國立臺灣大學理學院化學系研究所

碩士論文

Department of Chemistry
College of Science
National Taiwan University

Master Thesis

釕金屬誘發含異原子有機烯炔化合物之環化反應的研究

Study on Intramolecular Cyclization of Organic Hetero-Containing Enynes Induced by Ruthenium Metal Complexes

羅濟賢
Ji-Xian Lo

指導教授：林英智 博士
Advisor: Prof. Dr. Ying-Chih Lin

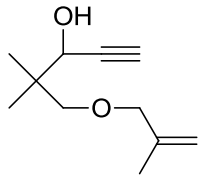
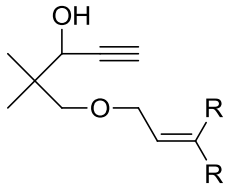
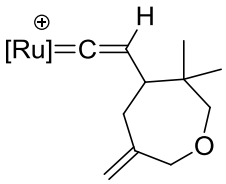
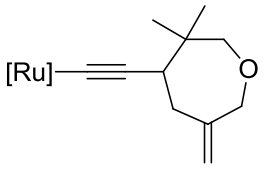
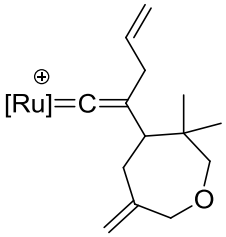
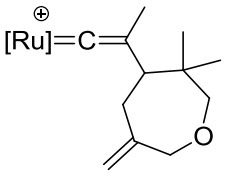
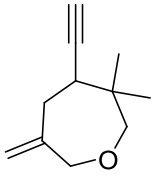
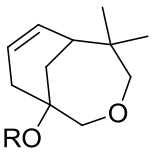
中華民國 102 年 7 月

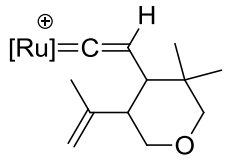
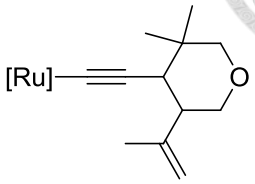
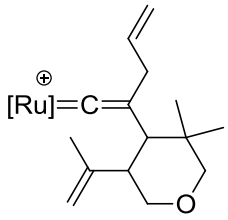
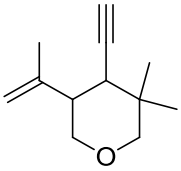
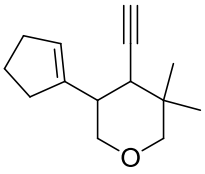
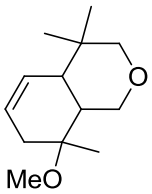
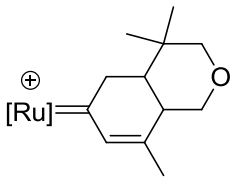
July, 2013

CONTENTS

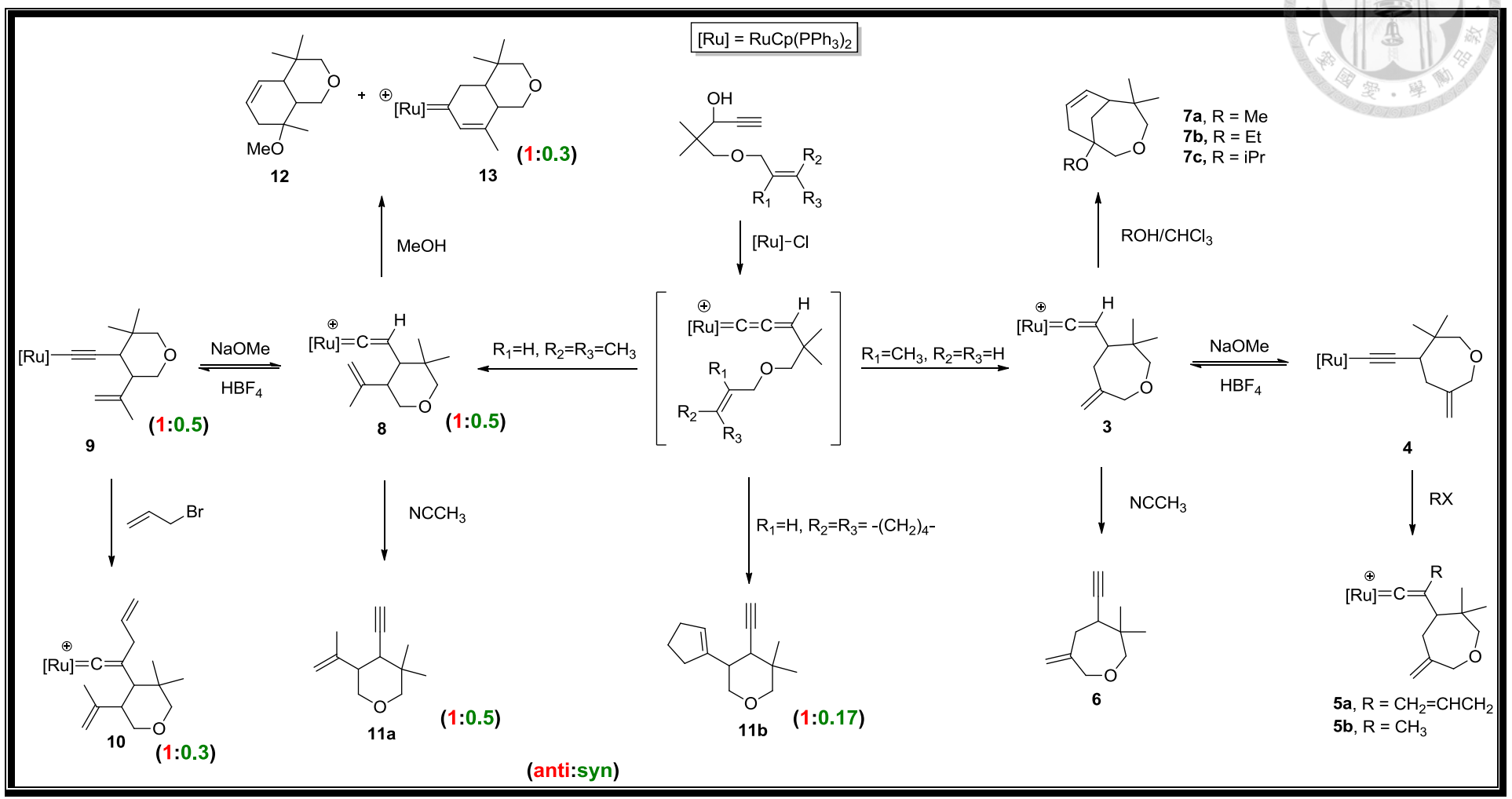
Numbering and Structure of Compounds

[Ru]=CpRu(PPh$_3$)$_2$

	 R= CH_3, **2a** R= -$(CH_2)_4$-, **2b**
1a	**2a-2b**
	
3	**4**
	
5a	**5b**
	 R= Me **7a** R= Et **7b** R= *i*-Pr **7c**
6	**7a-7c**

	
8	**9**
	
10	**11a**
	
11b	**12**
	
13	

Reaction Scheme



中文摘要

本篇論文探討藉由釕金屬錯合物誘發含異原子 1,8-烯炔化合物進行分子內環化反應而形成含氧雜環產物。利用釕金屬錯合物[Ru]Cl ([Ru] = $Cp(PPh_3)_2Ru$)與尾端烯類官能基有甲基取代的化合物 **1** 反應，可得到含氧七環的釕金屬亞乙烯基錯合物 **3**。此反應經由亞丙二烯中間體接著由親電性加成環化在 Cγ 上，並且是一溫和的反應過程。因為在乙烯上有甲基取代，因此環化所形成的中間體有三級碳陽離子的生成而穩定此過程。利用金屬錯合物 **3** 在乙腈中加熱或將$[Ru]NCCH_3^+$和化合物 **1** 在氯仿下加熱，皆可產生環化烯炔產物 **6**。此外，相同的反應在氯仿及甲醇的共溶劑環境下，經由甲氧基親核加成而得到二次環化有機產物 **7a**。另一方面，使用末端烯類官能基有兩甲基取代的化合物 **2a** 與[Ru]Cl 進行反應，得到以反式為主要產物的錯合物 **8**，。將$[Ru]NCCH_3^+$和化合物 **2a** 在氯仿加熱可生成 **11a** (反式：順式＝2/1)。推測此反應機制是經由六元環椅式過渡態，而使得立體障礙為主要的選擇性因素。因此，使用含有較大的五環取代基化合物 **2b**，可使得異構體比例大大的增加為 10：1.8。在溶劑為甲醇的環境下，化合物 **2a** 可產生相對應的雙環化合物 **12** 和錯合物 **13**。錯合物 **3** 和 **8** 加入甲醇鈉可分別得到相對應的乙炔基錯合物 **4** 和 **9**。此外，將錯合物 **3** 和 **8** 加入烷基化試劑可分別得到相對應的亞乙烯基錯合物 **5a-b** 和 **10**.

關鍵字:釕金屬、催化、雜環、烯炔、亞乙烯基

Abstract

The intramolecular cyclization of 1,8-enyne containing hetero-atom mediated by ruthenium complex, leading to the formation of the oxygen heterocycle is described. In the [Ru]Cl-induced ([Ru] = $Cp(PPh_3)_2Ru$) reactions of enyne **1**, with an internal methyl group on the olefinic group, the vinylidene complex **3** containing an oxepane moiety, bonded at Cβ is isolated. The reaction proceeds via the formation of an allenylidene intermediate followed by a cyclization at Cγ under mild condition. Stabilization of the cationic charge by the presence of methyl substituents clearly controls the reaction pathway. The reaction of **3** with NaOMe produces the acetylide complex **4**. The alkylation of **4** by allyl bromide and methyl iodide as alkylation reagents induced the formation of **5a** and **5b**, respectively. Heating complex **3** in CH_3CN or treatment of **1** with $[Ru]NCCH_3^+$ in $CHCl_3$ at 50 ℃ gave the organic enyne **6** as the cyclized product. Furthermore, the same reaction in $CHCl_3$/MeOH leads to the organic product **7a** by tandem cyclization, formed possibly via sequential allenylidene/vinylidene cyclization followed by a nucleophilic addition of a methoxide.

In the reaction of [Ru]Cl with enyne **2a**, containing two terminal methyl groups on the olefinic parts, the vinylidene complex **8** with a new oxane ring is obtained as a mixture of two diastereoisomers and the *anti*-isomer is the major product. Mild thermolysis of **2a** in $CHCl_3$ at 50 ℃ in the presence of $[Ru]NCCH_3^+$ gave **11a**

(*anti*-**11a**/*syn*-**11a** = 2/1). The proposed mechanism is via the formation of a six-membered ring chair-like transition state with the most bulkiest group in the pseudoequatorial position to reduce the 1,3 diaxial interactions. Hence, in the reaction of propargylic alcohol **2b**, the isomer ratio was greatly improved to 10:1.8 due to the steric effect of the bulkier cyclopentyl tether. Treatment of **2a** with [Ru]$NCCH_3^+$ in MeOH afforded two products, the hexahydro isochromene compound **12** with a methoxide group and the carbene complex **13**, both containing a newly formed bicyclic ring. The same reaction of **2b** in MeOH afforded no corresponding bicyclic ring products, but **11b** was obtained. Similarly, the reaction of **8** with NaOMe produces the acetylide complex **9** and alkylation of **9** by allyl bromide as alkylation reagent gives **10**.

Keywords: Ruthenium, catalysis, heterocycle, enyne, vinylidene.

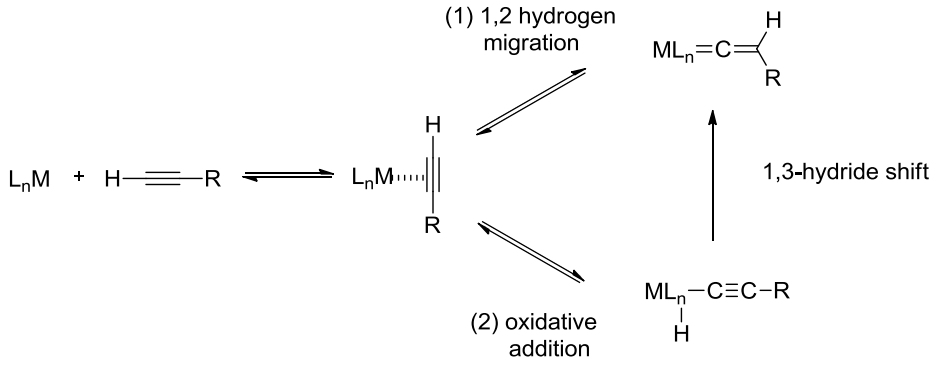
Introduction:

Metal Vinylidene Complexes

The chemistry of transition metal containing unsaturated carbenes such as vinylidene and allenylidene complexes has attracted a great deal of attention because the possibility of development of new types of organometallic intermediates as emphasized in several publications.[1]

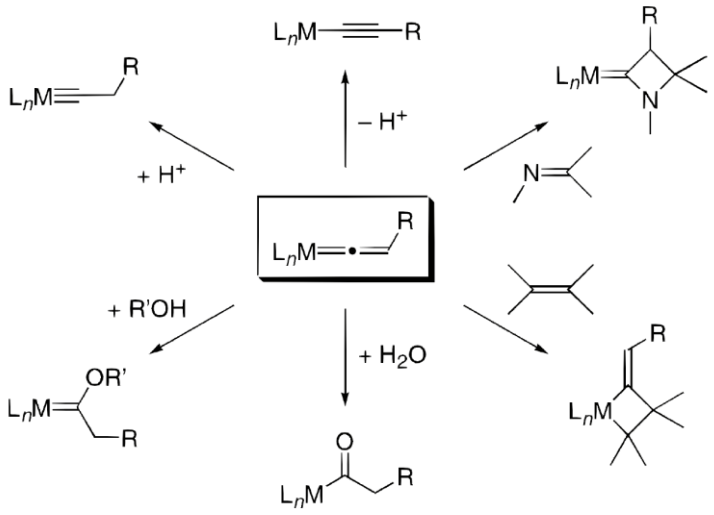
During the past decade, the direct simple formation of metal vinylidene intermediates from terminal alkynes has possible the transfer from stoichiometric to catalytic reactions. Since the first mononuclear metal vinylidene complex reported in 1972,[2] there are two major methods for the preparation, such as (1) the activation of a terminal alkyne to give an initial η^2-coordinated alkyne intermediate followed by a direct 1,2-hydrogen migration over the carbon-carbon triple bond; (2) by oxidative addition of the terminal alkynyl C-H bond to the metal center with subsequent 1,3-hydride shift to the alkynyl lignad.[3] (Scheme1).

Scheme 1



The coordinated vinylidene is considered as an electron-withdrawing ligand stabilized by electron-rich metal fragments[5], and the reactivity of the metal vinylidene complexes largely depends on the nature of the metal. The resulting complexes exhibit a variety of reactivities, which are rationalized by taking electrophilicity of α-vinylidene carbon, nucleophilicity of β-vinylidene carbon. These features boost C-C coupling and C-heteroatom coupling of vinylidene complexes into various metal complexes (Scheme 1-2).

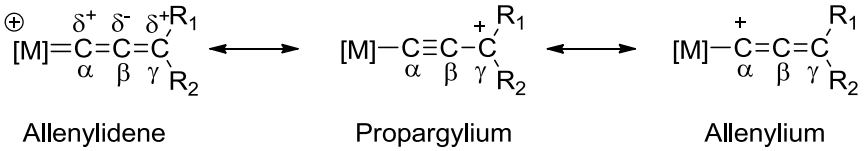
Scheme 1-2



Metal Allenylidene Complexes

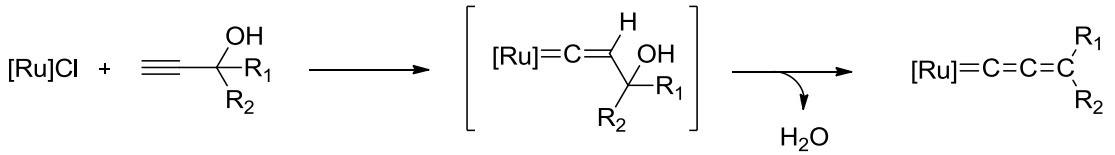
Allenylidene ligands are also cumulogous, more extended versions of carbenes and consist of three cumulated carbon atoms. Just like carbenes, these attach to metal via a formal M=C double bond. Further experimental[6] and theoretical evidence[7] shows that the carbon atoms of the allenylidene ligands are alternatively electron-deficient and

electron-rich when moving along the unsaturated chain starting from the metal center. This behavior is easily rationalized by the contribution of three resonance forms, namely, allenylidene, propargylium and allenylium structure.



The most useful and general method for the synthesis of metal-allenylidene complexes was reported by Selegue in 1982[8] for the preparation of $[Cp(PMe_3)Ru=C=C=CPh_2][PF_6]$. After η^2-coordinated of the 2-propyn-1-ol to a 16 electron metal center, the spontaneous dehydration of propargylic alcohol, via the hydroxyl vinylidnen intermediate occurs (Scheme 1-3). However, other metals such as Os[9a], Mo[9b], W[9c] have also been reported to give similar complexes.

Scheme 1-3



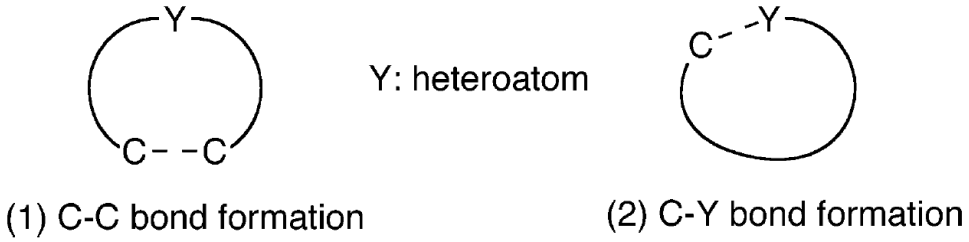
Heterocycles

The development of effective strategies for the synthesis of heterocyclic compounds containing oxygen, sulfur and nitrogen is a very important challenge for modern organic and natural products synthesis.[10] For example, chromane, thiochromane, and 1,2,3,4-tetrahydroquinoline derivatives are widely found in many natural and

biologically active compounds.[11] Some derivatives of chromane ring are well-known to exhibit extensive range of biological activities including anticancer,[12] antioxidative,[13] and significant pharmacological potential.[14]

The catalytic construction of heterocyclic skeletions is classified into two major processes, as ahown in Scheme 1-4: (1) C-C bond formation from the corresponding acyclic precursors and (2) C-Y bond formation from the corresponding acyclic precursors.[15]

Scheme 1-4 Two major processes of heterocycle synthesis.



Transition-Metal-catalyzed Reaction in Heterocyclic Synthesis

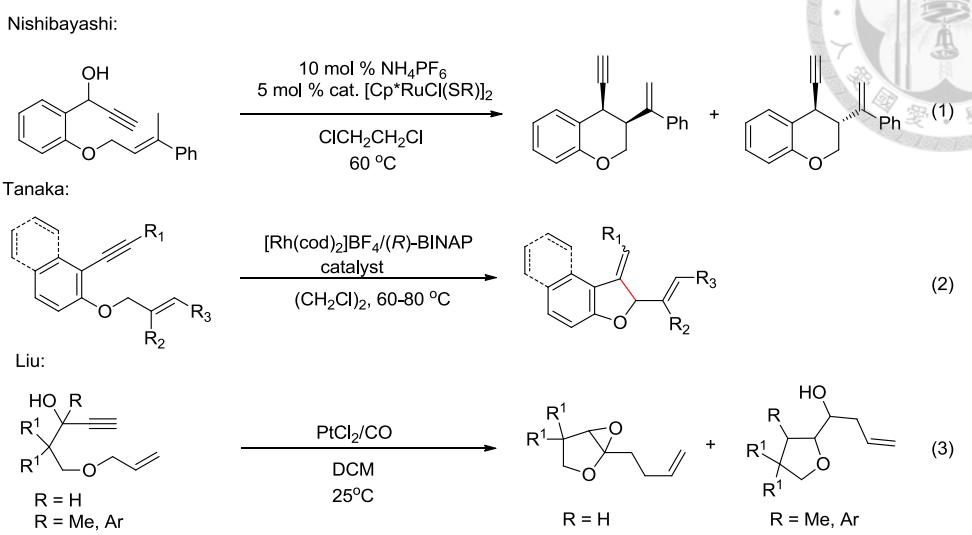
Recently, metal-catalyzed cycloisomerization of enynes represents an efficient synthetic strategy for a variety of carbo-[16] and heterocycles.[17] Because of the presence of metal stabilized "nonclassical" cationic intermediate, the metal-catalyzed cycloisomerization of enynes often leads to various skeleton rearrangements.[18] Additionally, a variety of Ru-based transition metal have been proposed as the key intermediate in catalyzed intra and intermolecular carbon-carbon bond forming

reactions between alkynes and alkenes.[19] Besides, a variety of preparative methods have been reported including its asymmetric version for the optically active heterocycles.[20]

More recently, Nishibayashi demonstrated that a thiolate-bridged diruthenium complex catalyzed cyclization of the enyne compounds via allenylidene-ene pathway to form chromane deravitives with high enantioselectivity. (Scheme 1-5, eq1)[20a-b] In addition, Tanaka and his co-workers have found that asymmetric synthesis of phenol- or naphthol-linked 1,7-enynes by the cationic rhodium(I)/(*R*)-BINAP complex catalyzed olefin isomerization/enantioselective intramolecular reaction giving substituted dihydrobenzofurans and dihydronaphthofurans. (Scheme 1-5, eq2)[21] Also, Liu et al have developed Pt-catalyzed cycloisomerization of linear 1,8-enynes via ally-rearrangement to produce dihydrofuryl alcohols and epoxide product (Scheme 1-5, eq3).[22] Therefore, the development of new, rapid, methods to generate heterocyclic products as a precursor of natural products would be a useful contribution to the synthetic community.

Furthermore, the construction of more complicated ring systems, such as fused or bridged rings, is also useful for synthesizing natural products.[23] To build these fused rings, photo-rearrangement[24]/thermal[25] rearrangement and the use of Lewis acids,[26] and transition metals[27] have been developed. These exhaustive efforts have resulted in elegant methods for intricate bicyclic systems.

Scheme 1-5. Synthesis of *O*-containing heteocyclic compounds.

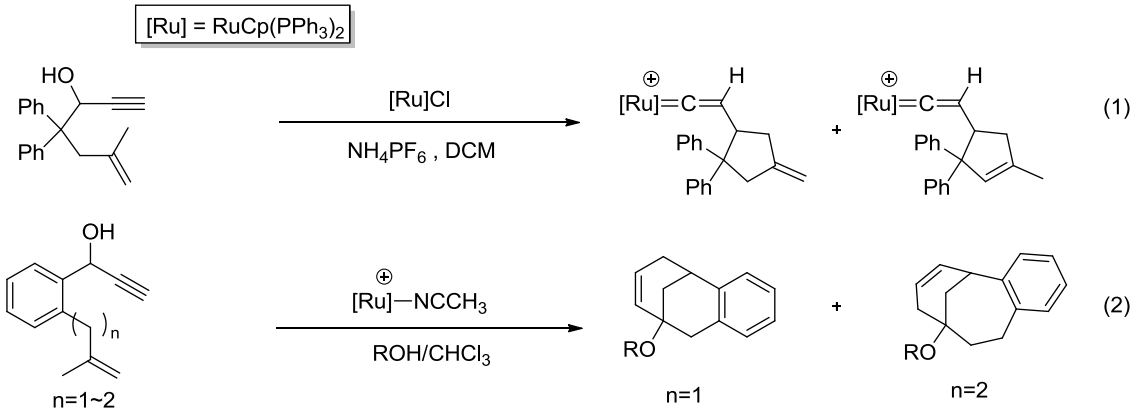


Motivation of This Thesis

Previously, we developed the ruthenium-mediated of 1,5-enynes, which was proposed via a intramolecular cyclization, affording the vinylidene complex with a five-membered ring containing an unsaturated methylene group on the ring.[28a] (Scheme 1-6, eq1) Potentially, this vinylidene ligand may undergo further cyclization yet to observe. In a recent study, we found a ruthenium-catalyzed tandem cyclization reaction of 1,n-enynes (n=7~8) with a methyl group at the terminal vinyl group produced tricyclic products in MeOH/$CHCl_3$.[28b] (Schene 1-6, eq2) As an extension of our previous study, we have explored the ruthenium-mediated reactions of linear 1,8-enyne propargylic alcohols, with an allylic alkoxy moiety, affording the corresponding cycloisomerization products. Herein,the results were reported on the

study of the reactions of [Ru]Cl with linear oxygen-containing enynes also with a propargyl alcohol group.

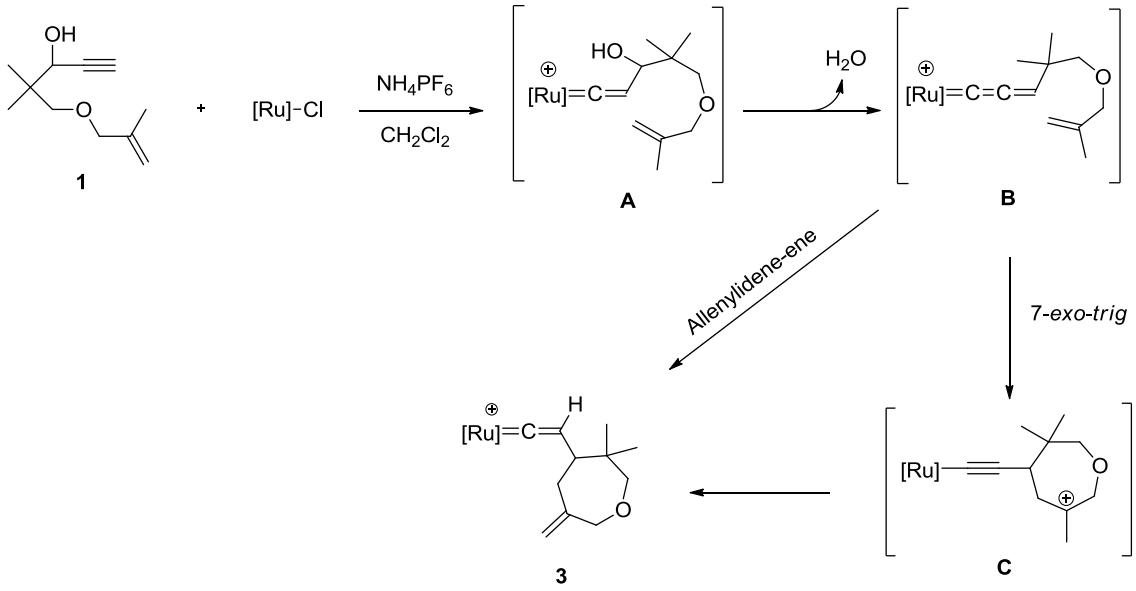
Scheme 1-6



Results and Discussion：

Formation of Vinylidene Complex Containing an Oxepane Group

Scheme 2

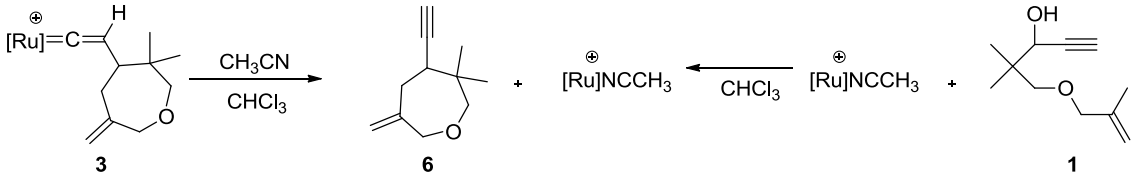


Treatment of [Ru]Cl ([Ru] = $Cp(PPh_3)_2Ru$) with **1** in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature for one day afforded the vinylidene complex **3** containing an oxepane moiety. The mechanism of the formation of **3** is shown in Scheme 2. The reaction presumably proceeds via the formation of the γ-hydroxyvinylidene intermediate **A**, followed by the formation of the allenylidene intermediate **B** by a dehydration at Cβ and Cγ. Subsequently, the intramolecular attack of the alkene portion onto the electrophilic Cγ of the allenylidene ligand in **B**, resulting in a C-C bond formation to give the alkynyl complex **C** bearing a cationic charge at the methyl-substituted tertiary carbon of the oxepane moiety. This is followed by a

1,5-hydrogen shift of one of the terminal protons into the acetylide moiety to give the corresponding vinylidene complex **3**. Stabilization of the tertiary carbocationic intermediate by the presence of methyl substituents could assist the cyclization process. Alternatively, direct allenylidene-ene process[20a-b] might be the other pathway for this cyclization. The structure of complex **3** is determined by NMR spectroscopy. The ^{31}P NMR spectrum of **3**, displays two doublet resonances at δ 43.24 and 43.02 with $^{2}J_{PP}$ = 26.35 Hz indicates the presence of a stereogenic center. In the 2D-HMBC NMR spectrum, the triplet resonance at δ 343.94 with $^{2}J_{CP}$ = 15.21 Hz assigned to Cα, shows correlation with the multiplet ^{1}H resonance at δ 2.35 assigned to CγH. The chemical shift of Cα is similar to many Cα resonances of other ruthenium vinylidene complexes.[29]

Formation of Oxepane Derivative Compound

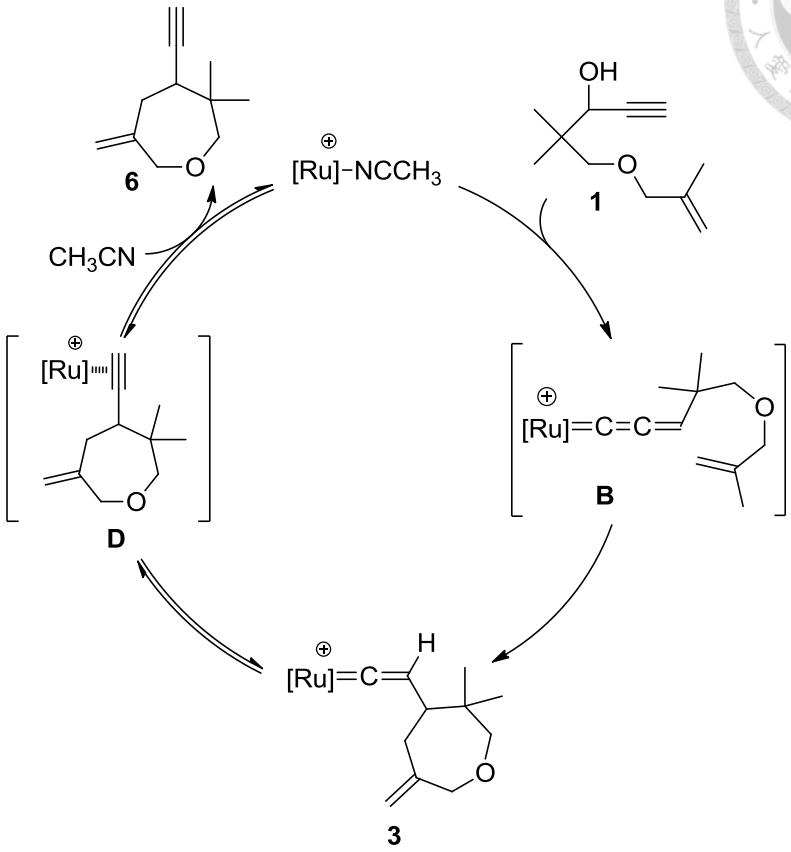
Scheme 3-1



Heating the vinylidene complex **3** in a cosolvent of $CHCl_3/CH_3CN$ for a day afforded the ethynyloxepane derivatives **6** and the cationic complex $[Ru](CH_3CN)[PF_6]$ as shown in Scheme 3-1. Formation of alkyne from a metal vinylidene complex has been reported in thermolysis of the analogous metal vinylidene complex in CH_3CN.[30]

Alternatively, direct treatment of **1** with a 30 mol% of [Ru]$NCCH_3^+$ in $CHCl_3$ at 50°C for a day also afforded **6**, but with slightly lower yield (78%). In this reaction, a small amount of **3** and other impurities are also produced. Presumably, treatment of [Ru]Cl with acetonitrile produced [Ru]$NCCH_3^+$ in the beginning which then catalyzed the cyclization reaction. The spectroscopic data of **6** are in agreement with the proposed structures. In the ^{1}H NMR spectrum of **6**, the characteristic acetylenic proton resonance appears as a doublet at δ 2.10 with $^4J_{HH}$ = 2.5 Hz. Two multiplet resonances at δ 4.92 and δ 4.83 are assigned to two olefinic methylene protons bonded to the oxepane moiety. Catalytic cyclization of analogous compound has been reported on an intramolecular Nicholas reaction via the acid treatment of *exo*-$Co_2(CO)_6$-propargyl alcohols, leading to the formation of ethynyloxepane derivatives[31]. However, their preparation required 3 steps and mixtures of diastereomers were produced. In our case, formation of **6** requires only one step with [Ru]$NCCH_3^+$ as a catalyst under mild condition.

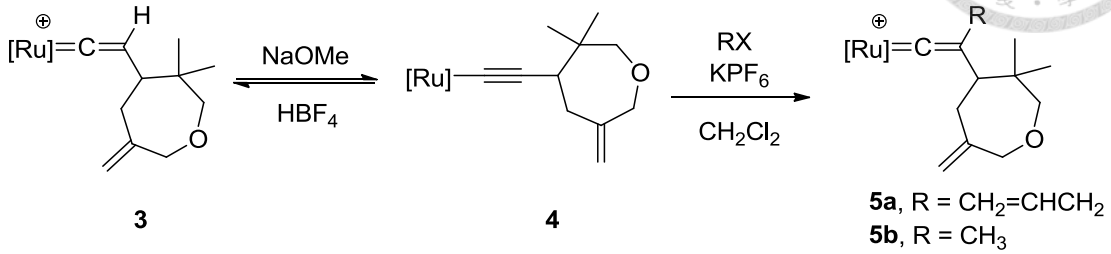
Scheme 3-2 Catalytic Cycle for the Formation of The Oxepane Derivative.



The proposed mechanism for the cyclization of compound **1** to give **6** is illustrated in Scheme 3-2. Cyclization of **1**, catalyzed by $[Ru]NCCH_3^+$, proceeds by the production of the allenylidene intermediate **B** followed by the cyclization to yield the vinylidene complex **3**. Finally, an isomerization of the vinylidene ligand gives the π-coordinated alkyne which is replaced by CH_3CN to produce **6**, finishing the catalytic cycle. Complex $[Ru]NCCH_3^+$ is therefore successfully used to catalyze the cyclization of **1** affording enyne **6**.

Formation of Vinylidene Complex by Alkylation

Scheme 4



Treatment of **3** with NaOMe/MeOH for 10 mins afforded the acetylide complex **4** by deprotonation and color of the solution changed from light orange to yellow. Complex **4** could be converted back to the vinylidene complex **3** by protonation with HBF_4 in diethyl ether. The structure of **4** is confirmed by ^1H NMR and ^{31}P NMR spectra. The ^{31}P NMR spectrum of **4**, with a stereogenic center, yet displays a broad resonance at δ 51.94. This may be due to the distant stereogenic center away from the phosphine ligands or the rotation of the C-C single bond. The resonance of CβH at δ 4.57 in the ^1H NMR spectrum of **3** disappears in the ^1H NMR spectrum of **4**.

Then, treatment of **4** separately with allyl bromide and methyl iodide as alkylation reagents in the presence of KPF_6 afforded the corresponding cationic vinylidene complexes **5a** and **5b** as shown in Scheme 4. Complexes **5a** and **5b** are stable under thermolytic condition, and show the similar NMR data. Fortunately, single crystals of **5a**, tethering an ally group at Cβ, are obtained at ambient temperature in diethyl ether/CH_2Cl_2 solution, and the structure is determined by a single crystal X-ray

diffraction study. An ORTEP type view of the cationic complex **5a** is shown in Figure 1, with selected bond distances and angles. Complex **5a** has distorted three-legged piano-stool coordination geometry around the ruthenium center which bound to a Cp, two PPh_3 and the vinylidene ligand with a oxepane moiety. The bond lengths of Ru(1)-C(1) and C(1)-C(2) of 1.864 (3) and 1.308 (5) Å, respectively, show a typical vinylidene bond skeletal. The bond length of C(3)-C(4) of 1.539 (6) Å attests the C-C bond formation and the C(5)-C(9) of 1.367 (9) Å corresponds to a double bond. From the crystal structure, the presence of the seven-membered oxepane ring in the vinylidene ligand is confirmed.

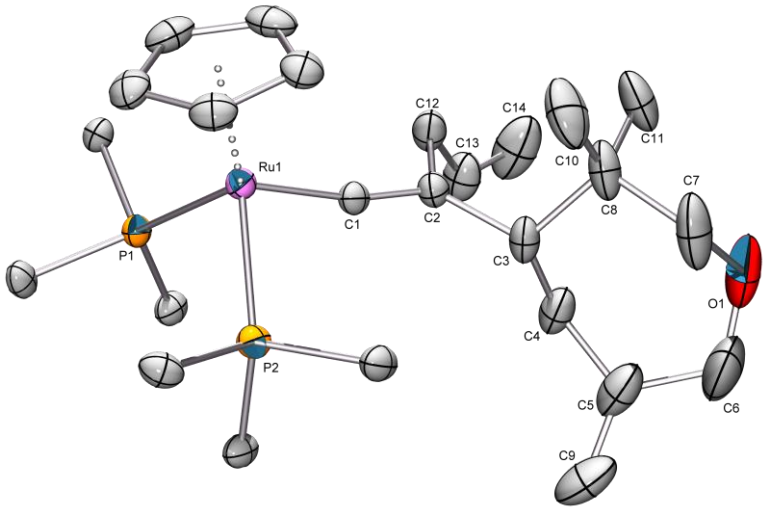
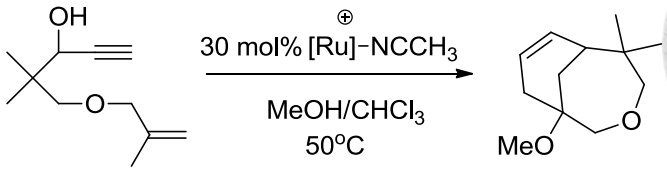


Figure 1. An ORTEP drawing of the cationic complex **5a**. For clarity, PF_6^- and phenyl groups of the triphenylphosphine ligands on Ru except the ipso carbons are omitted (thermal ellipsoid is set at the 25% probability level). Selected bond distances (Å) and angles (deg): Ru(1)-C(1), 1.864 (3); C(1)-C(2), 1.308 (5); C(2)-C(12), 1.536 (5); C(3)-C(4), 1.539 (6); C(5)-C(9), 1.367 (9); C(13)-C(14), 1.241 (7); Ru(1)-C(1)-C(2), 168.0 (3); C(4)-C(3)-C(8), 115.4 (3); C(6)-C(5)-C(4), 117.0 (6); C(6)-O(1)-C(7), 115.5 (6).

Scheme 5-1 Formation of the Cascade Cyclization Compound



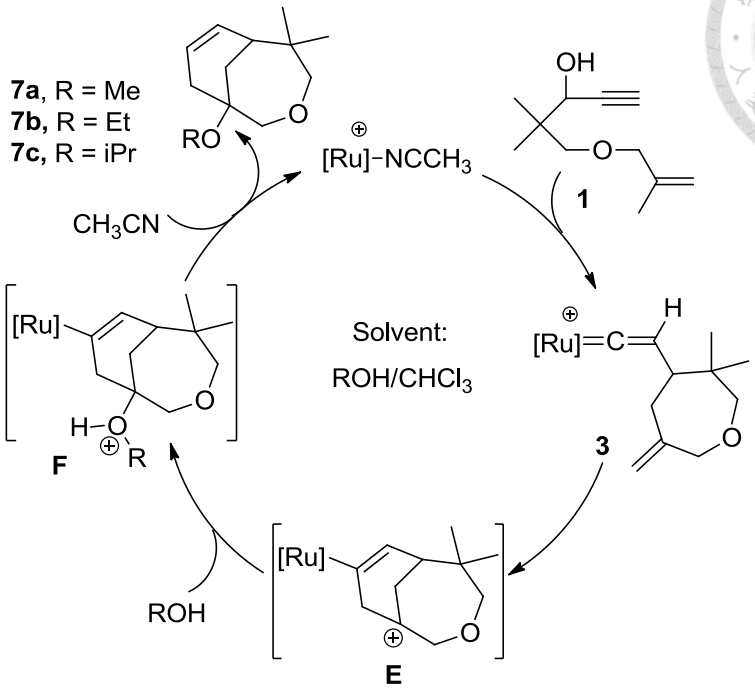
1 **7a**

As mentioned above, in the conversion of **1** to **3** or **6**, two unsaturated groups are retained after the first cyclization reaction. The enyne groups in **6** are in closer proximity for cyclization than those in **1**. Therefore, we have tried to explore further cyclization reaction. Thermolysis of **3** in $CHCl_3$/MeOH at 50 ^oC generates the 1-methoxy- 5,5-dimethyl-3-oxabicyclo[4.3.1]dec-7-ene product, **7a** with 90% yield shown in Scheme 5-1. In addition, a mixture of **6** and 30 mol% of $[Ru]NCCH_3^+$ in $CHCl_3$/MeOH at 50 ^oC could also afford **7a** in high yield. Compound **7a** is obtained from the treatment of **1** and $[Ru]NCCH_3^+$ in $CHCl_3$/MeOH as well, but with a lower isolated yield (70%) together with side products. In the ^1H NMR spectrum of the crude product mixtures of new olefinic multiplet resonances at δ 5.81, 5.70 and a methoxy singlet resonance at δ 3.28 appeared, at the cost of the characteristic terminal olefinic resonances at δ 4.87, 4.91 of **1**. The structure of **7a** is determined by spectroscopic methods. In the newly formed six-membered ring, the methylene protons near the double bond display two multiplet resonances at δ 2.12 and 1.92 because of the newly formed stereogenic center at the bridged head carbon with the OMe group. Treatment of **1** with $[Ru]NCCH_3^+$ in two other alcohols ROH (R = Et, iPr) also serve as nucleophiles

afforded **7b** and **7c**, respectively. The yield of **7c** decreased to about 30% because of bulkier *i*-Pr group. No cyclization product was observed in *tert*-butyl alcohol, propargylic amine or acetone. Furthermore, treatment of disubstituted vinylidene complexes **5a**-**b**, in $CHCl_3$/MeOH at 50 ^oC generated no tandem cyclization products which confirms the less reactive characteristics of disubstituted vinylidene complexes.[32]

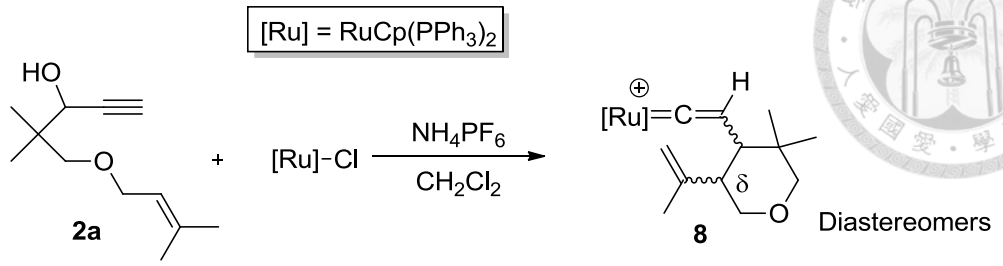
The seven-membered oxacycle is a novel structural feature of natural products in their molecular architecture. Structures range from fused structures janoxepin, oxepinamide C, and isoprelaurefucin to the functionalized monocycles such as lobatrienetriol and armatol A.[33] Recently, Stončius et al.[34] investigated the formation of the oxabicyclo[4.3.1]decane skeleton via the Baeyer–Villiger oxidation of bicyclooctane diketones. Besides, the reaction using SmI_2 as a reagent for promoting intermolecular reaction to make bicyclic product was reported.[35] Herein, we provided an accessible method under mild condition to generate the oxabicyclo[4.3.1]decane moiety by intramolecular cyclization with moderate yields.

Scheme 5-2



In order to further understand the mechanism of the formation of **7a**, we carried out the cyclization of **1** with $[Ru]NCCH_3^+$ in $CDCl_3/CD_3OD$ yielding **7a-D**, where both olefinic protons and the methoxy group are deuterated. According to these results, a plausible mechanism of the tandem cyclization for **1** is shown in Scheme 5-2. The tandem cyclization of **1** first yields the vinylidene complex **3**. Then, nucleophilic addition of the unsaturated double bond to Cα gives the intermediate **E**, with a bicyclic ring containing a cationic charge on the tertiary carbon. This is followed by a methanol attack to this carbon to give **F**. Finally, the ligand exchange reaction between **F** and **1** occurs to give the corresponding fused product **7a** accompanied by regeneration of the ruthenium catalyst.

Scheme 6-1 Formation of Vinylidene Complex Containing an Oxane Group



To extent our previous study, reaction of the propargyl alcohol **2a** bearing two methyl groups on the terminal carbon of the tethering alkyl group as the starting compound is investigated. Treatment of [Ru]Cl with **2a** in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature for one day afforded the vinylidene complex **8** containing a newly formed oxane moiety as a mixture of two diastereoisomers. The ratio of major and minor isomers is 1:0.5. The structure and configuration of **8** is determined by NMR spectroscopy. The ^{31}P NMR spectrum of **8**, with two stereogenic centers, displays two sets of two doublets at δ 43.75, 43.12 ($^2J_{PP}$ =26.4 Hz) for the major complex and at δ 45.22, 43.50 ($^2J_{PP}$ =26.7 Hz) for the minor complex. In the ^{13}C NMR spectrum of **8**, two triplet resonances at δ 343.71 ($^2J_{CP}$=14.86 Hz) and 342.67 ($^2J_{CP}$=15.08 Hz) are assigned to the Cα for the major and minor complexes, respectively. In the ^1H NMR spectrum as shown in Figure 2-1, resonances at δ 4.23, 2.67 and 2.18 are assigned to the protons at Cβ, Cγ and Cδ for the major complex and resonances at δ 4.44, 2.96 and 2.79 for the minor one, respectively. In the COSY NMR spectrum (Figure 2-2), the proton of Cγ correlates only with protons of Cβ and Cδ in both diastereomers as shown in Figure 2-2.

For the major complex, the proton coupling constants of Cγ (doublet of doublets) are 9.78 and 11.20 Hz and the former one shows correlations to Cβ ($^3J_{HH}$=9.78 Hz). Hence, we could conclude that the proton coupling constant of Cγ and Cδ is 11.20 Hz within the range of two protons at axial positions (Figure 3) shown in Karplus Curve[36] (Figure 2-3). Similarly, the proton coupling constant of Cγ and Cδ in the minor complex is 3.55 Hz which is assigned to the *syn*-isomer and supposedly, the dihedral angel of two protons of Cγ and Cδ is approximately 60°.

