UNIVERSITY OF ZULULAND

Synthesis and Evaluation of Pd(II) and Ni(II) complexes as catalyst for Ethylene Polymerization

By

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Declaration

I, Zanele Felicia Dube, declare that the work presented in this Masters degree is, to the best of my knowledge my own work. It has not been submitted to any academic institutions for a degree award. Sources of information used have been acknowledged using appropriate referencing methods.

Signature: …….

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Dedication

To my Parents (Mr Elijah Dube and Mrs Eldah Dube) and Siblings

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List of Symbols and Abbreviations

^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance
FT-IR	Fourier transform infrared
GC	gas chromatography
MS	mass spectrometry
FID	flame ionisation detector
ESI	electron spray ionisation
cm^{-1}	reciprocal centimetre
Kg	Kilograms
g	grams
THF	Tetrahydrofuran
DCM	Dichloromethane
ppm	parts per million
TBAB	tetrabutylammonium bromide
NBS	N-bromo succinamide
$EtAlCl_2$	ethylaluminium dichloride
δ	chemical shift downfield from tetrametyl silane in ppm
cm^{-1}	reciprocal centimetre
J	coupling constant in hertz
s	singlet
d	doublet
t	triplet
m	multiplet
mL	millilitre
M	molar
Hz	Hertz
mol	mole
W	watts
ATR	attenuated total reflection
°C	degrees celsius
min	minutes

Ph	phenyl
^{t}Bu	tertiary butyl
Me	methyl
r.t	room temperature
pz	pyrazolyl
PI	polarity index

List of Formulae

$MgSO_4$	Magnesium sulphate
$NaHCO_3$	Sodium hydrogen carbonate
NaCl	Sodium chloride
Na_2CO_3	Sodium carbonate
$PdCl_2(NCMe)_2$	Palladium(II) dichloride acetonitrile
$NiCl_2$.DME	Nickel(II) chloride dimethoxyethane
$SOCl_2$	Thionyl chloride
NaOH	Sodium hydroxide
P_2O_5	Phosphorus pentoxide

Abstract

This study entailed the synthesis and evaluation of asymmetric palladium(II) and nickel(II) pyrazolyl hydrazide complexes, **C1-C6**, as catalyst for ethylene transformation reactions. The complexes were prepared from their respective pyrazolyl hydrazide ligands **L5a**, **L5b** and **L5c**, which were also prepared in this study. The synthesis of all ligands was achieved in five (5) steps from 3-bromomethyl benzoate, **L2**. Compound **L2** was prepared from bromination of methyl 3-methyl benzoate **L1**, using NBS. Benzene methylene pyrazolyl acids (**L3a-L3c**) were prepared from the reaction of **L2** with different pyrazolyl moieties, namely 3,5-dimethyl pyrazole $(Me)_2Pz$ = **L3a**, 3,5-diphenyl pyrazole $(Ph)_2Pz$ = **L3b** and 3,5-ditertiarybutyl pyrazole $(^tBu)_2Pz$ = **L3c**, under basic reaction conditions and were obtained in good yields of between 75-80%. Interestingly, the basic conditions used to anchor the pyrazole moieties readily hydrolyses the ester groups back to their corresponding acids. This meant the esterification reaction to be repeated to turn the acids back to esters for hydrozonolysis to be possible. Thus, preparation of the pyrazolyl hydrazide ligands **L5a**, **L5b** and **L5c** was successfully carried out from the corresponding pyrazolyl esters **L4a**, **L4b** and **L4c**, and the ligands were obtained in moderate yields of between 53-63%. All compounds including the final ligands were characterised using common analytical techniques.

The pyrazolyl hydrazide ligands **L5a-L5c** were successfully complexed with $PdCl_2(NCMe)_2$ and $NiCl_2$.DME giving square planar complexes **C1-C3** and tetrahedral metal complexes **C4-C5**, respectively, with a general formula $MLCl_2$. The complexes were obtained in moderate yields of 49-63% and were also characterised using appropriate analytical techniques.

The pyrazolyl hydrazide complexes (**C1-C6**) were successfully evaluated in the ethylene transformation reactions where the catalyst structure, type of solvent used and reaction conditions were found to play a vital role in activity and product distribution. For example, when toluene was used as solvent a mixture of hexene and alkylated toluene products were obtained with hexene and butyltoluenes being the major products. On the other hand running the reactions using chlorobenzene displayed better activities to produce C_{10}-C_{20} oligomers. The pyrazolyl hydrazide nickel(II) complexes, **C4-C6**, generally showed better activities when compared to the palladium(II) analogues.

CHAPTER 1

REVIEW ON TRANSITION METAL COMPLEXES AS CATALYST FOR ETHYLENE TRANSFORMATION REACTIONS

1 A Literature Review

1.1 Catalysis

Catalysis is a broad field that is subcategorized into two types namely, (i) homogeneous catalysis and (ii) heterogeneous catalysis. Heterogeneous catalysis is where the chemical state of the catalyst differs from that of the reactants, normally the catalyst will be supported in the solid state and the reactant is introduced in either the gas or liquid state. As a result, in heterogeneous catalysis separation of products is easy, and the catalyst is easily recycled but then the selectivity is poor. In homogeneous catalysis, the catalyst is in the same chemical state as the reactants, here separation of products is hard, and hence the catalysts are expensive to recycle. Nevertheless, the selectivity is very high.[1] In general, the former is preferred due to its advantages that outweigh those of the latter.[2] However, with homogeneous catalysis the advantage is that it has a wide spectral range of ligand-metal combinations to choose from to suit a specific need. In these combinations, the ligand can be endowned with properties that limit or induce steric hindrance and thus allowing the ligand to achieve a specific coordination geometry when bound to the metal centre.[3] This property is one of the most important features that is required for catalysts used in homogeneous catalysis.

Homogeneous catalysis is further divided into classes based on principle of the process, e.g. coupling reactions, hydrogenation, etc. The most studied homogeneous catalytic processes are polymerisation and oligomerisation reactions due to a high industrial demand of the materials produced using these processes.[4] As a result, development of cost-effective and highly efficient catalytic systems still remain the key focus in this area. To achieve this, some of the strategies that have been devised focus on ligand design optimazation. Plenty of ligands have been prepared and their complexes have been used as catalyst in polymerisation and oligomerisation reactions.[5] However, there is still room for improvement, from the perspective of ligand manipulation and optimization. The cost of ligand depends on the type of atoms present, for example phosphine containing ligands are more expensive as compared to the ones containing

[1] M. Clugston, R Flemming, *Advanced Chemistry*, (**2000**) 270.

[2] N.T. Phan, M. Van Der Sluys, C.W. Jones, *Adv. Synt & Cat*. 348 (**2006**) 609.

[3] (a) J. Tornatzky, A. Kannenberg, S. Blechert, *Dalton Trans.* 41 (**2012**) 8215. (b) Ragone, A. Poater, L. Cavallo, 2010. *J. Am. Chem. Soc*. 132 (**2010**) 4249.

[4] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Ingew. Chem. Int. Ed.* 38 (**1999**) 428.

[5] S.D. Ittel, L.K. Johnson, M Ittel, *Chem. Rev*. 100 (**2000**) 1169.

nitrogen. To reduce the total catalyst cost, the catalyst contaning both expensive metals and ligands should be avoided by simply complexing chepear ligands with expensive metals and expensive ligands with cheaper metals.

1.2 Polymerisation and oligomerisation reactions of ethylene using metal complexes

As already mentioned, olefin oligomerisation and polymerisation are industrial processes that require catalyst for the reaction to take place. Ethylene oligomers are short chained compounds while polymers are long chained carbon compounds. The differences in chain sizes (oligomers have units between 5 and 100 and polymers have more than 100 units) of these molecules lead to different chemical properties and applications. In general ethylene oligomers are used in other chemicals such as detergents and lubricants.[6] Ethylene polymers are used in the coating industry and also in plastic materials.[7]

Polymerisation of ethylene is a reaction where ethylene is converted into a polymer in the presence of a catalyst; mostly transition metal complexes are used. The first active catalyst for polyolefin reactions was introduced by Natta *et al*.[8] when they discovered that a combination of transition metal salts ($TiCl_3$, $AlCl_3$) and aluminium alkyls ($AlEt_2Cl$ and $AlEt_3$) can polymerise ethylene at low temperature and pressure. Soon after this discovery, metallocene complexes of the group IV transition metals were reported as catalyst for ethylene polymerisation and were again activated with aluminium alkyls. However, their activity and stability was very low and they received no attention as useful catalysts for ethylene polymerisation.[9] Kamisky *et al*.[10] reported the activation of zirconocene complexes with ethylaluminoxane (MAO) as a co-catalyst and observed high catalyst activities.

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[6] G.A. Olah, A, Molnar, *Hydrocarbon Chemistry*, Wiley-Interscience, New York, (**1995**) 421.

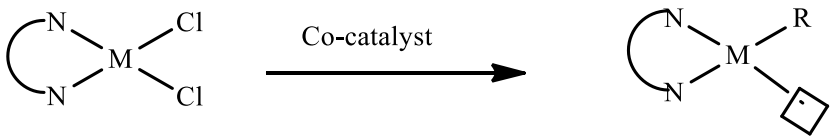
[7] J. Lange, Y. Wyser, *Package. Technol. Sc*.16 (**2003**) 149.

[8] G. Natta, P. Pino, G. Mazzanti, U. Giannini, *J. Am. Chem. Soc*. 79 (**1957**) 2975.

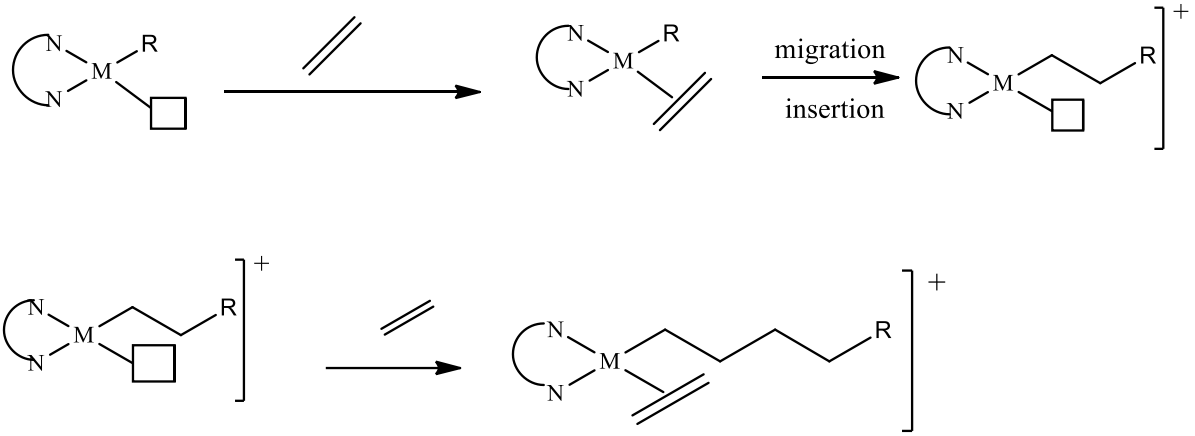
[9] (a) A. Andresen, H.G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.J. Vollmer, *Angew. Chem. Int. Ed*. 88 (**1976**) 688. (b) H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, *Angew. Chem. Int. Ed*. 92 (**1980**) 396.

[10] W. Kamisky, *J. Chem. Soc., Dalton Trans.,* (**1998**) 1413.

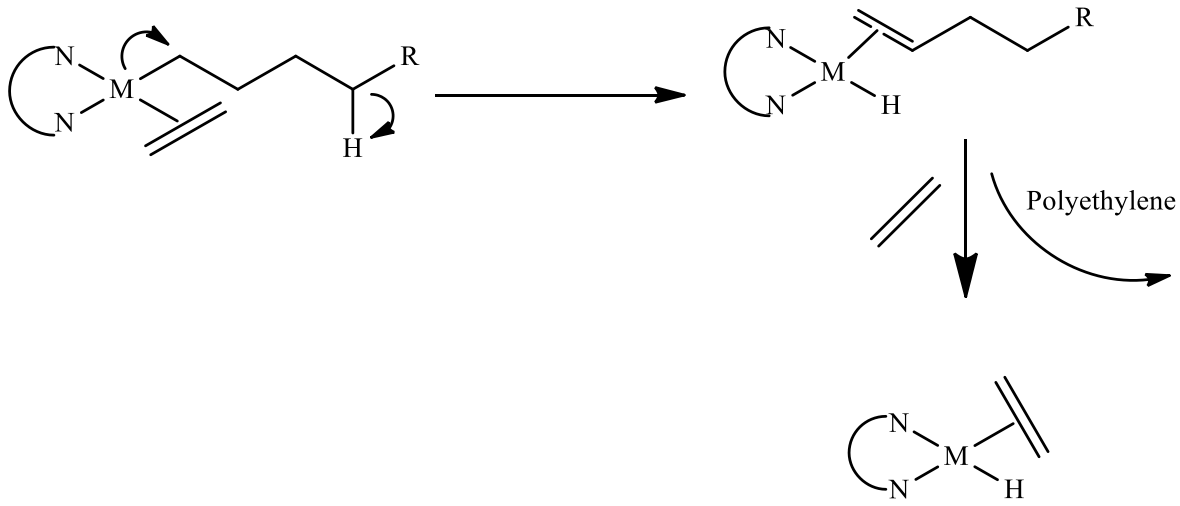
Initiation



Chain Propagation



Chain Termination



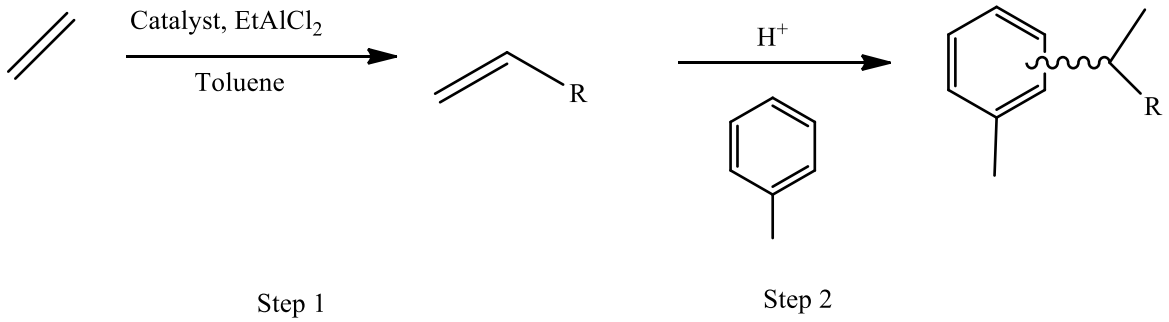
Scheme 1.1: Mechanism for olefin polymerisation

A mechanism that describes ethylene polymerisation reaction using a bidentate complex like those used in this study as an example is shown in Scheme 1.1. The overall mechanism is divided into three main steps, namely: initiation, chain propagation and chain termination. During initiation, the catalyst first undergoes activation by a co-catalyst through halide abstraction and formation of metal carbon bond by a co-catalyst. The role played by co-catalyst

on activity and product distribution will be discussed later in this chapter. The next step (chain propagation) after catalyst activation is the coordination of the ethylene to the metal centre. Ethylene uses the electrons in the p-orbitals to coordinate to the metal centre. At this stage, the metal atom is formally bonded to both carbons of the olefin. The second step involves "migration" of the alkyl group (R) from the metal atom to a carbon atom of the ethylene. This step results in destruction of the ethylene pi-bond, and the metal atom is left bonding only to one carbon and open a coordination site. This step also involves the rotation of the single bond of the extended alkyl group and it occurs at about the α-β position of the single bond. This moves the R group out of the way so that another ethylene molecule can coordinate to metal in the next step. Another alkyl migration can take place so to open another site for the next ethylene to bind and the reaction continues for the polymer to grow longer.[11] The last step (chain termination) is β-hydride elimination, which involves migration of a hydrogen atom on the β-carbon of the alkyl (growing polymer) chain back to the metal centre, followed by dissociation of the polymer from the metal centre.

1.3 Friedel-Craft alkylation of oligomers

During ethylene transformation reactions in cases where oligomers are obtained as products, under certain conditions the oligomers can be coupled to toluene when toluene is used as a solvent to form alkylated toluenes. The mechanism for the formation of alkylated toluene products shows that the two reactions takes place one after another, here the first step is ethylene oligomerisation followed by the alkylation of the formed oligomers to the toluene solvent.[12]



Scheme 1.2: Mechanism for Friedel-Craft alkylation of oligomers in toluene

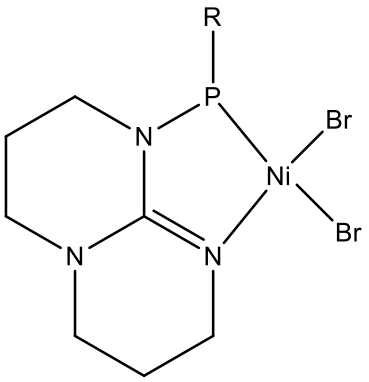
[11] (a) G.W. Coates, R.M. Weymouth, *J. Am. Chem. Soc*. 115 (**1995**) 6465. (b) R. Cramer, *J. Am. Chem. Soc*. 87 (**1965**) 4717.

[12] P.W. Dyer, J. Fawcett, M.J. Hanton, *Organometallics* 27 (**2008**) 5082.

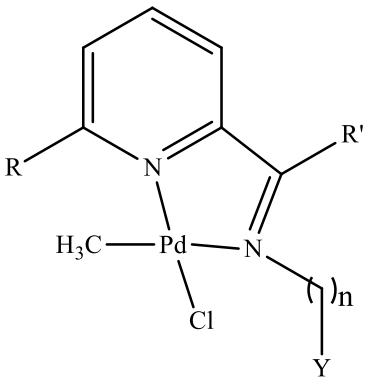
The combination of both neutral chelating P^N and N^N-ligands with Ni(II) has been shown to be very effective for the catalytic oligomerization of ethylene, manipulating the electronic and steric properties of these ligands can be used to control reaction activity and products selectivity. In catalytic transformation reactions, factors such as type of co-catalyst and solvent have been reported the major factors to play a vital role in product selectivity and catalyst activities as well.

1.3.1 The role played by catalyst structure on product selectivity

The role played by catalyst structure in product selectivity has been shown by Dyer *et al.*[11] using N-Phosphino Guanidine nickel(II) catalysts **1a-c** in toluene and $EtAlCl_2$ as co-catalyst. They observed that the Ni(II) catalyst gave different mixtures of butenes (C_4), hexenes (C_6), and traces of octenes (C_8) as products. Product selectivity depended on the nature of the phosphorus-donor atom; here only catalyst **1b** gave alkylated products with all the catalysts showing reasonable selectivity towards C_4. Obuah *et al.*[13] used *bis*-(3,5-dimethylpyrazol-1-ylmethyl)benzene nickel(II) catalyst and $EtAlCl_2$ as co-catalyst and observed C_4, C_6 and mixture of alkylated products. They observed that product selectivity depended on both the substituents on the pyrazole ring and the metal halide. For example Catalyst **2a** selectively gave alkylated products and no oligomers were observed.

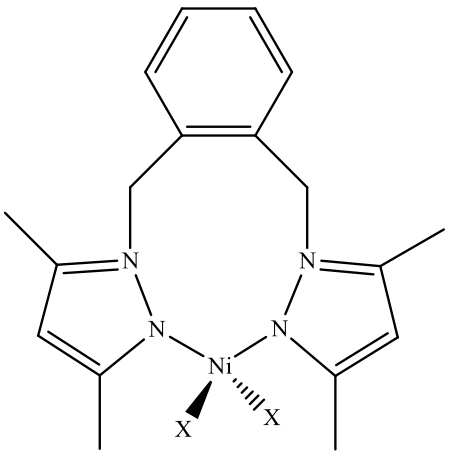


R = Ph **1a**
R = Ph_2N **1b**
R = *i*-Pr_2N **1c**

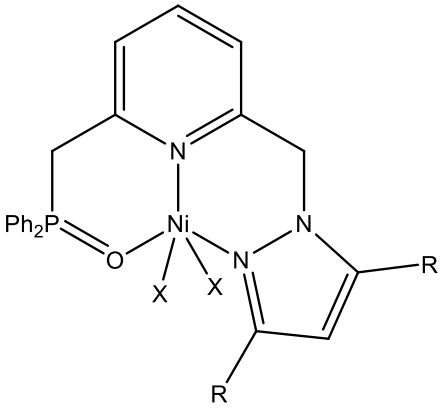


R = H, R' = Me, n = 2, Y = OMe **2a**
R = H, R' = H, n = 2, Y = NEt_2 **2b**

[13] A. Budhai, B.Omondi, S.O. Ojwach, C. Obuah, E.Y. Osei-Twum, J. Darkwa, *Catal. Sci. Technol.* 3 (**2013**) 313.



X = Cl **3a**
X = Br **3b**



R = Me, X = Cl **4a**
R = Me, X = Br **4b**
R = Ph, X = Br **4c**

Figure 1.1: Examples of the Ni(II) and Pd(II) complexes as catalysts for Ethylene transformation reactions

Nyamato *et al.*[14] used hemilabile (imino) pyridine palladium(II) complexes **2a** and **2b** and observed that they selectively dimerise ethylene when activated with MAO in toluene solvent. When the ester group in catalyst **2a** was replaced with bulkier substituent, the percentage of the C_4 product increased from 84% to 91%. Current trends favour the use of Ni(II) complexes over Pd(II) complexes in ethylene transformation reactions because of higher activities normally observed with the former. It is therefore not clear how Pd(II) complexes behave especially when activated with $EtAlCl_2$ towards oligomerisation and alkylation when reactions are done in toluene. One area of focus in this thesis will be to explore to see if there is any correlation in activities between the Ni(II) and Pd(II) complexes.

The role played by the co-catalyst has been reported by Nyamato *et al.*[15] using (pyrazolyl)-(phosphinoyl)pyridine nickel(II) catalysts **4a-c.** Different co-catalysts such as MAO, $EtAlCl_2$ and $EtAlMe_3$ were used for these reactions and they reported different activities and products selectivity where the reactions were done in toluene using different co-catalysts. They obtained alkylated toluene products only when $EtAlCl_2$ was used as a co-catalyst and oligomers were produced when MAO and $EtAlMe_2$ co-catalysts were used.

[14] G.S. Nyamato, S.O. Ojwach, M.P. Akerman, *Organometallics* 34 (**2015**) 5641.

[15] G.S. Nyamato, M.G. Alam, S.O. Ojwach, M.P. Akerman, *J. Organomet. Chem*. 783 (**2015**) 64.

1.3.2 Role played by different reaction conditions on product selectivity

Different reaction conditions such as time, temperature and pressure are known to play an important role on product selectivity as well. Most of all temperature has been reported to have great influence on the formation of alkylated products when toluene is used as solvent for ethylene transformation reactions. Gau *et al.*[16]observed alkylation of toluene to occur only at a temperature of 50 °C and they suggested that at elevated temperature the co-catalyst creates an acidic condition which triggers alkylation of toluene.

1.4 Early transition metal catalysts

It was Ziegler and Natta who discovered that trialkylaluminium activated based catalysts were highly active in olefin polymerisation reactions.[17] Their discovery laid a foundation of a catalyst known as the Ziegler-Natta Catalyst that is still being used in industry today. In spite of their great discovery. This multiple site catalyst led to the incoporation of co-monomers in the resultant co-polymers. The discovery of metalocene compounds provided a solution to the issue of non-uniform incoporation of monomers.

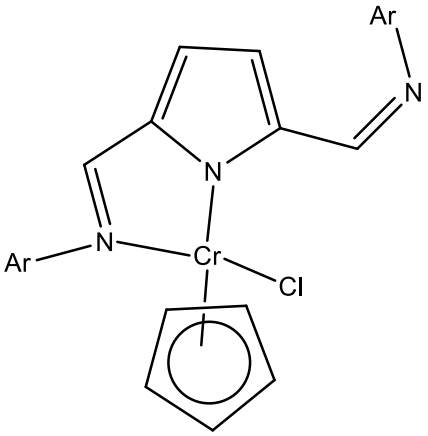
1.5 Mixed half-sandwiched compounds as catalyst for ethylene polymerisation

The mixed half sandwiched compounds consist of a ring bridged to the cyclopentadiene (Cp) ring similar to the metallocene compounds. Developments in Cp-based catalyst have been made using ligands containing an additional neutral donor, either bridged or unbridged to the Cp unit. Example is the bis(imino) pyrole ligands in Figure 1.2 which are related to the cyclopentadiene ligands both from electronic and steric perspectives.[18] These ligands are bidentate with one of the imino nitrogen atoms forming a sigma (σ) bond when coordinated to the Cr metal. These complexes adopt a pseudo-octahedral coordination environment with three-legged piano stool geometry in the solid state. In the complex, Figure 1.2, both the cyclopentadienyl group and the anionic donor ligand control the behaviour of such complexes towards polymerization of ethylene when used as catalyst

[16] K. Song, H. Gao, F. Liu, J. Barn, L. Guo, S. Zai, Q. Wu, *Eur. J. Inorg. Chem*. 20 (**2009**) 3016.

[17] (a) K. Zingler, E. Holzkaamp, H. Martin, H Breil, *Angew. Chem*. 67 (**1955**) 541. (b) G. Natta, *Angew. Chem*. 68 (**1956**) 393.

[18] W.K. Reagan, EP 0 417 477 (Phillips Petroleum Combarny), March 20 (**1991**).



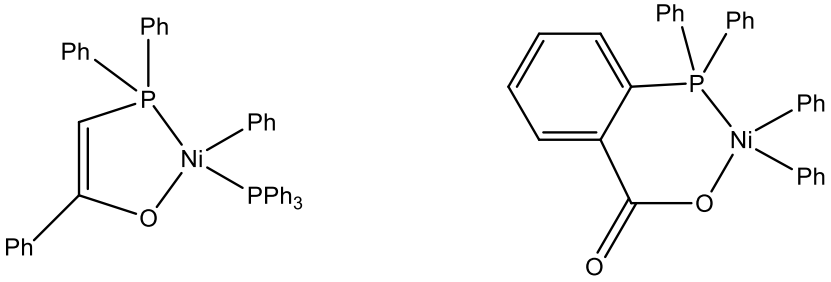
Ar	
C_5H_5	**5a**
2,6-Me_2-C_6H_3	**5b**

Figure 1.2: Half-Sandwich Cr(III) complexes

Increasing the bulkiness on catalyst **5a** increased activities from 1170 kg.mol^{-1}.h^{-1} to 1320 kg.mol^{-1}.h^{-1} for catalyst **5b**. High molecular weight polymers with unimodal molecular weight distributions were obtained for both the catalysts, indicating that the nature of the polymerization was single site.[19]

1.6 Late transition metals as catalyst for polyethylene reactions

Shell Higher Olefin Process (SHOP), contributes about 30% of linear α-olefin production worldwide every year. SHOP is a chemical process which was discovered by Shell Development Emeryville and is used for the production of linear α-olefins using both the



6 **7**

Figure 1.3: Examples of SHOP Catalyst

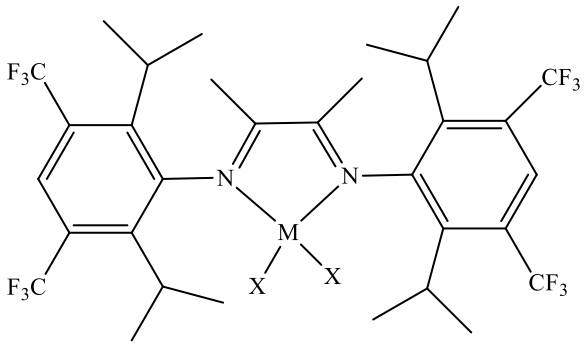
[19] J.Y. Liu, P. Tao, Y.X. Wang, Y.S. Li, *RSC Adv.* 4 (**2014**) 19433.

ethylene oligomerisation and metathesis processes which were first discovered by Royal Dutch Shell. In this reaction olefin products are first converted to fatty aldehydes then latter to fatty alcohols using the nickel catalysts such as **6** and **7** shown in Figure 1.3.

In 1977, Keim reported the use of the P^O cationic Ni(II) complexes as catalyst for ethylene polymerisation.[20] These complexes have an ability to control the selectivity for ethylene oligomerisation which makes them better than other phosphine ligands which only stabilise the catalyst. After the Keim's system other phosphorus late transition metal catalysts were developed to be used as catalyst for preparing polyethylenes. However, phosphines being expensive opened a window of opportunity for a search of suitable donor atom to replace phosphines and nitrogen donor ligands have been shown to be appropriate cheaper substitutes.

1.7 Nitrogen donor late transition metals catalysts

One of the well-known late transition metal catalysts that contain the nitrogen donor atoms is the α-diimine system which was designed in 1995 by Brookhart *et al.*[21] Moderate to high activities were reported when these ligands were incorporated in catalysts used for polyethylene production. It was observed that activity in this system was depended on the size of the substituents attached to the ligands. This behaviour emphasized the role played by ligands on the performance of the catalysts in olefin polymerisation reactions.



M	X	
Pd	NCMe	**8a**
Ni	Br	**8b**

Figure 1.4: Example of an α-diimine late transition metal catalyst

[20] W. Keim, F.H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl*. 17 (**1978**) 466.

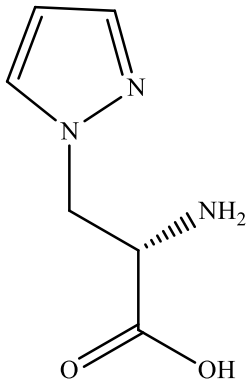
[21] F. Rix, M. Brookhart, *J. Am. Chem. Soc.* 117 (**1995**) 1137.

The other type of Ni(II) diimine complexes were reported with less bulky substituents, by the same group.[22] The report demonstrated that sterically unhindered Ni(II) catalysts dimerized propylene; this revealed the flexibility of this class of catalysts and confirmed their sensitivity to steric tuning. The discovery of these highly active nickel and palladium diimine olefin polymerization catalysts by Brookhart and co-workers led to an expansion of interest in the use of late transition metal catalysts, especially Ni(II) and Pd(II) complexes with nitrogen donor atoms in olefin transformation reactions in general.

1.8 Pyrazole and pyrazolyl late transition metal catalyst

1.8.1 Pyrazoles occurrence and preparation

Simple pyrazole ligands are 5 membered heterocyclic compounds with two nitrogen atoms in adjacent positions.[23] They are classified as alkaloids, a naturally occurring type of organic compounds. The 1-pyrazolyl-alanine, **9** Figure 1.5 is one of the few naturally occurring pyrazolyl compounds. It was isolated as an amino acid from dry seeds of water melon by Noe *et al*.[24] Only a few pyrazole derivatives have been found to occur naturally, most of them are prepared in laboratories using classical methods of synthesis and are also commercially available.



9

Figure 1.5: Structure of 1-pyrazolyl alanine

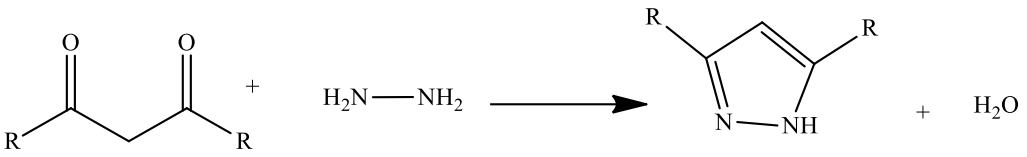
[22] M. Brookhart, S.A. Svejda, *Organometallics* 18 (**1999**) 65.

[23] Y. Han, H.V. Huynh, *Dalton Trans*. 40 (**2011**) 2141.

[24] F.F. Noe, L. Fowden, *Biochem. J*. 77 (**1960**) 543.

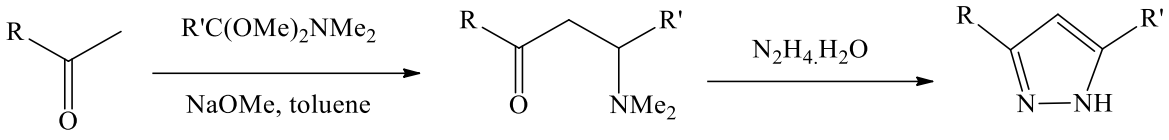
Pyrazoles can be prepared easily in the laboratory using two different methods, from the reaction of hydrazine with diketones or by the Villsmell reaction, as shown in Scheme 1.3.

(a)



Where R = Me, Ph and ^{t}Bu

(b)



Where R = R' = Me, Ph and ^{t}Bu

Scheme 1.3: General synthesis of simple pyrazoles by (a) Condensation of 1,3-diketones with hydrazine.[25] (b) The Villsmell reaction.[26]

1.8.2 Pyrazole as ligands

Pyrazole compounds as ligands have been used to prepare complexes for ethylene polymerisation and oligomerisation. One of the examples is the palladium pyrazolyl catalysts with different substituents on the 3 and 5 positions of the pyrazole ring (**10a** and **10b**) in Figure 1.6 reported by Li *et al.*[27] However, the polymerisation activities were not as high as those reported for diimine catalysts because of the weak basic nature of pyrazole rings as compared to pyridines and imines.[28] The low activities with late transition metal pyrazole catalyst shifted the research focus to incorporate motifs with linkers to enable pyrazole ligands to be anchored to these and to ascertain if this would improve the activity. For that reason pyrazole compounds as moieties were then anchored on different backbones with or without linkers to tune them for

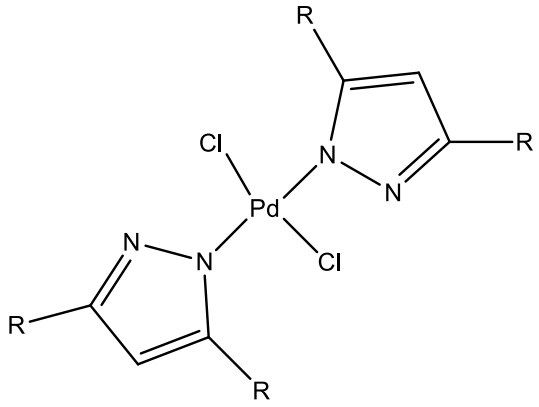
[25] D.J. Babinski, H.R. Aguilar, R. Still, D.E. Frantz, *J. Org. Chem*. 76 (**2011**) 5915.

[26] D.L. Reger, J.R. Gardinier, T.C. Grattan, M.R. Smith, M.D. Smith, *New J. Chem*. 27 (**2003**) 1670.

[27] K. Li, J. Darkwa, I.A. Guzei, S.F. Mapolie, *Organometallics* 660 (**2002**) 108.

[28] J. Perez, L. Riera, *Chem. Rev*. 37 (**2008**) 2658.

better activities, this included the use of pyridine and benzene rings as backbones for pyrazole containing compounds.[29]



R = Me (**10a**), R = ^{t}Bu (**10b**)

Figure 1.6: Example of complexes with pyrazole ligands

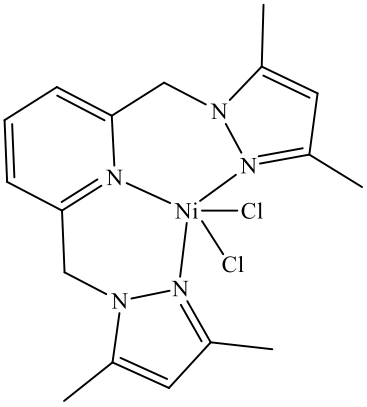
An attractive feature of polypyrazolyl ligands is their ability to stabilise transition metal centres at both low and high oxidation states.[30] The pyrazole ligands are easily modified and can be anchored on different backbones such as pyridine and benzene. Metal complexes bearing pyrazolyl ligands, when used as catalyst for ethylene transformation reactions their activity is dependent on the type of backbone a pyrazole moiety is anchored on. The nature of the backbone controls the stability and flexibility of the ligand while the substituents on the pyrazole contribute to the activity of the metal complex which can be improved by changing substituents on the pyrazole ring.

Pyridine pyrazolyl catalysts have been reported as better ligands to catalyse olefin transformation reactions, because of the strong σ donor ability from their nitrogen atom which allow fast coordination of the substrates before they are converted into products.[31]

[29] S.O. Ojwach, J. Darkwa, *Inorg. Chim. Acta*.363 (**2010**) 1947.

[30] T.A. Hafeli, F.R. Keene. *Aust. J. Chem*. 41 (**1988**) 1379.

[31] S. Tsuji, D.C. Swenson, R.F. Jordan, *Organometallics* 18 (**1999**) 4758.



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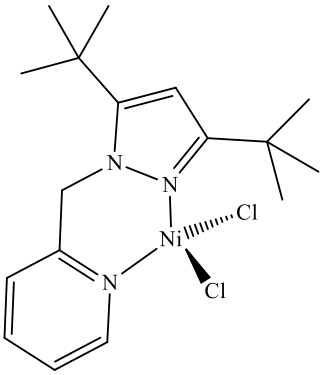

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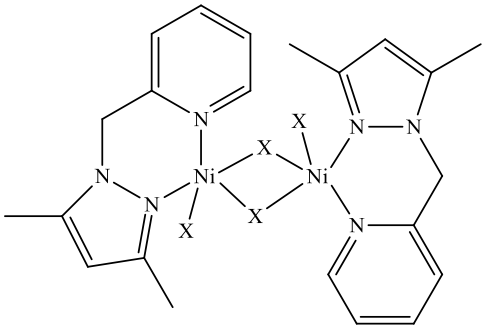


X = Cl **13a**

X = Br **13b**

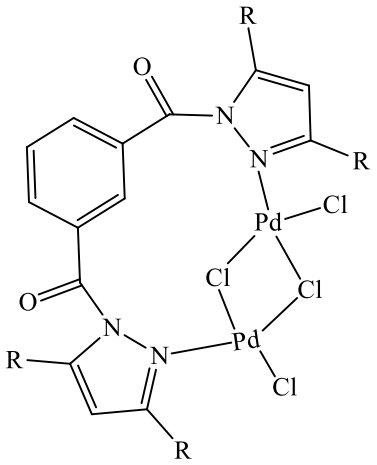
Figure 1.7: Selected examples of pyridine methylene pyrazolyl ligands

Changing bulkiness on the substituents of the ligands, affect the type of olefin product obtained. Steric hindrance on these ligands has been observed to prevent β-hydride elimination leading to the formation of high molecular weight polymers. On the other hand the absence of steric hindrance permits β-hydride elimination leading to the formation of oligomers. Ojwach *et al*.[32] reported the use of pyridine methylene pyrazolyl nickel(II) complexes **11-13** as catalysts for polyethylene reactions. The complexes when activated with $EtAlCl_2$ oligomerize ethylene to C_4, C_6 and C_8 products. Using complexes **12** and **13** displayed in Figure 1.7, the products subsequently undergo complete alkylation in toluene to form alkyltoluenes.

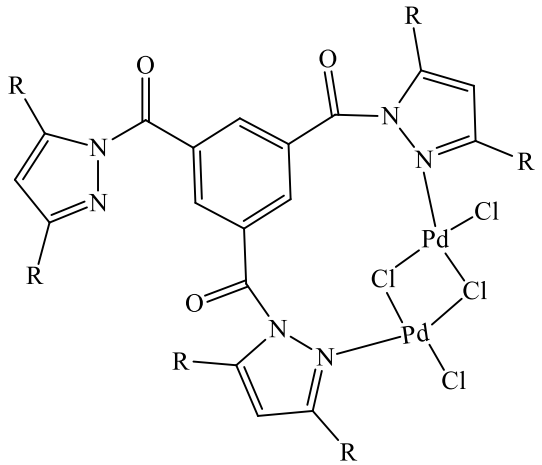
[32] (a) S.O. Ojwach, I.A. Guzei, J. Darkwa, S.F. Mapolie, *Polyhedron*. 26 (**2007**) 851. (b) L.C. Spencer, I.A. Guzei, S.O. Ojwach, J. Darkwa, *Acta Crystallogr*. 64 (**2008**) 114.

