การสังเคราะห์สติลบีนคราวน์อีเธอร์คาลิกซ์[4]เอรีนเพื่อใช้เป็นสารตัวรับที่สวิตช์ได้

นายโรจน์ฤทธิ์ โรจนธเนศ

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SYNTHESIS OF STILBENE CROWN ETHER CALIX[4]ARENES AS SWITCHABLE RECEPTORS

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โรจน์ฤทธิ์ โรจนธเนศ : การสังเคราะห์สติลบีนคราวน์อีเธอร์คาลิกซ์[4]เอรีนเพื่อเป็นสารตัวรับที่สวิตช์ได้ (SYNTHESIS OF STILBENE CROWN ETHER CALIX[4]ARENES AS SWITCHABLE RECEPTORS) อ.ที่ปรึกษา : ผศ.ดร.มงคล สุขวัฒนาสินิทธิ์, อ.ที่ปรึกษาร่วม : ผศ.ดร.ธวัชชัย ตันฑุลานิ; 189 หน้า. ISBN 974-17-6187-2

เริ่มต้นจากบิสเบนซาลดีไฮด์และบิสไนโตรเบนซีนของ *พารา-เทอร์เชียรี*-บิวทิลคาลิกซ์[4]เอรีน (**1** และ **2**) *พารา-เทอร์เชียรี*-บิวทิลคาลิกซ์[4]เอรีนที่มีสะพานเชื่อมเป็นสติลบีนและ เอโซ-เบนซีน (**3** และ **4**) ที่สวิตช์ได้ด้วยแสงสังเคราะห์ได้จากปฏิกิริยารีดักชันคู่ควบ ทั้ง*ซิส*- และ*ทรานส์*-**3** ได้จากปฏิกิริยารีดักชันคู่ควบของ*ออร์โธ*-**1** และ *เมตา*-**1** โดยได้ไอโซเมอร์*ซิส*เป็นหลักสำหรับเรจิโอไอโซเมอร์ทั้งสอง ในขณะที่ปฏิกิริยาคู่ควบของ*พารา*-**1** ให้ผลิตภัณฑ์เฉพาะ*ซิส*- ผลิตภัณฑ์ที่แยกออกมาได้จากการรีดักชันคู่ควบของ*ออร์โธ*-**2** และ *เมตา*-**2** คือ*ทรานส์*-**4** ในขณะที่ผลิตภัณฑ์จากปฏิกิริยาคู่ควบของ*พารา*-**2** ไม่เสถียร การระบุโครงสร้างเชิงเรขาคณิตจากโปรตอนเอ็นเอ็มอาร์สอดคล้องกับโครงสร้างผลึกจากรังสีเอกซ์ สารที่สังเคราะห์ขึ้นทั้งหมดแสดงสภาวะสมดุลเชิงแสงของการเปลี่ยนไอโซเมอร์*ซิส-ทรานส์* พบการเกิดสารเชิงซ้อนกับไอออนของโลหะแอลคาไลเฉพาะในอนุพันธ์*ออร์โธ*-**4** แสดงว่าอิเล็กตรอนคู่โดดเดี่ยวของอะตอมไนโตรเจนบนสะพานเอโซเบนซีน น่าจะมีส่วนร่วมในการเกิดสารเชิงซ้อน พบการเกิดสารเชิงซ้อนกับอะซีโตไนไตรล์และไนโตรมีเทนสำหรับ*ซิส*- และ*ทรานส์-ออร์โธ*-**3** และ*ซิส-เมตา*-**3** ได้หาค่าคงที่การเกิดสารเชิงซ้อนโดยการไทเทรทด้วยโปรตอนเอ็นเอ็มอาร์ *เมตา*-**3** แสดงการเกิดสารเชิงซ้อนกับ อะซีโตไนไตรล์ และ ไนโตรมีเทนที่สวิตช์ได้เพราะ*ซิส-เมตา*-**3** สามารถเกิดสารเชิงซ้อนกับสารทั้งสองได้ แต่*ทรานส์-เมตา*-**3** ไม่สามารถเกิดได้ ปฏิกิริยาของ*เมตา*-**1** ที่มีโพแทสเซียมไซยาไนด์ (20% โมล) ในตัวทำละลายแอลกอฮอล์ ให้ผลิตภัณฑ์เป็นโมโนเอสเทอร์ซึ่งเป็นผลมาจากการเกิดออกซิเดชันบนหมู่แอลดีไฮด์หนึ่งหมู่ แล้วตามด้วยการเกิดเอสเทอร์กับตัวทำละลายแอลกอฮอล์ทันที

ภาควิชาเคมี ลายมือชื่อนิสิต.....

สาขาวิชาเคมี ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา 2547 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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ROJRIT ROJANATHANES : SYNTHESIS OF STILBENE CROWN ETHER CALIX[4]ARENES AS SWITCHABLE RECEPTORS. DISSERTATION ADVISOR : ASST.PROF. MONGKOL SUKWATTANASINITT, Ph.D.; DISSERTATION ADVISOR : ASST.PROF. THAWATCHAI TUNTULANI, Ph.D., 189 pp. ISBN 974-17-6187-2

Starting from bisbenzaldehyde and bisnitrobenzene-*p*-*tert*-butylcalix[4]arenes (**1** and **2**), photoswitchable stilbene-bridged and azobenzene-bridged *p*-*tert*-butylcalix[4]arenes (**3** and **4**) were synthesised through reductive coupling reactions. Both *cis*- and *trans*-**3** were produced from the reductive coupling of the *ortho*-**1** and *meta*-**1** with *cis*-isomer being predominant for both regioisomers while the coupling of *para*-**1** gave only *cis*-product. The only isolable product obtained from the reductive coupling of *ortho*-**2** and *meta*-**2** was the corresponding *trans*-**4**, while the coupling product from *para*-**2** was not stable. The geometrical assignment from ^{1}H-NMR is in agreement with X-ray crystal structures. All the synthesised compounds showed photostationary state of their *cis*-*trans* isomerisation. The complexation with alkali metal ion was observed for only the *ortho*-**4** derivative, suggesting that the lone pair of N-atom in the azobenzene bridge participated in the complexation. The complexation with acetonitrile and nitromethane was observed for *cis*- and *trans*-*ortho*-**3** and *cis*-*meta*-**3**. The complexation constants were determined by ^{1}H-NMR titration. The *meta*-**3** displayed photoswitchable complexation with acetonitrile and nitromethane as *cis*-*meta*-**3** could complex with both compounds but *trans*-*meta*-**3** could complex with neither one. The reaction of *meta*-**1** with KCN (20% mole) in alcoholic solvent gave a monoester product resulting from a selective oxidation of one of the aldehyde groups followed by an intramolecular acid catalysis esterification with the alcoholic solvent.

Department……Chemistry…….Student's signature…….

Field of study....Chemistry…….Advisor's signature…….

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CONTENTS

Chapter II Experimental Section

Chapter III Results and Discussion

List of Schemes

List of Figures

List of Tables

List of Abbreviations and Signs

Å	Angstrom
bp	Boiling point
^{o}C	Degree Celsius
^{13}C-NMR	Carbon nuclear magnetic resonance
cm	Centimetre
δ	Chemical shift
J	Coupling constant
K_{eq}	Equilibrium constant
g	Gram
Hz	Hertz
kcal	Kilocalorie
mp	Melting point
mL	Millilitre
mM	millimolar
mmol	Millimole
M	Molar
ε	Molar extinction coefficient
nm	Nanometre
ppm	Part per million
cm^{-1}	Per centimetre
M^{-1}	Per molar
^{1}H-NMR	Proton nuclear magnetic resonance
UV-Vis	Ultra violet-visible
λ	Wave length

List of Numbered Compounds

o-**1**	*ortho*-bisbenzaldehyde-*p*-*tert*-butylcalix[4]arene
m-**1**	*meta*-bisbenzaldehyde-*p*-*tert*-butylcalix[4]arene
p-**1**	*para*-bisbenzaldehyde-*p*-*tert*-butylcalix[4]arene
o-**2**	*ortho*-bisnitrobenzene-*p*-*tert*-butylcalix[4]arene
m-**2**	*meta*-bisnitrobenzene-*p*-*tert*-butylcalix[4]arene
p-**2**	*para*-bisnitrobenzene-*p*-*tert*-butylcalix[4]arene
cis-*o*-**3**	*cis*-*ortho*-stilbene crown ether *p*-*tert*-butylcalix[4]arene
trans-*o*-**3**	*trans*-*ortho*-stilbene crown ether *p*-*tert*-butylcalix[4]arene
cis-*m*-**3**	*cis*-*meta*-stilbene crown ether *p*-*tert*-butylcalix[4]arene
trans-*m*-**3**	*trans*-*meta*-stilbene crown ether *p*-*tert*-butylcalix[4]arene
cis-*p*-**3**	*cis*-*para*-stilbene crown ether *p*-*tert*-butylcalix[4]arene
trans-*o*-**4**	*trans*-*ortho*-azobenzene crown ether *p*-*tert*-butylcalix[4]arene
trans-*m*-**4**	*trans*-*meta*-azobenzene crown ether *p*-*tert*-butylcalix[4]arene
Ethyl-**5**	monobenzaldehyde monoethylbenzoate *p*-*tert*-butylcalix[4]arene
*i*Propyl-**5**	monobenzaldehyde mono-*iso*-propylbenzoate *p*-*tert*-butylcalix[4]arene
6	monobenzylalcohol monobenzoic acid *p*-*tert*-butylcalix[4]arene
7	bisbenzylalcohol *p*-*tert*-butylcalix[4]arene
8	bisbenzoic acid *p*-*tert*-butylcalix[4]arene

CHAPTER I

INTRODUCTION

1.1 Switchable Molecules

The switchable molecule is a molecule that can be changed from one state to another when it was triggered by an external stimulus. A molecular switch is analogous to an everyday-life electrical switch. This molecular-scale switch functions in the same fashion, turning on and off the molecular device.

The basic requirement of a molecular switch is bistability. In other word, the molecule has two different stable forms which can be inter-converted through variety of mechanisms such as electron transfer, isomerism and complexation. Each bistable state can be inter-converted using an external stimulus, which maybe pH, heat, pressure, magnetic or electric field, chemical reaction or light.[1] These external stimuli can also be used as criteria to categorise these molecular-scale switches. Examples of molecular switches are;

1.1.1 pH Switches : Using the change of pH to switch the molecule from one to the other bistable state

The bispyridine derivative and copper (II) ion can be switched between a free form and a complex form easily by changing the proton concentration in the solution (**Figure 1.1.1**). The water molecules, depicted as "S", act as ligands for the Cu^{2+} ion. In a pH 2 solution the free form is found but in a pH 7 solution the complexation takes place. This inter-conversion can be operated in both forward and backward directions.[2]

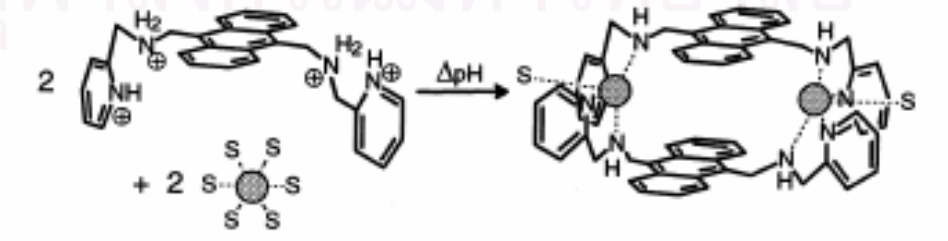


Figure 1.1.1: A pH switchable molecular box

Another example is a polymeric molecular capsule synthesised by Rudkevich and co-workers in 2003 (**Figure 1.1.2**).[3]

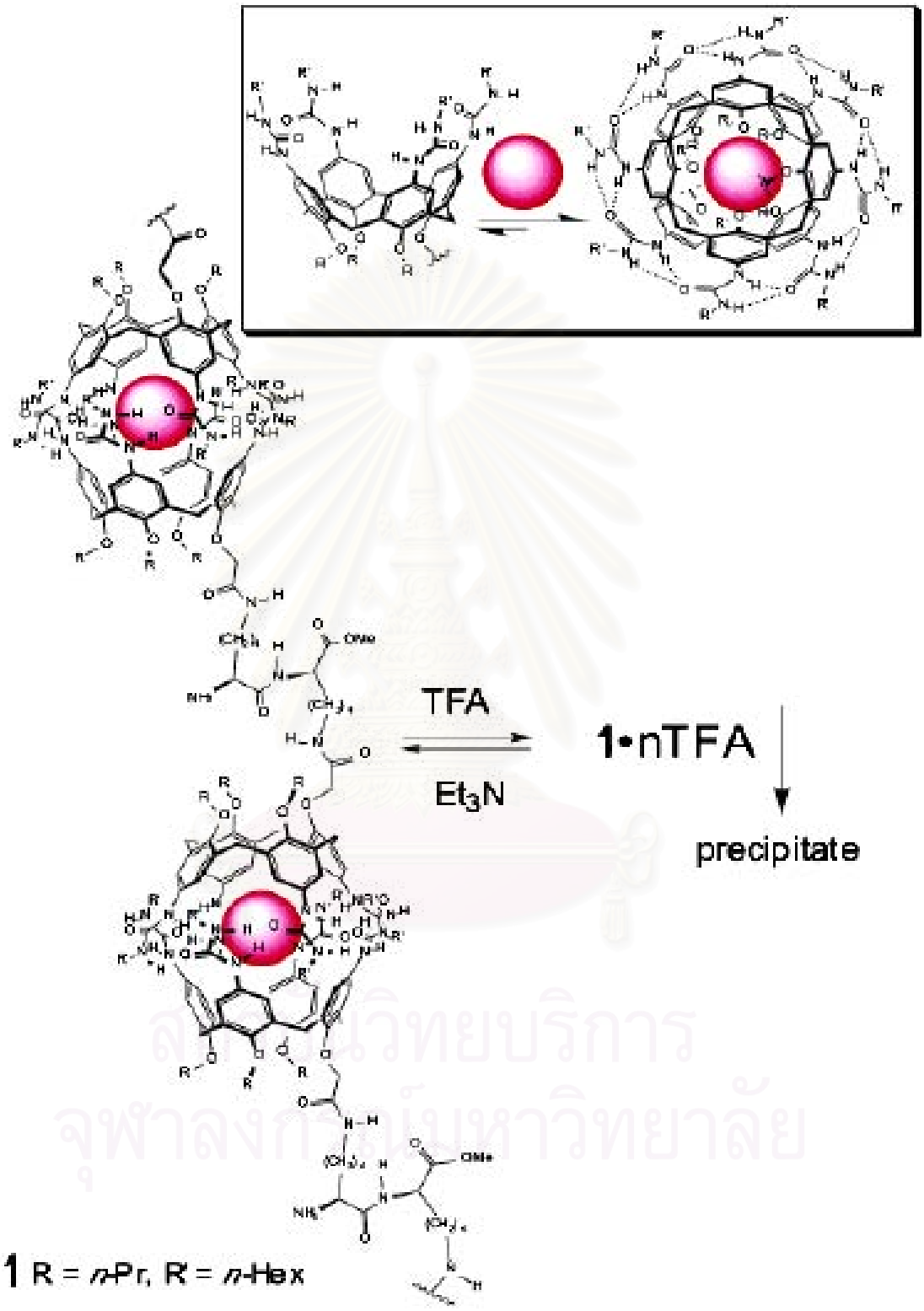


Figure 1.1.2: A pH switchable polymeric capsule

The molecular assembly can be triggered by pH. The capsule was formed in non-polar solvent. After a treatment with trifluoroacetic acid, the polymeric capsule precipitated out. In triethyl amine basic solution, the polymeric capsule solution was then reformed. The pH switch in this system was operated through the interaction between peptidic NH group.

1.1.2 Redox Switches : Using the changing of the electronic state to switch the molecule from one to another bistable state

Metallocene based molecules have been widely developed to be employed in a wide variety of applications as molecular redox switch. The central metal atom can basically be switched from one electronic state to another by an applied voltage, e.g. via cyclic voltammetry. The whole electronic state of the molecule can then be changed and, so the molecular properties.

The bis-pyridine metallocene (**Figure 1.1.3**) in neutral and positively charged state have different hydrogen bonding properties. The positively charged form bond with glutaric acid via hydrogen bonding stronger than the uncharged form did.[4]

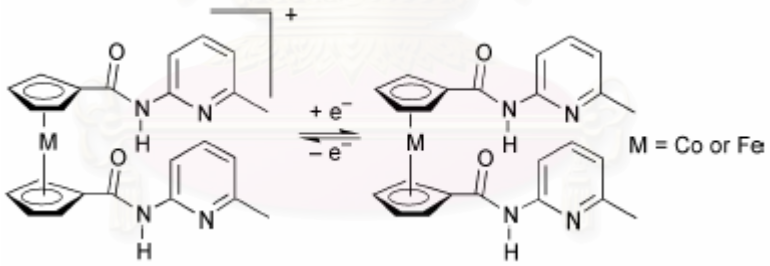


Figure 1.1.3: Redox switchable glutaric receptor

The charged cobaltocenium derivatives complexed with glutaric approximately 20 times stronger than the uncharged species with the log K value of 4.99 $\pm$ 0.04 and 3.66 $\pm$ 0.02, respectively.[4]

Another type of redox switch besides the metallocene family is organic redox active molecules, such as the paraquat derivatives. The paraquat receptors have been illustrated as outstanding organic redox switchable host molecules. An early example of this paraquat family is the macrocycle cyclobis(paraquat-*p*-phenylene), $CBPQT^{4+}$ (**Figure**

1.1.4).[5] which has become one of the most popular unit to be included in organic redox switchable molecules because of its rigid π-acceptor cavity.

cyclobis(paraquat-*p*-phenylene), $CBPQT^{4+}$

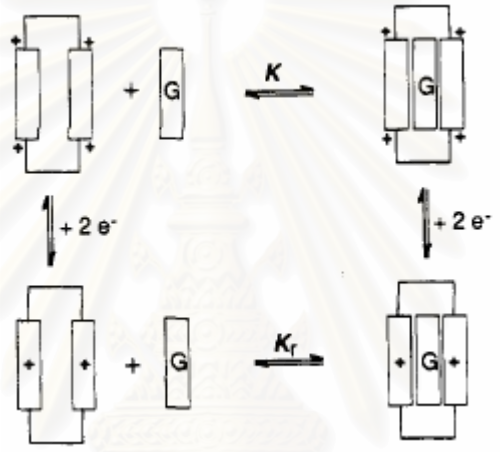


Figure 1.1.4: Complexation between indoles and $CBPQT^{4+}$

With indole as a guest molecule at pH 7, the complexation with the $CBPQT^{4+}$ (K) was stronger than its reductive form (K_r), $CBPQT^{2+}$, due to the stabilising charge-transfer interaction between the macrocycle and the indole, π-donor guest. This molecule is also noted as the first reported example of the redox-switchable molecular receptor.

1.1.3 *Ion switches* : Using the changing of complexed ion to switch the molecule from one to another bistable state

The following switchable fluorescence uses a metal ion as a stimulus to switch on the fluorescence (**Figure 1.1.5**). When the Cu^{2+} ion was added into the acetonitrile solution of the fluorescent host, the emission spectra of pyrene excimer was enhanced due to the closer distance of two pyrene moieties. The Cu^{2+} ion was wrapped around by the

oxygen atoms of the glycol chains which were designed to form an ion pocket. The complexation automatically brought two pyrene units together facilitating a formation of an excimer.(6)

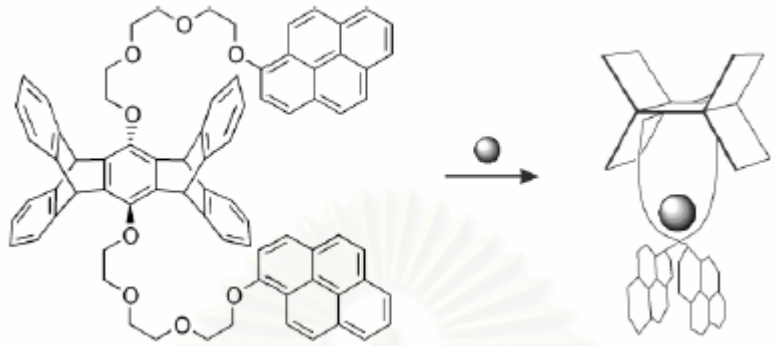


Figure 1.1.5: Cu^{2+} ion induces fluorescence switching

Besides the metal ions, molecular ions were also used as an external stimulus. In this case, the deprotonated nucleobase was a guest molecule complexed with the host, acridine-attached Zn(II) cyclen complex (**Figure 1.1.6**). This complexation led to considerable quenching of the fluorescent signal of the host molecule.(7)

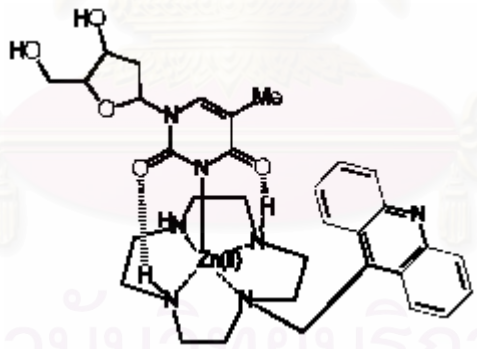


Figure 1.1.6: Deprotonated nucleobase and Zn(II) cyclen complex

1.1.4 Photoswitches : Using light to switch the molecule from one to another bistable state

The first example is a diheteroarylethene photoswitch (**Figure 1.1.7**). This unit functions as an on-off switch for the fluorescence resonance energy transfer (FRET). The opened form, on the left, was switched to the closed form, on the right, upon near-UV irradiation, and reversibly the closed form can also be switched back to the opened form

under visible light. The closed form acts as an energy acceptor from the "Lucifer Yellow", energy donor group on the left end of the molecule. Both on and off state are thermally stable.[8]

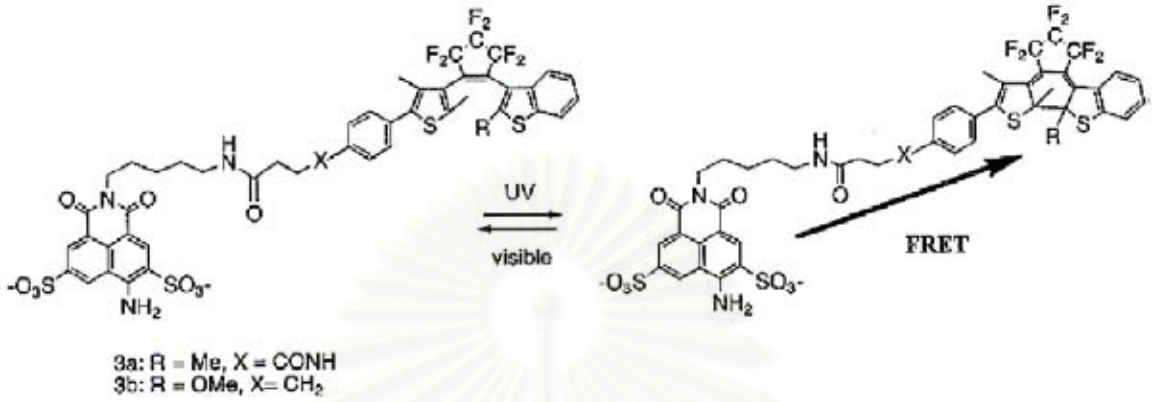


Figure 1.1.7: Diheteroarylethene photoswitch

There are also some applications in the biological system.[9] A nitrospiropyran was used as a photoswitch attached on a flavoenzyme glucose oxidase. This switchable enzyme was attached in monolayer fashion onto a gold electrode. The spiro structure of this switch allows the enzyme to function as a glucose oxidase, but the opened structure inhibits the enzyme activity by blocking the electron transfer from the gold electrode (**Figure 1.1.8**).[10]

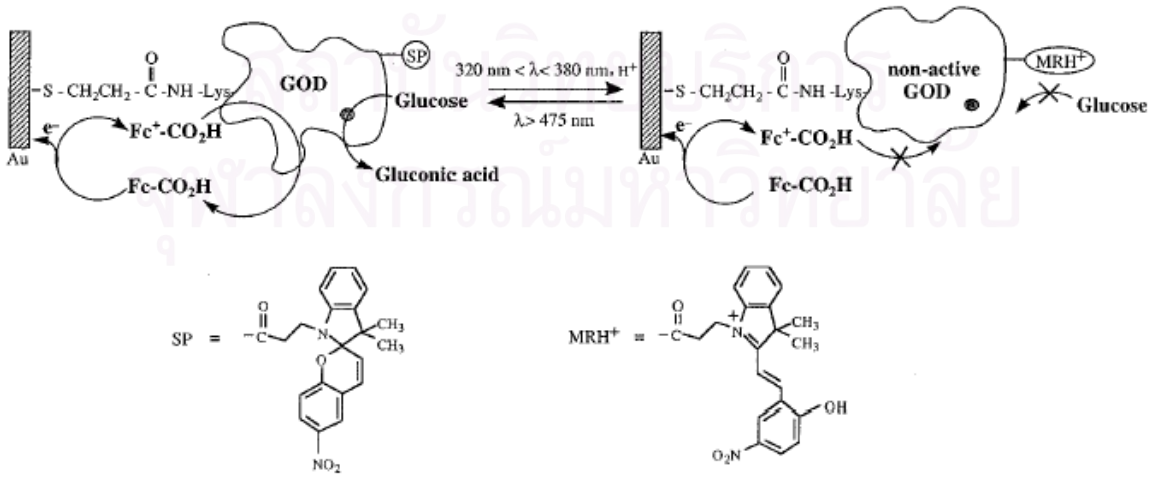


Figure 1.1.8: Photoswitchable enzyme as an electrochemical sensor for glucose

Another interesting example of the application of the photoswitchable molecule is zeolite-azobenzene photoswitchable membrane (**Figure 1.1.9**). The *cis-trans* isomerisation structure switching of the embedded azobenzene in faujasite (FAU) type microporous membrane leads to the change of gas permeation. The Na-X zeolite with *trans*-azobenzene gives the separation factor of CH_4/CO_2 = 3.30. On the other hand, the *cis*-isomer gives only 1.90. The reversible *trans-cis* photoisomerisation over numerous cycles can be obtained.[11]

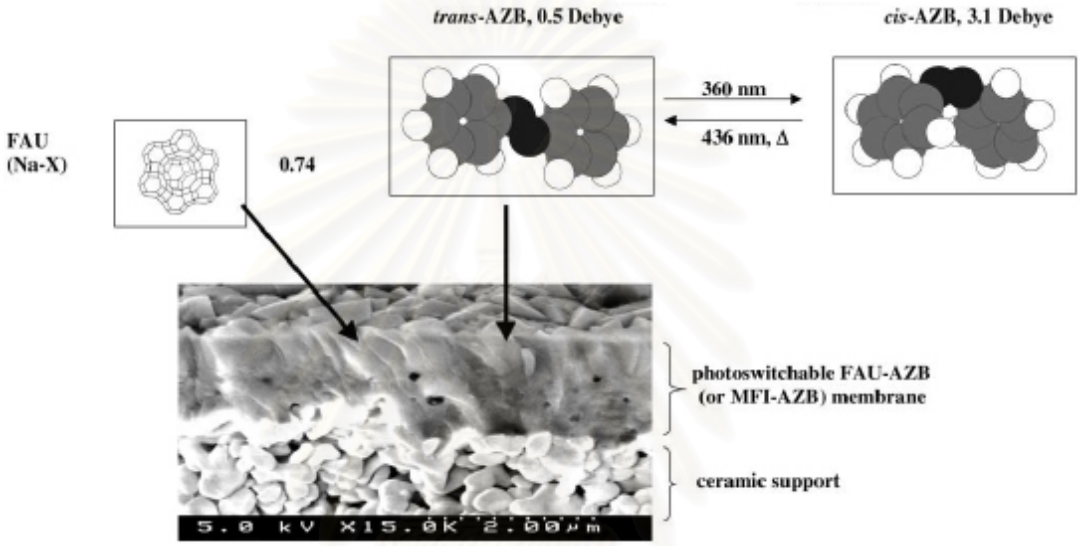


Figure 1.1.9: Photoswitchable zeolite-azobenzene membrane

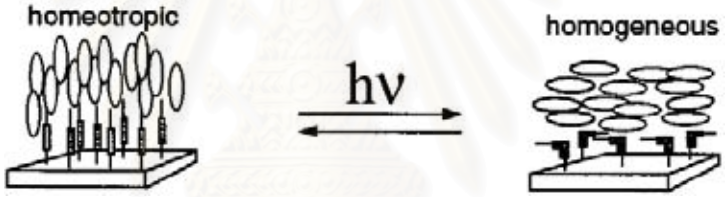
1.2 Photoswitchable Molecules

The photoswitchable compounds are the compounds that have two stable states; conformers, tautomers or structures (the absorption spectra of two states are completely different) which can be inter-converted between the two based on photochemically induced interconversions or, at least, one direction being induced by an electromagnetic irradiation. This type of switching mode, consequently, seems to be the most appealing choice among others thus far, because of the easy-to-operate switching mode.

