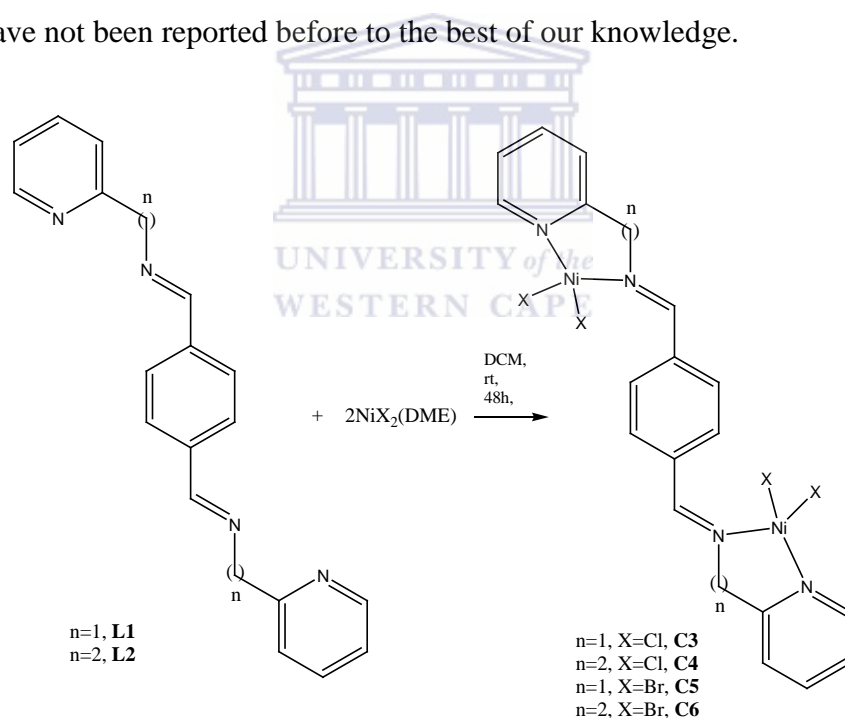


Scheme 3.4: Possible fragmentation pattern for **C2**



3.3.2 Bimetallic Iminopyridyl Ni(II) complexes

The iminopyridyl nickel(II) complexes were synthesized by using mixed procedures of Pelletier *et al.* and Bahuleyan *et al.* (Scheme.5) [2, 21]. The ligands were reacted in 2 equivalent moles of either NiCl₂(DME) or NiBr₂(DME), which gave formation of new Ni(II) complexes [22]. All of the NiCl₂ complexes were isolated as blue or green solids. All the NiBr₂ complexes were isolated as brown or yellow solids. These complexes decompose in the temperature range of 105 °C – 225 °C. All of these complexes are only partially soluble in DMSO and insoluble in most organic solvents. The new complexes were characterized by: FTIR; elemental analysis; melting point and mass spectroscopy. Due to these complexes being paramagnetic, NMR could not be used as a characterization technique. Again these complexes have not been reported before to the best of our knowledge.



Scheme 3.5: Synthesis of tetrahydrophenyl-linked iminopyridyl nickel(II) complexes

3.3.2.1 FTIR studies of Bimetallic Iminopyridyl Ni(II) complexes

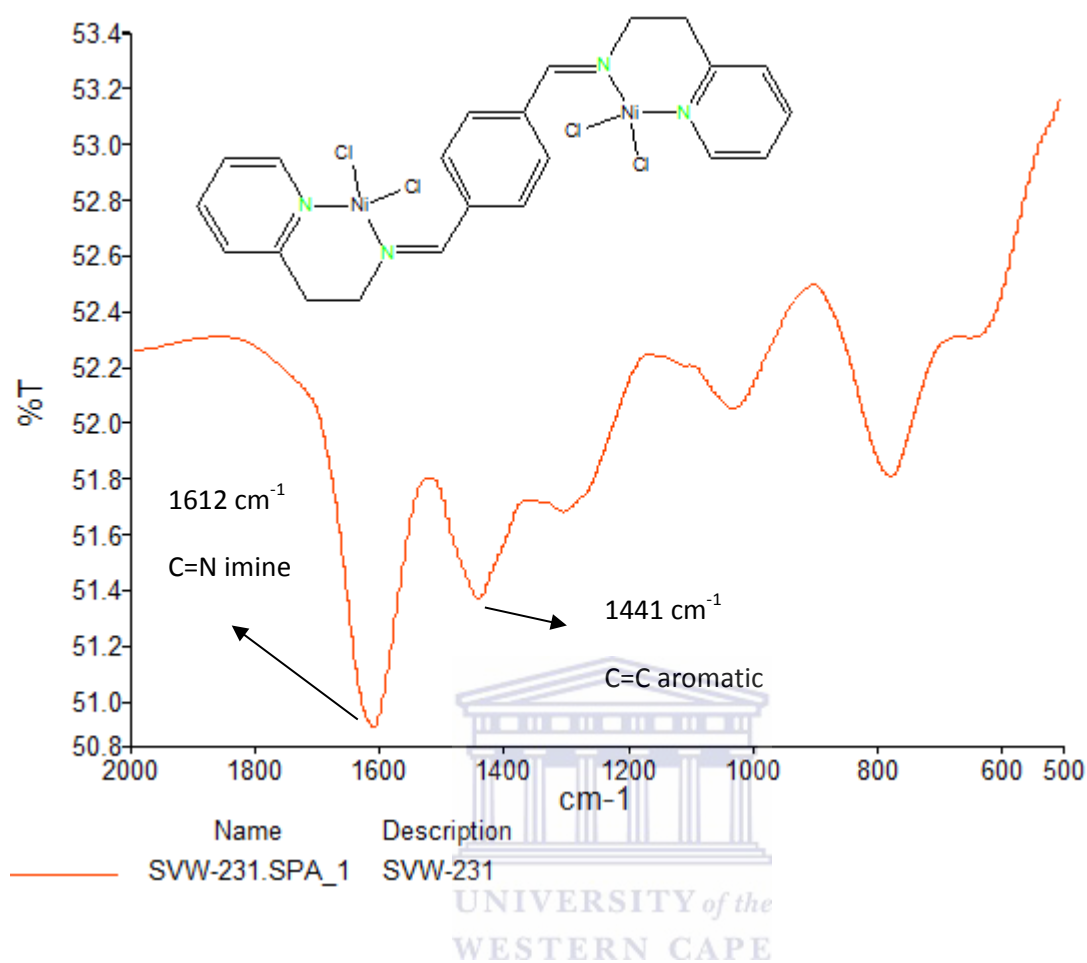


Figure 3.19: FTIR spectrum of complex C4

Table 3.13: Summary of FTIR data of complexes C3-C6

Complex	%Yield	(C=N) cm^{-1} <i>Imine</i>
C3	94	1614
C4	73	1612
C5	66	1618
C6	61	1616

Infra-red spectra of all pyridyl-imine palladium complexes showed a red shift of the $\nu(\text{C}=\text{N})$ band which occurs around $1640 - 1650 \text{ cm}^{-1}$ in the free ligand and upon coordination occurs around 1614 cm^{-1} for **C3** and 1618 cm^{-1} for **C5** which is a shift of 27 cm^{-1} and 23 cm^{-1} respectively. This indicated that nickel(II) chloride coordinated more strongly to **L1** than nickel(II) bromide did. This was not as big a shift compared to the monometallic complexes synthesized by Motswainyana *et al.* where the wavenumber decreased from 1648 cm^{-1} to 1598 cm^{-1} from the ligand to the complex respectively [1]. This indicates that the coordination is not as strong in this work, which is likely due to the absence of a hemi-labile ligand whereas in the work by Motswainyana *et al.* a thiophene was incorporated as the hemi-labile ligand [1]. There was also a blue shift for complexes **C4** and **C6** from 1641 cm^{-1} for the free ligand to 1612 cm^{-1} and 1616 cm^{-1} respectively which once again indicated that nickel(II) chloride coordinated more strongly to **L2** than nickel(II) bromide did. Once again this was not as big a shift compared to the monometallic complexes synthesized by Motswainyana *et al.* where the wavenumber decreased from 1650 cm^{-1} to 1599 cm^{-1} from the ligand to the complex respectively [1]. A similar case could be made for the lack of a hemi-labile ligand [1]. Disappearance of the imino C=N absorption in the IR spectra might be ascribed to an inactive C=N vibration in the Ni (II) complexes as a result of coordination of the ligand to the metal centre as well as a reduction in electron density in the C=N bond arising from electron density flowing from the ligand to the metal centre. This can be corroborated using reports by Pelletier *et al.* and Bahuleyan *et al.* [2, 21].

3.3.2.2 UV-Vis Studies of bimetallic Ni(II) complexes

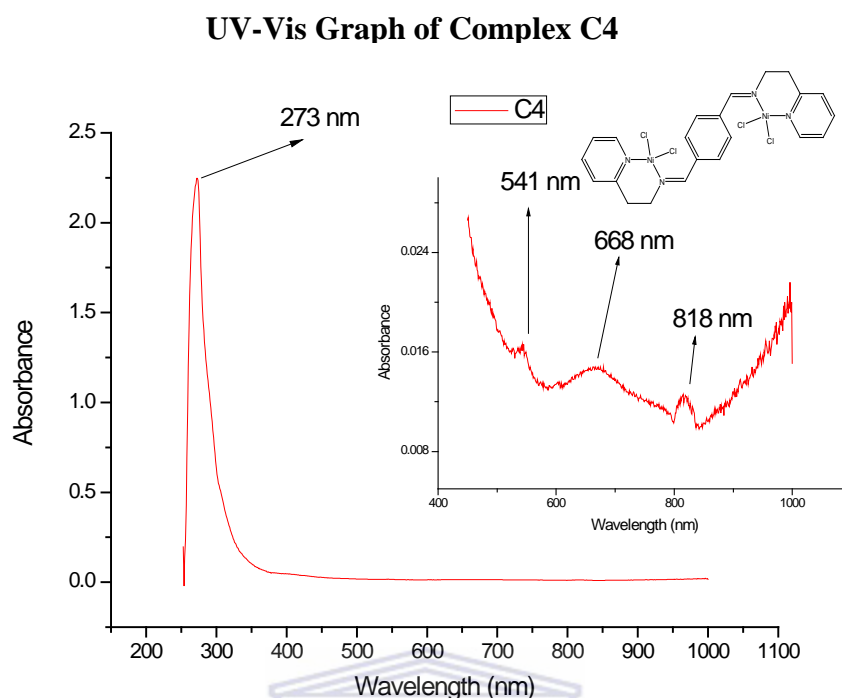


Figure 3.20: UV-Vis Spectrum of tetrachloro-[(2-Pyridin-2-yl-ethyl)-{4-[(2-pyridin-2-yl-ethylimino)-methyl]-benzylidene}-amine]dinickel(II) (**C4**)

Table 3.13: Summary of UV-Vis Data for **C3** and **C4**

Complex	λ_{max1} (nm)	λ_{max2} (nm)
C3	273	625
C4	273	668

The peaks at 273 nm are most likely from the π to π^* transitions while the peaks around 668 nm are likely from metal-to-ligand ((Ni(d π)-L(π^*)) charge transfer transitions which in a report by Mandal *et al.* appears at around 652 nm [23]. This large difference shows how changing the linker between the two C=N by just one carbon can have a significant effect on coordination of nickel chlorides to iminopyridines.

3.3.2.4 Mass spectroscopic analysis of iminopyridyl nickel(II) complexes

Mass spectroscopy was used to characterize the bimetallic iminopyridyl nickel complexes **C3** – **C6**. An example of the mass spectrum (Fig 3.23) and possible fragmentation pattern of **C6** (Scheme 3.6) are showed below. The molecular weight ion peak is observed at $m/z = 782$. The scheme below shows a fragmentation pattern of a charged complex, with first fragmentation of bromide ion coordinated to the nickel metal centre resulting to $m/z = 702$ ion peak, and then followed by the loss of another bromide as well as nickel showing an ion peak attributed at $m/z = 561$. This followed similar fragmentation pattern to a report by Radebe where first the two bromines are fragmented with two losses of $m/z = 80$ followed by the fragmentation of the metal with a loss of $m/z = 80$ eventually resulting in the molecular ion for the original ligand [20]. Further fragmentation resulted in a loss of another bromide with an ion peak at $m/z = 481$. This was followed by the loss of the remaining bromide peak with an ion peak at $m/z = 401$. Further fragmentation resulted in demetallation of the nickel centre attributed by an ion peak at 343 which corresponds to the molecular ion peak of the ligand **L2**.

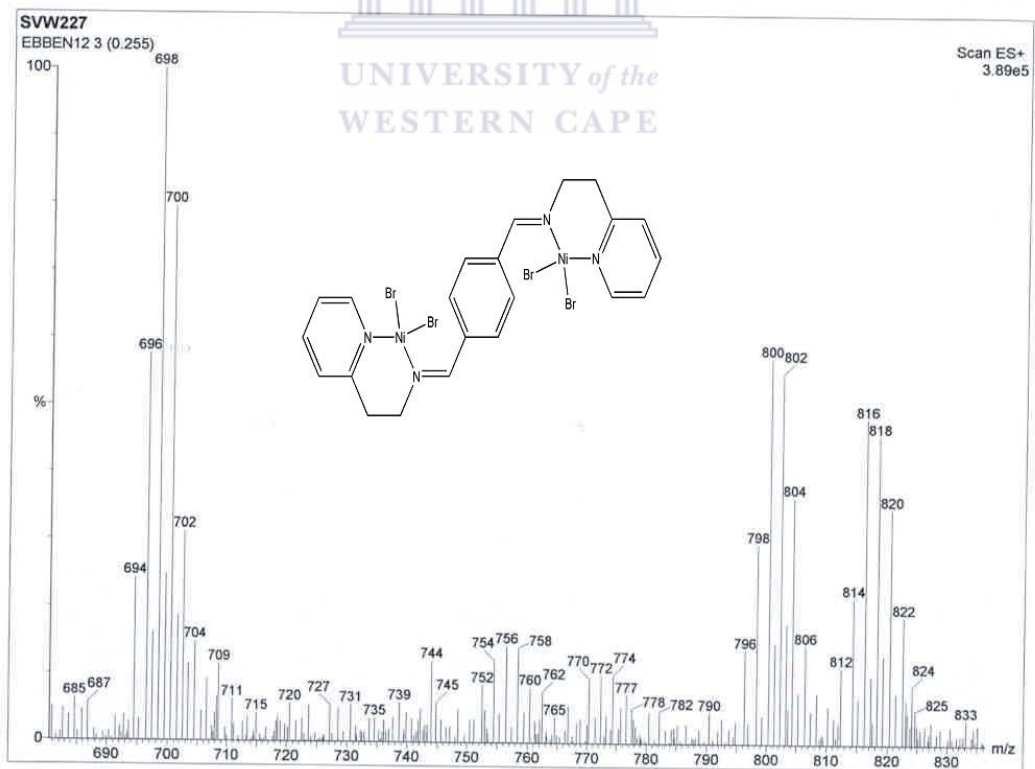
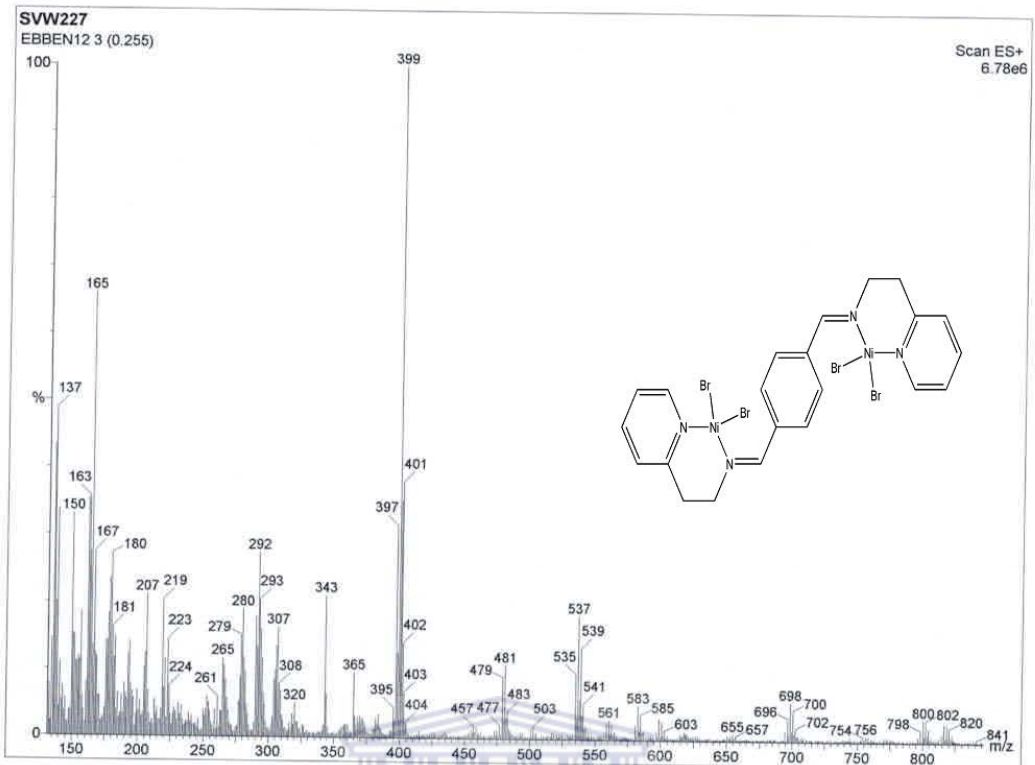
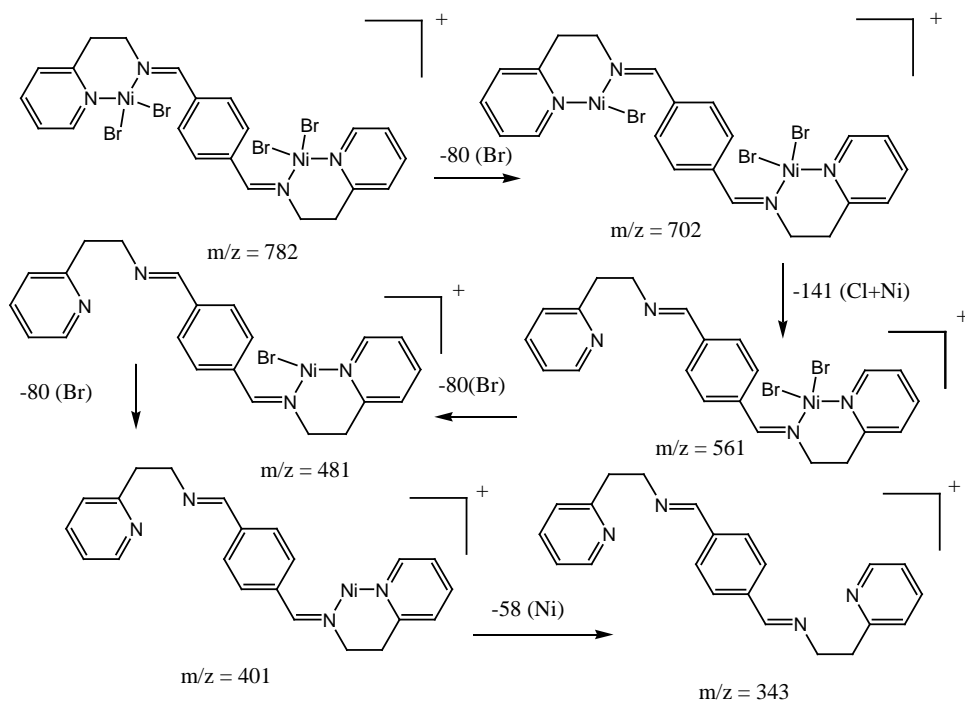