1.8.3 Poly(pyrazolyl) compounds with benzene backbone

Darkwa and co-workers have used a lot of benzene pyrazolyl-containing compounds as catalysts for ethylene polymerisation. Some of the catalysts the group reported are displayed in Figure 1.8. Li *et al*.[33] reported the preparation and catalytic evaluation of benzene 1,3-dicarbonyl pyrazolyl ligands complexed with Pd(II) and Ni(II) metals. The complexes were first activated using methylaluminoxane (MAO) as a co-catalyst, prior to ethylene polymerisation reactions. The bulkiness on the pyrazole ring help increase the solubility of these catalysts when toluene is used as a solvent thus increasing activity of the catalyst towards transformation reactions. The activity of the catalysts decreased in the order **14a** > **15** > **14b** in Figure 1.7. High density polyethylene olefin was obtained when these complexes were used as catalyst.



14a R= Me, **14b** R= ^{t}Bu



15 R= ^{t}Bu

Figure 1.8: Examples of Benzene carbonyl pyrazolyl catalyst

The same group reported the trisubstituted derivative of this catalyst where the carboxypyrazolyl moieties are anchored at 1, 3 and 5 positions on the benzene ring, **15**. However, the activity of this complex when activated with MAO towards ethylene polymerisation was reported to be less than that of its disubstituted analogue. The resulting benzene 1,3,5-tris-carboxy pyrazolyl ligand was expected to show similar reactivity as the di-

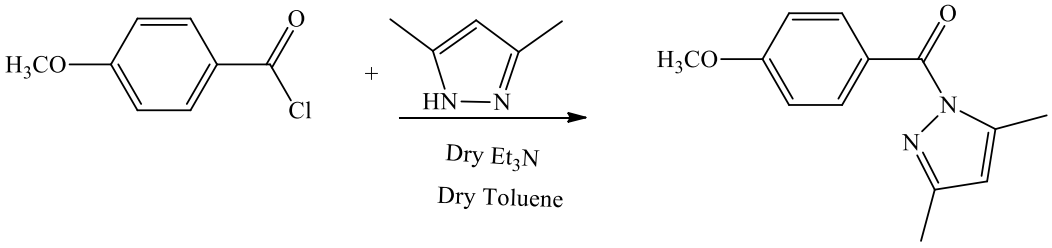
[33] I.A. Guzei, K. Li, G.A. Bikzhanova, J. Darkwa, S.F. Mapolie. *Dalton Trans*. 4 (**2003**) 715.

substituted analogue when activated towards ethylene polymerisation as only the two pyrazole moieties participate in coordination to metal centre, and they both have carboxypyrazolyl moieties at meta positions on the benzene ring.

However, the activity of the bidentate ligand was twice that of tridentate ligand. This was believed to be caused by the uncoordinated carboxypyrazolyl moiety which complexed with the co-catalyst (MAO), in that way reducing the amount of active palladium catalyst being generated for ethylene polymerization.[33] One of the disadvantages with this system that they not stable at high temperatures due to the electron withdrawing carbonyl linker in the system.[32]

1.8.4 Preparation of benzene carbonyl ligands

Benzene carbonyl pyrazolyl compounds are usually formed upon the reaction of their corresponding acids with pyrazolyl moieties. The mechanism is the same as that of the Preparation of amides from the corresponding acyl chlorides. The first step on the mechanism is the deprotonation of the amine (nucleophile) group by the base (i.e tertiary amine).



Scheme 1.4: Nucleophilic acyl substitution reaction

This step activates the nitrogen of a nucleophile to react with the carbonyl carbon. This is a very fast reaction and requires dry conditions in an inert atmosphere to avoid hydrolysis of the acyl chlorides to the corresponding carboxylic acids, Scheme 1.4.

Complexes with carbonyl linkers on their ligands have improved activities when used as catalyst for olefin transformation reactions because of the electron withdrawing nature of the linker which weakens the metal centre and promote easy dissociation of the ligand from the metal centre during polymer insertion. Example of some complexes of pyrazolyl carbonyl compounds which have been prepared this way that are reported as catalyst for ethylene polymerisation includes the benzene carbonyl pyrazolyl complexes reported by Mkoyi *et al*.[34]

[34] H.D. Mkoyi, S.O. Ojwach, I.A. Guzei, J. Darkwa, *J. Org. Chem.* 724 (**2013**) 95.

in Scheme 1.4. The pyrazolyl dicarbonyl benzene and pyridine compounds were also prepared by Darkwa *et al*.[35] following the nucleophilic acyl substitution mechanism.

1.8.5 Preparation of benzene methylene ligands

Stark and Markhosza reported the phase transfer reaction in the mid 1960 as the reaction between reaction between acidic methylene compounds and pyrazole derivatives to get the pyrazolyl methylene compounds.[36] Later on in 1970's, Hartson and Steel extended the use of the method in the preparation of benzenes pyrazolyl methylene ligands, Figure 1.9**.**

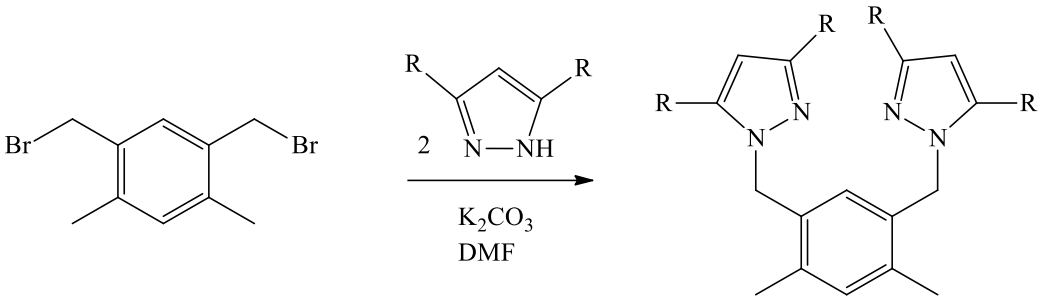


Figure 1.9: An example for the preparation of benzene methylene pyrazolyl ligand

Since then, phase transfer reactions have been adopted for the preparation of compounds with methylene linker or spacer from their corresponding alkyl halides. The presence of a methylene linker in the ligand stabilizes their metal complexes because of the electron donating nature of the methylene linker, which strengthen the metal-ligand bond of their complexes.

1.9 Geometric variation of d^8 metal complexes and their magnetic behaviour

The geometry in d^8 metal complexes such as those of nickel(II) and palladium(II) can be rationalized using crystal field theory. For example, the splitting of d orbitals in square planar and tetrahedral fields is shown in Figure 2.15. The size of the energy difference between the upper and the lower level in tetrahedral field is smaller than that for an octahedral field.

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[35] (a) I.A. Guzei, K. Li, G. Bikzhanova, J. Darkwa, S.F. Mapolie, *Dalton Trans*. 4 (**2003**) 715. (b) M.S. Mohlala, I.A. Guzei, J. Darkwa, S.F. Mapolie, *J. Mol. Catal. A: Chem*. 241 (**2005**) 93.

[36] (a) M. Makosza, *Tetrahedron Lett*. 7 (**1966**) 4621. (b) M. Makosza, *Tetrahedron Lett*. 7 (**1966**) 5489. (c) M. Makosza, *Tetrahedron Lett*. 10 (**1969**) 4659.

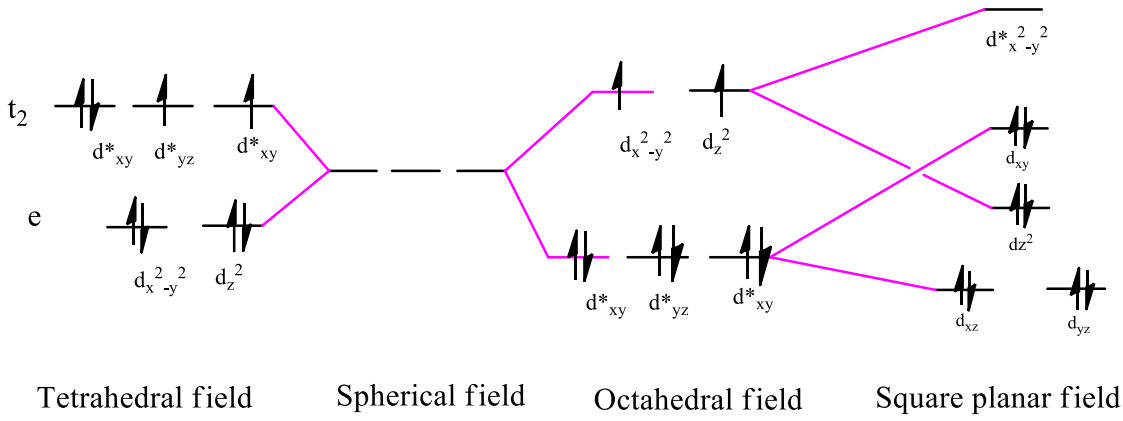

Figure 1.10: Splitting of d-orbitals in different fields for d^8 metal complexes

The square planar field on the other hand can be regarded as having been derived from the octahedral field by removing the electrons located along the z-axis of their complexes. As a result the two e_g orbitals do not have the same energy. The *d* orbitals in complexes in a square-planar form, have their ligands with a strong σ-interaction with the metal $d_{x^2-y^2}$ function and the resulting σ* ($d_{x^2-y^2}$) orbital is left unoccupied at the expense of pairing up of the eight *d*-electrons in the lower energy orbitals. This causes the lack of σ* electrons leading to strong bonds. In tetrahedral complexes, the degeneracy of the highest energy *d*-orbitals means that single occupation is preferred and all orbitals are being single occupied before paring and the resulting σ* orbitals remain half field. The ligand field theory predicts that in a tetrahedral field five-fold degenerate orbital of the single *d*-electron will be split into triply degenerate t_2 orbitals and lower energy doubly degenerate *e* orbitals. While in square planar field, the five-fold degenerate orbitals of the single *d*-orbitals will split into one higher energy orbital and four lower energy orbitals. Filling these orbitals following both the Hund's rule and Pauli's principle, for a tetrahedral complex there are six pared electrons and two unpaired electrons giving S = 1 and for the square planar complex, there are 4 pairs of paired electrons with no unpaired electrons, giving S = 0.[37] The crystal field theory can also be used to figure out the magnetic behaviour of a certain compound, bearing in mind that compounds are paramagnetic when they have one or more unpaired electrons and they are diamagnetic when they have all the electron paired. The spin free magnetic moment can be calculated from the number of unpared electrions, for example Ni^{2+} ion has a calculated moment of 2.83 B.M. and the value can range of 2.9-4.2 B.M. with different ligand systems. Obuah *et al.*[13] reported paramagnetic

[37] C.R. Dillard, D.E. Goldberg, Chemistry Reactions, Structure and Properties. 2nd edition. C Macmallian. (**1978**).

complexes of bis(3,5-dimethylpyrazol-1-ylmethyl)benzenenickel(II) complexes with μ_{eff} (298 K) between 3.00 and 4.10 BM.

1.10 Rationale of the Study

Over the years, synthetic chemistry has provided a broad range of ligands which have been exploited in various research fields such as anti-cancer drugs, industrial waste-water purification, mineral extraction processes and catalysis.[38] As a result of their diversity, a simplistic approach to classification of ligands has been established; ligands are classified mostly by the type of the incorporated donor atom, followed by that of the backbone.[39] These classes are not application-specific, that is, the ligands are used or shared among various fields, depending on the objectives. However, the research community has observed a considerably high exploitation of ligands in catalytic research studies than in other fields. This is mainly due to simple reasons that have been highlighted in this review. Ligands, regardless of their classes, are able to control the catalytic capabilities of the transition metal through manipulation of electronic and steric properties.[40] The main focus is on the electronic and steric effects brought by the bidentate nitrogen ligands and how this influences the catalytic activities of their complexes in catalytic transformation such as oligomerisation and polymerisation of ethylene. The use of benzene as ligand backbone as well as mixing different linkers on the same ligand system will be the focus of the current study. The present study take cognisance of all challenges therefore aim to design active and stable bidentate nitrogen donor late transition metal catalyst. The full aims of the study are:

(i) Synthesize and characterize an organic scaffold suitable to anchor both the hydrazide and pyrazoles nitrogen donor atoms.
(ii) Judiciously incorporating pyrazole and hydrazide functionalities into the ligand and fully characterizing the resulting ligands.

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[38] (a) M.G. Delroisse, B.L. Feringa, R. Hage, R.M. Hermant, R.E. Kalmeijer, J.H. Koek, C. Lamers, M.T. Rispens, S.W. Russell and R.T. Vliet, *Google Patents*, (**2000**). (b) PeindyáN'Dongo, H.W. *Chem. Commun*. 15 (**2008**) 1798. (c) D.L Jameson, K.A Goldsby. *J. Org. Chem.* 55 (**1990**) 4992. (d) N. Ajellal, M.C. Kuhn, A.D. Boff, M. Hörner, C.M Thomas, J.F. Carpentier, O.L. Casagrande, *Organometallics* 25 (**2006**) 1213.

[39] G.J. Britovsek, V.C. Gibson, D.F. Wass. *Angew. Chem. Int. Ed*. 38 (**1999**) 428.

[40] K. Li, J. Darkwa, I.A. Guzei, S.F. Mapolie . *J. organomet*. 660 (**2002**) 108.

(iii) Preparation and characterization of Ni(II) and Pd(II) complexes resulting from the above ligands.

(iv) Using $EtAlCl_2$ as a co-catalyst to activate and evaluate the activity and selectivity of the complexes as catalyst in olefin transformation reactions.

CHAPTER 2

PREPARATION AND CHARACTERISATION OF ASYMMETRIC BENZENE PYRAZOLYL LIGANDS AND THEIR Pd(II) AND Ni(II) METAL COMPLEXES

2.1 Introduction

2.1.1 Nitrogen compounds in polyolefin reactions

The nitrogen containing ligands and their complexes when used as catalyst in polymerisation of olefins such as ethylene can be easily modified to give polyethylene with different microstructures and high molecular weights.[41] A couple of such ligands and their corresponding metal complexes have been reported as good catalysts for olefin polymerization.[42] The use of nitrogen based complexes as catalysts for polyolefin reaction has been substantially reviewed.[43] However, most of the reviews on nitrogen donor ligand catalysts have mainly focused on imine and pyridine systems and not much has been reported on pyrazolyl-based nitrogen donor catalysts. For example, pyridine is a stronger base (pKa = 5.23) than pyrazole (pKa = 2.47) and also a better π-acceptor, which makes the pyridine ligand to strongly co-ordinate to the metal centre and thus making pyridine complexes less electrophilic. The electrophilic nature of pyridine complexes when used as catalyst allows them to rapidly coordinate to substrates before they are transformed into products.[44] Even though the pyrazolyl complexes are less electrophilic as catalysts for polyeolefin, they are still good candidates for olefin polymerisation reaction. This is mainly because of the possibility of tuning the electrophilic and steric properties of their compounds by changing the nature of the substituents on the various positions of the pyrazole ring. Ojwach *et al*.[45] presented a comprehensive review on the use of pyrazolyl complexes as catalyst.

2.1.2 Pyrazolyl benzene compounds

In systems where the pyrazole ring is attached to a benzene backbone to form ligands, the resulting N-pyrazolylbenzene structure can be divided into two types. The first type is where the pyrazole ring is directly linked to the phenyl ring and in the second type there is a linker between the pyrazole and the benzene rings, Figure 2.1. An example of the first type is the

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[41] L.K. Johnson, C.M. Killian, M. Brookhart, *J. Am. Chem. Soc*. 117 (**1995**) 6414.

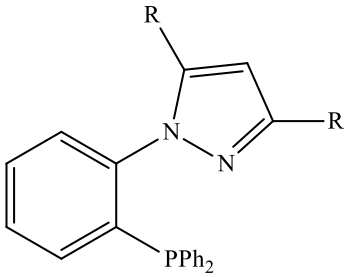
[42] (a) A. Koppl, H.G. Alt, *J. Mol. Catal. A: Chem*. 154 (**2000**) 45. (b) C.M. Killian, L.K. Johnson, M. Brookhart, *Organometallics* 16 (**1997**) 2005.

[43] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev*. 38 (**2009**) 1450.

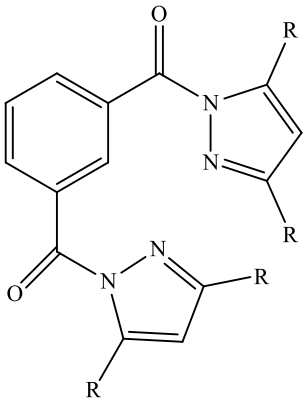
[44] S. Tsuji, D.C. Swenson, R.F. Jordan, *Organometallics* 18 (**1999**) 4758.

[45] S.O. Ojwach, J. Darkwa, *Inorg. Chim. Acta.* 363 (**2010**) 1947.

pyrazole-tethered aryl-phosphine ligand **16** developed by Mukherjee *et al*.[46] A lot of different ligands can be prepared from second type and the focus on this project is on modifying compounds **17** and **18** by introducing a ligand system bearing both the methylene and carbonyl linkers in between two different nitrogen donor moieties.[47] The poly pyrazolyl ligands **17**, having a carbonyl linker were studied by Darkwa *et al*.[48] and poly pyrazolyl ligands **18**, having methylene linkers were first studied by Steel *et al*.[49]

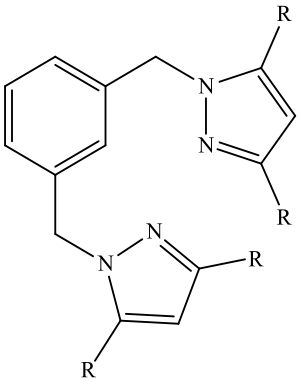


16



17

R= H, Me, ^{t}Bu



18

R= H, Me, ^{t}Bu

Figure 2.1: Examples of N-pyrazolylbenzene ligands

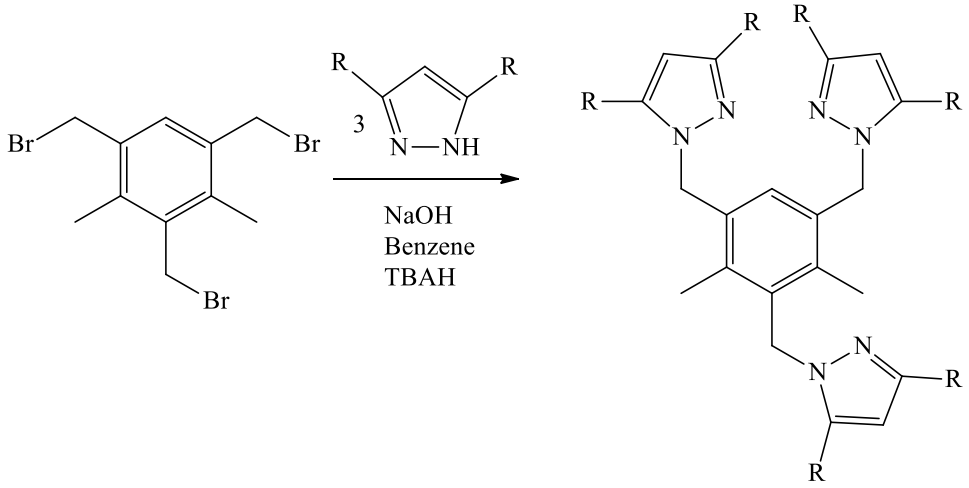
[46] A. Mukherjee, A. Sarkar, *Tetrahedron. Lett*. 45 (**2004**) 9525.

[47] C.M. Hartshorn, P.J. Steel, *Austr. J. Chem*. 48 (**1995**) 1587.

[48] I.A. Guzei, K. Li, G. Bikzhanova, J. Darkwa, S.F. Mapolie, *Dalton Trans*. 4 (**2003**) 715.

[49] C.M. Hartshorn, P.J. Steel, *Organometallics* 17 (**1998**) 3487.

N-pyrazolylbenzene compounds have various uses, including being employed as ligands for catalysts that are used for ethylene polymerisation reactions. A practical method for the preparation of these compounds is of great interest in synthetic organic chemistry. Synthetic protocol on the preparation of these ligands was reported by Hartshorn.[7] An example is the trisubstituted pyrazolyl methylene benzene ligands in Figure 2.2.



R = H, Me

Figure 2.2: Preparation of tri-substituted pyrazolyl methylene benzene ligands.[50]

Another set of closely similar ligands were reported by Motsoane and co-workers using the same procedure by Hartshorn and co-workers and were used for preparation of 1,3 and 1,2-bis(3,5-dimethyl-1H-pyrazol-1-ylmethyl) benzene complexes with palladium(II) in square-planar environment.[51] These complexes were tested as catalysts in Heck coupling reactions and were reported to be efficient catalysts for this reaction. Chang *et al*.[52] studied the coordination properties of cobalt(II) and copper(II) complexes of the 1,2-bis(3,5-dimethyl-1H-pyrazol-1-ylmethyl)benzene ligands but did not expand the scope of their work to include any catalytic application. The Cu(II) and Co(II) unbridged complexes of these ligands displayed distorted tetrahedral geometry while the bridged Cu(II) complex displayed distorted square-pyramidal geometry.

[50] C.M. Hartshorn, P.J. Steel, *Inorg Chem*. 35 (**1996**) 6902.

[51] N.M. Motsoane, I.A. Guzei, J. Darkwa, *Z. Naturforsch. Teil B*. 62 (**2007**) 323.

[52] W.-K. Chang, G.-H. Lee, Y. Wang, T.-I. Ho, Y.O. Su, Y.-C. Lin, *Inorg. Chim. Acta*. 223 (**1994**) 139.

Complexes of pyrazolyl carbonyl benzene ligands have been reported as active compounds in catalysis. The presence of the carbonyl group in these compounds reduces the sigma (σ) donor ability of the nitrogen bond to assist coordination of the substrate to the metal centre, thus increasing the activity of these compounds in catalytic reactions.[47] Other than the pyrazolyl carbonyl benzene compounds there is another class of nitrogen containing carbonyl benzene compounds known as hydrazides. They are organic compounds with a general formula ($RCONHNH_2$) and their analogues have attracted attention in the literature because of their ability to readily coordinate to a variety of transition metals using carbonyl oxygen and amino nitrogen as donor atoms forming five-membered ring.[53] Their complexes have been used mostly in biological applications,[54] and have not yet exploited in catalysis.

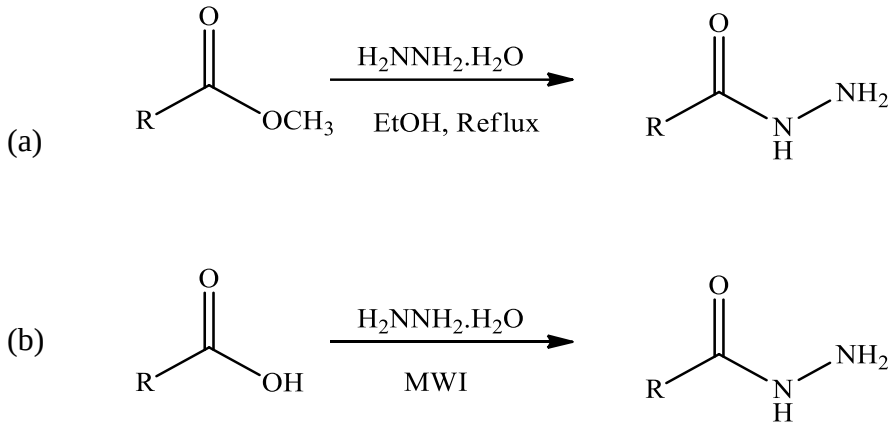


Figure 2.3: Different routes for the Preparation of hydrazides.[55]

[53] (a) A. Kermagoret, P. Braunstein, *Dalton Trans*. 22 (**2008**) 2945. (b) F. Speiser, P. Braunstein, L. Saussine, *Organometallics* 23 (**2004**) 2633.

[54] (a) D.G. Rando, D.N. Sato, L. Siqueira, A. Malvezzi,. C.Q. Leite, A.T. Amaral, E.I. Ferreira, L.C. Tavares, *Bio. Org. Med. Chem*, 10 (**2002**) 557. (b) M.G. Mamolo, V. Falagiani, D. Zanpier, , L. Vio, F. Banfi, *Farmaco*, 56 (**2001**) 587. (c) S. Rollas, N. Gulerman, H. Edeniz, *Farmaco*, 57 (**2002**) 171.

[55] (a) H.A. Saad, N.A. Osman, A.H. Moustafa, *Molecules* 16 (**2011**) 10187. (b) A. Saha, R. Kumar, C. Devakumar. *Indian J. Chem.* 49 (**2010**) 526.

They can be synthesized from different acyl derivatives and can serve as an intermediate for the preparation of the pyrazolyl carbonyl benzene ligands. Simple hydrazinolysis of esters allows esters to react with different hydrazine derivatives to form corresponding hydrazides as shown in Figure 2.3(a). Claesen and co-workers reported preparation of hydrazides from hydrazinolysis of esters using hydrazine monohydrate in low yields 16%.[56] Later, Maxwell reported preparation of the same hydrazides with improved yields of 40% using methyl hydrazine.[57] However recent procedures reported good yields up to 80% from hydrazinolysis of ester using hydrazine monohydrate.[54(a)] There are other different methods reported for the preparation of hydrazides straight from their carboxylic acids which are aimed at improving the yields.[58] For example, Kumar and co-workers showed that hydrazides can also be prepared directly from their corresponding acids under microwaves irradiation (MWI) in the absence of organic solvents, Figure 2.3 (b).[54(b)] This method can be considered as a greener route for the synthesis of hydrazides and excludes the step where acids are being converted to esters.

This chapter reports on the synthesis of new pyrazolyl hydrazide ligands with carbonyl and methylene linkers on the 1,3-positions of the benzene ring, The Pd(II) and Ni(II) complexes of these ligands are also reported.

2.2 Experimental methods and synthesis

2.2.1 Instrumentation

Fourier Transform Infrared (FT-IR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Gas Chromatography-Mass Spectrometry (GC-MS) and Elemental analyses (CHN) techniques were used for the characterization of the synthesized ligands and complexes.

[56] M. Claesen, P. Van Dijck, H. Vanderhaeghe, *J. Pharm. Pharmacol*. 6 (**1954**) 127.

[57] M.D. Maxwell. *Proc. Okla. Acad. Sci.* 38 (**2015**) 103.

[58](a) C. Naegeli, G. Stefanovich, *Helv. Chim. Acta*. 11 (**1928**) 609. (b) H.L. Yale, K. Losee, J. Martins, M. Holsing, F.M. Perry, J. Bernstein, *J. Am. Chem. Soc.* 75 (**1953**) 1933. (c) B.B. Furniss, V. Rogers, P.W.G. Smith, A.R. Tatchell, *Vogel's textbook of practical organic chemistry*, 5th Ed.(Longman Scientific and Technical, Essex England), (**1989**).

2.2.1.1 FT-IR Spectroscopy

FT-IR Spectroscopy analyses were carried out in-house on a Bruker Tensor 27 FT-IR spectrometer using a standard ATR cell; the samples were analysed in their original form at the mid-IR range of 500-4000 cm^{-1}.

2.2.1.2 NMR Spectroscopy

^{1}H and ^{13}C NMR spectroscopy analyses of samples prepared in $CDCl_3$ were performed at the University of KwaZulu-Natal Westville campus, South Africa, on a Bruker Advance III 400 MHz and 600 MHz spectrometers. The residual peak of $CDCl_3$ at 7.24 ppm was used to reference ^{1}H chemical shifts. Tetramethylsilane (TMS) was used as an external reference for ^{1}H NMR chemical shifts.

2.2.1.3 GC-MS

MS (GC) analyses were performed in-house on an Agilent 7890A gas chromatograph fitted with a 5975C VL mass selective detector (MSD). The type of column installed was a HP-5,5% phenyl methyl siloxane with dimensions: 30 m × 250 μm × 0.25 μm. Helium was used as a carrier gas at a flow rate of 0.7 mL/min. The injection source and detector temperatures were 250 °C and 230 °C, respectively. The initial oven temperature at 60 °C was held constant for 2 min then ramped-up to the final temperature of 300 °C, at a rate of 10 °C/min.

MS (ESI) analysis was performed at the University of Stellenbosch (South Africa) on a Waters Synapt G2 at a core voltage of 15 V, as well as in-house on a Agilent 7890A gas chromatograph fitted with a 5975C VL mass selective detector (MSD).

2.2.1.4 Elemental Analysis

Elemental analyses were carried out in-house on a Perkin-Elmer 2400 Series II CHNS/O analyser.

2.2.1.5 Melting Point

The melting points were carried out in a Stuart melting point SMP 11 (LASEC) at 10° C/min and are reported uncorrected.

2.3 Materials

2.3.1 Reagents

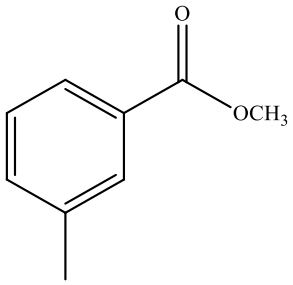
All the reagents used were of laboratory grade quality and were purchased from either Sigma Aldrich or Merck, and were used as received, except thionyl chloride which was purified by simple distillation and stored in a well ventilated fume hood before use. $NiCl_2$.DME was purchased from Sigma Aldrich and used as receive while the $PdCl_2(NCMe)_2$ was prepared a following literature procedure.[59]

2.3.2 Solvents

For reactions where dry solvents were required, the required solvent was first distilled under nitrogen atmosphere. Tetrahydrofuran (THF) and Toluene were dried over sodium benzophenone ketyl. Dichloromethane was distilled over phosphorus pentoxide (P_2O_5) and stored over molecular sieves. The rest of the solvents were of analytical grade and were used as received.

2.4 Preparation of ligands

2.4.1 Preparation of methyl 3-methylbenzoate, ***(L1)***



General procedure

A sample of 3-methylbenzoic acid (10.1 g, 73.5 mmol) was refluxed overnight for 20 hrs in methanol (100 mL) in the presence of a catalytic amount of H_2SO_4 (5 drops). The solution was then cooled and poured into a saturated solution of $NaHCO_3$ (150 mL), and the pH was adjusted to pH = 9 by slow addition of solid $NaHCO_3$. This solution was extracted with dichloromethane (3 × 100 mL), and the organic extracts were first washed with a saturated solution of $NaHCO_3$ (2 × 50 mL) followed by washing with brine (2 × 50 mL). The organic phase was collected and

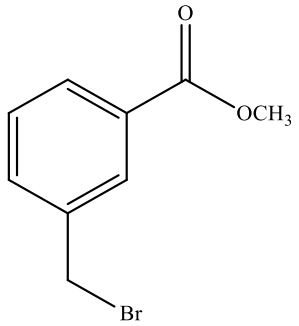
[59] D. Drew, J. R. Doyle, *Inorg. Synth*. 13 (**1972**) 47.

dried over $MgSO_4$ for 30 minutes. It was then filtered and the solvent was removed under reduced pressure to obtain the product **L1** as a yellowish liquid. Yield = 9.65 g (87%).

Alternative Procedure

A sample of 3-methylbenzoyl chloride (10.0 g, 64.7 mmol) was dissolved in methanol (100 mL) by heating to reflux for 30 min. Then, thionyl chloride (5 mL) was added dropwise and the reaction was refluxed overnight. The solvent and the excess $SOCl_2$ were removed under reduced pressure. A saturated solution of $NaHCO_3$ (150 mL) was added to the residue, and the mixture was extracted with dichloromethane (3 × 100 mL), upon evaporation of the solvent a colourless liquid of **L1** was obtained. Yield = 8.96 g (92 %). MS (GC): *m*/*z* = 150.17. FT/IR: υ(C=O) 1718 cm^{-1}, υ(C-H) 3000 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H, Ph), 7.82 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.33 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.28 (t, 1H, Ph, $^3J_{HH}$ = 16 Hz), 3.87 (s, 3H, -OCH_3), 2.35 (s, 3H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.10 (-$COCH_3$), 137.97 (Ph), 133.52 (Ph), 129.97 (Ph), 129.94 (Ph), 128.11 (Ph), 126.56 (Ph), 51.85 (-OCH_3), 21.08 (CH_3).

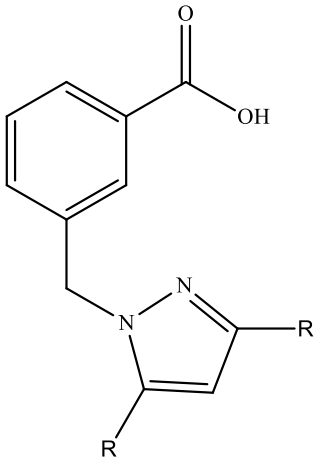
2.4.2 Preparation of methyl 3-(bromomethyl)benzoate, ***(L2)***



To a suspension of compound **L1** (9.00 g, 59.9 mmol) in water (20 mL) was added N-bromosuccinamide (NBS) (10.7 g, 59.9 mmol) and the solution was stirred at 500 rpm with a 150 W halogen lamp placed 15 cm away from the flask for 4 hrs. The resultant yellowish oil was separated from water using a separating funnel. The crude oil was re-dissolved in hot hexane, and immediately placed in a fridge freezer overnight. The excess hexane was decanted from which the amorphous crystals formed which were recrystallized from ethanol at room temperature. Colourless crystals of **L2** formed after 12 hrs and were dried in vacuum. Yield = 7.23 g (53 %). Mp: 41-42 °C. MS (GC): *m*/*z* = 227.8. Anal. Cal. for $C_9H_9BrO_2$: C = 47.19%, H = 3.96%. Found: C = 47.29%, H = 3.81%. FT/IR: υ(C=O) 1715 cm^{-1}, υ(C-Br) 515 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H, Ph), 7.95 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.57 (d, 1H, Ph,

$^{3}J_{HH}$ = 8 Hz), 7.40 (t, 1H, Ph, $^{3}J_{HH}$ = 16 Hz), 4.49 (s, 2H, -CH_2-), 3.90 (s, 3H, OCH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.41 (-$COCH_3$), 138.14 (Ph), 133.39 (Ph), 130.70 (Ph), 130.02 (Ph), 129.47 (Ph), 128.91 (Ph), 52.19 (-CH_2-), 32.43 (-OCH_3).

2.4.3 Preparation of 3-{(3,5-dimethyl-1H-pyrazol-1-yl)methyl)}benzoic acid, ***(L3a)***



R	
Me	**L3a**
Ph	**L3b**
^{t}Bu	**L3c**

To a basic solution containing of NaOH (2.10 g, 52.3 mmol) and Na_2CO_3 (5.55 g, 52.3 mmol) in THF (80 mL), was added 3,5-dimethyl pyrazole (1.29 g, 13.1 mmol), methyl 3-(bromomethyl)benzoate (**L2**) (3.00 g, 13.1 mmol) and TBAB (0.345 g, 1.07 mmol) which was used as a phase transfer catalyst. The solution was refluxed overnight for 22 hrs, after which the solvent was removed under reduced pressure to obtain a pale yellow powder. The yellow powder was redissolved in deionised water (50 mL) and acidified to pH = 2 with 5M HCl (20 mL). A white precipitate formed and was filtered and dried under vacuum to give a white solid. The solid was recrystallized from hot ethanol to obtain an analytically pure sample of **L3a** as a white solid. Yield = 1.97 g (62%). Mp = 190-192 °C. MS (GC): *m*/*z* = 229.29. Anal. Cal. for $C_{13}H_{14}N_2O_2$: C = 67.81%, H = 6.13%, N= 12.17%. Found C = 68.07%, H = 5.67%, N = 11.6%. FT/IR: υ(C=O) 1679 cm^{-1}, υ(-OH) 3395 cm^{-1}, υ(C-H) 3057 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, 1H; $^{3}J_{HH}$ = 8 Hz, Ph), 7.68 (s, 1H, Ph), 7.44 (t, 1H, $^{3}J_{HH}$ = 8 Hz, Ph), 7.33 (d, 1H, Ph, $^{3}J_{HH}$ = 16 Hz), 5.84 (s, 1H, Pz), 5.25 (s, 2H, -CH_2-), 2.14 (s, 3H, Pz), 2.09 (s, 3H, Pz). ^{13}C NMR (400 MHz, DMSO-d_6) δ 167.11 (-COOH), 146.25 (Pz), 138.80 (Pz), 138.47 (Ph), 131.29 (Ph), 131.07 (Ph), 128.81 (Ph), 128.21 (Ph), 127.66 (Ph), 105.14 (Pz), 51.16 (-CH_2-), 13.32 (CH_3), 10.60 (CH_3).

*2.4.4 Preparation of 3-{(3,5-diphenyl-1H-pyrazol-1-yl)methyl}benzoic acid, **(L3b)***

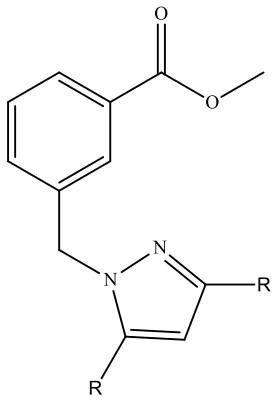
Compound **L3b** was prepared from the reaction of 3,5-diphenyl pyrazole (0.962 g, 6.55 mmol), methyl-3-(bromomethyl) benzoate (1.50 g, 6.55 mmol), $NaHCO_3$ (2.78 g, 26.2 mmol), NaOH (1.05 g, 26.2 mmol) and a catalytic amount of TBAB (0.23 g, 0.713 mmol) in THF (50 mL). The mixture was stirred for 22 hrs but changed colour from white to off-white after few hours of stirring. The solvent was removed completely under pressure. The crude was redissolved in distilled water and the undissolved white solid was filtered. To the aqueous solution drops of concentrated HCl were added until the acid precipitated as a light yellow gum. The gum was stirred in ethanol at room temperature for 10 minutes to obtain the desired product **L3b** as a white solid. Yield = 1.53 g (66%). Mp = 250-252 °C. MS (GC): *m/z* = 368.19. Anal. Cal. for $C_{23}H_{18}N_2O_2$: C = 77.95%, H = 5.12%, N = 7.90%. Found: C = 78.17%, H = 5.46%, N = 7.62%. FT/IR: υ(C=O) 1689 cm^{-1}, υ(-OH) 3039 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.82 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.65 (s, 1H, Ph), δ 7.45 (m, 8H, Ph), 7.31 (d, 2H, Ph, $^3J_{HH}$ = 8 Hz), 7.26 (d, 2H, Ph, $^3J_{HH}$ = 8 Hz), 6.97 (s, 1H, Pz), 5.50 (s, 2H, -CH_2-). ^{13}C NMR (400 MHz, DMSO-d_6) δ 167.00 (-COOH), 149.99 (Pz), 145.08 (Pz), 138.15 (Ph), 132.96 (Ph), 131.34 (Pz-Ph), 130.81 (Ph), 129.87 (Ph), 129.87 (Ph), 128.85 (Pz-Ph), 128.79 (Pz-Ph), 128.76 (Pz-Ph), 128.65 (Pz-Ph), 128.25 (Pz-Ph), 127.68 (Pz-Ph), 127.38 (Pz-Ph), 125.16 (Pz-Ph), 103.84 (Pz-Ph), 52.49 (-CH_2-).