There are varieties of photoswitchable molecules operated by different photoreaction processes, such as;

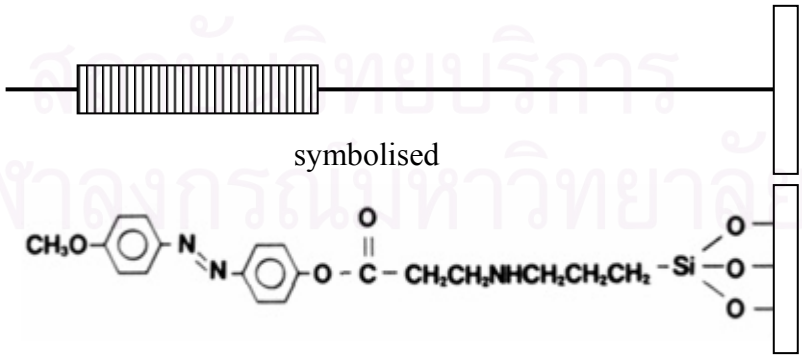
1.2.1 *cis-trans* isomerisation : e.g., stilbenes, azobenzenes

The photoisomerisation is basically the most convenient mechanism to switch the photochromic molecules. The *cis-trans* isomerisation of stilbenes and azobenzenes is one well known the simplest photochemical reaction that has been widely used.[12] This *cis-trans* photoisomerisation has been applied to many liquid crystal systems in order to obtain the transformation of liquid crystal orientation. An example of azobenzene functionalised silylating agent was demonstrated. The liquid crystal molecule was triggered by photochromic azobenzene derivative tethered on the supporting glass surface (**Figure 1.2.1**). The system was switched by alternating irradiation with linearly polarised UV light and non-polarised light. Upon an irradiation the azobenzene was isomerised on the surface, hence the liquid crystal alignment was also triggered to reorient via this azobenzene isomerisation.[13]



trans-conformation *cis*-conformation

(Liquid crystal mesogens, structural switchable part corresponding to the following azobenzene derivative)



liquid crystal mesogen, *trans*-azobenzene, *cis*-azobenzene

Figure 1.2.1: Homeotropic and homogeneous liquid crystal switched by azobenzene isomerisation

1.2.2 Electrocyclic Reaction : e.g., spirobenzopyrans, benzopyrans, fulgides

There are many possible electrocyclic reactions, but the leading candidates that have been applied to be used as a molecular switch thus far are 1,5-electrocyclic reaction and 1,3,5-hexatriene - 1,3-cyclohexadiene interconversion (**Figure 1.2.2**).

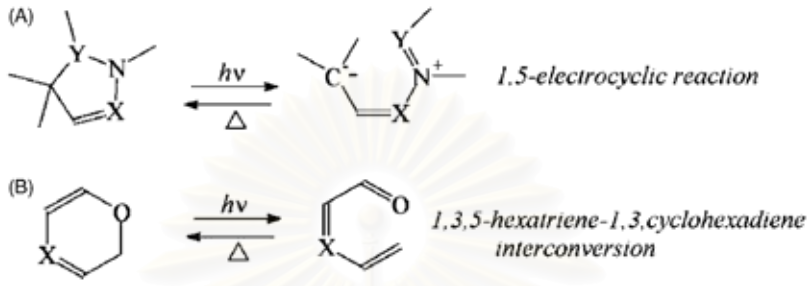


Figure 1.2.2: Examples of electrocyclic reaction using as a switching unit

Spirobenzopyrans are widely used as a switching unit. A crown-ether attached with a spirobenzopyrans was synthesised as a photoswitchable ionophore (**Figure 1.2.3**). The binding of alkali metal ions led to isomerisation of the spirobenzopyrans unit even in the dark. After an irradiation with light, the complex was switched back to the former free ligand state. The reversibility of the structural inter-conversion between these two states provides a tool for controlling the ion complexation ability.[14]

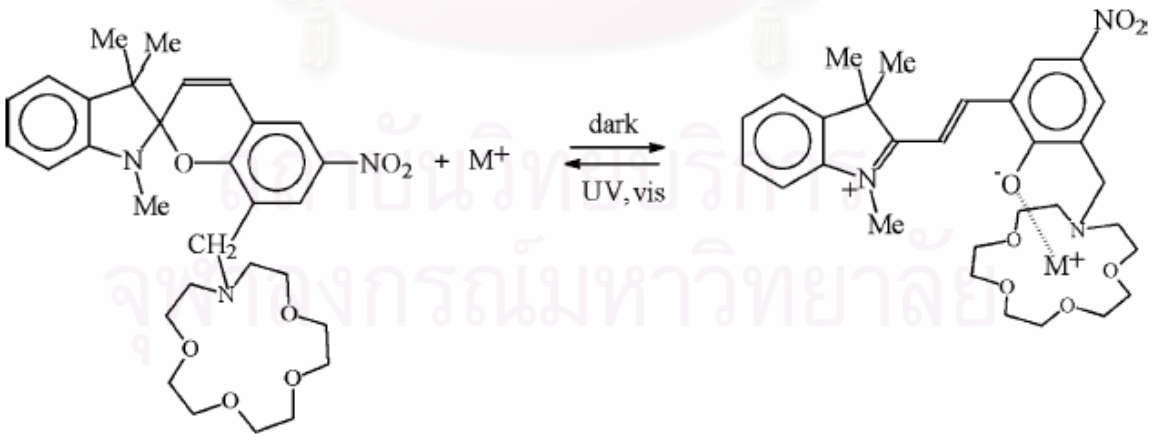


Figure 1.2.3: Spirobenzopyrans based photoswitchable ionophore

1.2.3 Cyclo Addition : e.g., diarylethylenes, anthracenes

Cyclo addition is another important class of the reaction which was used in a photoswitchable system. Both [4+4] and [2+2] have been commonly applied to the system.

A [4+4] photo cyclo addition of two anthracene units was designed as a switch in a cation receptor molecule (**Figure 1.2.4**). The irradiation of the ligand in the presence of lithium ion led to a photodimerisation. After heating, lithium ion was released and the dimer was also reversed back to the original bis-anthracene form.[15]

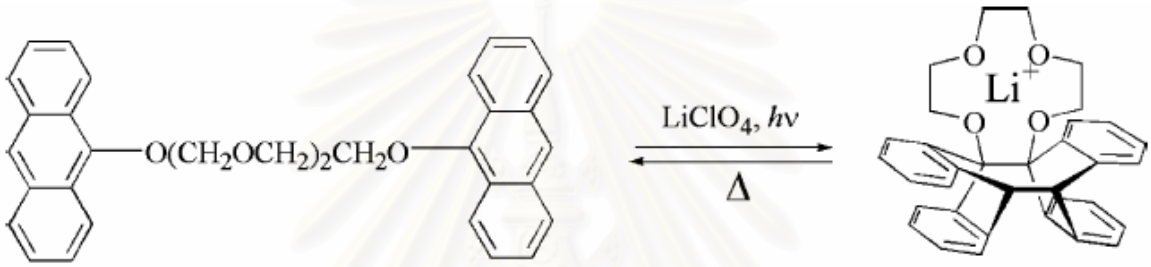


Figure 1.2.4: Photodimerisation as a switching process of bis-anthracene ionophore.

There are some essential requirements for a photoswitching molecule to function properly as a trigger element. A few most important criteria are as followed:

- Both bistable states should be stable enough under the studied or applied condition. Side reaction or decomposition should not dominate the transformation.
- The molecules should have fatigue resistance to survive numerous inter-conversion cycles.
- Immediate response is also required in order to operate in practical applications.
- One important characteristic of photoswitchable molecule is high quantum yield which is a straight forward indicator to reveal the efficiency of the inter-conversion process.

Together with those critical requirements, one may also expect some more additional factors as a decisive criterion such as the retention of photochemical properties when the photochromic compound is incorporated in, e.g., a polymeric matrix, organised surface or multi-component assembly.

1.3 Supramolecular Chemistry

Supramolecular chemistry is the chemistry beyond the molecular chemistry. The topic is about non-covalent interactions between molecules or ions, such as hydrogen bond or π-π interaction. These interactions hold molecules or ions together as complexes. In many cases there are self-assembles between many molecules or ions by these non-covalent interactions forming a well defined array or even a three dimensional sophisticated architecture.[18], [19], [20]

To understand the supramolecular chemistry, major non-covalent interactions may be categorised as followed.

1.3.1 Hydrogen Bond

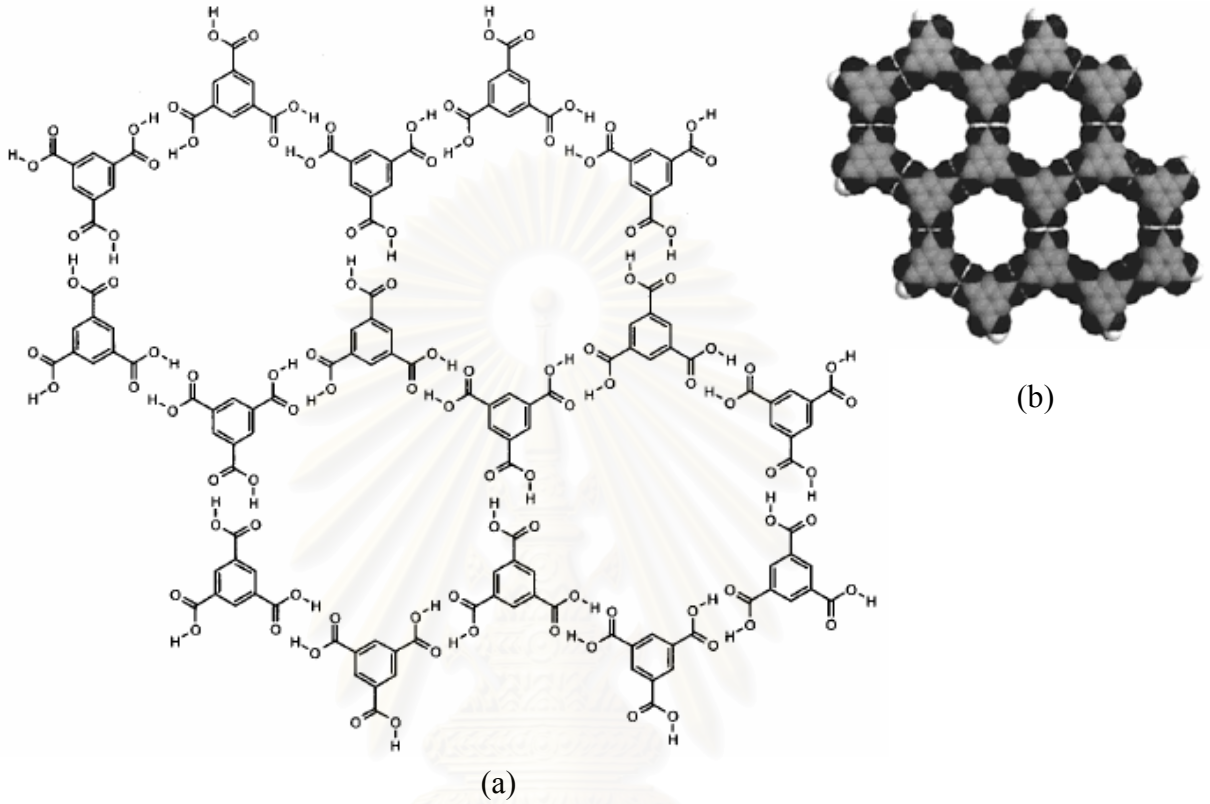
This interaction is very important in many cases and has been widely investigated. There are many interesting examples for this interaction due to a wide variety of applications in many different fields.

Hydrogen bond is a relatively weak interaction involving an electronegative donor, X, connected with a hydrogen atom and the electronegative receptor, Y.[16]

$$R{-}X{-}H\cdots{:}Y{-}R'$$

In molecular crystal, experimental evidence for hydrogen bond is the approach of hydrogen in one molecule to an electronegative atom in the other molecule significantly closer than the sum of van de Waals radii of both hydrogen and the electronegative atom. An obvious example is ice where the hydrogen bond distance is 1.75 Å is much closer than the sum of van de Waals radii (2.6 Å).[17]

In some cases, hydrogen bonds can form molecular array (**Figure 1.3.1)**. The honey comb network formed by hydrogen bonding in BTC (1,3,5-benzenetricarboxylic acid) crystal.[18]



(a) (b)

Figure 1.3.1: Crystal structure of BTC: a) schematic representation of hydrogen bond pattern and b) space-filling model illustrating the hexagon channels.

The oxygen or nitrogen is typical electronegative group promoting the hydrogen bond. However, there are also some hydrogen bonds formed without this electronegative atom.

The nitro-imidazolium receptor was synthesised to be an anion receptor using hydrogen bonding.[19] The receptor showed strong affinity and high selectivity for chloride ion. The complexation constant was 1.1 x 10^6 M^{-1}.

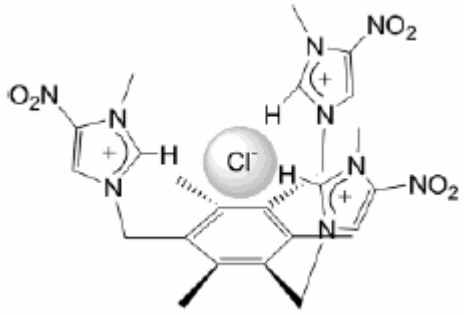
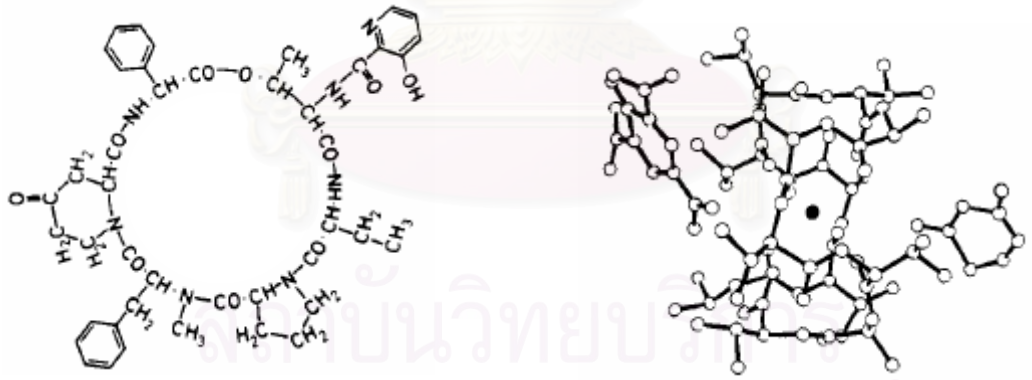


Figure 1.3.2: Nitro-imidazolium complex with chloride ion in a polar solvent.

1.3.2 Ion-Dipole Interaction

This interaction formed between an ion and a polar molecule. This interaction is widely used in designing an ion trap molecule. A specific ion can bound tightly with a host molecule because of a fit polar pocket.

The well known natural molecule is valinomycin.[20] This natural occurring molecule can bind selectively with potassium ion based on the proper size of potassium locked into the polar pocket.(**Figure 1.3.3**)



Free valinomycin

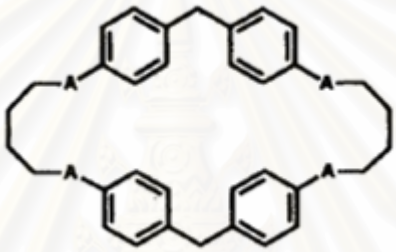
Valinomycin / K^+ complex
X-ray structure
(Cocrystallised with *m*-xylene)

Figure 1.3.3: Naturally occurred Valinomycin complexing agent for potassium ion

1.3.3 π-π Interaction[21]

This is a weak interaction, basically, between aromatic π systems. This weak interaction holds two or more aromatic rings together in storey as saw in graphite sheets. The π-π interaction is commonly found in aromatic crystal structure due to its aromatic π system. The most common example is DNA strand that contain π- π interaction throughout the strand and this interaction plays important role in holding the DNA in double stranded twist structure in cooperation with the hydrogen bonding.[22]

Many cyclophane systems can also bind with aromatic molecule such as benzene. The synthetic cyclophane (**Figure 1.3.4**)can trap the benzene ring in the π cavity in the middle of the molecule in D_2O with complexation constant around 1,000 M^{-1}.[23]



A = $NH_2^+Cl^-$

Figure 1.3.4: The benzene receptor

1.3.4 Ion-π Interaction[24]

This is also a weak interaction between cation and electron rich aromatic π system. From experimental measurement in gas phase, the complex between potassium cation and a benzene ring (**Figure 1.3.5**) gave the binding energy equal to 18 kcal/mole.[25]

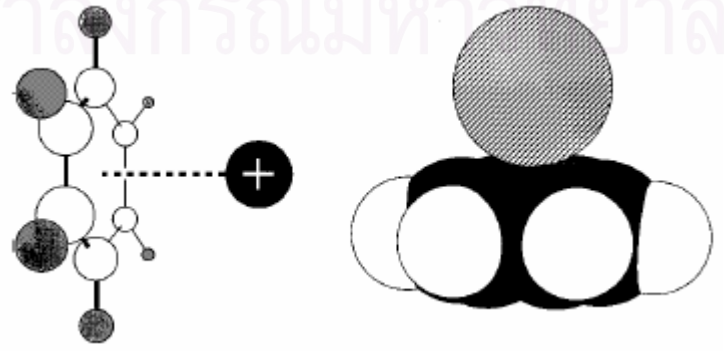


Figure 1.3.5: Schematic of K^+/benzene complex in the gas phase

This ion-π interaction can also be found in many biological systems. An example is a well-known neuroreceptor called nicotinic acetylcholine receptor (nAChR). The binding site of this protein is composed of 8 aromatic side chains from its amino acid sub-units. This π pocket acts as an effective receptor for many cation such as the positive-charged diazonium salt (**Figure 1.3.6**).[24]

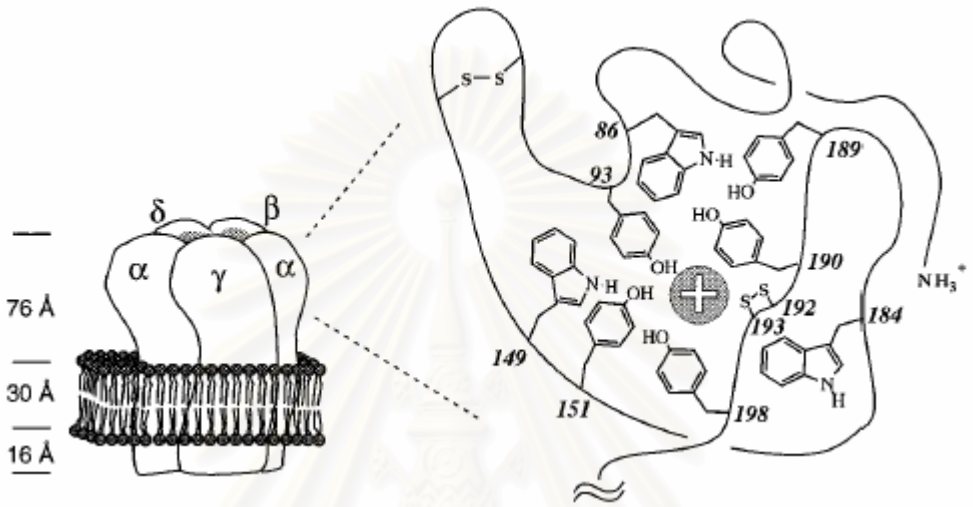


Figure 1.3.6: The complexation of a cation into the nAChR binding site.

1.3.5 Charge Transfer Interaction

Charge transfer interaction is the interaction between two π-electron systems, one is electron deficient and the other is electron rich. This can be categorised as a sub-type of π- π interaction but significantly stronger. This interaction is widely used in rotaxane chemistry for self-assembling the macrocycle and the thread (**Figure 1.3.7**).[26]

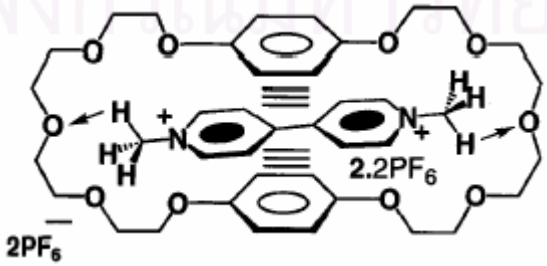


Figure 1.3.7: Rotaxane self-assemble with charge transfer interaction.

1.3.6 Lipophilic Interaction

This comparative weak interaction is also play an important role in biological system as found in phospholipids cell membranes.

There are several host molecule constructed to bind with a specific guest by this type of interaction to obtain shape or size selectivity. One type of these host molecules called cucurbituril family which is a cyclic polymeric compound synthesised by self assemble acid polymerisation reaction between glycoluril and formaldehyde. Its heptameric macrocycle can bind with oxaliplatin anticancer drug with complexation constant around 2 x 10^5 M^{-1}.[27] The interaction between cyclohexane ring in oxaplatin and the cucurbituril is the lipophilic interaction (**Figure 1.3.8**).

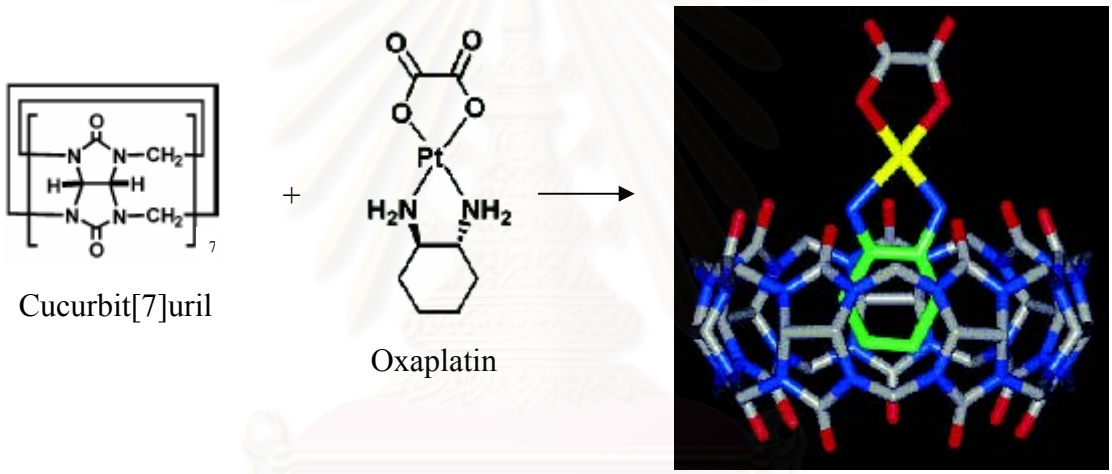


Figure 1.3.8: Complex of cucurbit[7]uril with oxaplatin anticancer drug.

There are some other types of interactions that take minority in supramolecular chemistry as well, such as hydrogen-π interaction which was also found in *bis-o*-nitrobenzenecalix[4]arene,[28] halogen–nitrogen interaction[29] but these specific interactions can be found in only some specific systems.

1.4 Calixarene

Calixarenes are cyclic products from base catalysed condensation of phenol and formaldehyde. These cyclic oligomers contain various number of repeating unit. The calix[*n*]arene, thus, means calixarene that contain n repeating units (**Figure 1.4.1**).[30]

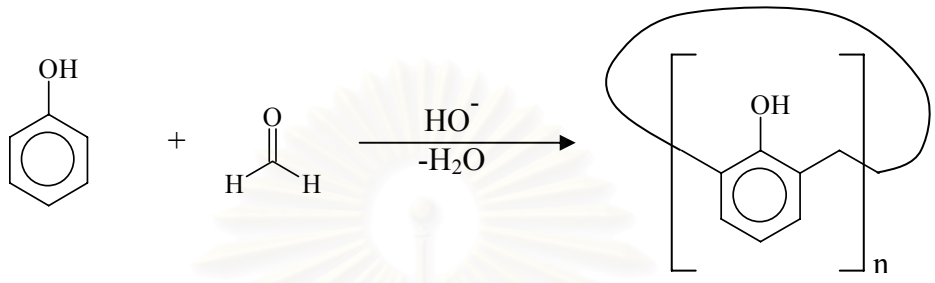


Figure 1.4.1: Synthesis of calix[n]arene from condensation of phenol and formaldehyde

The most common calixarene is calix[4]arene which contains 4 phenol groups in the cyclic structure. This calixarene has 4 main conformers: cone, partial cone, 1,2-alternate and 1,3-alternate conformers (**Figure 1.4.2**).

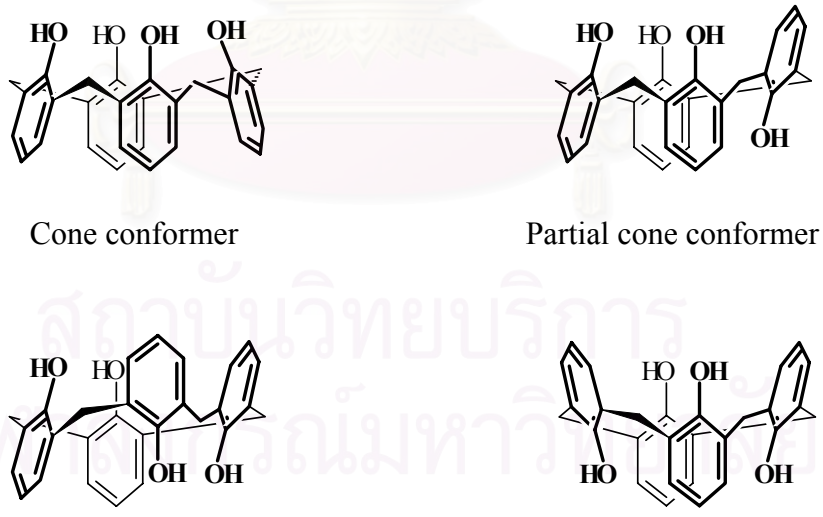


Figure 1.4.2: Four main conformers of calix[4]arene

Normally, to avoid the formation of polymeric products, polyphenolformaldehyde resin (Bakelite), the *para* position of phenol usually substituted by an alkyl or aryl group, such as *tert*-butyl, phenyl; or propyl group. If this group is bulky enough, the steric effect will also prevent the conformational change as well.

The simplest and the most well-known substituted-calix[4]arene is *p-tert*-butylcalix[4]arene. The *p-tert*-butylcalix[4]arene favourably adopts a cone conformation because of the hydrogen bonds among 4 hydroxy groups and this conformer, thus, has a π-cavity in the middle of molecules.[31]

The *p-tert*-butylcalix[4]arene itself can weakly bind with some guest as in its crystalline state several solvent (toluene, acetonitrile, anisole, etc.) can be included in the π-cavity.[32]

In tetra O-alkylation, because of the absence of such intramolecular hydrogen bonds the conformation is not locked in the cone conformation but easily able to rotate. The tetra O-methylation of calix[4]arene can complex with many cation in different conformation (**Figure 1.4.3**).[31]

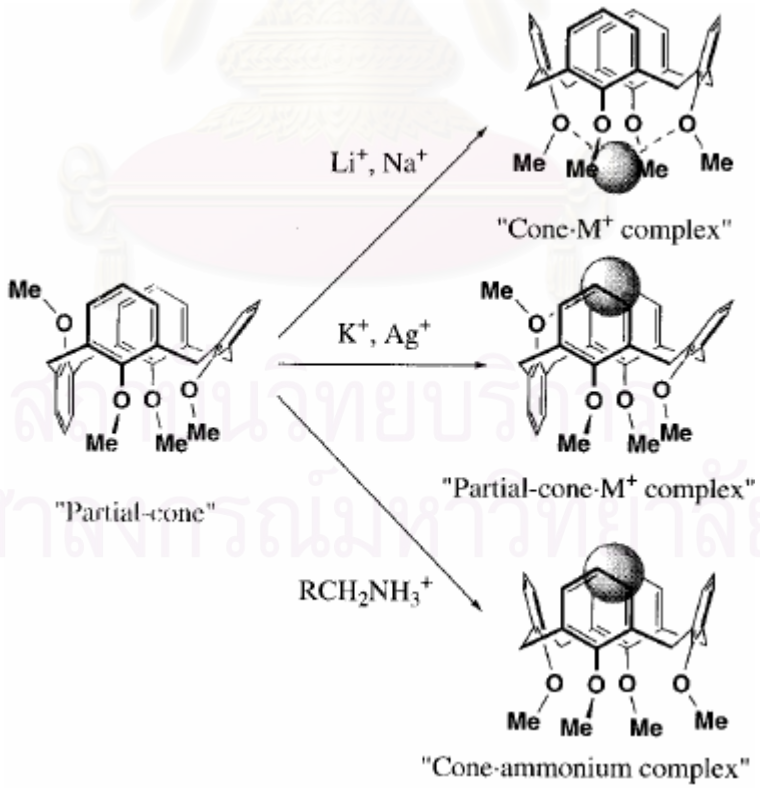
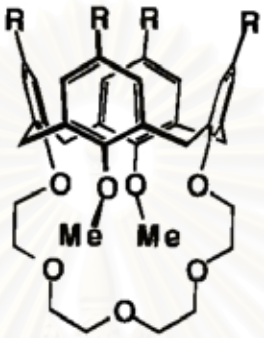


Figure 1.4.3: Various conformer of calixarene complex with different guest ions.

The *p-tert*-butylcalix[4]arene has been widely used as a molecular platform, owing to its pre-organized structure, for synthesis of other host molecules for specific guests. An interesting example is the derivative attached a crown ether onto the phenyl rings constructing a cesium cation host molecule (**Figure 1.4.4**). This molecule can complex with cesium picrate selectively over other cation.[33] The complex conformation is 1,3-alternate based on the stabilization of ion-π interaction between cesium ion and calix π-cavity.

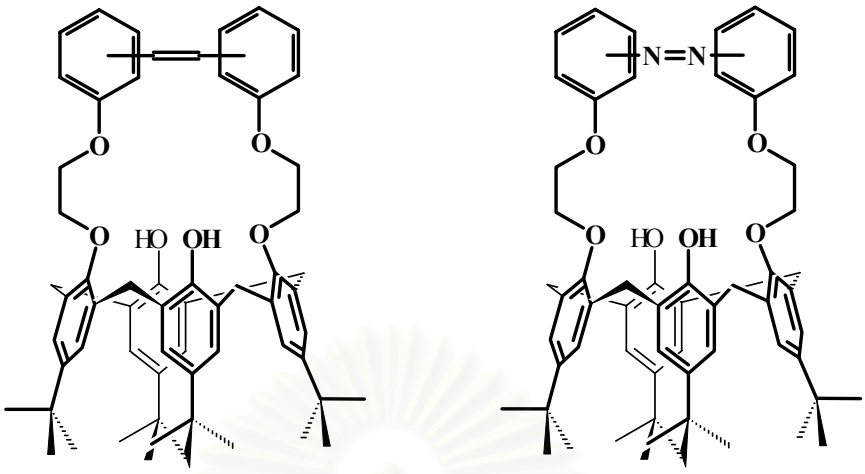


R = *p-tert*-butyl group

Figure 1.4.4: 1,3-Dimethoxy-*p-tert*-butylcalix[4]arene crowns-6

As shown in early example calixarene can use either its π-cavity or functionalised group to complex with many types of guest molecules or ions. Thus, it is interesting to construct a host molecule with two receptor pocket, π-cavity and a crown-ether on the phenolic side for complexing with electron deficient guest.

