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作品名稱：含環胺—亞胺雙牙配基及其鎳錯合物的合成、結構鑑定及烯烴催化聚合反應的研究

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作 者 簡 介

我從小具有追根究底個性，喜歡用不一樣的眼光看事情。國小資源班啓蒙我對科學的興趣，國中數理資源班則培養我研究的方法。到高中，選擇了化學作爲專題研究的科目。

一年半的實驗室生活是難得的經驗。在老師和學長姐的指導下從一次次的失敗中嚐到豐美的成果；爲了解實驗原理我努力研讀書籍，讓我在國際化學奧林匹亞中拿到好成績；理論之完備嚴謹，實驗之變化多端，我從中反覆印證兩者的一體兩面。

烯烴催化的研究告一段落，但研究的態度和精神已在我的生活根深蒂固。在我的人生，我願與研究相隨！

含環胺—亞胺雙牙配基及其鎳錯合物的合成、結構鑑定及烯烴催化聚合反應的研究

摘要

本研究合成含環形胺—亞胺雙牙配基鎳金屬催化劑，用以催化烯烴聚合反應。將 2-甲基丙醛經由溴化、胺化及亞胺化的步驟合成含胺—亞胺的雙牙配基，$Et_2NCMe_2CH=N(2,6\text{-}^iPr_2C_6H_3)$ (3a)、$(c\text{-}C_4H_8)N\text{-}\ CMe_2CH=NPh$ (3b)、$RNCMe_2CH=N(2,6\text{-}Me_2C_6H_3)$ (R = c-C_4H_8 3c，c-C_5H_{10} 3d)。再將配基和 $Ni(DME)Br_2$ (DME = 1,2-二甲烷氧基乙烷)反應，形成鎳金屬錯合物 $Ni[Et_2NCMe_2CH=N(2,6\text{-}^iPr_2C_6H_3)]Br_2$ (4a)、$Ni[RNCMe_2CH=N\ (2,6\text{-}Me_2C_6H_3)]Br_2$ (R = c-C_4H_8 4c，c-C_5H_{10} 4d)，並作結構鑑定。其中 3b、3c、3d、4c、4d 均爲合成的新化合物，4d 獲得 X 光單晶繞射結構。

以合成之鎳錯合物作爲催化劑，催化乙烯或降冰片烯(C_7H_{10})的聚合反應，探討反應活性和高分子產物的性質。與含相同碳數的錯合物比較，在胺基具環形取代基的錯合物對乙烯的催化活性較佳，聚乙烯產物分子量較高，分子量分布範圍狹窄；其對降冰片烯的催化活性略遜於非環形者。同爲環形取代基時，六環較五環者對乙烯的催化活性較差，但對降冰片烯的催化活性較佳。顯示乙烯聚合與降冰片烯聚合有不同的反應決定步驟。催化劑及配基的設計的確可以操控聚合反應及其高分子產物的性質。

Nickel Complexes Bearing Amine-Imine Bidentate Ligand - Syntheses, Structure, and Reactivity for Olefin Polymerization

Abstract

The synthesis of α-amino aldeimines $Et_2NCMe_2CH=N(2,6\text{-}^iPr_2C_6H_3)$ (**3a**), $(c\text{-}C_4H_8)NCMe_2CH=NPh$ (**3b**), $RNCMe_2CH=N(2,6\text{-}Me_2C_6H_3)$ (R = $c\text{-}C_4H_8$ **3c**, $c\text{-}C_5H_{10}$ **3d**), as well as the nickel complexes $Ni[Et_2NCMe_2C\text{-}H=N(2,6\text{-}^iPr_2C_6H_3)]Br_2$ (**4a**), $Ni[RNCMe_2CH=N(2,6\text{-}Me_2C_6H_3)]Br_2$ (R = $c\text{-}C_4H_8$ **4c**, $c\text{-}C_5H_{10}$ **4d**) has been succeeded. Their structures were mainly determined by spectroscopy or elemental analysis. The complex **4d** was characterized by X-ray crystallographic analysis. It shows that the nickel complex has distorted tetrahedral configuration.

The catalytic reactions of ethylene or norbornene polymerization using the newly synthesized nickel complexes are studied. All catalyts show high activity toward studied olefin polymerization. Comparing the data of the catalytic ethylene polymerization for complex **4c** with those of its isomer complex **4a**, the former is found to results in higher activity as well as the larger molecular weight of the PE products with the narrower dispersity. On the contrary, **4c** shows lower activity in the reactions of norbornene polymerization than **4a**. For the cyclic amine derivatives, **4c** of five-membered amino group shows better catalytic activity toward ethylene polymerization than **4d** of six-membered amino group. But **4d** gives better perfomance for norbornene polymerization than **4c**. Such results indicate that the processes of ethylene and norbornene polymerization might have different rate-determining steps. These study confirms that the design of ligand and catalyst are crucial with respect to the control of the catalytic olefin polymerization and the properties of the polymeric products.

含環胺—亞胺雙牙配基及其鎳錯合物的合成、結構鑑定及烯烴催化聚合反應的研究

壹、背景介紹

自 1950 年代，Ziegler 及 Natta 發現 Ti-Al 組成的非勻相觸媒對烯烴聚合的催化反應以來，化學家繼續找尋催化效果好、產物具特殊性能之聚合反應觸媒[1]。1980 年，Sinn 及 Kaminsky 發現 Ti-Al 及 Zr-Al 組成的勻相觸媒系統，可聚合 Ziegler-Natta 觸媒無法聚合之單體如苯乙烯等，開創了合成聚合反應觸媒的新紀元[2]。到了 1990 年代，化學家開始著手研究「後過渡金屬」(8~11 族)的觸媒系統，Brookhart 發展具高度立體效應的雙亞胺基的鎳、鈀及鐵錯合物的乙烯聚合[3]；Grubbs 則以碳烯基釕錯合物(含 Ru=C 基)開闢了開環聚合反應[4]。由於許多過渡金屬輔以適合的配基，即展現了特定的催化效能，如何找尋適當的配基與金屬配合便成爲研究開發新催化劑的重要課題。

貳、研究動機

一般認爲，配基必須能穩定金屬陽離子、金屬錯合物幾何結構，並扮演控制催化劑氧化數、活性位置立體條件等角色。在考量配基的立體控制功能上，非對稱的混合雙牙配基(hybrid bidentate)是開發新催化劑的重點。由於文獻中沒有對胺－亞胺雙牙配基催化劑烯烴聚合反應的相關研究，目前已知的例子均爲台大化學系陳竹亭教授實驗室所首創，因此，希望能就此種非對稱的雙牙配位基系統，尋求有效的烯烴聚合新催化劑。

參、研究目的

合成新的含環形胺－亞胺非對稱雙牙配基及其過渡金屬錯合物催化劑，探討相關合成反應及新催化劑對乙烯及降冰片烯的催化活性。

肆、文獻探討

一、高分子聚合物基本特性[5]

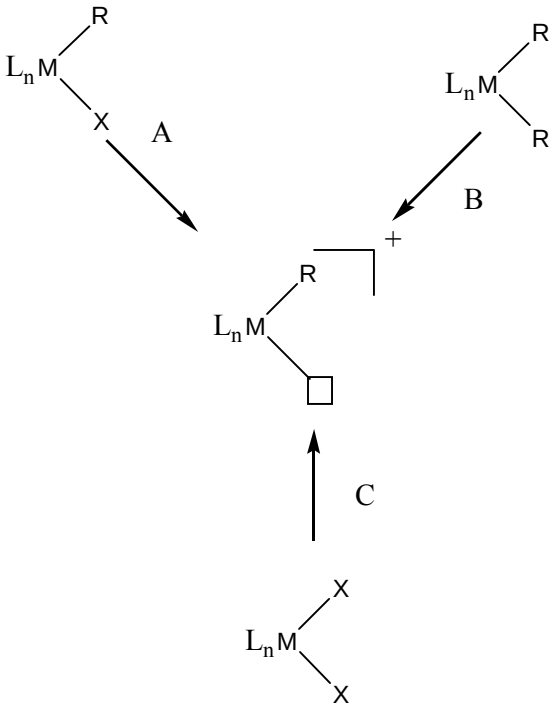
比起一般的化合物，聚合物多是由不同分子量的長鏈所組成的混合物，所以沒有一特定的分子量，而是分布於一個範圍；分子量也意味著聚合物中單體的數量，這兩者均影響聚合物的物理及材料性質而進一步影響其工業用途。例如分子量高於 10000 的耐綸才有實用價值，低於此值的產物爲易碎的固體。

聚合物的熔點和玻璃轉換溫度(T_g) 反應出聚合物的晶型，也反應出材料的彈性、受力強度及適用溫度。線性結晶型聚合物密度高、熔點高、規則性高；相反的，非晶型固體通常其分支較多，堆疊不緊密。一般的聚合物皆含有晶型和非晶型的區域。

二、過渡金屬催化劑的活化步驟

1.活化位的形成[6]

嚴格說來，所合成的金屬錯合物是催化劑的前驅物，必須形成如$[L_nMR]^+$的有機金屬化合物，催化反應才能進行。得到$[L_nMR]^+$ 的形式有三種方法，如右圖所示：



A:藉鹽基消去法(salt elimination)除去帶負電的配基，如鹵素。

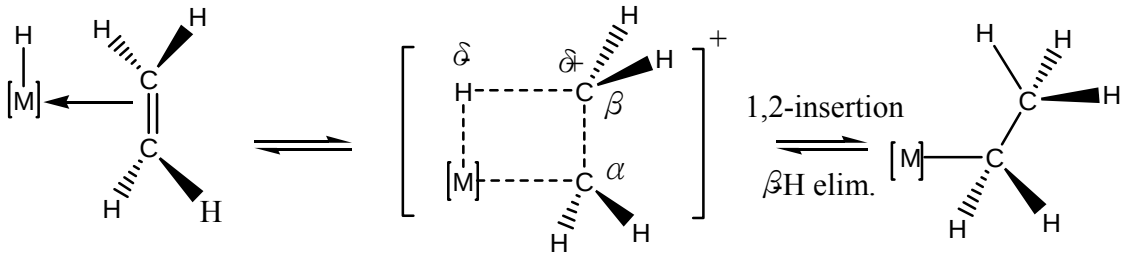
B:藉含氟硼烷 $B(C_6F_5)_3$ 等作摘離劑(abstracting reagent)除去烷基。

C:先以烷基化試劑處理再以摘離劑(abstracting reagent)除去烷基，如以三烷基鋁再以 $B(C_6F_5)_3$ 處理；而有機鋁氧烷(MAO)等試劑可以同時完成兩個步驟。本研究所採用的方法即爲路徑 C。

2.催化聚合反應之進行

2-1 基本概念[7]

在烯烴的聚合中，主要涉及兩種形式的有機金屬反應基本步驟：1,2-插入反應(1,2-insertion)和 β-H 消去反應(β-hydride elimination)。在烯烴類的插入反應中，該烯烴通常在插入前必須先配位；插入反應使金屬上的 H 或 C 轉移加成至烯烴的 β-碳上，因而氫基-烯烴基或烷基-烯烴基錯合物轉化成烷基錯合物。而 β-H 消去反應即是烯烴插入 M-H 鍵的逆向反應。

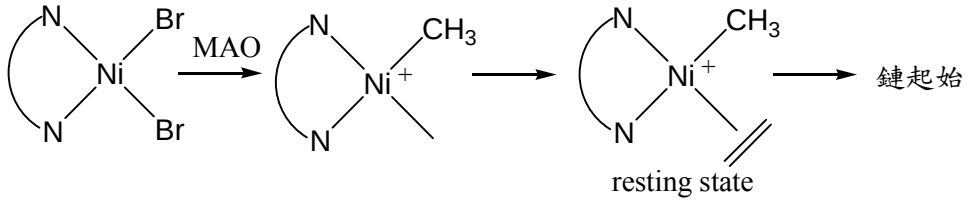


2-2 聚乙烯催化機制

聚合反應的機制包括鏈的起始(initialization)、延續(propagation)、終止(termination)，以及碳鍵分支的產生是幾大重點。下列機制爲 M. Brookhart 針對雙亞胺基鎳金屬錯合物催化劑所提出來的[8]，包括鏈起始(chain initialization)、鏈成長(chain growth)、鏈分支(chain walking)、鏈轉移(chain transfer)幾個步驟。

A. 鏈起始(chain initialization)

如下圖，鎳金屬錯合物以 MAO 處理後，形成烷基錯合物，接著乙烯進行配位，形成烷基-乙烯錯合物的休息態。

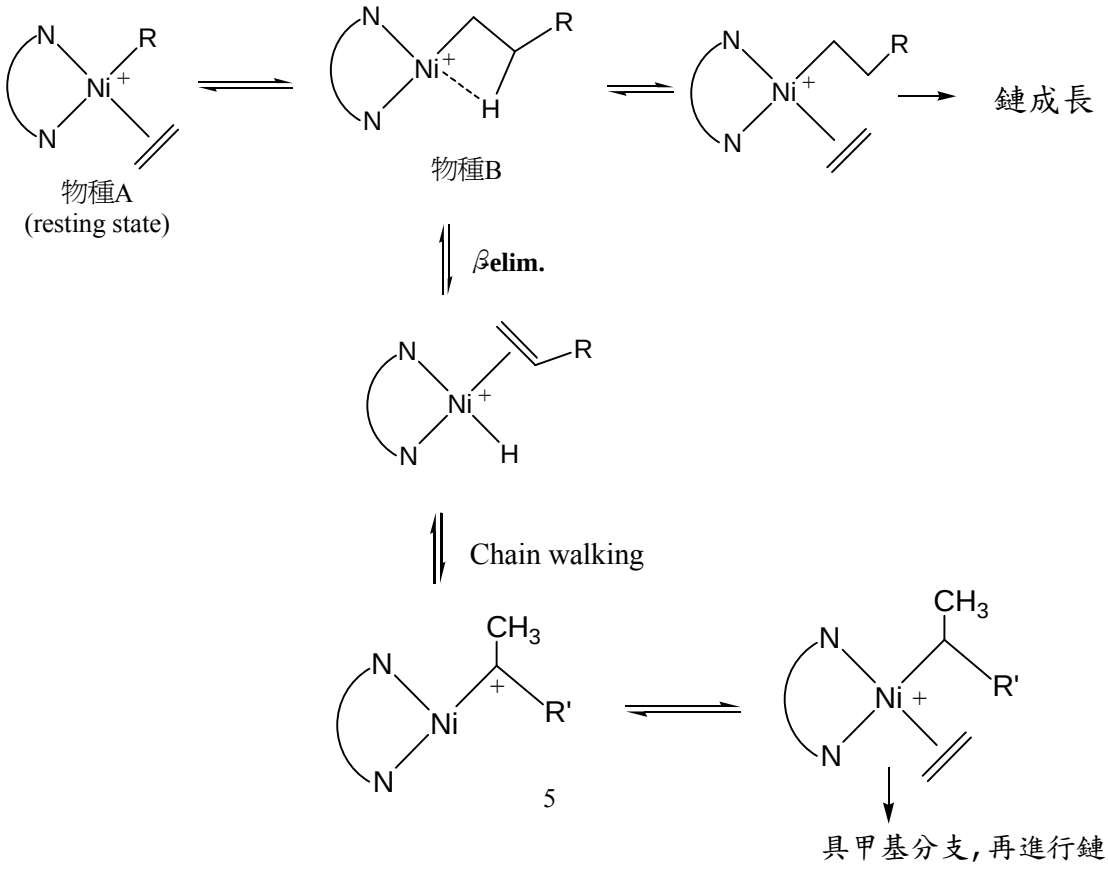


B. 鏈成長(chain growth)

如下圖，乙烯與金屬配位，形成烷基-乙烯錯合物的休息態物種 A(resting state)，經移動插入反應(migration insertion reaction)，形成物種 B。若乙烯配位後繼續重複此兩步驟反應，即爲鏈成長的機制。

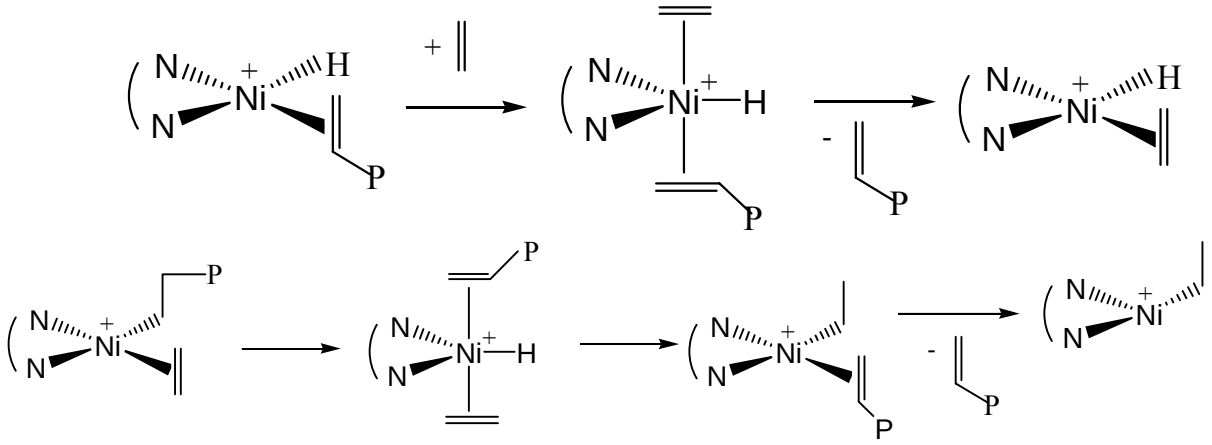
C. 鏈分支(Chain walking)

物種 B 後若進行 C-H 消去反應和再加成(β-hydride elimination and re-addition)，就會形成分支，再進行鏈成長。



D. 鏈轉移(Chain transfer)

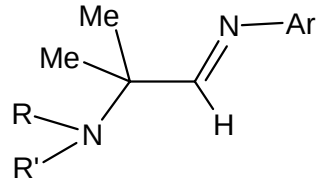
鏈轉移有兩種可能的途徑：第一種末端具不飽和鏈的物種 C 與單體的置換反應，第二種是在物種 A (resting state)時聚合物將 β-氫轉移給單體。兩者結果都使聚合物從金屬活性位置脫離，完成終結步驟，空出反應位進行新的聚合。此步驟特別需要額外的配位空位，Brookhart 在配基上設計的亞胺取代基以立體效應遮蔽配位空位，故能阻止鏈轉移步驟，提昇催化活性，本研究則探究胺取代基的影響。



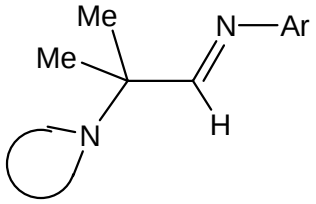
伍、研究方法

一、合成含「胺」及「亞胺」混合官能基之雙牙配基

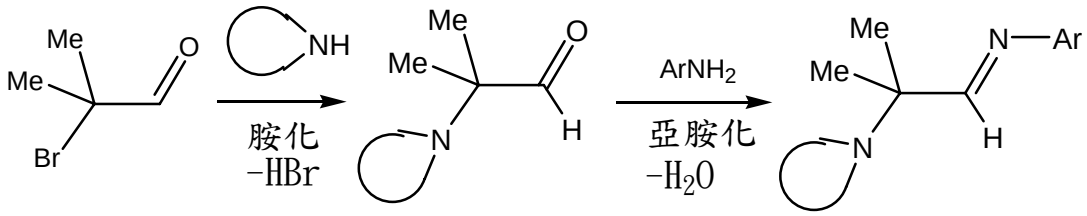
已有一系列具下方結構（A）的胺－亞胺雙牙配基被合成，並且和鎳金屬配位後成爲良好之烯烴催化劑。本計劃擬合成具「環基胺」的新配基（B）。其合成程序分三步：α-溴化醛→胺化→亞胺化，如式(1)，環基胺包括五員環和六員環胺基。



(A)



(B)

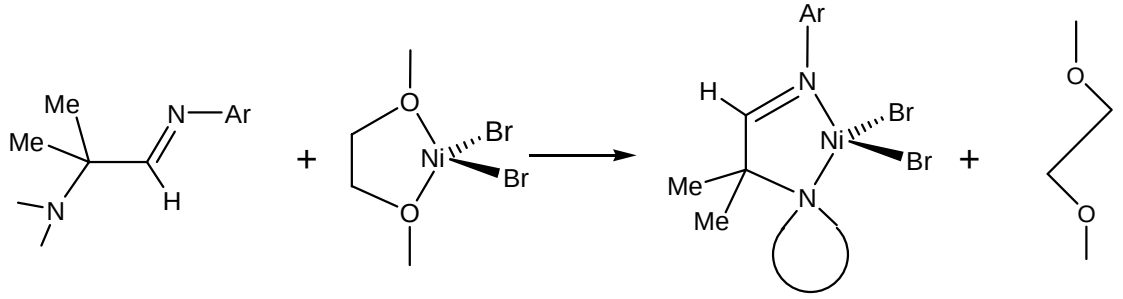


式(1)

(B)

二、合成及鑑定過渡金屬錯合物催化劑

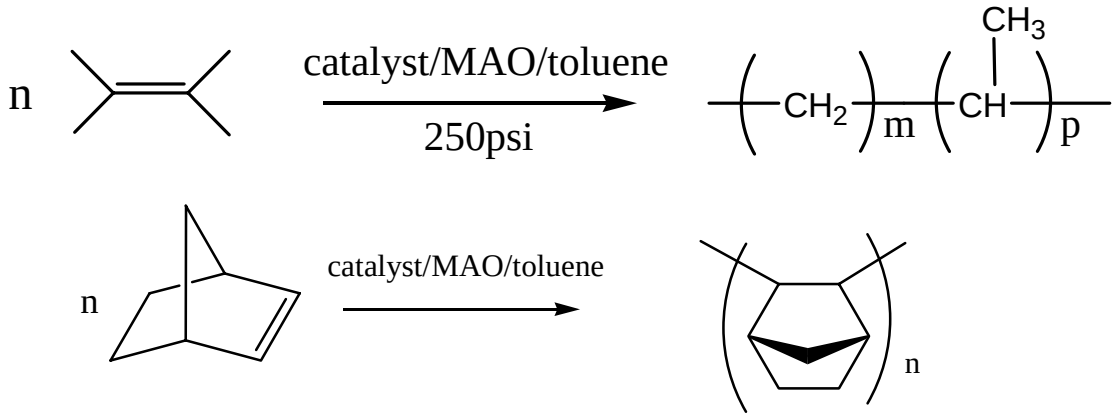
以無機合成的方式將合成的新配基和鎳金屬錯合物 $Ni(DME)Br_2$ 發生取代反應，形成催化劑(C)。



(C)

三、聚合烯烴催化反應

新合成之催化劑以有機鋁氧烷 MAO 爲助催化劑，催化乙烯和降冰片烯聚合反應，測試其活性並檢驗產物性質。



陸、一般實驗程序

一、本實驗所用之藥品皆由廠商直接購得的試藥級藥品。

二、合成錯合物催化劑時所用的無水溶劑皆在氮氣下以適當乾燥劑進行除水：乙醚、甲苯以鈉處理，並加入二苯基甲酮爲指示劑，氮氣下迴流至呈現藍黑色再蒸餾收集；二氯甲烷則以五氧化二磷處理，沸騰迴流再蒸餾收集至棕色瓶防光保存。

三、進行對空氣、水氣敏感的合成時，在無氧無水的氮氣系統操作，包括乾燥箱與 Shlenck 真空管及合成裝置。

柒、分析儀器

一、核磁共振光譜儀：Bruker AC-200, AC-300

二、質譜儀：Finnigan TSQ-46C MASS；Jeol SX-102A MASS

三、元素分析儀：Perkin Elmer 2400

四、X-光單晶繞射儀：荷蘭 Enraf Nonious CAD-4 Kappa Axis XRD(FR 586,FR590)；德國 Siemens Smart CCD XRD

五、紫外光-可見光電子光譜儀： Shimazn U-3010 Spectrophotometer

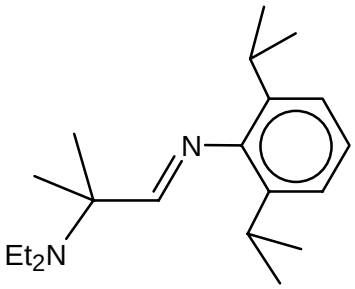
六、凝膠穿透層析儀：Model 2000 Refractive Index Detector

七、微差掃描熱分析儀

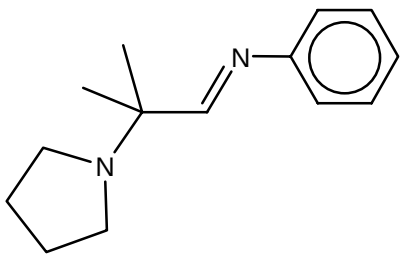
八、研究成果及討論

一、胺-亞胺雙牙配基之合成及鑑定

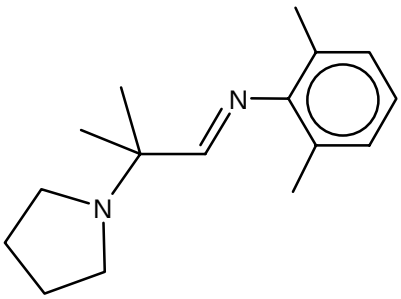
共合成下列四個配基，其中配基 3a 爲已知[9]，根據相同的程序合成新的配基 3b、3c 和 3d。



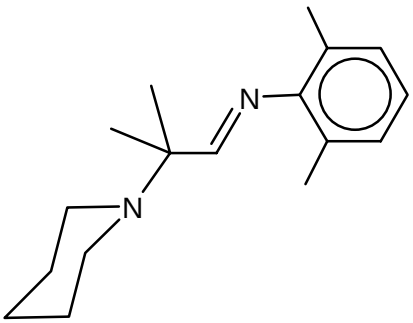
3a



3b



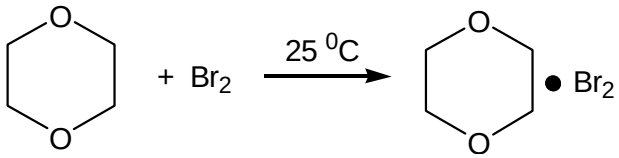
3c



3d

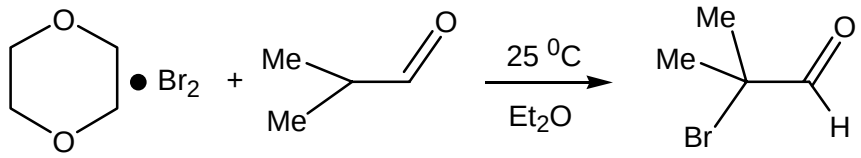
1.起始物：2-溴-2-甲基丙醛($BrCMe_2CHO$) (1)

(a)取 10 mL 1.4-二氧陸圜放入培養皿，將 6 mL 溴緩慢滴入，並以玻棒攪拌均勻，得到揮發性黃色固體。產率 76%。



式(2)

(b)取 6.41 mL 2-甲基丙醛置於錐形瓶，以乙醚爲溶劑，加入合成之黃色二氧六圜溴固體，形成淡黃色溶液，用冰水萃取三次，取有機層，再以無水硫酸鎂除水，過濾，濃縮抽去溶劑。產率 89%。



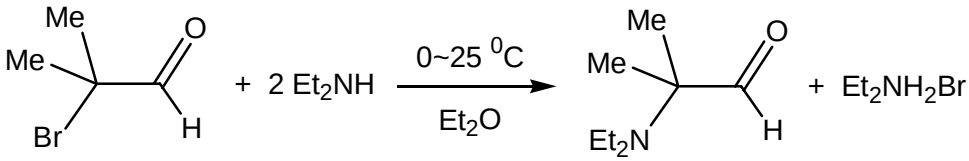
式(3)

產物以 NMR 鑑定

^{1}H NMR ($CDCl_3$)： δ 9.35 (s, 1H, C<u>H</u>O), 1.78 (s, 6H, C<u>H$_3$</u>)

2-A　2-二乙基胺-2-甲基丙醛(Et_2NCMe_2CHO) (2a)

將 11.93g $BrCMe_2CHO$ (1)以乙醚爲溶劑，在冰浴下緩慢加入兩當量的二乙基胺，室溫下攪拌 6 小時，產生白色鹽類沉澱，過濾，濃縮抽去溶劑，得淡黃色液體，產率爲 86%。



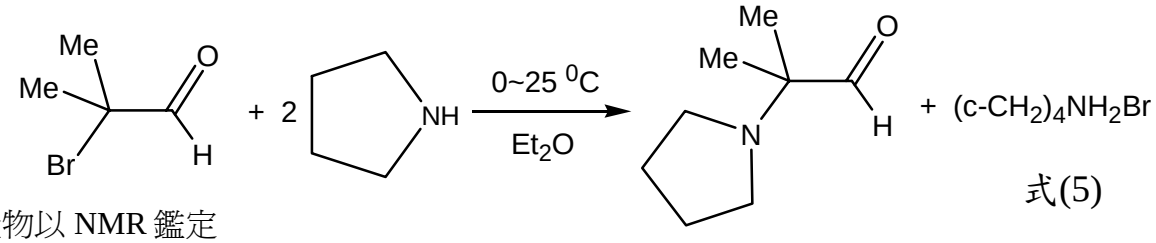
式(4)