Figure 3.21: ESI-MS Spectra of C6



Scheme 3.6: Possible fragmentation pattern of C6



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Chapter 4

4. Catalytic Application of the Iminopyridyl Complexes

4.1 Ethylene Oligomerization Reactions

4.1.1 Background

Catalysis can be described as an acceleration of a chemical reaction by lowering the activation energy of the process in the presence of a catalyst [1]. Catalysis has in the past few decades played a pivotal role in the industrial production of liquid fuels and fine chemicals. Homogeneous and heterogeneous catalytic processes have been used to form desired petrochemicals and fine chemicals products [1]. Homogeneous catalysis has become increasingly popular recently, this is true especially in certain C-C coupling reactions such as Heck coupling, Suzuki coupling and ethylene oligomerization/polymerization [2-4]. This section will focus on ethylene oligomerization/polymerization reactions. The catalytic reaction for the prepared Ni(II) and Pd(II) iminopyridyl complexes can be best represented by the following scheme (Scheme 1). The end products are known as oligoethylenes (C_4 - C_{20}) and polyethylenes ($C_{>20}$). Polyethylene is the most common plastic known. Many kinds of polyethylene are documented, with most having the chemical formula $(C_2H_4)_n$. The annual global production is 80 million tons [5]. Polyethylene was first synthesized by the German chemist Hans von Pechmann who prepared it by accident in 1898 while investigating diazomethane [6-7].

They are mainly used in packaging. Polyethylenes are placed into many categories based mostly on density and branching but the most important ones are high density polyethylenes (HDPEs) [8a], low density polyethylenes(LDPEs) [8b] and linear low density polyethylenes(LLDPEs) [8c]. Their various uses are illustrated below (Fig 4.1 and Table 4.1).

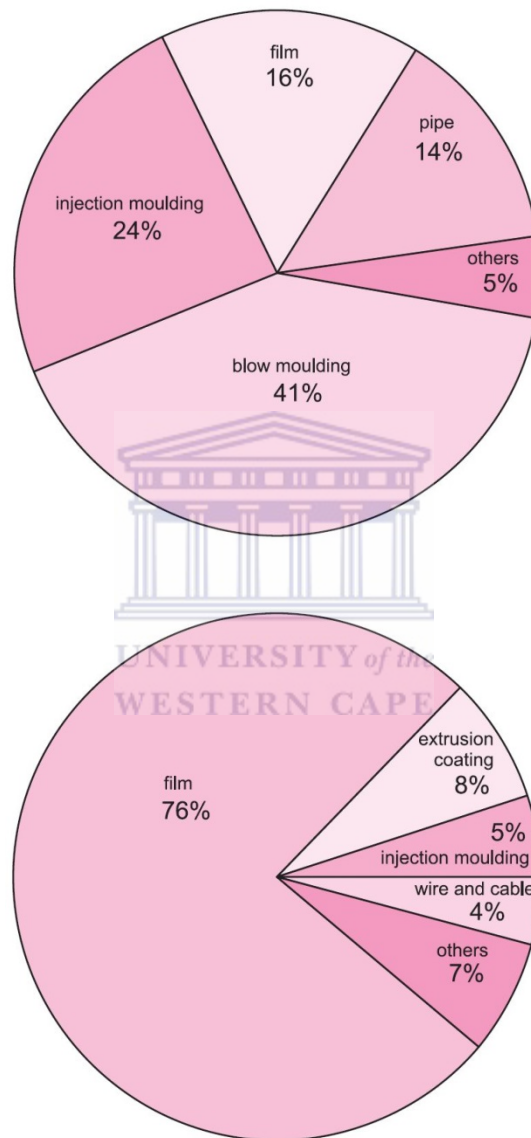


Figure 4.1: % distribution of processes of polyethylene for HDPE and LLDPE/LDPE [9]

EADC resulted in higher activity than MAO. As a result all four precatalysts were tested for catalytic activity of ethylene oligomerization using EADC as the cocatalyst, this is represented in **Fig 4.5**.

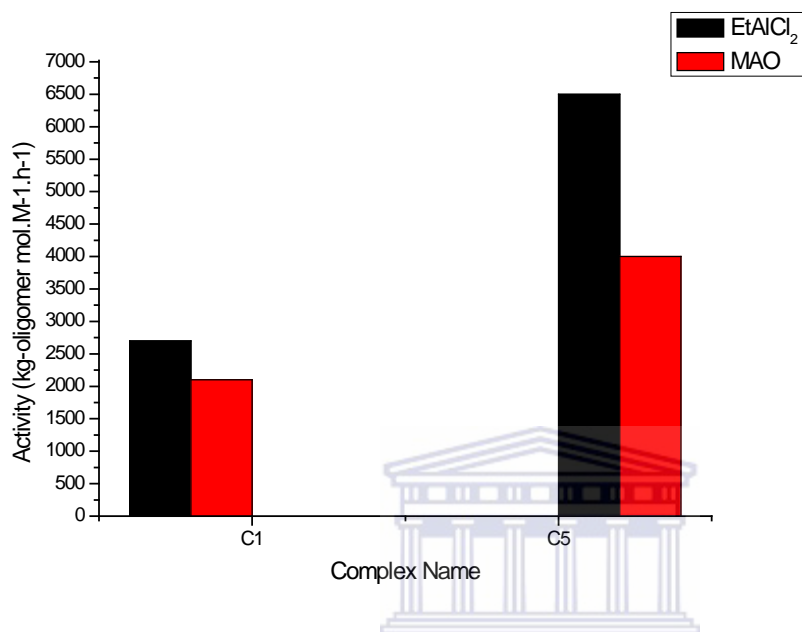


Figure 4.3: Activities of trial reactions involving C1 and C5 where EADC and MAO were used as cocatalysts

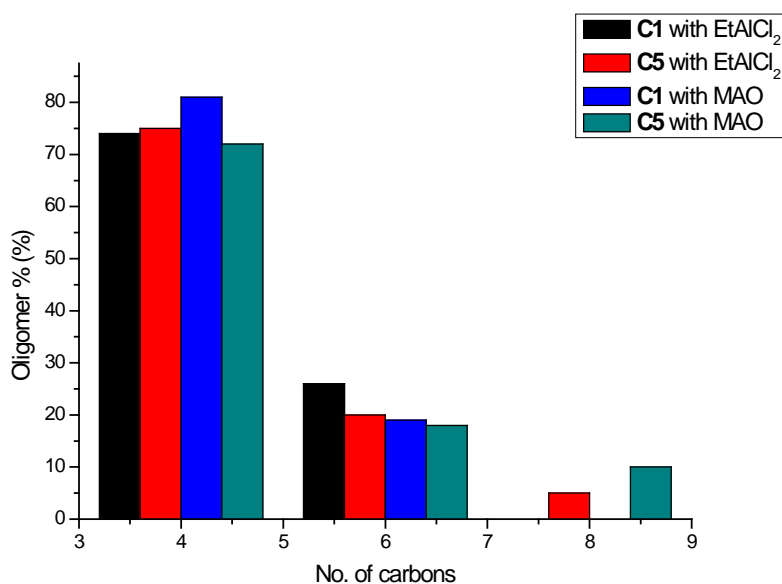


Figure 4.4: Oligomer selectivities of trial reactions involving C1 and C5 where EADC and MAO were used as cocatalysts

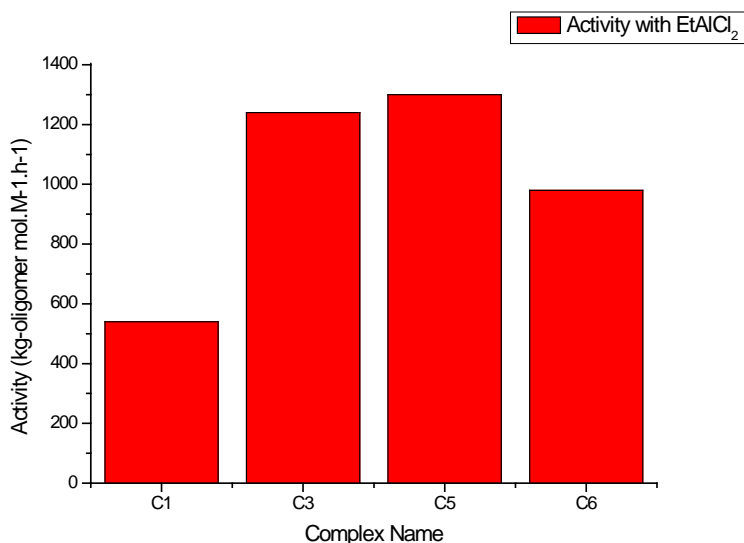
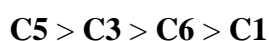


Figure 4.5: Bar graph of oligomerization activity when EADC is used as the cocatalyst

All four complexes were highly active as precatalysts for ethylene oligomerization reactions. The most active of them was **C5** while the least active was **C1**. One of the trends noticed was that the palladium precatalyst **C1** was less active than its nickel analogue **C3**. This is likely attributed to the energy barrier for ethylene insertion being lower for nickel complexes than for their palladium counterparts. Due to ethylene insertion being the turnover limiting step, the activity would thus be lower for palladium precatalysts than for nickel precatalysts. This theory can be corroborated using reports by Ittel *et al.* and Ivanchev [3, 11-14]. In a report involving similar compounds by Irrgang *et al.* the activities for the palladium(II) chlorides were found to range from 12-20 $\text{kgmol}_{\text{cat}}^{-1}\text{h}^{-1}\text{bar}^{-1}$ while their nickel(II) chloride analogues had activities that ranged from 140-156 $\text{kgmol}_{\text{cat}}^{-1}\text{h}^{-1}\text{bar}^{-1}$ [15]. With the nickel dibromide catalyst **C5** only having a slightly higher activity than its nickel chloride counterpart **C3**, this was unexpected since there were many literature reports in which a higher activity was achieved with the nickel chloride analogue [16-17]. An example of this can be found in a report by Nyamoto *et al.* where the nickel(II) chloride precatalyst had an activity of 1072 kg-

oligomer mol.M⁻¹.h⁻¹ while the nickel(II) bromide analogue achieved an activity of 871 kg-oligomer mol.M⁻¹.h⁻¹ [16]. A possible explanation for the higher activity of the nickel(II) bromide can be found in a report by Mungwe [17]. It was pointed out that although chloride is a better leaving group than bromide and thus resulting in faster formation of vacant sites and active complexes, bromine is less electrophilic, which in turn makes it easier to remove leading to more active catalysts in theory [17]. One other trend that was noticed was that **C6** had a much lower activity than **C5** which indicates that the length of the spacer between the imine nitrogen and pyridyl nitrogen does have a significant effect on catalytic activity. When an ethylene spacer was used the activity was lower as opposed to a methylene spacer. This is likely due to the imines of the ligand in **C6** causing the metal centre to be less electrophilic due to itself being less nucleophilic. This notion of lower nucleophilicity is further corroborated using the ¹H NMR spectra for ligands **L1** and **L2** found in the **Appendix** and in the **Chapter 2** respectively. As a result it will not be able to donate electron density to the metal as well as **C5**. In turn the metal in **C6** will not be as strong a back donor to the π-acceptor ethylene group as **C5** [18]. In a report by Bluhm *et al.*, when the chain length was increased by one carbon the activity decreased from a turnover frequency of 9526 h⁻¹ to 43 h⁻¹ [19]. This trend is also observed in this work but the difference in altering the chain length was not nearly as vast. Due to this phenomenon migratory insertion is inhibited and activity is lowered.

The catalytic activity of these precatalysts in ethylene oligomerization reactions can be summarized in the order of increasing magnitude when EADC is used as the cocatalyst:



The oligomer selectivity was then determined using GC-MS (**Fig 4.6**). All precatalysts produced oligomers not longer than C₈ with stronger selectivity for C₄ oligomers. This is likely due to there being no bulky groups *ortho* to the imine nitrogens. This aided chain

termination and thus the lower molecular weight. There was generally a high degree of branching for the C₄ oligomers, but for C₆ oligomers there was a low degree of branching. This was also likely due to the lack of steric bulk *ortho* to the imine nitrogens. The data is summarized in **Table 4.3** and **Fig 4.7**.

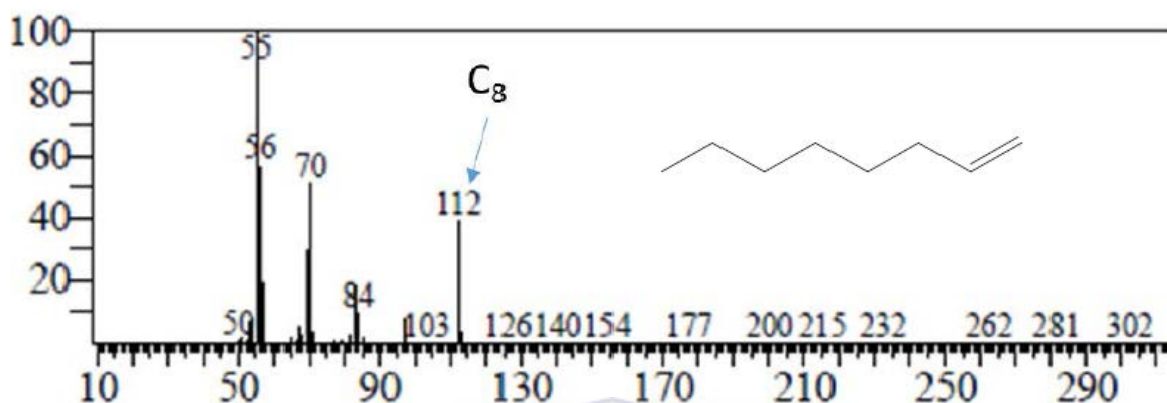


Figure 4.6: GC-MS spectrum of the product formed using catalyst **5** at 30 °C and 20 bar for 1 h confirming the formation of octene.

Table 4.3: Ethylene oligomerization selectivity data for complexes **C1**, **C3**, **C5** and **C6**^a

Entry	Catalyst	Al:M	Pressure (bar)	MW ^b (g.mol ⁻¹)	%Oligomer distribution ^c		
					C ₄ (α -C ₄)	C ₆ (α -C ₆)	C ₈
1	1	200	20	63.4	74(89)	26(92)	-
2	3	200	20	63.1	78(71)	19(23)	3
3	5	200	20	64.5	75(75)	20(26)	5
4	6	200	20	65.1	71(80)	26(21)	3

^a Reaction conditions: 5 μ mol M; solvent, toluene, 80 mL; time, 1 h; temperature, 30 °C. ^b Weighted average.