And also with the continually increment of interest in the molecular switch, the switch-embedded host molecules have been synthesised to control the complexation ability. When an outer stimulant stimulates the switching unit, the complexation constant can be altered. One of the most convenient switching modes is the photoswitching system, which is the most easy-to-operate system. Among the various types of switching units, two simplest but useful types of double bonds, C=C and N=N, have mainly been used due to their *cis-trans*-isomerizable properties. Synthesis and study of calix[4]arene derivatives containing stilbene (PhCH=CHPh) switching unit in comparison to the azobenzene (PhN=NPh) switching unit are the main focus of this research work (**Figure 1.4.5**).



Stilbene derivatives Azobenzene derivatives

Figure 1.4.5: The target molecules

1.5 Determination of Stability Constant *via* NMR Spectroscopy[34]

Determination of equilibrium constants for complexation is a key experiment in supramolecular research. Nuclear magnetic resonance (NMR) spectroscopy is one of the most useful techniques for this purpose. It is an invaluable tool for investigating of dynamic molecular processes. At least, the NMR data gives qualitative idea about the "exchange" effect in dynamic reversible process. With proper mathematical data process, the complexation constant can also be determined by the NMR spectroscopic technique.

To determine an equilibrium constant from NMR signals, the simplest system is the two-site exchanging system.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Complexation constant $(K) = \frac{k_1}{k_{-1}}$ Rate constant for interconversion $(k) = k_1 + k_{-1}$

At any equilibrium, the reaction rates of the forward and backward reactions are equal and the molar concentration of both product and starting material are constant.

Thus, the molar concentration ratio of product over reactant is also constant. Moreover, the ratio of the rate constant of forward over backward reaction is constant, too.

The sum of forward and backward rate constants is called interconversion rate constant. This value refers to the rate of interconversion between these two states.

Under the "slow-exchange" conditions the individual exchanging nucleus provides two signals in a ^{1}H-NMR spectrum: one for species A at the chemical shift δ_a and one for the species B at the chemical shift δ_b. On the other hand, in the "fast-exchange" process, there is just only one signal at the population-averaged chemical shift, $\delta = n_a\delta_a + n_b\delta_b$, where *n* represents the mole fraction of each species.

To distinguish between fast and slow exchange system, the difference of the two chemical shift δ_a and δ_b is a criteria. If the difference in hertz is much bigger than the interconversion rate constant, then the system is called slow exchange. In contrast, if the difference in hertz is much smaller than the interconversion rate constant, then the system is called fast exchange.

Slow exchange	A is at the chemical shift δ_a B is at the chemical shift δ_b
	$\Delta\delta = \delta_a - \delta_b >> k$
Fast exchange	$\delta = n_a\delta_a + n_b\delta_b$ (1) where n represent the mole fraction
	$\Delta\delta = \delta_a - \delta_b << k$

Slow exchange

Under a slow exchange condition, it is possible to observe both δ_a and δ_b directly from a ^{1}H-NMR spectrum. Furthermore, the equilibrium constant (*K*) can, basically, be calculated from the signal integrals (*I*) of the two signals.

$$(K) = \frac{[B]}{[A]} = \frac{I_b}{I_a}$$

Fast exchange

As the rate of exchange increases, the equilibrium constant for the fast-exchange system can be calculated only if the δ_a and δ_b are known.

Since the $n_b = 1 - n_a$, equation (1) can be rewritten as

$$\begin{aligned}\delta &= n_a\delta_a + (1-n_a)\delta_b \\ &= n_a\delta_a + (1-n_a)\delta_b \\ &= n_a\delta_a + \delta_b - n_a\delta_b \\ &= n_a(\Delta\delta) + \delta_b \end{aligned} \quad (2)$$

Thus,

$$n_a = \frac{\delta - \delta_b}{\delta_a - \delta_b} = \frac{\delta - \delta_b}{\Delta\delta} \quad (3)$$

$$n_b = \frac{\delta_a - \delta}{\delta_a - \delta_b} = \frac{\delta_a - \delta}{\Delta\delta} \quad (4)$$

Then

$$K = \frac{n_b}{n_a} = \frac{\delta_a - \delta}{\delta - \delta_b} \quad (5)$$

Complexation

In the complexation process, the system is also divided into slow and fast exchange systems. The chemical equation can be represented as

$$H + G \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \quad (6)$$

H represents a host, *G* represents a guest and *C* represents a complex.

Because the initial concentration of the host is equal to the sum of the concentration of the host and the complex in equilibrium, then the relationship between the concentration of the host and the complex species in equilibrium can be written according to the following equation.

$$[H] = n_h[H]_0$$

$$[C] = n_c[H]_0$$

The value *n* represents the mole fraction of each species.

The equilibrium constant can then be calculated related to the initial concentration of the host.

$$K = \frac{k_1}{k_{-1}} = \frac{[C]}{[H][G]} = \frac{n_c[H]_0}{n_h[H]_0[G]}$$

$$= \frac{n_c}{n_h[G]} = \frac{n_c}{(1-n_c)[G]} \quad (7)$$

Slow exchange

Equation (7) can be rewritten as

$$K = \frac{[C]}{([H]_0 - [C])([G]_0 - [C])} \quad (8)$$

The $[H]_0$ and $[G]_0$ represents the initial host and guest concentration, while the initial concentration of the complex $[C]_0$ is equal to zero.

The relative signal integrals at δ_h and δ_c give

And because $$[C] = n_c[H]_0 \quad (9)$$

Thus, equation (8) can be re written as

$$K = \frac{n_c[H]_0}{([H]_0 - n_c[H]_0)([G]_0 - n_c[H]_0)}$$

$$= \frac{n_c[H]_0}{(1-n_c)[H]_0\left(\frac{[G]_0}{[H]_0} - n_c\right)[H]_0}$$

$$= \frac{n_c/[H]_0}{(1-n_c)(R-n_c)} \qquad \text{where } R = [G]_0/[H]_0 \qquad (10)$$

The n_c can be calculated from the integral ratio of the signals at δ_h and δ_c according to the following equation.

$$\frac{I_c}{I_c + I_h} = n_c \qquad (11)$$

This means, the complexation constant can basically be calculated directly from the initial concentration of the host and the guest along with the integral of the host and the complex signals without any other parameters.

Fast exchange

From equations (4), substitute *h* for *a*, and *c* for *b*, then

$$n_c = \frac{\delta_h - \delta}{\delta_h - \delta_c} \qquad (12)$$

As shown in the slow exchange system, the observed chemical shift δ can be used to calculate the K value from equation (10) and (11). But in the fast exchange there is just only one signal at the population-averaged chemical shift. Thus, the signal integral of the host and the complex cannot be observed directly.

The equilibrium constant can be obtained as follows.

Applying n_h and n_c in place of n_a and n_p in equation (1) to obtain

$$\delta = n_h\delta_h + n_c\delta_c \tag{1a}$$

Since $n_c = 1 - n_h$, equation (1a) can be rewritten as

$$\begin{aligned}\delta &= (1-n_c)\delta_h + n_c\delta_c \\ &= \delta_h - n_c\delta_h + n_c\delta_c \\ &= \delta_h - n_c(\Delta\delta)\end{aligned} \tag{2a}$$

From equation (10)

$$\begin{aligned}\frac{n_c}{K[H]_0} &= (1-n_c)(R-n_c) \\ &= R - n_cR - n_c + (n_c)^2\end{aligned}$$

or

$$= R - (R+1)n_c + (n_c)^2$$

$$(n_c)^2 - \left(1 + R + \frac{1}{K[H]_0}\right)n_c + R = 0 \tag{13}$$

The real root of this quadratic equation is given by

$$n_c = \frac{b - \sqrt{b^2 - 4R}}{2} \tag{14}$$

Where

$$b = 1 + R + \frac{1}{K[H]_0}$$

Substitution of n_c from equation (14) into equation (2a) gives

$$\delta = \delta_h - \frac{b - \sqrt{b^2 - 4R}}{2}(\Delta\delta)$$

$$= \delta_h - \left(\frac{\Delta\delta}{2}\right)\left(b - \sqrt{b^2 - 4R}\right) \qquad (15)$$

In equation (15) the signal integral is not involved. This means from the initial concentration of the host and the guest along with the chemical shifts the K value can be calculated. The host chemical shift is obtained from a ^{1}H-NMR spectrum of the pure host solution. The $\Delta\delta$ value however cannot be observed directly from the spectrum, because the complex will never exist in a pure form at the equilibrium. The $\Delta\delta$ (or δ_c) has thus to be estimated from numerical simulation method for nonlinear curve fitting.

1.5.1 Non-Linear Curve Fitting

It is possible to use a nonlinear curve fitting to iteratively determine the values of K and δ_c that best simulate the experimental data set of δ vs. $[G]_0$ and $[H]_0$ (n data points), along with the value of δ_h and an estimated starting value of K (**Figure 1.4.1**).

Initial host concentration ($[H]_0$) and the chemical shift of pure host solution δ_h are constant values in each titration. From n data points titration, a set of initial guest concentration ($[G]_0$) along with a set of observed δ (δ_{obs}) each with n data was collected.

First step of calculation is manually estimated the K value and put into the calculation process. From this estimated K along with the $[H]_0$ and a set of $[G]_0$ from each titration datapoints, *via* equation 14, a sets of n_c values for each data points can be calculated. Substitution of these calculated n_c values into equation 12, then the n values of δ_c for all n data points can be calculated. Now, these δ_c values, all $[G]_0$ for every data points, the $[H]_0$ and the given estimated K value in the first step are all put together into the equation 15. The calculation gives n values of the calculated δ (δ_{calc}) for each data points. If the sum of the all (δ_{obs} - δ_{calc}) from n ata points is positive, the value of K is incremented geometrically giving a new estimated K value. On the other hand, if the sum of these differences is negative, the value of K is decremented geometrically giving a new

estimated K value. The entire process is repeated until the successive change in K less than 1 percent.

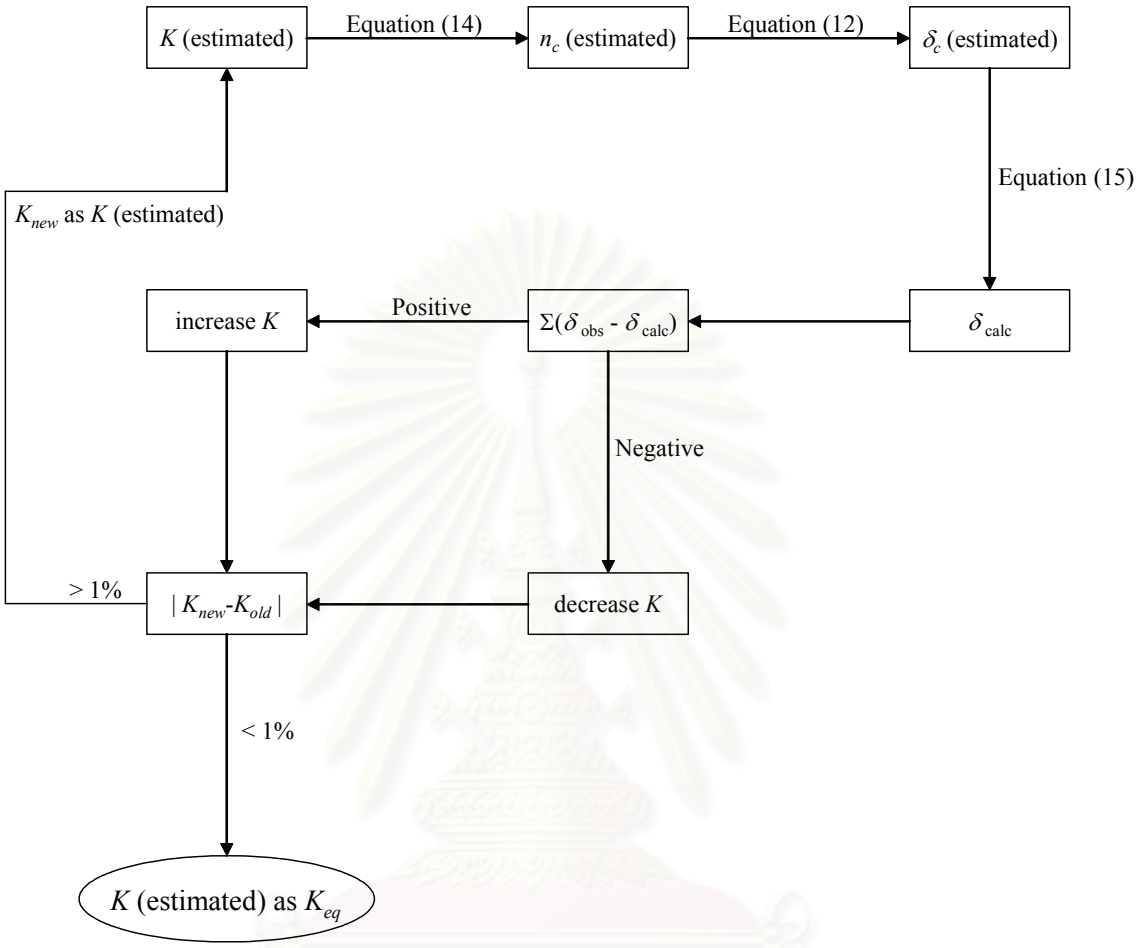


Figure 1.5.1: Schematic diagram showing the complexation constant calculation process.

From calculation, this curve fitting approach will be most accurate when the $[H]_0$ is about $0.1/K$ with $[G]_0$ spanning the range $0.1/K$ to $10/K$.

CHAPTER II

Experimental Section

2.1 Synthesis

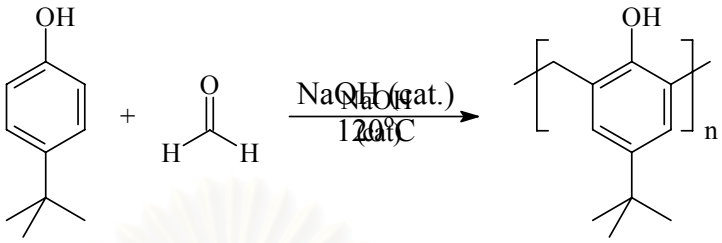
All reagents were purchased from Fluka® (Buch, Switzerland) and Merck® (Darmstadt, Germany). Solvents such as acetonitrile, methylene chloride and alcohols were reagent grade stored over molecular sieves. All reactions were carried out under N_2 atmosphere using a balloon filled with N_2 unless specified otherwise. In anhydrous reactions, solvents were dried by standard procedures and distilled before use. For extraction and chromatography, solvents were commercial grade and were distilled prior to use. The melting points were determined using an Electrothermal 900 melting point apparatus (Electrothermal Engineering, Essex, UK). Elemental analyses were performed on Perkin-Elmer PE 2400 Series II (Perkin-Elmer, Massachusetts, USA). Infrared spectrophotometry experiments were done on a Nicolet Impact 410 FT-IR (Thermo Nicolet, Wisconsin, USA), using thin film of neat samples cast from solutions in methylene chloride on KBr windows. Mass analyses were carried out on a FISONS VG TRIO 2000 mass spectrometer (Fisons, Sussex, UK). The NMR spectra were acquired on a Bruker ACF 200 NMR (Bruker, Fällanden, Switzerland) or Varian YH 400 (Varian, California, USA), using $CDCl_3$ as a solvent unless specified otherwise. All column chromatography were operated using silica gel 60, Merck®.

p-tert-Butylcalix[4]arene and picrate salts were prepared according to the literatures.[35], [36]

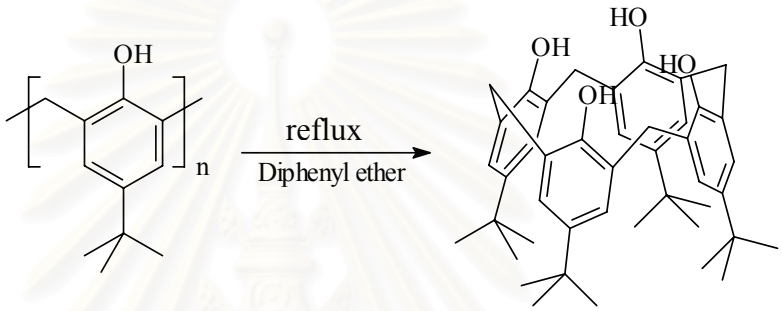
2.1.1 Preparation of Bisbenzaldehydecalix[4]arene and Bisnitrobenzenecalix[4]arene

Preparation of calix[4]arene[35]

Polymerisation



Cracking



overall 62% yield

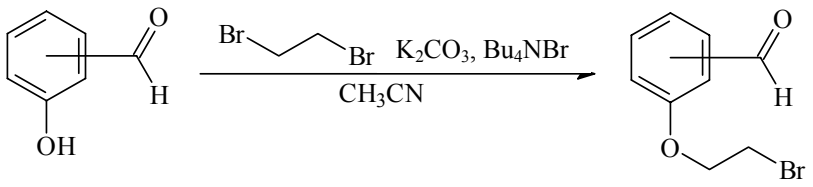
First step: polymerisation

In a 1 L, round-bottomed flask equipped with a magnetic stirring bar a mixture of *p-tert*-butylphenol (0.166 mmol, 25.00 g), 37% formaldehyde in ethanol (0.2 mol, 15.50 mL) and sodium hydroxide (7.5 mmol, 0.30 g) was stirred. The flask was left open and stirred during heating at 100-120°C on a heating mantle to allow the water by-product to escape from the reaction mixture. The stirring and heating was continued until a colourless liquid turned to spongy crispy yellow solid as the water evaporated. Then the reaction was cool down to room temperature. Over heating resulted in low yield of the desired product in the following step due to the formation of green polymeric materials. The small amount of green polymer by-product, if formed, was disposed and only the yellow part of the precursor was brought to the next step, cracking. The precursor prepared should be used within one or two days to assure the high yield of *p-tert*-butylcalix[4]arene.

Second step: cracking

Two batches of the yellow polymer from the first step was crushed to powder and combined. In a 2 L, two-necked, round-bottomed flask equipped with a magnetic stirring bar, condenser and a Dean-Stark trap, the precursor from polymerisation process (25.00 g) was stirred in diphenyl ether (250 mL). The reaction flask and the Dean-Stark side arm were wrapped with heating jacket and cotton wool in aluminium foil in order to maintain the temperature. Then the mixture was refluxed on a heating mantle. The cracking process produced “pop” sound as the water was removed to from the highly viscous mixture. When the “pop” sound was completely subsided, the reaction was allowed to cool to room temperature. The pale brown colour product was precipitated out by addition of ethyl acetate (400 mL). The product was washed with ethyl acetate and 25% acetic acid in ethyl acetate yielding a white solid. The *p-tert*-butylcalix[4]arene was further purified by crystallisation in toluene giving a white crystal as a product in 62% yield.

Preparation of (2-Bromoethoxy)benzaldehyde[37]



ortho = 80%, *meta* = 76%

para = 88%

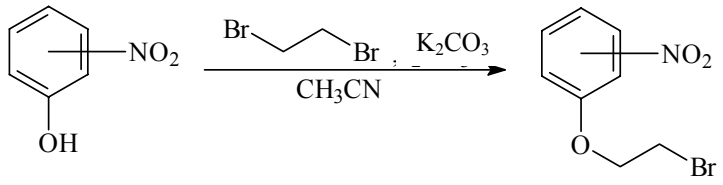
In a 1 L round-bottomed flask equipped with a magnetic bar and a reflux condenser, hydroxybenzaldehyde (199.8 mmol, 24.40 g), K_2CO_3 (209.8 mmol, 29.00 g) and Bu_4NBr (20 mmol, 0.65 g.) were dissolved in CH_3CN (800 mL). The mixture was stirred for 30 minutes at room temperature and dibromoethane (1600.0 mmol, 104.60 mL) was then added all at once to avoid the disubstitution by-product. The mixture was refluxed for 48 hours and allowed to cool to room temperature. The mixture was filtered and washed with CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with aqueous NaOH (4 M, 4 x 25 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by a column chromatography using 20% ethyl acetate in hexane as an eluent yielding a white solid as the product (*m*-isomer yielded yellow liquid).

2-(2-bromoethoxy)benzaldehyde (159.8 mmol, 36.61 g., 80%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.67 (t, 2H, C$\underline{H}_2$Br, *J* = 6.0 Hz), 4.38 (t, 2H, C$\underline{H}_2$OAr, *J* = 6.0 Hz), 6.92 (d, 1H, Ar$\underline{H}$, *J* = 8.5 Hz), 7.03 (t, 1H, Ar$\underline{H}$, *J* = 7.5 Hz), 7.52 (dt, 1H, Ar$\underline{H}$, *J* = 8.5, 2.0 Hz), 7.81 (dt, 1H, Ar$\underline{H}$, *J* = 7.5, 2.0 Hz), 10.50 (s, 1H, ArC$\underline{H}$O,); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 29.0 ($\underline{C}H_2$Br), 68.2 (C$\underline{H}_2$OAr), 112.7 (Ar$\underline{C}$), 121.5 (Ar$\underline{C}$), 125.1 (Ar$\underline{C}$), 128.3 (Ar$\underline{C}$), 136.0 (Ar$\underline{C}$), 160.4 (Ar$\underline{C}$), 189.6 (Ar$\underline{C}$HO).

3-(2-bromoethoxy)benzaldehyde (152.8 mmol, 35.00 g., 76%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.65 (t, 2H, C$\underline{H}_2$Br, *J* = 6.0 Hz), 4.33 (t, 2H, C$\underline{H}_2$OAr, *J* = 6.0 Hz), 7.13–7.47 (m, 4H, Ar$\underline{H}$), 9.95 (s, 1H, ArC$\underline{H}$O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.9 ($\underline{C}H_2$Br), 68.0 (C$\underline{H}_2$OAr), 112.9 (Ar$\underline{C}$), 122.0 (Ar$\underline{C}$), 124.1 (Ar$\underline{C}$), 130.3 (Ar$\underline{C}$), 137.8 (Ar$\underline{C}$), 158.7 (Ar$\underline{C}$), 191.9 (Ar$\underline{C}$HO); IR (neat) 3070, 2925, 2853 (aldehydic C-H stretching), 2735 (aldehydic C-H stretching), 1696 (aldehydic C=O stretching), 1609, 1588, 1491, 1450 cm^{-1}.

4-(2-bromoethoxy)benzaldehyde (176.9 mmol, 40.53 g., 88%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.65 (t, 2H, C$\underline{H}_2$Br, *J* = 6.0 Hz), 4.36 (t, 2H, C$\underline{H}_2$OAr, *J* = 6.0 Hz), 7.00 (d, 2H, ArC$\underline{H}$, *J* = 9.0 Hz), 7.84 (d, 2H, ArC$\underline{H}$, *J* = 9.0 Hz), 9.88 (s, 1H, ArC$\underline{H}$O).

Preparation of (2-Bromoethoxy)nitrobenzene[37]



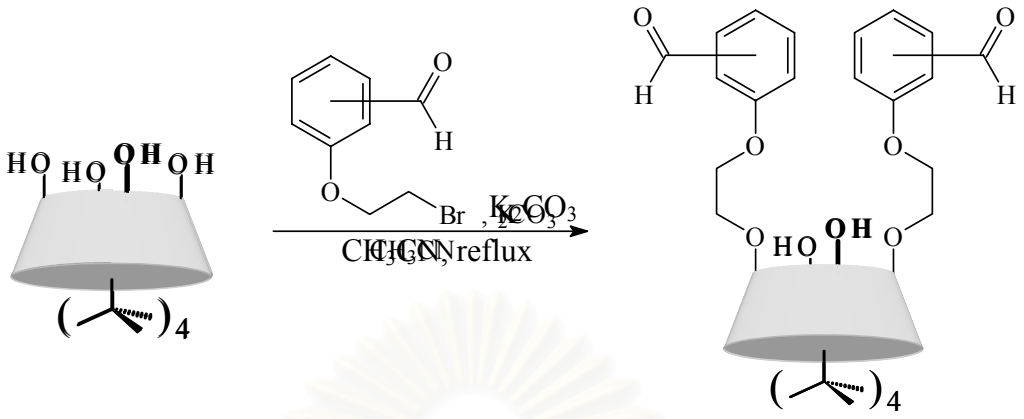
meta = 83%, *para* = 71%

In a 1 L round-bottomed flask equipped with a magnetic bar and a reflux condenser, a mixture of potassium carbonate (128 mmol, 17.70 g), 1,2-dibromoethane (640 mmol, 122.22 g) and hydroxynitrobenzene (64 mmol, 8.90 g) were stirred in dried acetonitrile (400 mL). The mixture was stirred at reflux temperature for 6 hours. The mixture was allowed to cool to room temperature and filtered off and then washed with CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with aqueous NaOH (4 M, 4 x 25 mL). The combined organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was further purified by a column chromatography using 20% ethyl acetate in hexane as an eluent.

3-(2-bromoethoxy)nitrobenzene as a yellow oil (52.83 mmol, 13.0 g., 83%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.66 (t, 2H, C<u>H</u>$_2$Br, *J* = 6.0 Hz), 4.34 (t, 2H, C<u>H</u>$_2$OAr, *J* = 6.0 Hz), 7.22 (ddd, 1H, Ar<u>H</u>, *J* = 8.0, 2.5, 1.0 Hz), 7.42 (t, 1H, Ar<u>H</u>, *J* = 8.0 Hz), 7.69 (t, 1H, Ar<u>H</u>, *J* = 2.5 Hz), 7.81 (ddd, 1H, Ar<u>H</u>, *J* = 8.0, 2.5, 1.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.7 (<u>C</u>H$_2$Br), 68.4 (<u>C</u>H$_2$OAr), 109.0 (Ar<u>C</u>), 116.4 (Ar<u>C</u>), 121.7 (Ar<u>C</u>), 130.2 (Ar<u>C</u>), 149.1 (Ar<u>C</u>), 158.6 (Ar<u>C</u>), along with 1,2-di-(3'-nitrophenoxy)ethane (2.83 mmol, 0.86 g, 4 %): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.44 (s, 4H, C<u>H</u>$_2$), 7.24-7.30 (m, 2H, Ar<u>H</u>), 7.44 (t, 2H, Ar<u>H</u>, *J* = 8.0 Hz), 7.78-7.88 (m, 4H, Ar<u>H</u>).

