A DOCTORAL DISSERTATION

Mn(III)-Catalyzed Olefin Oxidations by Using Molecular Oxygen in the Presence of $NaBH_4$

Department of Chemistry

GRADUATE SCHOOL
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$NaBH_4$ 존재 하에서 산소 분자 및 Mn(III) 촉매를 이용한 올레핀 산화반응

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이 논문을 이학 박사학위 논문으로 제출함

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(Supervised by Professor Nam Ho Lee)

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ABSTRACT

Molecular oxygen plays a pivot role in the biological systems. In addition, it is probably the most desirable oxidant in organic synthesis in terms of economical and environmental viewpoints. Therefore, lots of efforts have long been focused to utilize molecular oxygen for the oxidation of organic compounds especially using transition metals as an activator.

In nature, molecular oxygen is employed as an effective oxidant. In this biological process, an enzyme such as cytochrome P-450 is catalytically involved to activate molecular oxygen, where one-oxygen reductant such as NAD(P)H is necessarily consumed.

In this study, we have developed the oxidation method for the conversion of olefin to the corresponding alcohol under the oxygen. In this reaction used were the (salen)Mn(III) complex as the catalyst and $NaBH_4$ as a hydride source. Vinyl arenes undergo effective oxygenation under this condition, however, other simple olefins do not experience the desirable conversion due to low reactivity. In order to improve the scope of the olefin oxygenation procedure by development of the more effective catalyst, we have synthesized various (schiff-base)Mn(III) complexes, and examined the complexes as the catalyst for the oxygenation of olefins. As a result, newly synthesized Mn(III) complex **10** was proved to be effective catalyst for this method. Various type of olefins were effectively converted to alcohols using the catalyst **10** in the presence of molecular oxygen. We also have developed more practical oxygenation method, where readily avaliable Mn salt,

$Mn(OAc)_3 \cdot 2H_2O$ or $Mn(OAc)_2 \cdot 4H_2O$ was employed as the catalyst in the presence of catalytic amount of schiff-base ligand. This process affords the flexible reaction, because different type of ligands can be employed to various olefinic substrates as required.

α,β-Unsaturated carbonyl compound were oxidized to the saturated α-hydroxy esters by O_2 with reducing agent ($NaBH_4$ or $PhSiH_3$) in the presence of (schiff-base)Mn(III) complex **10**. The reaction proceeded in good yield under mild reaction conditions.

Mechanistically, the oxidation mechanism was consider to proceed *via* Mn(II) and Mn(III) interconversion as the catalytic cycle. In addition, hydride radical and peroxo radicals are considered to play a pivot role in this oxygenation system. The suggested mechanism was supported by the deuterium incorporation in the products obtained using $NaBD_4$.

When the reaction was examined using homochiral Jacobsen's catalyst, the chirality transfer was not observed.

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Symbols and Abbreviations

salen	bis(salicylidene)ethylenediaminato
t-Bu	*tertiary*-butyl
BHT	butylated hydroxytoluene
cat.	catalyst
DMSO	dimethyl sulfoxide
ee	enantiomeric excess
equiv.	equivalence
$Eu(hfc)_3$	Europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate
f.c.c.	flash column chromatography
i-PrOH	isopropyl alcohol
GC	gas chromatography
GC/MSD	gas chromatography / mass selective detector
TPP	*meso*-tetraphenylporphyrinato
TMPyP	*meso*-tetrakis(4-*N*-methylpyridyl)porphyrinato
Me	methyl
NADH	nicotinamide adenine dinucleotide reduced
NMR	nuclear magnetic resonance
Ph	phenyl group, C_6H_5-
rt	room temperature

Ⅰ. Introduction

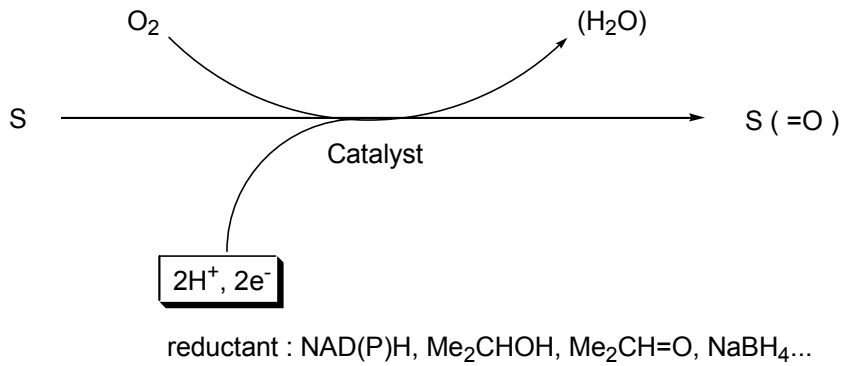
Molecular oxygen is vital element to almost all animals on earth as the biological oxidant to provide energy for life. In addition, it is probably the most desirable oxidant in organic synthesis in terms of economical and environmental point of view. As molecular oxygen is notably a very good oxidizing agent being cheap, abundant and readily available, lots of efforts have long been focused to utilize molecular oxygen for the oxidation of organic compounds. In industries, oxygen is used in large extent as the cheapest oxidizing agent. For example, ethylene oxide has been obtained by the aerobic oxidation of ethylene catalyzed by silver salt,[1] and phenol has been produced by the cumene process, which involves an aerobic auto-oxidation of cumene into "cumene hydroperoxide" in a key step.[2] The aerobic oxidation of *p*-xylene into terephthalic acid by using manganese and cobalt salts as catalysts has also been used in industrial processes.[3] These successful processes, however, have some limitations, because they are operated under severe conditions of temperature and/or pressure and also require selected experimental devices and suitable reactant that can endure extreme conditions. Therefore, recent studies have been directed to the development of more mild and efficient oxygenation procedures,[4] and indeed some excellent methods have been published very recently in the case of alcohol oxidation. For example, Marko et al. reported the oxidation method using Cu(I) or Ru(VII) complex as a catalyst under molecular oxygen.[5, 6] Sheldon et al. also reported, quite recently, the aerobic oxidation of various alcohols using a water-soluble Pd(II).[7] As in these methods only molecular oxygen is used as the

stoichiometric oxidant, they are economical and environmental-friendly. Furthermore, biological study on utilizing molecular oxygen in human being has long been undertaken.[8] The results of this study may become helpful to understand oxygenation mechanism in human being. Therefore, the study of oxygenation will be of great importance in view of understanding biological oxidation and development of novel and mild oxygenation methods.

The ground state of molecular oxygen is a triplet with two unpaired electrons having parallel spins. Therefore, the direct reaction of molecular oxygen with singlet organic molecule is a spin-forbidden process.[9] On the other hand, the radical chain reaction is one practical process by which organic compounds may be oxidized with molecular oxygen using transition-metal salt catalysts. Hence, many methods have been studied to make active molecular oxygen and also successful results of oxygenation using transition-metal catalyst have been reported.[10] As one of the methods utilizing molecular oxygen, the catalyst can incorporate one of its oxygen atoms into a substrate, and reduce the second oxygen to a water molecule. In this case, the catalyst with more than one equivalent reductant is necessary (Scheme 1).

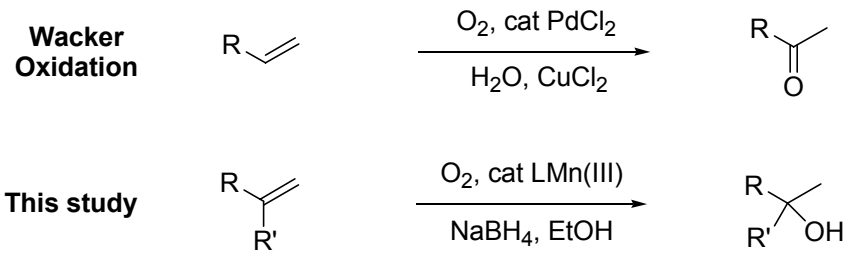
In nature, molecular oxygen is employed as an effective oxidant. In this biological process, an enzyme such as cytochrome P-450 is catalytically involved to activate molecular oxygen, where one-oxygen reductant such as NAD(P)H is necessarily consumed. It was reported that a variety of reductants such as alcohol,[11] aldehyde,[12] triethylsilane[13] or phenylsilane[14] has been used with molecular oxygen for the metal complex catalytic oxygenation methods. Especially, in case of epoxidation of olefin using various metallic catalyst, aldehydes have widely been used as a reductant.[4(a)] Recently, Neumann et al. reported that epoxidation

reaction using Ru-substituted polyoxometalate as a catalyst, does not require the stoichiometric amount of reductant and is of great interest.[15]



Scheme 1. The biomimetic oxygenation using molecular oxygen as the oxidant.

The carbonylation or hydration of olefins, mediated by O_2 is another reaction that has been investigated in organic synthesis. The carbonylation of olefins is known well as Wacker-type reaction, which convert ethylene to aldehyde using palladium(II) chloride and copper(II) chloride as catalysts under an oxygen atmosphere and is already applied as industrial method (Scheme 2).[16] Our study has similarity to Wacker-type oxidation, where ketone is obtained. On the other hand, this reaction provides alcohol as the product. Therefore, development of this

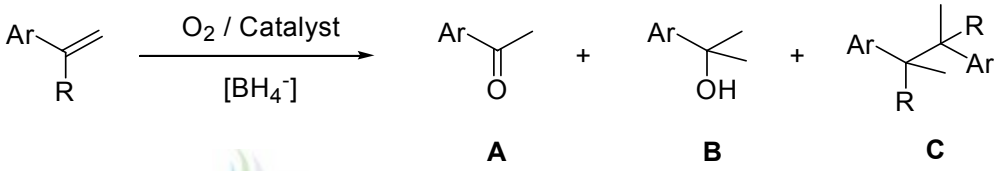


Scheme 2. Similarity of Wacker oxidation and this study.

reaction will provide useful olefin hydration method in organic synthesis. In case of the hydration of olefins, use of Co(II) as a catalyst and alcohol as a reductant has been reported.[17]

Tabushi and Koga,[18] during study of biomimetic oxidations, elucidated that the oxygenation of olefins is possible using the metal-porphyrins as a catalyst and $NaBH_4$ as a reductant. The model system proposed by Tabushi and Koga has further been studied by several groups (Table 1). While these studies have

Table 1. Literature survey of olefin oxygenation in the presence of borohydride.



Entry	Ar	R	Catalyst	Product(Yield %)	Ref.
1	Ph	H	Mn(TPP)Cl	**A**(700)[a] + **B**(1700)[a]	19
2	Ph	Me	Mn(TPP)Cl	**B**(64) + **C**(16)	20
3	*p*-Chlorophenyl	H	Fe(TMPyP)Cl	**A**(39) + **B**(34)	21
4	Ph	Me	Mn(TPP)Cl	**B**(69) + **C**(26)	22
5	Ph	Me	$Mn(OAc)_2$ + L[b]	**B**(19)	23

[a]Yield based on the amount of catalyst used.
[b]Pyridinedicarboxamide derivative was used as an external ligand.

an advantage of better understanding of the behavior of an enzyme such as cytochrome P-450 in biology, but in aspect of synthetical applications did not attract interest. Most of these studies were focused on the reaction mechanism to

access the better understanding of the biological oxidation process, few synthetically useful procedure were developed partly due to low reactivities or product selectivities, for example, providing olefin dimer as a side product. To overcome such problems, we tried to develop new catalyst that convert olefins to alcohols under molecular oxygen.

In this study, we elucidated for the first time that (salen)Mn(III) complexes can be used as new catalyst of oxygenation.[24] (Salen)Mn(III) complexes were known to have features in common with metalloporphyrins with respect to their electronic structure and catalytic activity. In asymmetric epoxidation of olefins using chiral salen complexes as catalyst, Jacobsen has shown that chiral salen-Mn provided far better selectivity than chiral metalloporphyrins.[25] The advantage of using (salen)Mn(III) complexes is that it is more convenient to prepare analogues containing a wide variety of electron-withdrawing or electron-donating or sterically different substituents which would be expected to regulate the catalytic properties.[26]

In this study, we used (salen)Mn(III) complexes as the catalyst and $NaBH_4$ as the reductant under molecular oxygen. On the basis of catalytic properties of the (salen)Mn(III) complexes, we have synthesized various Mn(III)(salen) type complexes and screened their reactivity. We have used simple olefins, cyclic, or non-cyclic olefins as substrate. A variety of reaction condition have been investigated in order to optimize reaction condition of olefin oxygenation. To get the more practical oxygenation method, we have examined a readily available manganese salt such as $Mn(OAc)_3$ or $Mn(OAc)_2$ as the catalyst. Also, we used α,β-unsaturated esters as substrate in order to expand the scope of our method.

In order to clarify the mechanism for (salen)Mn-catalyzed oxidation of olefins

by molecular oxygen with $NaBH_4$, the deuterium incorporation was studied using $NaBD_4$.

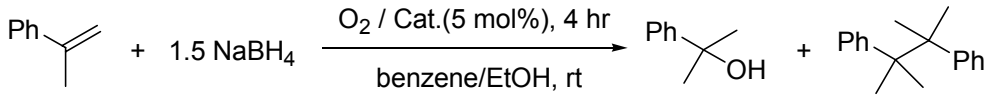
Results and Discussion

I. The oxygenation of vinyl arenes catalyzed by (salen)Mn(III) complexes.

For the screening of the catalytic activity, we have synthesized several (salen) Mn(III) type complexes. Usually the ligands were prepared by the coupling of salicyl aldehydes and corresponding diamine compounds. The prepared salen-type ligands were treated with manganese(II) acetate followed by air oxidation to provide Mn(III)(salen)-type complexes.[27] The catalytic activity of the complexes was examined using α-methylstyrene as a model substrate (Table 2). The reaction was carried out using 5 mol% Mn(III) complexes and 1.5 equiv. of $NaBH_4$ under balloon pressure of O_2 at room temperature. The reaction was monitored using gas chromatography. The results are summarized in Table 2. In all the cases, we obtained the corresponding alcohols as a major product (entries 1-4). Using complexes **1**, **2** as a catalyst, alcohols were obtained in 76% and 70% yield, respectively. Olefin dimer frequently observed as a by-product in the previous Mn(porphyrin)-catalyzed reaction was not detected (entries 1, 2). When the complexes **3**, **4** were tried as the catalyst, more substrate conversion was observed. However, in case of using **3**, **4** as a catalyst, we obtained rather lower yields and also dimer as a by-product (entries 3, 4). Among them, complex **1** showed the best result. These results suggested that choice of the catalyst is critical to achieve the desired oxygenation. The origin of the reactivity difference for these (salen)Mn(III) complexes is not clear at this point. It might be ascribed

to their differences in electronic/steric properties around the Mn metal or in their physical properties, such as solubility in the reaction.[28]

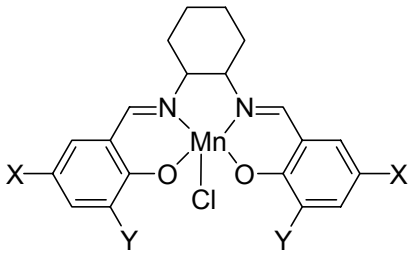
Table 2. Screening of the (salen)Mn(III) complexes for the catalyst of the olefin oxygenation.



1a **1b** **1c**

Entry	Catalyst	Conversion (%)[a]	Yield(%)[a]	
			1b	**1c**
1	**1**	93	76	0
2	**2**	93	70	0
3	**3**	99	57	11
4	**4**	99	59	12

[a]Based on GC analysis



1 X = H, Y = H

2 = *t*-Bu, = *t*-Bu

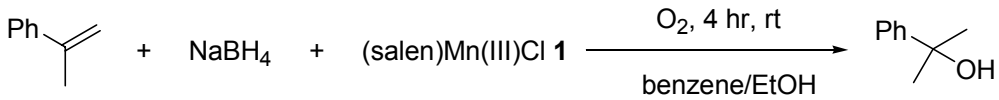
3 = Cl, = H

4 = Cl, = Cl

From the results in Table 1, our investigation began with an effort to get optimized reaction conditions for the oxidation of vinyl arenes using catalytic

salen-manganese complex **1** and stoichiometric $NaBH_4$ under O_2 atmosphere. α-Methylstyrene and styrene were chosen as model substrates to give the

Table 3. Examination of the different reaction conditions for the oxygenation of α-methylstyrene.



Entry	$NaBH_4$ (equiv.)	Complex **1** (mol %)	Benzene (mL)	EtOH (mL)	Product (Yield %)[a]
1	0.5	10	10	2.0	38
2	1.0	10	10	2.0	53
3	1.5	10	10	2.0	92
4	1.5	5	10	2.0	84
5	1.5	5	1.0	2.0	94
6	1.5	10	1.0	0	39
7	1.5	10	10	0.5	67
8	1.5	10	10	1.0	92
9	1.5	10	10	2.0	7[b]
10	1.5	10	10	2.0	34[c]

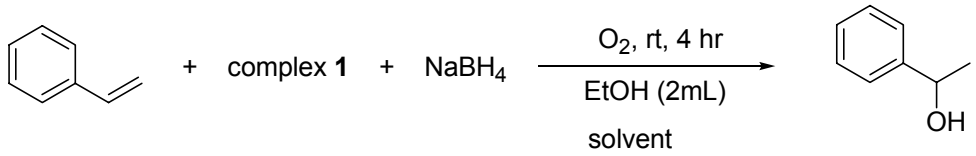
[a]GC yields using dodecane as an internal standard. [b]Reaction under N_2 gas in place of O_2. [c]Reaction under air in place of oxygen gas.

oxidized product, 2-phenyl-2-propanol and *sec*-phenethyl alcohol. The results are summarized in Table 3 and Table 4.

The first experiment was carried out with the variable amount of $NaBH_4$ as a hydride source (entries 1-3). It proved that 1.5 equivalent of sodium borohydride is necessary to complete the reaction. Ethanol was found to be necessary in this reaction, which is presumably due to the increased solubility of the catalyst at least in part (entries 6-8). Oxygen gas, which was supplied *via* a balloon, was of course indispensable for this procedure. For example, when the reaction was performed under nitrogen gas atmosphere, very low conversion was obtained (entry 9). Use of air in place of oxygen in an identical condition gave worse result (entry 10). We also found that the amount of benzene is another important factor, *i.e.* improved result was obtained with less amount of solvent (entries 4, 5). As seen in Table 4, we also examined reaction conditions for the oxygenation of styrene. When solvent was reduced to 3 mL, the result was improved (entry 2). Using toluene as the solvent instead of benzene, the corresponding alcohol was obtained lower, *i.e.* in 75% yield (entry 3). On the other hand, addition of LiCl salt[29] which was known to regulate reactivity of hydride through the substitution with $NaBH_4$, the styrene reactivity was decreased sharply (entry 4). In this case, some starting material was obtained along with 20% acetophenone as a by-product. When 2 mL of solvent was used, the result was slightly improved. In case of entry 6, the best result was obtained in 97% yield. In this reaction, we also found that the amount of solvent is important factor and also proved that 2.0 equivalent of sodium borohydride is necessary to complete the reaction. As seen in Table 3 and Table 4, the required amount of $NaBH_4$ was dependent on the substrates, *i.e.* there needed 1.5 equiv. sodium borohydride for α-methylstyrene

whereas 2.0 equivalence was necessary for styrene. In fact, using the condition in Table 3 entry 5 and Table 4 entry 6 as the optimized ones, we were able to let the reaction go for completion with 5 mol% of the complex **1**.

Table 4. Reaction conditions examined for the oxygenation of styrene.



Entry	$NaBH_4$ (equiv.)	Complex **1** (mol %)	Solvent (mL)	Product Yield (%)[a]
1	2.0	10	benzene (5)	80
2	2.0	10	benzene (3)	86
3	2.0	10	toluene (3)	75
4[b]	2.0	10	benzene (3)	22
5	1.5	5	benzene (2)	91
6	2.0	5	benzene (2)	97

[a]GC yields using dodecane as an internal standard.
[b]LiCl (2 equiv.) was added as the additive

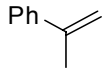
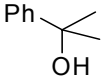
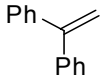
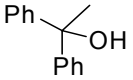
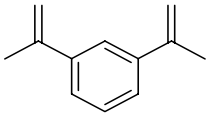
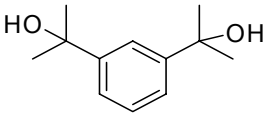
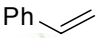
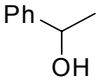
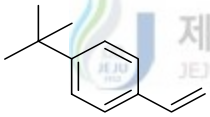
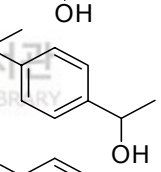
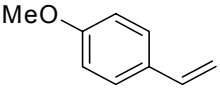
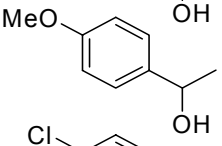
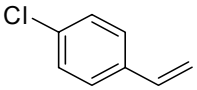
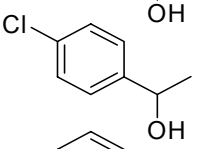
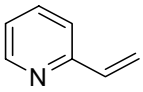
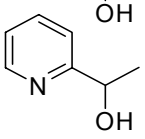
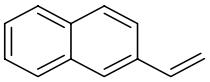
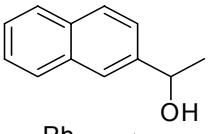
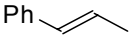
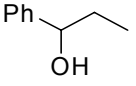
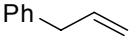
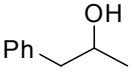
Different types of vinyl substrates were subjected to the reaction conditions examined above. As seen in Table 5, the complex **1** coupled with $NaBH_4$ proved to be an efficient catalyst to affect the oxygenation of styrene derivatives to give

the alcoholic compounds. 1.5 Equiv. and 2.0 equivalence sodium borohydride were used for the oxygenation of α-substituted styrenes and vinyl derivatives, respectively. Also with 4.0 equiv. of reductant, double oxygenation was efficiently achieved (entry 3). This reaction was generally applicable to other aromatic compounds such as pyridinyl and naphthyl derivatives (entries 8, 9). Functionality change in the benzene ring did not affect the reactivity showing low electronic effect in this reaction (entries 4-7). However, the styrene reactivity was decreased sharply by introduction of a substitution at terminal carbon of C=C bond (entry 10). For the non-conjugated vinyl compound, this procedure displays very low conversion leaving most of the starting material intact (entry 11).

This oxygenation procedure turned out to be a very clean reaction, *e.g.* following the reaction by GC and GC-MS, the only distinguished side product, dimers were usually observed in less than 5% yields.

Table 5. The oxygenation of styrene derivatives catalyzed by (salen)Mn(III) complex **1** in the presence of $NaBH_4$.[24]

Substrate + $NaBH_4$ + 5 mol% Complex **1** —(O_2 (1atm), rt, 4 hr; benzene/EtOH)→ Product

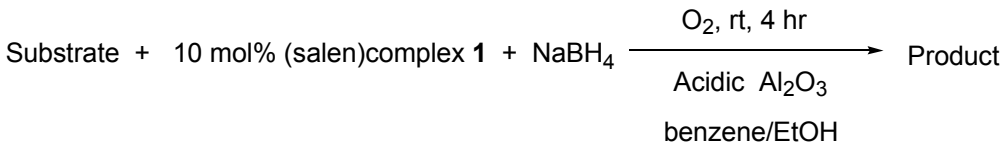
Entry	Substrate	$NaBH_4$ (equiv.)	Product	Isolated Yield (%)
1		1.5		85
2		1.5		90
3		4.0		77
4		2.0		81
5		2.0		80
6		2.0		87
7		2.0		87
8		2.0		73
9		2.0		79
10		2.0		35
11		2.0		7

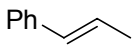
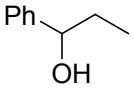
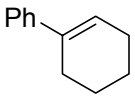
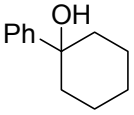
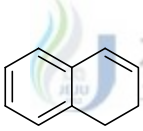
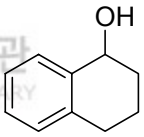
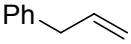
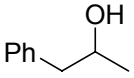
2. Development of (schiff-base)Mn(III) catalysts.

As seen in Table 5, only conjugated vinyl arene substrates were oxidized with high efficiency. Other olefin substrates, for example, non-conjugated or non-vinylic olefins, showed very low yields under mild conditions (Table 5, entries 10, 11). Therefore, we investigated a method to increase product yields. At first, some methods were reported on solid supports as an additive in order to improve reactivity in olefin epoxidations.[30, 31] Concerning the similar effect of solid supports, we examined acidic alumina as an additive in our reaction condition. The results are summarized in Table 6. In all the cases, the products were produced in 7-35% yields in the absence of acidic alumina. But, by addition of acidic alumina, big improvement in product yield was observed. For example, conjugated internal olefin compound, *trans*-β-methylstyrene gave the corresponding alcohol in 75% yield (entry 1). Conjugated cyclic compounds such as 1-phenyl-1-cyclohexene and 1,2-dihydronaphthalene were converted to the corresponding alcohol in 71% and 77% yield, respectively (entries 2, 3). Non conjugated olefin, allyl benzene, was also converted to the corresponding alcohol in 69% yield (entry 4).

With the results in Table 6, several other solid supports were screened using allyl benzene as a model substrate. These results are summarized in Table 7. In case of the absence of additives (entry 1) and raised temperature at 50℃ (entry 2), they showed 10% yield and no reaction, respectively. While, similar results were observed when acidic alumina or molecular sieve 4Å was added (entries 4, 8). The reactivity differences of solid supports may be ascribed by proposing that they inhibit catalyst's decomposition or oxidative degradation[32] or dimerization.[33]

Table 6. Reaction under acidic Al_2O_3.



Entry	Substrate	$NaBH_4$ (equiv.)	Product	Yield(%)[a]
1		2.0		75
2		1.5		71
3		2.0		77
4		2.0		69

[a]Based on GC yield.

Unfortunately, we were not able to improve the results further. Therefore, we decided to develop other method, which is development of new catalyst applicable to simple olefins such as allyl benzene.

For the screening of the catalytic activity, we have synthesized several Mn (III)(salen)-type complexes.[34] As shown in Scheme 3, usually the ligands were prepared by the coupling of salicyl aldehydes and corresponding diamine

compounds.[27] The prepared salen-type ligands were treated with manganese(II)

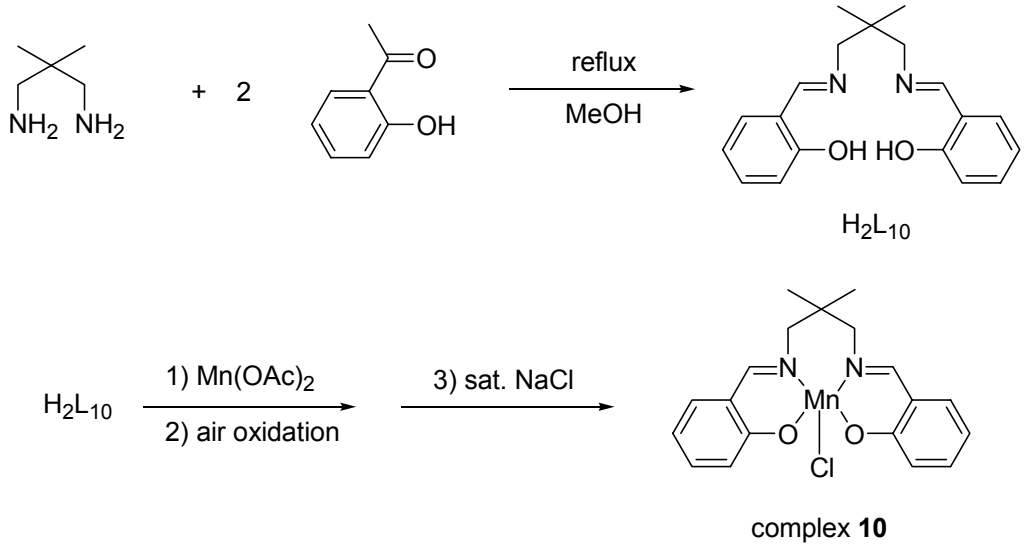
Table 7. Additive effect for the olefin oxygenation.

Entry	Benzene (mL)	Additive (g)	Product Yield (%)[a]
1	3	No	10
2[b]	3	No	0
3	3	MS 4Å (0.5)	35
4	1	MS 4Å (0.5)	69
5	1	MS 4Å (0.25)	32
6	1	MS 3Å (0.5)	43
7	1	Basic Al_2O_3(0.5)	21
8	1	Acidic Al_2O_3 (0.2)	63
9	1	Acidic Al_2O_3 (0.5)	39

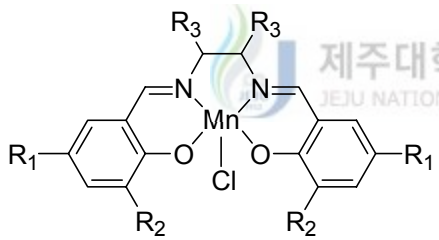
[a]GC yields. [b]Reaction at 50°C

acetate followed by air oxidation to provide Mn(III)(salen)-type complexes.

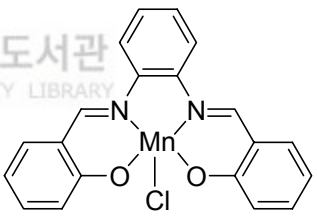
As shown in Figure 1, the prepared manganese complexes are divided into



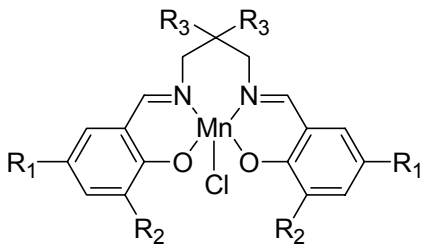
Scheme 3. Example of (salen)Mn(III)Cl complex synthesis.



5 R_1 = H, R_2 = H, R_3 = H



6 R_1 = H, R_2 = H

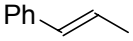


7 R_1 = H, R_2 = H, R_3 = H
8 R_1 = *t*-Bu, R_2 = *t*-Bu, R_3 = H
9 R_1 = Cl, R_2 = H, R_3 = H
10 R_1 = H, R_2 = H, R_3 = CH_3
11 R_1 = *t*-Bu, R_2 = *t*-Bu, R_3 = CH_3
12 R_1 = Cl, R_2 = H, R_3 = CH_3

Figure 1. (Salen)Mn(III) complexes.

three different categories, *i.e.* diaminoethane-derived Mn complex **5**, diamino-benzene-derived Mn complex **6**, and diaminopropane-derived Mn complexes **7**-**12**. The catalytic activity of the complexes was examined using *trans*-β-methyl-styrene (**2a**) and allyl benzene (**3a**) as the model substrate (Table 8).

Table 8. Screening of the Mn(III)(salen)-type complexes for the oxidation catalyst using the *trans*-β-methylstyrene and allyl benzene.

Entry	Mn(III) complex	Conversion (%)[a]	
		Ph  **2a**	Ph  **3a**
1	**5**	5	1
2	**6**	18	0
3	**7**	86	38
4	**8**	30	21
5	**9**	95	58
6	**10**	96	70
7	**11**	13	12
8	**12**	85	66

[a]Based on GC analysis.

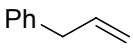
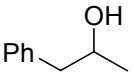
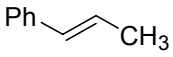
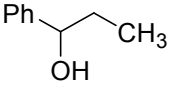
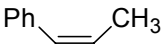
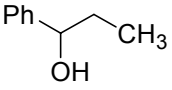
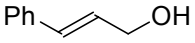
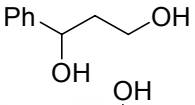
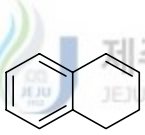
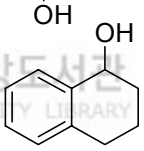
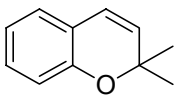
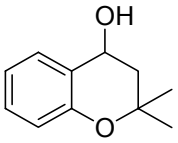
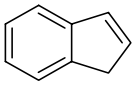
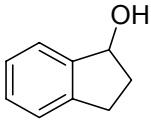
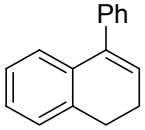
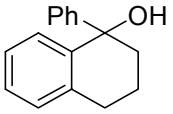
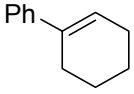
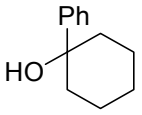
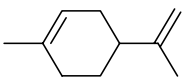
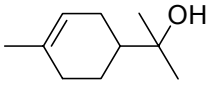
The reaction was carried out using **5** mol% Mn(III) complexes and 1.5 equiv. of $NaBH_4$ under balloon pressure of O_2 at room temperature for 4 hr. The

reaction was monitored using gas chromatography. These results are summarized in Table 8. In the previous experiment, employing the (salen)Mn(III) complex **1** as the catalyst, the compounds **2a** and **3a** were oxidized in only 35% and 7% conversion yield, respectively (see Table 5, entries 10, 11). When the Mn(III)-salen complex **5** was tried as the catalyst, rather lower substrate conversion was observed (entry 1). Diaminobenzene-derived Mn(III) complex **6** also gave lower reactivity (entry 2). However, diaminopropane-derived Mn(III) complex **7** showed big improvement in the conversion yield. For example, using complex **7**, we converted olefins **2a** and **3a** in 86% and 38% yield, respectively (entry 3). Different types of related complexes were examined (entries 4-8), taking the complex **7** as the leading compound. From this screening, it was concluded that dimethyl-substituted complex analogue **10** has the best catalytic activity among the complexes in Table 8. It is interesting to observe that introduction of bulky and electron-rich *tert*-butyl group, as shown in **8** and **11**, resulted in activity decrease. Another interesting observation was that electron poor Cl-substituted complexes, such as **9** and **12**, showed comparable but no better catalytic activity over the simple complex **10**. From the results in Table 8, we concluded that complex **10** is the best choice for a catalyst for this oxidation system. Although the higher reactivity of complex **10** compared to other complexes is not clear, but the combination of electronic and steric environments around the salen-type ligand would account for the reactivity difference.[28]

With the result in Table 8 at hand, we carried out the oxidation with various type of olefin substrates in the presence of the complex **10** and 1.5 equivalent of $NaBH_4$ under O_2. The results are summarized in Table 9. Non-conjugated vinyl compound, allyl benzene, gave the corresponding alcohol in 61% isolated yield

Table 9. Examples of olefin oxygenation reactions using the Mn(III) complex **10** as the catalyst.[35]

Olefins + 5 mol% Mn(III) complex **10** + 1.5 $NaBH_4$ $\xrightarrow[\text{benzene/EtOH}]{O_2,\ rt,\ 4\ hr}$ Alcohols

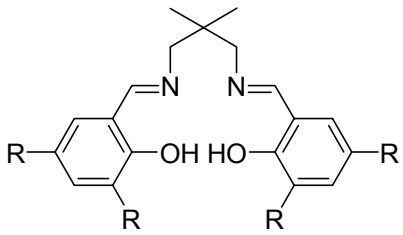
Entry	Olefins	Alcohols	Isolated Yield (%)
1			61
2			72
3			71
4			65
5			82
6			65
7			81
8			70
9			38
10			20

(entry 1). This reaction was very regiospecific, giving only Markovnikov type hydration product. Conjugated internal olefin, *trans*-β-methylstyrene, was also well oxidized in 72% yield (entry 2). This conversion was also regioselective; only the compound oxidized at the benzylic position was observed. *Cis*-β-methylstyrene was also oxidized in about the same yield as *trans* substrate (entry 3). Cinnamyl alcohol was converted to the corresponding alcohol in 65% yield, which shows that alcohol functionality rarely affects the reactivity (entry 4). Conjugated cyclic olefins, such as 1,2-dihydronaphthalene, indene, and 2,2-dimethylchromene were also good substrates for this oxidation procedure, providing the corresponding alcohols in 82%, 65% and 81% yield, respectively (entries 5-7). In case of 2,2-dimethylchromene, the corresponding ketone was obtained in 20% yield as the side product. This could be explained assuming that at least some ketone was produced as the initial product, which was subsequently reduced by $NaBH_4$ to the alcohol. Tertiary alcohol was also obtained from the *tri*-substituted olefins. For example, 1-phenyl-3,4-dihydronaphthalene gave the alcohol in 70% yield (entry 8). When 1-phenyl-1-cyclohexene (entry 9) was used as the substrate, the expected alcohol and C-C cleaved ring-open product were isolated in 38% and 30% yield, respectively. But limonene showed poor conversion (entry 10). In this case, we obtained several products, and the major compound in 20% isolated yield was identified to be tertiary alcohol resulting from the oxygenation on vinylic olefin over the electron-rich *tri*-substituted one.