^c Determined by GC.

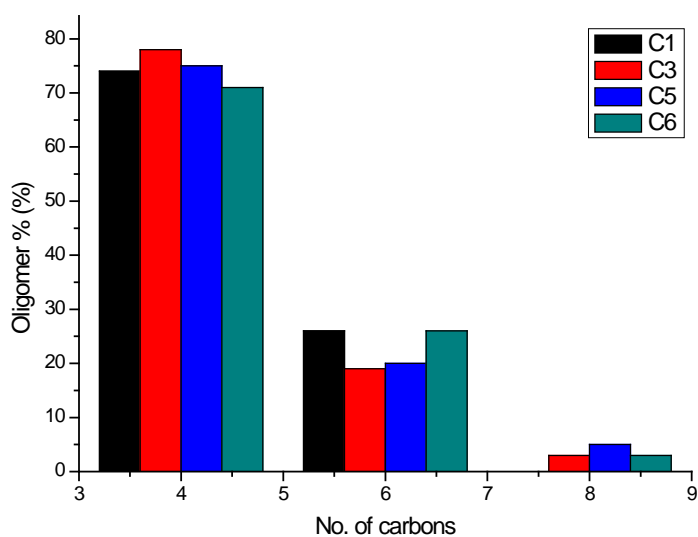


Figure 4.7: Graph of oligomer selectivity for **C1**, **C3**, **C5** and **C6** when EADC is used

When comparing the effects of the metal it was found that **C1** and **C3** have similar molecular weights but **C3** has a higher selectivity for C_8 oligomers than **C1**. In fact **C1** does not produce any C_8 oligomers. There was also a higher degree of branching that resulted from **C1** than **C3**. This was particularly the case for C_6 oligomers. This phenomenon is likely due to the agostic metal alkyl species undergoing numerous β -hydrogen eliminations and additions. This phenomenon is referred to as metal migrating or “chain walking”. This was expected to be the case as can be found in reports by Ittel *et al.* and Ivanchev [3, 11-14]. This is in agreement with a report by Johnson *et al.* where the branching decreased from 116 branches per 1000 carbons to 6 branches per 1000 carbons for the palladium and nickel catalysts respectively [13]. There were no significant differences when the halides were used, only a slight increase in molecular weight and selectivity for C_8 oligomers, as well as slightly more branching when the bromide **C5** was used compared to the chloride **C3**. In precatalysts **C5** and **C6**, it was found that **C6** produced higher molecular weight polymers while **C5** resulted in higher selectivity for C_8 oligomers. The former phenomenon was possibly due to the larger ethylene

spacer in **C6** found *ortho* to the pyridyl nitrogen donor compared to the methyl spacer found in **C5**. This would have led to inhibition of chain termination, hence the lower molecular weight. The latter phenomenon is likely due to the six-membered ring about the metal centre in **C6** being less stable than the five-membered ring found in **C5** due to the chelate effect of five-membered rings containing metals. This could have led to **C6** destabilizing more often before the third oligomerization cycle is reached.

To summarize the average molecular weights of the oligomers produced by these precatalysts are in the following order when EADC is used as the cocatalyst:



Due to **C3** and **C5** being most active precatalysts as well as having similar activities, it was decided to carry out the optimization on **C3** only. The following effects were explored namely: pressure effects and Al:M ratio

Pressure effects

The catalytic activities and oligomer selectivities of **C3** were studied by varying the pressure to 10, 20 and 30 bar using EADC as the cocatalyst. The data is summarized in **Table 4.4**

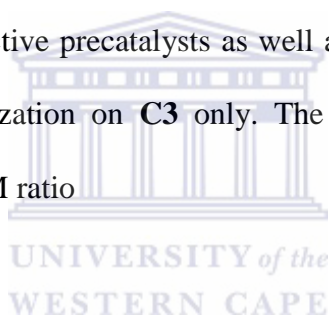
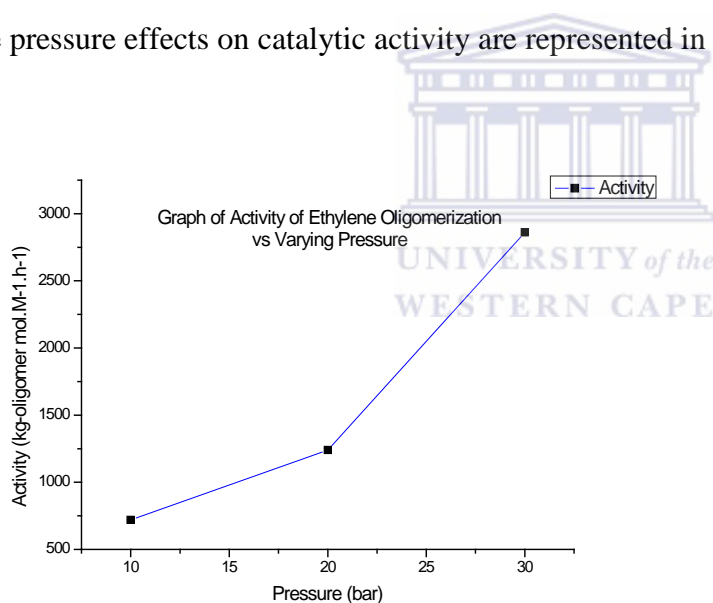


Table 4.4: Activity and oligomer selectivities for at various pressures^a

Entry	Catalyst	Al:M	Pressure (bar)	Yield (g)	Activity ^b	%Oligomer distribution ^c		
						C ₄ (α -C ₄)	C ₆ (α -C ₆)	C ₈
1	3	200	10	3.6	720	70(76)	26(26)	4
2	3	200	20	6.2	1 240	78(71)	19(23)	3
3	3	200	30	14.3	2 860	81(72)	17(23)	2

^a Reaction conditions: 5 $\mu\text{mol M}$; solvent, toluene, 80 mL; time, 1 h; temperature, 30 °C. ^b kg-oligomer mol.M⁻¹.h⁻¹. ^c Determined by GC.

The pressure effects on catalytic activity are represented in **Fig 4.8**

**Figure 4.8** Catalytic activity of C3 at various pressures

It was found that the activity increased as the pressure increased, especially when the pressure was increased from 20 to 30 bar where the activity more than doubled. This is likely due to the higher pressure aiding ethylene trapping. This in turn aids chain propagation [12]. This is in agreement with experiments carried by Nyamoto *et al.* where the activities were 473 kg-oligomer mol.M⁻¹.h⁻¹, 1072 kg-oligomer mol.M⁻¹.h⁻¹, 1743 kg-oligomer mol.M⁻¹.h⁻¹

and 2462 kg-oligomer mol.M⁻¹.h⁻¹ when the pressures were 5 bar, 10 bar, 20 bar and 30 bar respectively [16]. From 5-20 bar the activities from Nyamoto *et al.* were higher than the values achieved in this work but at 30 bar the activities in this work were higher [16].

The effects on the activity on **C3** can be summarized in the following way:

$$30 \text{ bar} > 20 \text{ bar} > 10 \text{ bar}$$

The pressure effects on oligomer selectivity are represented in **Fig 4.9**

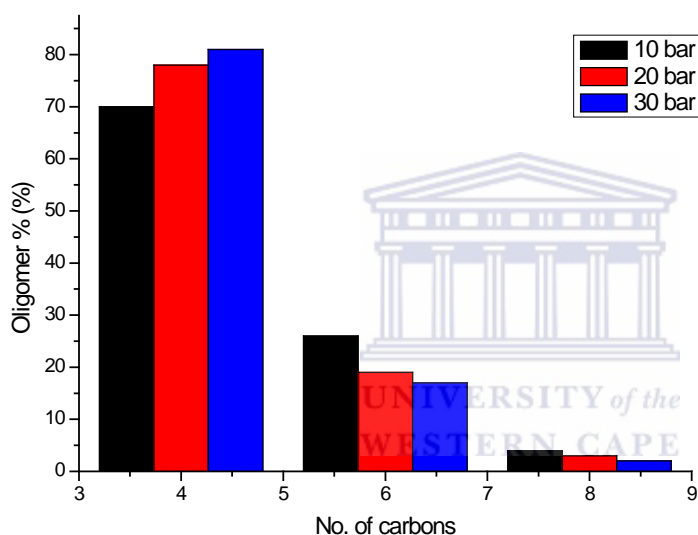


Figure 4.9: Oligomer selectivities resulting from **C3** at various pressures

It was found that the highest molecular weight and selectivity for C₈ oligomers was achieved at 10 bar (65.65 g.mol⁻¹ and 4% respectively). The selectivity towards C₄ increased as pressure increased. In fact as the pressure increased, the molecular weight, C₈ oligomer selectivity and branching decreased. This is likely due to the increased pressure aiding trapping of ethylene while overcoming chain transfer. The results and this notion are in agreement with a report by Johnson *et al.* where the branching when α -diimine nickel

complexes decreased from 24 branches per 1000 carbons to 5 branches per 1000 carbons when the pressure was increased from 1 atm to 4 atm [13].

To summarize the average molecular weights of the oligomers produced by **C3** are in the following order:

$$10 \text{ bar} > 20 \text{ bar} > 30 \text{ bar}$$

Effects of Al:Ni ratio

Table 4.5: Activity and oligomer selectivities for **C3** at various Al:Ni ratios^a

Entry	Catalyst	Al:Ni	Pressure (bar)	Yield (g)	Activity ^b	%Oligomer distribution ^c		
						C ₄ (α -C ₄)	C ₆ (α -C ₆)	C ₈
1	3	100	20	2.1	420	80(89)	16(26)	4
2	3	200	20	6.2	1 240	78(71)	19(23)	3
3	3	250	20	6.8	1 360	77(72)	19(20)	4

^a Reaction conditions: 5 $\mu\text{mol M}$; solvent, toluene, 80 mL; time, 1 h; temperature, 30 °C. ^b kg-oligomer mol.M⁻¹.h⁻¹. ^c Determined by GC.

The effects on catalytic activity are represented by **Fig 4.10**

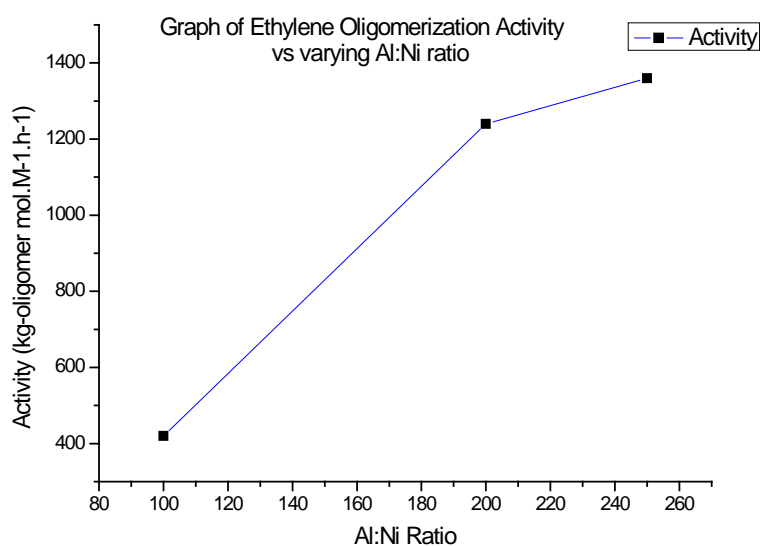


Figure 4.10: Catalytic activity of **C3** at various Al:Ni ratios

When the Al:Ni was increased from 100 to 200 the activity nearly tripled from 420 kg-oligomer mol.M⁻¹.h⁻¹ to 1240 kg-oligomer mol.M⁻¹.h⁻¹ while it plateaued from 1240 kg-oligomer mol.M⁻¹.h⁻¹ to 1360 kg-oligomer mol.M⁻¹.h⁻¹. From this it can be determined that 250 is the ideal Al:Ni ratio for ethylene oligomerization.

The activity effects on **C3** can be summarized in the following way in terms of Al:Ni ratios:

$$100 \ll 200 < 250$$

The effects on oligomer selectivity are represented by **Fig 4.11**

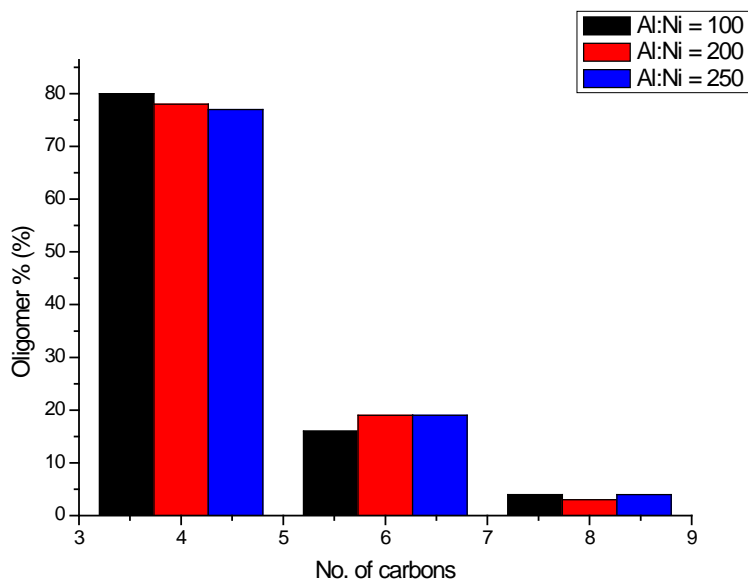


Figure 4.11: Oligomer selectivities resulting from **C3** at various Al:Ni ratios

While studying these effects there was no significant change in the molecular weight when the Al:Ni ratio was varied. Selectivity for C₈ oligomers as well as branching decreased as the Al:Ni ratio increased. The only significant change was that there was less branching as the Al:Ni ratio was increased. This indicates that increasing the Al:Ni ratio somehow inhibited chain transfer [20]. When comparing this to a report by Wang *et al.* where the Al:Ni ratios were 200, 400, 600, 800 and 1000 the selectivity towards C₄ increased (79.1%, 84.4%, 87.0, 88.4% and 89.0%) while in this work selectivity for C₄ decreased when the Al:Ni increased from 100 to 250 [20]. This decrease was possibly due to an excessive amount of cocatalyst interfering with formation of the active metal species and/or caused their over-reduction which caused the lower selectivity [20].

4.3 References

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Chapter 5

5. Conclusion and recommendations

5.1 Conclusion

The study involved synthesis of new iminopyridyl palladium (II) and nickel (II) complexes which could act as catalysts for Heck coupling reactions. Tetrahydrophenyl-linked iminopyridyl ligands **L1** – **L2** were successfully synthesized and obtained as a white and yellow solid respectively in good yields from 69-87%. They were observed to be air and moisture stable, but light sensitive. Alkyl-linked iminopyridyl ligands **L3** – **L5** were successfully synthesized with two of them obtained as red oils and one of them as an orange solid in low to moderate yields from 25-50%. These compounds were fully characterized by FTIR, ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, mass spectroscopy, and elemental analysis.

The formation of the ligands **L1** – **L5** was confirmed by the presence of an imine absorption band around $1641 - 1655 \text{ cm}^{-1}$ in the IR spectra. ^1H NMR further confirmed the formation of the imine moiety (**HC=N**) by observing proton signals at around 8.20 to 8.55 ppm (singlet) and around 8.40 to 8.63 ppm (doublet) attributed to pyridyl ring imine proton. The ^{13}C NMR spectra showed imine carbons downfield chemical shifts around 160.00 – 165.00 ppm and mass spectra of the synthesized compounds were in good agreement with the calculated molecular weight m/z values.

The ligands were reacted with two molar equivalents of $\text{PdCl}_2(\text{COD})$, $\text{NiCl}_2(\text{DME})$, and $\text{NiBr}_2(\text{DME})$ to give palladium (II) and nickel complexes **C1** – **C6** in moderate to high yields of 58-93%. All the complexes were observed to be stable both as solid and in liquid. The iminopyridyl complexes were characterized by FTIR, ^1H NMR spectroscopy, ^{13}C NMR

spectroscopy, thermogravimetric analysis, mass spectroscopy and elemental analysis. Coordination of the ligands to the metal centre was confirmed by red shift of the imine absorption band to around 1612 – 1619 cm^{-1} respectively. The proton NMR analysis of complex **C1** – **C2** showed a proton signal in the region of 8.74 – 8.91 ppm as a singlet peak which provided evidence of coordination of ligand to the metal.

Iminopyridyl nickel (II) complex **C3** – **C6** could not be analyzed using NMR spectroscopy suggesting that they were paramagnetic. Mass spectroscopic analyses were in good agreement with the calculated molecular weight of all analyzed the iminopyridyl complexes.

