อิพอกซิเดชันอย่างเลือกจำเพาะของเทอร์มินัลแอลคีนที่เร่งปฏิกิริยา
ด้วยสารประกอบเชิงซ้อนโคบอลต์

นางสาวสุมลรัตน์ ทิพย์ทินกร

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SELECTIVE EPOXIDATION OF TERMINAL ALKENES
CATALYZED BY COBALT COMPLEXES

Miss Sumonrut Thipthinnakorn

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

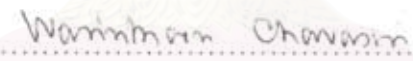Chulalongkorn University

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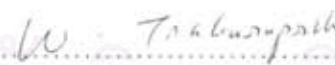
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ชวศิริ, 54 หน้า

ได้ศึกษาปฏิกิริยาอิพอกซิเดชันอย่างเลือกจำเพาะของเทอร์มินัลแอลคีนที่เร่งปฏิกิริยาด้วย
สารประกอบเชิงซ้อนโคบอลต์ที่มี 2-เอทิลบิวทิลแอลดีไฮด์กับออกซิเจนเป็นตัวออกซิไดซ์ภายใต้
ภาวะที่ไม่รุนแรง สารประกอบเชิงซ้อนโคบอลต์คาลิกซ์[4]พิโรล หรือเบนซิมิดาโซนซึ่งพบว่าไม่
เคยมีรายงานมาก่อนในการใช้เร่งปฏิกิริยาอิพอกซิเดชันของเทอร์มินัลแอลคีนสามารถใช้เป็นตัวเร่ง
ปฏิกิริยาที่มีประสิทธิภาพ ภายใต้ภาวะที่ได้พัฒนาขึ้น สารต้นแบบ 1-โดเดกซีนเปลี่ยนรูปเป็น
1-โดเดกซีนออกไซด์เพียงผลิตภัณฑ์เดียวได้ในปริมาณสูง และมีความเลือกจำเพาะที่ดีมาก เมื่อนำ
ระบบอิพอกซิเดชันที่ได้พัฒนาขึ้นมาประยุกต์กับเทอร์มินัลแอลคีนชนิดอื่นๆ ได้อิพอกไซด์ใน
ปริมาณปานกลางถึงสูง การศึกษาการเลือกจำเพาะในการเกิดปฏิกิริยาอิพอกซิเดชันของ 4-ไวนิล
ไซโคลเฮกซีนพบว่าพันธะคู่ที่ตำแหน่งเทอร์มินัลมีความว่องไวน้อยกว่าพันธะคู่ในวง

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต......................................
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SUMONRUT THIPTHINNAKORN: SELECTIVE EPOXIDATION OF TERMINAL ALKENES CATALYZED BY COBALT COMPLEXES. THESIS ADVISOR: ASST. PROF. WARINTHORN CHAVASIRI, Ph.D., 54 pp.

The selective epoxidation of terminal alkenes catalyzed by cobalt(II) complexes in the presence of 2-ethylbutyraldehyde/oxygen as oxidant was examined under mild conditions. Cobalt calix[4]pyrrole or benzimidazole with no previous report as a catalyst for terminal alkene epoxidation have been disclosed to be effective catalysts. Under the developed conditions, 1-dodecene as a chemical model was transformed into 1-dodecene oxide as a sole product with high yield and excellent selectivity. Applications of this developed epoxidation could be accomplished with various terminal alkenes and gave the desired products in moderate to high yield. Regioselectivity study performed using 4-vinylcyclohexene implied that terminal double bond was less reactive than endocyclic double bond.

Field of study Petrochemistry and Polymer Science Student's signature Sumonrut Thipthinnakorn

Academic year................2006.................... Advisor's signature W. Chavasiri

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br	broad (IR)
BuLi	butyllithium
δ	chemical shift
J	coupling constant (NMR)
^{o}C	degree Celsius
$CDCl_3$	deuterated chloroform
d	doublet (NMR)
dd	doublet of doublets (NMR)
GC	gas chromatography
g	gram(s)
^{1}H NMR	proton nuclear magnetic resonance
Hz	Hertz
h	hour(s)
IR	infrared
MS	mass spectrometry
m/z	mass to charge ratio
m	medium (IR)
m.p.	melting point
m-CPBA	*meta*-chloroperbenzoic acid
mL	milliliter(s)
mmol	millimole(s)
mg	milligram(s)
min	minute(s)
m	multiplet (NMR)
q	quartet (NMR)
s	singlet (NMR)
s	strong (IR)
t	triplet (NMR)
w	weak (IR)

CHAPTER I
INTRODUCTION

1.1 General background

The epoxidation of alkenes is a fundamental reaction in laboratory as well as in chemical industry. That is because epoxides are widely used as raw materials such as epoxy resins, paints, surfactants, and are very essential key intermediates in many important organic transformation reactions. In addition, the derived chemicals are widely used in industry for manufacturing various types of products, ranging from perfumery to polymeric materials. Although a number of epoxidation processes have been based on a chlorine-using non-catalytic process (the chlorohydrin process), catalytic processes employing organic peroxides, and peracids are still used extensively. These processes have disadvantages from the economical viewpoint because they are very capital intensive. Furthermore the chlorohydrin process has environmental disadvantages due to the large output of chloride laden sewage [1]. Then, the method of epoxidation has been improved with the use of transition metal catalysts, and green oxidant for example molecular oxygen/aldehyde. Transition metal catalysts have thus been developed, and dramatically enhanced the selectivity, and the rate of epoxidation.

The need for cleaner chemical processes in industry is obvious. Chemical transformations, which produce in addition to the desired product, large amounts of byproducts, and waste, are less desirable. Selective transformations using catalytic processes eliminate the requirement of stoichiometric auxiliary reagents in many current processes, and can eventually help to decrease the amounts of waste.

In pharmaceutical, and agrochemical industries, the need for selective transformations is even larger since delicate bioactive compounds are often not robust enough to stand the conditions used in bulk chemistry. Moreover, pharmaceuticals, and agrochemicals have to be enantiomerically pure if they contain stereogenic centers. The use of enantioselective catalytic processes can improve the efficiency of the production of fine chemicals, and pharmaceuticals.

The aim of this chapter is not to give a complete survey of the catalytic oxidation of terminal alkenes but to give a summary of the developments achieved in

the last decades. An overview will be presented including the most prominent, and synthetically applicable catalytic oxidation reactions for the preparation of functionalized organic compounds from terminal alkenes.

This present work describes the efforts to establish a new catalytic system capable of achieving epoxidation of terminal alkenes with high selectivity using aldehyde, and oxygen as oxidant. Cobalt complexes are focused since the precedent work of Buranaprasertsuk [2] revealed his success of employing cobalt complexes in epoxidation of alkenes [3]. Nonetheless, for terminal alkenes which are less reactive, the reaction conditions were needed to be optimized.

1.2 Epoxidation of alkenes

Epoxides are compounds which contain a saturated three-membered ring having one oxygen atom, and two carbon atoms.

The simplest imaginable case of epoxidation of a double bond is the industrial production of ethylene oxide from ethylene and oxygen in the presence of silver oxide on alumina at 270 $^{\circ}$C [4].

In the laboratory, epoxidations of alkenes are usually accomplished by H_2O_2 or its derivatives. H_2O_2 is applied to an alkaline medium so that it reacts as an anionic nucleophile.

$$\text{C=C} + \bar{\text{O}}\text{-O-H} \longrightarrow \overset{}{\underset{O}{\text{C-C}}} + \bar{\text{O}}\text{H}$$

In the presence of a nitrile, alkaline H_2O_2 froms peroxycarboximidic acid, which in the presence of an alkene gives an epoxide and a carboxamide.

$$CH_3CN + H_2O_2 \xrightarrow[\text{pH 8}]{\bar{\text{O}}\text{H}} \underset{\text{OOH}}{\overset{\text{NH}}{CH_3\text{C}}} \xrightarrow{\text{C=C}} \overset{}{\underset{O}{\text{C-C}}} + CH_3CONH_2$$
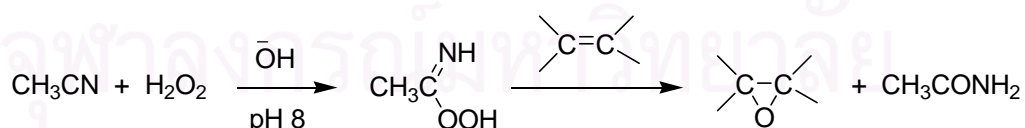
Using oxidant in the epoxidation reaction of alkenes developed improvement in yields, and selectivities. General oxidants were used in this reaction such as perbenzoic acids, dioxiranes, alkylhydroperoxides, H_2O_2 [5] for example peroxyacetic, and peroxybenzoic, bleach [6], iodosylbenzene [7], and molecular

oxygen [8]. Most of them suffer from the disadvantage that besides oxygenated products, stoichiometric amounts of waste products are formed which has to be separated from the epoxides.

$$\underset{\underset{-\overset{O}{C}=O}{\underset{\displaystyle O\,\diagdown H}{}}}{\overset{\displaystyle}{\text{C}=\text{C}}} \longrightarrow \overset{\displaystyle}{\underset{O}{\text{C}-\text{C}}} \;+\; \underset{R-\overset{\displaystyle O}{\underset{\|}{C}}-O^{\diagup H}}{}$$
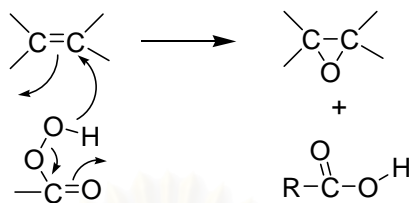
Molecular oxygen is the most attractive oxidant, and used on large scale in industry. Many epoxides are produced *via* the corresponding halohydrins. Molecular oxygen does not react with alkenes spontaneously but has to be activated with a suitable catalyst. For instance, in the case of the industrial conversion of ethylene to ethylene oxide, one oxygen atom is transferred by a silver catalyst to ethylene to form the desired product. The other oxygen atom cannot produce more epoxide but it oxidizes ethylene to CO and water. This process is only applicable with alkenes without α-hydrogen atoms present.

Epoxidation of alkenes in the laboratory is usually accomplished with peracids. *Meta*-chloroperbenzoic acid (*m*-CPBA) is the most commonly used oxidant, and most olefins react readily with this reagent to give the desired epoxide in good yields. Alternatives for *m*-CPBA include various peracids with higher or lesser reactivity. *m*-CPBA is, however, not safe for use on industrial scale.

Bleach is a very cheap, and easy to use oxidant but suffers from the facts that stoichiometric amounts of salt are formed during reactions, and the oxidant is highly diluted. Also the basicity of the reaction medium (pH > 10) can be a problem.

The oxidant of choice is H_2O_2, which can be handled easily, and leaves only water as the byproduct. Separation of water from the products is almost never a problem. H_2O_2, however, is often partially destroyed by catalase type activity, a common side-reaction caused by several epoxidation catalysts. In this reaction, two molecules of H_2O_2 are converted into two molecules of water, and molecular oxygen.

$$2\,H_2O_2 \xrightarrow{\text{Catalyst}} 2\,H_2O \;+\; O_2$$
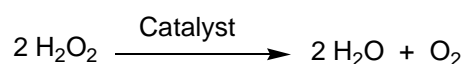
1.3 Literature review on the epoxidation of alkenes

Epoxides are cyclic ethers with three-membered ring. Oxygen is added to carbon-carbon double bonds to form epoxides [8]. The simplest epoxide, ethylene oxide, is one of the oldest-established ethylene-based petrochemicals [9]. It has been made in USA since about 1925. In 1930, improvement using Ag catalyst was employed in the process. Ethylene oxide is prepared industrially by direct air oxidation of ethylene over a hot silver catalyst [4].

$$H_2C{=}CH_2 \;+\; O_2 \quad \xrightarrow[\text{250-330 }^0\text{C}]{\text{Ag Catalyst}} \quad H_2C{-}CH_2 \atop O$$
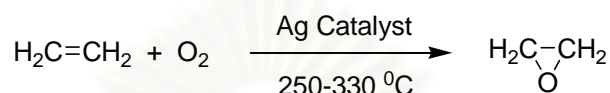
The most widely used method for synthesizing epoxides is the reaction of alkenes with an organic peroxy acid (or peracid), and peroxide.

1.3.1 Literature review on the epoxidation of alkenes with peroxy acids

The reaction of alkenes with peroxy acid to produce epoxides has been known for almost 90 years. It provides the most convenient method for the preparation of epoxides. Epoxidations with commercially available peroxy acids such as peroxyacetic acid, peroxybenzoic acid [10], peroxyfluoroacetic acid, m-CPBA [11], and m-nitroperoxybenzoic acid are among well-known examples. Oxygen atom transferred from a peroxy acid to an alkene is facilitated by electron-donating substituents on the carbon-carbon double bond, and electron-withdrawing groups on the peroxy acid.

$$RHC{=}CHR \;+\; R'{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}H \quad \xrightarrow{\text{epoxidation}} \quad RHC{-}CHR \atop O \;+\; R'COOH$$
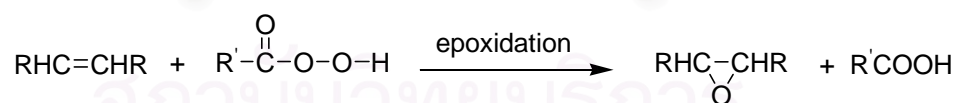
Bach, and co-workers [12] reported the epoxidation of 1-nonene by m-CPBA in the presence of either CCl₃COOH (TCA) or CF₃COOH (TFA) in benzene. Reaction rates were monitored by following the formation of 1,2-epoxynonane, and it was found that the reaction was second order, and the addition was stereospecific of oxygen. Some typical epoxidations with peroxy acids are shown below.
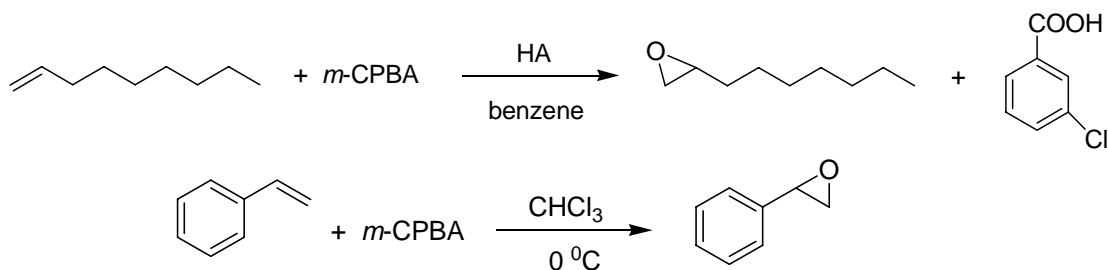
In addition, Carison and colleagues [13] reported that peroxybenzimidic acid appears to be a relatively indiscriminate reagent, and was not the reagent of choice for selective epoxidation of polyunsaturated substrates. Peroxybenzimic acid appeared to be less selective than other peroxy acid for the epoxidation of olefins. For example, the comparative epoxidation study of 4-vinylcyclohexene and limonene with *m*-CPBA gave predominantly 1,2-epoxide in 87% yield while peroxybenzimidic acid is less selective reagent for the epoxidation of double bonds than are peracids. The epoxidation of 4-vinylcyclohexene with *m*-CPBA furnished 1,2-epoxide in 88% yield and 7,8-epoxide in 2% yield.

