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

釕金屬錯合物與含酚之丙炔亞胺反應之研究

Reactions of Ruthenium Complexes with Propargylic Imines Containing a Phenol Substituent

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Structures and Numbering of Complexes

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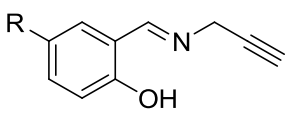
<tr><td> 

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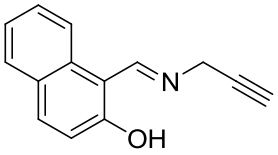
NO_2 **1c**</td><td> 
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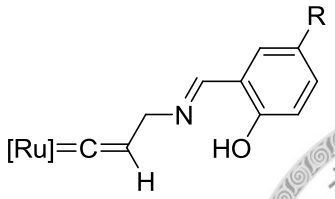
<tr><td> 

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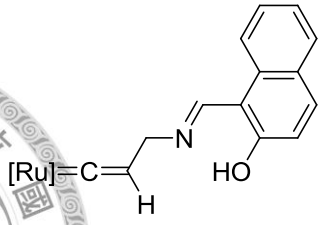
NO_2 **2c**</td><td> 
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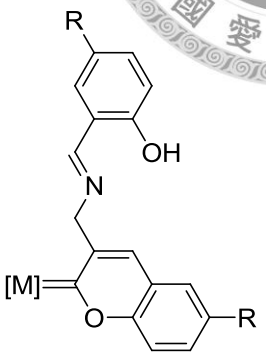
R = H **3a**, **3a'**
OMe **3b**, **3b'**
NO_2 **3c**, **3c'**
 
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 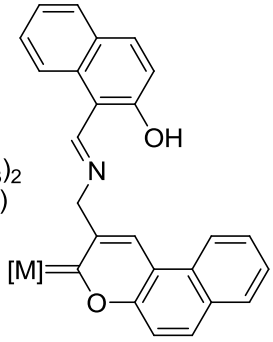
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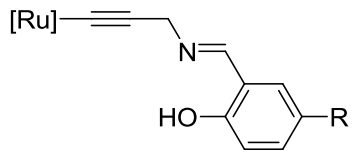
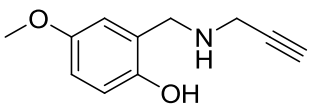
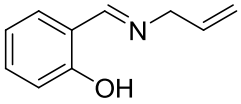
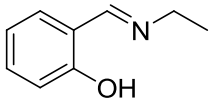
 R = H **4a** OMe **4b**	
4a, 4b	**5b**
	
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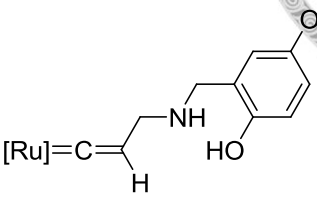	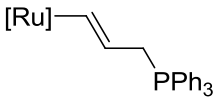
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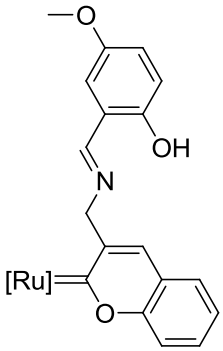	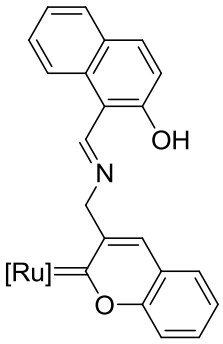

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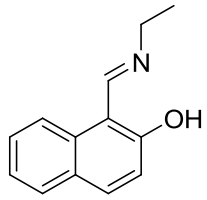	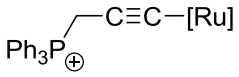
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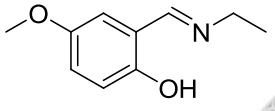	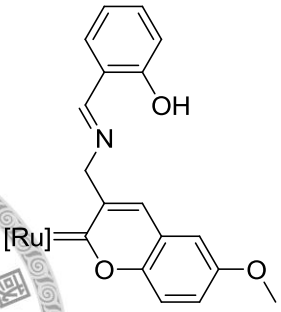
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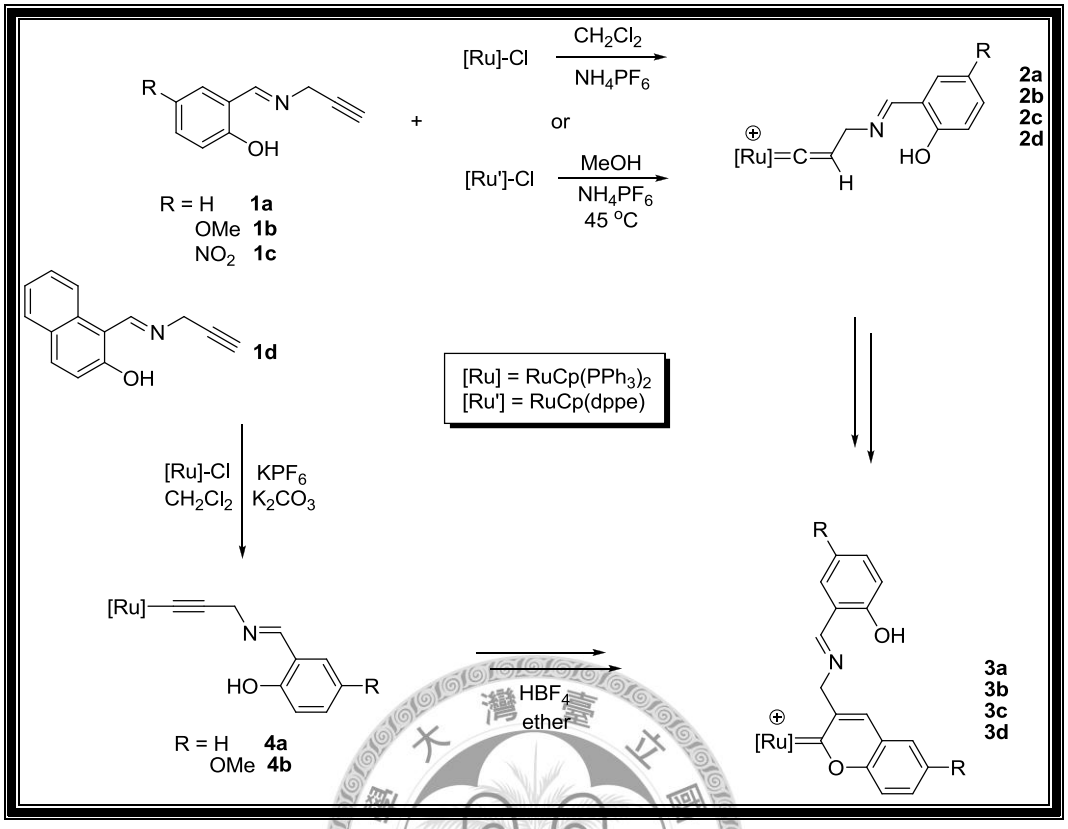

[Ru]-Cl
CH2Cl2
NH4PF6
or
[Ru']-Cl
MeOH
NH4PF6
45 °C
R = H 1a
OMe 1b
NO2 1c
1d
2a
2b
2c
2d
[Ru] = RuCp(PPh3)2
[Ru'] = RuCp(dppe)
[Ru]-Cl
CH2Cl2
KPF6
K2CO3
HBF4
ether
R = H 4a
OMe 4b
3a
3b
3c
3d


[Ru]-Cl, PPh3
CH2Cl2, KPF6
45 °C
5b
9

Abstract

Compound 2-((prop-2-ynylimino)methyl)phenol (**1a**), a propargyl aldimine, is prepared from the condensation of 2-hydroxy benzaldehyde and propargyl amine. Three analogous compounds **1b**, **1c** and **1d** are prepared similarly, using different aldehydes as starting materials. The reactions of compounds **1a** – **1c** with [Ru]-Cl ([Ru] = $RuCp(PPh_3)_2$) in the presence of NH_4PF_6 in CH_2Cl_2 at room temperature for one day afford the corresponding carbene complexes **3a** – **3c** as the major products and the vinylidene complexes **2a** - **2c** as the minor products, respectively. For a longer reaction time, the same reaction afforded, in high yield, the carbene complexes **3a** – **3c** without **2a** – **2c**. Interestingly, the overnight reaction of compound **1d** under the same reaction condition affords complex **2d** as the only product. Lengthening the time for 7 days results in similar carbene complex **3d** with some by-products. Structures of complexes **2a** – **2d** and **3a** – **3d** are proposed on the basis of spectroscopic data. The vinylidene ligand of complex **2** is from complete conversion of **1**. The ligand in complex **3** resulted from addition of a *o*-cresol moiety to Cα and Cβ of the vinylidene ligand of **2** to yield a substituted 2*H*-chromene unit, with various substituents on the 3,6-positions. In the mass spectrum of **3b**, the parent peak at *m/z* 1014.24 confirms the proposed structure.

Through our study, the added *o*-cresol portion comes from the organic imine compounds **1**, instead of aldehyde. When two imines with different substituents were used in the reaction, new cross carbene complex formed from coupling of two imine molecules as evidenced by the mass spectrum. Therefore, the imine group plays a decisive role when the addition of an *o*-cresol moiety to the vinylidene ligand occurs.

Furthermore, the amine analogue **5b**, which retains the propargyl group and phenol moiety, is treated with [Ru]-Cl under the same reaction condition. Completely different reactivities are observed when the imine functionality of the Schiff base used in our study is transformed to the corresponding amine group.

Keywords: Imine, vinylidene, ruthenium, oxocarbene, cyclization.

中文摘要

利用水楊醛 (2-hydroxybenzaldehyde) 及丙炔胺進行脫水反應，我們製備出了一個含有酚環在其上的丙炔亞胺化合物 **1a**，且隨著醛類起始物選擇的不同，相似於 **1a** 的另外三種丙炔亞胺化合物 **1b** – **1d** 亦被合成出來。當我們將 **1a** – **1c** 與 [Ru]-Cl 反應一夜後，會得到一組由陽離子釕金屬亞乙烯基錯合物([Ru]=C=CHR) **2a** – **2c** 及碳烯 (carbene) 錯合物 **3a** – **3c** 組成之混合物為反應後之產物，其中碳烯 (carbene) 錯合物 **3a** – **3c** 為主要產物，而亞乙烯基錯合物 ([Ru]=C=CHR) **2a** – **2c** 為次要產物。隨著反應時間的加長，我們可以得到 **3a** – **3c** 為最終的產物。有趣的是，當相同的反應條件用以操作在 **1d** 與[Ru]-Cl 的反應時，一夜的反應時間後，我們得到亞乙烯基錯合物 **2d** 為單一產物。然而，當反應時間拉長至 7 天，

其他無法辨識的副產物除外，我們仍然可以觀察到相似的 **3d** 產物生成。亞乙烯基錯合物 **2** 及碳烯錯合物 **3** 的鑑定是藉由 ^{31}P NMR、^{1}H NMR 以及 2D NMR 光譜的數據資料。亞乙烯基錯合物 **2** 上的配基是從 **1** 的分子轉換而來；碳烯錯合物 **3** 上的配基則是在 **2** 的α碳及β碳之間加上一鄰-甲酚結構的分子碎片進而得到一個含”色烯(2*H*-chromene)”分子單元的配基，分別在”色烯(2*H*-chromene)”分子單元的 3 號跟 6 號位置有若干個不同的取代基。在 **3b** 的質譜中，*m/z* 1014.24 的訊號亦與我們推測的結構相符。

在我們的研究中，加成上去的鄰-甲酚分子是來自有機亞胺化合物而非醛類化合物。當兩個不同丙炔亞胺化合物同時加到反應系統中與[Ru]-Cl 進行反應時，我們可以得到一個新的碳烯錯合物。從質譜上的數據來觀察，此碳烯錯合物是由不同的丙炔亞胺錯合物中個擷取部分分子結構而形成交錯碳烯錯合物。因此，我們相信，在亞乙烯基錯合物 **2** 上進一步進行加成上鄰-甲酚分子，進而得到碳烯錯合物 **3** 的反應過程中，亞胺的官能基想必扮演著相當重要的角色。

此外，針對 **1b** 的亞胺官能基進行還原反應後，我們合成出相對的丙炔胺化合物 **5b** 以進行上述反應之研究。**5b** 的丙炔及酚的官能基都是被保留的。隨著亞胺官能基的轉變，我們觀察到不同的反應性。

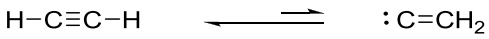
關鍵字: 亞胺, 亞乙烯基錯合物, 釘, 含氧碳烯基, 環化

Contents

Introduction

Metal Vinylidene Complexes

Vinylidene (:C=CH_2) is the simplest unsaturated carbene, and is tautomeric with ethyne (HC≡CH). It is formed by the formal 1,2-shift of the alkyne hydrogen from C(1) to C(2).

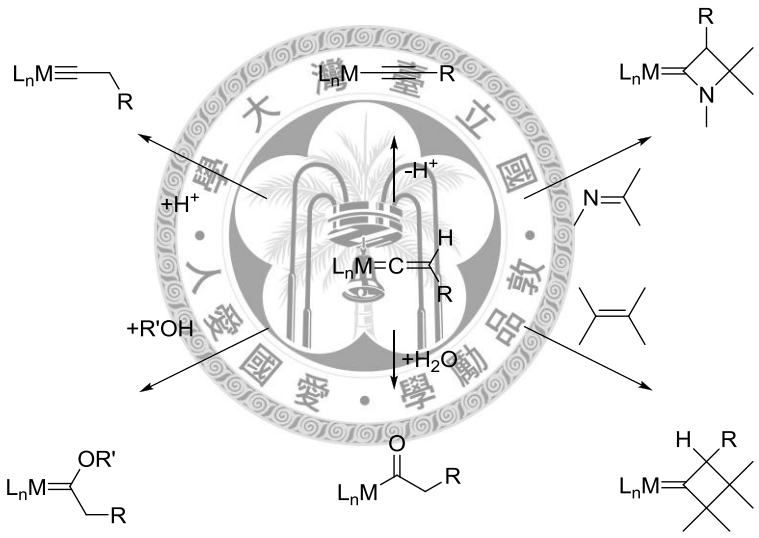


While in the free state the lifetime of the vinylidene is extremely short (~10^{-10} s), stabilization of organic vinylidene species via coordination to a metal center is now a well-known feature which has been encountered with many transition metals (Mo, W, Fe, Ru, Os…etc).[1] Activation of terminal alkynes following the similar pathway mentioned above also give the vinylidene metal derivatives, which now becomes one of the most straightforward method to synthesize the metal vinylidene complexes. During the last decade, the chemistry of ruthenium vinylidene [Ru]=C=CRR' has experienced important developments due to their involvement as the key intermediate in the stoichiometric reactions and in selective catalytic transformation reactions of terminal alkynes.[2] Such [Ru]-complexes can easily be obtained from terminal alkynes and electron-rich Ru precursors such as [RuCl(Cp)L_2] [L_2 = 2 × PPh_3 or dppe {1,2-bis(diphenyl-phosphino)ethane}]. The kinetic stability of these vinylidene complexes is enhanced by the presence of bulky ligands e.g. PPh_3, dppe, which offer

steric protection to Cα of the vinylidene moiety.

The reactivity of the metal vinylidene complexes depends largely on the nature of the metal. The resulting complexes exhibit a variety of reactivities (Scheme 1-1), which are rationalized by taking electrophilicity of α-vinylidene carbon, nucleophilicity of β-vinylidene carbon, and highly unsaturated structures of the vinylidene ligands into consideration.

Scheme 1-1



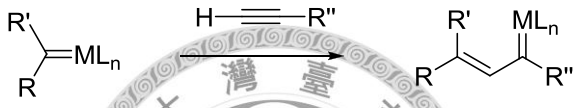
The mono-substituted vinylidene complexes prepared via the reaction of terminal alkyne contain a vinylidene hydrogen, which is acidic enough to be deprotonated by means of weak base, such as NEt_3.[3] Since the earlier research in the preparation of bi-substituted vinylidene via electrophilic attack of metal acetylide β carbon atom, the diversity and applications of metal vinylidene complexes have been further expanded. Besides, they play a key role in numerous carbon-carbon and carbon-hetero atom

coupling reactions such as [2+2] cycloaddition reactions.[1, 4]

Metal Carbene Complexes

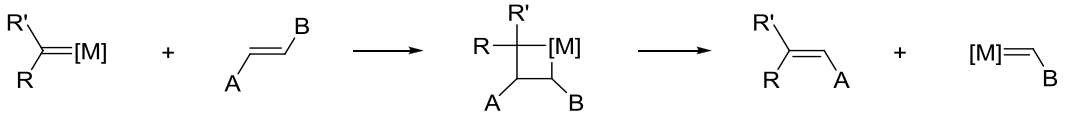
The reactivity of metal carbene complexes have been extensively investigated and a number of general and useful transformations have been reported.[5] Many transition metal carbene complexes readily react with alkynes, generally resulting in the formation of vinylcarbene complex (Scheme 1-2).

Scheme 1-2



Transition metal carbene complexes are capable of reacting with alkenes in a number of different ways. The two major reaction pathways that have been reported are alkene cyclopropanation and olefin metathesis. The olefin metathesis mechanism involves the [2+2] cycloaddition of an alkene double bond to a transiton metal carbene complex to form a metallocyclobutane intermediate. Subsequent retro [2+2] cyclization leads to a new alkene and a new carbene complex (Scheme 1-3).[6]

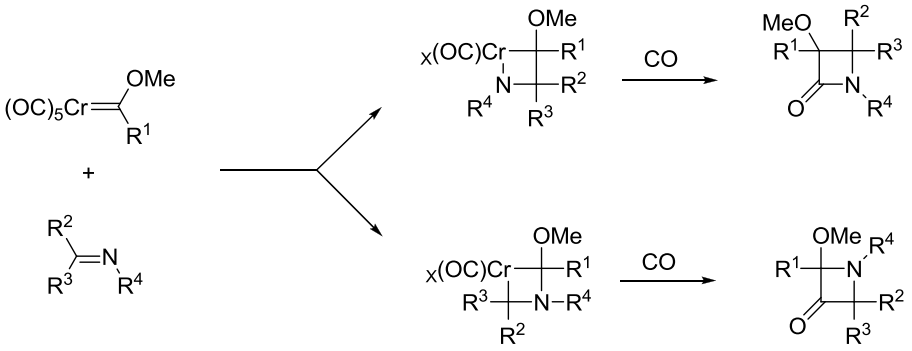
Scheme 1-3



Metal carbene complexes also react with N=C bouble-bond system, such as imines, carbodiimides, diaza dienes, in different ways.[7] As we shown in Scheme 1-4, Hegedus

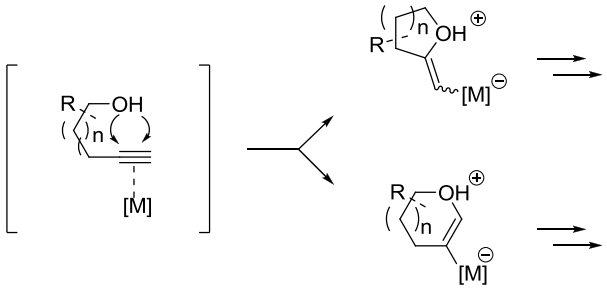
et al. proposed that on photolysis of $(CO)_5M$-[C(R)R'] in the presence of imines, β-lactams are formed.[8]

Scheme 1-4



Transition metal-catalyzed electrophilic activation of alkynes towards the attack of nucleophiles has been a subject of extensive study due to their high utility as useful methods for the construction of carbon frameworks. As shown in Scheme 1-5, oxygen-containing heterocycles utilizing the intramolecular variation of the reaction enhances the utility of the reaction, and a variety of methods for the preparation of useful compounds have been developed so far.[9]

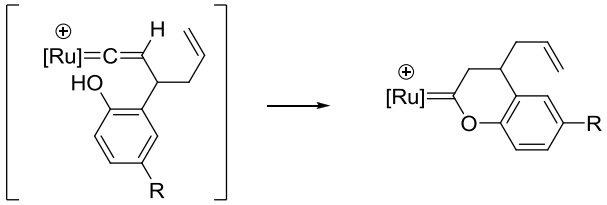
Scheme 1-5



In the previous researches, ruthenium alkoxy carbene complexes could be obtained from two pathways: (1) from vinylidene complexes and (2) from allenylidene

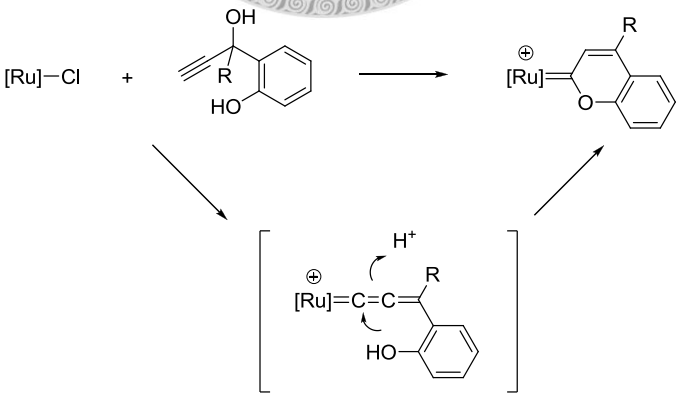
complexes. Examples are shown in Scheme 1-6 and Scheme 1-7 respectively.

Scheme 1-6



Nishibayashi and his co-workers reported many reactions of the diruthenium allenylidene complexes with a variety of nucleophiles, which attack either Cα or Cγ atom of the allenylidene ligands to afford Fischer-type carbenes or alkynyl complexes, respectively.[10] A similar result, shown in Scheme 1-7, using [Ru]Cl ([Ru] = $RuCp(PPh_3)_2$) to obtain cyclic alkoxy carbene complex via a ruthenium allenylidene complex, has been observed in our lab.

Scheme 1-7

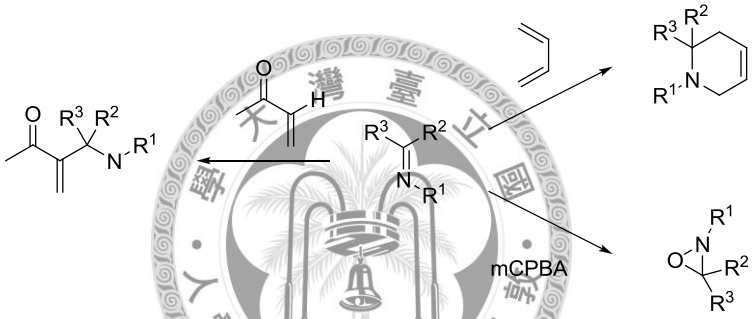


Imine Chemistry

Imines are typically prepared by the condensation of primary amines with aldehydes and, less commonly, with ketones.[11] The equilibrium in this reaction

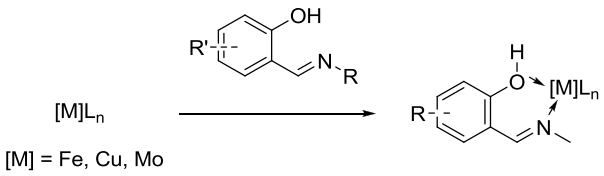
usually prefers the carbonyl compound and amine, so that use of dehydrating agent such as molecular sieves is required to push the reaction in favor of imine formation. As to the reactivity of imine, Scheme 1-8 shows many reactions of the imine functional group. The aza-Baylis-Hilman reaction[12] is analogous to the reaction of aldehyde and ketone and the aza Diels-Alder reaction[13] generates tetrahydropyridine ring. Treatment of imine with mCPBA could further give oxaziridine.[14]

Scheme 1-8



Also, imine compound is widely used in organic reaction. For instance, general synthesis of β-lactame via ketene-imine cycloaddition has been studied by Benito *et. al.*.[15] Mannich reaction which consists of an β-amino-ketone via imine intermediate is well-known, too.[16] As a chiral catalyst, proline is used, and asymmetric Mannich reactions could further afford the enantioselective product.[17]

At the same time, Schiff-base, containing an imine functionality and a hydroxy group, is a common ligand widely used in coordination chemistry. A variety of transition metal complexes of cobalt, molybdenum and copper, using Schiff base as a good bi-dentate ligand, are broadly studied.[18]

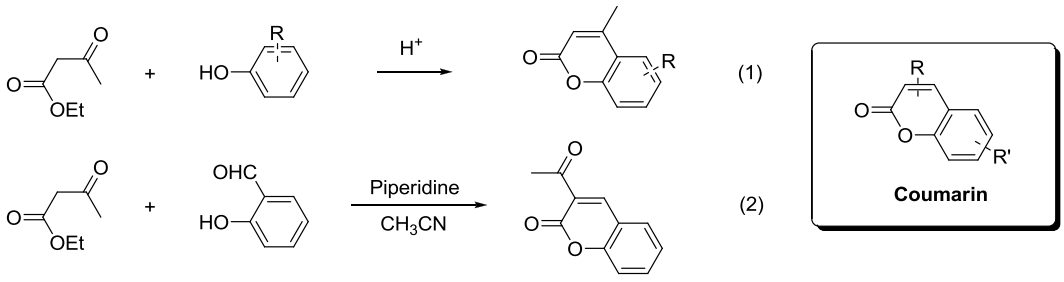


We report the reaction of the Schiff base **1** tethering a propargyl group with $Cp(PPh_3)_2RuCl$. Unlike a regular Schiff base, such a Schiff base with a propargyl group displays distinctive reactivity.

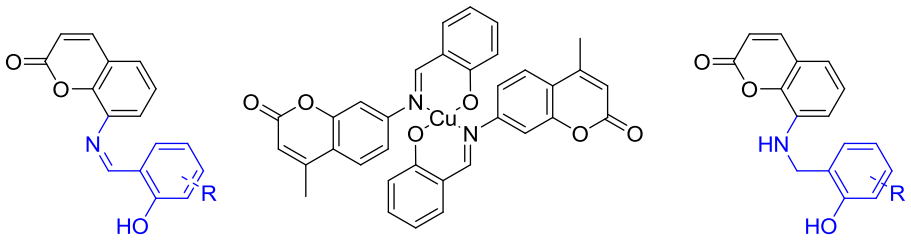
Coumarin

Coumarins, a class of fused ring heterocycles, occur widely in nature and show interesting biological activity.[19] Such a chemical fragment could be easily found in many compounds isolated from plants such as tonka bean and vanilla grass. Coumarins vary in structure due to the various types of substituents on their basic frames, which can influence their biological activity. Besides the biosynthesis in plants, coumarins could be prepared by many approaches e.g. Pechmann condensation[20] (see Scheme 1-9, eq.1) or Raju *et al.* hve done[21] (see Scheme 1-9, eq.2). Coumarin is also used as gain medium in some dye lasers, it is well documented that coumarin-type dyes possess excellent fluorescence quantum yield.[22]

Scheme 1-9



Coumarin derivatives are well known to possess a diverse array of pharmacological properties therefore chemistry of coumarins has been well studied. Recently, Bernadette and his co-workers have developed a series of coumarin-derived Schiff bases **a** and their Cu(II) complexes **b**, with the structure shown below. These coumarin derivatives were found to show significant activity against *Candida albicans* comparable to that of commercially available drug, Amphotericin B.[23] The corresponding amine ligands **c** from reduction of the imine functionality also have been studied. Though the anti-*Candida* activity is lower, the cytotoxicity studies reveal its ability to inhibit the growth of human colon cancer and human breast cancer cells, further unveil the chemotherapeutic potential.[24] Therefore, the biological activity of the chemicals which contains a coumarin fragment and a Schiff-base moiety is well documented.



a **b** **c**

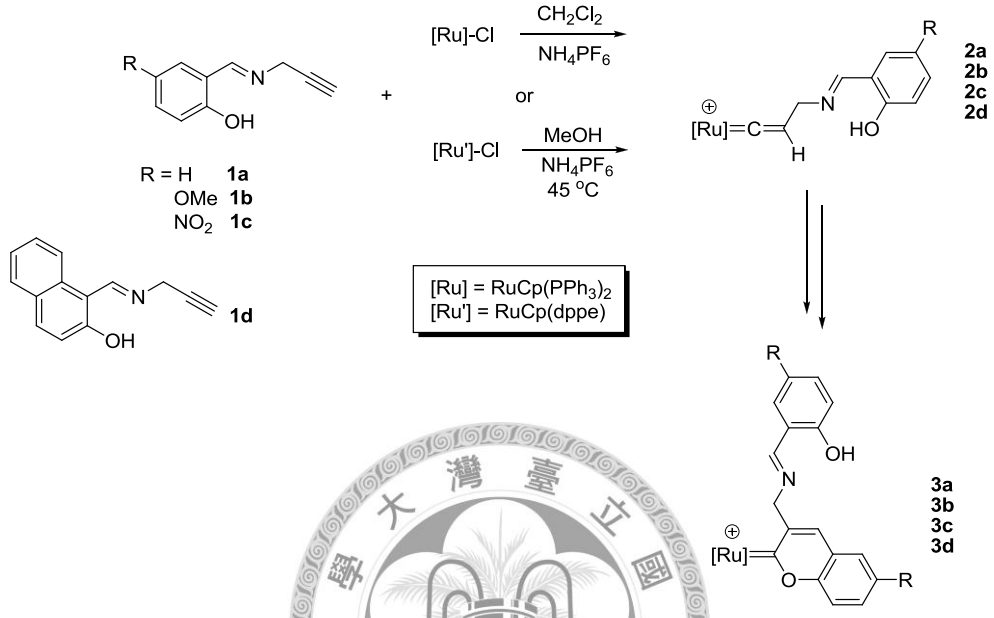
In this report, a series of Schiff base, each tethered a propargyl group on the nitrogen atom, are treated with the [Ru]-Cl to afford the alkoxy carbene complexes with polycyclic structure containing coumarin skeleton. Main structural feature of the Schiff base is retained (Scheme 2-1). The organic moiety of the ligand, which might

be a precursor for useful chemical, has not been reported before. In our preliminary trial, oxygenation has been attempted, however, no cleavage of the organic ligand from the ruthenium metal center is observed.

Results and Discussion

Reactions of Propargylic Imines Containing a Phenol Substituent.

Scheme 2-1



Compound 2-((prop-2-ynylimino)methyl)phenol (**1a**), a propargylaldimine, is prepared from the condensation of 2-hydroxy benzaldehyde and propargyl amine. Three analogous compounds **1b - 1d** are prepared similarly, using different aldehydes as starting materials. The ^{1}H signal at δ 8.66 of compound **1a** is assigned to the proton of the imine functionality. Treatment of excess **1a** with [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) and NH_4PF_6 in CH_2Cl_2 overnight afforded the carbene complex **3a** as the major product and the vinylidene complex **2a** as a minor product. The two singlet ^{31}P NMR signals at δ 42.97 and 49.00 are assigned to **2a** and **3a**, respectively**.** Additional small signals at around δ 16 and δ 50 are also seen in the ^{31}P NMR spectrum. Nevertheless, the intensity of these ^{31}P signals at around δ 16 and δ 50 is too small for identification

using other spectroscopic method. For a longer reaction time, the same reaction afforded, in high yield, the carbene complex **3a** without **2a**. The solution with only the carbene complex **3a** was filtered through Celite to remove the insoluble precipitates, then, the residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation via addition of a co-solvent of diethyl ether and hexane. If the solution still contains trace quantity of the vinylidene complex **2a**, reprecipitation should proceed in diethyl ether for purification because the solubility of **2a** in diethyl ether is higher than that of **3a**. Although the yield is lowered by dissolving a small quantity of **3a** in the solvent, higher purity of **3a** is achieved by ensuring that the residue does not contain complex **2a**. But when the quantity of **2a** is substantial such that its resonance can be easily seen in the NMR spectrum, the powder, obtained even after reprecipitation from only diethyl ether, will still consist of a mixture of two complexes. Only when the ratio of complex **3a** to complex **2a** is significantly high in the solution, pure **3a** can be obtained as the single product.

Formation of **3a** most likely proceeds through the vinylidene complex **2a**. Spectroscopic data, such as ^{1}H and ^{31}P NMR data, of complex **2a** in the reaction mixture could be obtained. However, attempts to isolate **2a** failed. Treatments of **1b**, and **1c** separately with [Ru]-Cl similarly yield complexes **3b** and **3c**, respectively. Interestingly, when **1d** is used in the reaction under the same reaction condition with

the same length of time i.e. overnight, the vinylidene complex **2d** is isolated, using the same purification procedure, and is characterized by spectroscopic method. But for a longer reaction time i.e. up to 7 days, the carbene complex **3d** becomes the major product with some by-products. If the starting material [Ru']-Cl ([Ru'] = Cp(dppe)Ru), instead of [Ru]-Cl, is used, the reaction condition should be modified, because of the slower reaction rate under the condition described above. Upon heating to 45 ℃ in MeOH, reactions of [Ru']-Cl with **1a** - **1d** speed up. Reactions overnight result in similar outcomes, and carbene complexes **3a'** – **3d'** are observed. Single crystals of **3a'** are obtained from a bi-layer solution of ether/CH_2Cl_2. The structure of complex **3a'** is confirmed by an X-ray diffraction analysis. An ORTEP drawing of **3a'** is shown in Figure 1. The bond length of Ru(1)-C(1) (1.986(2) Å) is between a single and a double metal-carbon bond, most likely because of the conjugated system of the ring structure. The bond length of the newly formed C(2)-C(3) bond (1.358(3) Å) is also between a single and double bond. The bond length of N(1)-C(11) (1.269(3) Å) reveals the nitrogen-carbon double bond of an imine group. A similar cyclic carbene complex has been reported by Bustelo et. al. and Pino-Chamorro et. al., obtained from the direct reaction of resorcinal with alkenylcarbyne complexes.[36]

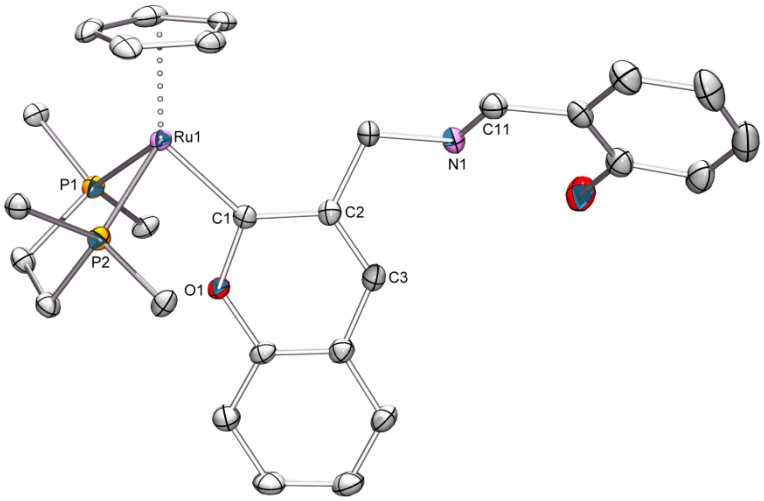
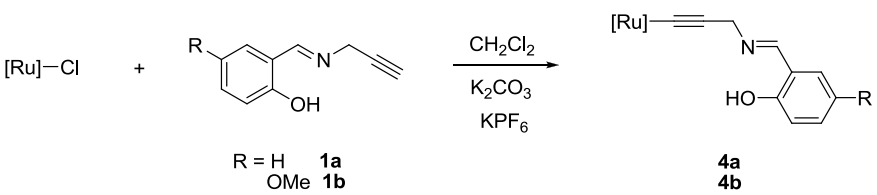


Figure 1. An ORTEP drawing of the cationic complex **3a'**. For clarity, aryl groups of the 1,2-bis(diphenylphosphino)ethane ligands on Ru except the *ipso* carbons, hydrogens and PF_6^- are omitted (thermal ellipsoid is set at the 50% probability level). Selected distances Å) and angles (deg): Ru(1)-C(1), 1.986(2); C(1)-C(2), 1.462(3); C(2)-C(3), 1.358(3); O(1)-C(1), 1.374(3); N(1)-C(11), 1.269(3). C(2)-C(1)-Ru(1), 132.01(17).

In the mass spectrum of **3b**, the parent peak at *m/z* 1014.24 reveals the composition of the ligand on the metal which should result from dimerization of **1b** accompanied with loss of a propargyl amine group. In the ^{1}H NMR spectrum of **3b**, resonances at δ 3.82 and δ 3.75 are assigned to two methoxy groups. The relative down field singlet peak at δ 8.83 is assigned to N=CH. In the ^{31}P NMR spectrum, a singlet peak is observed at δ 48.72 for **3b**. The Cα resonance in the ^{13}C NMR spectrum appears as a triplet at δ 260.70 with $^2J_{CP}$ = 14.5 Hz for **3b**. Complexes **3a**, **3c** and **3d** show similar NMR data.

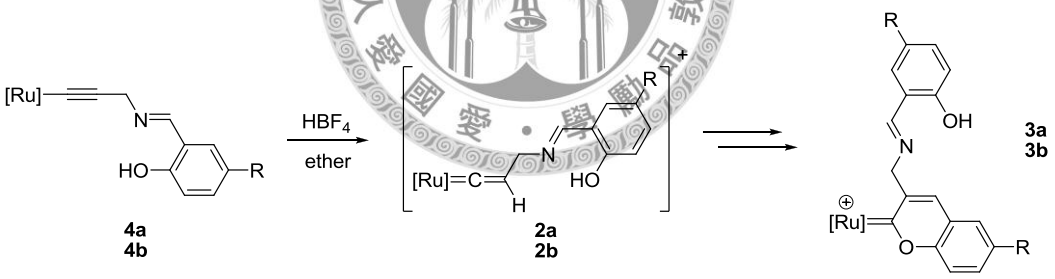
Scheme 2-2



Since we expect the formation of carbene complexes **3a** – **3d** from the vinyledene complexes **2a** – **2d**, attempts are thus made to prepare vinylidene complexes **2**. However, the vinylidene complexes are not isolated except when **1d** is used as the starting material. As expected from the previous report, the deprotonation can be easily achieved at Cβ of the vinylidene ligands in the presence of base giving the neutral acetylide complexes.[31] Therefore, we add base to the reaction system in order to trap the acetylide complex by deprotonation of the vinylidene intermediate. Presumably, it is easier to purify and isolate the neutral acetylide complex from a mixture of the cationic carbine complex and other cationic side products by reprecipitation method. Thereafter protonation is supposed to give the pure vinylidene complex. We first tried the conditions of using K_2CO_3 as a base source, methanol as a solvent and NH_4PF_6 as a salt in the beginning of the reaction. [Ru]-NH_3^+ becomes the major product because deprotonation takes place in the cationic ammonium NH_4^+ salt to give NH_3 thus reacting with [Ru]-Cl to yield the observed product. When NH_4PF_6 is replaced by KPF_6, which is not a protic salt, [Ru]-H rapidly forms. Probably base promotes coordination of methanol molecule to the ruthenium center which is followed by a β-hydrogen elimination to give [Ru]-H and formaldehyde.[32] Therefore, we choose the reaction condition by adding K_2CO_3 to the system with KPF_6 in CH_2Cl_2 at the beginning of the reaction to carry out the synthesis as shown in Scheme

2-2. Pure acetylide complexes **4a** and **4b** are obtained without the carbene complexes **3a** and **3b**. It is clear that, in these reactions, the vinylidene complexes **2a** and **2b** form first, then the deprotonation occurs readily. These results indirectly support the intermediate of the vinylidene complexes for the formation of the carbene complexes. The above-mentioned results are proposed on the basis of spectroscopic data. Singlet ^{31}P signal at δ 51.10 is assigned to the phosphine ligand of the neutral complex **4b**, different from that of **3b** which shows the ^{31}P singlet signal at δ 48.72. And the ^{1}H NMR spectrum of **4b** shows only one methoxy resonance instead of two methoxy peaks in the ^{1}H NMR spectrum of **3b**.

