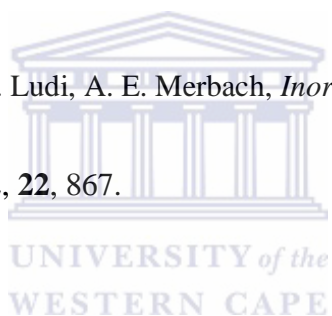


References:

1. M. J. Chitanda, D.E.Prokopchuk, *Organomet.*, 2008, **27**, 2337.
2. (a) T. P. Noon and E. N. Jacobsen, *Science*, 2003, **299**, 1691; (b) A. J. Swarts, *Mononuclear and Multinuclear Palladacycles as Catalyst Precursors*, MSc Thesis, Stellenbosch University, **2011**; (c) N. Mketi, *Palladium and Copper complexes based on a dendrimeric and monofunctional N,N'-chelating ligands as potential catalysts in the oxidative carbonylation of alcohols*, MSc Thesis, **2010**.
3. D. M. Haddleton, D. J. Duncalf, *Eur. J. Inorg. Chem.*, 1998, 1799.
4. W. Massa, S. Dehgampour, *Inorg.Chem.*, 2009, **362**, 2872.
5. R. Chen, J. Bacsá, S.F. Mapolie, *Polyhedr.*, 2003, **22**, 2855.
6. J. Cloete, S.F. Mapolie, *J. Mol. Catal. A:*, 2006, **243**, 221.
7. G. Smith, R. Chen and S. Mapolie, *J. Organomet. Chem.*, **2003**, 673, 111.
8. D. Prema, A.V. Wiznycia, *Dalton Trans.*, 2007, 4788.
9. V. Amandola, C. Mangano, *Inorg.Chem.*, 2003, **42**, 6056.
10. G. S. Smith and S. F. Mapolie, *J. Mol. Catal. A: Chem.*, 2004, **213**, 187.
11. C–J. Qui, Y–C. Zhang, Y. Gao, J–Q. Zhao, *J. Organomet. Chem.*, 2009, **694**, 3418.
12. (a) A. Capape, M. D. Zhou, S. L. Zhang, F. E. Kühn, *J. Organomet. Chem.*, 2008, **693**, 3240. (b) P. Ferreira, W. M. Xue, E. Bencze, F. E. Kühn, *Inorg. Chem.*, 2001, **40**, 5834.

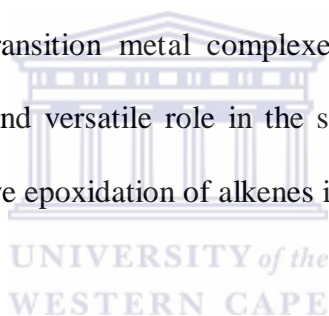
13. E. Buhleier and W. Wehner, *Synthesis*, 1978, 155.
14. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.*, 1985, **17**, 117.
15. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Macromolecules*, 1986, **19**, 2466.
16. D. A. Tomalia, A. M. Naylor and W. A. Goddard, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 138.
17. C. Hawker and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.*, 1990, 1010.
18. C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.
19. C. J. Hawker and J. M. J. Frechet, *Macromolecules*, 1990, **23**, 4726.
20. J. M. J. Frechet, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3713.
21. E.M.N. de-van Brabander Berg, E.W. Meijer, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1308.
22. G. R. Newkome, C. D. Shreiner, *Polymer*, 2008, **49**, 1.
23. A. Morean, *Electrochim, Acta*, 1998, **26**, 1609.
24. H. S. Li, T.A.Konovalova, *J. Phys. Chem.*, 2009, **113**, 5358.
25. R. Malgas-Enus, S. F. Mapolie and G. S. Smith, *J. Organomet. Chem.*, 2008, **693**, 2279-2286.
26. J. N. Mugo, S. F. Mapolie and J. L. van Wyk, *Inorg. Chim. Acta*, 2010, **363**, 2643.

27. P. Govender, A. K. Renfrew, C. M. Clavel, P. J. Dyson, B. Therrien, G. S. Smith, *Dalton Trans.*, 2011, **40**, 1158.
28. Murahashi, S.-I.; Komiya, N.; Hayashi, Y. H.; Kumano, T. *Pure Appl. Chem.* 2001, **73** (2), 311.
29. R. E. Connick, C. R. Hurley, *J. Am. Chem. Soc.*, 1952, **74**, 5012.
30. A. G. F. Shoir and R. H. Mohamed, *Synthetic Communications*, 2006, **36**, 59.
31. (a) M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.*, 1985, **21**, 75;(b) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, P. A. Tucker, *Inorg. Chem.*, 1980, **10**, 1014.
32. N. Aebischer, G. Laurency, A. Ludi, A. E. Merbach, *Inorg. Chem.*, 1993, **32**, 2810.
33. S. Pal, S. Pal, *Polyhedr.*, 2002, **22**, 867.



3.1 Introduction.

The constant endeavour, both in industry and academia, to catalytically transform C-C double bonds has developed into an active area of research. One area that is constantly developing due to “new” discoveries is the catalyzed oxidation of alkenes. Important oxidation reactions include the transformation of alcohols to either the corresponding carbonyl compounds or carboxylic acids, the oxidation of sulfides to sulfoxides and alkenes to epoxides and diols. Various studies have been devoted to oxidation of alkenes to the corresponding epoxides using transition metal complexes. The epoxide class of organic compounds plays an important and versatile role in the synthesis of intermediates for fine chemicals and as such the selective epoxidation of alkenes is a major area of research [1].



3.2 Rhenium complexes in the catalysed epoxidation reactions of olefins

The discovery of the catalytic ability of MTO by Herrmann *et al.* paved a way for exploration of MTO derivatives as inorganic rhenium compounds like Re_2O_7 or ReO_3 were long considered to have negligible catalytic oxidation activity with H_2O_2 [2]. The catalytic activity of MTO was quickly recognised and as a result further researches concerning the understanding of its active species was undertaken. The active catalyst was discovered to be the monoperoxo (**A**) and bis-peroxo (**B**) rhenium complex formed by the reaction of MTO with H_2O_2 [3]. The latter intermediate active catalyst has been fully characterised by X-ray studies [4-6].

The acidity of the rhenium centre restricted its use only to anhydrous H₂O₂ because low yield of the acid sensitive epoxide were obtained. Thus efforts made were aimed at improving the catalytic oxidation of sensitive alkenes by employing an urea-H₂O₂ adduct to circumvent the deleterious ring opening of epoxides. This process requires long reaction times. Other endeavours introduced the use of an additional tertiary base to suppress the epoxide ring opening and this resulted in the unfavourable detriment on the catalyst activity [3]. Sharpless *et al.* reported an improvement in selectivity by adding a large excess of pyridine with respect to the catalyst, without inhibition of the catalyst activity [7a]. This discovery led to the synthesis of sensitive epoxides with only 1.5 equivalents of aqueous H₂O₂ even at low catalyst loading [7a,b]. It was observed that higher catalyst loadings were necessary in the presence of bipyridine *N,N'*-dioxide as the *N,N'*-oxide suppresses the epoxide ring-opening [8]. This also ensured that unreactive terminal alkenes were converted to corresponding epoxides by making use of a less basic pyridine derivatives like 3-cyanopyridine [9].

The enhancement of the catalyst activity by an additive was further investigated by Herrmann's group. They reported the use of pyrazole as the most efficient additive and proposed a bis(peroxo)rhenium(VII)/pyrazole complex as the active oxidation species [10]. After a careful examination and comparison of the finding by Herrmann's group, Sharpless *et al.* [11] showed through mechanistic investigations [5], that incorporating the positive pyridine effect

[12], minimises the formation of the perrhenate (ReO_4^-) [12a] with the MTO decomposition thereby retaining high catalyst activity. The increased rate in the presence of pyridine was attributed to its intrinsic Brønsted basicity thus increasing the HO_2^- concentration. The HO_2^- is more nucleophilic and therefore more reactive with MTO compared to H_2O_2 . This characteristic of pyridine and related additives lowers the concentration of hydronium ions and as a result reducing the sensitivity of epoxides towards decomposition via ring-opening.

3.2.1 Mechanism of epoxidation reaction

The field of olefin epoxidation has been explored and a vast range of transitional metal catalysts have been tested and applied at both laboratory and industrial levels. Thus it has become certain to include compounds such as methyltrioxorhenium (CH_3ReO_3 , MTO) and MoO_3 as far as catalyzed oxidation reactions are concerned. These and other prominent catalysts in the field have been applied in industrial epoxidation of alkenes using the oxidants hydrogen peroxide and tertbutylhydroperoxide (TBHP) [3a,3d].

As mentioned (*vide supra*), Herrmann *et al.* have done extensive work on the subject of epoxidation with MTO [3,12c,13-15] consequently, its mechanism with H_2O_2 has been reported (Fig. 3.1) [16]. The mechanism discusses two important intermediates (*vide supra*) that have been isolated and studied as active catalysts [4], a bisperoxo complex of stoichiometry $(\text{CH}_3)\text{Re}(\text{O}_2)_2\text{O}\cdot\text{H}_2\text{O}(\mathbf{B})$ [4] obtained by reaction of MTO with excess H_2O_2 and a monoperoxo complex of composition $(\text{CH}_3)\text{Re}(\text{O})_2\text{O}_2(\mathbf{A})$ [12c, 25] obtained by reaction of MTO with 1 equiv. of H_2O_2 . Experimental data indicate that these intermediates have

similar rate constants in magnitude [12c,25,27]. Further work was pursued by density functional calculation in order to validate these findings [17,18,26]. The mechanism involves a nucleophilic attack on MTO by H_2O_2 as an activation parameter for the coordination of H_2O_2 to MTO. The protons lost in the conversion of H_2O_2 to a coordinated peroxo ligand, O_2^{2-} , are then transferred to one of the terminal oxygen atoms, which remain on the Re as an aqua ligand. The rate of this reaction is not pH dependent [19].

The concentration of the H_2O_2 used in the epoxidation reactions has been shown to be important because it directs the pathway the reaction will follow. The concentration dependent pathways can be categorised in two: high H_2O_2 and low H_2O_2 concentrations [16]. The isolable bisperoxo (**B**, path A) complex is responsible for the oxidation activity at high H_2O_2 concentration (85 wt%), while the monoperoxo (**A**) complex is responsible for epoxidation at low H_2O_2 concentration (<30 wt%) for the (path B). The studies of both catalytic pathways support a concerted mechanism in which the electron-rich double bond of the alkene electrophilically attacks a peroxidic oxygen of the complex possibly through a spiro arrangement [17-20].

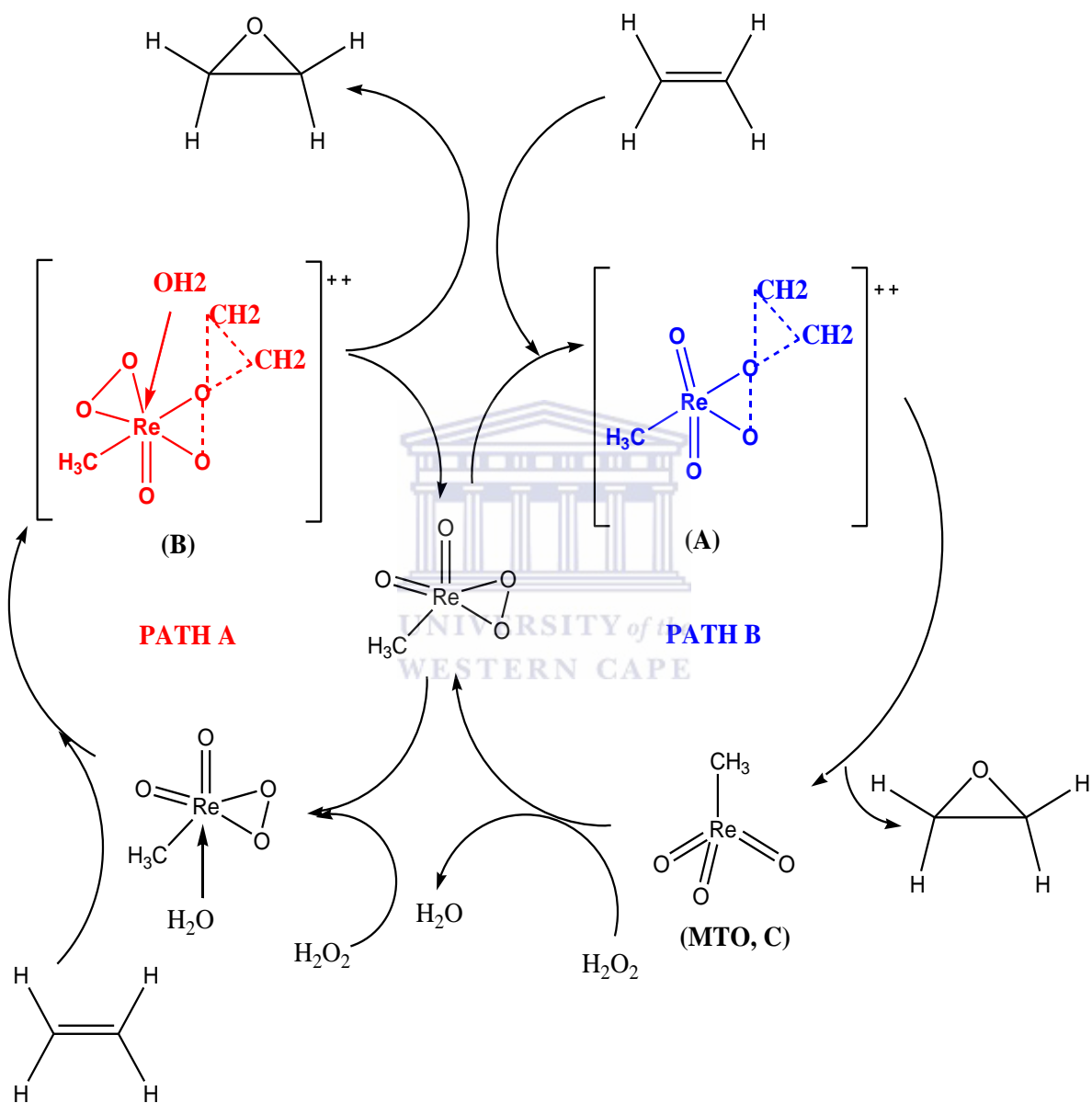
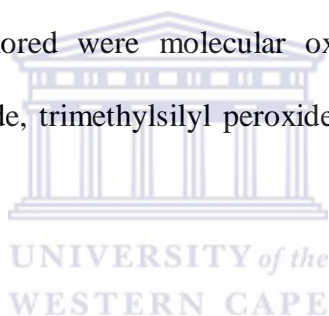


Figure 3.1: Suggested mechanism of methyltrioxorhenium (MTO, C) catalyzed epoxidation of alkenes [21,22].

