TRANSITION METAL CATALYZED GREENER APPROACH FOR THE SYNTHESIS OF ARYL KETONES AND AMIDES

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Candidate’s Declaration

I, **Munsaf Ali,** declare that this thesis titled **“TRANSITION METAL CATALYZED GREENER APPROACH FOR THE SYNTHESIS OF ARYL KETONES AND AMIDES”** and the work presented in it, are my own. I confirm that:

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This is to certify that the work incorporated in the thesis entitled "**TRANSITION METAL CATALYZED GREENER APPROACH FOR THE SYNTHESIS OF ARYL KETONES AND AMIDES**" which is being submitted to the Malaviya National Institute of Technology Jaipur, Jaipur, Rajasthan, for the award of the degree of **Doctor of Philosophy** in Chemistry by **Munsaf Ali** was carried out under my supervision at Department of Chemistry, Malaviya National Institute of Technology Jaipur. The matter embodied in this thesis is original and has not been submitted to any other university or institute for the award of any other degree.

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Abstract

Cost effective, greener and facile synthetic methods for the synthesis of amides and ketones have been devised with adopting various techniques including the thermal, photochemical and high pressure autoclave methods. In this thesis, we have demonstrated a much economical and green strategy for the hydration of terminal and internal alkynes. A ferrocene containing Schiff base water-soluble rhodium (I) catalyst was synthesised and used for alkyne hydration in photochemical conditions. The formation of the desired ketone was obtained in a very short time (20-30 minute) under UV irradiation. Moreover, water insoluble ironchalcogenidecarbonyl complexes ($Fe_3E_2(CO)_9$ (E=S, Se, Te)) were also explored for the hydration of alkynes and highly significant results were obtained than previously reported. Both the complexes Rh(I) and $Fe_3(E_2(CO)_9$ were isolated and reused further without any further activation. Here, the catalytic reactions were conducted under aqueous and aerobic conditions. Moreover, a highly economic autoclave method for the hydration of alkynes was also discovered. This method simply works without a metal/catalyst/reagent at 11 bar pressure of nitrogen and 150 °C. Apart from, the three new, novel, robust, air and water insensitive Chalcogen functionalized pyrazole-based Ru(II) half-sandwich complexes containing the S, Se and Te Chalcogen donor sites were designed and synthesised. All the complexes were characterized by the ^1H, ^{13}C NMR, mass and FT-IR analytical techniques. Moreover, and single crystal X-ray diffraction analysis of these complexes was also conducted and reveals the pseudo-octahedral half sandwich piano-stool geometry at Ru centre. The complexes were found to be highly efficient for the catalytic conversion of aldehyde to primary amide in high yield.

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LIST OF ABBREVIATIONS

Abbreviated Form	**Extended Form**
Δ	Chemical Shift
υ	Frequency
υ cm^{-1}	Wavenumber
λ nm	Wavelength
Å	Angstrom
API	Active Pharmaceutical Drug
Bs	Broad singlet
Cm	Centimetre
CH_2Cl_2	Dichloromethane
$CHCl_3$	Chloroform
CH_3CN	Acetonitrile
CO_2	Carbon di oxide
D	Doublet
DMF	Dimethylformamide
DMSO	Dimethyl Sulphoxide
e.g.	for example
G	Gram
h	Hour
HR-MS	High Resolution Mass Spectra
^1H NMR	Proton Nuclear Magnetic Resonance Spectroscopy
Hz	Hertz
FT-IR	Fourier Transform Infrared
M	Multiplet
m/z	Mass/Charge
MHz	Megahertz
M^+	Molecular Ion
M	Molar

Abbreviated Form	**Extended Form**
Mmol	Millimole
mL	Millilitre
m.p.	Melting Point
MW	Microwave
NHC	N-Heterocycle Carbine
nm	Nanometre
NP	Nano-Particle
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	Phenyl
ppm	Part per million
Q	Quartet
T	Triplet
TiO_2	Titanium Oxide
THF	Tetrahydrofuron
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
UV	Ultra –Violet

Chapter -1

Introduction

1.1 Introduction

The phenomenon called ‘catalysis’ was recognized from a previous era, even though people knew nothing about the underlying mechanism and the chemical process involved in it. A catalyst accelerates a chemical reaction while actually not being consumed, the process is called ‘catalysis’ [1]. By using catalytic reagents, one can reduce the temperature of a transformation, reduce reagent based waste, enhance the selectivity of a reaction, allowing reactions to occur faster, cheaper and greener [2]. Catalysis has a key enabling role in environmental protection, particularly in recycling waste and reduction of greenhouse gases. Anastas and Warner in 1998 suggested a set of twelve principles which is the main philosophy of green chemistry to reduce or eliminate chemicals and chemical processes that have negative environmental impacts. Designing and development of noval ideal catalyst is one of the prior application of green chemistry. According to these principles, highly selective catalytic reagents are superior than that of stoichiometric reagents. Stoichiometric reagents are used in high amounts and are not reusable while catalytic reagents are used in small amounts in some cases and can carry out a single reaction multiple times [3]. Catalysis is the most interdisciplinary and overarching technology famously playing a key role in chemical transformations and lies at the heart of countless chemical protocols, academic research at laboratories level to the chemical industry level [4]. Catalysis research underpins several strategic industrial sectors: from energy to the manufacturing of materials and industrial processes like petrochemical, pharmaceutical and chemical industries.

Catalysis history contained a long time: Swedish chemist Jöns Jacob Berzelius first time coined new term catalysis in 1835 [5]. He summarised his concepts on ‘catalysis’ as a novel force, Berzelius wrote:

“It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action, they produce, in these bodies, decompositions of their elements and different recombination of these same elements to which they remain indifferent.” He called this new force as ‘catalytic force’ [6].

He used it to describe a wide range of observed phenomena, both in homogeneous systems, where the catalysts and the reactants happen to be in the same phase and in heterogeneous systems, where the phase differs. Berzelius recognized those common principles were involved, but the two branches of catalysis have developed independently and offer the chemical industry different strengths and weaknesses [7]. The findings formulated by Berzelius were concluded through discussions and experimental work with contemporary scientists in Europe [8]. The modern definition of the catalyst was described by Wilhelm Ostwald in 1894. He generalized the definition and classified catalysts as species which enhance the rate of a chemical reaction through the formation of intermediates that is restored at the end of the reaction. In 1909, Ostwald was awarded the Nobel Prize for his work on catalysis, chemical equilibrium and reaction velocities [9]. A significant number of Nobel laureates including Haber (1918), Bergius and Bosch (1931), Natta and Ziegler (1963), Fischer and Wilkinson (1973), Knowles, Noyori and Sharpless (2001), Chauvin, Grubbs and Schrock (2005) and recently, G.Ertl (2007), followed Ostwald contributing majorly to the field of catalysis [1, 6, 10].

In fact, we can describe the catalytic reaction as a cyclic event in terms of conventional catalysis theory [11] in which the catalyst involved in the reaction is recovered in its original state at the end of the cycle. Let us consider the catalytic reaction between two molecules reactant and reagent to give a product in Figure 1.1. The cycle starts with the bonding of molecules with the catalyst and forms the intermediates and finally gives the product. In the final step, product detaches from the catalyst, thus leaving the reaction cycle in its original state.

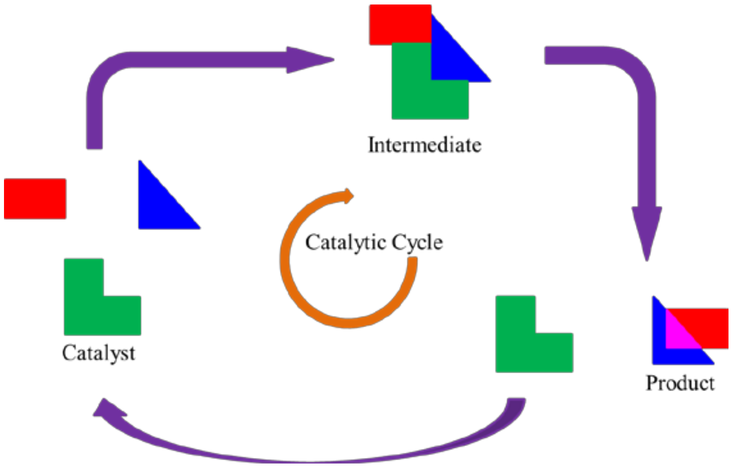


Figure 1.1: Generalized block schematic representation of energy for catalytic reaction as a sequence of elementary steps.

1.2 Catalysis: Homogenous vs Heterogeneous

Catalysis can be bifurcated into two categories depending on the phase homogeneity of the substrate(s) and the catalyst:

1. Homogeneous catalysis – involving a catalyst having phase coherence to that of a phase of reactant(s) in the reaction mixture.

2. Heterogeneous catalysis – involving a catalyst in a different phase to the reactants in the reaction mixture

These ideas brief the affiliation of reactants and catalysts; initially looking to be opposing each other, but in reality, they rather form a duo which acts in tandem quite well. Catalysts can occur in any physical form and are known as homogenous catalysts if they happen to be in the same state as the reagent phase in the reaction which is being promoted. During heterogeneous catalysis, a solid catalyst is used to accelerate a gas phase or liquid phase reaction. Generally the catalysts consist of tiny metal particles dispersed on an inert support material such as silica or alumina. The use of support material aids to enhance the metal surface area additionally leading to increase thermal stability.

1.2.1 Homogeneous catalysis

The first industrial homogeneous catalyst used as part of the lead chamber process for making sulphuric acid. In 1746, Birmingham-based British industrialist John Roebuck explored the catalytic effect of nitrogen oxide gases on the reaction between moist sulphur dioxide [12], air and most of the catalyst designs can be found today in the field of homogeneous catalysis due to metal complexes [13-15].A vital role by the metal catalyst is played in catalysis in elementary reactions such as oxidative additions of reactants, reductive elimination of products, as well as by large number but a well-classified rearrangement of the atoms and chemical bonds in the coordination with a sphere of metal atoms [16]. Homogeneous catalysis has some important properties like high selectivity of the products, good accessibility to catalytically active sites, etc. Homogeneous catalysts have superior defined active sites and usually include all of the metal atoms available for catalysis, and the steric and electronic vicinity of the metal atom can be, at least in principle, altered widely [17].The domain of homogeneous catalysts includes acids to sophisticated transition metal complexes, with a common feature of high amount of catalytically active sites and relatively high activity. The main disadvantage of such homogeneous transition metal complex catalysts is the inability to function at elevated temperatures and the problem of separating it. Other associated problems like corrosion, toxicity, regeneration and reuse, high cost, the creation large amount of solid waste in case of a homogeneous catalyst, make it unsuitable for application in industrial situations in today's environmentally conscious and economically pressured world. This leads to conclusion that the immobilization of homogeneous catalyst on polymer matrix may increase the possibility of their applications in industry [6,18-22]. Pros and Cons are associated with every methodology, heterogenizing through anchoring on a solid support increases the applicability of homogeneous catalyst to certain extent but also increases the number of synthesis steps for catalyst preparation. The multistep synthesis and use of solid support increases the cost of catalyst and hence it less attractive for the commercial applications. A reusable homogeneous catalyst could be an effective alternative. Due to the fact in homogeneous catalysis every active site is available for catalysis; therefore a reusable homogeneous catalyst can be a better alternative to heterogeneous catalysts. A homogeneous reusable catalyst could be more influential in combination to the biphasic reaction methodology. Designing such homogeneous catalysts may improve reusability but confines the application of catalyst to a limited set of solvents.

1.2.2 Heterogeneous Catalysis

One of the classical examples involving heterogeneous catalysts was the observation that red-hot metals such as iron or platinum could catalyse the decomposition of ammonia, recorded in 1813 by French chemist Louis Jacques Thenard [6]. Heterogeneous catalysts have played a vital role in organic transformations and have a major impact on the quality of human life as well as on economic progress. More than 90% of the processes in the petroleum, petrochemical, fertilizers, and food industries are catalytically induced. Synthesis and application of heterogeneous catalysis is an interdisciplinary science. Designing heterogeneous catalysts requires a good knowledge of chemistry and physics. Heterogeneous catalysts are compatible with a variety of reactors and reactions methodologies. These properties are quite tempting for industries to utilize heterogeneous catalysts at a commercial scale.

1.3 Alternate methodology

1.3.1 Photocatalysis reactions

The chemical reactions are initiated by the application of some form of energy like thermal [23], photochemical [24] and microwave [25]etc. The present investigation based on the use of photo-catalytic methods for organic synthesis, which are the alternative to popular thermal methods, in accordance with the fundamental principles of green chemistry. Unusual photo-assisted reactions such as isomerization around C-C double bond [26], activation of C-C triple bond [24, 27]also the cycloadditions [28]in the synthetic chemistry.

1.3.2 Microwave reactions

Microwave-Induced Organic Reaction Enhancement (MORE) chemistry can be considered as one way of improving the synthesis or as a concerted application to improve energy efficiency. Microwave aided chemistry has developed into a practical technique for numerous well known number of applications in organic transformations. Microwave irradiation produces well organized internal thermal excitation by the direct coupling of the polar molecules(e.g., solvents, chemical reagents and catalysts) with microwave energy involved in the reaction mixture. Hence, it improves the yield as well as decreases the time of the chemical transformations over conventional heating techniques [25, 29-31].

1.3.3 Autoclave reactions

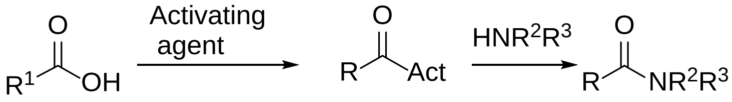
Autoclave curing is the globally used method of producing in bulk scale chemicals production in industry. The autoclave could be used with high temperature and high pressure for the reaction. The use of autoclave technique for hydrogenation [32], hydration [33] and various other reactions is quite common. Moreover, these methodologies outstandingly reduce the cost and formation of undesired by-products and chemical waste in the reaction. Recently, most autoclaves popularly used for hydrothermal or solvothermal synthesis in the laboratory [34].

The carbonyl functional group remains one of the most versatile functionalities available to the organic chemist [4, 35]. The importance of this functionality not only from its own inherent reactivity, being susceptible to both nucleophilic attack at carbon and electrophilic attack at oxygen, but also from the polarizing effect it has on neighboring atoms and functional groups, particularly its ability to stabilize an adjacent carbanion by charge delocalization into the C=O double bond [36]. To synthesize the carbonyl compounds like amide, ketones there were many reports available like hydroformylation [37], Wacker oxidation[38], hydration of nitrile [38, 39], hydration of alkyne [40-42] and carbonylation [27, 43].

A wide range of organic compounds has been catalytically synthesised by use of metal or catalyst in one and multistep by following the classical and advanced methodologies. There is always a demand the provide the feasible, economical method for the synthesis of industrially important value added organic compounds due to their huge demand as a precursor in verities of reactions. Amides and ketones are also considered the highly important value added compounds due to their extensive use in various chemical and pharmaceutical industries. Hence, here we have focused on the catalytic synthesis of amides and the ketones and developed some new methodologies those are superior in term economic and feasibility of the process.

1.4 Section A: Catalytic formation of amides

The amide belongs to the most privileged functional groups in carbonyl chemistry. It holds not only a crucial role in nature but also is a backbone in proteins such as enzymes. It is found in numerous natural products [44, 45] as a key chemical link in nitrogen-pertaining biomolecules [45] like Atorvastatin [46], Lisinopril [47], Valsartan [48] and Diltiazem [49] different commercially available pharmaceutical drugs [47, 49, 50] and polymers [51, 52] shows tremendous prevalence of amide bond formation in the field of synthetic chemistry. Despite their prominent importance, in previously most of the amide bond syntheses involve activation of carboxylic acid using carbodiimide as a coupling reagent and subsequent coupling of the activated species with amine (Scheme 1).

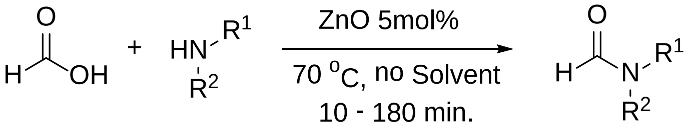


Scheme 1: Representation of activation of carboxylic acid

Although a large extent of method development has been devoted to fine-tuning of these coupling reagents for more efficient amide synthesis, this procedure involves inherent drawback of producing waste along with the desired amide [53] and also associated problems like increased costs and significant by-products which need to be eliminated. Finding an alternative to enzymes and coupling reagents in amide bond synthesis, non-metal catalysts such as organo-catalysts and boron reagents [54, 55] have been reported and these reports are also suffering from low atom efficiency and difficult isolations. Shorting this limitation for a possible solution is metal catalysis, which does not only include the advantage of atom-economical behaviour but also the low cost and more eco-friendly approach. These drawbacks encouraged the efforts towards the development of superior atom-efficient, cost friendly, a catalytic methodology for amide bond formation, as revealed by the increasing number of publications in this area in recent years.

1.4.1 Amide from carboxylic acid

The instantaneous formation of the amides is not possible via combining the two functional groups at ambient temperature, due to the presence of water elimination step that takes place at a very high temperature (≥200 °C) [56].The yield reflects the formation of undesired products as well as an inefficient atom economy for such a process which ultimately restricts their industrial application. Hence, the development of highly atom economically efficient catalytic approaches for amide formation is highly desired in modern synthetic chemistry [44, 57].There have been limited reports published in the field of metal catalysts for this transformation. However, formic acid as the formulating agent using for the N-formylation of amines has recently been reported to proceed under catalytic conditions. In 2006 reported the first example for this reaction using zinc-oxide as a metal catalyst under solvent-free neat reaction at 70 °C, reducing the time scale and obtaining excellent results (Scheme 2) [58] also demonstrated the reusability feature of the zinc-oxide.



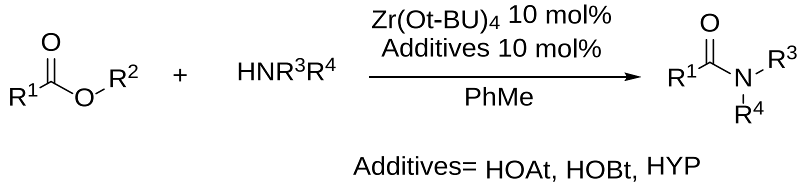
Scheme 2: Representation of N-formylation of an amine with formic acid using zinc-oxide catalyst

In 2009, Rao and Co-workers reported an article on series of Lewis acid catalysts for the same transformation, investigating the dichloride complexes of tin, iron, aluminum,nickel, zinc, and lanthanum to produce yields up to 80–100% [59]. They achieved the excellent results, obtained using zinc-chloride as a catalyst under solvent free reactions at 70 °C, Hosseini- Sarvari and Sharghi had employed and decreased the catalyst loading from 50 mol% (ZnO) to 10 mol% ($ZnCl_2$). Kim and Jang published a report on the amidation in presence of In (indium) metal as a catalyst again under solventless conditions at 70 °C [60] and resulted in an excellent yield using 10 mol% of indium metal, which they hypothesize that indium metal reacts with the formic acid for formation of $In(O_2CH)_3$ and acts as a Lewis acid in the reaction.

1.4.2 Amide from ester

The catalytic synthes of an amide from carboxylic acids is not convenient, as the alternative of carboxylic acid and their derivatives, particularly esters, have been already studied extensively in the catalytic synthesis of amides.

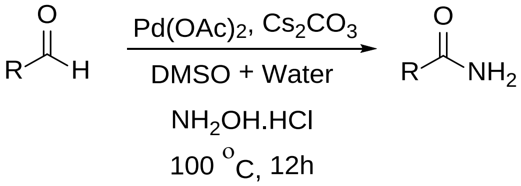
In 2003, Ranu and Co-workers, published a convenient methodology for the transformation of esters into secondary amides using the catalytic amount of indium tri-iodide and an enhanced amount of the amine [61]. The removal of hazardous reagents and simplified nature made this procedure an indigenous approach as an alternative for the methods known in that era. For a large number of amides having functional groups using their excellent yields was reported, but these conditions were not successful with secondary amines for the formation of tertiary amides. In 2005, a similar conversion was published by Gupta and Co-workers employed reusable zinc catalyst under either microwave or conventional heating [62]. They used only aromatic esters and amines, however a modest range of amides were synthesized and again the method was not optimized for tertiary amide synthesis. Despite having limited the substrate scope, the reaction procedure was advantageous in terms of having zinc catalyst being reusable up to six cycles. Porco and Co-workers also in the same year published their investigation of the group (IV) metal alkoxide complexes which, in combination with an activator and employed for the formation of amides from esters and amines (Scheme 3) [63]. They represented a variety of substrate domain.



Scheme 3: Zirconium catalyzed coupling of esters and amines

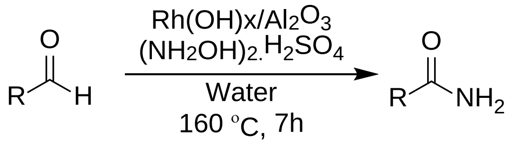
1.4.3 Amide from aldehydes

Due to their non-toxic nature and abundance aldehydes are desirable precursors in amide synthesis. In the previous decades, catalytic systems to effect this transformation have been substantially developed applied in useful organic transformations. The first metal catalyst system reported to be employed in this reaction was $Pd(OAc)_2$ (5 mol%), PPh_3 (15 mol%), K_2CO_3 with aryl bromide as the oxidant [64]. In 2008, Torisawa and Co-workers using another palladium catalyst with improved reaction conditions to form the corresponding amides from aldehydes coupled with morpholine. They use the oxidant H_2O_2 in urea in combination with $PdCl_2$(2.5 mol%) and xantphos(2.5 mol%) with decrementation of time and reaction temperature, as well as explore the range of aldehydes [65]. In later year Punniyamurthy and Co-workers reported one-pot conversion of an aldehyde with hydroxylamine hydrochloride to primary amide using $Pd(OAc)_2$ as a catalyst in aqueous DMSO at a moderate temperature(Scheme 4).



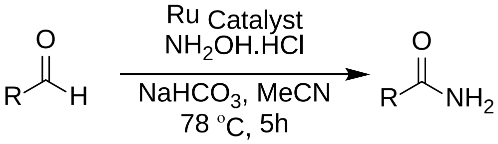
Scheme 4: $Pd(OAc)_2$ Catalyzed aldehyde activation

This protocol applies for the conversion of aliphatic as well as aryl aldehydes to corresponding amides and free from additives or chelating ligands [66]. In 2016, Saikia and Co-workers synthesized palladium nanoparticles immobilized on an amino-functionalized nanoscale MOF (metal-organic framework) MIL-101(Cr) employed as an active heterogeneous catalyst to perform the oxidative amination of aldehydes under solvent-free conditions [67]. Mizuno and Co-workers published a report in which, $Rh(OH)_x/Al_2O_3$ catalyzed one-pot conversion of amides from hydroxylamine and different kinds of aldehydes, including aliphatic, aromatic, unsaturated and heterocyclic ones, into corresponding amides in high yield and in the presence of only one equivalent of hydroxylamine with respect to the aldehyde(Scheme 5)[68].



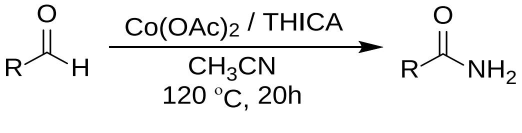
Scheme 5: Rh Catalyzed amide synthesis in an aqueous medium

In 2015, Semeril and Co-workers designed air stable, recyclable homogenous Ru(II) pyridoxal thiosemicarbazone complex(0.1mol%) that efficiently catalyses the conversion of aldehydes to primary amides with yields up to 91% (Scheme 6)[69].



Scheme 6: One pot Conversion of aldehyde into amide using Ru catalyst

Wong and Co-workers designed a method involving an efficient gold-catalyzed amide synthesis from the reaction of aromatic, aliphatic and polyhydroxy oligosaccharide-based aldehydes with secondary amines in the aqueous medium [70]. In Later Kobayashi and Co-workers reported gold-nanoparticles (medium size, 4.5–11 nm diameters) for the selective oxidative amidation of aldehydes and amines. An enhanced range of substrate combinations was employed. In particular, the availability of formaldehyde, aliphatic aldehydes, and primary amines [71]. In recent year Zhang and Co-workers published an article on oxidative amidation of aldehydes using Co(OAc)$_2$ (1 mol%), THICA (3 mol%) as a catalyst with 2 atm of O$_2$ at 120˚C. Orthoformates and secondary amines were successfully used as alkoxy and amino sources to couple with aldehydes without an acidic co-catalyst (Scheme 7)[72].

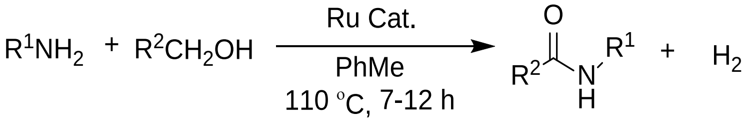


Scheme 7: Co(OAc)$_2$ Catalyzed aldehyde activation

A copper-catalyzed amide synthesis from aldehyde has been reported [64, 73] using *tert*-butyl hydro-peroxide as an oxidizing agent in aqueous and the employment of amine hydrochloride salts for minimization of competing for reaction, oxidation of the amine. In case of aliphatic or electron-poor aryl-aldehyde the yields decreased. Currently, lanthanide metal to be used as a catalyst for oxidative coupling of aldehydes and amines at room temperature have been also reported [74]. The advantage for the method is that no external oxidant is required, in the proposed catalytic cycle as the aldehyde itself behave as a hydrogen acceptor. Marks and Seo synthesized homoleptic lanthanide-amido complex $La[N(TMS)_2]_3$ performed for amide formation at room temperature in deuterated benzene [75]. Excess of aldehyde was required because it acts as a hydrogen acceptor. In 2010, Shen and Co-workers [74, 76] discovered several heterobimetallic lanthanide complexes used for the amination at1 mol% catalyst loading at room temperature.

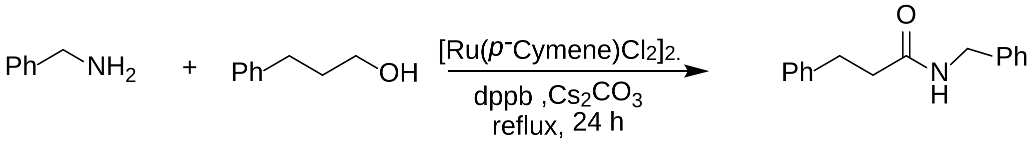
1.4.4 Amide from alcohol

In 1991, Murahasi and Naota reported the use of $RuH_2(PPh_3)_4$ for the synthesis of five and six-member lactams from an intramolecular reaction of 1-4, and 1-5 amino alcohols [77]. The same work repeated by Yamaguchi and Co-workers in 2004 with the rhodium complexes for the formation of several five-, six-, and seven-membered lactams from aromatic amino alcohols [78]. They used $[Cp^*RhCl_2]_2$(5 mol%)/K_2CO_3 (10 mol%), with acetone at 100 ˚C but the intermolecular reaction catalyzed by dearomatized PNN-Ru(II) hydride complex was demonstrated in 2007 by Milstein and Co-workers [79].



Scheme 8: Ru Catalyst for onepot conversion of alcohols into amides

In the proposed designed method, no special requirement for either acidic or basic additives also hydrogen acceptor and only molecular hydrogen were formed as a by-product during this reaction. This exceptionally simple and neat methodology has been further repeated by numerous other research groups since Milstein's original reports. An alternative ruthenium catalyst system was discovered by Madsen and Co-workers (Scheme 8)[80]. Combining of N-heterocyclic carbenes (NHC) with ruthenium complexes employed for an efficient catalytic design to synthesize a series of carboxiamides from different alcohols and primary amines. Optically pure substrates can be used without detected racemization, although this has been the first commercially available catalyst in this reaction, there were hardly significant acheivement obtained in terms of scope for the reaction and yield of reagents after the Milstein report. Later year, the Hong and Co-workers [81] have also investigated the behaviour of several NHC-based ruthenium complexes in amide formation. This type of work focuses some light on the reaction mechanism, which proposes that alcohol substrate holds a key role during the catalyst activation and the requirement of a strong base (NaH or KOtBu) may be associated to the ruthenium-alkoxide species activation and just not only associated with the in-situ generations of NHCs from the imidazolium. Again the same research group has also integrated easily available $RuCl_3$ (5 mol%) with NHCs and pyridine in the presence of NaH [82]. As far as hindered substrates are concerned, the employment of a less bulky NHC allowed moderate to superior results. Enhanced temperature (165 °C in mesitylene) was required for aniline and encumbered amine substrates. The employment of $[Ru(p\text{-cymene})Cl_2]_2$(2.5 mol%) in unification with dppb(5mol%), Cs_2CO_3(10 mol%) and a hydrogen acceptor produced the carboxymide products upto 81% yields(Scheme 9)[83].

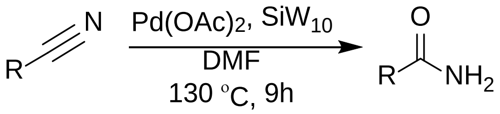


Scheme 9: Ru-Catalyzed oxidative formation of amide

Reactivity of this Ru-complex toward secondary amine was not at par, and low yield of the expected amide was obtained. In 2009, Grutzmacher and Co-workers demonstrated methodlogy for primary amide formation [84] using Rh(I)-diolefinamido complex $[Rh(trop_2N)(PPh_3)]$ [$trop_2N$=bis(5-H dibenzo[a,d]cyclohepten-5-yl)-amide] (0.2 mol%) and obtaining nitrogen from ammonia, primary amides were obtained in moderate to good yields in just 4 hours and at an ambient temperature. These catalytic systems highly chemo-selective in the direction of amide formation, difficult to handle, can be expensive and do not allow to secondary amines well. In the same year some of these disadvantages were addressed by Satsuma and Co-workers in their research report on γ-alumina supported silver cluster [85]. They used a heterogeneous, re-usable, catalyst for secondary amine, which forms the tertiary amides in good yields.

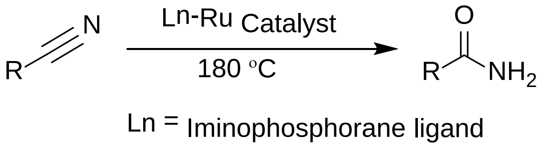
1.4.5 Amide from Nitrile

A very simplified and cost effective procedure for synthesizing primary amides is the nitrile hydration process. A number of metal complexes have been discovered to make this transformation efficiently and in-depth review is done by Kukushk in and Pombeiro in 2005 [86]. In 2008, Saito and Co-workers reported the use of Rh catalysts which involves the hydration of organonitriles under mild reaction conditions [87] and reducing the reaction time to 2 hours under microwave irradiation [88], moreover, the nitriles can also serve for amide synthesis. Mizuno and Co-workers designed Palladium(II) Containing γ-Keggin Silicodecatungstate [89] catalyst system for high catalytic conversion of hydration of numerous kinds of structurally diverse nitriles including aromatic, aliphatic, hetero-aromatic and double bond-containing ones(Scheme 10).



Scheme 10: Pd(II) Containing γ-Keggin Silicodecatungstate catalyzed nitrile hydration

In 2013 a different approach was demonstrated by Hong and Co-workers using Ruthenium-catalyzed synthesis of amides from nitriles and alcohols [90].On the basis of investigation and practical experience, a redox-neutral mechanism involving both the reduction of the nitrile and the alcohol oxidation to aldehyde is involved. Singh and Co-workers reported the magnetic nanoparticles of Ru complexes used for nitrile hydration in aqueous medium [91].Which can be easily separated by using the external magnet. In recent, the highly stable iminophosphoranes based Ru complexes perform nitrile hydration in aqueous (100 °C, 24 h) and 1,2-dimethoxyethane (180 °C, 3 h) and neat reaction conditions (180 °C, 3 h) all cases obtained results in the selectivily synthesized benzamide with yields of up to 96% (Scheme 11) [92].



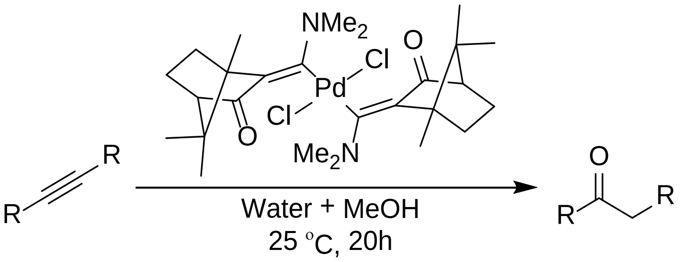
Scheme11: Iminophosphoranes based Ru catalyst-promoted nitrile hydration

1.5 Section B: Hydration of alkyne

The alkyne hydration reaction which is a route to the synthesis of carbonyl derivatives, is of prime interest because of the enhanced availability of alkyne substrates and the important role of the carbonyl compounds for both the bulk and fine chemical industries [93]. In this respect, Markovnikov addition of water on alkynes is an ideal method for the formation of ketones; in alkyne hydration water used as a reagent with 100% atom economy if a suitable catalyst is available [94]. Berthelot was the first to report an alkyne hydration reaction in 1862, which was classically catalyzed by Hg(II) salts used as a lewis acid in aqueous sulphuric acid solution [95-97]. Mercury promoted hydration of alkynes often suffer a significant drawback where certain acid-labile functional groups are not compatible with the harsh acidic conditions. Moreover, the reaction proceeds under stringent conditions, i.e. high temperatures (> 100 °C), prolonged reaction time as well as requires a large excess of acid and water. To circumvent these drawbacks, various transition-metal-based catalysts [24, 41, 98 -104] have been developed as environmentally benign alternatives to mercuric catalysts in the hydration of alkynes. These metals provide a more accessible, mild, greener and efficient protocol for the hydration of simple alkynes. In selected cases, aryl alkynes posed several challenges giving reduced yields, lower selectivity, higher catalyst loading and elevated temperatures etc. The hydration of terminal alkynes usually occurs via Markovnikov addition, giving methyl ketones, with symmetric internal alkynes selectively yielding single ketone products. It is generally accepted that the hydration proceeds via an enol intermedaite, which immediately transforms into the more stable ketone via tautomerism, with the metal ketone complexes being the key intermediates, in the presence of metal catalysts [105].

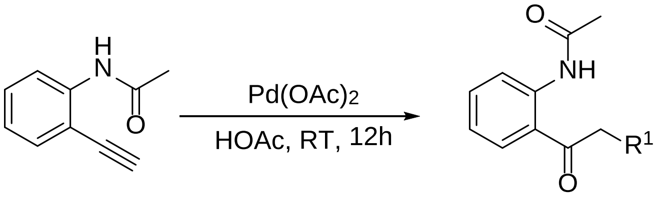
1.5.1 Pd Catalyzed alkyne hydration

Association of water with the C-C triple bond Catalyzed by transition-metal catalysts is an important approach from the non-toxic nature of water to both the user and the environment, its relative abundance compared to other solvents, as well as the compatibility with various organic substrates, could proceed with 100% atom economy which is need of fundamental principles of "green chemistry" [106, 107]. The palladium-catalyzed alkyne hydration is the easy way for generating ketones through alkynes [108]. A procedure of alkyne hydration was reported in 1987 reported, where the $PdCl_2(MeCN)_2$(5 mol%) was used in aqueous acetonitrile under microwave irradiation for to lead the 1,4-diketone [109]. In 1993, Marineli and Co-workers used the bi-phasic reaction media for the hydration of a hydroxylated alkyne [110] and then Marsella and Co-workers used nafion/palladium(II) resin in water-ethanol mixture for the hydration of 2-methylbut-3-yn-2-ol to 3-hydroxy-3-methylbutan-2-one [111]. Stepnica and Co-workers also reported the Markovnikov addition of ethynylferrocene to synthesis of acetylferrocene using camphor hydrazone-derivedpalladium(II) complex(10-25 mol%) in a water-methanol mixture at room temperature. Other simple terminal acetylenes such as oct-1-yne of several ethynylbenzenes and 1-ferrocenylprop-1-yne were not affected or polymerized (Scheme 12)[112].



Scheme 12: Camphor hydrazine derived Pd(II) complex catalyzed alkyne hydration

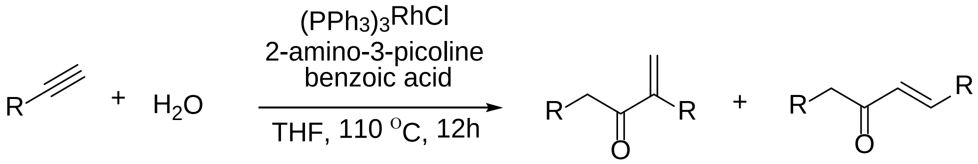
Amide oxygen-assisted palladium-catalyzed alkyne hydration developed in 2015 via an oxypalladation under mild reaction conditions with good functionality. This was an improved and convenient route for the synthesis of ortho-acylacetanilide derivatives in moderate to superior yields with single regio-selectivity (Scheme 13)[113].



Scheme13: Amide oxygen-assisted Pd catalyzed alkyne hydration

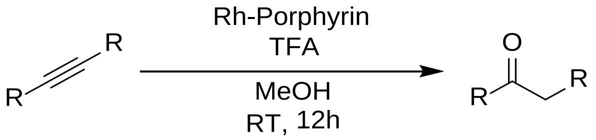
1.5.2 Rh Catalyzed alkyne hydration

Rhodium-catalyzed carbonyl synthesis through the addition of water on alkynes is a desirable method and sensitive towards the functional group tolerance of the metal and the high activity and selectivity demonstrated under amiable reaction conditions [114]. Jun and Co-workers discovered the chelation-assisted catalytic system with Rh(I)(5 mol%)and 2-amino-3-picoline(1equiv) used for an intermolecular hydrating dimerization reaction of 1-alkyne to give α,β-enones at 100 ˚C. This methodology demonstrated a new reaction pathway for the synthesis α,β-enones(Scheme 14) [115].



Scheme 14: Representation of chelation-assisted hydration of alkyne forming α, β-enones using Rh(I) Catalyst

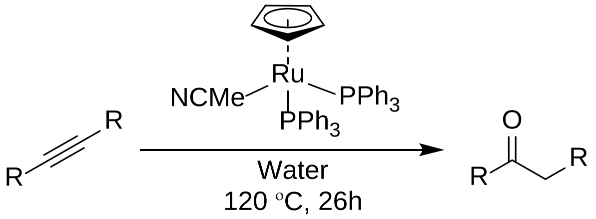
In 2010, Breit and Co-workers designed the first rhodium catalyst system for the intermolecular hydro-oxycarbonylation process of terminal alkynes to the corresponding Z-anti-Markovnikov fashioned enol esters in remarkable yield with an excellent stereo-selectivity at 100 ˚C in 16 hours. This catalytic system was generalized on the various substrate and showed a wide functional group tolerance [116]. In 2015, reducing the time period and the temperature, the first Rh catalyze visible light promoted hydration of alkynes was developed. The rhodium ketonyl intermediates were observed from photo-cleavage of Rh-C bonds in an acidic solution to produce corresponding products. This alkyne hydration under visible light irradiation provides a green approach for organometallic catalysis(Scheme 15)[41].



Scheme15: Visible light promoted alkyne hydration catalyzed by Rh(III) porphyrin complex

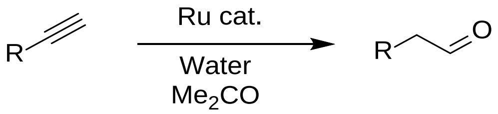
1.5.3 Ru Catalyzed alkyne hydration

On the basis of the Markovnikov fashion of water on alkynes, Trost and Co-workers designed a novel three-component reaction using a terminal alkyne, water, and methyl vinyl ketone, for to synthesised the corresponding 1,5-diketones with employing of CpRu(COD)Cl and $In(OTf)_3$ at 100 ˚C [117]. In the presence of indenyl ruthenium(II) catalyst, various aryl and aliphatic alkynes hydrated and selectively produce the corresponding ketones in moderate to excellent yield (77-98%)[118]. Wakatsuki and Co-workers reported anti-Markovnikov addition of water on terminal alkynes catalyzed by ruthenium(II) complexes(10 mol%) in the presence of $(C_6F_5)PPh_2$(30 mol%). This method was also found applicable to a broad substrate scope, but phenylacetylene and *tert*-butylacetylene gave less yield of the corresponding aldehydes [119, 120]. The remarkable enhancement in activity, as well as selectivity in the above procedure, was practically done by using CpRu(dppm)Cl (1 mol%) complexes bearing bidentate or monodentate phosphine ligands (Scheme 16)[121, 122].



Scheme 16: Ru-Catalyzed hydration of alkynes

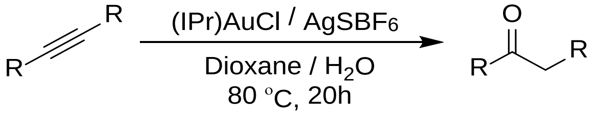
In the same year, Grotjahn and Co-workers published the same work with the use of ruthenium(II) catalyst, however, the procedure does not require electron-rich phosphine and tolerance for acid sensitive functionality [123]. In the case of alkyl-substituted alkynes the yield was good to excellent, but for *tert*-butylacetylene and phenylacetylene, there was no significant improvement. It was proposed that the imidazole groups in the catalyst play key role in the catalysis. In 2002,the conversion of propargyl alcohols to the corresponding α,β-unsaturated aldehydes in a stereoselective manner in aqueous solution was reported with the use of $CpRu(PMe_3)_2Cl$ as catalyst[124]. Gimeno and Co-workers also reported a modified way to control the regio-selectivity for alkynes hydration with the help of indenyl ruthenium(II) complex bearing π-acidic COD ligand and the addition of water to both terminal alkynes and propargyl alcohols in an anti-Markovnikov fashion when the reaction completed at 60 °C in an aqueous micellar environment [125]. In 2006, Hintermann and Co-workers also introduced a series of more active in-situ complexes for the anti-Markovnikov addition of alkynes using $[CpRu(naphthalene)]PF_6$ bearing 6-aryl-2-diphenyl phosphinopyridine ligands [126]. These in-situ active catalysts are similar to previously reported Grotjahn's complex. However, this catalyst system was four times more active than the previous one for the anti-Markovnikov hydration (Scheme 17).



Scheme 17: *anti*-Markovnikov addition of water on alkynes by Ru catalyst

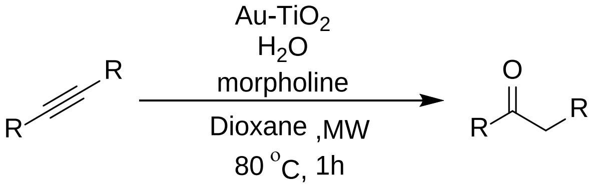
1.5.4 Au Catalyzed alkyne hydration

In 1991,Utimoto and co-workers designed a method that produces effective outcome when the reaction was executed with Au (gold) catalyst instead of a Pd (palladium) catalyst in aqueous methanol mixture, moreover, the internal alkynes were also hydrated with 1:1 mixture of region-isomers [127]. In the same year, the conversion of methyl propargyl ethers into α,β-unsaturated ketones regio-selectively using gold catalyst(5 mol%) in aqueous methanol reaction conditions was also reported [128]. In 1998, a new and very efficient class of Au(I) catalysts bearing phosphane, phosphite, or arsine as ligands were published. These were the quite few excellent catalysts employed for the addition of alcohols to alkynes under amiable reaction conditions [129]. In 2002, Hayashi and co-workers discovered the Au(I) acid catalytic system, which has effectively hydrate the large variety of alkynes with significant turnover frequencies than the *cis*-$(TPPTS)_2PtCl_2$ [130]. Laguna and co-workers demonstrate that Au(III) complexes, which was acting similarly to lewis acids, they have shown the catalytic nature of Au(III) and Au(I) in additions of nucleophiles to double and triple bonds [131]. In 2007, Nolan and co-workers designed the first series of well-defined N-heterocyclic gold complexes. They use the (NHC)Au(III) complexes along with silver salt as co-catalyst(2 mol%) and catalyze the alkyne hydration in aqueous methanol under reflux condition [132]. Later on, the same group discovered new (NHC)Au(I) complex and design new strategy for alkyne hydration with various functionality under acid-free conditions and at very low catalyst amount (Scheme 18)[133].



Scheme18: [(NHC)Au(I)] Catalyzed acid-free alkyne hydration

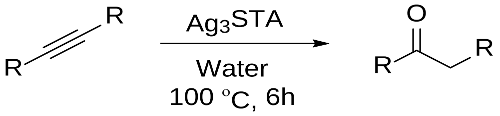
Hong and Co-workers prepared two new air-stable abnormal (NHC) AuCl complexes via transmetalation from the corresponding silver carbene complexes. These abnormal NHC gold complexes showed the catalytic activity in the hydration of alkynes which worse than those of the normal gold NHC complexes. This investigation was utilized for further studies on the structural diversity and enhanced catalytic activity of carbene based gold complexes were synthesised [134]. Corma and co-workers reported isolable Au(I) phosphine complexes, which were used at room temperature for ketone synthesis without using acidic promoters and also found suitable for sensitive acid-labile containing functional groups. This reported procedure was amiable, more convenient, selective and easier to handle than those published before [135]. In 2015, the neutral Au(I) complex instead of cationic ones as catalysts was also found efficient for the activation of C-C triple bonds for regio-selective ketone synthesis [136]. In the same year, Xu and Co-workers published a report on the gold nanoparticles, those can effectively and heterogeneously catalyze the acid-sensitive functional alkyne under basic conditions. These gold nanoparticles were easily to handle, air and moisture stable, reused by easy filtration and also efficiently worked in flow reactors(Scheme 19)[137].



Scheme 19: TiO_2 Supported Au-NPs catalyzed alkyne hydration under basic conditions

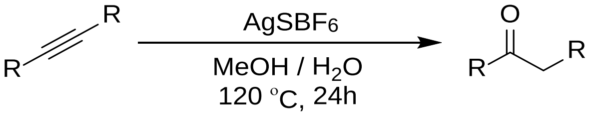
1.5.5 Ag Catalyzed alkyne hydration

Silver salts for the alkyne hydration to corresponding ketones were also explored with limited examples. In 1993, Marsella and co-workers reported hydration of acetylenic compounds, they found during catalyst screening that AgOTf could hydrate 2-methylbut-3yn-2ol with 44% conversion after 70 hours [111]. In 2012, a simple silver salt of heteropoly tungstate was discovered as a more effective heterogeneous catalyst for ketone synthesis via hydration of various structural derivatives of alkynes at 100 ˚C in neat condition and absence of mineral acid. The catalytic behaviour of the catalyst was depended upon acidity and the number of brønsted and lewis acid sites available. The positive properties of this methodology is the easy synthesis of the catalyst, this environmentally nature, recyclablity and being highly suitable for organic transformations (Scheme 20)[138].



Scheme 20: Hydration of alkynes in solvent free condition using heterogeneous Ag exchanged silico-tungstic acid catalyst

Wagner and co-workers designed a simple and efficient methodology for the chemo-selective ketone formation using $AgSbF_6$ as a catalyst in aqueous methanol at 75 ˚C in 36 to 48 hours. This reaction proceeds smoothly and afford moderate to excellent yield, it does not require any co-catalysts, catalyst activators or ligands. As the silver salts had drawn attention that these could be used as effective catalyst, hence, the role of silver as a co-catalyst has been undervalued in Au promoted hydration (Scheme 21)[139].



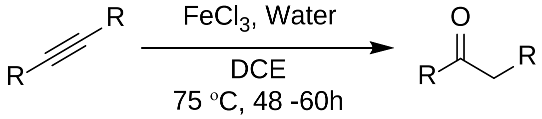
Scheme 21: Hydration of alkynes catalyzed byAgSbF$_6$

Later on, Chakraborty and co-workers reported the first gold-free silver catalysis for the alkyne hydration of corresponding Markovnikov's addition product i.e. ketone with better results. The large substrate scope like aliphatic, alicyclic, aromatic, hetero-aromatic alkynes tolerate the reaction conditions [140]. Xian Liu and co-workers presented a general and facile procedure for the regioselective synthesis of methyl ketones from the simple terminal alkynes in excellent yields using $AgBF_4$(5 mol%) at 110 ˚C [141]. In 2014, Bera and co-workers reported that $AgBAr^F$ display remarkable catalytic activity in water but being ineffective in common organic solvents. Alkynes which are in liquid state do not require the additives or co-solvents whereas the solid alkynes need a tiny amount of ethyl acetate for to promote the reaction [142]. In 2015, Xu and co-workers developed microemulsion containing silver catalyst for the selective hydration of both terminal as well as for internal alkynes. This procedure proceeds smoothly and afford better results, further more, the catalytic microemulsion system can be reused for several reactions [98].

1.5.6 Fe Catalyzed alkyne hydration

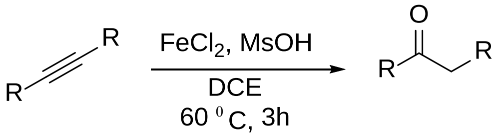
In 1966, iron was for the first time used for alkyne hydration, the stoichiometric amount of $FeCl_3$ was used in a water solvent. The most prominent features of the methods consisted the (i) $FeCl_3$ has efficiently catalyzed the reaction but neither the [$FeCl_3.6H_2O$] aqua catalyst nor $FeCl_2$; (ii) The hydration of aromatic alkynes was much faster than that of aliphatic alkynes [143]. In 2005, Martin and co-workers proved that Fe(III) halides are excellent catalysts for the combination of acetylenic compound and aldehydes at room temperature. In this process when terminal non-oxygenated acetylenes were used, the stereoselective (E,Z)-1,5-dihalo-1,4-dienes were obtained as a major product. Although internal aromatic alkynes were exclusively converted into tri-substituted (E)-α,β-unsaturated ketones as under the catalytic conditions [144]. In 2009, Darcel and co-workers report a simple and facile $FeCl_3$ promoted Markovnikov hydration of various alkynes to ketones with good regioselectivity in significant yields. As an initial investigation to improve this

$FeCl_3$ catalyzed the hydration of alkynes, using phenylacetylene (1 mmol) in a 1,2-dichloroethane was allowed to react with water (3 equiv.) at 75 ˚C in 67 hours employing anhydrous $FeCl_3$ (10 mol%) under a small pressure of air(Scheme 22)[145].



Scheme22: $FeCl_3$ Catalyzed hydration of alkynes

Later, the $[Fe(NTf_2)_3]$ complex was also used as a metal catalyst for the Markovnikov fashion of water on the terminal and internal aryl-alkyl alkynes, it also completes the reaction in quite lesser time period than the previously reported methods. Hydrolysis of the salts speedily occurs to give catalytically active protons, moreover, the use of triphenylphosphane oxide allows the reuse of the catalyst [146]. In 2013, Lee and co-workers presented $FeCl_2.4H_2O$(5 mol%) in combination with methanesulfonic acid as a catalytic system for the hydration of a numerous number of alkynes in 1,2 dichloroethane, under aimable conditions to produce ketones. Iron catalysts, are cost-effective, non-hazardous, and eco-friendly and quite significant from the view point of environmental and sustainable chemistry (Scheme 23)[147].

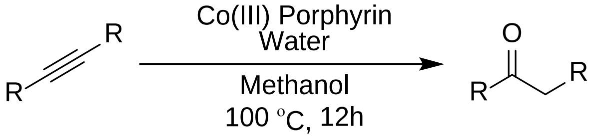


Scheme 23: $FeCl_2$ Catalyzed hydration of alkynes assisted with methanesulfonic acid

The Bassetti and co-workers have also demonstrated the catalytic nature of iron salts in acetic acid, as the brønsted acidic provides the acidic medium, this source is environmentally more benign than halogenated solvents. Phenylacetylene was transformed into acetophenone in high yield by reaction with stoichiometric amounts of both Fe(III) sulfate and acetic acid [103].

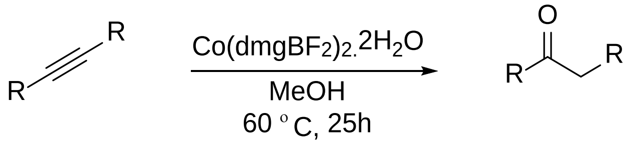
1.5.7 Co Catalyzed alkyne hydration

In 2013, Naka and co-workers developed for the first time a water-soluble cobalt porphyrin complex for alkyne hydration to corresponding ketones. This catalyst performs reaction under aerobic and mild acidic conditions that enables this catalyst to produce results with acid-labile functionalities(Scheme 24)[148].



Scheme 24: Alkyne hydration catalyzed by water-soluble cobalt porphyrin complex

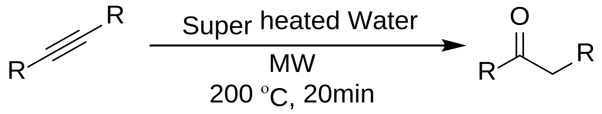
Later, a series of porous twofold cobalt porphyrin complexes as heterogeneous catalysts were discovered and studied for the hydration of various diversified terminal alkynes at low catalyst loading. The twofold interpenetration anticipated metalloporphyrin catalytically active sites adjacent to each other, allowing concerted activation, which enhanced results in excellent efficiency compared to their homogeneous analogs and before ones [149]. In 2014, Lei and co-workers were developed water soluble salen Co(III) complex(2 mol%) for the Markonikov fashion of water on terminal alkynes with various functionality using acid (2 mol%) as a co-catalyst at 80 ˚C for 20 hours. The catalyst could be reused up to three fold with significant results[150]. In 2015, Weck and co-workers demonstrated a core-shell micellar support Co-Rh catalyzed a tandem reaction. The micelle core and shell anticipated different micro environments for the conversion. Co-catalyzed alkyne hydration carry out in the hydrophobic core, while the Rh-catalyzed asymmetric transfer hydrogenation of the intermediate ketone into chiral alcohol occurs in the hydrophilic shell [151]. In 2017, Li and co-workers had discovered a series of cobaloxime catalyst and applied on terminal alkyne hydration under acid-free conditions. A large number of alkynes bearing different functionality especially with acid-sensitive ones were transformed to methyl ketones in moderate to excellent yield with complete regioselectivity. The readily available cobaloxime catalysts are bench stable and demonstrated the high synthetic potential in organic synthesis (Scheme 25)[152].



Scheme 25: Cobaloxime catalyzed hydration of alkynes without acidic promoters

1.5.8 Metal/Catalyst/Reagent-free ketone synthesis

There were many methodology presents that demonstrate the applications of green and sustainable approach for laboratory and industrial productions too. Practicing many cost-effective and eco-friendly benign reaction methodologies have unveiled a new era in the field of chemistry [153]. Optimizing reaction conditions to achieve results without using chemical reagents or catalyst; this phenomenon is interesting as well as significantly crucial from a commercial and economic perspective. Reordering the temperature and pressure associated with the reaction may forward to new insights into catalyst-free organic transformations. In 2004, Vasudevan and co-workers led catalyst-free approach which exclusively works for hydration of alkynes to the corresponding ketones. The alkynes treated in superheated water at 200 ˚C in a microwave reactor for 20 minutes to produce the ketones. Although the catalyst-free alkyne hydration was reported for the first time (Scheme 26)[25].



Scheme 26: Metal-free alkyne hydration under MW irradiation in superheated water

The Scope of the Work

Sustainable and economical synthetic methodologies are highly desired requisites of the modern chemical industries. The searches for new, improved and economic catalysts are the prime requirements in the present scenario. Finding other applications of the metal complexes and search for cost-effective alternative catalyst or developing reaction methodologies to work economically and with high efficiency are the critical goals of this research. Development of new and active catalysts that can be used for industrial applications is the motivation for this study.

Due to the great importance of carbonyl compound like amide and ketone, various synthetic approaches have been reported. The present thesis describes a straight forward and more efficient methodology for one-pot synthesis of the amides from aldehydes, which can effectively reduce the formation of hazardous wastage and use the detrimental reagents. The present ruthenium catalysts are economically better as compare to the reported Rh/Ir/Pd metals based catalysts for amide transformations and develop new catalytic methodologies for alkyne hydration reducing the time period and enhance the reusability of the catalyst also optimized the hydration of alkynes upto gram scale in an autoclave. The detail investigations and results are presented in the subsequent chapters.

1.6 References

[1] I. Chorkendorff, J.W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics.* Second Edition ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim **2007**.

[2] K. Hemalatha, G. Madhumitha, A. Kajbafvala, N. Anupama, R. Sompalle, S. Mohana Roopan, Function of Nanocatalyst in Chemistry of Organic Compounds Revolution: An Overview. *J. Nanomater.* **2013**, *2013*, 23.

[3] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*. Oxford University Press: New York, **1998**.

[4] S. Patai, *The Chemistry of the Carbonyl Group*. Wiley-Interscience: New York **1966**.

[5] J.J. Berzelius, *Årsberättelsen Om Framsteg I Fysik Och Kemi*. Royal Swedish Academy of Sciences: **1835**.

[6] A.J.B. Robertson, The Early History of Catalysis. *Platin. Met. Rev.* **1975,** *19*, 64.

[7] S. Green, *Industrial Catalysis*. Macmillan Company: New York, **1928**.

[8] J.J. Berzelius, *Reseanteckningar*. P. A. Norstedt & Söne: Stockholm, **1903**.

[9] J. Van Houten, A Century of Chemical Dynamics Traced through the Nobel Prizes. **1903**: Svante Arrhenius. *J. Chem. Educ.* **2002**, *79*, 21.

[10] R.V. Santen, *Catalysis in Perspective: Historic Review*. Wiley-VCH Verlag: Weinheim, **2012**.

[11] D.E. Koshland Jr., The Key–Lock Theory and the Induced Fit Theory. *Angew. Chem. Int. Ed. in English* **1995**, *33*, 2375-2378.

[12] E.M. Jones, Chamber Process Manufacture of Sulfuric Acid. *Industrial & Engineering Chemist* **1950**, *42*, 2208-2210.

[13] A. Nakamura, M. Tsulsui, *Principles and Applications of Homogeneous Catalysis*. Wiley: New York, **1980**.

[14] C. Masters, *Homogeneous Transition Metal Catalysis*. Chapman and Hall London **1981**.

[15] G.H. Olive, S. Olive, *Coordination and Catalysis*. Verlag Chemie: New York, **1977**.

[16] R.S. Nyholm, Proc. 3rd Internat. Congr. Catalysis, North-Holland Publ. Co., Amsterdam, **1965**.

[17] P.D. Frisch, A Review Of: "Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes. George W. Parshall, John Wiley & Sons, New York, N.Y., **1980**, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **1981**, *11*, 179-180.

[18] J.A. Widegren, R.G. Finke, A Review of the Problem of Distinguishing True Homogeneous Catalysis from Soluble or Other Metal-Particle Heterogeneous Catalysis under Reducing Conditions. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317-341.

[19] N. Mizuno, M. Misono, Heterogeneous Catalysis. *Chem. Rev.* **1998**, *98*, 199-218.

[20] M.K. Samantaray, E. Pump, A. Bendjeriou-Sedjerari, V. D'Elia, J.D.A. Pelletier, M. Guidotti, R. Psaro, J.-M. Basset, Surface Organometallic Chemistry in Heterogeneous Catalysis. *Chem. Soc. Rev.* **2018**, *47*, 8403-8437.

[21] H. Knozinger, *Heterogeneous Catalysis and Solid Catalysts*.Wiley-VCH Verlag Gmb: **2009**.

[22] A.J.B. Robertson, The Development of Ideas on Heterogeneous Catalysis. *Platin. Met. Rev.***1983**, *27*, 31–39.

[23] X. Jin, T. Oishi, K. Yamaguchi, N. Mizuno, Heterogeneously Catalyzed Efficient Hydration of Alkynes to Ketones by Tin–Tungsten Mixed Oxides. *Chem. Eur. J.* **2011**, *17*, 1261-1267.

[24] R.K. Joshi, N. Satrawala, One Pot Synthesis of Important Retinoid Synthon by the Catalytic Regioselective Bi-Functionalization of Acetylenes, Alcohol and Carbon Monoxide. *Tetrahedron Lett.* **2017**, *58*, 2931-2935.

[25] A. Vasudevan, M.K. Verzal, Neutral, Metal-Free Hydration of Alkynes Using Microwave Irradiation in Superheated Water. *Synlett* **2004**, *2004*, 631-634.

[26] T. Szymańska-Buzar, M. Jaroszewski, A.J. Downs, T.M. Greene, L.J. Morris, Photo-Reversible Isomerisation of *trans*- to *cis*-[W(Co)$_4$(H$_2$-Alkene)$_2$] Complexes in Low-Temperature Matrices. *J. Organomet. Chem.* **1997**, *531*, 207-216.

[27] B.N. Jha, A. Raghuvanshi, R.K. Joshi, S.M. Mobin, P. Mathur, A Photochemical Route to Ferrocenyl-Substituted Ferrapyrrolinone Complexes. *Appl. Organomet. Chem.* **2017**, *31*, e3805.

[28] M.H. Mir, L.L. Koh, G.K. Tan, J.J. Vittal, Single-Crystal to Single-Crystal Photochemical Structural Transformations of Interpenetrated 3 D Coordination Polymers by [2+2] Cycloaddition Reactions. *Angew. Chem. Int. Ed.* **2010**, *49*, 390-393.

[29] C.O. Kappe, Controlled Microwave Heating in Modern Organic Synthesis. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250-6284.

[30] C.O. Kappe, D. Dallinger, The Impact of Microwave Synthesis on Drug Discovery. *Nat. Rev. Drug Discov.* **2005**, *5*, 51.

[31] S. Kumar, S. Sharma, P. Das, Supported Gold Nanoparticles-Catalyzed Microwave-Assisted Hydration of Nitriles to Amides under Base-Free Conditions. *Adv. Synth. Catal.* **2016**, *358*, 2889-2894.

[32] R.V. Jagadeesh, T. Stemmler, A.-E. Surkus, H. Junge, K. Junge, M. Beller, Hydrogenation Using Iron Oxide–Based Nanocatalysts for the Synthesis of Amines. *Nat. Protoc.* **2015**, *10*, 548.

[33] Z.K. Wickens, B. Morandi, R.H. Grubbs, Aldehyde-Selective Wacker-Type Oxidation of Unbiased Alkenes Enabled by a Nitrite Co-Catalyst. *Angew. Chem. Int. Ed.* **2013**, *52*, 11257-11260.

[34] S.H. Feng, G.H. Li, Chapter 4 - Hydrothermal and Solvothermal Syntheses. In *Modern Inorganic Synthetic Chemistry (Second Edition)*, R. Xu, Y. Xu, Eds. Elsevier: Amsterdam, **2017**; 73-104.

[35] S. Warren, *Chemistry of the Carbonyl Group*. Wiley London, **1974**.

[36] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, *Carbonylation Direct Synthesis of Carbonyl Compounds* springer: US, **1991**.

[37] S. Pandey, K.V. Raj, D.R. Shinde, K. Vanka, V. Kashyap, S. Kurungot, C.P. Vinod, S.H. Chikkali, Iron Catalyzed Hydroformylation of Alkenes under Mild Conditions: Evidence of an Fe(II) Catalyzed Process. *J. Am. Chem. Soc.* **2018**, *140*, 4430-4439.

[38] T.V. Baiju, E. Gravel, E. Doris, I. Namboothiri, *Recent Developments in Tsuji-Wacker Oxidation*. **2016**; *57*.

[39] J. Lee, M. Kim, S. Chang, H.-Y. Lee, Anhydrous Hydration of Nitriles to Amides Using Aldoximes as the Water Source. *Org. Lett.* **2009**, *11*, 5598-5601.

[40] R. Chinchilla, C. Nájera, Chemicals from Alkynes with Palladium Catalysts. *Chem. Rev.* **2014**, *114*, 1783-1826.

[41] X. Liu, L. Liu, Z. Wang, X. Fu, Visible Light Promoted Hydration of Alkynes Catalyzed by Rhodium(III) Porphyrins. *Chem. Commun.* **2015**, *51*, 11896-11898.

[42] F. Chevallier, B. Breit, Self-Assembled Bidentate Ligands for Ru-Catalyzed Anti-Markovnikov Hydration of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2006**, *45*, 1599-1602.

[43] C.F.J. Barnard, Palladium-Catalyzed Carbonylation—a Reaction Come of Age. *Organometallics* **2008**, *27*, 5402-5422.

[44] J.S. Carey, D. Laffan, C. Thomson, M.T. Williams, Analysis of the Reactions Used for the Preparation of Drug Candidate Molecules. *Org. Biomol. Chem.* **2006**, *4*, 2337-2347.

[45] T. Wieland, M. Bodanszky, *The World of Peptides: A Brief History of Peptide Chemistry*. Springer: **1991**.

[46] A. Graul, J. Castaner, *Drug. Future* **1997**, *22*, 956–968.

[47] A.A. Patchett, Excursions in Drug Discovery. *J. Med. Chem.* **1993**, *36*, 2051-2058.

[48] M. de Gasparo, S. Whitebread, Binding of Valsartan to Mammalian Angiotensin At1 Receptors. *Regul. Pept.* **1995**, *59*, 303-311.

[49] V.S. Ananthanarayanan, S. Tetreault, A. Saint-Jean, Interaction of Calcium Channel Antagonists with Calcium: Spectroscopic and Modeling Studies on Diltiazem and Its Ca^{2+} Complex. *J. Med. Chem.* **1993**, *36*, 1324-1332.

[50] B.D. Roth, 1 the Discovery and Development of Atorvastatin, a Potent Novel Hypolipidemic Agent. *Prog. Med. Chem.*, F.D. King, A.W. Oxford, A.B. Reitz, S.L. Dax, Eds. Elsevier: **2002**, *40*, *1-22*.

[51] B.L. Deopura, 2 - Polyamide Fibers. In *Polyesters and Polyamides*, Woodhead Publishing: **2008**, 41-61.

[52] A.K. Agrawal, M. Jassal, 4 - Manufacture of Polyamide Fibres. In *Polyesters and Polyamides*, Woodhead Publishing: **2008**, 97-139.

[53] E. Valeur, M. Bradley, Amide Bond Formation: Beyond the Myth of Coupling Reagents. *Chem. Soc. Rev.* **2009**, *38*, 606-631.

[54] J.E. Anderson, R. Davis, R.N. Fitzgerald, J.M. Haberman, Selective Phenol Alkylation: An Improved Preparation of Efaproxiral. *Synth. Commun.* **2006**, *36*, 2129-2133.

[55] R.M. de Figueiredo, J.-S. Suppo, J.-M. Campagne, Nonclassical Routes for Amide Bond Formation. *Chem. Rev.* **2016**, *116*, 12029-12122.

[56] B.S. Jursic, Z. Zdravkovski, A Simple Preparation of Amides from Acids and Amines by Heating of Their Mixture. *Synth. Commun.* **1993**, *23*, 2761-2770.

[57] V.R. Pattabiraman, J.W. Bode, Rethinking Amide Bond Synthesis. *Nature* **2011**, *480*, 471.

[58] M. Hosseini-Sarvari, H. Sharghi, ZnO as a New Catalyst for N-Formylation of Amines under Solvent-Free Conditions. *J. Org. Chem.* **2006**, *71*, 6652-6654.

[59] A. Chandra Shekhar, A. Ravi Kumar, G. Sathaiah, V. Luke Paul, M. Sridhar, P. Shanthan Rao, Facile N-Formylation of Amines Using Lewis Acids as Novel Catalysts. *Tetrahedron Lett.* **2009**, *50*, 7099-7101.

[60] J.G. Kim, D.O. Jang, Indium-Catalyzed N-Formylation of Amines under Solvent-Free Conditions. *Synlett* **2010**, *2010*, 1231-1234.

[61] B.C. Ranu, P. Dutta, A Simple and Convenient Procedure for the Conversion of Esters to Secondary Amides. *Synth. Commun.* **2003**, *33*, 297-301.

[62] R. Arora, S. Paul, R. Gupta, A Mild and Efficient Procedure for the Conversion of Aromatic Carboxylic Esters to Secondary Amides. *Can. J. Chem.* **2005**, *83*, 1137-1140.

[63] C. Han, J.P. Lee, E. Lobkovsky, J.A. Porco, Catalytic Ester−Amide Exchange Using Group (IV) Metal Alkoxide−Activator Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 10039-10044.

[64] K. Ekoue-Kovi, C. Wolf, One-Pot Oxidative Esterification and Amidation of Aldehydes. *Chem. Eur. J.* **2008**, *14*, 6302-6315.

[65] Y. Suto, N. Yamagiwa, Y. Torisawa, Pd-Catalyzed Oxidative Amidation of Aldehydes with Hydrogen Peroxide. *Tetrahedron Lett.* **2008**, *49*, 5732-5735.

[66] M.A. Ali, T. Punniyamurthy, Palladium-Catalyzed One-Pot Conversion of Aldehydes to Amides. *Adv. Synth. Catal.* **2010**, *352*, 288-292.

[67] M. Saikia, L. Saikia, Palladium Nanoparticles Immobilized on an Amine-Functionalized Mil-101(Cr) as a Highly Active Catalyst for Oxidative Amination of Aldehydes. *RSC Adv.* **2016**, *6*, 14937-14947.

[68] H. Fujiwara, Y. Ogasawara, K. Yamaguchi, N. Mizuno, A One-Pot Synthesis of Primary Amides from Aldoximes or Aldehydes in Water in the Presence of a Supported Rhodium Catalyst. *Angew. Chem. Int. Ed.* **2007**, *46*, 5202-5205.

[69] A. Kanchanadevi, R. Ramesh, D. Semeril, Synthesis of Ru(II) Pyridoxal Thiosemicarbazone Complex and Its Catalytic Application to One-Pot Conversion of Aldehydes to Primary Amides. *Inorg. Chem. Commun.* **2015**, *56*, 116-119.

[70] G.L. Li, K.K.Y. Kung, M.K. Wong, Gold-Catalyzed Amide Synthesis from Aldehydes and Amines in Aqueous Medium. *Chem. Commun.* **2012**, *48*, 4112-4114.

[71] H. Miyamura, H. Min, J.F. Soulé, S. Kobayashi, Size of Gold Nanoparticles Driving Selective Amide Synthesis through Aerobic Condensation of Aldehydes and Amines. *Angew. Chem. Int. Ed.* **2015**, *54*, 7564-7567.

[72] B.-L. Jiang, B.-H. Xu, M.-L. Wang, Z.-X. Li, D.-S. Liu, S.-J. Zhang, Cobalt(II)/N,N′,N″-Trihydroxyisocyanuric Acid Catalyzed Aerobic Oxidative Esterification and Amidation of Aldehydes. *Asian J. Org. Chem.* **2018**, *7*, 977-983.

[73] W.-J. Yoo, C.-J. Li, Highly Efficient Oxidative Amidation of Aldehydes with Amine Hydrochloride Salts. *J. Am. Chem. Soc.* **2006**, *128*, 13064-13065.

[74] C. Qian, X. Zhang, Y. Zhang, Q. Shen, Heterobimetallic Complexes of Lanthanide and Lithium Metals with Dianionic Guanidinate Ligands: Syntheses, Structures and Catalytic Activity for Amidation of Aldehydes with Amines. *J. Organomet. Chem.* **2010**, *695*, 747-752.

[75] S. Seo, T. Marks, Mild Amidation of Aldehydes with Amines Mediated by Lanthanide Catalysts. *Org. Lett.* **2008**, *10*, 317 – 319.

[76] C.L. Allen, J.M.J. Williams, Metal-Catalysed Approaches to Amide Bond Formation. *Chem. Soc. Rev.* **2011**, *40*, 3405-3415.

[77] T. Naota, S.I. Murahashi, Ruthenium-Catalyzed Transformations of Amino Alcohols to Lactams. *Synlett* **1991**, *1991*, 693-694.

[78] K.I. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, Synthesis of Five-, Six-, and Seven-Membered Ring Lactams by Cp*Rh Complex-Catalyzed Oxidative N-Heterocyclization of Amino Alcohols. *Org. Lett.* **2004**, *6*, 2785-2788.

[79] C. Gunanathan, Y. Ben-David, D. Milstein, Direct Synthesis of Amides from Alcohols and Amines with Liberation of H_2. *Science* **2007**, *317*, 790-792.

[80] L.U. Nordstrøm, H. Vogt, R. Madsen, Amide Synthesis from Alcohols and Amines by the Extrusion of Dihydrogen. *J. Am. Chem. Soc.* **2008**, *130*, 17672-17673.

[81] Y. Zhang, C. Chen, S.C. Ghosh, Y. Li, S.H. Hong, Well-Defined N-Heterocyclic Carbene Based Ruthenium Catalysts for Direct Amide Synthesis from Alcohols and Amines. *Organometallics* **2010**, *29*, 1374-1378.

[82] S.C. Ghosh, S.H. Hong, Simple $RuCl_3$-Catalyzed Amide Synthesis from Alcohols and Amines. *Eur. J. Org. Chem.* **2010**, *2010*, 4266-4270.

[83] A.J.A. Watson, A.C. Maxwell, J.M.J. Williams, Ruthenium-Catalyzed Oxidation of Alcohols into Amides. *Org. Lett.* **2009**, *11*, 2667-2670.

[84] T. Zweifel, J.-V. Naubron, H. Grützmacher, Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines. *Angew. Chem.* **2009**, *121*, 567-571.

[85] K.-I. Shimizu, K. Ohshima, A. Satsuma, Direct Dehydrogenative Amide Synthesis from Alcohols and Amines Catalyzed by γ-Alumina Supported Silver Cluster. *Chem. Eur. J.* **2009**, *15*, 9977-9980.

[86] V.Y. Kukushkin, A.J.L. Pombeiro, Metal-Mediated and Metal-Catalyzed Hydrolysis of Nitriles. *Inorg. Chim. Acta* **2005**, *358*, 1-21.

[87] A. Goto, K. Endo, S. Saito, Rh(I)-Catalyzed Hydration of Organonitriles under Ambient Conditions. *Angew. Chem. Int. Ed.* **2008**, *47*, 3607-3609.

[88] C. Dash, M.M. Shaikh, R.J. Butcher, P. Ghosh, Highly Convenient Regioselective Intermolecular Hydroamination of Alkynes Yielding Ketimines Catalyzed by Gold(I) Complexes of 1,2,4-Triazole Based N-Heterocyclic Carbenes. *Inorg. Chem.* **2010**, *49*, 4972-4983.

[89] T. Hirano, K. Uehara, K. Kamata, N. Mizuno, Palladium(II) Containing γ-Keggin Silicodecatungstate That Efficiently Catalyzes Hydration of Nitriles. *J. Am. Chem. Soc.* **2012**, *134*, 6425-6433.

[90] B. Kang, Z. Fu, S.H. Hong, Ruthenium-Catalyzed Redox-Neutral and Single-Step Amide Synthesis from Alcohol and Nitrile with Complete Atom Economy. *J. Am. Chem. Soc.* **2013**, *135*, 11704-11707.

[91] H. Joshi, K.N. Sharma, A.K. Sharma, O. Prakash, A. Kumar, A.K. Singh, Magnetite Nanoparticles Coated with Ruthenium via Se-ph Layer as a Magnetically Retrievable Catalyst for the Selective Synthesis of Primary Amides in an Aqueous Medium. *Dalton Trans.* **2014**, *43*, 12365-12372.

[92] M.K. Rong, K. Van Duin, T. Van Dijk, J.J.M. de Pater, B.-J. Deelman, M. Nieger, A.W. Ehlers, J.C. Slootweg, K. Lammertsma, Iminophosphanes: Synthesis, Rhodium Complexes, and Ruthenium(II)-Catalyzed Hydration of Nitriles. *Organometallics* **2017**, *36*, 1079-1090.

[93] J.Otera, *Modern Carbonyl Chemistry*. Wiley-VCH: Weinheim: Germany, **2000**.

[94] B. Trost, The Atom Economy-a Search for Synthetic Efficiency. *Science* **1991**, *254*, 1471-1477.

[95] W.L. Budde, R.E. Dessy, The Homogeneously Catalyzed Hydration of Acetylenes by Mercuric Perchlorate-Perchloric Acid: Evidence for a *bis*-(Acetylene)-Mercuric Ion Complex as an Intermediate. *J. Am. Chem. Soc.* **1963**, *85*, 3964-3970.

[96] S.E. Denmark, T.K. Jones, (E)-3-(Trimethylsilyl)-2-Propen-1-Ol. An Improved Preparation. *J. Org. Chem.* **1982**, *47*, 4595-4597.

[97] K. Namba, H. Yamamoto, I. Sasaki, K. Mori, H. Imagawa, M. Nishizawa, $Hg(OTf)_2$-Catalyzed Arylene Cyclization. *Org. Lett.* **2008**, *10*, 1767-1770.

[98] Q. Dong, N. Li, R. Qiu, J. Wang, C. Guo, X. Xu, Silver-Containing Microemulsion as a High-Efficient and Recyclable Catalytic System for Hydration of Alkynes. *J. Organomet. Chem.* **2015**, *799-800*, 122-127.

[99] T.-F. Niu, D.-Y. Jiang, S.-Y. Li, X.-G. Shu, H. Li, A.-l. Zhang, J.-Y. Xu, B.-Q. Ni, Visible Light Promoted Copper-Catalyzed Markovnikov Hydration of Alkynes at Room Temperature. *Tetrahedron Lett.* **2017**, *58*, 1156-1159.

[100] T. Chen, C. Cai, Catalytic Hydration of Alkynes to Ketones by a Salen–Gold(III) Complex. *Catal. Commun.* **2015**, *65*, 102-104.

[101] M. Zeng, R.-X. Huang, W.-Y. Li, X.-W. Liu, F.-L. He, Y.-Y. Zhang, F. Xiao, In(OTf)$_3$/Acid Co-Catalyzed Hydration of 1-Haloalkynes to α-Halomethyl Ketones. *Tetrahedron* **2016**, *72*, 3818-3822.

[102] A. Labonne, T. Kribber, L. Hintermann, Highly Active in-Situ Catalysts for Anti-Markovnikov Hydration of Terminal Alkynes. *Org. Lett.* **2006**, *8*, 5853-5856.

[103] M. Bassetti, S. Ciceri, F. Lancia, C. Pasquini, Hydration of Aromatic Terminal Alkynes Catalyzed by Iron(III) Sulfate Hydrate under Chlorine-Free Conditions. *Tetrahedron Lett.* **2014**, *55*, 1608-1612.

[104] P. Mathur, R.K. Joshi, D.K. Rai, B. Jha, S.M. Mobin, One Pot Synthesis of Maleimide and Hydantoin by Fe(CO)$_5$ Catalyzed [2 + 2 + 1] Co-Cyclization of Acetylene, Isocyanate and CO. *Dalton Trans.* **2012**, *41*, 5045-5054.

[105] H. Kanemitsu, K. Uehara, S. Fukuzumi, S. Ogo, Isolation and Crystal Structures of Both Enol and Keto Tautomer Intermediates in a Hydration of an Alkyne−Carboxylic Acid Ester Catalyzed by Iridium Complexes in Water. *J. Am. Chem. Soc.* **2008**, *130*, 17141–17147.

[106] F. Alonso, I.P. Beletskaya, M. Yus, Transition-Metal-Catalyzed Addition of Hetero atom−Hydrogen Bonds to Alkynes. *Chem. Rev.* **2004**, *104,* 3079-3160.

[107] M. Beller, J. Seayad, A. Tillack, H. Jiao, Catalytic Markovnikov and Anti-Markovnikov Functionalization of Alkenes and Alkynes: Recent Developments and Trends. *Angew. Chem. Int. Ed.* **2004**, *43*, 3368-3398.

[108] L. Hintermann, A. Labonne, Catalytic Hydration of Alkynes and Its Application in Synthesis. *Synthesis* **2007**, *2007*, 1121-1150.

[109] K. Imi, K. Imai, K. Utimoto, Regioselective Hydration of Alkynones by Palladium Catalysis. *Tetrahedron Lett.* **1987**, *28*, 3127-3130.

[110] A. Arcadi, S. Cacchi, F. Marinelli, The Conversion of Vinyl Triflates into γ'-Hydroxy-α,β-Enones. *Tetrahedron* **1993**, *49*, 4955-4964.

[111] I.K. Meier, J.A. Marsella, Hydration of Acetylenic Compounds without Using Mercury. *J. Mol. Catal.* **1993**, *78*, 31-42.

[112] J. Tauchman, M.F.N.N. Carvalho, P. Štěpnička, Selective Hydration of Ferrocenylethyne Mediated by a Palladium Complex with a Camphor hydrazone Ligand. *Collect. Czech. Chem. Commun.* **2011**, *76*, 1277-1283.

[113] Z. Zhang, L. Wu, J. Liao, W. Wu, H. Jiang, J. Li, J. Li, Amide Oxygen-Assisted Palladium-Catalyzed Hydration of Alkynes. *J. Org. Chem.* **2015**, *80*, 7594-7603.

[114] I. Ojima, A.T. Vu, D. Bonafoux, *In Science of Synthesis*. Georg Thieme Verlag KG: **2001**; 531-616.

[115] Y.J. Park, B.-I. Kwon, J.-A. Ahn, H. Lee, C.-H. Jun, Chelation-Assisted Hydrative Dimerization of 1-Alkyne Forming α,β-Enones by an Rh(I) Catalyst. *J. Am. Chem. Soc.* **2004**, *126*, 13892-13893.

[116] A. Lumbroso, N.R. Vautravers, B. Breit, Rhodium-Catalyzed Selective Anti-Markovnikov Addition of Carboxylic Acids to Alkynes. *Org. Lett.* **2010**, *12*, 5498-5501.

[117] B.M. Trost, M. Portnoy, H. Kurihara, A Ru-Catalyzed Three-Component Addition to Form 1,5-Diketones. *J. Am. Chem. Soc.* **1997**, *119*, 836-837.

[118] P. Alvarez, J. Gimeno, E. Lastra, S. García-Granda, J.F. Van der Maelen, M. Bassetti, Synthesis and Reactivity of Indenyl Ruthenium(II) Complexes Containing the Labile Ligand 1,5-Cyclooctadiene (COD): Catalytic Activity of [Ru(η^5-C_9H_7)Cl(COD)]. *Organometallics* **2001**, *20*, 3762-3771.