產物以 NMR 鑑定

^{1}H NMR ($CDCl_3$)： δ 9.39　(s, 1H, C<u>H</u>O), 2.50 (q, $J_{H\text{-}H}$ = 7.1 Hz, 4H, NC<u>H$_2$</u>CH_3), 1.07 (s, 6H, C<u>H$_3$</u>), 1.02 (t, $J_{H\text{-}H}$ = 7.1 Hz, 6H, NCH_2C<u>H$_3$</u>)

2-B,C　2-環丁基胺-2-甲基丙醛(c-$(CH_2)_4NCMe_2CHO$) (2b)

將 5.87 g $BrCMe_2CHO$ (1)以乙醚爲溶劑，在冰浴下緩慢加入兩當量的環丁胺(pyrolidine)，室溫下攪拌 6 小時，產生分層，取上層，濃縮抽去溶劑，得淡黃色液體，產率爲 89%。



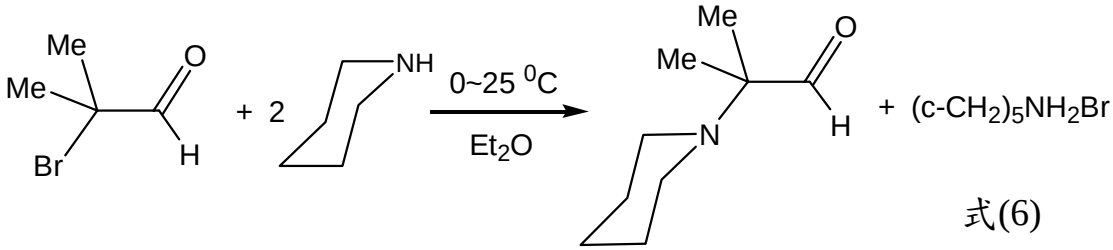
式(5)

產物以 NMR 鑑定

^1H NMR ($CDCl_3$)：δ 9.50 (s, 1H, C<u>H</u>O), 2.63, 1.76 (m, m, 4H, 4H, c-$C_4\underline{H}_8N$) 6H, $C\underline{H}_3$)

2-D　2-環戊基胺-2-甲基丙醛(c-$(CH_2)_5NCMe_2CHO$) (2d)

將 5.02g $BrCMe_2CHO$ (1)以乙醚爲溶劑，在冰浴下緩慢加入兩當量的呱啶(piperidine)，室溫攪拌 2 小時，產生白色鹽類沉澱，過濾，濃縮抽去溶劑，得淡黃色液體，產率爲 79%。



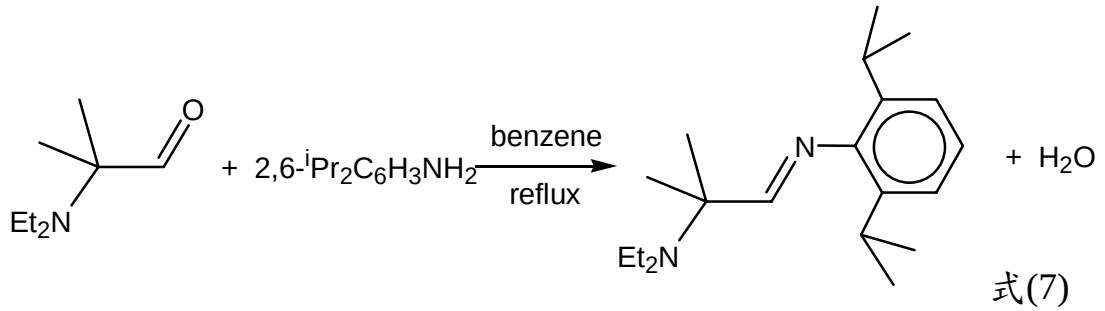
式(6)

產物以 NMR 鑑定

^1H NMR ($CDCl_3$)：δ 9.40 (s, 1H, C<u>H</u>O), 2.37, 1.53, 1.43 (m, m, m, 4H, 4H, 2H, c-$C_5\underline{H}_{10}N$), 1.02 (s, 6H, $C\underline{H}_3$)

3-A　$Et_2NCMe_2CN(2,6\text{-}^iPr_2C_6H_3)$ (<u>3a</u>)

將 9.71 g Et_2NCMe_2CHO (<u>2a</u>) 以苯當溶劑，加入 2,6-二異丙基苯胺，數滴濃硫酸，架設 Dean-Stark 除水器，以油浴加溫至 120℃除水迴流 6 小時，上真空線抽去溶劑，減壓蒸餾收集沸點 100-120℃的液體，得黃色粘稠狀液體，產率爲 51%。



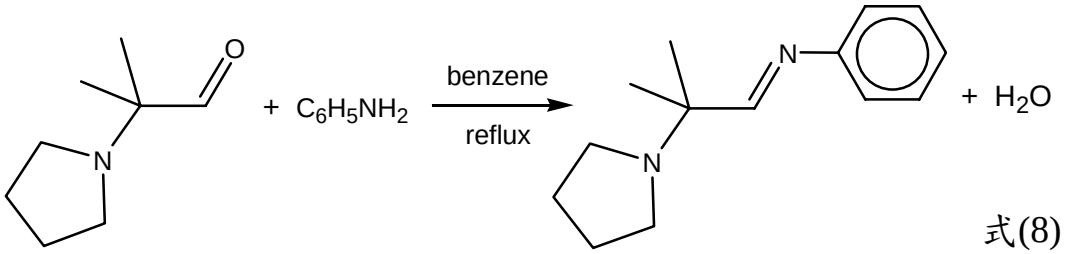
式(7)

產物以 NMR 鑑定

^{1}H NMR ($CDCl_3$)：δ 7.56 (s, 1H, C<u>H</u>=N), 7.10-7.03 (m, 3H, phenyl-<u>H</u>), 2.87 (m, J_{H-H} = 6.8 Hz, 2H, C<u>H</u>$(CH_3)_2$), 2.64 (q, J_{H-H} = 7.2 Hz, 4H, NC<u>H</u>$_2$CH_3), 1.33 (s, 6H, C<u>H</u>$_3$), 1.14 (d, J_{H-H} = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.05 (t, J_{H-H} = 7.2 Hz, 6H, NCH$_2$C<u>H</u>$_3$)

3-B c-$(CH_2)_4$NCMe_2CNPh (<u>3b</u>)

將 4.89 g c-$(CH_2)_4$NCMe_2CHO (<u>2b</u>)以甲苯當溶劑，加入苯胺，數滴濃硫酸，架設 Dean-Start 除水器，以油浴加溫至 150℃除水迴流 6 小時，上真空線抽去溶劑，減壓蒸餾收集沸點 120-140℃的液體，得黃褐色粘稠狀液體，產率：60%。



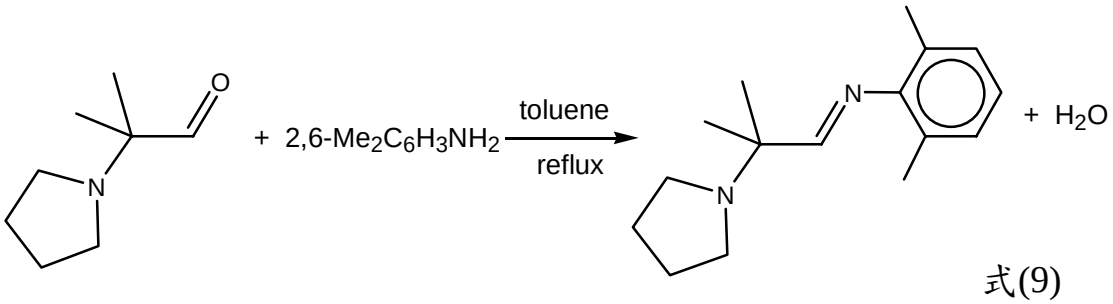
式(8)

產物以 NMR 鑑定

^{1}H NMR ($CDCl_3$)：δ 7.83 (s, 1H, C<u>H</u>=N), 7.35-7.00 (m, 5H, phenyl-<u>H</u>), 2.74, 1.77 (m, m, 4H, 4H, c-C_4<u>H</u>$_8$N), 1.33 (s, 6H, C<u>H</u>$_3$)

3-C c-$(CH_2)_4$NCMe_2CN(2,6-$Me_2C_6H_3$) (<u>3c</u>)

將 4.89 g c-$(CH_2)_4$NCMe_2CHO (<u>2b</u>)以甲苯當溶劑，加入 2,6-二甲基苯胺，以及數滴濃硫酸，架設 Dean-Stark 除水器，以油浴加溫至 150℃除水迴流 6 小時，上真空線抽去溶劑，減壓蒸餾收集沸點 120-130℃的液體，得淡黃色粘稠狀液體，產率爲 69%。



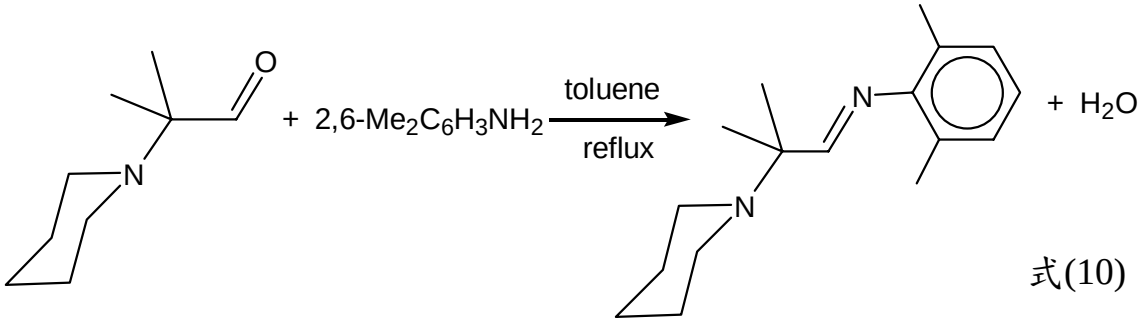
式(9)

產物以 NMR 鑑定

^{1}H NMR ($CDCl_3$)：δ 7.66 (s, 1H, C<u>H</u>=N), 6.99 (d, J_{H-H} = 7.5 Hz, 2H, phenyl-<u>H</u>), 6.87 (t, J_{H-H} = 7.5 Hz, 1H, phenyl-<u>H</u>), 2.77, 1.77 (m, m, 4H, 4H, c-C_4<u>H_8</u>N), 1.37 (s, 6H, C<u>H_3</u>)

3-D　c-$(CH_2)_5NCMe_2CN(2,6\text{-}Me_2C_6H_3)$ (<u>3d</u>)

將 4.07 g c-$(CH_2)_5NCMe_2CHO$ (<u>2c</u>)以甲苯當溶劑，加入 2,6-二甲基苯胺，以及數滴濃硫酸，架設 Dean-Stark 除水器，以油浴加溫至 150℃除水迴流 6 小時，上真空線抽去溶劑，減壓蒸餾收集沸點 106-120℃的液體，得淡黃色粘稠狀液體，產率爲 60%。



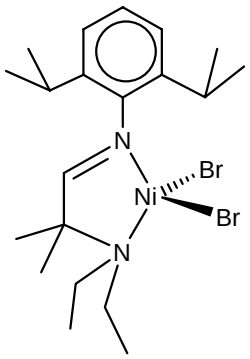
式(10)

產物以 NMR 鑑定

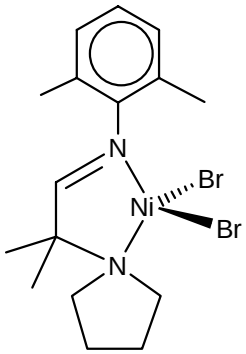
^{1}H NMR ($CDCl_3$)：δ 7.60 (s, 1H, C<u>H</u>=N), 7.00 (d, J_{H-H} = 7.5 Hz, 2H, phenyl-<u>H</u>), 6.91 (t, J_{H-H} = 7.5 Hz, 1H, phenyl-<u>H</u>), 2.09 (s, 6H, CC<u>H_3</u>),　2.57, 1.59, 1.46 (m, m, m, 4H, 4H, 2H, c-C_5<u>H_{10}</u>N), 1.31 (s, 6H, C<u>H_3</u>)

<u>二、過渡金屬錯合物催化劑之合成</u>

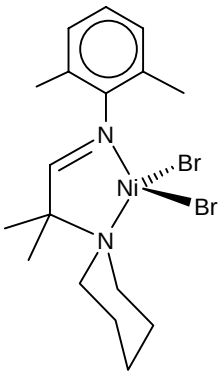
共合成下列三個催化劑，其中催化劑 <u>4a</u> 法爲已知[9]，以相同的程序合成新催化劑 <u>4c</u> 和 <u>4d</u>。



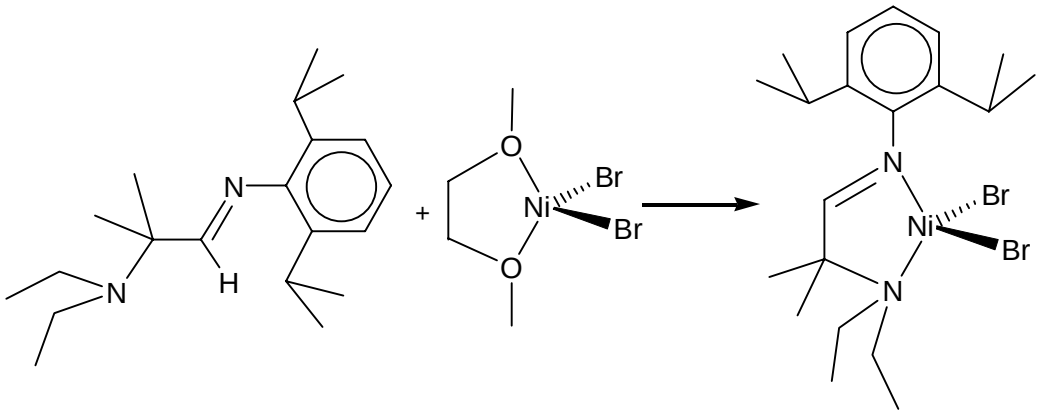
4a



4c



4d



式(11)

A [$Et_2NCMe_2CN(2,6\text{-}^iPr_2C_6H_3)$]$NiBr_2$ (4a)[9]

在乾燥箱中取 150 mg (0.486 mmol) $Ni(DME)Br_2$，裝入無氧反應器，在真空線上無氧無水的條件下反應，以無水二氯甲烷作溶劑，加入 1 當量(146.8 μL, 0.486 mmol)的配基 **3a**，攪拌 2 小時，得紫色溶液，過濾，濃縮溶劑，以無水乙醚作再結晶，超音波震盪十分鐘，得紫色固體，過濾，抽乾溶劑。產率爲 28%。

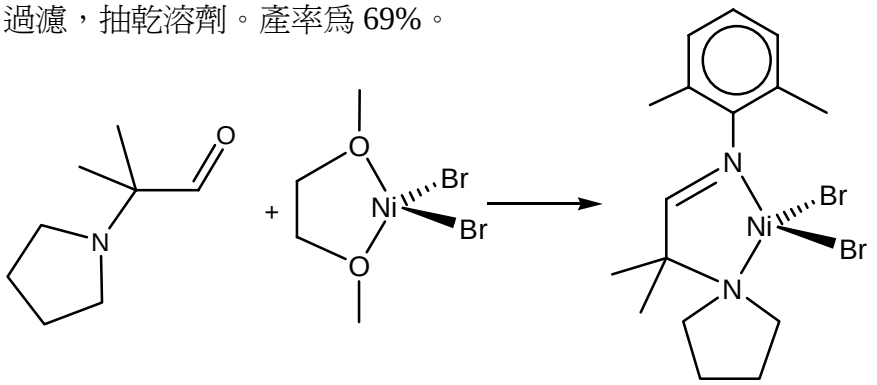
產物以 NMR 鑑定[9]

^1H NMR ($CDCl_3$)：δ 8.28 (s, 1H, C<u>H</u>=N), 7.13 (br, 3H, phenyl-<u>H</u>), 3.48,3.12 (m, 4H, $J_{H\text{-}H}$ =6.5, N(C<u>H</u>$_2$CH$_3$)$_2$), 2.73 (m, 1H, $J_{H\text{-}H}$=6.8, N(2,6-C_6H_3(C<u>H</u>(CH$_3$)$_2$))), 1.12 (d, 6H, $J_{H\text{-}H}$ =6.8, N(2,6-C_6H_3(CH$_2$C<u>H</u>$_3$)$_2$))), 1.05 (t, 6H, $J_{H\text{-}H}$ =6.5, N(CH$_2$C<u>H</u>$_3$)$_2$)

^{13}C NMR ($CDCl_3$)：δ 163.8 (<u>C</u>H=N), 145.8,136.0-122.5 (phenyl-<u>C</u>), 70.0 (<u>C</u>(CH$_3$)$_2$), 46.5 (N(<u>C</u>H$_2$CH$_3$)$_2$), 29.1 (N(2,6-C_6H_3(<u>C</u>H(CH3)2))), 23.0 (N (2,6-C_6H_3(CH(<u>C</u>H$_3$)$_2$))), 21.3 (C(<u>C</u>H$_3$)$_2$), 12.0 (N (CH$_2$<u>C</u>H$_3$)$_2$)

C [c-$(CH_2)_4NCMe_2CN(2,6\text{-}Me_2C_6H_3)]NiBr_2$ (4c)

在乾燥箱中取 150 mg $Ni(DME)Br_2$，裝入無氧反應器，在真空線上無氧無水的條件下反應，以無水二氯甲烷作溶劑，加入 1.5 當量(180 μL, 0.729 mmol)的配基 3c，攪拌 2 小時，得紫紅色溶液，過濾，濃縮溶劑，以無水乙醚作再結晶，超音波震盪十分鐘，得桃紅色固體，過濾，抽乾溶劑。產率爲 69%。



式(12)

MS(FAB, m/z)：381,383(M+1-Br)

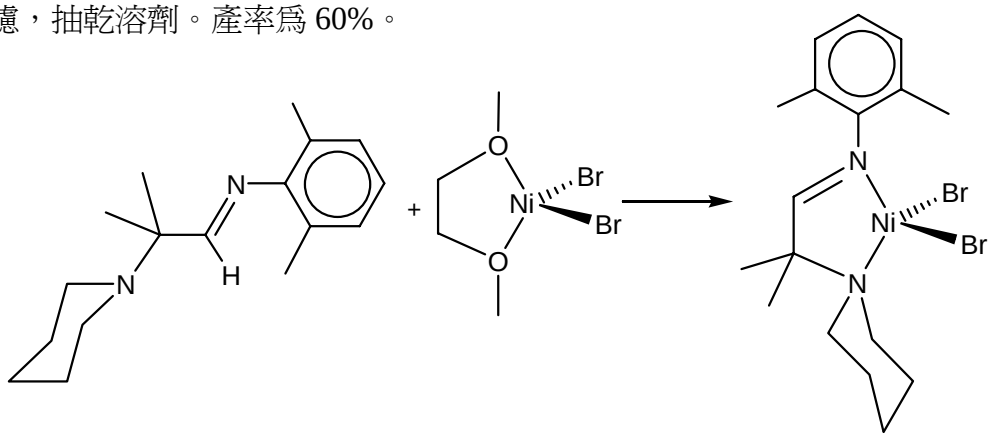
UV-Visible： λ_{max}=517.5 nm

EA：實驗值：N, 5.53, C, 40.99, H, 4.33

理論值：N, 6.05, C, 41.52, H, 5.23

D [c-$(CH_2)_5NCMe_2CN(2,6\text{-}Me_2C_6H_3)]NiBr_2$ (4d)

在乾燥箱中取 150mg $Ni(DME)Br_2$，裝入無氧反應器，在真空線上無氧無水的條件下反應，以無水二氯甲烷作溶劑，加入 0.778mmol(200 μL)的配基 3d，攪拌 2 小時，得紫色溶液，過濾，濃縮溶劑，以無水乙醚作再結晶，超音波震盪十分鐘，得紫色固體，過濾，抽乾溶劑。產率爲 60%。



式(13)

UV-Visible： λ_{max}=516 nm

X-Ray：

取約 5 mg 紫色固體溶於無水二氯甲烷，置於養晶瓶，外層置乙醚，靜置三天後得紫色單晶，送測。

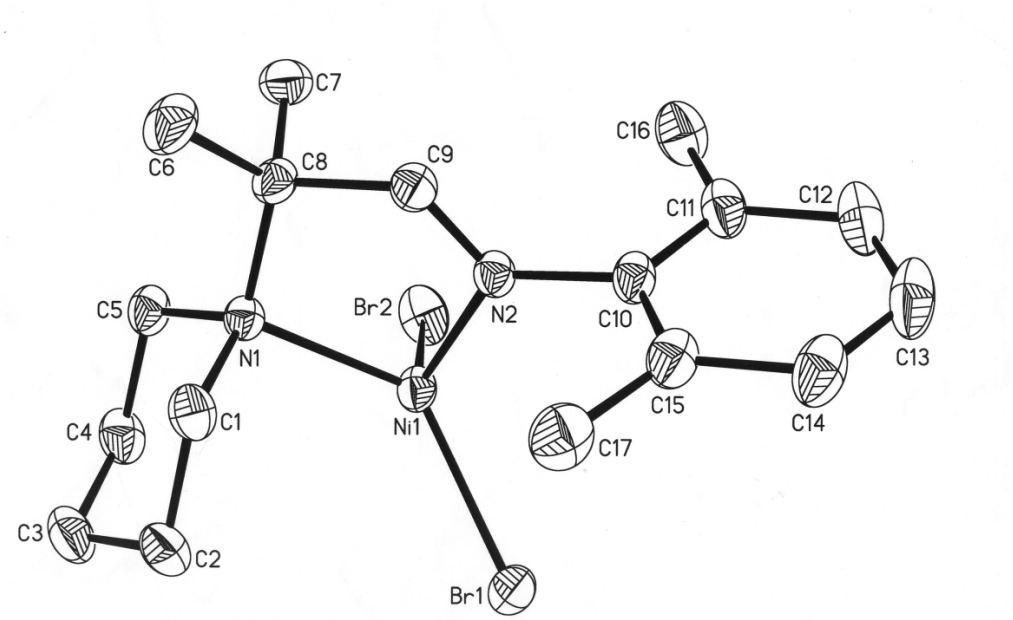
此錯合物大致上爲四面體構形，配基以雙牙鉗合鎳金屬形成五員環，重要鍵長鍵角如下，ORTEP 圖如後：

鍵角：

N(2)-Ni-Br(1)	N(1)-Ni-Br(2)	N(2)-Ni-Br(2)	N(1)-Ni-Br(1)	Br(1)-Ni-Br(2)	N(1)-Ni-N(2)
106.03(7)	104.51(6)	130.28(6)	130.28(6)	113.74(2)	82.41(9)

鍵長：

Br(1)-Ni	Br(2)-Ni	Ni-N(2)	Ni-N(1)
2.3527(5)	2.3638(5)	1.997(2)	2.084(2)



圖一

三、烯烴催化反應

1.乙烯的聚合反應

於乾燥箱中將 10 mg 的錯合物催化劑置入高壓反應瓶，以 50 mL 甲苯爲溶劑，再用針筒打入 5.6 mL 濃度 10% 的助催化劑 MAO(Ni：Al＝1：480)，將反應瓶鎖好後移出乾燥箱，灌入乙烯，維持恆壓 250 psi，以攪拌子攪拌。

反應一段時間後打開反應器，以甲醇和鹽酸停止反應，產生分層，取上層有機液，以丙酮沉澱出產物，過濾抽乾，秤重。測 GPC 以得知分子量及其分布範圍(PDI 值)，測 NMR 計算聚乙烯的分支數，測 TGA 以得其重量損失及分解溫度，催化劑 4c 和 4d 的產物在 400℃後分解。測 DSC 以得 Tg 點。相關數據列於表一。

表一 • 250 psi，25 ℃，Ni：Al＝1：480，50mL 甲苯

催化劑	反應時間 (hr)	產量 (g)	活性 (kg/mol・hr)	Mn	PDI (Mw/Mn)	Tg (℃)	分支數 (per 1000 C)
4a(22 μmol)[9]	3	2.9	51.5	238000	1.69	—	143
4c(21 μmol)	1	3.5	162.0	391400	1.26	38.5	117
4d(22 μmol)	1	0.08	3.8	—	—	—	106
4d(22 μmol)	3	0.87	13.8	95500	1.43	30.0	108

2.降冰片烯的聚合反應

取 250 mL 單頸瓶，於乾燥箱中置入 10 mg 錯合物催化劑，以 50 mL 甲苯爲溶劑，加入 5 g 降冰片烯，再用針筒打入助催化劑 MAO(Ni：Al＝1：480)，封口，移出乾燥箱，以攪拌子攪拌。

以甲醇和鹽酸停止反應，出現白色沉澱物，過濾抽乾，秤重。僅 4c 反應所得的產物微溶於甲苯，可以 GPC 測其分子量及 PDI。測 TGA 以得其重量損失及分解，溫度催化劑 4c 和 4d 的產物在 400℃後分解。以 DSC 測 Tg 點，4d 的產物 Tg 點過高無法測得。

表二

催化劑	反應時間 (hr)	Ni：Al	活性 (kg/mol・hr)	Mn	PDI (Mw/Mn)	Tg (℃)
4a(22 μmol)	0.25	1：230	331.6	—	—	—
4c(21 μmol)	1	1：480	23.1	53158	1.91	322.0
4d(22 μmol)	1	1：480	57.1	—	—	—

註：催化劑 4a 的數據引用自參考資料九

玖、討論

一、配基和錯合物的純化及鑑定

配基合成反應第一步溴化的產物用萃取的方式進行純化(乙醚／冰水)。第二步胺化會產生難溶性胺鹽或產生分層，分層或過濾洗滌除去雜質。主要的純化步驟是在亞胺化後，以減壓蒸餾的方式，收集沸點不同的液體，再以 NMR 鑑定以確定產物。進行錯合物合成前，因錯合物對水敏感，以微量蒸餾器純化配基。合成錯合物時，先以過濾除去固體的鎳起始物，再將產物沉澱出，留下液體的配基。

本實驗中配基的鑑定方法主要是利用 ^{1}H NMR，溶劑使用 $CDCl_3$。溴化步驟完成後，原二甲基丙醛被溴所取代的氫的訊號消失，可由此確定反應進行的情形；胺化步驟則會使醛基氫的化學位移改變；經過亞胺化步驟後，此醛基的氫位移(δ～9)消失，高場出現亞胺碳上的氫(δ～7)。錯合物的鑑定，除了 4a 以外，4c 和 4d 無法測 NMR，所以用 MASS 和 X-RAY 來鑑定。

二、烯烴聚合結果討論

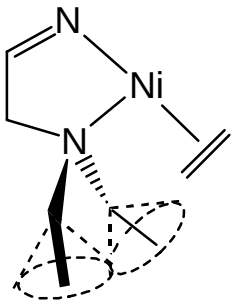
1.聚乙烯的催化

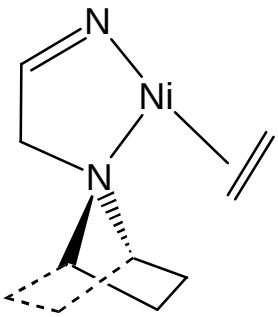
表三 • 250psi，25℃，catalyst：MAO＝1：480，50mL 甲苯

催化劑	反應時間 (hr)	活性 (kg/mol • hr)	Mn	PDI (Mw/Mn)	Tg (℃)	分支數 (per 1000 C)
A[9]	3	95.49	164000	1.31		149
4a	3	51.54	238000	1.69		143
4c	1	162.04	391400	1.26	38.5	117
4d	3	13.81	95500	1.43	30.0	108

1-1 環形胺取代基和非環形胺取代基催化效果比較

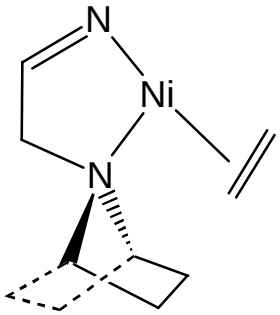
催化劑 A[9]和催化劑 4c 碳數相同，結構類似，僅胺基的部分爲非環形取代基。相較這兩者，催化劑 4a 在亞胺苯環上的取代基略有不同。由上表可以看出，催化劑 4c 的活性、分子量皆爲最高，PDI 分佈值最小，分支數最少。可能是因爲催化劑 A 胺基上之取代基的轉動會影響乙烯配位。而環形取代基自由度較小，如下圖，無法自由轉動，立體效應亦小，比起線型取代基較不干擾乙烯的配位，因而活性較大，鏈成長的速率相較起鏈分支、鏈轉移的速率更大，造成分支數少分子量高。