Scheme 2-3

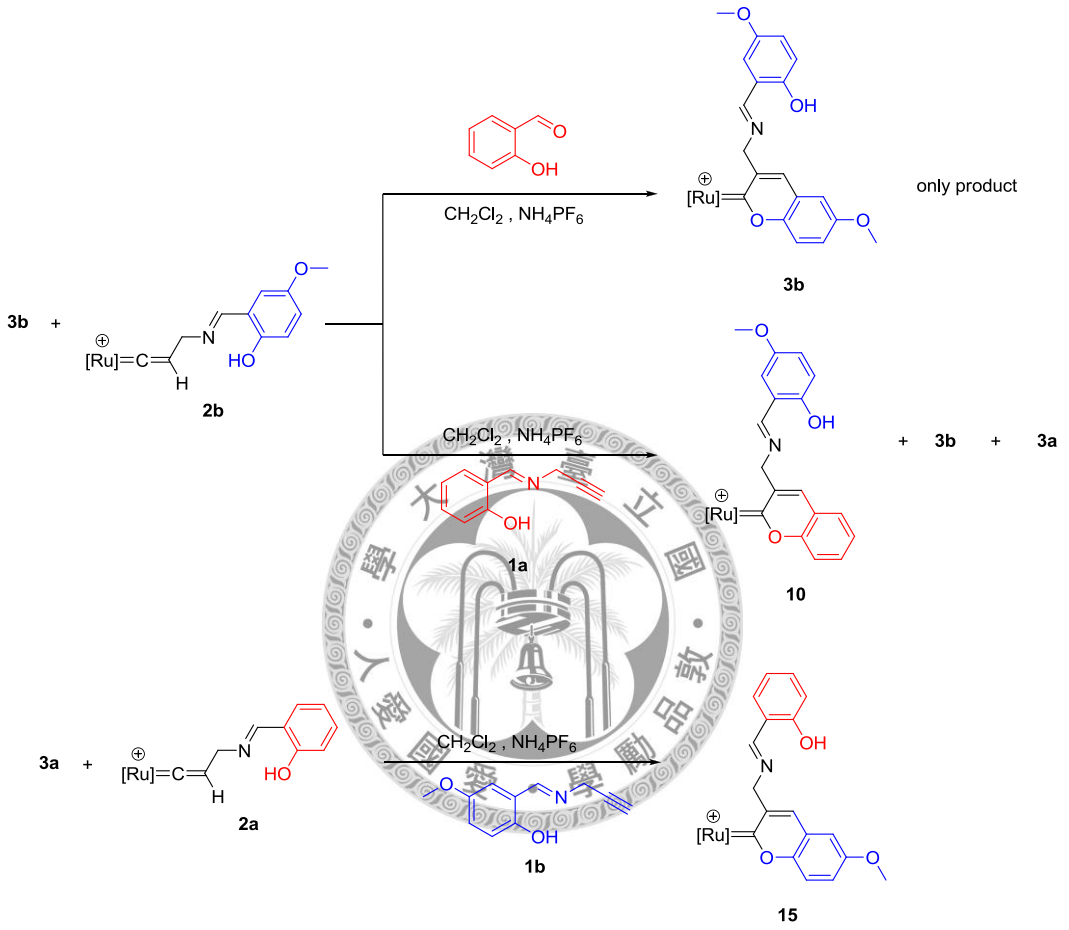


Protonation of complexes **4a** and **4b** is anticipated to form the corresponding vinylidene complexes **2a** and **2b**. However, as shown in Scheme 2-3, carbene complexes **3a** and **3b** are again isolated as the final product. Therefore, it is clear that formation of the vinylidene complex is readily followed by a further reaction to yield the observed carbene complex. It is also clear that the vinylidene complex with an imine group is much more reactive than the corresponding acetylide complex.

As formation of complex **3** involves a C-C bond formation as well as a cyclization reaction, it is interesting to explore further how complex **3** is formed. The vinylidene ligand of complex **2** is from complete conversion of **1**. The ligand in complex **3** resulted from addition of a *o*-cresol moiety to Cα and Cβ of the vinylidene ligand of **2** to yield a substituted 2*H*-chromene unit, with various substituents on the 3,6-positions. Several possible pathways are considered feasible for the formation of **3**. First, the carbene complexes could be formed by the addition of an aldehyde molecule to the proposed vinylidene intermediate. Presumably hydrolysis of the initial imine compound generates the aldehyde. However, as shown in Scheme 2-4, addition of other aldehyde i.e. the starting material of **1a**, namely 2-hydroxybenzaldehyde, to the vinylidene complex **2b** which resulted in no cross addition to give the mixed carbene complex **10**. Instead, the carbene complex **3b** is isolated as the only product; therefore, adding aldehyde seems to have no effect in the reaction. Addition of two other aldehydes which are use to synthesize **1c** and **1d** give the same results. Interestingly when the other imine **1a** is added to the system (**2b** + **3b**) as shown in Scheme below, in addition to the carbene complexes **3a** and **3b**, new mixed carbene complex **10** formed as evidenced by mass spectra. We also treat a mixture containing mostly the vinylidene complex **2a** with **1b** as shown in Scheme 2-4, and the very similar reaction give the mixed carbene **15**. Therefore, we believe that compounds with the imine

group, not with the aldehyde group, should play the key role for the addition to the vinylidene complexes to give the carbene products.

Scheme 2-4

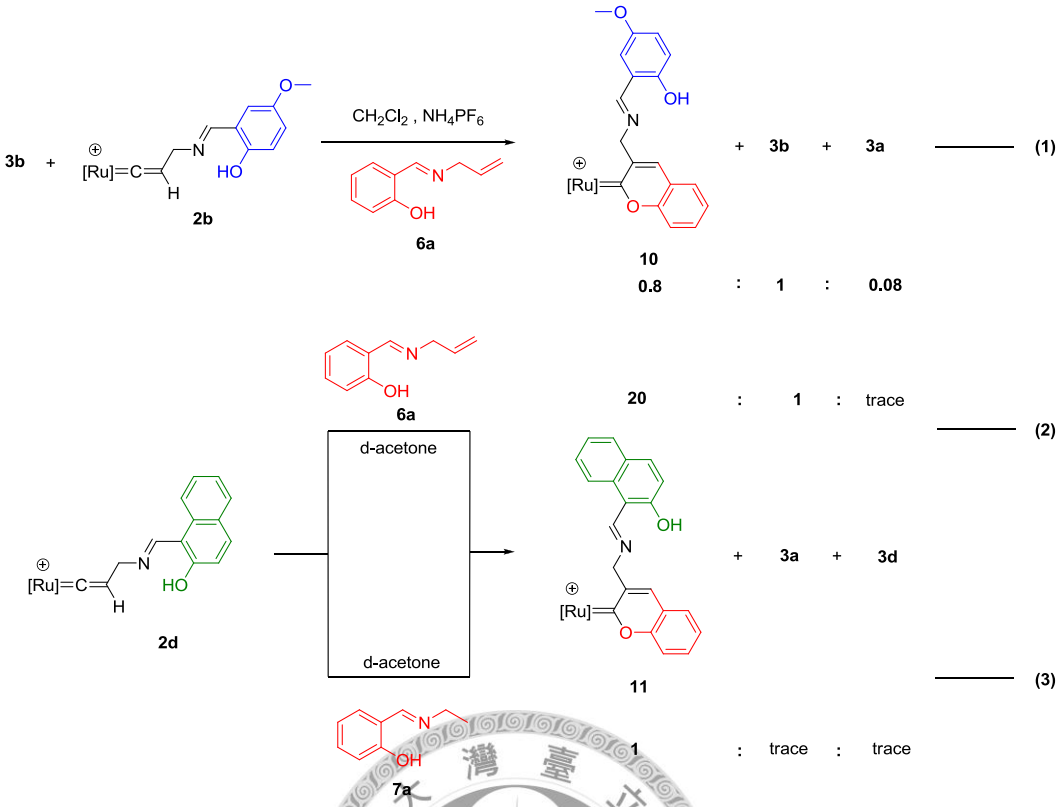


As mentioned before, the imine group should play a decisive role in the addition reaction to the vinylidene complexes **2** to form of carbene complexes **3**. As there are two possible imine sources exist in our reaction system i.e. the organic imine compounds **1a** – **1d** and the organometallic vinylidene complexes **2a** – **2d**, it is interesting to elucidate the role of imine.

If the organic propargylic imine **1a** is used, exchange of the whole ligand of the

vinylidene complex **2b** with **1a** should generate the vinylidene complex **2a** leading to the observed **3a**, as shown in Scheme 2-4. It is therefore not possible to designate the source of the aromatic group on the imine functionality on the metal, i.e. either from the organic imine compounds or from the vinylidene complexes. Therefore, the imine compound **6a** with an allyl group[4] is synthesized which is reacted with the vinylidene complex **2b** for one day as shown in equation (1) of Scheme 2-5. However, the carbene complex **3a** is nonetheless observed. The formation of **3a** will be discussed below. The ratio of these three carbene complexes **10**:**3b**:**3a** is approximately 1:0.8:0.08 from the ^{31}P NMR spectrum and three complexes are inseparable. Therefore, simple ^{1}H NMR spectrum of **10** is not easily obtained for characterization. So another vinylidene complex **2d**, which is more stable, is chosen to undergo cyclization in d-acetone for overnight as shown in equation (2) and (3) of Scheme 2-5. Complex **2d** is treated with the allyl imine **6a** and ethyl imine **7a**[5] separately, and in both experiments, all three different carbene complexes **11**, **3a**, **3d** can be detected from mass spectra. In both case, complex **11** is the major product. Hence, the reactant with the vinylidene complexes **2** to give the carbene complexes **3** should require an imine moiety.

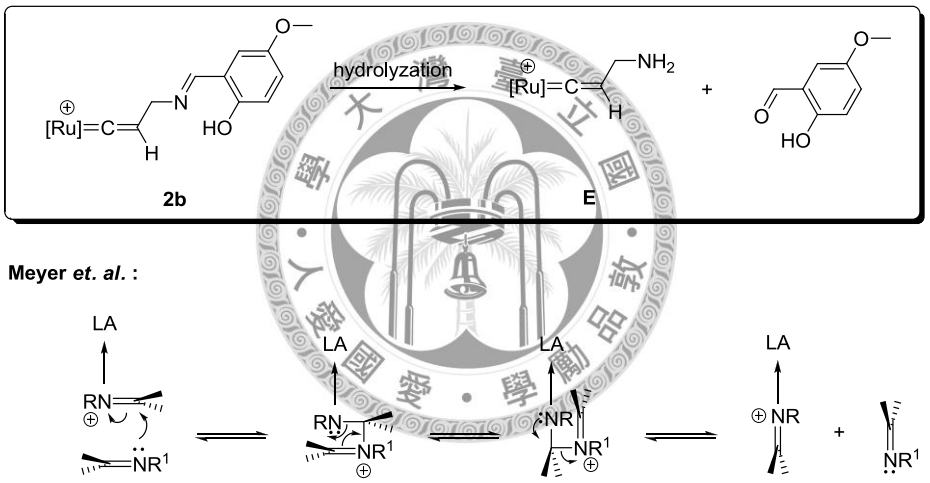
Scheme 2-5



It is interesting that the carbene complex **3a** is observed in all three reactions in Scheme 2-5. The added imines **6a**, with an allyl group, or **7a**, with an ethyl group, used in all three reactions contain no propargyl group. Seemingly ligand exchange would not be possible to generate **2a** in the reaction which could further give complex **3a**. However, as shown in Eqs. (1) (2) and (3), complex **3a**, other than the expected **10**, **3b**, **11** and **3d**, is nevertheless observed. It is clear that the formation of **3a** should require **2a**. It is also well known that imine is readily hydrolyzed to yield aldehyde. If hydrolysis of **2b** proceeds similarly, a vinylidene complex **E** (see Scheme 2-6) with an amine group will be obtained which could further react with aldehyde from hydrolysis of **6a** to give **2a**. However, an attempted preparation of **E** by directly treating propargyl amine with [Ru]-Cl afforded a complicated mixture, as

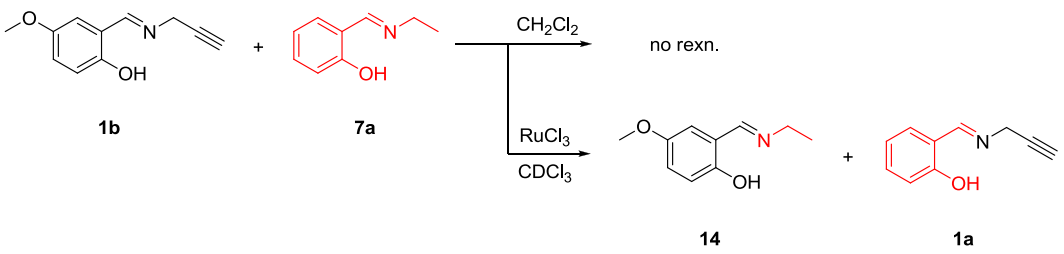
a result, complex **E** is believed to be very unstable. Therefore, the pathway via hydrolysis for the formation of complex **2a** is considered not feasible. On the other hand, Meyer *et. al.* have discovered that imine metathesis takes place in the presence of Lewis acid with the proposed mechanism shown in Scheme 2-6.[29b] Consequently the imine metathesis pathway is considered as the main route to give complex **2a** in our case.[3]

Scheme 2-6



Interestingly, as shown in Scheme 2-7, exchange reaction between two organic imine compounds **1b** and **7a** in the absence of Lewis acid is not observed in CH_2Cl_2. But, the same exchange reaction in the presence of $RuCl_3$ in $CDCl_3$ gives new imine compounds **14** and **1a** in 6% conversion overnight and 32% conversion in three days.

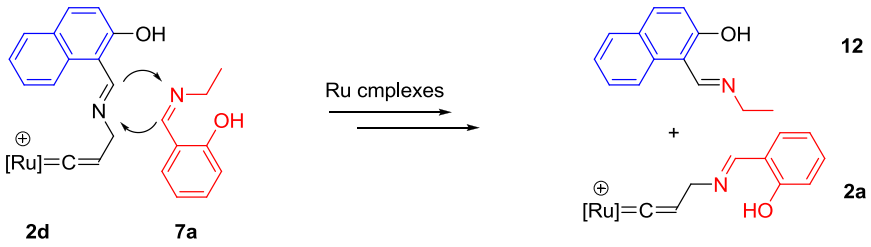
Scheme 2-7



1b **7a** **14** **1a**

The reaction pathway shown in Scheme 2-8 is proposed on the basis of our observation shown in Scheme 2-7 and previous results of Meyer *et. al*. The direct imine metathesis reaction between the two imine functionalities of complex **2d** and **7a** probably afford **12** and complex **2a**, which further gives complex **3a**. Compound **12** can be purified and isolated by column chromatography of the residue. The quartet ^{1}H signal at δ 3.65 and triplet ^{1}H signal at δ 1.40 with $^3J_{HH}$ = 7.34 Hz are assigned to the protons of the ethyl group of **12**, and the parent peak at *m/z* 199.13 in the mass spectrum also support the structure we proposed. Since the imine functionality is easily hydrolyzed when passing through a silica gel column, small ^{1}H signals of 2-hydroxy-1-naphthaldehyde is also seen in the ^{1}H NMR spectrum of **12**. Therefore, complex **3a** in the reactions shown in Scheme 2-5 is believed to come from the imine metathesis reaction between the organometallic vinylidene complex with an imine functionality and organic imine. Probably organometallic species in the reaction may play the role of Lewis acid.

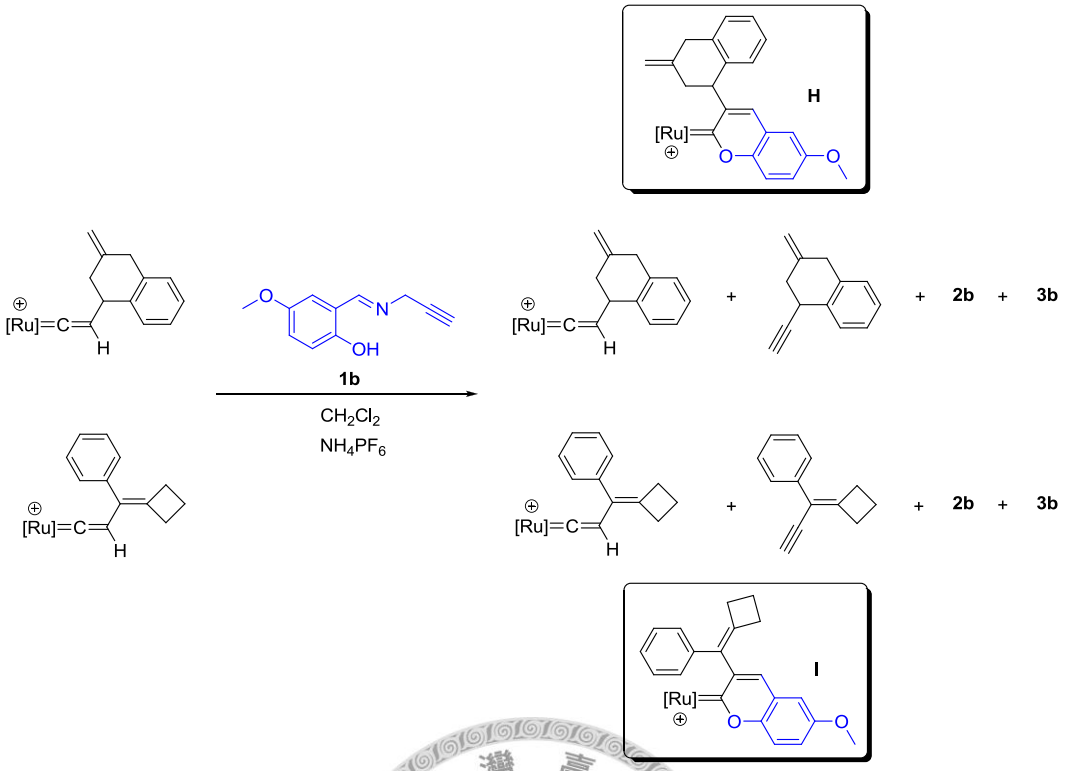
Scheme 2-8



Recapitulate the results in Scheme 2-5 and Scheme 2-8, with the aforementioned metathesis process, the organometallic imine **2a** could serve as the source of added portion for the mixed carbene complex, even the organic imine (**6a** or **7a**) which has no propargyl group is chosen to react with **2d** and **2b**. The elucidation of the role of the added imine should be clarified by other method, which will be discussed later.

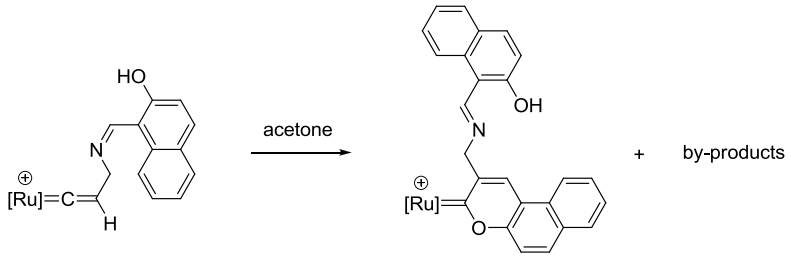
In addition, the necessity of an imine functional group within the vinylidene complex for such a cyclization should be checked. Therefore, we carried out the experiments shown in Scheme 2-9. Two different vinylidene complexes without the imine group are, separately, reacted with the imine compound **1b**. If the imine group on the vinylidene complex **2** is not important, we should observe the similar cyclization between vinylidene complex and imine compound **1b** which presumably gives the corresponding mixed carbene complexes **H** or **I**. However, neither **H** nor **I** were observed. Ligand exchange generates the vinylidene complex **2b**, and the carbene complex **3b** is also seen. As a result, the imine functionality on the vinylidene complex **2** is essential.

Scheme 2-9



Moreover, the isolated vinylidene complex **2d** in acetone was stirred under nitrogen without any other added organic imine reactants for 7 days, as shown in Scheme 2-10. Formation of the carbene complex **3d** and some other by-products with disappearance of complex **2d** is observed. However, since there exists an equilibrium between the vinylidene complex **2d** and its π-coordinated isomer, which might release the free imine ligand **1d**, so, formation of **3d**, shown in Scheme 2-10, may result from coupling of free **1d** with **2d**. For that reason, direct coupling of two vinylidene complexes **2d** may not be the only way to yield **3d**.

Scheme 2-10

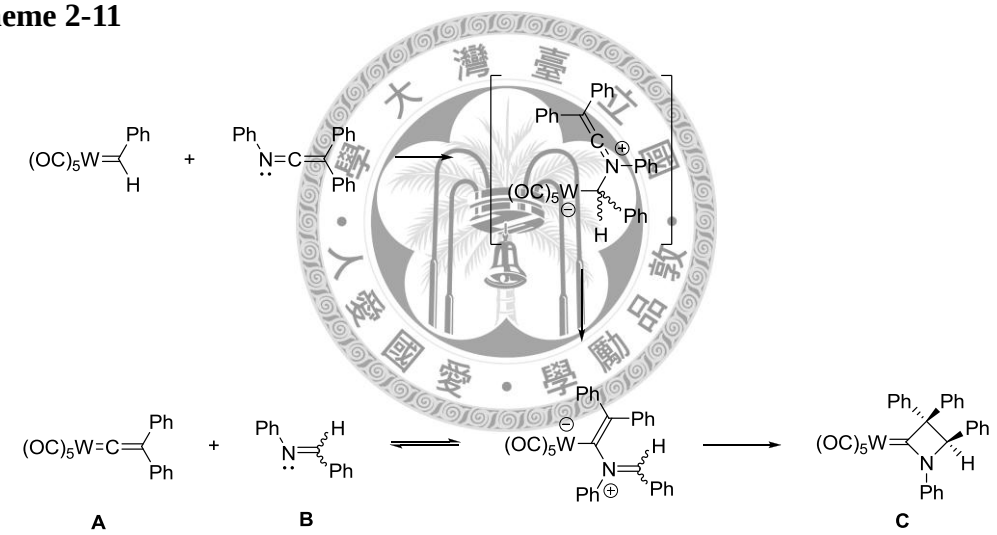


2d **3d**

Additionally, when we first run the reaction of Scheme 2-1, in addition to the vinylidene complex and the carbene complex, an impurity in trace quantity was observed and from the ^{31}P NMR spectrum, namely, small signals around δ 16 and δ 50 can be seen. However, this complex cannot be identified by spectroscopic method, even after purification by reprecipitation. When a larger quantity of starting material was used in the reaction, mixture of the crude product was further run through a neutral Al_2O_3 column to give two bands. The first band, containing this side product, was eluted by CH_2Cl_2 and acetone in the ratio 100:1. The second band consists of a mixture of the vinylidene complex **2** and the carbene complex **3**. The ^{31}P NMR spectrum of the first band, which displays a ^{31}P triplet signal at δ 16.08 assigned to the phosphonium group, and a ^{31}P doublet signal at δ 50.02 assigned to the phosphine ligand on the ruthenium metal, shows the pattern expected for a cationic phosphine addition product. The structure of this addition product is proposed as **13**, as shown in Mechanism 1-1. And the parent peat at *m/z* 991.23 in the mass spectrum of this acetylide complex **13** is also consistent with the formula of the structure. On the basis of these experimental results, we propose the mechanism for the formation

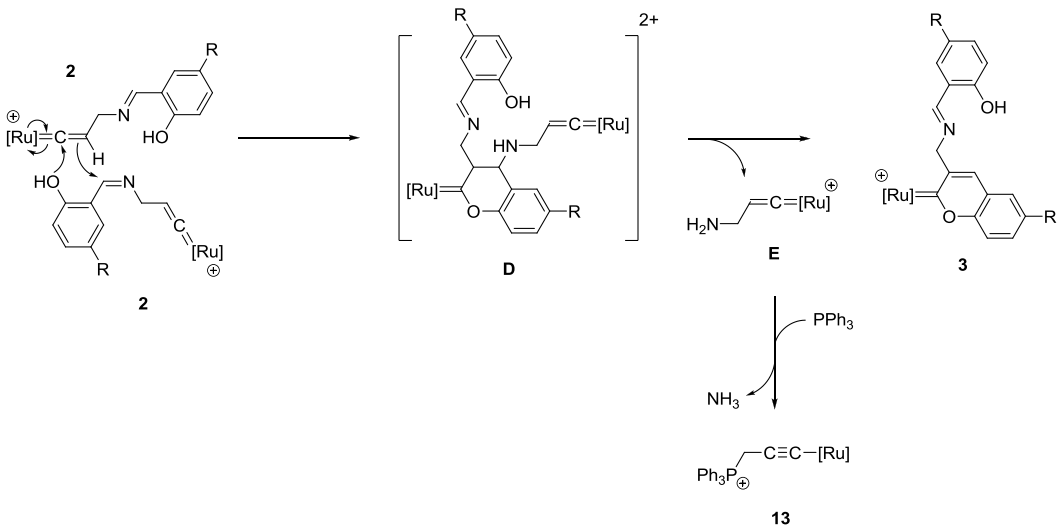
of carbene complex, as shown in Mechanism 1-1. The vinylidene complex first formed from terminal alkyne, then the two vinylidene complexes may dimerize to give dinuclear carbene vinylidene complex **D**, via the vinylidene ligand and the imine/phenol groups. Previously, as shown in Scheme 2-11, metathesis between a tungsten vinylidene complex **A** and an imine compound **B** via a C-C bond formation has been reported.[1] But the nucleophilic role is played by the lone pair on nitrogen atom of imine to afford compound **C**.

Scheme 2-11



Then the intermediate **D** undergoes an elimination of the vinylidene moiety to afford the final carbene complex **3**. Namely, cleavage of the ruthenium complex **E** in which the vinylidene ligand bonds to an amine group from the dinuclear complex **D** takes place. Deamination of **E** is followed by nucleophilic substitution of a phosphine molecule to give the acetylide complex **13** with a phosphonium group.

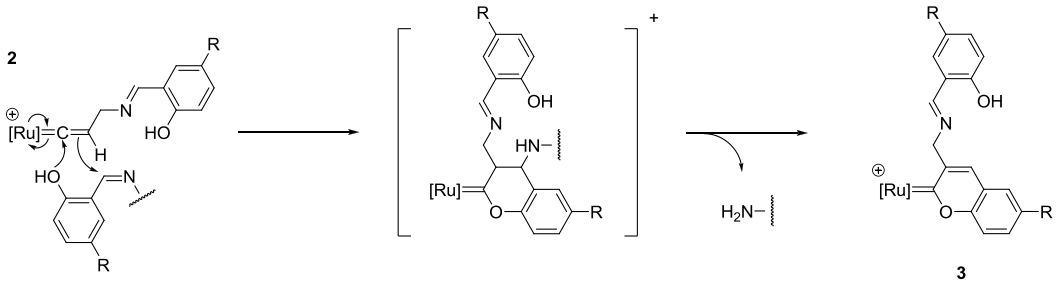
Mechanism 1-1



The summary of the overall reaction outcome is, the formation of the carbene complexes **3** should be formed from the vinylidene complex **2** with an imine functionality. And the added molecule to complexes **2** should have the imine group, too. As we already talked before, the role of the added imine compound should be elucidate by another method. Mechanism 1-1 we proposed indicates that the added imine compound is another vinylidene complex which could explain the formation of complex **13**, but depends on the reaction pathway, the yield of the carbene complexes **3** and **13** should be equal and 50% yield top. However, the high yield which over 50% of the carbene complexes **3** is observed, and the quantity divergence between **3** and **13** is also seen. Therefore, a general Mechanism 1-2 is proposed bellowed. The added compound to achieve the cyclization with the vinylidene complexes **2** could come from both the organometallic imine and organic imine molecules. The major source of added compound is believed to come from organic imine molecule since the high

yield, and the minor source which comes from organometallic imine molecule is contemplated on the basis of the trace quantity of complex **13**.

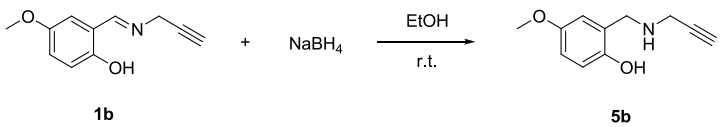
Mechanism 1-2



Reactions of the Amine Analogue.

As the imine functional group plays a key role on the reaction, it is interesting to compare the reactivities of propargylic imine and the corresponding amine. Transformation of the imine functional group into an amine group could be readily achieved by a simple reduction. As shown in Scheme 2-12, we use sodium borohydride as the reducing agent[2] to reduce the propargylic imine **1b** to the corresponding amine **5b**, 4-methoxy-2-((prop-2-ynylamino)methyl)phenol. Then compound **5b** was reacted with the ruthenium chloride.

Scheme 2-12

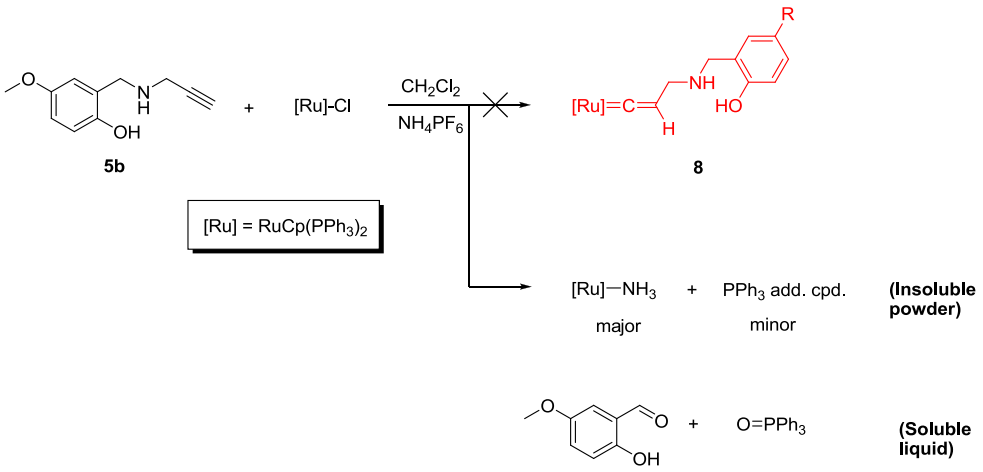


1b **5b**

Under the same reaction condition as that in the imine system, the amine compound **5b** was reacted with [Ru]-Cl ([Ru] = $Cp(PPh_3)_2Ru$) and NH_4PF_6 in CH_2Cl_2 overnight. However, the reaction rate is slow at room temperature. Thus, the temperature was

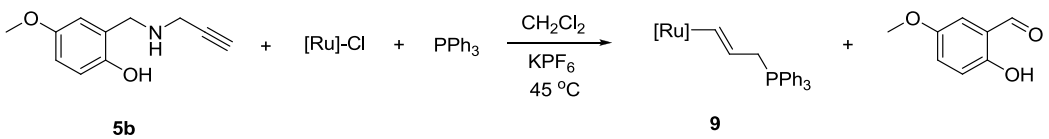
raised to 40 ^{o}C for 12 hours. After the same purification procedure, using diethyl ether to reprecipitate the residue, insoluble powder and liquid are separated. Instead of the desired vinylidene complex **8**, as shown in Scheme 2-13, a mixture containing [Ru]-NH_3 as the major product was isolated, and the minor product shows the ^{31}P NMR pattern expected for a cationic phosphine addition, also shown in Scheme 2-13. The formation of [Ru]-NH_3 is probably due to the basicity of amine ligand that deprotonates the ammonium NH_4^+ salt, leading to the formation of [Ru]-NH_3. In the ^{31}P NMR spectrum of the powder, a signal at δ 45.63 is assigned to [Ru]-NH_3. The ^{31}P NMR spectrum of the minor product shows a triplet signal at δ 14.92 and a doublet signal at δ 52.64. This is different with that of complex **13** shown in Mechanism 1. In addition, in the ^{1}H NMR spectrum of the soluble liquid, besides the signals of phosphine oxide, two down field signals at δ 9.84 and δ 10.62 are observed. After we further run through silica gel to remove the phosphine oxide, we find that the organic compound is identified as the starting material 5-methoxy-2-hydroxybenzaldehyde.

Scheme 2-13



In order to enhance the yield of the minor product which shows the pattern expected for a cationic phosphine addition product, as shown in Scheme 2-13, the salt NH_4PF_6 is replaced by KPF_6, and excess free phosphine is added in the beginning of the reaction as shown in Scheme 2-14. The mixture was heated to 45°C for 3 days, followed by purification using diethyl ether to reprecipitate. The acetylide complex **9** and the organic compound 5-methoxy-2-hydroxybenzaldehyde, shown below, were obtained. The triplet ^{31}P NMR signal at δ 14.92 is assigned to the phosphonium group, and the doublet signal at δ 52.64 assigned to the phosphine ligand on the ruthenium metal. In the ^{1}H NMR spectrum of **9**, a multiplet signal at δ 8.22 is assigned to CαH. In the mass spectrum, the parent peak at *m/z* 993.25 also support the structure of **9**, we proposed.

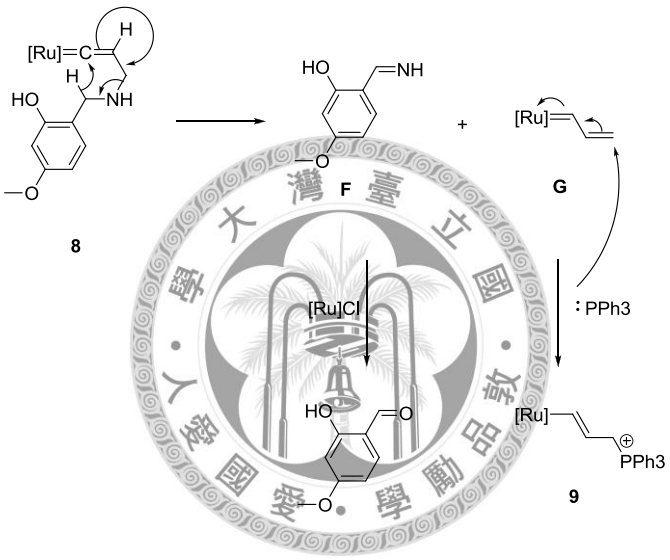
Scheme 2-14



The proposed mechanism for the reaction with the amine ligand is thus shown in

Mechanism 2, based on the previous research from our group.[33] Probably, the vinylidene complex **8** formed at first, then a 1,5-hydrogen shift takes place to give the imine compound **F** and the intermediate **G**. Free phosphine in solution attacks Cγ of complex **G** readily to give the final product **9**, and the imine compound undergoes hydrolysis to give 5-methoxy-2-hydroxybenzaldehyde.

Mechanism 2



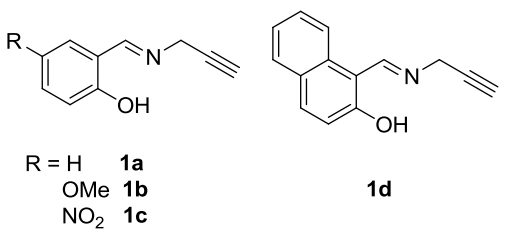
Conclusion

In summary, we report distinctive reactivity of the Schiff base-type compounds containing a propargyl moiety in the reaction with [Ru]-Cl. First, the vinylidene complexes **2** are formed, followed by an addition reaction, which added an *o*-cresol moiety between the Cα and Cβ of **2**, to give the carbene complexes **3** as the final product. The added cresol portion should come from a molecule which also has an imine functionality, instead of an aldehyde group. When two imines with different substituents were used in the reaction, new cross carbene complex formed from coupling of two imine molecules as evidenced by the mass spectrum. If formation of **3** is from the dimerization of two vinylidene complexes, one would obtain the vinylidene complex **E**. The acetylide complex **13** with a phosphonium group, presumably formed by deamination and phosphine addition to **E**, was indeed observed as a minor product. However, the fact, that yields of complexes **13** and **3** are unequal, and the yield of the carbene complexes **3** is over 50%, indicates that the source of the added *o*-cresol moiety most likely comes from an organic imine. In addition, reaction of the amine analogue **5b**, which retains the propargyl group and phenol moiety, with [Ru]Cl is also explored. The cationic phosphine addition product **9**, instead of the carbene complex **3**, is obtained. Different reactivities are observed between the reactions of imine and amine.

Experimental section

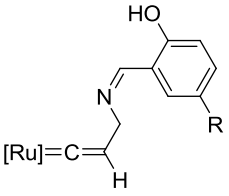
General Procedures. The manipulation were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques unless mentioned otherwise. Solvent were dried by standard methods and were distilled under nitrogen before use. All reagents were obtained from commercial supplier and were used without further purification. NMR spectra were recoreded on Brucker AC-300 instrument, Bruker DPX-400, AVIII-400FT-NMR spectrometer at room temperature and are reported in units of δ with residual protons in the solvents as a standard. Electrospray ionization mass spectrometry, elemental analysis and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University. According to the literature methods, [Ru]Cl ([Ru] = $Cp(PPh_3)_2Ru$)[34] were prepared from $RuCl_3 \cdot xH_2O$ which was purchased from Steam Chemicals.[Ru]Cl ([Ru] = Cp(dppe)Ru)[35] were prepared from Cp(PPh3)2RuCl according to the procedure described in references.