[119] M. Tokunaga, Y. Wakatsuki, The First Anti-Markovnikov Hydration of Terminal Alkynes: Formation of Aldehydes Catalyzed by a Ruthenium(II)/Phosphane Mixture. *Angew. Chem. Int. Ed.* **1998**, *37*, 2867-2869.

[120] M. Tokunaga, Y. Wakatsuki, in: C. Abstr. (Ed.) JP Patent Japan, **1999**.

[121] T. Suzuki, M. Tokunaga, Y. Wakatsuki, Ruthenium Complex-Catalyzed Anti-Markovnikov Hydration of Terminal Alkynes. *Org. Lett.* **2001**, *3*, 735-737.

[122] T. Suzuki, M. Tokunaga, Y. Wakatsuki, in: C. Abstr. (Ed.) JP Patent Japan, **2002**.

[123] D.B. Grotjahn, C.D. Incarvito, A.L. Rheingold, Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-Markovnikov Hydration of Terminal Alkynes. *Angew. Chem.* **2001**, *113*, 4002-4005.

[124] T. Suzuki, M. Tokunaga, Y. Wakatsuki, Efficient Transformation of Propargylic Alcohols to α,β-Unsaturated Aldehydes Catalyzed by Ruthenium/Water under Neutral Conditions. *Tetrahedron Lett.* **2002**, *43*, 7531-7533.

[125] P. Alvarez, M. Bassetti, J. Gimeno, G. Mancini, Hydration of Terminal Alkynes to Aldehydes in Aqueous Micellar Solutions by Ruthenium(II) Catalysis; First Anti-Markovnikov Addition of Water to Propargylic Alcohols. *Tetrahedron Lett.* **2001**, *42*, 8467-8470.

[126] A. Labonne, T. Kribber, L. Hintermann, Highly Active in-Situ Catalysts for Anti-Markovnikov Hydration of Terminal Alkynes. *Org. Lett.* **2006**, *8*, 5853-5856.

[127] Y. Fukuda, K. Utimoto, Effective Transformation of Unactivated Alkynes into Ketones or Acetals with a Gold(III) Catalyst. *J. Org. Chem.* **1991**, *56*, 3729-3731.

[128] F. Yukitoshi, U. Kiitiro, Efficient Transformation of Methyl Propargyl Ethers into α,β-Unsaturated Ketones. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2013-2015.

[129] J.H. Teles, S. Brode, M. Chabanas, Cationic Gold(I) Complexes: Highly Efficient Catalysts for the Addition of Alcohols to Alkynes. *Angew. Chem. Int. Ed.* **1998**, *37*, 1415-1418.

[130] E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, Highly Efficient AuI-Catalyzed Hydration of Alkynes. *Angew. Chem.* **2002**, *114*, 4745-4747.

[131] R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, Organometallic Gold(III) Compounds as Catalysts for the Addition of Water and Methanol to Terminal Alkynes. *J. Am. Chem. Soc.* **2003**, *125*, 11925-11935.

[132] P. de Frémont, R. Singh, E.D. Stevens, J.L. Petersen, S.P. Nolan, Synthesis, Characterization and Reactivity of N-Heterocyclic Carbene Gold(III) Complexes. *Organometallics* **2007**, *26*, 1376-1385.

[133] N. Marion, R.S. Ramón, S.P. Nolan, [(NHC)Au(I)]-Catalyzed Acid-Free Alkyne Hydration at Part-Per-Million Catalyst Loadings. *J. Am. Chem. Soc.* **2009**, *131*, 448-449.

[134] X. Xu, S.H. Kim, X. Zhang, A.K. Das, H. Hirao, S.H. Hong, Abnormal N-Heterocyclic Carbene Gold(I) Complexes: Synthesis, Structure, and Catalysis in Hydration of Alkynes. *Organometallics* **2013**, *32*, 164-171.

[135] A. Leyva, A. Corma, Isolable Gold(I) Complexes Having One Low-Coordinating Ligand as Catalysts for the Selective Hydration of Substituted Alkynes at Room Temperature without Acidic Promoters. *J. Org. Chem.* **2009**, *74*, 2067-2074.

[136] F. Li, N. Wang, L. Lu, G. Zhu, Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot Synthesis of Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(R,R)-TsDPEN]. *J. Org. Chem.* **2015**, *80*, 3538-3546.

[137] S. Liang, J. Jasinski, G.B. Hammond, B. Xu, Supported Gold Nanoparticle-Catalyzed Hydration of Alkynes under Basic Conditions. *Org. Lett.* **2015**, *17*, 162-165.

[138] K.T. Venkateswara Rao, P.S. Sai Prasad, N. Lingaiah, Solvent-Free Hydration of Alkynes over a Heterogeneous Silver Exchanged Silicotungstic Acid Catalyst. *Green Chem.* **2012**, *14*, 1507-1514.

[139] M.B.T. Thuong, A. Mann, A. Wagner, Mild Chemo-Selective Hydration of Terminal Alkynes Catalysed by $AgSbF_6$. *Chem. Commun.* **2012**, *48*, 434-436.

[140] R. Das, D. Chakraborty, AgOTf Catalyzed Hydration of Terminal Alkynes. *Appl. Organomet. Chem.* **2012**, *26*, 722-726.

[141] Z.-W. Chen, D.-N. Ye, Y.-P. Qian, M. Ye, L.-X. Liu, Highly Efficient $AgBF_4$-Catalyzed Synthesis of Methyl Ketones from Terminal Alkynes. *Tetrahedron* **2013**, *69*, 6116-6120.

[142] S. Saha, A. Sarbajna, J.K. Bera, Bulky, Spherical, and Fluorinated Anion Barf Induces ‘on-Water’ Activity of Silver Salt for the Hydration of Terminal Alkynes. *Tetrahedron Lett.* **2014**, *55*, 1444-1447.

[143] J. Pierre Damiano, M. Postel, $FeCl_3.H_2O$: A Specific System for Arylacetylene Hydration. *J. Organomet. Chem.* **1996**, *522*, 303-305.

[144] P.O. Miranda, D.D. Díaz, J.I. Padrón, M.A. Ramírez, V.S. Martín, Fe(III) Halides as Effective Catalysts in Carbon−Carbon Bond Formation: Synthesis of 1,5-

Dihalo-1,4-Dienes, α,β-Unsaturated Ketones, and Cyclic Ethers. *J. Org. Chem.* **2005**, *70*, 57-62.

[145] X.-F. Wu, D. Bezier, C. Darcel, Development of the First Iron Chloride-Catalyzed Hydration of Terminal Alkynes. *Adv. Synth. Catal.* **2009**, *351*, 367-370.

[146] J.R. Cabrero-Antonino, A. Leyva-Pérez, A. Corma, Regioselective Hydration of Alkynes by Iron(III) Lewis/Brønsted Catalysis. *Chem. Eur. J.* **2012**, *18*, 11107-11114.

[147] J. Park, J. Yeon, P.H. Lee, K. Lee, Iron-Catalyzed Indirect Hydration of Alkynes in Presence of Methanesulfonic Acid. *Tetrahedron Lett.* **2013**, *54,* 4414-4417.

[148] T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **2013**, *135,* 50-53.

[149] Z. Lin, Z.-M. Zhang, Y.-S. Chen, W. Lin, Highly Efficient Cooperative Catalysis by Co^{III}(Porphyrin) Pairs inInterpenetrating Metal–Organic Frameworks. *Angew.Chem.Int.Ed.* **2016**, *55,* 1-6.

[150] S. Wang, C. Miao, W. Wang, Z. Lei, W. Sun, A Salen–Co^{3+} Catalyst for the Hydration of Terminal Alkynes and in Tandem Catalysis with Ru–TsDPEN for the One-Pot Transformation of Alkynes into Chiral Alcohols. *Chem. Cat. Chem.* **2014**, *6*, 1612-1616.

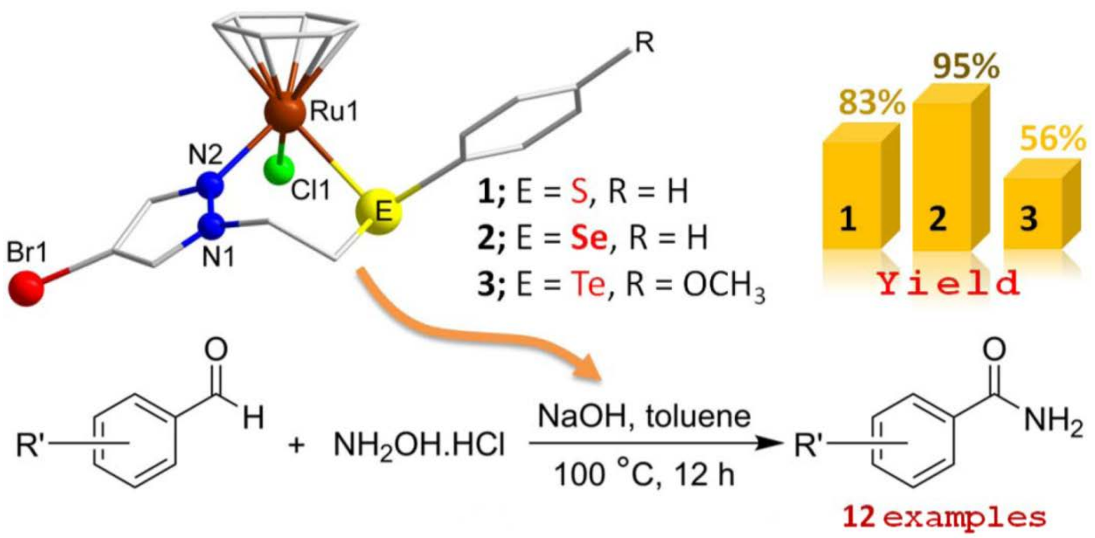
[151] J. Lu, J. Dimroth, M. Weck, Compartmentalization of Incompatible Catalytic Transformations for Tandem Catalysis. *J.Am. Chem. Soc.* **2015**, *137*, 12984-12989.

[152] S. Hou, H. Yang, B. Cheng, H. Zhai, Y. Li, Cobaloxime-Catalyzed Hydration of Terminal Alkynes without Acidic Promoters. *Chem. Commun.* **2017**, *53*, 6926-6929.

[153] N. Satrawala, K.N. Sharma, L.C. Matsinha, L. Maqeda, S. Siangwata, G.S. Smith, R.K. Joshi, Base-Catalyzed Cross Coupling of Secondary Alcohols and Aryl-Aldehydes with Concomitant Oxidation of Alcohols to Ketones: An Alternative Route for Synthesis of the Claisen-Schmidt Condensation Products. *Tetrahedron Lett.* **2017**, *58*, 2761-2764.

Chapter-2

(η^6-Benzene)Ru(II) Half-Sandwich Complexes of Pyrazolated Chalcogeno-ethers: Synthesis, Structure and Catalytic One-Pot Conversion of Aldehydes into Amides



2 .1 Introduction

Amides are amongst the most important organic compounds which have been extensively explored as synthetic building blocks in various organic transformations [1-3]. The presence of the amide functional group [4-9] as a key chemical connection in nitrogen containing biologically active compounds [10], various commercially available pharmaceutical drugs [11-13], and polymers [14, 15], is illustrated by the high prevalence of amide bond formation in synthetic chemistry. Classically, amides are synthesized by a stoichiometric reaction of carboxylic acid or its derivatives (halides, esters or anhydrides) with amines [16].The spontaneous formation of the amides is not possible through reacting these two functional groups at ambient temperature, because the essential water elimination step takes place at very high temperature (≥200 °C) [17]. The formation of undesired products and low atom economy in such a process restrict their employability in industrial applications. Hence, the development of advance atom-efficient catalytic methods for amide formation are highly desired in modern synthetic chemistry [18, 19]. In this context, several metal-catalyzed approaches for amide synthesis have been developed [20]. Many transition metal catalysts including scandium [21], nickel [22], copper [23-25], zinc [26], and palladium [27] have been reported for the catalytic transformation of aldehyde [24, 25, 27-30] or oxime [22, 23,28] into corresponding amide. Alumina-supported rhodium [31,32], titanosilicates loaded with rhodium [33], and $[Ir(Cp^*)Cl_2]_2$ [34] were found potential candidates for amide synthesis. However, the prime requisite of an inert atmosphere to handle the air-sensitive metal catalysts and harsh reaction conditions etc. are some of the major disadvantages of these protocols. Moreover, some functional groups do not withstand under such severe ambience and the selectivity of the desired product decreases. Moreover, the high catalyst loading and stoichiometric amount of additional reagents also produce the significant quantity of undesired products. Crabtree and Co-workers has developed a ruthenium complex of terpyridine based NNN type pincer ligand which efficiently carry out an additives free one-pot conversion of amide from aldehyde [35]. The prime goal of the present work is to develop an elegant and more efficient method for one-pot synthesis of amide from aldehyde which can effectively reduce the formation of hazardous wastage and use of detrimental additive reagents. The present ruthenium catalysts are economically better as compare to the reported Rh/Ir/Pd metals catalysts for amide transformations. The half sandwich ruthenium(II) complex of terdentate N-heterocyclic organo-chalcogen ligands had shown promising catalytic activity in various catalytic reactions such as asymmetric catalysis and hydration of nitrile [36, 37], transfer hydrogenation of ketones and oxidation of alcohols [38, 39]. The promising catalytic potential of various metal complexes of pyrozole containing ligands has been already proven explicitly in various earlier reports [40-48]. The strong donor properties of chalcogen ligands make them suitable candidates for catalysis of organic transformations [49-56]. Apart from efficiency, organochalcogen based catalytic systems are quite attractive due to their insensitivity towards the air and moisture, good solubility in various organic solvents and high stability in organic solutions. The catalytic strength of metal complexes of organochalcogen ligands for this particular transformation has not been investigated so far. Also, to the best in our knowledge, we are the first to report the ruthenium complexes of pyrazole-based organochalcogen ligands. Therefore, moving towards the ligand chemistry and application potential of N-heterocycles containing chalcogenated ligand, we have synthesised three new and novel mononuclear Ru(II) half-sanwich complexes of pyrazole based organochalcogen ligands and investigated their catalytic potential for aldehyde to amide transformation. The comparative study of the catalytic efficiency of these three complexes has also been investigated. Moreover, the present catalytic systems do not require any hazardous additives, and convert the aldehyde into the corresponding amide in good to excellent amount underaerobic reaction conditions.

2.2 Experimental

2.2.1 Materials and reagents

4-Bromopyrazole, phenyl diselenide, thiophenol, sodium borohydride, ruthenium chloride, ammonium hexafluorophosphate were procured from Sigma-Aldrich (USA), and used as received. Bis(4-methoxyphenyl) ditelluride, **L1**, **L2** and **L3** were prepared by previously reported methods [46, 47]. Prior to their use, all the solvents were dried and distilled by standard procedures [57]. The common chemicals and reagents which are available commercially within the country were used as received.

2.2.2 Synthesis of complexes [(η^6-C_6H_6)Ru(L1/L2/L3)Cl].PF_6 (1-3)

Brick red solid [Ru(η^6-C_6H_6)Cl_2]$_2$(0.050 g, 0.1 mmol) was added to a solution of **L1** (0.057 g, 0.2 mmol) / **L2** (0.066 g, 0.2 mmol) / **L3** (0.082 g, 0.2 mmol) prepared in 25 mL of methanol and resulting reaction mixture was stirred for 12 h at ambient temperature. The resulting reaction mixture was filtered, and the volume of the filtrate was reduced to 5 mL at the rotary evaporator. It was mixed with solid NH_4PF_6 (0.032 g, 0.2 mmol) and further stirred at room temperature for 3h. The resulting precipitated solid was filtered, washed with 5 mL of ice-cold methanol, and dried in vacuo. Single crystals of complexes **2** and **3** were obtained by slow evaporation of a saturated methanolic solution of the 2 and 3.

2.2.3 Procedure for the catalytic reaction

In an oven-dried 100 mL two-neck round bottom flask, a mixture of aryl-aldehyde (1.0 mmol), $NH_2OH.HCl$ (1.0 mmol), NaOH (1.0 mmol), catalyst (0.1mol%) and solvent (5 ml) were heated at 100 °C with continuous stirring for 12 h in air. The progress of the reaction was continuously monitored by TLC until the maximum conversion of the desired product observed. After completion, the reaction mixture was cooled to room temperature and extracted in ethyl acetate (2 × 25 mL). This extract was further washed with water and dried over anhydrous Na_2SO_4. The product was purified by column chromatography after removing the solvent on a rotary evaporator under reduced pressure. All the desired products obtained as white solids were further authenticated by HR-MS, ^{1}H, and ^{13}C NMR spectroscopy.

2.2.4 Instrumentation

2.2.4.1 Melting point determination

The melting points of all synthesized compounds were determined in an electrically heated melting point apparatus (accuracy ± 2°C) by taking the sample in a glass capillary sealed at one end and are reported as such.

2.2.4.2 Nuclear Magnetic Resonance Spectroscopy

Multinuclear NMR spectra were recorded by using JEOL ECS-400 spectrometer (operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C).

2.2.4.3 Infra-red Spectroscopy

IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin Elmer 10.4.00 FT-IR spectrometer as KBr pellets of the sample.

2.2.4.4 High Resolution Mass Spectrometry

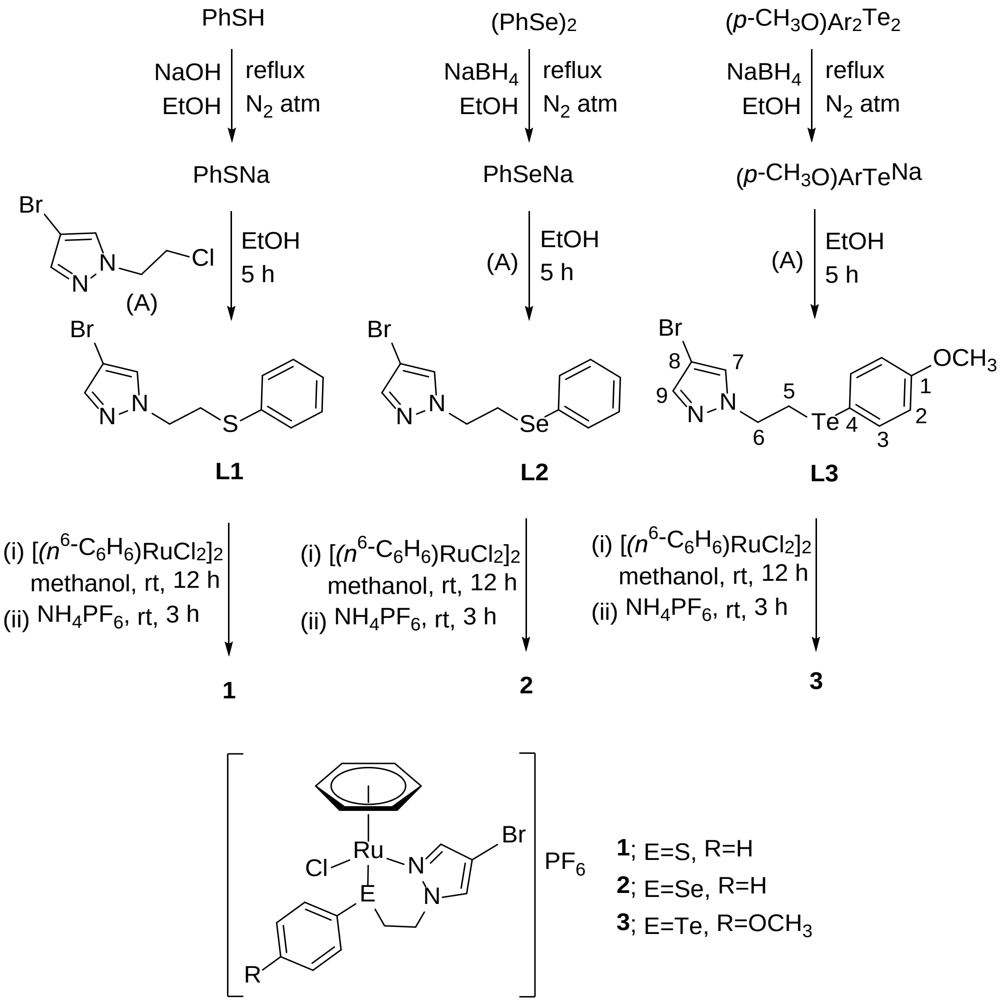
High resolution electron Impact Mass spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA) with the use of appropriate spectroscopy grade solvent.

2.3.4.5 Single-Crystal XRD Studies

The diffraction data were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo−*K*α radiations (0.71073 Å) at 298 (2) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements [58-60]. All non–hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The least–squares refinement cycles on F^2 were performed until the model converged. The CIF containing supplementary material *i.e.*, atomic coordinates and anisotropic displacement parameters and hydrogen coordinates etc.

2.3 Results and discussion

The systematic methodology adopted for the synthesis of Ru(II) complexes (**1-3**) is illustrated in Scheme 1. The previously reported methods [46, 61] were used to prepare the pyrazole based thio/seleno/telluro-ether functionalized bidentate ligands (**L1-L3)**. Three new half-sandwich (η^6-benzene)ruthenium(II) complexes (**1**-**3**) were synthesized by reacting $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with a methanolic solution of **L1**/**L2**/**L3** under ambient reaction conditions. All the complexes were characterized by using the NMR, Mass spectrometry and FT-IR techniques. The NMR and mass spectra of complexes **1**-**3** have been provided in a Compact Disc (CD) appended at the end of the thesis. Which were found to be consistent with their molecular structures illustrated in Scheme 1.



Scheme 1: Synthesis of half-sandwich (η^6-benzene)ruthenium(II) complexes **1**-**3**.

Due to the low solubility of **1**-**3** in $CDCl_3$, their NMR spectra were recorded in CD_3CN. As compared to the corresponding free ligands [46, 61], the deshielded NMR signals appeared in ^{1}H and ^{13}C spectra of **1**-**3** at 0.9 ppm and 8.6 ppm, respectively, corroborating the coordination of ligand with Ru(II) in a bidentate chelate mode.The four methylene protons (each H_5 and H_6 group) of –N–CH_2–CH_2–E– part of chelate ring were recorded as four multiplets in ^{1}H NMR spectra of complex **1**-**3**, which confirmed their diastereotopic nature which is arisen due to the rigid conformation of the coordinated ligand and inherent chirality associated with the asymmetric molecular structure of each of the three Ru complexes. Moreover, in ^{13}C NMR spectra, signals of C_9, C_6 and C_5 were found more deshielded relative to those of other carbon atoms of the complex. The protons attached to these carbons also appeared somewhat more deshielded than other protons present in the complexes. The high magnitude shift for these carbon atoms and proton is probably due to their closeness to the chalcogen donor atoms (N and S/Se/Te). Additionally, ^{1}H and ^{13}C NMR of each of the complexes **1**-**3** show a typical resonance (most intense signal) for six protons and carbons of η^6-benzene in the range of 5.59-5.90 ppm and 86.2-87.3 ppm, respectively which is in close agreement with the earlier reported half-sandwich ruthenium complex of η^6-benzene [62].The intense mass peaks at (*m*/*z*) 496.9025, 544.8474 and 624.8472 appeared in mass spectra of **1**, **2** and **3**, respectively, are attributable to $[M{-}PF_6]^+$ cations in each of the three complexes.

2.3.1 Crystal structures

The solubility of complexes **1-3** were found to be good in acetonitrile, DMF and DMSO, while close to negligible in dichloromethane, chloroform and methanol, and completely insoluble in diethyl ether and *n*-hexane. The suitable quality single crystals of complexes **2** and **3** were grown by slow evaporation of their saturated solution in acetonitrile/methanol (1:1) and subjected to analysis through single crystal X-ray crystallography. The thermal ellipsoid diagrams of **2** and **3** are depicted in figures 1 and 2 with some selected bond lengths and bond angles. Additional parameters are provided in Table 1. The bidentate coordination of ligand through N of pyrazole ring and Se/Te with Ru results in the formation of a six membered chelate ring in each case. In the cation of each complex, Ru adopts a pseudo-octahedral half-sandwich “pianostool” geometry. The observed bond lengths for Ru-Se and Ru-Te bonds in **2** and **3**, are 2.511 Ǻ and 2.648 Ǻ, respectively, which falls in the range of previously reported ruthenium complexes [38, 63].

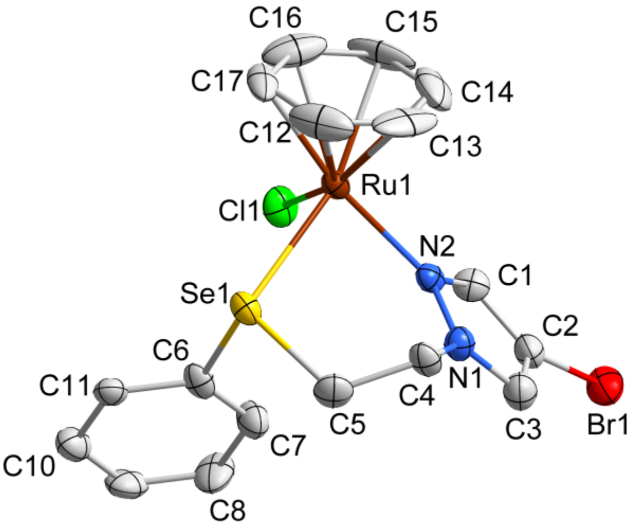


Figure 1: The molecular structure of **2** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity. Bond lengths (Å): Ru(1)–N(2)2.105(11), Ru(1)–Se(1) 2.5106(17); Bond angles (°): N(2)–Ru(1)–Se(1) 87.0(3), Se(1)–Ru(1)–Cl(1) 91.59(11).

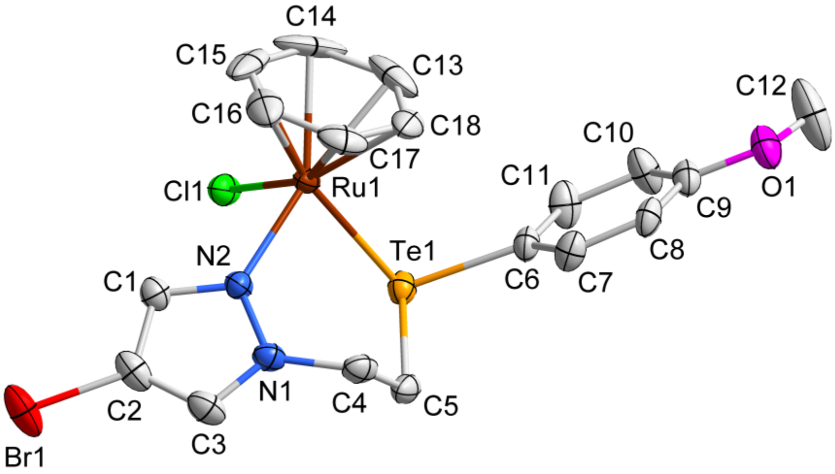


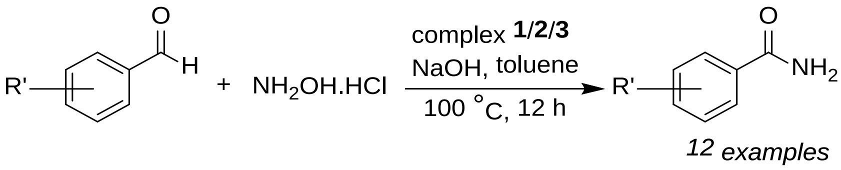
Figure 2: The molecular structure of **3** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity. Bond lengths (Å): Ru(1)–N(2)2.105(5), Ru(1)–Te(1) 2.6486(10); Bond angles (°): N(2)–Ru(1)–Te(1) 86.0(17), Te(1)–Ru(1)–Cl(1) 81.6(6).

Table 1 Crystal data and structural refinement parameters for 2 and 3

Compound	Complex **2**	Complex **3**
Empirical formula	$C_{17}H_{17}BrClN_2RuSe$**.** PF_6	$C_{18}H_{19}BrClN_2ORuTe$**.** PF_6
Formula Wt.	689.68	768.34
Crystal size [mm]	0.31×0.25×0.21	0.29×0.28×0.22
Crystal system	Triclinic	Monoclinic
Space group	P1	$P2_1/n$
Unit cell dimension	a = 7.583(2)Å b = 7.862(2)Å c = 9.861(3)Å α = 102.363(5)° β = 101.494(5)° γ = 91.189(5)°	a = 10.808(4)Å b = 10.070(4)Å c = 22.907(9)Å α = 90.00° β = 98.559(7)° γ = 90.00°
Cell volume [$Å^3$]	561.5(3)	2465.6(17)
Z	1	4
Density (Calc.) [$Mg{\cdot}m^{-3}$]	2.040	2.070
Absorption coeff. [mm^{-1}]	4.344	3.649
F(000)	332	1464
θ Range [°]	3.030–24.998	2.21–25.14
Index ranges	$-8 \le h \le 9$ $-9 \le k \le 9$ $-11 \le l \le 11$	$-12 \le h \le 12$ $-11 \le k \le 11$ $-27 \le l \le 27$
Reflections collected	5359	19039
Independent reflections ($R_{int.}$)	3964 (0.0319)	4064(0.1195)
Max./Min. transmission	0.405/0.247	0.451/0.331
Data/Restraints/Parameters	3874/0/271	4064/0/290
Goodness-of-Fit on F^2	1.003	1.017
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0525, wR_2 = 0.1044	R_1 = 0.0524, wR_2 = 0.1185
R Indices (All Data)	R_1 = 0.0601, wR_2 = 0.1083	R_1 = 0.0833, wR_2 = 0.1331
Largest diff. peak/Hole [$e.Å^{-3}$]	0.786/–0.621	1.134/–1.485

2.3.2 Evaluation of the catalytic potential of Ru(II) complexes (1-3) for amide synthesis

Previously, the half-sandwich Ru(II) complexes have been found to be promising candidates for the catalysis of various organic transformations including conversion of aldehyde to amides which were traditionally achieved by the reaction of carboxylic acid or its derivatives (anhydrides, esters or halides) with amines at high temperature [16, 17]. In this context, metal-based homogeneous [20-25] as well as heterogeneous [31-33] catalysts have been developed. Most of the methods suffer from several disadvantages like the requirement of inert atmosphere, high catalyst loading, a stoichiometric amount of additional reagents, harsh reaction conditions etc. which all are detrimental to the integrity of the substrate. Therefore, for the employment of the strong σ-donor properties of soft chalcogen donor sites of N-heterocycles based organo-chalcogen ligands, insensitivity of their metal complexes towards the air and moisture, the catalytic activity of current Ru(II) complexes (**1**-**3**) was explored for conversion of aryl aldehydes to corresponding amides (Scheme 2).



Scheme 2: Aldehyde to amide transformation catalyzed with **1**-**3**.

All three complexes were found to be highly efficient at the 0.1 mol% loading of catalyst at 100 °C under the aerobic conditions. Moreover, the present catalytic reaction does not demand any hazardous additives and produce the amides in good to excellent yields without generating any by-products. For the optimizations of reaction parameters, initially, the benzaldehyde was chosen as a model substrate and a series of the reactions using the ruthenium complexes **1**, **2** and **3** as catalyst were performed (Table 2& 3).

Table 2 Optimization of the base, solvent and temperature for aldehyde to amide transformation.

Entry	Base	Solvent	Temp. (˚C)	Yield[a] (%)
1	NaOH	Toluene	100	95
2	NaOH	THF	100	83
3	NaOH	Acetonitrile	100	45
4	NaOH	1,4-dioxane	100	25
5	NaOH	Water	100	Nd
6	NaOH	DMF	100	Nd
7	$NaHCO_3$	Toluene	100	80
8	KOH	Toluene	100	40
9	K_2CO_3	Toluene	100	50
10	Cs_2CO_3	Toluene	100	10
11	Base free	Toluene	100	Nd
12	K^tOBu	Toluene	100	Nd
13	NaOH	Toluene	80	17
14	NaOH	Toluene	Rt	Nd

Reaction Conditions:Aldehyde (1.0 mmol, 0.106 g), $NH_2OH.HCl$ (1.0 mmol, 0.064 g), catalyst **2** (0.1 mol%), base (1.0 mmol.), solvent (5 ml), time (12 h), nd (not detected), [a] isolated yields after purification.

The maximum conversion of aldehyde to amides was obtained with the use of 0.1 mol% amount of the catalyst, while below to 0.1 mol%, the yield of the desired product was significantly reduced. Moreover, the continuous increase in mol% of the catalyst (0.1 to 0.5) does not help further to improve the yield of the desired product. Furthermore, during the solvent optimization, the highest yield of product was obtained in toluene (Table 2, Entry 1). The desired product was also produced when solvents including the THF, acetonitrile and 1, 4-dioxane were used (Table 2, Entry 2-4), but yield of the desired product was substantially reduced. Water and DMF were also checked as solvent but the reaction was not initiated and failed to produce the desired product (Table 2, Entry 4-5). The effect of various bases was also investigated, the highest yield (95%) of benzamide was obtained with NaOH (Table 2, Entry 1). Other bases including the $NaHCO_3$, KOH, K_2CO_3 and Cs_2CO_3 afforded relatively low yield of desired product 80%, 40%, 50% and 10%, respectively (Table 2, Entries 7-10). It was also noticed that the reaction did not produce any product in the absence of base (Table 2, Entry 11). Hence, careful selection of the base is a prime requisite for the present transformation reaction. Furthermore, the highest yield of the amide was obtained at 95-100 ˚C temperature. The drastic changes in the yield were observed when the temperature was reduced to 80 ˚C (Yield 17%, Table 2, entry 13), and further lowering the temperature of the reaction failed to bring the desired transformations (Table 2, entry 14).

Figure 3 shown below represents the time profile of the catalytic reaction of model substrate producing benzamide under optimized rection conditions. The initial formation of the desired compound was detected after 4 h. A continuous increase in the yield was observed with time and after 12 h the yield of the reaction was found to be constant (95%).

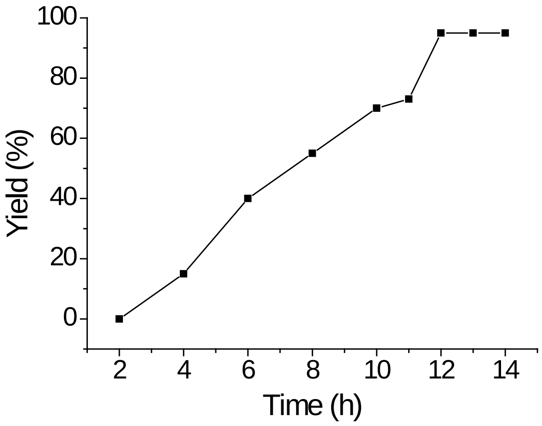
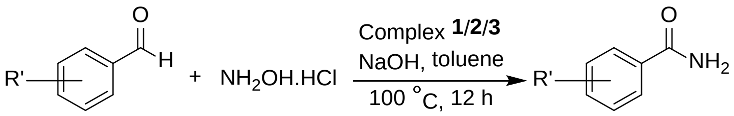


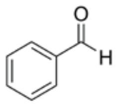
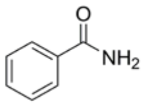
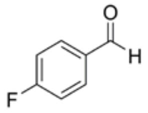
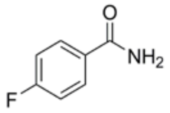
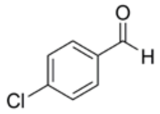
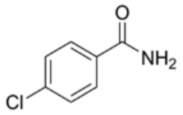
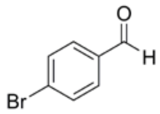
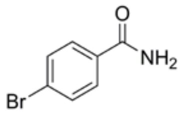
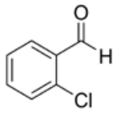
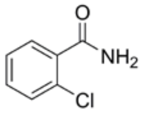
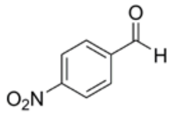
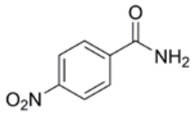
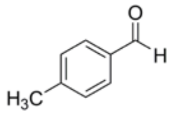
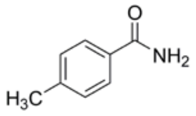
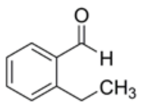
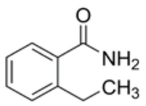
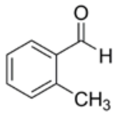
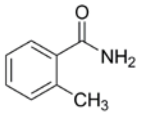
Figure 3: Time profile of the synthesis of benzamide using complex **2** as a catalyst.

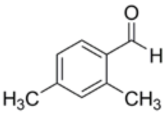
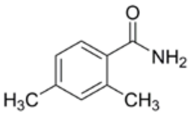
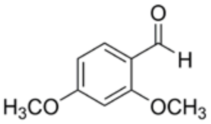
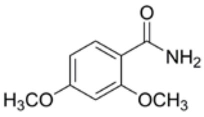
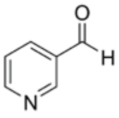
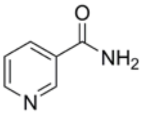
In order to check the wide scopes of the reaction, various functionally different aldehydes were used under the optimized reaction conditions and the reaction was completely generalized on wide range of substrate scope (Table 3). A One pot methodology for the synthesis of the primary amides from various aldehydes was developed by using the Ru(II) complexes (**1-3**). It seems that the substituent present on the aromatic ring of benzaldehyde does not affect the formation of the product. However, some minor differences in the product's yields were observed.

The catalytic activity of **1**, **2** and **3** was found to be in the order of **2** (Se)>**1** (S) >**3** (Te). Such variations are arisen due to the difference in the σ-donor properties of S/Se/Te as the other donor sites (N of pyrazole moiety of **L1-L3)** are common in all the three complexes. A similar trend of catalytic activity for Pd complexes of S/Se/Te donor analogues ligands towards the C-C coupling reaction has also been reported by Singh and Co-workers [64]. An another Pd(II) complex with Te ligand [65] has also been reported which had shown much lower catalytic efficiency than the S/Se analogues [66, 67]. The high catalytic activity of the selenium based ligand over the sulphur analogue for transfer hydrogenation has also been established through the experimental as well as the theoretical calculations by Singh and Co-workers [68].The catalytic studies on the Se based systems [67, 69, 70] have been indicated the excellent reactivity of selenium towards catalytic reactions [67] and sometimes, Se based systems had shown their outperformance to the phosphine based analogue [71]. The lower catalytic activity of present Te containing Ru complex is probably due to the steric effect of large size of Te which causes a lower electronic charge density accumulation over the central metal atom [64].

Table 3 Aldehyde to amide transformations using **1**, **2** and **3** as the catalyst.



Entry	Substrate	Product	Yield[a] (%)		
			1	**2**	**3**
1			83	95	56
2			80	89	50
3			86	91	47
4			84	94	59
5			80	93	58
6			85	90	48
7			82	88	45
8			82	85	42
9			81	94	42

10			89	92	41
11			86	94	47
12			84	91	35

Reaction Conditions: Aldehyde (1.0 mmol), $NH_2OH.HCl$ (1.0 mmol), catalyst (0.1 mol%), NaOH (1.0 mmol), toulene (5 ml), time (12 h), temperature (100 ˚C), [a] Isolated Yield.

2.3.3 Plausible reaction mechanism

Based on the available literature evidence for such metal catalyzed reactions [31, 72,73], the proposed mechanistic pathway for the present ruthenium catalyzed transformation of aldehyde to amide is depicted in figure 4. Here, it is assumed that, the OH group of aldoxime which is generated in-situ from the reaction of aldehyde and hydroxyl amine hydrochloride in the presence of base [35], coordinates to the ruthenium(II) catalyst (**1**/**2**/**3**) to form (η^6-C_6H_6)Ru(**L**)(−O−N=CHR') species **I** together with the elimination of HCl (step 1). In the next step, species **I** eliminates the nitrile and resulted the intermediate (**II**) [(η^6-C_6H_6)Ru(**L**)(OH)] [73]. The simultaneous nucleophilic attack of nitrile over the coordinated hydroxide resulted a ruthenium iminolate species(**III**) in step 3 [31, 72]. Under similar reaction conditions, the formation of benzamide was also noted when benzonitrile was directly used as a substrate with Ru catalyst (**2**). This experiment further strengethen and confirmed the reaction proceed through a nitrile intermediate. Finally, in step 4, the hydrolysis of the ruthenium iminolate species (**III**) leads to the regeneration of the catalyst with concomitant formation of the final product.

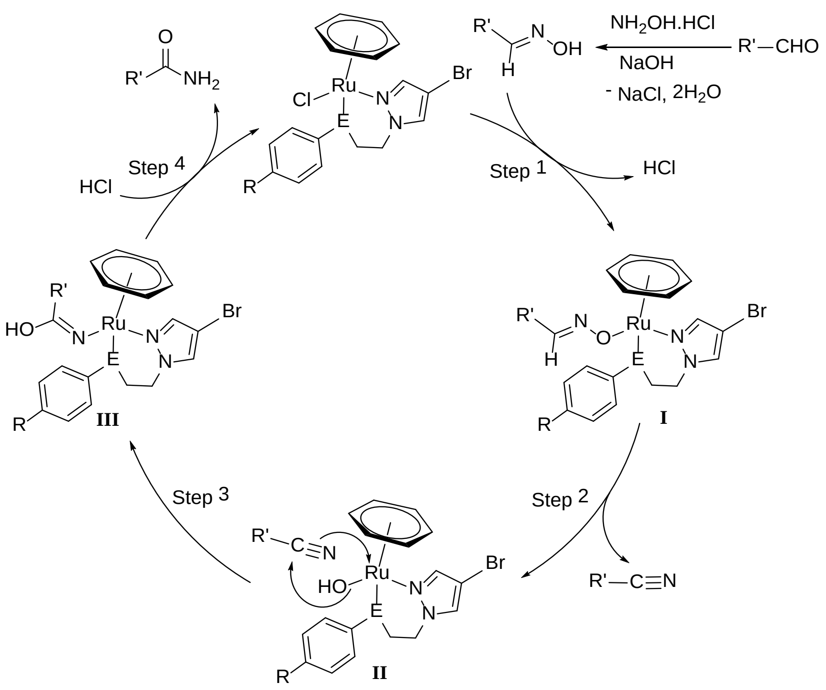


Figure 4: A plausible mechanism for aldehyde to amide transformation catalyzed with **1**/**2**/**3**. PF_6 Counter anion is omitted for clarity in each step.

2.3.4 Comparison of catalytic efficiency of present Ru catalysts (1-3) with previously reported catalytic systems for aldehyde to amide transformations

The catalytic transformation of aldehydes to amides with the present Ru(II) complexes **1**/**2**/**3** is quite efficient in terms of catalyst loading, reaction time, reaction temperature and use of additives in comparison to reported metal-based catalysts for amide synthesis [22, 34, 74, 75]. The first metal catalyzed transformation of aldoximes to amides was carried out in xylene at high temperature (138 °C) with a high catalyst loading of nickel acetate (5.6 mol%). Moreover, the formation of by-products was also observed during the catalytic process [22]. The iridium catalyst $[Ir(Cp^*)Cl_2]_2$ [34] has also been used for the amide synthesis with a higher catalyst loading (2.5 mol %). Williams and co-workers [74] have also reported a Ru catalyst that catalyzed the rearrangement of aldoximes to amides, but *p*-toluenesulfonic acid as an additive was used, and a considerable amount of nitrile was also obtained with amides. Crabtree and co-workers reported the ruthenium catalyst based on NNN pincer ligand $[terpyRu(PPh_3)Cl_2]$, which was found to be effective in the catalysis of aldehyde to amide transformation in 17 h. The maximum yields were observed when an additive $NaHCO_3$was used with1.0 mol% of catalyst loading. Moreover, a

η^6-arene-ruthenium(II) complex [RuCl$_2$(η^6-C$_6$Me$_6$){P(NMe$_2$)$_3$}] has also been established [75] as an effective catalyst for aldoxime to primary amides in the water at 100 °C with high catalyst loading (5 mol%). The present ruthenium half-sandwich complexes (**1-3**) show in execllent amide formation in 12h with 0.1 mol% of Ru catalyst under the aerobic reaction conditions, therefore, can be considered highly effective in the catalysis of aldehyde to amide transformation.

2.3.5 Supplementary data

Complex 1.Yellow solid, Yield: 0.096 g, 75%. mp: 195 °C. **^{1}H NMR (400 MHz, CD$_3$CN)**δ (ppm): 8.08 (s, 1H, H$_9$), 7.89 (s, 1H, H$_7$), 7.63-7.46 (m, 5H, H$_{1\text{-}3}$), 5.92 (s, 6H, η^6-C$_6\underline{H}_6$), 4.83-4.78 (m, 1H, H$_6$), 4.46-4.35 (m, 1H, H$_6$), 3.45-3.42 (m, 1H, H$_5$), 2.98-2.92 (m, 1H, H$_5$). **^{13}C NMR (100 MHz, CD$_3$CN)** δ (ppm): 148.5 (C$_9$), 136.7 (C$_7$), 130.8 (C$_3$), 130.6 (C$_2$), 129.7 (C$_1$), 125.9 (C$_4$), 93.7 (C$_8$), 86.2 (η^6-$\underline{C}_6$H$_6$), 49.9 (C$_6$), 34.5 (C$_5$). HR-MS (CH$_3$CN) [M−PF$_6$]$^+$ (*m/z*) Found: 496.9025; Calc. value for [C$_{17}$H$_{17}$BrClN$_2$RuS]$^+$: 496.9028. FT-IR (KBr, ν_{max}/cm^{-1}): 3093 (m, $\nu_{\text{C–H aromatic}}$), 2926 (m, $\nu_{\text{C–H aliphatic}}$), 1579 (m, $\nu_{\text{C=N aromatic}}$), 1440 (s, $\nu_{\text{C=C aromatic}}$), 1303 (m, $\nu_{\text{C–N aliphatic}}$), 823 (s, $\nu_{\text{C–H aromatic, bending}}$).

Complex 2.Yellow solid, Yield: 0.099 g, 72%. mp: 190 °C. **^{1}H NMR (400 MHz, CD$_3$CN)** δ (ppm): 8.08 (s, 1H, H$_9$), 7.90 (s, 1H, H$_7$), 7.79-7.76 (m, 2H, H$_3$), 7.62-7.60 (m, 3H, H$_1$ and H$_2$), 5.59 (s, 6H, η^6-C$_6\underline{H}_6$), 5.11-5.05 (m, 1H, H$_6$), 4.57-4.51 (m, 1H, H$_6$), 3.34-3.29 (m, 1H, H$_5$), 3.02-2.95 (m, 1H, H$_5$). **^{13}C NMR (100 MHz, CD$_3$CN)** δ (ppm): 148.3 (C$_9$), 136.8 (C$_7$), 132.2 (C$_3$), 130.8 (C$_2$), 129.1 (C$_1$), 124.8 (C$_4$), 93.8 (C$_8$), 87.3 (η^6-$\underline{C}_6$H$_6$), 52.0 (C$_6$), 29.0 (C$_5$).HR-MS (CH$_3$CN) [M−PF$_6$]$^+$ (*m/z*) Found: 544.8474; Calc. value for [C$_{17}$H$_{17}$BrClN$_2$RuSe]$^+$: 544.8472. FT-IR (KBr, ν_{max}/cm^{-1}): 3098 (m, $\nu_{\text{C–H aromatic}}$), 2958 (m, $\nu_{\text{C–H aliphatic}}$), 1574 (m, $\nu_{\text{C=N aromatic}}$), 1437 (s, $\nu_{\text{C=C aromatic}}$), 1299 (m, $\nu_{\text{C–N aliphatic}}$), 834 (s, $\nu_{\text{C–H aromatic, bending}}$).

Complex 3.Yellow solid, Yield: 0.114 g, 74%. mp: 193 °C. **^{1}H NMR (400 MHz, CD$_3$CN)** δ (ppm): 8.10 (s, 1H, H$_9$), 7.89 (s, 1H, H$_7$), 7.72 (d, $^{3J}{}_{\text{H–H}}$ = 6.6 Hz, 2H, H$_3$), 7.12 (d, $^3J_{\text{H–H}}$ = 6.7 Hz, 2H, H$_2$), 5.60 (s, 6H, η^6-C$_6\underline{H}_6$), 5.33-5.29 (m, 1H, H$_6$), 4.53-4.46 (m, 1H, H$_6$), 3.85 (s, 3H, OC$\underline{H}_3$), 3.03-2.99 (m, 1H, H$_5$), 2.92-2.85 (m, 1H, H$_5$). **^{13}C NMR (100 MHz, CD$_3$CN)** δ (ppm): 161.9 (C$_4$), 148.2 (C$_9$), 136.0 (C$_3$), 128.4 (C$_7$), 116.5 (C$_2$), 103.1 (C$_1$), 93.5 (C$_8$), 87.3 (η^6-$\underline{C}_6$H$_6$), 55.4 (O$\underline{C}$H$_3$), 53.2 (C_6), 13.0 (C_5). HR-MS (CH_3CN) $[M-PF_6]^+$ (*m/z*) Found: 624.8472; Calc. value for $[C_{18}H_{19}BrClN_2ORuTe]^+$: 624.8475.FT-IR (KBr, ν_{max}/cm^{-1}): 3087 (m, $\nu_{C-H\ aromatic}$), 2958 (m, $\nu_{C-H\ aliphatic}$), 1580 (m, $\nu_{C=N\ aromatic}$), 1491 (s, $\nu_{C=C\ aromatic}$), 1297 (m, $\nu_{C-N\ aliphatic}$), 822 (s, $\nu_{C-H\ aromatic\ (bending)}$).

1. Benzamide[27]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm): 7.84 – 7.81 (m, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.43 (m, 2H), 6.31 (br s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm): 169.68, 133.32, 131.95, 128.58, 127.29.

2. 4-Fluorobenzamide[27]

White Solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 – 7.72 (m, 2H), 6.95 – 6.88 (m, 2H), 6.39 (br s, 1H), 4.11 (br s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6)** δ 168.39, 165.82, 163.31, 129.95 (d, J = 8.9 Hz), 129.59, 115.18, 114.97.

3. 4-Chlorobenzamide[27]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm): 8.32 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 7.99 (d, 8.6 Hz, 2H), 6.13 (br s, 1H), 5.83 (br s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6)** δ (ppm): 167.01, 149.30, 139.22, 128.68, 123.22.

4. 4-Bromobenzamide[27]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm): 7.69 (d, 2H, $^3J_{H-H}$ = 8.5 Hz), 7.60 (d, 2H, $^3J_{H-H}$ = 8.5 Hz), 6.02 (br s, 1H), 5.81 (br s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6)** δ (ppm) 166.94, 133.40, 131.26, 129.62, 125.04.

5. 2-Chlorobenzamide[27]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm): 7.77 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, 1.6 Hz), 7.46 – 7.32 (m, 3H), 6.41 (br s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm): 168.24, 133.76, 131.78, 130.77, 130.59, 130.36, 127.12.

6. 4-Nitrobenzamide[34]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm): 7.84 – 7.75 (m, 2H), 7.53 – 7.43 (m, 2H), 6.03 (br s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6)** δ (ppm): 168.12, 137.42, 131.87, 128.84, 128.24.

7. 4-Methylbenzamide[27]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.42 (br s, 1H), 4.19 (br s, 1H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6)** δ 169.60, 142.25, 129.92, 128.88, 127.40, 21.22

8. 2-Ethylbenzamide[76]

^{1}H NMR (400 MHz, $CDCl_3$)δ 8.16 (dd, J = 7.8, 1.9 Hz, 1H), 7.88 (br s, 1H), 7.40 (ddd, J = 8.4, 7.4, 1.9 Hz, 1H), 7.05 – 6.977 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**δ 167.83, 157.47, 133.43, 132.39, 121.05, 120.77, 112.39, 64.76, 14.87.

9. 2-Methylbenzamide[77]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)**δ (ppm): 7.45 (d, 1H $^{3}J_{H–H}$ = 7.6 Hz), 7.35 – 7.32 (m, 1H), 7.25 – 7.19 (m, 2H), 6.20 (br s, 1H), 5.85 (br s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**δ (ppm): 172.19, 136.28, 135.15, 131.17, 130.24, 126.91, 125.70, 19.95.

10. 2,4-Dimethylbenzamide[78]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm): 7.37 (d, 1H, $^{3}J_{H–H}$ = 7.7 Hz), 7.05 (s, 1H), 7.02 (d, 1H, $^{3}J_{H–H}$ = 7.8 Hz), 5.95 (br s, 1H), 5.79 (br s, 1H), 2.47 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm): 172.02, 140.51, 136.55, 132.05, 127.14, 126.33, 125.71, 21.23, 20.06.

11. 2,4-Dimethoxybenzamide[79]

White solid, **^{1}H NMR (400 MHz, $CDCl_3$)**δ (ppm): 8.09 (d, 1H, $^{3}J_{H–H}$ = 8.8 Hz), 7.55 (br s, 1H), 6.51 (dd, 1H, $^{3}J_{H–H}$ = 8.8 Hz, 2.3 Hz), 6.41 (d, 1H, $^{3}J_{H–H}$ = 2.2 Hz 6.25 (br s, 1H), 3.85 (s, 3H), 3.77 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm): 167.03, 163.72, 159.12, 134.03, 113.70, 105.14, 98.41, 55.78, 55.43.

12. Nicotinamide[34]

^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) δ 9.02 (s, 1H), 8.64 – 8.63 (m, 1H), 8.13 (dt, J = 7.9, 1.8 Hz, 1H), 7.37 (br s, 1H), 7.32 – 7.28 (m, 1H), 6.36 (br s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$+ DMSO-d_6)** δ 167.69, 152.24, 148.86, 135.57, 129.46, 123.34.

2.4 Conclusion

Three new Ru(II) half-sandwich complexes have been synthesized in high yield by reacting pyrazole-based chalcogenoethers with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ in methanol under ambient reaction conditions and authenticated with ^{1}H, ^{13}C NMR, mass and FT-IR analytical techniques. Single crystal X-ray diffraction analysis of **2** and **3** revealed pseudo-octahedral half sandwich piano-stool geometry at Ru metal centre in both the complexes. The complexes **1-3** have been found efficient, thermally robust and moisture/air insensitive catalysts for the transformation of aldehyde to primary amide in high yield (95%). Complex **2**, consisting the selenium ligand has been found more efficient than their sulphur and tellurium analogues.

2.5 References

[1] E.L. Baker, M.M. Yamano, Y. Zhou, S.M. Anthony, N.K. Garg, A Two-step Approach to Achieve Secondary Amide Transamidation Enabled by Nickel Catalysis. *Nat. Commun.* **2016**, *7*, 11554.

[2] S.A. Ruider, N. Maulide, Strong Bonds Made Weak: Towards the General Utility of Amides as Synthetic Modules. *Angew. Chem. Int. Ed.* **2015**, *54*, 13856-13858.

[3] P.-Q. Huang, Y.-H. Huang, H. Geng, J.-L. Ye, Metal-Free C–H Alkyliminylation and Acylation of Alkenes with Secondary Amides. *Sci. Rep.* **2016**, *6*, 28801.

[4] A. Greenberg, C.M. Breneman, J.F. Liebman, *The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Materials Science*. Wiley-Interscience: New York: **2000**.

[5] J.M. Humphrey, A.R. Chamberlin, Chemical Synthesis of Natural Product Peptides: Coupling Methods for the Incorporation of Noncoded Amino Acids into Peptides. *Chem.Rev.***1997**, *97*, 2243-2266.

[6] P.S. Chaudhari, S.D. Salim, R.V. Sawant, K.G. Akamanchi, Sulfated Tungstate: A New Solid Heterogeneous Catalyst for Amide Synthesis. *Green Chem.* **2010**, *12*, 1707-1710.

[7] H. Lundberg, F. Tinnis, N. Selander, H. Adolfsson, Catalytic Amide Formation From Non-Activated Carboxylic Acids and Amines. *Chem. Soc. Rev.* **2014**, *43*, 2714-2742.

[8] A. Ojeda-Porras, D. Gamba-Sánchez, Recent Developments in Amide Synthesis Using Nonactivated Starting Materials. *J. Org. Chem.* **2016**, *81*, 11548-11555.

[9] E. Valeur, M. Bradley, Amide bond formation: beyond the myth of coupling reagents. *Chem. Soc. Rev.* **2009**, *38*, 606-631.

[10] T. Wieland, M. Bodanszky, *The World of Peptides: A Brief History of Peptide Chemistry*. Springer: **1991**.

[11] B.D. Roth, 1 The Discovery and Development of Atorvastatin, A Potent Novel Hypolipidemic Agent. *Prog. Med. Chem.* F.D. King, A.W. Oxford, A.B. Reitz, S.L. Dax, Eds. Elsevier: **2002**, *40*, 1-22.

[12] A.A. Patchett, Excursions in drug discovery. *J. Med. Chem.* **1993**, *36*, 2051-2058.

[13] V.S. Ananthanarayanan, S. Tetreault, A. Saint-Jean, Interaction of calcium channel antagonists with calcium: spectroscopic and modeling studies on diltiazem and its Ca^{2+} complex. *J. Med. Chem.* **1993**, *36*, 1324-1332.

[14] B.L. Deopura, 2 - Polyamide fibers. In *Polyesters and Polyamides*, Woodhead Publishing: **2008**, 41-61.

[15] A.K. Agrawal, M. Jassal, 4 - Manufacture of polyamide fibres. In *Polyesters and Polyamides*, Woodhead Publishing: **2008**, 97-139.

[16] F.A. Carey*, Organic Chemistry, McGraw-Hill*. New York, **2005**, 871.

[17] B.S. Jursic, Z. Zdravkovski, A Simple Preparation of Amides from Acids and Amines by Heating of Their Mixture. *Synth. Commun.* **1993**, *23,* 2761-2770.

[18] V.R. Pattabiraman, J.W. Bode, Rethinking amide bond synthesis. *Nature* **2011**, *480*, 471.

[19] J.S. Carey, D. Laffan, C. Thomson, M.T. Williams, Analysis of the Reactions Used for the Preparation of Drug Candidate Molecules. *Org. Biomol. Chem.* **2006**, *4*, 2337-2347.

[20] C.L. Allen, J.M.J. Williams, Metal-Catalyzed Approaches to Amide Bond Formation. *Chem. Soc. Rev.* **2011**, *40,* 3405-3415.

[21] B.K. Allam, K.N. Singh, Highly efficient One-pot Synthesis of Primary Amides Catalyzed by Scandium(III) triflate under Controlled MW. *Tetrahedron Lett.* **2011**, *52*, 5851-5854.

[22] L. Field, P.B. Hughmark, S.H. Shumaker, W.S. Marshall, Isomerization of Aldoximes to Amides under Substantially Neutral Conditions. *J. Am. Chem. Soc.* **1961**, *83,* 1983-1987.

[23] S.K. Sharma, S.D. Bishopp, C. Liana Allen, R. Lawrence, M.J. Bamford, A.A. Lapkin, P. Plucinski, R.J. Watson, J.M.J. Williams, Copper-Catalyzed Rearrangement of Oximes into Primary Amides. *Tetrahedron Lett.* **2011**, *52*, 4252-4255.

[24] N.C. Ganguly, S. Roy, P. Mondal, An Efficient Copper(II)-Catalyzed Direct Access to Primary Amides from Aldehydes under Neat Conditions. *Tetrahedron Lett.* **2012**, *53*, 1413-1416.

[25] A. Martínez-Asencio, M. Yus, D.J. Ramón, Copper(II) Acetate-Catalyzed One-Pot Conversion of Aldehydes Into Primary Amides Through A Beckmann-Type Rearrangement. *Tetrahedron* **2012**, *68*, 3948-3951.

[26] C.L. Allen, C. Burel, J.M.J. Williams, Cost Efficient Synthesis of Amides from Oximes with Indium or Zinc Catalysts. *Tetrahedron Lett.* **2010**, *51*, 2724-2726.

[27] M.A. Ali, T. Punniyamurthy, Palladium-Catalyzed One-Pot Conversion of Aldehydes to Amides. *Adv. Synth. Catal.* **2010**, *352*, 288-292.

[28] J.F. Hull, S.T. Hilton, R.H. Crabtree, A Simple Ru Catalyst for the Conversion of Aldehydes or Oximes to Primary Amides. *Inorg. Chim. Acta* **2010**, *363*, 1243-1245.

[29] A. Kanchanadevi, R. Ramesh, D. Semeril, Synthesis of Ru(II) Pyridoxal Thiosemicarbazone Complex and Its Catalytic Application to One-Pot Conversion of Aldehydes to Primary Amides. *Inorg. Chem. Commun.* **2015**, *56*, 116-119.

[30] W. Wang, X.-M. Zhao, J.-L. Wang, X. Geng, J.-F. Gong, X.-Q. Hao, M.-P. Song, Transition Metal-Free Synthesis of Primary Amides from Aldehydes And Hydroxylamine Hydrochloride. *Tetrahedron Lett.* **2014**, *55*, 3192-3194.

[31] H. Fujiwara, Y. Ogasawara, K. Yamaguchi, N. Mizuno, A One-Pot Synthesis of Primary Amides from Aldoximes or Aldehydes in Water in the Presence of a Supported Rhodium Catalyst. *Angew. Chem. Int. Ed.* **2007**, *46*, 5202-5205.

[32] H. Fujiwara, Y. Ogasawara, M. Kotani, K. Yamaguchi, N. Mizuno, A Supported Rhodium Hydroxide Catalyst: Preparation, Characterization, and Scope of the Synthesis of Primary Amides from Aldoximes or Aldehydes. *Chem. Asian J.* **2008**, *3*, 1715-1721.

[33] L. Xu, N. Li, H.-g. Peng, P. Wu, Clean Synthesis of Amides over Bifunctional Catalysts of Rhodium-Loaded Titanosilicates. *Chem.Cat.Chem* **2013**, *5*, 2462-2470.

[34] N.A. Owston, A.J. Parker, J.M.J. Williams, Iridium-Catalyzed Conversion of Alcohols into Amides via Oximes. *Org. Lett.* **2007**, *9*, 73-75.

[35] D. Gnanamgari, R.H. Crabtree, Terpyridine Ruthenium-Catalyzed One-Pot Conversion of Aldehydes into Amides. *Organometallics* **2009**, *28*, 922-924.

[36] A.J. Davenport, D.L. Davies, J. Fawcett, D.R. Russell, Arene-Ruthenium Complexes with Salicyloxazolines: Diastereoselective Synthesis, Configurational Stability and Applications as Asymmetric Catalysts for Diels-Alder Reactions. *Dalton Trans.* **2004**, 1481-1492.

[37] H. Joshi, K.N. Sharma, A.K. Sharma, O. Prakash, A. Kumar, A.K. Singh, Magnetite Nanoparticles Coated with Ruthenium via Se-ph Layer as A Magnetically Retrievable Catalyst for the Selective Synthesis of Primary Amides in An Aqueous Medium. *Dalton Trans.* **2014**, *43*, 12365-12372.

[38] P. Singh, A.K. Singh, Transfer Hydrogenation of Ketones and Catalytic Oxidation of Alcohols with Half-Sandwich Complexes of Ruthenium(II) Designed Using Benzene and Tridentate (S, N, E) Type Ligands (E = S, Se, Te). *Organometallics* **2010**, *29*, 6433-6442.

[39] P. Singh, A.K. Singh, "Piano-Stool" Complexes of Ruthenium(II) Designed with Arenes and N-[2-(Arylchalcogeno)ethyl] morpholines: Highly Active Catalysts for the Oxidation of Alcohols with N-Methylmorpholine N-Oxide, tert-Butyl Hydroperoxide and Sodium Periodate and Oxychloride. *Eur. J. Inorg. Chem.* **2010**, *2010*, 4187-4195.

[40] O. Prakash, K.N. Sharma, H. Joshi, P.L. Gupta, A.K. Singh, Half Sandwich Complexes of Chalcogenated Pyridine Based Bi-(N, S/Se) and Terdentate (N, S/Se, N) Ligands with (η^6-Benzene)Ruthenium(II): Synthesis, Structure and Catalysis of Transfer Hydrogenation of Ketones and Oxidation of Alcohols. *Dalton Trans.* **2013**, *42*, 8736-8747.

[41] O. Prakash, K.N. Sharma, H. Joshi, P.L. Gupta, A.K. Singh, (η^5-Cp*)Rh(III)/Ir(III) Complexes with Bis(chalcogenoethers) (E, E′ Ligands: E = S/Se; E′ = S/Se): Synthesis, Structure, and Applications in Catalytic Oppenauer-Type Oxidation and Transfer Hydrogenation. *Organometallics* **2014**, *33*, 983-993.

[42] K. Nomura, H. Okumura, T. Komatsu, N. Naga, Ethylene/Styrene Copolymerization by Various (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−MAO Catalyst Systems. *Macromolecules* **2002**, *35*, 5388-5395.

[43] A.A. Tregubov, K.Q. Vuong, E. Luais, J.J. Gooding, B.A. Messerle, Rh(I) Complexes Bearing N,N and N,P Ligands Anchored on Glassy Carbon Electrodes:

Toward Recyclable Hydroamination Catalysts. *J. Am. Chem. Soc.* **2013**, *135*, 16429-16437.

[44] S. Kotha, K. Lahiri, D. Kashinath, Recent Applications of the Suzuki–Miyaura Cross-Coupling Reaction in Organic Synthesis. *Tetrahedron* **2002**,*58*, 9633-9695.

[45] J. García-Álvarez, Deep Eutectic Mixtures: Promising Sustainable Solvents for Metal-Catalysed and Metal-Mediated Organic Reactions. *Eur. J. Inorg. Chem.* **2015**, *2015*, 5147-5157.

[46] K.N. Sharma, H. Joshi, V.V. Singh, P. Singh, A.K. Singh, Palladium(II) Complexes Of Pyrazolated Thio/Selenoethers: Syntheses, Structures, Single Source Precursors Of Pd_4Se and PdSe Nano-Particles and Potential for Catalyzing Suzuki-Miyaura Coupling.*Dalton Trans.* **2013**, *42*, 3908-3918.

[47] K.N. Sharma, H. Joshi, A.K. Sharma, O. Prakash, A.K. Singh, Single Source Precursor Routes for Synthesis of PdTe Nanorods and Particles: Solvent Dependent Control of Shapes. *Chem. Commun.* **2013**, *49*, 9344-9346.

[48] K. Nayan Sharma, H. Joshi, O. Prakash, A.K. Sharma, R. Bhaskar, A.K. Singh, Pyrazole-Stabilized Dinuclear Palladium(II) Chalcogenolates Formed by Oxidative Addition of Bis[2-(4-bromopyrazol-1-yl)ethyl] Dichalcogenides to Palladium(II) – Tailoring of Pd–S/Se Nanoparticles. *Eur. J. Inorg. Chem.* **2015**, *2015*, 4829-4838.

[49] G.K. Rao, A. Kumar, B. Kumar, D. Kumar, A.K. Singh, Palladium(II)-Selenated Schiff Base Complex Catalyzed Suzuki-Miyaura Coupling: Dependence of Efficiency on Alkyl Chain Length of Ligand. *Dalton Trans.* **2012**, *41*, 1931-1937.

[50] D.V. Aleksanyan, V.A. Kozlov, Y.V. Nelyubina, K.A. Lyssenko, L.N. Puntus, E.I. Gutsul, N.E. Shepel, A.A. Vasil'ev, P.V. Petrovskii, I.L. Odinets, Synthesis, Catalytic Activity, and Photophysical Properties of 5,6-Membered Pd And Pt SCS[Prime or Minute]-Pincer Complexes Based on Thiophosphorylated 3-Amino(Hydroxy)Benzoic Acid Thioanilides. *Dalton Trans.* **2011**, *40*, 1535-1546.

[51] D. Yuan, H.V. Huynh, Dinuclear and Tetranuclear Palladium(II) Complexes of a Thiolato-Functionalized, Benzannulated N-Heterocyclic Carbene Ligand and Their Activities toward Suzuki−Miyaura Coupling. *Organometallics* **2010**, *29*, 6020-6027.

[52] G.K. Rao, A. Kumar, J. Ahmed, A.K. Singh, Palladacycle Containing Nitrogen and Selenium: Highly Active Pre-Catalyst for the Suzuki-Miyaura Coupling

Reaction and Unprecedented Conversion into Nano-Sized $Pd_{17}Se_{15}$. *Chem. Commun.* **2010**, *46*, 5954-5956.

[53] V.A. Kozlov, D.V. Aleksanyan, Y.V. Nelyubina, K.A. Lyssenko, A.A. Vasil'ev, P.V. Petrovskii, I.L. Odinets, Cyclopalladation of meta-(Diphenylthiophosphoryloxy)benzaldimines: NCS and Unexpected NCO 5,6-Membered Pincer Palladium Complexes. *Organometallics* **2010**, *29*, 2054-2062.

[54] V.V. Singh, G.K. Rao, A. Kumar, A.K. Singh, Palladium(II)-Selenoether Complexes as New Single Source Precursors: First Synthesis of Pd_4Se And Pd_7Se_4 Nanoparticles. *Dalton Trans.* **2012**, *41*, 1142-1145.

[55] K.N. Sharma, H. Joshi, A.K. Sharma, O. Prakash, A.K. Singh, Selenium-Containing N-Heterocyclic Carbenes and Their First Palladium(II) Complexes: Synthesis, Structure, and Pendent Alkyl Chain Length Dependent Catalytic Activity for Suzuki–Miyaura Coupling. *Organometallics* **2013**, *32*, 2443-2451.

[56] N.S. Kamal, S. Naveen, K.J. Raj, Thioether–NHC-Ligated Pd(II) Complex for Crafting a Filtration-Free Magnetically Retrievable Catalyst for Suzuki–Miyaura Coupling in Water. *Eur. J. Org. Chem.* **2018**, *2018*, 1743-1751.

[57] S.G. M., Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Cryst. A.***1990**, *46*, 467-473.

[58] G. Sheldrick, A Short History of SHELX. *Acta Cryst. A.* **2008**, *64*, 112-122.

[59] G.M. Sheldrick, *Acta Cryst. A.* **2008**, *A64*, 112-122.

[60] H. Joshi, K.N. Sharma, A.K. Sharma, O. Prakash, A.K. Singh, Graphene Oxide Grafted with $Pd_{17}Se_{15}$ Nano-Particles Generated from A Single Source Precursor as A Recyclable and Efficient Catalyst for C-O Coupling in O-Arylation at Room Temperature. *Chem. Commun.* **2013**, *49*, 7483-7485.

[61] A.K. Sharma, H. Joshi, K.N. Sharma, P.L. Gupta, A.K. Singh, 2-Propanol vs Glycerol as Hydrogen Source in Catalytic Activation of Transfer Hydrogenation with (η^6-Benzene)ruthenium(II) Complexes of Unsymmetrical Bidentate Chalcogen Ligands. *Organometallics* **2014**, *33*, 3629-3639.

[62] F. Saleem, G.K. Rao, S. Kumar, M.P. Singh, A.K. Singh, Complexes of (η^6-Benzene)Ruthenium(II) with 1,4-Bis(Phenylthio/Seleno-Methyl)-1,2,3-Triazoles: Synthesis, Structure and Applications in Catalytic Activation of Oxidation and Transfer Hydrogenation. *Dalton Trans.* **2015**, *44*, 19141-19152.

[63] S. Kumar, G.K. Rao, A. Kumar, M.P. Singh, A.K. Singh, Palladium(II)-(E,N,E) Pincer Ligand (E = S/Se/Te) Complex Catalyzed Suzuki Coupling Reactions in Water via In-Situ Generated Palladium Quantum Dots. *Dalton Trans.* **2013**, *42*, 16939-16948.

[64] G.K. Rao, A. Kumar, M.P. Singh, A.K. Singh, Palladium(II) Complex of an Organotellurium Ligand as A Catalyst for Suzuki Miyaura Coupling: Generation and Role of Nano-Sized Pd_3Te_2. *J. Organomet. Chem.* **2014**, *749*, 1-6.

[65] G.K. Rao, A. Kumar, S. Kumar, U.B. Dupare, A.K. Singh, Palladacycles of Thioethers Catalyzing Suzuki–Miyaura C–C Coupling: Generation and Catalytic Activity of Nanoparticles. *Organometallics* **2013**, *32*, 2452-2458.

[66] G.K. Rao, A. Kumar, J. Ahmed, A.K. Singh, Palladacycle Containing Nitrogen and Selenium: Highly Active Pre-Catalyst for the Suzuki–Miyaura Coupling Reaction and Unprecedented Conversion into Nano-Sized $Pd_{17}Se_{15}$. *Chem. Commun.* **2010**, *46*, 5954-5956.

[67] O. Prakash, K.N. Sharma, H. Joshi, P.L. Gupta, A.K. Singh, Half Sandwich Complexes of Chalcogenated Pyridine Based Bi-(N, S/Se) and Terdentate (N, S/Se, N) Ligands with (η^6-Benzene)Ruthenium(II): Synthesis, Structure and Catalysis of Transfer Hydrogenation of Ketones and Oxidation of Alcohols. *Dalton Trans.* **2013**, *42*, 8736-8747.

[68] Q. Yao, E.P. Kinney, C. Zheng, Selenium-Ligated Palladium(II) Complexes as Highly Active Catalysts for Carbon−Carbon Coupling Reactions: The Heck Reaction. *Org. Lett.* **2004**, *6*, 2997-2999.

[69] Q. Yao, M. Sheets, A SeCSe−Pd(II) Pincer Complex as a Highly Efficient Catalyst for Allylation of Aldehydes with Allyltributyltin. *J. Org. Chem.* **2006**, *71*, 5384-5387.

[70] M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, Highly Active Pd(II) PCP-Type Catalysts for the Heck Reaction. *J. Am. Chem. Soc.* **1997**, *119*, 11687-11688.

[71] K. Yamaguchi, M. Matsushita, N. Mizuno, Efficient Hydration of Nitriles to Amides in Water, Catalyzed by Ruthenium Hydroxide Supported on Alumina. *Angew. Chem. Int. Ed.* **2004**, *43*, 1576-1580.

[72] E. Choi, C. Lee, Y. Na, S. Chang, [RuCl$_2$(p-cymene)]$_2$ on Carbon: An Efficient, Selective, Reusable, and Environmentally Versatile Heterogeneous Catalyst. *Org. Lett.* **2002**, *4*, 2369-2371.

[73] N.A. Owston, A.J. Parker, J.M.J. Williams, Highly Efficient Ruthenium-Catalyzed Oxime to Amide Rearrangement. *Org. Lett.* **2007**, *9*, 3599-3601.

[74] R. García-Álvarez, A.E. Díaz-Álvarez, J. Borge, P. Crochet, V. Cadierno, Ruthenium-Catalyzed Rearrangement of Aldoximes to Primary Amides in Water. *Organometallics* **2012**, *31*, 6482-6490.

[75] B.S.Furniss, A.J.H.P.W.G. Smith, A.R.Tatchell, *Vogel's Textbook of Practical Organic Chemistry, 5th ed.* ELBS, Longman Group U K Ltd: **1989**.

[76] T. Xu, H. Alper, Palladium-Catalyzed Aminocarbonylation of Aryl Iodides Using Aqueous Ammonia. *Tetrahedron Lett.* **2013**, *54*, 5496-5499.

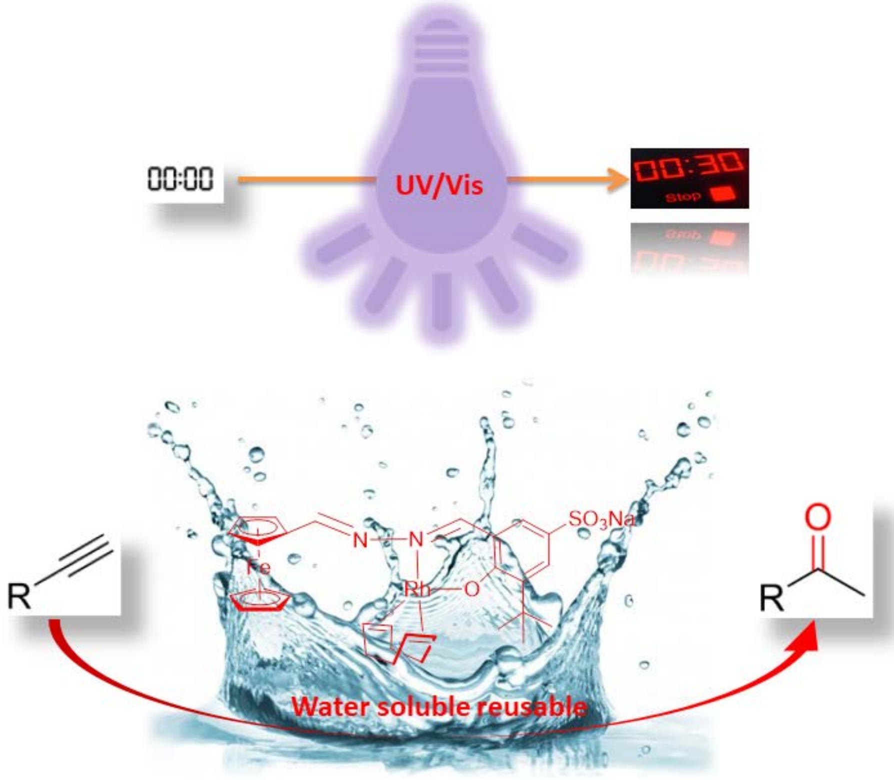
[77] G.F. Rebeca, C. Pascale, C. Victorio, M.M. Isabel, L. Ramón, Phosphinous Acid-Assisted Hydration of Nitriles: Understanding the Controversial Reactivity of Osmium and Ruthenium Catalysts. *A Eur. J. Chem*. **2017**, *23*, 15210-15221.

[78] Q. Xinxin, A. Han-Jun, C. Chuang-Xu, P. Jin-Bao, Y. Jun, W. Xiao-Feng, A Convenient Palladium-Catalyzed Aminocarbonylation of Aryl Iodides to Primary Amides under Gas-Free Conditions. *Eur. J. Org. Chem***.** **2017**, *2017*, 7222-7225.

[79] M. Rezaei, K. Amani, K. Darvishi, One–Pot Green Catalytic Synthesis of Primary Amides in Aqueous Medium by Cu(II)–Immobilized Silica–Based Magnetic Retrievable Nanocatalyst. *Catal. Commun.* **2017**, *91*, 38-42.

Chapter-3

A Water Soluble Rh(I) Catalyst for Photochemically Induced Hydration of Alkynes



3.1 Introduction

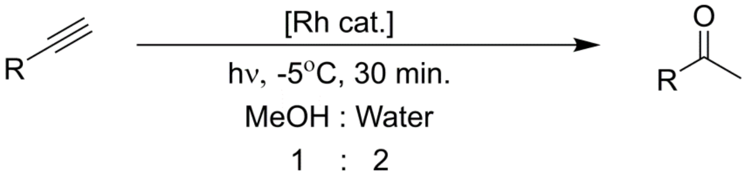
Chemical transformations that use water as a reagent or reaction medium continue to attract attention in organic synthesis [1]. This stems from the non-toxic nature of water to both the user and the environment, its relative abundance compared to other solvents, as well as the compatibility with various organic substrates. The atom-economical hydration of alkynes (with all of the reactant atoms found in the desired products) represents one of the most important reactions that utilize water in organic synthesis. This well-established reaction is classically catalyzed by the toxic and environmentally-destructive metal-containing mercuric sulphate or a strong acid catalyst. In the presence of sulphuric acid, the hydration of alkynes leads to industrially relevant carbonyl compounds, used in the bulk and fine chemical industries [2]. Mercury promoted hydration of alkynes often suffers a major drawback where certain acid-labile functional groups are not compatible with the harsh acidic conditions. Moreover, the reaction proceeds under stringent conditions, i.e. high temperatures (> 100 °C), prolonged reaction time as well as requiring a large excess of acid and water. To circumvent these drawbacks, various transition-metal-based catalysts have been developed as environmentally benign alternatives to mercuric catalysts in the hydration of alkynes, and these include Ag [3], Pt [4], Cu [5], Au [6], Fe [7-12], Ir [13], In [14],Ru[15-17] and Rh[18-23] complexes. These metals provide a much easier, mild, greener and efficient protocol for the hydration of simple alkynes. In selected cases, aryl alkynes posed several challenges giving reduced yields, lower selectivity or requiring higher catalyst loading and elevated temperatures. The hydration of terminal alkynes usually occurs via Markovnikov addition, giving methyl ketones, with symmetric internal alkynes selectively yielding single ketone products. It is generally accepted that the hydration proceeds via an enol which immediately transforms into the more stable ketone via tautomerism, with the metal ketonyl complexes being the key intermediates, in the presence of metal catalysts [24]. Rhodium-mediated addition of water to alkynes is attractive owing to the well-known good functional group tolerance of the metal, as well as the high activity and selectivity demonstrated under mild reaction conditions in various homogeneous catalytic transformations [25]. Complexing the metal to chelating schiff base ligands is a very popular approach because of the good stability and versatility afforded by the ligands, often leading to excellent catalytic activity [26]. Herein, we report the photolytic hydration of various alkynes using a previously synthesized, reusable, water-soluble N,O-chelate Rh(I)–Schiff base catalyst precursor bearing ferrocene as an ancillary support [27]. Using this rhodium catalyst, the hydration of alkynes proceeded in 30 minutes under irradiation, yielding methyl ketones.

3.2 Experimental

3.2.1 Materials and reagents

All chemical reagents were of analytical grade and used without further purification.

3.2.2 General Procedure for the Catalytic Reaction*:*



To a 100 mL capacity borosilicate immersion well of UV reactor 80 mL aqueous methanol MeOH:H_2O (1:2), alkyne (1 mmol), Rh catalyst (1.5 mol %) was added, The reaction mixture was first to cool down at -5 °C then it was exposed to the Hg vapour UV lamp, 125W, 289nm for 30 min with continuous stirring. After completion of the reaction; reaction mixture was brought up to the room temperature and then concentrated *in vacuo* to remove methanol then extracted with dichloromethane and water, the organic phase was dried with anhydrous $Na_2SO_{4,}$ concentrated at reduced pressure, and purified by flash column chromatography with hexanes/ethyl acetate as eluent to obtain the corresponding product.

3.2.3 Instrumentation

3.2.3.1 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C).