Figure 2-1 Part of ^{1}H NMR of complex **8**

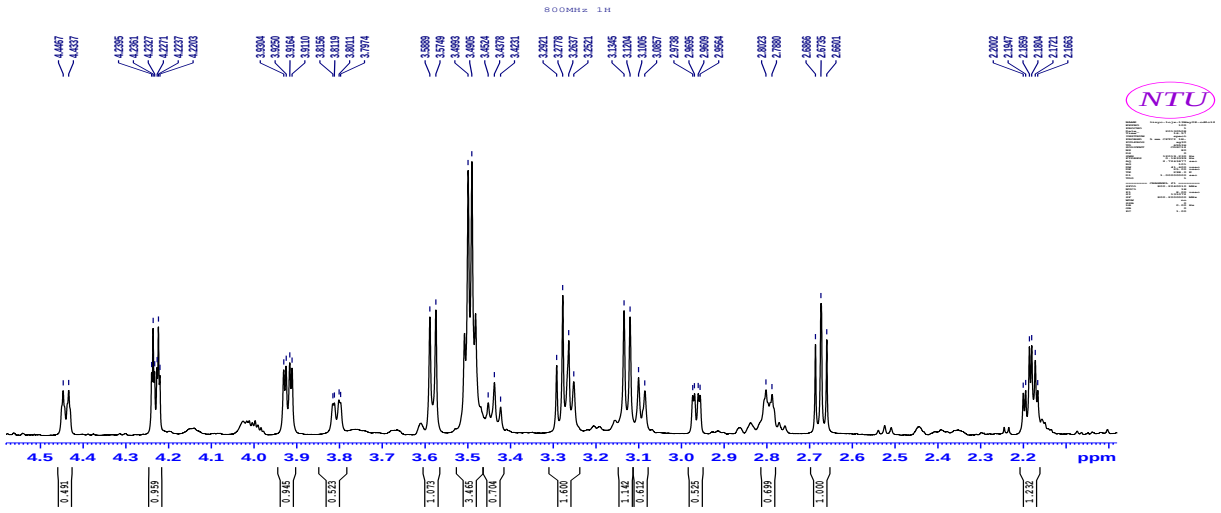


Figure 2-2 Part of ^{1}H, ^{1}H-COSY NMR of complex **8.** (inevitable noise with high concentration)

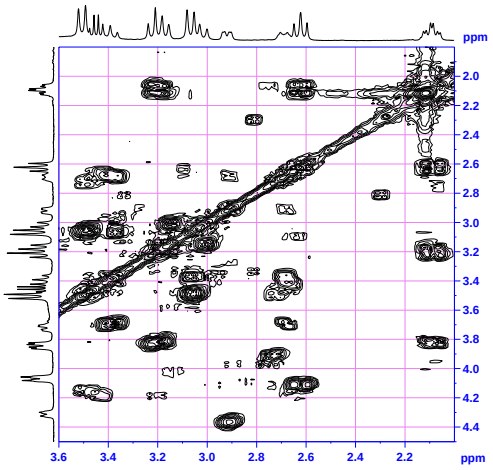
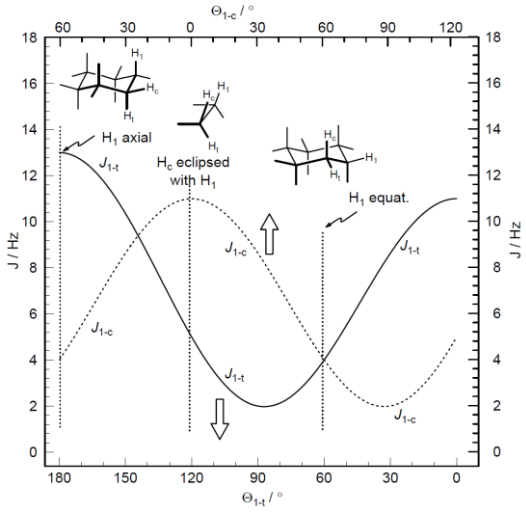


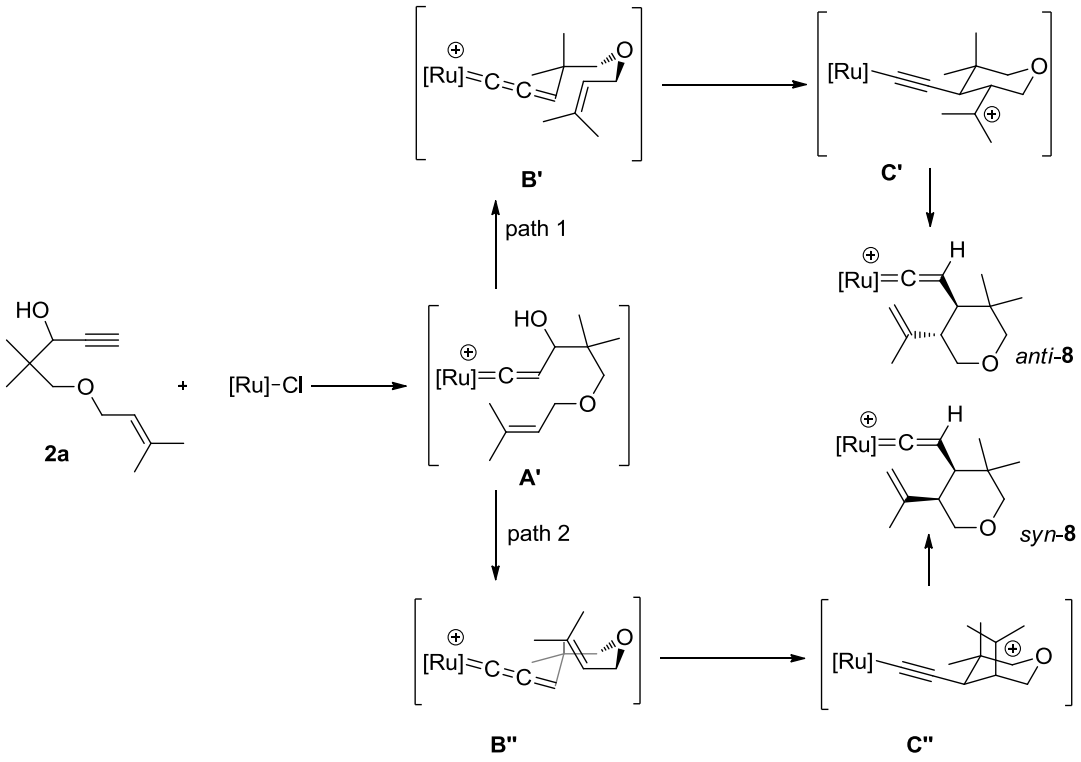
Figure 2-3 Karplus Curve for Vicinal coupling in Cycloalkanes.



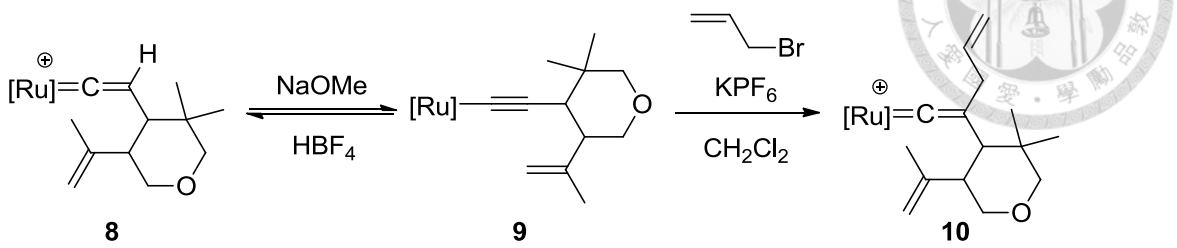
According to the Zimmerman-Traxler[37] transition state model, the aldol addition reaction proceeds via a chair-like, pericyclic process with the bulkier group occupying a pseudoequatorial rather than a pseudoaxial position to avoid potential 1,3-diaxial steric interactions. Hence, the cyclization mechanism of **8** may proceed via the formation of intermediate **A'** followed by a dehydration to give two possible chair-like allenylidene

transition states **B'** and **B''**. (Scheme 6-2). The highly demanding bulkier ruthenium complex group is thus located in a equatorial position after cyclization from a steric viewpoint.[38] In path 1, the intramolecular addition of alkene to Cγ in **B'** gives the acetylide intermediate **C'** with the tertiary cationic substituent at the equatorial position. This is followed by a 1,5-hydrogen shift of one of the methyl protons to Cβ of the acetylide ligand to give a less hindered product *anti*-**8**. In path 2, the intramolecular addition of the olefinic moiety to Cγ in **B''** similarly affords the corresponding **C''** but with the cationic group in the axial position. The larger steric repulsion of the axial groups of the transition state elevates the energy of intermediate **C''**. As a result, complex *anti*-**8** was obtained as the major product.

Scheme 6-2



Scheme 7



8 **9** **10**

Treatment of **8** with NaOMe/MeOH for 10 mins afforded the acetylide complex **9** by deprotonation and color of the solution changed from deep yellow to light yellow with similar isomer ratio (*anti*:*syn*=1:0.5). Complex **9** could be converted back to the vinylidene complex **8** by protonation with HBF_4 in diethyl ether. The structure of **9** is confirmed by NMR spectra. The ^{31}P NMR spectrum of **9**, with two stereogenic centers, displays a resonance at δ 51.22 and doublets resonances at δ 52.16, 50.34 with $^{2}J_{PP}$ = 37.9 Hz, for the *anti*- and *syn*-isomer respectively. We can see two sets of resonances in all spectra attributed to two diastereomers in a ratio of 1:0.5 and only spectroscopic data of the major product is described below. The proton resonance of CβH at δ 4.07 in the ^{1}H NMR spectrum of **8** disappears in the ^{1}H NMR spectrum of **9**. In the ^{1}H NMR spectrum of **9**, the proton coupling constant of Cγ and Cδ of the *anti*-isomer is 11.36 Hz. The ^{13}C NMR spectrum of **9** shows the triplet resonance at δ 92.19 with $^{2}J_{CP}$=24.98 Hz for Cα and the singlet resonance at δ 110.58 for Cβ.

Then, treatment of **9** with allyl bromide as alkylation reagents, as shown in Scheme 6, afforded the cationic vinylidene complex **10** (*anti*:*syn*=1:0.3). Color of the solution

changed from yellow to brown. The structure of **10** is determined by NMR spectra. The ^{31}P NMR spectrum of *anti*-**10**, displays a broad resonance at δ 40.56. In the ^{1}H NMR spectrum, multiplet resonance at δ 6.09 is assigned to one of the vinyl hydrogen of the allyl group and the proton coupling constant of CγH and CδH is 10.9 Hz. Resonances in the ^{13}C NMR spectrum of **10** at δ 349.91 and 94.36 are assigned to Cα as a triplet with $^{3}J_{CP}$=12.18 Hz, and to Cp as a singlet, respectively.

Isomers of the complex **10** are stable under thermolytic condition. Fortunately, single crystals of *anti*-isomer were obtained at ambient temperature in toluene/CH_2Cl_2 solution. The structure of *anti*-**10** is determined by a single crystal X-ray diffraction study. An ORTEP type view of the cationic complex *anti*-**10** is shown in Figure 3, with selected bond distances and angles. The *anti*-**10** has distorted three-legged piano-stool coordination geometry around the ruthenium center which bound to a Cp, two PPh_3 and the vinylidene ligand with a oxane moiety. From the crystal structure, two hydrogen atoms at Cγ and Cδ are at axial position. The bond lengths of Ru(1)-C(1) and C(1)-C(2) show a typical vinylidene bond skeletal. The bond length of C(6)-C(10) of 1.578 (12) Å attests the C-C bond formation and the C(11)-C(13) of 1.376 (8) Å corresponds to a double bond.

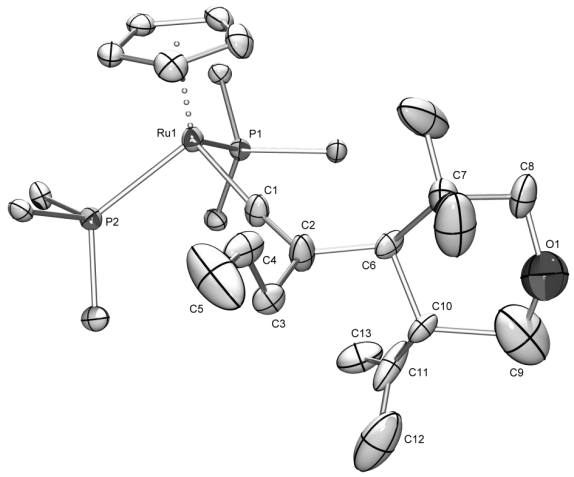
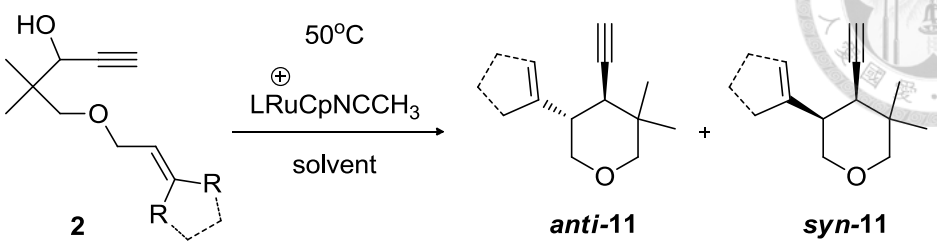


Figure 3. An ORTEP drawing of the cationic complex *anti*-**10**. For clarity, phenyl groups of the triphenylphosphine ligands on Ru except the ipso carbons and PF_6^- are omitted (thermal ellipsoid is set at the 25% probability level). Selected bond distances (Å) and angles (deg): Ru(1)-C(1), 1.886 (3); C(1)-C(2), 1.301 (5); C(6)-C(10), 1.578 (12); C(11)-C(13), 1.376 (8); C11-C12, 1.488 (11); Ru(1)-C(1)-C(2), 168.6 (4); C(7)-C(6)-C(10), 108.9 (6); C(6)-C(10)-C(9), 117.0 (7); C(10)-C(11)-C(12), 99.2 (6); C(8)-O(1)-C(9), 140.2 (8).

Table 1 Formation of the Ethynyloxane Derivatives from 2.



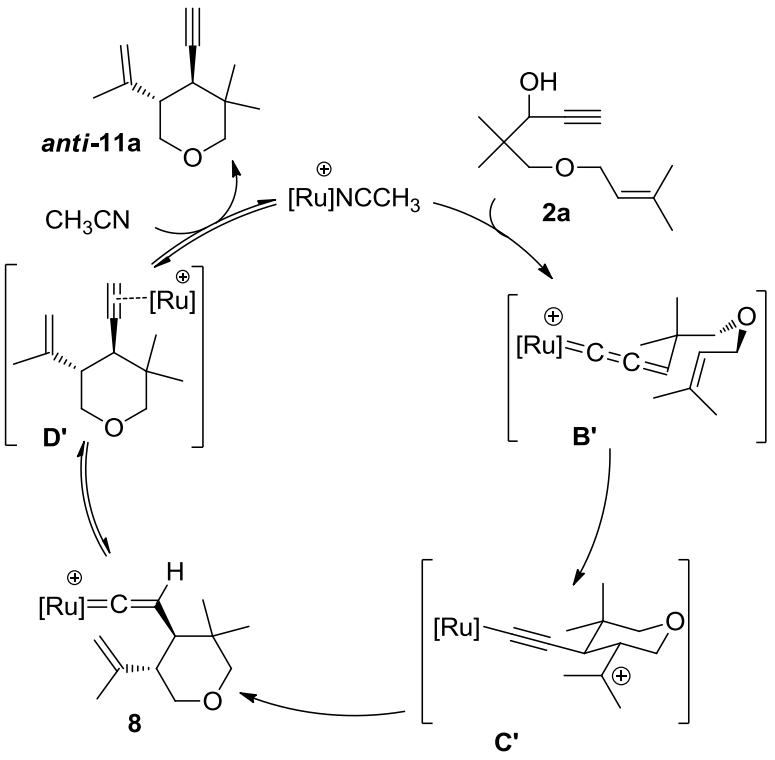
entry	substrate	L (ligand)	solvent	yields of **11** (%)[b]	ratio of isomers (anti:syn)[c]
1	**2a**, R=CH_3	2 PPh_3	$CHCl_3$	**11a**, 80	66:33
2	**2a**, R=CH_3	*S*-BINAP	$CHCl_3$	**11a**, 80	66:33
3	**2a**, R=CH_3	*R*-BINAP	$CHCl_3$	**11a**, 80	66:33
4	**2b**, 2R= -$(CH_2)_4$-	2 PPh_3	$CHCl_3$	**11b**, 45	85:15
5	**2a**, R=CH_3	2 PPh_3	MeOH	-[d]	-
6	2b, 2R= -$(CH_2)_4$-	2 PPh_3	MeOH	**11b**, 45	85:15

[a] All of the reactions were carried out at 50 ℃ for 12 h in the presence of 30 mol % $LRuCpNCCH_3^+$ except for entry 5 with 50 mol%. [b] Isolated yields as a mixture of *syn*- and *anti*-isomers. [c] The ratio of two stereoisomers was determined by ^{1}H NMR. [d] Products **12** and **13** were obtained in Scheme 9.

Heating **2a** in $CHCl_3$ at 50 ℃ for 12 h in the presence of 30 mol % of [Ru]$NCCH_3^+$ complex gave a mixture of diastereoisomers of 5,5-dimethyl-4-ethynyl-3-(1-methylethenyl)-oxane (**11a**) in 80% isolated yield. The *anti*-isomer is the major product with the ratio of *anti*-**11a**:*syn*-**11a** = 2:1. (Table 1, entry1) Alternatively, use of the complex bearing optically active phosphine ligands such as *S*-BINAP and *R*-BINAP

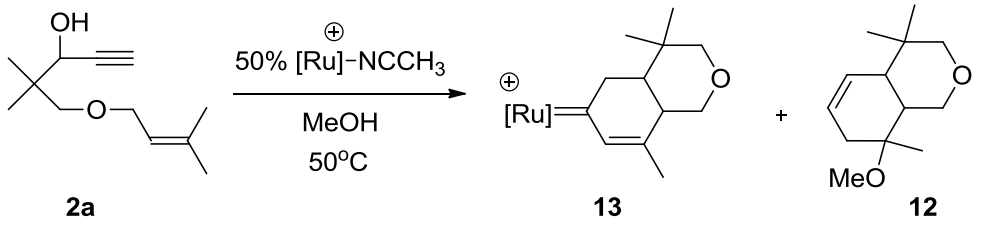
did not afford satisfactory results in isomer selectivity (Table 1, entry 2-3). According to the chair-like transition state model, the diastereoselectives of product may relate to the steric hindrance by minimizing 1,3-diaxial interactions. Hence, in the reaction of the propargylic alcohol **2b** with bulkier cyclopentyl tether, the isomer ratio was greatly improved to 17:3 due to the steric effect (Table 1, entry 4). The structures of **11a** and **11b** are determined by NMR spectra. In the ^{1}H NMR spectrum of **11a** and **11b**, the characteristic acetylenic proton resonances appear both as a doublet at δ 2.08 with $^{4}J_{HH}$ = 2.4 Hz and 2.04 with $^{4}J_{HH}$ = 2.1 Hz, respectively. Two singlet resonances at δ 4.93 and δ 4.84 are assigned to two olefinic methylene protons in **11a** and a singlet resonance at δ 5.52 is assigned to the olefinic proton of cyclopentene.

Scheme 8 Catalytic Cycle for the Formation of the *anti*-11a.



The proposed mechanism for the cyclization of the *anti*-**11a** is illustrated in Scheme 8. The reaction may, firstly, proceed by the production of the allenylidene intermediate **B'** and the intramolecular attack to give the corresponding alkynyl complex **C'** which is followed by a 1,5-hydrogen shift to give the corresponding *anti*-**8**. Finally, an isomerization of the vinylidene ligand gives the π-coordinated alkyne **D'** and replaced by CH_3CN to produce *anti*-**11a**, finishing the catalytic cycle.

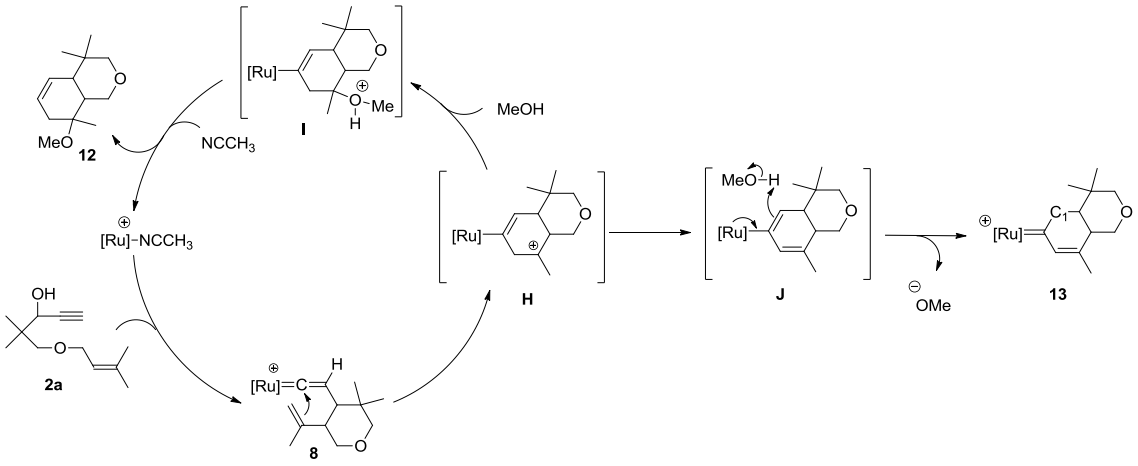
Scheme 9-1 Formation of the Bicyclic Ring Products



Interestingly, treatment of **2a** with $[Ru]NCCH_3^+$ in MeOH (Table 1, entry 5) afforded two products, the hexahydro isochromene compound **12** with a OMe group and the carbene complex **13**, both containing a newly formed bicyclic ring shown in Scheme 9-1. About 50 mol% of $[Ru]NCCH_3^+$ is required to completely consume **2a**. Otherwise, treatment of **2b** with a bulkier substituent with $[Ru]NCCH_3^+$ in MeOH afforded no corresponding product with bicyclic ring, but compound **11b** with the oxane moiety was obtained. (Table 1, entry 6). The ratio of **13** and **12** is 2: 1 as determined by the ^1H NMR spectrum. The structures of **13** and **12** are determined by various 2D NMR spectra. For **13**, with two stereogenic centers, there are two sets of resonances in all spectra

attributed to two diastereomers in a ratio of 1:0.3. The ^{31}P NMR spectrum displays two doublets at δ 45.26, 45.02 with $^{2}J_{PP}$ = 29.1 Hz. In the HMBC NMR spectrum, the singlet resonance at δ 6.73 assigned to =CH shows correlations with three ^{13}C resonances at δ 59.66, 41.11 and 20.62 assigned to methylene, the bridgehead CH and methyl carbon atoms. In the ^{1}H NMR spectrum, two multiplet resonances at δ 1.71 and 1.34 are assigned to the two bridgehead CH. The ^{13}C NMR spectrum shows triplet resonance at δ 317.61 with $^{2}J_{CP}$=9.66 Hz for Cα. For **12**, the multiplet resonance at δ 5.62, assigned to two =CH, shows correlations with the neighboring methylene group in the COSY NMR spectrum. And in the ^{1}H NMR spectrum, the singlet resonances at δ 3.20 and 1.10 are assigned to the methoxy and methyl groups, respectively. These correlations clearly revealing the C-C bond formation.

Scheme 9-2



Complex **13** and compound **12** are formed by a tandem cyclization of **2a** possibly via **8**. The second cyclization presumably takes place between the terminal double bond

and Cα of the vinylidene ligand of **8**. In order to better understand the mechanism of the formation of **13** and **12**, we treated **2a** with [Ru]Cl and KPF_6 in $CDCl_3/CD_3OD$ yielding **13-D**, where two hydrogens at C_1 are deuterated and **12-D** where both olefinic protons and methoxy group are deuterated. According previous evidence, the reaction presumably proceeds via formation of the vinylidene complex **8** and then the nucleophilic addition of the unsaturated double bond to Cα gives the acetylide intermediate **H**, forming a newly bicyclic skeleton, with methyl substituted tertiary carbocation. However, there are two different path ways from here on, i.e. the catalytic cycle and the formation of **13**, as shown in Scheme 9-2. In the catalytic path way, a methanol attack to the carbocation forms the intermediate **I**, which is followed by protonation to give **12** and $[Ru]NCCH_3^+$**.** In the formation of **13**, proton migration possibly assisted by MeOH and the presence of Ru yields the carbene complex **13**. The dehydrogenation reaction of the intermediate **H** of the methylene group proceeded to form the more stable intermediate **J** with two conjugated double bonds which may cause a higher yield of **13**. Finally, the reaction proceeds the protonation by methanol to form the carbene complex **13**.[39]

Similar reaction for the formation of fused polycyclic compounds was also proposed by Nishibayashi et al.[21a-b] However, in their case, an optically active thiolate-bridged diruthenium complex promoted catalytic cyclization process and

afforded *syn*-enynes as the major product in the first step. Then Pt complex was required to catalyze cycloisomerization of the enyne product in the second step. But, in our case, the first cyclization produces the *anti*-isomer as the major product and the tandem cyclization readily take place in methanol.

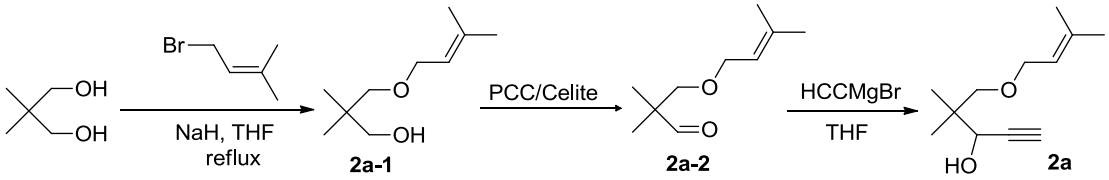
Conclusion

In summary, treatment of [Ru]Cl with enyne **1**, containing propargylic alcohol and allylic alkoxy moiety, in CH_2Cl_2 in the presence of NH_4PF_6 affords the vinylidene complex **3** with an oxepane mioety. Furthermore, from the same reaction of **2a**, the vinylidene complex **8** with a newly oxane ring is obtained as a mixture of two diastereoisomers and the *anti*-isomer is the major product. Additionally, the ruthenium-catalyzed cyclization of **1** generates organic enyne **6** in chloroform and in alcohol yields the organic product **7** by a tandem cyclization. Otherwise in the same reaction of **2a-b** gives **11a** and **11b**, respectively. And the isomer ratio of **11b** was greatly improved to 10:1.8 by the steric effect. Alternatively, the same reaction with **2a** in methanol affords the hexahydro isochromene compound **12** with a methoxy group and the carbene complex **13**, both containing a newly formed bicyclic ring. However, no corresponding bicyclic ring product was isolated from the reaction of **2b.**

Experimental Section：

General procedures: Manipulations were performed under an atmosphere of dry nitrogen by using vacuum-line and standard Schlenk techniques unless mentioned otherwise. All reagents were obtained from commercial suppliers and were used without further purification. Solvents were dried by standard methods and were distilled under nitrogen before use. NMR spectra were recorded on Brucker DPX-400, AVIII-400, DMX-500 or on AVIII-800 FT-NMR spectrometer at room temperature and were reported in units of δ with residual protons in the solvents as a standard. Electrospray ionization mass spectrometry and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at National Taiwan University. The ruthenium complex $Cp(PPh_3)_2RuCl$[40] and compound **1**[23] were prepared by following the method reported in the literature.

Synthesis of Compound 2a.



At room temperature, to a suspension of NaH (1.48 g, 37.2 mmol) in THF (10 mL) was added dropwise to a THF solution (30 mL) of 2,2-dimethyl-1,3-propandiol (5.00 g, 33.8 mmol) with stirring for 30 min, and the resulting mixture was then heated to reflux for 1h. After cooling to room temperature, to this solution was added

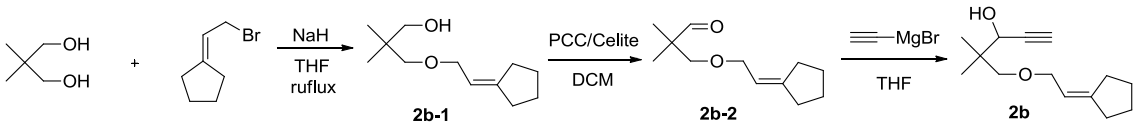
1-bromo-3-methyl-2-butene (4.7 ml, 40.5 mmol) slowly in 1 h, and the mixture was refluxed for 8 h. The resulting solution was treated with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and concentrated under reduced pressure to afford crude product **2a-1** (3.49 g, 60 %) that was purified by chromatography through a silica column (hexane/EA: 4/1). Spectroscopic data of **2a-1**: ^{1}H NMR (δ, $CDCl_3$): 5.28 (t, 1H, $^{3}J_{HH}$ = 6.79 Hz, HC=); 3.91 (d, 2H, $^{3}J_{HH}$ = 6.79 Hz, OCH_2); 3.42 (d, 2H, $^{3}J_{HH}$ = 5.47 Hz, OCH_2); 3.24 (s, 2H, OCH_2); 2.81 (t, 1H, $^{3}J_{HH}$ = 5.47 Hz, OH); 1.71, 1.63, 0.88 (s, 12H, 4 CH_3). ^{13}C NMR (δ, $CDCl_3$): 136.97 (C=); 120.93 (HC=); 79.67, 72.19, 68.00 (OCH_2); 36.02 (C); 25.71, 21.92, 18.03 (4 CH_3). MS (ESI^+) m/z: 195.1506 $(M+Na)^+$.

Compound **2a-1** (3.49 g, 20.3 mmol) was dissolved in CH_2Cl_2 (50 mL) and to this solution was slowly added PCC/celite (1:1 w/w, 6.51 g, 30.4 mmol). The resulting mixture was stirred for 3 h, and the resulting solution was diluted with hexane (50 mL) and purified by flash column to give **2a-2** (3.28 g, 95 %.) Spectroscopic data of **2a-2**: ^{1}H NMR (δ, $CDCl_3$): 9.51 (s, 1H, CHO); 5.24 (m, 1H, HC=); 3.90 (d, 2H, $^{3}J_{HH}$ = 7.07 Hz, OCH_2); 3.36 (s, 2H, OCH_2); 1.69, 1.60, 1.03 (s, 12H, 4 CH_3). ^{13}C NMR (δ, $CDCl_3$): 205.52 (CH=O); 136.85 (C=); 120.92 (CH=); 74.89, 67.92 (2 OCH_2); 47.03 (C); 25.69, 19.03, 17.99 (4 CH_3). MS (ESI^+) m/z: 193.1305 $(M+Na)^+$.

To a solution of compound **2a-2** (3.28 g, 19.3 mmol) in THF (30 mL), was added

ethynylmagnesium bromide (46.2 ml, 23.1 mmol) at room temperature and under nitrogen. The solution was stirred for 14h. After quenching by aqueous NH_4Cl solution (30 mL), the solution was extracted with ether (3x20 mL), then dried over sodium sulfate and concentrated under reduced pressure and eluted through a silica column (hexane/EA: 4/1) to give compound **2a** (3.39 g, 90 % yields). Spectroscopic data of **2a**: ^{1}H NMR (δ, $CDCl_3$): 5.29 (m, 1H, HC=); 4.14 (dd, 1H, $^3J_{HH}$ = 7.11 Hz, $^4J_{HH}$ = 1.96 Hz, CH); 3.94 (m, 2H, OCH_2); 3.77 (d, 1H, $^3J_{HH}$ = 7.11 Hz, OH); 3.58, 3.20 (2d, 2H, $^2J_{HH}$ = 8.93 Hz, OCH_2); 2.41 (d, 1H, $^4J_{HH}$ = 1.96 Hz, ≡CH); 1.71, 1.64, 1.06, 0.94 (s, 12H, $4CH_3$). ^{13}C NMR (δ, $CDCl_3$): 137.39 (=C); 120.61 (HC=); 83.48 (≡C); 77.85 (HC≡); 73.26, 70.84 (2 OCH_2); 67.96 (CH); 38.70 (C); 25.69, 22.19, 20.99, 18.03 (4 CH_3). MS (ESI^+) m/z: 219.1359 $(M+Na)^+$.

Synthesis of Compound 2c



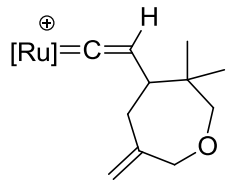
At room temperature, to a suspension of NaH (1.18 g, 18.6 mmol) in THF (10 mL) was added dropwise to a THF solution (30 mL) of 2,2-dimethyl-1,3-propandiol (2.79 g, 26.8 mmol) with stirring for 30 min, and the resulting mixture was then heated to reflux for 1h. After cooling to room temperature, to this solution was added (2-Bromoethylidene)cyclopentane (3.5 ml, 29.5 mmol) slowly in 1 h, and the mixture

was refluxed for 8 h. The resulting solution was treated with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate and concentrated under reduced pressure to afford crude product **2b-1** (3.18 g, 60 %) that was purified by chromatography through a silica column (hexane/EA: 4/1). Spectroscopic data of **2b-1**: ^{1}H NMR (δ, $CDCl_3$): 5.38 (m, 1H, HC=); 3.91 (m, 2H, OCH_2); 3.47 (s, 1H, OH); 3.41 (d, 2H, $^{2}J_{HH}$ = 5.84 Hz, OCH_2); 3.25 (s, 2H, OCH_2); 2.22, 1.62 (m, 8H, 4 CH_2); 0.89 (s, 6H, 2 CH_3). ^{13}C NMR (δ, $CDCl_3$): 139.70 (=C); 119.77 (HC=); 77.52, 72.15, 69.27 (3 OCH_2); 39.58 (C); 33.49, 26.10, 25.82 (4 CH_2); 22.57 (2 CH_3). MS (ESI^+) m/z: 221.1652 $(M+Na)^+$.

Compound **2b-1** (3.18 g, 16.1 mmol) was dissolved in CH_2Cl_2 (50 mL) and to this solution was slowly added PCC/celite (1:1 w/w, 6.91 g, 32.1 mmol). The resulting mixture was stirred for 3 h, and the resulting solution was diluted with hexane (50 mL) and purified by flash column to give **2b-2** (2.99 g, 95 %.) Spectroscopic data of **2b-2**: ^{1}H NMR (δ, $CDCl_3$): 9.53 (s, 1H, CHO); 5.36 (m, 1H, HC=); 3.90 (m, 2H, OCH_2): 3.38 (s, 2H, OCH_2); 2.22, 1.61 (m, 8H, 4 CH_2); 1.05 (s, 6H, 2 CH_3). ^{13}C NMR (δ, $CDCl_3$): 206.42 (CHO); 142.36 (=C); 123.54 (HC=); 77.52, 68.15 (2 OCH_2); 42.13 (C); 33.49, 28.62, 25.82 (4 CH_2); 18.62 (2 CH_3). MS (ESI^+) m/z: 219.1562 $(M+Na)^+$.

To a solution of compound **2b-2** (2.99 g, 15.2 mmol) in THF (30 mL), was added ethynylmagnesium bromide (38.4 ml, 19.2 mmol) at room temperature and under

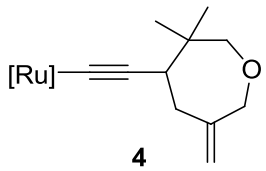
nitrogen. The solution was stirred for 14h. After quenching by aqueous NH_4Cl solution (30 mL), the solution was extracted with ether (3x20 mL), then dried over sodium sulfate and concentrated under reduced pressure and eluted through a silica column (hexane/EA: 4/1) to give compound **2b** (3.04 g, 90 % yields). Spectroscopic data of **2b**: ^{1}H NMR (δ, $CDCl_3$): 5.36-5.42 (m, 1H, HC=); 4.15 (dd, 1H, $^3J_{HH}$ = 7.10 Hz, $^4J_{HH}$ = 2.00 Hz, CH); 3.93 (m, 2H, OCH_2); 3.74 (d, 1H, $^3J_{HH}$ = 7.10 Hz, OH); 3.58, 3.21 (2d, 2H, $^2J_{HH}$ = 9.09 Hz, OCH_2); 4.15 (d, 1H, $^4J_{HH}$ = 2.00 Hz, ≡CH); 2.22 (dt, 4H, $^3J_{HH}$ = 19.12 Hz, $^4J_{HH}$ = 6.67 Hz, 2 CH_2); 1.63 (m, 4H, 2 CH_2). ^{13}C NMR (δ, $CDCl_3$): 148.40 (=C); 115.97 (HC=); 83.33 (≡C); 77.52, 69.27 (2 OCH_2); 73.13 (≡CH); 70.25 (CH); 38.58 (C); 33.49, 28.63, 26.10, 25.82 (4 CH_2); 21.92, 20.70 (2 CH_3). MS (ESI^+) m/z: 245.1508 $(M+Na)^+$.



3

Synthesis of Complex 3. A mixture of [Ru]Cl (250 mg, 0.34 mmol), **1** (61 mg, 0.34 mmol), and NH_4PF_6 (81 mg, 0.50 mmol), in CH_2Cl_2 (20 mL) was stirred at ambient temperature for one day. The resulting brown solution was filtered through a bed of Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under vacuum and the solid

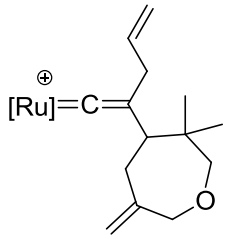
residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by a 50 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexane 1:1 and dried under vacuum. The final product can be obtained as a light orange powder identified as **3** (210 mg, 70% yields). Spectroscopic data of **3**: ^{1}H NMR (δ, $CDCl_3$): 6.94-7.66 (m, 34H, Ph); 5.13 (s, 5H, Cp); 4.57 (d, 1H, $^{3}J_{HH}$ = 10.47 Hz, CβH); 4.76, 4.54 (s, 2H, =CH_2); 4.12 (t, 2H, $^{3}J_{HH}$=15.11 Hz, CH_2); 3.30, 3.16 (2d, 2H, $^{2}J_{HH}$=12.71 Hz, CH_2); 2.35, 2.15 (m, 2H, CH_2); 0.99, 0.97 (s, 6H, 2CH_3). ^{13}C NMR (δ, $CDCl_3$): 343.94 (t, $^{3}J_{CP}$=15.21 Hz, Cα); 147.04 (C=); 128.21-134.61 (Ph); 115.64 (Cβ); 112.92 (CH_2=); 94.32 (Cp); 76.80, 74.43, 38.69 (3 CH_2); 44.23 (CH); 38.16, 26.09 (2 CH_3); 21.90 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 43.24, 43.02 (2d, $^{2}J_{PP}$=26.35 Hz, PPh_3). MS (ESI^{+}) m/z: 855.2453 (M)$^{+}$.



4

Synthesis of Complex 4. The mixture of **3** (85 mg, 0.099 mmol) and NaOMe (6.0 mg, 0.11 mmol) in MeOH (30 mL) was stirred for 5 m at room temperature. After that, solvent of the solution was removed under vacuum and then 20 mL of diethyl ether was added and the mixture was stirred using an ultrasonic cleaner. The solution was filtered through neutral Al_2O_3 to remove the insoluble salts, and then solvent of the filtrate was removed under vacuum. The final product can be obtained as a yellow solid identified

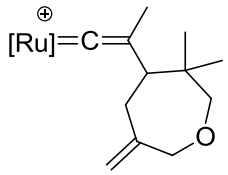
as **4** (77 mg, 90% yield). Spectroscopic data of **4**: ^{1}H NMR (δ, C_6D_6): 7.69-7.73 (m, 12H, Ph); 6.92-6.98 (m, 18H, Ph); 5.00, 4.79 (s, 2H, =CH_2); 4.39 (s, 5H, Cp); 4.59, 4.26 (2d, 2H, $^{2}J_{HH}$=14.17 Hz, OCH_2); 3.90, 3.33 (2d, 2H, $^{2}J_{HH}$=11.81 Hz, OCH_2); 2.86 (m, 2H, CH_2); 2.76 (m, 1H, CγH); 1.51 (s, 3H, CH_3); 1.22 (s, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 127.39-140.12 (Ph); 113.45 (Cβ); 92.69 (t, $^{2}J_{CP}$=24.43 Hz, Cα); 85.44 (Cp); 110.72 (CH_2=), 151.45 (C=); 78.96, 75.42, 39.64 (3 CH_2); 26.63, 21.74 (2 CH_3); 39.59 (C). ^{31}P NMR (δ, C_6D_6): 51.94 (s, PPh_3). MS (ESI^+) m/z: 855.2469 $(M+1)^+$.



5a

Synthesis of Complex 5a. Complex **4** (110 mg, 0.13 mmol) and KPF_6 (26 mg, 0.14 mmol) were added into a Schlenk flask, and CH_2Cl_2 (20 mL) was added under nitrogen atmosphere. Allyl bromide (17 mg, 0.14 mmol) was added to the resulting solution which was stirred for 8 h. After that, the solution was filtered through a bed of Celite to remove the insoluble salts, then the solvent of the filtrate was removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by adding to a 50 mL of stirred ethyl ether. Precipitates thus formed were collected in a glass frit, washed with ethyl ether/hexane 1:1 and dried under

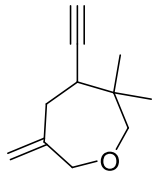
vacuum. The final product was obtained as a deep yellow powder identified as **5a** (100 mg, 90% yield). Spectroscopic data of **5a**: ^{1}H NMR (δ, $CDCl_3$): 7.74-6.79 (m, 49H, Ph); 5.89 (m, 1H, =C(C)H); 5.11 (s, 5H, Cp); 5.11 (m, 2H, $=CH_2$); 4.63, 4.55 (s, 2H, $=CH_2$); 4.16, 3.75 (2d, 2H, $^{2}J_{HH}$=14.25 Hz, OCH_2); 3.26, 2.72 (2d, 2H, $^{2}J_{HH}$=12.21 Hz, OCH_2); 3.13, 2.77 (dd, 2H, $^{2}J_{HH}$=16.79 Hz, $^{3}J_{HH}$=6.11 Hz, CH_2); 2.65, 2.25 (m, 2H, CH_2); 2.22 (d, $^{3}J_{HH}$=6.11 Hz, 1H, CH) 1.04, 0.83 (s, 6H, $2CH_3$). ^{13}C NMR (δ, $CDCl_3$): 349.67 (t, $^{3}J_{CP}$=14.04 Hz, Cα); 148.16-111.99 (Cβ, Ph, $=C(CH_2)_2$, $=CH_2$); 94.02 (Cp); 81.98 (OCH_2); 74.50 (OCH_2); 4.77 (CH); 39.97 (CH_2); 38.33 (C); 27.56 (CH_2); 26.46 (CH_3); 21.00 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 41.38, 40.68 (2d, $^{2}J_{PP}$=27.68 Hz, PPh_3). MS (ESI^+) m/z: 895.2813 $(M)^+$.



5b

Synthesis of Complex 5b. Complex **5b** (120 mg, 93% yield) was similarly prepared from **4** (130 mg, 0.15 mmol), KPF_6 (31 mg, 0.18 mmol) and methyl iodide (26 mg, 0.18 mmol). Spectroscopic data of **5b**: ^{1}H NMR (δ, $CDCl_3$):7.77-6.93 (m, 42H, Ph); 5.14 (s, 5H, Cp); 4.63, 4.41 (s, 2H, $=CH_2$); 4.18, 3.87 (2d, 2H, $^{2}J_{HH}$=14.18 Hz, OCH_2); 3.34, 2.92 (2d, 2H, $^{2}J_{HH}$=12.02 Hz, OCH_2); 2.49 (t, 1H, $^{3}J_{HH}$=12.91 Hz, CH); 2.20, 1.86 (2d, 2H, $^{2}J_{HH}$=11.57 Hz, CH_2); 1.76, 1.04, 0.93 (s, 9H, $3CH_3$). ^{13}C NMR (δ, $CDCl_3$): 350.81

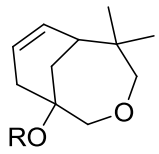
(t, $^{3}J_{CP}$=15.19 Hz, Cα); 148.22 (=C(CH_2)$_2$); 135.23-128.42 (Cβ, Ph); 112.23 (=CH_2); 93.93 (Cp); 81.00 (OCH_2); 74.59 (OCH_2); 43.85 (CH_2); 40.15 (CH_2); 36.34 (C); 27.12 (CH_3); 21.65 (CH_3); 7.98 (CH_3). ^{31}P NMR (δ, $CDCl_3$): 42.43, 41.44 (2d, $^{2}J_{PP}$=26.42 Hz, PPh_3). MS (ESI^+) m/z: 869.2641 $(M)^+$.



6

Synthesis of Compound 6. The solution of complex **3** (150 mg, 0.17 mmol) in $CDCl_3$ (1.5 mL) and CH_3CN (121 mg, 3.0 mmol, 0.15 mL) in an NMR tube was heated at 60°C for 24 h. Then $CDCl_3$ and CH_3CN were removed *in vacuo* and CH_2Cl_2 (1.0 mL) was used to extract the product and diethyl ether (6.0 mL) was then added. The pale-orange precipitates thus formed was filtered and washed with diethyl ether and dried under vacuum to give [Ru]$NCCH_3^+$. The filtrate was evaporated to dryness under vacuum and the crude product purified by flash chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **6** (26 mg, 92%). Spectroscopic data for **6**: ^{1}H NMR (δ, $CDCl_3$): 4.92, 4.83 (s, 2H, =CH_2); 4.23, 4.13 (2d, 2H, $^{2}J_{HH}$=14.51 Hz, OCH_2); 3.35, 3.13 (2d, 2H, $^{2}J_{HH}$=12.51 Hz, OCH_2); 2.48 (m, 2H, CH_2); 2.23 (dt, 1H, $^{3}J_{HH}$=9.54 Hz, $^{4}J_{HH}$= 2.50 Hz, CH); 2.10 (d, 1H, $^{4}J_{HH}$=2.50 Hz, HC≡); 1.03, 0.94 (s, 6H, 2CH_3). ^{13}C NMR (δ, $CDCl_3$): 147.49 (=C); 112.67 (H_2C=); 85.72 (≡C); 77.28, 74.59, 36.23 (3CH_2); 70.97 (HC≡); 34.21 (≡C);

37.74 (C); 25.31, 20.92 (3 CH_3). MS (ESI^+) m/z: 165.1217(M+1).



7a, R = Me
7b, R = Et
7c, R = iPr

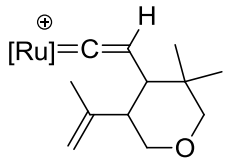
Synthesis of Compound 7a. The solution of **1** (65 mg, 0.36 mmol) and $[Ru]NCCH_3^+$ (78 mg, 0.11 mmol) in a 2:1 cosolvent of $CHCl_3$/MeOH was heated to 50 ^oC for 1 day. Then the solvent was removed under vacuum and 1 mL of CH_2Cl_2 was used to extract the crude product. This is followed by re-precipitation by a 10 mL of stirred diethyl ether. The pale-orange precipitates thus formed were filtered and washed with diethyl ether and dried under vacuum to give $[Ru]NCCH_3^+$. The filtrate was evaporated to dryness under vacuum and the crude product purified by flash chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **7a** (55 mg, 77%). Spectroscopic data for **7a**: ^1H NMR (δ, $CDCl_3$): 5.81 (m, 1H, =C(C)H); 5.70 (m, 1H, =C(C)H); 4.12, 3.19 (2d, 2H, $^2J_{HH}$=14.07 Hz, OCH_2); 3.44, 3.11 (2d, 2H, $^2J_{HH}$=12.27 Hz, OCH_2); 3.28 (s, 3H, OCH_3); 2.62 (2d, 1H, $^2J_{HH}$=12.82 Hz, CH_2); 2.12, 1.92 (m, 2H, CH_2); 2.05 (br, 1H, CH); 1.43 (dd, 1H, $^2J_{HH}$=12.82 Hz, $^3J_{HH}$=7.31 Hz, CH_2); 1.14, 0.81 (s, 6H, $2CH_3$). ^{13}C NMR (δ, $CDCl_3$): 128.96, 126.25 (2C=); 83.09, 81.60 ($2OCH_2$); 78.42 (C); 49.29 (OCH_3); 44.46 (CH); 38.01 (C); 36.57, 28.91 ($2CH_2$); 26.67, 23.75 ($2CH_3$). MS (ESI^+) m/z: 197.8102

$(M+H)^+$.

Synthesis of Compound 7b. Compound **7b** (49 mg, 70% yield) was similarly prepared from **1** (61 mg, 0.33 mmol), $[Ru]NCCH_3^+$ (73 mg, 0.10 mmol) in a 2:1 cosolvent of $CHCl_3$/EtOH, and the solution was heated to 50 ^oC for 1 day. Spectroscopic data of **7b**: ^1H NMR (δ, $CDCl_3$): 5.80 (m, 1H, =C(C)H); 5.70 (m, 1H, =C(C)H); 4.11, 3.22 (2d, 2H, $^2J_{HH}$=13.96 Hz, OCH_2); 3.53 (m, 2H, OCH_2); 3.43, 3.11 (2d, $^2J_{HH}$=12.16 Hz, 2H, OCH_2); 2.61 (d, 1H, $^2J_{HH}$=12.77 Hz, CH_2); 2.14, 1.93 (m, 2H, CH_2); 2.04 (br, 1H, CH); 1.47 (dd, 1H, $^2J_{HH}$=13.30 Hz, $^3J_{HH}$=7.48 Hz, CH_2); 1.15 (t, 3H, $^3J_{HH}$=7.06 Hz, CH_3); 1.13 (s, 3H, CH_3); 0.81 (s, 3H, CH_3). ^{13}C NMR (δ, $CDCl_3$): 128.94, 126.34 (2C=); 83.08, 81.60 (2 OCH_2); 78.42 (C); 49.29 (OCH_3); 44.46 (CH); 38.01 (C); 36.57, 28.91 (2 CH_2); 26.67, 23.75 (2 CH_3). MS (ESI^+) m/z: 211.8102 $(M+H)^+$.

Synthesis of Compound 7c. Compound **7c** (30 mg, 43% yield) was similarly prepared from **1** (57 mg, 0.31 mmol), $[Ru]NCCH_3^+$ (68 mg, 0.093 mmol) in a 2:1 cosolvent of $CHCl_3$/*i*-PrOH, and the solution was heated to 50 ^oC for 1 day. Spectroscopic data of **7c**: ^1H NMR (δ, $CDCl_3$): 5.78 (m, 1H, =C(C)H); 5.68 (m, 1H, =C(C)H); 4.11, 3.23 (2d, 2H, $^2J_{HH}$=13.95 Hz, OCH_2); 3.94 (Septet, 1H, $^3J_{HH}$=6.18 Hz, CH); 3.44, 3.12 (2d, 2H, $^2J_{HH}$=12.12 Hz, OCH_2); 2.58 (d, 1H, $^2J_{HH}$=12.68 Hz, CH_2); 2.12, 1.91 (m, 2H, CH_2); 2.03 (br, 1H, CH); 1.51 (dd, 1H, $^2J_{HH}$=12.51 Hz, $^3J_{HH}$=7.33 Hz, CH_2); 1.14(s, 3H,

CH_3);0.81 (s, 3H, CH_3); 1.13 (s, 6H, 2 CH_3). ^{13}C NMR (δ, $CDCl_3$): 128.86, 126.38 (2C=); 83.16, 83.07 (2 OCH_2); 79.03 (C); 64.23 (OCH); 44.53 (CH); 37.98 (C); 37.64, 31.07 (2 CH_2); 26.70, 25.54, 25.33, 23.76 (4 CH_3). MS (ESI^+) m/z: 247.1661 $(M+Na)^+$.



8

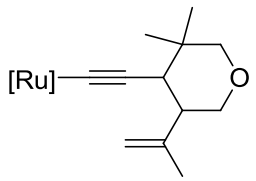
Synthesis of Complex 8. A mixture of [Ru]Cl (148 mg, 0.21 mmol), **2a** (50 mg, 0.25 mmol), and NH_4PF_6 (85 mg, 0.32 mmol), in CH_2Cl_2 (20 mL) was stirred at ambient temperature for one day. The resulting brown solution was filtered through a bed of Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by a 50 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether/hexane 1:1 and dried under vacuum. The final product can be obtained as a deep yellow powder identified as **8** (147 mg, 68% yields).

The ratio of *anti*- and *syn*- isomers is 1:0.5.

