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碩士論文

Department of Chemistry

College of Science

National Taiwan University

Master Thesis

鈎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



Hsin-Tzu Hsu

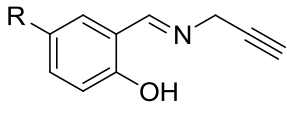
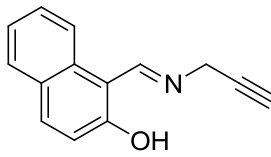
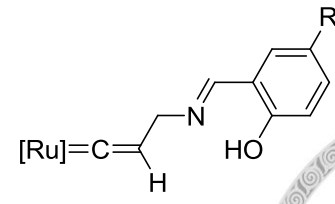
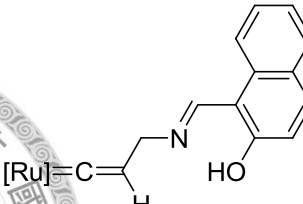
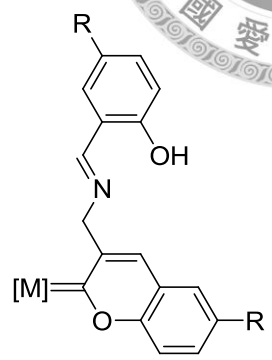
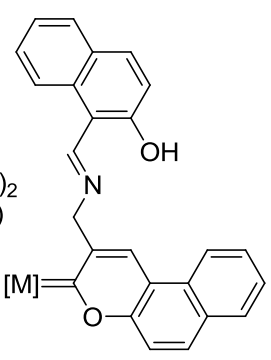
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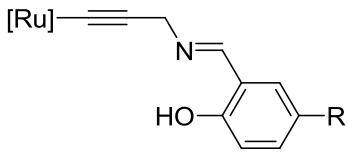
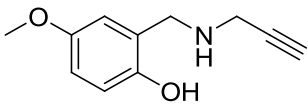
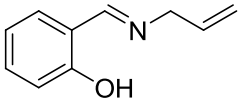
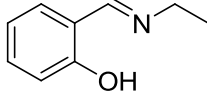
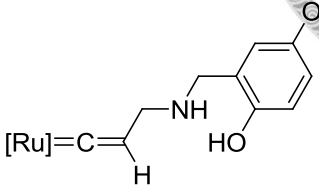
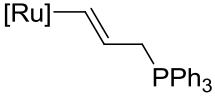
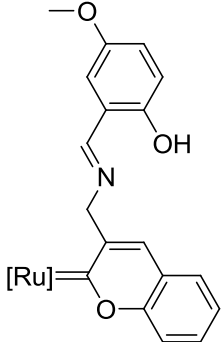
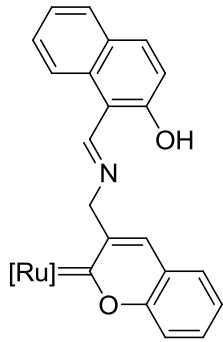
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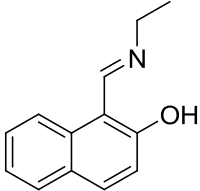
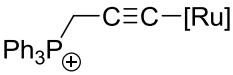
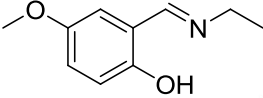
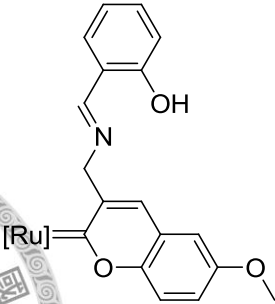
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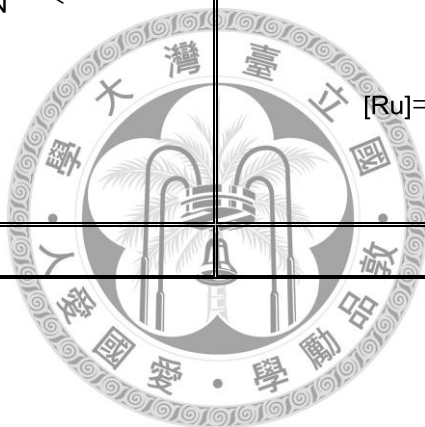
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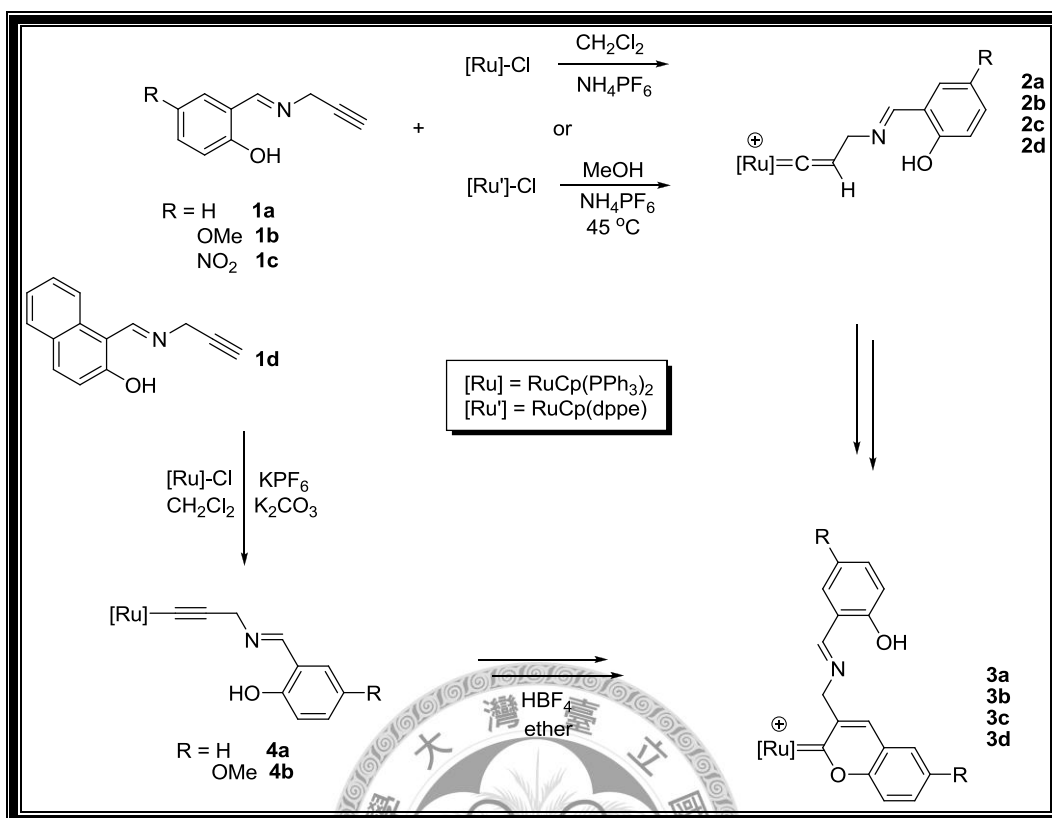
Structures and Numbering of Complexes

 <p>R = H 1a OMe 1b NO₂ 1c</p>	
1a – 1c	1d
 <p>R = H 2a OMe 2b NO₂ 2c</p>	
2a – 2c	2d
<p>[M] = RuCp(PPh₃)₂ RuCp(dppe)</p> <p>R = H 3a, 3a' OMe 3b, 3b' NO₂ 3c, 3c'</p> 	<p>[M] = RuCp(PPh₃)₂ RuCp(dppe)</p> 
3a – 3c, 3a' – 3c'	3d, 3d'

 <p>[Ru]—C≡C—CH₂—N=CH—C₆H₃(OH)—R</p> <p>R = H 4a OMe 4b</p>	
4a, 4b	5b
	
6a	7a
	
8	9
	

10	11
	
12	13
	
14	15





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(PPh₃)₂) in the presence of NH₄PF₆ in CH₂Cl₂ 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 C α and C β 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鈦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、 ^1H 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(2H-chromene)”分子單元的配基，分別在”色烯(2H-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, 鈦, 含氧碳烯基, 環化

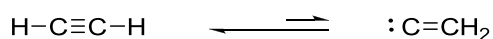
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Introduction

Metal Vinylidene Complexes

Vinylidene (:C=CH₂) 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).

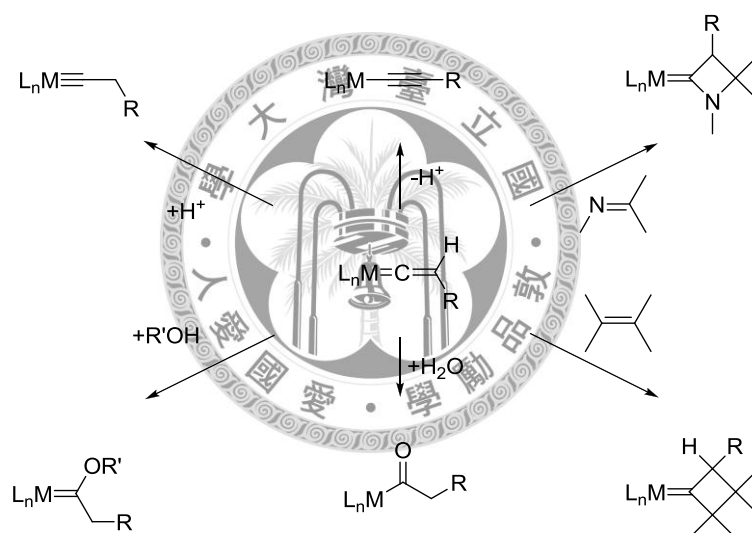


While in the free state the lifetime of the vinylidene is extremely short (~10⁻¹⁰ s), stabilization of organic vinylidene species via coordination to a metal center is now a well-known feature which has been encountered with many transition metals (Mo, W, Fe, Ru, Os...etc).¹ Activation of terminal alkynes 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)L₂] [L₂ = 2 × PPh₃ 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. PPh₃, dppe, which offer

steric protection to C α 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

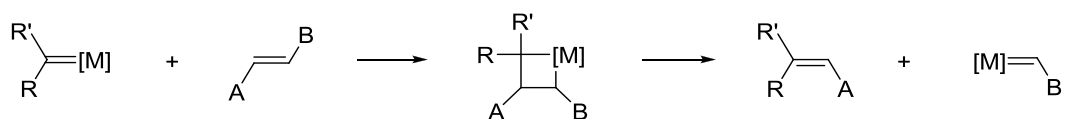
The reactivity of metal carbene complexes have been extensively investigated and a number of general and useful transformations have been reported.⁵ Many transition metal carbene complexes readily react with alkynes, generally resulting in the formation of vinylcarbene complex (Scheme 1-2).

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 transition metal carbene complex to form a metallacyclobutane intermediate. Subsequent retro [2+2] cyclization leads to a new alkene and a new carbene complex (Scheme 1-3).⁶

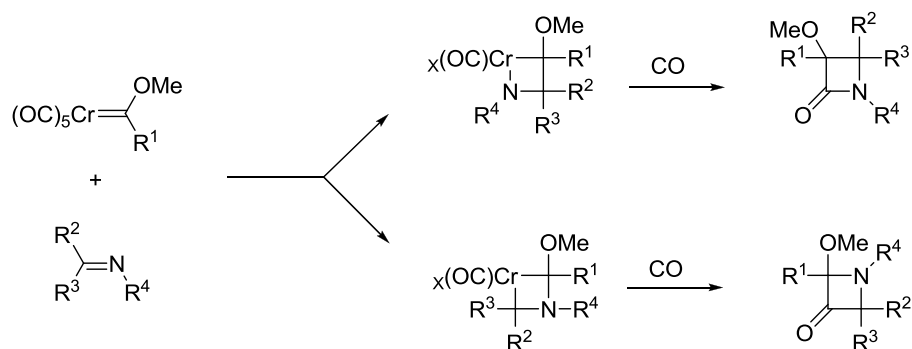
Scheme 1-3



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

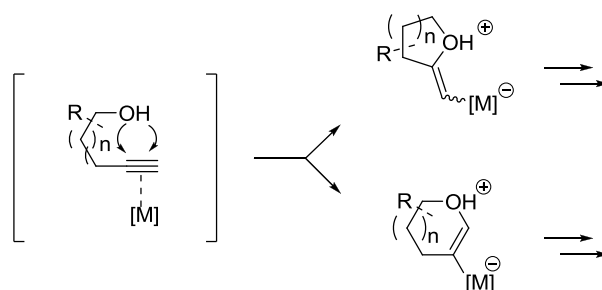
et al. proposed that on photolysis of $(\text{CO})_5\text{M}-[\text{C}(\text{R})\text{R}']$ in the presence of imines, β -lactams are formed.⁸

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

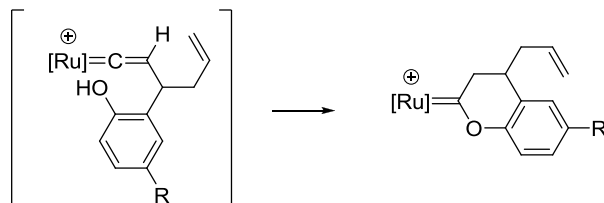
Scheme 1-5



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

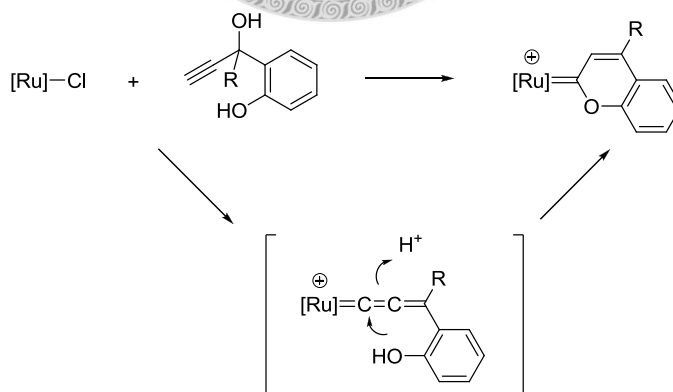
complexes. Examples are shown in Scheme 1-6 and Scheme 1-7 respectively.

Scheme 1-6



Nishibayashi and his co-workers reported many reactions of the diruthenium allenylidene complexes with a variety of nucleophiles, which attack either C α or C γ 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(PPh₃)₂) to obtain cyclic alkoxy carbene complex via a ruthenium allenylidene complex, has been observed in our lab.

Scheme 1-7



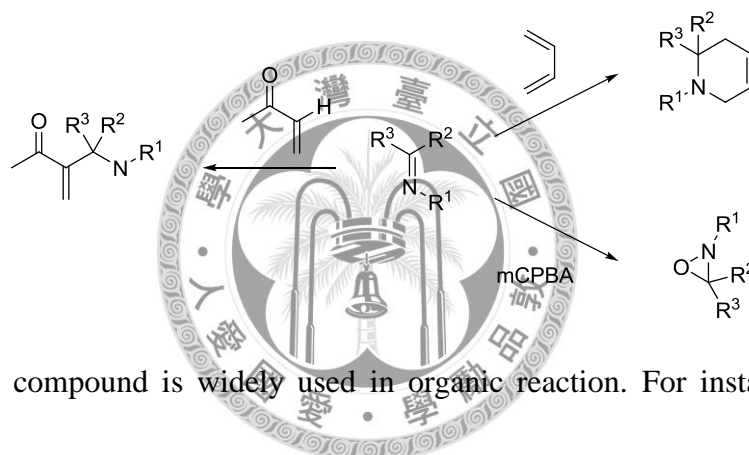
Imine Chemistry

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.

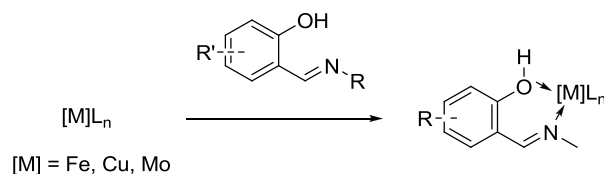
As to the reactivity of imine, Scheme 1-8 shows many reactions of the imine functional group. The aza-Baylis-Hilman reaction¹² is analogous to the reaction of aldehyde and ketone and the aza Diels-Alder reaction¹³ generates tetrahydropyridine ring. Treatment of imine with mCPBA could further give oxaziridine.¹⁴

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

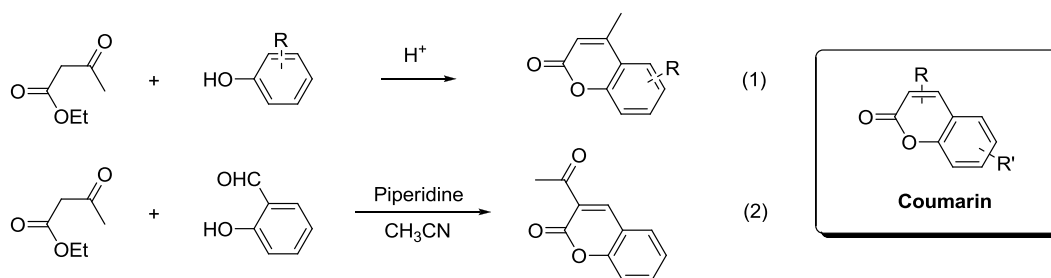


We report the reaction of the Schiff base **1** tethering a propargyl group with Cp(PPh₃)₂RuCl. Unlike a regular Schiff base, such a Schiff base with a propargyl group displays distinctive reactivity.

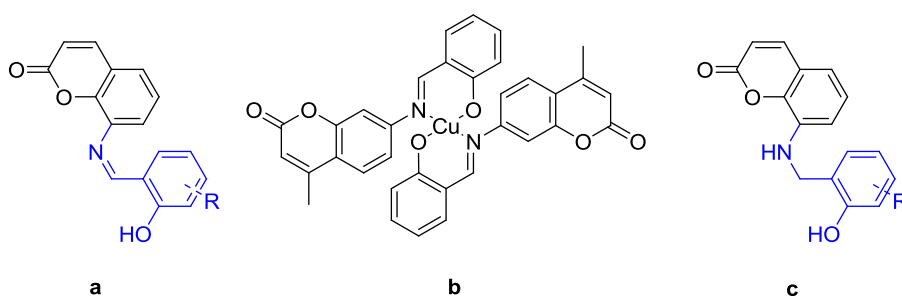
Coumarin

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 condensation²⁰ (see Scheme 1-9, eq.1) or Raju *et al.* have done²¹ (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.



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

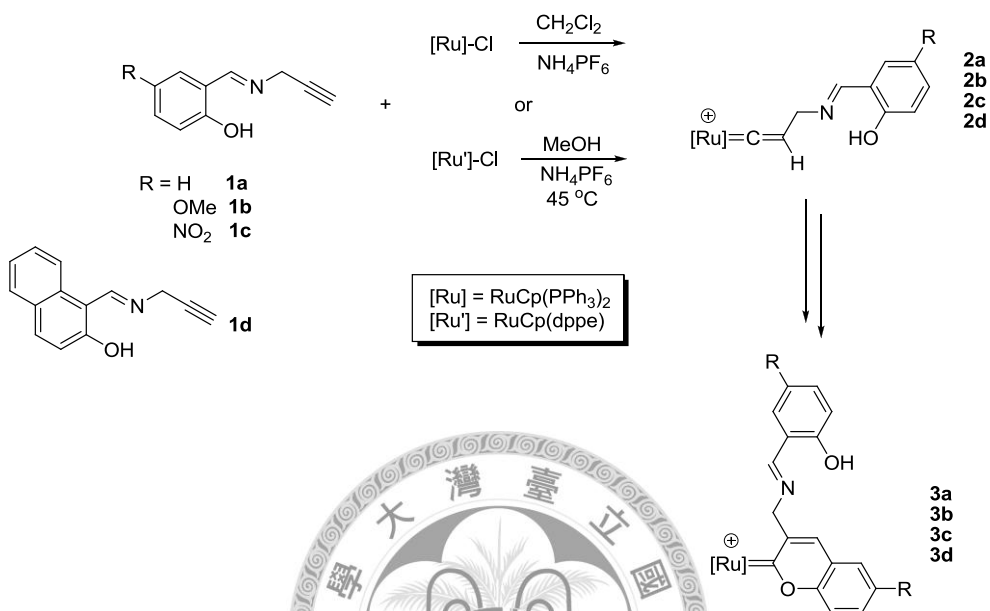
be a precursor for useful chemical, has not been reported before. In our preliminary trial, oxygenation has been attempted, however, no cleavage of the organic ligand from the ruthenium metal center is observed.



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 ¹H 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(PPh₃)₂Ru) and NH₄PF₆ in CH₂Cl₂ overnight afforded the carbene complex **3a** as the major product and the vinylidene complex **2a** as a minor product. The two singlet ³¹P 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 ³¹P NMR spectrum. Nevertheless, the intensity of these ³¹P 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 CH₂Cl₂ 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.

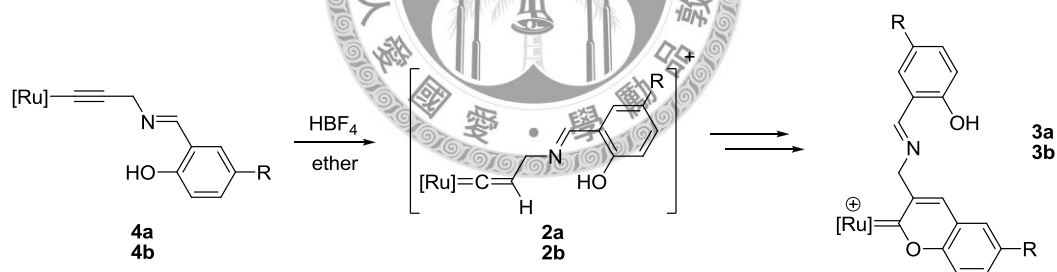
Formation of **3a** most likely proceeds through the vinylidene complex **2a**. Spectroscopic data, such as ¹H and ³¹P NMR data, of complex **2a** in the reaction mixture could be obtained. However, attempts to isolate **2a** failed. Treatments of **1b**, and **1c** separately with [Ru]-Cl similarly 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 °C 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/CH₂Cl₂. 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 resorcinol with alkenylcarbyne complexes.³⁶

Since we expect the formation of carbene complexes **3a** – **3d** from the vinylidene 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 C β 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 carbene 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 K₂CO₃ as a base source, methanol as a solvent and NH₄PF₆ as a salt in the beginning of the reaction. [Ru]-NH₃⁺ becomes the major product because deprotonation takes place in the cationic ammonium NH₄⁺ salt to give NH₃ thus reacting with [Ru]-Cl to yield the observed product. When NH₄PF₆ is replaced by KPF₆, 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 K₂CO₃ to the system with KPF₆ in CH₂Cl₂ 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 ^1H NMR spectrum of **4b** shows only one methoxy resonance instead of two methoxy peaks in the ^1H NMR spectrum of **3b**.

Scheme 2-3

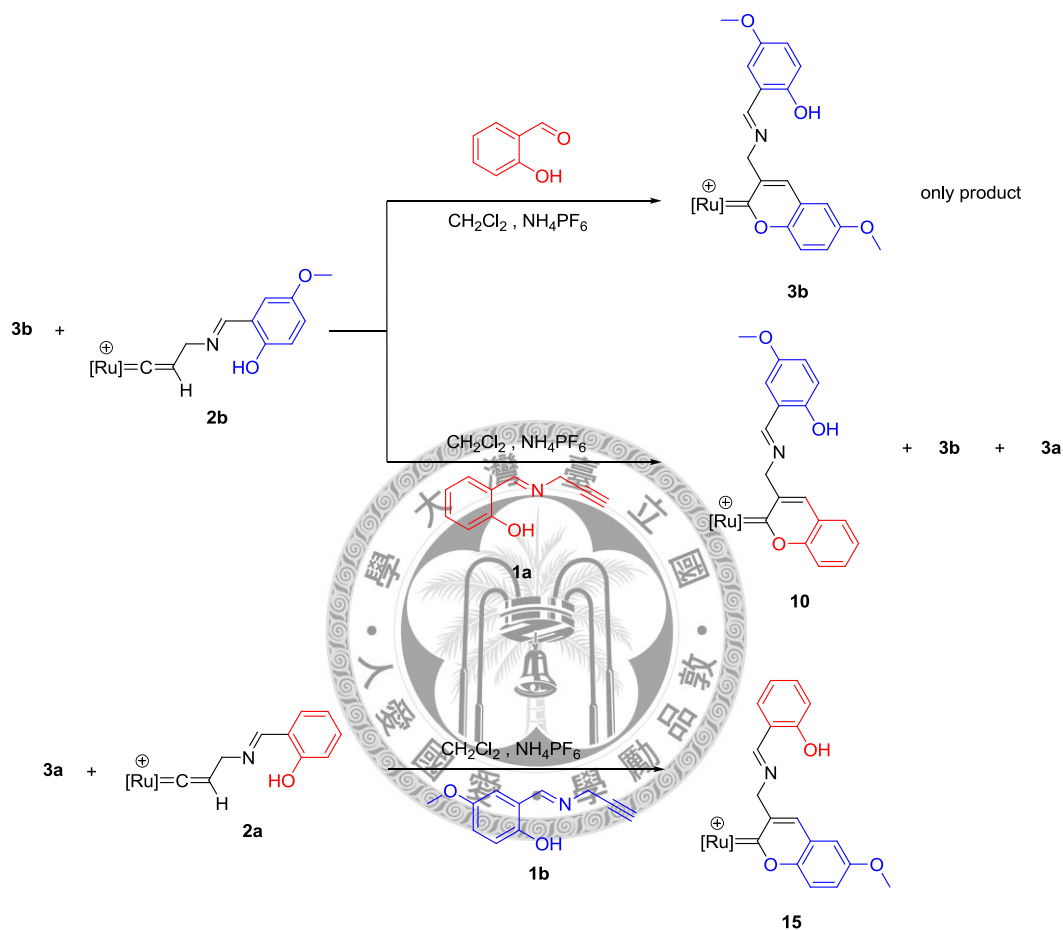


Protonation of complexes **4a** and **4b** is anticipated to form the corresponding vinylidene complexes **2a** and **2b**. However, as shown in Scheme 2-3, carbene complexes **3a** and **3b** are again isolated as the final product. Therefore, it is clear that formation of the vinylidene complex is 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 C α and C β of the vinylidene ligand of **2** to yield a substituted *2H*-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

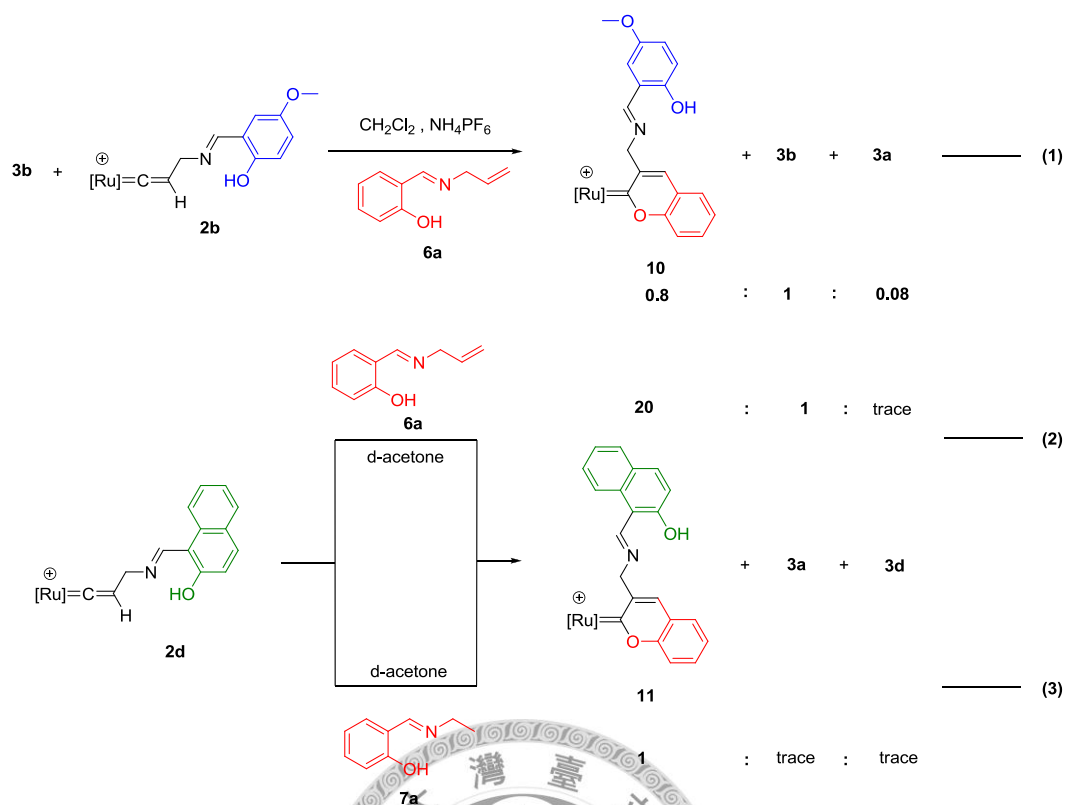


As mentioned before, the imine group should play a decisive role in the addition reaction to the vinylidene complexes **2** to form of carbene complexes **3**. As there are two possible imine sources exist in our reaction system i.e. the organic imine compounds **1a** – **1d** and the organometallic 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 group⁴ 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 ³¹P NMR spectrum and three complexes are inseparable. Therefore, simple ¹H 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.