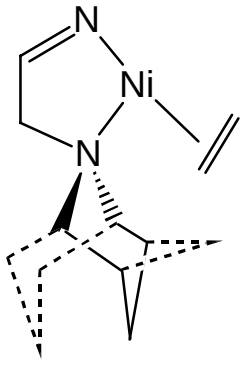




1-2 五員環胺取代基和六員胺取代基催化效果比較

由上表可知，催化劑 4c 的活性較催化劑 4d 高了一個數量級，分子量較大，分布範圍小，分支數相仿。原因可能是因爲六員環自由度較五員環高，具椅形、半椅形、船形等多種構形，較容易干擾乙烯的配位，因此造成活性較低。





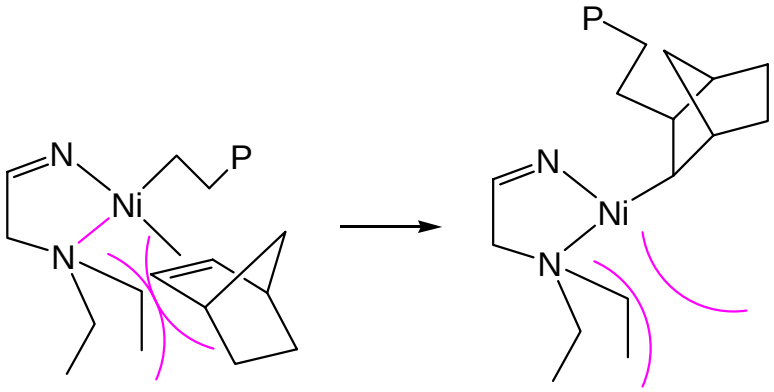
2.聚降冰片烯的催化

表四

催化劑	反應時間 (hr)	Ni：Al	活性 (kg/mol・hr)	Mn	PDI (Mw/Mn)	Tg (℃)
A[9]	0.25	1：230	209.2	—	—	—
4a	0.25	1：230	331.6	—	—	—
4c	1	1：480	23.1	53158	1.91	322.0
4d	1	1：480	57.1	—	—	—

2-1 環形胺取代基和非環形胺取代基催化效果比較

由表四可以看出，催化劑 **4c** 在活性上較催化劑 A 和催化劑 **4a** 低了一個數量級，分子量也較小。催化劑 A 和催化劑 **4a** 的產物分子量較大，不溶於甲苯，常溫下無法測 GPC。而催化劑 **4c** 的產物實際平均分子量可能較此數據高，因分子量較大的產物無法溶於甲苯。造成活性及分子量的原因可能是降冰片烯的立體障礙較大，但配位能力較好，所以速率決定步驟是鏈成長過程的插入反應，立體效應大的配機會促使配位降冰片烯快速插入，配位數減少，可降低立體效應之張力。



2-2 五員環胺取代基和六員胺取代基催化效果比較

由表四可知，催化劑 4c 的活性較催化劑 4d 略低，分子量應較小 因催化劑 4d 的產物不溶於甲苯。同理，由於六員環的自由度稍大，會驅使立體效應大的降冰片烯較快速的進行插入反應而提昇了活性與分子量。

拾、結論

一、.成功合成具五員環和六員環胺基-亞胺基雙牙配基 $Et_2NCMe_2CH=N(2,6\text{-}^{i}Pr_2C_6H_3)$ (**3a**)、$(c\text{-}C_4H_8)NCMe_2CH=NPh$ (**3b**)、$RNCMe_2CH=N(2,6\text{-}Me_2C_6H_3)$ (R = c-C_4H_8 **3c**，c-C_5H_{10} **3d**)，及其鎳金屬錯合物 $Ni[Et_2NCMe_2CH=N(2,6\text{-}^{i}Pr_2C_6H_3)]Br_2$ (**4a**)、$Ni[RNCMe_2CH=N\ (2,6\text{-}Me_2C_6H_3)]Br_2$ (R = c-C_4H_8 **4c**，c-C_5H_{10} **4d**)。

二、新合成的配基及鎳錯合物催化劑的純化及結構鑑定，其中 $Ni[c\text{-}C_4H_8NCMe_2CH=N(2,6\text{-}Me_2C_6H_3)]Br_2$(**4d**)爲紫色單晶，其結構經 X-光單晶繞射確定是近四面體構形。

三、所合成錯合物在 MAO 的活化下，展現了對催化乙烯聚合及降冰片烯聚合反應的高度活性。對乙烯的催化活性 10^4~10^5 g/molNi • h 平均分子量約 10^5，PDI 值約 1.4，分支數約在 100/per 1000 C。對降冰片烯的催化活性 10^4~10^5g/molNi • h，分子量超過 10^4。

四、催化劑中相同碳數的錯合物比較，吡咯烷(pyrrolidine)具環形取代基者，與雙乙基胺者相較，乙烯聚合的催化活性較好，分子量較高，PDI 值較小。降冰片烯聚合的催化活

性則相反。

五、催化劑中同是環形胺的吡咯烷與哌啶(piperidine)的取代基相較，較大的六環哌啶之乙烯聚合催化活性較差，降冰片烯聚合催化活性較好。

六、結果顯示乙烯聚合催化反應的速率決定步驟較可能在鏈起始的配位反應；而立體效應大且配位效果好的降冰片烯聚合之速率決定步驟可能在鏈生成的烯烴插入反應，胺上的環形取代基確能對烯烴催化聚合反應有直接的影響。

拾壹、誌謝

感謝陳竹亭教授和黃進松老師在研究方向、理論指導及報告修改上給予大力協助。還要感謝指導我各項實驗技巧及儀器操作的虹儀學姊、小翼學姊，和帶我作催化的師淇學姊，以及實驗室所有學長姐的鼓勵和包容，讓我一年半的實驗進行順利。當然還要跟愛我的爸媽說聲謝謝，給我支持鼓勵，並在我作實驗到晚上十點十一點時，從化學系接我回家。最後感謝崇友文教基金會提供研究經費。

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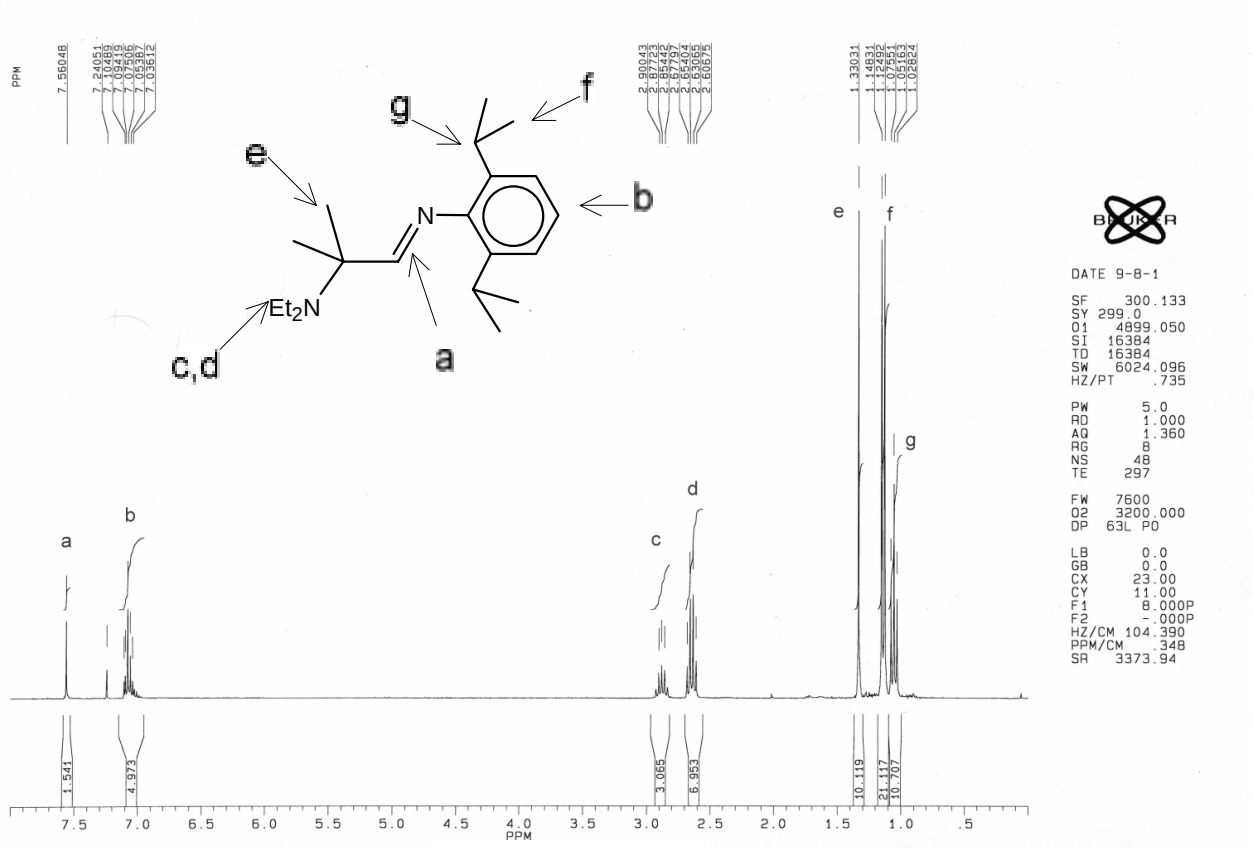
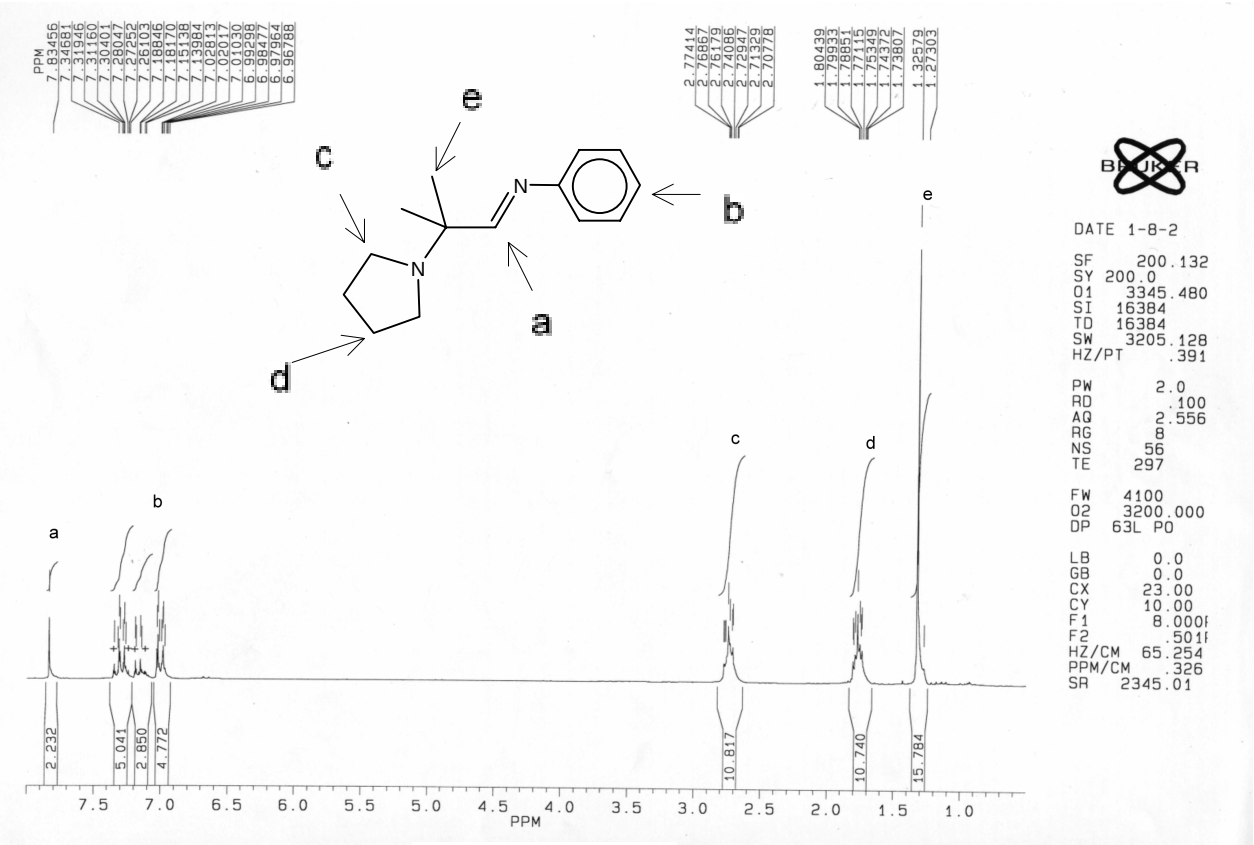


配基 3a ^{1}H NMR



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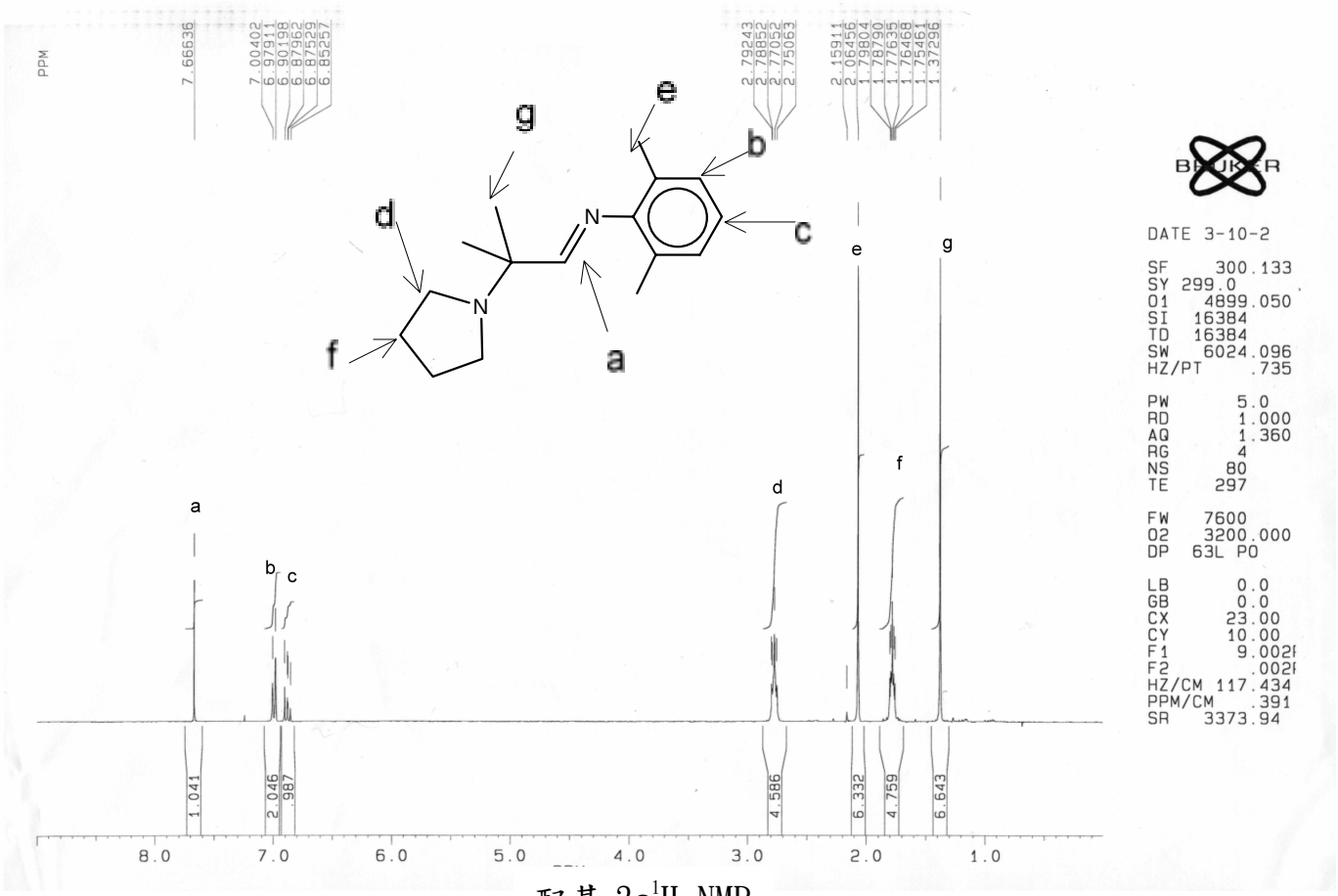

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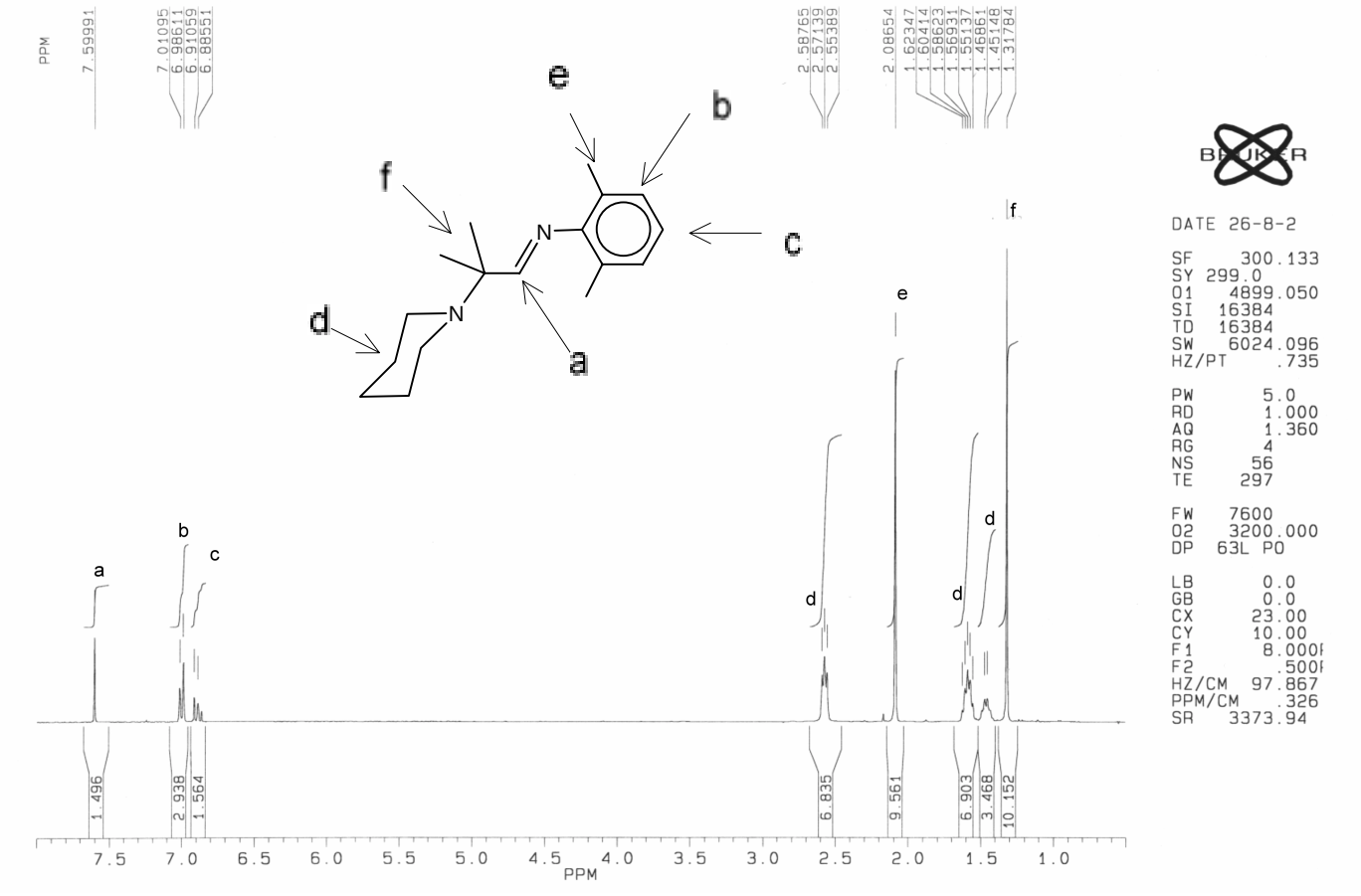

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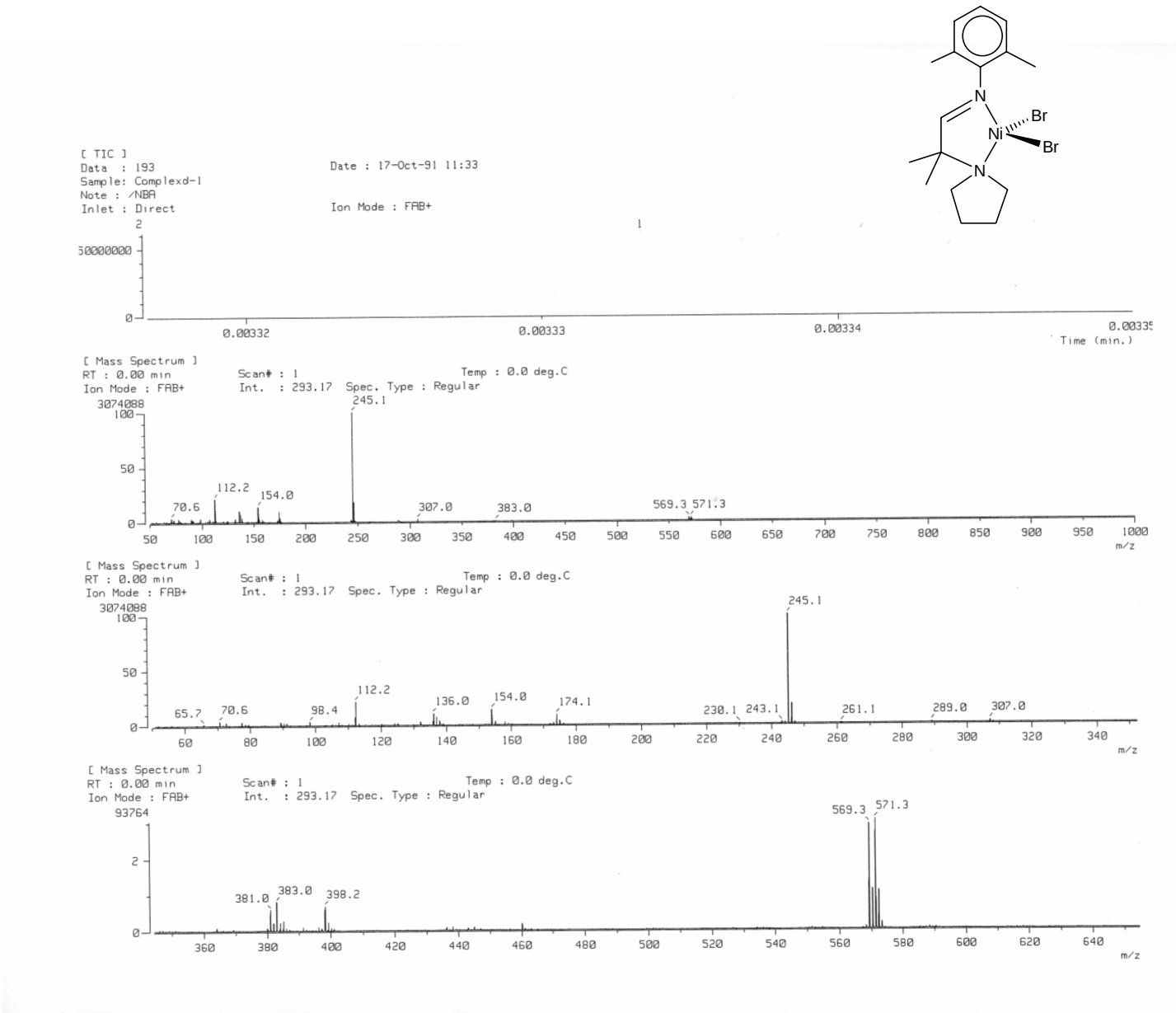
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m/z

催化劑 4c MASS

錯合物 4d X-RAY 資料

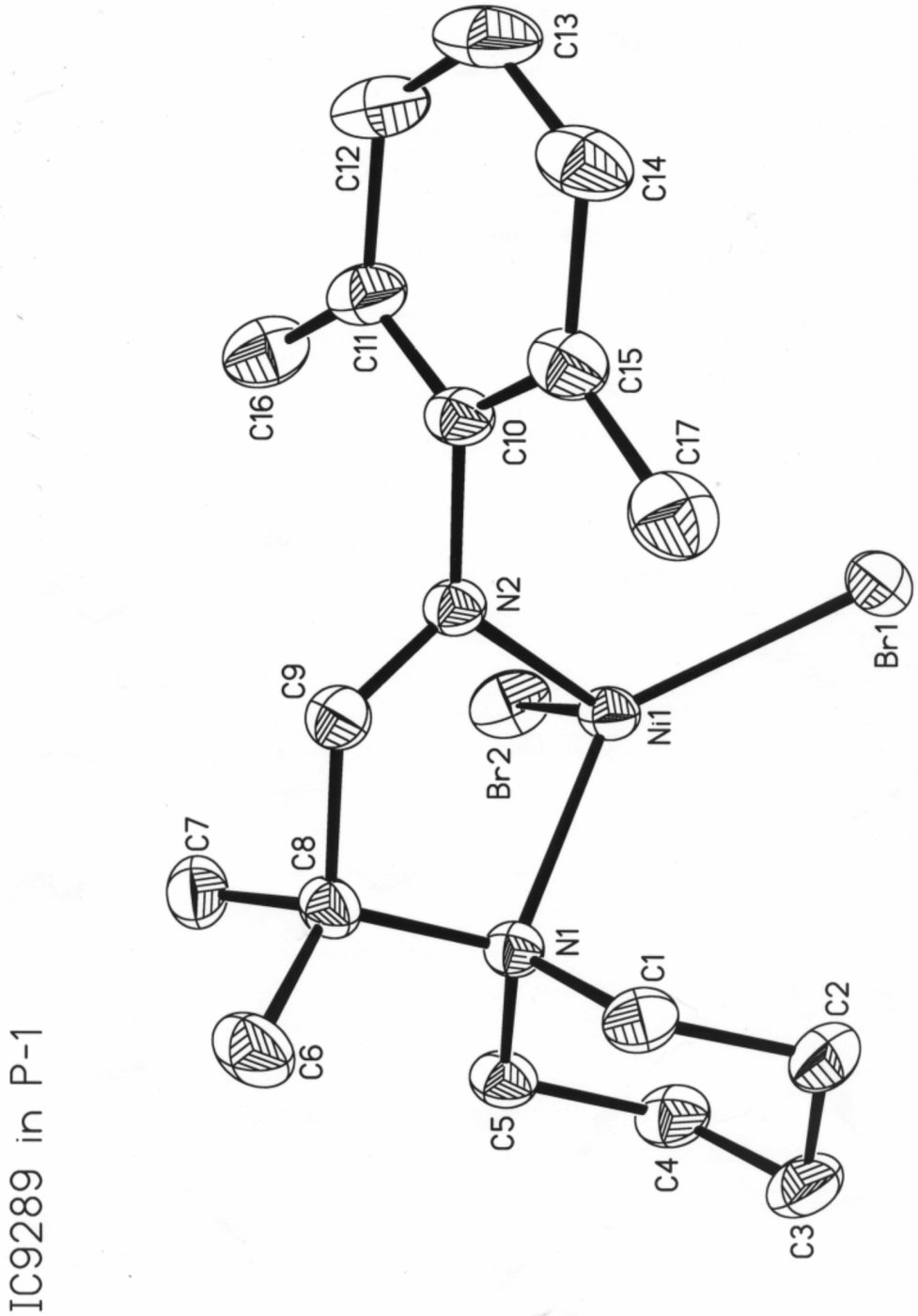


Table 1. Crystal data and structure refinement for IC9289.

Identification code	ic9289
Diffractometer used	Nonius KappaCCD
Empirical formula	$C_{17}H_{26}Br_2N_2Ni$
Formula weight	476.93
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.10100(10) Å alpha = 100.4700(10)° b = 8.68800(10) Å beta = 93.7440(10)° c = 15.2850(2) Å gamma = 113.1160(10)°
Volume, Z	961.77(2) $Å^3$, 2
Density (calculated)	1.647 Mg/m^3
Absorption coefficient	5.162 mm^{-1}
F(000)	480
Crystal size	0.30 x 0.27 x 0.25 mm
θ range for data collection	4.11 to 27.48°
Limiting indices	$-10 \le h \le 10$, $-11 \le k \le 11$, $-19 \le l \le 19$
Reflections collected	19983
Independent reflections	4390 (R_{int} = 0.0542)
Absorption correction	Multi-scan
Max. and min. transmission	0.293 and 0.220
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4380 / 0 / 201
Goodness-of-fit on F^2	0.987
Final R indices [I>2σ(I)]	R1 = 0.0345, wR2 = 0.0863
R indices (all data)	R1 = 0.0433, wR2 = 0.0925
Extinction coefficient	0.0153(14)
Largest diff. peak and hole	1.230 and -0.804 $eÅ^{-3}$

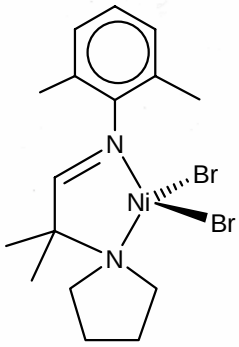
Table 2. Bond lengths [Å] and angles [°] for 9289.