[Ru']Cl: CpRu(dppe)Cl (dppe = 1,2-Bis(diphenylphosphino)ethane)

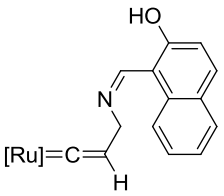


R = H **1a**
OMe **1b**
NO_2 **1c**

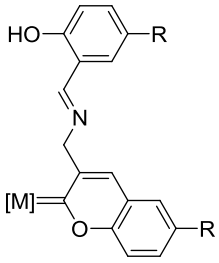
1d



R = H **2a**
OMe **2b**
NO_2 **2c**

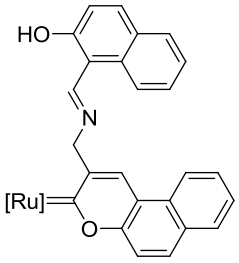


2d

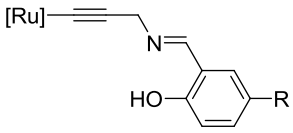


R = H **3a**, **3a'**
OMe **3b**, **3b'**
NO_2 **3c**

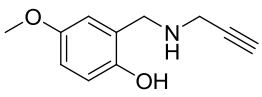
[M] = $RuCp(PPh_3)_2$
RuCp(dppe)



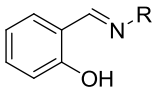
3d



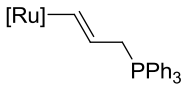
R = H **4a**
OMe **4b**



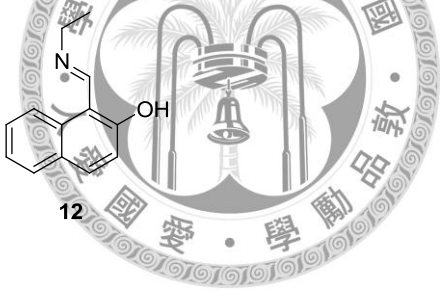
5



R = $-CH_2-CH=CH_2$ **6a**
Et **7a**



9



12

Synthesis of Compound 1a. To a Schlenk flask charged with 2-hydroxy-benzaldehyde (1.98 g, 0.016 mole) and propargyl amine (1.07 g, 0.019 mole) in the presence of $MgSO_4$, then 30 mL of toluene were added under nitrogen. The resulting solution was stirred at room temperature overnight. The reaction mixture was extracted with EA, and organic phase was washed with aqueous NH_4Cl and dried over $MgSO_4$. Solvent was then removed under reduced pressur to give compound **1a** (2.45 g, 0.015 mole, 95% yield). Then Spectroscopic data for **1a**: ^1H NMR (δ, $CDCl_3$): 12.87 (s, 1H, OH); 8.66 (t, $^4J_{HH}$ = 2.12 Hz, 1H, N=CH); 6.86 - 7.33

(m, 4H, Ph); 4.52 (t, $^4J_{HH}$ = 2.12 Hz, 2H, CH_2); 2.55 (t, $^4J_{HH}$ = 2.12 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 165.73 (N=C); 160.65 (Ph - OH); 132.53, 131.70, 118.75, 116.99 (Ph, =C); 77.47, (C≡); 76.51 (≡CH); 45.38 (CH_2).

Compound **1b** (1.31 g, 6.93 mmole, 94% yield) was similarly prepared from 2-hydroxy-5-methoxybenzaldehyde (1.12 g, 7.37 mmole) and propargyl amine (0.47 g, 8.53 mmole) with $MgSO_4$ in toluene. Spectroscopic data for **1b**: ^{1}H NMR (δ, $CDCl_3$): 12.38 (s, 1H, OH); 8.62 (t, $^4J_{HH}$ = 2.12 Hz, 1H, N=CH); 6.82 – 6.94 (m, 3H, Ph); 4.52 (t, $^4J_{HH}$ = 2.12 Hz, 2H, CH_2); 3.77 (s, 3H, OCH_3); 2.56 (t, $^4J_{HH}$ = 2.12 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 165.44 (N=C); 154.80, 152.09 (Ph – OH, Ph – OCH_3); 119.64, 118.33, 117.76, 115.16 (Ph, =C); 77.45 (C≡); 76.60 (≡CH); 55.94 (-OCH_3); 45.43 (CH_2).

Compound **1c** (1.21 g, 5.93 mmole, 95% yield) was similarly prepared from 2-hydroxy-5-nitrobenzaldehyde (1.04 g, 6.22 mmole) and propargyl amine (0.41 g, 7.44 mmole) with $MgSO_4$ in toluene. Spectroscopic data for **1c**: ^{1}H NMR (δ, $CDCl_3$): 13.98 (s, 1H, OH); 8.78 (t, $^4J_{HH}$ = 2.14 Hz, 1H, N=CH); 8.32 (d, $^4J_{HH}$ = 2.72 Hz, 1H, Ph); 8.22 (dd, $^3J_{HH}$ = 9.16 Hz, $^4J_{HH}$ = 2.72 Hz, 1H, Ph); 7.03 (d, $^3J_{HH}$ = 9.16 Hz, 1H, Ph); 4.60 (t, $^4J_{HH}$ = 2.14 Hz, 2H, CH_2); 2.65 (t, $^4J_{HH}$ = 2.14 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 170.09 (Ph – OH); 165.90 (N=C); 138.70, 129.95, 129.32, 120.14, 117.97 (Ph, =C); 79.63, (C≡); 78.87 (≡CH); 44.77 (CH_2).

Compound **1d** (1.17 g, 5.60 mmole, 89% yield) was similarly prepared from 2-hydroxy-1-naphthaldehyde (1.08 g, 6.28 mmole) and propargyl amine (0.42 g, 7.63 mmole) with $MgSO_4$ in toluene. The remained 2-hydroxy-1-naphthaldehyde with **1d** in a ratio of 1:10 can not be removed even further purified by column chromatography. Spectroscopic data for **1d**: ^{1}H NMR (δ, $CDCl_3$): 14.68 (s, 1H, OH); 9.57 (br, 1H, N=CH); 7.04 – 9.57 (m, 6H, Ph); 4.65 (dd, $^4J_{HH}$ = 2.44 Hz, $^4J_{HH}$ = 1.44 Hz, 2H, CH_2); 3.11 (t, $^4J_{HH}$ = 2.44 Hz, 1H, ≡CH). ^{13}C NMR (δ, CD_2Cl_3): 166.44 (N=C); 161.59 (Ph – OH); 135.62, 133.62, 129.65, 128.35, 127.94, 123.79, 121.40, 119.62, 108.85 (Ph, =C); 78.27 (C≡); 76.59(≡CH); 44.88 (CH_2).

Synthesis of Complex 2a. To a Schlenk flask charged with [Ru]Cl (0.097 g, 0.13 mmole) and NH_4PF_6 (0.054 g, 0.33 mmole), 1.2 equiv of heteroenyne **1a** (0.025 g, 0.16 mmole) and 2.4 equiv of 2-hydroxybenzaldehyde (0.041 g, 0.33 mmole) and 10 mL of CH_2Cl_2 were added under nitrogen. The resulting solution was stirred at room temperature overnight. The solution was filtered through Celite to remove the insoluble precipitates, then the volatiles were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by addition of 70 mL of diethyl ether and hexane (1:1). Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a mixture of complex **2a** and **3a** in a ratio of 3.6:1. (0.104

g). However, complex **2a** undergoes further reaction to give **3a** easily when collecting the ^{13}C NMR spectrum. Spectroscopic data for **2a**: ^{1}H NMR (δ, $CDCl_3$): 13.22 (s, 1H, OH); 8.14 (s, 1H, N=CH); 6.83 - 7.75 (m, 34H, Ph); 5.15 (s, 5H, Cp); 5.00 (t, $^{3}J_{HH}$ = 8.12 Hz, 1H, CβH); 4.40 (d, $^{3}J_{HH}$ = 8.12 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.68 (s, PPh_3). MS (ESI^+) *m/z*: 850.20. Anal.Calcd for $C_{51}H_{44}F_6NOP_3Ru$: C, 61.57; H, 4.46.

Complex **2b** (0.18 g) was similarly prepared from 1.2 equiv of **1b** (0.047 g, 0.25 mmole) and 2.4 equiv of 5-methoxy-2-hydroxybenzaldehyde (0.079 g, 0.52 mmole) and [Ru]Cl (0.152 g, 0.21 mmole) in the presence of NH_4PF_6 (0.091 g, 0.56 mmole) in CH_2Cl_2. The final product can be obtained as a mixture of complex **2b** and **3b** in a ratio of 1.8:1. However, complex **2b** undergoes further reaction to give **3b** easily when collecting the ^{13}C NMR spectrum. Spectroscopic data for **2b**: ^{1}H NMR (δ, $CDCl_3$): 12.70 (s, 1H, OH); 8.17 (s, 1H, N=CH); 6.62 - 7.84 (m, 36H, Ph); 5.14 (s, 5H, Cp); 5.00 (t, $^{3}J_{HH}$ = 8.00 Hz, 1H, CβH); 4.38 (d, $^{3}J_{HH}$ = 8.00 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.72 (s, PPh_3). MS (ESI^+) *m/z*: 880.20. Anal.Calcd for $C_{52}H_{46}F_6NO_2P_3Ru$: C, 60.94; H, 4.52.

Complex **2c** (0.16 g) was similarly prepared from 1.2 equiv of **1c** (0.085 g, 0.42 mmole) and 2.4 equiv of 2-hydroxy-5-nitrobenzaldehyde (0.14 g, 0.82 mmole) and [Ru]Cl (0.148 g, 0.20 mmole) in the presence of NH_4PF_6 (0.088 g, 0.54 mmole) in CH_2Cl_2. The final product can be obtained as a mixture of complex **2c** and **3c** in a

ratio of 4.1:1. However, complex **2c** undergoes further reaction to give **3c** easily when collecting the ^{13}C NMR spectrum. Spectroscopic data for **2c**: ^{1}H NMR (δ, $CDCl_3$): 14.00 (s, 1H, OH); 8.78 (s, 1H, N=CH); 6.89 - 7.40 (m, 33H, Ph); 5.19 (s, 5H, Cp); 5.08 (t, $^{3}J_{HH}$ = 7.95 Hz, 1H, CβH); 4.45 (d, $^{3}J_{HH}$ = 7.95 Hz, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.69 (s, PPh_3). MS (ESI^+) *m/z*: 895.18. Anal.Calcd for $C_{51}H_{43}F_6N_2O_3P_3Ru$: C, 58.91; H, 4.17.

Synthesis of Complex 2d. To a Schlenk flask charged with [Ru]Cl (0.097 g, 0.13 mmole) and NH_4PF_6 (0.058 g, 0.36 mmole), 2 equiv of heteroenyne **1d** (0.070 g, 0.335 mmole) and 10 mL of CH_2Cl_2 were added under nitrogen. The resulting solution was stirred at room temperature overnight. The solution was filtered through Celite to remove the insoluble precipitates, then the volatiles were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by addition of 70 mL of diethyl ether and hexane (1:1). Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as an orange powder **2d** (0.104 g, 0.12 mmole, 84% yield). Spectroscopic data for **2d**: ^{1}H NMR (δ, $CDCl_3$): 14.37 (s, 1H, OH); 8.62 (s, 1H, N=CH); 7.75 (d, $^{3}J_{HH}$ = 8.25 Hz, 1H, Ph); 7.69 (d, $^{3}J_{HH}$ = 9.27 Hz, 1H, Ph); 7.58 (d, $^{3}J_{HH}$ = 8.25 Hz, 1H, Ph); 6.93 - 7.76 (m, 32H, Ph); 6.95 (d, $^{3}J_{HH}$ = 9.27 Hz, 1H, Ph); 5.17 (s, 5H, Cp); 5.08 (t, $^{3}J_{HH}$ = 8.11 Hz, 1H, CβH); 4.42 (d, $^{3}J_{HH}$ =

8.11 Hz, 2H, CH_2). ^{13}C NMR (δ, $CDCl_3$): 345.72 (t, $^2J_{CP}$ = 15.3 Hz, Cα); 158.53 (N=C);107.00 – 133.61 (Ph, =C); 94.85 (Cp); 44.42 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 42.07 (s, PPh_3). MS (ESI^+) *m/z*: 900.21. Anal.Calcd for $C_{55}H_{46}F_6NOP_3Ru$: C, 63.22; H, 4.44.

Complex **3a** (0.15 g, 0.16 mmole, 83% yield) was similarly prepared from 2.5 equiv of **1a** (0.067 g, 0.42 mmole) and [Ru]Cl (0.14 g, 0.19 mmole) and NH_4PF_6 (0.083 g, 0.51 mmole) in CH_2Cl_2. Spectroscopic data of **3a**: ^1H NMR (δ, $CDCl_3$): 13.18 (s, 1H, OH); 8.83 (s, 1H, N=CH); 6.92 - 7.67 (m, 38H, Ph); 5.99 (d, $^3J_{HH}$ = 8.49 Hz, 1H, Ph); 5.18 (s, 2H, CH_2); 4.75 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 264.40 (t, $^2J_{CP}$ = 14.73 Hz, Cα); 169.71 (N=C); 160.91, 160.29 (Ph – OH, Ph - OCα); 147.63 (Ph, =C); 114.97 – 136.41 (Ph, =C); 89.21 (Cp); 62.91 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.93 (s, PPh_3). MS (ESI^+) *m/z*: 954.22. Anal.Calcd for $C_{58}H_{48}F_6NO_2P_3Ru$: C, 63.39; H, 4.40.

Complex **3b** (0.059 g, 0.058 mmole, 85% yield) was similarly prepared from 2.5 equiv of **1b** (0.031 g, 0.164 mmole) and [Ru]Cl (0.048 g, 0.066 mmole) and NH_4PF_6 (0.028 g, 0.17 mmole) in CH_2Cl_2. Spectroscopic data for **3b**: ^1H NMR (δ, $CDCl_3$): 12.71 (s, 1H, OH); 8.83 (s, 1H, N=CH); 7.64 (s, 1H, Cγ*H*); 6.62 - 7.67 (m, 48H, Ph); 5.92 (d, $^3J_{HH}$ = 9.26 Hz, 1H, Ph); 5.13 (s, 2H, CH_2); 4.73 (s, 5H, Cp); 3.82, 3.75 (2 s, 6H, 2 OCH_3). ^{13}C NMR (δ, $CDCl_3$): 260.63 (t, $^2J_{CP}$ = 14.66 Hz, Cα); 169.58 (N=C); 156.99, 156.64, 154.98, 152.45 (Ph – OH, Ph - OCα, 2Ph - OMe); 147.57 (Ph, =C);

107.64 - 136.49 (Ph, =C); 88.72 (Cp); 63.06 (CH_2); 55.99, 55.81 (2 OCH_3). ^{31}P NMR (δ, $CDCl_3$): 48.72 (s, PPh_3). MS (ESI^+) *m/z*: 1014.24. Anal.Calcd for $C_{60}H_{52}F_6NO_4P_3Ru$: C, 62.18; H, 4.52.

Complex **3c** (0.138 g, 0.13 mmole, 66% yield) was similarly prepared from 2.5 equiv of **1c** (0.105 g, 0.52 mmole) and [Ru]Cl (0.146 g, 0.20 mmole) and NH_4PF_6 (0.091 g, 0.56 mmole) in CH_2Cl_2. Spectroscopic data for **3c**: ^{1}H NMR (δ, $(CD_3)_2CO$): 14.38 (s, 1H, OH); 9.08 (s, 1H, N=CH);8.75, 8.55 (2d, $^4J_{HH}$ = 2.77 Hz, 2H, Ph);8.30 (m, 1H, Ph); 8.13 (s, 1H, Cγ*H*); 7.05 – 8.04 (m, 32H, Ph); 6.37 (d, $^3J_{HH}$ = 9.26 Hz, 1H, Ph); 5.63 (s, 2H, CH_2); 5.17 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 268.12 (t, $^2J_{CP}$ = 13.9Hz, Cα); 169.08 (N=C); 167.53, 161.03 (Ph - OH, Ph - OCα); 148.86, 144.31 (Ph); 115.82 – 139.53 (Ph, =C); 90.49 (Cp); 61.96 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.27 (s, PPh_3). MS (ESI^+) *m/z*: 1044.19. Anal.Calcd for $C_{58}H_{46}F_6N_3O_6P_3Ru$: C, 58.59; H, 3.90.

Complex **3d**. (0.090 g, 0.086 mmole, 43% yield) was similarly prepared from 2.5 equiv of **1d** (0.109 g, 0.52 mmole) and [Ru]Cl (0.145 g, 0.20 mmole) and NH_4PF_6 (0.110 g, 0.67 mmole) in CH_2Cl_2. Spectroscopic data for **3d**: ^{1}H NMR (δ, $CDCl_3$): 14.94 (s, 1H, OH); 9.58 (s, 1H, N=CH); 8.45 (s, 1H, Cγ*H*); 6.78 – 7.79 (m, 41H, Ph); 6.05 (d, $^3J_{HH}$ = 9.06 Hz, 1H, Ph); 5.32 (s, 2H, CH_2); 4.78 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 258.31 (t, $^2J_{CP}$ = 15.35 Hz, Cα); 171.12 (N=C); 163.16, 162.27 (Ph - OH, Ph - OCα); 147.31 (Ph); 114.66 – 136.64 (Ph, =C); 88.94 (Cp); 59.35 (CH_2). ^{31}P NMR (δ,

$CDCl_3$): 48.69 (s, PPh_3). MS (ESI^+) *m/z*: 1054.25. Anal.Calcd for $C_{66}H_{52}F_6NO_2P_3Ru$: C, 66.11; H, 4.37.

Synthesis of Complex 3a'. To a Schlenk flask charged with [Ru']Cl (0.097 g, 0.16 mmole) and NH_4PF_6 (0.068 g, 0.417 mmole) was added 2.5 equiv heteroenyne **1a** (0.064 g, 0.402 mmole) and 10 mL MeOH under nitrogen. The resulting solution was stirred at 45℃ overnight and MeOH was then removed under vacuum. The product was dissolved in dichloromethane and the mixture was filtered through Celite to remove the insoluble precipitates. The volatiles were removed under vacuum and the solid residue was extracted with a small volume of dichloromethane followed by reprecipitation by addition of 70 mL of diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product **3a'** (0.112 g, 0.135 mmole, 84% yield) can be obtained as a red powder. Spectroscopic data of **3a'**: ^{1}H NMR (δ, $CDCl_3$): 13.13 (s, 1H, OH); 8.72 (s, 1H, N=CH); 6.85 - 7.49 (m, 26H, Ph); 6.33 (d, $^3J_{HH}$ = 8.53 Hz, 1H, Ph); 4.96 (s, 5H, Cp); 4.89 (d, 2H, CH_2); 3.22, 2.98 (two m, 4H, 2 dppe CH_2). ^{13}C NMR (δ, $CDCl_3$): 264.86 (t, $^2J_{CP}$ = 13.2 Hz, Cα); 169.43 (N=C); 115.21 – 147.13 (Ph, =C); 89.35 (Cp); 64.31 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 90.59 (s, dppe). MS (ESI^+) *m/z*: 828.17. Anal.Calcd for $C_{48}H_{42}F_6NO_2P_3Ru$: C, 59.26; H, 4.35.

Complex **3b'** (0.179 g, 0.202 mmole, 82% yield) was similarly prepared from 2.5

equiv of **1b** (0.116 g, 0.613 mmole) and [Ru']Cl (0.147 g, 0.245 mmole) and NH_4PF_6 (0.102 g, 0.626 mmole) in MeOH at 45 ℃. Spectroscopic data for **3b'**: ^{1}H NMR (δ, $CDCl_3$): 12.72 (s, 1H, OH); 8.70 (s, 1H, N=CH); 6.66 – 7.72 (m, 27H, Ph); 6.25 (d, $^3J_{HH}$ = 9.14 Hz, 1H, Ph); 5.00 (s, 5H, Cp); 4.85 (s, 2H, CH_2); 3.81, 3.68 (2 s, 2H, 2 OCH_3); 3.16, 2.96 (two m, 4H, 2 dppe CH_2). ^{13}C NMR (δ, $CDCl_3$): 260.13 (t, $^2J_{CP}$ = 13.2 Hz, Cα); 168.87 (N=C); 107.63 – 139.74 (Ph, =C); 87.61 (Cp); 63.07 (CH_2); 55.88, 55.64 (2 OCH_3); 28.97 (t, $^2J_{CP}$ = 22.1 Hz, dppe).^{31}P NMR (δ, $CDCl_3$): 90.34 (s, dppe). MS (ESI^+) *m/z*: 888.20. Anal.Calcd for $C_{50}H_{46}F_6NO_4P_3Ru$: C, 58.14; H, 4.49.

Synthesis of Complex 4a. To a Schlenk flask charged with [Ru]Cl (0.147 g, 0.19 mmole) and KPF_6 (0.095 g, 0.52 mmole) was added 1.5 quiv heteroenyne **1a** (0.048 g, 0.30 mmole) and 15 mL CH_2Cl_2 under nitrogen. The resulting solution was stirred at roomtemperature for 3 days and CH_2Cl_2 was then removed under vacuum. The product was dissolved in dichloromethane and the mixture was filtered through Celite to remove the insoluble precipitates. The volatiles were removed under vacuum and the solid residue was extracted with a small volume of dichloromethane followed by reprecipitation by addition of 50 mL of MeOH. Precipitates thus formed were collected in a glass frit, washed with MeOH, and dried under vacuum. The final product **4a** (0.105 g, 0.124 mmole, 61% yield) can be obtained as a light yellow powder. Spectroscopic data for **4a**: ^{1}H NMR (δ, $CDCl_3$): 14.20 (s, 1H, OH); 8.80 (t,

$^4J_{HH}$ = 1.80 Hz, 1H, N=CH); 7.06 – 7.46 (m, 31H, Ph); 6.90 (d, $^3J_{HH}$ = 8.31 Hz, 1H, Ph); 6.61 (m, 1H, Ph); 6.50 (m, 1H, Ph); 4.74 (d, $^4J_{HH}$ = 1.80 Hz, 2H, CH_2); 4.31 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 164.16 (N=C); 161.73 (Ph - OH); 116.79 – 139.32 (Ph, =C); 109.39 (t, $^2J_{CP}$ = 24.54 Hz, Cα); 103.66 (Cβ); 84.94 (Cp); 48.80 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 50.63 (s, PPh_3). MS (ESI^+) *m/z*: 850.19. Anal.Calcd for $C_{51}H_{43}NOP_2Ru$: C, 72.16; H, 5.11.

Complex **4b** (0.114 g, 0.130 mmole, 62% yield) was similarly prepared from 1.5 equiv of **1b** (0.059 g, 0.31 mmole) and [Ru]Cl (0.152 g, 0.21 mmole) and KPF_6 (0.102 g, 0.55 mmole) in CH_2Cl_2 at roomtemperature. Spectroscopic data for **4b**: ^{1}H NMR (δ, $CDCl_3$): 13.57 (s, 1H, OH); 8.72 (s, 1H, N=CH); 6.74 – 7.48 (m, 32H, Ph); 5.86 (d, $^4J_{HH}$ = 2.96 Hz, 1H, Ph); 4.77 (s, 2H, CH_2); 4.30 (s, 5H, Cp); 3.37 (s, 3H, OCH_3). ^{13}C NMR (δ, $CDCl_3$): 163.99 (N=C); 155.43 (Ph - OH); 151.24 (Ph - OMe); 114.15 – 139.40 (Ph, =C); 109.14 (t, $^2J_{CP}$ = 24.34 Hz, Cα); 103.89 (Cβ); 85.05 (Cp); 55.64 (CH_2); 48.92 (OCH_3). ^{31}P NMR (δ, $CDCl_3$): 50.40 (s, PPh_3). MS (ESI^+) *m/z*: 880.20. Anal.Calcd for $C_{52}H_{45}NO_2P_2Ru$: C, 71.06; H, 5.16.

Synthesis of Compound 5b. To a Schlenk flask charged with **1b** (0.026 g, 1.38 mmole) in the presence of 0.5 equiv $NaBH_4$ (0.11g, 2.89 mmole), then 20 mL of EtOH were added under nitrogen. The resulting solution was stirred at room temperature overnight. The reaction mixture was extracted with ether, and organic

phase was washed with aqueous NH_4Cl and dried over $MgSO_4$. Solvent was then removed under reduced pressur to give compound **5b** (0.23 g, 1.20 mmole, 87% yield). Spectroscopic data for **5b**: ^{1}H NMR (δ, $CDCl_3$): 6.52 – 6.76 (m, 3H, Ph); 5.34 (br, 2H, OH and NH); 4.02 (s, 2H, Ph – CH_2); 3.72 (s, 3H, OCH_3); 3.43 (d, $^4J_{HH}$ = 2.41 Hz, 2H, CH_2); 2.28 (t, $^4J_{HH}$ = 2.41 Hz, 1H, ≡CH). ^{13}C NMR (δ, $CDCl_3$): 152.51, 151.57 (Ph – OH, Ph – OCH_3); 122.26, 116.69, 114.60, 113.80 (Ph, =C); 80.15 (C≡); 72.71 (≡CH); 55.66 (OCH_3); 50.73 (Ph – CH_2); 36.44 (CH_2).

Synthesis of Complex 9. To a Schlenk flask charged with [Ru]Cl (0.097 g, 0.13 mmole) and KPF_6 (0.068 g, 0.37 mmole) was added 1.1 equiv **5** (0.031 g, 0.16 mmole) in the presence of PPh_3 (0.18 g, 0.69 mmole) and 10 mL CH_2Cl_2 under nitrogen. The resulting solution was stirred at room temperature for 6 days. The solution was filtered through Celite to remove the insoluble precipitates, then the volatiles were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by addition of 70 mL of diethyl ether. Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a yellow powder **9** (0.095 g, 0.096 mmole, 72% yield). Spectroscopic data for **9**: ^{1}H NMR (δ, $CDCl_3$): 8.21 (m, 1H, Cα - H); 6.96 – 7.77 (m, H, Ph); 5.24 (m, 1H, Cβ - H); 4.06 (s, 5H, Cp); 3.83 (dd, $^2J_{HP}$ = 12.59 Hz, $^3J_{HH}$ = 6.35 Hz, 2H, CH_2). ^{13}C NMR (δ, $CDCl_3$): 165.27 (m, Cα); 138.75

(m, Cβ); 118.56 – 134.83 (Ph, =C); 85.60 (Cp); 33.25 (d, $^{2}J_{CP}$ = 42.38 Hz, CH_2). ^{31}P NMR (δ, $CDCl_3$): 52.64 (d, J_{PP} = 4.31 Hz, 2P, 2Ru - PPh3); 14.93 (t, J_{PP} = 4.31 Hz, 1P, PPh3). MS (ESI^+) *m/z*: 993.25. Anal.Calcd for $C_{62}H_{54}F_6P_4Ru$: C, 65.43; H, 4.78.

Synthesis of Complex 11. To an NMR tube charged with **2d** (0.062 g, 0.069 mmole) was added 2.3 equiv **7a** (0.024 g, 0.16 mmole) in 1.5 mL $CDCl_3$. The resulting solution was reacted at room temperature overnight. The solution was filtered through Celite to remove the insoluble precipitates, then the volatiles were removed under vacuum and the solid residue was extracted with a small volume of CH_2Cl_2 followed by reprecipitation by addition of 70 mL of diethyl ether and hexane (1:1). Precipitates thus formed were collected in a glass frit, washed with diethyl ether, and dried under vacuum. The final product can be obtained as a orange powder **11** (0.052 g, 0.052 mmole, 75% yield). Spectroscopic data for **11**: ^{1}H NMR (δ, $CDCl_3$): 14.77 (s, 1H, OH); 9.40 (s, 1H, N=CH); 8.32 (d, $^{3}J_{HH}$ = 8.40 Hz, 1H, Ph); 7.77 (d, $^{3}J_{HH}$ = 9.20 Hz, 1H, Ph); 7.65 (s, 1H, Cγ*H*); 6.92 - 7.63 (m, 37H, Ph); 6.02 (d, $^{3}J_{HH}$ = 8.40 Hz, 1H, Ph); 5.16 (s, 2H, CH_2); 4.80 (s, 5H, Cp). ^{13}C NMR (δ, $CDCl_3$): 264.16 (t, $^{2}J_{CP}$ = 14.54 Hz, Cα); 172.12 (N=C); 163.00, 160.33 (Ph – OH, Ph - OCα); 147.21 (Ph, =C); 108.28 - 136.95 (Ph, =C); 89.35 (Cp); 58.55 (CH_2). ^{31}P NMR (δ, $CDCl_3$): 48.44 (s, PPh_3). MS (ESI^+) *m/z*: 1004.25. Anal.Calcd for $C_{62}H_{50}F_6NO_2P_3Ru$: C, 64.81; H, 4.39.

Single-Crystal X-ray Diffraction Analyses.

Single crystal of complex **3a'** suitable for X-ray diffraction study were grown as mentioned above. All of these X-ray diffraction studies are operated by similar process. A single crystal of dimensions was glued to a glass fiber and mounted on a SMART CCD diffractometer. The diffraction data were collected using 3-Kw sealed-tube Mo K_α radiation (T = 295 K). Exposure time was 5 s per frame. SADABS[37] (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[38] program. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. Crystal data and related parameters of complex **3a'** is listed in Table 1.

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Table 1. Crystal Data and Refinement Parameters for Complex **3a'**

	3a'
Formula	$C_{49}H_{44}Cl_2F_6NO_2P_3Ru$
Formula weight	1057.73
Crystal system	Triclinic
Space group	$R\bar{3}$
a(Å)	11.9919(4)
b(Å)	12.4210(5)
c(Å)	17.8817(5)
α(deg)	98.958(3)
β(deg)	97.484(3)
γ(deg)	118.856(4)
V(Å^3)	2238.45(13)
Z	2
reflns collected	15643
Indep reflns (Rint)	9713(0.0241)
Goodness-of-fit on F^2	1.004
R_1/wR_2 [$I>2\sigma(I)$]	0.0341/0.0761
R_1/wR_2 (all data)	0.0448/0.0819

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.
2. (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.*, **2004**, *248*, 1627 – 1657. (b) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.*, **2004**, *248*, 1703 – 1715.
3. (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.*, **1978**, *100*, 7763 – 7765. (b) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276 – 3285.
4. Barrett, A. G. M.; Mortier, J.; Sabat, M.; Sturgess, M.A. *Organometallics*, **1988**, *7*, 2553 - 2561.
5. Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.*, **1988**, *60*, 137 – 144.
6. (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.*, **1992**, *114*, 3974 – 3975. (b) Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem. Int. Ed.*, **2002**, *41*, 4038 – 4040. (c) Bieniek, M.; Bujok, R.; Cabaj, M.; Lugan, N.; Lavigne, G.; Arlt, D.; Grela, K. *J. Am. Chem. Soc.*, **2006**, *128*, 13652 – 13653.
7. (a) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.*, **1982**, *104*, 5538 – 5540. (b) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron*, **1985**, *41*, 5833 –

5838.

8. Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. J. *J. Am. Chem. Soc.*, **1984**, *106*, 2680 – 2687.

9. (a) McDonald, F. E. *Chem. Eur. J.*, **1999**, 5, 3103 – 3106. (b) Zeni, G.; Larock, R. C. *Chem. Rev.*, **2004**, *104*, 2285 – 2310. (c) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.*, **2004**, *104*, 3079 – 3160. (d) Kusama, H.; Iwasawa, N. *Chem. Lett.*, **2006**, *35*, 1082 – 1087.

10. (a) Touchard, D.; Haquette, P.; Daridor, A.; Romero, A.; Dixneuf, P. H. *Organometallics*, **1998**, *17*, 3844 – 3852. (b) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Lopez, C.; Rios, I.; Romerosa, A. *Chem. Commun.*, **1999**, 443 – 444. (c) Bruce, M. I.; Low, P. J.; Tiekink, E. R. T. *J. Organomet. Chem.*, **1999**, *572*, 3 – 10.

11. (a) Gotthardt, H.; Hoffman, N. *Liebigs Ann. Chem.*, **1985**, 901 – 912. (b) Kitson, T. M.; Freeman, G. H. *Bioorg. Chem.*, **1993**, *21*, 354- 365. (c) van den Goorbergh, J. A. M.; van der Steeg, M.; van der Gen, A. *Synthesis*, **1987**, *3*, 314 – 317.

12. (a) Matsui, K.; Takizawa, S.; Sasai, H. *J. Am. Chem. Soc.*, **2005**, *127*, 3680 – 3681. (b) Buskens, P.; Klankermayer, J.; Leitner, W. *J. Am. Chem. Soc.*, **2005**, *127*, 16762 – 16763.

13. (a) Kobayashi, S.; Ishitani, H. *Chem. Rev.*, **1999**, *99*, 1069 – 1094. (b) Jørgensen,

K. A. *Angew. Chem. Int. Ed.*, **2000**, *39*, 3558 – 3588. (c) He, Y.-H.; Hu, W.; Guan, Z. *J. Org. Chem.*, **2012**, *77*, 200 – 207.

14. (a) Emmons, W. D. *J. Am. Chem. Soc.*, **1956**, *78*, 6208 –6209. (b) Pews, R. G. *J. Org. Chem.*, **1967**, *32*, 1628 – 1628. (c) Nongkunsarn, P.; Ramsden, C. A. *Tetrahedron*, **1997**, *53*, 3805 – 3830.
15. (a) Alcaide, B.; Almendros, P.; Salgado, N. R. *Tetrahedron Lett.* **2001**, *42*, 1503 – 1505. (b) Alcaide, B.; Rodríguez-Vicente, A. *Tetrahedron Lett.*, **1999**, *40*, 2005 – 2006.
16. List, B. *J. Am. Chem. Soc.*, **2000**, *122*, 9336 –9337.
17. List, B.; Pojarliev, P.; Biller, W. T.; Martin, H. J. *J. Am. Chem. Soc.*, **2002**, *124*, 827 –833.
18. (a) Qin, D.-D.; Yang, Z.-Y.; Zhang, F.-H.; Du. B.; Wang, P.; Li, T.-R. *Inorg. Chem. Commun.*, **2010**, *13*, 727 – 729. (b) Rezaeifard, A.; Sheikhshoaie, I.; Monadi, N.; Alipour, M. *Polyhedron*, **2010**, *29*, 2703 – 2709. (c) Thakurta, S.; Butcher, R. J.; Pilet, G.; Mitra, S. *J. Mol. Struct.*, **2009**, *929*, 112 – 119.
19. Kotali, A.; Nasiopoulou, D. A.; Harris, P. A.; Helliwell, M.; Joule, J. A. *Tetrahedron*, **2012**, *68*, 761 – 766.
20. (a) Daru, J.; Stirling, A. *J. Org. Chem.*, **2011**, *76*, 8749 – 8755. (b) Kuarm, B. S.; Madhav, J. V.; Rajitha, B. *Synth. Commun.*, **2012**, *42*, 1770 – 1777.

21. Raju, B. C.; Tiwari, A. K.; Kumar, J. A.; Ali, A. Z.; Agawane, S. B. *Bioorg. Med. Chem.*, **2010**, *18*, 358 – 365.

22. (a) Jang, Y.-J.; Syu, S.; Chen, Y.-J.; Yang, M.-C.; Lin, W. *Org. Biomol. Chem.*, **2012**, *10*, 843 – 847. (b) Suzuki, K.; Ubukata, T.; Yokoyama, Y. *Chem. Commun.*, **2012**, *48*, 765 – 767.

23. Creaven, B. S.; Devereux, M.; Karcz, D.; Kellett, A.; McCann, M.; Nobel, A.; Walsh, M. *J. Inorg. Biochem.*, **2009**, *103*, 1196 – 1203.

24. Creaven, B. S.; Czegldéi, E.; Devereux, M.; Enyedy, É. A.; Kia, A. F.-A.; Karcz, D.; Kellett, A.; McClean, S.; Nagy, N. V.; Nobel, A.; Rockenbauer, A.; Szabó-Plánka, T.; Walsh, M. *Dalton Trans.*, **2010**, *39*, 10854 – 10865.

25. Chang, L.-H.; Yeh, C.-W.; Ma, H.-W.; Liu, S.-Y.; Lin, Y.-C.; Wang, Y.; Liu, Y.-H. *Organometallics*, **2010**, *29*, 1092 – 1099.

26. (a) Pearson, D. M.; Waymouth, R. M. *Organometallics*, **2009**, *28*, 3896 – 3900. (b) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.*, **2008**, *693*, 399 – 407.

27. More detail experimental data of compound **6a**, see Poulter, N.; Donaldson, M.; Mulley, G.; Luis Duque, L.; Waterfield, N.; Shard, A. G.; Spencer, S.; Jenkins, A. T. A.; Johnson, A. L. *New J. Chem.*, **2011**, *35*, 1477–1484.

28. More detail experimental data of compound **7a**, see Singh, R. V.; Tandon, J. P.

Monatsh. Chem., **1980**, *111*, 1391 – 1397.

29. (a) Burland, M. C.; Meyer, T.Y. *Inorg. Chem.*, **2003**, *42*, 3438 – 3444. (b) Krska, S. W.; Zuckerman, R. L.; Bergman, R. G. *J. Am. Chem. Soc.*, **1998**, *120*, 11828 – 11829.

30. More detail experimental data of compound **12**, see Yamada, S.; Takeuchi, A. *Bull. Chem. Soc. Jpn.*, **1969**, *42*, 2549 – 2551.

31. Helmut, F.; Andreas, S.; Wolfgang, B.; Angelika, F. *Organometallics*, **1991**, *10*, 389 - 391.

32. Andreu, R.; Ronda, J. C. *Synth. Commun.*, **2008**, *38*, 2316 - 2329.

33. (a) Chung, C.-P.; Chen, C.-C.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y. *J. Am. Chem. Soc.*, **2009**, *131*, 18366 – 18375. (b) Hyber, I.; Jimnez-Tenorio, M.; Puerta, M. C.; Valerga, P. Organometallics, **2011**, *30*, 726 – 737.

34. Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R.; Ittel, S.D. *Inorg. Synth.*, **1990**, *28*, 270 – 272.

35. Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.*, **1979**, *32*, 1003 – 1016.

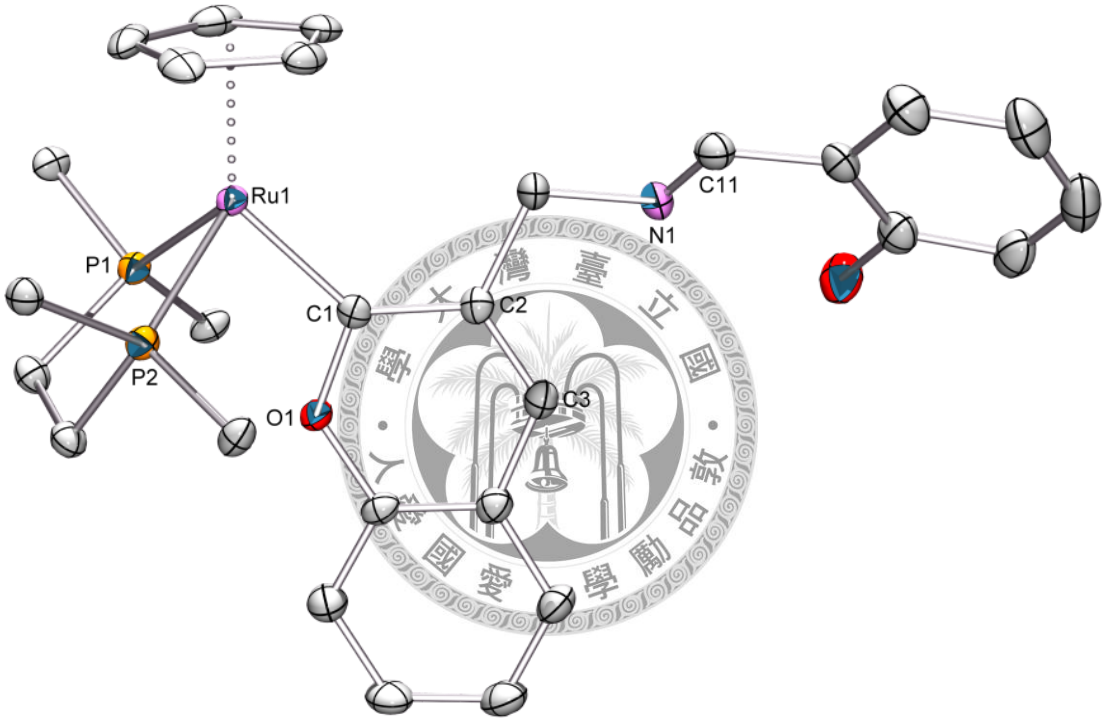
36. (a) Bustelo, E.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics*, **2007**, *26*, 4300 – 4309. (b) Pino-Chamorro, J. A.; Bustelo, E.; Puerta, M. C.;Valerga, P. *Organometallics*, **2009**, *28*, 1546 – 1557.

37. The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A.*, **1995**, 51, 33 – 38.

38. *SHELXTL: Structure Analysis Program*, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, **1995**.

Appendix I: X-ray Crystallographic Data

ORTEP drawing of the cationic complex **3a'**.



For clarity, aryl groups of the 1,2-bis(diphenylphosphino)ethane ligands on Ru except the *ipso* carbons, hydrogens and PF_6^- are omitted (thermal ellipsoid is set at the 50% probability level).

Table 1. Crystal data and structure refinement for ic15549.

Identification code	ic15549
Empirical formula	$C_{49}H_{44}Cl_2F_6NO_2P_3Ru$
Formula weight	1057.73
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.9919(4) Å alpha = 98.958(3)° b = 12.4210(5) Å beta = 97.484(3)° c = 17.8817(5) Å gamma = 118.856(4)°
Volume, Z	2238.45(13) $Å^3$, 2
Density (calculated)	1.569 Mg/m^3
Absorption coefficient	0.644 mm^{-1}
F(000)	1076
Crystal size	0.25 x 0.20 x 0.15 mm
Θ range for data collection	3.08 to 27.50°
Limiting indices	$-15 \le h \le 10$, $-16 \le k \le 16$, $-22 \le l \le 2$
Reflections collected	15643
Independent reflections	9713 (R_{int} = 0.0241)
Completeness to Θ = 27.50°	94.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.99274
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9713 / 0 / 581
Goodness-of-fit on F^2	1.004
Final R indices [I>2σ(I)]	R1 = 0.0341, wR2 = 0.0761
R indices (all data)	R1 = 0.0448, wR2 = 0.0819
Largest diff. peak and hole	0.627 and -0.479 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropi displacement parameters [$Å^2$ x 10^3] for ic15549. U(eq) is define as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	4050(1)	7771(1)	2988(1)	15(1)
P(1)	1981(1)	6365(1)	3058(1)	17(1)
P(2)	4579(1)	6412(1)	3429(1)	16(1)
O(1)	3022(2)	5474(1)	1820(1)	18(1)
O(2)	4745(2)	8121(2)	-1024(1)	34(1)
N(1)	5177(2)	8719(2)	478(1)	23(1)
C(1)	3738(2)	6768(2)	1923(1)	17(1)
C(2)	4200(2)	7144(2)	1238(1)	17(1)
C(3)	4081(2)	6274(2)	621(1)	21(1)
C(4)	3403(2)	4950(2)	575(1)	21(1)
C(5)	3209(3)	3999(2)	-59(1)	26(1)
C(6)	2466(3)	2739(3)	-69(1)	29(1)
C(7)	1886(3)	2393(2)	554(1)	29(1)
C(8)	2055(2)	3307(2)	1180(1)	26(1)
C(9)	2824(2)	4573(2)	1182(1)	19(1)
C(10)	4802(2)	8524(2)	1212(1)	23(1)
C(11)	6331(2)	9590(2)	504(1)	23(1)
C(12)	6816(2)	9793(2)	-200(1)	24(1)
C(13)	6017(2)	8996(2)	-936(1)	26(1)
C(14)	6546(3)	9106(3)	-1586(2)	31(1)
C(15)	7828(3)	10026(3)	-1518(2)	37(1)
C(16)	8616(3)	10846(3)	-799(2)	38(1)
C(17)	8117(3)	10715(3)	-147(2)	32(1)
C(18)	3909(3)	9495(2)	3388(2)	29(1)
C(19)	4524(3)	9297(2)	4041(1)	30(1)
C(20)	5709(3)	9438(2)	3909(1)	28(1)
C(21)	5851(2)	9734(2)	3181(1)	23(1)
C(22)	4735(2)	9784(2)	2868(1)	24(1)
C(23)	1980(2)	5146(2)	3535(1)	20(1)
C(24)	3095(2)	4915(2)	3413(1)	20(1)
C(25)	692(2)	5508(2)	2154(1)	21(1)
C(26)	708(2)	6148(3)	1577(1)	26(1)
C(27)	-261(3)	5540(3)	886(1)	33(1)
C(28)	-1231(3)	4283(3)	763(2)	35(1)
C(29)	-1260(3)	3645(3)	1331(2)	33(1)
C(30)	-303(2)	4256(2)	2027(1)	25(1)
C(31)	1295(2)	7113(2)	3667(1)	19(1)
C(32)	546(2)	7574(2)	3334(1)	26(1)
C(33)	174(3)	8293(3)	3792(2)	32(1)
C(34)	537(3)	8553(3)	4595(2)	33(1)
C(35)	1239(3)	8080(3)	4935(2)	29(1)
C(36)	1619(2)	7367(2)	4478(1)	25(1)
C(37)	5536(2)	5952(2)	2893(1)	20(1)
C(38)	6486(2)	6860(2)	2603(1)	24(1)
C(39)	7251(3)	6562(3)	2197(1)	30(1)
C(40)	7054(3)	5358(3)	2066(2)	35(1)
C(41)	6118(3)	4451(3)	2351(2)	38(1)
C(42)	5362(3)	4743(3)	2768(2)	29(1)

C(43)	5531(2)	6975(2)	4442(1)	19(1)
C(44)	6828(2)	7293(3)	4634(1)	29(1)
C(45)	7519(3)	7748(3)	5407(2)	34(1)
C(46)	6921(3)	7890(3)	5995(1)	28(1)
C(47)	5639(3)	7575(3)	5811(1)	29(1)
C(48)	4949(2)	7132(3)	5042(1)	27(1)
P(3)	9352(1)	694(1)	2429(1)	28(1)
F(1)	8548(2)	1391(2)	2311(1)	57(1)
F(2)	10123(2)	-31(2)	2544(1)	56(1)
F(3)	9617(2)	763(2)	1586(1)	62(1)
F(5)	9051(2)	577(2)	3259(1)	65(1)
F(4)	8015(2)	-623(2)	2043(1)	50(1)
F(6)	10670(2)	2010(2)	2795(1)	81(1)
C(49)	8493(3)	4463(3)	3772(2)	45(1)
Cl(1)	7363(1)	2825(1)	3460(1)	46(1)
Cl(2)	8048(1)	5229(1)	4472(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for ic15549.

Ru(1)-C(1)	1.986(2)	Ru(1)-C(19)	2.243(2)
Ru(1)-C(18)	2.243(3)	Ru(1)-C(20)	2.251(2)
Ru(1)-P(1)	2.2773(6)	Ru(1)-P(2)	2.2784(6)
Ru(1)-C(21)	2.279(2)	Ru(1)-C(22)	2.281(2)
P(1)-C(25)	1.832(2)	P(1)-C(31)	1.839(2)
P(1)-C(23)	1.849(2)	P(2)-C(37)	1.820(2)
P(2)-C(43)	1.835(2)	P(2)-C(24)	1.845(2)
O(1)-C(9)	1.374(3)	O(1)-C(1)	1.374(3)
O(2)-C(13)	1.348(3)	N(1)-C(11)	1.269(3)
N(1)-C(10)	1.461(3)	C(1)-C(2)	1.462(3)
C(2)-C(3)	1.358(3)	C(2)-C(10)	1.516(3)
C(3)-C(4)	1.422(3)	C(4)-C(9)	1.385(3)
C(4)-C(5)	1.408(3)	C(5)-C(6)	1.372(4)
C(6)-C(7)	1.404(4)	C(7)-C(8)	1.381(4)
C(8)-C(9)	1.386(3)	C(11)-C(12)	1.459(3)
C(12)-C(17)	1.400(4)	C(12)-C(13)	1.408(3)
C(13)-C(14)	1.388(4)	C(14)-C(15)	1.377(4)
C(15)-C(16)	1.389(4)	C(16)-C(17)	1.376(4)
C(18)-C(22)	1.405(4)	C(18)-C(19)	1.417(4)
C(19)-C(20)	1.402(4)	C(20)-C(21)	1.415(3)
C(21)-C(22)	1.415(3)	C(23)-C(24)	1.531(3)
C(25)-C(30)	1.386(3)	C(25)-C(26)	1.394(3)
C(26)-C(27)	1.392(3)	C(27)-C(28)	1.383(4)
C(28)-C(29)	1.376(4)	C(29)-C(30)	1.391(3)
C(31)-C(36)	1.396(3)	C(31)-C(32)	1.397(3)
C(32)-C(33)	1.385(4)	C(33)-C(34)	1.384(4)
C(34)-C(35)	1.371(4)	C(35)-C(36)	1.387(4)
C(37)-C(42)	1.389(3)	C(37)-C(38)	1.391(3)
C(38)-C(39)	1.386(3)	C(39)-C(40)	1.372(4)
C(40)-C(41)	1.376(4)	C(41)-C(42)	1.387(4)
C(43)-C(44)	1.385(3)	C(43)-C(48)	1.392(3)
C(44)-C(45)	1.386(3)	C(45)-C(46)	1.384(4)
C(46)-C(47)	1.368(4)	C(47)-C(48)	1.380(3)
P(3)-F(6)	1.581(2)	P(3)-F(5)	1.5834(18)
P(3)-F(3)	1.5879(18)	P(3)-F(2)	1.5881(18)
P(3)-F(1)	1.5916(19)	P(3)-F(4)	1.5973(18)
C(49)-Cl(2)	1.747(3)	C(49)-Cl(1)	1.754(3)

C(1)-Ru(1)-C(19)	165.64(9)	C(1)-Ru(1)-C(18)	130.86(9)
C(19)-Ru(1)-C(18)	36.84(10)	C(1)-Ru(1)-C(20)	139.17(10)
C(19)-Ru(1)-C(20)	36.35(10)	C(18)-Ru(1)-C(20)	60.82(10)
C(1)-Ru(1)-P(1)	90.55(7)	C(19)-Ru(1)-P(1)	97.47(7)
C(18)-Ru(1)-P(1)	94.75(7)	C(20)-Ru(1)-P(1)	129.86(7)
C(1)-Ru(1)-P(2)	86.35(6)	C(19)-Ru(1)-P(2)	106.17(7)
C(18)-Ru(1)-P(2)	142.77(7)	C(20)-Ru(1)-P(2)	91.24(7)
P(1)-Ru(1)-P(2)	84.76(2)	C(1)-Ru(1)-C(21)	108.30(9)
C(19)-Ru(1)-C(21)	60.92(9)	C(18)-Ru(1)-C(21)	60.81(9)
C(20)-Ru(1)-C(21)	36.42(9)	P(1)-Ru(1)-C(21)	155.21(7)
P(2)-Ru(1)-C(21)	111.70(6)	C(1)-Ru(1)-C(22)	105.03(9)
C(19)-Ru(1)-C(22)	60.62(9)	C(18)-Ru(1)-C(22)	36.18(9)
C(20)-Ru(1)-C(22)	60.26(9)	P(1)-Ru(1)-C(22)	124.39(7)
P(2)-Ru(1)-C(22)	147.71(7)	C(21)-Ru(1)-C(22)	36.15(9)
C(25)-P(1)-C(31)	102.81(10)	C(25)-P(1)-C(23)	106.51(11)
C(31)-P(1)-C(23)	104.48(11)	C(25)-P(1)-Ru(1)	118.64(8)
C(31)-P(1)-Ru(1)	112.72(8)	C(23)-P(1)-Ru(1)	110.49(8)

C(37)-P(2)-C(43)	103.16(10)	C(37)-P(2)-C(24)	105.80(11)
C(43)-P(2)-C(24)	103.79(10)	C(37)-P(2)-Ru(1)	116.12(7)
C(43)-P(2)-Ru(1)	115.69(8)	C(24)-P(2)-Ru(1)	111.05(8)
C(9)-O(1)-C(1)	126.21(17)	C(11)-N(1)-C(10)	118.4(2)
O(1)-C(1)-C(2)	113.27(19)	O(1)-C(1)-Ru(1)	114.58(14)
C(2)-C(1)-Ru(1)	132.01(17)	C(3)-C(2)-C(1)	120.9(2)
C(3)-C(2)-C(10)	119.8(2)	C(1)-C(2)-C(10)	119.3(2)
C(2)-C(3)-C(4)	122.3(2)	C(9)-C(4)-C(5)	118.0(2)
C(9)-C(4)-C(3)	116.8(2)	C(5)-C(4)-C(3)	125.0(2)
C(6)-C(5)-C(4)	120.5(2)	C(5)-C(6)-C(7)	119.9(2)
C(8)-C(7)-C(6)	120.7(2)	C(7)-C(8)-C(9)	118.3(2)
O(1)-C(9)-C(4)	119.7(2)	O(1)-C(9)-C(8)	117.8(2)
C(4)-C(9)-C(8)	122.5(2)	N(1)-C(10)-C(2)	111.74(19)
N(1)-C(11)-C(12)	121.9(2)	C(17)-C(12)-C(13)	118.8(2)
C(17)-C(12)-C(11)	120.4(2)	C(13)-C(12)-C(11)	120.6(2)
O(2)-C(13)-C(14)	119.2(2)	O(2)-C(13)-C(12)	121.2(2)
C(14)-C(13)-C(12)	119.6(2)	C(15)-C(14)-C(13)	120.3(3)
C(14)-C(15)-C(16)	120.7(2)	C(17)-C(16)-C(15)	119.5(3)
C(16)-C(17)-C(12)	121.0(3)	C(22)-C(18)-C(19)	108.0(2)
C(22)-C(18)-Ru(1)	73.37(14)	C(19)-C(18)-Ru(1)	71.56(15)
C(20)-C(19)-C(18)	107.6(2)	C(20)-C(19)-Ru(1)	72.13(14)
C(18)-C(19)-Ru(1)	71.60(14)	C(19)-C(20)-C(21)	108.9(2)
C(19)-C(20)-Ru(1)	71.52(14)	C(21)-C(20)-Ru(1)	72.88(13)
C(22)-C(21)-C(20)	107.0(2)	C(22)-C(21)-Ru(1)	72.01(13)
C(20)-C(21)-Ru(1)	70.71(13)	C(18)-C(22)-C(21)	108.5(2)
C(18)-C(22)-Ru(1)	70.45(14)	C(21)-C(22)-Ru(1)	71.84(13)
C(24)-C(23)-P(1)	112.05(15)	C(23)-C(24)-P(2)	110.67(16)
C(30)-C(25)-C(26)	118.9(2)	C(30)-C(25)-P(1)	122.61(18)
C(26)-C(25)-P(1)	118.52(18)	C(27)-C(26)-C(25)	120.5(2)
C(28)-C(27)-C(26)	119.8(2)	C(29)-C(28)-C(27)	120.1(2)
C(28)-C(29)-C(30)	120.2(3)	C(25)-C(30)-C(29)	120.5(2)
C(36)-C(31)-C(32)	117.6(2)	C(36)-C(31)-P(1)	121.51(18)
C(32)-C(31)-P(1)	120.49(18)	C(33)-C(32)-C(31)	121.3(2)
C(34)-C(33)-C(32)	119.7(2)	C(35)-C(34)-C(33)	120.1(3)
C(34)-C(35)-C(36)	120.3(2)	C(35)-C(36)-C(31)	120.9(2)
C(42)-C(37)-C(38)	119.1(2)	C(42)-C(37)-P(2)	122.78(19)
C(38)-C(37)-P(2)	118.15(18)	C(39)-C(38)-C(37)	120.4(2)
C(40)-C(39)-C(38)	120.0(3)	C(39)-C(40)-C(41)	120.2(3)
C(40)-C(41)-C(42)	120.3(3)	C(41)-C(42)-C(37)	120.0(2)
C(44)-C(43)-C(48)	118.3(2)	C(44)-C(43)-P(2)	122.49(18)
C(48)-C(43)-P(2)	119.14(17)	C(43)-C(44)-C(45)	120.4(2)
C(46)-C(45)-C(44)	120.4(2)	C(47)-C(46)-C(45)	119.6(2)
C(46)-C(47)-C(48)	120.3(2)	C(47)-C(48)-C(43)	121.0(2)
F(6)-P(3)-F(5)	91.79(13)	F(6)-P(3)-F(3)	90.05(13)
F(5)-P(3)-F(3)	178.10(13)	F(6)-P(3)-F(2)	89.98(12)
F(5)-P(3)-F(2)	88.81(11)	F(3)-P(3)-F(2)	90.71(11)
F(6)-P(3)-F(1)	91.30(12)	F(5)-P(3)-F(1)	90.82(12)
F(3)-P(3)-F(1)	89.62(11)	F(2)-P(3)-F(1)	178.68(12)
F(6)-P(3)-F(4)	178.73(11)	F(5)-P(3)-F(4)	89.22(11)
F(3)-P(3)-F(4)	88.94(11)	F(2)-P(3)-F(4)	90.80(11)
F(1)-P(3)-F(4)	87.93(10)	Cl(2)-C(49)-Cl(1)	112.05(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic15549.

The anisotropic displacement factor exponent takes the form:

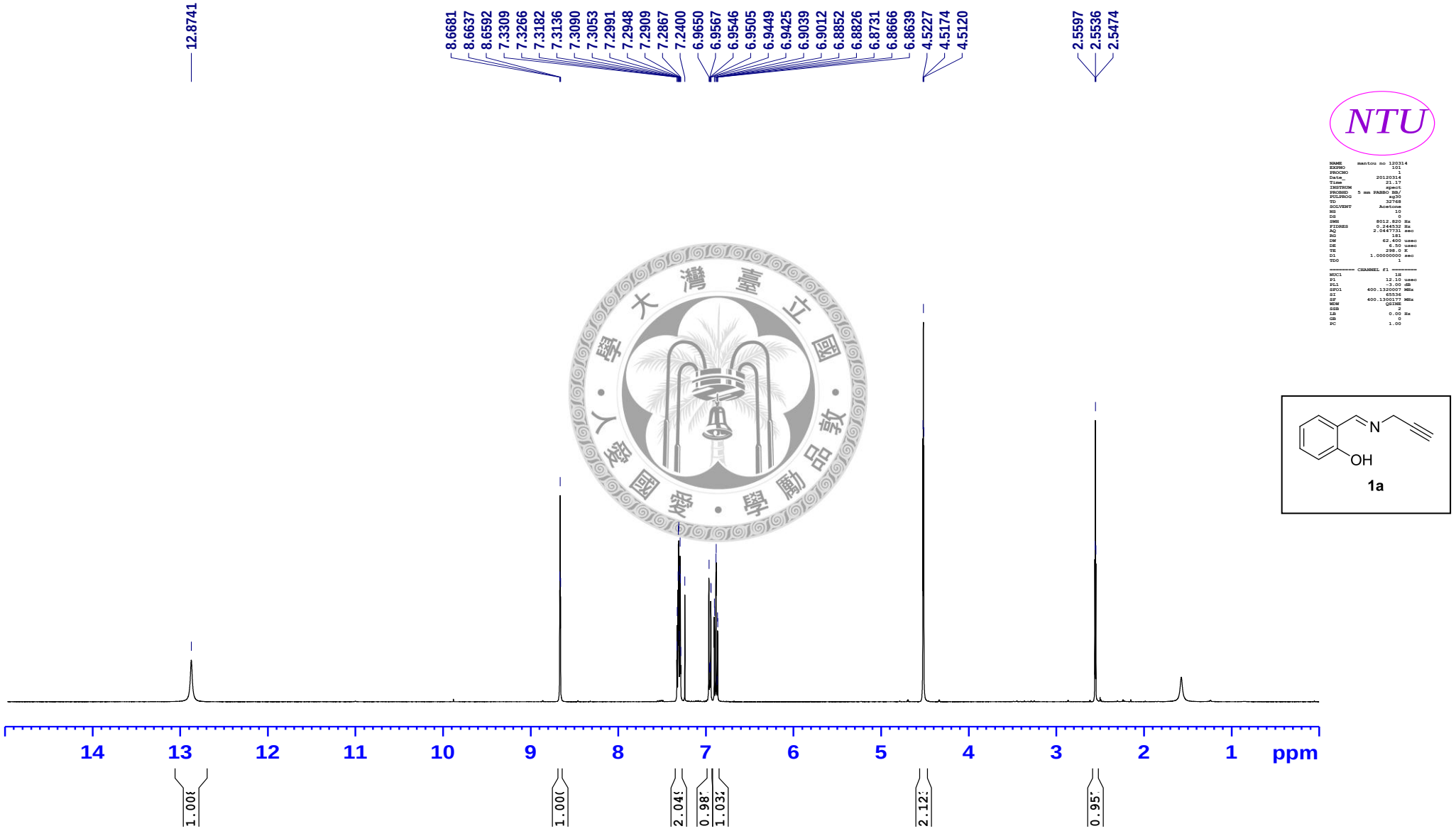
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru(1)	15(1)	13(1)	14(1)	1(1)	3(1)	6(1)
P(1)	15(1)	16(1)	16(1)	2(1)	3(1)	6(1)
P(2)	16(1)	17(1)	16(1)	3(1)	3(1)	8(1)
O(1)	19(1)	15(1)	15(1)	1(1)	5(1)	6(1)
O(2)	32(1)	35(1)	23(1)	2(1)	4(1)	9(1)
N(1)	29(1)	20(1)	19(1)	8(1)	9(1)	11(1)
C(1)	16(1)	18(1)	17(1)	5(1)	3(1)	10(1)
C(2)	15(1)	19(1)	15(1)	3(1)	1(1)	8(1)
C(3)	23(1)	24(1)	17(1)	6(1)	6(1)	13(1)
C(4)	23(1)	22(1)	18(1)	3(1)	3(1)	13(1)
C(5)	33(1)	27(1)	19(1)	1(1)	7(1)	17(1)
C(6)	38(2)	25(1)	24(1)	-2(1)	2(1)	19(1)
C(7)	33(2)	16(1)	29(1)	0(1)	1(1)	9(1)
C(8)	29(1)	22(1)	23(1)	4(1)	5(1)	10(1)
C(9)	19(1)	19(1)	16(1)	0(1)	0(1)	11(1)
C(10)	32(1)	20(1)	17(1)	7(1)	9(1)	12(1)
C(11)	27(1)	20(1)	21(1)	4(1)	4(1)	11(1)
C(12)	29(1)	23(1)	24(1)	10(1)	8(1)	14(1)
C(13)	29(1)	29(1)	23(1)	10(1)	6(1)	17(1)
C(14)	44(2)	38(2)	22(1)	10(1)	9(1)	27(1)
C(15)	47(2)	53(2)	35(2)	26(1)	23(1)	36(2)
C(16)	31(2)	44(2)	44(2)	25(1)	18(1)	17(1)
C(17)	28(1)	30(2)	34(1)	11(1)	7(1)	12(1)
C(18)	25(1)	16(1)	40(2)	-4(1)	9(1)	7(1)
C(19)	35(2)	16(1)	23(1)	-5(1)	11(1)	2(1)
C(20)	28(1)	12(1)	22(1)	-2(1)	-6(1)	0(1)
C(21)	19(1)	14(1)	28(1)	1(1)	7(1)	4(1)
C(22)	31(1)	12(1)	24(1)	2(1)	4(1)	10(1)
C(23)	17(1)	19(1)	23(1)	8(1)	5(1)	7(1)
C(24)	20(1)	16(1)	20(1)	6(1)	4(1)	6(1)
C(25)	16(1)	21(1)	20(1)	-2(1)	1(1)	9(1)
C(26)	23(1)	28(1)	23(1)	4(1)	4(1)	12(1)
C(27)	33(2)	51(2)	21(1)	8(1)	5(1)	27(2)
C(28)	25(1)	47(2)	25(1)	-11(1)	-6(1)	21(1)
C(29)	23(1)	28(2)	36(2)	-10(1)	-2(1)	11(1)
C(30)	22(1)	24(1)	26(1)	0(1)	3(1)	11(1)
C(31)	13(1)	17(1)	23(1)	3(1)	6(1)	5(1)
C(32)	26(1)	29(1)	25(1)	7(1)	8(1)	16(1)
C(33)	31(2)	33(2)	40(2)	11(1)	12(1)	21(1)
C(34)	32(2)	25(1)	40(2)	1(1)	16(1)	14(1)
C(35)	27(1)	28(1)	26(1)	0(1)	8(1)	11(1)
C(36)	20(1)	27(1)	25(1)	1(1)	4(1)	11(1)
C(37)	22(1)	26(1)	15(1)	3(1)	3(1)	16(1)
C(38)	25(1)	27(1)	23(1)	6(1)	7(1)	15(1)
C(39)	28(1)	40(2)	27(1)	11(1)	11(1)	20(1)
C(40)	41(2)	49(2)	26(1)	6(1)	13(1)	32(2)
C(41)	50(2)	32(2)	40(2)	2(1)	13(1)	29(2)
C(42)	33(2)	25(1)	33(1)	6(1)	11(1)	17(1)

C(43)	20(1)	19(1)	18(1)	5(1)	3(1)	10(1)
C(44)	25(1)	41(2)	23(1)	8(1)	7(1)	19(1)
C(45)	20(1)	49(2)	29(1)	8(1)	1(1)	17(1)
C(46)	30(1)	30(2)	18(1)	4(1)	-2(1)	13(1)
C(47)	32(1)	31(2)	21(1)	3(1)	5(1)	16(1)
C(48)	20(1)	37(2)	22(1)	4(1)	3(1)	15(1)
P(3)	22(1)	28(1)	33(1)	12(1)	6(1)	11(1)
F(1)	56(1)	43(1)	73(1)	7(1)	-2(1)	35(1)
F(2)	54(1)	80(2)	73(1)	44(1)	33(1)	53(1)
F(3)	54(1)	95(2)	51(1)	46(1)	28(1)	36(1)
F(5)	73(1)	110(2)	35(1)	23(1)	23(1)	61(1)
F(4)	39(1)	31(1)	63(1)	15(1)	4(1)	7(1)
F(6)	45(1)	44(1)	104(2)	19(1)	-29(1)	-3(1)
C(49)	36(2)	36(2)	54(2)	8(1)	19(1)	9(2)
Cl(1)	50(1)	30(1)	55(1)	8(1)	14(1)	18(1)
Cl(2)	67(1)	34(1)	44(1)	10(1)	25(1)	20(1)

Appendix II: Spectra Data

400MHz 1H no 120314(101) CDCl3

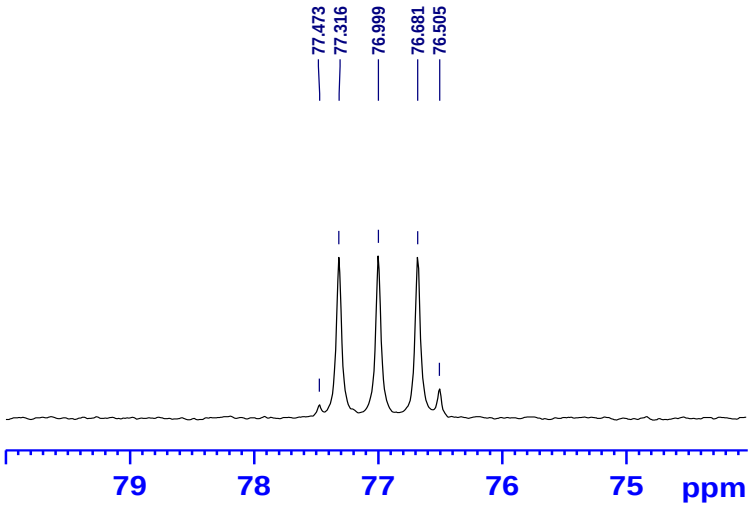


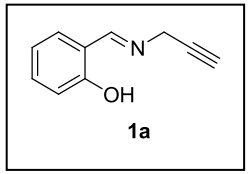
NTU

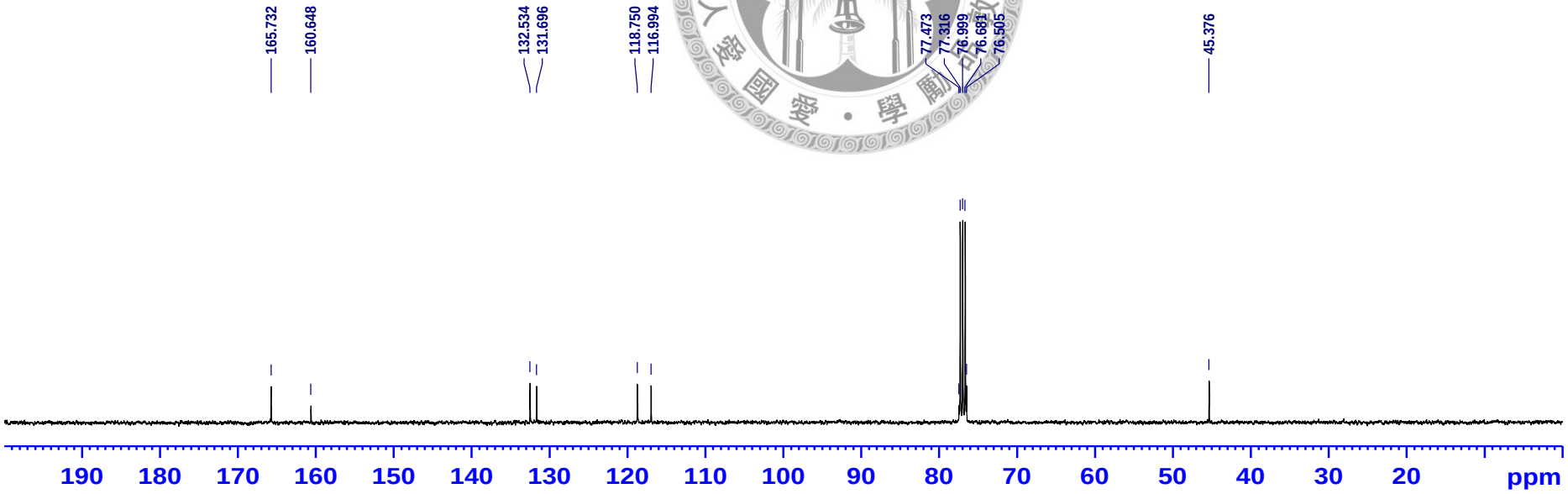
```
NAME        mantou no 120314
EXPNO               101
PROCNO                1
Date_          20120314
Time_             21.17
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               32768
SOLVENT        Acetone
NS                   10
DS                    0
SWH           8012.820 Hz
FIDRES        0.244532 Hz
AQ            2.0447104 sec
RG                  181
DW             62.400 usec
DE              6.50 usec
TE             298.0 K
D1          1.00000000 sec
TD0                   1
========== CHANNEL f1 ========
NUC1                 1H
P1              12.10 usec
PL1             -3.00 dB
SFO1        400.1320007 MHz
SI                65536
SF          400.1300177 MHz
WDW                 QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
PC                 1.00
```