Spectroscopic data for the *anti*-isomers: ^1H NMR (δ, CD_2Cl_2): 7.93- 6.99 (m, 70H, Ph); 5.12 (s, 5H, Cp); 5.10, 4.89 (s, 2H, 2 HC=); 4.23 (dt, 1H, $^3J_{HH}$=9.78 Hz, $^4J_{HP}$=2.69 Hz, CβH); 3.92 (dd, 1H, $^2J_{HH}$=11.38 Hz, $^3J_{HH}$=4.36 Hz, OCH_2); 3.58 (2d, 1H, $^2J_{HH}$=11.09

Hz, OCH_2); 3.27 (m, 1H, OCH_2); 3.12 (2d, 1H, $^2J_{HH}$=11.45 Hz, OCH_2); 2.67 (dd, 1H, $^3J_{HH}$=9.78 Hz, $^3J_{HH}$=11.20 Hz, CH); 2.18 (dt, 1H, $^3J_{HH}$=11.20 Hz, $^3J_{HH}$=4.36 Hz, CH); 1.73, 0.97, 0.82 (s, 9H, $3CH_3$). ^{13}C NMR (δ, CD_2Cl_2): 343.71 (t, $^2J_{CP}$=14.86 Hz, Cα); 145.33 (=C); 135.38-128.27 (Ph); 114.31 (Cβ); 113.07 (CH_2=); 94.70 (Cp); 78.73, 72.34 (2 OCH_2); 47.55, 45.66 (2 CH); 35.27 (C); 25.97, 22.72, 19.34 (3 CH_3). ^{31}P NMR (δ, CD_2Cl_2): 43.75, 43.12 (2d, $^2J_{PP}$=26.49 Hz, PPh_3). MS (ESI^+) m/z: 869.2624 $(M)^+$.

Spectroscopic data for the *syn*-isomer: ^{1}H NMR (δ, CD_2Cl_2): 7.93- 6.99 (m, 70H, Ph); 5.12 (s, 5H, Cp); 5.10, 4.68 (s, 2H, 2 HC=); 4.44 (d, 1H, $^3J_{HH}$=10.46 Hz, CβH); 3.80 (dd, 1H, $^2J_{HH}$=11.87 Hz, $^3J_{HH}$=3.39 Hz, OCH_2); 3.43 (t, 1H, $^2J_{HH}$=11.87 Hz, OCH_2); 3.25 (m, 1H, OCH_2); 3.09 (2d, 1H, $^2J_{HH}$=11.97 Hz, OCH_2); 2.96 (dd, 1H, $^3J_{HH}$=10.46 Hz, $^3J_{HH}$=3.55 Hz, CH); 2.79 (br, 1H, CH); 1.80, 1.21, 0.86 (s, 9H, $3CH_3$). ^{13}C NMR (δ, CD_2Cl_2): 342.67 (t, $^2J_{CP}$=15.08 Hz, Cα); 145.26 (=C); 135.38-128.27 (Ph); 111.24 (Cβ); 111.01 (CH_2=); 94.61 (Cp); 72.54, 65.93 (2 OCH_2); 43.06, 42.18 (2 CH); 34.38 (C); 26.26, 24.39, 23.21 (3 CH_3). ^{31}P NMR (δ, CD_2Cl_2): 45.22, 43.50 (2d, $^2J_{PP}$=26.79 Hz, PPh_3). MS (ESI^+) m/z: 869.2624 $(M)^+$.



9

Synthesis of Complex 9. The mixture of **8** (75 mg, 0.086 mmol) and NaOMe (6 mg,

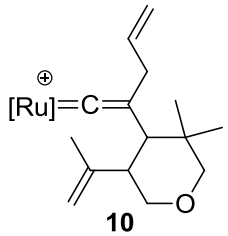
0.11 mmol) in MeOH (30 mL) was stirred for 5 m at room temperature. After that, solvent of the solution was removed under vacuum and then 20 mL of diethyl ether was added and the mixture was stirred using an ultrasonic cleaner. The solution was filtered through neutral Al_2O_3 to remove the insoluble salts, and then solvent of the filtrate was removed under vacuum. The yellow final product can be obtained and was identified as **9** (67 mg, 90% yield). Spectroscopic data of **9**:

The ratio of *anti*- and *syn*- isomers is 1:0.5.

Spectroscopic data for the *anti*-isomer: ^{1}H NMR (δ, C_6D_6): 7.56-7.65 (m, 20H, Ph); 6.95-6.96 (m, 30H, Ph); 4.96, 4.93 (s, 2H, $=CH_2$); 4.40 (s, 5H, Cp); 4.11,3.35 (dd, 2H, $^{2}J_{HH}$=11.37 Hz, $^{3}J_{HH}$=4.60, OCH_2); 3.70, 3.16 (2d, 2H, $^{2}J_{HH}$=10.79 Hz, OCH_2); 2.81 (m, 1H, CH); 2.69 (d, 1H, $^{3}J_{HH}$=11.36 Hz, CH); 1.79 (s, 3H,CH_3); 1.43 (s, 3H, CH_3); 1.07 (s, 3H, CH_3). ^{13}C NMR (δ, C_6D_6): 146.24 (=C); 127.50-140.52 (Ph); 112.72 ($=CH_2$); 110.58 (Cβ); 92.19 (t, $^{2}J_{CP}$=24.98 Hz, Cα); 85.69 (Cp); 79.07 (OCH_2); 73.46 (OCH_2); 48.72 (CH); 46.15 (CH); 35.64 (C); 26.334, 20.93, 20.71 ($3CH_3$). ^{31}P NMR (δ, C_6D_6): 51.22 (s, PPh_3). MS (ESI^+) m/z: 869.2634 $(M+1)^+$.

Spectroscopic data for the *syn*-isomer: ^{1}H NMR (δ, C_6D_6): 7.56-7.65 (m, 20H, Ph); 6.95-6.96 (m, 30H, Ph); 4.93, 4.66 (s, 2H, $=CH_2$); 4.41 (s, 5H, Cp); 4.37,4.28 (dd, 2H, $^{2}J_{HH}$=10.60 Hz, $^{3}J_{HH}$=3.34 Hz, OCH_2); 4.03, 3.41 (2d, 2H, $^{2}J_{HH}$=10.78 Hz, OCH_2); 3.05 (br, 1H, CH); 2.81 (m, 1H, CH); 1.91 (s, 3H,CH_3); 1.29 (s, 3H, CH_3); 1.01 (s, 3H, CH_3).

^{13}C NMR (δ, C_6D_6): 146.69 (=C); 127.50-140.52 (Ph); 109.13 (H_2C=); 108.51 (Cβ); 93.83 (t, $^2J_{CP}$=24.98 Hz, Cα); 85.69 (Cp); 74.07 (OCH_2); 67.76 (OCH_2); 44.81 (CH); 42.57 (CH); 35.22 (C); 26.74, 25.61, 22.61 ($3CH_3$). ^{31}P NMR (δ, C_6D_6): 52.16, 50.34 (2d, $^2J_{PP}$=37.98 Hz, PPh_3). MS (ESI^+) m/z: 869.2634 $(M+1)^+$.



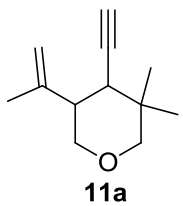
10

Synthesis of Complex 10. Complex **9** (165 mg, 0.19 mmol) and KPF_6 (39 mg, 0.21 mmol) were added into a Schlenk flask, and CH_2Cl_2 (20 mL) was added under nitrogen atmosphere. Allyl bromide (26 mg, 0.21 mmol) was added to the resulting solution which was stirred for 8 h. After that, the solution was filtered through a bed of Celite to remove the insoluble salts, then the solvent of the filtrate was removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by adding to a 50 mL of stirred ethyl ether. Precipitates thus formed were collected in a glass frit, washed with ethyl ether/hexane 1:1 and dried under vacuum. The final product was obtained as a light pink powder identified as **10** (160 mg, 93% yield). Spectroscopic data of **10**:

The ratio of *anti*- and *syn*- isomers is 1:0.3.

Spectroscopic data for the *anti*-isomer: ^{1}H NMR (δ, $CDCl_3$): 6.68-7.75 (m, 50H, Ph); 6.09 (m, 1H, =C(C)H); 5.13 (s, 5H, Cp); 5.28-4.91 (m, 4H, 2 =CH_2); 3.90,2.86 (2d, 2H, $^{2}J_{HH}$=10.29 Hz, OCH_2); 3.27, 2.69 (2d, 2H, $^{2}J_{HH}$=10.85 Hz, OCH_2); 2.44 (br, 2H, 2 CH); 1.81, 1.10, 0.63 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 349.91 (t, $^{3}J_{CP}$=12.18 Hz, Cα); 144.24 (=C); 139.19(=C(C)H); 122.36-135.13 (Ph, Cβ, =C); 116.54, 113.72 (2 =CH_2); 94.36 (Cp); 80.60, 73.89 (2 OCH_2); 42.91, 42.85 (2 CH); 36.73 (C); 28.43 (CH_2); 26.46, 23.57, 22.11 (3 CH_3). ^{31}P NMR (δ, $CDCl_3$): 40.56 (br, PPh_3). MS (ESI^+) m/z: 909.2948 $(M)^+$.

Spectroscopic data for the *syn*-isomer: ^{1}H NMR (δ, $CDCl_3$): 6.68-7.75 (m, 50H, Ph); 5.95 (m, 1H, =C(C)H); 5.38, 5.04 (m, 4H, 2 =CH_2); 5.17 (s, 5H, Cp); 3.79-3.04 (m, 6H, CH_2, 2 OCH_2); 2.67, 2.50 (m, 2H, 2CH); 1.81, 0.96, 0.92 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 351.04 (m, Cα); 145.56 (=C); 137.83 (=C(C)H); 122.36-135.13 (Ph, Cβ , =C); 94.10 (Cp); 73.88, 69.59 (2 OCH_2); 44.99, 39.61 (2 CH); 35.85 (C); 29.72 (CH_2); 28.12, 24.89, 24.14 (3 CH_3). ^{31}P NMR (δ, $CDCl_3$): 40.91 (br, PPh_3). MS (ESI^+) m/z: 909.2948 $(M)^+$.



11a

Synthesis of Compound 11a. The solution of complex **8** (150 mg, 0.16 mmol) in

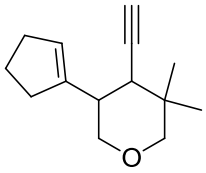
$CDCl_3$ (1.5 mL) and CH_3CN (97 mg, 2.4 mmol, 0.12 mL) in an NMR tube was heated at 50°C for 24 h. Then $CDCl_3$ and CH_3CN were removed *in vacuo* and CH_2Cl_2 (1 mL) was used to extract the product and diethyl ether (6 mL) was then added. The pale-orange precipitates thus formed was filtered and washed with diethyl ether and dried under vacuum to give [Ru]$NCCH_3^+$. The filtrate was evaporated to dryness under vacuum and the crude product purified by flash chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **11a** (26 mg, 93%). Spectroscopic data of **11a**:

The ratio of *anti*- and *syn*- isomers is 1:0.5.

Spectroscopic data for the *anti*-isomer: ^{1}H NMR (δ, $CDCl_3$): 4.93, 4.84 (s, 2H, $=CH_2$); 3.86 (m, 1H, OCH_2); 3.53, 3.07 (2d, 2H, $^2J_{HH}$=11.42 Hz, OCH_2); 3.12 (t, 1H, $^2J_{HH}$=11.35 Hz, OCH_2); 2.47 (td, 1H, $^2J_{HH}$=11.35 Hz, $^3J_{HH}$=4.49 Hz, CH); 2.28 (dd, 1H, $^2J_{HH}$=11.35 Hz, $^4J_{HH}$=2.39 Hz, CH); 2.08 (d, 1H, $^4J_{HH}$=2.39 Hz, ≡CH); 1.75, 1.13, 0.97 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 143.42 (=C); 113.19 ($=CH_2$); 83.26 (≡C); 78.02, 72.15 (2 OCH_2); 71.14 (≡CH); 45.22, 42.48 (2CH); 33.71 (C); 25.17, 21.13, 19.75 (3 CH_3). MS (ESI^+) m/z: 179.1422 $(M+1)^+$.

Spectroscopic data for the *syn*-isomer: ^{1}H NMR (δ, $CDCl_3$): 4.86, 4.54 (s, 2H, $=CH_2$); 3.86 (m, 1H, OCH_2); 3.64 (t, 1H, $^2J_{HH}$=10.95 Hz, OCH_2); 3.48, 3.25 (2d, 2H, $^2J_{HH}$=11.51 Hz, OCH_2); 2.60 (br, 2H, 2CH); 2.13 (d, 1H, $^4J_{HH}$=2.39 Hz, ≡CH); 1.74, 1.16, 1.01 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 143.63 (=C); 110.63 ($=CH_2$); 81.93 (≡

C); 73.32, 73.25 (2 OCH_2); 66.83 (≡CH); 40.79, 40.20 (2CH); 33.40 (C); 24.80, 22.00, 21.13 (3 CH_3). MS (ESI^+) m/z: 179.1422 $(M+1)^+$.



11b

Synthesis of Compound 11b. The solution of compound **2b** (55 mg, 0.24 mmol) and [Ru]$NCCH_3^+$ (55 mg, 0.07 mmol) in cosolvent of $CHCl_3$/MeOH in an NMR tube was heated at 60°C for 24 h. Then $CHCl_3$ and MeOH were removed *in vacuo* and CH_2Cl_2 (1.0 mL) was used to extract the product and diethyl ether (6.0 mL) was then added. The filtrate was evaporated to dryness under vacuum and the crude product purified by flash chromatography (silica gel, hexanes/EtOAc = 10/1) to afford **11b** (22 mg, 45%).

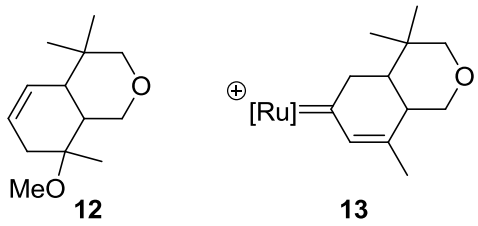
Spectroscopic data of **11b**:

The ratio of *anti*- and *syn*- isomers is 1:0.18.

Spectroscopic data for the *anti*-isomer: ^{1}H NMR (δ, $CDCl_3$): 5.52 (s, 1H, HC=); 3.84 (dd, 1H, $^2J_{HH}$=11.54 Hz, $^3J_{HH}$=4.59 Hz, OCH_2); 3.08 (t, 1H, $^2J_{HH}$=11.54 Hz, OCH_2); 3.50, 3.04 (2d, 2H, $^2J_{HH}$=11.28 Hz, OCH_2); 2.62 (td, 1H, $^3J_{HH}$=11.50 Hz, $^3J_{HH}$=4.59 Hz, CH); 2.29 (br, 4H, 2 CH_2); 2.24 (dd, 1H, $^3J_{HH}$=11.50 Hz, $^4J_{HH}$=2.11 Hz, CH); 2.04 (d, 1H, $^4J_{HH}$=2.11 Hz, HC≡); 1.82 (quintet, 2H, $^3J_{HH}$=7.37 Hz, CH_2); 1.11, 0.93 (s, 6H,

$2CH_3$). ^{13}C NMR (δ, $CDCl_3$): 142.05 (C=); 126.84 (HC=); 83.68 (C≡); 78.01, 72.00 (2 OCH_2); 71.03 (HC≡); 42.97, 39.85 (2 CH); 33.65 (C); 33.14, 32.26, 23.15 (3 CH_2); 25.09, 19.74 (2 CH_3). MS (ESI^+) m/z: 227.1406 $(M+Na)^+$.

Spectroscopic data for the *syn*-isomer: ^1H NMR (δ, $CDCl_3$): 2.06 (d, 1H, $^4J_{HH}$=2.41 Hz, HC≡). MS (ESI^+) m/z: 227.1406 $(M+Na)^+$.



12 **13**

Synthesis of compound 12 and complex 13 and. A mixture of [Ru]Cl (230 mg, 0.32 mmol), **2a** (62 mg, 0.32 mmol), and KPF_6 (77 mg, 0.42 mmol), in MeOH (30 mL) was stirred at 50°C for one day. After that, the solvent of the solution was removed under reduced pressure and then 20mL of CH_2Cl_2 was added. The solution was filtered through a bed of Celite to remove the insoluble salts, and the pad was eluted with CH_2Cl_2 until the eluent was colorless, then the solvent of the filtrate were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by re-precipitation by a 50 mL of stirred diethyl ether. Precipitates thus formed were collected in a glass frit and dried under vacuum. The final product was obtained as a deep red powder identified as **13** (167 mg, 60% yields). The filtrate was evaporated to dryness under vacuum and the crude product purified by chromatography (silica gel,

hexanes/EtOAc = 10/1) to afford **12** (20 mg, 30% yields).

Spectroscopic data of **13**:

The ratio of *anti*- and *syn*-isomers is 1:0.3.

Spectroscopic data for the *anti*-isomer: ^{1}H NMR (δ, $CDCl_3$): 6.89-7.49 (m, 40H, Ph); 6.73 (s, 1H, HC(C)=); 4.86 (s, 5H, Cp); 4.41, 2.27 (2d, 2H, $^{2}J_{HH}$=16.49 Hz, CH_2); 4.01 (dd, 1H, $^{2}J_{HH}$=10.91 Hz, $^{3}J_{HH}$=4.42 Hz, OCH_2); 2.72 (t, 1H, $^{2}J_{HH}$=10.91 Hz, OCH_2); 3.43, 2.97 (2d, 2H, $^{2}J_{HH}$=11.28 Hz, OCH_2); 1.71 (br, 1H, CH); 1.34 (t, 1H, $^{3}J_{HH}$= 11.12 Hz, CH_2); 0.99, 0.91, 0.81 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 317.61 (t, $^{2}J_{CP}$=9.66 Hz, Cα); 151.48 (HC=); 148.19 (C=); 128.20-135.84 (Ph); 94.54 (Cp); 79.30 (OCH_2); 69.04 (OCH_2); 59.66 (CH_2); 48.44 (CH); 41.11 (CH); 32.92 (C); 23.32, 20.62, 18.90 (3 CH_3). ^{31}P NMR (δ, $CDCl_3$): 45.26, 45.02 (2d, $^{2}J_{PP}$=29.05 Hz, PPh_3). MS (ESI^+) m/z: 869.2615 $(M)^+$.

Spectroscopic data for the *syn*-isomer: ^{1}H NMR (δ, $CDCl_3$): 6.89-7.49 (m, 40H, Ph, HC(C)=); 4.86 (s, 5H, Cp); 4.17, 2.80 (2d, 2H, $^{2}J_{PP}$=18.58 Hz, $^{3}J_{PP}$=3.26 Hz, CH_2); 3.61 (2d, 1H, $^{2}J_{HH}$=11.06 Hz, $^{3}J_{HH}$=4.81 Hz, OCH_2); 3.03 (t, 1H, $^{2}J_{HH}$=11.18 Hz, OCH_2); 3.43, 3.24 (2d, 2H, $^{2}J_{HH}$=12.51 Hz, OCH_2); 2.34 (m, 1H, CH); 1.71 (br, 1H, CH); 1.07, 0.95, 0.87 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 316.67 (t, $^{2}J_{CP}$=9.66 Hz, Cα); 151.48 (HC=); 148.36 (C=); 128.20-135.84 (Ph); 94.78 (Cp); 72.44 (OCH_2); 63.19 (OCH_2); 54.57 (CH_2); 42.04 (CH); 39.54 (CH); 31.33 (C); 26.16, 23.56, 23.05 (3 CH_3). ^{31}P NMR

(δ, $CDCl_3$): 46.63, 44.56 (2d, $^2J_{PP}$=29.05 Hz, 2 PPh_3). MS (ESI^+) m/z: 869.2615 $(M)^+$.

Spectroscopic data for the major diastereomer 12: ^1H NMR (δ, $CDCl_3$): 5.62 (m, 2H, 2 HC=); 3.86 (dd, 1H, $^2J_{HH}$=11.39 Hz, $^3J_{HH}$=4.64Hz, OCH_2); 3.20 (s, 3H, OCH_3); 3.15-3.04 (m, 3H, 2 OCH_2); 2.32 (m, 1H, CH); 1.97 (m, 2H, CH_2); 1.93 (m, 1H, CH); 1.12, 1.10, 0.89 (s, 9H, 3 CH_3). ^{13}C NMR (δ, $CDCl_3$): 126.55, 124.76 (2 CH=); 74.88 (C); 74.01, 65.33 (2 OCH_2); 48.10 (OCH_3); 43.45, 36.76 (2 CH); 34.98 (CH_2); 33.30 (C); 26.22, 23.95, 21.39 (3 CH_3). MS (ESI^+) m/z: 223.1507 $(M+Na)^+$.

References：

1. (a) Bruce, M. I. *Chem. Rev*. **1991**, *91*, 197-257. (b) Bruneau, C.; Dixneuf P. H. *Acc Chem Res*. **1999**, *32*, 311-323. (c) Cadierno, V.; Diex, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *Coord. Chem. Rev*. **1999**, *193-195*, 147-205.
2. King, R. B.; Saran, M. S. *J. Chem. Soc. Chem. Commum*. **1972**, *19*, 1053-1072.
3. (a) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc*. **1994**, *116*, 8105-8111. (b) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc*. **1997**, *119*, 360-366. (c) Jiménez Tenorio, M. A.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1997**, *16*, 5528-5535. (d) Antonova, A. B.; Koloboba, N. E. ; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Orgaomet. Chem*. 1997, *137*, 55-67.
4. (a) Alonso , F.; Beleskaya, I. P.; Yus, M. *Chem. Rev*. **2004**, *104*, 3079-3160. (b) katayama, H.; Ozawa, F. *Coord. Chem. Rev*. **2004**, *248*, 1703-1715. (c) Bruneau, C.; Dixneuf P. H. *Angew. Chem. Int. Ed*. **2006**, *45*, 2176-2203.
5. (a) Rigaut, S.; Touchard, D; Dixneuf, P. *Coord. Chem. Rev*. **2004**, *248*, 1585-1601. (b) Bruce, M. I. ; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59-128. (c) Barrett, A. G. M.; Mortier, J.; Sabat, M.; Sturgess, M.A. *Organometallics* **1988**, *7*, 2553 - 2561.
6. Winter, R. F.; Záliš, S. *Coord. Chem. Rev*. **2004**, *248*, 1565-1583.
7. (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granada, S.; Pérex-Carreno, E. *Organometallics* **1996**, *15*, 2137-2147. (b) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826-5835. (c) Auger, N.; Touchard, D.; Rigaut, S.; Halet, J.; Saillard, J. *Organometallics* **2003**, *22*, 1638-1644.
8. Selegue, J. P. *Organometallics* **1982**, *1*, 217-218.

9. (a) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M.; Oñate, E.; *Organometallics* **2008**, *27*, 795-798. (b) Ojo, W. S.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2006**, *25*, 5503-5505. (c) Szesni, N.; Drexler, M.; Maurer, J.; Winter, R. F.; Montigny, F.; Lapinte, C.; Steffens, S.; Heck, J.; Weibert, B.; Fisher, H. *Organometallics* **2006**, *25*, 5774-5787.
10. (a) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed*. **2007**, *46*, 3410-3449. (b) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed*. **2006**, *45*, 7896-7936. (c) Nakamura, I.; Yamamoto, Y. *Chem. Rev*. **2004**, *104*, 2127-2198. (d) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev*. **2008**, *108*, 3351-3378. (e) Patil, N. T.; Yamamoto, Y. *Chem. Rev*. **2008**, *108*, 3395-3442.
11. (a) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127-2198. (b) Deiters, A.; Martin, S. F. *Chem. Rev.* **2004**, *104*, 2199-2238. (c) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. *Chem. Rev.* **2004**, *104*, 2239-2258. (d) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644-4680. (e) D'Souza, D. M.; Müller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095-1108. (f) Mihovilovic, M. D.; Stanetty, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 3612-3645.
12. (a) Cichewicz, R. H.; Kenyon, V. A.; Whitman, S.; Morales, N. M.; Arguello, J. F.; Holman, T. R.; Crews, P. *J. Am. Chem. Soc.* **2004**, *126*, 14910–14920. (b) Maloney, D. J.; Deng, J. Z.; Starck, S. R.; Gao, Z.; Hecht, S. M. *J. Am. Chem. Soc.* **2005**, *127*, 4140–4141.
13. (a) Tafazoli, S.; Wright, J. S.; O'Brien, P. J. *Chem. Res. Toxicol.* **2005,** *18*, 1567–1574. (b) Tulio, A. Z.; JR., Reese, R. N.; Wyzgoski, F. J.; Rinaldi, P. L.; Fu, R.; Cheerens, J. C.; Miller, A. R. *J. Agric. Food Chem.* **2008**, *56*, 1880–1888.
14. (a) Leopoldini, M.; Russo, N.; Toscano, M. *J. Agric. Food Chem.* **2007,** *55*, 7944–7949. (b) Ott, D.; Floersheim, P.; Inderbitzin, W.; Stoehr, N.; Francotte, E.;

Lecis, G.; Richert, P.; Rihs, G.; Flor, P. J.; Kuhn, R.; Gasparini, F. *J. Med. Chem.* **2000,** *43,* 4428–4436. (c) Zhao, Q.; Han, F.; Romero, D. L. *J. Org. Chem.* **2002,** *67,* 3317–3322. (d) Asolkar, R. N.; Kamat, V. P.; Wagner-Dobler, I.; Laatsch, H. *J. Nat. Prod.* **2002,** *65,* 1664–1666.

15. Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004,** *104,* 2127-2198.
16. (a) Datta, S.; Odedra, A.; Liu, R. S. *J. Am. Chem. Soc.* **2005**, *127*, 11606-11607. (b) Odedra, A.; Datta, S.; Liu, R. S. *J. Org. Chem.* **2007**, *72*, 3289-3292. (c) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 2534-2537. (d) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178-6179. (e) Lin, M. Y.; Das, A.; Liu, R. –S. *J. Am. Chem. Soc.* **2006**, *128*, 9340-9341. (f) Jiménez-Núñez, E.; Claverie, C. K.; Bour, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 7892-7895. (g) Ma, H. W.; Lin, Y. C.; Huang, S. L. *Org. Lett.* **2012**, *14*, 3846-3849.
17. (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49-92. (b) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813-834. (c) Geis, O.; Schmalz, H. G. *Angew. Chem. Int. Ed.* **1998**, *37*, 911-914. (d) Fruhauf, H. W. *Chem. Rev.* **1997**, *97*, 523-596.
18. (a) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. *J. Chem. Rev.* **1996**, *96*, 635-662. (b) Trost, B. M.; Krische, M. *J. Synlett* **1998**, 1-16. (c) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704-3709. (d) Michelet, V.; Toullec, P. Y.; Genêt, J. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268-4315. (e) Zhang, Z.; Zhu, G.; Tong, X.; Wang, F.; Xie, X.; Wang, J.; Jiang, L. *Curr. Chem.* **2006**, *10*, 1457-1478. (f) Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núñez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677-1693.

19. (a) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680–11683. (b) Shen, H.-C.; Pal, S.; Lian, J.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 15762–15763. (c) Madhushaw, R. J.; Lin, M.-Y.; Sohel, S. M. A.; Liu, R.-S. *J. Am. Chem. Soc*., **2004**, *126*, 6895–6899. (d) Le Paih, J.; Derien, S.; Demerseman, B.; Bruneau, C.; Dixneuf, P. H.; Toupet, L.; Dazinger, G.; Kirchner, K. *Chem. Eur. J.* **2005**, *11*, 1312–1324. (e) Inada, Y.; Yoshikawa, M.; Milton, D. M.; Nishibayashi, Y.;Sakae Uemura, S. *Eur. J. Org. Chem*. **2006**, *4*, 881–890.

20. (a) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2004**, *126*, 16066-16072. (b) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 10498-10499. (c) *New Frontiers in Asymmetric Catalysis*; Mikami, K., Lautens, M., Eds.; Wiley-Interscience: New Jersey, 2007. (d) Pohlhaus, P. D.; Johnson, J. S.; *J. Am. Chem. Soc*., **2005**, *127*, 16014–16015. (e) Liu, Z.; Wasmuth, A. S.; Nelson, S. G.; *J. Am. Chem. Soc*., **2005**, *128*, 10352–10353. (f) Bonne,D.; Constantieux, T.; Coquerel Y.; Rodriguez, J. *Org. Biomol. Chem*., **2012**, *10*, 3969–3973.

21. Okamoto, R.; Okazaki, E.; Noguchi, K.; Tanaka, K. *Org. Lett*. **2011**, *13*, 4894-4897.

22. Ting, C.-M.; Wang, C.-D.; Chaudhuri, R.; Liu, R.-S. *Org. Lett*., **2011**, *13*, 1702-1705.

23. (a) Jimenez, J. I.; Huber, U.; Moore, R. E.; Patterson, G. M. L. J. *Nat. Prod*. **1999**, *62*, 569–572. (b) Bhat, V.; Allan, K. M.; Rawal, V. H. *J. Am. Chem. Soc*. **2011**, *133*, 5798–5801. (c) Huters, A. D.; Quasdorf, K. W.; Styduhar, E. D.; Garg, N. K. *J. Am. Chem. Soc*. **2011**, *133*, 15797–15799.

24. Jackson, S. R.; Johnson, M. G.; Mikami, M.; Shiokawa, S.; Carreira, E. M. *Angew. Chem., Int. Ed*. **2001**, *40*, 2694–2697.

25. Demirci-Gültekin, D.; Günbaś, D. D.; Taśkesenligil, Y.; Balci, M. *Tetrahedron*

2007, *63*, 8151–8156.

26. (a) Warner, P. M.; Palmer, R. F.; Lu, S.-L. *J. Am. Chem. Soc*. **1977**, *99*, 3773–3778. (b) Xing, S.; Pan, W.; Liu, C.; Ren, J.; Wang, Z. *Angew. Chem., Int. Ed*. **2010,** *49*, 3215–3218.
27. (a) Matsuda, T.; Makino, M.; Murakami. M. *Angew. Chem., Int. Ed*. **2005,** *44*, 4608-4611. (b) Evans, P. A.; Lawler, M. J. *Angew. Chem., Int. Ed*. **2006,** *45*, 4970-4972
28. (a) Chung, C. –P.; Chen, C. –C.; Lin, Y. –C.; Liu, Y. –H.; Wamg, Y. *J. Am. Chem. Soc.* **2009**, *131*, 18366-18375. (b) Ma, H.-W.; Lin, Y.-C.; Huang, S.-L. *Org. Lett*. **2012**, *14*, 3846-3849.
29. (a) Yen, Y.-S.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y *Organometallics*, 2007, 26, 1250-1255. (b) Borguet, Y; Sauvage, X.; Zaragoza, G.; Demonceau, A; Delaude, L. *Organometallics* **2011**, *30*, 2730-2738.
30. Cadierno, V; Conejero, S; Gamasa, M. P.; Gimeno, J. *J. Organometallics* **2002**, *21*, 3837-3840. (b) Cadierno, V.; Gamasa, M.P.; Gimeno, J. *Organometallics* **1999**, *18*, 2821-2832.
31. (a) Diaz, D. D.; Betancourt, J. M.; Crisostomo, F. R. P.; Martin, T.; Martin, V. S. *Tetrahedron* **2002**, *58*, 1913–1919. (b) Kira, K.; Isobe, M. *Tetrahedron Lett*. **2000**, *41*, 5951–5955.
32. Chang, S.-H.; Tsai, W.-R.; Lin, Y.-C.; Huang, S.-L.; Liu, Y.-H.; Wang, Y. *Organometallics*, 2009, 28, 1863–1871.
33. (a) Snyder, N. L.; Haines, H. M.; Peczuh, M. W. *Tetrahedron* **2006**, *62*, 9301–9320. (b) Venkateswarlu, Y.; Reddy, M. V. R.; Ramesh, P.; Rao, J. V. *Indian J. Chem., Sect. B* **1999**, *38*, 254–256. (c) Edrada, R. A.; Proksch, P.; Wray, V.; Witte, L.; Ofwegen, L. *J. Nat. Prod.* **1998**, *61*, 358–361.

34. (a) Stephens, P. J.; McCann, D. M.; Devlin, F. J.; Flood, T. C.; Butkus, E.; Stončius, S.; Cheeseman, J. R. *J. Org. Chem.* **2005**, *70*, 3903-3913. (b) Butkus, E.; Stončius, S. *J. Chem. Soc*., *Perkin Trans. 1*, **2001**, 1885–1888. (c) Stončius, S.; Berg, U.; Butkus, E. *Tetrahedron: Asymmetry* **2004**, *15*, 2405–2413.
35. Gary A. Molander, G. A.; Alija, C. A. *J. Org. Chem.* **1998**, *63*, 4366-4373.
36. Karplus, M. *J. Chem. Phys*. **1959**, *30*, 11-15. (b) Karplus, M. *J. Am. Chem. Soc.*, **1963**, *18*, 2870–2871 (c) Reich, H. J. *U.Wisc. Chem 2010.*
37. (a) Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920–1923. (b) Dubois, J. E.; Fellman, P. *Tetrahedron Lett*. **1975**, 1225-1228. (c) Heathcock, C. H.; Buse, C. T.; Kleschnick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem*. **1980**, *45*, 1066-1081
38. Díaz, D.; Martín, V. S. *Org. Lett.* **2000**, *3*, 335-337.
39. Cheng, C. W.; Kuo, Y. C.; Chang, S. H.; Lin, Y. C. *J. Am. Chem. Soc*. **2007**, *129*, 14974-14980.
40. Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485.

Appendix I

X-Ray Crystallographic Data

An ORTEP drawing and crystal data of **5a**

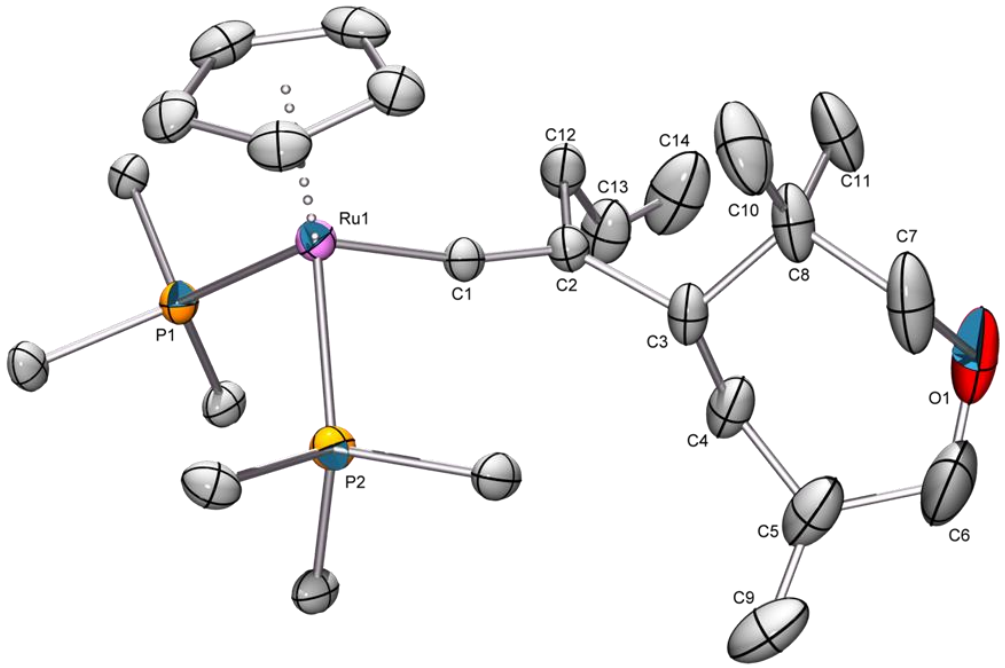


Table 1. Crystal data and structure refinement for ic15954.

Identification code	ic15954
Empirical formula	$C_{55}H_{55}F_6OP_3Ru$
Formula weight	1039.97
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.8600(3) Å alpha = 90° b = 18.1133(4) Å beta = 99.838(2)° c = 21.1609(5) Å gamma = 90°
Volume, Z	4856.67(19) $Å^3$, 4
Density (calculated)	1.422 Mg/m^3
Absorption coefficient	0.484 mm^{-1}
F(000)	2144
Crystal size	0.20 x 0.15 x 0.10 mm
Θ range for data collection	2.84 to 27.50°
Limiting indices	$-16 \le h \le 15$, $-23 \le k \le 22$, $-27 \le l \le 23$
Reflections collected	37353
Independent reflections	10981 (R_{int} = 0.0367)
Completeness to Θ = 27.50°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.98693
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10981 / 0 / 595
Goodness-of-fit on F^2	1.042
Final R indices [I>2σ(I)]	R1 = 0.0496, wR2 = 0.1142
R indices (all data)	R1 = 0.0771, wR2 = 0.1336
Largest diff. peak and hole	0.643 and -0.302 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for icl5954. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2623(1)	3533(1)	627(1)	39(1)
P(1)	959(1)	3015(1)	231(1)	42(1)
P(2)	2936(1)	2869(1)	1594(1)	44(1)
O(1)	7238(3)	1528(4)	193(3)	139(2)
C(1)	3398(2)	2892(2)	198(2)	43(1)
C(2)	4018(3)	2570(2)	-148(2)	51(1)
C(3)	5036(3)	2200(2)	185(2)	62(1)
C(4)	5027(4)	1367(3)	41(2)	82(1)
C(5)	5736(5)	903(4)	524(3)	107(2)
C(6)	6879(6)	884(6)	473(5)	175(4)
C(7)	7016(4)	2209(4)	478(3)	125(2)
C(8)	6060(3)	2617(3)	95(2)	83(1)
C(9)	5341(6)	477(3)	961(3)	131(2)
C(10)	6036(4)	3384(3)	377(3)	119(2)
C(11)	6225(4)	2668(4)	-597(3)	109(2)
C(12)	3672(3)	2589(2)	-879(2)	66(1)
C(13)	3614(4)	1849(3)	-1216(2)	83(1)
C(14)	4026(6)	1680(4)	-1685(3)	135(3)
C(15)	3115(3)	4577(2)	1194(2)	60(1)
C(16)	3797(3)	4473(2)	754(2)	64(1)
C(17)	3183(4)	4518(2)	134(2)	71(1)
C(18)	2144(4)	4636(2)	205(2)	70(1)
C(19)	2087(3)	4682(2)	863(2)	65(1)
C(20)	745(3)	2046(2)	-18(2)	50(1)
C(21)	1455(3)	1720(2)	-349(2)	74(1)
C(22)	1249(4)	1031(3)	-631(3)	93(2)
C(23)	357(4)	673(3)	-589(3)	86(2)
C(24)	-357(4)	976(2)	-257(3)	88(2)
C(25)	-182(3)	1670(2)	24(2)	67(1)
C(26)	280(3)	3422(2)	-530(2)	45(1)
C(27)	848(3)	3698(2)	-970(2)	56(1)
C(28)	325(4)	3959(2)	-1560(2)	66(1)
C(29)	-756(3)	3919(2)	-1707(2)	66(1)
C(30)	-1318(3)	3622(2)	-1279(2)	60(1)
C(31)	-805(3)	3376(2)	-693(2)	53(1)
C(32)	18(2)	3186(2)	772(2)	48(1)
C(33)	-466(3)	3876(2)	771(2)	55(1)
C(34)	-1124(3)	4032(3)	1204(2)	66(1)
C(35)	-1299(3)	3514(3)	1643(2)	73(1)
C(36)	-813(3)	2842(3)	1664(2)	72(1)
C(37)	-153(3)	2675(2)	1230(2)	58(1)
C(38)	4346(3)	2713(2)	1886(2)	53(1)
C(39)	4983(3)	3307(3)	2098(3)	86(2)
C(40)	6046(4)	3207(3)	2347(3)	97(2)
C(41)	6478(3)	2520(3)	2371(2)	84(1)
C(42)	5868(3)	1931(3)	2142(2)	75(1)
C(43)	4802(3)	2030(2)	1909(2)	62(1)
C(44)	2371(3)	1945(2)	1634(2)	49(1)

C(45)	2485(3)	1441(2)	1165(2)	63(1)
C(46)	2096(4)	728(2)	1192(3)	83(1)
C(47)	1579(4)	533(3)	1683(3)	88(2)
C(48)	1446(3)	1030(3)	2142(2)	78(1)
C(49)	1849(3)	1743(2)	2128(2)	60(1)
C(50)	2528(3)	3335(2)	2284(2)	53(1)
C(51)	3049(4)	3197(2)	2905(2)	70(1)
C(52)	2657(5)	3500(3)	3417(2)	85(2)
C(53)	1786(5)	3938(3)	3329(2)	89(2)
C(54)	1271(4)	4073(3)	2724(2)	76(1)
C(55)	1634(3)	3776(2)	2202(2)	59(1)
P(3)	3563(1)	4519(1)	7938(1)	91(1)
F(1)	2604(4)	4897(3)	7547(3)	189(2)
F(2)	4510(4)	4184(3)	8375(4)	246(3)
F(3)	4359(4)	4931(2)	7606(3)	198(2)
F(4)	3590(4)	5206(3)	8386(3)	183(2)
F(5)	2817(3)	4108(3)	8314(3)	187(2)
F(6)	3530(6)	3877(3)	7505(4)	258(4)

Table 3. Bond lengths [Å] and angles [°] for ic15954.

Ru(1)-C(1)	1.864(3)	Ru(1)-C(18)	2.233(4)
Ru(1)-C(17)	2.246(4)	Ru(1)-C(16)	2.262(4)
Ru(1)-C(15)	2.272(3)	Ru(1)-C(19)	2.274(4)
Ru(1)-P(2)	2.3487(9)	Ru(1)-P(1)	2.3557(8)
P(1)-C(32)	1.831(3)	P(1)-C(20)	1.838(3)
P(1)-C(26)	1.848(3)	P(2)-C(44)	1.831(3)
P(2)-C(38)	1.835(3)	P(2)-C(50)	1.840(4)
O(1)-C(6)	1.420(9)	O(1)-C(7)	1.424(8)
C(1)-C(2)	1.308(5)	C(2)-C(3)	1.530(5)
C(2)-C(12)	1.536(5)	C(3)-C(4)	1.539(6)
C(3)-C(8)	1.559(6)	C(4)-C(5)	1.504(7)
C(5)-C(9)	1.367(9)	C(5)-C(6)	1.493(9)
C(7)-C(8)	1.543(7)	C(8)-C(10)	1.514(7)
C(8)-C(11)	1.516(7)	C(12)-C(13)	1.513(6)
C(13)-C(14)	1.241(7)	C(15)-C(16)	1.398(6)
C(15)-C(19)	1.399(6)	C(16)-C(17)	1.413(6)
C(17)-C(18)	1.386(6)	C(18)-C(19)	1.409(6)
C(20)-C(21)	1.376(5)	C(20)-C(25)	1.389(5)
C(21)-C(22)	1.390(6)	C(22)-C(23)	1.333(7)
C(23)-C(24)	1.363(7)	C(24)-C(25)	1.392(6)
C(26)-C(27)	1.373(5)	C(26)-C(31)	1.382(5)
C(27)-C(28)	1.395(5)	C(28)-C(29)	1.374(6)
C(29)-C(30)	1.364(6)	C(30)-C(31)	1.375(5)
C(32)-C(37)	1.384(5)	C(32)-C(33)	1.397(5)
C(33)-C(34)	1.378(5)	C(34)-C(35)	1.366(6)
C(35)-C(36)	1.367(6)	C(36)-C(37)	1.386(6)
C(38)-C(43)	1.366(5)	C(38)-C(39)	1.381(5)
C(39)-C(40)	1.390(6)	C(40)-C(41)	1.360(7)
C(41)-C(42)	1.364(6)	C(42)-C(43)	1.387(5)
C(44)-C(45)	1.375(5)	C(44)-C(49)	1.384(5)
C(45)-C(46)	1.390(6)	C(46)-C(47)	1.371(7)
C(47)-C(48)	1.356(7)	C(48)-C(49)	1.394(6)
C(50)-C(55)	1.386(5)	C(50)-C(51)	1.391(5)
C(51)-C(52)	1.385(7)	C(52)-C(53)	1.360(7)
C(53)-C(54)	1.360(7)	C(54)-C(55)	1.380(5)
P(3)-F(6)	1.477(5)	P(3)-F(2)	1.524(5)
P(3)-F(1)	1.525(5)	P(3)-F(3)	1.531(4)
P(3)-F(5)	1.539(4)	P(3)-F(4)	1.561(4)

C(1)-Ru(1)-C(18)	119.81(16)	C(1)-Ru(1)-C(17)	91.65(15)
C(18)-Ru(1)-C(17)	36.06(16)	C(1)-Ru(1)-C(16)	97.21(14)
C(18)-Ru(1)-C(16)	60.43(16)	C(17)-Ru(1)-C(16)	36.54(15)
C(1)-Ru(1)-C(15)	130.73(14)	C(18)-Ru(1)-C(15)	59.93(15)
C(17)-Ru(1)-C(15)	60.10(15)	C(16)-Ru(1)-C(15)	35.91(14)
C(1)-Ru(1)-C(19)	152.16(15)	C(18)-Ru(1)-C(19)	36.42(15)
C(17)-Ru(1)-C(19)	60.53(16)	C(16)-Ru(1)-C(19)	60.40(15)
C(15)-Ru(1)-C(19)	35.86(14)	C(1)-Ru(1)-P(2)	94.54(10)
C(18)-Ru(1)-P(2)	143.26(12)	C(17)-Ru(1)-P(2)	142.23(12)
C(16)-Ru(1)-P(2)	105.69(11)	C(15)-Ru(1)-P(2)	88.56(10)
C(19)-Ru(1)-P(2)	106.87(12)	C(1)-Ru(1)-P(1)	96.14(10)
C(18)-Ru(1)-P(1)	92.44(12)	C(17)-Ru(1)-P(1)	119.67(13)
C(16)-Ru(1)-P(1)	152.86(11)	C(15)-Ru(1)-P(1)	132.37(11)
C(19)-Ru(1)-P(1)	98.74(11)	P(2)-Ru(1)-P(1)	96.66(3)
C(32)-P(1)-C(20)	104.95(16)	C(32)-P(1)-C(26)	102.29(15)
C(20)-P(1)-C(26)	96.09(15)	C(32)-P(1)-Ru(1)	111.56(11)

C(20)-P(1)-Ru(1)	124.38(11)	C(26)-P(1)-Ru(1)	114.59(11)
C(44)-P(2)-C(38)	102.74(16)	C(44)-P(2)-C(50)	102.32(16)
C(38)-P(2)-C(50)	101.71(17)	C(44)-P(2)-Ru(1)	119.86(12)
C(38)-P(2)-Ru(1)	112.62(11)	C(50)-P(2)-Ru(1)	115.29(12)
C(6)-O(1)-C(7)	115.5(6)	C(2)-C(1)-Ru(1)	168.0(3)
C(1)-C(2)-C(3)	119.5(3)	C(1)-C(2)-C(12)	117.0(3)
C(3)-C(2)-C(12)	123.5(3)	C(2)-C(3)-C(4)	111.1(3)
C(2)-C(3)-C(8)	113.9(4)	C(4)-C(3)-C(8)	115.4(3)
C(5)-C(4)-C(3)	115.5(4)	C(9)-C(5)-C(6)	121.3(6)
C(9)-C(5)-C(4)	121.5(6)	C(6)-C(5)-C(4)	117.0(6)
O(1)-C(6)-C(5)	113.9(6)	O(1)-C(7)-C(8)	113.1(5)
C(10)-C(8)-C(11)	110.0(5)	C(10)-C(8)-C(7)	107.5(5)
C(11)-C(8)-C(7)	107.9(4)	C(10)-C(8)-C(3)	108.8(4)
C(11)-C(8)-C(3)	114.1(4)	C(7)-C(8)-C(3)	108.5(5)
C(13)-C(12)-C(2)	115.9(3)	C(14)-C(13)-C(12)	127.0(6)
C(16)-C(15)-C(19)	109.3(4)	C(16)-C(15)-Ru(1)	71.6(2)
C(19)-C(15)-Ru(1)	72.2(2)	C(15)-C(16)-C(17)	107.2(4)
C(15)-C(16)-Ru(1)	72.4(2)	C(17)-C(16)-Ru(1)	71.1(2)
C(18)-C(17)-C(16)	107.8(4)	C(18)-C(17)-Ru(1)	71.4(2)
C(16)-C(17)-Ru(1)	72.3(2)	C(17)-C(18)-C(19)	109.2(4)
C(17)-C(18)-Ru(1)	72.5(2)	C(19)-C(18)-Ru(1)	73.4(2)
C(15)-C(19)-C(18)	106.5(4)	C(15)-C(19)-Ru(1)	72.0(2)
C(18)-C(19)-Ru(1)	70.2(2)	C(21)-C(20)-C(25)	118.3(4)
C(21)-C(20)-P(1)	118.4(3)	C(25)-C(20)-P(1)	122.5(3)
C(20)-C(21)-C(22)	120.7(4)	C(23)-C(22)-C(21)	120.7(5)
C(22)-C(23)-C(24)	120.1(4)	C(23)-C(24)-C(25)	120.7(4)
C(20)-C(25)-C(24)	119.5(4)	C(27)-C(26)-C(31)	118.9(3)
C(27)-C(26)-P(1)	120.6(3)	C(31)-C(26)-P(1)	120.0(3)
C(26)-C(27)-C(28)	120.0(4)	C(29)-C(28)-C(27)	119.9(4)
C(30)-C(29)-C(28)	120.1(4)	C(29)-C(30)-C(31)	120.0(4)
C(30)-C(31)-C(26)	121.0(4)	C(37)-C(32)-C(33)	118.5(3)
C(37)-C(32)-P(1)	121.7(3)	C(33)-C(32)-P(1)	119.5(3)
C(34)-C(33)-C(32)	120.4(4)	C(35)-C(34)-C(33)	120.2(4)
C(36)-C(35)-C(34)	120.4(4)	C(35)-C(36)-C(37)	120.1(4)
C(32)-C(37)-C(36)	120.4(4)	C(43)-C(38)-C(39)	117.8(4)
C(43)-C(38)-P(2)	123.1(3)	C(39)-C(38)-P(2)	119.1(3)
C(38)-C(39)-C(40)	120.8(5)	C(41)-C(40)-C(39)	120.2(5)
C(40)-C(41)-C(42)	119.8(4)	C(41)-C(42)-C(43)	119.9(4)
C(38)-C(43)-C(42)	121.5(4)	C(45)-C(44)-C(49)	119.7(3)
C(45)-C(44)-P(2)	118.7(3)	C(49)-C(44)-P(2)	121.6(3)
C(44)-C(45)-C(46)	120.2(4)	C(47)-C(46)-C(45)	119.7(5)
C(48)-C(47)-C(46)	120.6(4)	C(47)-C(48)-C(49)	120.5(4)
C(44)-C(49)-C(48)	119.4(4)	C(55)-C(50)-C(51)	118.6(4)
C(55)-C(50)-P(2)	120.5(3)	C(51)-C(50)-P(2)	120.7(3)
C(52)-C(51)-C(50)	119.2(5)	C(53)-C(52)-C(51)	121.7(5)
C(52)-C(53)-C(54)	119.5(5)	C(53)-C(54)-C(55)	120.4(5)
C(54)-C(55)-C(50)	120.7(4)	F(6)-P(3)-F(2)	89.9(4)
F(6)-P(3)-F(1)	94.7(4)	F(2)-P(3)-F(1)	175.2(4)
F(6)-P(3)-F(3)	92.9(3)	F(2)-P(3)-F(3)	86.9(3)
F(1)-P(3)-F(3)	94.3(3)	F(6)-P(3)-F(5)	89.2(3)
F(2)-P(3)-F(5)	89.9(3)	F(1)-P(3)-F(5)	88.9(3)
F(3)-P(3)-F(5)	176.1(4)	F(6)-P(3)-F(4)	179.1(4)
F(2)-P(3)-F(4)	90.9(4)	F(1)-P(3)-F(4)	84.5(3)
F(3)-P(3)-F(4)	86.7(3)	F(5)-P(3)-F(4)	91.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic15954.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + $2hka^*b^*U_{12}$]