Br(1)-Ni(1)	2.3527(5)	Br(2)-Ni(1)	2.3638(5)
Ni(1)-N(2)	1.997(2)	Ni(1)-N(1)	2.084(2)
N(1)-C(5)	1.492(3)	N(1)-C(1)	1.499(4)
N(1)-C(8)	1.527(3)	N(2)-C(9)	1.261(4)
N(2)-C(10)	1.456(3)	C(1)-C(2)	1.514(5)
C(2)-C(3)	1.515(5)	C(3)-C(4)	1.517(5)
C(4)-C(5)	1.518(4)	C(6)-C(8)	1.533(4)
C(7)-C(8)	1.542(4)	C(8)-C(9)	1.503(4)
C(10)-C(15)	1.389(4)	C(10)-C(11)	1.394(4)
C(11)-C(12)	1.403(5)	C(11)-C(16)	1.498(5)
C(12)-C(13)	1.373(6)	C(13)-C(14)	1.371(6)
C(14)-C(15)	1.393(5)	C(15)-C(17)	1.501(5)

N(2)-Ni(1)-N(1)	82.41(9)	N(2)-Ni(1)-Br(1)	106.03(7)
N(1)-Ni(1)-Br(1)	130.28(6)	N(2)-Ni(1)-Br(2)	116.53(7)
N(1)-Ni(1)-Br(2)	104.51(6)	Br(1)-Ni(1)-Br(2)	113.74(2)
C(5)-N(1)-C(1)	108.6(2)	C(5)-N(1)-C(8)	112.0(2)
C(1)-N(1)-C(8)	110.2(2)	C(5)-N(1)-Ni(1)	113.9(2)
C(1)-N(1)-Ni(1)	106.7(2)	C(8)-N(1)-Ni(1)	105.4(2)
C(9)-N(2)-C(10)	120.2(2)	C(9)-N(2)-Ni(1)	113.4(2)
C(10)-N(2)-Ni(1)	126.4(2)	N(1)-C(1)-C(2)	112.6(2)
C(1)-C(2)-C(3)	110.8(3)	C(2)-C(3)-C(4)	109.4(3)
C(3)-C(4)-C(5)	112.5(3)	N(1)-C(5)-C(4)	111.4(2)
C(9)-C(8)-N(1)	106.9(2)	C(9)-C(8)-C(6)	109.7(2)
N(1)-C(8)-C(6)	114.5(3)	C(9)-C(8)-C(7)	104.8(2)
N(1)-C(8)-C(7)	111.8(2)	C(6)-C(8)-C(7)	108.7(3)
N(2)-C(9)-C(8)	121.5(2)	C(15)-C(10)-C(11)	123.5(3)
C(15)-C(10)-N(2)	118.3(3)	C(11)-C(10)-N(2)	118.2(3)
C(10)-C(11)-C(12)	116.4(3)	C(10)-C(11)-C(16)	122.8(3)
C(12)-C(11)-C(16)	120.9(3)	C(13)-C(12)-C(11)	121.5(4)
C(14)-C(13)-C(12)	120.1(3)	C(13)-C(14)-C(15)	121.4(4)
C(10)-C(15)-C(14)	117.1(3)	C(10)-C(15)-C(17)	122.1(3)
C(14)-C(15)-C(17)	120.8(3)		

Symmetry transformations used to generate equivalent atoms:

錯合物 4c 催化乙烯聚合一小時之 GPC



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Mw (重量平均分子量值) = 494389
Mz (Z 平均分子量值) = 598988
Mv (黏度平均分子量值) = 494389
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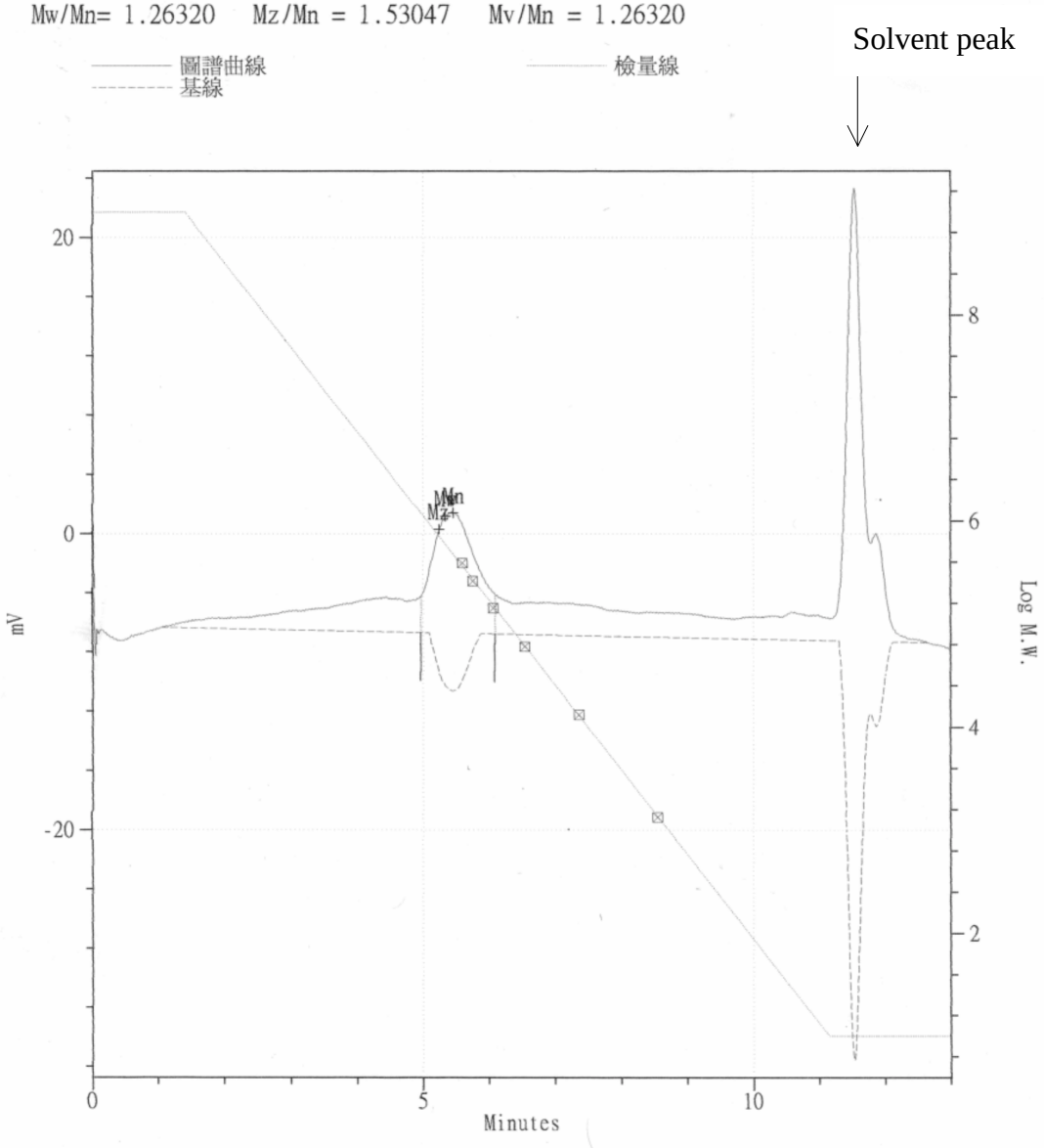
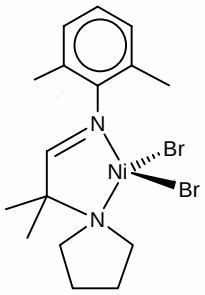
Dispersity 和 其它比值

Mw/Mn= 1.26320 Mz/Mn = 1.53047 Mv/Mn = 1.26320



錯合物 4c 催化降冰片烯聚合一小時之 GPC



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平均分子量值

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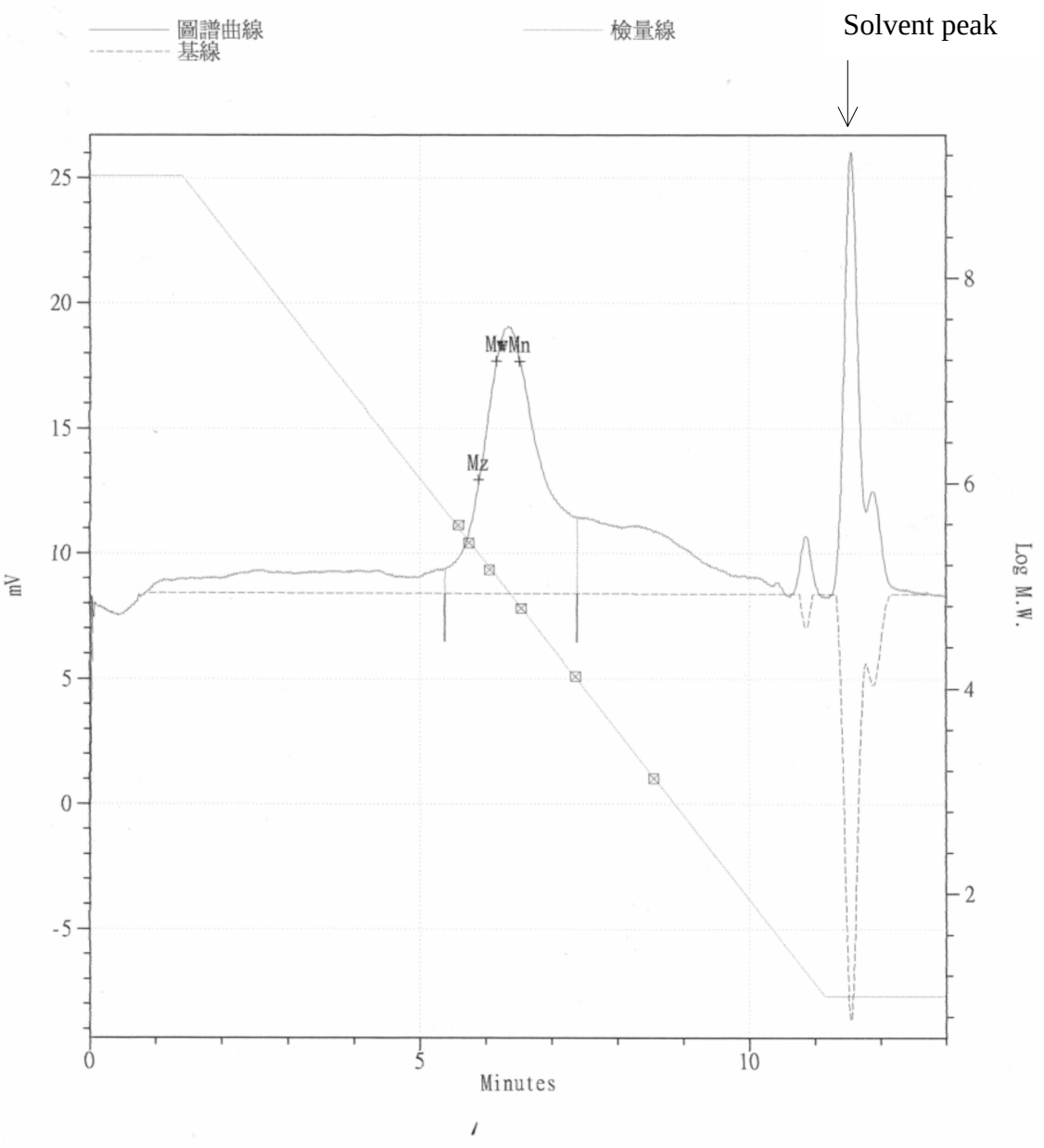
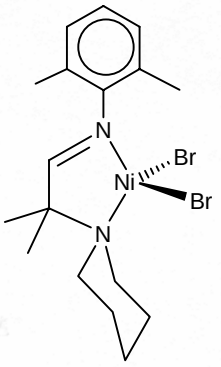
Mw (重量平均分子量值) = 101324
Mz (Z 平均分子量值) = 173621
Mv (黏度平均分子量值) = 101324
I.V (固有黏度) = 101324

Dispersity 和 其它比值

Mw/Mn= 1.90609 Mz/Mn = 3.26613 Mv/Mn = 1.90609



錯合物 4d 催化乙烯聚合三小時之 GPC



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平均分子量值

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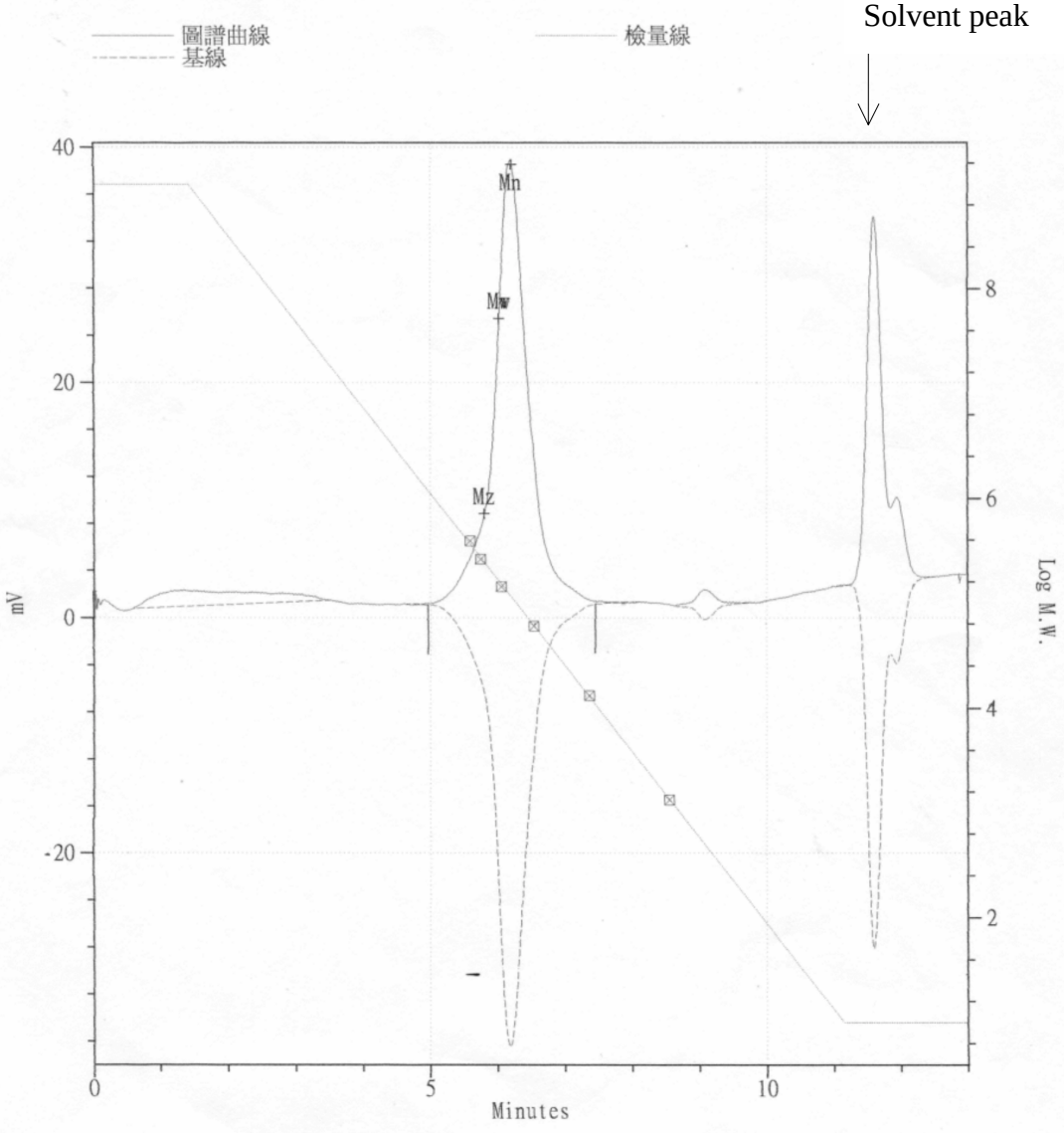
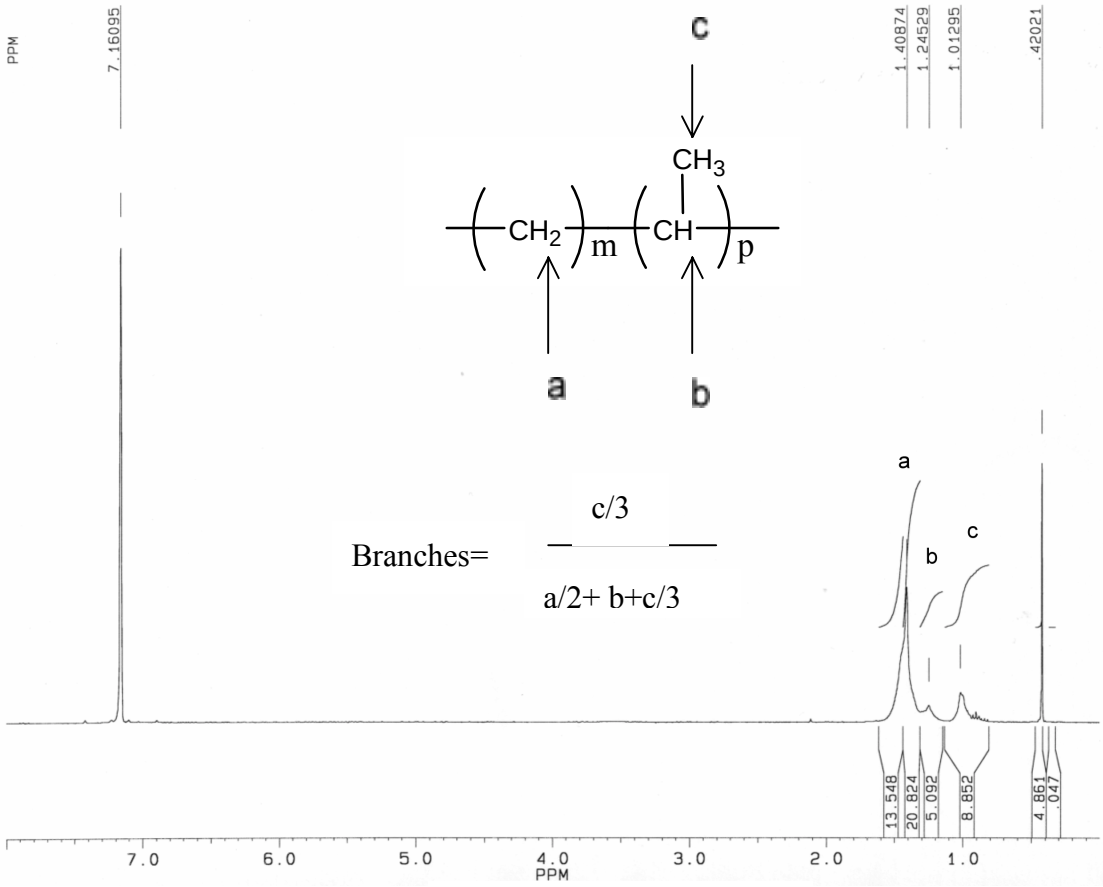
Mw	(重量平均分子量值)	= 137528
Mz	(Z 平均分子量值)	= 205811
Mv	(黏度平均分子量值)	= 137528
I.V.	(固有黏度)	= 137528

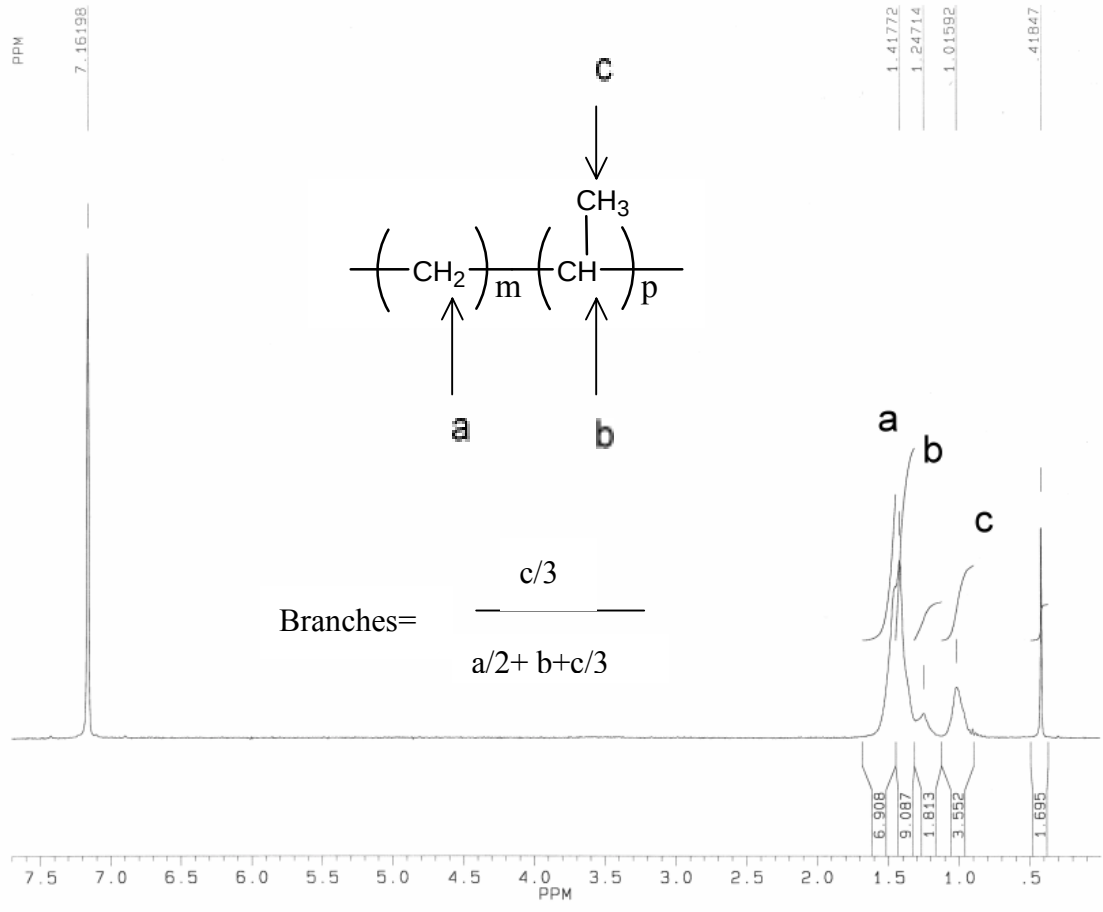
Dispersity 和 其它比值

Mw/Mn= 1.43973 Mz/Mn = 2.15456 Mv/Mn = 1.43973

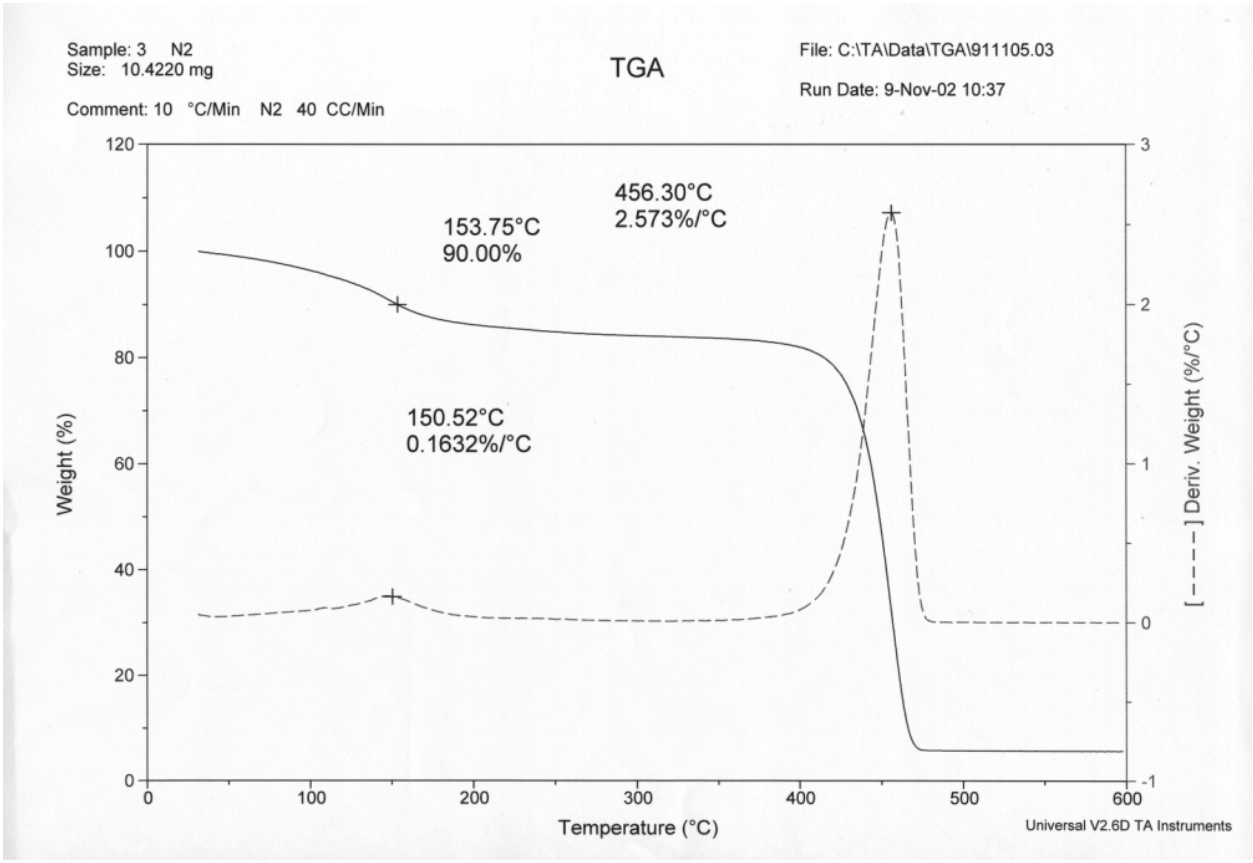




錯合物 3c PE ^{1}H NMR



錯合物 4d PE ^{1}H NMR



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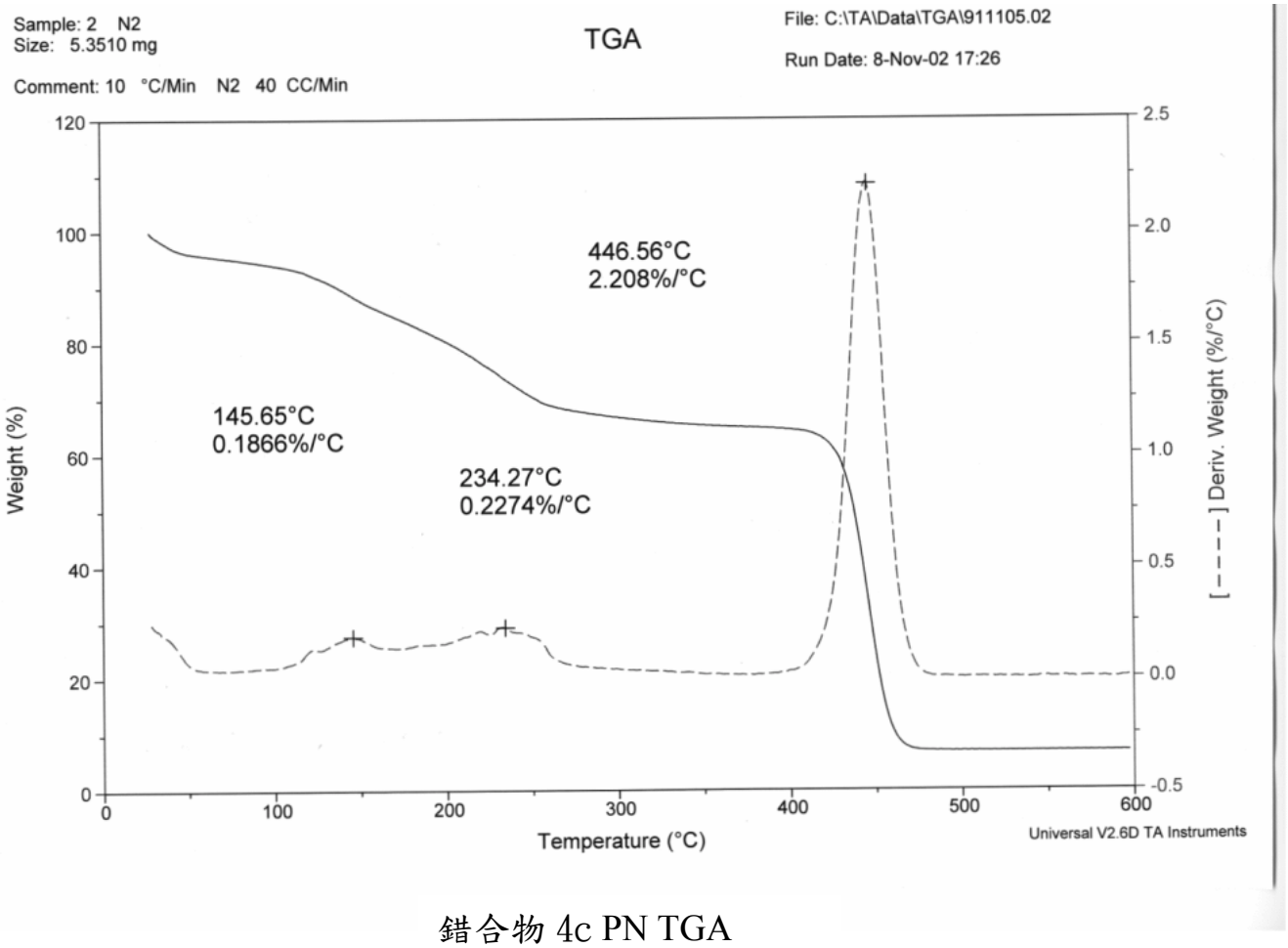

