91 Ir(III) DPPP dichloride with butyl ether. The peak at 744.92 is due to loss of butyl radical and 672.67 is the iridium complex.



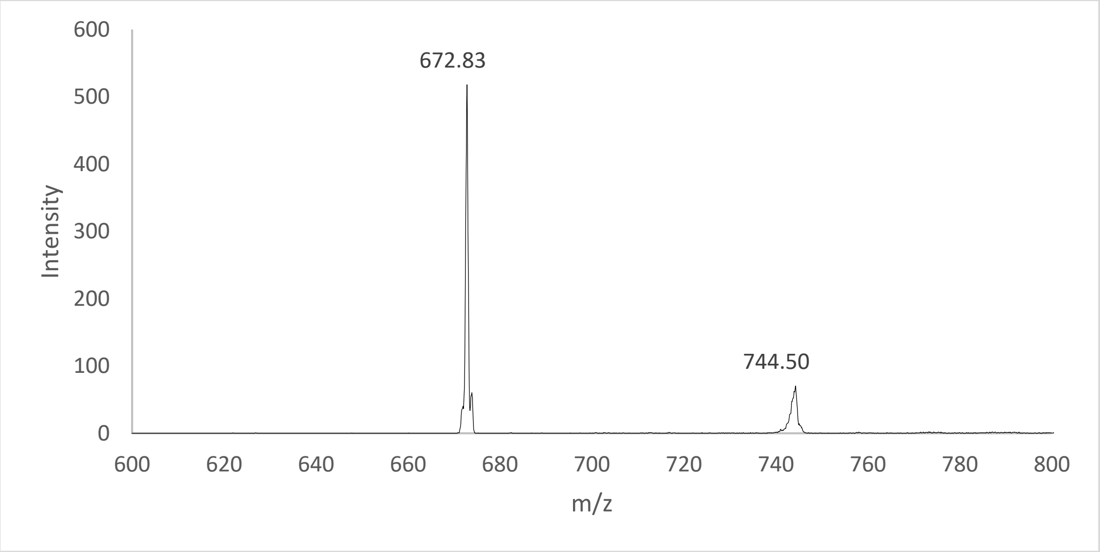
A 92 Ir(III) DPPP dichloride with methoxypropane. The peak at 731.25 is due to loss of methyl radical, 702.42 and 744.08 are adducts of one methanol molecule and two methanol molecules respectively and 672.67 is the iridium complex.



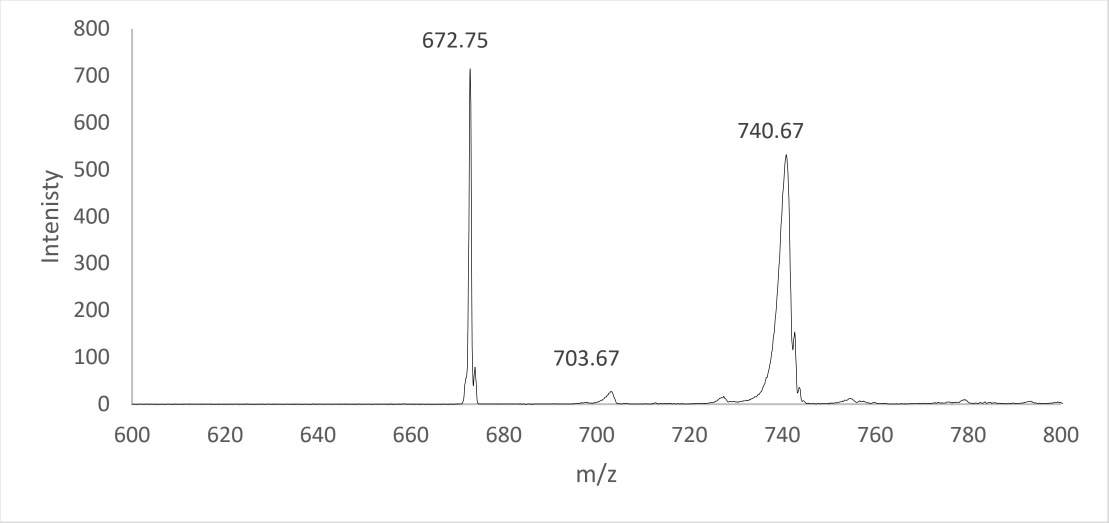
A 93 Ir(III) DPPP dichloride with propyl ether. The peak at 673.27 is the iridium complex.



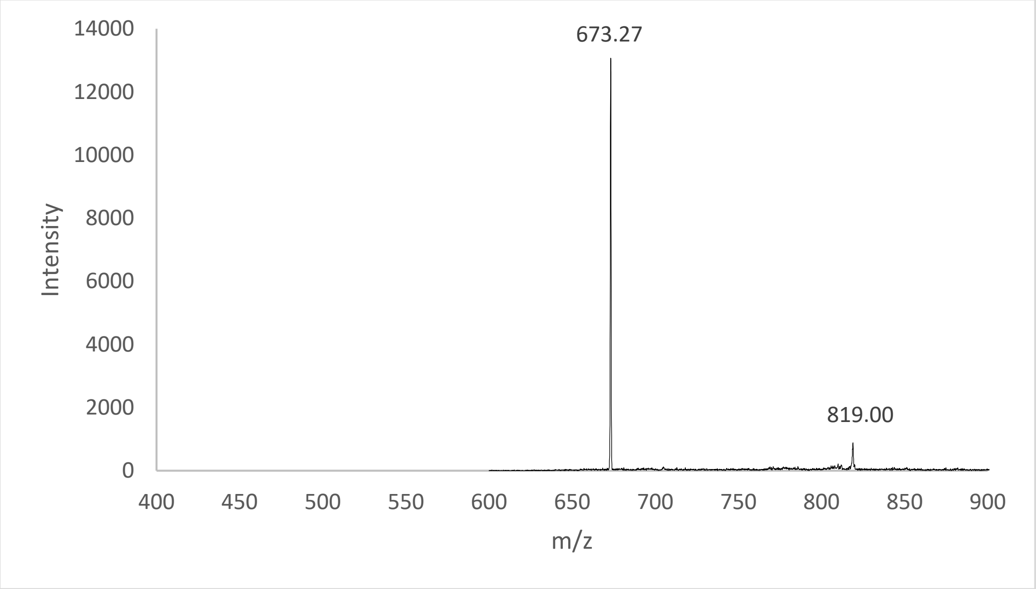
A 94 Ir(III) DPPP dichloride with ethyl ether. The peak at 672.75 is the iridium complex.



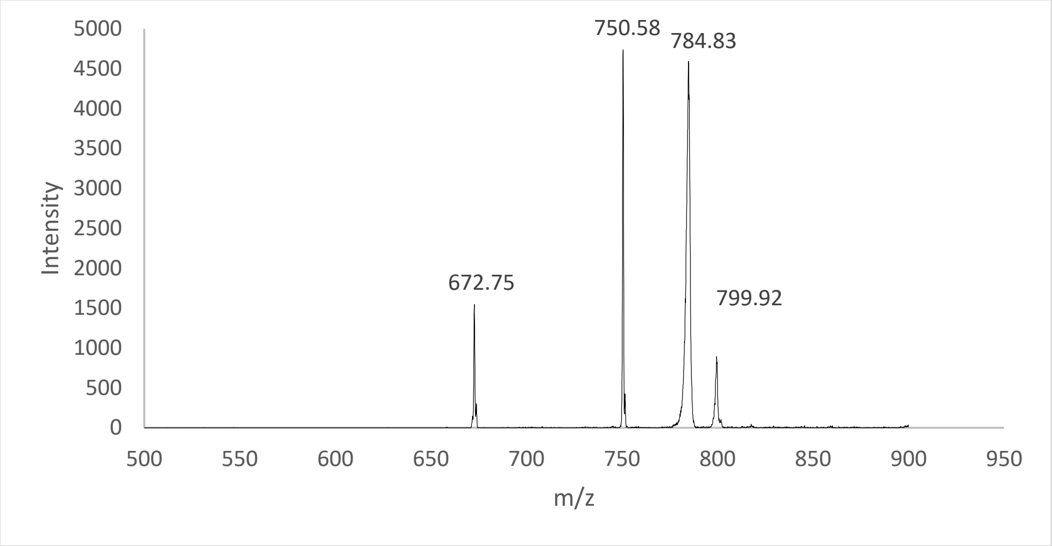
A 95 Ir(III) DPPP dichloride with ethyl vinyl ether. The peak at 744.50 is an adduct of four water molecules and 672.83 is the iridium complex.



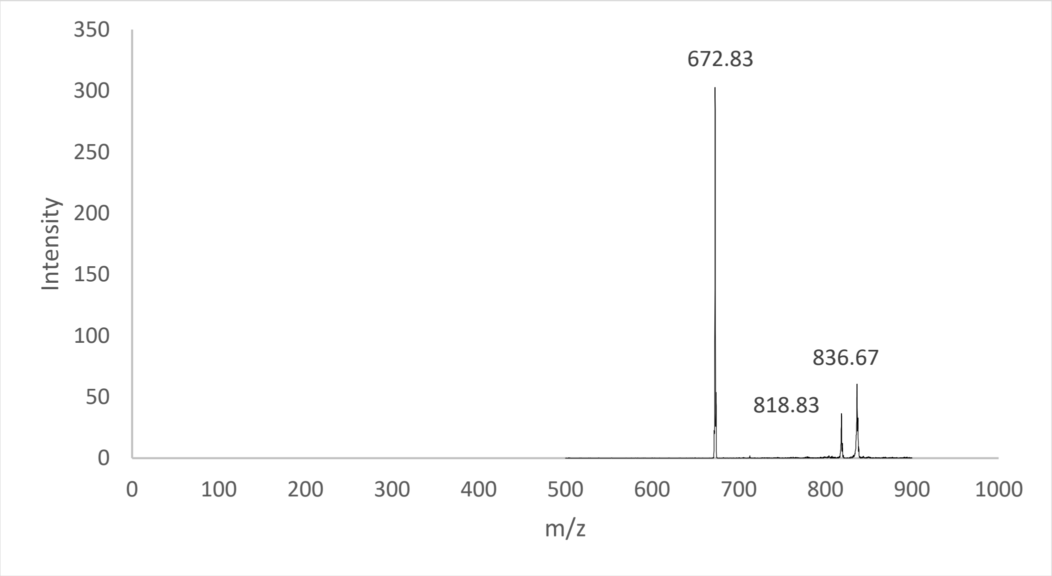
A 96 Ir(III) DPPP dichloride with methyl propargyl ether. The peak at 740.67 is the ether adduct, 703.67 is a methanol adduct and 672.75 is the iridium complex.



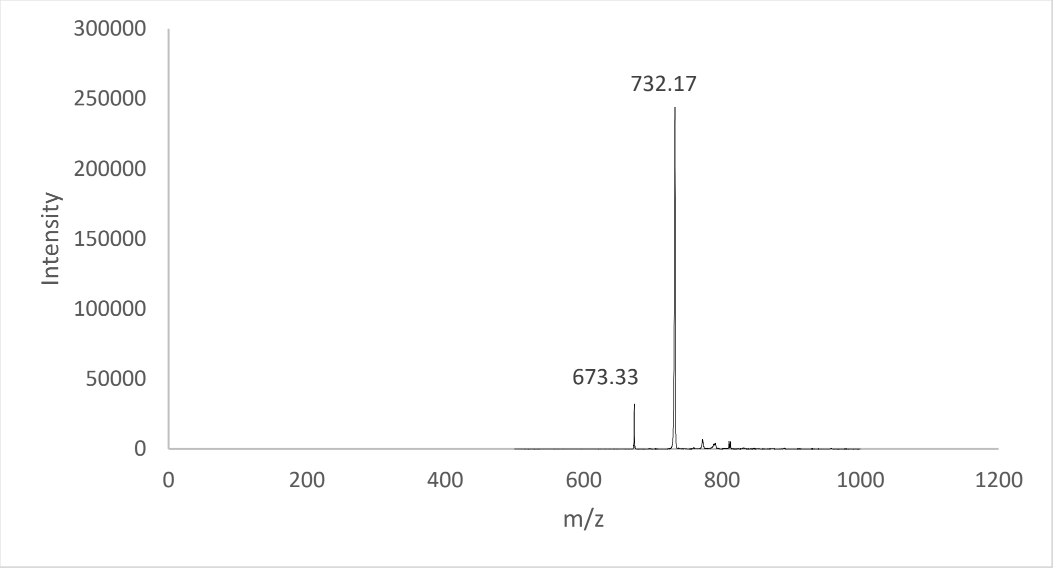
A 97 Ir(III) DPPP dichloride with benzyl propargyl ether. The peak at 819.00 is the ether adduct and 673.27 is the iridium complex.



A 98 Ir(III) DPPP dichloride with allyl butyl ether. The peak at 750.58 is C-H activation due to loss of HCl, 784.83 and 799.92 are adducts of the C-H activated complex with one methanol and one water and methanol molecule respectively, 672.75 is the iridium complex.



A 99 Ir(III) DPPP dichloride with benzyl butyl ether. The peak at 836.67 is the ether adduct, 818.83 is an artifact (ether from the previous runs) and 672.83 is the iridium complex.



A 100 Ir(III) DPPP dichloride with allyl propyl ether. The peak at 732.17 is C-H activation due to loss of allyl radical and 673.33 is the iridium complex.

Appendix B -Computational data

Appendix B1 – Computational data for chapter 3

XYZ coordinates of iridium(III)-1,10-phenanthroline dichloride

Energy: -1595.871456

H	1.09761	-4.48699	0.00040
C	1.21328	-3.40987	0.00011
H	3.35651	-3.44037	-0.00007
C	2.46075	-2.82684	-0.00014
N	0.15636	-1.29590	-0.00020
C	2.57223	-1.42525	-0.00037
C	0.06046	-2.61927	0.00003
C	1.37824	-0.70248	-0.00032
C	3.79422	-0.67951	-0.00051
H	-0.93768	-3.04589	0.00024
C	3.79422	0.67952	-0.00036
H	4.73116	-1.22754	-0.00069
H	4.73115	1.22755	-0.00042
C	2.57222	1.42525	-0.00004
C	2.46074	2.82685	0.00048
C	1.37824	0.70249	-0.00015
C	1.21328	3.40987	0.00086
H	3.35650	3.44038	0.00066
H	1.09760	4.48699	0.00136
C	0.06045	2.61927	0.00064
H	-0.93769	3.04589	0.00092
N	0.15636	1.29590	0.00014
Ir	-1.32841	-0.00000	-0.00006
Cl	-1.59234	-0.00066	2.31322
Cl	-1.59274	0.00066	-2.31314

XYZ coordinates of 1-butanol

Energy: -233.4708331

C	2.49089	-0.29317	-0.00020
C	1.21551	0.52871	0.00041
C	-0.03087	-0.33918	-0.00014
C	-1.30218	0.47095	-0.00027
O	-2.39684	-0.42184	0.00058
H	-3.21475	0.07810	-0.00235
H	2.53937	-0.94195	0.88169
H	3.38499	0.33692	0.00082
H	2.53991	-0.93988	-0.88357
H	1.19985	1.19073	0.87813
H	1.19983	1.19198	-0.87637
H	-0.03319	-0.99817	0.87910
H	-0.03269	-0.99790	-0.87959
H	-1.32458	1.12503	-0.88833
H	-1.32407	1.12604	0.88708

XYZ coordinates of the delta transition state of 1-butanol

Energy: -1829.474381

Imaginary frequency: 365.53cm^{-1}

N	0.81118	1.31020	0.02398
C	2.02691	0.69034	-0.01249
C	2.05283	-0.73373	-0.03826
C	0.76872	2.63388	0.10562
H	-0.21372	3.08728	0.16752
C	3.23132	1.40976	-0.00725
C	1.92417	3.41657	0.11882

C	3.15370	2.81097	0.05356
H	4.06663	3.39914	0.05867
C	0.84144	-2.69664	-0.02982
H	-0.13907	-3.16479	-0.01144
C	2.01473	-3.45880	-0.07003
H	1.94708	-4.54008	-0.08064
C	3.27845	-1.41488	-0.07529
C	3.22994	-2.82018	-0.09216
H	4.15639	-3.38657	-0.12057
C	4.49159	-0.66104	-0.08729
H	5.43514	-1.19734	-0.11956
C	4.46765	0.69319	-0.05262
H	5.39112	1.26407	-0.05510
H	1.82642	4.49355	0.18228
N	0.86321	-1.37690	-0.01537
Ir	-0.78177	0.03578	0.03443
Cl	-0.90464	0.15426	-2.48999
O	-2.23668	-1.51921	0.23942
H	-2.27373	-1.63066	1.20644
Cl	-0.73961	-0.06437	2.36733
C	-3.59104	-1.39033	-0.26703
C	-4.27920	-0.15564	0.25595
C	-3.72109	1.14100	-0.31118
C	-2.33619	1.52345	0.19141
H	-4.11619	-2.30813	0.01405
H	-3.48704	-1.37468	-1.35606
H	-4.22957	-0.14697	1.35543
H	-5.34184	-0.24324	0.00042
H	-4.40906	1.95725	-0.05475
H	-3.74026	1.08007	-1.41003
H	-2.36571	1.72074	1.26969
H	-2.05078	2.47157	-0.28910
H	-1.45856	0.92861	-1.39049

XYZ coordinates of the gamma transition state of 1-butanol

Energy: -1829.469579

Imaginary frequency: 246.10cm^{-1}

N	0.65016	1.28579	0.06809
C	1.92242	0.79797	0.01857
C	2.09146	-0.61354	-0.04494
C	0.47498	2.59207	0.21511
H	-0.54814	2.93472	0.29812
C	3.04749	1.63489	0.05077
C	1.54340	3.48854	0.26568
C	2.82824	3.01714	0.16896
H	3.67633	3.69483	0.19630
C	1.07609	-2.67935	-0.10268
H	0.15094	-3.24941	-0.11102
C	2.31533	-3.32311	-0.18321
H	2.35055	-4.40442	-0.24065
C	3.37773	-1.16915	-0.11671
C	3.46439	-2.57070	-0.18528
H	4.44012	-3.04466	-0.24191
C	4.50866	-0.29606	-0.11042
H	5.50101	-0.73290	-0.16829
C	4.34881	1.04665	-0.02441
H	5.21106	1.70616	-0.00904
H	1.33510	4.54561	0.37889
N	0.96889	-1.36538	-0.02643
Ir	-0.82168	-0.12922	0.03118

Cl	-0.91308	-0.06329	-2.46090
C	-2.70242	0.98760	0.15126
C	-2.95179	2.28883	-0.59830
H	-2.88724	2.17827	-1.68889
H	-3.96793	2.64157	-0.38157
H	-2.28345	3.10264	-0.30719
C	-3.77477	-0.02665	-0.24100
H	-4.76952	0.36865	0.00636
H	-3.77085	-0.19436	-1.32761
C	-3.58078	-1.32623	0.47164
H	-3.67181	-1.20371	1.55677
H	-4.24945	-2.11852	0.12784
O	-2.21032	-1.75538	0.17742
H	-1.90966	-2.28452	0.93025
Cl	-0.77299	-0.19497	2.37360
H	-2.74798	1.17806	1.23028
H	-1.51322	0.72916	-1.28644

XYZ coordinates of gamma activated 1-butanol

Energy: -1829.395963

N	0.65016	1.28579	0.06809
C	1.92242	0.79797	0.01857
C	2.09146	-0.61354	-0.04494
C	0.47498	2.59207	0.21511
H	-0.54814	2.93472	0.29812
C	3.04749	1.63489	0.05077
C	1.54340	3.48854	0.26568
C	2.82824	3.01714	0.16896
H	3.67633	3.69483	0.19630
C	1.07609	-2.67935	-0.10268
H	0.15094	-3.24941	-0.11102
C	2.31533	-3.32311	-0.18321
H	2.35055	-4.40442	-0.24065
C	3.37773	-1.16915	-0.11671
C	3.46439	-2.57070	-0.18528
H	4.44012	-3.04466	-0.24191
C	4.50866	-0.29606	-0.11042
H	5.50101	-0.73290	-0.16829
C	4.34881	1.04665	-0.02441
H	5.21106	1.70616	-0.00904
H	1.33510	4.54561	0.37889
N	0.96889	-1.36538	-0.02643
Ir	-0.82168	-0.12922	0.03118
Cl	-0.91308	-0.06329	-2.46090
C	-2.70242	0.98760	0.15126
C	-2.95179	2.28883	-0.59830
H	-2.88724	2.17827	-1.68889
H	-3.96793	2.64157	-0.38157
H	-2.28345	3.10264	-0.30719
C	-3.77477	-0.02665	-0.24100
H	-4.76952	0.36865	0.00636
H	-3.77085	-0.19436	-1.32761
C	-3.58078	-1.32623	0.47164
H	-3.67181	-1.20371	1.55677
H	-4.24945	-2.11852	0.12784
O	-2.21032	-1.75538	0.17742
H	-1.90966	-2.28452	0.93025
Cl	-0.77299	-0.19497	2.37360
H	-2.74798	1.17806	1.23028
H	-1.51322	0.72916	-1.28644

XYZ coordinates of delta activated 1-butanol

Energy: -1829.398193

N	0.81118	1.31020	0.02398
C	2.02691	0.69034	-0.01249
C	2.05283	-0.73373	-0.03826
C	0.76872	2.63388	0.10562
H	-0.21372	3.08728	0.16752
C	3.23132	1.40976	-0.00725
C	1.92417	3.41657	0.11882
C	3.15370	2.81097	0.05356
H	4.06663	3.39914	0.05867
C	0.84144	-2.69664	-0.02982
H	-0.13907	-3.16479	-0.01144
C	2.01473	-3.45880	-0.07003
H	1.94708	-4.54008	-0.08064
C	3.27845	-1.41488	-0.07529
C	3.22994	-2.82018	-0.09216
H	4.15639	-3.38657	-0.12057
C	4.49159	-0.66104	-0.08729
H	5.43514	-1.19734	-0.11956
C	4.46765	0.69319	-0.05262
H	5.39112	1.26407	-0.05510
H	1.82642	4.49355	0.18228
N	0.86321	-1.37690	-0.01537
Ir	-0.78177	0.03578	0.03443
Cl	-0.90464	0.15426	-2.48999
O	-2.23668	-1.51921	0.23942
H	-2.27373	-1.63066	1.20644
Cl	-0.73961	-0.06437	2.36733
C	-3.59104	-1.39033	-0.26703
C	-4.27920	-0.15564	0.25595
C	-3.72109	1.14100	-0.31118
C	-2.33619	1.52345	0.19141
H	-4.11619	-2.30813	0.01405
H	-3.48704	-1.37468	-1.35606
H	-4.22957	-0.14697	1.35543
H	-5.34184	-0.24324	0.00042
H	-4.40906	1.95725	-0.05475
H	-3.74026	1.08007	-1.41003
H	-2.36571	1.72074	1.26969
H	-2.05078	2.47157	-0.28910
H	-1.45856	0.92861	-1.39049

XYZ coordinates of 1-methoxybutane

Energy: -272.7294241

C	3.04319	0.12713	0.00001
O	1.79287	-0.55302	-0.00000
C	0.70361	0.36748	-0.00000
C	-0.60845	-0.41017	0.00000
C	-1.80665	0.53965	-0.00000
C	-3.12787	-0.20855	0.00000
H	3.14223	0.74767	0.89656
H	3.84381	-0.61642	0.00001
H	3.14223	0.74767	-0.89656
H	0.76250	1.00062	-0.89279
H	0.76250	1.00062	0.89280
H	-0.64392	-1.06925	0.87688
H	-0.64392	-1.06925	-0.87687
H	-1.76202	1.18736	0.88355
H	-1.76202	1.18737	-0.88355

H	-3.96405	0.49771	-0.00000
H	-3.22167	-0.84158	0.88803
H	-3.22167	-0.84158	-0.88803

XYZ coordinates of the delta transition state of 1-methoxybutane

Energy: -1868.716591

Imaginary frequency: 675.28cm^{-1}

N	0.95449	-1.30364	-0.02574
C	2.13376	-0.61914	-0.00158
C	2.07782	0.80420	0.01232
C	0.98231	-2.62897	-0.10008
H	0.02565	-3.13642	-0.14336
C	3.37550	-1.27183	-0.02864
C	2.17829	-3.34728	-0.12533
C	3.37404	-2.67515	-0.08367
H	4.31798	-3.21164	-0.10439
C	0.76486	2.69204	-0.08818
H	-0.23553	3.11115	-0.14544
C	1.89322	3.51756	-0.13711
H	1.76476	4.59065	-0.21430
C	3.26513	1.55123	-0.02647
C	3.14230	2.94984	-0.08997
H	4.03704	3.56483	-0.12063
C	4.51840	0.86616	-0.02546
H	5.43014	1.45553	-0.03910
C	4.57039	-0.48755	-0.02341
H	5.52420	-1.00595	-0.03340
H	2.13848	-4.42834	-0.18229
N	0.85186	1.37792	0.01426
Ir	-0.70673	-0.14611	0.03652
Cl	-0.85892	-0.52895	2.56593
O	-2.36614	1.23291	0.14149
Cl	-0.63748	0.02724	-2.29016
C	-3.62116	1.13499	-0.58223
C	-3.86426	-0.24383	-1.13538
C	-3.56884	-1.34114	-0.12014
C	-2.11069	-1.76474	-0.12831
H	-3.61104	1.90434	-1.36283
H	-4.40674	1.38175	0.14453
H	-3.27950	-0.40595	-2.04602
H	-4.91876	-0.26686	-1.43315
H	-4.18708	-2.21902	-0.34585
H	-3.87543	-1.01336	0.88637
H	-1.42918	-1.20684	1.45957
C	-2.43915	2.17018	1.21325
H	-1.44646	2.27211	1.65155
H	-3.13572	1.81308	1.98088
H	-2.77913	3.13854	0.82961
H	-1.97534	-2.59185	0.59444
H	-1.84839	-2.18878	-1.10594

XYZ coordinates of the gamma transition state of 1-methoxybutane

Energy: -1868.717320

Imaginary frequency: 389.58cm^{-1}

N	-0.79822	1.28851	0.05500
C	-2.03712	0.73203	-0.02397
C	-2.12508	-0.68665	0.01063
C	-0.69190	2.61293	0.08331
H	0.30712	3.02392	0.16378
C	-3.20212	1.51017	-0.11066

C	-1.80308	3.45196	0.00995
C	-3.05772	2.90605	-0.09789
H	-3.93889	3.53711	-0.16470
C	-1.03320	-2.69851	0.17971
H	-0.09703	-3.23451	0.27118
C	-2.23980	-3.40265	0.11733
H	-2.22409	-4.48495	0.16465
C	-3.38334	-1.30554	-0.05833
C	-3.41632	-2.70857	-0.00471
H	-4.36996	-3.22552	-0.05860
C	-4.55511	-0.49676	-0.17126
H	-5.51957	-0.99172	-0.23110
C	-4.46836	0.85440	-0.19472
H	-5.36075	1.46765	-0.27222
H	-1.65189	4.52430	0.03535
N	-0.96671	-1.38000	0.12846
Ir	0.76072	-0.01321	0.10905
Cl	0.92233	0.30608	2.57811
C	3.68513	0.69456	0.26931
H	4.55113	1.25654	-0.10334
H	3.82802	0.56021	1.34861
C	3.65672	-0.65658	-0.37800
H	3.57008	-0.61090	-1.47167
H	4.52531	-1.26631	-0.10831
Cl	0.65014	-0.30741	-2.22202
H	2.32706	2.26337	0.74164
H	2.70539	1.48077	-2.17575
C	2.43606	2.16326	-1.36760
H	1.48354	2.61733	-1.65347
H	3.18950	2.96035	-1.33100
O	2.48173	-1.32648	0.14646
C	2.38379	-2.68224	-0.28719
H	3.38713	-3.11382	-0.32857
H	1.91120	-2.73857	-1.27400
H	1.81191	-3.22576	0.46544
C	2.39609	1.46049	-0.01973
H	1.48978	1.00230	1.33902

XYZ coordinates of delta activated 1-methoxybutane

Energy: -1868.648032

N	0.91502	-1.30300	0.00200
C	2.12200	-0.66718	-0.01108
C	2.13487	0.76030	0.00998
C	0.89343	-2.63030	-0.07713
H	-0.08098	-3.10185	-0.09645
C	3.33417	-1.37620	-0.07717
C	2.05478	-3.39883	-0.14018
C	3.27700	-2.77714	-0.13440
H	4.19871	-3.34893	-0.18654
C	0.94177	2.71933	-0.01237
H	-0.02544	3.20920	-0.01207
C	2.11042	3.48354	-0.09630
H	2.03826	4.56327	-0.15239
C	3.36293	1.44214	-0.06148
C	3.32379	2.84558	-0.10572
H	4.25293	3.40525	-0.16220
C	4.58064	0.69859	-0.10550
H	5.51820	1.24466	-0.14681
C	4.56624	-0.65447	-0.10903
H	5.49136	-1.22101	-0.15159

H	1.96654	-4.47694	-0.19993
N	0.94228	1.40036	0.06358
Ir	-0.73957	-0.12520	0.06832
Cl	-0.83249	-0.27908	2.58447
O	-2.50603	1.12631	0.19156
Cl	-0.68275	0.05480	-2.25311
C	-3.61998	1.02147	-0.73281
C	-3.90572	-0.41362	-1.10626
C	-3.55009	-1.38815	0.00785
C	-2.07045	-1.72737	-0.00515
H	-3.39577	1.64441	-1.60805
H	-4.47287	1.45867	-0.19690
H	-3.35597	-0.68697	-2.01271
H	-4.97126	-0.47275	-1.35198
H	-4.12477	-2.31351	-0.12776
H	-3.86445	-0.98024	0.98052
H	-1.73954	-1.20251	2.71282
C	-2.37846	2.45423	0.67540
H	-1.59165	2.46914	1.43056
H	-3.32215	2.76525	1.13555
H	-2.13938	3.14042	-0.14789
H	-1.84169	-2.41251	0.83087
H	-1.85128	-2.27325	-0.93390

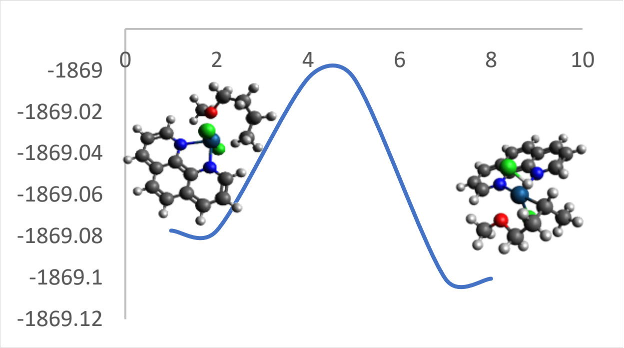
XYZ coordinates of gamma activated 1-methoxybutane

Energy: -1868.654333

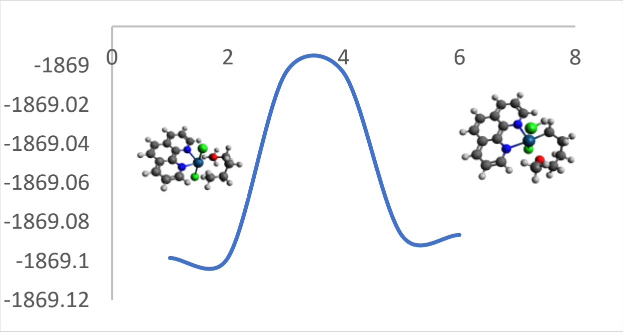
N	0.77745	-1.28508	0.09942
C	2.02572	-0.74493	0.00340
C	2.14579	0.67621	0.02641
C	0.65860	-2.60989	0.12697
H	-0.34577	-3.00701	0.20676
C	3.17773	-1.54340	-0.09734
C	1.75620	-3.46519	0.04570
C	3.01643	-2.93703	-0.07791
H	3.88881	-3.57878	-0.15719
C	1.11013	2.71440	0.20614
H	0.18761	3.27275	0.32278
C	2.32943	3.39290	0.10802
H	2.34148	4.47575	0.14571
C	3.41768	1.26620	-0.07415
C	3.48512	2.66848	-0.03527
H	4.45000	3.16061	-0.11624
C	4.57085	0.43417	-0.20350
H	5.54364	0.90878	-0.28932
C	4.45534	-0.91429	-0.21079
H	5.33254	-1.54755	-0.30087
H	1.58953	-4.53539	0.07021
N	1.00926	1.39820	0.16620
Ir	-0.78651	0.01525	0.09220
Cl	-0.91685	-0.06253	2.60237
C	-3.63758	-0.68892	0.34076
H	-4.50497	-1.29189	0.04009
H	-3.74358	-0.49785	1.41649
C	-3.67888	0.62691	-0.37543
H	-3.63954	0.51607	-1.46755
H	-4.54641	1.23839	-0.10418
Cl	-0.61574	0.21072	-2.22813
H	-2.12572	-2.12555	0.84022
H	-2.81643	-1.58932	-2.09656
C	-2.46332	-2.21043	-1.26873

H	-1.52178	-2.65309	-1.60746
H	-3.18789	-3.02445	-1.13178
O	-2.49248	1.34543	0.04948
C	-2.39549	2.63167	-0.56302
H	-3.38272	3.10201	-0.55106
H	-2.02679	2.54222	-1.59004
H	-1.71915	3.23493	0.04153
C	-2.32721	-1.41367	0.01721
H	-1.60359	-1.14844	2.80119

IRC of gamma transition state for 1-1-methoxybutane



IRC of delta transition state for 1-1-methoxybutane



XYZ coordinates of butyl acetate

Energy: -386.0775324

C	-3.25933	-0.92388	-0.00047
C	-2.18554	0.11824	-0.00011
O	-2.35906	1.30636	-0.00094
O	-0.97067	-0.45402	0.00098
C	0.14939	0.43762	0.00145
C	1.40538	-0.39235	-0.00028
C	2.65483	0.47254	-0.00004
C	3.92643	-0.35485	-0.00059
H	-3.16016	-1.56170	0.88173
H	-3.15391	-1.56837	-0.87704
H	-4.23759	-0.44536	-0.00547
H	0.09271	1.08689	0.88448
H	0.09174	1.08914	-0.87984
H	1.40379	-1.04957	-0.88065
H	1.40493	-1.05174	0.87846
H	2.64004	1.13457	0.87718
H	2.63981	1.13537	-0.87663
H	3.97343	-1.00224	-0.88354
H	4.82202	0.27275	-0.00088
H	3.97410	-1.00241	0.88220