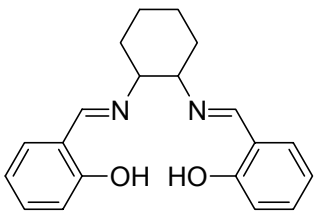
3. Development of manganese(III) acetate as the catalyst.

Previously, we have reported the oxidative conversion of olefins to the alcohols, where molecular oxygen was used as the oxidant. In this process, (schiff-base)Mn(III)Cl complexes were used as the catalyst and sodium boro-hydride was employed as the required hydride source.[24, 35] As a continuous effort for searching the more practical oxygenation method, we have decided to carry on the experiment with a readily available manganese salt such as $Mn(OAc)_3$ or $Mn(OAc)_2$ as the catalyst.[36]

For the screening of the oxidation conditions, *trans*-β-methylstyrene was selected as the model compounds. The olefin oxidation was performed using O_2 (1 atm), metal salt, schiff-base ligand and $NaBH_4$ in the organic solvent (benzene/EtOH) at room temperature. The reaction was monitored using gas chromato-graphy, and the product yields were obtained using dodecane as the internal standard. The results are summarized in Table 10.



13 R = H, **14** R = *t*-Bu, **15** R = NO_2



16

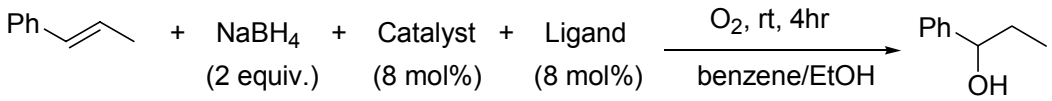
Figure 2. Schiff-base ligands were used for oxidation.

As the initial trial, the reaction was conducted in the absence of external

ligands (entries 1-3). The salt of Mn(II) or Mn(III) species rarely provided the expected alcohol. Employment of one equivalent of Mn(III) salt also provided only 11% yield of the product (entry 2). However, addition of schiff-base type ligands led to great improvement in product yield. We have screened schiff-bases **13**-**16**, effective ligands in the (schiff-base)Mn(III) complexes employed previously.[24, 35] Among them, diaminopropane-derived ligand **13** showed the best result. For example, using **13**, the starting material was almost consumed (93% conversion) and the desired product was obtained in 91% yield (entry 4). The analogous ligands **14** and **15**, having electron rich and electron poor properties compared to **13**, were selected for reactivity comparison. With these ligands, lower conversion of the olefin were observed (entries 5, 6). Trial of salen type ligand **16** also provided the lower reactivity (entry 7). These results suggested that choice of the ligand is critical to achieve the desired oxygenation. Examination of Mn(II) species as the catalyst, in the presence of ligand **13**, also afforded the good result giving the product in 85% yield (entry 8). This could be explained assuming that part of Mn(II)L is initially oxidized to Mn(III)L by O_2 under reaction conditions. Once Mn(III) species is developed, it could initiate oxidation system where Mn(III) and Mn(II) species are alternatively involved in the catalytic cycle. When other metal species such as Fe(III) or Co(II) were tried as the catalyst, the expected oxidation was not observed with lower conversion of the starting material (entries 9, 10).

In this process, (schiff-base)Mn(III) complexes formed *in situ* during the reaction is considered to be the active catalyst, otherwise the reactivity differences observed with ligand change could not be explained. The corresponding LMn(III)Cl (L = **13**, **14**, **16**) complexes were prepared, and the catalytic

Table 10. Examination of reaction conditions for the oxygenation of *trans*-β-methylstyrene.



Entry	Catalyst	Ligand	Conversion(%)[a]	Yield(%)[b]
1	$Mn(OAc)_3 \cdot 2H_2O$	No	8	2
2[c]	$Mn(OAc)_3 \cdot 2H_2O$	No	18	11
3	$Mn(OAc)_2 \cdot 4H_2O$	No	7	1
4	$Mn(OAc)_3 \cdot 2H_2O$	**13**	93	91(75)[d]
5	$Mn(OAc)_3 \cdot 2H_2O$	**14**	23	19(22)[d]
6	$Mn(OAc)_3 \cdot 2H_2O$	**15**	61	49
7	$Mn(OAc)_3 \cdot 2H_2O$	**16**	42	24(60)[d]
8	$Mn(OAc)_2 \cdot 4H_2O$	**13**	89	85
9	$FeCl_3$	**13**	23	0
10	$Co(OAc)_2 \cdot 4H_2O$	**13**	38	3

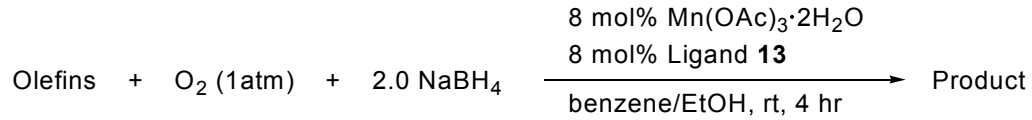
[a]Conversion based on GC analysis using dodecane as an internal standard. [b]GC yields using dodecane as an internal standard. [c]100 mol% Mn(III) was employed. [d]Yields obtained using the corresponding (schiff-base)Mn(III)Cl complex (8 mol%) as the catalyst.

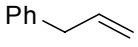
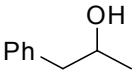
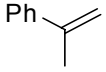
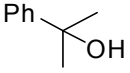
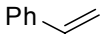
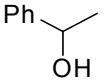
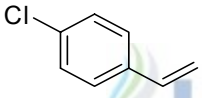
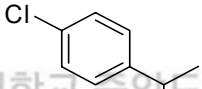
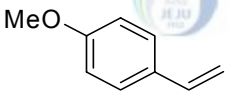
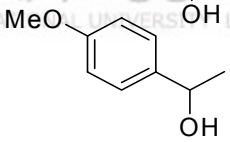
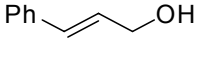
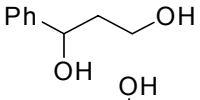
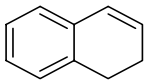
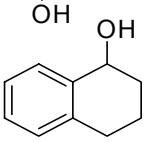
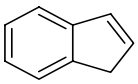
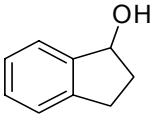
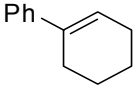
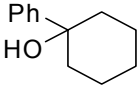
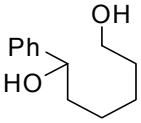
activity was compared (entries 4, 5, 7).[37] In this reaction, the alcohol was obtained in 75%, 22%, and 60% yield, respectively, which is showing the similar reactivity trend. In addition, the complexation stabilities of the ligand **13**-**16** to the

$Mn(OAc)_3$ could be partly responsible for the activity differences shown in Table 10.

Using the reaction condition of entry 4 in Table 10, various types of olefins were examined to achieve the desired oxidation. The results are summarized in Table 11. When allyl benzene (**3a**), a non-conjugated olefin, was tried as the substrate, the secondary alcohol **3b** was obtained as the major product in 58% yield. As a major side product, a reduced alkane (1-phenylpropane) was observed (entry 1). Examination of other ligands **14-16** in **3a** led to the same reactivity trend described in Table 10. α-Methylstyrene was subjected to the reaction condition, the desired product was obtained in 78% yield (entry 2). In this case, non oxidized dimeric product, 2,3-dimethyl-2,3-diphenylbutane, was isolated as the minor product. From our experience, dimeric product was obtained when substrate is too reactive under reaction condition. Thus, the less reactive ligand **16** was tried. As expected, the dimeric impurity was disappeared and the product **1b** was isolated in 90% yield (entry 2). For the styrene type substrates, the desired phenethyl alcohols were obtained in 62-88% yields (entries 3-5). In the case of 4-methoxystyrene (**6a**), the corresponding ketone was obtained in 15% yield along with the expected alcohol **6b** (entry 5). This could be explained assuming that at least some ketone was produced as the initial product, which was subsequently reduced by $NaBH_4$ to the alcohol. Compared to styrene, introduction of the methoxy group at *p*-position of the aromatic ring in **6a** made the carbonyl less electrophilic, which caused the carbonyl less reactive to hydride-mediated reduction. Cinnamyl alcohol (**7a**) was oxidized to give diol **7b**, which shows that the hydroxy functionality is tolerable to the reaction condition (entry 6). Cyclic olefins also proved to be good substrates to provide the oxidation at the benzylic

Table 11. Oxidation of olefins using $Mn(OAc)_3 \cdot 2H_2O$ and schiff-base **13** as the catalyst.[38]



Entry	Olefins		Product		Conv.[a] (%)	Yield[b] (%)
1		**3a**		**3b**	100	58
2		**1a**		**1b**	100	78 (90)[c]
3		**4a**		**4b**	100	88
4		**5a**		**5b**	100	71
5		**6a**		**6b**	98	62[d]
6		**7a**		**7b**	100	64
7		**8a**		**8b**	99	78
8		**9a**		**9b**	99	76
9		**10a**		**10b**	97	**10b** + **10c** (33) (31)
				**10c**		

[a]Based on GC analysis. [b]Isolated yields. [c]Isolated yield obtained when ligand **16** was employed instead of lignad **13**. [d]As a minor product, corresponding ketone was isolated in 15% yield.

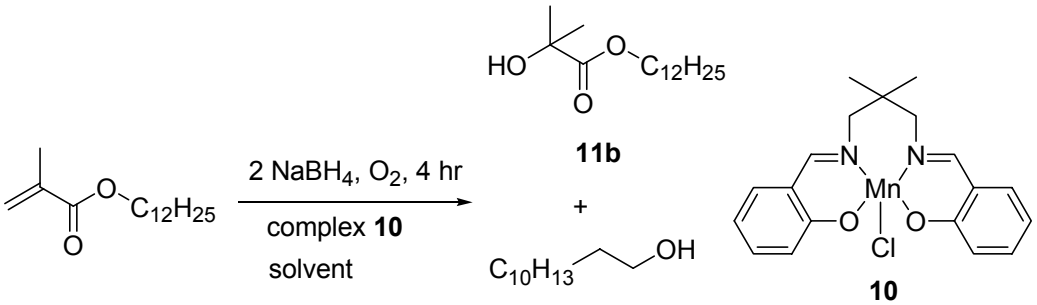
carbon with high selectivity as shown in entries 7 and 8. When 1-phenyl-1-cyclohexene (**10a**) was used as the substrate, the expected alcohol **10b** and C-C cleaved product **10c** were isolated in 33% and 31% yield. As seen in Table 11, this procedure comprises a mild oxygenation method converting the olefins to the hydration products with high efficiency.

4. The oxygenation of α,β-unsaturated esters.

α-Hydroxycarbonyl compound can be found in various natural products, and therefore, their various preparative methods have been reported.[39] For example, the stereoselective oxidation of the corresponding enolates has been examined.[40] However, few reports were found about the direct synthesis of α-hydroxycarboxy-lates with molecular oxygen by the use of transition metal catalysts. From the synthetic point of view, it is interesting to develop an efficient method for hydration of olefinic bond having electron withdrawing substituents, such as esters and ketones. As a part of our continuous effort to extend the scope of olefin oxygenation, we have decided to examine α,β-unsaturated esters.

Our investigation began with an effort to optimize reaction condition for the oxygenation of α,β-unsaturated esters using catalytic (salpro)Mn(III) complex **10** which showed the best result of the oxygenation of various olefins and $NaBH_4$ under O_2. Lauryl methacrylate was chosen as a model substrate to give the oxidized product, dodecyl 2-hydroxy-2-methylpropanoate. The results are summarized in Table 12. The first examined was the amount of catalyst (entries 1, 2).

Table 12. Examination of reaction conditions for the oxygenation of lauryl methacrylate.



11a **11c**

Entry	Temp.	Complex **10** (mol %)	Solvent (mL)	(Yield %)[a]	
				11b	**11c**
1	rt	8	MeCN/EtOH (10/2)	93	trace
2	rt	10	MeCN/EtOH (10/2)	97	trace
3	rt	10	MeCN/EtOH (2/1)	74	11
4	rt	10	MeCN (10)	96	trace
5	O^0C	10	MeCN/EtOH (10/2)	98	trace
6	O^0C	10	EtOH (10)	99	trace

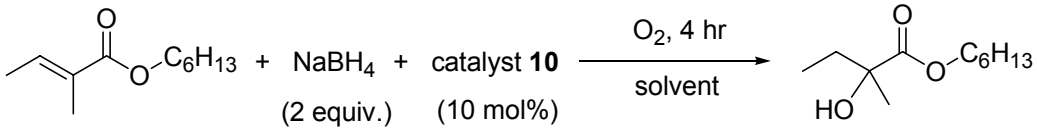
[a]Based on GC analysis

When 10 mol% of complex **10** was employed, the starting material was almost completely consumed. When the amount of solvent was reduced, the expected product **11b** was obtained in 74% yield and the reduced alcohol **11c** as a by-product was increased (entry 3). In case of entries 4, 5 and 6, the alcohol **11b**

was obtained in respective 96%, 98%, and 99% yield, which is showing the similar results.

Using the reaction condition of entry 6 in Table 12, we performed the oxidation of hexyl tigrate, including internal olefin. The result was obtained low conversion yield in 75%. Therefore, we had to find other reaction condition which

Table 13. Examination of reaction conditions for the oxygenation of hexyl tigrate.



Entry	Temp.	Solvent (mL)	Conv.[a] (%)	Yield[a] (%)
1	O^0C	MeCN/EtOH (10/2)	24	22
2	O^0C	*i*-PrOH (10)	34	27
3	O^0C	CH_2Cl_2/EtOH (5/5)	43	41
4	O^0C	benzene/EtOH (2/2)	88	84
5	rt	benzene/EtOH (2/2)	82	77
6	O^0C	benzene/EtOH (1/1)	92	89
7	O^0C	benzene/EtOH (2/2)	quant	77[b]
8	O^0C	$CHCl_3$ (4)	99	89

[a]Based on GC analysis. [b]Acidic alumina (300mg) was added as the additve.

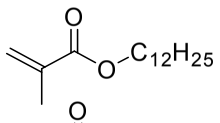
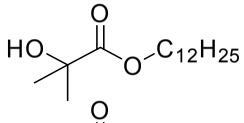
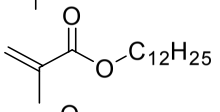
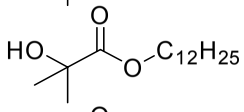
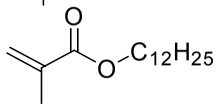
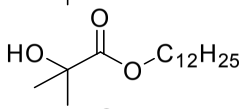
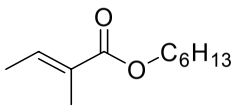
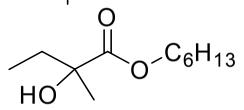
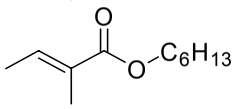
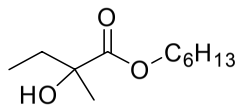
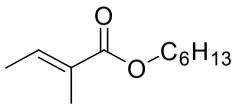
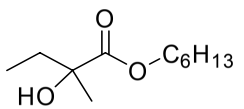
could be applied here. The examined results using hexyl tigrate are shown in Table 13.

As shown in Table 13, use of MeCN, *i*-PrOH, CH_2Cl_2 as a solvent, displayed low conversion in 24 %, 34 % and 43 % yield, respectively (entries 1-3). When benzene was used as the solvent, improvement in conversion and yield was observed (entry 4). When raising the reaction temperature to room temperature in reaction condition (entry 5), the conversion and yield became somewhat lower. We found that the amount of solvent is another important factor, *i.e.* improved result was obtained with less amount of solvent (entry 6). Addition of acidic alumina gave improved conversion and an increase in the reduced alkane as a by-product (entry 7). Using $CHCl_3$ as the solvent, the starting material was almost completely consumed. The expected product was obtained in 89% yield with 99% conversion by GC analysis and also the reduced alkane as a by-product was obtained in 8% yield.

To investigate the reactivity difference of other reducing agent, phenylsilane and tetrabutylammonium borohydride were further examined. The results are summarized in Table 14. In case of using hexyl tigrate as the substrate, the reductant gave almost comparable yield (74% and 73%, respectively, in entries 4 and 6). But, using $PhSiH_3$, the corresponding alcohol was in 32% yield and there left some starting material intact. Based on the results, it proved that sodium borohydride is proper reductant in our system.

Using the reaction condition of entry 8 in Table 13, various α,β-unsaturated esters were examined to achieve the desired oxidation. The results are summarized in Table 15. Methacrylate-type esters converted to the corresponding *tert*-alcohol was obtained good in 74%, 83%, and 80% yield, respectively (entries 1-3).

Table 14. Using various reductants for the oxygenation reaction.

Entry	STM	[Red] (equiv.)	Temp.	Solvent	Product	Yield (%)[a]
1		2 $NaBH_4$	0^0C	$CHCl_3$ (4 mL)		83
2		1.2 $PhSiH_3$	rt	*i*-PrOH/EtOH (2 mL/2 mL)		76
3		2 n-Bu_4NBH_4	0^0C	$CHCl_3$/EtOH (4 mL/1 mL)		79
4		2 $NaBH_4$	0^0C	$CHCl_3$ (4 mL)		74
5		1.2 $PhSiH_3$	rt	*i*-PrOH/EtOH (2 mL/2 mL)		32(50[b])
6		2 n-Bu_4NBH_4	0^0C	$CHCl_3$/EtOH (4 mL/1 mL)		73

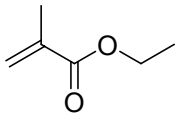
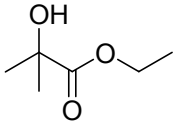
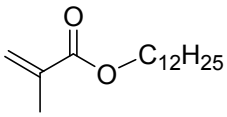
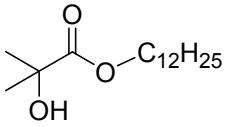
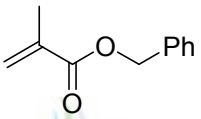
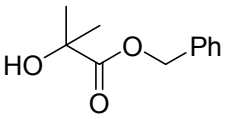
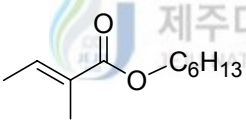
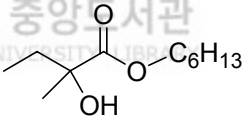
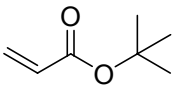
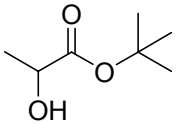
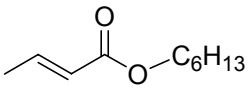
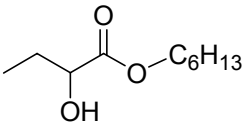
[a]Isolated yield. [b]Conversion yield was detected by GC

This reaction was very regioselective to give only Markovnikov type hydration product. Hexyl tigrate was also good substrate to give the product in 74% yield (entry 4). Acrylate-type ester, *tert*-butyl acrylate, was also well oxidized in 73% yield (entry 5). However, α,β-unsaturated esters that have internal double bond is converted to *sec*-alcohol with decreased yield (entry 6). In case of entry 6, low conversion was obtained in 36% yield with 47% conversion. Furthermore, the corresponding ketone was also found as a by-product. Interestingly, in case of using ligand **17** that substituted electron-withdrawing nitro group to ligand **13** and Mn(III) acetate as a catalyst instead of complex **10**, yield improvement was observed giving 75% yield (entry 6), and the corresponding ketone was also obtained in 10% yield.

This reaction provides a new and convenient method for the direct preparation of various α-hydroxycarboxylic acid esters starting from α,β-unsaturated esters.

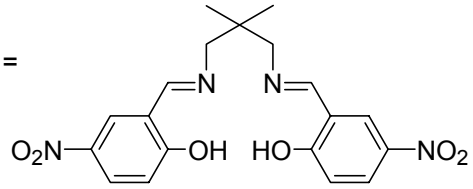
Table 15. The oxygenation of various α,β-unsaturated esters.

STM + 2 $NaBH_4$ + 10 mol % cat. **10** $\xrightarrow[CHCl_3\ (4mL)]{0^0C,\ O_2,\ 4\ hr}$ Product

Entry	STM	Porduct	Isolated Yield (%)
1			74[a]
2			83
3			80
4			74
5			73
6			36(75[b])

[a]GC yield using dodecane as an internal standard. [b]Using 15 mol% schiff-base ligand **17** along with 15 mol% Mn(III) acetate as the catalyst instead of complex **10**

schiff-base Ligand =



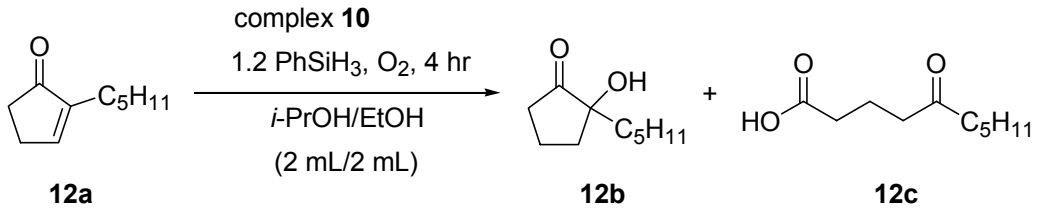
17

5. The oxygenation of 2-pentyl-2-cyclopenten-1-one in the $O_2/PhSiH_3$/ catalyst system.

We also examined the oxygenation of 2-pentyl-2-cyclopenten-1-one as the substrate using $O_2/PhSiH_3$ and complex **10** as the catalyst. The results are summarized in Table 16. In all the cases, we obtained the expected α-hydroxyl ketone **12b** and C-C cleaved ring-open product **12c**. When this reaction was conducted using complex **10** as the catalyst, the poor conversion was showed (entries 1-5). Increasing the amount of catalyst, the conversion result was similar (compare entry 1 and entry 2). With addition of acidic alumina, the yield was rather decreased (entry 3). Trial of lower temperature to 0℃ also provided the lower conversion (entry 4). In case of raising temperature to 50℃, the result was slightly improved (entry 5). Interestingly, using 15 mol% schiff-base ligand **15** which has electron poor dinitro substitutent compared to ligand **13** along with 15 mol% Mn(III) salt as the catalyst instead of complex **10**, big improvement in product yield was observed (entry 6). The expected alcohol **12b** and C-C cleaved ring-open product **12c** were isolated in 42% and 40% yield.

Further studies to extend the scope of the oxygenation method of various α,β-unsaturated carbonyl compound are in progress.

Table 16. The oxygenation of 2-pentyl-2-cyclopenten-1-one.

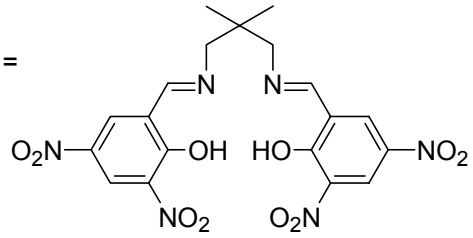


12a **12b** **12c**

Entry	Temp. (^{0}C)	Complex **10** (mol %)	Conv. (%)[a]	Yield (%)[a]	
				12b	**12c**
1	rt	8	29	3	26
2	rt	15	30	8	21
3[b]	rt	8	10	6	4
4	0	8	22	12	10
5	50	8	43	12	30
6[c]	rt	-	98	42[d]	40[d]

[a]Based on GC yield. [b]Added acidic alumina (300mg). [c]Using 15 mol% (schiff-base) ligand **15** along with 15 mol% Mn(III) acetate instead of complex **10** for 12 hr. [d]Isolated yield.

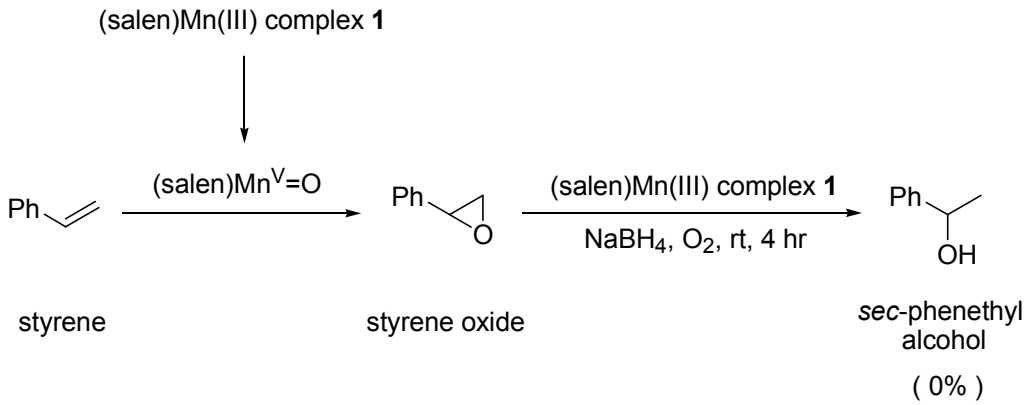
schiff-base Ligand =



15

6. Proposed reaction mechanism.

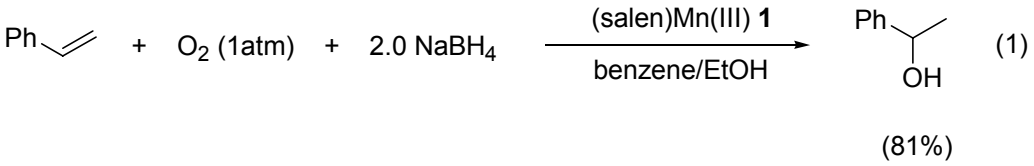
(Salen)Mn(III) complexes have been well known to catalyze various oxidation reactions such as epoxidation of olefins, oxidation of saturated hydrocarbon and alcohols. A high-valent oxomanganese(V) species has been believed as an active species.[25] Therefore, we considered possibility that vinyl arene reacting with oxo-manganese(V) species yields epoxide, which is reduced with $NaBH_4$ to give alcohol. We examined whether ring opening reaction of epoxide occurred or not in our system (Scheme 4). When the oxygenation of styrene oxide was proceeded in our system, no reduced alcohol was observed and starting material was recovered intact. This result indicated a mechanism which does not involve a oxomanga-nese(V) species.

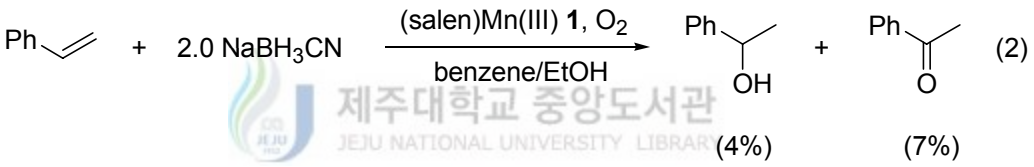


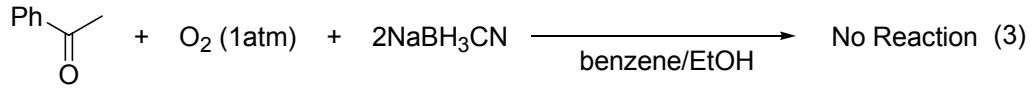
Scheme 4. Possible mechanism involving Mn^{V}=O species as the intermediate.

In case of styrene, a small amount of acetophenone (< 5%) was detected by GC analysis. On the basis of that result, the reaction product was alcohol

resulting from the reduction of the acetophenone by $NaBH_4$. Since the ketones are hardly reduced by $NaBH_3CN$, the reaction was performed using $NaBH_3CN$ as the reducing agent instead of $NaBH_4$ in order to capture this reaction intermediate. As a result, the corresponding ketone was formed along with the corresponding alcohol (Eq. 2). This result implies that the alcohol and ketone are obtained in different synthetic pathways (see Scheme 6).

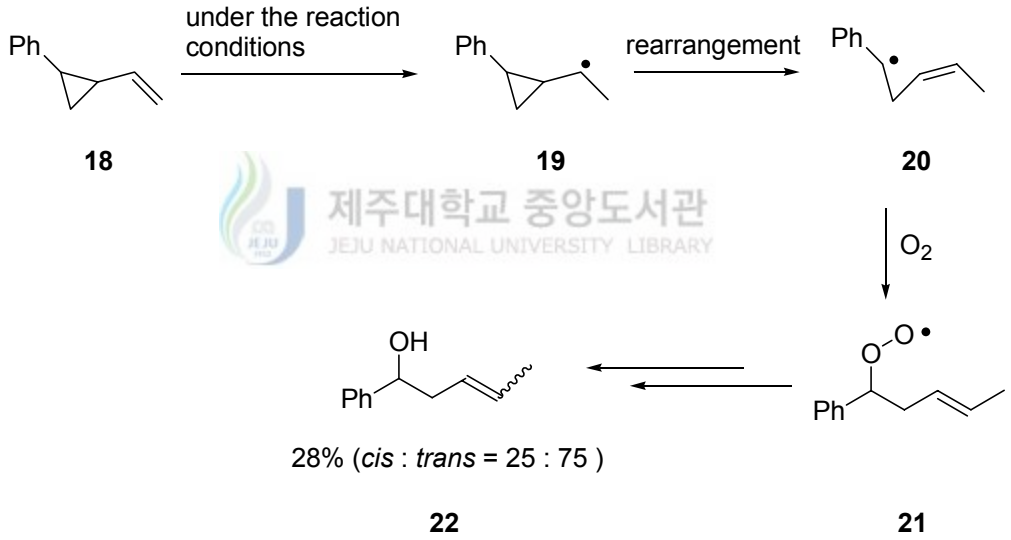






In our reaction conditions, it is assumed that Mn(III) and Mn(II) species are involved in the catalytic cycle.[22, 41] The color change between colorless and dark brown was observed during the reaction, which also suggested the involvement of colorless Mn(II) and dark brownish Mn(III) complexes. When the oxidation of styrene was conducted in the presence of BHT, a phenolic radical scavenger, no desired product was observed rendering the starting material intact. Thus, it is assumed that some radical species are involved as the reaction intermediate.

In order to confirm the generation of radical, we used 2-phenyl-1-vinyl-cyclopropane that was well known as an efficient radical clock[42] as a substrate in our reaction conditions. When the olefin **18** was subjected to our reaction condition (see Table 9), the benzylic alcohol **22** was obtained as the major product (28% yield) along with some unidentified minor products. The reaction of vinylcyclopropane **18** provides **22** presumably *via* a unsaturated peroxyl radical **21**, which is produced by the rapid ring opening of the cyclopropylmethyl radical **19** followed by reaction with O_2 (Scheme 5).



Scheme 5. Proposed mechanism for the oxygenation of vinylcyclopropane **18**.

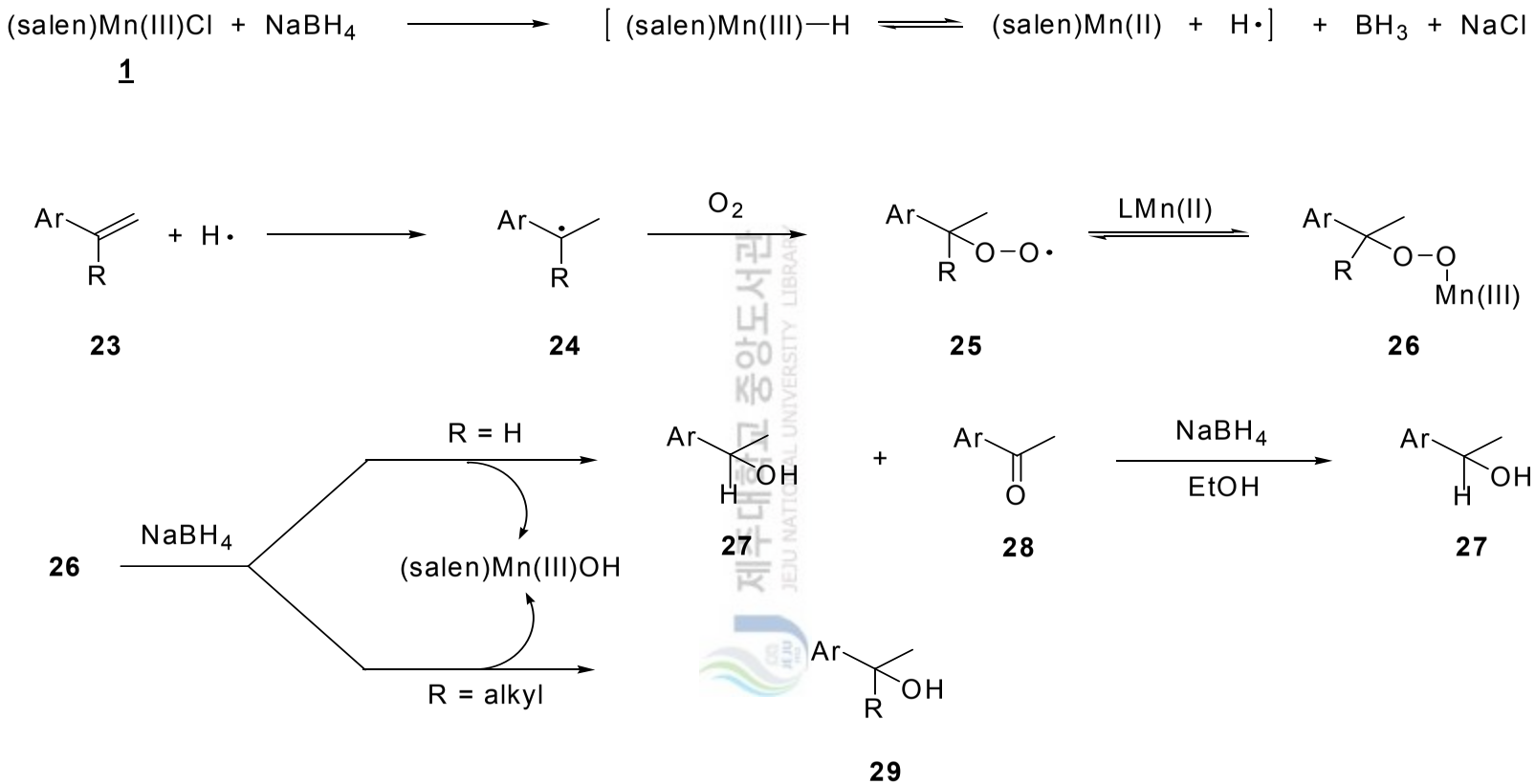
On the basis of the results, we propose the reaction mechanism of the oxygenation of vinyl arenes in our reaction conditions as following (Scheme 6).

(Salen)Mn(III) complex **1** reacting as the oxidant is converting hydride to hydrogen radical and is reduced to (salen)Mn(II). Then the resulting hydrogen

radical forms benzyl radical **24** being added to vinyl arene compound. Benzyl radical is stabilized by resonance. The stabilized radical **24** should easily react with dioxygen to yield peroxyl radical **25**,[43] which may be converted to (alkylperoxo)-(salen)Mn(III) **26** being captured to (salen)Mn(II). The formation of (alkylperoxo)-(salen)Mn(III) **26** may take place with two probable pathway: (1) (salen)LMn(II) coordinated with peroxyl radical is oxidized to LMn(III) by electron transfer of dioxygen. (2) electron-rich LMn(II) combined with dioxygen forms (peroxo)-LMn(III) radical, which reacting with radical **24** may form (alkylperoxo)-(salen)Mn(III) **26** which may be stabilized in a form of (alkylperoxo)-(salen)Mn(III) **26**.[44]

The O-O bond of the intermediate **26** derived from vinyl arene may homolytically cleavage to form ketone (**28**) and dispropotionation process to form corresponding alcohol (**27**). The formed ketone **28** is reduced to corresponding alcohol (**27**) by $NaBH_4$ under reaction conditions. Meanwhile, since the intermediate **26** generated from α-substituted vinyl arene such as α-methylstyrene, may directly be reduced by $NaBH_4$ to yield *tert*-alcohol (**29**). The formation of small amount of acetophenone was observed in the oxygenation of styrene. It is quite reasonable to consider that acetophenone is the precursor of the final oxygenation product, 1-phenylethanol. In order to confirm this, the deuterium incorporation was studied using $NaBD_4$. The reaction conditions were the same as those described in experimental section, except for the use of $NaBD_4$ in place of $NaBH_4$. The structures of the oxygenation products of styrene and α-methylstyrene were determined by means of ^1H NMR and GC-MSD.

The results are revealed in Eq. 4 and Eq. 5. In case of styrene, two molecular

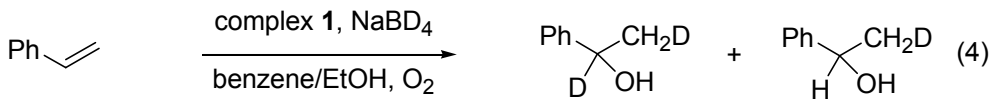


Scheme 6. Proposed mechanism of the oxygenation of vinyl arenes.