4-(2-bromoethoxy)nitrobenzene as a yellow crystal (45.5 mmol, 11.20 g, 71%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.66 (t, 2H, C<u>H</u>$_2$Br, *J* = 6.0 Hz), 4.37 (t, 2H, C<u>H</u>$_2$OAr *J* = 6.0 Hz), 6.96 (d, 2H, Ar<u>H</u>, *J* = 9.0 Hz), 8.20 (d, 2H, Ar<u>H</u>, *J* = 9.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.2 (C<u>H</u>$_2$Br), 68.3 (C<u>H</u>$_2$OAr), 114.6 (Ar<u>C</u>), 126.0 (Ar<u>C</u>), 142.0 (Ar<u>C</u>), 163.0 (Ar<u>C</u>), along with 1,2-di-(4'-nitrophenoxy)ethane (8.0 mmol, 2.43 g, 25%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.45 (s, 4H, C<u>H</u>$_2$), 7.00 (d, 4H, Ar<u>C</u>, *J* = 9.0 Hz), 8.21 (d, 4H, (Ar<u>C</u>), *J* = 9.0 Hz)

Preparation of Bisbenzaldehydecalix[4]arene[38]



o-**1** = 70%, *m*-**1** = 60%

p-**1** = 55%

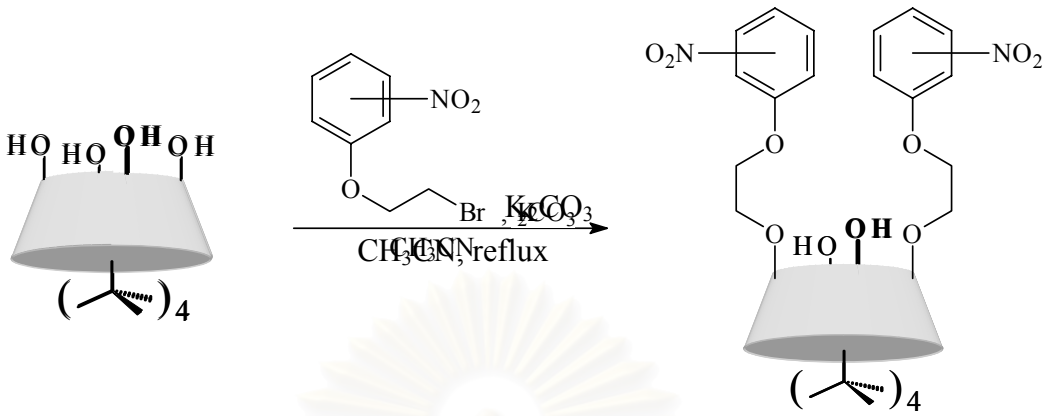
In a two-necked 1 L round-bottomed flask equipped with a magnetic bar and a reflux condenser, *p-tert*-butylcalix[4]arene (7.8 mmol, 5.00 g) and K_2CO_3 (57.9 mmol, 8.00 g) were dissolved in CH_3CN (300 mL). The mixture was stirred for 30 minutes at room temperature and (2-bromoethoxy)-benzaldehyde (17.5 mmol, 4.00 g) was then added dropwise. The mixture was refluxed for 60 hours and then allowed to cool to room temperature. The mixture was filtered and washed with acetone and CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and extracted with aqueous HCl (2 M, 4 x 25 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by crystallization in CH_2Cl_2/CH_3OH yielding a white solid as the product.

o-**1** (5.5 mmol, 5.16 g., 70%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H, C(C<u>H</u>$_3$)$_3$), 1.24 (s, 18H, C(C<u>H</u>$_3$)$_3$), 3.29 (d, 4H, Ar$_2$C<u>H</u>$_2$, *J* = 13.0 Hz), 4.29 (d, 4H, Ar$_2$C<u>H</u>$_2$, *J* = 13.0 Hz), 4.38-4.40 (m, 8H, OC<u>H</u>$_2$), 6.85 (s, 4H, calix-Ar<u>H</u>), 7.00 (s, 4H, calix-Ar<u>H</u>) 6.94–7.04 (m, 4H, benzaldehyde-Ar<u>C</u>), 7.50 (s, 2H, O<u>H</u>), 7.45-7.55 (m, 2H, benzaldehyde-Ar<u>H</u>), 7.82 (dd, 2H, benzaldehyde-Ar<u>C</u>, *J* = 7.5, 2.0 Hz), 10.48 (s, 2H, ArC<u>H</u>O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.1 (C(<u>C</u>H$_3$)$_3$), 31.7 (C(<u>C</u>H$_3$)$_3$), 31.8 (<u>C</u>(CH$_3$)$_3$), 33.8 (Ar$_2$<u>C</u>H$_2$), 34.0 (Ar$_2$<u>C</u>H$_2$), 67.5 (O<u>C</u>H$_2$), 73.6 (O<u>C</u>H$_2$), 112.4 (benzaldehyde-Ar<u>C</u>), 121.0 (benzaldehyde-Ar<u>C</u>), 125.2 (calix-Ar<u>C</u>), 125.8 (calix-Ar<u>C</u>), 127.7 (calix-Ar<u>C</u>), 128.2 (benzaldehyde-Ar<u>C</u>), 132.6 (calix-Ar<u>C</u>), 135.8 (benzaldehyde-Ar<u>C</u>), 141.7 (calix-Ar<u>C</u>), 147.3 (calix-Ar<u>C</u>), 149.8 (calix-Ar<u>C</u>),150.3 (calix-Ar<u>C</u>), 160.8 (benzaldehyde-Ar<u>C</u>), 190.2 (Ar<u>C</u>HO).

m-**1** (4.7 mmol, 4.42 g., 60%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H, C(C<u>H</u>$_3$)$_3$), 1.27 (s, 18H, C(C<u>H</u>$_3$)$_3$), 3.32 (d, 4H, Ar$_2$C<u>H</u>$_2$, *J* = 13.0 Hz), 4.30-4.40 (m, 12H, Ar$_2$C<u>H</u>$_2$ and OC<u>H</u>$_2$), 6.85 (s, 4H, calix-Ar<u>H</u>), 7.04 (s, 4H, calix-Ar<u>H</u>) 7.20–7.45 (m, 8H, calix-Ar<u>H</u> and benzaldehyde-Ar<u>H</u>), 9.93 (s, 1H, ArC<u>H</u>O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.1 (C(<u>C</u>H$_3$)$_3$), 31.7 (C(<u>C</u>H$_3$)$_3$), 31.7 (<u>C</u>(CH$_3$)$_3$), 33.8 (Ar$_2$<u>C</u>H$_2$), 34.0 (Ar$_2$<u>C</u>H$_2$), 66.9 (O<u>C</u>H$_2$), 73.7 (O<u>C</u>H$_2$), 113.4 (benzaldehyde-Ar<u>C</u>), 122.4 (benzaldehyde-Ar<u>C</u>), 123.6 (benzaldehyde-Ar<u>C</u>), 125.2 (calix-Ar<u>C</u>), 125.7 (calix-Ar<u>C</u>), 127.8 (benzaldehyde-Ar<u>C</u>), 130.2 (calix-Ar<u>C</u>), 132.8 (benzaldehyde-Ar<u>C</u>), 137.8 (benzaldehyde-Ar<u>C</u>), 141.5 (calix-Ar<u>C</u>), 147.1 (calix-Ar<u>C</u>), 149.7 (calix-Ar<u>C</u>), 150.5 (calix-Ar<u>C</u>), 159.2 (benzaldehyde-Ar<u>C</u>), 192.1 (Ar<u>C</u>HO); IR (neat) ν_{max} 3336 (phenolic O-H stretching), 3050, 2958, 2869 (aldehydic C-H stretching), 2731 (aldehydic C-H stretching), 1697 (aldehydic C=O stretching), 1597, 1485, 1450, 1265 cm^{-1}; Anal. Calcd for $C_{62}H_{72}O_8 \cdot H_2O$: C, 77.31; H, 7.74; Found: C, 76.80; H, 7.95; mp (decomposed) = 184.8-185.3 ºC.

p-**1** (4.3 mmol, 4.05 g., 55%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.18 (s, 18H, C(C<u>H</u>$_3$)$_3$), 1.50 (s, 18H, C(C<u>H</u>$_3$)$_3$), 3.49 (d, 4H, Ar$_2$C<u>H</u>$_2$, *J* = 13.0 Hz), 4.80-4.52 (m, 8H, OC<u>H</u>$_2$,), 4.54 (d, 4H, Ar$_2$C<u>H</u>$_2$, *J* = 13.0 Hz), 7.02 (s, 4H, calix-Ar<u>H</u>), 7.19 (d, 4H, benzaldehyde-Ar<u>H</u>, *J* = 8.5 Hz), 7.24 (s, 4H, calix-Ar<u>H</u>), 7.42 (s, 2H, O<u>H</u>), 8.00 (d, 2H, benzaldehyde-Ar<u>H</u>, *J* = 8.5 Hz) 10.06 (s, 2H, ArC<u>H</u>O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.0 (C(<u>C</u>H$_3$)$_3$), 31.5 (<u>C</u>(CH$_3$)$_3$), 31.7 (C(<u>C</u>H$_3$)$_3$), 33.8 (Ar$_2$<u>C</u>H$_2$), 34.0 (Ar$_2$<u>C</u>H$_2$), 66.9 (O<u>C</u>H$_2$), 73.5 (O<u>C</u>H$_2$), 115.1 (benzaldehyde-Ar<u>C</u>), 125.2 (calix-Ar<u>C</u>), 125.7 (calix-Ar<u>C</u>), 127.8 (calix-Ar<u>C</u>), 130.2 (benzaldehyde-Ar<u>C</u>), 131.9 (benzaldehyde-Ar<u>C</u>), 132.6 (calix-Ar<u>C</u>), 141.6 (calix-Ar<u>C</u>), 147.2 (calix-Ar<u>C</u>), 149.6 (calix-Ar<u>C</u>), 150.4 (calix-Ar<u>C</u>), 163.5 (benzaldehyde-Ar<u>C</u>), 190.8 (Ar<u>C</u>HO).

Preparation of Bisnitrobenzenecalix[4]arene[39]



m-**2** = 70%, *p*-**2** = 80%

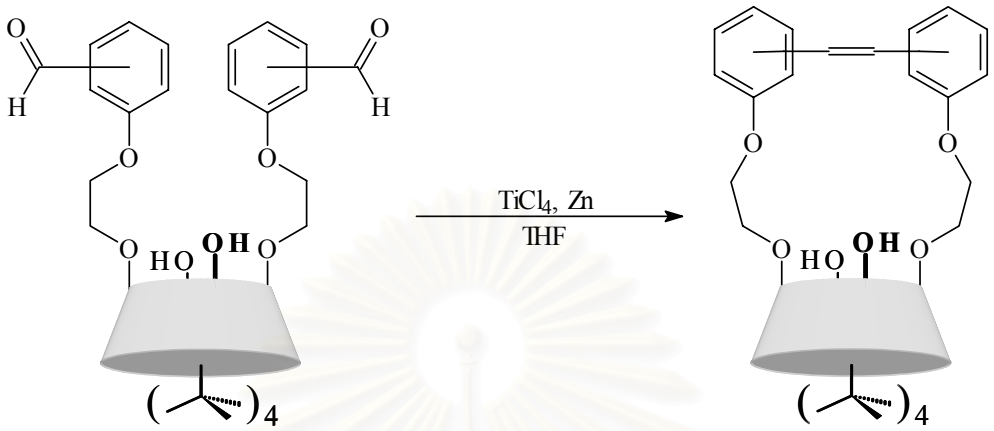
In a 500 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser, a mixture of potassium carbonate (0.43 mmol, 6.0 g), (2-bromoethoxy)nitrobenzene (40.64 mmol, 10.0 g) and *p-tert*-butylcalix[4]arene (18.85 mmol, 8.0 g) were stirred in CH_3CN (200 mL). The mixture was kept stirring at reflux temperature overnight. Then, the mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with water for several times. The combined organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was further purified by crystallization in CH_2Cl_2/CH_3OH yielding a yellow solid as the product.

m-**2** (13.28 mmol, 13.0 g., 70%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.99 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.26 (s, 18H, C(C$\underline{H}_3$)$_3$), 3.31 (d, 4H, Ar$_2$C$\underline{H}_2$, *J* = 13.0 Hz), 4.33 (s, 8H, OC$\underline{H}_2$), 4.35 (d, 4H, Ar$_2$C$\underline{H}_2$, *J* = 13.0 Hz), 6.85 (s, 4H, calix-Ar$\underline{H}$), 7.03 (s, 4H, calix-Ar$\underline{H}$), 7.24 (ddd, 2H, nitrobenzene-Ar$\underline{H}$, *J* = 8.0, 2.0, 1.0 Hz), 7.35 (s, 2H, O$\underline{H}$), 7.40 (t, 2H, nitrobenzene-Ar$\underline{H}$, *J* = 8.0 Hz), 7.74 (t, 2H, nitrobenzene-Ar$\underline{H}$, 2.0 Hz), 7.81 (ddd, 2H, nitrobenzene-Ar$\underline{H}$, 8.0, 2.0, 1.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.1 (C($\underline{C}$H$_3$)$_3$), 31.7 (C($\underline{C}$H$_3$)$_3$), 31.7 ($\underline{C}$(CH$_3$)$_3$), 33.9 (Ar$_2\underline{C}$H$_2$), 34.0 (Ar$_2\underline{C}$H$_2$), 67.4 (O$\underline{C}$H$_2$), 73.4 (O$\underline{C}$H$_2$), 109.1 (nitrobenzene-Ar$\underline{C}$), 116.2 (nitrobenzene-Ar$\underline{C}$), 122.2 (nitrobenzene-Ar$\underline{C}$), 125.2 (calix-Ar$\underline{C}$), 125.8 (calix-Ar$\underline{C}$), 127.8 (calix-Ar$\underline{C}$), 130.0 (nitrobenzene-Ar$\underline{C}$), 132.8 (calix-Ar$\underline{C}$), 141.8 (calix-Ar$\underline{C}$), 147.5 (calix-Ar$\underline{C}$), 149.1 (nitrobenzene-Ar$\underline{C}$), 149.5 (calix-Ar$\underline{C}$), 150.3 (calix-Ar$\underline{C}$), 159.1 (nitrobenzene-Ar$\underline{C}$).

p-**2** (15.1 mmol, 14.8 g., 80%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.96 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.27 (s, 18H, C(C$\underline{H}_3$)$_3$), 3.30 (d, 4H, Ar$_2$C$\underline{H}_2$, *J* = 13.0 Hz), 4.31 (m, 8H, OC$\underline{H}_2$), 4.35 (d, 4H, Ar$_2$C$\underline{H}_2$, *J* = 13.0 Hz), 6.80 (s, 4H, calix-Ar$\underline{H}$), 6.98 (d, 4H, nitrobenzene-Ar$\underline{H}$, *J* = 9.0 Hz), 7.05 (s, 4H, calix-Ar$\underline{H}$), 7.07 (s, 2H, O$\underline{H}$), 8.18 (d, 4H, nitrobenzene-Ar$\underline{H}$, *J* = 9.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.0 (C($\underline{C}$H$_3$)$_3$), 31.5 ($\underline{C}$(CH$_3$)$_3$), 31.7 (C($\underline{C}$H$_3$)$_3$), 33.9 (Ar$_2\underline{C}$H$_2$), 34.0 (Ar$_2\underline{C}$H$_2$), 67.4 (O$\underline{C}$H$_2$), 73.5 (O$\underline{C}$H$_2$), 114.8 (nitrobenzene-Ar$\underline{C}$), 125.2 (calix-Ar$\underline{C}$), 125.7 (nitrobenzene-Ar$\underline{C}$), 125.9 (calix-Ar$\underline{C}$), 127.7 (calix-Ar$\underline{C}$), 132.5 (calix-Ar$\underline{C}$), 141.8 (nitrobenzene-Ar$\underline{C}$), 141.8 (calix-Ar$\underline{C}$), 147.3 (calix-Ar$\underline{C}$), 149.4 (calix-Ar$\underline{C}$), 150.4 (calix-Ar$\underline{C}$), 163.5 (nitrobenzene-Ar$\underline{C}$).

2.1.2 Preparation of the Bridged Calix[4]arene

Preparation of the Stilbene-Bridged Calix[4]arene[40), (41)]



cis-o-**3** = 57%, *trans-o*-**3** = 10%,
cis-m-**3** = 20%, *trans-m*-**3** = 8%,
cis-p-**3** = 51%

$TiCl_4$ (3.17 mmol, 0.60 g) was feeded under N_2 atmosphere in to a dried two-necked 500 mL round-bottomed flask equipped with a magnetic bar, anhydrous THF (30 mL) was added dropwise. After a completion of THF addition, activated Zn powder (6.35 mmol, 0.41 g) was added cautiously. The starting Ti(IV) was bright yellow which was gradually turned to green and finally to deep purple or black colour of Ti(0) upon refluxing with Zn powder. After 1 hour of reflux, the *bis*benzaldehyde (1.06 mmol, 1.00 g) in THF (10 mL) was added dropwise. The mixture was refluxed for additional 15 hours and it was allowed to cool to room temperature. A solution of K_2CO_3 (15% w/v) was added to quench the excess $TiCl_4$. The mixture was slowly turned from grey to white or pale yellow. The precipitate was filtered over celite and washed with acetone and CH_2Cl_2. The acetone washing prior to wash with CH_2Cl_2 is necessary to avoid the formation of muddy sticky gum. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product. The reaction produced both *cis*- and *trans*-isomers for *o*- and *m*-isomer which were separated by column chromatography using 5% ethyl acetate in hexane as eluent (*cis*-isomer has a higher R_f value). For *p*-isomer, only *cis*-isomer was formed and isolated.

cis-o-**3** (0.60 mmol, 0.55 g., 57%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.03 (s, 18H, C($C\underline{H}_3$)$_3$), 1.22 (s, 18H, C($C\underline{H}_3$)$_3$), 3.25 (d, 4H, $Ar_2C\underline{H}_2$, *J* = 13.0 Hz), 4.16 (broad, 4H, $OC\underline{H}_2$), 4.26 (broad, 4H, $OC\underline{H}_2$), 4.35 (d, 4H, $Ar_2C\underline{H}_2$, *J* = 13.0 Hz), 6.83 (t, 2H, stilbene-Ar$\underline{H}$, *J* = 7.5 Hz), 6.88 (d, 2H, stilbene-Ar$\underline{H}$, *J* = 7.5 Hz), 6.90 (s, 4H, calix-Ar$\underline{H}$), 6.97 (s, 4H, calix-Ar$\underline{H}$), 7.17 (t, 2H, stilbene-Ar$\underline{H}$, *J* = 7.5 Hz), 7.25 (s, 2H, C$\underline{H}$=C$\underline{H}$), 7.29 (d, 2H, stilbene-Ar$\underline{H}$, *J* = 7.5 Hz), 7.70 (s, 2H, O$\underline{H}$) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.1 (C($\underline{C}H_3$)$_3$), 31.7 (C($\underline{C}H_3$)$_3$), 31.9 ($Ar_2\underline{C}H_2$), 33.8 ($\underline{C}(CH_3)_3$), 34.0 ($\underline{C}$(CH3)3), 67.8 ($O\underline{C}H_2$), 74.1 ($O\underline{C}H_2$), 113.4 (stilbene-Ar$\underline{C}$), 120.8 (stilbene-Ar$\underline{C}$), 125.1 (calix-Ar$\underline{C}$), 125.4 ($\underline{C}$H=$\underline{C}$H), 125.7 (calix-Ar$\underline{C}$), 127.7 (calix-Ar$\underline{C}$), 127.9 (stilbene-Ar$\underline{C}$), 129.0 (stilbene-Ar$\underline{C}$), 129.5 (stilbene-Ar$\underline{C}$), 133.3 (stilbene-Ar$\underline{C}$), 141.0 (calix-Ar$\underline{C}$), 147.0 (calix-Ar$\underline{C}$), 149.6 (calix-Ar$\underline{C}$), 150.8 (calix-Ar$\underline{C}$), 155.7 (stilbene-Ar$\underline{C}$) ; Anal. Calcd for $C_{62}H_{72}O_6 \bullet CH_2Cl_2$: C, 75.88;H, 7.38; Found: C, 76.12; H, 7.25: mp = 292-294 ^{o}C (decomposed).

trans-o-**3** (0.11 mmol, 0.10 g., 10%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.06 (s, 18H, C($C\underline{H}_3$)$_3$), 1.18 (s, 18H, C($C\underline{H}_3$)$_3$), 3.21 (d, 4H, $Ar_2C\underline{H}_2$, *J* = 12.5 Hz), 4.23 (d, 4H, $Ar_2C\underline{H}_2$, *J* = 12.5 Hz), 4.51 (broad, 4H, $OC\underline{H}_2$), 4.68 (broad, 4H, $OC\underline{H}_2$), 6.82 (d, 2H, stilbene-Ar$\underline{H}$, *J* = 8.0 Hz), 6.93 (m, 4H, calix-Ar$\underline{H}$ & 2 stilbene-Ar$\underline{H}$), 6.97 (s, 4H, calix-Ar$\underline{H}$), 7.15 (t, 2H, stilbene-Ar$\underline{H}$, *J* = 8.0 Hz), 7.50 (d, 2H, stilbene-Ar$\underline{H}$, *J* = 8.0 Hz), 7.74 (s, 2H, C$\underline{H}$=C$\underline{H}$), 8.43 (s, 2H, O$\underline{H}$) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.2 (C($\underline{C}H_3$)$_3$), 31.6 (C($\underline{C}H_3$)$_3$), 32.1 ($Ar_2\underline{C}H_2$), 33.8 ($\underline{C}(CH_3)_3$), 34.1 ($\underline{C}(CH_3)_3$), 66.6 ($O\underline{C}H_2$), 73.6 ($O\underline{C}H_2$), 111.1 (stilbene-Ar$\underline{C}$), 120.8 (stilbene-Ar$\underline{C}$), 125.0 (calix-Ar$\underline{C}$), 125.9 (calix-Ar$\underline{C}$), 127.5 (calix-Ar$\underline{C}$), 127.5 ($\underline{C}$H=$\underline{C}$H), 127.7 (stilbene-Ar$\underline{C}$), 128.0 (stilbene-Ar$\underline{C}$), 129.6 (stilbene-Ar$\underline{C}$), 133.7 (calix-Ar$\underline{C}$), 141.2 (calix-Ar$\underline{C}$), 147.4 (calix-Ar$\underline{C}$), 149.3 (calix-Ar$\underline{C}$), 150.7 (calix-Ar$\underline{C}$), 155.9 (stilbene-Ar$\underline{C}$) ; Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.41; H, 7.94: mp = 278-280 ^{o}C (decomposed).

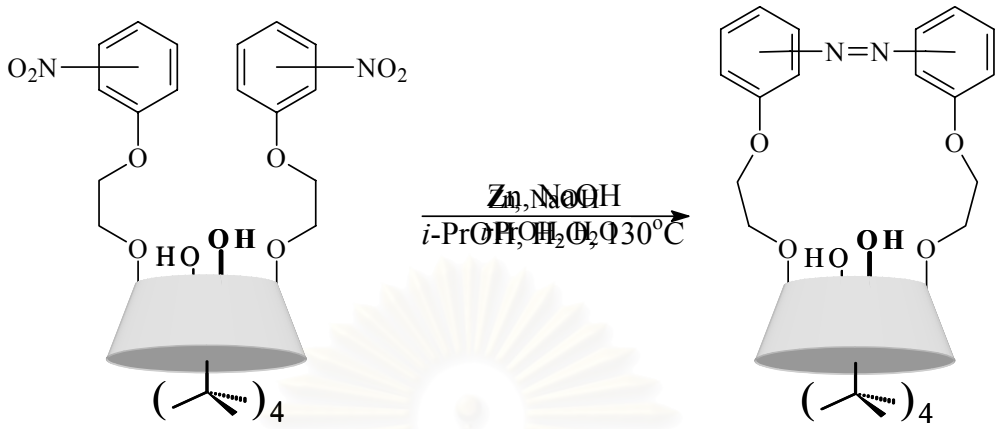
cis-m-**3** (0.21 mmol, 0.19 g., 20%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.09 (s, 18 C($C\underline{H}_3$)$_3$), 1.25 (s, 18 C($C\underline{H}_3$)$_3$), 3.32 (d, 4 $Ar_2C\underline{H}_2$, *J* = 12.5 Hz), 3.94 (broad, 4 $OC\underline{H}_2$), 4.12 (broad, 4 $OC\underline{H}_2$), 4.38 (d, 4 $Ar_2C\underline{H}_2$, *J* = 12.5 Hz), 6.69 (broad, 2 stilbene-Ar$\underline{H}$), 6.71 (s, 2 C$\underline{H}$=C$\underline{H}$), 6.89 (m, 4 stilbene-Ar$\underline{H}$), 6.97 (s, 4 calix-Ar$\underline{H}$), 7.02 (s, 4 calix-Ar$\underline{H}$), 7.24 (t, 2 stilbene-Ar$\underline{H}$, *J* = 8.5 Hz), 8.08 (s, 2 O$\underline{H}$) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.2 (C($\underline{C}H_3$)$_3$), 31.7 (C($\underline{C}H_3$)$_3$), 31.7 ($Ar_2\underline{C}H_2$), 33.8 ($\underline{C}(CH_3)_3$), 34.1 ($\underline{C}(CH_3)_3$), 66.2 ($O\underline{C}H_2$), 73.7 ($O\underline{C}H_2$), 111.8 (stilbene-Ar$\underline{C}$), 117.0 (stilbene-Ar$\underline{C}$), 121.5 (stilbene-Ar$\underline{C}$), 125.0 (calix-

ArC), 125.7 (calix-ArC), 127.3 (calix-ArC), 129.6 (CH=CH), 130.9 (stilbene-ArC), 133.5 (calix-ArC), 138.3 (stilbene-ArC), 140.9 (calix-ArC), 147.2 (calix-ArC), 149.2 (calix-ArC), 151.1 (calix-ArC), 158.2 (stilbene-ArC) ; Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.48; H, 7.92: mp = 264-265 ºC.

trans-m-**3** (0.08 mmol, 0.08 g., 8%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.83 (s, 18H, $C(CH_3)_3$), 1.31 (s, 18H, $C(CH_3)_3$), 3.29 (d, 4H, Ar_2CH_2, J = 13.5 Hz), 4.25 (t, 4H, OCH_2, J = 5.0 Hz), 4.41 (d, 4H, Ar_2CH_2, J = 13.5 Hz), 4.57 (t, 4H, OCH_2, J = 5.0 Hz), 5.84 (s, 2H, OH), 6.60 (s, 4H, calix-ArH), 6.87 (t, 2H, stilbene-ArH, J = 8.5 Hz), 7.06 (s, 4H, calix-ArH), 7.14 (d, 2H, stilbene-ArH, J = 7.5 Hz), 7.24 (s, 2H, CH=CH), 7.25 (t, 2H, stilbene-ArH, J = 7.5 Hz), 7.74 (s, 2H, stilbene-ArH) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 30.8 ($C(CH_3)_3$), 31.2 (Ar_2CH_2), 31.7 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 69.3 (OCH_2), 75.0 (OCH_2), 114.3 (stilbene-ArC), 118.0 (stilbene-ArC), 119.9 (stilbene-ArC), 125.3 (calix-ArC), 125.4 (calix-ArC), 128.5 (calix-ArC), 128.9 (CH=CH), 129.8 (stilbene-ArC), 131.6 (calix-ArC), 139.1 (stilbene-ArC), 141.8 (calix-ArC), 146.7 (calix-ArC), 150.3 (calix-ArC), 150.8 (calix-ArC), 158.8 (stilbene-ArC) ; Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.59; H, 8.00: mp = 281-283^{o}C (decomposed).

cis-p-**3** (0.54 mmol, 0.49 g., 51%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.85 (s, 18H, $C(CH_3)_3$), 1.31 (s, 18H, $C(CH_3)_3$), 3.28 (d, 4H, Ar_2CH_2, J = 13.5 Hz), 4.17 (t, 4H, OCH_2, J = 4.0 Hz), 4.38 (d, 4H, Ar_2CH_2, J = 13.5 Hz), 4.45 (t, 4H, OCH_2, J = 4.0 Hz), 6.29 (s, 2H, OH), 6.66 (s, 4H, calix-ArH), 6.68 (s, 2H, CH=CH), 6.85 (d, 4H, stilbene-ArH, J = 9.0 Hz), 6.93 (d, 4H, stilbene-ArH, J = 9.0 Hz), 7.06 (s, 4H, calix-ArH) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.0 ($C(CH_3)_3$), 31.1 (Ar_2CH_2), 31.8 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 68.4 (OCH_2), 74.8 (OCH_2), 115.8 (stilbene-ArC), 125.2 (calix-ArC), 125.4 (calix-ArC), 128.1 (calix-ArC), 130.4 (stilbene-ArC), 130.8 (CH=CH), 131.3 (stilbene-ArC), 132.0 (calix-ArC), 141.4 (calix-ArC), 146.8 (calix-ArC), 149.9 (calix-ArC), 150.5 (calix-ArC), 157.7 (stilbene-ArC) ; Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.57; H, 8.14: mp = 290-291 ºC (decomposed).

Preparation of the Azobenzene-Bridged Calix[4]arene[41]



trans-m-**4** = 59%

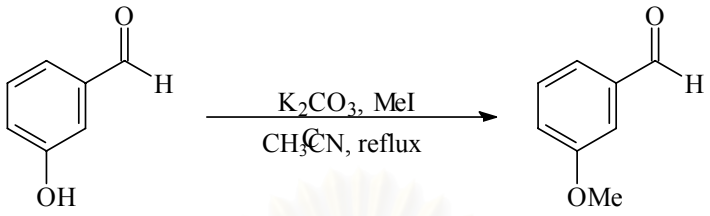
In a high-pressure glass tube equipped with a magnetic bar and pressure gauge, a mixture of *bis*nitrobenzene, (0.87 mmol, 0.85 g) in *i*-propanol (12 mL), sodium hydroxide (8.7 mmol, 0.35g) in water (6 mL) and zinc (3.58 mmol, 0.23 g) was stirred. The reactor was heated to 130 ^{o}C and stirred under 3 atm. nitrogen atmosphere overnight and it was then allowed to cool to room temperature. The mixture was filtered and washed with CH_2Cl_2. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with 2M HCl (2 x 20 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product, which was purified by column chromatography using 5% ethyl acetate in hexane as eluent. The *trans*-isomers can be separated. The product was further purified by crystallization in CH_2Cl_2/CH_3OH yielding an orange crystal as the product.

trans-m-**4** (0.51 mmol, 0.47 g., 59%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.83 (s, 18H, $C(C\underline{H}_3)_3$), 1.28 (s, 18H, $C(C\underline{H}_3)_3$), 3.26 (d, 4H, $Ar_2C\underline{H}_2$, *J* = 13.0 Hz), 4.38 (t, 4H, $OC\underline{H}_2$, *J* = 5.0 Hz) , 4.34 (d, 4H, $Ar_2C\underline{H}_2$, *J* = 13.0 Hz), 4.66 (t, 4H, $OC\underline{H}_2$, *J* = 5.0 Hz) , 6.07 (s, 2H, O<u>H</u>) , 6.61 (s, 4H, calix-Ar<u>H</u>), 7.03 (s, 4H, calix-Ar<u>H</u>), 7.08 (d, 2H, azobenzene-Ar<u>H</u>, *J* = 8.0 Hz), 7.39 (t, 2H, azobenzene-Ar<u>H</u>, *J* = 8.0 Hz), 7.60 (d, 2H, azobenzene-Ar<u>H</u>, *J* = 8.0 Hz) , 8.19 (s, 2H, azobenzene-Ar<u>H</u>) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 30.9 ($C(\underline{C}H_3)_3$), 31.2 ($Ar_2\underline{C}H_2$), 31.7 ($C(\underline{C}H_3)_3$), 33.8 ($\underline{C}(CH_3)_3$), 33.8 ($\underline{C}(CH_3)_3$), 69.1 ($O\underline{C}H_2$), 74.4 ($O\underline{C}H_2$), 110.9 (azobenzene-Ar<u>C</u>), 116.2 (azobenzene-Ar<u>C</u>), 121.4 (azobenzene-Ar<u>C</u>), 125.2 (calix-Ar<u>C</u>), 125.5 (calix-Ar<u>C</u>), 128.2 (calix-Ar<u>C</u>), 129.8 (azobenzene-Ar<u>C</u>), 131.7 (calix-Ar<u>C</u>), 141.6 (calix-Ar<u>C</u>), 146.7 (calix-Ar<u>C</u>), 150.4 (calix-Ar<u>C</u>), 150.7 (calix-Ar<u>C</u>), 153.7 (azobenzene-Ar<u>C</u>), 159.4 (azobenzene -Ar<u>C</u>) ; Anal. Calcd for $C_{60}H_{70}N_2O_6$: C, 78.74; H, 7.71; N, 3.06 Found: C, 78.41; H, 7.78, N 3.01 mp: 351-352 ^{o}C.

p-**4** was not stable upon exposure to ambient atmosphere.