3.2.3.2 Infra-red Spectroscopy

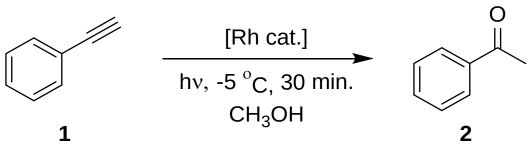
IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin Elmer 10.4.00 FT-IR spectrometer as KBr pellets of the sample.

3.2.3.3 High Resolution Mass Spectroscopy

High Resolution Electron Impact Mass Spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA) with the sample taken up in CH_3CN.

3.3 **Result and discussion**

Based on previous reports of water-soluble Rh salts [19] and Rh complexes [20] used for hydration reactions, various methods were attempted to improve the yield of these transformations. However, these methods have significant limitations which include slow processes, long reaction time (12-24 hr), and the loss of volatile alkynes at high temperatures during the long reaction hours. However, after studying a series of reported reactions with our Rh catalyst, we found insignificant changes to the product yield; hence it was decided to adopt a different strategy. This entailed the preliminary screening of hydration reactions in a UV reactor (containing 125 W, Hg vapour lamp ≈ 289 nm) which produced some unprecedented results.



Scheme 1: Photochemical hydration of phenylacetylene with Rh(I) catalyst in methanol

Scheme 1 depicts our preliminary reaction in which the hydration of phenyl acetylene (1) resulted in the formation of acetophenone (2). When a methanol solution of phenylacetylene containing a catalytic amount of Rh catalyst was exposed to UV radiation for 30 min. at -5˚C, the formation of acetophenone was unequivocally observed. Phenylacetylene was used as a model reactant for the optimization of various reaction parameters in different reaction conditions. The feasibility of the catalytic reaction is summarized in Table 1. At a very low catalyst loading (0.2 mol%, entry 2), the yield of phenyl acetylene was very poor. However, the yield was proportionally improved with an incremental catalyst loading up to 1.5 mol% (entries 3-6). Moreover, a further increase of catalyst loading to 2.5 mol% (entry 7,8) does not show any significant effect on the product yield. For the solvent optimizations, when water was used as a solvent, the substrate does not undergo any chemical reaction. This may be ascribed to the insolubility of phenylacetylene in water (entry 9). However, a water and methanol (1:1) solvent mixture substantially increase the yield up to 70% of the desired acetophenone (entry 10,11).

Table 1: Optimization of different reaction parameters with phenylacetylene

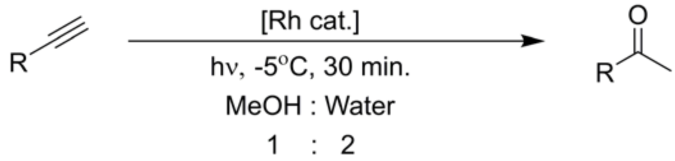
Entry	mol (%) Catalyst	Solvent Ratio (MeOH:Water)	Time (min.)	Temp (˚C)	Yield[a] (%)
1.	-	1:2	30	-5	Nd
2.	0.2	1:2	30	-5	30
3.	0.5	1:2	30	-5	50
4.	0.7	1:2	30	-5	60
5.	1.0	1:2	30	-5	70
6.	1.5	1:2	30	-5	78
7.	2	1:2	30	-5	78
8.	2.5	1:2	30	-5	78
9.	1.5	0:1	30	-5	Nd
10.	1.5	1:1	30	-5	70
11.	1.5	1:2	30	-5	78
12.	1.5	2:1	30	-5	40
13.	1.5	1:0	30	-5	08
14.	1.5	1:2	15	-5	20
15.	1.5	1:2	20	-5	37
16.	1.5	1:2	25	-5	60
17.	1.5	1:2	30	-5	78
18.	1.5	1:2	35	-5	77
19.	1.5	1:2	40	-5	75
20.	1.5	1:2	30	0	53
21.	1.5	1:2	30	-5	78
22.	1.5	1:2	30	-10	77

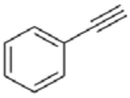
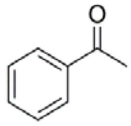
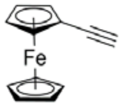
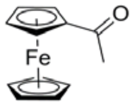
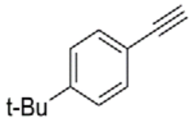
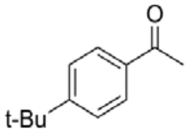
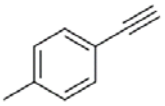
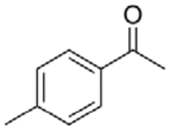
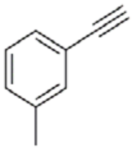
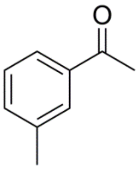
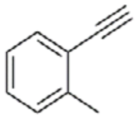
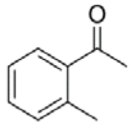
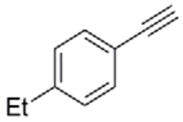
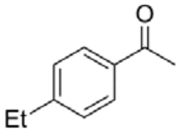
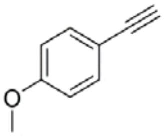
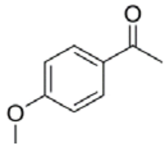
[a]isolated Yields

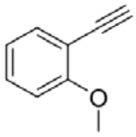
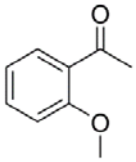
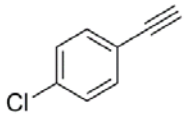
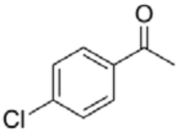
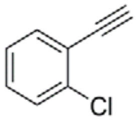
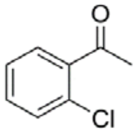
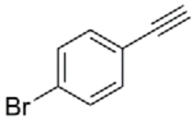
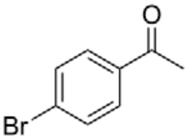
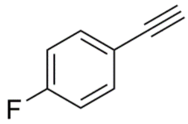
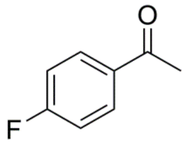
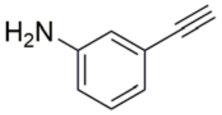
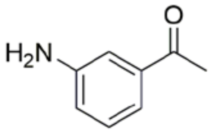
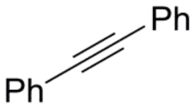
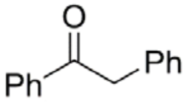
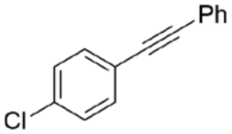
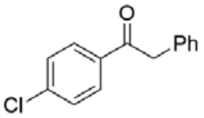
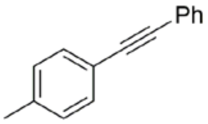
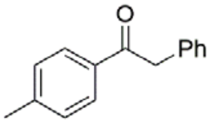
In an attempt to optimize the yield of the desired product, various other combinations of water and methanol were investigated for this reaction. Furthermore, increasing the water in the solvent mixture does not bring any changes to the yield of the product. A higher ratio of methanol in the solvent mixture decreased the yield of acetophenone to a certain extent, while 1:2 ratio of methanol and water produced the highest yield (entry 12,13). Other alcohols like ethanol, propanol and butanol in combination with water were also studied as a solvent, but unfortunately low-yielding transformations were obtained. Moreover, reactions in the presence of branched alcohols, isopropanol and *tert*-butanol also failed to result in a favorable transformation. Nonetheless, the obtained results from various trial experiments reveal a new strategy to pursue hydration reactions, which motivated us explore a wider scope of the hydration reaction. In optimizing the parameters for alkyne hydration, a set of trial reactions were carried out at various times and temperatures. Increasing the reaction time from 15 to 30 min (entries 14-18) consistently affords an increased yield, while longer periods of photolysis of the reaction mixture does not affect the course of the reaction. In assessing the effect of temperature, a series of reactions in the range -10 ˚C to 10 ˚C was tested and it was noted that the product yield was higher at lower temperatures. Moreover, the yield of the desired product was almost constant between -5 to -10 °C, while increasing the temperature to 0 °C drastically deaccelerates the rate of hydration (entry 21-22). Under the optimized reaction parameters (1.5mol%, 1:2 MeOH-H_2O, 30 min, -5 °C), a selective formation of acetophenone was recorded for the hydration of phenyl acetylene. Using the established optimized reaction conditions, we examined the hydration of a variety of alkynes and the results are summarized in Table 2. Both terminal and internal alkynes are efficiently and selectively converted to their corresponding ketones in high yields, in the presence of a range of electron-donating or withdrawing functional groups, demonstrating a high tolerance for a variety of functional groups. Substituted phenylacetylenes, such as 2- and 4-methoxy phenylacetylene gave the corresponding ketones in 82%, and 84% yields respectively (Table 2, entry8,9). Similarly, ortho-, meta-, and para-substituted methyl-phenylacetylene reacted smoothly; producing the corresponding methyl ketones in 83%, 82%, and 83% yields respectively (Table 2, entries 4-6). The highest yield (85%) was achieved using 4-*tert*-butylphenylacetylene (Table 2, entry 3). The 4-ethylphenylacetylene and 3-aminophenylacetylene also reacted favorably and formed the corresponding ketone in 82% and 79% yields respectively (Table 2, entry 7, 14). The hydration of ferrocenylacetylene also reacted successfully and yielded 80% of keto product (entry 2). The same reaction conditions were applied to halo-substituted phenylacetylenes, such as 4-fluoro-, 4-chloro-, 4-bromo and 2-chloro phenylacetylene to give 81%, 73%, 75% and 74% yields (Table 2, entry 10-13) respectively. The hydration of internal alkynes yielded the corresponding diphenylacetylene in yield of about 76, 81% of the corresponding hydrated product

(Table 2, entry 15 - 17). However, this reaction was not found feasible for the hydration of aliphatic alkynes under the present reaction condition.

Table 2: Scope of alkynes hydration for various terminal and internal alkynes



Entry	Reactant	Product	Yield[a]
1.			78
2.			80
3.			85
4.			83
5.			82
6.			83
7.			82
8.			82

9.			84
10.			75
11.			74
12.			73
13.			81
14.			79
15.			76
16.			77
17.			81

Reaction Conditions: Rh-Catalyst 1.5 mol%,Solvent (80mL) MeOH: Water (1:2 ratio), Temp. -5˚C, hυ, 0.5h., [a]Isolated Yield

The recyclability of the catalyst was studied, using phenylacetylene as a model reactant under the optimized reaction conditions. In a typical experiment, the water-soluble rhodium complex was recovered at the end of the reaction by liquid-liquid extraction using dichloromethane and water. The separated aqueous phase was directly used in a new catalytic run. The catalyst showed good recyclability and could be used up to 4 times before a decrease in product yield was observed. The catalyst was rendered ineffective after the seventh cycle due to possibly metal leaching or decomposition of metal complex. Previous Rh metal based catalysts do not show such promising catalysis and recyclability, with such a less amount of catalyst and short duration of the reaction.

No.of Cycles	1	2	3	4	5	6	7	8
Product Yield[a]	78	78	72	70	60	50	20	Trace

Condition: Catalyst 1.5 mol%, Solvent (80mL) MeOH: Water (1:2), Temp. -5˚C, hυ, 30 min, [a]Isolated Yields

Table 3: Comparisons of reported alkyne hydration reactions with present reaction

Entry	**Metal catalyst**	**Catalyst (mol%)**	**Solvent**	**Temp. (˚C)**	**Time (h)**	**condition (Δ, hν, MW)**	**Yield (%)**	**Ref.**
1.	Hg(II)	5	MeCN	Rt	12	Δ	100	[28]
2.	Sn-W	50	cycloocatane	100	0.5 - 24	Δ	91	[29]
3.	Co(III)	2	MeOH	80	5 – 36	Δ	99	[30]
4.	Fe(III)	10	DCE	75	67	Δ	96	[31]
5.	Ag(I)	10	MeOH	75	36 – 48	Δ	94	[32]
6.	Pt(II)	0.8	THF	60	12	Δ	55:45	[33]
7.	Rh(III)	4	THF	110	16 – 24	Δ	93	[19]
8.	Rh(I)	5	THF	110	2	Δ	100	[23]
9.	Rh(III)	20	MeOH	Rt	12	Hν	91	[20]
10.	Ru(I)	1 – 5	IPA	100	12 – 36	Δ	99	[34]
11.	Ru(II)	5	PEG-400	Rt	12 – 48	Δ	89	[35]
12.	Pd(II)	5	MeOH	50	1 – 51	Δ	99	[36]
13.	Au(I)	0.1	Dioxane	120	18	Δ	97	[37]
14.	Au-TiO_2	1	Dioxane	120	1	Mw	97	[38]
15.	Au(III)	1.6 – 4.5	MeOH	70	1.5 – 4	Δ	98	[39]
16.	**Rh(I)**	**1.5**	**MeOH**	**-5**	**0.5**	**Hν**	**85**	**---**

In comparison to the previous reports catalyst reported here show better activity in many terms. This catalyst is required in very low amount for this particular reaction. This catalyst produces excellent yields with wide functional group compatibility at very low temperature and in minimum time in comparison to other catalysts. Moreover this catalysis methodology is highly time and energy efficient. While comparing the recyclability of the present catalyst, there was only 2 heterogeneous recyclable catalyst are reports earlier (Table 3, Entry 2 and Entry 14), no homogeneous recyclable catalyst is reported yet. This will be the first report of a homogeneous recyclable catalyst which can produce promising results up to 7 straight catalytic cycles, there is no need to separated or activated this catalyst. While the previous catalysts had shown activity up to 3 and 4 cycles respectively. (Table 3 Entry 2 and Entry 14). In comparison to the other Rh based catalyst ($RhCl_3$ and Rh complexes) [19, 20, 22, 23] most of them does not produce a substantial yield in aqueous solvents. However all the previous Rh based catalysts are homogeneous similar to the present catalyst but they not reusable. Moreover the previous catalysts required high catalyst loading of up to 20 mol% in comparison to 1.5 mol% of the present catalyst. The only previous methodology to perform this reaction under UV irradiation in the presence of Rh (III) catalyst and Triflouroacetic acid (TFA) takes 24 hr to complete [20]. But the present catalytic methodology produces the same results in 0.5h without any need of organic or mineral acids.

3.3.1 Mechanism

A plausible mechanism is envisioned with the aid of previous reports in the literature (Figure 2). It is suggested that hydration of alkynes can be conducted under UV [20], MW [40] and Thermal [41] conditions. Methanol [20] and water [42] are found suitable for alkyne hydrations. In general, metal catalysts are employed with polar aprotic solvents with a stoichiometric amount of water in the reaction. There are multiple intermediates with water and methanol that have been investigated in previous reports. This suggests the formation of intermediates b to d which are possible in the presence of water as well as methanol [20]. Various possible pathways for the formation of d as an intermediate complex with water and methanol are depicted and discussed.

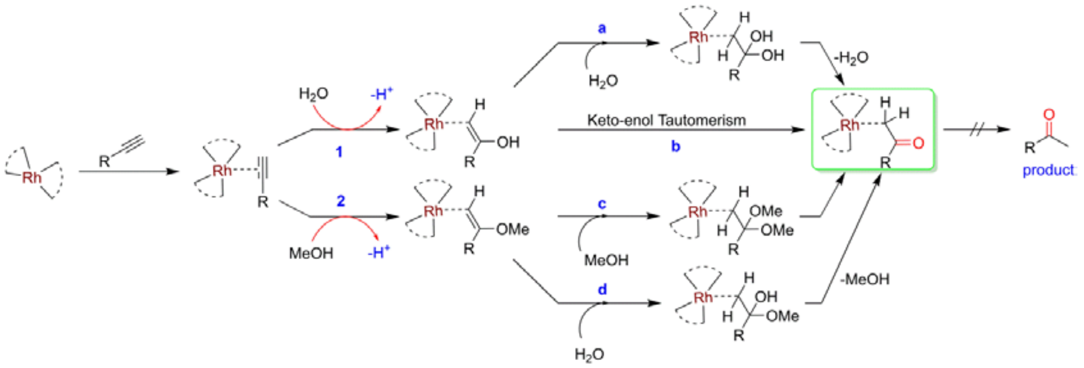


Figure 1: Possible pathways for the formations intermediates

Pathway 2 followed by addition of methanol (c) or water (d) can form two different intermediates which upon loss of MeOH leads to the formation of desire intermediate. The most suitable pathway 1 followed by keto-enol tautomerism can form the intermediate. Further homolytic cleavage of Rh–C bond under the influence of UV radiation produces a $PhCOCH_2$ radical [20]. Formation of complexes e and f occurs at high concentration of methanol [41, 43-45]. Complex e and f behave as H radical carrier which is transferred to the $PhCOCH_2$ radical [20].

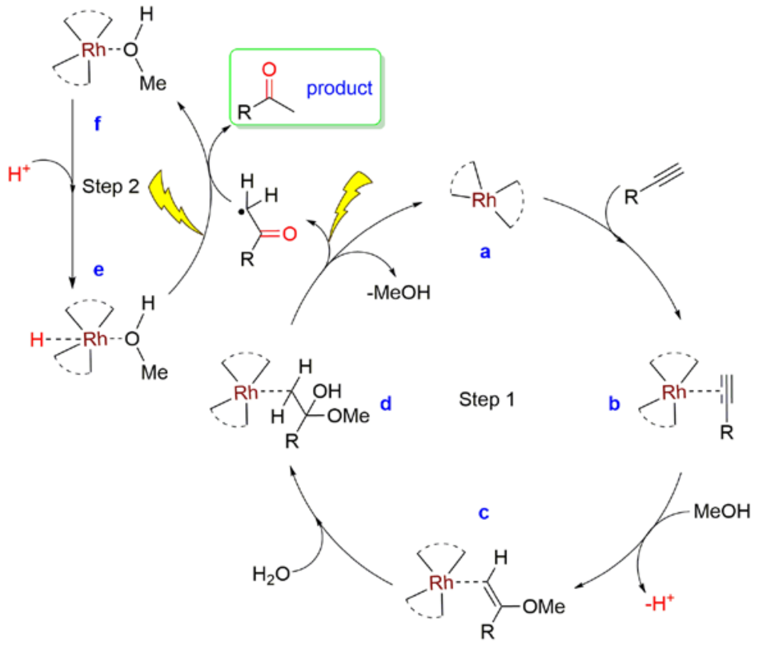


Figure2: Plausible reaction mechanism for Rh (I) catalyzed alkyne hydration

Reaction temperatures of -5 ˚C make this reaction a more favourable approach when working with low boiling alkynes. Hence, this methodology has shown its ability to overcome the challenges of earlier metal mediated and metal free methods reported for the hydration of alkynes [40, 46].

3.3.2 Supplementary data

Acetophenone [31]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.92 – 7.90 (m, 2H), 7.53 – 7.49 (m, 1H), 7.43 – 7.39 (m, 2H), 2.55 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 198.21, 137.13, 133.19, 128.64, 128.37, 26.68.

Acetyl Ferrocene [47]

^{1}H NMR (400MHz, $CDCl_3$): δ = 4.74 (s, 2H), 4.48 (s, 2H), 4.18 (s, 5H), 2.37 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 202.30, 72.46 69.96, 69.70, 27.55.

1-(4-(tert-butyl)phenyl)ethan-1-one[31]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.90 – 7.88(m, 2H), 7.47 – 7.45 (m, 2H), 2.57 (s, 3H), 1.33 (s, 9H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 198.05, 156.92, 134.66, 131.95, 130.14, 128.41, 125.60, 35.18, 31.17, 26.64.

1-(p-tolyl)ethan-1-one [48]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.77 - 7.74 (m, 2H), 7.14 – 7.11 (m, 2H), 2.44 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 197.32, 143.66, 134.65, 129.18, 128.38, 26.29, 21.44.

1-(m-tolyl)ethan-1-one [48]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.71 – 7.68 (m, 2H), 7.29 – 7.28 (m, 2H), 2.52 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 198.36, 138.36, 137.16, 133.92, 128.82, 128.50, 125.64, 26.70, 21.36.

1-(o-tolyl)ethan-1-one [29]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.64 – 7.62 (m, 1H), 7.33 – 7.29 (m, 1H), 7.22 – 7.16 (m, 2H), 2.51 (s, 3H), 2.48 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 201.68, 138.47, 137.63, 132.11, 131.60, 129.48, 125.79, 29.56, 21.68.

1-(4-ethylphenyl)ethan-1-one [48]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.87 – 7.85 (m, 2H), 7.26 – 7.24 (m, 2H), 2.71 – 2.65 (q, 2H), 2.55 (s, 3H), 1.25 – 1.21 (t, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 197.93, 150.12, 134.98, 128.62, 128.13, 29.01, 26.62, 15.30.

1-(4-chlorophenyl)ethan-1-one [48]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.73 – 7.69 (m, 2H), 7.25 – 7.21(m, 2H), 2.43 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 196.43, 139.22, 135.30, 129.65, 128.69, 26.34.

1-(2-chlorophenyl)ethan-1-one

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.45 – 7.41 (m, 1H), 7.27 – 7.16 (m, 3H), 2.50 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 199.92, 138.91, 132.01, 131.05, 130.56, 129.40, 126.96, 30.51.

1-(4-methoxyphenyl)ethan-1-one [48]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.86 – 7.83 (m, 2H), 6.85 – 6.82 (m, 2H), 3.77 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.75, 163.51, 130.59, 130.29, 113.69, 55.46, 26.33.

1-(2-methoxyphenyl)ethan-1-one [48]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.64 – 7.62 (m, 1H), 7.33 – 7.29 (m, 1H), 7.22 – 7.16 (m, 2H), 2.51 (s, 3H), 2.48 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 199.69, 158.97, 133.77, 130.27, 128.13, 120.49, 111.66, 55.46, 31.87.

1-(3-aminophenyl)ethan-1-one [48]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.30 – 7.18 (m, 3H), 6.85 – 6.83 (m, 1H), 3.86 (s, 2H), 2.52 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 198.69, 146.94, 138.25, 129.52, 119.76, 118.84, 114.07, 26.81.

1-(4-bromophenyl)ethan-1-one [48]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.80 – 7.77 (m, 2H), 7.58 – 7.56 (m, 2H), 2.55 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.13, 135.87, 131.97, 129.93, 128.39, 26.66.

1-(4-fluorophenyl)ethan-1-one [48]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.96 – 7.92 (m, 2H), 7.10 – 7.06(m, 2H), 2.55 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.54, 165.80 (d, J_{C-F} = 253 Hz), 133.63 (d, J_{C-F} = 2.7 Hz), 131.00 (d, J_{C-F} = 9.4 Hz), 115.69 (d, J_{C-F} = 22 Hz), 26.58.

1,2-diphenylethan-1-one [48]

^{1}H NMR (400MHz, CDCl$_3$): δ = 8.04 – 8.03 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 7.36 – 7.25 (m, 5H), 4.30 (s, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.77, 136.68, 134.66, 133.31, 129.61, 128.80, 128.78, 128.74, 127.02, 45.61.

1-(4-chlorophenyl)-2-phenylethan-1-one [49]

^{1}H NMR (400MHz, CDCl$_3$): δ = 4.25 (s, 2H), 7.23 – 7.34 (m, 5H), 7.40 – 7.43 (m, 2H), 7.92 – 7.95 (m, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.53, 139.72, 134.90, 134.25, 130.14, 129.47, 129.07, 128.87, 127.14, 45.64

2-phenyl-1-(p-tolyl)ethan-1-one [50]

^{1}H NMR (400MHz, CDCl$_3$): δ = 3.01 (s, 3H), 4.25 (s, 2H), 7.13 – 7.18 (m, 4H), 7.43 – 7.47 (m, 2H), 7.53 – 7.55 (m, 1H), 8.01 – 8.03 (m, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.96, 136.69, 136.59, 133.22, 131.52, 129.51, 129.42, 128.73, 45.24, 21.20.

3.4 Conclusion

In conclusion, we have demonstrated a novel and green strategy for the hydration of terminal and internal alkynes to produce the ketones, using a water-soluble rhodium (I) catalyst. This represents the first example of a UV-assisted alkyne hydration in the presence of a water-soluble and reusable rhodium (I) catalyst. The catalytic conversion occurs under aqueous, aerobic conditions and the catalyst can be reused up to 4 cycles without any regeneration, which reflects the green and robust nature of the catalyst. Furthermore, this catalyst produces excellent, selective, high-yielding results with terminal, internal and substituted aryl alkynes via a one-pot hydration in 30 minutes, which is far quicker in comparison with earlier reports.

3.5 References

[1] R.N. Butler, A.G. Coyne, Water: Nature's Reaction Enforcer—Comparative Effects for Organic Synthesis "In-Water" and "On-Water". *Chem.Rev.* **2010**, *110*, 6302-6337.

[2] R. Mello, A. Alcalde-Aragonés, M.E. González-Núñez, Silica-Supported $HgSO_4/H_2SO_4$: A Convenient Reagent for the Hydration of Alkynes Under Mild Conditions. *Tetrahedron Lett.* **2010**, *51*, 4281-4283.

[3] Q. Dong, N. Li, R. Qiu, J. Wang, C. Guo, X. Xu, Silver-Containing Microemulsion as A High-Efficient and Recyclable Catalytic System for Hydration of Alkynes. *J. Organomet. Chem.* **2015**, *799-800*, 122-127.

[4] L.W. Francisco, D.A. Moreno, J.D. Atwood, Synthesis, Characterization and Reaction Chemistry of $PtCl_2[P(m\text{-}C_6H_4SO_3Na)_3]_2$, an Alkyne Hydration Catalyst. *Organometallics* **2001**, *20*, 4237-4245.

[5] T.-F. Niu, D.-Y. Jiang, S.-Y. Li, X.-G. Shu, H. Li, A.-L. Zhang, J.-Y. Xu, B.-Q. Ni, Visible Light Promoted Copper-Catalyzed Markovnikov Hydration of Alkynes at Room Temperature. *Tetrahedron Lett.* **2017**, *58*, 1156-1159.

[6] T. Chen, C. Cai, Catalytic Hydration of Alkynes to Ketones by A Salen–Gold(III) Complex. *Catal. Commun.* **2015**, *65*, 102-104.

[7] M. Bassetti, S. Ciceri, F. Lancia, C. Pasquini, Hydration of Aromatic Terminal Alkynes Catalyzed by Iron(III) Sulfate Hydrate Under Chlorine-Free Conditions. *Tetrahedron Lett.* **2014**, *55*, 1608-1612.

[8] P. Mathur, B. Jha, A. Raghuvanshi, R.K. Joshi, S.M. Mobin, Photolytic Reaction of Substituted (Ethynyl)Benzaldehyde and $Fe(CO)_5$: Formation of Indenone and Chelated Iron Complexes. *J. Organomet. Chem.* **2012**, *712*, 7-14.

[9] P. Mathur, R.K. Joshi, D.K. Rai, B. Jha, S.M. Mobin, One Pot Synthesis of Maleimide and Hydantoin by $Fe(CO)_5$ Catalyzed [2 + 2 + 1] Co-Cyclization of Acetylene, Isocyanate and CO. *Dalton Trans.* **2012**, *41*, 5045-5054.

[10] P. Mathur, R.K. Joshi, B. Jha, A.K. Singh, S.M. Mobin, Towards the Catalytic Formation of α,β-Vinylesters and Alkoxy Substituted γ-Lactones. *J. Organomet. Chem.* **2010**, *695*, 2687-2694.

[11] B.N. Jha, A. Raghuvanshi, R.K. Joshi, S.M. Mobin, P. Mathur, A Photochemical Route to Ferrocenyl-Substituted Ferrapyrrolinone Complexes. *Appl. Organomet. Chem.* **2017**, *31*, e3805.

[12] R.K. Joshi, N. Satrawala, One Pot Synthesis of Important Retinoid Synthon by the Catalytic Regioselective Bi-Functionalization of Acetylenes, Alcohol and Carbon Monoxide. *Tetrahedron Lett.* **2017**, *58*, 2931-2935.

[13] S. Ogo, K. Uehara, T. Abura, Y. Watanabe, S. Fukuzumi, pH-Selective Synthesis and Structures of Alkynyl, Acyl, and Ketonyl Intermediates in Anti-Markovnikov and Markovnikov Hydrations of a Terminal Alkyne with a Water-Soluble Iridium Aqua Complex in Water. *J. Am. Chem. Soc.* **2004**, *126*, 16520-16527.

[14] M. Zeng, R.-X. Huang, W.-Y. Li, X.-W. Liu, F.-L. He, Y.-Y. Zhang, F. Xiao, $In(OTf)_3$/Acid Co-Catalyzed Hydration of 1-haloalkynes to α-halomethyl Ketones. *Tetrahedron* **2016**, *72*, 3818-3822.

[15] M. Tokunaga, Y. Wakatsuki, The First Anti-Markovnikov Hydration of Terminal Alkynes: Formation of Aldehydes Catalyzed by a Ruthenium(II)/Phosphane Mixture. *Angew. Chem. Int. Ed.* **1998**, *37*, 2867-2869.

[16] F. Boeck, T. Kribber, L. Xiao, L. Hintermann, Mixed Phosphane η^5-$CpRuCl(PR_3)_2$ Complexes as Ambifunctional Catalysts for Anti-Markovnikov Hydration of Terminal Alkynes. *J. Am.Chem. Soc.* **2011**, *133*, 8138-8141.

[17] D.B. Grotjahn, C.D. Incarvito, A.L. Rheingold, Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-

Markovnikov Hydration of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2001**, *40*, 3884-3887.

[18] Y. Zhou, Q. Liu, W. Lv, Q. Pang, R. Ben, Y. Qian, J. Zhao, Indazolin-s-ylidene–N-Heterocyclic Carbene Complexes of Rhodium, Palladium, and Gold: Synthesis, Characterization, and Catalytic Hydration of Alkynes. *Organometallics* **2013**, *32*, 3753-3759.

[19] A. Lumbroso, N.R. Vautravers, B. Breit, Rhodium-Catalyzed Selective anti-Markovnikov Addition of Carboxylic Acids to Alkynes. *Org. Lett.* **2010**, *12*, 5498-5501.

[20] X. Liu, L. Liu, Z. Wang, X. Fu, Visible Light Promoted Hydration of Alkynes Catalyzed by Rhodium(III) Porphyrins. *Chem. Commun.* **2015**, *51*, 11896-11898.

[21] M. Setty-Fichman, Y. Sasson, J. Blum, Double Bond Migration, Cyclohexadiene Disproportionation and Alkyne Hydration by Dowex® 1-$RhCl_3$ Ion Pair Catalysts. *J. Mol. Catal. A: Chem.* **1997**, *126*, 27-36.

[22] J. Blum, H. Huminer, H. Alper, Alkyne Hydration Promoted by $RhCl_3$ and Quaternary Ammonium Salts. *J. Mol. Catal.* **1992**, *75*, 153-160.

[23] Y.J. Park, B.-I. Kwon, J.-A. Ahn, H. Lee, C.-H. Jun, Chelation-Assisted Hydrative Dimerization of 1-Alkyne Forming α,β-Enones by an Rh(I) Catalyst. *J. Am. Chem. Soc.* **2004**, *126*, 13892-13893.

[24] H. Kanemitsu, K. Uehara, S. Fukuzumi, S. Ogo, Isolation and Crystal Structures of Both Enol and Keto Tautomer Intermediates in a Hydration of an Alkyne−Carboxylic Acid Ester Catalyzed by Iridium Complexes in Water. *J. Am. Chem. Soc.* **2008**, *130*, 17141-17147.

[25] Product Class 5: Organometallic Complexes of Rhodium. In *Category 1, Organometallics*, **2001**.; M. Lautens, Ed. Georg Thieme Verlag: Stuttgart, **2001**, *1*.

[26] K.C. Gupta, A.K. Sutar, Catalytic Activities of Schiff Base Transition Metal Complexes. *Coord. Chem. Rev.* **2008**, *252*, 1420-1450.

[27] S. Siangwata, N. Baartzes, B.C.E. Makhubela, G.S. Smith, Synthesis, Characterisation and Reactivity of Water-Soluble Ferrocenylimine-Rh(I) Complexes as Aqueous-Biphasic Hydroformylation Catalyst Precursors. *J. Organomet. Chem.* **2015**, *796*, 26-32.

[28] N. Mugio, S. Mariusz, I. Hiroshi, S. Takumichi, Mercuric Triflate-TMU Catalyzed Hydration of Terminal Alkyne to give Methyl Ketone under Mild Conditions. *Chem. Lett.* **2002**, *31*, 12-13.

[29] X. Jin, T. Oishi, K. Yamaguchi, N. Mizuno, Heterogeneously Catalyzed Efficient Hydration of Alkynes to Ketones by Tin–Tungsten Mixed Oxides. *Chem. Eur. J.* **2011**, *17*, 1261-1267.

[30] T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 50-53.

[31] X.-F. Wu, D. Bezier, C. Darcel, Development of the First Iron Chloride-Catalyzed Hydration of Terminal Alkynes. *Adv. Synth. Catal.* **2009**, *351*, 367-370.

[32] M.B.T. Thuong, A. Mann, A. Wagner, Mild Chemo-Selective Hydration of Terminal Alkynes Catalyzed by $AgSbf_6$. *Chem. Commun.* **2012**, *48*, 434-436.

[33] P.W. Jennings, J.W. Hartman, W.C. Hiscox, Alkyne Hydration Using Pt(II) Catalysts. *Inorg. Chim. Acta* **1994**, *222*, 317-322.

[34] T. Suzuki, M. Tokunaga, Y. Wakatsuki, Ruthenium Complex-Catalyzed anti-Markovnikov Hydration of Terminal Alkynes. *Org. Lett.* **2001**, *3*, 735-737.

[35] P.S. Mainkar, V. Chippala, R. Chegondi, S. Chandrasekhar, Ruthenium(II)-Catalyzed Hydration of Terminal Alkynes in PEG-400. *Synlett* **2016**, *27*, 1969-1972.

[36] T. Kusakabe, Y. Ito, M. Kamimura, T. Shirai, K. Takahashi, T. Mochida, K. Kato, Palladium(II) Bis(oxazoline) Complexes that Catalyze the Hydration of Alkynes. *Asian J. Org. Chem.* **2017**, *6*, 1086-1090.

[37] N. Marion, R.S. Ramón, S.P. Nolan, [(NHC)Au(I)]-Catalyzed Acid-Free Alkyne Hydration at Part-Per-Million Catalyst Loadings. *J. Am. Chem. Soc.* **2009**, *131*, 448-449.

[38] S. Liang, J. Jasinski, G.B. Hammond, B. Xu, Supported Gold Nanoparticle-Catalyzed Hydration of Alkynes under Basic Conditions. *Org. Lett.* **2015**, *17*, 162-165.

[39] R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, Organometallic Gold(III) Compounds as Catalysts for the Addition of Water and Methanol to Terminal Alkynes. *J. Am. Chem. Soc.* **2003**, *125*, 11925-11935.

[40] A. Vasudevan, M.K. Verzal, Neutral, Metal-free Hydration of Alkynes Using Microwave Irradiation in Superheated Water. *Synlett* **2004**, *2004*, 631-634.

[41] J. Zhang, S. Li, X. Fu, B.B. Wayland, Aerobic Oxidation of Alkenes Mediated by Porphyrin Rhodium(III) Complexes in Water. *Dalton Trans.* **2009**, 3661-3663.

[42] A. Leyva, A. Corma, Isolable Gold(I) Complexes Having One Low-Coordinating Ligand as Catalysts for the Selective Hydration of Substituted Alkynes at Room Temperature without Acidic Promoters. *J. Org. Chem.* **2009**, *74*, 2067-2074.

[43] J. Zhang, B.B. Wayland, L. Yun, S. Li, X. Fu, Reactivity and Kinetic–Mechanistic Studies of Regioselective Reactions of Rhodium Porphyrins with Unactivated Olefins in Water that form β-Hydroxyalkyl Complexes and Conversion to Ketones and Epoxides. *Dalton Trans.* **2010**, *39*, 477-483.

[44] S. Li, W. Cui, B.B. Wayland, Competitive O–H and C–H Oxidative Addition of CH_3OH to Rhodium(II) Porphyrins. *Chem. Commun.* **2007**, 4024-4025.

[45] S. Li, S. Sarkar, B.B. Wayland, Methanol as a Reaction Medium and Reagent in Substrate Reactions of Rhodium Porphyrins. *Inorg. Chem.* **2009**, *48*, 8550-8558.

[46] M. Ali, A.K. Srivastava, R.K. Joshi, Metal/Catalyst/Reagent Free Hydration of Alkynes up to Gram Scale Under Temperature and Pressure Controlled Condition. *Tetrahedron Lett.* **2018**, *59*, 2075-2078.

[47] J. Polin, H. Schottenberger, Conversion of Methyl Ketones into Terminal Acetylenes: Ethynylferrocene. *Org. Synth.* **1996**, *9*, 411 - 414.

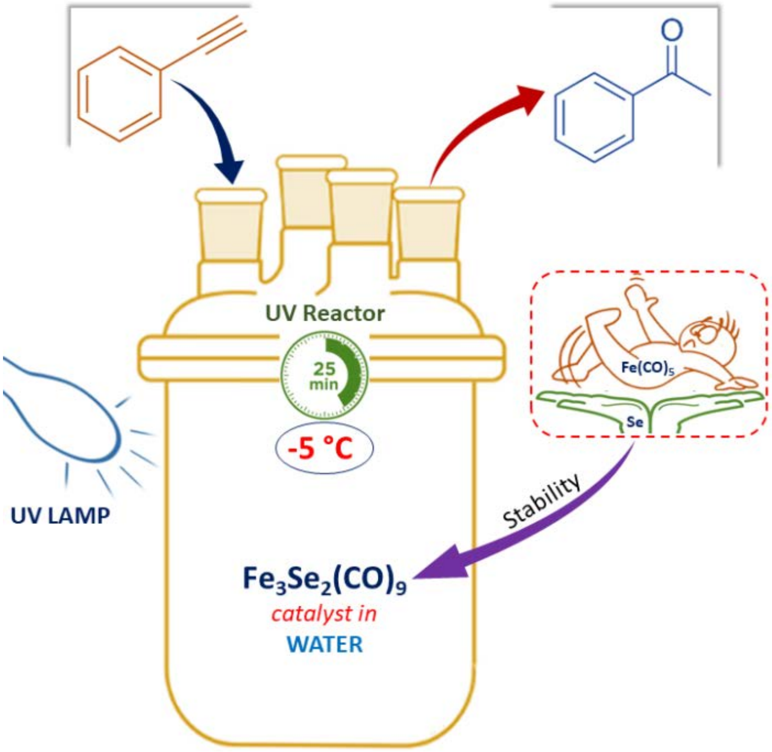
[48] F. Li, N. Wang, L. Lu, G. Zhu, Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot Synthesis of Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(R,R)-TsDPEN]. *J. Org. Chem.* **2015**, *80*, 3538-3546.

[49] O. Israelsohn, K.P.C. Vollhardt, J. Blum, Further Studies on Hydration of Alkynes by the $PtCl_4$–CO Catalyst. *J. Mol. Catal. A: Chem.* **2002**, *184*, 1-10.

[50] M. Jacubert, O. Provot, J.-F. Peyrat, A. Hamze, J.-D. Brion, M. Alami, p-Toluenesulfonic Acid-Promoted Selective Functionalization of Unsymmetrical Arylalkynes: a Regioselective Access to Various Arylketones and Heterocycles. *Tetrahedron* **2010**, *66*, 3775-3787.

Chapter-4

An Efficient, Cost-Effective and Green Approach for Hydration of Alkynes by Chalcogenated Metal cluster in Photo Chemical Conditions



4.1 Introduction

Association of water and alkynes is difficult due to their different affinities [1], the chemical union of these molecules produces carbonyls in the form of ketones or aldehydes depending upon the nature of addition (Markonikov or anti-Markonikov). Hydration reactions are the most facile methodology to create C–O bonds. Ketones are one of the crucial motifs for the modern pharmaceutical and chemical industries. Synthesis of ketones has wide fundamental importance for various pharmaceutical and API Industries [2]. Synthesis of fexofenadine, benperidol, droperidol, azaperone and other related drugs requires alkyne hydration as one of the crucial steps for synthesis [2]. Hydrations reactions are slow even in the presence of catalysts; the reason is their reconcilable polarities of reagents used in the reaction. Solving this problem requires a specific property of catalyst to induce polarity to the alkyne used in the reaction [1]. Hydrations of alkynes using mineral acids or organic acids are known since the discovery of alkynes. Metal catalyzed hydrations of alkynes is well established; classically toxic reagents catalyzed such reactions conventionally $Hg^{2+}$and mercury-based complexes are used [3]. Conventional catalysis techniques like the use of acids and mercury restrict the substrate scope of the reaction; acid-labile functionalities are not compatible with such reaction conditions. To circumvent the flaws of previous synthesis methodologies, the opted alternate is the transition metal based catalysis. In the 1960's Kemp *et al.* reported the use of Ru(III) published several reports showing catalytic applications of Ru(II) complexes for alkyne hydrations [6-9]. Pt(IV), Au(III), Pd(II), Cu(II) and Ag(I) were also used for similar reactions during the same decade [10-16]. However, these methodologies were not found adequately efficient for such reactions.

Tanaka *et al.* reported a highly efficient Au(I) catalyst for alkyne hydrations in the year 2002, but this catalyst performs hydrations in the presence of mineral acids [2]. Since then Au(I) complexes had emerged as a promising substitute for the previous toxic and inefficient catalysts. In the later years, Au(I) complexes with NHC and Phosphine ligands were also reported for their exceptional catalytic ability towards alkyne hydrations [17-21]. The need of co-catalysts as halide scavenger and non-reusable nature are the major drawbacks associated with these catalysts. Heavy metals and expensive catalysts are unsustainable from the view of green chemistry.

Therefore, many efforts towards the development of an economic catalyst have been made in recent years. Ag(I), Fe(III), Fe(II), Co(III) and Sn(II) are presented as a valid alternative for the previous expensive catalysts [22-27]. Naka *et al.* reported for the first time a Co(III) porphyrin complex for alkyne hydration; this catalyst performs reaction under mild acidic reaction condition that enables this catalyst to work with acid-labile functionalities [28]. Most of these catalysts are not reusable while; few are the highly sensitive metal-ligand complexes. Hence, many other research groups aimed to produce even more sustainable methodologies.

As it is very familiar that the use of different reaction methodologies (like Photochemical, Microwave) that can improve the productivity of reactions. In the year 2004, Vasudevan *et al.* reported a catalyst-free reaction methodology for alkyne hydration using superheated water under microwave irradiation [29]. Joshi *et al.* in the year 2018 reported a modified catalyst-free reaction methodology optimised up to gram scale in an autoclave [30]. These methodologies use harsh reaction conditions for catalytic conversion. Fu *et al.* reported the use of a Rh(III) porphyrin complex in mild acidic condition as a catalyst for alkyne hydration under UV-Visible irradiation [31]. Recently Joshi *et al.* reported an Rh(I) Schiff base complex for acid-free alkyne hydrations UV irradiation [3]. These reactions use methanol as a solvent, and most of the other examples reported with aqueous methanol. As the hydration, reactions need water as one of the reactants, and water is an appreciated solvent. Non-toxic nature, abundance and easy separation of water make it a most favoured solvent. Performing alkyne hydration reactions under neat reaction condition stems the sustainable approach towards methodology development.

Metal Carbonyls are the well-implemented catalysts in the laboratory as well as the commercial synthesis of various organic compounds. Chikkali *et al.* in the present year reported an Iron carbonyl catalyzed hydroformylations reaction [32]. alkoxycarbonylations of alkyl bromides, and synthesis of γ-lactones using iron carbonyls are also reported in this same year [33, 34]. Monoatomic 3d transition clusters are sometimes considered toxic, but bi- or triatomic clusters are highly stable at ambient temperatures. Additionally, these metal carbonyls can be made stable at ambient conditions by introducing Chalcogen between metal-metal bonds. Moreover, the use of chalcogens (especially S and Se) is well established for cluster growth reactions. As the literature suggests metal carbonyls under UV irradiation forms a catalytically active species [35]. Reports are available highlighting the catalytic properties of metal carbonyls under UV irradiation. Masuda *et al.* (1980) and Geoffroy *et al.*(1985) reported photo induced alkyne polymerisation using $M(CO)_6$ where M= Cr, Mo and W [36, 37]. But there are certain drawbacks of using $M(CO)_6$ under photochemical conditions. These metal carbonyls may undergo irreversible chemical changes during the reaction, and they are not soluble in aqueous solvents.

In terms of finding a stable alternate of metalcarbonyls that can perform reactions under aqueous and photochemical condition. Metal Chalcogenide carbonyl clusters could be the possible alternate of metal carbonyls $[M(CO)_x]$ for such applications, but the use of these complexes as catalysts is not very common and to our knowledge; these complexes have not yet used as a catalyst under such reaction conditions. *In this chapter,* we wish to report an iron chalcogenide carbonyl cluster for hydration of alkyne, which works as a heterogeneous catalyst in aqueous media and produce excellent results under UV irradiation.

4.2 Experimental

4.2.1 Materials and reagents

Reactants, reagents, chemicals and solvents available commercially within the country were used. Methanol used in this reaction is HPLC grade and purchased from Fischer Scientific. De-ionised water is obtained from Aqua Maxx basic 360 series water purification system manufactured by Young Lin Instrument Co. Ltd., South Korea.

4.2.2 General Procedure for the Catalytic Reaction:

General Procedure for the Catalytic Reaction: To a 100 mL borosilicate immersion well of UV reactor, 80 mL water was used as a solvent, alkyne (1 mmol), $Fe_3Se_2(CO)_9$ catalyst (5 mol%) was added. The reaction mixture was first cooled down at -5 °C then it was exposed to the Hg vapour UV lamp, 125 W, 289 nm for 25 min with continuous stirring. After completion of the reaction, the catalyst was separated through filtration and product was extracted through solvent extraction with ethyl acetate. The extracted solvent was dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. The residue was subjected to column chromatography with hexanes/ethyl acetate as eluent to obtain the corresponding desired product.

4.2.3 Instrumentation

4.2.3.1 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C).

4.2.3.2 Infra-red Spectroscopy

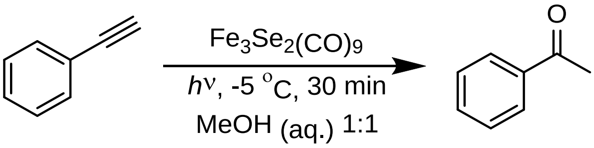
IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin Elmer 10.4.00 FT-IR spectrometer as KBr pellets of the sample.

4.2.3.3 High Resolution Mass Spectroscopy

High Resolution Electron Impact Mass Spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA) in HPLC grade acetonitrile solvent.

4.3 Results and Discussion

The initial test reactions with phenylacetylene and the $Fe(CO)_5$ in aqueous methanol under photo-catalytic conditions do not produce any results. Other iron carbonyl clusters were also used for the trail reaction under the same reaction conditions but did not mimic any chemical change in the reaction (Table 1, Entry 1 - 5).



Scheme 1: Reaction of phenyl acetylene under UV irradiation

The change of the catalyst to $Fe_3Se_2(CO)_9$ for the same reactions leads to instant success (Scheme 1). However, the obtained yield was considerably low. To increase the yield of acetophenone, different combinations of the solvent ratio mixtures of aqueous methanol were investigated, but no substantial increase in the yield was obtained. Use of methanol as a solvent decreases the yield, while water as solvent significantly enhances the product yield.

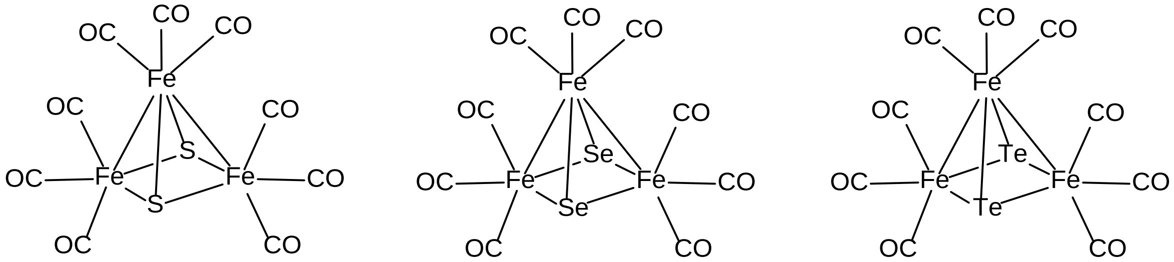


Figure 1: The structure of the iron chalcogenide carbonyl complex used as catalyst

As observed, the presented catalyst is found inactive for this reaction in methanol; however in methanol catalyst was completely soluble. However, this catalyst was insoluble in water and behaved as a heterogeneous catalyst as well as shows catalysis towards the hydration of acetylene. The complex used as the catalyst is synthesised as per the procedure reported in the previous literature [38]. The three chalcogens (S, Se and Te) are used for the synthesis of the complex. Complex with the selenide bridging shows excellent catalysis activity in comparison to the S and Te bridging complexes (Table 1, Entry 6 - 8).The reason could be the difference in the electron donor properties of S, Se and Te. The literature suggests going down to the chalcogen metal group, the HOMO – LUMO band gap decreases which support the higher activity of selenium. The reduced catalytic activity of Te complex can be explained by the increased atomic size, which tends to reduce the electron density on the central metal atom [39-46].

Reaction parameters Optimization. Various parameters to scale up the yield of the desired product were further investigated. It was noted that 5 mol% of catalyst was sufficient enough to bring about the desired organic transformations with significant yields. Further addition of the catalyst amount does not affect the product yield while the lower quantity of catalyst substantially decreases the product yield. Amount less than 2 mol% of catalyst only indicates the traces of the desired organic transformation. Gradually increasing the catalyst amount (up to 5 mol %) improves the yield in significant amount (Table 1, Entry 9 - 14).The scope of the reaction was again explored concerning the reaction temperature. The present reaction was found to be sensitive towards the increase in reaction temperature; at 0 °C, the reaction produces an average yield of the desired product. However, lowering the reaction temperature to -5 °C significantly increase the yield of the desired transformation.

Hence, all experiments were conducted at a low temperature of -5 °C; further decreasing the temperature does not show any considerable changes in the yield of desire reaction product(Table 1, Entry 15 - 17).

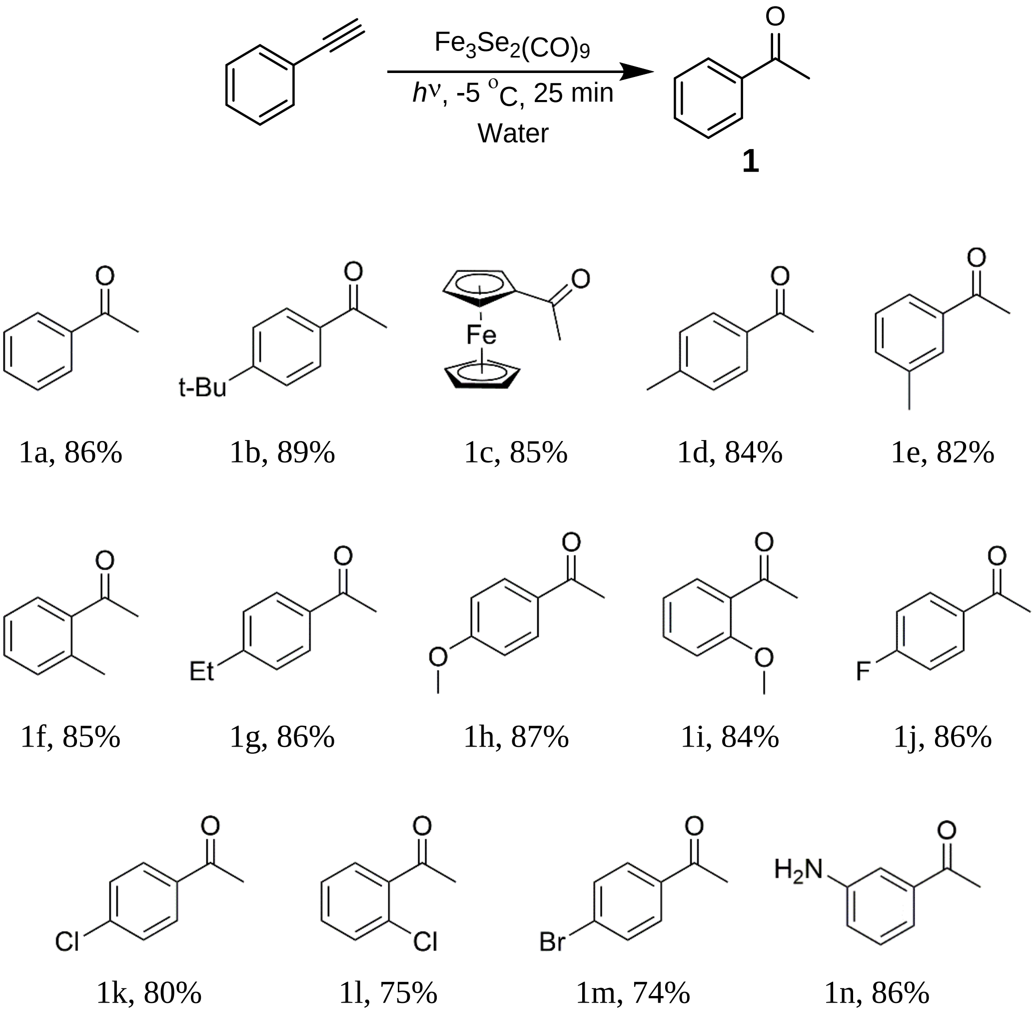
Table 1: Optimizations of reaction parameters for alkyne hydrations

Entry	**Catalyst**	**Cat. Amt. (mol%)**	**Temp. (°C)**	**Time (min.)**	**Yield[a] (%)**
1.	-	-	-5	25	-
2.	**$Fe(CO)_5$**	5	-5	25	-
3.	**Se**	5	-5	25	-
4.	**$Fe_2(CO)_9$**	5	-5	25	-
5.	**$Fe_3(CO)_{12}$**	5	-5	25	-
6.	**$Fe_3Se_2(CO)_9$**	**5**	**-5**	**25**	**86**
7.	**$Fe_3S_2(CO)_9$**	5	-5	25	29
8.	**$Fe_3Te_2(CO)_9$**	5	-5	25	13
9.	$Fe_3Se_2(CO)_9$	**1**	-5	25	-
10.	$Fe_3Se_2(CO)_9$	**2**	-5	25	15
11.	$Fe_3Se_2(CO)_9$	**3**	-5	25	65
12.	$Fe_3Se_2(CO)_9$	**4**	-5	25	76
13.	**$Fe_3Se_2(CO)_9$**	**5**	**-5**	**25**	**86**
14.	$Fe_3Se_2(CO)_9$	**6**	-5	25	86
15.	$Fe_3Se_2(CO)_9$	5	**0**	25	45
16.	**$Fe_3Se_2(CO)_9$**	**5**	**-5**	**25**	**86**
17.	$Fe_3Se_2(CO)_9$	5	**-10**	25	86
18.	$Fe_3Se_2(CO)_9$	5	-5	**10**	26
19.	$Fe_3Se_2(CO)_9$	5	-5	**15**	59
20.	$Fe_3Se_2(CO)_9$	5	-5	**20**	76
21.	**$Fe_3Se_2(CO)_9$**	**5**	**-5**	**25**	**86**
22.	$Fe_3Se_2(CO)_9$	5	-5	**30**	87

[a] Isolated Yields, Phenylacetylene (1 equiv), catalyst (5 mol%), Water Solvent, 25 min., -5 °C

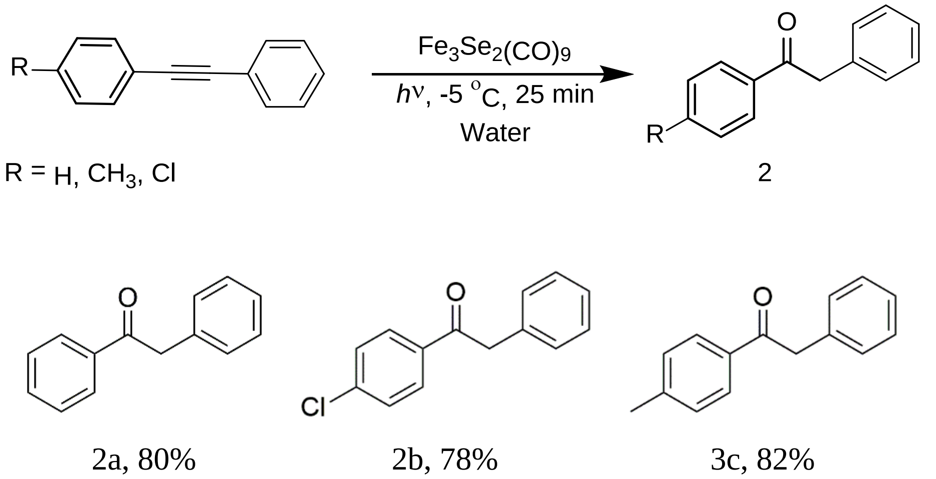
Using alternate reaction methodologies have extensive benefits in comparison to the classical thermal reaction methods. Alternate sources like a microwave or UV-Vis irradiation are a possible and efficient way of providing energy to the reaction mixture. Hg vapour lamp is one of the authoritative sources for providing UV-Vis irradiation. In this optimised reaction conditions methodology, we have used a 125 W, high-pressure Hg vapour lamp as a UV source, which produced 289 nm wavelength UV-Vis irradiation. This enables us to pursue reactions in a very short duration. Under these photochemical conditions, a maximum of 86% yield was recorded during optimisation in 25 minutes. In the first 10 minutes, 26% yield was recorded, moreover, it was further increased up to 86 % in next 15 min. There was no sizeable change obtained for the yield of the desired product beyond the further exposure of the irradiations (Table 1, Entry 18 - 22).

Substrate Scope: Next, to explore is the substrate scope, the optimised reaction conditions were employed for the reactions of various alkynes. The functionally substituted alkynes are having electron donating and withdrawing groups at any of the *ortho*-, *meta*- and *para*- positions proceeds smoothly to produce corresponding ketones. It was noteworthy that *para*-*tert*-Butyl-phenyl acetylene and ethynylferrocene were compatible with the reaction and produced 89% and 85% yield of their corresponding ketones (1b and 1c). Other alkyls the *ortho*-, *meta*- and *para*- methyl substitutions participated smoothly in the reaction and yields 85%, 82% and 84% of the desired ketones (1d, 1e and 1f). Similarly, *para*-ethyl, *para*-methoxy and *ortho*-methoxy efficiently worked for this reaction producing 86%, 87% and 84% yield of ketones (1g, 1h and 1i). Strongly electron withdrawing functionality the *para*-flouro substitution produces excellent results through this reaction as it produces the 86% of the desired product (1j). Other halogens *ortho*- and *para*-chloro, *para*-bromo shows slightly reduced yields of their corresponding products, 80%, 75% and 74% yields were recorded with these functionalities (1k, 1l and 1m). The *meta*- substituted 3-aminophenyl acetylene also produces 86% yield of the keto product (1n).



Scheme 2: Generalization of the scope of reaction with various terminal acetylenes

This reaction was extended to internal alkynes, three different internal alkynes were used for the hydration reaction and excellent yields of their corresponding ketones



Scheme 3: Generalization of the scope of reaction with various Internal acetylenes

was recorded. It was also noted that the symmetric internal alkyne produces 80% its corresponding ketone (2a), while the *para*-chloro and *para*- methyl substituted asymmetric internal alkynes produces 78% and 82% of their corresponding ketones (2b and 2c). The recyclability of the catalyst was studied, using phenylacetylene as a model substrate under the optimized reaction conditions. In a typical experiment, the water-insoluble iron chalcogenide complex was recovered at the end of the reaction by filtration and directly used in a new catalytic run. The catalyst showed good recyclability and not deactivated much up to 6 catalytic cycles, moreover, up to 50% product transformations were noted in 8th catalytic cycles. We have used the same catalyst up to 9 catalytic cycles and 31% product formation was obtained in the 9th catalytic run. This reusability test indicates the catalytic system is highly robust and active in nature as it can even work after 9 catalytic cycles and do not require any specific treatment for to separate the catalyst as well as the reactivation of the catalyst.

No. of Cycles	1	2	3	4	5	6	7	8	9
Product Yield[a]	86	86	84	84	79	70	60	49	31

Condition: [a]Isolated Yields, Phenylacetylene (1 equiv), catalyst (5 mol%), Water Solvent, 25 min., -5 °C

Most of the iron-based catalysts reported earlier are non-reusable and performs the reaction in organic media at highly thermal condition with prolonged time [24, 58, 25, 26] (Table 2, Entry 4, Entry 18, Entry 19, and Entry 20). In comparison to the previous reports the presented catalyst has shown better activity in many terms. The catalyst produces excellent yields of the desired product and shows wide functional group compatibility at very low temperature. This catalytic methodology needs very less time in comparison to other reported catalysts (Table 2, Entry1-20), hence the present methodology is time and energy efficient. It was also noticed that the presented catalyst behaves as a heterogeneous catalyst in aqueous media and can be reused up to several catalytic cycles. Moreover, the catalyst can be isolated from the reaction through filtration and it does not require any chemical or thermal activation and can be used the next catalytic cycle.

Table 2: Comparison of various alkyne hydration reactions with the present reaction

Entry	Metal catalyst	Catalyst (mol%)	Solvent	Temp. (˚C)	Time (h)	condition (Δ, hν, MW)	Yield (%)	Ref.
1.	Hg(II)	5	MeCN	Rt	12	Δ	100	47
2.	Sn-W	50	cycloocatane	100	0.5 –	Δ	91	48*
3.	Co(III)	2	MeOH	80	5 – 36	Δ	99	49
4.	Fe(III)	10	DCE	75	67	Δ	96	24
5.	Ag(I)	10	MeOH	75	36 – 48	Δ	94	22
6.	Pt(II)	0.8	THF	60	12	Δ	55:45	50
7.	Rh(III)	4	THF	110	16 – 24	Δ	93	51
8.	Rh(I)	5	THF	110	2	Δ	100	52
9.	Rh(III)	20	MeOH	Rt	12	Hν	91	31
10.	Ru(I)	1 – 5	IPA	100	12 – 36	Δ	99	8
11.	Ru(II)	5	PEG-400	Rt	12 – 48	Δ	89	53
12.	Pd(II)	5	MeOH	50	1 – 51	Δ	99	54
13.	Au(I)	0.1	Dioxane	120	18	Δ	97	55
14.	Au-TiO_2	1	Dioxane	120	1	Mw	97	56*
15.	Au(III)	1.6 – 4.5	MeOH	70	1.5 – 4	Δ	98	57
16.	Rh(I)	1.5	MeOH	-5	0.5	Hν	85	3#
17.	Fe(III)	100	DCM	Rt	24	Δ	92	23
18.	Fe(II)	5	DCE	60	1	Δ	92	58
19.	Fe(III)	10	Dioxane	80	20	Δ	96	25
20.	Fe(III)	9	AcOH	95	24	Δ	99	26
21.	**Fe(0)**	**5**	**Water**	**-5**	**0.42**	**Hν**	**86**	**--**

*Heterogeneous reusable catalyst, #Homogeneous reusable catalyst

While comparing the reusability of the present catalyst with the other two reported heterogeneous [48, 56] (Table 2, Entry 2 and Entry 14) and as well as one homogeneous [3] (Table 2, Entry 16) catalyst, the present catalyst is a unique and a rare example of heterogeneous reusable catalyst in aqueous media. While, the present catalyst is the first ever example of performing alkyne hydration in neat water.

4.3.1 Supplementary Data

Acetophenone [24]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.87 – 7.85 (m, 2H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 2H), 2.50 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 198.34, 137.26, 133.32, 128.77, 128.50, 26.81.

Acetyl Ferrocene [59]

^{1}H NMR (400MHz, $CDCl_3$): δ = 4.77 (s, 2H), 4.51 (s, 2H), 4.21 (s, 5H), 2.40 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 202.16, 72.29 69.80, 69.54, 27.38.

1-(4-(tert-butyl)phenyl)ethan-1-one [24]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.82 – 7.80(m, 2H), 7.39 – 7.37 (m, 2H), 2.48 (s, 3H), 1.24 (s, 9H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 197.66, 156.52, 134.27, 131.55, 129.75, 128.02, 125.21, 34.79, 30.78, 26.25.

1-(p-tolyl)ethan-1-one [60]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.87 - 7.85 (m, 2H), 7.26 – 7.24 (m, 2H), 2.57 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 197.50, 143.54, 134.33, 128.91, 128.10, 26.18, 21.28.

1-(m-tolyl)ethan-1-one [60]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.75 – 7.72 (m, 2H), 7.34 – 7.32 (m, 2H), 2.56 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 198.21, 138.21, 137.01, 133.77, 128.67, 128.35, 125.49, 26.55, 21.21.

1-(o-tolyl)ethan-1-one [61]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.68 – 7.67 (m, 1H), 7.37 – 7.33 (m, 1H), 7.26 – 7.20 (m, 2H), 2.55 (s, 3H), 2.53 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 201.60, 138.38, 137.44, 132.02, 131.52, 129.40, 125.70, 29.48, 21.60.

1-(4-ethylphenyl)ethan-1-one [60]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.89 – 7.87 (m, 2H), 7.29 – 7.27 (m, 2H), 2.73 – 2.67 (q, 2H), 2.57 (s, 3H), 1.27 – 1.23 (t, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 198.07, 150.26, 135.12, 128.76, 128.27, 29.15, 26.76, 15.43.

1-(4-chlorophenyl)ethan-1-one [60]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.93 – 7.91 (m, 2H), 7.47 – 7.45(m, 2H), 2.62 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 196.71, 139.40, 135.26, 129.62, 128.75, 26.45

1-(2-chlorophenyl)ethan-1-one [3]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.55 – 7.53 (m, 1H), 7.41 – 7.29 (m, 3H), 2.64 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 200.32, 138.94, 131.91, 131.13, 130.52, 129.29, 126.83, 30.58.

1-(4-methoxyphenyl)ethan-1-one [60]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.93 – 7.91 (m, 2H), 6.92 – 6.90 (m, 2H), 3.84 (s, 3H), 2.53 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ = 196.88, 163.63, 130.72, 130.42, 113.82, 55.58, 26.46.

1-(2-methoxyphenyl)ethan-1-one [60]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.71 – 7.69 (m, 1H), 7.43 – 7.39 (m, 1H), 6.95 – 6.90 (m, 2H), 3.84 (s, 3H), 2.57 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 199.83, 159.11, 133.91, 130.41, 128.26, 120.63, 111.80, 55.59, 32.01.

1-(3-aminophenyl)ethan-1-one [60]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.32 – 7.20 (m, 3H), 6.87 – 6.85 (m, 1H), 3.88 (s, 2H), 2.55 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 198.53, 146.78, 138.08, 129.35, 119.60, 118.67, 113.91, 26.65

1-(4-bromophenyl)ethan-1-one [60]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.83 – 7.81 (m, 2H), 7.61 – 7.59 (m, 2H), 2.59 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.26, 136.00, 132.11, 130.07, 128.53, 26.79.

1-(4-fluorophenyl)ethan-1-one [60]

^{1}H NMR (400MHz, CDCl$_3$): δ = 8.0 – 7.97 (m, 2H), 7.15 – 7.11(m, 2H), 2.59 (s, 3H).**^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.67, 165.94 (d, J C – F = 254 Hz), 133.76 (d, J C – F = 3.0 Hz), 131.13 (d, J C – F = 9.0 Hz), 115.83 (d, J C – F = 22 Hz), 26.71.

1,2-diphenylethan-1-one[60]

^{1}H NMR (400MHz, CDCl$_3$): δ = 8.01 – 7.99 (m, 2H), 7.54 – 7.51 (m, 1H), 7.45 – 7.41 (m, 2H), 7.33 – 7.21 (m, 5H), 4.26 (s, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.37, 136.27, 134.25, 132.91, 129.20, 128.39, 128.37, 128.34, 126.01, 45.21.

1-(4-chlorophenyl)-2-phenylethan-1-one [62]

^{1}H NMR (400MHz, CDCl$_3$): δ = 4.25 (s, 2H), 7.24 – 7.35 (m, 5H), 7.41 – 7.44 (m, 2H), 7.93 – 7.96 (m, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.46, 139.65, 134.83, 134.18, 130.07, 129.40, 128.99, 128.79, 127.07, 45.56

2-phenyl-1-(p-tolyl)ethan-1-one [63]

^{1}H NMR (400MHz, CDCl$_3$): δ = 2.30 (s, 3H), 4.22 (s, 2H), 7.10 – 7.15 (m, 4H), 7.40 – 7.44 (m, 2H), 7.50 – 7.52 (m, 1H), 7.98 – 8.00 (m, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.79, 136.52, 136.42, 133.05, 131.35, 129.34, 129.25, 128.56, 45.07, 21.03.

4.4 Conclusion

We have developed a catalytic methodology for the alkyne hydration under UV irradiation. For the first time Iron chalcogenide carbonyl complexes as catalyst were used for such reaction. This catalytic methodology is found active towards the terminal and internal alkynes having various functional groups at different positions (*ortho-*, *meta-* and *para-*) are used in the reaction. This methodology produces excellent yields and shows compatibility towards the wide range of functionalities. The presented catalyst behaves as a heterogeneous catalyst in aqueous media. Moreover, the presented catalyst is reusable up to several cycles and easily separated through filtrations as well as the reaction completes in minor duration.

4.5 References

1. L. Hintermann, A. Labonne, Catalytic Hydration of Alkynes and Its Application in Synthesis. *Synthesis* **2007**, *8*, 1121-1150.

2. E.Mizushima, K. Sato, T. Hayashi, M. Tanaka, Highly Efficient Au(I) Catalyzed Hydration of Alkynes. *Angew. Chem.* **2002**, *114*, 4745-4747.

3. M. Ali, A. K. Srivastava, S. Siangwata, G. S. Smith, R. K. Joshi, Photo Induced Alkyne Hydration Reactions Mediated by a Water Soluble, Reusable Rhodium (I) Catalyst. *Catal. Commun.* **2018**, *115*, 78-81.

4. J. Halpern, B. R. James, A. L. W. Kemp, Catalysis of the Hydration of Acetylenic Compounds by Ruthenium(III) Chloride. *J. Am. Chem. Soc.* **1961**, *83*, 4097-4098.

5. J. Halpern, B. R. James, A. L. W. Kemp, Formation and Properties of Some Chloro carbonyl Complexes of Ruthenium(II) and Ruthenium(III). *J. Am. Chem. Soc.* **1966**, *88*, 5142-5147.

6. D. B. Grotjahn, C. D. Incarvito, A. L. Rheingold, Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-Markovnikov Hydration of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2001**, *113*, 4002-4005

7. M. Tokunaga, Y. Wakatsuki, The First Anti-Markovnikov Hydration of Terminal Alkynes: Formation of Aldehydes Catalyzed by a Ruthenium(II)/Phosphane Mixture. *Angew. Chem. Int. Ed.* **1998**, *37*, 2867-2869.

8. T. Suzuki, M. Tokunaga, Y.Wakatsuki, Ruthenium Complex-Catalyzed anti-Markovnikov Hydration of Terminal Alkynes. *Org. Lett.* **2001**, *3*, 735-737.

9. M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi, Y. Wakatsuki, Ruthenium-Catalyzed Hydration of 1-Alkynes to Give Aldehydes: Insight into anti-Markovnikov Regiochemistry. *J. Am. Chem. Soc.* **2001**, *123*, 11917-11924.

10. W. Hiscox, P. W. Jennings, Catalytic Hydration of Alkynes with Zeise's Dimer. *Organometalics.* **1990**, *9*, 1997-1999.

11. W. Baidossi, M. Lahav, J. Blum, Hydration of Alkynes by a $PtCl_4$−CO Catalyst. *J. Org. Chem.* **1997**, *62*, 669-672.

12. L. W.Francisco, D. A. Moreno, J. D. Atwood, Synthesis, Characterization, and Reaction Chemistry of $PtCl_2[P(m\text{-}C_6H_4SO_3Na)_3]_2$, an Alkyne Hydration Catalyst. *Organometalics.* **2001**, *20*, 4237-4245.

13. Y. Fukuda, K. Utimoto, Effective Transformation of Unactivated Alkynes into Ketones or Acetals with A Gold(III) Catalyst. *J. Org. Chem.* **1991**, *56*, 3729-3731.

14. Y. Fukuda, K. Utimoto, Efficient Transformation of Methyl Propargyl Ethers into α,β-Unsaturated Ketones. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2013-2015.

15. K. Imi, K. Imai, K. Utimoto, Regioselective Hydration of Alkynones by Palladium Catalysis. *Tetrahedron Lett.* **1987**, *28,* 3127-3130.

16. I. K. Meier, J. A. Marsella, Hydration of Acetylenic Compounds without Using Mercury. *J. Mol. Catal.* **1993**, *78,* 31-42.

17. N.Ghosh, S. Nayak, A. K. Sahoo, Gold-Catalyzed Regioselective Hydration of Propargyl Acetates Assisted by a Neighbouring Carbonyl Group: Access to α-Acyloxy Methyl Ketones and Synthesis of (±)-Actinopolymorphol B. *J. Org. Chem.* **2011**, *76,* 500-511.

18. A. Leyva, A. Corma, Isolable Gold(I) Complexes Having One Low-Coordinating Ligand as Catalysts for the Selective Hydration of Substituted Alkynes at Room Temperature without Acidic Promoters. *J. Org. Chem.* **2009**, *74*, 2067-2074.

19. P. Nun, R. S.Ramón, S. Gaillard, S. P.Nolan, Efficient Silver-Free Gold(I)-Catalyzed Hydration of Alkynes at Low Catalyst Loading. *J. Organomet. Chem.* **2011**, *696*, 7-11.

20. F. Li, N. Wang, L. Lu, G. Zhu, Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot Synthesis of Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(R,R)-TsDPEN]. *J. Org. Chem.* **2015**, *80*, 3538-3546.

21. M. Gatto, W. Baratta, P. Belanzoni, L. Belpassi, A. D. Zotto, F. Tarantelli, D. Zuccaccia, Hydration and Alkoxylation of Alkynes Catalyzed by NHC–Au–OTf. *Green Chem.* **2018**, *20*, 2125-2134.

22. M. B. T. Thuong, A. Mann, A. Wagner, Mild Chemo-Selective Hydration of Terminal Alkynes Catalysed by $AgSbF_6$. *Chem. Commun.* **2012**, *48*, 434-436.

23. J. P. Damiano, M. Pastel, $FeCl_3.H_2O$: A Specific System for Arylacetylene Hydration. *J. Organomet. Chem.* **1996**, *522*, 303-305.

24. X. Wu, D. Bezier, C.Darcel, Development of the First Iron Chloride Catalyzed Hydration of Terminal Alkynes. *Adv. Synth. Catal.* **2009**, *351*, 367-370.

25. J. R. C. Antonino, A. L. Perez, A. Corma, Regioselective Hydration of Alkynes by Iron(III) Lewis/Brønsted Catalysis. *Chem. Eur. J.* **2012**, *18*, 11107-11114.

26. M. Bassetti, S. Ciceri, F. Lancia, C. Pasquini, Hydration of Aromatic Terminal Alkynes Catalyzed by Iron(III) Sulfate Hydrate Under Chlorine-Free Conditions. *Tetrahedron Lett.* **2014**, *55*, 1608-1612.

27. S. Hou, H. Yang, B. Cheng, H. Zhai, Y. Li, Cobaloxime-Catalyzed Hydration of Terminal Alkynes Without Acidic Promoters. *Chem. Commun.* **2017**, *53*, 6926-6929.

28. T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 50-53.

29. A. Vasudevan, M. K. Verzal, Neutral, Metal-free Hydration of Alkynes Using Microwave Irradiation in -Superheated Water. *Synlett* **2004**, *4*, 631-634.

30. M. Ali, A. K. Srivastava, R. K. Joshi, Metal/Catalyst/Reagent Free Hydration of Alkynes upto Gram Scale Under Temperature and Pressure Controlled Condition. *Tetrahedron Lett.* **2018**, *59*, 2075-2078.

31. X. Liu, L. Liu, Z. Wang, X. Fu, Visible Light Promoted Hydration of Alkynes Catalysed by Rhodium(III) Porphyrins. *Chem. Commun.* **2015**, *51*, 11896-11898.

32. S. Pandey, K. V. Raj, D. R. Shinde, K. Vanka, V. Kashyap, S. Kurungot, C. P. Vinod, S. H. Chikkali, Iron Catalyzed Hydroformylations of Alkenes under Mild Conditions: Evidence of an Fe(II) Catalysed Process. *J. Am. Chem. Soc.* **2018**, *140*, 4430-4439.

33. Y. Li, X. F. Wu, Copper/Iron Co-Catalyzed Alkoxycarbonylation of Inactivated Alkyl Bromides. *Communications Chemistry* **2018**, *1*, 39

34. M. Iwasaki, N. Miki, Y. Ikemoto, Y. Ura, Y. Nishihara, Regioselective Synthesis of γ-Lactones by Iron-Catalyzed Radical Annulation of Alkenes with α-Halocarboxylic Acids and their Derivatives. *Org. Lett.* **2018**, *20*, 3848-3852.

35. K. Xu, H. Peng, J. W. Y. Lam, T. W. H. Poon, Y. Dong, H. Xu, Q. Sun, K. K. L. Cheuk, F. Salhi, P. P. S. Lee, B. Z. Tang,Transition Metal Carbonyl Catalysts for Polymerizations of Substituted Acetylenes. *Macromolecules* **2000**, *33*, 6918-6924.

36. T. Masuda, Y.Kuwane, K. Yamamoto, T. Higashimura, Polymerization of Acetylene Derivatives Induced by UV Irradiation via Metal Carbonyls. *Polym. Bull.* **1980**, *2*, 823-827.

37. S. J. Landon, P. M. Shulman, G. L. Geoffrey, Photo-assisted Polymerization of Terminal Alkynes by $W(CO)_6$ Involving Catalyst Generation by an Alkyne to Vinylidene Ligand Rearrangement. *J. Am. Chem. Soc.* **1985**, *107*, 6739-6740.

38. P. Mathur, D. Chakrabarty, M.M. Hossain, Mixed Chalcogen Carbonyl Compounds: Synthesis and Characterisation of $(CO)_6Fe_2(\mu_3\text{-Se})(\mu_3\text{-Te})Pt(PPh_3)_2$ and $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-Se})(\mu_3\text{-Te})$. *J.Organomett. Chem.* **1991,** 401, 167-172.

39. S. Kumar, G.K. Rao, A. Kumar, M.P. Singh, A.K. Singh, Palladium(II)-(E,N,E) Pincer Ligand (E = S/Se/Te) Complex Catalysed Suzuki Coupling Reactions in Water via in Situ Generated Palladium Quantum Dots. *Dalton Trans.* **2013**, *42*, 16939-16948.

40. G.K. Rao, A. Kumar, M.P. Singh, A.K. Singh, Palladium(II) Complex of an Organotellurium Ligand as a Catalyst for Suzuki Miyaura Coupling: Generation and Role of Nano-Sized Pd_3Te_2. *J. Organomet. Chem.* **2014**, *749*, 1-6.

41. G. K. Rao, A. Kumar, S. Kumar, U. B. Dupare, A.K. Singh, Palladacycles of Thioethers Catalysing Suzuki–Miyaura C–C Coupling: Generation and Catalytic Activity of Nanoparticles. *Organometallics* **2013**, *32*, 2452-2458.

42. G. K. Rao, A. Kumar, J. Ahmed, A. K. Singh, Palladacycle Containing Nitrogen and Selenium: Highly Active Pre-Catalyst for the Suzuki–Miyaura Coupling Reaction and Unprecedented Conversion into Nano-Sized $Pd_{17}Se_{15}$. *Chem. Commun*. **2010**, *46*, 5954-5956.

43. O. Prakash, K.N. Sharma, H. Joshi, P.L. Gupta, A.K. Singh, Half Sandwich Complexes of Chalcogenated Pyridine Based Bi-(N, S/Se) and Terdentate (N, S/Se, N) Ligands with (η^6-Benzene)Ruthenium(II): Synthesis, Structure and Catalysis of Transfer Hydrogenation of Ketones and Oxidation of Alcohols. *Dalton Trans*. **2013**, *42*, 8736-8747.

44. Q. Yao, E.P. Kinney, C. Zheng, Selenium-Ligated Palladium(II) Complexes as Highly Active Catalysts for Carbon−Carbon Coupling Reactions: The Heck Reaction. *Org. Lett*. **2004**, *6*, 2997-2999.

45. Q. Yao, M. Sheets, A SeCSe−Pd(II) Pincer Complex as a Highly Efficient Catalyst for Allylation of Aldehydes with Allyltributyltin. *J. Org. Chem*. **2006**, *71*, 5384-5387.

46. M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, Highly Active Pd(II) PCP-Type Catalysts for the Heck Reaction. *J. Am. Chem. Soc.* **1997**, *119*, 11687-11688.

47. M. Nishizawa, M. Skwarczynski, H. Imagawa, T. Sugihara, Mercuric Triflate-TMU Catalyzed Hydration of Terminal Alkyne to give Methyl Ketone under Mild Conditions. *Chem. Lett.* **2002**, *31*, 12 –13.

48. X. Jin, T. Oishi, K. Yamaguchi, N. Mizuno, Heterogeneously Catalysed Efficient Hydration of Alkynes to Ketones by Tin–Tungsten Mixed Oxides. *Chem. Eur. J.* **2011**, *17*, 1261 – 1267.

49. T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 50–53.

50. P. W. Jennings, J. W. Hartman, W. C. Hiscox, Alkyne Hydration using Pt(II) Catalysts *Inorg. Chim. Acta* **1994**, *222*, 317 - 322.

51. A. Lumbroso, N. R. Vautravers, B. Breit, Rhodium-Catalyzed Selective anti-Markovnikov Addition of Carboxylic Acids to Alkynes. *Org. Lett*. **2010**, *12*, 5498 - 5501.

52. Young Jun Park, Bong-Il Kwon, Jeong-AeAhn, Hyuk Lee, Chul-Ho Jun, Chelation-Assisted Hydrative Dimerization of 1-Alkyne Forming α,β-Enones by an Rh(I) Catalyst. *J. Am. Chem. Soc*. **2004**, *126*, 13892-13893.