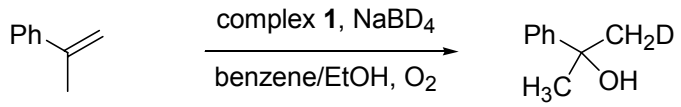
peaks were observed at m/e = 123 and 124 (relative intensity; 1.6:1), which correspond to $C_6H_5CH(OH)(CH_2D)$ and $C_6H_5CD(OH)(CH_2D)$, respectively. The fragmentation peaks due to the $C_6H_5CH(OH)$ and $C_6H_5CD(OH)$ radical ions were also observed at m/e = 107 and 108 (relative intensity: 1.7:1), respectively.

If 1-phenylethanol is necessarily formed *via* acetophenone, the molecular-ion peak should be observed only at m/e = 124. The result of deuterium incorporation indicates that there are, at least, two pathways for formation of 1-phenylethanol. Since the mass spectroscopy applied in this study can not provide the correct ratio of $C_6H_5CH(OH)(CH_2D)$ to $C_6H_5CD(OH)(CH_2D)$,[45] the reaction product were analyzed by means of ^1H NMR spectroscopy. The NMR signal were assigned to $C_6H_5CH(OH)(CH_2D)$ and $C_6H_5CD(OH)(CH_2D)$. The signal due to -CH(OH)- appeared at 4.85 ppm. The comparison of the signal intensity at 4.85 ppm due to -CH(OH)- with that at 1.45 ppm due to $-(CH_2D)-$ suggests that the ratio of the formation of $C_6H_5CH(OH)(CH_2D)$ to $C_6H_5CD(OH)(CH_2D)$ is 1:1.

In the oxygenation of α-methylstyrene in the presence of $NaBD_4$, 1-deuterio-2-phenyl-2-propanol was the sole oxygenation product under same conditions.



(4)

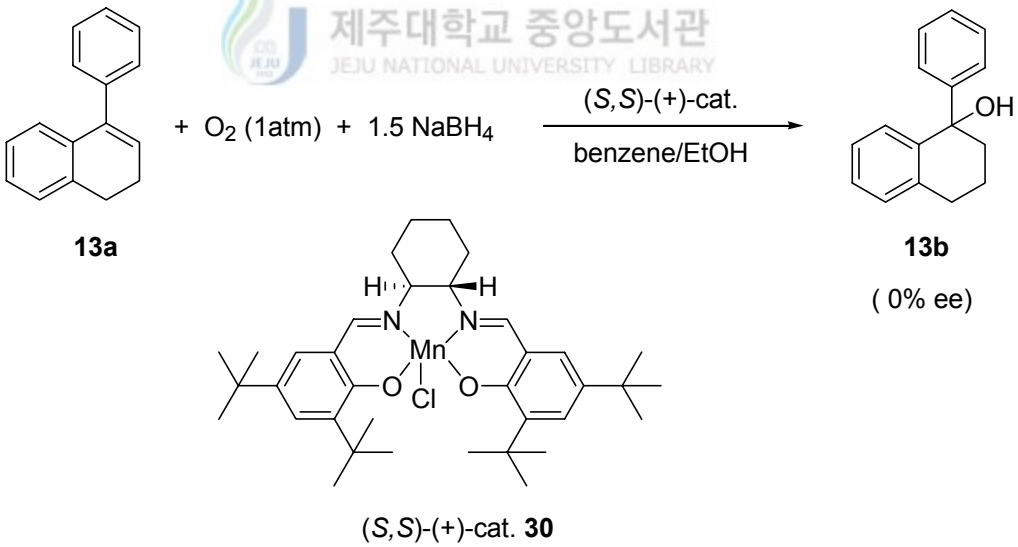


(5)

In the process of the formation of benzyl radical **24** and peroxy radical **25**, it

is possible to assume another pathway in which the mechanism involving (σ-alkyl)Mn(III)-complex[46] which is formed by the coordination of olefin and (salen) Mn(II). If coordination is done, it is assumed that chirality is somewhat transferred in the experiment using optical active (salen)Mn complex as the catalyst. But the optical yield (ee's) of the alcohol **13b** was not obtained (Scheme 7). Judging from this result, the coordination of (salen)Mn(II) with olefin do not occur.

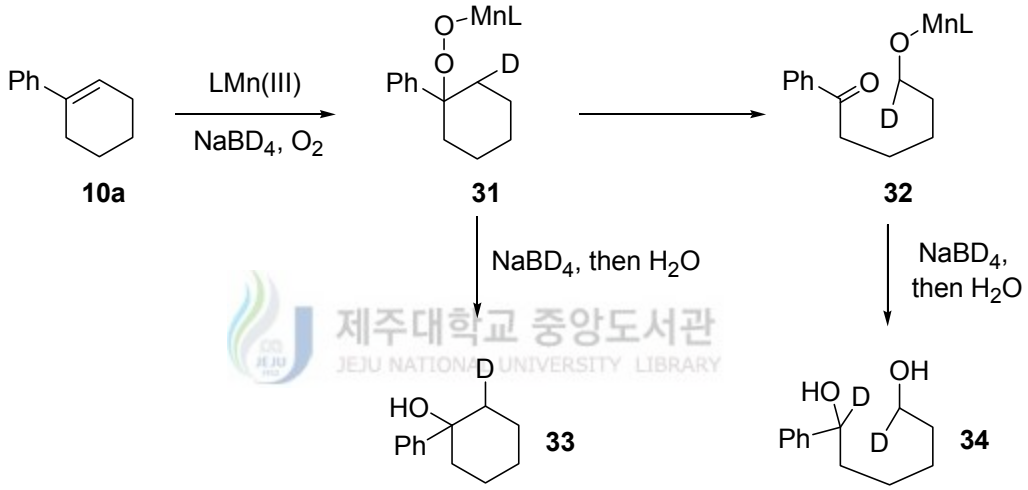
In case of 1-phenyl-1-cyclohexene was used as the substrate, the expected alcohol and C-C bond cleaved product were isolated. The product obtained from 1-phenyl-1-cyclohexene could be derived through the pathway described in Scheme 8. The suggested pathway was supported by the analysis of the products



Scheme 7. The asymmetric oxygenation of 1-phenyl-3,4-dihydronaphthalene.

using $NaBD_4$. Involvement of LMn(III), $NaBD_4$ and O_2 produced the peroxo-Mn

intermediate **31** which could be derived either from O_2-oxidation of corresponding C-Mn intermediate or from a pathway involving carbon and C-O-O· radical species, which could be either reduced to **33** or fragmented to give an intermediate **32**. The ketone **32** could be further reduced to the diol **34** by $NaBD_4$. Incorporation of deuterium in **33** and **34** was confirmed by ^1H and ^{13}C NMR analysis.

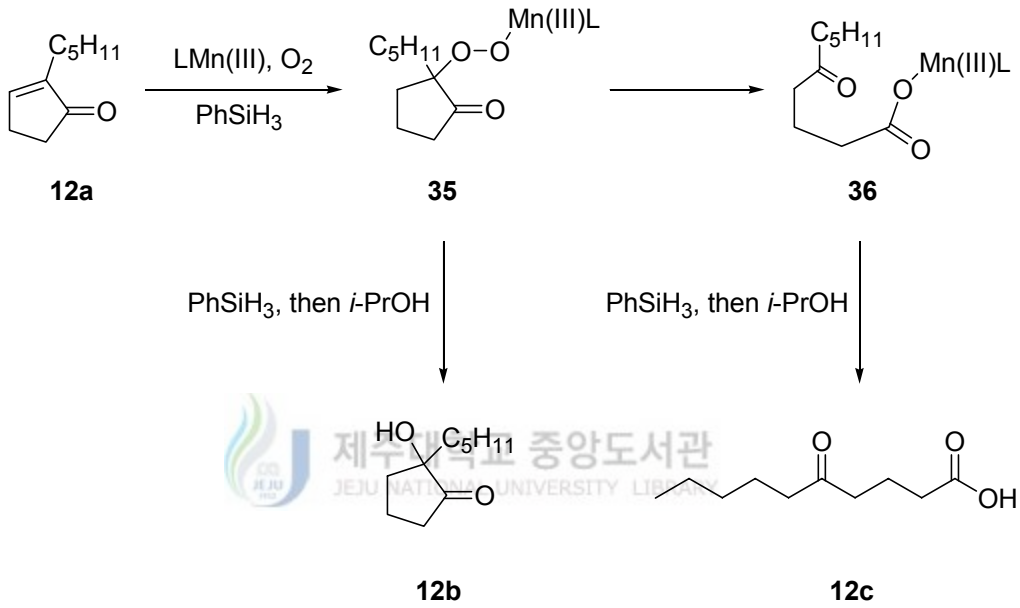


Scheme 8. Proposed mechanism of the oxygenation of 1-phenyl-1-cyclohexene.

Using 2-pentyl-2-cyclopenten-1-one as the substrate also produced the expected alcohol and C-C cleaved ring-open product were isolated. The product obtained from 2-pentyl-2-cyclopenten-1-one could be derived through the pathway describe in Scheme 9.

The result of the deuterium incorporation for the reaction of styrene can be understood by these two mechanisms. Using 1-phenyl-1-cyclohexene or 2-pentyl-2-cyclopenten-1-one as a substrate, indicate that there are, at least, two

pathways for formation of corresponding products. Since no high-valent oxo-manganese(V) complex is generated, the epoxidation does not proceed in our system. Further investigation is needed to identify the detailed reaction mechanism.



Scheme 9. Proposed mechanism of the oxygenation of 2-pentyl-2-cyclopenten-1-one.

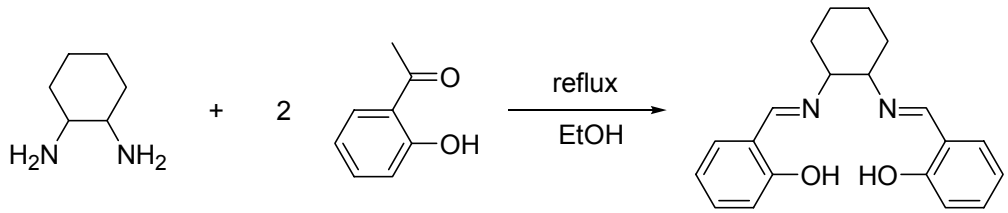
Ⅲ. Experimental

1. General

The reagents and solvent for oxygenations and syntheses were purchased from Aldrich Co. in highest purity and used without further purification. 2,2-dimethyl-chromene was prepared by reported procedure.[47] All the ligands and complexes were prepared as reported with some modification.[28] All solvents were used after drying by the appropriate methods. Thin layer chromatography was performed on Merck prepared plates (silica gel 60 F-254 on aluminum). Column chromatography was performed using Merck silica gel 60 (230-400 mesh). The elemental analyses were carried out using LECO CHN-900 analyzer. The IR spectra were recorded on a Bruker FSS66 FT-IR spectrometer in the range 4000-370 cm^{-1} using KBr pellets. The UV-visible spectra were recorded on a KONTRON UVIKON 860 UV-VIS spectrometer. NMR spectra were recorded on a JEOL model LAMBDA NMR spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. GC/MSD analyses were carried out Hewlett-Packard 5772A gas chromatograph with a mass selective detector equipped with a HP-5 capillary column. The GC analyses were carried out on a YoungLin 600D instrument equipped with a FID detector using HP-5 capillary column. The optical yield (ee's) of the product was determined by ^{1}H NMR spectroscopy using chiral NMR shift reagent $Eu(hfc)_3$.

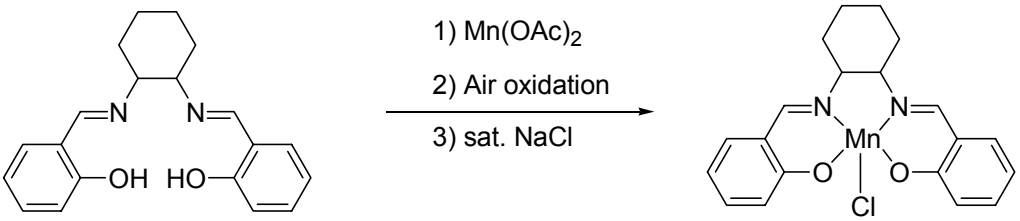
2. Synthesis of ligands and complexes.

1) Synthesis of *N,N'*-cyclohexylbis(salicyaldimine) (H_2L_1)



In a 300 mL round bottom flask were placed salicylaldehyde (2.44 g, 20 mmol) in ethanol (100 mL). A solution of (±)-*trans*-1,2-diaminocyclohexane (1.14 g, 10 mmol) in ethanol (10 mL) was added. The mixture was heated to reflux for 2 hr. The reaction mixture was cooled in an ice bath, the yellow solid began to precipitate and was collected by vacuum filtration and washed with ethanol. The ligand H_2L_1 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (2.51 g, 78% yield): Anal. Calcd (found, %) for $C_{20}H_{22}N_2O_2$: C, 74.51 (74.55); H, 6.88 (6.79); N, 8.69 (8.61)

Synthesis of $Mn(L_1)Cl$ (complex 1)



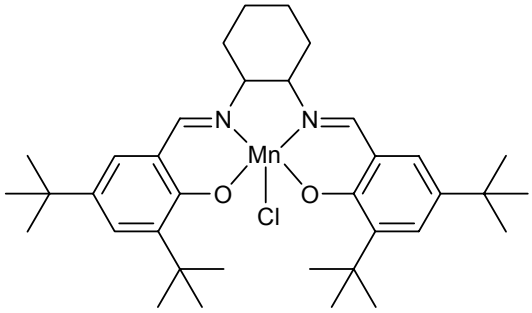
In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with $Mn(OAc)_2 \cdot 4H_2O$ (3.55 g, 14.5 mmol) and ethanol (50 mL). The stirred solution was heated to reflux (80-85℃) with heating mantle, and a solution of ligand H_2L_1 (1.56 g, 4.84 mmol) in toluene (50 mL) was added in a slow stream over 20 min. The mixture was stirred at reflux for 2 hr and air was bubbled through the reaction mixture for 1 hr. After addition of brine solution (20 mL), the mixture was cooled to room temperature and the precipitated brown solid was collected by filtration and washed with toluene (30 mL) and H_2O (50 mL). The complex **1** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (1.74 g, 88% yield): Anal. Calcd (found, %) for $C_{20}H_{20}N_2O_2MnCl$: C, 58.48 (58.15); H, 4.91 (4.87); N, 6.82 (6.60)

2) Synthesis of *N,N′*-cyclohexylbis(3,5-di-*tert*-butylsalicyaldimine) (H_2L_2)

In a 300 mL round bottom flask were placed 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (4.69 g, 20 mmol) in ethanol (100 mL). A solution of (±)-*trans*-1,2-diaminocyclohexane (1.14 g, 10 mmol) in ethanol (10 mL) was added. The mixture was heated to reflux for 2 hr. The reaction mixture was cooled in an ice bath and the precipitated yellow solid was collected by vacuum filtration and washed with ethanol. The ligand H_2L_2 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (4.54 g, 83% yield): Anal. Calcd (found, %) for $C_{36}H_{54}N_2O_2$: C, 79.07 (79.02); H, 9.95 (9.90); N, 5.12 (5.10)

Synthesis of $Mn(L_2)Cl$ (complex 2)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with $Mn(OAc)_2 \cdot 4H_2O$ (3.68 g, 15 mmol) and ethanol



complex **2**

(50 mL). The stirred solution was heated to reflux (80-85℃) with heating mantle, and a solution of ligand H_2L_2 (2.73 g, 5 mmol) in toluene (50 mL) was added in a slow stream over 20 min. The mixture was stirred at reflux for 2 hr and air was bubbled through the reaction mixture for 1 hr. After addition of brine solution (20 mL), the mixture was cooled to room temperature and rinsed into a separatory funnel with toluene (20 mL). The brown organic layer was washed with H_2O (3 × 50 mL) and then dried over Na_2SO_4. Solvent removal in *vacuo* yielded a brown solid which was redissolved completely in CH_2Cl_2 (50 mL). To this solution heptane (50 mL) was added, and the resulting mixture was concentrated by rotary evaporation to a volume of ≈ 15 mL. The mixture was cooled in an ice bath for 1 hr and the precipitated brown solid was collected by filtration and washed with toluene (30 mL) and H_2O (50 mL). The complex **2** was dried under high vacuum at 10 0℃ for 12 hr to yield the desired product (2.79 g, 88% yield): Anal. Calcd (found, %) for $C_{36}H_{52}N_2O_2MnCl$: C, 68.07 (67.96); H, 8.25 (8.35); N, 4.41 (4.20)

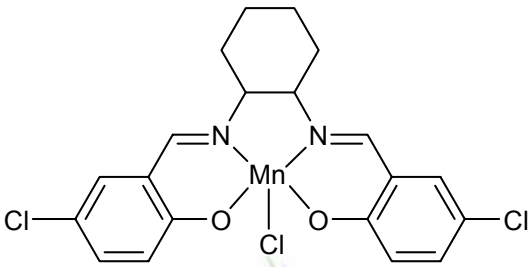
3) Synthesis of *N,N′*-cyclohexylbis(5-chlorosalicyaldimine) (H_2L_3)

In a 300 mL round bottom flask were placed 5-chlorosalicylaldehyde (3.13 g, 20 mmol) in ethanol (100 mL). A solution of (±)-*trans*-1,2-diaminocyclohexane (1.14 g, 10 mmol) in ethanol (10 mL) was added. The mixture was heated to reflux for 2 hr. The reaction mixture was cooled in an ice bath and the precipitated yellow solid was collected by vacuum filtration and washed with

ethanol. The ligand H_2L_3 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (2.15 g, 55% yield): Anal. Calcd (found, %) for $C_{20}H_{20}N_2O_2Cl_2$: C, 61.39 (61.30); H, 5.15 (5.12); N, 7.16 (7.11)

Synthesis of $Mn(L_3)Cl$ (complex 3)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with $Mn(OAc)_2 \cdot 4H_2O$ (3.68 g, 15 mmol) and ethanol (50 mL). The stirred solution was heated to reflux (80-85℃) with heating mantle, and a solution of ligand H_2L_3 (1.96 g, 5 mmol) in toluene (50 mL) was added in a slow stream over 20 min. The mixture was stirred at reflux for 2 hr and air was bubbled through the reaction mixture for 1 hr. After addition of brine solution (20 mL), the mixture was cooled to room temperature and the precipitated brown solid was collected by filtration and washed with toluene (30 mL) and H_2O (50 mL). The complex **3** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (1.78 g, 74% yield): Anal. Calcd (found, %) for $C_{20}H_{18}N_2O_2Cl_2MnCl$: C, 50.08 (50.15); H, 3.78 (3.80); N, 5.84 (5.89)



complex **3**

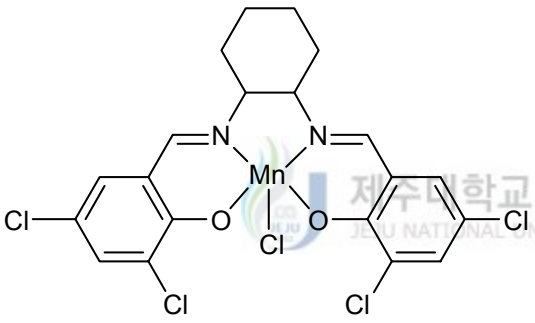
4) Synthesis of *N,N′*-cyclohexylbis(3,5-dichlorosalicyaldimine) (H_2L_4)

In a 300 mL round bottom flask were placed 3,5-dichlorosalicylaldehyde (3.82 g, 20 mmol) in ethanol (100 mL). A solution of (±)-*trans*-1,2-diaminocyclohexane (1.14 g, 10 mmol) in ethanol (10 mL) was added. The mixture was heated to

reflux for 2 hr. The reaction mixture was cooled in an ice bath and the precipitated yellow solid was collected by vacuum filtration and washed with ethanol. The ligand H_2L_4 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (4.05 g, 88% yield): Anal. Calcd (found, %) for $C_{20}H_{18}N_2O_2Cl_4$: C, 52.20 (52.18); H, 3.94 (4.01); N, 6.09 (6.05)

Synthesis of $Mn(L_4)Cl$ (complex 4)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with $Mn(OAc)_2 \cdot 4H_2O$ (3.68 g, 15 mmol) and ethanol (34 mL). The stirred solution was heated to reflux (80-85℃) with heating mantle, and a solution of ligand H_2L_4 (2.3 g, 5 mmol) in toluene (50 mL) was added in a slow stream over 20 min. The mixture was stirred at reflux for 2 hr and air was bubbled through the reaction mixture for 1 hr. After addition of brine solution (20 mL), the mixture was cooled to room temperature and the precipitated brown solid was collected by filtration and washed with toluene (30 mL) and H_2O (50 mL). The complex **4** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (2.19 g, 80% yield): Anal. Calcd (found, %) for $C_{20}H_{16}N_2O_2Cl_4MnCl$: C, 43.79 (43.84); H, 2.94 (2.91); N, 5.11 (5.18)



complex **4**

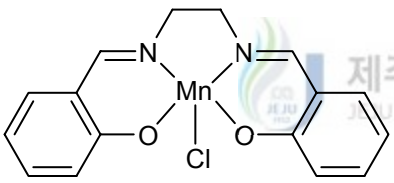
5) Synthesis of *N,N′*-ethylbis(salicylaldimine) ($H_2L_5 \cdot 1/4H_2O$)

In a 300 mL round bottom flask were placed salicylaldehyde (6.11 g, 50 mmol)

in methanol (100 mL). A solution of ethylenediamine (1.5 g, 25 mmol) in methanol (10 mL) was added. The mixture was heated to reflux for 2 hr. The reaction mixture was cooled to room temperature and began to precipitate the yellow solid. The product was collected by vacuum filtration and washed with methanol. The ligand H_2L_5 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (5.05 g, 74% yield): Anal. Calcd (found, %) for $C_{16}H_{16}N_2O_2 \cdot 1/4H_2O$: C, 70.44 (70.28); H, 6.10 (6.18); N, 10.27 (10.35)

Synthesis of $Mn(L_5)Cl$ (complex 5)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_5 (4.09 g, 15 mmol) and toluene (50 mL). The stirred solution was heated to reflux with heating mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (3.68 g, 15 mmol) in methanol (30 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (20 mL) was added and the solution was refluxed for 1 hr. After cooling the mixture to room temperature, solvent was removed in *vacuo*. H_2O (100 mL) was added with stirring for 10 min. The solution was concentrated by rotary evaporation to a volume of ≈ 20 mL, The precipitated reddish brown solid was collected by filtration and washed with a small portion of cold H_2O. The complex **5** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (4.06 g, 74% yield): Anal. Calcd (found, %) for $C_{16}H_{14}N_2O_2MnCl \cdot 1/2H_2O$: C, 52.55 (53.07); H, 4.13 (4.65); N, 7.66 (7.85)



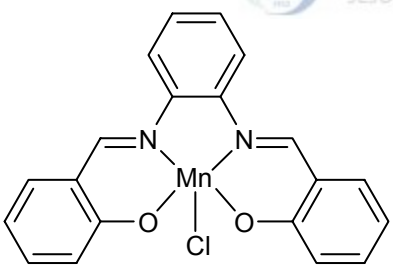
complex **5**

6) Synthesis of *N,N′*-phenylbis(salicylaldimine) ($H_2L_6 \cdot 1/2H_2O$)

In a 300 mL round bottom flask were placed salicylaldehyde (6.11 g, 50 mmol) in methanol (100 mL). A solution of *o*-phenylethylenediamine (2.70 g, 25 mmol) in methanol (10 mL) was added. The mixture was heated to reflux for 2 hr. The reaction mixture was cooled in an ice bath. The deep red product that precipitated from the resulting solution was collected by vacuum filtration and washed with methanol. The ligand H_2L_6 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (6.24 g, 77% yield): Anal. Calcd (found, %) for $C_{20}H_{16}N_2O_2 \cdot 1/2H_2O$: C, 73.83 (73.75); H, 5.27 (5.51); N, 8.61 (8.78)

Synthesis of $Mn(L_6)Cl$ (complex 6)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_6 (4.88 g, 15 mmol) and toluene (50 mL). The stirred solution was heated to reflux with heating mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (11.03 g, 45 mmol) in methanol (100 mL) was added in a slow stream over 20 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (20 mL) was added and the solution was refluxed for 1 hr. After cooling the mixture to room temperature, the solution was concentrated by rotary evaporation to a volume of ≈ 20 mL. After addition of H_2O (100 mL), the solution was stirred for 10 min, whereupon the complex began to precipitate. The precipitated reddish brown solid was collected by filtration. The complex **6** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (4.75 g,



complex **6**

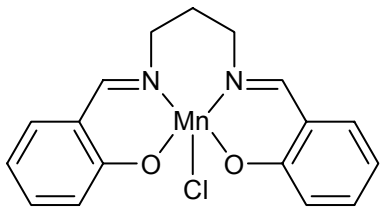
75% yield): Anal. Calcd (found, %) for $C_{20}H_{14}N_2O_2MnCl \cdot H_2O$: C, 56.82 (56.47); H, 3.81 (4.00); N, 6.63 (6.35)

7) Synthesis of *N,N'*-propylbis(salicylaldimine) ($H_2L_7 \cdot 3/4H_2O$)

In a 300 mL round bottom flask were placed salicylaldehyde (6.11 g, 50 mmol) in methanol (100 mL). A solution of 1,3-diaminopropane (1.85 g, 25 mmol) in methanol (10 mL) was added. The mixture was heated to reflux for 2 hr. The solution was concentrated by rotary evaporation to a volume of ≈ 20 mL. After cooling the solution in an ice bath, H_2O (100 mL) was added, and the mixture was stirred. The product was obtained as a yellow precipitate, which was collected by vacuum filtration and washed with H_2O. The ligand H_2L_7 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (6.03 g, 82% yield): Anal. Calcd (found, %) for $C_{17}H_{18}N_2O_2 \cdot 3/4H_2O$: C, 69.02 (69.21); H, 6.64 (6.74); N, 9.47 (9.85)

Synthesis of $Mn(L_7)Cl$ (complex 7)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_7 (4.44 g, 15 mmol) and toluene (50 mL). The stirred solution was heated to reflux with heating mantle and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (3.67 g, 15 mmol) in methanol (100 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (20 mL) was added and the solution was refluxed for 1 hr. After cooling



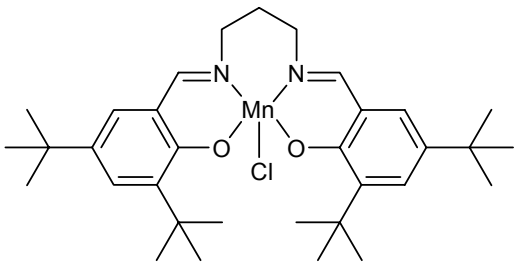
complex **7**

the mixture to room temperature, the solution was concentrated by rotary evaporation to a volume of ≈ 20 mL. After addition of 50 mL of H_2O was stirred for 10 min, whereupon the product began to precipitate. The precipitated dark reddish brown solid was collected by filtration. The complex **7** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (3.87 g, 66% yield): Anal. Calcd (found, %) for $C_{17}H_{16}N_2O_2MnCl \cdot H_2O$: C, 52.53 (52.52); H, 4.67 (4.83); N, 7.21 (7.49)

8) Synthesis of *N,N′*-propylbis(3,5-di-*tert*-butylsalicylaldimine) (H_2L_8)

In a 300 mL round bottom flask were placed 3,5-di-*tert*-butyl-2-hydroxybenz-aldehyde (2.34 g, 10 mmol) in methanol (100 mL). A solution of 1,3-diamino-propane (0.37 g, 5 mmol) in methanol (10 mL) was added. The mixture was heated to reflux for 3 hr. The reaction mixture was cooled to room temperature. The orange precipitate from the resulting solution was filtered off and washed with cold methanol. The ligand H_2L_8 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (2.26 g, 89% yield): Anal. Calcd (found, %) for $C_{33}H_{50}N_2O_2$: C, 78.21 (78.00); H, 9.94 (9.81); N, 5.53 (5.60)

Synthesis of Mn(L_8)Cl (complex 8)



complex **8**

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_8 (1.01 g, 2 mmol) and toluene (100 mL). The stirred solution was heated to reflux with heating

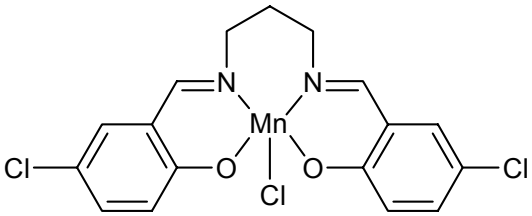
mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (2.21 g, 9 mmol) in methanol (30 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (4 mL) was added and the solution was refluxed for 1 hr. After cooling the mixture to room temperature, the solution was concentrated by rotary evaporation to a volume of ≈ 20 mL. After addition of H_2O (100 mL), the solution stirred for 10 min, whereupon the product began to precipitate. The precipitated dark reddish brown solid that was collected by filtration and washed with H_2O. It was recrystallized from acetone. The complex **8** was dried under high vacuum at 10 0℃ for 12 hr to yield the desired product (0.58 g, 48% yield): Anal. Calcd (found, %) for $C_{33}H_{48}N_2O_2MnCl \cdot 1/2H_2O$: C, 65.61 (65.13); H, 8.17 (7.83); N, 4.64 (4.48)

9) Synthesis of *N,N′*-propylbis(5-chlorosalicylaldimine) ($H_2L_9 \cdot 1/4H_2O$)

In a 500 mL round bottom flask were placed 5-chlorosalicylaldehyde (7.83 g, 50 mmol) in methanol (200 mL). A solution of 1,3-diaminopropane (1.85 g, 25 mmol) in methanol (20 mL) was added. The mixture was heated to reflux for 3 hr. The reaction mixture was cooled to room temperature. The yellow product that precipitated from the resulting solution was filtered off and washed with methanol. The ligand H_2L_9 was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (7.69 g, 87% yield): Anal. Calcd (found, %) for $C_{17}H_{16}N_2O_2Cl_2 \cdot 1/4H_2O$: C, 57.40 (57.17); H, 4.67 (4.64); N, 7.87 (7.80)

Synthesis of $Mn(L_9)Cl$ (complex 9)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_9 (3.56 g, 10 mmol) and toluene (50



complex **9**

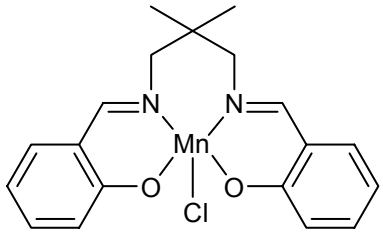
mL). The stirred solution was heated to reflux with heating mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (4.90 g, 20 mmol) in methanol (20 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (15 mL) was added and the solution was refluxed for 1 hr. After cooling the mixture to room temperature, the solution was concentrated by rotary evaporation to a volume of ≈ 20 mL. After addition of 100 mL of H_2O, the solution was stirred for 10 min, whereupon the product began to precipitate. The precipitated green solid was collected by filtration and washed with cold H_2O. It was recrystallized from methanol. The complex **9** was dried under high vacuum at 10 0℃ for 12 hr to yield the desired product (2.23 g, 51% yield): Anal. Calcd (found, %) for $C_{17}H_{14}N_2O_2Cl_2MnCl$: C, 46.45 (46.17); H, 3.21 (3.78); N, 6.37 (6.55)

10) Synthesis of *N,N′*-2,2-dimethylproylbis(salicylaldimine) ($H_2L_{10} \cdot 1/4H_2O$)

In a 500 mL round bottom flask were placed salicylaldehyde (6.11 g, 50 mmol) in methanol (150 mL). A solution of 2,2-dimethyl-1,3-propanediamine (2.55 g, 25 mmol) in methanol (20 mL) as a solvent. The mixture was heated to reflux for 3 hr. The reaction mixture was cooled to room temperature. The yellow product that precipitated from the resulting solution was filtered off and washed with cold methanol. The ligand H_2L_{10} was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (5.98 g, 76% yield): Anal. Calcd (found, %) for $C_{19}H_{22}N_2O_2 \cdot 1/4H_2O$: C, 72.47 (72.65); H, 7.20 (7.23); N, 8.90 (8.96)

Synthesis of $Mn(L_{10})Cl$ (complex 10)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_{10} (2.20 g, 7 mmol) and methanol (50 mL). The stirred solution was heated to reflux with heating mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (5.14 g, 21 mmol) in methanol (50 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30min and air was bubbled through the reaction mixture for 1 hr. Brine solution (10 mL) was added and the solution was refluxed for 1 hr. The reaction mixture was cooled to room temperature and concentrated by rotary evaporation to a volume of ≈ 20 mL. After addition of MeOH (100 mL), and the mixture was stirred for 10 min, and then the solution was filtered. The filtrate was removed from solvent in *vacuo* and yielded the dark yellowish green product, which was washed with diethyl ether and recrystallized from CH_2Cl_2. The complex **10** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (1.67 g, 60% yield): Anal. Calcd (found, %) for $C_{19}H_{20}N_2O_2MnCl$: C, 57.23 (57.20); H, 5.06 (4.78); N, 7.03 (7.09)



complex **10**

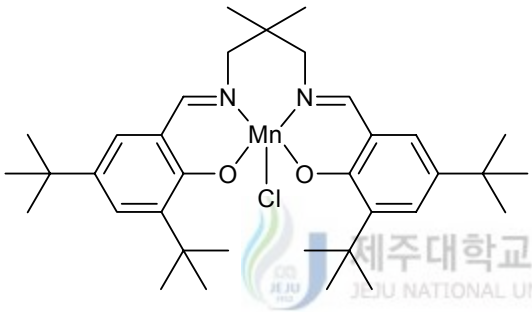
11) Synthesis of *N,N′*-2,2-dimethylpropylbis(3,5-di-*tert*-butylsalicylaldimine) (H_2L_{11})

In a 300 mL round bottom flask were placed 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) in methanol (100 mL). A solution of 2,2-dimethyl-1,3-propanediamine (0.51 g, 5 mmol) in methanol (10 mL) was added. The mixture was stirred at room temperature for 3 hr. The yellow product that

precipitated from the resulting solution was filtered off and washed with cold methanol. The ligand H_2L_{11} was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (2.46 g, 92% yield): Anal. Calcd (found, %) for $C_{35}H_{54}N_2O_2$: C, 78.65 (78.70); H, 10.11 (10.44); N, 5.24 (5.33)

Synthesis of $Mn(L_{11})Cl$ (complex 11)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_{11} (1.07 g, 2 mmol) and methanol (10 mL). The stirred solution was heated to reflux with heating mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (0.49 g, 2 mmol) in methanol (30 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (2 mL) was added and the solution was refluxed for 1 hr. After cooling the mixture to room temperature, the solution was concentrated by rotary evaporation. After addition of 50 mL of H_2O, the solution was stirred for 10 min, whereupon the complex began to precipitate. The precipitated dark green solid was collected by filtration and washed with H_2O. It was recrystallized from CH_2Cl_2. The complex **11** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (0.47 g, 38% yield): Anal. Calcd (found, %) for $C_{35}H_{52}N_2O_2MnCl$: C, 67.46 (68.49); H, 8.41 (8.90); N, 4.50 (4.11)



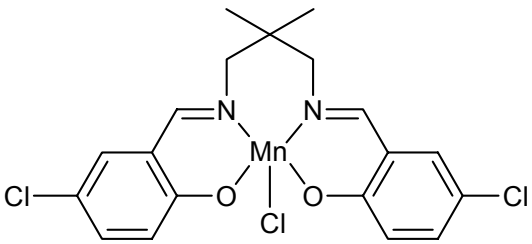
complex **11**

12) Synthesis of *N,N′*-2,2-dimethylpropylbis(5-chlorosalicylaldimine) (H_2L_{12} · $1/4H_2O$)

In a 300 mL round bottom flask were placed 5-chlorosalicylaldehyde (3.13 g, 20 mmol) in methanol (150 mL), A solution of 2,2-dimethyl-1,3-propanediamine (1.02 g, 10 mmol) in methanol (15 mL) as a solvent. The mixture was stirred at room temperature for 1 day. The precipitated yellow solid was collected by vacuum filtration and washed with cold methanol. The ligand H_2L_{12} was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (1.68 g, 44% yield): Anal. Calcd (found, %) for $C_{19}H_{20}N_2O_2Cl_2$ · $1/4H_2O$: C, 59.46 (59.65); H, 5.38 (5.48); N, 7.30 (7.40)

Synthesis of $Mn(L_{12})Cl$ (complex 12)

In a 300 mL three necked flask equipped with a reflux condenser, and an addition funnel was charged with ligand H_2L_{12} (0.77 g, 2 mmol) and toluene (10 mL). The stirred solution was heated to reflux with heating mantle, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (0.49 g, 2 mmol) in methanol (20 mL) was added in a slow stream over 10 min. The mixture was stirred at reflux for 30 min and air was bubbled through the reaction mixture for 1 hr. Brine solution (2 mL) was added and the solution was refluxed for 1 hr. After cooling the mixture to room temperature, the solution was concentrated by rotary evaporation. After addition of 50 mL of H_2O, the solution was stirred for 10 min, whereupon the product began to precipitate. The precipitate was collected by filtration and



complex **12**

washed with H_2O. The complex **12** was dried under high vacuum at 100℃ for 12 hr to yield the desired product (0.8 g, 86% yield): Anal. Calcd (found, %) for $C_{19}H_{18}N_2O_2Cl_2$ MnCl: C, 48.80 (48.94); H, 3.88 (3.81); N, 5.99 (6.02)

13) Synthesis of *N,N′*-2,2-dimethylpropylbis(5-nitrosalicylaldimine) (H_2L_{13})

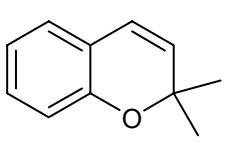
In a 300 mL round bottom flask were placed 2-hydroxy-5-nitrobenzaldehyde (1.02 g, 6.1 mmol) in benzene (100 mL). A solution of 2,2-dimethyl-1,3-propanediamine (0.31 g, 3 mmol) in methanol (10 mL) was added. The mixture was stirred at reflux for 4 hr. The precipitated yellow solid was collected by vacuum filtration and washed with methanol and benzene. The ligand H_2L_{13} was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (0.84 g, 70% yield): Anal. Calcd (found, %) for $C_{19}H_{20}N_4O_6$: C, 57.00 (57.65); H, 5.03 (5.18); N, 13.99 (13.85)

14) Synthesis of *N,N′*-2,2-dimethylpropylbis(3,5-di-nitrosalicylaldimine) (H_2L_{14})

In a 300 mL round bottom flask were placed 3,5-di-nitrobenzaldehyde (1.28 g, 6 mmol) in ethanol (50 mL), A solution of 2,2-dimethyl-1,3-propanediamine (0.31 g, 3 mmol) in ethanol (5 mL) was added, whereupon the product began to precipitate. The mixture was stirred at reflux for 2 hr. The reaction mixture was cooled in an ice bath and the precipitated yellow solid was collected by vacuum filtration and washed with ethanol. The ligand H_2L_{14} was dried under vacuum at 40 ℃ for 12 hr to yield the desired product (1.15 g, 78% yield): Anal. Calcd (found, %) for $C_{19}H_{18}N_6O_{10}$: C, 46.54 (46.29); H, 3.70 (3.82); N, 17.14 (17.40)

3. Synthesis of the substrates.

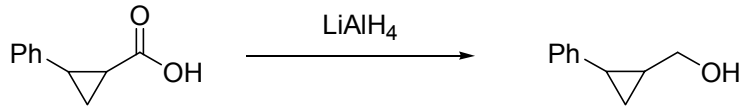
1) Synthesis of 2,2-dimethylchromene.