XYZ coordinates of alpha activated butyl acetate

Energy: -2139.120918

N	-0.23658	1.25499	0.11361
C	-1.59340	1.19841	0.03447
C	-2.19185	-0.09504	0.02139
C	0.33601	2.45005	0.16508
H	1.42029	2.46201	0.23715
C	-2.38505	2.35227	-0.02987
C	-0.36837	3.65795	0.12153
C	-1.75368	3.61926	0.00844
C	-1.85550	-2.36450	0.05896
H	-1.13720	-3.18096	0.10508

C	-3.22744	-2.63228	-0.06445
C	-3.57866	-0.24672	-0.09227
C	-4.11078	-1.56029	-0.13095
C	-4.36784	0.94285	-0.17132
H	-5.44535	0.85872	-0.26163
C	-3.80080	2.17531	-0.13696
H	-4.43643	3.05174	-0.19637
N	-1.35190	-1.14688	0.11589
Ir	0.73058	-0.54730	0.10576
Cl	0.83393	-0.54506	2.63561
O	3.52503	-1.27914	-0.00534
C	2.87063	-2.38819	0.00614
Cl	0.58051	-0.64535	-2.21759
H	3.04548	0.45064	0.96712
H	3.26252	0.18000	-2.03031
C	3.25717	0.81454	-1.13830
H	2.54537	1.61873	-1.37079
O	1.62792	-2.43285	0.09514
C	2.71549	-0.00255	0.01377
H	1.93673	0.10414	2.86177
C	3.67578	-3.62640	-0.10597
H	3.10796	-4.48007	0.26141
H	3.90669	-3.78934	-1.16348
H	4.62055	-3.52322	0.42885
C	4.63510	1.41586	-0.87800
H	5.06708	1.73627	-1.83278
H	5.30787	0.64057	-0.48941
C	4.59138	2.60136	0.07093
H	3.96412	3.40347	-0.33881
H	4.18712	2.33226	1.05534
H	5.58559	3.02180	0.24326
C	-3.67555	-4.05898	-0.12268
H	-4.34210	-4.30833	0.70935
H	-4.21697	-4.27285	-1.04957
H	-2.82186	-4.73840	-0.07651
C	-5.58498	-1.75972	-0.25756
H	-5.86645	-2.81105	-0.21679
H	-6.12280	-1.24032	0.54261
H	-5.95283	-1.35459	-1.20713
C	-2.57371	4.86367	-0.06858
H	-3.28627	4.91588	0.76203
H	-1.96398	5.76555	-0.03892
H	-3.15886	4.88825	-0.99431
C	0.40891	4.93610	0.18317
H	0.26708	5.53658	-0.72105
H	0.10580	5.55275	1.03515
H	1.47910	4.73992	0.28224

XYZ coordinates of the transition state for butyl acetate

Energy: -1981.999176

Imaginary frequency: 577.80cm^{-1}

N	-0.82010	1.32627	0.12049
C	-2.13689	1.00716	-0.01290
C	-2.47807	-0.37039	-0.07715
C	-0.47373	2.60562	0.18390
H	0.58405	2.82365	0.29562
C	-3.14341	1.98140	-0.08454
C	-1.41489	3.63309	0.11634
C	-2.74687	3.32688	-0.01833
H	-3.49626	4.11104	-0.07257

C	-1.71218	-2.54834	-0.04648
H	-0.85540	-3.21267	0.02049
C	-3.01798	-3.03556	-0.17483
H	-3.18334	-4.10572	-0.20931
C	-3.81509	-0.76686	-0.20402
C	-4.06540	-2.15007	-0.25406
H	-5.08687	-2.50560	-0.35462
C	-4.82600	0.24103	-0.27337
H	-5.86184	-0.06914	-0.37158
C	-4.50281	1.55650	-0.21781
H	-5.27470	2.31798	-0.27219
H	-1.07459	4.65987	0.17417
N	-1.46043	-1.25336	-0.00329
Ir	0.45854	-0.29074	0.14931
Cl	0.31792	-0.66514	2.55700
Cl	0.44105	-0.19204	-2.21282
H	2.96211	0.98769	-1.91965
C	2.85907	1.46682	-0.94202
H	2.03818	2.18512	-1.06385
C	2.46809	0.41076	0.06588
H	0.96384	0.58276	1.37017
C	4.12934	2.21267	-0.54422
H	4.51699	2.74193	-1.42153
H	4.90627	1.49026	-0.26158
C	3.89040	3.20535	0.58063
H	3.16565	3.97024	0.27469
H	3.50298	2.72426	1.48812
H	4.80829	3.72424	0.86775
O	3.29918	-0.78417	-0.24011
C	2.73930	-1.93876	-0.19088
O	1.51826	-2.06810	0.03092
C	3.61713	-3.11203	-0.38292
H	4.36693	-2.90049	-1.14637
H	3.02584	-3.98656	-0.64899
H	4.14302	-3.31042	0.55644
H	2.84257	0.68676	1.06064

Appendix B2 – Computational data for chapter 4

XYZ coordinates of iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride

Energy: -1674.436572

C	-1.96238	-3.21354	0.10759
C	-3.12546	-2.46947	0.08256
C	-3.05265	-1.05710	0.09136
C	-1.76554	-0.50658	0.13893
N	-0.62115	-1.25480	0.18215
C	-0.68763	-2.60015	0.14721
C	-4.16342	-0.15277	0.04063
C	-3.97033	1.20232	0.02169
C	-2.65211	1.76522	0.05259
C	-1.56663	0.88268	0.12165
C	-2.33656	3.14217	0.00214
C	-1.01505	3.53911	0.00693
C	0.04933	2.60747	0.07063
N	-0.25581	1.29368	0.15362
Ir	1.11239	-0.18094	0.22134
Cl	3.39157	0.04852	0.56379
Cl	1.15981	-0.30488	-2.11124
C	0.57760	-3.38556	0.13849
C	1.47082	3.04535	0.04281

H	-2.00222	-4.29722	0.08926
H	-4.09295	-2.96158	0.04748
H	-5.16764	-0.56467	0.00967
H	-4.81950	1.87749	-0.02480
H	-3.13242	3.87918	-0.05145
H	-0.75661	4.59086	-0.04698
H	0.37063	-4.45676	0.19756
H	1.22641	-3.11979	0.98378
H	1.14397	-3.19853	-0.78403
H	2.00519	2.59560	-0.80417
H	1.53190	4.13194	-0.04880
H	2.00433	2.74730	0.95427

XYZ coordinates of delta activated 1-butanol by iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride

Energy: -2748.611478

N	0.85021	1.34254	-0.14925
C	2.07459	0.73709	0.01507
C	2.13641	-0.68616	-0.03469
C	0.84197	2.65415	-0.36273
Cl	-0.59539	3.44601	-0.87368
C	3.26475	1.46796	0.14541
C	1.98660	3.45430	-0.24327
C	3.18431	2.86785	0.04989
H	4.08159	3.46858	0.16435
C	1.02795	-2.65443	-0.44716
Cl	-0.41683	-3.48822	-0.86615
C	2.21500	-3.39960	-0.33842
H	2.18236	-4.47248	-0.48284
C	3.37407	-1.33519	0.07885
C	3.37746	-2.73753	-0.05990
H	4.31270	-3.28173	0.03440
C	4.55559	-0.57105	0.29576
H	5.49982	-1.09378	0.41210
C	4.50160	0.78241	0.32382
H	5.40153	1.37392	0.45938
H	1.89030	4.52227	-0.39361
N	0.97821	-1.35514	-0.26670
Ir	-0.73699	0.04175	0.14763
Cl	-1.35166	0.09799	-2.24444
O	-2.17838	-1.44305	0.61584
H	-2.19215	-1.52716	1.58348
Cl	-0.08257	-0.19925	2.39613
C	-3.52696	-1.38531	0.07794
C	-4.30059	-0.20949	0.61618
C	-3.65537	1.14337	0.34304
C	-2.28000	1.29429	0.96689
H	-4.00113	-2.33974	0.32539
H	-3.39124	-1.33972	-1.00598
H	-4.43499	-0.33476	1.70112
H	-5.30557	-0.24877	0.18022
H	-4.30254	1.91732	0.77752
H	-3.64589	1.34518	-0.73802
H	-2.31142	0.98272	2.01615
H	-1.94674	2.33095	0.95720
H	-1.53435	1.01834	-0.93545

XYZ coordinates of gamma activated 1-butanol by iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride

Energy: -1907.947398

N	0.61372	-1.31404	-0.29979
C	1.88569	-0.86283	-0.02980
C	2.10690	0.54787	0.00709
C	0.45929	-2.59017	-0.67987
C	2.98192	-1.72665	0.10334
C	1.53099	-3.49863	-0.56044
C	2.75862	-3.09550	-0.12462
H	3.57567	-3.80215	-0.01193
C	1.23846	2.66127	-0.38404
C	2.50948	3.23073	-0.17862
H	2.62494	4.30418	-0.28255
C	3.40428	1.04336	0.22069
C	3.57646	2.43630	0.14017
H	4.56133	2.86420	0.30483
C	4.47950	0.13855	0.45822
H	5.46763	0.54424	0.65297
C	4.27431	-1.19834	0.39695
H	5.09417	-1.89629	0.53674
H	1.34686	-4.53205	-0.83447
N	1.04706	1.35307	-0.25668
Ir	-0.83651	0.13485	-0.03903
Cl	-0.30985	0.27920	2.43357
C	-2.54722	-1.01430	0.40485
C	-3.62626	-0.05959	0.92376
H	-4.61335	-0.54138	0.91358
H	-3.42740	0.22134	1.96842
C	-3.65719	1.18273	0.09481
H	-3.89263	0.96580	-0.95352
H	-4.32524	1.95730	0.47995
Cl	-1.33554	0.22828	-2.31829
O	-2.29216	1.70255	0.16152
H	-2.90107	-1.41974	-0.55139
C	0.07988	3.52229	-0.75579
H	0.41447	4.50699	-1.08720
H	-0.48086	3.05962	-1.57596
H	-0.58289	3.67565	0.10431
C	-0.80560	-3.09712	-1.27962
H	-1.41251	-2.29310	-1.68922
H	-0.54716	-3.78304	-2.09125
H	-1.39918	-3.66998	-0.56037
H	-2.16201	2.31589	-0.57515
C	-2.37160	-2.14998	1.40728
H	-1.42629	-2.69372	1.31411
H	-2.45024	-1.79130	2.44510
H	-3.17512	-2.89226	1.31135
H	-0.86192	-0.82411	2.84393

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride

Energy: -1947.191649

N	0.91775	-1.34556	0.16828
C	2.10634	-0.67082	0.00541
C	2.10226	0.75156	0.13033
C	0.95059	-2.67404	0.31576
C	3.32625	-1.33357	-0.18966
C	2.15232	-3.38460	0.13471
C	3.31606	-2.73783	-0.15938
H	4.23807	-3.28688	-0.32675
C	0.90005	2.64911	0.70435
C	2.06999	3.42929	0.60556

H	2.00765	4.49110	0.82140
C	3.30836	1.46164	0.02540
C	3.25473	2.84974	0.24951
H	4.16209	3.44056	0.16147
C	4.51814	0.76829	-0.26664
H	5.43301	1.34188	-0.38012
C	4.52525	-0.58171	-0.36562
H	5.44687	-1.12304	-0.55656
H	2.11995	-4.46476	0.23124
N	0.91953	1.35149	0.42649
Ir	-0.71714	-0.12542	-0.09950
Cl	-1.16752	-0.20918	2.41593
C	-3.40044	-1.57364	0.05684
C	-4.02080	-0.21926	0.43282
H	-5.10952	-0.31253	0.51111
H	-3.69405	0.13773	1.41728
C	-3.73840	0.87205	-0.56103
H	-3.95471	0.55299	-1.59014
H	-4.33964	1.76441	-0.34911
Cl	-0.04923	0.02848	-2.33038
H	-2.13418	-1.05660	2.59731
H	-3.21643	-2.16090	0.97050
H	-2.42738	-1.07112	-1.78798
C	-2.15137	-1.46507	-0.80139
H	-1.72736	-2.44977	-1.00828
O	-2.35509	1.29298	-0.49457
C	-2.10775	2.31189	-1.47380
H	-2.30192	1.92565	-2.47901
H	-1.06208	2.60519	-1.40835
H	-2.76000	3.16502	-1.25814
H	-4.14779	-2.16000	-0.49671
C	-0.36267	3.28605	1.17802
H	-0.25881	3.55406	2.23603
H	-0.56075	4.21767	0.63818
H	-1.22159	2.62243	1.07411
C	-0.24562	-3.46124	0.72546
H	-0.58895	-4.10954	-0.08718
H	0.03643	-4.11660	1.55583
H	-1.07411	-2.83006	1.03476

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride

Energy: -1947.199129

N	-0.80745	1.34632	0.34973
C	-2.00969	0.76922	0.00948
C	-2.10682	-0.65575	0.01758
C	-0.78088	2.66386	0.58939
C	-3.16316	1.52189	-0.25640
C	-1.91075	3.46178	0.33554
C	-3.07375	2.91523	-0.12456
H	-3.93800	3.53494	-0.34463
C	-1.08695	-2.65493	0.59586
C	-2.29123	-3.34645	0.36041
H	-2.32156	-4.41685	0.53661
C	-3.34091	-1.27512	-0.23294
C	-3.39652	-2.67179	-0.07906
H	-4.32735	-3.19459	-0.27994
C	-4.47135	-0.48501	-0.59005
H	-5.40556	-0.98650	-0.82345
C	-4.38228	0.86520	-0.60065

H	-5.24390	1.48011	-0.84191
H	-1.82920	4.52826	0.51352
N	-0.99505	-1.35078	0.36435
Ir	0.77031	0.02701	0.06659
Cl	1.28134	-0.17274	2.53783
C	3.68677	0.39669	-0.07094
H	4.58187	0.94352	-0.39851
H	3.88756	0.07585	0.96148
C	3.51435	-0.81964	-0.92279
H	3.42565	-0.56053	-1.98643
H	4.30961	-1.56398	-0.80212
Cl	0.21690	0.12178	-2.20348
H	2.46246	1.94022	0.72146
H	2.65918	1.59527	-2.31213
C	2.49705	2.17214	-1.39712
H	1.56977	2.73014	-1.55972
H	3.31944	2.89626	-1.31148
O	2.27013	-1.43706	-0.51004
C	1.92411	-2.50521	-1.40324
H	1.95212	-2.15467	-2.43819
H	0.91407	-2.83624	-1.17605
H	2.63623	-3.32288	-1.25227
C	2.44276	1.29089	-0.16259
H	2.46601	0.35097	2.63814
C	0.41937	3.32996	1.16424
H	1.14388	3.60200	0.39207
H	0.11555	4.25045	1.66677
H	0.91550	2.68962	1.89412
C	0.07660	-3.38904	1.17468
H	-0.13335	-3.61893	2.22625
H	0.23578	-4.34713	0.67060
H	0.99619	-2.80457	1.13550

XYZ coordinates of alpha activated butyl acetate by iridium(III)-2,9-dimethyl-1,10-phenanthroline dichloride

Energy: -1599.736886

C	-2.63077	-2.77590	0.01270
C	-3.60049	-1.85239	0.29441
C	-3.30066	-0.48202	0.17870
C	-2.00130	-0.16168	-0.21538
N	-1.03796	-1.09311	-0.48024
C	-1.32951	-2.39521	-0.37500
C	-4.21854	0.58669	0.41712
C	-3.84698	1.88282	0.24447
C	-2.52474	2.21757	-0.18029
C	-1.61435	1.17993	-0.38892
C	-2.05478	3.51906	-0.43117
C	-0.77259	3.69244	-0.88640
C	0.09234	2.59920	-1.08347
N	-0.33055	1.36347	-0.79880
Ir	0.78346	-0.35368	-0.94387
Cl	2.61869	-1.55986	-1.55284
C	1.37009	-0.23758	1.04732
C	2.52898	0.71121	1.21226
C	3.19077	0.55320	2.58206
C	4.35928	1.50572	2.74875
O	0.32596	0.20677	1.88124
C	-0.45492	-0.71477	2.51109
C	-1.39529	-0.04108	3.45153
O	-0.36782	-1.89288	2.31317

H	-2.83857	-3.83676	0.09467
H	-4.59478	-2.16610	0.59841
H	-5.22896	0.33928	0.72802
H	-4.55584	2.68736	0.41488
H	-2.71087	4.37132	-0.28100
H	-0.39727	4.68462	-1.11136
H	1.62778	-1.27528	1.29401
H	3.27594	0.52212	0.43148
H	2.17433	1.74524	1.09709
H	2.44350	0.72763	3.36607
H	3.52880	-0.48491	2.69690
H	4.83319	1.38849	3.72639
H	4.03589	2.54875	2.66041
H	5.12551	1.32932	1.98641
H	-1.85020	0.83804	2.98766
H	-0.83794	0.30902	4.32597
H	-2.15924	-0.74603	3.77814
C	1.45870	2.78650	-1.64191
H	1.68706	3.84679	-1.76056
H	2.22699	2.33877	-1.00443
H	1.53618	2.31032	-2.62599
C	-0.28971	-3.41996	-0.63778
H	0.20463	-3.25814	-1.59961
H	0.48137	-3.37767	0.13938
H	-0.73060	-4.41754	-0.62888

XYZ coordinates of iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2515.108078

C	0.34981	3.72323	-0.05056
C	1.72399	3.59801	-0.01933
C	2.31006	2.31066	-0.05146
C	1.42954	1.22245	-0.12373
N	0.05832	1.34896	-0.17467
C	-0.46793	2.58084	-0.11956
C	3.71481	2.02968	-0.00162
C	4.18447	0.74318	-0.01195
C	3.28600	-0.37117	-0.07253
C	1.91306	-0.09477	-0.13270
C	3.65413	-1.73824	-0.06363
C	2.67577	-2.71405	-0.10662
C	1.32192	-2.34304	-0.16229
N	0.94647	-1.06321	-0.18885
Ir	-0.97938	-0.38541	-0.19606
Cl	-0.92153	-0.46170	2.14086
Cl	-3.24878	-0.67105	-0.44137
Cl	-2.21521	2.76900	-0.13712
Cl	0.05005	-3.56607	-0.20106
H	-0.13029	4.69411	-0.01681
H	2.35221	4.48168	0.03786
H	4.40671	2.86479	0.05069
H	5.25178	0.54912	0.03175
H	4.70199	-2.01860	-0.01639
H	2.92579	-3.76838	-0.09211

XYZ coordinates of delta activated 1-butanol by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2287.785701

C	-1.43612	-3.43730	-0.71304
C	-2.70746	-2.92420	-0.68407
C	-2.88997	-1.52891	-0.62379

C	-1.73274	-0.74849	-0.61718
N	-0.46387	-1.25203	-0.67480
C	-0.32830	-2.57534	-0.70114
C	-4.15053	-0.85907	-0.55786
C	-4.22267	0.49603	-0.46590
C	-3.04061	1.29718	-0.43285
C	-1.80790	0.64991	-0.52131
C	-3.00743	2.69995	-0.30786
C	-1.79832	3.34562	-0.27319
C	-0.60505	2.61173	-0.37640
N	-0.60022	1.28895	-0.51000
Ir	1.04007	0.11127	-0.77070
Cl	3.22336	0.18732	-1.31685
Cl	1.25108	-3.22544	-0.72043
Cl	0.89885	3.42238	-0.33021
C	1.49923	0.01393	1.25474
C	0.34903	-0.11988	2.21773
C	0.88667	-0.20318	3.64354
C	-0.21442	-0.31755	4.67291
O	0.40303	-0.40066	5.93061
H	-1.25409	-4.50460	-0.74635
H	-3.56825	-3.58618	-0.69822
H	-5.05590	-1.45774	-0.57807
H	-5.18657	0.99286	-0.41265
H	-3.93364	3.26270	-0.23725
H	-1.73033	4.42228	-0.17209
H	2.18736	-0.83834	1.32002
H	2.07231	0.93414	1.42788
H	-0.33405	0.73929	2.13728
H	-0.24181	-1.02283	2.00278
H	1.49149	0.68317	3.87457
H	1.55332	-1.06915	3.74618
H	-0.82876	-1.21046	4.46290
H	-0.87937	0.56090	4.60488
H	-0.25912	-0.46220	6.62224

XYZ coordinates of gamma activated 1-butanol by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2748.611786

N	0.58208	1.42961	-0.22240
C	1.88139	1.02970	0.01579
C	2.19028	-0.35923	-0.07037
C	0.39903	2.73331	-0.38696
Cl	-1.08443	3.31520	-1.00956
C	2.92504	1.93392	0.26611
C	1.37900	3.70430	-0.13683
C	2.63001	3.30651	0.23051
H	3.40660	4.03361	0.44719
C	1.46784	-2.46761	-0.57349
Cl	0.18698	-3.53947	-1.05709
C	2.74836	-3.01412	-0.42443
H	2.90393	-4.07254	-0.59272
C	3.51221	-0.80084	0.11077
C	3.76561	-2.17300	-0.06403
H	4.77372	-2.55288	0.07336
C	4.53305	0.13537	0.43827
H	5.54178	-0.22874	0.60554
C	4.24541	1.45550	0.51200
H	5.01848	2.18323	0.73809
H	1.11442	4.74798	-0.25116

N	1.17622	-1.20288	-0.38676
Ir	-0.78931	-0.14895	0.07504
Cl	-1.59002	-0.29578	-2.29213
C	-2.63697	0.67682	0.80538
C	-3.57742	1.47815	-0.08265
H	-3.91105	0.91391	-0.96831
H	-4.50537	1.66814	0.47496
H	-3.21021	2.44882	-0.39596
C	-3.51641	-0.48330	1.33281
H	-4.11013	-0.14023	2.18848
H	-4.23247	-0.76030	0.54644
C	-2.75718	-1.71680	1.69152
H	-2.14089	-1.60486	2.58687
H	-3.39249	-2.60298	1.77350
O	-1.88554	-1.90443	0.53871
H	-1.29677	-2.66198	0.66219
Cl	-0.01958	-0.10958	2.29254
H	-2.31540	1.30559	1.64414
H	-2.60669	0.51257	-2.21685

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2748.613478

Imaginary frequency: 165.57cm^{-1}

N	0.85021	1.34254	-0.14925
C	2.07459	0.73709	0.01507
C	2.13641	-0.68616	-0.03469
C	0.84197	2.65415	-0.36273
Cl	-0.59539	3.44601	-0.87368
C	3.26475	1.46796	0.14541
C	1.98660	3.45430	-0.24327
C	3.18431	2.86785	0.04989
H	4.08159	3.46858	0.16435
C	1.02795	-2.65443	-0.44716
Cl	-0.41683	-3.48822	-0.86615
C	2.21500	-3.39960	-0.33842
H	2.18236	-4.47248	-0.48284
C	3.37407	-1.33519	0.07885
C	3.37746	-2.73753	-0.05990
H	4.31270	-3.28173	0.03440
C	4.55559	-0.57105	0.29576
H	5.49982	-1.09378	0.41210
C	4.50160	0.78241	0.32382
H	5.40153	1.37392	0.45938
H	1.89030	4.52227	-0.39361
N	0.97821	-1.35514	-0.26670
Ir	-0.73699	0.04175	0.14763
Cl	-1.35166	0.09799	-2.24444
O	-2.17838	-1.44305	0.61584
H	-2.19215	-1.52716	1.58348
Cl	-0.08257	-0.19925	2.39613
C	-3.52696	-1.38531	0.07794
C	-4.30059	-0.20949	0.61618
C	-3.65537	1.14337	0.34304
C	-2.28000	1.29429	0.96689
H	-4.00113	-2.33974	0.32539
H	-3.39124	-1.33972	-1.00598
H	-4.43499	-0.33476	1.70112
H	-5.30557	-0.24877	0.18022
H	-4.30254	1.91732	0.77752

H	-3.64589	1.34518	-0.73802
H	-2.31142	0.98272	2.01615
H	-1.94674	2.33095	0.95720
H	-1.53435	1.01834	-0.93545

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2787.862843

N	1.11162	-1.25323	-0.16169
C	2.21780	-0.46738	0.08164
C	2.06257	0.95029	0.04436
C	1.32389	-2.54502	-0.39777
Cl	0.06447	-3.55161	-0.96052
C	3.49945	-1.00492	0.27108
C	2.57895	-3.15432	-0.22812
C	3.64967	-2.39789	0.14390
H	4.62392	-2.85197	0.29826
C	0.71273	2.72556	-0.49831
Cl	-0.78783	3.34286	-1.07306
C	1.77224	3.63762	-0.34603
H	1.59664	4.68818	-0.54299
C	3.18419	1.77851	0.21203
C	2.99451	3.16323	0.03512
H	3.83338	3.84009	0.16836
C	4.45346	1.20385	0.50132
H	5.29936	1.86382	0.66625
C	4.60421	-0.14205	0.52623
H	5.57514	-0.59199	0.70878
H	2.65946	-4.22030	-0.40138
N	0.82800	1.43904	-0.25240
Ir	-0.66558	-0.20208	0.03233
Cl	-0.23087	-0.22854	2.55639
O	-2.35450	1.09817	0.23159
Cl	-0.97099	-0.32273	-2.27522
C	-3.58595	0.69372	-0.41262
C	-4.31282	-0.37519	0.37642
C	-3.36702	-1.34149	1.08633
C	-2.13369	-1.75942	0.30176
H	-3.27407	0.34108	-1.39703
H	-4.18519	1.60085	-0.54870
H	-4.94601	-0.92078	-0.33333
H	-4.99565	0.07078	1.10867
H	-3.93385	-2.24848	1.33335
H	-3.07467	-0.92787	2.06117
H	-0.81616	-1.12580	1.57206
C	-2.53878	1.90497	1.39422
H	-1.56185	2.27928	1.70108
H	-2.98274	1.33321	2.21526
H	-3.18663	2.74681	1.13119
H	-1.70177	-2.64706	0.77953
H	-2.38455	-2.05577	-0.72268

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2327.049457

C	-2.53462	-2.38130	-1.05908
C	-3.43490	-1.35116	-1.13445
C	-2.99240	-0.03253	-0.93779
C	-1.62982	0.14763	-0.69257
N	-0.72066	-0.87587	-0.63200

C	-1.18180	-2.11963	-0.79563
C	-3.83794	1.11704	-0.95219
C	-3.33579	2.36257	-0.74658
C	-1.93885	2.56117	-0.53316
C	-1.10758	1.43982	-0.50976
C	-1.31701	3.81343	-0.36717
C	0.04706	3.87860	-0.23949
C	0.80036	2.69648	-0.25171
N	0.24447	1.49542	-0.33912
Ir	1.20045	-0.32332	-0.34432
Cl	-0.10534	-3.43475	-0.66538
Cl	2.89506	-1.82776	-0.59691
Cl	2.51284	2.77845	-0.19172
C	1.27135	-0.46696	1.75988
C	2.51816	0.27659	2.18209
C	0.05260	0.01569	2.51460
C	-1.15751	-0.90779	2.54285
O	-2.29508	-0.20291	2.10082
C	-3.48856	-0.89763	2.35908
H	-2.83538	-3.41314	-1.19458
H	-4.48318	-1.54979	-1.33690
H	-4.89891	0.97337	-1.13314
H	-3.98730	3.23052	-0.75933
H	-1.91391	4.72024	-0.36299
H	0.56710	4.82388	-0.14108
H	1.40513	-1.55057	1.88001
H	2.77897	-0.03859	3.20252
H	3.38935	0.06324	1.55755
H	2.35830	1.35936	2.20916
H	0.38929	0.18837	3.54746
H	-0.26913	1.00616	2.16792
H	-1.33373	-1.28252	3.56271
H	-0.99650	-1.80033	1.91097
H	-3.62638	-1.06808	3.43578
H	-4.31847	-0.28881	1.99300
H	-3.50597	-1.87462	1.84916

XYZ coordinates of alpha activated butyl acetate by iridium(III)-2,9-dichloro-1,10-phenanthroline dichloride

Energy: -2440.404606

C	-2.95707	-2.49470	0.03857
C	-3.84096	-1.47409	0.25053
C	-3.40268	-0.14063	0.12288
C	-2.06549	0.05097	-0.22891
N	-1.17863	-0.97025	-0.44737
C	-1.62070	-2.21858	-0.30275
C	-4.22142	1.01166	0.32404
C	-3.72073	2.26738	0.17532
C	-2.35573	2.47350	-0.18655
C	-1.54743	1.35003	-0.37621
C	-1.74550	3.72926	-0.37827
C	-0.42726	3.79250	-0.74838
C	0.30207	2.60537	-0.91738
N	-0.22968	1.40911	-0.71684
Ir	0.71551	-0.40548	-0.87779
Cl	-0.54499	-3.51525	-0.52268
Cl	1.93939	2.66898	-1.42212
Cl	2.34660	-1.86432	-1.48834
C	1.28562	-0.35740	1.12531
C	2.61174	0.34001	1.27743

C	3.19769	0.11554	2.67361
C	4.54475	0.79623	2.82423
O	0.34203	0.31817	1.92410
C	-0.62647	-0.39927	2.55997
C	-1.42006	0.48379	3.46181
O	-0.78990	-1.57394	2.39182
H	-3.25022	-3.53285	0.13601
H	-4.87178	-1.68450	0.51918
H	-5.26222	0.86263	0.59499
H	-4.35554	3.13529	0.32466
H	-2.32255	4.63909	-0.24269
H	0.07315	4.73788	-0.92121
H	1.31598	-1.41983	1.39860
H	3.31572	-0.03925	0.52770
H	2.49226	1.41743	1.09918
H	2.49403	0.49351	3.42585
H	3.29705	-0.96332	2.85086
H	4.96514	0.63195	3.81956
H	4.46095	1.87801	2.67357
H	5.26490	0.41395	2.09315
H	-1.61514	1.45312	2.99572
H	-0.84253	0.67505	4.37203
H	-2.35140	-0.01148	3.73679

XYZ coordinates of iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1674.42937

C	0.29043	3.47779	0.08719
C	1.65908	3.21953	0.09500
C	2.07635	1.85862	0.00572
C	1.08123	0.87540	-0.09080
N	-0.25982	1.17341	-0.11528
C	-0.65680	2.45429	-0.01030
C	3.43699	1.40640	0.01971
C	3.75140	0.07526	-0.04514
C	2.73487	-0.93194	-0.12692
C	1.40287	-0.49524	-0.15226
C	2.96798	-2.33865	-0.17354
C	1.85577	-3.17303	-0.23004
C	0.55124	-2.66099	-0.24340
N	0.33095	-1.34212	-0.22181
Ir	-1.48303	-0.37915	-0.21424
Cl	-1.52860	-0.92048	2.05401
Cl	-3.59432	0.50500	-0.65531
C	2.65295	4.32691	0.20417
C	4.35355	-2.89415	-0.15181
H	-0.06739	4.49917	0.16130
H	-1.72373	2.64411	-0.01078
H	4.23177	2.14234	0.08730
H	4.79269	-0.23042	-0.02952
H	1.98989	-4.24926	-0.25534
H	-0.31966	-3.30809	-0.26523
H	3.27194	4.21647	1.10387
H	2.15943	5.30016	0.25537
H	3.33176	4.33847	-0.65818
H	4.34363	-3.98566	-0.19893
H	4.94346	-2.52693	-1.00130
H	4.88409	-2.60324	0.76390

XYZ coordinates of delta activated 1-butanol by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1907.954674

N	-0.51261	1.29597	0.00783
C	-1.74371	0.70050	0.04258
C	-1.79251	-0.72869	0.05394
C	-0.45691	2.61744	-0.09732
H	0.53058	3.05803	-0.17374
C	-2.93467	1.44412	0.02766
C	-1.59693	3.41574	-0.12016
C	-2.85489	2.85816	-0.04659
C	-0.60886	-2.69853	-0.01008
H	0.36448	-3.18232	-0.04598
C	-1.78842	-3.44569	0.00150
H	-1.72828	-4.52872	-0.02658
C	-3.02601	-1.39879	0.06536
C	-3.01553	-2.81839	0.04142
C	-4.21990	-0.61858	0.08335
H	-5.18069	-1.12168	0.10157
C	-4.17438	0.73691	0.06340
H	-5.09941	1.30287	0.06535
H	-1.47557	4.49053	-0.20343
N	-0.60644	-1.38015	0.02391
Ir	1.07981	0.02862	-0.03221
Cl	1.17793	0.01152	2.47872
O	2.54029	-1.52816	-0.31326
H	2.51644	-1.60221	-1.28479
Cl	1.02042	-0.01472	-2.36241
C	3.92048	-1.40707	0.10748
C	4.54420	-0.10506	-0.32458
C	3.95701	1.10429	0.38898
C	2.56046	1.50539	-0.06566
H	4.45064	-2.27533	-0.29628
H	3.89757	-1.50218	1.19783
H	4.44674	0.00755	-1.41467
H	5.61917	-0.17679	-0.11886
H	4.63086	1.95933	0.24133
H	3.98183	0.90451	1.47284
H	2.61323	1.89493	-1.09214
H	2.23000	2.34383	0.57156
H	1.82888	1.11278	2.70342
C	-4.28353	-3.60242	0.04961
H	-4.08282	-4.67479	0.03536
H	-4.88148	-3.38178	0.94034
H	-4.90183	-3.36322	-0.82232
C	-4.07793	3.70879	-0.06787
H	-4.68546	3.55334	0.83008
H	-3.81944	4.76737	-0.12210
H	-4.70963	3.47059	-0.93044

XYZ coordinates of gamma activated 1-butanol by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1907.952577

N	-0.34370	1.23887	-0.03439
C	-1.62936	0.77944	0.02714
C	-1.82446	-0.63581	0.03400
C	-0.15768	2.53850	-0.23057
H	0.86500	2.86511	-0.37398
C	-2.73692	1.64204	0.01981
C	-1.20814	3.45075	-0.26551
C	-2.51331	3.03605	-0.11127
C	-0.85580	-2.71238	-0.08897