53. P. S. Manikar, V. Chippala, R. Chegondi, S. Chandrasekher, Ruthenium(II)-Catalyzed Hydration of Terminal Alkynes in PEG-400. *Synlett* **2016**, *27*, 1969-1972.

54. T. Kusakabe, Y. Ito, M. Kamimura, T. Shirai, K. Takahashi, T. Mochida, K. Kato, Palladium(II) Bis(oxazoline) Complexes that Catalyze the Hydration of Alkynes. *Asian J. Org. Chem*. **2017**, *6*, 1086 - 1090.

55. N. Marion, R. S. Ramon, S. P. Nolan, [(NHC)Au(I)]-Catalyzed Acid-Free Alkyne Hydration at Part-Per-Million Catalyst Loadings. *J. Am. Chem. Soc*. **2009**, *131*, 448–449.

56. S. Liang, J. Jasinski, G. B. Hammond, B. Xu Supported Gold Nanoparticle-Catalyzed Hydration of Alkynes under Basic Conditions. *Org. Lett.* **2015**, *17*, 162–165.

57. R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, Organometallic Gold(III) Compounds as Catalysts for the Addition of Water and Methanol to Terminal Alkynes. *J. Am. Chem. Soc.* **2003**, *125*, 11925 - 11935.

58. J. Park, J. Yeon, P. H. Lee, K. Lee, Iron-Catalyzed Indirect Hydration of Alkynes in Presence of Methanesulfonic Acid. *Tetrahedron Lett*. **2013**, *54*, 4414 – 4417.

59. J. Polin, H. Schottenberger, Conversion of Methyl Ketones into Terminal Acetylenes: Ethynylferrocene *Org. Synth.***1998**, *9*, 411-414.

60. F. Li, N. Wang, L. Lu, G. Zhu, Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot

Synthesis of Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(R,R)-TsDPEN]. *J. Org. Chem.* **2015**, *80*, 3538-3546.

61. X. Jin, T. Oishi, K. Yamaguchi, N. Mizuno, Heterogeneously Catalyzed Efficient Hydration of Alkynes to Ketones by Tin–Tungsten Mixed Oxides. *Chem. Eur. J.* **2011**, *17*, 1261-1267.

62. O. Israelsohn, K. P. C. Vollhardt, J. Blum, Further Studies on Hydration of Alkynes by the $PtCl_4$–CO Catalyst. *J. Mol. Cat. A: Chem*. **2002**, *184*, 1–10.

63. M. Jacubert, O. Provot, J. F. Peyrat, A. Hamze, J. D. Brion, M. Alami, P-Toluenesulfonic Acid-Promoted Selective Functionalization of Unsymmetrical Arylalkynes: A Regioselective Access to Various Arylketones and Heterocycles. *Tetrahedron* **2010**, *66*, 3775–3787

Chapter-5

Temperature and Pressure Controlled Hydration of Alkynes: A Sustainable Strategy for the Ketone Synthesis

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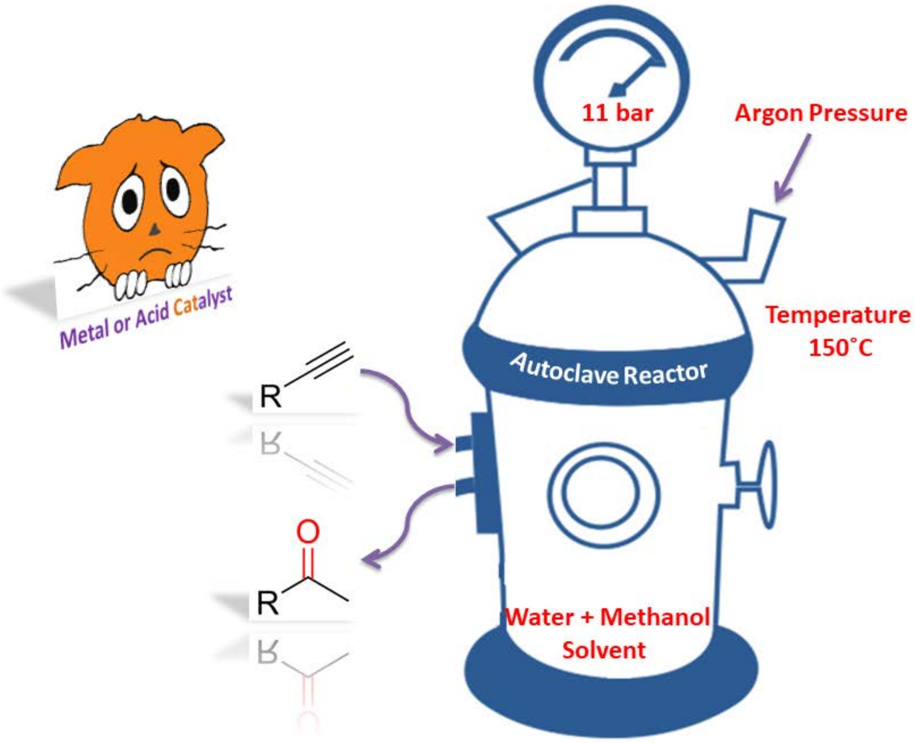


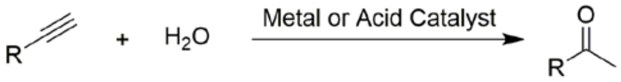
5.1 Introduction

Increasing the amount of product with minimising the amount of catalyst and the raw material is required one of the critical aspects among the 12 principles of green chemistry [1]. There were many reports available that demonstrate the applications of green and sustainable methodologies for laboratory and industrial productions. Practising various inexpensive and environmentally benign reaction methodologies have unveiled a new era in the field of chemistry [2]. Optimizing reaction conditions to accomplish without any chemical activation, i.e. without using additional chemical reagents or catalyst to perform chemical changes; this phenomenon is interesting as well as significantly crucial from a commercial and economic perspective. Reordering the physical parameters (temperature and pressure) associated with the reaction may lead to new insights in catalyst-free organic transformation. The use of high pressure techniques for hydrogenation [3], hydration [4] and various other catalytic reactions is quite common. Moreover, these methodologies dramatically reduce the cost and formation of undesired by-products and chemical waste in the reaction.

The Wacker oxidation of alkenes and metal mediated carbonylation of alkynes are extensively used to generate the carbonyl compounds including the ketones, esters, lactone, and melamide [4-11]. The hydration of alkynes had developed a paramount interest worldwide among various research groups, and it is a well-established and more advanced method for the production of ketones. Due to their diversified applications, ketones are the linchpins for various organic syntheses. Moreover, they also serve as versatile intermediates in a wide range of chemical syntheses such as natural products, drugs and other valuable industrial products [12]. A vast diversity of alkyne substrates are precursors for hydration reactions, and the applications of obtained carbonyls in organic syntheses [13, 14] is an essential aspect of traditional synthetic chemistry. Transition metals and other metal complexes are extensively used in hydration reactions. Before 1980's mercury compounds such as $Hg(OTf)_2$ [15], $HgSO_4$ [16] and $Hg(OAc)_2$ [17] were utilised for hydration reactions. Due to the toxicity and hazards to the environment; search the greener, and more economical catalysts is undergoing for many years. There is surplus literature accumulated over the last two decades dealing with alkyne hydrations from a variety of transition metals such as Pd [18-22], Pt [23, 24], Rh [24-27], Ru [28], Au [29-39]. However, these metal catalysts are precious and the use thereof not economically viable. Although some economical alternatives of a metal catalyst such as Ag [40, 41], Fe [42], Co [43], Sn and W mix-oxides [44] have also been reported in recent past. In some recent reports, acid catalyzed [45-48] and *para*-methoxybenzenetellurinic acid anhydride [49] indicates that alkyne hydration can be done by metal-free conditions. However, most of the reactions have suffered from at least one or more following drawbacks: (i) Use of expensive transition metals (Ru, Rh, Pd, Pt, Au, Ir, Ag) predominantly the recovery and reusability of catalysts and the indispensable use of acid co-catalysts, additives, and promoter; (ii) High price and the light sensitivity of silver salts and other acid salts; (iii) limited functional group compatibility; (iv) Requirement of large excess of acidic additive besides the metal complexes if any.

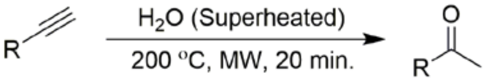
In the year 2004, Vasudevan and Co-workers [50] reported a catalyst-free methodology, which exclusively works for terminal alkynes. The alkynes in superheated water were heated at 200 ˚C in a microwave reactor for 20 minutes to produces the ketones. Although the catalyst-free alkyne hydration was reported for the first time, due to the harsh reaction conditions, the high temperature, unknown pressure, it cannot be implemented for large scale synthesis etc. Moreover, this method does not work for internal alkynes. All these shortfalls made this method inappropriate for the metal-free bulk synthesis of ketones.

Earlier Methodologies

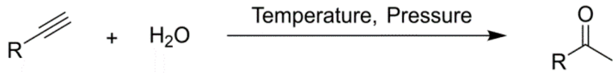


Metal Catalyst or Acid Catalyst: (1) Au, (2) Pd, (3) Pt, (4) Rh, (5) Ru, (6)CF_3SO_3H

In Recent Past



The Present Work



Reaction carried out in Autoclave, without any catalyst

Herein, we have investigated a catalyst-free methodology for hydration of terminal and internal alkynes without using any metal or acid catalyst. The present reaction is carried out in an autoclave at high temperature and pressure. Apart from the reactants, the present methodology needs only water/methanol mixture as a solvent. The present method has excellent functional group compatibility and also works for both the terminal and internal alkynes and do not produce any unwanted by-product.

5.2 Experimental

5.2.1 Materials and reagents

Reactants, reagents, chemicals and solvents available commercially within the country were used. Methanol used in this reaction is HPLC grade and purchased from Fischer Scientific. De-ionised water is obtained from Aqua Maxx basic 360 series water purification system manufactured by Young Lin Instrument Co. Ltd., South Korea.

5.2.2 General Procedure for the Catalytic Reaction*:*

A typical procedure for the hydration of various alkynes: To initial alkyne (1 mmol) dissolve in MeOH and H_2O (1:2) (60ml) were placed in a 100 mL stainless-steel autoclave. The vessel was pressurized to 11 bar of Ar, and then the mixture was vigorously stirred at 150˚C for 14 h. After the reaction, the reactor was cooled to room temperature and then the Ar pressure was carefully released to the atmospheric pressure. Methanol from the reaction mixture is removed using rotatory evaporator. Then work up with ethyl acetate and the products were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. The resultant crude mixture was purified by column chromatography (silica gel) using ethyl acetate/n-hexane as the eluent to obtain pure ketone.

5.2.3 Instrumentation

5.2.3.1 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C).

5.2.3.2 Infra-red Spectroscopy

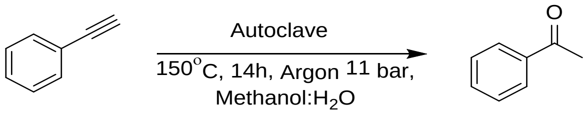
IR spectra in the range 4000–400 cm^{-1}were recorded on a Perkin Elmer 10.4.00 FT-IR spectrometer as KBr pellets of the sample.

5.2.3.3 High Resolution Mass Spectroscopy

High Resolution Electron Impact Mass Spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA). with the sample taken up in CH_3CN.

5.4 Result and discussion

To follow the principles of green chemistry, we were interested in developing a metal-free reaction method for hydration of alkynes. Phenylacetylene was chosen as a model substrate for all the optimisation. After some reactions under different conditions with no results, our series of the trail is interrupted by a trace product obtained in a reaction carried out in an autoclave. Desired product acetophenone was obtained through a reaction of phenylacetylene in an autoclave at 150 ˚C and 11 bar of argon gas pressure in 14 hr. Here, methanol was used as a solvent in the reaction. Scheme 1 represents the parameters where the desired alkyne hydration product was obtained. (Table 1, entry 9)



Scheme 1: Temperature and pressure controlled the formation of ketones

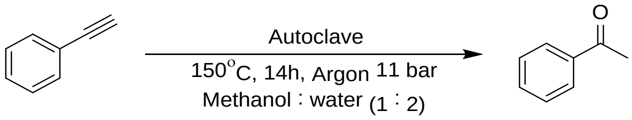
In the reaction, the inert gas pressure plays an important role. During the pressure optimisation, it was found that product yield was proportionally increased with continuously increasing pressure from 0 to 11 bar (table 1, entry 1-6). Pressure below 9 bar does not initiate the reaction, while a small quantity of product was obtained at 9 bar pressure of inert gas. Increasing the pressure up to 11 bar increases the product yield. However, the further increase in pressure does not produce any change in the yield (Table 1, entry 7-9). We investigated argon, nitrogen and CO_2 gas to generate the desired pressure but irrespective of the nature of gas the product formation was consistent and hardly brings any changes in the yield of transformed product. Since, the phenylacetylene is a volatile and low boiling liquid, at low pressure and high temperature; it vaporizes, and in the gaseous phase, it is quite unlikely to react with the liquid water present in the solvent mixture. While in present reaction conditions, the moderate pressure and high temperature restricted the vaporization of alkynes which is unable to react it in its vapor form, hence, under the reaction conditions it can undergo a hydration reaction. In our opinion, it could be the best possible effect of pressure on the reaction. The optimised value of pressure to get the highest yield of desired product is 11 bar, while the higher pressure of inert gas does not affect the product yield and supports our proposed hypothesis. Another reason for this reaction may be the higher ionisation of water molecules at higher pressure. In the earlier reports related to the studies of ionisation of water at various pressure and temperatures [51] suggested that ionisation of water molecules increases at higher pressure and the ionization of water increases with the increasing temperature. Here, both the facts again support the present hypothesis of the high yield of hydrated product at a relatively high temperature and moderate to high pressure.

Using pure water as a solvent result in no transformation taking place. (Table 1, entry 10). Hence, a mixture of water and methanol was used as a solvent. Gratifyingly, the 1:1 ratio of water and methanol as solvent enormously increases the yield of the desired product (Table 1, entry 11). The presence of methanol in the reaction mixture enhances the solubility of the acetylenes in water. Moreover, it also helps in the ionisation of water which directly favours the hydration reactions [52, 53]. As it is reported earlier that ionisation in water can be increased by increasing temperature, pressure or both and by adding alcohols [54]. Also by increasing these parameters viscosity and surface tension of water decreases and dielectric constant increases which improves the solubility of organic compounds in water [55]. Decreasing the amount of water in solvent mixture produces moderate product yield (Table 1, entry 12). Inversely, the increasing the amount of water in the solvent mixture improves the product yield and the maximum recorded yield of 79% was obtained with 1:2 ratio of methanol and water (Table 1, entry 13). Use of other alcohols, ethanol, isopropyl alcohol and *tert*-butanol showed a substantial decrease in the yield.

Further optimisation of temperature and time was carried out. Temperature up to 110 ˚C does not produce even a trace of the desired product. Increasing the temperature to 120 ˚C leads to a low yield of the phenylacetylene obtained. Amount of product was consistently increased with increasing the temperature up to 150 ˚C (Table 1, entry 14-17), furthermore increase of temperature up to 180 ˚C does not show any changes in the yield of product (Table 1, entry 18-20). Duration of reaction up to 14 hr or more produces a consistent yield (Table 1, entry 21-25), while the least 4-8 hr reaction produces below to average yield. However, it further increases up to 14 hr and then become consistent (Table 1, entry 26-28).

The present methodology was also found compatible with a wide variety functionalities. The substrate scope of this reaction is represented in Table 2. Phenyl acetylenes substituted with electron-donating or withdrawing groups produces excellent yield of their corresponding methyl ketones. Besides the phenyl acetylene, other aromatic alkynes (both terminal and internal), including the functional groups like fluoro, chloro, bromo, amino, alkyl, alkoxy also undergo hydration and affords excellent yields. The ferrocenyl acetylene yield acetylferrocene in 83% (Table 2, entries 2). *ortho*-, *meta*- and *para*- methyl-phenyl acetylene reacted smoothly, forming the corresponding methyl ketones in 84 %, 82 % and 83 % respectively (Table 2, entries 3-5). Halo-substituted phenyl acetylenes such as 4-fluoro-, 4-chloro-, 4-bromo and 2-chlorophenyl acetylene yielded 78 %, 76 %, 73 % and 72 % respectively (Table 2, entries 6-9). *ortho*- and *para*- methoxyphenylacetylene gave the corresponding products by 84 % and 83 % yield (Table 2, entries 10, 11). 4-ethylphenylacetylene reacted easily and formed the corresponding ketones in 85% yields (Table 2, entries 12). The 4-*tert*-butylphenylacetylene gave the corresponding ketones in 89 % (Table 2, entries 13); while the 3-aminophenylacetylene yielded 80 % of the hydrated product (Table 2, entries 14). The symmetrical diphenyl acetylene while 80 % yield of the hydrated product was recorded with the unsymmetrical 1-methyl-4-(phenylethynyl)benzene respectively (Table 2, entries 15 and 16).

Table 1: Optimization of reaction parameters with phenylacetylene

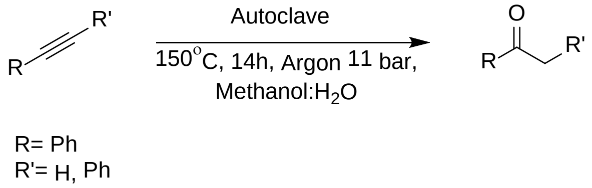


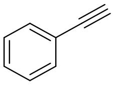
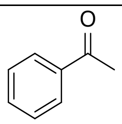
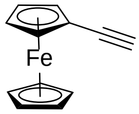
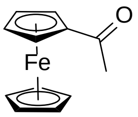
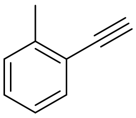
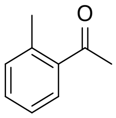
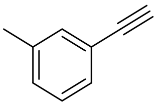
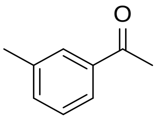
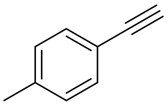
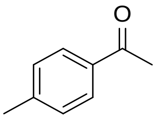
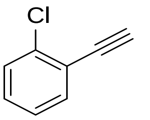
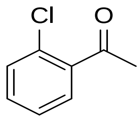
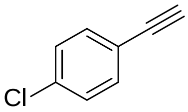
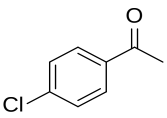
Entry	Ar Pressure	Solvent Ratio	Temp	Time	Yield[a]
1.	00	1:2	150	14	nd
2.	9.0	1:2	150	14	23
3.	9.5	1:2	150	14	34
4.	10.0	1:2	150	14	45
5.	10.5	1:2	150	14	60
6.	11.0	1:2	150	14	79
7.	11.5	1:2	150	14	79
8.	11.0	1:2	150	14	79
9.	11.0	1:0	150	14	Trace
10.	11.5	0:1	150	14	nd
11.	12.0	1:1	150	14	69
12.	11.0	2:1	150	14	45
13.	11.0	1:2	150	14	79
14.	11.0	1:2	120	14	20
15.	11.0	1:2	130	14	50
16.	11.0	1:2	140	14	60
17.	11.0	1:2	150	14	79
18.	11.0	1:2	160	14	79
19.	11.0	1:2	170	14	79
20.	11.0	1:2	180	14	79
21.	11.0	1:2	150	4	nd
22.	11.0	1:2	150	8	23
23.	11.0	1:2	150	10	43
24.	11.0	1:2	150	12	67
25.	11.0	1:2	150	14	79
26.	11.0	1:2	150	16	79
27.	11.0	1:2	150	18	79
28.	11.0	1:2	150	20	79

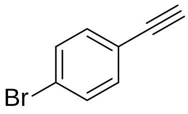
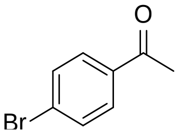
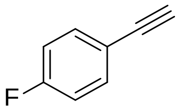
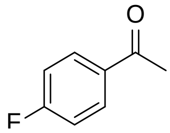
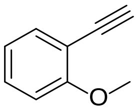
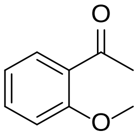
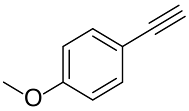
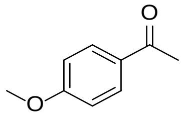
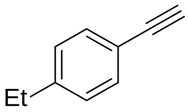
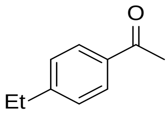
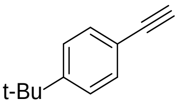
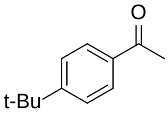
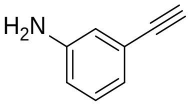
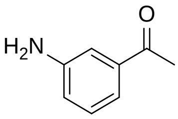
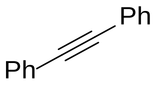
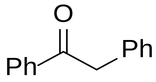
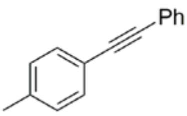
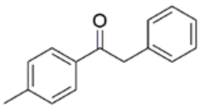
Reaction Condition: Solvent MeOH: Water (1:2), Temperature 150 ˚C, 11.0 bar argon, 14 h, [a]Isolated yield, nd = not detected

The reaction was further extended to the internal alkynes with maintaining the similar reaction parameters, a significant conversion of 78 % was obtained Here, hydration of both the symmetrical and unsymmetrical diarylacetylene regioselectively forms only one product and the formation of carbonyl group is preferred at the position where carbonyl is conjugated with a substituted phenyl group[56, 57]

Table 2: Substrate scope of hydration reaction in an autoclave



Entry	**Reactant**	**Product**	**Yield[a] (%)**
1.			79
2.			83
3.			84
4.			82
5.			83
6.			72
7.			76

8.			73
9.			78
10.			84
11.			83
12.			85
13.			89
14.			80
15.			78
16.			80

Reaction Condition: Solvent MeOH: Water (1:2), Temperature 150 ˚C, 11.0 bar argon, 14 h, [a]isolated yield

We attempt to address the issue of scalability of the method which was the limitation of the previous approach, [56] by performing reaction on 1 g scale of phenyl acetylene under considered optimised reaction parameters. After the completion of the reaction, a yield 70% of acetophenone was isolated. This indicates the present method can be utilized for the bulk production in relevant industries.

5.3.1 Supplimentary Data

Acetophenone [12]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.92 – 7.90 (m, 2H), 7.50 – 7.49 (m, 1H), 7.42 – 7.38 (m, 2H), 2.54 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.92, 136.93, 132.97, 128.43, 128.15, 26.44.

1,2-diphenylethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 8.01 – 7.99 (m, 2H), 7.53 – 7.51 (m, 1H), 7.45 – 7.41 (m, 2H), 7.33 – 7.22 (m, 5H), 4.27 (s, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.61, 136.52, 134.50, 133.15, 129.45, 128.64, 128.62, 128.58, 126.86, 45.45.

Acetyl Ferrocene [58]

^{1}H NMR (400MHz, CDCl$_3$): δ = 4.77 (s, 2H), 4.50 (s, 2H), 4.20 (s, 5H), 2.39 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 202.09, 72.26 69.77, 69.50, 27.36.

1-(o-tolyl)ethan-1-one [44]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.65 – 7.62 (m, 1H), 7.33 – 7.31 (m, 1H), 7.29 – 7.16 (m, 2H), 2.51 (s, 3H), 2.48 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 201.68, 138.45, 137.59, 132.10, 131.60, 129.50, 125.78, 29.53, 21.69.

1-(m-tolyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.76 – 7.73 (m, 2H), 7.34 – 7.32 (m, 2H), 2.57 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 198.40, 138.39, 137.19, 133.93, 128.84, 128.51, 125.65, 26.72, 21.38.

1-(p-tolyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.59 - 7.57 (m, 2H), 6.96 – 6.94 (m, 2H), 2.26 (s, 3H), 2.11 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.25, 143.57, 134.55, 129.09, 128.28, 26.20, 21.35.

1-(2-chlorophenyl)ethan-1-one

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.35 – 7.33 (m, 1H), 7.17 – 7.07 (m, 3H), 2.41 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 199.94, 138.90, 131.99, 131.04, 130.54, 129.37, 126.94, 30.50.

1-(4-chlorophenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.62 – 7.60 (m, 2H), 7.14 – 7.12 (m, 2H), 2.32 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.41, 139.20, 135.27, 129.63, 128.67, 26.34.

1-(4-bromophenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.83 – 7.81 (m, 2H), 7.61 – 7.59 (m, 2H), 2.59 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.94, 135.69, 131.79, 129.75, 128.21, 26.48.

1-(4-fluorophenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 8.00 – 7.97 (m, 2H), 7.15 – 7.11 (m, 2H), 2.55 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.54, 165.80 (d, J_{C-F} = 253 Hz), 133.63 (d, J_{C-F} = 2.7 Hz), 131.00 (d, J_{C-F} = 9.4 Hz), 115.69 (d, J_{C-F} = 22 Hz), 26.58.

1-(2-methoxyphenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.71 – 7.68 (m, 1H), 7.43 – 7.38 (m, 1H), 6.95 – 6.90 (m, 2H), 3.84 (s, 3H), 2.57 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 199.69, 158.97, 133.77, 130.27, 128.13, 120.49, 111.66, 55.46, 31.87.

1-(4-methoxyphenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.85 – 7.83 (m, 2H), 6.85 – 6.83 (m, 2H), 3.77 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 196.75, 163.51, 130.59, 130.29, 113.69, 55.46, 26.33.

1-(4-ethylphenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.89 – 7.87 (m, 2H), 7.29 – 7.27 (m, 2H), 2.73 – 2.67 (q, 2H), 2.57 (s, 3H), 1.27 – 1.23 (t, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.93, 150.12, 134.98, 128.62, 128.13, 29.01, 26.62, 15.30.

1-(4-(tert-butyl)phenyl)ethan-1-one [12]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.90 – 7.88(m, 2H), 7.47 – 7.45 (m, 2H), 2.57 (s, 3H), 1.33 (s, 9H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 198.05, 156.92, 134.66, 131.95, 130.14, 128.41, 125.60, 35.18, 31.17, 26.64.

1-(3-aminophenyl)ethan-1-one [29]

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.32 – 7.20 (m, 3H), 6.87 – 6.85 (m, 1H), 3.88 (s, 2H), 2.55 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 199.53, 146.78, 138.08, 129.35, 119.60, 118.67, 113.91, 26.65.

2-phenyl-1-(p-tolyl)ethan-1-one

^{1}H NMR (400MHz, CDCl$_3$): δ = 3.01 (s, 3H), 4.25 (s, 2H), 7.13 – 7.18 (m, 4H), 7.43 – 7.47 (m, 2H), 7.53 – 7.55 (m, 1H), 8.01 – 8.03 (m, 2H). **^{13}C NMR (100MHz, CDCl$_3$)**: δ = 197.96, 136.69, 136.59, 133.22, 131.52, 129.51, 129.42, 128.73, 45.24, 21.20.

5.4 Conclusion

In this note, we report the development of new metal/catalyst/ acid reagent-free methodology for hydration of alkynes at possible reaction conditions. Transformation of acetylene to ketone was entirely controlled by tuning the temperature and pressure of the reaction. The reaction shows excellent functional group compatibility and works smoothly for aryl containing either electron donating or withdrawing functional groups. Moreover, a significant yield of the product was also obtained, irrespective of the position of functional group attached to benzene. Hence, reaction indicates the robustness nature towards all possible alkynes. Apart from alkyne substrate, the present method needs only mixture of water and methanol as solvent and does not form any by-product. This method offers high atom economy and successfully implemented for the bulk synthesis of ketone in fine chemical industries.

5.5 References

[1] B.M. Trost, On Inventing Reactions for Atom Economy. *Acc. Chem. Res.* **2002**, *35*, 695-705.

[2] N. Satrawala, K.N. Sharma, L.C. Matsinha, L. Maqeda, S. Siangwata, G.S. Smith, R.K. Joshi, Base-Catalyzed Cross Coupling of Secondary Alcohols and Aryl-Aldehydes with Concomitant Oxidation of Alcohols to Ketones: An Alternative Route for Synthesis of the Claisen-Schmidt Condensation Products. *Tetrahedron Lett.* **2017**, *58*, 2761-2764.

[3] R.V. Jagadeesh, T. Stemmler, A.-E. Surkus, H. Junge, K. Junge, M. Beller, Hydrogenation using Iron Oxide–Based Nanocatalysts for the Synthesis of Amines. *Nat. Protoc.* **2015**, *10*, 548.

[4] B. Morandi, Z.K. Wickens, R.H. Grubbs, Practical and General Palladium-Catalyzed Synthesis of Ketones from Internal Olefins. *Angew. Chem.* **2013**, *125*, 3016-3020.

[5] T. Mitsudome, K. Mizumoto, T. Mizugaki, K. Jitsukawa, K. Kaneda, Wacker-Type Oxidation of Internal Olefins using a $PdCl_2$/N,N-Dimethylacetamide Catalyst System under Copper-Free Reaction Conditions. *Angew. Chem.* **2010**, *122*, 1260-1262.

[6] R.J. DeLuca, J.L. Edwards, L.D. Steffens, B.W. Michel, X. Qiao, C. Zhu, S.P. Cook, M.S. Sigman, Wacker-Type Oxidation of Internal Alkenes using Pd(Quinox) and TBHP. *J. Org. Chem.* **2013**, *78*, 1682-1686.

[7] P. Mathur, B. Jha, A. Raghuvanshi, R.K. Joshi, S.M. Mobin, Photolytic Reaction of Substituted (Ethynyl)Benzaldehyde and $Fe(CO)_5$: Formation of Indenone and Chelated Iron Complexes. *J. Organomet. Chem.* **2012**, *712*, 7-14.

[8] B.N. Jha, A. Raghuvanshi, R.K. Joshi, S.M. Mobin, P. Mathur, A Photochemical Route to Ferrocenyl-Substituted Ferrapyrrolinone Complexes. *Appl. Organomet. Chem.* **2017**, *31*, e3805.

[9] C. Crudden, H. Alper, Carbonylation. Direct Synthesis of Carbonyl Compounds. Von H. M. Colquhoun, D. J. Thompson und M. V. Twigg. Plenum Press, New York, **1991**. ISBN 0-306-43747-3. *Angew. Chem.* **1992**, *104,* 1122-1122.

[10] I. Wender, P. Pino, *Organic Synthesis via Metal Carbonyls,* Wiley Interscience, New York, **1977**.

[11] R.K. Joshi, N. Satrawala, One Pot Synthesis of Important Retinoid Synthon by the Catalytic Regioselective Bi-Functionalization of Acetylenes, Alcohol and Carbon Monoxide. *Tetrahedron Lett.* **2017**, *58*, 2931-2935.

[12] X.-F. Wu, D. Bezier, C. Darcel, Development of the First Iron Chloride-Catalyzed Hydration of Terminal Alkynes. *Adv. Synth. Catal.* **2009**, *351,* 367-370.

[13] F. Alonso, I.P. Beletskaya, M. Yus, Transition-Metal-Catalyzed Addition of Heteroatom−Hydrogen Bonds to Alkynes. *Chem. Rev.* **2004**, *104*, 3079-3160.

[14] M. Beller, J. Seayad, A. Tillack, H. Jiao, Catalytic Markovnikov and anti-Markovnikov Functionalization of Alkenes and Alkynes: Recent Developments and Trends. *Angew. Chem. Int. Ed.* **2004**, *43,* 3368-3398.

[15] N. Mugio, S. Mariusz, I. Hiroshi, S. Takumichi, Mercuric Triflate-TMU Catalyzed Hydration of Terminal Alkyne to give Methyl Ketone under Mild Conditions. *Chem. Lett.* **2002**, *31*, 12-13.

[16] J.P. Wasacz, V.G. Badding, A Hydration of An Alkyne Illustrating Steam and Vacuum Distillation. *J. Chem. Educ.* **1982**, *59*, 694.

[17] R.D. Bach, R.A. Woodard, T.J. Anderson, M.D. Glick, Stereochemistry of the Acetoxymercuration of Alkynes. A Synthesis of Vinyl Acetates. *J. Org. Chem.* **1982**, *47*, 3707-3712.

[18] I. Kadota, L.M. Lutete, A. Shibuya, Y. Yamamoto, Palladium/Benzoic Acid-Catalyzed Hydroalkoxylation of Alkynes. *Tetrahedron Lett.* **2001**, *42*, 6207-6210.

[19] Y. Fukuda, H. Shiragami, K. Utimoto, H. Nozaki, Synthesis of Substituted Furans by Palladium-Catalyzed Cyclization of Acetylenic Ketones. *J. Org. Chem.* **1991**, *56*, 5816-5819.

[20] K. Yasutaka, M. Osamu, O. Masataka, Y. Tsuneaki, T. Kazuhide, Stereoselective Addition of Alcohol to Alkyne Catalyzed by Dicationic Platinum and Palladium Complexes. *Chem. Lett.* **1994**, *23*, 1283-1284.

[21] A.K. Das, S. Park, S. Muthaiah, S.H. Hong, Ligand- and Acid-Free Gold(I) Chloride Catalyzed Hydration of Terminal Alkynes. *Synlett* **2015**, *26*, 2517-2520.

[22] M.J. Rodríguez-Álvarez, N. Ríos-Lombardía, S. Schumacher, D. Pérez-Iglesias, F. Morís, V. Cadierno, J. García-Álvarez, J. González-Sabín, Combination of Metal-Catalyzed Cycloisomerizations and Biocatalysis in Aqueous Media: Asymmetric Construction of Chiral Alcohols, Lactones, and γ-Hydroxy-Carbonyl Compounds. *ACS Catal.* **2017**, *7*, 7753-7759.

[23] W. Hiscox, P.W. Jennings, Catalytic Hydration of Alkynes With Zeise's Dimer. *Organometallics* **1990**, *9*, 1997-1999.

[24] P.W. Jennings, J.W. Hartman, W.C. Hiscox, Alkyne Hydration using Pt(II) Catalysts. *Inorg. Chim. Acta* **1994**, *222*, 317-322.

[25] A. Lumbroso, N.R. Vautravers, B. Breit, Rhodium-Catalyzed Selective anti-Markovnikov Addition of Carboxylic Acids to Alkynes. *Org. Lett.* **2010**, *12*, 5498-5501.

[26] F.Y. Kwong, Y.M. Li, W.H. Lam, L. Qiu, H.W. Lee, C.H. Yeung, K.S. Chan, A.S.C. Chan, Rhodium-Catalyzed Asymmetric Aqueous Pauson–Khand-Type Reaction. *Chem. Eur. J.* **2005**, *11*, 3872-3880.

[27] I. Omae, Three Characteristic Reactions of Alkynes with Metal Compounds in Organic Synthesis. *Appl. Organomet. Chem.* **2008**, *22*, 149-166.

[28] C. Bruneau, P. H. Dixneuf, Selective Transformations of Alkynes with Ruthenium Catalysts. *Chem. Commun.* **1997**, 507-512.

[29] F. Li, N. Wang, L. Lu, G. Zhu, Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot Synthesis of

Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(R,R)-TsDPEN]. *J. Org. Chem.* **2015**, *80*, 3538-3546.

[30] S. Liang, J. Jasinski, G.B. Hammond, B. Xu, Supported Gold Nanoparticle-Catalyzed Hydration of Alkynes under Basic Conditions. *Org. Lett.* **2015**, *17,* 162-165.

[31] W. Wang, G.B. Hammond, B. Xu, Ligand Effects and Ligand Design in Homogeneous Gold(I) Catalysis. *J. Am. Chem. Soc.* **2012**, *134*, 5697-5705.

[32] N. Marion, R.S. Ramón, S.P. Nolan, [(NHC)AuI]-Catalyzed Acid-Free Alkyne Hydration at Part-Per-Million Catalyst Loadings. *J. Am. Chem. Soc.* **2009**, *131*, 448-449.

[33] A. Leyva, A. Corma, Isolable Gold(I) Complexes Having One Low-Coordinating Ligand as Catalysts for the Selective Hydration of Substituted Alkynes at Room Temperature without Acidic Promoters. *J. Org. Chem.* **2009**, *74,* 2067-2074.

[34] E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, Highly Efficient Au(I)-Catalyzed Hydration of Alkynes. *Angew. Chem.* **2002**, *114*, 4745-4747.

[35] J.H. Teles, S. Brode, M. Chabanas, Cationic Gold(I) Complexes: Highly Efficient Catalysts for the Addition of Alcohols to Alkynes. *Angew. Chem. Int. Ed.* **1998**, *37*, 1415-1418.

[36] X. Xu, S.H. Kim, X. Zhang, A.K. Das, H. Hirao, S.H. Hong, Abnormal N-Heterocyclic Carbene Gold(I) Complexes: Synthesis, Structure, and Catalysis in Hydration of Alkynes. *Organometallics* **2013**, *32*, 164-171.

[37] Y. Fukuda, K. Utimoto, Effective Transformation of Unactivated Alkynes into Ketones or Acetals with A Gold(III) Catalyst. *J. Org. Chem.* **1991**, *56,* 3729-3731.

[38] R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, Organometallic Gold(III) Compounds as Catalysts for the Addition of Water and Methanol to Terminal Alkynes. *J. Am. Chem. Soc.* **2003**, *125*, 11925-11935.

[39] P. de Frémont, R. Singh, E.D. Stevens, J.L. Petersen, S.P. Nolan, Synthesis, Characterization and Reactivity of N-Heterocyclic Carbene Gold(III) Complexes. *Organometallics* **2007**, *26*, 1376-1385.

[40] K.T. Venkateswara Rao, P.S. Sai Prasad, N. Lingaiah, Solvent-Free Hydration of Alkynes over A Heterogeneous Silver Exchanged Silicotungstic Acid Catalyst. *Green Chem.* **2012**, *14*, 1507-1514.

[41] M.B.T. Thuong, A. Mann, A. Wagner, Mild Chemo-Selective Hydration of Terminal Alkynes Catalysed by $AgSbf_6$. *Chem. Commun.* **2012**, *48*, 434-436.

[42] J. Pierre Damiano, M. Postel, $FeCl_3.H_2O$: A Specific System for Arylacetylene Hydration. *J. Organomet. Chem.* **1996**, *522*, 303-305.

[43] T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 50-53.

[44] X. Jin, T. Oishi, K. Yamaguchi, N. Mizuno, Heterogeneously Catalyzed Efficient Hydration of Alkynes to Ketones by Tin–Tungsten Mixed Oxides. *Chem. Eur. J.* **2011**, *17*, 1261-1267.

[45] W. Liu, H. Wang, C.-J. Li, Metal-Free Markovnikov-Type Alkyne Hydration under Mild Conditions. *Org. Lett.* **2016**, *18*, 2184-2187.

[46] D.-Q. Chen, C.-H. Guo, H.-R. Zhang, D.-P. Jin, X.-S. Li, P. Gao, X.-X. Wu, X.-Y. Liu, Y.-M. Liang, A Metal-Free Transformation of Alkynes to Carbonyls Directed by Remote OH Group. *Green Chem.* **2016**, *18*, 4176-4180.

[47] J. An, L. Bagnell, T. Cablewski, C.R. Strauss, R.W. Trainor, Applications of High-Temperature Aqueous Media for Synthetic Organic Reactions. *J. Org. Chem.* **1997**, *62*, 2505-2511.

[48] M. Ye, Y. Wen, H. Li, Y. Fu, Q. Wang, Metal-Free Hydration of Aromatic Haloalkynes to α-halomethyl Ketones. *Tetrahedron Lett.* **2016**, *57*, 4983-4986.

[49] N.X. Hu, Y. Aso, T. Otsubo, F. Ogura, Novel Oxidizing Properties of p-Methoxybenzenetellurinic Acid Anhydride. *Tetrahedron Lett.* **1986**, *27*, 6099-6102.

[50] A. Vasudevan, M.K. Verzal, Neutral, Metal-free Hydration of Alkynes Using Microwave Irradiation in Superheated Water. *Synlett* **2004**, *2004*, 631-634.

[51] F.J. Millero, E.V. Hoff, L. Kahn, The Effect of Pressure on the Ionization of Water At Various Temperatures from Molal-Volume Data[1]. *J. Solution Chem.* **1972**, *1*, 309-327.

[52] A. Farajtaba, F. Gharib, Autoprotolysis Constants Determination of Water-Methanol Mixtures and Solvent Effect. *J. Taibah Univ. Sci.* **2009**, *2*, 7-13.

[53] C.H. Rochester, D.N. Wilson, Ionization Constants of Phenols in Methanol + Water Mixtures. *J. Chem. Soc. Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1976**, *72*, 2930-2938.

[54] S. Gbashi, P. Njobeh, P. Steenkamp, H. Tutu, N. Madala, The Effect of Temperature and Methanol–Water Mixture on Pressurized Hot Water Extraction (PHWE) of anti-HIV Analogoues From Bidens Pilosa. *Chem. Cent. J.* **2016**, *10*, 37.

[55] A.V. Bandura, S.N. Lvov, The Ionization Constant of Water over Wide Ranges of Temperature and Density. *J. Phys. Chem. Ref. Data* **2006**, *35*, 15-30.

[56] G. Le Bras, O. Provot, J.-F. Peyrat, M. Alami, J.-D. Brion, Rapid Microwave Assisted Hydration of Internal Arylalkynes in the Presence of PTSA: An Efficient Regioselective Access to Carbonyl Compounds. *Tetrahedron Lett.* **2006**, *47*, 5497-5501.

[57] O. Israelsohn, K.P.C. Vollhardt, J. Blum, Further Studies on Hydration of Alkynes by the $PtCl_4$–CO Catalyst. *J. Mol. Catal. A: Chem.* **2002**, *184*, 1-10.

[58] J. Polin, H. Schottenberger, Conversion of Methyl Ketones into Terminal Acetylenes: Ethynylferrocene. *Org. Synth.* **1996**, *9*, 411 - 414.

SUMMARY

This thesis presented a cost effective, facile synthetic methodology and greener approach for ketone synthesis and report on the design of three new robust complexes for one pot conversion of aldehyde to amide synthesis.

- We have synthesised three new and novel mononuclear Ru(II) half-sandwich complexes of pyrazole based organo-chalcogens ligands and investigated their catalytic potential for aldehyde to amide transformations. The comparative study of different Chalcogen based metal complexes the catalytic efficiency of these three complexes has also been investigated. Moreover, the present catalytic systems do not require any hazardous additives, and convert the aldehydes into corresponding amides in good to excellent yields under aerobic reaction conditions.
- We report the photolytic hydration of various alkynes using a previously synthesized, reusable, water-soluble N,O-chelate Rh(I)–Schiff base catalyst precursor bearing ferrocene as ancillary support. Using this rhodium catalyst, the hydration of alkynes proceeded in 30 minutes under irradiation, yielding methyl ketones.
- We developed a catalytic methodology for the alkyne hydration under UV irradiation. For the first time Iron Chalcogenide carbonyl complexes as catalysts were used for such a reaction. This catalytic methodology is found effective towards terminal and internal alkynes having a wide range of functionalities. The reported catalyst behaves as a heterogeneous catalyst in aqueous media. Moreover, the catalyst is reusable up to several cycles and can be easily separated through filtration as well as the reaction is completed in short reaction times.
- We had devised a new metal/catalyst/ acid reagent free methodology for hydration of alkynes at feasible reaction conditions. Transformation of acetylene to ketone was fully controlled by tuning the temperature and pressure of the reaction. This methodology optimized up to gram scale.

List of Publications

Research Paper Published:

1. Metal/Catalyst/Reagent Free Hydration Of Alkynes Up To Gram Scale Under Temperature And Pressure Controlled Condition, **M. Ali**, A. K. Srivastava, R. K. Joshi, *Tetrahedron Lett.* 2018, 59, 2075–2078
2. Photo Induced Alkyne Hydration Reactions Mediated by A Water Soluble, Reusable Rhodium (I) Catalyst, **M. Ali**, A. K. Srivastava, S. Siangawata, G. S. Smith, R. K. Joshi, *Catal. Commun.* 2018,115, 78–81
3. (η^6-Benzene)Ru(II) Half-Sandwich Complexes of Pyrazolated Chalcogenoethers for Catalytic Activation of Aldehydes to Amides Transformation, K. N. Sharma, **M. Ali**, A. K. Srivastava, R. K. Joshi, *J. Organomet. Chem.* 2019, 879, 69-77
4. Metal-Free, PTSA Catalyzed Facile Synthesis of β-Ketoacetal from β-Chlorocinnamaldehyde, A. K. Srivastava, **M. Ali**, K. N. Sharma, R. K. Joshi, *Tetrahedron Lett.* 2018, 59, 3188–3193
5. Pd(II) Ligated First (Se,CNHC,N−) Type Pincer Frame-worked Selenoether-NHC for Efficient Catalytic Activation of Aryl/Heteroaryl Bromides and Chlorides to Mizoroki-Heck Coupling in Neat Water, K. N. Sharma, N. Satrawala, A. K. Srivastava, **M. Ali**, R. K. Joshi (10.1039/C9OB01674K)

Research Papers Submitted:

1. Iron Chalcogenide Carbonyl Complexes as a Heterogeneous Photo Catalyst for Alkyne Hydrations in Aqueous Media, **M. Ali**, A. K. Srivastava, R. K. Joshi.

Conferences, Seminar and Short-term course:

1. Attended and participated in an Oral presentation in Two days Inter-National conference on “Frontiers at the Chemistry-Allied Sciences (FCASI-2018)” from 21st- 22nd August, 2018 organized by department of chemistry, University of Rajasthan, Jaipur
2. Attended and participated in poster presentation in three days International conference on “The 13th Anniversary india-Japan International conference

on Sustainable development BICON -2018"organized by biyani group of college, Jaipur- Rajasthan India from 26th- 28th Nov., 2017.

3. Attended five days short term course on "Properties of Nano Materials- Why & How They Differ from their bulk Counter Part" organized by Materials Research Centre, MNIT, Jaipur from 13th -17th Nov., 2018.
4. Attended and participated in poster presentation International conference on "Chemical Science in New Era" organized by Department of PG Studies and Department of chemistry, PACIFIC University, Udaipur and ICS, Kolkata on 5-6 Oct., 2018.
5. Participated in National Seminar on "Recent Trends & Advances in Chemical Science and their Impact on Environment" (RTACIE-2018) organized by department of chemistry, Amity University, Jaipur on 13th April, 2018
6. Attended five days short term course on "Nano Forms of Carbon" organized by Materials Research Centre, MNIT, Jaipur from 19th March-23rd March, 2018.
7. Attended and participated in poster presentation in four days national conference on "Modern Trends in Inorganic Chemistry",(MTIC-XVII,2017) organized by CSIR-NCL Pune and IISER Pune from 11th- 14th December, 2017.
8. Participated in "Indo-Australia Workshop on Nano Structured Material for Energy Storage Application "organized by Manipal University, Jaipur on 13th August 2017.
9. Attended and participated in poster presentation in three days National conference on "Recent Advancement in Chemical Sciences (RAICS-2015)" from 21st- 23rd August, 2015 organized by department of chemistry, MNIT Jaipur and got the Best Poster Award.
10. Attended in four days short term course on "Electron Microscopy" organized by Materials Research Centre, MNIT, Jaipur from 31stjan.-3rd Feb., 2014.

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Under Supervision of **Dr. Raj Kumar Joshi** , Department of Chemistry, **MNIT Jaipur**

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Thesis Title: Transition Metal Catalyzed Greeneer Approach for the Synthesis of Aryl ketones and Amides

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ACADEMIC ACHIEVEMENTS

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2. Awarded MANF-UGC SRF: April2016−March 2019
3. Published 05 research papers in peer reviewed international journals
4. Visited abroad for research work under DST sponsored Indo-South African Research project at the University of Cape Town, Cape Town, South Africa.

RESEARCH WORK, INSTRUMENT HANDLING AND SOFTWARE SKILLS

- Development of new catalytic methodology with a transition metal or without.
- Expertise in the characterization of newly prepared materials by using analytical techniques such as C, H and N analysis, FT-IR, UV/Visible, multinuclei NMR, mass spectra, SEM, EDX, TEM, XPS, AAS, ICP-AES etc.
- Familiar with sophisticated instruments such as NMR Spectrometer (JEOL ECS-400) (operating at 400 MHz for 1H and 100 MHz for 13C). IR spectrometer(Perkin Elmer) MASS Spectrometer(Xevo G2-S Q-Tof (Waters, USA).

- Diamond, Mercury, MNOVA, EndNote, ChemDraw, Origin, PCPDFWIN (For JCPDS) etc. Diploma in Computer: RS-CIT

PUBLICATIONS IN PEER REVIEWED JOURNALS

1. Metal/catalyst/reagent free hydration of alkynes up to gram scale under temperature and pressure controlled condition, M. Ali, A. K. Srivastav, R. K. Joshi, *Tetrahedron Lett.* 2018, 59, 2075–2078
2. Photo induced alkyne hydration reactions mediated by a water soluble, reusable Rhodium (I) catalyst, M. Ali, A. K. Srivastava, S. Siangawata, G. S. Smith, R. K. Joshi*, *Catal. Commun.* 2018,115, 78–81
3. (η^6-Benzene)Ru(II) half-sandwich complexes of pyrazolated chalcogenoethers for catalytic activation of aldehydes to amides transformation, K. N. Sharma, M. Ali, A. K. Srivastava, R. K. Joshi, *J. Organomet. Chem.* 2019, 879, 69-77
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Research Papers Submitted:

1. Iron Chalcogenide Carbonyl Complexes as a heterogeneous Photo catalyst for alkyne hydrations in aqueous media,M. Ali, A. K. Srivastav, R. K. Joshi

CONFERENCES, SEMINAR, SHORT-TERM COURSE AND SYMPOSIUM

1. Attended and participated in an Oral presentation in Two days Inter-National conference on “Frontiers at the Chemistry-Allied Sciences(FCASI-2018)” from 21st-22nd August, 2018 organized by department of chemistry, University of Rajasthan, Jaipur
2. Attended and participated in poster presentation in three days International conference on “The 13th Anniversary india-Japan International conference on

Sustainable development BICON -2018"organized by biyani group of college, Jaipur- Rajasthan India from 2^{6th}- 28th Nov., 2017.

3. Attended five days short term course on "Properties of Nano Materials- Why & How They Differ from their bulk Counter Part" organized by Materials Research Centre, MNIT, Jaipur from 13th -17th Nov., 2018.

4. Attended and participated in poster presentation International conference on "Chemical Science in New Era" organized by Department of PG Studies and Department of chemistry, PACIFIC University, Udaipur and ICS, Kolkata on 5 th-6 th Oct., 2018.

5. Participated in National Seminar on "Recent Trends & Advances in Chemical Science and their Impact on Environment" (RTACIE-2018) organized by department of chemistry, Amity University, Jaipur on 13th April, 2018.

6. Attended five days short term course on "Nano Forms of Carbon" organized by Materials Research Centre, MNIT, Jaipur from 19th -23rd March, 2018.

7. Attended and participated in poster presentation in four days national conference on "Modern Trends in Inorganic Chemistry",(MTIC-XVII,2017) organized by CSIR-NCL Pune and IISER Pune from 11th- 14th December, 2017.

8. Participated in "Indo-Australia Workshop on Nano Structured Material for Energy Storage Application" Organized by Manipal University, Jaipur on 13th August 2017.

9. Attended and participated in poster presentation in three days National conference on "Recent Advancement in Chemical Sciences (RAICS-2015)" from 21st- 23rd August, 2015 organized by department of chemistry, MNIT Jaipur and got the Best Poster Award.

10. Attended in four days short term course on on "Electron Microscopy" organized by Materials Research Centre, MNIT, Jaipur from 31stjan.-^{3rd} Feb., 2014.

Declaration:

I hereby declare that the above-mentioned all the information about me is correct in my knowledge.

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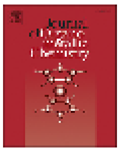

(η^6-Benzene)Ru(II) half-sandwich complexes of pyrazolated chalcogenoethers for catalytic activation of aldehydes to amides transformation

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The reaction of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ with chalcogenoether substituted 1*H*-pyrazole ligands (**L1-L3**) in methanol have yielded three novel Ru(II) half-sandwich complexes $[(\eta^6\text{-}C_6H_6)RuCl(L)]PF_6$ (**1–3**) in high yield under the ambient reaction conditions. The NMR, MS and FT-IR analytical techniques were used to identify their structures. The molecular structures of the complexes **2** and **3** were established with X-ray crystallographic analysis and revealed a pseudo-octahedral half sandwich piano-stool geometry around ruthenium in each complex. Complexes **1–3** are thermally robust and were found to be insensitive towards the air and moisture. All the complexes were found to be catalytically active and produced the excellent yields of amides (up to 95%) from corresponding aldehydes. In contrast to the previous reported catalytic systems for aldehyde to amide transformation, the present complexes **1–3** are very efficient and have several advantages in terms of low catalyst loading, reaction time, temperature and wide applicability for various substituted aldehydes. Owing to the stronger σ-donor coordination properties of selenium containing ligands, the complex **2** was found to be more efficient as compare to the sulphur and tellurium analogues.

1. Introduction

Amides are amongst the most important organic compounds which have been extensively explored as synthetic building blocks in various organic transformations [1–3]. The presence of amide functional group [4–9] is a key chemical connection in nitrogen containing biologically active compounds [10], various commercially available pharmaceutical drugs [11–13], and polymers [14,15], show as immense prevalence of amide bond formation in synthetic chemistry. Classically, amides are synthesized by a stoichiometric reaction of carboxylic acid or its derivatives (halides, esters or anhydrides) with amines [16]. The spontaneous formation of the amides is not possible through unifying these two functional groups at ambient temperature, because the essential water elimination step takes place at very high temperature (≥200 °C) [17]. The formation of undesired products and low atom economy in such process restrict their employability in industrial applications. Hence, the development of advance atom-efficient catalytic methods for amide formation are highly desired in modern synthetic chemistry [18,19]. In this context, several metal-catalyzed approaches for amide synthesis have been developed [20]. Many of transition metals including scandium [21], nickel [22], copper [23–25], zinc [26], and palladium [27] based catalysts have been reported for the catalytic transformations of aldehydes [24,25,27–30] or oximes [22,23,28] into corresponding amides. Alumina-supported rhodium [31,32], titanosilicates loaded with rhodium [33], and $[Ir(Cp^*)Cl_2]_2$ [34] have been found to be potential candidates for amide synthesis. However, the prime requisite of an inert atmosphere to handle the air-sensitive metal catalysts and harsh reaction conditions are some of the major disadvantages of these protocols. Moreover, some functional groups do not withstand under such severe ambience and the selectivity of the desire product decreases. Also, the high catalyst loading and stoichiometric amount of additional reagents produce the significant quantity of undesired products. Crabtree and co-workers has developed a ruthenium complex of terpyridine based NNN type pincer ligand which efficiently carry out an additives free one-pot conversion of amides from aldehydes [35]. The prime goal of present work is to develop an elegant and more efficient method for

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Short communication

Photo induced alkyne hydration reactions mediated by a water soluble, reusable Rhodium (I) catalyst

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ABSTRACT

Under photochemical irradiation, the hydration of aryl alkynes in the presence of water proceeds in good yields to afford the corresponding ketone, using a water-soluble rhodium (I) catalyst. The catalyst is effective for internal and terminal alkynes and showed high functional group compatibility. A low catalyst loading, low temperature and shorter duration of photolysis are ideal feature of reaction. The catalyst can be reused several times under aerobic and aqueous conditions, exemplifying the robust nature of the catalyst. In comparison with known Rh and other metal catalysts, the present reaction provides a remarkable green approach for alkyne hydration reactions.

1. Introduction

Chemical transformations that use water as a reagent or reaction medium continue to attract attention in organic synthesis [1]. This stems from the non-toxic nature of water to both the user and the environment, its relative abundance compared to other solvents, as well as the compatibility with various organic substrates. The atom-economical hydration of alkynes (with all of the reactant atoms found in the desired products) represents one of the most important reactions that utilize water in organic synthesis. This well-established reaction is classically catalyzed by the toxic and environmentally-destructive metal-containing mercuric sulfate or a strong acid catalyst. In the presence of sulfuric acid, the hydration of alkynes leads to industrially relevant carbonyl compounds, used in the bulk and fine chemical industries [2]. Mercury promoted hydration of alkynes often suffer a major drawback where certain acid-labile functional groups are not compatible with the harsh acidic conditions. Moreover, the reaction proceeds under stringent conditions, i.e. high temperatures (> 100 °C), prolonged reaction time as well as requiring a large excess of acid and water. To circumvent these drawbacks, various transition-metal-based catalysts have been developed as environmentally benign alternatives to mercuric catalysts in the hydration of alkynes, and these include Ag [3], Pt [4], Cu [5], Au [6], Fe [7–12], Ir [13], In [14], Ru [15–17] and Rh [18–23] complexes. These metals provide a much easier, mild, greener and efficient protocol for the hydration of simple alkynes. In selected cases, aryl alkynes posed several challenges giving reduced yields, lower selectivity or requiring higher catalyst loading and elevated temperatures. The hydration of terminal alkynes usually occurs via Markovnikov addition, giving methyl ketones, with symmetric internal alkynes selectively yielding single ketone products. It is generally accepted that the hydration proceeds via an enol which immediately transforms into the more stable ketone via tautomerism, with the metal ketonyl complexes being the key intermediates, in the presence of metal catalysts [24]. Rhodium-mediated addition of water to alkynes is attractive owing to the well-known good functional group tolerance of the metal, as well as the high activity and selectivity demonstrated under mild reaction conditions in various homogeneous catalytic transformations [25]. Complexing the metal to chelating Schiff base ligands is a very popular approach because of the good stability and versatility afforded by the ligands, often leading to excellent catalytic activity [26]. Herein, we report the photolytic hydration of various alkynes using a previously synthesized, reusable, water-soluble *N,O*-chelate Rh(I)–Schiff base catalyst precursor bearing ferrocene as an ancillary support [27]. Using this rhodium catalyst, the hydration of alkynes proceeded in 30 min under irradiation, yielding methyl ketones.

Based on previous reports of water-soluble Rh salts [19] and Rh complexes [20] used for hydration reactions, various methods were attempted to improve the yield of these transformations. However, these methods have significant limitations which include slow processes, long reaction time (12–24 h), and the loss of volatile alkynes at high temperatures during the long reaction hours. However, after studying a series of reported reactions with our Rh catalyst, we found

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Metal/catalyst/reagent free hydration of alkynes up to gram scale under temperature and pressure controlled condition

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ABSTRACT

A new green water-mediated metal/catalyst/reagent-free methodology for hydration of alkyne is devised. The remarkable yields of various ketones were achieved when alkynes were heated at 150 °C under 11 bar pressure in an autoclave for 14 h in water-methanol solution. Outstanding functional group compatibility for both the terminal and internal alkynes was established. This methodology produces excellent yields up to gram scale under optimised reaction condition.

Introduction

Increasing the amount of product with minimising the role of catalyst and raw material is one of the critical aspects among the 12 principles of green chemistry.[1] There were many reports available that demonstrate the applications of green and sustainable methodologies for laboratory and industrial productions. Practising various inexpensive and environmentally benign reaction methodologies have unveiled a new era in the field of chemistry.[2] Optimizing reaction conditions to accomplish without any chemical activation, i.e. without using chemical reagents or catalyst to perform chemical changes; this phenomenon is interesting as well as significantly crucial from commercial and economic perspective. Reordering the physical parameters (temperature and pressure) associated with the reaction may lead to new insights in catalyst-free organic transformation. The use of autoclave technique for hydrogenation,[3] hydration[4] and various other reactions is quite common. Moreover, these methodologies outstandingly reduce the cost and formation of undesired by-products and chemical waste in the reaction.

The Wacker oxidation of alkenes and metal mediated carbonylation of alkynes is extensively used to generate the carbonyl compounds including the ketones, esters, lactone, and melamide.[4,5] The hydration of alkynes had developed a paramount interest worldwide among various research groups, and it is a well-established and more advanced method for the production of ketones. Due to their diversified applications, ketones are the linchpins for various organic syntheses. Moreover, they also serve as versatile intermediates in a wide range of chemical syntheses such as natural products, drugs and other valuable industrial products.[6] The vast diversity of alkyne substrates are a precursor for hydration reactions, and the applications of obtained carbonyls in organic syntheses[7] is an essential aspect of traditional synthetic chemistry. Transition metals and other metal complexes are extensively used for hydration reactions. Before 1980's mercury compounds such as $Hg(OTf)_2$,[8a] $HgSO_4$,[8b] and $Hg(OAc)_2$[8c] were utilised for hydration reactions. While due to the toxicity and hazards to the environment; search for the green, and the economic catalyst is undergoing from many years. There is surplus literature congregated in last two decades representing alkyne hydrations from a variety of transition metals such as Pd,[9] Pt,[10] Rh,[11] Ru,[12] Au.[13] However, these metal catalysts are rare and not economically viable. Although some economical alternatives of metal catalyst such as Ag,[14] Fe,[15] Co,[16] Sn and W mix-oxides[17] also been reported in recent past. In some recent reports, acid catalyzed[18] and *para*-methoxybenzenetellurinic acid anhydride[19] indicates that alkyne hydration can be done by metal-free conditions. However, most of the reactions have suffered from at least one or more following drawbacks: (i) Use expensive transition metals (Ru, Rh, Pd, Pt, Au, Ir, Ag) predominantly the recovery and reusability of catalysts and the indispensable use of acid co-catalysts, additives, and promoter;

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Metal-free, PTSA catalyzed facile synthesis of β-ketoacetal from β-chlorocinnamaldehyde

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ABSTRACT

A toluene solution of β-chlorocinnamaldehyde and dihydroxy alcohols in the catalytic presence of *para*-toluenesulphonic acid (PTSA) yield the β-ketoacetal in good to outstanding amount. The catalyst (PTSA), first selectively protect the aldehydic group to form the β-chloroacetal and the subsequent dechlorination by H_2O result the β-ketoacetal. Significant transformation was achieved with electron donating substituent attached at the *para*-position of cinnamaldehyde. The selective formation of β-keto-1,3-acetal was also obtained with a mixture of 1, 2- and 1, 3- diol. The present reaction consists of a metal-free, economical, robustly feasible, sizeable functional group tolerance and high yield properties. Moreover, the use of different dihydroxy alcohols made this process more benign and valuable towards the metal-free development of ketones. First, of its kind, a rare and unusual multitasking nature of PTSA is observed.

Introduction

Protection and deprotection of the carbonyl functionalities are quite common in multistep organic synthesis [1]. The protection of carbonyls group is usually carried out either in the presence of Lewis acid or protonic acid [2]. Various reagents including the tetrabutylammonium tribromide [1], $ZrCl_4$ [2], $PdCl_2Ce(OTf)_3$ [3], $PhICl_2$ [4], $(EtO)_3CH$ – DDQ [5], $(EtO)_3CH$ – NBS [6], I_2 [7] and Sc $(NTf_2)_3$ [8] used as common reagents for the protection/deprotection of carbonyls. Literature evident the protection of large numbers of general and functionalized carbonyl groups [9], but surprisingly the protection of β-chlorocinnamaldehydes is still not reported. Hence, it motivated us to investigate the protection of carbonyl functionality present in β-chlorocinnamaldehyde and the synthesis of β-chloroacetal was our prime expectation from this reaction. However, quite a few reports are available for the synthesis of β-chloroacetals [10,11] but all reports consists of the multistep process and need quite expensive reagents and catalyst (Di-*tert*-ButylPeroxide) [10]. Hence, a promising alternative and inexpensive catalysts are highly desired for the chloroacetal formation. PTSA is very cheap and most common catalyst [12] used for the protection of carbonyl groups, moreover, it was not explored for the protection of cinnamaldehyde, hence, use of PTSA as a catalyst becomes an ideal choice for the desired transformations. But, unlike to our expectations, a different product, a β-ketoacetal was formed in reaction trials. Since there is no previous report available for the direct synthesis of β-ketoacetal and β-chloroacetal from β-chlorocinnamaldehyde using PTSA or any other catalyst. These observations encouraged us to investigate this particular reaction. The panorama of the methodology developed through this scheme shows that it will be equally beneficial for the synthesis of both the products.

β-Ketoacetals are more valuable synthons than β-chloroacetal and have great diversity as a precursor for many natural and biologically active compounds [13]. Nevertheless, as per literature concern, the β-chloroacetals also have significant but limited applications [11]. Moreover, the synthesis of β-ketoacetal recorded several patents in last few decades [14–16]. Reported methods mostly use the precious metals, i.e. $PdCl_2$-$CuCl_2$-O_2 [17], $PdCl_2$-$(MeCN)_2$-O_2 [18], however, quite a few also reported with $SiO_2.H_2SO_4$ – DDQ [19] and K_2CO_3 or KOH [19] catalysts. Moreover, the used reactant already consist of a ketonic functional group which is economically not viable and difficult to synthesize. Literature indicates, the synthesis of β-ketoacetal was first reported by Nells et al. in 1937, while, other synthetic methods up to 1960 for the β-ketoacetal are only available in patent forms. The first cyclic β-ketoethyleneacetals was synthesized by Kochetkov et al. [13] in 1957, by reaction of β-chlorovinylketone and ethandiol in the presence of K_2CO_3 or KOH base. Hosokawa et al. [17] reported $PdCl_2$-$CuCl_2$ catalyzed the synthesis of β-ketoacetal from terminal olefins, the same research group also reported the modified synthesis with $PdCl_2$-$Me(CN)_2$ [18] catalyst in the O_2 environment. The most recent method was reported in 1993 by Campi et al. [19], an

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ARTICLE

Palladium(II) ligated with selenated NHC based (Se, C_{NHC}, N^-) type pincer: An efficient catalyst for Mizoroki-Heck and Suzuki Miyaura coupling in water

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A new 1-[*N*-benzylacetamido]-3-[1-(2-phenylselenylethyl)] benzimidazolium chloride (**L**), the precursor of a novel (Se,C_{NHC},N^-) type first pincer ligand (**L**) has been synthesized in high yield through a sequence of consecutive reactions of 1*H*-benzimidazole with ethylene dichloride, sodium selenophenolate, and *N*-benzyl-2-chloroacetamide. The palladium promoted reaction of **L** with $PdCl_2$ has resulted in a moisture and air insensitive complex [Pd(**L**–H_2Cl)Cl] (**1**) which has demonstrated outstanding catalytic potential for Mizoroki-Heck of aromatic bromides/chlorides (Yields up to 94%/70%) at very low catalyst loading (0.2 mol%) under mild reaction conditions in water. The complex **1** has also been explored for the Suzuki-Miyaura coupling and found to be selectively efficient (Yields up to 94%) for Suzuki-Miyaura coupling of aromatic bromides at 0.01 mol% of **1** in water. All coupling reactions were carried out in green and economical solvent water, which is highly desired for bulk synthesis of complexed molecules in industries. During the catalytic process, the complex **1** in situ converted into Pd-Se nanoparticles (NPs, size range 5-6 nm). The morphology and composition of these NPs were analysed through HR-TEM and TEM-EDX, respectively. The core-level X-ray photoelectron spectroscopic (XPS) analysis has confirmed the presence of stable Pd^0 and Pd^{+2} oxidation states in these Pd-Se NPs. Based on further experimental investigations, these nanoparticles were found to work as a stock of true catalytic species. The hot-filtration, as well as two-phase test, have confirmed the largely homogeneous nature of the catalytic process which most probably proceeds by leaching of solution-phase Pd species from these NPs.

Introduction

The Mizoroki-Heck reaction[1, 2] has grown as an indispensable and prominent standard protocol for organic synthesis in the industry as well as academia.[3, 4] Various synthetic applications of the Mizoroki-Heck coupling for the synthesis of olefinic cross-coupled products which are the main building blocks of wide range of complex molecules including natural products and fine chemicals are worth mentioning.[5, 6] Several bulky electron-rich phosphine based palladium catalysts,[7-9] and palladacycles[8, 10, 11] catalysts have been reported for the Heck coupling but the certain drawbacks are associated with them such as the use of toxic solvents, strongly desired air/moisture-free conditions and limited reactivity for readily available inexpensive aryl chloride as substrates. Hence, due to the economic concerns and environmental sustainability, there is a high demand to develop the economic, air/moisture insensitive catalysts those can efficiently surpass the challenges of sophisticated catalysts and can work in non-flammable and less noxious green solvents. According to the traditional proponents of principles of green chemistry,[12] water is the greenest and best alternative solvent for organic solvents.[13-15] Owing to the unique two-electron σ-donor and negligible π-acceptor properties, NHCs usually form the metal complexes with an enhanced thermal and air/moisture stability and also allow access to the metal complexes, outstanding in the catalysis.[16-18] From the last several decades, NHCs are enjoying the status of most indispensable tool in catalyst design in organometallic catalysis. The investigations of NHCs are mainly on track after the first metal-NHC complexes reported by Wanzlick,[19] Öfele,[20] Lappert,[21] and the isolation of the first free NHC by Arduengo[22] in 1991. The pincer frame-work designed using NHC ligands are known as a useful motif to provide electronic, topological versatility and protective sheltered environment to the metal centre which in turn affords their metal complexes, high stability, and catalytic activity.[23] An assorted collections of N, P donor functionalized NHC based pincer type such as CNC,[24] CCC,[25] PCP,[26] and CNC[27] have been shown the terrific catalytic activity for organic reactions. Comparable to the NHC, the organochalcogen ligated metal complexes have also been recognized as potential candidates for the catalysis of Suzuki-Miyaura

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† Electronic Supplementary Information (ESI) available: NMR spectra, mass spectra, crystal and refinement data, bond lengths and bond angles, NMR data of all the Mizoroki-Heck coupling products and CIF of **1** (CCDC 1876803) are provided as ESI.
See DOI: 10.1039/x0xx00000x

Chapter 2

(η^6-Benzene)Ru(II) Half-Sandwich Complexes of Pyrazolated Chalcogenoethers for Catalytic Activation of Aldehydes to Amides Transformation

Supporting Information

^{1}H and ^{13}C NMR Spectra of Complexes and Compounds

SCXRD of Complexes 2 and 3

Mass Spectra of Complexes of 1-3

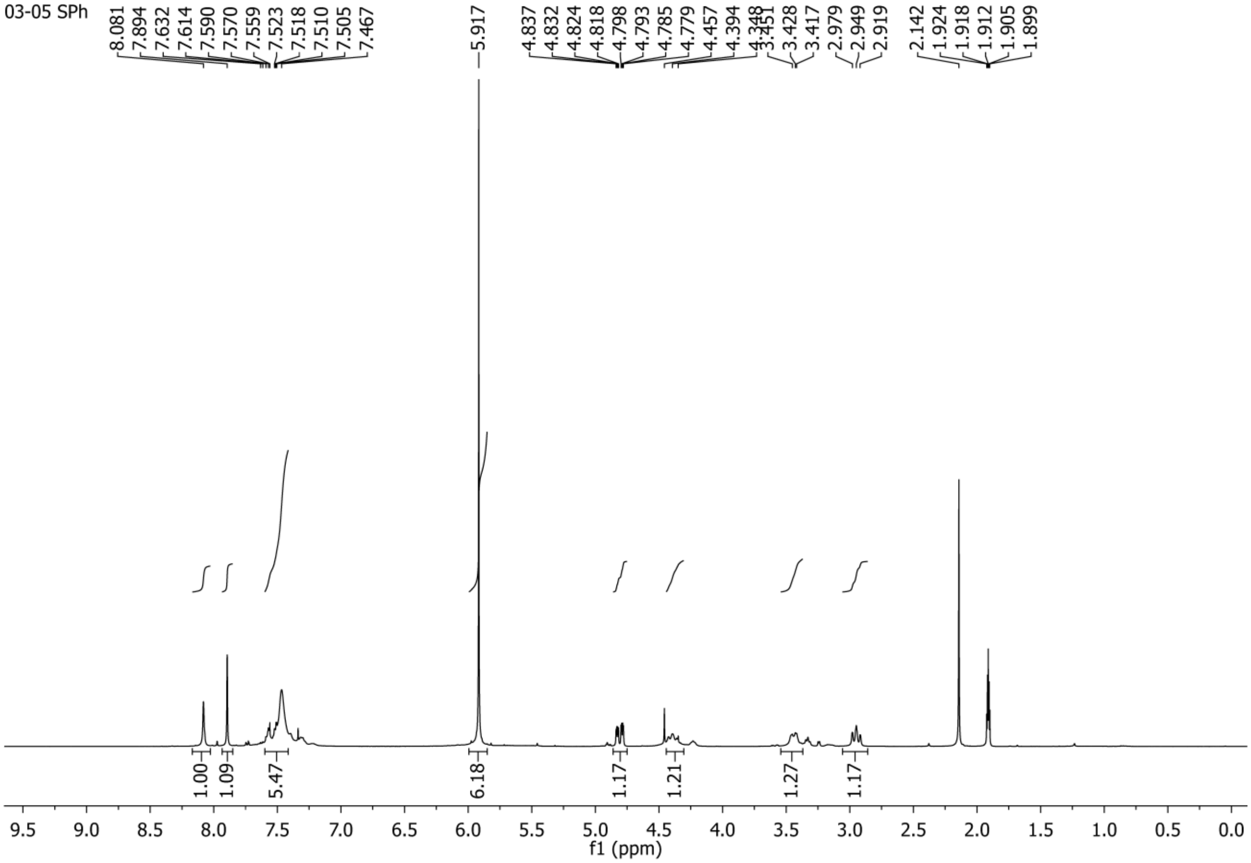


Figure S1: ^{1}H NMR (400 MHz, CD$_3$CN) of complex **1**.

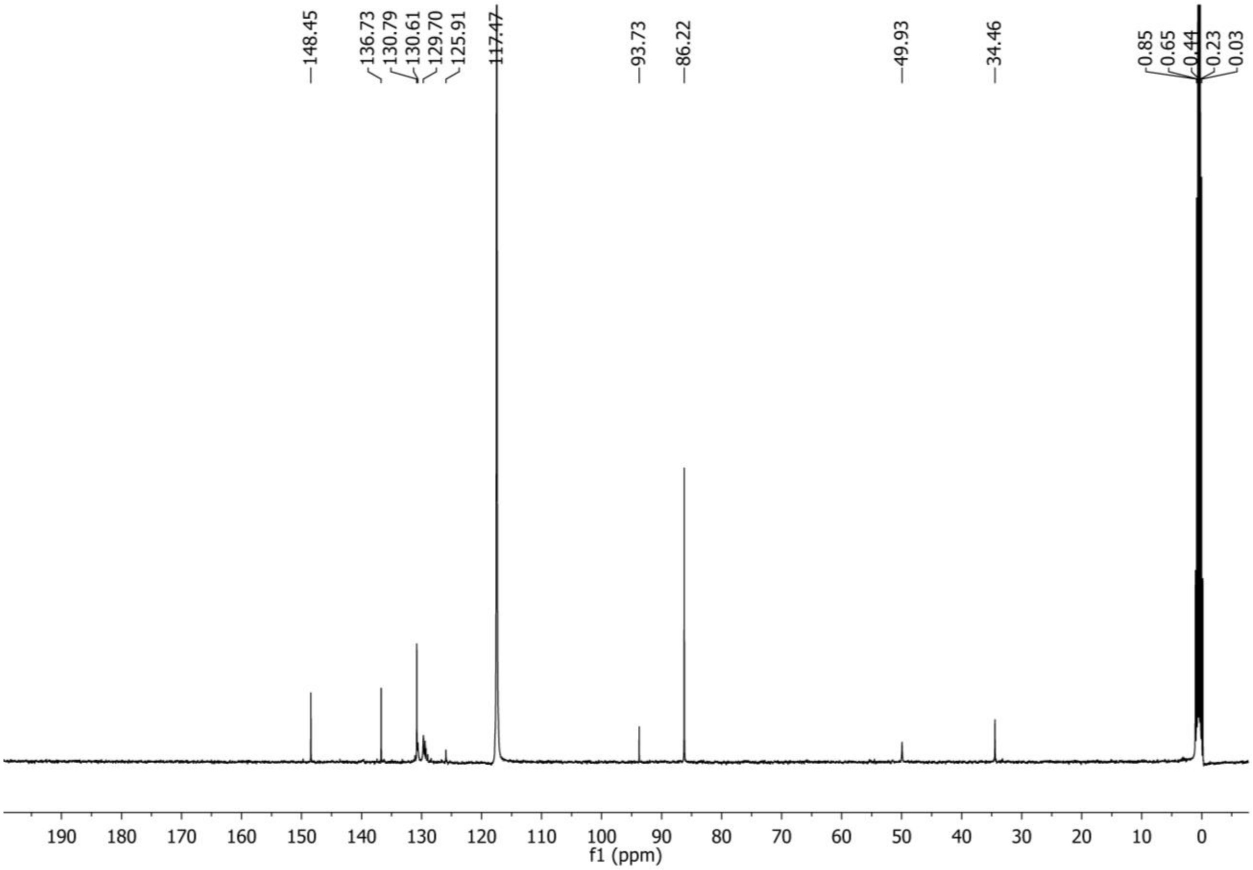


Figure S2: ^{13}C NMR (101 MHz, CD$_3$CN) of complex **1**.

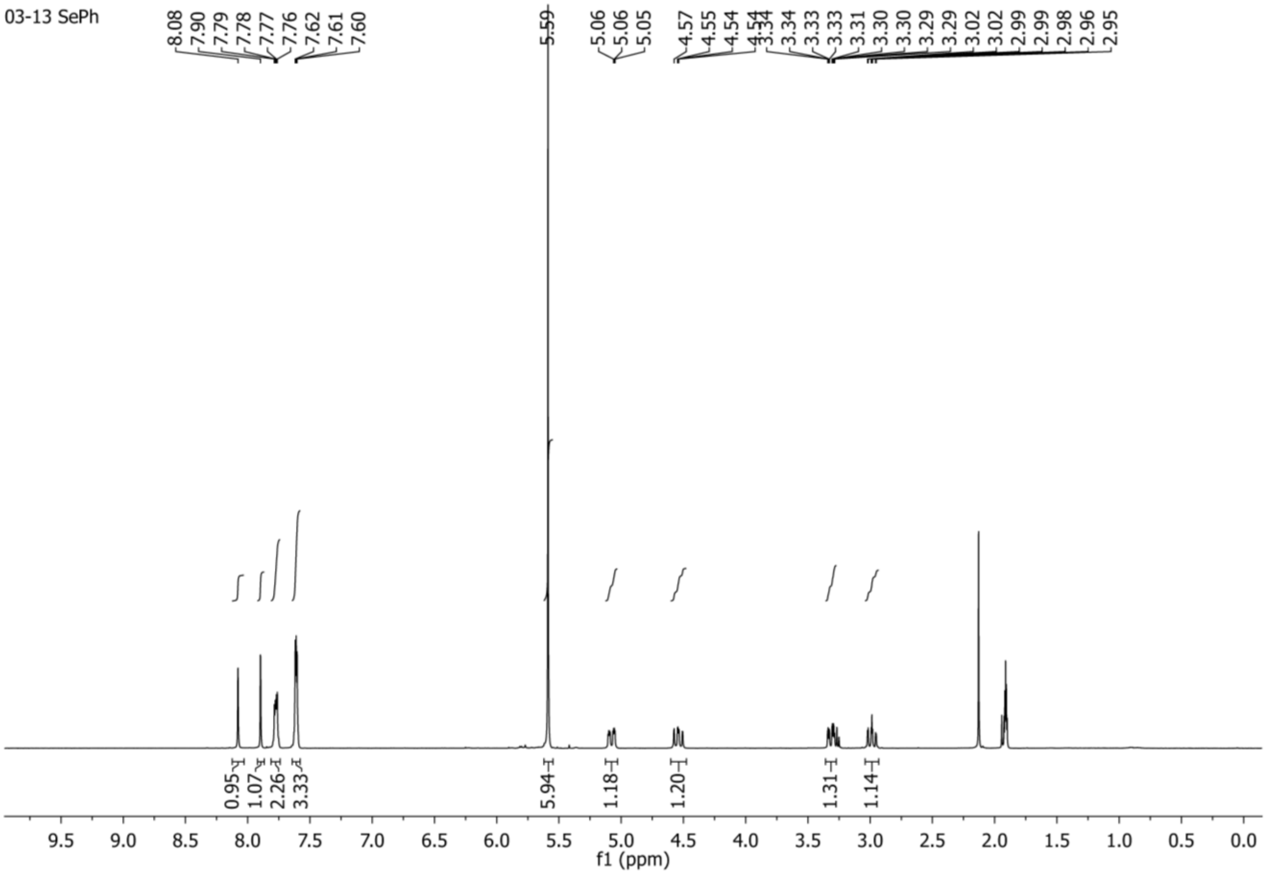


Figure S3: ^{1}H NMR (400 MHz, CD_3CN) of complex **2**.