2.1.3 *Reaction of the Model Compounds*

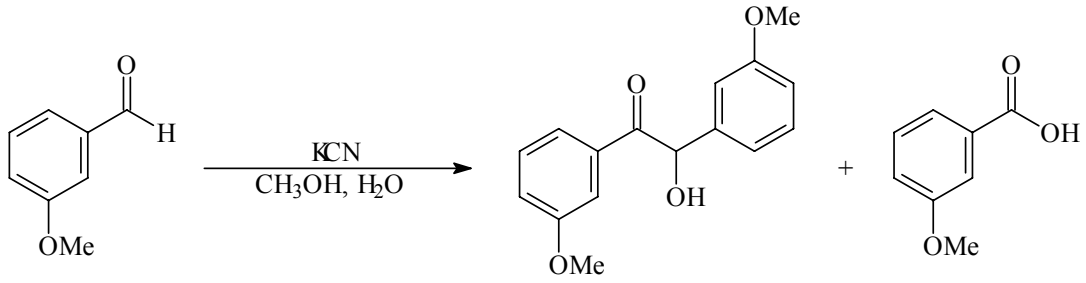
Preparation of Model Compound, 3-Methoxybenzaldehyde



81%

In a 1 L round-bottomed flask equipped with a magnetic bar and a reflux condenser, hydroxybenzaldehyde (245.7 mmol, 30.00 g) and K_2CO_3 (289.4 mmol, 40.00 g) were dissolved in CH_3CN (800 mL). The mixture was refluxed for 30 minutes and methyl iodide (959.6 mmol, 60.00 mL) was then added dropwise. The mixture was refluxed overnight and then allowed to cool to room temperature. The mixture was filtered and washed with CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with aqueous NaOH (4 M, 4 x 25 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by vacuum distillation yielding a colourless liquid as the product (198.3 mmol, 27.00 mL, 81%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 3H, OC<u>H</u>$_3$), 7.05–7.37 (m, 4H, Ar<u>H</u>), 9.88 (s, 1H, ArC<u>H</u>O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.3 (O<u>C</u>H$_3$), 112.1 (Ar<u>C</u>), 121.3 (Ar<u>C</u>), 123.3 (Ar<u>C</u>), 130.0 (Ar<u>C</u>), 137.8 (Ar<u>C</u>), 160.1 (Ar<u>C</u>), 192.1 (Ar<u>C</u>HO); IR (neat) 3070, 3006, 2962, 2942, 2838 (aldehydic C-H stretching), 2733 (aldehydic C-H stretching), 1702 (aldehydic C=O stretching), 1587, 1485, 1464, 1260 cm^{-1}: bp (0.8 bar) = 74 ºC.

Benzoin Condensation[42]



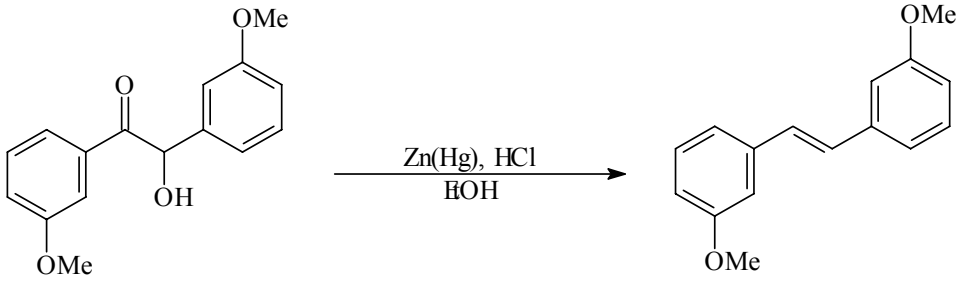
42% 20%

In a 50 mL, round-bottomed flask equipped with a magnetic bar and a reflux condenser, 3-methoxybenzaldehyde (7.34 mmol, 1.00 g) and KCN (1.56 mmol, 0.10 g) were dissolved in 95% ethanol (4.00 mL). The mixture was refluxed for 24 hours and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and then extracted with aqueous NaOH (4 M, 3 x 20 mL). Both organic and aqueous phase were collected.

The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by column chromatography using 30% ethyl acetate in hexane as an eluent yielding a yellow liquid as the desired product, 3,3'-dimethoxybenzoin (1.6 mmol, 0.42 g., 42%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.73 (s, 3H, OC<u>H</u>$_3$), 3.77 (s, 3H, OC<u>H</u>$_3$), 4.52 (d, 1H, O<u>H</u>, *J* = 5.5 Hz), 5.87 (d, 1H, C<u>H</u>OH, *J* = 5.0 Hz), 6.75–7.48 (m, 8H, Ar<u>H</u>) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.2 (O<u>C</u>H$_3$), 55.4 (O<u>C</u>H$_3$), 76.2 (<u>C</u>HOH), 113.1 (Ar<u>C</u>), 113.3 (Ar<u>C</u>), 114.1 (Ar<u>C</u>), 120.1 (Ar<u>C</u>), 120.5 (Ar<u>C</u>), 121.7 (Ar<u>C</u>), 129.6 (Ar<u>C</u>), 130.2 (Ar<u>C</u>), 134.7 (Ar<u>C</u>), 140.4 (Ar<u>C</u>), 159.7 (Ar<u>C</u>), 160.1 (Ar<u>C</u>), 198.7 (<u>C</u>=O).

The aqueous phase was acidified and extracted with CH_2Cl_2 (4 x 25 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by crystallization in CH_2Cl_2/CH_3OH yielding the 3,methoxybenzoic acid as a white solid (1.47 mmol, 0.22 g., 20%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.82 (s, 3H, OC<u>H</u>$_3$), 7.14 (dd, 1H, Ar<u>H</u>, *J* = 8.5, 2.0 Hz), 7.36 (t, 1H, Ar<u>H</u>, *J* = 8.0 Hz), 7.61 (m, 1H, Ar<u>H</u>), 7.71 (d, 1H, Ar<u>H</u>, *J* = 6.5 Hz), 11.17 (br, 1H, ArCOO<u>H</u>) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.4 (O<u>C</u>H$_3$), 114.4 (ArC), 120.4 (ArC), 122.7 (ArC), 129.5 (ArC), 130.6 (ArC), 159.6 (ArC), 172.2 (Ar<u>C</u>OOH).

Preparation of 3,3'-Dimethoxystilbene by Clemmensen Reduction[43]



62%

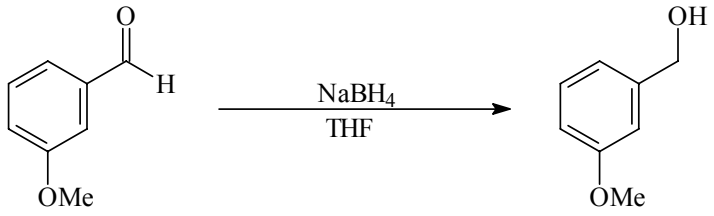
Preparation of Zn(Hg)

In a 50 mL, beaker equipped with a magnetic bar and a reflux condenser, $HgCl_2$ (0.74 mmol, 0.16 g) was stirred in water (10.00 mL) at room temperature and the activated zinc dust (9.79 mmol, 0.64 g) was added rapidly. The mixture was stirred until $HgCl_2$ disappeared. The amalgam was filtered out and washed with water.

Clemmensen Reduction ;

In a 100 mL round-bottomed flask equipped with a magnetic bar freshly prepared amalgam was stirred in 95% ethanol (1.6 mL) and 32% HCl (1.6 mL) at below 15 ^oC in an ice bath. Dimethoxybenzoin (1.54 mmol, 0.42 g) was added slowly. The mixture was stirred for additional 2 hours. The cold water (50 mL) was then added to stop the reaction. The mixture was filtered with Büchner funnel. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and then extracted with water (3 x 20 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by crystallisation in hot EtOH yielding white crystals of *trans-m*-dimethoxybenzoin (0.96 mmol, 0.23 g., 62%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 6H, $OC\underline{H}_3$), 6.81 (ddd, 2H, Ar$\underline{H}$, J = 8.0, 2.5, 1.0 Hz), 7.04 (t, 2H, Ar$\underline{H}$, J = 2.5 Hz), 7.06 (s, 2H, $\underline{H}C{=}C\underline{H}$), 7.10 (dt, 2H, Ar$\underline{H}$, J = 8.0, 1.0 Hz), 7.27 (t, 2H, Ar$\underline{H}$, J = 8.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.3 ($O\underline{C}H_3$), 111.8 (Ar$\underline{C}$H), 113.4 (Ar$\underline{C}$H), 119.3 (Ar$\underline{C}$H), 128.9 ($H\underline{C}{=}\underline{C}H$), 129.7 (Ar$\underline{C}$H), 138.7 (Ar$\underline{C}$), 159.9 (Ar$\underline{C}$).

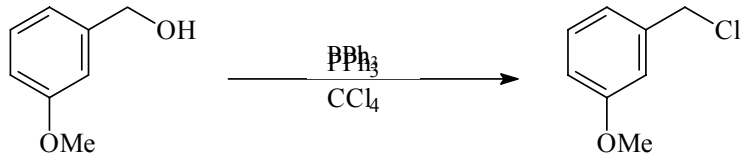
Reduction of 3-Methoxybenzaldehyde[44]



94%

In a 50 mL, round-bottomed flask equipped with a magnetic bar, 3-methoxybenzaldehyde (38.9 mmol, 5.3 g) and $NaBH_4$ (13.2 mmol, 0.50 g.) were dissolved in THF (50 mL). The mixture was stirred for 2 hours at room temperature. Then, the mixture was filtered and washed with CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and then extracted with water (3 x 20 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. Without any further purification, the solvent was evaporated under reduced pressure yielding colourless oil as the product (36.4 mmol, 5.03 g., 94%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 3H, OC<u>H</u>$_3$), 4.62 (d, 2H, C<u>H</u>$_2$OH, *J* = 5.0 Hz), 6.79–7.29 (m, 4H, Ar<u>H</u>) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.2 (O<u>C</u>H$_3$), 64.8 (<u>C</u>H$_2$OH), 112.2 (Ar<u>C</u>), 113.1 (Ar<u>C</u>), 119.1 (Ar<u>C</u>), 129.5 (Ar<u>C</u>), 142.7 (Ar<u>C</u>), 159.7 (Ar<u>C</u>) ; IR (neat) 3070 (br, OH stretching), 3057, 2960, 2832, 2733, 1600, 1488, 1458, 1435 cm^{-1}.

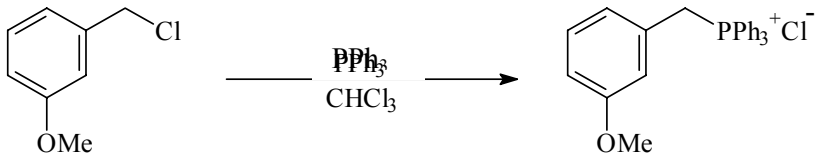
Preparation of 3-Methoxybenzyl chloride[45]



78%

In a 100 mL round-bottomed flask equipped with a magnetic bar, 3-methoxybenzylalcohol (36.2 mmol, 5.00 g) and PPh_3 (36.2 mmol, 9.50 g.) were dissolved in CCl_4 (8.00 mL). The mixture was stirred for 2 hours at room temperature. Then, the mixture was filtered and washed with CCl_4. The filtrate was combined and the solvent was evaporated under reduced pressure. The product was further purified by column chromatography using CH_2Cl_2 as an eluent yielding a colourless liquid as the desired product (28.4 mmol, 4.00 g., 78%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.81 (s, 3H, OC<u>H</u>$_3$), 4.56 (s, 2H, C<u>H</u>$_2$Cl), 6.85–7.31 (m, 4H, Ar<u>H</u>) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 46.2 (O<u>C</u>H$_3$), 55.3 (<u>C</u>H$_2$Cl), 114.0 (Ar<u>C</u>), 114.1 (Ar<u>C</u>), 120.8 (Ar<u>C</u>), 129.8 (Ar<u>C</u>), 138.9 (Ar<u>C</u>), 159.8 (Ar<u>C</u>) ; IR (neat) 3005, 2958, 2834, 1600, 1492, 1454, 1434 cm^{-1}.

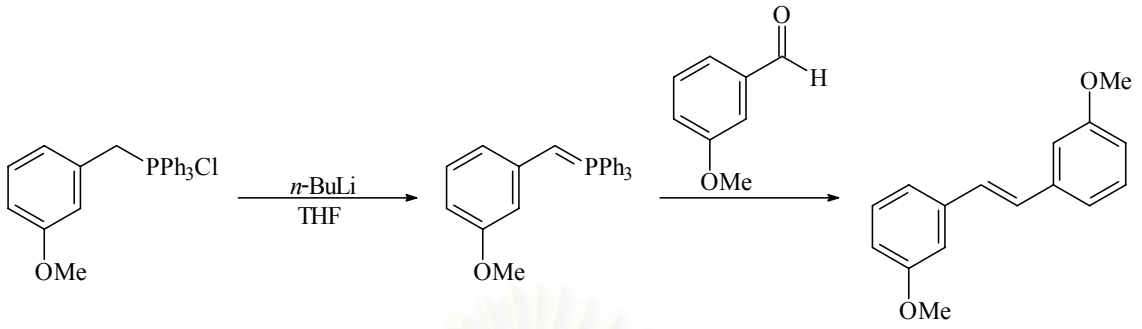
Preparation of 3-Methoxybenzyltriphenylphosphonium Chloride[46]



94%

In a 100 mL round-bottomed flask equipped with a magnetic bar, PPh_3 (28. 5 mmol, 7.50 g.) was dissolved in $CHCl_3$ (15 mL). The mixture was stirred at room temperature and the 3-methoxybenzyl chloride (28. 5 mmol, 4.00 g) was then added slowly. The mixture was stirred for 2 hours at room temperature. The solvent was then evaporated under reduced pressure. The product can be further purified by crystallization in ethyl acetate yielding white crystals (26.7 mmol, 11.20 g., 94%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.52 (s, 3H, OC$\underline{H}_3$), 5.18 (d, 2H, PC$\underline{H}_2$, *J* = 15.5 Hz), 6.49 (s, 1H, Ar$\underline{H}$), 6.60 (d, 2H, Ar$\underline{H}$, *J* = 7.5 Hz), 6.84 (d, 2H, Ar$\underline{H}$, *J* = 8.0 Hz), 7.14 (t, 2H, Ar$\underline{H}$, *J* = 8.0 Hz), 7.63–7.89 (m, 15H, PPh$\underline{H}$).

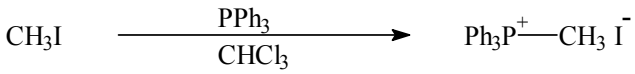
Preparation of 3,3'-Dimethoxystilbene by Wittig Reaction[46]



31%

In a dried two-necked 250 mL round-bottomed flask equipped with a magnetic bar, an ethereal solution of *n*-butyl lithium (1.46 M, 15.00 mL) was dissolved in anhydrous THF (20 mL). The mixture was stirred and 3-methoxybenzyltriphenyl phosphonium chloride (22.7 mmol, 9.50 g) was added cautiously. The mixture turned red after stirring for 4 hours at 50 ^{o}C as the ylide was formed. Freshly distilled 3-methoxybenzaldehyde (22.0 mmol, 3.00 g) was added dropwise using a syringe at 0 ^{o}C and continued stirring for an hour at room temperature. Then, the mixture was filtered and washed with diethyl ether. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in diethyl ether (150 mL) and then extracted with water. The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was further purified by column chromatography using 20% ethyl acetate in hexane as eluent yielding a white crystal as the desired product (7.1 mmol, 1.70 g., 31%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 6H, OC$\underline{H}_3$), 6.81 (ddd, 2H, Ar$\underline{H}$, *J* = 8.0, 2.5, 1.0 Hz), 7.04 (t, 2H, Ar$\underline{H}$, *J* = 2.5 Hz), 7.06 (s, 2H, $\underline{H}$C=C$\underline{H}$), 7.10 (dt, 2H, Ar$\underline{H}$, *J* = 8.0, 1.0 Hz), 7.27 (t, 2H, Ar$\underline{H}$, *J* = 8.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.3 (O$\underline{C}H_3$), 111.8 (Ar$\underline{C}$H), 113.4 (Ar$\underline{C}$H), 119.3 (Ar$\underline{C}$H), 128.9 (H$\underline{C}$=$\underline{C}$H), 129.7 (Ar$\underline{C}$H), 138.7 (Ar$\underline{C}$), 159.9 (Ar$\underline{C}$).

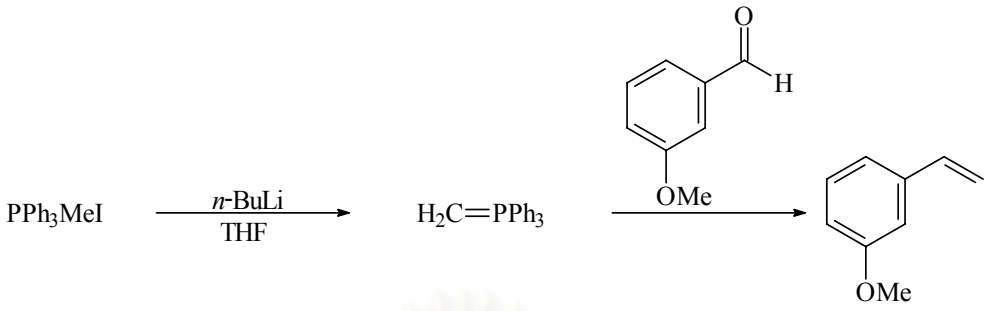
Preparation of Methyltriphenylphosphonium Iodide[46]



95%

In a 100 mL round-bottomed flask equipped with a magnetic bar, PPh_3 (115.6 mmol, 30.33 g.) was dissolved in $CHCl_3$ (10 mL). The mixture was stirred at room temperature and the methyl iodide (159.9 mmol, 29.70 g) was then added slowly. The mixture was stirred for 2 hours at room temperature. The solvent was then evaporated under reduced pressure. The product can be further purified by crystallization in acetone yielding white crystals (151.9 mmol, 61.41 g., 95%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.12 (d, 3H, C<u>H</u>$_3$, J = 13.0 Hz), 7.64–7.80 (m, 15H, Ar<u>H</u>).

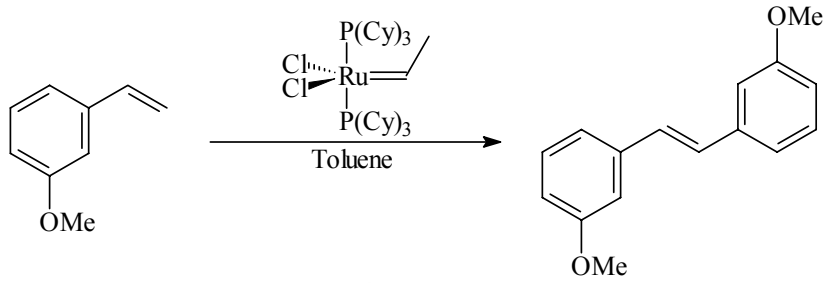
Preparation of 3-Methoxystyrene[46]



45%

In a dried two-necked 100 mL round-bottomed flask equipped with a magnetic bar, an ethereal solution of *n*-butyl lithium (1.25 M, 16.05 mL) was dissolved in anhydrous THF (20 mL). The mixture was stirred and methyltriphenylphosphonium iodide (21.5 mmol, 8.71 g) was added cautiously. The mixture turned red after stirring for 4 hours at room temperature. Freshly distilled 3-methoxybenzaldehyde (29.4 mmol, 4.00 g) was added dropwise using a syringe at 0 ^{o}C and continued stirring for an hour at room temperature. Then, the mixture was filtered and washed with diethyl ether. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in diethyl ether (150 mL) and then extracted with water. The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was further purified by column chromatography using 20% ethyl acetate in hexane as eluent yielding a colourless liquid as the desired product (9.7 mmol, 1.30 g., 45%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.82 (s, 3H, OC$\underline{H}_3$), 5.27 (d, 1H, ArCH=C$\underline{H}_2$, *J* = 11.0 Hz), 5.77 (d, 1H, ArCH=C$\underline{H}_2$, *J* = 17.5 Hz), 6.72 (dd, 1H, ArC$\underline{H}$=CH_2, *J* = 17.5, 11.0 Hz), 6.83 (dd, 1H, Ar$\underline{H}$, *J* = 8.0, 2.5 Hz), 6.98-7.05 (m, 2H, Ar$\underline{H}$), 7.26 (t, 1H, Ar$\underline{H}$, *J* = 8.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.2 (O$\underline{C}H_3$), 111.6 (Ar$\underline{C}$), 113.5 (CH=$\underline{C}H_2$), 114.1 (Ar$\underline{C}$), 118.9 (Ar$\underline{C}$), 129.5 (Ar$\underline{C}$), 136.8 (Ar$\underline{C}$H=CH_2), 139.1 (Ar$\underline{C}$), 159.9 (Ar$\underline{C}$).

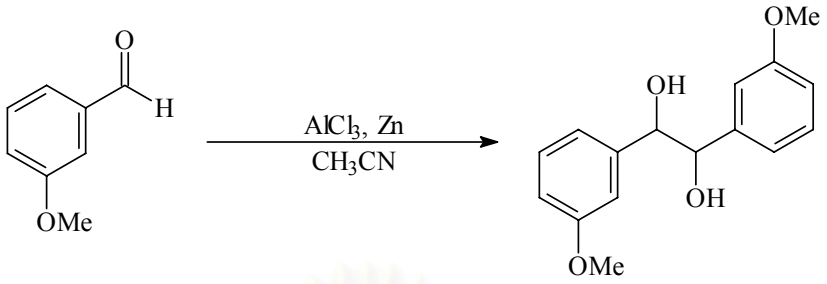
Reaction of 3, -Methoxystyrene with Grubb's Catalyst[47]



no reaction

In a dried 100 mL round-bottomed flask equipped with a magnetic bar, 3-methoxybenzaldehyde (7.45 mmol, 1.00 g) was dissolved in dried toluene (20 mL). The mixture was stirred and Grubb's catalyst (0.61 mmol, 0.50 g) was added. The mixture was stirred at room temperature overnight. The reaction was monitored by TLC showing only starting material on a TLC plate. The reaction was refluxed overnight but the TLC of the reaction mixture still showed only starting material on the TLC plate.

Condensation of 3-Methoxybenzaldehyde by $AlCl_3/Zn$[48]



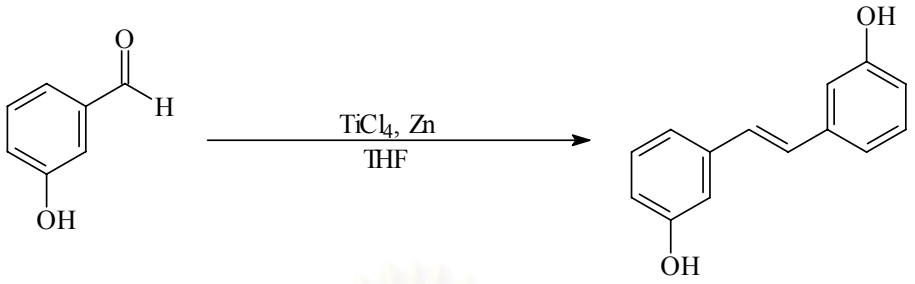
84%

In a dried two-necked 100 mL round-bottomed flask equipped with a magnetic bar, $AlCl_3$ (7.34 mmol, 0.98 g) and activated Zn powder (7.34 mmol, 0.48 g) was added under N_2 atmosphere into dried CH_3CN (25 mL). The mixture was stirred at room temperature and 3-methoxybenzaldehyde (3.67 mmol, 0.50 g) in CH_3CN (5 mL) was added dropwise. The mixture was refluxed overnight. The mixture was then allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and extracted with water for several times. The combined organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was further purified by column chromatography using 20% ethyl acetate in hexane as eluent yielding a white solid as a mixture of diastereomer pinacol products in 1:1 ratio, in stead of the desired stilbene derivative, (overall 1.54 mmol, 0.42 g., 84%):

diastereomer 1: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.67 (s, 6H, OC<u>H</u>$_3$), 4.60 (s, 2H, C<u>H</u>OH), 6.65-6.82 (m, 6H, Ar<u>H</u>), 7.11 (d, Ar<u>H</u>, *J* = 8.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.2 (O<u>C</u>H$_3$), 77.8 (<u>C</u>HOH), 112.3 (Ar<u>C</u>H), 113.6 (Ar<u>C</u>H), 119.3 (Ar<u>C</u>H), 129.0 (Ar<u>C</u>H), 141.4 (Ar<u>C</u>H), 159.3 (Ar<u>C</u>).

diastereomer 2: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.69 (s, 6H, OC<u>H</u>$_3$), 4.75 (s, 2H, C<u>H</u>OH), 6.65-6.82 (m, 6H, Ar<u>H</u>), 7.19 (d, Ar<u>H</u>, *J* = 8.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.2 (O<u>C</u>H$_3$), 78.8 (<u>C</u>HOH), 112.3 (Ar<u>C</u>H), 113.8 (Ar<u>C</u>H), 119.5 (Ar<u>C</u>H), 129.0 (Ar<u>C</u>H), 141.6 (Ar<u>C</u>H), 159.4 (Ar<u>C</u>).

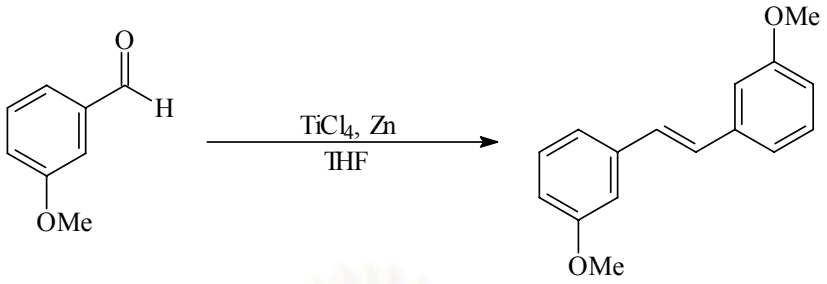
Reaction of 3 -Hydroxybenzaldehyde with TiCl4/Zn [49]



complex mixture

In a dried two-necked 250 mL round-bottomed flask equipped with a magnetic bar, $TiCl_4$ (12.3 mmol, 2.33 g) was added under N_2 atmosphere. Anhydrous THF (30 mL) was added dropwise and activated Zn powder (24.6 mmol, 1.61 g) was added cautiously. The starting Ti(IV) was bright yellow which was gradually turned to green and finally to deep purple or black of Ti(0) upon refluxing with Zn powder for 1 hour. Then, 3-hydroxybenzaldehyde (4.1 mmol, 0.50 g) in THF (10 mL) was added dropwise. The mixture was refluxed for additional 15 hours and it was allowed to cool to room temperature. A solution of K_2CO_3 (15% w/v) was added to quench the excess $TiCl_4$. The mixture was slowly turned from grey to white or pale yellow. The precipitate was filtered over celite and washed with acetone and CH_2Cl_2. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product that showed many decomposed products on the TLC plate.

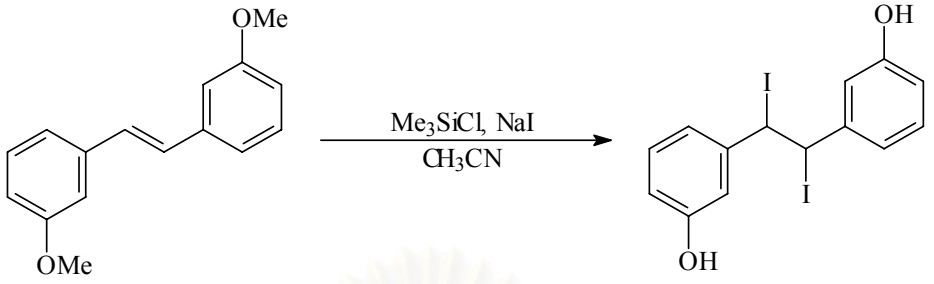
McMurry Coupling of 3,3'-Dimethoxystilbene[49]



80%

In a dried two-necked 500 mL round-bottomed flask equipped with a magnetic bar, $TiCl_4$ (22.0 mmol, 4.18 g) was added under N_2 atmosphere. Anhydrous THF (50 mL) was added dropwise and activated Zn powder (44.1 mmol, 2.88 g) was added cautiously. The starting Ti(IV) was bright yellow which was gradually turned to green and finally to deep purple or black of Ti(0) upon refluxing with Zn powder for 1 hour. Then, 3-methoxybenzaldehyde (7.3 mmol, 1.00 g) in THF (10 mL) was added dropwise. The mixture was refluxed for additional 15 hours and it was allowed to cool to room temperature. A solution of K_2CO_3 (15% w/v) was added to quench the excess $TiCl_4$. The mixture was slowly turned from grey to white or pale yellow. The precipitate was filtered over celite and washed with acetone and CH_2Cl_2. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give a white solid of the *trans*-3,3dimethoxystilbene (5.88 mmol, 1.41 g., 80%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 6H, OC<u>H</u>$_3$), 6.81 (ddd, 2H, Ar<u>H</u>, *J* = 8.0, 2.5, 1.0 Hz), 7.04 (t, 2H, Ar<u>H</u>, *J* = 2.5 Hz), 7.06 (s, 2H, <u>H</u>C=C<u>H</u>), 7.10 (dt, 2H, Ar<u>H</u>, *J* = 8.0, 1.0 Hz), 7.27 (t, 2H, Ar<u>H</u>, *J* = 8.0 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 55.3 (O<u>C</u>H$_3$), 111.8 (Ar<u>C</u>H), 113.4 (Ar<u>C</u>H), 119.3 (Ar<u>C</u>H), 128.9 (H<u>C</u>=<u>C</u>H), 129.7 (Ar<u>C</u>H), 138.7 (Ar<u>C</u>), 159.9 (Ar<u>C</u>).