H	0.05416	-3.30423	-0.15707
C	-2.10287	-3.33639	-0.03184
H	-2.15359	-4.41976	-0.06365
C	-3.11974	-1.17538	0.08696
C	-3.25729	-2.58735	0.05639
C	-4.22528	-0.27595	0.14693
H	-5.23138	-0.67705	0.20452
C	-4.04110	1.06720	0.10765
H	-4.90236	1.72590	0.13103
H	-0.97836	4.50003	-0.41709
N	-0.71155	-1.40097	-0.05604
Ir	1.13082	-0.16307	-0.05614
Cl	1.08683	-0.47524	2.44729
C	2.86043	1.03389	0.04659
C	2.93206	2.08551	1.14483
H	3.12895	1.63824	2.13188
H	3.77692	2.76724	0.97862
H	2.03802	2.70989	1.23925
C	4.05521	0.08749	0.20787
H	5.00028	0.59838	-0.02238
H	4.13242	-0.24807	1.25333
C	3.91179	-1.11709	-0.66689
H	3.88040	-0.84521	-1.72786
H	4.67568	-1.87950	-0.49469
O	2.61648	-1.70203	-0.30875
H	2.32508	-2.24329	-1.05508
Cl	1.12999	-0.02421	-2.38267
H	2.93725	1.52957	-0.93272
H	1.74097	0.58224	2.82667
C	-4.59757	-3.23757	0.10920
H	-4.50879	-4.32479	0.08650
H	-5.13763	-2.96075	1.02094
H	-5.21844	-2.93168	-0.73976
C	-3.64033	4.01042	-0.12286
H	-4.22173	3.95539	0.80373
H	-3.27500	5.03261	-0.23240
H	-4.32984	3.80764	-0.94947

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1907.947779

Imaginary frequency: 318.78cm^{-1}

N	0.52839	-1.30369	-0.01831
C	1.75184	-0.69504	0.01500
C	1.77965	0.73165	0.02547
C	0.48319	-2.62622	-0.09412
H	-0.50012	-3.07790	-0.15812
C	2.95032	-1.42391	0.01777
C	1.63178	-3.41241	-0.09768
C	2.88397	-2.84041	-0.03105
C	0.56226	2.68442	-0.01122
H	-0.41832	3.15262	-0.03761
C	1.73043	3.44773	0.01849
H	1.65317	4.52984	0.01253
C	3.00148	1.41998	0.05413
C	2.96774	2.83968	0.05081
C	4.20629	0.65653	0.07674
H	5.16002	1.17248	0.10419
C	4.18036	-0.69977	0.05749
H	5.11283	-1.25341	0.06853

H	1.52196	-4.49000	-0.15462
N	0.58378	1.36570	-0.00602
Ir	-1.06427	-0.03352	-0.03889
Cl	-1.16316	-0.11676	2.49999
O	-2.52155	1.52174	-0.25560
H	-2.56700	1.61760	-1.22379
Cl	-1.03417	0.03731	-2.37097
C	-3.86966	1.40154	0.26640
C	-4.56539	0.15989	-0.22963
C	-3.99967	-1.12905	0.34744
C	-2.62058	-1.51605	-0.16907
H	-4.39830	2.31541	-0.02129
H	-3.75365	1.40120	1.35446
H	-4.52990	0.13545	-1.32949
H	-5.62464	0.25216	0.03848
H	-4.69207	-1.94819	0.11265
H	-4.00427	-1.05220	1.44571
H	-2.66847	-1.72987	-1.24375
H	-2.32951	-2.45854	0.31967
H	-1.72114	-0.90534	1.44267
C	4.22082	3.64560	0.07791
H	4.00080	4.71419	0.07192
H	4.81352	3.42730	0.97276
H	4.85139	3.42537	-0.79010
C	4.11441	-3.67943	-0.02476
H	4.70984	-3.50096	0.87697
H	3.86632	-4.74117	-0.06141
H	4.75276	-3.45084	-0.88492

XYZ coordinates of the gamma transition state of 1-butanol by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1907.944259

Imaginary frequency: 226.68cm^{-1}

N	-0.37238	1.25540	-0.05031
C	-1.64913	0.77599	-0.00517
C	-1.81665	-0.63964	0.00629
C	-0.19637	2.56082	-0.19460
H	0.82575	2.90334	-0.29752
C	-2.76853	1.62058	-0.00716
C	-1.25957	3.45850	-0.22156
C	-2.56132	3.02047	-0.10520
C	-0.79376	-2.69589	-0.04465
H	0.13003	-3.26756	-0.07766
C	-2.02645	-3.34468	0.02969
H	-2.05082	-4.42914	0.04130
C	-3.09808	-1.20609	0.07307
C	-3.20009	-2.62181	0.08492
C	-4.22065	-0.32599	0.11728
H	-5.21917	-0.74522	0.17746
C	-4.06237	1.02062	0.07071
H	-4.93706	1.66139	0.09051
H	-1.04275	4.51560	-0.33158
N	-0.68670	-1.38097	-0.06462
Ir	1.10193	-0.15144	-0.03621
Cl	1.10524	-0.25815	2.45031
C	2.96691	0.99490	-0.04191
C	3.17645	2.22386	0.83287
H	3.17577	1.98318	1.90404

H	4.15575	2.66711	0.61299
H	2.43819	3.01439	0.67636
C	4.05293	-0.02913	0.27873
H	5.04341	0.39540	0.06447
H	4.04534	-0.27206	1.35115
C	3.87657	-1.28186	-0.51720
H	3.94920	-1.08639	-1.59284
H	4.56514	-2.08104	-0.23350
O	2.51922	-1.75435	-0.23245
H	2.22895	-2.26764	-0.99962
Cl	1.11982	-0.08398	-2.38061
H	3.02254	1.28388	-1.09860
H	1.72767	0.63154	1.33258
C	-4.52287	-3.30297	0.15836
H	-4.40770	-4.38785	0.16388
H	-5.06607	-3.01541	1.06503
H	-5.15384	-3.03385	-0.69559
C	-3.70127	3.97846	-0.10808
H	-4.28107	3.90370	0.81826
H	-3.35099	5.00705	-0.20549
H	-4.38749	3.77356	-0.93670

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1947.204285

N	0.63599	-1.30014	0.01390
C	1.85039	-0.67539	0.02063
C	1.86205	0.75437	0.04197
C	0.61251	-2.62522	-0.07161
H	-0.36247	-3.09511	-0.10863
C	3.05836	-1.39264	-0.02828
C	1.76891	-3.39632	-0.11799
C	3.01375	-2.80778	-0.09204
C	0.65590	2.69874	-0.01048
H	-0.31330	3.18487	-0.03094
C	1.81864	3.46675	-0.08095
H	1.73409	4.54654	-0.14643
C	3.08502	1.44643	-0.01304
C	3.05607	2.86338	-0.06759
C	4.29622	0.69445	-0.03371
H	5.24413	1.22088	-0.05752
C	4.28272	-0.66050	-0.03671
H	5.21946	-1.20610	-0.06128
H	1.66993	-4.47464	-0.18302
N	0.66033	1.38165	0.07602
Ir	-1.01765	-0.12395	0.06703
Cl	-1.12840	-0.29066	2.58079
O	-2.78487	1.13301	0.18423
Cl	-0.94549	0.05755	-2.25484
C	-3.89294	1.03519	-0.74622
C	-4.17905	-0.39786	-1.12755
C	-3.83546	-1.37745	-0.01385
C	-2.35636	-1.72128	-0.01731
H	-3.66285	1.66169	-1.61752
H	-4.74885	1.47120	-0.21383
H	-3.62152	-0.66913	-2.02987
H	-5.24254	-0.45318	-1.38324
H	-4.41400	-2.29949	-0.15582
H	-4.15457	-0.97029	0.95774
H	-2.02472	-1.22738	2.68761

C	-2.66524	2.45361	0.68825
H	-1.87535	2.46282	1.44023
H	-3.60954	2.75085	1.15653
H	-2.43370	3.15528	-0.12412
H	-2.13701	-2.41060	0.81842
H	-2.13370	-2.26804	-0.94487
C	4.30990	3.66729	-0.12873
H	4.89799	3.41645	-1.01806
H	4.08990	4.73550	-0.16156
H	4.94562	3.47924	0.74310
C	4.25657	-3.62797	-0.14616
H	4.02236	-4.69308	-0.17941
H	4.85181	-3.38542	-1.03310
H	4.89091	-3.44732	0.72821

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1947.210761

N	-0.50296	1.26365	0.12831
C	-1.75752	0.73398	0.03574
C	-1.87550	-0.68959	0.05505
C	-0.38277	2.58618	0.16356
H	0.62224	2.98282	0.24073
C	-2.90506	1.53963	-0.05625
C	-1.47570	3.44298	0.09253
C	-2.75571	2.94866	-0.03284
C	-0.82480	-2.71434	0.23226
H	0.10012	-3.26973	0.34708
C	-2.03789	-3.39776	0.14301
H	-2.03668	-4.48199	0.18492
C	-3.14253	-1.29063	-0.03861
C	-3.22027	-2.70612	-0.00063
C	-4.28907	-0.45148	-0.16189
H	-5.26985	-0.90655	-0.24678
C	-4.17533	0.89904	-0.16650
H	-5.06565	1.51196	-0.25327
H	-1.29848	4.51277	0.12357
N	-0.72837	-1.39929	0.18663
Ir	1.06191	-0.03249	0.09352
Cl	1.22063	0.02975	2.60147
C	3.91783	0.66755	0.31941
H	4.78384	1.27262	0.01845
H	4.03187	0.46500	1.39231
C	3.95266	-0.64077	-0.41072
H	3.90417	-0.51685	-1.50119
H	4.82293	-1.25513	-0.15458
Cl	0.86142	-0.20563	-2.22706
H	2.41318	2.10192	0.84337
H	3.07072	1.58627	-2.10448
C	2.73039	2.20222	-1.26739
H	1.78622	2.65077	-1.59085
H	3.45984	3.01249	-1.13317
O	2.77055	-1.36478	0.01486
C	2.66831	-2.63821	-0.62218
H	3.65194	-3.11643	-0.61150
H	2.30779	-2.52672	-1.64995
H	1.98159	-3.24782	-0.03639
C	2.60496	1.39505	0.01337
H	1.90758	1.11652	2.79582
C	-4.52533	-3.41840	-0.10699

H	-4.38769	-4.49973	-0.05917
H	-5.20379	-3.12771	0.70221
H	-5.02832	-3.18314	-1.05105
C	-3.92884	3.86162	-0.13414
H	-4.46995	3.70658	-1.07374
H	-4.63966	3.68756	0.68076
H	-3.61770	4.90660	-0.09346

XYZ coordinates of the delta transition state of 1-methoxybutane by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1947.198192

Imaginary frequency: 657.08cm^{-1}

N	0.67225	-1.31064	-0.01218
C	1.86221	-0.64236	0.01555
C	1.81475	0.78369	0.03145
C	0.69114	-2.63470	-0.08765
H	-0.26859	-3.13591	-0.13608
C	3.09567	-1.31115	-0.00682
C	1.87689	-3.36254	-0.10837
C	3.09982	-2.72843	-0.06399
C	0.50475	2.66640	-0.07573
H	-0.49350	3.09009	-0.14031
C	1.63230	3.48723	-0.11903
H	1.49939	4.56115	-0.19774
C	3.00135	1.53159	0.00009
C	2.89896	2.94583	-0.06494
C	4.24393	0.82972	0.00776
H	5.16949	1.39515	0.00242
C	4.28773	-0.52593	0.00750
H	5.24806	-1.02989	0.00381
H	1.81983	-4.44417	-0.16565
N	0.58466	1.35359	0.02958
Ir	-0.98476	-0.14906	0.03923
Cl	-1.13998	-0.52436	2.57477
O	-2.64476	1.23669	0.12340
Cl	-0.90912	0.02083	-2.28698
C	-3.89915	1.13456	-0.60006
C	-4.13783	-0.24321	-1.15678
C	-3.85190	-1.34188	-0.14017
C	-2.39310	-1.76327	-0.13313
H	-3.89267	1.90646	-1.37815
H	-4.68602	1.37558	0.12727
H	-3.54589	-0.40463	-2.06292
H	-5.19010	-0.26478	-1.46290
H	-4.46738	-2.21980	-0.37378
H	-4.17034	-1.01621	0.86350
H	-1.71231	-1.20316	1.47736
C	-2.72639	2.16896	1.19833
H	-1.73679	2.27017	1.64394
H	-3.42900	1.80838	1.95900
H	-3.06514	3.13867	0.81678
H	-2.26450	-2.58655	0.59536
H	-2.12481	-2.19423	-1.10618
C	4.11124	3.81169	-0.09655
H	4.73303	3.58906	-0.97037
H	3.83954	4.86759	-0.13720
H	4.73277	3.65527	0.79147
C	4.37047	-3.50506	-0.08836
H	4.17430	-4.57764	-0.12535
H	4.97755	-3.24244	-0.96150

H	4.97682	-3.30173	0.80072

XYZ coordinates of the gamma transition state of 1-methoxybutane by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -1947.199828

Imaginary frequency: 327.06cm^{-1}

N	-0.52893	1.27391	0.07180
C	-1.77338	0.72413	0.00016
C	-1.85490	-0.69814	0.02558
C	-0.42627	2.59638	0.11274
H	0.57227	3.01012	0.18749
C	-2.93712	1.50520	-0.07008
C	-1.53622	3.43286	0.06098
C	-2.81023	2.91691	-0.04358
C	-0.74171	-2.69390	0.17354
H	0.19962	-3.22158	0.25699
C	-1.93806	-3.40733	0.10974
H	-1.90473	-4.49102	0.14719
C	-3.10549	-1.33260	-0.04287
C	-3.14305	-2.74998	-0.00301
C	-4.27390	-0.51996	-0.14322
H	-5.24549	-0.99781	-0.20670
C	-4.19386	0.83340	-0.15268
H	-5.10107	1.42346	-0.22049
H	-1.37856	4.50539	0.09824
N	-0.68503	-1.37607	0.13387
Ir	1.03718	-0.01952	0.10993
Cl	1.19712	0.27212	2.58626
C	3.96416	0.69569	0.23146
H	4.82397	1.25730	-0.15612
H	4.12299	0.56537	1.30915
C	3.92797	-0.65860	-0.40881
H	3.81426	-0.61770	-1.50017
H	4.80510	-1.26358	-0.15635
Cl	0.92018	-0.31497	-2.21950
H	2.59866	2.25598	0.71805
H	2.97005	1.47283	-2.19995
C	2.69383	2.15497	-1.39354
H	1.73227	2.59213	-1.67565
H	3.43590	2.96307	-1.36352
O	2.76764	-1.32792	0.14607
C	2.67331	-2.69271	-0.25519
H	3.67814	-3.12157	-0.29089
H	2.19636	-2.77642	-1.23822
H	2.10589	-3.21994	0.51258
C	2.66871	1.45566	-0.04436
H	1.76022	0.97000	1.35633
C	-4.42822	-3.49942	-0.07801
H	-4.25868	-4.57594	-0.02585
H	-5.09790	-3.22208	0.74306
H	-4.95670	-3.28536	-1.01331
C	-4.00115	3.80840	-0.11196
H	-4.56547	3.64317	-1.03601
H	-4.68467	3.61922	0.72270
H	-3.70894	4.85894	-0.07780

XYZ coordinates of alpha activated butyl acetate by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -2060.572059

N	-0.54367	1.20785	0.13752

C	-1.87553	0.92260	0.05266
C	-2.24288	-0.45507	0.01081
C	-0.18171	2.48206	0.21126
H	0.88246	2.68355	0.28324
C	-2.86203	1.91888	0.00938
C	-1.10379	3.52479	0.19009
C	-2.45575	3.27547	0.07713
C	-1.51264	-2.63567	0.00843
H	-0.66785	-3.31875	0.04173
C	-2.82281	-3.10091	-0.12005
H	-2.99765	-4.17007	-0.17887
C	-3.58684	-0.83335	-0.11040
C	-3.88291	-2.21986	-0.17638
C	-4.57178	0.19802	-0.16761
H	-5.61749	-0.07475	-0.26158
C	-4.22558	1.50884	-0.10548
H	-4.99877	2.26821	-0.14786
H	-0.73686	4.54382	0.25165
N	-1.23021	-1.34857	0.08787
Ir	0.71754	-0.40206	0.09410
Cl	0.82659	-0.44850	2.62617
Cl	0.57692	-0.46532	-2.23020
H	3.07926	0.77715	-2.02050
C	2.99065	1.38234	-1.11257
H	2.16739	2.08046	-1.31909
C	2.58508	0.46797	0.02173
H	1.76512	0.41488	2.87578
C	4.27026	2.17025	-0.84645
H	4.63688	2.57696	-1.79567
H	5.05339	1.48911	-0.48989
C	4.07172	3.30861	0.13947
H	3.33558	4.02875	-0.23895
H	3.72003	2.95592	1.11756
H	5.00022	3.85691	0.31848
O	3.59560	-0.65609	-0.01462
C	3.13619	-1.85770	-0.02343
O	1.91594	-2.10902	0.04472
C	4.13033	-2.95451	-0.09490
H	3.80735	-3.68467	-0.83907
H	4.16551	-3.46509	0.87181
H	5.12056	-2.57275	-0.33747
H	2.83194	0.95183	0.98486
C	-5.28535	-2.70606	-0.31257
H	-5.32292	-3.79596	-0.34593
H	-5.90456	-2.37128	0.52660
H	-5.74829	-2.32391	-1.22876
C	-3.44510	4.38829	0.03015
H	-2.95153	5.35826	0.10706
H	-4.01265	4.37074	-0.90657
H	-4.16957	4.30989	0.84783

XYZ coordinates of the alpha transition state of butyl acetate by iridium(III)-4,7-dimethyl-1,10-phenanthroline dichloride

Energy: -2060.546178

Imaginary frequency: 376.57cm^{-1}

N	-0.55989	1.24116	0.13975
C	-1.89448	0.92469	0.03957
C	-2.22870	-0.45665	-0.00423
C	-0.20800	2.53356	0.18393
H	0.85253	2.75223	0.25701

C	-2.90268	1.90583	-0.01929
C	-1.15891	3.55675	0.13441
C	-2.51507	3.27581	0.02832
C	-1.42396	-2.64255	0.00728
H	-0.55790	-3.29561	0.04430
C	-2.73188	-3.13679	-0.10020
H	-2.88705	-4.20994	-0.14007
C	-3.56637	-0.87528	-0.11353
C	-3.82166	-2.27755	-0.16239
C	-4.57939	0.13472	-0.17300
H	-5.61903	-0.16561	-0.25681
C	-4.26110	1.46286	-0.12732
H	-5.05080	2.20568	-0.17528
H	-0.81921	4.58630	0.17533
N	-1.18471	-1.33151	0.06112
Ir	0.71324	-0.36911	0.09926
Cl	0.78973	-0.53378	2.77011
Cl	0.62092	-0.26821	-2.26335
H	3.16582	0.87288	-1.96990
C	3.06827	1.42788	-1.02966
H	2.25879	2.15344	-1.20713
C	2.63879	0.45838	0.05548
C	4.36323	2.17732	-0.68972
H	4.75734	2.63731	-1.60514
H	5.12151	1.45475	-0.35642
C	4.15459	3.25821	0.36877
H	3.44830	4.02090	0.01129
H	3.76062	2.84588	1.30929
H	5.09221	3.76823	0.61365
O	3.60948	-0.74675	-0.10611
C	3.09005	-1.94620	-0.12733
O	1.82560	-2.11570	-0.00946
C	4.01035	-3.08739	-0.30821
H	3.51519	-4.01834	-0.03086
H	4.91806	-2.94197	0.28246
H	4.30844	-3.14556	-1.36203
H	2.96096	0.82941	1.04333
C	-5.21554	-2.80435	-0.28242
H	-5.22277	-3.89691	-0.30704
H	-5.83838	-2.48401	0.56241
H	-5.69951	-2.44564	-1.19967
C	-3.52802	4.37199	-0.03461
H	-3.05107	5.35371	0.01980
H	-4.10208	4.32930	-0.96893
H	-4.24591	4.30074	0.79230
H	1.02836	0.51292	1.85318

XYZ coordinates of iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride

Energy: -1746.346862

C	1.16874	3.38632	0.08411
C	2.42721	2.80286	0.04942
C	2.52478	1.38766	0.07342
C	1.32568	0.68799	0.14516
N	0.10000	1.26790	0.20291
C	0.02955	2.59413	0.15246
C	3.73735	0.64047	0.01221
C	3.71681	-0.72098	0.00869
C	2.49032	-1.45035	0.06547
C	1.30613	-0.71759	0.14098
C	2.34551	-2.86335	0.03542

C	1.06778	-3.40711	0.06702
C	-0.04542	-2.58761	0.13793
N	0.06588	-1.26073	0.19505
O	3.56352	3.47754	-0.01587
O	3.36242	-3.70616	-0.03154
Ir	-1.51349	0.02028	0.23455
Cl	-3.73371	-0.01772	0.49071
Cl	-1.53531	0.05235	-2.05035
H	1.05637	4.46506	0.05160
H	-0.96462	3.03114	0.16593
H	4.67757	1.17771	-0.03804
H	4.66473	-1.24933	-0.04465
H	0.95028	-4.48342	0.02869
H	-1.05257	-2.99328	0.14930
H	3.42582	4.43244	-0.03843
H	4.21946	-3.26646	-0.06085

XYZ coordinates of delta activated 1-butanol by iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride

Energy: -1979.856109

N	-0.52987	1.29501	0.01695
C	-1.75919	0.70353	0.04316
C	-1.80950	-0.72879	0.05651
C	-0.47383	2.62229	-0.08663
H	0.51530	3.05968	-0.15824
C	-2.95431	1.44016	0.02288
C	-1.59786	3.42694	-0.11508
C	-2.85261	2.85290	-0.04824
C	-0.63199	-2.70247	0.01098
H	0.34161	-3.18556	-0.01621
C	-1.79764	-3.45418	0.01624
H	-1.76669	-4.53689	-0.00787
C	-3.04904	-1.38964	0.06289
C	-3.01946	-2.80878	0.04321
C	-4.24280	-0.61400	0.07245
H	-5.21658	-1.09554	0.08982
C	-4.19562	0.74065	0.05081
H	-5.13405	1.28789	0.05085
H	-1.50357	4.50287	-0.19788
N	-0.62657	-1.37817	0.03891
Ir	1.06718	0.02768	-0.03005
Cl	1.18196	0.01519	2.48122
O	2.52481	-1.52751	-0.31813
H	2.49596	-1.60357	-1.28936
Cl	0.98715	-0.02045	-2.35936
C	3.90761	-1.40671	0.09520
C	4.52980	-0.10686	-0.34521
C	3.94699	1.10519	0.36713
C	2.54698	1.50366	-0.07905
H	4.43426	-2.27715	-0.30839
H	3.89004	-1.49787	1.18595
H	4.42628	0.00170	-1.43517
H	5.60587	-0.17826	-0.14528
H	4.61892	1.96014	0.21064
H	3.97935	0.91067	1.45167
H	2.59177	1.89004	-1.10710
H	2.22124	2.34382	0.55848
H	1.83398	1.11644	2.70300
O	-4.11241	-3.56684	0.04647
H	-4.92539	-3.05174	0.03924

O	-3.90051	3.66821	-0.06960
H	-4.74116	3.19956	-0.04642

XYZ coordinates of gamma activated 1-butanol by iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride

Energy: -1979.853534

N	-0.36595	1.24523	0.00901
C	-1.64917	0.78596	0.03879
C	-1.84372	-0.63272	0.03115
C	-0.18017	2.55438	-0.15988
H	0.84402	2.88297	-0.28218
C	-2.76397	1.63941	0.02741
C	-1.21575	3.46951	-0.19439
C	-2.52018	3.03297	-0.06903
C	-0.87224	-2.70994	-0.05103
H	0.04235	-3.29704	-0.08905
C	-2.10500	-3.34374	-0.01895
H	-2.18114	-4.42421	-0.04156
C	-3.14294	-1.16622	0.06207
C	-3.25628	-2.58013	0.03226
C	-4.25221	-0.27470	0.10425
H	-5.26883	-0.65587	0.14387
C	-4.06867	1.06815	0.07969
H	-4.94683	1.70755	0.09519
H	-1.01264	4.52593	-0.32092
N	-0.73018	-1.39267	-0.03186
Ir	1.12016	-0.15282	-0.05157
Cl	1.09393	-0.55209	2.45409
C	2.84233	1.05279	0.02423
C	2.93247	2.06886	1.15165
H	3.04885	1.59159	2.13269
H	3.81509	2.70991	1.02132
H	2.06796	2.73342	1.23263
C	4.05399	0.11809	0.11658
H	4.98048	0.64362	-0.15203
H	4.19536	-0.22410	1.15476
C	3.88414	-1.08054	-0.76151
H	3.80215	-0.79869	-1.81700
H	4.66117	-1.83817	-0.63172
O	2.61072	-1.67892	-0.34931
H	2.29769	-2.23441	-1.07604
Cl	1.05960	0.02512	-2.37312
H	2.88509	1.57522	-0.94340
H	2.34851	-0.47799	2.77272
O	-4.41843	-3.22570	0.05315
H	-5.17614	-2.63211	0.06066
O	-3.47824	3.95236	-0.07676
H	-4.36096	3.57550	-0.00199

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride

Energy: -2019.10599

N	0.65267	-1.29864	0.04467
C	1.86499	-0.67823	0.02300
C	1.87908	0.75457	0.05066
C	0.62797	-2.63049	-0.02018
H	-0.34883	-3.09770	-0.03039
C	3.07562	-1.38916	-0.04632
C	1.76743	-3.40920	-0.08161
C	3.00812	-2.80391	-0.09427

C	0.68266	2.70486	0.06551
H	-0.28517	3.19282	0.08299
C	1.83035	3.47692	-0.02481
H	1.77480	4.55784	-0.07165
C	3.10731	1.43662	-0.02627
C	3.06068	2.85341	-0.06105
C	4.31693	0.68875	-0.07957
H	5.27829	1.19330	-0.11865
C	4.30130	-0.66536	-0.08497
H	5.25045	-1.19195	-0.12749
H	1.69449	-4.48874	-0.13187
N	0.68271	1.38055	0.12528
Ir	-1.00668	-0.12251	0.07783
Cl	-1.17916	-0.31036	2.58670
O	-2.77751	1.12951	0.16089
Cl	-0.87492	0.07994	-2.24030
C	-3.85715	1.04054	-0.80404
C	-4.13373	-0.38910	-1.20455
C	-3.82043	-1.37718	-0.08969
C	-2.34144	-1.71880	-0.05355
H	-3.59958	1.67318	-1.66307
H	-4.72776	1.47433	-0.29427
H	-3.55223	-0.65373	-2.09357
H	-5.18999	-0.44196	-1.48896
H	-4.39259	-2.29915	-0.25567
H	-4.16780	-0.97852	0.87568
H	-2.09425	-1.23147	2.66431
C	-2.66282	2.45006	0.66626
H	-1.90397	2.45161	1.44985
H	-3.62138	2.75941	1.09601
H	-2.39137	3.14641	-0.13840
H	-2.14623	-2.41250	0.78454
H	-2.09085	-2.25961	-0.97751
O	4.14040	3.62620	-0.13539
H	4.95762	3.12183	-0.19926
O	4.07439	-3.59334	-0.15783
H	4.90278	-3.10356	-0.18241

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride

Energy: -2019.118704

N	-0.51512	1.26895	0.11857
C	-1.76990	0.73536	0.03358
C	-1.88882	-0.68651	0.05328
C	-0.40112	2.59330	0.14139
H	0.60257	2.99491	0.21146
C	-2.92382	1.52472	-0.05661
C	-1.48791	3.45281	0.07099
C	-2.76060	2.93117	-0.04188
C	-0.85315	-2.72000	0.20708
H	0.06695	-3.28560	0.30926
C	-2.06372	-3.40224	0.11764
H	-2.07418	-4.48717	0.14748
C	-3.16264	-1.26601	-0.03898
C	-3.23180	-2.68071	-0.01075
C	-4.31773	-0.44418	-0.15269
H	-5.28834	-0.92026	-0.23018
C	-4.20224	0.90731	-0.15730
H	-5.07730	1.54148	-0.23672
H	-1.31884	4.52452	0.09219

N	-0.74442	-1.40407	0.17775
Ir	1.05137	-0.03244	0.09251
Cl	1.18830	0.03583	2.60176
C	3.90488	0.66878	0.32968
H	4.77177	1.27241	0.02831
H	4.01635	0.47052	1.40366
C	3.94132	-0.64303	-0.39474
H	3.89415	-0.52450	-1.48585
H	4.81143	-1.25580	-0.13416
Cl	0.86519	-0.21343	-2.22857
H	2.39763	2.10385	0.84613
H	3.06928	1.58306	-2.09773
C	2.72321	2.20027	-1.26393
H	1.77982	2.64546	-1.59448
H	3.45020	3.01250	-1.12782
O	2.75887	-1.36448	0.03366
C	2.65573	-2.64388	-0.58977
H	3.64056	-3.11979	-0.58243
H	2.28661	-2.54393	-1.61580
H	1.97580	-3.24883	0.00931
C	2.59250	1.39537	0.01796
H	1.88024	1.11849	2.80086
O	-4.44275	-3.22426	-0.10742
H	-4.40433	-4.18707	-0.08877
O	-3.86430	3.66664	-0.13327
H	-3.66773	4.61017	-0.12983

XYZ coordinates of alpha activated butyl acetate by iridium(III)-4,7-dihydroxy-1,10-phenanthroline dichloride

Energy: -2132.481538

N	-0.55289	1.21593	0.14003
C	-1.88536	0.92935	0.04827
C	-2.25599	-0.44584	0.00987
C	-0.19555	2.49258	0.20924
H	0.86726	2.69808	0.28906
C	-2.87913	1.91256	-0.00522
C	-1.10905	3.53827	0.17781
C	-2.45784	3.26368	0.05772
C	-1.54465	-2.63198	0.01417
H	-0.70707	-3.32350	0.05180
C	-2.85100	-3.09562	-0.11950
C	-3.60265	-0.80121	-0.11591
C	-3.89123	-2.18813	-0.17922
C	-4.59577	0.21634	-0.18263
H	-5.63500	-0.07575	-0.28058
C	-4.24555	1.52732	-0.12375
H	-4.99872	2.30523	-0.17044
N	-1.24880	-1.34647	0.09481
Ir	0.70580	-0.40208	0.10163
Cl	0.80648	-0.43555	2.63329
O	3.58092	-0.66382	-0.00308
C	3.11708	-1.86488	-0.02628
Cl	0.56897	-0.46904	-2.22308
H	2.82092	0.94807	0.99579
H	3.06904	0.77255	-2.00898
C	2.98110	1.37769	-1.10095
H	2.15869	2.07675	-1.30805
O	1.89758	-2.11346	0.05146
C	2.57327	0.46349	0.03279
H	1.88103	0.25678	2.86871

C	4.11326	-2.95220	-0.16323
H	3.69816	-3.89185	0.19886
H	4.35235	-3.06400	-1.22563
H	5.03552	-2.70125	0.36160
C	4.26138	2.16394	-0.83356
H	4.63206	2.56745	-1.78258
H	5.04205	1.48232	-0.47248
C	4.06130	3.30528	0.14863
H	3.33023	4.02720	-0.23636
H	3.70169	2.95605	1.12506
H	4.99057	3.85077	0.33223
O	-3.40677	4.19242	0.00136
H	-3.04079	5.08333	0.03918
O	-5.17224	-2.52696	-0.30122
H	-5.28558	-3.48262	-0.35412
H	-0.74861	4.56018	0.23601
H	-3.03877	-4.16296	-0.17966

XYZ coordinates of iridium(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride

Energy: -1752.993519

C	3.22675	1.54198	-0.07086
C	2.47377	2.71738	-0.05039
C	1.06132	2.60825	-0.07340
C	0.50813	1.33242	-0.13903
N	1.24771	0.20095	-0.18852
C	2.56869	0.30628	-0.13701
C	0.13015	3.69616	-0.01599
C	-1.21510	3.49346	-0.01652
C	-1.78802	2.17974	-0.07449
C	-0.88060	1.12178	-0.13915
C	-3.16752	1.85866	-0.05529
C	-3.53264	0.50953	-0.06996
C	-2.54034	-0.47418	-0.13322
N	-1.24786	-0.17850	-0.18759
C	4.72236	1.54399	-0.01761
C	3.11228	4.06234	0.02238
C	-4.21980	2.91027	0.01628
C	-4.96383	0.08258	-0.01494
Ir	0.24010	-1.56369	-0.23191
Cl	0.57766	-3.75831	-0.50954
Cl	0.24441	-1.59352	2.05343
H	3.12783	-0.62617	-0.14549
H	0.50901	4.71096	0.03952
H	-1.87176	4.35398	0.04024
H	-2.79565	-1.53105	-0.13822
H	5.15343	2.05754	-0.88300
H	5.11805	0.52668	-0.00739
H	5.08892	2.05067	0.88035
H	2.70444	4.73263	-0.74070
H	2.91643	4.52726	0.99614
H	4.19198	4.01997	-0.11278
H	-5.05135	2.68009	-0.65531
H	-3.84865	3.90216	-0.23955
H	-4.63889	2.96137	1.02903
H	-5.05309	-1.00296	0.05584
H	-5.51054	0.40340	-0.90856
H	-5.47608	0.51792	0.84888

XYZ coordinates of delta activated 1-butanol by iridium(III)-3,4,7,8-

tetramethyl-1,10-phenanthroline dichloride

Energy: -1986.506081

N	-0.38796	1.30909	0.02327
C	-1.63100	0.74920	0.06354
C	-1.72261	-0.67669	0.06070
C	-0.29707	2.62818	-0.07990
H	0.70553	3.03526	-0.16343
C	-2.79269	1.53490	0.06370
C	-1.39886	3.48995	-0.09593
C	-2.67309	2.94494	-0.00296
C	-0.61047	-2.68077	-0.04296
H	0.34941	-3.19275	-0.09551
C	-1.80226	-3.42178	-0.03409
C	-2.97054	-1.31551	0.07504
C	-3.00701	-2.73265	0.03349
C	-4.13874	-0.49402	0.10995
H	-5.11654	-0.96257	0.12834
C	-4.05239	0.85936	0.10277
H	-4.96284	1.44788	0.11404
N	-0.56185	-1.36496	0.01114
Ir	1.16616	-0.00542	-0.02685
Cl	1.24368	-0.05214	2.48403
O	2.58250	-1.60202	-0.32161
H	2.55986	-1.66010	-1.29430
Cl	1.12120	-0.01752	-2.35785
C	3.96338	-1.52661	0.10593
C	4.62608	-0.23574	-0.30095
C	4.06908	0.97828	0.42881
C	2.68934	1.42779	-0.03136
H	4.47128	-2.40229	-0.31050
H	3.93394	-1.63955	1.19448
H	4.53811	-0.10256	-1.38952
H	5.69738	-0.34160	-0.09050
H	4.77009	1.81478	0.30244
H	4.07606	0.75907	1.50909
H	2.76215	1.82889	-1.05225
H	2.37847	2.26766	0.61400
C	-1.72070	-4.91447	-0.10277
H	-2.24179	-5.30657	-0.98194
H	-0.68188	-5.24659	-0.16110
H	-2.16874	-5.38555	0.77813
C	-4.32090	-3.44220	0.04616
H	-4.20650	-4.52513	0.06656
H	-4.91623	-3.15485	0.91922
H	-4.91029	-3.18818	-0.84217
C	-3.89598	3.80044	-0.00256
H	-4.52977	3.58306	0.86335
H	-3.65715	4.86280	0.02027
H	-4.50112	3.61591	-0.89765
C	-1.14911	4.96084	-0.21954
H	-0.08144	5.17106	-0.31090
H	-1.64317	5.37864	-1.10221
H	-1.52091	5.50870	0.65241
H	1.90064	1.04279	2.72148