1a

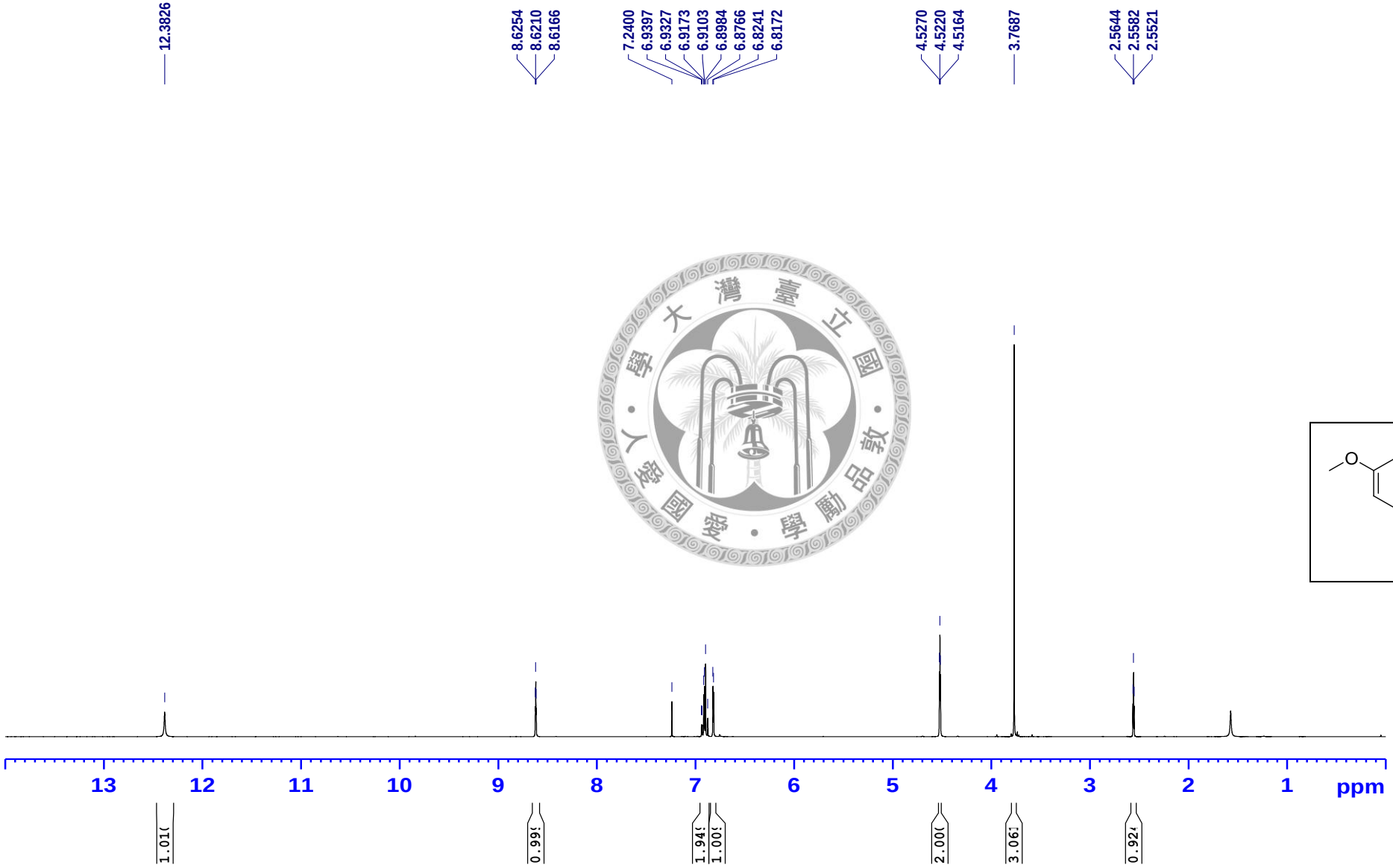
400MHz 13C no 120314 CDCl3



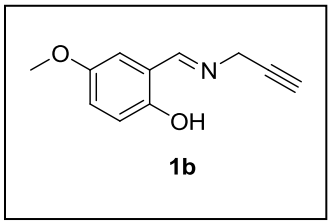




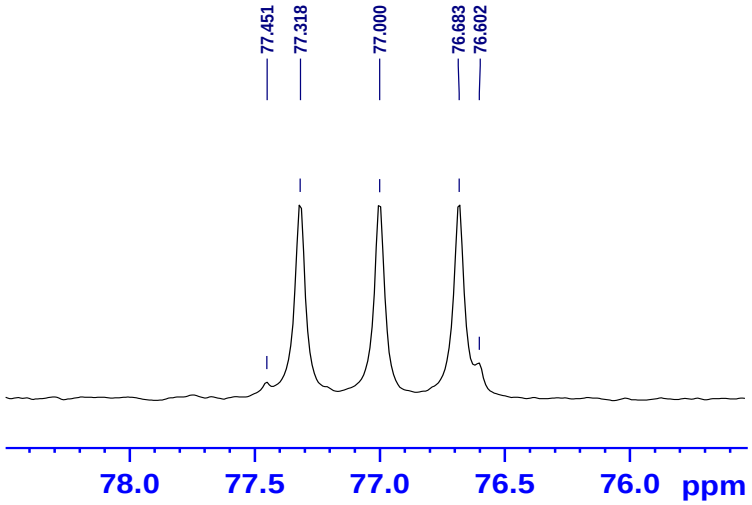
400MHz 1H OMe 120314 CDCl3

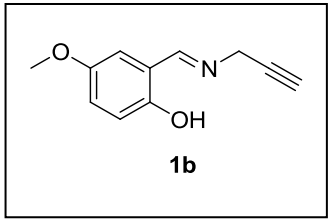


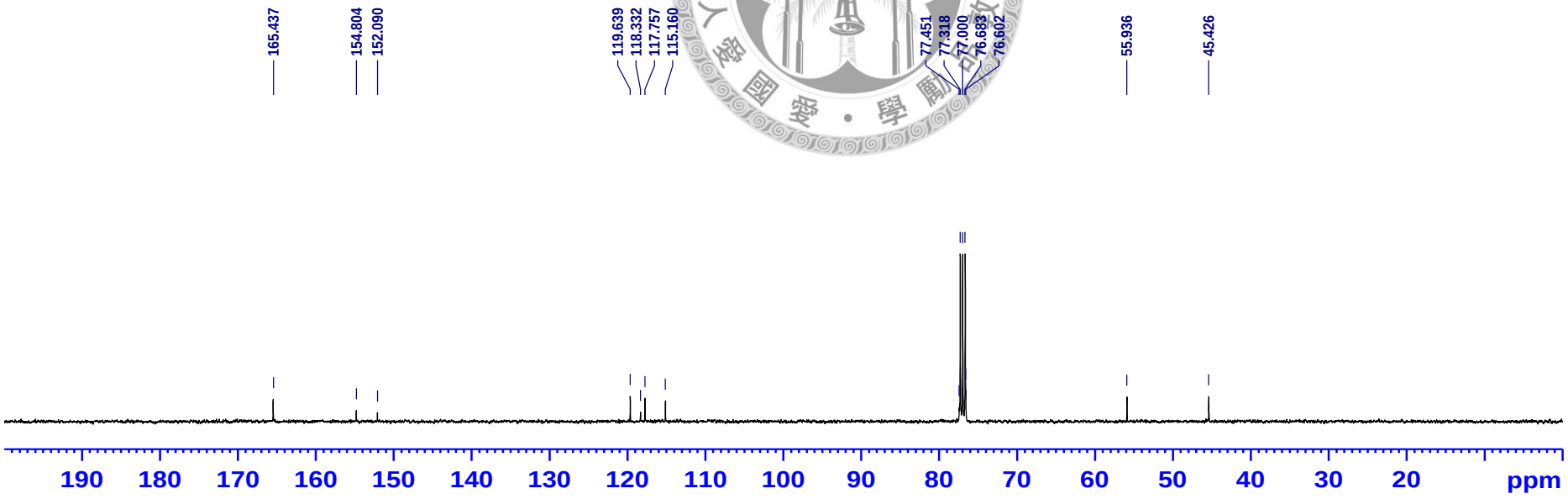

```
NAME        mantou OMe 120314
EXPNO                    100
PROCNO                     1
Date_               20120314
Time_                 10.12
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT            Acetone
NS                        16
DS                         0
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 2.0447731 sec
RG                     228.1
DW                  62.400 usec
DE                   6.50 usec
TE                   298.3 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.10 usec
PL1                    7.00 dB
SFO1              400.1320007 MHz
SI                       65536
SF                400.1300178 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```



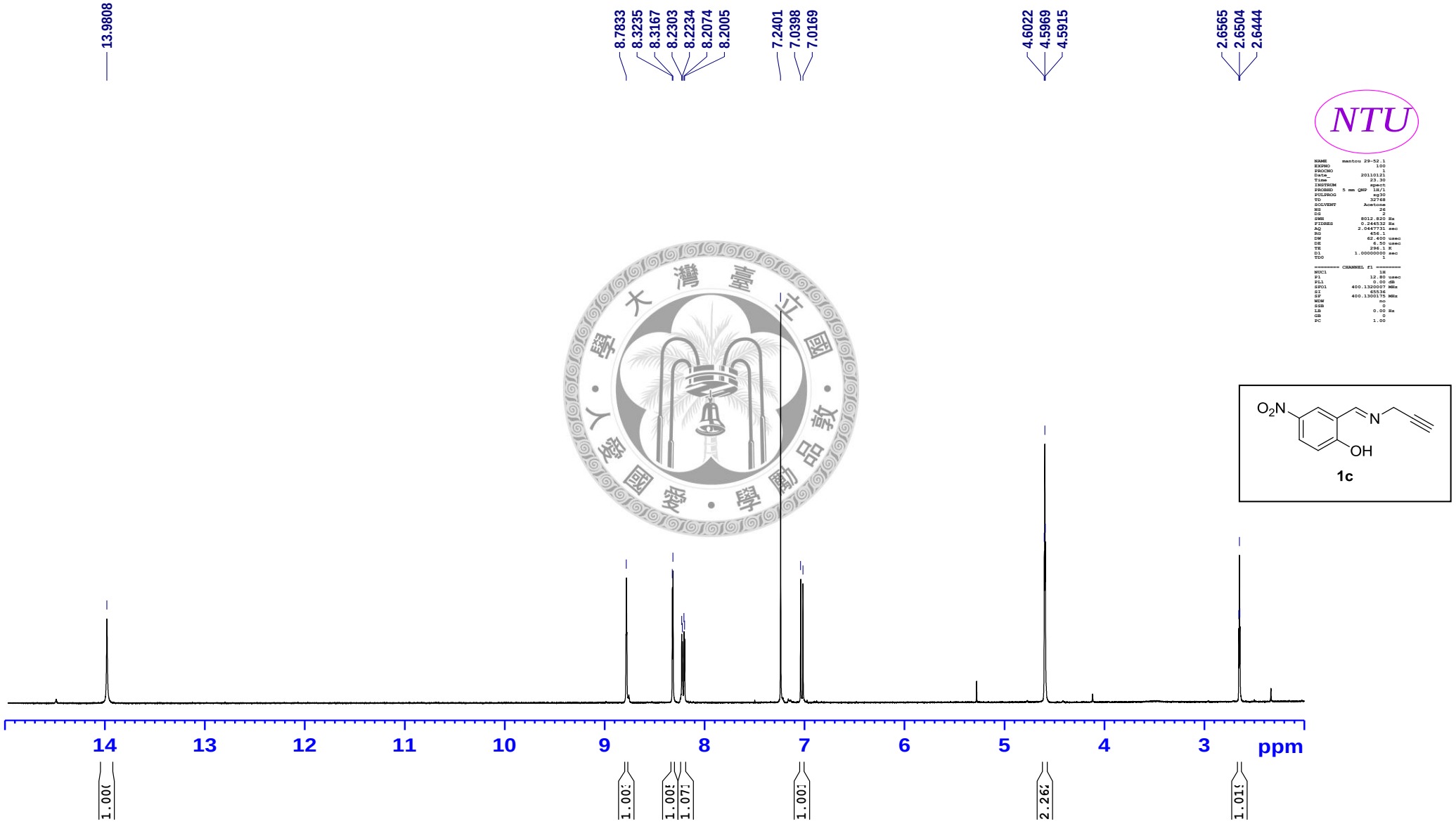
400MHz 13C OMe 120314 CDCl3



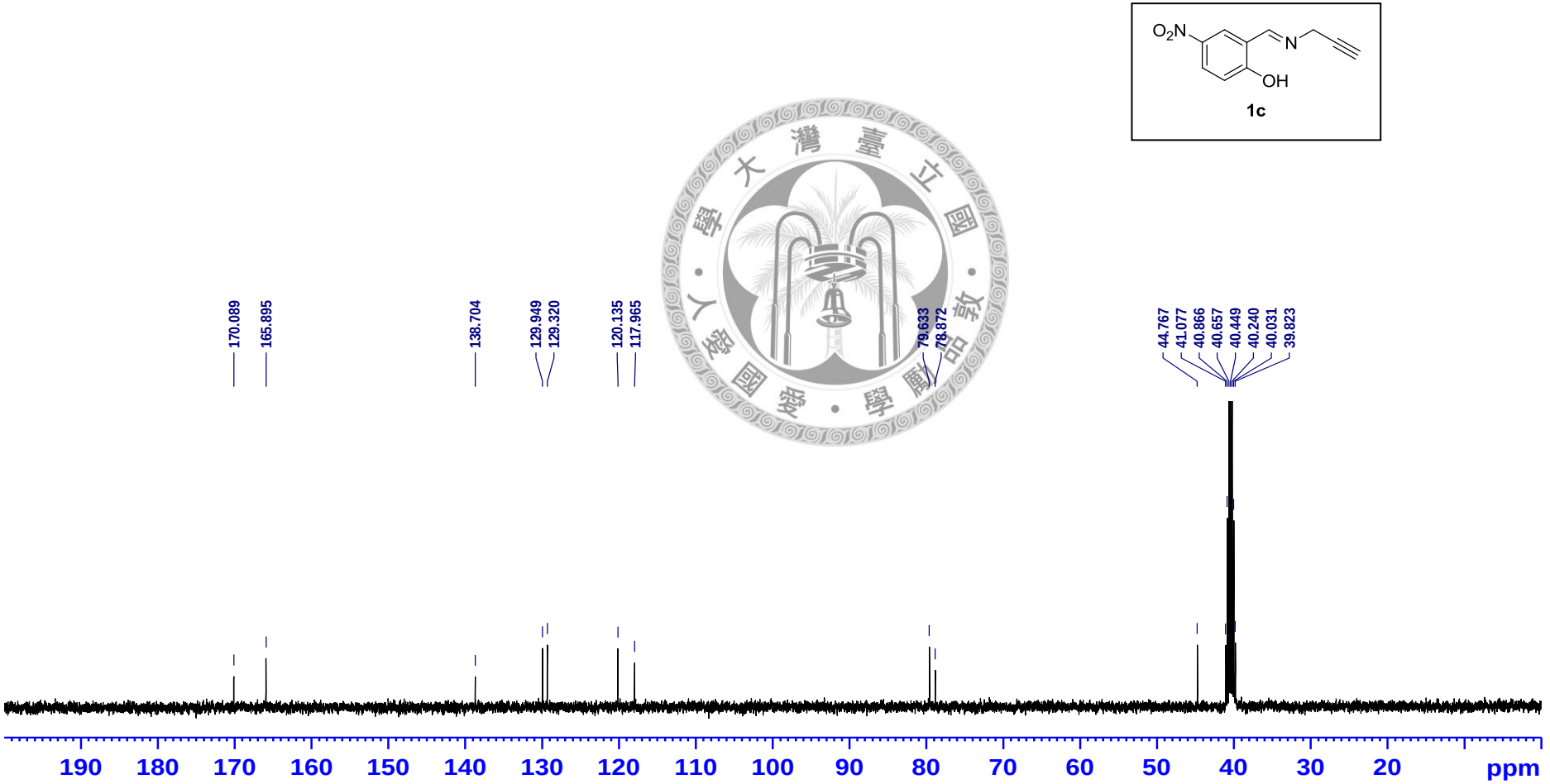




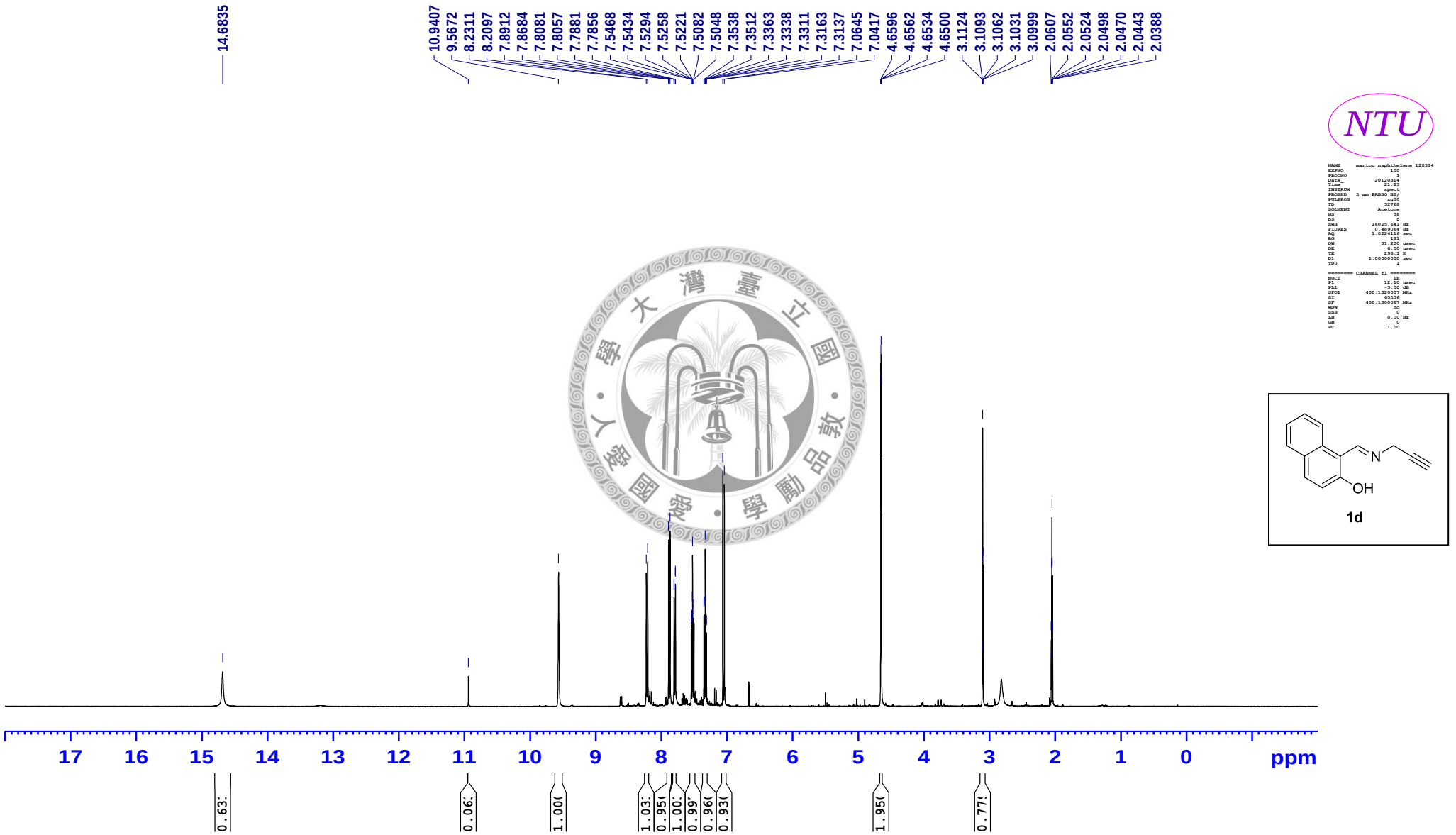
400MHz 1H CDCL3 29-52.1



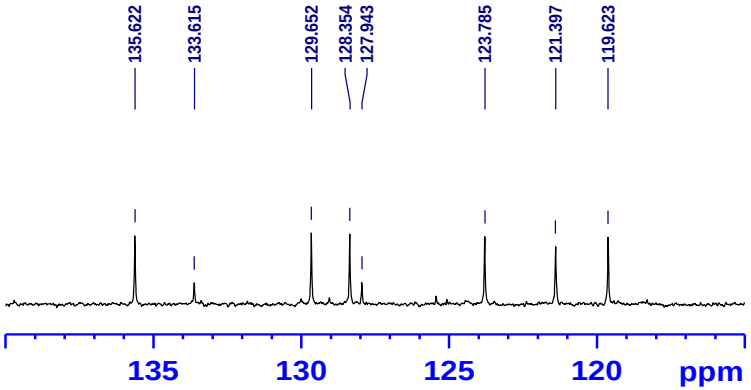
400MHz 13C NO2 120319 d-DMSO

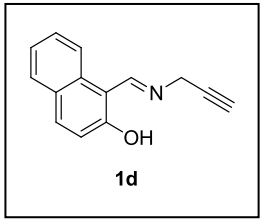


400MHz 1H naph 120314 CDCl3

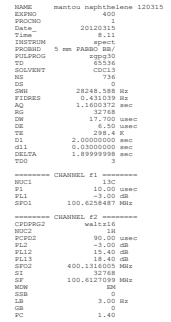


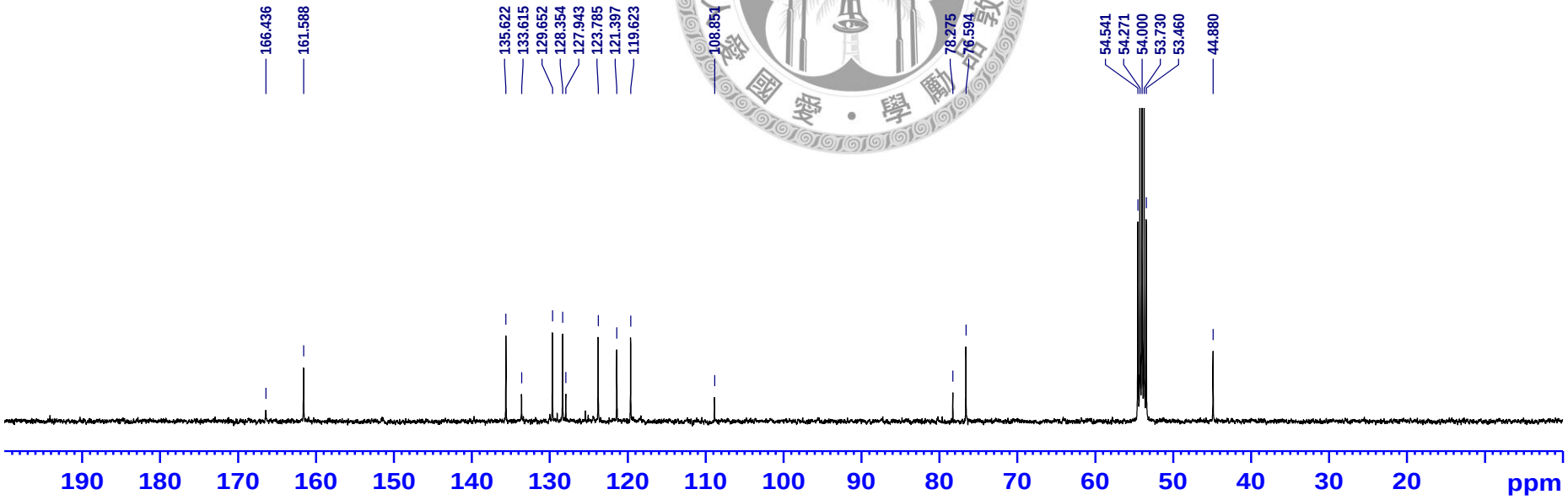
400MHz 13C naph 120315(400) CD2Cl2



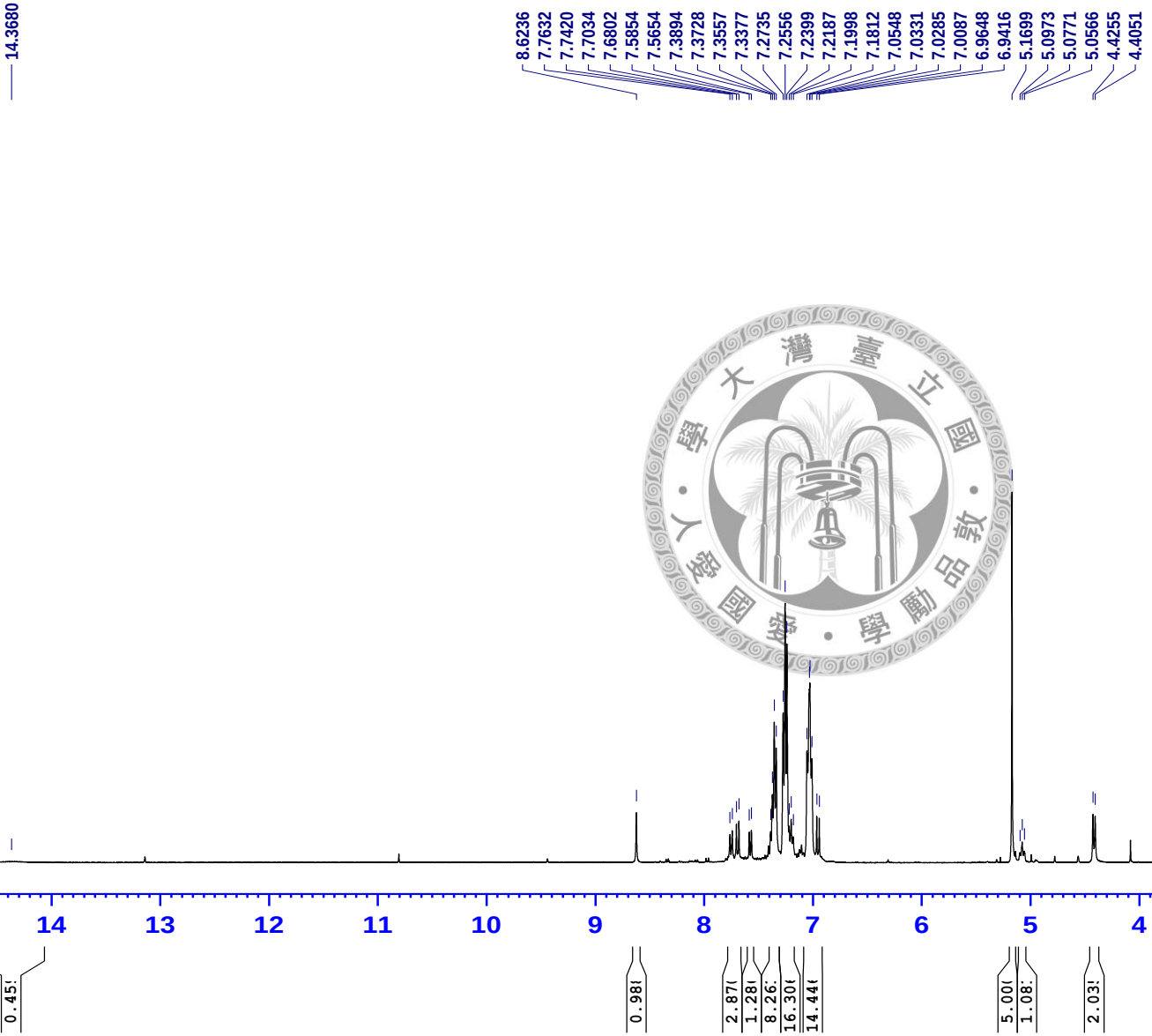


NTU



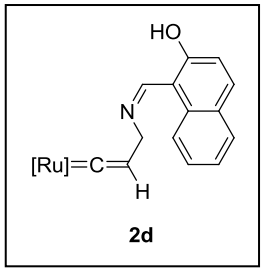


400MHz 1H 24-164.1 CDCl3



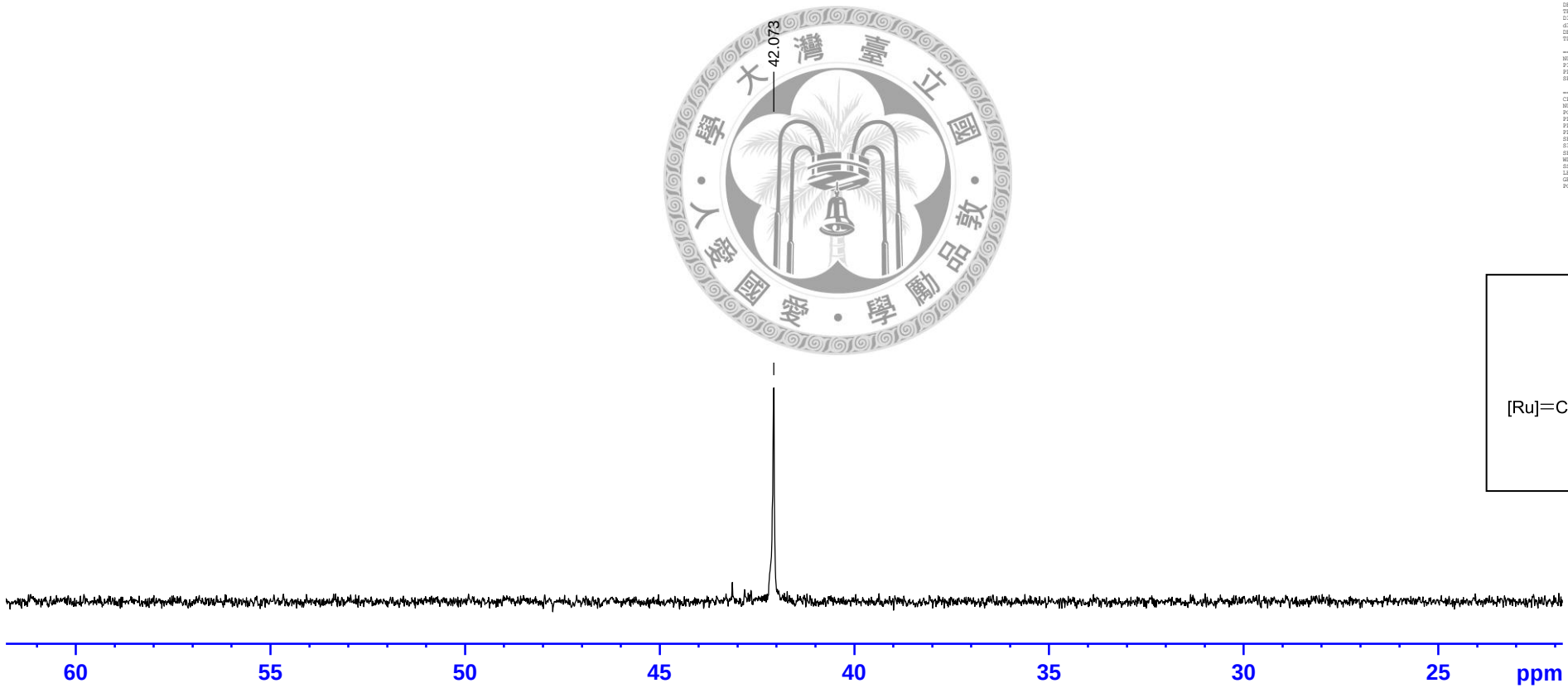
NTU

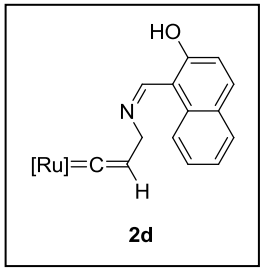
NAME mantou 24-164.1
EXPNO 100
PROCNO 1
Date_ 20111124
Time 21.37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 24
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 228.5
DW 62.400 usec
DE 6.00 usec
TE 304.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.10 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300179 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



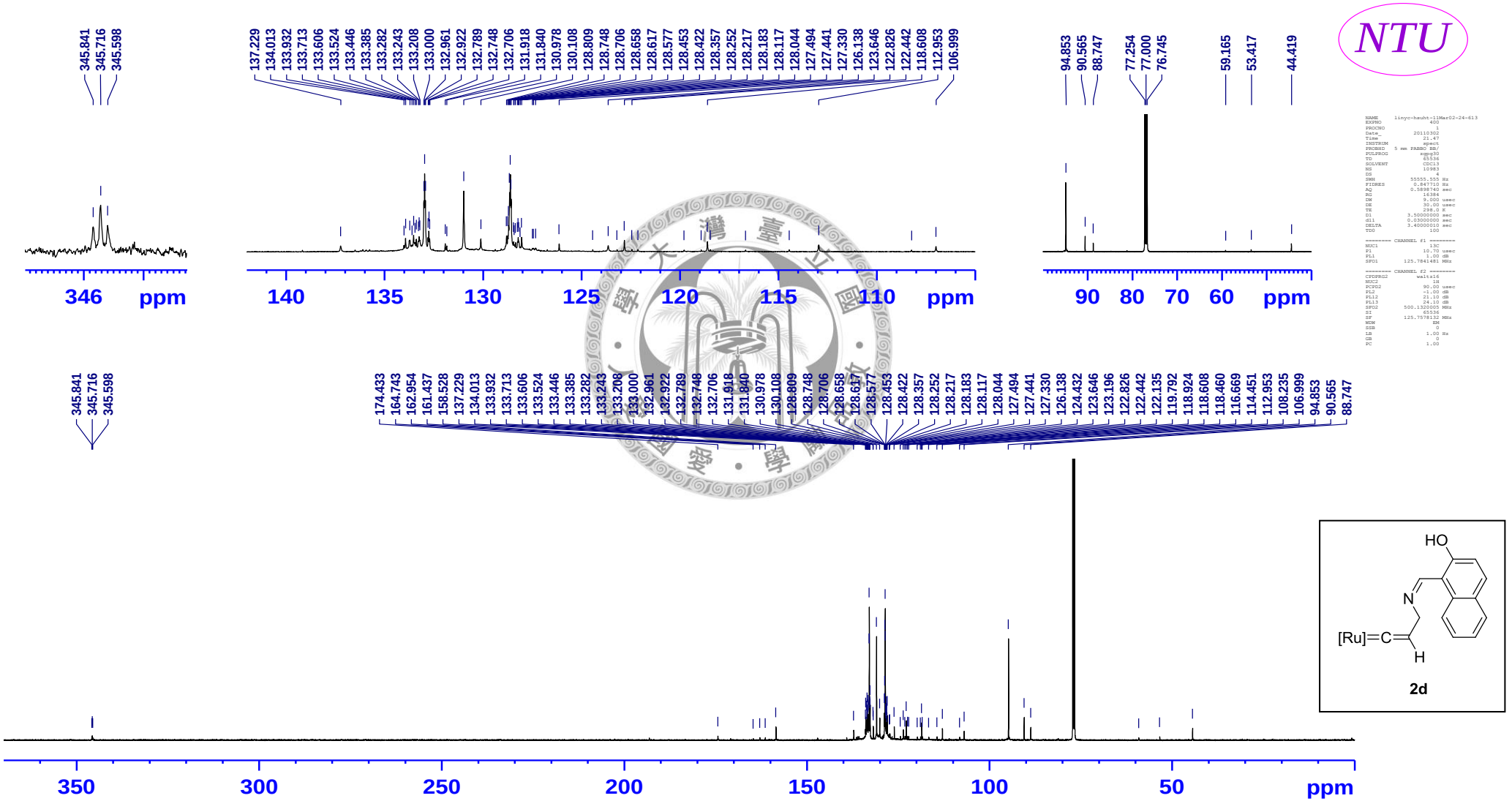
2d

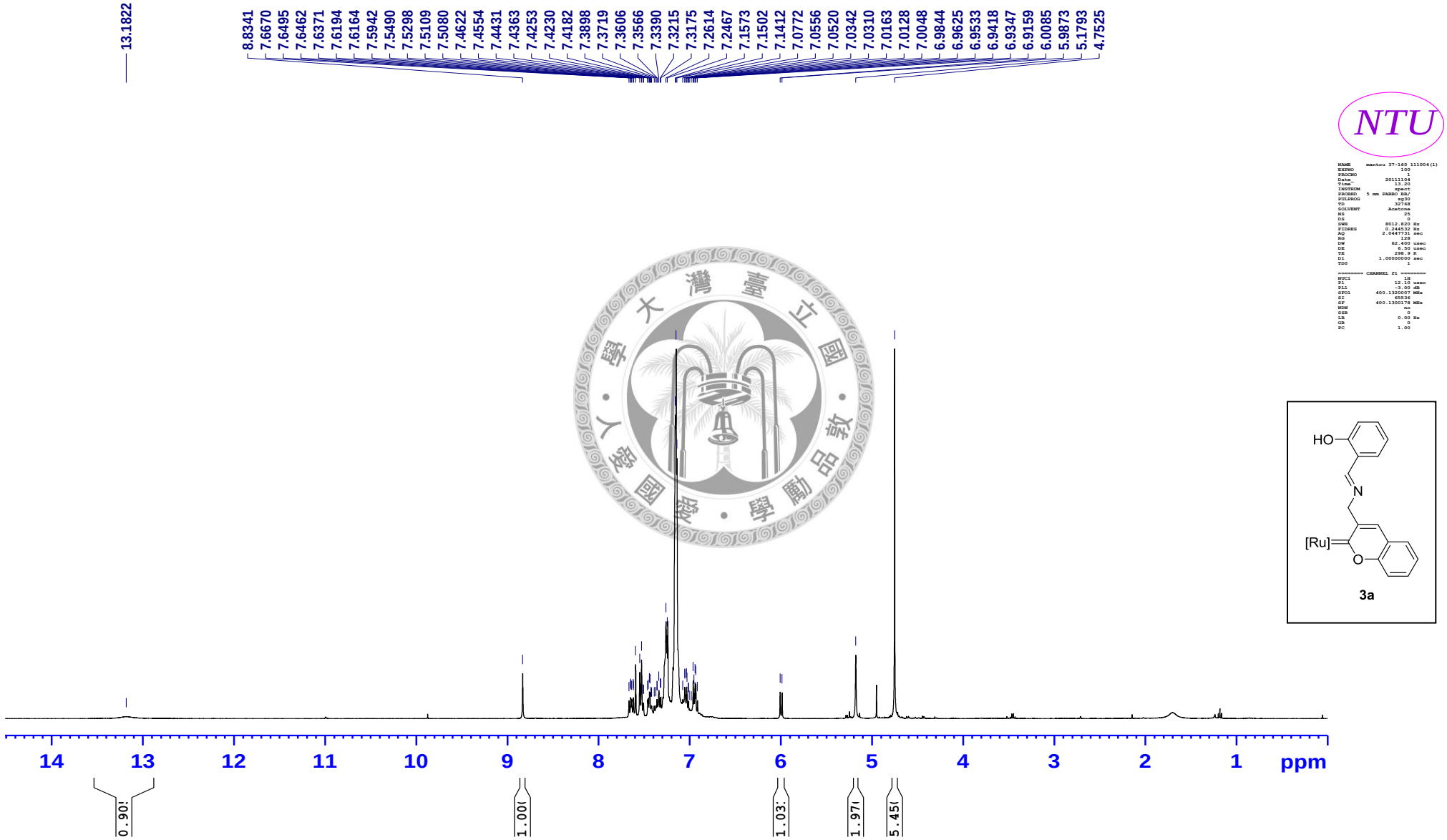
400MHz P31 24-39.2 CDCl3



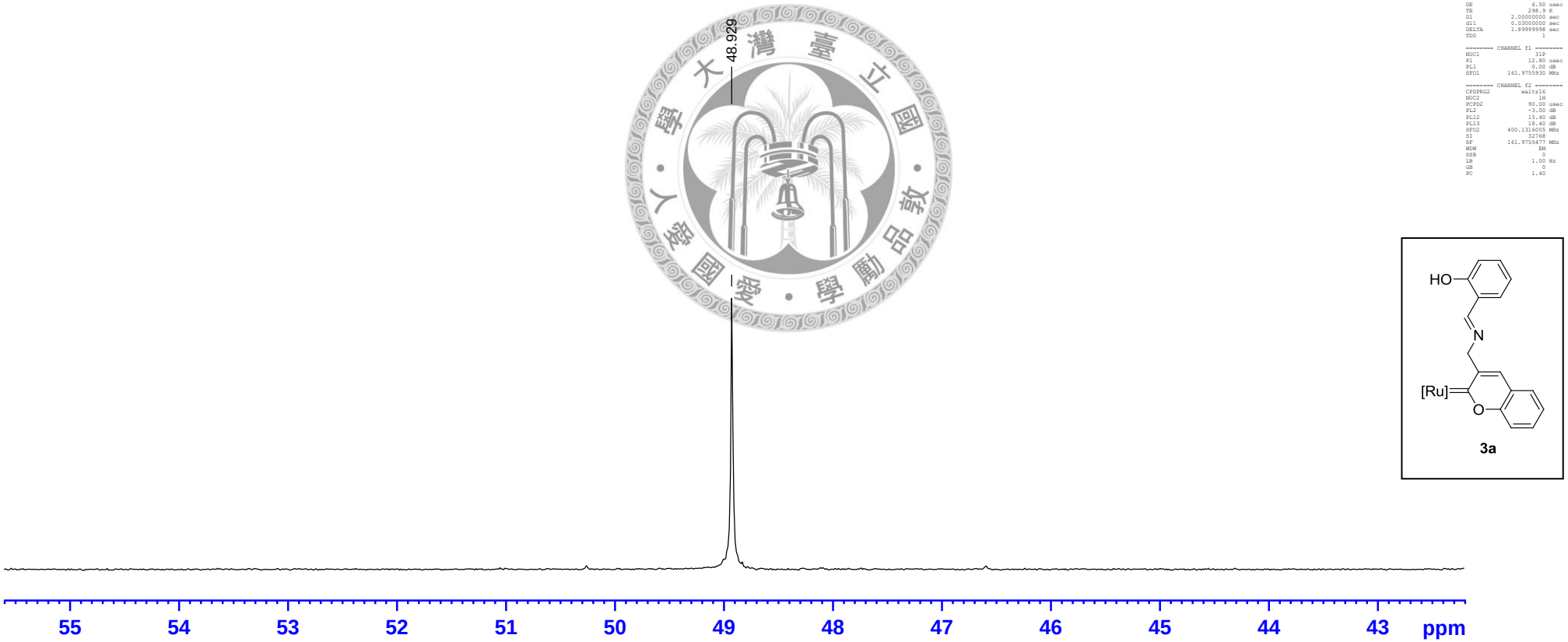


2d


345.841
345.716
345.598
137.229
134.013
133.932
133.713
133.606
133.524
133.446
133.385
133.282
133.243
133.208
133.000
132.961
132.922
132.789
132.748
132.706
131.918
131.840
130.978
130.108
128.809
128.748
128.706
128.658
128.617
128.577
128.453
128.422
128.357
128.252
128.217
128.183
128.117
128.044
127.494
127.441
127.330
126.138
123.646
122.826
122.442
118.608
112.953
106.999
94.853
90.565
88.747
77.254
77.000
76.745
59.165
53.417
44.419
346 ppm
140 135 130 125 120 115 110 ppm
90 80 70 60 ppm
174.433
164.743
162.954
161.437
158.528
137.229
134.013
133.932
133.713
133.606
133.524
133.446
133.385
133.282
133.243
133.208
133.000
132.961
132.922
132.789
132.748
132.706
131.918
131.840
130.978
130.108
128.809
128.748
128.706
128.658
128.617
128.577
128.453
128.422
128.357
128.252
128.217
128.183
128.117
128.044
127.494
127.441
127.330
126.138
124.432
123.646
123.196
122.826
122.442
122.135
119.792
118.924
118.608
118.460
116.669
114.451
112.953
108.235
106.999
94.853
90.565
88.747
350 300 250 200 150 100 50 ppm
HO
N
[Ru]=C
H
2d


13.1822
8.8341
7.6670
7.6495
7.6462
7.6371
7.6194
7.6164
7.5942
7.5490
7.5298
7.5109
7.5080
7.4622
7.4554
7.4431
7.4363
7.4253
7.4230
7.4182
7.3898
7.3719
7.3606
7.3566
7.3390
7.3215
7.3175
7.2614
7.2467
7.1573
7.1502
7.1412
7.0772
7.0556
7.0520
7.0342
7.0310
7.0163
7.0128
7.0048
6.9844
6.9625
6.9533
6.9418
6.9347
6.9159
6.0085
5.9873
5.1793
4.7525
NTU
NAME mantou 37-160 111004(1)
EXPNO 100
PROCNO 1
Date_ 20111104
Time 13.20
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 8
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 298.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.10 usec
PL1 -3.00 dB
SFO1 400.1320007 MHz
SI 65536
SF 400.1300178 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
HO
N
[Ru]
O
3a
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.90
1.00
1.03
1.97
5.45

400MHz P31 37-160 111104(1) CDCl3



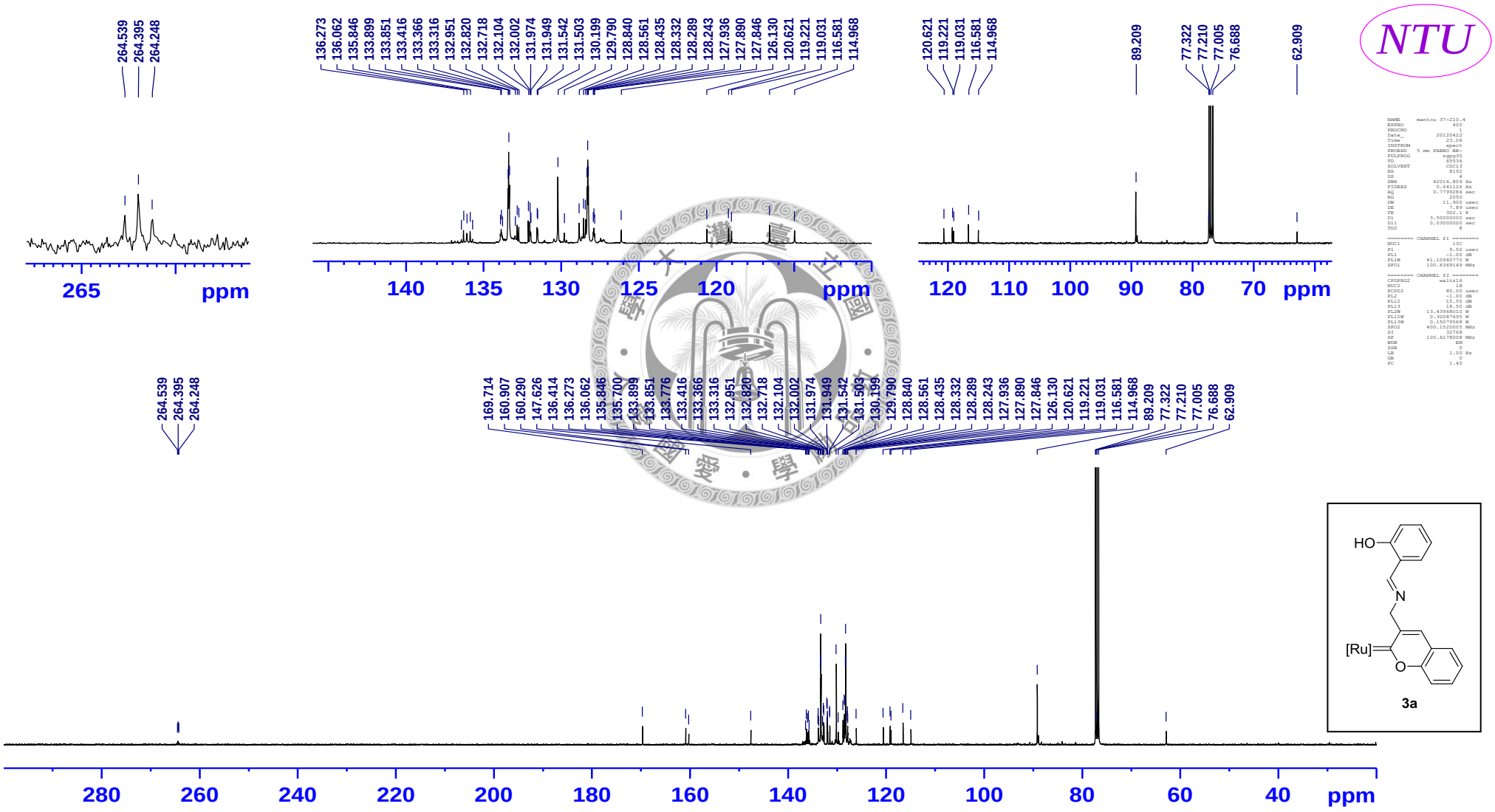
NAME mantou 37-160 111004(1)
EXPNO 300
PROCNO 1
Date 20111104
Time 13.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 24
DS 4
SWH 58479.531 Hz
FIDRES 0.892327 Hz
AQ 0.5603828 sec
RG 8192
DW 8.550 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 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

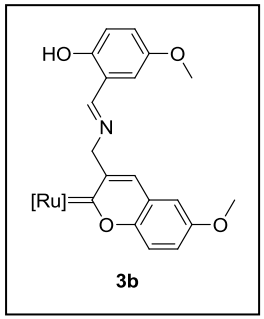
3a

400MHz 13C 37-210.4 CDCl3

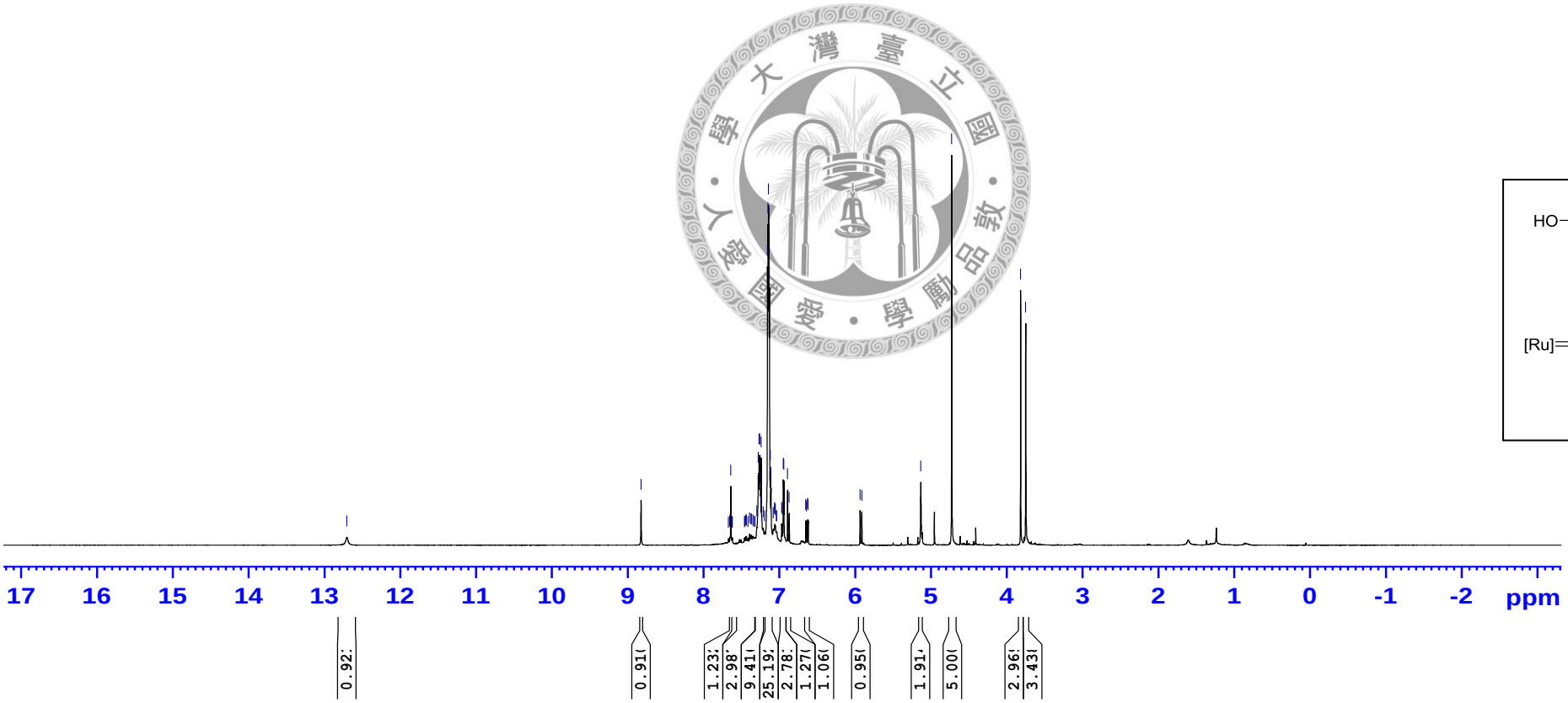


400MHz 1H 27-211 120424.2 CDCl3

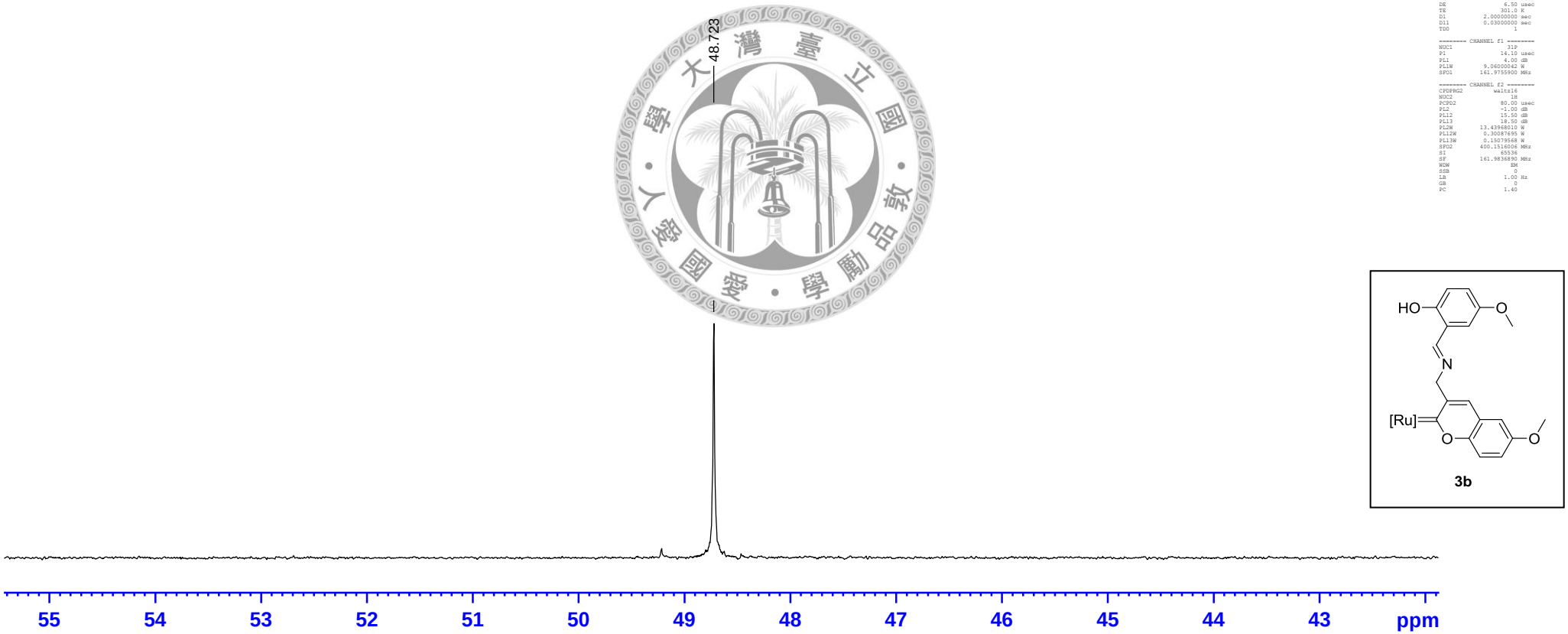