*2.4.5 Preparation of 3-((3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl)benzoic acid, **(L3c)***

Compound **L3c** was prepared from the reaction of 3,5-di-tertiatybutylpyrazole (0.657 g, 9.95 mmol), methyl 3-(bromomethyl) benzoate (1.50 g, 6.55 mmol), Na_2CO_3 (2.78 g, 26.2 mmol), NaOH (1.05 g, 26.2 mmol) and a catalytic amount of TBAB (0.173 g, 0.655 mmol) in THF (70 mL). The mixture was stirred for 22 hours but changed colour from white to light yellow after few hrs of stirring. After evaporation of solvent under reduced pressure, a yellow solid was obtained and which was then redissolved in water (100 mL). To the resulting aqueous solution was added ethanol (20 mL) followed by dichloromethane (20 mL). The organic phase which contained some of the unreacted pyrazole was separated and discarded. The aqueous phase was then acidified with concentrated HCl (2 mL). To the acidic solution was added diethyl ether (30 mL) to extract the product, on evaporation of the ether extracts, the desired product **L3c** was obtained as yellow solid. Yield = 0.98 g (48%). Mp = 145°C. MS (GC): *m/z* = 316.1. Anal. Cal. for $C_{19}H_{26}N_2O_2$: C = 72.58%, H = 8.33%, N = 8.91%. Found: C = 72.03%, H = 8.22%, N = 8.63%. FT/IR: υ(C=O) 1690 cm^{-1}, υ(-OH) 3396 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 7.88 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.57 (s, 1H, Ph), 7.42 (t, 1H, Ph, $^3J_{HH}$ = 16 Hz), 7.15 (d, 1H, Ph,

$^{3}J_{HH}$ = 8 Hz), 5.95 (s, 1H, Pz), δ: 5.47 (s, 2H,-CH_2-), δ: 1.21 (d, 18H, CH_3, $^{3}J_{HH}$ = 2.8 Hz). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 167.23 (-COOH), 159.11 (Pz), 151.47 (Pz), 140.02 (Ph), 130.87 (Ph), 130.79 (Ph), 130.35 (Ph), 128.64 (Ph), 127.05 (Ph), 99.71 (Pz), 53.11 (-CH_2-), 31.65 ($\underline{C}(CH_3)_3$), 30.93 ($\underline{C}(CH_3)_3$), 30.46 (C($\underline{C}H_3)_3$), 30.01 (C($\underline{C}H_3)_3$).

2.4.6 Preparation of methyl 3-{(3,5-dimethyl-1H-pyrazol-1-yl)methyl}benzoate, ***(L4a)***



R	
Me	**L4a**
Ph	**L4b**
^{t}Bu	**L4c**

To a solution of **L3a** (1.50 g, 6.51 mmol) in methanol (50 mL) was added a catalytic amount of H_2SO_4 (5 drops). The solution was refluxed overnight for 19 hrs, cooled and poured into a saturated solution of $NaHCO_3$ (50 mL). The pH was adjusted to pH = 9 by slow addition of solid $NaHCO_3$. The solution was then extracted with dichloromethane (2 × 20 mL). The organic extracts were dried over $MgSO_4$ for 30 min and then filtered. The organic solvent was removed under reduced pressure to obtain the product **L4a** as red oil. Yield = 1.13 g (75%). GC (MS): *m*/*z* = 244.1. FT/IR: υ(C=O) 1718.cm^{-1}, υ(C-H) 2951 cm^{-1}, υ(-OCH_3) 2817 cm^{-1}. ^{1}H NMR (400 MHz, MeOD-d_4) δ: 7.90 (d, 1H, Ph, $^{3}J_{HH}$ = 4 Hz), 7.73 (s, 1H, Ph), 7.41 (t, 1H, Ph, $^{3}J_{HH}$ = 12 Hz), 7.29 (d, 1H, Ph, $^{3}J_{HH}$ = 4 Hz), 5.91 (s, 1H, Pz), 5.27 (s, 2H,-CH_2-), 3.86 (s, 3H,-OCH_3), 2.18 (s, 3H, pz), 2.16 (s, 3H, Pz). ^{13}C NMR (400 MHz, MeOD-d_4) δ: 168.10 (-$COOCH_3$), 149.22 (Pz), 141.59 (Pz), 139.51 (Ph), 132.40 (Ph), 131.88 (Ph), 130.03 (Ph), 129.68 (Ph), 128.66 (Ph), 106.80 (Pz), 52.68 (-CH_2-), 52.55 (-OCH_3), 13.21 (CH_3), 10.97 (CH_3).

2.4.7 Preparation of methyl 3-{(3,5-diphenyl-1H-pyrazol-1-yl)methyl)}benzoate, ***(L4b)***

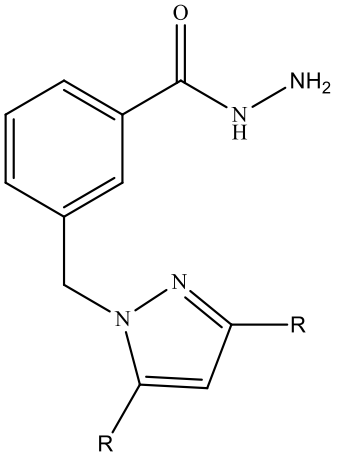
Compound **L4b** was prepared in a similar manner to **L4a** by refluxing the carboxylic acid **L3b** (1.50 g, 6.94 mmol) in methanol (50 mL). The product was obtained as brown oil which solidified upon standing. The solid crude product was redissolved in hot ethanol and as the ethanol cooled down to room temperature, the product **L4b** precipitated out as white solid. Yield = 1.25 g (80%). Mp = 132-133 °C. FT-IR: υ(C=O) 1719 cm^{-1}, υ(-OCH_3) 2783 cm^{-1}. GC

(MS): *m/z* = 368.43. Anal. Cal. for $C_{24}H_{20}N_2O_2$: C = 78.24%, H = 5.47%, N = 7.60%. Found: C = 77.57%, H = 5.63%, N = 7.51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.86 (d, 2H, Ph, $^3J_{HH}$ = 8 Hz), 7.78 (s, 1H, Ph), 7.42-7.24 (m, 10H, Ph-Pz), 6.66 (s, 1H, Pz), 5.41 (s, 2H, -CH_2-). 3.87 (s, 3H, -OCH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.70 (-$COOCH_3$), 151.21 (Pz), 145.51 (Pz), 138.03 (Ph), 133.31 (Ph-Pz), 131.29 (Ph), 130.42 (Ph), 128.74 (Ph), 128.73 (Ph-Pz), 128.69 (Ph-Pz), 128.16 (Ph-Pz), 127.90 (Ph-Pz), 127.32 (Ph-Pz), 125.24 (Ph), 52.88 (-CH_2-), 52.08 (-OCH_3).

2.4.8 Preparation of methyl 3-((3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl)benzoate, ***(L4c)***

Compound **L4c** was prepared in a similar manner to **L4a** from the reaction of **L3c** (1.20 g, 3.82 mmol) in methanol (60 mL). A red oil of **L4c** was washed with saturated solution of $NaHCO_3$ (30 mL). Yield = 0.96 g (77%), GC (MS): *m/z* = 328, FT/IR = υ(C=O) 1716 cm^{-1}, υ(OCH_3) 2819 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.62 (s, 1H, Ph), 7.30 (t, 1H, Ph, $^3J_{HH}$ = 16 Hz), 7.00 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 5.91 (s, 1H, Pz), 5.48 (s, 2H, -CH_2-), 3.88 (s, 3H, -OCH_3), 1.30 (s, 9H, -C(C$\underline{H_3}$)$_3$), 1.22 (s, 9H, -C(C$\underline{H_3}$)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.23 (-$COOCH_3$), 158.97 (Pz), 150.93 (Pz), 137.61 (Ph), 132.91 (Ph), 131.23 (Ph), 131.14 (Ph), 129.50 (Ph), 127.91 (Ph), 100.37 (Pz), 58.11 (-CH_2-), 52.43 (-OCH_3), 36.13 (-$\underline{C}(CH_3)_3$), 33.67 (-$\underline{C}(CH_3)_3$), 30.94 (-C($\underline{C}H_3)_3$), 30.54 (-C($\underline{C}H_3)_3$)

2.4.9 Preparation of 3-{(3,5-dimethyl-1H-pyrazol-1-yl)methyl}benzohydrazide, ***(L5a)***



R	
Me	**L5a**
Ph	**L5b**
^{t}Bu	**L5c**

General procedure

To a solution of **L4a** (1.44 g, 6.47 mmol) in methanol (10 mL) was added drop wise a solution of hydrazine monohydrate (0.730 g, 14.8 mmol). The resulting solution was refluxed for 19 hrs. The solvent was then removed under reduced pressure to give the desired product as yellow oil which solidified upon standing at room temperature. The yellow solid that was obtained was stirred in ethanol for 5-10 min to obtain the desired product **L5a** as a white solid. Yield = 1.22 g (84%).

Alternative procedure

To a solution of hydrazine sulphate (5.00 g, 38.4 mmol) in water (45 mL) was added pellets of sodium hydroxide (3.074 g, 76.9 mmol) and the mixture was stirred until all reagents dissolved. The solution was stirred in an ice-bath for an hour. Ethanol (40 mL) was then added to precipitate sodium sulphate impurities which were removed by vacuum filtration. To the resultant filtrate was added **L4a** (1.88 g, 7.69 mol) and the solution was refluxed for 18 hrs. After the specified time, the reaction was cooled and solvent evaporated under reduced pressure to get the crude product as an off white solid. The crude product was stirred in cold ethanol to obtain white powder of **L5a.** Yield = 1.03 g (55%). Mp = 114 °C. *m/z* = 244.03. Anal.Cal. for $C_{13}H_{16}N_4O$: C = 63.91%, H = 6.60%, N = 22.93%. Found: C = 64.03%, H = 6.65%, N = 23.01%. FT/IR: υ(C=O) 1617 cm^{-1}, υ(N-H) 3346 cm^{-1}. MS (GC): *m/z* = 244.10. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.79 (s, 1H, -NH-), 7.69 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.58 (s, 1H, Ph,), 7.38 (t, 1H, Ph, $^3J_{HH}$ = 16 Hz), 7.20 (d, 1H, Ph, ^3J = 8.0 Hz), 5.84 (s, 1H, Pz), 5.20 (s, 2H, CH_2), 4.49 (s, 2H, -NH_2,), 2.14 (s, 3H, Pz), 2.08 (s, 3H, Pz).^{13}C NMR (400 MHz, $CDCl_3$) δ 168.15 (-$CONHNH_2$), 147.93 (Pz), 139.27 (Pz), 137.93 (Ph), 133.17 (Ph), 129.94 (Ph), 129.04 (Ph), 126.19 (Ph), 125.23 (Ph), 105.73 (Pz), 51.98 (-CH_2-), 13.38 (CH_3), 11.04 (CH_3).

Compound **L5b** and **L5c** were prepared following the general procedure described for **L5a**

2.4.10 Preparation of 3-{(3,5-diphenyl-1H-pyrazol-1-yl)methyl}benzohydrazide, ***(L5b)***

Compound **L5b** was prepared from the reaction of **L4b** (2.00 g, 5.43 mmol) and hydrazine monohydrate (0.680 g, 13.6 mmol) in ethanol (10 mL). The crude product was redissolved in hot methanol and was precipitated by allowing the solvent to cool to room temperature to obtain pure white solid of **L5b**. Yield = 1.25 g (63%). Mp = 217-218.5 °C. GC/MS: *m/z* = 368.59. Anal.Cal. for: $C_{23}H_{20}N_4O$: C = 74.98%, H = 5.47 %, N = 15.21%. Found: C = 75.33%, H = 5.61%, N = 15.34%. FT/IR: υ(C=O) 1605 cm^{-1}, υ(N-H) 3327 cm^{-1}. ^{1}H NMR (400 MHz,

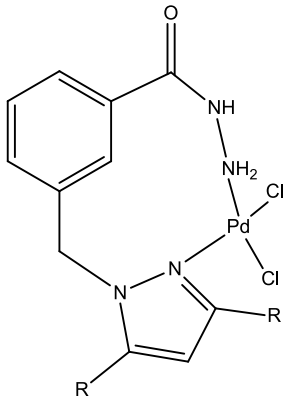
DMSO-d_6) δ 9.76 (s, 1H, -NH-), 7.88 (d, 2H, Ph, $^3J_{HH}$ = 8 Hz), 7.70 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.60 (s, 1H, Ph), 7.50-720 (m, 9H, Pz), 7.14 (d, 1H, $^3J_{HH}$ = 8 Hz, Ph), 6.98 (s, 1H, Pz), 5.47 (s, 2H,-CH_2-), 4.49 (s, 1H, Pz). ^{13}C NMR (400 MHz, DMSO-d_6) δ 165.92 (-CONHNH_2), 150.06 (Pz), 145.13 (Pz), 138.44 (Ph), 132.95 (Ph), 131.46 (Ph), 129.86 (Ph), 129.11 (Ph), 128.92 (Ph), 128.83 (Ph), 128.71 (Ph), 128.47 (Ph), 128.15 (Ph), 127.75 (Ph), 127.32 (Ph), 103.94 (Pz), 52.45 (-CH_2-).

2.4.11 Preparation of 3-((3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl)benzohydrazide, ***(L5c)***

To a solution of **L4c** (0.812 g, 2.47 mmol) in methanol (10 mL) was added drop-wise a solution of hydrazine monohydrate (0.247 g, 4.94 mmol). The resulting solution was refluxed overnight for 22 hrs. The solvent was then removed under reduced pressure to give yellowish oil, which solidified upon standing at room temperature. The crude solid was redissolved in DCM, the undissolved hydrolysed starting material was filtered and filtrate was evaporated under reduced pressure to give the product, **L5c** as white solid. Yield = 0.481 g (59%). Mp = 107-109 °C. GC (MS): *m/z* = 328. Anal.Cal. for: $C_{19}H_{28}N_4O$: C = 69.48%, H = 8.59%, N = 17.06%. Found: C = 69.71%, H = 8.34%, N = 17.89%. FT/IR: υ(C=O) 1622 cm^{-1}, υ(N-H) 2956 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 (s, 1H, -NH-), 7.64 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 7.54 (s, 1H, Ph), 7.35 (t, 1H, Ph, $^3J_{HH}$ = 16 Hz), 6.95 (d, 1H, Ph, $^3J_{HH}$ = 8 Hz), 5.95 (s, 1H, Pz), 5.44 (s, 2H, -CH_2-), 4.45 (s, 2H, -NH_2), 1.22 (s, 9H, CH_3), 1.20 (s, 9H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6) δ 165.84 (-CONHNH_2), 159.03 (Pz), 151.40 (Pz), 139.79 (Ph), 133.29 (Ph), 128.52 (Ph), 128.17 (Ph), 125.30 (Ph), 125.00 (Ph), 99.67 (Pz), 53.30 (-CH_2-), 31.65 ($\underline{C}(CH_3)_3$), 30.94 ($\underline{C}(CH_3)_3$), 30.49 (C($\underline{C}H_3)_3$), 30.04 (C($\underline{C}H_3)_3$).

2.5 Preparation of complexes

2.5.1 Preparation of dichloro-{3-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)benzohydrazide)} palladium(II) complex, ***(C1)***



R	
Me	**C1**
Ph	**C2**
^{t}Bu	**C3**

To a solution of $[PdCl_2(NCMe)_2]$ (0.212 g, 0.819 mmol) in dichloromethane (15 mL) was added a solution of **L5a** (0.200 g, 0.819 mmol) in dichloromethane (15 mL). The resultant yellow solution was stirred for 6 hrs at room temperature. The yellow precipitate that formed was filtered and dried in air. Yield = 0.193 g (53%). Mp = 210-215 °C. FT/IR: υ(C=O) 1618 cm^{-1}, υ(N-H) 3347 cm^{-1}. GC (FID): *m/z* = 421. Anal.Cal. for: $C_{13}H_{16}Cl_2N_4OPd.¼CH_2Cl_2$: C = 35.52%, H = 4.13 %, N = 12.74%. Found: C = 36.07%, H = 3.65%, N = 12.63%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H, NH), 7.89-7.83 (m, 1H, Ph), 7.49-7.49 (m, 1H, Ph), 7.31-7.24 (m, 1H, Ph), 7.04-6.93 (m, 1H, Ph), 5.21 (s, 2H, CH_2), 2.64 (s, 2H, NH_2), 2.15 (s, 3H, CH_3), 2.08 (s, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6) δ 164.30 (-COONHNH$_2$), 146.40 (Pz), 138.93 (Pz), 138.52 (Ph), 136.44 (Ph), 130.55 (Ph), 128.83 (Ph), 126.74 (Ph), 126.23 (Ph), 107.93 (Pz), 48.71 (-CH_2-), 14.79 (C(CH_3)), 13.45 (C(CH_3)). 11.58 (C(CH_3)), 10.79 (C(CH_3)).

2.5.2 Preparation of dicloro (3-(3,5-diphenyl-1H-pyrazol-1-yl) methyl) benzohydrazide) palladium (II) complex, ***(C2)***

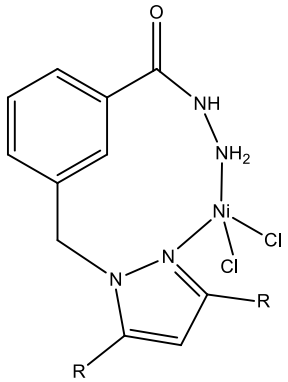
Complex **C2** was prepared in a similar manner to **C1** using $[PdCl_2(NCMe)_2]$ (0.141 g, 0.543 mmol) and **L5b** (0.200 g, 0.543 mmol). Yield = 0.170 g (58%). Mp = 201-202 °C. GC (FID): *m/z* = 544. FT/IR: υ(C=O) 1632 cm^{-1}, υ(-N-H) 3211 cm^{-1}. Anal. Cal. for: $C_{23}H_{20}N_4OPdCl_2.CH_2Cl_2$: C = 45.71%, H = 3.52 %, N = 8.88%. Found: C = 45.93%, H = 3.67%, N = 9.13%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86-7.84 (d, 2H, Ph, $^{3}J_{HH}$ = 3.6 Hz), 7.69-7.65 (m, 1H, Ph), 7.57-7.54 (m, 1H, Ph), 7.46-7.30 (m, 8H, Ph), 7.17-7.16 (d, 1H, Ph, $^{3}J_{HH}$ = 3.0 Hz), 6.97-6.96 (d, 1H, Ph, $^{3}J_{HH}$ = 2.4 Hz), 5.47 (s, 2H, CH_2). ^{13}C NMR (400 MHz, DMSO-d_6) δ 150.11 (-CO), 145.22 (Pz), 138.26 (Pz), 133.00 (Ph-Pz), 129.93 (Ph-Pz), 129.00

(Ph-Pz), 128.89 (Ph-Pz), 128.76 (Ph-Pz), 128.53 (Ph-Pz), 127.81 (Ph), 125.27 (Ph), 103.00 (Pz), 52.58 (CH_2).

2.5.3 Preparation of dichloro-3-((3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl)benzohydrazide palladium(II) complex, ***(C3)***

To a solution of [$PdCl_2(NCMe)_2$] (0.158 g, 0.609 mmol) in dichloromethane (10 mL) was added a solution of **L5c** (0.200 g, 0.609 mmol) in dichloromethane (5 mL) and the resulting yellow solution was stirred at room temperature for 6 hours at room temperature. The solvent was removed under reduced pressure to obtain a red powder. Slow diffusion of hexane into a dichloromethane solution containing the red powder produced analytically pure red powder. Yield = 0.149 g (61%). Mp = 175-178 °C. FT/IR: υ(C=O) 1609 cm^{-1}, υ(N-H) 2914 cm^{-1}. GC (FID): *m/z* = 504. Anal.Cal. for: $C_{19}H_{28}N_4OPdCl_2$. ½CH_2Cl_2: C = 42.72%, H = 5.33 %, N = 10.22%. Found: C = 43.13%, H = 5.85%, N = 10.57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H, NH), 7.45-6.94 (m, 12H, Ph), 6.03-5.08 (s, 1H, Pz, Pz), 5.27-5.08 (dd, 2H, CH_2), 4.08 (s, 2H, NH_2), 2.29-1.23 (m, 36H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 164.12 (-$CONHNH_2$), 137.07 (Pz), 135.13 (Pz), 129.52 (Ph), 128.98 (Ph), 128.83 (Ph), 125.95 (Ph), 125.70 (Ph), 124.96 (Ph), 104.15 (Pz), 31.65 (CH), 30.49 (CH_3), 30.04 (CH_3).

2.5.4 Preparation of dichloro-{3-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)benzohydrazide)} nickel (II)complex, ***(C4)***



R	
Me	**C4**
Ph	**C5**
^{t}Bu	**C6**

To a solution of **L5a** (0.200 g, 0.819 mmol) in dry dichloromethane (10 mL) was added $NiCl_2$.(DME) (0.180 g, 0.819 mmol). The yellow mixture was stirred at room temperature and changed from yellow to green after 4 hrs of stirring. It was stirred for a further 18 hrs after which the unreacted yellow solid of $NiCl_2$.(DME) was filtered and the organic solvent was removed under reduced pressure to obtain a green solid. The solid was washed with diethyl ether (5 mL × 2). Yield = 0.192 g (63%). Mp = 130-134 °C. FT/IR: υ(CO) 1641 cm^{-1}, υ(N-H)

3134 cm^{-1}. GC (FID): *m/z* = 374. Anal.Cal. for $C_{13}H_{16}Cl_2N_4ONi$: C = 41.76%, H = 4.08%, N = 15.24%. Found: C = 43.13%, H = 4.13%, N = 15.03%.

2.5.5 Preparation of dichloro 3-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)benzohydrazide)} nickel(II) complex, ***(C5)***

Complex **C5** was prepared in a similar manner to **C4** from the reaction of and **L5a** (0.300 g, 0.814 mmol) with $NiCl_2$.(DME) (0.179 g, 0.814 mmol). Yield = 0.213 g (53%). Mp = 77-80 °C. FT/IR: υ(CO) 1641 cm^{-1}, υ(N-H) 3148 cm^{-1}. GC (FID): *m/z* = 498. Anal.Cal. for $C_{23}H_{20}Cl_2N_4ONi$: C = 55.47%, H = 4.05 %, N = 11.25%. Found: C = 55.22%, H = 4.42%, N = 11.92%.

2.5.6 Preparation of dichloro 3-((3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl)benzohydrazide)} nickel (II)complex, ***(C6)***

Complex **C6** was prepared in a similar manner to **C4** and **C5** from the reaction of **L5a** (0.200 g, 0.609 mmol) with $NiCl_2$.DME (0.134 g, 0.609 mmol). Yield = 0.137 g (49 %). Mp = 127-131 °C. FT/IR = υ(CO) 1643 cm^{-1}, υ(N-H) 3142 cm^{-1}. GC (FID): *m/z* = 466. Anal.Cal. for $C_{19}H_{28}Cl_2N_4ONi$: C = 49.82%, H = 6.16 %, N = 12.23%. Found: C = 50.23%, H = 6.53%, N = 12.64%.

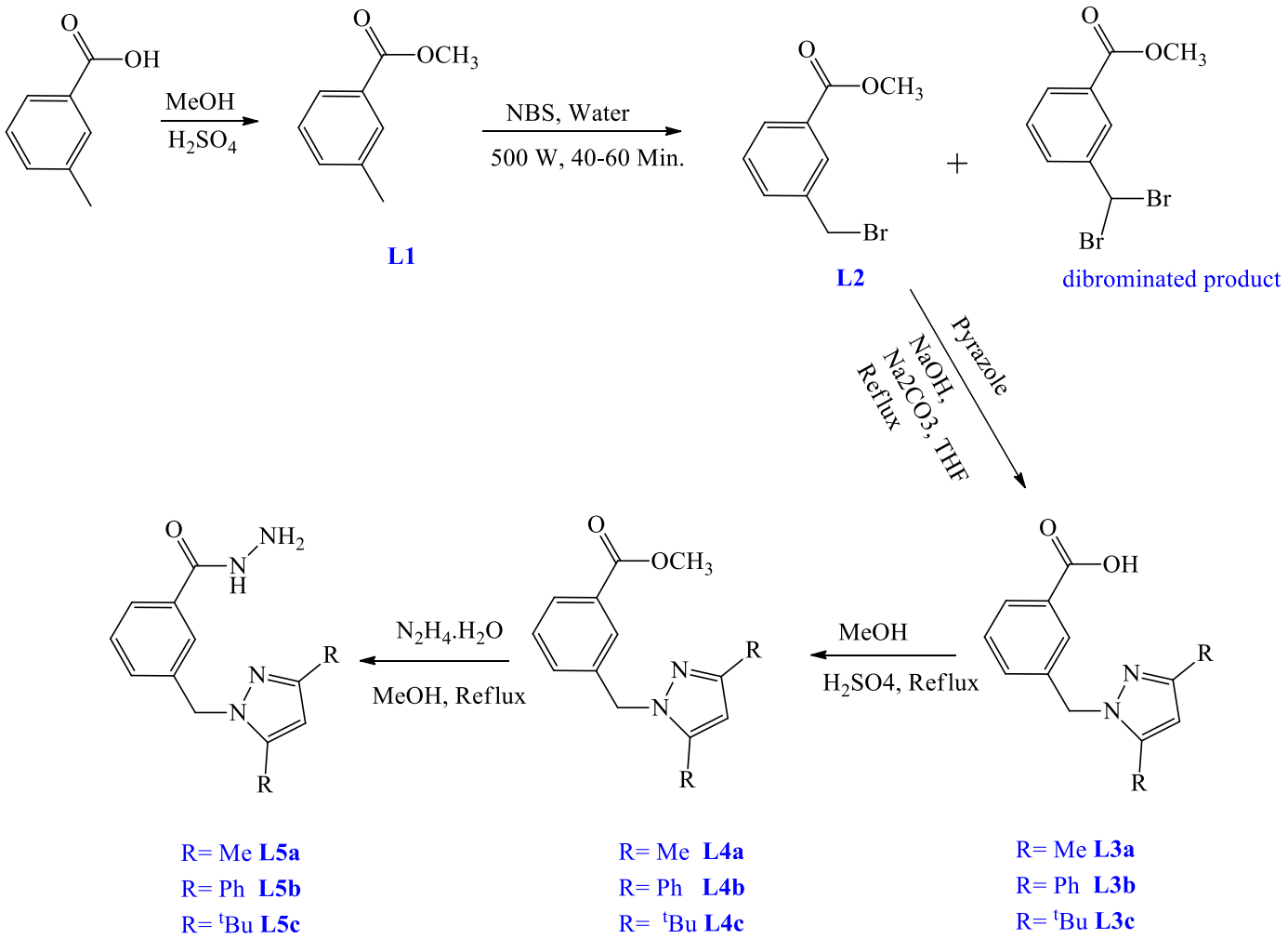
2.6 Results and Discussions

2.6.1 Synthesis of ligands and complexes

The rationale for this work was to prepare asymmetric pyrazolyl hydrazide ligands bearing different linkers. Different synthetic methods were explored to prepare these ligands. In all explored precedures, the synthetic protocol made use of the synthon in which a pyrazole derivative was bridged to the benzene ring via a methylene linker, and the benzene ring itself carried a carboxylic group in the *meta* position. The presence of the carboxylic group made the introduction of the hydrazide group easy, Figure 2.4.

Compounds **L1** and **L2** were prepared following modified literature procedures.[60] Compound **L1** was obtained from esterification of the corresponding acid in methanol using sulphuric acid as catalyst. The same compound can be obtained from the reaction of its corresponding

[60] (a) J.A. Mikroyannidis, *J. Appl. Polym. Sci.* 101 (**2006**) 3842. (b) A. Podgoršek, S. Stavber, M. Zubarn, J. Iskra. *Tetrahedron Lett.* 47 (**2006**) 1097.



Scheme 2.1: The stepwise synthesis of ligands

acyl chloride in methanol in the presence of an excess thionyl chloride. Slightly better yields were obtained with the latter (92%) as compared to the former (87%).

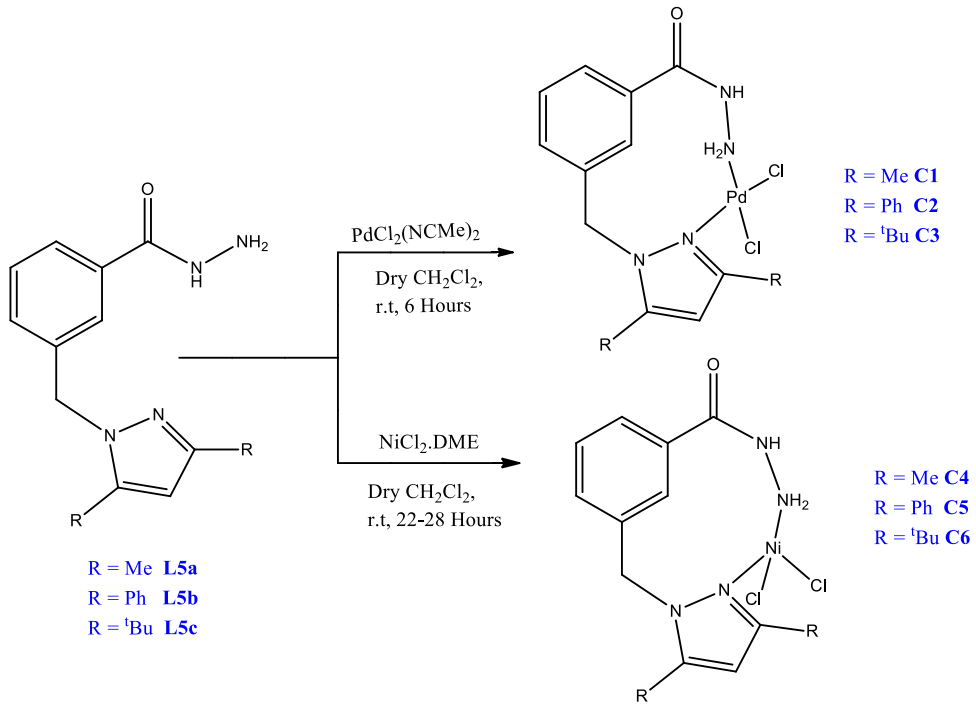
Compound **L2**, was obtained from the bromination of the methyl ester (**L1)** under light irradiation using a halogen lamp. When a 150 watt halogen lamp was used the reaction took between 3-4 hrs to reach completion, while with a 500 watts lamp the reaction only took between 40-60 minutes. The reaction also gave a dibrominated product that was analysed using GC/MS. The chromatogram gave two peaks corresponding to both the dibrominated by-product and desired monobrominated product **(L2)**, Figure A10. The separation of the desired product from the dibrominated analogue was done by extracting the crude with hot hexane and cooling down the hexane extracts below -10 ^{o}C. This allowed the desired product to precipitate out, leaving the oily dibrominated by product in solution. An analytically pure sample of **L2** was obtained in 53% yield after recrystallization from ethanol at room temperature.

The pyrazolyl benzoic acids, (**L3a**, **L3b** and **L3c**), were also prepared from a modified literature procedure.[61] The procedure incorporated two steps at once. Firstly, it involved anchoring a pyrazole moiety followed by the hydrolysis of the ester group into a carboxylic acid. Complete hydrolysis was carried out to avoid obtaining a product mixture containing unhydrolysed esters and hydrolysed carboxylic acids. The hydrolysis depends on the mole ratio of the bases (NaOH and Na_2CO_3) used, and was observed to occur when four mole equivalents of each base were added. The carboxylic acid group in **L3a**, **L3b** and **L3c** was again esterified and further converted to the corresponding hydrazides, through hydrozonolysis of esters, and were obtained in good yields of between 75-80%. The hydrazides were prepared in absolute ethanol or methanol, and were obtained in moderate yields of between 55-63 %. The reaction for the hydrozonolysis of esters **L4a-c** can be done with either hydrazine monohydrate or hydrazine sulphate salt, with hydrazine monohydrate giving better yields as compared to the hydrazine sulphate salt.

The pyrazolyl hydrazide ligands (**L5a-c**) were all obtained as white solids, their solubility depends on the substituents on the pyrazole rings, for example the hydrazide with di-tertiary butyl substituents is soluble in cold alcohols but the diphenyl and dimethyl were only soluble in hot ethanol and methanol. All the pyrazolyl hydrazides were soluble in other slightly polar

[61] P.J. Steel, M.C. Hartshorn, *J. Austr. Chem*. 48 (**1995**) 1587.

solvents like dichloromethane, chloroform and THF. The pyrazolyl hydrazide ligands (**L5a**, **L5b** and **L5c**) were all stable at room temperature and could be stored in vials for two weeks without requiring any extra precautions.



Scheme 2.2: Synthesis of palladium(II) and nickel(II) complexes

The pyrazolyl hydrazide ligands **L5a-c** reacted with palladium acetonitrile salt $PdCl_2(CH_3CN)_2$ in a 1:1 ratio to form the Pd(II) complexes **C1-C2**. The complexes **C1** and **C2** with dimethyl and diphenyl pyrazole moieties were obtained as yellow powders while the palladium complex with ditertiary butyl pyrazole **C3** was obtained as red powder. All the complexes are non-hygroscopic and fairly stable in air at room temperature. The solubility test showed that the solubility of the Pd(II) complexes (**C1**, **C2** and **C3**) depend on the substituents of the pyrazole moiety, for example the solubility of the Pd(II) complexes in dichloromethane decreased in the order ditertiary butyl complex > diphenyl complex > dimethyl complex. The dimethyl and diphenyl complexes (**C1** and **C2**) dissolved in THF and more polar solvents like DMF, and DMSO, while the ditertiary butyl complex (**C2**) easily dissolved in most of the common solvents like dichloromethane, chloroform and methanol. The complexes were obtained in moderate yields of 53-63%.

The nickel complexes **C4-C6** were also prepared in 1:1 ratio from the reaction of pyrazolyl hydrazide ligands (**L5a**, **L5b** and **L5c**) with $NiCl_2$.DME. Preparation of the complexes using $NiCl_2.6H_2O$ was not successful because the ligands were readily hydrolysed back to their corresponding carboxylic acids under wet conditions. The complexes (**C4**, **C5** and **C6**) were therefore prepared using $NiCl_2$.DME salt in dry dichloromethane as a solvent. The nickel(II) complexes were obtained as solids of various shades of green and were soluble in most organic solvents such as dichloromethane, chloroform, methanol, THF and DMSO. The nickel(II) complexes are also non-hygroscopic and fairly stable in air at room temperature and were obtained in moderate yields that were between 49-63 %.

2.6.2 Characterisation of ligands and complexes

2.6.2.1 Characterisation by FT-IR spectroscopic technique

FT-IR spectroscopy is the most common spectroscopic techniques used by chemists to determine the functional groups in their samples. The transitions responsible for infrared bands are due to molecular absorption, such as periodic motions involving stretching or bending of bonds. Absorption strength depends on the nature of bonds. For example, polar bonds are associated with strong absorption while symmetrical bonds might not absorb at all.[62] Using various sampling accessories, infrared spectrometers can be modified to be used with a wide range of sample types such as gases, liquids and solids. Given that the majority of compounds prepared in this study were either liquids or solids, infrared spectroscopy served as an important tool for functional group identification.

All of the compounds prepared in this study contained a derivative of the carbonyl (C=O) group. Using IR spectroscopy, the C=O stretching frequencies generally appear in the region between 2000 cm^{-1} and 1500 cm^{-1}. Several other vibrations, such as C=C vibrations, also occur in this region. However, C=O stretching is normally more intense than any other vibrations in this region. The position and intensity of C=O stretching depends upon the type of substituent or group attached to the carbonyl group. For example the stretching frequency due to carbonyl group of **L2** shifted from 1715 cm^{-1} to 1679 cm^{-1} after the ester group was converted into a carboxylic acid in **L3a**, Figure 2.5. The C=O stretching frequencies of the ester carbonyl groups

[62] S. Sternhell, J.R. Kalman, Organic Structures from Spectra, John Wiley & Sons Inc, United State, (**1986**).

are generally observed in the range 1716 cm^{-1} to 1719 cm^{-1} while those for the carboxylic acids and amides are observed at the region between 1605-1690 cm^{-1}.[63]

The appearance of the band at 557.91 cm^{-1} in **L2** confirmed the successful bromination of CH_3 to CH_2Br, Figure 2.4. While the appearance of the broad υ(OH) band at 3395 cm^{-1} for **L3a** in Figure 2.5 confirms successful conversion of the ester group in 3-bromomethyl methyl benzoate into a carboxylic acid. Concurrently, under the same conditions substitution of bromine by 3,5-dimethyl pyrazole occurred. Successful substitution was confirmed by the appearance of the υ(CN) band of the pyrazole at 1360 cm^{-1}. Further esterification of **L3a** is confirmed by the disappearance of the broad υ(OH) band at 3395 cm^{-1} and the appearance of $-OCH_3$ at 2867 cm^{-1}, Figure 2.6.

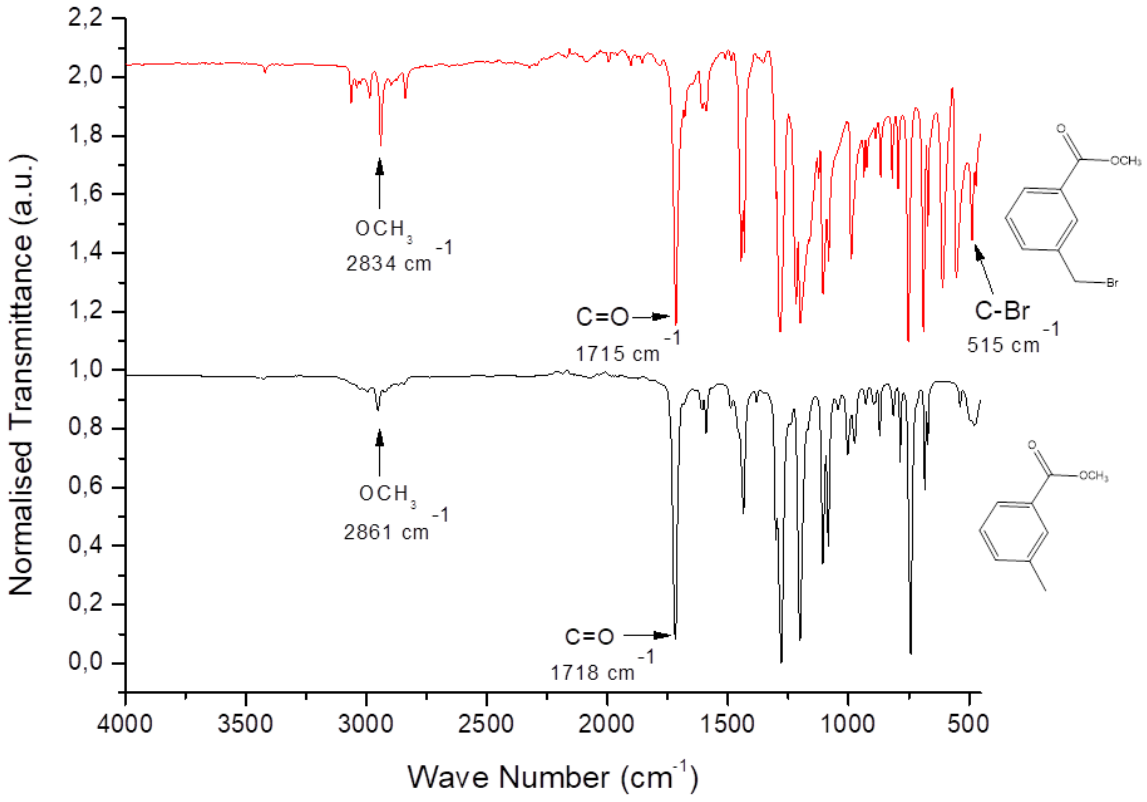


Figure 2.4: The FT-IR spectra of compound **L1** (black) and **L2** (red)

[63] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric identification of organic compounds, John Wiley & Sons Inc, Canada, (**1963**).