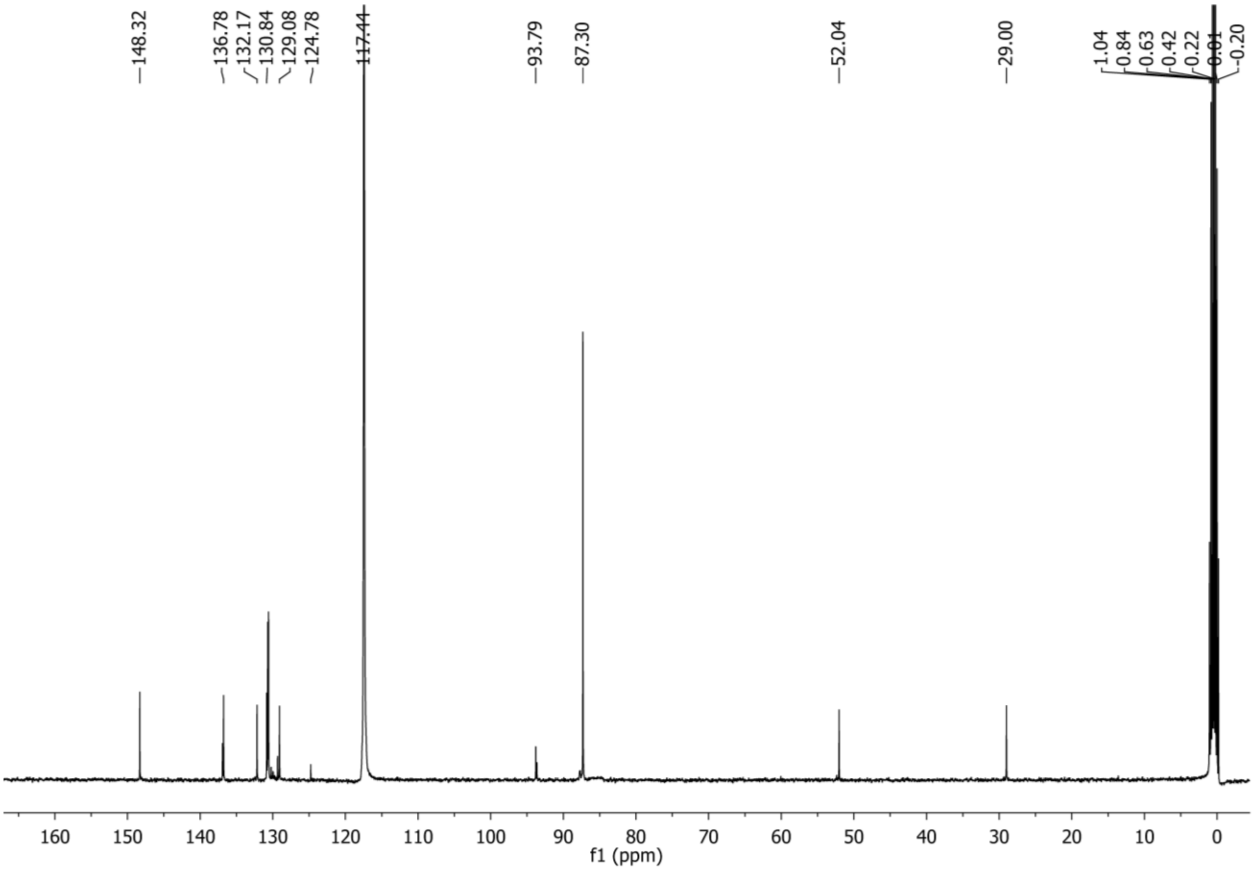


Figure S4: ^{13}C NMR (101 MHz, CD_3CN) of complex **2**.

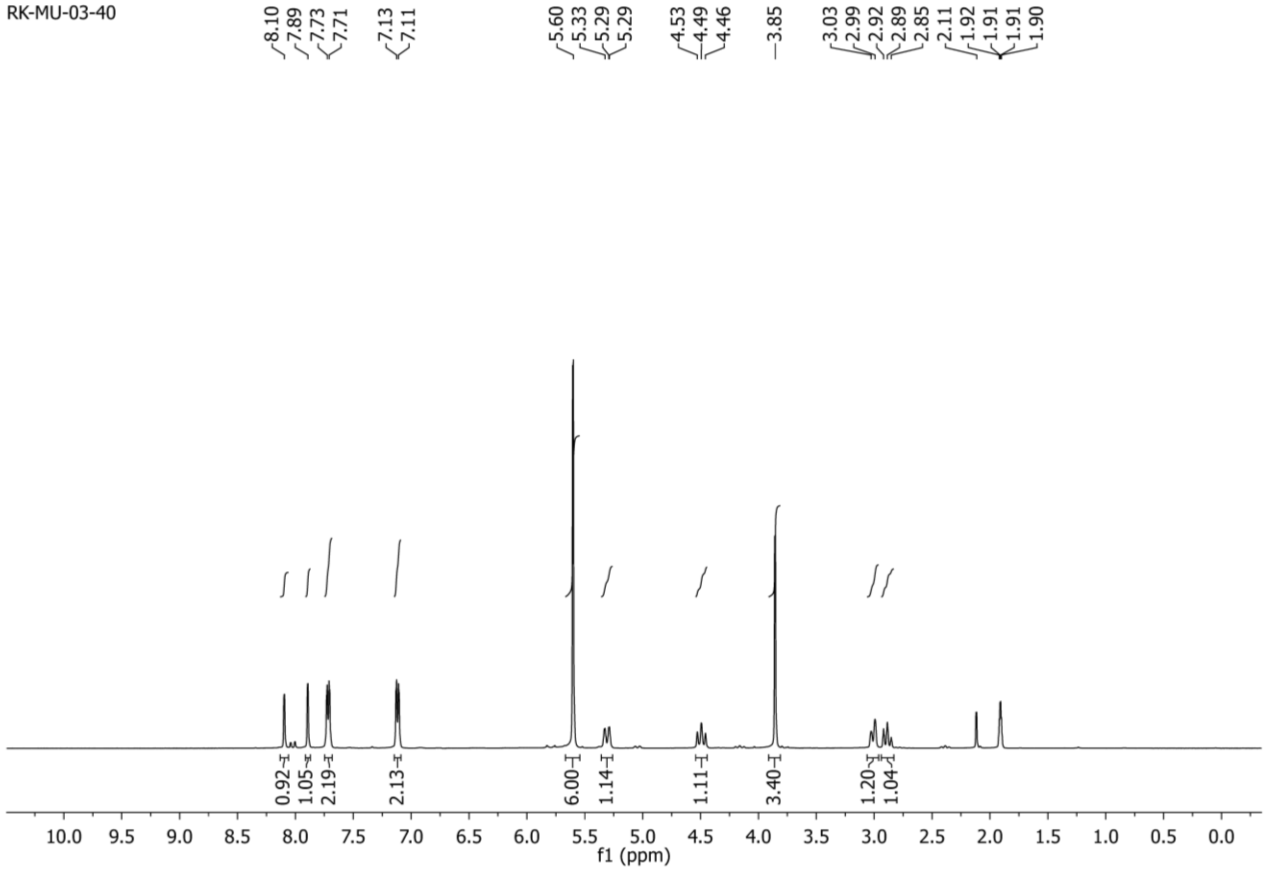


Figure S5: ^{1}H NMR (400 MHz, CD_3CN) of complex **3**.

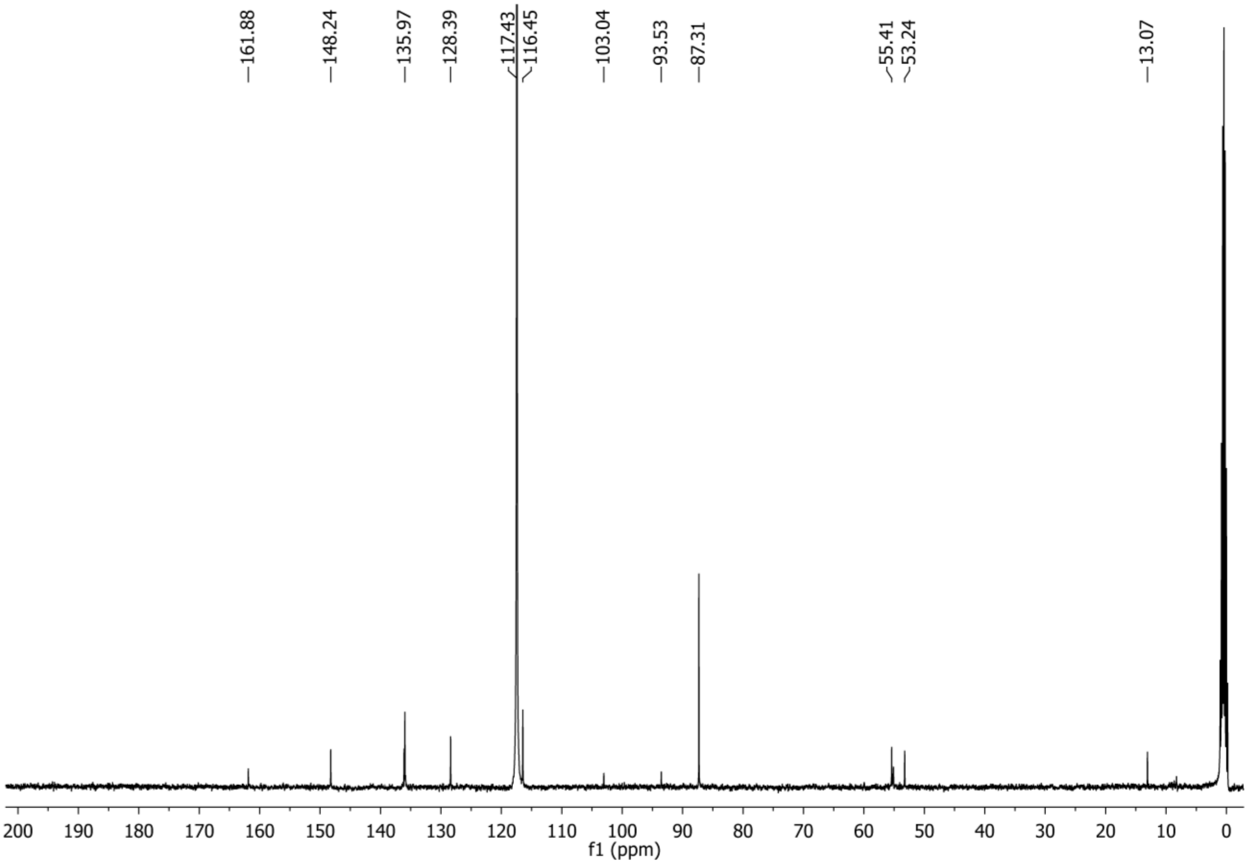


Figure S6: ^{13}C NMR (101 MHz, CD_3CN) of complex **3**.

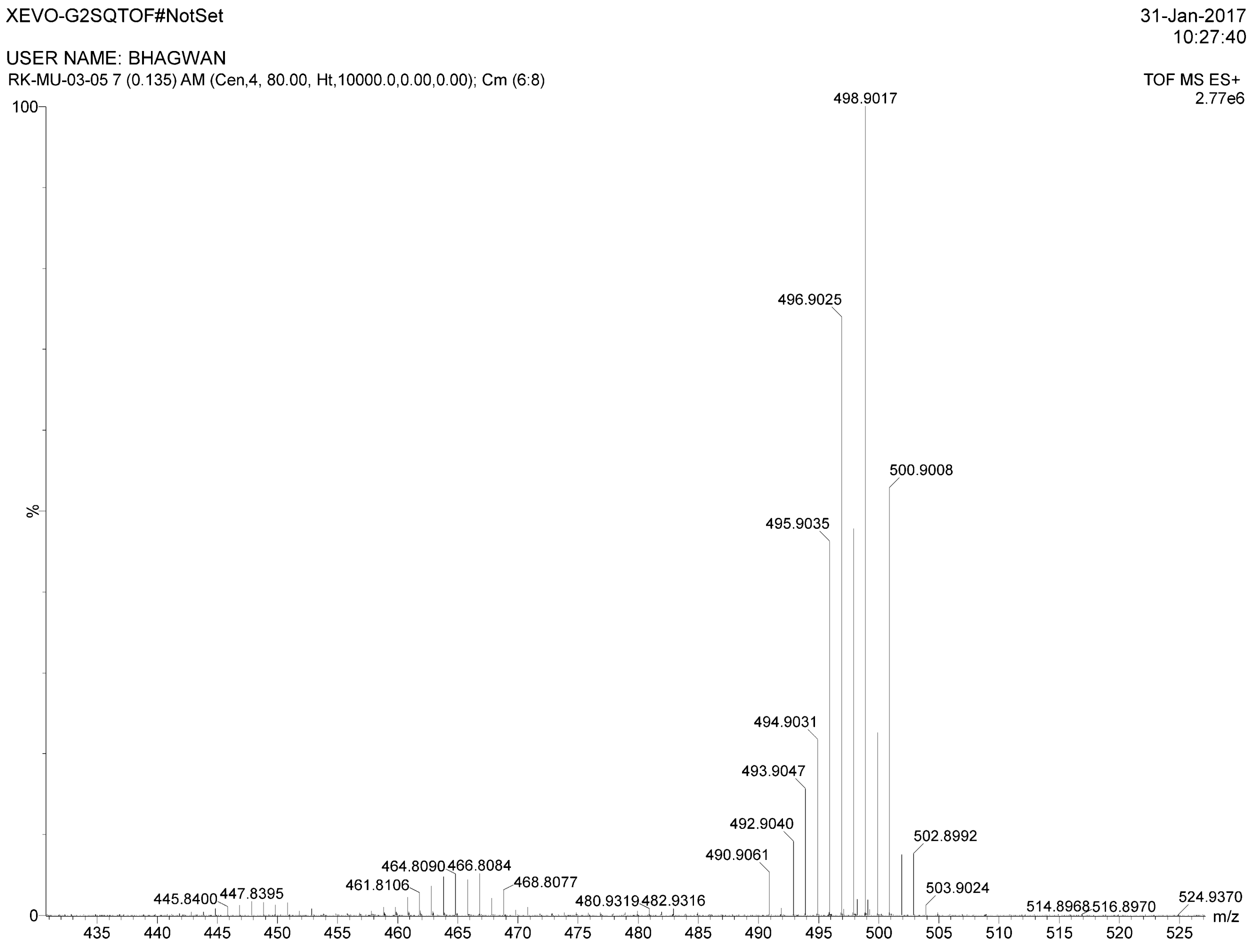


Figure S7: Mass spectrum of complex **1**.

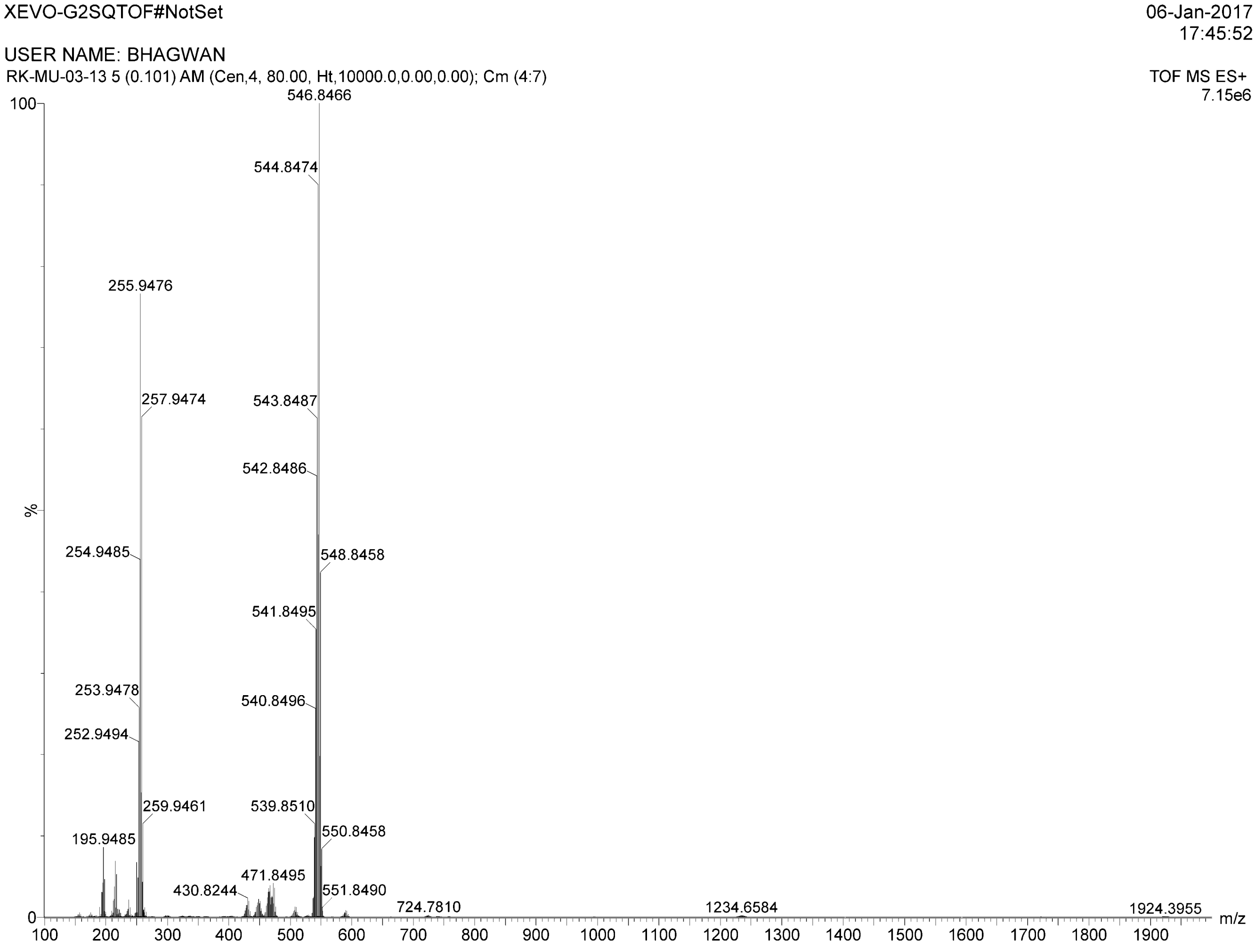


Figure S8: Mass spectrum of complex **2**.

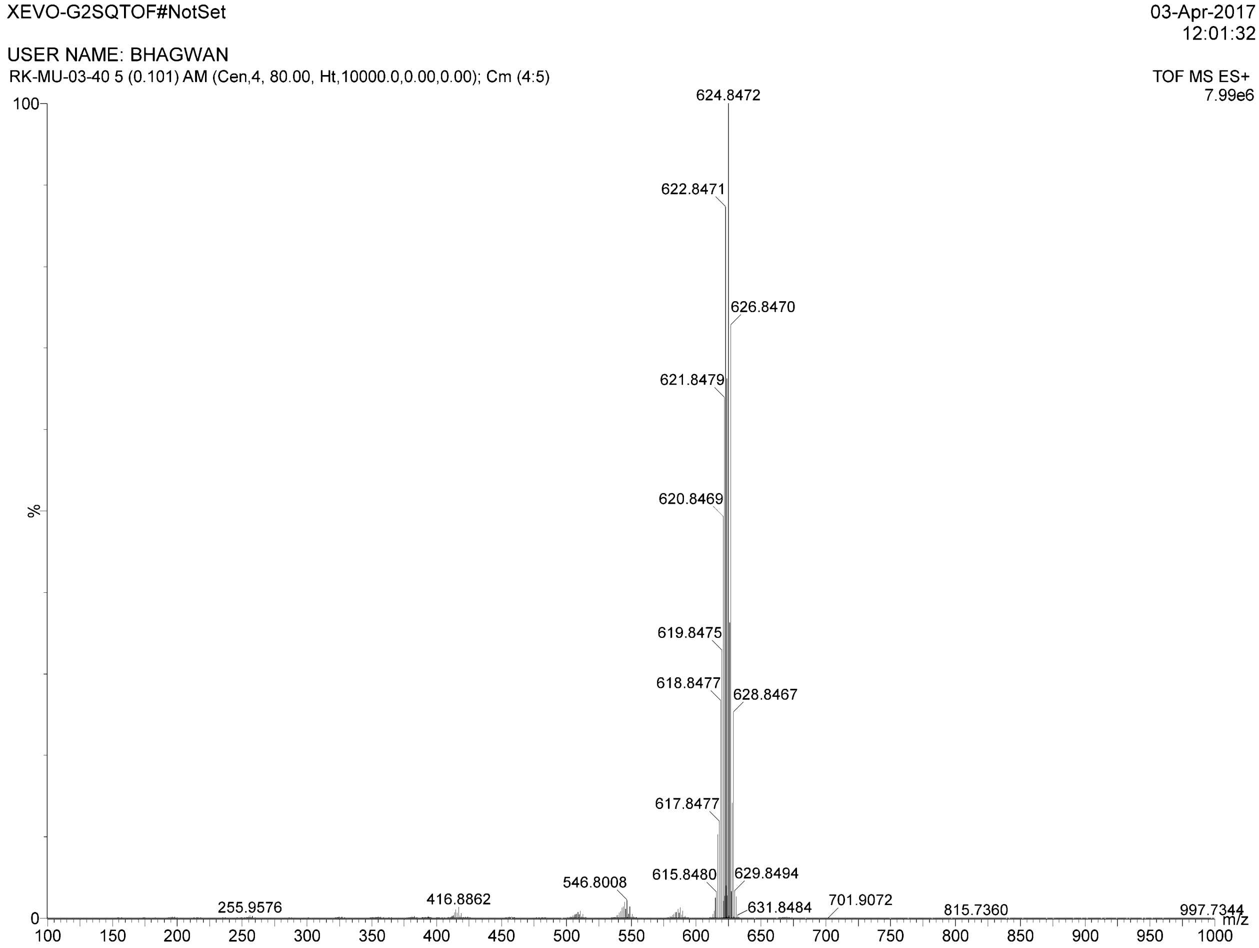


Figure S9: Mass spectrum of complex **3**

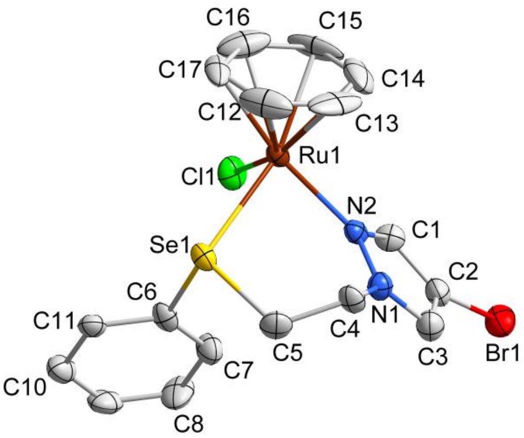


Figure S10: The molecular structure of **2** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity

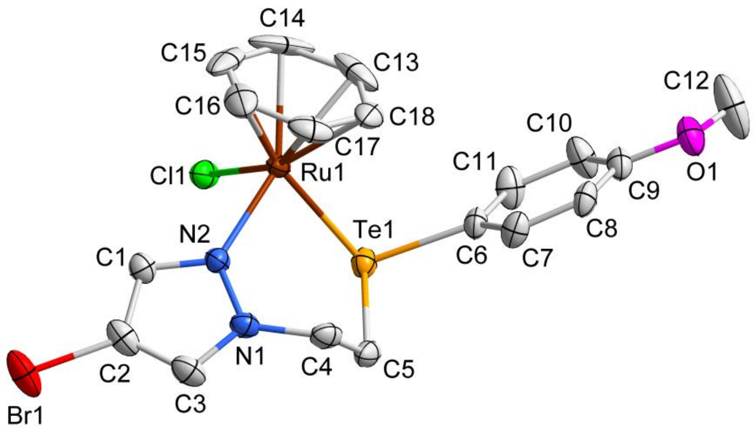
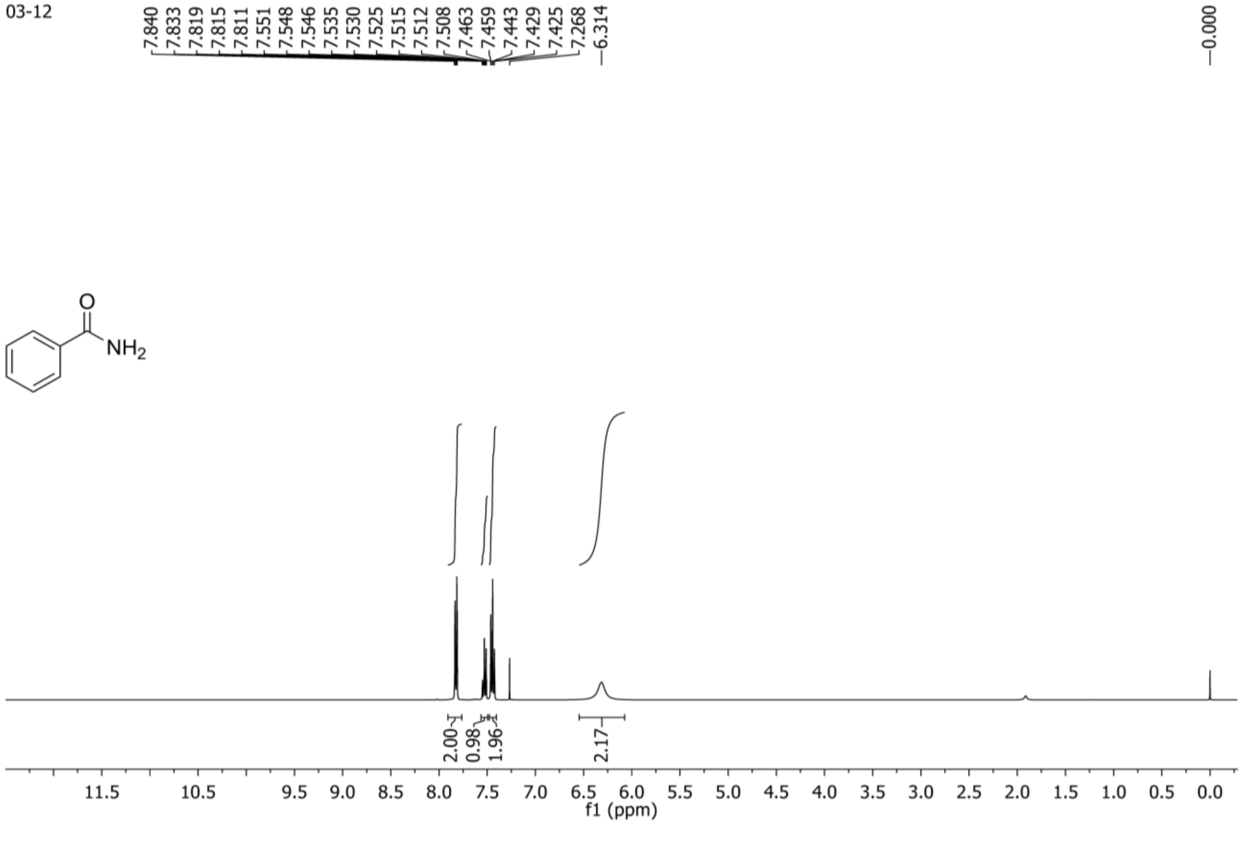


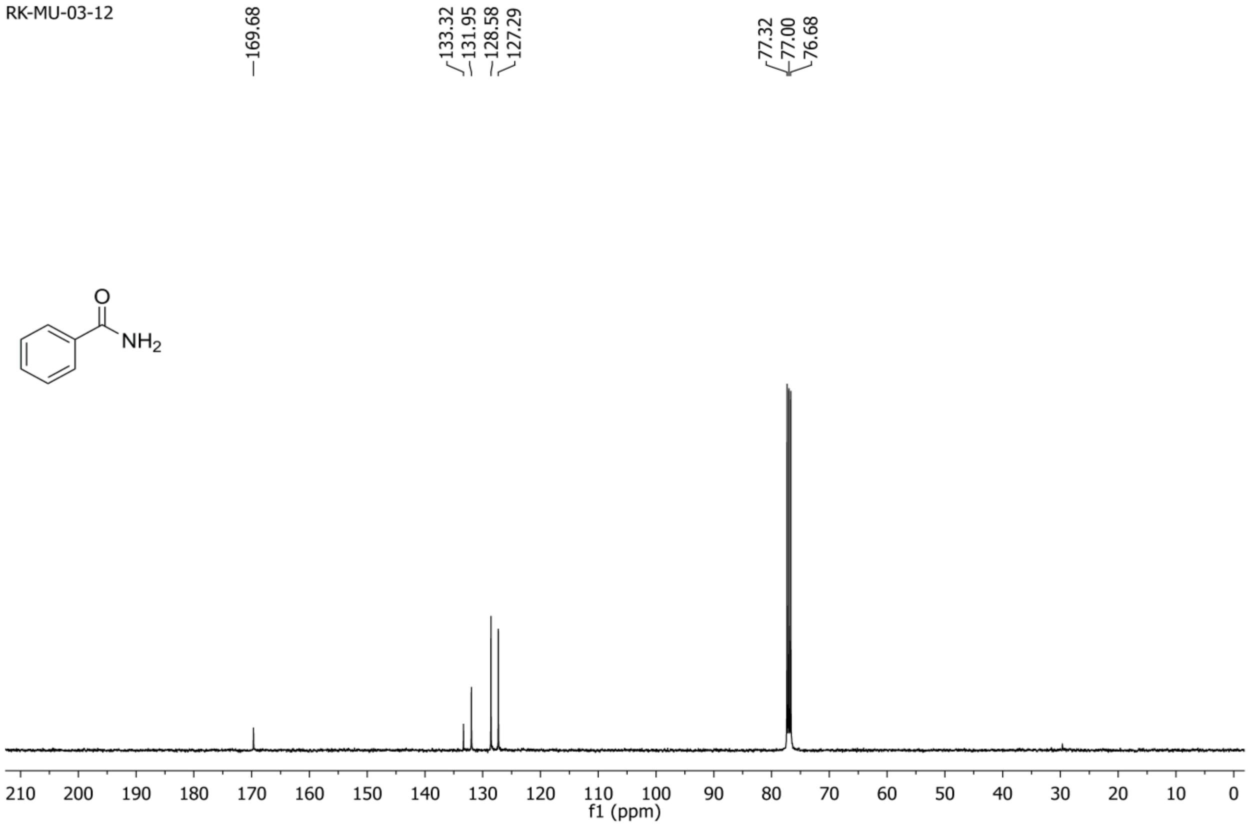
Figure S11: The molecular structure of **3** with thermal ellipsoids set at the 30% probability level. H atoms and PF_6 counter anion are omitted for clarity

Table S1 Selected Bond Lengths [Å] and Bond Angles [°] for 2 and 3

Complex	Bond Length [Å]		Bond Angle [°]	
2	Ru(1)—Cl(1)	2.392(4)	Cl(1)—Ru(1)—Se(1)	91.59(11)
	Ru(1)—Se(1)	2.5106(17)	N(2)—Ru(1)—Cl(1)	85.5(3)
	Ru(1)—N(2)	2.105(11)	N(2)—Ru(1)—Se(1)	87.0(3)
	Ru(1)—C(12)	2.16(2)	C(5)—Se(1)—Ru(1)	103.8(5)
	Ru(1)—C(13)	2.16(2)	C(6)—Se(1)—C(5)	98.0(7)
	Ru(1)—C(14)	2.15(2)	C(6)—Se(1)—Ru(1)	111.9(4)
	Ru(1)—C(15)	2.159(18)	C(1)—N(2)—N(1)	106.0(13)
	Ru(1)—C(16)	2.169(19)	C(1)—N(2)—Ru(1)	126.7(10)
	N(1)—N(2)	1.362(7)	N(1)—N(2)—Ru(1)	127.3(9)
	N(2)—C(1)	1.316(19)	C(3)—N(1)—C(4)	126.7(13)
	N(1)—C(4)	1.472(17)	N(2)—N(1)—C(3)	111.6(12)
	Se(1)—C(5)	1.973(15)	N(2)—N(1)—C(4)	121.7(11)
	Se(1)—C(6)	1.948(16)	C(7)—C(6)—C(11)	122.6(16)
	C(4)—C(5)	1.49(2)	C(7)—C(6)—Se(1)	121.6(12)
			C(11)—C(6)—Se(1)	115.8(12)
			C(1)—C(2)—Br(1)	126.1(13)
			C(1)—C(2)—C(3)	107.5(15)
3	Ru(1)—Cl(1)	2.403(2)	Cl(1)—Ru(1)—Te(1)	81.6(6)
	Ru(1)—Te(1)	2.6486(10)	N(2)—Ru(1)—Cl(1)	86.3(17)

Ru(1)—N(2)	2.105(5)	N(2)—Ru(1)—Te(1)	86.0(17)
Ru(1)—C(13)	2.16(8)	C(5)—Te(1)—Ru(1)	99.9(2)
Ru(1)—C(14)	2.16(8)	C(6)—Te(1)—C(5)	97.3(3)
Ru(1)—C(15)	2.19(10)	C(6)—Te(1)—Ru(1)	104.2(2)
Ru(1)—C(16)	2.21(10)	C(1)—N(2)—N(1)	105.9(5)
Ru(1)—C(17)	2.17(9)	C(1)—N(2)—Ru(1)	126.0(4)
Ru(1)—C(18)	2.18(8)	N(1)—N(2)—Ru(1)	128.1(4)
N(1)—N(2)	1.362(7)	C(3)—N(1)—C(4)	128.4(6)
N(2)—C(1)	1.333(8)	N(2)—N(1)—C(3)	110.4(6)
N(1)—C(4)	1.468(9)	N(2)—N(1)—C(4)	121.1(5)
Te(1)—C(5)	2.165(7)	C(7)—C(6)—C(11)	118.5(7)
Te(1)—C(6)	2.126(7)	C(7)—C(6)—Te(1)	124.7(6)
C(4)—C(5)		C(11)—C(6)—Te(1)	116.8(6)
		C(1)—C(2)—Br(1)	124.9(7)
		C(1)—C(2)—C(3)	106.2(7)

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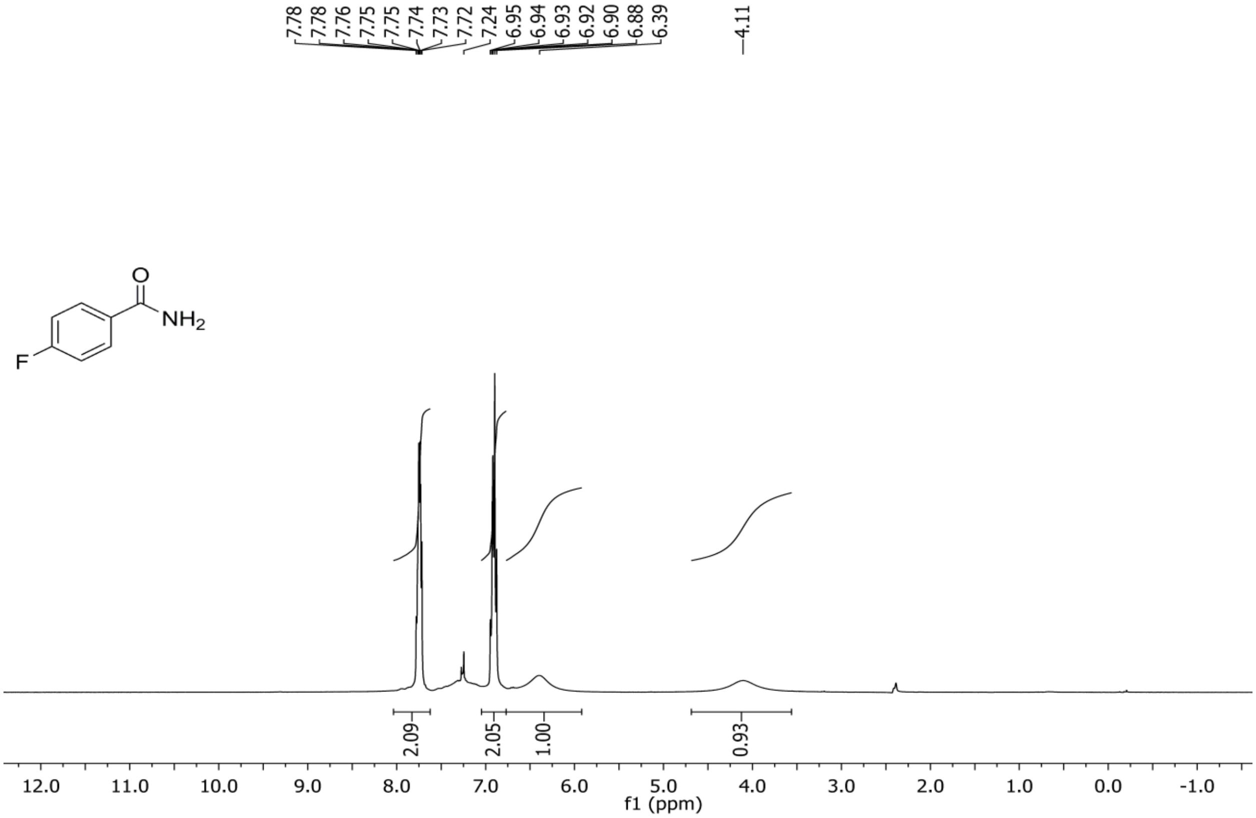
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6.90
6.88
6.39
4.11
O
NH2
F
2.09
2.05
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0.93
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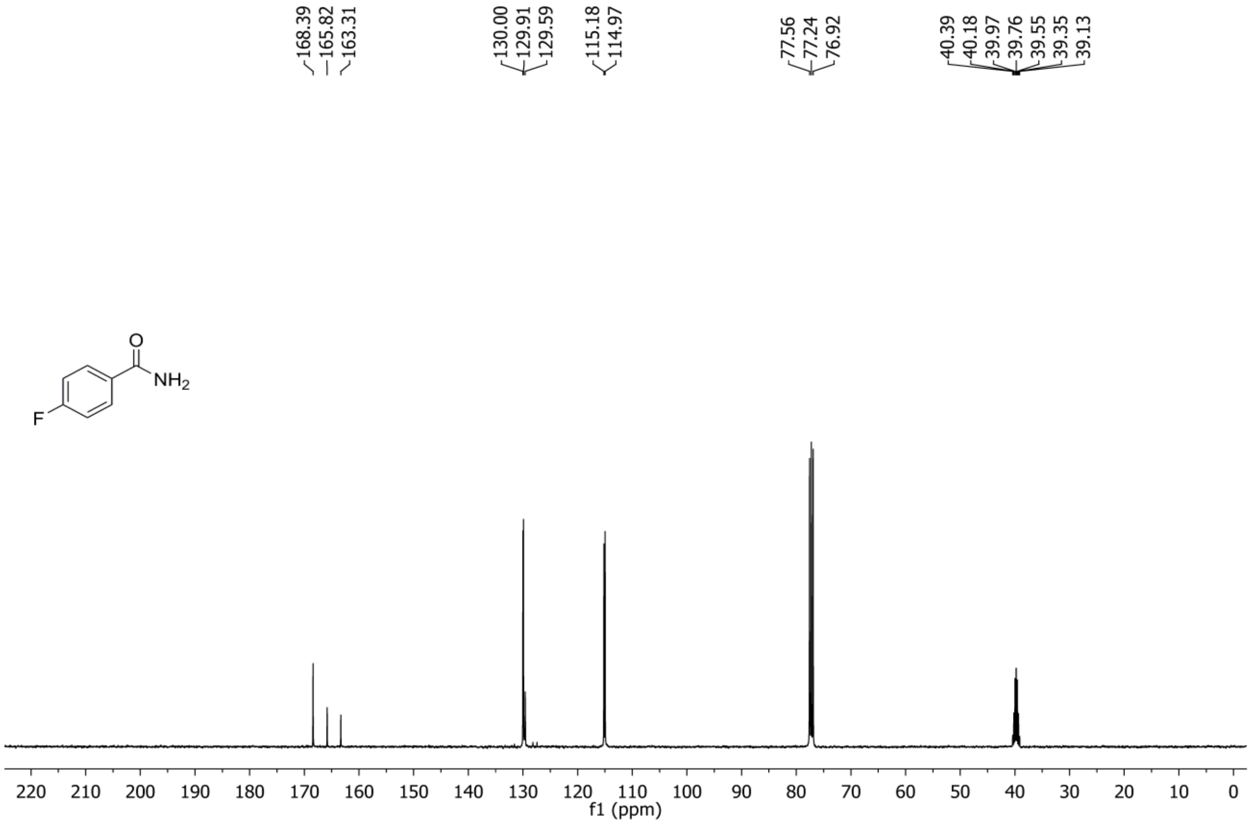
f1 (ppm)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39.97
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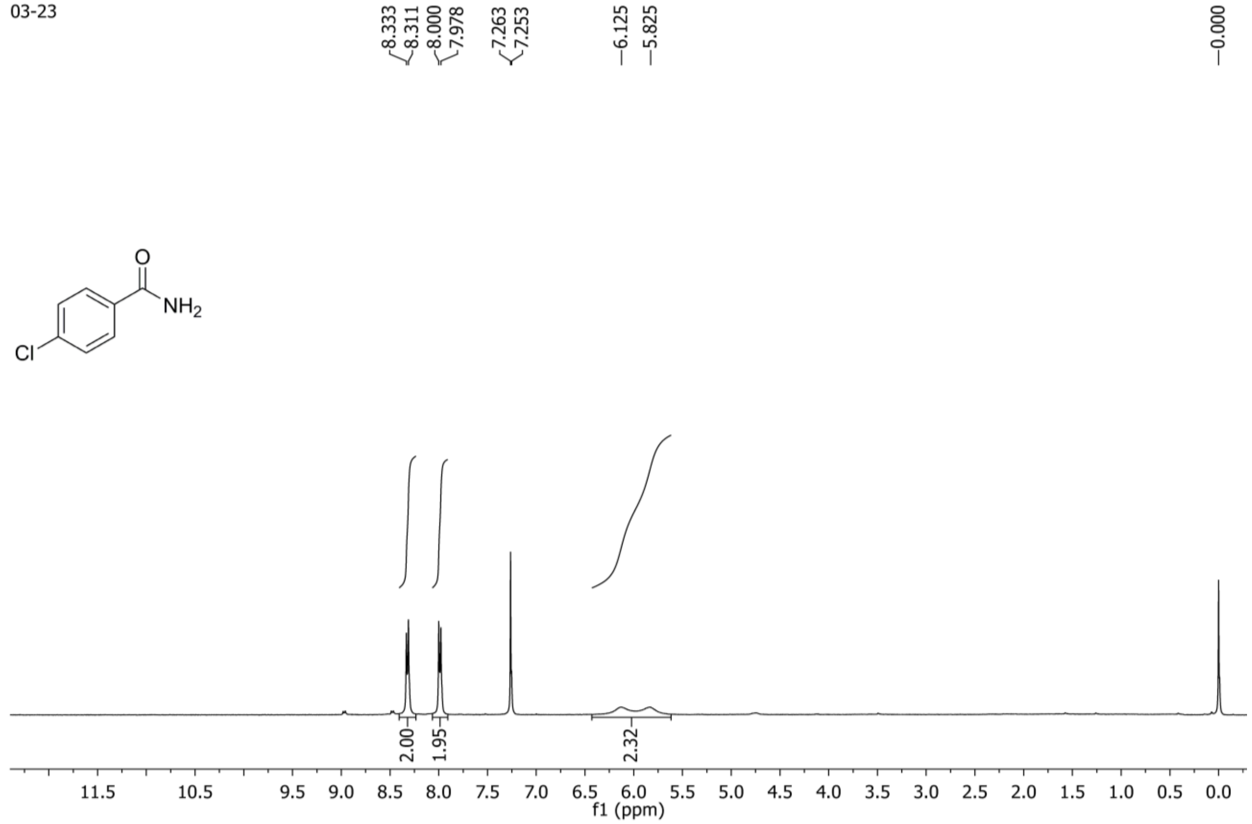
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1.95
2.32
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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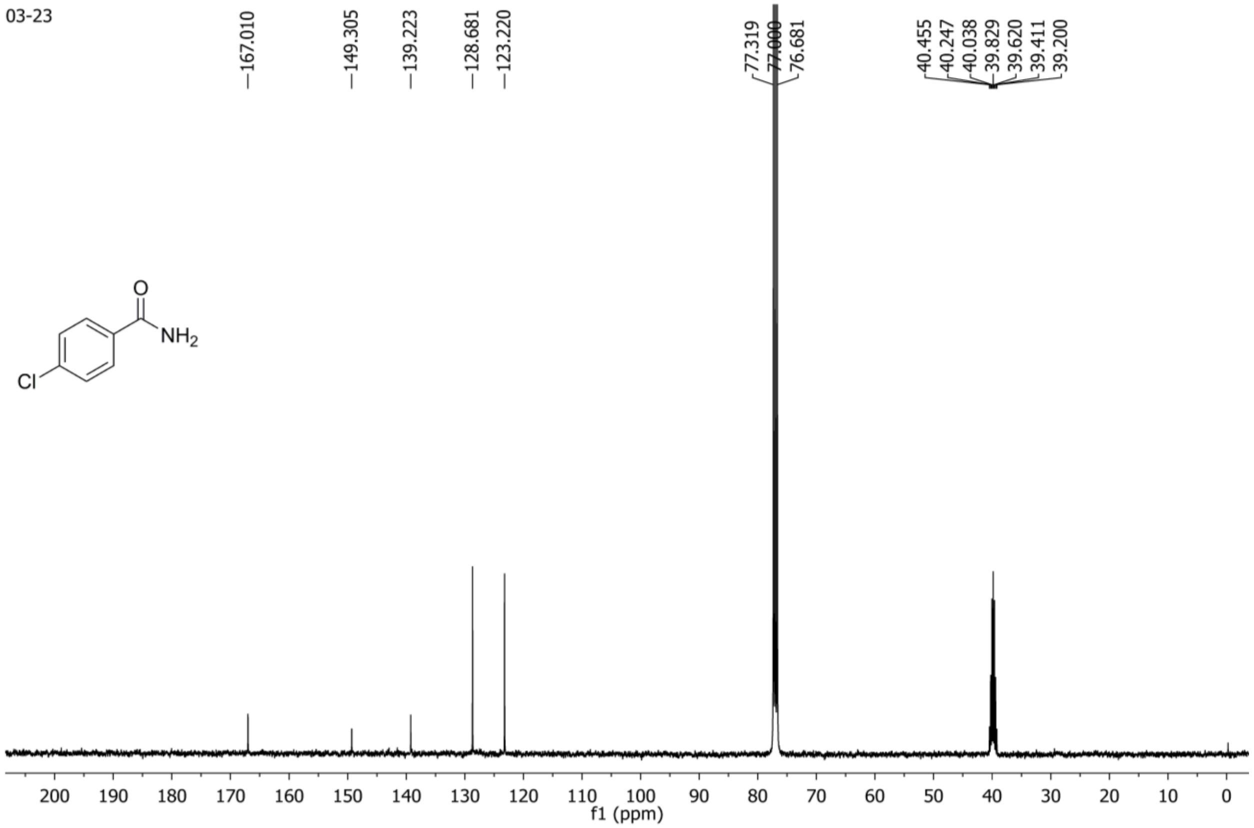
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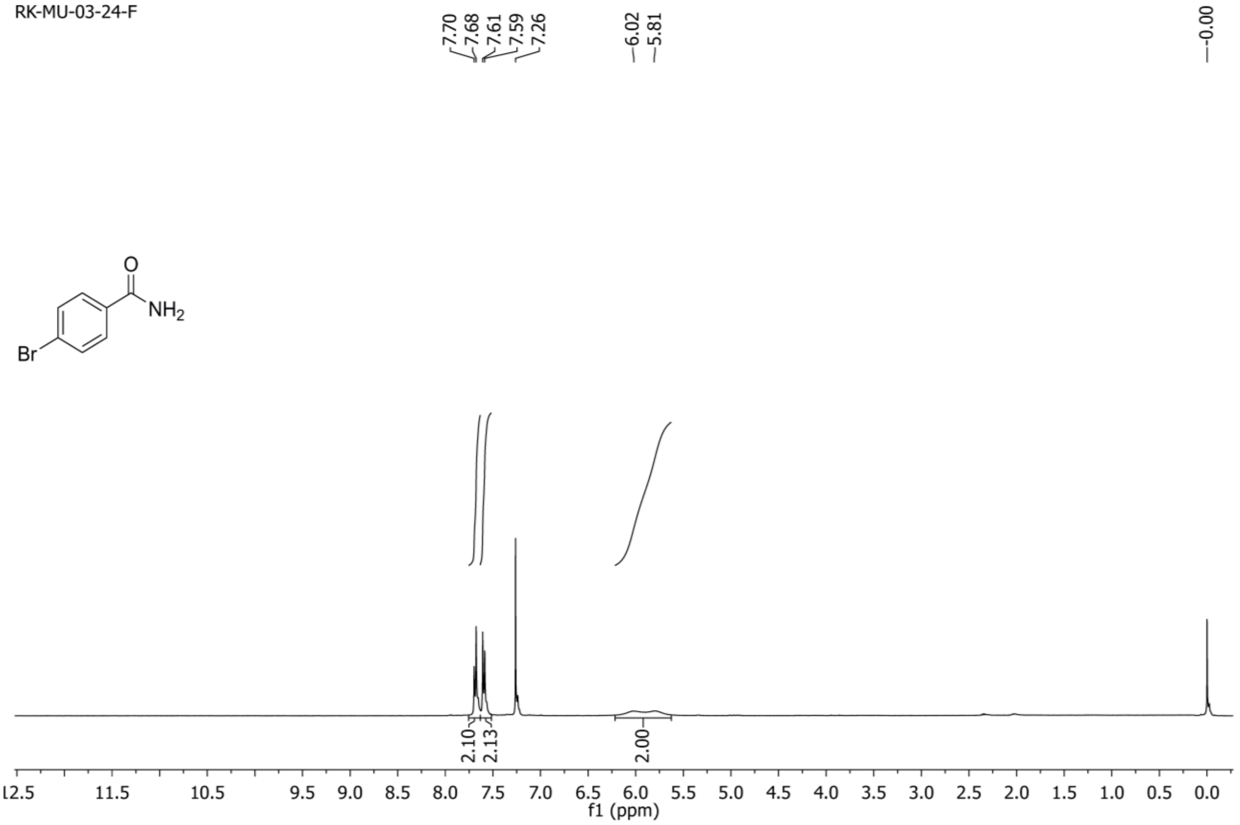
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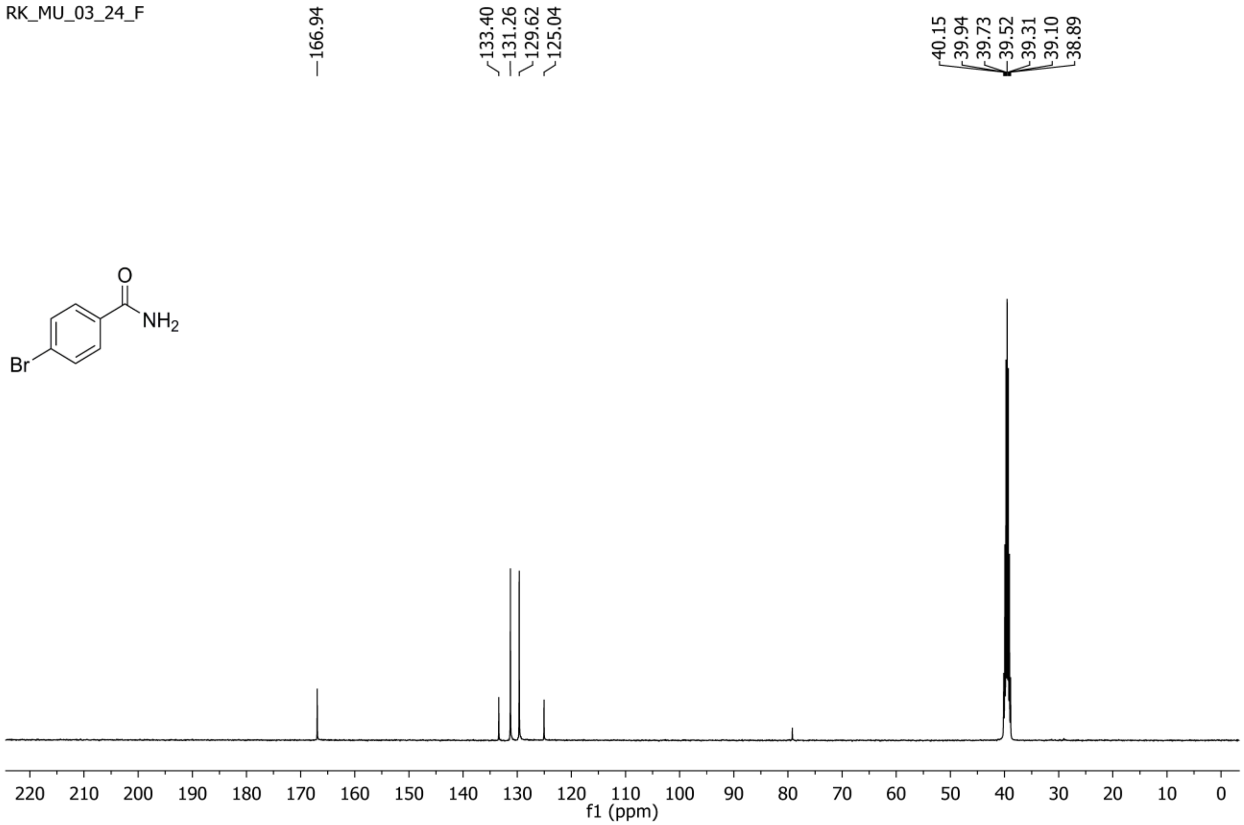
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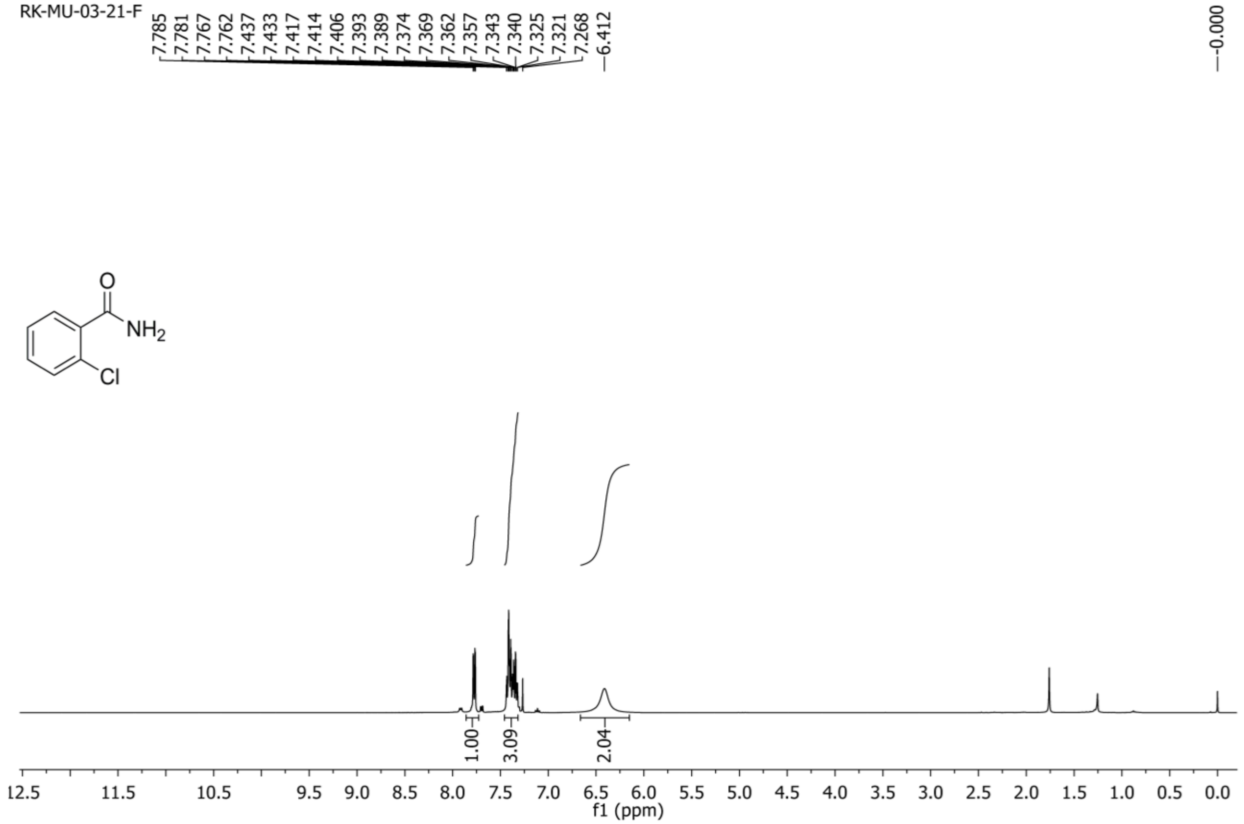
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Cl
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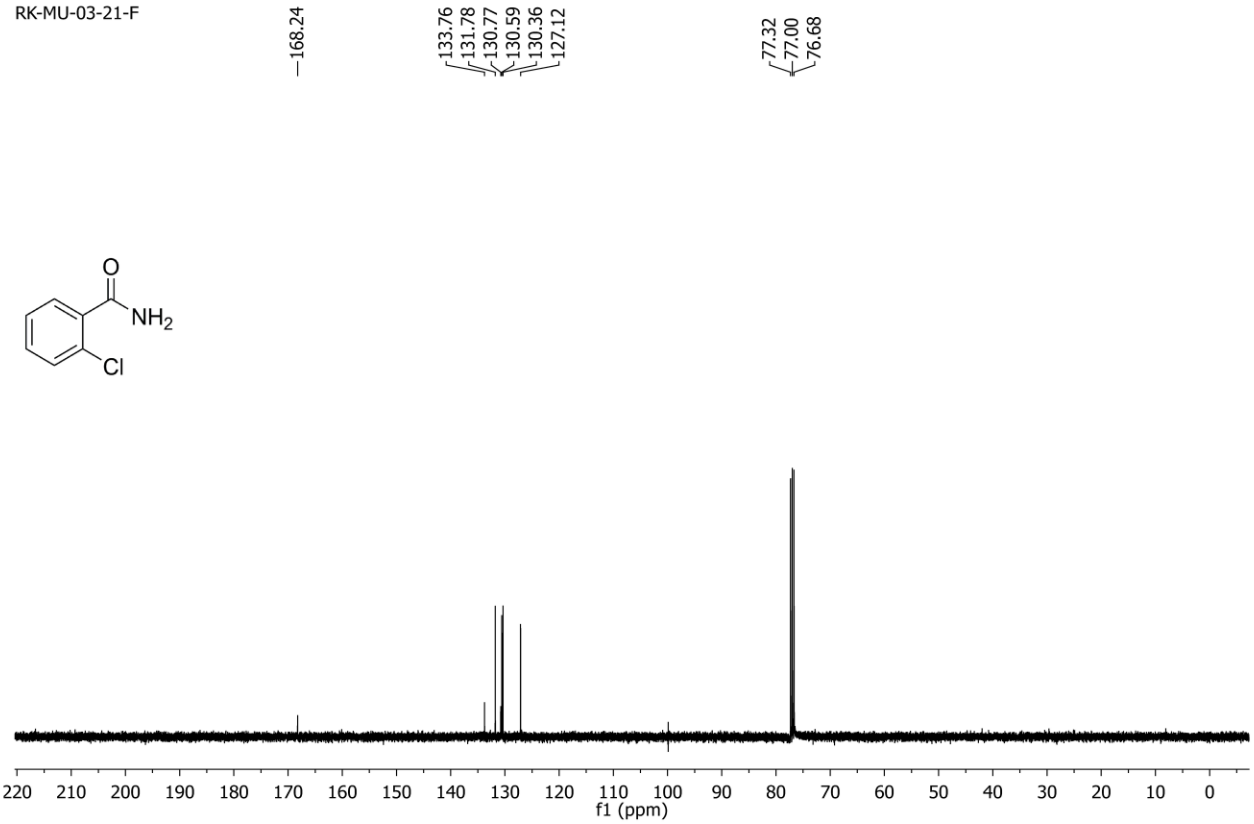
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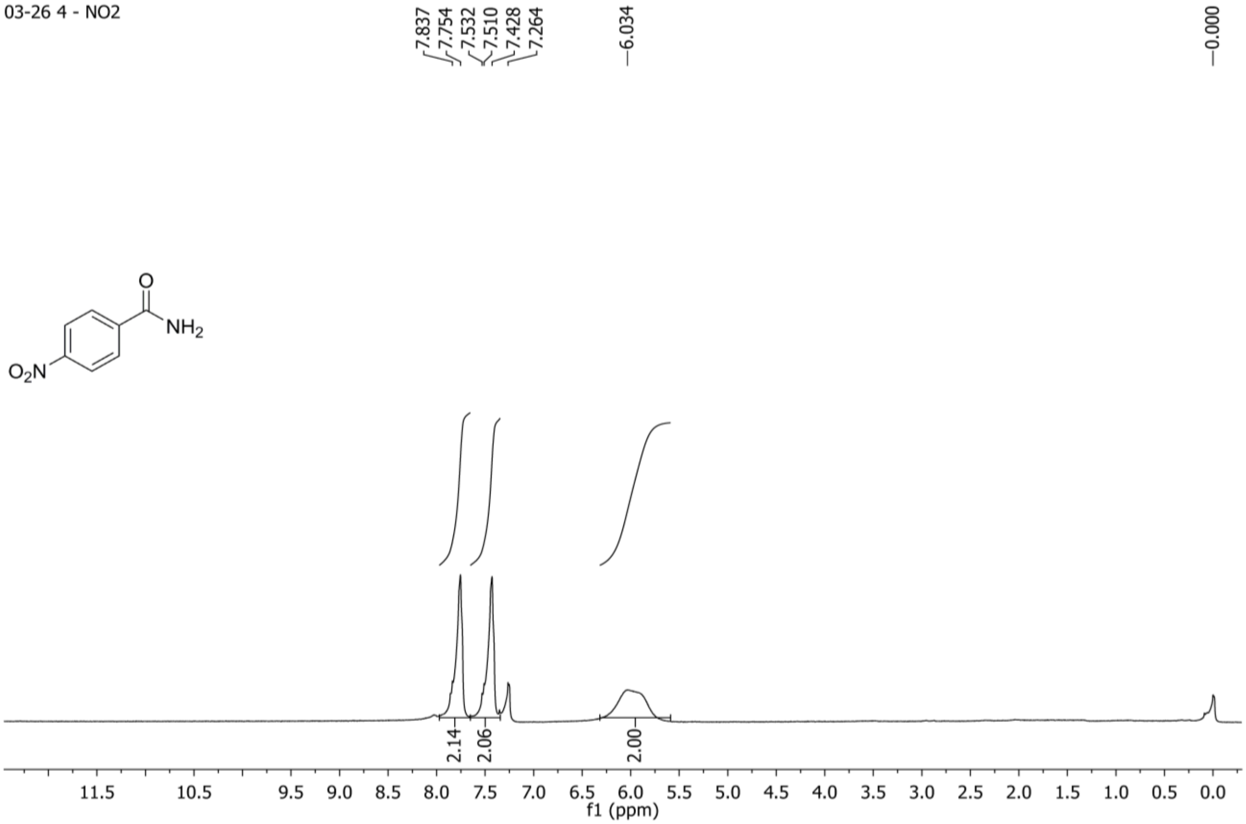
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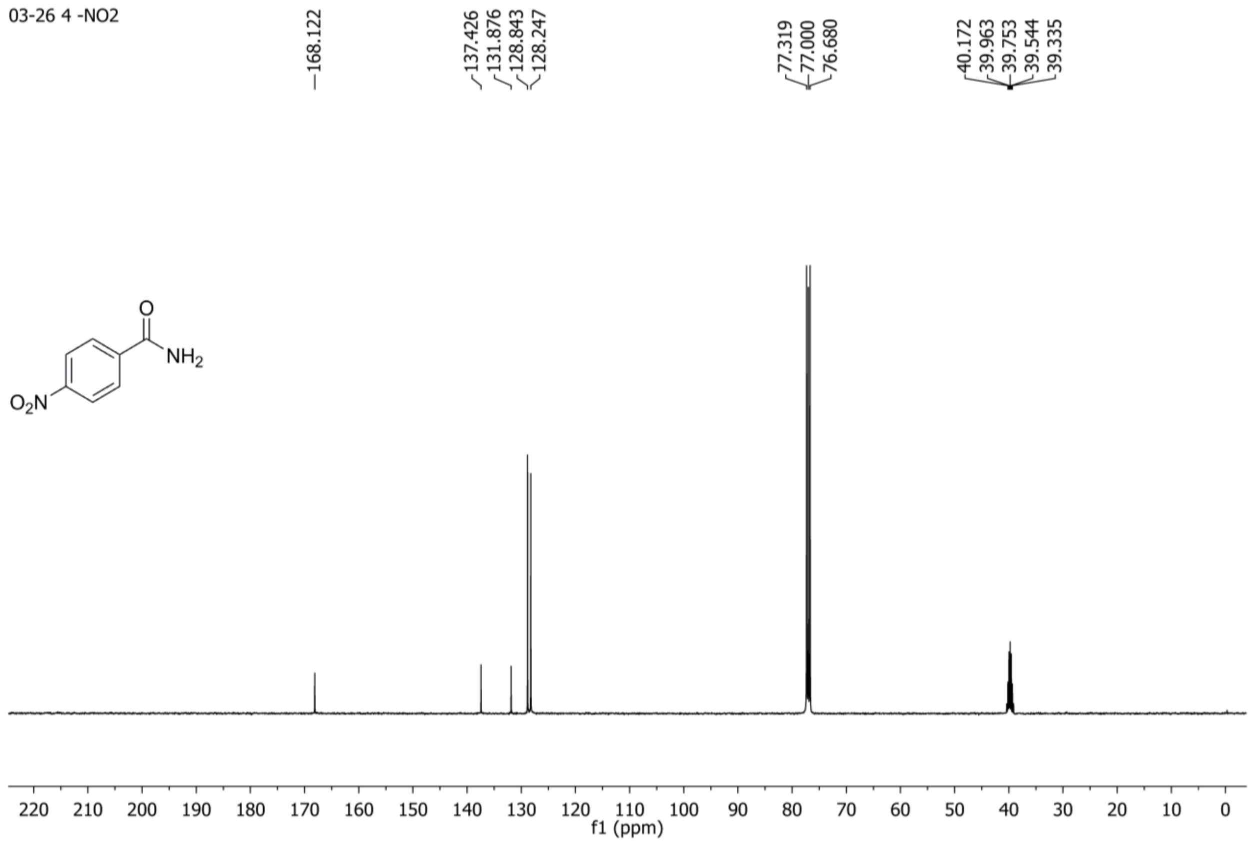
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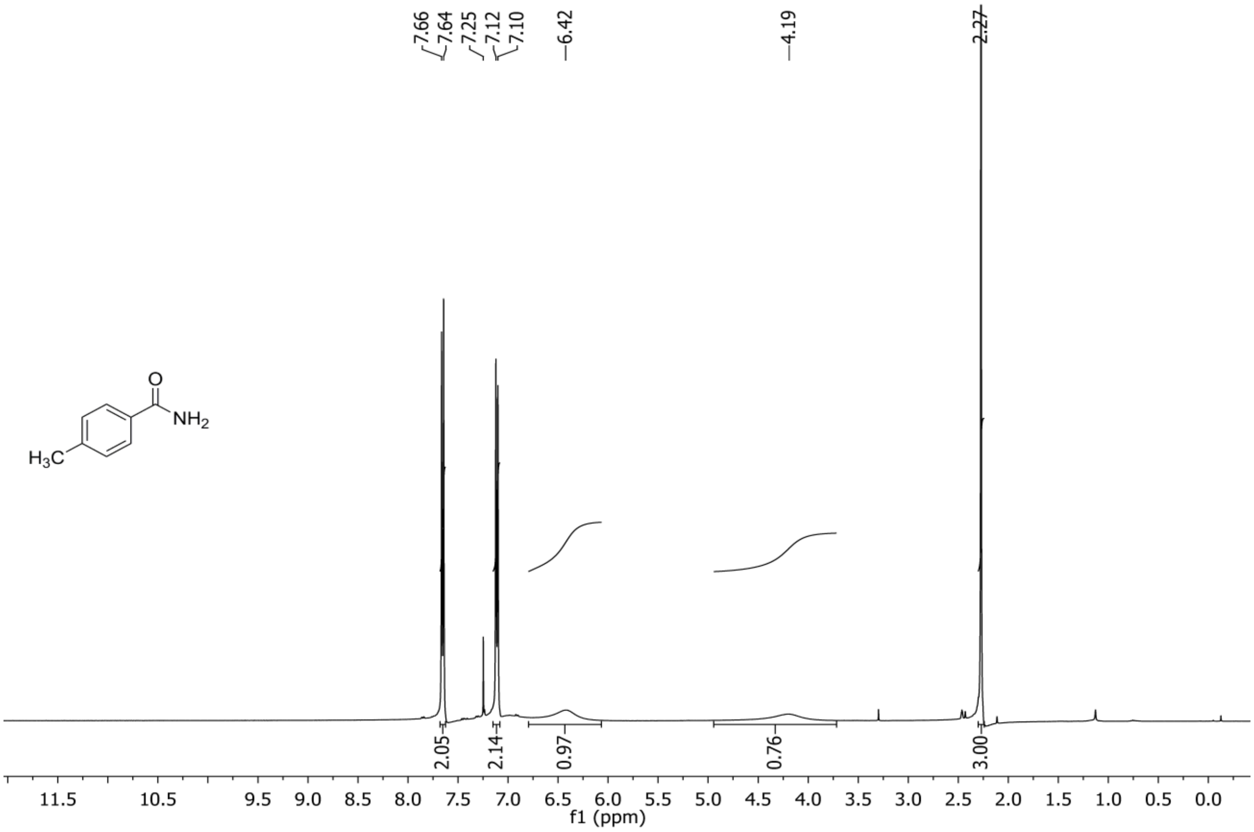
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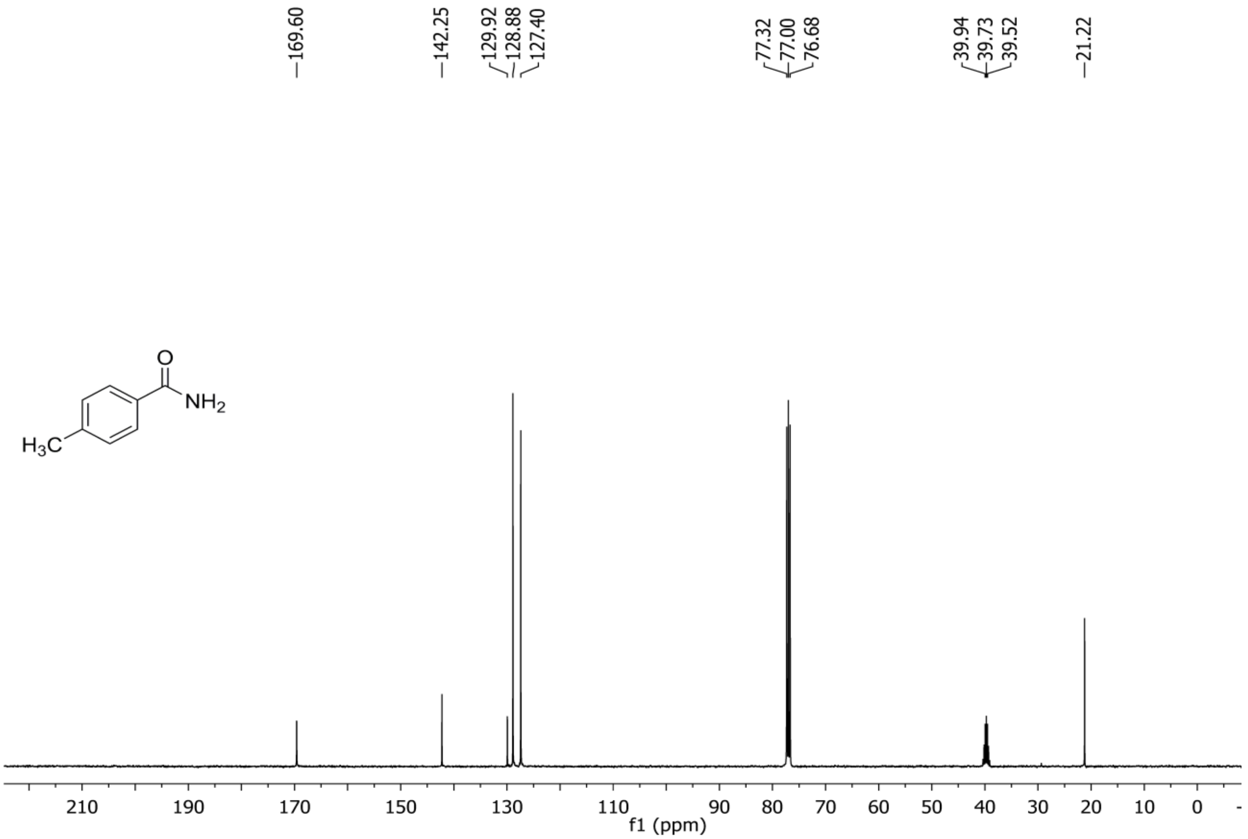
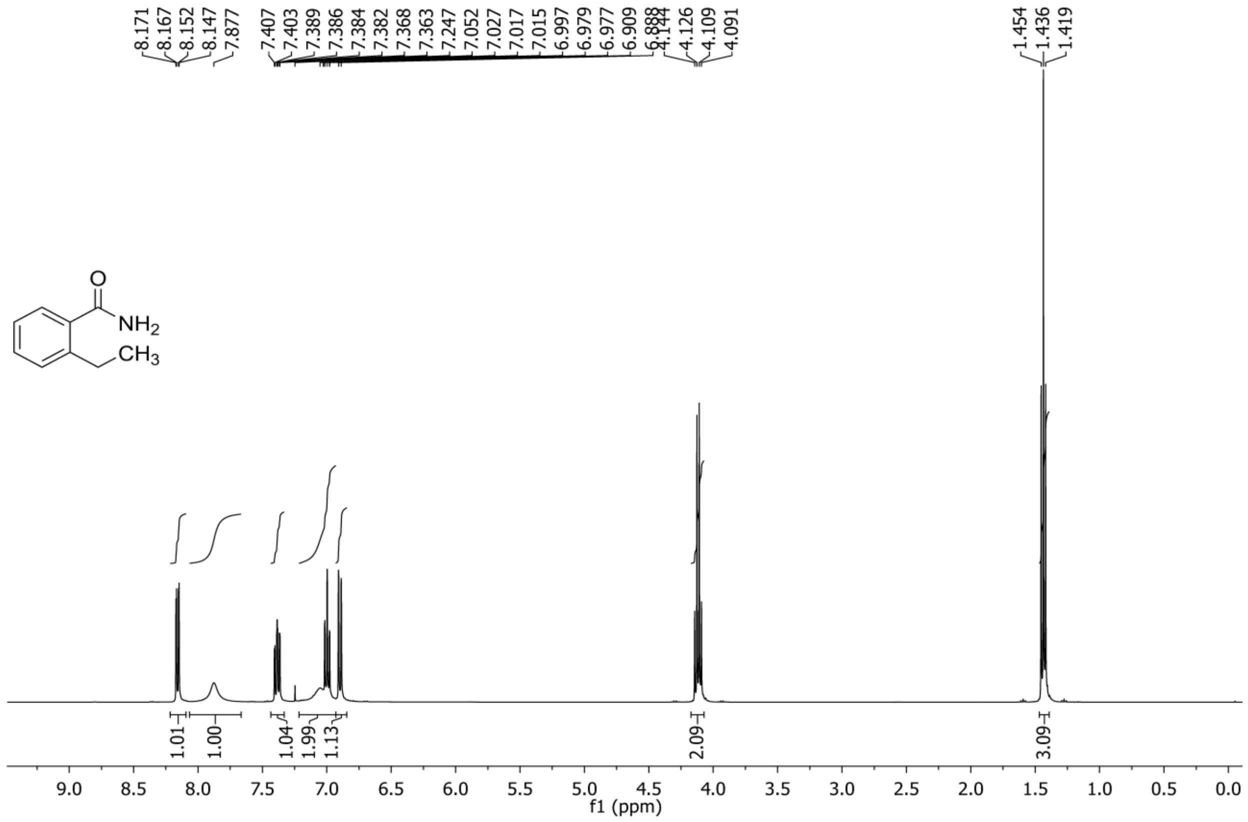
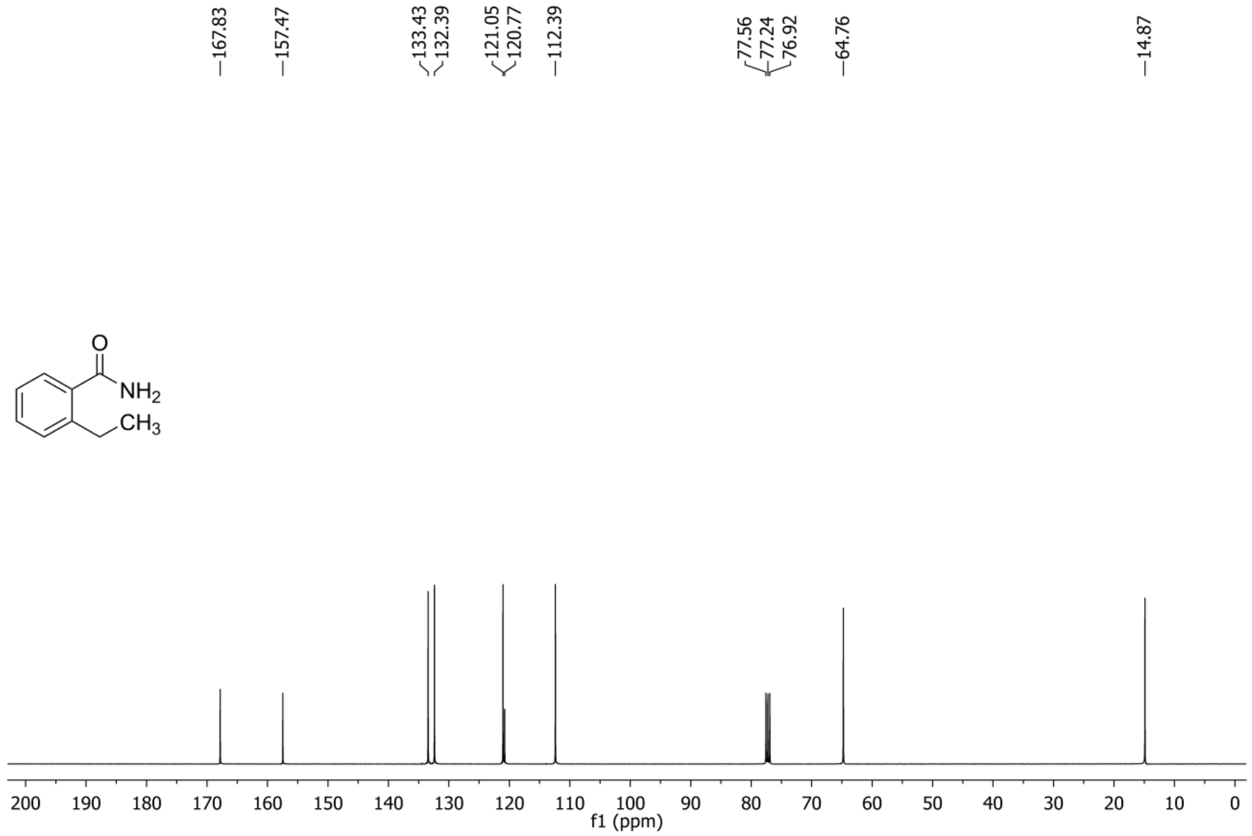
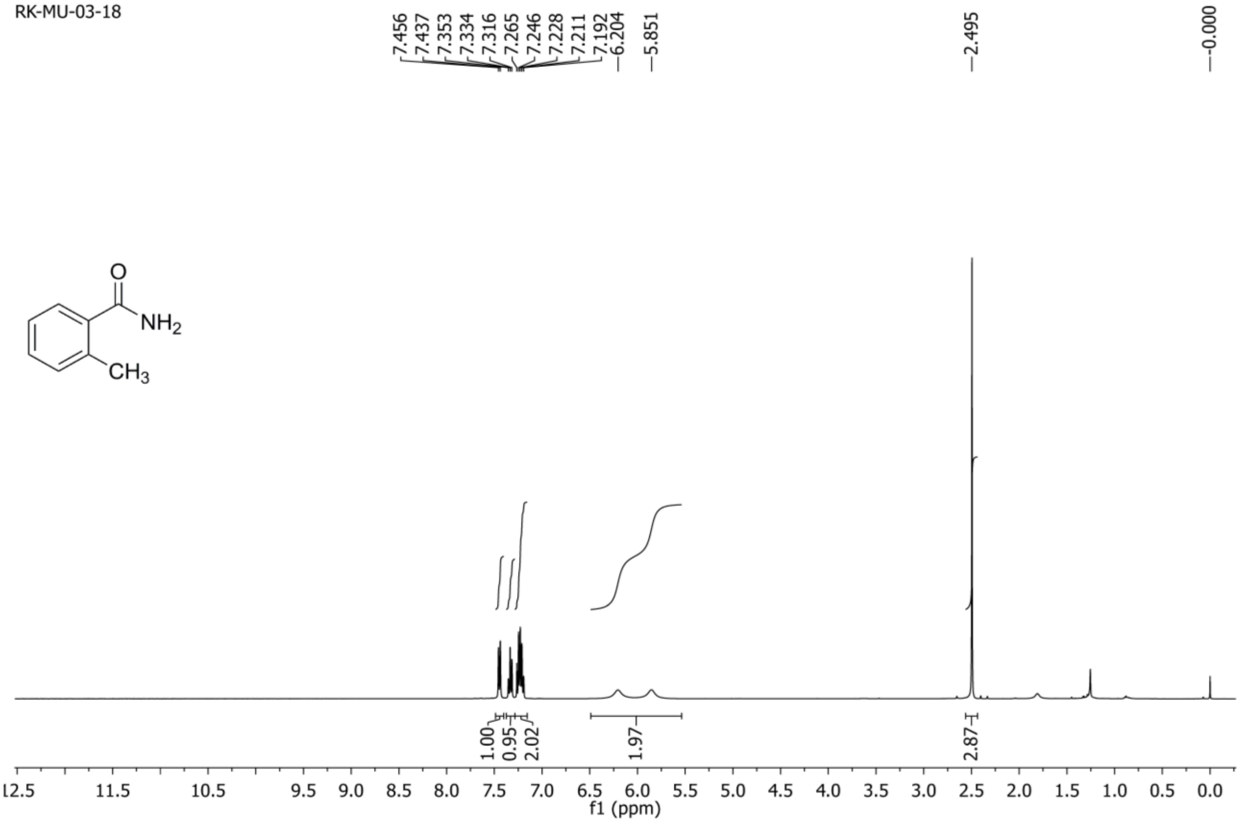
2.14
0.97
0.76
3.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