Coumarin (5 g, 34.2 mmol) was dissolved in a mixture of anhydrous ether (60 mL) and toluene (40 mL) under nitrogen atmosphere and with a bath temperature of 38-40℃. To this was added a solution of methyllithium in ether (1.5 M solution) by syringe over 5 minutes. After 3 minutes, the reaction flask was cooled in ice bath, and a mixture of water (10 mL) and THF (10 mL) was added by syringe over 3 minutes. The temperature was allowed to rise to room temperature and 10% aqueous KH_2PO_4 solution was added to make pH below 7.0. The mixture was poured into water (100 mL) and NaCl was added to saturation. The mixture was extracted 3 times with ethyl acetate (total volume 180 mL) and extracts were dried over Na_2SO_4 and filtered. The solvent was removed in *vacuo*. and the residue in hexane (150 mL) was refluxed with stirring under nitrogen in the presence of silica gel (70 g) for 12 hours. The silica gel was removed by filtration and washed with hexane. Evaporation of the filtrates under reduced pressure afforded crude 2,2-dimethyl-chromene. The yield of pure 2,2-dimethylchromene obtained after f. c. c. was 75% (4.12g).

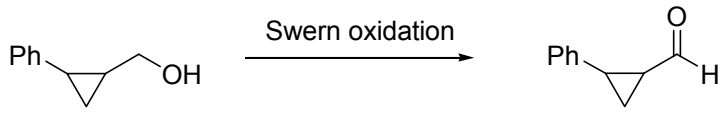
2) Synthesis of 2-phenyl-1-vinylcyclopropane.

(1). Synthesis of 2-phenylcyclopropanemethanol.



A 500 mL three-necked round-bottomed flask equipped with a reflux condenser, and addition funnel. In this flask were placed $LiAlH_4$ (4.71 g, 0.12 mol) in dried ether (150 mL). After the mixture has been stirred for 15 min, a milky suspension is produced. A solution of *trans*-2-phenyl-1-cyclopropanecarboxylic acid (9.74 g, 0.06 mol) in dried ether (50 mL) was added from the dropping funnel slowly with vigorous stirring for 2 hr under nitrogen atmosphere. The excess $LiAlH_4$ is decomposed by adding 40 mL of water slowly with stirring and then 6*N* hydrochloric acid (50 mL) was added slowly to the mass. Stirring is continued for 30 min, and the solution becomes clear during this period. This mixture is transferred to a separatory funnel. Brine solution (100 mL) was added and extracted with diethyl ether. The organic layer concentrated in *vacuo* and purified by flash column chromatography to give 2-phenylcyclopropanemethanol (7.99 g, 90% yield).

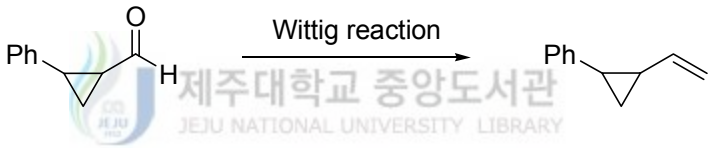
(2) Synthesis of 2-phenylcyclopropanecarbaldehyde.



A solution of oxalyl chloride (5.91 g, 46.5 mmol) in 50 mL of CH_2Cl_2 was placed in a 250 mL round bottom flask, the flask was cooled in immersion cooler,

and DMSO (4.4 mL, 62 mmol) was added. The reaction mixture was stirred for 15 min at this temp, and then alcohol (4.6 g, 31 mmol) in 40 mL of CH_2Cl_2 was added. Stirring continued for 30 min and then Et_3N (12.9 mL, 93 mmol) was added. The reaction mixture was stirred for 30 min. It was poured into H_2O and extracted with CH_2Cl_2 and the combined organic extracts were washed with brine solution and dried over Na_2SO_4. The organic layer was concentrated in *vacuo* and purified by flash column chromatography to give 2-phenylcyclopropanecarbalde-hyde (3.53 g, 78% yield) as the product.

(3) Synthesis of 2-phenyl-1-vinylcyclopropane.



A 300mL three-necked round bottomed flask is fitted with a reflux condenser, an addition funnel. A etheral solution of *n*-butyllithium (about 120 mL, 12 mmol) and 30 mL of anhydride diethyl ether was added to the flask under nitrogen atmosphere. The solution of triphenylmethylphosphonium bromide (4.3 g, 12 mmol) in diethyl ether (50 mL) was added cautiously over a 5 minute period. The solution was stirred for 4 hr at room temperature. And then, 2-phenylcyclo-propanecarbaldehyde (1.5 g, 10 mmol) was added dropwise. The mixture was heated under reflux for 4 hr, allowed to cool at room temperature, and the yellow precipitate was removed by suction filtration. The filtrate was washed with brine solution (3 × 50 mL) and then dried over Na_2SO_4. The solvent was removed in *vacuo* and purified by flash column chromatography to give 2-phenyl-1-vinyl-

cyclopropane (0.43 g, 30% yield) as the product.

4. General procedure.

1) The oxygenation of vinyl arenes.

In a 50 mL round bottom flask were placed α-methylstyrene (118 mg, 1.0 mmol), racemic (salen)Mn(III)Cl complex **1** (20 mg, 0.05 mmol) and benzene/ EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, flushing the vessel with O_2 was under taken by evacuation/ charging procedure three times. To this was added *via* syringe $NaBH_4$ (56 mg, 1.5 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, it was poured into sat. NH_4Cl solution and extracted with diethyl ether. The organic layer was dried with Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography to give 2-phenyl-2-propanol (116 mg, 85% yield) as the product.

2) The oxygenation of various olefins.

In a 50 mL round bottom flask were placed *trans*-β-methylstyrene (118 mg, 1.0 mmol), (salpro)Mn(III)Cl complex **10** (20 mg, 0.05 mmol) and benzene/ EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, flushing the vessel with O_2 was under taken by evacuation/charging procedure three times. To this was added *via* syringe $NaBH_4$ (56 mg, 1.5 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was

stirred for 4 hr at rt, it was poured into sat. NH_4Cl solution and extracted with diethyl ether. The organic layer was dried with Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography to give 1-phenyl-1-propanol (99 mg, 73% yield) as the product.

3) The oxygenation of olefins using Mn(III) salt along with schiff-base ligands as the catalyst.

In a 50 mL round bottom flask were placed α-methylstyrene (118 mg, 1.0 mmol), ligand **13** (26 mg, 0.08 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (22 mg, 0.08 mmol) and benzene/EtOH (10 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, the vessel was flushed three times by O_2. To this was added *via* syringe $NaBH_4$ (74 mg, 2 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, the reaction was quenched by adding sat. NH_4Cl solution. The organic layer extracted with diethyl ether was dried with Na_2SO_4, concentrated, and then purified by flash column chromatography to give 2-phenyl-2-propanol (106 mg, 78% yield) as the product.

4) The Oxygenation of α,β-unsaturated esters.

In a 50 mL round bottom flask were placed lauryl methacrylate (254 mg, 1.0 mmol), (salpro)Mn(III)Cl complex **10** (39 mg, 0.1 mmol), and $CHCl_3$ (4 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, flushing the vessel with O_2 was under taken by evacuation/charging procedure three times. To this was added *via* syringe $NaBH_4$ (74 mg, 2 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, it was poured into sat. NH_4Cl solution and extracted with diethyl ether. The organic

layer was dried with Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography to give dodecyl 2-hydroxy-2-methylpropanoate (226 mg, 83% yield) as the product.

5) The Oxygenation of 2-pentyl-2-cyclopenten-1-one.

In a 50 mL round bottom flask were placed 2-pentyl-2-cyclopenten-1-one (152 mg, 1.0 mmol), schiff-base ligand **15** (74 mg, 0.15 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (40 mg, 0.15 mmol), and *i*-PrOH/EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, flushing the vessel with O_2 was under taken by evacuation/charging procedure three times. After the mixture was stirred for 12 hr at rt, it was poured into sat. NH_4Cl solution and extracted with diethyl ether. The organic layer was dried with Na_2SO_4, concentrated in *vacuo* and purified by flash column chromatography to give 2-hydroxy-2-pentylcyclopentan-one (72 mg, 42% yield) along with 5-oxo-decanoic acid (74 mg, 40% yield) as the product.

6) The asymmetric oxygenation of 1-phenyl-3,4-dihydronaphthalene.

In a 25 mL round bottom flask were placed 1-phenyl-3,4-dihydronaphtalene (206 mg, 1 mmol), (*s,s*)-(+)-Jacobsen's catalyst (32 mg, 0.05 mmol), and benzene/EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, the vessel was flushed three times by O_2. To this was added *via* syringe $NaBH_4$ (74 mg, 2 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, the reaction was quenched by adding sat. NH_4Cl solution. The organic layer extracted with diethyl ether was dried with Na_2SO_4, concentrated, and then purified by flash column chromato-

graphy to give 1-phenyl-1,2,3,4-tetrahydro-1-naphthalenol (54 mg, 24% yield) as the product. The optical yield (ee's) of the product was determined by ^{1}H NMR spectroscopy using chiral NMR shift reagent $Eu(hfc)_3$.

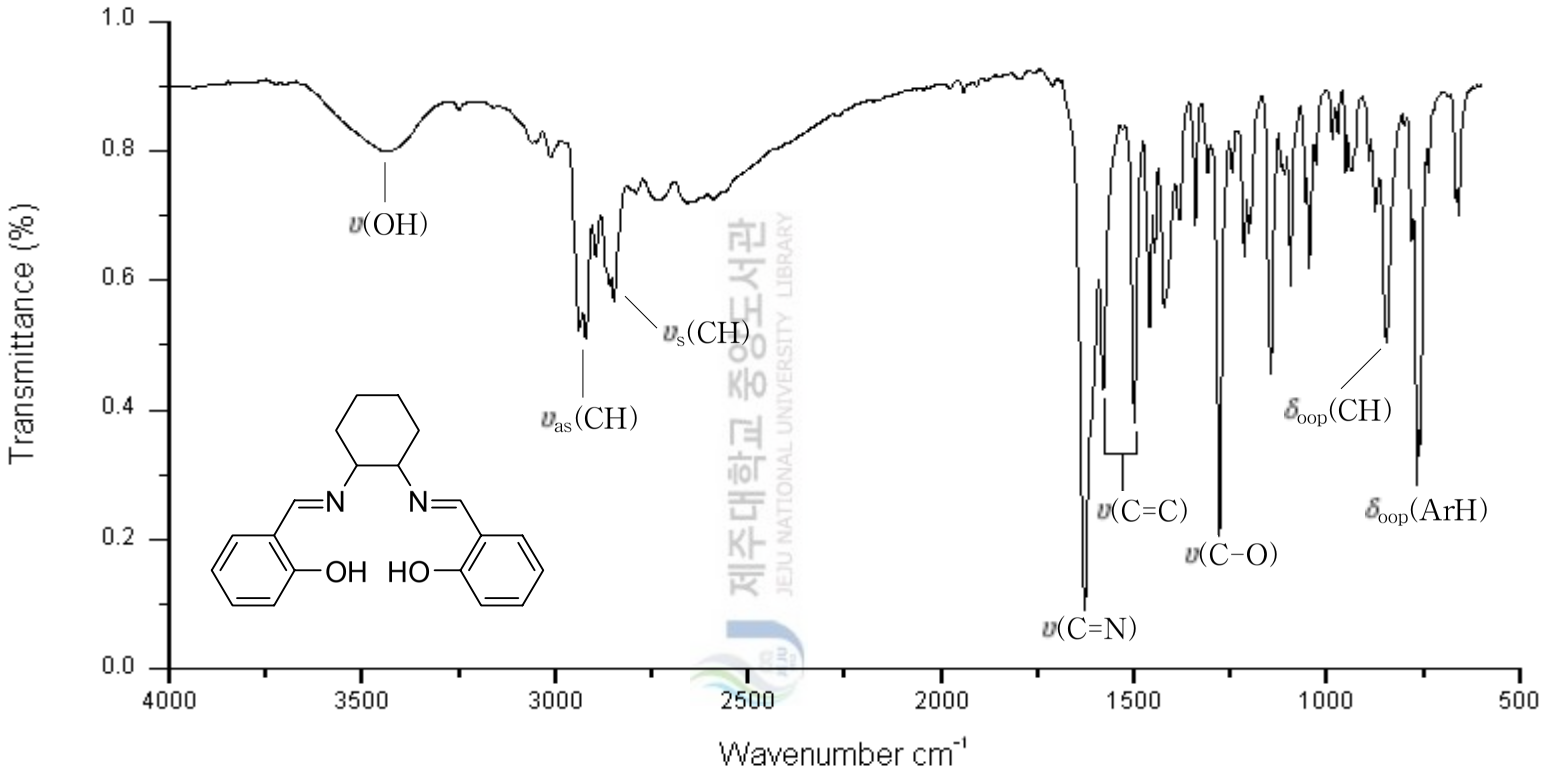


Figure 3. FT-IR spectrum of ligand **16**.

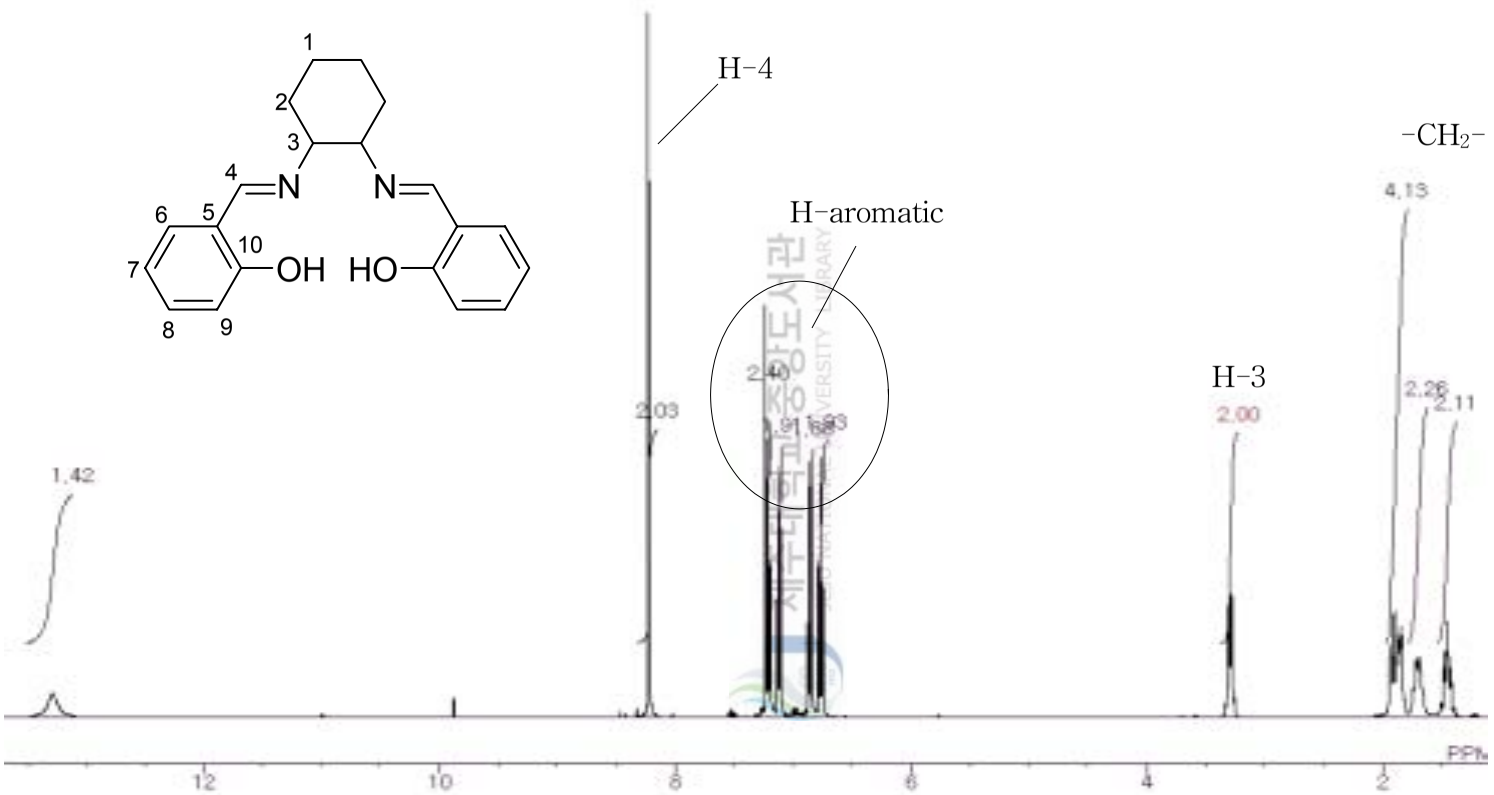


Figure 4. ^{1}H NMR spectrum (400 MHz) of lignad **16** in $CDCl_3$.

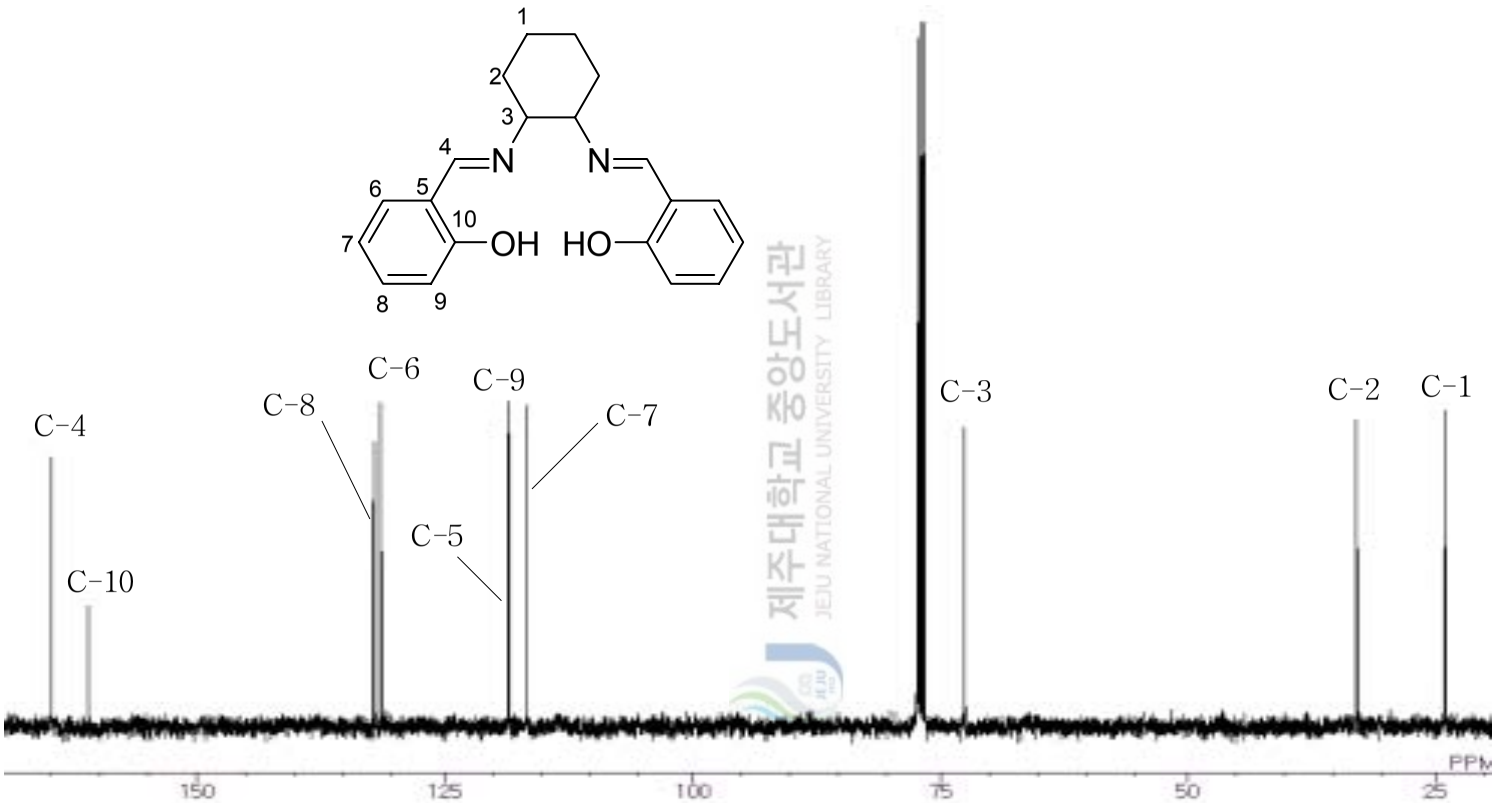


Figure 5. ^{13}C NMR spectrum (100 MHz) of ligand **16** in $CDCl_3$.

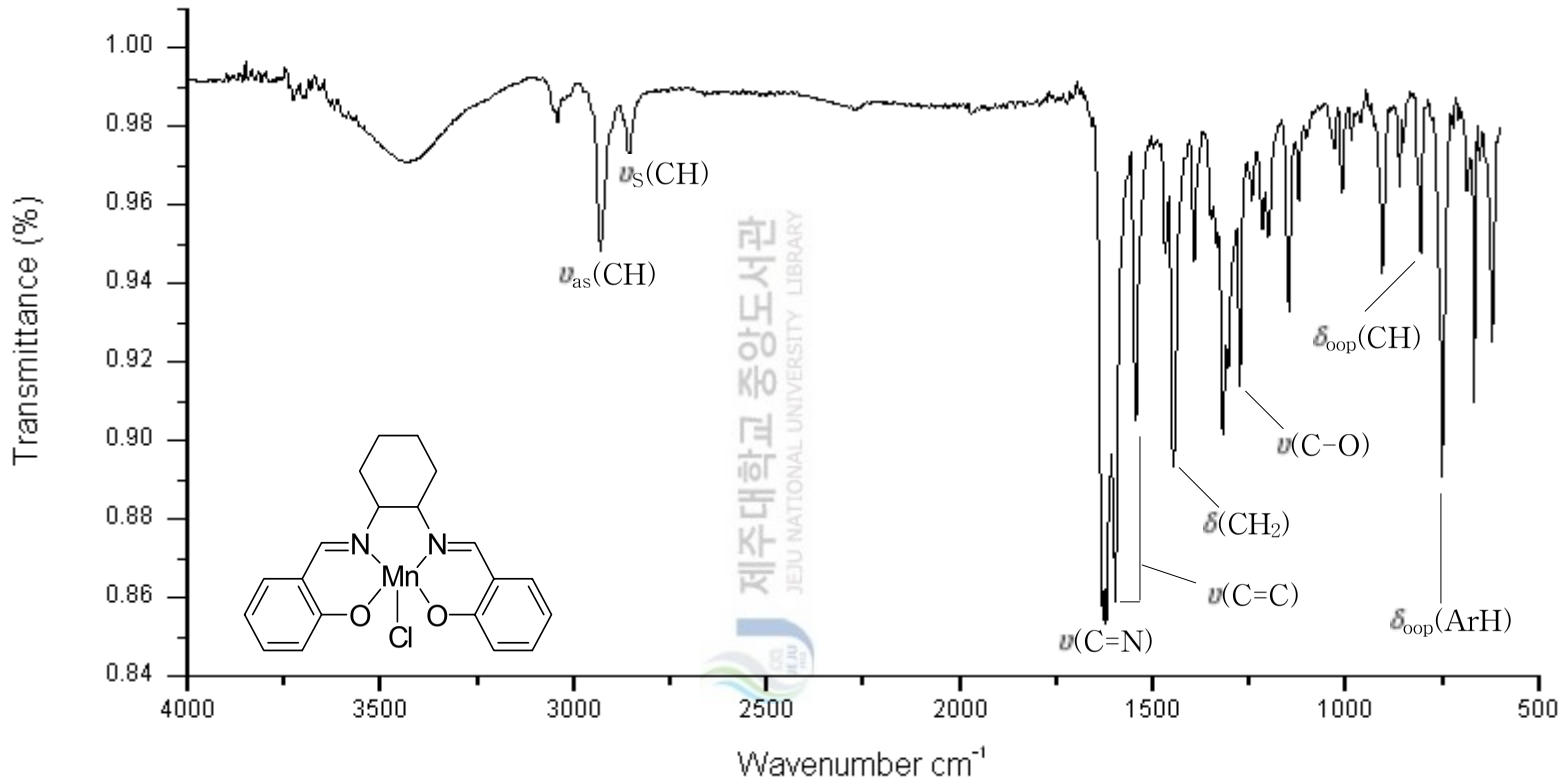


Figure 6. FT-IR spectrum of complex **1**.

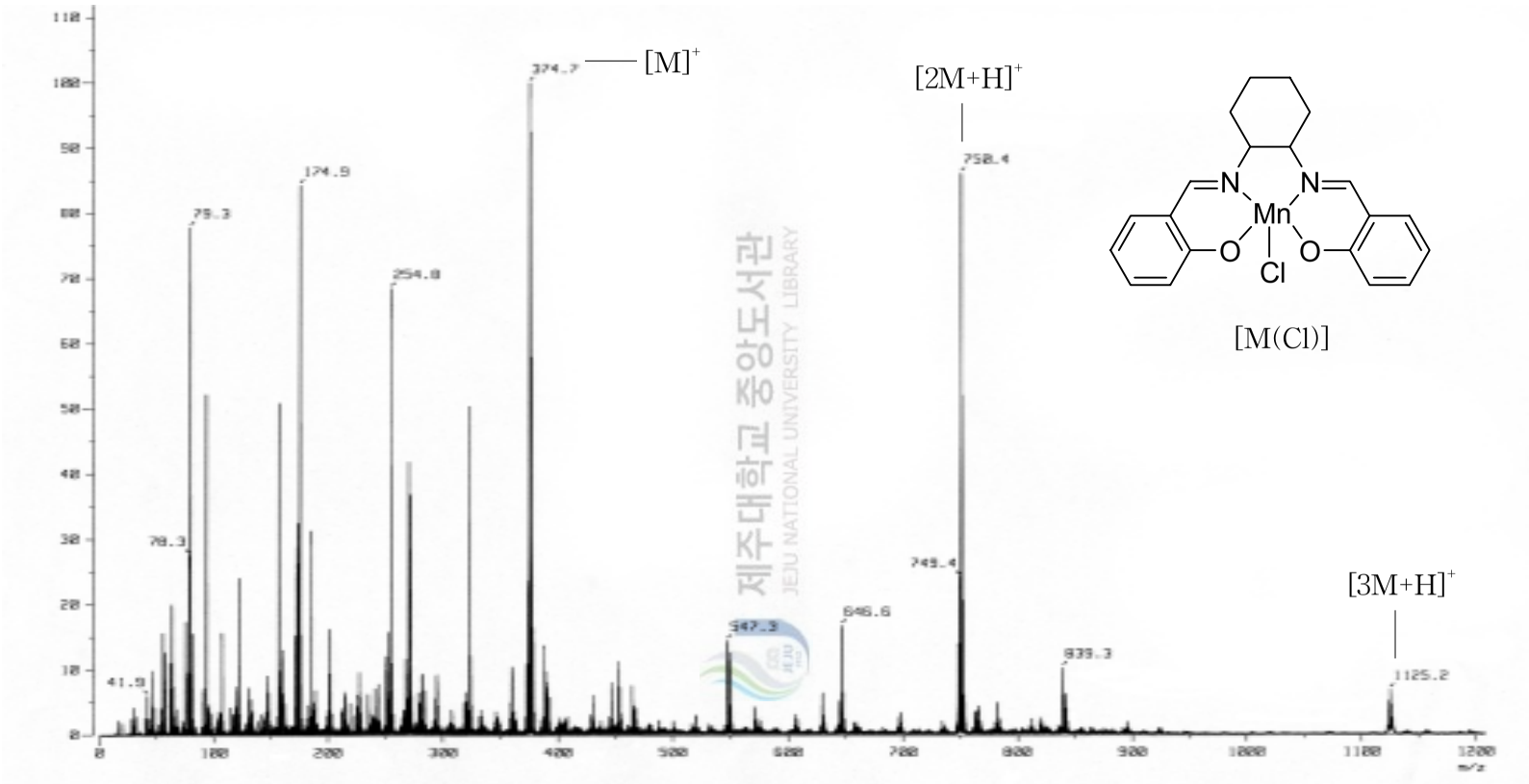


Figure 7. Mass spectrum of complex **1**.

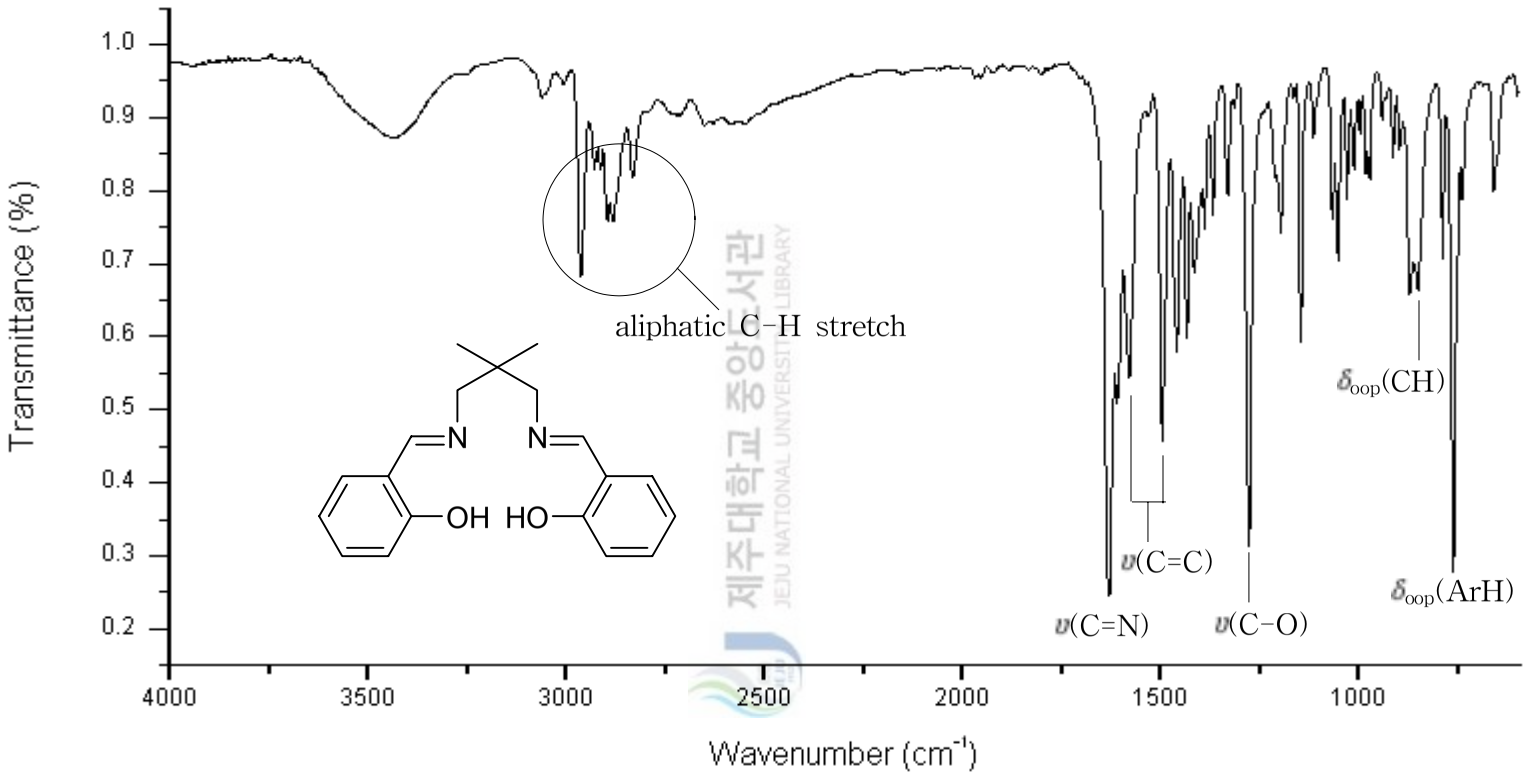


Figure 8. FT-IR spectrum of ligand **13**.

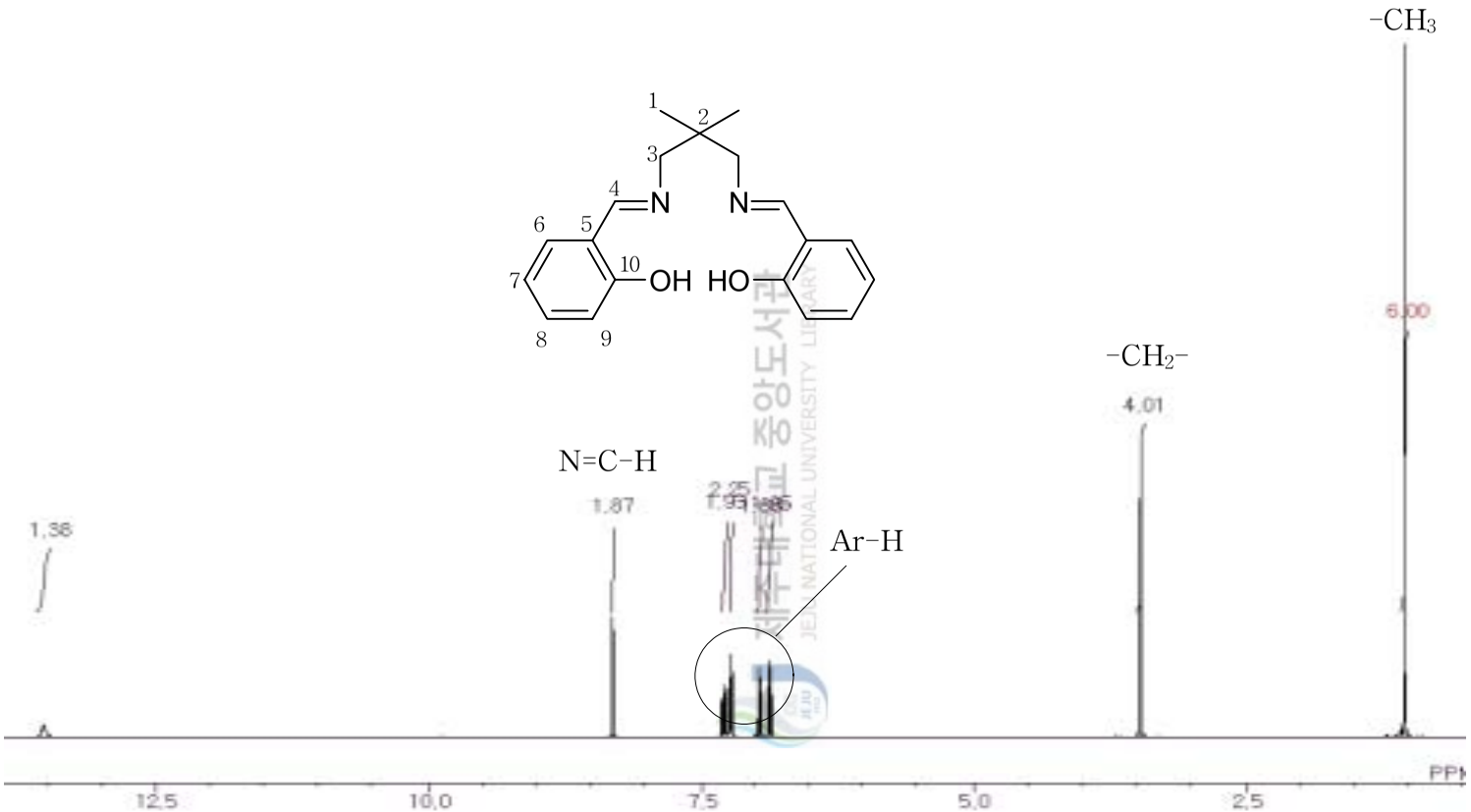


Figure 9. ^{1}H NMR spectrum (400 MHz) of ligand **13** in $CDCl_3$.