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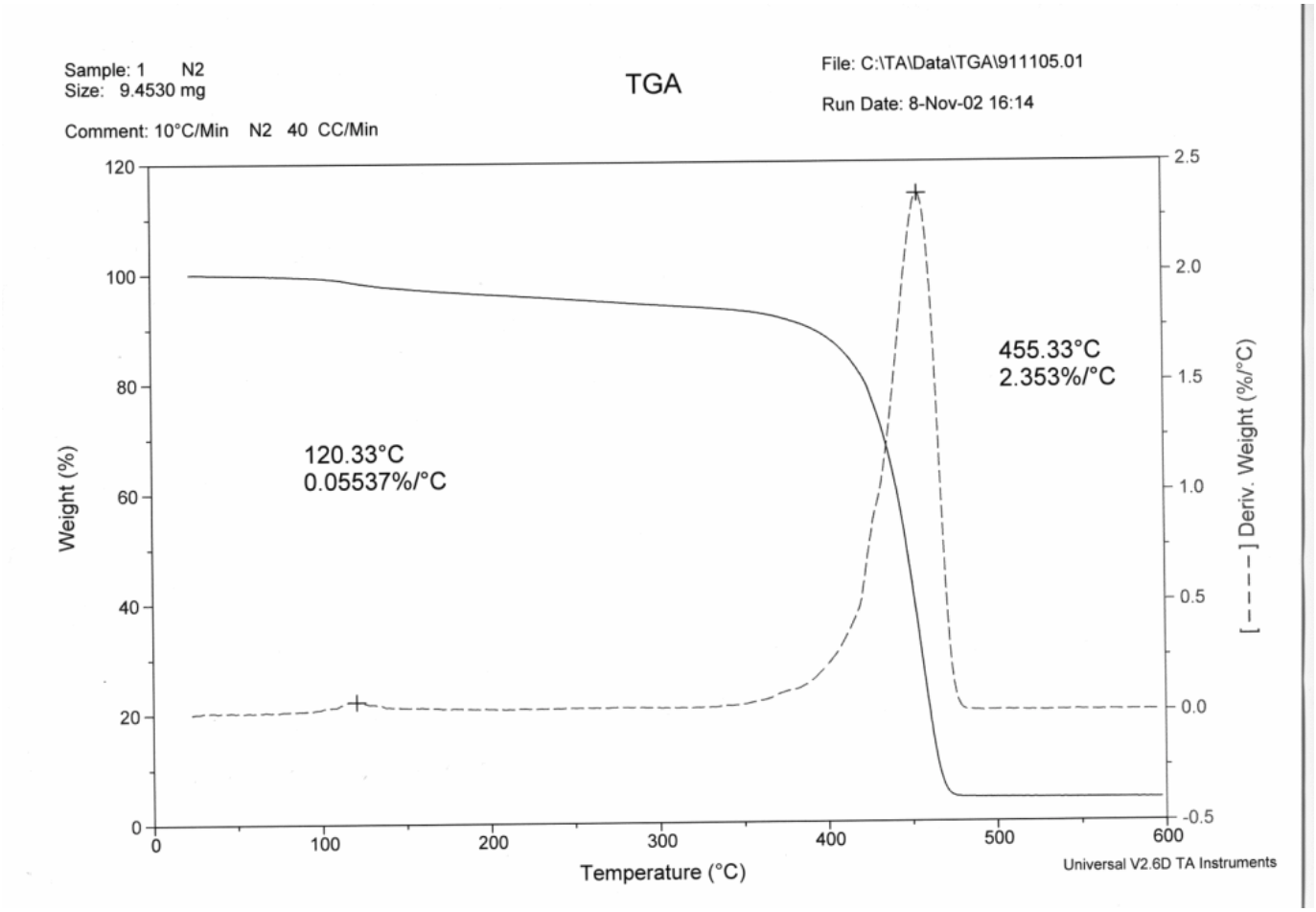

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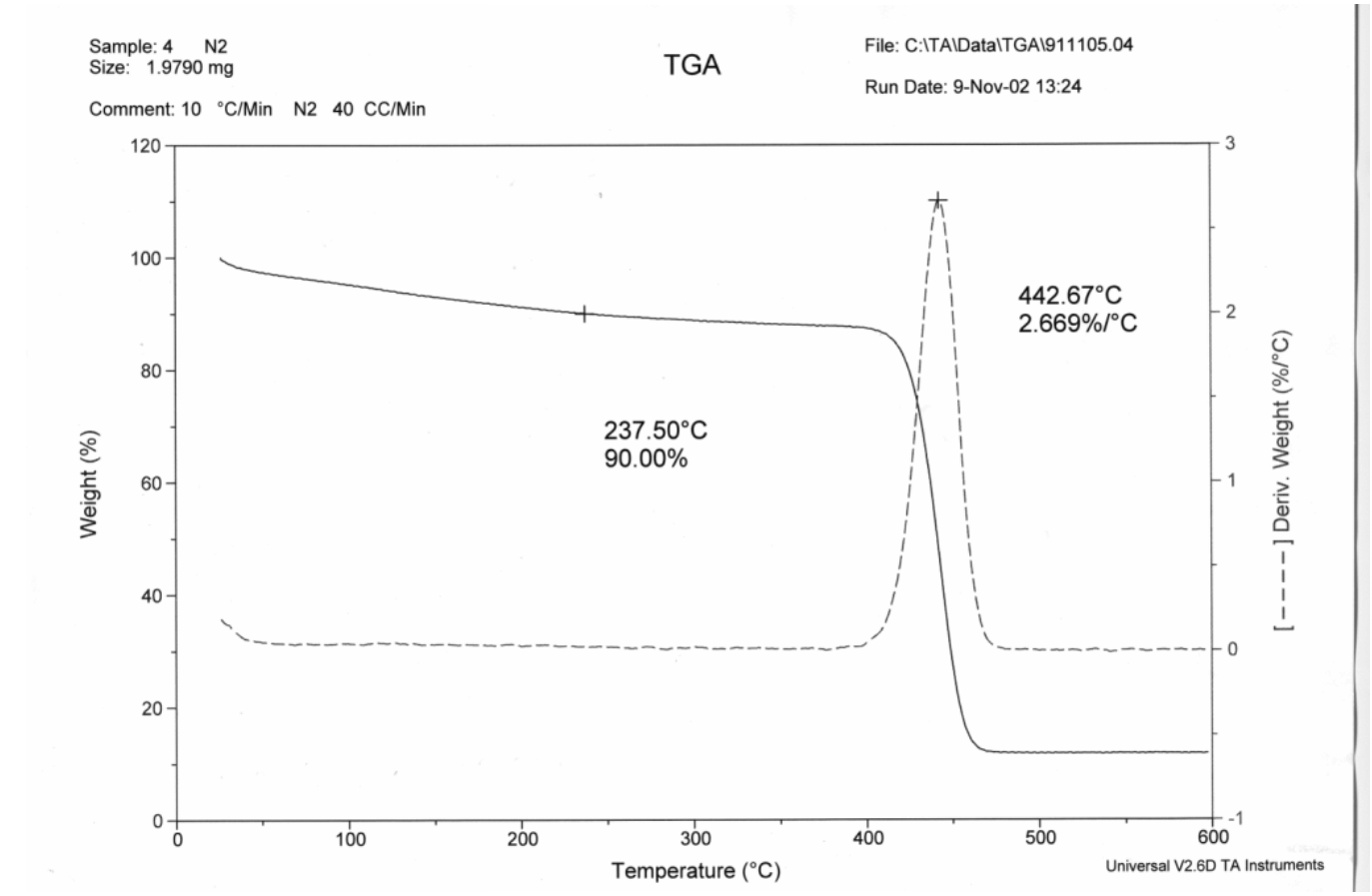

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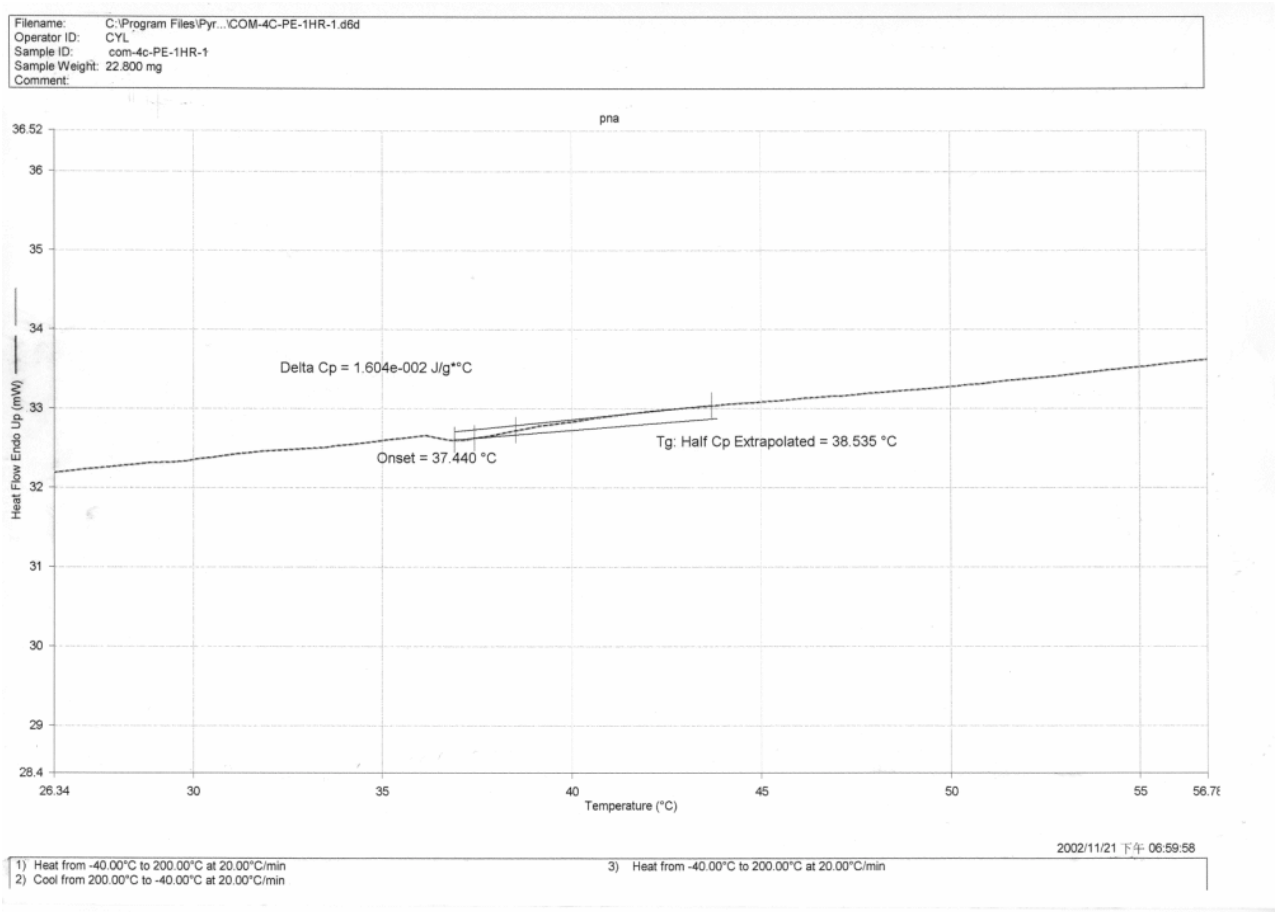
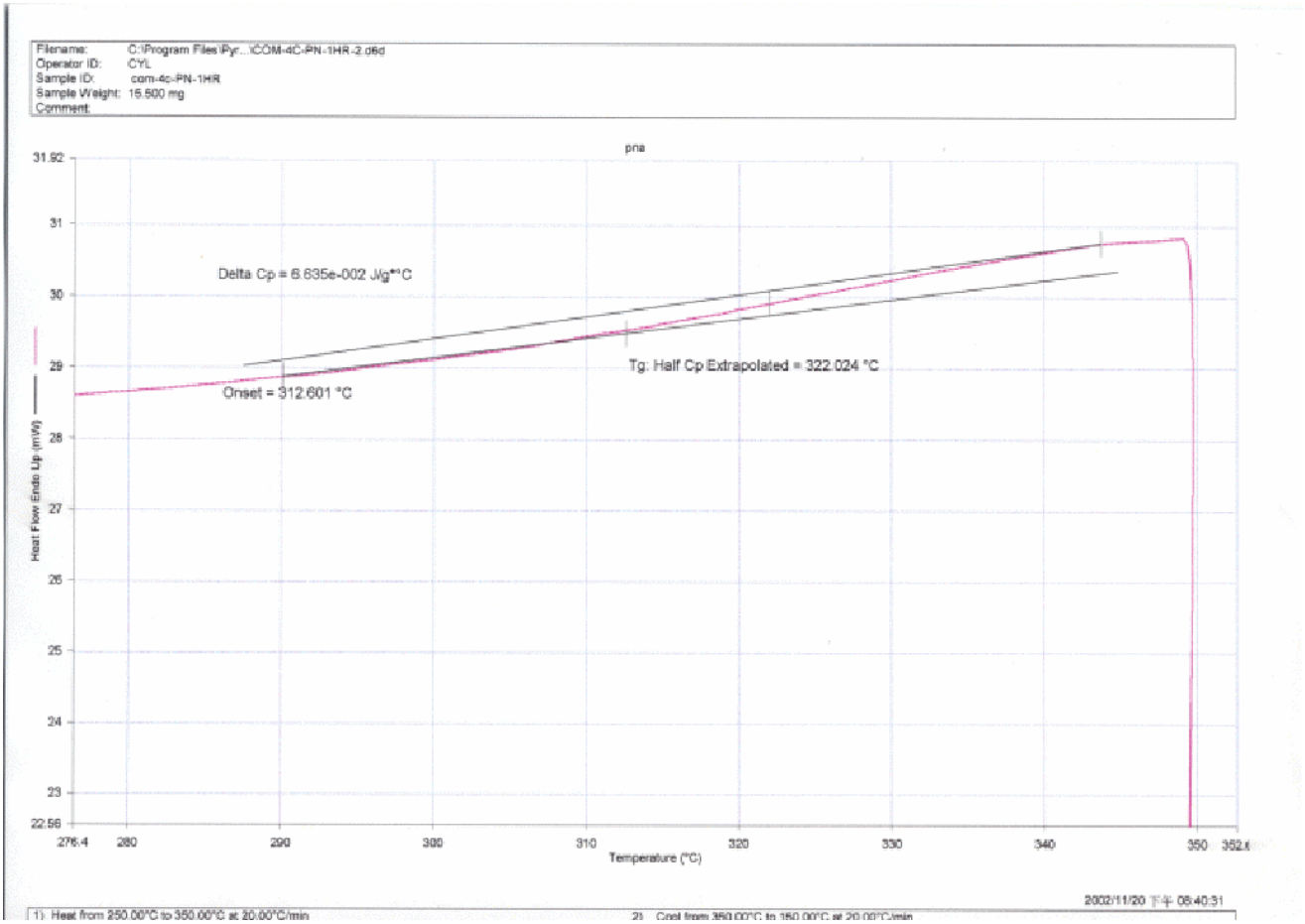
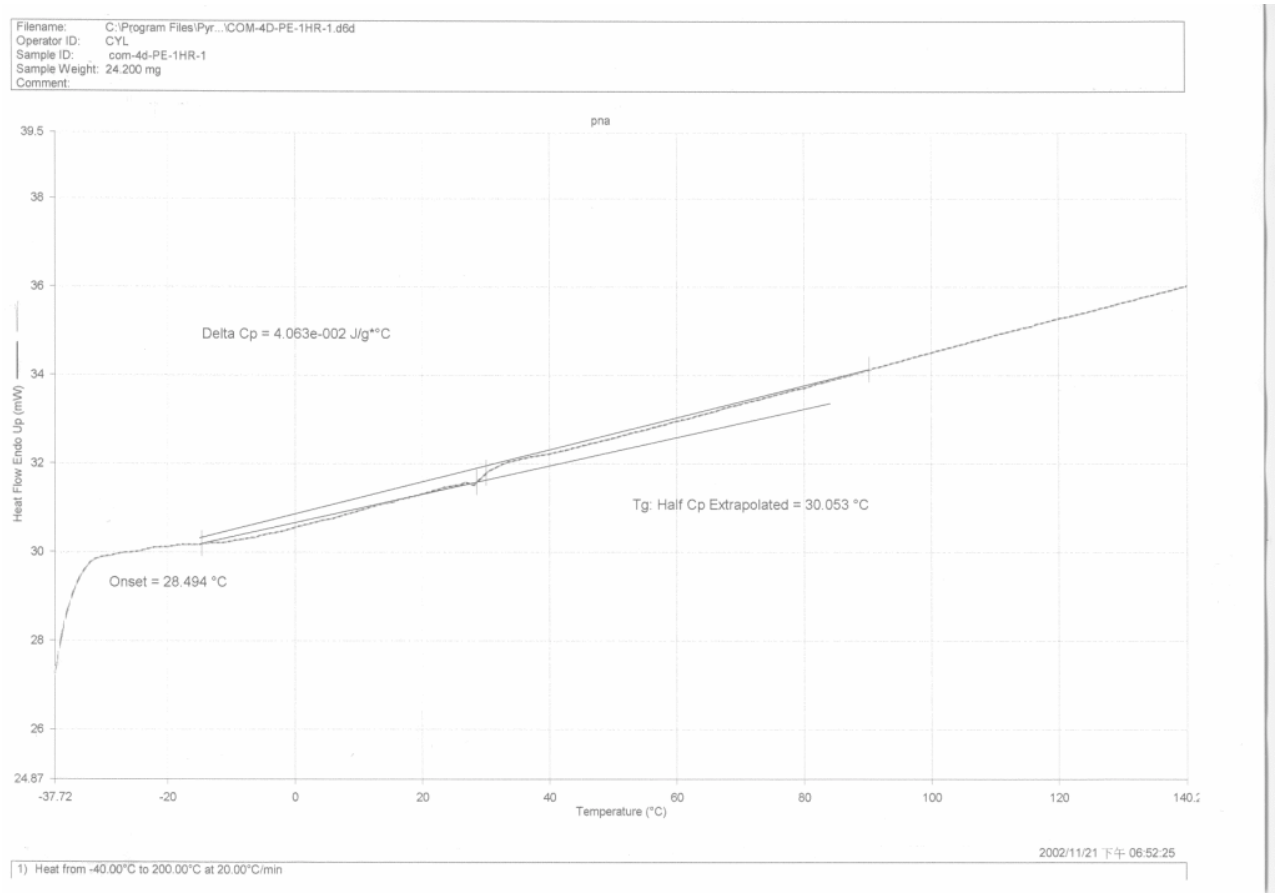


錯合物 4c PE DSC



錯合物 4c PN DSC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pna
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Tg: Half Cp Extrapolated = 30.053 °C
Onset = 28.494 °C
Heat Flow Endo Up (mW)
Temperature (°C)
2002/11/21 下午 06:52:25
1) Heat from -40.00°C to 200.00°C at 20.00°C/min

錯合物 4d PE DSC

Nickel Complexes Bearing Amine-Imine Hybrid Bidentate Ligand - Synthesis, Structure, and Reactivity for Olefin Polymerization

Abstract

Two derivatives of α-amino aldeimine in the form of c-$C_nH_{2n}NCMe_2CH$═N (2,6-$Me_2C_6H_3$) (n = 4 (**3c**), n = 5 (**3d**)) and their nickel complexes [c-$C_nH_{2n}NCMe_2CH$═N (2,6-$Me_2C_6H_3$)]$NiBr_2$ (n = 4 (**4c**), n = 5 (**4d**)) have been successfully synthesized. The structures of these compounds have been determined by spectroscopy and X-ray crystallography. The nickel complexes show high catalytic activity toward polymerization of ethylene and norbornene with the assistance of methyaluminoxanes (MAO). Complex **4c** shows better activity than **4d** for polyethylene formation. But opposite activity order was found for the polynorborylene formation. It indicates that the processes of polymerization for ethylene and for norbornene might have different rate-determining steps.

Introduction

Polymers play important roles in modern world. Since Ziegler and Natta discovered the olefin polymerization using heterogeneous catalysts of Ti-Al mixtures in 1950s, scientists have been continuing to seek for new catalysts.[1] In 1980, Sinn and Kaminsky found that the homogeneous catalysts of Ti or Zr activated with methyl aluminoxane (MAO) could polymerize monomers that Ziegler-Natta catalysts could not.[2] Late transition-metal catalysts used for olefin polymerization acquired little progress until mid eighties. Grubbs and Schrock established ring opening metathesis polymerization using ruthenium-carbene complexes, which could catalyze the polymerization of polar monomers.[3] Brookhart found that nickel, palladium, and iron complexes bearing α-diimine ligands with bulky substituents could effectively catalyze ethylene polymerization.[4] Ligand design has become crucial to the development of new catalysts for olefin polymerization.

Generally speaking, the ligand can provide fundamental influence in a metal complex in three aspects: 1) stabilize the metal cation; 2) control the coordination geometry, and 3) control the oxidation state. All these factors may profoundly influence the catalytic activity and selectivity. In this study, the nickel complexes bearing hybrid bidentate ligands containing amine-imine functionalities are employed for olefin polymerization.Some preliminary results have demonstrated that the aliphatic amino substituents of the nickel complexes in the form of [$RNCMe_2CH{=}N(2,6\text{-}Me_2C_6H_3)$]$NiBr_2$ can influence the activity of the reactions of ethylene or norbornene polymerization. In this work, the preparation of the nickel complexes with cyclic aliphatic amino substituents has been done. The synthesis and characterization of two new derivatives of the nickel catalysts as well as their reactivity towards the polymerization of ethylene and norbornene have been studied.

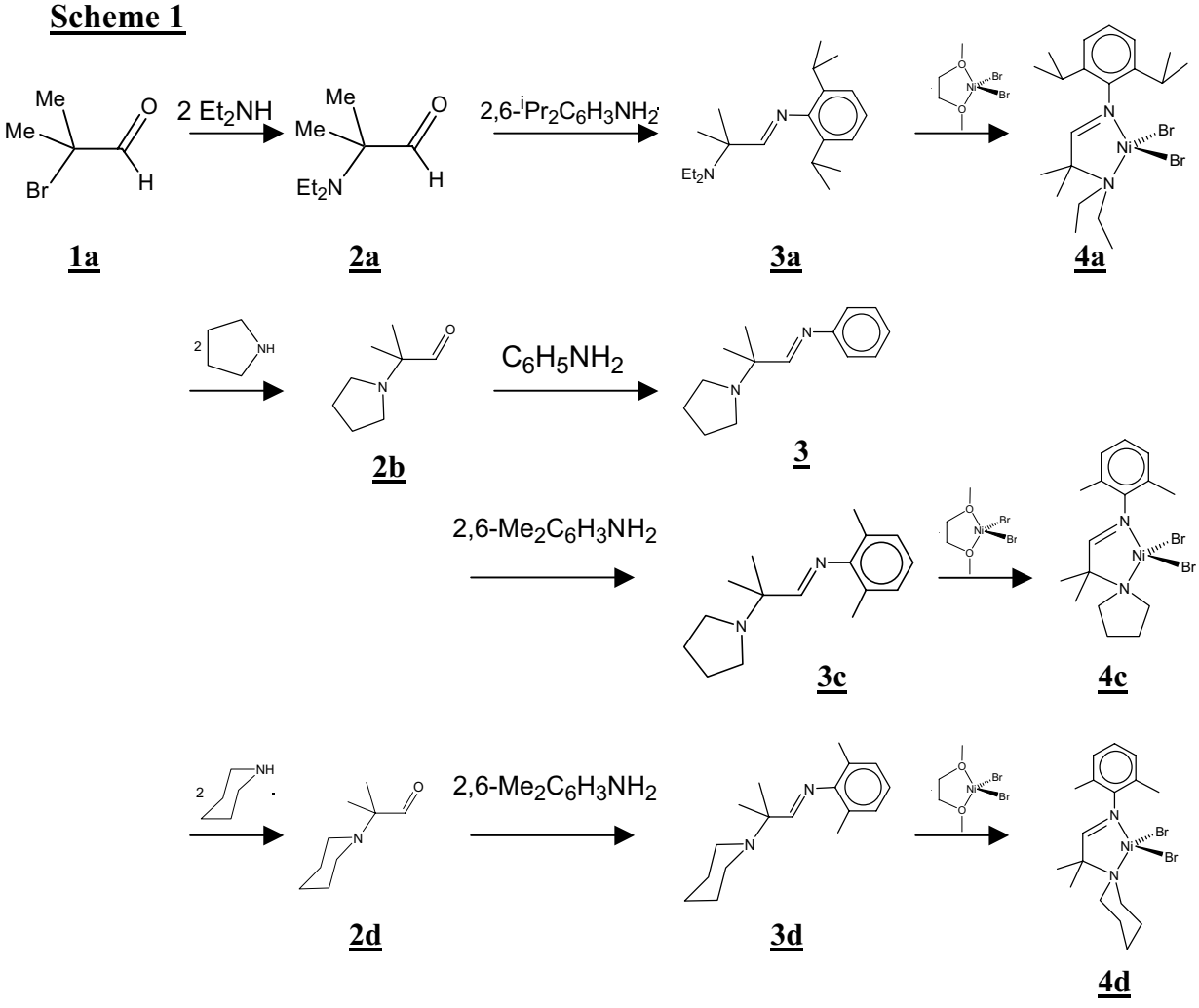
Experiment

Instrumentation

1. Nuclear Magnetic Resonance Spectrometer: Bruker AC-200, AC-300
2. Mass Spectrometer: Finnigan TSQ-46C MASS；Jeol SX-102A MASS
3. X-Ray Single Crystal Diffractometer: Dutch Enraf Nonious CAD-4 Kappa Axis XRD(FR 586,FR590)；Germany Siemens Smart CCD XRD
4. Elemental Analyzer: Perkin Elmer 2400
5. UV-VIS Spectrophotometer: Shimazu U-3010 Spectrophotometer
6. Gel Permeation Chromatography: ENSH INE SuperCO-150
7. Differential Scanning Analysis: Perkin Elmer Pyris 6 DSC

Synthetic Procedures of Ligands and Complexes

Scheme 1



Ligands **3a**, **3b**, **3c**, and **3d** have been synthesized first by amination of α-bromoaldehyde, then followed by condensation with aniline derivatives as shown in Scheme I. The nickel complexes **4a**, **4c**, and **4d** are formed by substitution reactions of $Ni(DME)Br_2$ with the synthesized ligands in inert atmosphere. The typical procedures for the ligands **3c** and complex **4c** are described below.

1. $BrCMe_2CHO$(1a)

To a petri dish, 6 mL of bromine was slowly added into 10 mL of dioxane and mixed thoroughly to give orange solid product. In an Erlenmeyer flask, the solid was added to 6.41 mL of 2-methylpropanal with ether as solvent. The mixture was extracted by cold water, and the organic layer was collected. A minute amount of anhydrous magnesium sulfate was added to remove water. The solution was filtered and the solvent was evaporated.

2. c-$(CH_2)_4NCMe_2CHO$(2b)

$BrCMe_2CHO$ (**1a**) (5.87 g) was placed in a flask with ether as solvent. Pyrrolidine of two equivalents was added in the aliquot of a few drops at a time with use of the ice bath. The solution was then stirred for 6 hours at room temperature. Two layers of solution were resulted. The upper one was collected; and the solvent was evaporated.