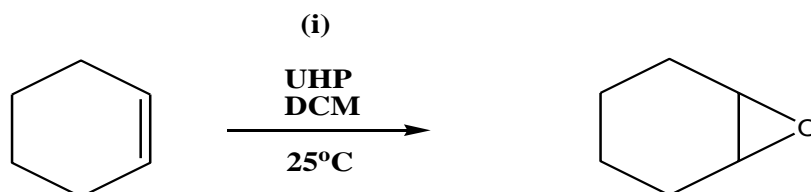
The above scheme of the suggested mechanism clearly indicates that the oxygen atom of the oxidant is activated by the catalyst in preparation to incorporate alkene/substrate to the activated oxygen atom. For both pathways, the presence of the metal is vital as it is a prerequisite for the facilitation of the transfer of the oxygen atom from the oxidant to the alkene/substrate [21,22].

Different sources of oxygen donors were used in the previous inventions for the transition metal catalyzed epoxidation reactions in order to obtain epoxides as desired products. Some of the oxidants that were explored were molecular oxygen, hydrogen peroxide, alkyl peroxides, urea-hydrogen peroxide, trimethylsilyl peroxide and sodium hypochlorite among others [23].



Deductions from the previous inventions serve as rudimentary tools for a better understanding of the epoxidation reactions of alkenes and the improvement of selectivity over the deleterious concomitant epoxide ring opening into diols. We herein report the use of MTO mono-(**C1**), bi-(**C2**), and multinuclear dendritic (**DC1** and **DC2**) catalysts (Figure. 3.3 and 3.5). To our knowledge, these MTO complexes, except **C1**, are reported herein for the first time and their catalytic activity is evaluated for the first time towards epoxidation reactions on selected cyclic substrates/alkenes.

3.3 Results and Discussion: Epoxidation of cyclohexene and cis-cyclohexene.



(i) **C1-C2** and **DC1-DC2**

Figure 3.2: A general epoxidation reaction of the alkene substrates.

This section documents the results obtained from the catalytic evaluation of the compounds **C1** and **C2** towards the epoxidation of selected cyclic alkenes (Figure 3.2) with isooctane as an internal standard. GC-FID was employed in the analysis and determination of conversion as the consumption of the substrates (cyclohexene and cis-cyclooctene, respectively) was monitored as a function of time.

3.3.1 Epoxidation reactions catalysed by mono- (**C1**) and bi-nuclear (**C2**) MTO Complexes.

Schiff-base complexes of MTO that were synthesized, **C1** and **C2**, were examined as catalysts for the epoxidation of two cyclic substrates i.e cyclohexene and cis-cyclooctene, respectively. These complexes were examined in the epoxidation reaction with urea hydrogen peroxide adduct (UHP) as the oxidant. A similar catalytic setup that was employed by Qui

et. al., a catalyst: oxidant: substrate ratio of 1:200:100, for all catalytic reactions was used. The catalysts were found to be activity as epoxidation catalysts for the transformation of the two selected olefins/substrates.

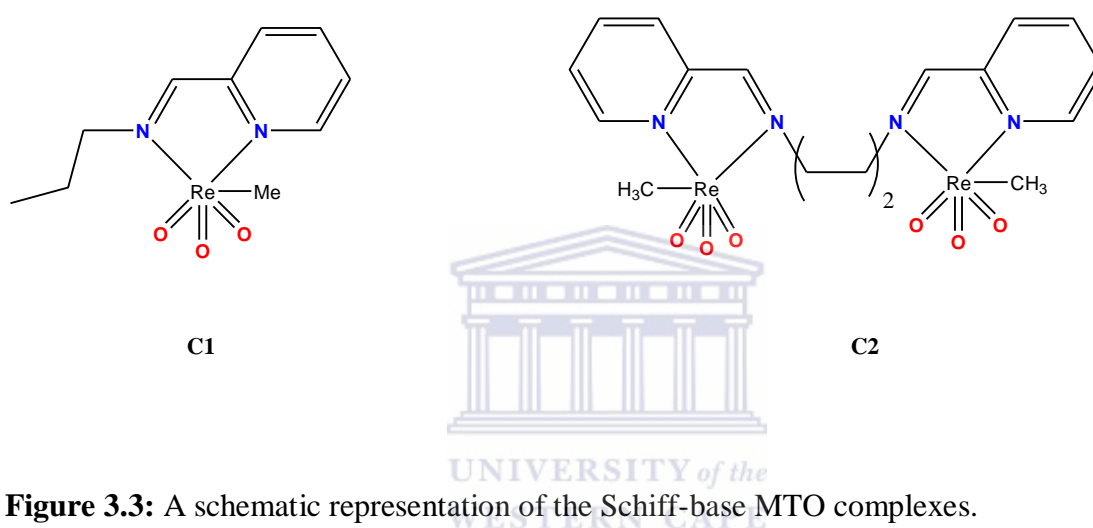


Figure 3.3: A schematic representation of the Schiff-base MTO complexes.

Complex **C1** is known and was first resolved crystallographically and tested as a catalyst for both cyclic substrates by Qui *et. al.* [24]. Herein the complex is synthesized as a benchmark for the novel synthesized homobimetallic MTO complex **C2**.

C1 was used as a catalyst for the epoxidation of the cyclic substrates i.e. cyclohexene and cis-cyclooctene, respectively. As like the previously reported protocol [24], the suitable oxidant used for the epoxidation reaction of the olefinic substrates was Urea-hydrogen peroxide adduct (UHP). The use of hydrogen peroxide (H_2O_2) as an oxidant was avoided as this is commercially available as an aqueous solution and tends to favour the further reaction of the epoxides to subsequent diols. Hydrogen peroxide needs specialized instruments or

procedures to dry and the alternative route of using urea-hydrogen peroxide as the source of hydrogen peroxide was opted. This resulted in no significant amount of diols formed for both cyclic olefinic substrates. All catalytic reactions reached completion within 4 h, exhibiting elevated reaction rates with 98 % conversion. The epoxide yield reached up to 100 % after 4h, showing the same trend reported [24].

The catalytic activity of complex **C2** followed the same trend as with **C1**, with notable completion of the catalytic reaction in a shorter time (Table 3.1). Synergy between the two rhenium centres in complex **C2**, that has been afforded by the bifunctional ligand, in the epoxidation reactions of the cyclic substrates/alkenes under the buffering effect of urea-hydrogen peroxide, afforded conversions to reaching 99 % with also no significant diols amount observed. At selected time intervals, the novel Schiff-base complex of MTO (**C2**) performed better than the benchmark complex **C1**.

Table 3.1: Catalytic data of the epoxidation of cyclohexene with MTO(C) and catalysts **C1** and **C2**.

Entry	Catalyst	Oxidant	Time (h)	Conversion (%) ^a	Selectivity (%) ^b
1	MTO	UHP	2.5	>99	>99
2	C1	UHP	2.5	72	97
3	C2	UHP	2.5	76	97
4	C1	UHP	8	>99	>99
5	C2	UHP	6.5	>99	>99

Reaction conditions: 0.955 mmol of cyclohexene; 1.9 mmol of oxidant; 0.00928 mmol of catalyst; 4 mL of DCM; 25 °C. ^aCalculated by GC. ^bCalculated by GC.

The activity of the catalysts was observed to increase as a function of time with the highest conversion being greater than 99% observed for both catalysts. Comparison of the catalytic activity of the synthesized Schiff-base complexes of MTO (C1 and C2), with that of the free MTO (in the absence of the imine ligand) showed that the free MTO performed better as the highest conversion was reached within the shortest amount of time. This is documented in the literature with other reported Schiff-base complexes of MTO [24]. A detailed trend is exhibited in the figure below (Figure 3.4).

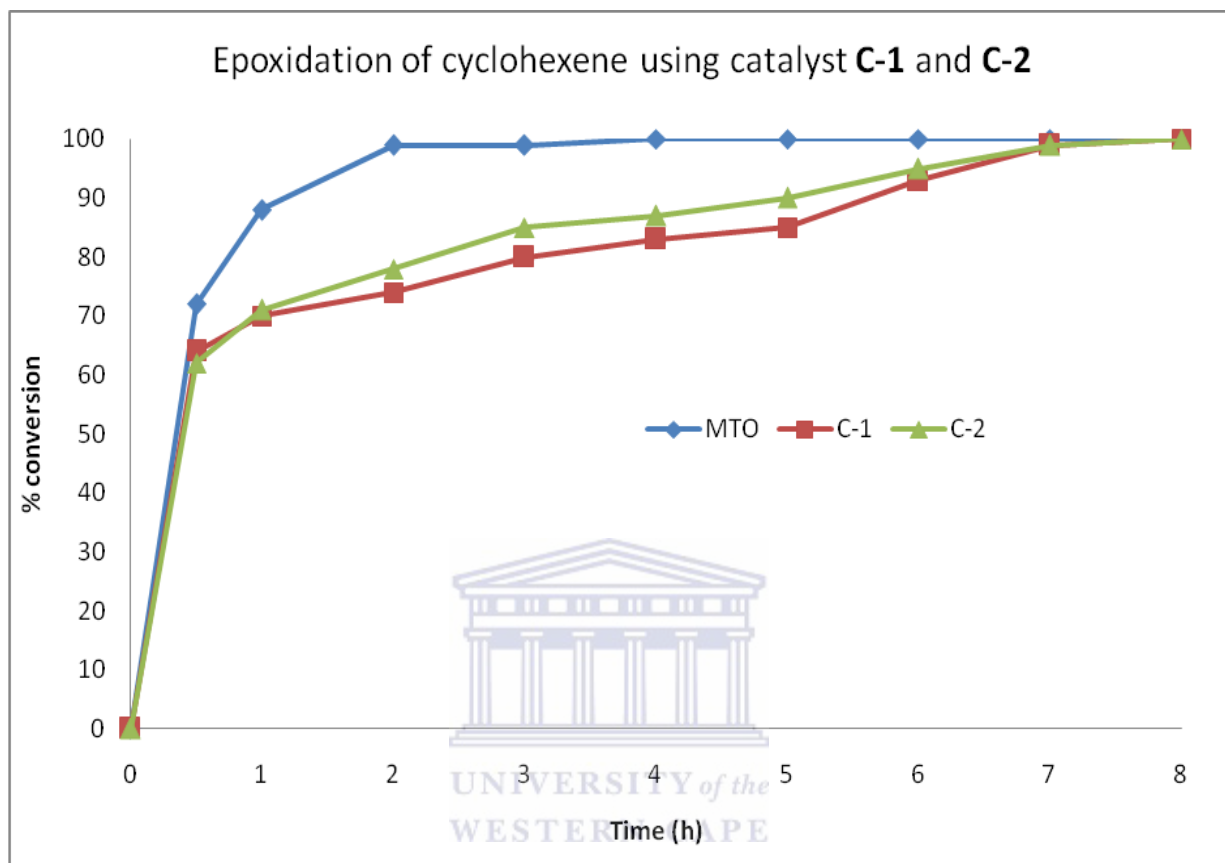


Figure 3.4: Plot of the consumption of cyclohexene as a function of time.

The reason for the lower catalytic activity of the prepared complexes is similar to what is documented in the literature [24]. Complexes derived from alkylamine (strong electron donating) tend to exhibit low catalytic activity as compared to weak electron donating ligands as the former tends to form stronger Re-N bond thus leading to a lower reactivity of the catalysts, hence the reaction times had to be prolonged in order to ensure 100% epoxide yields. This is explainable by the fact that the ligands exert their influence on the Lewis acidity of the Re atom and the immediate surroundings of terminal ligands. The formation of the catalytically

active mono and bisperoxo species is hindered as the Lewis acidity of the metal centre (Re) is reduced. Hence a decrease in the electron deficiency of the peroxy-oxygen results in the catalyst being less activated to be attacked by the nucleophilic olefin.

Complexes **C1** and **C2** showed similar trend when applied as catalyst in the epoxidation of cyclooctene. The catalytic reactions showed high reaction rate and completion within the indicated time (Table 3.2). Complexes **C1** and **C2** showed similar catalytic activity for the epoxidation of cyclooctene, and the epoxides yield reached 100% when the reaction times were prolonged.