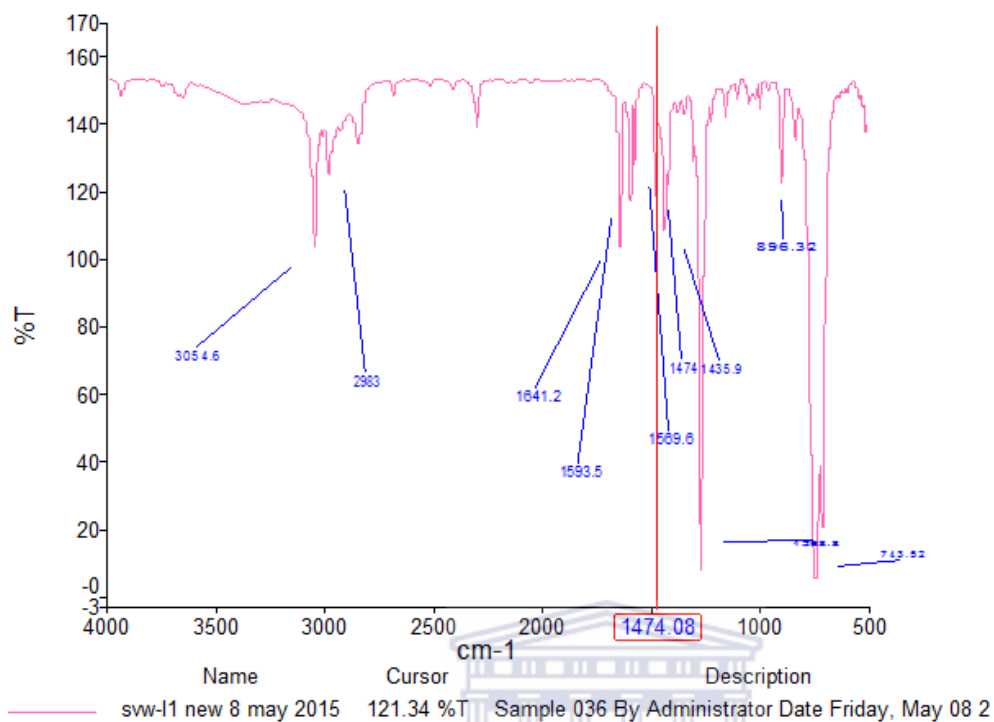
All four complexes were highly active as catalysts for ethylene oligomerization. They were most active when EADC was used as the cocatalyst compared to MAO. **C5** was the most active (1300 kg-oligomer $\text{mol.M}^{-1}.\text{h}^{-1}$), followed by **C3** (1240 kg-oligomer $\text{mol.M}^{-1}.\text{h}^{-1}$), **C6** (980 kg-oligomer $\text{mol.M}^{-1}.\text{h}^{-1}$) and lastly the palladium complex **C1** (540 kg-oligomer $\text{mol.M}^{-1}.\text{h}^{-1}$). All four complexes had good selectivity for C_4 oligomers with all the nickel precatalysts producing a small amount of C_8 oligomers while the palladium precatalyst only produced C_4 and C_8 oligomers. The palladium precatalyst **C1** produced highly branched oligomers while the nickel precatalysts, **C1**, **C3** and **C5** produced oligomers with significantly less branching. The pressure and Al:Ni optimization studies were carried out using **C3** as the precatalyst. When the pressure was increased the activity increased (maximum 2860 kg-oligomer $\text{mol.M}^{-1}.\text{h}^{-1}$) and branching decreased with the optimum pressure being 30 bar. When the Al:Ni was varied it was found that increasing the ratio to 250 led to the highest activity (1360 kg-oligomer $\text{mol.M}^{-1}.\text{h}^{-1}$) with slightly decreased branching.

5.2 Recommendations

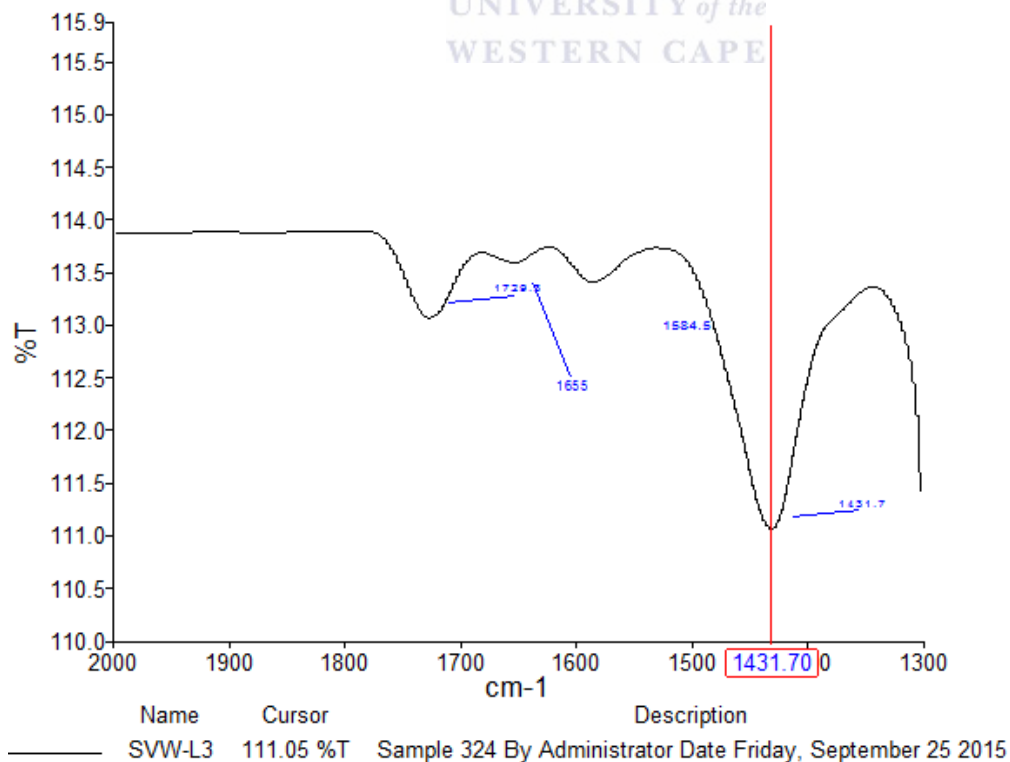
Palladium (II) and nickel (II) iminopyridyl complexes were synthesized and characterized by various analytical and spectroscopic techniques. Some of the complexes were tested for ethylene oligomerization reactions, and showed high activity to become ethylene oligomerization reaction catalysts. However, we recommend the following future work on this project:

1. Test the remaining two bimetallic iminopyridyl complexes as well as the monometallic analogues of **C1-C6** for ethylene oligomerization to study the cooperative effect
2. Synthesize bimetallic nickel and palladium complexes from alkyl linked iminopyridyl ligands **L3-L5**
3. Single X-ray diffraction studies should be done on the nickel and palladium complexes to confirm the coordination mode of the ligands to the metal to support the spectroscopic analysis results
4. Investigate the catalytic activity of heterobimetallic nickel(II) and palladium(II) complexes for ethylene oligomerization/polymerization
5. The complexes should also be investigated for Heck coupling

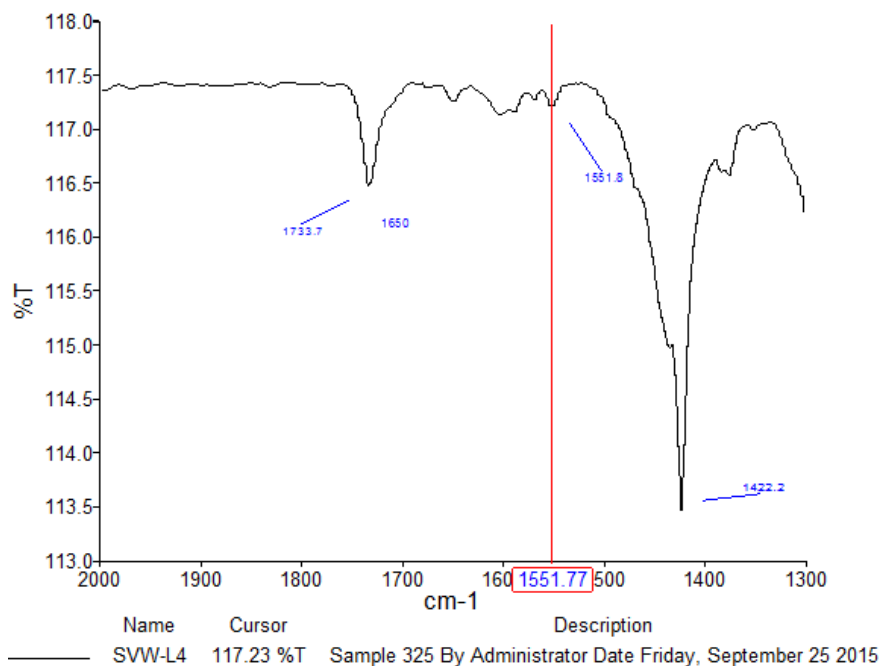
Appendix



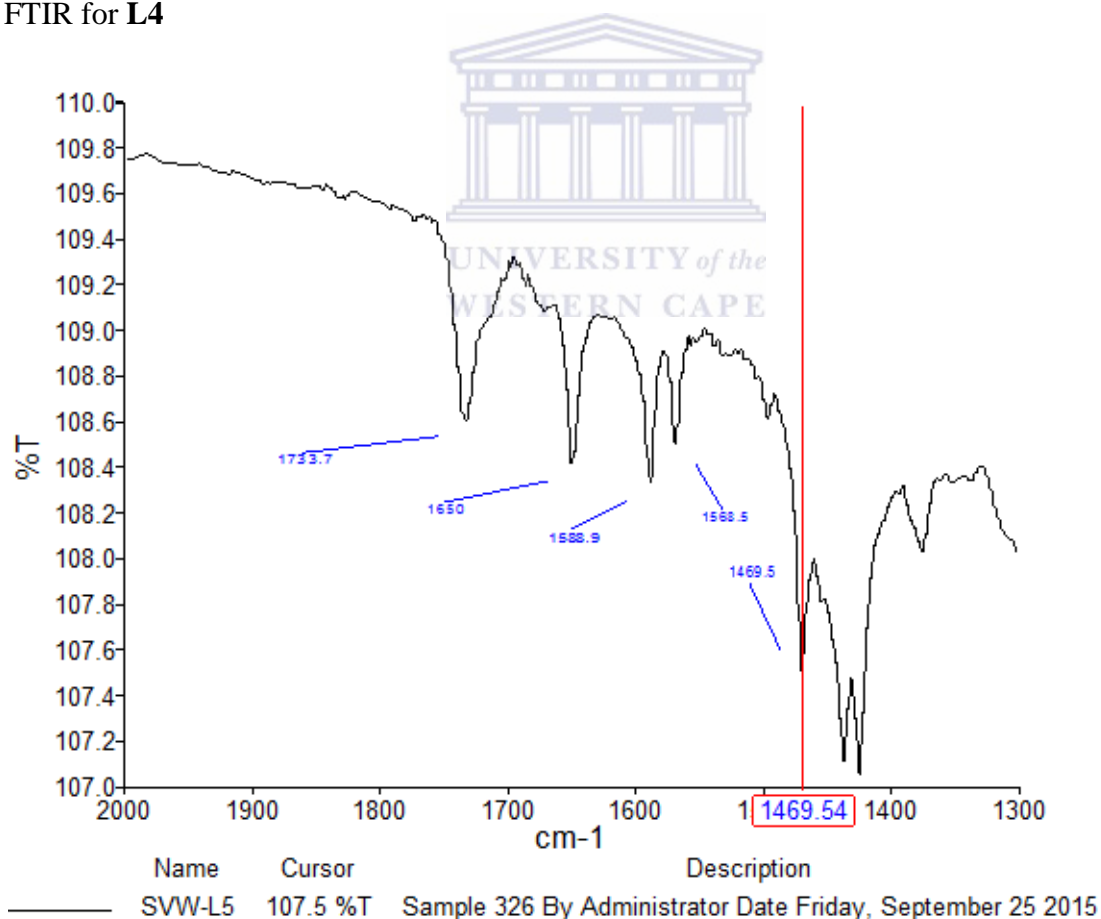
FTIR for L1



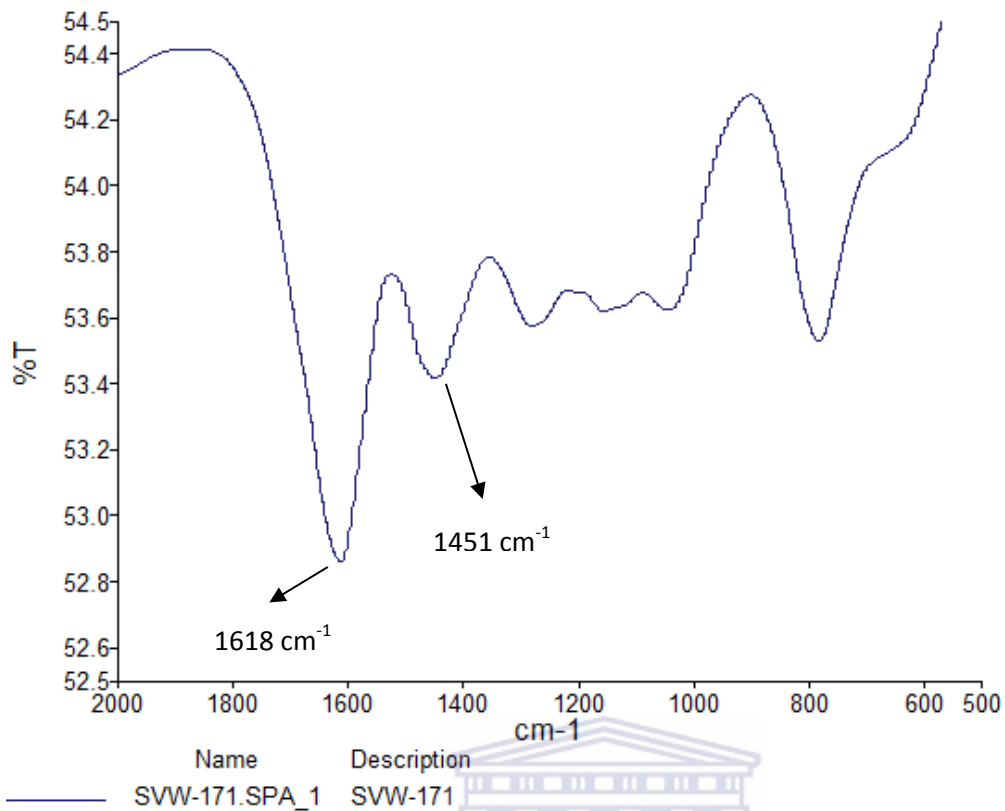
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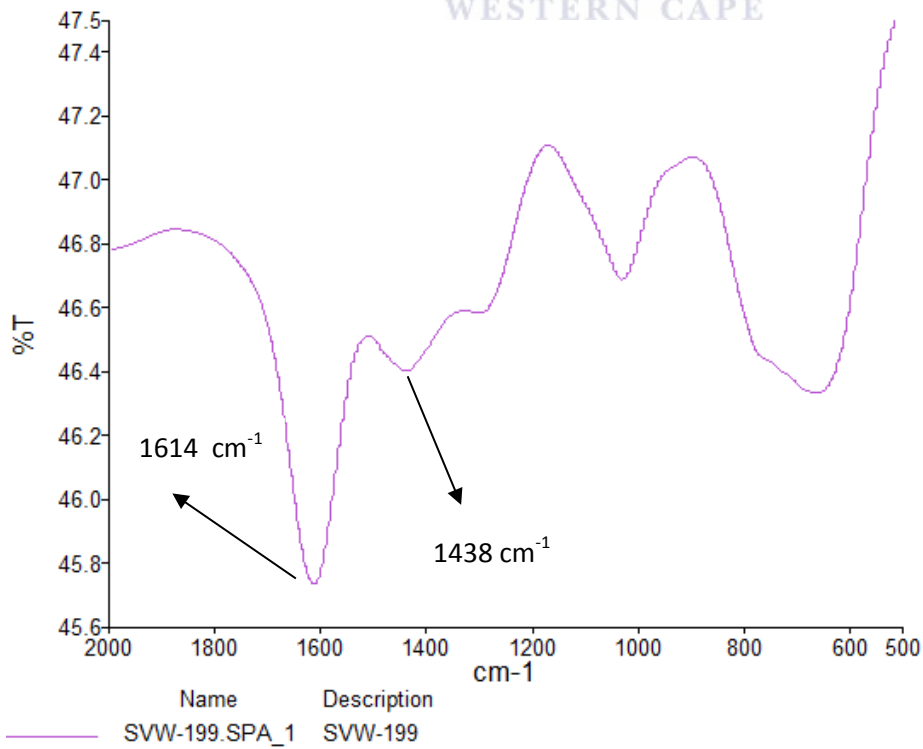
FTIR for L4