4-vinylcyclohexene attacked by *m*-CPBA   4-vinylcyclohexene attacked by peroxybenzimidic acid

limonene attacked by *m*-CPBA   limonene attacked by peroxybenzimidic acid
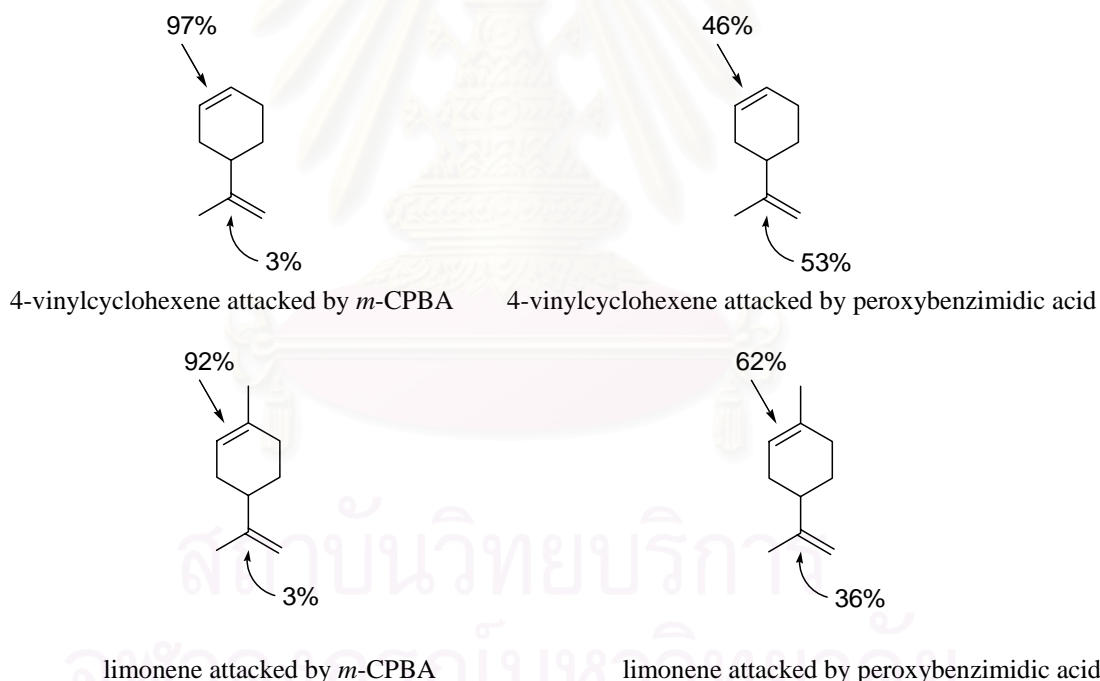
1.3.2 Literature review on the epoxidation of alkenes with peroxides

Besides peroxy acids, hydroperoxides are used in epoxidation of alkenes especially, H_2O_2, and *tert*-alkyl hydroperoxides. H_2O_2 are available to use for epoxidation. Using aqueous H_2O_2 as the oxidant is appreciated because water is the sole expected side product, and it is the oxygen source for alkene epoxidation. Only a few alkenes undergo epoxidation reaction using H_2O_2 alone. Moreover, H_2O_2 is too

expensive to be used in a bulk process. Many epoxidation reactions used H_2O_2 as a primary oxidant combined with inorganic reagents such as Na_2WO_4-H_3PO_4-quaternary ammonium chloride.

$$R\diagup\!\!\diagdown\!\!\diagup + H_2O_2 \xrightarrow[\text{NH}_2\text{CH}_2\text{PO}_3\text{H}_2,\ 90\ ^0\text{C}]{\begin{array}{c}\text{Na}_2\text{WO}_4 \\ [\text{CH}_3(n\text{-}\text{C}_8\text{H}_{17})_3\text{N}]\text{HSO}_4\end{array}} R\diagup\!\!\triangle\!\!O + H_2O$$
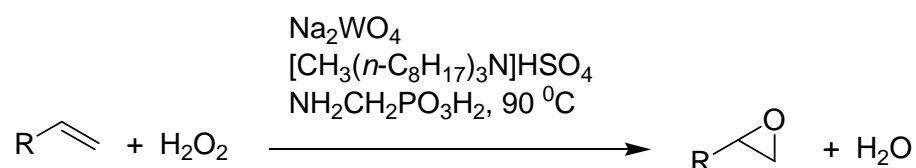
The epoxidation of terminal olefins with 30% H_2O_2 under halide-free conditions was also addressed. Catalytic systems consist simply of Na_2WO_4 dihydrate, (aminomethyl)phosphonic acid, and methyltri-*n*-octylammonium hydrogensulfate in a 2:1:1 molar ratio and is free from any organic or inorganic chlorides. The biphasic epoxidation of simple terminal olefins can be carried out at 90 ^{o}C with 150 mol% of H_2O_2, and 0.2-2 mol% of catalyst without organic solvents or alternatively by adding toluene. Terminal olefins, which are normally least reactive, were epoxidized in 94-99% yield (based on olefin charged) with 2 mol% of the catalyst [14]. This method is operationally very simple, and uses an environmentally friendly oxidant.

1.3.3 Literature review on the epoxidation of alkenes catalyzed by metal complexes

Epoxidations of alkenes using methyltrioxorhenium (MTO) were found as an outstanding epoxidation catalyst using H_2O_2 as oxidant. The acid catalyzed ring opening of the epoxide was however found to be a severe problem, and in some cases, the diol was formed quantitatively. The addition of bases was found to suppress this ring opening but the activity of the catalyst diminished using low amounts of bases.

The activity, and stability of MTO were enhanced by the addition of excess pyridine to the reaction mixture with respect to the catalyst and also the selectivity of the reaction benefits from the addition of base, suppressing the competing acid catalyzed ring opening of the epoxides. Besides the desired epoxide, a considerable amount of pyridine *N*-oxide was formed, and the reaction has been used to prepare the *N*-oxides on a preparative scale [15].

$$\text{Cyclohexyl-CH=CH}_2 \xrightarrow[\text{1.5 eq 30\% aq H}_2\text{O}_2,\ 25\ ^0\text{C, CH}_2\text{Cl}_2]{\text{MTO (0.5\%), 3-CNC}_5\text{H}_5\text{N (12\%)}} \text{Cyclohexyl-epoxide}$$

86%
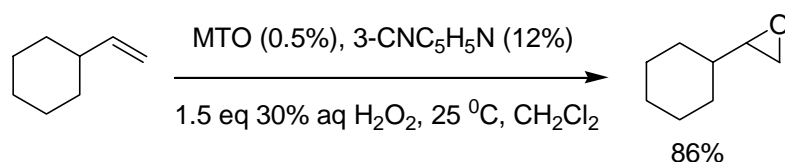
In numerous cases quantitative yields of epoxides can be obtained from styrenes, internal and terminal aliphatic olefins, and even tetrasubstituted alkenes. Only 1.5 equivalent of H_2O_2 are necessary, and typically 0.5 mol% of MTO is used.

In the epoxidation system of $[\pi\text{-}C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ / molecular oxygen / recyclable reductant (2-ethylanthrahydroquinone), terminal olefin for example 1-dodecene, 1-octene, and 1-hexene all underwent epoxidation reactions smoothly under mild conditions. Good selectivities to epoxides, and high reductant utilization efficiencies (72.6-94.5%) were achieved. From 1-dodecene to 1-hexene, the epoxidation reactivity of the olefin, and the efficiency of the reductant increased with the decrease of carbon atoms in terminal olefins. Studies showed that H_2O_2 produced by the oxidation of 2-ethylanthrahydroquinone (EAHQ) with molecular oxygen was the key intermediate that afforded the direct epoxidation of substrate. The unique characteristic of this system was the use of a recyclable reductant. After the epoxidation reaction, the oxidation product of the reductant, for example 2-ethylanthraquinone (EAQ), could be easily regenerated to the original reductant *via* a simple catalytic hydrogenation, and then could be reused [4].
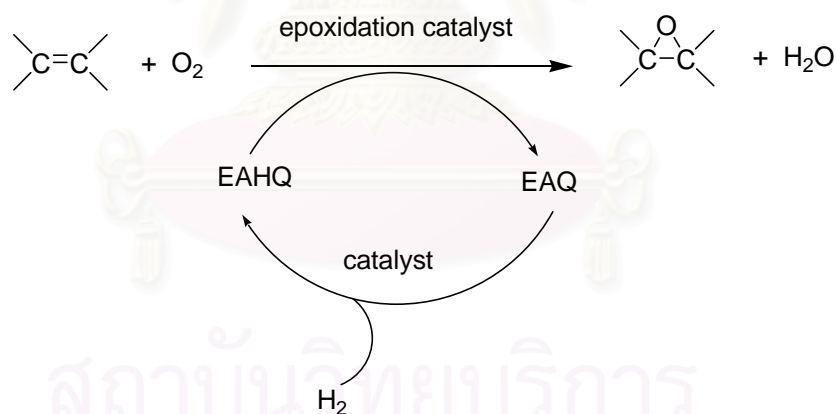
The epoxidation of linear terminal alkenes for example 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undene, and 1-dodecene by an $O_2\text{-}O_3$ mixture at room temperatures was catalyzed by Fe(TMP)Cl (TMP is the dianion of 5,10,15,20-tetramesitylporphyrin). The epoxidation of linear terminal alkenes gave low yield of epoxide, 10-25% [16].

Fe(TMP)Cl

CH$_2$Cl$_2$, RT

$+$ O$_2$-O$_3$

Fe(TMP)Cl

CH$_2$Cl$_2$, RT

$+$ O$_2$-O$_3$
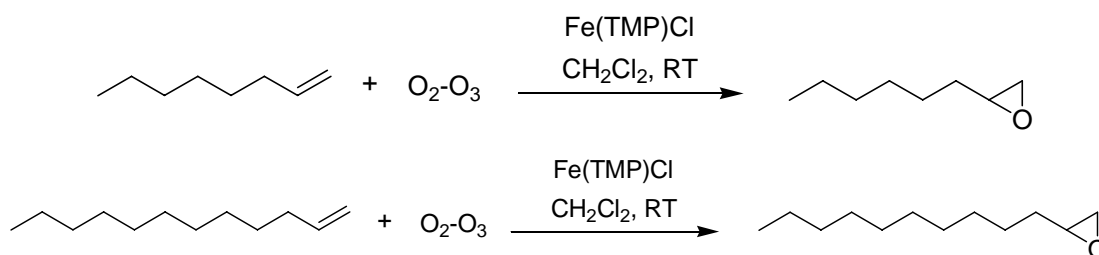
Methyltrioxorhenium-catalysed epoxidation of 1-dodecene with hydrogen peroxide at 0 ^{o}C used hexafluoro-2-propanol as a solvent. Quantitative conversion of 1-dodecene can be obtained with only 30% H$_2$O$_2$, and 0.1 mol% of catalyst [17].

H$_2$O$_2$/MeReO$_3$/

HFIP, 0 ^{0}C
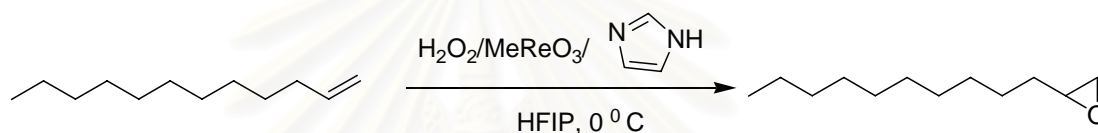
The epoxidation of olefins using Mn-salen complexes was published by Kochi [18]. Later on, the groups of Jacobsen [19], and Katsuki published at about the same time their first articles on asymmetric epoxidation using Mn-salen complexes (Figure 1.1). Since then, epoxidation chemistry using chiral Mn-salen complexes has been expanded, and has proven to be a valuable tool in asymmetric synthesis. In general Mn-salen complexes provide the epoxide in yields above 80%, and the *ee* usually exceeds 90 %. The complexes can be used with a variety of oxidants including bleach, persulfates, *m*-CPBA [20], periodates, dimethyldioxirane, dioxygen, and iodosylbenzene [8]. Special conditions make it possible to use H$_2$O$_2$ in the epoxidation reaction catalyzed by Mn-salen complexes. Additives like Me-imidazole, and carboxylates are used. Although turnover numbers are not as high as with bleach or iodosylbenzene, enantioselectivities ranging from 60 % to 96 % have been reached.
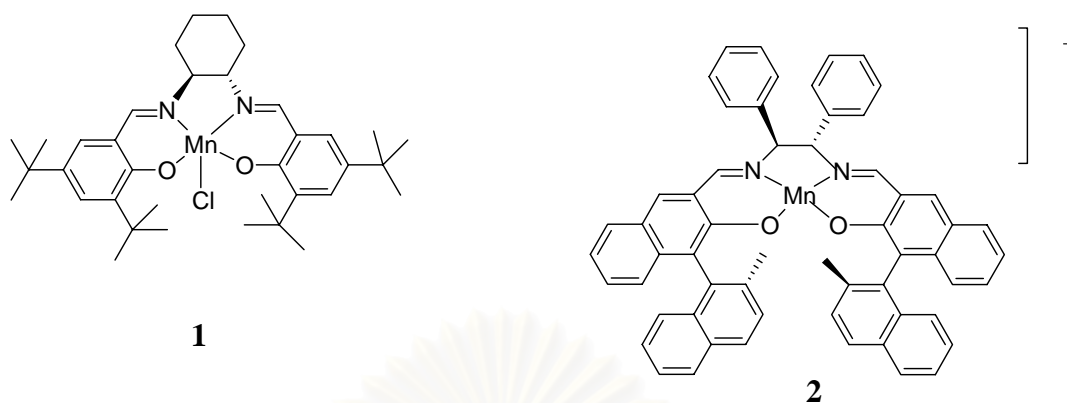
Figure 1.1 The Mn-complexes used in epoxidation reaction by the groups of
Jacobsen, and Katsuki.

The group of Mukaiyama developed a system that uses dioxygen as oxidant in combination with a reductant. The manganese complexes used as catalysts are prepared from simple aldimines or ketimines (Figure 1.2). Moderate enantioselectivity has been reached using complex **3**, and the enantioselectivity increased with the introduction of more steric bulk in the ester group [21]. Catalyst efficiency however is not high. Dihydronaphthalene epoxide was obtained in 70% yield with 64% *ee* using 8 mol% of catalyst. The same catalyst can be used in the aerobic oxidation of sulfides in an enantioselective fashion. Thioanisole was converted to its sulfoxide in 66% yield with 51% *ee* using 18 mol% of complex **3**.
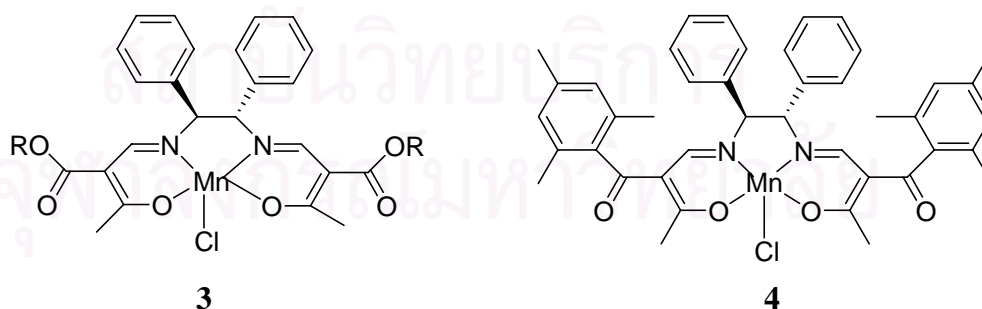
Figure 1.2 Aldimindinato Mn complexes.