	U11	U22	U33	U23	U13	U12
Ru(1)	35(1)	37(1)	45(1)	1(1)	6(1)	-1(1)
P(1)	33(1)	45(1)	47(1)	3(1)	5(1)	1(1)
P(2)	37(1)	43(1)	50(1)	5(1)	2(1)	-5(1)
O(1)	73(3)	202(6)	140(4)	-24(4)	18(3)	60(3)
C(1)	34(2)	47(2)	47(2)	4(1)	2(1)	-2(1)
C(2)	41(2)	53(2)	58(2)	1(2)	11(2)	1(2)
C(3)	40(2)	83(3)	61(2)	-10(2)	6(2)	12(2)
C(4)	67(3)	90(3)	86(3)	1(3)	7(2)	29(2)
C(5)	107(5)	107(4)	102(4)	2(4)	2(3)	52(4)
C(6)	106(6)	223(10)	198(9)	64(8)	27(6)	93(7)
C(7)	47(3)	216(8)	107(4)	-45(5)	4(3)	13(4)
C(8)	40(2)	122(4)	89(3)	-30(3)	12(2)	0(2)
C(9)	165(7)	80(4)	137(6)	20(4)	-1(5)	45(4)
C(10)	63(3)	135(5)	163(6)	-57(4)	32(4)	-33(3)
C(11)	58(3)	168(6)	110(4)	-15(4)	38(3)	-19(3)
C(12)	56(2)	85(3)	58(2)	5(2)	12(2)	15(2)
C(13)	80(3)	107(4)	60(3)	-13(3)	9(2)	22(3)
C(14)	140(6)	176(7)	79(4)	-25(4)	-9(4)	67(5)
C(15)	75(3)	41(2)	62(2)	-6(2)	7(2)	-11(2)
C(16)	59(2)	46(2)	87(3)	-1(2)	13(2)	-15(2)
C(17)	102(4)	43(2)	72(3)	4(2)	29(3)	-18(2)
C(18)	84(3)	40(2)	77(3)	9(2)	-9(2)	3(2)
C(19)	68(3)	35(2)	93(3)	-5(2)	17(2)	3(2)
C(20)	37(2)	47(2)	63(2)	2(2)	-3(2)	-3(1)
C(21)	63(3)	64(3)	95(3)	-20(2)	18(2)	-14(2)
C(22)	92(4)	67(3)	122(4)	-37(3)	23(3)	-11(3)
C(23)	71(3)	56(3)	119(4)	-24(3)	-15(3)	-9(2)
C(24)	64(3)	58(3)	130(4)	3(3)	-14(3)	-23(2)
C(25)	45(2)	59(2)	94(3)	5(2)	-1(2)	-5(2)
C(26)	42(2)	46(2)	47(2)	-1(1)	4(1)	5(1)
C(27)	49(2)	65(2)	53(2)	-2(2)	9(2)	-1(2)
C(28)	77(3)	74(3)	48(2)	1(2)	11(2)	-6(2)
C(29)	75(3)	71(3)	45(2)	-3(2)	-5(2)	6(2)
C(30)	50(2)	66(2)	58(2)	-7(2)	-5(2)	5(2)
C(31)	46(2)	60(2)	51(2)	3(2)	1(2)	1(2)
C(32)	29(2)	64(2)	48(2)	2(2)	3(1)	-2(1)
C(33)	48(2)	63(2)	53(2)	3(2)	9(2)	4(2)
C(34)	51(2)	82(3)	67(2)	-7(2)	10(2)	12(2)
C(35)	51(2)	117(4)	54(2)	0(2)	18(2)	3(2)
C(36)	50(2)	111(4)	54(2)	18(2)	8(2)	-8(2)
C(37)	38(2)	77(3)	57(2)	14(2)	2(2)	-2(2)
C(38)	40(2)	58(2)	57(2)	14(2)	-1(2)	-4(2)
C(39)	53(3)	71(3)	125(4)	21(3)	-13(3)	-16(2)
C(40)	50(3)	87(3)	141(5)	24(3)	-17(3)	-24(2)
C(41)	40(2)	111(4)	93(3)	32(3)	-8(2)	-7(2)
C(42)	52(2)	89(3)	83(3)	23(2)	3(2)	11(2)
C(43)	42(2)	72(3)	68(2)	14(2)	-4(2)	-3(2)
C(44)	35(2)	46(2)	61(2)	10(2)	-5(2)	-4(1)

C(45)	57(2)	50(2)	76(3)	-1(2)	-4(2)	-4(2)
C(46)	88(3)	51(2)	101(4)	-5(2)	-7(3)	-8(2)
C(47)	84(3)	53(3)	115(4)	14(3)	-14(3)	-26(2)
C(48)	59(3)	73(3)	98(3)	30(3)	-1(2)	-20(2)
C(49)	48(2)	61(2)	70(2)	18(2)	0(2)	-10(2)
C(50)	57(2)	53(2)	47(2)	1(2)	6(2)	-15(2)
C(51)	74(3)	76(3)	57(2)	2(2)	1(2)	-12(2)
C(52)	105(4)	102(4)	47(2)	-6(2)	7(2)	-34(3)
C(53)	105(4)	97(4)	72(3)	-20(3)	38(3)	-27(3)
C(54)	81(3)	80(3)	72(3)	-15(2)	30(2)	-14(2)
C(55)	54(2)	67(2)	55(2)	-6(2)	11(2)	-9(2)
P(3)	67(1)	77(1)	134(1)	-4(1)	28(1)	-19(1)
F(1)	161(4)	189(5)	198(5)	45(4)	-21(3)	26(4)
F(2)	102(3)	212(6)	396(9)	125(6)	-40(4)	-16(3)
F(3)	200(5)	112(3)	330(7)	-2(4)	182(5)	-21(3)
F(4)	181(5)	166(4)	215(5)	-70(4)	70(4)	-26(3)
F(5)	115(3)	190(4)	272(6)	96(4)	77(3)	-15(3)
F(6)	283(8)	155(4)	368(9)	-150(5)	149(7)	-79(5)

An OROTEP drawing and crystal data of *anti*-**10**

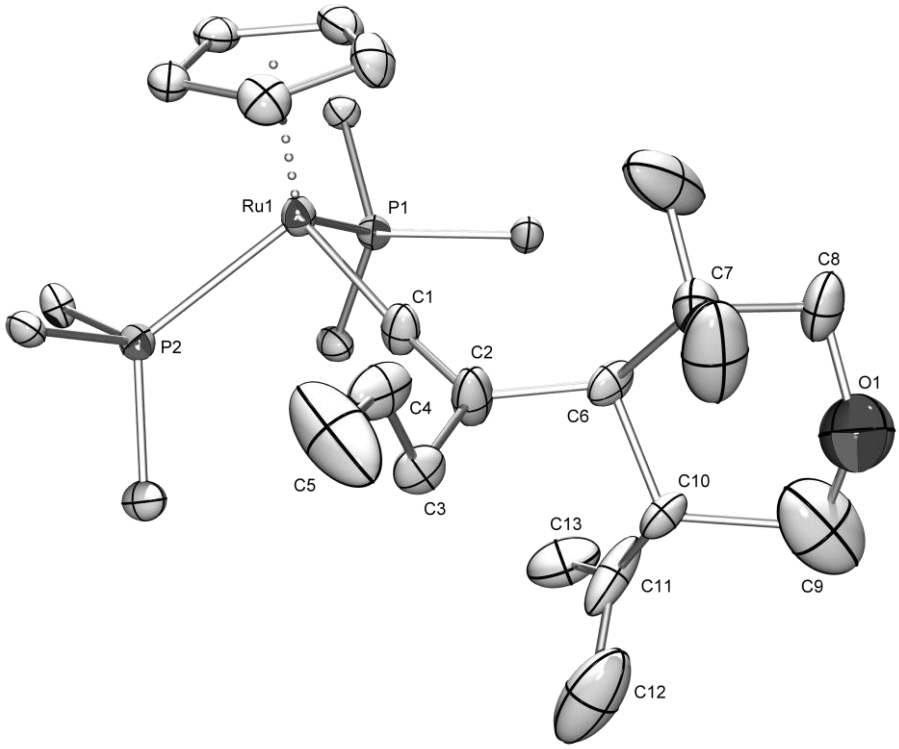


Table 1. Crystal data and structure refinement for ic16023.

Identification code	ic16023
Empirical formula	$C_{56}H_{57}F_6OP_3Ru$
Formula weight	1054.00
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 14.2112(4) Å alpha = 90°
	b = 17.5594(7) Å beta = 90°
	c = 19.6273(7) Å gamma = 90°
Volume, Z	4897.8(3) $Å^3$, 4
Density (calculated)	1.429 Mg/m^3
Absorption coefficient	0.481 mm^{-1}
F(000)	2176
Crystal size	0.25 x 0.20 x 0.15 mm
Θ range for data collection	2.73 to 27.50°
Limiting indices	$-18 \le h \le 14$, $-22 \le k \le 18$, $-19 \le l \le 25$
Reflections collected	24222
Independent reflections	10126 (R_{int} = 0.0378)
Completeness to Θ = 27.50°	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.86978
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10126 / 0 / 632
Goodness-of-fit on F^2	1.031
Final R indices [I>2σ(I)]	R1 = 0.0425, wR2 = 0.0983
R indices (all data)	R1 = 0.0503, wR2 = 0.1035
Absolute structure parameter	-0.06(3)
Largest diff. peak and hole	0.546 and -0.387 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic16023. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	6609(1)	4621(1)	463(1)	28(1)
P(1)	6797(1)	5926(1)	230(1)	28(1)
P(2)	6816(1)	4690(1)	1653(1)	28(1)
C(1)	5282(2)	4612(2)	470(2)	39(1)
C(2)	4386(3)	4469(3)	424(2)	54(1)
C(3)	3947(3)	3856(3)	883(2)	42(1)
C(4)	4213(3)	3055(3)	723(3)	57(1)
C(5)	3894(8)	2461(4)	1007(4)	123(4)
O(1)	2325(5)	5119(5)	-987(4)	118(2)
C(6)	3808(5)	4719(6)	-185(5)	37(2)
C(8)	3092(6)	4725(7)	-1324(5)	63(3)
C(9)	2175(6)	5677(5)	-497(4)	135(3)
C(10)	2891(5)	5108(5)	107(5)	39(2)
O(1')	2175(6)	5677(5)	-497(4)	135(3)
C(6')	3716(6)	5113(7)	40(6)	40(3)
C(8')	2622(7)	6208(7)	-92(7)	67(4)
C(9')	2325(5)	5119(5)	-987(4)	118(2)
C(10')	3049(7)	4662(7)	-404(6)	63(3)
C(7)	3507(4)	4128(3)	-798(2)	57(1)
C(11)	3048(3)	5695(3)	562(4)	75(2)
C(12)	2359(4)	5477(5)	1099(5)	121(3)
C(13)	3652(4)	6267(3)	742(3)	76(2)
C(14)	2873(5)	3481(5)	-687(4)	108(3)
C(15)	4339(4)	3958(5)	-1142(3)	106(3)
C(16)	6790(3)	3395(3)	133(2)	45(1)
C(17)	6695(3)	3858(2)	-457(2)	47(1)
C(18)	7445(3)	4372(2)	-472(2)	42(1)
C(19)	8043(3)	4218(2)	87(2)	36(1)
C(20)	7628(3)	3626(2)	458(2)	37(1)
C(21)	6009(2)	6278(2)	-439(2)	32(1)
C(22)	5787(3)	5807(3)	-984(2)	38(1)
C(23)	5259(3)	6079(3)	-1533(2)	42(1)
C(24)	4938(3)	6817(3)	-1534(2)	50(1)
C(25)	5143(4)	7286(3)	-989(2)	59(1)
C(26)	5681(3)	7021(3)	-440(2)	47(1)
C(27)	7961(2)	6140(2)	-132(2)	28(1)
C(28)	8071(3)	6453(2)	-773(2)	30(1)
C(29)	8965(3)	6574(2)	-1039(2)	37(1)
C(30)	9754(3)	6380(2)	-663(2)	38(1)
C(31)	9645(3)	6079(3)	-19(2)	41(1)
C(32)	8754(3)	5963(2)	242(2)	37(1)
C(33)	6682(3)	6641(2)	895(2)	33(1)
C(34)	7332(3)	7215(3)	1009(2)	46(1)
C(35)	7195(4)	7742(3)	1533(2)	55(1)
C(36)	6412(4)	7701(3)	1938(2)	55(1)
C(37)	5760(4)	7137(3)	1822(3)	57(1)
C(38)	5886(3)	6610(3)	1304(2)	44(1)
C(39)	7877(3)	5204(2)	1914(2)	31(1)

C(40)	8761(3)	4909(2)	1753(2)	36(1)
C(41)	9582(3)	5314(3)	1906(2)	45(1)
C(42)	9516(4)	6019(3)	2213(3)	59(1)
C(43)	8642(4)	6323(3)	2369(3)	60(1)
C(44)	7835(3)	5923(3)	2220(2)	46(1)
C(45)	6960(3)	3716(2)	1989(2)	30(1)
C(46)	6265(3)	3192(2)	1819(2)	35(1)
C(47)	6319(3)	2441(2)	2044(2)	39(1)
C(48)	7064(3)	2221(2)	2444(2)	42(1)
C(49)	7745(3)	2728(2)	2628(2)	39(1)
C(50)	7691(3)	3485(2)	2409(2)	33(1)
C(51)	5934(3)	5017(2)	2260(2)	36(1)
C(52)	4996(3)	5121(2)	2086(3)	46(1)
C(53)	4345(3)	5318(3)	2576(3)	60(1)
C(54)	4613(3)	5419(3)	3243(3)	59(1)
C(55)	5530(3)	5314(3)	3424(2)	56(1)
C(56)	6181(3)	5104(3)	2945(2)	53(1)
P(3)	646(1)	3327(1)	1141(1)	62(1)
F(1)	325(3)	4126(2)	814(2)	88(1)
F(2)	936(4)	2544(2)	1442(3)	131(2)
F(3)	1642(3)	3462(3)	866(4)	164(2)
F(4)	397(4)	2914(3)	462(3)	148(2)
F(5)	-383(3)	3224(3)	1387(4)	167(3)
F(6)	856(6)	3747(3)	1810(3)	183(3)

Table 3. Bond lengths [Å] and angles [°] for ic16023.

Ru(1)-C(1)	1.886(3)	Ru(1)-C(18)	2.229(4)
Ru(1)-C(17)	2.251(4)	Ru(1)-C(16)	2.264(4)
Ru(1)-C(20)	2.270(4)	Ru(1)-C(19)	2.280(4)
Ru(1)-P(1)	2.3512(10)	Ru(1)-P(2)	2.3569(9)
P(1)-C(33)	1.819(4)	P(1)-C(21)	1.833(4)
P(1)-C(27)	1.839(3)	P(2)-C(51)	1.823(4)
P(2)-C(39)	1.831(4)	P(2)-C(45)	1.845(4)
C(1)-C(2)	1.301(5)	C(2)-C(6)	1.515(10)
C(2)-C(3)	1.535(6)	C(2)-C(6')	1.659(11)
C(3)-C(4)	1.489(7)	C(4)-C(5)	1.268(9)
O(1)-C(9)	1.390(10)	O(1)-C(8)	1.451(12)
C(6)-C(10)	1.578(12)	C(6)-C(7)	1.646(11)
C(8)-C(7)	1.586(11)	C(9)-C(10)	1.855(11)
C(10)-C(11)	1.382(10)	C(6')-C(10')	1.513(15)
C(6')-C(11)	1.730(14)	C(8')-C(11)	1.682(12)
C(10')-C(7)	1.379(14)	C(7)-C(15)	1.394(8)
C(7)-C(14)	1.465(8)	C(11)-C(13)	1.367(8)
C(11)-C(12)	1.488(11)	C(16)-C(20)	1.410(6)
C(16)-C(17)	1.421(6)	C(17)-C(18)	1.396(6)
C(18)-C(19)	1.413(6)	C(19)-C(20)	1.399(6)
C(21)-C(26)	1.384(6)	C(21)-C(22)	1.389(6)
C(22)-C(23)	1.396(6)	C(23)-C(24)	1.373(7)
C(24)-C(25)	1.382(7)	C(25)-C(26)	1.400(6)
C(27)-C(32)	1.381(5)	C(27)-C(28)	1.382(5)
C(28)-C(29)	1.389(5)	C(29)-C(30)	1.385(6)
C(30)-C(31)	1.378(6)	C(31)-C(32)	1.382(5)
C(33)-C(34)	1.384(6)	C(33)-C(38)	1.388(5)
C(34)-C(35)	1.397(6)	C(35)-C(36)	1.370(7)
C(36)-C(37)	1.376(8)	C(37)-C(38)	1.387(7)
C(39)-C(40)	1.395(5)	C(39)-C(44)	1.398(6)
C(40)-C(41)	1.399(5)	C(41)-C(42)	1.381(8)
C(42)-C(43)	1.385(8)	C(43)-C(44)	1.376(7)
C(45)-C(50)	1.386(5)	C(45)-C(46)	1.391(5)
C(46)-C(47)	1.393(6)	C(47)-C(48)	1.374(6)
C(48)-C(49)	1.364(6)	C(49)-C(50)	1.398(6)
C(51)-C(52)	1.389(6)	C(51)-C(56)	1.396(6)
C(52)-C(53)	1.379(6)	C(53)-C(54)	1.375(7)
C(54)-C(55)	1.364(7)	C(55)-C(56)	1.369(6)
P(3)-F(3)	1.533(4)	P(3)-F(6)	1.535(5)
P(3)-F(2)	1.551(4)	P(3)-F(5)	1.550(4)
P(3)-F(4)	1.557(5)	P(3)-F(1)	1.608(4)

C(1)-Ru(1)-C(18)	122.49(17)	C(1)-Ru(1)-C(17)	93.13(18)
C(18)-Ru(1)-C(17)	36.31(16)	C(1)-Ru(1)-C(16)	96.16(18)
C(18)-Ru(1)-C(16)	61.10(16)	C(17)-Ru(1)-C(16)	36.70(15)
C(1)-Ru(1)-C(20)	129.11(17)	C(18)-Ru(1)-C(20)	60.31(16)
C(17)-Ru(1)-C(20)	60.23(15)	C(16)-Ru(1)-C(20)	36.23(15)
C(1)-Ru(1)-C(19)	153.27(17)	C(18)-Ru(1)-C(19)	36.50(15)
C(17)-Ru(1)-C(19)	60.47(15)	C(16)-Ru(1)-C(19)	60.66(16)
C(20)-Ru(1)-C(19)	35.82(15)	C(1)-Ru(1)-P(1)	97.14(13)
C(18)-Ru(1)-P(1)	88.34(11)	C(17)-Ru(1)-P(1)	114.70(12)
C(16)-Ru(1)-P(1)	149.14(11)	C(20)-Ru(1)-P(1)	132.59(11)
C(19)-Ru(1)-P(1)	97.93(11)	C(1)-Ru(1)-P(2)	96.76(13)
C(18)-Ru(1)-P(2)	139.38(11)	C(17)-Ru(1)-P(2)	144.89(11)
C(16)-Ru(1)-P(2)	108.52(11)	C(20)-Ru(1)-P(2)	87.95(11)

C(19)-Ru(1)-P(2)	103.02(10)	P(1)-Ru(1)-P(2)	97.40(3)
C(33)-P(1)-C(21)	103.09(18)	C(33)-P(1)-C(27)	102.50(18)
C(21)-P(1)-C(27)	101.76(16)	C(33)-P(1)-Ru(1)	121.52(12)
C(21)-P(1)-Ru(1)	113.49(13)	C(27)-P(1)-Ru(1)	112.14(13)
C(51)-P(2)-C(39)	103.15(18)	C(51)-P(2)-C(45)	97.69(17)
C(39)-P(2)-C(45)	105.36(17)	C(51)-P(2)-Ru(1)	125.36(14)
C(39)-P(2)-Ru(1)	113.94(12)	C(45)-P(2)-Ru(1)	108.75(12)
C(2)-C(1)-Ru(1)	168.6(4)	C(1)-C(2)-C(6)	122.0(5)
C(1)-C(2)-C(3)	119.4(4)	C(6)-C(2)-C(3)	116.5(4)
C(1)-C(2)-C(6')	117.5(5)	C(6)-C(2)-C(6')	29.9(4)
C(3)-C(2)-C(6')	120.8(4)	C(4)-C(3)-C(2)	115.8(4)
C(5)-C(4)-C(3)	126.5(6)	C(9)-O(1)-C(8)	140.2(8)
C(2)-C(6)-C(10)	106.7(7)	C(2)-C(6)-C(7)	122.3(7)
C(10)-C(6)-C(7)	108.9(6)	O(1)-C(8)-C(7)	107.3(7)
O(1)-C(9)-C(10)	88.7(6)	C(11)-C(10)-C(6)	115.0(6)
C(11)-C(10)-C(9)	95.8(6)	C(6)-C(10)-C(9)	117.0(7)
C(10')-C(6')-C(2)	105.3(9)	C(10')-C(6')-C(11)	107.9(7)
C(2)-C(6')-C(11)	116.6(7)	C(7)-C(10')-C(6')	112.6(9)
C(10')-C(7)-C(15)	144.8(7)	C(10')-C(7)-C(14)	98.9(7)
C(15)-C(7)-C(14)	115.3(7)	C(10')-C(7)-C(8)	74.9(7)
C(15)-C(7)-C(8)	98.1(6)	C(14)-C(7)-C(8)	112.4(5)
C(10')-C(7)-C(6)	44.2(5)	C(15)-C(7)-C(6)	105.5(5)
C(14)-C(7)-C(6)	122.7(6)	C(8)-C(7)-C(6)	98.9(6)
C(13)-C(11)-C(10)	144.7(7)	C(13)-C(11)-C(12)	114.8(7)
C(10)-C(11)-C(12)	99.2(6)	C(13)-C(11)-C(8')	91.7(6)
C(10)-C(11)-C(8')	81.2(6)	C(12)-C(11)-C(8')	116.1(6)
C(13)-C(11)-C(6')	104.0(5)	C(10)-C(11)-C(6')	42.8(5)
C(12)-C(11)-C(6')	128.9(6)	C(8')-C(11)-C(6')	93.6(7)
C(20)-C(16)-C(17)	106.5(4)	C(20)-C(16)-Ru(1)	72.1(2)
C(17)-C(16)-Ru(1)	71.2(2)	C(18)-C(17)-C(16)	108.3(4)
C(18)-C(17)-Ru(1)	71.0(2)	C(16)-C(17)-Ru(1)	72.1(2)
C(17)-C(18)-C(19)	108.6(4)	C(17)-C(18)-Ru(1)	72.7(3)
C(19)-C(18)-Ru(1)	73.7(2)	C(20)-C(19)-C(18)	107.0(4)
C(20)-C(19)-Ru(1)	71.7(2)	C(18)-C(19)-Ru(1)	69.8(2)
C(19)-C(20)-C(16)	109.6(4)	C(19)-C(20)-Ru(1)	72.5(2)
C(16)-C(20)-Ru(1)	71.7(2)	C(26)-C(21)-C(22)	118.9(4)
C(26)-C(21)-P(1)	121.6(3)	C(22)-C(21)-P(1)	119.3(3)
C(21)-C(22)-C(23)	120.8(4)	C(24)-C(23)-C(22)	120.2(4)
C(23)-C(24)-C(25)	119.5(4)	C(24)-C(25)-C(26)	120.7(5)
C(21)-C(26)-C(25)	119.9(5)	C(32)-C(27)-C(28)	118.8(3)
C(32)-C(27)-P(1)	118.8(3)	C(28)-C(27)-P(1)	122.3(3)
C(27)-C(28)-C(29)	120.4(3)	C(30)-C(29)-C(28)	120.2(3)
C(31)-C(30)-C(29)	119.5(3)	C(30)-C(31)-C(32)	120.0(4)
C(27)-C(32)-C(31)	121.1(4)	C(34)-C(33)-C(38)	118.6(4)
C(34)-C(33)-P(1)	124.0(3)	C(38)-C(33)-P(1)	117.4(3)
C(33)-C(34)-C(35)	120.6(4)	C(36)-C(35)-C(34)	120.4(5)
C(35)-C(36)-C(37)	119.2(4)	C(36)-C(37)-C(38)	121.0(4)
C(37)-C(38)-C(33)	120.2(4)	C(40)-C(39)-C(44)	118.1(4)
C(40)-C(39)-P(2)	119.6(3)	C(44)-C(39)-P(2)	122.0(3)
C(39)-C(40)-C(41)	120.9(4)	C(42)-C(41)-C(40)	119.5(4)
C(41)-C(42)-C(43)	120.2(4)	C(44)-C(43)-C(42)	120.3(5)
C(43)-C(44)-C(39)	121.0(5)	C(50)-C(45)-C(46)	118.8(4)
C(50)-C(45)-P(2)	124.6(3)	C(46)-C(45)-P(2)	116.6(3)
C(45)-C(46)-C(47)	120.7(4)	C(48)-C(47)-C(46)	119.3(4)
C(49)-C(48)-C(47)	120.9(4)	C(48)-C(49)-C(50)	120.1(4)
C(45)-C(50)-C(49)	120.1(4)	C(52)-C(51)-C(56)	117.7(4)
C(52)-C(51)-P(2)	122.7(3)	C(56)-C(51)-P(2)	119.4(3)
C(53)-C(52)-C(51)	120.3(5)	C(54)-C(53)-C(52)	120.8(4)
C(55)-C(54)-C(53)	119.6(4)	C(54)-C(55)-C(56)	120.2(5)

C(55)-C(56)-C(51)	121.4(4)	F(3)-P(3)-F(6)	92.8(4)
F(3)-P(3)-F(2)	91.5(3)	F(6)-P(3)-F(2)	92.8(3)
F(3)-P(3)-F(5)	176.6(4)	F(6)-P(3)-F(5)	88.5(4)
F(2)-P(3)-F(5)	91.7(3)	F(3)-P(3)-F(4)	88.9(4)
F(6)-P(3)-F(4)	177.9(4)	F(2)-P(3)-F(4)	88.5(3)
F(5)-P(3)-F(4)	89.8(4)	F(3)-P(3)-F(1)	89.2(3)
F(6)-P(3)-F(1)	88.7(2)	F(2)-P(3)-F(1)	178.3(3)
F(5)-P(3)-F(1)	87.6(3)	F(4)-P(3)-F(1)	90.0(3)

Symmetry transformations used to generate equivalent atoms:

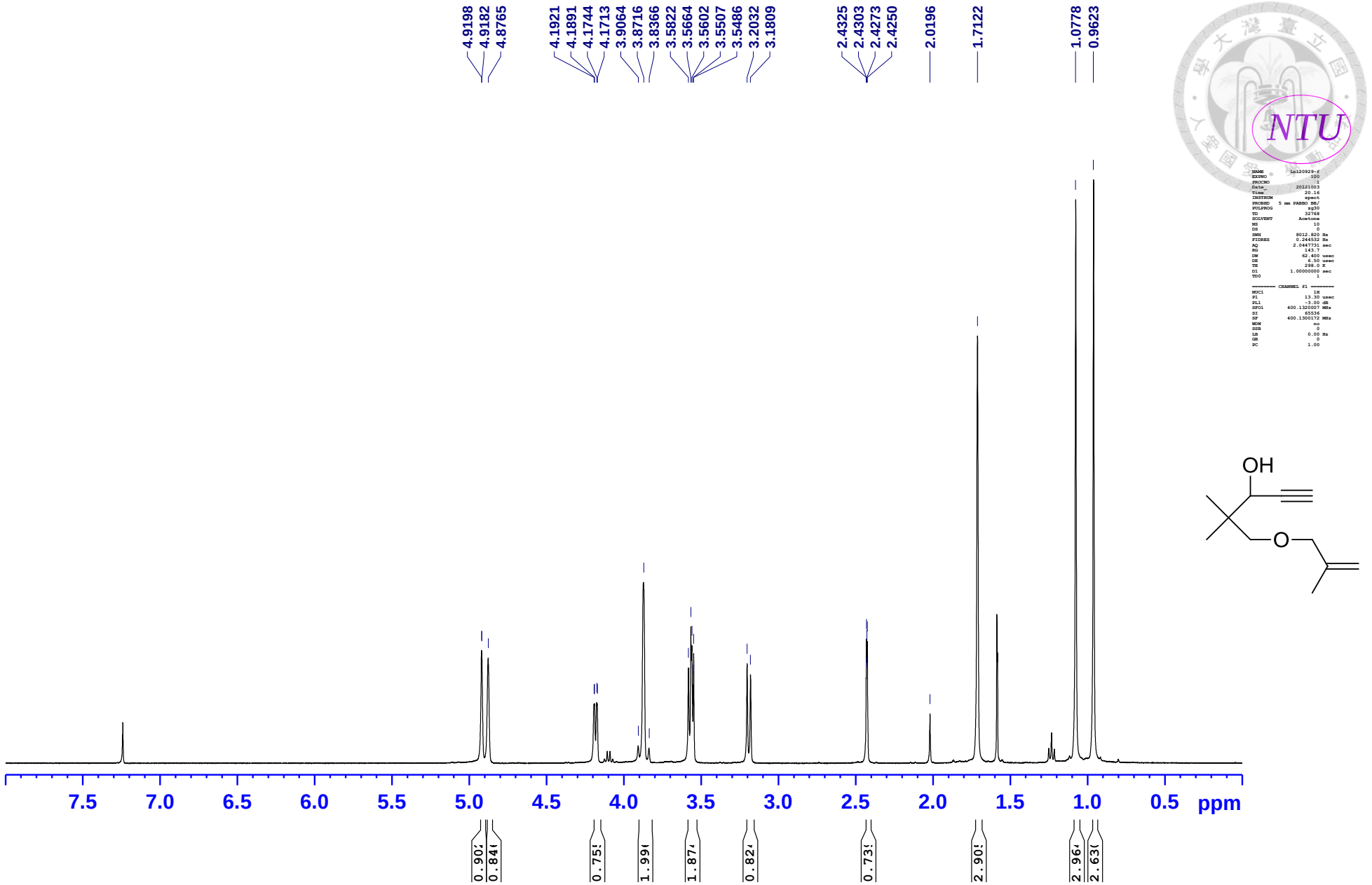
Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic16023.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + $2hka^*b^*U_{12}$]

	U11	U22	U33	U23	U13	U12
Ru(1)	24(1)	33(1)	27(1)	3(1)	-3(1)	-4(1)
P(1)	24(1)	34(1)	26(1)	5(1)	1(1)	-1(1)
P(2)	27(1)	29(1)	27(1)	3(1)	1(1)	1(1)
C(1)	33(2)	43(2)	41(2)	18(2)	-5(2)	-7(2)
C(2)	32(2)	80(4)	49(2)	23(3)	-10(2)	-15(2)
C(3)	31(2)	45(2)	49(2)	1(2)	1(2)	-13(2)
C(4)	35(2)	65(3)	72(3)	-30(3)	-7(2)	-8(2)
C(5)	255(12)	42(3)	71(4)	-1(3)	-10(6)	9(5)
O(1)	124(5)	126(6)	103(5)	43(5)	8(4)	44(5)
C(6)	21(3)	36(5)	52(5)	-8(4)	-4(3)	-5(4)
C(8)	42(5)	74(7)	74(6)	12(6)	-24(5)	-3(5)
C(9)	161(7)	136(6)	108(5)	-5(5)	-9(5)	-85(5)
C(10)	20(4)	38(5)	59(5)	-3(4)	-3(3)	1(3)
O(1')	161(7)	136(6)	108(5)	-5(5)	-9(5)	-85(5)
C(6')	27(4)	50(7)	44(5)	14(5)	-11(4)	-4(4)
C(8')	46(6)	52(6)	104(10)	22(7)	-28(6)	4(5)
C(9')	124(5)	126(6)	103(5)	43(5)	8(4)	44(5)
C(10')	55(6)	60(7)	75(7)	11(8)	-25(6)	-19(5)
C(7)	49(3)	76(3)	46(2)	2(3)	-11(2)	0(3)
C(11)	39(2)	39(2)	146(6)	-21(3)	-41(3)	13(2)
C(12)	54(3)	94(6)	215(10)	54(7)	-18(5)	-17(4)
C(13)	61(3)	60(3)	105(5)	-11(3)	22(3)	7(3)
C(14)	78(4)	130(7)	116(6)	55(5)	-30(4)	-53(4)
C(15)	71(4)	186(9)	62(3)	-45(5)	11(3)	-56(5)
C(16)	53(3)	34(2)	46(2)	-6(2)	-1(2)	-4(2)
C(17)	57(2)	46(2)	37(2)	-9(2)	-15(2)	-3(2)
C(18)	51(2)	47(2)	29(2)	-5(2)	4(2)	3(2)
C(19)	34(2)	41(2)	33(2)	-10(2)	4(2)	2(2)
C(20)	41(2)	40(2)	31(2)	-6(2)	-2(2)	11(2)
C(21)	23(2)	47(2)	28(2)	11(2)	2(2)	1(2)
C(22)	28(2)	48(2)	39(2)	8(2)	-4(2)	-5(2)
C(23)	30(2)	59(3)	38(2)	10(2)	-5(2)	-9(2)
C(24)	35(2)	75(4)	39(2)	10(2)	-10(2)	13(2)
C(25)	56(3)	68(3)	53(3)	15(3)	-3(2)	32(3)
C(26)	51(2)	55(3)	36(2)	4(2)	-3(2)	16(2)
C(27)	25(2)	31(2)	28(2)	1(2)	3(1)	-6(2)
C(28)	28(2)	30(2)	33(2)	5(2)	-3(2)	-1(2)
C(29)	38(2)	43(2)	32(2)	7(2)	9(2)	-4(2)
C(30)	27(2)	44(2)	41(2)	1(2)	9(2)	-7(2)
C(31)	30(2)	53(3)	41(2)	9(2)	-6(2)	-7(2)
C(32)	32(2)	46(2)	32(2)	12(2)	-3(2)	-10(2)
C(33)	40(2)	32(2)	27(2)	4(2)	4(2)	4(2)
C(34)	49(2)	51(3)	37(2)	-5(2)	7(2)	-5(2)
C(35)	68(3)	50(3)	46(3)	-10(2)	-1(2)	2(2)
C(36)	81(4)	44(2)	40(2)	-1(2)	4(2)	23(3)
C(37)	68(3)	51(3)	51(3)	9(2)	26(3)	18(3)
C(38)	45(2)	39(2)	49(2)	9(2)	16(2)	9(2)
C(39)	38(2)	29(2)	26(2)	4(2)	-6(2)	-8(2)

C(40)	36(2)	43(2)	28(2)	7(2)	-4(2)	-8(2)
C(41)	42(2)	57(3)	38(2)	15(2)	-16(2)	-15(2)
C(42)	61(3)	55(3)	61(3)	17(3)	-33(3)	-26(3)
C(43)	82(4)	36(2)	63(3)	-1(2)	-34(3)	-13(2)
C(44)	58(3)	34(2)	47(2)	-1(2)	-16(2)	6(2)
C(45)	33(2)	34(2)	22(2)	3(2)	5(2)	0(2)
C(46)	34(2)	43(2)	29(2)	1(2)	2(2)	-4(2)
C(47)	46(2)	34(2)	38(2)	-1(2)	9(2)	-10(2)
C(48)	59(3)	31(2)	35(2)	7(2)	10(2)	6(2)
C(49)	45(2)	38(2)	35(2)	8(2)	-2(2)	7(2)
C(50)	36(2)	34(2)	29(2)	1(2)	1(2)	1(2)
C(51)	40(2)	29(2)	39(2)	7(2)	8(2)	4(2)
C(52)	38(2)	39(2)	61(3)	-8(2)	9(2)	-4(2)
C(53)	34(2)	57(3)	87(4)	-9(3)	19(2)	0(2)
C(54)	61(3)	52(3)	63(3)	-6(3)	34(2)	-2(3)
C(55)	60(3)	67(3)	42(2)	5(3)	15(2)	15(3)
C(56)	53(2)	69(3)	37(2)	8(2)	5(2)	25(2)
P(3)	48(1)	55(1)	84(1)	-6(1)	4(1)	-4(1)
F(1)	95(2)	81(2)	89(2)	8(2)	8(2)	19(2)
F(2)	171(4)	74(3)	148(4)	25(3)	9(4)	40(3)
F(3)	55(2)	151(4)	286(7)	58(5)	44(3)	11(3)
F(4)	185(5)	121(4)	138(4)	-67(4)	-37(4)	48(4)
F(5)	103(3)	84(3)	314(8)	15(4)	95(5)	8(3)
F(6)	328(9)	109(4)	113(4)	-19(3)	-110(5)	48(5)

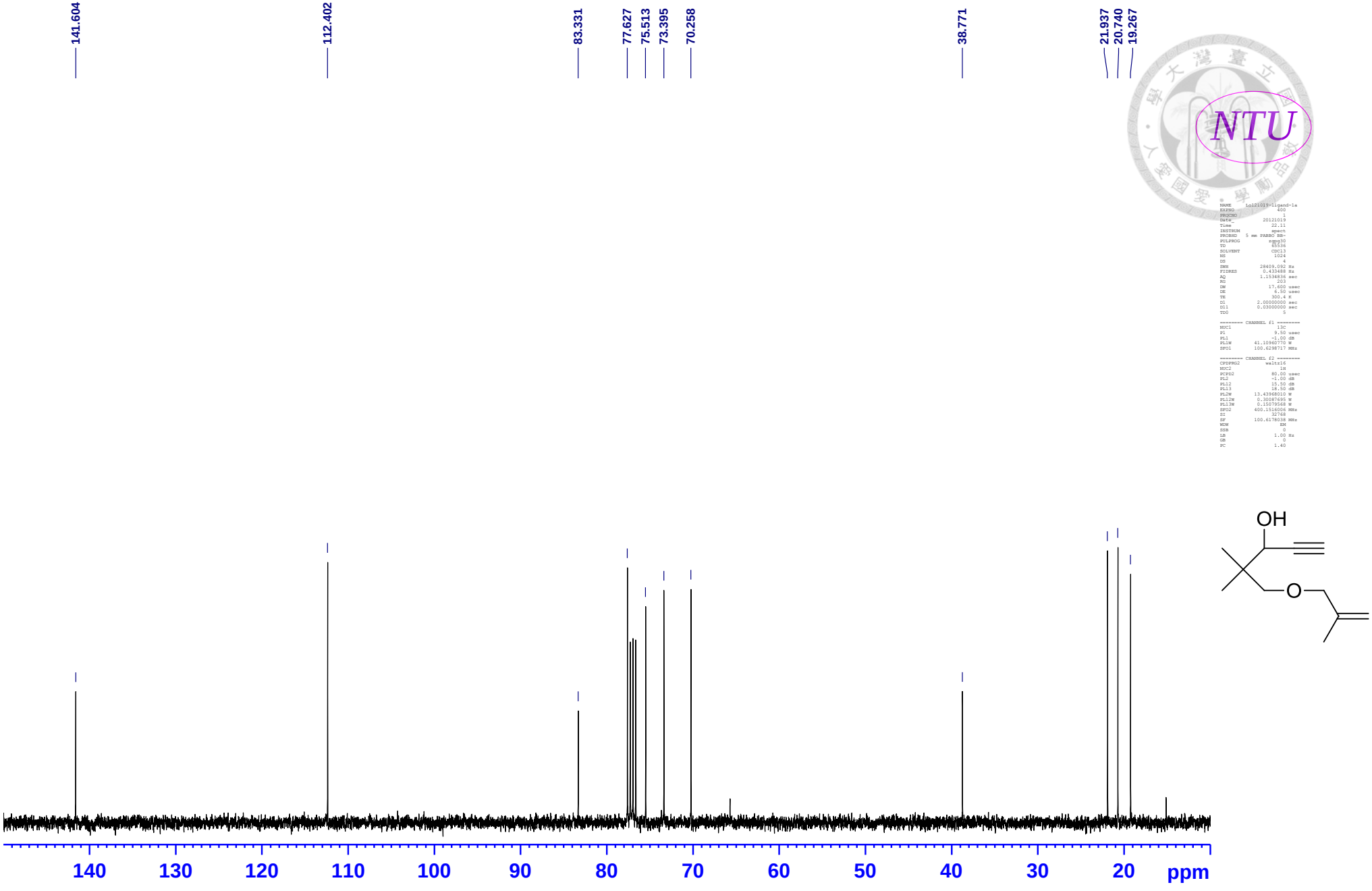
Appendix II: Spectra Data

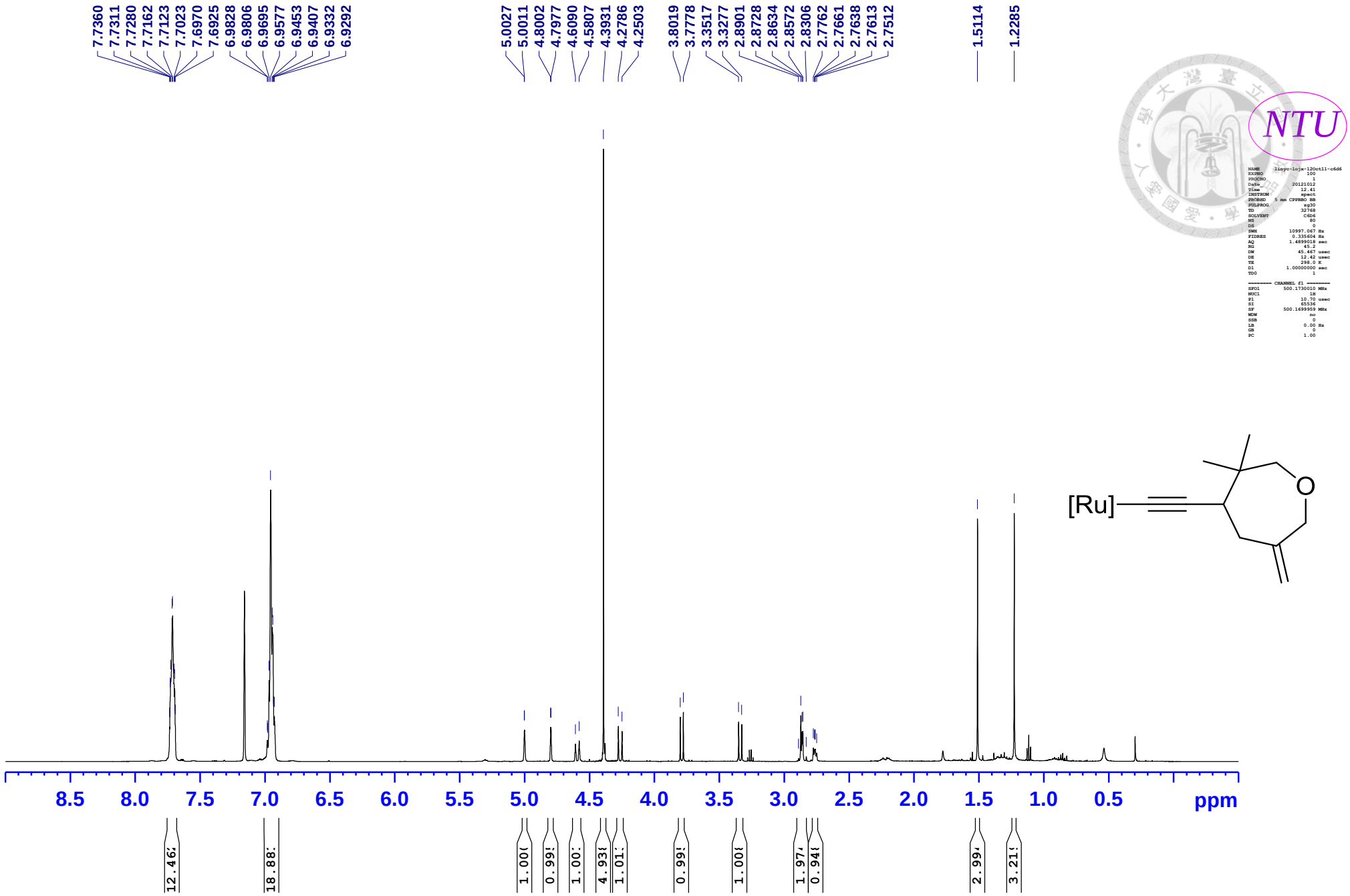
400MHz 1H



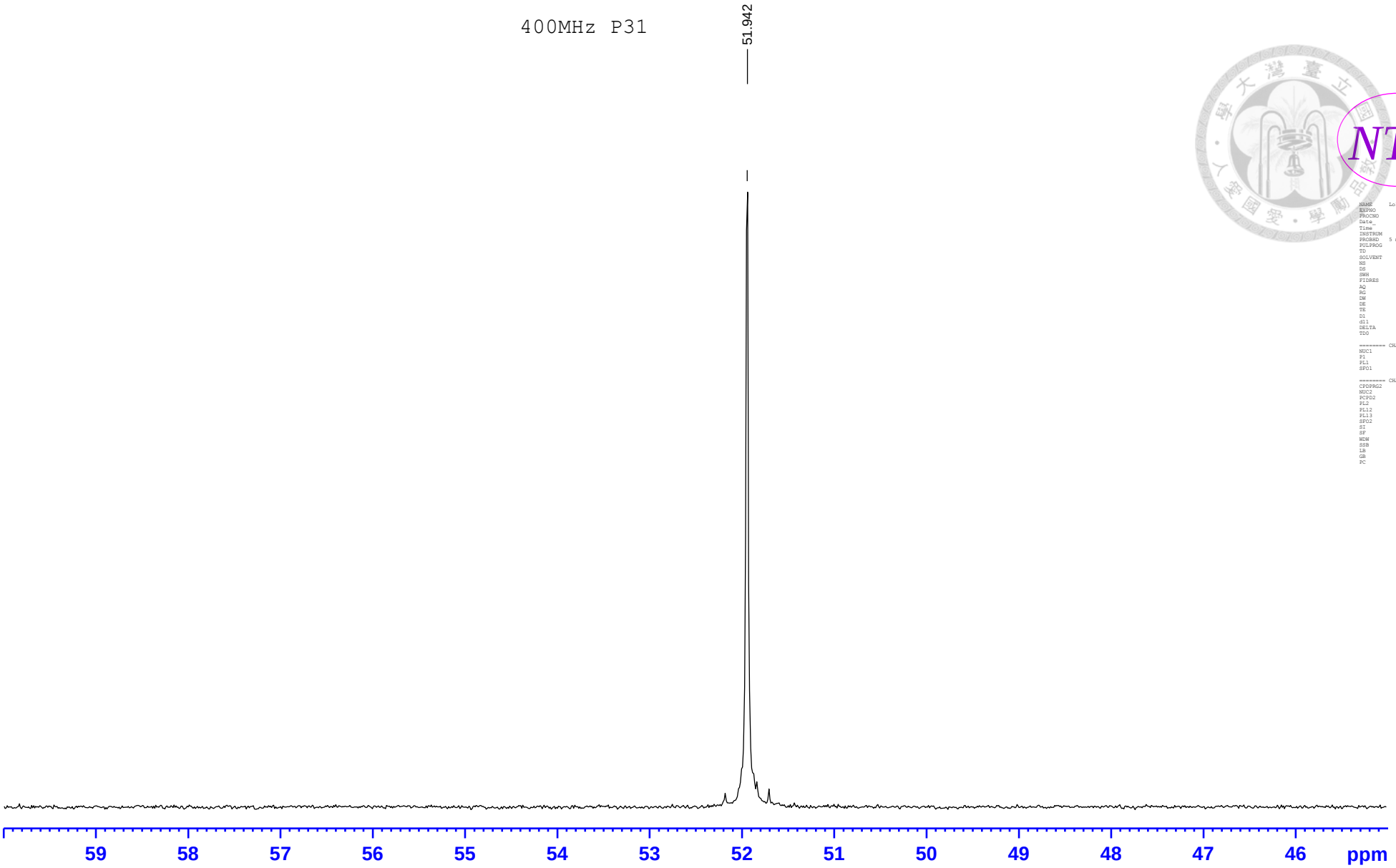

```
NAME                  Lo120929-f
EXPNO                        100
PROCNO                         1
Date_               20121003
Time                      20.14
INSTRUM                    spect
PROBHD     5 mm PABBO BB/
PULPROG                    zg30
TD                        32768
SOLVENT                 Acetone
NS                             10
DS                              0
SWH                  8012.820 Hz
FIDRES               0.244532 Hz
AQ                   2.0447731 sec
RG                         143.7
DW                      62.400 usec
DE                       6.50 usec
TE                       298.0 K
D1                   1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         1H
P1                       13.30 usec
PL1                       -3.00 dB
SFO1                400.1320007 MHz
SI                         65536
SF                  400.1300172 MHz
WDW                           no
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.00
```