```
NAME        mantou 27-211 120424.2
EXPNO             100
PROCNO              1
Date_        20120424
Time              22.02
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              32768
SOLVENT         CDCl3
NS                 24
DS                  0
SWH           8223.685 Hz
FIDRES        0.250967 Hz
AQ            1.9923444 sec
RG                 90.5
DW               60.850 usec
DE                6.50 usec
TE                301.1 K
D1            1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              12.00 usec
PL1             -1.00 dB
PLW1        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
```



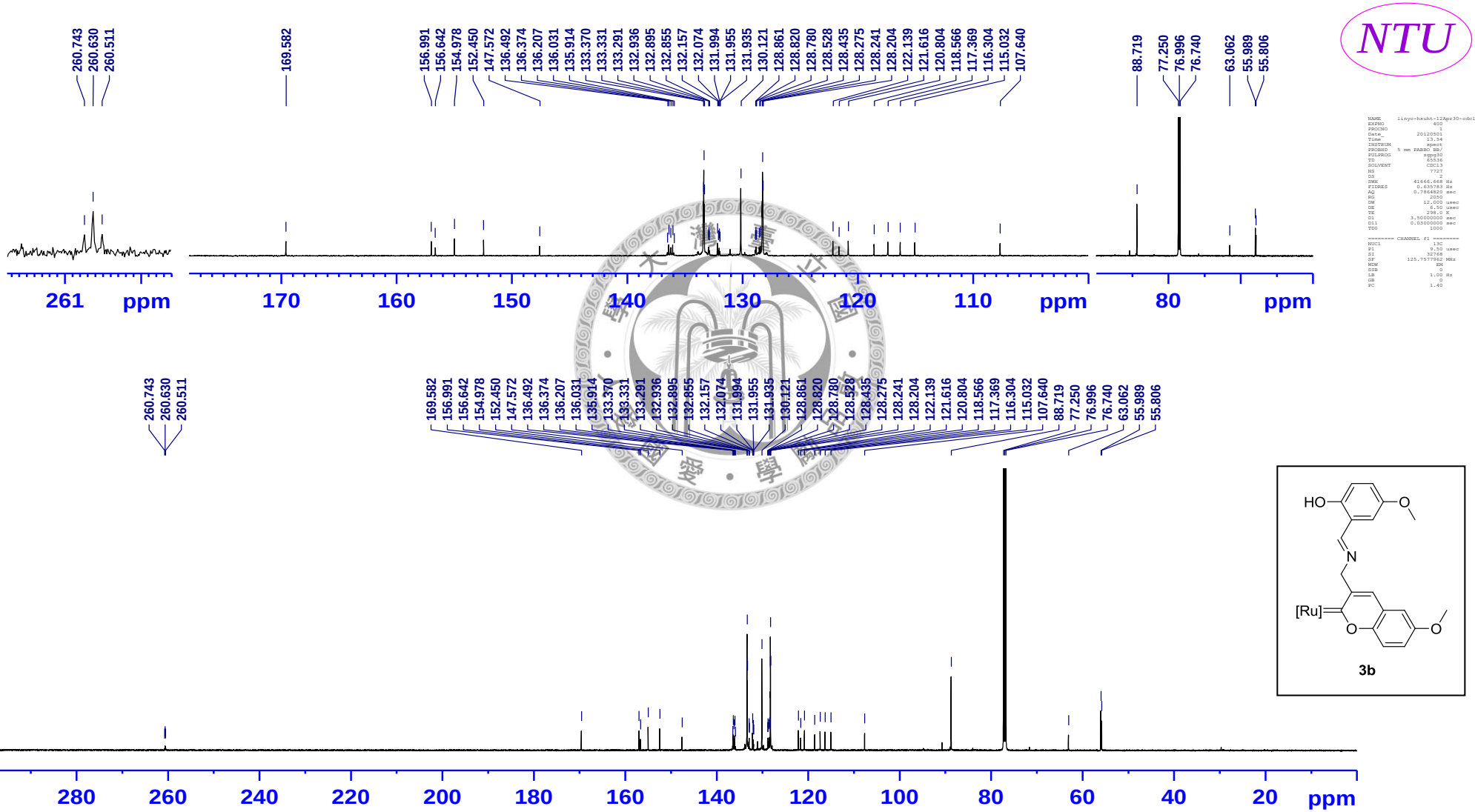
3b



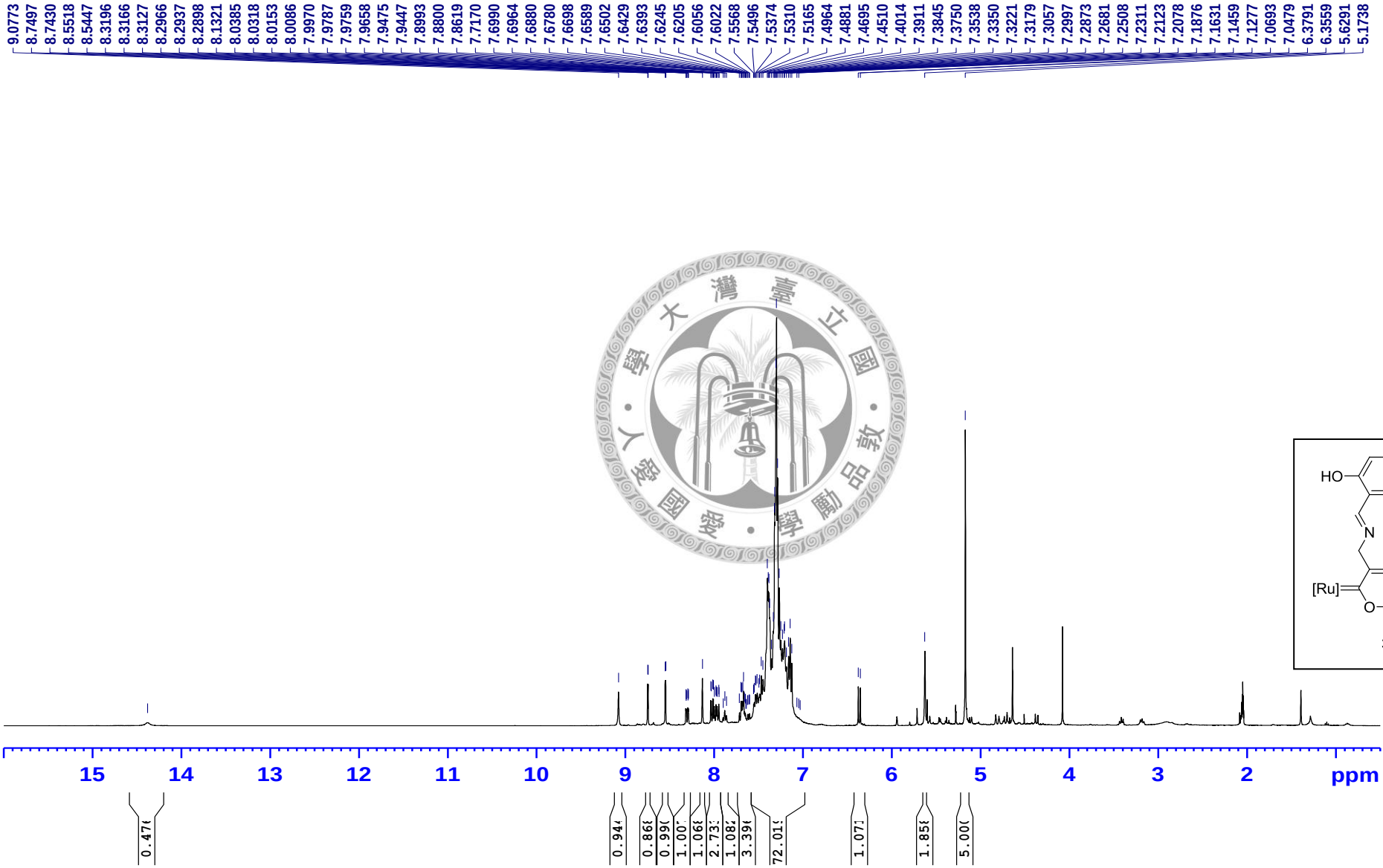
400MHz 31P 27-211 120424.2 CDCl3



3b

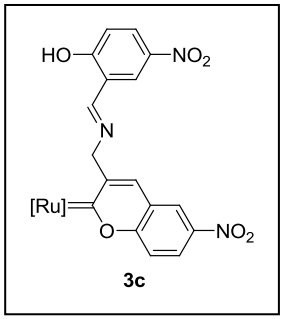

260.743
260.630
260.511
169.582
156.991
156.642
154.978
152.450
147.572
136.492
136.374
136.207
136.031
135.914
133.370
133.331
133.291
132.936
132.895
132.855
132.157
132.074
131.994
131.955
131.935
130.121
128.861
128.820
128.780
128.528
128.435
128.275
128.241
128.204
122.139
121.616
120.804
118.566
117.369
116.304
115.032
107.640
88.719
77.250
76.996
76.740
63.062
55.989
55.806
261 ppm
170
160
150
140
130
120
110 ppm
80 ppm
280
260
240
220
200
180
160
140
120
100
80
60
40
20 ppm
HO
O
N
[Ru]
O
O
3b

400MHz 1H 30-213.7(1) d-acetone



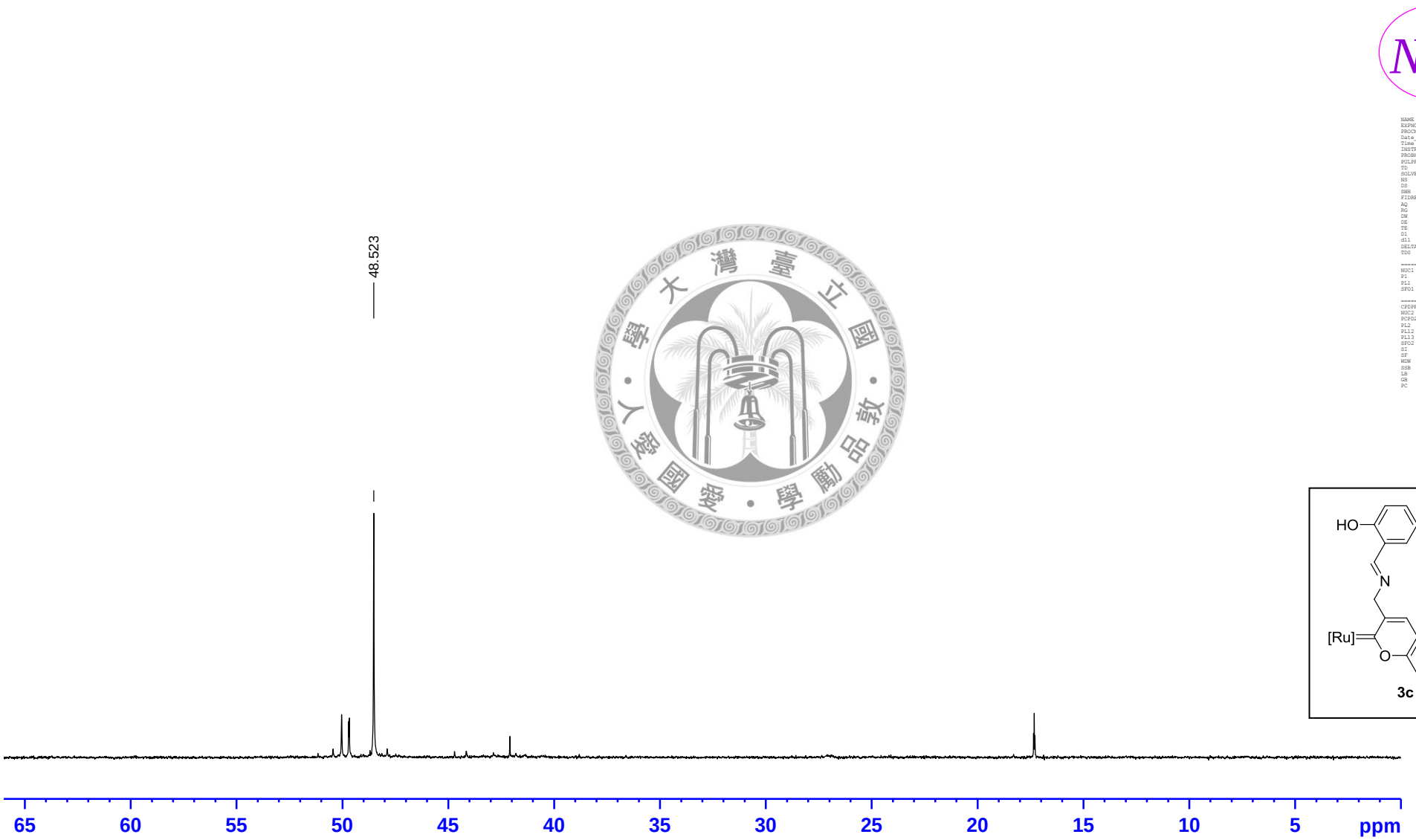
NTU

```
NAME        mantou 30-213.7(1)
EXPNO              100
PROCNO               1
Date_         20120427
Time             11.33
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD               32768
SOLVENT        Acetone
NS                  23
DS                   0
SWH          16025.641 Hz
FIDRES        0.489056 Hz
AQ            1.0224116 sec
RG                 7168
DW               31.200 usec
DE                6.50 usec
TE                 301.2 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                12.10 usec
PL1               -3.00 dB
SFO1        400.1320007 MHz
SI                 65536
SF          400.1300068 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```



3c

400MHz P31 30-213.7(1) d-acetone



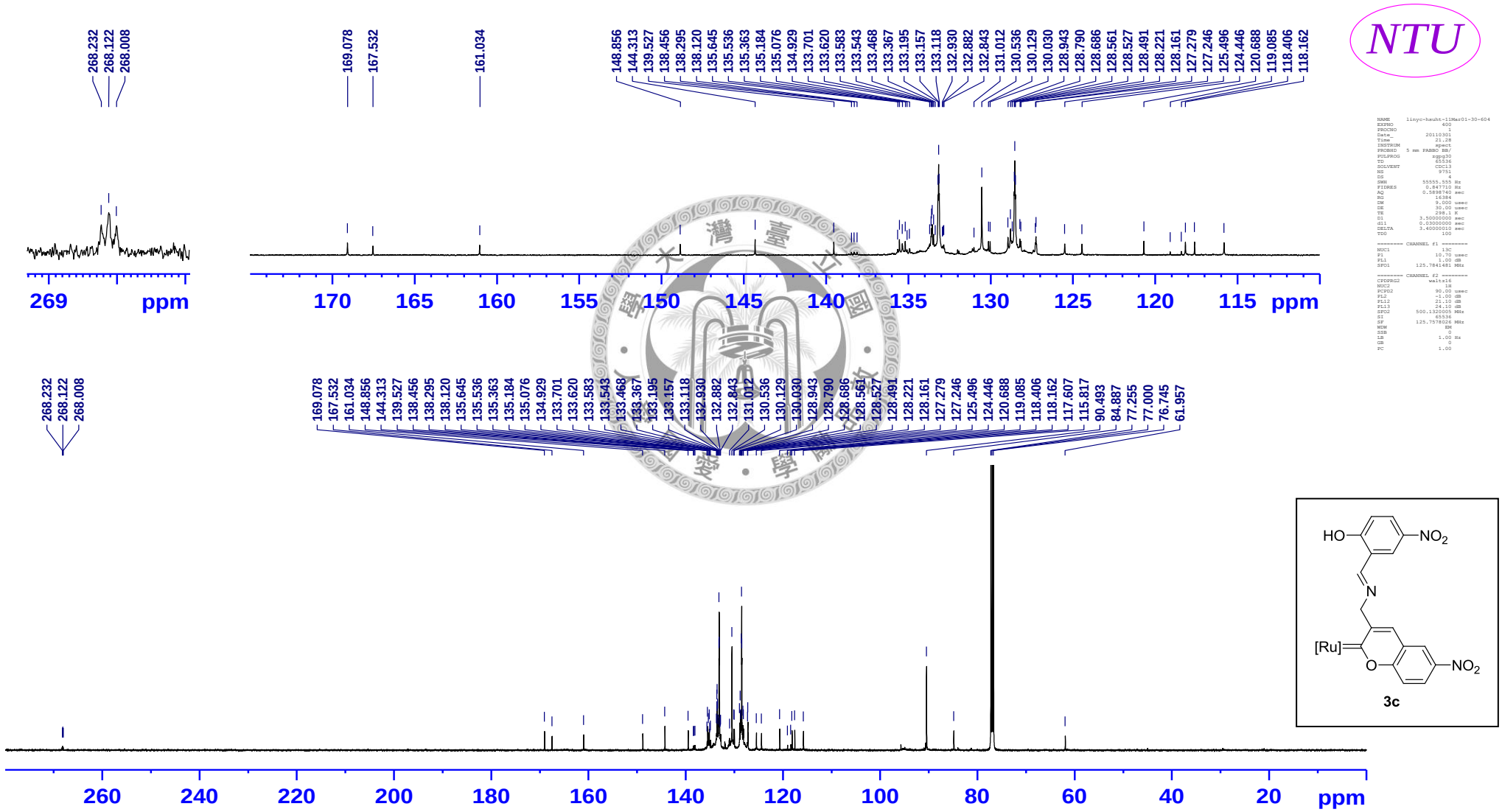
NAME mantou 30-213.7(1)
EXPNO 300
PROCNO 1
Date_ 20120427
Time_ 11.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 22
DS 4
SWH 58479.531 Hz
FIDRES 0.892327 Hz
AQ 0.5603828 sec
RG 8192
DW 8.550 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 12.80 usec
PL1 0.00 dB
SFO1 161.9755930 MHz

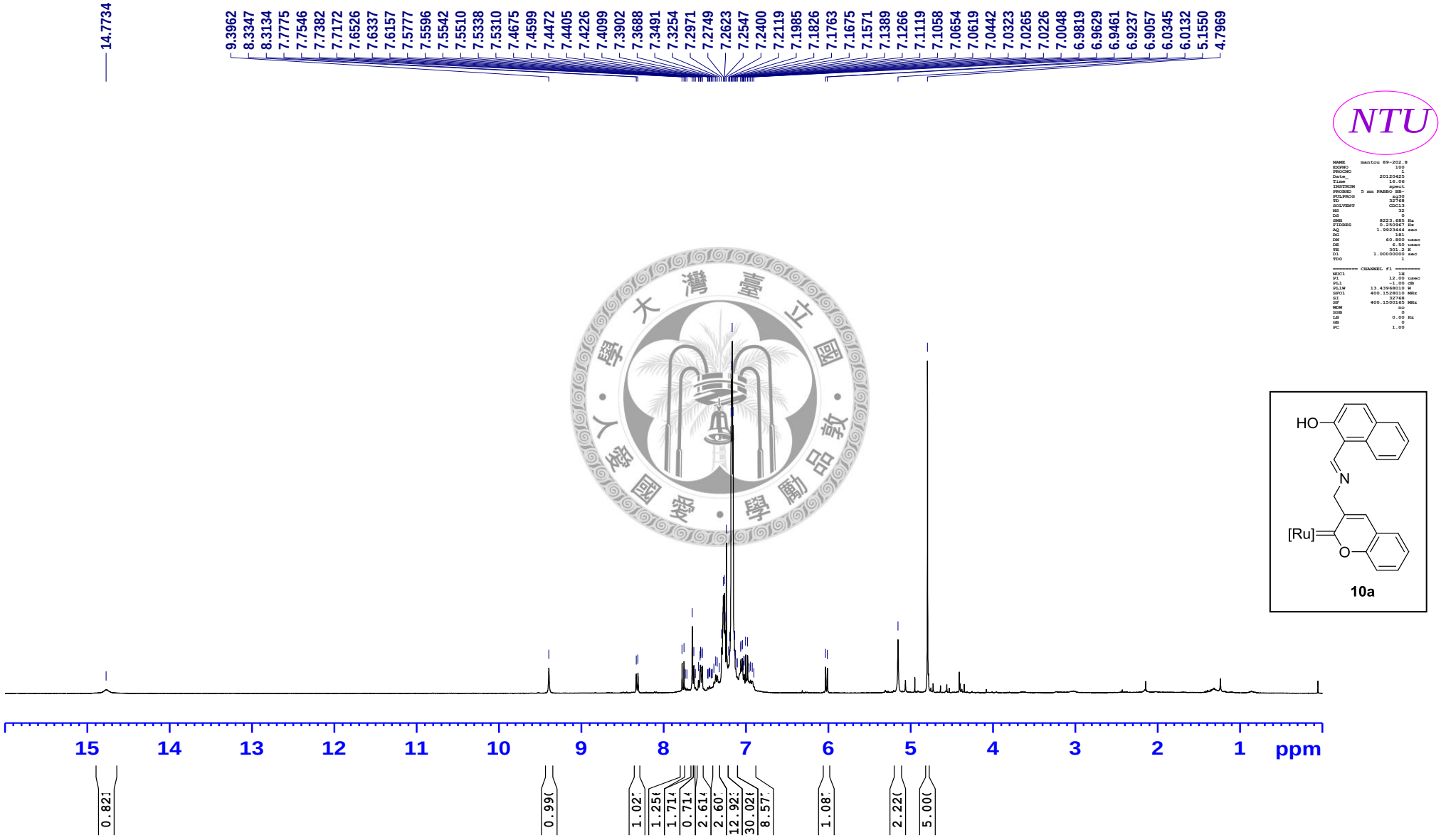
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.40 dB
PL13 18.40 dB
SFO2 400.1316005 MHz
SI 32768
SF 161.9755477 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3c