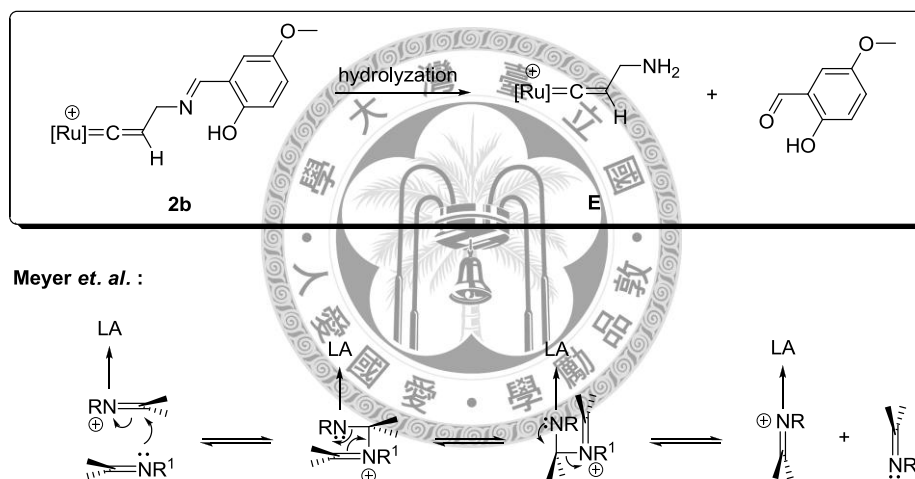
Scheme 2-5



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

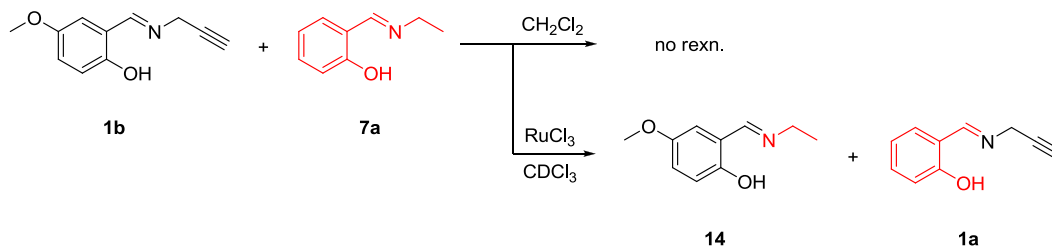
a result, complex **E** is believed to be very unstable. Therefore, the pathway via hydrolysis for the formation of complex **2a** is considered not feasible. On the other hand, Meyer *et. al.* have discovered that imine metathesis takes place in the presence of Lewis acid with the proposed mechanism 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



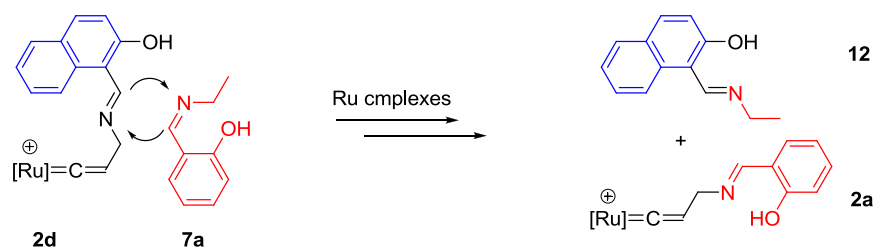
Interestingly, as shown in Scheme 2-7, exchange reaction between two organic imine compounds **1b** and **7a** in the absence of Lewis acid is not observed in CH_2Cl_2 . But, the same exchange reaction in the presence of RuCl_3 in CDCl_3 gives new imine compounds **14** and **1a** in 6% conversion overnight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

Scheme 2-7



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 ^1H signal at δ 3.65 and triplet ^1H signal at δ 1.40 with $^3J_{\text{HH}} = 7.34$ 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 ^1H signals of 2-hydroxy-1-naphthaldehyde is also seen in the ^1H 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.

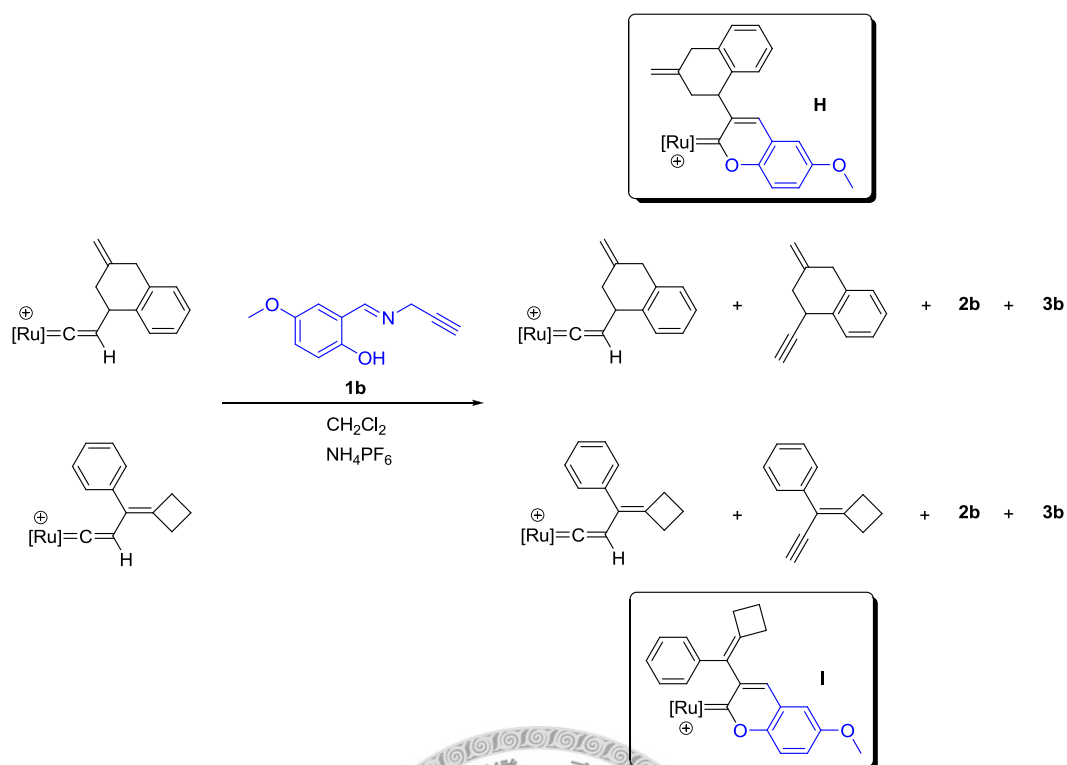
Scheme 2-8



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.

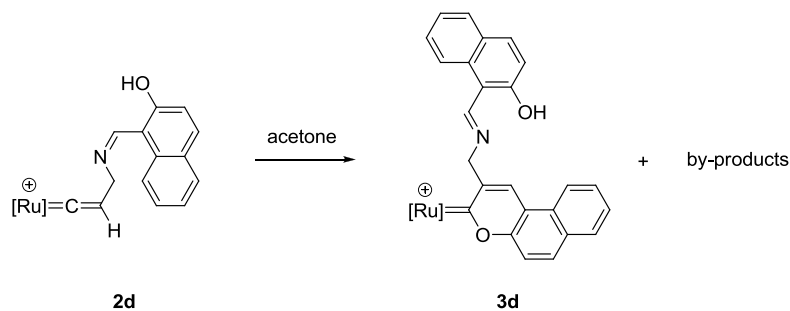
In addition, the necessity of an imine functional group within the vinylidene complex for such a cyclization should be checked. Therefore, we carried out the experiments shown in Scheme 2-9. Two different vinylidene complexes without the imine group are, separately, reacted with the imine compound **1b**. 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**.

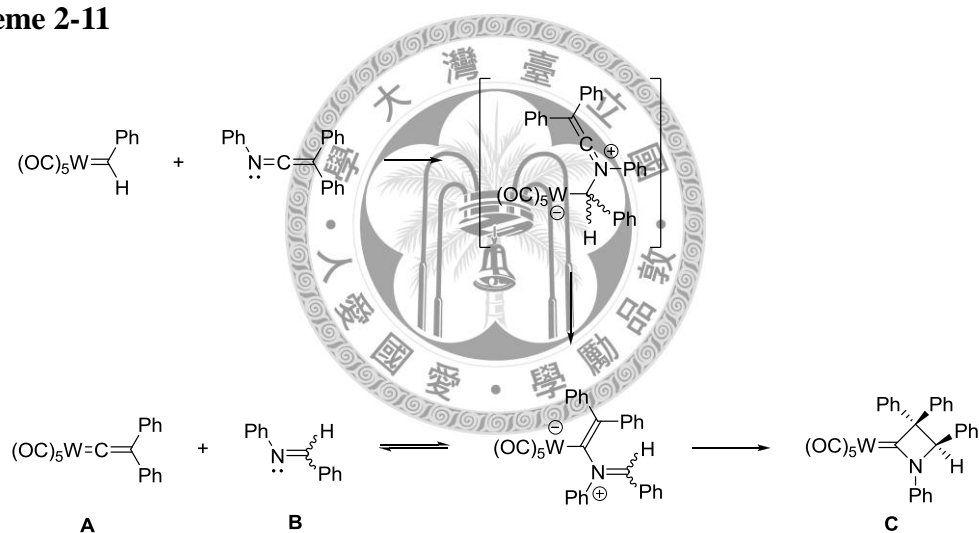
Scheme 2-10



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 peak 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

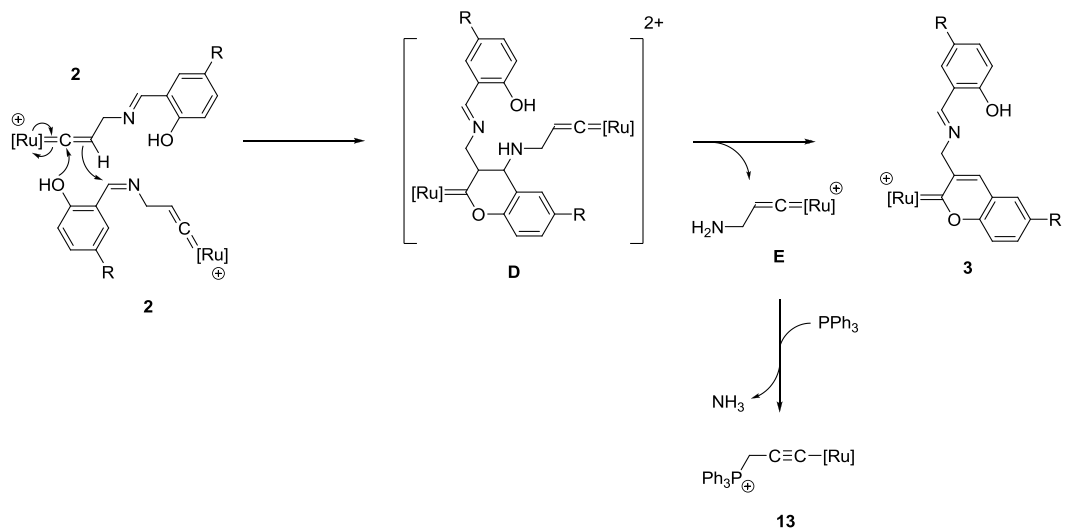
of carbene complex, as shown in Mechanism 1-1. The vinylidene complex first formed from terminal alkyne, then the two vinylidene complexes may dimerize to give dinuclear carbene vinylidene complex **D**, via the vinylidene ligand and the imine/phenol groups. Previously, as shown in Scheme 2-11, metathesis 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.

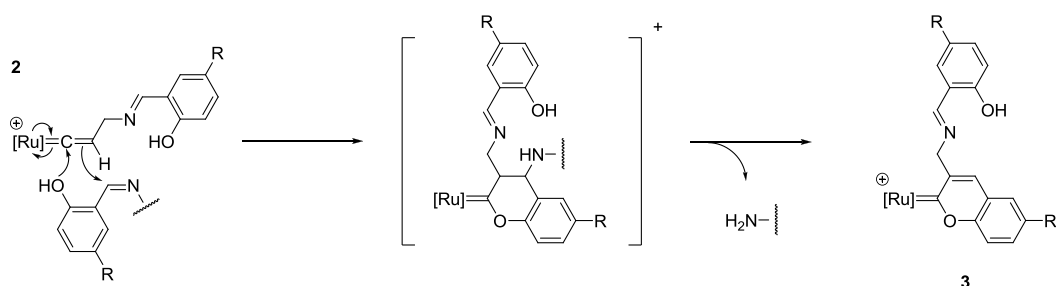
Mechanism 1-1



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**.

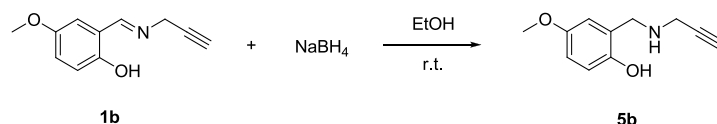
Mechanism 1-2



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 agent² 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.

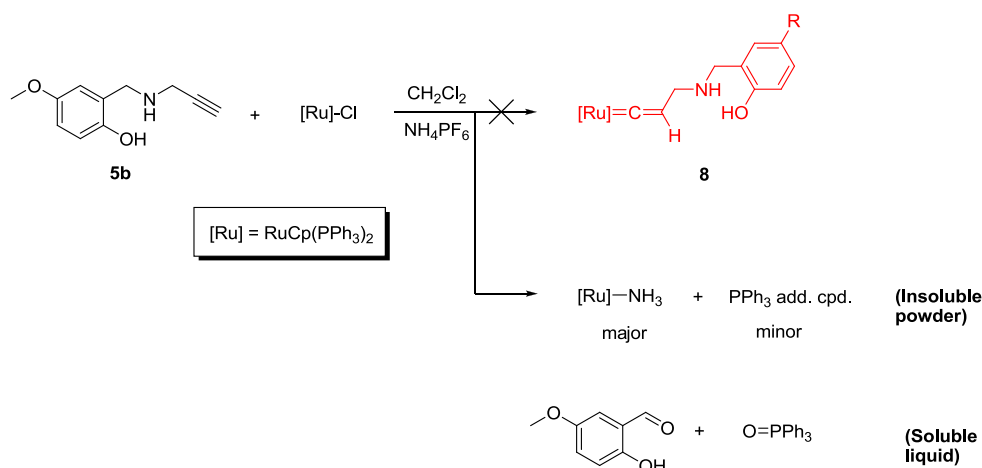
Scheme 2-12



Under the same reaction condition as that in the imine system, the amine compound **5b** was reacted with $[\text{Ru}]\text{-Cl}$ ($[\text{Ru}] = \text{Cp}(\text{PPh}_3)_2\text{Ru}$) and NH_4PF_6 in CH_2Cl_2 overnight. However, the reaction rate is slow at room temperature. Thus, the temperature was

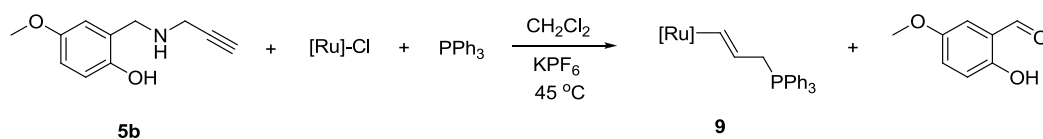
raised to 40 °C for 12 hours. After the same purification procedure, using diethyl ether to reprecipitate the residue, insoluble powder and liquid are separated. Instead of the desired vinylidene complex **8**, as shown in Scheme 2-13, a mixture containing [Ru]-NH₃ as the major product was isolated, and the minor product shows the ³¹P NMR pattern expected for a cationic phosphine addition, also shown in Scheme 2-13. The formation of [Ru]-NH₃ is probably due to the basicity of amine ligand that deprotonates the ammonium NH₄⁺ salt, leading to the formation of [Ru]-NH₃. In the ³¹P NMR spectrum of the powder, a signal at δ 45.63 is assigned to [Ru]-NH₃. The ³¹P 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 ¹H 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 $45^\circ C$ 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 1H NMR spectrum of **9**, a multiplet signal at δ 8.22 is assigned to $C\alpha H$. In the mass spectrum, the parent peak at m/z 993.25 also support the structure of **9**, we proposed.

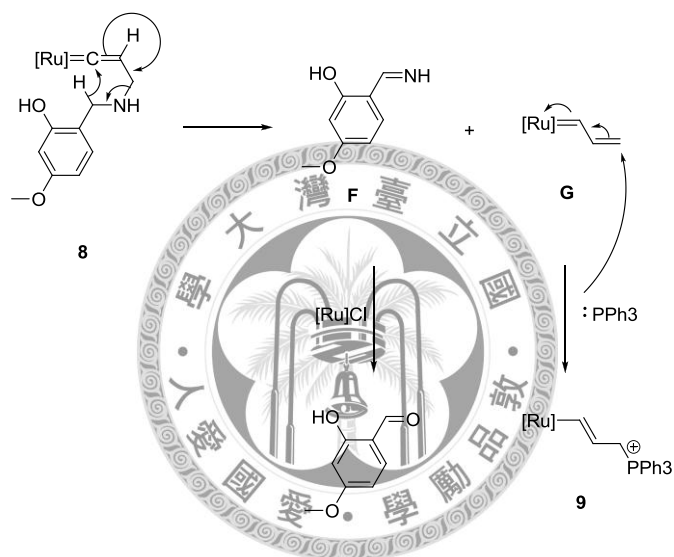
Scheme 2-14



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 C γ of complex **G** readily to give the final product **9**, and the imine compound undergoes hydrolysis to give 5-methoxy-2-hydroxybenzaldehyde.

Mechanism 2



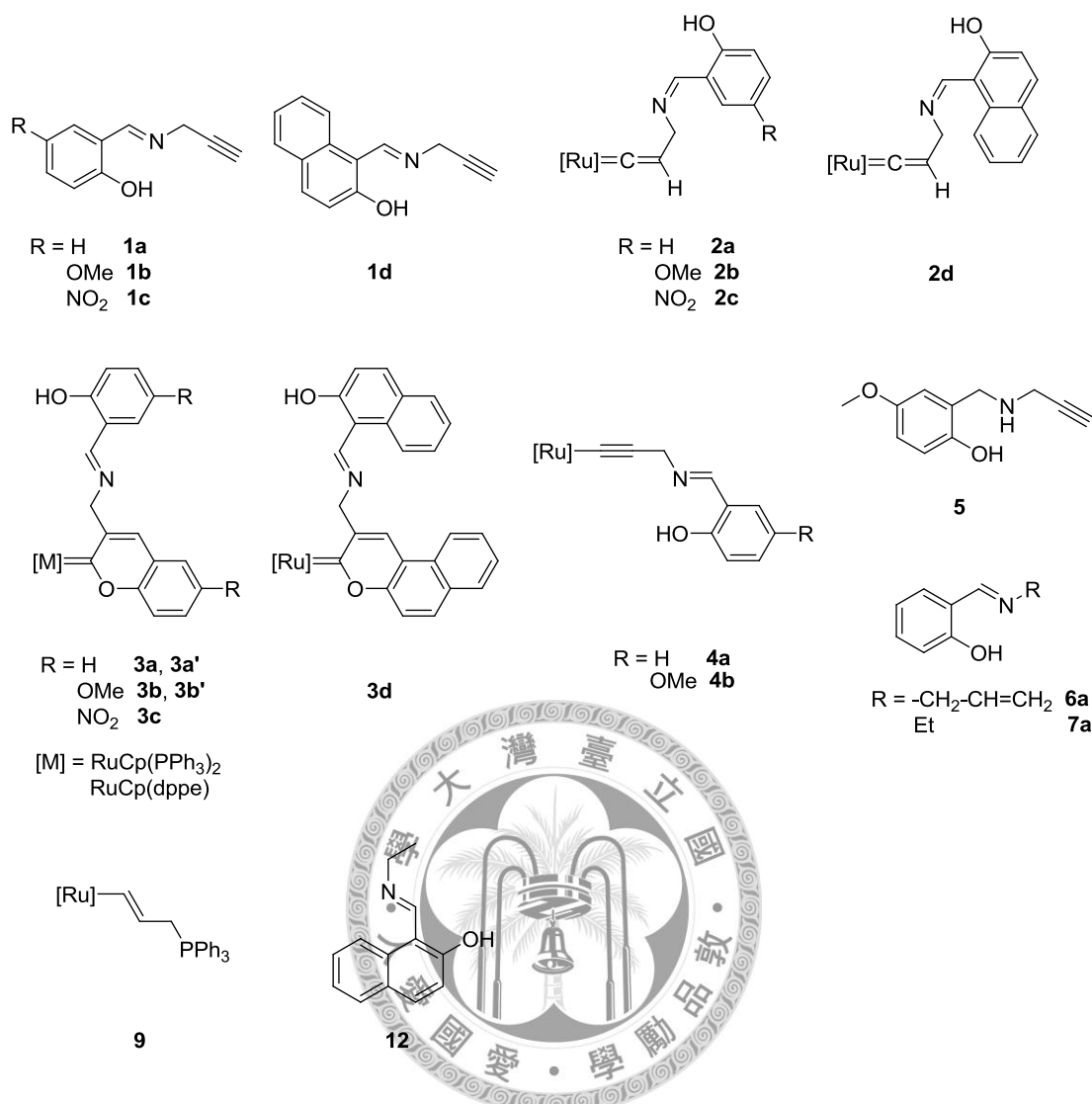
Conclusion

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 C α and C β 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 recorded on Bruker 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(PPh₃)₂Ru)³⁴ were prepared from RuCl₃ · xH₂O 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)



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 MgSO₄, 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 NH₄Cl and dried over MgSO₄. Solvent was then removed under reduced pressure to give compound **1a** (2.45 g, 0.015 mole, 95% yield). Then Spectroscopic data for **1a**: ¹H NMR (δ, CDCl₃): 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, $^4J_{\text{HH}} = 2.12$ Hz, 2H, CH₂); 2.55 (t, $^4J_{\text{HH}} = 2.12$ Hz, 1H, $\equiv\text{CH}$).

¹³C NMR (δ , CDCl₃): 165.73 (N=C); 160.65 (Ph - OH); 132.53, 131.70, 118.75, 116.99 (Ph, =C); 77.47, (C \equiv); 76.51 ($\equiv\text{CH}$); 45.38 (CH₂).

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 MgSO₄ in toluene. Spectroscopic data for **1b**: ¹H NMR (δ ,

CDCl₃): 12.38 (s, 1H, OH); 8.62 (t, $^4J_{\text{HH}} = 2.12$ Hz, 1H, N=CH); 6.82 – 6.94 (m, 3H,

Ph); 4.52 (t, $^4J_{\text{HH}} = 2.12$ Hz, 2H, CH₂); 3.77 (s, 3H, OCH₃); 2.56 (t, $^4J_{\text{HH}} = 2.12$ Hz,

1H, $\equiv\text{CH}$). ¹³C NMR (δ , CDCl₃): 165.44 (N=C); 154.80, 152.09 (Ph - OH, Ph -

OCH₃); 119.64, 118.33, 117.76, 115.16 (Ph, =C); 77.45 (C \equiv); 76.60 ($\equiv\text{CH}$); 55.94

(-OCH₃); 45.43 (CH₂).

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 MgSO₄ in toluene. Spectroscopic data for **1c**: ¹H NMR (δ , CDCl₃):

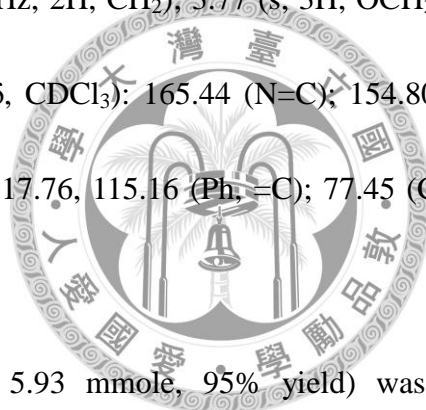
13.98 (s, 1H, OH); 8.78 (t, $^4J_{\text{HH}} = 2.14$ Hz, 1H, N=CH); 8.32 (d, $^4J_{\text{HH}} = 2.72$ Hz, 1H,

Ph); 8.22 (dd, $^3J_{\text{HH}} = 9.16$ Hz, $^4J_{\text{HH}} = 2.72$ Hz, 1H, Ph); 7.03 (d, $^3J_{\text{HH}} = 9.16$ Hz, 1H,

Ph); 4.60 (t, $^4J_{\text{HH}} = 2.14$ Hz, 2H, CH₂); 2.65 (t, $^4J_{\text{HH}} = 2.14$ Hz, 1H, $\equiv\text{CH}$). ¹³C NMR

(δ , CDCl₃): 170.09 (Ph - OH); 165.90 (N=C); 138.70, 129.95, 129.32, 120.14, 117.97

(Ph, =C); 79.63, (C \equiv); 78.87 ($\equiv\text{CH}$); 44.77 (CH₂).