The absorption bands located in the 3100-2800 cm^{-1} region are caused by the vibration of either the -OH, $-CH_2$, $-CH_3$ or -N-H groups. However the presence of the carboxylic acid (**L3a)** group (-OH) masks the expected absorptions peaks for $-CH_2$ and $-CH_3$ groups, Figure 2.5. Generally, the -N-H stretching frequencies of secondary amide are observed in the region 3370-3170 cm^{-1}. Successful conversion of esters to hydrazides is confirmed by the appearance of the N-H stretch at 3346 cm^{-1}, Figure 2.6.

Infrared spectral data of the ligands and their Pd(II) and Ni(II) complexes have been reported. All the pyrazolyl hydrazide ligands show a pair of fairly intense N-H stretching bands in the range of 2956-3641 cm^{-1}. All the complexes showed considerable positive or negative shift in bands (2914-3347 cm^{-1}) originating from amino N-H stretching frequency as compared to their free ligands. The shift of N-H bands observed on the infrared spectrum of ligands and complexes indicates the coordination of terminal amino nitrogen for both Pd(II) and Ni(II) complexes. An increase or decrease in amino N-H stretching frequency is due to increase or decrease in the stretching force constant of amino N-H respectively upon complexation. The bands originating from imino N-H stretching frequencies in complexes **C2** and **C5** are in the range of 3148 cm^{-1} to 3311 cm^{-1} for both the Pd(II) and Ni(II) complexes, Figure 2.7. The bands attributed to imino N-H in two complexes **C2** and **C5** were lower by roughly 40 cm^{-1} than the ones observed for their corresponding ligand **L2**. From this information, it shows that the $-NH_2$ of the hydrazide group participated in bonding to the metal centres. Ain *et al*.[64] reported both monodentate and bidentate hydrazide Pd(II) complexes. According to the report benzene and pyridine carbohydrazides can form two different square planner Pd(II) complexes. They also showed that both the nitrogen and oxygen atoms on the hydrazide group can participate towards bonding to the metal centre. They reported the NH bands ranging from 3216 cm^{-1} to 3011 cm^{-1} for the ligands and from 3499 cm^{-1} to 3095 cm^{-1} for the corresponding Pd(II) complexes. Vidal *et al*.[65] reported 5 co-ordinate distorted square planar and trigonal bipyrimidal Ni(II) complexes of dipicolinic acid hydrazide. From their results the bands assigned to NH stretching vibrations were observed as a broad bands between 3200 cm^{-1} to 3300 cm^{-1} for the ligands and from 3500 cm^{-1} to 3600 cm^{-1} for their corresponding Ni(II) complexes.

[64] Q.U. Ain, U. Ashiq, R.A. Jamal, M. Mahrooof-Tahir, Spectrochim. *Acta Mol. Biomol. Spectrosc*., 115 (**2013**) 683.

[65] S.K. Sahni, S.K. Sangal, S.P. Gupta, V.B. Rana, *J. Inorg. Nucl. Chem*. 39 (**1977**) 1098.

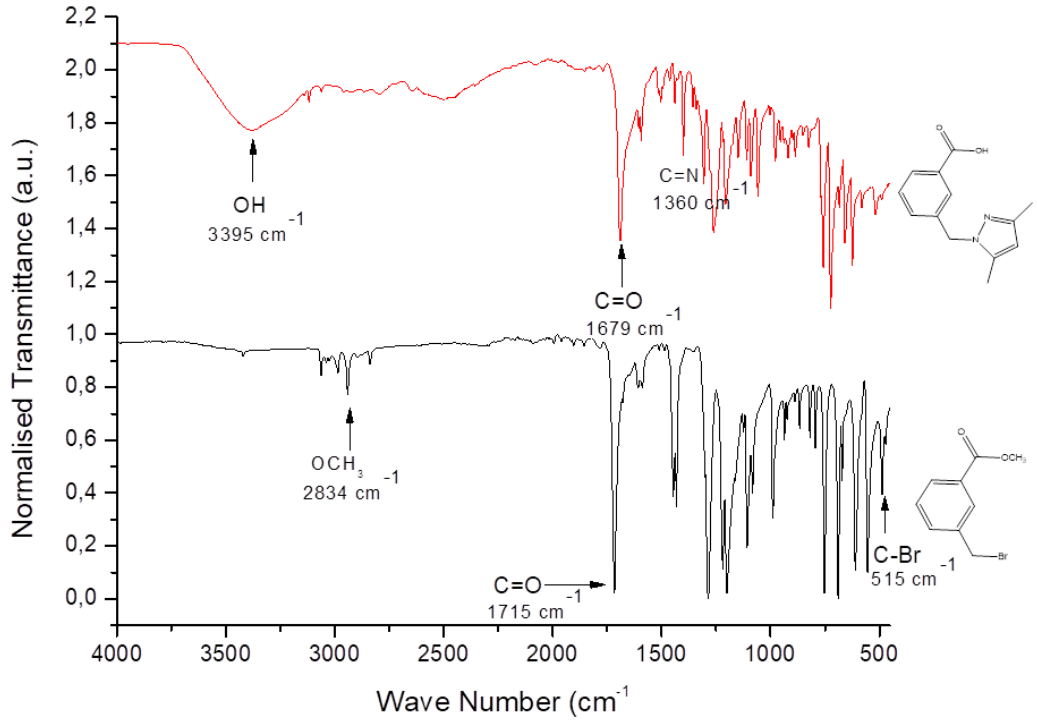


Figure 2.5: The FT-IR spectra of compound **L2** (black) and **L3a** (red)

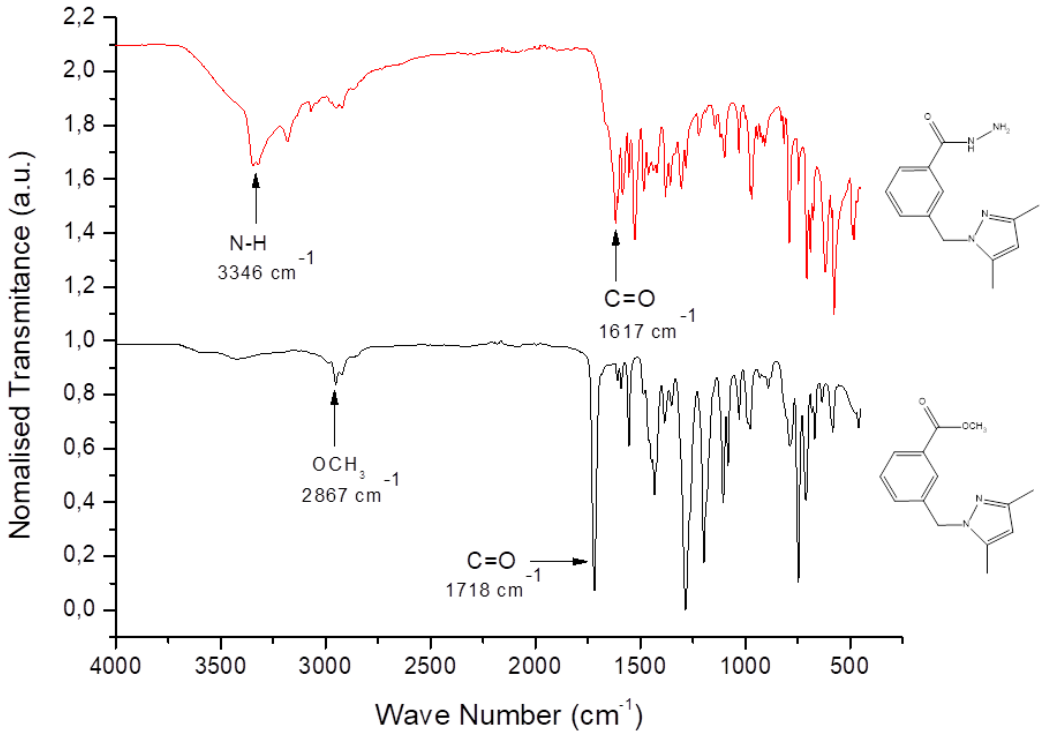


Figure 2.6: The FT-IR spectra of compound **L4a** (black) and **L5a** (red)

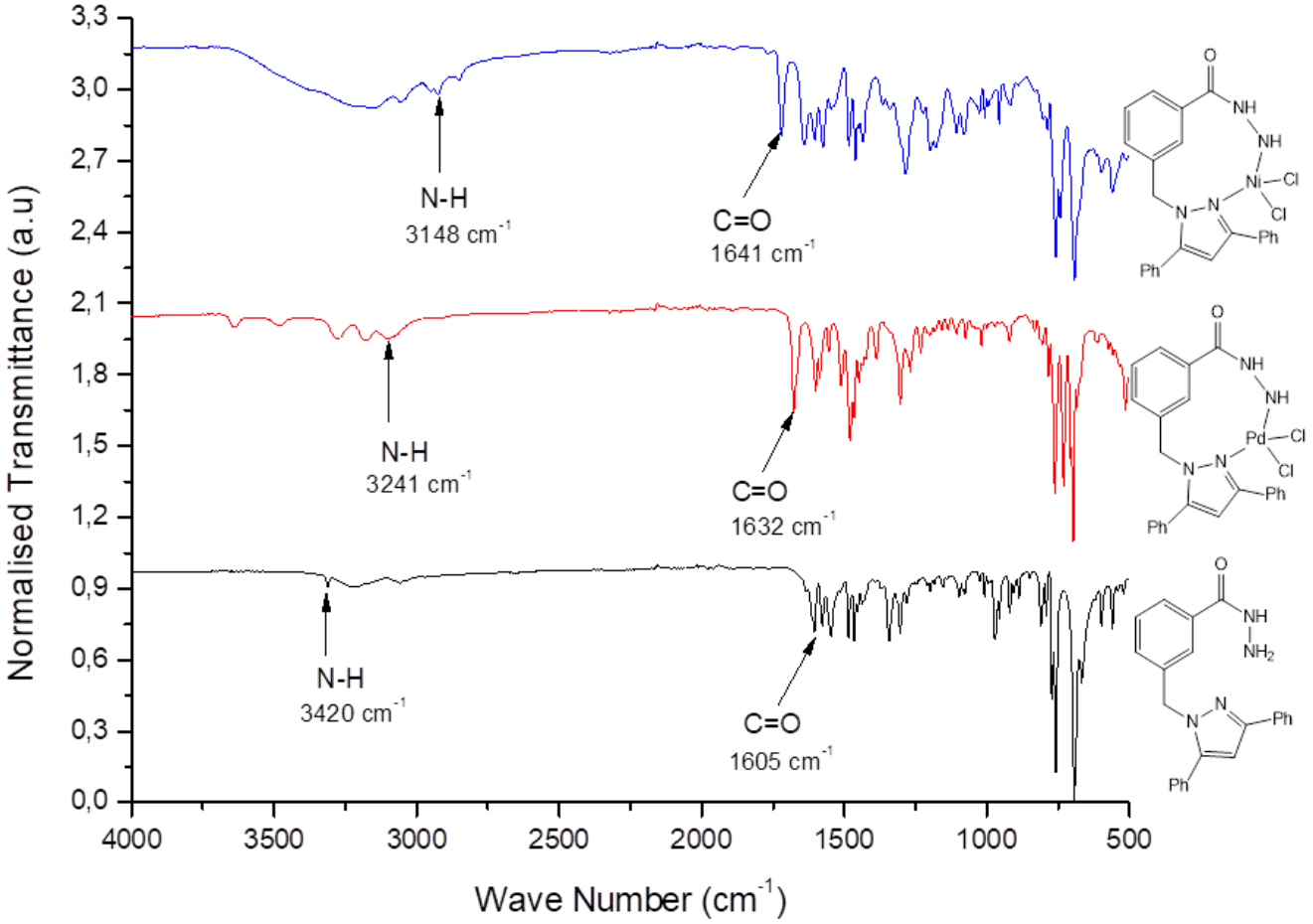


Figure 2.7: The FT-IR spectra of **L5b**, **C2** and **C5**

2.6.1.2 Characterisation by NMR spectroscopic technique

NMR spectroscopy is a research technique that exploits the magnetic properties of certain magnetic nuclei. It determines the chemical properties of the atoms or molecules in which atoms are contained. This technique also provides the detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.[66]

For elucidation of chemical structure, both ^{1}H NMR and ^{13}C NMR were used to confirm structures of all the compounds prepared. For example in the ^{1}H NMR spectrum of compound **L1**, the methyl protons of the tolyl group resonate at 2.25 ppm, and at 3.87 ppm for the methyl of the ester group, Figure A1. The successful preparation of **L2** was confirmed by the appearance of the peak for the methylene protons which is observed at 4.49 ppm and while the methyl peak from the ester group moved down field and resonated at 3.90 ppm in Figure 2.8. In the aromatic region, the protons from the phenyl ring are represented by four peaks, a singlet at 8.04 ppm, two doublets at 7.95 ppm and 7.57 ppm followed by a triplet at 7.40 ppm, as expected for a benzene ring with substituents on the 1,3 positions. The ^{13}C NMR spectrum in Figure A2 has 9 peaks as expected from the number of carbons present in compound **L2**; with the carbonyl carbon resonating at 166.41 ppm which is in the downfield region of the spectrum because of the oxygen being double bonded to this carbon. The ester carbon is observed at 32.43 ppm and the methylene carbon is observed at 52.20 ppm.

Further reaction of compound **L2** with different pyrazole moieties allowed for the substitution of the bromine group with different pyrazole moieties. The substitution caused the methylene protons of **L3a**, **L3b** and **L3c** to appear downfield when compared to those of **L2.** Figure 2.9, represents the ^{1}H NMR spectrum of **L3a** and as expected the methylene protons were observed at 5.25 ppm. Two distinct peaks are observed at 2.14 ppm and 2.09 ppm and these are due to the resonance of the protons of the two methyl groups which are substituents on the 3,5 positions of the pyrazole moiety. A peak assignable to the proton on the fourth position of the pyrazole was observed at 5.84 ppm. The aromatic protons shifted down field and were again observed as four different peaks with two doublets (7.84 ppm and 7.33 ppm), one singlet (7.68 ppm) and a triplet (7.44 ppm). Motsoane and co-workers also reported the pyrazolyl benzene

[66] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric identification of organic compounds, John Wiley & Sons Inc, Canada. (**1963**).

compounds with methylene linkers located at the 1,3 positions of the benzene ring {$C_6H_6(CH_2)_2(Pz)_2$}. They observed methylene protons at 5.12 ppm and the pyrazolyl proton at 5.90 ppm.[11] Furthermore, under basic condition the ester group was converted into a carboxylic group but unfortunately the resonance due to the OH protons of the carboxylic group was not observed but were confirmed using FT-IR spectroscopy as previously discussed. The ^{13}C NMR spectrum of compound **L3a** in Figure A3 does show the 13 protons as expected with the carbonyl carbon more deshielded because of the acidic proton on the carboxylic acid that was observed at 167.11 ppm. The peak assignable to a methylene carbon was observed at 51.16 ppm, while the peak assigned to the fourth carbon on the pyrazolyl ring appear at 105.14 ppm, and the two methyl carbons from the pyrazole ring were observed at 13.32 ppm and 10.60 ppm. Similar observations were observed for **L3b** and **L3c**.

To prepare the pyrazolyl hydrazides, the carboxylic acids (**L3a**, **L3b** and **L3c**) were again esterified and then reacted with hydrazine monohydrate, to get the final ligands. Introduction of the ester group slightly shifted the carbonyl carbon resonance from 167.11 ppm (**L3a**) to 168.10 ppm (**L4a**). The ^{1}HNMR spectrum in Figure 2.10 shows the methyl peaks at 3.86 ppm assignable to the methyl protons of the ester group. The same trend was observed with compounds **L4b** and **L4c**. The ^{13}C NMR spectrum of compound **L3a** shows the carbonyl carbon at 167.11 ppm and the methylene carbon at 51.16 ppm. The methyl carbons for the 2 methyl groups on the pyrazole were observed upfield at 10.60 ppm and 13.32 ppm. For compound **L4a** all the carbon NMR peaks were downfield as compared to the ones for compound **L3a**. A peak assignable to the ester carbonyl carbon was observed at 168.10 ppm, while the peak assignable to the methylene carbon was observed at 52.68 ppm and for the methyl carbons the peaks were observed at 13.21 ppm and 10.97 ppm, Figure A4.

Hydrozonolysis of the esters gave the corresponding pyrazolyl hydrazides and these were confirmed by the presence of the NH_2 and NH resonance. For compound **L5a**, a peak assignable to NH_2 protons is observed at 4.49 ppm while the peak at 9.79 ppm was assigned to an NH peak. Manojkumar *et al.*[67] using methyl coumarinyl-7-ocylic acid hydrazide ligands observed the NH protons of the hydrazides at 8.33 ppm in deuterated DMSO. Kumar and co-workers observed NH peak of benzoic hydrazides at 8.75 ppm in a mixture of deuterated DMSO and $CDCl_3$, they also reported the NH_2 peak at 4.65 ppm. Figure 2.12 represents the ^{13}C NMR of **L5a**, the peak assignable to the carbonyl carbon did not show any significant

[67] P. Manojkumar, T. Ravi, G. Subbuchettiar, *Acta. Pharm.* 59 (**2009**) 159.

change from that of compound **L4a**. The peak assignable to the fourth carbon the pyrazole ring moved slightly to the downfield region and resonated at 105.73 ppm. Another shift was observed for the methylene carbon at 51.98 ppm. Again for the methyl carbons of the pyrazole ring were observed at 11.05 ppm and 13.38 ppm regions with no significant shift comparable to the ones for **L4a**.

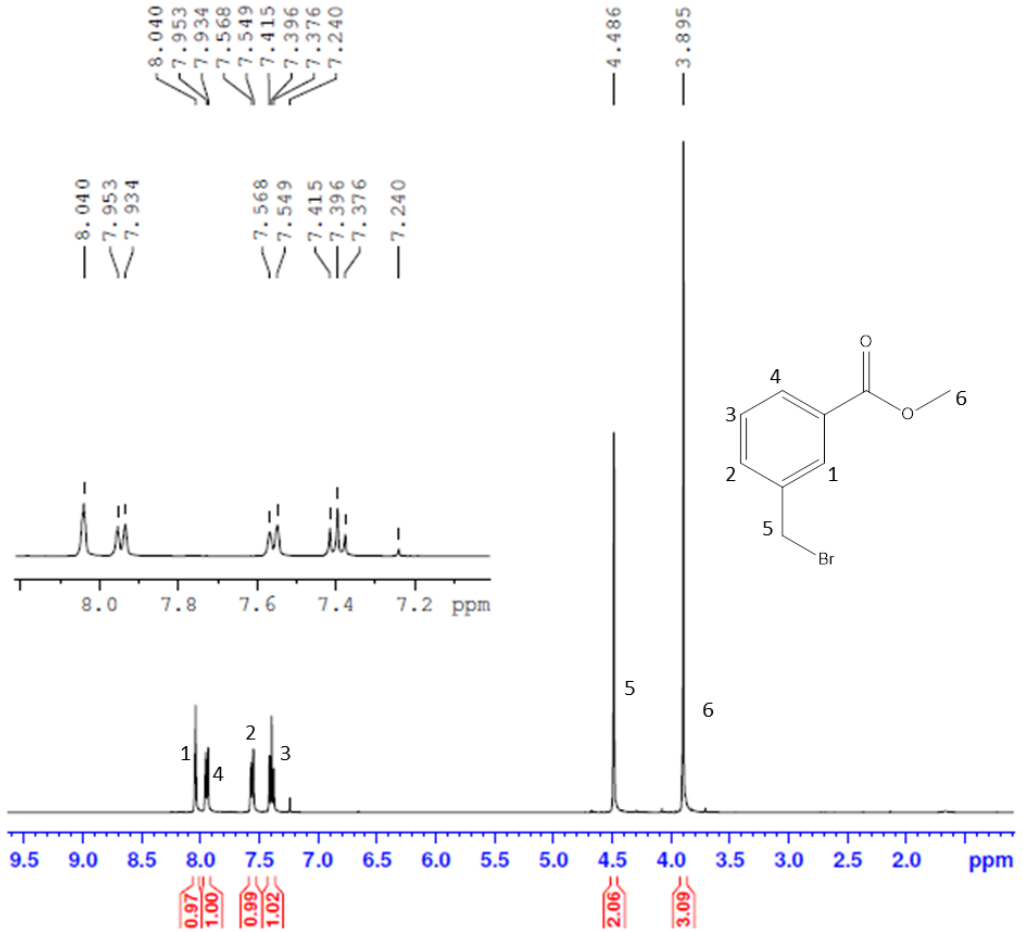


Figure 2.8: ^{1}H NMR spectrum of methyl 3-(bromomethyl) benzoate **L2 (**in $CDCl_3$)

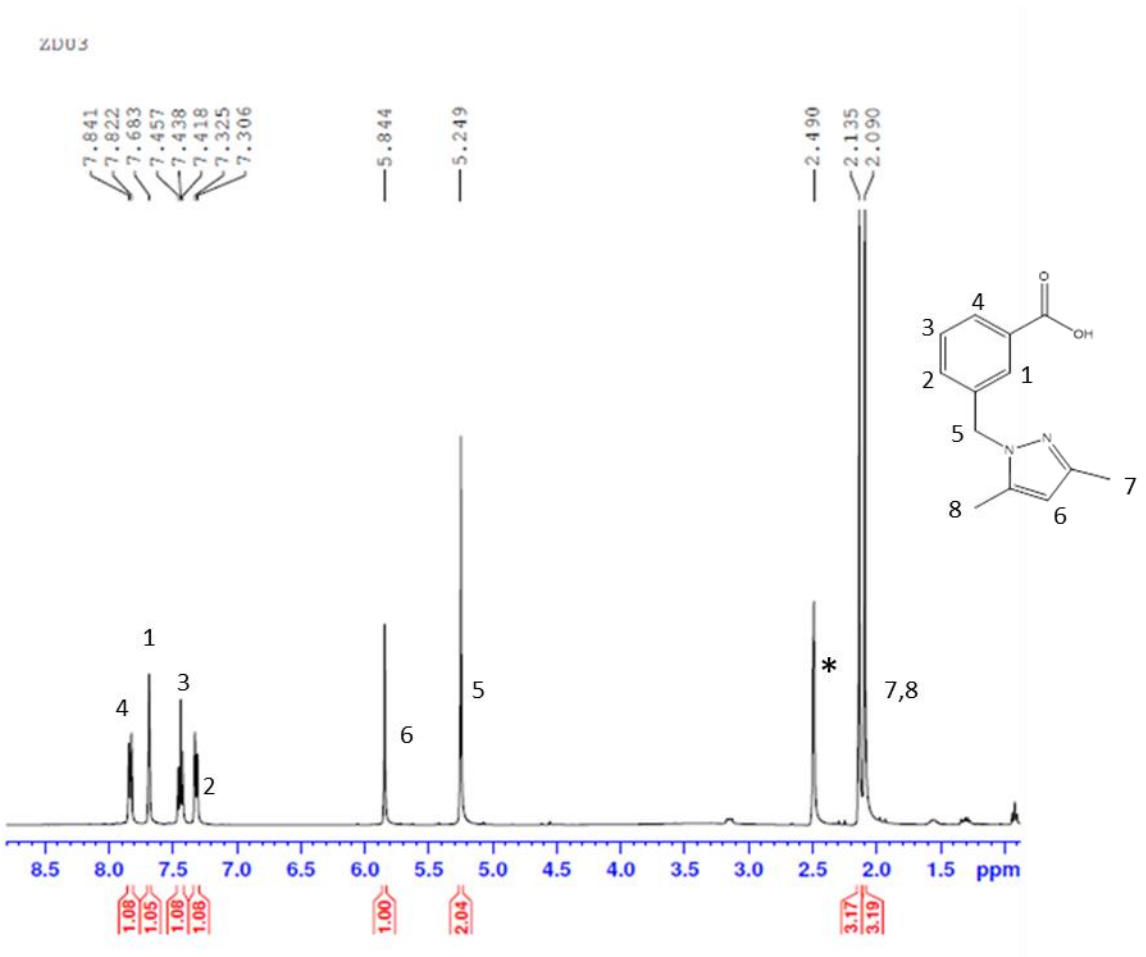


Figure 2.9: ^{1}H NMR spectrum of Compound **L3a** (in *DMSO-d_6)

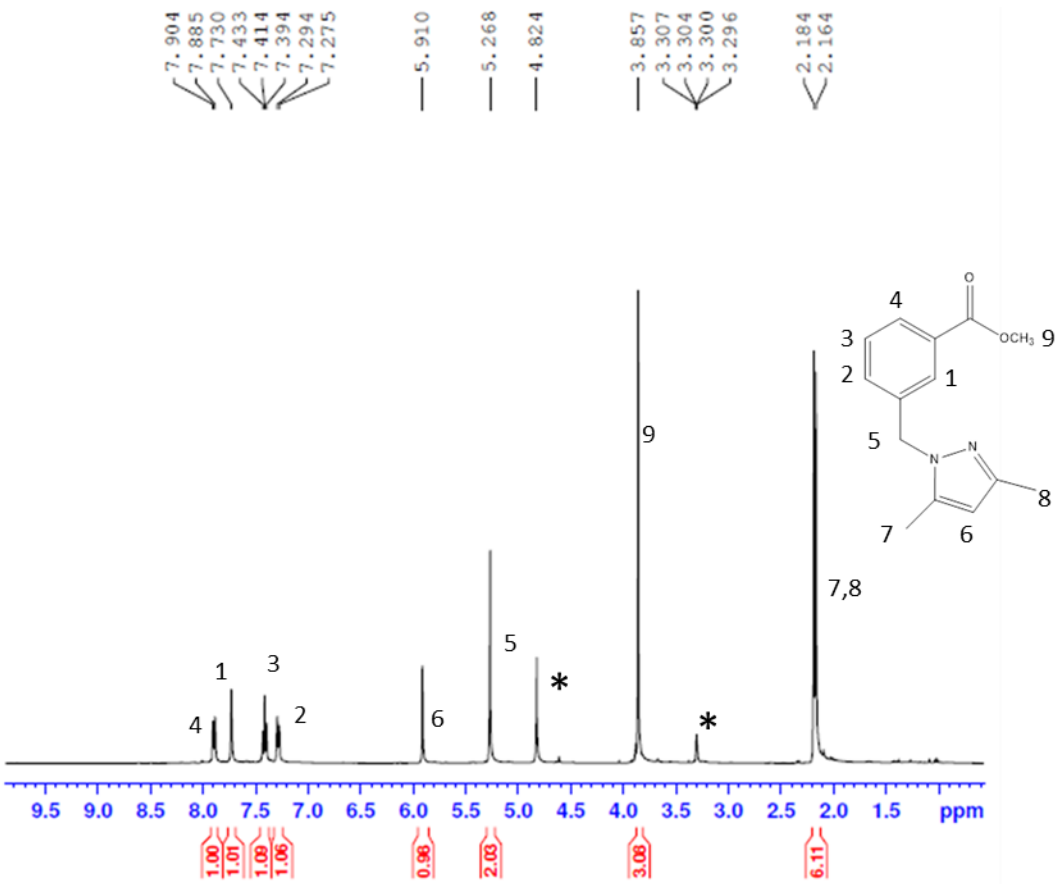


Figure 2.10: ^{1}H NMR spectrum of Compound **L4a** (in *MeOD-d_4)

After complexing with palladium metal to prepare complexes (**C1**, **C2** and **C3**), the CH_2 for complexes **C1** and **C3** signals appear between 5.92 ppm and 5.84 ppm as AB doublets.[68] Most of peaks on complex **C1** and **C2** appeared as doublets. This can be associated with the fluxionality of the molecule resulting from the presence AB type of protons from both the methylene and the amide groups. Figure 2.13 shows the spectrum of complex **C3** and a shift on the amide proton from 9.71 ppm in the ligand to give a pair of peaks at 8.89 ppm to 8.79 ppm. Another pair was observed for the methylene protons which appeared at 5.44 ppm and now appear as two peaks at 5.08 ppm and 5.22 ppm. Ain and co-workers reported palladium complexes of benzohydrazides. The signals assignable to methylene protons of the ligands were observed at 5.44 ppm and after complexation the signals shifted to 5.10 ppm and 5.27 ppm.[1] The proton from the fourth carbon of the di-tertiarybutyl pyrazole was observed at 5.95 ppm for the ligand and after complexation the proton shifted slightly downfield and was observed at 6.03 ppm.

The ^{13}C NMR spectra of pyrazolyl hydrazide ligands (**L5a**, **L5b** and **L5c**) and their palladium(II) complexes (**C1**, **C2** and **C3**) in deuterated DMSO confirm the bonding modes explained in ^{1}H NMR and IR spectra. The number of carbon peaks in ligands and complexes matches their expected values. The carbonyl carbon signals in the pyrazolyl hydrazide ligands (**L5a**, **L5b** and **L5c**) appear in the range of 168.15 ppm to 165.23 ppm and the phenyl carbons were observed in a range of 139.51 ppm to127.23 ppm. The peaks assignable to the methylele carbons of the pyrazolyl hydrazide ligands were observed in the range of 58.11 ppm to 32.43 ppm. This CH_2 carbon signal is shifted up-field from 32.43 ppm in **L2** to 58.11 ppm in the rest of the compounds (**L3's**, **L4's** and **L5's**); this shift is due to the substitution of the bromine group with the pyrazole moiety. For their Pd(II) complexes (**C1**, **C2** and **C3**), the peaks for the carbonyl carbons appears in the range of 150.11 ppm to 164.30 ppm. For their Pd(II) complexes (**C1**, **C2** and **C3**), the peaks for the carbonyl carbons appears in the range of 150.11 ppm to 164.30 ppm. Other aromatic carbon atoms in the free ligands and corresponding complexes resonate in nearly the same region. All the ligands have shown bidentate behaviour (N^N donor) forming metal hydrazide complexes in 1:1 ratio.

[68] S.O. Ojwach, I.A. Guzei, L.L. Benade, S.F. Mapolie. J. Darkwa, *Organometallics* 28 (**2009**) 2127.

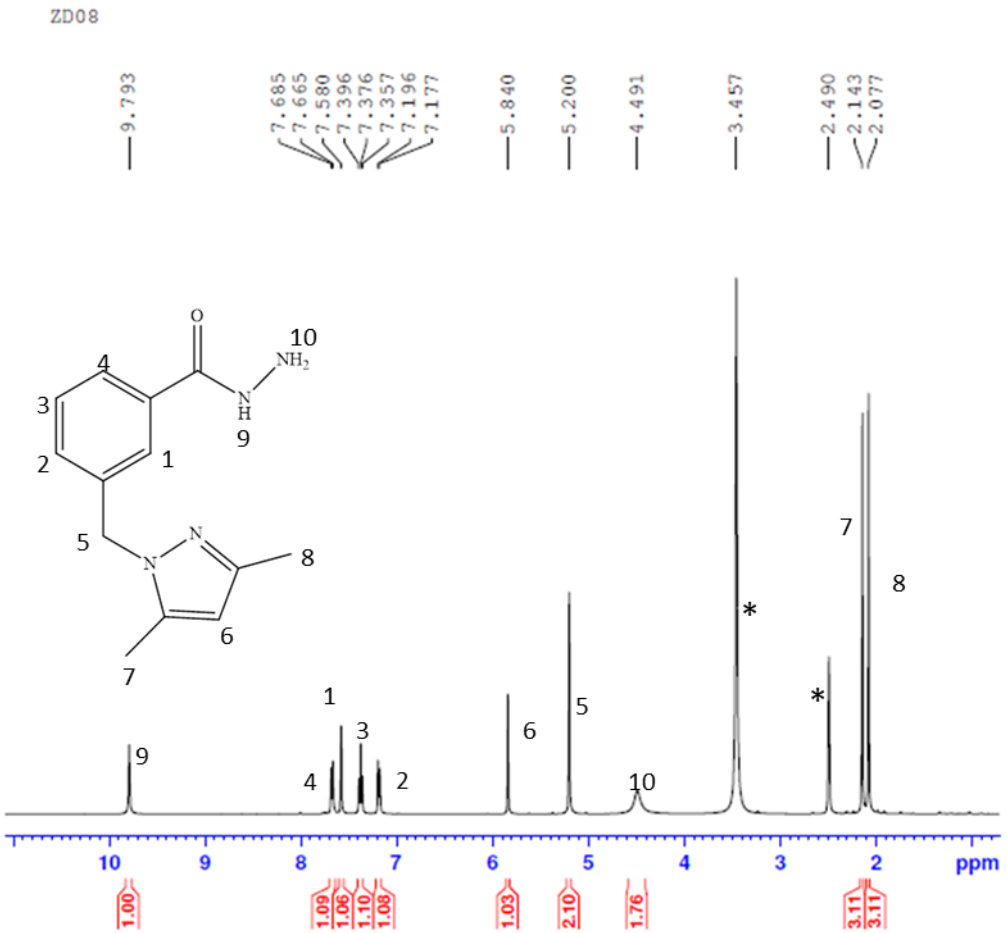


Figure 2.11: ^{1}H NMR spectrum of Compound **L5a** (in *DMSO-d_6)

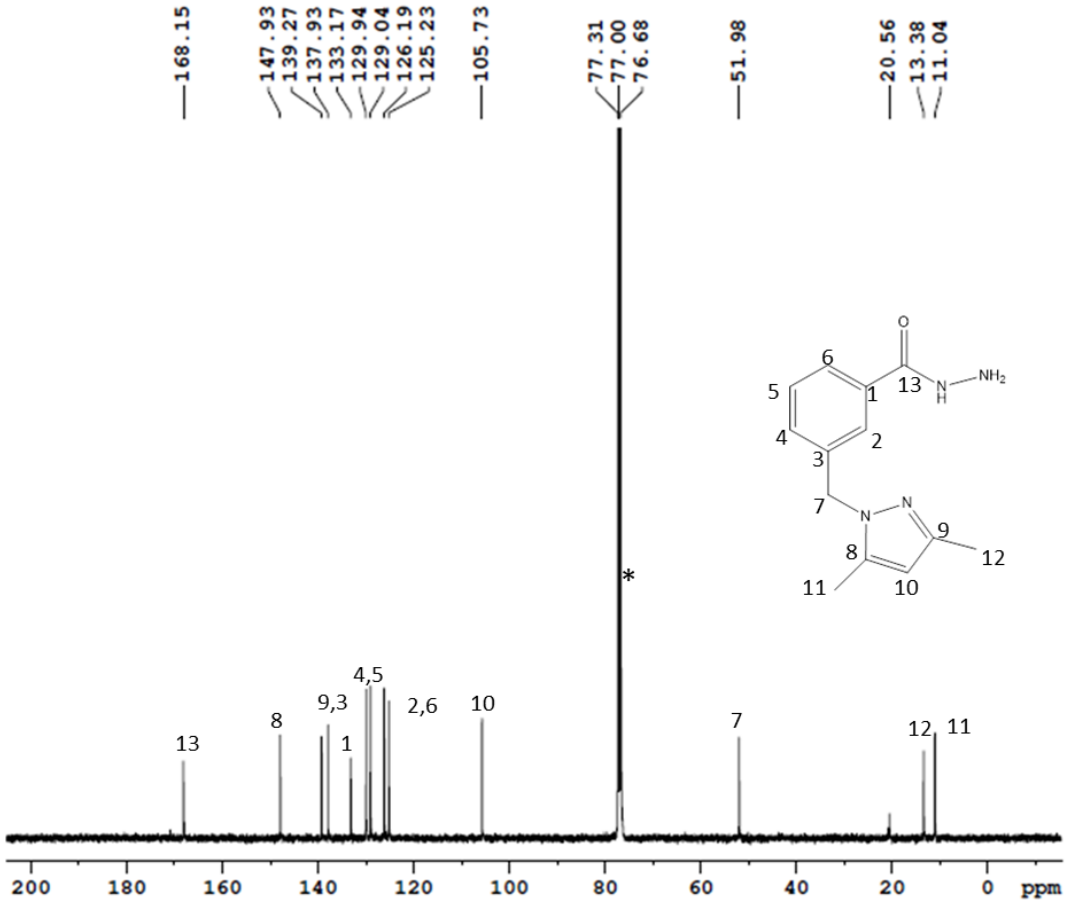


Figure 2.12: ^{13}C NMR spectrum of Compound **L5a** (in *$CDCl_3$)

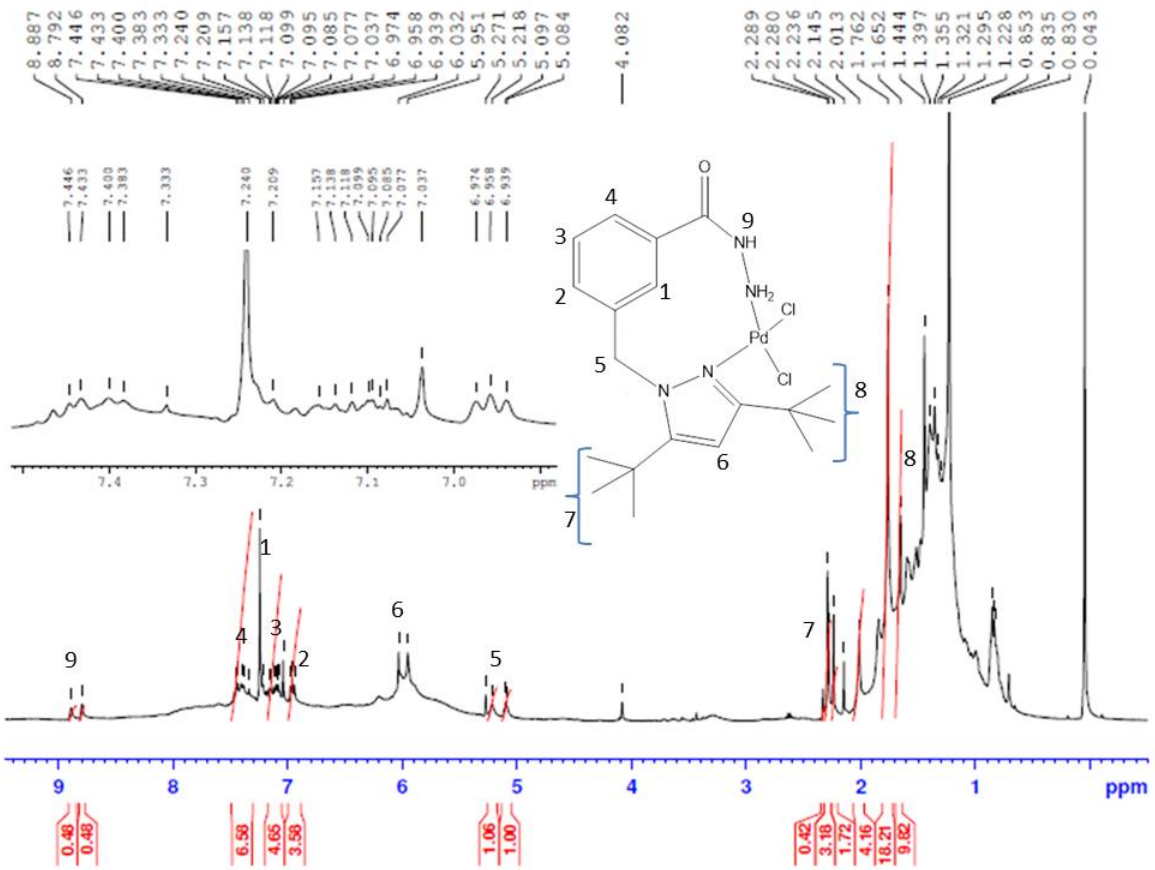


Figure 2.13: ^{1}H NMR Spectrum of Complex **C3** (in $CDCl_3$)

The ^{1}H NMR spectra of all the Ni(II) complexes showed the broad peaks, which were not easy to assign, this suggested that the complexes are paramagnetic. The magnetic behaviour of metal complexes can help to predict geometry of the corresponding complexes using valence bond theory as described in in the previous chapter.[69]

2.6.1.3 Characterisation by Mass spectroscopic technique

In a mass spectrometer the substance under investigation is bombarded with an electron beam and quantitatively records the results as a spectrum of positive ion fragments. This record is called a mass spectrum.[70]

GC-MS is one of the mostly used techniques for specific trace analysis in complex mixtures and is also called a tandem mass spectroscopy because it couples the gas chromatography and mass spectrometry. Only compounds that are sufficiently volatile for GC can be used in GC-MS.[71] This spectroscopy was also used to confirm the molecular weight of the expected compounds. When analysis was performed for compound **L5a**, the GC-MS spectrum of **L5a** shows the parent mass ion in (*m/z* = 244) as expected. Another peak assignable to the loss of the CH_3 group was observed at *m/z* = 229, this is followed by a loss of the NH_3 group at *m/z* = 213. The complete loss of the hydrazide group ($CONH_2NH_3$) was observed at *m/z* = 170. This was followed followed by the loss of C_4H_4 group and was observed at *m/z* = 135. A complete loss of the pyrazolyl ring was observed at *m/z* = 89 and after loosing two moles of C_2H_4 group, the resulting C_3H_3 was observed at *m/z* = 39.