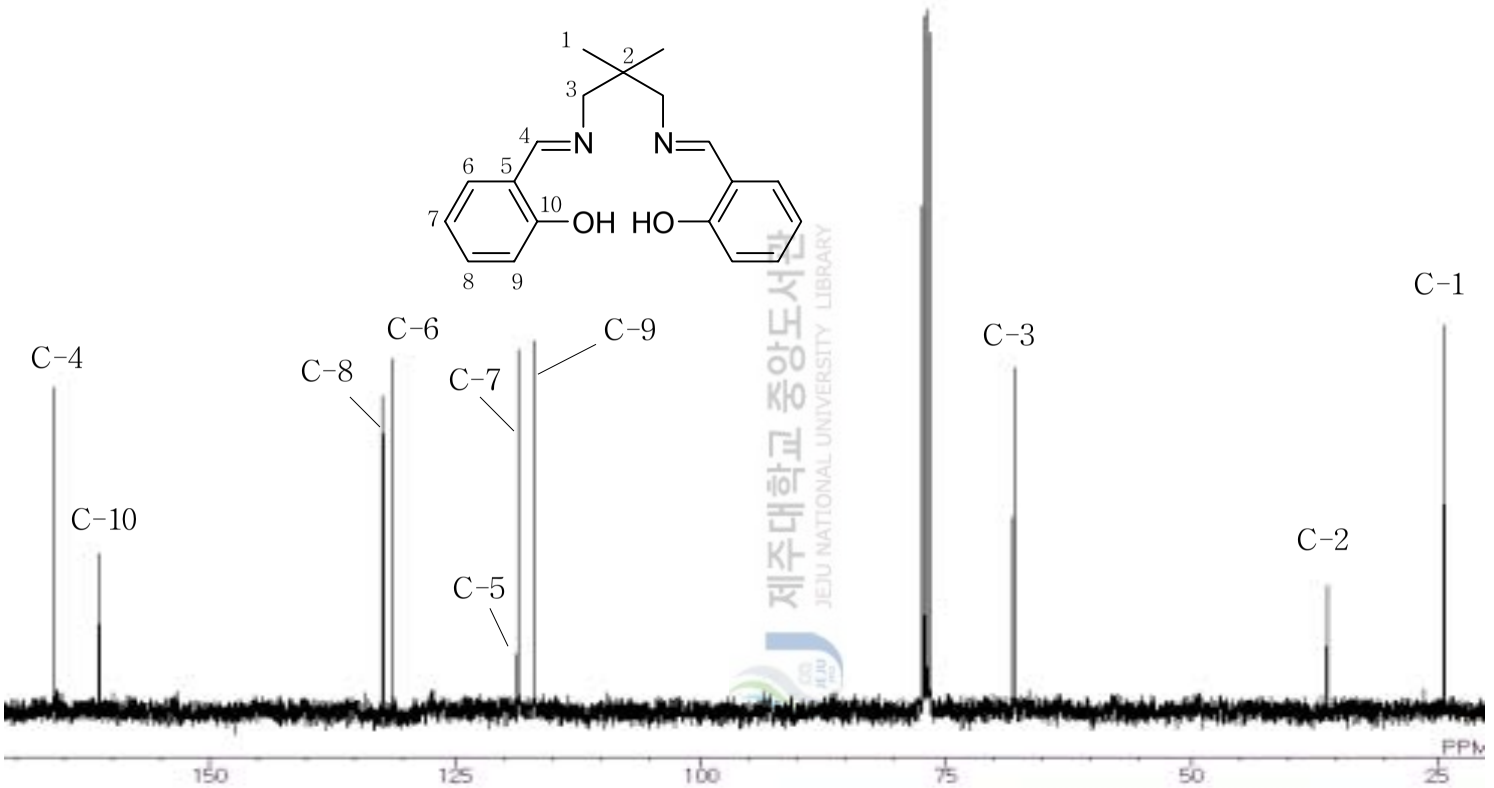


Figure 10. ^{13}C NMR spectrum (100 MHz) of ligand **13** in $CDCl_3$.

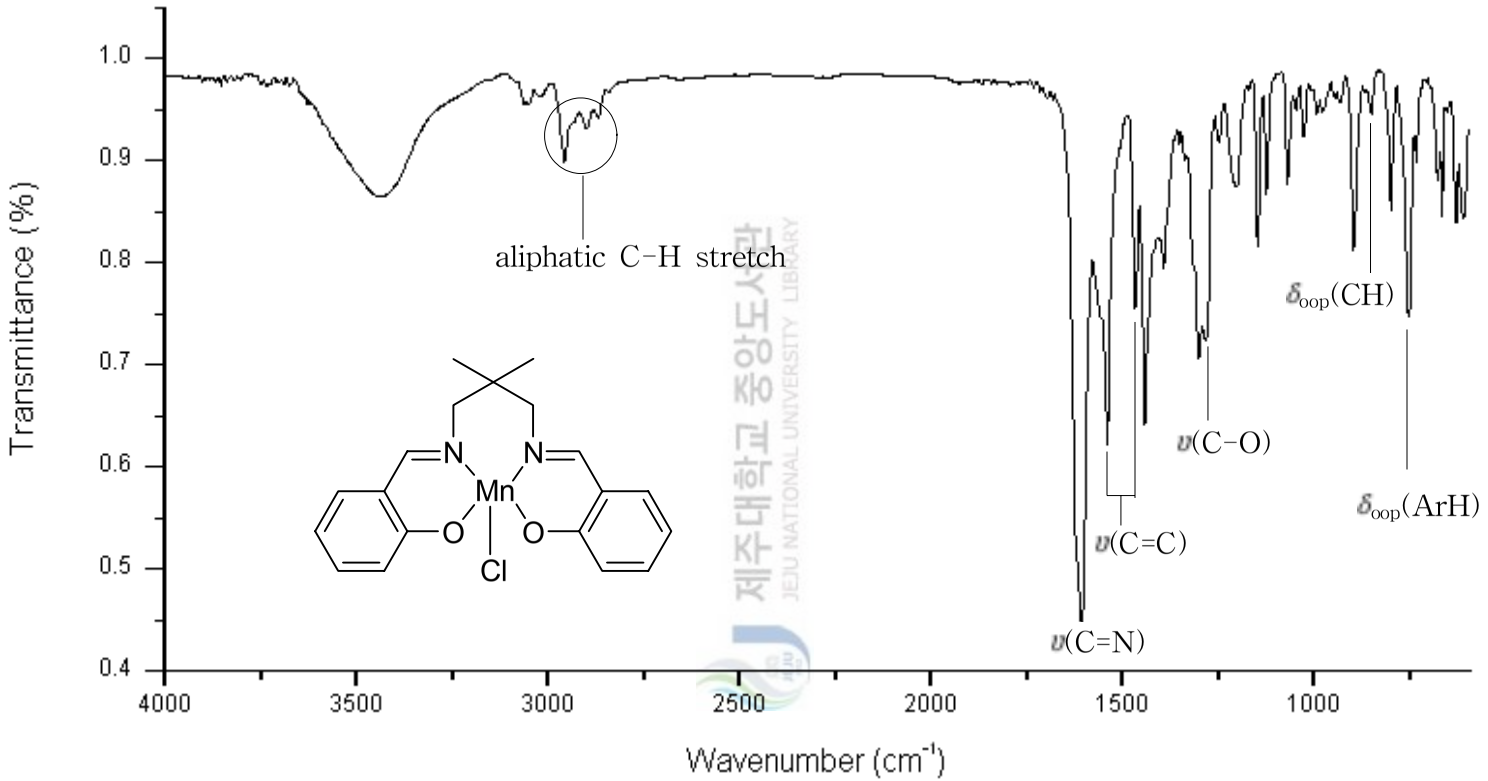


Figure 11. FT-IR spectrum of complex **10**.

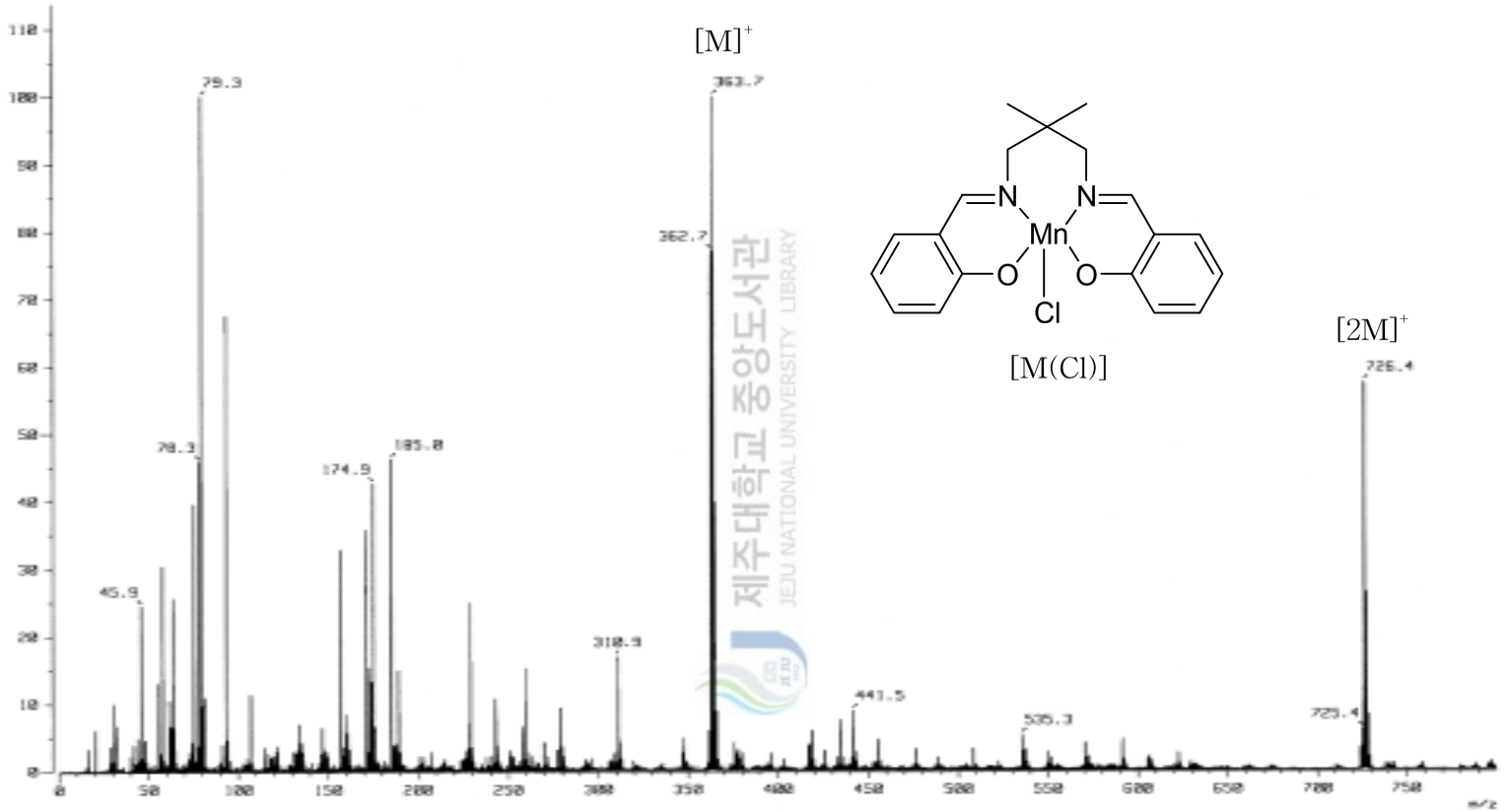


Figure 12. Mass spectrum of complex **10**.

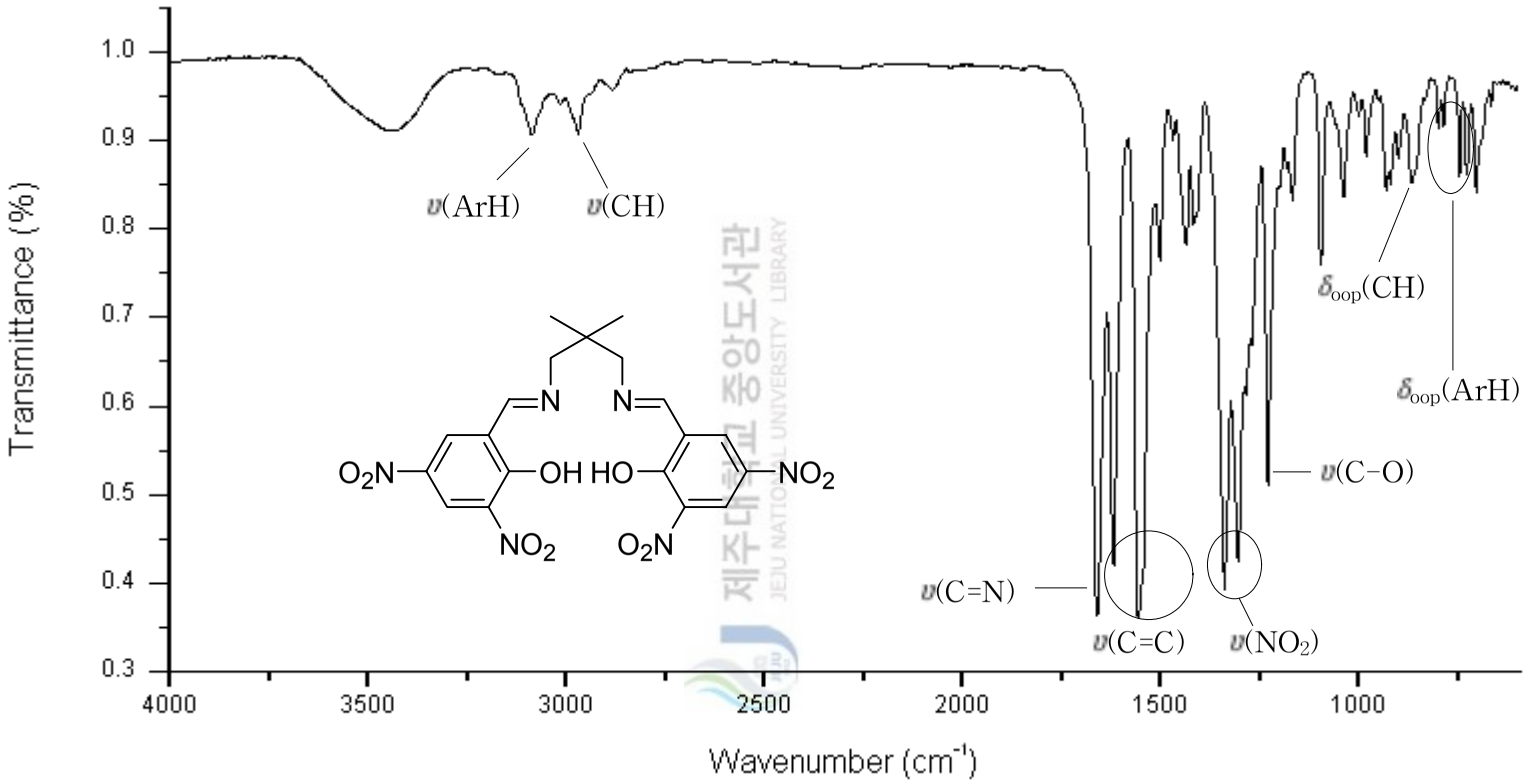


Figure 13. FT-IR spectrum of ligand **15**.

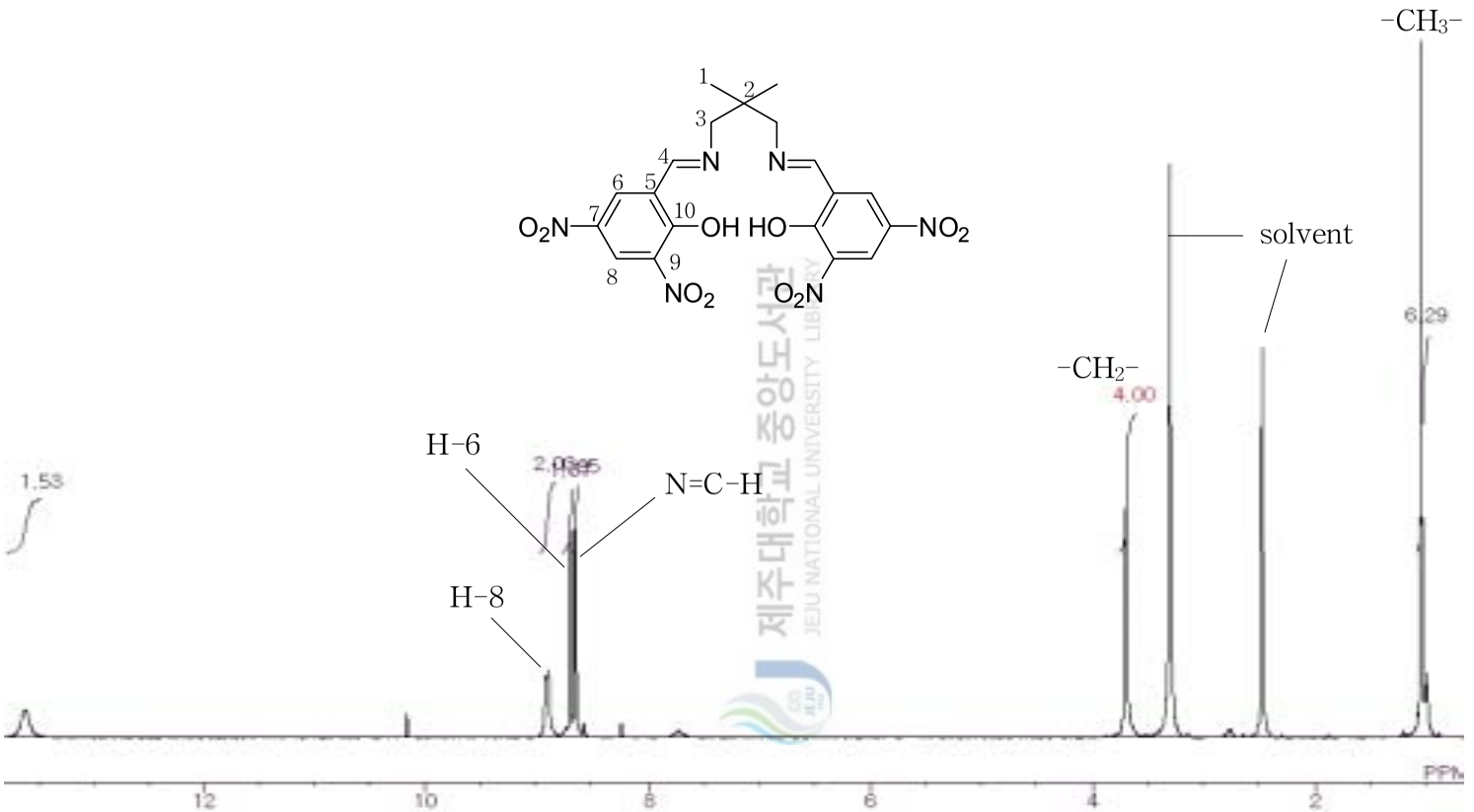


Figure 14. ^{1}H NMR spectrum (400 MHz) of ligand **15** in DMSO-d_6.

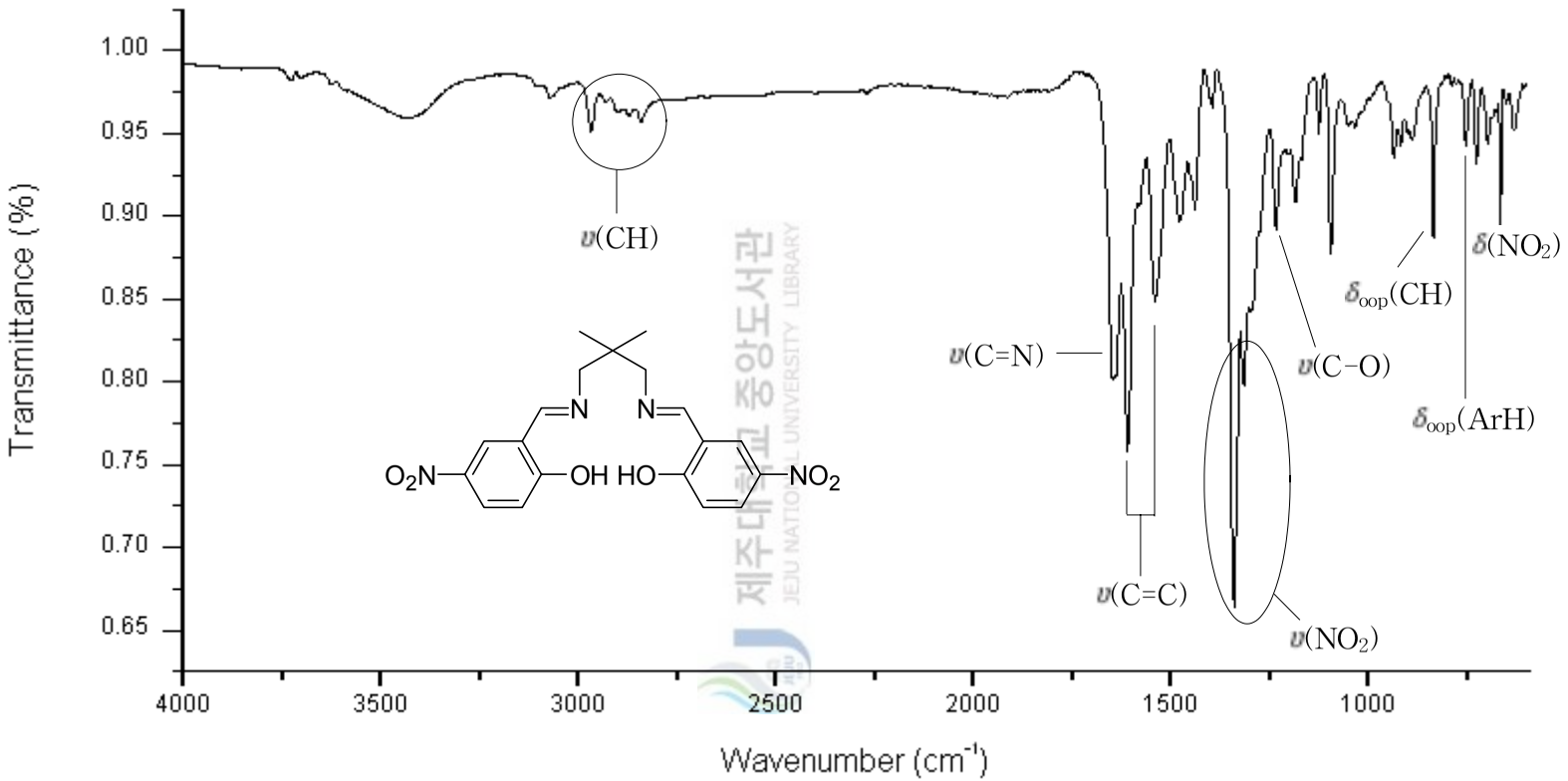


Figure 15. FT-IR spectrum of ligand **17**.

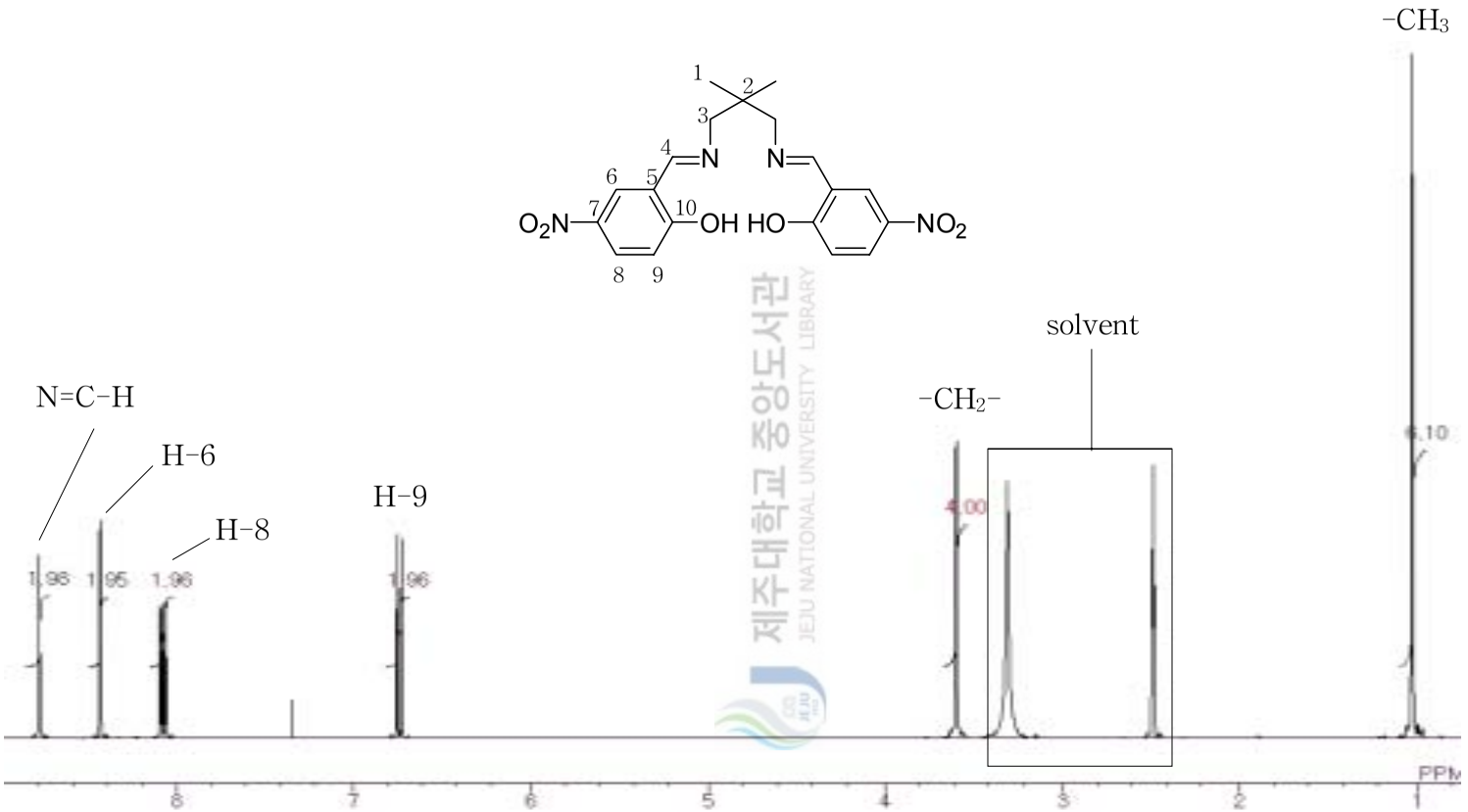


Figure 16. ^{1}H NMR spectrum (400 MHz) of ligand **17** in DMSO-d_6.

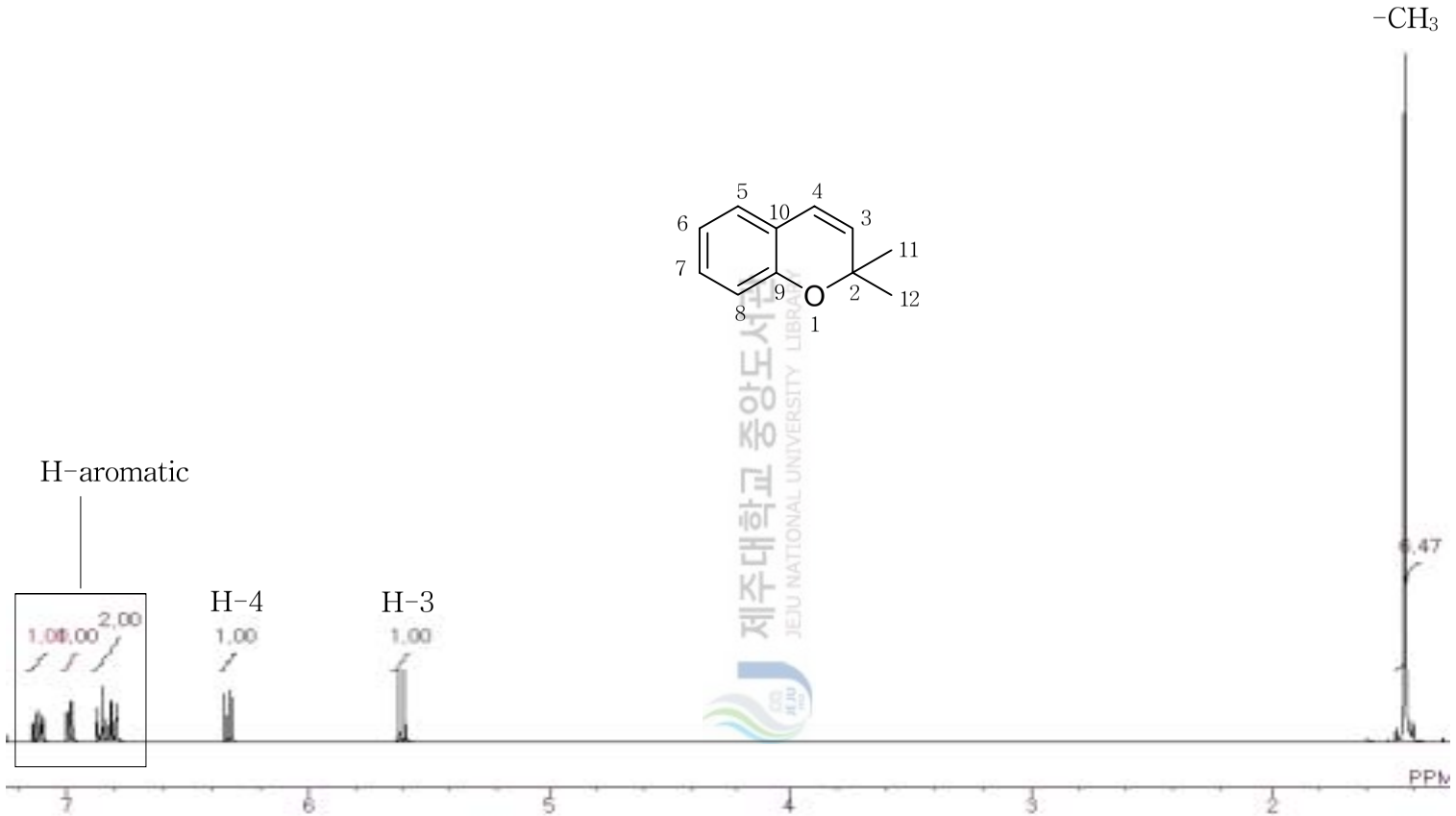


Figure 17. ^{1}H NMR spectrum (400 MHz) of 2,2-dimethylchromene in $CDCl_3$.

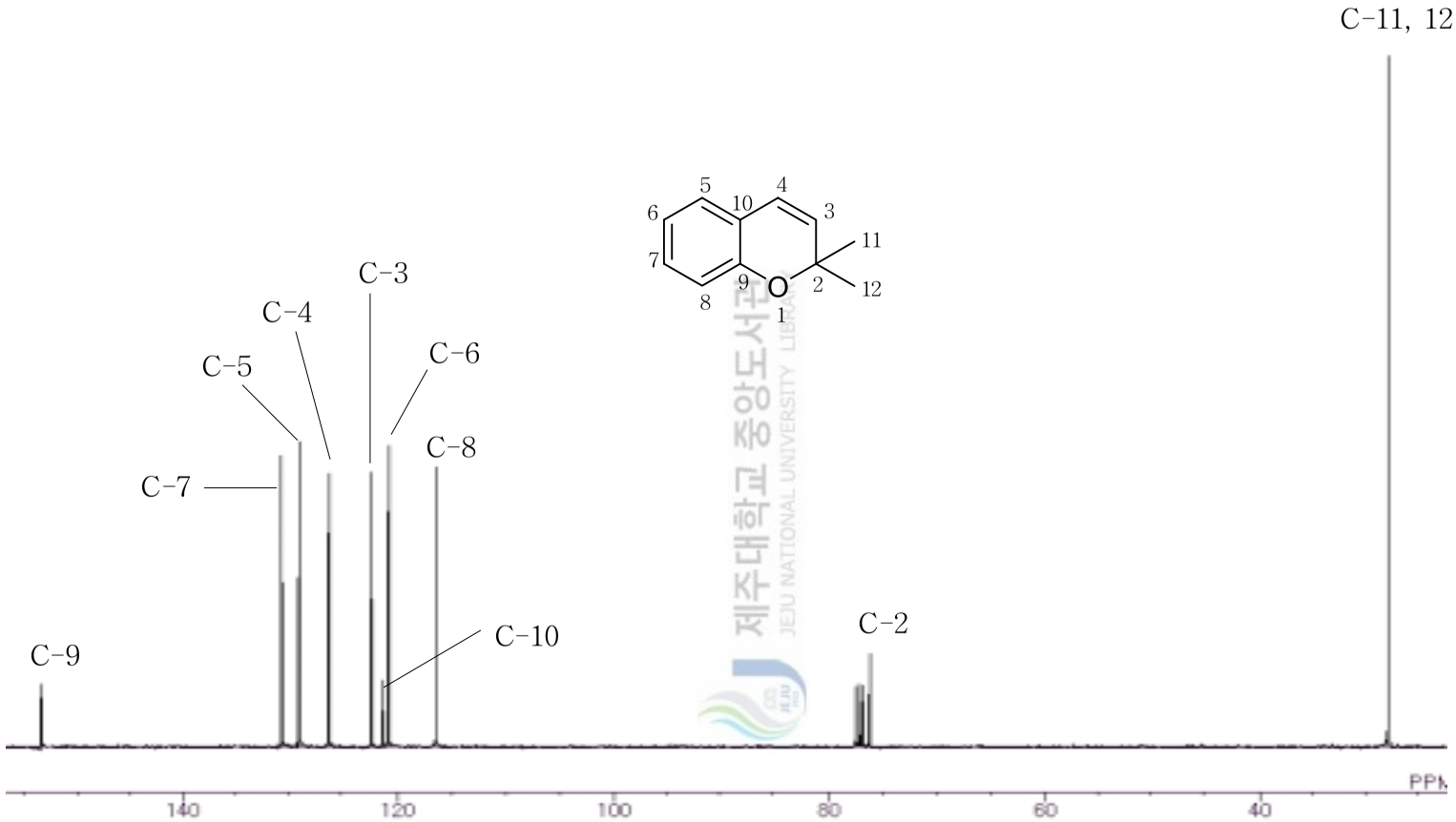


Figure 18. ^{13}C NMR spectrum (100 MHz) of 2,2-dimethylchromene in $CDCl_3$.