XYZ coordinates of gamma activated 1-butanol by iridium(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride

Energy: -1986.503739

N	-0.06285	1.26352	0.00296

C	-1.39979	1.00887	0.06679
C	-1.81492	-0.35692	0.04923
C	0.32102	2.52085	-0.17770
H	1.38322	2.67900	-0.32785
C	-2.34979	2.04000	0.08215
C	-0.55265	3.61265	-0.19737
C	-1.91172	3.38252	-0.02408
C	-1.19484	-2.55458	-0.12428
C	-2.52146	-3.00746	-0.07455
C	-3.17509	-0.69449	0.09921
C	-3.53550	-2.06422	0.04289
C	-4.12227	0.37226	0.17896
H	-5.18021	0.13967	0.22985
C	-3.72889	1.66996	0.16508
H	-4.48017	2.45090	0.19997
N	-0.84132	-1.28559	-0.06401
Ir	1.17268	-0.35297	-0.04689
Cl	1.07895	-0.68551	2.45298
C	3.07094	0.55105	0.07268
C	3.30767	1.56779	1.18044
H	3.42068	1.08657	2.16467
H	4.25469	2.10217	1.02553
H	2.52752	2.33005	1.27344
C	4.09741	-0.57688	0.22723
H	5.11395	-0.22165	0.00829
H	4.11297	-0.93313	1.26866
C	3.76921	-1.73156	-0.66509
H	3.79336	-1.44471	-1.72234
H	4.39912	-2.60906	-0.49815
O	2.39368	-2.10523	-0.32568
H	2.02245	-2.57359	-1.08575
Cl	1.19896	-0.17941	-2.37138
H	3.23056	1.03673	-0.90163
H	-0.38691	-3.27992	-0.21262
C	-2.78306	-4.47859	-0.15706
H	-1.84944	-5.03765	-0.25165
H	-3.29938	-4.84842	0.73461
H	-3.40602	-4.72941	-1.02148
C	-4.97504	-2.45712	0.09441
H	-5.10960	-3.53789	0.10316
H	-5.46233	-2.05438	0.98855
H	-5.51786	-2.06278	-0.77215
C	0.02074	4.97954	-0.40547
H	1.09831	4.93128	-0.57607
H	-0.42839	5.47455	-1.27196
H	-0.14810	5.62508	0.46280
C	-2.90088	4.49970	-0.00072
H	-3.56926	4.41965	0.86209
H	-2.41933	5.47583	0.04299
H	-3.53040	4.48128	-0.89832
H	1.86293	0.27830	2.83487

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride

Energy: -2025.753396

N	0.53620	-1.30722	0.01810
C	1.75067	-0.69197	0.04189
C	1.77448	0.73679	0.05988
C	0.50586	-2.63079	-0.07924
H	-0.47575	-3.08790	-0.13276

C	2.94679	-1.42630	0.00691
C	1.64352	-3.44178	-0.11975
C	2.89282	-2.83925	-0.06302
C	0.59473	2.69070	-0.03191
H	-0.37267	3.18268	-0.07496
C	1.75362	3.47771	-0.09688
C	2.99824	1.42447	0.01768
C	2.98463	2.83968	-0.04740
C	4.20179	0.65582	0.01570
H	5.15711	1.16850	0.00036
C	4.17649	-0.69871	0.01414
H	5.11156	-1.24691	-0.00088
N	0.58218	1.37573	0.07081
Ir	-1.10749	-0.11658	0.07248
Cl	-1.19296	-0.26608	2.58730
O	-2.86386	1.15781	0.19792
Cl	-1.05318	0.05185	-2.25074
C	-3.98094	1.06316	-0.72087
C	-4.28143	-0.36989	-1.09123
C	-3.93637	-1.34606	0.02517
C	-2.46026	-1.70290	0.00952
H	-3.75449	1.68241	-1.59839
H	-4.82884	1.50898	-0.18360
H	-3.73265	-0.65047	-1.99616
H	-5.34732	-0.41823	-1.33839
H	-4.52502	-2.26340	-0.10584
H	-4.24258	-0.93024	0.99730
H	-2.09807	-1.19187	2.71306
C	-2.72782	2.48031	0.69168
H	-1.92840	2.48829	1.43343
H	-3.66428	2.78842	1.16884
H	-2.49943	3.17439	-0.12803
H	-2.23803	-2.39025	0.84610
H	-2.25228	-2.25644	-0.91748
C	4.15386	-3.63692	-0.09856
H	3.96488	-4.70920	-0.07241
H	4.72495	-3.42339	-1.00939
H	4.80058	-3.39246	0.75038
C	1.45698	-4.92290	-0.23133
H	1.88183	-5.44942	0.62941
H	0.39760	-5.18192	-0.28658
H	1.94049	-5.32145	-1.12866
C	1.60946	4.96255	-0.21522
H	0.55729	5.25115	-0.26781
H	2.05158	5.48253	0.64098
H	2.09999	5.34420	-1.11613
C	4.26950	3.59915	-0.09028
H	4.82823	3.37053	-1.00508
H	4.11345	4.67676	-0.06082
H	4.91385	3.33404	0.75424

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride

Energy: -2025.760132

N	-0.28566	1.29984	0.13307
C	-1.58164	0.90020	0.01949
C	-1.84502	-0.50332	0.01552
C	-0.03360	2.60281	0.17398
H	1.00896	2.88867	0.26174
C	-2.63295	1.82496	-0.06999

C	-1.01476	3.59538	0.09763
C	-2.34242	3.20999	-0.03605
C	-1.01643	-2.62432	0.19881
H	-0.15044	-3.26957	0.33064
C	-2.28772	-3.21070	0.11873
C	-3.16237	-0.97832	-0.07707
C	-3.38656	-2.37671	-0.03937
C	-4.21424	-0.01901	-0.19544
H	-5.23839	-0.36430	-0.28291
C	-3.96182	1.31243	-0.19057
H	-4.78787	2.00933	-0.27550
N	-0.78112	-1.32850	0.13437
Ir	1.13669	-0.14980	0.07744
Cl	1.20812	-0.24641	2.59347
C	4.02480	0.20235	0.48320
H	4.97593	0.71500	0.28325
H	4.02805	-0.05945	1.54924
C	3.97578	-1.06376	-0.31740
H	4.05357	-0.87341	-1.39681
H	4.74024	-1.79320	-0.02649
Cl	0.96815	-0.16443	-2.25083
H	2.67254	1.79843	0.95385
H	3.42990	1.27273	-1.96967
C	3.13242	1.90627	-1.12922
H	2.27266	2.48401	-1.48208
H	3.95451	2.60855	-0.93443
O	2.68162	-1.66480	-0.06292
C	2.48986	-2.82294	-0.87630
H	3.30203	-3.52835	-0.67569
H	2.46890	-2.54733	-1.93511
H	1.53924	-3.27493	-0.60198
C	2.83149	1.09207	0.11687
H	1.97537	0.75987	2.88989
C	-2.39984	-4.70081	0.20041
H	-3.04520	-5.01363	1.02720
H	-2.81898	-5.12445	-0.71806
H	-1.42074	-5.15959	0.35578
C	-4.77498	-2.91370	-0.15428
H	-5.39836	-2.57229	0.67981
H	-5.25432	-2.56740	-1.07598
H	-4.79849	-4.00259	-0.15951
C	-0.58242	5.02775	0.14899
H	-0.86190	5.56394	-0.76347
H	-1.03847	5.55751	0.99134
H	0.50153	5.10700	0.25616
C	-3.44614	4.20909	-0.14177
H	-3.99376	4.08850	-1.08289
H	-4.17107	4.08194	0.66967
H	-3.08141	5.23445	-0.10148

XYZ coordinates of alpha activated butyl acetate by iridium(III)-3,4,7,8-tetramethyl-1,10-phenanthroline dichloride

Energy: -2139.120908

N	-0.23661	1.25498	0.11357
C	-1.59343	1.19839	0.03456
C	-2.19188	-0.09506	0.02138
C	0.33599	2.45005	0.16494
H	1.42028	2.46198	0.23681
C	-2.38510	2.35225	-0.02963
C	-0.36840	3.65793	0.12154

C	-1.75375	3.61923	0.00869
C	-1.85549	-2.36453	0.05843
H	-1.13716	-3.18098	0.10428
C	-3.22743	-2.63230	-0.06487
C	-3.57869	-0.24674	-0.09215
C	-4.11080	-1.56030	-0.13096
C	-4.36790	0.94284	-0.17096
H	-5.44542	0.85869	-0.26117
C	-3.80087	2.17530	-0.13655
H	-4.43651	3.05174	-0.19575
N	-1.35190	-1.14691	0.11562
Ir	0.73055	-0.54727	0.10566
Cl	0.83367	-0.54563	2.63555
O	3.52512	-1.27875	-0.00402
C	2.87086	-2.38790	0.00678
Cl	0.58054	-0.64525	-2.21769
H	3.04504	0.45162	0.96720
H	3.26264	0.17926	-2.03008
C	3.25726	0.81422	-1.13837
H	2.54553	1.61834	-1.37129
O	1.62809	-2.43277	0.09494
C	2.71540	-0.00229	0.01406
H	1.93678	0.10286	2.86220
C	3.67625	-3.62597	-0.10512
H	3.10870	-4.47965	0.26267
H	3.90685	-3.78922	-1.16266
H	4.62115	-3.52243	0.42939
C	4.63521	1.41555	-0.87825
H	5.06730	1.73541	-1.83317
H	5.30790	0.64044	-0.48918
C	4.59152	2.60160	0.07000
H	3.96427	3.40349	-0.34019
H	4.18727	2.33308	1.05458
H	5.58574	3.02213	0.24209
C	-3.67553	-4.05899	-0.12348
H	-4.34171	-4.30870	0.70874
H	-4.21734	-4.27247	-1.05024
H	-2.82180	-4.73841	-0.07797
C	-5.58501	-1.75974	-0.25747
H	-5.86648	-2.81106	-0.21650
H	-6.12280	-1.24018	0.54259
H	-5.95289	-1.35481	-1.20713
C	-2.57374	4.86369	-0.06802
H	-3.15949	4.88820	-0.99340
H	-3.28574	4.91613	0.76308
H	-1.96384	5.76553	-0.03897
C	0.40885	4.93609	0.18323
H	0.26686	5.53675	-0.72084
H	0.10586	5.55256	1.03539
H	1.47907	4.73992	0.28207

XYZ coordinates of iridium(III)-2,2'-bipyridine dichloride

Energy: -1519.689975

H	1.51957	4.46556	-0.04896
C	1.66320	3.39238	-0.07950
C	1.92296	0.66508	-0.13050
C	0.56015	2.56239	-0.14040
C	2.93021	2.82827	-0.05350
C	3.06142	1.44911	-0.07505
N	0.69410	1.23205	-0.18245

H	-0.45654	2.94338	-0.15412
H	3.81130	3.45879	-0.00720
H	4.04039	0.98483	-0.04136
C	1.86977	-0.78639	-0.12604
C	1.40630	-3.48804	-0.05843
N	0.60281	-1.26249	-0.17697
C	2.94580	-1.65385	-0.06274
C	2.71157	-3.01912	-0.03188
C	0.36856	-2.57919	-0.12780
H	3.95661	-1.26368	-0.02924
H	3.54302	-3.71311	0.02211
H	-0.67388	-2.88212	-0.14301
H	1.18281	-4.54722	-0.02134
Ir	-0.94110	0.03637	-0.23162
Cl	-3.15513	0.04079	-0.52033
Cl	-0.97291	0.06170	2.05495

XYZ coordinates of delta activated 1-butanol by iridium(III)-2,2’-bipyridine dichloride

Energy: -1753.197419

N	1.08373	-1.29227	0.00991
C	2.30735	-0.70324	0.05233
C	2.32525	0.76684	0.06993
C	0.99644	-2.62541	-0.07960
H	-0.00236	-3.03819	-0.14995
C	3.45772	-1.47727	0.04431
C	2.11150	-3.43964	-0.09375
C	3.36471	-2.85590	-0.02222
H	4.26197	-3.46480	-0.03113
C	1.01587	2.68128	-0.02035
H	0.00795	3.08195	-0.08109
C	2.12906	3.50098	0.04370
H	2.01078	4.57778	0.02762
C	3.48191	1.53000	0.14317
C	3.38012	2.91163	0.12927
H	4.27449	3.52270	0.18457
H	1.98592	-4.51308	-0.16647
N	1.11692	1.35390	-0.00521
Ir	-0.51971	-0.04150	-0.03616
Cl	-0.69161	-0.10604	2.49286
O	-1.98799	1.49936	-0.30596
H	-2.02184	1.56517	-1.27739
Cl	-0.46166	-0.01617	-2.36997
C	-3.34455	1.39819	0.20215
C	-4.03700	0.14648	-0.27034
C	-3.47641	-1.12784	0.34248
C	-2.08836	-1.52492	-0.14180
H	-3.86433	2.30592	-0.11884
H	-3.24445	1.42847	1.29121
H	-3.99489	0.09648	-1.36908
H	-5.09808	0.24468	-0.01187
H	-4.16167	-1.95440	0.11336
H	-3.49985	-1.02915	1.43863
H	-2.11335	-1.75562	-1.21376
H	-1.81157	-2.46130	0.36709
H	-1.23286	-0.90688	1.42360
H	4.42947	-1.00028	0.07768
H	4.45562	1.06006	0.21031

XYZ coordinates of gamma activated 1-butanol by iridium(III)-2,2’-bipyridine dichloride

Energy: -1753.201909

N	-0.76293	1.35398	-0.02888
C	-2.08021	1.03578	0.06602
C	-2.40463	-0.39846	0.08883
C	-0.41771	2.63024	-0.25552
C	-3.04879	2.02915	0.04901
C	-1.34261	3.65383	-0.29852
C	-2.68174	3.35233	-0.11618
C	-1.56140	-2.53530	-0.17945
C	-2.81584	-3.10322	-0.04252
C	-3.69043	-0.89812	0.25280
C	-3.89645	-2.26581	0.18559
N	-1.35883	-1.22055	-0.11272
Ir	0.58954	-0.16139	-0.07036
Cl	0.48362	-0.54848	2.42562
C	2.41178	0.87889	0.10952
C	2.53153	1.89993	1.23201
H	2.67121	1.41905	2.21256
H	3.42685	2.52190	1.10026
H	1.68257	2.58586	1.31691
C	3.51736	-0.16709	0.28218
H	4.50852	0.27016	0.09924
H	3.52972	-0.53752	1.31835
C	3.30486	-1.32757	-0.63656
H	3.33932	-1.02293	-1.68846
H	3.99135	-2.15968	-0.46201
O	1.94967	-1.80680	-0.34623
H	1.64074	-2.29156	-1.12390
Cl	0.65390	0.04532	-2.38980
H	2.55798	1.38399	-0.85708
H	1.15852	0.48193	2.84183
H	0.63571	2.81615	-0.42037
H	-4.09540	1.76345	0.13355
H	-1.00658	4.66722	-0.48184
H	-3.43524	4.13186	-0.13557
H	-0.68135	-3.15229	-0.34006
H	-2.93573	-4.17799	-0.10904
H	-4.52652	-0.23294	0.43267
H	-4.89392	-2.67325	0.30965

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-2,2’-bipyridine dichloride

Energy: -1753.19742

Imaginary frequency: 496.39cm^{-1}

N	1.08373	-1.29227	0.00991
C	2.30735	-0.70324	0.05233
C	2.32525	0.76684	0.06993
C	0.99644	-2.62541	-0.07960
H	-0.00236	-3.03819	-0.14995
C	3.45772	-1.47727	0.04431
C	2.11150	-3.43964	-0.09375
C	3.36471	-2.85590	-0.02222
H	4.26197	-3.46480	-0.03113
C	1.01587	2.68128	-0.02035
H	0.00795	3.08195	-0.08109
C	2.12906	3.50098	0.04370
H	2.01078	4.57778	0.02762

C	3.48191	1.53000	0.14317
C	3.38012	2.91163	0.12927
H	4.27449	3.52270	0.18457
H	1.98592	-4.51308	-0.16647
N	1.11692	1.35390	-0.00521
Ir	-0.51971	-0.04150	-0.03616
Cl	-0.69161	-0.10604	2.49286
O	-1.98799	1.49936	-0.30596
H	-2.02184	1.56517	-1.27739
Cl	-0.46166	-0.01617	-2.36997
C	-3.34455	1.39819	0.20215
C	-4.03700	0.14648	-0.27034
C	-3.47641	-1.12784	0.34248
C	-2.08836	-1.52492	-0.14180
H	-3.86433	2.30592	-0.11884
H	-3.24445	1.42847	1.29121
H	-3.99489	0.09648	-1.36908
H	-5.09808	0.24468	-0.01187
H	-4.16167	-1.95440	0.11336
H	-3.49985	-1.02915	1.43863
H	-2.11335	-1.75562	-1.21376
H	-1.81157	-2.46130	0.36709
H	-1.23286	-0.90688	1.42360
H	4.42947	-1.00028	0.07768
H	4.45562	1.06006	0.21031

XYZ coordinates of the gamma transition state of 1-butanol by iridium(III)-2,2’-bipyridine dichloride

Energy: -1753.193297

Imaginary frequency: 276.35cm^{-1}

N	-0.79251	1.35992	-0.03773
C	-2.10523	1.02493	0.03981
C	-2.40305	-0.41188	0.07831
C	-0.45215	2.63985	-0.23268
H	0.60291	2.83738	-0.36978
C	-3.08398	2.00666	0.01301
C	-1.38701	3.65471	-0.27702
C	-2.72608	3.33529	-0.13032
H	-3.48688	4.10760	-0.15390
C	-1.49937	-2.53836	-0.08639
H	-0.60192	-3.13998	-0.19437
C	-2.74091	-3.13034	0.05875
H	-2.83093	-4.20983	0.04601
C	-3.67690	-0.93795	0.24197
C	-3.84644	-2.31223	0.22814
H	-4.83496	-2.74019	0.35433
H	-1.05807	4.67501	-0.43212
N	-1.33638	-1.21652	-0.08343
Ir	0.55614	-0.16096	-0.04557
Cl	0.57244	-0.32636	2.44791
C	2.49762	0.85358	0.01008
C	2.78578	2.01692	0.95297
H	2.83131	1.70291	2.00381
H	3.76555	2.44822	0.71396
H	2.06053	2.83281	0.89401
C	3.52326	-0.24945	0.25996
H	4.53451	0.11868	0.03963
H	3.52312	-0.53652	1.32153
C	3.24709	-1.45549	-0.57915
H	3.30668	-1.22416	-1.64855

H	3.88787	-2.30799	-0.34234
O	1.86779	-1.84982	-0.27653
H	1.54141	-2.34677	-1.03951
Cl	0.59754	-0.03372	-2.38361
H	2.56366	1.19920	-1.02922
H	1.30634	0.47398	1.38249
H	-4.53082	-0.28690	0.38573
H	-4.12877	1.72898	0.07980

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-2,2’-bipyridine dichloride

Energy: -1792.45461

N	1.23532	-1.24150	-0.05141
C	2.41848	-0.57045	0.03346
C	2.33299	0.89903	0.03686
C	1.24672	-2.57804	-0.18455
H	0.28676	-3.06134	-0.27553
C	3.60455	-1.26711	0.00946
C	2.42580	-3.30905	-0.20340
C	3.62413	-2.64695	-0.08405
H	4.56912	-3.18520	-0.09272
C	0.92537	2.72745	-0.08915
H	-0.09591	3.07955	-0.14808
C	1.99182	3.60754	-0.17098
H	1.81213	4.66966	-0.27300
C	3.45275	1.72190	-0.03182
C	3.27753	3.09335	-0.12211
H	4.14152	3.74899	-0.17861
H	2.37232	-4.38673	-0.31599
N	1.09291	1.41222	0.04449
Ir	-0.46533	-0.15505	0.02961
Cl	-0.54973	-0.46046	2.53700
O	-2.19170	1.15731	0.13633
Cl	-0.41210	0.07106	-2.28909
C	-3.43345	1.00899	-0.59903
C	-3.63362	-0.39820	-1.09688
C	-3.25635	-1.43422	-0.04454
C	-1.77691	-1.77525	-0.09667
H	-3.42957	1.74798	-1.40852
H	-4.23377	1.26555	0.10828
H	-3.05746	-0.57058	-2.01176
H	-4.69151	-0.48018	-1.37046
H	-3.84074	-2.34918	-0.20693
H	-3.54602	-1.06959	0.95522
H	-1.26368	-1.54904	2.57313
C	-2.29227	2.13525	1.16264
H	-1.30328	2.28753	1.59649
H	-2.98278	1.79509	1.94468
H	-2.65559	3.07992	0.74268
H	-1.53980	-2.50440	0.70108
H	-1.57128	-2.28172	-1.05077
H	4.45270	1.30592	-0.03540
H	4.54898	-0.72237	0.09414

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-2,2’-bipyridine dichloride

Energy: -1792.460142

N	-0.96980	1.33769	0.12888
C	-2.23317	0.89297	-0.09224
C	-2.42283	-0.56532	-0.08827

C	-0.75169	2.65772	0.23071
H	0.27162	2.96211	0.41133
C	-3.27995	1.79149	-0.24612
C	-1.75921	3.59072	0.09890
C	-3.04738	3.15090	-0.15766
C	-1.42652	-2.60739	0.31355
H	-0.51481	-3.14161	0.56590
C	-2.62558	-3.28259	0.17318
H	-2.66220	-4.35767	0.30272
C	-3.65946	-1.17481	-0.26044
C	-3.75889	-2.54988	-0.13998
H	-4.71593	-3.04178	-0.27617
H	-1.52383	4.64444	0.18735
N	-1.31702	-1.28850	0.16495
Ir	0.53351	-0.02530	0.09506
Cl	0.65086	-0.10716	2.61110
C	3.41180	0.46777	0.45184
H	4.33125	1.02703	0.23100
H	3.45090	0.21134	1.51844
C	3.40929	-0.80186	-0.34288
H	3.45954	-0.61257	-1.42394
H	4.21044	-1.49476	-0.06250
Cl	0.33926	-0.06529	-2.23082
H	2.70776	1.51582	-1.99189
C	2.40244	2.12968	-1.13992
H	1.51008	2.67337	-1.46543
H	3.19671	2.86648	-0.95906
O	2.14702	-1.46082	-0.06527
C	2.00061	-2.63116	-0.87397
H	2.83236	-3.30830	-0.65803
H	1.98548	-2.36243	-1.93443
H	1.06067	-3.11185	-0.61227
C	2.16906	1.29603	0.10708
H	-4.54203	-0.58824	-0.48429
H	-4.28212	1.42582	-0.43091
H	-3.86187	3.85571	-0.28149
H	1.44438	0.88358	2.89136
H	1.98974	1.98979	0.95022

XYZ coordinates of the delta transition state of 1-methoxybutane by iridium(III)-2,2'-bipyridine dichloride

Energy:1792.447434

Imaginary frequency: 703.38cm^{-1}

N	1.26890	-1.22384	-0.06405
C	2.42878	-0.52044	0.00356
C	2.30019	0.94344	0.02455
C	1.31166	-2.55774	-0.18005
H	0.35796	-3.06466	-0.26130
C	3.64875	-1.17975	0.00331
C	2.50066	-3.25910	-0.19726
C	3.69060	-2.55902	-0.09230
H	4.64229	-3.07872	-0.09414
C	0.81461	2.71593	-0.10584
H	-0.22485	3.02020	-0.18046
C	1.84395	3.63874	-0.15258
H	1.62108	4.69479	-0.24647
C	3.38089	1.81426	-0.00772
C	3.14859	3.17719	-0.08535
H	3.98196	3.87069	-0.11369
H	2.48055	-4.33804	-0.29149

N	1.03669	1.40769	0.01119
Ir	-0.44635	-0.15726	0.02938
Cl	-0.54655	-0.60988	2.55186
O	-2.15700	1.15860	0.17525
Cl	-0.41719	0.05494	-2.29513
C	-3.40667	1.03135	-0.55758
C	-3.61696	-0.35345	-1.11079
C	-3.27725	-1.44294	-0.10130
C	-1.80593	-1.81955	-0.12885
H	-3.40759	1.80009	-1.33828
H	-4.20170	1.26140	0.16343
H	-3.03747	-0.49771	-2.02769
H	-4.67340	-0.40693	-1.39752
H	-3.87135	-2.33852	-0.32195
H	-3.58212	-1.12710	0.90960
H	-1.11690	-1.29509	1.45838
C	-2.28538	2.01291	1.31099
H	-1.29659	2.16302	1.74456
H	-2.94099	1.55250	2.05937
H	-2.70210	2.97592	0.99700
H	-1.63953	-2.65390	0.58016
H	-1.54440	-2.22741	-1.11372
H	4.39687	1.43880	0.00910
H	4.56909	-0.61274	0.06951

XYZ coordinates of the gamma transition state of 1-methoxybutane by iridium(III)-2,2’-bipyridine dichloride

Energy: -1792.44908

Imaginary frequency: 420.38cm^{-1}

N	-0.99935	1.32637	0.08123
C	-2.25570	0.85644	-0.10774
C	-2.40382	-0.60204	-0.07909
C	-0.80012	2.64893	0.17977
H	0.21771	2.97407	0.35419
C	-3.32165	1.73309	-0.25063
C	-1.82695	3.56214	0.06078
C	-3.11019	3.09689	-0.17478
H	-3.93924	3.78677	-0.28653
C	-1.33744	-2.61493	0.29644
H	-0.40754	-3.12573	0.51040
C	-2.52080	-3.32200	0.18154
H	-2.51975	-4.39828	0.30507
C	-3.62421	-1.24693	-0.22081
C	-3.68305	-2.62413	-0.09766
H	-4.62867	-3.14317	-0.20977
H	-1.61096	4.61997	0.14808
N	-1.27003	-1.29220	0.15618
Ir	0.51067	-0.02506	0.12078
Cl	0.74714	0.24754	2.59408
C	3.47058	0.55837	0.22510
H	4.35020	1.09118	-0.15850
H	3.63351	0.39901	1.29829
C	3.37170	-0.77762	-0.44454
H	3.26283	-0.70659	-1.53485
H	4.22019	-1.42741	-0.20652
Cl	0.34247	-0.27887	-2.21092
H	2.18555	2.16788	0.75724
H	2.46446	1.43332	-2.18340
C	2.24466	2.10826	-1.35413
H	1.30556	2.60941	-1.60393

H	3.03250	2.87153	-1.32057
O	2.18133	-1.41135	0.09216
C	2.01932	-2.74808	-0.38512
H	3.00600	-3.20215	-0.50541
H	1.48662	-2.75424	-1.34208
H	1.48098	-3.31014	0.37802
C	2.20623	1.37804	-0.02084
H	1.32566	0.92562	1.37277
H	-4.52647	-0.68331	-0.42355
H	-4.32066	1.34765	-0.41171

XYZ coordinates of alpha activated butyl acetate by iridium(III)-2,2’-bipyridine dichloride

Energy: -1905.821471

N	-0.84106	1.46181	0.10314
C	-2.18967	1.42055	-0.04569
C	-2.78833	0.08029	-0.11370
C	-0.23223	2.64963	0.22434
H	0.84490	2.62611	0.34941
C	-2.93042	2.59259	-0.09817
C	-0.92172	3.84467	0.18580
C	-2.29621	3.81625	0.01236
C	-2.34278	-2.19381	0.00704
H	-1.57990	-2.95756	0.12849
C	-3.67196	-2.51018	-0.21383
C	-4.13419	-0.16586	-0.34388
C	-4.57872	-1.47727	-0.39047
N	-1.92074	-0.93170	0.06742
Ir	0.15030	-0.32403	0.10772
Cl	0.23953	-0.33326	2.64013
O	2.94852	-1.05434	0.01205
C	2.29508	-2.16281	0.01991
Cl	0.02442	-0.41730	-2.21715
H	2.46008	0.66769	0.99283
H	2.67572	0.42761	-2.01114
C	2.69014	1.04564	-1.10774
H	1.99424	1.86965	-1.31925
O	1.05084	-2.20342	0.10456
C	2.13976	0.22040	0.03358
C	3.09602	-3.40290	-0.09107
H	2.53333	-4.25147	0.29573
H	3.30601	-3.57912	-1.15097
H	4.05054	-3.29519	0.42484
C	4.08415	1.61015	-0.84850
H	4.50746	1.94935	-1.80056
H	4.74489	0.80808	-0.49580
C	4.08488	2.76621	0.13678
H	3.47469	3.59821	-0.23625
H	3.69021	2.47743	1.11942
H	5.09295	3.15349	0.30562
H	-0.37988	4.77734	0.28617
H	-2.86910	4.73600	-0.02948
H	-4.00596	2.54623	-0.21844
H	-4.83031	0.64957	-0.49998
H	-5.62639	-1.68951	-0.57411
H	-3.98155	-3.54753	-0.25582
H	1.35327	0.29369	2.87653

XYZ coordinates of the alpha transition state of butyl acetate by iridium(III)-2,2’-bipyridine dichloride

Energy: -1905.811817

Imaginary frequency: 158.36cm^{-1}

N	-0.84063	1.47738	0.09877
C	-2.18624	1.42577	-0.07785
C	-2.77817	0.08231	-0.13176
C	-0.24164	2.67247	0.20626
H	0.83373	2.66054	0.35046
C	-2.93136	2.59245	-0.16883
C	-0.93687	3.86235	0.13389
C	-2.30714	3.82193	-0.06686
C	-2.31808	-2.18760	0.02118
H	-1.54859	-2.94500	0.14079
C	-3.65246	-2.51347	-0.15018
H	-3.95958	-3.55240	-0.15498
C	-4.12952	-0.17380	-0.31344
C	-4.56843	-1.48805	-0.32245
H	-0.40228	4.79967	0.22917
N	-1.90054	-0.92299	0.03265
Ir	0.16001	-0.31559	0.09247
Cl	0.16617	-0.48371	2.73982
Cl	0.10069	-0.27525	-2.22574
H	2.78177	0.57169	-1.95124
C	2.75282	1.10913	-0.99837
H	2.05479	1.94027	-1.16627
C	2.18318	0.17529	0.04749
H	0.69844	0.48647	2.02099
C	4.12705	1.66435	-0.63603
H	4.59019	2.08084	-1.53747
H	4.78034	0.84261	-0.31537
C	4.06280	2.73831	0.43616
H	3.47614	3.59895	0.09118
H	3.60490	2.37293	1.36466
H	5.05629	3.10857	0.70136
O	2.93797	-1.11488	-0.14735
C	2.25687	-2.20183	-0.12152
O	1.01610	-2.20529	0.03134
C	3.00283	-3.47299	-0.26289
H	4.04930	-3.29039	-0.49946
H	2.53443	-4.08053	-1.03980
H	2.93062	-4.03093	0.67492
H	2.54842	0.47867	1.04476
H	-2.88455	4.73702	-0.13837
H	-5.62060	-1.70816	-0.46691
H	-4.00312	2.53774	-0.31570
H	-4.83637	0.63536	-0.45264

XYZ coordinates of iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -1748.673369

C	1.21545	3.28696	-0.08625
C	2.46592	2.66106	-0.05894
C	2.51225	1.26030	-0.08005
C	1.34355	0.54549	-0.13814
N	0.13740	1.16959	-0.19271
C	0.08405	2.50454	-0.14643
C	1.21660	-0.90599	-0.14049
C	2.25982	-1.80795	-0.07915
C	1.96956	-3.17546	-0.06492
C	0.62572	-3.57490	-0.10503
C	-0.35613	-2.62451	-0.16463
N	-0.07063	-1.30994	-0.20001

Ir	-1.55677	0.06404	-0.22966
Cl	-1.57355	0.06437	2.05623
Cl	-3.77135	0.25869	-0.48794
H	1.10699	4.36325	-0.05562
H	3.47906	0.77160	-0.04247
H	-0.90927	2.94339	-0.15839
H	3.27940	-1.44612	-0.03466
H	0.37990	-4.62965	-0.08061
H	-1.40973	-2.88523	-0.18353
O	3.62767	3.28116	-0.00730
C	3.66166	4.70724	0.02172
H	3.15758	5.08744	0.91544
H	3.20386	5.12258	-0.88136
H	4.71428	4.97889	0.05429
O	2.86678	-4.13907	-0.00882
C	4.25105	-3.81365	0.06289
H	4.77972	-4.76380	0.09015
H	4.46862	-3.24954	0.97552
H	4.56414	-3.24889	-0.82115

XYZ coordinates of delta activated 1-butanol by iridium(III)-4,4'-dimethoxy-2,2'-bipyridine dichloride

Energy: -1982.180207

N	-0.42956	1.28724	0.02552
C	-1.66371	0.72645	0.05452
C	-1.71365	-0.75056	0.05524
C	-0.33489	2.62635	-0.07896
H	0.66785	3.02908	-0.15527
C	-2.80874	1.50757	0.03913
C	-1.42450	3.45389	-0.10521
C	-2.70274	2.89516	-0.03221
C	-0.46369	-2.69066	-0.04707
H	0.53174	-3.12297	-0.09701
C	-1.58495	-3.48122	-0.03777
H	-1.51987	-4.56181	-0.08357
C	-2.89893	-1.47392	0.07416
C	-2.83916	-2.86673	0.02665
H	-1.30889	4.52779	-0.19250
N	-0.51814	-1.35458	0.00613
Ir	1.17393	0.03203	-0.03170
Cl	1.27206	-0.02414	2.47963
O	2.63684	-1.51832	-0.34252
H	2.61631	-1.56778	-1.31580
Cl	1.11550	0.02923	-2.36250
C	4.01588	-1.41852	0.08673
C	4.65076	-0.11273	-0.31539
C	4.06308	1.08433	0.41726
C	2.66953	1.49723	-0.03678
H	4.54045	-2.28269	-0.33295
H	3.98745	-1.53615	1.17480
H	4.56106	0.02159	-1.40388
H	5.72388	-0.19410	-0.10387
H	4.73979	1.94030	0.28927
H	4.08139	0.86421	1.49731
H	2.72902	1.90321	-1.05667
H	2.34285	2.32825	0.61227
H	1.92232	1.07483	2.71711
H	-3.77967	1.03182	0.06347
H	-3.85387	-0.96743	0.11673
O	-3.89270	-3.67349	0.03534