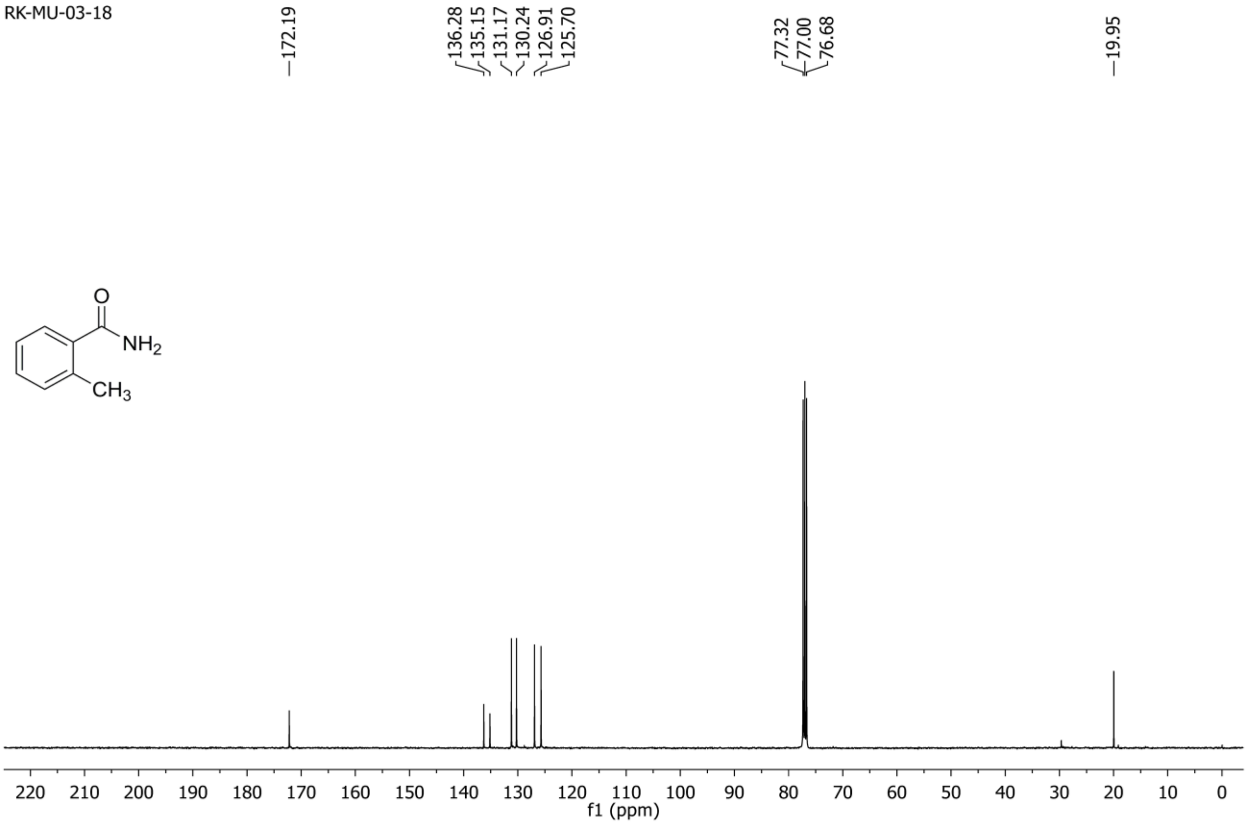

169.60
142.25
129.92
128.88
127.40
77.32
77.00
76.68
39.94
39.73
39.52
21.22
O
NH2
H3C
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.171
8.167
8.152
8.147
7.877
7.407
7.403
7.389
7.386
7.384
7.382
7.368
7.363
7.247
7.052
7.027
7.017
7.015
6.997
6.979
6.977
6.909
6.888
4.144
4.126
4.109
4.091
1.454
1.436
1.419
O
NH2
CH3
1.01
1.00
1.04
1.99
1.13
2.09
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

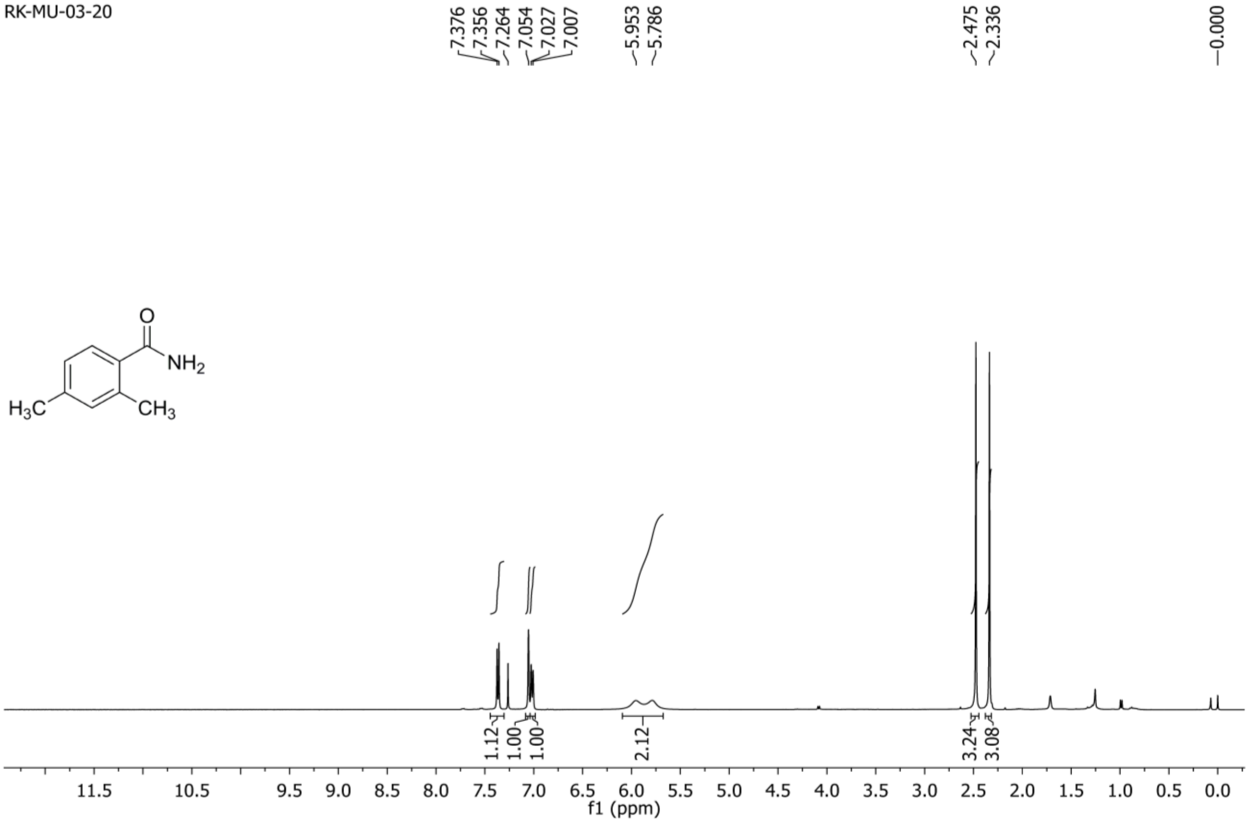

167.83
157.47
133.43
132.39
121.05
120.77
112.39
77.56
77.24
76.92
64.76
14.87
O
NH2
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

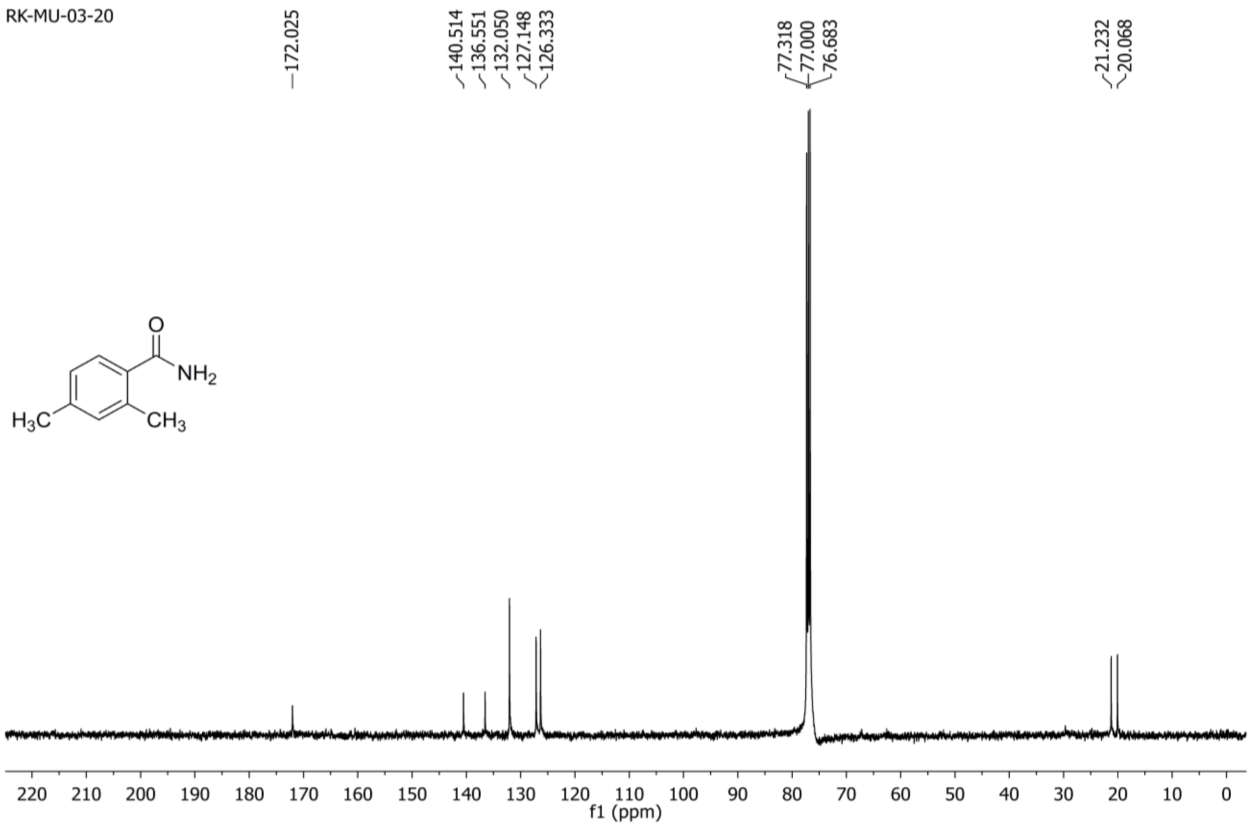

RK-MU-03-18
7.456
7.437
7.353
7.334
7.316
7.265
7.246
7.228
7.211
7.192
6.204
5.851
2.495
0.000
O
NH2
CH3
1.00
0.95
2.02
1.97
2.87
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

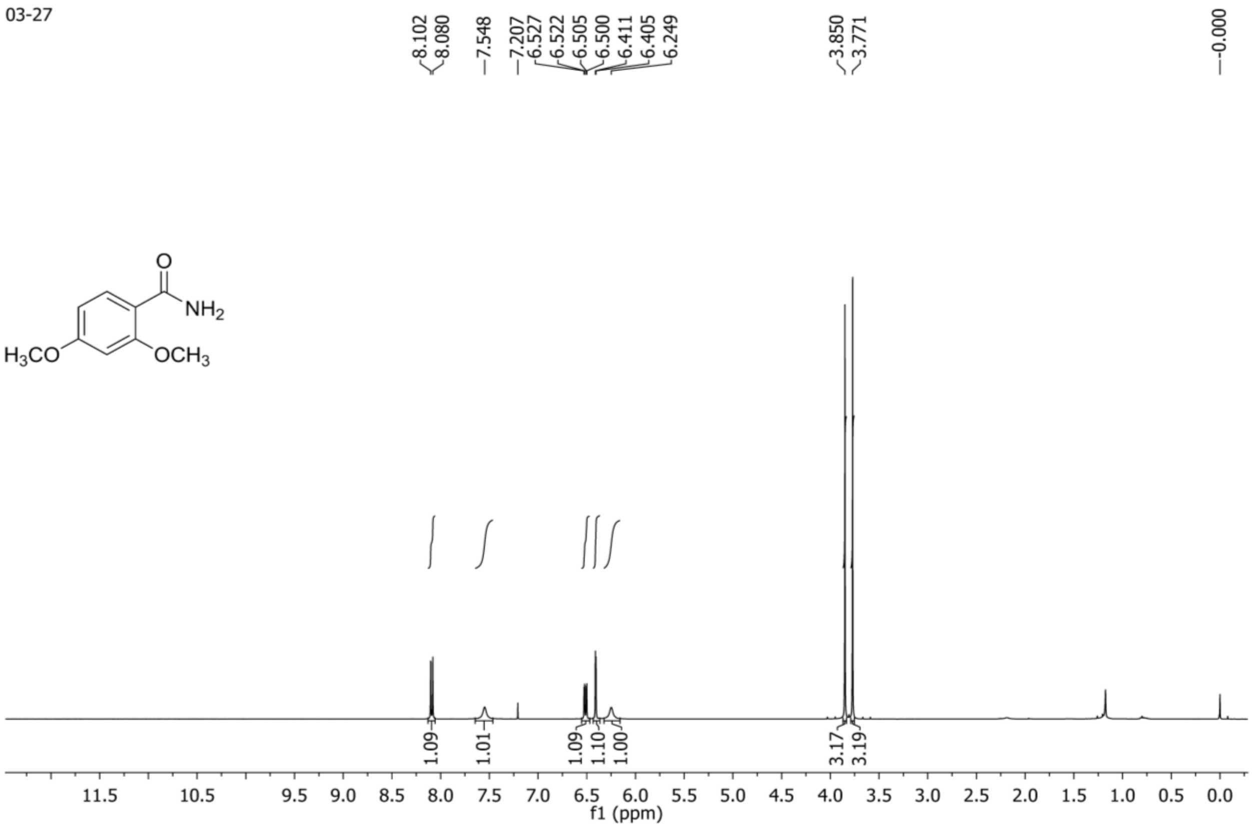
RK-MU-03-18



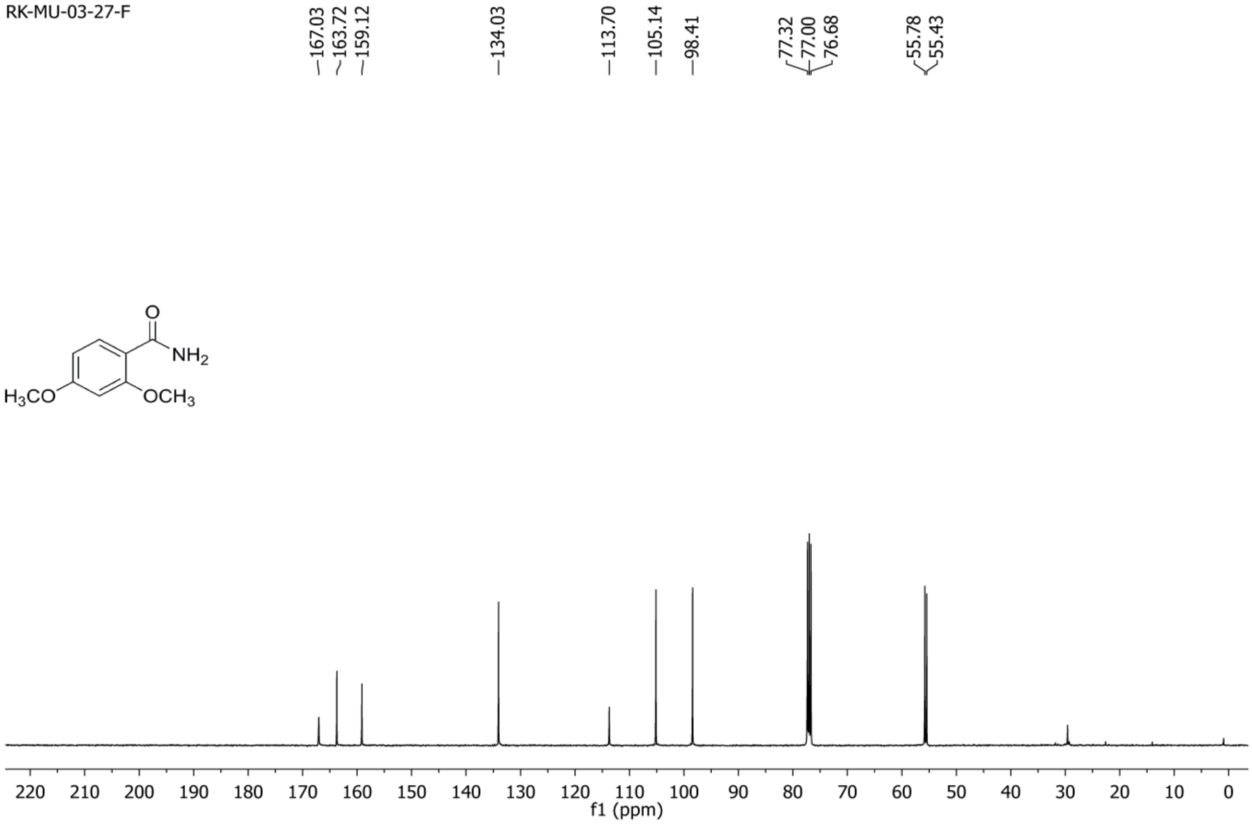
RK-MU-03-20



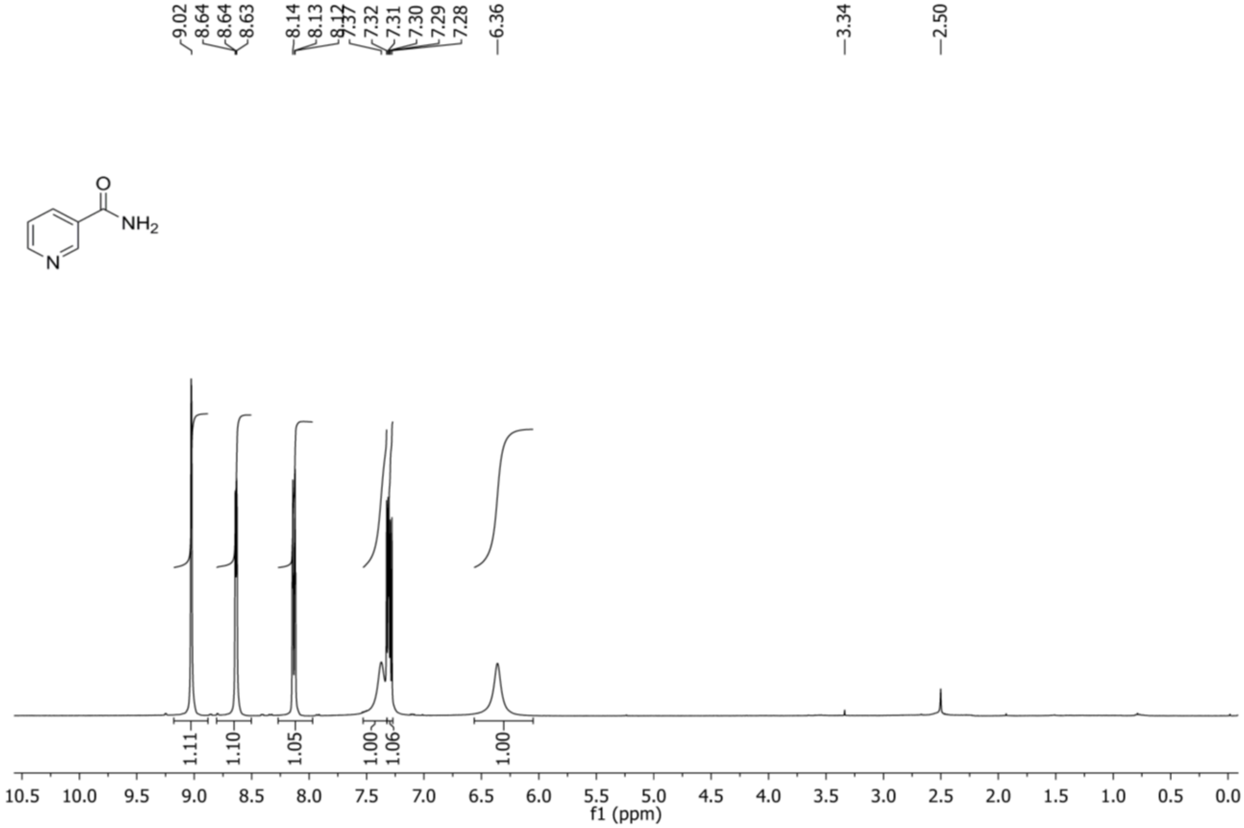

RK-MU-03-20
172.025
140.514
136.551
132.050
127.148
126.333
77.318
77.000
76.683
21.232
20.068
O
NH2
H3C
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


03-27
8.102
8.080
7.548
7.207
6.527
6.522
6.505
6.500
6.411
6.405
6.249
3.850
3.771
0.000
O
NH2
H3CO
OCH3
1.09
1.01
1.09
1.10
1.00
3.17
3.19
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

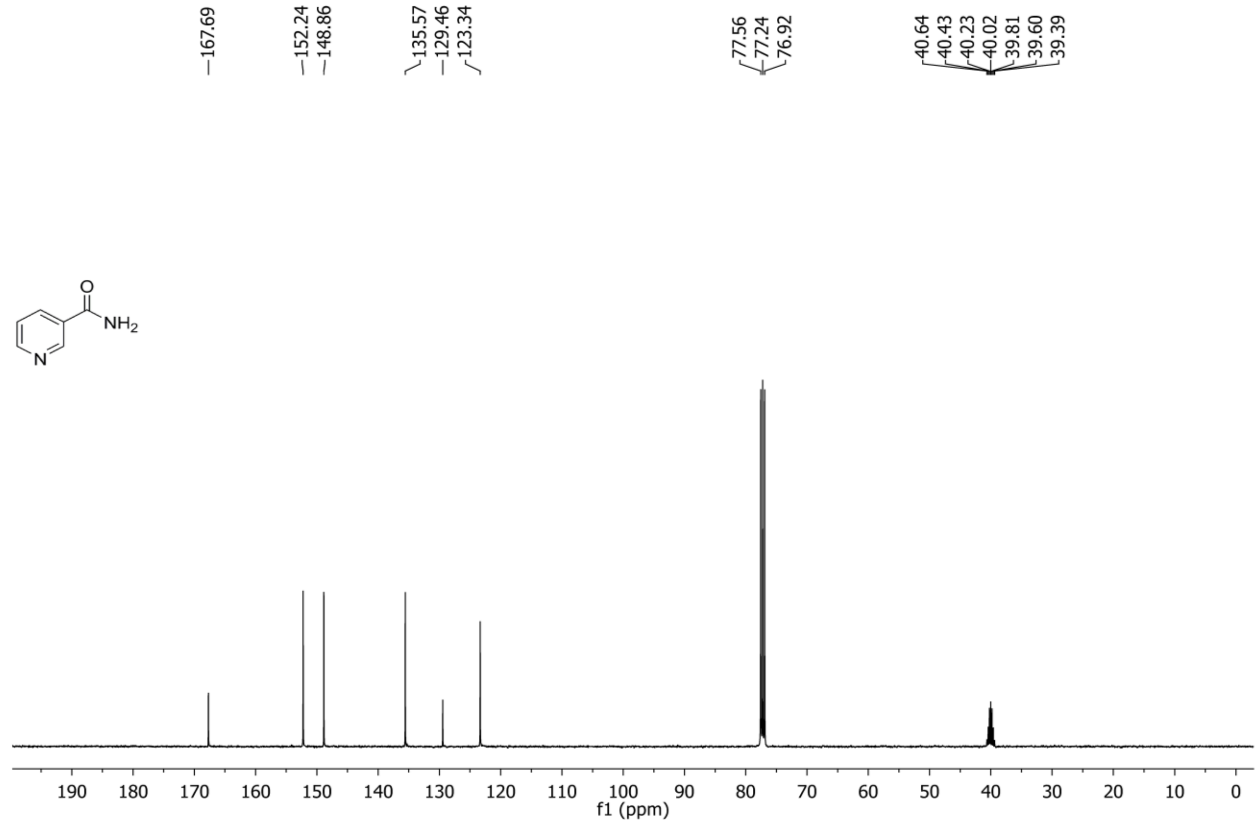
RK-MU-03-27-F



167.03
163.72
159.12
134.03
113.70
105.14
98.41
77.32
77.00
76.68
55.78
55.43
O
NH2
H3CO
OCH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



9.02
8.64
8.64
8.63
8.14
8.13
8.12
7.37
7.32
7.31
7.30
7.29
7.28
6.36
3.34
2.50
O
NH2
N
1.11
1.10
1.05
1.00
1.06
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



167.69
152.24
148.86
135.57
129.46
123.34
77.56
77.24
76.92
40.64
40.43
40.23
40.02
39.81
39.60
39.39
O
NH2
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

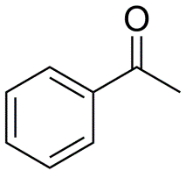
Chapter 3

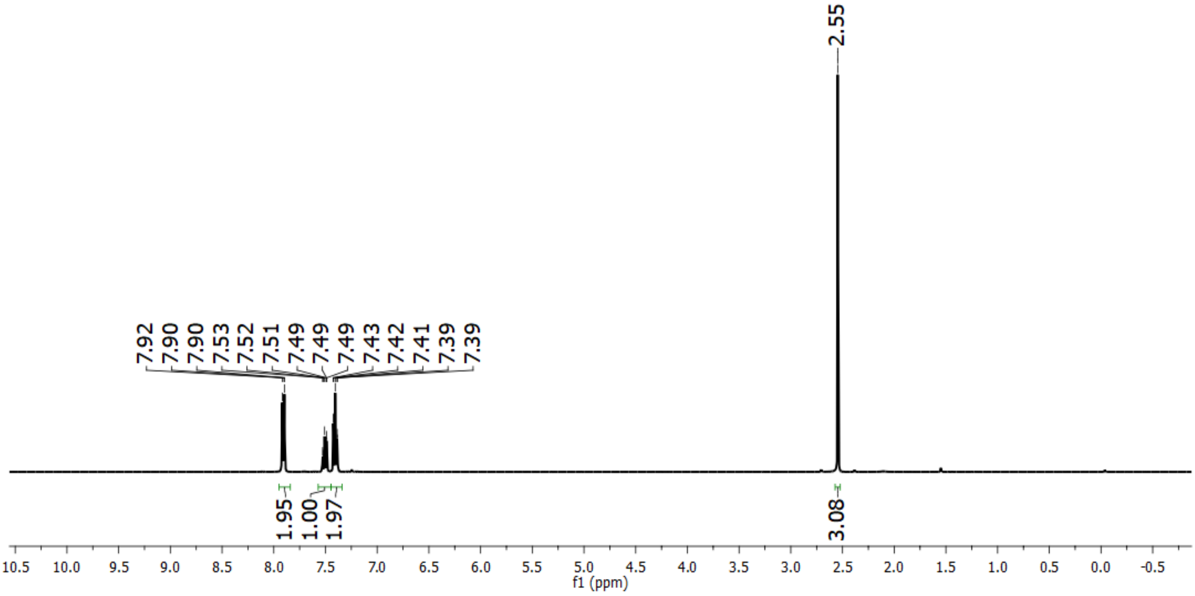
A Water Soluble Rh(I) Catalyst for Photochemically Induced Hydration of Alkynes

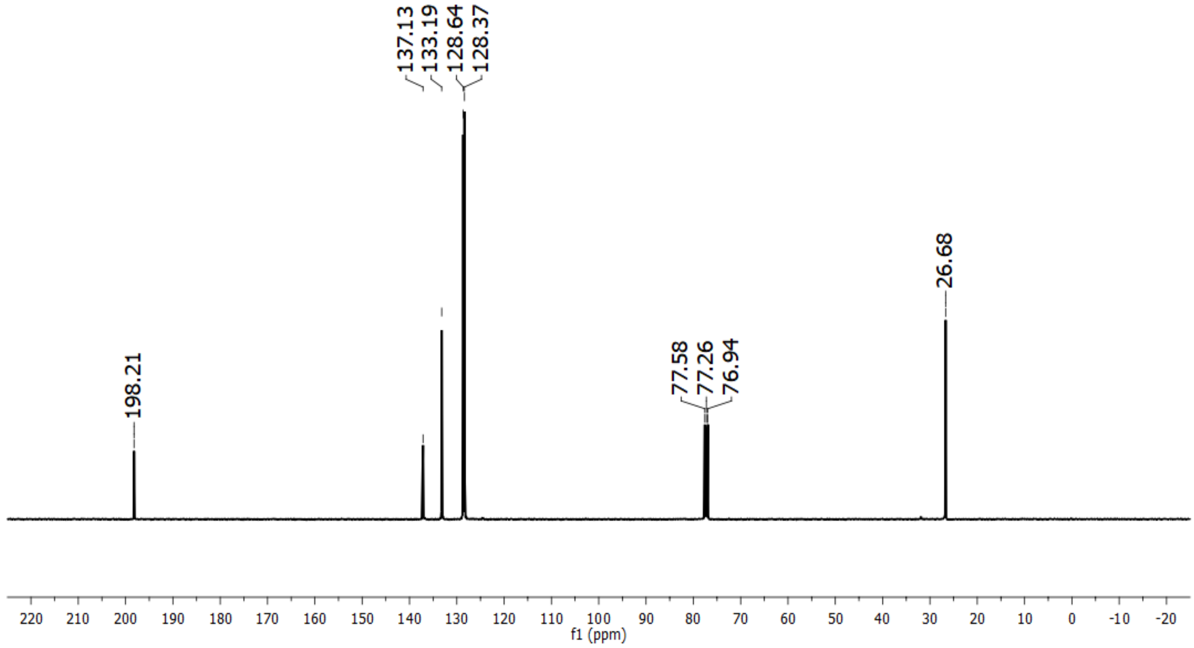
Supporting Information

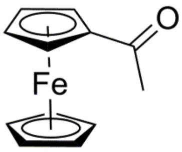
Photochemical reactor vessel (Capacity 100 mL)

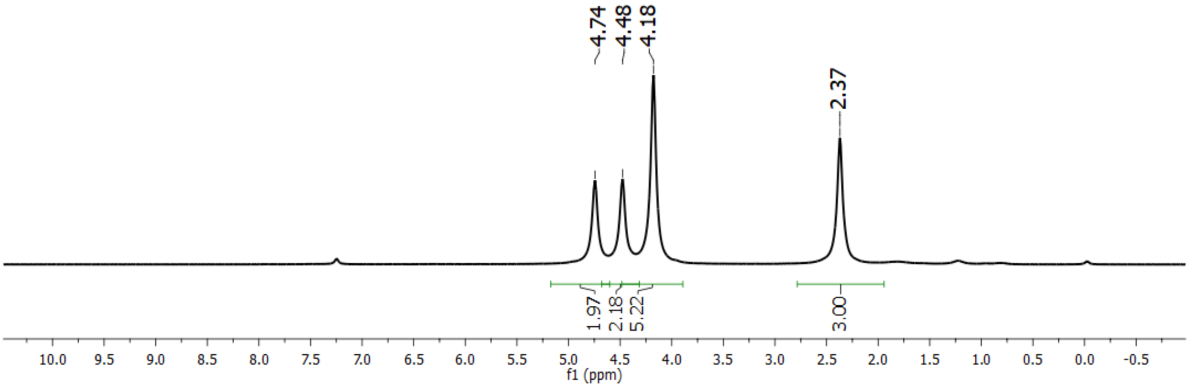
^{1}H and ^{13}C NMR Spectra of Compounds

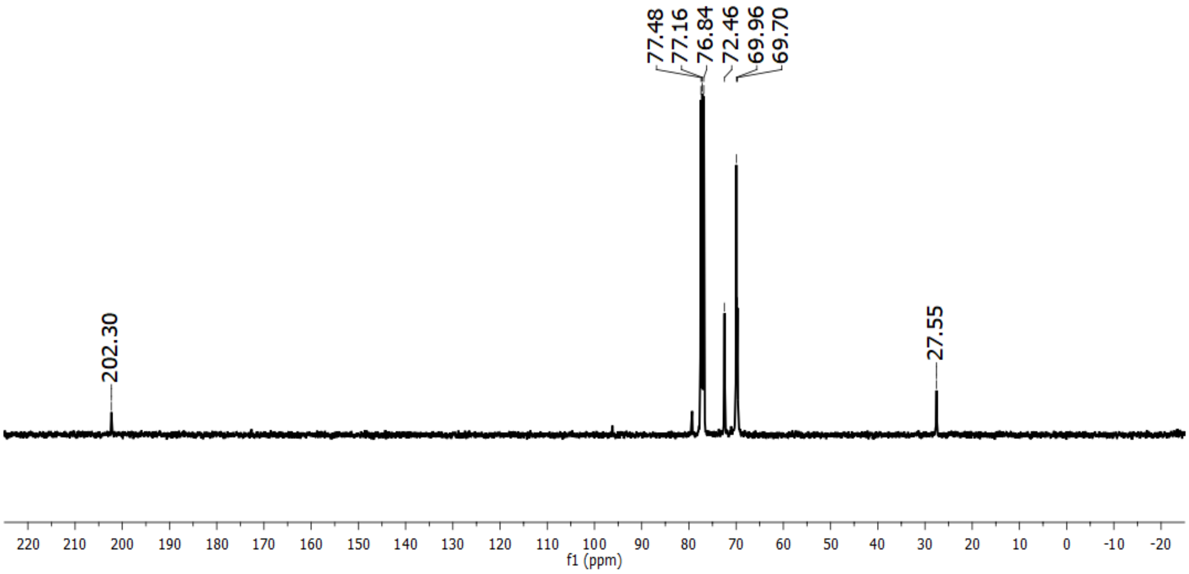

O

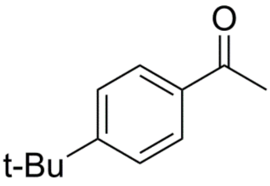

2.55
7.92
7.90
7.90
7.53
7.52
7.51
7.49
7.49
7.49
7.43
7.42
7.41
7.39
7.39
1.95
1.00
1.97
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

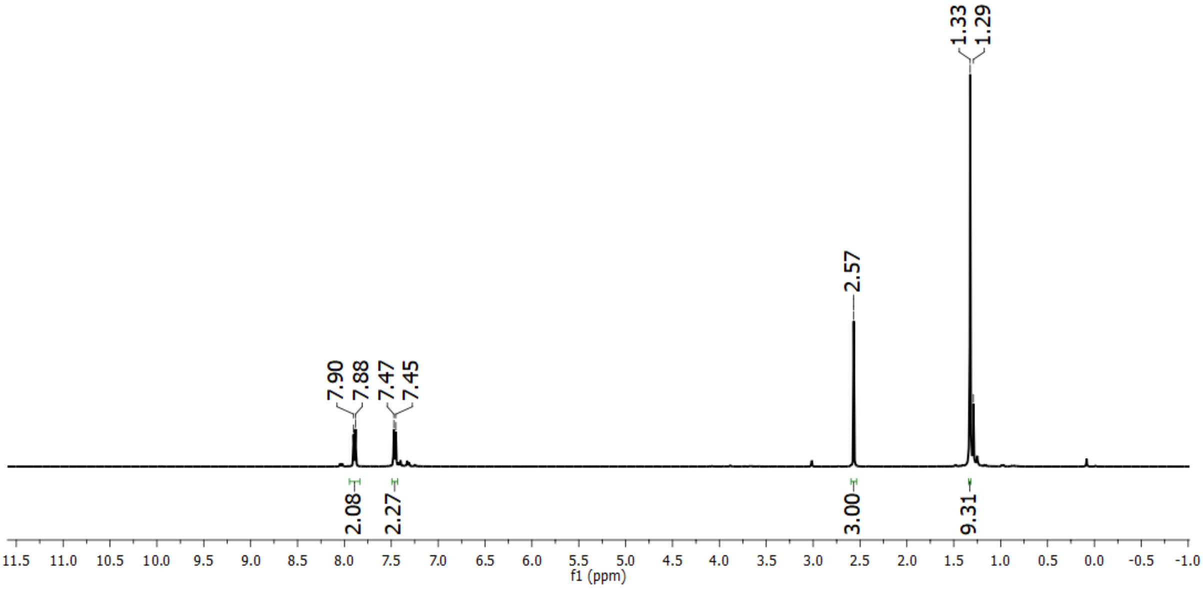

137.13
133.19
128.64
128.37
26.68
198.21
77.58
77.26
76.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

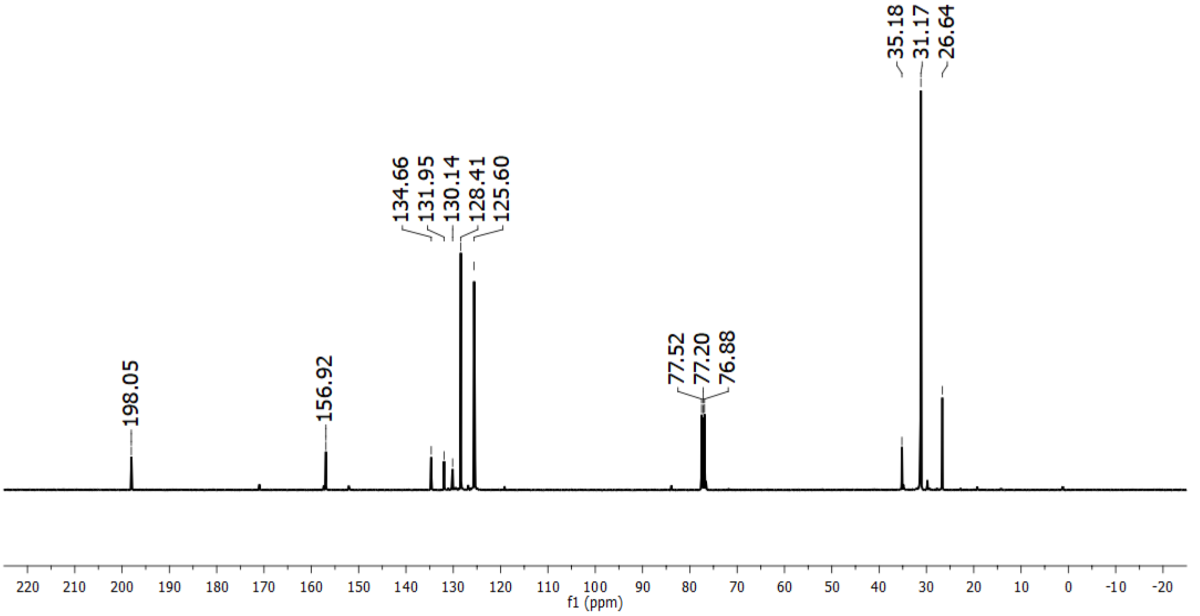

O
Fe

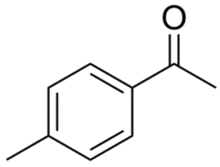

4.74
4.48
4.18
2.37
1.97
2.18
5.22
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

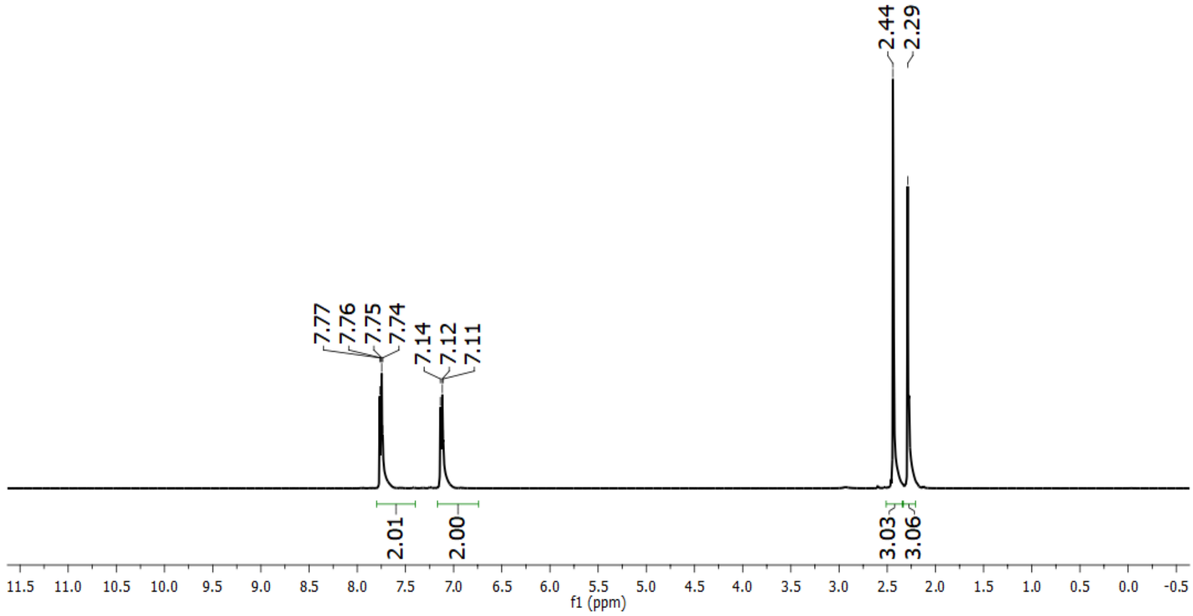

77.48
77.16
76.84
72.46
69.96
69.70
202.30
27.55
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


O
t-Bu


7.90
7.88
7.47
7.45
2.57
1.33
1.29
2.08
2.27
3.00
9.31
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


198.05
156.92
134.66
131.95
130.14
128.41
125.60
77.52
77.20
76.88
35.18
31.17
26.64
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O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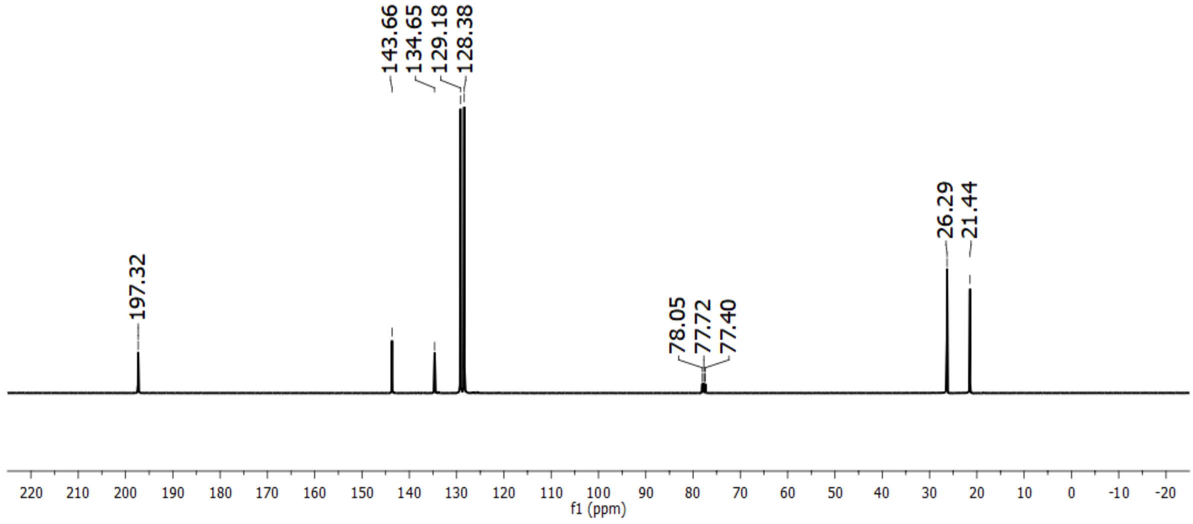
7.76
7.75
7.74
7.14
7.12
7.11
2.44
2.29
2.01
2.00
3.03
3.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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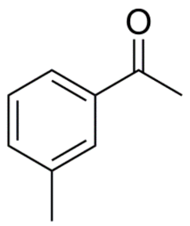
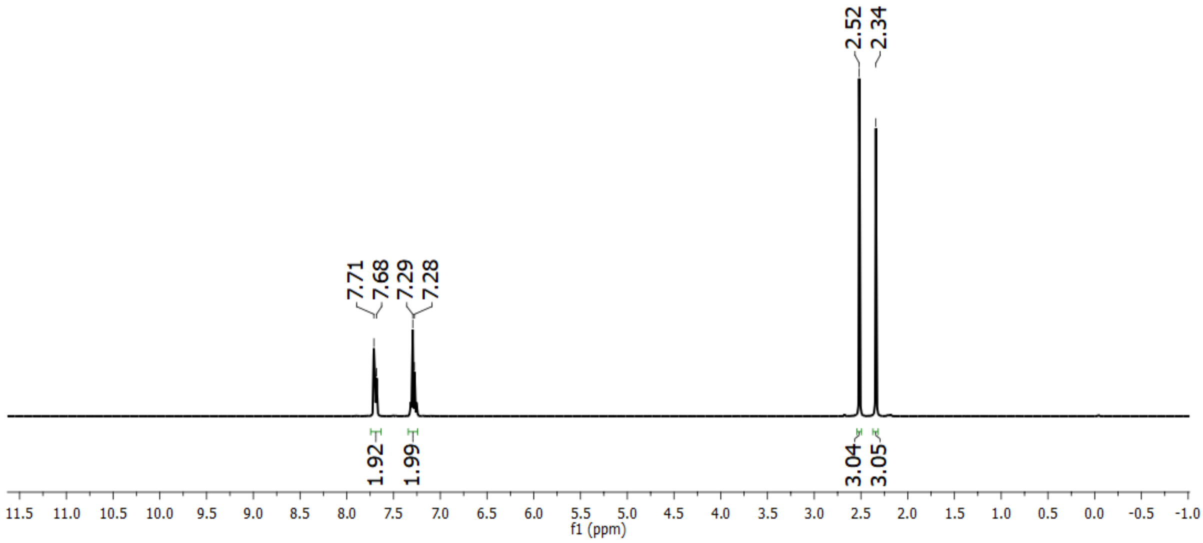
143.66
134.65
129.18
128.38
78.05
77.72
77.40
26.29
21.44
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

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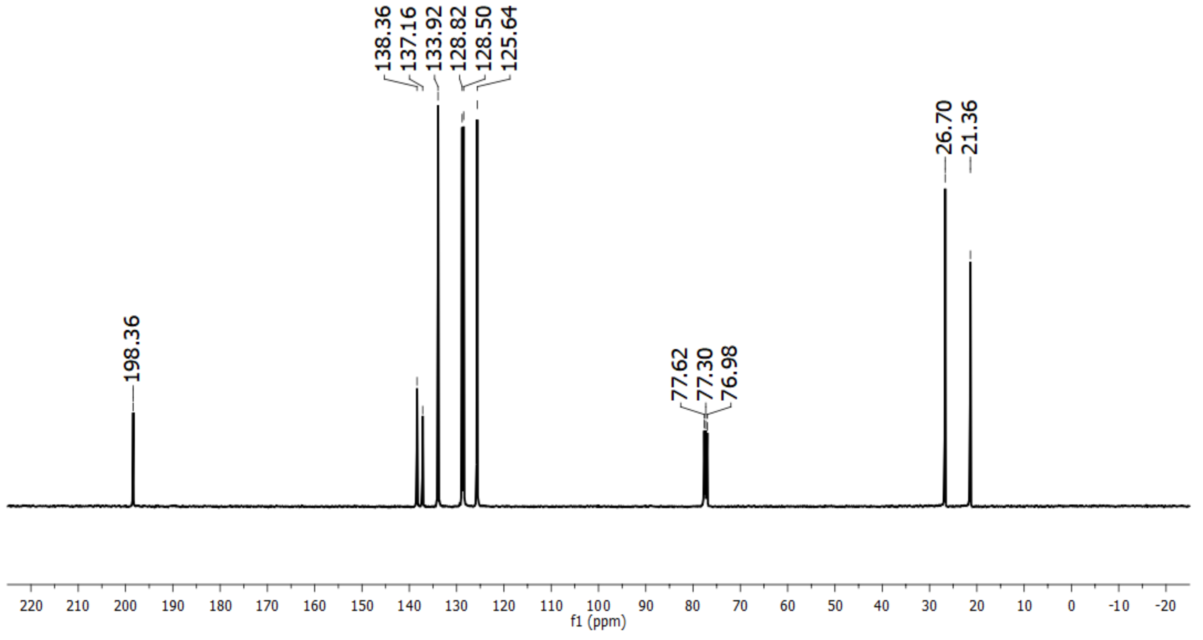
7.29
7.28
2.52
2.34
1.92
1.99
3.04
3.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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133.92
128.82
128.50
125.64
77.62
77.30
76.98
26.70
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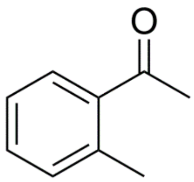
f1 (ppm)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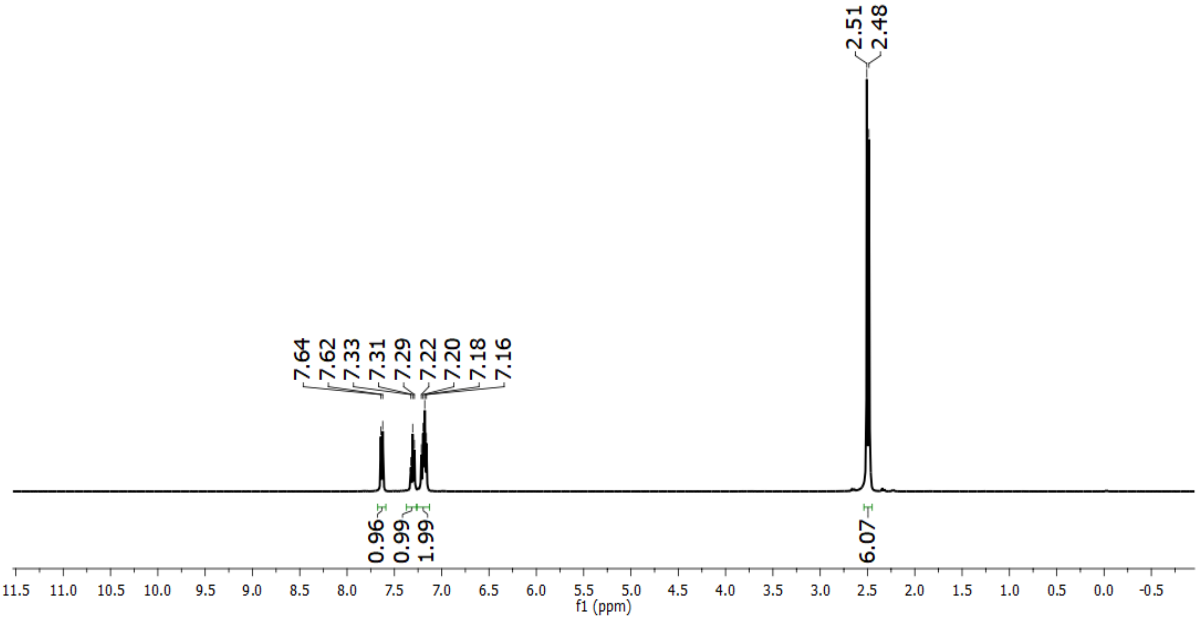
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7.33
7.31
7.29
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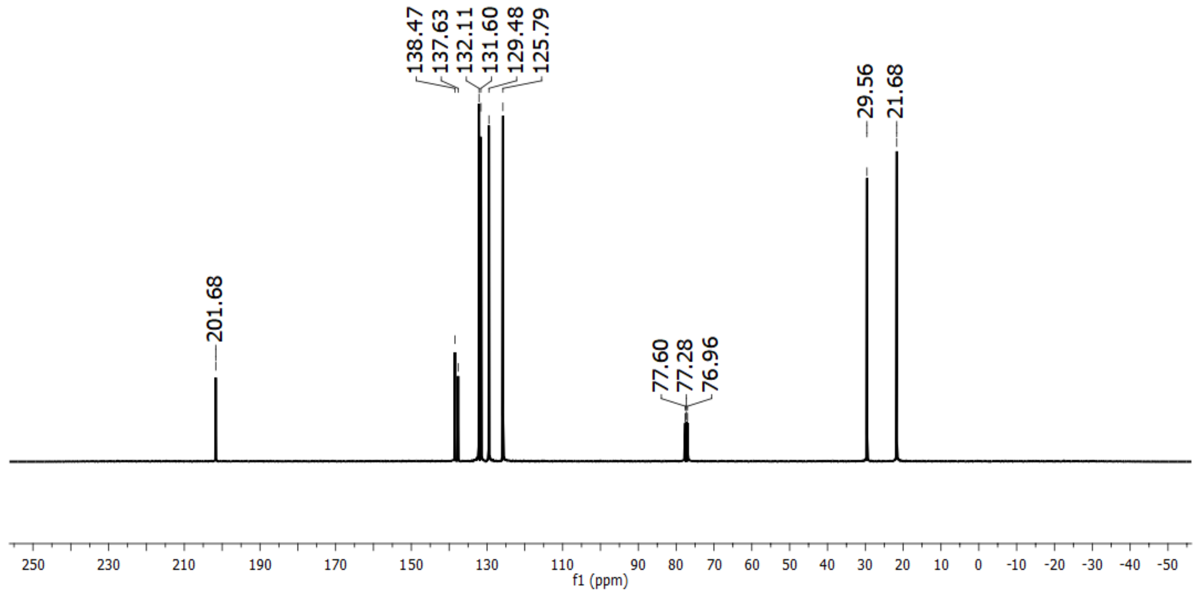
7.20
7.18
7.16
2.51
2.48
0.96
0.99
1.99
6.07
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


201.68
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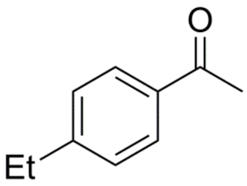
137.63
132.11
131.60
129.48
125.79
77.60
77.28
76.96
29.56
21.68
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)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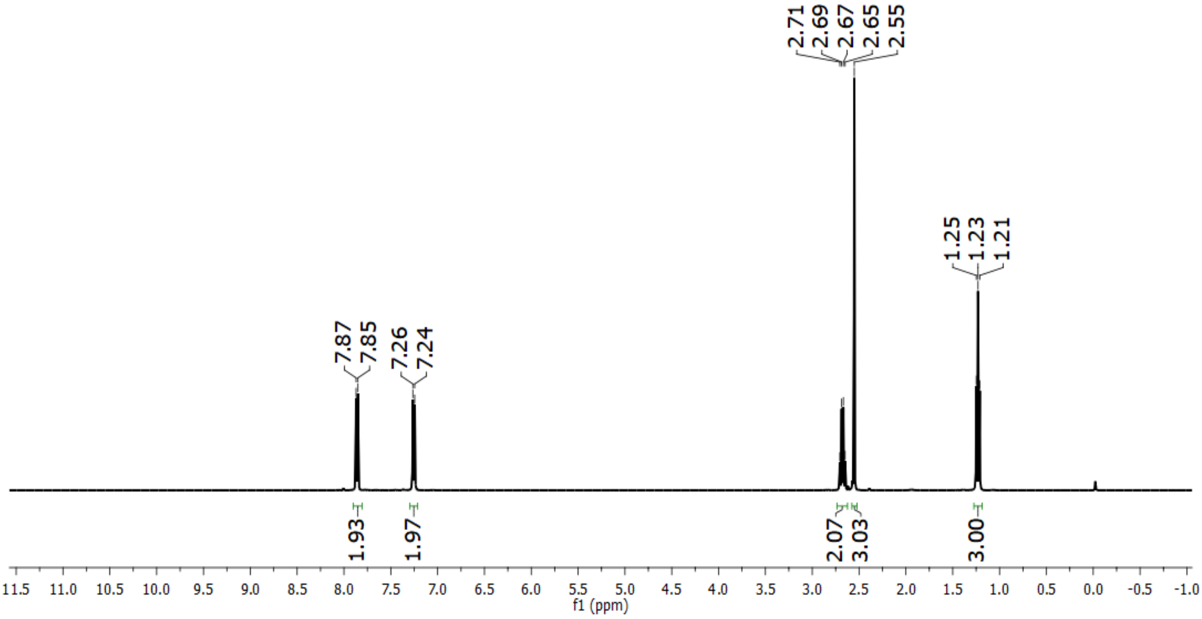
Et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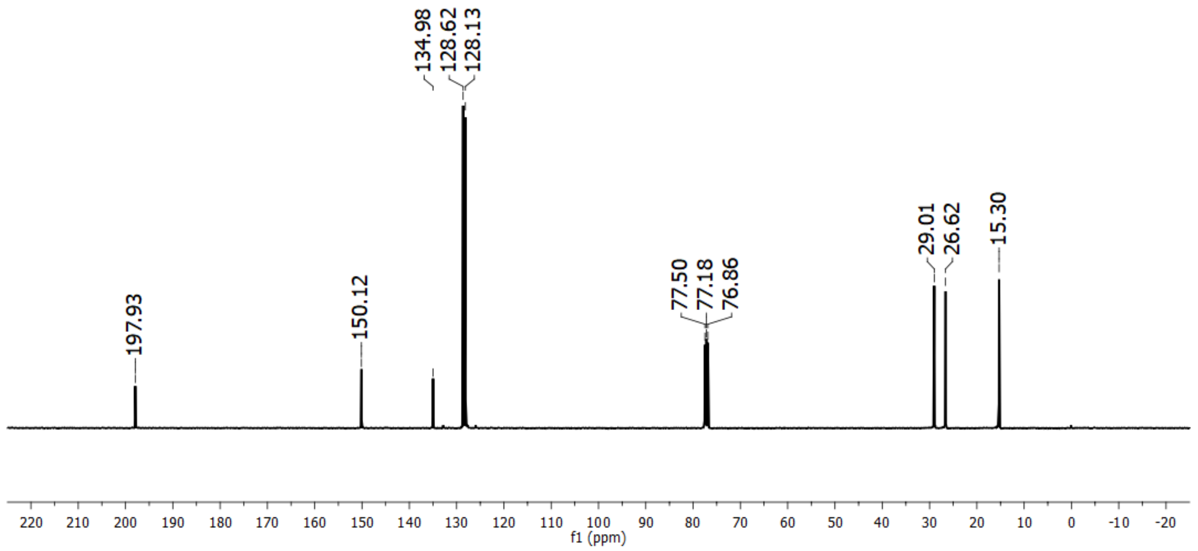
2.67
2.65
2.55
1.25
1.23
1.21
1.93
1.97
2.07
3.03
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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150.12
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128.62
128.13
77.50
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76.86
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26.62
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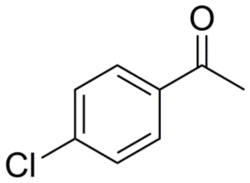
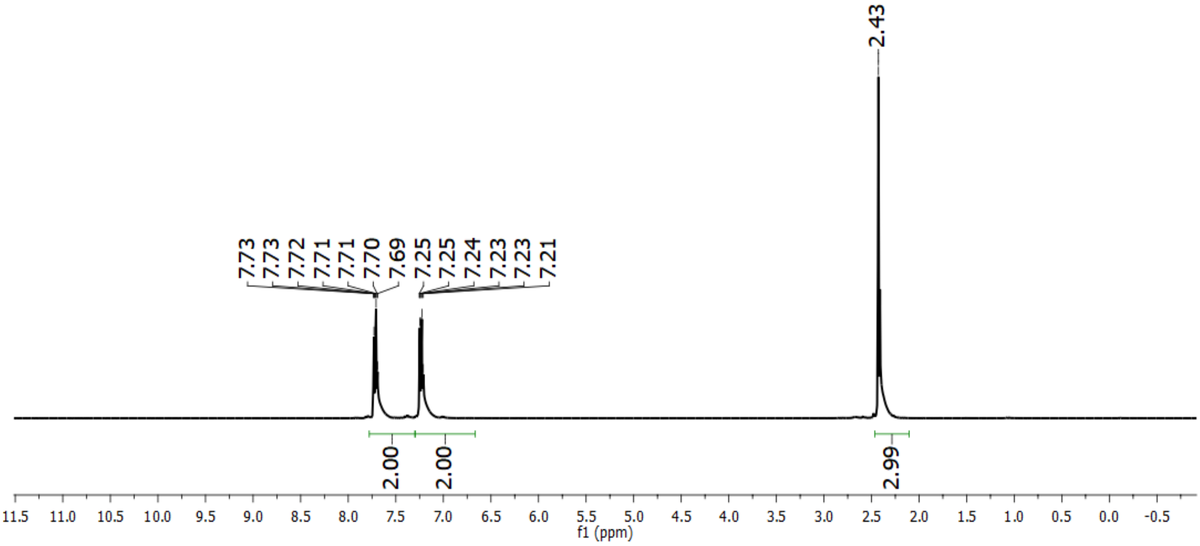
f1 (ppm)


O
Cl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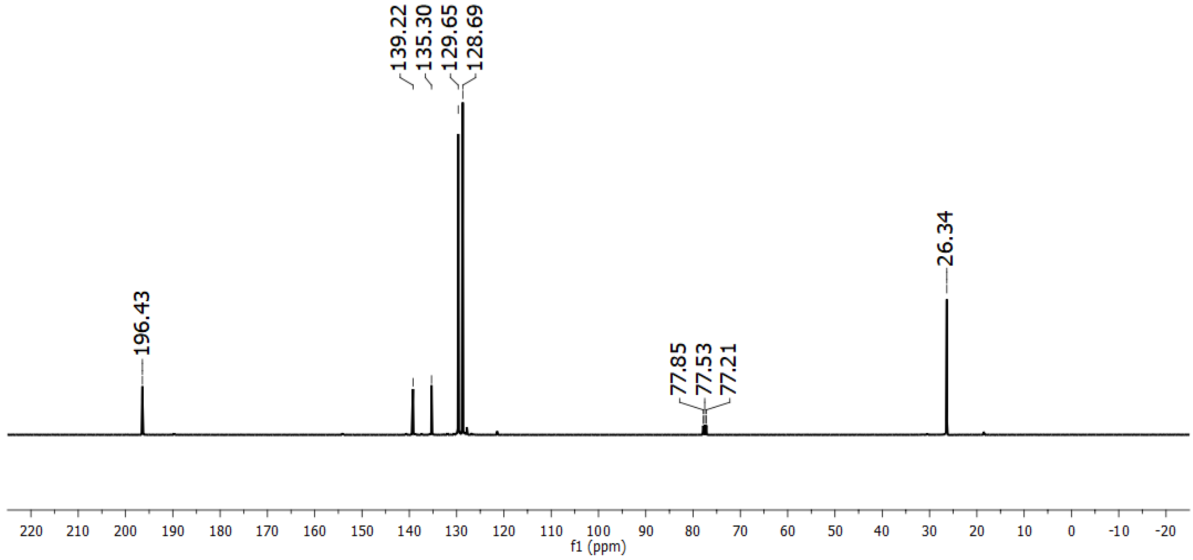
7.24
7.23
7.23
7.21
2.43
2.00
2.00
2.99
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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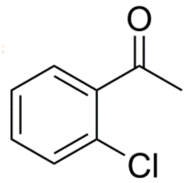
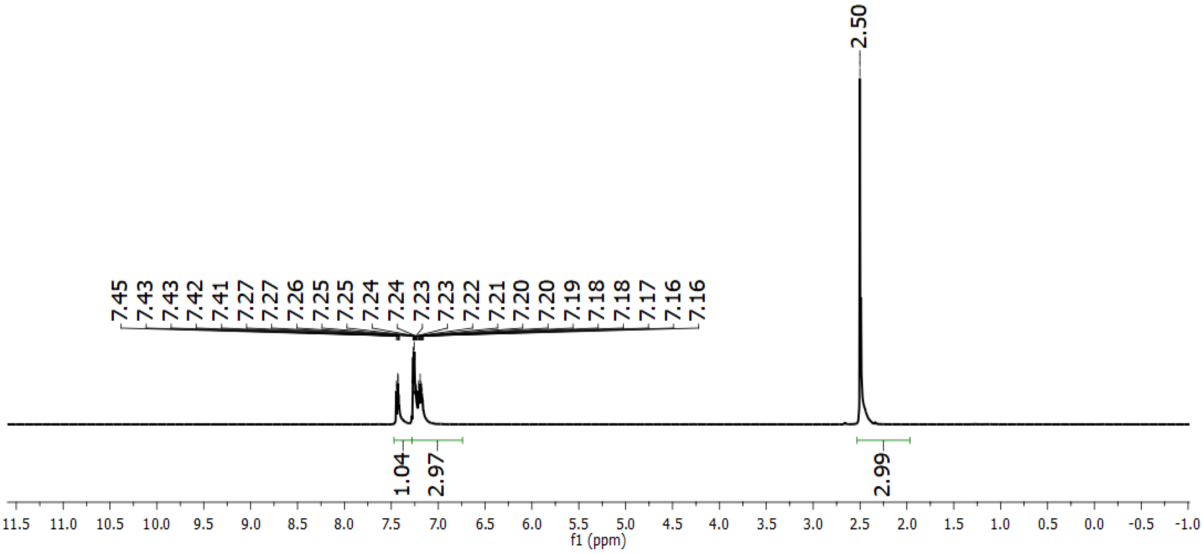
77.21
26.34
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
Cl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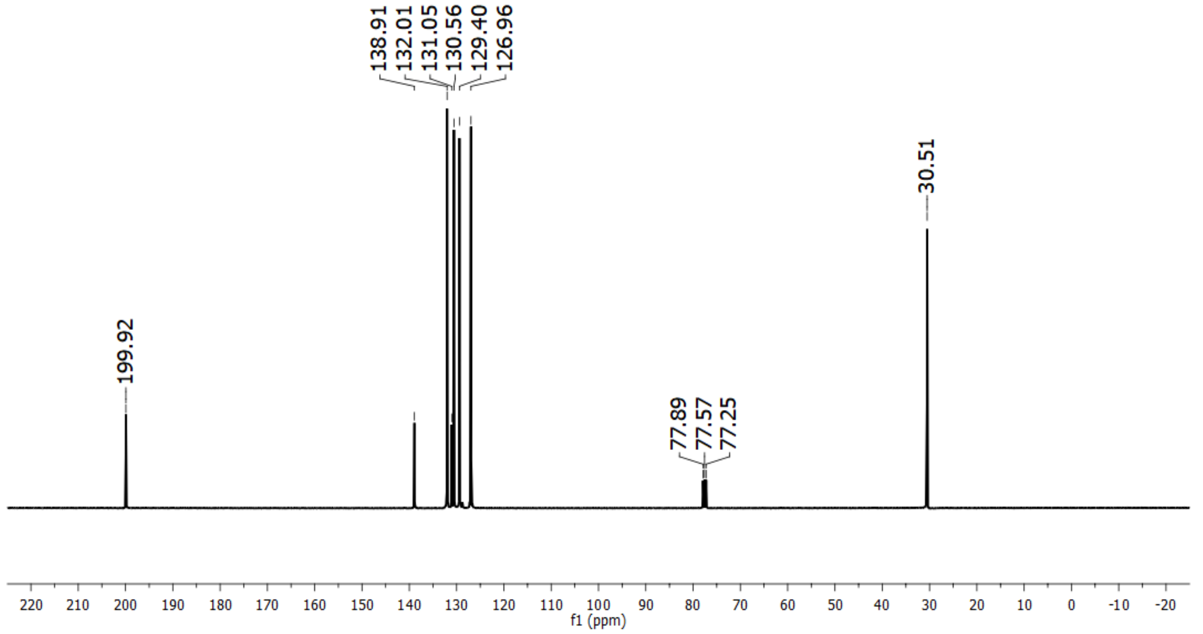
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.16
2.50
1.04
2.97
2.99
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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131.05
130.56
129.40
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77.89
77.57
77.25
30.51
220
210
200
190
180
170
160
150
140
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110
100
90
80
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60
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-20
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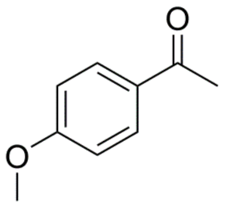
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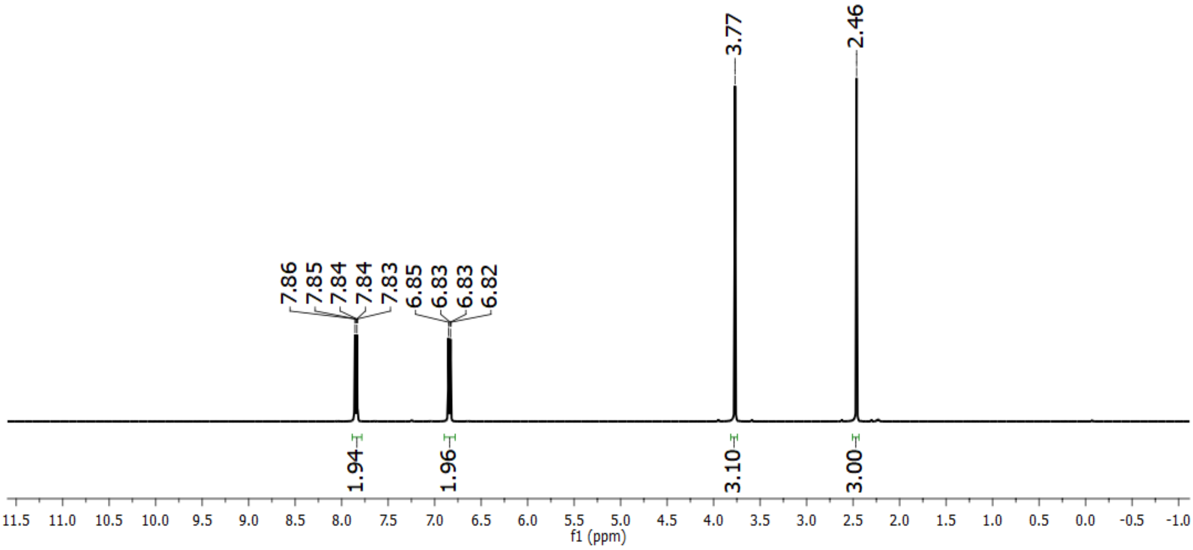
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1.96
3.10
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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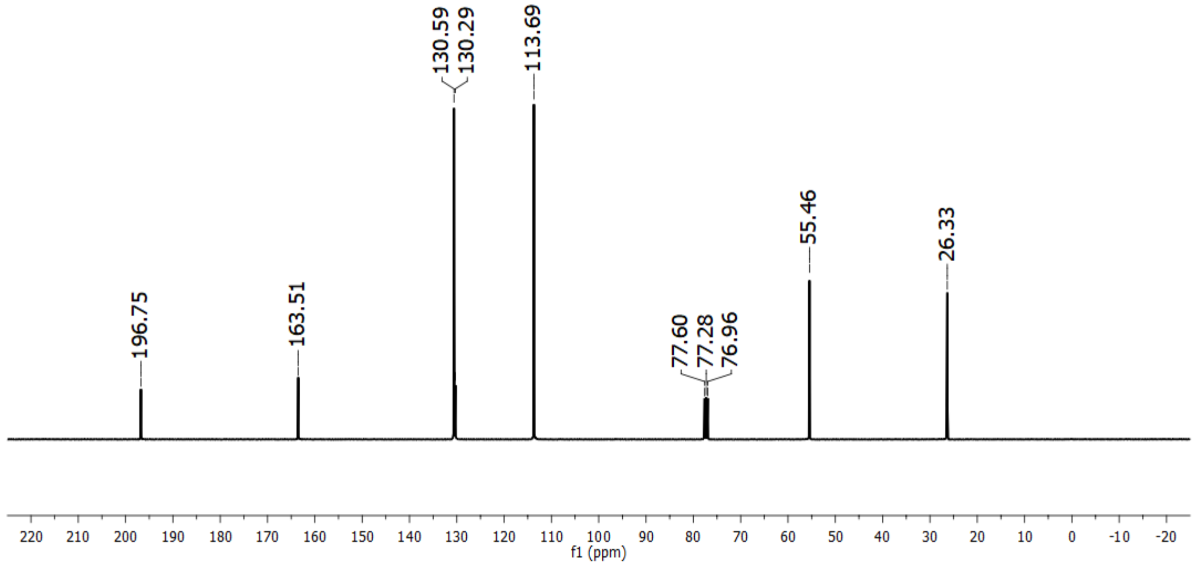
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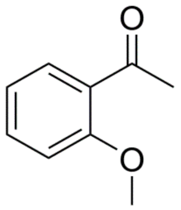
f1 (ppm)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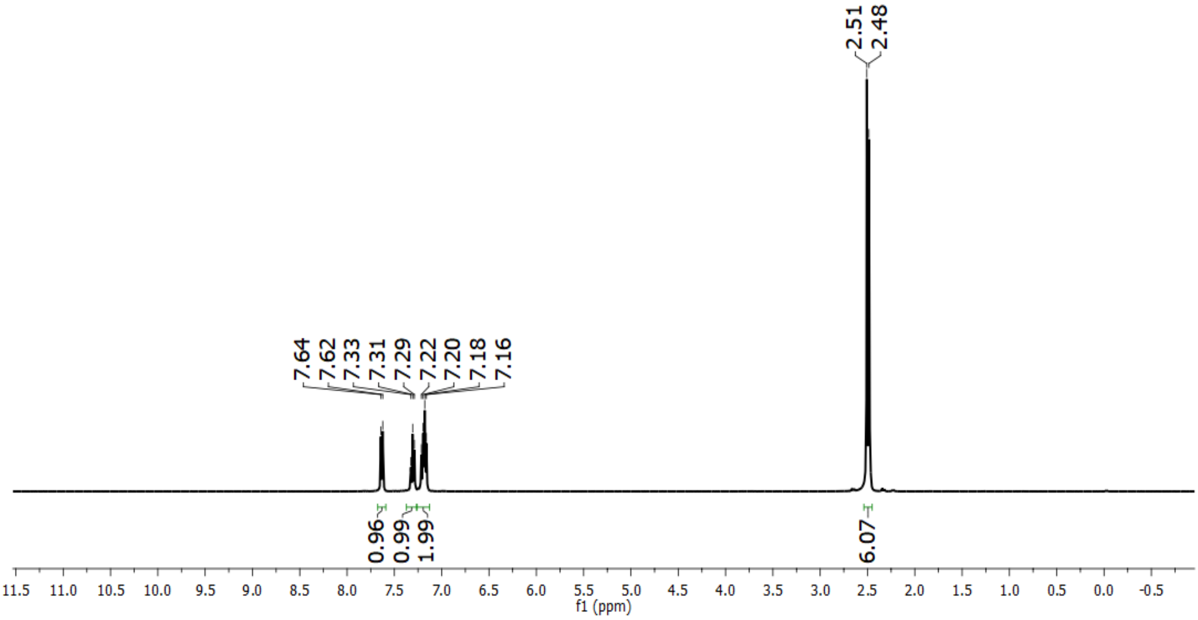
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7.22
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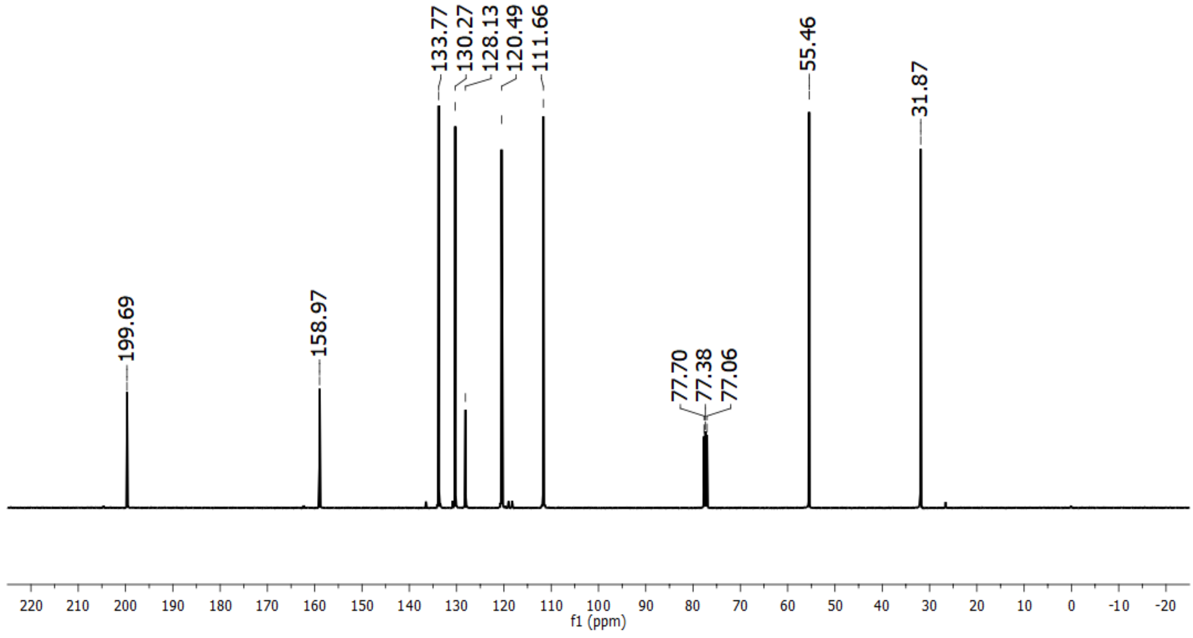
0.99
1.99
6.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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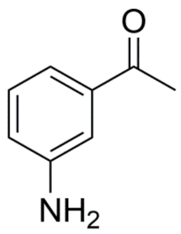
f1 (ppm)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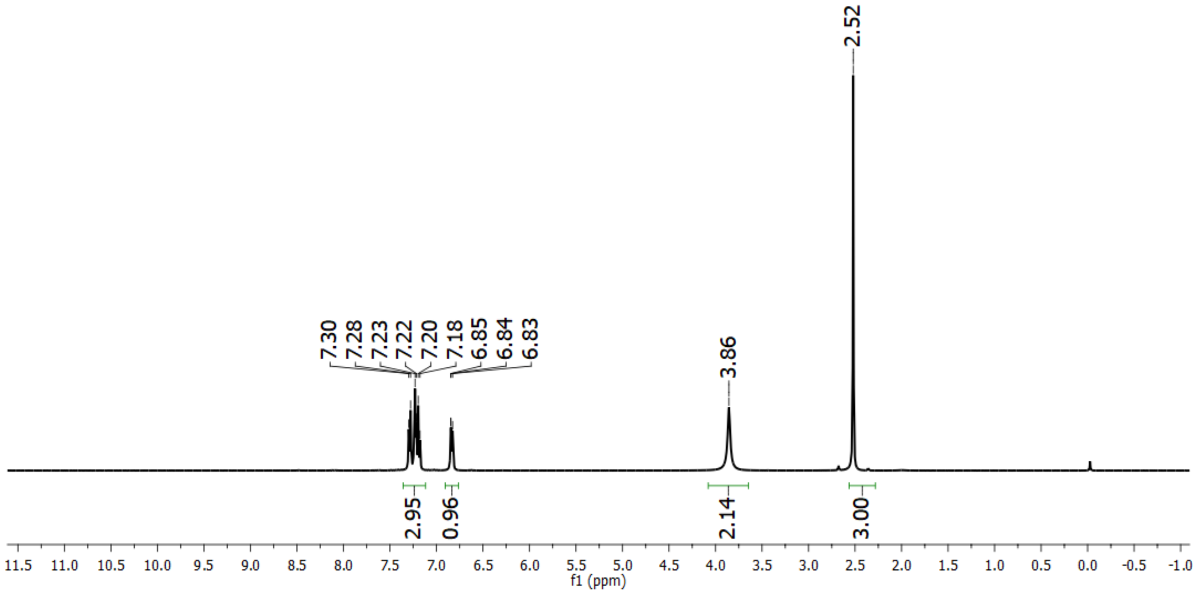
NH2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2.14
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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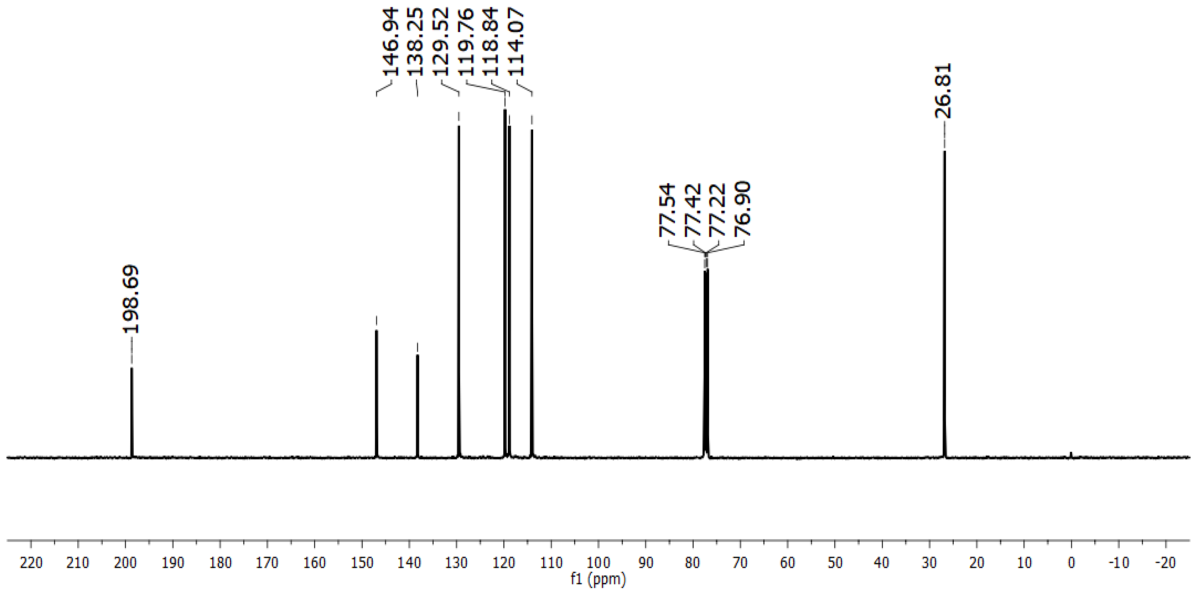
f1 (ppm)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200
190
180
170
160
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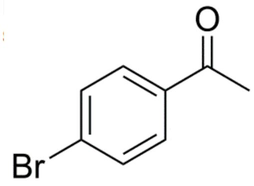
-20
f1 (ppm)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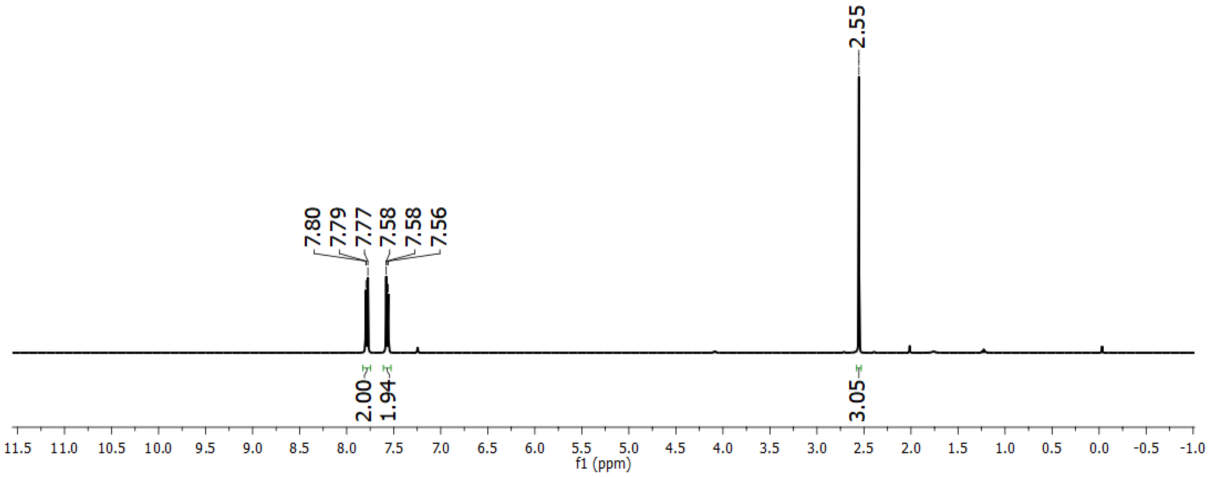
Br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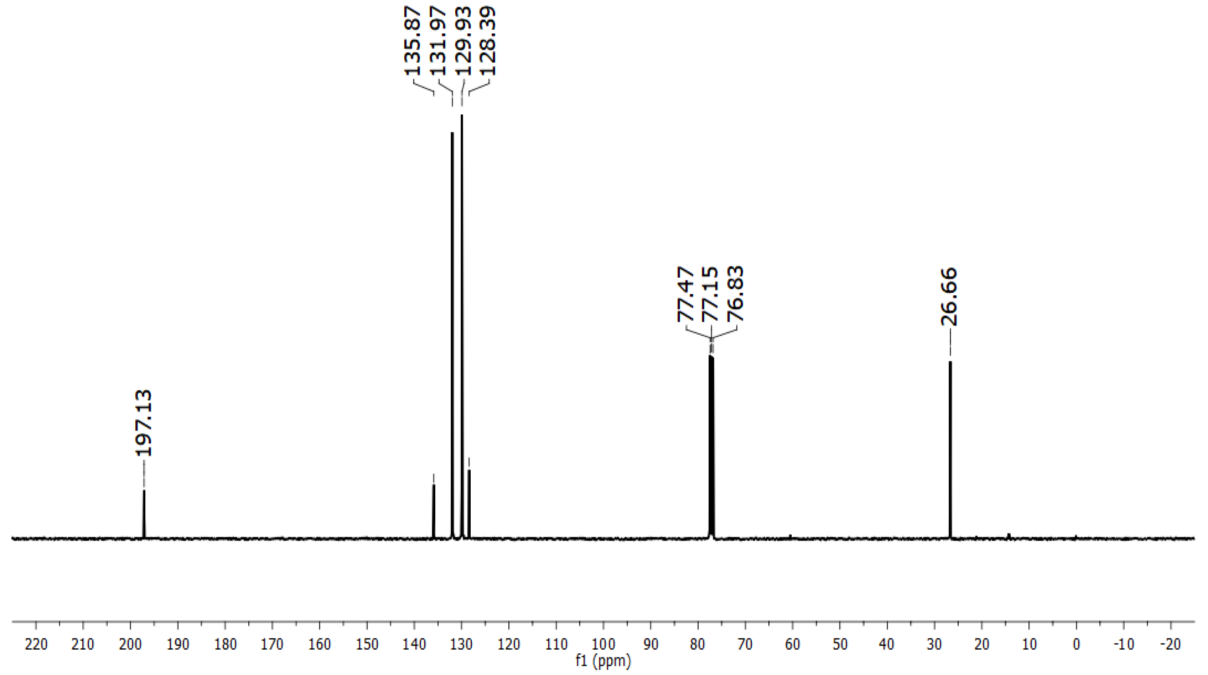
2.00
1.94
3.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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131.97
129.93
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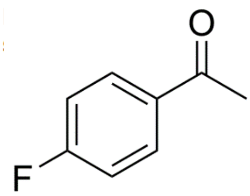
77.47
77.15
76.83
26.66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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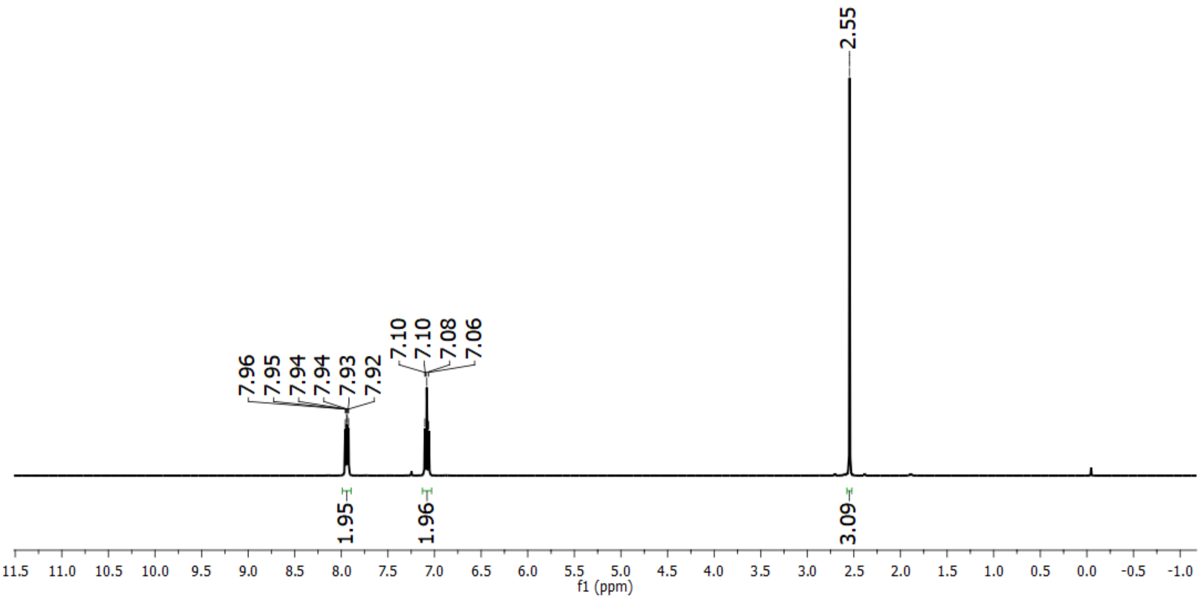
F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7.10
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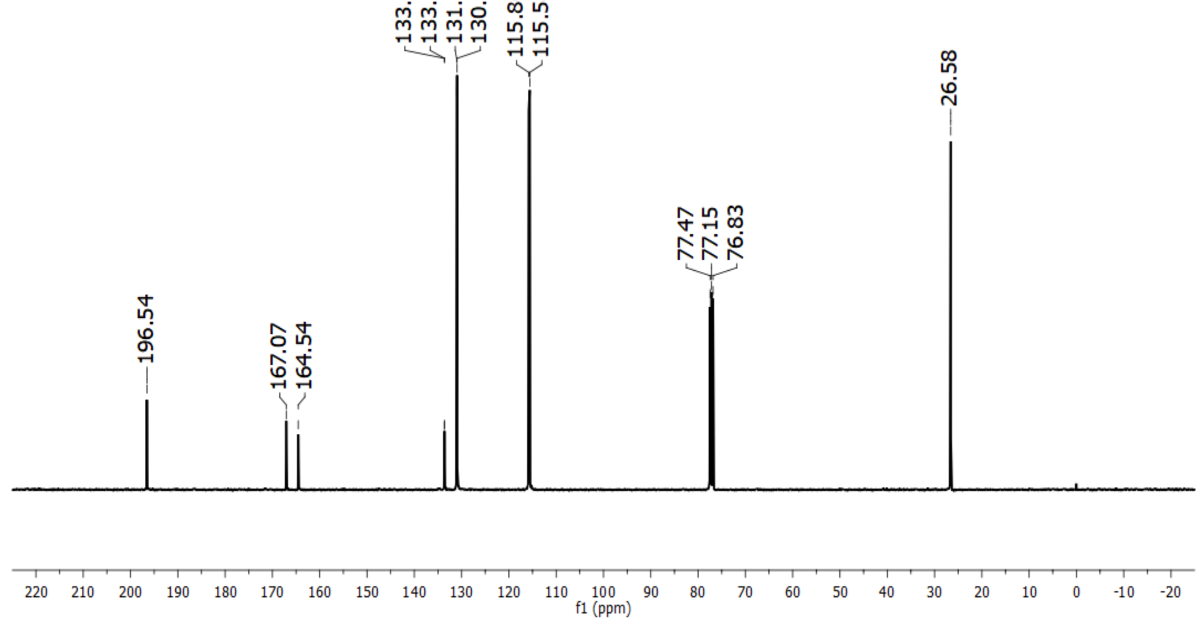
7.06
2.55
1.95
1.96
3.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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133.62
131.05
130.95
115.80
115.58
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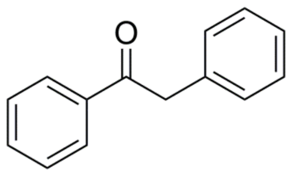
76.83
26.58
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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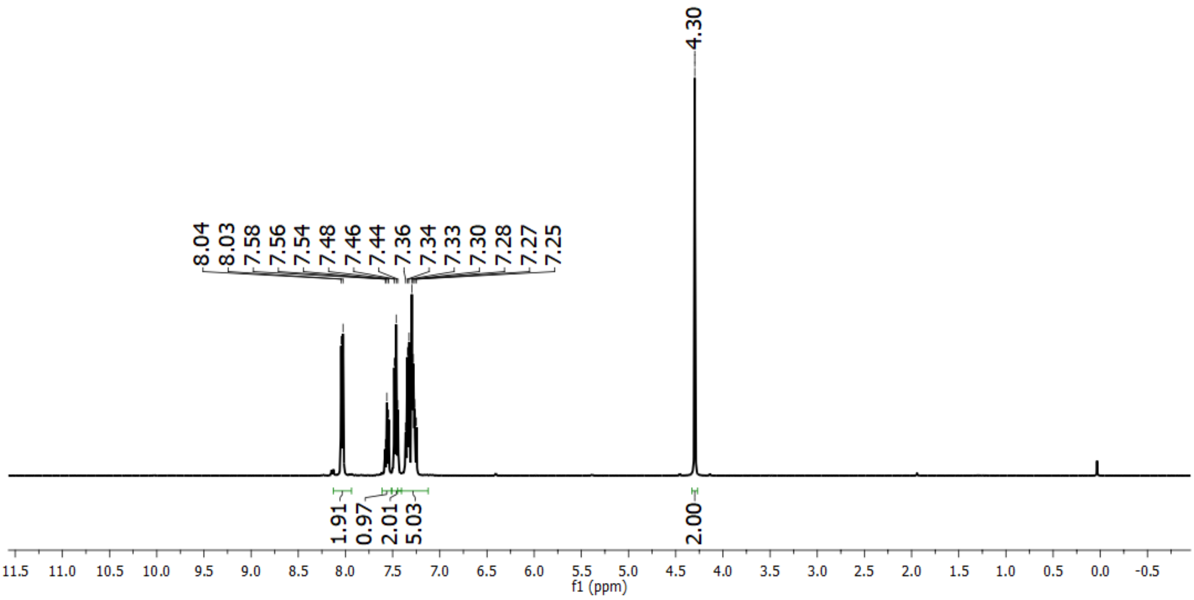
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8.03
7.58
7.56
7.54
7.48
7.46
7.44
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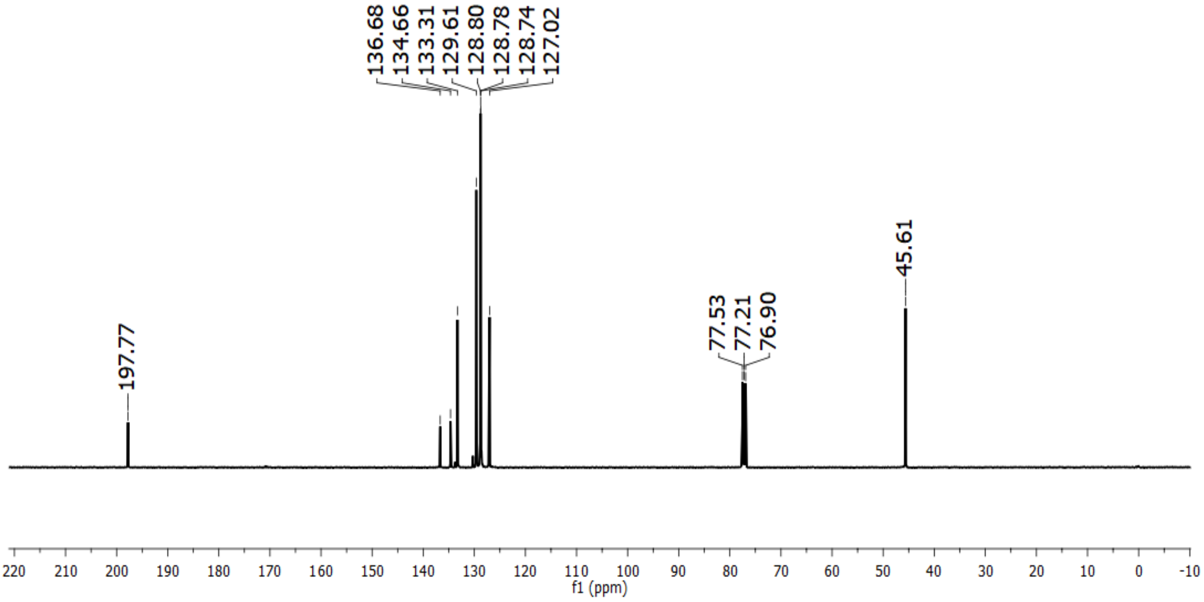
7.34
7.33
7.30
7.28
7.27
7.25
4.30
1.91
0.97
2.01
5.03
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.21
76.90
45.61
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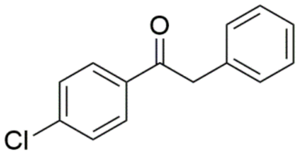
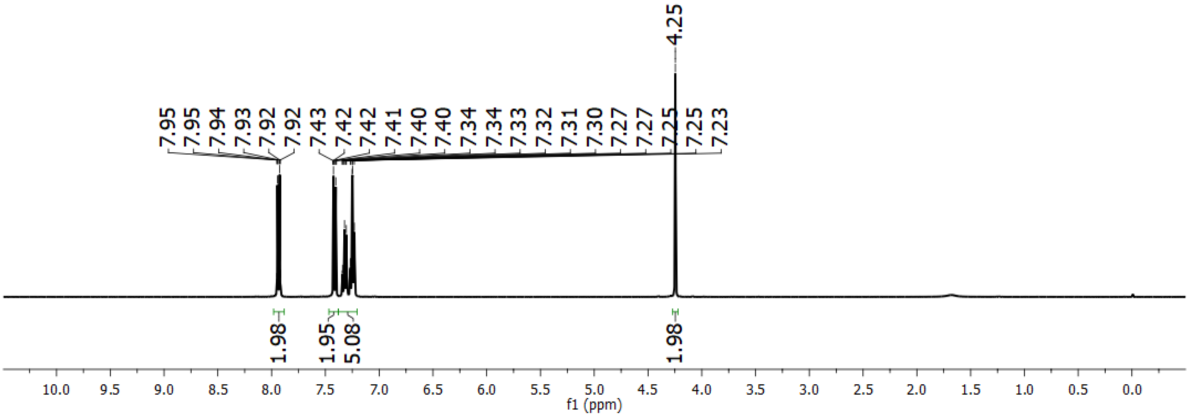
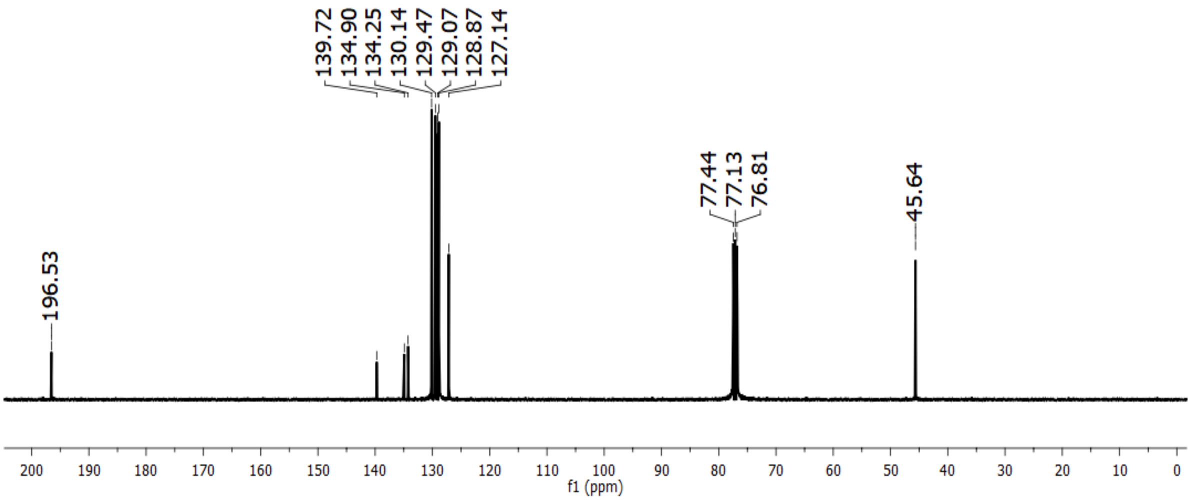
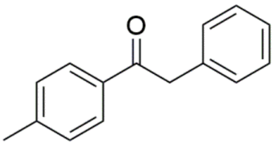
f1 (ppm)