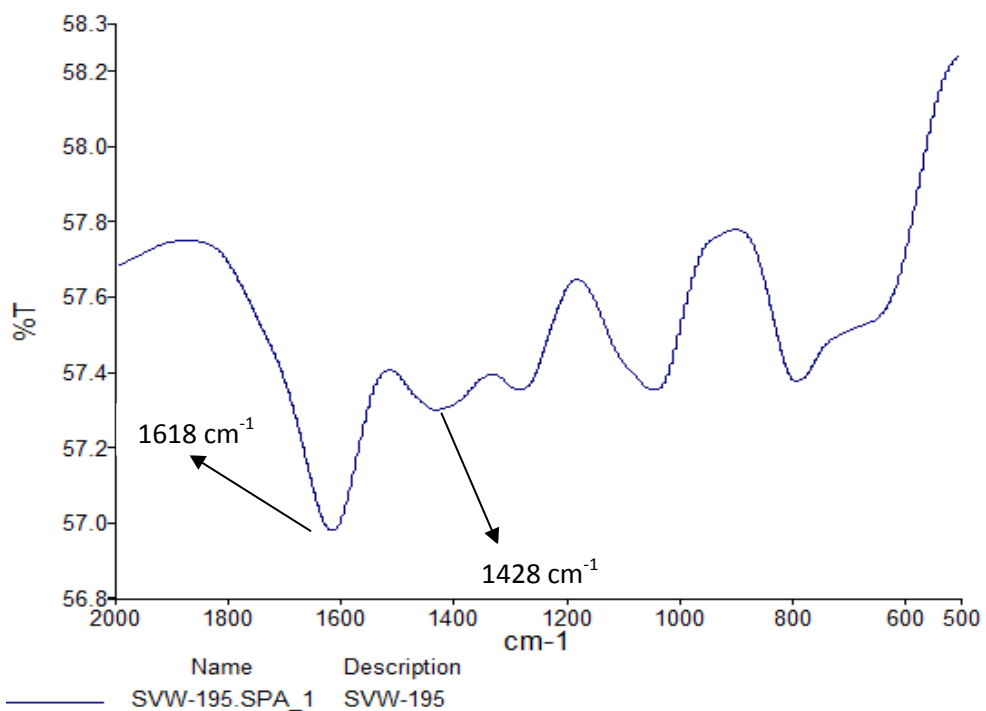
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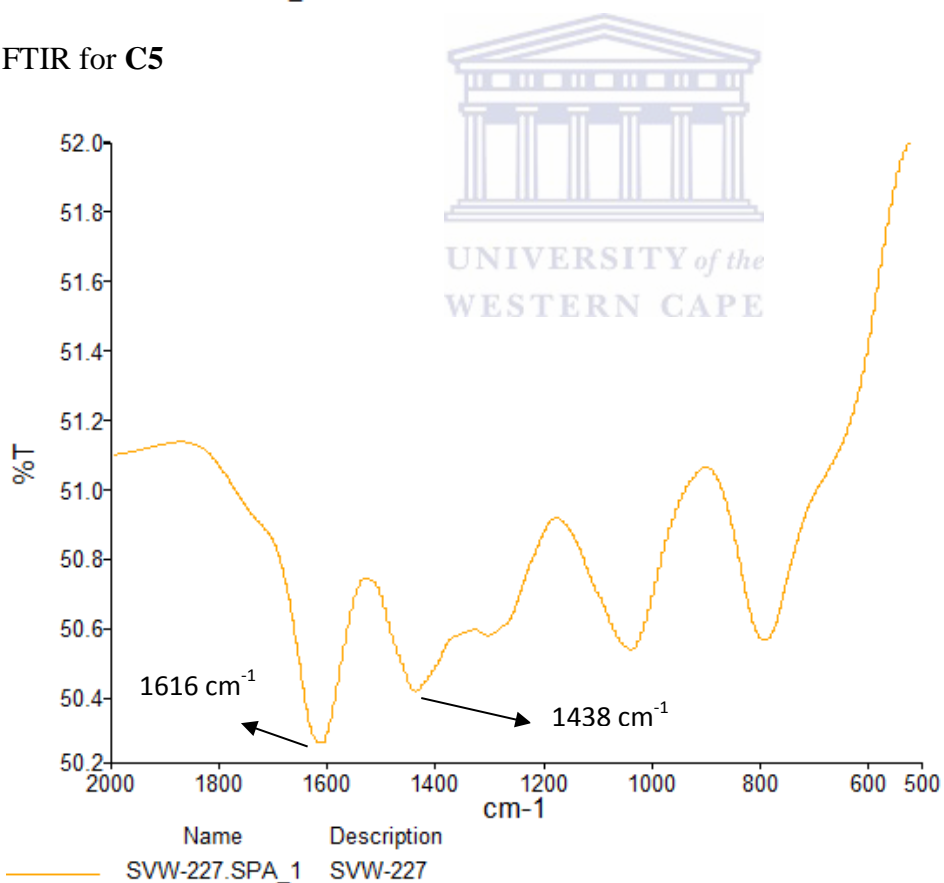
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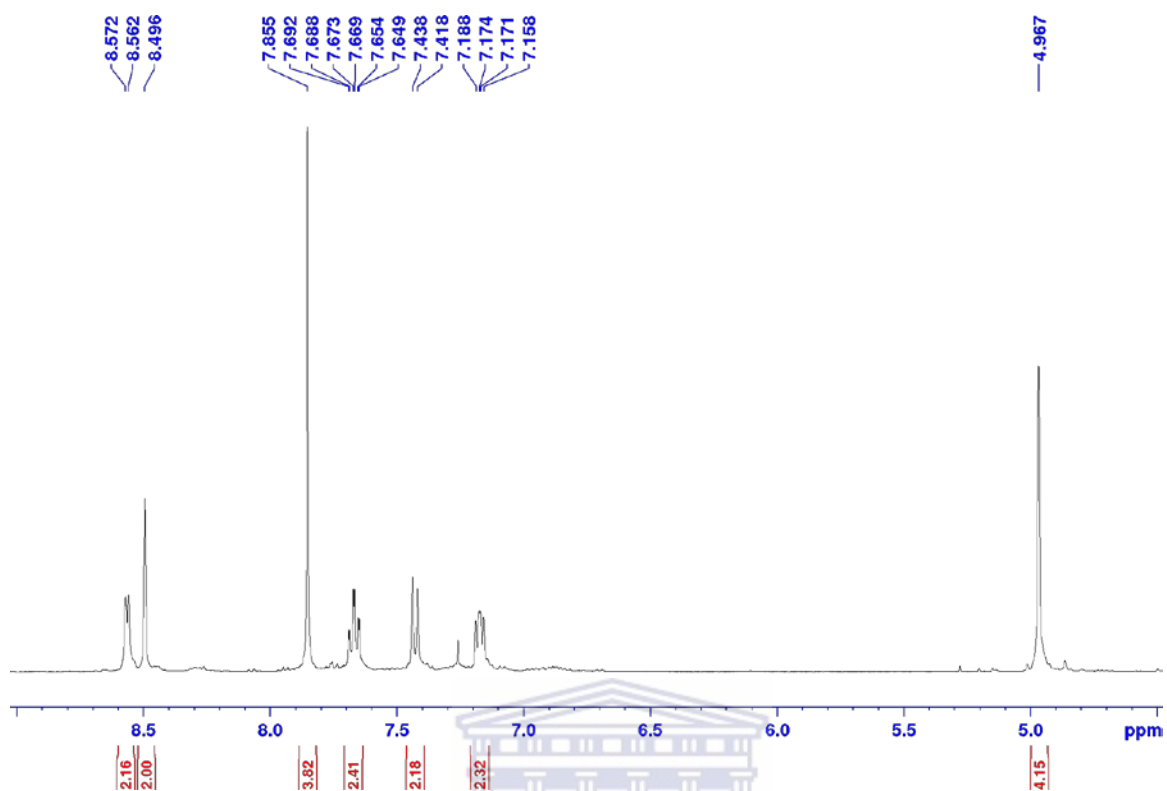
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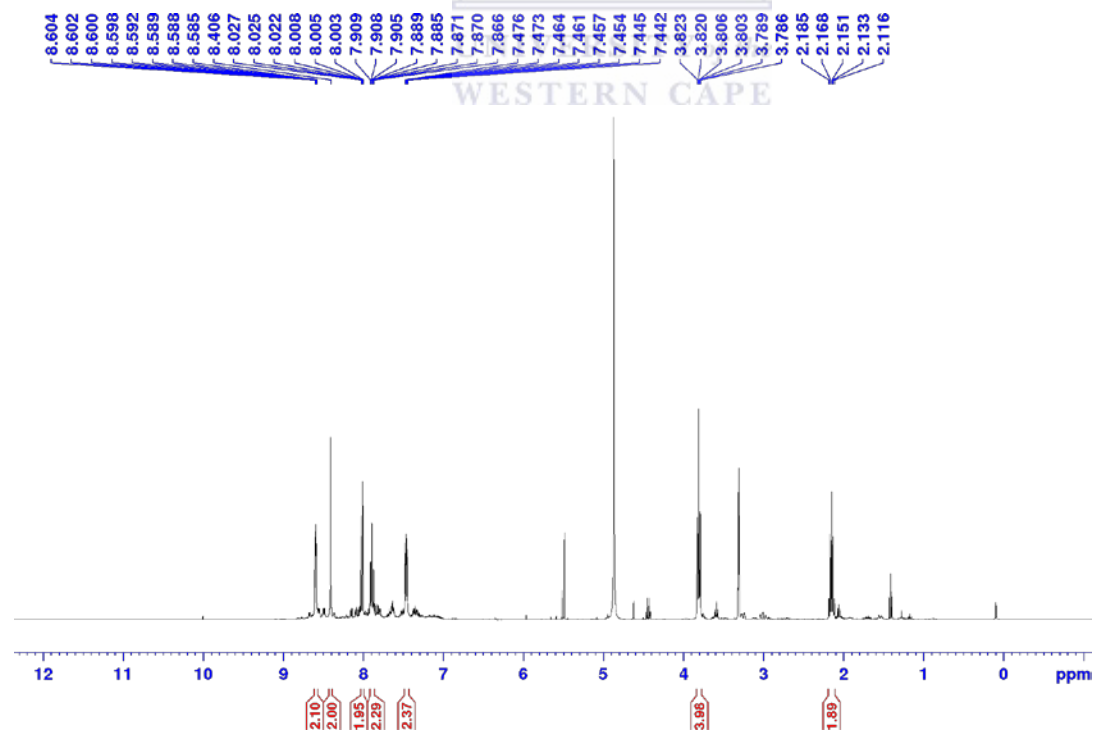
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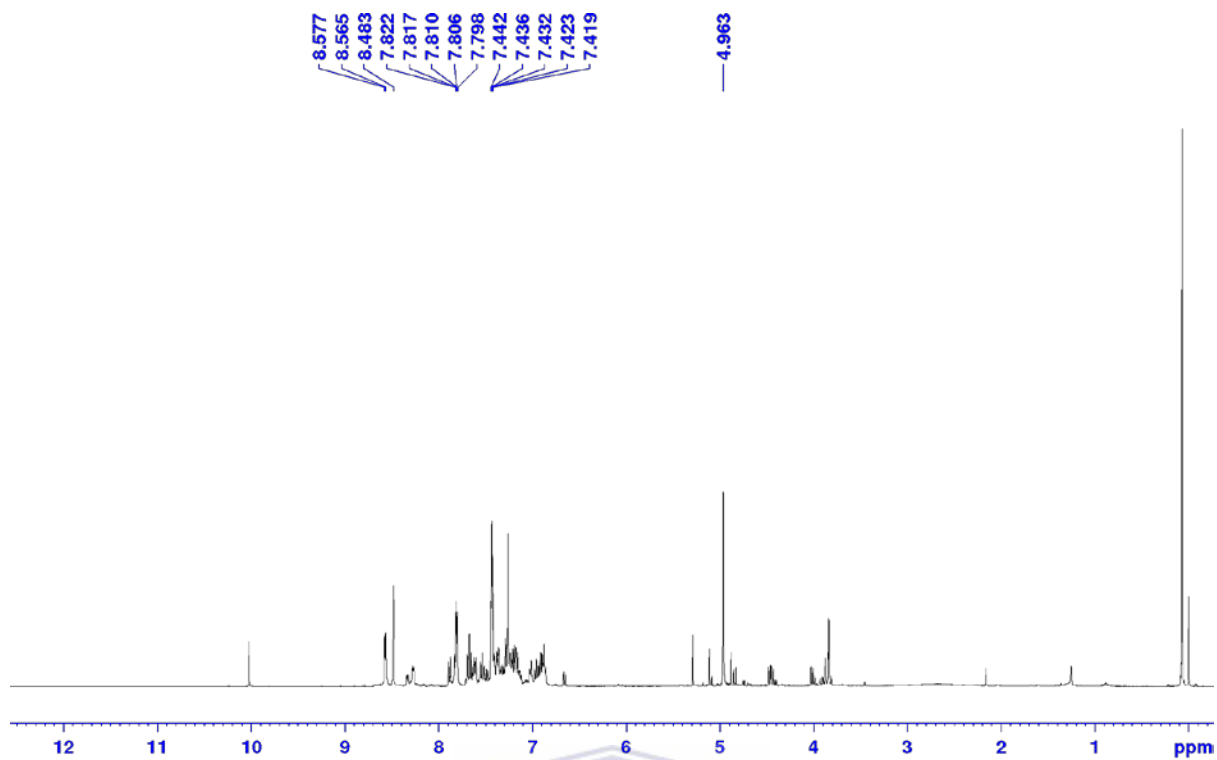
FTIR for C6