3. c-$(CH_2)_4NCMe_2CN(2,6\text{-}Me_2C_6H_3)$ (3c)

2,6-dimethylaniline (6.0 mL) was mixed with $(c\text{-}C_4H_8N)CMe_2CHO$ (**2b**) (6.84 g) with toluene as solvent. The solution was refluxed along with a few drops of sulfuric acid in a Dean-Stark set-up for 6 hours. The solvent was removed by distillation under reduced pressure. The product was collected between 120℃ and 130℃.

4. [c-$(CH_2)_4NCMe_2CN(2,6\text{-}Me_2C_6H_3)$]$NiBr_2$ (4c)

Into a Shlenck reactor, was placed $Ni(DME)Br_2$ (150 mg, 0.486mmol) in a dry box. Ligand **3c** of 1.5 equivalents in dried dichloromethane was added, and the reaction solution was stir for 2 hours. The purple solution was filtered and concentrated. Purple solid product was precipitated from diethyl ether.

The purification and identification of the ligands and complexes

The ligands were purified via distillation under reduced pressure. The resulting products were mainly identified by ^{1}H NMR. The nickel complexes are hygroscopic. Precaution for predrying the ligand before the synthesis of the inorganic complexes is necessary. The paramagetic nickel complexes are identified with MS, elemental analysis and/or X-ray crystallography.

Reactions of Polymerization

The nickel complexes activated with the co-catalyst, methyl aluminoxanes (MAO), were used to catalyze the polymerization of ethylene and norbornene in toluene at 25 ℃ under nitrogen atmosphere. The characterizations of the polymers were done by GPC, TGA, DSC, and/or NMR.

1. The polymerization of ethylene

In the dry box, 10 mg of nickel catalyst and 50 mL toluene were transferred into a Parr autoclave, followed with 5.6 mL of 10% MAO (Ni：Al＝1：480). The reactor was locked and taken out of the dry box. Ethylene was filled to the pressure of 250 psi and kept constant. The solution was stirred with a magnetic bar for 1 hour. The pressure was released. Methanol and hydrochloric acid were used to deactivate MAO. The organic layer was collected. Acetone was added to precipitate the product.

2. The polymerization of norbornene

In the dry box, 10 mg of nickel catalyst and 5 g of norbornene in 50 mL toluene were placed into a flask, followed with 5.6 mL of 10% MAO (Ni：Al＝1：480). The reaction solution was stirred at 25 ℃ for 1 hour. Methanol and hydrochloric acid were added to quench the reaction. White precipitate was collected.

Results and Discussion

Yield

3a-51%　　**3b**-50%　　**3c**-69%　　**3d**-60%

4a-28%　　**4c**-69%　　**4d**-73%

The Data of Characterization

1. ^{1}H NMR ($CDCl_3$) data for ligands：

3a— δ 7.56 (s, 1H, C<u>H</u>=N), 7.10-7.03 (m, 3H, phenyl-<u>H</u>), 2.87 (m, J_{H-H} = 6.8 Hz, 2H, C<u>H</u>$(CH_3)_2$), 2.64 (q, J_{H-H} = 7.2 Hz, 4H, NC<u>H</u>$_2$CH_3), 1.33 (s, 6H, C<u>H</u>$_3$), 1.14 (d, J_{H-H} = 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.05 (t, J_{H-H} = 7.2 Hz, 6H, NCH$_2$C<u>H</u>$_3$)

3b— δ 7.83 (s, 1H, C<u>H</u>=N), 7.35-7.00 (m, 5H, phenyl-<u>H</u>), 2.74, 1.77 (m, m, 4H, 4H, c-C$_4$<u>H</u>$_8$N), 1.33 (s, 6H, C<u>H</u>$_3$)

3c— δ 7.66 (s, 1H, C<u>H</u>=N), 6.99 (d, J_{H-H} = 7.5 Hz, 2H, phenyl-<u>H</u>), 6.87 (t, J_{H-H} = 7.5 Hz, 1H, phenyl-<u>H</u>), 2.77, 1.77 (m, m, 4H, 4H, c- C$_4$<u>H</u>$_8$N), 1.37 (s, 6H, C<u>H</u>$_3$)

3d— δ 7.60 (s, 1H, C<u>H</u>=N), 7.00 (d, J_{H-H} = 7.5 Hz, 2H, phenyl-<u>H</u>), 6.91 (t, J_{H-H} = 7.5 Hz, 1H, phenyl-<u>H</u>), 2.09 (s, 6H, CC<u>H</u>$_3$), 2.57, 1.59, 1.46 (m, m, m, 4H, 4H, 2H, c- C$_5$<u>H</u>$_{10}$N), 1.31 (s, 6H, C<u>H</u>$_3$)

2. Complexes

4a[5]— ^{1}H NMR ($CDCl_3$)：δ 8.28 (s, 1H, C<u>H</u>=N), 7.13 (br, 3H, phenyl-<u>H</u>), 3.48,3.12 (m, 4H, J_{H-H} = 6.5, NC<u>H</u>$_2$CH_3), 2.73 (m, 1H, J_{H-H} = 6.8, C<u>H</u>$(CH_3)_2$), 1.12 (d, 6H, J_{H-H} = 6.8, CH(C<u>H</u>$_3$)$_2$), 1.05 (t, 6H, J_{H-H} = 6.5, N(CH$_2$C<u>H</u>$_3$)$_2$)

^{13}C NMR ($CDCl_3$)：δ 163.8 (<u>C</u>H=N), 145.8, 136.0-122.5 (phenyl-<u>C</u>), 70.0 (<u>C</u>$(CH_3)_2$), 46.5 (N(<u>C</u>H$_2$CH$_3$)$_2$), 29.1 (<u>C</u>H$(CH_3)_2$), 23.0 (CH(<u>C</u>H$_3$)$_2$), 21.3 (C(<u>C</u>H$_3$)$_2$), 12.0 (N (CH$_2$<u>C</u>H$_3$)$_2$)

4c— MS(FAB, m/z)：381,383(M+1-Br)

UV-Visible：λ_{max} = 517.5 nm

EA：Found：N, 5.53, C, 40.99, H, 4.33

Calcd: N, 6.05, C, 41.52, H, 5.23

4d— UV-Visible：λ_{max} = 516 nm

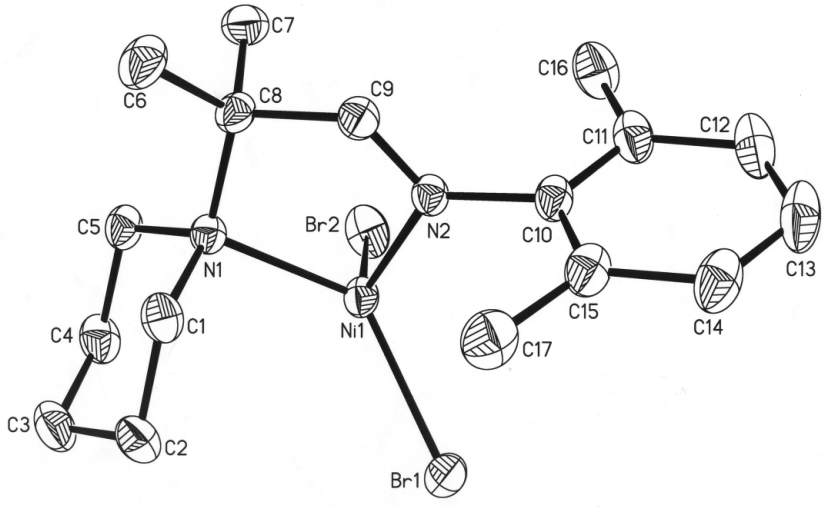
X-Ray：The configuration of the complex is approximately tetrahedral. The ligand chelates with nickel in bidentate mode and forms a five-member ring. Selected bond angles and lengths along with the ORTEP are shown below.

Bond angles (degree)

N(2)-Ni-Br(1)	N(1)-Ni-Br(2)	N(2)-Ni-Br(2)	N(1)-Ni-Br(1)	Br(1)-Ni-Br(2)	N(1)-Ni-N(2)
106.03(7)	104.51(6)	130.28(6)	130.28(6)	113.74(2)	82.41(9)

Bond lengths (Å)

Br(1)-Ni	Br(2)-Ni	Ni-N(2)	Ni-N(1)
2.3527(5)	2.3638(5)	1.997(2)	2.084(2)



Data for polymerization

Table 1 ethylene polymerization

Catalyst (μmol)	Reaction time(h)	Yield (g)	Activity (kg/mol Ni•hr)	M_n	PDI (M_w/M_n)	T_g (℃)	Branches (per 10^3 C)
4a (22)[5]	3	2.9	51.5	238000	1.69	—	143
4c (21)	1	3.5	162.0	391400	1.26	38.5	117
4d (22)	1	0.08	3.8	—	—	—	106
4d (22)	3	0.87	13.8	95500	1.43	30.0	108

Table 2 norbornene polymerization

Catalyst (μmol)	Reaction time (h)	Ni：Al	Activity (kg/mol Ni•hr)	M_n	PDI (M_w/M_n)	T_g (℃)
4a (22)	0.25	1：230	331.6	*	—	—
4c (21)	1	1：480	23.1	53200	1.91	322.0**
4d (22)	1	1：480	57.1	*	—	**

* The products are insoluble in toluene. The GPC data are not available.

** The T_g does not appear below 350 ℃.

Ligand Effect on Polymerizations of Ethylene and Norbornene

The amino substituent is acyclic in **4a**, but cyclic in **4c**. The data of ethylene polymerization show that **4c** gives better activity and the products of higher molecular weight; lower value of PDI and less branches than does **4a**.

On the other hand, **4d** with six-member amino ring shows poorer activity and gives the products of lower molecular weight than does **4c** with five-member amino ring. **4c** results in smaller value of PDI value. It suggests that ***the less steric and less free pyrrolidinyl substituent of 4c, might be favored for ethylene polymerization.***

The measurements for the molecular weight of polynorbornenes are not feasible owing to the poor solubility of PN in toluene. Despite of the limited data in Table 2, complex **4c** results in lower activity than either **4a** or **4d**, in contrast to the results of ethylene polymerization. Besides, complex **4a** with two ethyl substituents shows better activity than both complexes containing cyclic amino group. One could conclude that ***the more steric and more free amino substituents may be favored for norbornene polymerization.***

Such results might be explained by the different rate-determining step in the polymerization reactions of ethylene and norbornene.

Ethylene is a small weakly coordinating ligand. The steric effect of the amino substituent may hinder the rate-determining coordination of ethylene. In comparison with ethylene, norbornene is a strong bulky ligand. Its coordination to the metal is less interfered by ligand difference. Instead, the insertion of norbornene could be further accelerated in **4a** and **4d** than in **4c**, because the steric stress may be released when the coordination number decreases.

Conclusions

1. The amine-imine bidentate lignads, $Et_2NCMe_2CH=N(2,6\text{-}^{i}Pr_2C_6H_3)$ (**3a**), $(c\text{-}C_4H_8)NCMe_2CH=NPh$ (**3b**), $RNCMe_2CH=N(2,6\text{-}Me_2C_6H_3)$ (R = $c\text{-}C_4H_8$ **3c**, $c\text{-}C_5H_{10}$ **3d**), and its nickel complexes, $Ni[Et_2NCMe_2CH=N(2,6\text{-}^{i}Pr_2C_6H_3)]Br_2$ (**4a**), $Ni[RNCMe_2CH=N\ (2,6\text{-}Me_2C_6H_3)]Br_2$ (R = $c\text{-}C_4H_8$ **4c**, $c\text{-}C_5H_{10}$ **4d**) have been synthesized and fully characterized.

2. The single-crystal X-ray crystallographic analysis shows that **4d** has distorted tetrahedral structure. The bidentate ligand chelates with nickel and forms a five-member metallocyclic ring.

3. The nickel complexes activated by MAO exhibit high catalytic activity towards polymerization of ethylene and norbornene. For the former reactions, the activity reaches 10^5 g/mol Ni·h. The average molecular weight of PE is 10^5, and the PDI value is 1.4. There are over 100 branches per 10^3 C. For the reactions of norbornene polymerization, the activity is about 10^4~10^5 g/mol Ni·h. The average molecular weight of PN is about 10^4.

4.The less steric and less free amino substituent of the ligand appears to be favored for ethylene polymerization, but disfavored for norbornene polymerization.

5.The results suggest that the rate-determining step in the polymerization of ethylene might be different from the polymerization of norbornene.

6.The design of ligand and catalyst is crucial with respect to the control of the catalytic olefin polymerization and the properties of the polymeric products.

References

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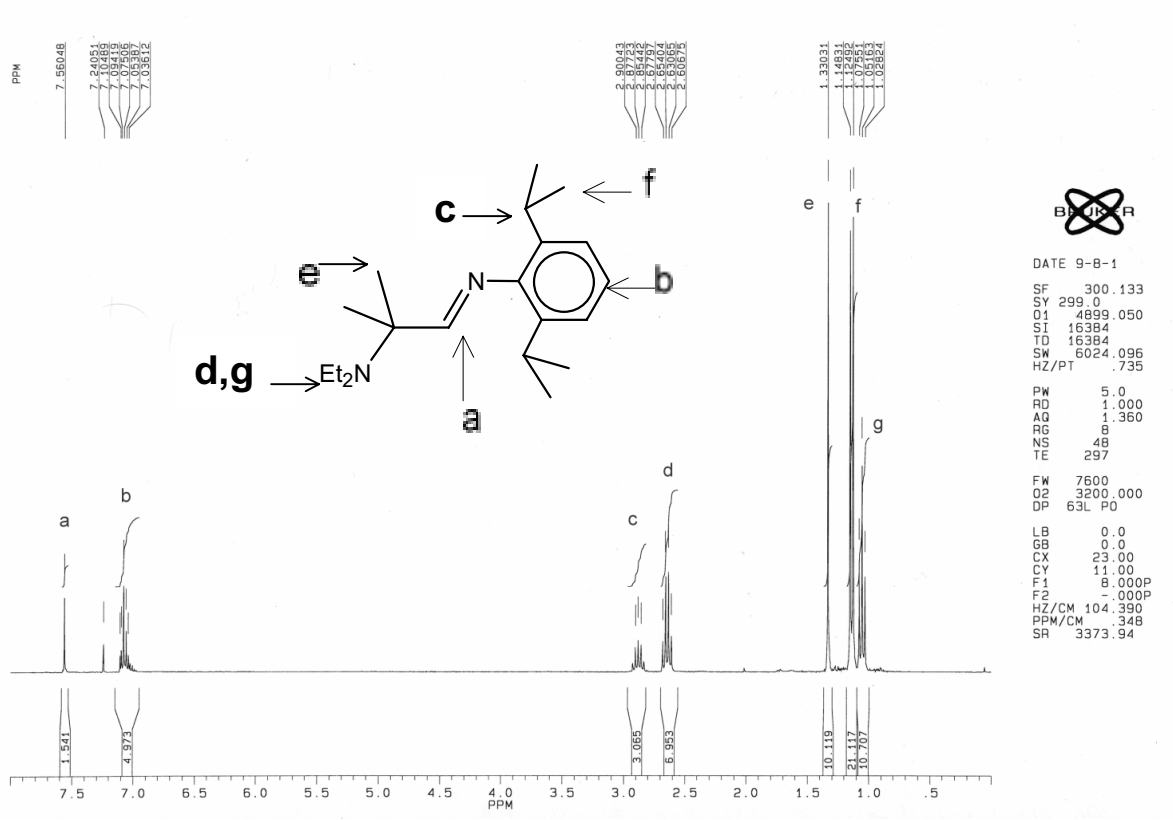
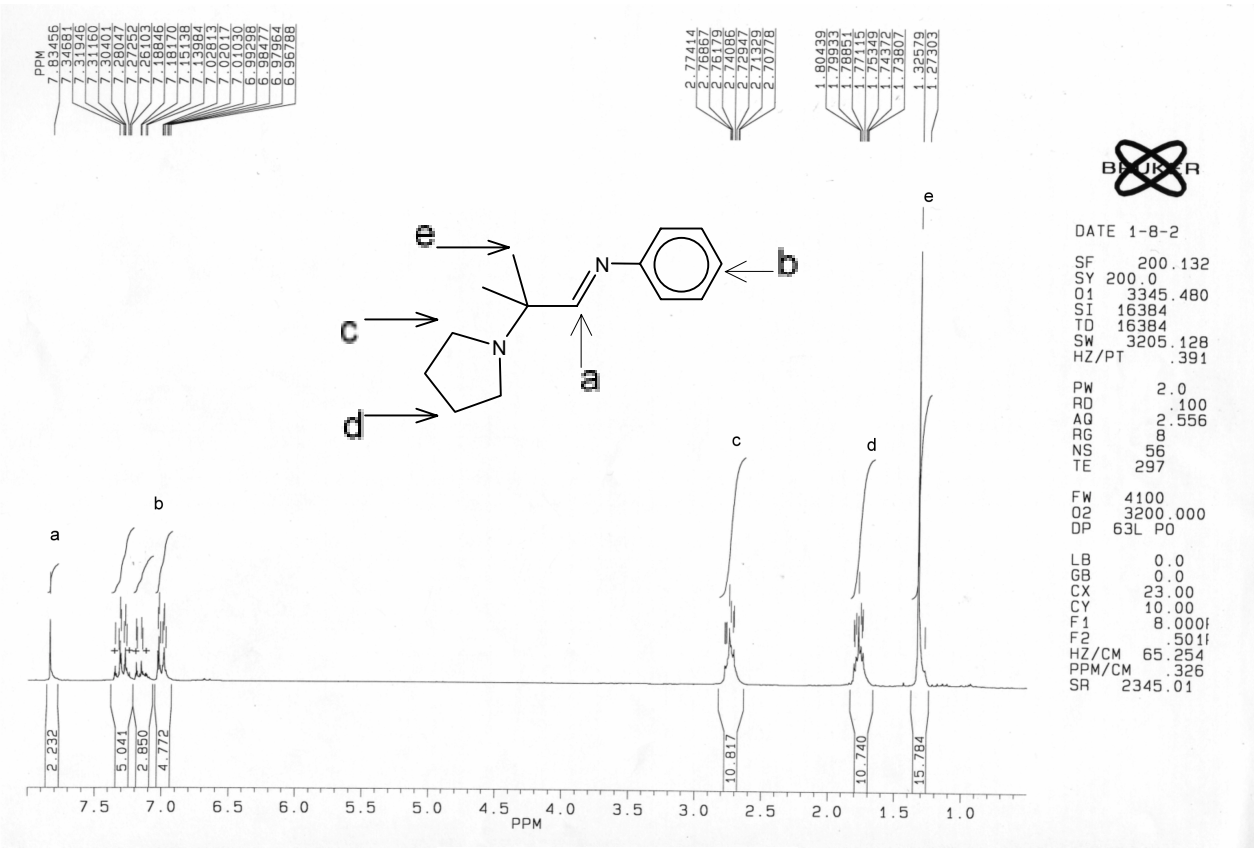
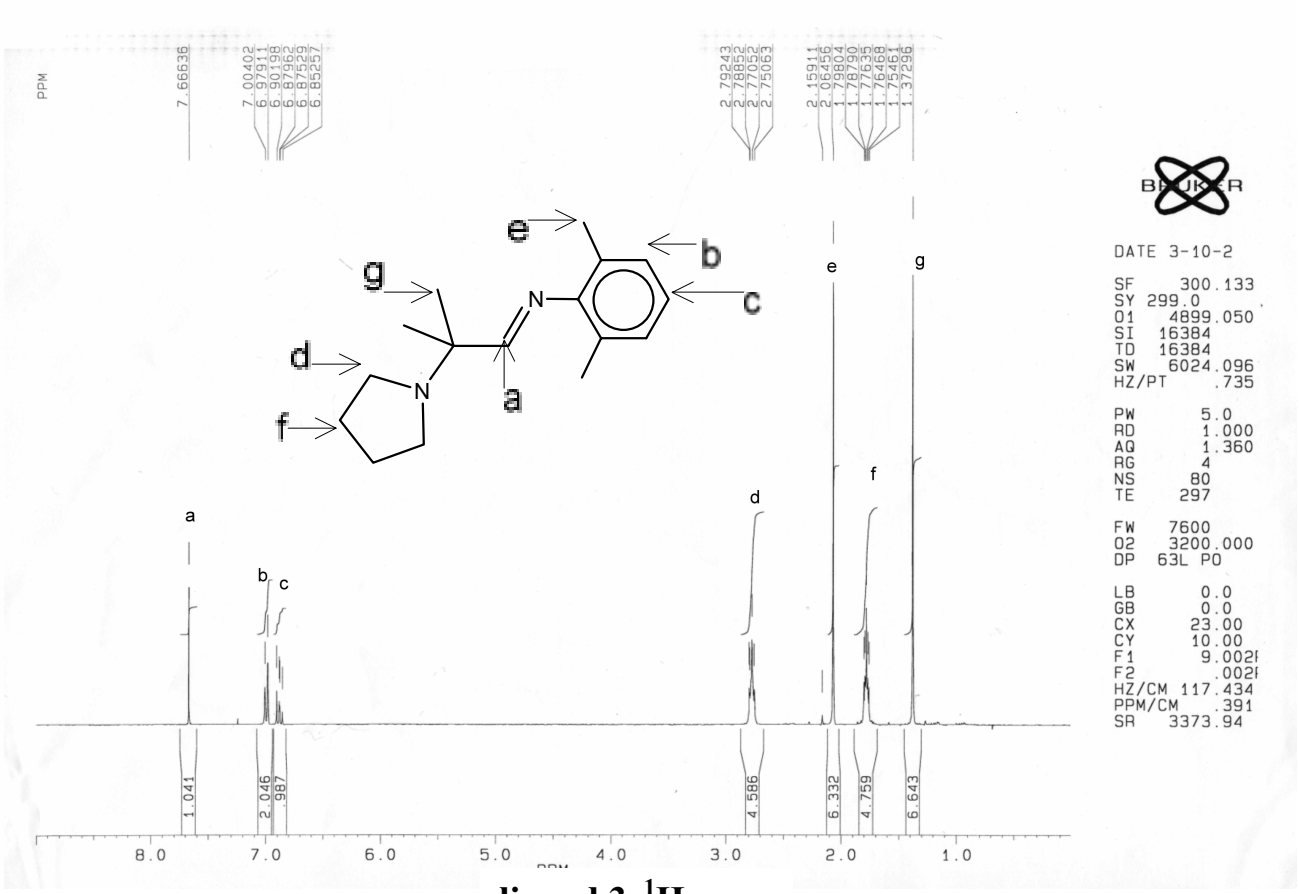
Appendix