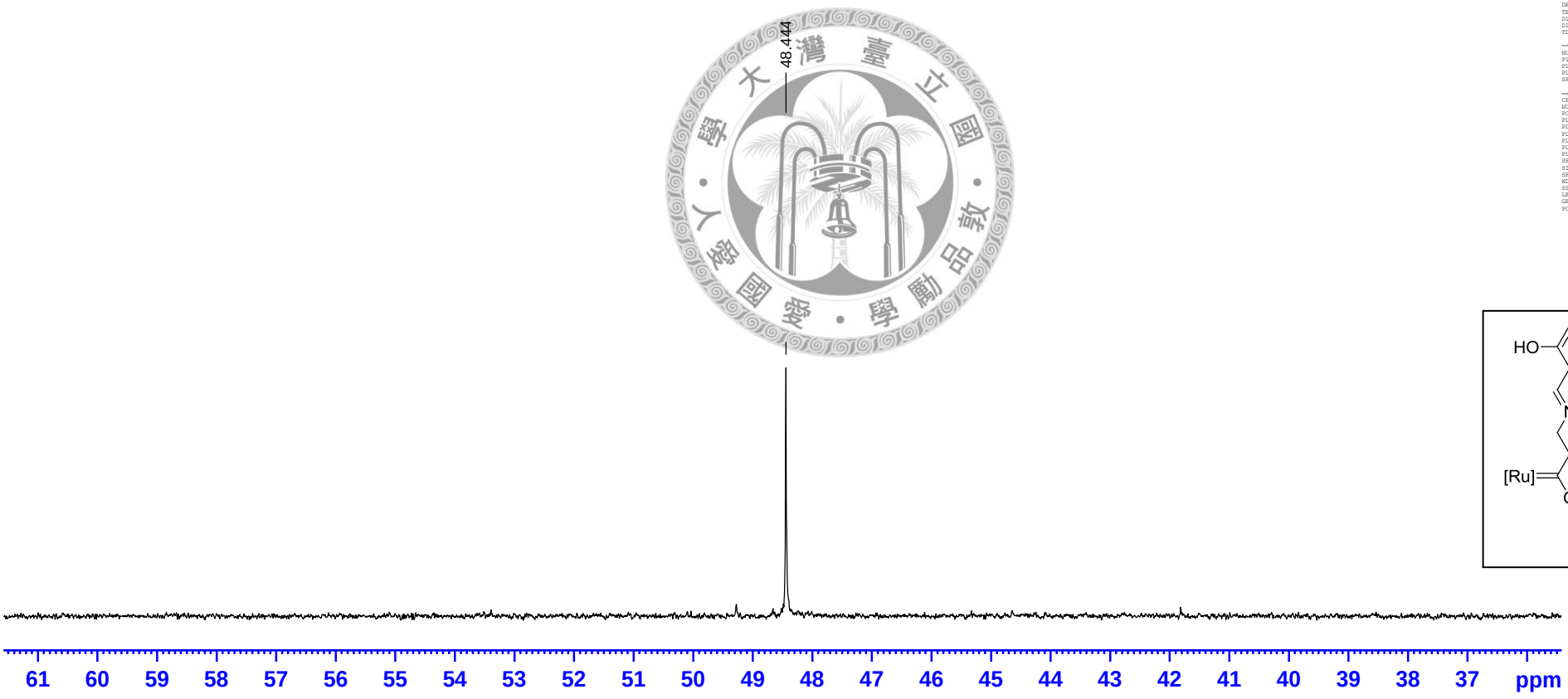
500MHz C13 CDCL3 30-60.4

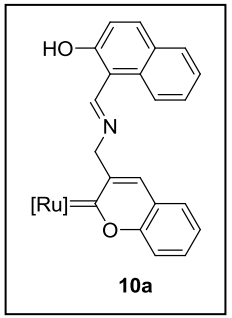


400MHz 1H 89-202.8 CDCl3



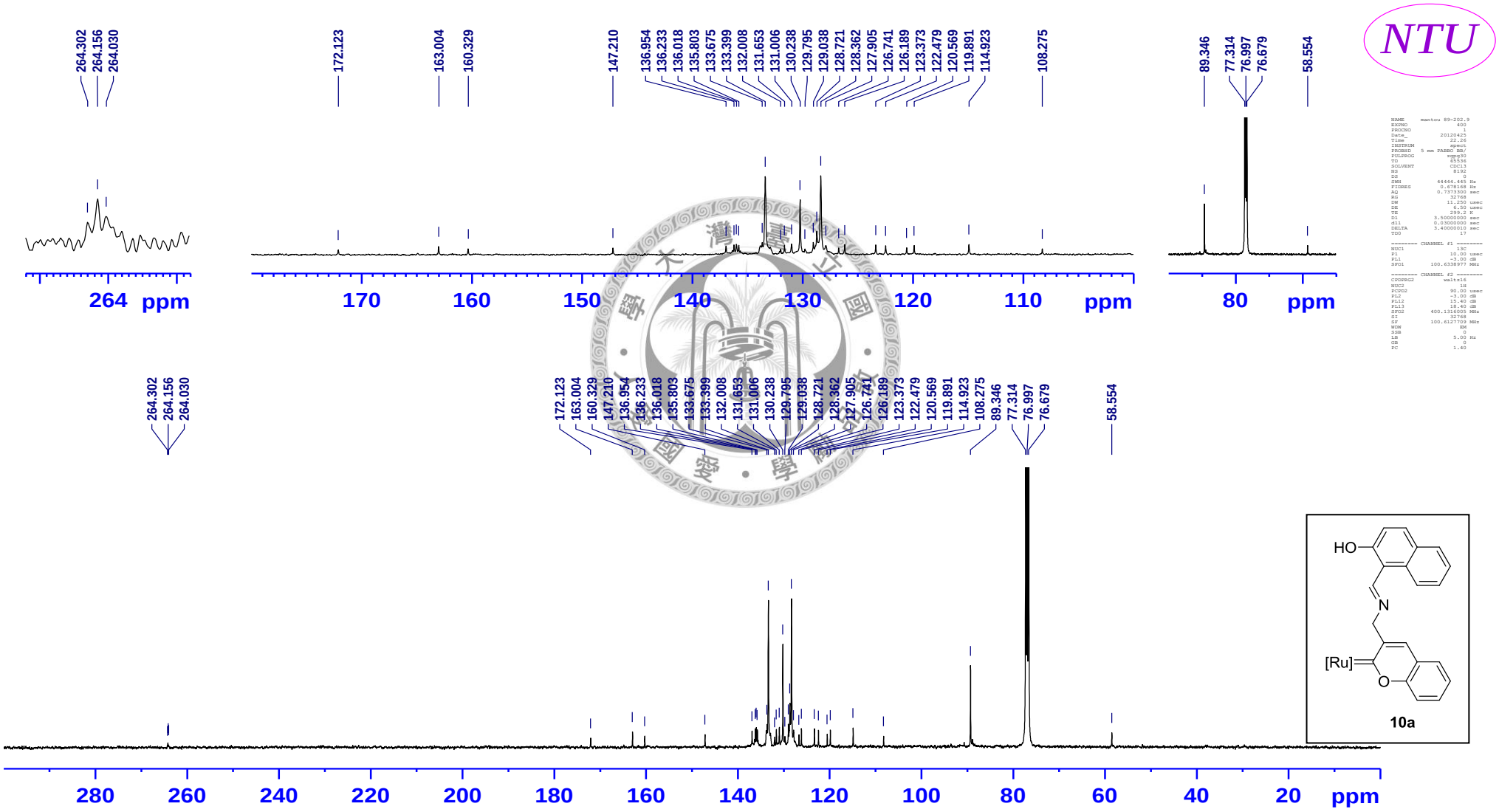
400MHz 31P 89-202.8 CDCl3



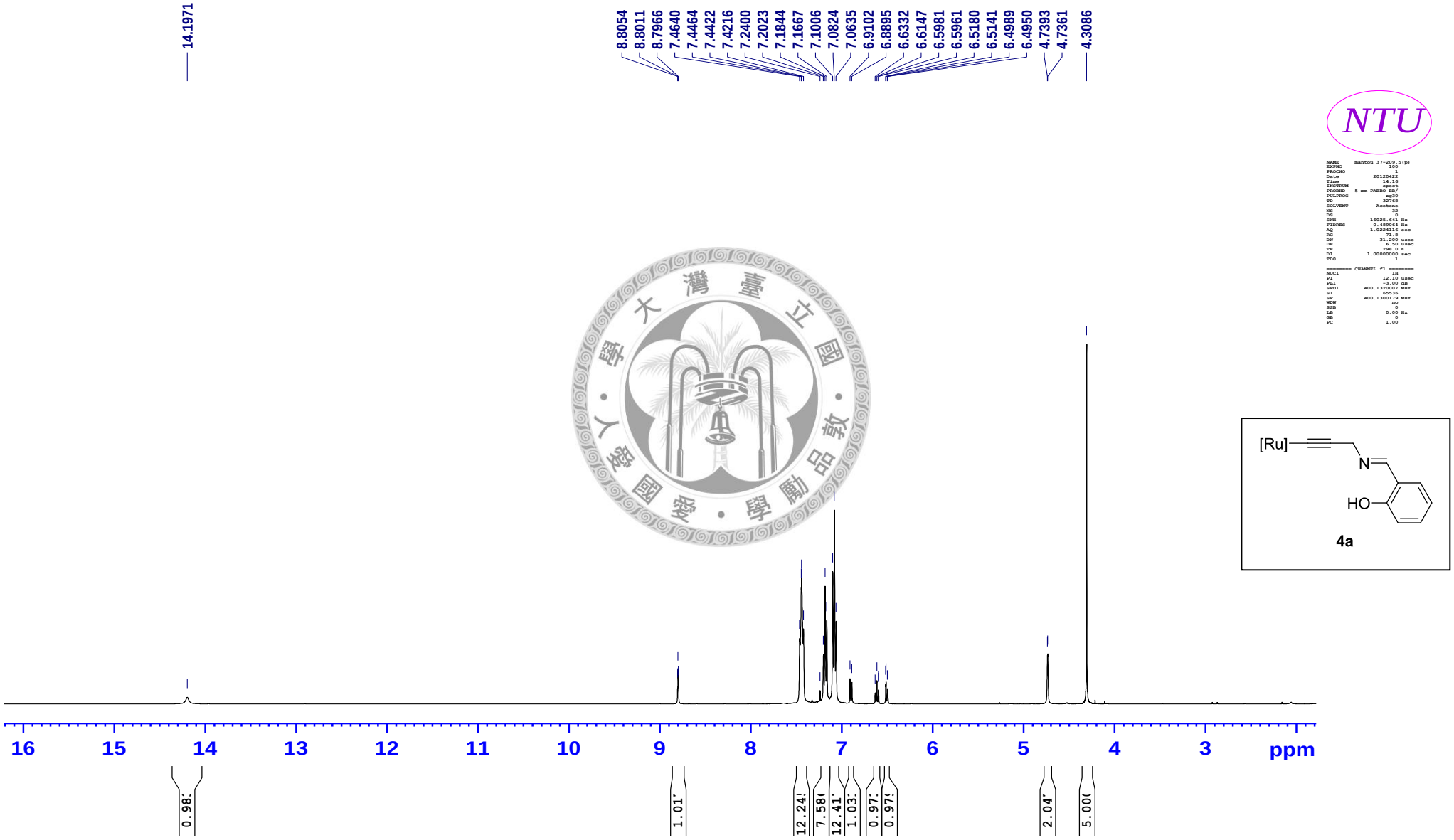


10a

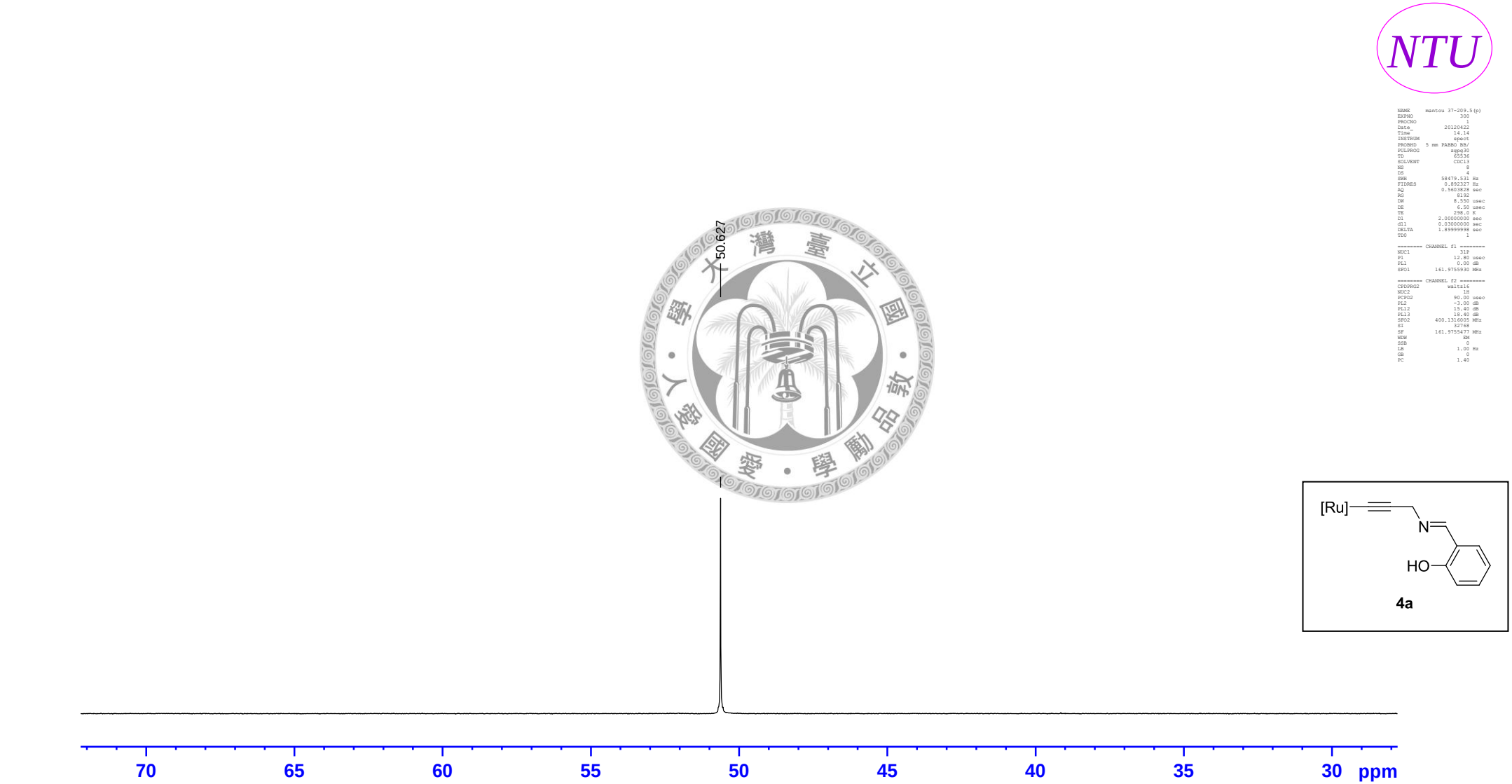
500MHz 13C 89-202.9 CDCl3



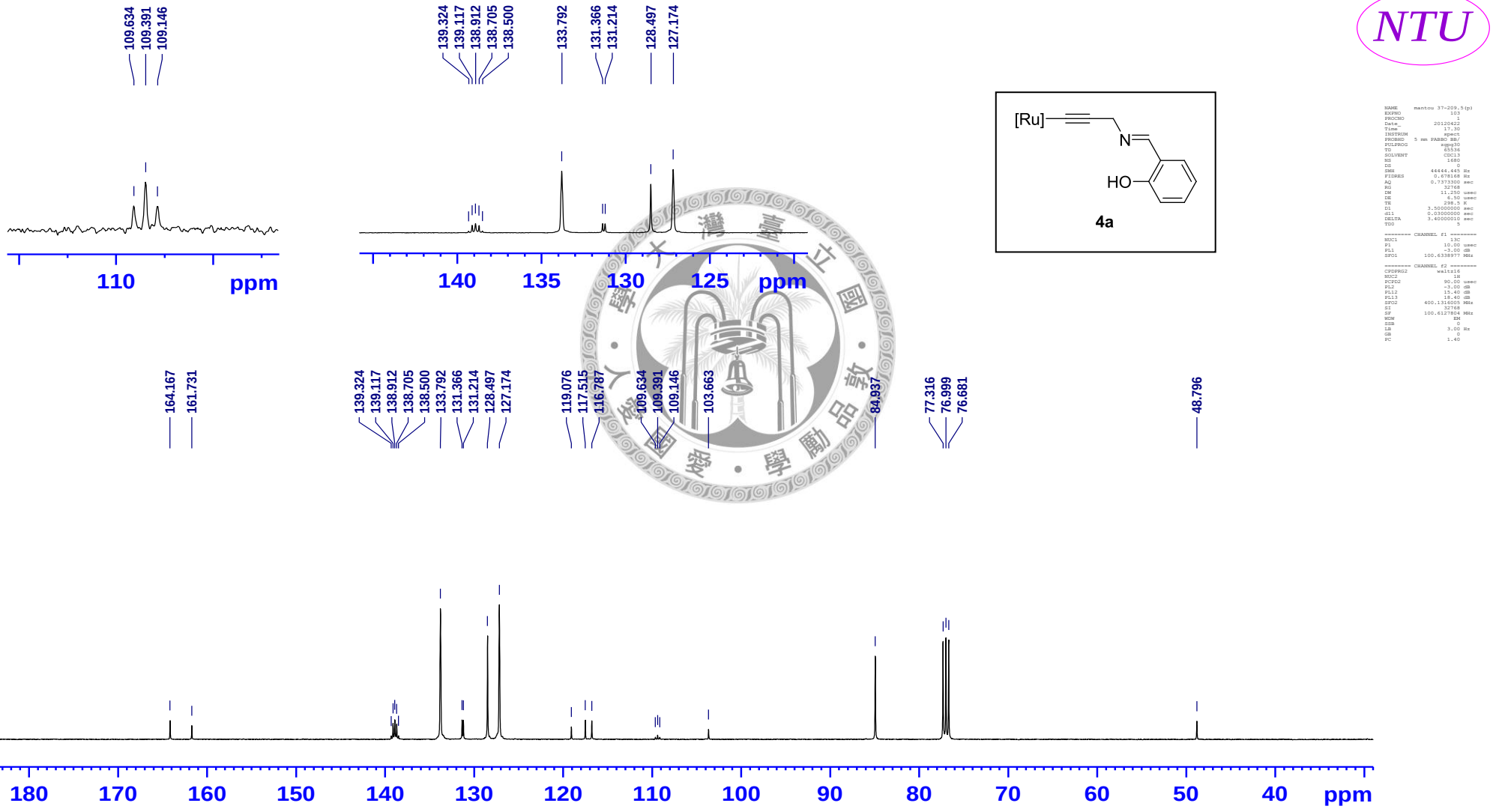
400MHz 1H 37-209.5(p) CDCl3



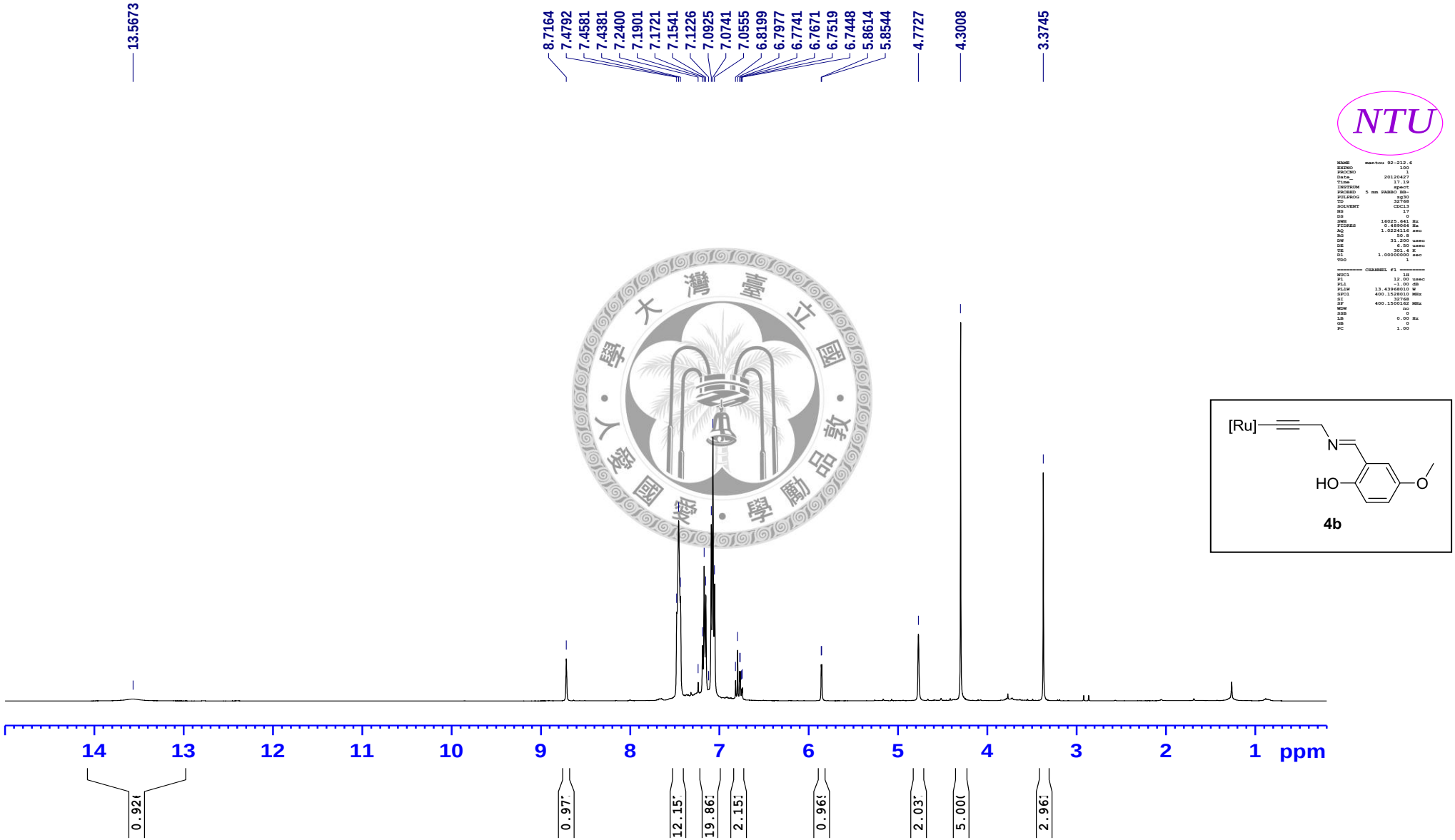
400MHz P31 37-209.5(p) CDCl3



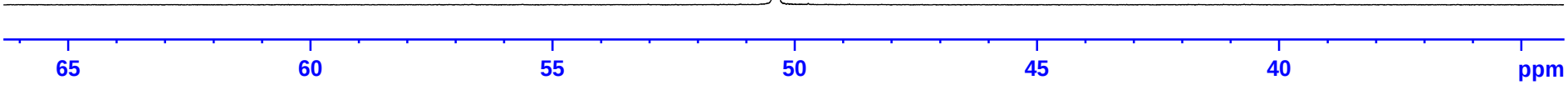
4a

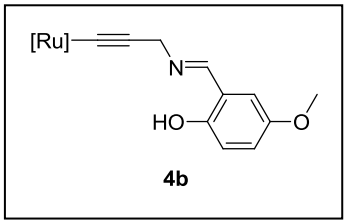

109.634
109.391
109.146
139.324
139.117
138.912
138.705
138.500
133.792
131.366
131.214
128.497
127.174
110
ppm
140
135
130
125
ppm
[Ru]
N
HO
4a
NTU
164.167
161.731
139.324
139.117
138.912
138.705
138.500
133.792
131.366
131.214
128.497
127.174
119.076
117.515
116.787
109.634
109.391
109.146
103.663
84.937
77.316
76.999
76.681
48.796
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

400MHz 1H 92-212.6 CDCl3

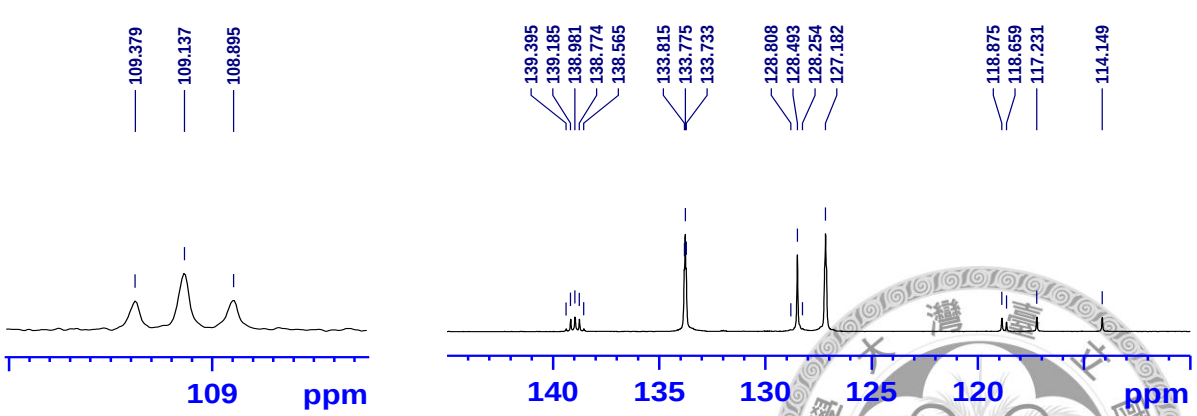


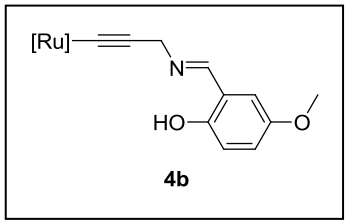
400MHz 31P 92-212.6 CDCl3

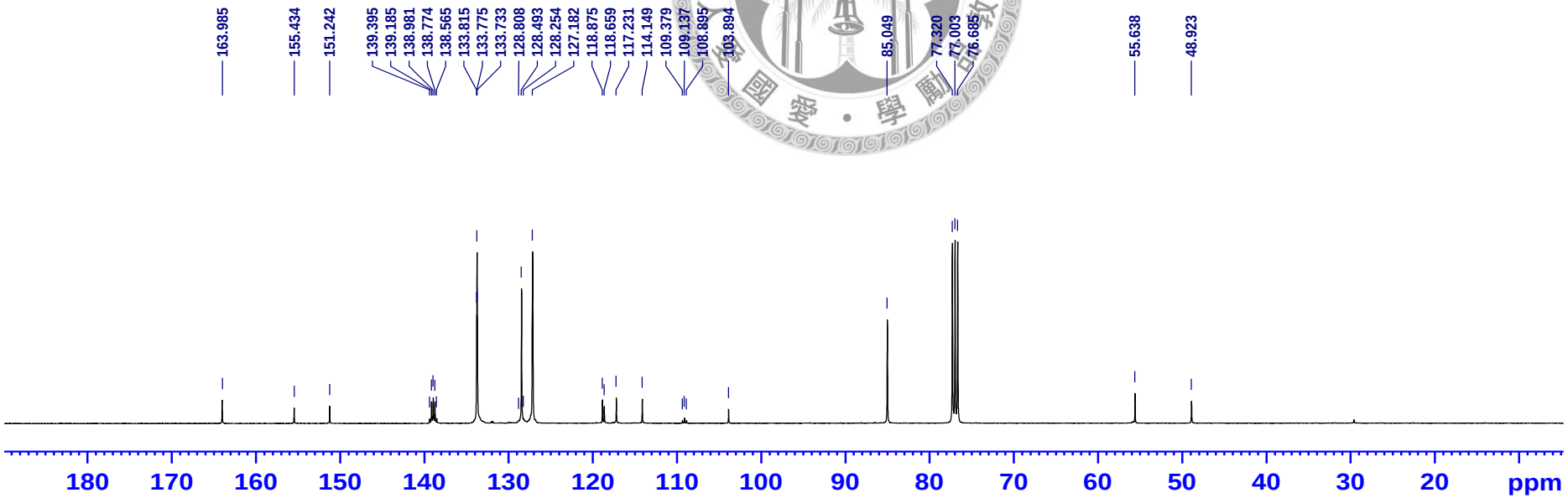




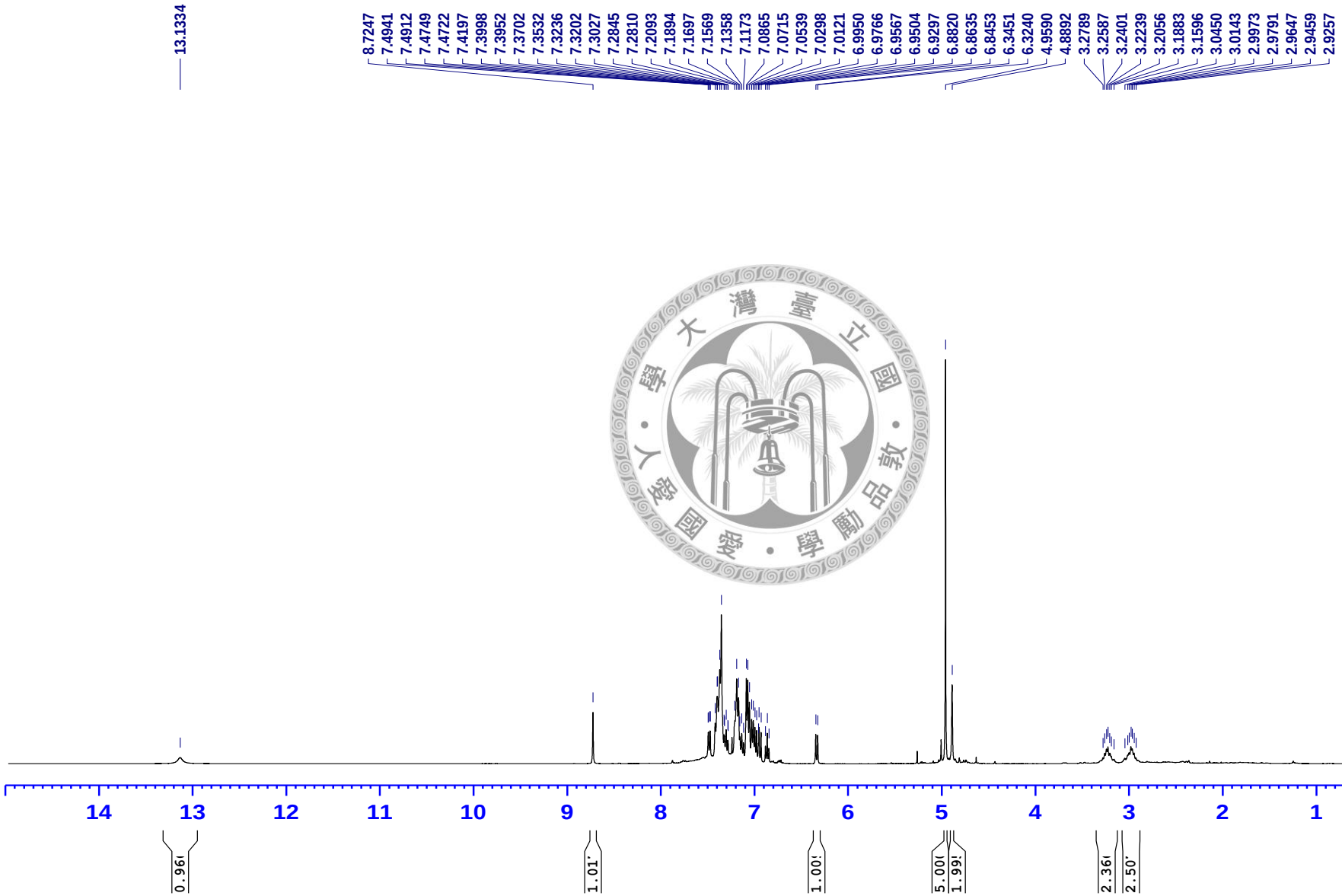
4b


109.379
109.137
108.895
139.395
139.185
138.981
138.774
138.565
133.815
133.775
133.733
128.808
128.493
128.254
127.182
118.875
118.659
117.231
114.149
109
ppm
140
135
130
125
120
ppm


[Ru]
N
HO
O
4b

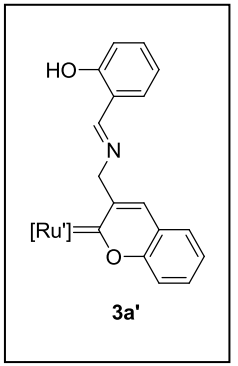

163.985
155.434
151.242
139.395
139.185
138.981
138.774
138.565
133.815
133.775
133.733
128.808
128.493
128.254
127.182
118.875
118.659
117.231
114.149
109.379
109.137
108.895
103.894
85.049
77.320
77.003
76.685
55.638
48.923
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

400MHz 1H 45-145 111029 CDCl3



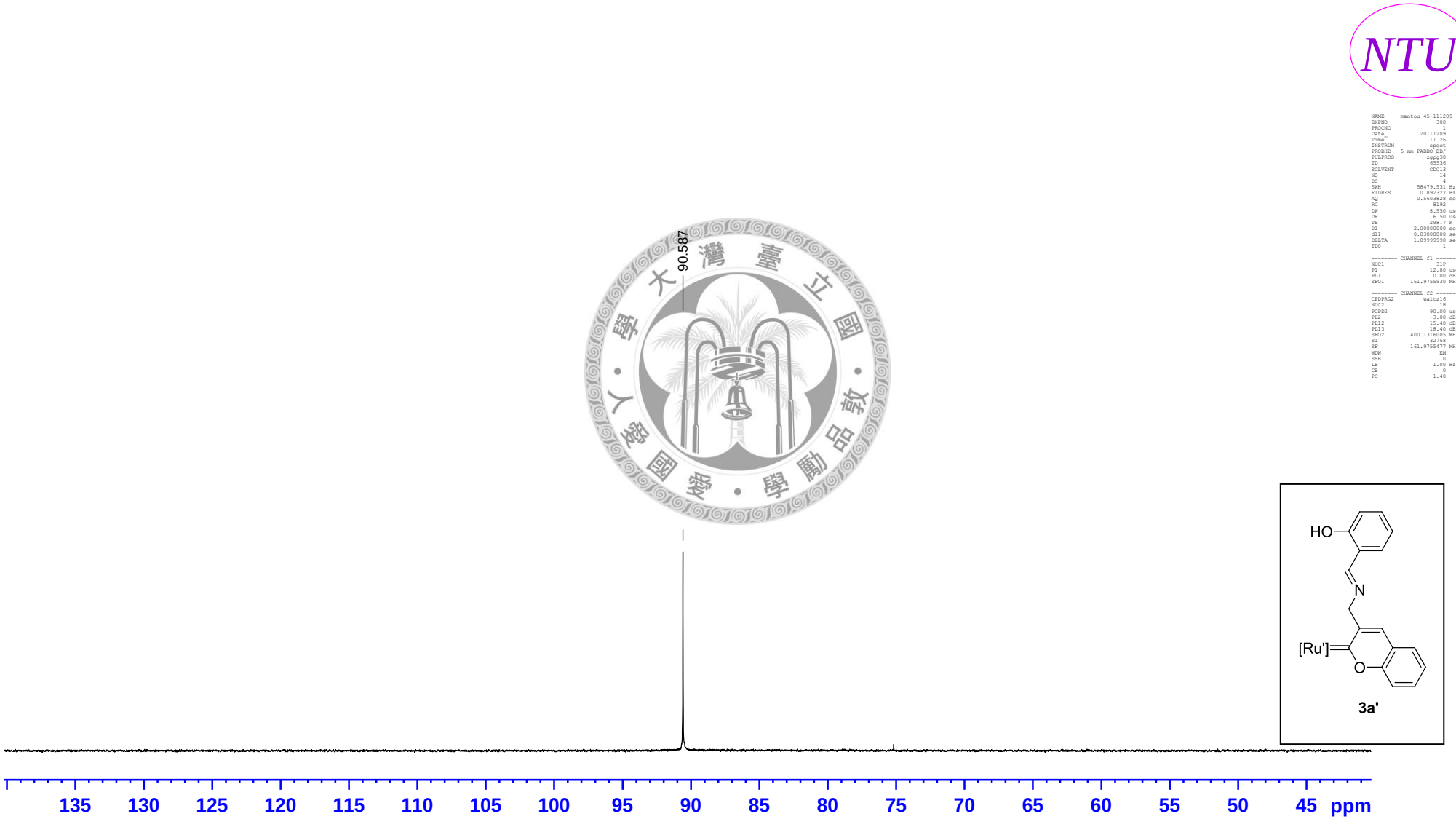
NTU

```
NAME        mantou 45-145 111029
EXPNO             100
PROCNO              1
Date_       20111029
Time              13.34
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zg30
TD                32768
SOLVENT         Acetone
NS                  40
DS                   0
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ             2.0447731 sec
RG                  71.8
DW               62.400 usec
DE                6.50 usec
TE              298.8 K
D1              1.00000000 sec
TD0                  1
======== CHANNEL f1 ========
NUC1                1H
P1                12.10 usec
PL1               -3.00 dB
SFO1        400.1320007 MHz
SI                 65536
SF          400.1300177 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00
```



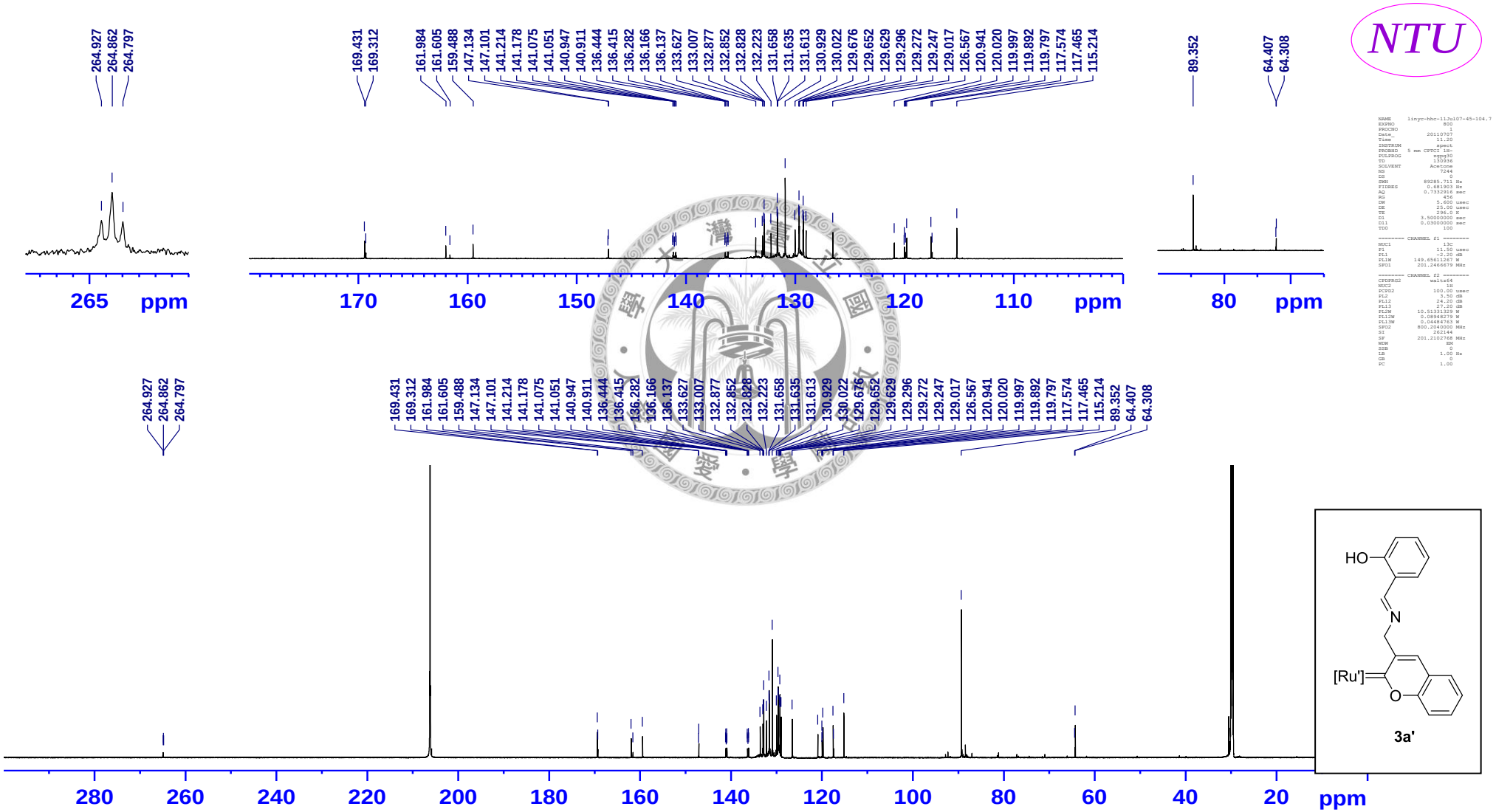
3a'