The new catalytic epoxidation system was developed. Isolated, and well characterized dinuclear manganese complexes depicted below catalyze the epoxidation with H_2O_2 as terminal oxidant under similar conditions as reported for

MnTMTACN complexes. Various alkenes such as styrene, cyclohexene, and 2-octene were all converted into their epoxides with good yields. Turnover numbers higher than 300 can be reached easily.

The mechanism of this epoxidation reaction is not known at the present but in the case of the epoxidation of *cis*-β-methylstyrene a considerable amount of *trans* epoxide is found, which is often attributed to radical intermediates [22].

5   (ClO$_4$)$_2$ **6**   (ClO$_4$)$_2$
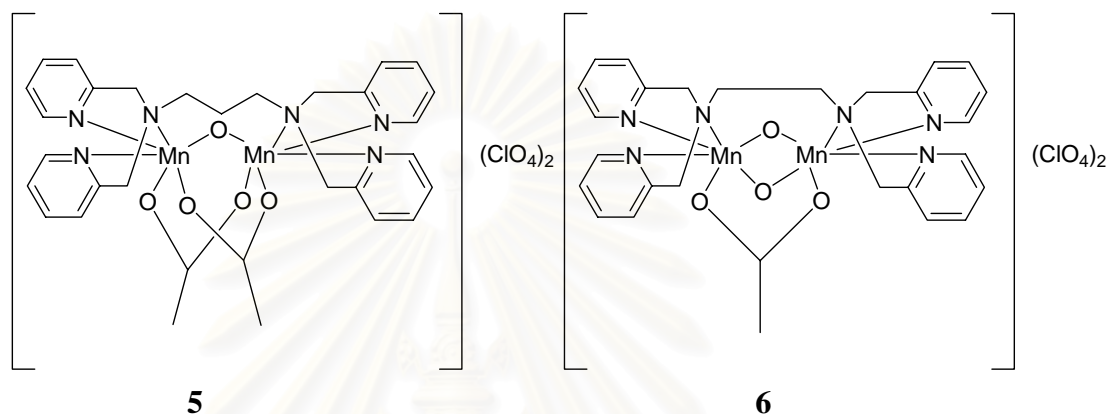
Moreover, the epoxidation of alkenes catalyzed by manganese porphyrins has recently been reported [23]. The manganese derivatives of chiral porphyrin catalyst were the most effective asymmetric catalysts in the epoxidation system. Monosubstituted alkenes were epoxidized by magnesium monoperoxyphthalate, like with other oxygen donor, and catalyzed by tetra-2,6-dichloro-phenyl-porphinato-manganese(III)acetate. Alkene conversion was nearly completed within 0.5-5 minutes at 0 ^{o}C, and provided good yields (60-93%). In addition, the epoxidation by threitol-strapped manganese porphyrins catalyzed for *cis*-disubstituted alkenes gave optical yield up to 88% *ee*, and proceeded greater than 80% conversion to oxidized products when iodosylbenzene was used as an oxidant. These were the highest *ee* in the epoxidation of these olefins such as styrene, *p*-chlorostyrene, α-methyl styrene, and 1,2-dihydronaphthalene. While *mono*- and *cis*-disubstituted alkenes were epoxidized with high degree of stereoselectivity, *trans*-disubstitued alkenes were poor substrates. For example, the epoxidation using threitol-strapped manganese porphyrins by iodosylbenzene as an oxidant was shown below.

82% yield, 70% ee
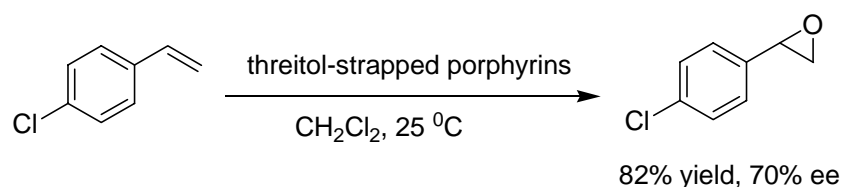
Catalysis was achieved by means of transition metal complexes with common oxygen sources while the stereoselectivity may be controlled either by an optically active oxidizing species or by a chiral substrate [24]. Stereocontrol using the diasteroselective epoxidation of chiral allylic alcohols had proved to be used of transition metal in the system [24]. Several catalytic [Ti(OiPr)$_4$ / TBHP, VO(acac)$_2$ / TBHP [25, 26], and non catalytic (DMD, m-CPBA) [27, 28, 29] methods have already been extensively studied. The valuable information on the geometry of the oxygen transfer process has been required. The mentioned catalytic oxidants including peroxy-, and peroxo-metal complexes were catalyzed by metal(Salen) or metal(porphyrin) complexes [24].

Recently, it was found that calix[4]pyrrole ligands have acquired special importance. It was useful to make anion binding agents, and especially neutral substrates [30, 31]. Calix[4]pyrroles provided useful precursors which play important role in the chemistry of biological process [32, 33]. The epoxidation reactions examined in this research were proceeded by the use of cobalt calix[4]pyrrole. The consideration derived from the structure of ligands is somewhat similar to porphyrin skeleton, in which be used in oxidation and biochemical systems.

Calix[4]pyrroles (meso-octaalkylporphyrinogens) [34, 35, 36] are stable tetrapyrrolic macrocycles first synthesized in the 19th century by Baeyer via acid-catalyzed condensation of pyrrole with acetone to produce $meso$-octamethylcalix[4]pyrrole [35, 36]. In the early 1970s, Brown reported a refined procedure that permitted them to obtain tetraspirocyclohexylcalix[4]pyrrole [37, 38]. Recently Floriani, and coworkers have made an extensive study on the chemistry of metal complexes of various deprotonated octaalkylporphyrinogens [39, 40]. Although porphyrinogen (5,10,15,20,22,24-hexahydro-porphyrin(H$_4$L)) is a well known precursor of porphyrin, its chemistry has never been explored. This is mainly due to its instability since it spontaneously forms porphyrin, the oxidation reaction being facile due to the presence of hydrogen atoms in the $meso$(5,10,15,20-) positions. However, a stable form of porphyrinogen has been known for more than a century [38] with alkyl groups at each $meso$ positions. Recent investigations by Floriani, and coworkers on the use of 5,5,10,10,15,15,20,20-octaalkyl-porphyrinogen in coordination and organometallic chemistry led to the discovery of their curious characteristics [39].

$$H_2L + 4LiBu^n \xrightarrow[-BuH]{THF} LLi_4 \cdot 4THF$$
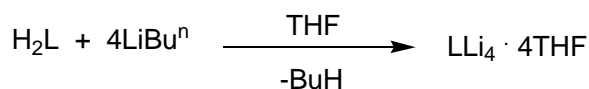
In order to obtain metal complexes of H_4L, a procedure often employed tetraanion in this synthesis to combine metal [41, 42]. In addition to the electronic flexibility, the use of tetraanion has advantage that it stabilized high oxidation states of metals, and favors the intramolecular interaction between unsaturated metal, and *meso*-alkyl substituents. In terms of catalysis for epoxidation of alkenes, in contrary to the case of porphyrin, porphyrinogen is able to use the periphery for binding metal [43, 44] atom, and substrates such as neutral molecules.

Manganese porphyrin supported on Merrifield, and Argogel resins as catalyst, and using $NaIO_4$ as oxidant have been demonstrated in alkene epoxidation [43]. %Yield of epoxide product of aromatic alkenes for example styrene, and α-methylstyrene were 80% and 51%, respectively (based on starting material consumed and by-products present). While %yield of terminal alkenes for example 1-hexene and 1-dodecene were 24% and 22%, respectively (based on starting material consumed, and by-products present) [42].

Mn(II) salen complex as catalyst is efficient for enantioselective epoxidation of alkenes. Epoxidation of styrene using aq NaOCl in CH_2Cl_2 as terminal oxidant at 20 ^{o}C provided 75% epoxide [43].

Epoxides desired from terminal alkenes, for example 1-undecene, and 1-heptene using manganese(II) porphyrin, and (*meso*-tetrakis(pentafluorophenyl) porphinato) manganese(III) chloride as catalyst could be achieved in 79% and 74%, respectively [6]. $PhI(OAc)_2$ in [bmim]/PF_6/$CHCl_2$ at room temperature could be used as oxidant in epoxidation of terminal alkenes.

Epoxidation of terminal alkenes for example 1-heptene, vinylcyclohexane, 1-octene, styrene, *trans*-β-methylstyrene, *cis*-β-methylstyrene, and 4-vinyl-1-cyclohexene by μ-oxo-iron(III) dimer, $[((phen)_2(H_2O)Fe^{III})_2(\mu\text{-}O)](ClO_4)_4$ was reported. The obtained epoxides occured about 63-74%. The oxidant used in this epoxidation reaction was peracetic acid at 0 ^{o}C, and reaction time was less than 5 minutes [44].

The aerobic epoxidation of linear terminal olefin such as 1-octene can be accomplished by *trans*-dioxo(tetramesitylporphyrinato)ruthenium(VI) ($Ru(TMP)O_2$) as catalyst with turn-over of 40 during 1 day [45].

The catalyst as *bis*[*N*,*O*-{(2´-pyridyl)pentan-3-olatalo}]dioxomolybdenum(VI) the epoxide is formed as the main product in the autoxidation process of 1-octene. The product selectivity is 58% (epoxide, autoxidation) upon treatment of 1-octene with molecular oxygen (1 bar and 100 ^{o}C) in the presence of catalyst [46].

The aerobic enantioselective epoxidation of 1-octene used Ni(II) symmetrical, and non-symmetrical chiral Schiff base complexes in the presence of molecular oxygen using isobutyraldehyde as sacrificial reductant. The catalyst gave very good conversion with 1-octene (75-95%) [47].

Catalytic activity of [brucine](S)-[Ru(PDTA-H)Cl], and [brucine](R)-[Ru(PDTA-H)Cl] for enantioselective epoxidation of non-functionalised alkenes such as styrene, 4-chloro-, 4-methyl-, and 4-nitrostyrene. Moderate conversions (58-78%) were obtained in the case of both the catalysts [48].

The synthesized dioxomolybdenum(VI) complexes of tetradentate Schiff-base derivatives of *trans*-1,2-diaminocyclohexane are found to be very selective catalysts for the epoxidation of 1-octene. For the epoxidation of 1-octene the yield was in the range 15-74%. An increase in the reaction temperature may lead to an increase in the yield of the epoxide. The complexes are stable in the solid state, however, they undergo decomposition during the reaction [48].

1,1-(2-thenyl)methyl-2-(2-thenyl)benzimidazole or benzimidazole was previously synthesized, and examined on its structure, bonding, and reactivity in transition-metal-inserted thiophene complexes [2, 49]. On the viewpoint of catalysis concerning this ligand, there was no report concerning the epoxidation of alkenes catalyzed by benzimidazole complex.

Encouraged by the facile synthesis of both calix[4]pyrrole, and benzimidazole ligands, together with there was no report cited in chemical literature to ulilize these cobalt calix[4]pyrrole, and cobalt benzimidazole complexes in the epoxidation reaction, the selectively catalytic epoxidation of terminal alkenes under mild condition will be thoroughly investigated in this research. 1-Dodecene was employed as a chemical model. The outcome of this work will certainly expand the use of these catalysts in the catalytic epoxidation.

There was no report concerning the use of cobalt calix[4]pyrrole, and benzimidazole on epoxidation of terminal alkenes. This research is concentrated in the epoxidation of terminal alkenes catalyzed by cobalt calix[4]pyrrole, and benzimidazole for development epoxide product in high yield, and selectivity.

1.4 Aims of this study

The aims of the research are to design and develop new cobalt-based epoxidation catalysts. The new catalysts should exhibit high selectivity towards epoxide formation from terminal alkenes with aldehyde/oxygen as oxidant.

CHAPTER II

EXPERIMENTAL

2.1 General procedure

Melting points were determined on Electrothermal 9100 melting point apparatus, and are uncorrected.

Chromatography: thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF_{254}). Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G), and aluminium oxide 90 (70-230 mesh ASTM). Gas chromatographic analysis was carried out on a GC-14A Shimadzu gas chromatograph equipped with flame ionization detector (FID) with nitrogen as a carrier gas. The column used was a capillary column type of DB-wax (30 m x 0.25 mm).

Spectrometers: the Fourier transform-infrared spectra (FT-IR) were recorded on Nicolet Impact 410 FT-IR spectrometer. The ^{1}H- and ^{13}C-NMR spectra were performed in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference on Varian nuclear magnetic resonance spectrometer, model Mercury plus 400 NMR spectrometer which was operated at 399.84 MHz for ^{1}H, and 100.54 MHz for ^{13}C nuclei. The chemical shifts (δ) are assigned by comparison with residue solvent protons.

2.2 Chemical reagents

All solvents used in this research were purified by standard methodology except for those which were reagent grades. The reagents utilized for synthesizing ligands, metal complexes and all alkenes were purchased from Fluka Chemical Company or otherwise stated, and were used without further purification.

2.3 Syntheses

2.3.1 Cobalt calix[4]pyrrole 9

The synthesis of cobalt calix[4]pyrrole **9** consisted of three steps. The preparation of ligand **7** in the first step employing acid-catalyzed condensation of pyrrole, and 4-methoxyacetophenone [50, 51]. The second step was the synthesis of polyanion **8** from **7** using *n*-BuLi, and the last step involved the complex formation with $CoCl_2 \cdot 6H_2O$ to furnish complex **9**.

<u>*meso*-Tetrakis(4-methoxyphenyl)-tetramethyl calix[4]pyrrole</u> **7** [50, 51]

Methanesulfonic acid (7% mol) was slowly added to the solution of 4-methoxyacetophenone 15.02 g (0.1 mol) and pyrrole 7.0 mL (0.1 mol) in EtOH 50 mL. The mixture was allowed to reflux for 4 h, and then cooled, the brown solid precipitated. The precipitate was filtered off, washed with several portions of EtOH, and dried at room temperature. Brown solid 19.82 g (99% yield) was obtained, m.p. 121-122 °C, and R_f 0.43 (hexane:EtOAc 8:2).

IR (KBr, cm^{-1}): 3431 (s), 2970 (s), 2832 (m), 1608 (s), 1456 (s), and 1250 (s); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.53 (s, 4H), 7.02 (d, $J = 8.7$ Hz, 8H), 6.78 (d, $J = 8.6$ Hz, 8H), 5.80 (s, 4H), 5.60 (s, 4H), 3.80 (s, 12H), and 1.82 (s, 12H); ^{13}C-NMR (CDCl$_3$) δ (ppm): 157.5, 139.4, 136.8, 128.3, 113.0, 105.5, 55.0, 43.6, and 17.8.