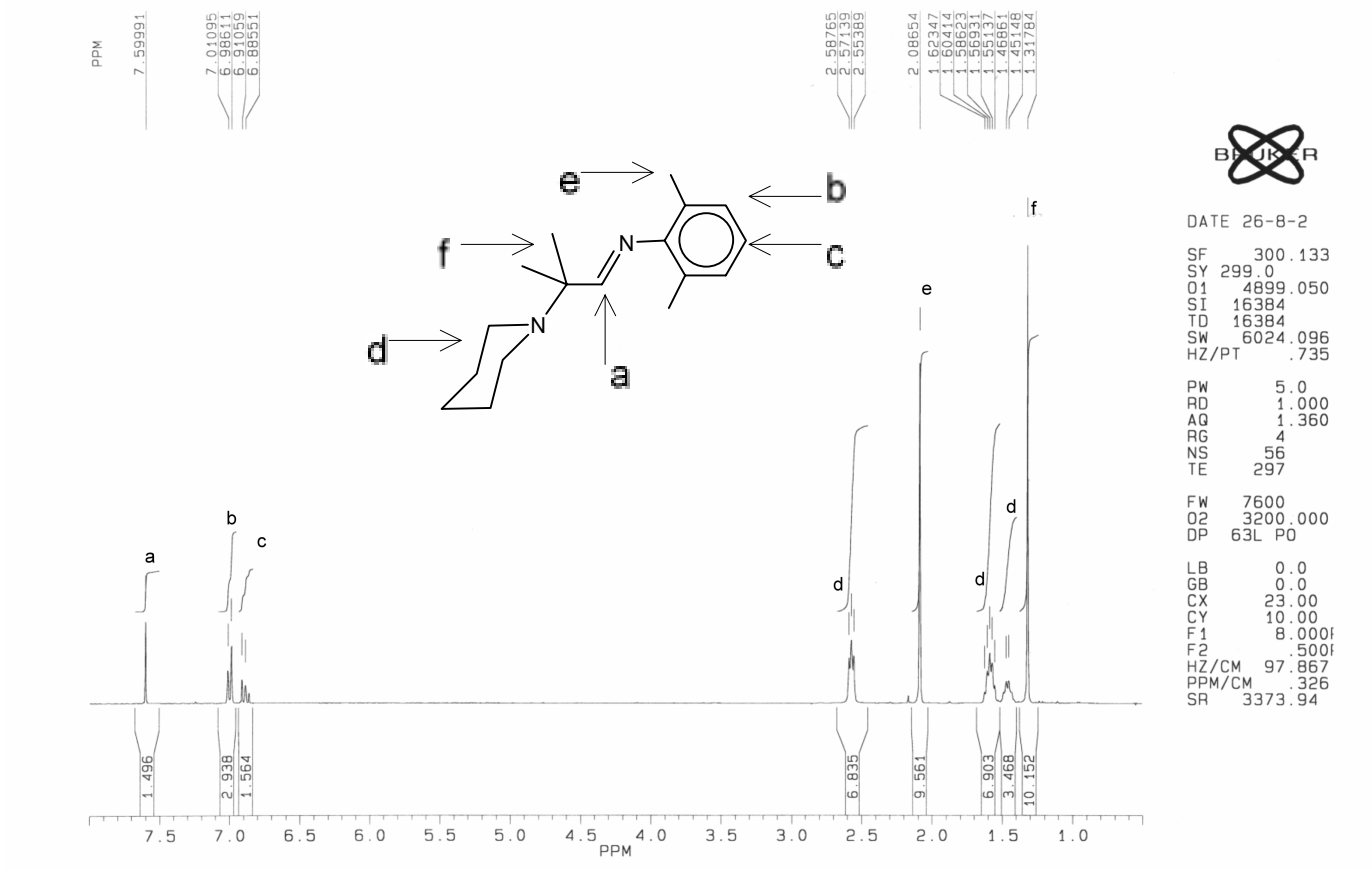
ligand 3a ^{1}H NMR



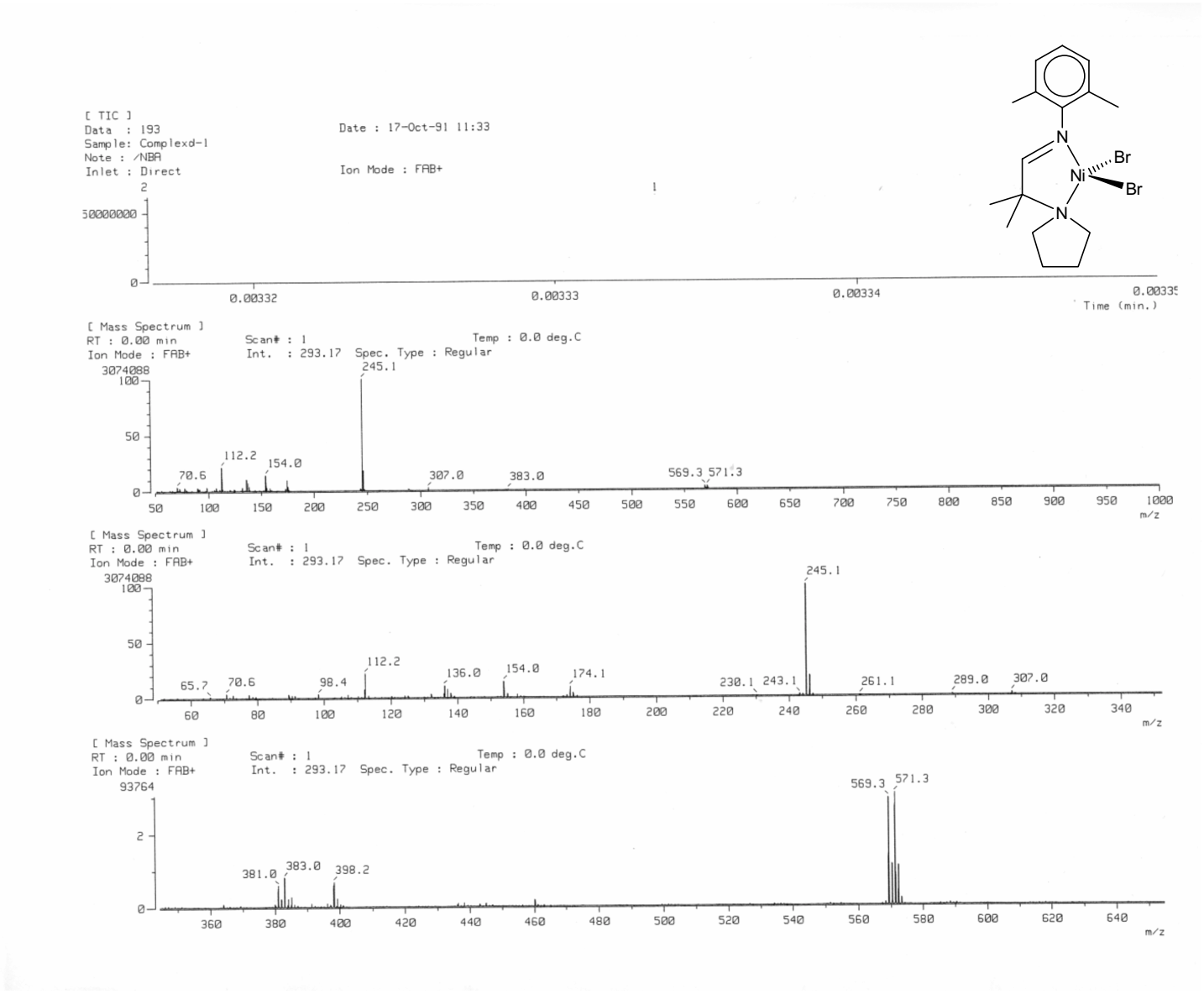
ligand 3b ^{1}H NMR



ligand 3c ^{1}H



ligand 3d ^{1}H NMR



complex <u>4c</u> MASS

complex 4d X-RAY data

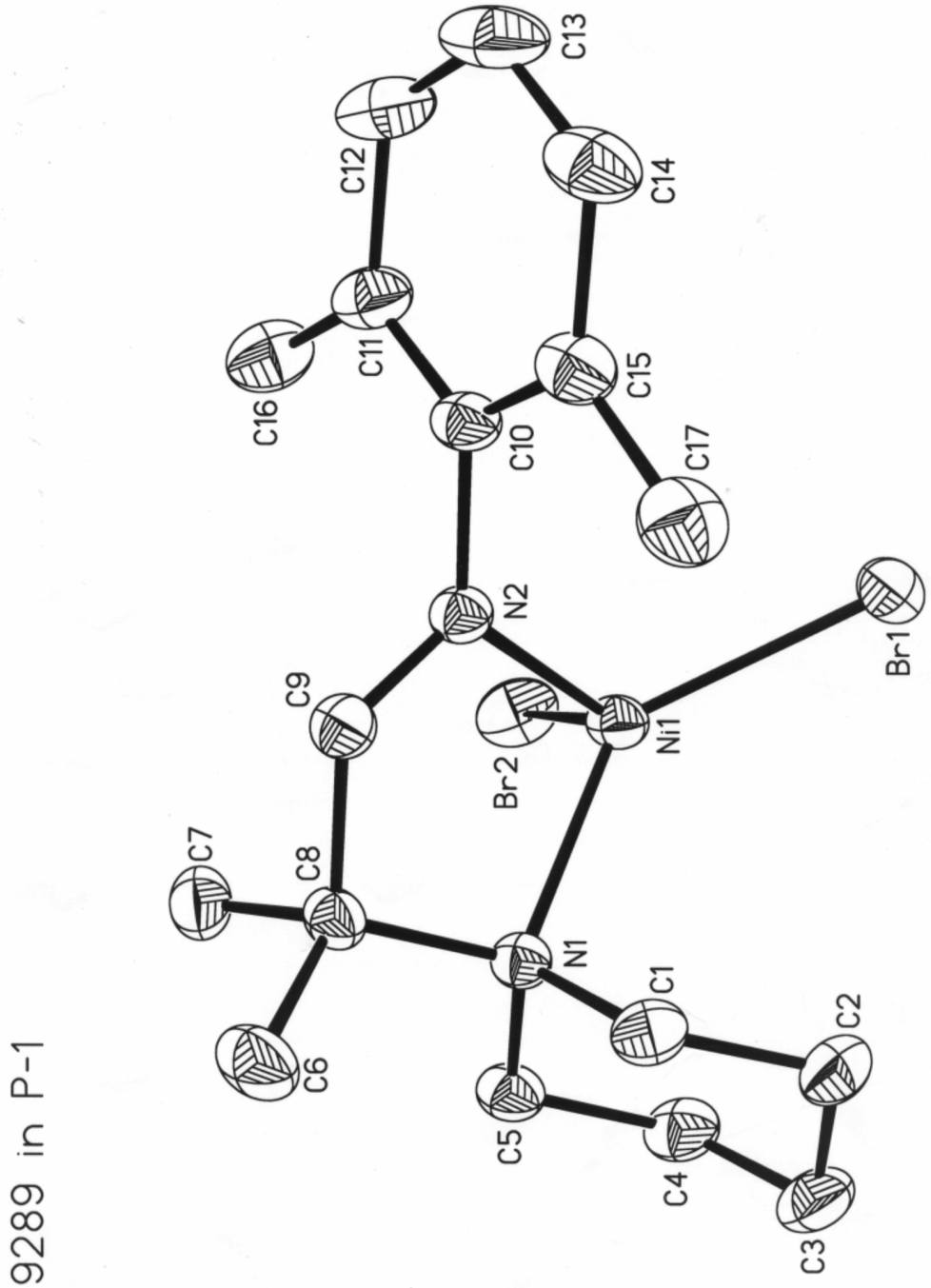


Table 1. Crystal data and structure refinement for IC9289.

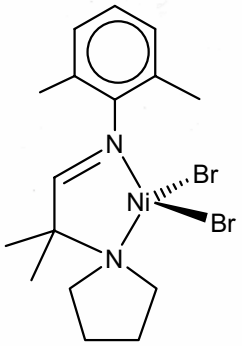
Identification code	ic9289
Diffractometer used	Nonius KappaCCD
Empirical formula	$C_{17}H_{26}Br_2N_2Ni$
Formula weight	476.93
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.10100(10) Å alpha = 100.4700(10)° b = 8.68800(10) Å beta = 93.7440(10)° c = 15.2850(2) Å gamma = 113.1160(10)°
Volume, Z	961.77(2) $Å^3$, 2
Density (calculated)	1.647 Mg/m^3
Absorption coefficient	5.162 mm^{-1}
F(000)	480
Crystal size	0.30 x 0.27 x 0.25 mm
θ range for data collection	4.11 to 27.48°
Limiting indices	$-10 \le h \le 10$, $-11 \le k \le 11$, $-19 \le l \le 19$
Reflections collected	19983
Independent reflections	4390 (R_{int} = 0.0542)
Absorption correction	Multi-scan
Max. and min. transmission	0.293 and 0.220
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4380 / 0 / 201
Goodness-of-fit on F^2	0.987
Final R indices [I>2σ(I)]	R1 = 0.0345, wR2 = 0.0863
R indices (all data)	R1 = 0.0433, wR2 = 0.0925
Extinction coefficient	0.0153(14)
Largest diff. peak and hole	1.230 and -0.804 $eÅ^{-3}$

Table 2. Bond lengths [Å] and angles [°] for 9289.

Br(1)-Ni(1)	2.3527(5)	Br(2)-Ni(1)	2.3638(5)
Ni(1)-N(2)	1.997(2)	Ni(1)-N(1)	2.084(2)
N(1)-C(5)	1.492(3)	N(1)-C(1)	1.499(4)
N(1)-C(8)	1.527(3)	N(2)-C(9)	1.261(4)
N(2)-C(10)	1.456(3)	C(1)-C(2)	1.514(5)
C(2)-C(3)	1.515(5)	C(3)-C(4)	1.517(5)
C(4)-C(5)	1.518(4)	C(6)-C(8)	1.533(4)
C(7)-C(8)	1.542(4)	C(8)-C(9)	1.503(4)
C(10)-C(15)	1.389(4)	C(10)-C(11)	1.394(4)
C(11)-C(12)	1.403(5)	C(11)-C(16)	1.498(5)
C(12)-C(13)	1.373(6)	C(13)-C(14)	1.371(6)
C(14)-C(15)	1.393(5)	C(15)-C(17)	1.501(5)
N(2)-Ni(1)-N(1)	82.41(9)	N(2)-Ni(1)-Br(1)	106.03(7)
N(1)-Ni(1)-Br(1)	130.28(6)	N(2)-Ni(1)-Br(2)	116.53(7)
N(1)-Ni(1)-Br(2)	104.51(6)	Br(1)-Ni(1)-Br(2)	113.74(2)
C(5)-N(1)-C(1)	108.6(2)	C(5)-N(1)-C(8)	112.0(2)
C(1)-N(1)-C(8)	110.2(2)	C(5)-N(1)-Ni(1)	113.9(2)
C(1)-N(1)-Ni(1)	106.7(2)	C(8)-N(1)-Ni(1)	105.4(2)
C(9)-N(2)-C(10)	120.2(2)	C(9)-N(2)-Ni(1)	113.4(2)
C(10)-N(2)-Ni(1)	126.4(2)	N(1)-C(1)-C(2)	112.6(2)
C(1)-C(2)-C(3)	110.8(3)	C(2)-C(3)-C(4)	109.4(3)
C(3)-C(4)-C(5)	112.5(3)	N(1)-C(5)-C(4)	111.4(2)
C(9)-C(8)-N(1)	106.9(2)	C(9)-C(8)-C(6)	109.7(2)
N(1)-C(8)-C(6)	114.5(3)	C(9)-C(8)-C(7)	104.8(2)
N(1)-C(8)-C(7)	111.8(2)	C(6)-C(8)-C(7)	108.7(3)
N(2)-C(9)-C(8)	121.5(2)	C(15)-C(10)-C(11)	123.5(3)
C(15)-C(10)-N(2)	118.3(3)	C(11)-C(10)-N(2)	118.2(3)
C(10)-C(11)-C(12)	116.4(3)	C(10)-C(11)-C(16)	122.8(3)
C(12)-C(11)-C(16)	120.9(3)	C(13)-C(12)-C(11)	121.5(4)
C(14)-C(13)-C(12)	120.1(3)	C(13)-C(14)-C(15)	121.4(4)
C(10)-C(15)-C(14)	117.1(3)	C(10)-C(15)-C(17)	122.1(3)
C(14)-C(15)-C(17)	120.8(3)		

Symmetry transformations used to generate equivalent atoms:

GPC data for PE using complex 4c



檔案名稱: COMPLEX-4C-PE-1HR.CHR
STD. 檔案名稱: JTC-GPC-IVAN.GSD
注射試樣時間: 10-24-2002 18:42:39
印表日期: 2002-10-24 印表時間: 19:01:47
切片範圍: 4.967 到 6.077 分鐘 切片時間: 0.200 分鐘
波峰最高時間: 6.623 分鐘 分子量 = 51482
Q 係數: 1.000 A 係數: 1.000 K 係數: 1.0000000

平均分子量值

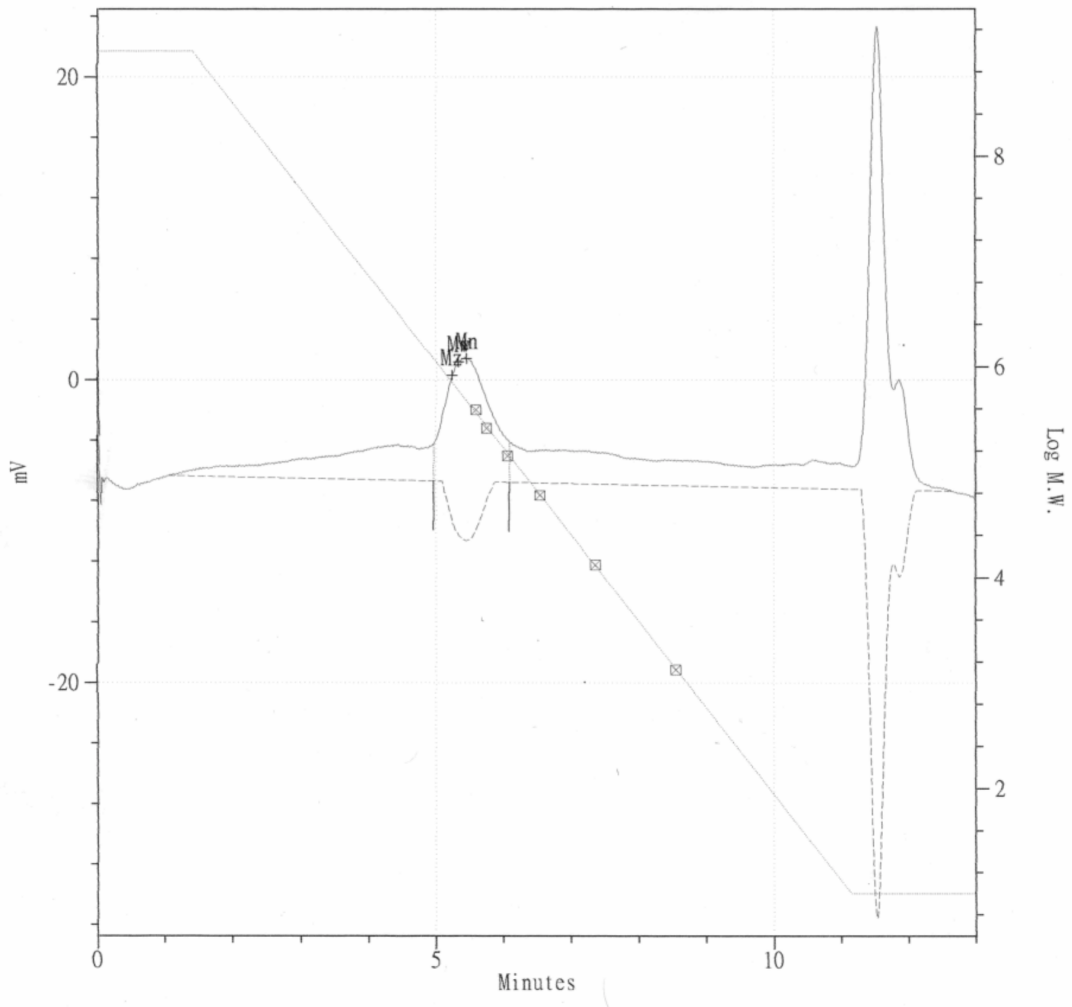
Mn	(數平均分子量值)	= 391377
Mw	(重量平均分子量值)	= 494389
Mz	(Z 平均分子量值)	= 598988
Mv	(黏度平均分子量值)	= 494389
I.V	(固有黏度)	= 494389

Dispersity 和 其它比值

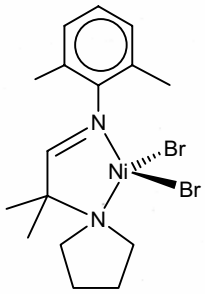
Mw/Mn= 1.26320 Mz/Mn = 1.53047 Mv/Mn = 1.26320

圖譜曲線 檢量線
基線

Solvent peak



GPC data for PN using complex 4c

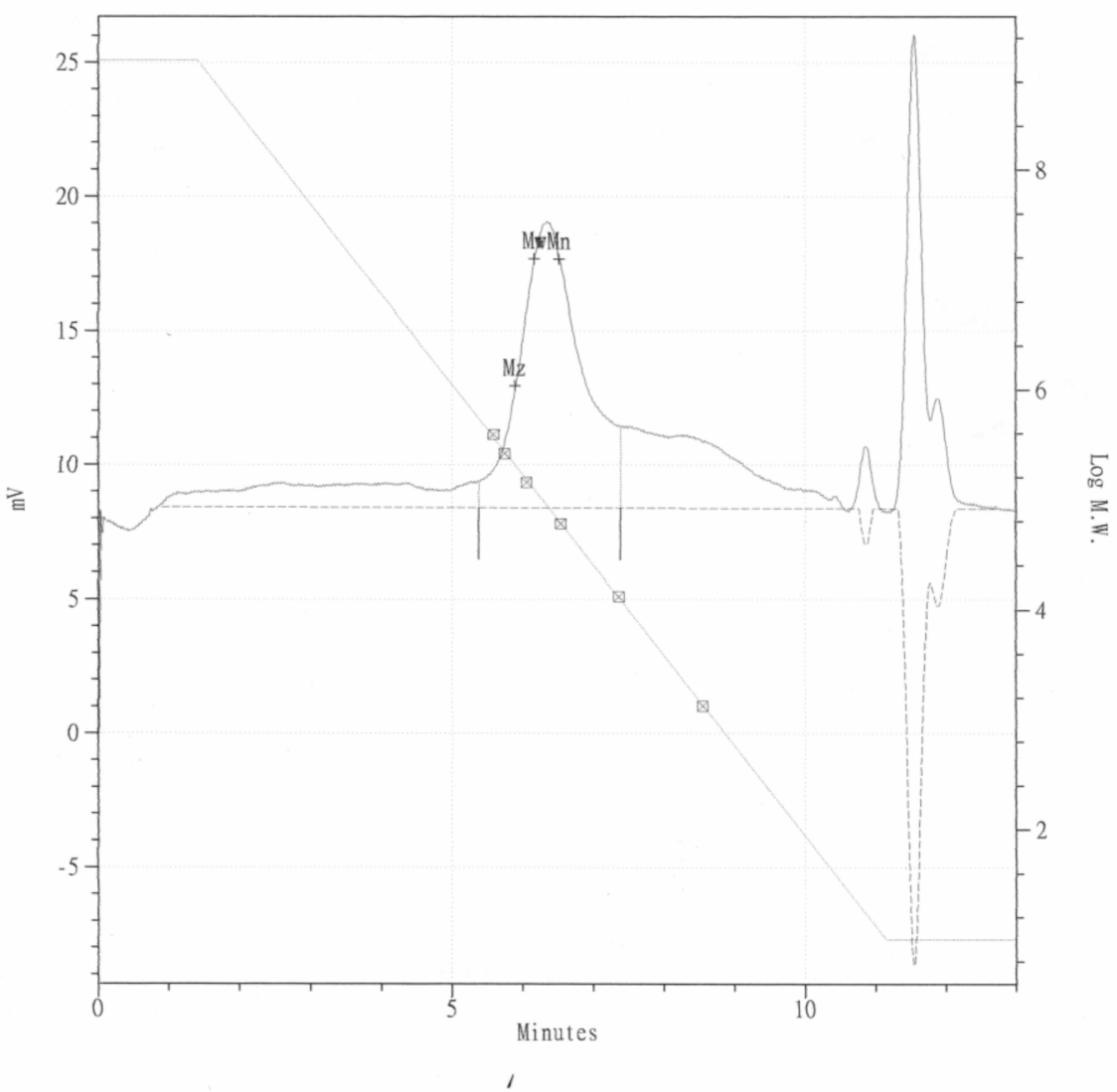


檔案名稱: COMPLEX-4C-PN-1HR.CHR
STD. 檔案名稱: JTC-GPC-IVAN.GSD
注射試樣時間: 10-23-2002 20:03:08
印表日期: 2002-10-23 印表時間: 20:20:55
切片範圍: 5.377 到 7.380 分鐘 切片時間: 0.200 分鐘
波峰最高時間: 6.333 分鐘 分子量 = 89049
Q 係數: 1.000 A 係數: 1.000 K 係數: 1.0000000

平均分子量值
Mn (數平均分子量值) = 53158
Mw (重量平均分子量值) = 101324
Mz (Z 平均分子量值) = 173621
Mv (黏度平均分子量值) = 101324
I.V (固有黏度) = 101324

Dispersity 和 其它比值
Mw/Mn= 1.90609 Mz/Mn = 3.26613 Mv/Mn = 1.90609

Solvent peak

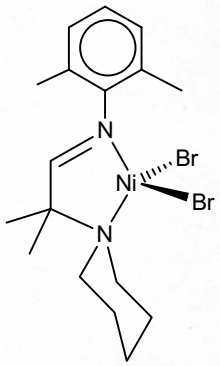


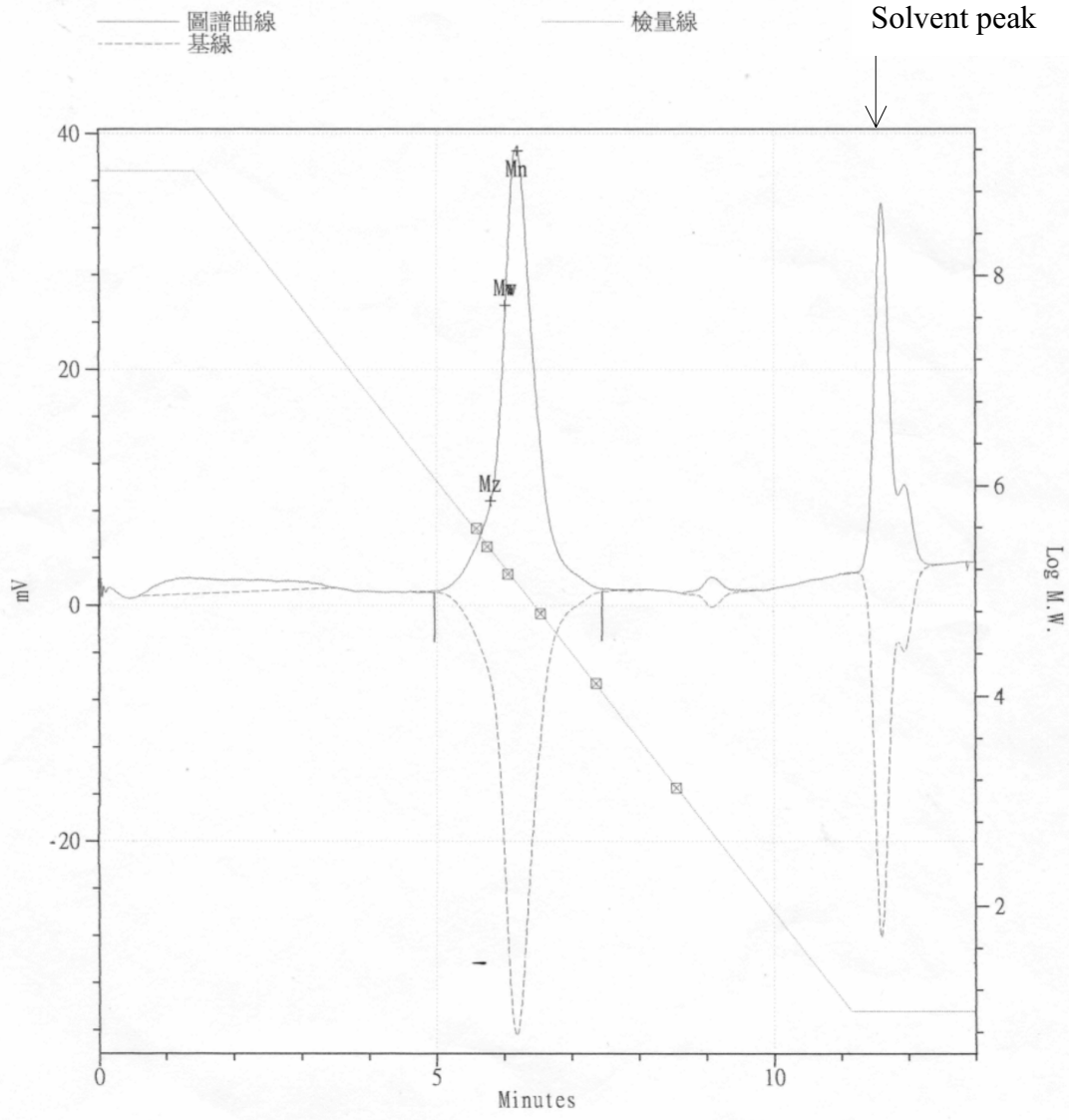
GPC data for PE using complex 4d

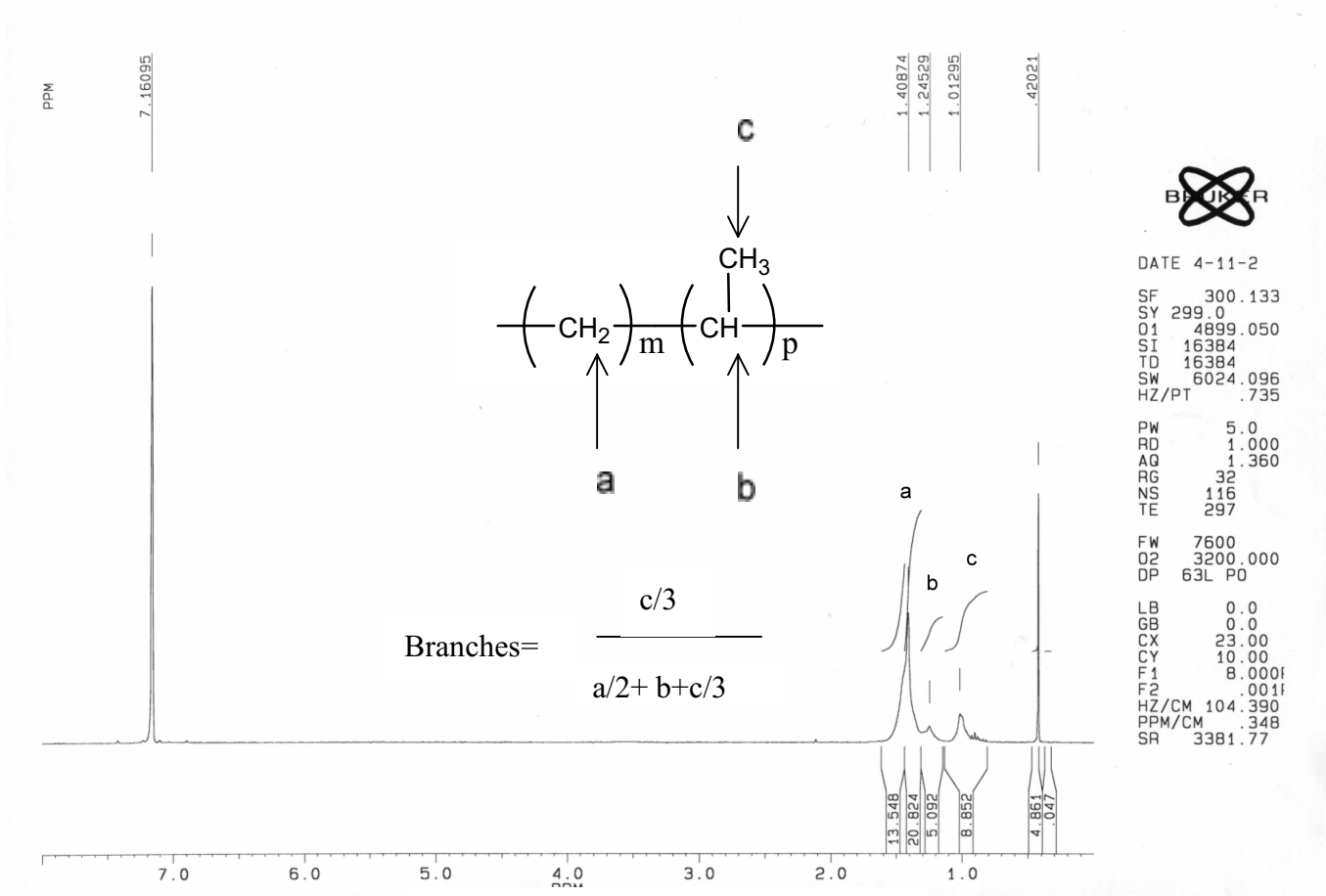
檔案名稱: COMPLEX-4D-PE-3HR.CHR
STD. 檔案名稱: JTC-GPC-IVAN.GSD
注射試樣時間: 09-25-2002 19:20:40
印表日期: 2002-09-25　　印表時間: 19:35:13
切片範圍: 4.967 到 7.450 分鐘　　切片時間: 0.200 分鐘
波峰最高時間: 1.333 分鐘　　分子量 = 1000000000
Q 係數: 1.000　　A 係數: 1.000　　K 係數: 1.0000000

平均分子量值
Mn (數平均分子量值) = 95523
Mw (重量平均分子量值) = 137528
Mz (Z 平均分子量值) = 205811
Mv (黏度平均分子量值) = 137528
I.V. (固有黏度) = 137528