Table 3.2: Catalytic data of the epoxidation of cis-cyclooctene with MTO(C) and catalysts C1 and C2.

Entry	Catalyst	Oxidant	Time (h)	Conversion (%) ^a	Selectivity (%) ^b
1	MTO	UHP	2.5	>99	>99
2	C1	UHP	2.5	77	97
3	C2	UHP	2.5	80	97
4	C1	UHP	8	>99	>99
5	C2	UHP	6	>99	>99

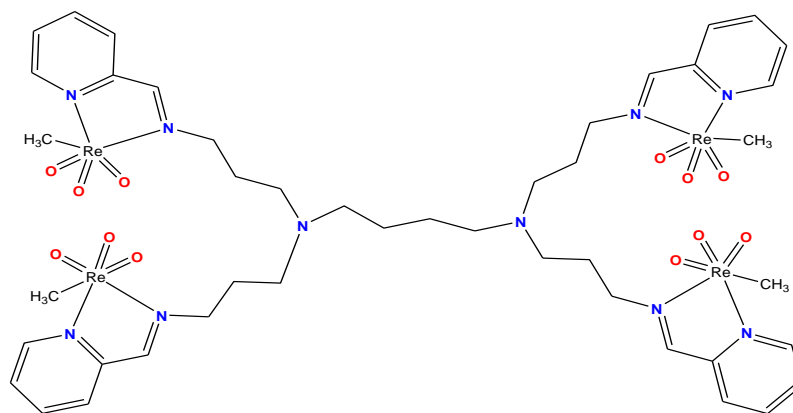
Reaction conditions: 0.955 mmol of cis-cyclooctene; 1.9 mmol of oxidant; 0.00928 mmol of catalyst; 4 mL of DCM; 25 °C. ^aCalculated by GC. ^bClaculated by GC

3.3.2 Epoxidation reactions catalysed by multinuclear Schiff-base complexes of MTO metallodendrimer, DC1 and DC2.

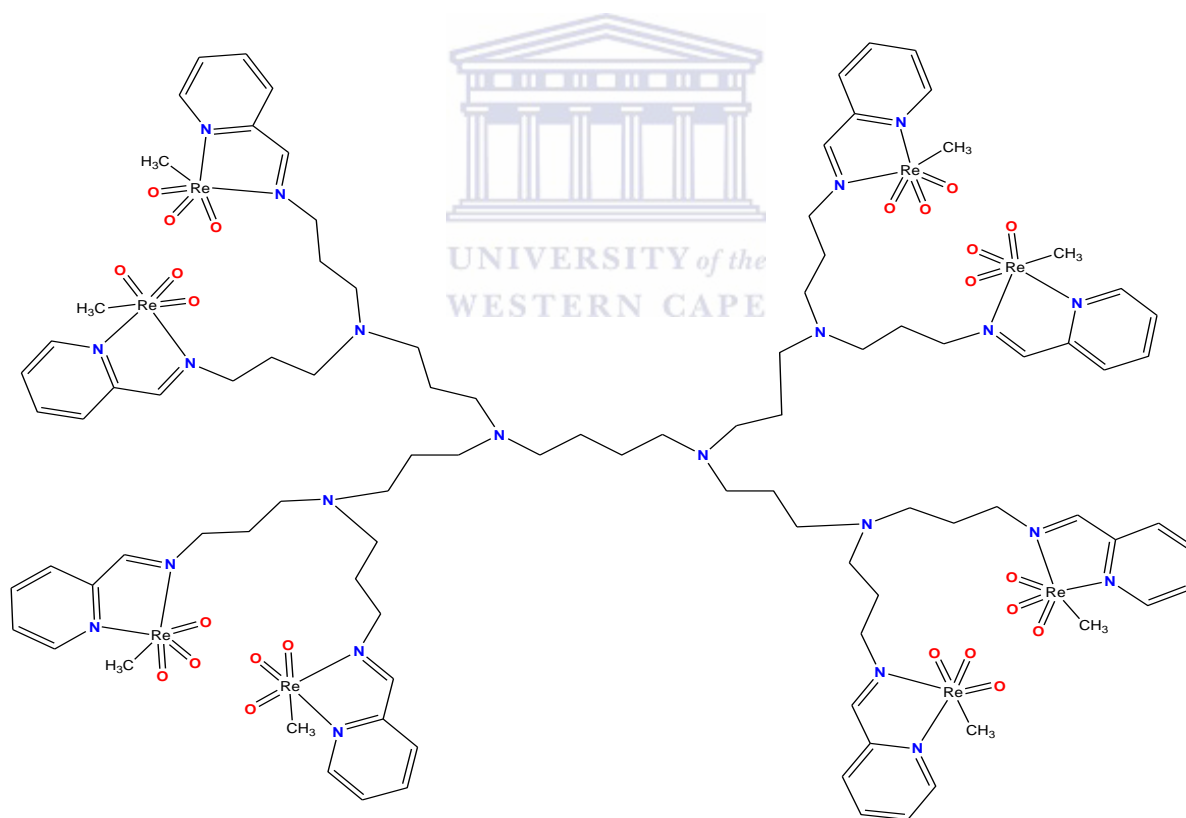
The 1st and the 2nd generation Schiff-base Re(VII) metallodendrimers were evaluated as catalysts in the epoxidation of cyclohexene and cis-cyclooctene, respectively. The dendritic catalysts were found to be highly active as catalysts in the epoxidation reactions of the two selected cyclic substrates/olefins.

The consumption and conversion of the cyclic substrates/olefins occurred within 4 hrs for all the dendritic catalyzed reactions. Drastic quantitative conversion of cyclohexene/cis-cyclooctene was observed within the first hour in comparison with the mono- and binuclear MTO complexes (Figure 3.5).





DC1



DC2

Figure 3.5: A representation of the novel 1st and 2nd generation Re(VII) metallodendrimer tested in the epoxidation of cyclohexene/cis-cyclooctene.

Table 3.3: Catalytic data of the epoxidation of cis-cyclooctene with MTO (C) and catalysts DC1 and DC2.

Entry	Catalyst	Oxidant	Time (h)	Conversion (%) ^a	Selectivity (%) ^b
1	MTO	UHP	2.5	>99	>99
2	DC1	UHP	2.5	82	98
3	DC2	UHP	2.5	85	98
4	DC1	UHP	4	>99	>99
5	DC2	UHP	3	>99	>99

Reaction conditions: 0.955 mmol of cyclohexene; 1.9 mmol of oxidant; 0.00928 mmol of catalyst; 4 mL of DCM; 25 °C. ^bCalculated by GC. ^cCalculated by GC

It was also noted that with time the pyridineimine moiety undergoes hydrolysis and this fragment was detected in the GC. This ease of hydrolysis was far more deferred in the case of the dendrimer indicating the stability impacted by the dendrimer ligand.

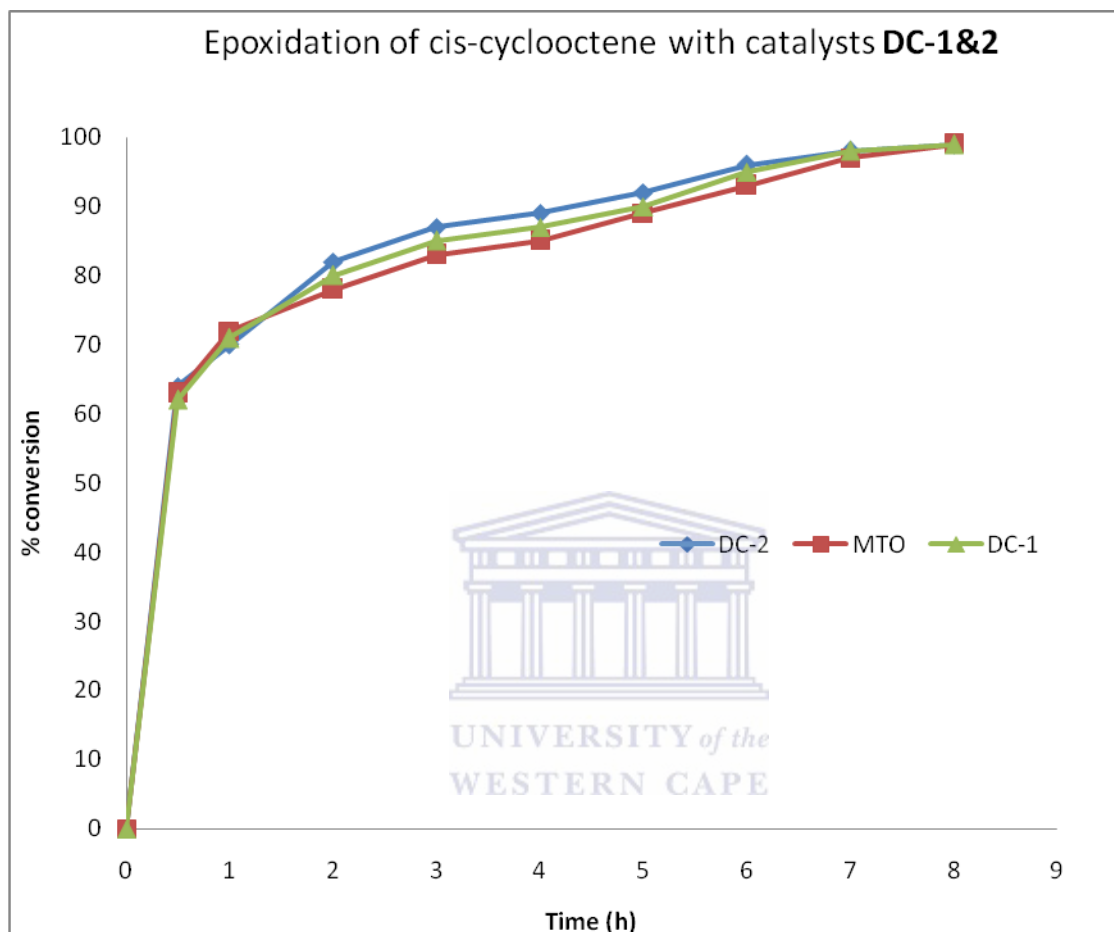


Figure3.6: Plot of the consumption of *cis*-cyclooctene as a function of time.

The activity of the dendritic catalysts yielded higher conversion as compared to the mono- and binuclear MTO complexes at any time. Although it was observed that MTO reaches the highest conversion in the least amount of time, it was also observed that the dendrimer catalysts give the highest conversion at any time but the only hindering was the prolonged reaction time in order to attain 100% epoxide yield.

Table 3.4: Catalytic data of the epoxidation of cyclohexene with MTO (**C**) and catalysts **DC1** and **DC2**.

Entry	Catalyst	Oxidant	Time (h)	Conversion (%) ^a	Selectivity (%) ^b
1	MTO	UHP	2.5	>99	>99
2	DC1	UHP	2.5	80	>99
3	DC2	UHP	2.5	82	>99
4	DC1	UHP	4	>99	>99
5	DC2	UHP	3	>99	>99

Reaction conditions: 0.955 mmol of cyclohexene; 1.9 mmol of oxidant; 0.00928 mmol of catalyst; 4 mL of DCM; 25 °C. ^bCalculated by GC. ^cCalculated by GC.

The rapid formation of the active species in the catalysis (a peroxo complex) renders these novel rhenium dendritic complexes useful in the catalyzed epoxidation of cyclohexene and cis-cyclooctene, respectively. High levels of conversion to epoxides were observed with no significant (less than 5%) diol formation.

3.4 Conclusion

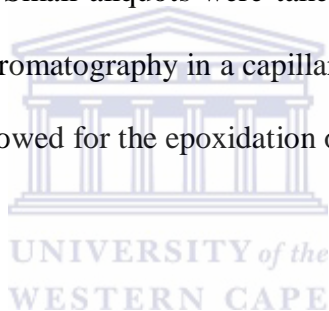
All the complexes synthesized were evaluated as catalysts in the epoxidation of cyclohexene/cis-cyclooctene reactions. The use of urea hydrogen peroxide as an oxidant resulted in all the complexes displaying high catalytic activity and selectivity when applied to the epoxidation of cyclohexene/cis-cyclooctene. No significant diols formation was observed.

3.5 Materials and Methods

Methyltrioxorhenium (MTO) was purchased from Sigma-Aldrich/Strem Chemicals. cyclohexene (99%), cyclohexene oxide (98%) cis-cyclooctene (95%), cyclooctene oxide (99%) isooctane (99.8%) were purchased from Aldrich and used without further purification. Dichloromethane was dried using standard procedures, distilled under nitrogen and kept over dried 3 Å molecule sieves. Other reagents were used as received. All preparations and manipulations were carried out under an oxygen and water free nitrogen atmosphere using the standard Schlenk techniques. The GC analysis was carried out on Agilent 7890, GC Column: Agilent 19091J-413; 325 °C: 30 m X 320 μm X 0.25 μm, 5% phenyl methyl Siloxan HP5-column.

3.5.1 *General procedure for the Epoxidation of cyclohexene/cis-cyclooctene*

The catalytic reactions were carried out under continuous stirring in a 50 ml r.b.f immersed in a water bath with temperature control. In a typical experiment, 0.025 mmol of the catalyst, 3.5 ml of methanol, and a given amount (5 mmol) of UHP were mixed in the flask under agitation until the reaction temperature was reached. At this time, 2.5 mmol of the substrate was added (time zero). Small aliquots were taken at selected reactions times. The products were analyzed by gas chromatography in a capillary column using a FID detector. A similar catalytic protocol was followed for the epoxidation of the substrates.