<u>Dilithium of *meso*-tetrakis(4-methoxyphenyl)-tetramethyl calix[4]pyrrole tetraanion</u> **8** [52]

n-BuLi 2.27 mL (28 mmol) was added dropwise to THF 40 mL of **7** 5.57 g (7 mmol). The reaction mixture was refluxed with stirring for 2 h. The solvent was evaporated *in vacuo*, and the residue was washed with dry hexane to afford a brown solid 5.67 g (76% yield), m.p. 112 °C, and R_f 0.45 (hexane:EtOAc 8:2).

IR (KBr, cm^{-1}): 3090 (w), 2631 (w), 1607 (w), 1456 (m), and 1250 (m); ^{1}H-NMR (CDCl$_3$) δ (ppm): 6.93-7.15 (m, 8H), 6.64-6.78 (m, 8H), 5.78-5.90 (m, 8H), 3.77 (m, 12H), 4.68 (br, THF, 16H), 1.86 (s, 12H), and 1.75 (br, THF, 16H).

<u>Cobalt complex of *meso*-(4-methoxyphenyl)-tetramethyl calix[4]pyrrole: cobalt calix[4]pyrrole</u> **9**

Polyanion **8** 4.43 g (4 mmol) was dissolved in EtOH followed by the addition of $CoCl_2 \cdot 6H_2O$ 0.78 g (3.3 mmol). The reaction mixture was stirred for 48 h. After the reaction was completed, the brown solid was filtered off, and washed with several portions of toluene. The filtrate was collected, and kept in refrigerator for 24 h. The

solvent was evaporated to give brown solid 3.99 g (87% yield), m.p. 116-117 °C, and R_f 0.43 (hexane:EtOAc 8:2).

IR (KBr, cm^{-1}): 2959 (w), 1724 (s), 1672 (m), 1597 (s), and 1254 (s); MALDI-TOF-MS: m/z 929 [M+Co^{2+}, 2Cl^{-} and H^{+}], and 797 [M+H^{+}]

2.3.2 Cobalt calix[4]pyrrole 13

Four steps were manipulated for the synthesis of cobalt calix[4]pyrrole **13**. The 4-*tert*-butylacetophenone **10** was prepared from acylation of *tert*-butylbenzene with acetyl chloride [50, 51]. Other steps were come out similar to those described previously (2.3.1).

4-*tert*-Butylacetophenone **10** [50, 51]

Anhydrous AlCl$_3$ (45.3 g, 0.34 mol) was suspended in 180 mL of stirred, anhydrous 1,2-DCE, and cooled to 0 °C. Acetyl chloride (21.2 g, 0.27 mol) was added in one portion, followed by dropwise addition of *tert*-butylbenzene (28.2 g, 0.21 mol) over a 30-min period. Stirring was continued for 2 h at room temperature. The reaction mixture was poured into 300 g of ice, and the precipitated Al(OH)$_3$ was dissolved by addition of conc HCl. The phases were separated, and the aqueous phase was extracted with 50 mL of CH$_2$Cl$_2$. The combined organic phases were washed with H$_2$O, and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated, and the residue was the light yellow oil. The yield was 27.8 g (82%) and R_f 0.45 (hexane:EtOAc 8:2).

IR (KBr, cm^{-1}): 2960 (s), 1685 (s), 1603 (m), 1350 (s), and 1270 (s); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.90 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 2.55 (s, 3H), and 1.34 (m, 9H); ^{13}C-NMR (CDCl$_3$) δ (ppm): 197.0 (1C), 157.0 (1C), 135.0 (1C), 128.0 (2C), 125.0 (2C), 35.0 (1C), 31.0 (3C), and 26.0 (1C); LC-MS : m/z 177 [M+H^{+}].

meso-Tetrakis(4-*tert*-butylacetophenone)-tetramethyl calix[4]pyrrole **11** [49, 50]

The brown solid 19.82 g (80% yield) was obtained, m.p. 115-116 °C, and R_f 0.53 (hexane:EtOAc 8:2)

IR (KBr, cm^{-1}): 3431 (s), 2970 (s), 1573 (m), 1265 (m), and 1199 (m); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.25 (d, J =8.4, 8H), 7.08 (d, J =8.4, 8H), 5.95 (s, 4H), 5.65 (s, 4H), 1.85-2.00 (s, 20H), and 1.25 (s, 36H) ; ^{13}C-NMR (CDCl$_3$) δ (ppm): 149.0, 142.0, 137.0, 136.0, 127.0, 124.0, 107.0, 105.0, 42.0, 35.0, 32.0, and 29.0; LC-MS : m/z 901 [M+H^{+}].

Dilithium of *meso*-tetrakis(4-*tert*-butylacetophenone)tetramethyl calix[4]pyrrole tetraanion **12** [38]

12 was the brown solid 5.67 g (77% yield), m.p. 102 °C, and R_f 0.55 (hexane:EtOAc 8:2).

^{1}H-NMR (CDCl$_3$) δ (ppm): 7.25 (d, *J* =8.4, 8H), 7.08 (d, *J* =8.4, 8H), 5.95 (s, 4H), 5.65 (s, 4H), 3.78 (m, THF, 16H), 1.85-2.00 (s, 20H), 1.42 (m, THF, 16H), and 1.25 (s, 36H); ^{13}C-NMR (CDCl$_3$) δ (ppm): 149.0, 142.0, 137.0, 136.0, 127.0, 124.0, 107.0, 105.0, 68, 42.0, 35.0, 32.0, 29.0, and 26.

Cobalt complex of *meso*-tetrakis(tetrahydrofuran)-α,β,γ,δ-tetrakis-(4-*tert*-utylacetophenone)-tetramethyl calix[4]pyrrole: cobalt calix[4]pyrrole **13**

The brown solid gave 3.99 g (87% yield), m.p. 112-114 °C, and R_f 0.53 (hexane:EtOAc 8:2).

MALDI-TOF-MS: *m/z* 1031 [*M*+Co^{2+}, and 2Cl$^-$], 971 [*M*+2Cl$^-$], and 901 [*M*+H$^+$].

2.3.3 Cobalt benzimidazole 15 [2, 49, 53]

The synthesis of benzimidazole **14** consisted of the two steps. The first step involved the synthesis of ligand **14** employing acid-catalyzed condensation of *o*-phenylenediamine, and thiophen-2-aldehyde. The second step was complex formation of **14**, and CoCl$_2$ to yield **15**.

1, 1-(2-Thenyl)methyl-2-(2-thenyl)benzimidazole: (benzimidazole) **14**

 o-Phenylenediamine 2.7 g (0.05 mol) in EtOH 30 mL was added to thiophen-2-aldehyde 5.6 g (0.05 mol) to give a dark green solution which was then heated on steam-bath for 30 min, whereupon the color was changed to red. The reaction mixture was cooled, and the clear red solution was decanted from a small amount of brown oil, and filtered. The filtrate on standing overnight deposited yellow needles 4.56 g (62% yield), m.p. 148-149 °C, and R_f 0.68 (EtOH).

IR (KBr, cm^{-1}): 3090-3050 (w), 2950 (w), 1630 (w), and 1225 (s); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.83 (dd, *J* = 6.9, and 1.8 Hz, 1H), 7.51 (dd, *J* = 5.0, and 1.2 Hz, 1H), 7.47 (dd, *J* = 3.8, and 1.2 Hz, 1H), 7.37 (dd, *J* = 7.3, and 1.2 Hz, 1H), 7.29 (m, 2H), 7.23 (dd, *J* = 4.9, and 1.2 Hz, 1H), 7.13 (t, *J* = 4.3 Hz, 1H), 6.94 (t, *J* = 4.4 Hz, 1H), 6.86 (dd, *J* = 3.4, and 1.2 Hz. 1H), and 5.70 (s, 2H); ^{13}C-NMR (CDCl$_3$) δ(ppm): 147.6, 143.0, 138.8, 125.4, 125.2, 123.3, 123.0, 119.9, 109.9, and 44.0.

Cobalt complex of 1,1-(2-thenyl)methyl-2-(2-thenyl)benzimidazole: cobalt benzimidazole **15**

The ethanolic solution (80 mL) of **14** (10 mmol) was mixed with an aqueous solution (80 mL) of $CoCl_2$ (10 mmol). Then a solution (42 mL) of $CH_3COONa.3H_2O$ (30 mmol) was added and refluxed for 2-3 h. After that the solution was cooled down to room temperature, and kept it for overnight to deposit green needles 2.13 g (60% yield).

IR (KBr, cm^{-1}): 3073 (w), 2945 (w), 1563 (w,) and 1221 (s); MALDI-TOF-MS: m/z 392 [M+Co^{2+}, Cl$^-$, and H$^+$], and 296 [M+H$^+$].

Other cobalt catalysts: cobalt complexes of salophen, and salen utilized in this work were kindly obtained from Mr. Jirasak Imurai [54].

2.4 Synthesis of authentic epoxides

General Procedure [2]

To a solution of alkene (9.7 mmol) in 50 mL of dry CH_2Cl_2 at 0°C was added 70% *m*-CPBA (2.22 mmol) in 40 mL of dry CH_2Cl_2 over a period of 30 min. After the solution was stirred for 3-4 h, the excess peracid was decomposed with 5 mL of 10% Na_2SO_3 solution. The combined CH_2Cl_2 was washed carefully with 100 mL of saturated $NaHCO_3$, the organic layer was separated, and the aqueous layer was washed twice with dry CH_2Cl_2. The organic layers were combined, washed with brine, dried and evaporated to yield the desired epoxide.

1-octadecene oxide: white waxy solid, R_f 0.53 (hexane:EtOAc 8:2) ^{1}H-NMR (CDCl$_3$) δ (ppm): 2.91 (t, J = 3.4 Hz, 1H), 2.74 (d, J = 4.1 Hz, 1H), 2.47 (d, J = 5.1 Hz, 1H), 1.53 (m, 1H), 1.46 (m, 1H), 1.31 (m, 28H), and 0.91 (t, J = 5.4 Hz, 3H)

1-dodecene oxide: colorless liquid, R_f 0.47 (hexane:EtOAc 8:2) ^{1}H-NMR (CDCl$_3$) δ (ppm): 2.91 (t, J = 3.5 Hz, 1H), 2.74 (d, J = 4.2 Hz, 1H), 2.47 (d, J = 5.2 Hz, 1H), 1.53 (m, 1H), 1.46 (m, 1H), 1.31 (m, 16H), and 0.91 (t, J = 5.4 Hz, 3H)

1-octene oxide: colorless liquid, R_f 0.43 (hexane:EtOAc 8:2) ^{1}H-NMR (CDCl$_3$) δ (ppm): 2.91 (t, J = 3.4 Hz, 1H), 2.74 (d, J = 4.2 Hz, 1H), 2.47 (d, J = 5.2 Hz, 1H), 1.53 (m, 1H), 1.46 (m, 1H), 1.31 (m, 8H), and 0.91 (t, J = 5.4 Hz, 3H)

vinylcyclohexene oxide: colorless liquid, R_f 0.43 (hexane) ^{1}H-NMR (CDCl$_3$) δ (ppm): 2.52 (m, 1H), 2.50 (t, J = 3.9 Hz, 2H), 1.85 (d, J = 10.5 Hz, 1H), 1.60-1.80 (m, 6H), and 1.10-1.28 (m, 4H)

4-chlorostyrene oxide: clear yellow liquid, R_f 0.43 (hexane:EtOAc 8:2) ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.35 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 3.87 (t, J = 3.8 Hz, 1H), 3.18 (t, J = 4.1 Hz, 1H), and 2.79 (m, 1H)

α-methylstyrene oxide: colorless liquid, R_f 0.36 (CHCl$_3$); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.23-7.42 (m, 5H), 2.98 (d, J = 5.4 Hz, 1H), 2.82 (d, J = 5.4 Hz, 1H), and 1.73 (s, 3H)

4-chloro-α-methylstyrene oxide: colorless liquid, R_f 0.41 (CHCl$_3$); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.85 (d, J = 4.1 Hz, 2H), 7.41 (d, J = 4.1 Hz, 2H), 2.98 (s, 1H), 2.78 (d, J = 5.4 Hz, 1H), and 1.73 (s, 3H)

allylbenzene oxide: colorless liquid, R_f 0.42 (hexane:EtOAc 8:2); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.22-7.40 (m, 5H), 3.2 (m, 2H), 2.90-2.97 (dd, J = 5.7 Hz, 2H), 2.82-2.85 (m, 1H), and 2.58 (m, 2H)

1,1-diphenylethylene oxide: colorless liquid, R_f 0.38 (hexane:EtOAc 7:3); ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.30 (m, 10H), and 3.21 (s, 2H)

2-methyl-3-buten-2-ol oxide: white solid, R_f 0.38 (hexane:EtOAc 7:3); ^{1}H-NMR (CDCl$_3$) δ (ppm): 2.97 (m, 1H), 2.83 (m, 1H), 2.78 (m, 1H), 1.42-1.75 (OH), and 1.20 (s, 6H)

2.5 The general procedure for the epoxidation of terminal alkenes

The epoxidation was carried out in CH$_3$CN (15 mL) containing alkenes (5 mmol), 2-ethylbutyraldehyde (20 mmol) under an oxygen atmosphere, and cobalt complex (0.05 mmol) at room temperature (30 ℃). The mixture was stirred for 24 h. After the reaction was completed, 1 mL of the reaction mixture was taken, and extracted with Et$_2$O. The combined extracts were washed with saturated NaHCO$_3$, and brine, respectively. The organic layer was dried over anhydrous Na$_2$SO$_4$, and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

2.6 Study on the optimum conditions for the epoxidation of 1-dodecene, and other terminal alkenes

2.6.1 Effect of type of catalyst

The epoxidation reaction was performed employing cobalt complexes such as cobalt calix[4]pyrroles **9**, **13**, benzimidazole **15**, cobalt acetate, cobalt chloride, cobalt phthalocyanine, cobalt salophen or cobalt salen as a catalyst.

2.6.2 Effect of solvent

The epoxidation reaction was carried out in the same manner as previously described but using various solvents, namely CH_2Cl_2, 1,2-DCE, EtOAc, acetone, $CHCl_3$, THF, EtOH, MeOH, a mixture of toluene, and CH_3CN, toluene, and hexane were employed instead of CH_3CN.

2.6.3 Effect of amount of 2-ethylbutyraldehyde

The epoxidation reaction was carried out in the same fashion as previously described but the amount of 2-ethylbutyraldehyde was varied (5, 10, 15, 20, 25, and 30 mmol).

2.7 Kinetic study on the epoxidation of terminal alkenes catalyzed by cobalt benzimidazole

The general epoxidation procedure utilizing cobalt benzimidazole as a catalyst, and 1-dodecene as a substrate were carried out. As the reaction proceeded (2, 4, 6, 8, 10, 12, 14, 16, and 24 h), an aliquot (1.0 mL) of the reaction mixture was taken, worked up, and analyzed by GC.

2.8 Application of developed epoxidation reaction for other terminal alkenes

Selected terminal alkenes including vinylcyclohexane, styrene, 4-chlorostyrene, 4-chloro-α-methylstyrene, 2-methyl-3-buten-2-ol, and allyl phenyl ether were subjected to this developed epoxidation reaction catalyzed by cobalt complexes of calix[4]pyrrole **9**, and benzimidazole **15**. Other procedures were carried out as previously described.