400MHz 13C

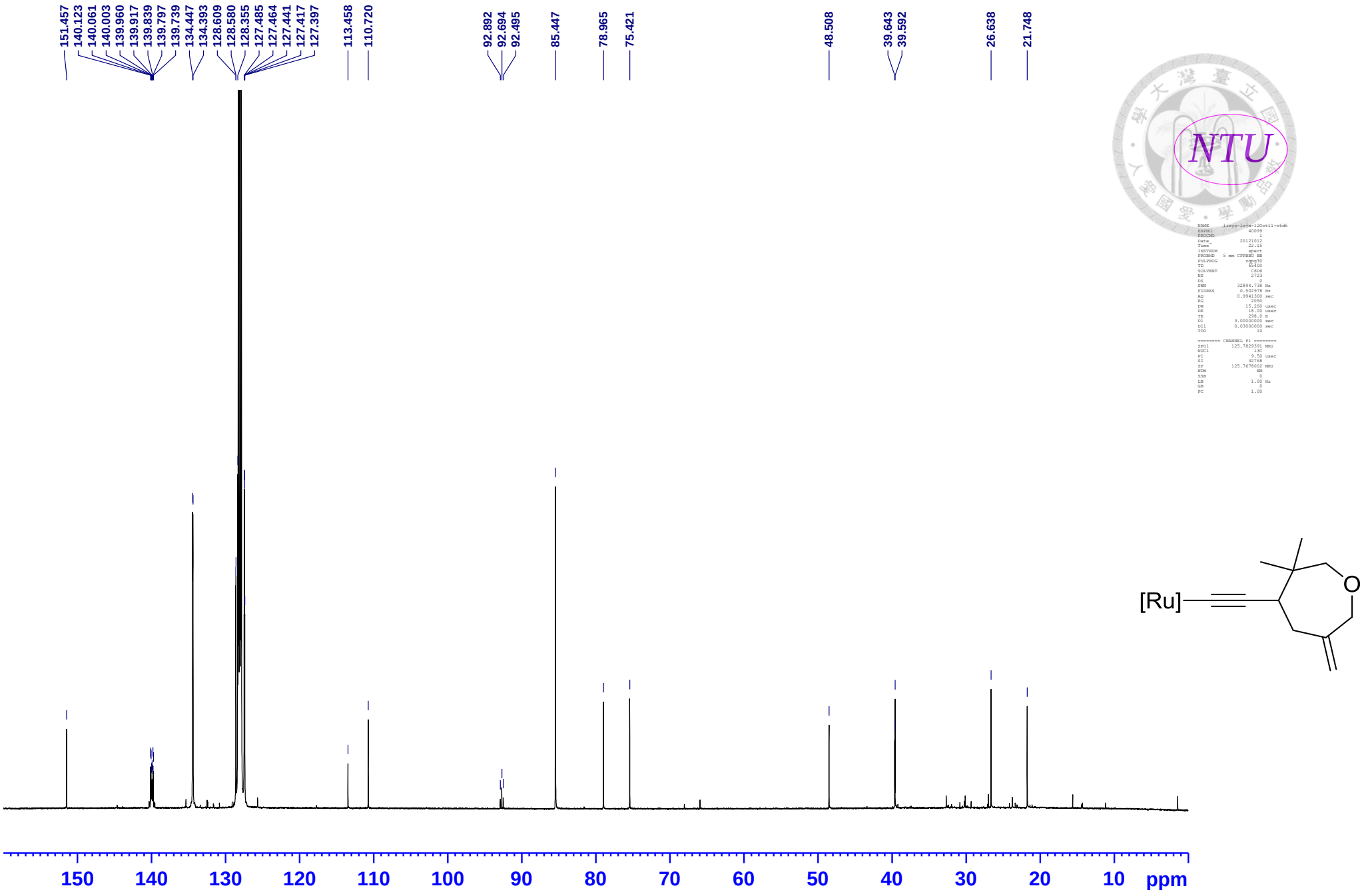

141.604
112.402
83.331
77.627
75.513
73.395
70.258
38.771
21.937
20.740
19.267
NTU
OH
O
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.7360
7.7311
7.7280
7.7162
7.7123
7.7023
7.6970
7.6925
6.9828
6.9806
6.9695
6.9577
6.9453
6.9407
6.9332
6.9292
5.0027
5.0011
4.8002
4.7977
4.6090
4.5807
4.3931
4.2786
4.2503
3.8019
3.7778
3.3517
3.3277
2.8901
2.8728
2.8634
2.8572
2.8306
2.7762
2.7661
2.7638
2.7613
2.7512
1.5114
1.2285
NTU
NAME liuyc-lojx-12Oct11-c6d6
EXPNO 100
PROCNO 1
Date_ 20121012
Time_ 12.41
INSTRUM spect
PROBHD 5 mm CPTBBO BB
PULPROG zg30
TD 32768
SOLVENT C6D6
NS 80
DS 0
SWH 10997.067 Hz
FIDRES 0.335604 Hz
AQ 1.4899018 sec
RG 45.2
DW 45.467 usec
DE 12.42 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1730010 MHz
NUC1 1H
P1 10.70 usec
SI 65536
SF 500.1699959 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
[Ru]
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
12.46
18.88
1.00
0.99
1.00
4.93
1.01
0.99
1.00
1.97
0.94
2.99
3.21

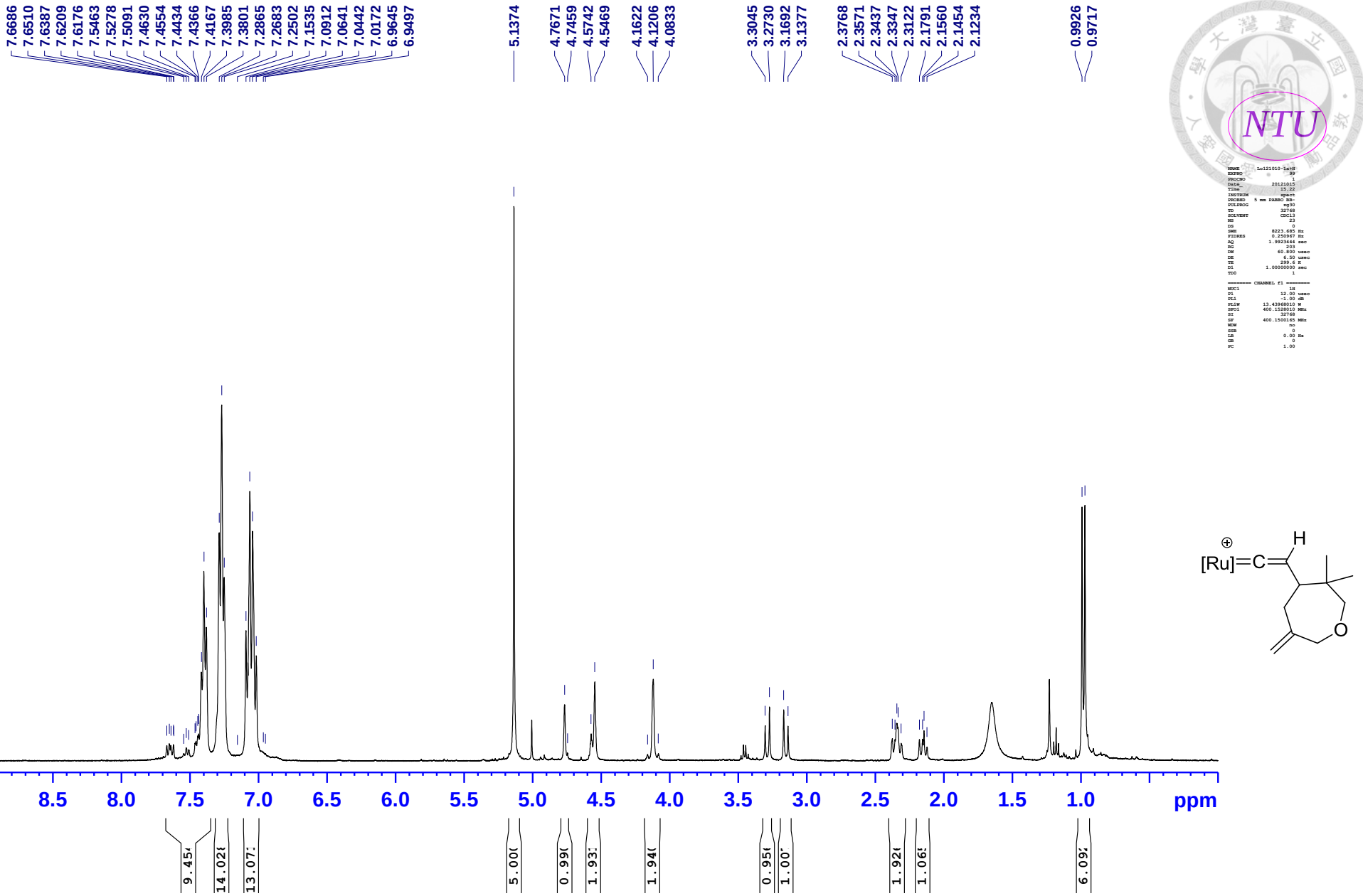
400MHz P31




```
NAME                 Lo121010-n-al2o3-1
EXPNO                               300
PROCNO                                1
Date_                          20121010
Time                              21.15
INSTRUM                           spect
PROBHD     5 mm PABBO BB/
PULPROG                         zgpg30
TD                               65536
SOLVENT                          CDCl3
NS                                  21
DS                                   0
SWH                        58479.531 Hz
FIDRES                      0.892327 Hz
AQ                          0.560328 sec
RG                                8192
DW                            8.550 usec
DE                            6.50 usec
TE                            298.2 K
D1                       2.00000000 sec
d11                      0.03000000 sec
DELTA                    1.89999998 sec
TD0                                  1

======== CHANNEL f1 ========
NUC1                               31P
P1                           12.80 usec
PL1                           0.00 dB
SFO1                    161.9759930 MHz

======== CHANNEL f2 ========
CPDPRG2                       waltz16
NUC2                               1H
PCPD2                        90.00 usec
PL2                          -3.00 dB
PL12                         19.40 dB
PL13                         18.40 dB
SFO2                    400.1316005 MHz
SI                                32768
SF                      161.9755477 MHz
WDW                                EM
SSB                                 0
LB                           1.00 Hz
GB                                  0
PC                                1.40
```


151.457
140.123
140.061
140.003
139.960
139.917
139.839
139.797
139.739
134.447
134.393
128.609
128.580
128.355
127.485
127.464
127.441
127.417
127.397
113.458
110.720
92.892
92.694
92.495
85.447
78.965
75.421
48.508
39.643
39.592
26.638
21.748
NTU
NAME liuyc-lajw-12oct11-c6d6
EXPNO 40099
PROCNO 1
Date_ 20121012
Time 22.15
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zgpg30
TD 65400
SOLVENT C6D6
NS 2723
DS 0
SWH 32894.738 Hz
FIDRES 0.502978 Hz
AQ 0.9941309 sec
RG 2050
DW 15.200 usec
DE 18.00 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 10
======== CHANNEL f1 ========
SFO1 125.7829391 MHz
NUC1 13C
P1 9.50 usec
SI 32768
SF 125.7678002 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
[Ru]
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

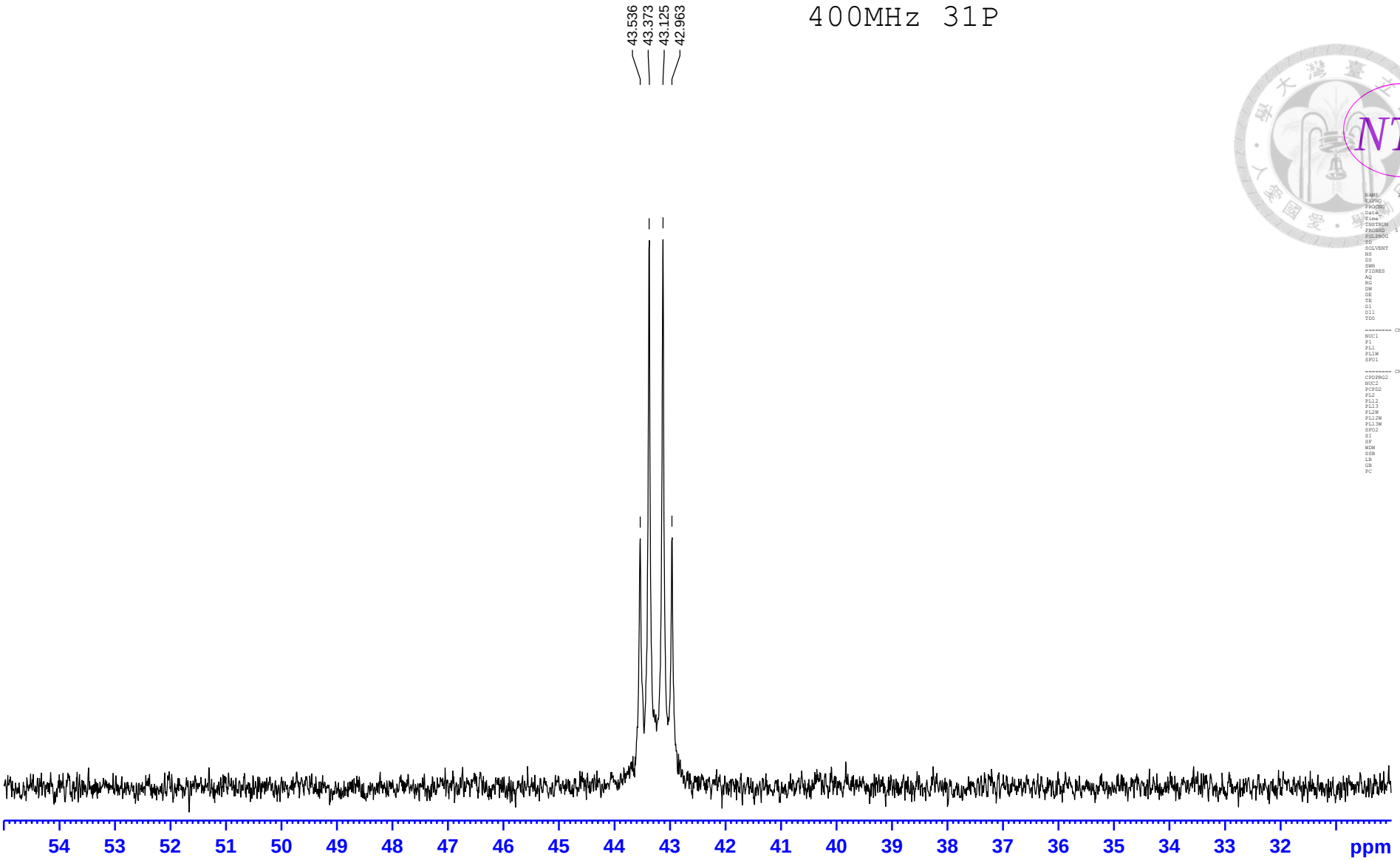
400MHz 1H


7.6686
7.6510
7.6387
7.6209
7.6176
7.5463
7.5278
7.5091
7.4630
7.4554
7.4434
7.4366
7.4167
7.3985
7.3801
7.2865
7.2683
7.2502
7.1535
7.0912
7.0641
7.0442
7.0172
6.9645
6.9497
5.1374
4.7671
4.7459
4.5742
4.5469
4.1622
4.1206
4.0833
3.3045
3.2730
3.1692
3.1377
2.3768
2.3571
2.3437
2.3347
2.3122
2.1791
2.1560
2.1454
2.1234
0.9926
0.9717
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
9.45
14.02
13.07
5.00
0.99
1.93
1.94
0.95
1.00
1.92
1.06
6.09

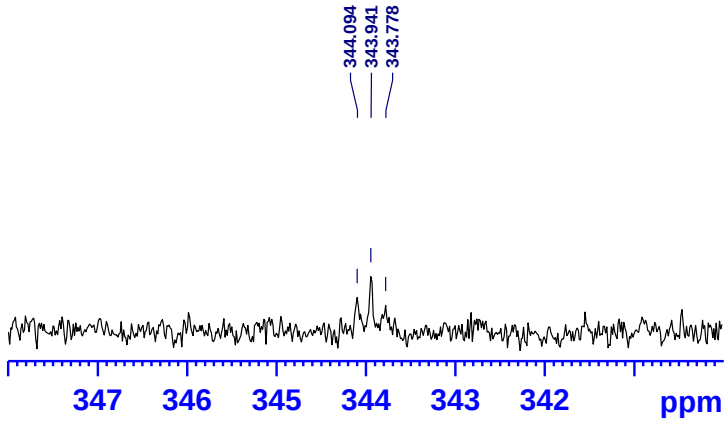
NTU
NAME Lo121010-1aHf
EXPNO 99
PROCNO 1
Date_ 20121015
Time 15.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 23
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 299.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.00 dB
PL1W 13.43968010 W
SFO1 400.1528010 MHz
SI 32768
SF 400.1500165 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

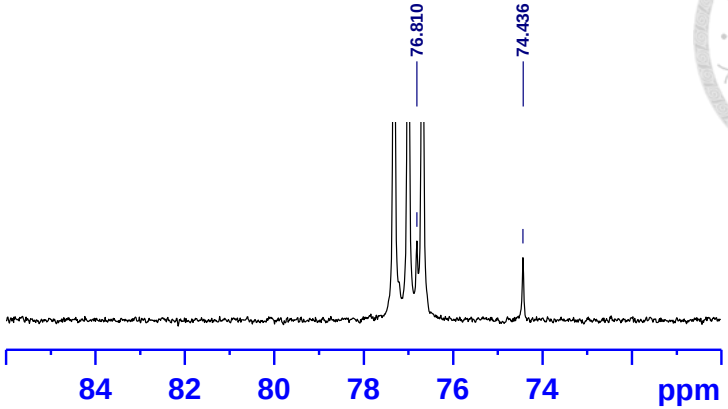
[Ru]=C
H
O

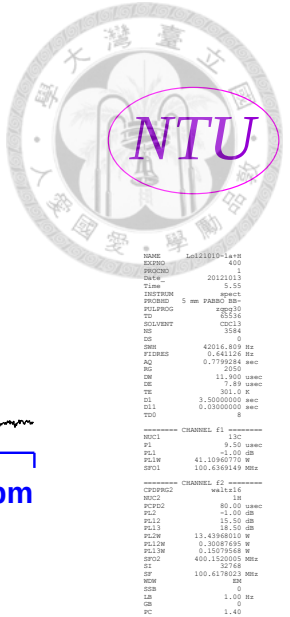
400MHz 31P

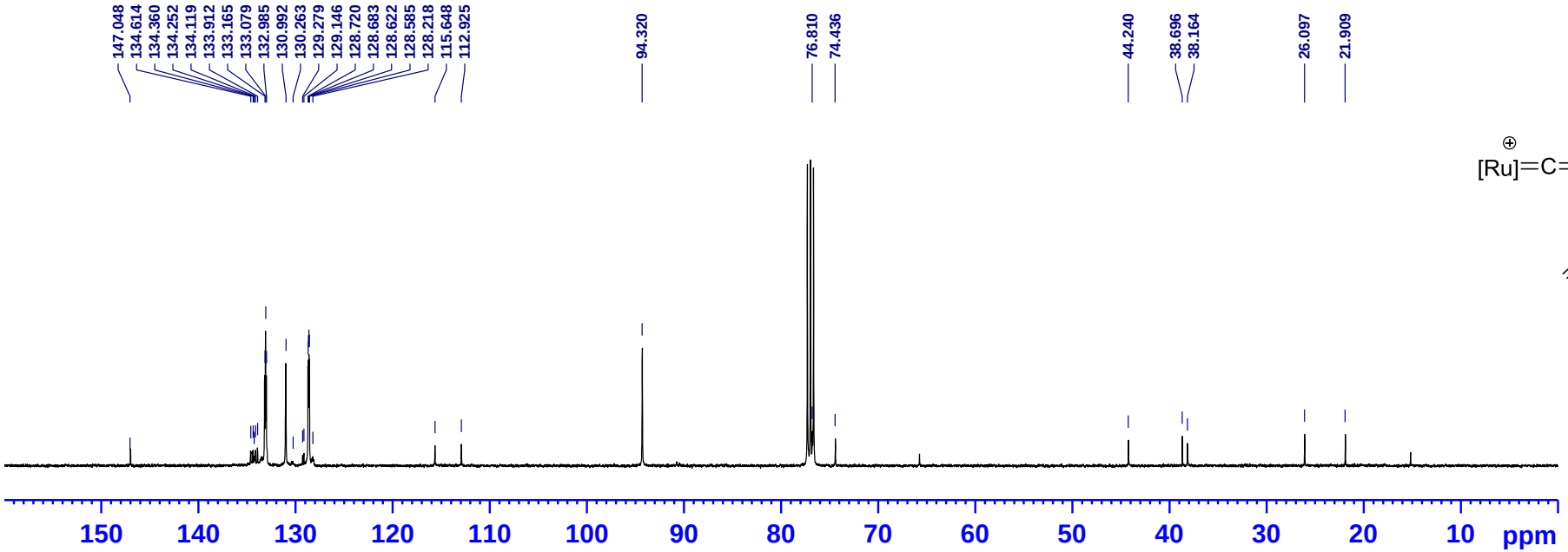


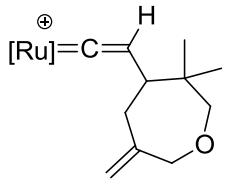
400MHz 13C


344.094
343.941
343.778
347
346
345
344
343
342
ppm

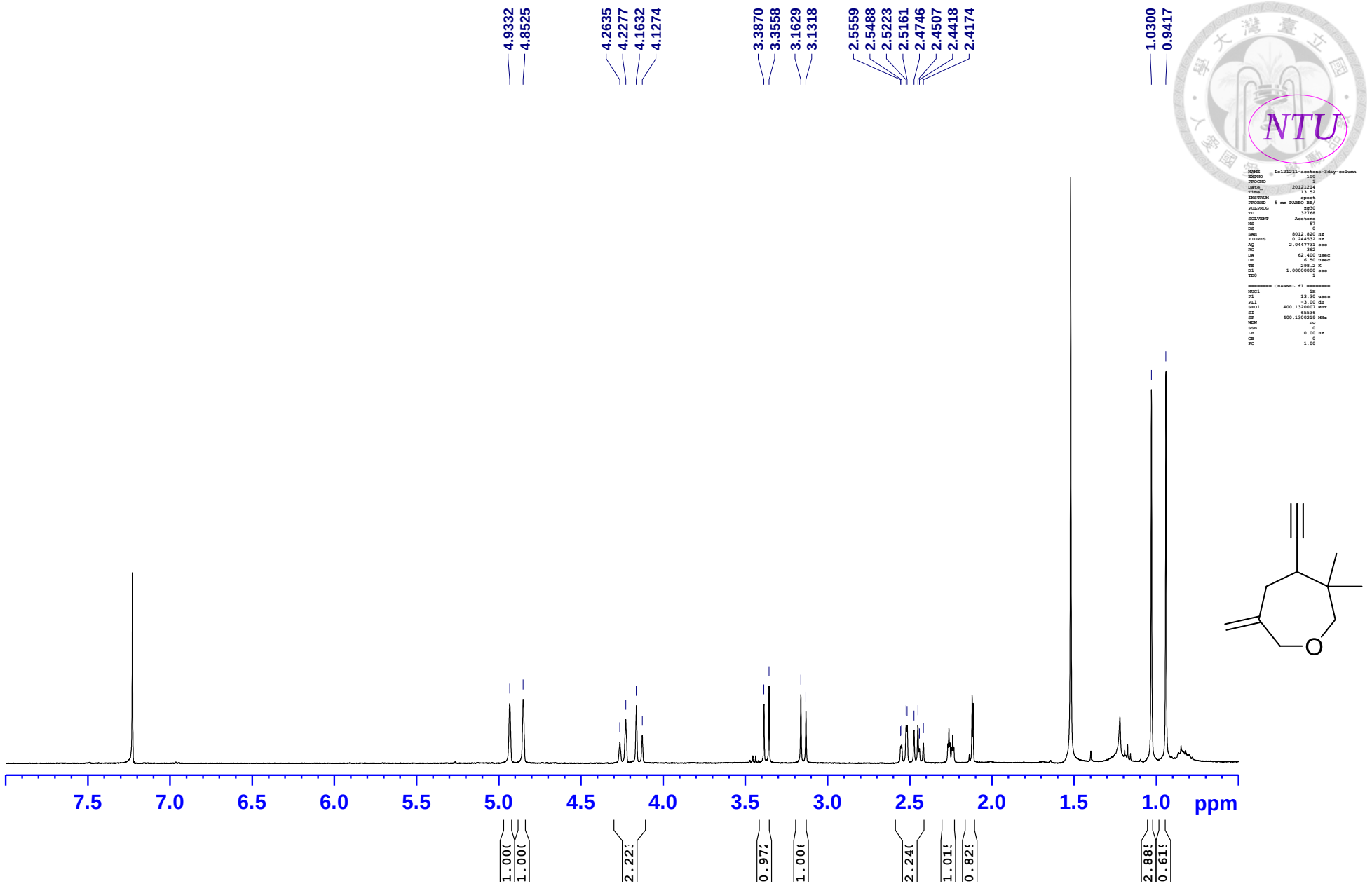

76.810
74.436
84
82
80
78
76
74
ppm


NTU

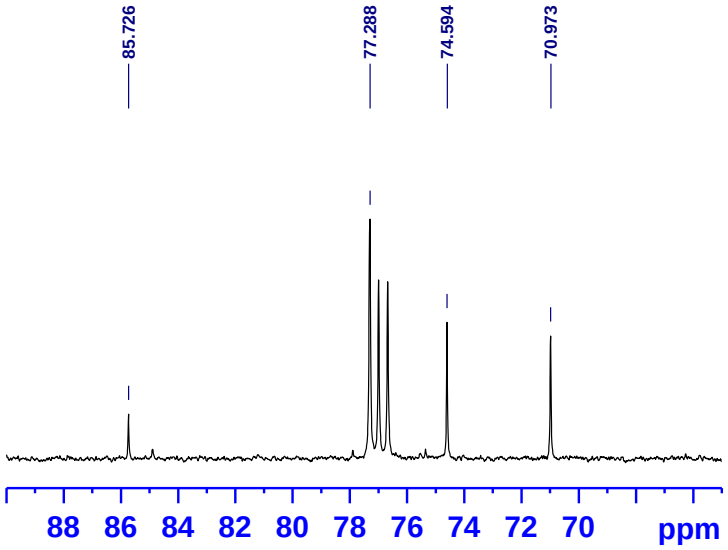

147.048
134.614
134.360
134.252
134.119
133.912
133.165
133.079
132.985
130.992
130.263
129.279
129.146
128.720
128.683
128.622
128.585
128.218
115.648
112.925
94.320
76.810
74.436
44.240
38.696
38.164
26.097
21.909
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


[Ru]=C
H
O

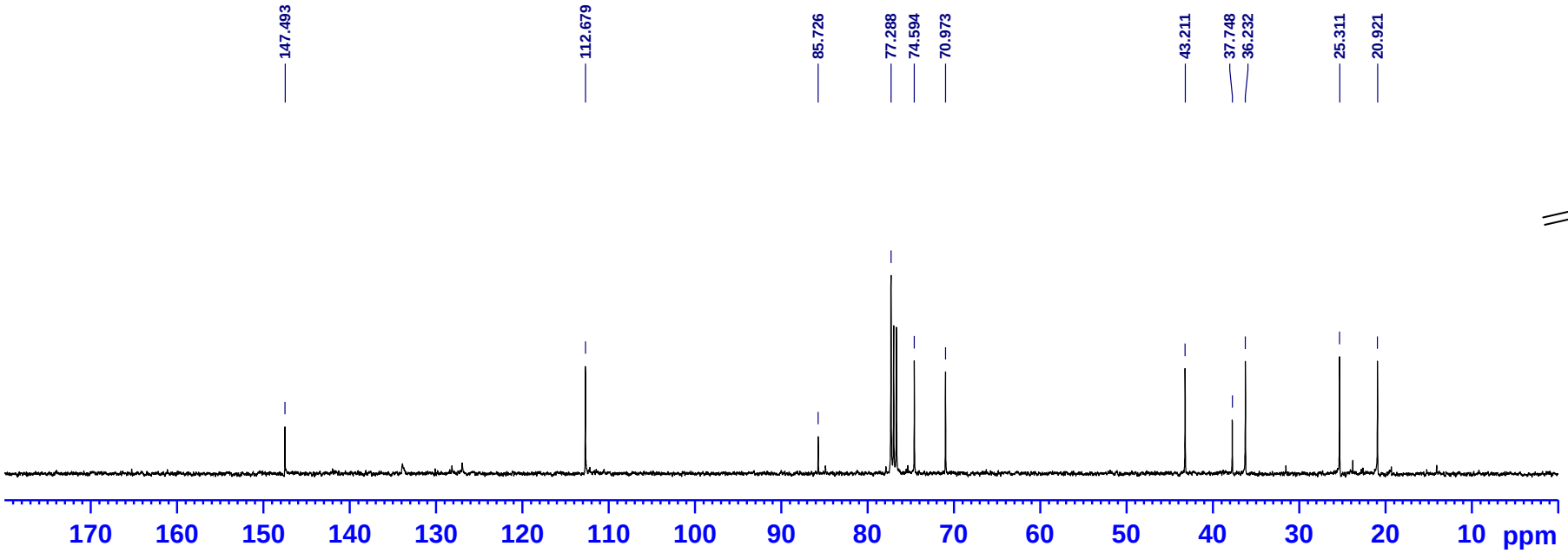
400MHz 1H

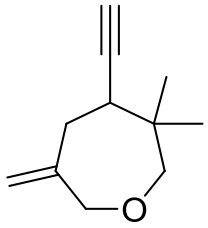

4.9332
4.8525
4.2635
4.2277
4.1632
4.1274
3.3870
3.3558
3.1629
3.1318
2.5559
2.5488
2.5223
2.5161
2.4746
2.4507
2.4418
2.4174
1.0300
0.9417
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
2.22
0.97
1.00
2.24
1.01
0.82
2.88
0.61

400MHz 13C

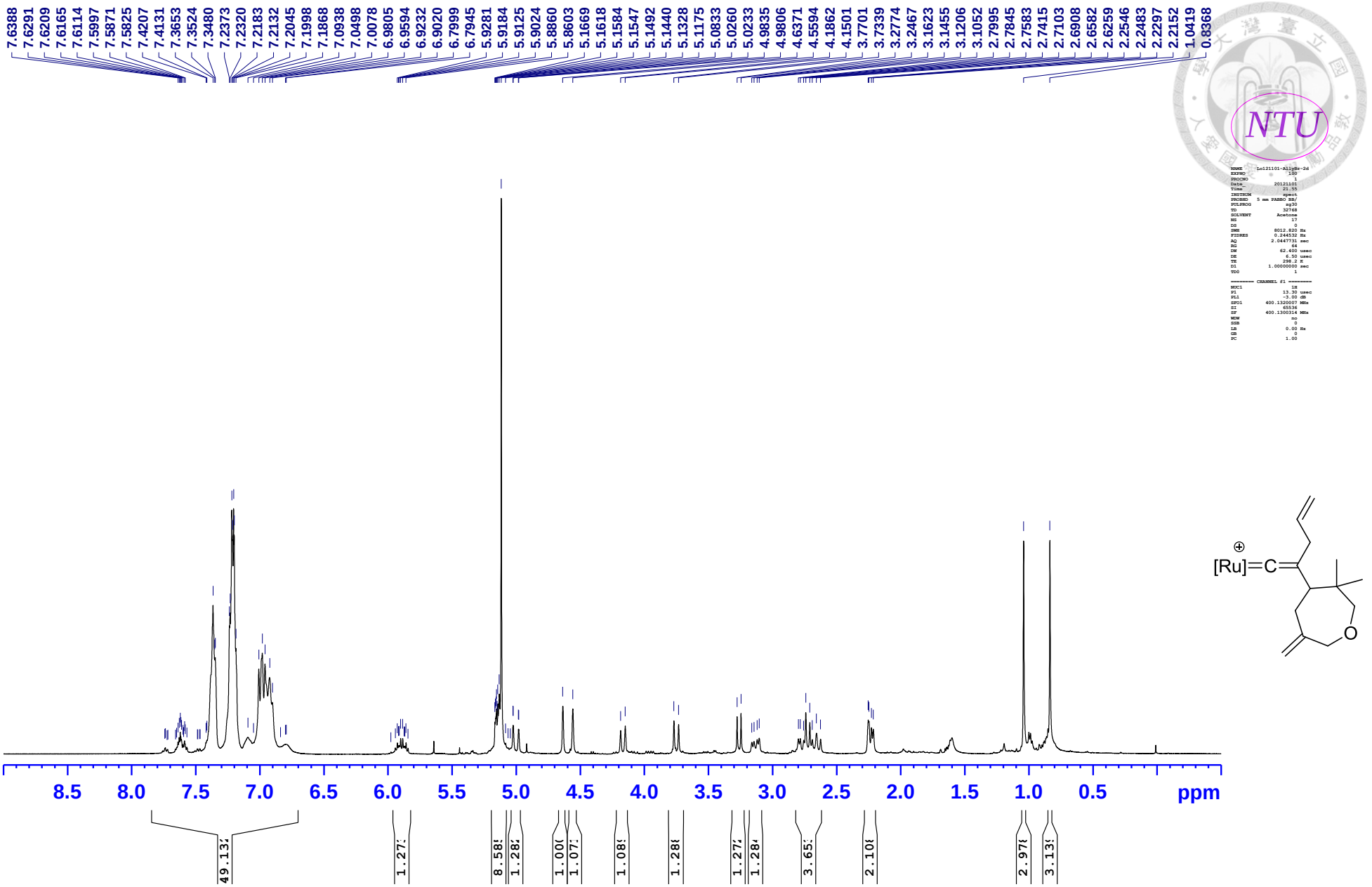

85.726
77.288
74.594
70.973
88 86 84 82 80 78 76 74 72 70 ppm

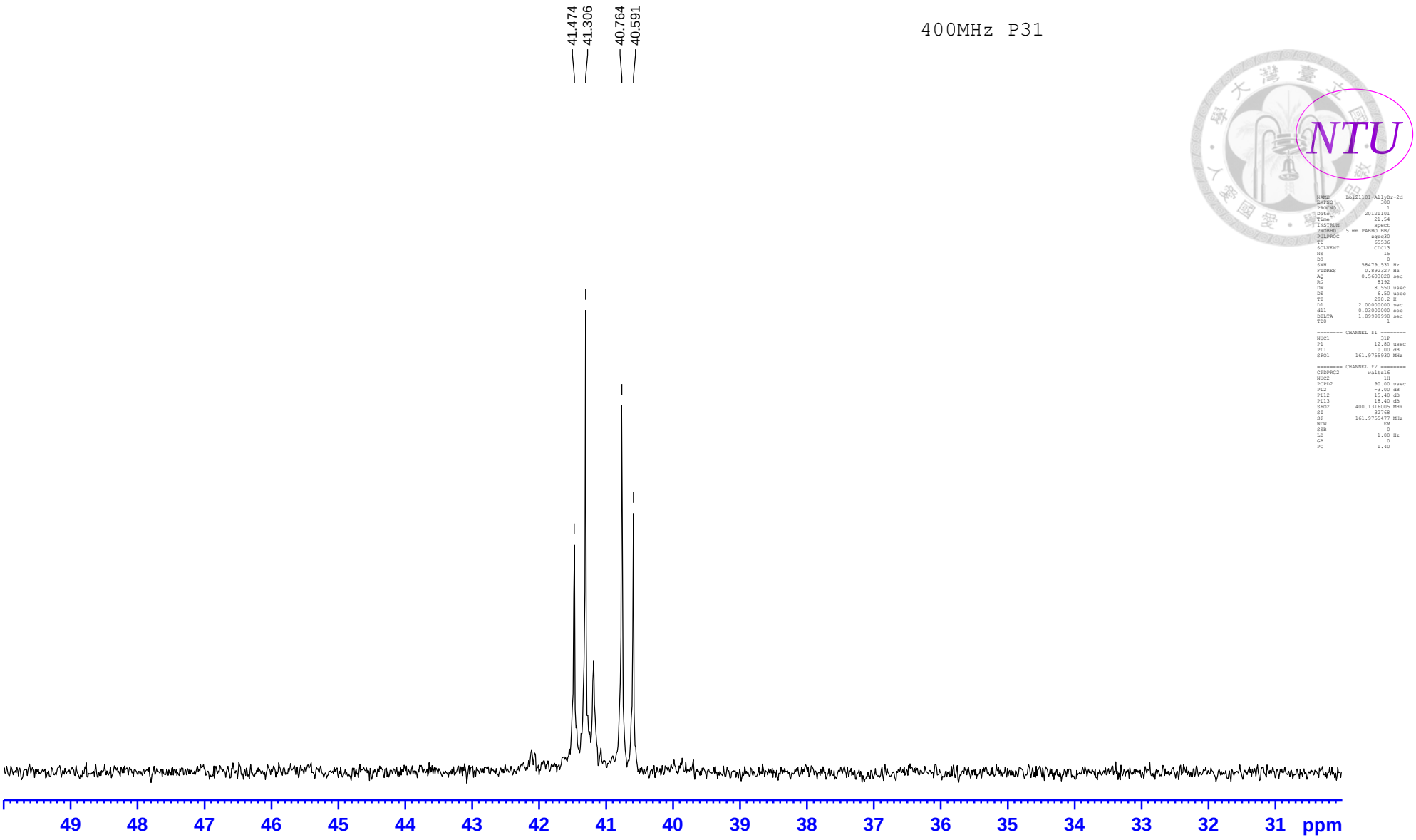

NTU

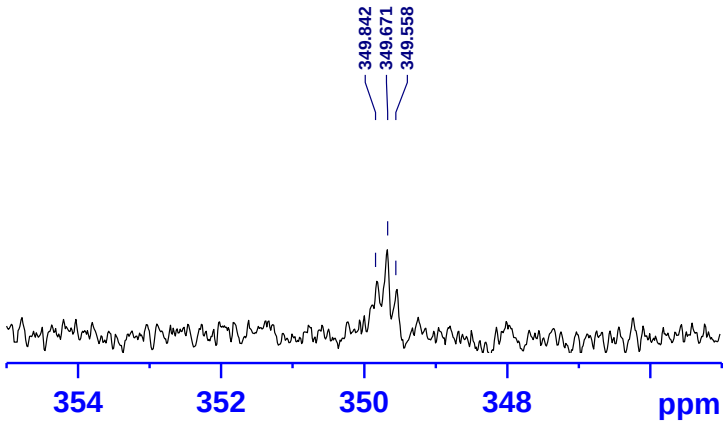

147.493
112.679
85.726
77.288
74.594
70.973
43.211
37.748
36.232
25.311
20.921
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

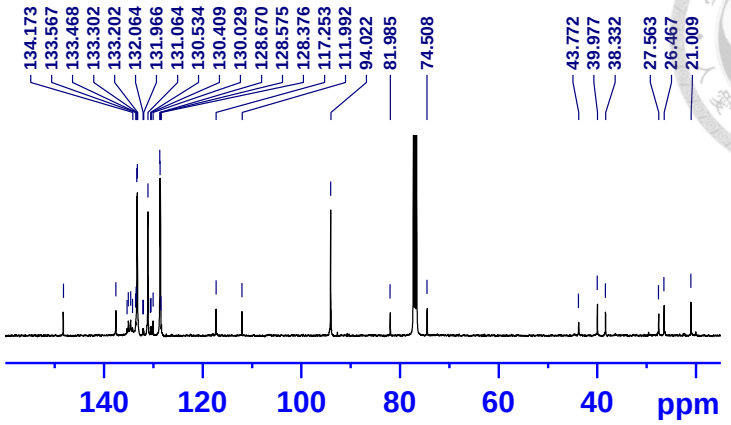

O

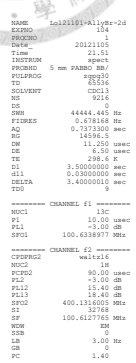
400MHz 1H

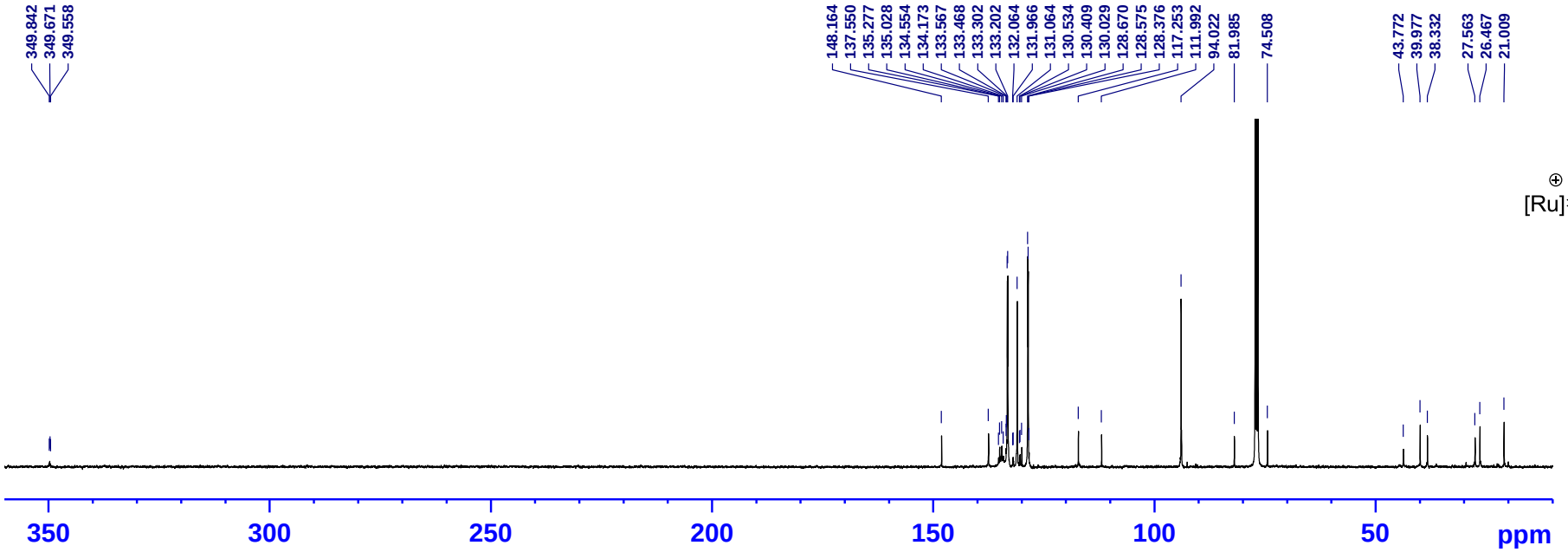

7.6388 7.6291 7.6209 7.6165 7.6114 7.5997 7.5871 7.5825 7.4207 7.4131 7.3653 7.3524 7.3480 7.2373 7.2320 7.2183 7.2132 7.2045 7.1998 7.1868 7.0938 7.0498 7.0078 6.9805 6.9594 6.9232 6.9020 6.7999 6.7945 5.9281 5.9184 5.9125 5.9024 5.8860 5.8603 5.1669 5.1618 5.1584 5.1547 5.1492 5.1440 5.1328 5.1175 5.0833 5.0260 5.0233 4.9835 4.9806 4.6371 4.5594 4.1862 4.1501 3.7701 3.7339 3.2774 3.2467 3.1623 3.1455 3.1206 3.1052 2.7995 2.7845 2.7583 2.7415 2.7103 2.6908 2.6582 2.6259 2.2546 2.2483 2.2297 2.2152 1.0419 0.8368
NTU
NAME Lo121101-Allydc-2d
EXPNO 100
PROCNO 1
Date_ 20121101
Time 21.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 17
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300314 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
[Ru]=C
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
49.13
1.27
8.58
1.28
1.00
1.07
1.08
1.28
1.27
1.28
3.65
2.10
2.97
3.13

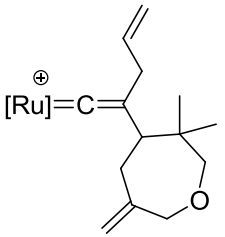

41.474
41.306
40.764
40.591
400MHz P31
NTU
NAME Le121101-AllylBr-2d
EXPNO 350
PROCNO 1
Date_ 20121101
Time 21.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 58479.531 Hz
FIDRES 0.892327 Hz
AQ 0.5603828 sec
RG 8192
DW 8.550 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 31P
P1 12.80 usec
PL1 0.00 dB
SFO1 161.9755930 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.40 dB
PL13 18.40 dB
SFO2 400.1316005 MHz
SI 32768
SF 161.9755477 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
49
48
47
46
45
44
43
42
41
40
39
38
37
36
35
34
33
32
31
ppm


349.842
349.671
349.558
354
352
350
348
ppm

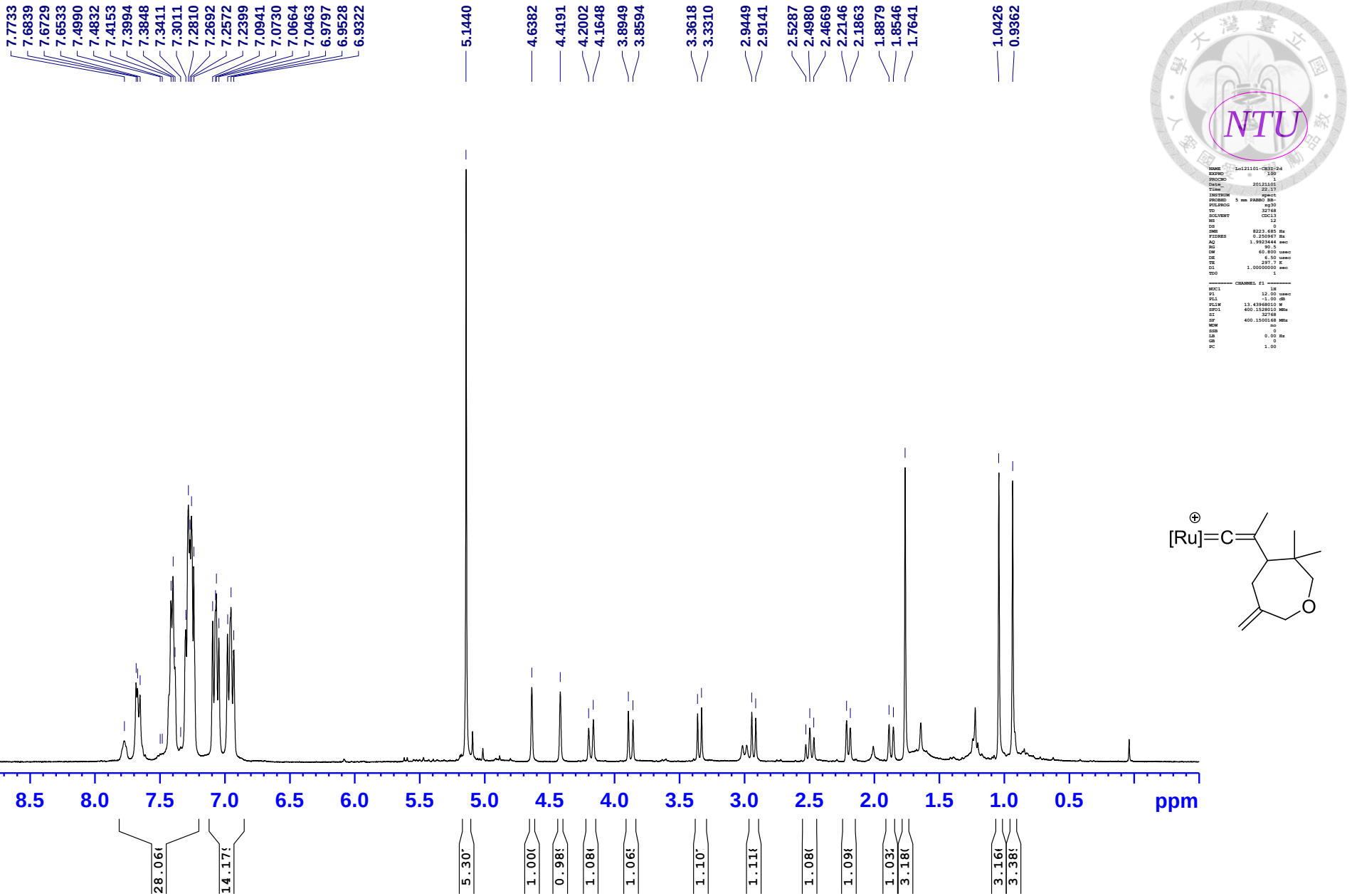

134.173
133.567
133.468
133.302
133.202
132.064
131.966
131.064
130.534
130.409
130.029
128.670
128.575
128.376
117.253
111.992
94.022
81.985
74.508
43.772
39.977
38.332
27.563
26.467
21.009
140
120
100
80
60
40
ppm