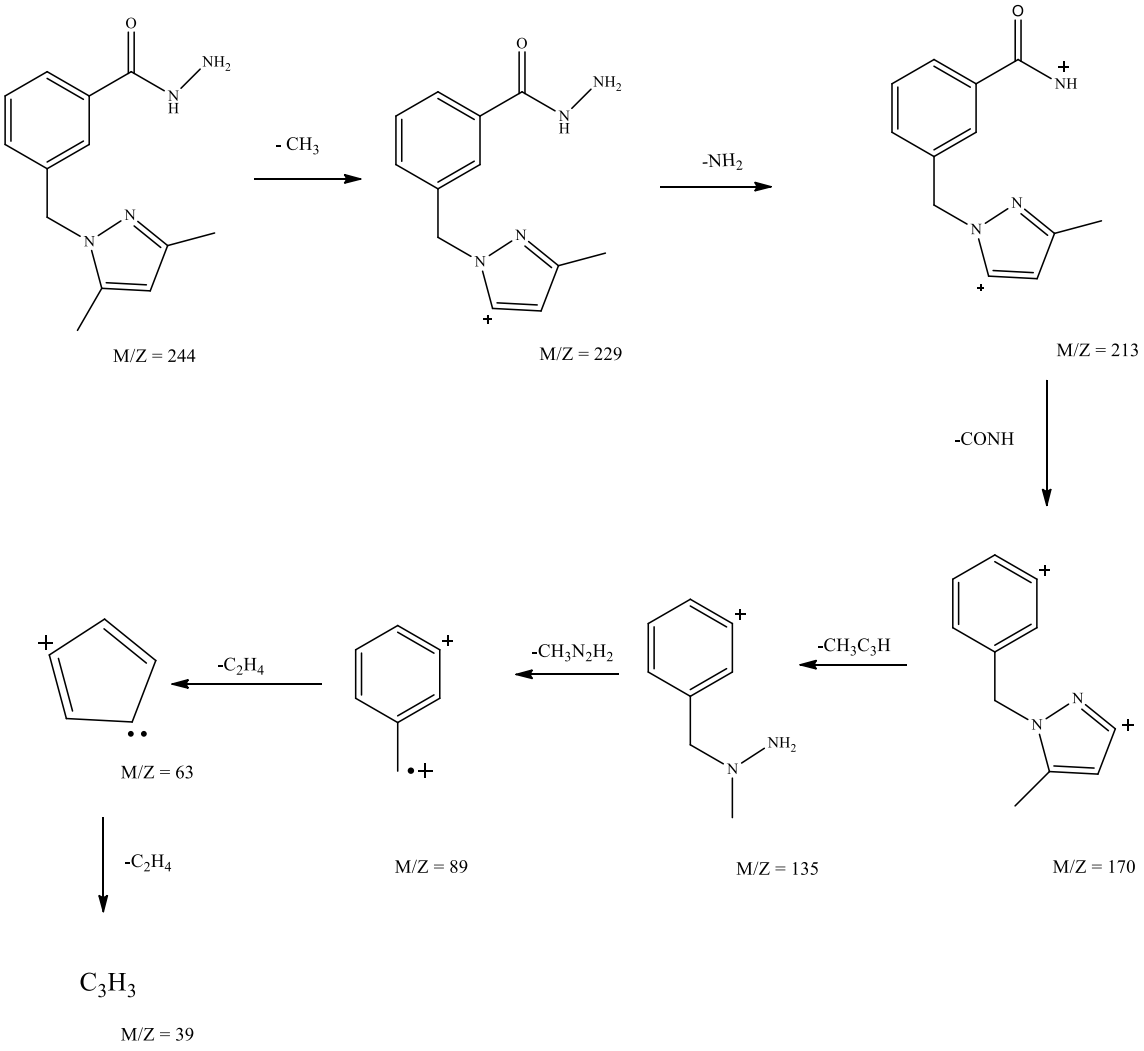
Structures of Pd(II) and Ni(II) complexes of these ligands were also predicted using mass spectrometry. The $[M^+]$ observed at *m/z* = 373 corresponding to the expected product in Figure 2.13 confirms successful complexation of the compound **L5a** with the nickel metal. The

[69] (a) R.G. Hayter, F.S. Humiec, *Inorg. Chem*. 4 (**1965**) 1701. (b) A. Togni, U Burckhardt, V. Pregosin, R.T. Pregosin, R.J. Salzmann, *J. Am. Chem. Soc.* 118 (**1996**) 1013.

[70] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric identification of organic compounds, John Wiley & Sons Inc, Canada, (**1963**).

[71] C.J.W. Brooks and C.G. Edmonds, B.S. Middleditch, in Practical Mass Spectrometry, Ed. Plenum, New York, (**1979**).

molecular ion not being a base peak may suggest the instability of this complex at high temperatures.



Scheme 2.3: The fragmentation pattern of compound **L5a**.[72]

[72] A. Saeed, M. Batool,. *Med. Chem. Res*. 16 (**2007**) 143

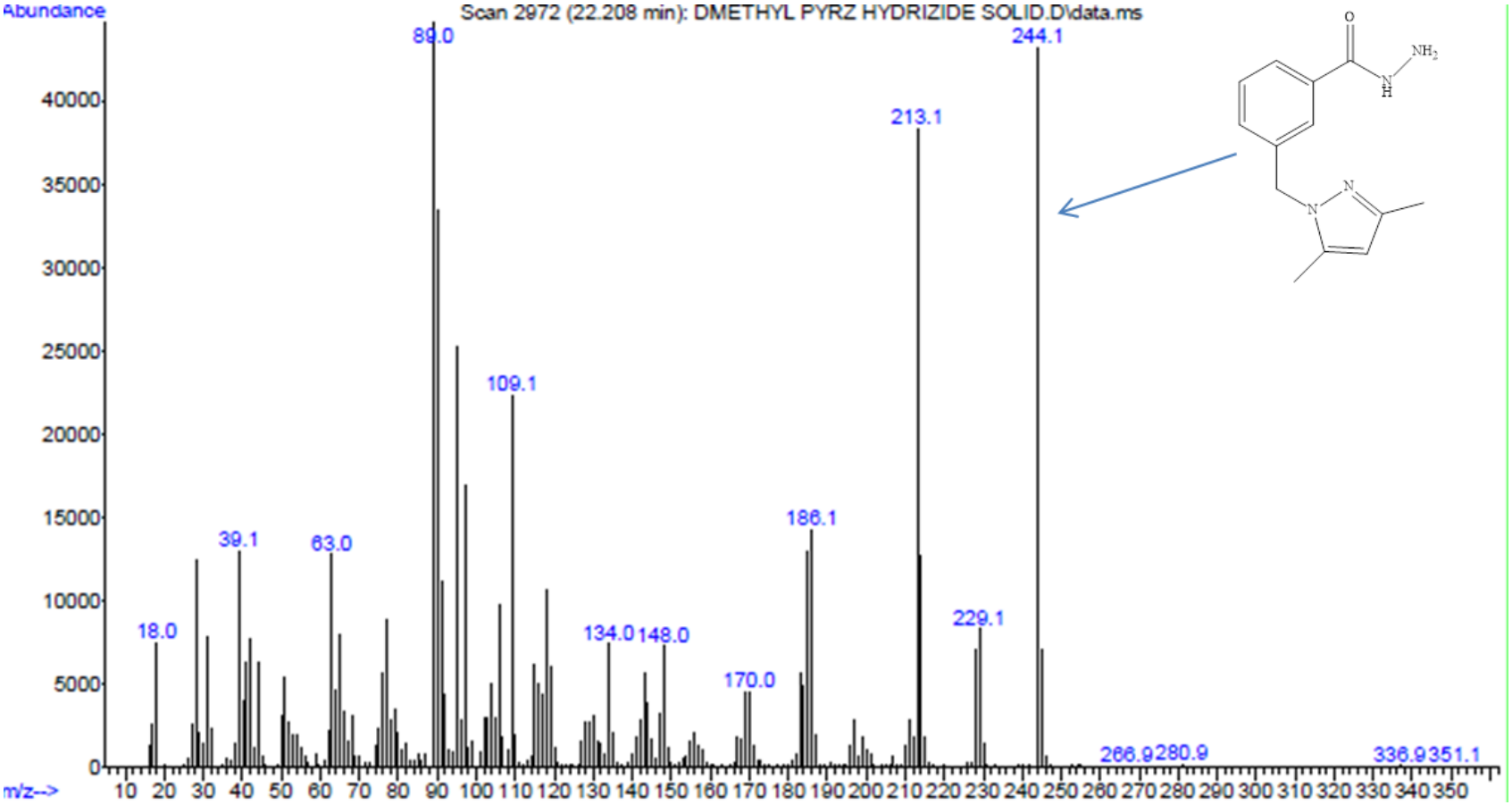


Figure 2.14: The GC-MS spectrum of Compound **L5a**

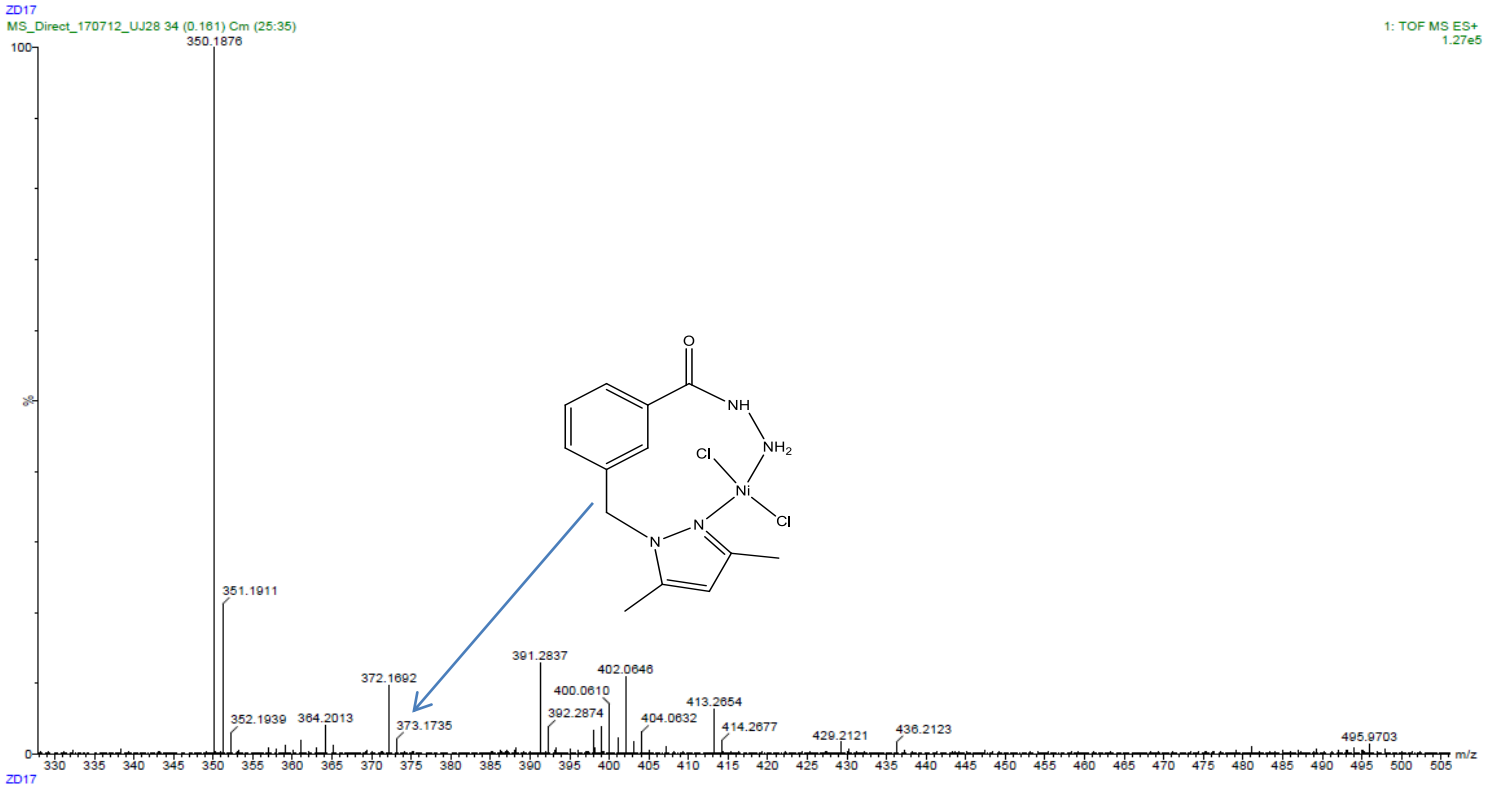


Figure 2.15: The ESI-MS spectrum of Compound **C1**

2.7 Conclusions

Asymmetric pyrazolyl hydrazide ligands (**L5a**, **L5b** and **L5c**) were successfully prepared and obtained in moderate yields (53-63%) using a multistep synthetic approach. Preparation of the pyrazolyl hydrazide ligands started from bromination of the 3-methyl benzoate (**L1)** using NBS in water. This was a greener method for the bromination of tolyl derivatives compared the use of Br_2. The other advantage with the use of this method is the easy separation of the brominated product from the excess succinamide. The by-product from succinamide dissolves in water and the final product is insoluble in water, thus separation of the brominated product is easy. The bromination reaction was followed by addition of the pyrazole moiety, and then the hydrazide functionality to generate the desired ligands. The ligands were characterized by FT-IR, melting point, multi-nuclear NMR spectroscopy, GC mass spectrometry and elemental analysis.

The pyrazolyl hydrazide ligands were successfully complexed with $PdCl_2(NCMe)_2$ and $NiCl_2$.DME giving **C1-C3** as square planar complexes and **C4-C6** as tetrahedral metal complexes respectively, with a general formula $MLCl_2$. The complexes were obtained in moderate yields (49-63%). The palladium(II) complexes **C1-C3** were characterized by FT-IR, melting point, multi-nuclear NMR spectroscopy, GC mass spectrometry and elemental analysis. For the tetrahedral nickel(II) complexes **C4-C6**, multi-nuclear NMR spectroscopy could not be used to characterize the complexes because of their paramagnetic nature.

CHAPTER 3

EVALUATION OF ASYMMETRIC PYRAZOLYL Pd(II) AND Ni(II) AS CATALYST FOR ETHYLENE TRANSFORMATION REACTIONS

3 Introduction

3.1 Oligomerisation and polymerisation of olefins

Over the years catalysis has played a very significant role in different chemical transformations that are crucial in many industrial processes. In catalysis, a catalyst is used to speed up the reaction by lowering the activation energy of a particular reaction.[73] Ethylene oligomerisation and polymerisation are examples of chemical transformation reactions that require catalyst for them to occur.

Polymerisation of olefins has made major technical advances over the past 50 years. Today production of material from this process accounts for more than $ 4 billion in which over 100 000 kilograms of polymers and elastomers (polymers with elastic properties) are produced.[74] The success story of olefin polymerisation started with the discovery of the Ziegler–Natta catalyst which was based on an early transition metal.[75] This catalyst has since been used in the commercial manufacture of various polyolefins. There are some different systems that are closely related to Ziegler-Natta that are currently in use, one such catalyst is the Philips's catalyst which was discovered by Hogan and Banks at the Phillips Petroleum Company in the late 1950's.[76] These together with metallocenes[77] and Ziegler-Natta are one of the most important industrial catalysts for polyethylene production.[78] A new class of late transition metal catalysts emerged when Brookhart and co-workers showed that complexes with α-diimine ligands could be used as catalyst for ethylene polymerisation reactions.[79]

The chemistry of late transition metals catalyst for ethylene polymerisation has been intensively researched since the mid 1990's and their reactivity has extensively been

[73] P.H. Emmett, P. Sabatier, E.E. Reid, Catalysis now and then, Franklin (**1965**).

[74] A. Forestiere, H. Oliver-Bourbigou, L. Saussine, *Oil Gas Sci. Technol*. 64 **(2009**) 649.

[75] K. Ziegler, E. Holzkamp, H. Martin, and H. Breil, *Angew. Chem.* 67 (**1955**) 541.

[76] J.P. Hogan, R.J. Banks, *United States Bartent US2,825,721 1958.*

[77] W. Kaminsky, *Macromol. Chem. Phys.*197 (**1996**) 3907.

[78] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.* 77 (**1955**) 1708. (b) D.S. Breslow, N.R. Newburg, *J. Am. Chem. Soc.* 79 (**1957**) 5072.

[79] L.K. Johnson, C.M. Killian, M Brookhart, *J. Am. Chem. Soc.* 117 (**1995**) 6414.

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reviewed.[80] After the pioneering work by Brookhart, nitrogen containing ligands such as diimines, pyridine and pyrazolyl compounds have received attention as ligands of choice in preparing catalyst for ethylene polymerisation.[81] There is still a lot of nitrogen containing compounds that can still be introduced in polyolefin industry. Nickel(II) and palladium(II) complexes have been judiciously chosen for their ability to tolerate polar groups and have been used successfully as catalyst for ethylene polymerisation.[82] The type of ligand and co-ordination chemistry plays a vital role in catalytic behaviour of the metal complexes. Type of ligand complexed with transition metal influences both the electron density and the physical environment around the metal centre.[83] Therefore the properties of the coordination complexes of transition metals are basically controlled by modifying the electron density around the metal centre. The presence of different linkers in between the benzene backbone and pyrazole moieties affects the properties of the resulting transition metal complexes differently.

When the pyrazolyl benzene ligands with methylene linkers chelate to the metal centre, the resulting complexes are more thermodynamically stable compared to those with a carbonyl as a linker.[84] This result from the electron donating nature of the methylene linkers which donates electrons towards a metal centre and increases the electron density towards the metal centre and strengthen the metal ligand bond. Whilst the electron withdrawing nature of carbonyl linker withdraws electrons from the metal centre and weaken the metal ligand bond, which makes the complexes less stable. These pyrazolyl benzene ligands with methylene linkers coordinate to the metal centre through a nitrogen donor atom of the pyrazolyl moieties which are common both in coordination chemistry and homogeneous catalysis.

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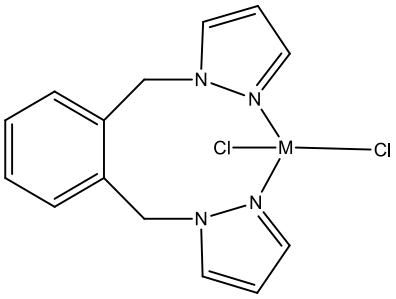
[80] S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (**2000**) 1169. (b) J.Y. Dong, Y. Hu, *Coord. Chem. Rev*. 250 (**2006**) 47. (c) C. Bianchini, G. Giambastiani, L. Luconi, A. Meli, *Coord. Chem. Rev*. 254 (**2010**) 431. (d) J. Zhang, X. Wang, G.X. Jin, *Coord. Chem. Rev.* 250 (**2006**) 95.

[81] G.J.P. Britovsek, M. Bruice, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, *J. Am. Chem. Soc.* 121 (**1999**) 8728.

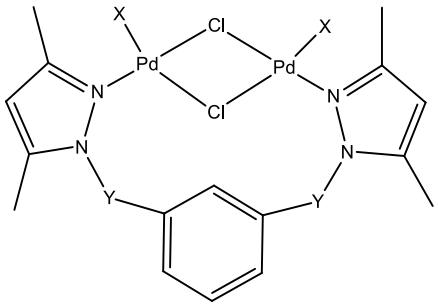
[82] Z. Guan, *J. Polym. Sci. A Polym. Chem*. 41 (**2003**) 3680.

[83] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc*. 120 (**1998**) 11122.

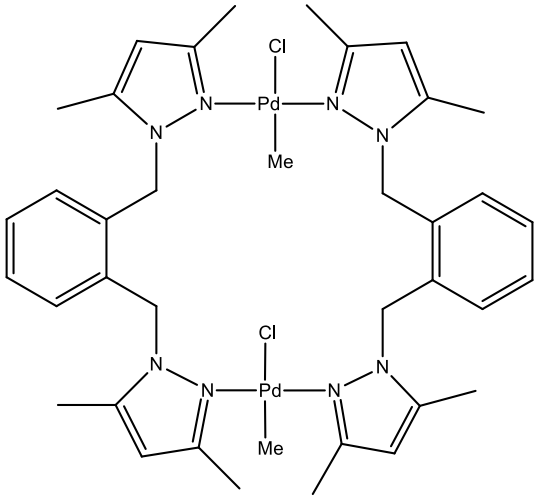
[84] S.O. Ojwach, J. Darkwa, *Inorg. Chim. Acta*. 363 (**2010**) 1947.



M = Co **(19),** M= Cu **(20)**



X = CH_3, Y = CH_2 **(21)**, X = CH_3, Y = CO **(21')**



(22)

Figure 3.1: Selected metal complexes of polypyrazolyl ligands

Chang *et al.*[85] reported the cobalt(II), **19** and copper(II), **20** analogues of the 1,2-bis(pyrazoly-l-methyl) benzene (L) ligand with the formula [$CuLCl_2$] for monomeric complex and [CuL_2Cl_4] for a dimeric complex. Both the monomeric Cu(II) and Co(II) complexes showed distorted tetrahedral geometry while the dimeric Cu(II) complex showed distorted square-pyramidal geometry. Another set of comparable complexes are the Pd(II) complexes with the same ligand type, reported by Motsoane *et al*.[86] The ligands coordinated to the metal centre in 3 different ways depending on the mode in which the bis(pyrazol-1-ylmethyl) units are attached to the benzene linker and the nature of the pyrazole. The 1,2-benzene linker ligands form the dimeric complex complexes [$Pd_2L_2Cl_4$] **22**, while the 1,3-benzene linker ligands form the chloro-

[85] W.K. Chang, G.H. Lee, Y. Wang, T.I. Ho, Y.O. Su, Y.C. Lin, *Inorg. Chim. Acta*. 223 (**1994**) 139.

[86] N.M. Motsoane, I.A. Guzei, J. Darkwa. *Z. Naturforsch. Teil B*, 62 (**2007**) 323.

bridged bimetallic complexes [$Pd_2LCl_2Me_2$], **21**. All the complexes showed a square planar geometry and were tested as catalyst for Heck and Suzuki coupling reactions. The report shows that the activity of these complexes as catalysts for coupling reactions depended mostly on both the size of the substituents on the pyrazole moiety and mode in which the bis(pyrazol-1-ylmethyl) units are attached to the benzene linker.

The nickel(II) complexes with the same ligand system was used by Obuah *et al*.[87] as catalyst for ethylene oligomerisation and Friedel-Craft alkylation reactions. They reported that these nickel(II) catalysts lead principally to dimerization and trimerization of ethylene; where 1-butene and 1- hexene are the dominant products followed by Friedel-Craft alkylation of the oligomers to toluene solvent when $EtAlCl_2$ was used as co-catalyst. The role played by the co-catalyst in these ethylene transformation reactions has been brought into focus by Dyer and co-workers.[88]

A similar pyrazolyl system, **21**, with carbonyl linkers on the 1,3 positions on the benzene ring has been reported together with its coordination chemistry and catalytic activity towards ethylene polymerisation reactions. The system once again showed that the activity of the complexes when used as catalyst for ethylene polymerisation depends on the stability and electrophilic behaviour of the resultant catalyst.[89] This serves as further indication of how ligand fine tuning affect the catalyst behaviour in catalytic transformation reactions. Moreover, these reactions are affected by reaction parameters such as catalyst to co-catalyst ratio, temperature, pressure and reaction time.

In our attempt to develop both active and stable catalysts for ethylene transformation reactions, we herein report the catalytic behaviour of new pyrazolyl hydrazide palladium(II) and nickel(II) complexes prepared in Chapter 2. Pyrazolyl benzene ligands with dicarbonyl and dimethylene linkers have already been tested by Darkwa *et al.*[90] The activity and stability of the two systems were not balanced. From their reports conclusions that were drawn suggested that benzene carbonyl systems are active but lack stability while the methylene system is stable

[87] A. Budhai, B. Omondi, S.O. Ojwach, C. Obuah, J. Darkwa, *Catal. Sci. Technol.* 3 (**2013**) 3130.

[88] P.W. Dyer, J. Fawcett, M.J. Hanton, *Organometallics* 27 (**2008**) 5082.

[89] I.A. Guzei, K. Li, G. Bikzhanova, J. Darkwa, S.F. Mapolie, *Dalton Trans*. 100 (**2003**) 715.

[90] S.O. Ojwach, J. Darkwa, *Inorg. Chim. Acta.* 363 (**2010**) 1947.

but less active as compared to the carbonyl. Finding balance between the two systems poses a challenge. It is on this basis that we undertook to study the ability of palladium(II) and nickel(II) complexes of pyrazolyl hydrazide ligands containing both methylene and carbonyl linker on 1,3 positions of the benzene backbone as catalysts for ethylene oligomerisation and polymerisation.

3.2 Experimental methods and synthesis

3.2.1 Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy, Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography-Flame Ionisation Detector (GC-FID) techniques were used for the characterization of the synthesized ethylene oligomers and Friedel-Craft acylation products.

3.2.1.1 NMR Spectroscopy

^{1}H and ^{3}C NMR spectroscopy analyses of samples prepared in $CDCl_3$ were performed at the University of KwaZulu-Natal Westville campus, South Africa, on a Bruker Advance III 400 MHz and 600 MHz spectrometers. The residual peak of $CDCl_3$ at 7.24 ppm was used to reference ^{1}H chemical shifts. Tetramethylsilane (TMS) was used as an external reference for ^{1}H NMR chemical shifts.

3.2.1.2 GC-MS/ FID

GC (MS) analyses were performed in-house on an Agilent 7890A gas chromatograph fitted with a 5975C VL mass selective detector (MSD). The type of column installed was a HP-5,5% phenyl methyl siloxane with dimensions: 30 m × 250 μm × 0.25 μm. Helium was used as a carrier gas at a flow rate of 0.7 mL/min. The injection source and detector temperatures were 250 °C and 230 °C, respectively. The initial oven temperature at 60 °C was held constant for 2 min then ramped-up to the final temperature at 300 °C, at a rate of 10 °C/min.

GC (FID) analysis was performed at the University of Stellenbosch (South Africa) on a Waters Synapt G2 at a core voltage of 15 V, as well as in-house on a Agilent 7890A gas chromatograph fitted with a 5975C VL mass selective detector (MSD).

3.3 Materials

3.3.1 Reagents

The co-catalyst used in this study was 10M $EtAlCl_2$ solution in hexanes and was purchased from Sigma Aldrich and used as received.

3.3.2 Solvents

For all the reactions dry solvents were required and were dried using general methods. Toluene and hexane were dried over sodium benzophenone ketyl and stored over molecular sieves. Chlorobenzene was HPLC grade and was stored under molecular sieves before use.

3.4 Experimental Section

3.4.1 General Method for ethylene transformation reaction

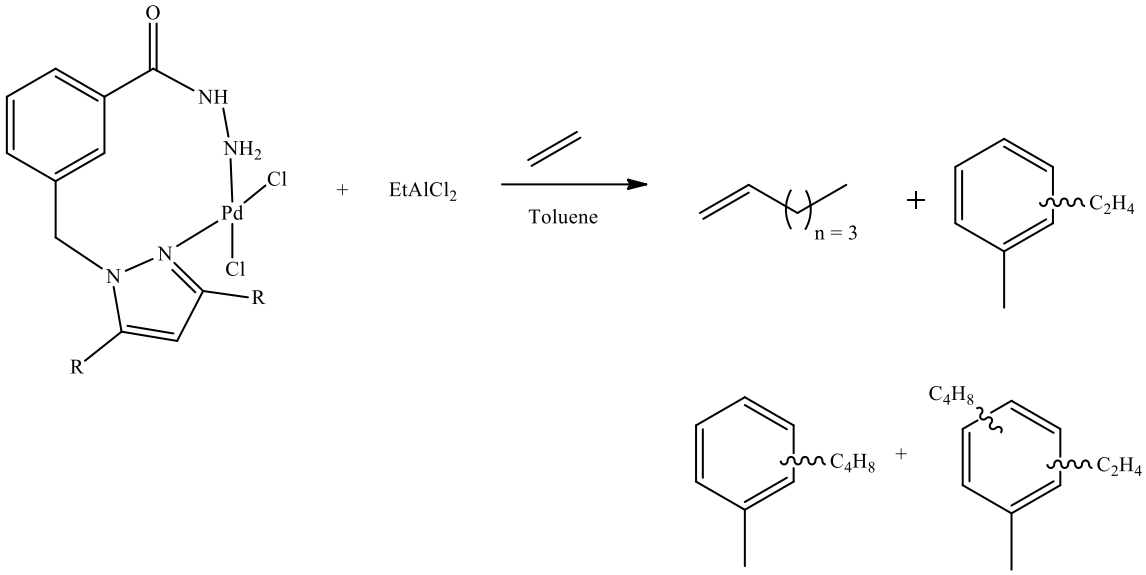
Ethylene oligomerization reactions were carried out in a 100 mL steel autoclave reactor equipped with a stirrer bar. In a typical experiment, the catalyst precursor **C1** (4.22 mg, 10 µmol) was weighed and transferred into a reactor; the reactor was closed and degassed by flushing with argon at least three times. To the reactor was added toluene (5-10 mL) and the resultant mixture was degassed again. Finally the co-catalyst, 10 M solution of $EtAlCl_2$ in hexanes (2 mL, 2 mmol) was added to the reactor to form the active catalytic species. The reactor was then flushed with ethylene gas at a pressure of 10 bar and temperature was set to 30 °C. The reaction was run for an hr. After the specified reaction time, the reactor was cooled for about 2 minutes in a chiller set to 8 °C. The reaction was then quenched by addition of 10% HCl in methanol until the solution stopped bubbling (about 5-10 mL was required). A portion of the reaction mixture was sampled for GC and GC-MS analyses to determine the size of oligomers formed. The amount of products formed was determined by mass difference of toluene and mass of final solution.

The same reaction conditions were repeated for all the catalyst (**C2**-**C6**) and reaction parameters were varied for the catalyst **C2** and **C5**

3.5 Results and Discussions

3.5.1 Ethylene transformation using palladium(II) complexes

Three pyrazolyl hydrazide palladium(II) complexes (**C1**, **C2** and **C3**) were first activated with $EtAlCl_2$ co-catalyst and were used as catalyst for ethylene transformation reactions. From the preliminary data, mixtures of oligomers and alkylated products were obtained, Scheme 3.1.

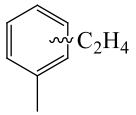
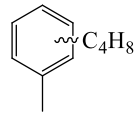
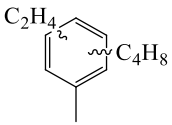


Scheme 3.1 Ethylene oligomerization and Friedel-Crafts alkylation of toluene with palladium(II) pre-catalysts **C1–C3**, and $EtAlCl_2$ as co-catalyst. [91]

A notable observation was the dependence of catalytic activity, product distribution and selectivity on different reaction conditions and nature of solvent used. A summary of the data obtained from evaluation of catalysts precursors **C1-C3** is presented in **Table 3.1**.

[91] P.W. Dyer, J. Fawcett, M.J. Hanton, *Organometallics* 27 (**2008**) 5082.

Table 3.1: Ethylene Transformation studies using catalyst C**1-C3** and $EtAlCl_2$ in hexanes as co-catalyst[a]

Entry	Catalyst	Time (h)	Temp (°C)	Al:Pd ratio	Pressure (bar)	[b]Yield (g)	Activity ($Kg.mol^{-1}.h^{-1}$)	[c]Products distribution in percentages			
								C_6	 **A**	 **B**	 **C**
1	**C1**	1	30	200	10	2.60	260	51.82	5.13	39.23	3.82
2	**C2**	1	30	200	10	3.03	300	62.78	5.78	29.41	2.03
3*	**C3**	1	30	200	10	3.06	310	1.34	9.52	73.04	9.05
4	**C2**	1	30	300	10	4.34	430	78.88	4.62	15.83	0.67
5*	**C2**	1	30	400	10	3.47	350	63.15	3.43	27.95	3.20
6	**C2**	1	30	500	10	3.03	300	74.21	25.72	–	0.07
7	**C2**	1	40	300	10	4.50	450	70.09	6.56	21.41	1.94
8	**C2**	1	50	300	10	2.60	260	66.34	–	33.66	–
9	**C2**	1	60	300	10	2.60	260	70.64	5.88	21.86	1.62
10*	**C2**	1	40	300	20	4.35	440	46.05	3.10	35.39	12.58
11	**C2**	1	40	300	30	3.47	350	37.84	14.38	29.83	17.95
12	**C2**	2	40	300	10	3.03	152	62.63	18.92	18.45	–
13*	**C2**	3	40	300	10	4.34	143	59.43	10.98	22.40	1.74
14	**C2**	4	40	300	10	4.34	108	60.82	5.25	30.48	3.45

[a]Reaction conditions: [Catalyst] = 10 µ mol; solvent, Toluene, 10 mL; [b]determined by mass difference of 10 mL Toluene (8.67 g) and mass of final solution. [c]Determined by GC-FID. *includes amounts of butyl-butyltoluenes which could not be resolved.

Initial studies carried out at 30 °C, 10 bar of ethylene pressure using catalyst to co-catalyst ratio of 1:200 indicated that these catalytic systems were reasonably active in ethylene oligomerization reactions to afford C_6 oligomer and butyltoluenes as major products and other alkylated toluenes made up the difference of the products obtained. Type of substituents present on the pyrazole ring seemed to have had a significant influence on product distribution and also on the catalytic activities of complexes **C1-C3**. Two opposite trends were observed. While the two steric bulk compounds resulted on better activities than complex **C1** but they gave a range of different products. For instance catalyst **Cl** and **C2** gave C_6 oligomers in higher percentage (52% and 63%, respectively) as compared to the alkylated products, Table 3.1, entries 1-2. Complex **C3** on the other hand exclusively gave alkylated toulenes as major products and only traces of C_6 oligomer (<2%). Butyl toluene was again obtained as the major alkylated product (73.04 %), Table 3.1, entry 3. It was based on the C_6 oligomer yields that **C2** was then used for the rest of ethylene transformation reactions.

Other groups have also reported ethylene oligomerization with oligomers further alkylated to toluene solvent, for example Ojwach and co-workers reported good selectivity of alkylation of toluene.[92] The results by Dyer and co-workers shows that it is not all Ni(II) complexes that is can perform ethylene oligomerization followed by Friedel–Crafts alkylation.[91] Their report highlighted the importance of catalyst structure on formation of Friedel–Crafts alkylation products. When Obuah and co-workers used pyrazolyl methyl benzene nickel(II) complexes, all the complexes performed ethylene transformation and was followed by alkylation of toluene.[93] This work suggested that the pyrazolyl ligands play a vital role in promoting alkylation of toluene in the presence of $EtAlCl_2$ co-catalyst. On the other hand Gau *et al.*[94] suggested that performing the ethylene transformation with the same $EtAlCl_2$ co-catalyst at elevated temperatures creates an acidic condition which triggers alkylation of toluene. From the reports cited above it is clear that type of catalyst used and reaction conditions in which the reaction is run plays a vital role of controlling alkylation of toluene in ethylene transformation reactions.

[92] S.O. Ojwach, I.A. Guzei, L.L. Benade, S.F. Mapolie, J. Darkwa, *Organometallics* 28 (**2009**) 2127. (b) M.K. Ainooson, S.O. Ojwach, I.A. Guzei, L.C. Spencer, J. Darkwa, *J. Organomet. Chem*. 696 (**2011**) 1528.

[93] A. Budhai, B. Omondi, S.O. Ojwach, C. Obuah, J. Darkwa, *Catal. Sci. Technol*. 3 (**2013**) 3130.

[94] K. Song, H. Gao, F. Liu, J. Barn, L. Guo, S. Zai, Q. Wu, *Eur. J. Inorg. Chem*. 20 (**2009**) 3016.

The elucidation of oligomerization products obtained was carried out using a combination of GC-FID, GC-MS and ^{1}H NMR spectroscopy techniques. For example, a typical ^{1}H NMR spectrum of the products obtained from catalyst **C2** (Table 3.1, entry 2) showed different methyl peaks in the range of 0.5 ppm to 3.0 ppm as an evidence for different alkylated toluene compounds. The presence of ethylene oligomers was identified by the appearance of small peaks around 4.0 ppm indicating characteristic peaks attributed to the terminal alkenes protons, Figure 3.3. Further analyses of the products by GC-MS confirmed the ethylene oligomerization products, hexene oligomers and mixture of alkylated products (A, B and C). The appearance of more than one peak in the same region of the GC chromatogram, for all the products suggests that the products exist as isomers, Figures 3.3.

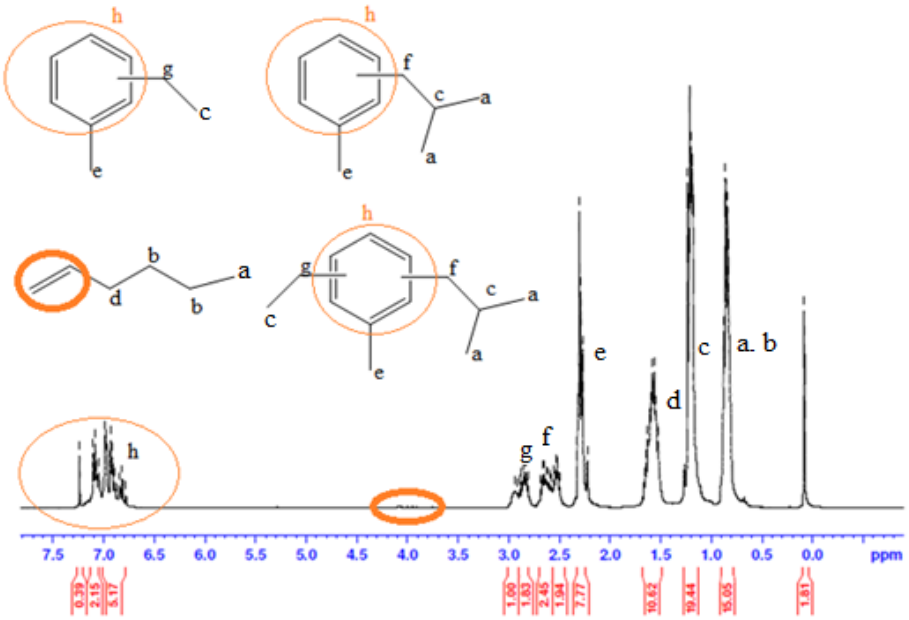


Figure 3.2: ^{1}H NMR spectrum of the products of catalyst **C2** from the reaction at Al:Pd ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 hr, solvent = toluene.