400MHz P31 45-111209 d-acetone

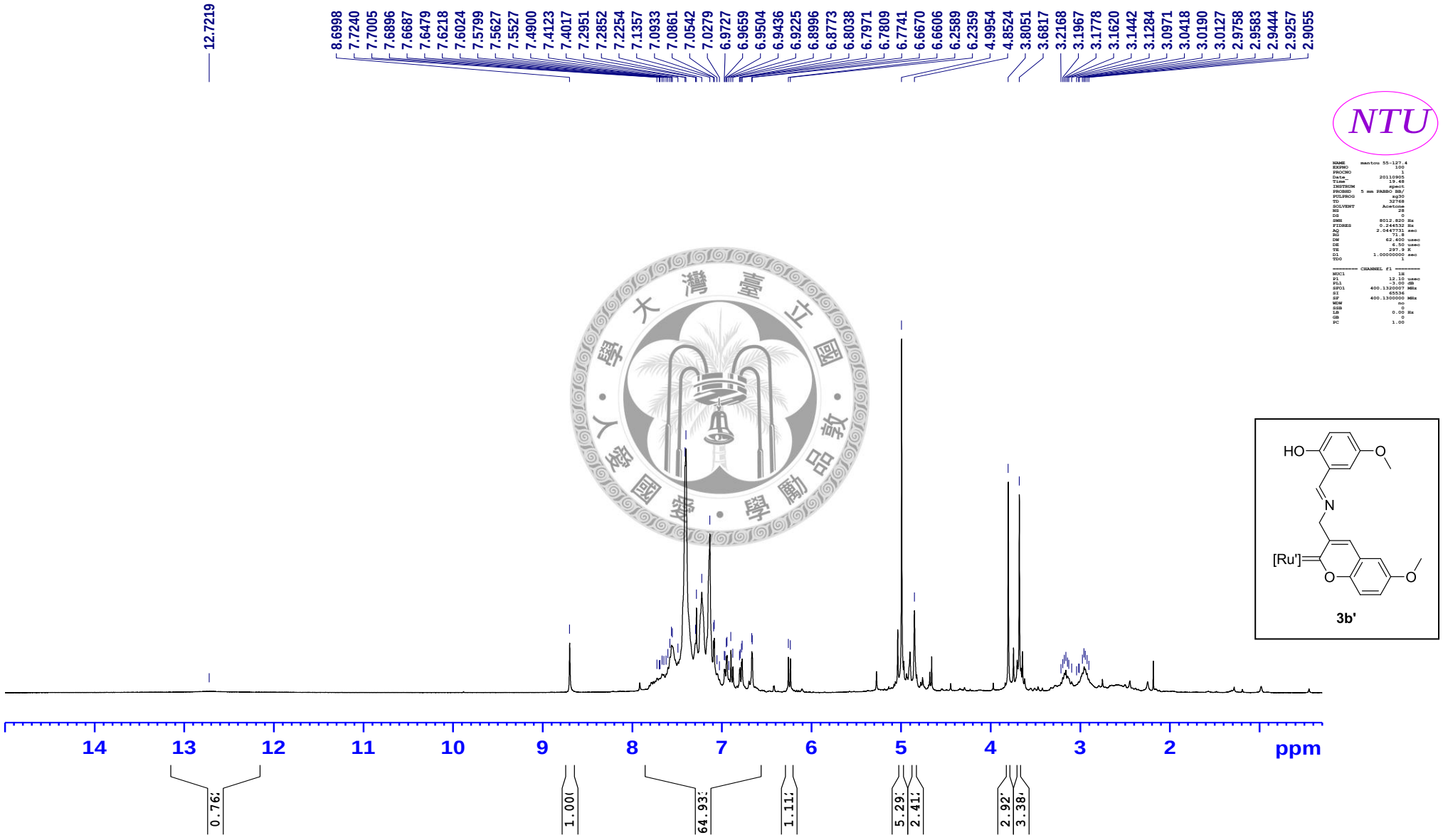


3a'

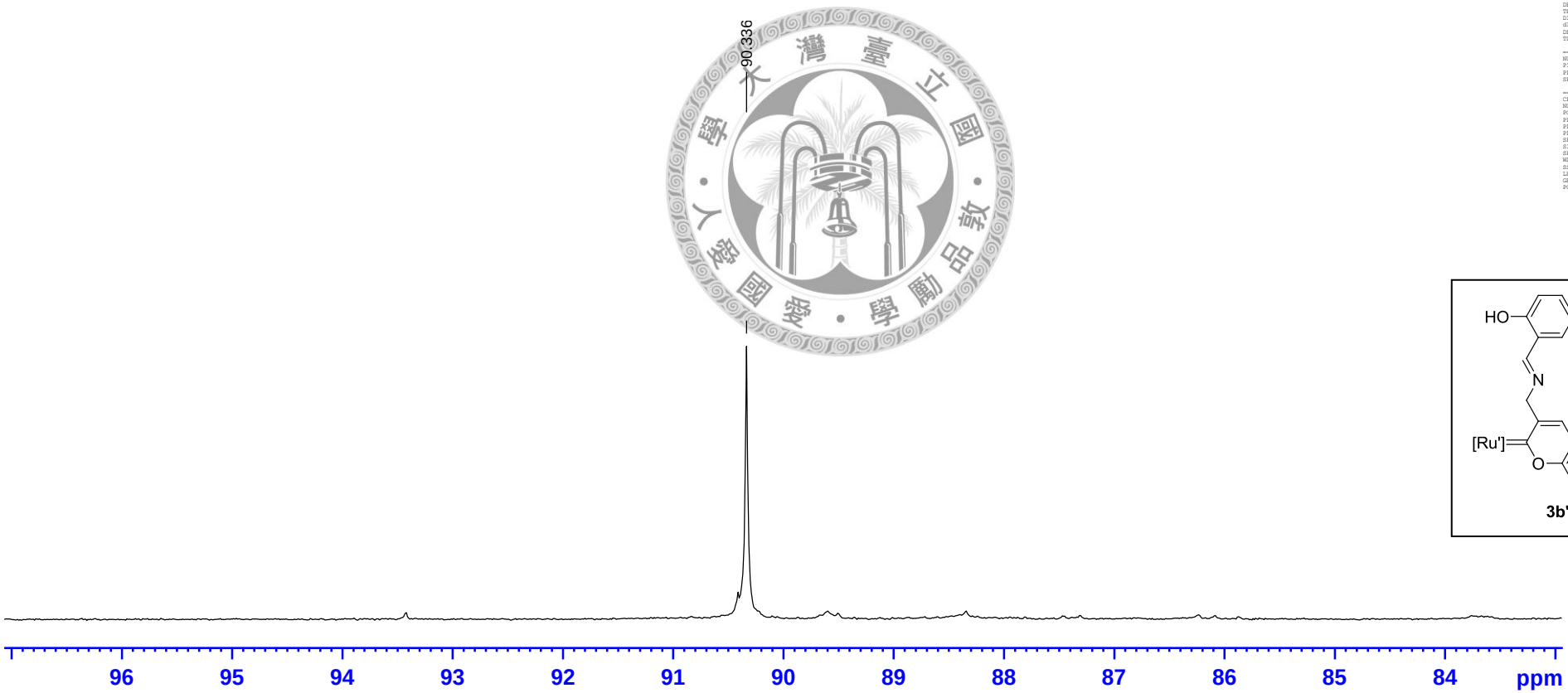
800MHz 13C 45-104.7 d-acetone



400MHz 1H 55-127.4 CDCl3



400MHz P31 55-127.3 CDCl3



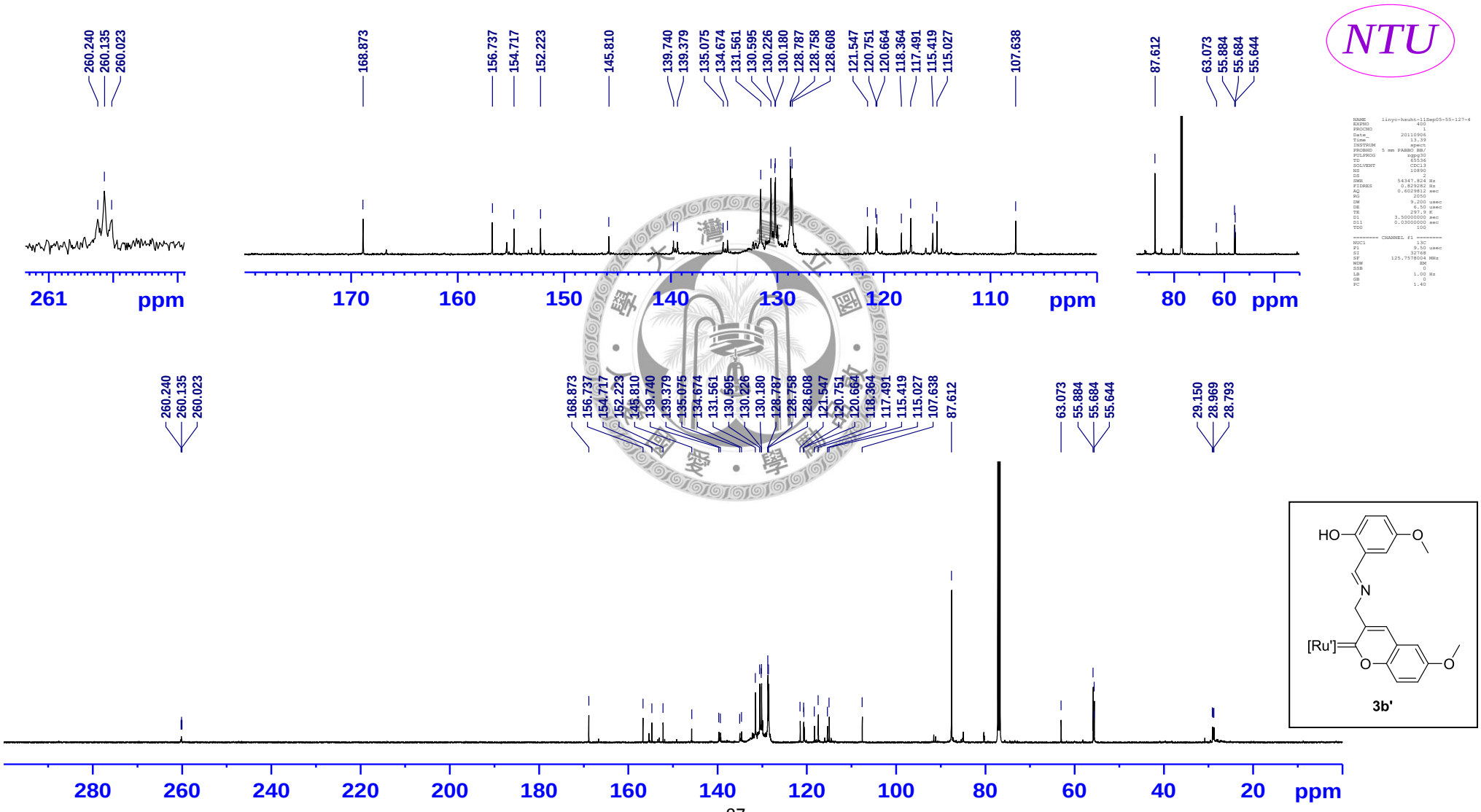
NAME mantou 55-127.3
EXPNO 300
PROCNO 1
Date_ 20110902
Time_ 16.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 4
SWH 58479.531 Hz
FIDRES 0.892327 Hz
AQ 0.5603828 sec
RG 8192
DW 8.550 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 12.80 usec
PL1 0.00 dB
SFO1 161.9755930 MHz

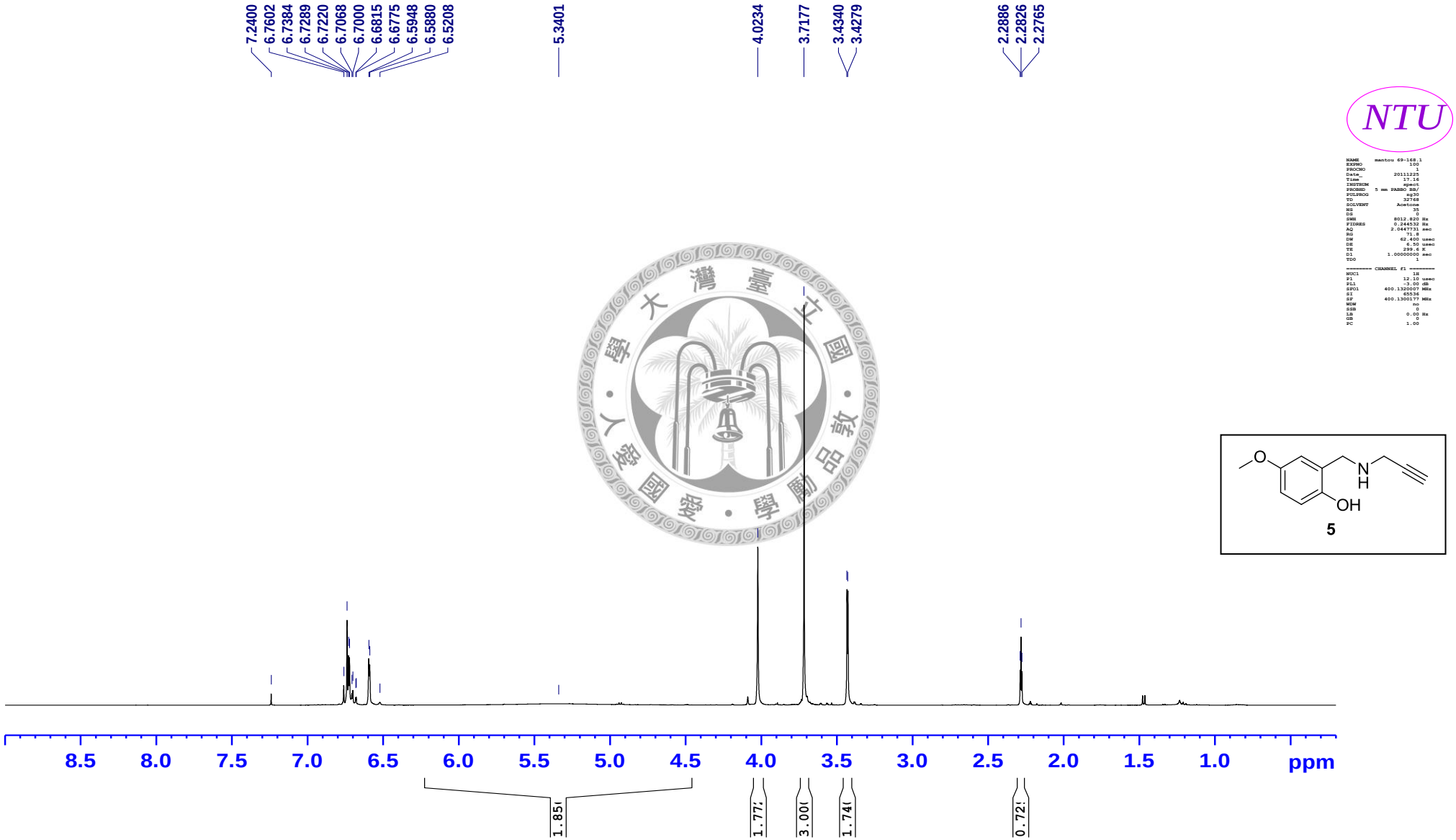
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.40 dB
PL13 18.40 dB
SFO2 400.1316005 MHz
SI 32768
SF 161.9755477 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3b'

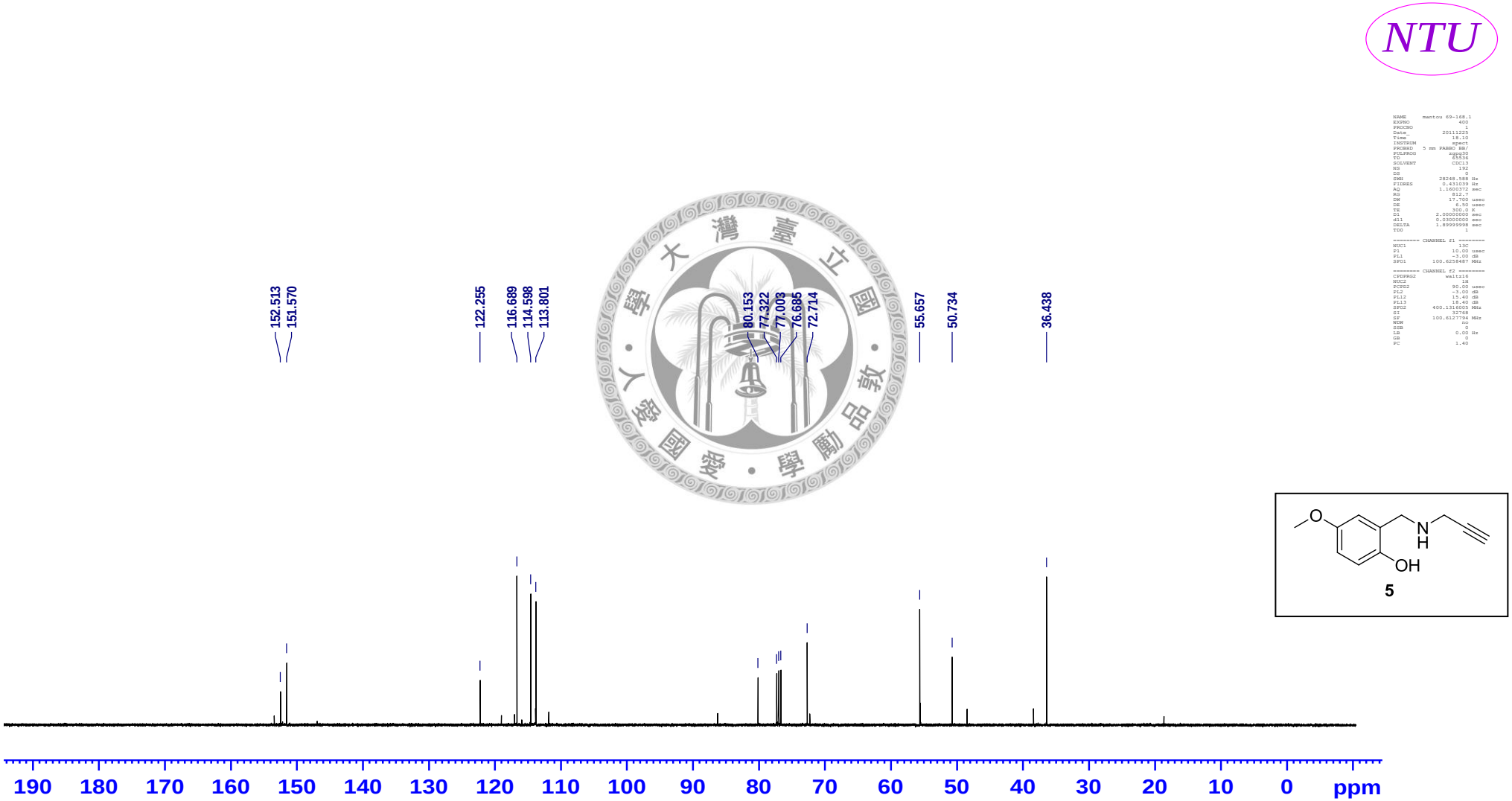
500\MHz 13C 55-127.4 CDCl3



400MHz 1H 69-168.1 CDCl3

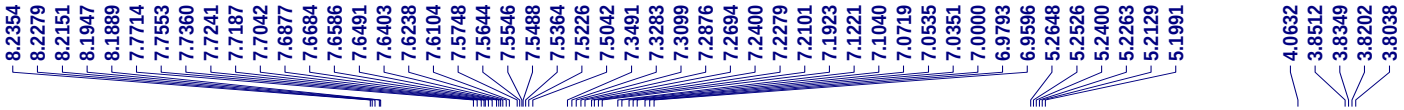


400MHz 13C 69-168.1 CDCl3

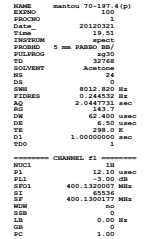


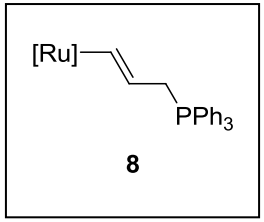
5

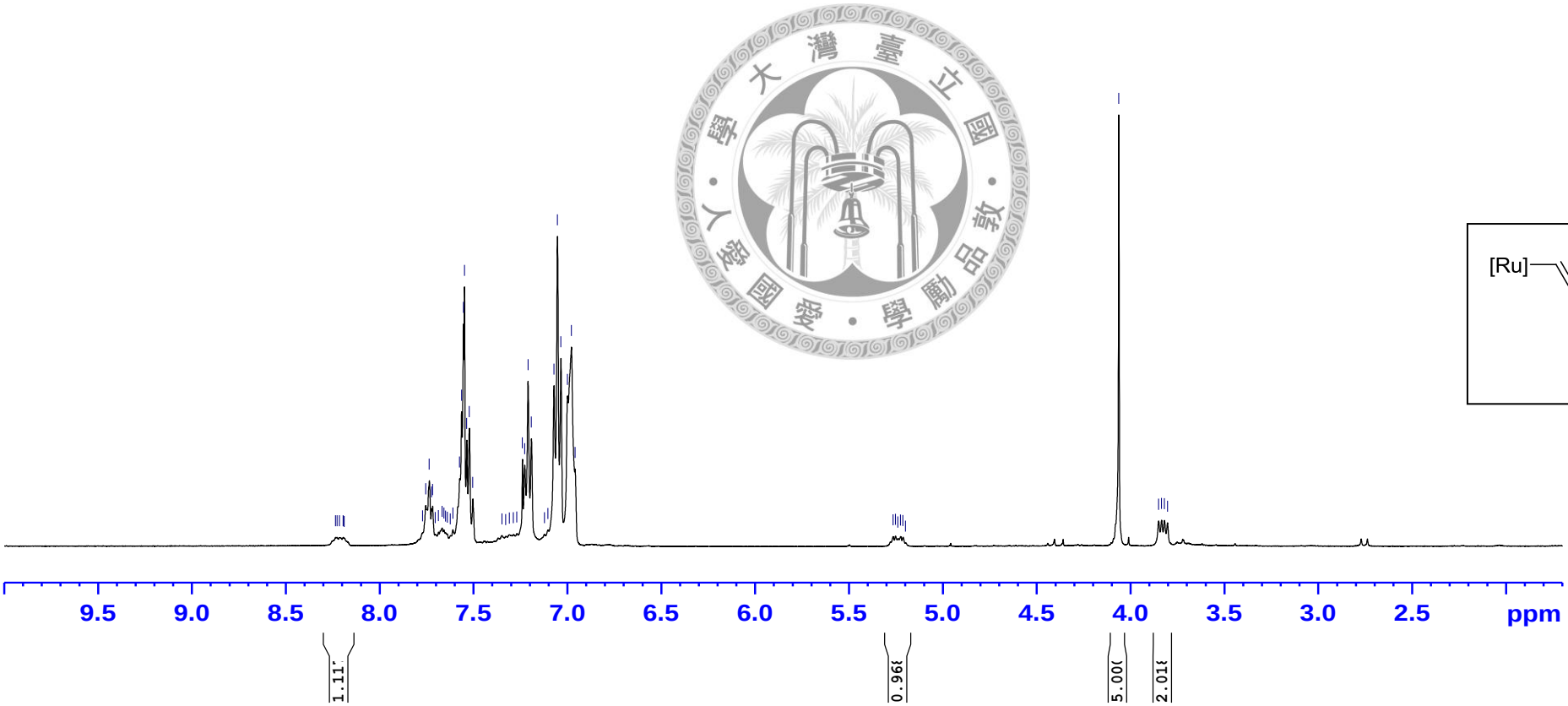
400MHz 1H 70-197.4(p) CDCl3



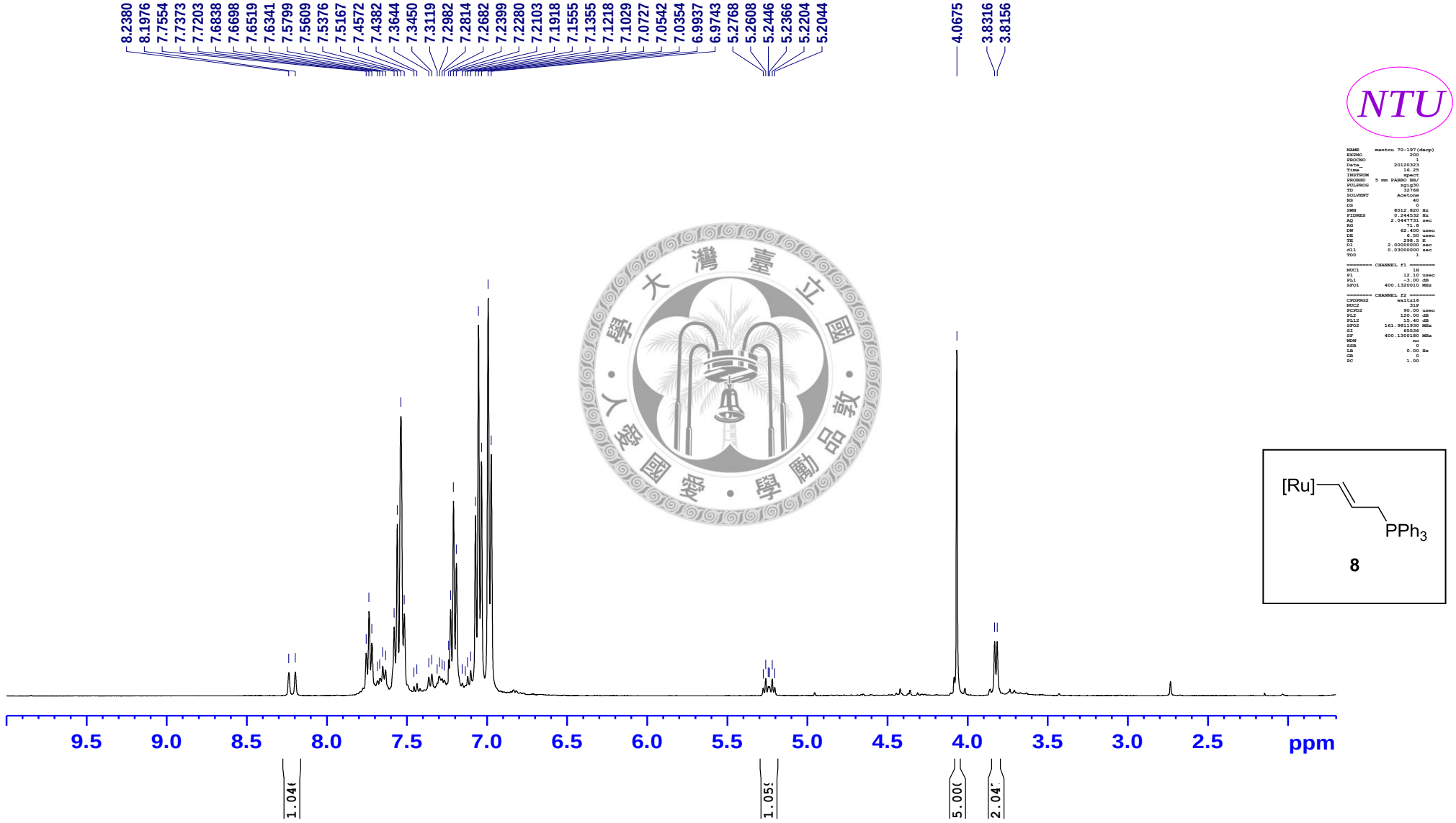
NTU



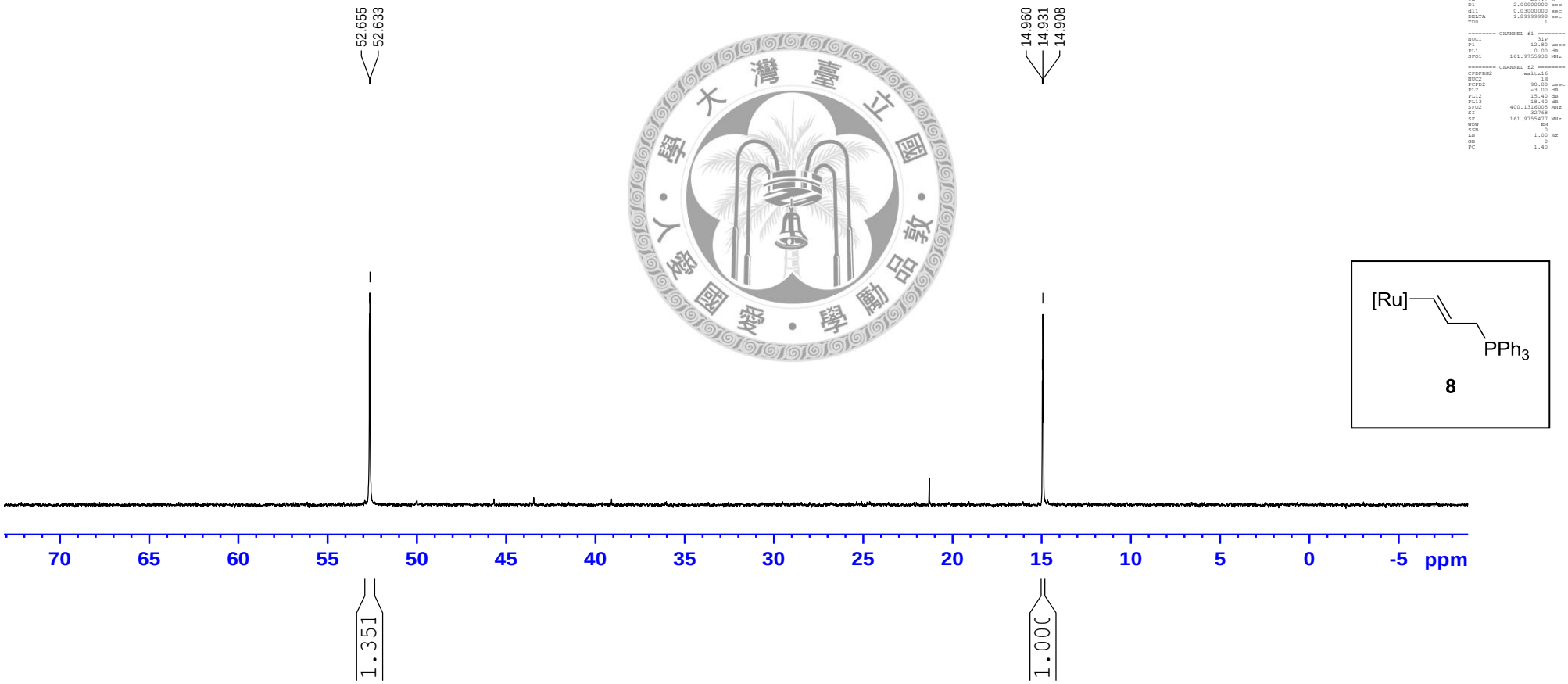




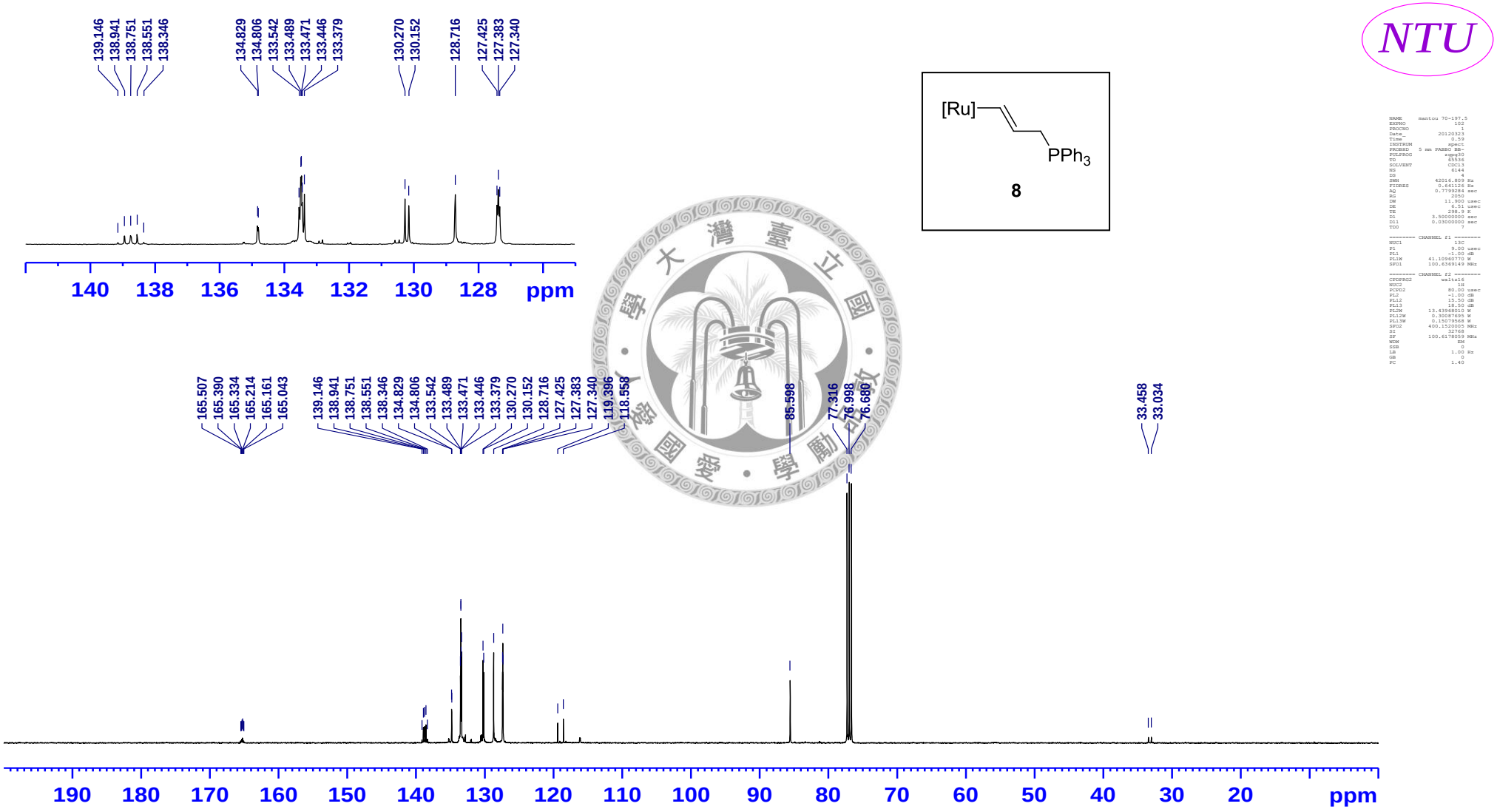
400MHz 1H 70-197(decp) (200) CDCl3



400MHz P31 70-197.4(p) CDCl3



8



8

NTU

Elemental Composition

File Edit View Process Help

Single Mass Analysis

Tolerance = 4.0 PPM / DBE: min = -1.5, max = 100.0

Selected filters: None

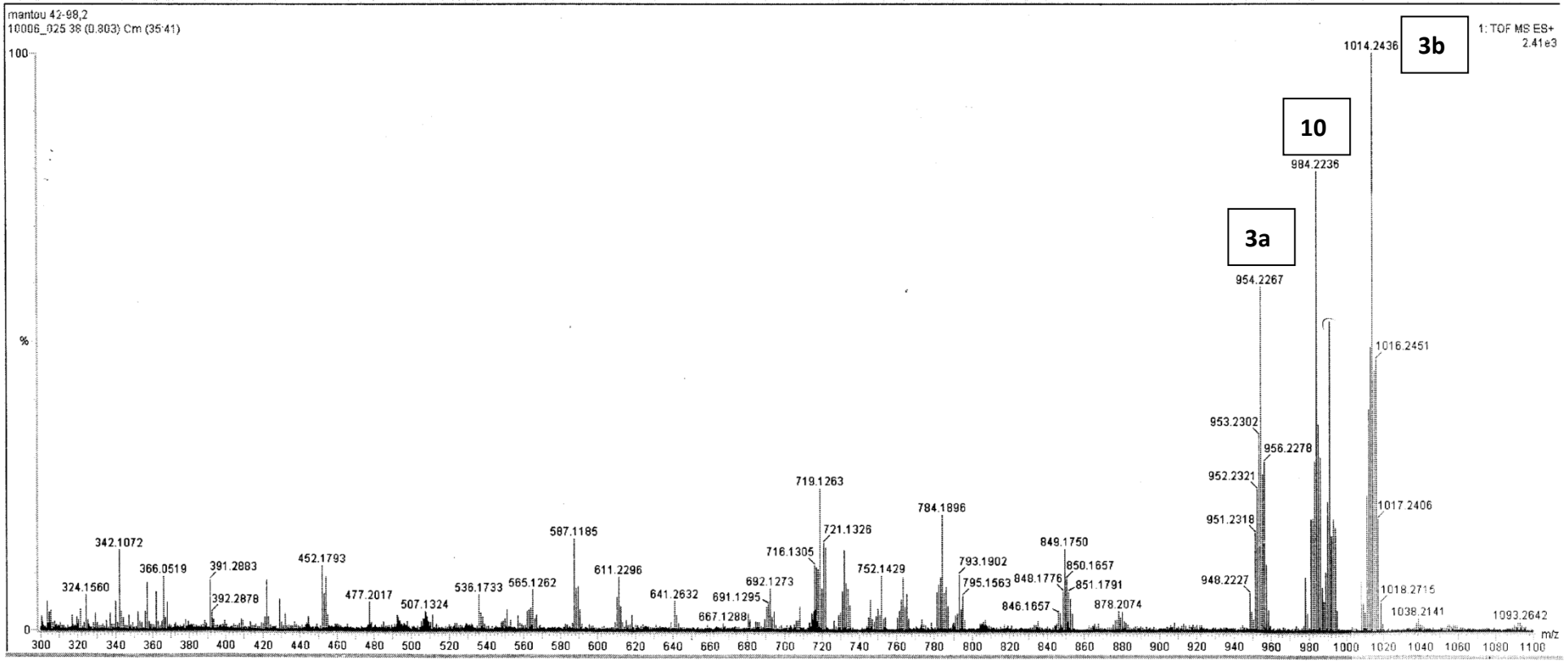
Monoisotopic Mass, Even Electron Ions

1131 formula(e) evaluated with 4 results within limits (up to 3 best isotopic matches for each mass)

Elements Used:

C: 3-80 H: 0-125 N: 0-2 O: 0-5 P: 0-2 102Ru: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	C	H	N	O	P	102Ru
1014.2436	1014.2415	2.1	2.1	36.5	C60 H52 N O4 P2 102Ru	27.2	60	52	1	4	2	1
	1014.2439	-0.3	-0.3	45.5	C67 H47 N O P 102Ru	42.4	67	47	1	1	1	1
	1014.2409	2.7	2.7	54.5	C71 H37 N O5 P	257.1	71	37	1	5	1	



Elemental Composition

File Edit View Process Help

Single Mass Analysis

Tolerance = 4.0 PPM / DBE: min = -1.5, max = 60.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

563 formula(e) evaluated with 3 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 50-100 H: 1-100 N: 1-10 O: 1-10 P: 2-2 102Ru: 1-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	C	H	N	O	P	102Ru
1004.2366	1004.2360	0.6	0.6	39.5	C62 H50 N O2 P2 102Ru	178.1	62	50	1	2	2	1
	1004.2379	-1.3	-1.3	26.5	C50 H54 N3 O9 P2 102Ru	87.0	50	54	3	9	2	1
	1004.2392	-2.6	-2.6	31.5	C51 H50 N7 O5 P2 102Ru	93.3	51	50	7	5	2	1