References:

1. (a) Gorzynski Smith, J. *Synthesis.*, 1984, 629. (b) Bonini, C.; Righi, G. *Synthesis* 1994, 225.
2. Lai, T. -S.; Zhang, R.; Cheung, K. -K.; Kwong, H. -L. Che, C. -M. *Chem. Commun.* 1998, 1583.
3. (a) W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 163. (b) W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal. A: Chem.* 1994, **86**, 243. (c) W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* **1997**, *30*, 169. (d) G. Grivani, S. Tangestaninejad, M. H. Habibi, V. Mirkhani, M. Moghadam, *Appl. Catal A: Gen.*, 2006, **299**, 131.
4. W. A. Herrmann, R. W. Fischer, W. Scherer, M. U. Rauch, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1157.
5. A. M. Al-Ajlouni, J. H. Espenson, *J. Org. Chem.*, 1996, **61**, 3969.
6. (a) Z. Zhu, J. H. Espenson, *J. Org. Chem.*, 1995, **60**, 1326. (b) M. M. Abu-Omar, J. H. Espenson, *J. Am. Chem. Soc.*, 1995, **117**, 272. (c) Wang, W. -D.; Espenson, J. H. *Inorg. Chem.*, 1997, **36**, 5069. (d) Van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Commun.*, 1999, 821.
7. (a) J. Rudolph, K. L. Reddy, J. P. Chiang, K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189. (b) A. L. Villa, D. E. Vos, C. Montes, P. A. Jacobs, *Tetrahedron Lett.*, 1998, **39**, 8521.
8. M. Nakajima, Y. Sasaki, H. Iwamoto, S. Hashimoto, *Tetrahedron Lett.*, 1998, **39**, 87.
9. C. Copéret, H. Adolfsson, K. B. Sharpless, *Chem. Commun.*, 1997, 1565.

10. W. A. Herrmann, R. M. Kratzer, H. Ding, W. Thiel, H. Glas, *J. Organomet. Chem.*, 1998, **555**, 293.
11. H. Adolfsson, A. Converso, K. B. Sharpless, *Tetrahedron Lett.*, 1999, **40**, 3991.
12. (a) W.-D. Wang, J. H. Espenson, *J. Am. Chem. Soc.*, 1998, **120**, 11335. (b) H. Tan, J. H. Espenson, *Inorg. Chem.*, 1998, **37**, 467. (c) Espenson, J. H. *Chem. Commun.* 1999, 479.
13. W.A. Herrmann, M. Dieter, W. Wagner, J.G. Kuchler, G. Weichselbaumer, R. Fischer, US Patent 5,155,247, Oct. 13, **1992**, To Hoechst Aktiengesellschaft.
14. F. E. Kuhn, A. M. Santos, W. A. Herrmann, *Dalton Trans.*, 2005, 2483.
15. J. B. Espenson, M. M. Abu-Omar, *Adv. Chem. Series*, Vol. 253, p. 99, *Am. Chem. Society*, Washington, DC, **1997**.
16. F. E. Kuhn, A. Scherbaum, W. A. Herrmann, *J. Organomet. Chem.*, 2004, **689**, 4149.
17. P. Gisdakis, N. Rosch, *Eur. J. Org. Chem.*, **2001**, 719.
18. C. di Valentin, R. Gandolfi, P. Gisdakis, N. Rosch, *J. Am. Chem. Soc.*, 2001, **123**, 2365.
19. O. Pestovski, R. V. Eldik, P. Huston, J. H. Espenson, *J. Chem. Soc. Dalton. Trans.*, 1995, 133.
20. P. Gisdakis, W. Antonczak, S. Kostlmeir, W. A. Herrmann, N. Rosch, *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 2211.
21. A. O. Bouh, A. Hassan, S. L. Scott, *Catalysis Of Organic reactions, Ed., Chemical Industries (Marcel Dekker)*, **2003**, 537.
22. R. Neumann, *A process for epoxidation of alkenes*, International patent WO,98/54165.
23. G. S. Owens, J. Arias, M. M. Abu-Omar, *Catal. Today*, 2000, **55**, 317.
24. C.-J. Qiu, Y.-C. Zhang, Y. Gao, J.-Q. Zhao, *J. Organomet. Chem.*, 2009, **694**, 3418.

25. A. Al-Ajlouni, H. Espenson, *J. Am. Chem. Soc.*, 1995, **117**, 9243.
26. P. Gisdakis, I. V. Yudonov, N. Rosch, *Inorg. Chem.*, 2001, **40**, 3755.
27. W. Adam, C. R. Saha-Moller, O. Weichold, *J. Org. Chem.*, 2000, **65**, 5001.
28. W.A. Herrmann, R.M. Kratzer, H. Ding, W. Thiel, H. Glas, , *J. Organomet. Chem.*, 1988, **555**, 293.



4.1 *Introduction.*

In Organic Synthesis, the craft of oxidative cleavage has grown tremendously elevating olefin transformation to become one of the most prevalent reactions in the field. The application of a variety of inorganic oxidizing agents to organic substrates has considerably broadened the selectivity with which such oxidations may be carried out. The extensive study documented in the literature highlights two main oxidative cleavage routes that can be summed up as conversion of olefins to vicinal diols and subsequent cleavage with NaIO_4 or other oxidants [1].

The use of ruthenium as the catalytic metal in this field of research can be attributed to its versatility, as it can catalyse a number of oxidative transformations *viz.* the oxidation of alkanes, the cleavage of double bonds, the asymmetric epoxidation of alkenes, the oxidation of alcohols and ethers and the oxidation of amines and amides [2].

4.2 *Catalytic Oxidative Cleavage of alkenes by ruthenium compounds.*

From the first example of a catalysed alkene cleavage using a form RuO_2 (aq.). $\text{Na}(\text{IO}_4)/\text{AcOH}(\text{I})$ system, the oxidative functionalization class has broaden into a field of fundamental transformations in organic chemistry. This topic has been extensively reviewed and applied in a myriad of various settings for the synthesis and production of valuable intermediates and chemical commodities [2-8].

The earliest inventions report on the use of RuO_4 as an active species generated *in situ* from the system (I) (*vide supra*) to cleave alkenes into corresponding alkenes [3-8].

4.2.1 *In situ* generated ruthenium tetroxide promoted oxidations.

The nature of the active species, RuO_4 (II), permits transformations such as oxygenation and hydrogen abstraction of an array of organic compounds because it is a powerful oxidant in the transformation of various organic substrates. Due to its reactive nature, the reaction conditions are normally mild and performed at room temperature. The catalytic reactions are known to conveniently take place in a biphasic solvent system (*vide infra*) employing a catalytic amount of RuCl_3 or RuO_2 in conjunction with oxidants such as NaIO_4 , HIO_4 , NaOCl and NaBrO_3 , or under electrochemical conditions (see Fig. 4.1).

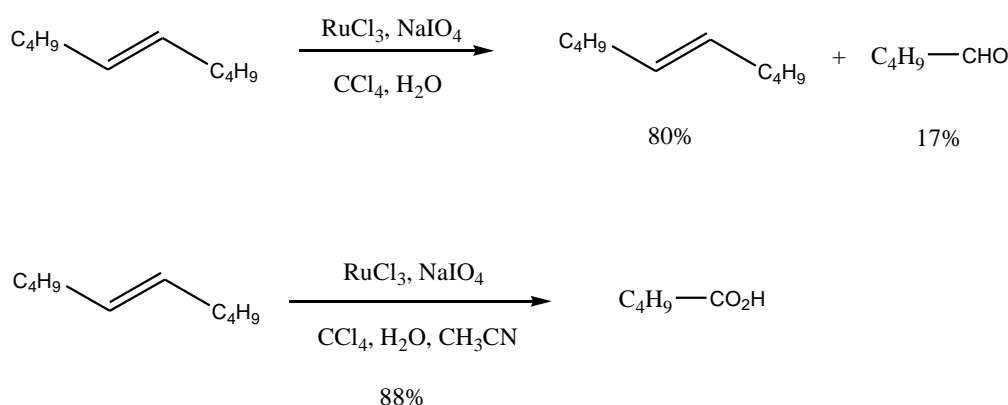


Figure 4.1: A general scheme showing the usage of catalytic amounts of RuCl_3 [10].

Addition of acetonitrile has indicated to favour the formation of carboxylic acids over aldehydes as the organic solvent, upon introduction into the reaction mixture, prevents the

inactivation of the ruthenium catalysts as this leads to sluggish, incomplete reactions by forming low-valent ruthenium carboxylate complexes [4].

4.2.1.1 Oxidative Cleavage of alkenes

The schematic depicted below (Figure 4.2) depicts olefins undergoing oxidative cleavage to afford the desired carbonyl complex in good yield. The cyclohexene reacts with a small amount of ruthenium trichloride in the presence of NaOCl dissolved in dichloromethane to give hexanedioic acid. This reaction is shown in fig. 4.2 below.

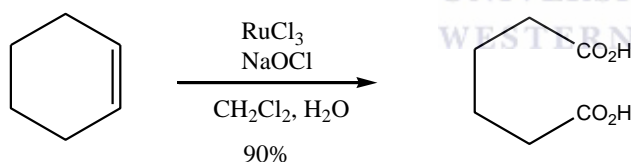


Figure 4.2: A general scheme pertaining to the synthesis of carboxylic acids [12].

The reaction conditions can be modified in order for the catalytic system to favour the formation of cis-diols/dialcohols and not acids. This occurs selectively when the reaction is carried out in short time. A typical example of such a reaction is shown below.

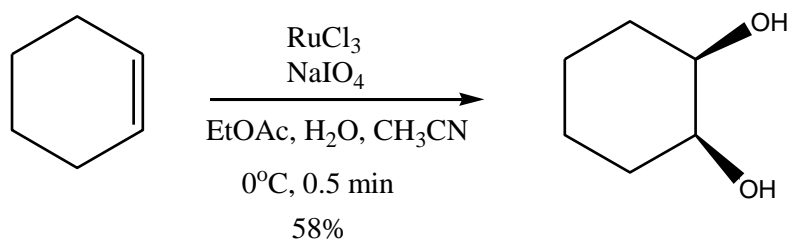


Figure 4.3: A general selective scheme for the synthesis of *cis*-dihydroxyls [11].

Epoxides can be achieved in a similar catalytic setup as for the production of carboxylic acids except that the use of a nitrogen ligand is employed in order to coordinate the active species that is generated *in situ*.

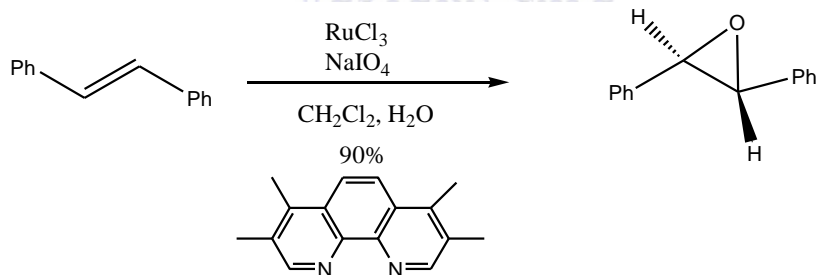


Figure 4.4: A general ruthenium scheme for the epoxidation of alkenes [13].

4.3 Mechanism of Catalyzed Oxidative Cleavage of Alkenes by ruthenium.

A stoichiometric amount of the potent oxidant, rutheniumtetroxide (**II**), has long been known to oxidatively fragment alkenes into corresponding carboxylic acids. This

transformation of olefins, catalyzed by ruthenium, has been achieved by assistances of a range of oxygen donors, e.g. NaIO₄ and NaOCl as primary oxidants [2-8]. The precise mechanistic study of reactions containing low-valent ruthenium complexes as catalysts is known, and proposes the formation of a metal-oxo (**II**) intermediate as the active species. This can be seen in the following catalytic cycle (Fig. 4.5).