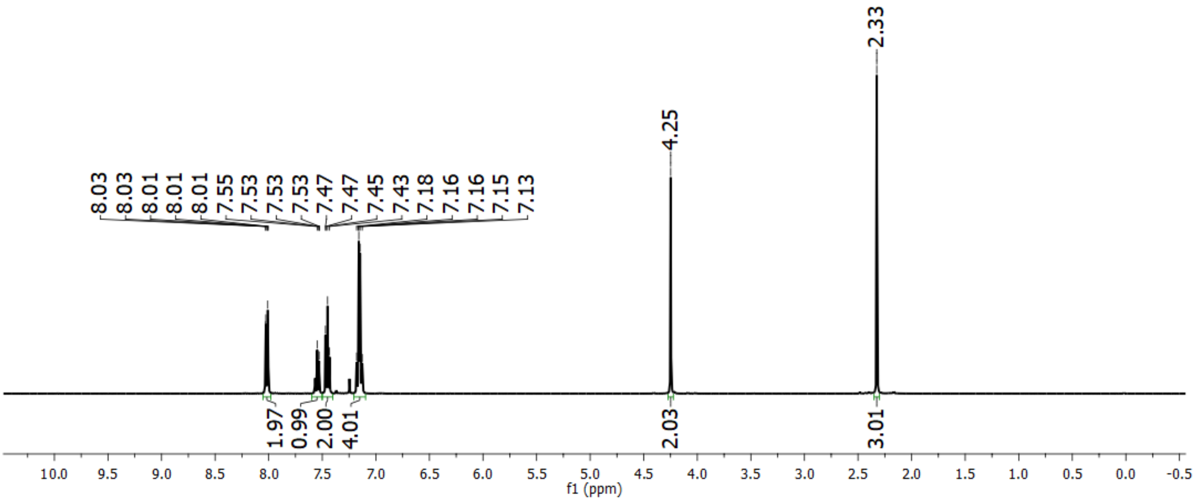




RK-MU-04-66
single pulse decoupled gated NOE







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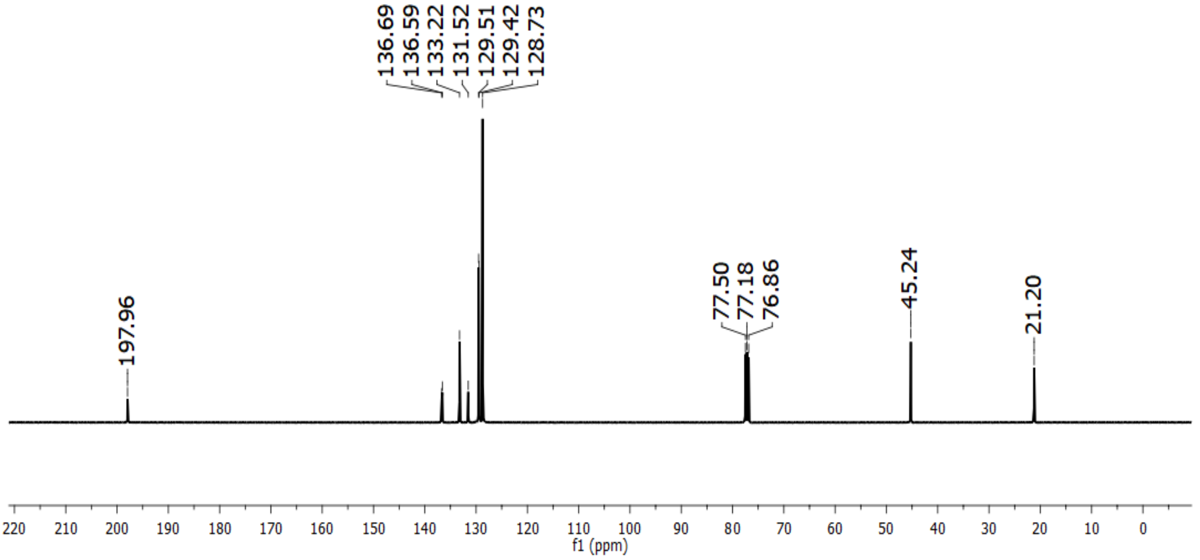
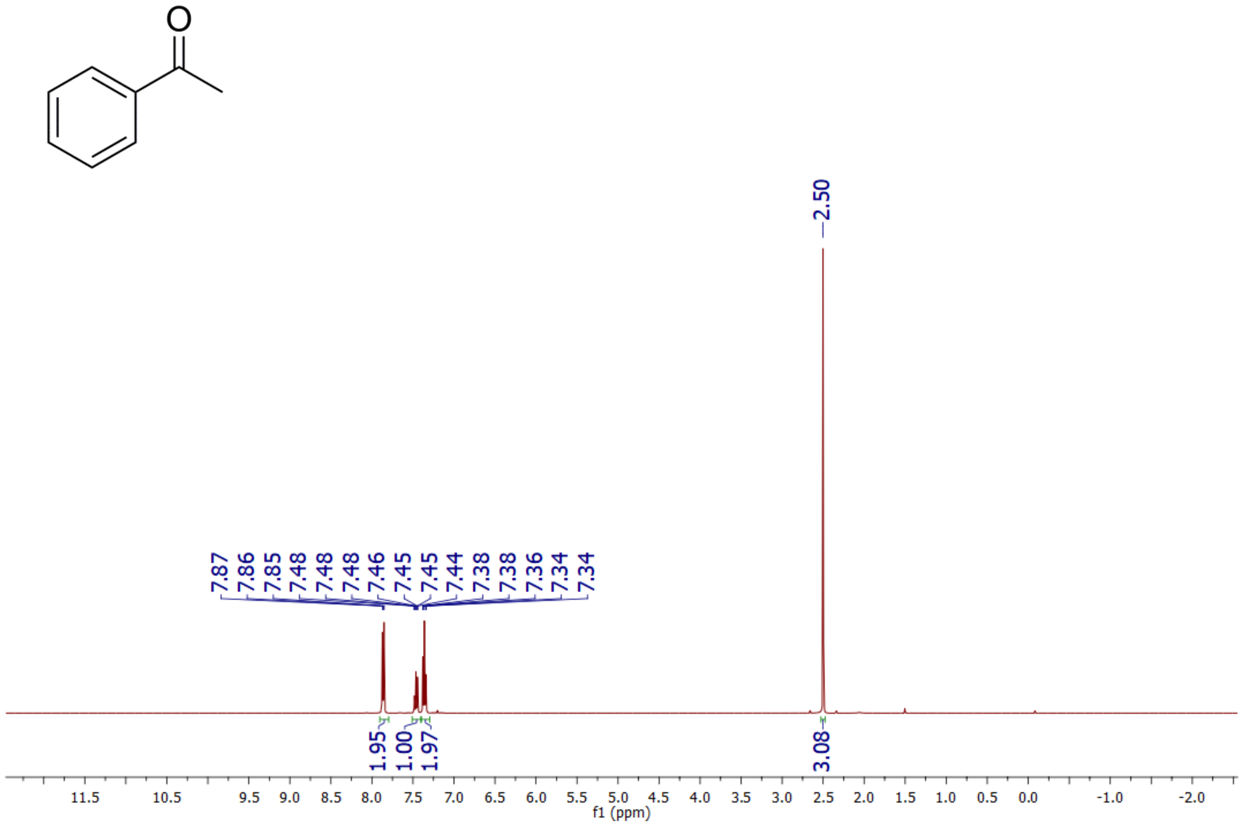


Chapter 4

Iron Chalcogenide Carbonyl Complexes as a heterogeneous Photo catalyst for alkyne hydrations in aqueous media

Supporting Information

^{1}H and ^{13}C NMR Spectra of Compounds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7.87
7.86
7.85
7.48
7.48
7.48
7.46
7.45
7.45
7.44
7.38
7.38
7.36
7.34
7.34
2.50
1.95
1.00
1.97
3.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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1.5
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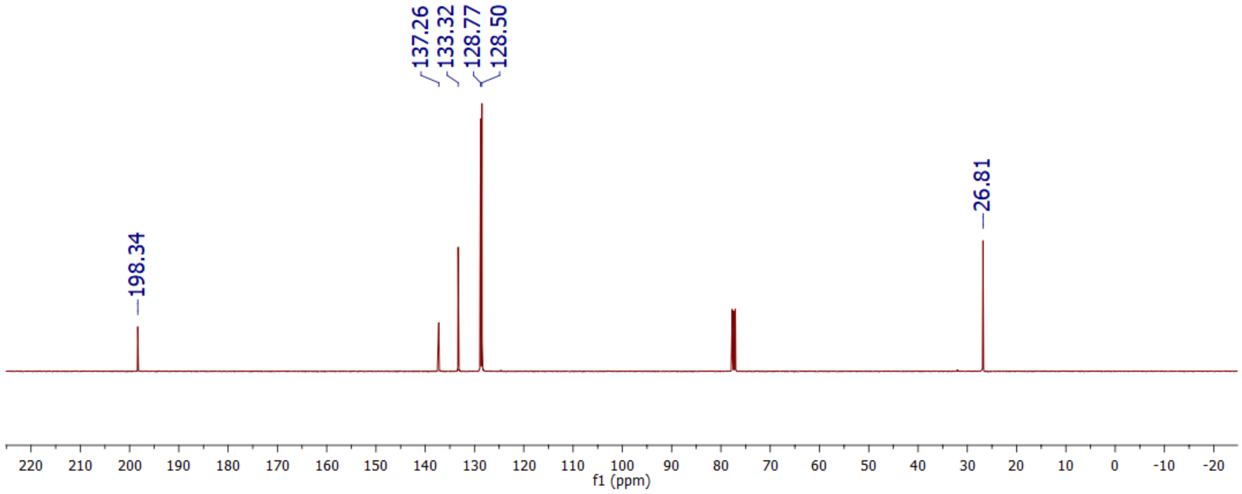
0.0
-1.0
-2.0
f1 (ppm)


137.26
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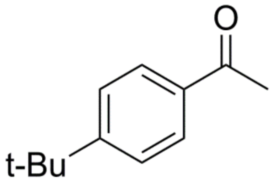
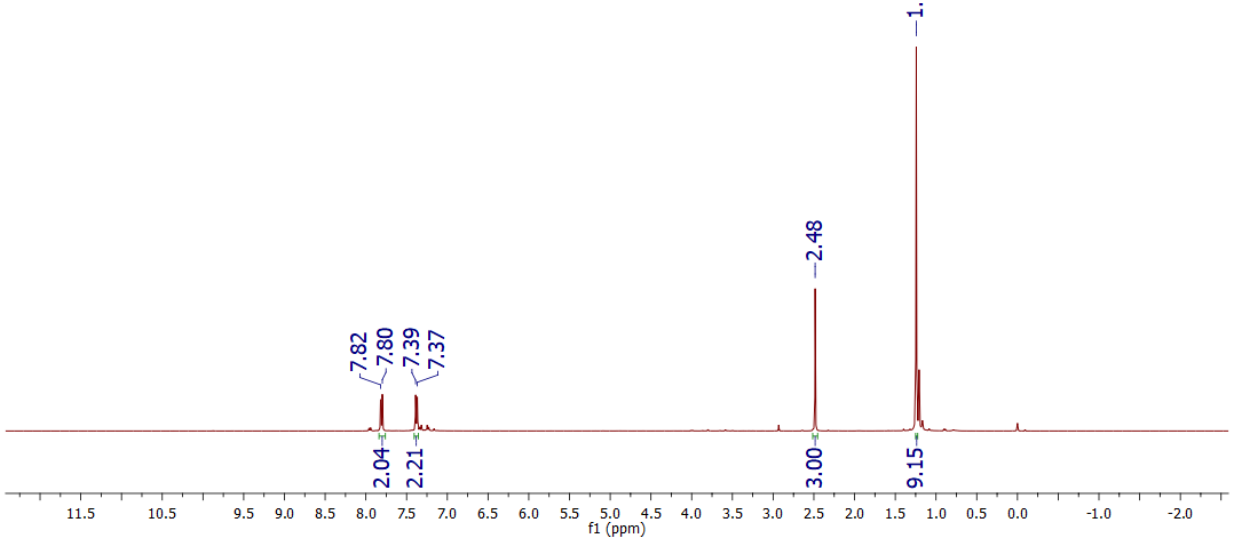
f1 (ppm)


O
t-Bu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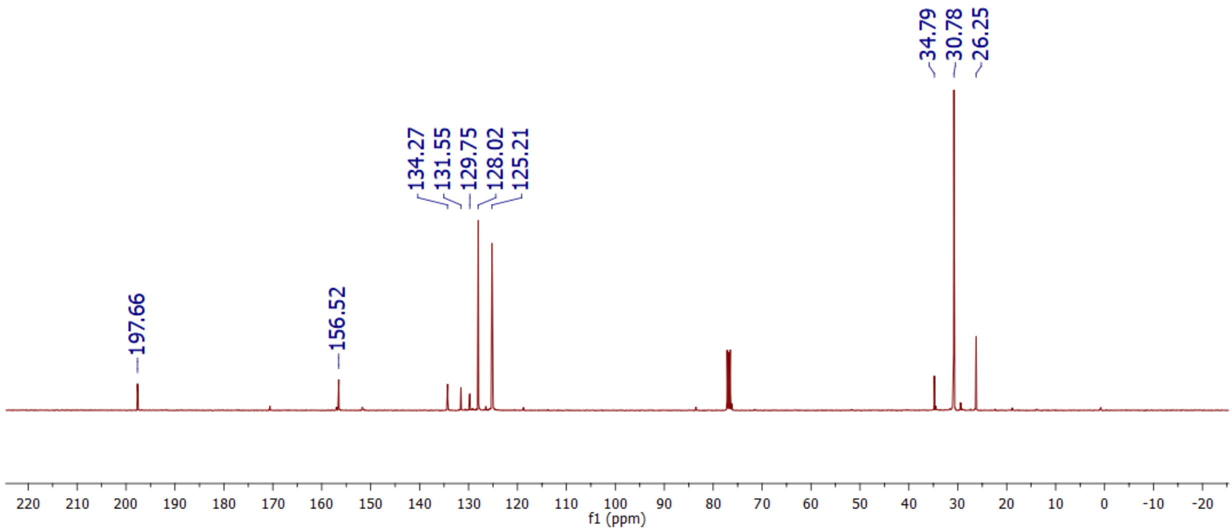
7.82
7.80
7.39
7.37
2.04
2.21
3.00
9.15
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0
f1 (ppm)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26.25
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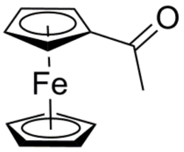
f1 (ppm)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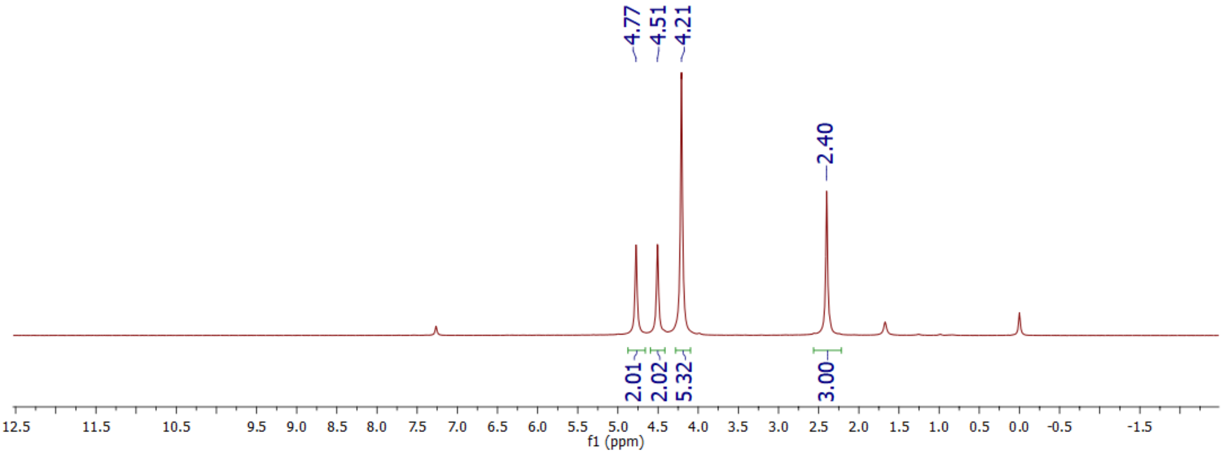
Fe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4.21
2.40
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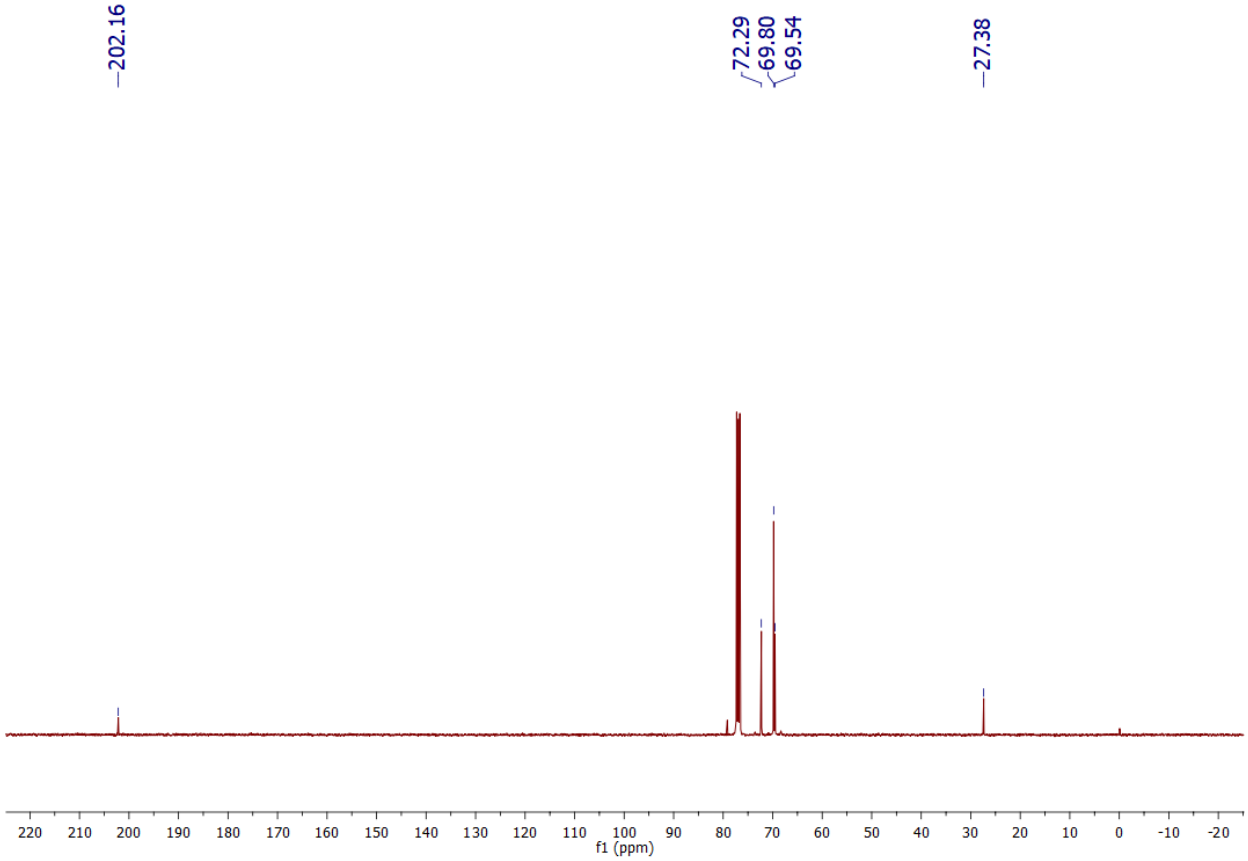
2.02
5.32
3.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)



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72.29
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69.54
27.38
220
210
200
190
180
170
160
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100
90
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70
60
50
40
30
20
10
0
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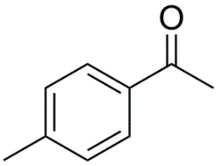
-20
f1 (ppm)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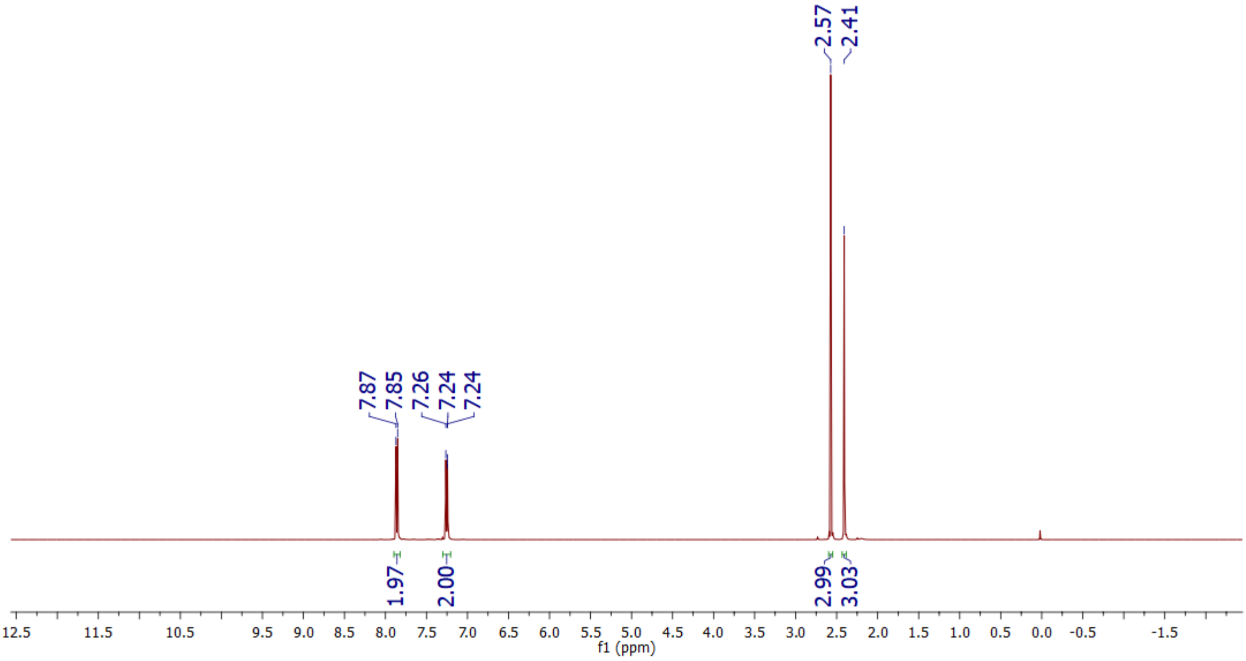
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10.5
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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5.0
4.5
4.0
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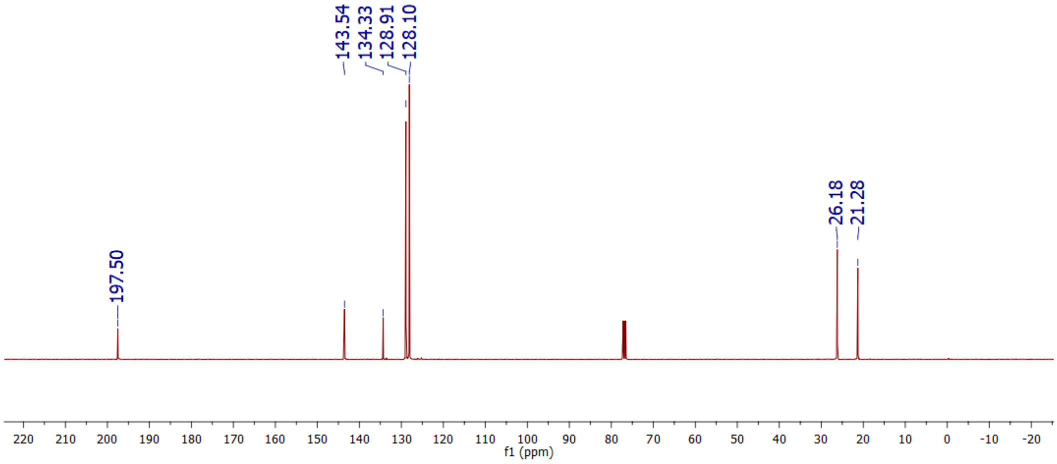
f1 (ppm)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0
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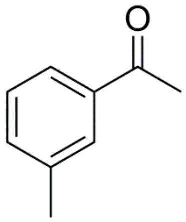
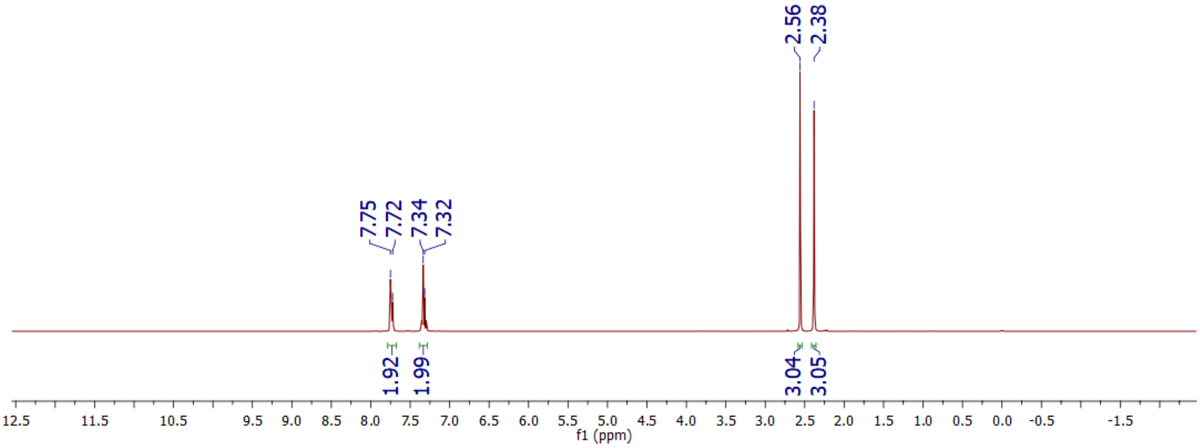
f1 (ppm)

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10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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0.0
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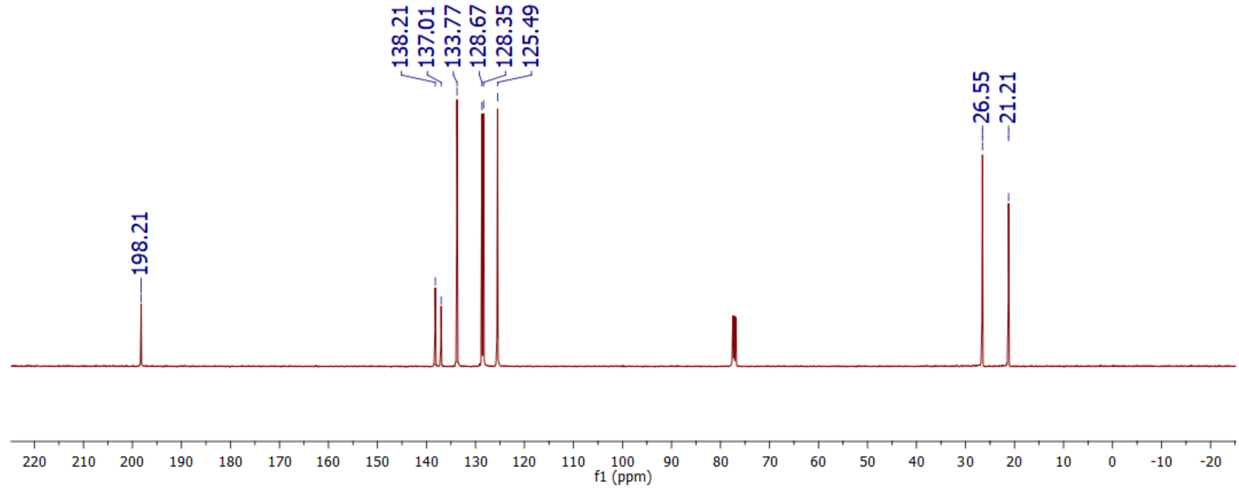
f1 (ppm)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160
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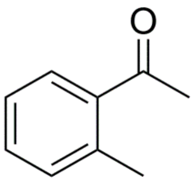
-20
f1 (ppm)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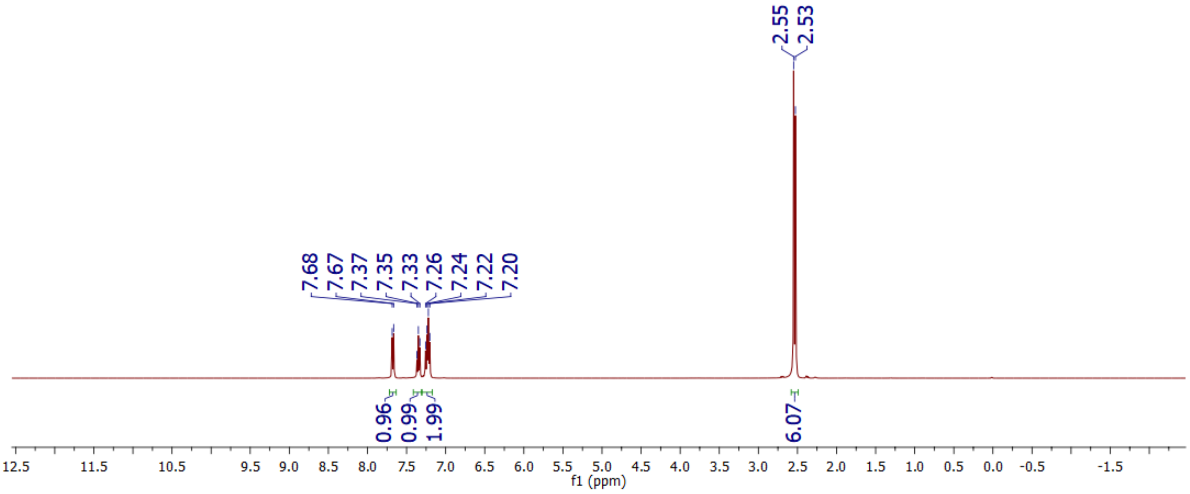
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0.99
1.99
6.07
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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0.0
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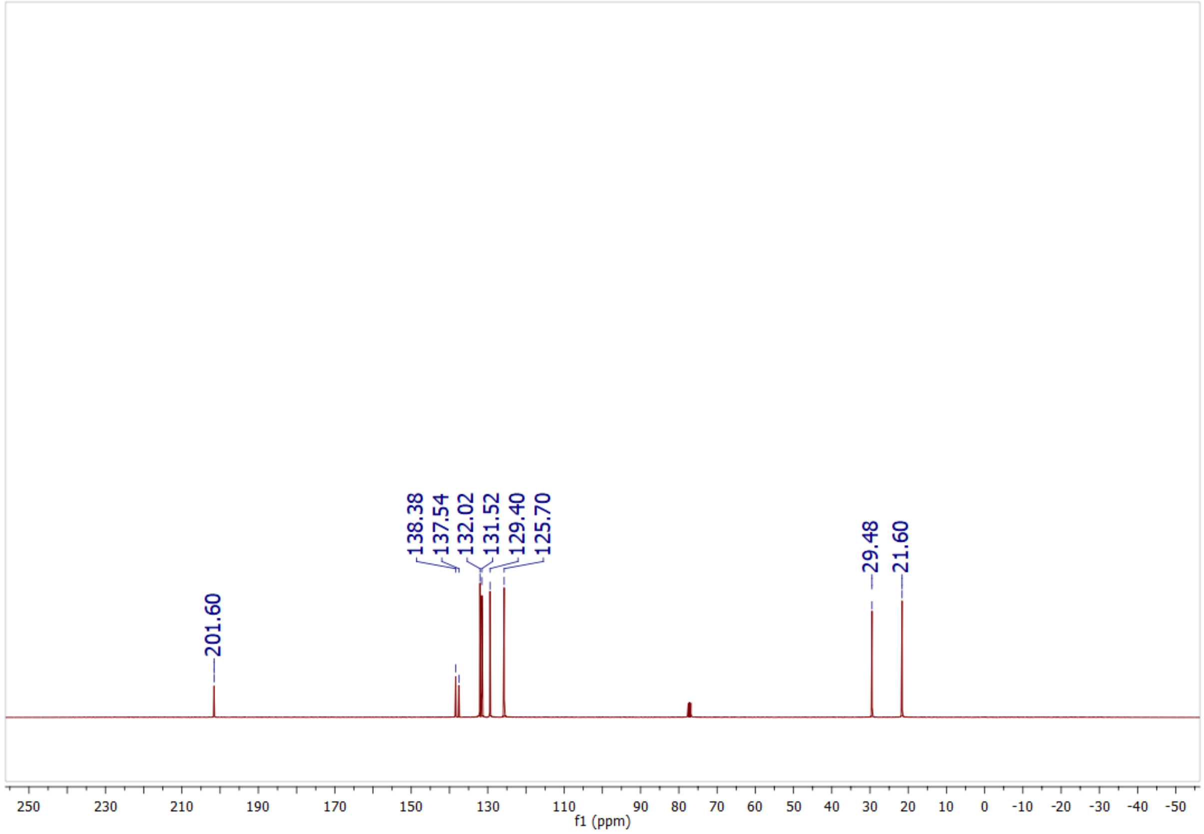
-1.5
f1 (ppm)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170
150
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-20
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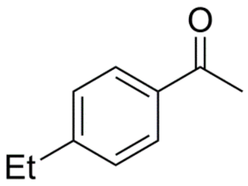
-40
-50
f1 (ppm)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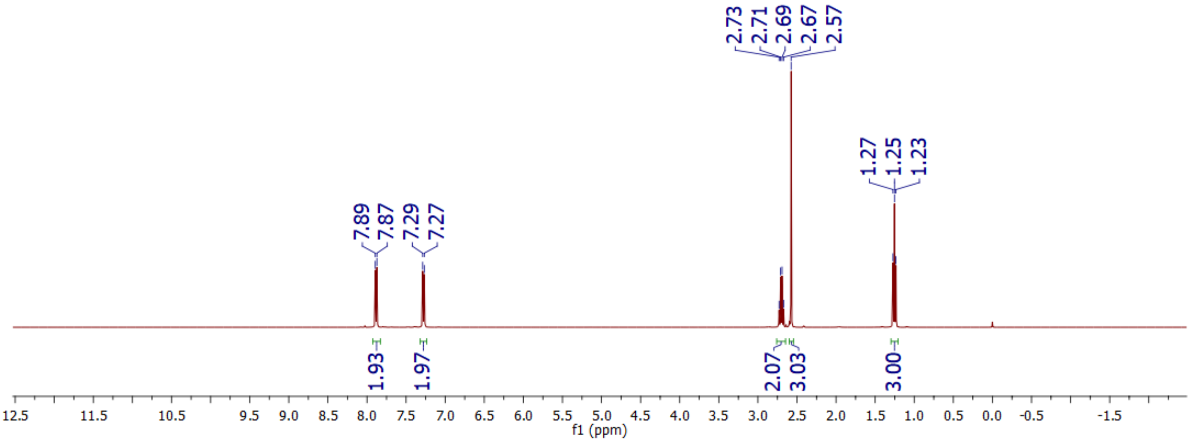
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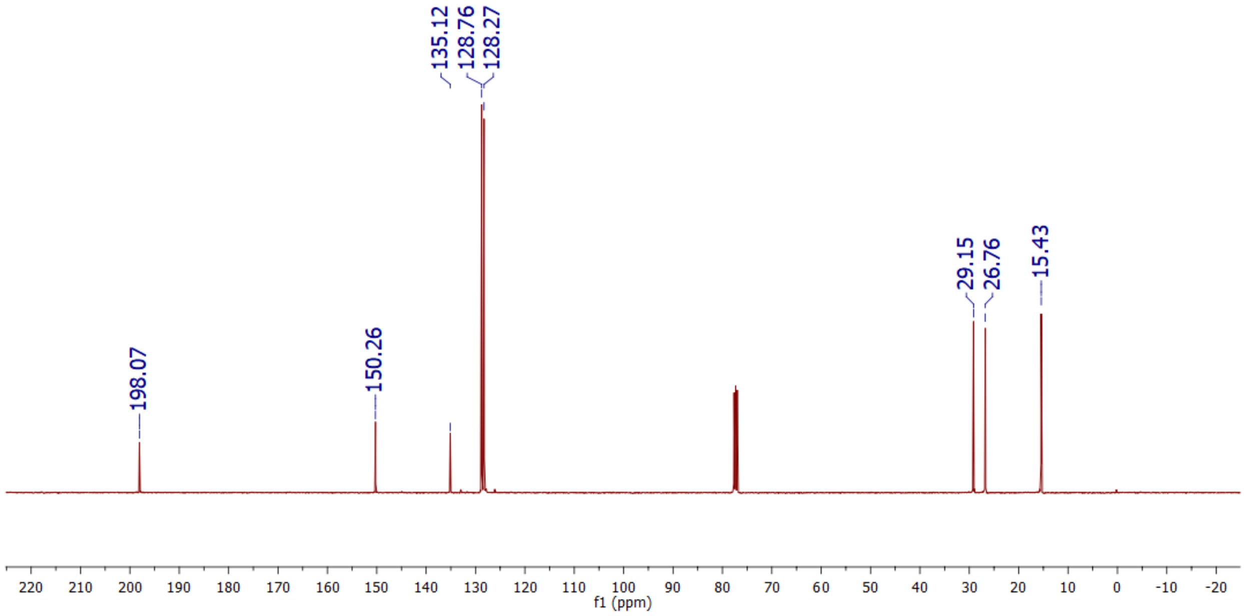
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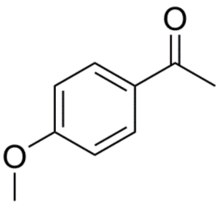
f1 (ppm)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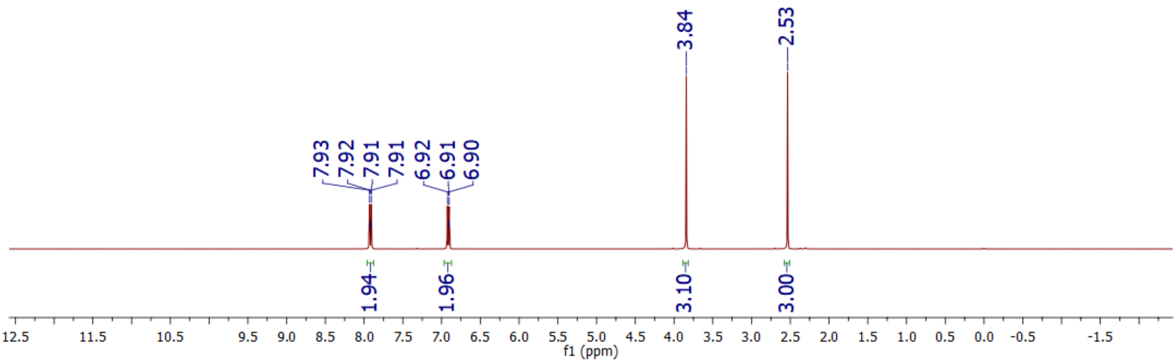
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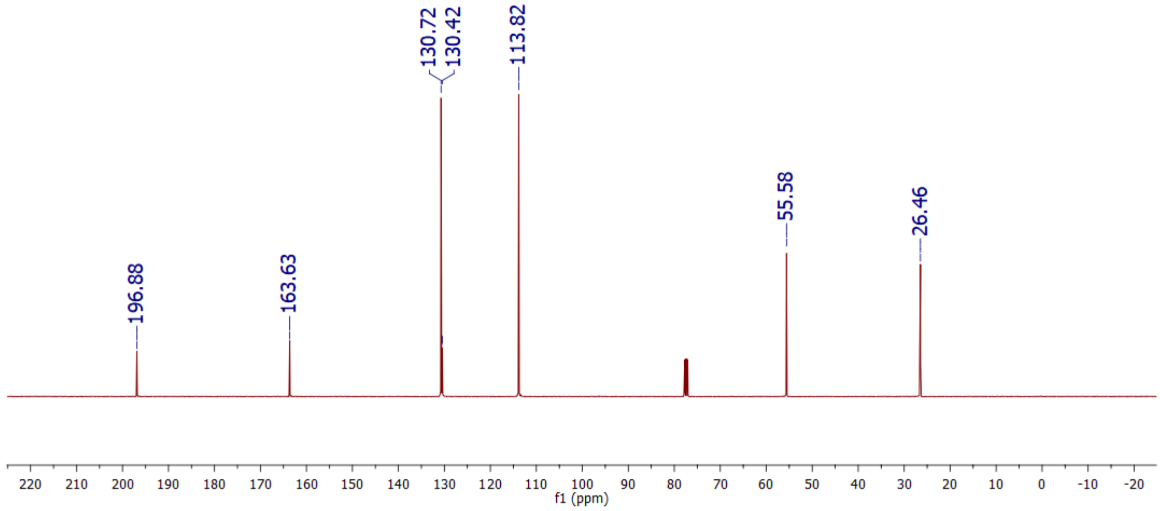
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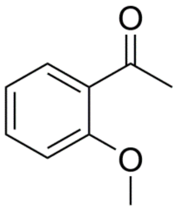

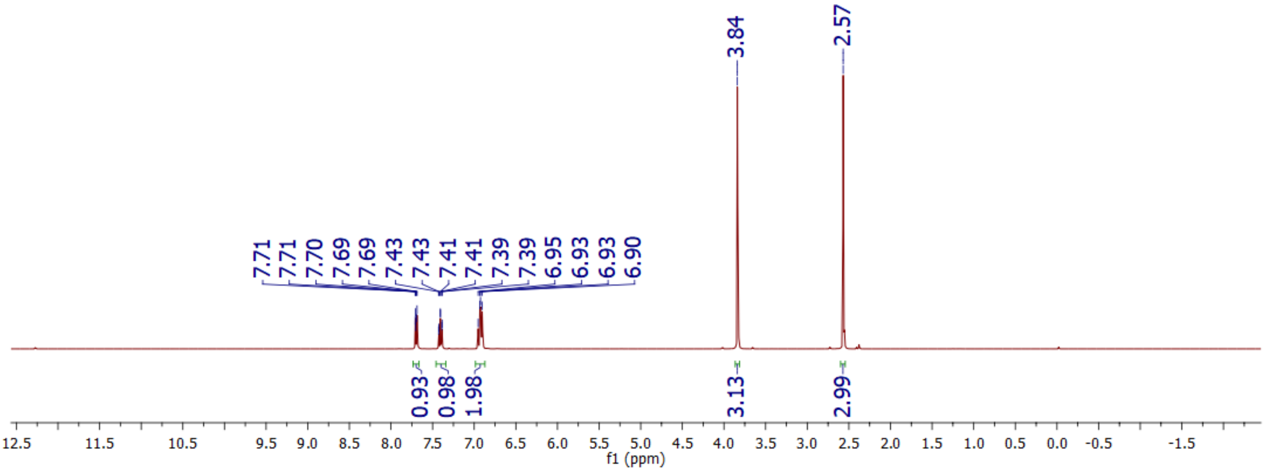
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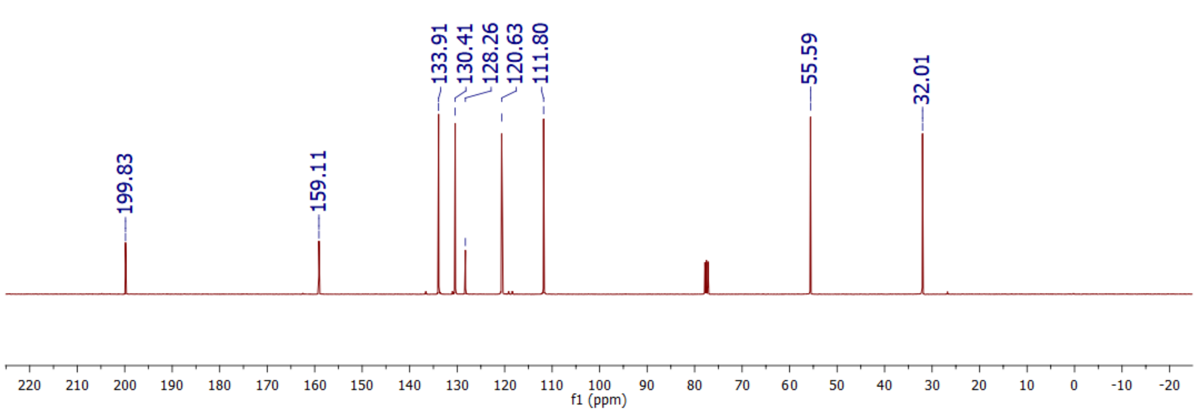
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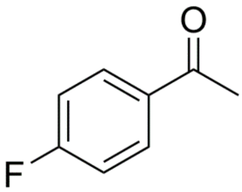
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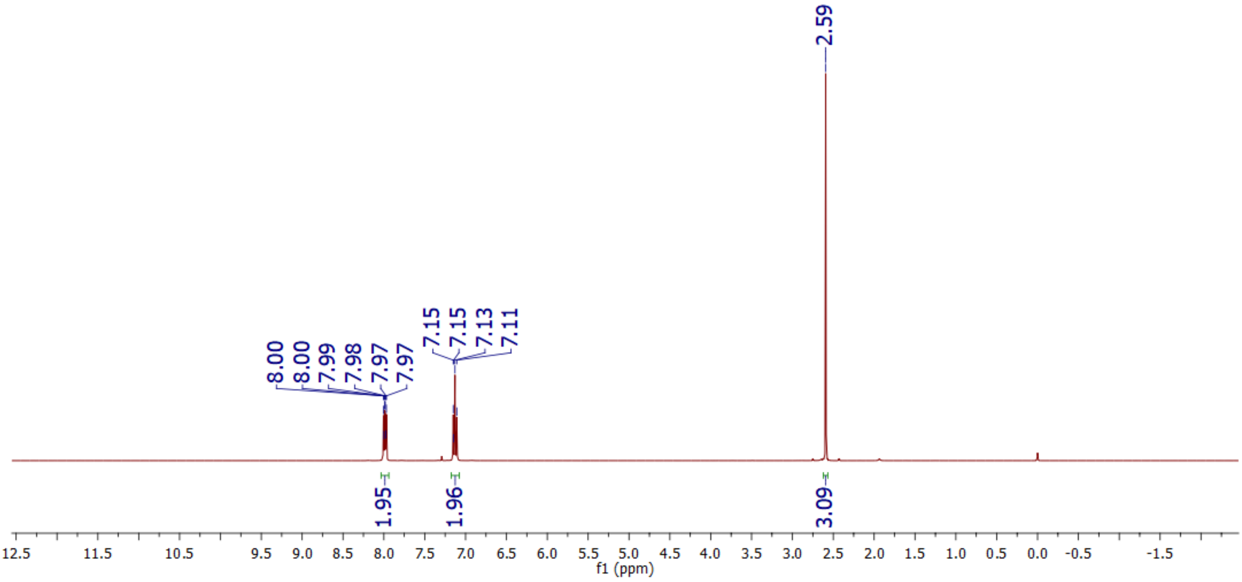
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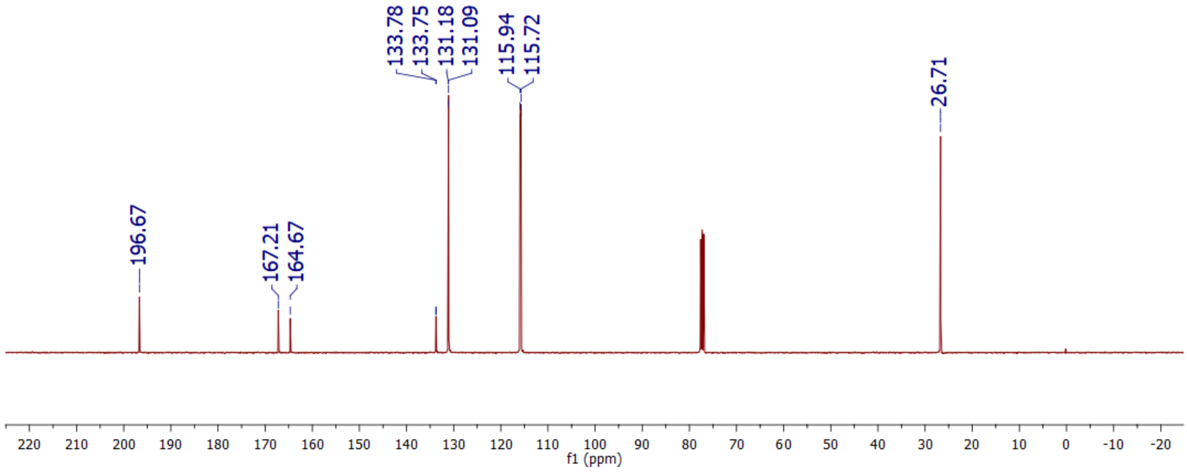
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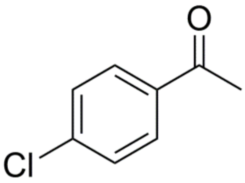
f1 (ppm)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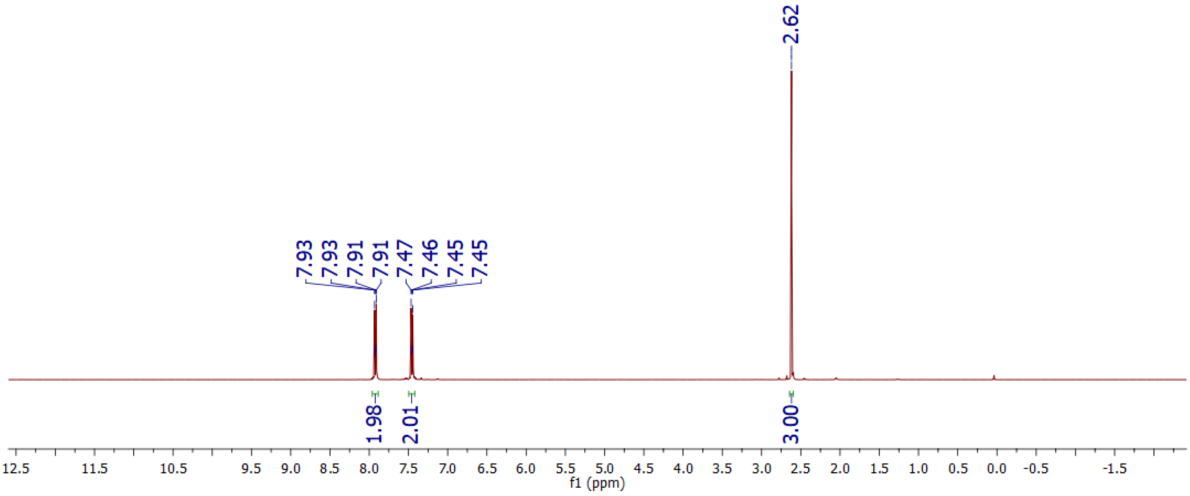
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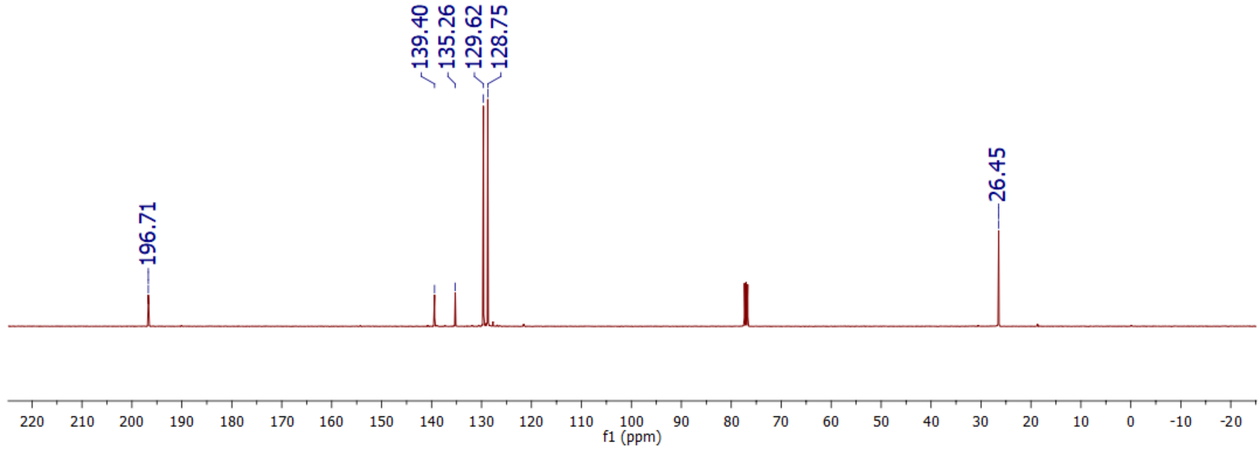
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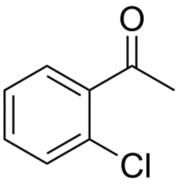
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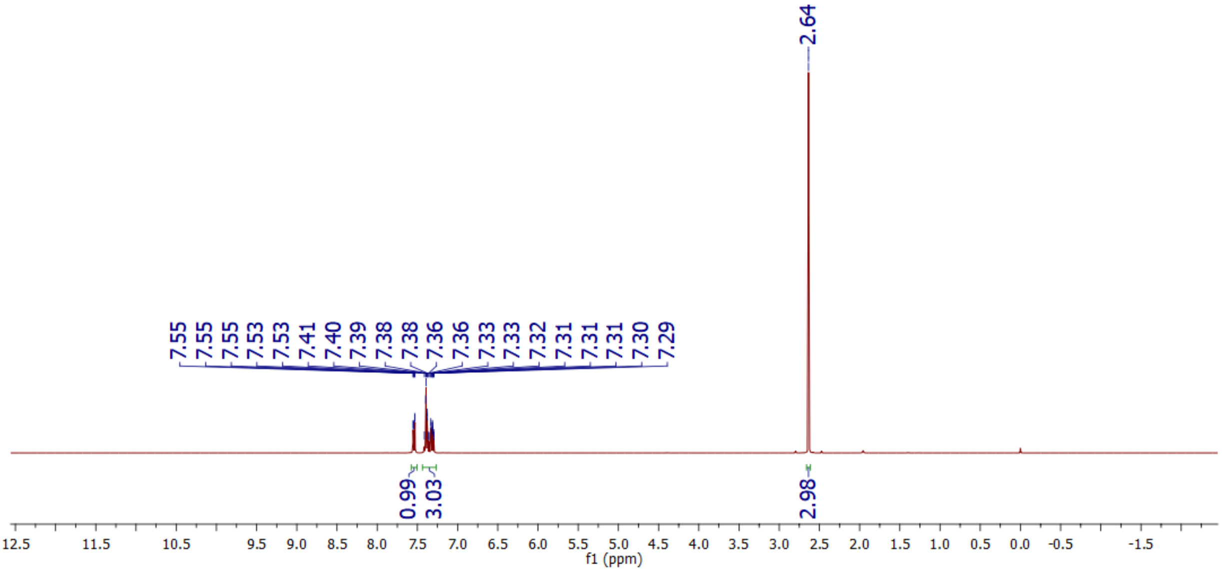
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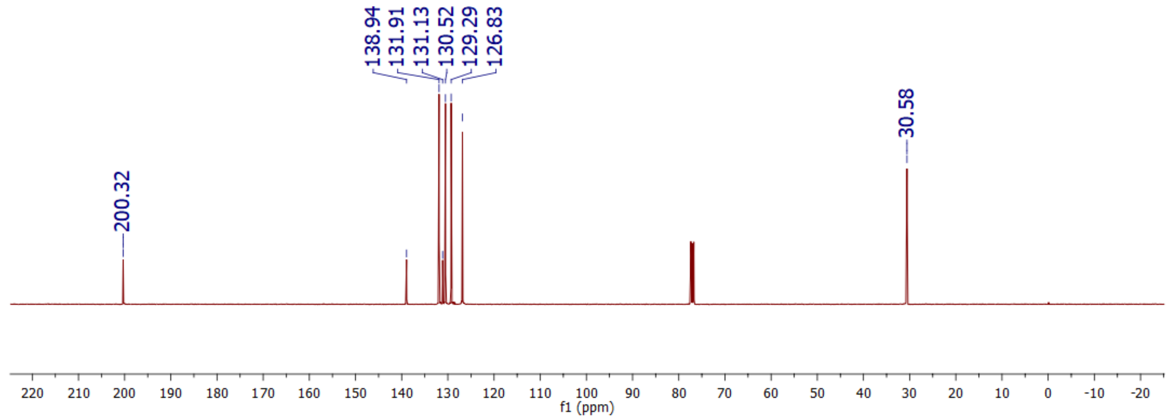
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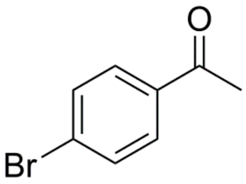
f1 (ppm)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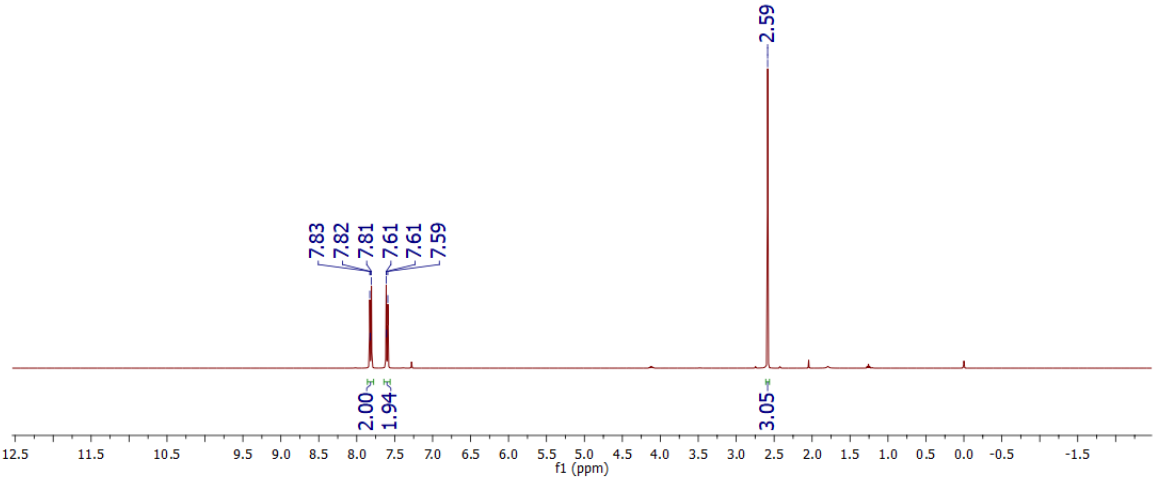
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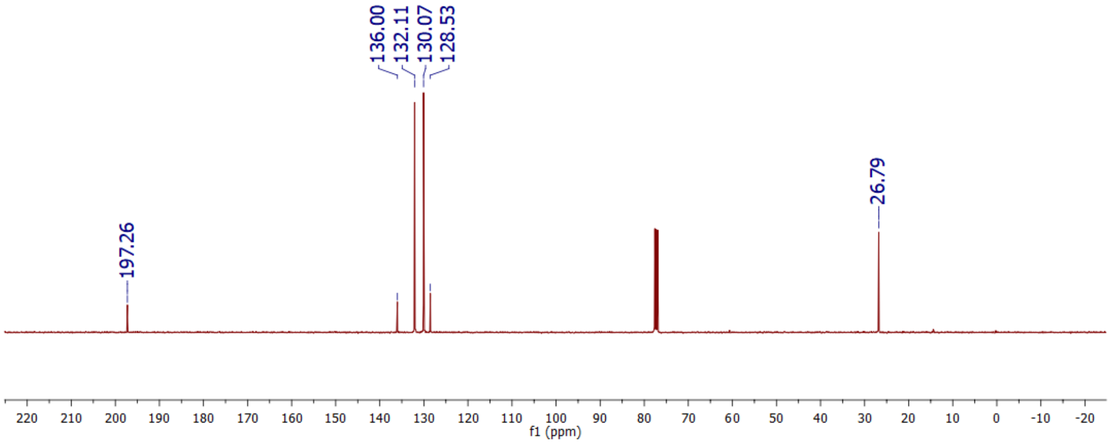
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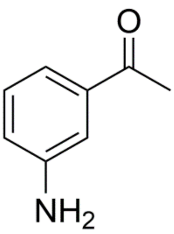
f1 (ppm)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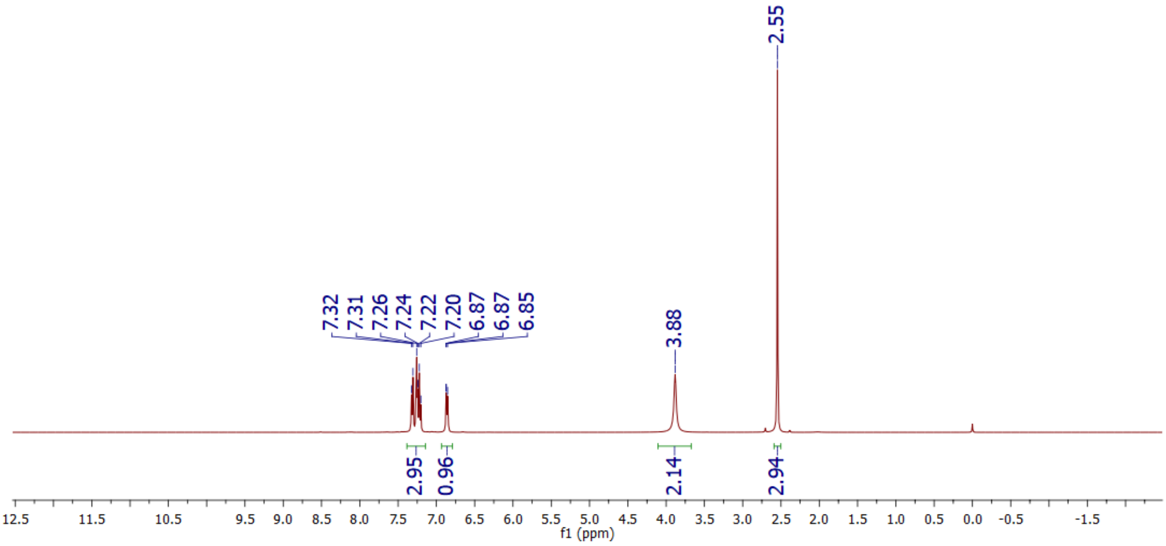
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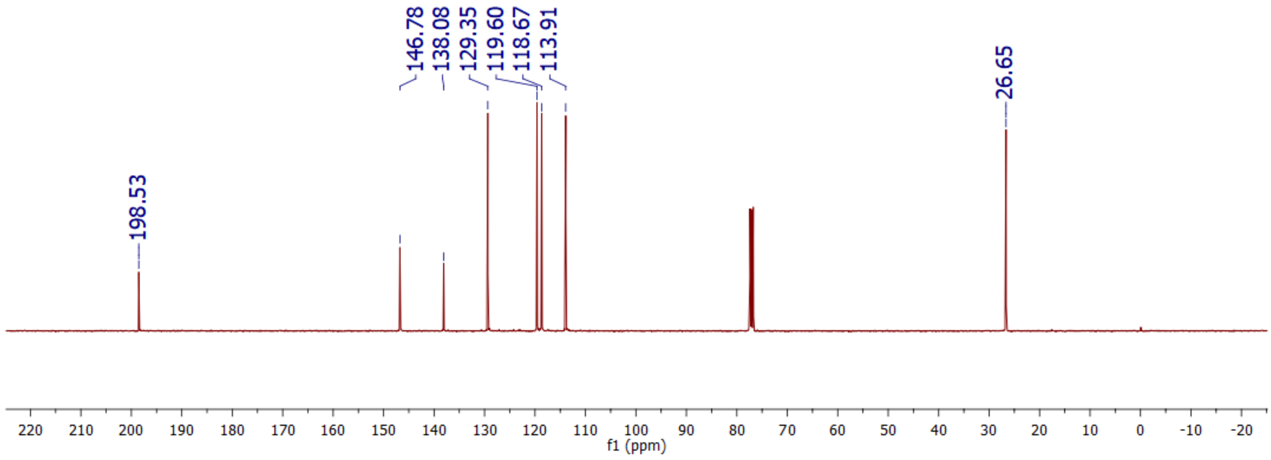
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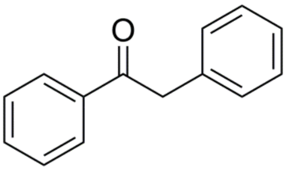
f1 (ppm)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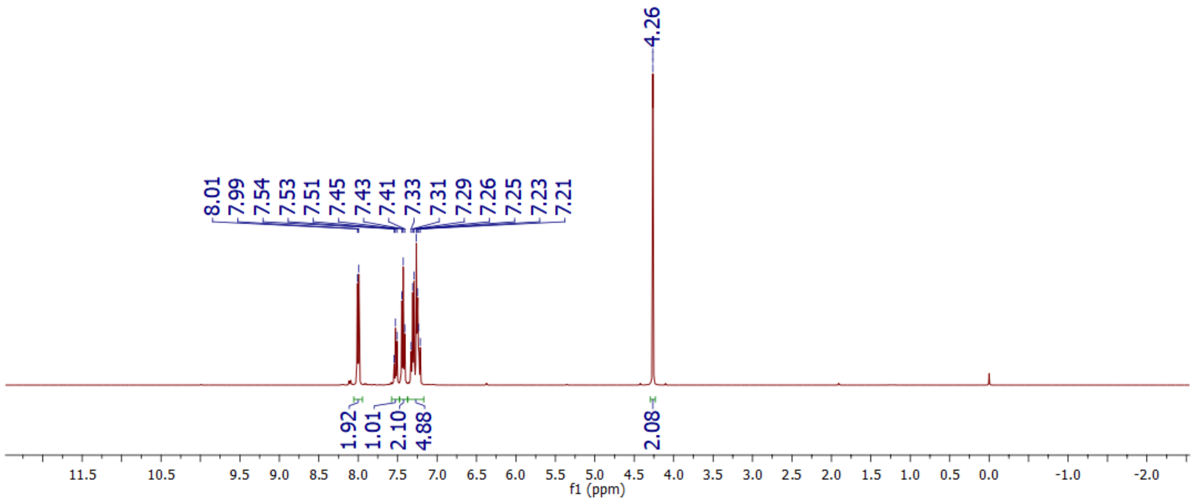
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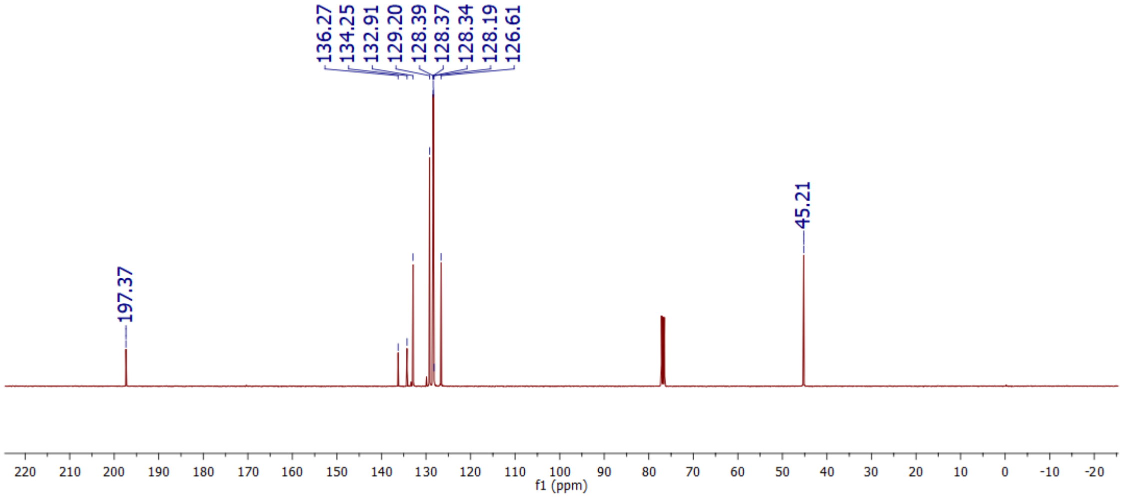
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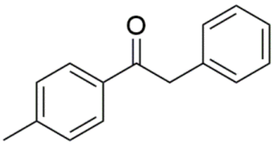
f1 (ppm)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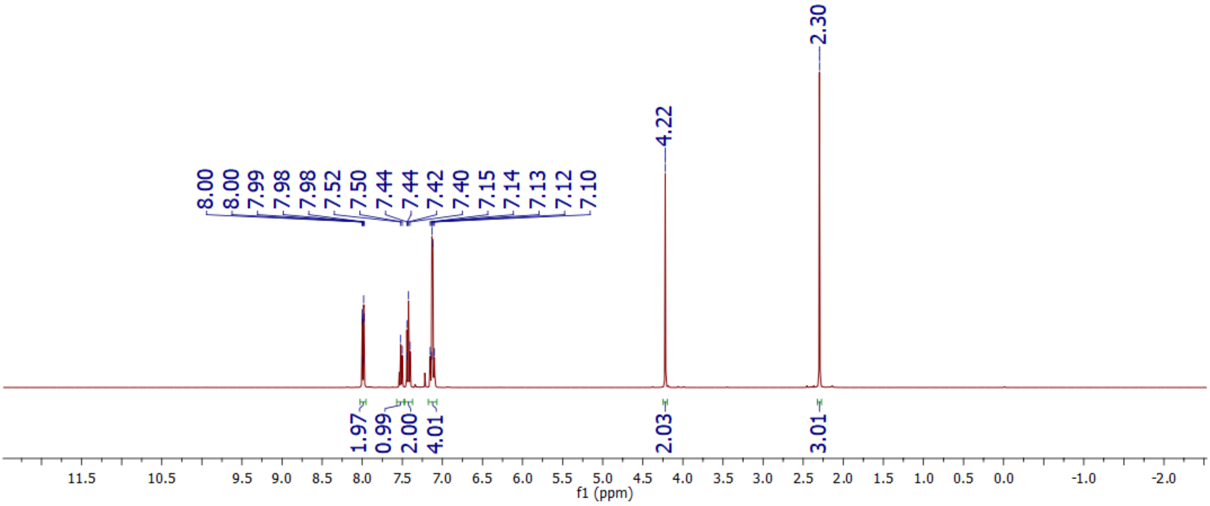
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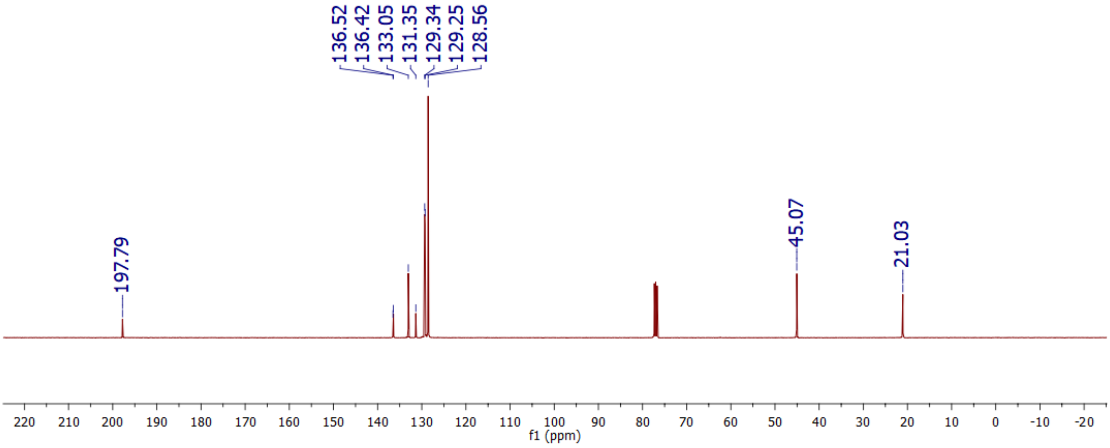
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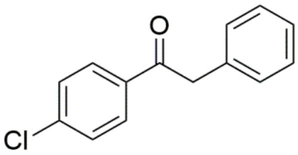
f1 (ppm)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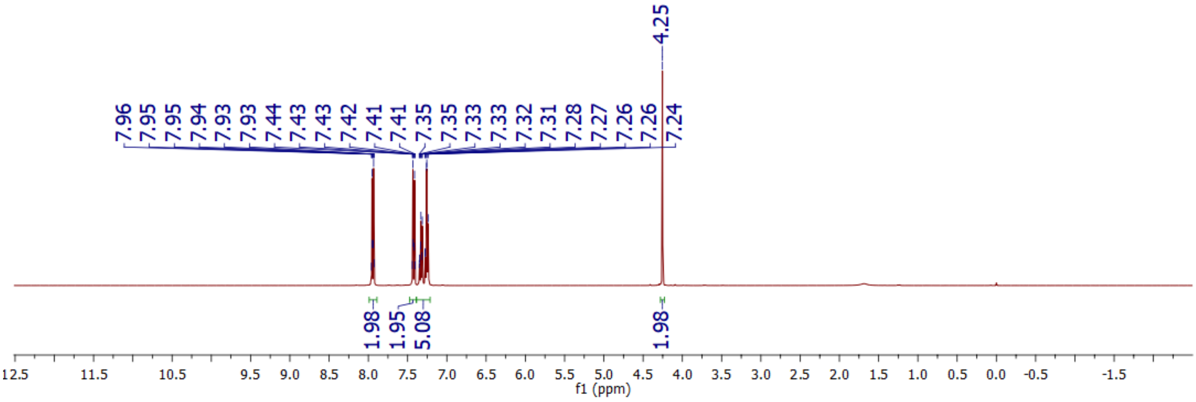
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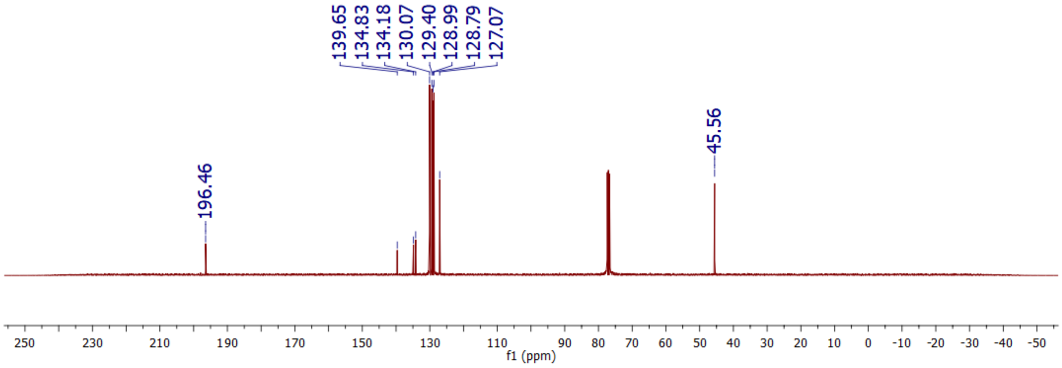
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45.56
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210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
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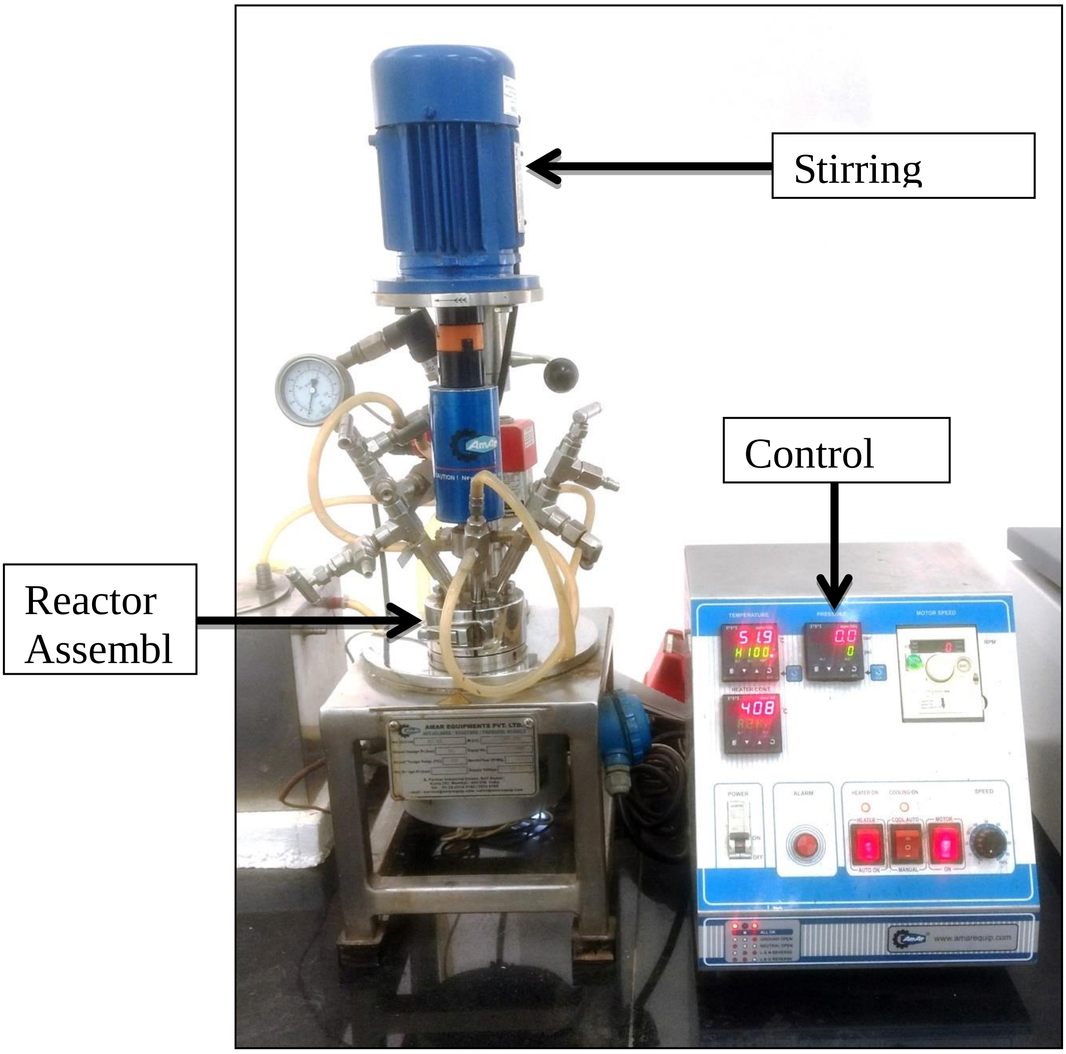
-40
-50
f1 (ppm)