Demethylation of 3,3'-Dimethoxystilbene[50]



88%

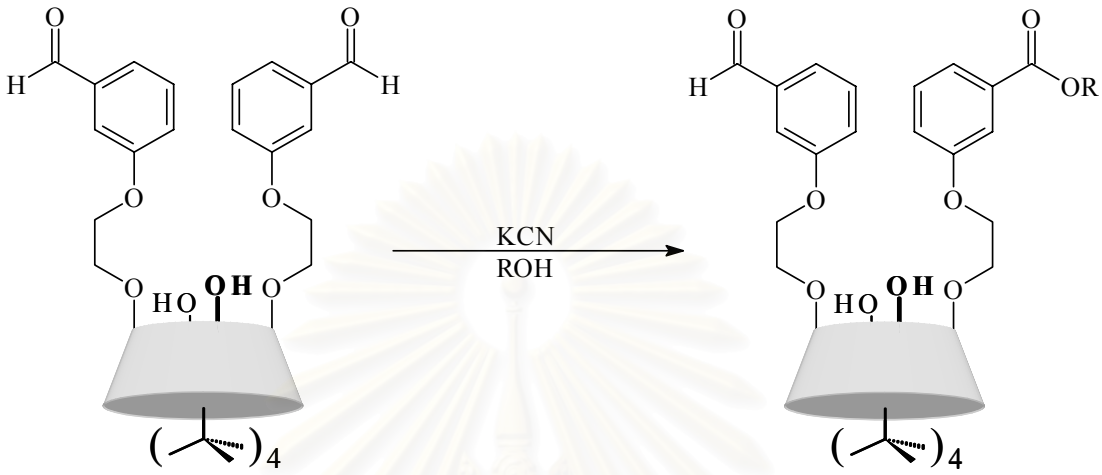
In a dried two-necked 250 mL round-bottomed flask equipped with a magnetic bar, 3,3'-dimethoxystilbene (2.08 mmol, 0.50 g) and NaI (16.64 mmol, 2.48 g) was added under N_2 atmosphere into dried CH_3CN (20 mL). The mixture stirred in the dark at room temperature and $SiMe_3Cl$ (16.64 mmol, 1.80 g) was added dropwise. The mixture was refluxed for 1 hour and it was allowed to cool to room temperature. The water (20 mL) was added to quench the reaction. The mixture was extracted with diethyl ether (3 x 20 mL). The organic phase was washed with aqueous $Na_2S_2O_3$ and brine and then dried over anhydrous Na_2SO_4. The solvent was removed to give a white solid. as a mixture of diastereomer 1,2-diiodo-1,2-di-(3,3'-dihydroxyphenyl)ethane in 3:1 ratio, in stead of the desired stilbene derivative (overall 0.94 mmol, 0.44 g., 88%):

diasteromer 1 (75%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.78 (s, 2H, C<u>H</u>I), 6.54-6.65 (m, 6H, Ar<u>H</u>), 7.04 (t, Ar<u>H</u>, *J* = 7.5 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 37.5 (<u>C</u>HI), 112.2 (Ar<u>C</u>H), 114.8 (Ar<u>C</u>H), 119.3 (Ar<u>C</u>H), 128.7 (Ar<u>C</u>H), 143.2 (Ar<u>C</u>H), 156.8 (Ar<u>C</u>).

diasteromer 2 (25%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.78 (s, 2H, C<u>H</u>I), 6.54-6.65 (m, 6H, Ar<u>H</u>), 7.05 (t, Ar<u>H</u>, *J* = 7.5 Hz) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 39.0 (<u>C</u>HI), 113.8 (Ar<u>C</u>H), 116.3 (Ar<u>C</u>H), 120.8 (Ar<u>C</u>H), 130.2 (Ar<u>C</u>H), 144.7 (Ar<u>C</u>H), 158.2 (Ar<u>C</u>).

2.1.4 Other Reactions of m-Bisbenzaldehydecalix[4]arene[38]

Reaction with KCN in Alcoholic solvent



Ethyl-**5** = 50%

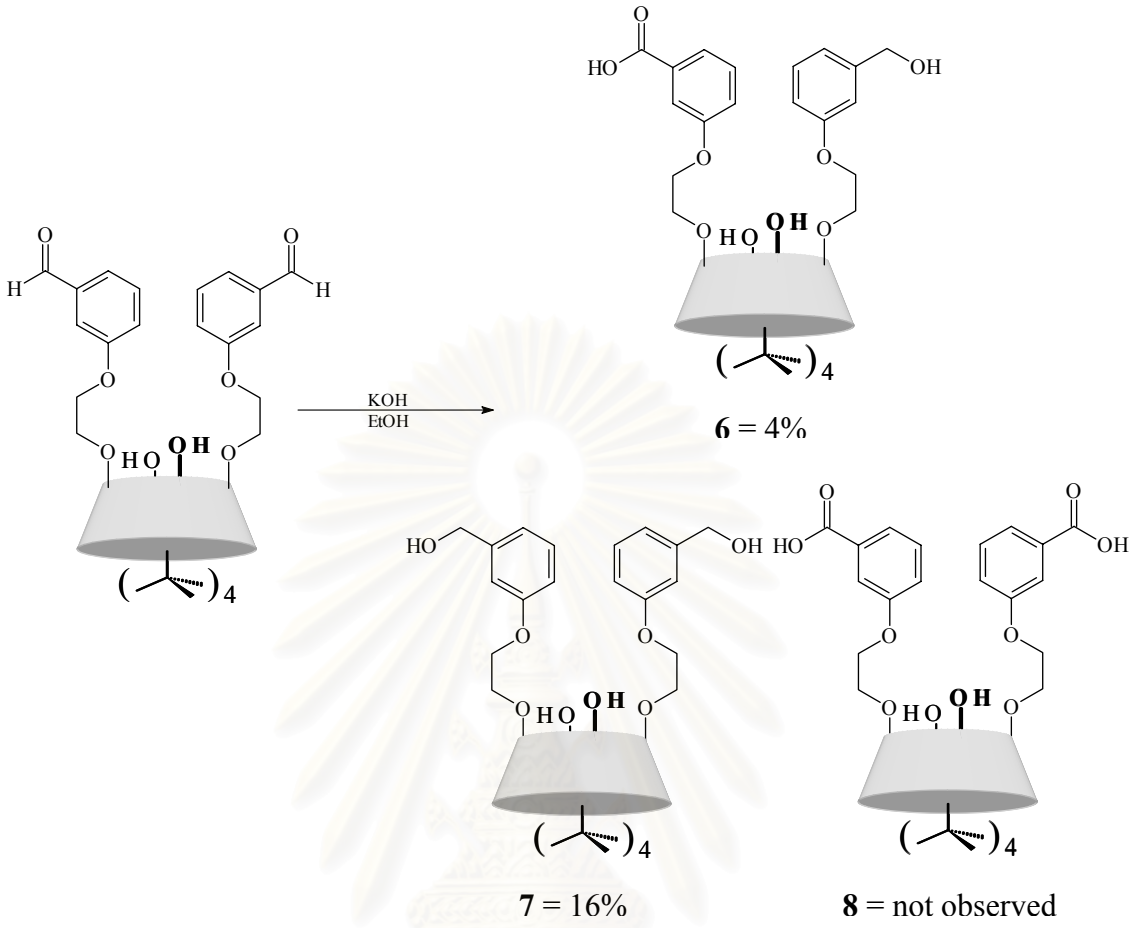
i-Propyl-**5** = 15%

In a 100 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser, bis-*m*-benzaldehyde (0.6 mmol, 0.50 g) and KCN (0.15 mmol, 0.01 g) were dissolved in 95% ethanol (20 mL). The mixture was refluxed for 24 hours and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and then extracted with aqueous HCl (2 M, 3 x 20 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by crystallisation in CH_2Cl_2/CH_3OH yielding the desired product as a white solid.

Ethyl-**5** (0.3 mmol, 0.25 g., 50%): mp(decomposed) = 133-134^{o}C.; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.03 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.30 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.40 (t, 3H, OCH$_2$C$\underline{H}_3$, *J* = 8.0 Hz), 3.34 (d, 4H, Ar$_2$C$\underline{H}_2$, *J* = 12.0 Hz), 4.34-4.43 (m, 14H, Ar$_2$C$\underline{H}_2$, OC$\underline{H}_2$ and OC$\underline{H}_2$CH$_3$), 6.88 (s, 4H, calix-Ar$\underline{H}$), 7.07 (s, 4H, calix-Ar$\underline{H}$), 7.18 (d, 1H, benzoate-Ar$\underline{H}$, *J* = 8.0 Hz), 7.25 (d, 1H, benzaldehyde-Ar$\underline{H}$, *J* = 8.0 Hz), 7.35 (t, 1H, benzoate-Ar$\underline{H}$, *J* = 8.0 Hz), 7.43-7.50 (m, 5H, benzaldehyde-Ar$\underline{H}$ and O$\underline{H}$), 7.61 (d, 1H, benzoate-Ar$\underline{H}$, *J* = 4.0 Hz), 7.67 (s, 1H, benzoate-Ar$\underline{H}$), 9.92 (s, 1H, ArC$\underline{H}$O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 14.2 (OCH$_2$$\underline{C}H_3$), 31.0 (C($\underline{C}H_3$)$_3$), 31.6 (C($\underline{C}H_3$)$_3$), 31.7 ($\underline{C}$(CH$_3$)$_3$), 33.8 (Ar$_2$$\underline{C}H_2$), 34.0 (Ar$_2$$\underline{C}H_2$), 53.2 (O$\underline{C}H_2CH_3$), 61.0 (O$\underline{C}H_2$), 66.8 (O$\underline{C}H_2$), 66.9 (O$\underline{C}H_2$), 73.7 (O$\underline{C}H_2$), 113.7 (benzaldehyde-Ar$\underline{C}$), 114.8 (benzoate-Ar$\underline{C}$), 120.3 (benzoate-Ar$\underline{C}$), 122.2 (benzaldehyde-Ar$\underline{C}$), 122.3 (benzoate-Ar$\underline{C}$), 123.3 (benzaldehyde-Ar$\underline{C}$), 125.1 (calix-Ar$\underline{C}$), 125.7 (calix-Ar$\underline{C}$), 127.7 (calix-Ar$\underline{C}$), 129.4 (benzoate-Ar$\underline{C}$), 130.1 (benzaldehyde-Ar$\underline{C}$), 131.7 (benzoate-Ar$\underline{C}$), 132.8 (calix-Ar$\underline{C}$), 137.7 (benzaldehyde-Ar$\underline{C}$), 141.4 (calix-Ar$\underline{C}$), 147.1 (calix-Ar$\underline{C}$), 149.7 (calix-Ar$\underline{C}$), 150.4 (calix-Ar$\underline{C}$), 158.5 (benzoate-Ar$\underline{C}$), 159.1 (benzaldehyde-Ar$\underline{C}$), 166.4 (Ar$\underline{C}$O$_2$Et), 192.1 (Ar$\underline{C}$HO); IR (KBr pellet) ν_{max} 3363 (Ar-OH), 3047, 2958, 2870 (aldehydic CH stretching), 2727 (aldehydic C-H stretching), 1716 (carboxylate C=O stretching), 1701 (aldehydic C=O stretching), 1589, 1485, 1446, 1277, 1200 cm-1; Anal. Calcd for $C_{64}H_{76}O_9$: C, 77.70; H, 7.74; Found: C, 77.80; H, 7.77.

i-propyl-**5** (0.1 mmol, 0.09 g, 15%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.25 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.33 (d, 6H, OCH(C$\underline{H}_3$)$_2$, *J* = 6.0 Hz), 3.29 (d, 4H, Ar$_2$$\underline{H}_2$, *J* = 13.0 Hz), 4.09-4.41 (m, 14H, Ar$_2$$\underline{H}_2$, OC$\underline{H}_2$ and OC$\underline{H}$(CH$_3$)$_2$), 6.84 (s, 4H, calix-Ar$\underline{H}$), 7.02 (s, 4H, calix-Ar$\underline{H}$), 7.20-7.43 (m, 8H, benzaldehyde-Ar$\underline{H}$ and benzoate-Ar$\underline{H}$), 7.55 (s, 1H, benzaldehyde-Ar$\underline{H}$), 7.62 (d, 1H, benzoate -Ar$\underline{H}$, *J* = 7.5 Hz), 9.92 (s, 1H, ArC$\underline{H}$O) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 21.9 (OCH(C$\underline{H}_3$)$_2$), 31.1 (C($\underline{C}$H$_3$)$_3$), 31.3 (C($\underline{C}$H$_3$)$_3$), 31.7 ($\underline{C}$(CH$_3$)$_3$), 33.8 (Ar$_2$$\underline{C}H_2$), 34.0 (Ar$_2$$\underline{C}H_2$), 66.8 (O$\underline{C}H_2$), 66.9 (O$\underline{C}H_2$), 68.5 (O$\underline{C}$H(CH$_3$)$_2$), 73.7 (O$\underline{C}H_2$), 113.7 (benzaldehyde-Ar$\underline{C}$), 114.9 (benzoate-Ar$\underline{C}$), 120.2 (benzoate-Ar$\underline{C}$), 122.2 (benzaldehyde-Ar$\underline{C}$), 122.3 (benzoate-Ar$\underline{C}$), 123.3 (benzaldehyde-Ar$\underline{C}$), 125.2 (calix-Ar$\underline{C}$), 125.7 (calix-Ar$\underline{C}$), 127.8 (calix-Ar$\underline{C}$), 129.4 (benzoate-Ar$\underline{C}$), 130.1 (benzaldehyde-Ar$\underline{C}$), 132.2 (benzoate-Ar$\underline{C}$), 132.9 (calix-Ar$\underline{C}$), 137.7 (benzaldehyde-Ar$\underline{C}$), 141.4 (calix-Ar$\underline{C}$), 147.1 (calix-Ar$\underline{C}$), 149.7 (calix-Ar$\underline{C}$), 150.6 (calix-Ar$\underline{C}$), 158.5 (benzoate-Ar$\underline{C}$), 159.2 (benzaldehyde-Ar$\underline{C}$), 165.9 (Ar$\underline{C}$O$_2$CH(CH$_3$)$_2$), 192.1 (Ar$\underline{C}$HO); Anal Calcd for $C_{65}H_{78}O_9.CH_2Cl_2$: C, 72.84; H, 7.41; Found: C, 73.25; H, 7.55.

Cannizzaro Reaction[51]



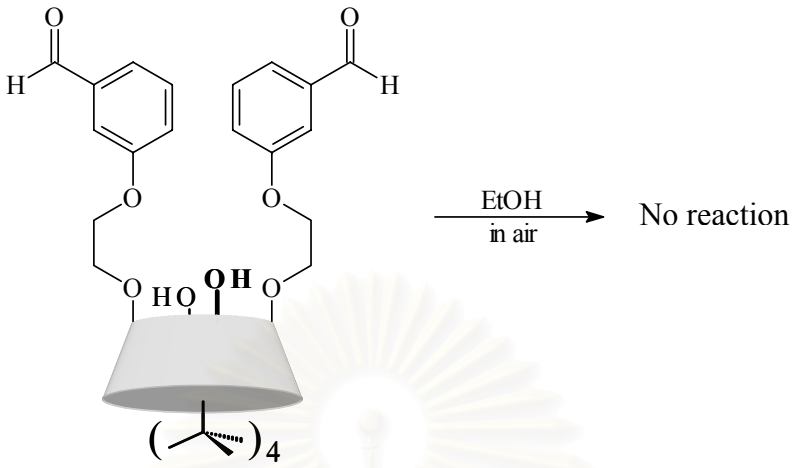
In a 100 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser, bis-*m*-benzaldehyde (0.6 mmol, 0.50 g) and KOH (3.6 mmol, 0.20 g) were dissolved in 95% ethanol (15 mL). The mixture was refluxed for 24 hours and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (50 mL) and then extracted with aqueous HCl (2 M, 3 x 20 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The products were further purified by column chromatography using 20% ethyl acetate in CH_2Cl_2 as an eluent yielding two products as white solids.

alcohol-acid (**6**) (0.02 mmol, 0.02 g, 4%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 18H, $C(C\underline{H}_3)_3$), 1.03 (s, 18H, $C(C\underline{H}_3)_3$), 3.30 (t, 4H, $Ar_2C\underline{H}_2$, J = 13, 6.5 Hz), 4.06 – 4.42 (m, 12H, $Ar_2C\underline{H}_2$ and $OC\underline{H}_2$), 4.66 (s, 2H, $ArC\underline{H}_2OH$), 7.05–7.11 (m, 4H, Ar$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 31.1 ($C(\underline{C}H_3)_3$), 31.7 ($C(\underline{C}H_3)_3$), 31.9 ($Ar_2\underline{C}H_2$), 33.8 ($\underline{C}(CH_3)_3$), 34.0 ($\underline{C}(CH_3)_3$), 65.1 ($Ar\underline{C}H_2OH$), 66.6 ($O\underline{C}H_2$), 67.0 ($O\underline{C}H_2$), 74.1 ($O\underline{C}H_2$), 74.1 ($O\underline{C}H_2$), 112.8 (benzyl alcohol-Ar$\underline{C}$), 114.4 (benzoic-Ar$\underline{C}$), 114.8 (benzyl alcohol-Ar$\underline{C}$), 119.6 (benzyl alcohol-Ar$\underline{C}$), 121.9 (benzoic-Ar$\underline{C}$), 122.9 (benzoic-Ar$\underline{C}$), 125.1 (calix-Ar$\underline{C}$), 125.7 (calix-Ar$\underline{C}$), 127.9 (calix-Ar$\underline{C}$), 129.5 (benzoic-Ar$\underline{C}$), 130.9 (benzyl alcohol-Ar$\underline{C}$), 132.8 (benzoic-Ar$\underline{C}$), 141.5 (benzyl alcohol-Ar$\underline{C}$), 142.2 (calix-Ar$\underline{C}$), 147.0 (calix-Ar$\underline{C}$), 147.0 (calix-Ar$\underline{C}$), 150.0 (calix-Ar$\underline{C}$), 150.5 (calix-Ar$\underline{C}$), 158.6 (benzoic-Ar$\underline{C}$), 158.7 (benzyl alcohol-Ar$\underline{C}$), 170.0 ($Ar\underline{C}O_2H$).

bisalcohol (**7**) (0.09 mmol, 0.08 g, 16%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H, $C(C\underline{H}_3)_3$), 1.25 (s, 18H, $C(C\underline{H}_3)_3$), 3.29 (d, 4H, $Ar_2C\underline{H}_2$, J = 13.0 Hz), 4.30-4.40 (m, 12H, $Ar_2C\underline{H}_2$ and $OC\underline{H}_2$), 4.60 (s, 4H, $ArC\underline{H}_2OH$), 6.84-7.02 (m, 16H, Ar$\underline{H}$), 7.20-7.29 (m, 2H, benzyl alcohol-Ar$\underline{H}$) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 30.9 ($C(\underline{C}H_3)_3$), 31.1 ($C(\underline{C}H_3)_3$), 31.7 (Ar_2CH_2), 33.8 ($C(\underline{C}H_3)_3$), 34.0 ($C(\underline{C}H_3)_3$), 64.9 ($Ar\underline{C}H_2OH$), 66.6 ($O\underline{C}H_2$), 74.0 ($O\underline{C}H_2$), 112.7 (benzyl alcohol-Ar$\underline{C}$), 114.6 (benzyl alcohol-Ar$\underline{C}$), 119.4 (benzyl alcohol-Ar$\underline{C}$), 125.2 (calix-Ar$\underline{C}$), 125.7 (calix-Ar$\underline{C}$), 128.3 (calix-Ar$\underline{C}$), 129.5 (benzyl alcohol-Ar$\underline{C}$), 132.9 (calix-Ar$\underline{C}$), 141.5 (calix-Ar$\underline{C}$), 142.7 (benzyl alcohol-Ar$\underline{C}$), 147.1 (calix-Ar$\underline{C}$), 149.9 (calix-Ar$\underline{C}$), 150.5 (calix-Ar$\underline{C}$), 158.8 (benzyl alcohol-Ar$\underline{C}$).

Bisacid (**8**) could not be separated from the column.

Reaction with Oxygen in Air



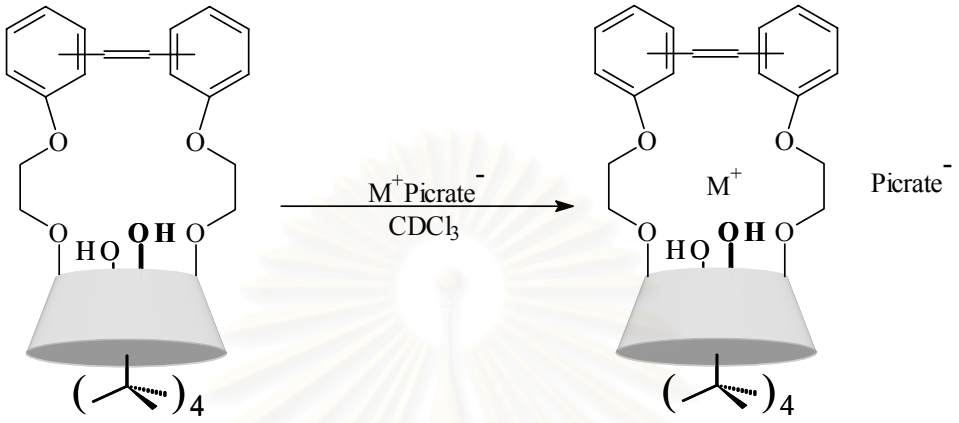
In a 100 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser, bis-*m*-benzaldehyde (0.6 mmol, 0.50 g) were refluxed with ethanol (15 mL) for 5 days and then allowed to cool to room temperature. The TLC trace did not show any products but only the un-reacted starting material.

2.1.5 Preparation of metal picrate salts[36]

In a 50 mL Erlenmayer flask, picric acid (8.73 mmol, 2.0 g) was dissolved in ethanol (20 mL). The solution was stirred at room temperature. The metal carbonate (4.36 mmol) was dissolved in small amount of ethanol (if the metal carbonate cannot completely dissolve in ethanol, tiny amount of water was added as a co-solvent). Then the metal carbonate solution was added dropwise into the stirring picric acid solution. The mixture was heated to slowly evaporate the ethanol. As a result, the picrate salt was obtained as yellow crystal in quantitative yield.

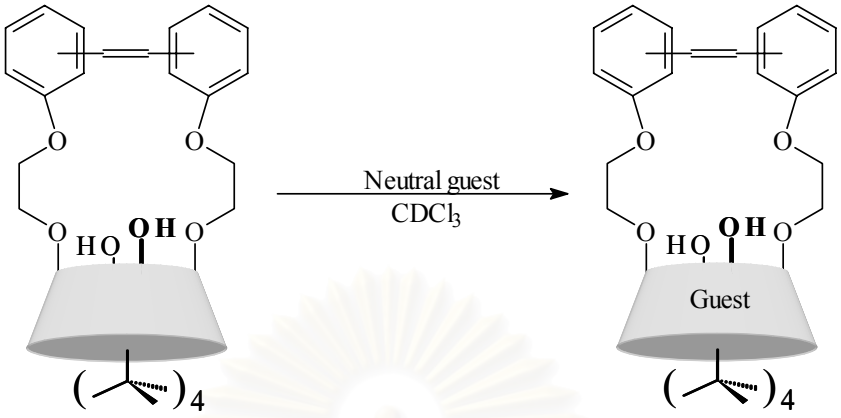
2.2 Complexation

2.2.1 Complexation with Metal Picrate[39]



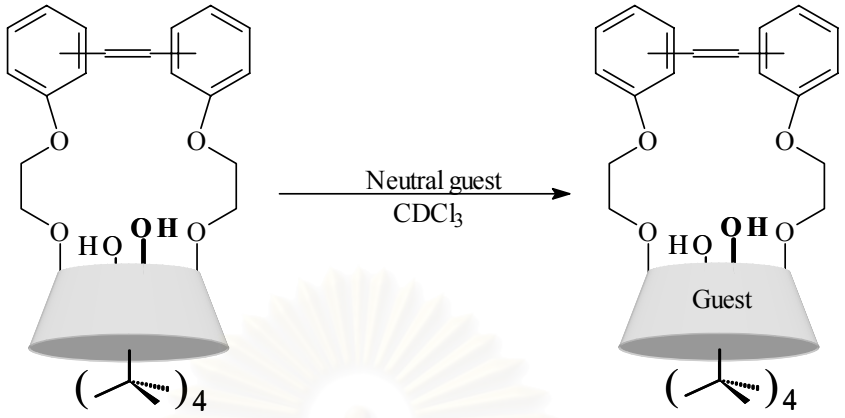
In an NMR tube, **3** (3.0 μmol, 2.74 mg) or **4** (3.0 μmol, 2.75 g) was dissolved with chloroform-*d* (0.70 mL). The metal picrate (30.0 μmol) was added as a solid into the solution. The mixture was sonicated for 1 hour at room temperature. The yellow colour solution of the picrate anion indicated the complexation. The NMR spectra of the complex were recorded.

2.2.2 Complexation with Neutral Molecules[41),(52)]



In an NMR tube, **3** (3.0 μmol, 2.74 mg) were dissolved with chloroform-*d* (0.70 mL). The ^{1}H-NMR spectrum was collected. One equivalent of neutral guest molecule (0.30 M, 10.00 μL) was added into the solution using a micro syringe. Since there was no colour indicator in complexation as in metal picrate, the ^{1}H-NMR spectrum of the mixture was collected to determine the complexation from the Δδ of the guest proton.

2.3 NMR Titration[34), (41)]



In an NMR tube, **3** (3.0 μmol, 2.74 mg) were dissolved into chloroform-*d* (0.70 mL) to make a 4.286 mM of the host solution. The mixture was titrated with neutral guest solution (85.71 mM) which was prepared by dissolving guest molecule (85.71 μmol) into $CDCl_3$ (1.0 mL) in a vial capped with a rubber septum. The guest solution (7 μL) was added stepwise into the host solution until the total volume of guest solution reached 70 μL. The addition volume was increased to 10 μL in each addition until the total guest solution reached 100 μL. The addition volume was increased again to 25 and 50 μL until the total volume of guest solution reached 350 μL. The increasing of addition volume was necessary to obtain significant Δδ towards the end of titration. The NMR spectra of the mixture were collected at every addition. The complexation constant was determined using EQNMR curve fitting program.[53] The program required concentration of total host and total guest molecule at each data point, together with the chemical shift of a host proton shifted during the titration. For the first cycle of calculation, an initial value of complexation constant was arbitrarily guessed and put in. The titration curved was plotted between the titrant volume and the chemical shift of a selected host proton. The calculated values from the program were a complexation constant with error and a 1:1 complex chemical shift with error.

2.4 Photoisomerisation[40]

2.4.1 Photostationary State Determination

In an NMR tube, **3** or **4** (3.0 μmol) were dissolved into chloroform-*d* (0.70 mL). The NMR spectrum of the solution was recorded. The solution was then exposed to the UV light using Hanovia 450 W medium pressure mercury lamp at 30 cm distance. The NMR spectra of the solution were collected at various time intervals to determine the photostationary state. The *cis*-: *trans*-ratio the compound was determined from integration of the appropriate corresponding signals to the *cis*- and *trans*-isomers.

2.4.2 Photoswitchable Complexation Study

In an NMR tube, **3** (3.0 μmol, 2.74 mg) were dissolved into chloroform-*d* (0.70 mL). The guest molecule, CH_3CN or CH_3NO_2 (3.0 μmol in 35 μL of $CDCl_3$) was added into the host solution. The NMR of the mixture was collected. The mixture was then exposed to the UV light using Hanovia 450 W medium pressure mercury lamp at 30 cm distance. The NMR spectra of the mixture were collected at the photostationary state. The *cis*-: *trans*-ratio the compound was determined from integration of the appropriate corresponding signals to the *cis*- and *trans*-isomers. The release of the guest molecules was determined from the chemical shift of the guest molecule in the solution mixture.

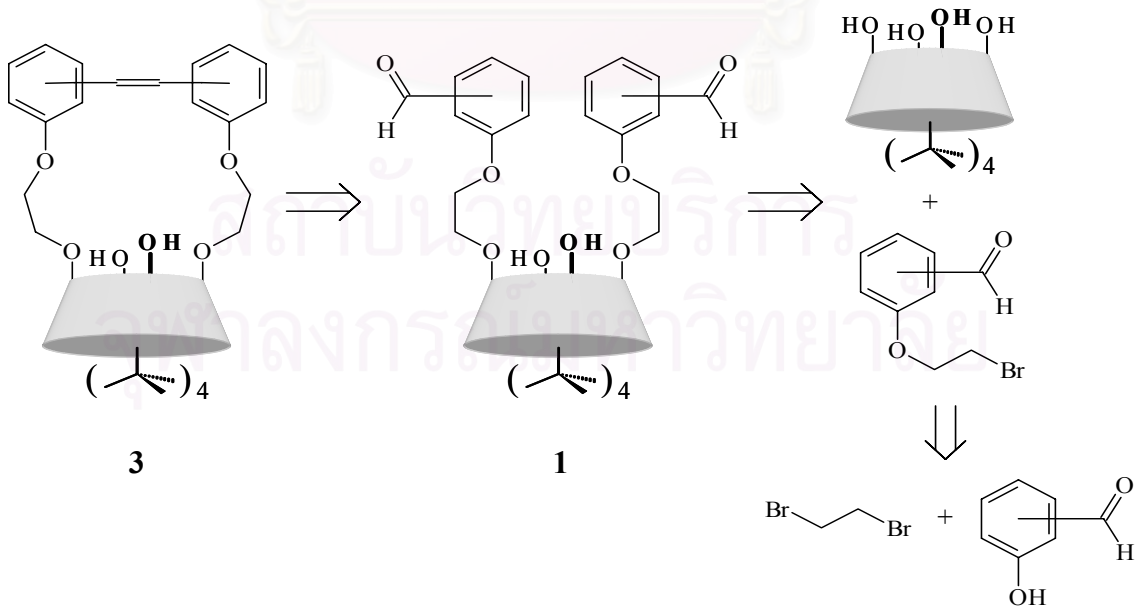
CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis

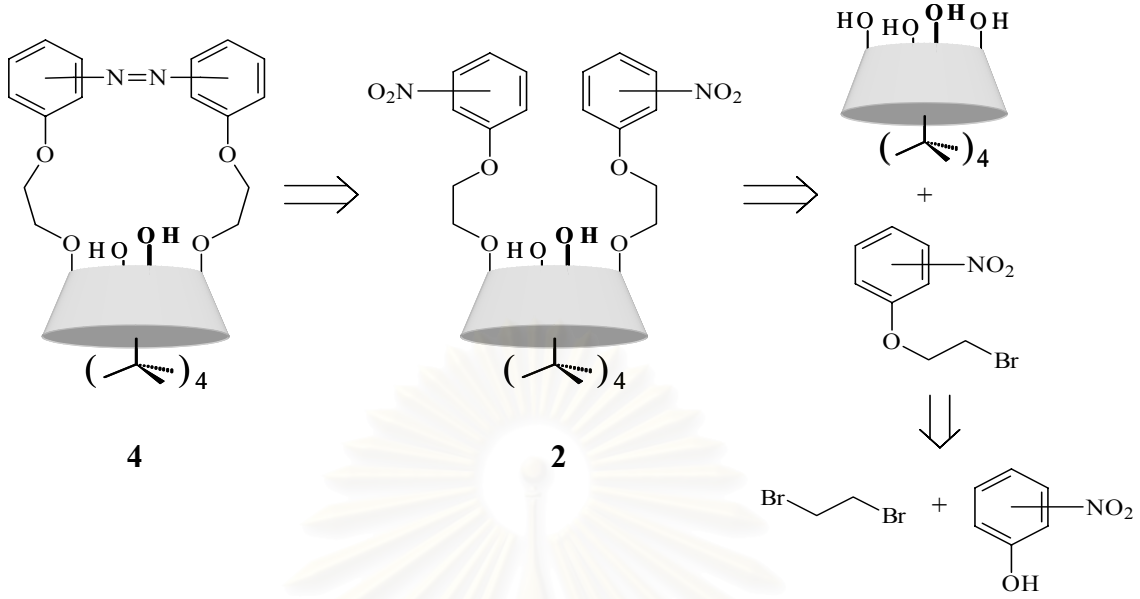
The retro-synthesis of the stilbene derivatives **3** (**Scheme 3.1.1**) started from breaking the bridging double bond into two aldehyde groups. These *bis*benzaldehyde derivatives were detached into *p-tert*-butylcalix[4]arene and two corresponding bromoethoxybenzaldehyde units. The bromoethoxybenzaldehyde was disconnected into two simple molecules, hydroxybenzaldehyde and 1,2-dibromoethane.