C	-5.19683	-3.11854	0.08566
H	-5.88382	-3.96248	0.07997
H	-5.38981	-2.49004	-0.79077
H	-5.34276	-2.54055	1.00500
O	-3.72360	3.73856	-0.05301
C	-5.04950	3.23360	-0.00686
H	-5.22476	2.67744	0.92047
H	-5.25652	2.59875	-0.87516
H	-5.70335	4.10293	-0.03357

XYZ coordinates of gamma activated 1-butanol by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -1982.180949

N	0.09751	1.27856	-0.02513
C	1.44663	1.09658	-0.09147
C	1.91564	-0.30007	-0.05398
C	-0.36312	2.52319	0.15011
C	2.30945	2.16810	-0.09814
C	0.44269	3.64070	0.16709
C	1.81794	3.47088	0.01169
C	1.29943	-2.49173	0.29401
C	2.60194	-2.94176	0.19548
H	2.81288	-3.99713	0.31078
C	3.23922	-0.65953	-0.18452
C	3.60311	-2.00339	-0.05777
H	-0.01091	4.61218	0.31451
N	0.94844	-1.21473	0.17206
Ir	-1.09603	-0.36792	0.07257
Cl	-0.90724	-0.82570	-2.40514
C	-3.01555	0.46567	-0.15805
C	-3.23317	1.42914	-1.31606
H	-3.29499	0.90516	-2.28288
H	-4.19815	1.94502	-1.22100
H	-2.46811	2.20648	-1.41093
C	-4.00161	-0.69806	-0.30206
H	-5.03698	-0.36434	-0.14663
H	-3.95917	-1.10662	-1.32328
C	-3.67953	-1.79395	0.66340
H	-3.76245	-1.45339	1.70166
H	-4.27288	-2.69988	0.51587
O	-2.27836	-2.13830	0.40787
H	-1.92835	-2.54159	1.21406
Cl	-1.20561	-0.08082	2.38273
H	-3.22910	0.98612	0.78797
H	3.38267	2.02991	-0.14732
H	4.02105	0.06445	-0.38116
O	4.89351	-2.27618	-0.19151
C	5.33204	-3.62194	-0.06083
H	6.41089	-3.60130	-0.20047
H	4.87785	-4.25713	-0.82856
H	5.10138	-4.01242	0.93582
O	2.71586	4.44337	-0.00823
C	2.28104	5.78909	0.14367
H	3.17864	6.40183	0.09305
H	1.79519	5.93417	1.11399
H	1.60025	6.07254	-0.66566
H	-1.71491	0.08228	-2.86625
H	0.49299	-3.19867	0.47251
H	-1.43170	2.61779	0.29835

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -1982.174575

Imaginary frequency: 433.27cm^{-1}

N	0.44410	-1.28992	0.02109
C	1.68668	-0.71360	0.03567
C	1.71058	0.75619	0.03076
C	0.34348	-2.64186	-0.05726
H	-0.65796	-3.04719	-0.12116
C	2.83695	-1.49493	0.02321
C	1.44776	-3.46325	-0.07436
C	2.72513	-2.88850	-0.02310
C	0.38292	2.68625	-0.07473
H	-0.62593	3.08119	-0.12863
C	1.49319	3.50380	-0.03497
H	1.41160	4.58358	-0.06352
C	2.87375	1.52022	0.08075
C	2.76441	2.91570	0.04523
H	1.35069	-4.54013	-0.13702
N	0.48726	1.33916	-0.04063
Ir	-1.14358	-0.03132	-0.05208
Cl	-1.33299	-0.11948	2.57716
O	-2.59086	1.50878	-0.36927
H	-2.59756	1.61959	-1.34685
Cl	-1.11623	-0.09494	-2.42522
C	-3.96706	1.45156	0.16716
C	-4.66742	0.17716	-0.25031
C	-4.11215	-1.07053	0.43821
C	-2.71218	-1.49985	-0.02984
H	-4.47442	2.35292	-0.19225
H	-3.84192	1.52537	1.25178
H	-4.60850	0.06450	-1.34496
H	-5.73327	0.28845	-0.00849
H	-4.80618	-1.90477	0.25761
H	-4.13767	-0.90124	1.52903
H	-2.76369	-1.81955	-1.08264
H	-2.43425	-2.41353	0.53463
H	-1.95941	-1.02223	1.73992
H	3.80993	-1.01906	0.03122
H	3.84489	1.04448	0.14655
O	3.81085	3.76999	0.08500
C	5.16631	3.26299	0.15896
H	5.79917	4.14796	0.17067
H	5.39860	2.65222	-0.72053
H	5.31455	2.68867	1.08024
O	3.76591	-3.74611	-0.03723
C	5.12778	-3.24780	-0.00996
H	5.31151	-2.67904	0.90814
H	5.33088	-2.63509	-0.89501
H	5.75406	-4.13726	-0.02511

XYZ coordinates of the gamma transition state of 1-butanol by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -1982.17082

Imaginary frequency: 353.17cm^{-1}

N	0.08766	1.25245	-0.01223
C	1.42186	1.04161	-0.15395
C	1.83947	-0.36201	-0.15599
C	-0.37345	2.55984	0.45691

H	-0.68041	2.42546	1.51920
C	2.34307	2.07517	-0.17595
C	0.61222	3.66659	0.33859
C	1.91497	3.41898	0.02200
C	1.11854	-2.63666	0.27180
H	0.70894	-2.88009	1.27357
C	2.55322	-3.03240	0.18708
H	2.78672	-4.08160	0.33851
C	3.17896	-0.73582	-0.22968
C	3.52640	-2.10529	-0.05848
H	0.25042	4.66689	0.55473
N	0.83729	-1.23091	0.02519
Ir	-1.09938	-0.34086	0.04593
Cl	-1.01377	-0.62188	-2.56741
C	-3.02523	0.55723	-0.02487
C	-3.30041	1.51215	-1.19278
H	-3.49682	0.96269	-2.13255
H	-4.21510	2.09899	-1.02074
H	-2.49241	2.22959	-1.38811
C	-4.10053	-0.55690	-0.05204
H	-5.06338	-0.17958	0.32345
H	-4.26996	-0.87604	-1.09400
C	-3.67468	-1.76288	0.74446
H	-3.57645	-1.55710	1.81426
H	-4.30276	-2.64451	0.58607
O	-2.30784	-2.07377	0.26365
H	-2.16206	-2.95311	-0.11252
Cl	-1.12301	-0.16481	2.40605
H	-3.12392	1.11617	0.91993
H	3.40063	1.90344	-0.33233
H	3.98087	-0.03271	-0.41675
O	4.86296	-2.35122	-0.15666
C	5.33787	-3.70455	0.02460
H	6.41838	-3.64921	-0.09218
H	4.91403	-4.36913	-0.73754
H	5.08922	-4.07071	1.02763
O	2.90887	4.34178	-0.10150
C	2.59618	5.73360	0.13524
H	3.53093	6.26967	-0.01631
H	2.24340	5.88103	1.16277
H	1.84303	6.08739	-0.57869
H	-1.30348	2.81883	-0.06461
H	0.51878	-3.24565	-0.43100
H	-2.01835	0.20229	-2.85242

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-4,4'-dimethoxy-2,2'-bipyridine dichloride

Energy: -2021.430058

N	-0.55529	-1.30680	0.14497
C	-1.75909	-0.69389	0.04444
C	-1.74524	0.78329	0.06657
C	-0.52021	-2.65217	0.19596
H	0.46207	-3.10256	0.26454
C	-2.93468	-1.42584	-0.02458
C	-1.64311	-3.43233	0.14494
C	-2.89066	-2.81725	0.01731
C	-0.44444	2.66895	0.32294
H	0.55603	3.07275	0.45287
C	-1.53615	3.49925	0.30996
H	-1.43705	4.57247	0.42095

C	-2.90396	1.54836	0.03054
C	-2.80374	2.93436	0.13975
H	-1.57487	-4.51274	0.18441
N	-0.52983	1.33958	0.18530
Ir	1.10339	-0.15275	-0.00075
Cl	0.81219	-0.24804	-2.31230
O	2.73368	1.27705	-0.25272
Cl	1.36168	-0.04710	2.50856
C	4.12451	1.08868	0.09766
C	4.43770	-0.32442	0.50804
C	3.88107	-1.34603	-0.47633
C	2.44795	-1.73133	-0.17075
H	4.37056	1.82192	0.87616
H	4.71038	1.33169	-0.79856
H	4.07906	-0.53091	1.52485
H	5.53089	-0.38549	0.56558
H	4.50893	-2.24658	-0.46318
H	3.94794	-0.94697	-1.49911
H	2.07995	-2.40576	-0.95460
C	2.59863	2.25852	-1.28582
H	1.53947	2.40862	-1.48582
H	3.07801	1.90314	-2.20393
H	3.06439	3.19250	-0.95217
H	2.43524	-2.30171	0.77961
H	-3.88125	-0.91001	-0.11036
H	-3.87144	1.07682	-0.07678
O	-3.94489	-3.61687	-0.05010
C	-5.23856	-3.05507	-0.20859
H	-5.92761	-3.89576	-0.25847
H	-5.30328	-2.47820	-1.13750
H	-5.49969	-2.42460	0.64847
O	-3.82761	3.77734	0.10879
C	-5.14082	3.27417	-0.07753
H	-5.79690	4.14228	-0.08977
H	-5.42976	2.61542	0.74890
H	-5.22540	2.74323	-1.03202
H	1.99865	-1.15375	2.75082

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -2021.429023

N	-0.38263	1.31189	0.13977
C	-1.67586	0.92490	-0.02132
C	-1.91148	-0.52554	-0.00718
C	-0.11350	2.61924	0.23793
H	0.92487	2.88911	0.38810
C	-2.68576	1.85204	-0.12817
C	-1.07479	3.60082	0.15151
C	-2.40041	3.21704	-0.05439
C	-0.96890	-2.59978	0.30601
H	-0.07279	-3.17979	0.48890
C	-2.18809	-3.24016	0.21094
H	-2.23269	-4.31611	0.31950
C	-3.16497	-1.08005	-0.12625
C	-3.32196	-2.46525	-0.02876
H	-0.77588	4.63699	0.24138
N	-0.80843	-1.28436	0.18886
Ir	1.04451	-0.13128	0.12503
Cl	1.31856	0.06289	2.60442
C	4.03068	0.26597	0.17683

H	4.93784	0.74806	-0.21038
H	4.19591	0.08035	1.24557
C	3.84160	-1.05163	-0.51016
H	3.71896	-0.95488	-1.59717
H	4.65432	-1.75446	-0.29822
Cl	0.81040	-0.32574	-2.20717
H	2.85457	1.94315	0.74733
H	3.04345	1.23082	-2.20708
C	2.88124	1.90739	-1.36577
H	1.97013	2.46801	-1.59283
H	3.71589	2.61980	-1.33750
O	2.62574	-1.62261	0.03724
C	2.36503	-2.92986	-0.47325
H	3.31583	-3.44773	-0.62324
H	1.81722	-2.87135	-1.41992
H	1.79951	-3.47460	0.28284
C	2.81600	1.16510	-0.04080
H	1.90878	0.73399	1.37971
H	-3.71823	1.55346	-0.26081
H	-4.04980	-0.47766	-0.29201
O	-4.55502	-2.92721	-0.16319
C	-4.78308	-4.32816	-0.07269
H	-5.85205	-4.46798	-0.21901
H	-4.49798	-4.70636	0.91445
H	-4.23515	-4.86319	-0.85515
O	-3.42761	4.04085	-0.17446
C	-3.20335	5.44452	-0.10472
H	-4.17821	5.91007	-0.23277
H	-2.53480	5.77181	-0.90745
H	-2.79089	5.72471	0.86992

XYZ coordinates of the delta transition state of 1-methoxybutane by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -2021.424413

Imaginary frequency: 627.58cm^{-1}

N	0.59310	-1.30296	-0.05645
C	1.78693	-0.66936	0.02075
C	1.73136	0.80457	0.04915
C	0.57663	-2.64311	-0.17999
H	-0.39894	-3.10420	-0.27285
C	2.97692	-1.37878	0.02516
C	1.71479	-3.40255	-0.19240
C	2.95491	-2.76893	-0.07634
C	0.34798	2.64860	-0.07443
H	-0.67213	3.01179	-0.15136
C	1.41020	3.51449	-0.11716
H	1.26730	4.58439	-0.21011
C	2.86185	1.60814	0.01870
C	2.70570	2.99254	-0.05228
H	1.66632	-4.48015	-0.29159
N	0.49307	1.32271	0.03982
Ir	-1.07451	-0.16107	0.03003
Cl	-1.19660	-0.60549	2.56270
O	-2.73114	1.22734	0.17465
Cl	-1.01867	0.06471	-2.29124
C	-3.98353	1.16023	-0.55722
C	-4.24647	-0.20724	-1.13008
C	-3.95674	-1.32162	-0.13206
C	-2.50154	-1.75686	-0.15711
H	-3.95666	1.94016	-1.32678

H	-4.76951	1.40950	0.16800
H	-3.66740	-0.36299	-2.04555
H	-5.30258	-0.21399	-1.42324
H	-4.58690	-2.18915	-0.36518
H	-4.25347	-1.00350	0.88076
H	-1.79345	-1.25362	1.47093
C	-2.81068	2.10831	1.29230
H	-1.81711	2.20103	1.73090
H	-3.50020	1.70560	2.04381
H	-3.16232	3.09111	0.95935
H	-2.37123	-2.59894	0.54972
H	-2.25646	-2.17073	-1.14396
H	3.91598	-0.84708	0.09869
H	3.84934	1.16660	0.02566
O	4.02361	-3.54950	-0.08009
C	5.31546	-2.96914	0.02449
H	6.01980	-3.79815	0.00292
H	5.42469	-2.42570	0.96925
H	5.51409	-2.30342	-0.82234
O	3.69877	3.86975	-0.08333
C	5.04049	3.40985	-0.03862
H	5.66479	4.30070	-0.06546
H	5.26876	2.78282	-0.90737
H	5.23547	2.85945	0.88831

XYZ coordinates of the gamma transition state of 1-methoxybutane by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -2021.429024

Imaginary frequency: 354.96cm^{-1}

N	-0.38263	1.31189	0.13977
C	-1.67586	0.92490	-0.02132
C	-1.91148	-0.52554	-0.00718
C	-0.11350	2.61924	0.23793
H	0.92487	2.88911	0.38810
C	-2.68576	1.85204	-0.12817
C	-1.07479	3.60082	0.15151
C	-2.40041	3.21704	-0.05439
C	-0.96890	-2.59978	0.30601
H	-0.07279	-3.17979	0.48890
C	-2.18809	-3.24016	0.21094
H	-2.23269	-4.31611	0.31950
C	-3.16497	-1.08005	-0.12625
C	-3.32196	-2.46525	-0.02876
H	-0.77588	4.63699	0.24138
N	-0.80843	-1.28436	0.18886
Ir	1.04451	-0.13128	0.12503
Cl	1.31856	0.06289	2.60442
C	4.03068	0.26597	0.17683
H	4.93784	0.74806	-0.21038
H	4.19591	0.08035	1.24557
C	3.84160	-1.05163	-0.51016
H	3.71896	-0.95488	-1.59717
H	4.65432	-1.75446	-0.29822
Cl	0.81040	-0.32574	-2.20717
H	2.85457	1.94315	0.74733
H	3.04345	1.23082	-2.20708
C	2.88124	1.90739	-1.36577
H	1.97013	2.46801	-1.59283
H	3.71589	2.61980	-1.33750
O	2.62574	-1.62261	0.03724

C	2.36503	-2.92986	-0.47325
H	3.31583	-3.44773	-0.62324
H	1.81722	-2.87135	-1.41992
H	1.79951	-3.47460	0.28284
C	2.81600	1.16510	-0.04080
H	1.90878	0.73399	1.37971
H	-3.71823	1.55346	-0.26081
H	-4.04980	-0.47766	-0.29201
O	-4.55502	-2.92721	-0.16319
C	-4.78308	-4.32816	-0.07269
H	-5.85205	-4.46799	-0.21901
H	-4.49798	-4.70636	0.91445
H	-4.23515	-4.86319	-0.85515
O	-3.42761	4.04085	-0.17446
C	-3.20335	5.44452	-0.10472
H	-4.17821	5.91007	-0.23277
H	-2.53480	5.77181	-0.90745
H	-2.79089	5.72471	0.86992

XYZ coordinates of alpha activated butyl acetate by iridium(III)-4,4'-dimethoxy-2,2'-bipyridine dichloride

Energy: -2134.800388

N	-0.28293	1.29549	0.12410
C	-1.64217	1.31460	0.03372
C	-2.29900	-0.00323	0.02455
C	0.36622	2.46299	0.18323
H	1.44677	2.40685	0.26510
C	-2.33543	2.50135	-0.01923
C	-0.26162	3.68875	0.13964
C	-1.65182	3.71858	0.02398
C	-1.95270	-2.28209	0.18349
H	-1.22839	-3.08409	0.29718
C	-3.29564	-2.55625	0.01251
C	-3.65093	-0.18614	-0.15556
C	-4.17176	-1.48430	-0.16143
N	-1.46112	-1.04601	0.20538
Ir	0.63427	-0.53261	0.13747
Cl	0.82687	-0.45877	2.66074
O	3.39547	-1.38236	-0.05387
C	2.69769	-2.46231	0.01218
Cl	0.40576	-0.68612	-2.17733
H	3.02087	0.38313	0.90058
H	3.09488	0.05906	-2.10125
C	3.17310	0.69896	-1.21655
H	2.50149	1.54462	-1.42113
O	1.45895	-2.45096	0.15210
C	2.63836	-0.07397	-0.03169
H	2.00843	0.06018	2.81661
C	3.44527	-3.73599	-0.09989
H	2.86233	-4.55397	0.32119
H	3.61537	-3.93967	-1.16190
H	4.41915	-3.65726	0.38433
C	4.59807	1.21302	-1.03226
H	4.99566	1.50638	-2.01042
H	5.24030	0.39545	-0.68079
C	4.68524	2.39679	-0.08433
H	4.09493	3.24193	-0.46004
H	4.31636	2.15359	0.92034
H	5.71409	2.74638	0.03468
H	0.33709	4.58886	0.19088

H	-3.41643	2.52237	-0.08831
H	-4.33340	0.64040	-0.31407
H	-3.63181	-3.58497	0.00367
O	-5.48092	-1.58711	-0.34486
C	-6.07308	-2.87839	-0.38744
H	-7.13640	-2.71587	-0.55129
H	-5.92751	-3.40661	0.56070
H	-5.66342	-3.46852	-1.21380
O	-2.39323	4.81335	-0.03986
C	-1.75581	6.08419	-0.00870
H	-2.55252	6.82130	-0.08366
H	-1.07308	6.19839	-0.85695
H	-1.21565	6.22669	0.93305

XYZ coordinates of the alpha transition state of butylacetate by iridium(III)-4,4’-dimethoxy-2,2’-bipyridine dichloride

Energy: -2134.791583

Imaginary frequency: 456.32cm^{-1}

N	-0.29042	1.29853	0.09868
C	-1.64977	1.31634	0.00738
C	-2.30128	-0.00332	-0.00571
C	0.35840	2.46617	0.16060
H	1.43907	2.41134	0.24420
C	-2.34424	2.50182	-0.04290
C	-0.27098	3.69108	0.12155
C	-1.66132	3.71986	0.00566
C	-1.93695	-2.28371	0.11905
H	-1.20415	-3.08093	0.20783
C	-3.28259	-2.56317	-0.01632
C	-3.65634	-0.19290	-0.14805
C	-4.16958	-1.49449	-0.15280
N	-1.45347	-1.04423	0.13803
Ir	0.61936	-0.53112	0.11987
Cl	0.81964	-0.39749	2.77029
O	3.39242	-1.40769	-0.02547
C	2.67745	-2.47890	0.02524
Cl	0.47362	-0.66584	-2.19464
H	3.10430	0.36579	0.92499
H	3.13691	0.05058	-2.06146
C	3.21335	0.68909	-1.17598
H	2.54751	1.53837	-1.38292
O	1.43742	-2.45168	0.14827
C	2.66652	-0.08769	0.00484
C	3.41173	-3.76023	-0.07976
H	2.80632	-4.57496	0.31483
H	3.61260	-3.95378	-1.13832
H	4.37102	-3.69845	0.43521
C	4.63914	1.19463	-0.98000
H	5.04616	1.48500	-1.95510
H	5.27410	0.37358	-0.62315
C	4.72275	2.37873	-0.03208
H	4.14286	3.22717	-0.41635
H	4.34064	2.14092	0.96895
H	5.75236	2.72135	0.09897
H	0.32658	4.59163	0.17741
H	-3.42509	2.52199	-0.11475
H	-4.34856	0.63150	-0.27163
H	-3.61367	-3.59353	-0.02423
O	-5.48258	-1.60295	-0.29648
C	-6.07041	-2.89699	-0.32719

H	-7.13937	-2.73803	-0.45326
H	-5.88986	-3.43017	0.61202
H	-5.68681	-3.47972	-1.17106
O	-2.40352	4.81337	-0.05433
C	-1.76842	6.08570	-0.01356
H	-2.56668	6.82145	-0.08460
H	-1.08491	6.20670	-0.86015
H	-1.23013	6.22234	0.93002
H	1.80562	-0.06808	1.97392

XYZ coordinates of iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1704.109675

C	-1.07022	-3.45503	-0.20092
C	-2.34407	-2.89000	-0.21652
C	-2.47157	-1.50680	-0.13367
C	-1.33558	-0.72633	-0.02872
N	-0.10166	-1.29480	0.00576
C	0.02742	-2.62915	-0.09096
C	-1.33437	0.72848	0.02861
C	-2.46902	1.51092	0.13353
C	-2.33909	2.89390	0.21651
C	-1.06427	3.45668	0.20118
C	0.03194	2.62892	0.09115
N	-0.09946	1.29479	-0.00579
Ir	1.45384	-0.00120	-0.00013
Cl	2.54579	-1.35211	1.41536
Cl	2.54854	1.34830	-1.41484
H	-0.93419	-4.52794	-0.26983
H	-3.45558	-1.05387	-0.16971
H	1.03543	-3.02418	-0.06414
H	-3.45378	1.05961	0.16945
H	-0.92640	4.52935	0.27027
H	1.04065	3.02218	0.06445
C	-3.49923	3.71536	0.32995
C	-3.50548	-3.70966	-0.32997
N	-4.44686	-4.36783	-0.42130
N	-4.43976	4.37477	0.42126

XYZ coordinates of delta activated 1-butanol by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1937.619872

N	-0.57412	1.29377	0.02791
C	-1.79783	0.73098	0.06782
C	-1.87054	-0.73748	0.05988
C	-0.44496	2.62859	-0.07976
H	0.54284	3.02502	-0.16542
C	-2.95585	1.52653	0.06520
C	-1.56927	3.46976	-0.09603
C	-2.82220	2.91156	-0.00887
C	-3.98001	3.71700	-0.00951
C	-0.62308	-2.69056	-0.07722
H	0.37112	-3.12162	-0.15021
C	-1.75831	-3.47861	-0.06631
H	-1.68705	-4.55848	-0.12771
C	-3.05143	-1.45863	0.08916
C	-2.99778	-2.84861	0.02644
C	-4.19846	-3.60850	0.05589
H	-1.41472	4.53711	-0.18494
N	-0.67831	-1.36004	-0.01182
Ir	1.02013	0.03176	-0.03572

Cl	1.14065	-0.08177	2.47991
O	2.46848	-1.51899	-0.36181
H	2.45773	-1.56419	-1.33529
Cl	0.95527	0.06523	-2.36285
C	3.84934	-1.43590	0.07942
C	4.49420	-0.13144	-0.30801
C	3.90933	1.06241	0.43193
C	2.52100	1.48858	-0.02311
H	4.36554	-2.30084	-0.34774
H	3.81145	-1.56560	1.16545
H	4.41404	0.01265	-1.39576
H	5.56503	-0.22042	-0.08956
H	4.58753	1.91762	0.30986
H	3.92511	0.83734	1.51050
H	2.58348	1.89907	-1.04051
H	2.19390	2.31327	0.63296
H	1.79874	1.00686	2.74353
H	-3.93071	1.07789	0.09941
H	-4.01863	-0.97056	0.15425
N	-5.18304	-4.22627	0.08356
N	-4.95298	4.40510	-0.00907

XYZ coordinates of gamma activated 1-butanol by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1937.609564

N	-0.35299	1.26519	0.04149
C	-1.67171	0.88036	0.05304
C	-1.92408	-0.56234	0.02373
C	-0.05114	2.58125	-0.05978
H	0.99876	2.82652	-0.13311
C	-2.68725	1.82940	0.04010
C	-1.02560	3.56554	-0.08472
C	-2.37244	3.19060	-0.01686
C	-3.40767	4.17047	-0.02707
C	-0.92261	-2.67341	-0.16549
H	0.00207	-3.23388	-0.25135
C	-2.15271	-3.31351	-0.09996
H	-2.21914	-4.39414	-0.15129
C	-3.18872	-1.13893	0.10530
C	-3.30797	-2.53235	0.03954
C	-4.59391	-3.14449	0.12172
H	-0.74307	4.60866	-0.16543
N	-0.81160	-1.33282	-0.10909
Ir	1.05264	-0.18615	-0.08576
Cl	1.06677	-0.69172	2.45537
C	2.85772	0.89884	0.07467
C	2.92147	2.00252	1.14896
H	2.08049	1.99100	1.86250
H	3.84595	1.92725	1.73960
H	2.93105	3.00842	0.71110
C	3.96598	-0.14548	0.32880
H	4.95739	0.31715	0.20930
H	3.92017	-0.52212	1.36290
C	3.83779	-1.30024	-0.62183
H	3.96357	-0.98468	-1.66481
H	4.48712	-2.14775	-0.39101
O	2.42789	-1.76923	-0.45697
H	2.14066	-2.28321	-1.23698
Cl	1.04678	0.11009	-2.43914
H	3.02980	1.34248	-0.91870

N	-4.26110	4.97383	-0.03073
N	-5.65224	-3.64300	0.19175
H	-3.72810	1.52646	0.05062
H	-4.08283	-0.53683	0.22347
H	1.89214	0.23814	2.92189

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1937.613225

Imaginary frequency: 608.43cm^{-1}

N	0.59745	-1.29448	0.02858
C	1.84038	-0.71012	0.04832
C	1.86370	0.75541	0.04299
C	0.49342	-2.64022	-0.04564
H	-0.50728	-3.04738	-0.10895
C	2.98737	-1.49430	0.04113
C	1.60640	-3.46592	-0.05912
C	2.88023	-2.88834	-0.00488
C	4.05235	-3.69984	-0.01056
C	0.52693	2.68545	-0.06674
H	-0.48287	3.07764	-0.12365
C	1.64364	3.51007	-0.02168
H	1.53680	4.58826	-0.05132
C	3.02096	1.52470	0.09768
C	2.91231	2.92110	0.06381
C	4.08632	3.72964	0.11837
H	1.48618	-4.54133	-0.11816
N	0.64023	1.34567	-0.03353
Ir	-0.98345	-0.03269	-0.05147
Cl	-1.23199	-0.12100	2.55905
O	-2.42227	1.50300	-0.37715
H	-2.43278	1.62067	-1.35394
Cl	-0.92626	-0.09770	-2.42338
C	-3.80193	1.45052	0.16296
C	-4.50863	0.18539	-0.26992
C	-3.96582	-1.07374	0.40714
C	-2.56053	-1.50203	-0.04654
H	-4.29995	2.35955	-0.18906
H	-3.67368	1.51408	1.24772
H	-4.44961	0.08456	-1.36566
H	-5.57413	0.30060	-0.02950
H	-4.65562	-1.90469	0.19953
H	-4.01030	-0.92559	1.49994
H	-2.59568	-1.80076	-1.10568
H	-2.29087	-2.42389	0.50645
H	-1.85759	-0.99281	1.66655
H	3.97069	-1.03813	0.05717
H	4.00380	1.07175	0.16625
N	5.05340	4.38998	0.16488
N	5.01816	-4.36372	-0.01246

XYZ coordinates of the gamma transition state of 1-butanol by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1937.6127

Imaginary frequency: 557.34cm^{-1}

N	-0.37752	1.26710	0.10326
C	-1.67443	0.87857	0.00178
C	-1.91219	-0.57082	0.00839
C	-0.08361	2.57342	0.16432
H	0.96542	2.83006	0.25092

C	-2.69028	1.81588	-0.06484
C	-1.05086	3.55413	0.11228
C	-2.38281	3.17072	-0.01286
C	-3.42162	4.14597	-0.07957
C	-0.90778	-2.65211	0.19929
H	0.01818	-3.20648	0.31863
C	-2.12474	-3.30339	0.14171
H	-2.17827	-4.38373	0.20347
C	-3.16911	-1.14862	-0.06190
C	-3.27693	-2.53501	-0.00049
C	-4.56036	-3.15506	-0.07470
H	-0.77057	4.59928	0.16448
N	-0.80451	-1.32631	0.12553
Ir	1.02208	-0.19512	0.07902
Cl	1.30179	0.02492	2.55623
C	2.89888	0.95069	0.00878
C	4.00626	-0.07109	0.29068
H	4.98315	0.33953	0.00391
H	4.06343	-0.30009	1.36212
C	3.77214	-1.34308	-0.46556
H	3.78632	-1.18862	-1.54981
H	4.47117	-2.13798	-0.19607
Cl	0.82251	-0.39164	-2.25373
H	1.93413	0.68990	1.38569
H	2.99405	1.72936	0.79429
H	3.18017	0.99274	-2.15289
C	3.08585	1.68117	-1.31083
H	2.25331	2.34868	-1.55206
H	3.99764	2.28958	-1.26537
O	2.42740	-1.80142	-0.09319
H	2.11516	-2.37670	-0.80649
H	-3.72495	1.50734	-0.15260
H	-4.06606	-0.54944	-0.16355
N	-5.59809	-3.65208	-0.13431
N	-4.26342	4.93096	-0.13230

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1976.87457

N	0.72859	-1.29245	-0.02974
C	1.92708	-0.65588	0.05505
C	1.89330	0.81531	0.09595
C	0.70767	-2.62643	-0.17640
H	-0.26774	-3.08410	-0.28131
C	3.11094	-1.37542	0.05627
C	1.85237	-3.39324	-0.19922
C	3.08324	-2.75922	-0.06511
C	0.54377	2.69040	0.04048
H	-0.46870	3.08044	0.01119
C	1.62985	3.54112	-0.04022
H	1.49147	4.61310	-0.11566
C	3.03629	1.59796	0.02516
C	2.90404	2.98166	-0.03106
H	1.78456	-4.46788	-0.31888
N	0.66766	1.36792	0.13769
Ir	-0.94486	-0.16097	0.03908
Cl	-1.13248	-0.54029	2.53676
O	-2.63820	1.17544	0.14100
Cl	-0.80040	0.15126	-2.26476
C	-3.84796	1.09729	-0.65880

C	-4.06925	-0.28416	-1.21630
C	-3.75609	-1.36891	-0.19313
C	-2.28405	-1.74131	-0.19847
H	-3.77945	1.86363	-1.43944
H	-4.67047	1.35803	0.02085
H	-3.46871	-0.43918	-2.11827
H	-5.11910	-0.32675	-1.52650
H	-4.34783	-2.26520	-0.41888
H	-4.08293	-1.04151	0.80780
H	-1.95488	-1.54908	2.53003
C	-2.73457	2.16473	1.15834
H	-1.76750	2.24910	1.65525
H	-3.49420	1.87614	1.89494
H	-3.00684	3.12982	0.71592
H	-2.09328	-2.50041	0.58205
H	-2.04809	-2.21383	-1.16257
H	4.06504	-0.87069	0.14534
H	4.02682	1.16106	-0.00968
C	4.29826	-3.50647	-0.06113
C	4.06456	3.80993	-0.10005
N	5.00309	4.47638	-0.15134
N	5.28114	-4.10788	-0.05405

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1976.883638

N	-0.52080	1.28354	0.15470
C	-1.78600	0.80931	0.02636
C	-1.94545	-0.65183	0.06993
C	-0.32782	2.61109	0.22282
H	0.69602	2.94413	0.33482
C	-2.86313	1.67603	-0.06905
C	-1.35722	3.52217	0.14285
C	-2.65581	3.04828	-0.01906
C	-0.91219	-2.66730	0.50103
H	0.00526	-3.18612	0.75511
C	-2.09128	-3.37246	0.35095
H	-2.11527	-4.44785	0.48096
C	-3.16695	-1.28147	-0.11661
C	-3.24090	-2.66370	0.01735
H	-1.15023	4.58404	0.19968
N	-0.82807	-1.34701	0.35177
Ir	1.00882	-0.04573	0.11085
Cl	1.35634	0.13951	2.59660
C	3.89884	0.57712	0.04947
H	4.74050	1.13952	-0.37567
H	4.12334	0.43582	1.11485
C	3.82632	-0.77206	-0.59665
H	3.67720	-0.71598	-1.68321
H	4.69681	-1.40076	-0.38156
Cl	0.64559	-0.34800	-2.17570
H	2.47875	2.06321	0.65484
H	2.84285	1.43345	-2.32183
C	2.59740	2.08472	-1.47868
H	1.63785	2.55036	-1.72392
H	3.35433	2.87932	-1.44146
O	2.66666	-1.42362	-0.01333
C	2.47716	-2.74236	-0.53211
H	3.44988	-3.23754	-0.59358
H	2.00602	-2.70337	-1.51951

H	1.85709	-3.29145	0.17520
C	2.58001	1.32635	-0.16365
H	2.27701	1.05433	2.67722
H	-3.87231	1.29607	-0.16893
H	-4.06124	-0.72615	-0.37183
C	-4.48431	-3.33791	-0.17495
C	-3.75864	3.94774	-0.11523
N	-5.48942	-3.87997	-0.32818
N	-4.65160	4.67221	-0.19022

XYZ coordinates of the delta transition state of 1-methoxybutane by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1976.869699