2.9 Competitive study on the epoxidation of 1-octene, 1-dodecene, and 1-octadecene

The equimolar amount (5 mmol) of 1-octene, and 1-dodecene, and 1-octadecene were used as competitive substrates in the reaction by comparing yield

of product. Other procedures were performed according to those described in Topic 2.5.

2.10 Regioselectivity study

The general epoxidation procedures using cobalt complexes, for example cobalt calix[4]pyrrole**s** **9**, **13**, and benzimidazole **15** as catalyst, and 4-vinylcyclohexene as substrate was carried out. An aliquot (1 mL) of the reaction mixture was taken, worked up, and analyzed by ^{1}H-NMR.

2.11 General isolation procedure

After the reaction was completed (followed by TLC), the epoxidation product was separated as follows: the whole reaction mixture was extracted according to that described in the general procedure, and all solvents were removed *in vaccuo*. The crude product was purified by silica gel column chromatography using hexane or a mixture of hexane-EtOAc as an eluent. The equivalent fractions monitored by TLC were combined, and the solvents were completely evaporated.

CHAPTER III
RESULTS AND DISCUSSION

This research was focused on the epoxidation of terminal alkenes using cobalt complexes as a catalyst. The epoxidation of terminal alkenes is a particularly challenging problem in organic chemistry, due to their relative inertness [4]. Since there was no report concerning the use of cobalt calix[4]pyrrole and cobalt benzimidazole as a catalyst for terminal alkene epoxidation, a systematic examination to optimize this developed system was scrunilized search for efficient catalyst. The system was composed of a catalyst, 2-ethylbutyraldehyde and O_2 as a source of an oxidant in a reaction medium. 1-Dodecene was selected as a chemical model for reaction conditions optimization. Other substrates including 1-octadecene, 1-octene, vinylcyclohexane, styrene, 4-chlorostyrene, α-methylstyrene, 4-chloro-α-methylstyrene, allylbenzene, diphenylethylene, vinylcyclohexene, 2-methyl-3-buten-2-ol, 3-methyl-3-buten-2-ol and allyl phenyl ether were chosen for examining the capability and exploring the scope of this developed epoxidation system.

Part I Selective epoxidation of terminal alkenes catalyzed by cobalt calix[4]pyrroles

3.1 Synthesis and characterization of calix[4]pyrroles

To extend the scope of the epoxidation of alkenes catalyzed by cobalt calix[4]pyrrole recently reported by Buranaprasertsuk [2], calix[4]pyrroles **7** and **11** were synthesized employing acid-catalyzed condensation of pyrrole with 4-methoxyacetophenone and 4-*tert*-butylacetophenone, respectively [51]. The polyanions of calix[4]pyrroles **8** and **12** were obtained from the reaction of **7** and **11** with *n*-BuLi which were then allowed to react with $CoCl_2 \cdot 6H_2O$ to yield the cobalt calix[4]pyrroles **9** and **13**.

Calix[4] pyrrole **7**

Calix[4]pyrrole **7** was synthesized by condensation of pyrrole with 4-methoxyacetophenone. The ^{1}H-NMR spectrum of calix[4]pyrrole **7** (Fig 3.1) visualized a singlet signal of methyl protons at δ_H 1.82 (s, 12H). A singlet signal at δ_H 3.80 was indicative of twelve protons of four methoxy groups. The protons on the pyrrole rings were detected at δ_H 5.60 (s, 4H) and δ_H 5.80 (s, 4H). The aromatic protons were found at δ_H 6.78 (d, J = 8.6 Hz, 8H) and δ_H 7.02 (d, J = 8.7 Hz, 8H). A broad singlet signal of N-H protons could be detected at δ_H 7.53 (s, 4H).
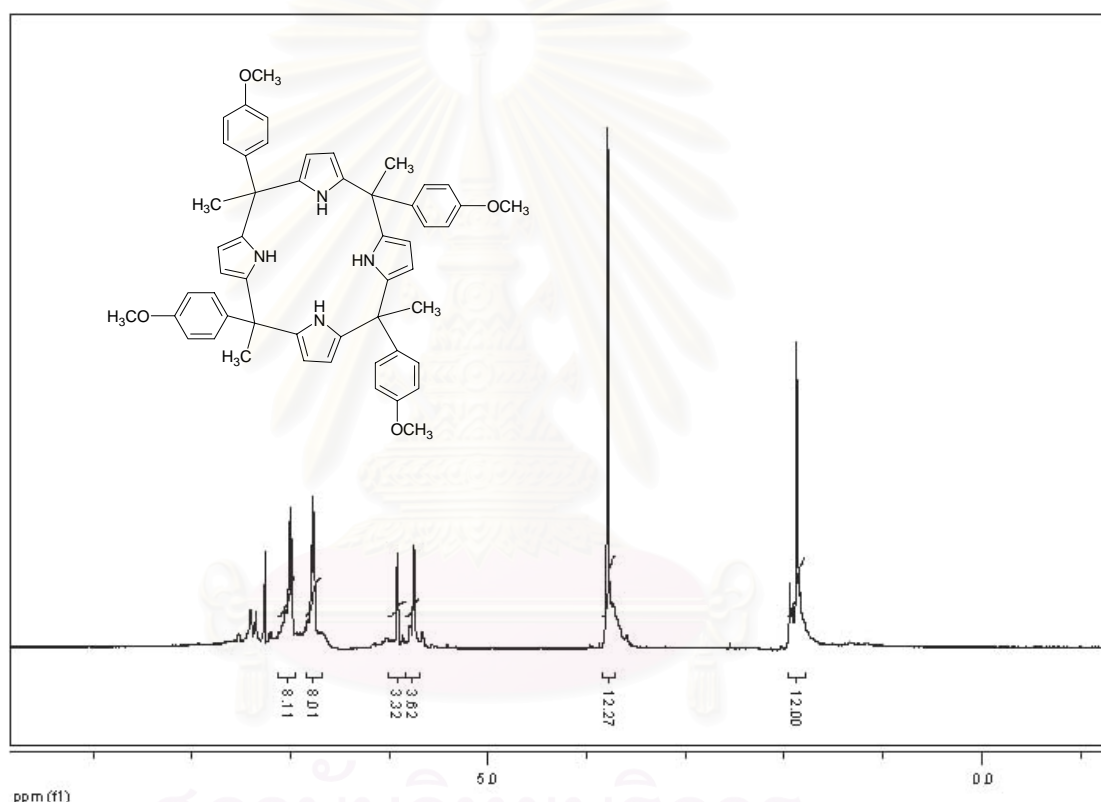
Figure 3.1 The ^{1}H-NMR spectrum of calix[4]pyrrole **7**.

4-*tert*-Butylacetophenone **10**

Since 4-*tert*-butylacetophenone **10** was not commercially available, it was synthesized from acetyl chloride and *tert*-butylbenzene by a Fridel craft acylation [50, 51]. The ^{1}H-NMR spectrum of 4-*tert*-butylacetophenone **10** (Fig 3.2) revealed a singlet signal of nine protons of tertiary butyl groups at δ_H 1.34. The singlet signal at δ_H 2.55 belonged to three protons on a carbon connecting with a carbonyl group. The

presence of four protons on an aromatic ring was observed as doublet at δ_H 7.25 (d, J = 8.5 Hz, 2H) and δ_H 7.90 (d, J = 8.5 Hz, 2H).
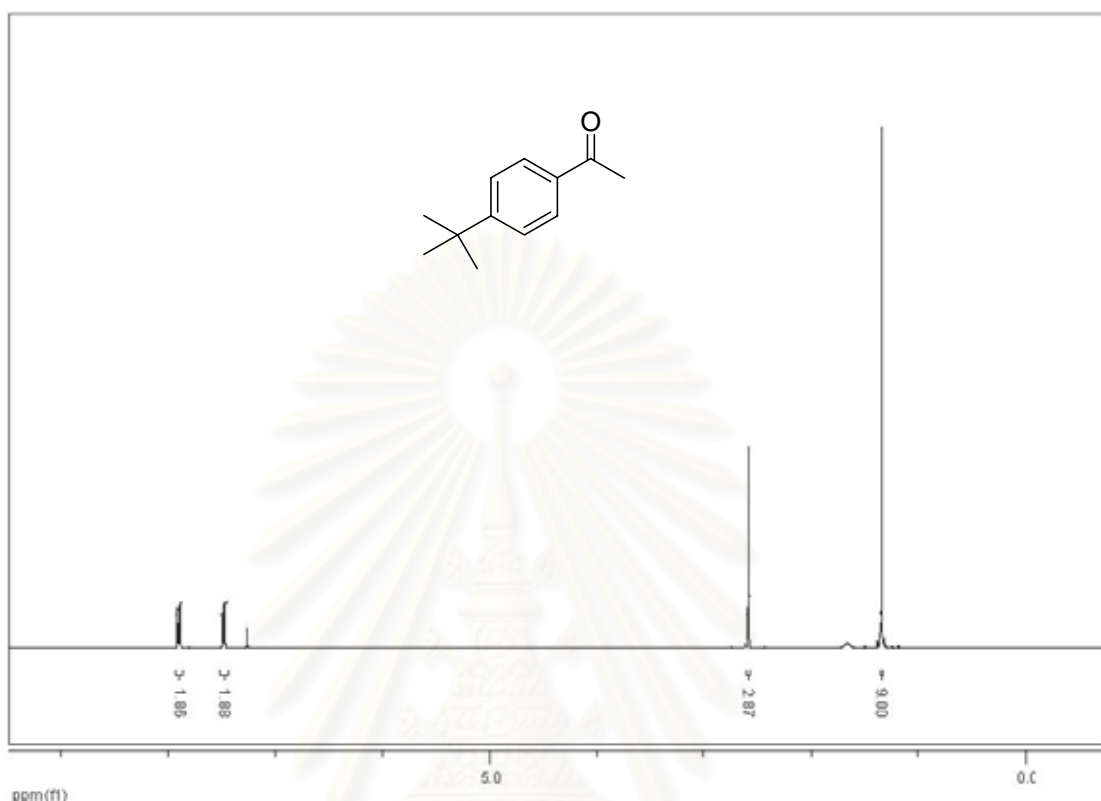
Figure 3.2 The ^{1}H-NMR spectrum of 4-*tert*-butylacetophenone **10**.

Calix[4]pyrrole **14**

Calix[4]pyrrole **14** was synthesized employing the same manner as that described for **7** using pyrrole and 4-*tert*-butylacetophenone **10**. The ^{1}H-NMR spectrum of *meso*-tetrakis(4-*tert*-butylacetophenone)-tetramethylcalix[4]pyrrole **11** (Fig 3.3) displayed a singlet signal at δ_H 1.25, indicating for thirty six protons of four tertiary butyl groups. The signals around δ_H 1.85-2.00 could be ascribed to twelve protons of four methyl groups. A pair of broad singlet signal at δ_H 5.65 and 5.95 was indicated to eight protons of four pyrrole rings. Two doublet signals of four phenyl groups were observed at δ_H 7.08 (d, J = 8.4 Hz) and δ_H 7.25 (d, J = 8.4 Hz).
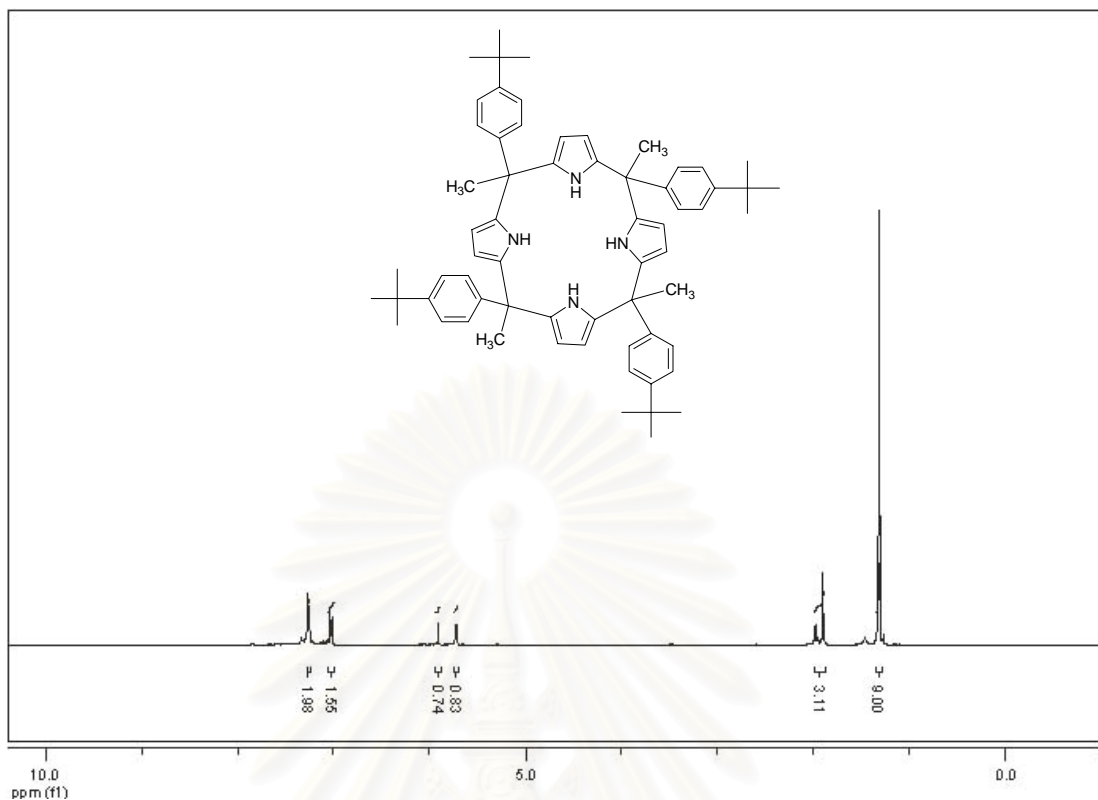
Figure 3.3 The ^{1}H-NMR spectrum of calix[4]pyrrole **11**.

The difference of ^{1}H-NMR spectra between those of calix[4]pyrroles **7** and **11** could be visualized by the proton signal of methoxy in calix[4]pyrrole **7** displaying at δ_H 3.80 while the protons of *tert*-butyl group in calix[4]pyrrole **11** could be observed at δ_H 1.29.

The ^{1}H-NMR spectra of calix[4]pyrrole in general displayed the proton signal of NH at δ_H 7.53. These proton signals had disappeared when this ligand was deprotonated by *n*-BuLi to polyanion. The polyanion was further treated with $CoCl_2 \cdot 6H_2O$ to yield the cobalt complex.

The structure of calix[4]pyrroles **7** and **11** are depicted as shown below.