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 MgSO₄ 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**: ¹H NMR (δ, CDCl₃): 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, CH₂); 3.11 (t, ⁴J_{HH} = 2.44 Hz, 1H, ≡CH). ¹³C NMR (δ, CD₂Cl₃): 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 (CH₂).

Synthesis of Complex 2a. To a Schlenk flask charged with [Ru]Cl (0.097 g, 0.13 mmole) and NH₄PF₆ (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 CH₂Cl₂ 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 CH₂Cl₂ 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**: ^1H 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, $^3J_{\text{HH}} = 8.12$ Hz, 1H, C β H); 4.40 (d, $^3J_{\text{HH}} = 8.12$ Hz, 2H, CH_2). ^{31}P NMR (δ , CDCl_3): 42.68 (s, PPh $_3$). MS (ESI $^+$) m/z : 850.20. Anal. Calcd for $\text{C}_{51}\text{H}_{44}\text{F}_6\text{NOP}_3\text{Ru}$: 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**: ^1H 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, $^3J_{\text{HH}} = 8.00$ Hz, 1H, C β H); 4.38 (d, $^3J_{\text{HH}} = 8.00$ Hz, 2H, CH_2). ^{31}P NMR (δ , CDCl_3): 42.72 (s, PPh $_3$). MS (ESI $^+$) m/z : 880.20. Anal. Calcd for $\text{C}_{52}\text{H}_{46}\text{F}_6\text{NO}_2\text{P}_3\text{Ru}$: 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**: ^1H 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, $^3J_{\text{HH}} = 7.95$ Hz, 1H, C β H); 4.45 (d, $^3J_{\text{HH}} = 7.95$ Hz, 2H, CH_2). ^{31}P NMR (δ , CDCl_3): 42.69 (s, PPh_3). MS (ESI $^+$) m/z : 895.18. Anal. Calcd for $\text{C}_{51}\text{H}_{43}\text{F}_6\text{N}_2\text{O}_3\text{P}_3\text{Ru}$: C, 58.91; H, 4.17.

Synthesis of Complex 2d. To a Schlenk flask charged with $[\text{Ru}]\text{Cl}$ (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**: ^1H NMR (δ , CDCl_3): 14.37 (s, 1H, OH); 8.62 (s, 1H, N=CH); 7.75 (d, $^3J_{\text{HH}} = 8.25$ Hz, 1H, Ph); 7.69 (d, $^3J_{\text{HH}} = 9.27$ Hz, 1H, Ph); 7.58 (d, $^3J_{\text{HH}} = 8.25$ Hz, 1H, Ph); 6.93 - 7.76 (m, 32H, Ph); 6.95 (d, $^3J_{\text{HH}} = 9.27$ Hz, 1H, Ph); 5.17 (s, 5H, Cp); 5.08 (t, $^3J_{\text{HH}} = 8.11$ Hz, 1H, C β H); 4.42 (d, $^3J_{\text{HH}} =$

8.11 Hz, 2H, CH₂). ¹³C NMR (δ, CDCl₃): 345.72 (t, ²J_{CP} = 15.3 Hz, Cα); 158.53 (N=C); 107.00 – 133.61 (Ph, =C); 94.85 (Cp); 44.42 (CH₂). ³¹P NMR (δ, CDCl₃): 42.07 (s, PPh₃). MS (ESI⁺) *m/z*: 900.21. Anal. Calcd for C₅₅H₄₆F₆NOP₃Ru: 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 NH₄PF₆ (0.083 g, 0.51 mmole) in CH₂Cl₂. Spectroscopic data of **3a**: ¹H NMR (δ, CDCl₃): 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, CH₂); 4.75 (s, 5H, Cp). ¹³C NMR (δ, CDCl₃): 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 (CH₂). ³¹P NMR (δ, CDCl₃): 48.93 (s, PPh₃). MS (ESI⁺) *m/z*: 954.22. Anal. Calcd for C₅₈H₄₈F₆NO₂P₃Ru: 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 NH₄PF₆ (0.028 g, 0.17 mmole) in CH₂Cl₂. Spectroscopic data for **3b**: ¹H NMR (δ, CDCl₃): 12.71 (s, 1H, OH); 8.83 (s, 1H, N=CH); 7.64 (s, 1H, C_γH); 6.62 - 7.67 (m, 48H, Ph); 5.92 (d, ³J_{HH} = 9.26 Hz, 1H, Ph); 5.13 (s, 2H, CH₂); 4.73 (s, 5H, Cp); 3.82, 3.75 (2 s, 6H, 2 OCH₃). ¹³C NMR (δ, CDCl₃): 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 (CH₂); 55.99, 55.81 (2 OCH₃). ³¹P NMR (δ, CDCl₃): 48.72 (s, PPh₃). MS (ESI⁺) *m/z*: 1014.24. Anal. Calcd for C₆₀H₅₂F₆NO₄P₃Ru: 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 NH₄PF₆ (0.091 g, 0.56 mmole) in CH₂Cl₂. Spectroscopic data for **3c**: ¹H NMR (δ, (CD₃)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, C_γH); 7.05 – 8.04 (m, 32H, Ph); 6.37 (d, ³J_{HH} = 9.26 Hz, 1H, Ph); 5.63 (s, 2H, CH₂); 5.17 (s, 5H, Cp). ¹³C NMR (δ, CDCl₃): 268.12 (t, ²J_{CP} = 13.9 Hz, C_α); 169.08 (N=C); 167.53, 161.03 (Ph - OH, Ph - OC_α); 148.86, 144.31 (Ph); 115.82 – 139.53 (Ph, =C); 90.49 (Cp); 61.96 (CH₂). ³¹P NMR (δ, CDCl₃): 48.27 (s, PPh₃). MS (ESI⁺) *m/z*: 1044.19. Anal. Calcd for C₅₈H₄₆F₆N₃O₆P₃Ru: 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 NH₄PF₆ (0.110 g, 0.67 mmole) in CH₂Cl₂. Spectroscopic data for **3d**: ¹H NMR (δ, CDCl₃): 14.94 (s, 1H, OH); 9.58 (s, 1H, N=CH); 8.45 (s, 1H, C_γH); 6.78 – 7.79 (m, 41H, Ph); 6.05 (d, ³J_{HH} = 9.06 Hz, 1H, Ph); 5.32 (s, 2H, CH₂); 4.78 (s, 5H, Cp). ¹³C NMR (δ, CDCl₃): 258.31 (t, ²J_{CP} = 15.35 Hz, C_α); 171.12 (N=C); 163.16, 162.27 (Ph - OH, Ph - OC_α); 147.31 (Ph); 114.66 – 136.64 (Ph, =C); 88.94 (Cp); 59.35 (CH₂). ³¹P NMR (δ,

CDCl₃): 48.69 (s, PPh₃). MS (ESI⁺) *m/z*: 1054.25. Anal.Calcd for C₆₆H₅₂F₆NO₂P₃Ru: 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 NH₄PF₆ (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°C 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'**: ¹H NMR (δ, CDCl₃): 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, CH₂); 3.22, 2.98 (two m, 4H, 2 dppe CH₂). ¹³C NMR (δ, CDCl₃): 264.86 (t, ²J_{CP} = 13.2 Hz, Cα); 169.43 (N=C); 115.21 – 147.13 (Ph, =C); 89.35 (Cp); 64.31 (CH₂). ³¹P NMR (δ, CDCl₃): 90.59 (s, dppe). MS (ESI⁺) *m/z*: 828.17. Anal.Calcd for C₄₈H₄₂F₆NO₂P₃Ru: 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 NH₄PF₆ (0.102 g, 0.626 mmole) in MeOH at 45 °C. Spectroscopic data for **3b'**: ¹H NMR (δ, CDCl₃): 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, CH₂); 3.81, 3.68 (2 s, 2H, 2 OCH₃); 3.16, 2.96 (two m, 4H, 2 dppe CH₂). ¹³C NMR (δ, CDCl₃): 260.13 (t, ²J_{CP} = 13.2 Hz, Cα); 168.87 (N=C); 107.63 – 139.74 (Ph, =C); 87.61 (Cp); 63.07 (CH₂); 55.88, 55.64 (2 OCH₃); 28.97 (t, ²J_{CP} = 22.1 Hz, dppe). ³¹P NMR (δ, CDCl₃): 90.34 (s, dppe). MS (ESI⁺) *m/z*: 888.20. Anal. Calcd for C₅₀H₄₆F₆NO₄P₃Ru: 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 KPF₆ (0.095 g, 0.52 mmole) was added 1.5 equiv heteroenyne **1a** (0.048 g, 0.30 mmole) and 15 mL CH₂Cl₂ under nitrogen. The resulting solution was stirred at roomtemperature for 3 days and CH₂Cl₂ 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**: ¹H NMR (δ, CDCl₃): 14.20 (s, 1H, OH); 8.80 (t,

$^4J_{\text{HH}} = 1.80$ Hz, 1H, N=CH); 7.06 – 7.46 (m, 31H, Ph); 6.90 (d, $^3J_{\text{HH}} = 8.31$ Hz, 1H, Ph); 6.61 (m, 1H, Ph); 6.50 (m, 1H, Ph); 4.74 (d, $^4J_{\text{HH}} = 1.80$ Hz, 2H, CH₂); 4.31 (s, 5H, Cp). ¹³C NMR (δ, CDCl₃): 164.16 (N=C); 161.73 (Ph - OH); 116.79 – 139.32 (Ph, =C); 109.39 (t, $^2J_{\text{CP}} = 24.54$ Hz, Cα); 103.66 (Cβ); 84.94 (Cp); 48.80 (CH₂). ³¹P NMR (δ, CDCl₃): 50.63 (s, PPh₃). MS (ESI⁺) *m/z*: 850.19. Anal. Calcd for C₅₁H₄₃NOP₂Ru: 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 KPF₆ (0.102 g, 0.55 mmole) in CH₂Cl₂ at roomtemperature. Spectroscopic data for **4b**: ¹H NMR (δ, CDCl₃): 13.57 (s, 1H, OH); 8.72 (s, 1H, N=CH); 6.74 – 7.48 (m, 32H, Ph); 5.86 (d, $^4J_{\text{HH}} = 2.96$ Hz, 1H, Ph); 4.77 (s, 2H, CH₂); 4.30 (s, 5H, Cp); 3.37 (s, 3H, OCH₃). ¹³C NMR (δ, CDCl₃): 163.99 (N=C); 155.43 (Ph - OH); 151.24 (Ph - OMe); 114.15 – 139.40 (Ph, =C); 109.14 (t, $^2J_{\text{CP}} = 24.34$ Hz, Cα); 103.89 (Cβ); 85.05 (Cp); 55.64 (CH₂); 48.92 (OCH₃). ³¹P NMR (δ, CDCl₃): 50.40 (s, PPh₃). MS (ESI⁺) *m/z*: 880.20. Anal. Calcd for C₅₂H₄₅NO₂P₂Ru: 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 NaBH₄ (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 pressure to give compound **5b** (0.23 g, 1.20 mmole, 87% yield). Spectroscopic data for **5b**: ^1H 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, $^4J_{\text{HH}} = 2.41$ Hz, 2H, CH_2); 2.28 (t, $^4J_{\text{HH}} = 2.41$ Hz, 1H, $\equiv\text{CH}$). ^{13}C NMR (δ , CDCl_3): 152.51, 151.57 (Ph – OH, Ph – OCH_3); 122.26, 116.69, 114.60, 113.80 (Ph, $=\text{C}$); 80.15 ($\text{C}\equiv$); 72.71 ($\equiv\text{CH}$); 55.66 (OCH_3); 50.73 (Ph – CH_2); 36.44 (CH_2).

Synthesis of Complex 9. To a Schlenk flask charged with $[\text{Ru}]\text{Cl}$ (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**: ^1H NMR (δ , CDCl_3): 8.21 (m, 1H, $\text{C}\alpha$ - H); 6.96 – 7.77 (m, H, Ph); 5.24 (m, 1H, $\text{C}\beta$ - H); 4.06 (s, 5H, Cp); 3.83 (dd, $^2J_{\text{HP}} = 12.59$ Hz, $^3J_{\text{HH}} = 6.35$ Hz, 2H, CH_2). ^{13}C NMR (δ , CDCl_3): 165.27 (m, $\text{C}\alpha$); 138.75

(m, C β); 118.56 – 134.83 (Ph, =C); 85.60 (Cp); 33.25 (d, $^2J_{CP}$ = 42.38 Hz, CH₂). ^{31}P NMR (δ , CDCl₃): 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 C₆₂H₅₄F₆P₄Ru: 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 CDCl₃. 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 CH₂Cl₂ 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**: ^1H NMR (δ , CDCl₃): 14.77 (s, 1H, OH); 9.40 (s, 1H, N=CH); 8.32 (d, $^3J_{HH}$ = 8.40 Hz, 1H, Ph); 7.77 (d, $^3J_{HH}$ = 9.20 Hz, 1H, Ph); 7.65 (s, 1H, C γ H); 6.92 - 7.63 (m, 37H, Ph); 6.02 (d, $^3J_{HH}$ = 8.40 Hz, 1H, Ph); 5.16 (s, 2H, CH₂); 4.80 (s, 5H, Cp). ^{13}C NMR (δ , CDCl₃): 264.16 (t, $^2J_{CP}$ = 14.54 Hz, C α); 172.12 (N=C); 163.00, 160.33 (Ph - OH, Ph - OC α); 147.21 (Ph, =C); 108.28 - 136.95 (Ph, =C); 89.35 (Cp); 58.55 (CH₂). ^{31}P NMR (δ , CDCl₃): 48.44 (s, PPh₃). MS (ESI⁺) m/z : 1004.25. Anal. Calcd for C₆₂H₅₀F₆NO₂P₃Ru: 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. SADABS³⁷ (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL³⁸ 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.

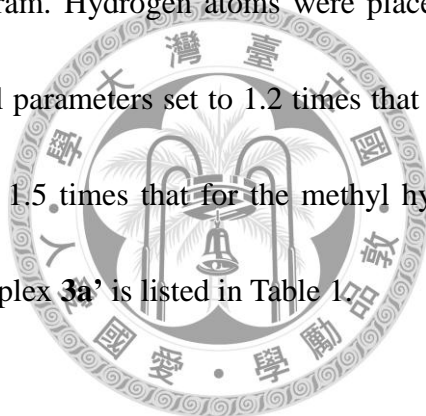
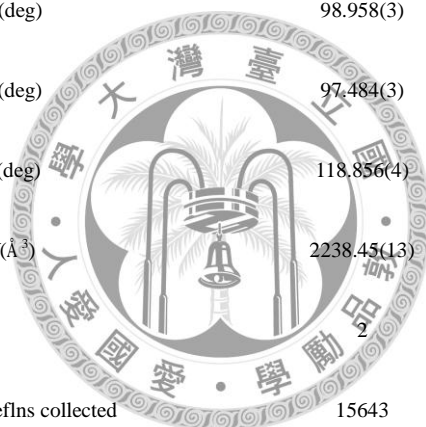


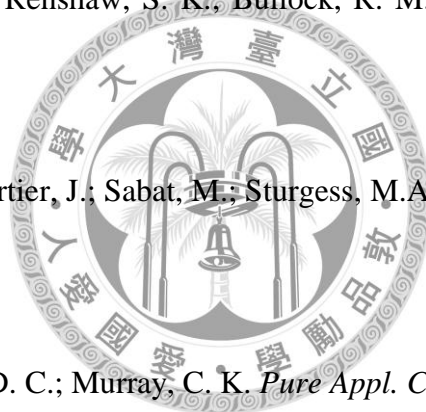
Table 1. Crystal Data and Refinement Parameters for Complex **3a'**

3a'	
Formula	C ₄₉ H ₄₄ Cl ₂ F ₆ NO ₂ P ₃ Ru
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>2σ(I)]	0.0341/0.0761
R ₁ /wR ₂ (all data)	0.0448/0.0819



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Appendix I: X-ray Crystallographic Data



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 $\alpha = 98.958(3)^\circ$ $b = 12.4210(5)$ Å $\beta = 97.484(3)^\circ$ $c = 17.8817(5)$ Å $\gamma = 118.856(4)^\circ$
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	$-15 \leq h \leq 10$, $-16 \leq k \leq 16$, $-22 \leq l \leq 21$
Reflections collected	15643
Independent reflections	9713 ($R_{int} = 0.0241$)
Completeness to $\theta = 27.50^\circ$	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 [$I > 2\sigma(I)$]	$R1 = 0.0341$, $wR2 = 0.0761$
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 [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for ic15549. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
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 icl5549.

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 [$\text{\AA}^2 \times 10^3$] for ic15549.

The anisotropic displacement factor exponent takes the form:

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

	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)
C1(1)	50(1)	30(1)	55(1)	8(1)	14(1)	18(1)
C1(2)	67(1)	34(1)	44(1)	10(1)	25(1)	20(1)



Appendix II: Spectra Data



400MHz 1H no 120314(101) CDC13

12.8741

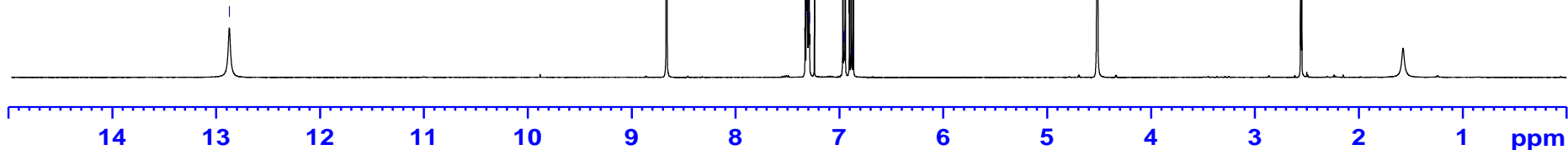
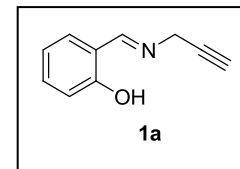
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8.6637
8.6592
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7.3266
7.3182
7.3136
7.3090
7.3053
7.2991
7.2948
7.2909
7.2867
7.2400
6.9650
6.9567
6.9546
6.9505
6.9449
6.9425
6.9039
6.9012
6.8852
6.8826
6.8731
6.8666
6.8639
4.5227
4.5174
4.5120

2.5597
2.5536
2.5474



NTU

```
NAME          manure no 120314
EXPNO         101
PROCNO        1
Date_         20120314
Time         21.17
INSTRUM       spect
PROCESSED     5 ml FAIMS0 80/
F2FREQU      400.1320000 MHz
SOLVENT       Acetone
SOLVENT       32768
NS            10
DS            8012.870 Hz
FIDRES       0.244532 Hz
AQ           2.0447111 sec
RG           381
DE           62.4000 umm
DC           288.0 Hz
DI           1.00000000 sec
TD           1
----- CHANNEL f1 -----
NUC1          1H
P1            12.10 umm
PL           -1.00 dB
SFO1          400.1320000 MHz
SI           6532
SF           400.1320175 MHz
WDW          COSYMP
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
```



1.00f

1.00f

2.04f

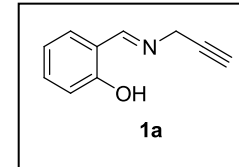
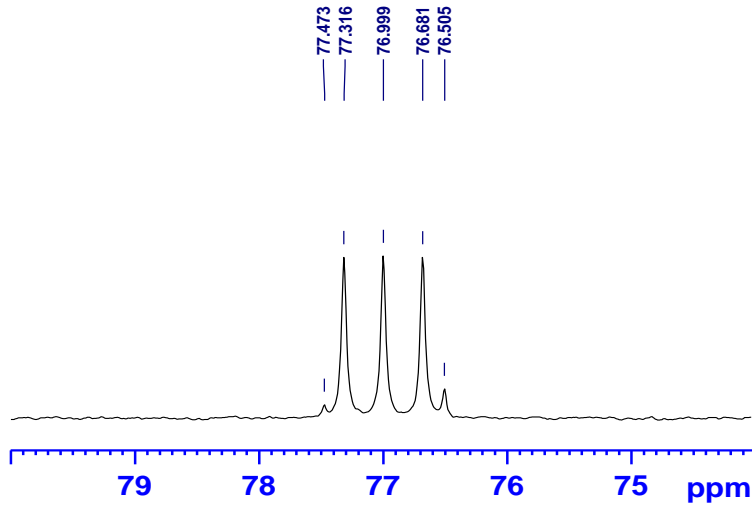
0.98f

1.03f

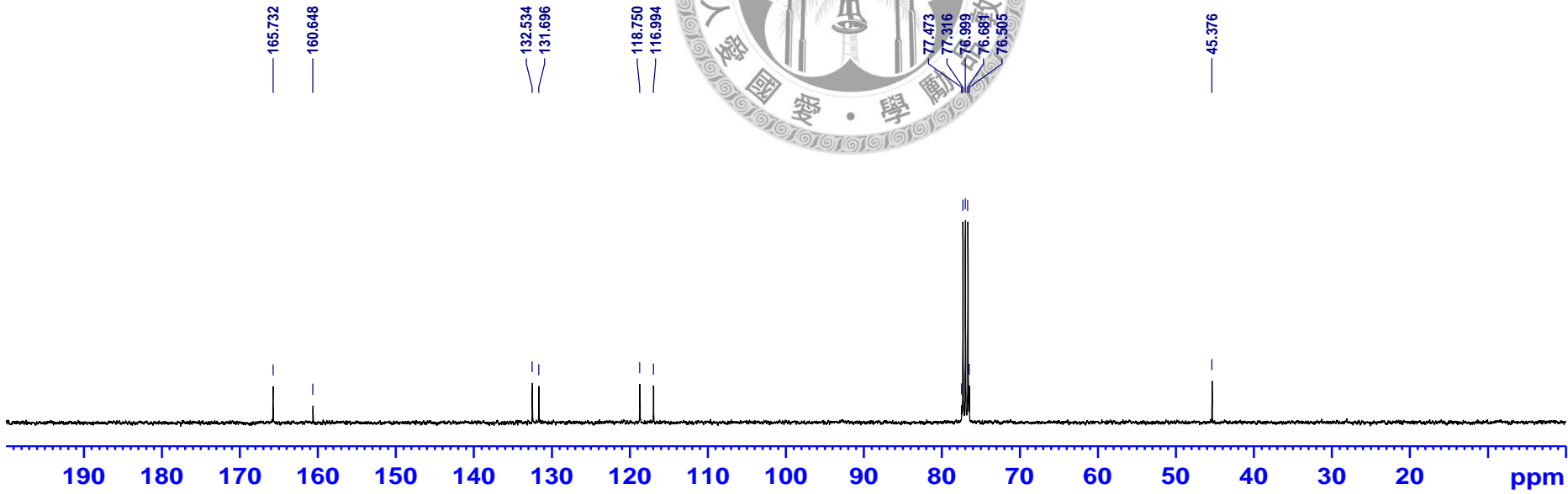
2.12f

0.95f

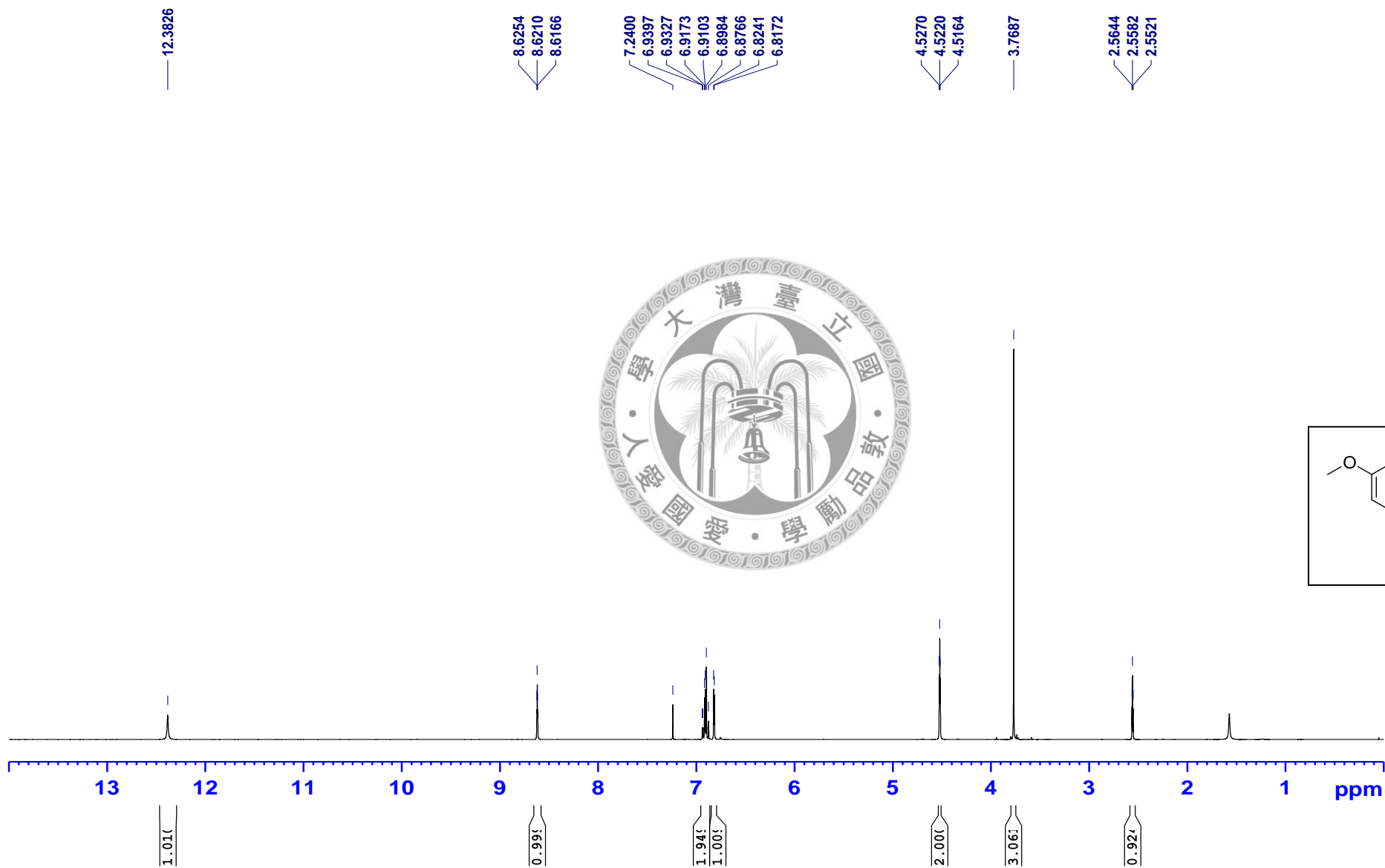
400MHz 13C no 120314 CDC13



```
NAME          nantou no 120314
EXPNO         400
PROCNO        1
Date_         20120114
Time          10:27
INSTRUM       spect
PROBHD        5 mm F4BBO BB/
PULPROG       zgpg30
TD            65535
SOLVENT       CDCl3
NS            120
DS            4
SWH           28248.160 Hz
FIDRES       0.431039 Hz
AQ           1.1462072 sec
RG            32768
SQ           17.700 usec
SM           8.50 usec
SFO           286.5 K
TE            7.00000000 sec
SI            0.03000000 sec
SFO           1.89999999 sec
TD            1
----- CHANNEL f1 -----
NUC1          13C
P1            60.00 usec
PL1           -3.00 dB
SFO1         100.6284847 MHz
----- CHANNEL f2 -----
CPDPRG2       waltz16
NUC2          1H
P2            90.00 usec
PL2           +1.00 dB
P3            90.00 usec
PL3           +1.00 dB
PL13          19.40 dB
SFO2         400.1340000 MHz
SI            32768
SF           100.6187127 MHz
RG            32768
SFO          400.1340000 MHz
PC            1.40
```