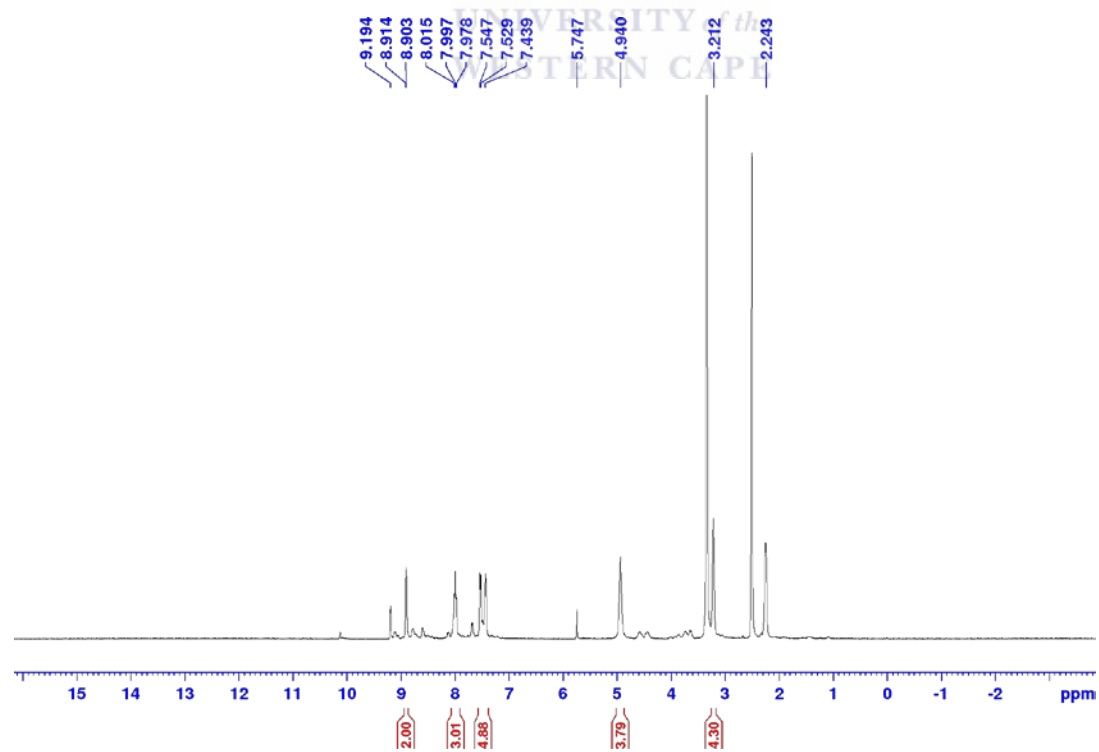
¹H NMR for L1



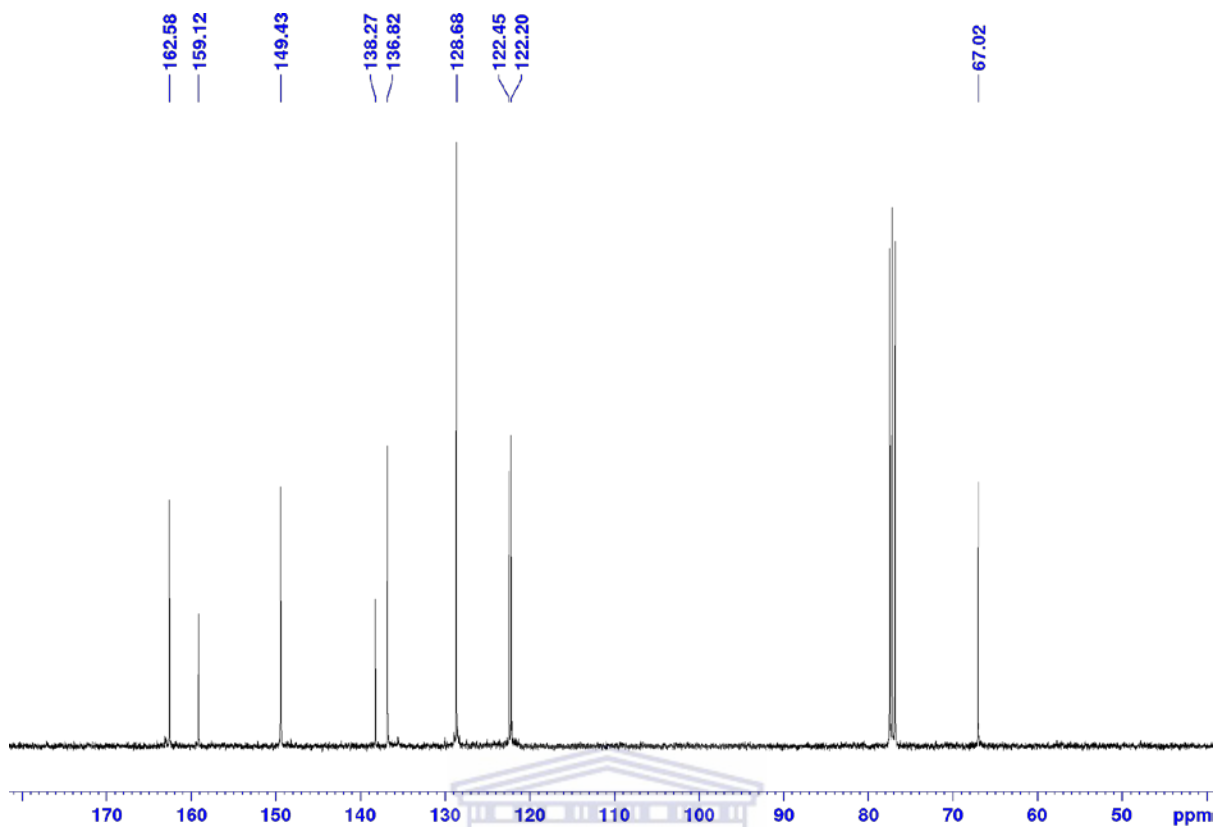
¹H NMR for L3



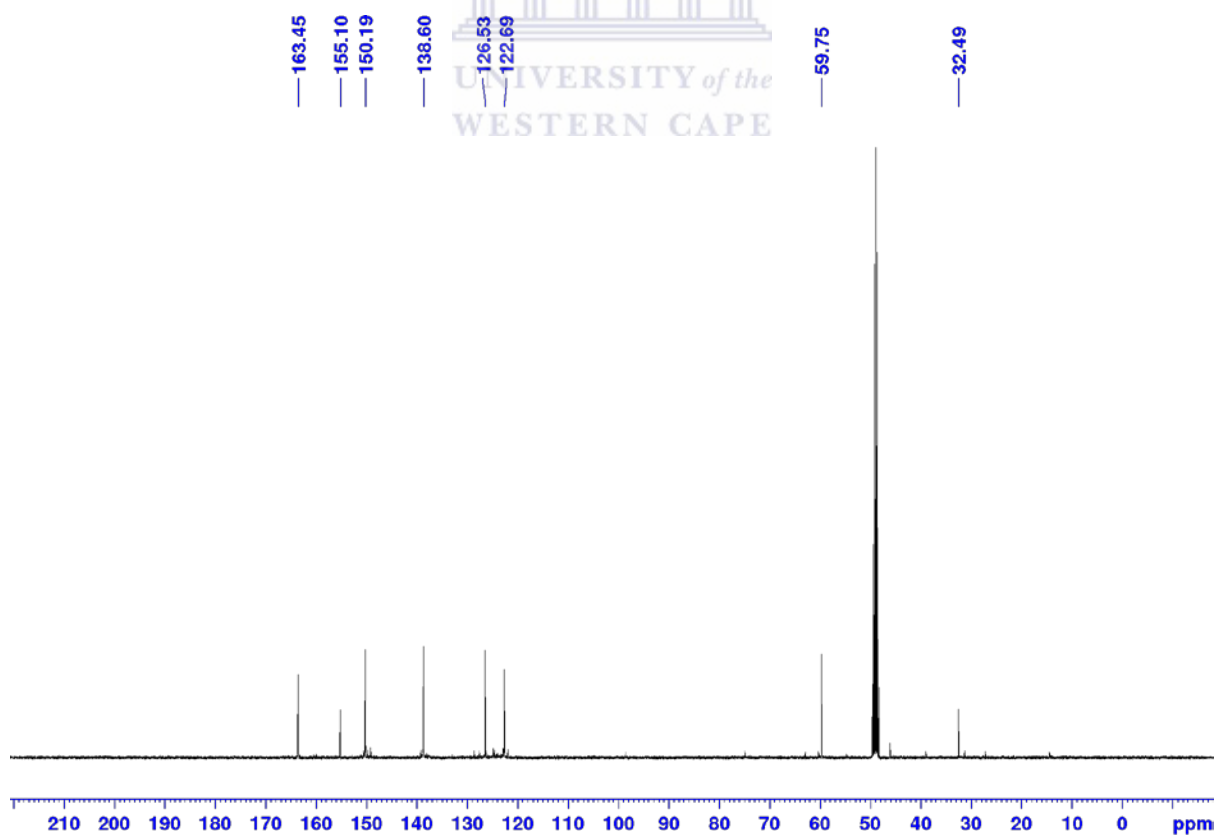
^1H NMR for L5



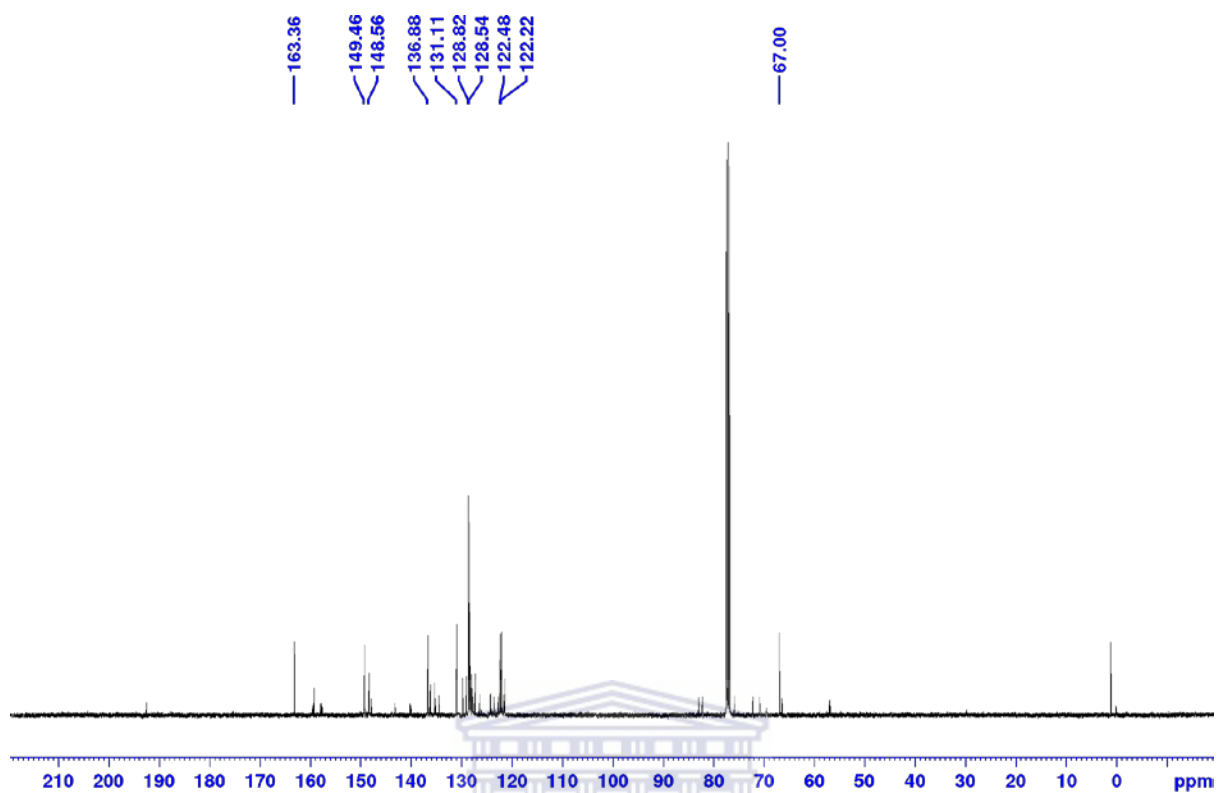
^1H NMR for C2



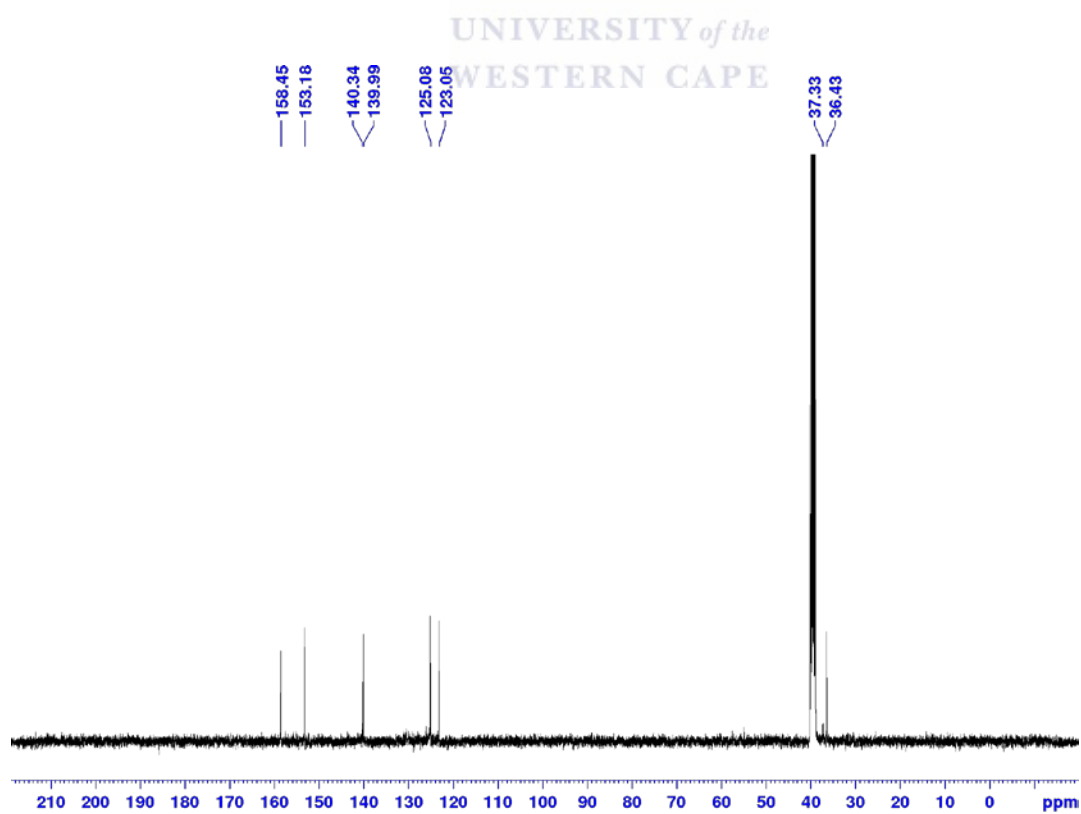
¹³C NMR for L1



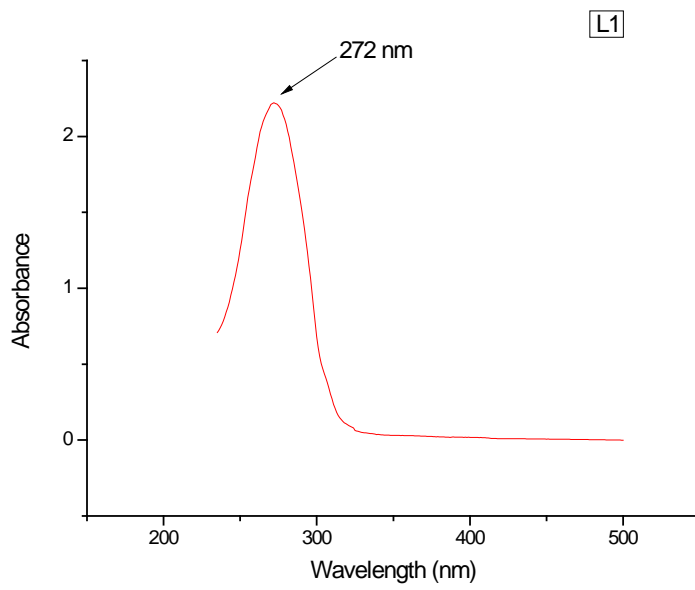
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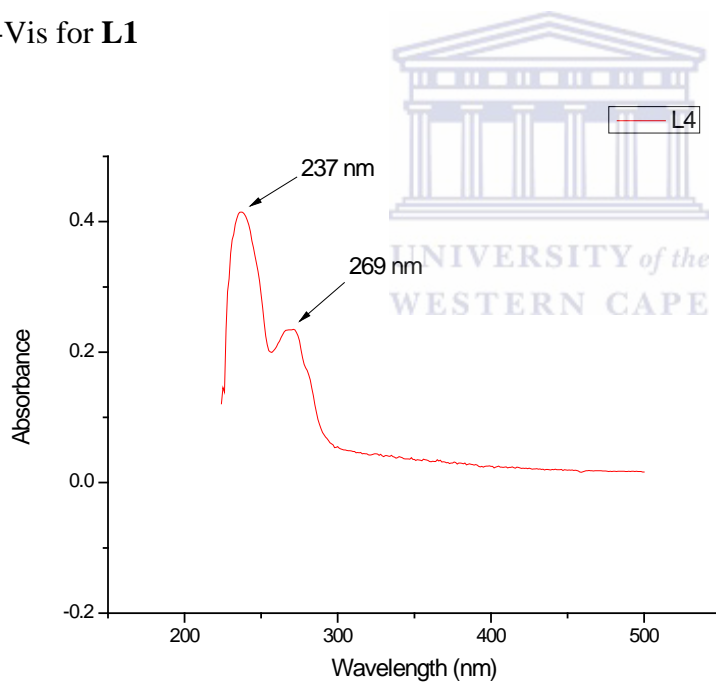
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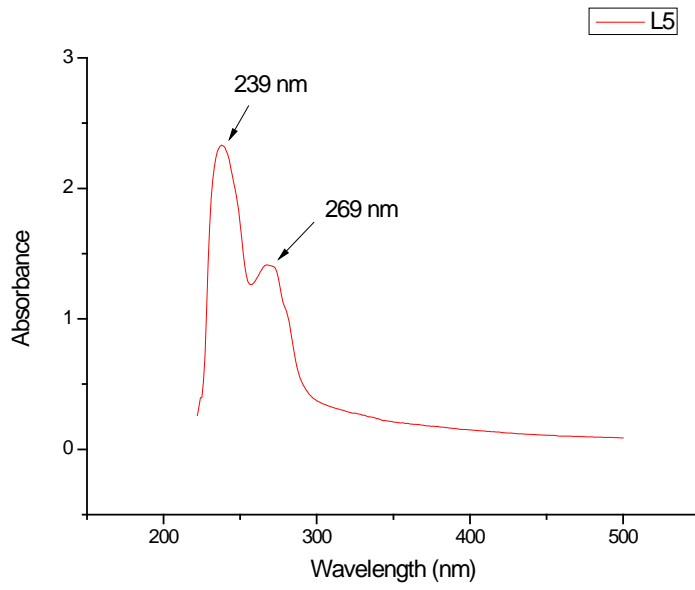
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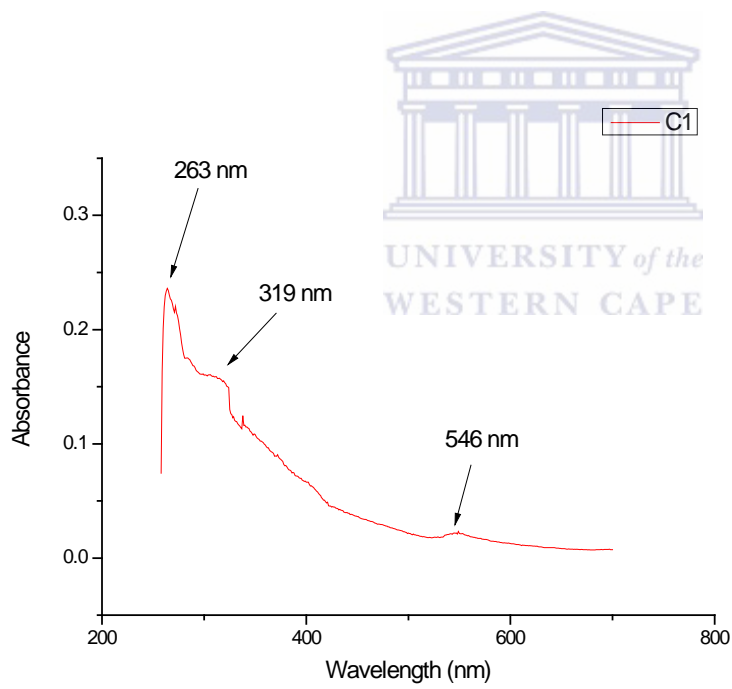
UV-Vis for L1