Calix[4]pyrrole **7**   Calix[4]pyrrole **11**
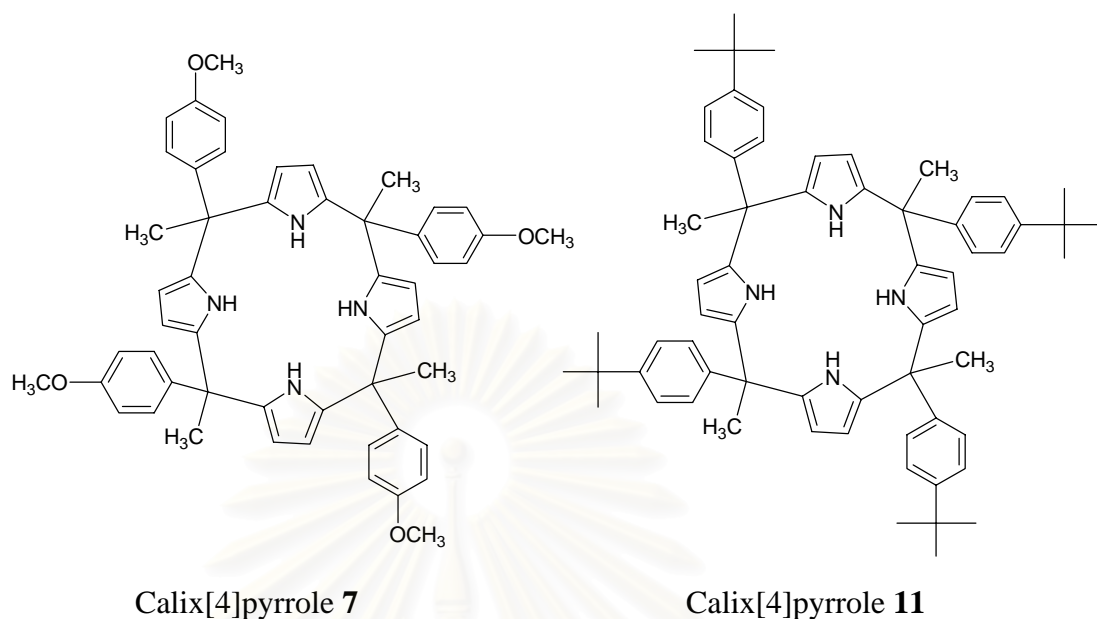
3.2 Optimum conditions for the epoxidation of terminal alkenes

In fact, various factors are required to reach the optimal conditions for the developed epoxidation reaction such as the amount of catalyst, reaction temperature, type of ligand, type of oxidant, type of solvent, and the amount of oxidant. The parameters studied in this research include effect of catalyst, the amount 2-ethylbutyraldehyde, solvent, and reaction time. 1-Dodecene was chosen as a chemical model.

3.2.1 Effect of type of catalyst

The epoxidation of alkenes catalyzed by metal complexes is emerging as a useful synthetic transformation. Nonetheless, not many studies devote to examine the epoxidation of terminal alkenes, possibly due to its unreactiveness compared with cyclic or other substituted alkenes. For instance, the epoxidation of 1-dodecene was reported to give quite a low yield of epoxide product of 25% [16, 45, 55]. According to preliminary results, the epoxidation of 1-dodecene catalyzed by cobalt calix[4]pyrroles **9** and **13** provided a reasonable yield of 1-dodecene oxide as a sole product. To ascertain the structure of the desired product, the reaction mixture was worked-up and subjected to silica gel column chromatography. The ^{1}H-NMR spectrum of the target molecule, 1-dodecene oxide (Fig 3.4) visualized a triplet signal of methyl protons at δ_H 0.91 (t, J = 5.5 Hz, 3H). The methylene protons could be

assigned around δ_H 1.20-1.40 (m, 18H). The oxirane ring protons were detected at δ_H 2.47 (d, J = 5.2 Hz, 1H), δ_H 2.74 (d, J = 4.2 Hz, 1H) and δ_H 2.91 (t, J = 3.45 Hz, 1H). The ^{13}C-NMR spectrum (Fig 3.5) displayed eleven signals for twelve carbons of 1-dodecene oxide. A signal of the methyl carbon was detected at δ_C 14.0 (1C). Eight signals of nine methylene carbons were found at δ_C 22.6 (1C), 26.0 (1C), 29.3 (1C), 29.4 (1C), 29.5 (2C), 29.6 (1C), 31.9 (1C) and 32.5 (1C), respectively. Two carbons of oxirane showed two signals at δ_C 47.0 and 52.5, respectively.
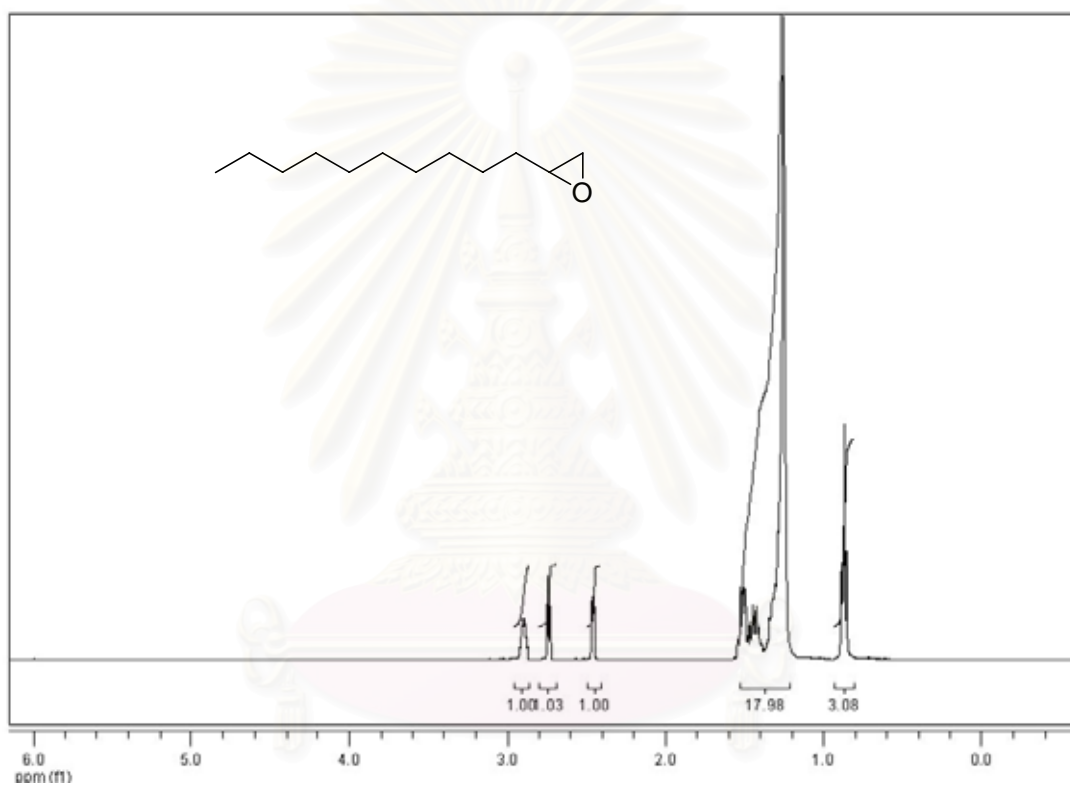
Figure 3.4 The ^{1}H-NMR spectrum of 1-dodecene oxide.
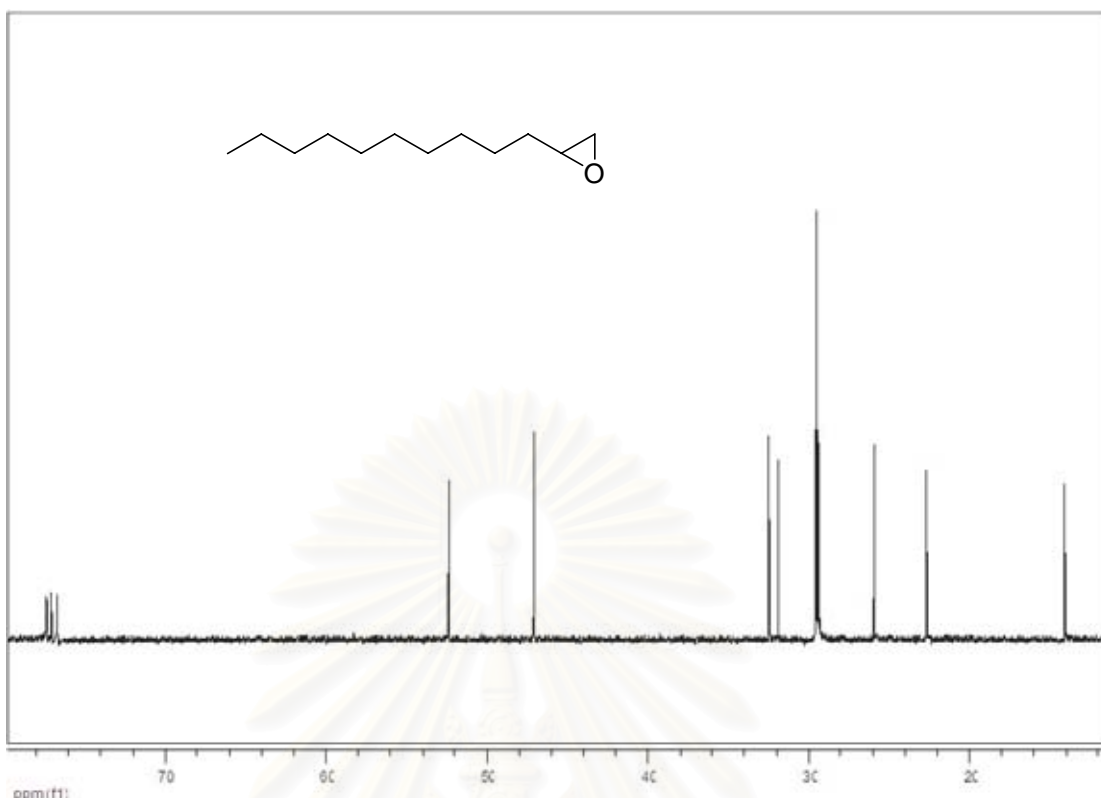
Figure 3.5 The ^{13}C-NMR spectrum of 1-dodecene oxide.

Since there was no report concerning the use of this class of catalyst for terminal alkenes epoxidation, certain cobalt salts and complexes were selected to compare their catalytic ability. The findings are collected in Table 3.1.

Table 3.1 Comparative study on 1-dodecene epoxidation catalyzed by various cobalt complexes

Entry	Catalyst	% Substrate (recovered)	% Yield 1-dodecene oxide	Mass Balance
1	none	100	0	100
2	**9**	16	80	96
3	**13**	82	21	103
4	cobalt acetate	101	0	101
5	cobalt chloride	84	15	99
6	cobalt phthalocyanine	80	18	98

Reaction conditions: 1-dodecene (5 mmol), catalyst (0.05 mmol), CH$_3$CN (15 mL), O$_2$ and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h

The observations obtained from Table 3.1 revealed that the epoxidation of 1-dodecene greatly depended on the type of cobalt complex. Without a catalyst in the system, the epoxidation of 1-dodecene did not occur (entry 1). Cobalt calix[4]pyrrole **9** recently reported as a good catalyst for epoxidation of cyclic alkenes [2] still gave high yield of terminal epoxide (entry 2). To our best knowledge, calix[4]pyrrole **11** and its cobalt complex **13** have never been reported. Thus, these two substances are new. Unfortunately cobalt calix[4]pyrrole **13** gave quite a low yield (entry 3) compared with cobalt calix[4]pyrrole **9**. This observation strongly implied that active site of cobalt calix[4]pyrrole **11** should be electrophilic in character more [2] than cobalt calix[4]pyrrole **13**. Other catalysts: $Co(OAc)_2$, $CoCl_2$, and cobalt phthalocyanine gave poor yield of epoxide under this studied conditions. The main reason was perhaps because of their low solubility in CH_3CN (entries 4-6).

3.2.2 Effect of solvent

Solvents always play an important role in catalytic reactions. The effect of various solvents on the epoxidation reaction of 1-dodecene was investigated and the results are displayed in Table 3.2.

Table 3.2 The effect of solvent on the epoxidation of 1-dodecene catalyzed by cobalt calix[4]pyrrole **9**

Entry	Solvent	% Substrate (recovered)	% Yield 1-dodecene oxide	Mass Balance
1	CH_3CN	16	80	96
2	EtOAc	81	30	101
3	EtOH	94	8	102
4	MeOH	100	0	100
5	toluene	64	33	97
6	hexane	72	29	101
7	THF	92	11	103

Reaction conditions: 1-dodecene (5 mmol), catalyst (0.05 mmol), solvent (15 mL), O_2 and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h

From Table 3.2, CH$_3$CN was found to be the best solvent (entry 1). This was probably related directly to the solubility of catalyst and substrate in a reaction medium.

3.2.3 Application of the developed epoxidation system for other terminal alkenes

The optimized conditions attained were further applied for the epoxidation of other selected terminal alkenes including vinylcyclohexane, styrene, α-methylstyrene, and allylbenzene. The results are accumulated in Table 3.3.
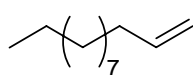
1-dodecene   vinylcyclohexane   styrene
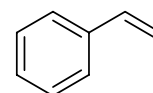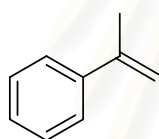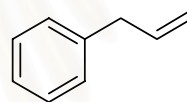
α-methylstyrene   allylbenzene

Table 3.3 The epoxidation of selected terminal alkenes catalyzed by cobalt calix[4]pyrrole **9**
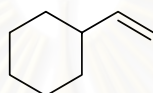
Entry	Substrate	% Yield of epoxide
1	1-dodecene	80
2	vinylcyclohexane	93
3	styrene	63[a]
4	α-methylstyrene	74
5	allylbenzene	38

Reaction conditions: substrate (5 mmol), cobalt calix[4]pyrrole **9** (0.05 mmol), CH$_3$CN (15 mL), O$_2$ and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h,

[a]1-phenylethanol 32% was detected

The results of the epoxidation of various terminal alkenes are shown in Table 3.3. All epoxide products were analyzed by GC compared with authentic specimen prepared from the reaction of *m*-CPBA and the corresponding alkenes [11]. Under this optimum condition, 1-dodecene and vinylcyclohexane (entries 1-2) could be transformed to their analogues epoxides in superior yields compared with previous reports. For instance, the epoxidation of 1-dodecene by an O_2-O_3 mixture at room temperature catalyzed by Fe(TMP)Cl (TMP is the dianion of 5,10,15,20-tetramesitylporphyrin) furnished the target epoxide product only 25% [4, 16]. Other selected terminal alkenes could also be epoxidized in moderate yield for example styrene and α-methylstyrene (entries 3-4). In the case of styrene, two main products identified as styrene oxide and 1-phenylethanol in the ratio of approximately 2:1 were obtained, while α-methylstyrene gave the corresponding epoxide in 74%. For allylbenzene, only 38% of the epoxide was achieved, the rest was the recovered substrate. In order to attain more desired product, a modification of the system should be performed.

This section of research clearly demonstrates the successful utilization of cobalt calix[4]pyrrole **9** as a catalyst in the epoxidation of terminal alkenes. The developed system was selective and found to provide the corresponding epoxides prevailing to other previous reported systems [4].

Part II Epoxidation of terminal alkenes catalyzed by cobalt benzimidazole

Encouraged by the facile synthesis of benzimidazole **14** and no report cited in chemical literature to ulilize cobalt benzimidazole **15** in the epoxidation reaction, the selective catalytic epoxidation of terminal alkenes under mild conditions was thoroughly investigated in this research.

3.1 Synthesis and characterization of benzimidazole 14

Benzimidazole **14** was synthesized by acid-catalyzed condensation between *o*-phenylenediamine and thiophen-2-aldehyde [55, 57].