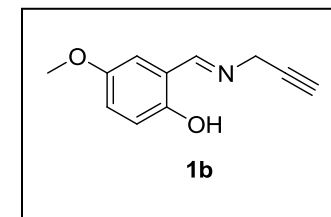


400MHz 1H OMe 120314 CDC13

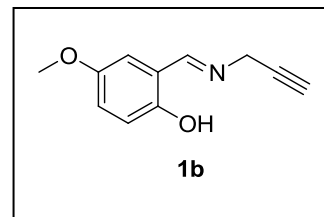
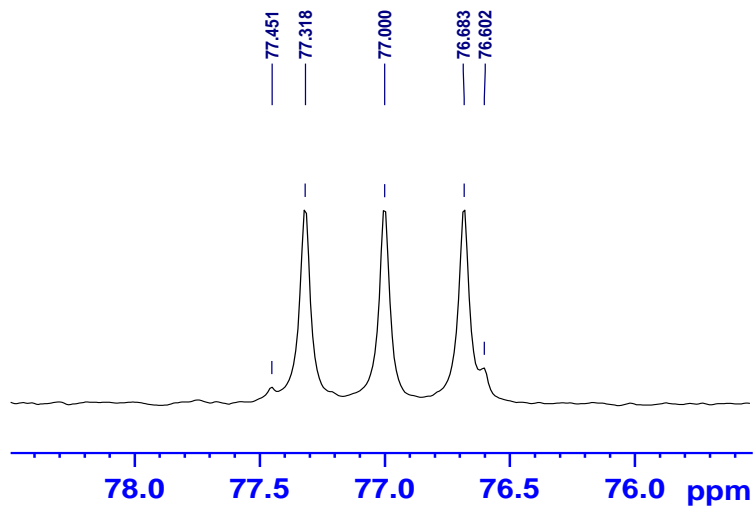


NTU

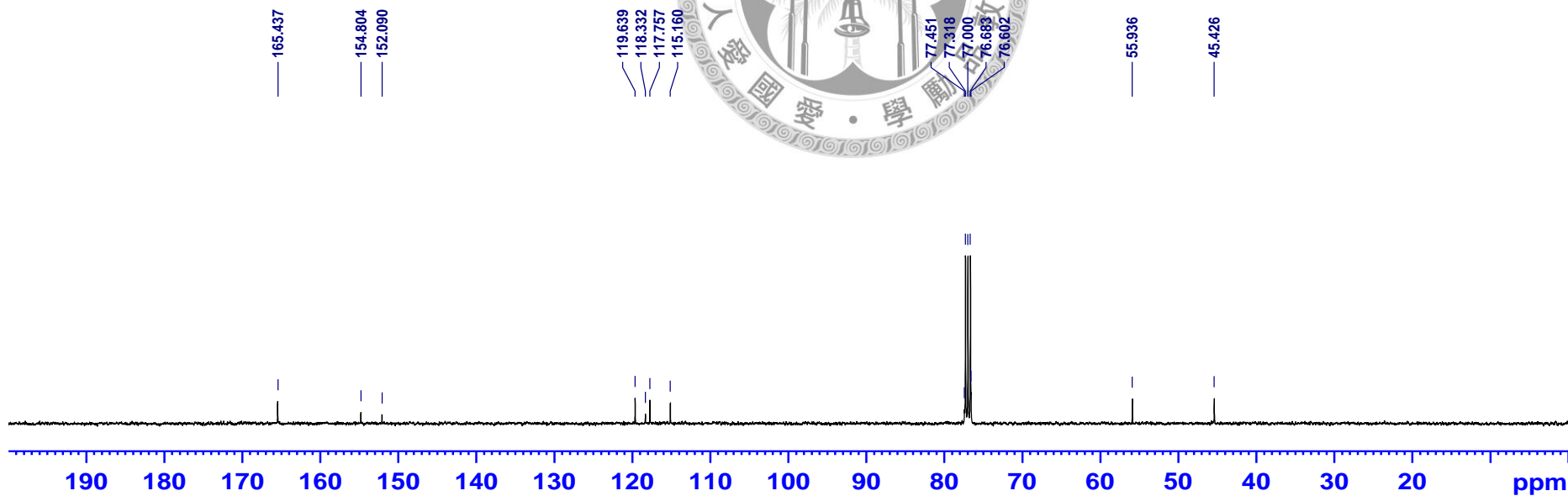
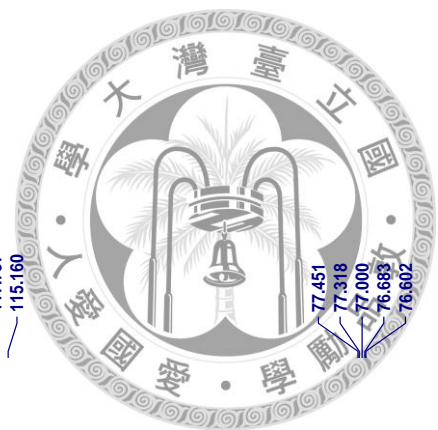
```
NAME:          methuu OMe 120314
EXPNO:         1
PROCNO:        1
Date_         20120314
Time:         15.15
INSTRUM:       spect
PROBHD:        5 mm PABBO BB7
PULPROG:       zgpg30
SOLVENT:       Acetone
SOLVENT:       3748
NS:            15
DS:            4
SWH:           8012.820 Hz
F2:            2.244532 Hz
AQ:            2.1641711 sec
RG:            228.1
AQ:            62.400
DE:            6.50 usec
TE:            298.2 K
D1:            1.0000000 sec
TD:            1
----- CHANNEL f1 -----
NUC1:          1H
P1:            12.10 usec
PL1:           -1.00 dB
SFO1:          400.1320070 MHz
SF:            400.132
WDW:           EM
SSB:           0
LB:            0.00 Hz
GB:            0
PC:            1.00
```



400MHz 13C OMe 120314 CDC13



```
NAME          120314
EXPNO         400
PROCNO        1
DATE_         20120114
TIME          10:15
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
FID           3253
SOLVENT       CDCl3
RG            120
DS            0
SFO          28248.268 Hz
FIDRES       0.431039 Hz
AQ           1.1402075 sec
RG           32768
SM           17.700 usec
DE           6.50 dB
TE           298.2 K
SI           2.0000000 sec
SFO          0.0300000 sec
SFO          1.8999998 sec
DELTA        1
TDO          0
===== CHANNEL F1 =====
NUC1          13C
P1            10.00 usec
PL1           -3.00 dB
SFO1         100.6284847 MHz
===== CHANNEL F2 =====
CPDPRG2      waltz16
NUC2          13C
P2            90.00 dB
PL2           +3.00 dB
PL12         19.40 dB
PL13         19.40 dB
SFO2         400.1316000 MHz
SI            27760
SF           100.6177122 MHz
SFO          0
SFO          3.00 Hz
GB            0
GB            1.40
PC            1.40
```



400MHz 1H CDCL3 29-52.1

13.9808

8.7833
8.3235
8.3167
8.2303
8.2234
8.2074
8.2005

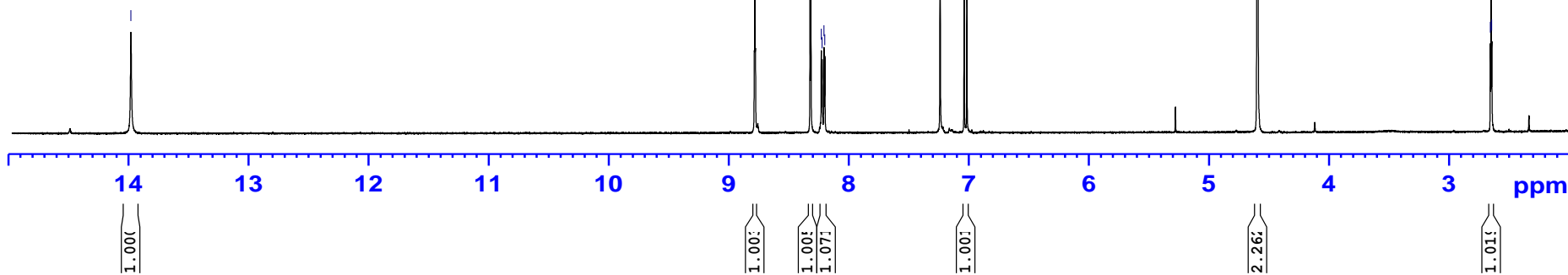
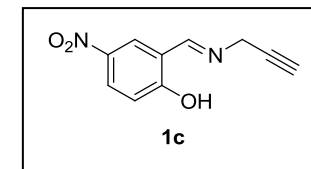
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7.0398
7.0169

4.6022
4.5969
4.5915

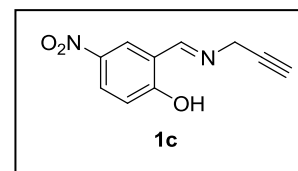
2.6565
2.6504
2.6444



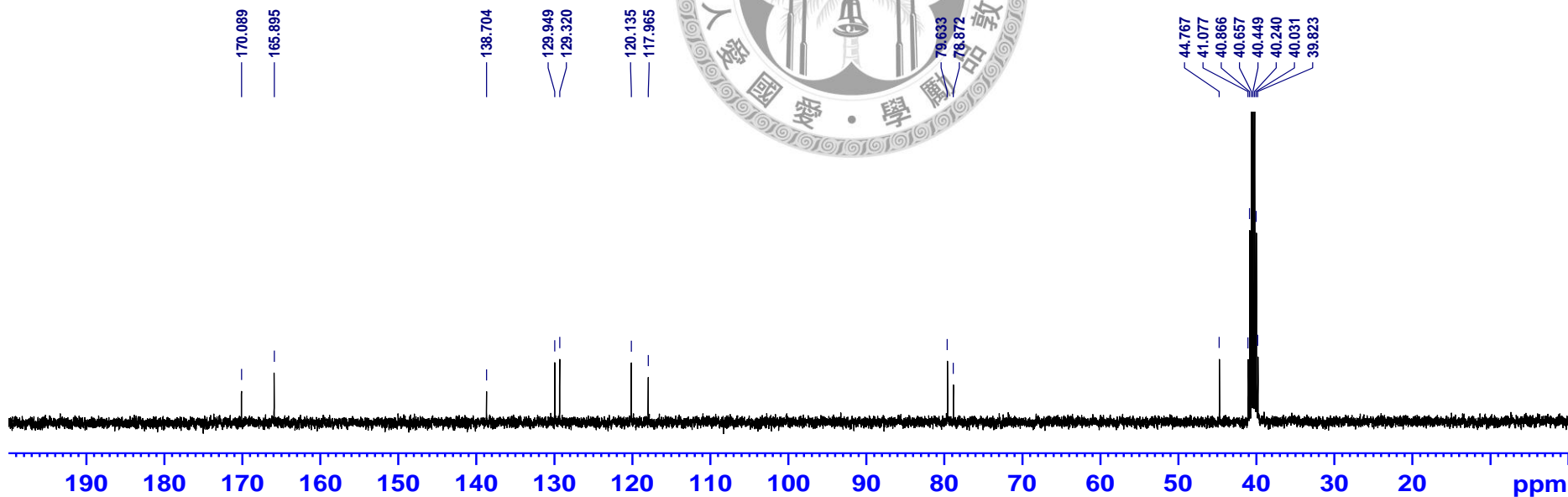
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EXPNO         100
PROCNO        1
DATE_         20110211
TIME          23.30
INSTRUM       spect
PROBHD        5 mm QNP 1H/1
PULPROG       zgpg30
TD            32768
SOLVENT       MeCN-d4
NS            25
DS            8012.00 Hz
F2FRES        0.244332 Hz
AQ            2.0647731 sec
RG            456.1
DW            62.400 usec
DE            456.1
TE            296.1 K
D1            1.00000000 sec
TDO           1
----- CHANNEL f1 -----
NUC1          13
P1            12.80 usec
PL1           0.00 dB
SFO1          400.1320007 MHz
SS            400.1300170 MHz
WDW           no
GB            0
LB            0.00 Hz
GB            0
PC            1.00
```



400MHz 13C NO2 120319 d-DMSO



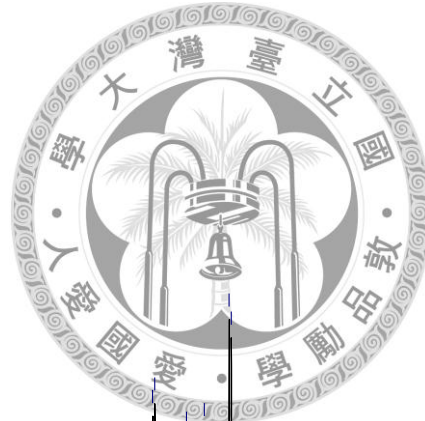
```
NAME      mantou NO2 120319
EXPNO     400
PROCNO    1
Date_     20120319
Time      15:15
INSTRUM   spect
PROBHD    5 mm PABBO MM
PULPROG   zgpg30
TD        65536
SOLVENT   DMSO
RG         32
DS         4
SWH        28439.002 Hz
FIDRES    0.433448 Hz
AQ         1.1334616 sec
RG         381
SW         17.400 usec
TE         4.00 usec
TE         298.4 K
D1         2.0000000 sec
D13        0.0300000 sec
TD0        1
----- CHANNEL f1 -----
NUC1       13C
P1         9.00 usec
PL1        -1.00 dB
PL1W       41.10960770 MHz
SFO1       100.6289717 MHz
----- CHANNEL f2 -----
CPCPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
P12        -1.00 dB
P12W       10.00 MHz
P13        18.00 dB
P13W       13.43916010 MHz
PCPDW      0.30087693 MHz
P14W       0.10079000 MHz
SFO2       400.1516000 MHz
SF         10766
SF         100.6277914 MHz
RG         0
SWH        1.00 Hz
LB         1.40
PC         1.40
```



400MHz 1H naph 120314 CDC13

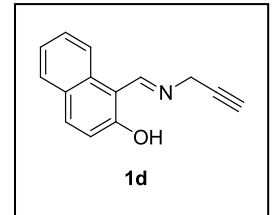
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9.5672
8.2311
8.2097
7.8912
7.8684
7.8081
7.8057
7.7881
7.7656
7.5468
7.5434
7.5294
7.5258
7.5221
7.5082
7.5048
7.3538
7.3512
7.3363
7.3338
7.3311
7.3163
7.3137
7.0645
7.0417
4.6596
4.6562
4.6534
4.6500
3.1124
3.1093
3.1062
3.1031
3.0999
2.0607
2.0552
2.0524
2.0498
2.0470
2.0443
2.0388



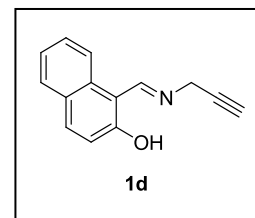
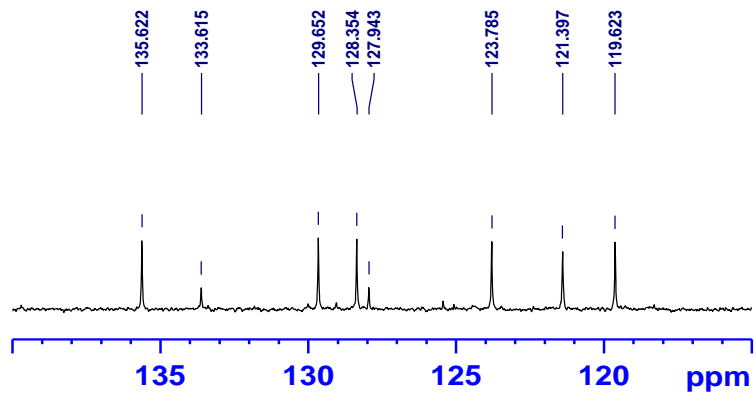
NTU

```
NAME          naxton naphthalene 120314
EXPNO         100
PROCNO        20122115
Date_         21_23
INSTRUM       spect
PROBHD        5 mm PABBO 5H/
PULPROG       zgpg30
TD            32768
SOLVENT       Acetone
NS            78
DS            28
SWH           16625.44 Hz
FIDRES       0.489264 Hz
AQ           1.522116 sec
RG            381
AQ           31.200 usec
DE           2.50 usec
TE           298.2 K
SI            1.00000000 usec
SI            1
----- CHANNEL f1 -----
NUC1          1H
P1            12.10 usec
PL            -2.00 dB
SFO1         400.130007 MHz
SI            65534
SF           400.1300047 MHz
WDW           no
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
```

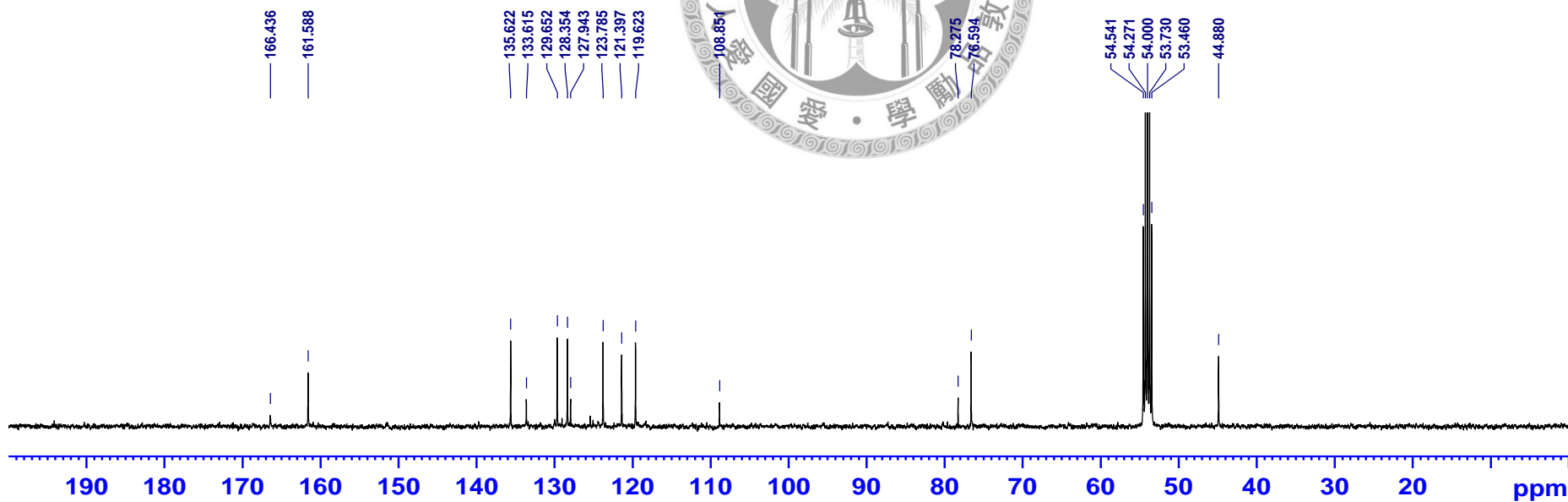
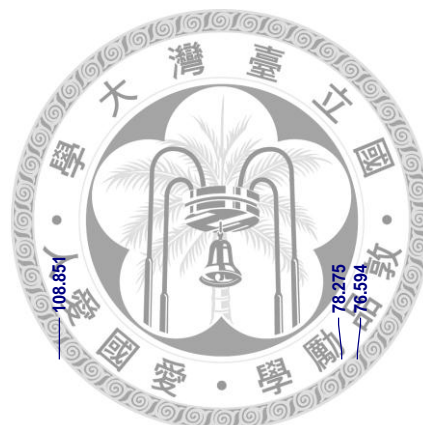


0.63
0.06
1.00
1.03
0.951
1.00
0.99
0.961
0.931
1.951
0.771

400MHz 13C naph 120315(400) CD2C12



```
NAME      Nantou naphthalene 120315
EXPNO    400
PROCNO   1
DATE_    20120111
TIME     8.11
INSTRUM  spect
PROBHD   5 mm PABBO/BB
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        342
DS        0
SWH       28248.388 Hz
FIDRES   0.431039 Hz
AQ        1.460077 sec
RG         32768
WDW       17.700 usec
SS         8.00 usec
TE        298.4 K
DQ        2.0000000 sec
delt1    0.0000000 sec
DELTA    1.8999998 sec
TQC       3
----- CHANNEL f1 -----
NUC1      13C
P1        10.00 usec
PL1       -1.00 dB
SFO1     100.628487 MHz
----- CHANNEL f2 -----
CFPPROG2 waltz16
NUC2      1H
P2        80.00 usec
PL2       -1.00 dB
PL12     19.40 dB
PL13     19.40 dB
SFO2     400.1316000 MHz
SFO3     32768
SF        100.627999 MHz
WDW       DM
SS        3.00 usec
DS        0
GB        0
PC        1.40
```



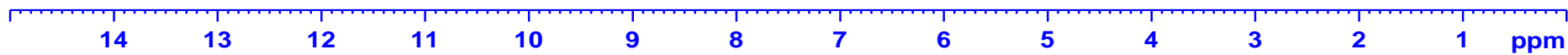
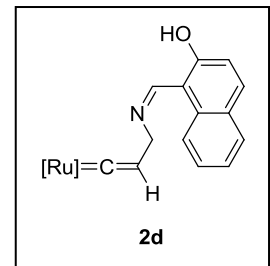
14.3680

400MHz 1H 24-164.1 CDC13

8.6236
7.7632
7.7420
7.7034
7.6802
7.5854
7.5654
7.3894
7.3728
7.3557
7.3377
7.2735
7.2556
7.2399
7.2187
7.1998
7.1812
7.0548
7.0331
7.0285
7.0087
6.9648
6.9416
5.1699
5.0973
5.0771
5.0566
4.4255
4.4051



```
NAME          hanton 24-164.1
EXPNO         100
PROCNO        2011124
DATE_         2011124
TIME          21.37
PROBHD        5 mm QNP1H
PULPROG       zgpg30
SOLVENT       Acetone
NS            32768
SOLVENTPROB   24
DE            8012.820 Hz
AQ            0.244333 sec
RG            2.0447731 sec
FIDRES        0.2511
AQ            2.0447731 sec
NUC1           1H
NUC2           13C
P1            12.00 usec
PL1           -2.00 dB
SFO1          400.132007 MHz
SI            65535
SF            400.1300179 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
```



0.45

0.98

2.87

1.28

8.26

16.30

14.44

5.00

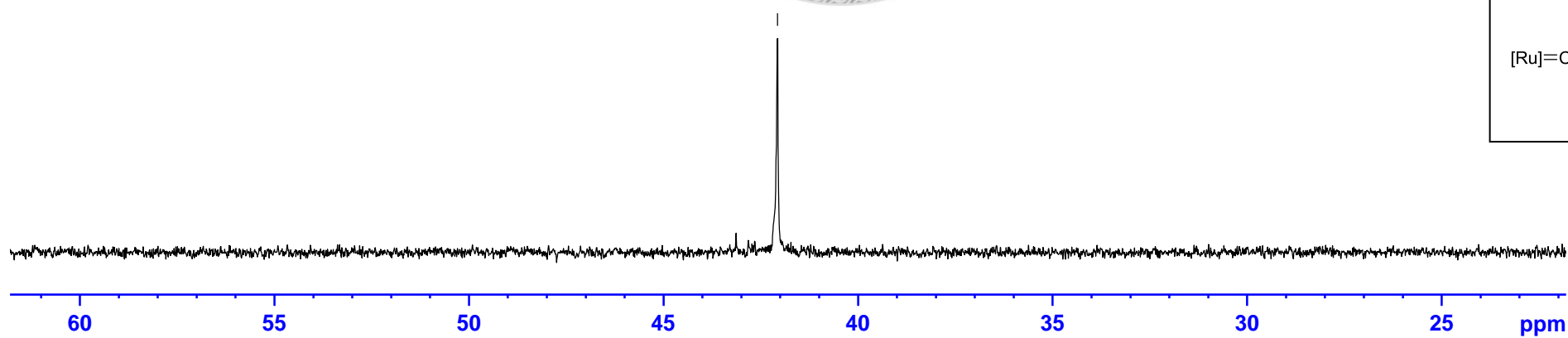
1.08

2.03

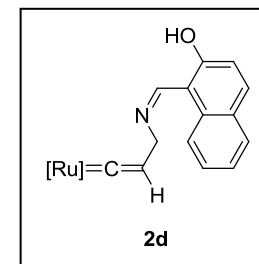
400MHz P31 24-39.2 CDC13



42.073



```
NAME mantou 24-39.2
EXPNO 300
PROCNO 1
Date_ 20101116
Time 20.22
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 40
DS 4
SWH 58479.531 Hz
FREQES 0.892327 Hz
AQ 0.5602828 sec
RG 41.90
DM 8.550 usec
DE 4.50 usec
TE 296.8 K
DQ 2.0000000 sec
d11 0.0300000 sec
DELTA 1.8999998 sec
TD0 1
----- CHANNEL f1 -----
NUC1 31P
P1 17.50 usec
PL1 +4.00 dB
SFO1 161.9756930 MHz
----- CHANNEL f2 -----
CH0PRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -0.70 dB
PL12 19.30 dB
SFO2 400.1314000 MHz
SI 32768
SF 161.9754777 MHz
DS 80
WON 0
SSB 1.00 Hz
LB 0
GB 1.40
PC 1.40
```



13.1822

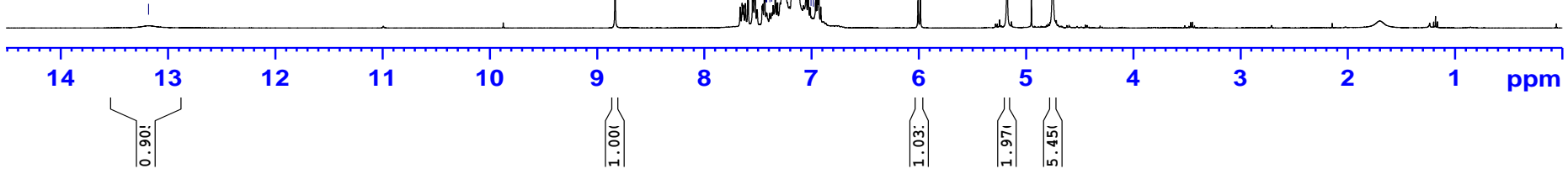
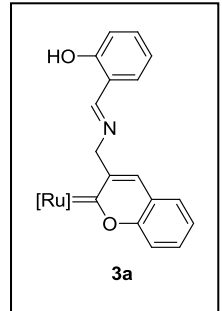
8.8341
7.6670
7.6495
7.6462
7.6371
7.6194
7.6164
7.5942
7.5490
7.5298
7.5109
7.5080
7.4622
7.4554
7.4431
7.4363
7.4253
7.4230
7.4182
7.3898
7.3719
7.3606
7.3566
7.3390
7.3215
7.3175
7.2614
7.2467
7.1573
7.1502
7.1412
7.0772
7.0556
7.0520
7.0342
7.0310
7.0163
7.0128
7.0048
6.9844
6.9625
6.9533
6.9418
6.9347
6.9159
6.0085
5.9873
5.1793
4.7525



NTU