Chapter 5

Temperature And Pressure Controlled Hydration Of Alkynes: A Sustainable Strategy For The Ketone Synthesis

Supporting Information

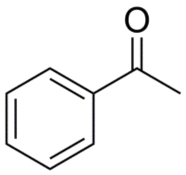
Autoclave Reactor

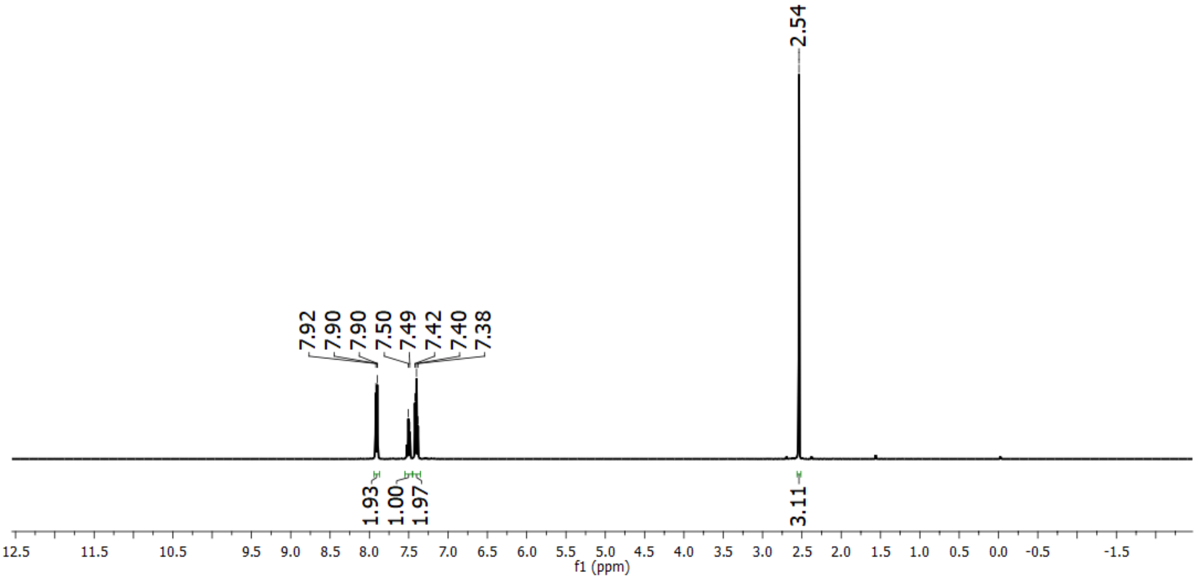


Autoclave Reactor Vessel

Autoclave reactor is purchased from Amar Equipment's Pvt. Ltd., India. This instrument is equipped with 100mL capacity reactor which can use up to 100bar at 350˚C.

^{1}H and ^{13}C NMR Spectra of Compounds





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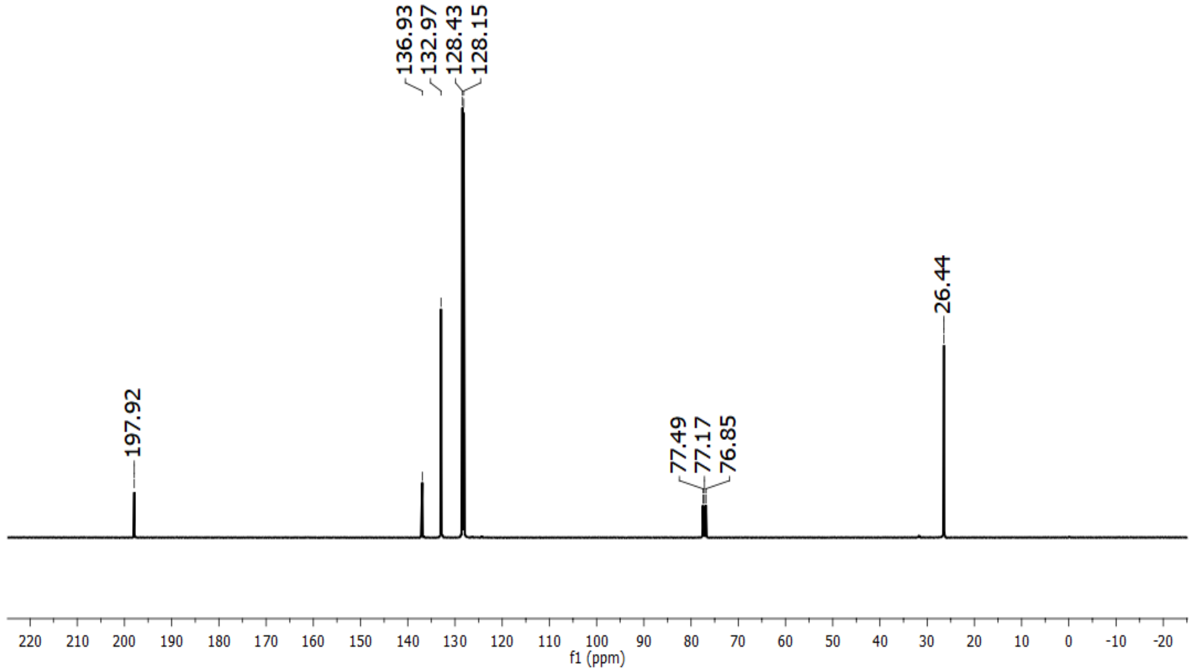

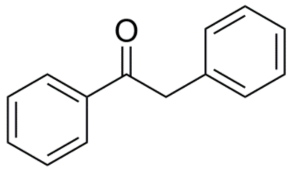

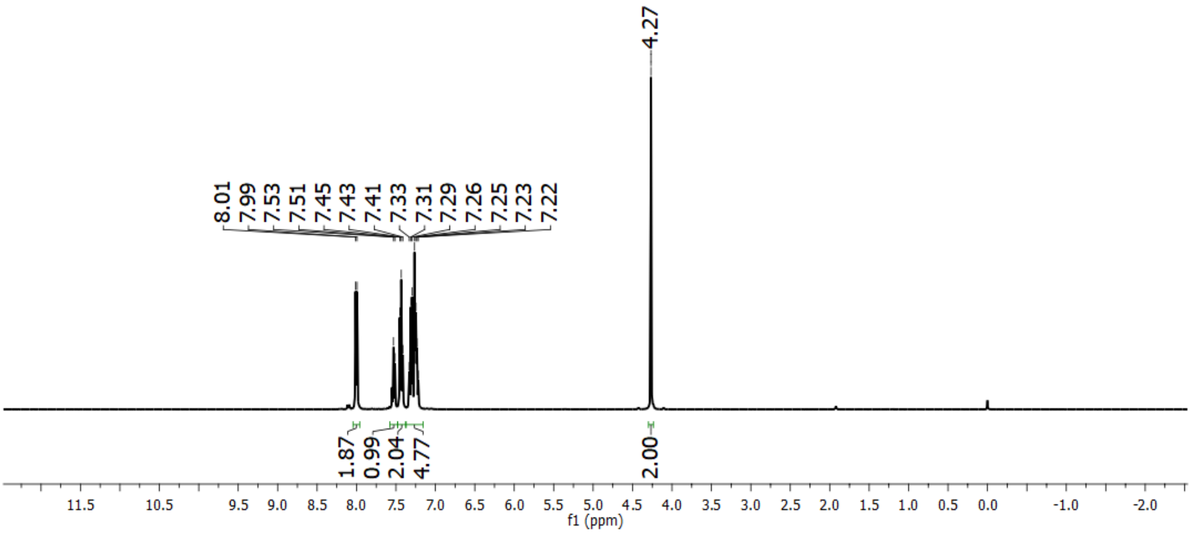

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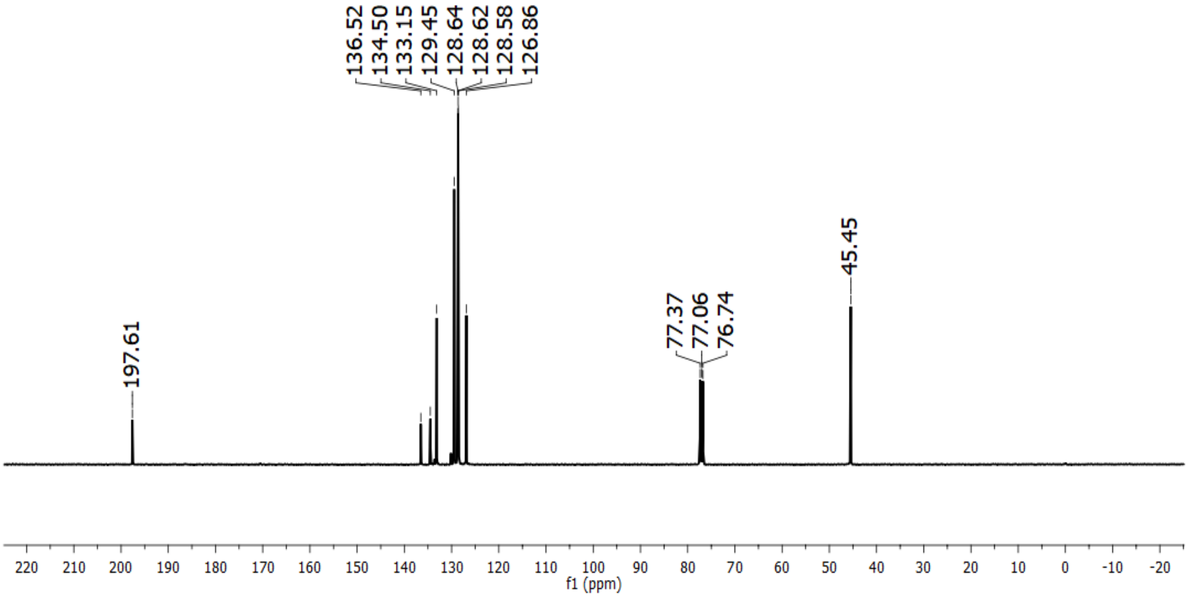
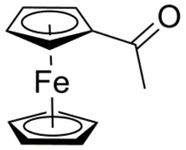
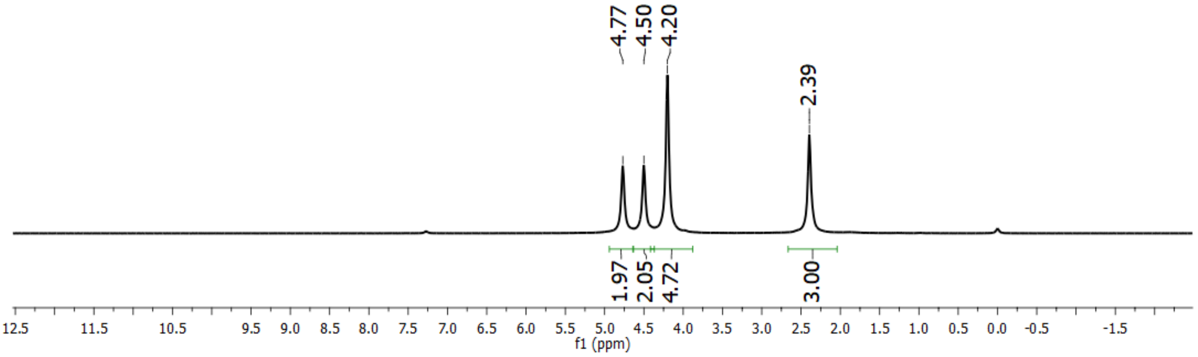
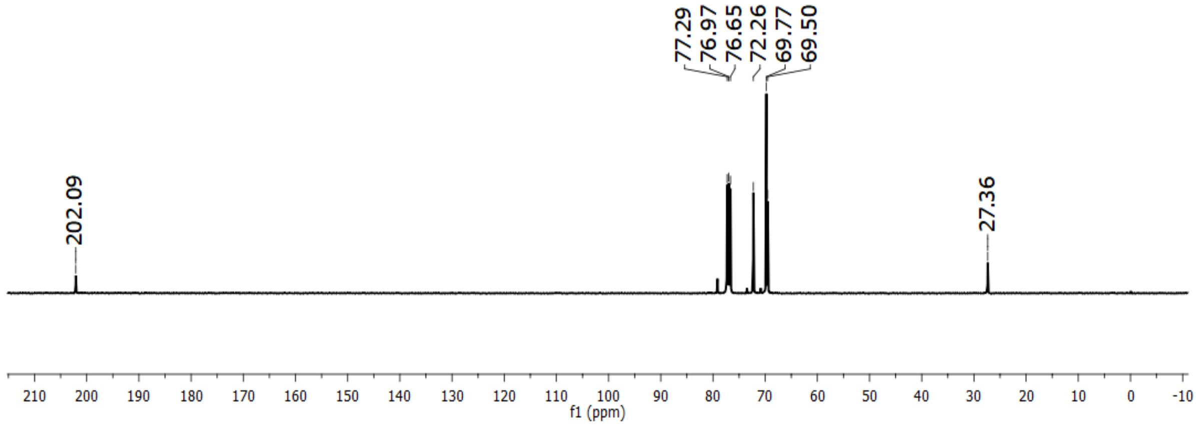
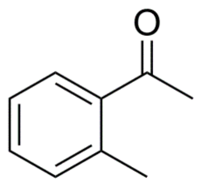


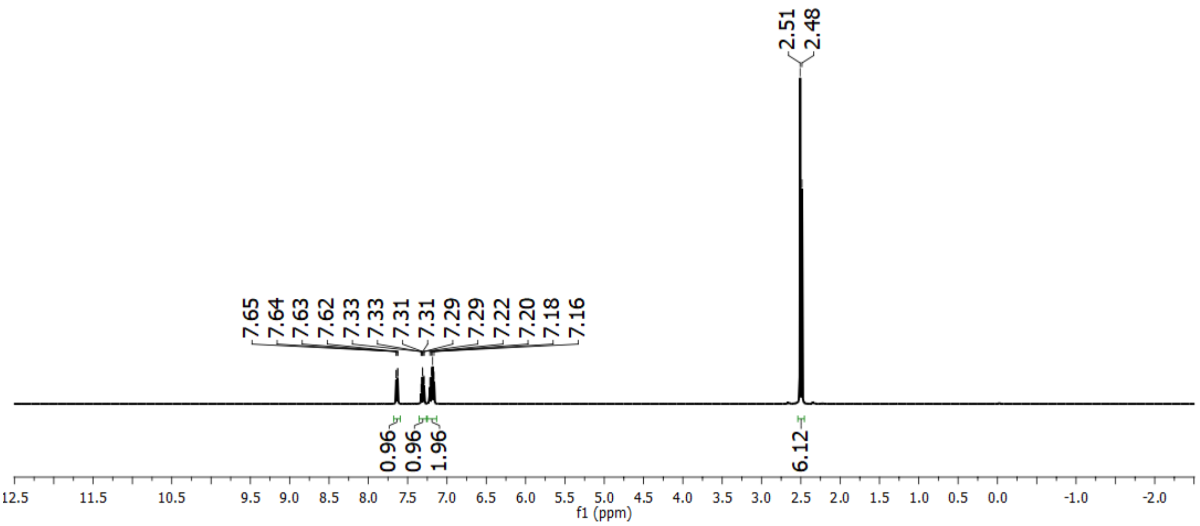




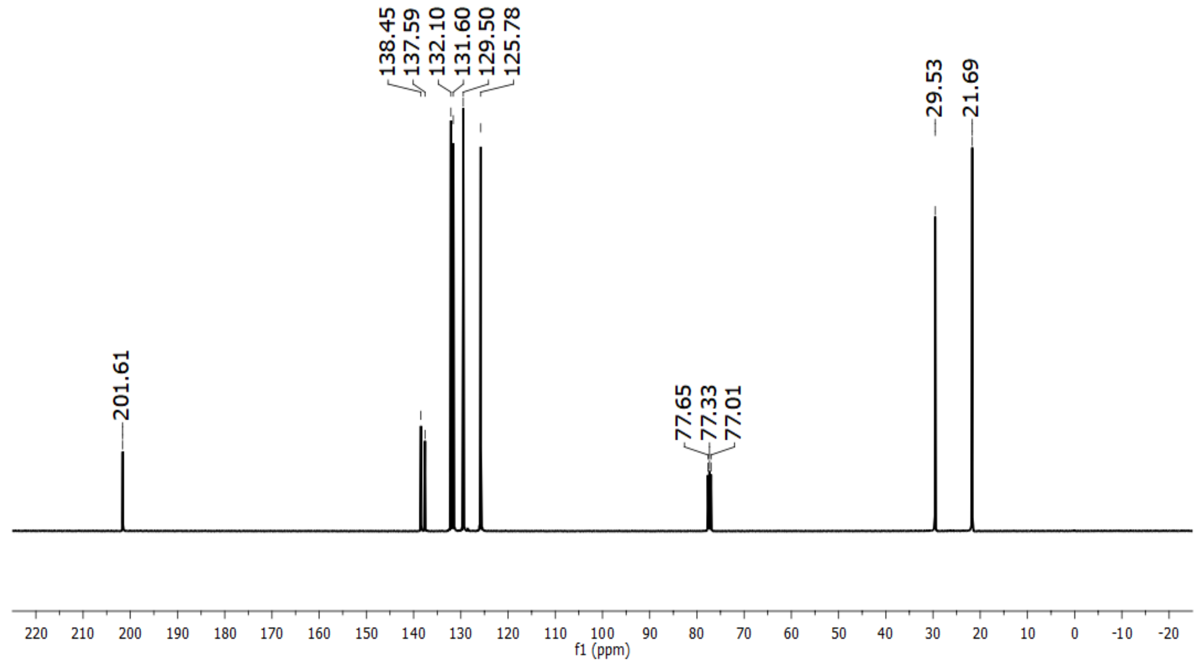
RK-MU-04-07-F
single pulse decoupled gated NOE

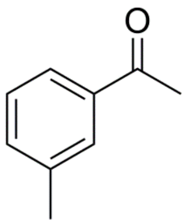


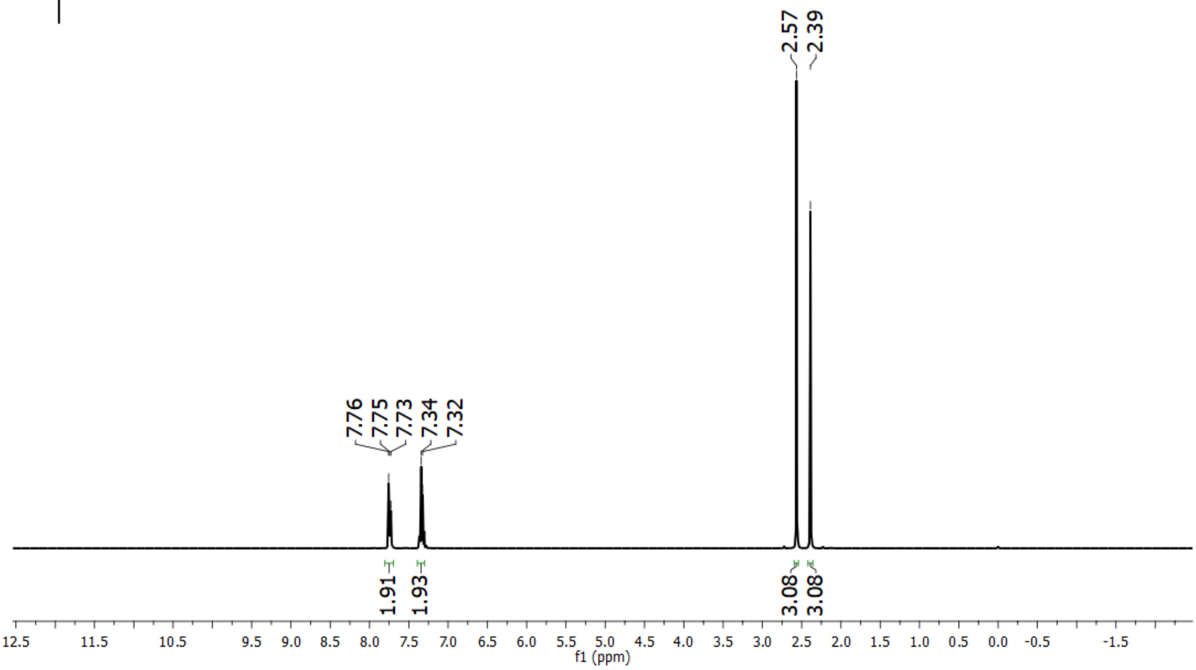




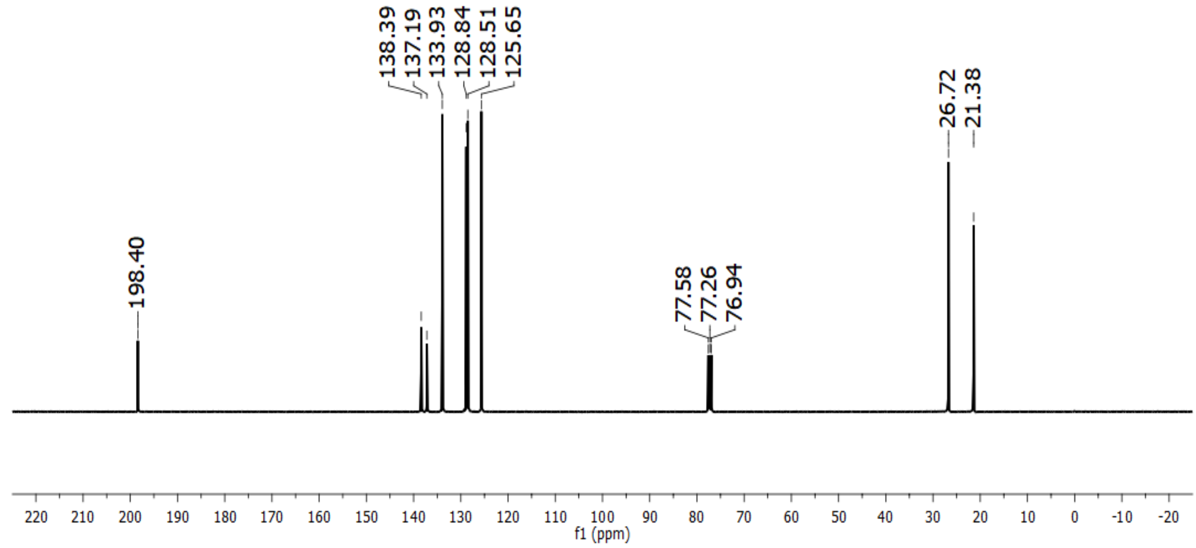
RK-MU-04-28
single pulse decoupled gated NOE

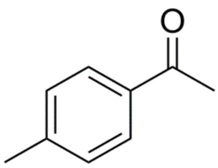


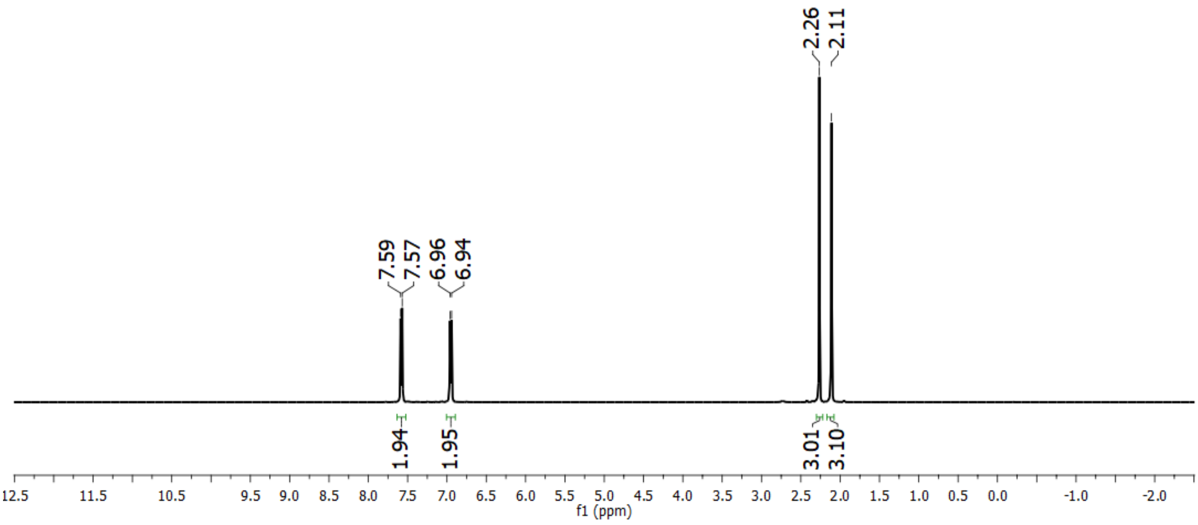




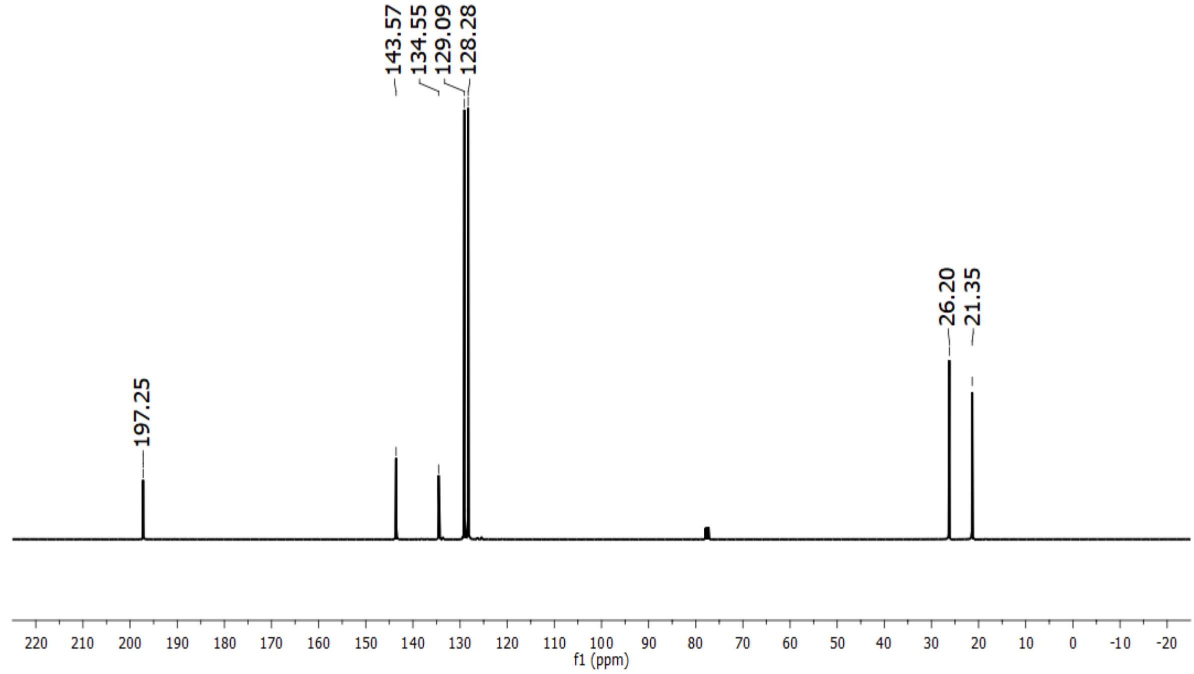
RK-MU-04-29-F
single pulse decoupled gated NOE

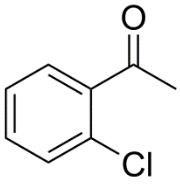


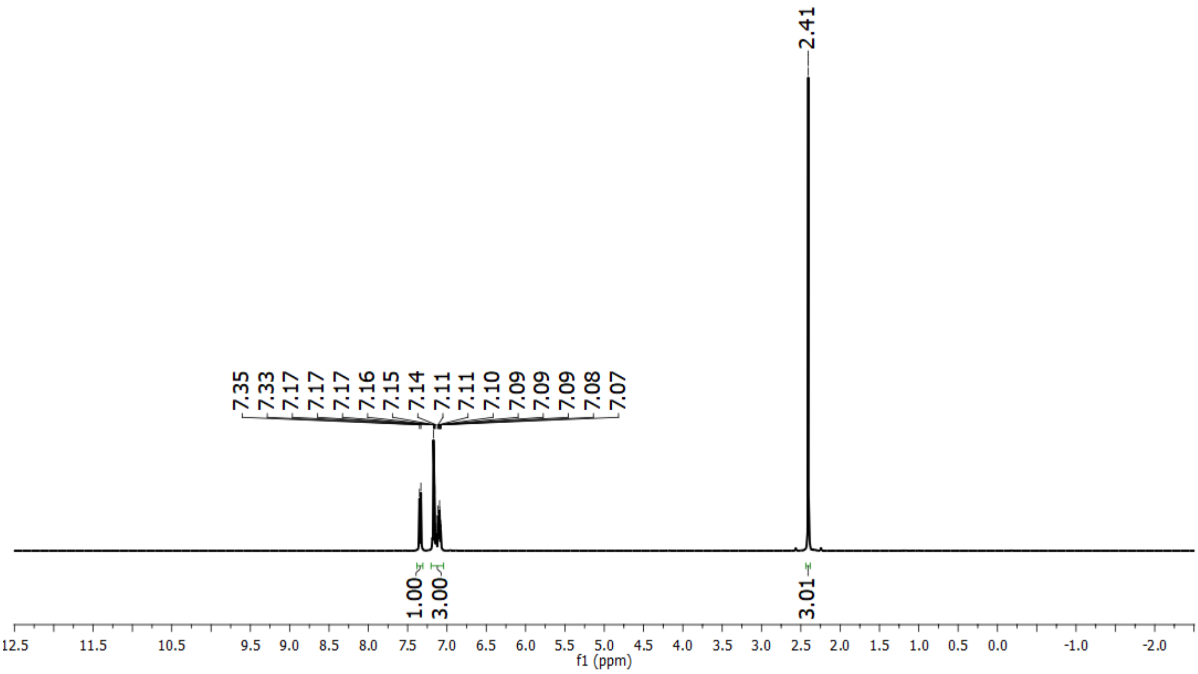




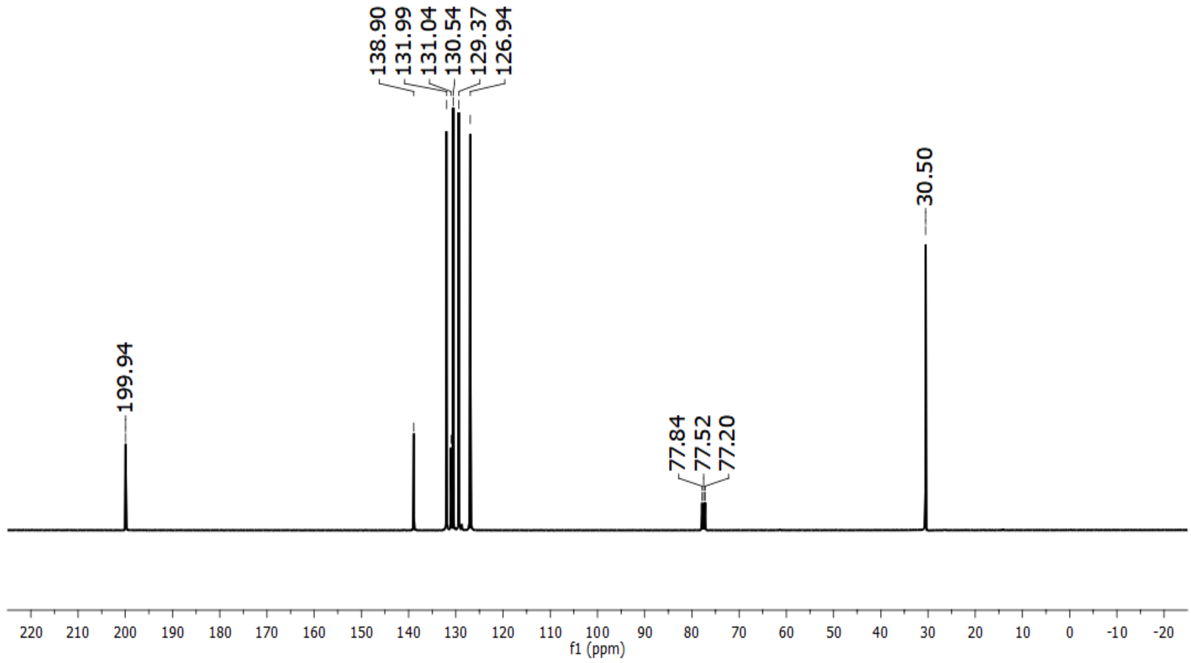
RK-MU-04-18-LF
single pulse decoupled gated NOE

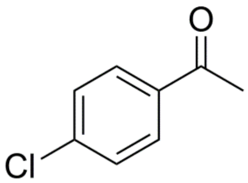


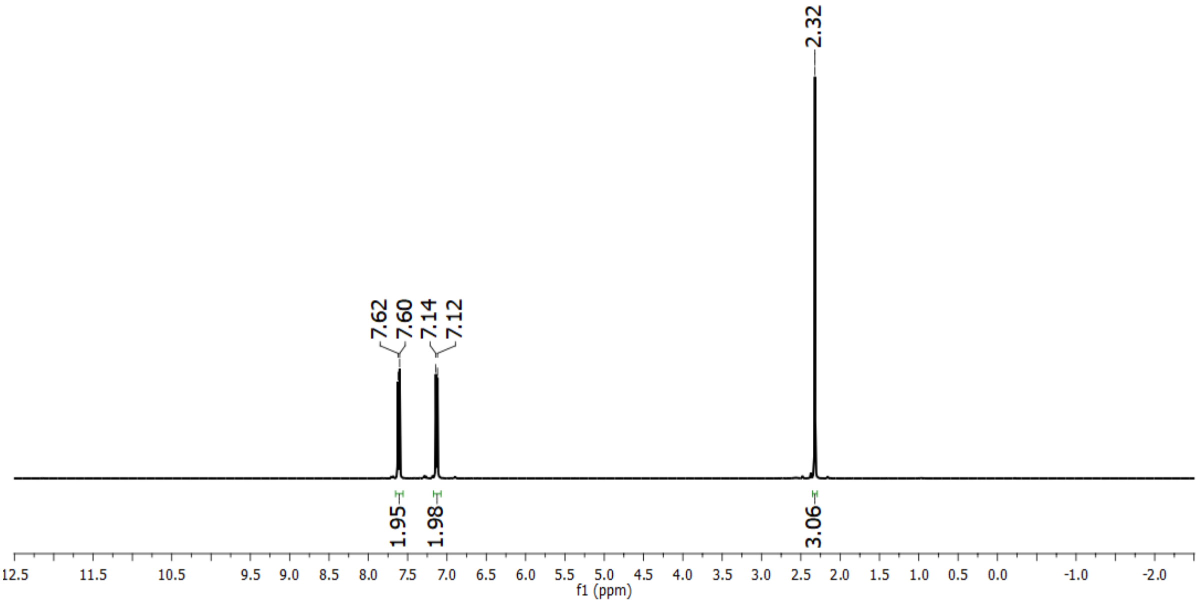




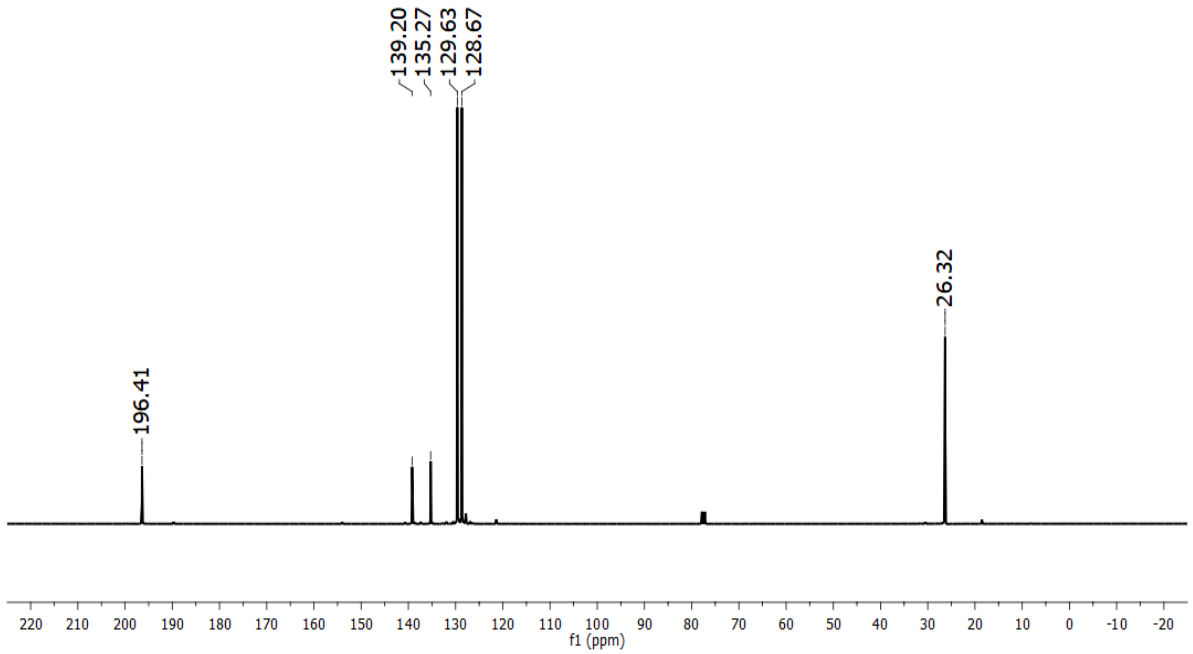
RK-MU-04-22-LF
single pulse decoupled gated NOE

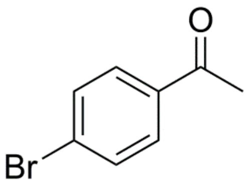


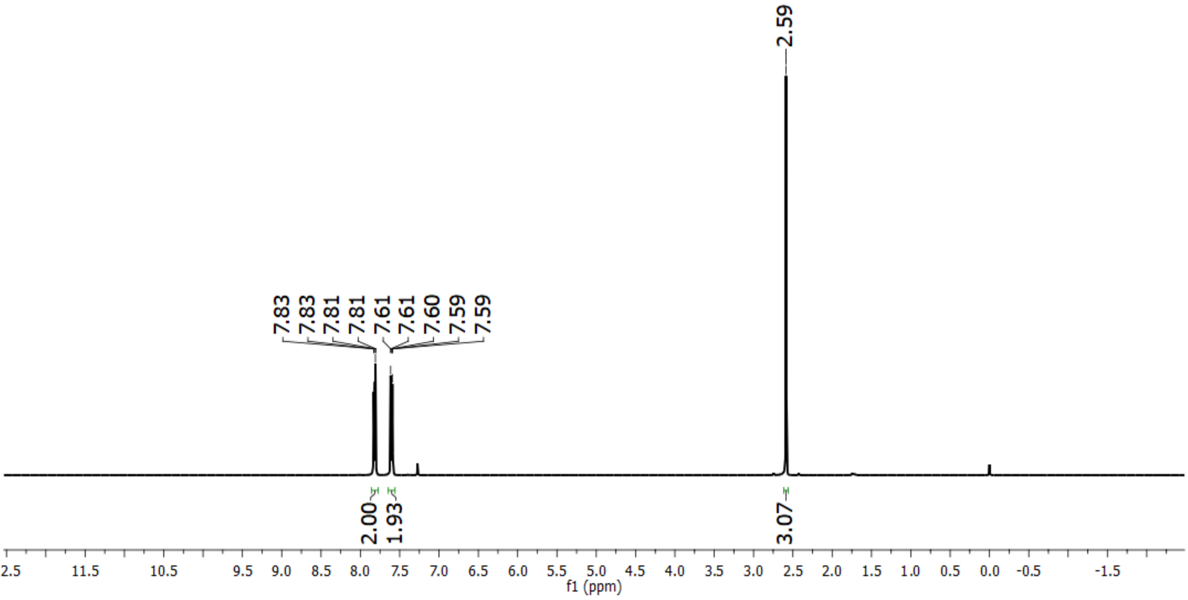




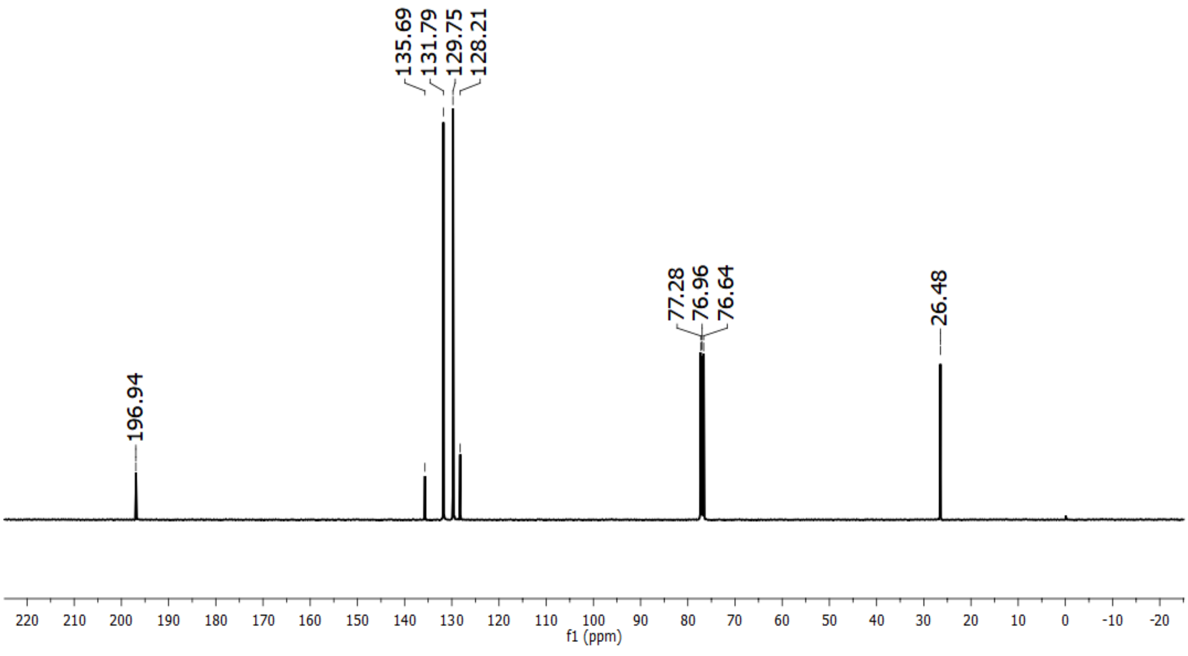
RK-MU-04-21-LF
single pulse decoupled gated NOE



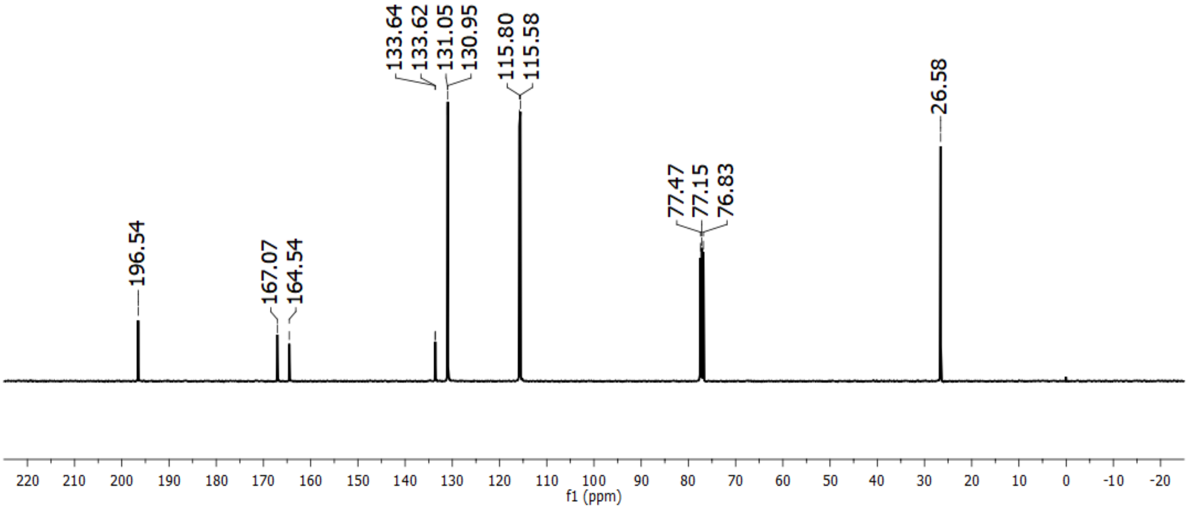


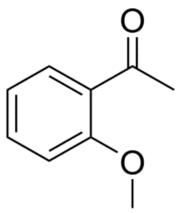


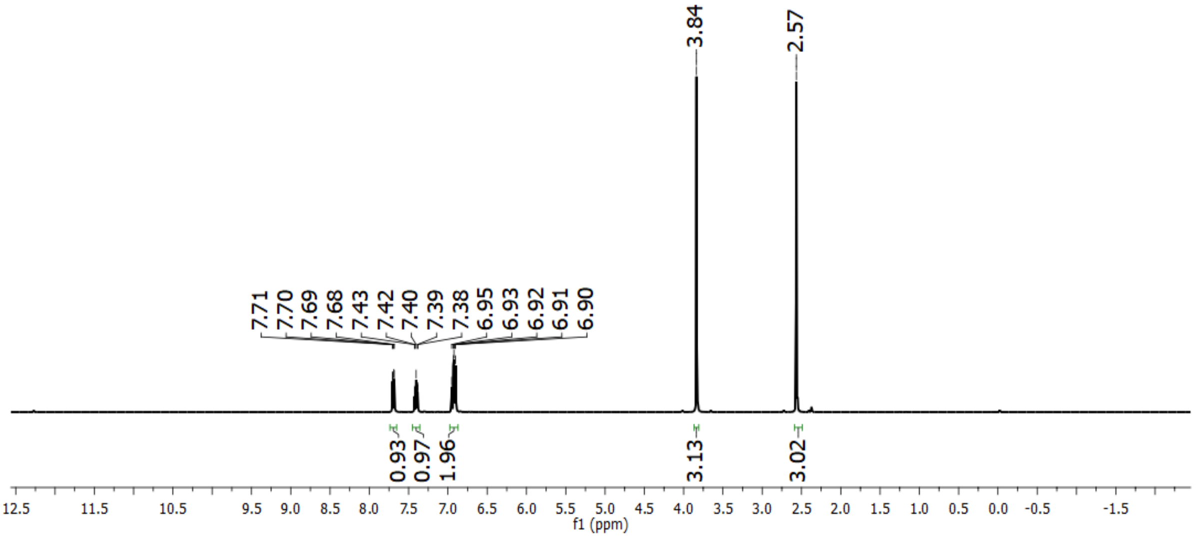
RK-MU-04-23-LF
single pulse decoupled gated NOE



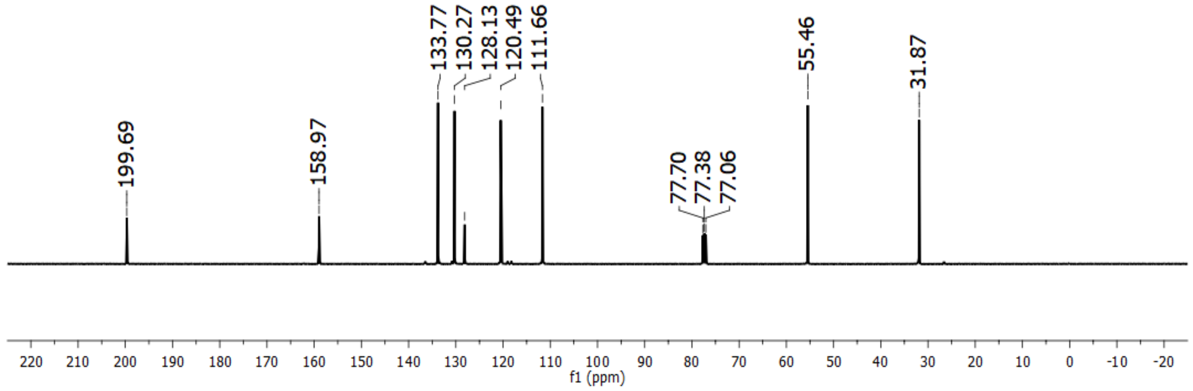
RK-MU-04-29-6
single pulse decoupled gated NOE

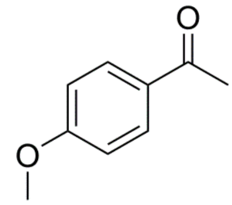


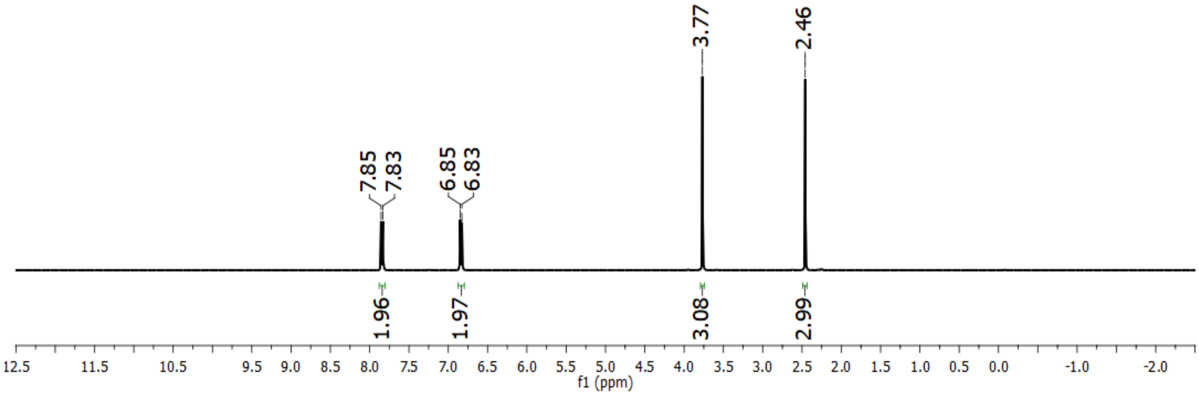




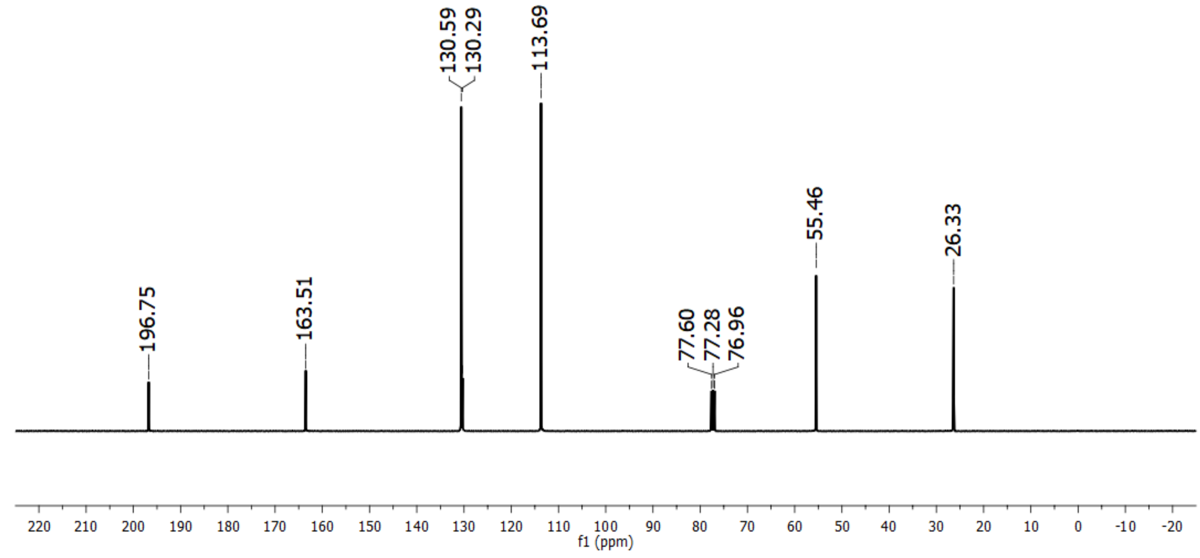
RK-MU-04-29-2
single pulse decoupled gated NOE

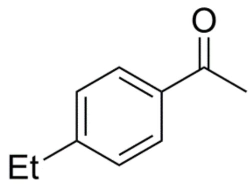


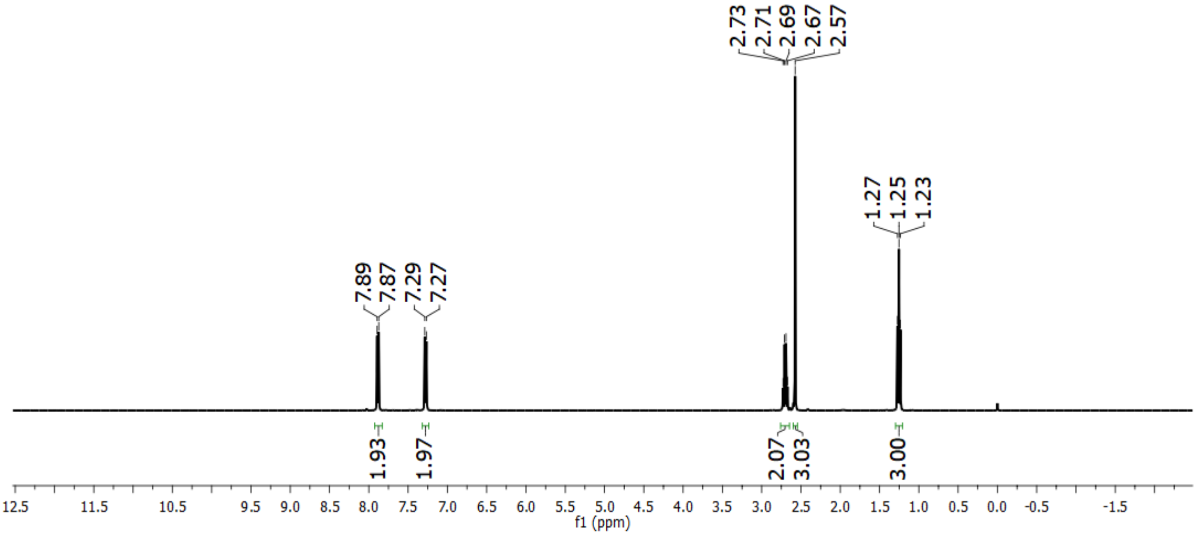




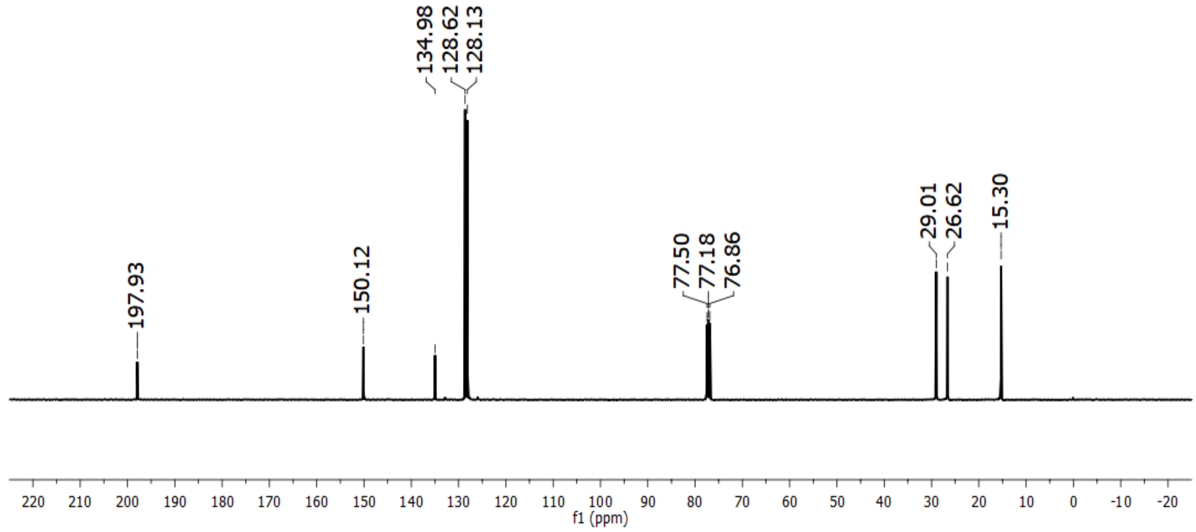
RK-MU-04-29-1
single pulse decoupled gated NOE

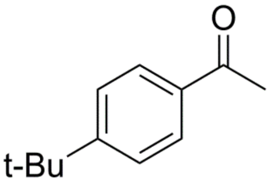


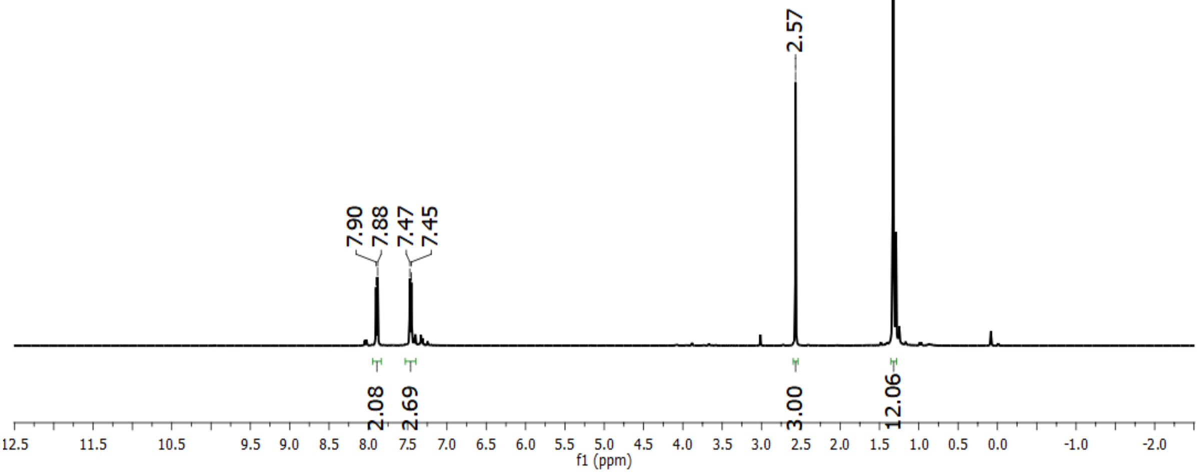




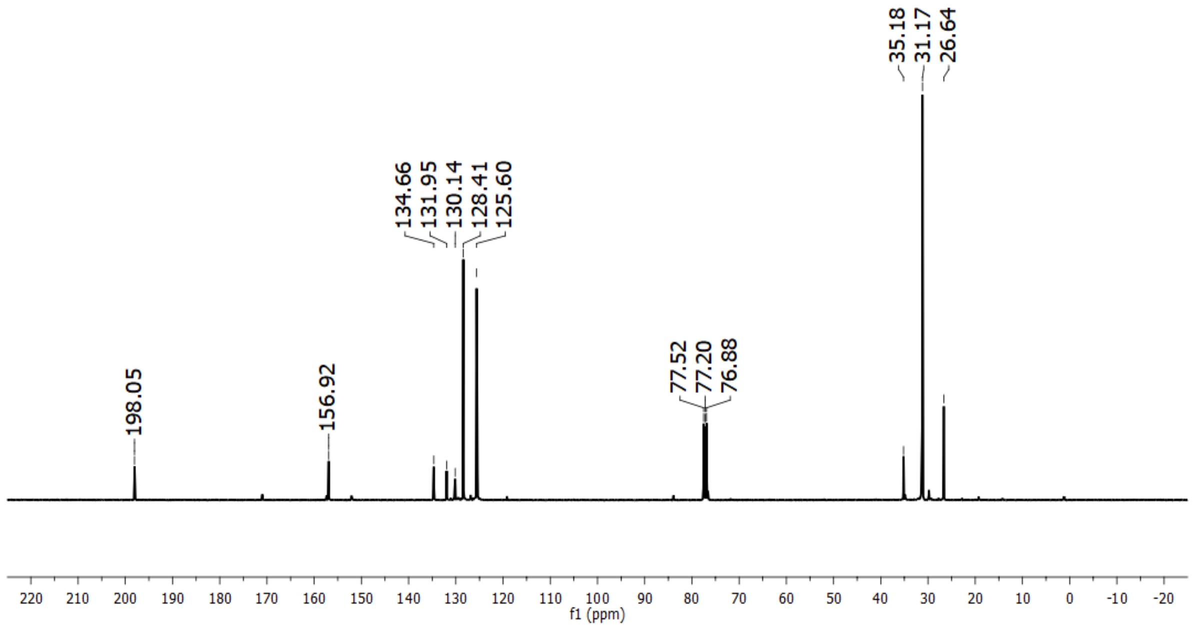
RK-MU-04-29-4
single pulse decoupled gated NOE

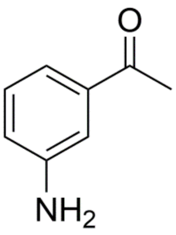


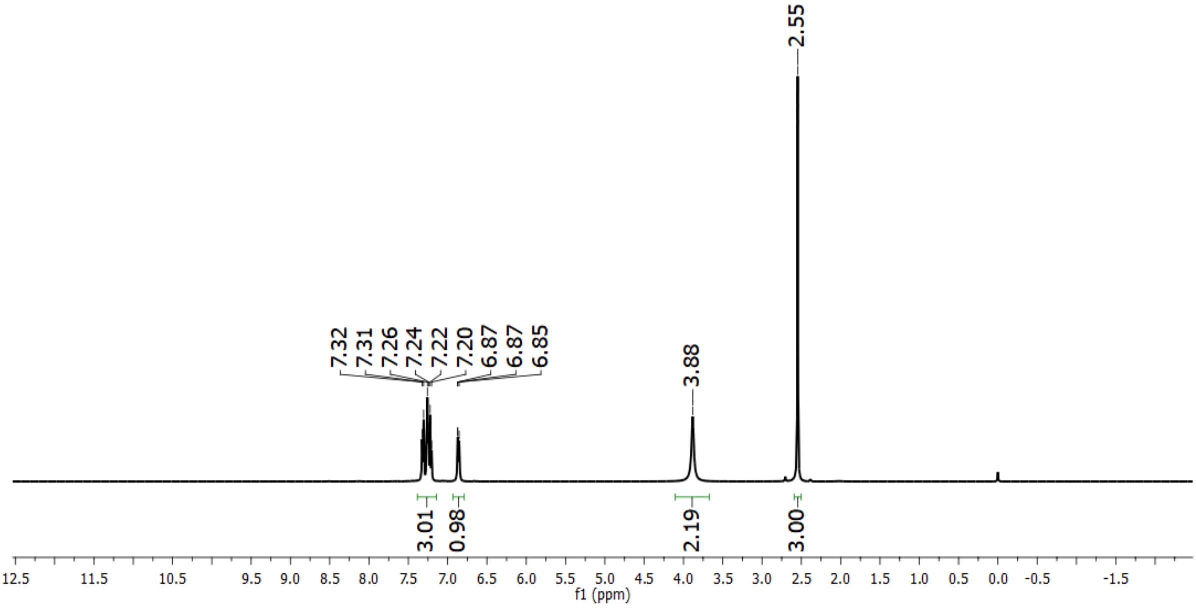




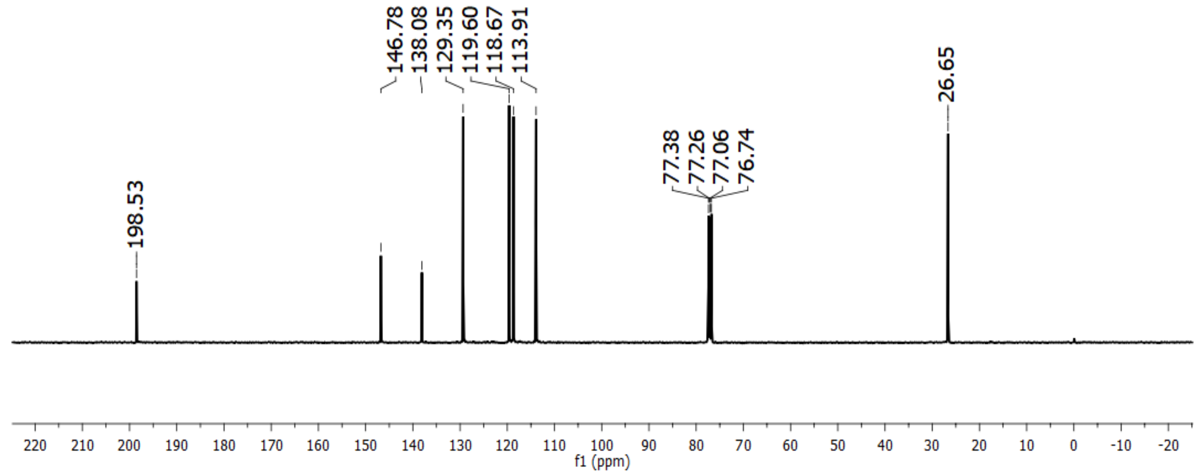
RK-MU-04-24
single pulse decoupled gated NOE

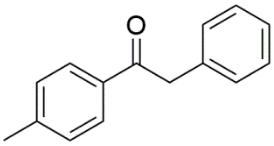


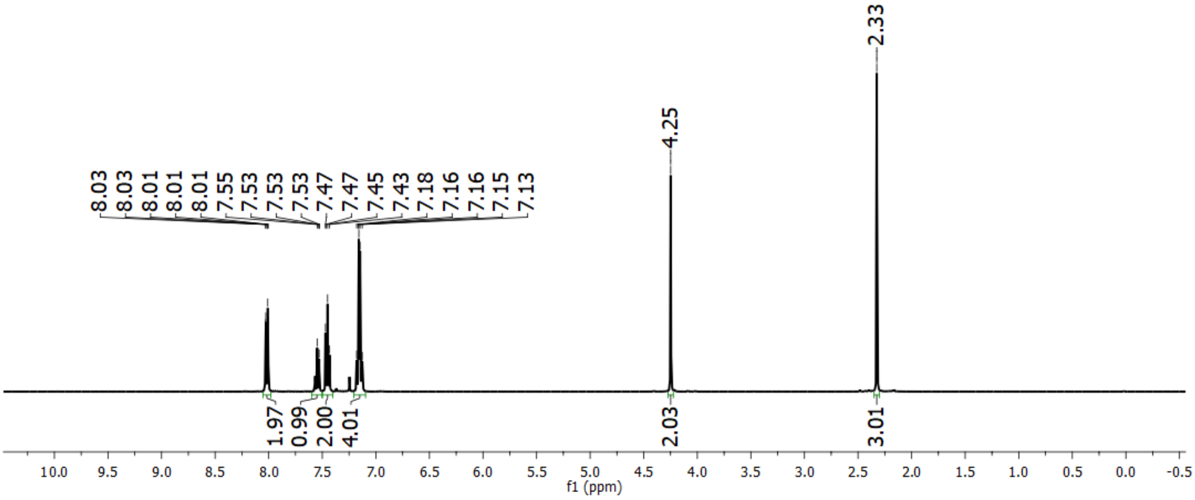




RK-MU-04-29-3
single pulse decoupled gated NOE







RK-MU-04-65
single pulse decoupled gated NOE