Imaginary frequency: 791.09cm^{-1}

N	0.76454	-1.28922	-0.04767
C	1.94612	-0.62321	0.03141
C	1.86238	0.84427	0.06273
C	0.76728	-2.62338	-0.17187
H	-0.19961	-3.10281	-0.26289
C	3.14588	-1.31321	0.03498
C	1.92968	-3.36470	-0.18578
C	3.14593	-2.69983	-0.06806
C	4.37710	-3.42027	-0.06200
C	0.43014	2.66197	-0.05957
H	-0.59886	2.99909	-0.13450
C	1.48235	3.55651	-0.09743
H	1.30176	4.62134	-0.18357
C	2.97046	1.67594	0.03975
C	2.77821	3.05283	-0.02881
C	3.90296	3.93128	-0.04892
H	1.88671	-4.44261	-0.28546
N	0.61365	1.34719	0.04988
Ir	-0.91584	-0.17101	0.03536
Cl	-1.08816	-0.67059	2.53385
O	-2.57888	1.19490	0.16453
Cl	-0.84032	0.07395	-2.28657
C	-3.81454	1.11850	-0.60479
C	-4.06608	-0.25463	-1.17031
C	-3.78511	-1.36296	-0.16387
C	-2.32764	-1.78932	-0.16221
H	-3.76126	1.88901	-1.38133
H	-4.61741	1.37868	0.09616
H	-3.47946	-0.41514	-2.07984
H	-5.11898	-0.26740	-1.47376
H	-4.40128	-2.23719	-0.40737
H	-4.10254	-1.04852	0.84325
H	-1.66755	-1.31783	1.40785
C	-2.71627	2.02096	1.32255
H	-1.73492	2.13875	1.78252
H	-3.39751	1.55384	2.04287
H	-3.10616	2.99983	1.02487
H	-2.20609	-2.63982	0.53726
H	-2.05245	-2.19093	-1.14577
H	4.08870	-0.78521	0.11077
H	3.97921	1.28113	0.05650
N	4.81305	4.63779	-0.06138
N	5.37302	-3.99970	-0.05469

XYZ coordinates of the gamma transition state of 1-methoxybutane by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -1976.868901

Imaginary frequency: 413.04cm^{-1}

N	-0.54662	1.28057	0.15303
C	-1.80215	0.79708	-0.01131
C	-1.93191	-0.66373	0.01569
C	-0.36362	2.60459	0.26834
H	0.65213	2.94380	0.42701
C	-2.88402	1.65458	-0.11986
C	-1.39997	3.50815	0.18505
C	-2.68791	3.02722	-0.03173
C	-0.83391	-2.66167	0.38346
H	0.10453	-3.16109	0.58565
C	-2.00626	-3.38736	0.29244
H	-2.00050	-4.46309	0.42112
C	-3.14674	-1.31780	-0.10613
C	-3.18619	-2.70201	0.02451
H	-1.20600	4.56948	0.28248
N	-0.78587	-1.33932	0.23354
Ir	0.97813	-0.05038	0.12617
Cl	1.35698	0.25384	2.57151
C	3.93801	0.56620	0.06528
H	4.78304	1.10881	-0.37697
H	4.17528	0.40890	1.12459
C	3.80681	-0.77043	-0.59710
H	3.62715	-0.70335	-1.67801
H	4.67290	-1.41352	-0.41159
Cl	0.69832	-0.31911	-2.19439
H	2.67652	2.16146	0.69054
H	2.76418	1.44760	-2.26618
C	2.59342	2.11544	-1.42004
H	1.63604	2.61045	-1.60393
H	3.37438	2.88587	-1.43270
O	2.65649	-1.41140	0.01727
C	2.48506	-2.75989	-0.42504
H	3.46925	-3.20410	-0.59156
H	1.90110	-2.79130	-1.35102
H	1.99916	-3.31288	0.37911
C	2.65293	1.37535	-0.09268
H	1.87718	0.92825	1.31482
H	-3.88601	1.26869	-0.26178
H	-4.06512	-0.77661	-0.29818
C	-4.42489	-3.39974	-0.10057
C	-3.79450	3.92023	-0.14369
N	-5.42636	-3.96049	-0.20090
N	-4.69092	4.63854	-0.23388

XYZ coordinates of alpha activated butyl acetate by iridium(III)-4,4’-dicyano-2,2’-bipyridine dichloride

Energy: -2090.242858

N	-0.51805	1.26218	0.13850
C	-1.86233	1.09853	0.03279
C	-2.34095	-0.29152	0.01175
C	-0.01475	2.50220	0.21969
H	1.06307	2.58008	0.31102
C	-2.70959	2.19276	-0.01553
C	-0.80407	3.63131	0.18243
C	-2.18164	3.47668	0.05357
C	-1.69049	-2.51325	0.18123
H	-0.86169	-3.20427	0.30460
C	-2.98737	-2.95719	0.00179

H	-3.21393	-4.01665	-0.00613
C	-3.66311	-0.65599	-0.18051
C	-3.99087	-2.00949	-0.18094
H	-0.35449	4.61476	0.24865
N	-1.38299	-1.21737	0.19849
Ir	0.62856	-0.42564	0.13929
Cl	0.83170	-0.37171	2.66745
Cl	0.40374	-0.58998	-2.17325
H	2.97389	0.50776	-2.11582
C	2.96777	1.14199	-1.22373
H	2.18618	1.89080	-1.41524
C	2.55437	0.28962	-0.04547
H	1.93683	0.28724	2.85347
C	4.31008	1.84360	-1.03634
H	4.65518	2.20369	-2.01176
H	5.06102	1.11599	-0.70330
C	4.24084	3.01254	-0.06905
H	3.53624	3.77420	-0.42575
H	3.92276	2.70613	0.93596
H	5.21216	3.49989	0.04629
O	3.46815	-0.90757	-0.09287
C	2.91883	-2.06873	-0.02498
O	1.68754	-2.21305	0.13096
C	3.81647	-3.23729	-0.15517
H	3.97033	-3.43043	-1.22192
H	3.35783	-4.11817	0.29217
H	4.78973	-3.02988	0.29030
H	2.87719	0.77990	0.89115
H	-3.78167	2.06002	-0.09842
H	-4.44062	0.08094	-0.34357
C	-5.34593	-2.41421	-0.37549
C	-3.04312	4.61268	0.00577
N	-6.44142	-2.73672	-0.52889
N	-3.74069	5.52912	-0.03006

XYZ coordinates of the alpha transition state of butylacetate by iridium(III)-4,4'-dicyano-2,2'-bipyridine dichloride

Energy: -2090.209587

Imaginary frequency: 473.08cm^{-1}

N	-0.54446	1.30808	0.15580
C	-1.89245	1.10967	0.01200
C	-2.32887	-0.28684	-0.03217
C	-0.05088	2.56337	0.23159
H	1.02302	2.65866	0.34684
C	-2.75761	2.19455	-0.06728
C	-0.87024	3.67852	0.16234
C	-2.24985	3.49605	0.00495
C	-1.56799	-2.51303	0.06981
H	-0.70349	-3.16344	0.15399
C	-2.86468	-2.99876	-0.04901
C	-3.64693	-0.70860	-0.15591
C	-3.91926	-2.08398	-0.16555
N	-1.32248	-1.19221	0.07714
Ir	0.62777	-0.37160	0.14919
Cl	0.63967	-0.65829	2.69170
O	3.46789	-1.03844	-0.20885
C	2.83134	-2.17850	-0.19223
Cl	0.54329	-0.24766	-2.23057
H	3.06849	0.54628	1.02139
H	3.15731	0.68154	-1.98916

C	3.12233	1.21629	-1.03353
H	2.36446	2.00306	-1.17080
O	1.56442	-2.20798	0.00626
C	2.66386	0.25015	0.04185
C	3.60940	-3.40878	-0.42901
H	3.05470	-4.27991	-0.07922
H	3.79172	-3.51658	-1.50555
H	4.58156	-3.34567	0.06538
C	4.47562	1.86086	-0.70358
H	4.88031	2.31586	-1.61645
H	5.18751	1.07667	-0.40915
C	4.36664	2.92308	0.38792
H	3.71311	3.74595	0.06549
H	3.96286	2.51584	1.32661
H	5.34357	3.35615	0.62577
H	-0.44541	4.67323	0.22823
H	-3.82482	2.04435	-0.18530
H	-4.46615	-0.00386	-0.24565
H	-3.05615	-4.06539	-0.05353
C	-5.26481	-2.54103	-0.29201
C	-3.12882	4.61564	-0.07562
H	1.14764	0.43592	1.54194
N	-6.37198	-2.91085	-0.39516
N	-3.85364	5.53425	-0.13981

XYZ coordinates of iridium(III)-DPPE dichloride

Energy: -1945.425837

P	-1.54082	-0.03397	-0.86295
P	1.55898	0.18931	-0.81864
Ir	-0.00620	-0.07377	0.76397

Cl	-0.26309	2.20481	1.24245
C	-0.69152	0.66114	-2.32736
C	0.69671	0.04299	-2.43024
C	2.37681	1.80042	-0.78403
C	2.86759	-1.05185	-0.78819
C	-2.17697	-1.66019	-1.33139
C	-2.97845	0.99199	-0.49867
H	-0.64083	1.74774	-2.18280
H	-1.29198	0.46925	-3.22388
H	1.30329	0.52408	-3.20587
H	0.64202	-1.02634	-2.67105
H	2.86086	1.94996	0.18448
H	1.65091	2.60383	-0.92545
H	3.13335	1.82116	-1.57670
H	2.43882	-2.05036	-0.89539
H	3.40416	-1.00411	0.16319
H	3.56689	-0.84210	-1.60574
H	-1.36902	-2.31866	-1.65720
H	-2.90498	-1.52609	-2.13973
H	-2.66633	-2.12865	-0.47377
H	-2.67021	2.02608	-0.33285
H	-3.47685	0.62466	0.40273
H	-3.67713	0.92812	-1.34074
Cl	0.22407	-2.39043	0.92452

XYZ coordinates of delta activated 1-butanol by iridium(III)-DPPE dichloride

Energy: -2178.896825

P	-1.31505	1.62121	-0.11066
P	-1.57472	-1.54487	0.18030
Ir	0.27698	0.02230	-0.01450

Cl	0.65835	0.22452	2.43971
O	1.76705	-1.65513	-0.14713
H	1.69731	-1.86563	-1.09238
Cl	0.17701	-0.32063	-2.34545
C	3.15950	-1.46563	0.17999
C	3.75384	-0.22419	-0.43945
C	3.21171	1.08011	0.13183
C	1.81608	1.46794	-0.33820
H	3.69390	-2.36910	-0.13135
H	3.19580	-1.42276	1.27381
H	3.60679	-0.24831	-1.52940
H	4.83752	-0.27506	-0.27772
H	3.90388	1.89014	-0.13694
H	3.27618	1.02194	1.23337
H	1.84784	1.65396	-1.41943
H	1.54317	2.42545	0.13367
H	1.59553	1.12903	2.46432
C	-2.97110	0.83453	0.11189
C	-3.00338	-0.57318	-0.46994
C	-2.13405	-2.09507	1.83162
C	-1.56207	-3.07479	-0.80232
C	-1.26699	2.91365	1.16737
C	-1.39889	2.54411	-1.66857
H	-3.73579	1.48188	-0.33384
H	-3.16505	0.81290	1.19320
H	-2.89560	-0.55035	-1.56188
H	-3.94949	-1.07713	-0.24121
H	-2.32316	-1.23355	2.47969
H	-1.35605	-2.70722	2.29724
H	-3.05091	-2.68902	1.75792
H	-0.80147	-3.75374	-0.40628
H	-1.31398	-2.83597	-1.83975
H	-2.53642	-3.57237	-0.76326
H	-1.30500	2.47124	2.16592
H	-2.12871	3.57795	1.04330
H	-0.35356	3.50677	1.06957
H	-1.63417	1.86905	-2.49372
H	-0.42914	3.00592	-1.87319
H	-2.16576	3.32147	-1.59049

XYZ coordinates of gamma activated 1-butanol by iridium(III)-DPPE dichloride

Energy: -2178.895724

P	-2.95591	1.72789	0.66933
P	-1.25828	-1.74013	0.03372
Ir	0.52965	-0.00598	-0.01368
Cl	1.32131	-0.65616	2.28425
C	2.08388	1.44211	-0.16728
C	2.16352	2.49938	0.91036
H	2.30846	2.09455	1.92579
H	3.02182	3.16479	0.74404
H	1.27389	3.13598	0.93745
C	3.38015	0.64522	-0.28679
H	4.20546	1.28921	-0.62334
H	3.69278	0.23240	0.68348
C	3.21084	-0.46807	-1.27373
H	2.98576	-0.08211	-2.27375
H	4.05293	-1.16270	-1.31526
O	2.04227	-1.24670	-0.82007
H	1.67386	-1.70952	-1.58666
Cl	-0.03944	0.46661	-2.24679

H	1.89390	1.94035	-1.12756
H	1.93031	0.43464	2.65471
C	-3.25459	0.22339	-0.39007
C	-2.96385	-1.09301	0.33043
C	-1.43551	-2.68787	-1.51618
C	-1.12817	-3.05035	1.30191
C	-2.66756	2.98502	-0.64476
C	-1.19885	1.41048	1.19339
H	-2.68358	0.30686	-1.32451
H	-4.31323	0.27206	-0.66721
H	-3.65630	-1.88235	0.01090
H	-3.10341	-0.99842	1.41696
H	-2.25845	-3.40543	-1.43565
H	-0.51421	-3.24295	-1.72062
H	-1.62009	-2.00829	-2.35178
H	-1.13905	-2.60674	2.30278
H	-0.19240	-3.60362	1.17734
H	-1.96524	-3.75221	1.22400
H	-3.60744	3.16642	-1.17382
H	-1.91309	2.66529	-1.37266
H	-2.36113	3.93202	-0.19238
H	-0.60974	1.36256	0.19200
H	-1.17544	0.57661	1.89104
H	-0.76605	2.28298	1.69204

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-DPPE dichloride

Energy: -2178.88981

Imaginary frequency: 638.51cm^{-1}

P	-1.36927	1.58751	-0.13789
P	-1.54122	-1.55408	0.21565
Ir	0.25509	0.01229	-0.01179
O	1.76475	-1.64223	-0.09599
H	1.71521	-1.89144	-1.03264
Cl	0.16540	-0.37191	-2.33559
C	3.15247	-1.42153	0.24482
C	3.76103	-0.23821	-0.46913
C	3.27858	1.11916	0.02641
C	1.85168	1.49128	-0.36842
H	3.68888	-2.34864	0.01839
H	3.16551	-1.28761	1.33118
H	3.59209	-0.33472	-1.55215
H	4.84653	-0.30651	-0.32795
H	3.95268	1.88966	-0.37096
H	3.42055	1.15776	1.11821
H	1.78949	1.57570	-1.45964
H	1.62321	2.49800	0.01749
C	-3.01090	0.76793	0.07690
C	-2.99893	-0.65662	-0.46128
C	-2.02920	-2.02498	1.90687
C	-1.47530	-3.12565	-0.69063
C	-1.34910	2.89125	1.12542
C	-1.45255	2.48768	-1.70865
H	-3.77847	1.38377	-0.40657
H	-3.22936	0.77728	1.15309
H	-2.89243	-0.66454	-1.55336
H	-3.92759	-1.18393	-0.21465
H	-2.22666	-1.13582	2.51256
H	-1.21704	-2.58445	2.37994
H	-2.92737	-2.65075	1.88932

H	-0.67086	-3.74502	-0.28388
H	-1.27012	-2.92836	-1.74598
H	-2.42178	-3.66778	-0.59689
H	-1.34513	2.45542	2.12739
H	-2.23983	3.51712	1.00753
H	-0.46223	3.51988	1.00664
H	-1.70556	1.80714	-2.52396
H	-0.48061	2.93836	-1.92761
H	-2.21055	3.27413	-1.63317
Cl	0.74464	0.41766	2.45903
H	1.27140	1.10599	1.38466

XYZ coordinates of delta activated 1-methoxybutane by iridium(III)-DPPE dichloride

Energy: -2218.150705

P	1.57342	-1.49848	-0.13878
P	1.41101	1.69333	-0.05020
Ir	-0.22065	-0.14287	0.06829
Cl	-0.31938	-0.23364	2.56443
O	-2.09383	1.10643	0.26488
Cl	-0.38562	0.05976	-2.27214
C	-3.30914	0.85196	-0.47468
C	-3.46631	-0.60214	-0.84673
C	-2.95717	-1.56225	0.22102
C	-1.47409	-1.86015	0.06291
H	-3.31038	1.49500	-1.36539
H	-4.12746	1.17353	0.18536
H	-2.95359	-0.80931	-1.79189
H	-4.53494	-0.75843	-1.03028
H	-3.51345	-2.50621	0.14761
H	-3.18963	-1.16177	1.22032
H	-1.14082	-1.23295	2.71554
C	-1.95388	2.49400	0.51973
H	-1.14359	2.62945	1.23858
H	-2.88043	2.88819	0.95219
H	-1.73199	3.03330	-0.41076
H	-1.15010	-2.55405	0.85752
H	-1.32757	-2.38963	-0.88804
C	2.91317	0.85462	-0.72278
C	3.11036	-0.48869	-0.03683
C	1.70504	-2.42817	-1.69026
C	1.78647	-2.76728	1.14543
C	2.03167	2.46111	1.49330
C	1.20041	3.11853	-1.16678
H	3.78984	1.50124	-0.60050
H	2.74561	0.72641	-1.79998
H	3.33632	-0.35666	1.03045
H	3.94159	-1.05722	-0.47085
H	1.78246	-1.74483	-2.53764
H	0.81220	-3.04259	-1.83145
H	2.58832	-3.07349	-1.64464
H	0.97240	-3.49515	1.09145
H	1.80214	-2.31502	2.14012
H	2.73423	-3.29055	0.98033
H	2.36614	1.69187	2.19636
H	1.23642	3.03762	1.97595
H	2.86913	3.13505	1.28438
H	0.78471	2.77474	-2.11762
H	2.16443	3.60722	-1.34248
H	0.51764	3.84766	-0.72250

XYZ coordinates of gamma activated 1-methoxybutane by iridium(III)-DPPE dichloride

Energy: -2218.155519

P	-1.12724	1.75676	-0.07785
P	-1.76483	-1.35833	-0.04214
Ir	0.27798	-0.00887	0.07298
Cl	0.30003	-0.00758	2.57241
C	3.19888	0.22436	0.56037
H	4.17159	0.67742	0.32280
H	3.21969	0.00345	1.63597
C	3.08229	-1.08235	-0.17062
H	3.10843	-0.95913	-1.26228
H	3.85481	-1.80136	0.12731
Cl	0.41401	-0.19005	-2.27196
H	1.91069	1.87268	1.05664
H	2.60171	1.43938	-1.89396
C	2.42338	2.04024	-0.99745
H	1.64246	2.76423	-1.25315
H	3.33756	2.61448	-0.79466
O	1.79943	-1.63499	0.19865
C	1.55919	-2.91037	-0.38467
H	2.40502	-3.57110	-0.16956
H	1.41645	-2.82230	-1.46796
H	0.66114	-3.31913	0.08269
C	2.05600	1.18738	0.20048
H	1.23866	0.86717	2.80400
C	-2.82627	1.17377	0.32993
C	-3.10625	-0.13517	-0.39511
C	-0.82554	3.13892	1.06322
C	-1.30917	2.55031	-1.70045
C	-2.34290	-2.18722	1.48365
C	-2.01186	-2.62646	-1.32672
H	-3.55146	1.95376	0.06800
H	-2.87214	1.04161	1.42001
H	-3.11819	0.01558	-1.48255
H	-4.08001	-0.55380	-0.11632
H	-0.82669	2.79027	2.09918
H	-1.61290	3.89068	0.94510
H	0.13945	3.60241	0.84080
H	-1.67094	1.83130	-2.43755
H	-0.34681	2.92721	-2.05250
H	-2.01778	3.38001	-1.60800
H	-2.47309	-1.45764	2.28893
H	-1.60535	-2.92732	1.80970
H	-3.29837	-2.69398	1.31327
H	-1.67798	-2.23540	-2.29118
H	-3.06995	-2.90244	-1.38411
H	-1.42988	-3.52192	-1.09323

XYZ coordinates of alpha activated butyl acetate by iridium(III)-DPPE dichloride

Energy: -2331.506723

P	-0.95304	1.94081	-0.09932
P	-2.41479	-0.85954	-0.05804
Ir	-0.10434	-0.16773	0.07687
Cl	-0.14795	-0.31048	2.58641
O	2.63936	-1.10951	-0.13998
C	1.92289	-2.18643	-0.12212
Cl	0.06881	-0.23323	-2.26942
H	2.26136	0.34047	1.24336

H	2.34078	1.16387	-1.68437
C	2.66445	1.24150	-0.63993
H	2.29344	2.20623	-0.25847
O	0.69975	-2.17772	0.09209
C	1.97520	0.18712	0.18492
H	1.05212	0.09740	2.88928
C	2.65586	-3.44378	-0.40295
H	2.08085	-4.30055	-0.05490
H	2.78310	-3.52549	-1.48737
H	3.64880	-3.42612	0.04750
C	4.18963	1.24997	-0.56091
H	4.55005	2.07697	-1.18384
H	4.58379	0.33619	-1.01917
C	4.73411	1.40037	0.84834
H	4.29282	2.26792	1.35592
H	4.53566	0.51498	1.46268
H	5.81739	1.54487	0.84173
C	-2.72601	1.81657	-0.59715
C	-3.42593	0.67356	0.12319
C	-3.04788	-2.00059	1.21316
C	-2.94445	-1.61414	-1.62367
C	-0.95237	2.90104	1.44737
C	-0.26395	3.08722	-1.32483
H	-2.72238	1.65126	-1.68299
H	-3.21616	2.78132	-0.41891
H	-4.44208	0.51758	-0.25627
H	-3.51002	0.88044	1.19921
H	-2.94868	-1.55951	2.20918
H	-2.46611	-2.92670	1.18405
H	-4.10207	-2.23719	1.03738
H	-2.75216	-0.93275	-2.45510
H	-4.00835	-1.86768	-1.58243
H	-2.35652	-2.51978	-1.79835
H	-1.52200	2.38969	2.22740
H	-1.38960	3.88940	1.27278
H	0.07862	3.02759	1.79397
H	-0.18854	2.59062	-2.29447
H	0.72859	3.42645	-1.02236
H	-0.92769	3.95512	-1.40182

XYZ coordinates of iridium(III)-1,10-phenanthroline di(trifluoroacetate)

Energy: -1727.870422

N	-1.22925	0.78378	1.32433
C	-1.63238	1.72115	0.42928
C	-0.91139	1.76985	-0.78157
C	-1.90237	0.63771	2.45542
H	-1.57248	-0.14732	3.12931
C	-2.71686	2.57419	0.64772
C	-2.99438	1.45758	2.75937
C	-3.40013	2.42400	1.86859
H	-4.24953	3.06220	2.09327
C	0.78354	0.80111	-2.06151
H	1.55081	0.03786	-2.13584
C	0.48204	1.66586	-3.11679
H	1.05723	1.58029	-4.03076
C	-1.26846	2.65905	-1.79789
C	-0.52692	2.59222	-2.99117
H	-0.76484	3.26359	-3.81085
C	-2.36478	3.54523	-1.55222
H	-2.64196	4.24837	-2.33142
C	-3.05573	3.50633	-0.38331

H	-3.89098	4.17935	-0.21680
H	-3.51199	1.30911	3.69938
N	0.10596	0.87790	-0.92159
Ir	0.37857	-0.27717	0.65850
O	-0.98566	-1.70866	0.40435
C	-1.13286	-2.25932	-0.77309
O	-0.63128	-1.90781	-1.80395
C	-2.12014	-3.44519	-0.68364
F	-3.32788	-2.98198	-0.35428
F	-2.20604	-4.06926	-1.83713
F	-1.73512	-4.30641	0.24948
O	2.26778	-1.05378	0.02118
C	2.85123	-0.02300	0.45295
O	2.17343	0.87675	1.00948
C	4.34964	0.16154	0.19737
F	4.98919	-0.97954	0.33195
F	4.47558	0.58590	-1.06236
F	4.86012	1.06183	1.00734

XYZ coordinates of iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -1278.095088

N	1.60237	-1.16539	-0.22948
C	2.46245	-0.11594	-0.18202
C	1.85383	1.13915	0.00212
C	2.09395	-2.37836	-0.46169
H	1.37541	-3.19088	-0.52077
C	3.84942	-0.24210	-0.29649
C	3.46765	-2.59281	-0.60991
C	4.34888	-1.53932	-0.51151
H	5.41908	-1.70126	-0.60178
C	-0.13822	2.28989	0.28639
H	-1.21856	2.25541	0.37300
C	0.56672	3.49322	0.37915
H	0.00685	4.40876	0.52792
C	2.62992	2.29608	0.10223
C	1.94054	3.50586	0.29778
H	2.49467	4.43570	0.38944
C	4.05309	2.15818	0.01747
H	4.66352	3.05078	0.11558
C	4.63689	0.94658	-0.17590
H	5.71757	0.85999	-0.23623
H	3.81863	-3.60167	-0.79208
N	0.49149	1.12995	0.10124
Ir	-0.35585	-0.72107	0.08955
O	-2.33488	-1.00756	0.29609
C	-3.48039	-0.64779	-0.22946
O	-4.35881	-1.37380	-0.57745
C	-3.62915	0.88855	-0.32737
F	-4.84756	1.26508	-0.61618
F	-3.26267	1.47361	0.82950
F	-2.79475	1.36183	-1.27572
H	-1.47739	-2.43748	1.80262
O	-0.53100	-2.39685	1.57756
H	-0.04776	-2.19526	2.39220

XYZ coordinates of the dissociated trifluoroacetate

Energy: -526.170425

O	-2.36054	-1.08467	0.00665
C	-2.87805	-0.05072	-0.02880
O	-3.39303	0.98361	-0.06448
C	1.60160	0.08708	-0.03551
F	2.13565	1.22563	0.33775
F	1.69571	-0.81764	0.91201
F	2.13389	-0.34239	-1.15549

XYZ coordinates of the transition state for the formation of iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -1804.243218

Imaginary frequency: 472.24cm^{-1}

N	-1.81989	-0.85637	-0.58429
C	-2.68554	0.11581	-0.18484
C	-2.12934	1.37431	0.16534
C	-2.29723	-2.04731	-0.92291
H	-1.57285	-2.79674	-1.22679
C	-4.06880	-0.08748	-0.11163
C	-3.66438	-2.32969	-0.87899
C	-4.54896	-1.35880	-0.47503
H	-5.61487	-1.56259	-0.43155
C	-0.20031	2.64635	0.40360
H	0.88222	2.68497	0.31967
C	-0.95630	3.73841	0.84189
H	-0.44480	4.65644	1.10557
C	-2.95330	2.42028	0.59428
C	-2.32289	3.63114	0.93656
H	-2.92274	4.46980	1.27774
C	-4.36345	2.19384	0.66321
H	-5.00103	3.00692	0.99644
C	-4.89741	0.99363	0.32446
H	-5.96922	0.83084	0.38161
H	-4.00467	-3.31865	-1.16175
N	-0.77872	1.50069	0.07102
Ir	0.14227	-0.22215	-0.52351
O	0.97465	-2.03084	-1.05160
C	1.20793	-2.63725	0.00816
O	1.66203	-3.61220	0.44606
C	0.33770	-1.75642	1.59189
F	0.00799	-0.44649	1.95620
F	-0.80897	-2.44031	1.69422
F	1.15395	-2.16378	2.51701
O	1.97407	0.70132	-0.57426
C	2.98364	0.24759	0.11525
O	3.01569	-0.73648	0.79914
C	4.19568	1.19309	-0.03913
F	4.54819	1.27807	-1.32187
F	3.85712	2.42008	0.37475
F	5.22366	0.77955	0.66057
H	1.11024	0.97403	-2.48610
O	0.23095	0.54531	-2.47538
H	0.25456	-0.15543	-3.14405

XYZ coordinates of delta activated 1-butanol by iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -1511.564091

N	-0.02707	1.71301	-0.56775
C	1.15069	1.67728	0.12133
C	1.21774	0.80504	1.24090
C	-0.11468	2.53139	-1.61198
H	-1.06237	2.54523	-2.13946
C	2.27806	2.41611	-0.25698
C	0.95319	3.32624	-2.03230
C	2.15435	3.26331	-1.36975
H	3.00621	3.85180	-1.69663
C	0.11115	-0.74262	2.56149
H	-0.81828	-1.26637	2.76760
C	1.26877	-0.97313	3.30816
H	1.24427	-1.69260	4.11790
C	2.42086	0.63590	1.93934
C	2.41982	-0.28533	3.00140

H	3.33390	-0.45318	3.56374
C	3.56655	1.38147	1.52285
H	4.49843	1.24393	2.06265
C	3.49252	2.24149	0.47701
H	4.36529	2.80743	0.16580
H	0.81865	3.97005	-2.89329
N	0.08378	0.12789	1.56050
Ir	-1.44611	0.42805	0.10951
O	0.75054	-1.94571	-0.75851
O	-2.86436	-0.90924	0.98582
H	-3.70477	-0.41990	1.13467
C	-3.16394	-2.14389	0.29902
C	-3.69858	-1.91424	-1.09421
C	-2.67555	-1.35631	-2.07200
C	-2.18497	0.04771	-1.76899
H	-3.88115	-2.69165	0.91977
H	-2.22492	-2.71029	0.28625
H	-4.57162	-1.24788	-1.03356
H	-4.07381	-2.87581	-1.46501
H	-3.11829	-1.36297	-3.07812
H	-1.82287	-2.04946	-2.13323
H	-3.03818	0.76265	-1.77010
H	-1.48299	0.37848	-2.54584
H	0.00206	-1.30394	-0.81803
C	1.83520	-1.38782	-1.26506
C	3.06811	-2.25428	-0.93921
O	1.90863	-0.34452	-1.84129
F	4.14198	-1.77325	-1.52769
F	2.89215	-3.51238	-1.30670
F	3.26189	-2.22414	0.38628
H	-5.94307	0.38748	1.63996
O	-5.13491	0.54585	1.14469
H	-5.11238	1.48745	0.95496

XYZ coordinates of gamma activated 1-butanol by iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -1511.570614

N	-0.12763	-1.85410	0.14558
C	1.11069	-1.66411	-0.40260
C	1.25664	-0.58053	-1.31054
C	-0.30218	-2.91647	0.92920
H	-1.30105	-3.06747	1.32400
C	2.20774	-2.48717	-0.11423
C	0.73276	-3.79802	1.24336
C	1.99323	-3.57910	0.74291
H	2.81773	-4.24089	0.98996
C	0.23212	1.16386	-2.43644
H	-0.67898	1.72372	-2.62524
C	1.43776	1.51259	-3.04925
H	1.46058	2.35138	-3.73458
C	2.50387	-0.30359	-1.88741
C	2.57186	0.78517	-2.77406
H	3.52121	1.03805	-3.23757
C	3.61771	-1.13387	-1.55360
H	4.58225	-0.90983	-1.99883
C	3.47238	-2.18374	-0.70929
H	4.31831	-2.82005	-0.46781
H	0.52279	-4.64087	1.89111
N	0.14208	0.14776	-1.58645
Ir	-1.51903	-0.46326	-0.37811
O	0.69871	0.73889	1.72271
C	-2.72869	-0.46838	1.29744
C	-3.68488	0.72002	1.22649

H	-4.55662	0.56282	1.87827
H	-3.17440	1.62040	1.60189
C	-4.12153	0.94934	-0.19295
H	-4.72692	0.12082	-0.57416
H	-4.67564	1.88052	-0.34043
O	-2.93507	0.98616	-1.02439
H	-2.53348	1.88626	-0.95602
H	-0.17574	0.58770	1.27214
C	1.25616	1.84055	1.29129
C	2.72983	1.90420	1.74527
O	0.76700	2.68661	0.59400
F	2.84712	1.66654	3.03960
F	3.25610	3.07514	1.46497
F	3.40383	0.95974	1.07694
C	-2.17513	-0.64061	2.69433
H	-1.70532	0.28653	3.04446
H	-2.97846	-0.86736	3.40806
H	-1.42927	-1.43520	2.78137
H	-3.27975	-1.38958	0.98392
H	-0.80723	3.20979	-0.22045
O	-1.61854	3.27382	-0.75253
H	-1.85844	4.20102	-0.81147

XYZ coordinates of delta activated 1-methoxybutane by iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -947.583926

N	0.87807	-1.29690	-0.18272
C	2.02325	-0.57089	-0.00613
C	1.88810	0.84169	0.06665
C	0.99194	-2.61734	-0.31510
H	0.07157	-3.16848	-0.47379
C	3.29210	-1.15777	0.08686
C	2.22234	-3.27386	-0.25080
C	3.37314	-2.55489	-0.03816
H	4.33870	-3.04720	0.02632
C	0.46003	2.65916	-0.00625
H	-0.55939	3.01477	-0.12911
C	1.52212	3.53973	0.21095
H	1.32901	4.60476	0.26134
C	3.01294	1.65276	0.27452
C	2.79656	3.03962	0.34704
H	3.63987	3.70461	0.51025
C	4.29519	1.03279	0.39253
H	5.16340	1.66444	0.55405
C	4.42745	-0.31288	0.29573
H	5.40502	-0.77863	0.37558
H	2.24553	-4.35116	-0.36505
N	0.63721	1.34695	-0.08257
Ir	-0.82325	-0.21042	-0.26301
O	-2.55682	1.05656	-0.42777
C	-3.39117	1.13924	0.75067
C	-3.99579	-0.18572	1.14730
C	-2.98153	-1.21260	1.62834
C	-1.97900	-1.67577	0.58679
H	-4.15960	1.89367	0.54251
H	-2.72985	1.52348	1.53588
H	-4.58997	-0.59061	0.31619
H	-4.71648	0.02181	1.94779
H	-3.53052	-2.08566	2.00872
H	-2.44084	-0.80480	2.49461
H	-2.49706	-2.09622	-0.30216
H	-1.35860	-2.47702	1.00703
C	-3.28850	0.93114	-1.65174

H	-3.75392	-0.05601	-1.73715
H	-4.05573	1.71090	-1.69000
H	-2.57876	1.07031	-2.46745

XYZ coordinates of trifluoroacetate

Energy: -526.7999568

C	-0.57853	-0.00794	-0.00000
C	0.96424	-0.15202	-0.00000
O	1.45675	-1.23014	-0.00000
O	1.64365	0.98857	0.00000
F	-1.08899	-0.57922	-1.07554
F	-1.08899	-0.57922	1.07554
F	-0.95202	1.28500	-0.00000
H	1.05251	1.75332	-0.00000

XYZ coordinates of water

Energy: -76.40673701

H	0.00000	0.76080	-0.46656
O	0.00000	0.00000	0.11664
H	-0.00000	-0.76080	-0.46656

XYZ coordinates of gamma activated 1-methoxybutane by iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -1550.803125