NAME Ls121101-AllyBr-2d
EXPNO 104
PROCNO 1
Date_ 20121105
Time_ 21.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 9216
DS 0
SWH 44444.445 Hz
FIDRES 0.678168 Hz
AQ 0.7373300 sec
RG 14596.5
DW 11.250 usec
DE 6.50 usec
TE 298.6 K
D1 3.50000000 sec
d11 0.03000000 sec
DELTA 3.40000010 sec
TD0 9
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.00 dB
SFO1 100.6338977 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.40 dB
PL13 18.40 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127765 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40


349.842
349.671
349.558
148.164
137.550
135.277
135.028
134.554
134.173
133.567
133.468
133.302
133.202
132.064
131.966
131.064
130.534
130.409
130.029
128.670
128.575
128.376
117.253
111.992
94.022
81.985
74.508
43.772
39.977
38.332
27.563
26.467
21.009
350
300
250
200
150
100
50
ppm

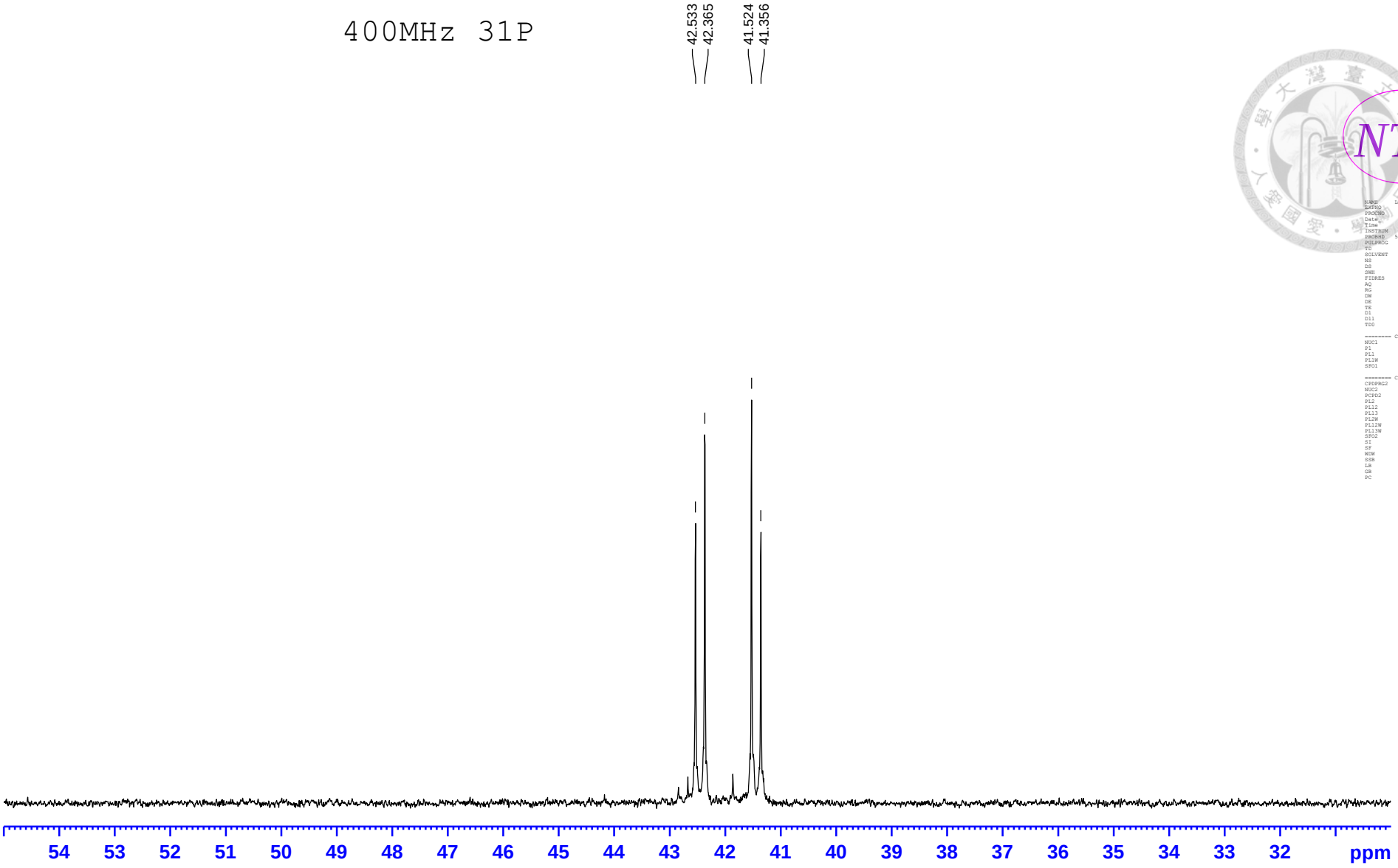

[Ru]=C
O

400MHz 1H



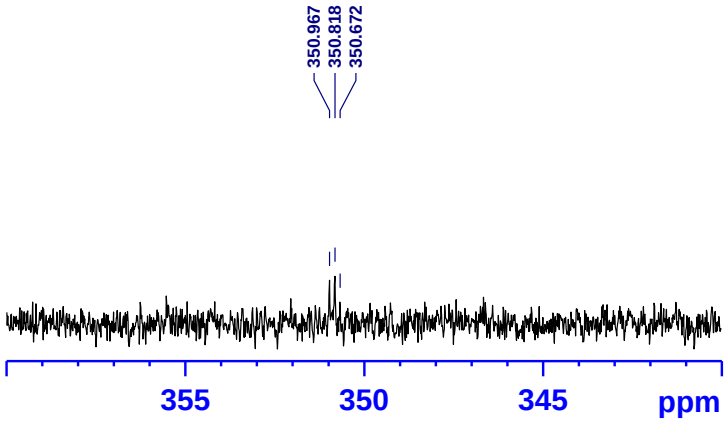

```
NAME        Lo121101-CH31-2d
EXPNO             100
PROCNO              1
Date_          20121101
Time              22.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD               32768
SOLVENT          CDCl3
NS                  12
DS                   0
SWH           8223.685 Hz
FIDRES        0.250967 Hz
AQ            1.9923444 sec
RG                90.5
DW               60.800 usec
DE                6.50 usec
TE              297.7 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                12.00 usec
PL1               -1.00 dB
PL1W        13.43968010 W
SFO1        400.1528010 MHz
SI               32768
SF          400.1500168 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00
```

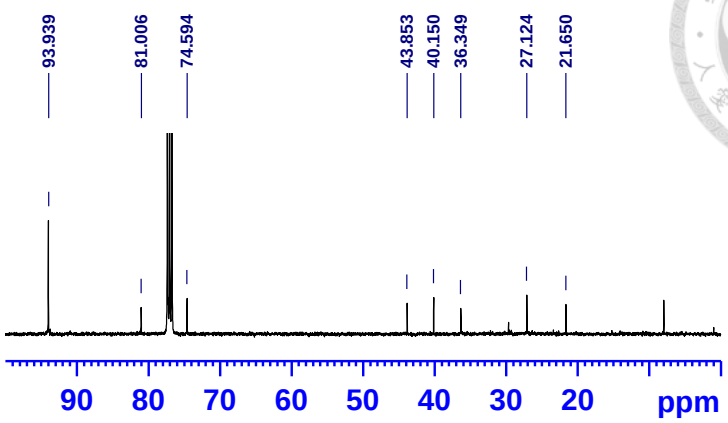
400MHz 31P



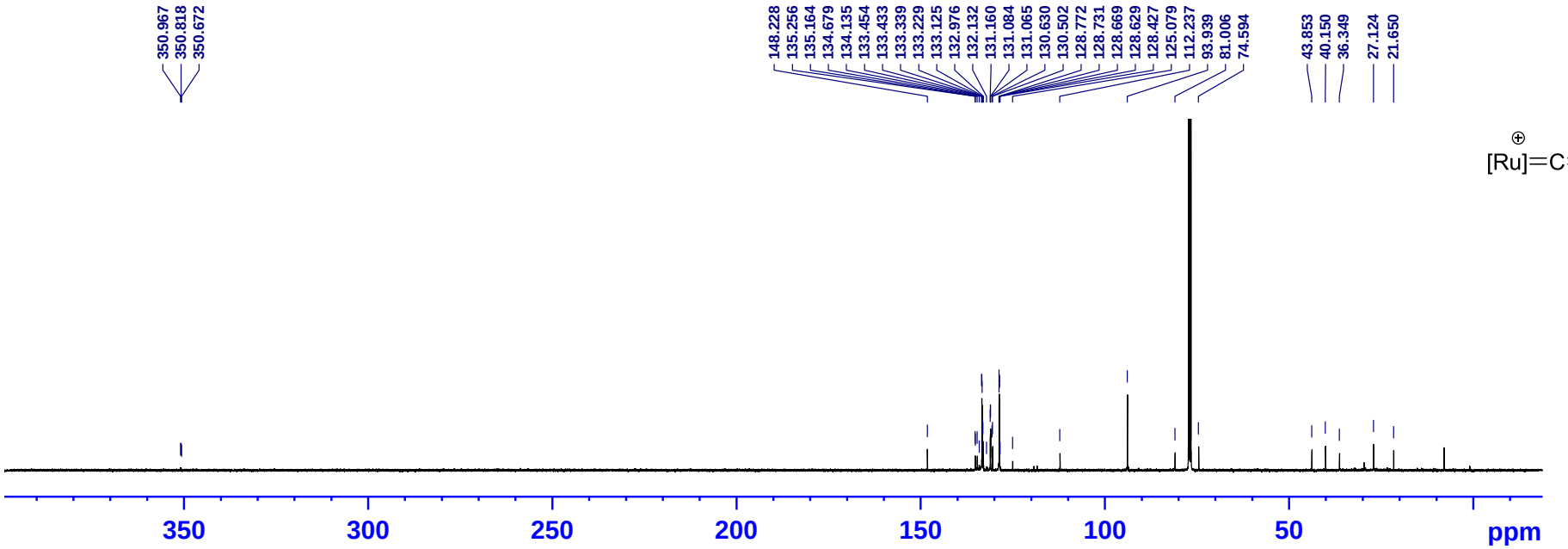

```
NAME                 Le121101-CH3I-2d
EXPNO                             300
PROCNO                              1
Date_                        20121101
Time                            22.14
INSTRUM                         spect
PROBHD     5 mm PABBO BB-
PULPROG                         zgpg30
TD                              65536
SOLVENT                         CDCl3
NS                                 42
DS                                  0
SWH                         64102.563 Hz
FIDRES                      0.978127 Hz
AQ                          0.5112308 sec
RG                                2050
DW                           7.800 usec
DE                           6.50 usec
TE                             297.4 K
D1                       2.00000000 sec
D11                      0.03000000 sec
TD0                                 1

======== CHANNEL f1 ========
NUC1                              31P
P1                           14.10 usec
PL1                           4.00 dB
PL1W                     9.06000042 W
SFO1                   161.9755900 MHz

======== CHANNEL f2 ========
CPDPRG2                       waltz16
NUC2                              1H
PCPD2                        80.00 usec
PL2                          -1.00 dB
PL12                         15.50 dB
PL13                         18.50 dB
PL2W                    13.43968010 W
PL12W                    0.3008769
PL13W                    0.1507956
SFO2                   400.1516006 MHz
SI                                65536
SF                     161.9836890 MHz
WDW                               EM
SSB                                0
LB                            1.00 Hz
GB                                 0
PC                              1.40
```

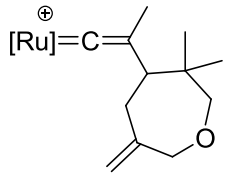
400MHz 13C


350.967
350.818
350.672
355
350
345
ppm

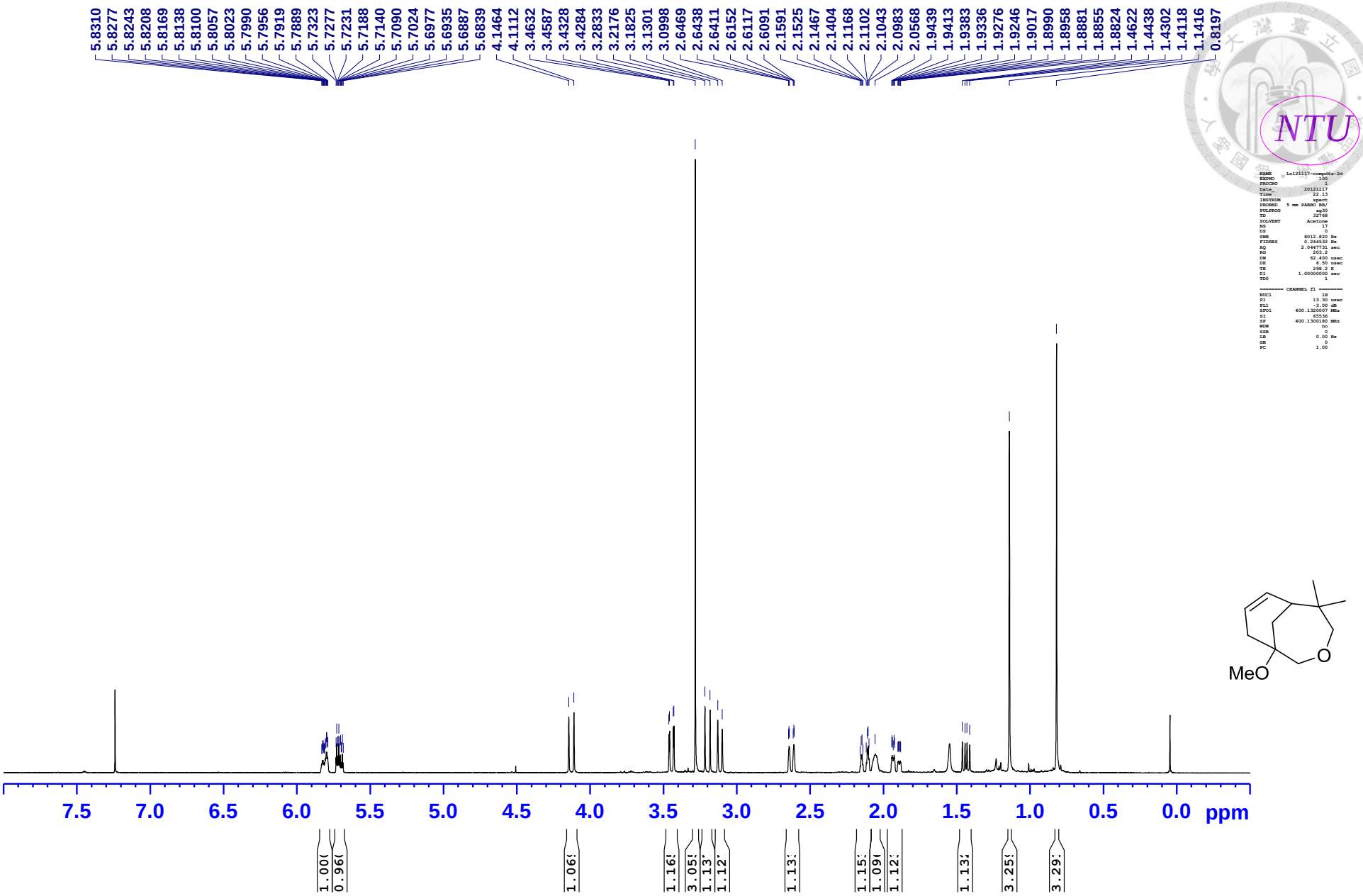

93.939
81.006
74.594
43.853
40.150
36.349
27.124
21.650
90
80
70
60
50
40
30
20
ppm

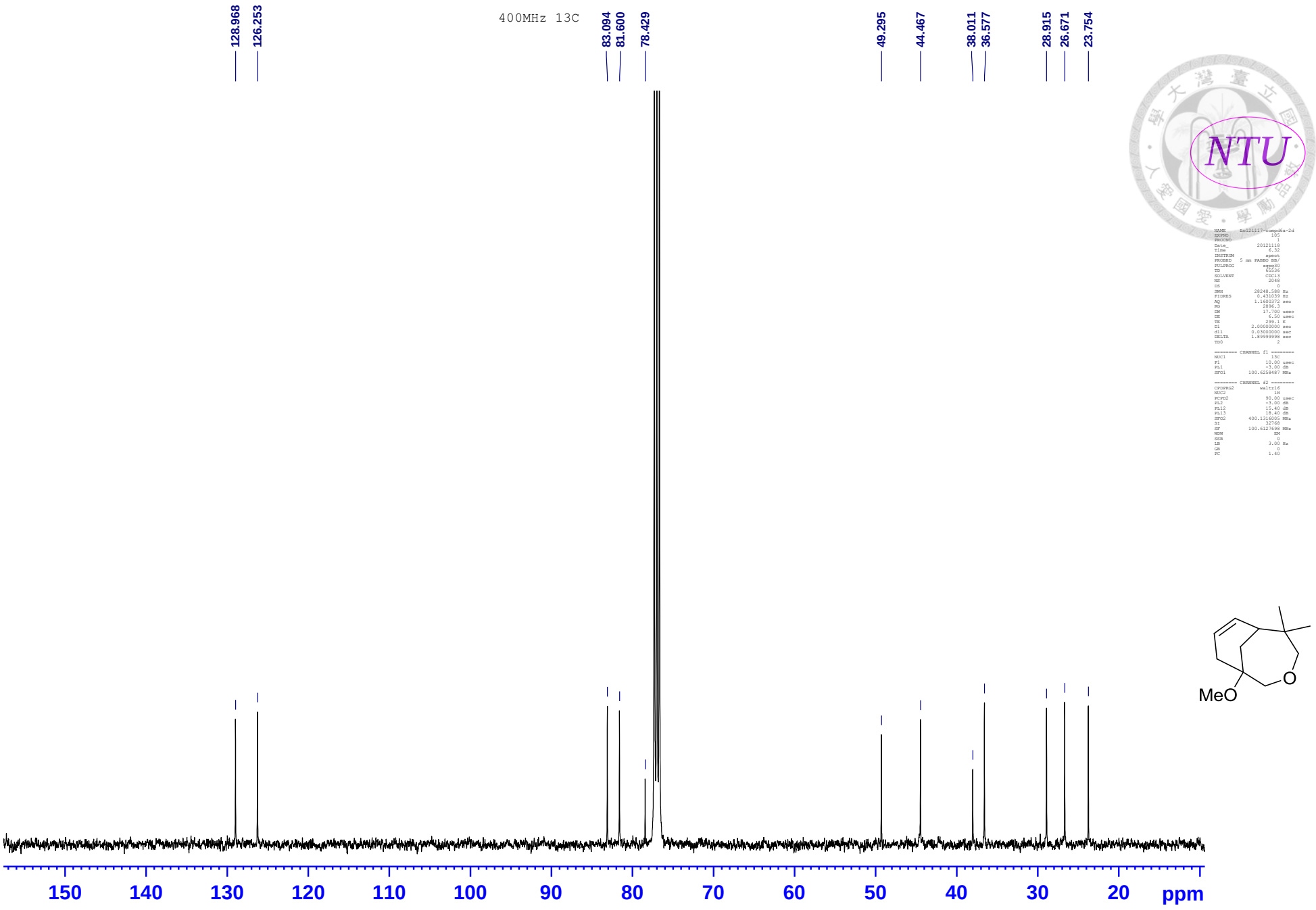

NTU


350.967
350.818
350.672
148.228
135.256
135.164
134.679
134.135
133.454
133.433
133.339
133.229
133.125
132.976
132.132
131.160
131.084
131.065
130.630
130.502
128.772
128.731
128.669
128.629
128.427
125.079
112.237
93.939
81.006
74.594
43.853
40.150
36.349
27.124
21.650
350
300
250
200
150
100
50
ppm

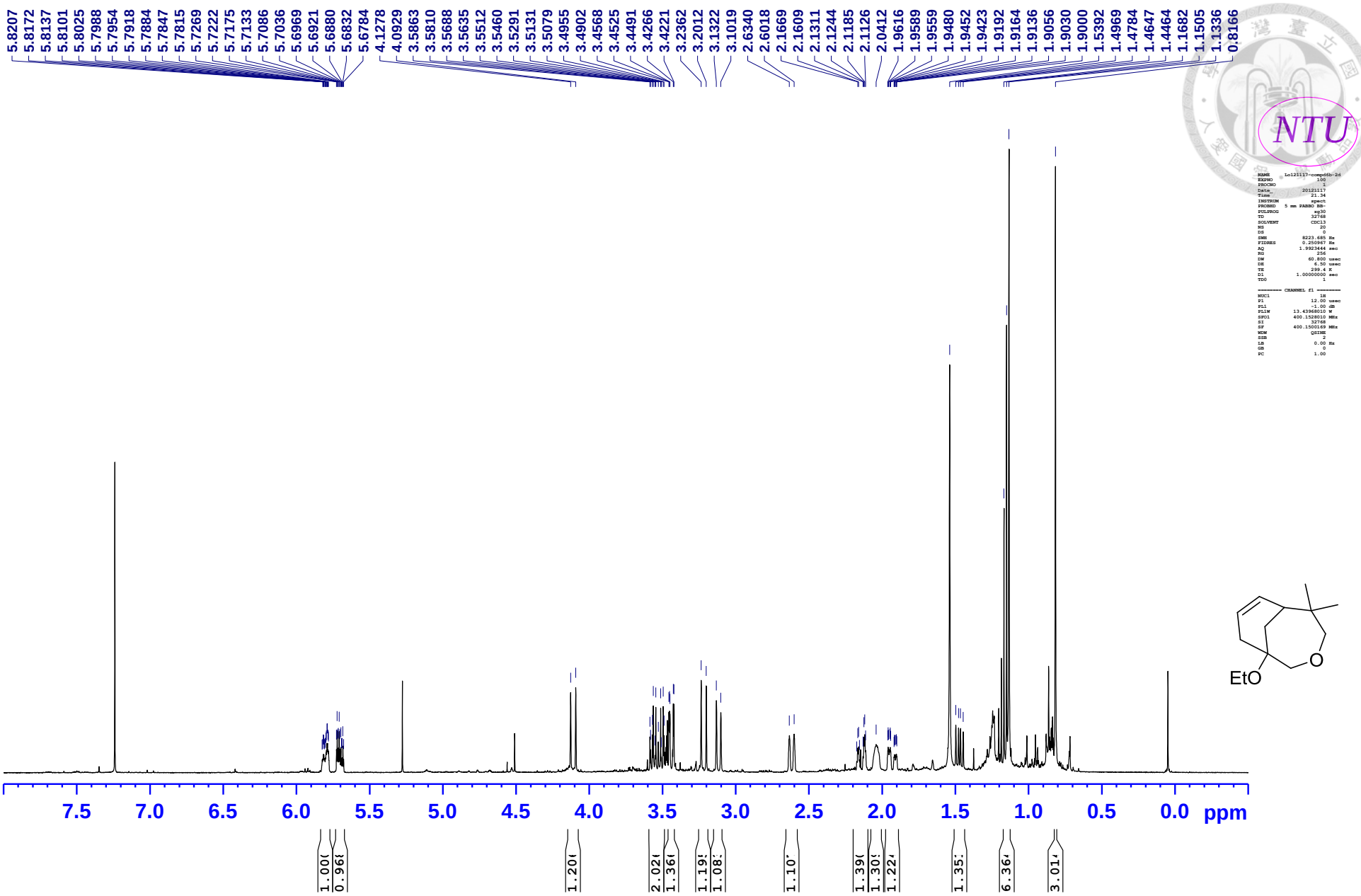

[Ru]=C
O

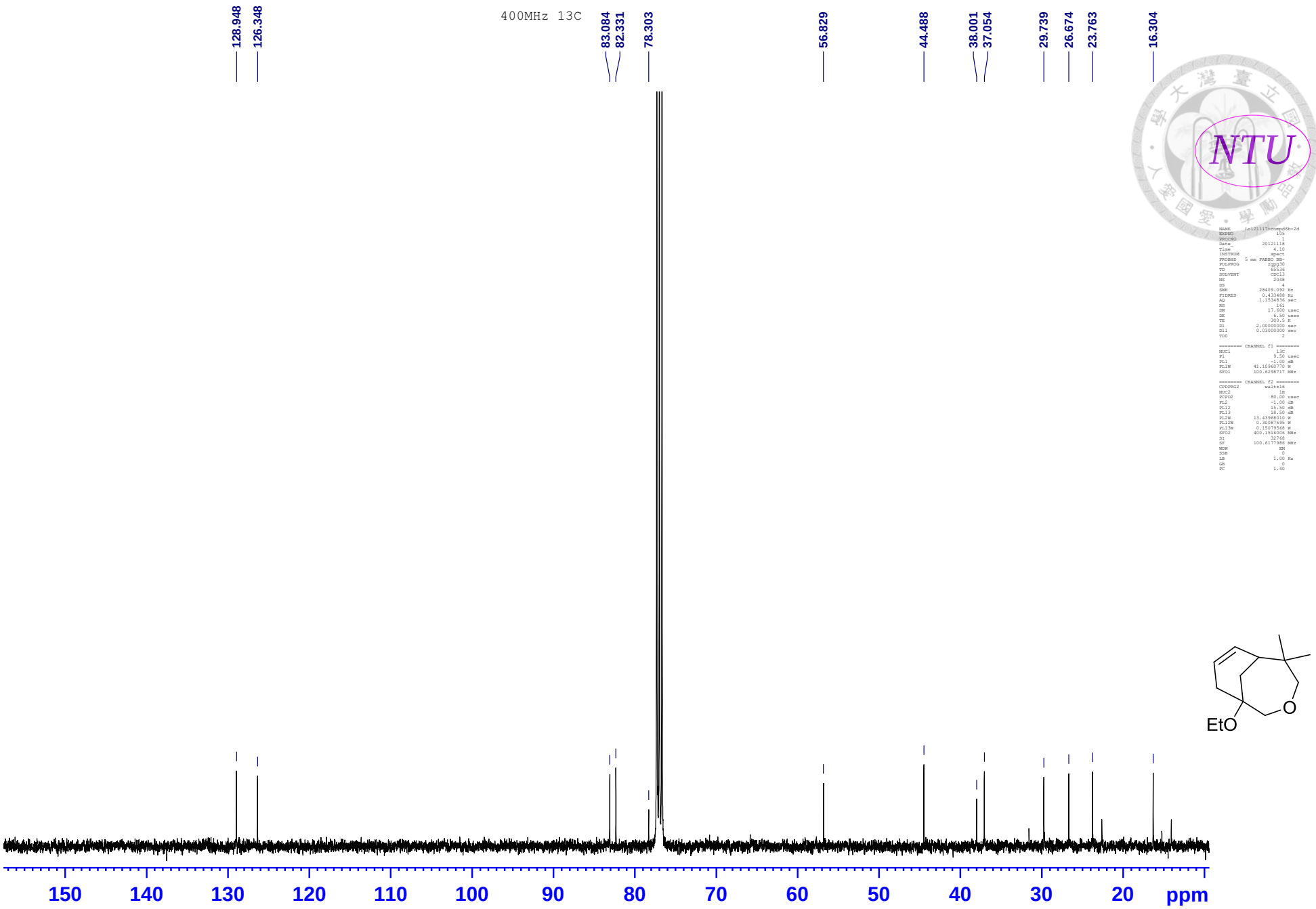
400MHz 1H


5.8310 5.8277 5.8243 5.8208 5.8169 5.8138 5.8100 5.8057 5.8023 5.7990 5.7956 5.7919 5.7889 5.7323 5.7277 5.7231 5.7188 5.7140 5.7090 5.7024 5.6977 5.6935 5.6887 5.6839 4.1464 4.1112 3.4632 3.4587 3.4328 3.4284 3.2833 3.2176 3.1825 3.1301 3.0998 2.6469 2.6438 2.6411 2.6152 2.6117 2.6091 2.1591 2.1525 2.1467 2.1404 2.1168 2.1102 2.1043 2.0983 2.0568 1.9439 1.9413 1.9383 1.9336 1.9276 1.9246 1.9017 1.8990 1.8958 1.8881 1.8855 1.8824 1.4622 1.4438 1.4302 1.4118 1.1416 0.8197
NAME Lo121117-compd6a-2d
EXPNO 100
PROCNO 1
Date_ 20121117
Time_ 22.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 17
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 203.2
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300180 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
MeO
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 0.96 1.06 1.16 3.05 1.13 1.12 1.13 1.15 1.09 1.12 1.13 3.25 3.29

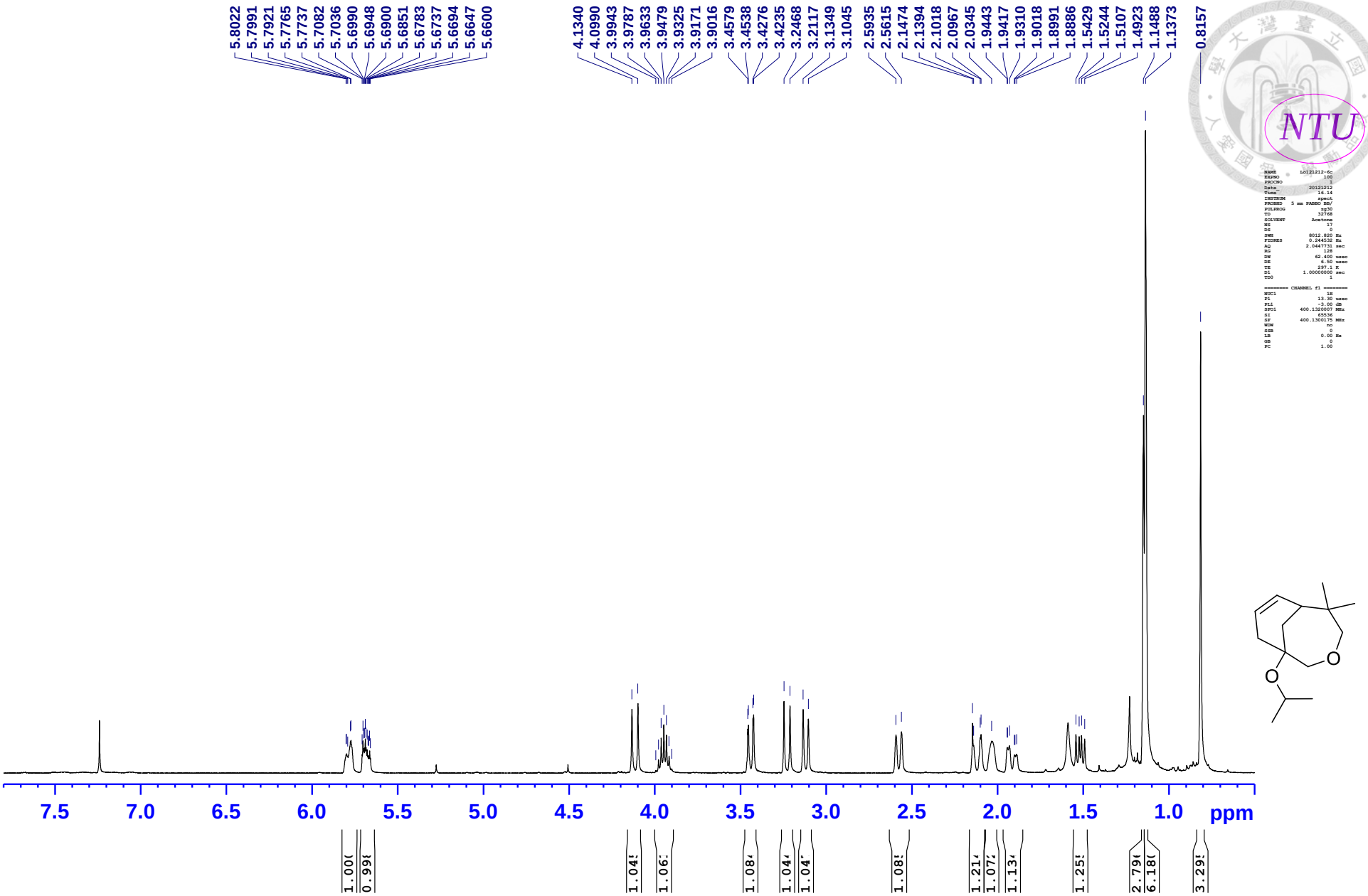

400MHz 13C
128.968
126.253
83.094
81.600
78.429
49.295
44.467
38.011
36.577
28.915
26.671
23.754
NTU
MeO
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

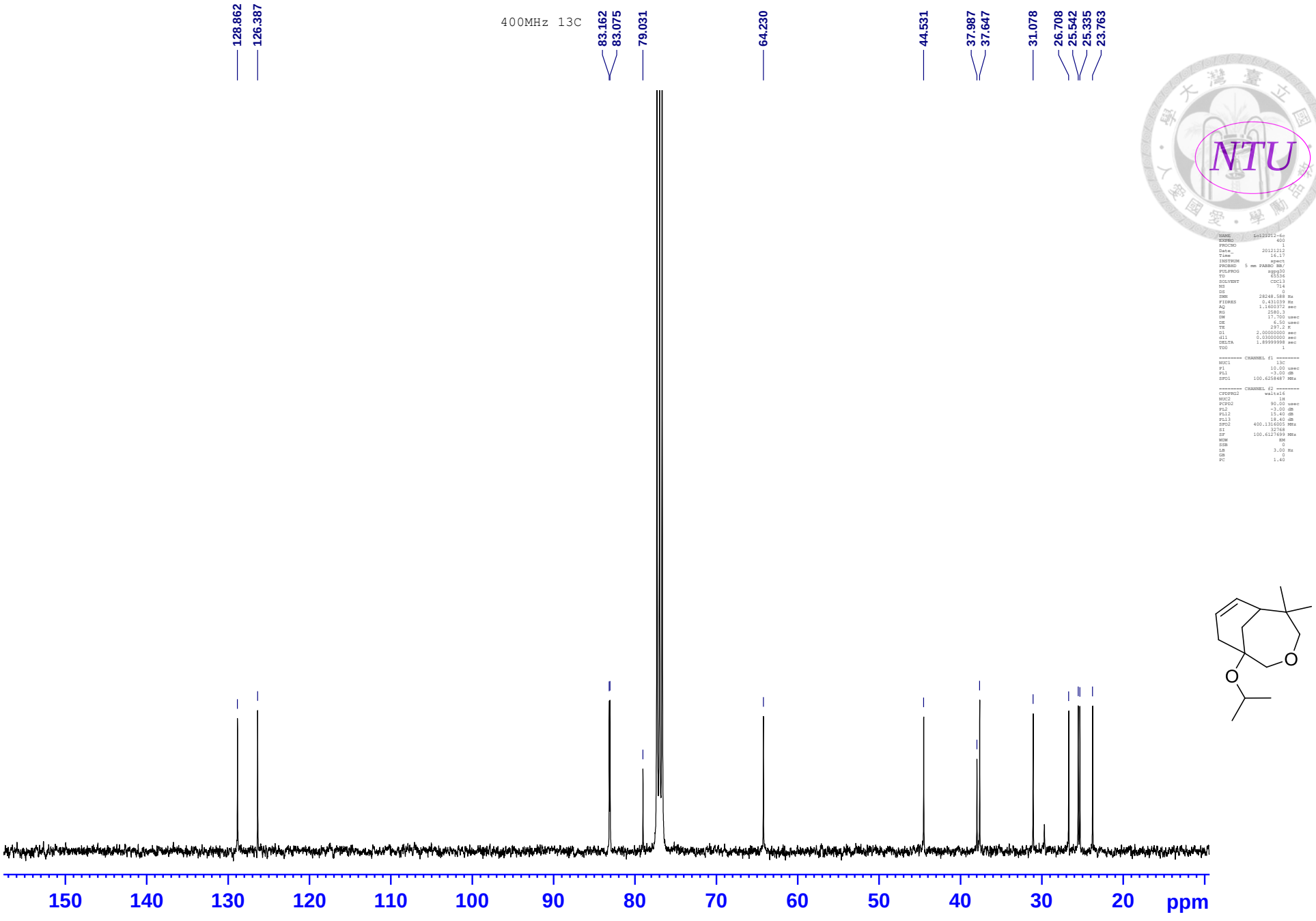
400MHz 1H


5.8207 5.8172 5.8137 5.8101 5.8025 5.7988 5.7954 5.7918 5.7884 5.7847 5.7815 5.7269 5.7222 5.7175 5.7133 5.7086 5.7036 5.6969 5.6921 5.6880 5.6832 5.6784 4.1278 4.0929 3.5863 3.5810 3.5688 3.5635 3.5512 3.5460 3.5291 3.5131 3.5079 3.4955 3.4902 3.4568 3.4525 3.4491 3.4266 3.4221 3.2362 3.2012 3.1322 3.1019 2.6340 2.6018 2.1669 2.1609 2.1311 2.1244 2.1185 2.1126 2.0412 1.9616 1.9589 1.9559 1.9480 1.9452 1.9423 1.9192 1.9164 1.9136 1.9056 1.9030 1.9000 1.5392 1.4969 1.4784 1.4647 1.4464 1.1682 1.1505 1.1336 0.8166
NAME Lo121117-compd6b-2d
EXPNO 100
PROCNO 1
Date_ 20121117
Time_ 21.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 20
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 256
DW 60.800 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.00 dB
PL1W 13.43968010 W
SFO1 400.1528010 MHz
SI 32768
SF 400.1500169 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 0.96 1.20 2.02 1.36 1.19 1.08 1.10 1.39 1.30 1.22 1.35 6.36 3.01
EtO
O

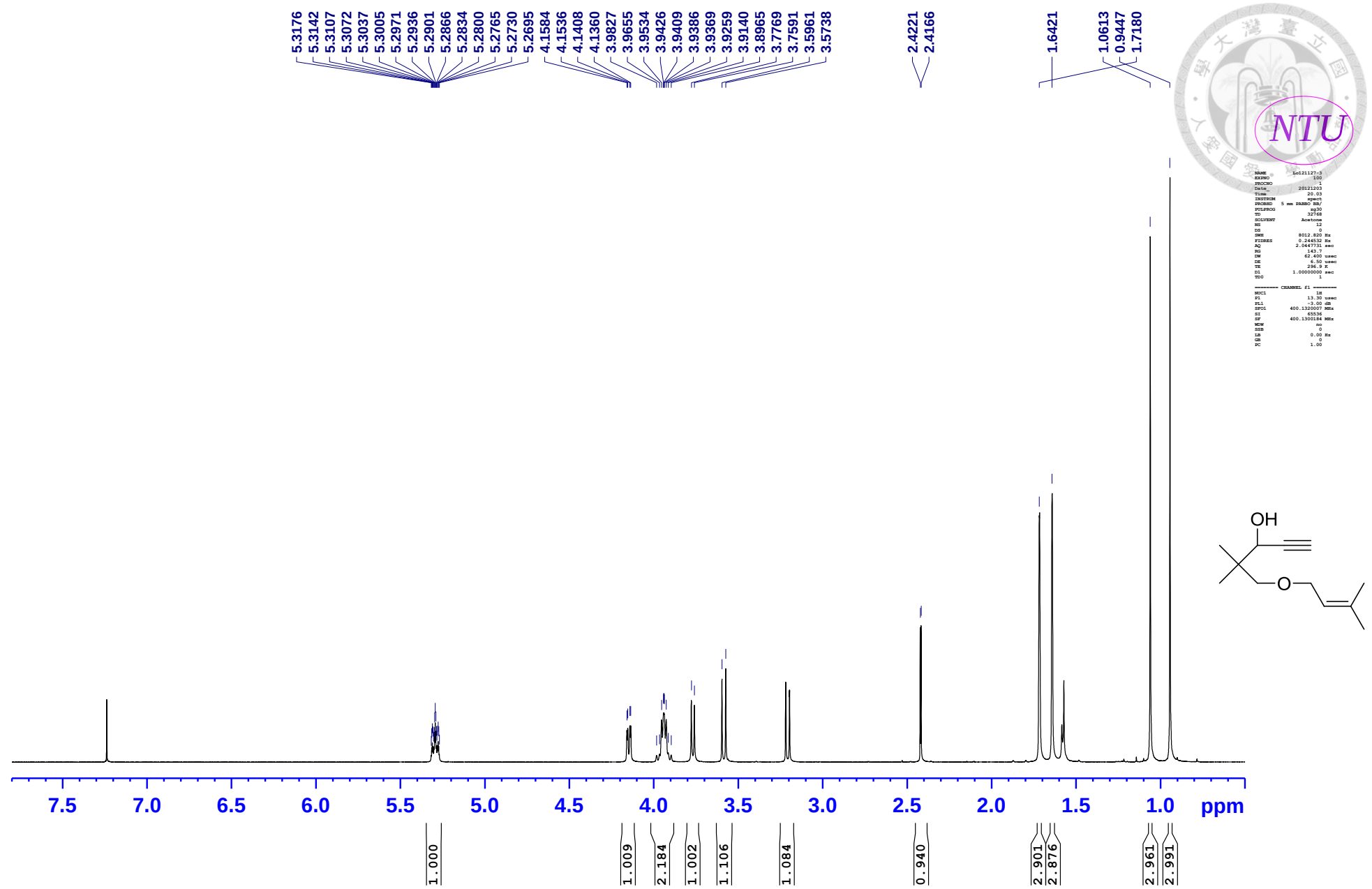

400MHz 13C
128.948
126.348
83.084
82.331
78.303
56.829
44.488
38.001
37.054
29.739
26.674
23.763
16.304
NAME Le121117-compd6b-2d
EXPNO 105
PROCNO 1
Date_ 20121118
Time 4.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 28409.092 Hz
FIDRES 0.433488 Hz
AQ 1.1534836 sec
RG 161
DW 17.600 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 2
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 +1.00 dB
PL1W 41.10960770 W
SFO1 100.6298717 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 +1.00 dB
PL12 15.50 dB
PL13 18.50 dB
PL2W 13.43968010 W
PL12W 0.30087695 W
PL13W 0.15079568 W
SFO2 400.1516006 MHz
SI 32768
SF 100.6177986 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
EtO
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

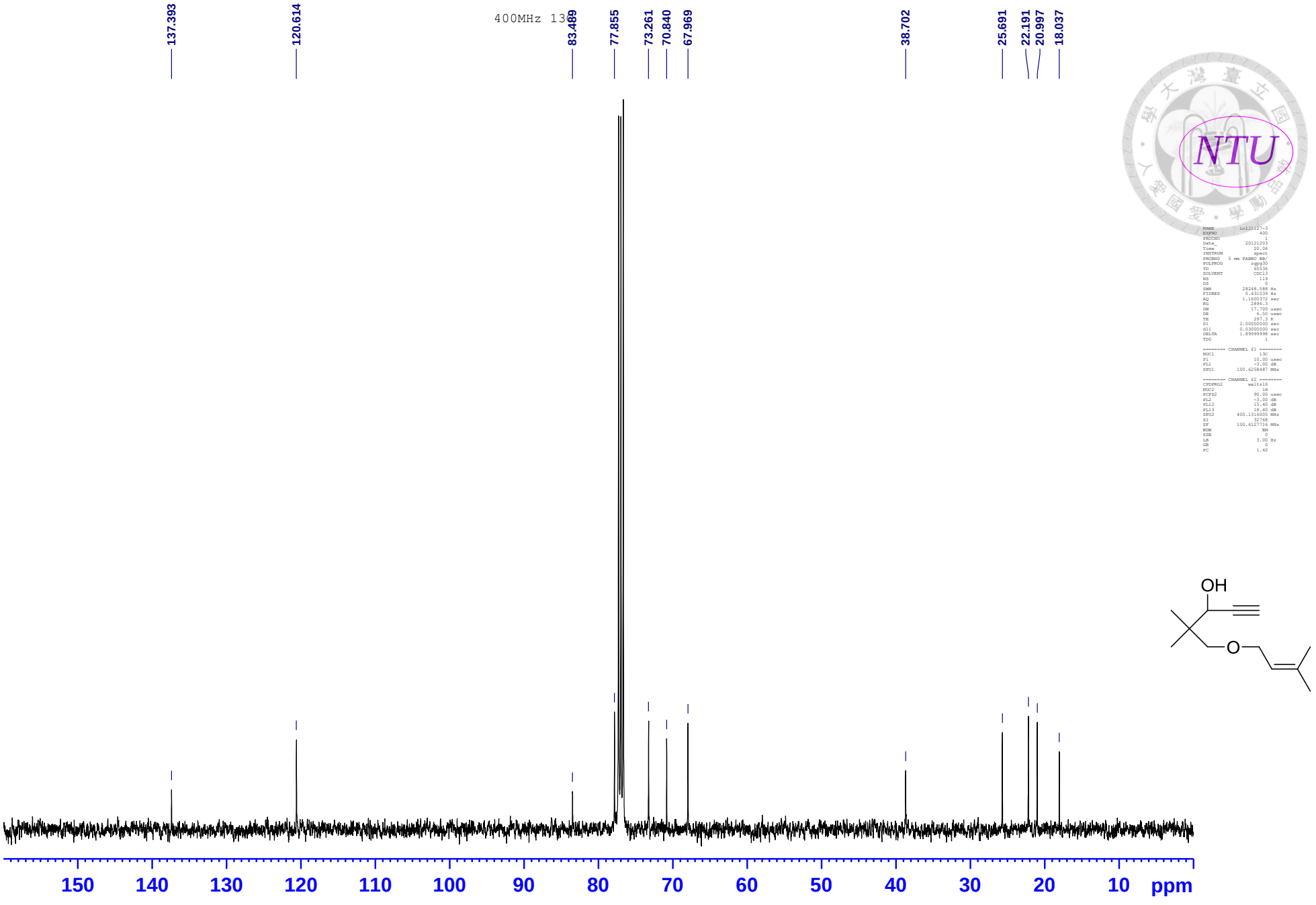
400MHz 1H


5.8022
5.7991
5.7921
5.7765
5.7737
5.7082
5.7036
5.6990
5.6948
5.6900
5.6851
5.6783
5.6737
5.6694
5.6647
5.6600
4.1340
4.0990
3.9943
3.9787
3.9633
3.9479
3.9325
3.9171
3.9016
3.4579
3.4538
3.4276
3.4235
3.2468
3.2117
3.1349
3.1045
2.5935
2.5615
2.1474
2.1394
2.1018
2.0967
2.0345
1.9443
1.9417
1.9310
1.9018
1.8991
1.8886
1.5429
1.5244
1.5107
1.4923
1.1488
1.1373
0.8157
NTU
NAME Lo121212-6c
EXPNO 100
PROCNO 1
Date_ 20121212
Time_ 16.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 17
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 128
DW 62.400 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
1.04
1.06
1.08
1.04
1.04
1.08
1.21
1.07
1.13
1.25
2.79
6.18
3.29
O
O

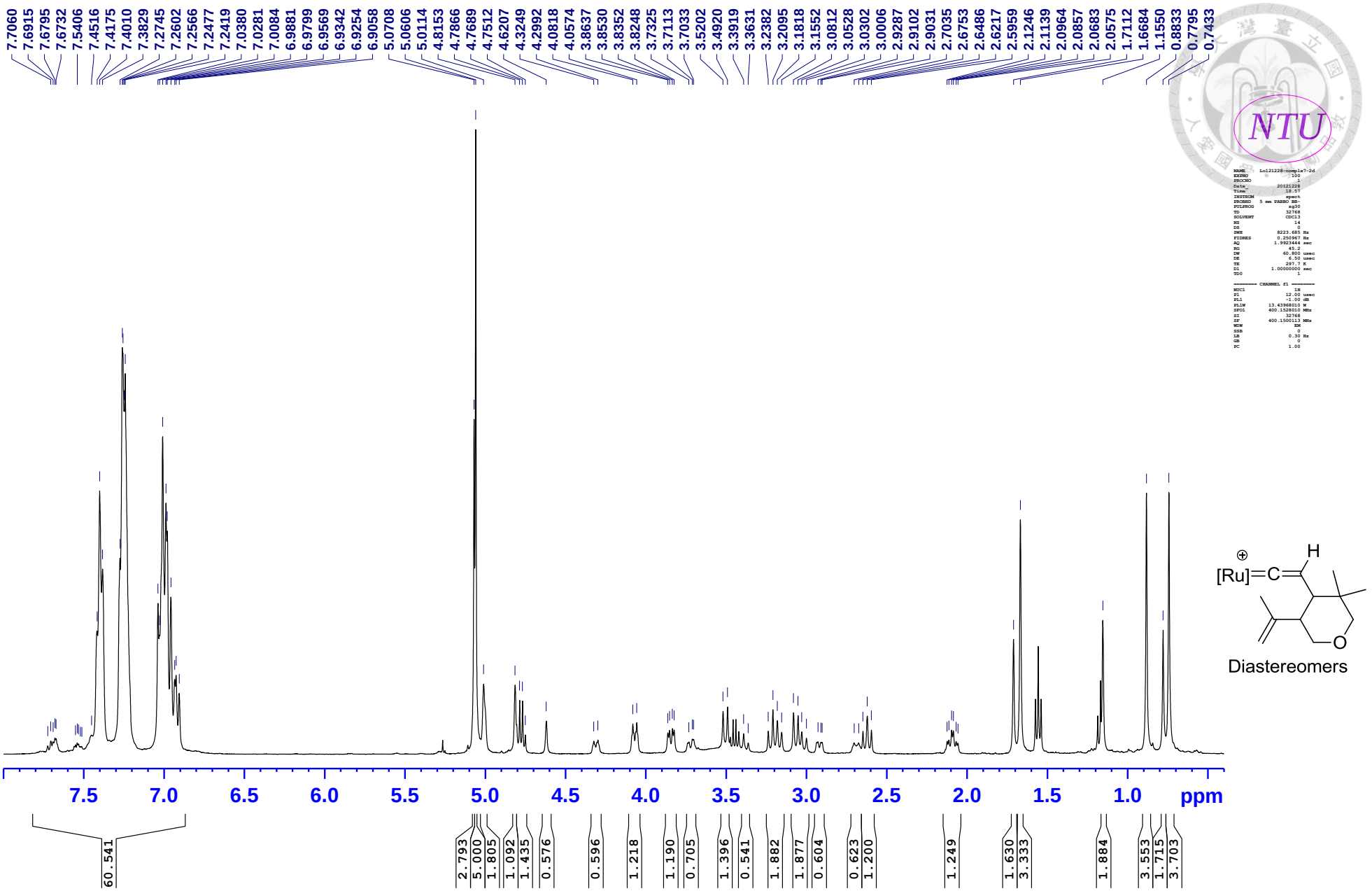

400MHz 13C
128.862
126.387
83.162
83.075
79.031
64.230
44.531
37.987
37.647
31.078
26.708
25.542
25.335
23.763
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