The ^{1}H-NMR spectrum of benzimidazole **14** (Fig 3.6) showed a singlet signal at δ_H 5.70 for two methylene protons. The three double doublet signals of thiophen protons next to methylene carbon connecting imidazole were observed at δ_H 7.23 (dd, J = 4.9 and 1.2 Hz, 1H), 7.37 (dd, J = 7.3 and 1.2 Hz, 1H) and 7.83 (dd, J = 6.9 and 1.8 Hz, 1H), respectively. The multiplet signals for three protons on the other

thiophen of benzimadazole ring were observed at δ_H 6.86 (dd, J = 3.4 and 1.2 Hz, 1H), 6.94 (t, J = 4.4 Hz, 1H) and 7.13 (t, J = 4.3 Hz, 1H), respectively. The multiplet signal at δ_H 7.29 (m, 2H), 7.47 (dd, J = 3.8 and 1.2 Hz, 1H) and 7.51 (dd, J = 5.0 and 1.2 Hz, 1H) belonged to four protons of imidazole.
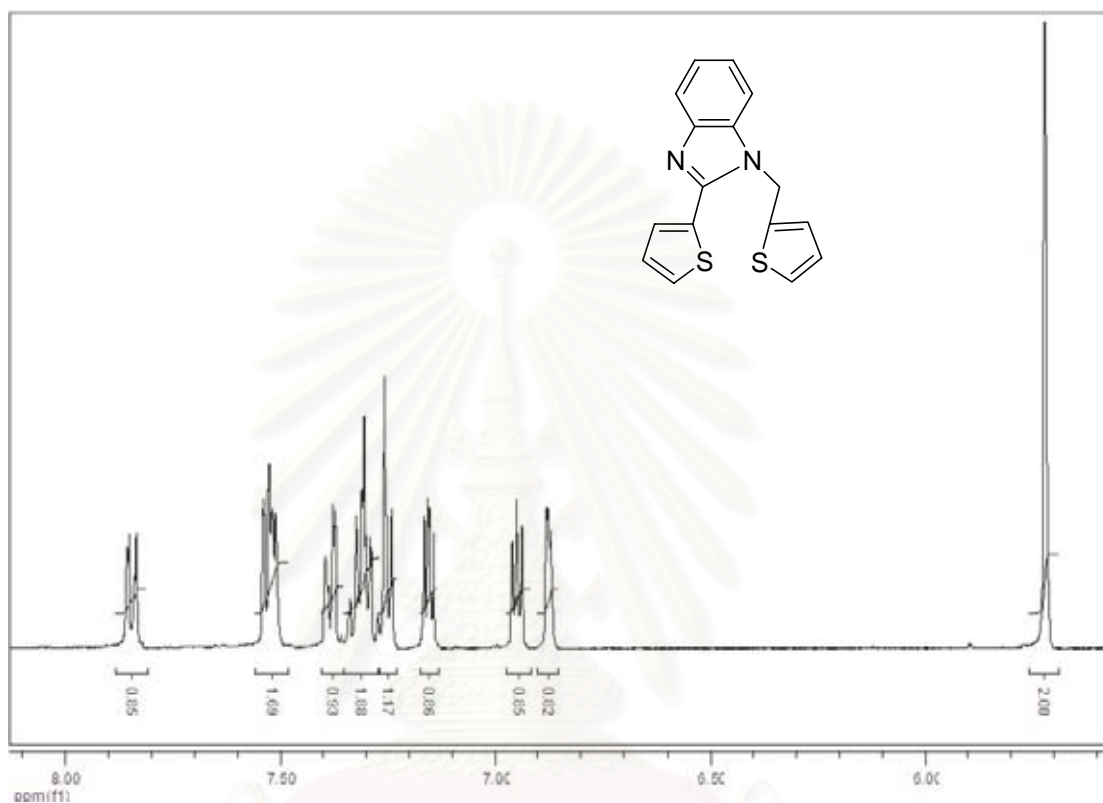
Figure 3.6 The ^{1}H-NMR spectrum of benzimidazole **14**.

Benzimidazole **14** was then reacted with $CoCl_2$ to furnish cobalt benzimidazole **15**. Cobalt benzimidazole **15** was characterized by MALDI-TOF-MS (MALDI-TOF-MS: m/z 392 [M+Co^{2+}, Cl$^-$, and H$^+$], and 296 [M+ H$^+$]).

3.2 Optimum conditions for the epoxidation of terminal alkenes catalyzed by cobalt benzimidazole 15

3.2.1 Effect of type of catalyst

Cobalt benzimidazole **15** has never been reported as a catalyst in alkene epoxidation. Typically, this ligand could be accomplishly synthesized by the same protocol for those of Schiff base's ligands [49, 53]. Therefore, it was rationalized to compare the catalytic capability of cobalt benzimidazole **15** with certain cobalt Schiff base's complexes. Two Schiff base-cobalt complexes, namely cobalt salophen, and

cobalt salen were kindly provided by Buranaprasertsuk [2]. 1-Dodecene was selected as a substrate and the findings are collected in Table 3.4.

All ligands **14**, **16,** and **17** used in this study are depicted as shown below.

benzimidazole **14**   Salophen **16**

Salen **17**
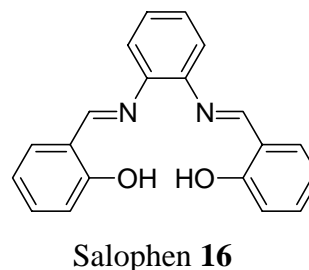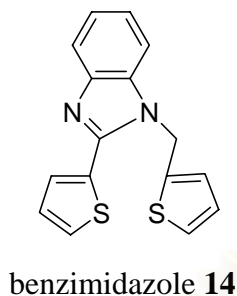
Table 3.4 Comparative study on 1-dodecene epoxidation catalyzed by various cobalt complexes

Entry	Catalyst	% Substrate (recovered)	% Yield 1-dodecene oxide	Mass Balance
1	none	100	0	100
2	**15**	9	84	93
3	cobalt salophen	97	8	105
4	cobalt salen	80	22	102

Reaction conditions: 1-dodecene (5 mmol), catalyst (0.05 mmol), CH_3CN (15 mL), O_2 and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h

From Table 3.4, the epoxidation of 1-dodecene clearly needed the proper catalyst. Without catalyst, this epoxidation did not take place (entry 1). Under this optimized condition, cobalt benzimidazole **15** provided good yield of epoxide product (entry 2), whereas cobalt salophen and cobalt salen (entries 3-4) gave poor yield of epoxide product.

Cobalt benzimidazole **15** was thus selected to use as a catalyst to further explore on the epoxidation of terminal alkenes.

3.2.2 Effect of amount of 2-ethylbutyraldehyde

The aldehyde coupled with O_2 was utilized as an oxidant in this reaction. The effect of the amount of 2-ethylbutyraldehyde on the epoxidation was summarized as shown in Table 3.5.

Table 3.5 The effect of the amount of 2-ethylbutyraldehyde on the epoxidation of 1-dodecene catalyzed by cobalt benzimidazole **15**

Entry	Oxidant (mmol)	% Substrate (recovered)	% Yield 1-dodecene oxide	Mass Balance
1	5	78	22	100
2	10	58	44	102
3	15	32	66	98
4	20	9	84	93
5	25	60	43	103
6	30	53	38	91

Reaction conditions: 1-dodecene (5 mmol), catalyst (0.05 mmol), CH_3CN (15 mL), O_2 and 2-ethylbutyraldehyde (varied) at 30 °C for 24 h

As a result from Table 3.5, the use of different amounts of 2-ethylbutyraldehyde affected the outcome of the reaction. The most appropriate conditions were observed when 2-ethylbutyraldehyde 20 mmol was employed, 1-dodecene was epoxidized to 1-dodecene oxide in 84% (entry 4). Epoxidation reactions with less amount of 2-ethylbutyraldehyde (entries 1-2) gave low yield of epoxide product due to the limit amount of the oxidant. On the other hand, when the amount of oxidant was increased (entries 5-6), the yield of epoxide was lower than using 20 mmol of oxidant. This was probably because more oxidizing agent may react with each other, and produced unwanted reactions. Therefore, 20 mmol of 2-ethylbutyraldehyde was kept constant for further investigation.

3.2.3 Effect of solvent

The choice of solvent that could provide a homogeneous reaction had a crucial effect on the reactivity, and the yield of product. Various solvents were tried, and the results are collected as shown in Table 3.6.

Table 3.6 The effect of solvent on the epoxidation of 1-dodecene catalyzed by cobalt benzimidazole **15**

Entry	Solvent	% Substrate (Recovered)	% Yield 1-dodecene oxide	Mass Balance
1	CH_3CN	9	84	93
2	CH_2Cl_2	95	5	100
3	1,2-DCE	87	14	101
4	EtOAc	47	54	101
5	acetone	80	23	103
6	$CHCl_3$	25	65	90
7	THF	100	0	100
8	EtOH	93	2	95
9	MeOH	86	12	98
10	toluene : CH_3CN (13:2)	65	35	100
11	toluene	90	12	102
12	hexane	70	32	102

Reaction conditions: 1-dodecene (5 mmol), catalyst (0.05 mmol), solvent (15 mL), O_2 and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h

Among several diverse solvents studied in Table 3.6, CH_3CN was the first solvent chosen as a reaction medium because it could dissolve both cobalt benzimidazole **15**, and a substrate. The yield of the desired product using CH_3CN as a solvent was higher than employing relatively nonpolar solvents such as toluene, and hexane or slightly polar solvents as CH_2Cl_2, 1,2-DCE, EtOAc, acetone, $CHCl_3$, and THF. Polar solvents for instance EtOH, and MeOH poorly dissolved a substrate, thus gave very low yield of the epoxide product.

3.2.4 Kinetic study of 1-dodecene epoxidation catalyzed by cobalt benzimidazole 15

The kinetic study of the epoxidation of 1-dodecene by cobalt benzimidazole **15** was conducted at room temperature. The results are shown in Fig 3.7.
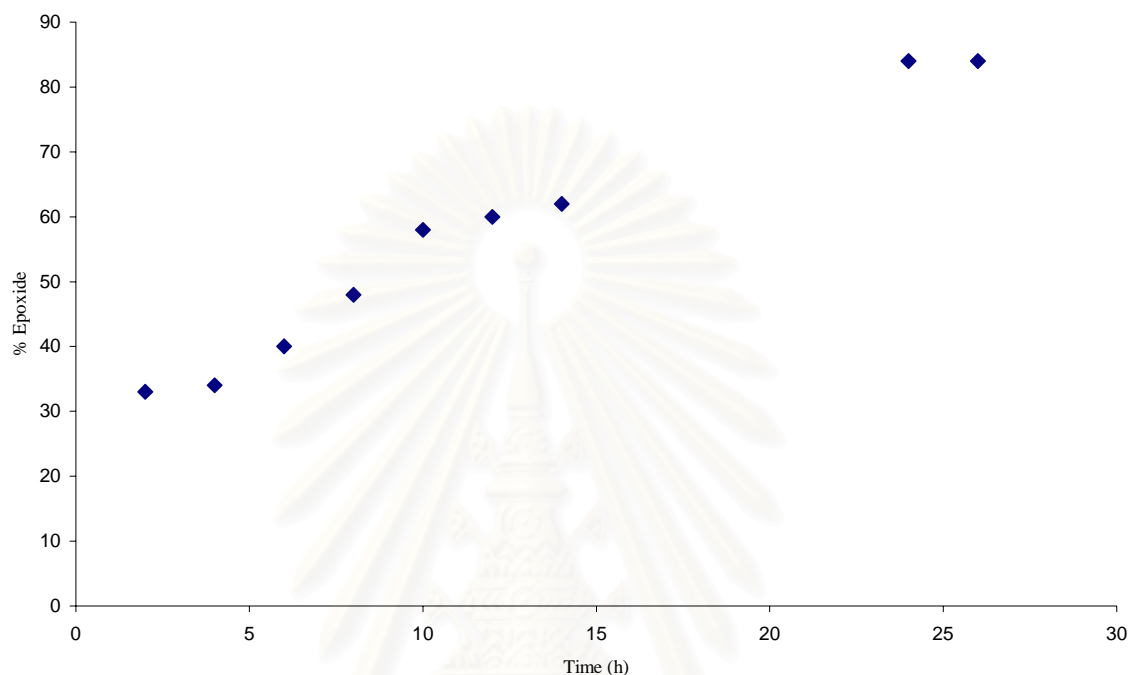

Figure 3.7 Kinetic study of 1-dodecene epoxidation catalyzed by cobalt benzimidazole **15**.

Fig 3.7 revealed that 1-dodecene was converted to 1-dodecene oxide in high yield. The maximum yield was about 84% using cobalt benzimidazole **15**. The half-life of the epoxidation reaction was approximately 8 h.

3.3 Application of developed epoxidation reaction for other terminal alkenes

As mentioned earlier, the optimum conditions for the epoxidaton of terminal alkenes by this catalyst has been developed. It would be more advantage to apply this finding system to other terminal alkenes. Twelve selected terminal alkenes including 1-octadecene, 1-dodecene, 1-octene, vinylcyclohexane, styrene, 4-chlorostyrene, α-methylstyrene, 4-chloro-α-methylstyrene, allylbenzene, diphenylethylene, 2-methyl-3-buten-2-ol, and allyl phenyl ether were conducted, and the results are accumulated in Table 3.7.
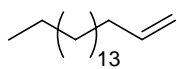
1-octadecene
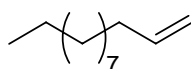
1-dodecene
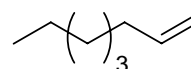
1-octene

vinylcyclohexane

styrene

4-chlorostyrene

α-methylstyrene

4-chloro-α-methylstyrene

allylbenzene

diphenylethylene

vinylcyclohexene

2-methyl-3-buten-2-ol
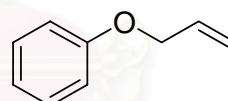
allyl phenyl ether

Table 3.7 The epoxidation of selected terminal alkenes catalyzed by cobalt benzimidazole **15**
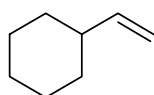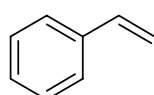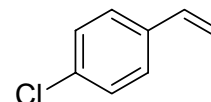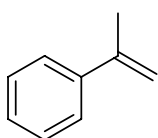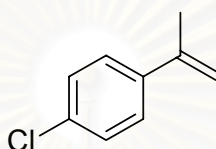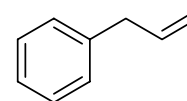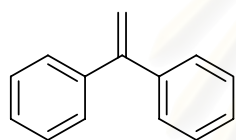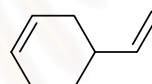
Entry	Substrate	% Substrate (recovered)	% Yield of epoxide	Mass Balance
1	1-octadecene	60	41	101
2	1-dodecene	9	84	93
3	1-octene	9	91	100
4	vinylcyclohexane	43	52	95
5	styrene	6	57[a]	93
6	4-chlorostyrene	23	28	51
7	α-methylstyrene	41	59	100
8	4-chloro-α-methylstyrene	16	34	50
9	diphenylethylene	62	36	98
10	2-methyl-3-buten-2-ol	29	70	99
11	allyl phenyl ether	100	0	100

Reaction conditions: substrate (5 mmol), catalyst (0.05 mmol), CH$_3$CN (15 mL), O$_2$ and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h

[a] 1-phenylethanol 30% was detected

The results of the epoxidation of various terminal alkenes are shown in Table 3.7. Epoxide products obtained in this system were analyzed by GC compared with anthentic specimen similar to those decribed previously (section 3.2.3). These data clearly showed that cobalt benzimidazole **15** could catalyze the epoxidation of various terminal alkenes to produce the desired epoxides in moderate to good yields. According to the above results, terminal alkenes studied could be divided into 4 groups. The first group was aliphatic terminal alkenes such as 1-octadecene, 1-dodecene, and 1-octene (entries 1-3). The yield of the epoxides went up from 41% to 91% for the compound having less carbon atoms in the substrate chain. This indicated that the reactivity was directly dependent upon the steric hindrance [4]. The second group consisted of vinylcyclohexane, and styrene (entries 4-5). It was found that the benzene ring had affected on the epoxidation reaction [56]. The activation process for styrene was found to be prevailing over vinylcyclohexane. Two main products were styrene oxide, and 1-phenylethanol. The latter was believed to derive

from the former. This observation was similar to that in the case of employing cobalt calix[4]pyrrole **9** (Table 3.3, entries 2-3). The third group was styrene derivatives including 4-chlorostyrene and α-methylstyrene. The yield of α-methylstyrene oxide was less than that of styrene (entries 5, 7). Whereas the yield of 4-chloro-α-methylstyrene oxide was lower than styrene oxide plausibly because the chloro group was an electron-withdrawing group. The low electron density of terminal alkene limited its reactivity for electrophilic oxygen transfer and often the epoxidation was further retarded by nearby electron-withdrawing group [58, 59]. The last group contained diphenylethylene, and allyl phenyl ether. This group gave low yield of epoxide or no epoxidation reaction occurred. The main reason for less activation of these substrates was steric effect. In addition, 2-methyl-3-buten-2-ol also gave high yield of epoxide. This may be due to the presence of oxygenated functional group as an electron donating group present.