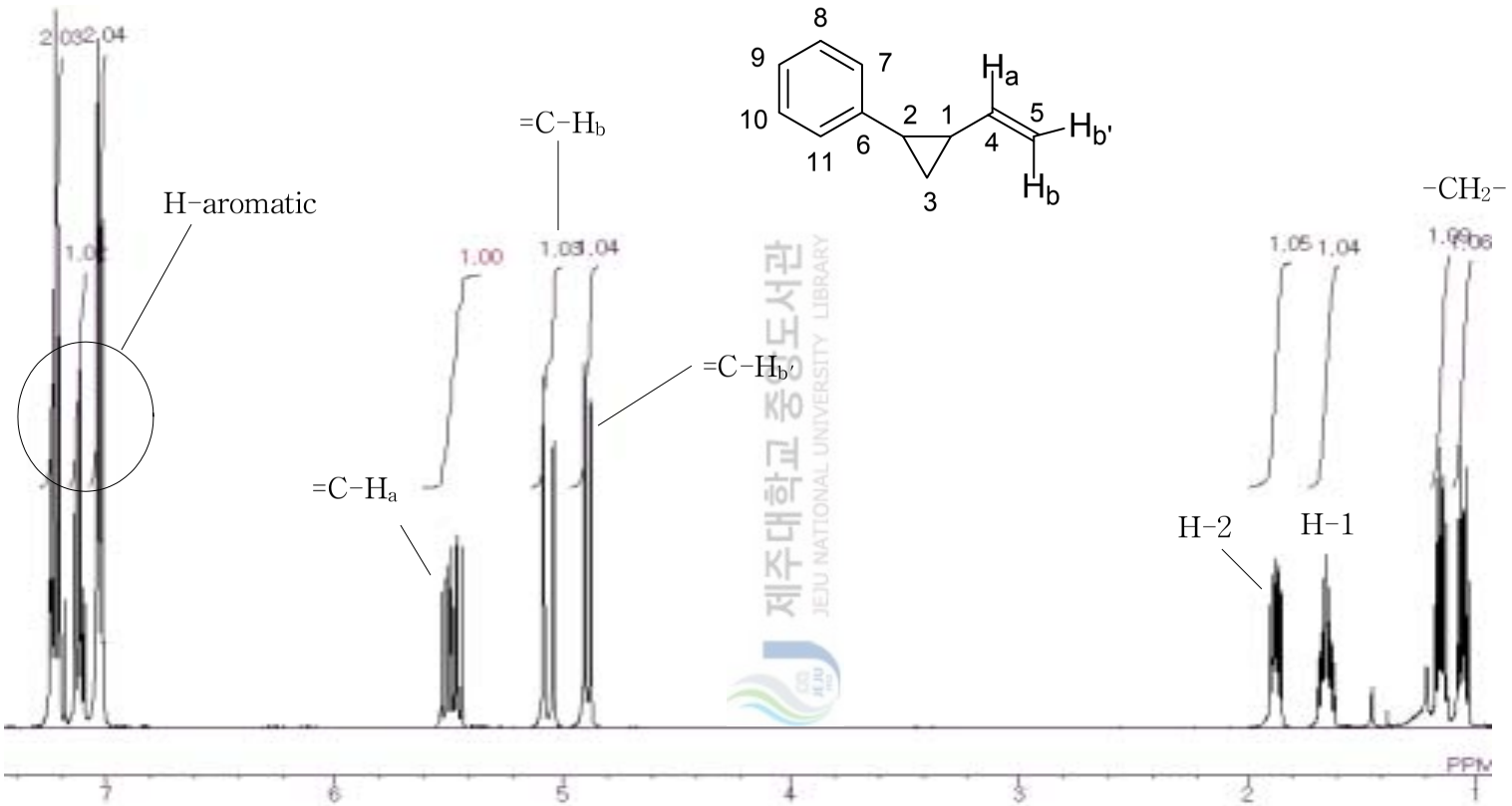


Figure 19. ^{1}H NMR spectrum (400 MHz) of 2-phenyl-1-vinylcyclopropane in $CDCl_3$.

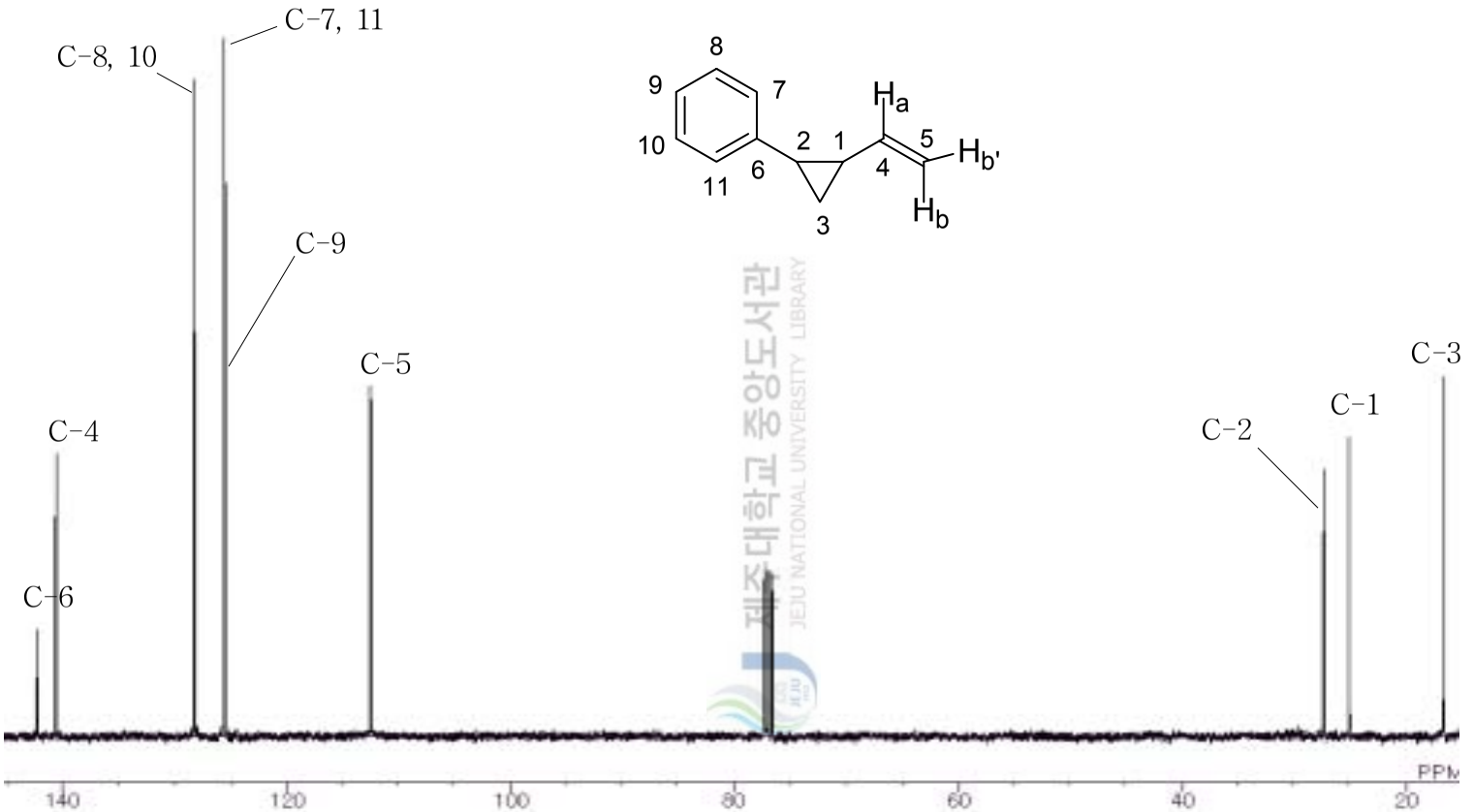


Figure 20. ^{13}C NMR spectrum (100 MHz) of 2-phenyl-1-vinylcyclopropane in $CDCl_3$.

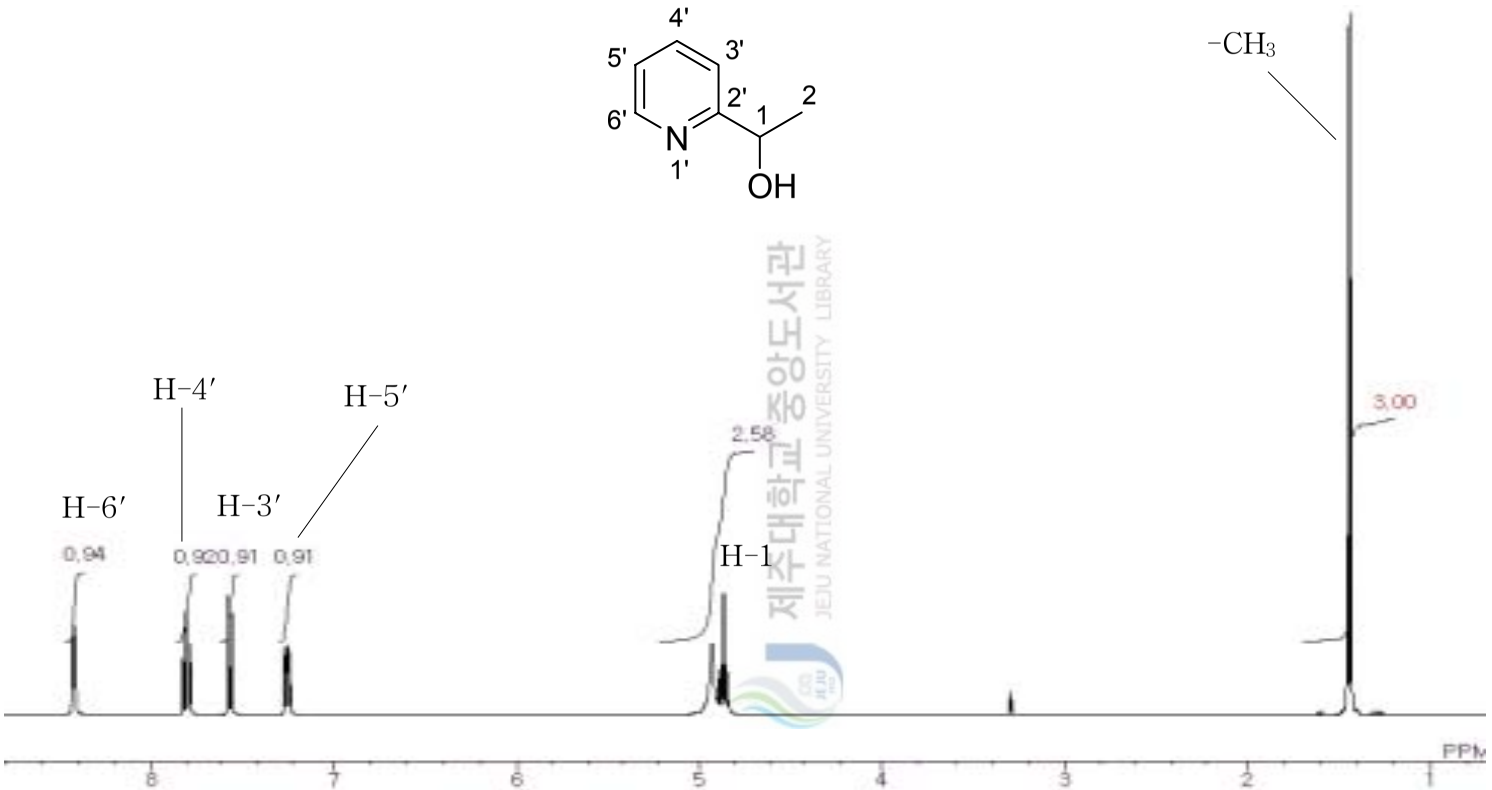


Figure 21. ^{1}H NMR spectrum (400 MHz) of 1-(2-pyridinyl)ethanol in CD_3OD.

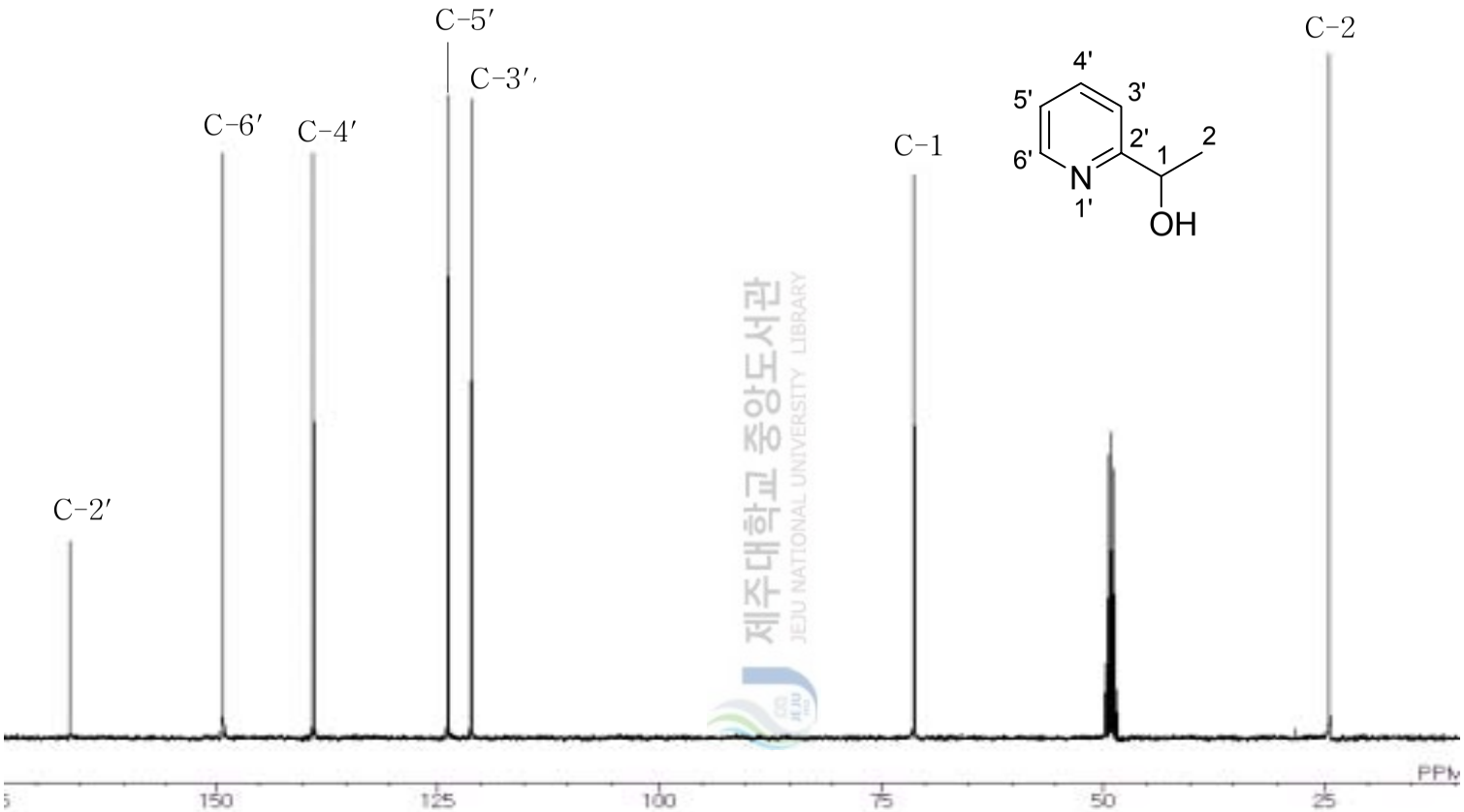


Figure 22. ^{13}C NMR spectrum (100 MHz) of 1-(2-pyridinyl)ethanol in CD_3OD.

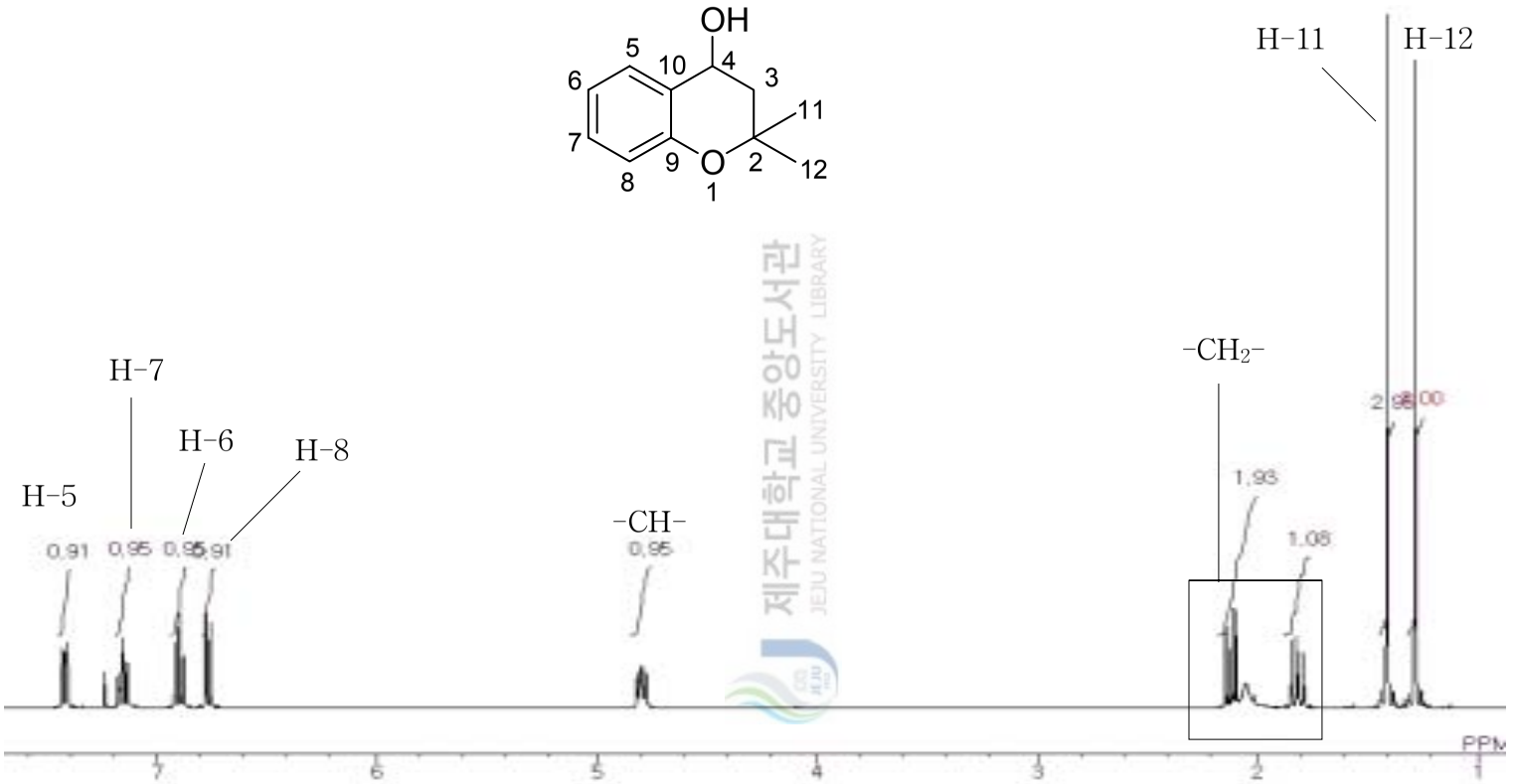


Figure 23. ^{1}H NMR spectrum (400 MHz) of 2,2-dimethyl-4-chromanol in $CDCl_3$.

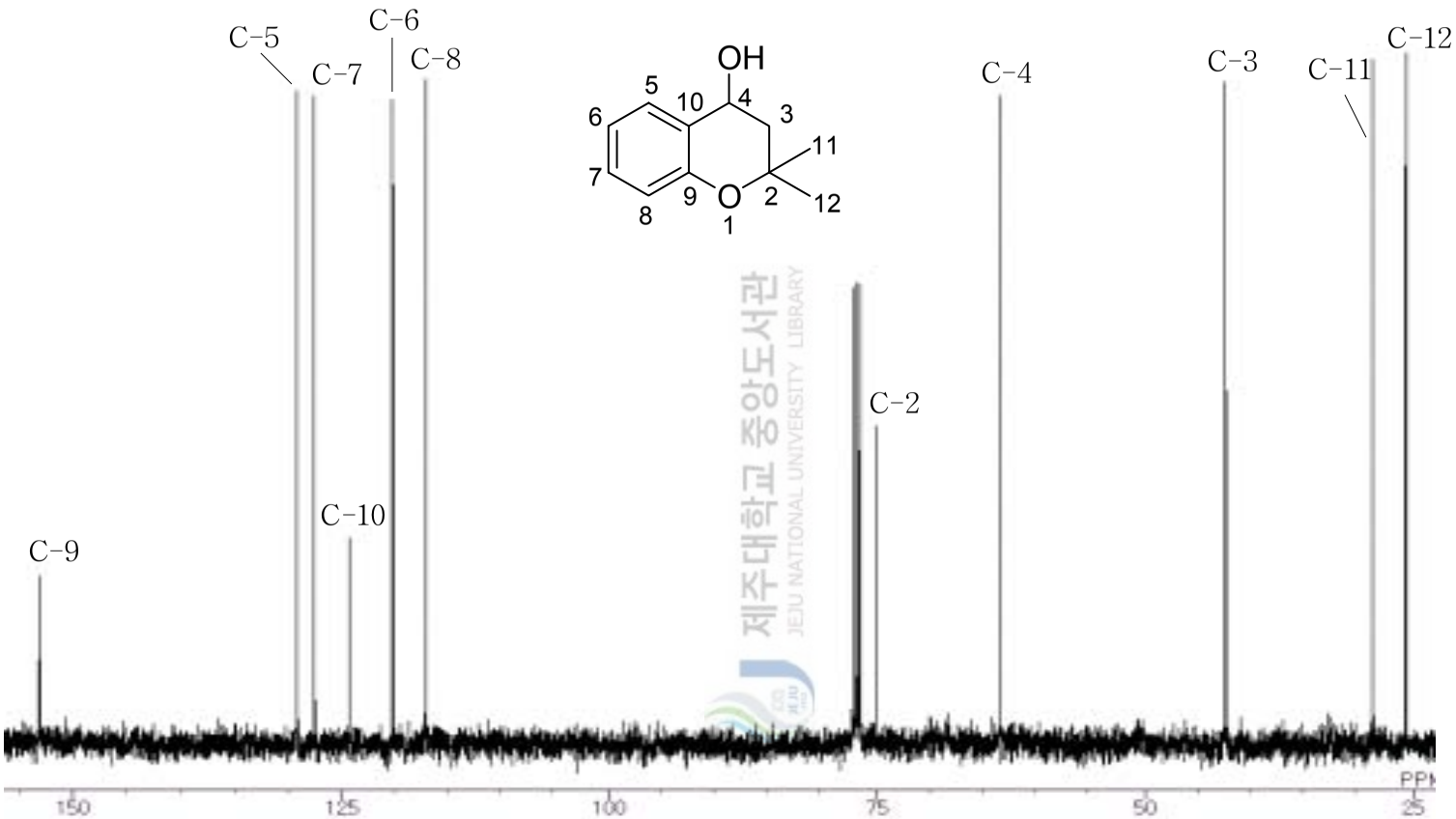


Figure 24. ^{13}C NMR spectrum (100 MHz) of 2,2-dimethyl-4-chromanol in $CDCl_3$.

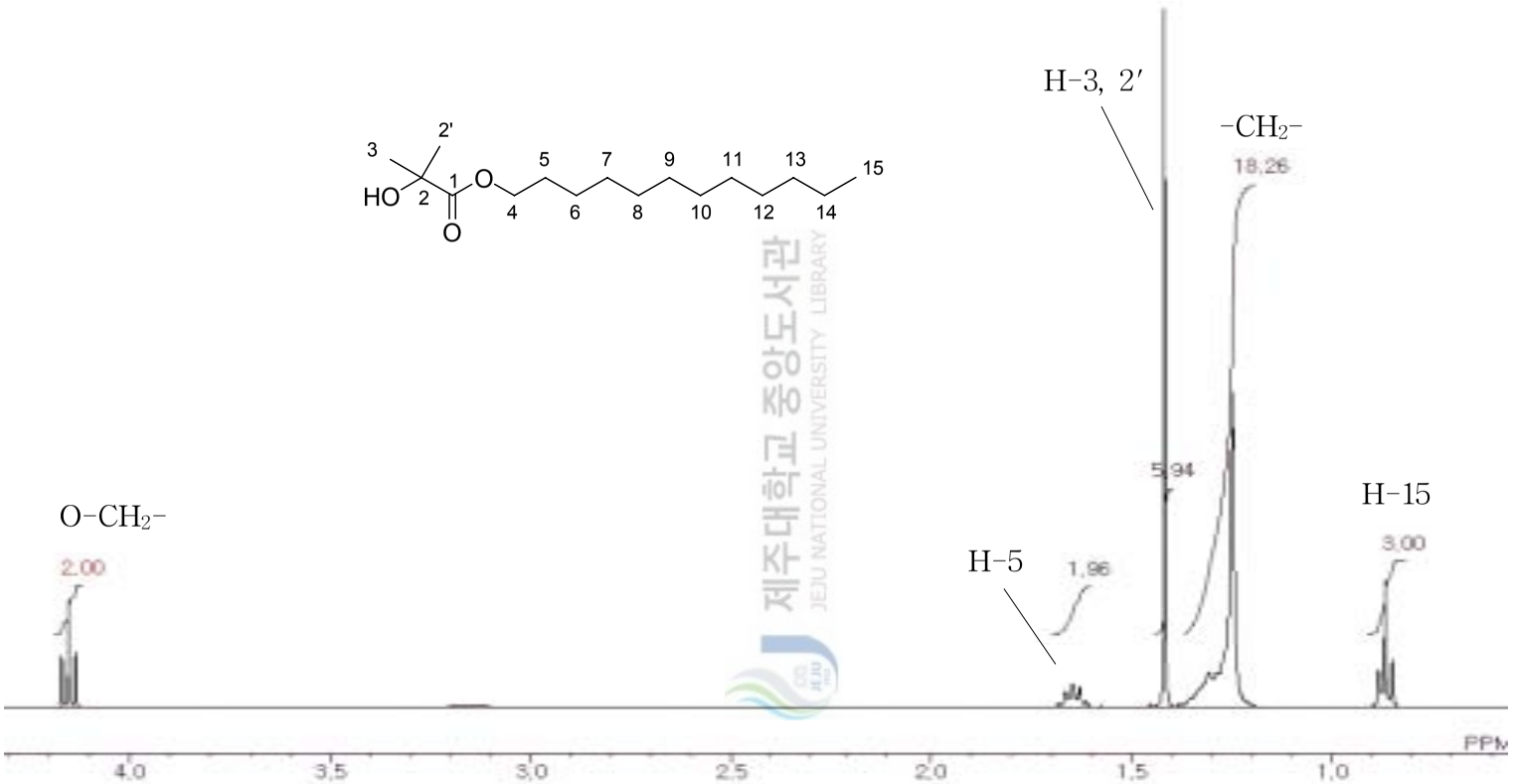


Figure 25. ^{1}H NMR spectrum (400 MHz) of dodecyl 2-hydroxy-2-methylpropanoate in $CDCl_3$.

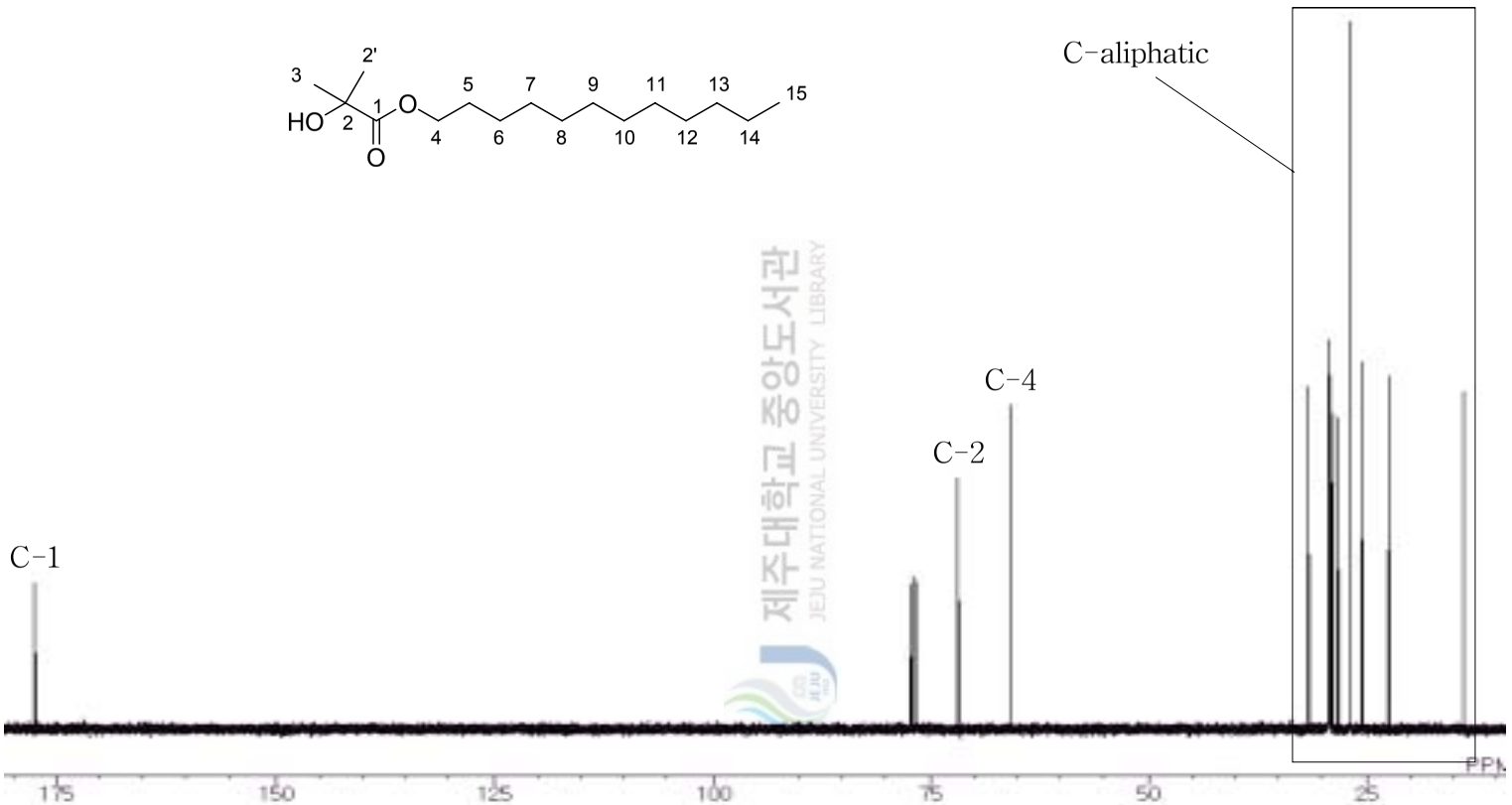


Figure 26. ^{13}C NMR spectrum (100 MHz) of dodecyl 2-hydroxy-2-methylpropanoate in $CDCl_3$.

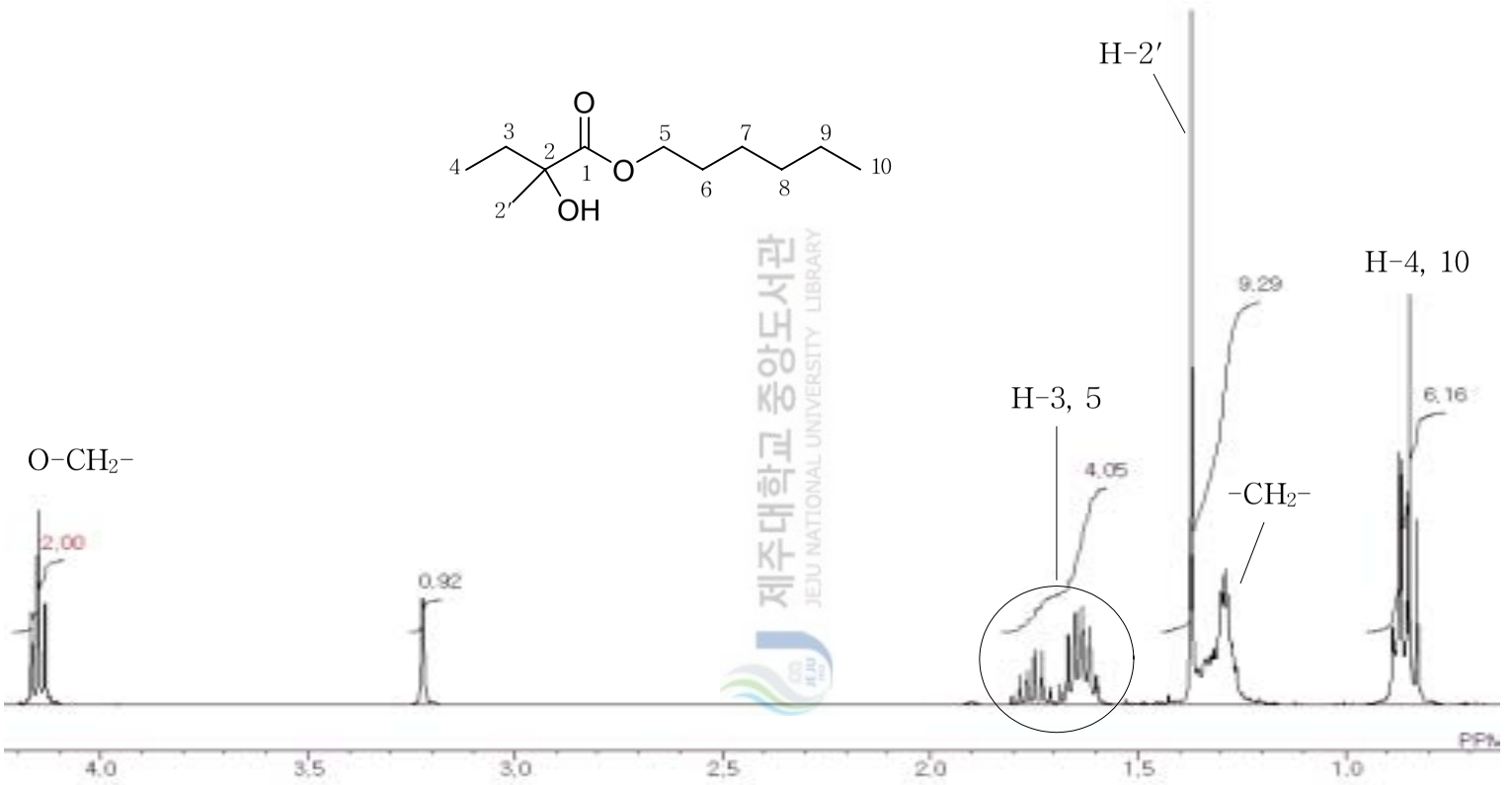


Figure 27. ^{1}H NMR spectrum (400 MHz) of hexyl 2-hydroxy-2-methylbutanoate in $CDCl_3$.