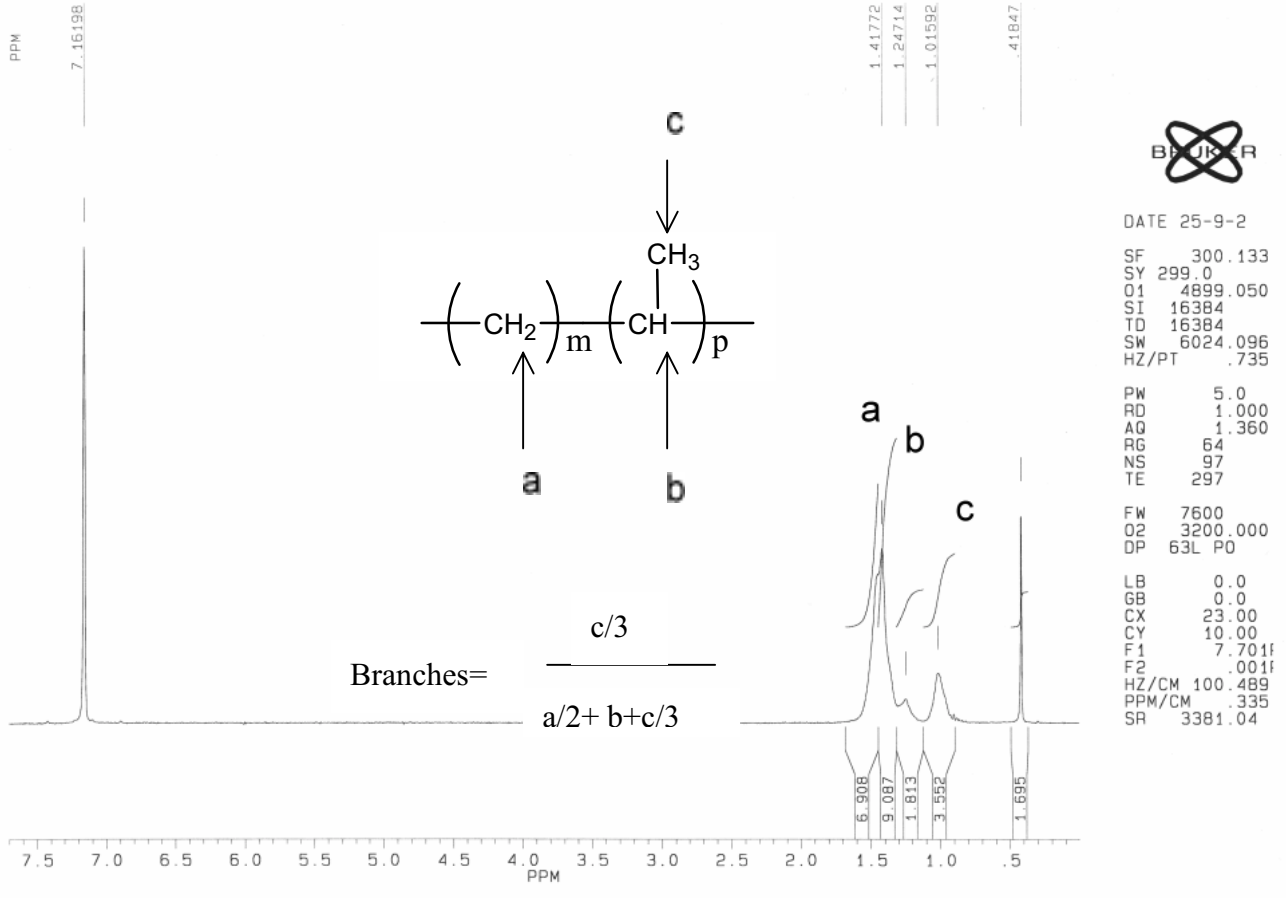
Dispersity 和 其它比值
Mw/Mn= 1.43973　　Mz/Mn = 2.15456　　Mv/Mn = 1.43973



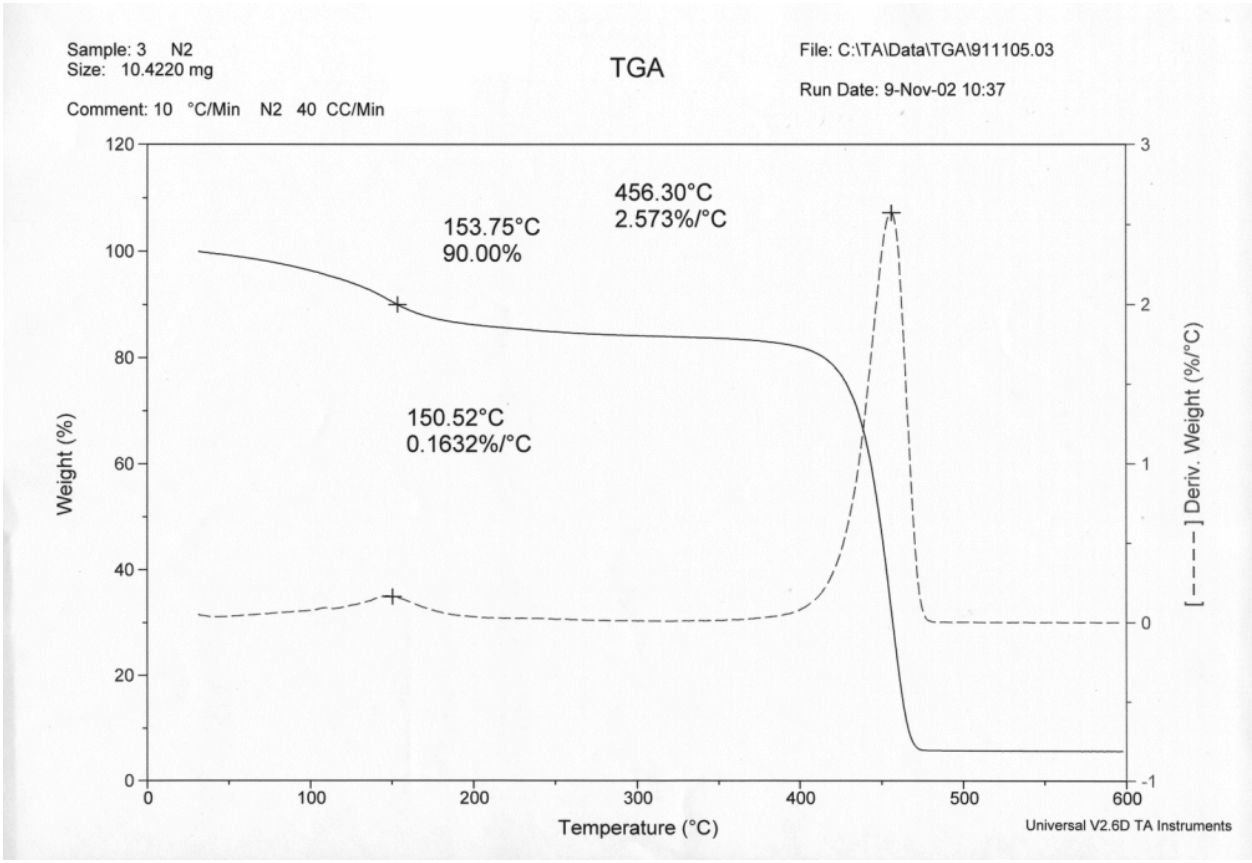




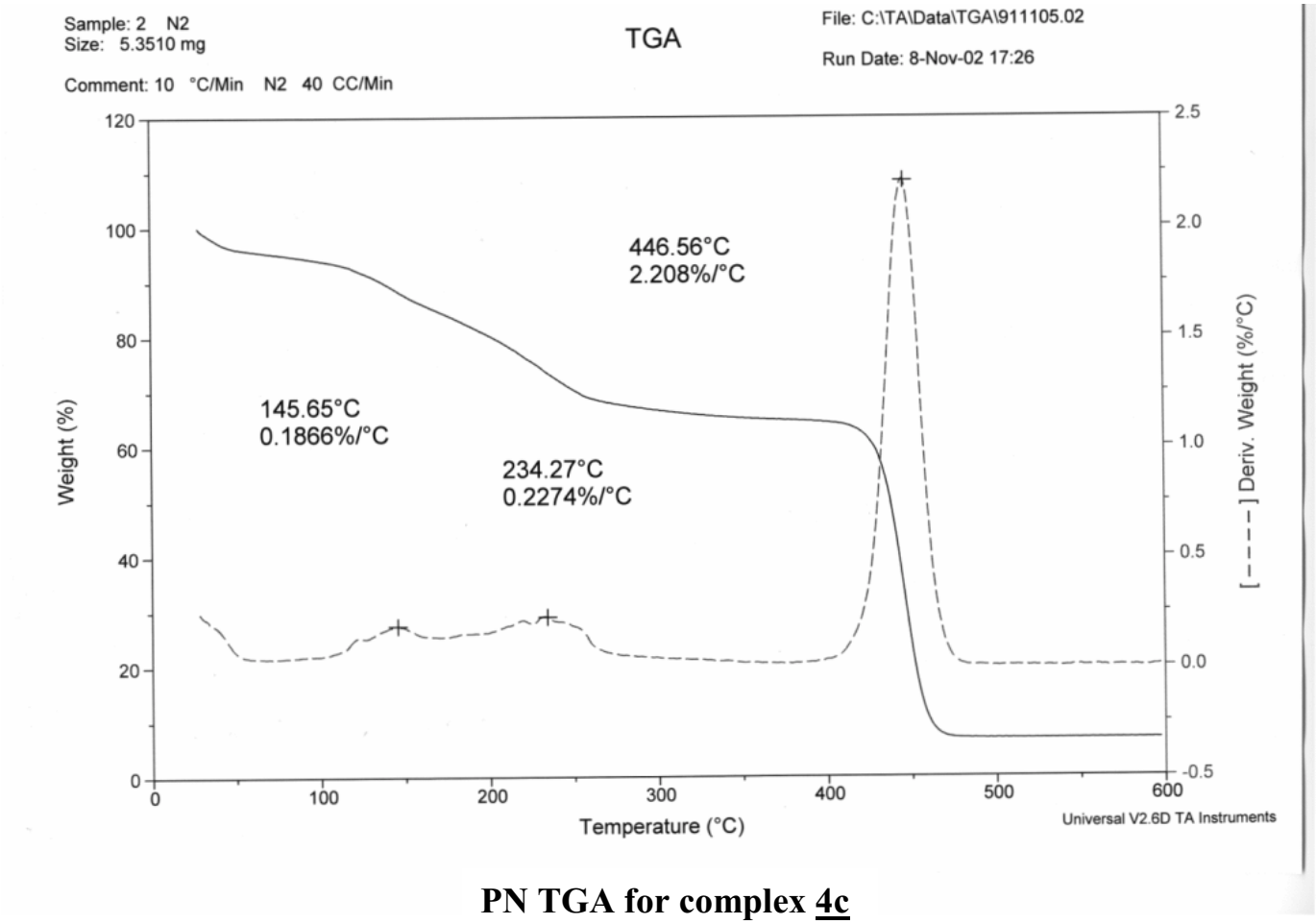
PE ^{1}H NMR for complex <u>4c</u>



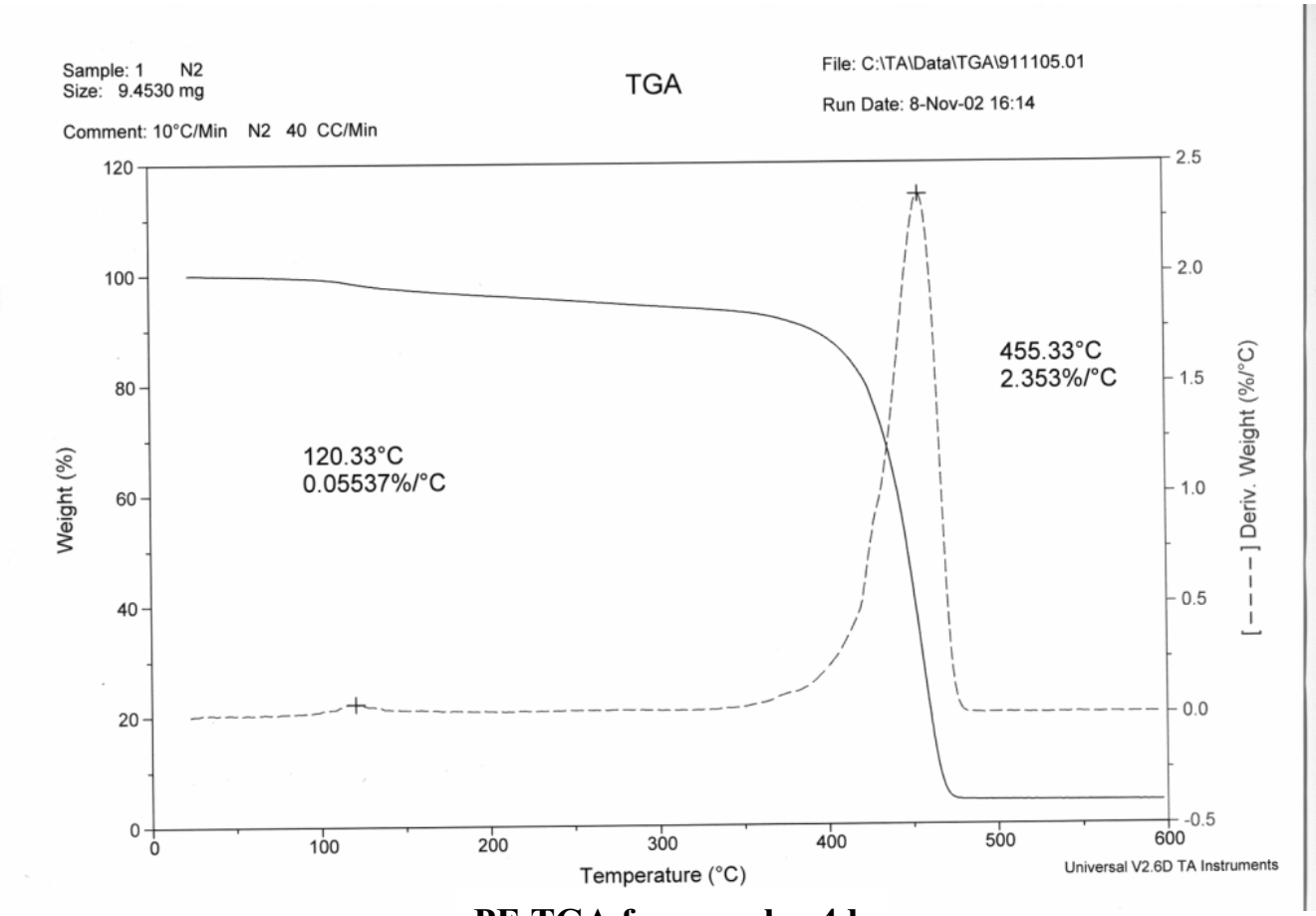
PE ^{1}H NMR for complex <u>4d</u>



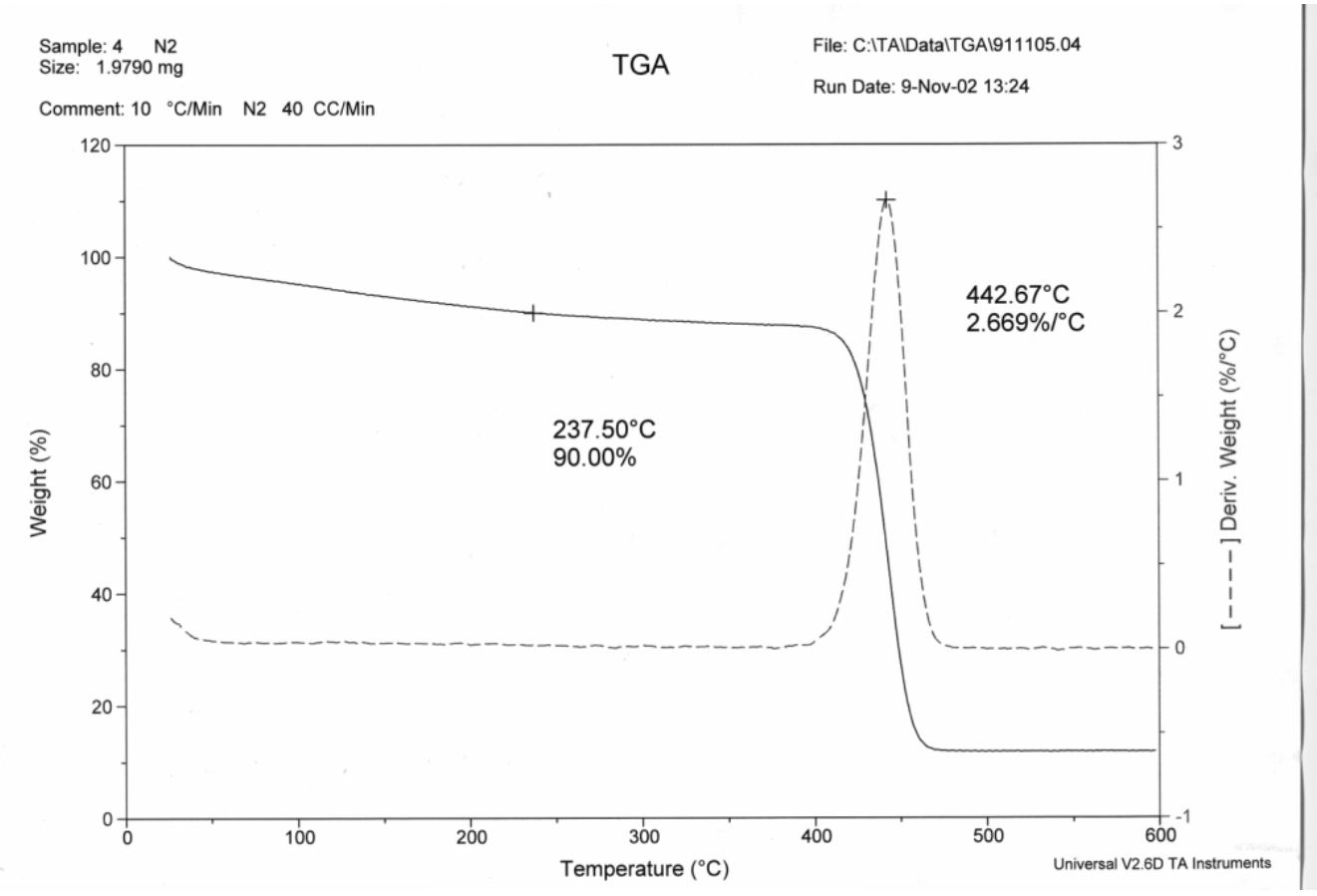
PE TGA for complex <u>4c</u>



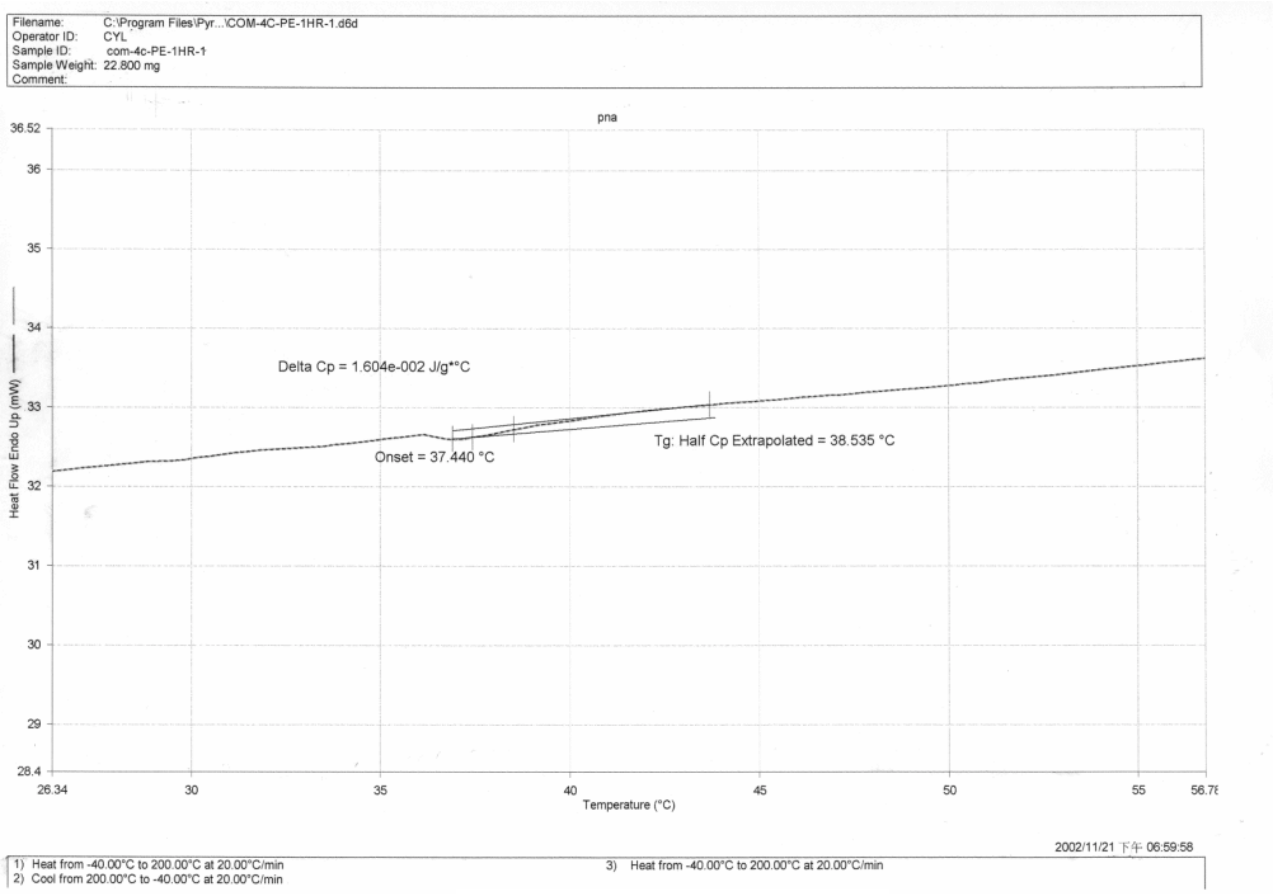
PN TGA for complex <u>4c</u>



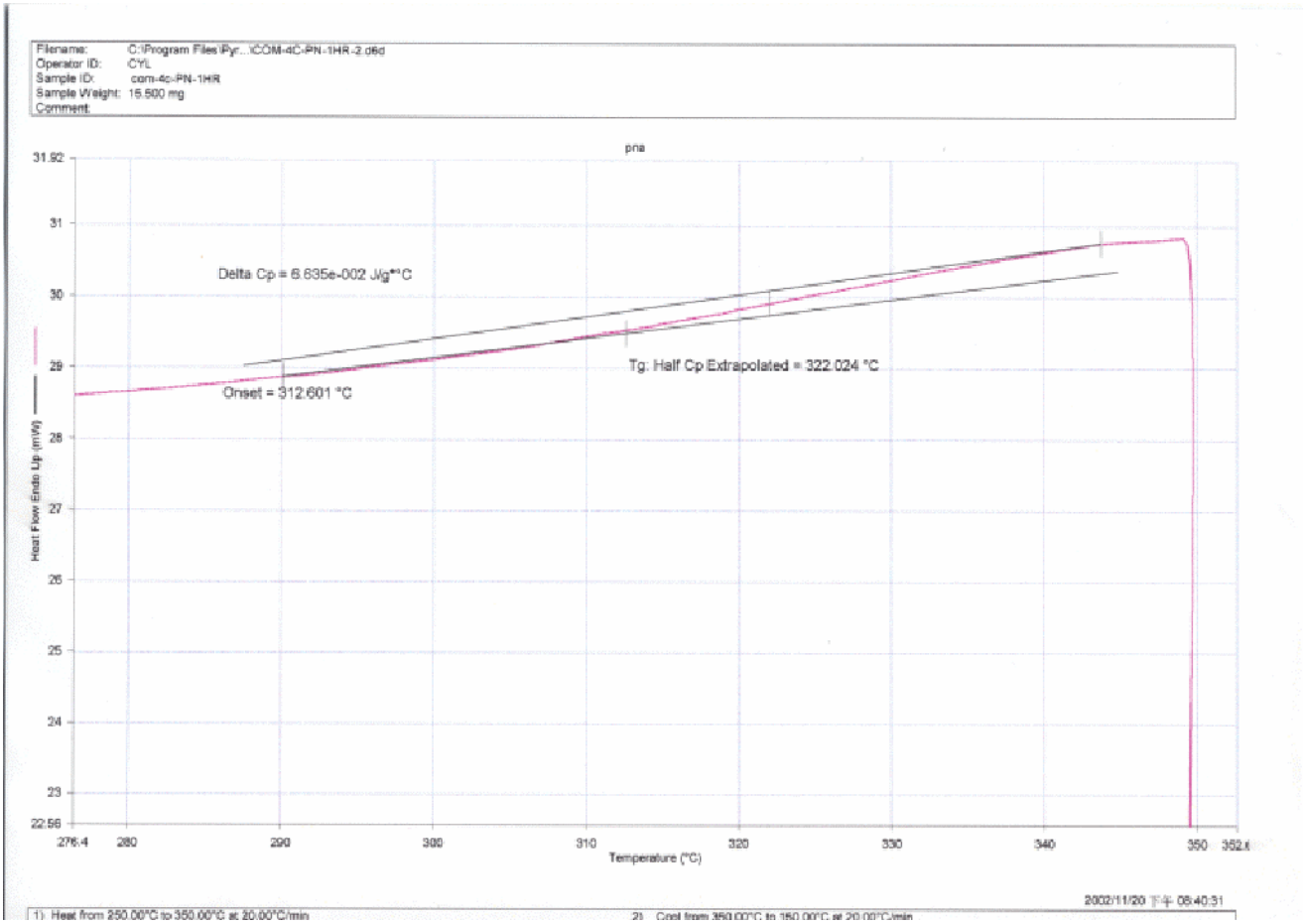
PE TGA for complex <u>4d</u>



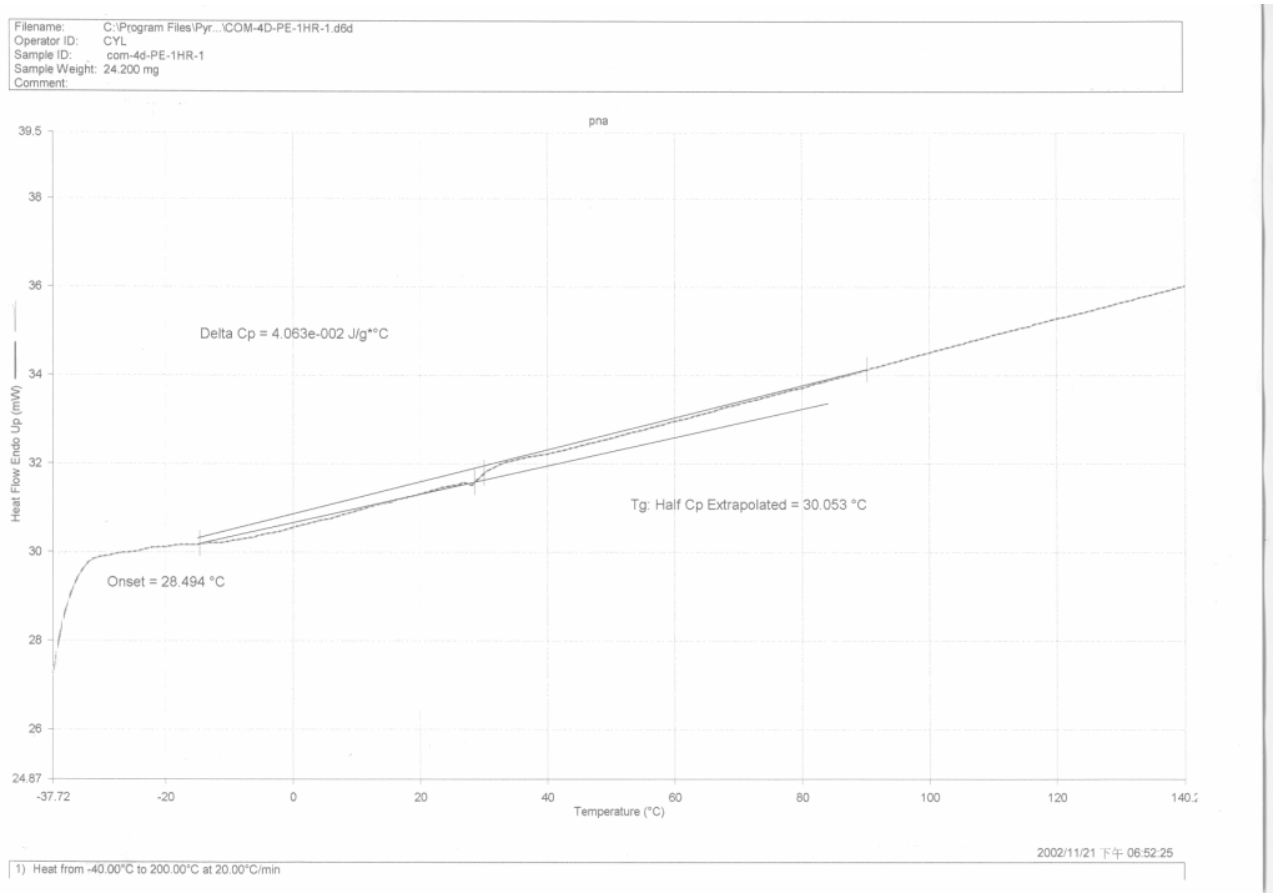
PN TGA for complex <u>4d</u>



PE DSC for complex 4c



PN DSC for complex 4c



PE DSC for complex <u>4d</u>

評 語

本作品探討亞胺配基的鎳錯合物之合成鑑定及聚合反應，工作內容紮實完整，開發新型的聚合觸媒且有潛力。作者對問題有深入的瞭解並且思考細節的問題，並化學結構對反應活性的影響是一個很完整的作品，實驗內容已具有大學或研究所的水平，使用研究型的儀器，引用之論文亦如國際之期刊，建議給予第二名。