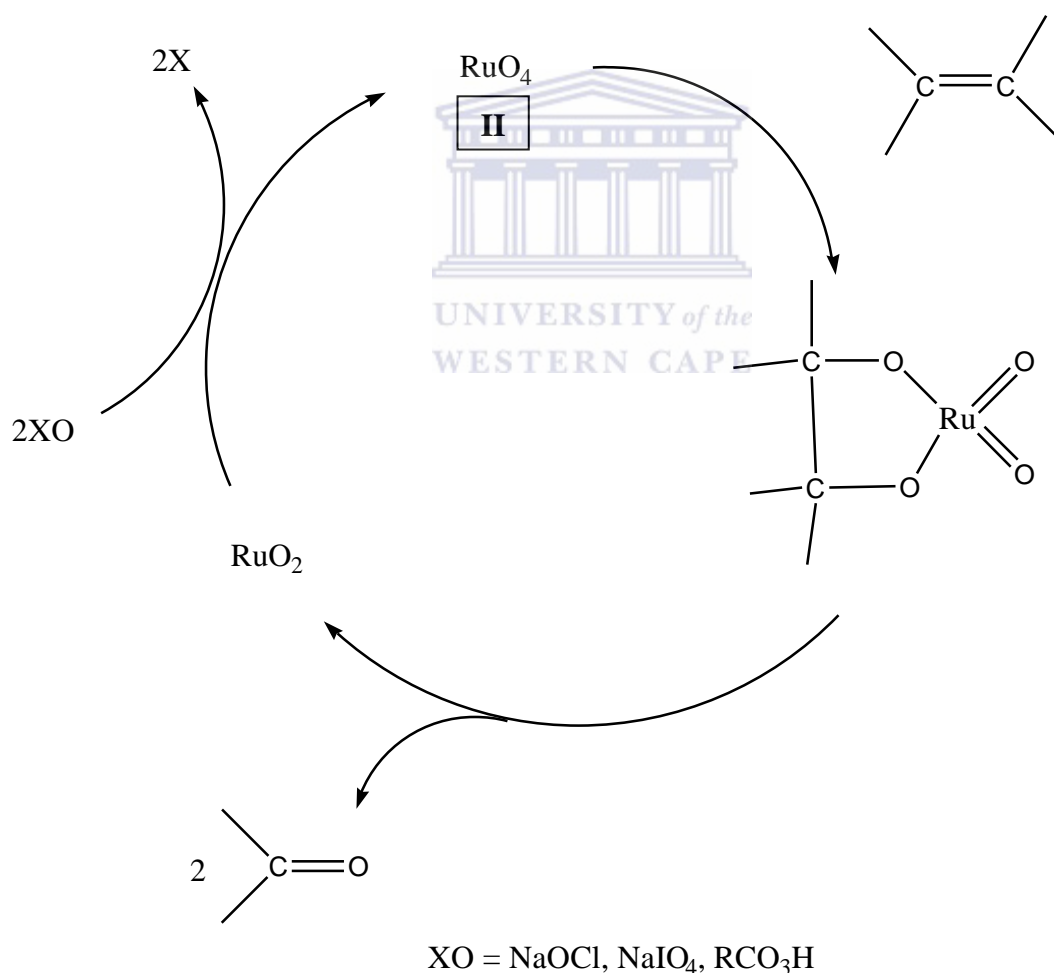


Figure 4.5: A catalytic cycle for ruthenium-catalyzed oxidative cleavage of olefins [7].

4.4 Results and Discussion: Oxidative Cleavage of 1-Octene by ruthenium catalyst

The following schematic diagram illustrates the oxidative cleavage of 1-octene to form the acid product. The reaction was carried out in a biphasic solvent system involving tetrachloromethane, acetonitrile and water.

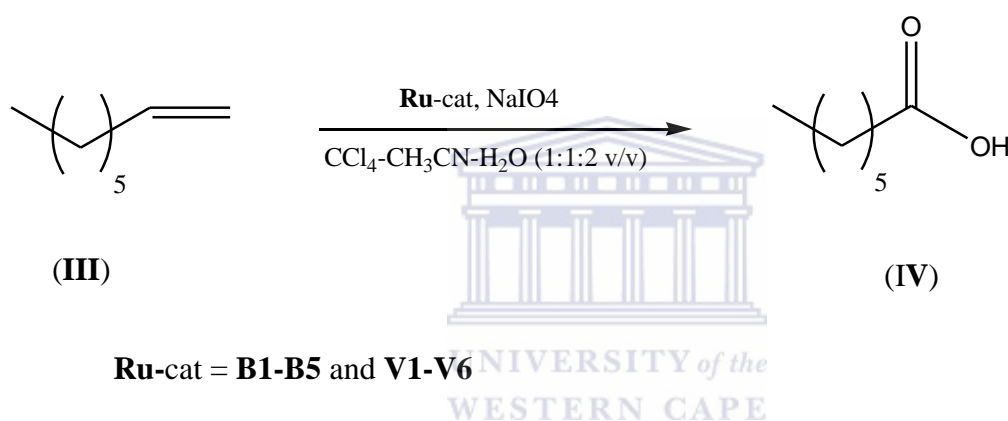


Figure 4.6: A general oxidative cleavage of 1-octene in a biphasic solvent.

The low-valent ruthenium complexes were used with sodium periodate (NaIO_4) as the cooxidant.

4.4.1 Oxidative cleavage of 1-octene by neutral and Cationic mono-, bi-, and multinuclear ruthenium catalysts.

Mononuclear chelating neutral (*N, N*) (**B1** and **B3**) and mono- and bi-nuclear cationic (*N, N*-) (**B2**, **B4** and **B5**) ruthenium (II) catalyst were evaluated as complexes for oxidative

cleavage of linear alkene (1-octene, **III**) at room temperature in a biphasic solvent (CCl₄-CH₃-H₂O). The catalytic systems were found to be highly active for oxidative cleavage of 1-octene with the chosen cooxidant (*vide supra*). The yields ranged from moderate to good, Table 4.1 summarizes the results obtained for the oxidation of the linear alkene (1-octene, **III**). The results are within the range as those previously reported and are comparable for the oxidation of the same linear olefinic substrate.



Chapter 4: Application of mono-, bi-, and multinuclear neutral and cationic Ru(II) catalysts in the oxidative cleavage of 1-octene.

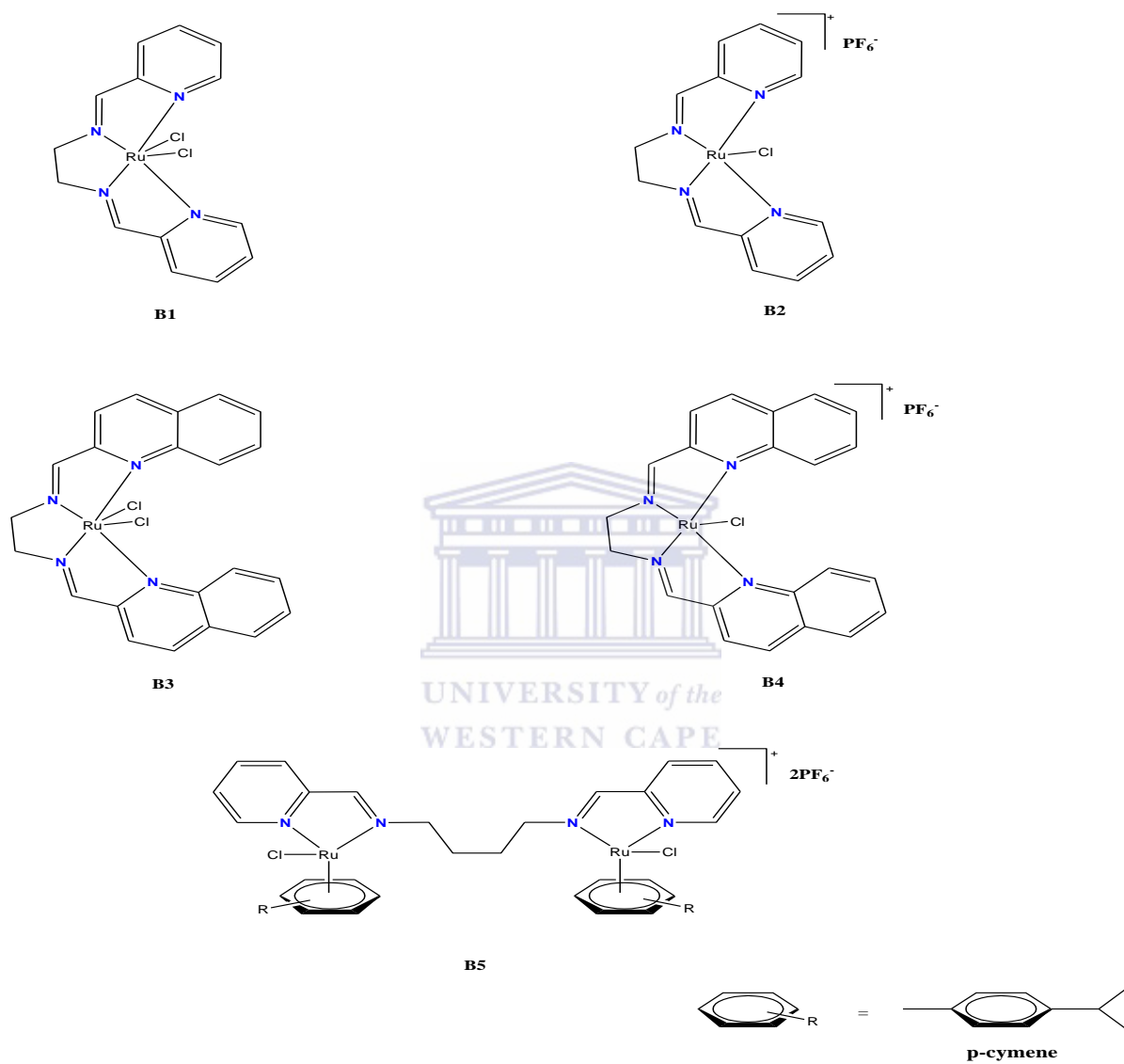


Figure 4.7(a): Scheme representing mono- and binuclear neutral and cationic (*N,N*) Ru(II) catalysts.

Chapter 4: Application of mono-, bi-, and multinuclear neutral and cationic Ru(II) catalysts in the oxidative cleavage of 1-octene.

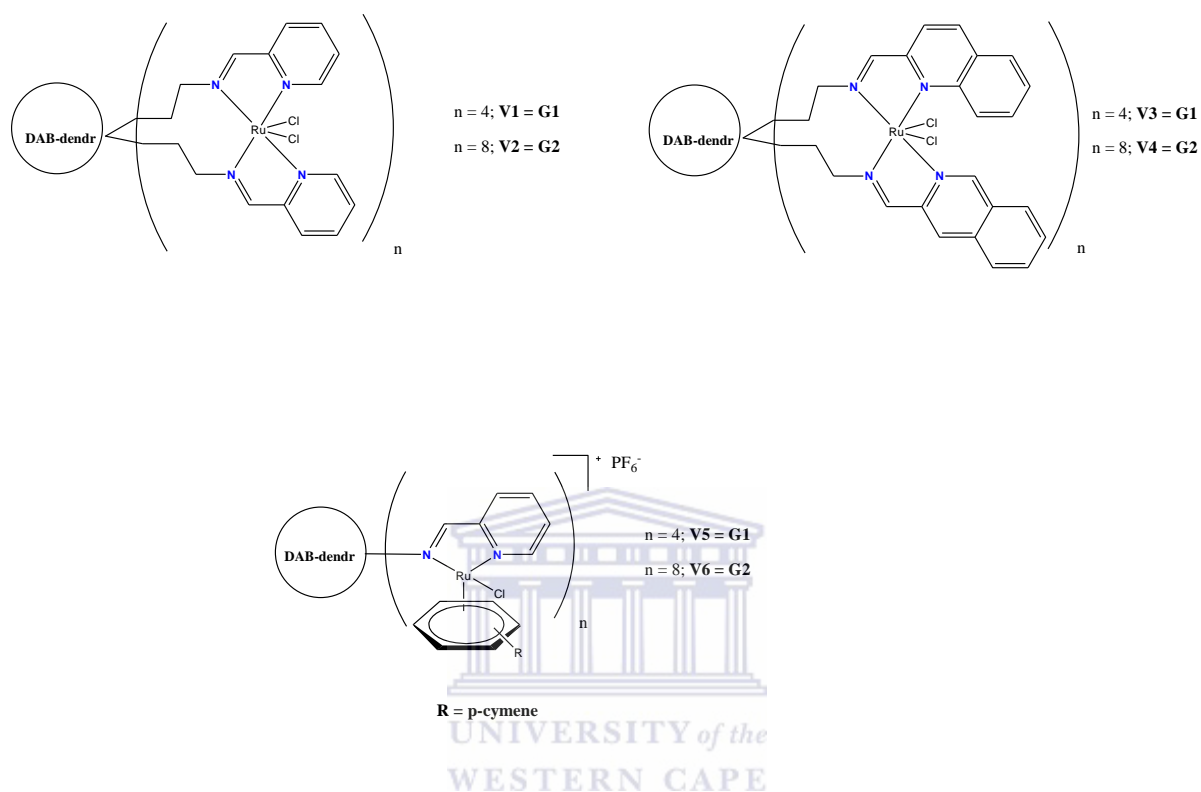


Figure 4.7(b): Scheme representing tetra- and octanuclear neutral and cationic (N,N) Ru(II) catalysts.

It was confirmed that the *in situ* generated active species, ruthenium tetroxide (**I**), under Sharpless conditions ensures the fragmentation of the C-C double bond to corresponding acids. It was also observed that there was an induction period (10-15 minutes) before the formation of the active species that was evident by the colour change to pale-yellow indicative of the presence of the active species. The colour of the catalytic reaction mixture changes from purple to yellow in the case of complex **B1-B4**. The experimental setup for the catalytic reactions is a less complex one, with the major products being the acids. The yields reported herein were higher than some of the previous reported reactions that employ a ruthenium system $[\text{RuCl}_2(\text{PPh}_3)_3]/\text{PhIO}$ [16].

Chapter 4: Application of mono-, bi-, and multinuclear neutral and cationic Ru(II) catalysts in the oxidative cleavage of 1-octene.

Competing reactions such as aldehydes formation were observed but in yields that were less than 5%. The presence of acetonitrile in the biphasic solvent system elevated the selectivity of acids over undesired products as reported for the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{IO}(\text{OH})_5$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{NaIO}_4$ systems respectively [10,12]. The completion of the catalytic reaction was confirmed by TLC.