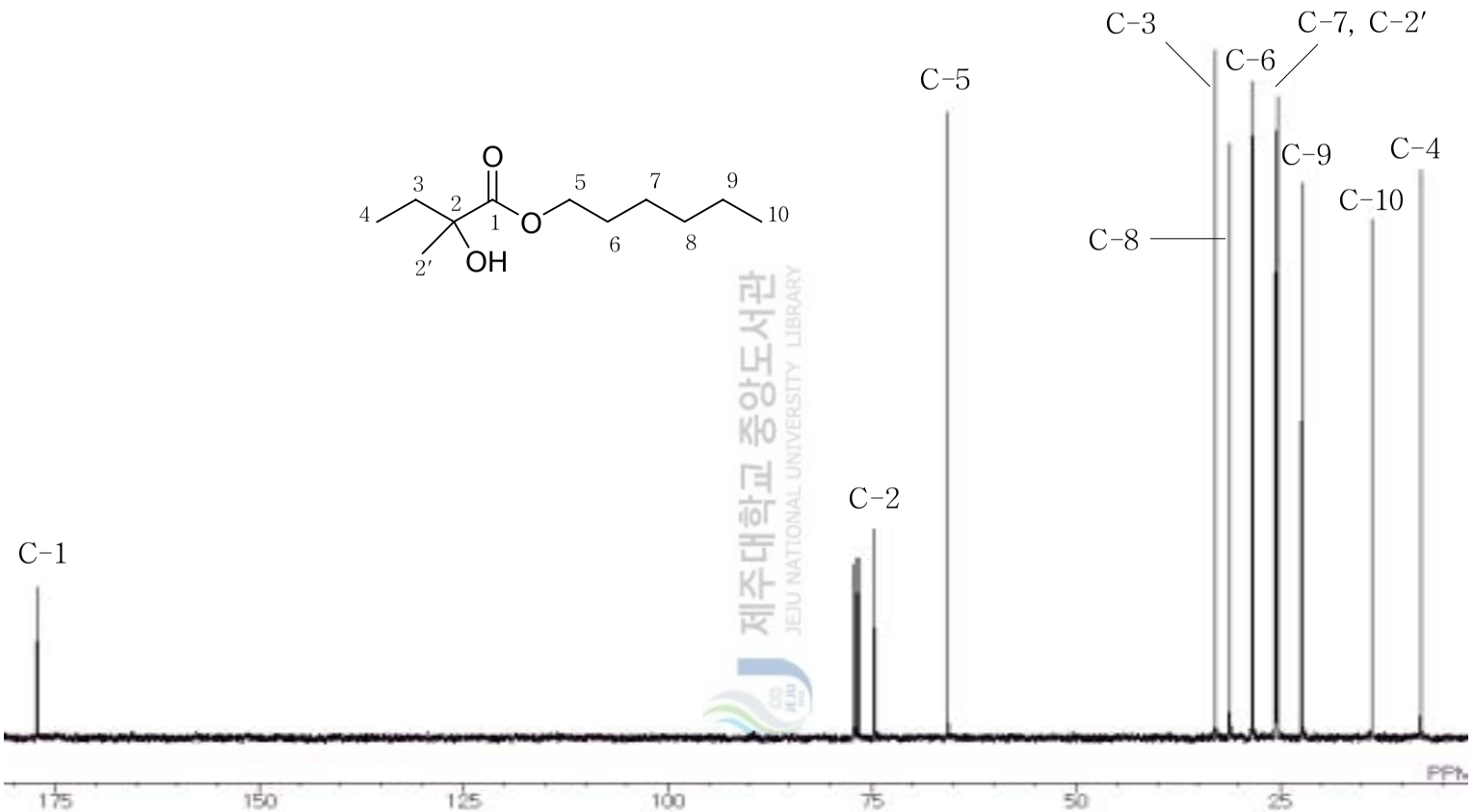


Figure 28. ^{13}C NMR spectrum (100 MHz) of hexyl 2-hydroxy-2-methylbutanoate in $CDCl_3$.

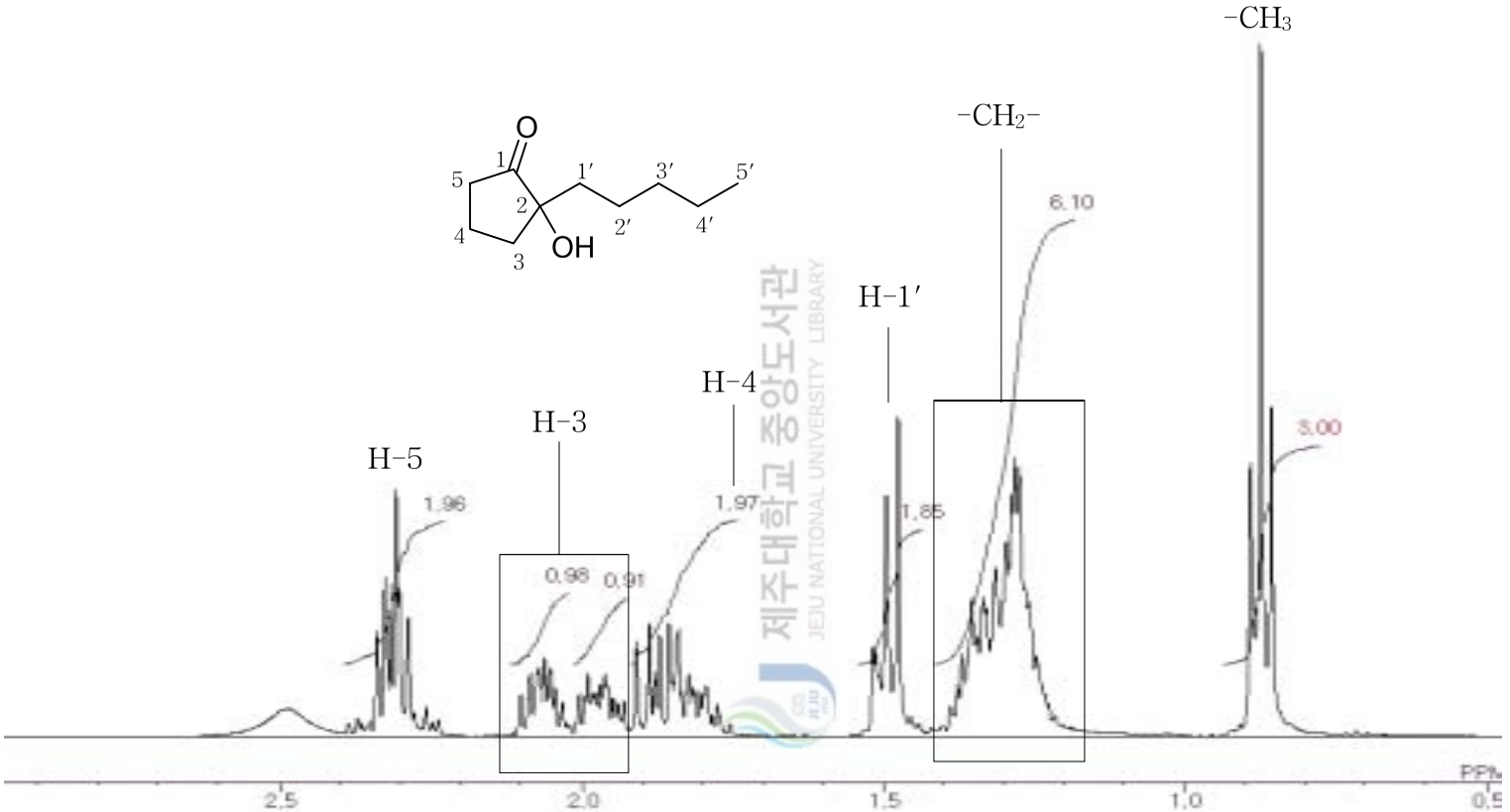


Figure 29. ^{1}H NMR spectrum (400 MHz) of 2-hydroxy-2-pentylcyclopentanone in $CDCl_3$.

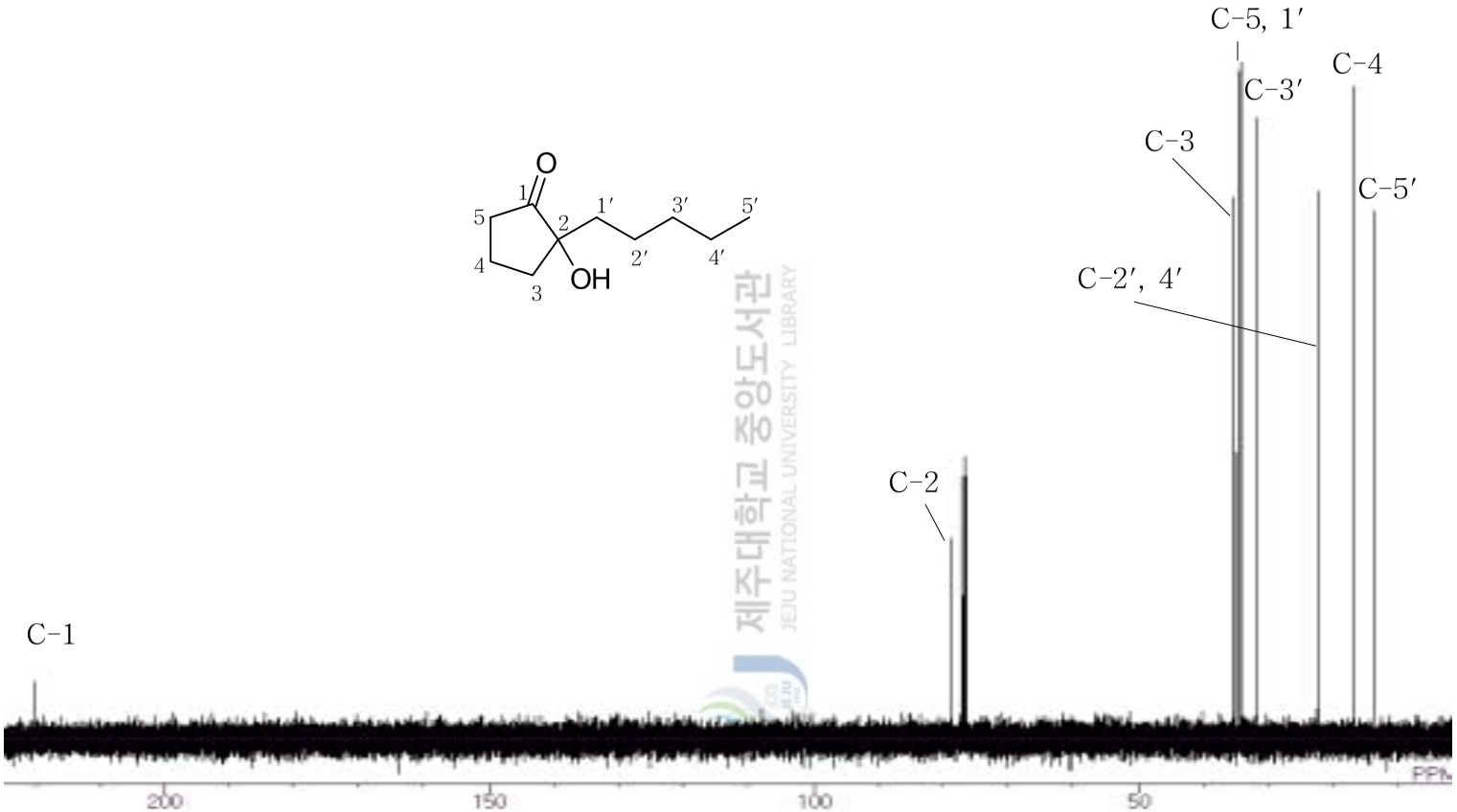


Figure 30. ^{13}C NMR spectrum (100 MHz) of 2-hydroxy-2-pentylcyclopentanone in $CDCl_3$.

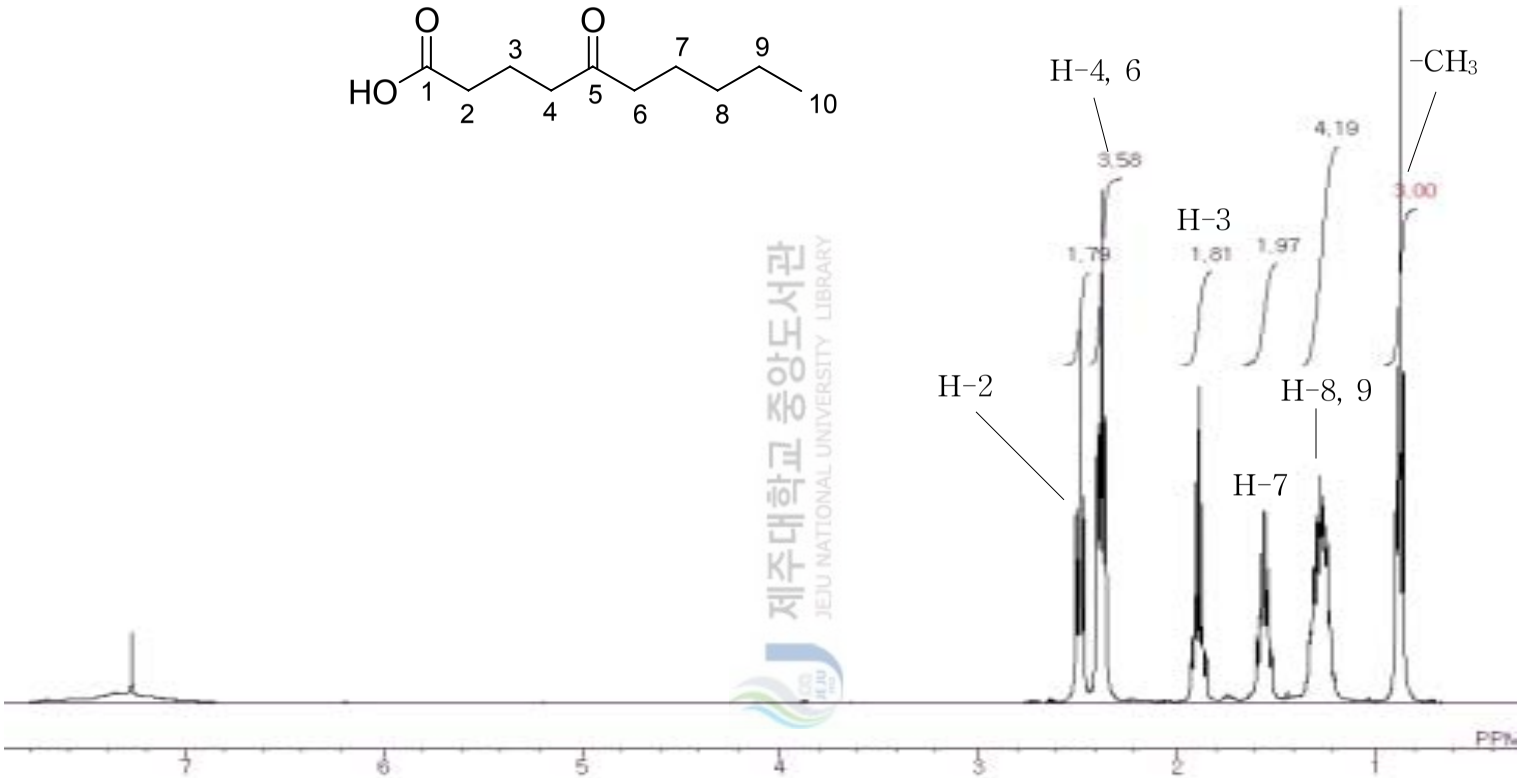


Figure 31. ^{1}H NMR spectrum (400 MHz) of 5-oxo-decanoic acid in $CDCl_3$.

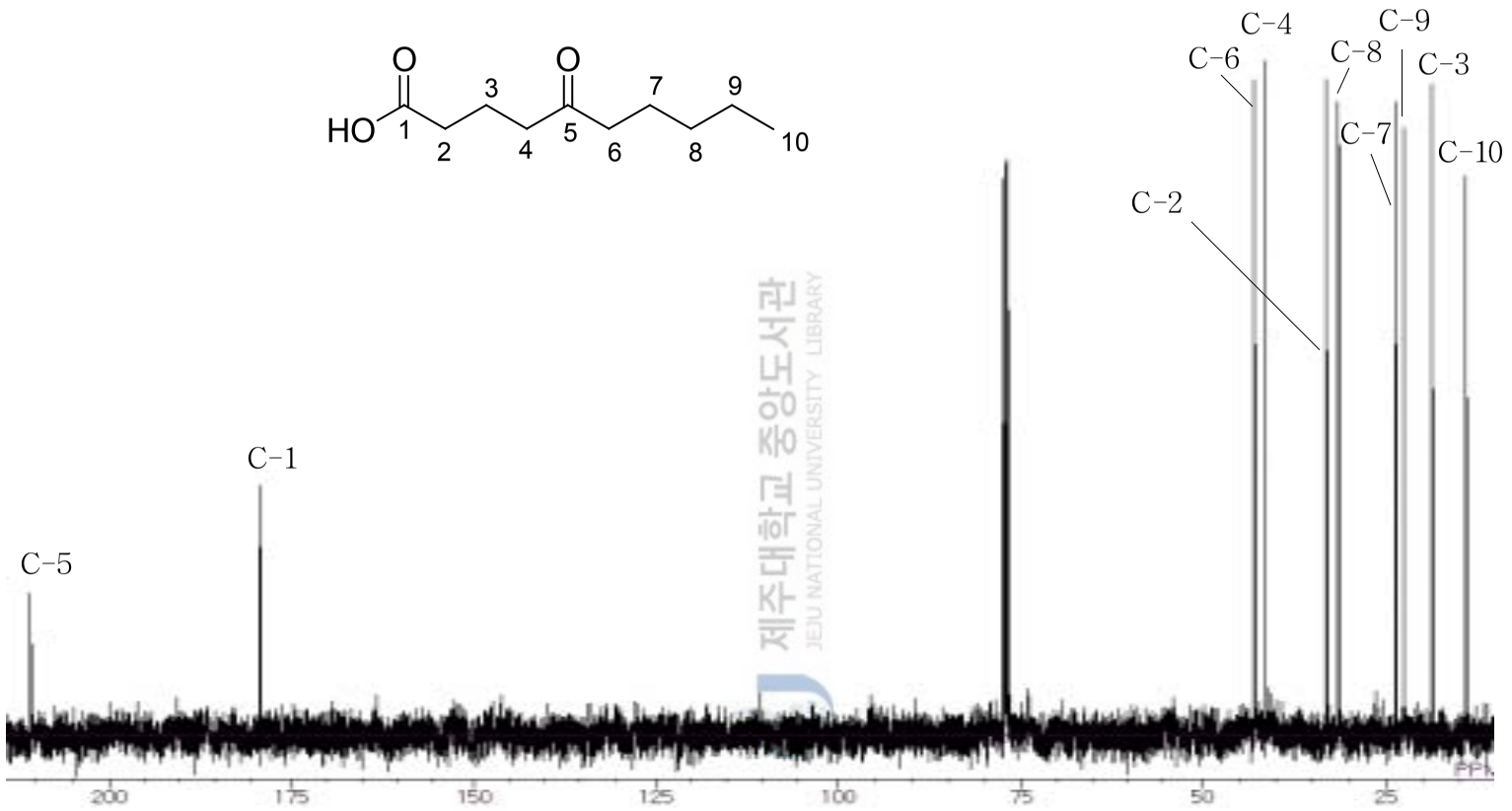


Figure 32. ^{13}C NMR spectrum (100 MHz) of 5-oxo-decanoic acid in $CDCl_3$.

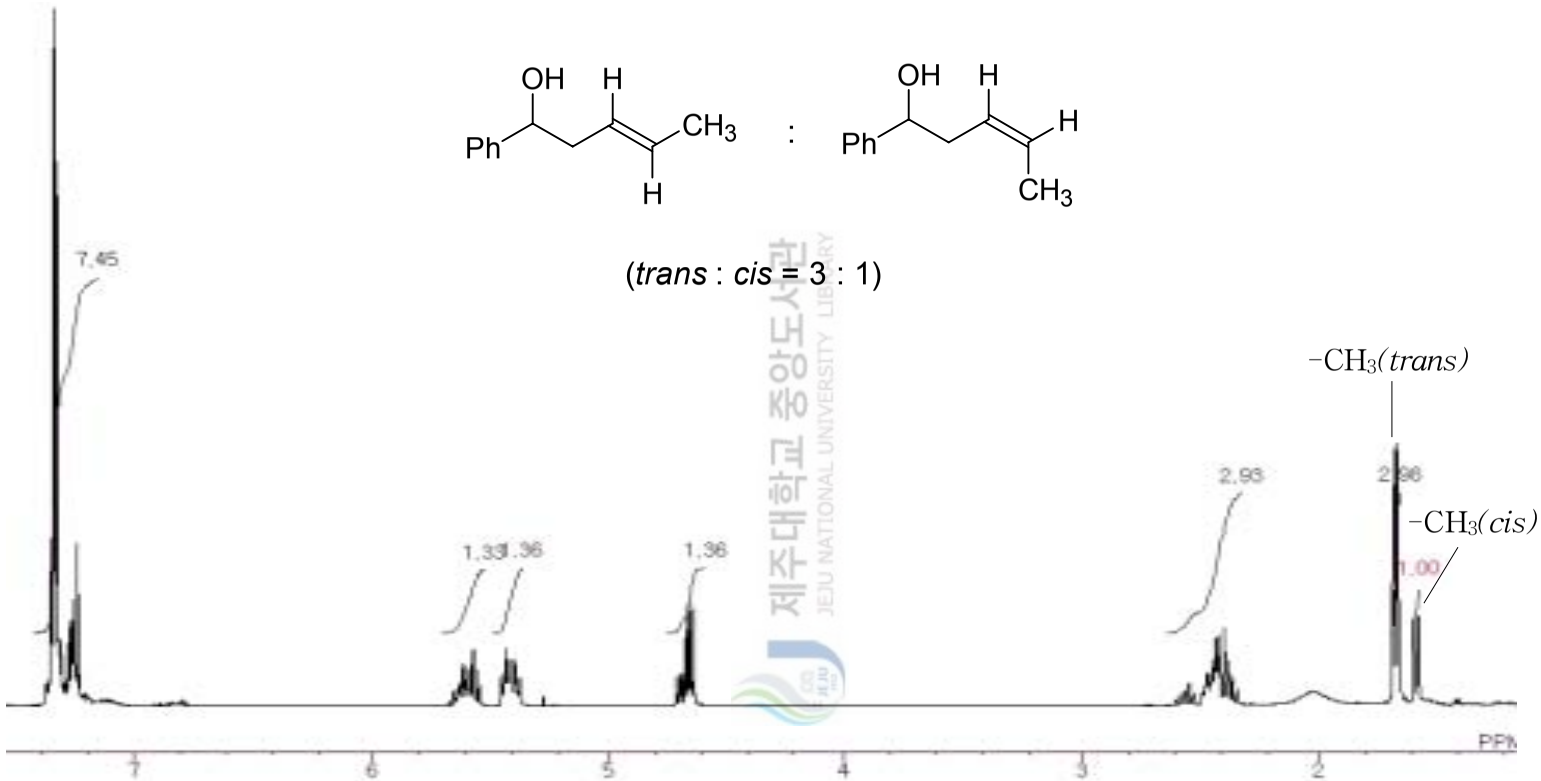


Figure 33. ^{1}H NMR spectrum (400 MHz) of compound **22** in $CDCl_3$.

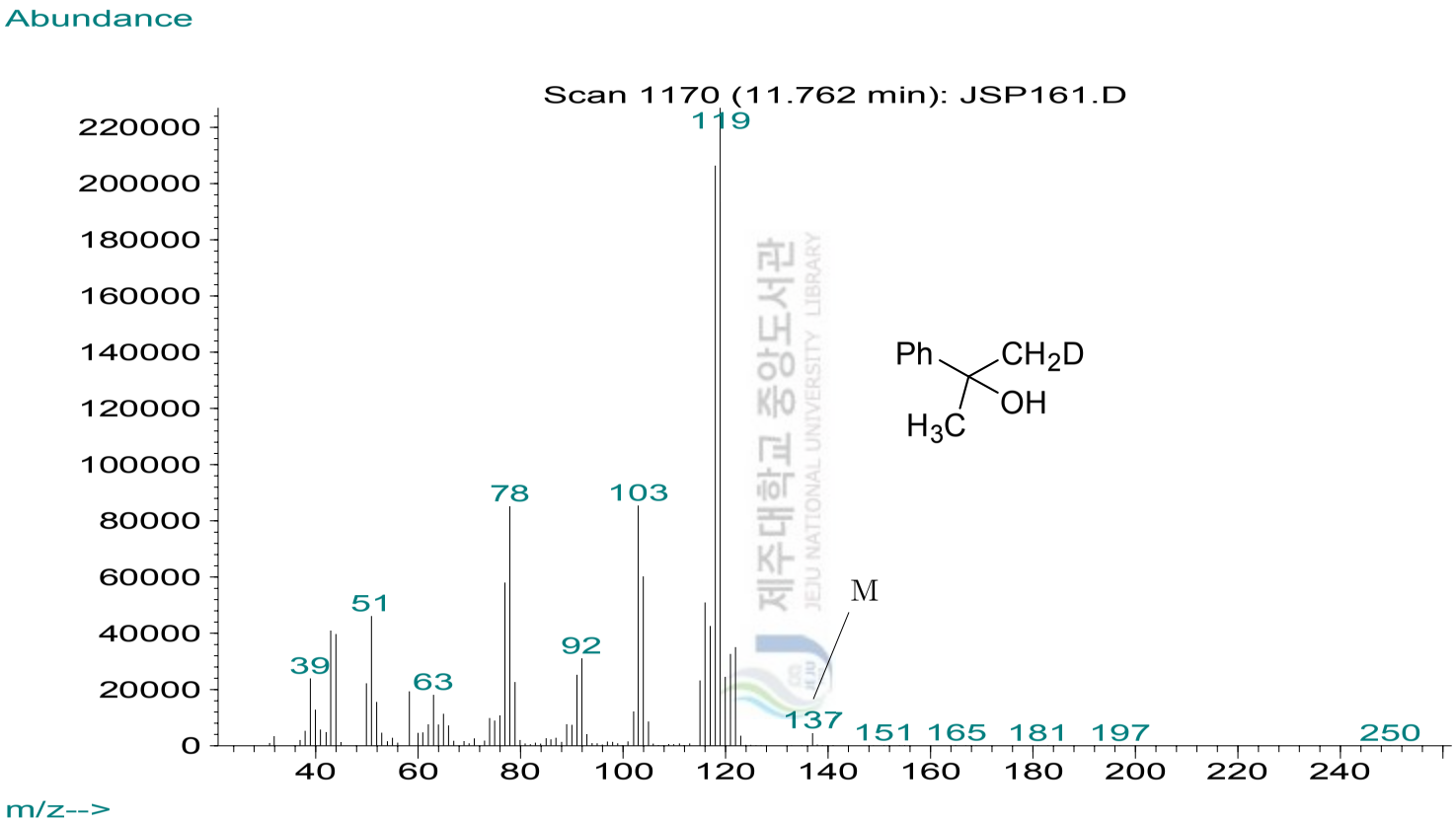


Figure 34. Mass spectrum of 1-deuterio-2-phenyl-2-propanol.

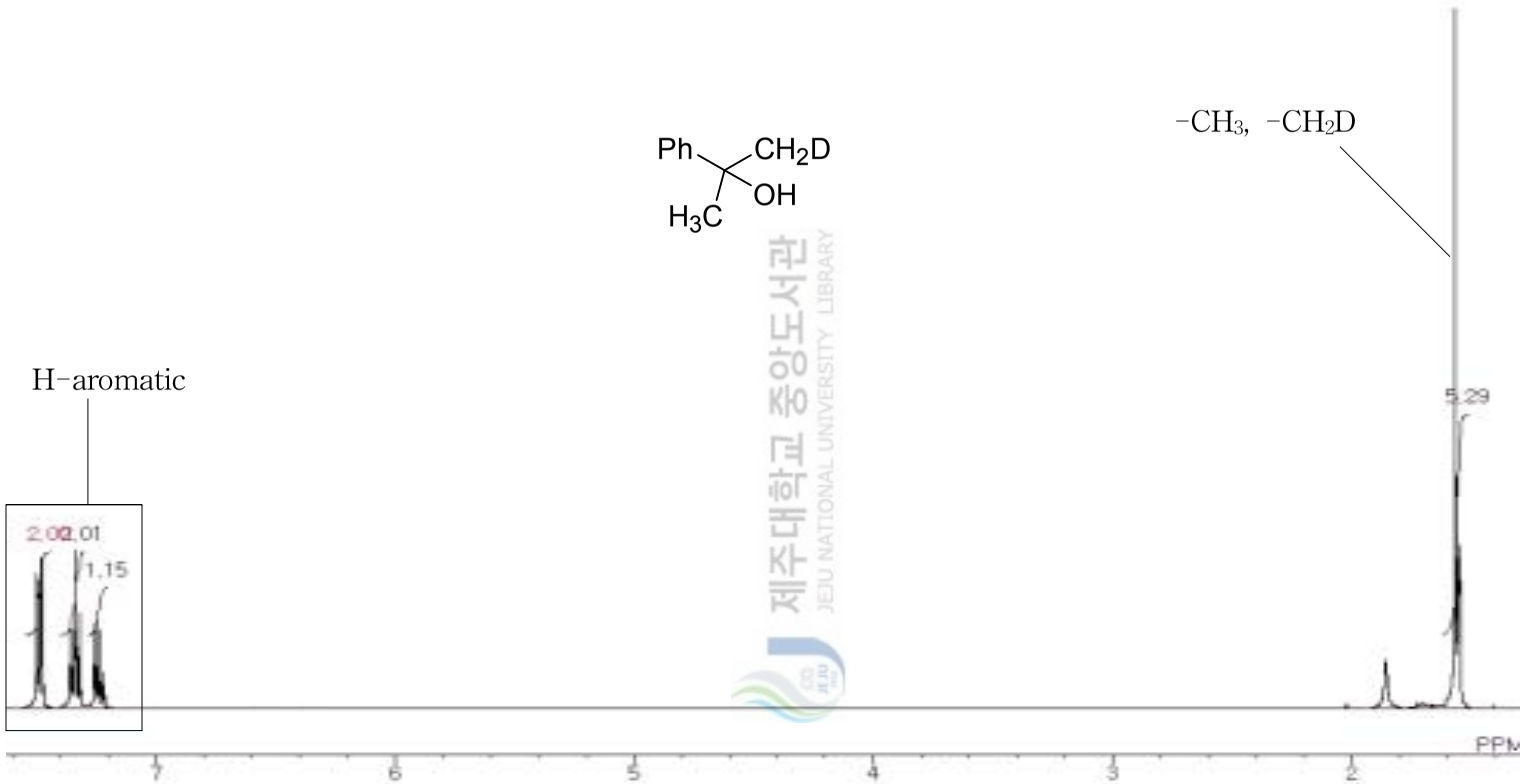


Figure 35. ^{1}H NMR spectrum (400 MHz) of 1-deuterio-2-phenyl-2-propanol in $CDCl_3$.

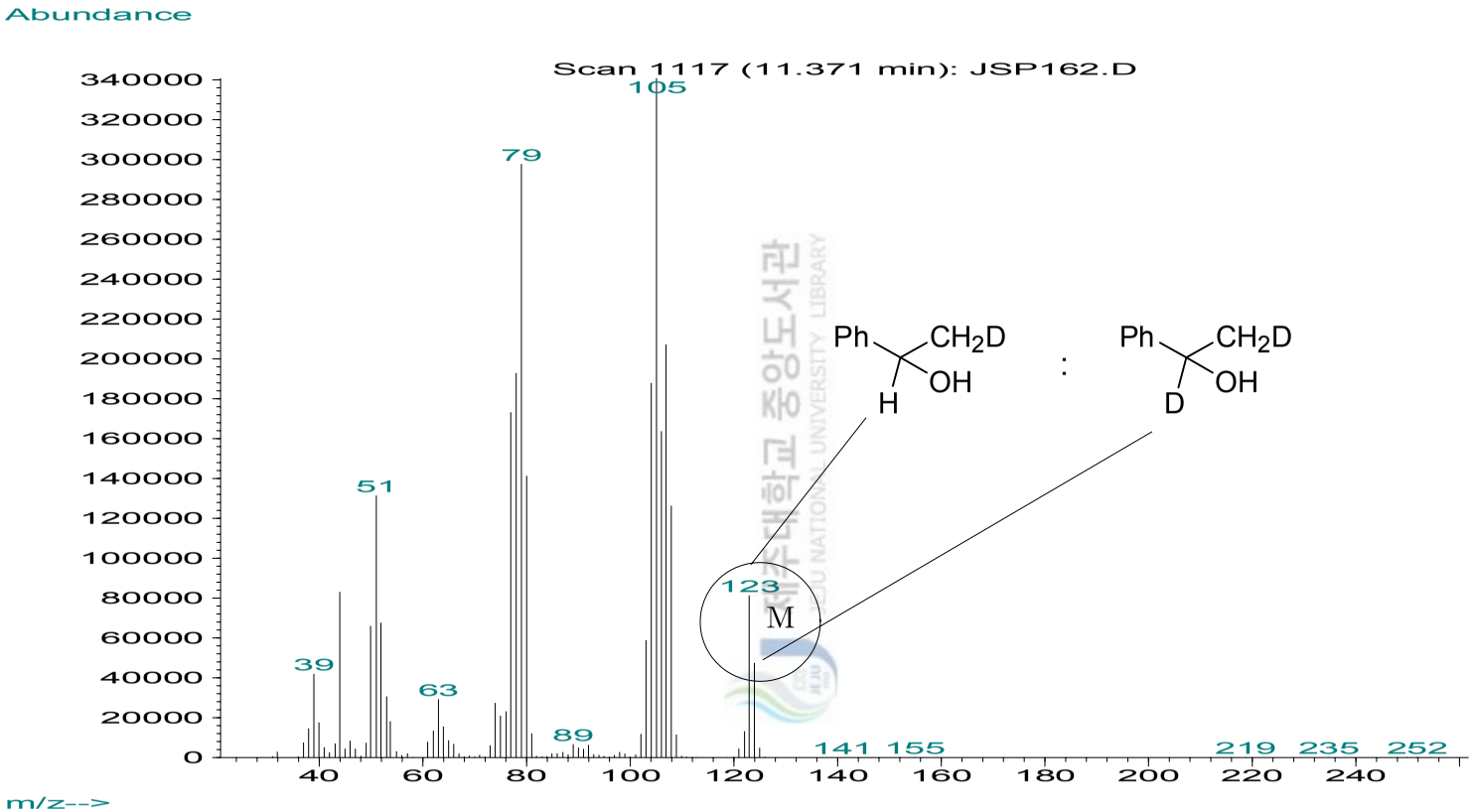


Figure 36. Mass spectrum of deuterium incorporated product of styrene oxygenation.

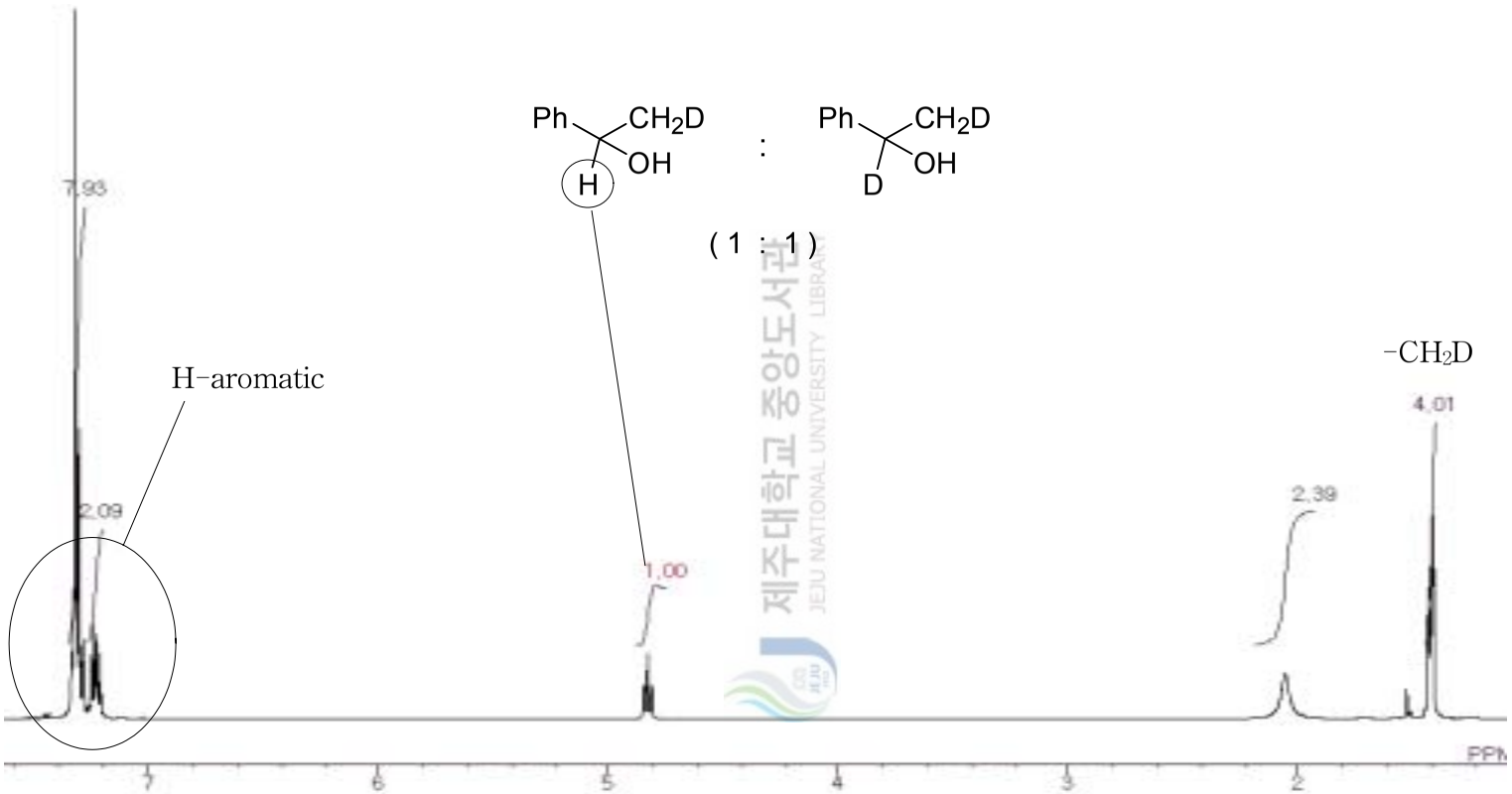


Figure 37. ^{1}H NMR spectrum (400 MHz) of deuterium incorporated product of styrene oxygenation in $CDCl_3$.