N	-0.51701	-0.19520	1.42874
C	-1.47464	0.72509	1.10091
C	-1.13624	1.68105	0.10628
C	-0.81328	-1.09543	2.36392
H	-0.04249	-1.82077	2.59965
C	-2.75064	0.73818	1.68241
C	-2.05110	-1.13154	3.00684
C	-3.02580	-0.22565	2.66688
H	-4.00169	-0.24618	3.14236
C	0.45852	2.45686	-1.37312
H	1.47330	2.37991	-1.75016
C	-0.43779	3.39317	-1.89368
H	-0.11650	4.04775	-2.69495
C	-2.09159	2.60478	-0.33702
C	-1.70702	3.47312	-1.37352
H	-2.42178	4.19533	-1.75766
C	-3.38680	2.60105	0.26512
H	-4.12037	3.32273	-0.08099
C	-3.69849	1.71241	1.23978
H	-4.68491	1.71151	1.69320
H	-2.22633	-1.89092	3.75963
N	0.12351	1.62574	-0.39786
Ir	1.22065	-0.04238	0.40106
O	-1.19566	-0.33618	-2.18962
C	2.57704	-2.27261	-0.84205
H	3.05588	-3.26319	-0.83202
H	1.91389	-2.25701	-1.71585
C	3.64523	-1.22426	-0.99463
H	4.43759	-1.34406	-0.24296
H	4.11003	-1.21126	-1.98662
H	0.90765	-2.69867	0.45832
H	3.44406	-1.51588	1.78697
C	2.61913	-2.23281	1.69554
H	2.03119	-2.15021	2.61513
H	3.06952	-3.23685	1.69294
O	3.01932	0.06580	-0.78113
C	3.96895	1.10051	-0.51388
H	4.66947	1.16941	-1.35281
H	4.51852	0.87332	0.40828
H	3.42608	2.03989	-0.39011
C	1.77735	-2.03018	0.43584

H	-0.37546	-0.83690	-2.04805
C	-2.27007	-1.02519	-1.82219
C	-2.00204	-2.47275	-1.34197
O	-3.37250	-0.58536	-1.81315
F	-2.07004	-2.50389	-0.01017
F	-0.77609	-2.89038	-1.69167
F	-2.88773	-3.30316	-1.83501
H	2.21743	3.93560	1.28386
O	2.42949	3.96154	0.34741
H	2.83463	4.82162	0.20915

XYZ coordinates of alpha activated butyl acetate by iridium(II)(aqua)-1,10-phenanthroline trifluoroacetate

Energy: -1060.9454

N	0.71774	1.22075	-0.18455
C	2.05154	0.95404	-0.04689
C	2.43232	-0.40959	0.07844
C	0.34963	2.49044	-0.34568
H	-0.71233	2.67750	-0.46782
C	3.03147	1.95699	-0.03490
C	1.26506	3.54307	-0.35880
C	2.60440	3.28523	-0.19479
C	1.74503	-2.61579	0.12484
H	0.91495	-3.31447	0.06997
C	3.06200	-3.05234	0.29012
C	3.78138	-0.75808	0.23431
C	4.07852	-2.12757	0.34382
C	4.76210	0.28087	0.26372
H	5.80505	0.00579	0.38802
C	4.40146	1.58062	0.13070
H	5.15061	2.36635	0.14533
N	1.43773	-1.33007	0.02127
Ir	-0.50498	-0.41796	-0.16062
O	-3.37430	-0.67388	-0.14763
C	-2.92069	-1.87662	-0.14031
H	-2.53002	0.96148	-1.05171
H	-2.75903	0.64781	1.97358
C	-2.73969	1.29214	1.08499
H	-1.93409	2.01791	1.26787
O	-1.69607	-2.12754	-0.13836
C	-2.34627	0.43431	-0.09780
C	-3.93082	-2.95937	-0.13960
H	-3.44387	-3.93233	-0.16700
H	-4.55262	-2.87655	0.75559
H	-4.59142	-2.84377	-1.00241
C	-4.06150	2.03789	0.92653
H	-4.35495	2.43934	1.90328
H	-4.84905	1.32973	0.64167
C	-3.98297	3.17160	-0.08064
H	-3.22302	3.90632	0.21423
H	-3.73335	2.81638	-1.08754
H	-4.93389	3.70421	-0.16127
H	0.89863	4.55363	-0.49474
H	3.33383	4.08959	-0.19306
H	3.26436	-4.11384	0.36889
H	5.11073	-2.44260	0.46740

XYZ coordinates of iridium(III)-1,10-phenanthroline diacetate

Energy: -1132.264663

N	0.71873	-0.90314	-0.87923
C	1.75168	-0.05486	-0.63202
C	1.49061	1.11496	0.13466
C	0.94486	-2.03196	-1.54323

H	0.09197	-2.68612	-1.69631
C	3.05254	-0.32108	-1.07982
C	2.21150	-2.36807	-2.01702
C	3.26386	-1.51380	-1.79032
H	4.26133	-1.75404	-2.14657
C	-0.06225	2.36845	1.29759
H	-1.09438	2.47005	1.62526
C	0.90891	3.31813	1.63415
H	0.63054	4.17704	2.23326
C	2.52939	2.01191	0.42622
C	2.20048	3.13884	1.19936
H	2.97480	3.85837	1.44968
C	3.84380	1.73201	-0.05955
H	4.64059	2.43346	0.16814
C	4.09373	0.61233	-0.77967
H	5.09519	0.39691	-1.13911
H	2.34406	-3.29988	-2.55311
N	0.23153	1.30504	0.57517
Ir	-1.12802	-0.36936	-0.16036
O	-1.01456	-1.61984	1.32361
C	0.08583	-1.95398	2.03047
O	1.17251	-1.48487	1.81373
O	-3.08966	0.39340	0.12944
C	-2.99757	1.09403	-0.92328
O	-1.87356	1.02116	-1.54010
C	-4.10164	1.93005	-1.42609
H	-4.85072	2.08362	-0.64984
H	-3.71472	2.88228	-1.79361
H	-4.56957	1.41861	-2.27339
C	-0.24010	-2.95061	3.09205
H	-0.68375	-3.84248	2.64212
H	0.65892	-3.21480	3.64691
H	-0.99064	-2.53254	3.76807

XYZ coordinates of iridium(II)-1,10-phenanthroline acetate

Energy: -903.8018052

N	-0.96634	-1.31096	-0.00016
C	-1.98742	-0.41536	0.00025
C	-1.59168	0.93527	0.00004
C	-1.26221	-2.60859	-0.00006
H	-0.42362	-3.29856	-0.00040
C	-3.33623	-0.76988	0.00078
C	-2.58518	-3.05660	0.00046
C	-3.62103	-2.14842	0.00089
H	-4.65308	-2.48714	0.00130
C	0.19224	2.39997	-0.00087
H	1.26826	2.53894	-0.00135
C	-0.68890	3.48490	-0.00064
H	-0.27615	4.48666	-0.00095
C	-2.54059	1.95933	0.00034
C	-2.04915	3.27675	-0.00001
H	-2.73995	4.11448	0.00019
C	-3.92347	1.58794	0.00093
H	-4.66875	2.37729	0.00119
C	-4.30492	0.28379	0.00114
H	-5.35788	0.01973	0.00158
H	-2.77667	-4.12284	0.00052
N	-0.24760	1.14489	-0.00051
Ir	0.92721	-0.50118	-0.00072
O	2.78738	-0.47077	-0.00012

C	4.04857	0.06334	0.00129
O	4.99665	-0.64995	0.00199
C	4.04166	1.55831	0.00174
H	3.52186	1.92869	-0.88784
H	3.52023	1.92816	0.89057
H	5.06568	1.92961	0.00278

XYZ coordinates of the transition state for formation of iridium(II)-1,10-phenanthroline acetate

Energy: -1132.229623

Imaginary frequency: 583.21cm^{-1}

N	-1.00055	-1.24145	-0.25653
C	-2.13541	-0.51110	-0.06847
C	-1.98526	0.89380	0.08377
C	-1.10304	-2.55228	-0.43845
H	-0.17856	-3.09663	-0.60849
C	-3.41197	-1.08703	-0.04884
C	-2.34011	-3.20422	-0.42790
C	-3.49064	-2.48003	-0.23049
H	-4.46051	-2.96863	-0.21968
C	-0.52421	2.70060	0.14926
H	0.50775	3.03366	0.09032
C	-1.59382	3.58307	0.32166
H	-1.39160	4.64393	0.40764
C	-3.10738	1.71267	0.25624
C	-2.87790	3.09570	0.38010
H	-3.72038	3.76738	0.51727
C	-4.40036	1.10394	0.28787
H	-5.26810	1.74143	0.42637
C	-4.54561	-0.23707	0.14207
H	-5.53186	-0.69041	0.16197
H	-2.36893	-4.27660	-0.57963
N	-0.71813	1.39162	0.03831
Ir	0.71697	-0.06122	-0.24837
O	2.00841	-1.58570	-0.62603
C	2.18027	-2.10127	0.52526
O	2.70913	-3.04806	0.97362
C	1.29956	-1.08367	1.58684
H	0.76375	-0.05604	1.64867
H	0.60518	-1.76074	2.08625
H	2.19572	-0.72472	2.11153
O	2.15693	1.28814	-0.56149
C	3.35798	1.24977	0.00467
O	3.59861	0.56247	0.97133
C	4.35469	2.13442	-0.67121
H	3.89434	3.05547	-1.03235
H	5.17741	2.35255	0.00924
H	4.75477	1.60338	-1.54056

XYZ coordinates of the iridium(III)-1,10-phenanthroline di(acetylacetonate)

Energy: -1366.712947

H	-2.73195	-4.36400	-0.25301
C	-2.74532	-3.28395	-0.18637
H	-4.87004	-3.17936	0.17809
C	-3.95880	-2.60622	0.05833
N	-1.62425	-1.20970	-0.25271
C	-3.98702	-1.20036	0.14941
C	-1.55574	-2.55656	-0.34309
C	-2.78485	-0.50584	-0.01176
C	-5.16768	-0.47360	0.39671

H	-0.61266	-3.05139	-0.53165
C	-5.14633	0.93491	0.48626
H	-6.10899	-0.99422	0.52375
H	-6.06953	1.46639	0.67978
C	-3.94646	1.65198	0.33157
C	-3.87755	3.16102	0.42744
C	-2.76971	0.95662	0.08311
C	-2.51420	3.82160	0.25847
H	-4.78377	3.77044	0.62664
H	-2.43802	4.90151	0.33137
C	-1.40831	3.09137	0.02102
H	-0.43814	3.56161	-0.10006
N	-1.54319	1.68875	-0.07039
Ir	-0.27610	0.22994	-0.39491
O	0.16550	-0.39663	2.19183
C	1.20346	-0.14021	2.78201
C	2.07071	0.99844	2.30169
C	3.44961	0.57490	1.85414
O	3.78682	-0.59987	1.85713
C	1.56959	-0.93433	4.00338
C	4.41992	1.61563	1.38615
O	2.05118	-1.72983	-0.50723
C	3.01594	-1.50731	-1.22492
C	3.19300	-0.17108	-1.90369
C	2.06458	0.81926	-1.58893
O	0.83852	0.32464	-2.03927
C	4.04506	-2.57629	-1.42939
C	2.31598	2.19059	-2.20525
H	2.16524	1.73465	3.12792
H	0.79773	-1.70566	4.21238
H	1.63910	-0.25578	4.87886
H	2.54247	-1.44635	3.86531
H	4.61492	2.33861	2.20551
H	3.99669	2.15781	0.51637
H	5.38203	1.14968	1.08338
H	4.15590	0.26251	-1.55775
H	3.77635	-3.49517	-0.86573
H	5.03291	-2.21539	-1.07404
H	4.11415	-2.82628	-2.50875
H	2.36024	2.11645	-3.31278
H	3.27229	2.61023	-1.82967
H	1.49369	2.88028	-1.92123
H	1.57631	1.50254	1.44241
H	3.24827	-0.32757	-3.00291

XYZ coordinates of delta activation of 1-butanol by iridium(III)-1,10-phenanthroline di(acetylacetonate)

Energy: -1254.001723

N	-1.322245	-1.625881	-0.083662
C	-2.423427	-0.868287	0.097325
C	-2.242703	0.504222	0.458372
C	-1.459299	-2.880035	-0.474044
H	-0.542323	-3.446593	-0.615829
C	-3.723870	-1.386986	-0.030180
C	-2.712150	-3.463358	-0.692654
C	-3.843236	-2.719639	-0.455499
H	-4.832518	-3.149822	-0.589586
C	-0.784205	2.237936	0.945100
H	0.248490	2.563126	0.996697
C	-1.836595	3.065122	1.330359

H	-1.619287	4.062795	1.692470
C	-3.357763	1.287980	0.794098
C	-3.126802	2.601051	1.230775
H	-3.969516	3.229314	1.501344
C	-4.666096	0.720623	0.690351
H	-5.516520	1.343837	0.948028
C	-4.843374	-0.555983	0.277973
H	-5.841158	-0.978462	0.191748
H	-2.775607	-4.492114	-1.025876
N	-0.979427	1.007156	0.485220
Ir	0.559994	-0.203445	-0.110461
O	2.191140	2.123216	-0.589894
H	2.550986	2.487802	0.236363
O	1.383221	0.066581	1.734759
C	1.660230	3.167136	-1.405696
C	1.177092	2.591204	-2.708102
C	0.011637	1.615193	-2.614192
C	0.352107	0.217197	-2.134914
H	2.430379	3.925507	-1.592558
H	0.823009	3.662060	-0.887359
H	2.021436	2.110553	-3.220345
H	0.874272	3.435117	-3.340869
H	-0.404704	1.539069	-3.624137
H	-0.802757	2.053382	-2.018400
H	1.260991	-0.149828	-2.636887
H	-0.469777	-0.475804	-2.401723
C	2.558989	-0.572103	2.107076
C	3.606750	-0.603197	0.967570
C	3.247804	-1.541600	-0.130486
O	2.127426	-1.527883	-0.652794
C	3.151818	0.147304	3.303611
C	4.245389	-2.517096	-0.646518
H	2.348183	-1.622750	2.393123
H	4.595055	-0.848569	1.366350
H	3.661641	0.406573	0.532698
H	4.019667	-0.383888	3.707302
H	2.399311	0.231700	4.090139
H	3.461177	1.160088	3.018922
H	5.041328	-2.720516	0.075551
H	4.709009	-2.077136	-1.543705
H	3.753305	-3.444486	-0.957371

XYZ coordinates of iridium(III)-1,10-phenanthroline dibromide

Energy: -5823.702268

N	-0.70560	1.27443	-0.32698
C	-1.92261	0.67922	-0.18805
C	-1.92187	-0.68081	0.18782
C	-0.64987	2.53806	-0.74332
H	0.33526	2.97745	-0.84621
C	-3.12892	1.35483	-0.41081
C	-1.80924	3.26782	-1.01040
C	-3.04530	2.69157	-0.83405
C	-0.64716	-2.53838	0.74288
H	0.33842	-2.97676	0.84558
C	-1.80573	-3.26929	1.01022
C	-3.12745	-1.35765	0.41087
C	-3.04242	-2.69428	0.83412
C	-4.35183	-0.64959	0.20205
H	-5.28610	-1.17639	0.36940
C	-4.35252	0.64556	-0.20173

H	-5.28737	1.17141	-0.36888
N	-0.70424	-1.27481	0.32645
Ir	0.85748	0.00040	-0.00052
Br	2.05393	1.75380	1.05133
Br	2.05730	-1.75211	-1.05002
H	-1.71016	4.29484	-1.34111
H	-3.95430	3.25455	-1.02363
H	-1.70554	-4.29620	1.34093
H	-3.95081	-3.25815	1.02391

XYZ coordinates of delta activation of 1-butanol by iridium(III)-1,10-phenanthroline dibromide

Energy: -6057.21322

N	0.89863	-1.30329	-0.08934
C	2.12267	-0.70357	0.00959
C	2.17214	0.71803	0.13165
C	0.84693	-2.61610	-0.28709
H	-0.13892	-3.05005	-0.40752
C	3.31891	-1.43727	-0.04389
C	1.99302	-3.40987	-0.34924
C	3.22832	-2.82778	-0.21726
H	4.13595	-3.42238	-0.26200
C	0.99995	2.70072	0.20989
H	0.02815	3.18846	0.20217
C	2.18564	3.44055	0.28852
H	2.13801	4.52180	0.34220
C	3.41071	1.37527	0.20654
C	3.38869	2.77881	0.29092
H	4.32593	3.32476	0.34901
C	4.61153	0.60309	0.17807
H	5.56320	1.12173	0.24390
C	4.56556	-0.74533	0.05769
H	5.47963	-1.33030	0.02444
H	1.88383	-4.47603	-0.50785
N	0.99396	1.38213	0.14267
Ir	-0.69494	-0.03208	-0.04822
Br	-0.83347	-0.20552	2.55084
O	-2.15958	1.54309	-0.19904
H	-2.12646	1.72041	-1.15688
Br	-0.58859	0.21964	-2.50125
C	-3.54579	1.37550	0.18872
C	-4.15638	0.11840	-0.37476
C	-3.57698	-1.15047	0.23417
C	-2.17116	-1.50878	-0.22678
H	-4.07425	2.27671	-0.13735
H	-3.53797	1.36460	1.28319
H	-4.04229	0.10903	-1.46882
H	-5.23471	0.16795	-0.18016
H	-4.24444	-1.98954	-0.00518
H	-3.62041	-1.05157	1.33064
H	-2.20642	-1.82040	-1.27988
H	-1.84643	-2.39047	0.35083
H	-1.53358	-1.45272	2.69484

XYZ coordinates of gamma activation of 1-butanol by iridium(III)-1,10-phenanthroline dibromide

Energy: -6057.200635

N	-0.72525	1.26093	0.24195
C	-2.01600	0.78451	0.19217
C	-2.20292	-0.59398	-0.10524

C	-0.53363	2.58557	0.34943
H	0.48883	2.93484	0.28830
C	-3.13425	1.62557	0.36580
C	-1.60131	3.47861	0.51307
C	-2.89819	3.00434	0.54765
H	-3.73738	3.68002	0.68407
C	-1.21156	-2.62588	-0.65901
H	-0.29654	-3.18136	-0.83850
C	-2.46828	-3.24915	-0.73544
H	-2.52661	-4.30182	-0.98673
C	-3.50159	-1.13919	-0.17336
C	-3.61120	-2.50954	-0.49476
H	-4.59380	-2.96850	-0.55590
C	-4.62386	-0.28050	0.06350
H	-5.62182	-0.70699	0.01904
C	-4.44593	1.04783	0.31548
H	-5.30004	1.70069	0.47063
H	-1.38884	4.53720	0.60483
N	-1.08140	-1.33163	-0.35405
Ir	0.73675	-0.10849	-0.08993
Br	0.71017	-0.92695	2.45081
C	2.48068	1.03712	0.27504
C	2.56652	1.85577	1.56957
H	2.83798	1.22561	2.43018
H	3.36255	2.61110	1.49546
H	1.64456	2.39482	1.82500
C	3.67533	0.05822	0.24918
H	4.62281	0.60891	0.14567
H	3.73006	-0.48968	1.20274
C	3.54984	-0.93592	-0.86830
H	3.55532	-0.45408	-1.85349
H	4.28138	-1.74674	-0.82600
O	2.20167	-1.55038	-0.66985
H	1.91781	-2.03024	-1.47097
Br	0.76156	0.65670	-2.46523
H	2.57038	1.72189	-0.58370
H	1.10420	0.31410	3.09351

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-1,10-phenanthroline dibromide

Energy: -6057.203961

Imaginary frequency: 417.21cm^{-1}

N	0.90710	-1.30119	0.16197
C	2.12392	-0.68179	0.12642
C	2.15389	0.73158	-0.06171
C	0.86743	-2.62567	0.25667
H	-0.11419	-3.08512	0.23654
C	3.32792	-1.39473	0.23710
C	2.02210	-3.40120	0.36905
C	3.25110	-2.79063	0.37107
H	4.16440	-3.37154	0.45949
C	0.94883	2.66732	-0.39788
H	-0.03088	3.12571	-0.50743
C	2.12302	3.42716	-0.46123
H	2.05842	4.49644	-0.62454
C	3.38141	1.40939	-0.11533
C	3.33646	2.80005	-0.31999
H	4.26411	3.36301	-0.36872
C	4.59205	0.66515	0.02636
H	5.53651	1.19945	-0.01155

C	4.56479	-0.67918	0.19316
H	5.48683	-1.24418	0.28994
H	1.92473	-4.47718	0.44904
N	0.96638	1.36226	-0.20181
Ir	-0.69475	-0.05816	-0.06244
Br	-0.75184	0.41615	2.63807
O	-2.16554	1.44115	-0.52318
H	-2.19594	1.39783	-1.49544
Br	-0.62584	-0.37996	-2.49746
C	-3.52422	1.39306	-0.01539
C	-4.19003	0.06703	-0.27671
C	-3.59015	-1.08089	0.52222
C	-2.21501	-1.54012	0.05631
H	-4.06083	2.22526	-0.48132
H	-3.43659	1.60199	1.05522
H	-4.15617	-0.15613	-1.35382
H	-5.25076	0.18312	-0.02324
H	-4.27448	-1.93811	0.46498
H	-3.57699	-0.79480	1.58580
H	-2.29756	-1.97482	-0.94819
H	-1.89864	-2.36505	0.71555
H	-1.25798	-0.72994	1.84808

XYZ coordinates of the gamma transition state of 1-butanol by iridium(III)-1,10-phenanthroline dibromide

Energy: -6057.192159

Imaginary frequency: 592.08cm^{-1}

N	-0.73069	1.20489	0.51154
C	-2.01490	0.76491	0.29414
C	-2.18247	-0.55069	-0.21774
C	-0.53997	2.44818	0.98083
H	0.48662	2.76611	1.11866
C	-3.14010	1.56953	0.56169
C	-1.61515	3.29972	1.26842
C	-2.91205	2.86834	1.06240
H	-3.75592	3.51722	1.27742
C	-1.15242	-2.51617	-0.92229
H	-0.22561	-3.05747	-1.08400
C	-2.40145	-3.10703	-1.17862
H	-2.44289	-4.12209	-1.55610
C	-3.47256	-1.06634	-0.45131
C	-3.55825	-2.38498	-0.94939
H	-4.53333	-2.82113	-1.14658
C	-4.60637	-0.23459	-0.17370
H	-5.59963	-0.63339	-0.35858
C	-4.44532	1.03046	0.31074
H	-5.30799	1.65716	0.51741
H	-1.40939	4.29416	1.64638
N	-1.04781	-1.26873	-0.45916
Ir	0.73554	-0.08499	-0.03191
Br	0.74901	-1.19910	2.53484
C	2.47403	1.06389	0.45687
C	3.63536	0.04455	0.51351
H	4.60306	0.56815	0.54652
H	3.57900	-0.57417	1.42040
C	3.60832	-0.85740	-0.69136
H	3.75710	-0.30524	-1.62715
H	4.30427	-1.69752	-0.62828
Br	0.60005	0.73305	-2.38101
H	1.28010	0.11863	2.06105

H	2.36659	1.48295	1.48004
H	3.08916	1.92023	-1.46390
C	2.81169	2.24349	-0.45458
H	1.96999	2.93616	-0.57741
H	3.65750	2.81064	-0.03813
O	2.22917	-1.43167	-0.71780
H	2.01415	-1.79927	-1.59639

XYZ coordinates of delta activation of 1-methoxybutane by iridium(III)-1,10-phenanthroline dibromide

Energy: -6096.462941

N	0.99694	-1.28307	-0.18078
C	2.21004	-0.66446	-0.09238
C	2.23591	0.75031	0.09737
C	0.96621	-2.58893	-0.43219
H	-0.01143	-3.04333	-0.53076
C	3.41703	-1.37371	-0.22352
C	2.12195	-3.35631	-0.56958
C	3.34932	-2.75557	-0.45769
H	4.26693	-3.32674	-0.56227
C	1.06378	2.71474	0.26865
H	0.10248	3.21451	0.29993
C	2.24152	3.46887	0.29690
H	2.18093	4.54895	0.35963
C	3.47208	1.42131	0.12935
C	3.44839	2.82100	0.24342
H	4.38423	3.37159	0.27051
C	4.68345	0.67398	0.02424
H	5.62663	1.21013	0.06738
C	4.65627	-0.66859	-0.14186
H	5.57659	-1.23712	-0.23391
H	2.02499	-4.41669	-0.76940
N	1.04815	1.39511	0.19768
Ir	-0.65211	-0.11194	0.02582
Br	-0.69656	-0.53237	2.61238
O	-2.42095	1.12854	0.29726
Br	-0.60009	0.35422	-2.39586
C	-3.57632	1.09746	-0.58118
C	-3.86680	-0.29301	-1.09059
C	-3.46519	-1.37643	-0.10047
C	-1.98672	-1.70149	-0.20586
H	-3.40240	1.81089	-1.39713
H	-4.40776	1.46392	0.03558
H	-3.35106	-0.46525	-2.04116
H	-4.94061	-0.33444	-1.30225
H	-4.04094	-2.28673	-0.31282
H	-3.74366	-1.07689	0.92120
H	-1.67211	-1.58750	2.67357
C	-2.26100	2.42303	0.85447
H	-1.47509	2.37596	1.60931
H	-3.19638	2.73174	1.33285
H	-2.00423	3.14724	0.06965
H	-1.72809	-2.47890	0.53329
H	-1.80206	-2.13234	-1.20042

XYZ coordinates of gamma activation of 1-methoxybutane by iridium(III)-1,10-phenanthroline dibromide

Energy: -6096.468506

N	0.87372	-1.29756	-0.04509
C	2.12375	-0.75237	-0.03667

C	2.23792	0.66155	0.11118
C	0.75802	-2.61821	-0.15711
H	-0.24765	-3.01976	-0.15936
C	3.28160	-1.53830	-0.16543
C	1.86115	-3.46234	-0.27607
C	3.12429	-2.92703	-0.28885
H	4.00127	-3.55895	-0.39234
C	1.18567	2.68226	0.37975
H	0.25544	3.23014	0.48453
C	2.40487	3.36783	0.37737
H	2.40992	4.44638	0.48158
C	3.51008	1.25979	0.10290
C	3.56936	2.65623	0.24008
H	4.53446	3.15448	0.23335
C	4.67080	0.44143	-0.04380
H	5.64442	0.92200	-0.05103
C	4.56048	-0.90177	-0.16861
H	5.44296	-1.52488	-0.27648
H	1.69653	-4.52929	-0.36704
N	1.09355	1.37010	0.25723
Ir	-0.69620	-0.00638	0.04875
Br	-0.81613	-0.28769	2.64478
C	-3.54959	-0.74279	0.23819
H	-4.41578	-1.31867	-0.11471
H	-3.65199	-0.65232	1.32724
C	-3.59962	0.63464	-0.35121
H	-3.56593	0.62955	-1.44923
H	-4.46865	1.21308	-0.01871
Br	-0.48956	0.42729	-2.37905
H	-2.03060	-2.20854	0.60603
H	-2.75672	-1.44252	-2.26881
C	-2.38813	-2.12397	-1.49702
H	-1.45165	-2.53756	-1.88375
H	-3.10882	-2.94887	-1.41344
O	-2.41485	1.31248	0.13800
C	-2.33298	2.66600	-0.30446
H	-3.32989	3.11341	-0.26018
H	-1.93832	2.71582	-1.32471
H	-1.68550	3.20087	0.39076
C	-2.23786	-1.43162	-0.15240
H	-1.55761	-1.51479	2.76582

XYZ coordinates of the delta transition state of 1-methoxybutane by iridium(III)-1,10-phenanthroline dibromide

Energy: -6096.454089

Imaginary frequency: 330.58cm^{-1}

N	1.00419	-1.29272	-0.14691
C	2.20458	-0.64725	-0.09186
C	2.19756	0.77641	-0.00534
C	0.99509	-2.61189	-0.31004
H	0.02527	-3.08827	-0.38300
C	3.42524	-1.33870	-0.16290
C	2.16674	-3.36467	-0.38487
C	3.38234	-2.73491	-0.30212
H	4.31012	-3.29650	-0.35760
C	0.96959	2.71680	-0.00872
H	-0.00764	3.18655	-0.03532
C	2.12849	3.50007	-0.02496
H	2.04118	4.57979	-0.05098
C	3.41535	1.47815	-0.01252

C	3.35258	2.88162	-0.00936
H	4.27284	3.45852	-0.01430
C	4.64365	0.75123	-0.04934
H	5.57498	1.30916	-0.03543
C	4.64763	-0.60068	-0.11891
H	5.58166	-1.15248	-0.16044
H	2.09158	-4.43793	-0.51157
N	0.99399	1.39634	0.02855
Ir	-0.64895	-0.12333	0.01256
Br	-0.54258	-0.35105	2.76180
O	-2.40129	1.12418	0.29984
Br	-0.67262	0.15557	-2.42959
C	-3.60570	1.07155	-0.50707
C	-3.89827	-0.32045	-1.01001
C	-3.48271	-1.40599	-0.02732
C	-2.00864	-1.74802	-0.15230
H	-3.49763	1.79527	-1.32552
H	-4.40819	1.41351	0.16004
H	-3.40509	-0.49223	-1.97219
H	-4.97633	-0.36165	-1.19991
H	-4.06770	-2.31243	-0.22907
H	-3.74086	-1.10714	0.99968
H	-1.32176	-1.05157	1.70068
C	-2.27173	2.39040	0.93256
H	-1.40391	2.35617	1.59119
H	-3.16694	2.58882	1.53095
H	-2.16138	3.18357	0.18157
H	-1.76183	-2.54670	0.56825
H	-1.82543	-2.16746	-1.15072

XYZ coordinates of the gamma transition state of 1-methoxybutane by iridium(III)-1,10-phenanthroline dibromide

Energy: -6096.458331

Imaginary frequency: 243.27cm^{-1}

N	0.88183	-1.30219	0.15353
C	2.12451	-0.75362	0.04760
C	2.22119	0.66160	-0.08768
C	0.77513	-2.62180	0.28342
H	-0.22732	-3.02471	0.36015
C	3.28978	-1.53820	0.06828
C	1.88603	-3.46316	0.31890
C	3.14414	-2.92680	0.20849
H	4.02684	-3.55904	0.22709
C	1.14164	2.68113	-0.22799
H	0.20465	3.22642	-0.24123
C	2.35374	3.36868	-0.35194
H	2.34542	4.44707	-0.45734
C	3.48616	1.26225	-0.20541
C	3.52766	2.65968	-0.34085
H	4.48675	3.16027	-0.43712
C	4.65642	0.44446	-0.18565
H	5.62495	0.92619	-0.27926
C	4.56172	-0.89951	-0.05345
H	5.45165	-1.52110	-0.03791
H	1.73169	-4.52987	0.42780
N	1.06759	1.36953	-0.09568
Ir	-0.69886	-0.02117	0.04915
Br	-0.64049	0.38833	2.75351
C	-2.27054	-1.48426	0.15398

C	-3.55475	-0.71823	0.47591
H	-4.43760	-1.33963	0.27448
H	-3.59963	-0.43565	1.53547
C	-3.63042	0.53092	-0.34880
H	-3.64596	0.33221	-1.42902
H	-4.48280	1.16607	-0.08498
Br	-0.59602	-0.10315	-2.41392
H	-1.12982	-0.69394	1.81817
H	-2.06533	-2.14869	1.01211
H	-2.85718	-1.83740	-1.91964
C	-2.46611	-2.38216	-1.05661
H	-1.54577	-2.86844	-1.39376
H	-3.18816	-3.17165	-0.80866
O	-2.42506	1.27526	-0.03877
C	-2.37165	2.54885	-0.67683
H	-3.37415	2.98521	-0.68081
H	-1.99815	2.45477	-1.70243
H	-1.72301	3.18792	-0.07662

XYZ coordinates of alpha activation of butylacetate by iridium(III)-1,10-phenanthroline dibromide

Energy: -6209.824987

N	0.84964	1.31279	-0.07829
C	2.18229	1.03397	-0.01206
C	2.56823	-0.33650	0.00103
C	0.47072	2.58523	-0.12125
H	-0.59653	2.77370	-0.17915
C	3.16222	2.03650	0.04348
C	1.38445	3.63957	-0.08631
C	2.72830	3.37121	0.00566
C	1.87719	-2.53510	-0.02801
H	1.04194	-3.22918	-0.06702
C	3.19917	-2.98154	0.08217
H	3.39863	-4.04581	0.12193
C	3.92075	-0.69010	0.10441
C	4.21955	-2.06343	0.14153
C	4.90085	0.34765	0.17195
H	5.94697	0.06767	0.25112
C	4.53673	1.65279	0.13765
H	5.28572	2.43732	0.18599
H	1.01344	4.65685	-0.12217
N	1.57502	-1.24969	-0.08264
Ir	-0.38855	-0.32059	-0.06857
Br	-0.53910	-0.23315	-2.69951
Br	-0.24798	-0.40277	2.39612
H	-2.83186	0.84462	2.05583
C	-2.71321	1.44068	1.14579
H	-1.89876	2.14267	1.37234
C	-2.27701	0.51874	0.02792
H	-1.56450	0.76423	-2.84896
C	-3.98501	2.22386	0.83075
H	-4.38648	2.63483	1.76384
H	-4.75314	1.53848	0.45019
C	-3.75374	3.35786	-0.15316
H	-3.03790	4.08475	0.25047
H	-3.36049	3.00226	-1.11469
H	-4.67730	3.89945	-0.37320
O	-3.26092	-0.62644	0.07197
C	-2.78047	-1.81989	0.05114
O	-1.55794	-2.04806	-0.05063

C	-3.75801	-2.92553	0.17227
H	-3.98932	-3.06185	1.23355
H	-3.33057	-3.85099	-0.21114
H	-4.68716	-2.67857	-0.34226
H	-2.53752	0.99007	-0.93585
H	3.45754	4.17481	0.04792
H	5.25383	-2.38442	0.22528

XYZ coordinates of the alpha transition state of butylacetate by iridium(III)-1,10-phenanthroline dibromide