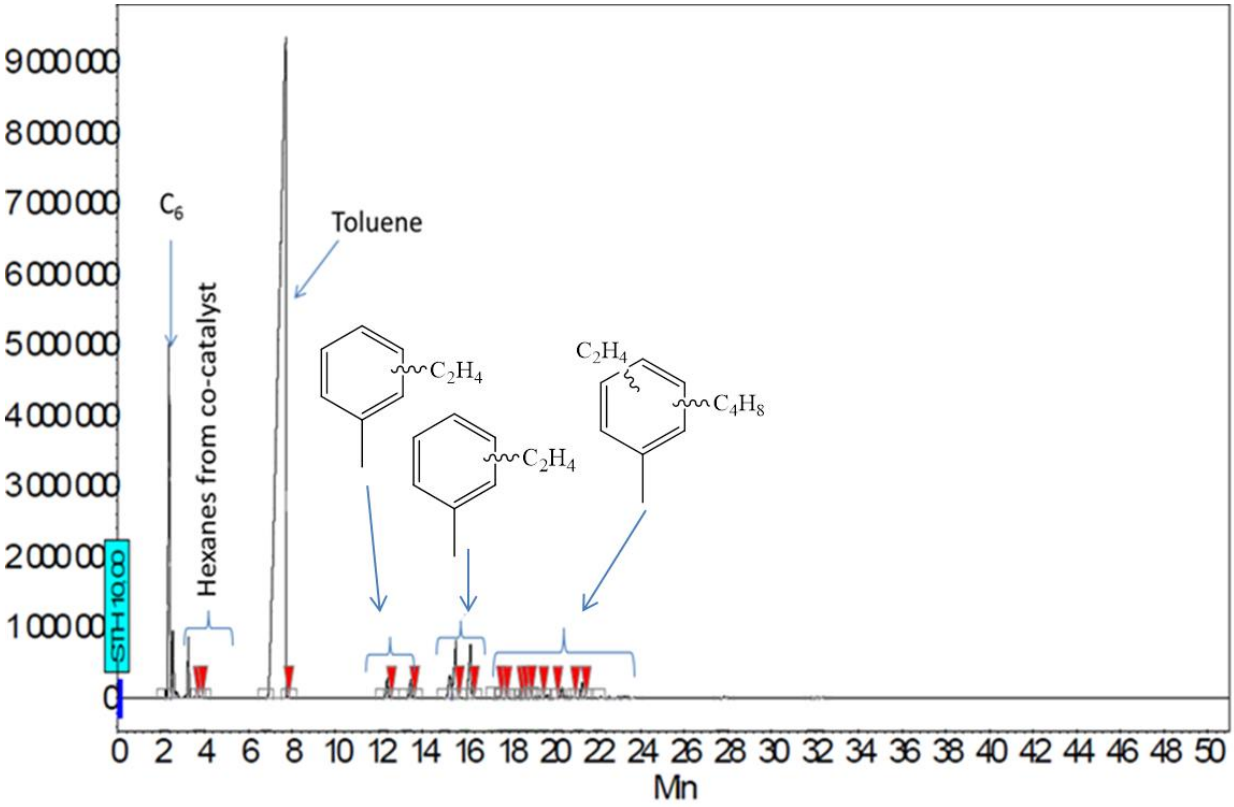


Figure 3.3: GC trace of oligomer and Alkylated toluene products of catalyst **2** from the reaction at Al:Ni ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 hr, solvent = toluene

Reaction conditions such as temperature, pressure, time and catalyst to co-catalyst ratios were varied to observe the yields and product distribution under these conditions. The effect of catalyst to co-catalyst ratios was evaluated by running the reaction at different ratios, Table 3.2, entries 4-6. An increase in catalyst to co-catalyst ratio from 1:200 to 1:300 resulted in an increase of both the catalyst activity from 300 $kg.mol^{-1}.h^{-1}$ to 430 $kg.mol^{-1}.h^{-1}$, and selectivity of C_6 oligomers from 62.78 % to 78.88 %, respectively. However, further increase of the co-catalyst ratio to 1:400 and 1:500 decreased the activities to 350 $kg.mol^{-1}.h^{-1}$ and 300 $kg.mol^{-1}.h^{-1}$, respectively. In fact doubling the co-catalyst ratio from 1:200 to1:400 resulted in only a slight increase in activity but the selectivity for the two major products (C_6 oligomers and **B**) were comparable, Table 3.1, entries 2 and 5. This decrease on activity with an increase on catalyst to co-catalyst ratio might be caused by high accumulation of the aluminium impurities which are known to deactivate the catalyst.[95]

[95] H.S. Abbo, S.J. Titinchi, *Molecules* 18 (**2013**) 4728.

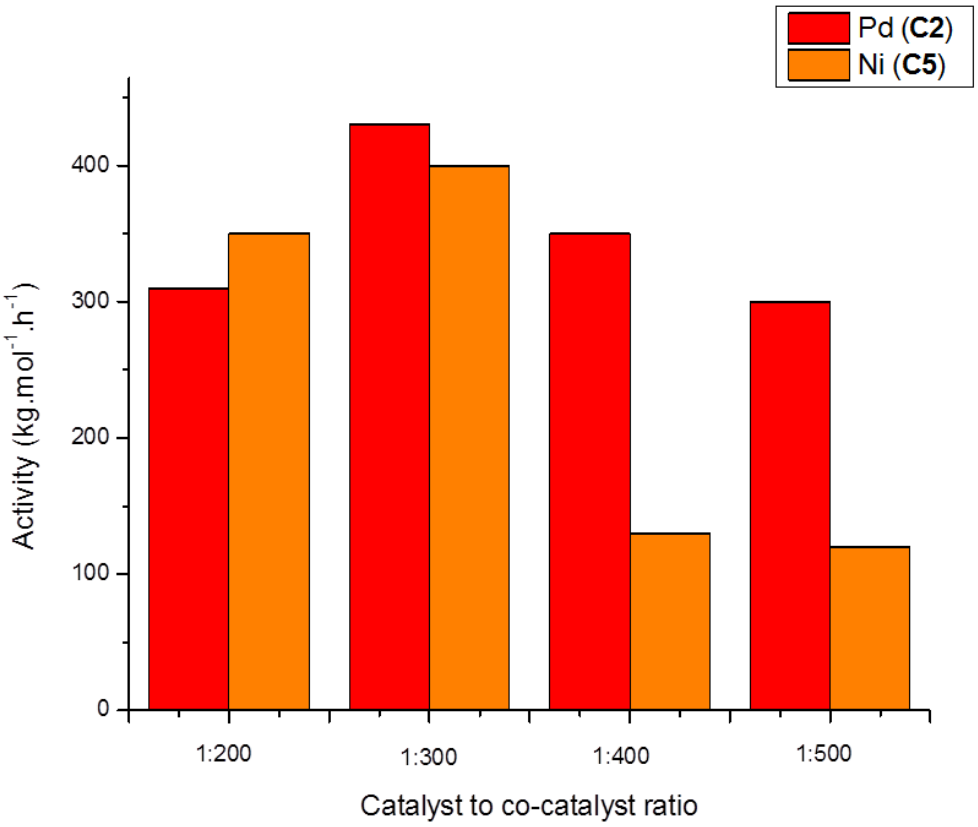


Figure 3.4: Effect of Catalyst to co-catalyst ratio on product yield using catalyst **C2** and **C5**

In this study an increase in temperature of the ethylene transformation from 30 °C to 40 °C showed a 50% increase on the activity of the catalyst from 300 $kg.mol^{-1}.h^{-1}$ to 450 $kg.mol^{-1}.h^{-1}$ and slight increase in the selectivity of the C_6 oligomers from 63% to 70%, respectively (Table 3.1, entries 2 and 7). Increasing the reaction temperature further to 50 °C and 60 °C only resulted in the decrease in activity from 450 $kg.mol^{-1}.h^{-1}$ to 260 $kg.mol^{-1}.h^{-1}$ (Table 3.1, entries 8 and 9). The selectivities in the cases involving an increase in temperature were essentially the same. Theoretically an increase in temperature of the reaction should increase the activity of the reaction due to possible high solubility of the reactants and catalyst in a particular solvent at high temperature. The observed decrease in activity with an increase on reaction temperature might be due to the possible catalyst deactivating at temperatures above 40 °C.[96]

[96] C. Obuah, J.H. Jordaan, J. Darkwa, *Catal. Sci. Tech*. 6 (**2016**) 4814.

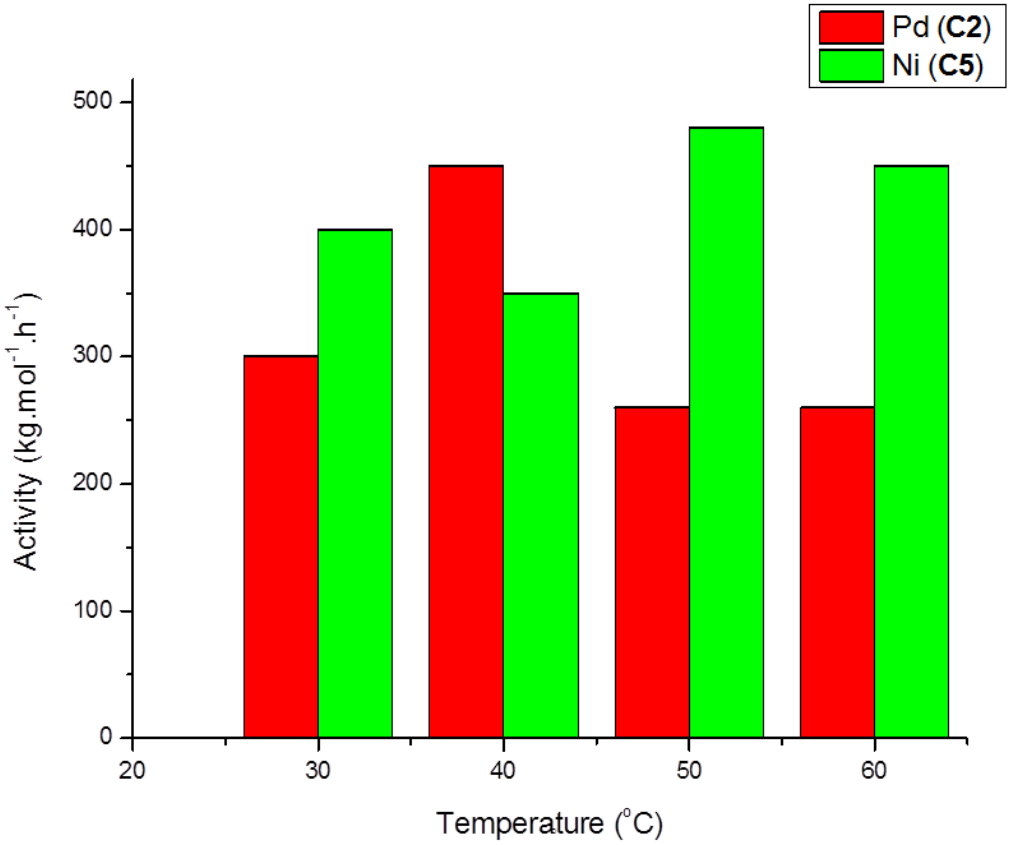


Figure 3.5: Effect of temperature on product yield using catalyst **C2** and **C5**

The reaction was also run at different pressures to study the effect of pressure on ethylene transformation activity and product distribution (Table 3.1, entries 7, 10-11). An increase in ethylene pressure from 10 bar to 20 bar decreased the activity from 450 $kg.mol^{-1}h^{-1}$ to 440 $kg.mol^{-1}h^{-1}$ while production of hexene oligomers dropped from 70% to 46%, respectively. Further increase of pressure to 30 bar decreased the activity to 350 $kg.mol^{-1}h^{-1}$ and production of hexene oligomers decreased to 38%. Although an increase in pressure resulted in the decrease in the selectivity of the major products, they were both still formed on the same proportion at 20 bar and 30 bar. In both cases, the C_6 oligomers were obtained at the ratio of 1.3 compared to the butyltoluenes. The decrease on activity with an increase in ethylene pressure can be associated with saturation of the reaction mixture by ethylene monomer.[97]

[97] J. Skupińska, *Chem. Rev*. 91 **(1991)** 613.

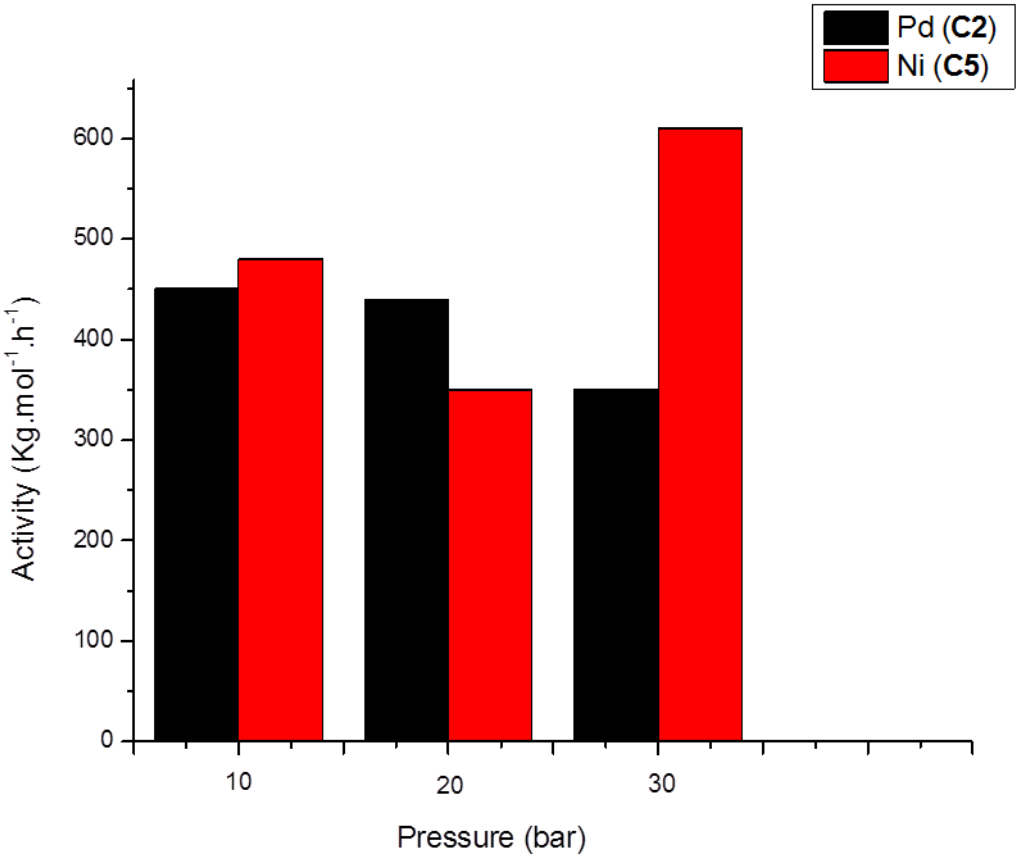


Figure 3.6: Effect of pressure on product yield using catalyst **C2** and **C5**

The stability of the active species was investigated using complex **C2** by varying reaction time from 1 hr to 4 hrs (Table 3.1, entries 11-14). Results from the current report shows that the catalyst activity decreases as expected with an increase in reaction time. For example the activity of 350 $kg.mol^{-1}h^{-1}$ was observed after 1 hr and running the reaction for 2 hrs decreased the activity to 152 $kg.mol^{-1}.h^{-1}$. An increase on C_6 production from 38% (2 hrs) to 59% (3 hrs) was observed and running the reaction longer increases the selectivity of C_6 up to 60%. Further increase on the time did not show a significant improvement on selectivity of the C_6 oligomers while an increase on the butyltoluenes was observed. The decrease of activities with time can be associated with possible catalyst deactivation over time. The observation of no significant increase with an increase on reaction time might be a sign that the catalyst get deactivated after 2 hrs thus running the reaction for more than 2 hrs only the co-catalyst is left alive and promote the Friedel-Craft alkylation of toluene solvent. This can be the reason explaining why when running reactions longer only shows an increase on butyl toluenes is observed.

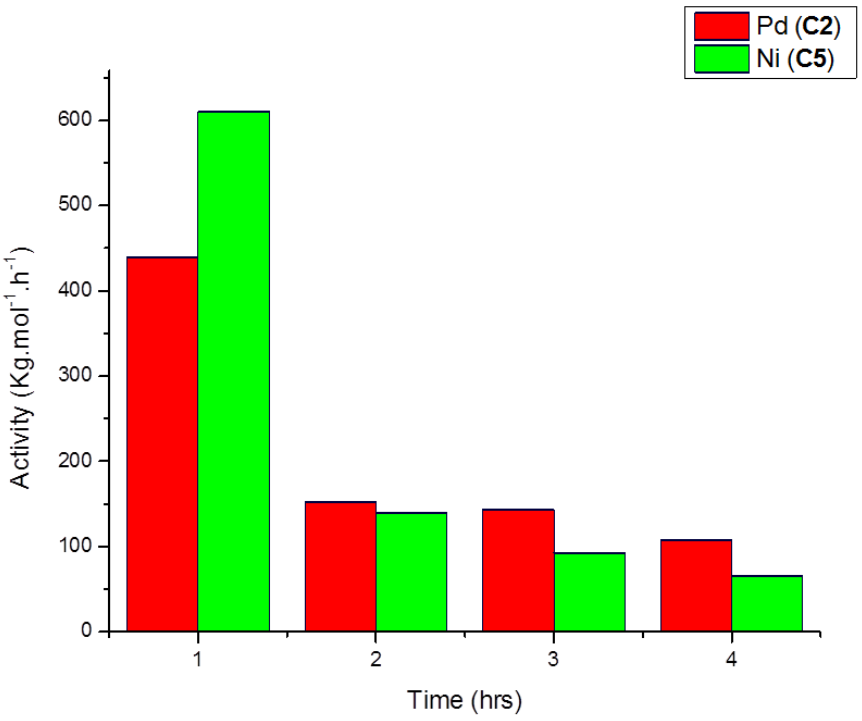
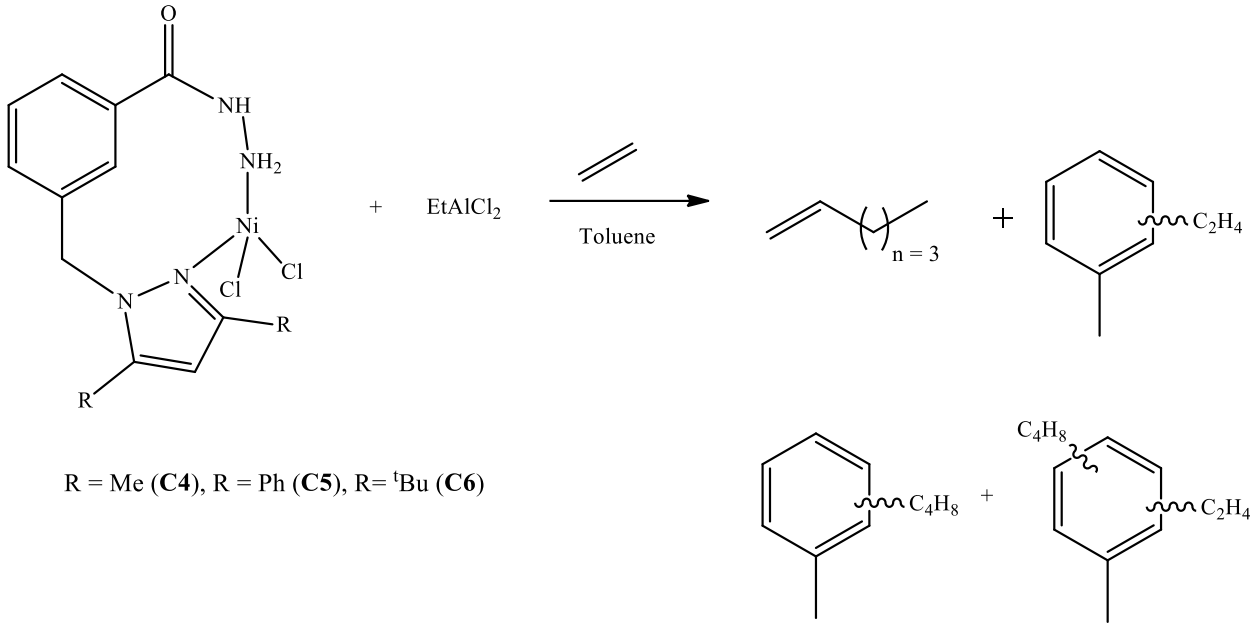


Figure 3.7: Effect of time on product yield using catalyst **C2** and **C5**

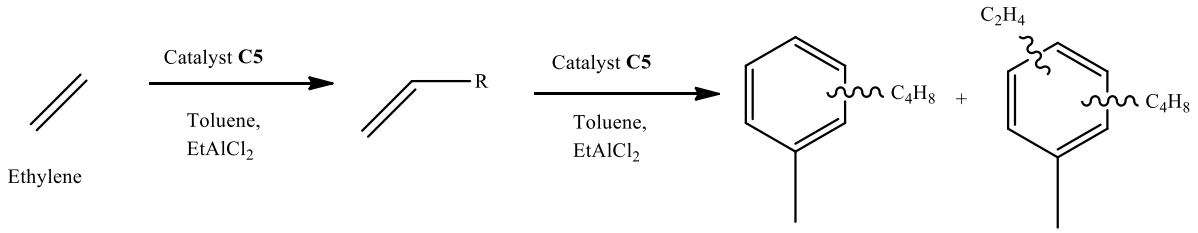
3.5.2 Evaluation of nickel(II) complexes C4-C6 as catalysts in ethylene oligomerization reactions

The pyrazolyl hydrazide nickel(II) complexes (**C4**, **C5** and **C6**) were also tested as catalysts for ethylene transformation reactions following the same procedure described for Palladium(II) complexes, In toluene the pyrazolyl hydrazide nickel(II) catalysts (**C4**, **C5** and **C6**) also produced C_6 oligomers and alkylated butyltoluenes as a major products, ethyltoluene and ethyl-butyltoluenes were observed as minor products, Scheme 3.2.



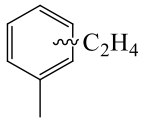
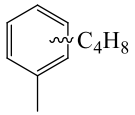
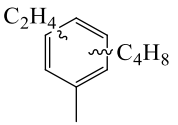
Scheme 3.2: Ethylene oligomerization and Friedel-Crafts alkylation of toluene with nickel(II) pre-catalysts **C4**–**C6** and $EtAlCl_2$ as co-catalyst.

The reaction is assumed to follow the mechanism in Scheme 3.3. In the current study no hexene oligomers were alkylated to toluene but such products are known in the literature.[20] GC and GC-MS analysis of products from toluene reactions indicates that the butene alkylation competes with direct alkylation of the ethylene to toluene and forms the butyl-ethyltoluene products.



Scheme 3.3: Oligomerization of ethylene followed by the Friedel-Crafts alkylation of toluene using complex **C5**, and $EtAlCl_2$ as co-catalyst

Table 3.2 : Ethylene Transformation studies using catalyst **C4-C6** in toluene and $EtAlCl_2$ in hexanes as co-catalyst.[a]

Entry	Catalyst	Time (hrs)	Temp (°C)	Al:Ni ratio	Pressure (bar)	Yield (g)	Activity[c] ($kg.mol^{-1}.h^{-1}$)	Products distribution and selectivity (%)[c]			
								C_6	 **A**	 **B**	 **C**
1	**C4**	1	30	200	10	2.76	280	78.06	14.84	7.10	–
2	**C5**	1	30	200	10	3.46	350	52.40	–	36.20	11.40
3	**C6**	1	30	200	10	3.46	350	57.62	4.96	33.65	3.77
4	**C5**	1	30	300	10	3.98	400	79.25	–	17.30	3.45
5*	**C5**	1	30	400	10	1.30	130	31.37	–	53.61	13.15
6	**C5**	1	30	500	10	1.21	120	26.16	–	43.01	30.83
7	**C5**	1	40	300	10	3.46	350	80.81	–	12.88	6.31
8	**C5**	1	50	300	10	4.84	480	80.58	–	14.08	5.34
9	**C5**	1	60	300	10	4.48	450	60.57	–	18.46	20.86
10	**C5**	1	50	300	20	3.46	350	25.94	–	43.75	30.31
11	**C5**	1	50	300	30	6.06	610	62.42	–	32.53	5.05
12*	**C5**	3	50	300	30	2.76	140	31.37	–	53.61	13.15
13	**C5**	4	50	300	30	2.76	93	40.10	–	47.91	11.99
14	**C5**	5	50	300	30	2.59	65	79.21	–	10.79	10.00

[a]Reaction conditions: [Catalyst] = 10 µmol; Solvent Toluene , 10 mL, [a]determined by mass difference of 5 mL Toluene (8.67 g) and mass of final solution. [b]Activity, kg oligomer.mol.$^{-1}$.catalyst.h^{-1}. [c]determined by GC. *includes amounts of butyl-butyltoluenes that could not be resolved.

Initial studies carried out at 30 °C, 10 bar of ethylene pressure using catalyst to co-catalyst ratio of 1:200 indicated that these catalytic systems were reasonably active in ethylene oligomerization reactions to afford C_6 oligomer and butyltoluene as major products and other alkylated toluenes made up the difference of the products obtained, Table 3.2, entries 1-3.
A similar trend on the activities of all the nickel(II) complexes with bulky substituents (**C5**and **C6**) on the pyrazole have higher activities than the less bulky substituted catalyst **C4** is also observed. However, product selectivity with the nickel(II) complexes was different when compared to its palladium(II) analogue. In case of the nickel(II) complexes the less bulky substituted pre-catalyst **C4** seemed to give high percentages of C_6 oligomers (78%) as compared to **C5** and **C6** with 52% and 58%, respectively (Table 3.2, entries 1-3). There were no butyl-ethyl toluene product observed with catalyst **C4** and interestingly catalyst **C5** gave no ethyltoluene product which normally results from direct alkylation of ethylene monomer on toluene. From the preliminary experiments using nickel(II) complexes as pre-catalyst for ethylene transformation in toluene, pre-catalysts **C5** just like **C4** was found to be limiting the number of alkylated products obtained under the above mentioned conditions but was more active and hence was used for the rest of the optimisation experiments.

Reaction conditions such as catalyst to co-catalyst ratios, temperature, pressure and time were varied to observe the yields and product distribution under different conditions using nickel complexes (**C4**, **C5** and **C6**). Catalyst to co-catalyst ratio was also varied to study how the variation in the ratio affects the activity and product selectivity, Table 3.2, entries 2, 4-6. An increase in catalyst to co-catalyst ratio from 1:200 to 1:300 ratios resulted in a slight increase in catalyst activity from 350 $kg.mol^{-1}.h^{-1}$ to 400 $kg.mol^{-1}.h^{-1}$, and selectivity of C_6 oligomers from 58% to 79%, respectively. Subsequent increments of the ratios to 1:400 and 1:500 further decreased the activities to 130 $kg.mol^{-1}.h^{-1}$ and 120 $kg.mol^{-1}.h^{-1}$, respectively. Further increase on the catalyst to co-catalyst ratio was found to decrease the selectivity on the C_6 oligomers. When the catalyst to co-catalyst ratio was increased to 1:400 and 1:500, the selectivity on the C_6 oligomers decreased to 26% and 31%, respectively. This increase in ratios favoured formation of butyl toluene over the C_6 oligomers which suggests that high Ni:Al ratio activate the Friedel-Craft acylation of toluene. This affirmation is supported by literature reports where low Al:Ni ratios have been used, typically 10-15 equivalents of $EtAlCl_2$, and no alkylated

toluene products were observed.[98] In fact doubling the ratio from 1:200 to 1:400 decreased the activity from 350 kg.mol^{-1}.h^{-1} to 130 C_6. kg.mol^{-1}.h^{-1}. This is contrary to the results observed with the Pd(II) catalyst earlier, where doubling the co-catalyst ratio slightly increase the activity. The behaviour of the two catalysts is confusing as the nickel complexes were expected to be far more active as compare to their palladium analogues. Surprisingly, the palladium complexes were found to be more active in some instances. This might possibly suggest that the high activities were associated with the $EtAlCl_2$ activating alkylation of the toluene solvent giving high yields of alkylated solvent than oligomers.

A study of an increase in temperature on the catalytic transformation from 30 °C to 40 °C decreased the activity 400 kg.mol^{-1}.h^{-1} to 350 kg.mol^{-1}.h^{-1} resulting in a slight increase in C_6 oligomers from 79% to 81%, Table 3.2, entries 4 and 7. The same decrease of activity with increase in temperature has been observed with Pd(II) complex **C2** discussed above. Obuah *et al*.[99] when using ferrocenylpyrazolyl nickel(II) catalyst observed the same trend where an increase in temperature resulted in decreased activities. They observed that catalytic activity decreased from 25°C (1989 kg.mol^{-1}.h^{-1}) to 50°C (634 kg.mol^{-1}.h^{-1}) using bis-(3,5-dimethylpyrazol-1-ylmethyl)benzene nickel(II) catalyst. Surprisingly in the present study further increase on reaction temperature to 50 °C showed an increase on the activity to 480 kg.mol^{-1}.h^{-1}. (Table 3.1, entries 7-8). Contrary, another 10 °C more increase of temperature to 60 °C resulted in both the activity and the formation of C_6 oligomers dropping down to 450 kg.mol^{-1}h^{-1} and 61%, respectively. In the case where decrease on C_6 oligomers was observed, alkylated toluene products were obtained in better percentages. For example, butyltoluenes (18%) and butyl-ethyltoluenes (21%) were observed at 60 °C.

The reactions were also run at different pressures using catalyst **C5** to study the effect of pressure on ethylene transformation activity and product distribution (Table 3.2, entries 7, 10-11). An increase in ethylene pressure from 10 bar to 20 bar increased the activity from 300 kg.mol^{-1}.h^{-1} to 440 kg.mol^{-1}.h^{-1} while production of C_6 oligomers dropped from 63% to 46%. Furthermore, increase of pressure to 30 bar decreased the activity to 350 kg.mol^{-1}h^{-1} and production of C_6 oligomers dropped from 46% (20 bar) to 38% (30 bar). This behaviour is

[98] (a) A. Kermagoret, P. Braunstein, *Organometallics* 27 (**2008**) 88. (b) F. Speiser, P. Braunstein, L. Saussine, *Organometallics* 23 (**2004**) 2625.

[99] C. Obuah, J.H. Jordaan, J. Darkwa, *Catal. Sci. Technol*. 6 (**2016**) 4814.

associated to saturation of the reaction mixture by ethylene monomer.[100] Obuah *et al.*[20] reported an increase of activity from 1890 Kg.mol^{-1}.h^{-1} (10 bar) to 9092 kg.mol^{-1}.h^{-1} (30 bar) using dimethyl pyrazol-yl benzene nickel(II) pre-catalyst with $EtAlCl_2$ co-catalyst. When they further increased pressure to 40 bar, only a slight increase of 9650 kg.mol^{-1}.h^{-1} was observed.[20] Ojwach *et al.*[101] reported impressing and good increase on activities with an increase on ethylene pressure using pyrazol-yl methyl pyridine nickel(II) catalyst and $EtAlCl_2$ co-catalyst. On their report doubling the ethylene pressure from 20 bar to 40 bar resulted on an increase on activity from 2929 kg.mol^{-1}.h^{-1}to 16 660 kg.mol^{-1}.h^{-1}.

The reactions were also run at different times to test the stability of the catalyst **C5** by varying reaction time from 1 hr to 4 hrs (Table 3.2, entries 8, 12-14). The results shows that the catalyst activity also decreased with an increase in reaction time as reported for Pd(II) catalyst. For example, the activity of 260 kg.mol^{-1}.h^{-1} was observed after 1 hr and running the reaction for 2 hrs decreased the activity to 152 kg.mol^{-1}.h^{-1}. Time was also observed to play a vital role in product distribution. Unexpected change on product selectivity when running the reaction for more for 4 hrs was observed. Here a decrease on percentage of C_6 oligomers was expected as observed for the **C5**, surprisingly a high percentage of 79% was obtained instead. This might be due to the catalyst deactivation over time and the co-catalyst in solution continues to activate alkylation of the toluene solvent and increase the amount of alkylated toluene products formed.

3.5.3 The effect of solvent on ethylene transformation activity and product distribution

Different solvents were used to study the effect of solvent on both activity and product selectivity. First toluene was substituted with chlorobenzene in an attempt to prevent the getting the oligomers being alkylated to toluene. The difference between toluene and chlorobenzene are the methyl and chloride substituents on the benzene ring. The methyl in toluene is an activating group and activates the benzene ring towards electrophilic substitution reactions and whiles the chloride in chlorobenzene leads to the ring being deactivated. Running the reactions in chlorobenzene afforded oligomers C_{10} to C_{18} with greater selectivity towards C_{10} oligomers. Secondly hexane was used as solvent for the same reactions to study the effect on solvent polarity towards activity and size of the oligomers. High activities were observed when

[100] J. Skupińska, *Chem. Rev*. 91 **(1991)** 613.

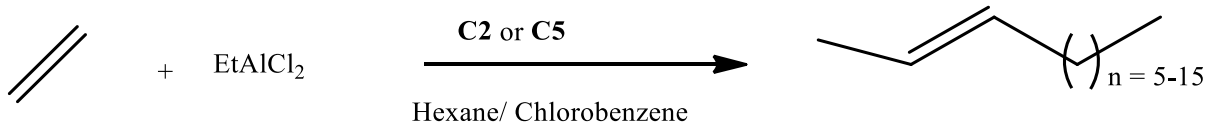
[101] S.O. Ojwach, I.A Guzei, L.L. Benade, S.F. Mapolie, J. Darkwa, *Organometallics* 28 (**2009**) 2127.

chlorobenzene (2.7 p.m) was used as solvent possibly because of it high polarity index as compared to both toluene (2.4 p.m) and hexane (0.1 p.m). The polarities of these solvents affected the solubility of the catalysts which the affected the activity of these catalyst in ethylene transformation reactions. The reactions on hexane afforded traces of C_{20}.

Table 3.3: Ethylene Transformation studies using catalyst **C2** and **C5** in chlorobenzene and $EtAlCl_2$ in hexanes as co-catalyst.[a]

Entry	Catalyst	Solvent	Al:Pd/ Ni ratio	[b]Yield (g)	Activity ($Kg.mol^{-1}.h^{-1}$)	[c]Product distributions (%)					
						C_{10}	**C_{12}**	**C_{14}**	**C_{16}**	**C_{18}**	**C_{20}**
1	**C2**	Hexane	200	2.30	230	35.41	13.48	37.78	9.30	2.18	1.85
2	**C5**	Hexane	200	2.63	260	43.41	6.48	29.11	10.72	8.97	1.07
3	**C2**	Chlorobenzene	200	5.59	560	50.26	10.51	28.18	5.89	4.16	–
4	**C5**	Chlorobenzene	200	6.76	680	51.57	5.20	29.23	11.23	2.77	–
5	**C5**	Chlorobenzene	300	21.09	2110	52.87	11.47	18.30	12.29	5.07	–

[a]Reaction conditions: [Catalyst] = 10 µmol; Solvents ,Toluene and Hexane ,10 mL, Pressure, 10 bar, [b]determined by mass difference of 10 mL Chlorobenzene (9.01 g) and hexane (15.27 g) and mass of final solutions. [c]determined by GC-FID.



Scheme 3.4: Ethylene oligomerization with nickel catalysts **C4–C6**, and $EtAlCl_2$ as co-catalyst in hexane and chlorobenzene

It was previously observed that when catalysts **C2** and **C5** were tested in toluene at optimum reaction conditions of Ni:Al = 1:200, for 1 hour, with precatalyst loading of 10 μmol and temperature set at 30 ^{o}C, the major products obtained from these reactions were hexenes, ethyltoluenes, butyltoluenes and butyl-ethyltoluenes with activities up to 610 kg.mol^{-1}.h^{-1} Table 3.1 and Table 3.2. When changing solvent to either hexane or chlorobenzene under the same reaction conditions described for reactions in toluene C_{10}-C_{20} oligomers were observed with activities up to 2110 kg.mol^{-1}.h^{-1}, Table 3.3, entries 1-5.

Again catalyst structure was found to play an important role in product distribution. For example using catalyst **C2** in hexane produced higher C_{14} (38%) than C_{10} (35%) oligomers while catalyst **C5** gave higher C_{10} (43%) oligomers as compared to the C_{14} (29) oligomers. Running the reactions in chlorobenzene using catalyst **C2** increased activities from 320 kg.mol^{-1}.h^{-1} in hexane to 560 kg.mol^{-1}.h^{-1} in chlorobenzene. Solvent also played a role in product selectivity; using catalyst **C2** in hexane produced 35% of C_{10} oligomers while using the same catalyst in chlorobenzene produced 50% of C_{10} oligomers, Table 3.3, entries 1 and 3. When catalyst **C5** was used under the same conditions in chlorobenzene the activity increased from 269 kg.mol^{-1}.h^{-1} (hexane) to 680 kg.mol^{-1}.h^{-1} (chlorobenzene). Again higher selectivity of C_{10} (52%) and C_{14} (29%) were observed. increasing the co-catalyst ratio from 1:200 to 1:300 increased the activity from 680 kg.mol^{-1}.h^{-1} to 2110 kg.mol^{-1}.h^{-1}, respectively. The selectivity on the oligomers was comparable to the ones observed at co-catalyst ratio of 1:200. In all the reaction C_{10} and C_{14} were obtained as major products. These results display the role played by the type of solvent in both activity and product distribution.

The identification of the oligomerization products was done using a combination of GC-FID, GC-MS and ^{1}H NMR spectroscopy. In, a typical ^{1}H NMR spectrum of the products obtained from catalyst **C5**, the spectrum showed a peak at a range of 5.0 ppm to 5.5 ppm as an evidence for internal alkene olefin protons, Figure 3.8. The olefin protons for terminal alkenes are expected at 4.6 ppm-5.0 ppm region and no peaks were observed around that region. It is clear that the oligomers obtained with hexane and chlorobenzene solvents are internal olefins.