```

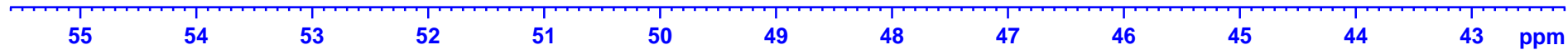
NAME      hantou 37-160 111004(1)
EXPNO     1
PROCNO    1
Date_     20111204
Time      13:25
INSTRUM   spect
PROBHD    5 mm PABBO BBI
PULPROG   zgpg30
TD         32768
SOLVENT   MeCN-d4
NS         25
DS         8
SWH        8012.842 Hz
F2RES     0.244332 Hz
AQ         2.0447131 sec
RG         62.400 umax
WDW        EM
SSB        0
DE         6.50 umax
TE         298.0 K
D1         1.00000000 sec
D11        1
D12        1
----- CHANNEL f1 -----
NUC1       13
P1         12.10 umax
PL1        -2.00 dB
PR1        400.130007 MHz
SI         65536
SF         400.1300178 MHz
WDW        EM
SSB        0
LB         0.00 Hz
GB         0
PC         1.00
    
```



400MHz P31 37-160 111104(1) CDC13



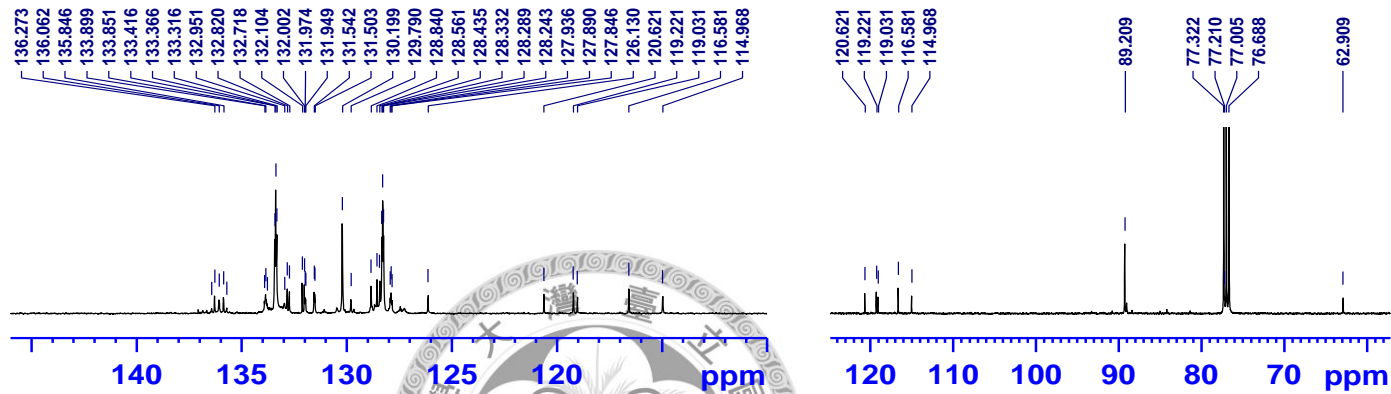
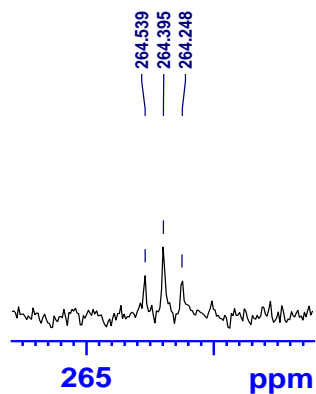
48.928



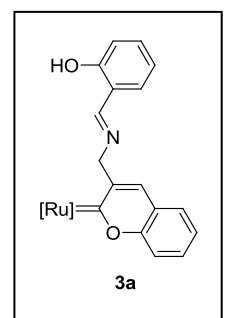
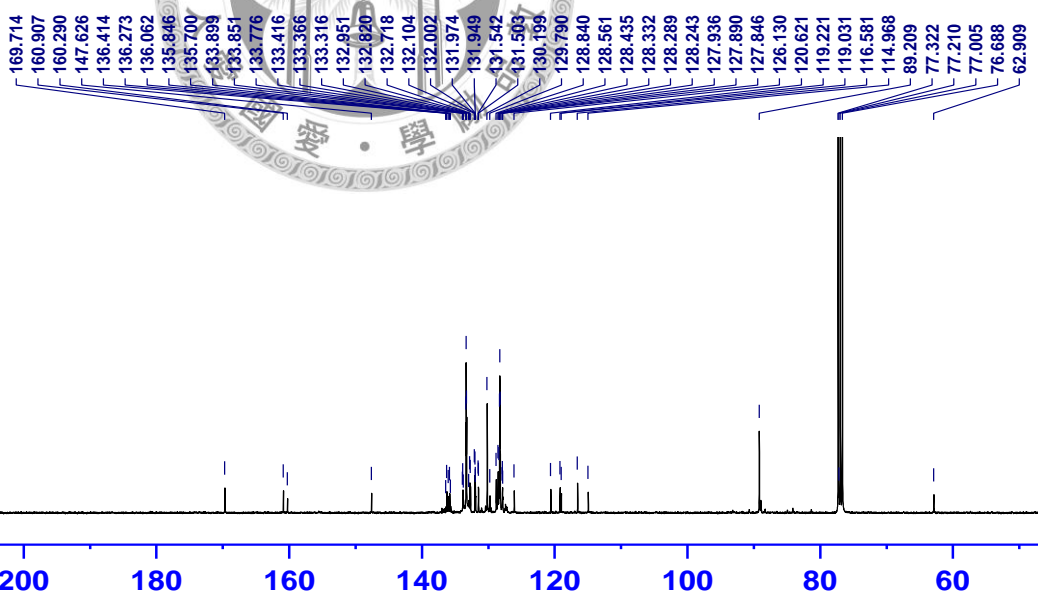
```
NAME      nantou 37-160_111104(1)
EXPNO     310
PROCNO    1
Date_     20111104
Time      13:18
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         24
DS         4
SWH        58479.531 Hz
FIDRES    0.892327 Hz
AQ         0.5603828 sec
RG         81.92
DM         8.550 usec
DE         6.50 usec
TE         298.9 K
SI         2.0000000 sec
dS1        0.0300000 sec
DELTA     1.8999998 sec
TDC        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        -1.00 dB
PL12       15.40 dB
PL13       18.40 dB
SFO2       400.1314605 MHz
SI         27168
SF         161.9755477 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```



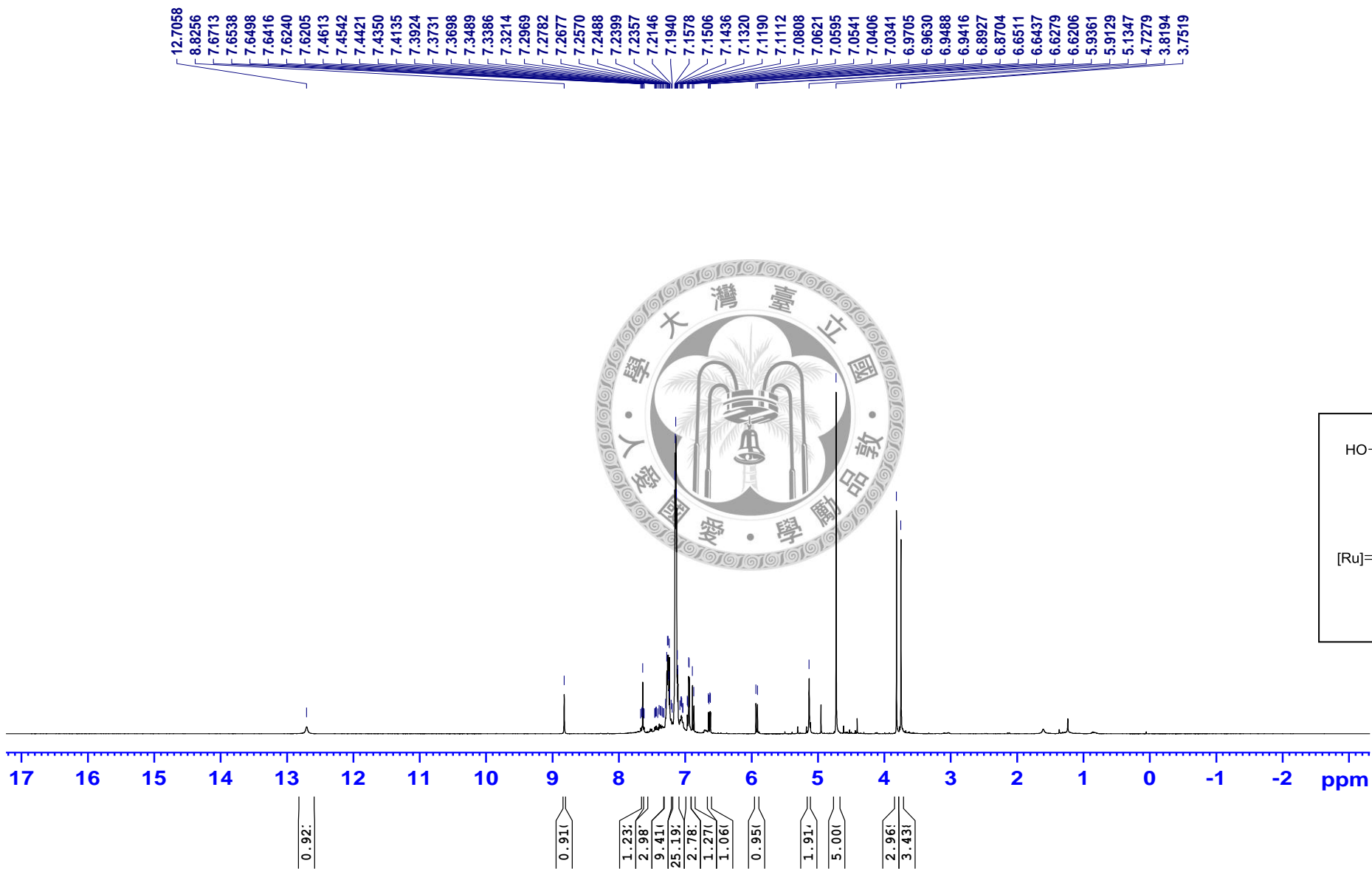
400MHz 13C 37-210.4 CDC13



```
NAME mantou 37-210.4
EXPNO 400
PROCNO 1
Date_ 20120421
Time 23.06
INSTRUM spect
PROBHD 5 mm PABBO MM
PULPROG zgpg30
TD 65536
SOLVENT CDC13
RG 612
DS 42016.809 Hz
FIDRES 0.441124 Hz
AQ 0.7192214 sec
RG 260
DM 11.900 usec
DE 7.49 usec
TE 302.1 K
DQ 3.5000000 sec
D11 0.0300000 sec
TD 8
===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
PL12 41.10560770 dB
SFO1 100.6260949 MHz
===== CHANNEL f2 =====
CPCPRG2 waltz16
NUC2 13C
P2 80.00 usec
PL2 1.00 dB
PL3 12.50 dB
PL4 18.50 dB
PL5 13.43168210 dB
PL12W 0.30087493 dB
PL13W 0.15043746 dB
SFO2 400.1500000 MHz
SF 100.6260949 MHz
SS 12769
SWH 100.6278058 MHz
GB 0
LB 1.00 Hz
GB 0
PC 1.40
```

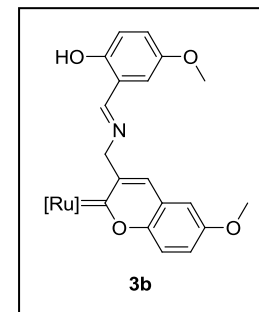


400MHz 1H 27-211 120424.2 CDC13



NTU

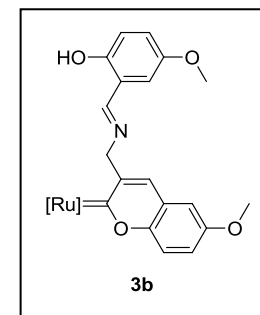
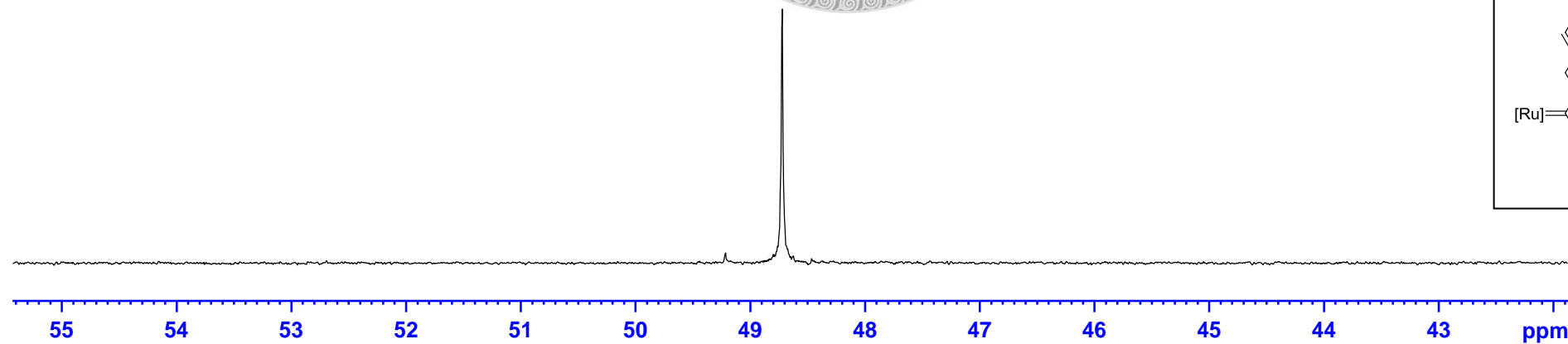
```
NAME          HANTOU 27-211 120424.2
EXPNO         150
PROCNO        1
Date_         20120424
Time         22:02
INSTRUM       spect
PROBHD        5 mm PABBO-5B
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
AQ            0.3768
RG            256
DS            0
FIDRES        0.230891 Hz
AQ           1.9923444 sec
RG           6.50
DM           60.800 usec
DE           6.50 usec
TE            301.1 K
SI            1.00000000 sec
TDO           1
----- CHANNEL f1 -----
NUC1          13C
P1            12.00 usec
PL1          -1.00 dB
PL12         13.4388810 dB
PL13         400.1382810 MHz
RF1          400.1382810 MHz
SF           400.1380162 MHz
WDW           PC
SSB           0
LB           0.00 Hz
GB           0
PC           1.00
```

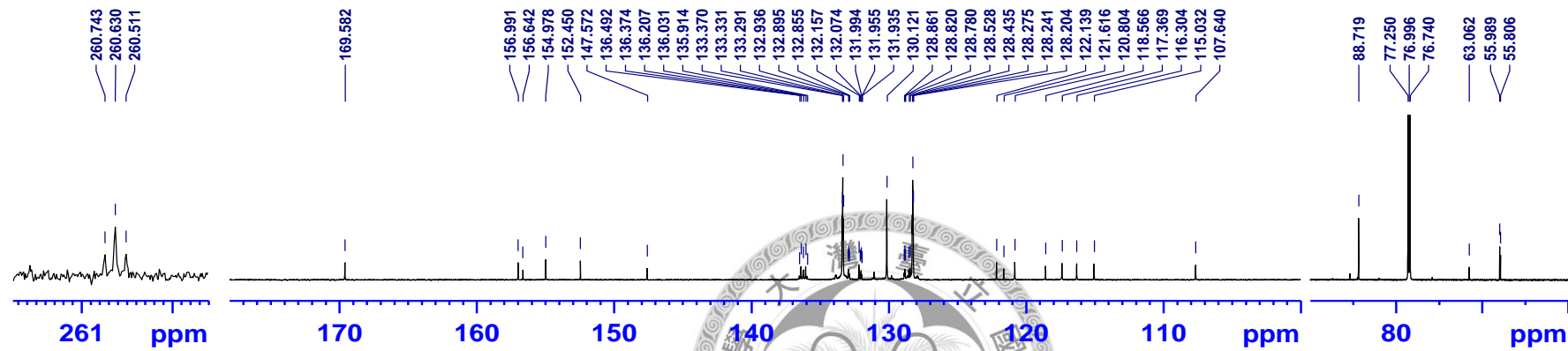


400MHz 31P 27-211 120424.2 CDC13



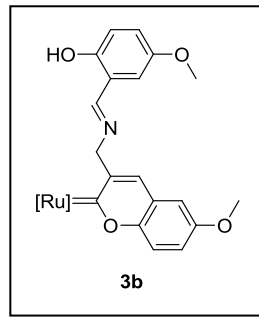
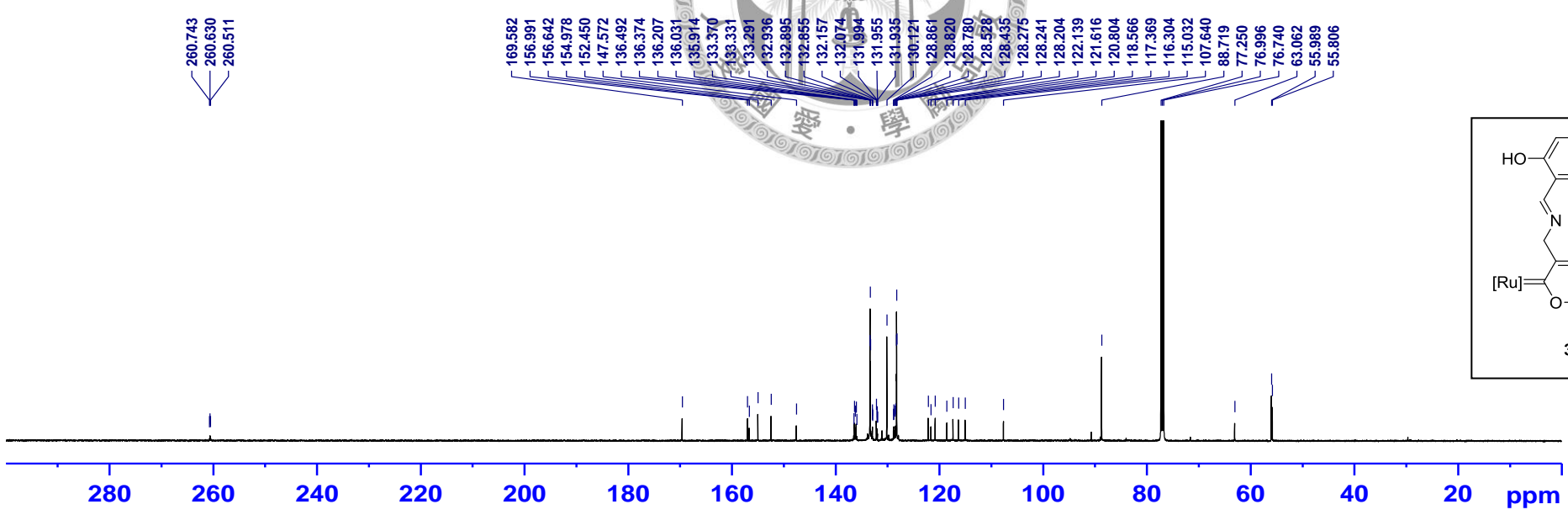
```
NAME mantou 27-211 120424.2
EXPNO 300
PROCNO 1
Date_ 20120424
Time 22.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 8
DS 4
SWH 64102.563 Hz
FIDRES 0.37827 Hz
AQ 0.5112208 sec
RG 2050
DW 7.800 usec
DE 6.50 usec
TE 301.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TD 1
----- CHANNEL f1 -----
NUC1 31P
P1 14.10 usec
P11 4.00 dB
P11W 8.0400000 W
SFO1 161.975590 MHz
----- CHANNEL f2 -----
C13FPRG2 waltz16
NUC2 13C
PCPD2 80.00 usec
P12 -1.00 dB
P12W 18.00 dB
P13 18.00 dB
P13W 12.4388800 W
P12W 0.30287695 W
P13W 0.15079568 W
SFO2 400.146000 MHz
SF 161.9836800 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
```





```

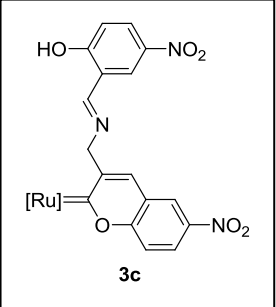
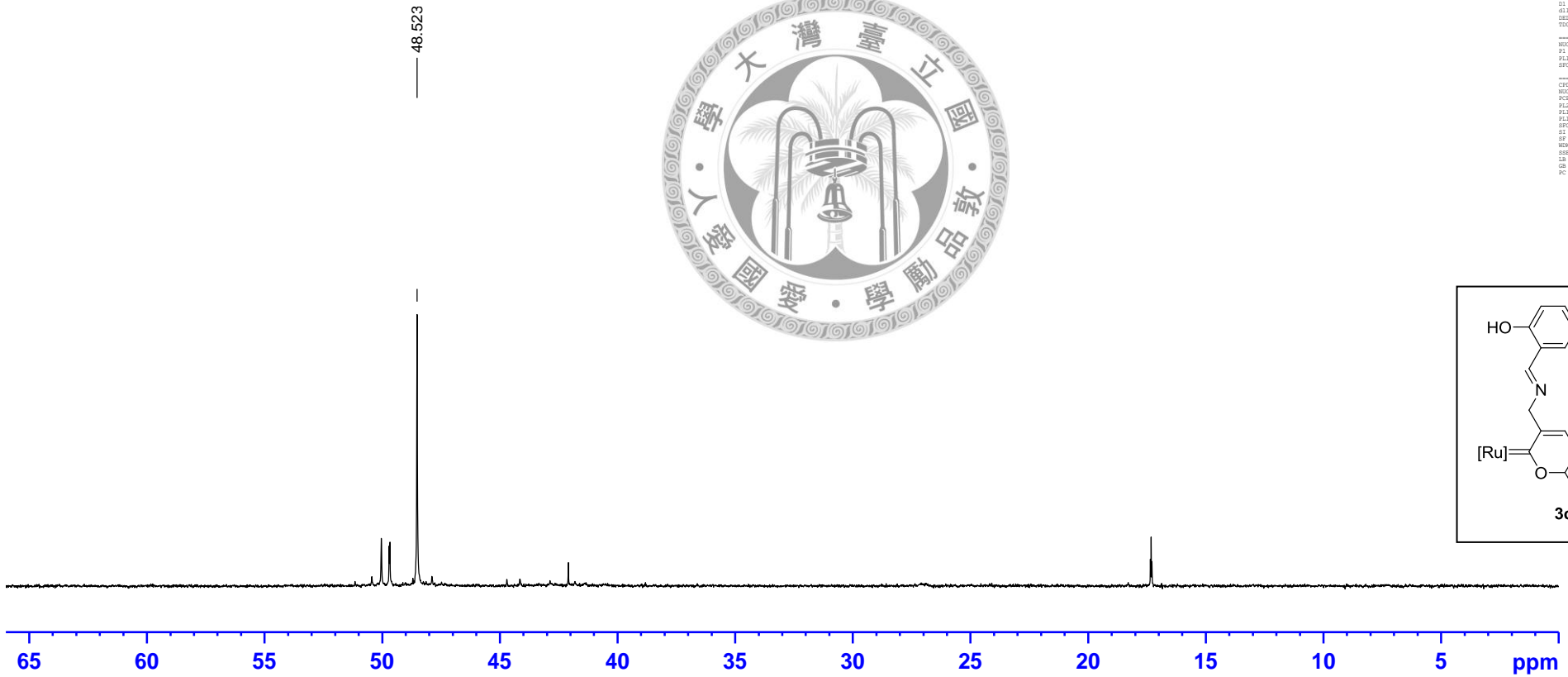
NAME linyo-hsuht-12Apr30-cdc13
PROCNO 400
Date_ 20120501
Time 11.14
INSTRUM spect
PROBHD 5 mm PABBO 501
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
F2 41666.668 Hz
F1 125.760 MHz
AQ 0.43183 sec
RG 0.784820 sec
DE 3200
DN 12.000 usec
DE 12.000 usec
TE 298.0 K
D1 3.5000000 sec
D11 0.0300000 sec
TSD 1000
===== CHANNEL f1 =====
NUC1 13C
P1 12.00 usec
PL 0.00 dB
RF 125.7577982 MHz
MW 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

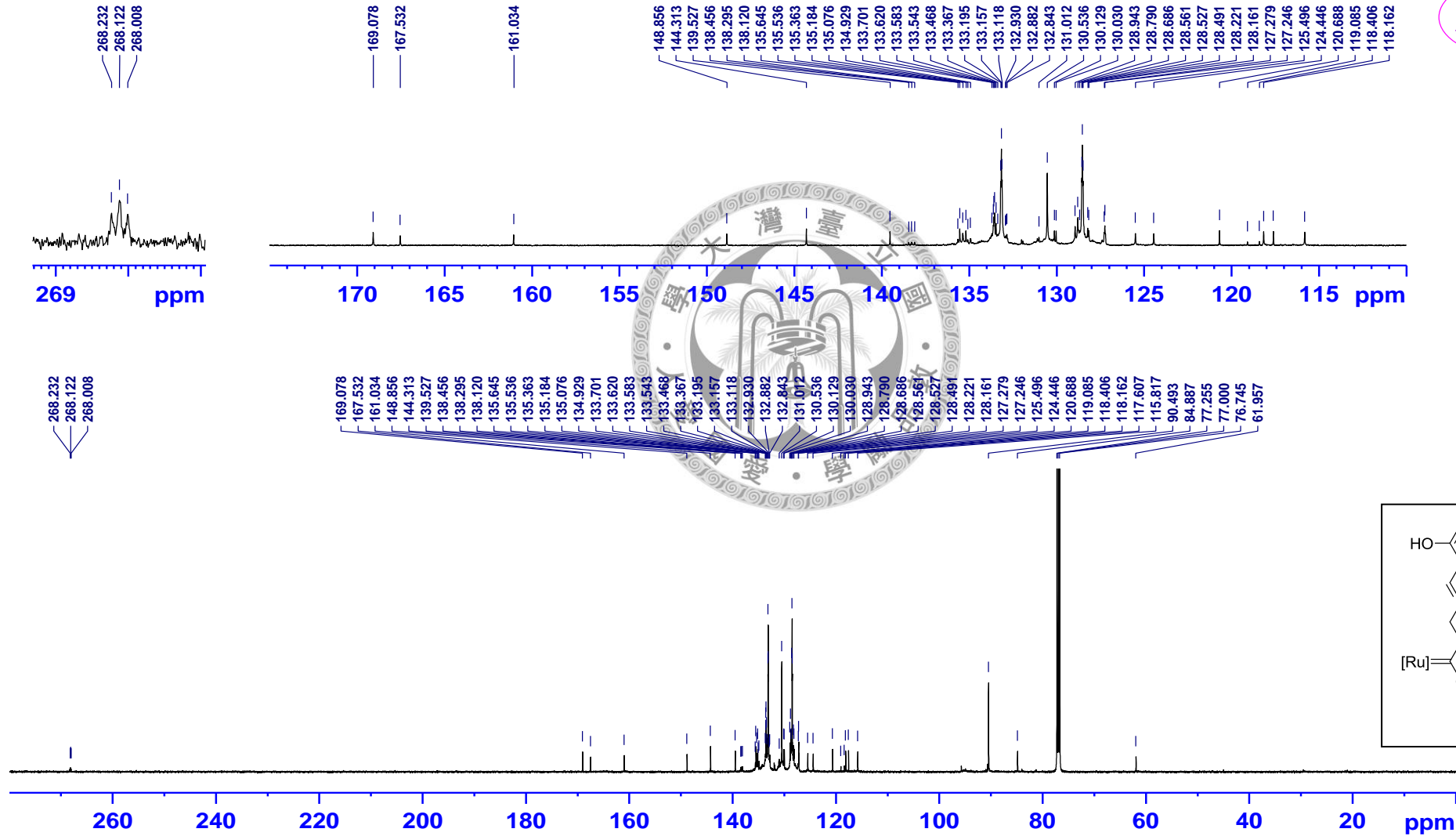


400MHz P31 30-213.7(1) d-acetone



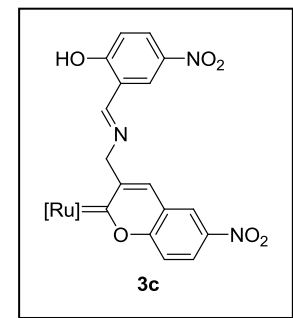
```
NAME mantou 30-213.7(1)
EXPNO 330
PROCNO 1
Date_ 20120427
Time 11.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 22
DS 4
SWH 58479.531 Hz
F2RES 0.892327 Hz
AQ 0.5603828 sec
RG 6192
DK 8.550 usec
DE 61.50 usec
TE 298.0 K
DQ1 2.0000000 sec
d11 0.0300000 sec
DELTA 1.8999998 sec
TD0 1
----- CHANNEL f1 -----
NUC1 31P
P1 12.80 usec
PL1 0.00 dB
SFO1 161.9759930 MHz
----- CHANNEL f2 -----
CH0RG2 waltz16
NUC2 1H
PULP2 90.00 usec
PL2 -3.00 dB
PL12 15.40 dB
PL13 18.40 dB
SFO2 400.1100000 MHz
SF 32768
SE 161.9754771 MHz
DS 80
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
```