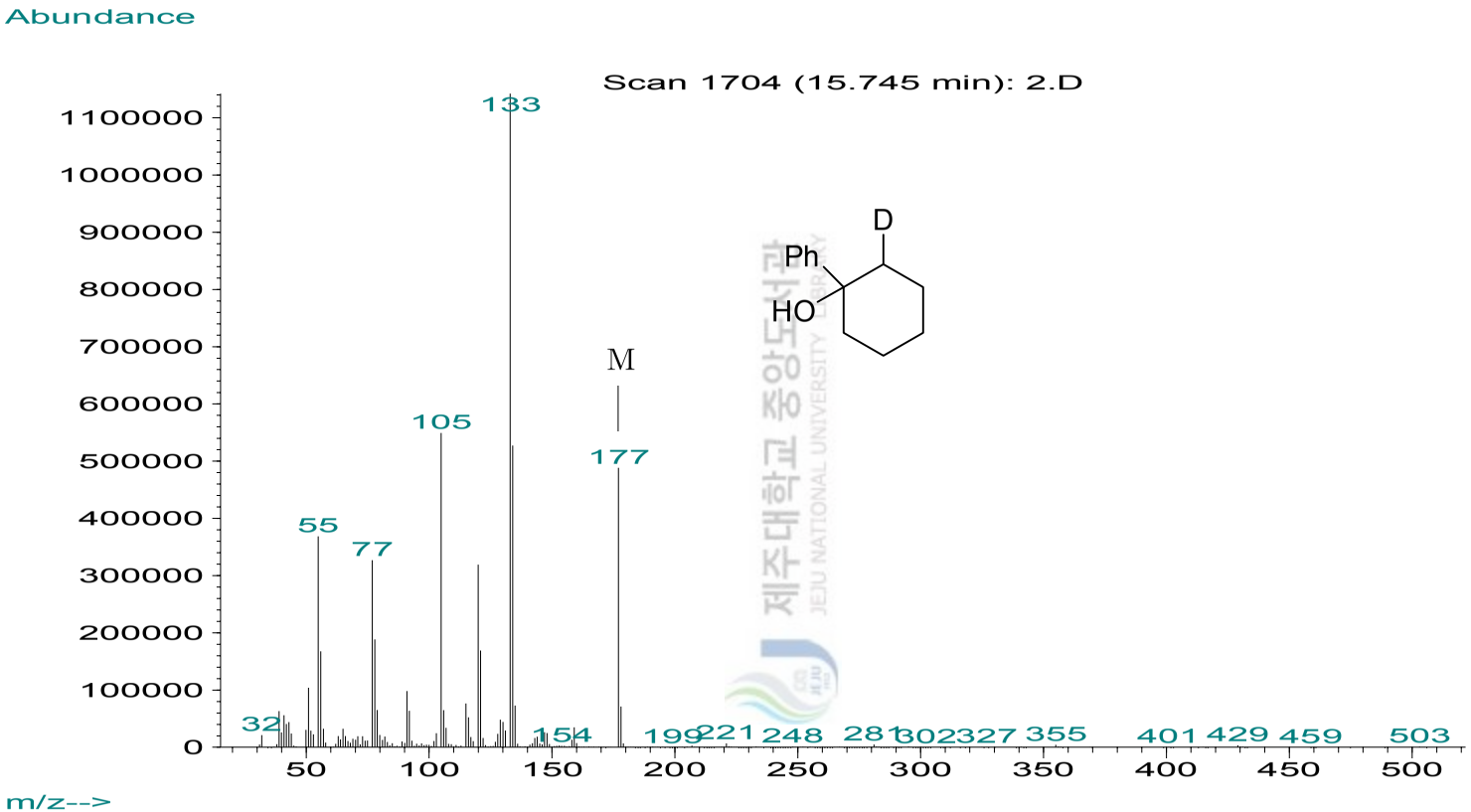


Figure 38. Mass spectrum of 1-deuterio-2-phenyl-2-cyclohexanol.

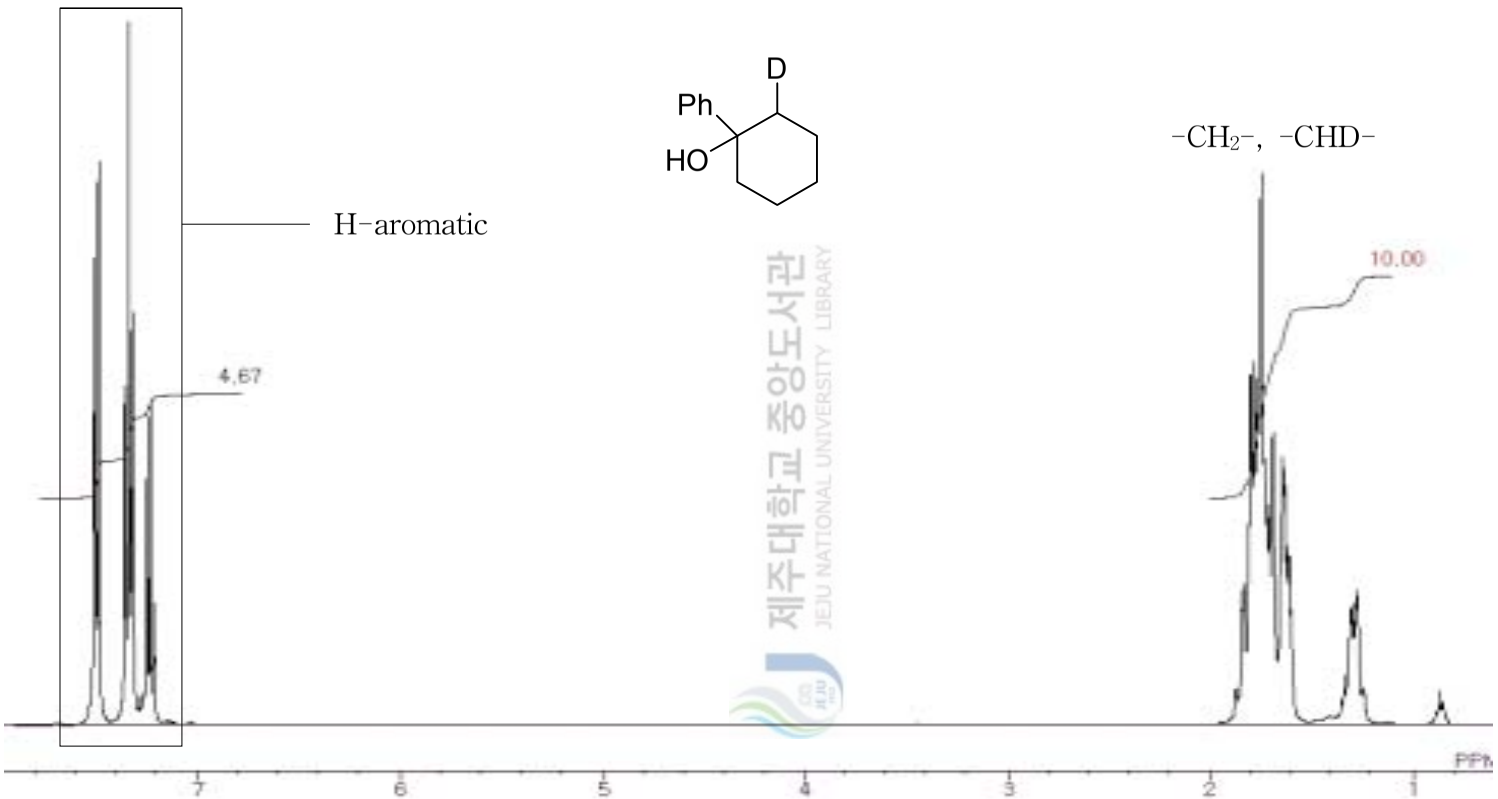


Figure 39. ^{1}H NMR spectrum (400 MHz) of 1-deuterio-2-phenyl-2-cyclohexanol in $CDCl_3$.

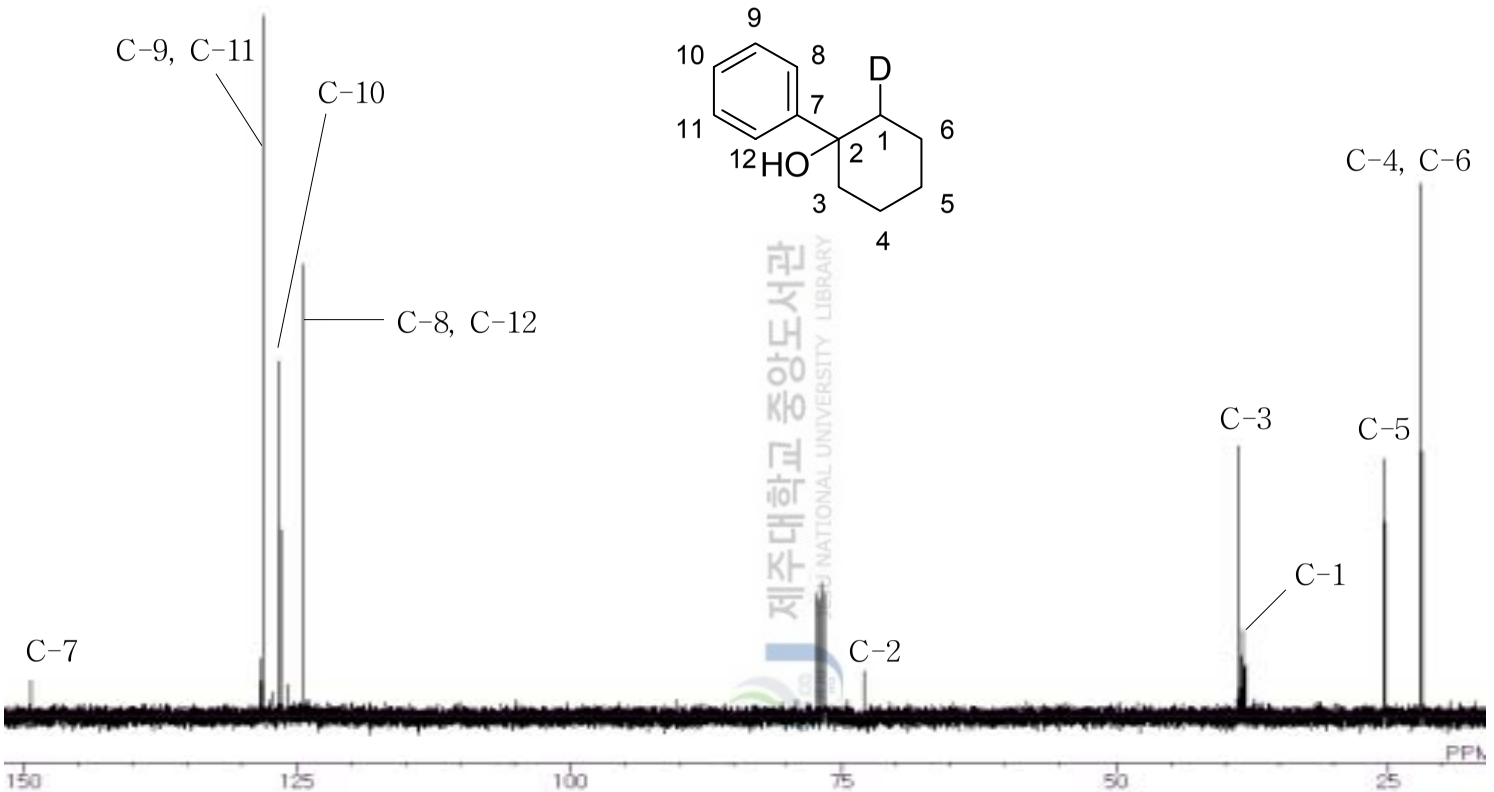


Figure 40. ^{13}C NMR spectrum (100 MHz) of 1-deuterio-2-phenyl-2-cyclohexanol in $CDCl_3$.

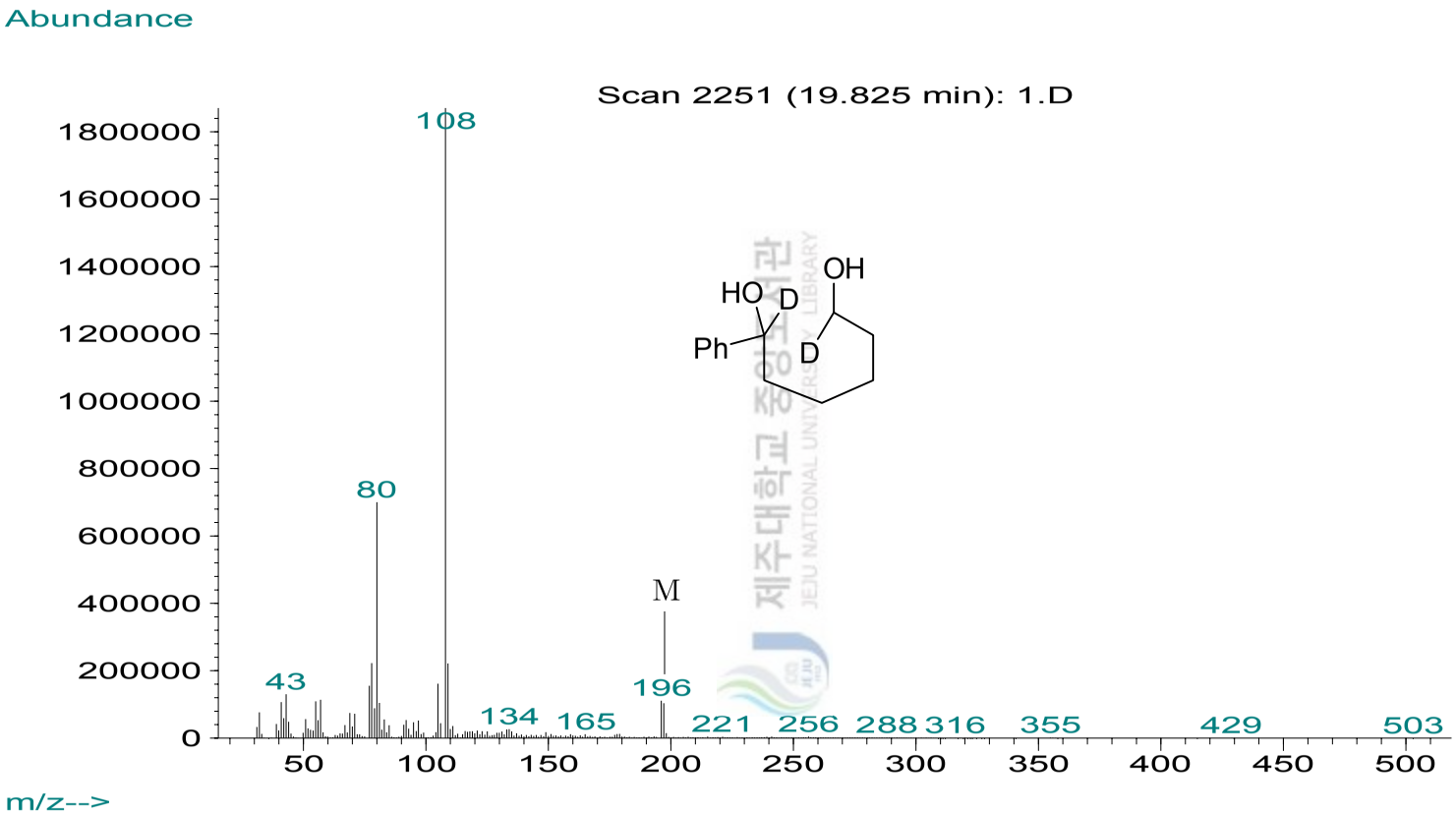


Figure 41. Mass spectrum of compound **34**.

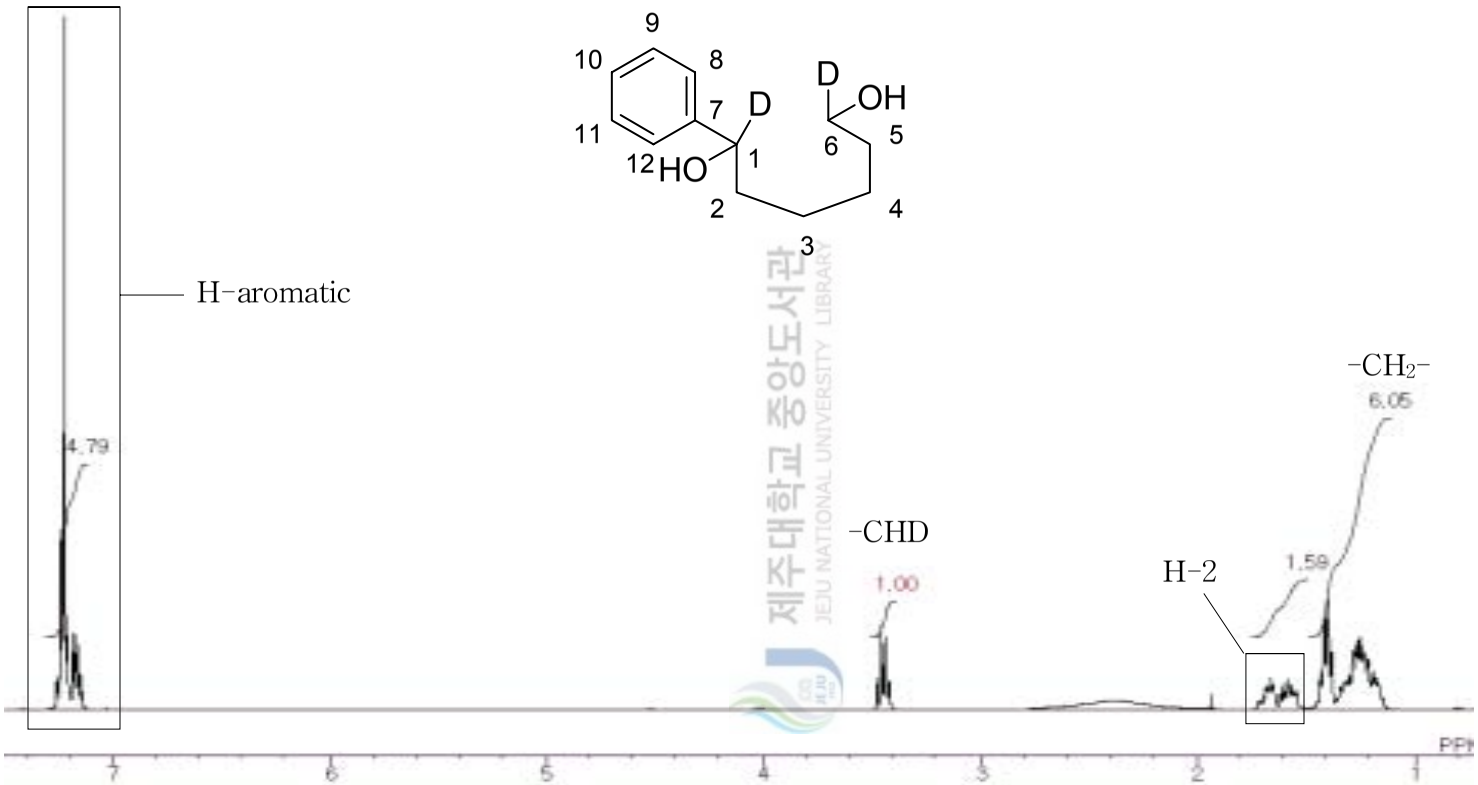


Figure 42. ^{1}H NMR spectrum (400 MHz) of compound **34** in $CDCl_3$.

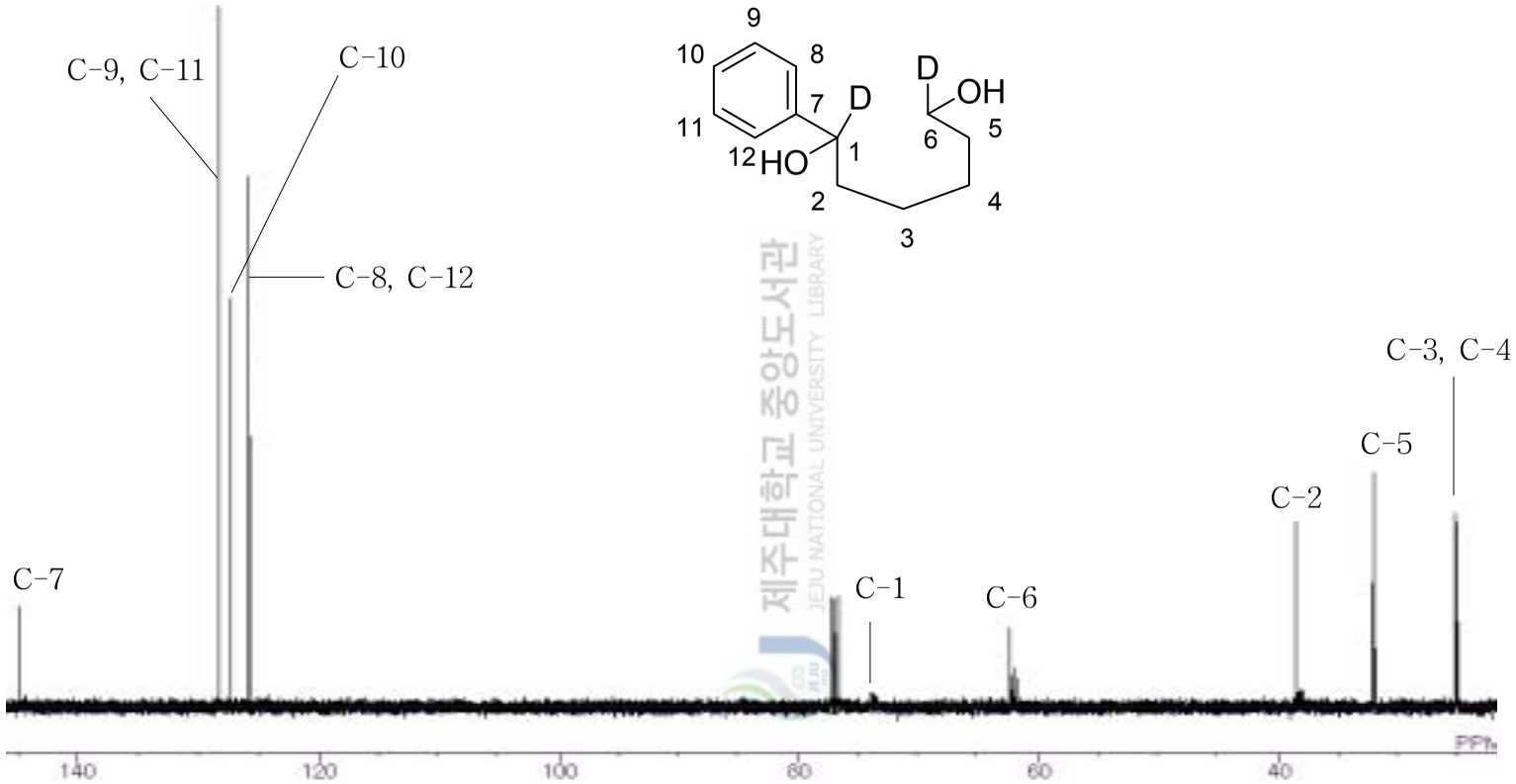


Figure 43. ^{13}C NMR spectrum (100 MHz) of compound **34** in $CDCl_3$.

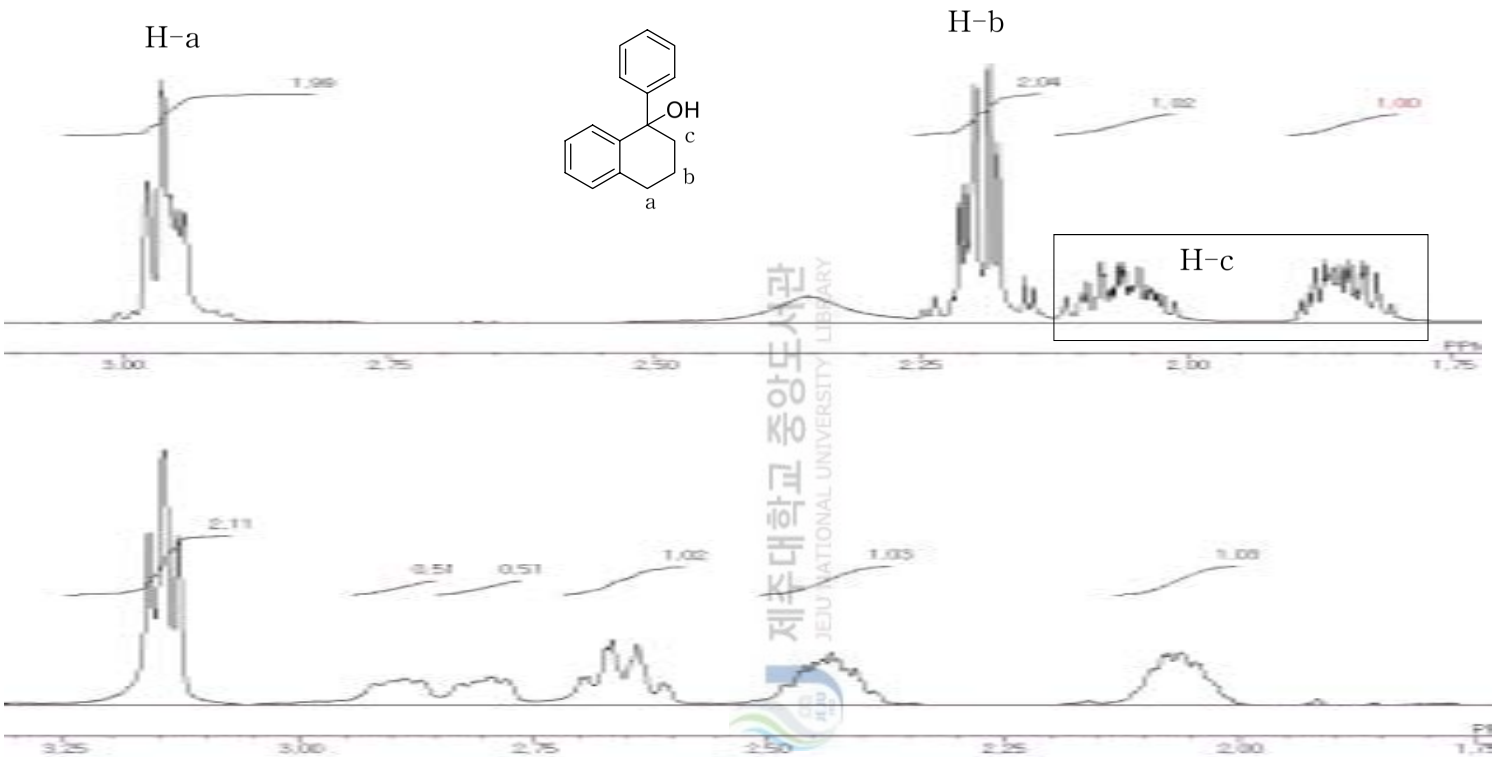


Figure 44. ^{1}H NMR spectrum (400 MHz) of **13b** in $CDCl_3$: (up) no shift reagent; (down) $Eu(hfc)_3$ was added.

Ⅳ. Conclusion

In this study, we wanted to develop a practical olefin oxidation method using molecular oxygen as an oxidant and metal complexes as a catalyst. Molecular oxygen is economically cheap and environment-friendly oxidant. In this reaction used were the (salen)Mn(III) complexes as the catalyst and $NaBH_4$ as the one-oxygen reductant.

We have shown the oxidation procedure for the conversion of olefin to the corresponding alcohol under the molecular oxygen. While vinyl arenes undergo effective oxygenation using complex **1** as the catalyst under mild condition, other simple olefins do not experience the desirable conversion due to low reactivity. Therefore, to extend the scope of the olefin oxygenation procedure by development of the more effective catalyst, we have synthesized several (schiff-base)Mn(III) complexes, and examined the complexes as the catalysts for the oxygenation of olefins. As a result, (salpro)Mn(III) complex **10** was a very good catalyst for our system. The complex **10** was found to be easy to handle due to its stability to moisture and air. Various types of olefins were effectively converted to olefins using the catalyst **10** in the presence of molecular oxygen under mild condition, *i.e.* balloon pressure of oxygen and room temperature.

We also have shown that readily available Mn salt, $Mn(OAc)_3 \cdot H_2O$ could be employed as the catalyst in the presence of appropriate schiff-base ligand. Atmospheric pressure of O_2 is used as the oxidant, and mild reducing agent $NaBH_4$ is used as the hydrogen source. The requried ligand such as **13** is easily

prepared from the condensation of diamine and salicyl aldehyde. This process affords the flexible reaction method, because different type of ligands can be employed to various olefinic substrates as needed.

α,β-Unsaturated ester was subjected to the reaction condition with O_2, and $NaBH_4$ catalyzed by complex **10**. Methacrylate-type and acrylate-type esters are converted to the corresponding *tert*-alcohol in good yield. However, crotonate-type esters having internal C=C bond is converted to *sec*-alcohol in low yield. But, using lignad **17** along with Mn(III) acetate instead of complex **10** as the catalyst provided good yield.

Mechanistically, the oxidation mechanism was considered to proceed *via* Mn(II) and Mn(III) interconversion as the catalytic cycle. The color change between colorless Mn(II) and brownish Mn(III) complexes. When the oxidation of styrene was conducted in the presence of BHT, a phenolic radical scavenger, no desired product was observed recovering much of the starting material. Thus, it is considered that some radical species are involved as the reaction mechanism. On the basis of the results, we propose the reaction mechanism of the oxygenation of vinyl arenes in our reaction conditions (Scheme 6). The mechanism involving a pair of alkyl radical and (salen)Mn(II) which is formed by the reaction of alkene, a hydride, and (salen)Mn(III). The radical reacts with dioxygen to form the (alkylperoxo)Mn(III) complex which is converted to acetophenone and directly reduced with $NaBH_4$ in the reaction of styrene. In case of α-methylstyrene is directly reduced with $NaBH_4$. The result of the deuterium incorporation for the reaction of styrene can be understood by these two mechanism. In case of 1-phenyl-1-cyclohexene, the result of deuterium incorporation indicates that there are, at least, two pathways for formation of corresponding products. No evidence

for formation of the (□-alkyl)Mn(III)-complex has been obtained in this study. Since no high-valent oxomanganese(V) complex is generated, the epoxidation does not proceed in our system. Further investigation is needed to identify the detailed reaction mechanism. When the reaction was examined using homochiral Jacobsen's catalyst, the chirality transfer was not observed.

If this oxygenation could be generally used in simple olefins, this could be important oxidation method in organic synthesis as well as in industry. This study also has a biological importance as a model in biomimetic oxidation pathway. We also believe this study will contribute to the development of related oxygenation studies by providing fundamental data.

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ABSTRACT

산소분자는 생체 내 산화과정에서 필수적으로 이용되고 있으며, 유기합성 분야에서도 가장 저렴하고 환경친화적인 산화제로서 유기합성에서 매우 중요하게 인식되고 있다. 따라서 산소분자를 산화제로 이용하고 전이금속을 활성화제로 이용한 실용적인 산화과정의 개발은 오랫동안 이어져 왔으며, 앞으로도 더욱 효율적이고 다양한 산소화 방법의 개발에 관심이 모아질 것이다. 생체 내의 산소화 과정에서는 산화효소가 촉매로 이용되고, NADH등이 환원제로 이용되고 산소를 활성화 시키고 있다. 이 때 이용되는 산화효소는 대부분 활성자리에 금속-착물이 자리 잡고 있다.

본 연구에서는 이러한 생체 내 산화 반응 시스템을 모방한 새로운 산소화 반응을 개발하였다. 반응의 촉매로서 (살렌)망간(+3) 착물을 이용하고, 환원제로서는 저렴하고 다루기 쉬운 $NaBH_4$를 이용하였다. 이러한 시스템을 이용하여 여러 가지 올레핀을 알코올로 산화시킬 수 있음을 발견하였다. 촉매로 (살렌)망간(+3) 착물 **1**을 사용한 경우, vinyl aren의 경우 효율적으로 반응이 진행된 반면 기타 올레핀의 경우 반응성이 감소하였다. 따라서 일반적인 올레핀에서도 고효율로 산소화 반응을 진행할 수 있는 다양한 schiff-base계의 리간드를 갖는 망간(+3) 착물들을 합성하여 올레핀 산화반응의 반응을 검색하였다. 검색 결과 망간 착물 **10**이 가장 효율적인 촉매임을 밝혀내었다. 망간 착물 **10**을 이용하여 여러 가지 타입의 올레핀이 산소 하에서 산화반응이 진행됨을 발견하였다. 또한, 망간(+3) 착물 대신에 망간(+2) 아세테이트 혹은 망간(+3) 아세테이트가 직접 촉매로 사용되는 보다 실용적인 산화반응을 개발하였다. 이 반응에서는 촉매량의 schiff-base가 리간드로 사용되어진다. 기질로 α,β-불포화 카르보닐 화합물을 사용한 경우에도 산화반응이 고효율로 진행됨을 확인하였다. 여러 가지 방법으로 반응 메카니즘을 추적한 결과, 망간(+2)과 망간(+3)이 상호 변환되는 촉매 순환을 한다고 판단된다. 또한 이 반응은 라디칼 중간체를 거쳐 진행된다고 판단

된다. 본 연구에서 제안된 산소화 반응 메카니즘은 중수소 합체 실험을 통하여 더욱 명확히 하였다.

감사의 글

입학을 한지가 엊그제 같은데 벌써 시간은 살같이 흘러 학위과정의 종착역에 서 있습니다. 어렵고 힘들었던 하지만 많은 즐거움이 함께 있었기에 많은 아쉬움이 남습니다. 하지만 이런 아쉬움들이 있기에 그것을 거울삼아 좀 더 나은 자기 자신을 찾을 수 있었고, 자신감 있는 발걸음으로 내일을 향해 한 걸음 내디딜 수 있는 계기가 된 시간이었던 것 같습니다. 졸업이 배움의 끝이 아니라 새로운 배움의 장으로 도약하는 첫걸음이라 생각하며, 대학원 생활을 잘 마무리 할 수 있도록 도와주신 많은 분들께 감사의 마음을 전하고자 합니다.

학위과정 중 학문의 길로 정진할 수 있는 연구 환경을 조성해주시고 모든 실험과 논문작성에 있어서 세밀하고, 자상하게 지도해주시고 연구자의 자세를 가르쳐 주신 이남호 지도교수님과 본 논문을 심사하시면서 많은 지적과 지도를 해주신 한성빈 교수님, 정덕상 교수님, 변종철 교수님, 그리고 한양대학교 오창호 교수님께 감사를 드립니다. 그리고 많은 애정과 관심을 가지고 늘 격려를 해주신 김덕수 교수님, 강창희 교수님, 이선주 교수님, 김원형 교수님께 감사를 드립니다.

부족한 선배를 잘 따라주고 수많은 부탁과 일거리를 말없이 묵묵히 해준 태헌, 정미, 지영, 영민, 그리고 항상 큰형처럼 생각한다며 잘 따라준 Bangladesh에서 온 Neaz, 졸업 후 직장생활을 열심히 하고 있는 진석, 홍철, 지금은 편입하여 다른 전공을 공부하고 있는 영국, 그리고 선배들의 실험하는데 애로사항이 없도록 항상 뒷바라지를 열심히 해주고 있는 학부생 형주, 성준, 성훈, 석봉, 재형, 촉매를 만드는데 있어서 같이 고민하고 많은 도움을 준 동기인 무기화학실험실의 충훈, 그리고 무기화학실험실의 창식과 기주, 모두들 행복하고 좋은 일만 있기를 바라며 이렇게나마 감사의 마음을 전합니다.

이날이 있기까지 항상 자식 잘되길 빌며 매일같이 기도해 주시는 어머니와 항상 친자식처럼 아껴주시고 사랑해주신 장인어른과 장모님, 그리고 항상 애정 어린 관심과 따듯한 정으로 대해주시고 여러 모로 도움을 주시고 밀어주신 식구들, 처갓집 식구들, 그리고 친지 어른들께 감사드립니다.

저의 인생의 반려자로 언제나 내 뒤에 서서 날 지켜봐 주고 믿어 주었으며, 내가 힘들어 할 때 마다 옆에서 항상 격려해주고 묵묵히 내조를 아끼지 않은 사랑하는 아내 정애와 오늘의 기쁨과 영광을 함께 나누고자 합니다.

이 밖에도 저를 도와주고 격려해주신 많은 분들께도 머리 숙여 감사드립니다.

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