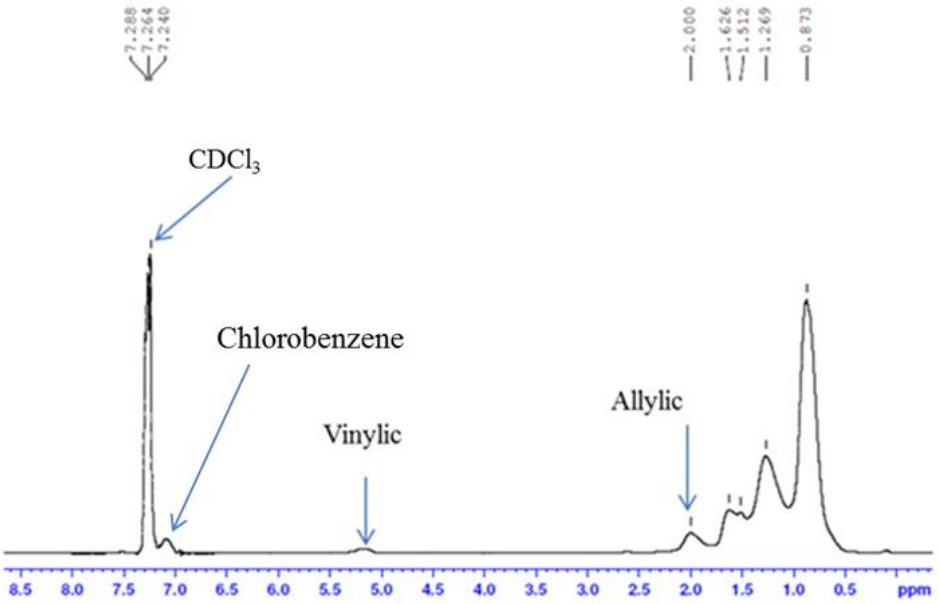


Figure 3.8 ^{1}H NMR spectrum of the products of catalyst **C5** from the reaction at Al:Ni ratio of 200:1, temperature = 30 °C, pressure = 10 bar, time = 1 hr, solvent = chlorobenzene.

Further analyses of the products by GC-MS confirmed the ethylene oligomerization products to be a range of ethylene oligomers from C_{10} to C_{20}. The chromatogram from GC-MS shows the distribution of products with C_{10} and C_{14} obtained at appreciable percentages. The chromatogram did not follow the Flory-Schulz distribution after C_{10}. Flory-Schulz distribution is a function describing the relative ratios of polymers with different lengths after complete polymerisation process based on their relative probability of occurrence. According to this distribution the shorter polymers are favoured over both the medium and long chained oligomers. In this report the C_{14} oligomers were favoured over the C_{12} oligomers, Figure 3.9.

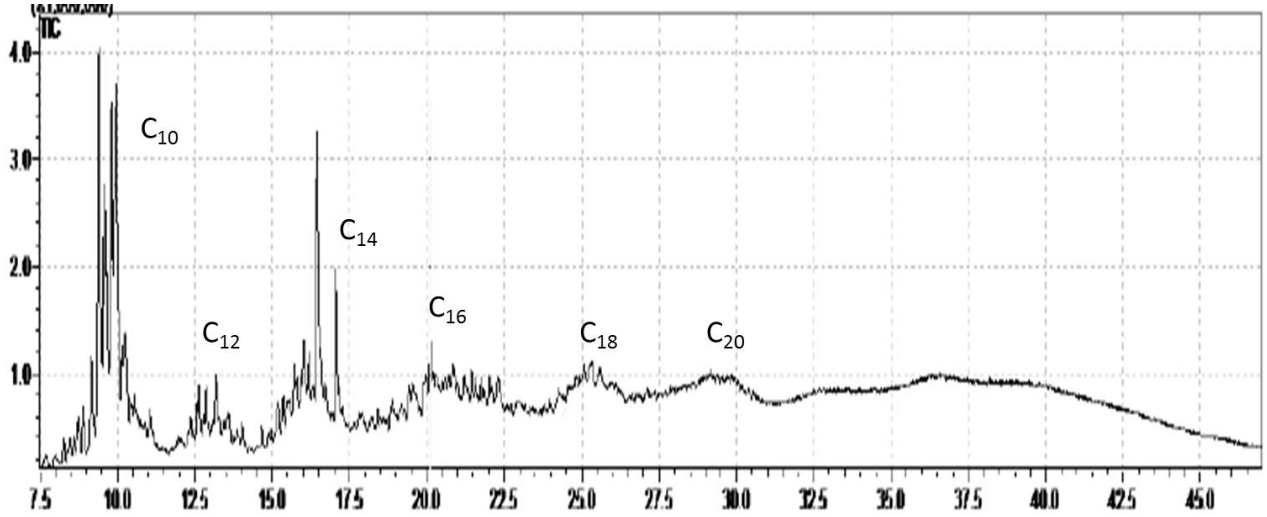


Figure 3.9 GC-MS chromatogram showing the products distribution obtained using catalyst **C5** in hexane

3.6 Conclusions

The complexes **C1-C6** were successfully evaluated in the ethylene transformation reactions where the catalyst structure, type of solvent used and reaction conditions were found to play a vital role in activity and product distribution. When toluene was used a solvent a mixture of hexene and alkylated toluene products were obtained, with hexene and butyltoluenes being obtained as major products. On the other hand running the reactions in hexane and chlorobenzene displayed better activities to produce C_{10}-C_{20} oligomers. The palladium(II) catalyst gave lower activities which were typically bellow 500 $kg.mol^{-1}.h^{-1}$ and nickel(II) catalysts gave activities up to 610 $kg.mol^{-1}.h^{-1}$ in toluene. When chlorobenzene was used as solvent better activities above 2000 $kg.mol^{-1}.h^{-1}$ were observed.

CHAPTER 4

SUMMARY, FUTURE WORK AND GENERAL CONCLUSION

4.1 Summary and Challenges

Symmetric poly pyrazolyl compounds in ethylene polymerisation have been used as catalyst for ethylene polymerisation. The problems encountered with stability and activity of these ligands opened a window for a search of different ligand system that can provide solutions to the problem at hand. In this study, synthesis of asymmetric pyrazolyl ligands and their complexes as catalyst for ethylene polymerisation was the main focus. Syntheses of these ligands have been a challenge. The main aim was to synthesize pyrazolyl ligands with different linkers and placing those pyrazole moieties at different times and has been a great challenge due to the lack of stability with the pyrazolyl hydrazide ligands.

For the preparation of the pyrazolyl hydrazide ligands two different starting materials were used, in **Route 1**, isophthaldehyde was used as a starting material. This was first reduced to 1,3-phenylenedimethanol using $LiAlH_4$ in THF and then MnO_2 was used as an oxidising agent following the procedure reported in the literature.[102] The aim with this route was to produce a scaffold with an alcohol and aldehyde group. The strategy was to anchor the pyrazole first after chlorination of the alcohol and later oxidise the aldehyde group to a carboxylic acid. After esterification the hydrazide group would be anchored as described in chapter 2. Unfortunately extensively low yields of the mono aldehyde discouraged us from continuing with this route. The low yields were caused by poor selectivity in the oxidation of 1,3-phenylenedimethanol. This decreased the yields of the 3-(hydroxymethyl) benzaldehyde to below 30%.

[102] A. Erxleben, D. Schumacher, *Eur. J. Inorg. Chem*. (**2001**) 3039.

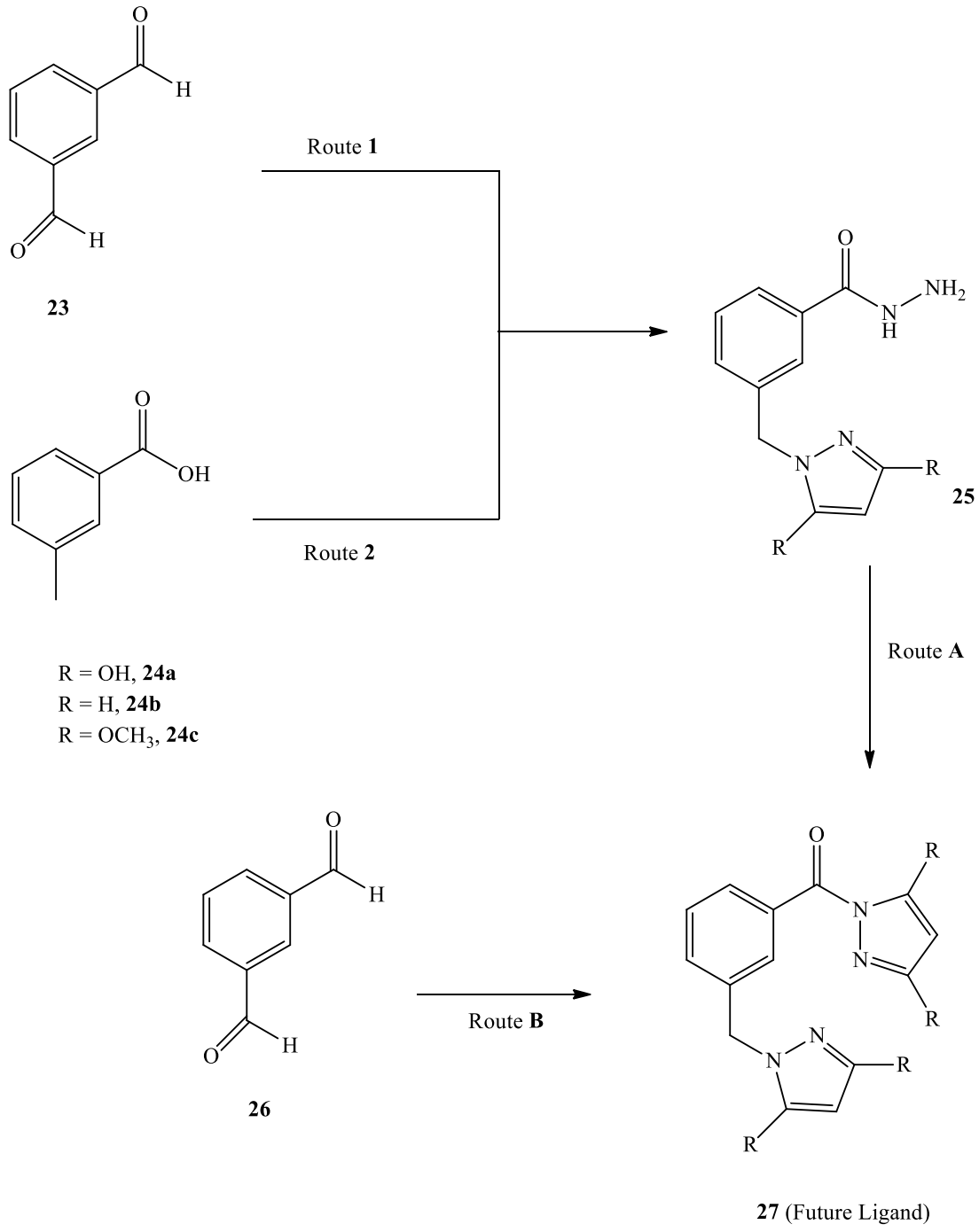


Figure 4.1: Different routes attempted for the preparation of pyrazolyl hydrazide ligand and possible attempts for the future ligand.

To resolve the issue of low yields, research was extended to using tolyl derivatives route as starting materials. Out of the tolyl derivatives use only the ester from 3-methylbenzoic acid **24c** in route **2** was successfully brominated with N-bromo succinamide (NBS) in water using

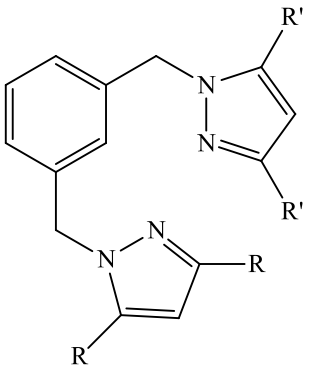
halogen light as an initiator.[103] The resultant methylene bromide allowed for the addition of the pyrazole moiety while the carbonyl group laid a foundation for the hydrazides. Other different carbonyl tolyl derivatives such as tolyl alcohol **24a** and tolyl aldehyde **24b** when reacted with NBS were oxidised into toluic acid. Toluic acid on the other hand when reacted with NBS under the same conditions under goes nuclear bromination. This can be considered as a greener method for oxidation of alcohols and aldehydes using NBS and light in water.

4.2 Future Outlook

In future it would be interesting to further prepare pyrazolyl methylene carbonyl benzene ligands from the reaction the hydrazides and different diketones, route A. This ligand could also be prepared using starting materials **25** and **26** as shown in Scheme 4.1.

Starting from isopthalic acid in **route B**, the acid will first be converted into a dimethyl isophthalate, followed by conversion of one ester group to a carboxylic acid, then chlorinated to give an acyl chloride which is then used to anchor the first pyrazole ring on the carbonyl linker. The remaining ester group will later be reduced into an alcohol, chlorinated and used to anchor the second pyrazole on the methylene linker. This would be a new family of N-Heterocyclic pyrazolyl ligands with mixed linkers or on the 1,3-positions of the benzene ring. Again it would be interesting to further reduce the carbonyl linker into a methylene linker and have two different pyrazoles on different positions of the benzene ring, Scheme 4.1. Evaluation of the complexes of both these ligand systems as catalyst for polymerisation reactions would be of great. This can possibly balance the stability and activity of the pyrazolyl benzene complexes when used as catalysts.

[103] A. Podgorsˇek, S. Stavber, M. Zupan, J. Iskra, *Tetrahedron Lett*. 47 (**2006**) 1097.



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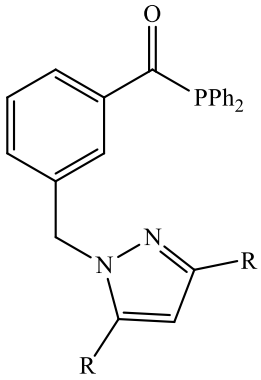

29

R or R'= Me, ^{t}Bu, Ph

Figure 4.2: Possible novel benzene pyrazolyl ligands

In addition, future investigation on the use of other hemilabile soft donor groups can be explored. A possible approach can be the use of the phosphine donor atom in place of the nitrogen donor from the hydrazide group, Figure 4.3. This would allow the soft phosphine donor atom to stabilise the metal centre while the hard nitrogen donor atom from pyrazole moiety creates a vacant site for the substrate to bind. Further analysis of the products obtained with the pyrazolyl hydrazides catalysts will need to be done in detail to determine the selectivity on the isomers formed. The alkylated products obtained with these catalysts reported in the current study were found to be isomeric mixtures and it was not clear which isomer was favoured over the other. If analytic techniques like HPLC could be used to separate the products, selectivity of isomers could be determined as well.

4.3 General Conclusions

In summary, a complete series of pyrazolyl hydrazide ligands have been synthesized using different routes and characterised fully. This reports new pyrazolyl-hydrazide nickel(II) and Palladium(II) complexes as potential catalysts for olefin transformation reactions. All the complexes were activated using $EtAlCl_2$ and gave mixture of oligomers and alkylated products in toluene. Running the same reactions in chlorobenzene gave longer chain oligomers. The role played by different solvents, type of co-catalyst, catalyst structure and reaction conditions has been shown to have effect on the products. For example Friedel-Craft alkylation was observed only in the case where toluene was a solvent. Both the ethylene oligomerisation and Friedel-Craft alkylation were observed to occur in tandem.

APPENDIX

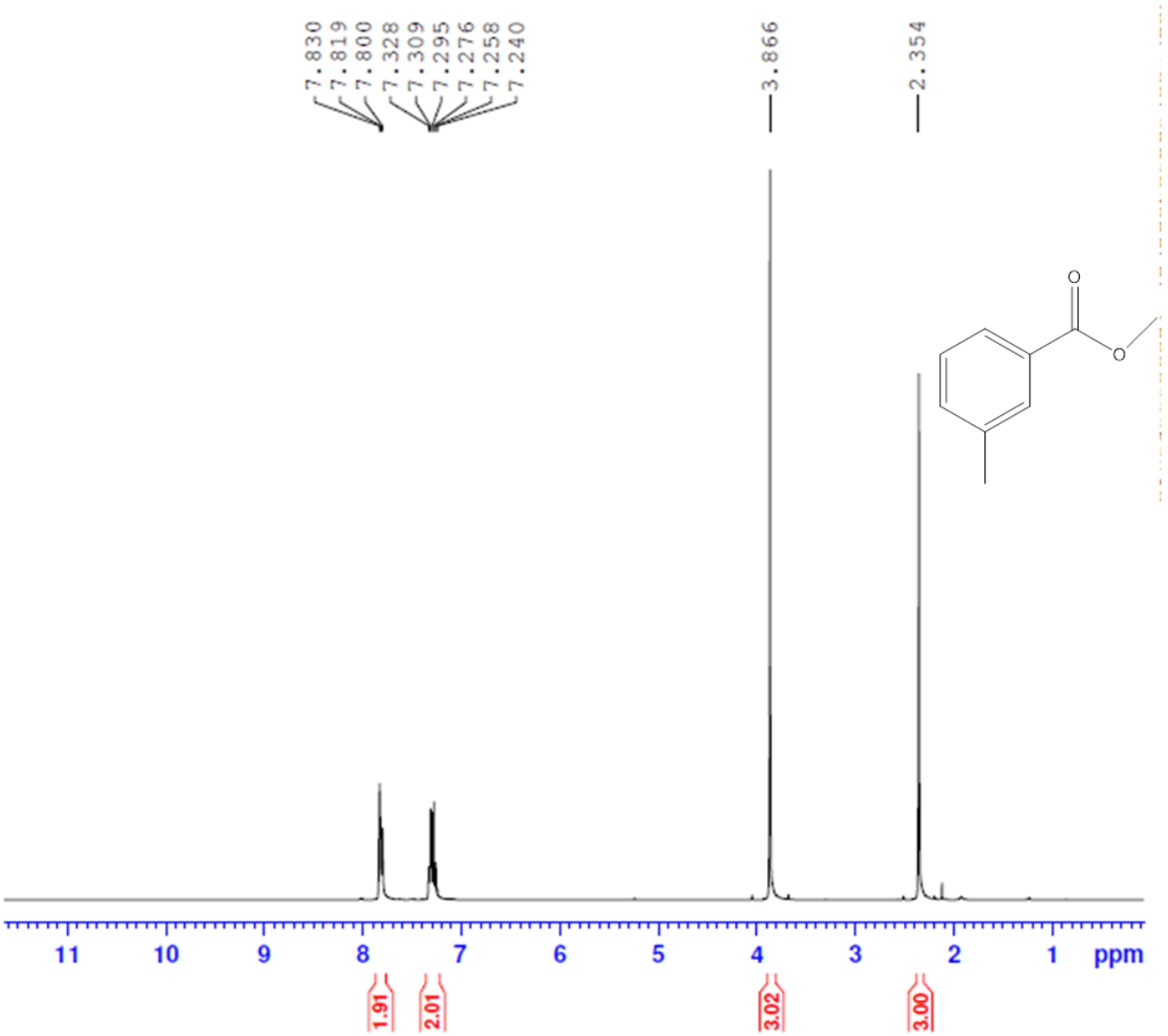

Figure A1: The ^{1}H NMR spectrum of spectrum of compound **L1** (in $CDCl_3$)

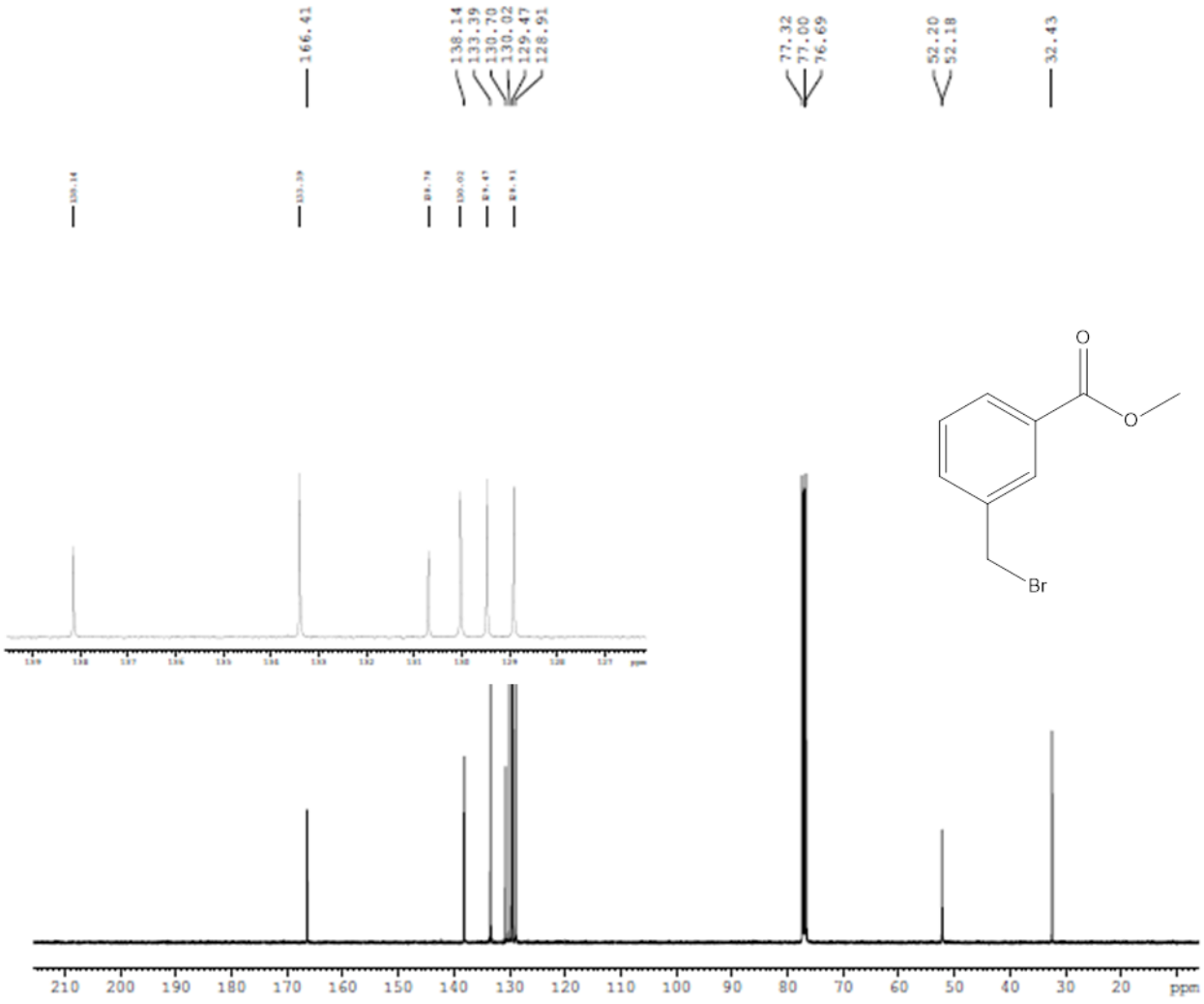

Figure A2: The ^{13}C NMR spectrum of methyl 3-(bromomethyl) benzoate **L2 (**in $CDCl_3$)

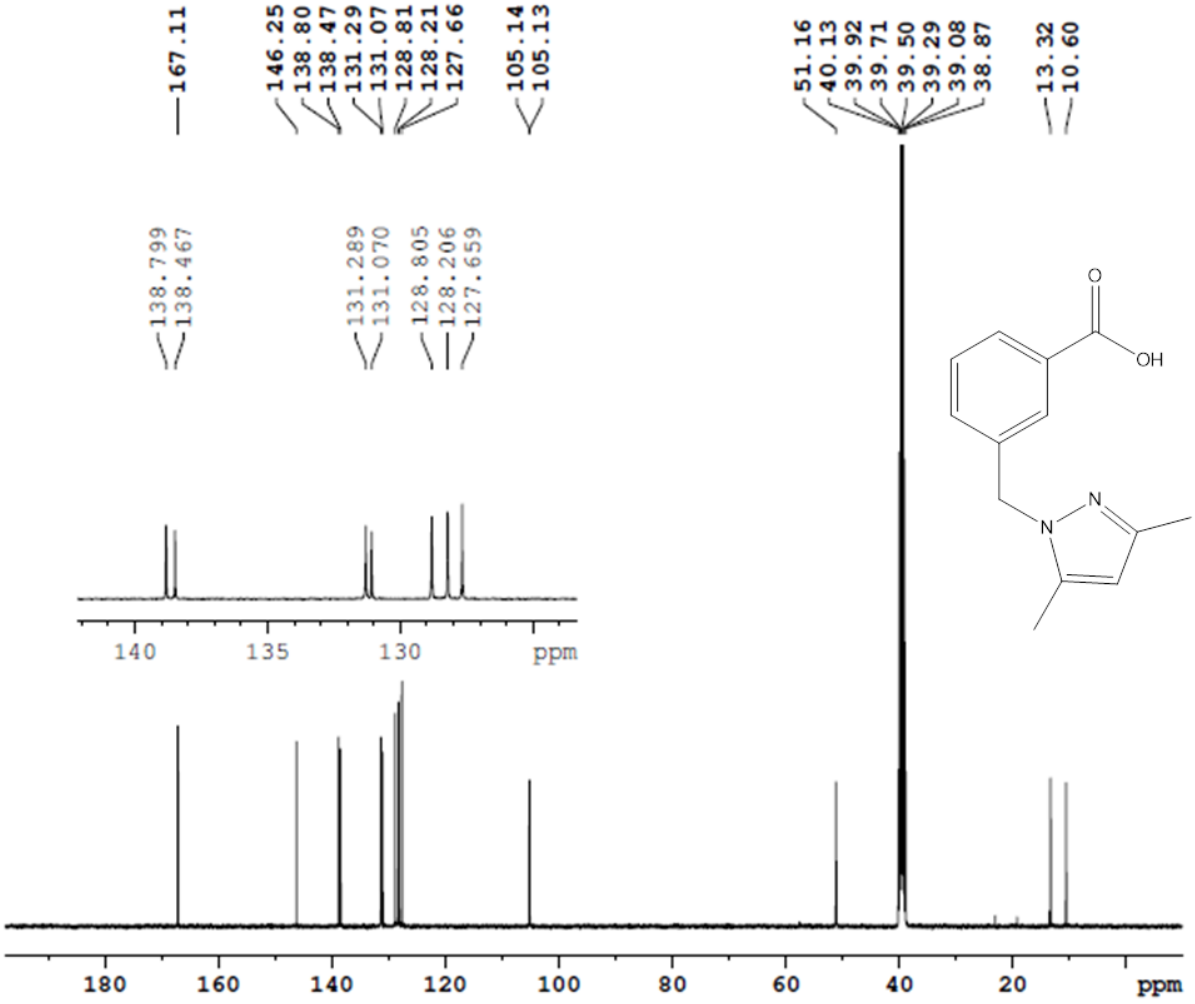

Figure A3: The ^{13}C NMR spectrum of Compound **L3a** (in DMSO-d_6)

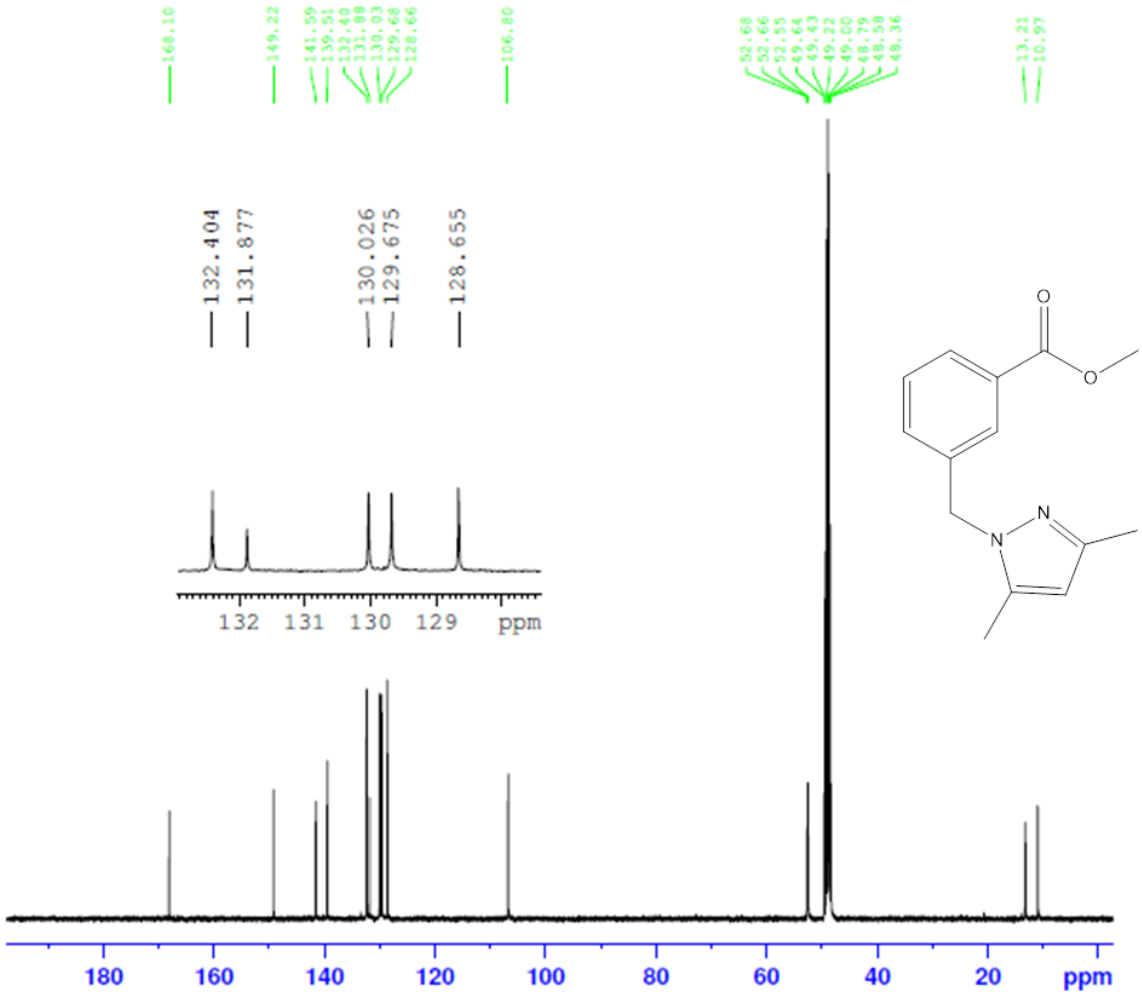

Figure A4: The ^{13}C NMR spectrum of Compound **L4a** (in MeOD-d_4)

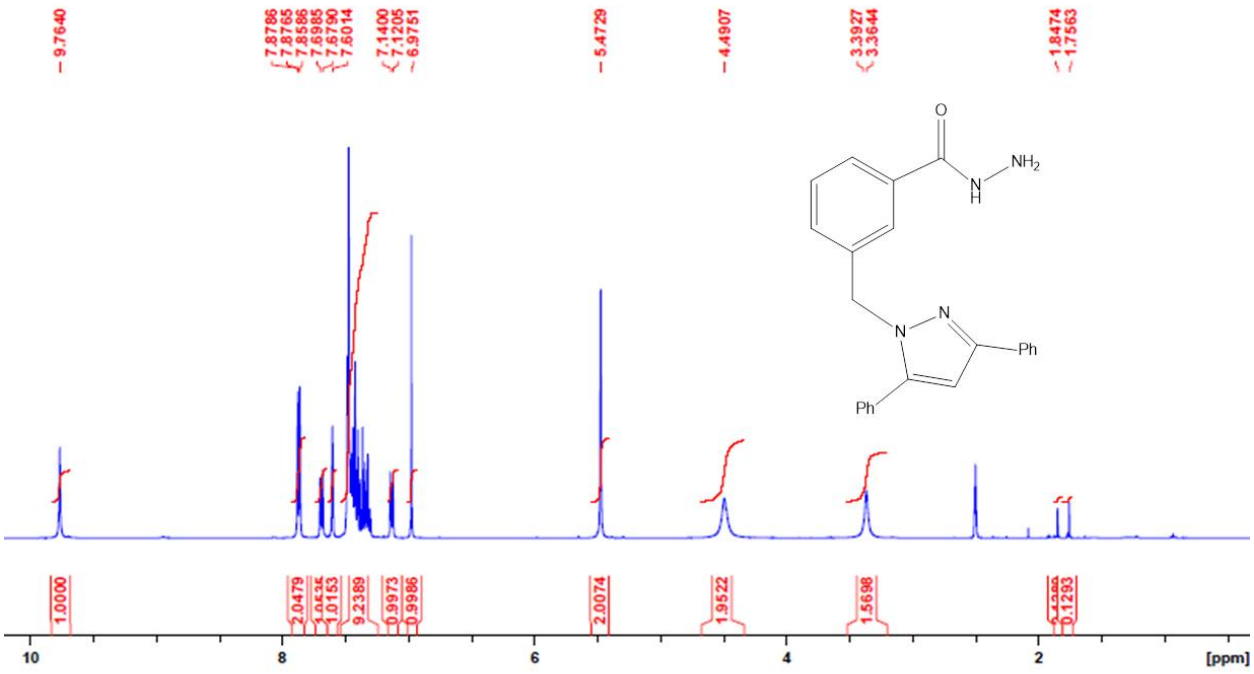

Figure A5: The ^{1}H NMR spectrum of compound **L5b** (in DMSO-d_6)

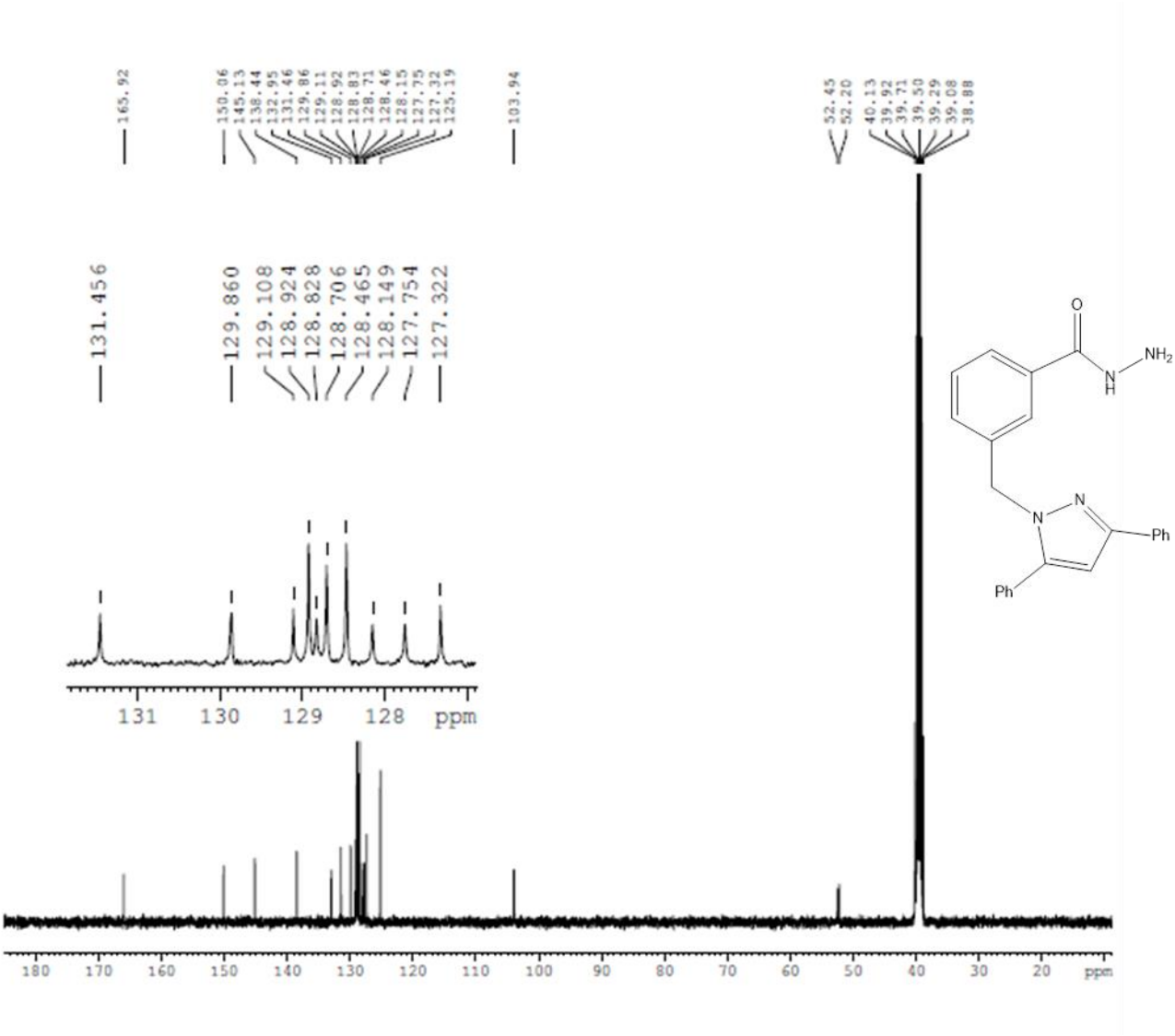

Figure A6: The ^{13}C NMR spectrum of compound **L5b** (in DMSO-d_6)

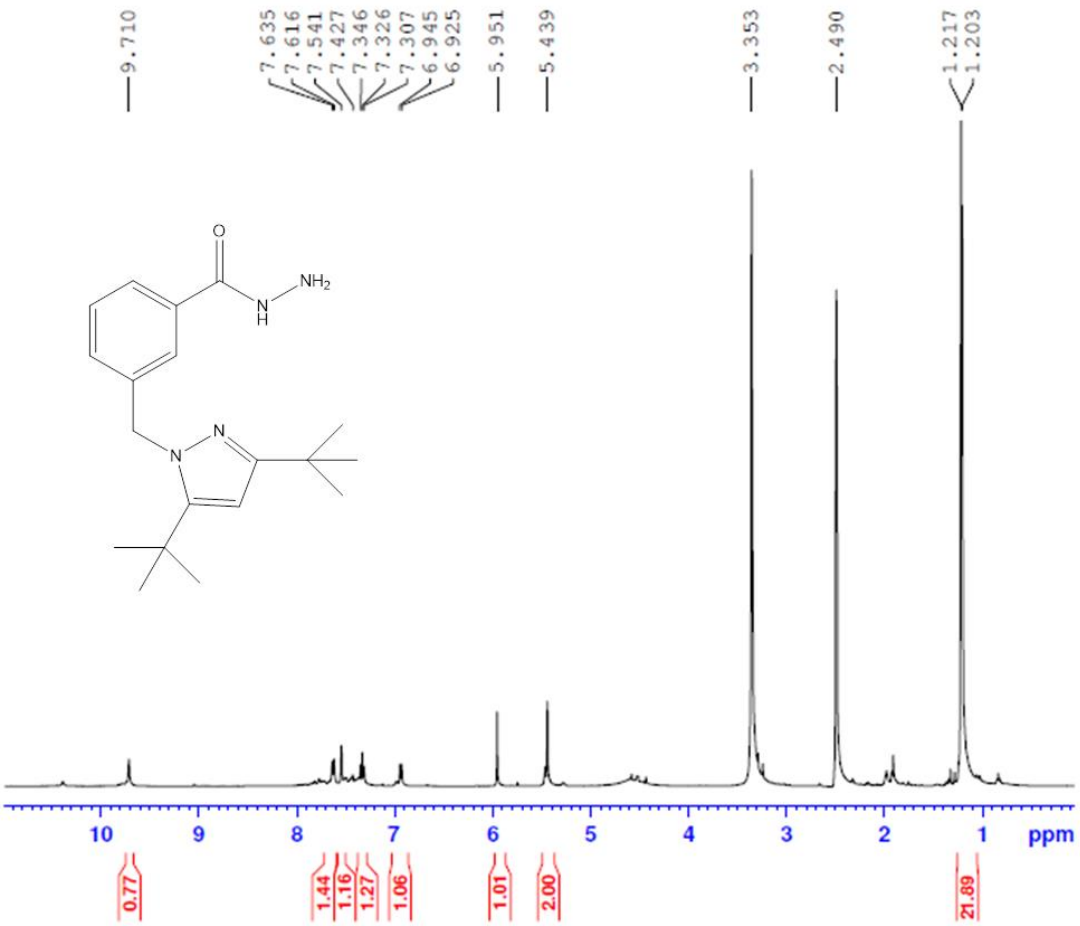

Figure A7: The ^{1}H NMR spectrum of compound **L5c** (in DMSO-d_6)