3.4 Competitive study on the epoxidation of 1-octadecene, 1-dodecene, and 1-octene

The effect of the number of carbon atom in terminal alkenes on the epoxidation was competitively studied using 1-octadecene, 1-dodecene and 1-octene as substrate. The results are presented in Table 3.8.

Table 3.8 Competitive study on the epoxidation of 1-octadecene, 1-dodecene and
1-octene catalyzed by cobalt benzimidazole **15**

Entry	Substrates	% Substrate (recovered)	% Yield of Oxide	Mass Balance
1		27/15	26/35	103
2		37/19	12/28	96
3		19/29	16/25	89
4		19/14/11	10/14/15	83
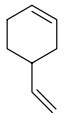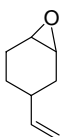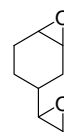
Reaction conditions: 1-octadecene, 1-dodecene and 1-octene (5 mmol), catalyst
(0.05 mmol), CH$_3$CN (15 mL), O$_2$ and 2-ethylbutyraldehyde (varied) at 30 °C for 24 h

From Table 3.8, the competitive study upon increasing number of carbon
atoms revealed that 1-octene gave the best yield of epoxide product.The reactivity
was enhanced possibly because of steric hindrance of the substrate. The epoxidation
was enhanced with the decrease of carbon atoms from 1-octadecene to 1-octene in
this epoxidation system.

3.5 Regioselectivity of 4-vinylcyclohexene catalyzed by cobalt complexes

A concern of the direction of chemical reaction to take place involved in the
regioselectivity study. Catalysts always play an important role in this regard.
4-Vinylcyclohexene was selected as a model for this purpose. Comparative studies
were carried out utilizing cobalt complexes **9**, **13**, and **15** as catalysts in CH$_3$CN. The
results are presented in Table 3.9.

Table 3.9 Regioselectivity study on the epoxidation of 4-vinylcyclohexene catalyzed by cobalt complexes of **9**, **13** and **15**

			% Yield		
Entry	catalyst	% Substrate (recovered)			Mass Balance
1	**9**	49	32	11	92
2[a]	**9**	6	82	12	100
3	**13**	50	32	16	98
4	**15**	44	49	9	102

Reaction conditions: 4-vinylcyclohexene (5 mmol), catalyst (0.05 mmol), CH_3CN (15 mL), O_2 and 2-ethylbutyraldehyde (20 mmol) at 30 °C for 24 h

[a] toluene : CH_3CN (13:2)

From Table 3.9, 4-vinylcyclohexene oxide was detected as a major product. This could be explained by the electron density in structure. The olefinic portion in the ring of cyclohexene has more electron density than at terminal site; therefore, the olefinic portion in the ring being an electrophilic in character would be a more reactive site. According to the isolation of the attained epoxides from the epoxidation reaction of 4-vinylcyclohexene catalyzed by **9**, a major product was 4-vinylcyclohexene oxide while 4-vinylcyclohexene dioxide was a minor product.

The epoxidation of 4-vinylcyclohexene by *m*-CPBA was previously reported [54], two products identified: 4-vinylcyclohexene oxide and 4-vinylcyclohexene dioxide were obtained in 97% and 3% selectivity, respectively. From Table 3.9, the isolation of epoxides from the reaction of 4-vinylcyclohexene catalyzed by cobalt complexes of **9**, **13** and **15** giving the major epoxide as 4-vinylcyclohexene oxide (74%, 67% and 84% selectivity, respectively) and 4-vinylcyclohexene dioxide (26%, 33% and 16% selectivity, respectively). The results manifestly displayed that the epoxidation at terminal site of 4-vinylcyclohexene was prevailed employing cobalt complexes **9**, **13** and **15** over using *m*-CPBA. Comparing the solvent used between CH_3CN and the mixture of toluene:CH_3CN (13:2) (entries 1-2), it was found that the solvent greatly affected the regioselectivity. To illustrate this, the use of toluene:

CH₃CN (13:2) clearly promoted the selective epoxidation at endocyclic double bond. Selectivity attained from the use of catalyst **15** was also better than that of **9**. This would be the direct influence from the structure of catalyst [49, 53].

4-Vinylcyclohexene oxide (Fig 3.8) displayed the characteristic chemical shift of the three olefinic protons at δ_H 4.95 and 5.65. The two protons of oxirane ring were observed at δ_H 3.20. The multiplet signals for seven protons of the cyclohexyl ring were detected at δ_H 1.50-2.20 and 5.70. 4-Vinylcyclohexene dioxide (Fig 3.9) showed five protons of oxirane ring at δ_H 2.42-3.10. The multiplet signals for seven protons of the cyclohexyl ring were observed at δ_H 1.00-2.20.
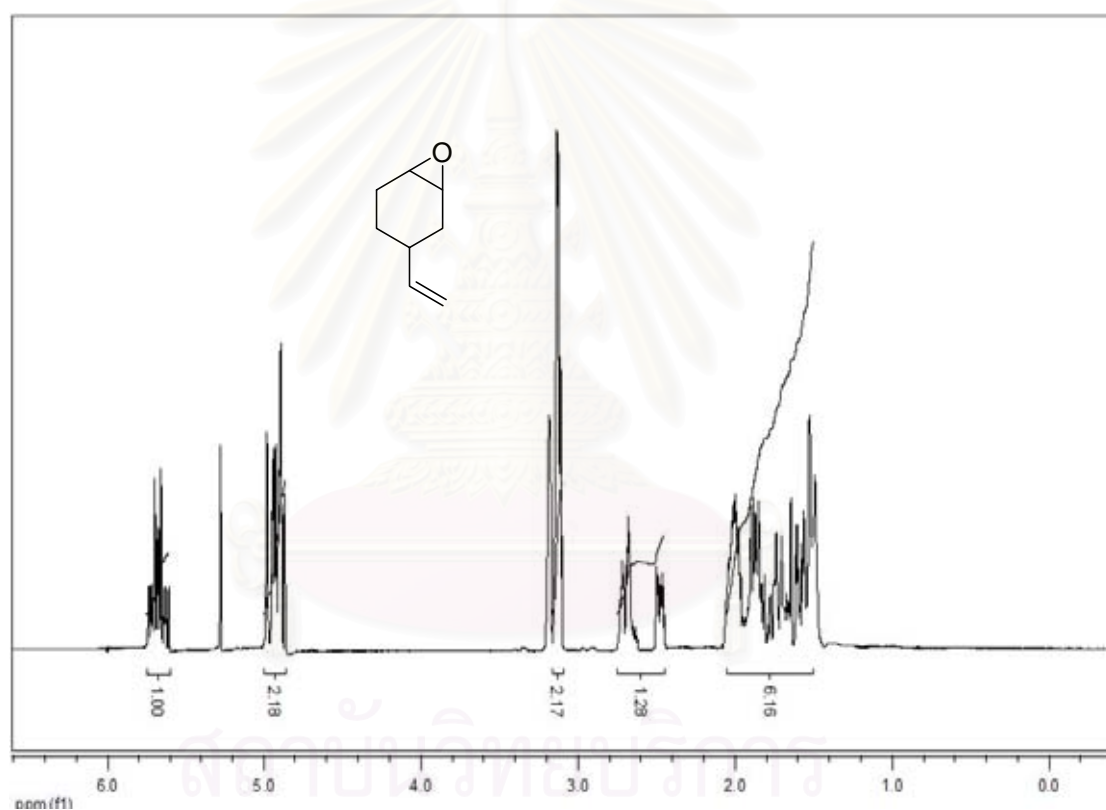
Figure 3.8 The ¹H-NMR spectrum of 4-vinylcyclohexene oxide.
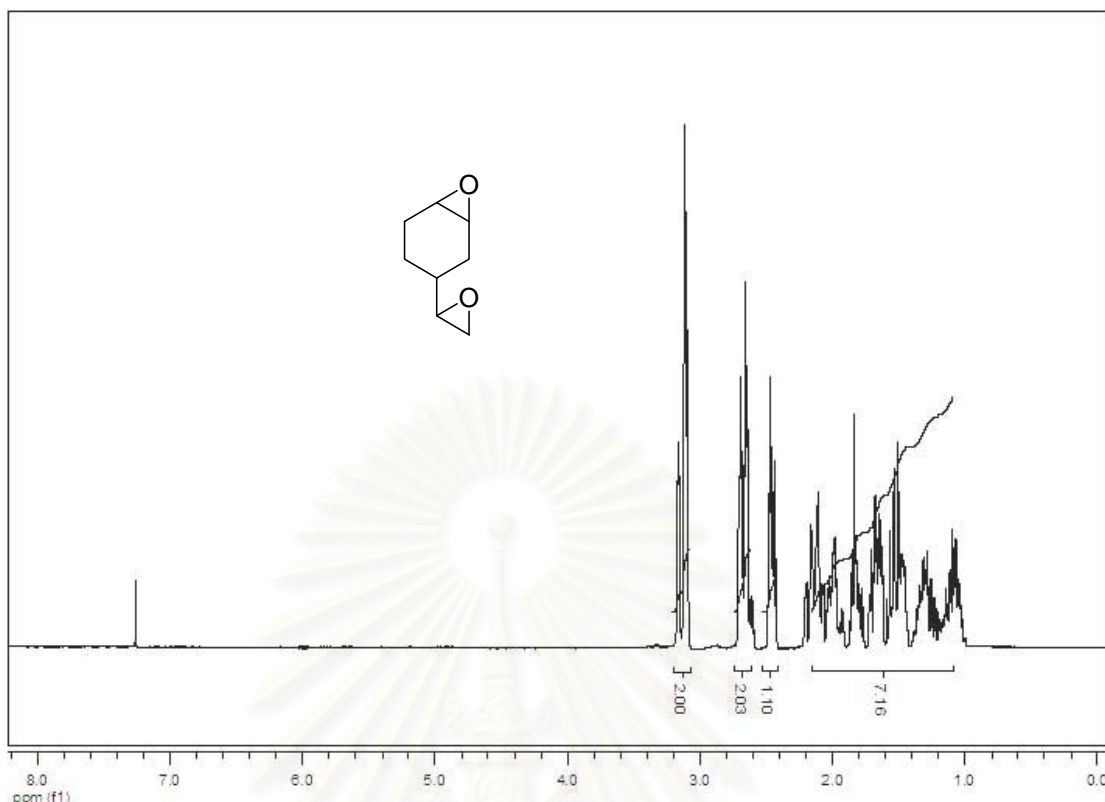
Figure 3.9 The ^{1}H-NMR spectrum of 4-vinylcyclohexene dioxide.

3.6 Proposed mechanism for cobalt complex catalyzed epoxidation of terminal alkenes

The mechanism was proposed as shown in Scheme 3.1. The mechanistic pathway proposed above as that postulated in literature [58] was believed that the cobalt complex played two major roles. First, the cobalt complex reacted with the aldehyde to generate an acyl radical (RC(O)•). The acyl radical then reacted with dioxygen to give an acylperoxy radical (RC(O)OO•). The acylperoxy radical acted as a carrier in a chain mechanism by reacting with another aldehyde molecule to give the peroxyacid, thereby generating another acyl radical. Oxygenation of substrate was assumed to occur *via* reactive high-valent cobalt oxo intermediates, which were produced by the reaction of the peroxyacid with the cobalt catalysts and which then reacted with the olefin in a fashion analogous to that observed previously for metal complex-catalyzed reactions of peroxy acids with olefins [59, 60].

Scheme 3.1 Proposed mechanism for cobalt complexes catalyzed epoxidation of terminal alkenes

CHAPTER IV
CONCLUSION

From the proceeding results and discussion, the main feature of this research is to search for the optimum conditions for selective epoxidation of terminal alkenes by cobalt complexes. The study was carried out in the homogeneous catalytic system with combination of an aldehyde, and oxygen as an oxidizing agent at room temperature. Cobalt calix[4]pyrrole **9** and benzimidazole **15** were the most effective catalyst under this developed condition in the epoxidation of terminal alkenes. 1-Dodecene 5 mmol as substrate, cobalt calix[4]pyrrole **9** or benzimidazole **15**, 0.05 mmol as catalyst, acetonitrile 15 mL as solvent, 2-ethylbutyraldehyde 20 mmol, and oxygen as oxidant in the reaction period of 24 h was discovered to the optimum condition. The highest yield, 84% of the corresponding epoxide was attained.

The epoxidation system was also widen to other types of terminal alkenes. Applications based upon the developed epoxidation of aliphatic terminal alkenes, cyclic terminal alkenes, aromatic terminal alkenes and terminal alkenes having hydroxy group and ether group were achieved and gave the desired products in moderate to high yield with excellent selectivity. In this research, the epoxidation of terminal alkenes favored less steric group or having electrophilic moiety in the molecule which would increase the reactivity. Electron-withdrawing group made low electron density of terminal alkenes and limited its reactivity for oxygen transfer. The regioselectivity study using 4-vinylcyclohexene implied that terminal double bond was less reactive than endocyclic double bond. Furthermore, it was shown that this developed epoxidation system could be employed for other terminal alkenes. Most terminal alkenes could transform to the corredponding epoxides in moderate to high yield.

Propose for the future work

From the overall studies, the epoxidation of terminal alkenes catalyzed by cobalt calix[4]pyrrole and cobalt benzimidazole could be applied in the large scale for chemical industry. The variety of alkenes, particularly those containing sensitive function groups are still required for further investigation to observe the scope of this developed epoxidation reaction.

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