400MHz 1H


5.3176
5.3142
5.3107
5.3072
5.3037
5.3005
5.2971
5.2936
5.2901
5.2866
5.2834
5.2800
5.2765
5.2730
5.2695
4.1584
4.1536
4.1408
4.1360
3.9827
3.9655
3.9534
3.9426
3.9409
3.9386
3.9369
3.9259
3.9140
3.8965
3.7769
3.7591
3.5961
3.5738
2.4221
2.4166
1.6421
1.0613
0.9447
1.7180
NTU
NAME 1o121127-3
EXPNO 100
PROCNO 1
Date_ 20121203
Time 20.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 12
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 143.7
DW 62.400 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300184 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
OH
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.000
1.009
2.184
1.002
1.106
1.084
0.940
2.901
2.876
2.961
2.991

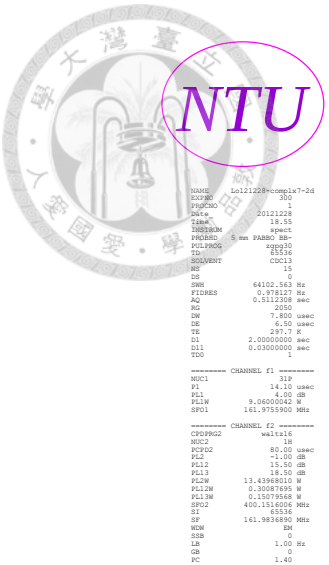

400MHz 13
137.393
120.614
83.489
77.855
73.261
70.840
67.969
38.702
25.691
22.191
20.997
18.037
NTU
OH
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

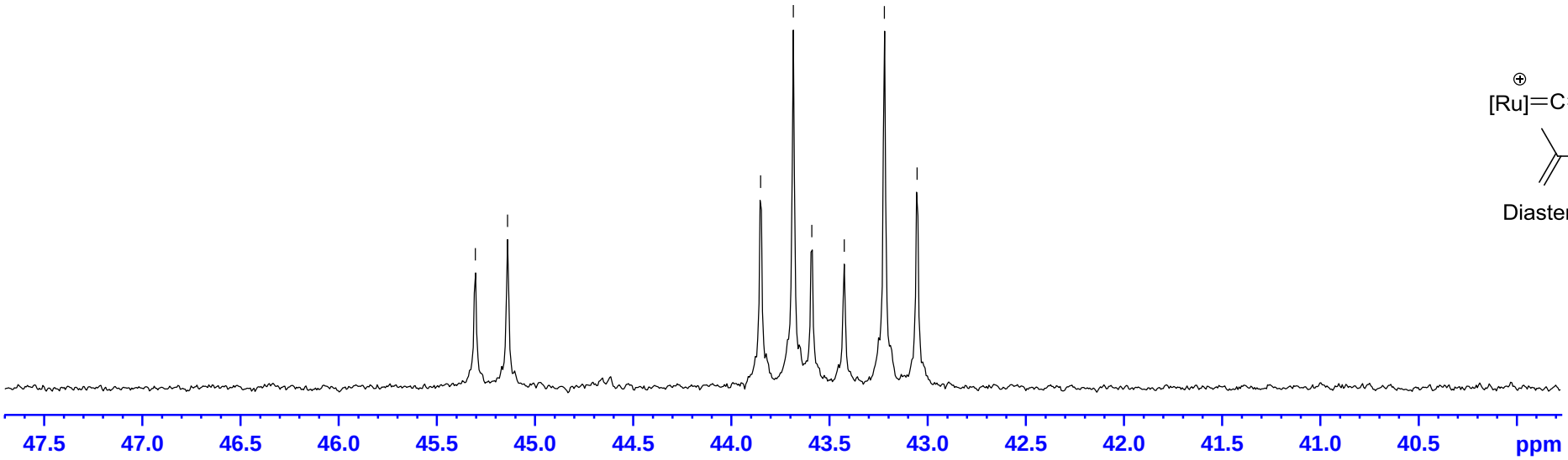
400MHz 1H

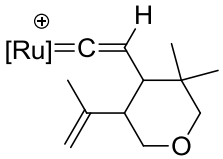

7.7060 7.6915 7.6795 7.6732 7.5406 7.4516 7.4175 7.4010 7.3829 7.2745 7.2602 7.2566 7.2477 7.2419 7.0380 7.0281 7.0084 6.9881 6.9799 6.9569 6.9342 6.9254 6.9058 5.0708 5.0606 5.0114 4.8153 4.7866 4.7689 4.7512 4.6207 4.3249 4.2992 4.0818 4.0574 3.8637 3.8530 3.8352 3.8248 3.7325 3.7113 3.7033 3.5202 3.4920 3.3919 3.3631 3.2382 3.2095 3.1818 3.1552 3.0812 3.0528 3.0302 3.0006 2.9287 2.9102 2.9031 2.7035 2.6753 2.6486 2.6217 2.5959 2.1246 2.1139 2.0964 2.0857 2.0683 2.0575 1.7112 1.6684 1.1550 0.8833 0.7795 0.7433
NTU
NAME Lo121228-comp1x7-2d
EXPNO 100
PROCNO 1
Date_ 20121228
Time_ 18.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 14
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 45.2
DW 60.800 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.00 dB
PLW 13.43968010 W
SFO1 400.1528010 MHz
SI 32768
SF 400.1500113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
[Ru]=C
H
O
Diastereomers
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
60.541
2.793 5.000 1.805 1.092 1.435 0.576 0.596 1.218 1.190 0.705 1.396 0.541 1.882 1.877 0.604 0.623 1.200 1.249 1.630 3.333 1.884 3.553 1.715 3.703

45.304
45.140
43.851
43.685
43.591
43.426
43.220
43.055

400MHz 31P

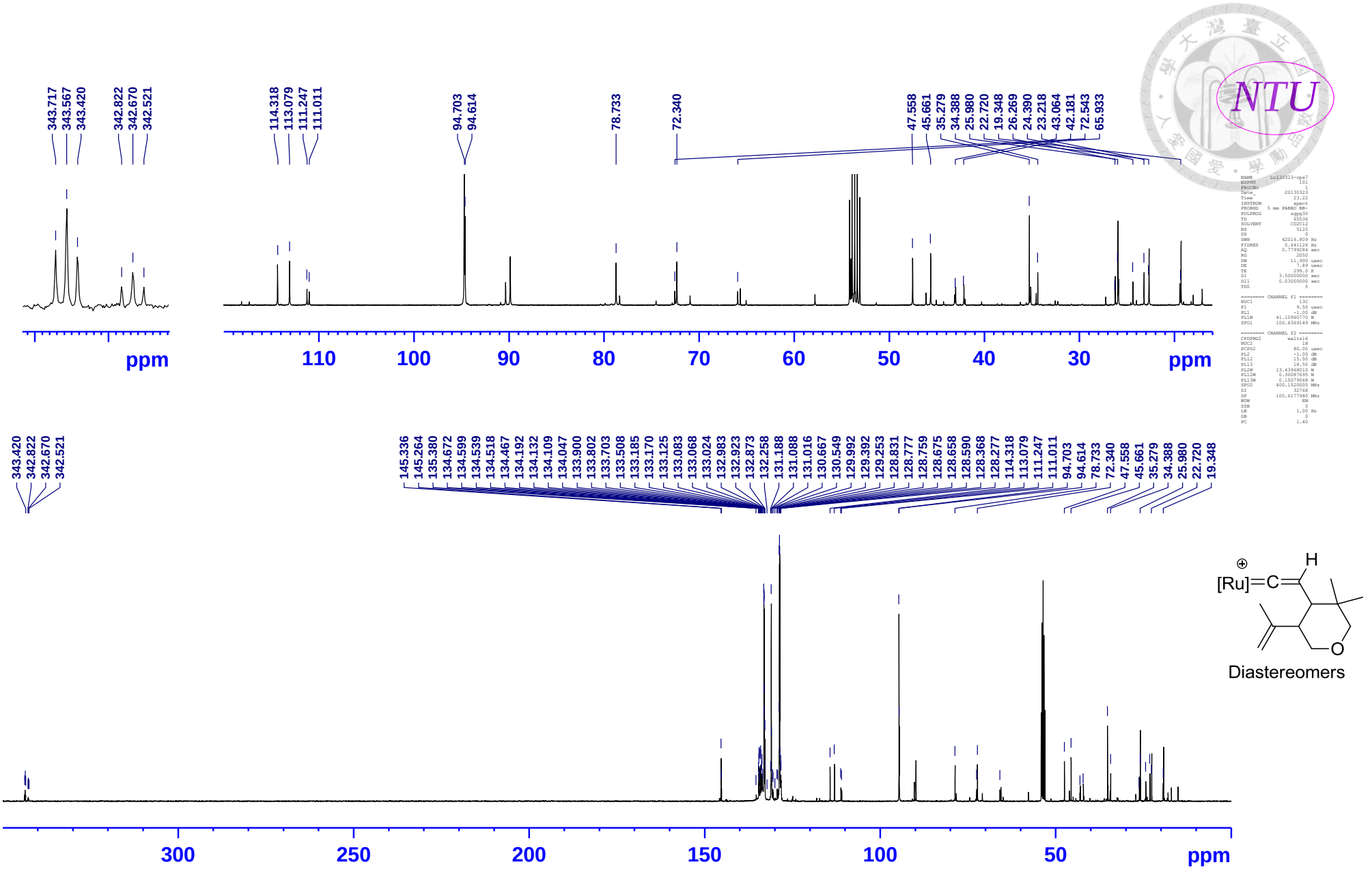






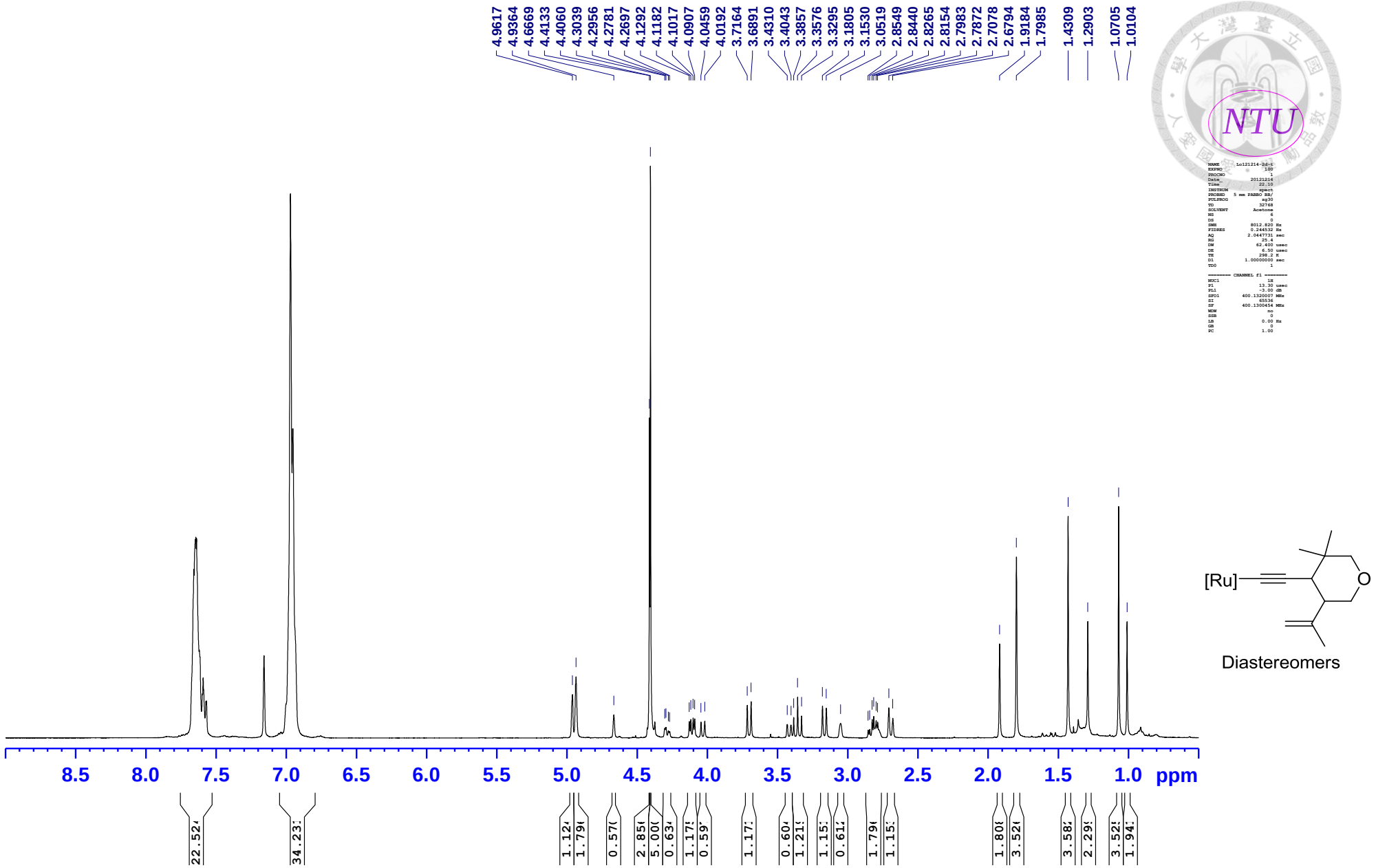
Diastereomers

400MHz 13C



Diastereomers

400MHz 1H

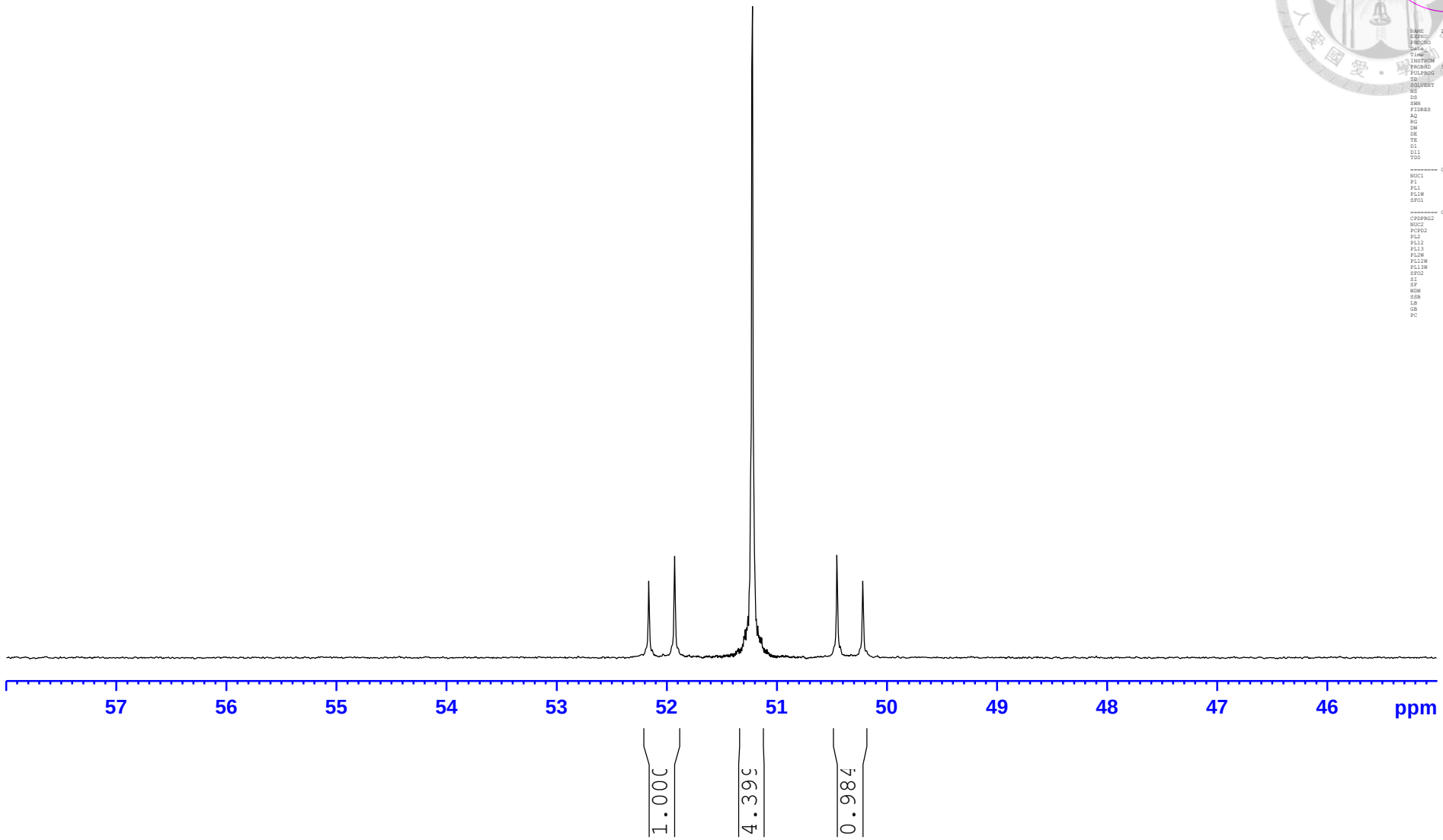


NTU

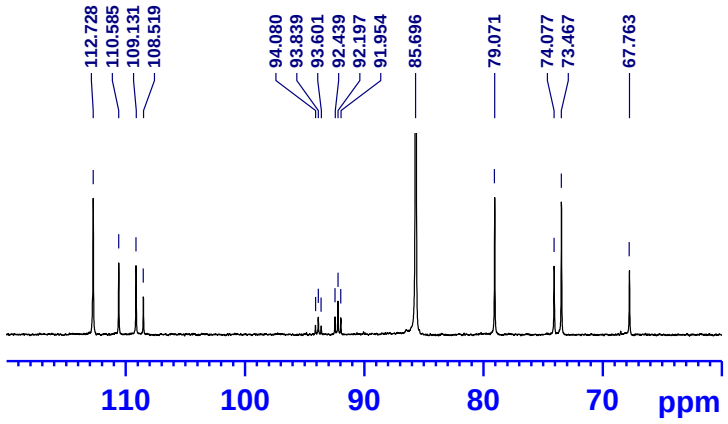
NAME Lo121214-2d-c
EXPNO 100
PROCNO 1
Date_ 20121214
Time 22.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 6
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 25.4
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300454 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

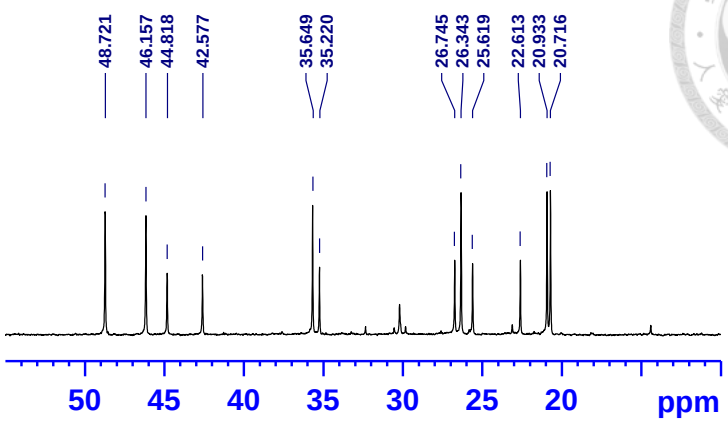
Diastereomers

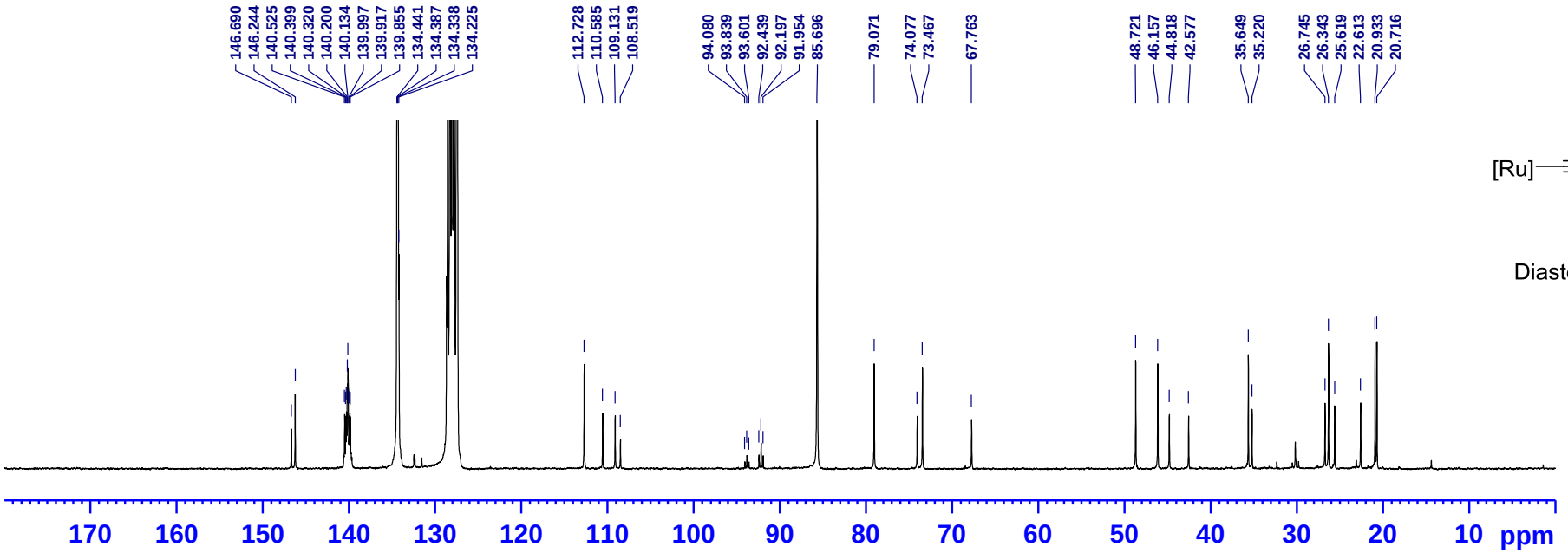
400MHz 31P

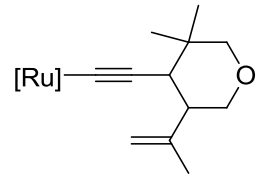


400MHz 13C



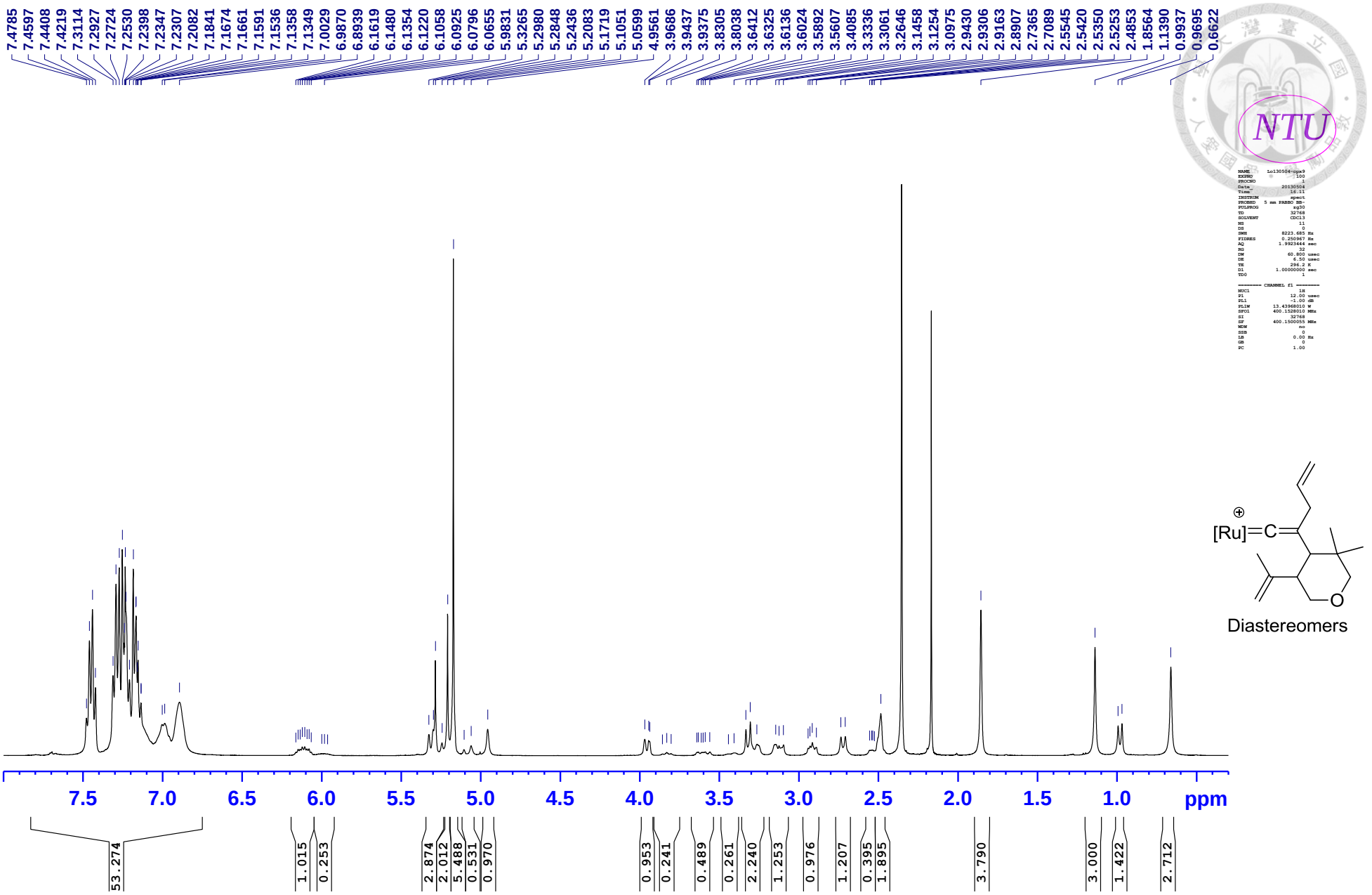




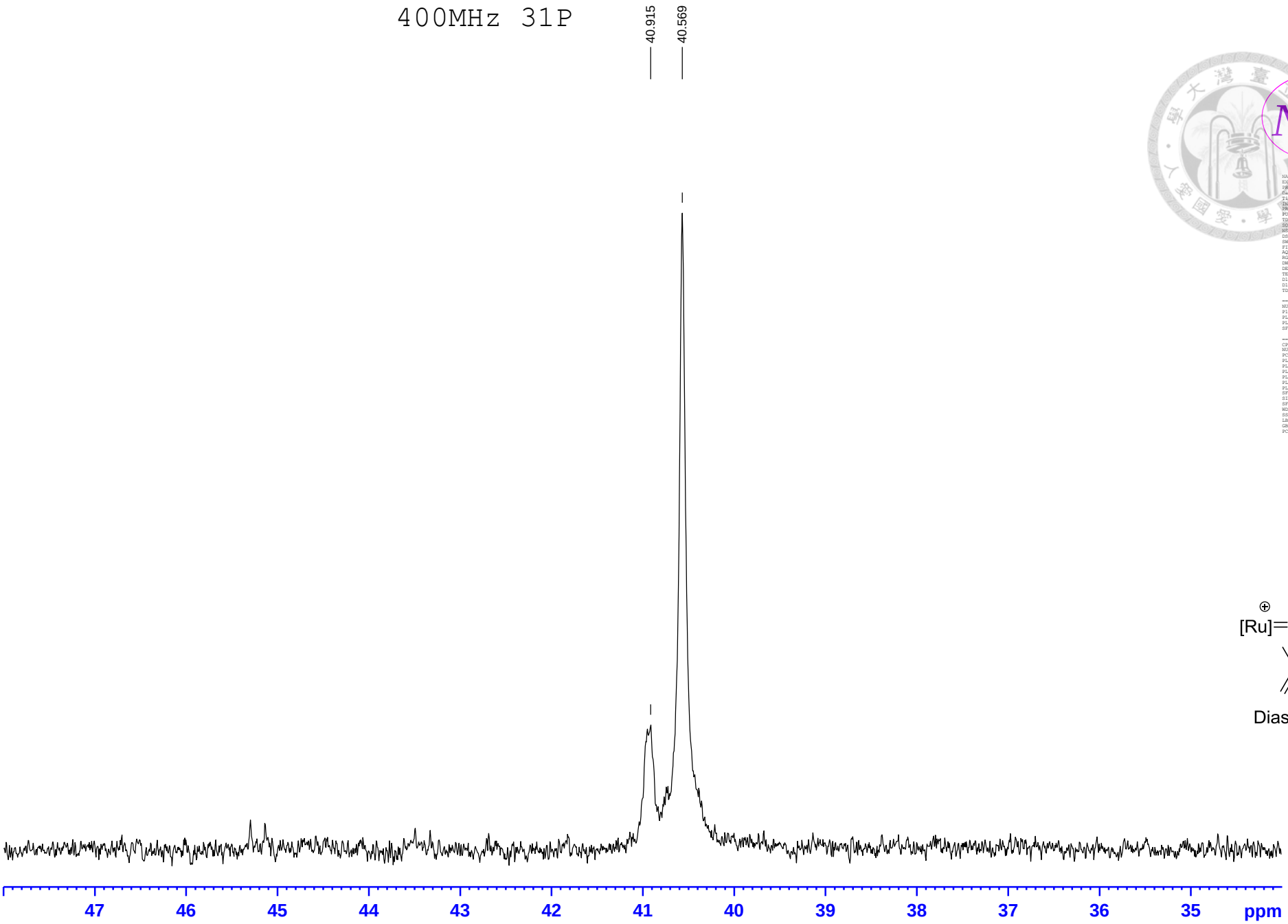


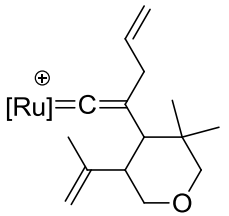
Diastereomers

400MHz 1H


7.4785 7.4597 7.4408 7.4219 7.3114 7.2927 7.2724 7.2530 7.2398 7.2347 7.2307 7.2082 7.1841 7.1674 7.1661 7.1591 7.1536 7.1358 7.1349 7.0029 6.9870 6.8939 6.1619 6.1480 6.1354 6.1220 6.1058 6.0925 6.0796 6.0655 5.9831 5.3265 5.2980 5.2848 5.2436 5.2083 5.1719 5.1051 5.0599 4.9561 3.9686 3.9437 3.9375 3.8305 3.8038 3.6412 3.6325 3.6136 3.6024 3.5892 3.5607 3.4085 3.3336 3.3061 3.2646 3.1458 3.1254 3.0975 2.9430 2.9306 2.9163 2.8907 2.7365 2.7089 2.5545 2.5420 2.5350 2.5253 2.4853 1.8564 1.1390 0.9937 0.9695 0.6622
NTU
NAME Lo130504-cpx9
EXPNO 100
PROCNO 1
Date_ 20130504
Time_ 16.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 11
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 12.00 usec
PL1 -1.00 dB
PLW 13.43968010 W
SFO1 400.1528010 MHz
SI 32768
SF 400.1500055 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
[Ru]=C
O
Diastereomers
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
53.274 1.015 0.253 2.874 2.012 5.488 0.531 0.970 0.953 0.241 0.489 0.261 2.240 1.253 0.976 1.207 0.395 1.895 3.790 3.000 1.422 2.712

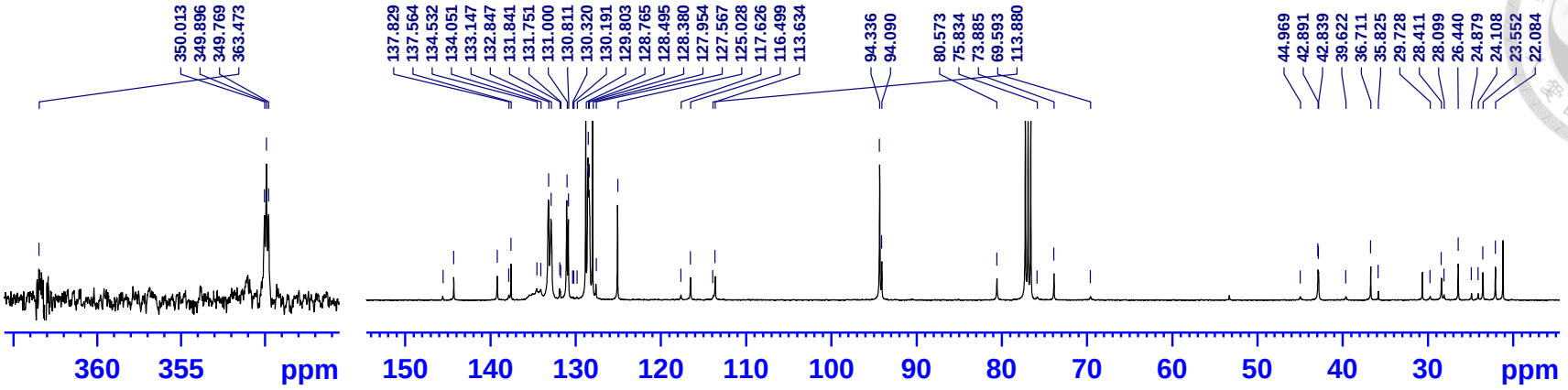
400MHz 31P

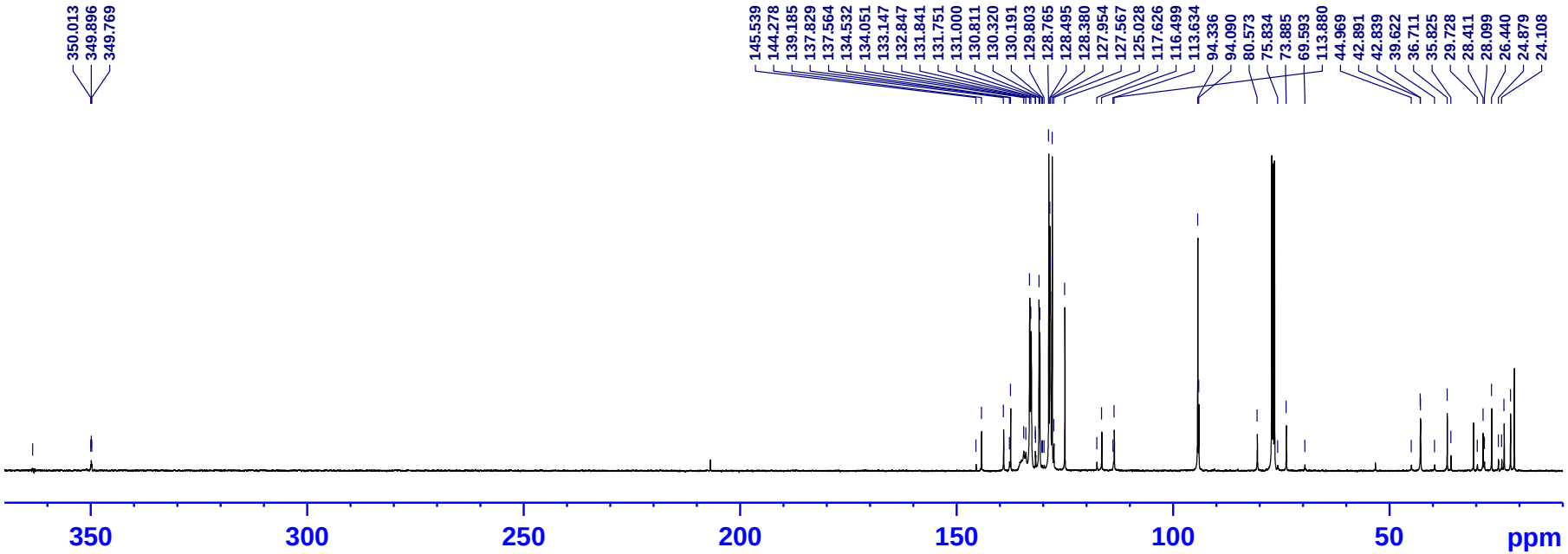


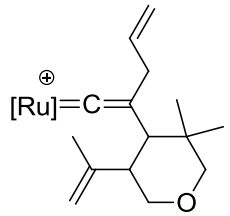


Diastereomers

500MHz 13C (420p to -10p)

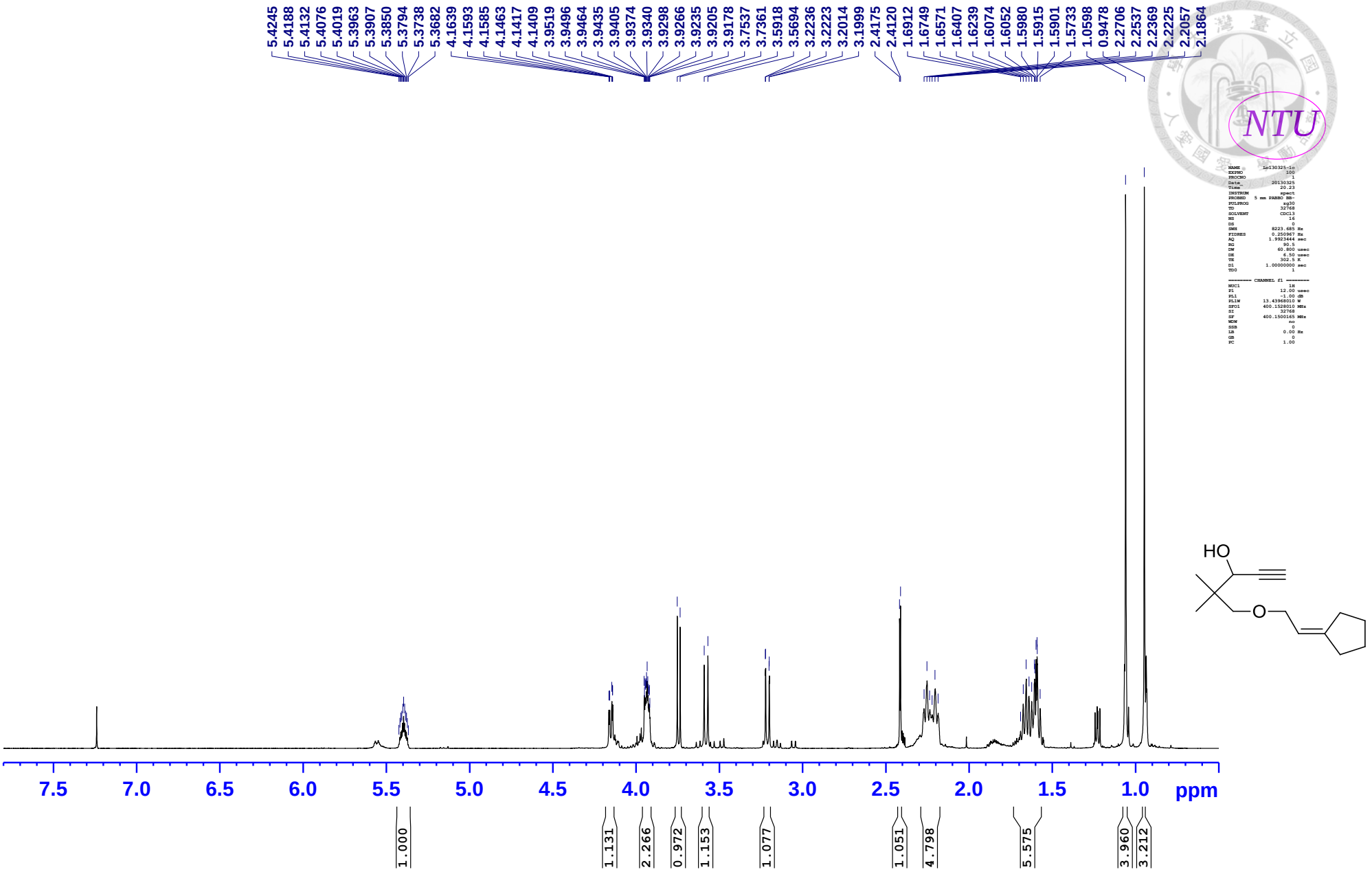


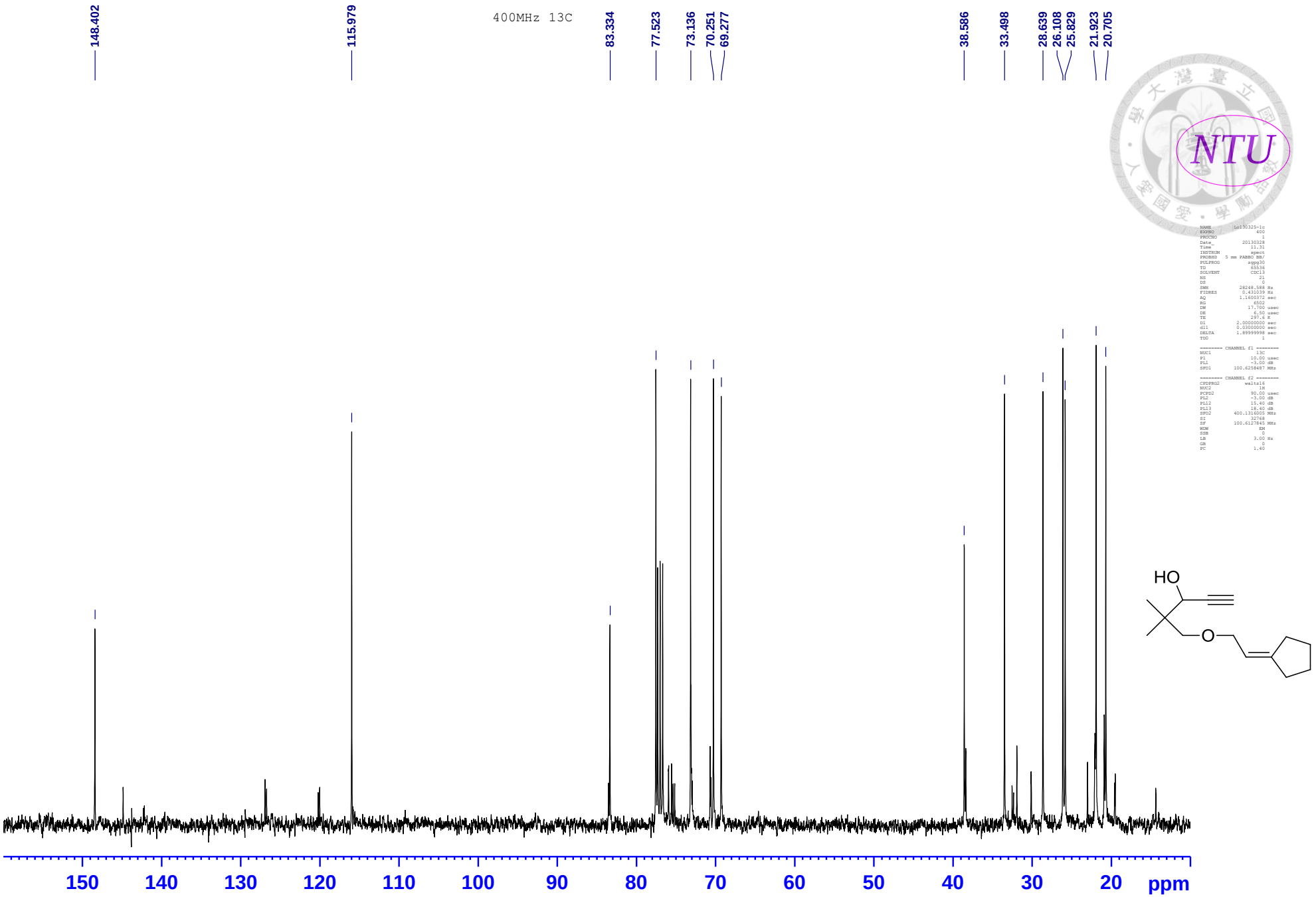




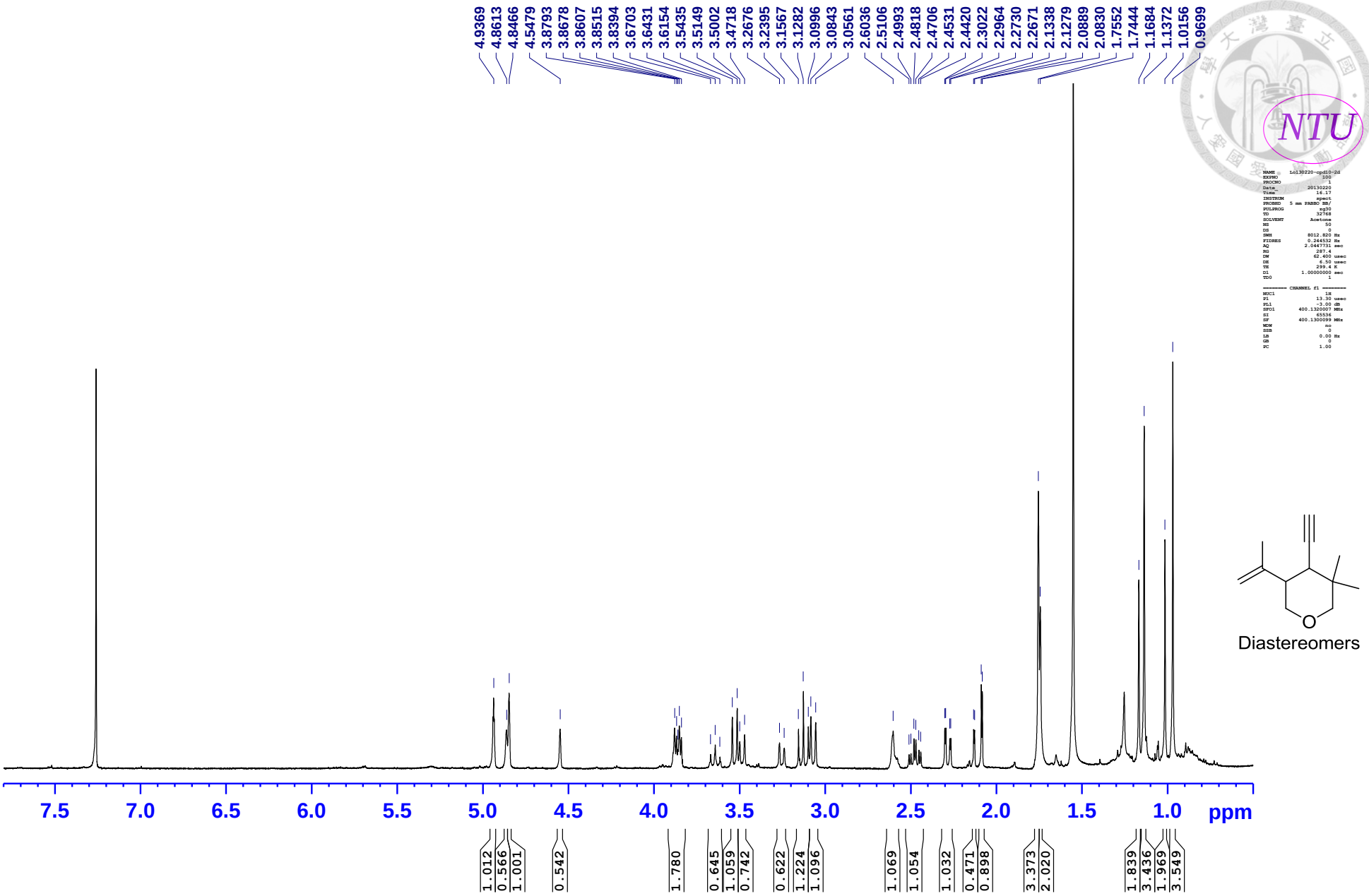
Diastereomers

400MHz 1H

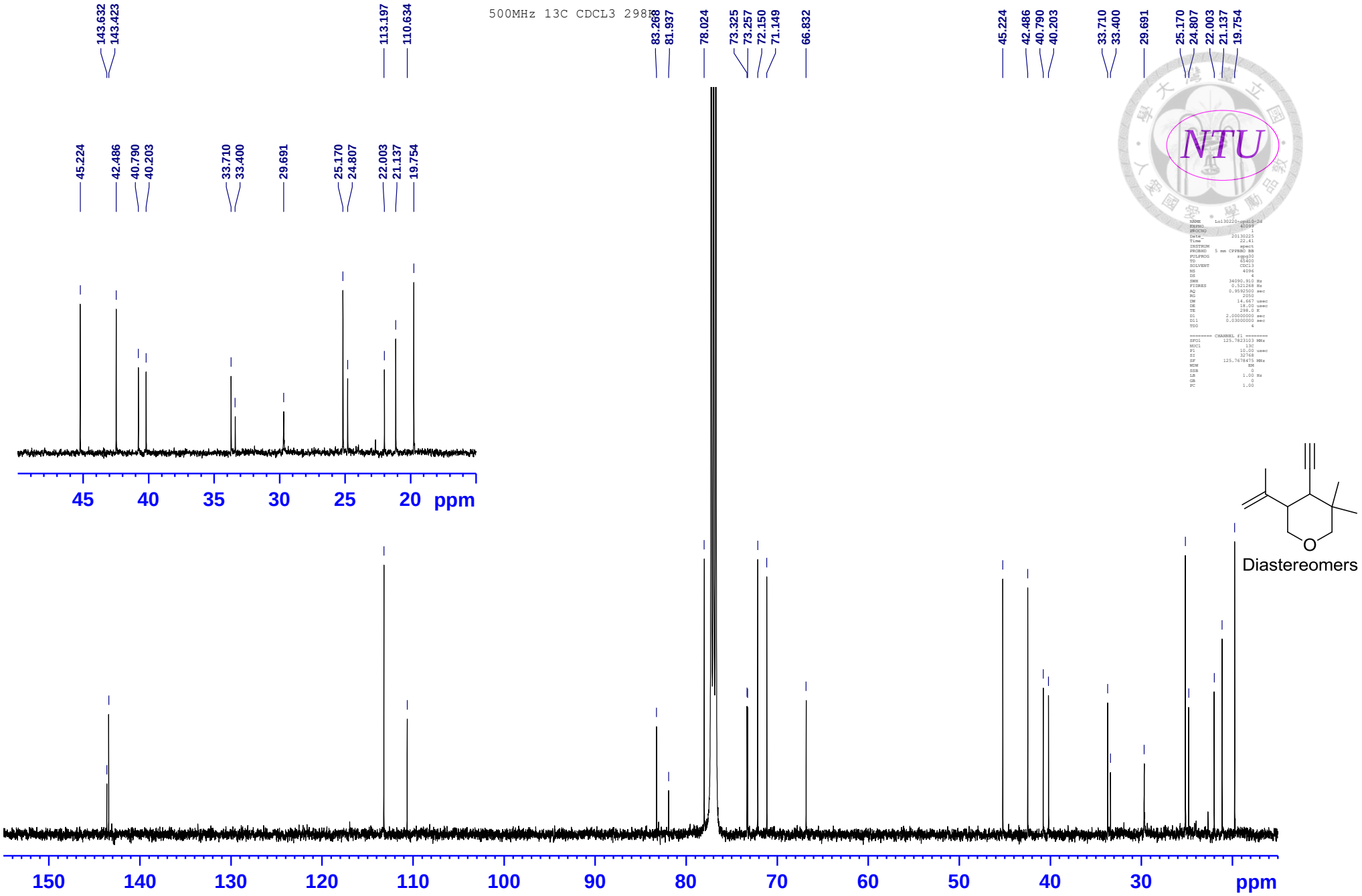

5.4245 5.4188 5.4132 5.4076 5.4019 5.3963 5.3907 5.3850 5.3794 5.3738 5.3682 4.1639 4.1593 4.1585 4.1463 4.1417 4.1409 3.9519 3.9496 3.9464 3.9435 3.9405 3.9374 3.9340 3.9298 3.9266 3.9235 3.9205 3.9178 3.7537 3.7361 3.5918 3.5694 3.2236 3.2223 3.2014 3.1999 2.4175 2.4120 1.6912 1.6749 1.6571 1.6407 1.6239 1.6074 1.6052 1.5980 1.5915 1.5901 1.5733 1.0598 0.9478 2.2706 2.2537 2.2369 2.2225 2.2057 2.1864
NTU
NAME Lp130325-1c
EXPNO 100
PROCNO 1
Date_ 20130325
Time 20.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 302.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.00 dB
PLLW 13.43968010 W
SFO1 400.1528010 MHz
SI 32768
SF 400.1500165 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
HO
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.000 1.131 2.266 0.972 1.153 1.077 1.051 4.798 5.575 3.960 3.212