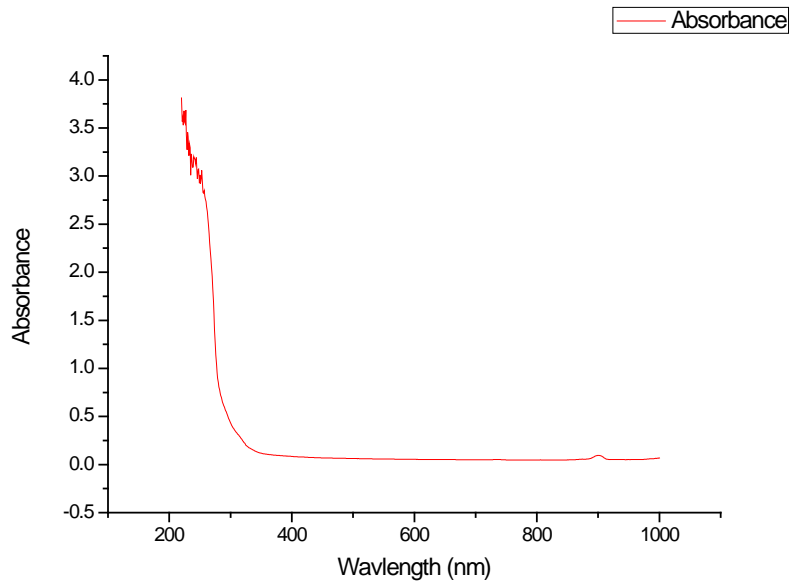
UV-Vis for L4



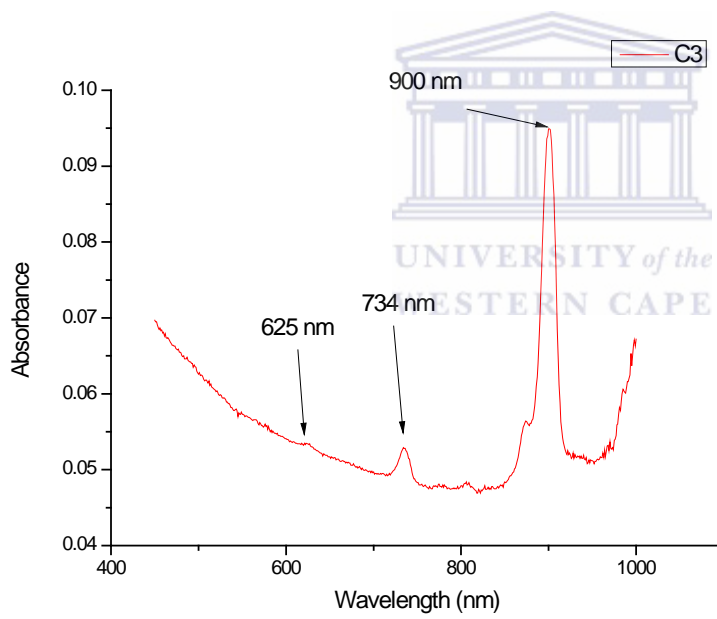
UV-Vis for **L5**



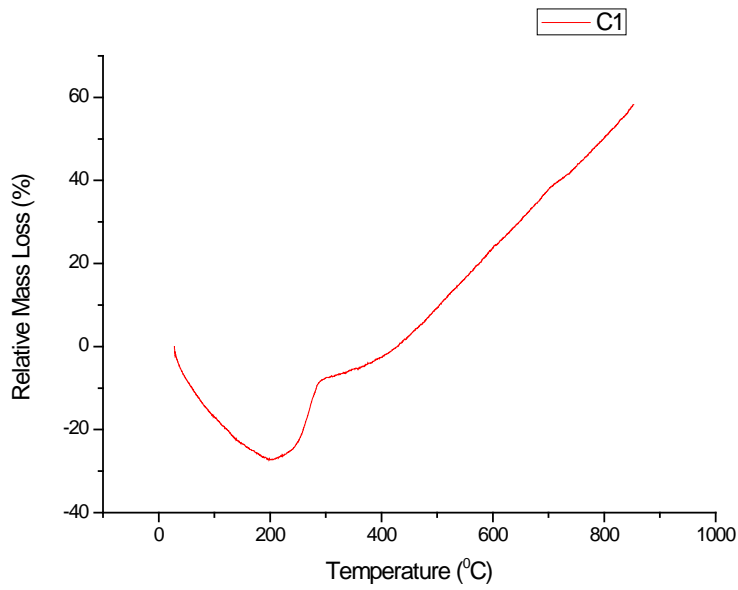
UV-Vis for **C1**



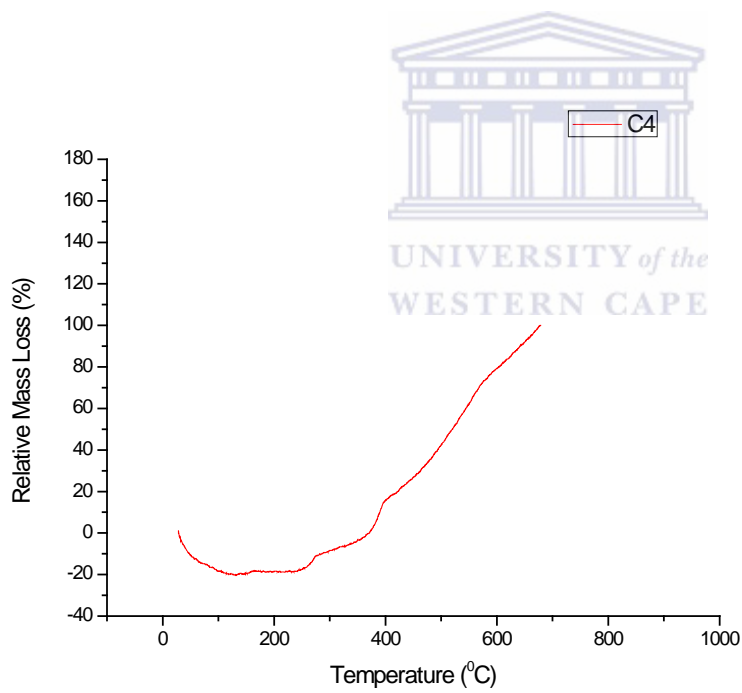
UV-Vis for C3



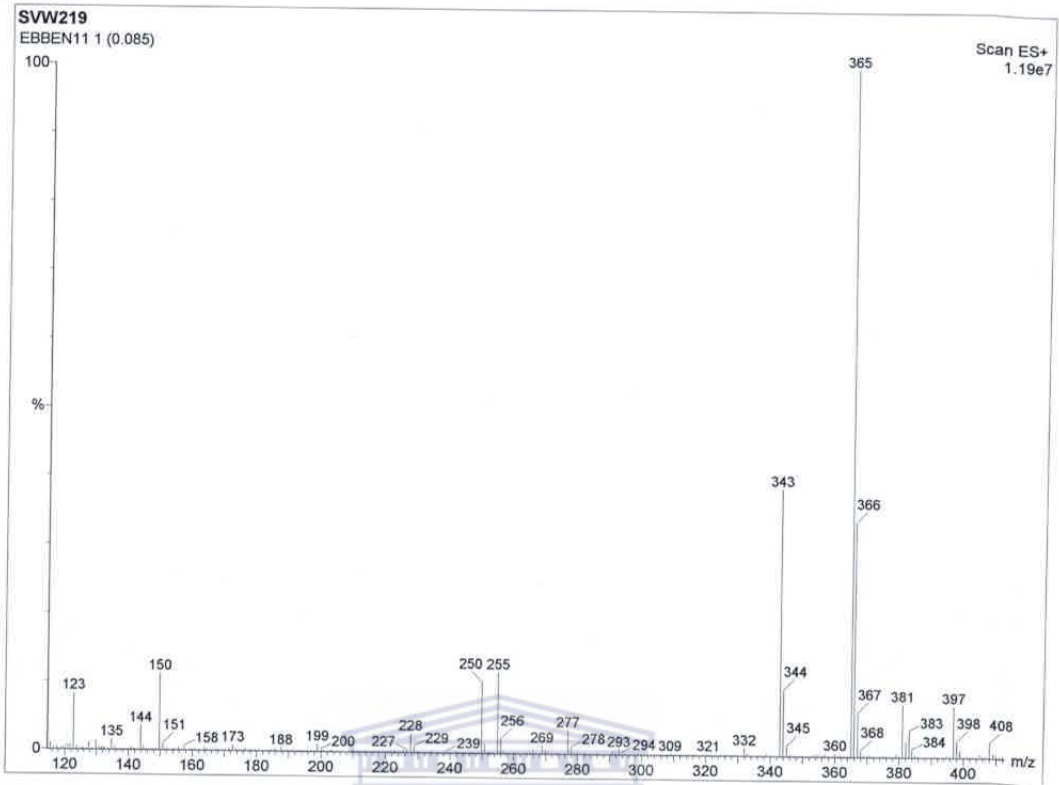
UV-Vis for C3 enlarged



TGA for **C1**



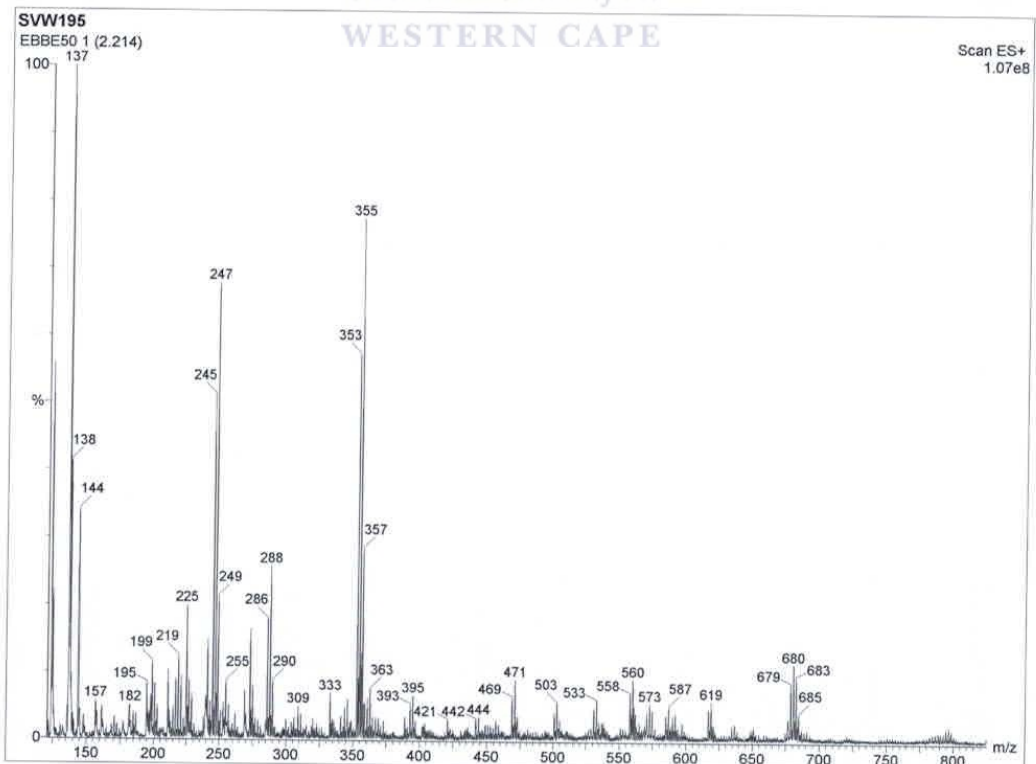
TGA for **C4**



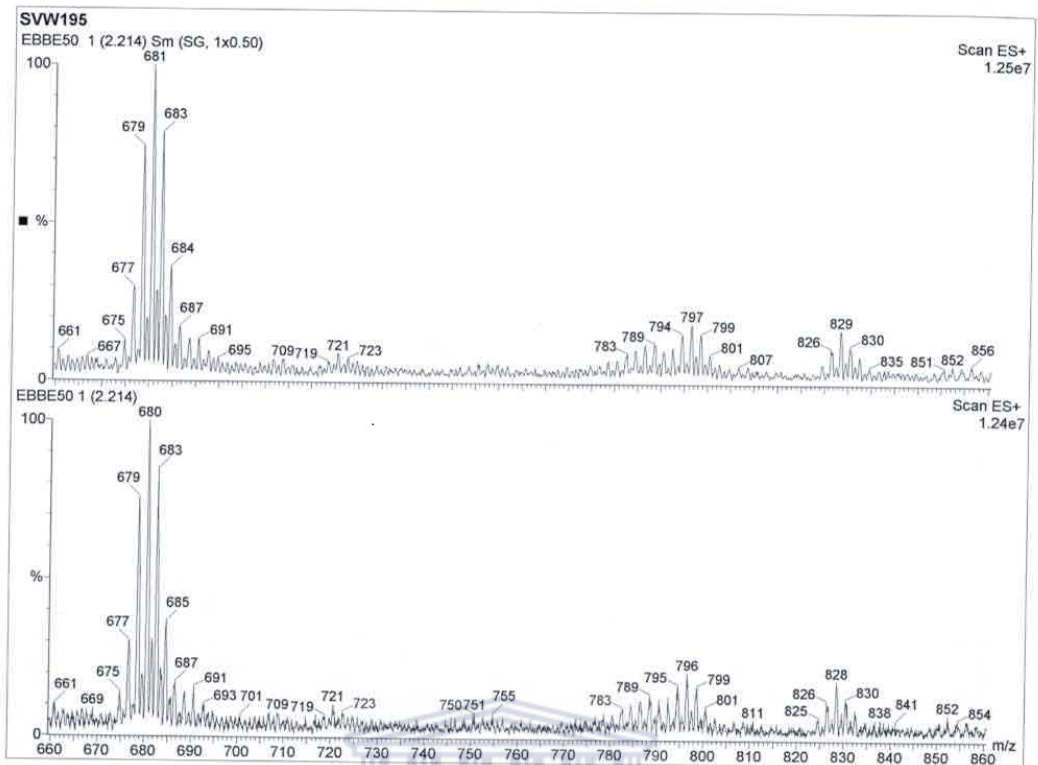
ESI-MS for L2



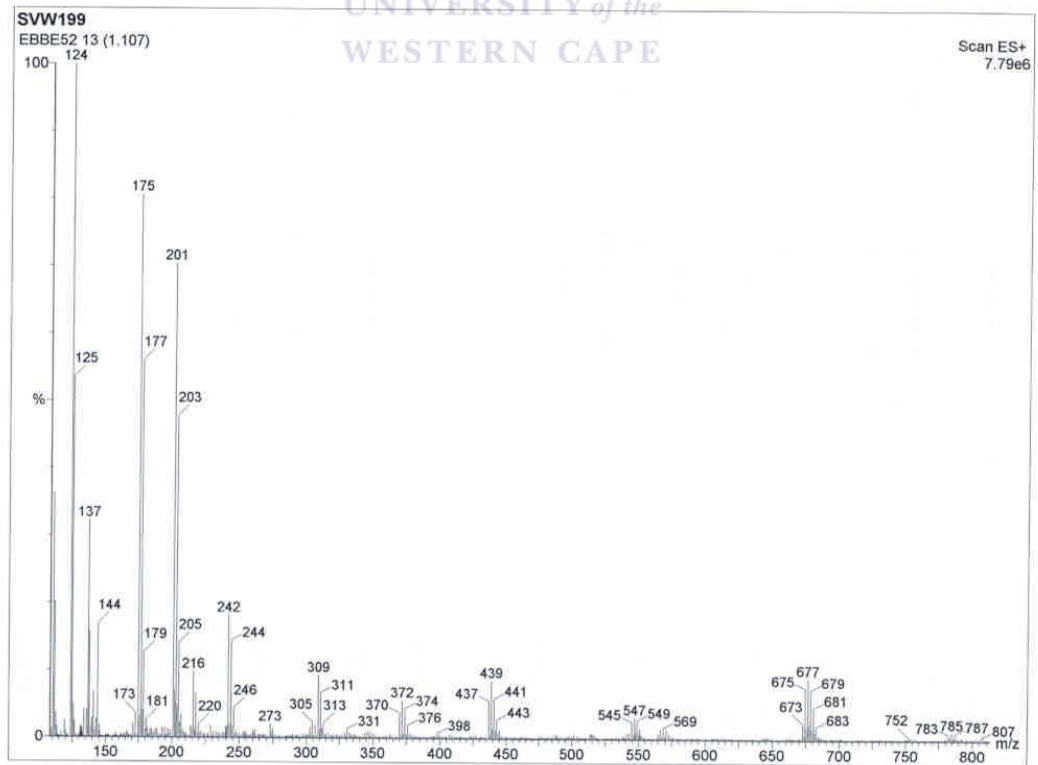
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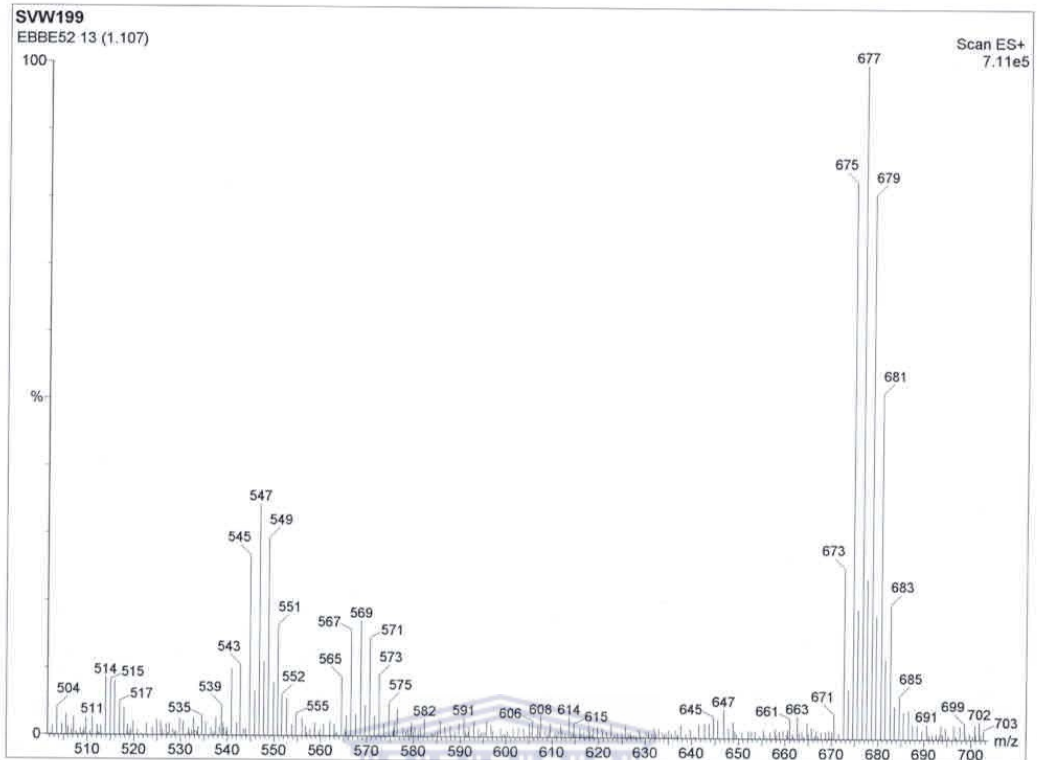
ESI-MS for C5



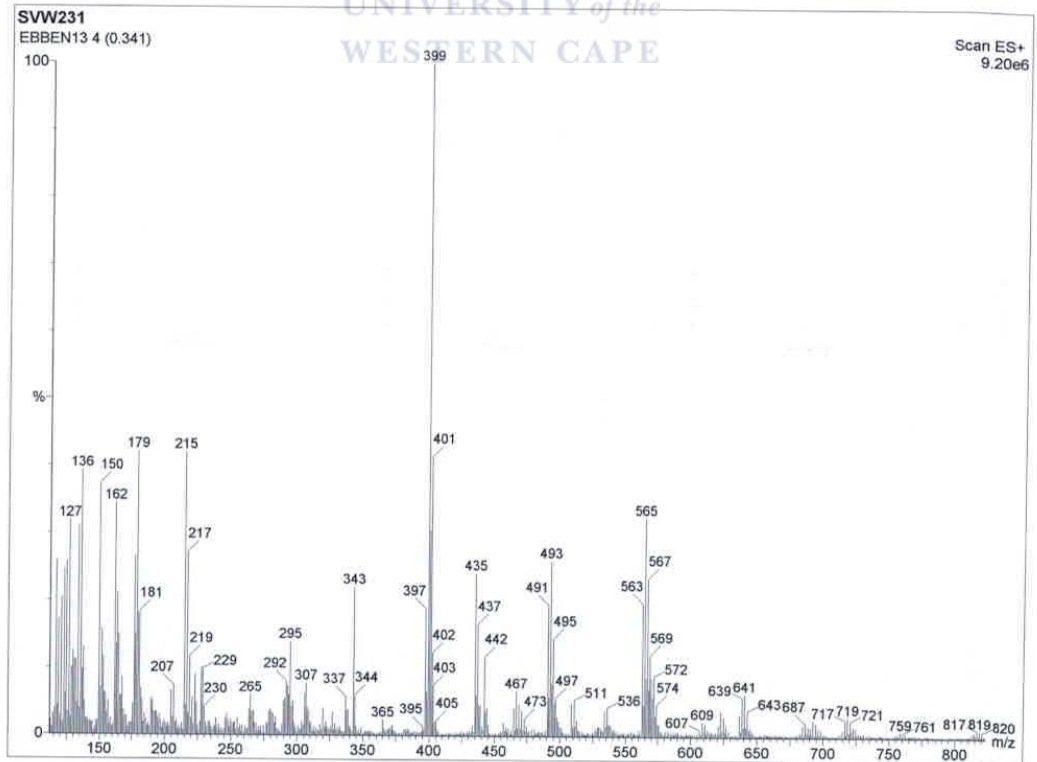