The *ortho*- isomer of the azobenzene derivatives were previously synthesised by Ms. Pipoosananakaton in 2000.[39] The same retro-synthesis was thus proposed to synthesise the *meta*- and *para*- analogues **4** (**Scheme 3.1.2**). The retro-synthesis started from breaking the bridging nitrogen double bond into two nitro groups. These bisnitrobenzene derivatives were detached into *p-tert*-butylcalix[4]arene and two corresponding bromoethoxynitrobenzene units. The bromoethoxynitrobenzene was disconnected into two simple molecules, hydroxynitrobenzene and 1,2-dibromoethane.



3 **1**

Scheme 3.1.1: Disconnection approach for stilbene bridged calix[4]arene



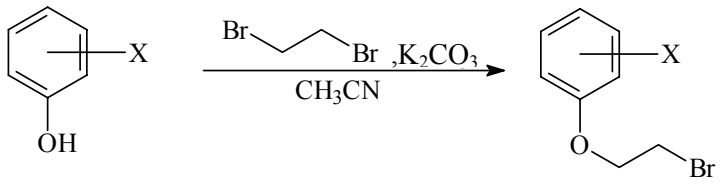
Scheme 3.1.2: Disconnection approach for azobenzene bridged calix[4]arene

3.1.1 Preparation of bisbenzaldehydecalix[4]arene and bisnitrobenzenecalix[4]arene

Both bisbenzaldehyde and bisnitrobenzenecalix[4]arenes were synthesised by nucleophilic substitution of the corresponding 2-bromoethoxyarene and *p-tert*-butylcalix[4]arene.[38],[39] The 2-bormoethoxyarene starting materials were synthesised by nucleophilic substitution of the corresponding hydroxyarenes and 1,2-dibromoethane.[37]

For the first step, nucleophilic substitution of dibromoethane (**Scheme 3.1.3**), all starting material should be mixed well before heating in order to reduce the disubstitution by-product. The completion of the reaction was simply indicated by the colour of the reaction mixture. The deep yellow colour of the phenolate anion disappeared toward the end of the reaction.

For benzaldehyde derivatives, the product was obtained in 80, 76 and 88% yields for *ortho*-, *meta*- and *para*- isomer respectively. Similarly, the nitrobenzene derivatives, the product was obtained in 83 and 71% yields for *meta*- and *para*- isomers respectively.



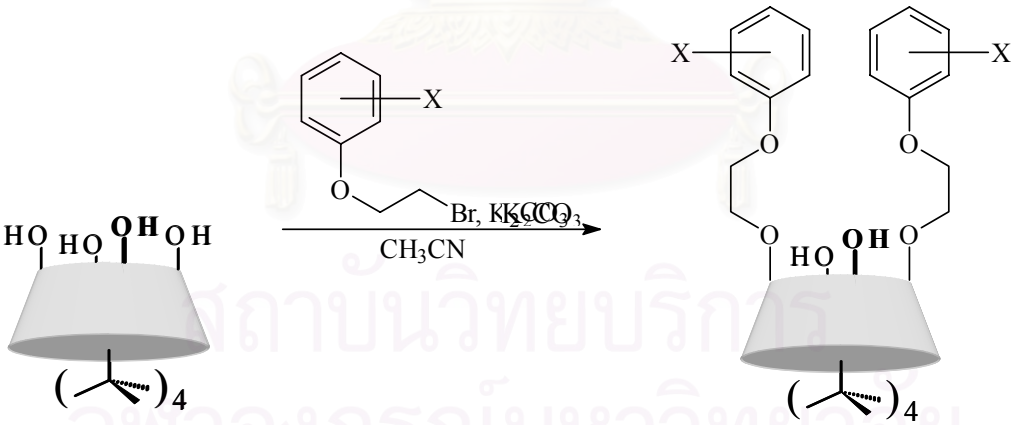
X = CHO : *o*- = 80%, *m*- = 76%, *p*- = 88%

X = NO_2 : *m*- = 83%, *p*- = 71%

Scheme 3.1.3: Nucleophilic substitution of dibromoethane

The second step was the nucleophilic substitution of bromoethoxybenzaldehyde and boromoethoxynitrobenzene on calix[4]arene ring (**Scheme 3.1.4**).

For benzaldehyde derivatives, the desired product was obtained in 70, 60 and 55% yield for *ortho-, meta-* and *para-* isomers respectively. And for the nitrobenzene derivatives, the product was obtained in 70 and 80% yields for *meta-* and *para-* isomers respectively.



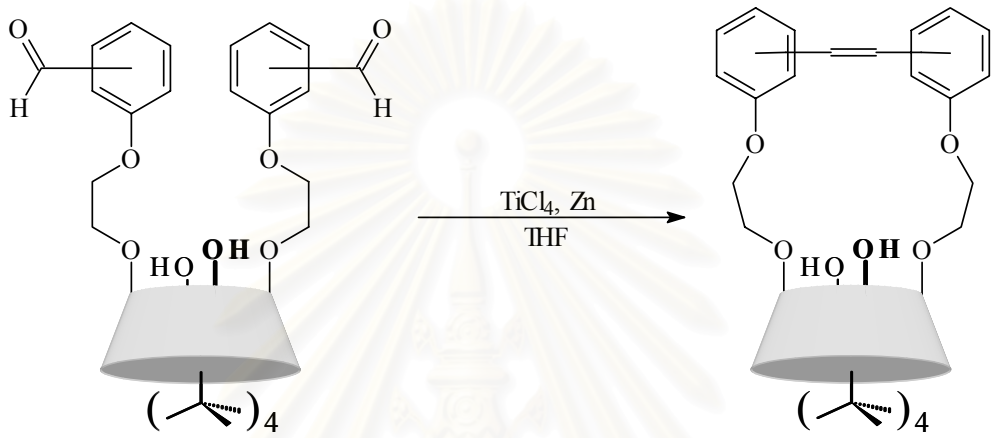
X = CHO : *o*-**1** = 70%, *m*-**1** = 60%, *p*-**1** = 55%

X = NO_2 : *m*-**2** = 70%, *p*-**2** = 80%

Scheme 3.1.4: Nucleophilic substitution of bromoethoxyarene derivatives on calix[4] arene

3.1.2 Preparation of the stilbene bridged calix[4]arene derivatives

There have been reports that McMurry coupling is not generally compatible with substrates containing phenolic proton.[54] Despite the presence of two phenolic OH group on the calix[4]arene, McMurry coupling between two aldehyde groups was surprisingly successful in all bisbenzaldehyde isomers conducted in this work (**Scheme 3.1.5**).[40), (41)



1

cis-o-**3** = 57%, *trans-o*-**3** = 10%,
cis-m-**3** = 20%, *trans-m*-**3** = 8%,
cis-p-**3** = 51%

Scheme 3.1.5: McMurry coupling of bisbenzaldehydecalix[4]arene

The *m*-stilbene bridged calix[4]arene was prepared under McMurry condition to give both *cis*- and *trans*-stilbenes in 28% yield (**Table 3.1.1**). The reaction also gave 20% of the corresponding pinacol by-product. This result also indicated that the pinacol was an intermediate of this reductive coupling. The coupling reaction of the *o*- and *p*-bisbenzaldehydes gave higher yields of stilbenes at 67% and 51%, respectively, without observable pinacol. Both *cis*- and *trans*-stilbenes were obtained from the coupling reaction of *o*- and *m*-bisbenzaldehydes but the *trans*-stilbene was not obtained from the *para*- isomer.

Table 3.1.1: Products from the synthesis of stilbene bridged calix[4]arenes

Products	% Yield		*cis*: trans ratio
	cis	***trans***	
o-**3**	57	10	85 : 15
m-**3**	20	8	73 : 27
p-**3**	51	0	100 : 0

All *cis*- and *trans*-stilbene derivatives possess C_2 axis, the coupling between two vinylic protons in ^{1}H-NMR spectra, which would normally be used for distinguishing between *cis*- and *trans*-isomers, does not exist. The assignment of *cis*- and *trans*-geometries was thus based on the chemical shift of the vinylic proton and the UV-Vis absorption using the parent *cis*- and *trans*-unsubstituted stilbenes as references. According to the chemical shifts observed for the unsubstituted stilbenes, the *cis*-geometry was assigned to the isomer possessing vinylic protons with lower chemical shift (**Table 3.1.2**).

Table 3.1.2: Chemical shifts of the vinylic protons of **3** and stilbene in $CDCl_3$

Compound	^{1}H-NMR (ppm)	
	cis-isomer	*trans*-isomer
o-**3**	7.25	7.74
m-**3**	6.71	7.24
p-**3**	6.68	-
Stilbene	6.57	7.15

This assignment is consistent with the data from UV-Vis spectra (as shown in **Figure 3.1.1**) that showed shorter λ_{max} and lower extinction coefficients for all *cis*-isomers (**Table 3.1.3**) due to the twisted geometry of the *cis*-isomers caused by the steric repulsion between two *ortho*- hydrogens on each benzene ring (**Figure 3.1.2**).

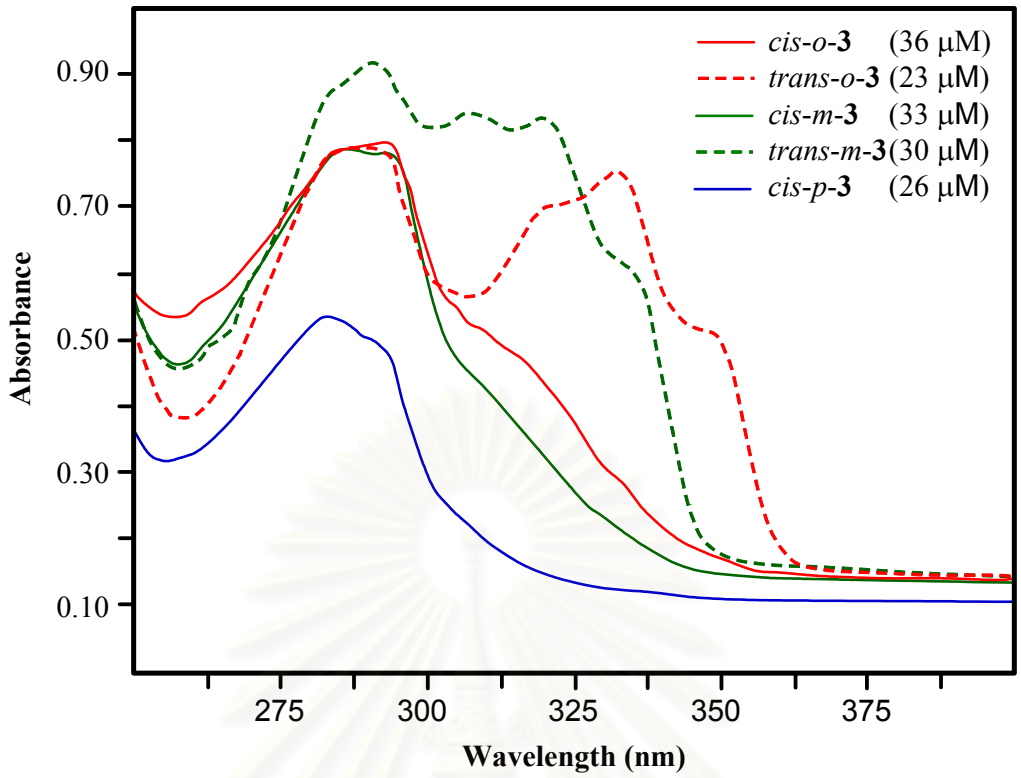
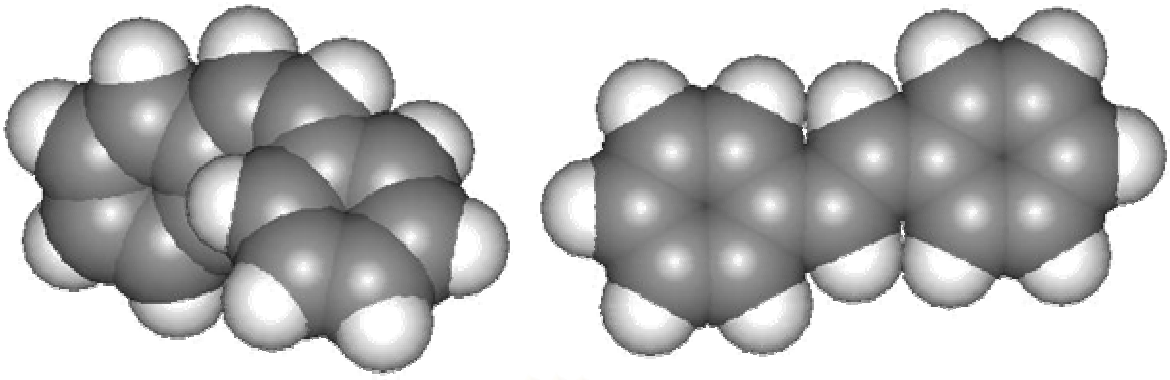


Figure 3.1.1: UV spectra of stilbenecalixarene **1**

Table 3.1.3: λ_{max} and Extinction coefficient (ε) of the stilbene products and stilbene (in CH_2Cl_2)

Compound	*cis*-isomer		*trans*-isomer	
	λ_{max} (nm)	ε (cm^{-1} M^{-1})	λ_{max} (nm)	ε (cm^{-1} M^{-1})
o-**3**	292	19321	291 333	30106 28492
m-**3**	286	20955	291 308 320	27488 24866 24629
p-**3**	283	16632	-	-
Stilbene[a]	223 276	20600 10900	227 294 307	21000 33200 32100

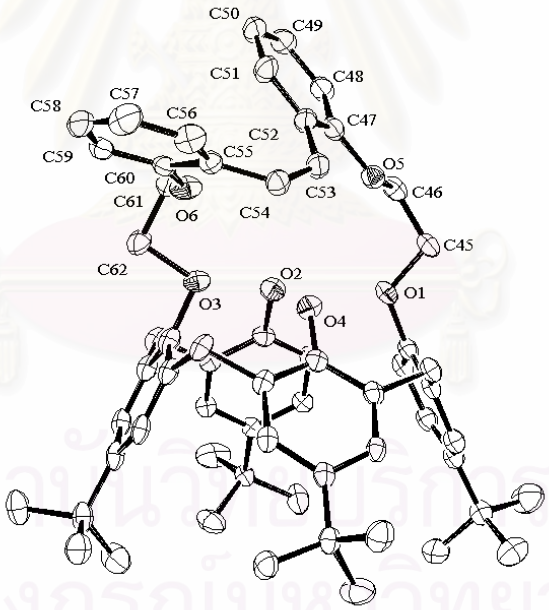
[a]measured in methanol.



cis-stilbene *trans*-stilbene

Figure 3.1.2: CPK models of *cis*- and *trans*-stilbene

This structural assignment was confirmed by X-ray crystallography. The compound proposed to be *cis*-*o*-stilbene bridged calix[4]arene was successfully crystallised as a single crystal. The X-ray crystal structure was in agreement with the proposed structure (**Figure 3.1.3**).[40]



cis-*o*-**3**

Figure 3.1.3: X-ray crystallographic structure of *cis*-*o*-stilbene bridged calix[4]arene

The predominant formation of the *cis*-over *trans*-products in the McMurry coupling reaction suggested that the pre-organised structure of the starting bisbenzaldehydecalix[4]arene should play an important role in controlling the geometry of the product. The short ethylene glycol linkages over the small and rigid lower rim of

the *p-tert*-butylcalix[4]arene are less likely to allow the formation of the *threo* orientation of the two benzaldehyde moieties (**Figure 3.1.4**) resulting in less *trans*-product. The situation becomes most obvious for the coupling of the bis-*p*-benzaldehyde in which no *trans*-isomer was observed as the *threo* like orientation would be most difficult to form.

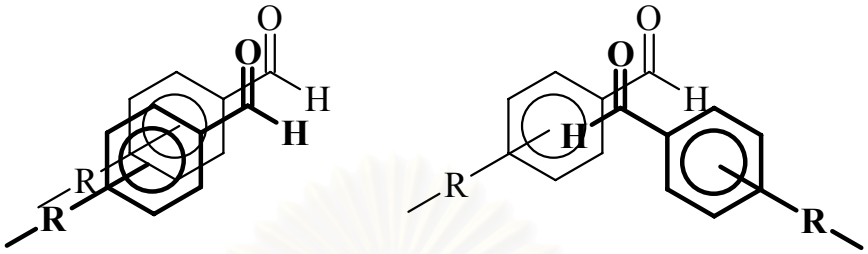


Figure 3.1.4: Proposed orientations of the two benzaldehyde groups that would lead to the formation of *cis*- and *trans*-products

3.1.3 Preparation of the azobenzene bridged calix[4]arene derivatives

The *ortho*- isomer was synthesised by Ms. Pipoosananakaton in 2000.[39] Therefore, the same methodology of the synthesis was utilised for *meta*- and *para*-isomers. The only problem was the very low yield from this reductive coupling method. From this method, the *ortho*- isomer gave only 8% yield (**Table 3.1.2**) and even worse; the *meta*- isomer gave completely 0%. When the reaction of *m*-bisnitrobenzene was conducted under elevated pressure (3 atm), *trans-m*-azobenzene analogue was obtained in 59% yield (**Table 3.1.4**)

Table 3.1.4 Yields in the synthesis of azobenzene bridged calix[4]arenes

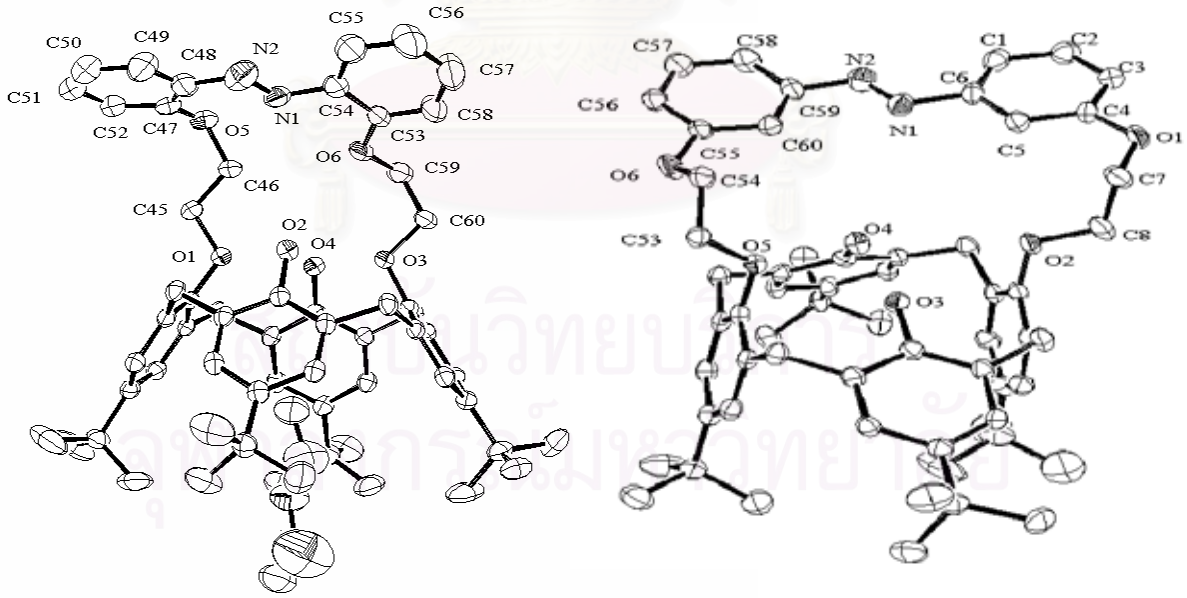
Products	% Yield	
	cis	*Trans*
o-**4**[a]	0	8
m-**4**	0	59
p-**4**	0	0

[a]ambient pressure method

This reaction was normally used *i*-propanol/water mixture media. The high pressure method was performed in a high-pressure glass tube and the reaction was operated under nitrogen pressure of 3 atm at 130 ºC. Under such an elevated pressure the temperature raised up to 130 ^{o}C, higher than the normal boiling point of the solvents. This might be a favourable thermodynamic factor for the reductive coupling process.

The reaction of bis-*m*-nitrobenzene at atmospheric pressure left only the starting nitrobenzene analogues. The reaction of *p*-bisnitrobenzene however seemed to give an unstable *p*-azobenzene product as the colour of the terminated reaction solution changed rapidly from bright orange to dark brown upon its exposure to the air and moisture and no desired product could be isolated afterwards.

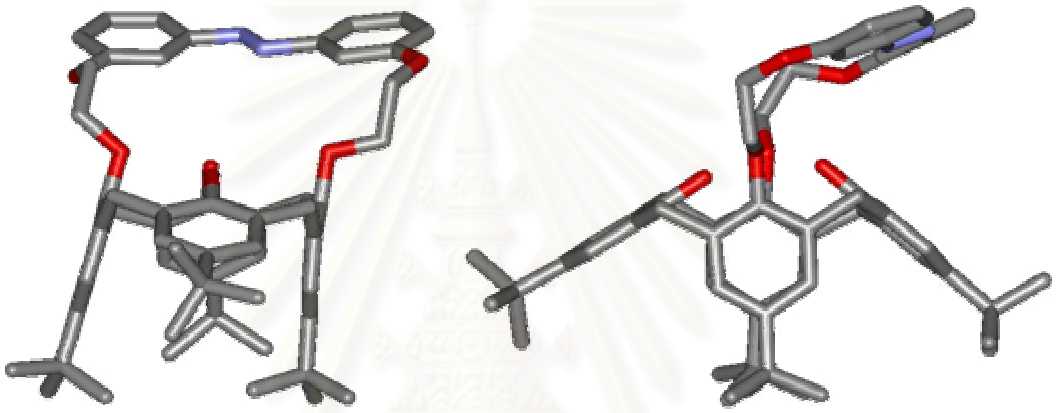
In cases of azobenzene derivatives, there was only one product isolated for each of the *o*-azobenzene and *m*-azobenzene bridged calix[4]arene. Since only one stereoisomer of the azobenzene is available and the nitrogen contains no proton to be observed by ^{1}H-NMR, the assignment of *cis*- and *trans*-isomer was only possible through X-ray crystallography. Fortunately, both azobenzene derivatives could be crystallised into single crystals suitable for X-rays crystallography. The X-rays structure of these azobenzene derivatives revealed that both compounds were the *trans*-isomers (**Figure 3.1.5**).[41]



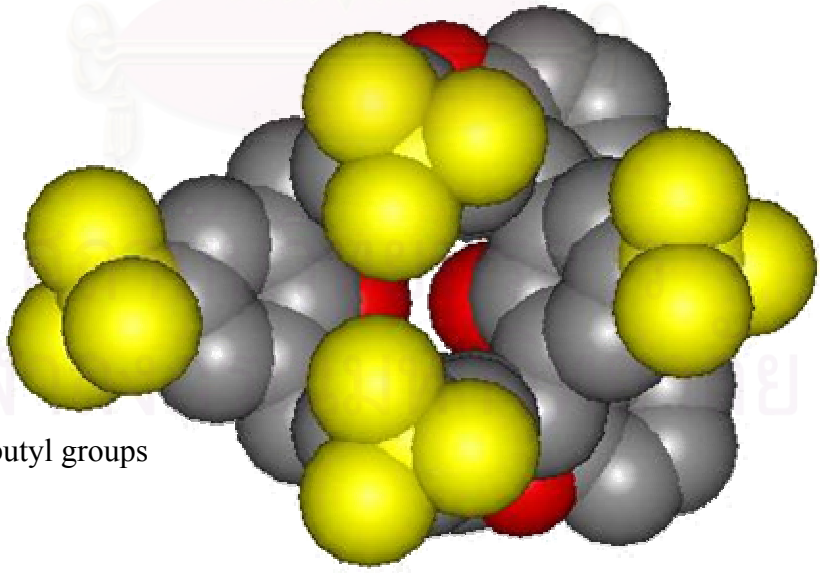
trans-o-**4** *trans-m*-**4**

Figure 3.1.5: X-ray crystal structures of *trans-o*-azobenzene and *trans-m*-azobenzenecalix[4]arene

It is of interest to point out here that the X-ray structure shows that *trans-o*-**4** is crystallised as an inclusion complex with the ethyl acetate solvent while *trans-m*-**4** crystallised as a single compound. The cone conformation of calix[4]arene is significantly distorted into a pinched cone conformation[31] for *trans-m*-**4**. The pinched cone conformation posses an oval shape of the wider rim of the calix[4]arene. The X-ray structure of *trans-m*-4 clearly shows that the oval shape of the wider is sterically unfavourable for the entrance of any molecule as two tert-butyl groups are so closed to each other (**Figure 3.1.6**). While the cone conformation of *trans-o*-**4** posses a circle shape of wider rim (**Figure 3.1.7**).



Front Side



Yellow = *tert*-butyl groups

Bottom (CPK)

Figure 3.1.6: Distortion of calix[4]arene ring in *trans-m*-azobenzenecalix[4]arene in X-ray structure

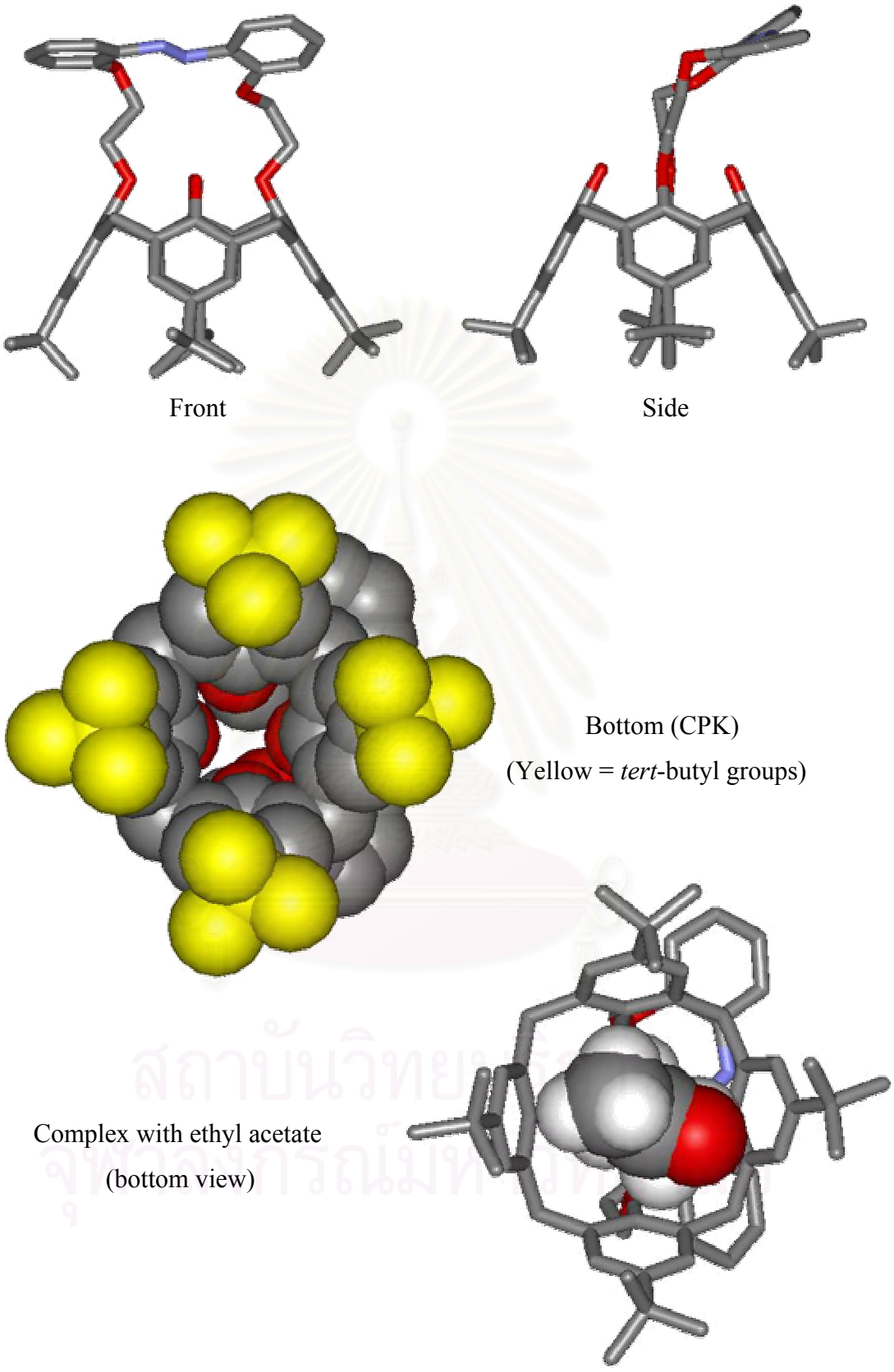
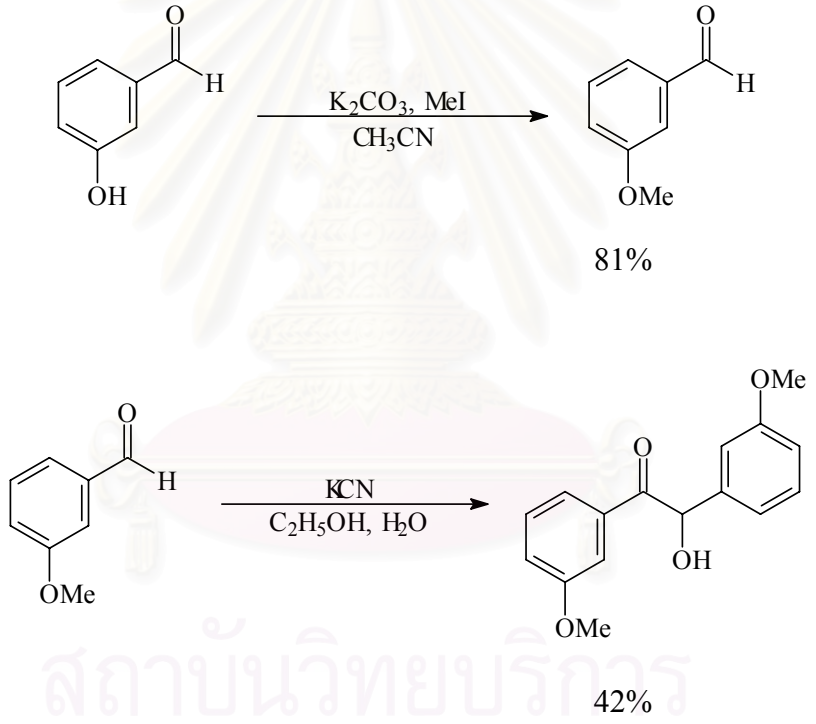


Figure 3.1.7: Circular cone shape of calix[4]arene ring in *trans*-*o*-azobenzenecalix[4] arene in X-ray structure

3.1.4 Approaches towards the construction of stilbene bridge across the calix[4]arene lower rim (The synthesis of model compounds and reactions of bisbenzaldehydecalix[4]arene)

During the attempt in synthesis of stilbene-bridged calix[4]arene, several reactions of aldehyde group were performed. A few interesting results merit for discussion are presented here. Initially, 3,3'-dimethoxystilbene was synthesised as a model compound. Synthetic approaches were carried out starting from 3-methoxybenzaldehyde. This 3-methoxybenzaldehyde was easily prepared by the same nucleophilic substitution condition as the preparation of 3-(2-bromoethoxy)-benzaldehyde (**Scheme 3.1.6**). The product was obtained in 81% yield.