```

NAME      linye-haueh-118a01-30-604
EXPNO    1
PROCNO   1
DATE_    20110921
TIME     21.28
INSTRUM  spect
PROBHD   5 mm PABBO 5B/
PULPROG  zgpg30
SOLVENT  CDCl3
NS       6536
DS       4
SWH      55555.162 Hz
FIDRES   0.847710 Hz
AQ       0.2839140 sec
RG        16384
WDW      8.000 useq
SSB      30.00 useq
TE       298.1 K
NUC1     13.0000000 MHz
NUC2     0.0000000 MHz
DETA     1.40000010 sec
TD       100
----- CHANNEL f1 -----
NUC1     13C2
P1       10.00 useq
PL1     125.001482 MHz
SFO1     125.761482 MHz
----- CHANNEL f2 -----
CPDPRG2  waltz16
NUC2     1H
PCPD2   90.00 useq
PL2     1.00 MHz
PL12    21.10 dB
PL13    24.10 dB
PL14    21.10 dB
SFO2    500.1360510 MHz
SI       6536
SF       125.761482 MHz
DE       0
MSW      0
DSB      0
LA       1.00 Hz
GB       0
PC       1.00
    
```



400MHz 1H 89-202.8 CDC13

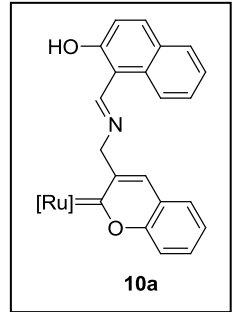
14.7734

9.3962
8.3347
8.3134
7.7775
7.7546
7.7382
7.7172
7.6526
7.6337
7.6157
7.5777
7.5596
7.5542
7.5510
7.5338
7.5310
7.4675
7.4599
7.4472
7.4405
7.4226
7.4099
7.3902
7.3688
7.3491
7.3254
7.2971
7.2749
7.2623
7.2547
7.2400
7.2119
7.1985
7.1826
7.1763
7.1675
7.1571
7.1389
7.1266
7.1119
7.1058
7.0654
7.0619
7.0442
7.0323
7.0265
7.0226
7.0048
6.9819
6.9629
6.9461
6.9237
6.9057
6.0345
6.0132
5.1550
4.7969



NTU

```
NAME          nantou 89-202.8
EXPNO         120
PROCNO        20120425
Date_         20120425
Time          16.04
PROBHD        5 mm QNP1H
PULPROG       zgpg30
SOLVENT       CDCl3
NS            1576
DS            4
SOLVENT       CDCl3
AQ            30
DE            8223.680 Hz
F2           0.234897 Hz
AQ           1.9923444 sec
RG            101
DW            60.800 usec
DE            0.50 usec
TE            301.2 K
DQ            1.00000000 sec
VFO          1
----- CHANNEL f1 -----
NUC1          13
P1            12.00 usec
PL1          -1.00 dB
PL12         13.43948010 dB
PL1M         400.1326010 MHz
NUC2          1H
P2            32760
PL2          0.00 dB
PL2M         400.1260160 MHz
MCW          no
SFO          0
LB            0.00 Hz
GB            0
PC            1.00
```



15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm

0.821

0.991

1.021

1.251

1.711

0.711

2.611

2.601

12.921

30.021

8.571

1.081

2.221

5.001

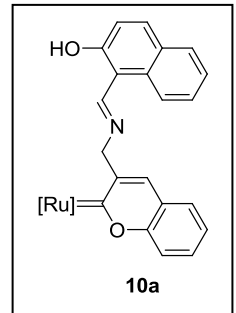
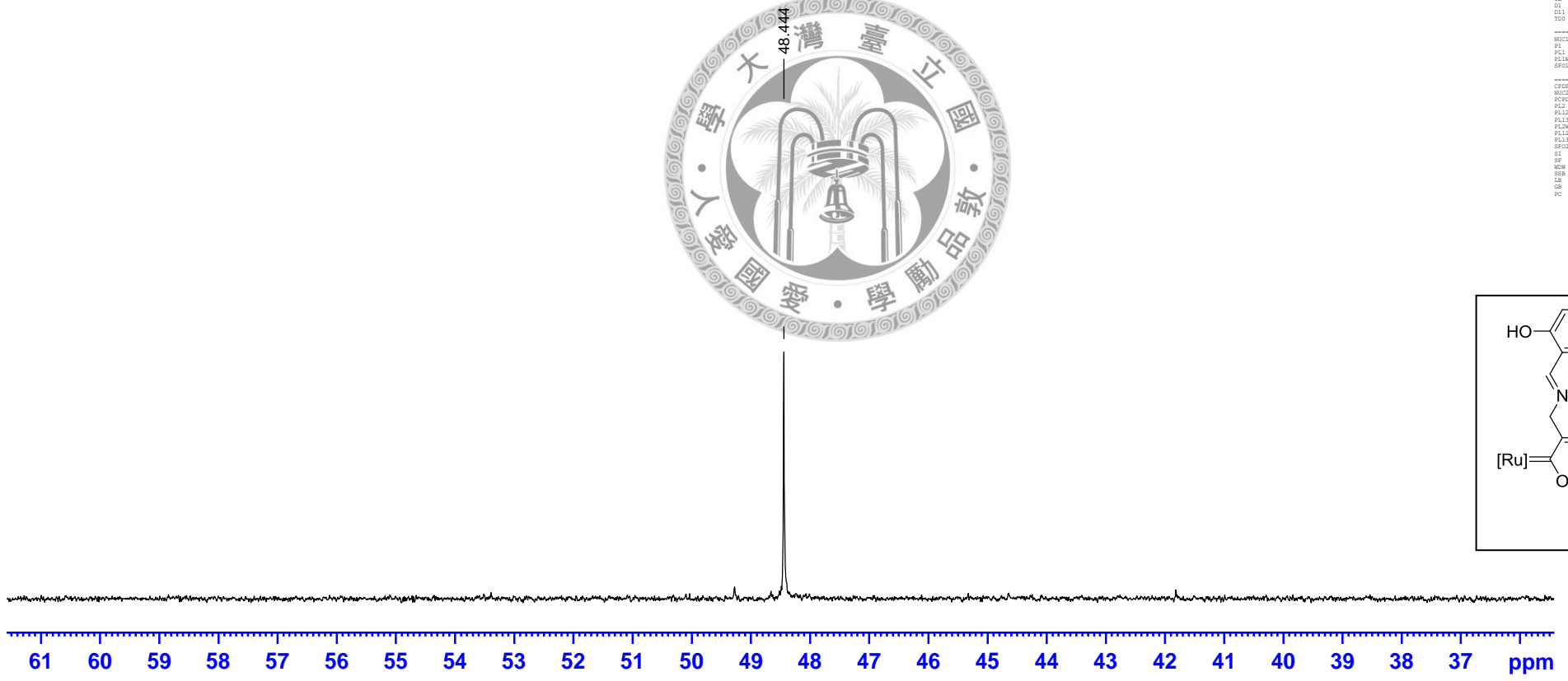
400MHz 31P 89-202.8 CDC13

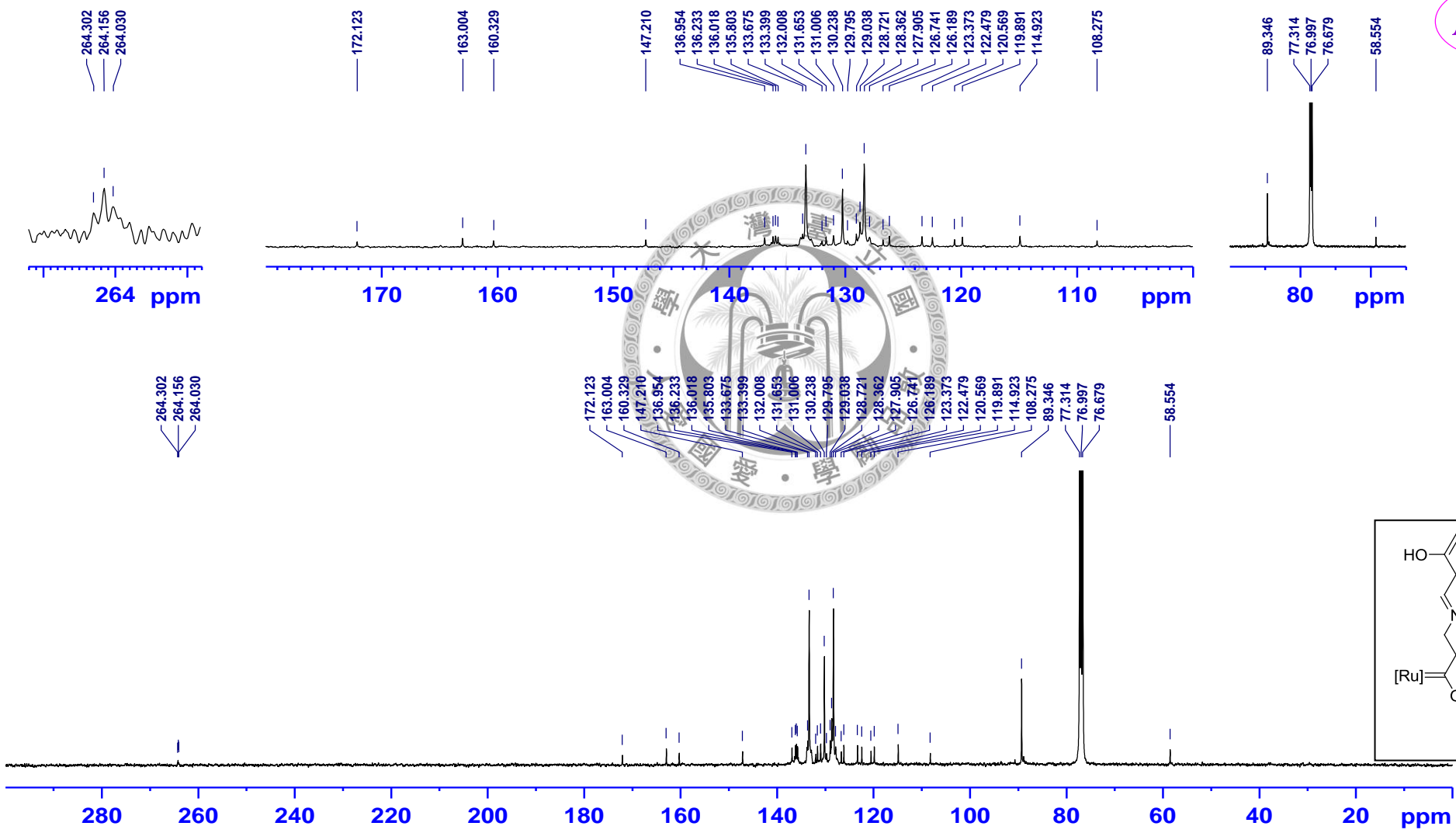


```
NAME      mantou 89-202.8
EXPNO     500
PROCNO    1
Date_     20120425
Time      16.05
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         5
DS         4
SFO1      64102.563 Hz
F2RES     0.378127 Hz
AQ         0.5112308 sec
RG         2500
DM         7.800 usec
DE         6.50 usec
TE         301.1 K
DQ         2.0000000 sec
D11        0.0300000 sec
TD0        1

----- CHANNEL f1 -----
NUC1       31P
P1         14.10 usec
P11        4.00 dB
P12        9.0600002 dB
SF01      161.975590 MHz

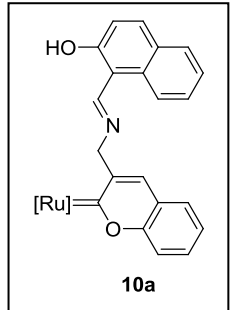
----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PC12      -1.00 dB
PC13      18.50 dB
PC14      18.50 dB
PC15      13.4388810 dB
PC16      0.30287895 dB
PC17      0.15079968 dB
PC18      400.1316016 MHz
SF        65536
RF         161.981690 MHz
WDW       EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```





```

NAME: mantou 89-202.9
EXPNO: 402
PROCNO: 20120425
Date_ : 22.04
INSTRUM: spect
PROBHD: 5 mm PABBO 101
PULPROG: zgpg30
TD: 65536
SOLVENT: CDC13
NS: 8192
DS: 4
F2: 44444.445 Hz
AQ: 0.072168 Hz
RG: 0.712300 Hz
DE: 20.00
CW: 11.250 usec
TE: 300.2 K
D1: 3.3000000 sec
d11: 0.0300000 sec
DELTA: 3.4000010 sec
TDO: 17
===== CHANNEL f1 =====
NUC1: 13C
P1: 10.00 usec
PL1: 10.00 dB
SFO1: 100.638987 MHz
===== CHANNEL f2 =====
CHRG2: 461144
NUC2: 1H
P2: 90.00 usec
PL2: -1.00 dB
PL12: 19.40 dB
SFO2: 400.147600 MHz
SI: 32768
SF: 100.638987 MHz
WDW: EM
SSB: RB
GB: 5.00
PC: 1.40
    
```



400MHz 1H 37-209.5 (p) CDC13

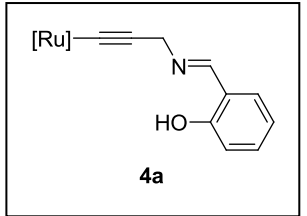
14.1971

8.8054
8.8011
8.7966
7.4640
7.4464
7.4422
7.4216
7.2400
7.2023
7.1844
7.1667
7.1006
7.0824
7.0635
6.9102
6.8895
6.6332
6.6147
6.5981
6.5961
6.5180
6.5141
6.4989
6.4950
4.7393
4.7361
4.3086



NTU

```
NAME mantou 37-209.5 (p)
EXPNO 1
PROCNO 1
DATA_ 012042
TIME 14.16
PROCURE
PROCNO 5
PULPROG zgpg30
TD 4920
SOLVENT Acetone
SI 32768
SF 16025.641 Hz
FIDRES 0.489058 Hz
AQ 1.0224114 sec
RG 71.8
DM 31.200 usec
DE 6.20 usec
TE 298.0 K
D1 1.00000000 sec
D11 1
===== CHANNEL f1 =====
NUC1 13
P1 12.10 usec
PL1 -3.00 dB
SFO1 400.130001 MHz
F2 1
PC 1
RF 400.1300176 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
```



16 15 14 13 12 11 10 9 8 7 6 5 4 3 ppm

0.98

1.01

12.24

7.58

12.41

1.03

0.97

0.97

2.04

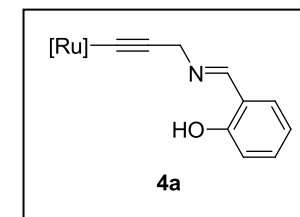
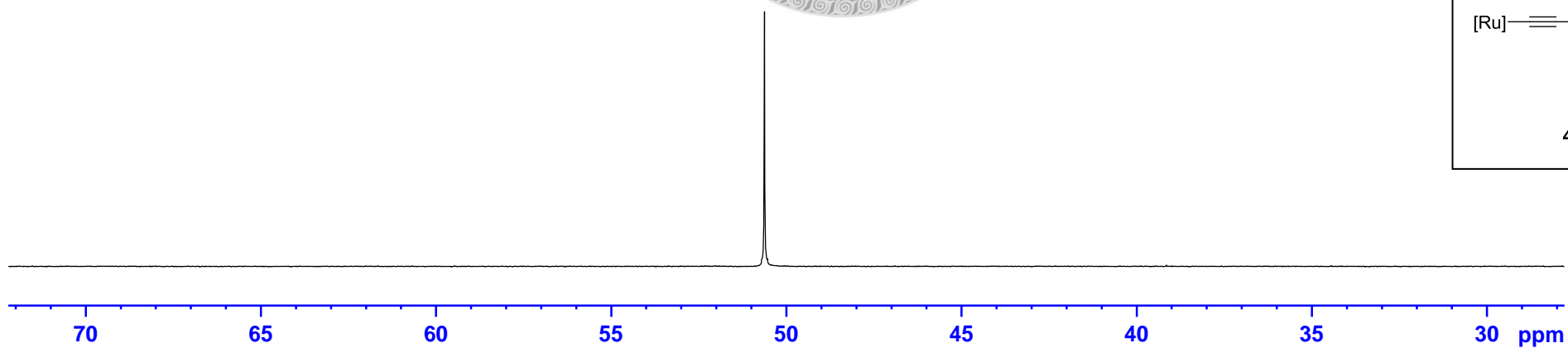
5.00

400MHz P31 37-209.5(p) CDC13

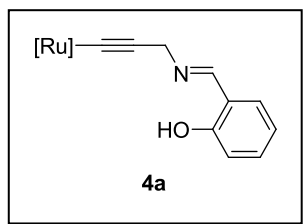
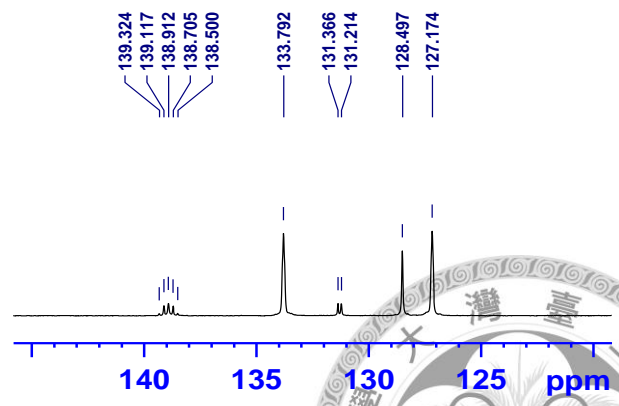
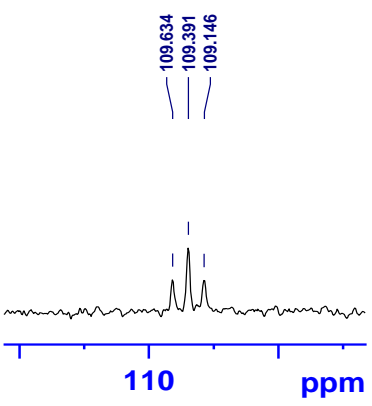


50.627

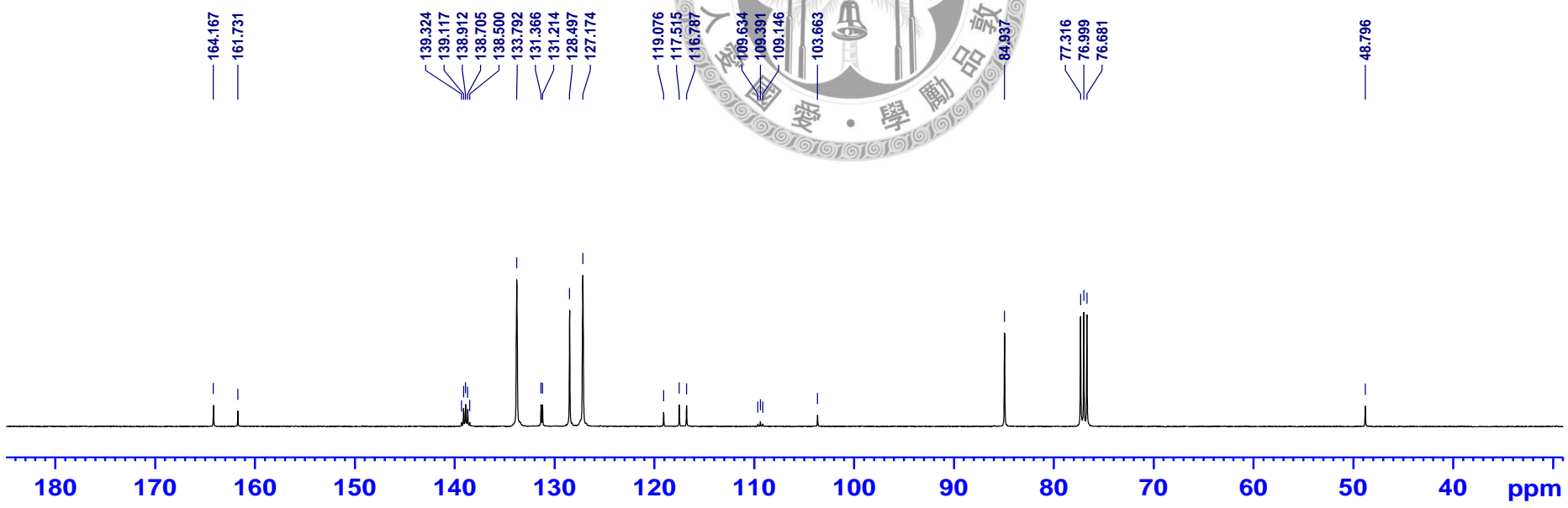
```
NAME      mantou 37-209.5(p)
EXPNO     1
PROCNO    1
Date_     20120412
Time      14.14
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         4
DS         4
SWH        58479.131 Hz
F2REQ2    0.892157 Hz
AQ         0.5603828 sec
RG         8192
DM         8.550 usec
DE         6.50 usec
TE         298.0 K
SI         2.0000000 sec
d11        0.0300000 sec
DELTA     1.8999998 sec
TDO        1
----- CHANNEL f1 -----
NUC1       31P
P1         12.80 usec
P11        0.00 dB
SFO1       161.9755930 MHz
----- CHANNEL f2 -----
CNUFREQ2   waltz16
NUC2        1H
PCPD2       90.00 usec
P12         -1.00 dB
P13         18.40 dB
SFO2       400.1314000 MHz
SI          32768
SF         161.9755477 MHz
DS          0
SSB         1.00 Hz
LB          0
GB          0
PC          1.40
```



500MHz 13C 37-209.5 (p) (103) CDC13



```
NAME mantou 37-209.5 (p)
EXPNO 1
PROCNO 1
DATA_ 20120422
TIME 11.30
INSTRUM spect
PROBHD 5 mm PABBO 1H1
PULPROG zgpg30
TD 65536
SOLVENT CDC13
SI 180
SF 500.135
F2 44444.444 Hz
FIDRES 0.476148 Hz
AQ 0.7373350 sec
RG 32768
DM 11.250 usec
DE 16.00 usec
TE 298.2 K
D1 3.50000000 sec
d11 0.03000000 sec
DELTA 3.40000010 sec
TDO 0
===== CHANNEL f1 =====
NUC1 13C
P1 16.00 usec
PL1 -2.00 dB
SFO1 100.6283701 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 12.00 usec
PL2 -1.00 dB
PL12 19.40 dB
PL13 19.40 dB
SFO2 400.1418910 MHz
SI 32768
SF 500.1357694 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
```



400MHz 1H 92-212.6 CDC13

13.5673

8.7164
7.4792
7.4581
7.4381
7.2400
7.1901
7.1721
7.1541
7.1226
7.0925
7.0741
7.0555
6.8199
6.7977
6.7741
6.7671
6.7519
6.7448
5.8614
5.8544