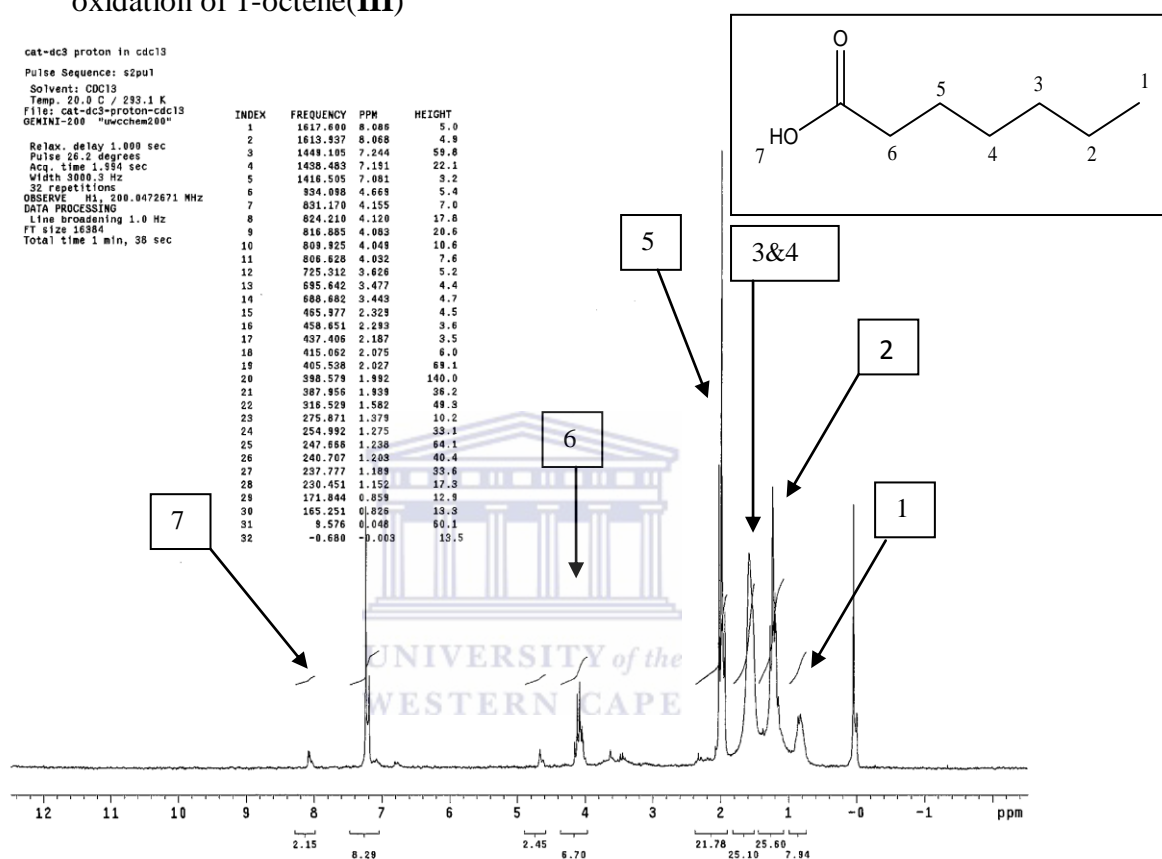


Table 4.1: Oxidative Cleavage of 1-octene to heptanoic acid by **B1-B5** and **V1-V6**/NaIO₄.

Entry	Catalysts	Yield (%) [TO]	Reaction time (h)
1	B1	70(140)	2
2	B2	70(140)	2
3	B3	78(156)	2
4	B4	78(156)	2
5	B5	80(160)	2
6	V1	84(168)	2
7	V2	86(172)	2
8	V3	87(174)	2
9	V4	89(178)	2
10	V5	90(197)	2
11	V6	91(180)	2

Reaction conditions: alkene (0.556 mmol), catalyst (0.00278 mmol, **V-1**), and periodic acid (2.78 mmol) were added to a mixture of CCl₄-CH₃CN-H₂O (1:1:2 v/v), stirring at room temperature for 2 h. TO = turnover = moles of the product/moles of the catalyst.

Figure 4.8: ^1H NMR spectra of the crude product(IV) obtained after the ruthenium-catalyzed oxidation of 1-octene(III)



Reaction conditions: (a) catalyst (0.00278 mmol, **V-4**), 1-octene (0.556 mmol), and periodic acid (2.78 mmol).

The ^1H NMR was employed in order to aid with the identification of the product. The spectra of the crude product confirm cleavage of 1-octene to heptanoic acid. All the catalyst evaluated for the catalyzed oxidative cleavage of 1-octene gave heptanoic acid as the major product. Complex **B3** and **B4** gave higher yields of the acid in comparison with complex **B1** and **B2**. The higher conversion of the substrate by the former mentioned complexes was

attributed to the steric bulkiness around the active metal centre. The dendritic catalysts, **V3** and **V4**, gave higher conversion of the substrate/alkene in comparison to the dendritic catalysts, **V1** and **V2**, further confirming the results obtained for the mononuclear complexes with the same quinoline moiety. The yields of the product reached 90%, catalyzed by complex **V6**.

Thus it can be concluded that the oxidative cleavage of 1-octene with the synthesized catalyst systems required only mild reaction conditions at room temperature to achieve the results.

4.5 Conclusion

The results of the present studies convincingly demonstrate the catalytic ability of Ruthenium II-complexes towards the catalyzed oxidative cleavage of 1-octenes with NaIO₄ as a cooxidant. Under the catalytic conditions setup for the oxidation of the substrate/alkene, it can be thus concluded that the catalyst system reported herein for the first time are able to oxidize the chosen substrate/alkene.

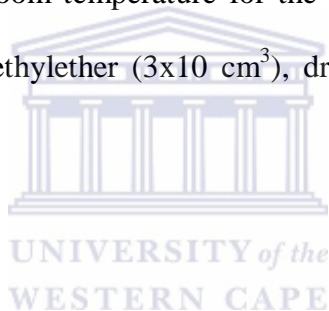
4.6 Materials and Methods

Infrared spectroscopic measurements in the range between 4000 and 450 cm⁻¹ were recorded on Perkin-Elmer spectrum-100 Series FT-IR spectrophotometer. The ¹H and ¹³C NMR measurements were recorded on a Varian XR200 MHz spectrometer. The ¹H and ¹³C

chemical shifts were referenced internally using the residual CDCl_3 (99.9%) and reported relative to the internal standard tetramethylsilane (TMS).

4.6.1 *General procedure for oxidative cleavage of 1-octene*

1-octene (0.556 mmol), catalyst (0.002782 mmol), and NaIO_4 (2.782 mmol) were added in a biphasic solvent system [CH_3CN (5 cm^3), CCl_4 (5 cm^3), and H_2O (10 cm^3)] with stirring. The reaction mixture was stirred at room temperature for the times specified in Table 4.1. The products were extracted with diethylether ($3 \times 10 \text{ cm}^3$), dried over MgSO_4 , and evaporated under reduced pressure.



References:

1. (a) R. Pappo, D. S. Allen, Jr., R. U. Lemieux and W. S. Johnson, *J. Org. Chem.*, 1956, **21**, 478; (b) T. M. K. Shing, in *Comprehensive Organic Synthesis*, B. M. Trost and I. Fleming, ed., Pergamon Press, Oxford, 1991, Vol. 7, pp 703-716.
2. J. L. Courtney, In: Mijs W. J. De Jonge CRHI (eds) *Organic Synthesis by oxidation with metal compounds*. Plenum Press, New York, pp 445-467.
3. F. E. Kuehn, R. W. Fischer, T. Weskamp, (2004) In: M. Beller, C. Bolm, (eds) *Transition metals for organic synthesis*, 2nd edn, Wiley-VHC Verlag GmbH, Weinheim, pp427-436.
4. R. W. Fischer, W. A. Herrmann, T. Weskamp, (1998) In: M. Beller, C. Bolm, (eds) *Transition metals for organic synthesis: building blocks and fine chemicals*, vol 2. Wiley, New York, pp282-289.
5. D. G. Lee, T. Chen, (1991) In: B. M. Trost, S.V. Ley, (eds) *Comprehensive organic synthesis*, vol 7. Pergamon Press, Oxford, pp 541-591.
6. H. Milmeum, (1987) In: G. Wilkison, R. D. Gillard, J. A. McCleverty, (eds) *Comprehensive coordination chemistry*, vol 6. Pergamon Press, Oxford, pp 317-410.
7. R. A. Sheldon, I. Arends, U. Hanefeld, *Green Chemistry and catalysis*,
8. E. S. Gore, *Platinum Metals Rev*, 1983, 27, 111.
9. P. N. Rylander, *Engelhard Tech Bull*, 1969, 135.
10. P. H. J. Carlsen, T. Katsuki, V. S. Martin, K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936.
11. L. F. Tietze, C. Schneider, A. Montenbruck, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 980.

12. S. Wolfe, S. K. Hasan, J. R. Campbell, *J. Chem. Soc. Chem. Commun.*, 1970, 1420.
13. A. F. Diaz, K. K. Kanazawa, G. P. Gardini, *J. Chem. Soc. Chem. Commun.*, 1985, **26**, 362.
14. T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.*, 1998, **98**, 2599.
15. J. Halpern, *Pure and Appl. Chem.*, 1987, **59**, 173.
16. P. Muller, J. Godoy, *Helv. Chim. Acta.*, 1981, **64**, 2531.



5.1 General Conclusions

The present study detailed the synthesis and catalytic application of mono-, bi- and multinuclear ruthenium(II) and rhenium(VII) metallodendrimers. These complexes were synthesized from Schiff-bases (**L1-L4** and **DL1-DL4**) that were synthesized by condensation of primary amines and aldehydes in good yields. These Schiff-bases were subsequently reacted with the respective metal precursors ($[\text{RuCl}_2(\text{dmsO})_4]$, $[(\text{p-cymene})\text{RuCl}_2]_2$ and $\text{CH}_3\text{ReO}_3(\text{MTO})$) and formed complexes with the metals via nitrogen lone pair electrons. The Schiff-base Re(VII) complexes, **C1**, **C2**, **DC1** and **DC2**, were evaluated in the epoxidation reactions of selected cyclic alkenes while the neutral and cationic mono-, bi- and multinuclear ruthenium(II), **B1-B5** and **V1-V6**, complexes were tested as catalysts in the oxidative cleavage of a selected straight chain alkene.

The mono-, binuclear Schiff-base complexes of methyltrioxorhenium (MTO), **C1** and **C2**, and 1st and 2nd generation Re(VII) metallodendrimers, **DC1** and **DC2**, were evaluated in a comparative study as catalysts in the epoxidation of selected cyclic substrates/alkenes, i.e. cyclohexene and *cis*-cyclooctene, respectively. These Schiff-base complexes of MTO, both the discrete mono- and binuclear as well as the metallodendrimers were efficient catalysts in the epoxidation reaction of cyclic substrates/alkenes. The Schiff-base Re(VII) metallodendrimers exhibited superior catalytic efficiency than the mono- and binuclear Schiff-base Re(VII) complexes, i.e. catalytic activity. The complexes, **C1**, **C2**, **DC1** and **DC2**, displayed high selectivity towards the formation of epoxides with no significant formation of side products.

The mono-(**B1-B4**), bi-(**B5**) and multinuclear(**V1-V6**) neutral and cationic Ru(II) complexes were also subjected to a comparative study as catalysts in the oxidative cleavage of 1-octene. The chelating neutral and cationic 1st- and 2nd-generation Ru(II) arene complexes based on the poly(propyleneimine) dendrimer scaffold gave higher yields in comparison to the mono-(**B1-B4**), and binuclear(**B5**) neutral and cationic Ru(II) complexes. In the catalyzed oxidative cleavage of 1-octene, the catalytic active species was confirmed to be ruthenium tetroxide, RuO₄.

In general, the thesis has clearly described the synthesis, characterization and catalytic application of various chelating flexible Schiff-base complexes of Ru(II) and Re(VII) as catalysts for the oxidative cleavage and epoxidation reactions, respectively. The thesis explores new possibilities of development of environmental friendly and efficient catalysts based on dendritic scaffold. In brief the thesis has contributed to Inorganic synthesis and homogeneous catalysis.

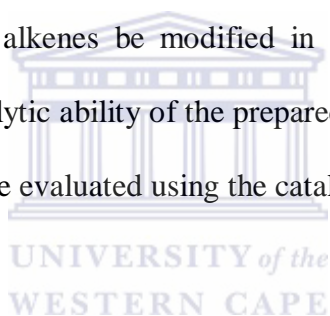
5.2 Recommendations

It is within the study of these synthesized complexes to try and better some of the shortcomings that arose from the study. It was discovered that the Schiff-base complexes of methyltrioxorhenium (MTO) were sensitive to moisture, light and temperature. The bi- and multinuclear Re(VII) complexes hindered thorough characterization as they decompose before they could be analyzed by some of the spectroscopic techniques at hand. It is recommended that a trial for stabilization of these Schiff-base MTO complexes should be

carried out to gain their better understanding. Also their crystal structures should be obtained through growing of crystals and resolving them crystallographically.

The scope of the epoxidation reactions should be widened to include more sensitive alkenes because the epoxidation catalysts behave extremely well during the study of cyclohexene and *cis*-cyclooctene, respectively. The investigation should involve the epoxidation of long chains alkenes and sterically hindered cyclic alkenes.

It is also recommended that in the future, the catalytic reaction conditions for the Ru(II) catalyzed oxidative cleavage of alkenes be modified in order to homogenize the solvent mixture so as to quantify the catalytic ability of the prepared complexes. Long chains alkenes (> C8) and cyclic alkenes are to be evaluated using the catalysts in the future.