Energy: -6209.806059

Imaginary frequency: 160.85cm^{-1}

N	-0.87551	1.36564	0.26002
C	-2.20204	1.05451	0.09640
C	-2.52774	-0.30632	-0.13284
C	-0.52358	2.63925	0.47938
H	0.53510	2.84257	0.60330
C	-3.21780	2.02865	0.14652
C	-1.48185	3.66045	0.54430
C	-2.82246	3.36366	0.37774
C	-1.71179	-2.48276	-0.36948
H	-0.83860	-3.12756	-0.38487
C	-3.01941	-2.96457	-0.55708
H	-3.17442	-4.02413	-0.72257
C	-3.86282	-0.70915	-0.31164
C	-4.08873	-2.08674	-0.53034
C	-4.88701	0.29315	-0.25911
H	-5.92000	-0.01234	-0.39760
C	-4.57654	1.60468	-0.03924
H	-5.35872	2.35710	-0.00044
H	-1.15314	4.67675	0.72574
N	-1.48777	-1.18422	-0.16399
Ir	0.39611	-0.23913	0.08103
Br	0.28599	-0.95765	2.64858
Br	0.34275	0.16964	-2.40204
H	2.89132	1.20996	-1.82961
C	2.84126	1.61793	-0.81440
H	2.06784	2.40167	-0.85199
C	2.38755	0.52233	0.12929
H	0.80609	0.40382	1.54302
C	4.18339	2.23473	-0.39788
H	4.58235	2.80939	-1.24362
H	4.90408	1.42699	-0.20681
C	4.06585	3.14436	0.82264
H	3.40191	3.99479	0.61403
H	3.67038	2.61424	1.70074
H	5.03998	3.55260	1.11175
O	3.28689	-0.68758	-0.20284
C	2.72431	-1.85432	-0.36621
O	1.45403	-1.98741	-0.26099
C	3.59015	-3.01064	-0.67371
H	4.63075	-2.70176	-0.76284
H	3.25736	-3.47485	-1.60811
H	3.48933	-3.76432	0.11418
H	2.72993	0.74343	1.15047
H	-3.57352	4.14665	0.42489
H	-5.10304	-2.44708	-0.67597

XYZ coordinates of iridium(III)-1,10-phenanthroline dimethoxide

Energy: -905.5470535

H	-1.36737	4.47481	-0.04715
C	-1.48914	3.39847	-0.06876
H	-3.63058	3.44093	0.05172
C	-2.73905	2.82426	-0.01324
N	-0.43314	1.27151	-0.18250
C	-2.85332	1.42341	-0.03007
C	-0.34708	2.59455	-0.14820
C	-1.66045	0.70302	-0.11459
C	-4.07476	0.67947	0.04462
H	0.65168	3.01874	-0.18015
C	-4.07476	-0.67946	0.04462
H	-5.00994	1.22731	0.10803
H	-5.00994	-1.22727	0.10803
C	-2.85332	-1.42340	-0.03007
C	-2.73906	-2.82425	-0.01324
C	-1.66045	-0.70302	-0.11460
C	-1.48916	-3.39847	-0.06876
H	-3.63060	-3.44092	0.05172
H	-1.36739	-4.47480	-0.04716
C	-0.34709	-2.59456	-0.14820
H	0.65167	-3.01875	-0.18015
N	-0.43315	-1.27151	-0.18250
Ir	1.19935	-0.00000	-0.20362
O	3.08994	-0.00000	-0.17399
C	3.78446	0.00001	-1.39722
H	4.41859	0.89075	-1.45719
H	3.09945	-0.00000	-2.26510
H	4.41860	-0.89074	-1.45719
O	1.13201	-0.00002	1.77983
C	2.33941	-0.00000	2.48446
H	2.03695	-0.00002	3.54120
H	2.95002	0.89257	2.29998
H	2.95005	-0.89254	2.29996

XYZ coordinates of delta activation of 1-butanol by iridium(III)-1,10-phenanthroline dimethoxide

Energy: -1139.093268

N	0.75520	-1.28409	0.05371
C	1.98025	-0.67028	0.02098
C	2.01544	0.75582	-0.00215
C	0.71824	-2.61450	0.04351
H	-0.26542	-3.07052	0.04259
C	3.18184	-1.39552	-0.01240
C	1.87075	-3.40035	0.01477
C	3.10358	-2.79795	-0.01134
H	4.01533	-3.38724	-0.03885
C	0.81992	2.72401	-0.02812
H	-0.15805	3.19873	-0.02391
C	1.99775	3.47939	-0.08682
H	1.93667	4.56061	-0.12751
C	3.24681	1.42895	-0.05578
C	3.20961	2.83381	-0.09640
H	4.14023	3.39231	-0.14162
C	4.45545	0.66817	-0.07809
H	5.40219	1.19859	-0.11929
C	4.42273	-0.68576	-0.05649
H	5.34201	-1.26321	-0.07933
H	1.76890	-4.47911	0.00608
N	0.82891	1.40449	0.02416
Ir	-0.84669	-0.02240	-0.00654

O	-2.28955	1.51498	-0.36505
H	-2.23446	1.43964	-1.34284
C	-3.66114	1.44343	0.07117
C	-4.32071	0.14094	-0.30268
C	-3.71472	-1.06357	0.40267
C	-2.33992	-1.47104	-0.11328
H	-4.18031	2.30589	-0.35957
H	-3.62603	1.57587	1.15749
H	-4.27137	0.00408	-1.39349
H	-5.38484	0.23049	-0.05245
H	-4.40118	-1.91446	0.29314
H	-3.68918	-0.85022	1.48412
H	-2.43439	-1.76792	-1.16790
H	-2.02969	-2.37464	0.43938
H	-1.54860	-0.97636	2.41850
O	-1.09209	-0.16010	2.18361
C	-0.00969	0.08535	3.08627
H	-0.37624	0.07931	4.11518
H	0.37900	1.07597	2.85042
H	0.78319	-0.66050	2.96683
O	-0.87290	0.26549	-1.98851
C	-0.36786	-0.70641	-2.84345
H	-0.58023	-0.40275	-3.87588
H	-0.82171	-1.70056	-2.69141
H	0.72720	-0.82167	-2.75571

XYZ coordinates of gamma activation of 1-butanol by iridium(III)-1,10-phenanthroline dimethoxide

Energy: -1139.088928

N	-0.59640	1.26957	0.07913
C	-1.87568	0.78033	0.01673
C	-2.05061	-0.63439	0.03524
C	-0.43823	2.59079	0.09868
H	0.58099	2.94975	0.14699
C	-3.00103	1.61567	-0.06563
C	-1.50861	3.48380	0.03509
C	-2.79025	3.00421	-0.05900
H	-3.63966	3.67763	-0.12518
C	-1.04142	-2.69816	0.16181
H	-0.11361	-3.25978	0.24313
C	-2.27983	-3.34642	0.08257
H	-2.31746	-4.42930	0.09982
C	-3.33658	-1.19295	-0.04274
C	-3.42613	-2.59574	-0.01871
H	-4.40080	-3.07128	-0.08310
C	-4.46385	-0.32116	-0.14287
H	-5.45511	-0.75940	-0.21136
C	-4.30073	1.02366	-0.15005
H	-5.15956	1.68430	-0.22201
H	-1.30265	4.54775	0.04878
N	-0.93193	-1.38232	0.14275
Ir	0.88126	-0.14197	-0.01331
C	2.69112	0.89734	-0.29294
C	2.90985	2.26833	0.31747
H	2.58727	2.34714	1.36814
H	3.97463	2.53869	0.31083
H	2.40059	3.06018	-0.24095
C	3.77080	-0.07529	0.19479
H	4.77653	0.31527	-0.01893
H	3.72127	-0.21234	1.28515

C	3.60641	-1.39854	-0.49114
H	3.83383	-1.31035	-1.55941
H	4.20519	-2.20346	-0.05976
O	2.20116	-1.78407	-0.36478
H	1.86907	-1.96072	-1.26672
H	2.80401	0.98674	-1.38449
H	1.76370	0.77989	2.38993
O	1.25168	-0.00441	2.16102
C	0.18881	-0.19209	3.10010
H	0.58819	-0.19285	4.11672
H	-0.25209	-1.16572	2.88699
H	-0.57300	0.58783	2.99613
O	0.69994	-0.49772	-1.97620
C	0.44747	0.55265	-2.85263
H	1.18480	1.37073	-2.78000
H	-0.55473	0.99442	-2.71248
H	0.48859	0.16326	-3.87751

XYZ coordinates of the delta transition state of 1-butanol by iridium(III)-1,10-phenanthroline dimethoxide

Energy: -1139.051975

Imaginary frequency: 1588.19cm^{-1}

N	-0.80033	-1.26577	0.07139
C	-2.01443	-0.64868	0.00047
C	-2.00407	0.76474	-0.09538
C	-0.77038	-2.58693	0.21020
H	0.20972	-3.04730	0.28041
C	-3.22844	-1.34546	0.04409
C	-1.93552	-3.35390	0.26345
C	-3.16388	-2.74243	0.17510
H	-4.08041	-3.32357	0.21250
C	-0.71195	2.68059	-0.16569
H	0.28523	3.10915	-0.15928
C	-1.86172	3.47353	-0.24070
H	-1.75365	4.55036	-0.29366
C	-3.20252	1.48369	-0.16331
C	-3.10346	2.88375	-0.24215
H	-4.00606	3.48494	-0.29798
C	-4.43328	0.75549	-0.13777
H	-5.36379	1.31207	-0.19482
C	-4.44527	-0.59716	-0.03659
H	-5.38511	-1.14005	-0.01028
H	-1.84955	-4.42820	0.37473
N	-0.78406	1.35959	-0.10387
Ir	0.76831	0.02276	0.01933
O	2.21616	1.56630	0.18276
H	2.22174	1.60883	1.16365
C	3.56043	1.42441	-0.33686
C	4.31165	0.26922	0.28484
C	3.92481	-1.10608	-0.23969
C	2.48982	-1.52255	0.07044
H	4.06478	2.37724	-0.14966
H	3.43581	1.30271	-1.41679
H	4.19594	0.31140	1.37890
H	5.37802	0.43451	0.09111
H	4.60854	-1.84823	0.18924
H	4.09261	-1.13090	-1.32485
H	2.31587	-2.57319	-0.20263
O	1.26545	-0.35779	-2.00087
C	0.36590	-1.04074	-2.82961

H	0.78726	-1.09920	-3.83935
H	-0.59977	-0.51762	-2.89474
H	0.17142	-2.07130	-2.48953
O	0.86113	0.48757	1.99791
C	0.23808	-0.31261	2.94490
H	0.47289	0.07126	3.94565
H	0.57328	-1.36599	2.91307
H	-0.86242	-0.31365	2.84749
H	2.30105	-1.46944	1.15031
H	1.88136	-1.08526	-1.00703

XYZ coordinates of delta activation of 1-methoxybutane by iridium(III)-1,10-phenanthroline dimethoxide

Energy: -1178.342156

N	0.87725	-1.27349	0.11858
C	2.07501	-0.62293	-0.00371
C	2.05801	0.80183	-0.08044
C	0.88658	-2.60480	0.19051
H	-0.07785	-3.09086	0.27838
C	3.29584	-1.31408	-0.08224
C	2.06024	-3.35388	0.13226
C	3.26723	-2.71584	-0.01118
H	4.19567	-3.27549	-0.07294
C	0.81913	2.73259	-0.12213
H	-0.15962	3.19918	-0.07888
C	1.96333	3.51398	-0.31916
H	1.86454	4.58817	-0.42303
C	3.26398	1.50234	-0.26133
C	3.18893	2.90028	-0.37662
H	4.09906	3.47530	-0.52099
C	4.49215	0.77766	-0.33394
H	5.41421	1.33508	-0.46924
C	4.50705	-0.57287	-0.24282
H	5.44090	-1.12369	-0.30104
H	1.99488	-4.43396	0.19015
N	0.85670	1.41946	0.01506
Ir	-0.78458	-0.12238	0.10759
O	-2.53753	1.12856	0.15266
C	-3.57482	1.03302	-0.84963
C	-3.81418	-0.40598	-1.24291
C	-3.58919	-1.36376	-0.07809
C	-2.11834	-1.71869	0.08043
H	-3.28801	1.65907	-1.70334
H	-4.47194	1.45863	-0.37905
H	-3.15663	-0.67753	-2.07473
H	-4.84391	-0.47202	-1.61037
H	-4.16424	-2.28307	-0.24814
H	-3.99113	-0.92566	0.84725
H	-1.51793	-0.97484	2.56335
C	-2.49864	2.40261	0.76958
H	-1.70854	2.38942	1.52227
H	-3.45806	2.60152	1.25938
H	-2.31072	3.18851	0.02605
H	-1.98912	-2.32516	0.99810
H	-1.83060	-2.37111	-0.75688
O	-1.02252	-0.18752	2.30537
C	0.09500	0.01566	3.17321
H	0.51859	0.98754	2.91542
H	0.85359	-0.76125	3.03172
H	-0.23581	0.03055	4.21420

O	-0.79607	0.14024	-1.87145
C	-0.30410	-0.85112	-2.70761
H	-0.45696	-0.52540	-3.74503
H	-0.81587	-1.82388	-2.59412
H	0.77995	-1.03388	-2.58589

XYZ coordinates of gamma activation of 1-methoxybutane by iridium(III)-1,10-phenanthroline dimethoxide

Energy: -1178.344988

N	0.85242	-1.30753	0.22259
C	2.07229	-0.71819	0.08070
C	2.12620	0.70598	0.01309
C	0.79650	-2.63120	0.34098
H	-0.18835	-3.06854	0.45020
C	3.26045	-1.46626	0.03039
C	1.93258	-3.43733	0.31332
C	3.16676	-2.86087	0.14758
H	4.06872	-3.46413	0.10909
C	1.00338	2.70392	0.08310
H	0.05579	3.22777	0.16557
C	2.18851	3.43035	-0.05778
H	2.15212	4.51311	-0.08292
C	3.37065	1.34762	-0.12462
C	3.37624	2.75016	-0.16571
H	4.31814	3.27934	-0.27844
C	4.56148	0.56293	-0.20712
H	5.51110	1.07599	-0.32498
C	4.50780	-0.78664	-0.12886
H	5.41354	-1.38320	-0.18093
H	1.81705	-4.51030	0.41203
N	0.95801	1.38268	0.11723
Ir	-0.75783	-0.09213	0.08178
C	-3.57907	-0.97166	0.21577
H	-4.38668	-1.63081	-0.13134
H	-3.75071	-0.81114	1.29008
C	-3.69274	0.35546	-0.47232
H	-3.63584	0.27449	-1.56650
H	-4.60391	0.90242	-0.20354
H	-2.01290	-2.32045	0.76093
H	-2.48457	-1.69600	-2.20799
C	-2.20414	-2.34590	-1.37320
H	-1.22078	-2.74753	-1.63219
H	-2.91872	-3.18004	-1.34231
O	-2.56085	1.13031	-0.00820
C	-2.62080	2.50010	-0.37926
H	-3.61883	2.88868	-0.15301
H	-2.40361	2.63443	-1.44415
H	-1.89179	3.03853	0.22764
C	-2.20405	-1.59620	-0.05274
H	-1.71537	-0.82135	2.52560
O	-0.33977	-0.19988	-1.88161
C	-0.76878	0.82684	-2.69599
H	-0.37134	0.65373	-3.70563
H	-0.41120	1.82655	-2.37968
H	-1.87142	0.88318	-2.79917
O	-1.06869	-0.15047	2.27803
C	-1.33668	1.06808	2.97681
H	-1.35131	0.88656	4.05402
H	-2.28623	1.50533	2.65220
H	-0.51806	1.74841	2.73926

XYZ coordinates of alpha activation of butyl acetate by iridium(III)-1,10-phenanthroline dimethoxide

Energy: -1291.710676

N	-0.79353	1.31015	0.27068
C	-2.11181	1.04500	0.05403
C	-2.49207	-0.31851	-0.10819
C	-0.42575	2.56847	0.48237
H	0.63056	2.74404	0.65736
C	-3.08664	2.05244	0.01264
C	-1.33701	3.62515	0.47271
C	-2.66494	3.37418	0.22682
C	-1.82099	-2.52144	-0.14538
H	-0.99756	-3.22807	-0.06830
C	-3.12992	-2.95006	-0.38942
C	-3.83455	-0.65402	-0.34000
C	-4.13640	-2.01852	-0.48534
C	-4.80622	0.39219	-0.40920
H	-5.84190	0.12537	-0.59708
C	-4.44746	1.68706	-0.23510
H	-5.19057	2.47756	-0.27862
N	-1.51179	-1.24363	-0.00350
Ir	0.44661	-0.29956	0.12751
O	3.32691	-0.51423	0.07499
C	2.88916	-1.71816	-0.03397
H	2.52343	1.08879	1.06355
H	2.67244	0.89503	-1.96199
C	2.64254	1.50129	-1.04964
H	1.80911	2.19917	-1.21006
O	1.67059	-1.99449	-0.01778
C	2.28208	0.59658	0.10442
H	1.55649	-0.30094	2.64310
C	3.90909	-2.77880	-0.20877
H	3.51684	-3.74124	0.11798
H	4.14410	-2.84857	-1.27649
H	4.82948	-2.52758	0.31884
C	3.94030	2.28116	-0.86149
H	4.24097	2.70030	-1.82853
H	4.74441	1.59408	-0.56881
C	3.81567	3.40640	0.15146
H	3.05008	4.12822	-0.15917
H	3.54339	3.04020	1.14918
H	4.75407	3.95592	0.26281
H	-5.16204	-2.32317	-0.67292
H	-3.39132	4.18103	0.20024
O	0.65662	-0.46073	2.33671
C	0.10863	-1.61146	2.99146
H	0.29769	-1.55514	4.06564
H	0.53049	-2.53258	2.57742
H	-0.96671	-1.59038	2.81469
O	0.20711	-0.02578	-1.84479
C	0.63915	-1.04835	-2.67385
H	0.32577	-0.80596	-3.69794
H	0.21029	-2.03444	-2.42088
H	1.74057	-1.16580	-2.69306
H	-0.97655	4.63142	0.64980
H	-3.33201	-4.00876	-0.50168

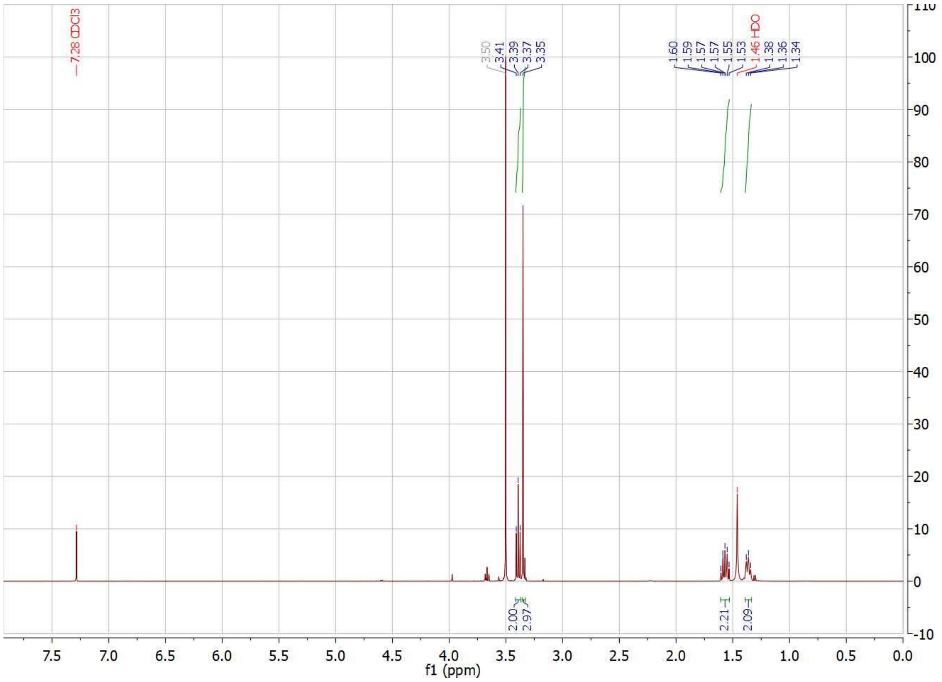
Appendix B3 – Computational data for chapter 5

Ir(III)-DPPP complex and methoxybutane

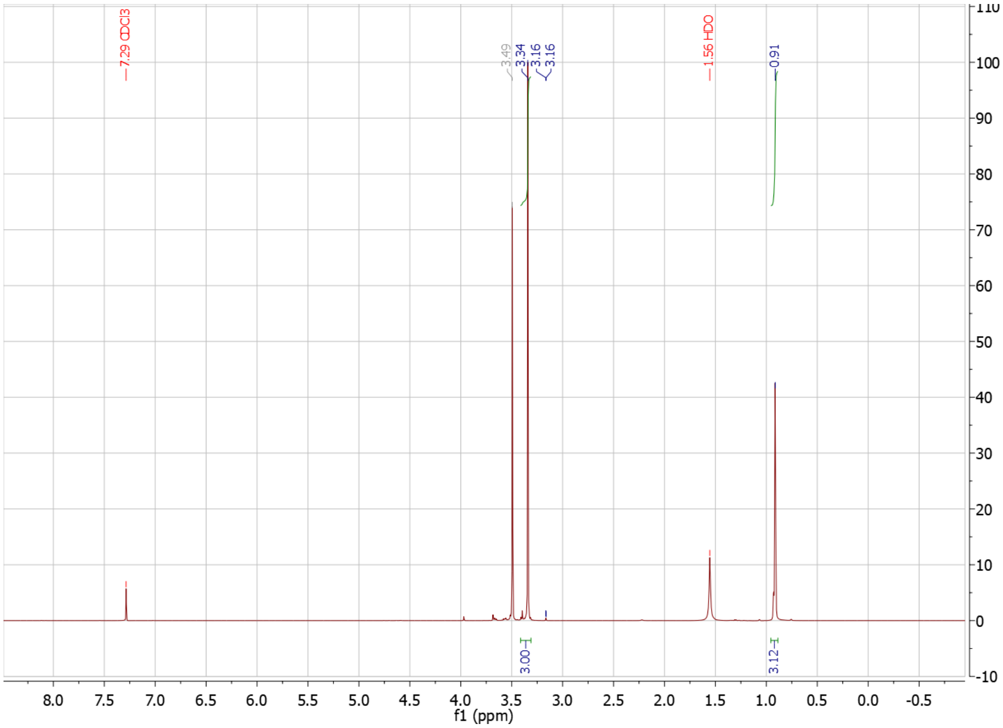
Energy: -2257.433403

Ir	0.07096	-0.09490	-0.21631
P	1.19707	1.38532	1.01094
P	1.78371	-1.58247	-0.15740
C	2.99005	1.04765	1.14435
C	3.63551	0.61481	-0.16810
C	3.43724	-0.86031	-0.51298
C	1.51196	-2.85628	-1.41719
C	1.98086	-2.50953	1.39114
C	0.60180	1.54202	2.71125
C	1.04685	3.03994	0.29141
Cl	0.90814	0.62404	-2.32407
Cl	-0.99630	-1.18884	1.59714
H	3.42769	1.98807	1.50575
H	3.14435	0.30964	1.94238
H	3.25764	1.23085	-0.99141
H	4.71085	0.81046	-0.11446
H	3.62143	-1.01418	-1.58153
H	4.15651	-1.48536	0.03258
H	1.43952	-2.39147	-2.40323
H	0.58198	-3.38855	-1.19567
H	2.34197	-3.57104	-1.40397
H	2.10333	-1.83629	2.24330
H	2.86010	-3.15690	1.30753
H	1.08990	-3.11431	1.57047
H	0.69243	0.58964	3.23771
H	-0.45174	1.83339	2.70412
H	1.19202	2.31380	3.21861
H	-0.01225	3.30096	0.22563
H	1.48104	3.06075	-0.71047
H	1.55834	3.75924	0.94047
O	-1.70416	1.33852	-0.42339
C	-1.94238	1.98928	-1.67722
H	-2.28976	1.27678	-2.43159
H	-1.00594	2.42806	-2.01774
H	-2.69329	2.77193	-1.52992
C	-2.92809	1.06763	0.29817
C	-3.77028	-0.00925	-0.33971
C	-4.90223	-0.43579	0.58314
C	-5.79312	-1.48645	-0.05158
H	-3.47535	2.01733	0.37149
H	-2.62124	0.76638	1.30239
H	-3.13169	-0.87813	-0.56084
H	-4.18608	0.33578	-1.29615
H	-5.49987	0.44451	0.85859
H	-4.47319	-0.81974	1.51887
H	-6.25734	-1.10970	-0.96936
H	-6.59586	-1.79510	0.62242
H	-5.21851	-2.38125	-0.31481

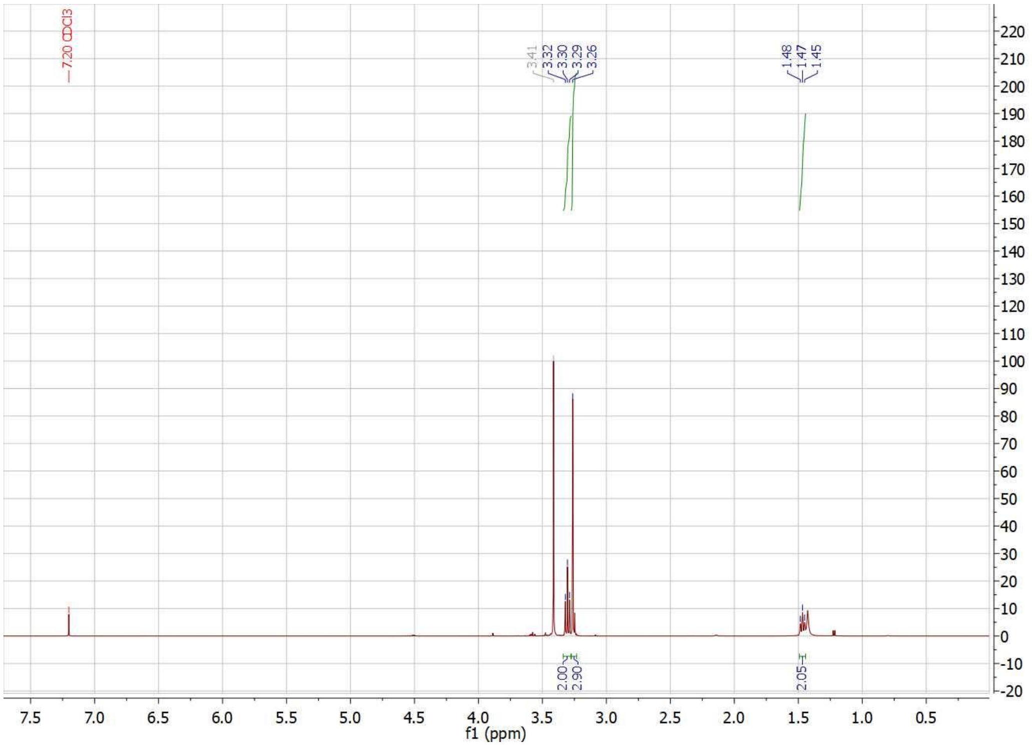
Appendix C – NMR



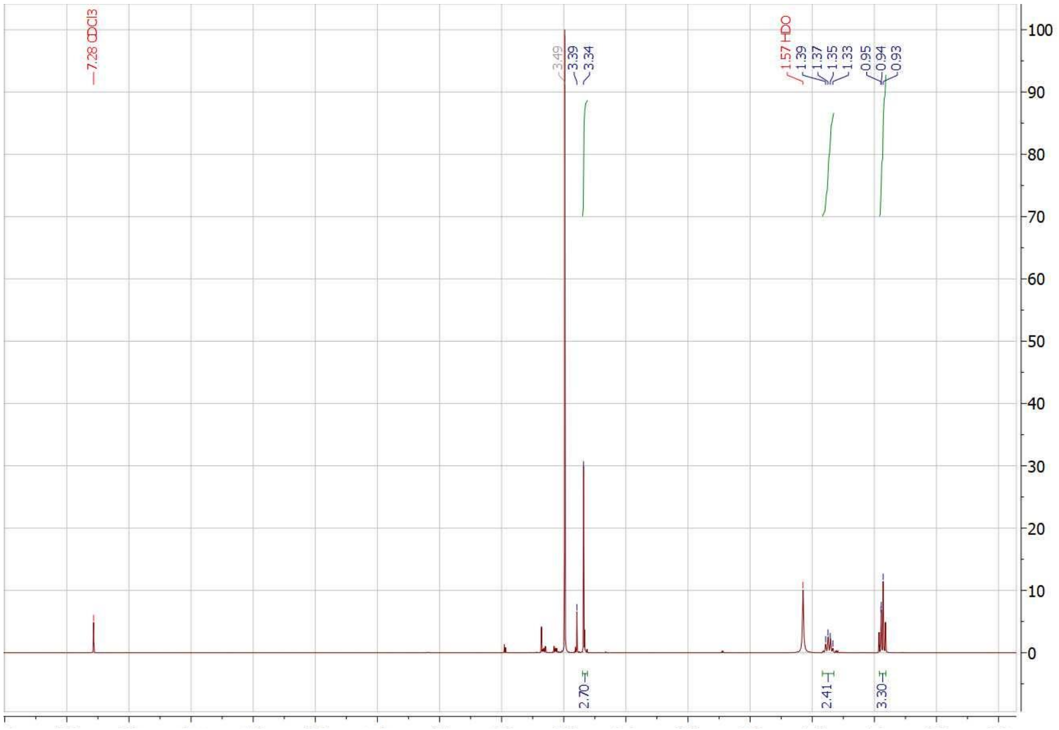
A 101 1H NMR of 1,1,2,2-d_4 1-methoxybutane in $CDCl_3$



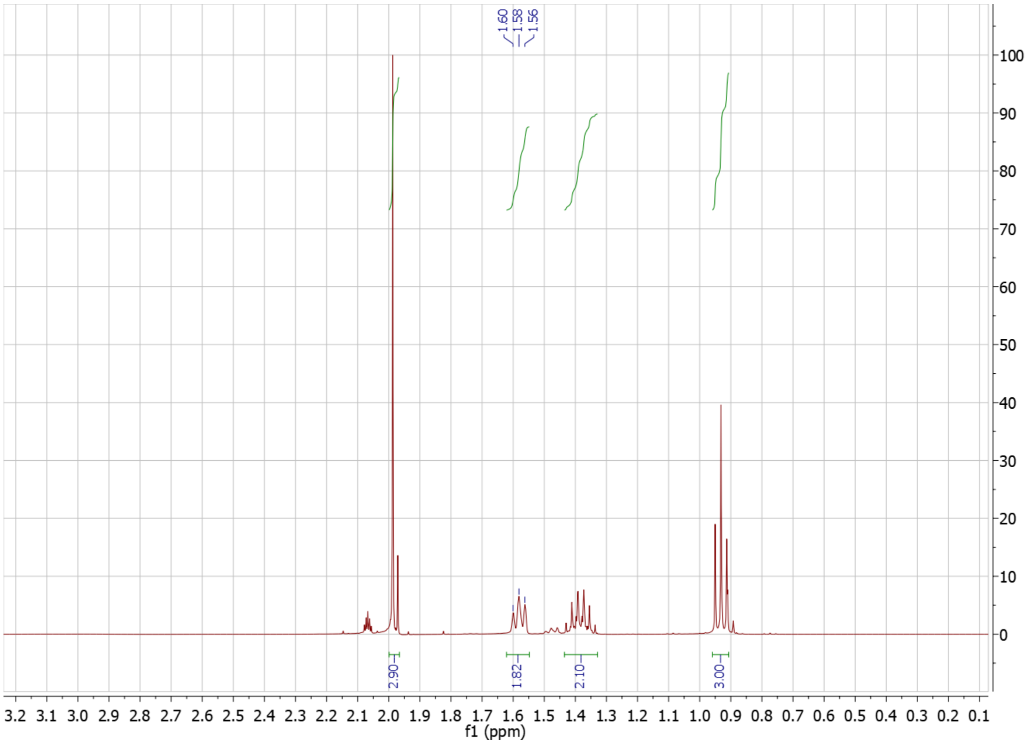
A 102 1H NMR of 1,1,2,2,3,3-d_6 1-methoxybutane in $CDCl_3$



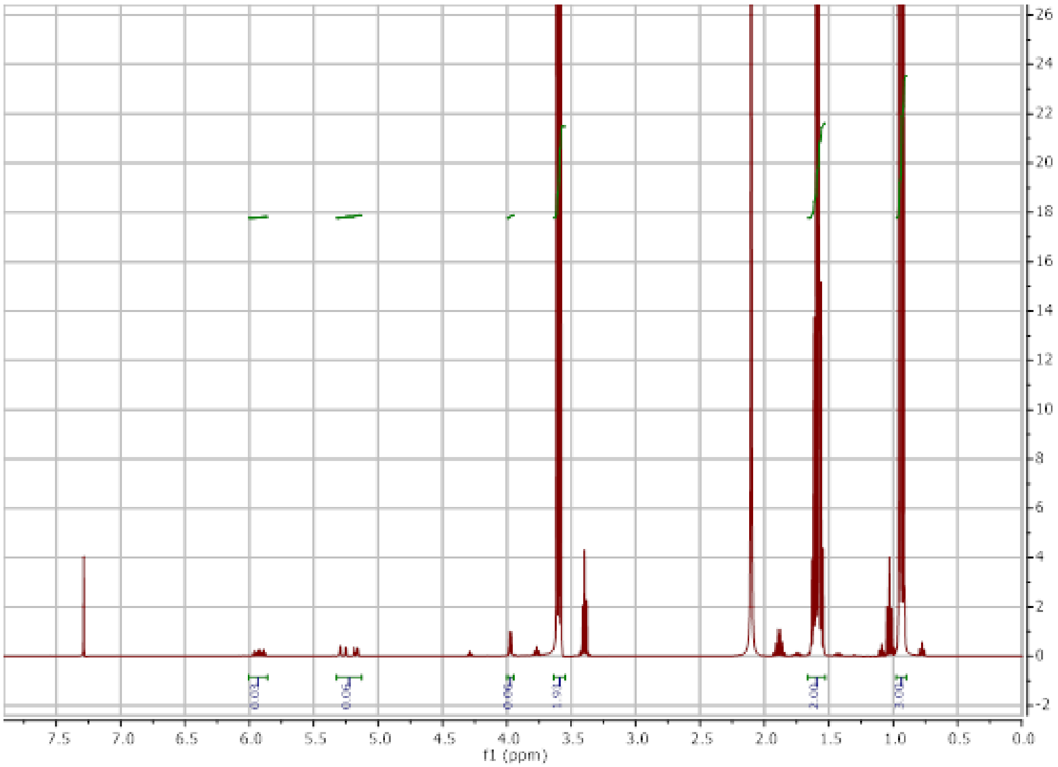
A 103 1H NMR of 3,3,4,4-d5 1-methoxybutane in $CDCl_3$



A 104 1H NMR of 4,4,4-d_3 1-methoxybutane in $CDCl_3$



A 105 1H NMR of 1,1-d_2 butyl acetate in acetone-d_6



A 106 1H NMR of allyl propyl ether in $CDCl_3$ Product distributions showing the regioselectivity of C-H activation of alcohols, ethers and esters by complex **M'**