4.7727

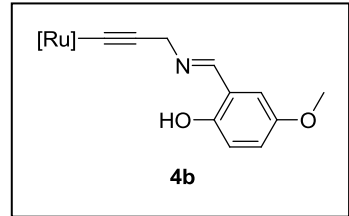
4.3008

3.3745



NTU

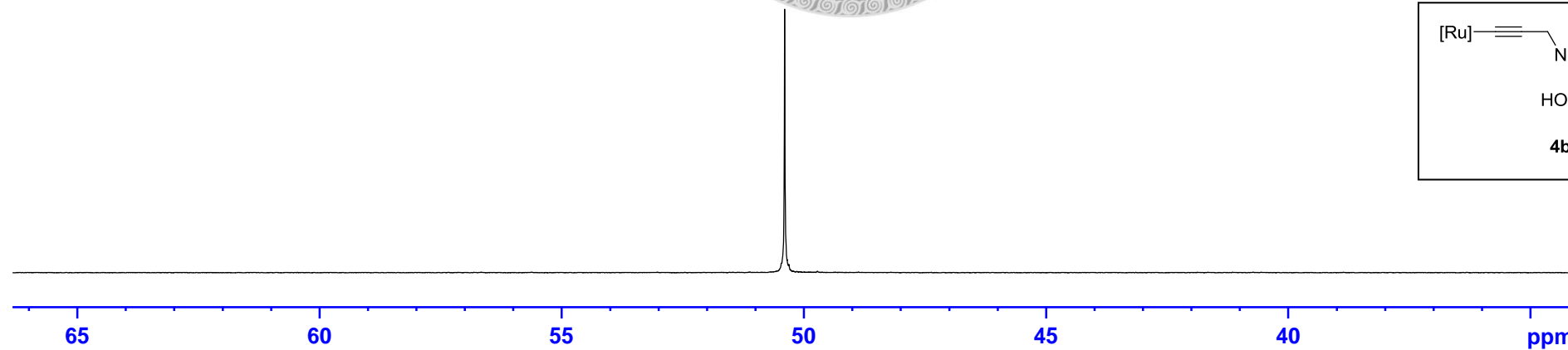
```
NAME          hanton 92-212.6
EXPNO         170
PROCNO        20120471
DATE_         17.10
TIME          09:01
PROBHD        5 mm QNP5
PULPROG       zgpg
SOLVENT       CDCl3
NS            1570
SOLVENT       CDCl3
AQ            0
DE            16025.640 Hz
NUC1          13
NUC2          13
F2          0.488468 MHz
AQ            1.0224114 sec
RG            512
DW            31.200 usec
DE            0.50 usec
TE            301.4 K
DQ            1.0000000 sec
SFO          400.146363 MHz
===== CHANNEL f1 =====
NUC1          13
P1            12.00 usec
PL1          -1.00 dB
PL12         13.43948010 MHz
NUC2          13
P2            32.760 usec
PL2          0.00 dB
MCW          no
SFO          400.146363 MHz
IR          0.00 Hz
GB            0
PC            1.00
```



14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm

0.92
0.97
12.15
19.86
2.15
0.96
2.03
5.00
2.96

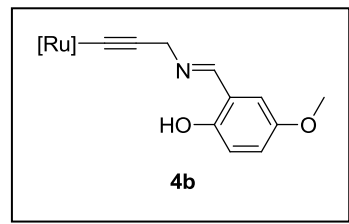
400MHz 31P 92-212.6 CDC13



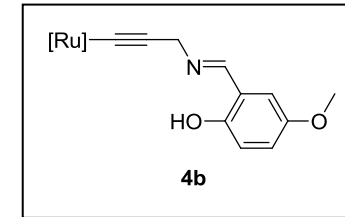
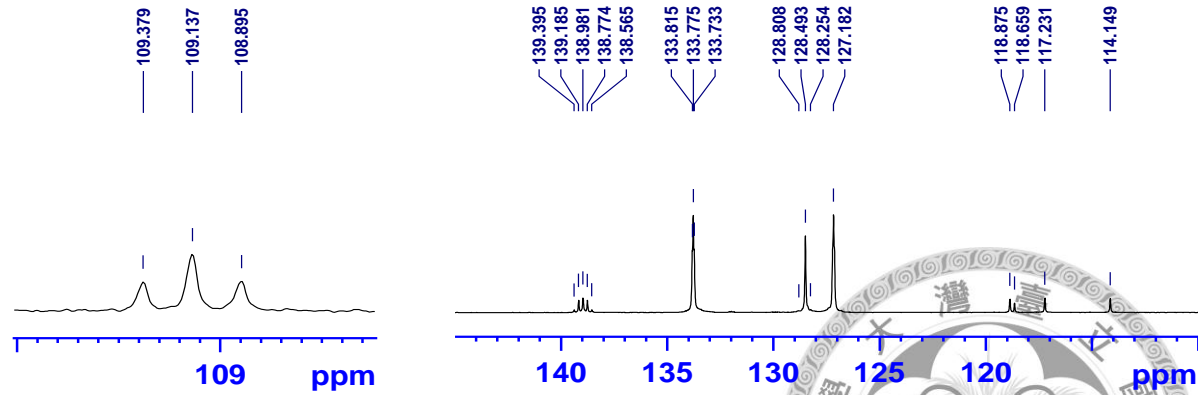
```
NAME mantou 92-212.6
EXPNO 1
PROCNO 1
Date_ 20120427
Time 17.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
PC 1
NS 4
DS 2
SWH 64102.163 Hz
F2RES 0.278127 Hz
AQ 0.5112108 sec
RG 2050
DM 7.800 usec
DE 6.50 usec
TE 301.3 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 31P
P1 14.10 usec
PL1 4.00 dB
PL1W 9.0600042 Hz
SFO1 161.9755900 MHz

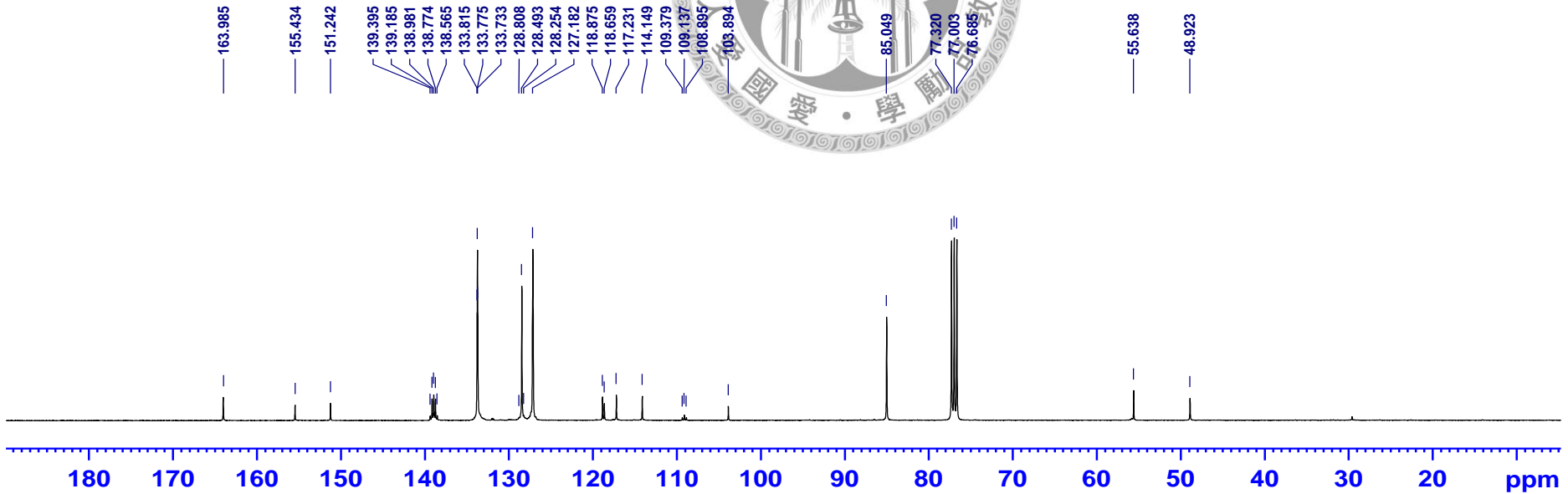
===== CHANNEL f2 =====
CNUFREQ2 waltz16
NUC2 1H
PCF02 80.00 usec
PL2 -1.00 dB
PL2 18.00 dB
PL3 18.00 dB
PL4 13.4398810 Hz
PL1W 0.30287695 Hz
PL1W 0.15079688 Hz
SFO2 400.1464004 MHz
SFO 650.36 MHz
SF 161.9836890 MHz
MSH 0
SBS 0
LB 1.00 Hz
GB 0
PC 1.40
```



400MHz 13C 92-212.7 CDC13



```
NAME mantou 92-212.7
EXPNO 402
PROCNO 1
Date_ 20120417
Time 23:31
INSTRUM spect
PROBHD 5 mm PABBO MM
PULPROG zgpg30
TD 65536
SOLVENT cdcl3
RG 320
DS 28248.588 Hz
FIDRES 0.431039 Hz
AQ 1.160272 sec
RG 320
AQ 1.160272 sec
DE 17.700 usec
TE 300.2 K
DE 17.700 usec
TE 300.2 K
SI 2.0000000 sec
SI 2.0000000 sec
DELTA 1.8999998 sec
DELTA 1.8999998 sec
TD 19
===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
P11 -3.00 dB
SFO1 100.628487 MHz
===== CHANNEL f2 =====
CPCPRG2 waltz16
NUC2 13C
P2 90.00 usec
P21 -3.00 dB
P22 3.00 dB
P23 3.00 dB
P24 3.00 dB
P25 3.00 dB
P26 3.00 dB
P27 3.00 dB
P28 3.00 dB
P29 3.00 dB
P30 3.00 dB
SFO2 400.1516003 MHz
SI 32768
SF 100.617786 MHz
RG 320
DS 0
DE 0
TE 300.2 K
SI 2.0000000 sec
SI 2.0000000 sec
DELTA 1.40
```



400MHz 1H 45-145 111029 CDC13

13.1334

8.7247
7.4941
7.4912
7.4749
7.4722
7.4197
7.3998
7.3952
7.3702
7.3532
7.3236
7.3202
7.3027
7.2845
7.2810
7.2093
7.1894
7.1697
7.1569
7.1358
7.1173
7.0865
7.0715
7.0539
7.0298
7.0121
6.9950
6.9766
6.9567
6.9504
6.9297
6.8820
6.8635
6.8453
6.3451
6.3240
4.9590
4.8892
3.2789
3.2587
3.2401
3.2239
3.2056
3.1883
3.1596
3.0450
3.0143
2.9973
2.9791
2.9647
2.9459
2.9257

NTU

```
NAME      hantou 45-145 111029
EXPNO     1
PROCNO    1
PROCNAME  20111029
TIME      13.34
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   Acetone-d6
DE        0
DS         4
F2       400.136298 MHz
F1       400.136298 MHz
AQ        0.244532 Hz
RG         62.400
RW         71.8
DN         6.50 usec
DE         298.2 K
TE         1.00000000 sec
D1         1
D11        1
D12        1
D13        1
D14        1
D15        1
D16        1
D17        1
D18        1
D19        1
D20        1
D21        1
D22        1
D23        1
D24        1
D25        1
D26        1
D27        1
D28        1
D29        1
D30        1
D31        1
D32        1
D33        1
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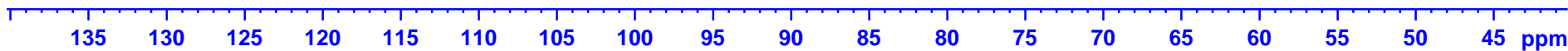
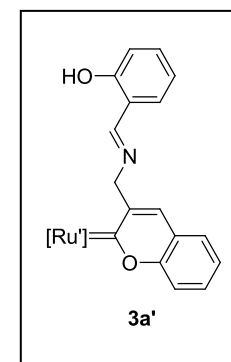
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400MHz P31 45-111209 d-acetone

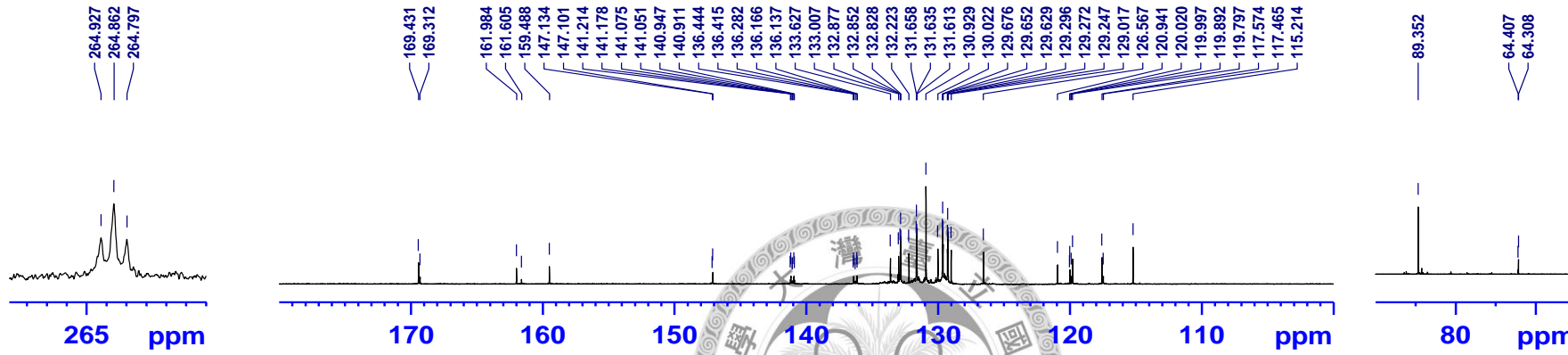


90.587

```
NAME      mantou 45-111209
EXPNO     1
PROCNO    1
Date_     20111209
Time      11.26
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
PC         4
NS         14
DS         4
SWH        58479.131 Hz
F2RES     0.892127 Hz
AQ         0.5603828 sec
RG         8192
DM         8.550 usec
DE         6.50 usec
TE         298.7 K
SI         2.0000000 sec
dS1        0.5300000 sec
DELTA     1.8999998 sec
TDO        1
===== CHANNEL f1 =====
NUC1       31P
P1         12.80 usec
P12        0.00 dB
SFO1      161.9755930 MHz
===== CHANNEL f2 =====
CPOPRG2    waltz16
NUC2        1H
PCPD2       90.00 usec
P122        -1.00 dB
P123        18.40 dB
P133        18.40 dB
SFO2      400.1314000 MHz
SI          32768
SF         161.9755477 MHz
WDW         EM
SSB         0
GB          1.00
PC          1.40
```



800MHz 13C 45-104.7 d-acetone

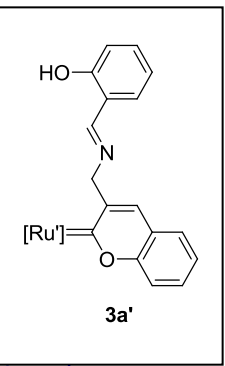
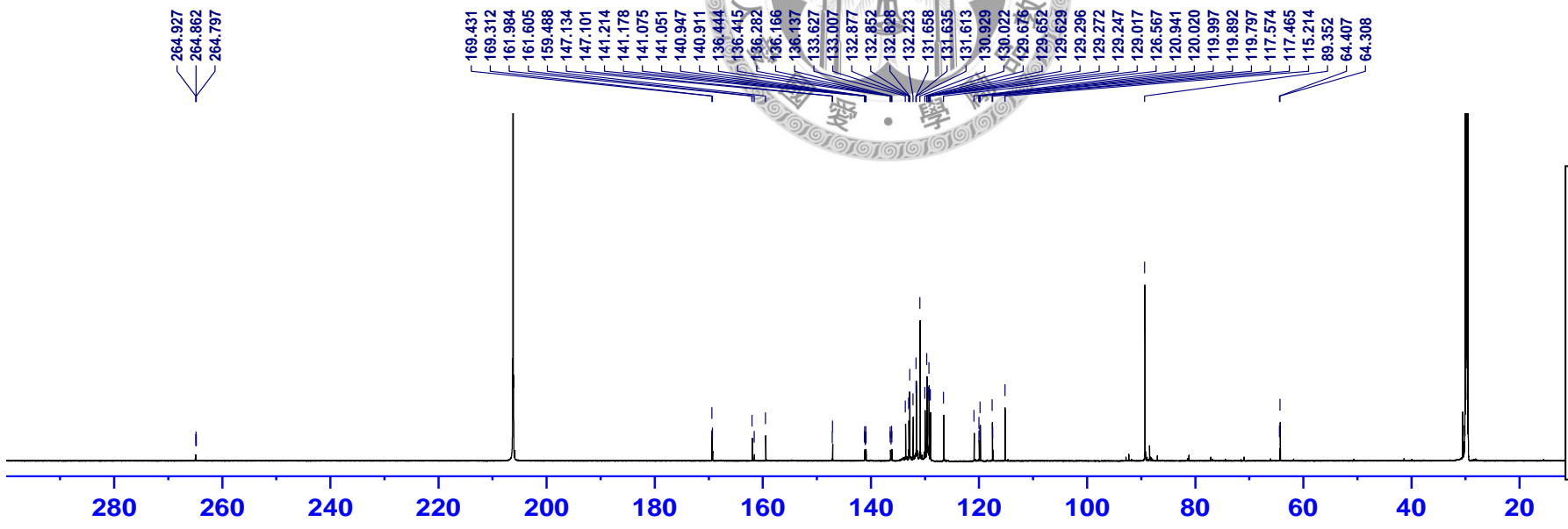


```

NAME      linyo-hbo-110107-45-104.7
EXPNO     1
PROCNO    1
DATE_     20110707
TIME      15.20
INSTRUM   spect
PROBHD    5 mm QNP1H 1H-
PULPROG   zgpg30
TD        65536
SOLVENT   Acetone
NS        144
DS        4
SWH        89285.111 Hz
FIDRES    0.6812003 Hz
AQ         0.132216 sec
RG         456
LW        25.000 uHz
GB         0
TE         296.0 K
DE         3.50000000 uHz
D11        0.03000000 sec
D15        0.03000000 sec
TD0        100

===== CHANNEL f1 =====
NUC1       13C
P1         11.00 uSec
PL1        -2.00 dB
PL12M     149.63611207 MHz
SFO1       201.2646479 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     100.00 uSec
PL2        0.00 dB
PL12      24.00 dB
PL13      27.00 dB
PL14      10.51812129 MHz
PL12M     0.08948279 MHz
PL13M     0.08484763 MHz
SFO2       800.2040000 MHz
Z1         0.02144
SF         201.2102768 MHz
WDW        EM
SSB        0
GB         1.00 Hz
PC         1.00
  
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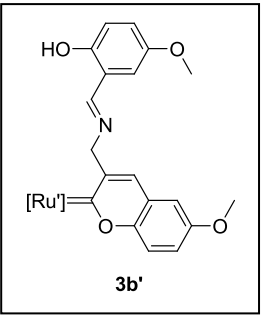
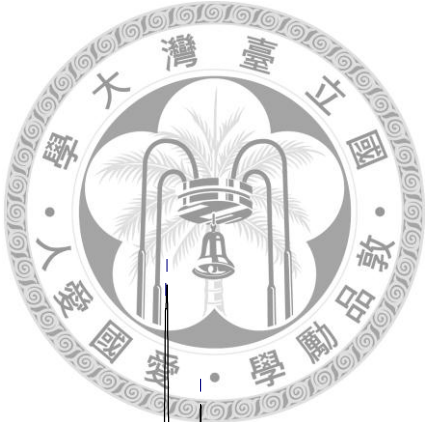
400MHz 1H 55-127.4 CDC13

12.7219

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2.9444
2.9257
2.9055



```
NAME          mantou 55-127.4
EXPNO         10
PROCNO        2011905
Date_         20110905
Time          19.44
PROBHD        5 mm QNP5B
PULPROG       zgpg30
SOLVENT       Acetone
SOLVENT2      Acetone
DE            0
FIDRES        0.248333 Hz
AQ            2.0447731 sec
RG            512
DS            4
SWH            62.400 MHz
DE            0.200 MHz
TE            297.2 K
DQ            1.0000000 sec
VFO           400.1300000 MHz
----- CHANNEL f1 -----
NUC1          13
P1            12.00 MHz
PL1           -2.00 dB
SFO1         400.1300000 MHz
SI            65536
SF           400.1300000 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            1.00
PC            1.00
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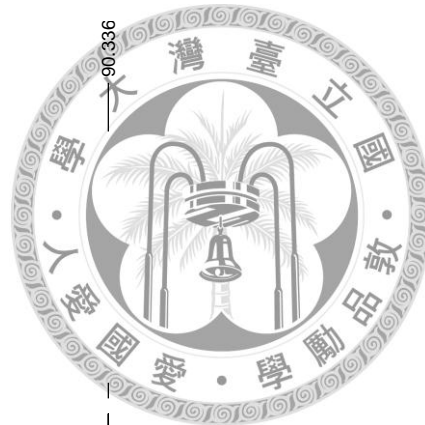


14 13 12 11 10 9 8 7 6 5 4 3 2 ppm

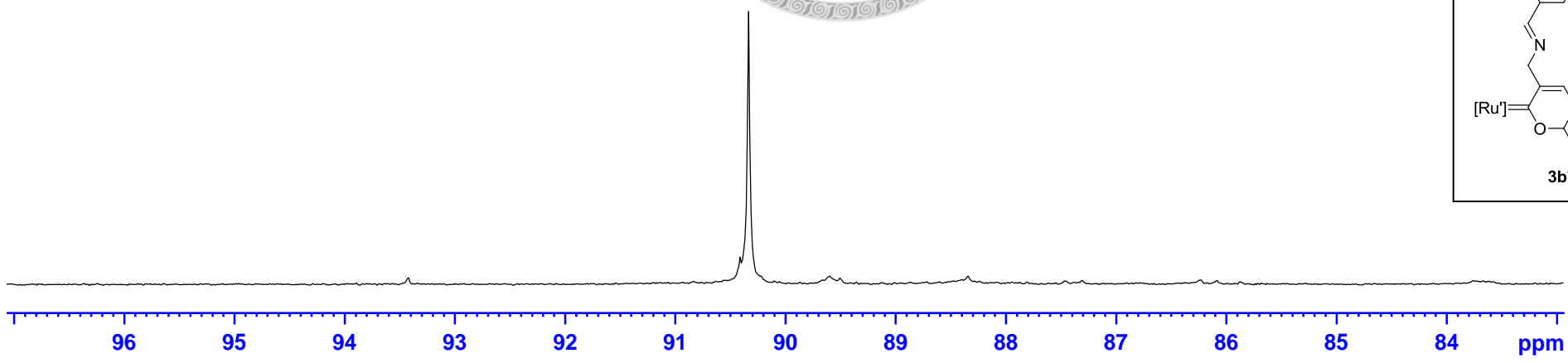
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1.11
5.29
2.41
2.92
3.38

95

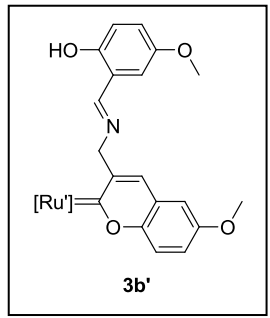
400MHz P31 55-127.3 CDCl3



90.336