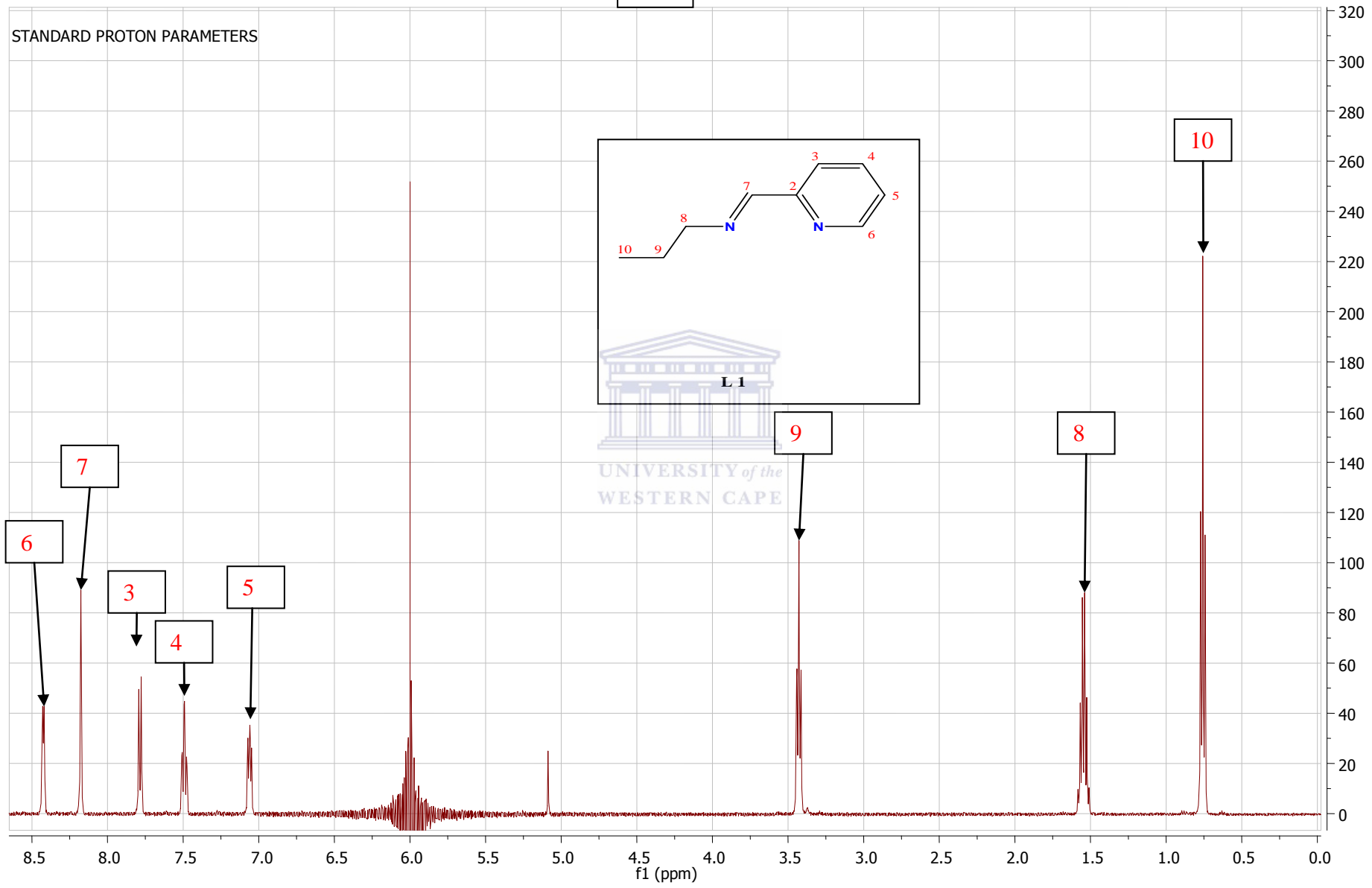


ANNEXURE: Chapter 2

- A** ^1H NMR spectrum of the ligand **L1**.
- B** ^1H NMR spectrum of the ligand **L3**.
- C** ^1H NMR spectrum of the dendrimeric quinoline based ligand **DL3**.
- D** ^1H NMR spectrum of the neutral mononuclear ruthenium complex **B2**.
- E** ESI-MS spectrum of ligand **L4** showing $[\text{M}+\text{H}]^+$ fragment (indicated by arrow).
- F** ESI-MS spectrum of dendrimeric ligand **DL4** showing $[\text{M}+\text{H}]^+$ fragment (indicated by arrow)
- G** ESI-MS spectrum of the neutral dendritic complex **V4** showing $[\text{M}+\text{H}]^+$ fragment (indicated by arrow).
- H** ESI-MS spectrum of the homobimetallic complex **B5** showing $[\text{M}+\text{H}]^+$ fragment (indicated by arrow).



A



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32 repetitions

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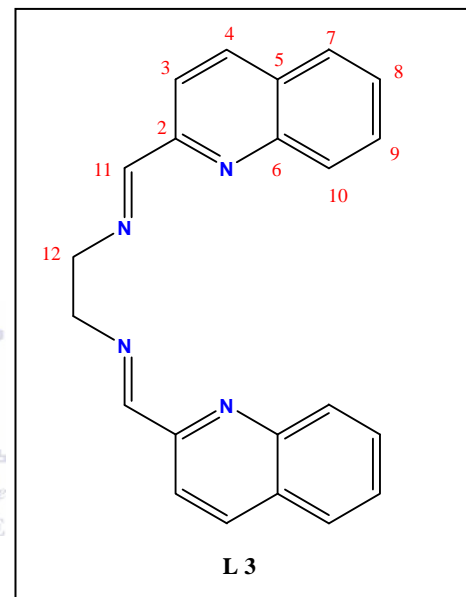
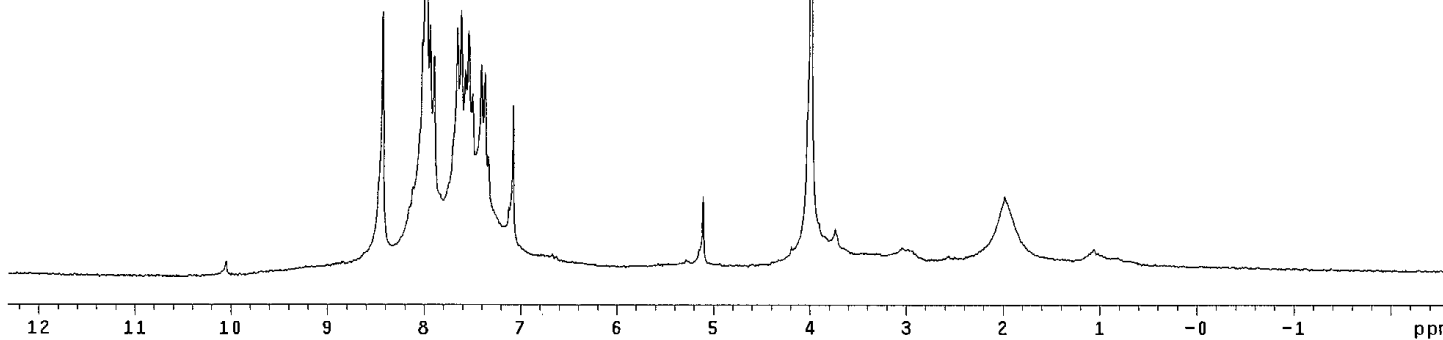
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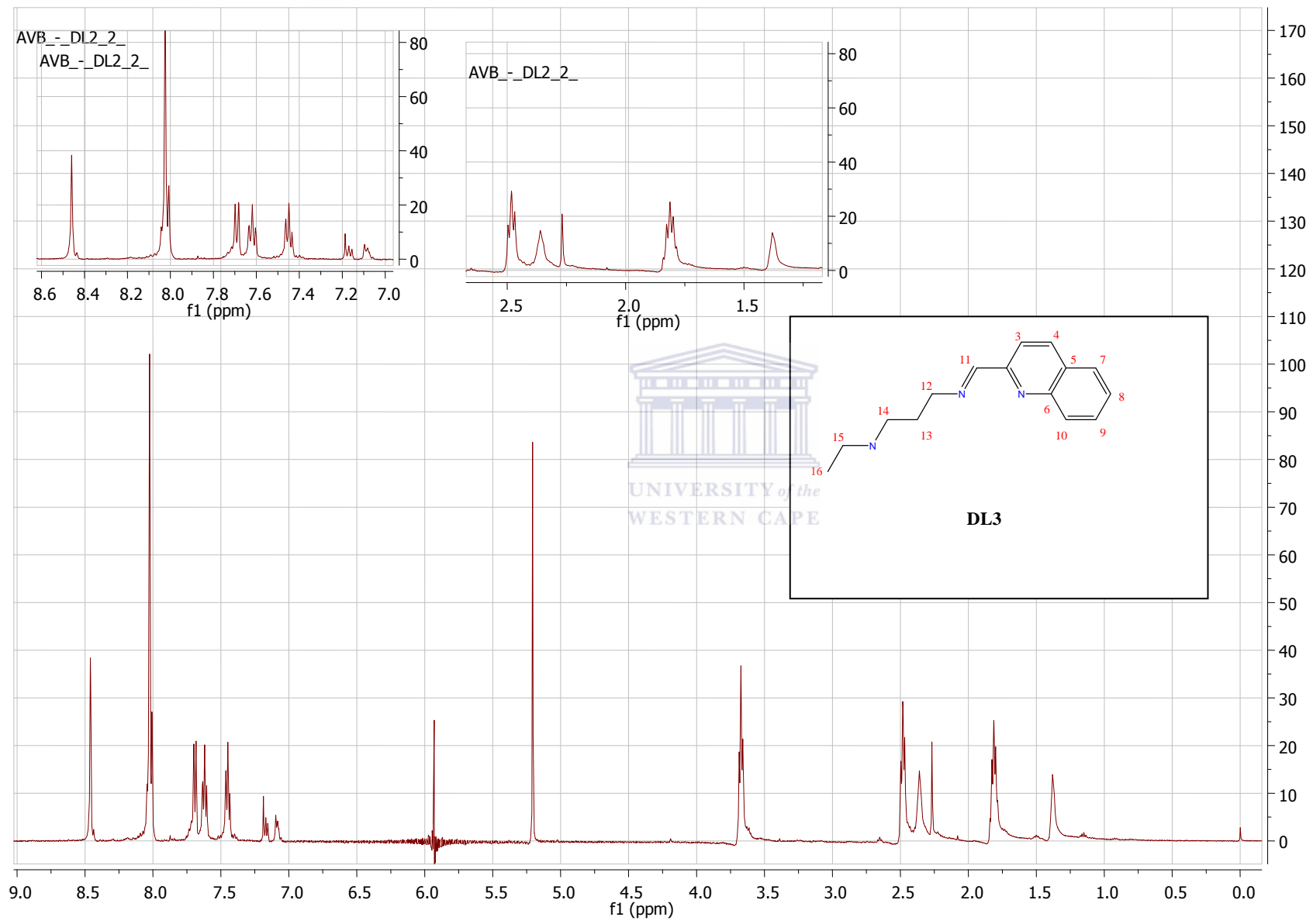
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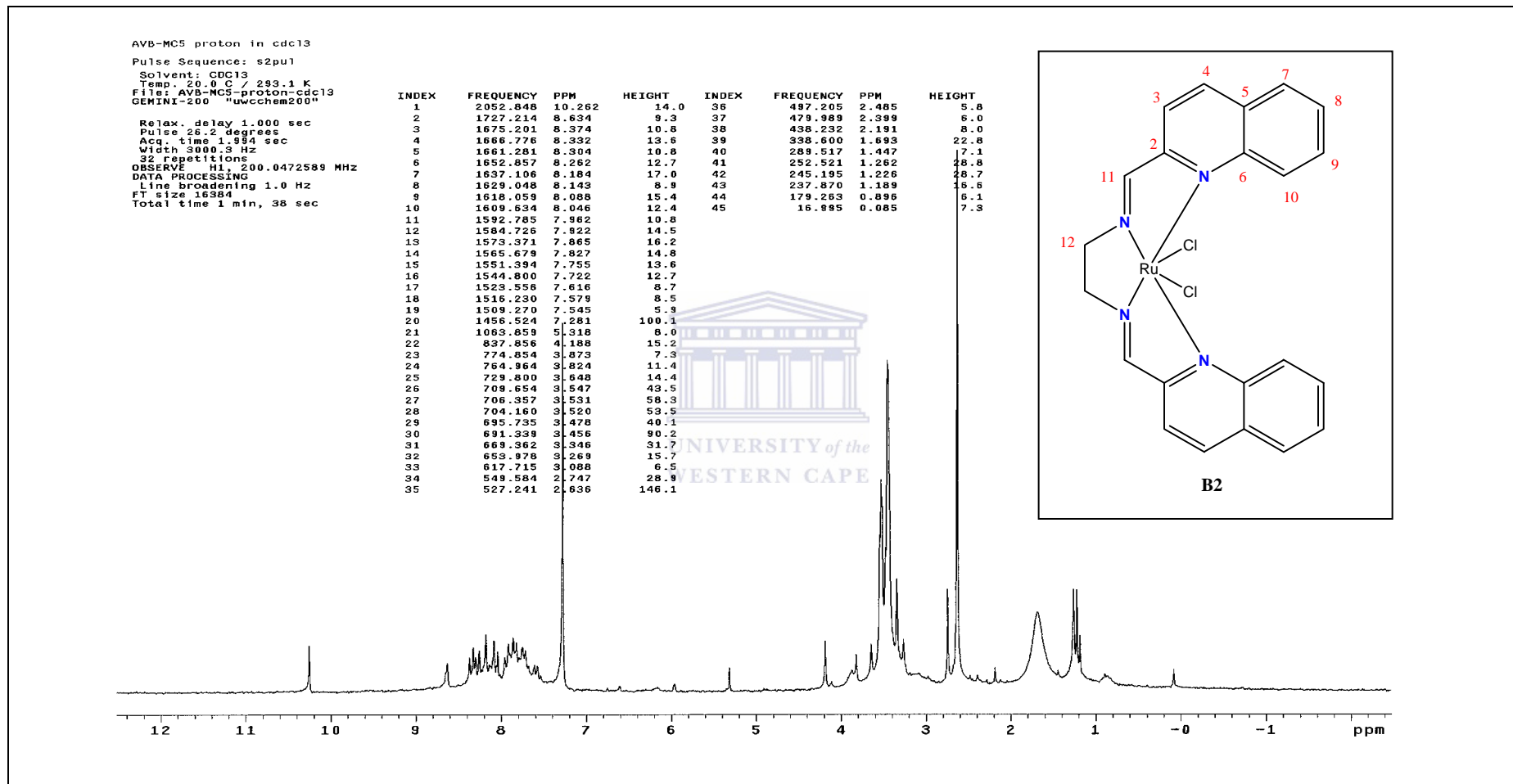
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6	1578.714	7.892	38.5
7	1530.730	7.652	43.2
8	1522.671	7.612	46.3
9	1514.247	7.569	36.1
10	1507.287	7.535	42.7
11	1499.229	7.494	31.9
12	1480.914	7.403	36.9
13	1473.222	7.364	35.6
14	1465.896	7.328	21.1
15	1423.406	7.115	12.2
16	1414.615	7.071	29.9
17	1333.665	6.667	4.0
18	1114.256	5.570	2.4
19	1056.381	5.281	3.0
20	1020.851	5.103	14.1
21	837.705	4.188	5.2
22	795.948	3.979	95.2
23	746.498	3.732	8.3
24	607.673	3.038	5.0
25	511.705	2.558	3.6
26	395.224	1.976	14.1
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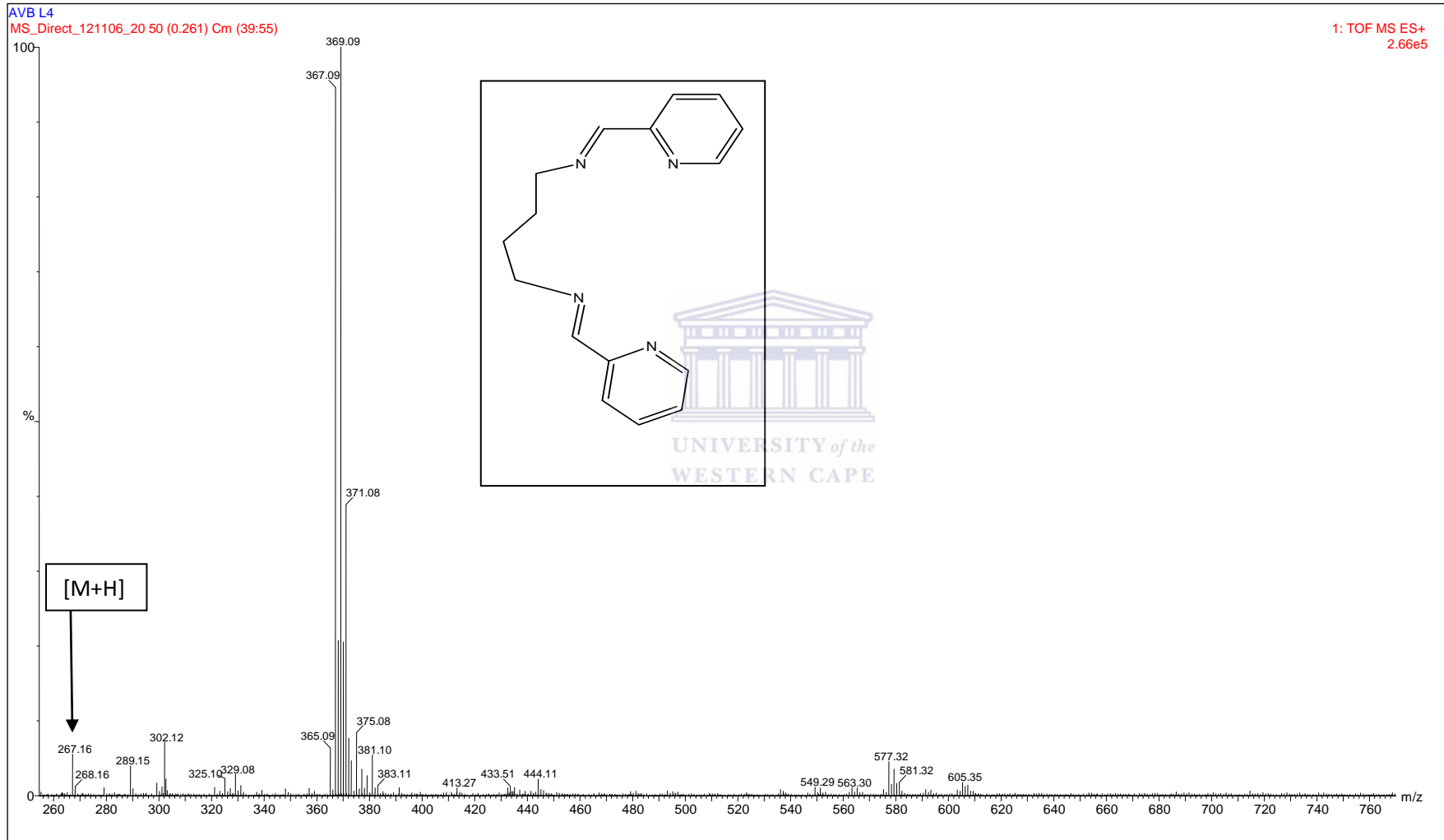