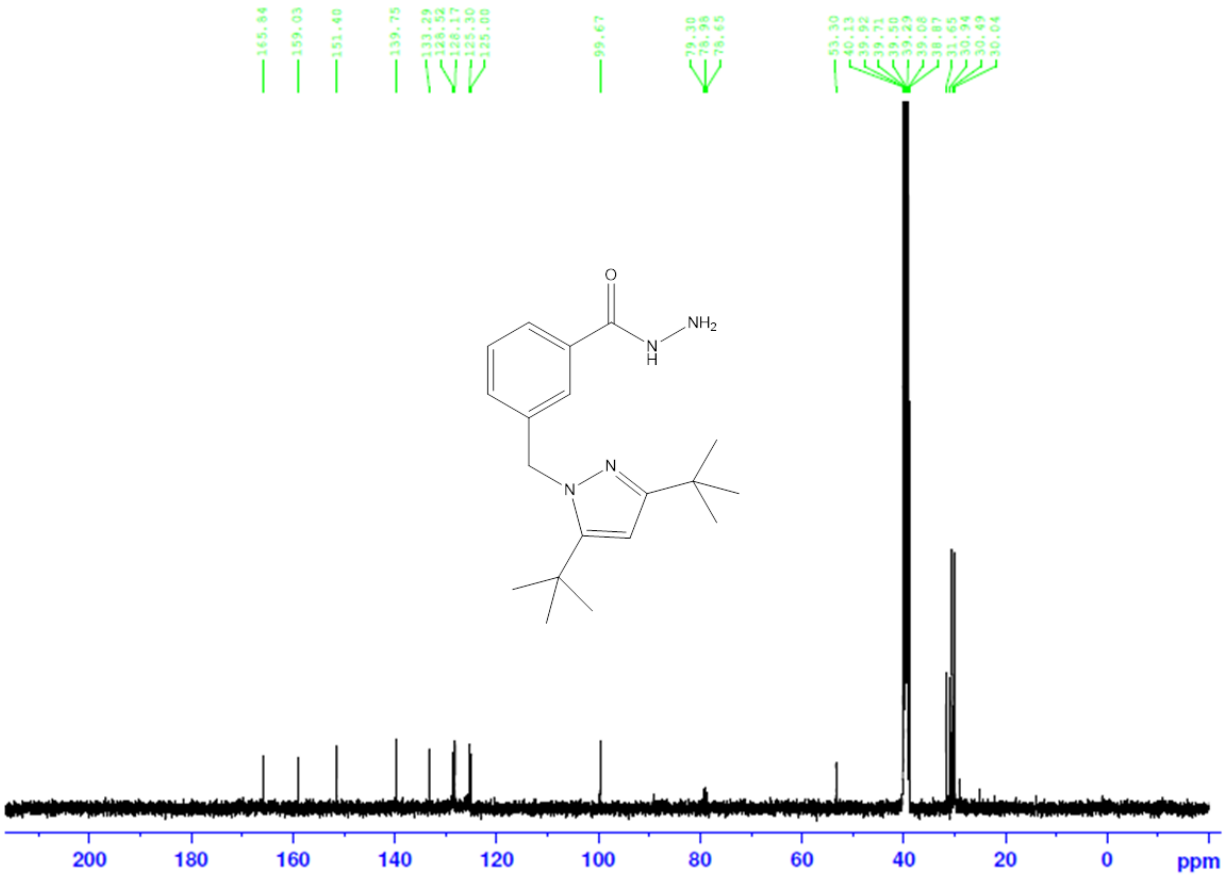

Figure A8: The ^{13}C NMR spectrum of compound **L5c** (in DMSO-d_6)

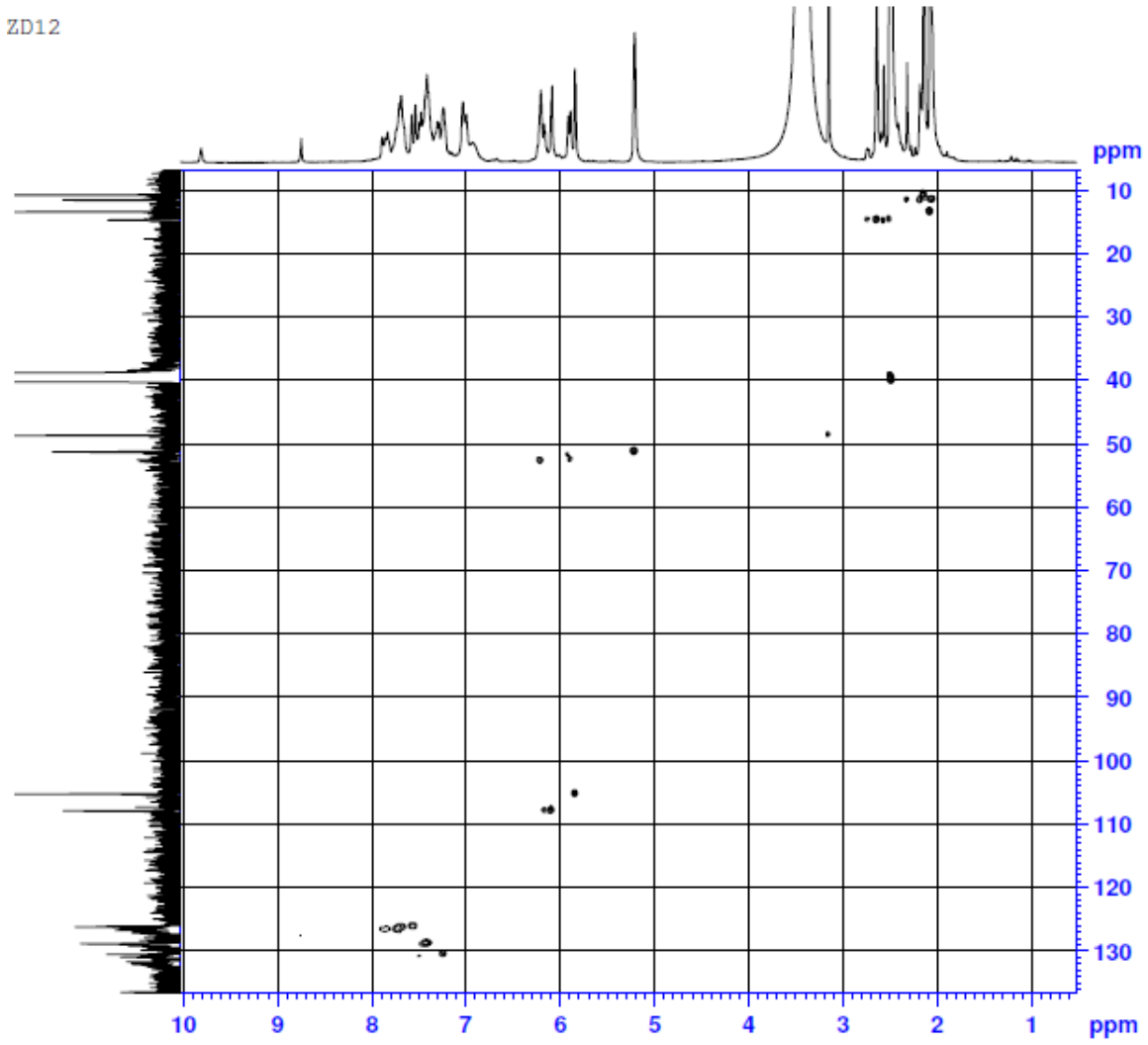

Figure A9: The HSQC NMR spectrum of complex **C1** (in DMSO-d_6)

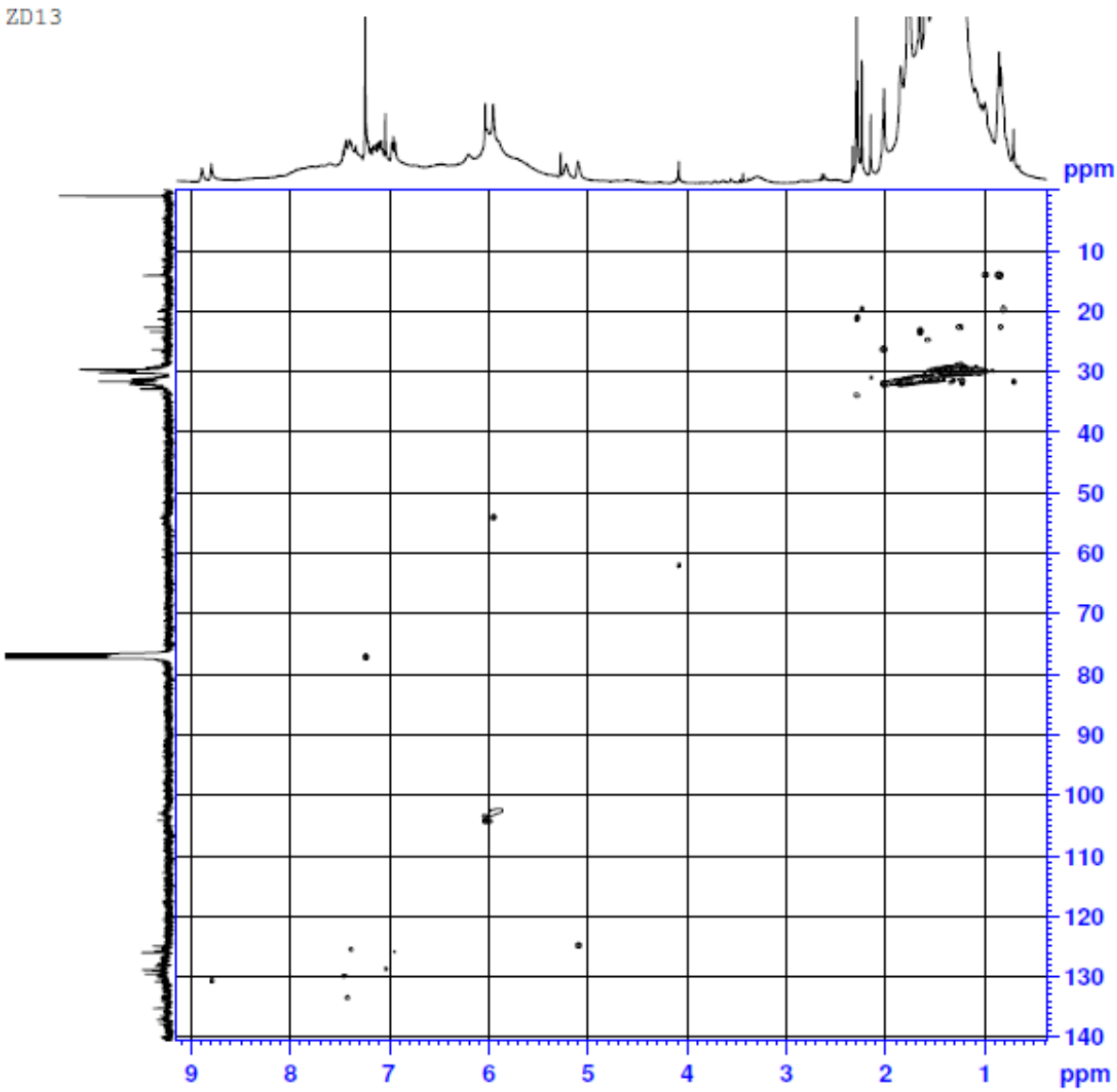

Figure A10: The HSQC NMR spectrum of complex **C3** (in $CDCl_3$)

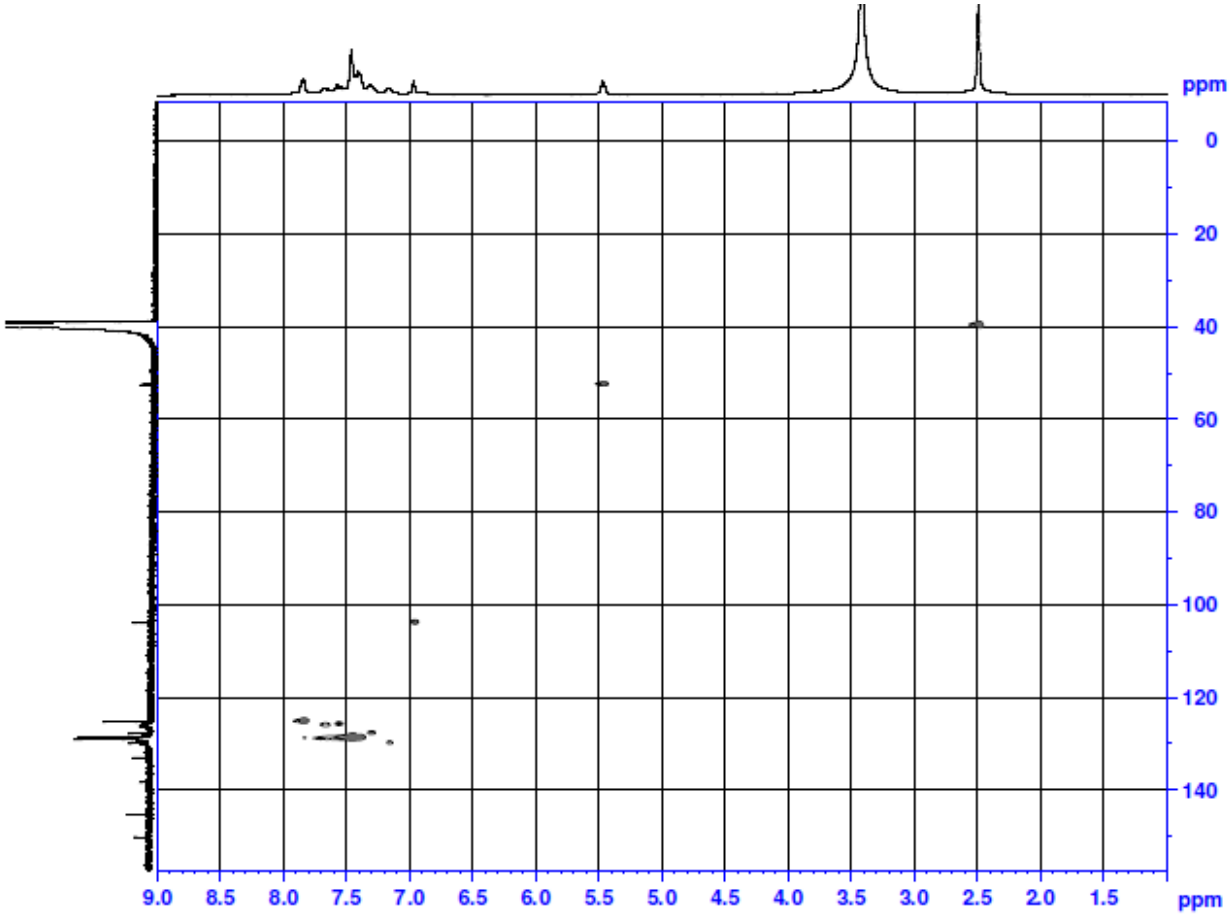

Figure A11: The HSQC NMR spectrum of complex **C2** (in DMSO-d_6)

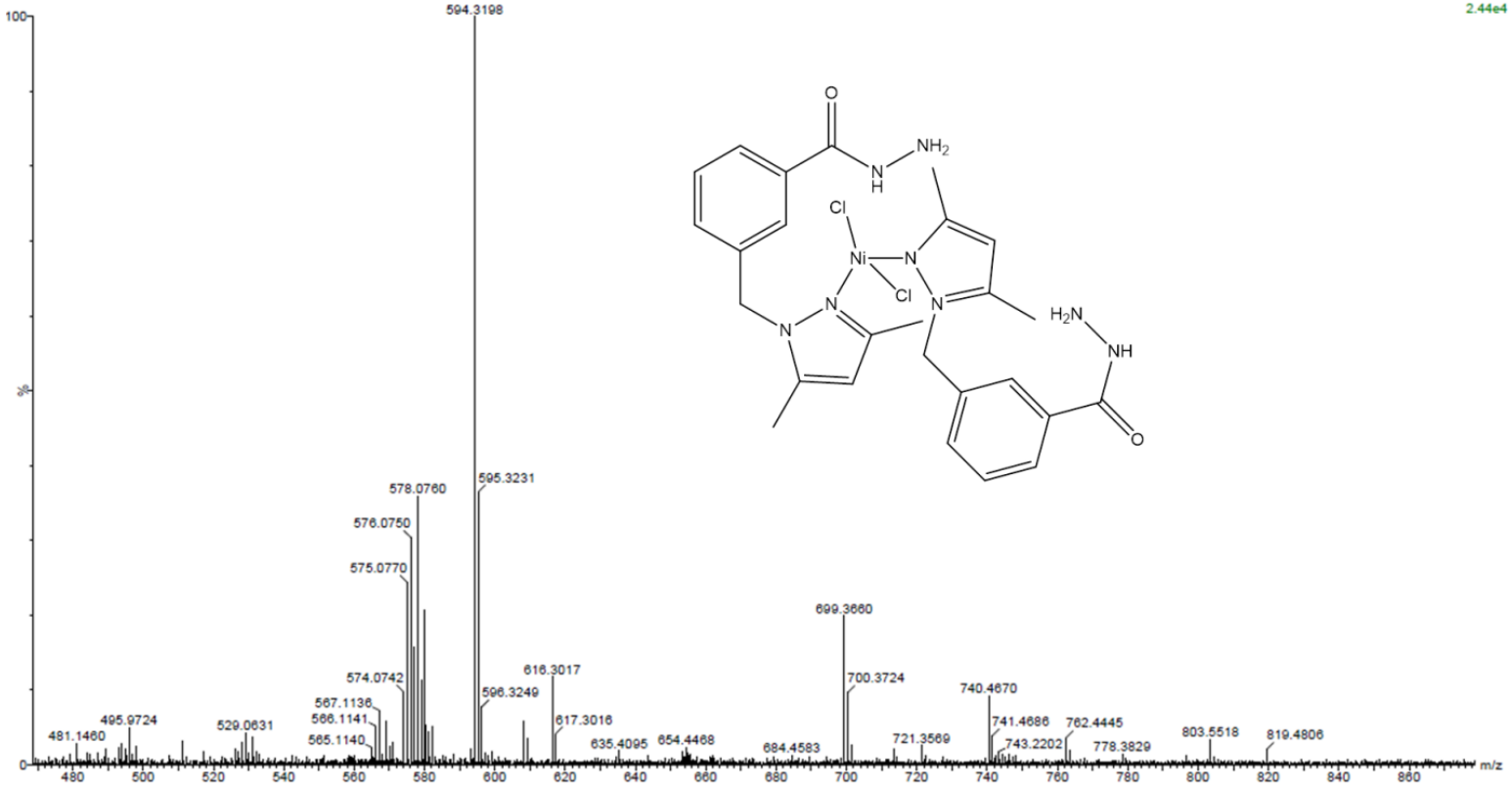

Figure A12: The MS/EIS spectrum of complex **C4**

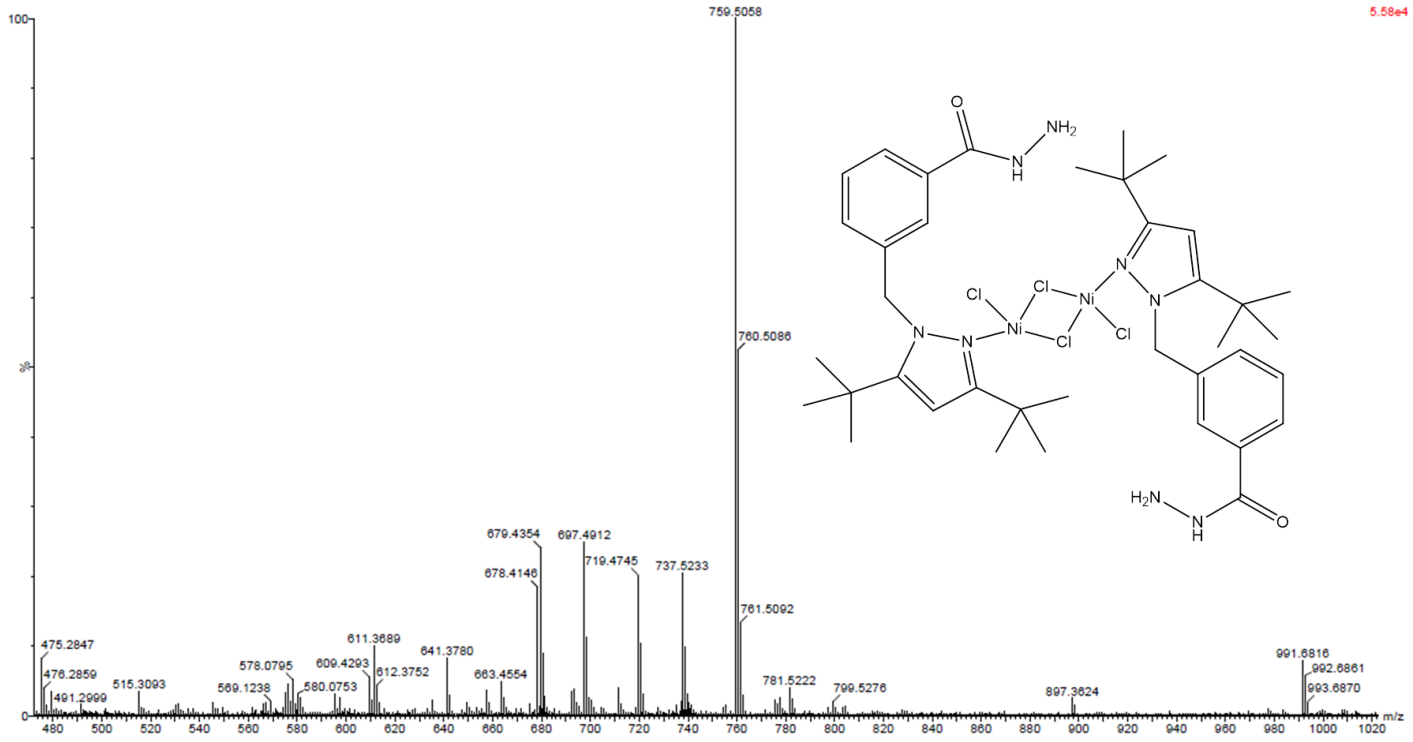

Figure A13: The MS/EIS spectrum of complex **C6**

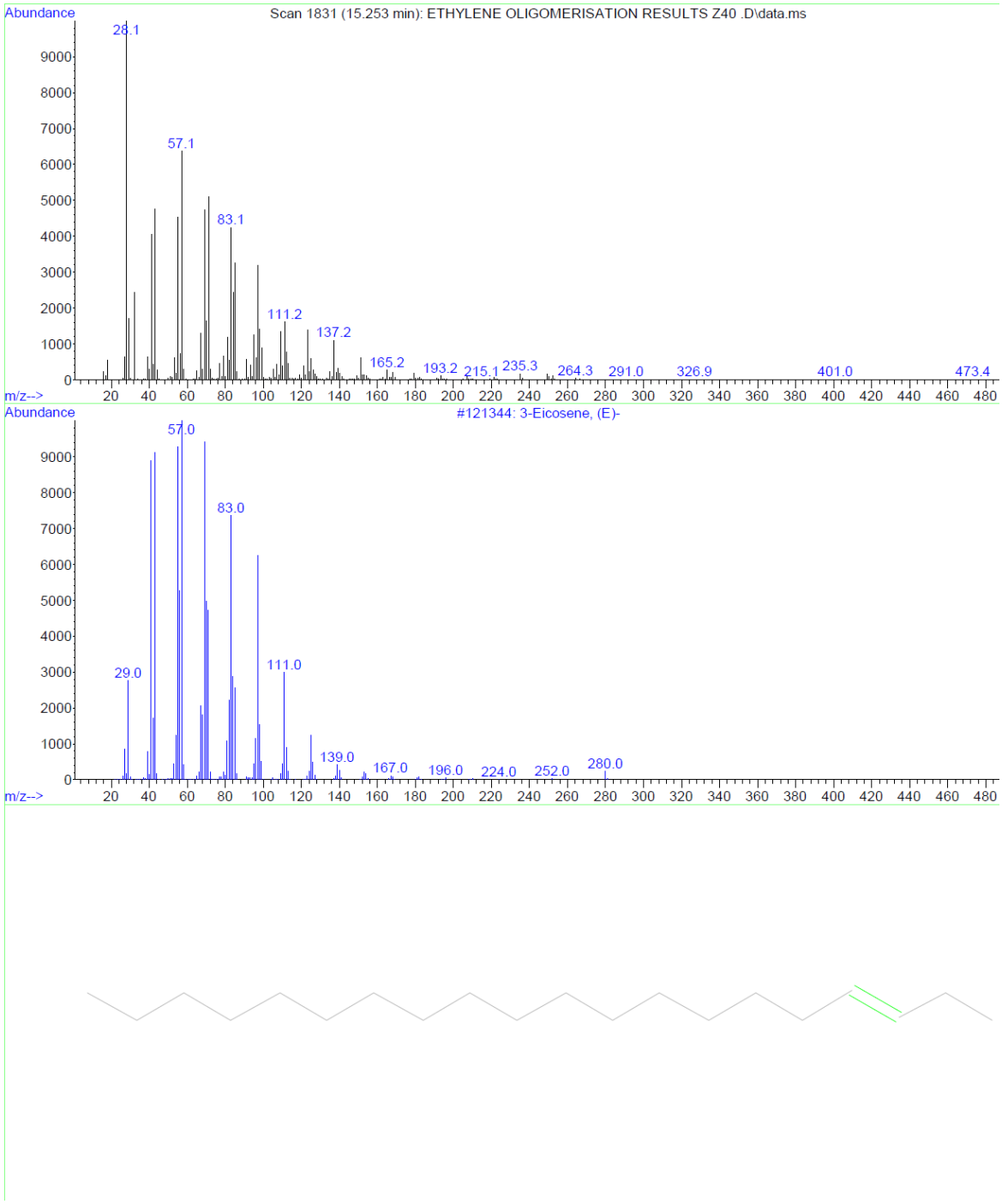

Figure A14: GC MS Spectrum GC trace of oligomer products of catalyst 2 from the reaction at Al:Ni ratio of 1:200, temperature = 30 °C, pressure = 10 bar, time = 1 hr, solvent = chlorobenzene

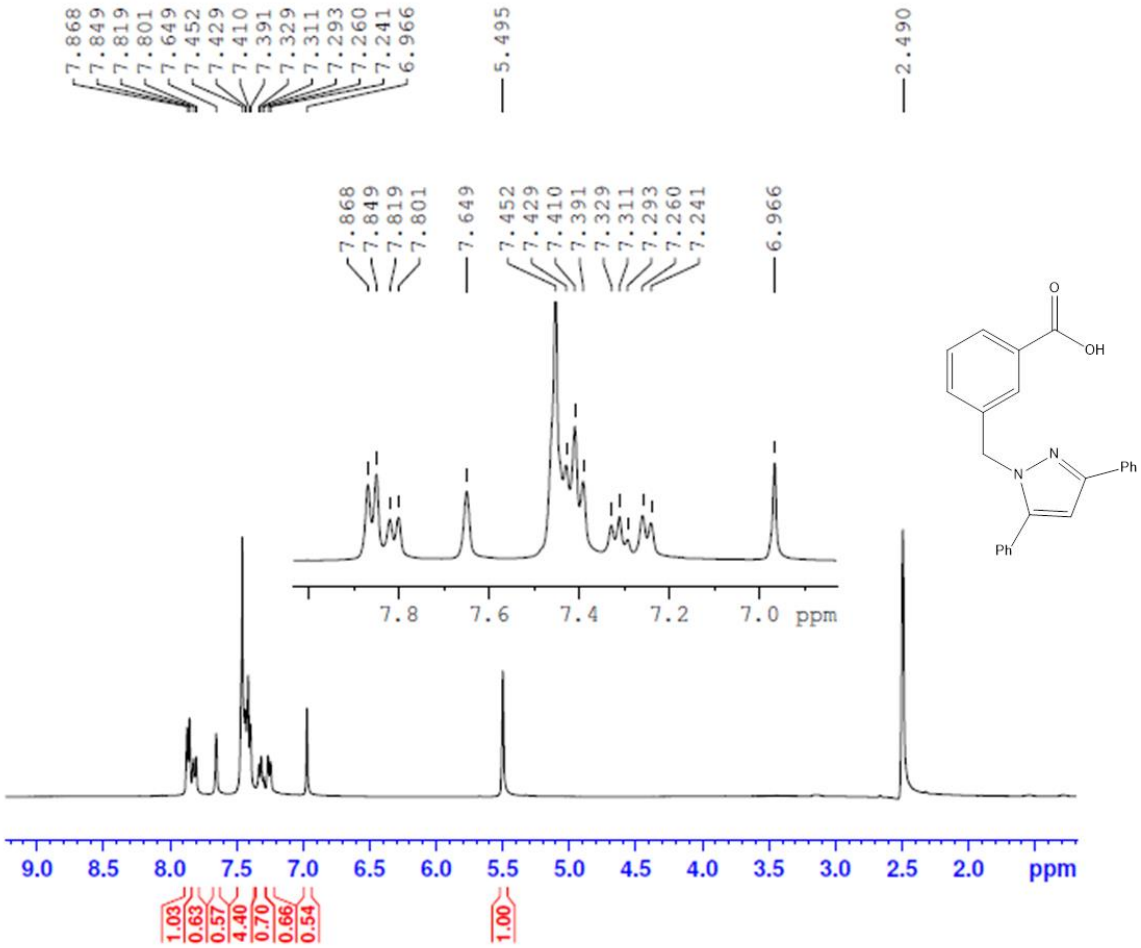

Figure A14: The ^{1}H NMR spectrum of compound **L3b** (in DMSO-d_6)

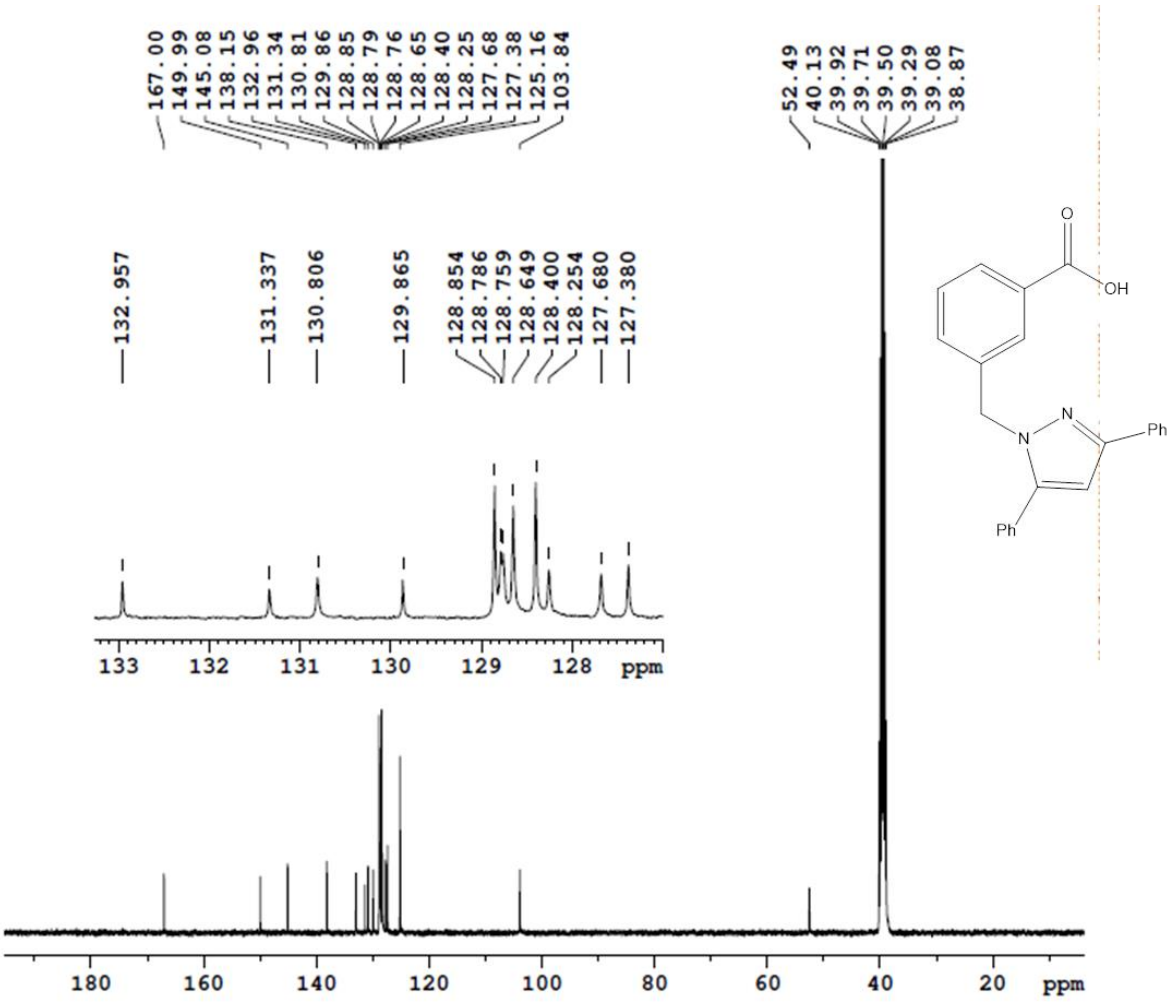

Figure A15: The ^{13}C NMR spectrum of compound **L3b** (in DMSO-d_6)

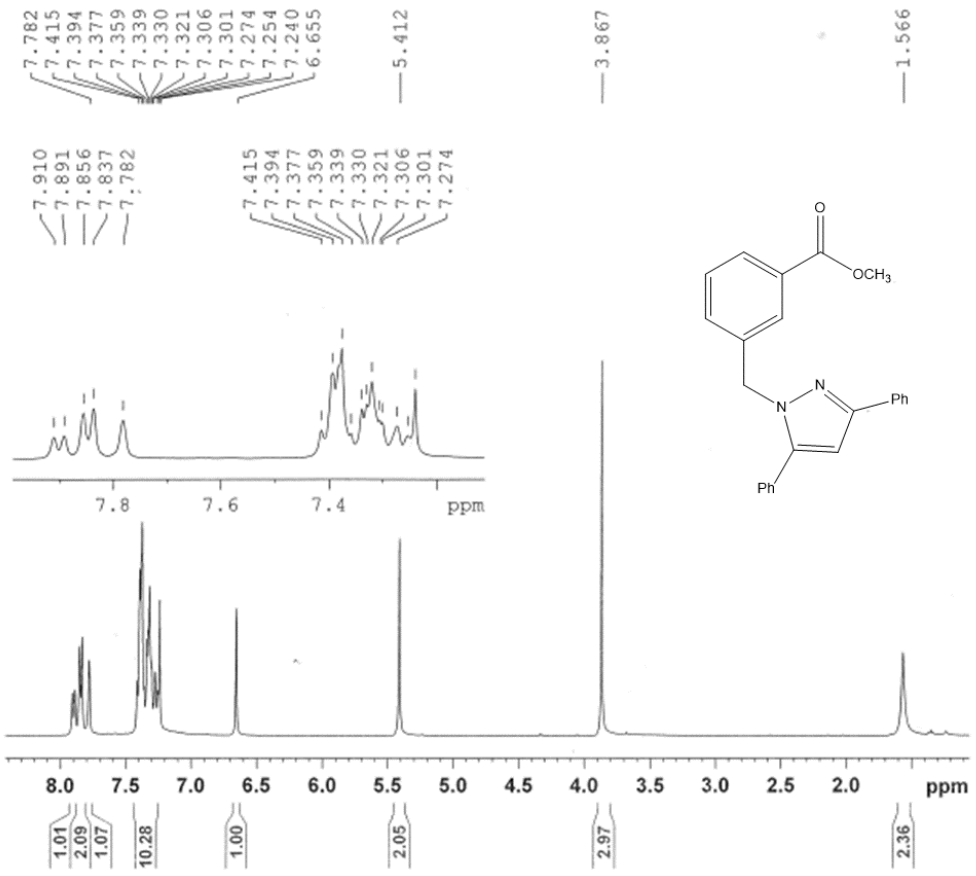

Figure A16: The ^{1}H NMR spectrum of compound **L4b** (in $CDCl_3$)

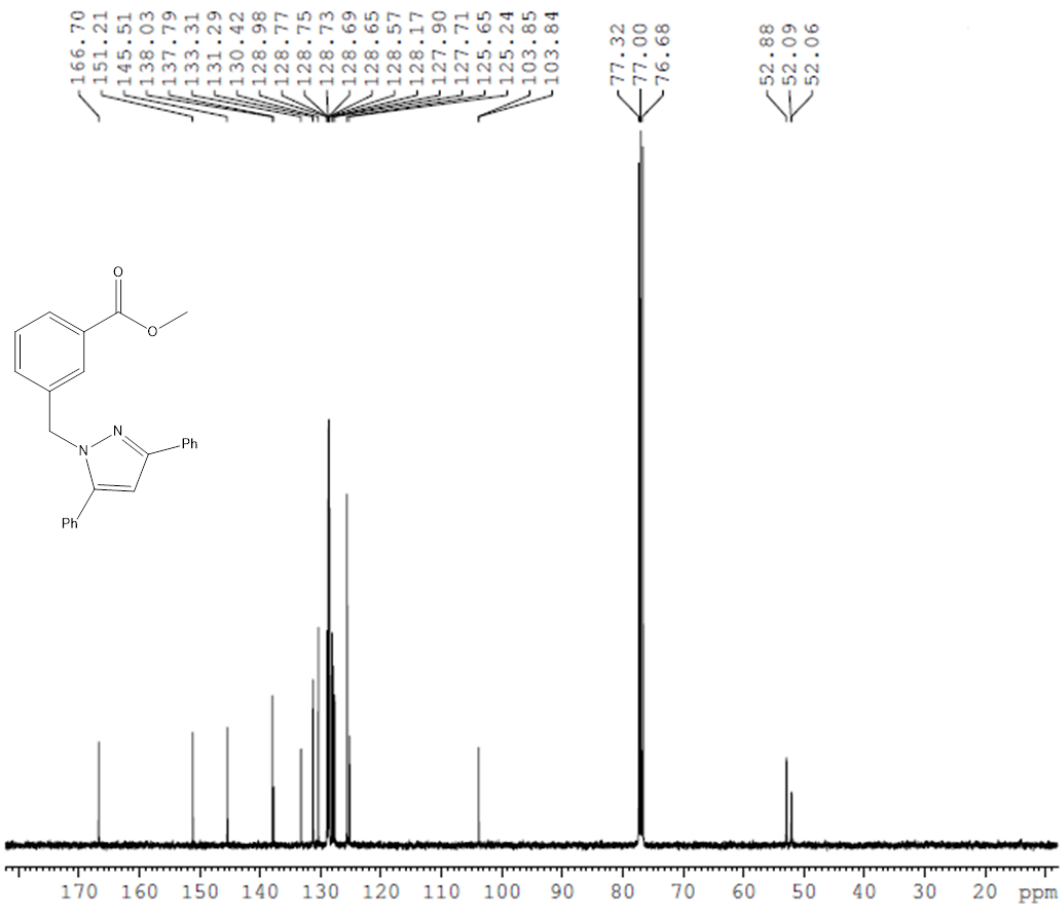

Figure A17: The ^{13}C NMR spectrum of compound **L4b** (in $CDCl_3$)