400MHz 13C
148.402
115.979
83.334
77.523
73.136
70.251
69.277
38.586
33.498
28.639
26.108
25.829
21.923
20.705
HO
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

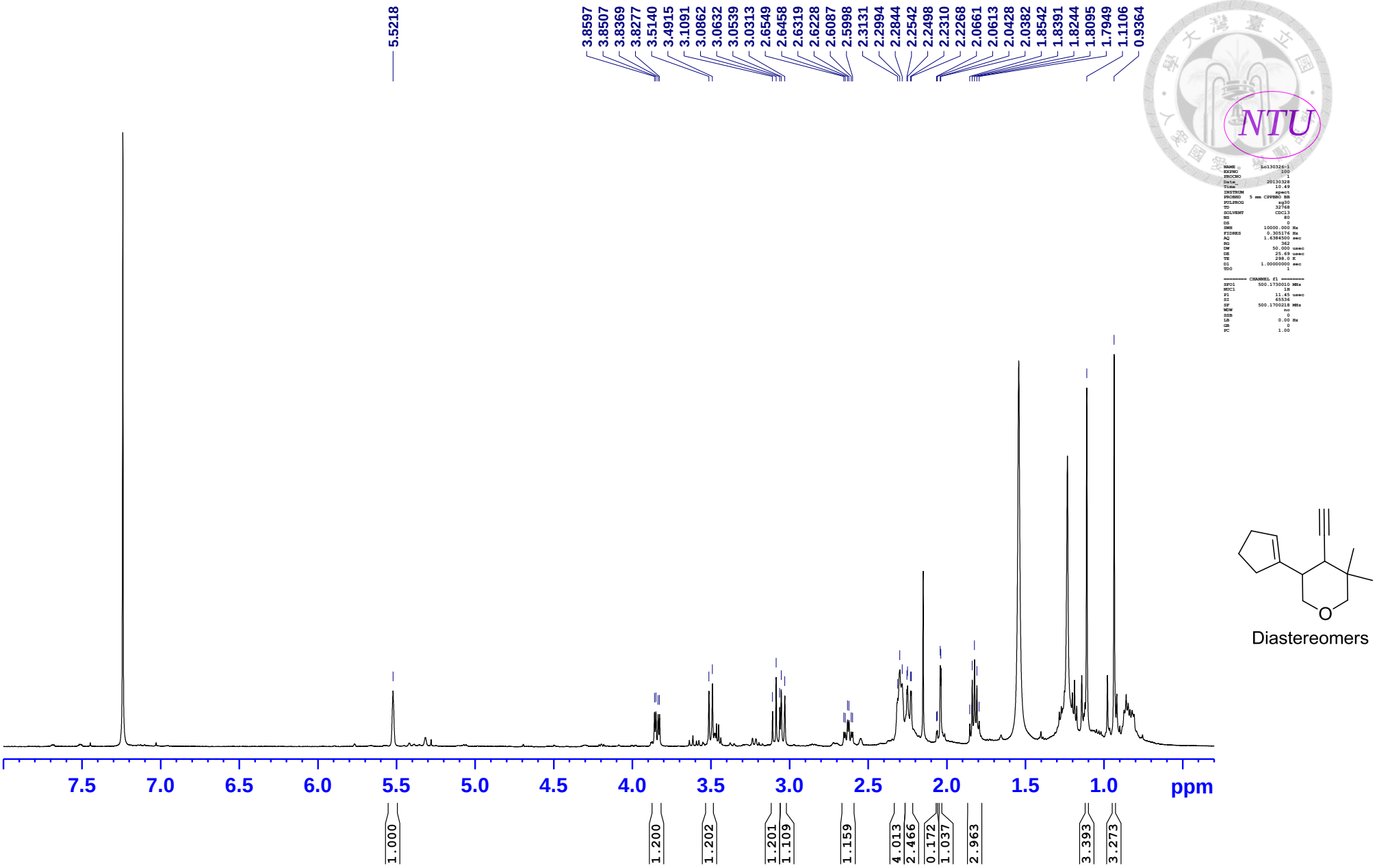
400MHz 1H



Diastereomers

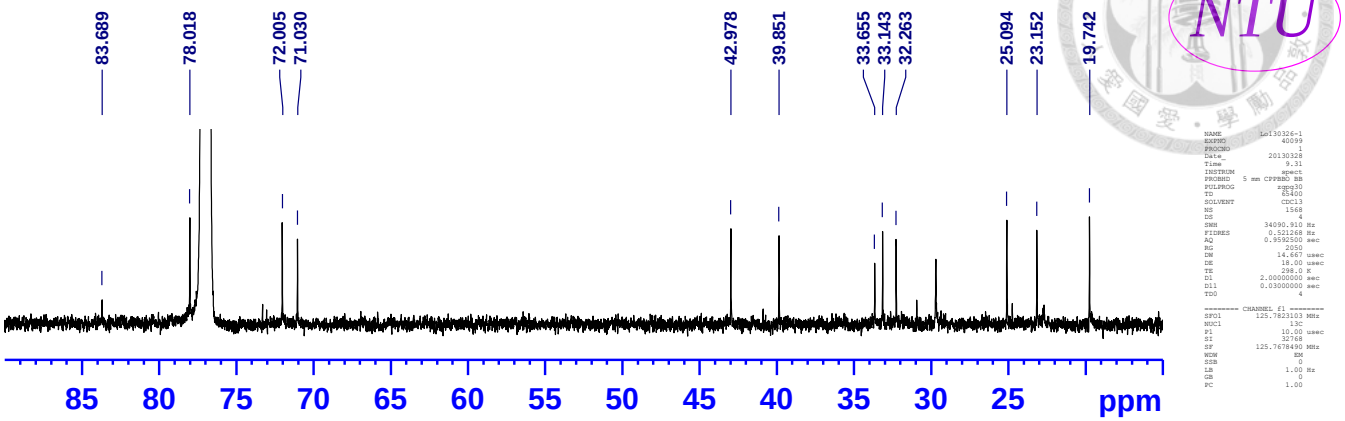

500MHz 13C CDCL3 29888
143.632
143.423
113.197
110.634
83.268
81.937
78.024
73.325
73.257
72.150
71.149
66.832
45.224
42.486
40.790
40.203
33.710
33.400
29.691
25.170
24.807
22.003
21.137
19.754
45
40
35
30
25
20
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm
Diastereomers

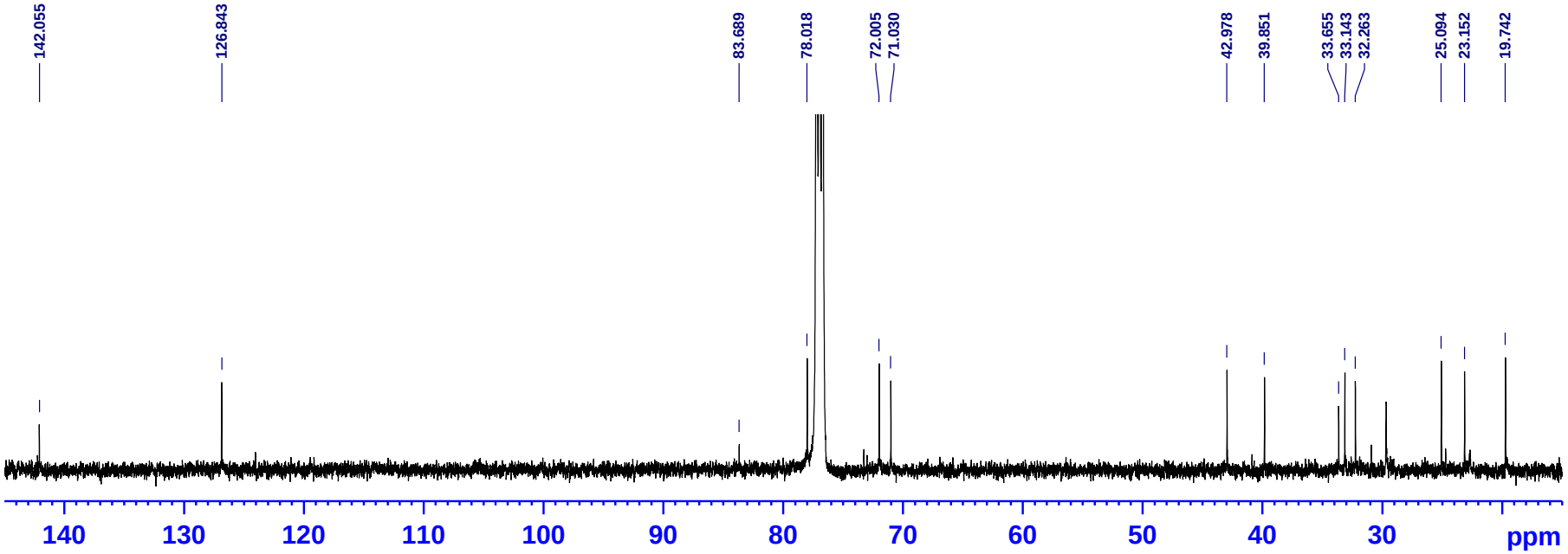
500MHz 1H CDCL3 298K

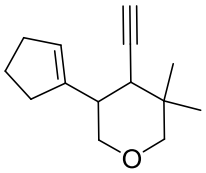


Diastereomers

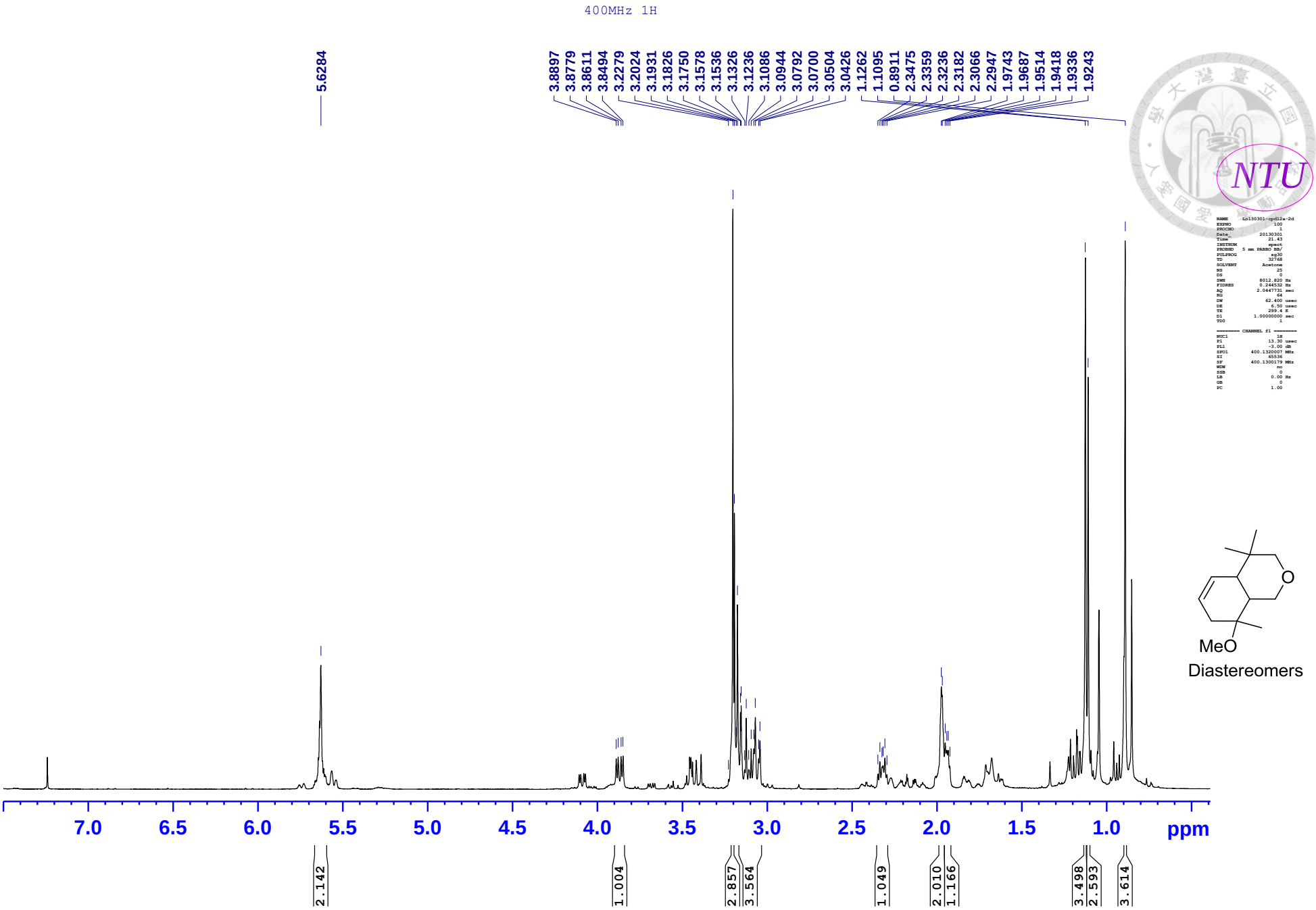
500MHz 13C CDCL3 298K



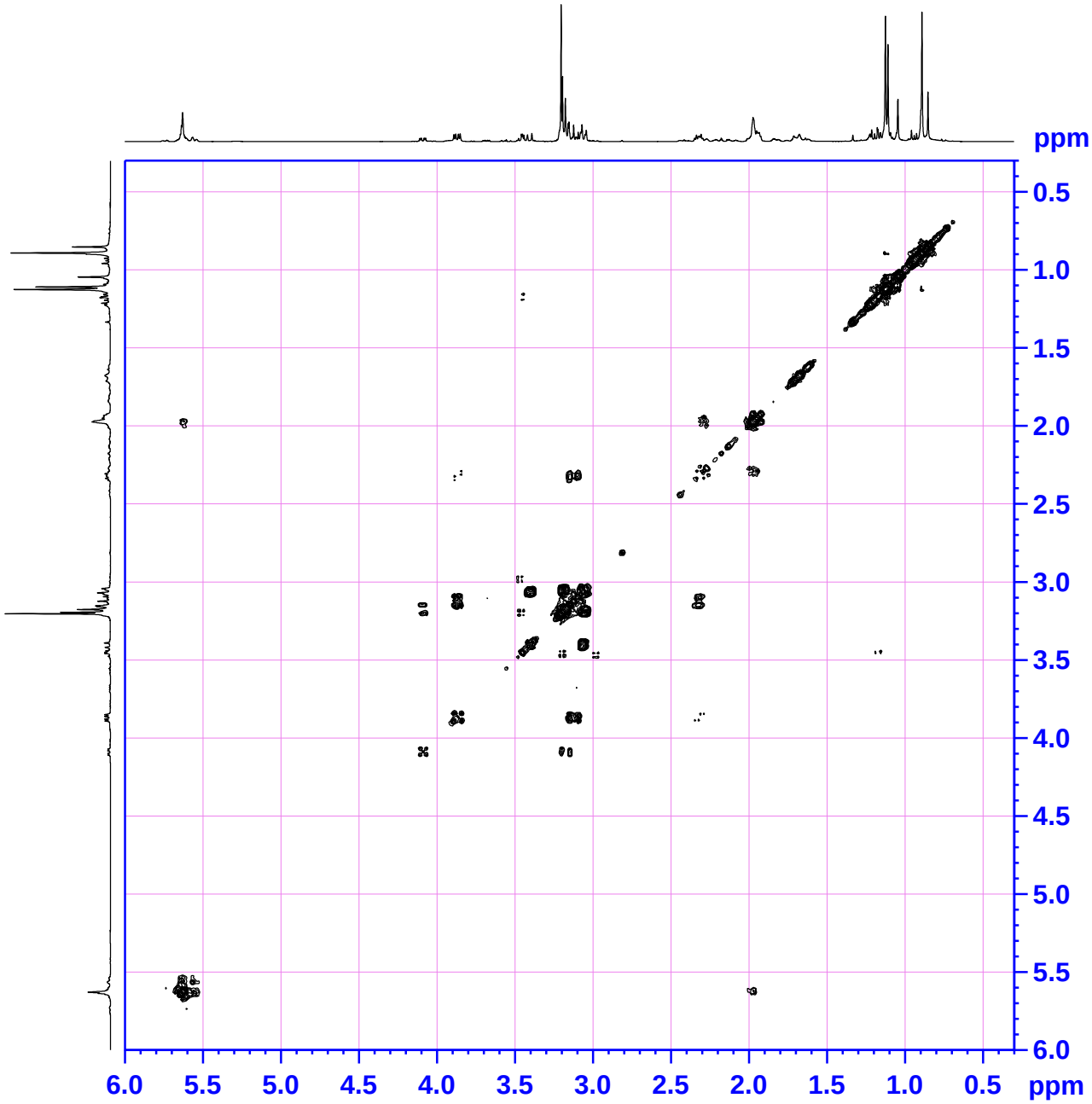




Diastereomers


400MHz 1H
5.6284
3.8897
3.8779
3.8611
3.8494
3.2279
3.2024
3.1931
3.1826
3.1750
3.1578
3.1536
3.1326
3.1236
3.1086
3.0944
3.0792
3.0700
3.0504
3.0426
1.1262
1.1095
0.8911
2.3475
2.3359
2.3236
2.3182
2.3066
2.2947
1.9743
1.9687
1.9514
1.9418
1.9336
1.9243
NTU
NAME kp130301-cpd12a-2d
EXPNO 100
PROCNO 1
Date 20130301
Time 21.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 25
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300179 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
O
MeO
Diastereomers
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.142
1.004
2.857
3.564
1.049
2.010
1.166
3.498
2.593
3.614

400MHz COSY

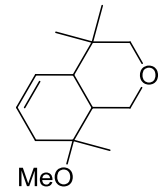


NTU

NAME Lo130301-cpd12a-2d
EXPNO 102
PROCNO 1
Date_ 20130301
Time 21.53
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG cosygpqf
TD 2048
SOLVENT MeOD
NS 4
DS 0
SWH 4789.272 Hz
FIDRES 2.338512 Hz
AQ 0.2138612 sec
RG 101.6
DW 104.400 usec
DE 6.50 usec
TE 299.3 K
d0 0.00000300 sec
D1 1.50000000 sec
d13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00020880 sec

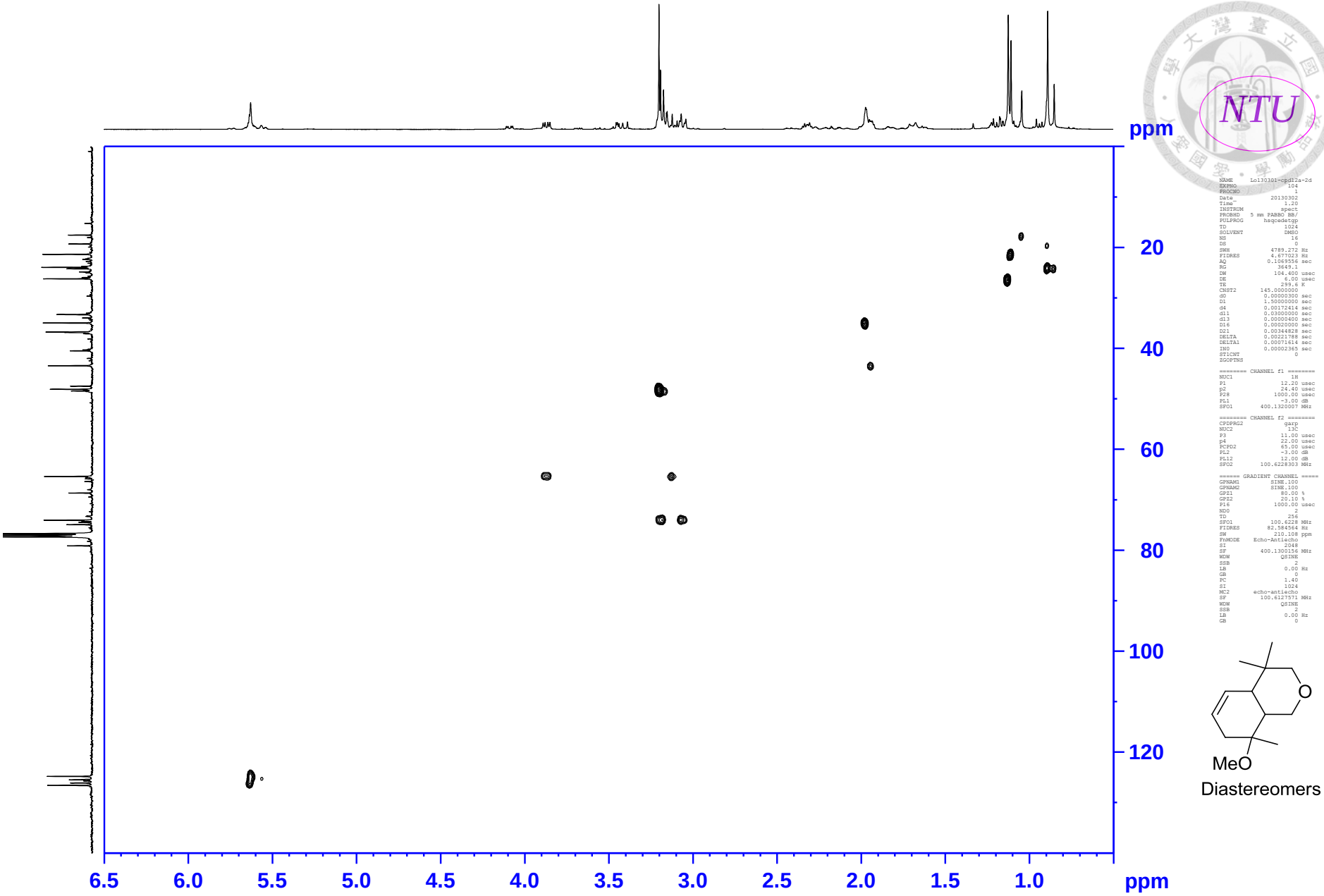
======== CHANNEL f1 ========
NUC1 1H
P0 13.30 usec
P1 13.30 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
ND0 1
TD 256
SFO1 400.132 MHz
FIDRES 18.708094 Hz
SW 11.969 ppm
FnMODE QF
SI 1024
SF 400.1300172 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 QF
SF 400.1300164 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0



Diastereomers

400MHz HSQC



NAME Lo130301-cpd12a-2d
EXPNO 104
PROCNO 1
Date_ 20130302
Time_ 1.20
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hsqcedetgp
TD 1024
SOLVENT DMSO
NS 16
DS 0
SWH 4789.272 Hz
FIDRES 4.677023 Hz
AQ 0.1069556 sec
RG 3649.1
DW 104.400 usec
DE 6.00 usec
TE 299.6 K
CNST2 145.0000000
d0 0.00000300 sec
D1 1.50000000 sec
d4 0.00172414 sec
d11 0.03000000 sec
d13 0.00000400 sec
D16 0.00020000 sec
D21 0.00344828 sec
DELTA 0.00221788 sec
DELTA1 0.00071614 sec
IN0 0.00002365 sec
ST1CNT 0
SGOPTNS

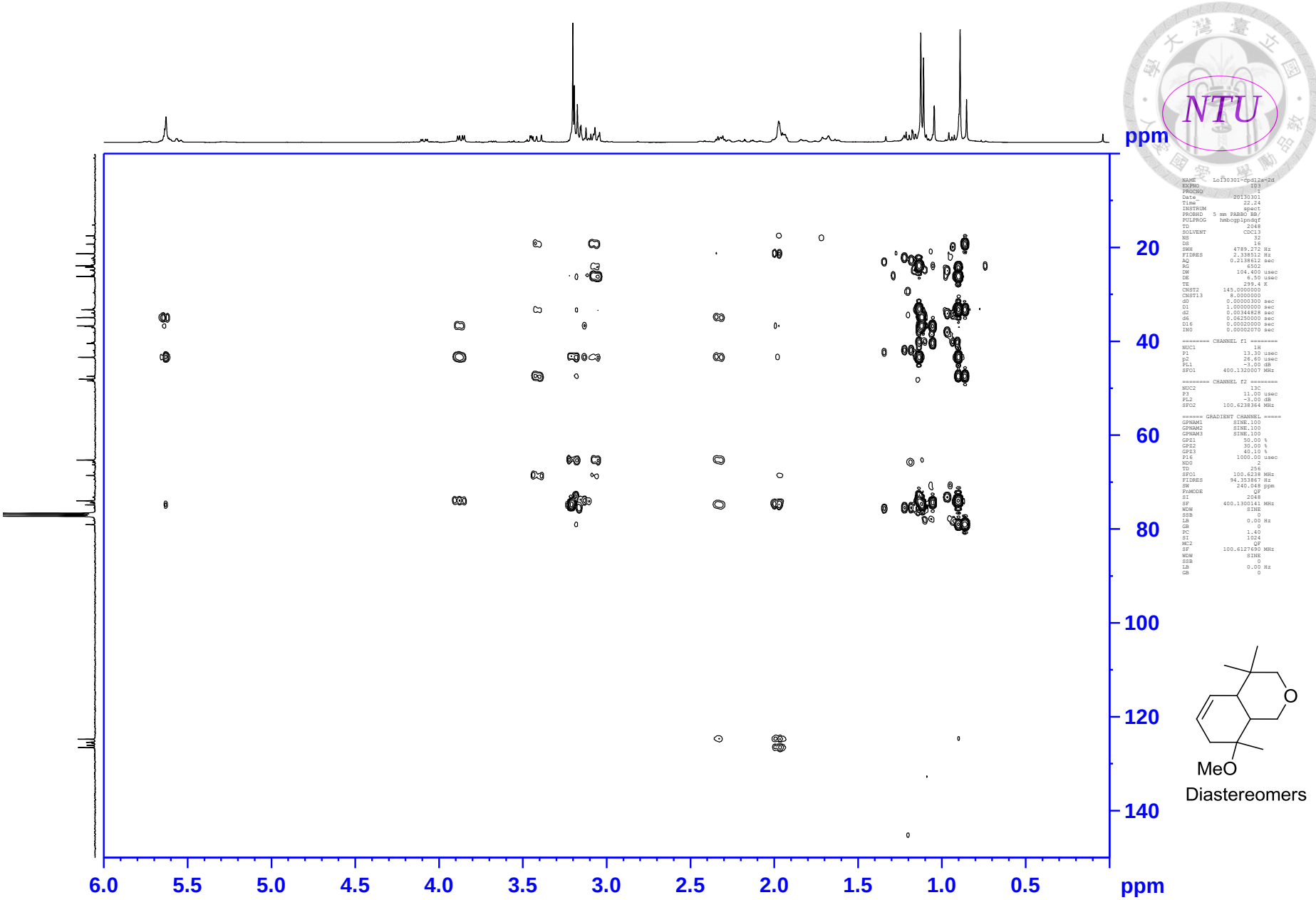
======== CHANNEL f1 ========
NUC1 1H
P1 12.20 usec
p2 24.40 usec
P28 1000.00 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG2 garp
NUC2 13C
P3 11.00 usec
p4 22.00 usec
PCPD2 65.00 usec
PL2 -3.00 dB
PL12 12.00 dB
SFO2 100.6228303 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 80.00 %
GPZ2 20.10 %
P16 1000.00 usec
NDO 2
TD 256
SFO1 100.6228 MHz
FIDRES 82.584564 Hz
SW 210.108 ppm
FnMODE Echo-Antiecho
SI 2048
SF 400.1300156 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 echo-antiecho
SF 100.6127571 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

Diastereomers

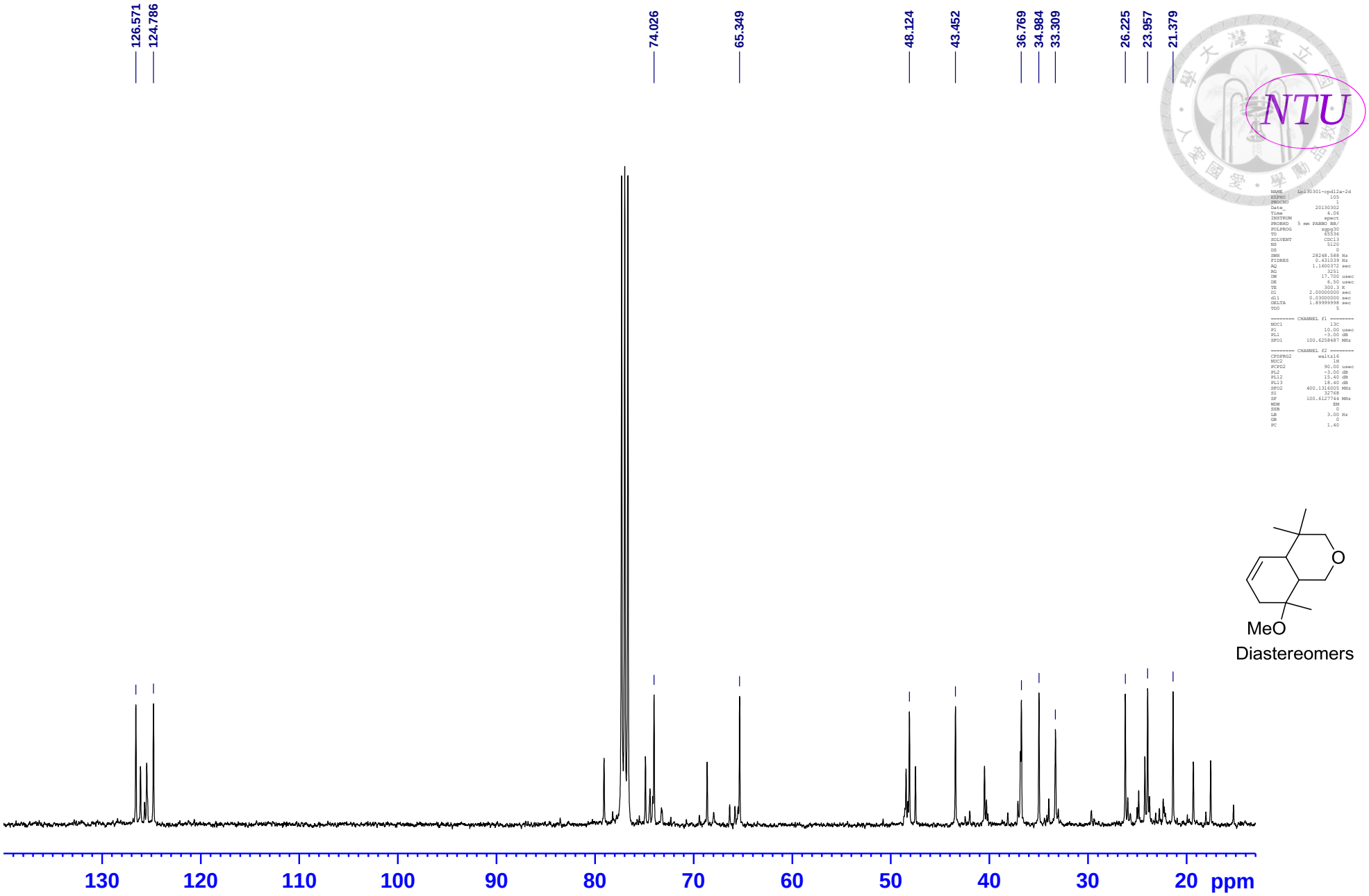
400MHz HMBCLPND



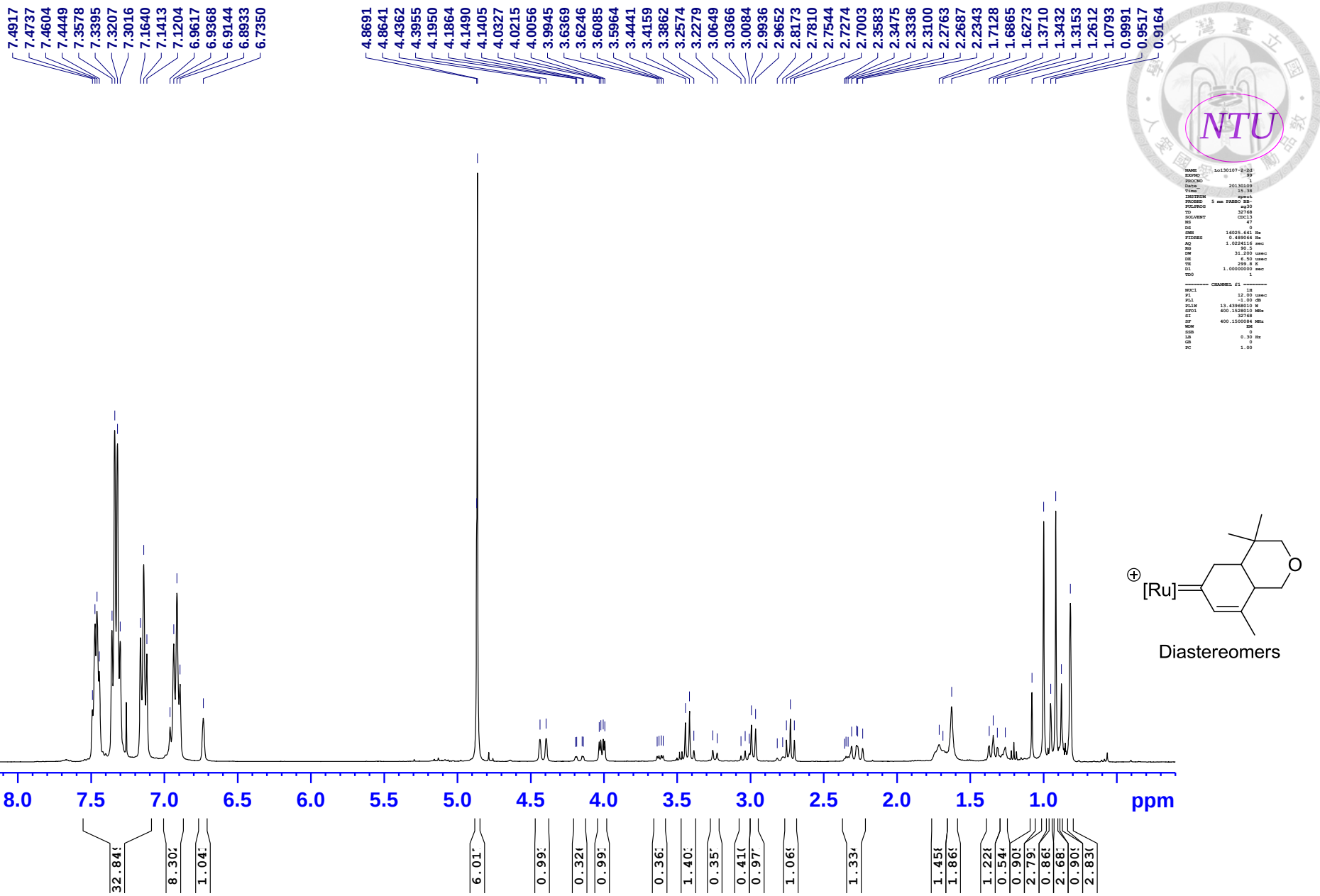
NAME Lo130301-cpd12a-2d
EXPNO 103
PROCNO 1
Date_ 20130301
Time 22.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hmbcgplpndqf
TD 2048
SOLVENT CDCl3
NS 32
DS 16
SWH 4789.272 Hz
FIDRES 2.338512 Hz
AQ 0.2138612 sec
RG 6502
DW 104.400 usec
DE 6.50 usec
TE 299.4 K
CNST2 145.0000000
CNST13 8.0000000
d0 0.00000300 sec
D1 1.00000000 sec
d2 0.00344828 sec
d6 0.06250000 sec
D16 0.00020000 sec
IN0 0.00002070 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
p2 26.60 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
======== CHANNEL f2 ========
NUC2 13C
P3 11.00 usec
PL2 -3.00 dB
SFO2 100.6238364 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 50.00 %
GPZ2 30.00 %
GPZ3 40.10 %
P16 1000.00 usec
NDO 2
TD 256
SFO1 100.6238 MHz
FIDRES 94.353867 Hz
SW 240.048 ppm
FnMODE QF
SI 2048
SF 400.1300141 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 QF
SF 100.6127690 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

Diastereomers

400MHz 13C

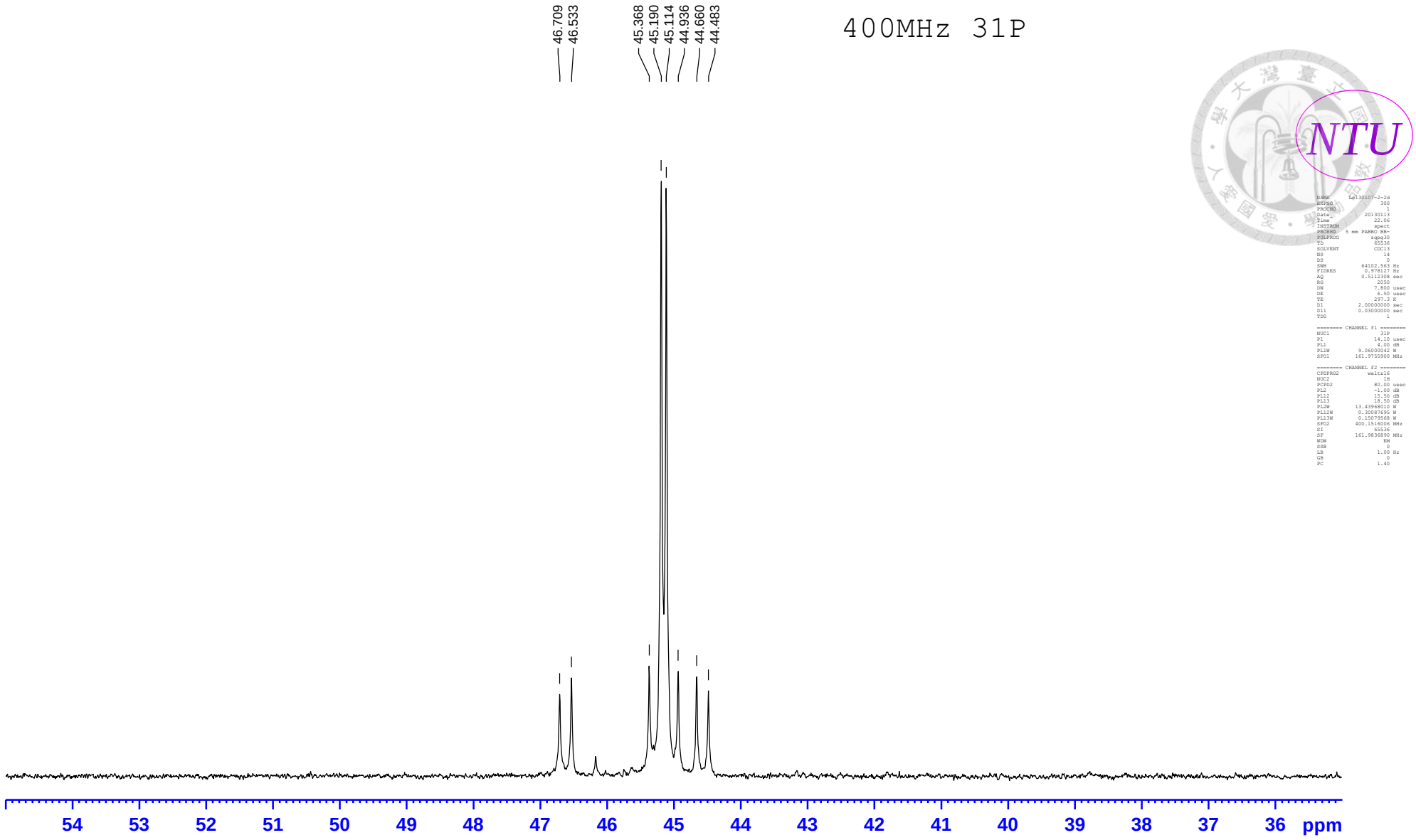

126.571
124.786
74.026
65.349
48.124
43.452
36.769
34.984
33.309
26.225
23.957
21.379
NTU
NAME Lo130301-cpd12a-2d
EXPNO 105
PROCNO 1
Date_ 20130302
Time_ 4.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5120
DS 0
SWH 28248.588 Hz
FIDRES 0.431039 Hz
AQ 1.1600372 sec
RG 3251
DW 17.700 usec
DE 6.50 usec
TE 300.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 5
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 +3.00 dB
SFO1 100.6258487 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 +3.00 dB
PL12 15.40 dB
PL13 18.40 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127744 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
O
MeO
Diastereomers
130
120
110
100
90
80
70
60
50
40
30
20
ppm

400MHz 1H

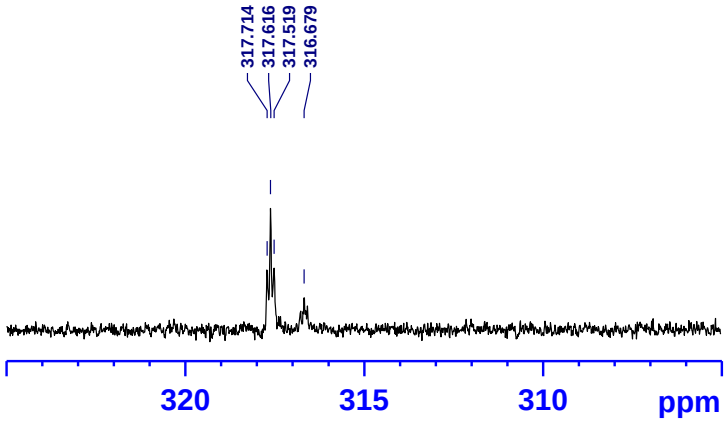


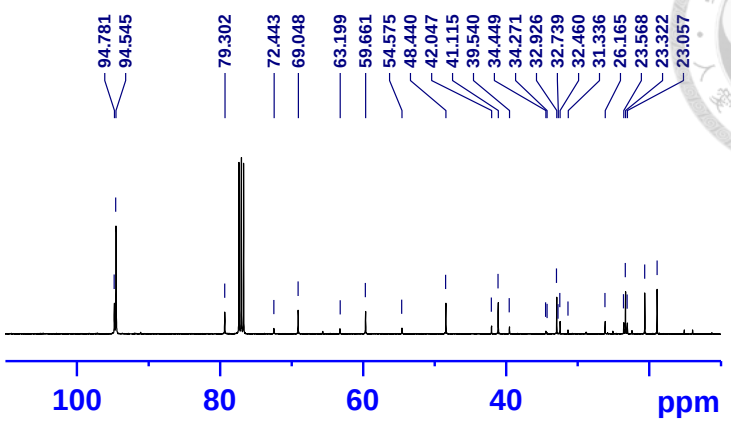

```
NAME          Lo130107-2-2d
EXPNO                   99
PROCNO                   1
Date_          20130109
Time               15.38
INSTRUM            spect
PROBHD     5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    47
DS                     0
SWH           16025.641 Hz
FIDRES        0.489064 Hz
AQ            1.0224116 sec
RG                  90.5
DW             31.200 usec
DE              6.50 usec
TE             299.8 K
D1          1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1             12.00 usec
PL1            -1.00 dB
PL1W       13.43968010 W
SFO1       400.1528010 MHz
SI                 32768
SF         400.1500084 MHz
WDW                   EM
SSB                    0
LB              0.30 Hz
GB                     0
PC                  1.00
```

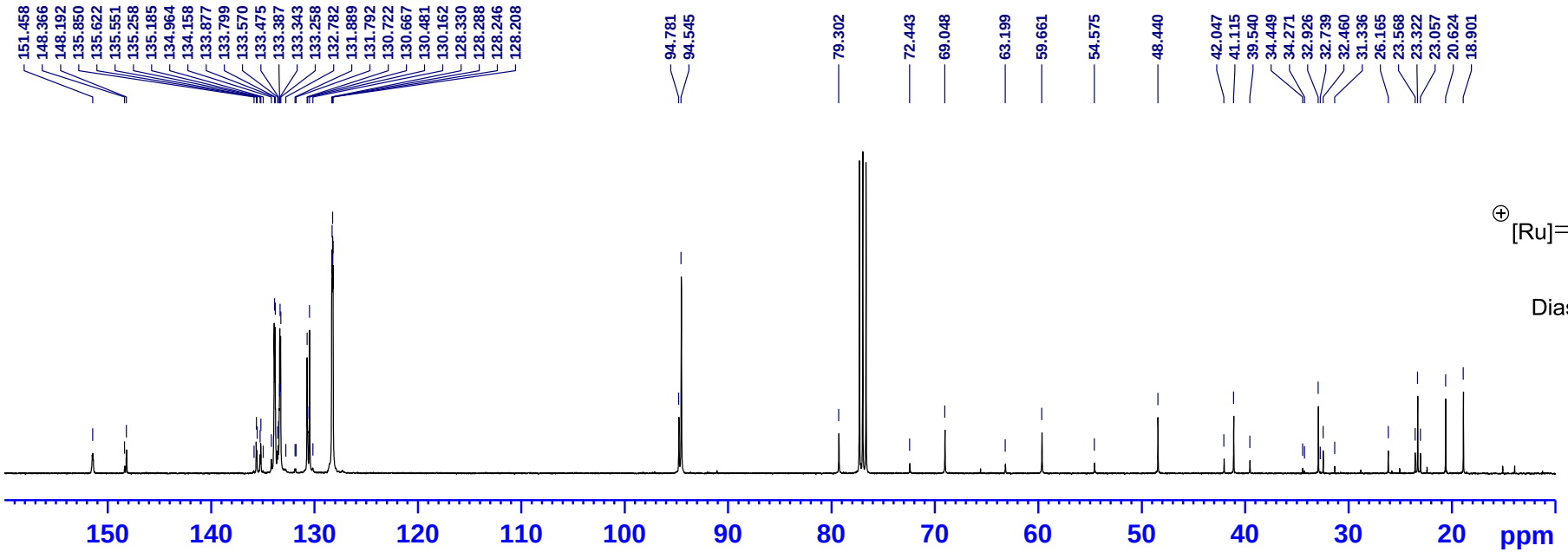

Diastereomers

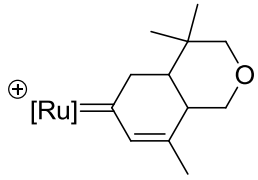

46.709
46.533
45.368
45.190
45.114
44.936
44.660
44.483
400MHz 31P
NTU
54
53
52
51
50
49
48
47
46
45
44
43
42
41
40
39
38
37
36
ppm

400MHz 13C









Diastereomers