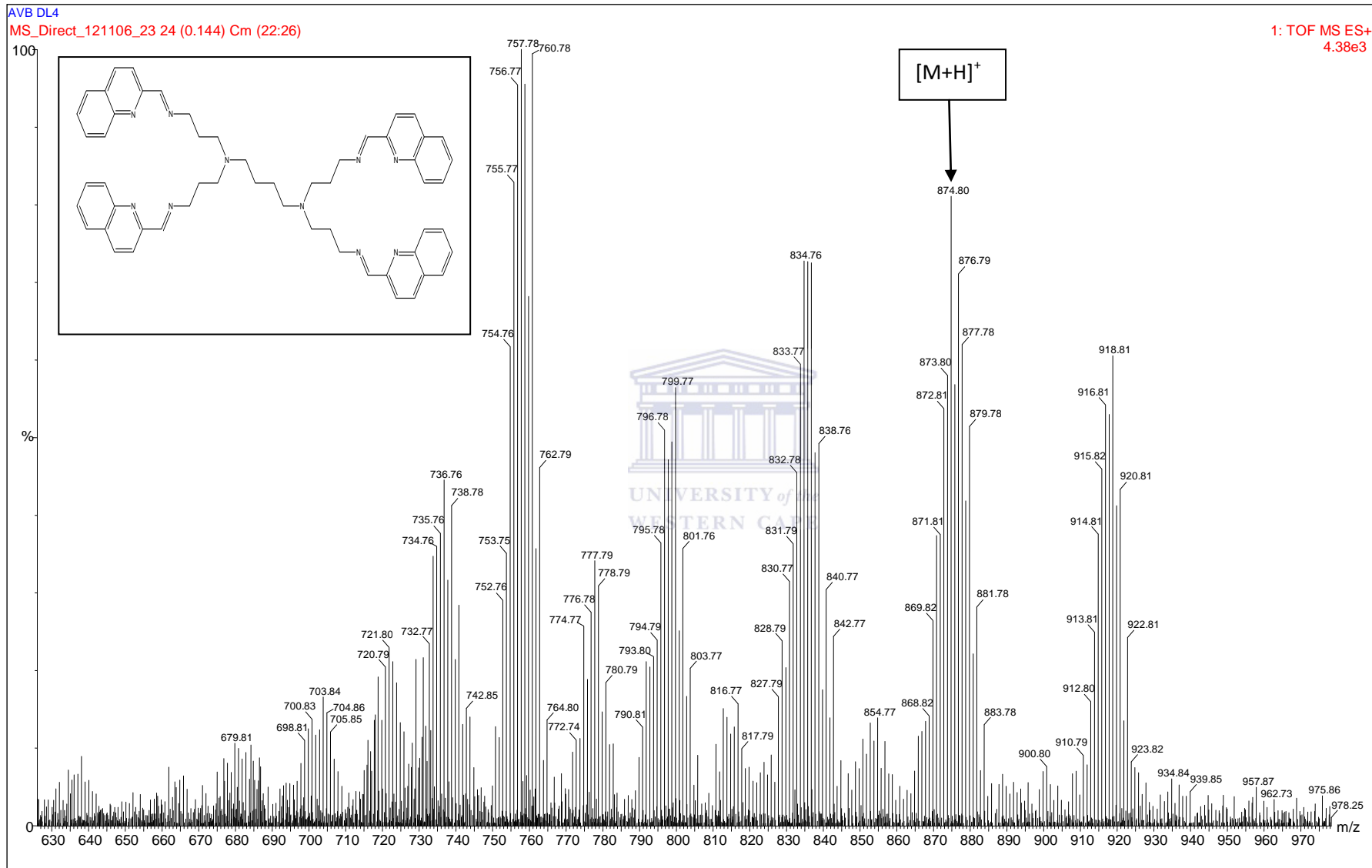
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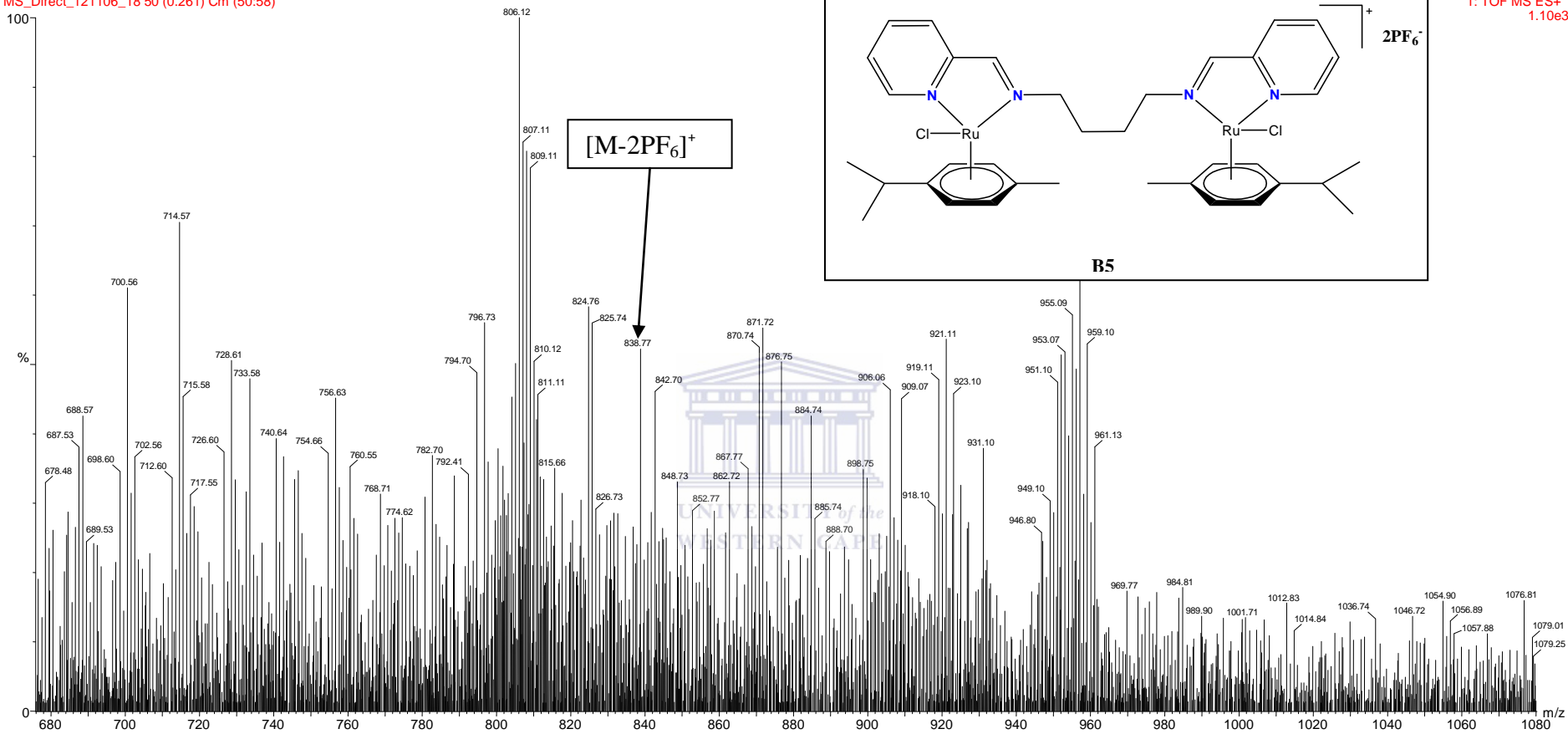


F



H

AVB BCZ
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