ESI-MS for C5 enlarged



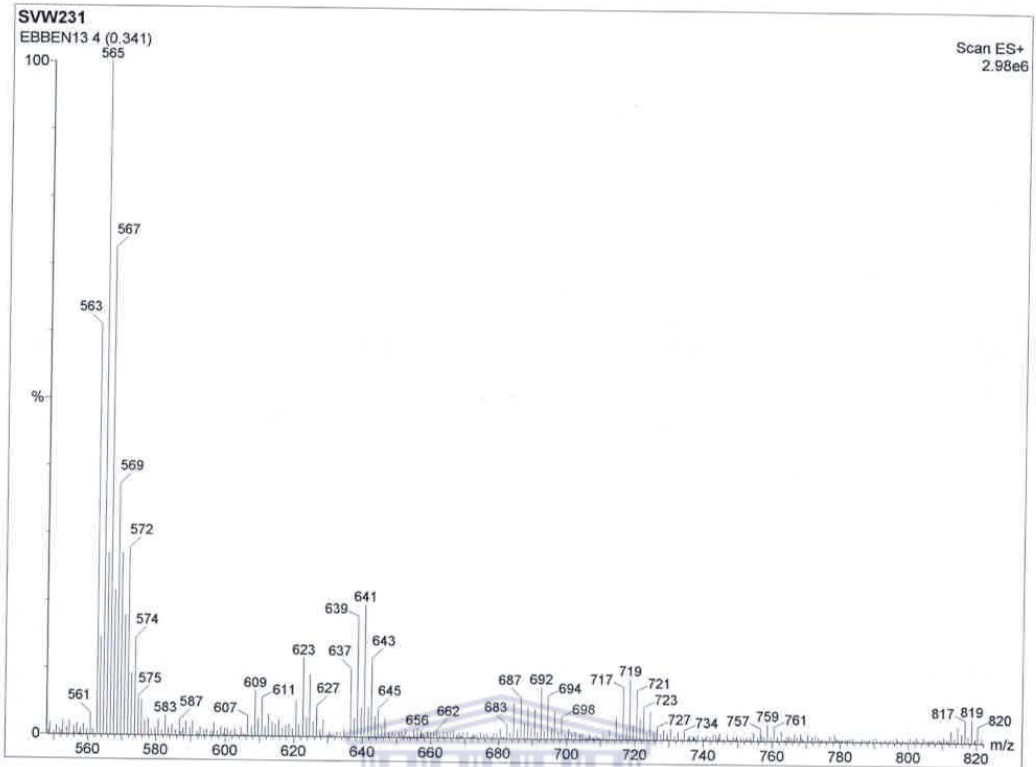
ESI-MS for C3



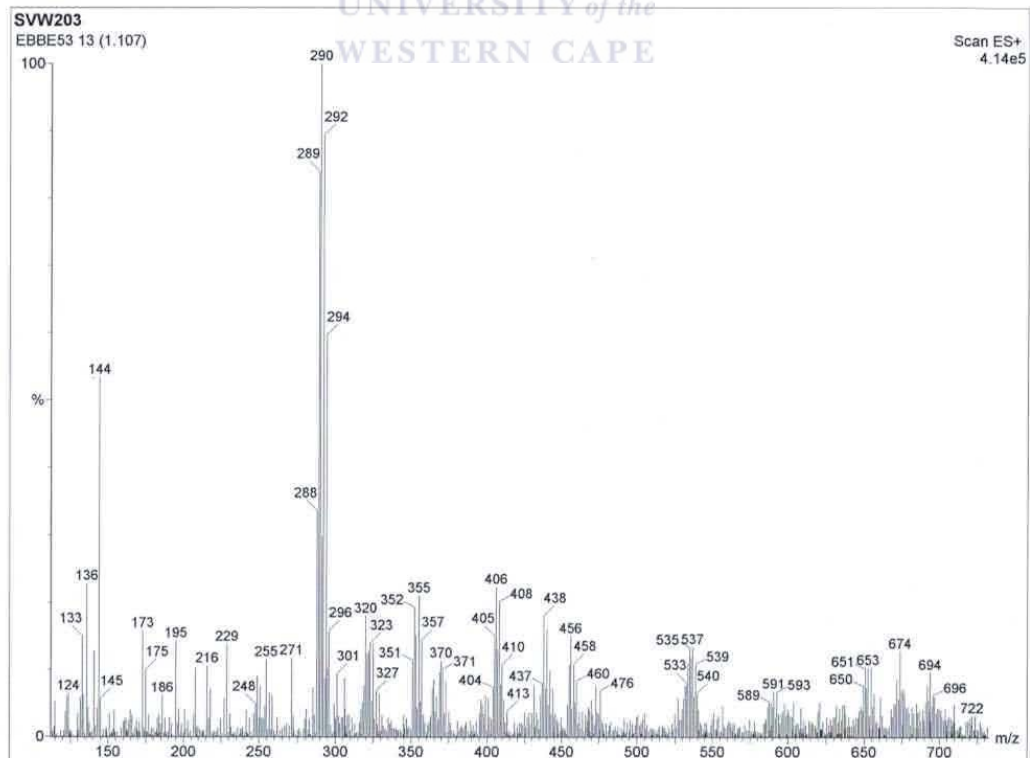
ESI-MS for C3 enlarged



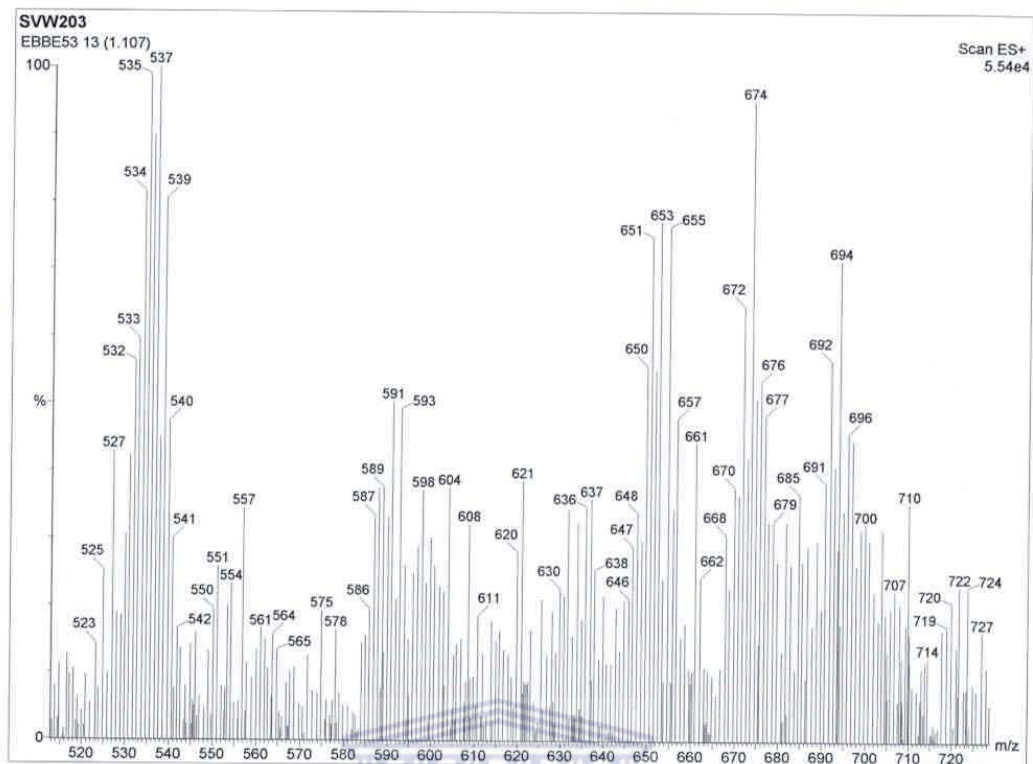
ESI-MS for C4



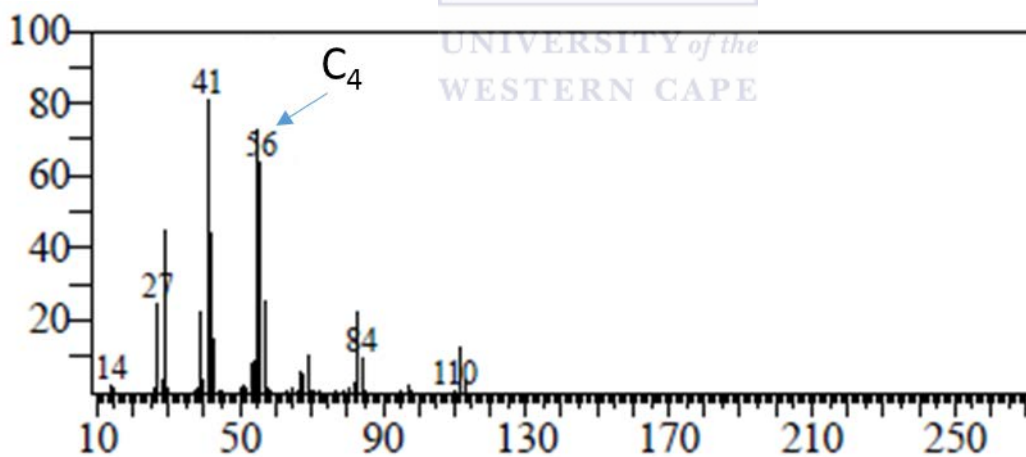
ESI-MS for C4 enlarged



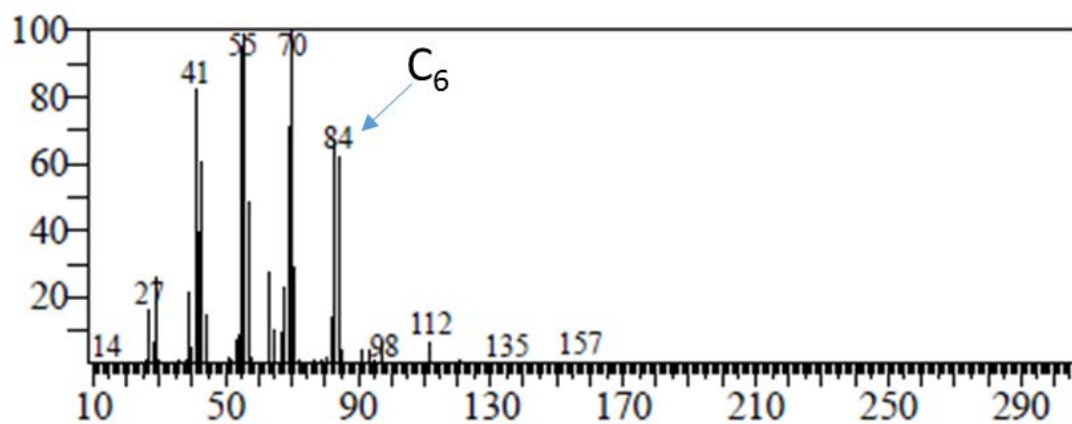
ESI-MS for C1



ESI-MS for C1 enlarged



Typical GC-MS spectrum of the product formed using catalyst **3** at 30 °C and 20 bar for 1 h confirming the formation of butene.



Typical GC-MS spectrum of the product formed using catalyst **5** at 30 °C and 20 bar for 1 h confirming the formation of hexene.