```
NAME mantou 55-127.3
EXPNO 1
PROCNO 1
Date_ 20110802
Time 16.18
INSTRUM spect
PROBHD 5 mm PABBO 5B/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
AQ 0.5603828 sec
RG 6192
DS 8.350 usec
DE 6.50 usec
TE 297.7 K
D1 2.0000000 sec
d11 0.5300000 sec
DELTA 1.8999998 sec
TD0 1
----- CHANNEL f1 -----
NUC1 31P
P1 12.80 usec
P12 0.00 dB
SFO1 161.9755930 MHz
----- CHANNEL f2 -----
CPOPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
P12 -3.00 dB
P12 18.40 dB
P13 18.40 dB
SFO2 400.1314000 MHz
SI 32768
SF 161.9755477 MHz
SSB 0
LB 0
GB 1.00 Hz
PC 1.40
```



400MHz 1H 69-168.1 CDC13

7.2400
6.7602
6.7384
6.7289
6.7220
6.7068
6.7000
6.6815
6.6775
6.5948
6.5880
6.5208

5.3401

4.0234

3.7177

3.4340

3.4279

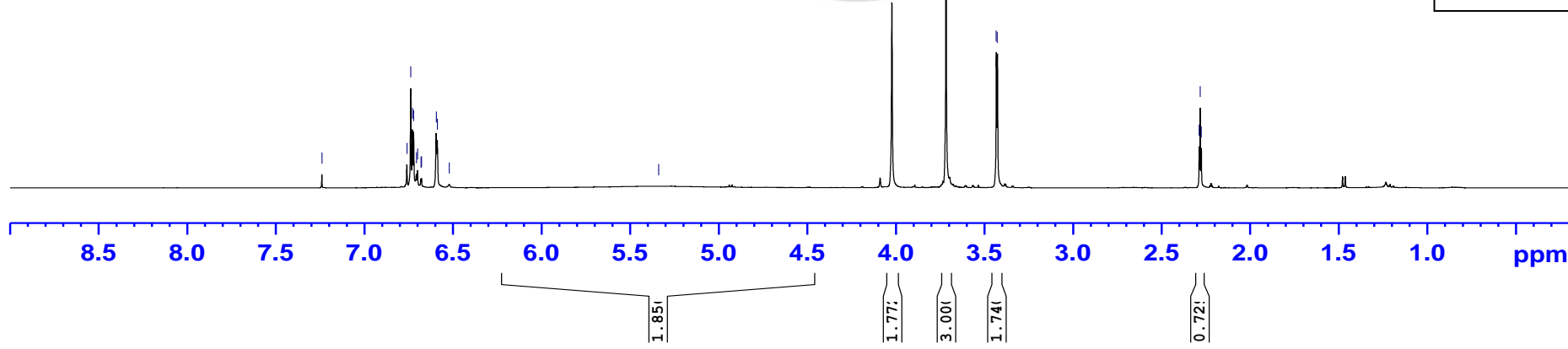
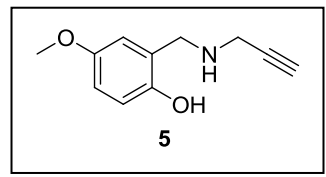
2.2886

2.2826

2.2765

NTU

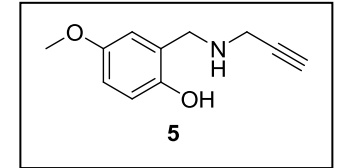
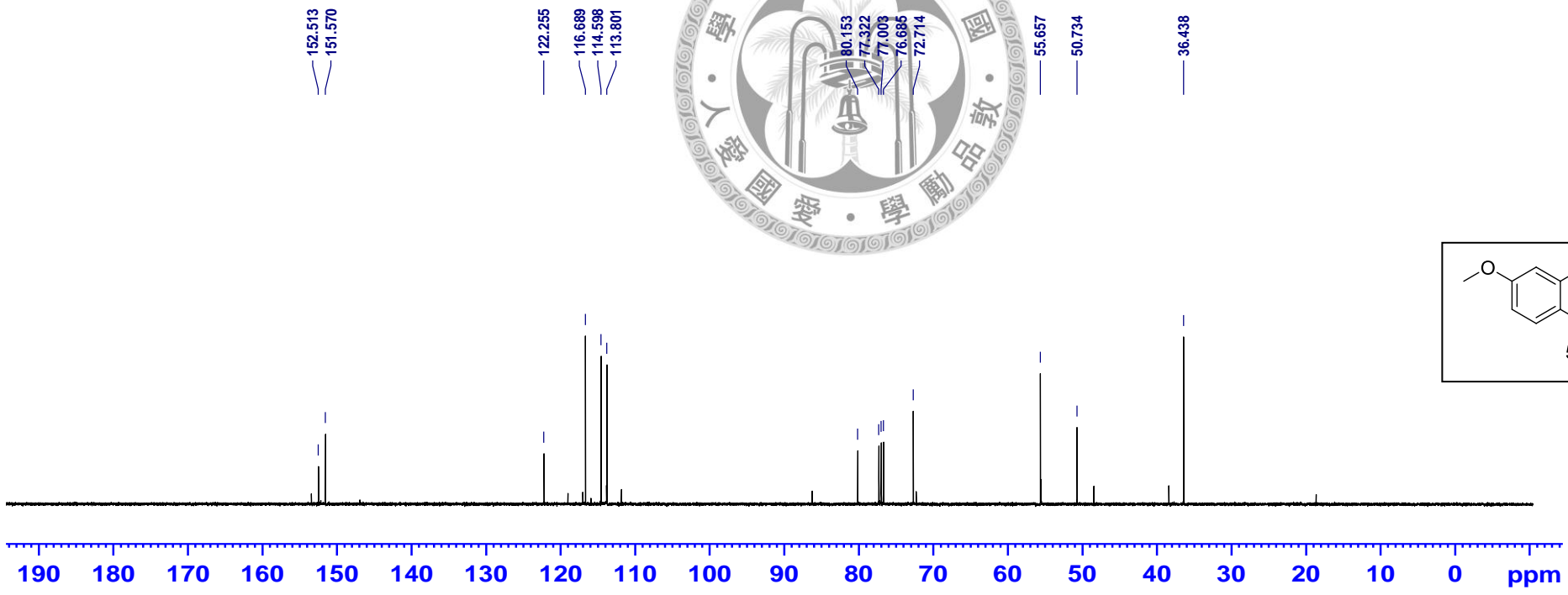
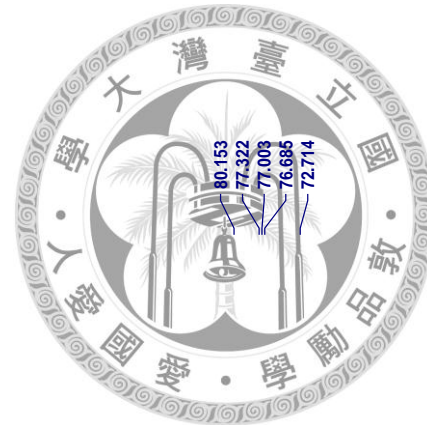
```
NAME      hantou 69-168.1
EXPNO     1
PROCNO    1
Date_     20111125
Time      17.16
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         32768
SOLVENT   MeCN-d3
NS         25
DS         2
SWH        8032.820 Hz
FIDRES     0.244532 Hz
AQ         2.0447131 sec
RG         62.600
DSH        1.8
DE         6.50 usec
TE         298.6 K
T2        1.00000000 sec
T3         1
TDO        1
----- CHANNEL f1 -----
NUC1       1H
P1         12.10 usec
PL1        -2.50 dB
PR1        400.330007 MHz
SI         65036
SF         400.330077 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.00
```



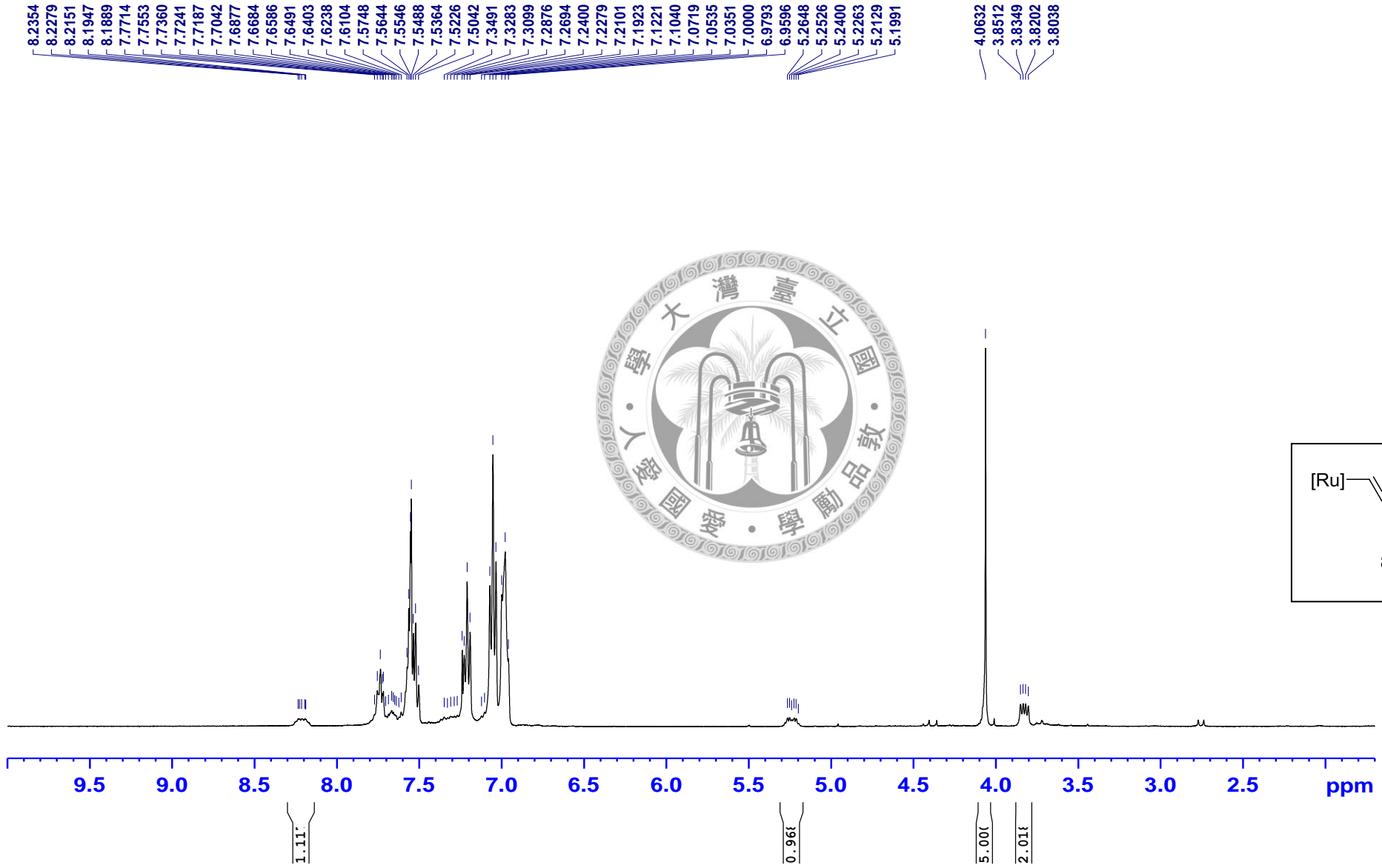
400MHz 13C 69-168.1 CDC13



```
NAME      man100 69-168.1
EXPNO     400
PROCNO    2011121
Date_    18.10
INSTRUM   spect
PROBHD    5 mm PABBO BB7
PULPROG   zgpg30
SOLVENT   CDCl3
NS        150
DS        4
SWH        25244.848 Hz
FIDRES    0.431019 Hz
AQ        1.1620372 sec
RG        812.5
DE        37.700 usec
TE        300.2 K
DELTA     2.0000000 sec
d11       0.0300000 sec
DELTA     1.8999998 sec
TD        1
----- CHANNEL f1 -----
NUC1       13C
P1         19.00 usec
PL1        +1.00 dB
SFO1       100.628467 MHz
----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
P2         90.00 usec
PL2        +1.00 dB
PL12       18.00 dB
PL13       18.00 dB
SFO2       400.1416000 MHz
SI         100.627768 MHz
RF         400.1416000 MHz
WDW        EM
SSB        0
GB         0.00 Hz
PC         1.40
```

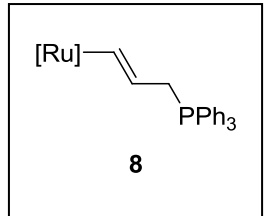


400MHz 1H 70-197.4(p) CDC13

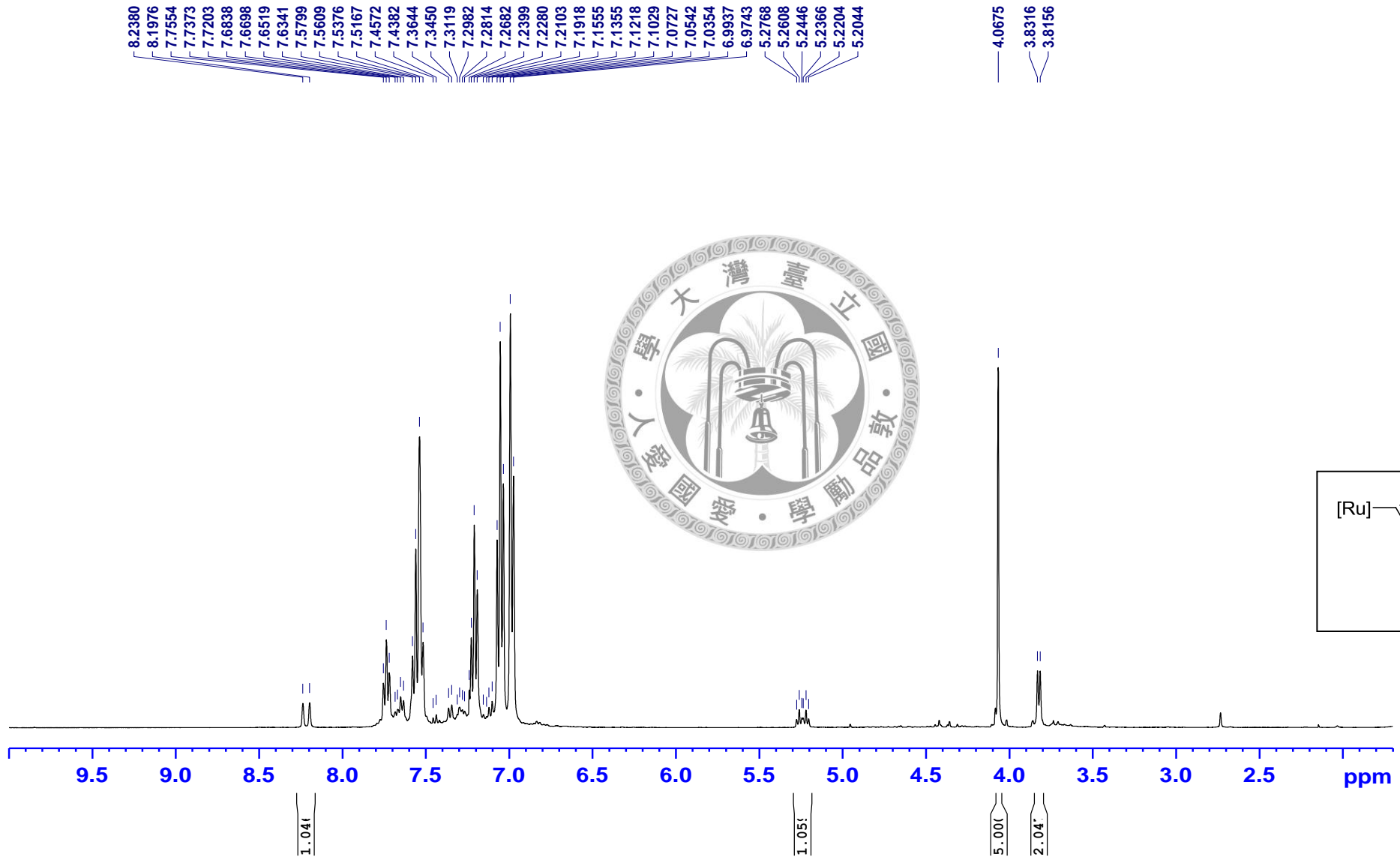


NTU

```
NAME          mantou 70-197.4(p)
EXPNO         1
PROCNO        1
Date_         20120221
Time          15:51
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zg30
TD            32768
SOLVENT       Acetone
NS            24
DS            0
SWH           8012.800 Hz
FIDRES       0.244532 Hz
AQ           0.0447131 sec
RG           143.7
SQ           42.400 sec
DS           8.00 sec
TE           298.0 K
SI           1.00000000
SFO          400.1300000 MHz
----- CHANNEL f1 -----
NUC1          1H
P1           12.10 usec
PL           -1.00 dB
PR1          400.1300000 MHz
SF           400.1300000 MHz
WDW          po
SSB           0
LB           0.00 Hz
GB           0
PC           1.00
```



400MHz 1H 70-197 (dec) (200) CDC13

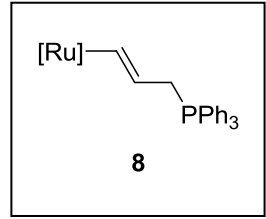


NTU

```
NAME          nantou 70-197 (dec)
EXPNO         200
PROCNO        1
Date_         20120323
Time          16:25
INSTRUM       spect
PROBHD        5 mm PABBO 4B/
PULPROG       zgpg30
TD            32768
SOLVENT       Acetone-d6
AQ            0
DS            0
SWH           8012.800 Hz
F2DRS         0.244532 Hz
AQ           2.0447711 sec
RG            71.8
DE           42.400 sec
TE           8.50 sec
TE           288.5 K
SI            2.0000000 sec
AQ           0.03000000 sec
TD           1

===== CHANNEL f1 =====
NUC1          1H
P1            12.10 usec
PL1           -2.10 dB
SFO1          400.1326010 MHz

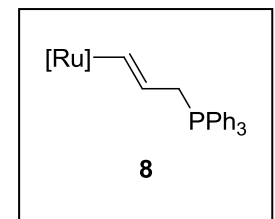
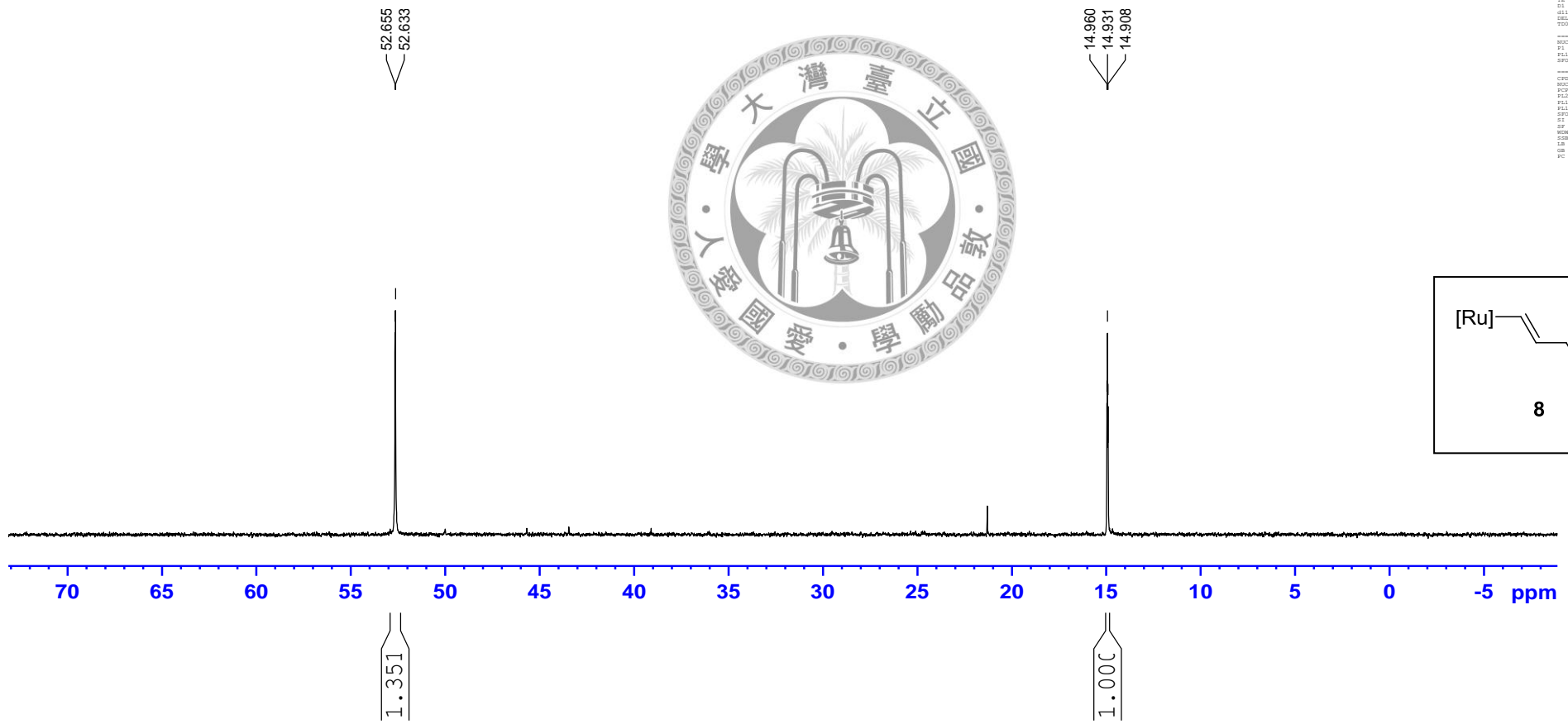
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          13C
PCPD2         90.00 usec
PL2           120.00 dB
PL12          15.40 dB
SFO2          101.6261200 MHz
SI            65536
SF            400.1300900 MHz
WDW           no
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
```



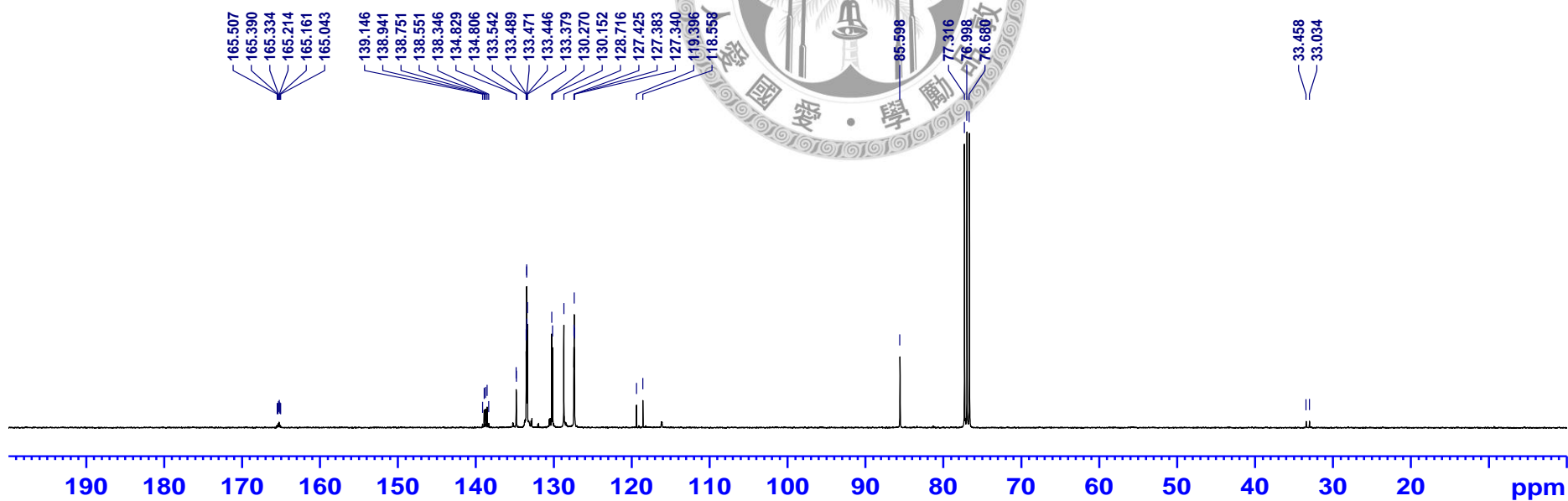
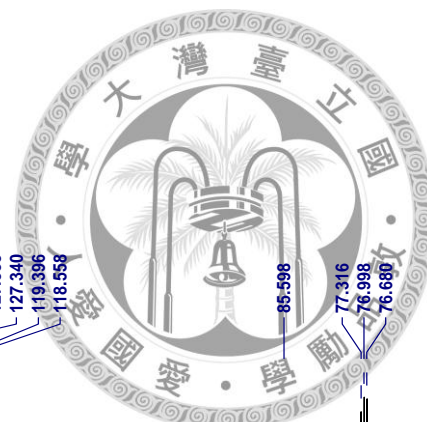
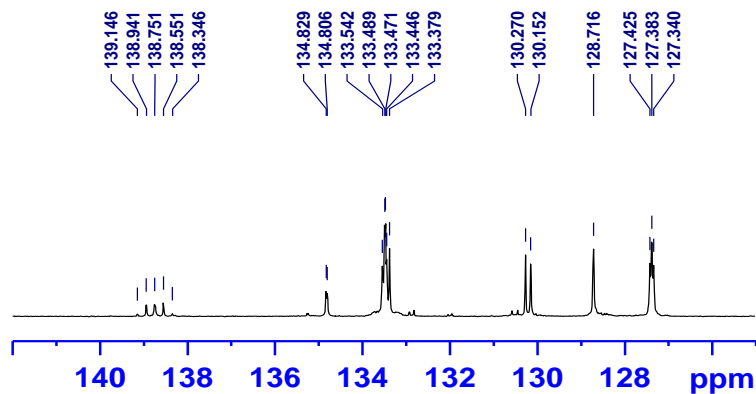
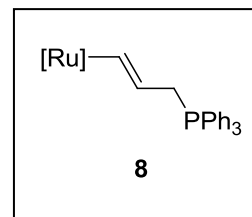
400MHz P31 70-197.4 (p) CDC13



```
NAME mantou 70-197.4(p)
PROCNO 302
Date_ 20120321
Time_ 19.49
INSTRUM spect
PROBHD 5 mm PABBO-DE/
PULPROG zgpg30
TD 65524
SOLVENT CDC13
NS 4
DS 58479.531 Hz
FIDRES 0.82123 Hz
AQ 0.5603228 sec
RG 819
SM 8.150 uV/cm
SE 6.20 uV/cm
TE 297.2 K
SI 2.00000000 sec
d11 0.03000000 sec
DELTA 1.8999998 sec
TD0 1
----- CHANNEL f1 -----
NUC1 31P
P1 12.00 uV/cm
PL1 0.00 dB
SFO1 161.975350 MHz
----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 uV/cm
PL2 -1.00 dB
PL12 18.40 dB
PL13 18.40 dB
SFO2 400.136050 MHz
SI 0.2768 sec
RF 161.975347 MHz
WDW EM
GB 0
LB 1.00 Hz
GB 0
PC 1.40
```



400MHz 13C 70-197.5(102) CDC13



```
NAME mantou 70-197.5
EXPNO 1
PROCNO 1
Date_ 20120311
Time 0.59
INSTRUM spect
PROBHD 5 mm PABBO MM-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 6144
DS 4
SWH 42016.809 Hz
FIDRES 0.441124 Hz
AQ 0.778264 sec
RG 2560
DM 11.900 usec
DE 6.51 usec
TE 298.2 K
D1 3.5000000 sec
D11 0.0300000 sec
TD0
----- CHANNEL f1 -----
NUC1 13C
P1 9.00 usec
PC1 -1.00 dB
PL1 41.10560770 dB
SFO1 100.6260949 MHz
----- CHANNEL f2 -----
PCPGR2 waltz16
NUC2 1H
P2 80.00 usec
PC2 -1.00 dB
PL2 19.00 dB
SFO2 400.1500000 MHz
P12W 0.30087693 u
PL12W 0.15000000 dB
SFO2 400.1500000 MHz
IS 12769
SS 100.6278059 MHz
RSH EM
SFO 100.6278059 MHz
LB 1.00 Hz
GB 0
PC 1.40
```

Single Mass Analysis

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

Selected filters: None

Monoisotopic Mass, Even Electron Ions

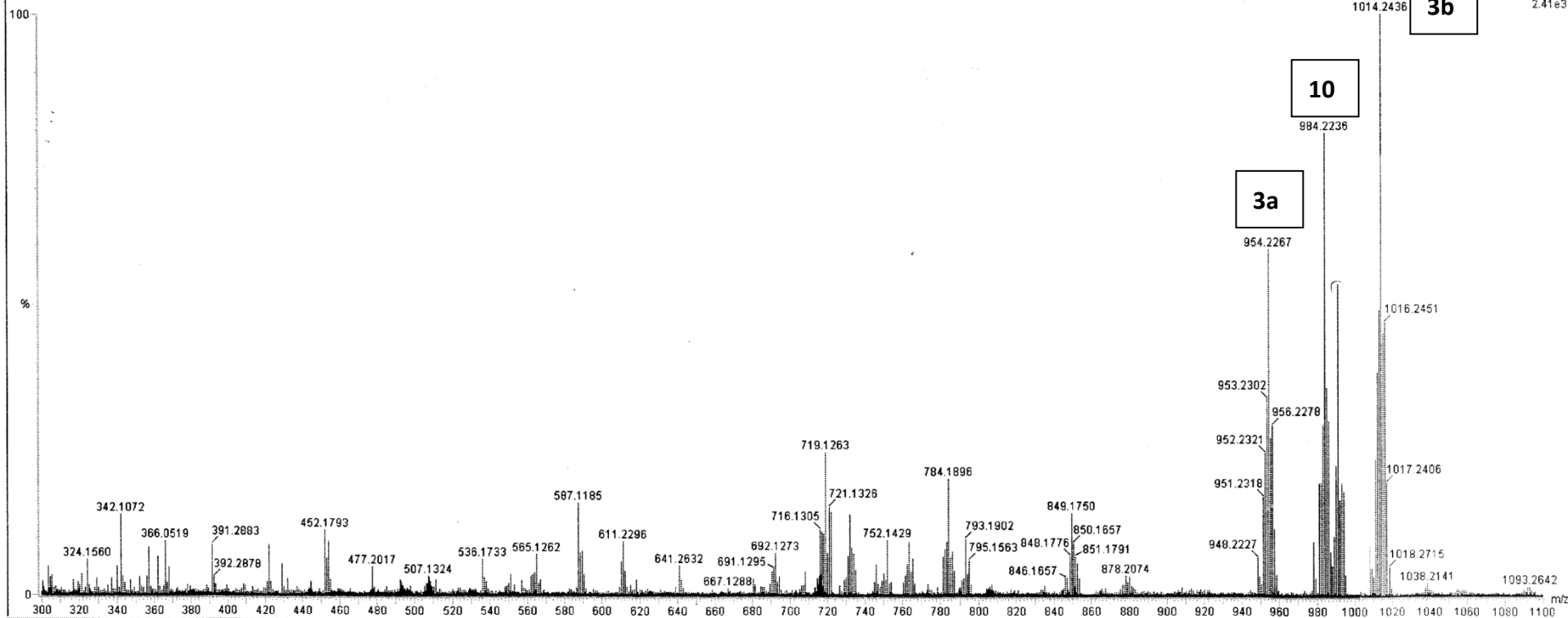
1131 formula(e) evaluated with 4 results within limits (up to 3 best isotopic matches for each mass)

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 04 P2 102Ru	27.2	60	52	1	4	2	1
	1014.2439	-0.3	-0.3	45.5	C67 H47 N 0 P 102Ru	42.4	67	47	1	1	1	1
	1014.2409	2.7	2.7	54.5	C71 H37 N 05 P	257.1	71	37	1	5	1	

mantou 42-98,2
10006_025 38 (0.803) Cm (35:41)



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