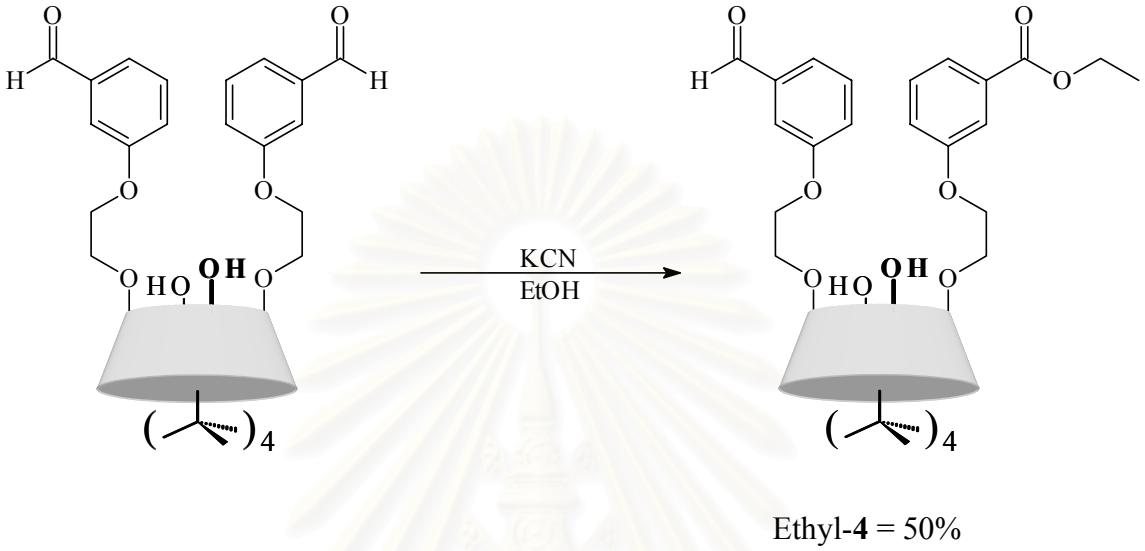


Scheme 3.1.6: Synthesis of 3,3'-dimethoxybenzoin

The first method selected for the synthesis of the model stilbene was the benzoin coupling[42] followed by Clemmensen reduction.[43] Using the 3-methoxybenzaldehyde as a starting material, the corresponding benzoin can be synthesised in 42% yield using KCN (20% mol) as a catalyst in ethanol (**Scheme 3.1.6**).

The benzoin condensation of bis-*m*-benzaldehydecalix[4]arene was performed under the same condition as that used in the condensation of the model compound. Thus, the benzoin coupling was applied to bis-*m*-benzaldehydecalix[4]arene. There was only

one product observed on TLC which was isolated by re-crystallisation in methanol/CH_2Cl_2 to give a white crystalline material. The ^{1}H-NMR and ^{13}C-NMR spectra of the isolated material suggested that it was not the expected benzoin but the mono-ethyl ester (**Scheme 3.1.7**). The yield was approximately 50%.[38]



Scheme 3.1.7: Reaction of bis-*m*-benzaldehydecalix[4]arene with KCN in ethanol

The structure of product was elucidated by NMR spectroscopy. From the ^{1}H-NMR spectrum, the aldehydic proton was still observed around 10 ppm but with the integral of only one half of the original signal of the starting bisbenzaldehyde. This indicated the presence of one aldehyde group remained unreacted. However, the *tert*-butyl groups showed only 2 signals instead of the expected 3 signals for the unsymmetrical 1,3-substituted *tert*-butylcalix[4]arene. This may be due to the fact that the reaction on the benzaldehyde groups did too little effect to change the environment of the *tert*-butyl group.

There were also 2 new signals resembled to the ethyl group of ethyl acetate but there was no observable methyl signal corresponding to the acetate group. These two proton signal remained in the spectrum in spite of removal of all volatile substances under vacuum. Therefore the ^{13}C-NMR spectrum was collected and the 2 sp^3 carbon signals of ethyl group were clearly observed at 15 and 60 ppm (**Figure 3.1.8**).

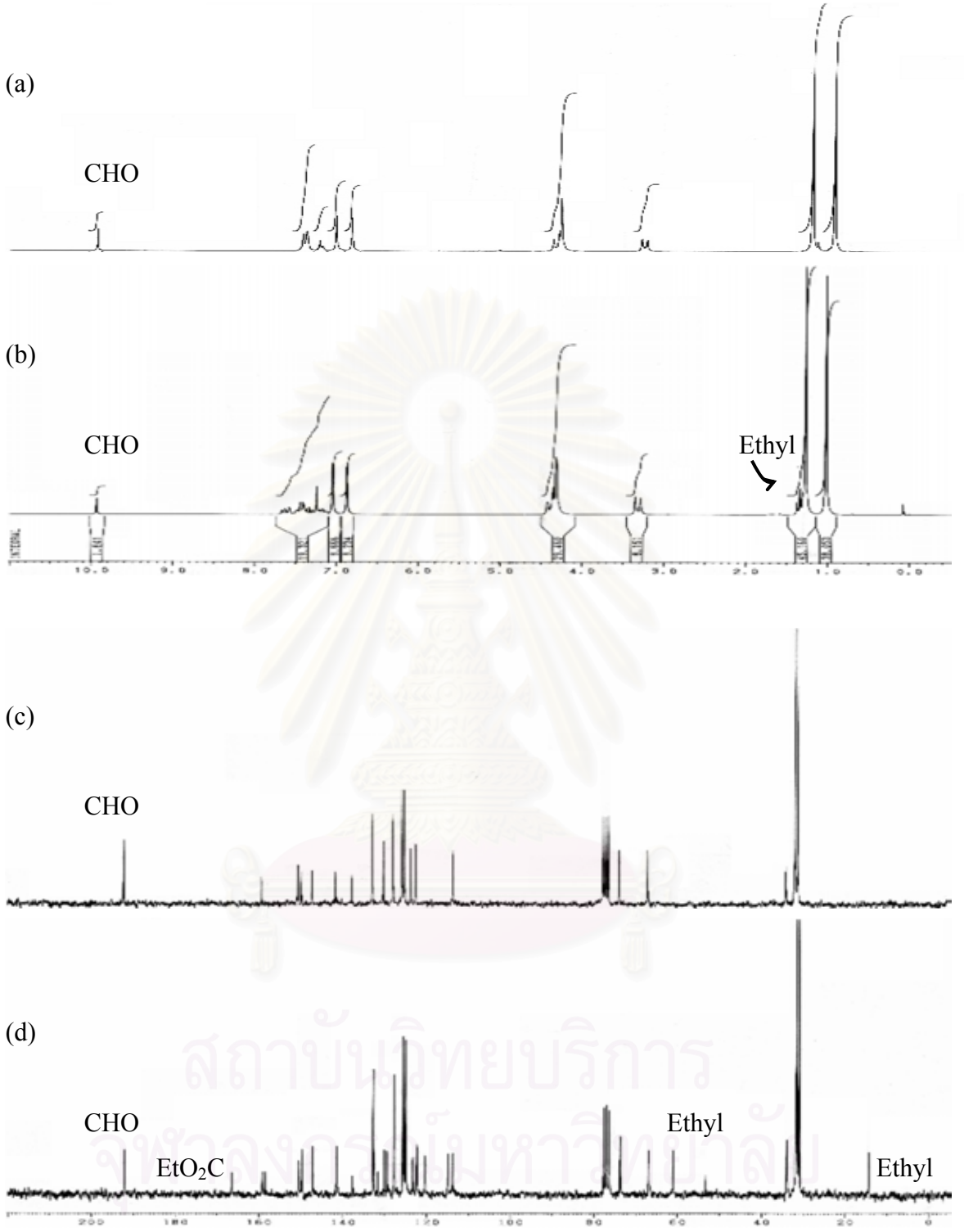


Figure 3.1.8: ^{1}H-NMR spectra of KCN catalysed selective oxidation: (a) ^{1}H-NMR of *m*-**1** (b) ^{1}H-NMR of ethyl-**5** (c) ^{13}C-NMR spectrum of *m*-**1** and (c) ^{13}C-NMR spectrum of ethyl-**5**

From the 1D-NMR evidences the mono ethyl ester was proposed to be the product. To confirm the functionality of this product the IR spectrum was collected. There were 2 carbonyl signals belonging to the aldehyde and ester at 1699 and 1716 cm^{-1}, respectively.

Another basic characterisation was elemental analysis. The EA gave 77.80% C and 7.77% H, while the calculation for the mono ethyl ester ($C_{64}H_{76}O_9$) gave 77.70% C and 7.74% H.

All signals in ^{1}H-NMR and ^{13}C-NMR were assigned corresponding to the proposed structure of the product with the aid of 2D-NMR. (**Figure 3.1.9**, **Figure 3.1.10** and **Figure 3.1.11**)

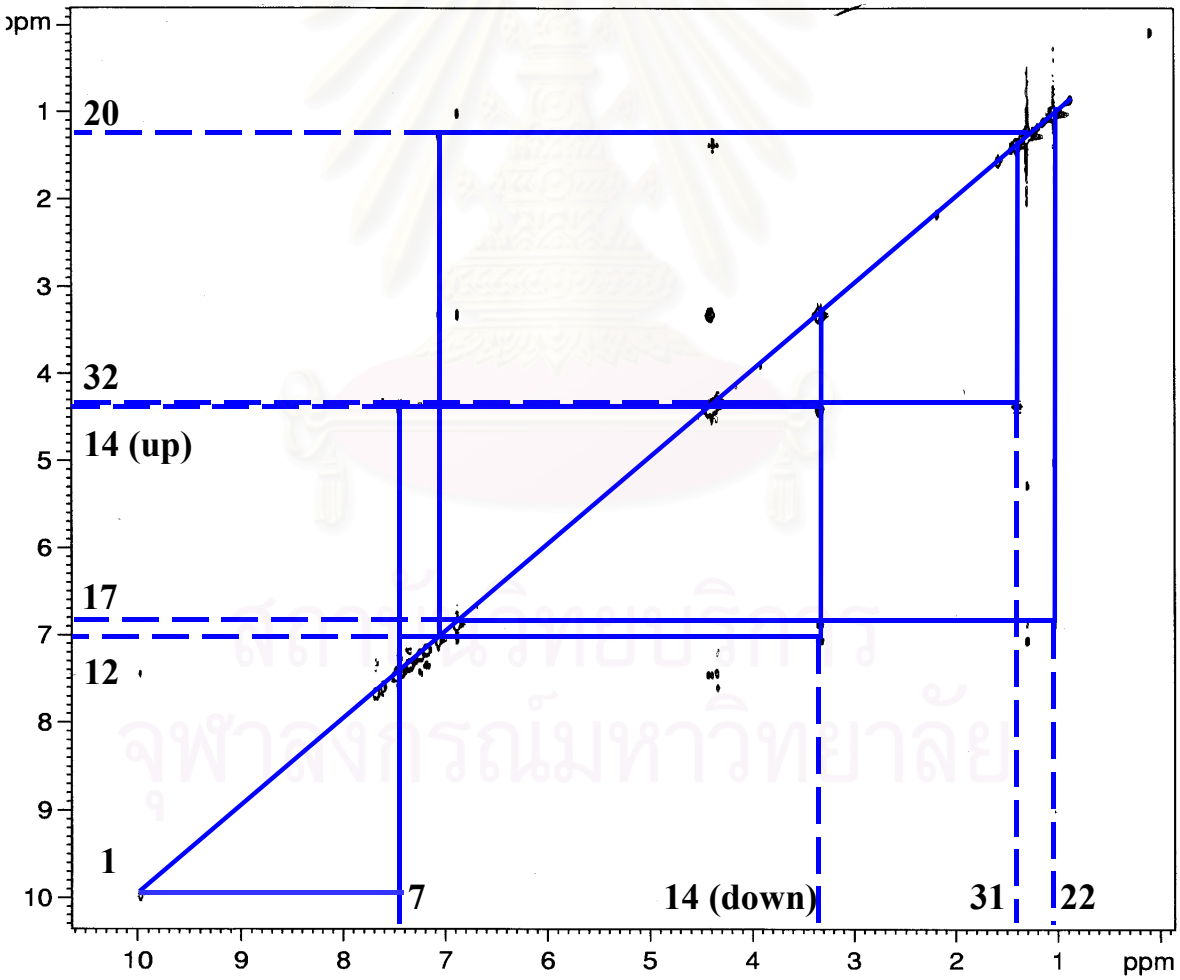


Figure 3.1.9: NOESY correlation of product ethyl-**5**

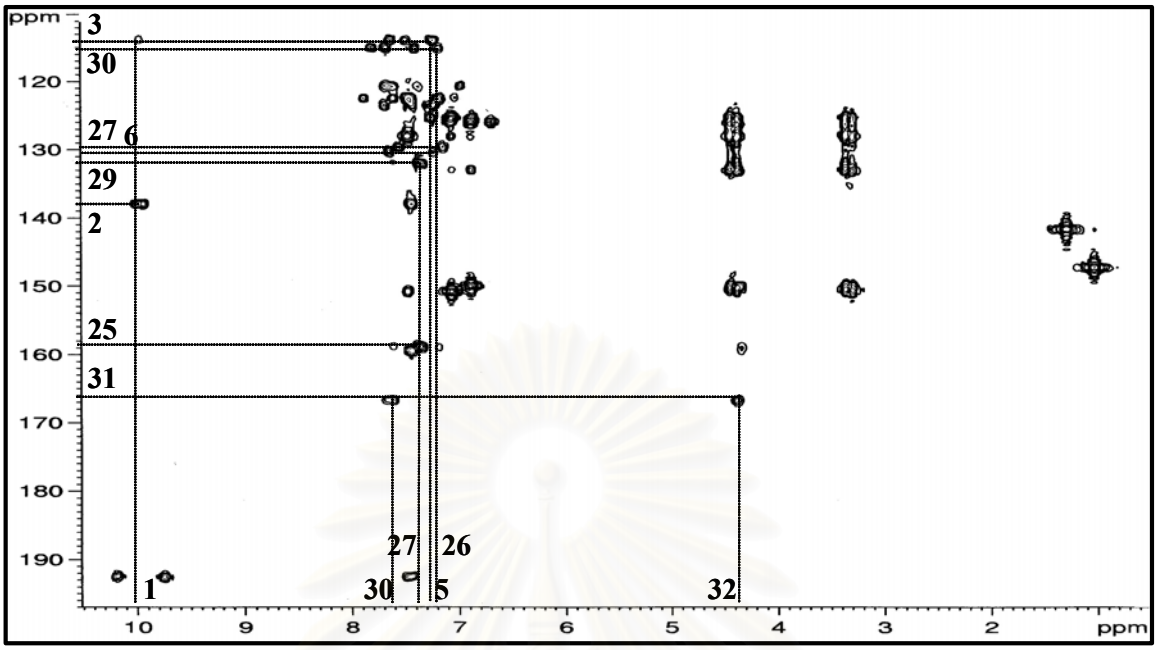


Figure 3.1.10: HMBC correlation of product ethyl-**5**

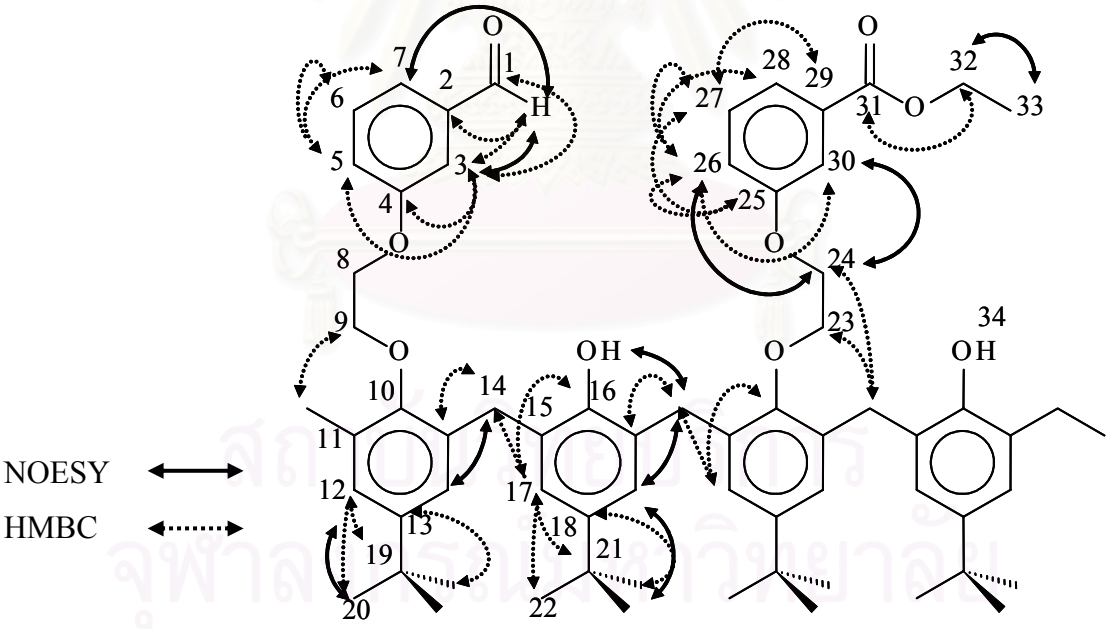


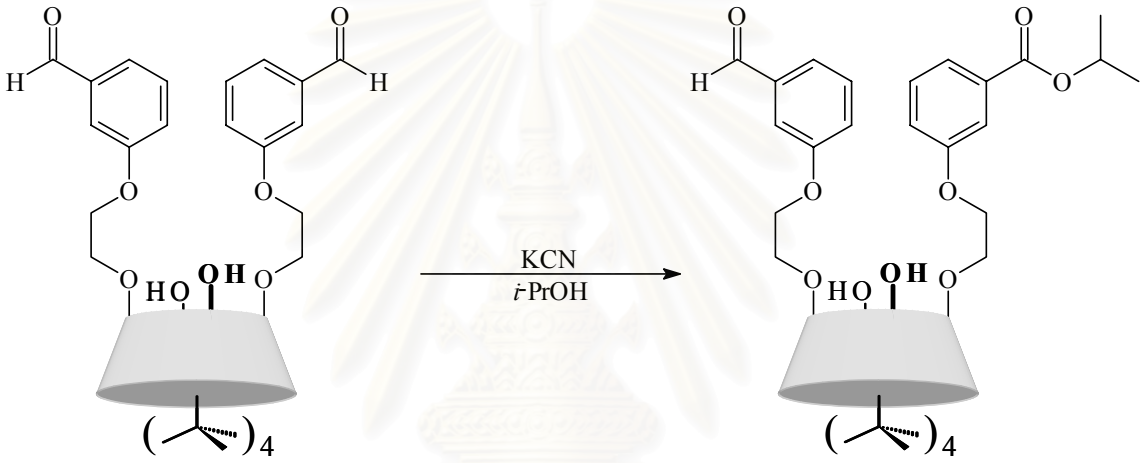
Figure 3.1.11: 2D-NMR correlation of product ethyl-**5**

This 2D-correlation diagram showed the relationship from both NOESY and HMBC. The proton of ethyl group at position 32 correlated to the carbonyl carbon position 31. Thus, the ethyl ester was confirmed that it was attached onto the

bisbenzaldehyde and the ethyl signal was not from ethyl acetate impurity by this direct evidence.

Additionally, the aldehydic proton at position 1 had a close relationship to carbon position 2 and 3. This relationship associate with the ethyl group correlation, the aromatic side arms of calix[4]arene can be distinguished and clearly assigned.

To confirm the generality of this unexpected reaction, the mono-*i*-propyl ester was also synthesised using the reaction of KCN and bis-*m*-benzaldehyde with *i*-propanol as a solvent (**Scheme 3.1.8**). Nonetheless, this *i*-propyl derivative gave lower yield of the *i*-propyl ester (15%).[38]

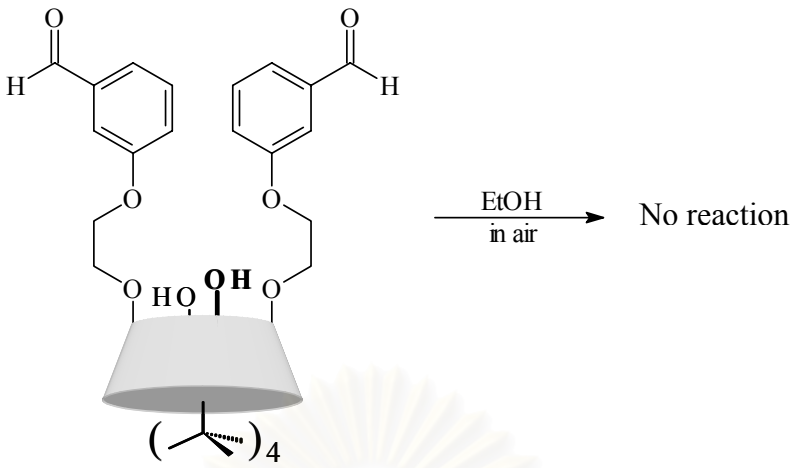


Scheme 3.1.8: Reaction of bis-*m*-benzaldehydecalix[4]arene with KCN in *i*-propanol

As the mono ester product from the reaction condition of benzoin coupling was unpredicted and the reaction showed rather unusual selectivity, this reaction was investigated in further detail.

Two mechanistically different types of reactions, Cannizzaro reaction[51] and auto-oxidation, may be responsible for the formation of the observed product.

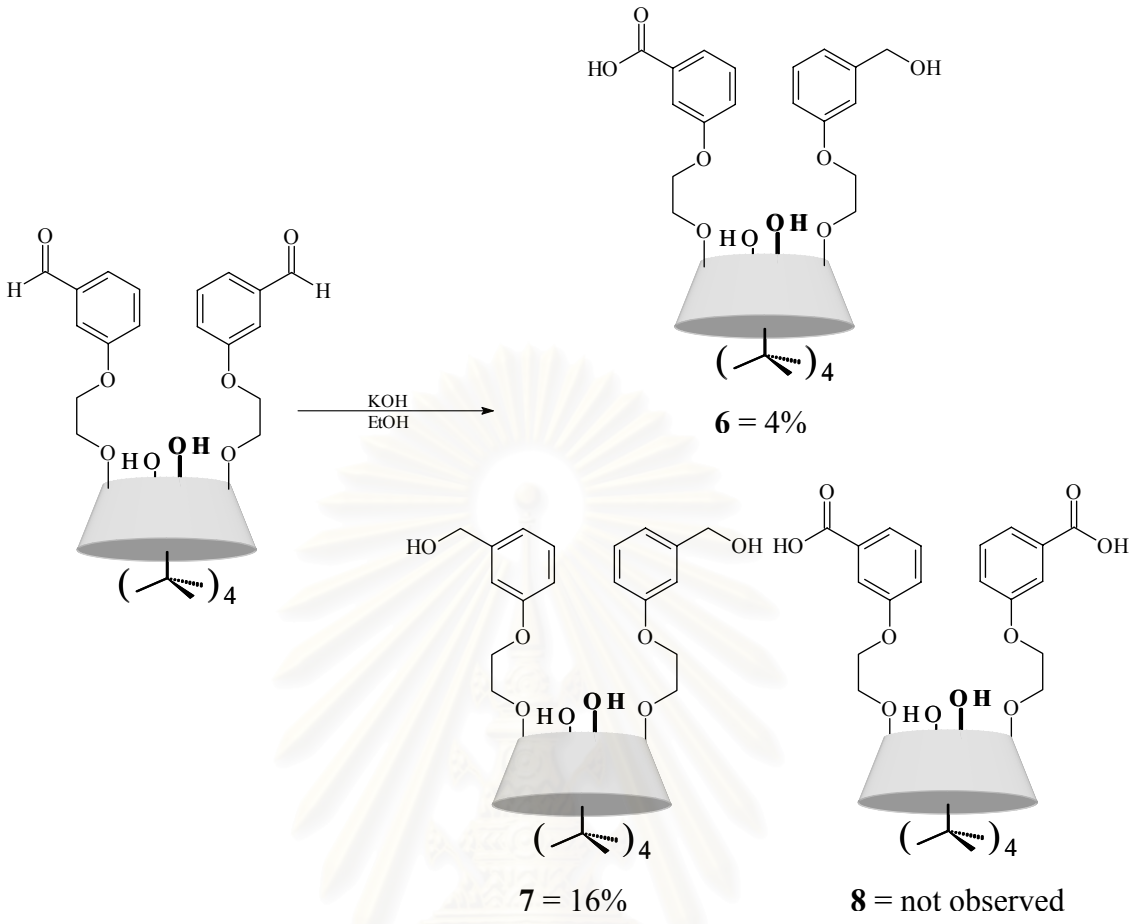
When the auto-oxidation reaction of bis-*m*-benzaldehydecalix[4]arene was performed by refluxing the bis-*m*-benzaldehydecalix[4]arene in ethanol in the presence of air but without KCN, the TLC trace did not show any product but only the un-reacted starting bis-*m*-benzaldehyde, even after 5 days of reflux (**Scheme 3.1.9**). This result indicated that the auto-oxidation of bis-*m*-benzaldehydecalix[4]arene did not proceed without KCN.



Scheme 3.1.9: Reaction of bis-*m*-benzaldehydecalix[4]arene with oxygen in air

The Cannizzaro reaction of bis-*m*-benzaldehydecalix[4]arene was also performed in ethanol using a strong base KOH instead of KCN.[38] The reaction gave two products as white solids. The first product was the bisbenzyl alcohol (16% yield) and the second isolated product was the corresponding mono-alcohol mono-acid (4% yield). The observation of the bisbenzyl alcohol suggested that there should be another product, the bisbenzoic acid (**Scheme 3.1.10**). However, attempts to isolate this bisbenzoic acid were not successful.

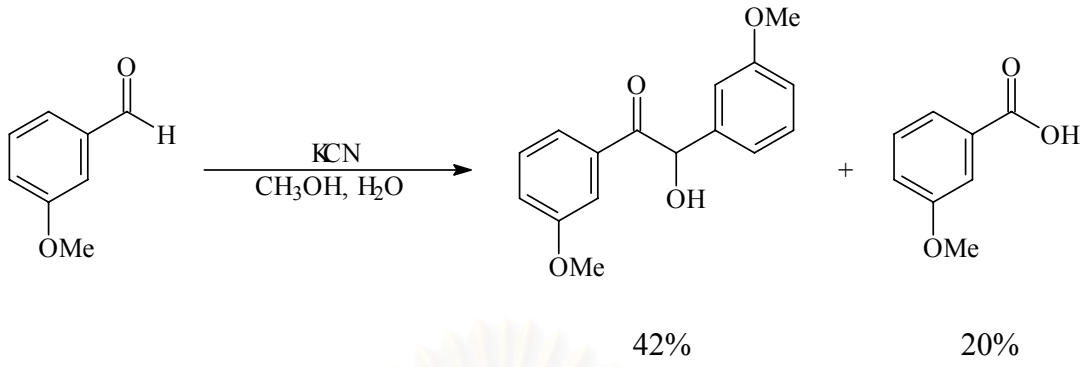
As this reaction did not produce the mono-ethyl ester, the Cannizzaro reaction can not account for the formation of the mono-ester derivatives from the bis-*m*-benzaldehydecalix[4]arene.



Scheme 3.1.10: Cannizzaro reaction of bis-*m*-benzaldehydecalix[4]arene

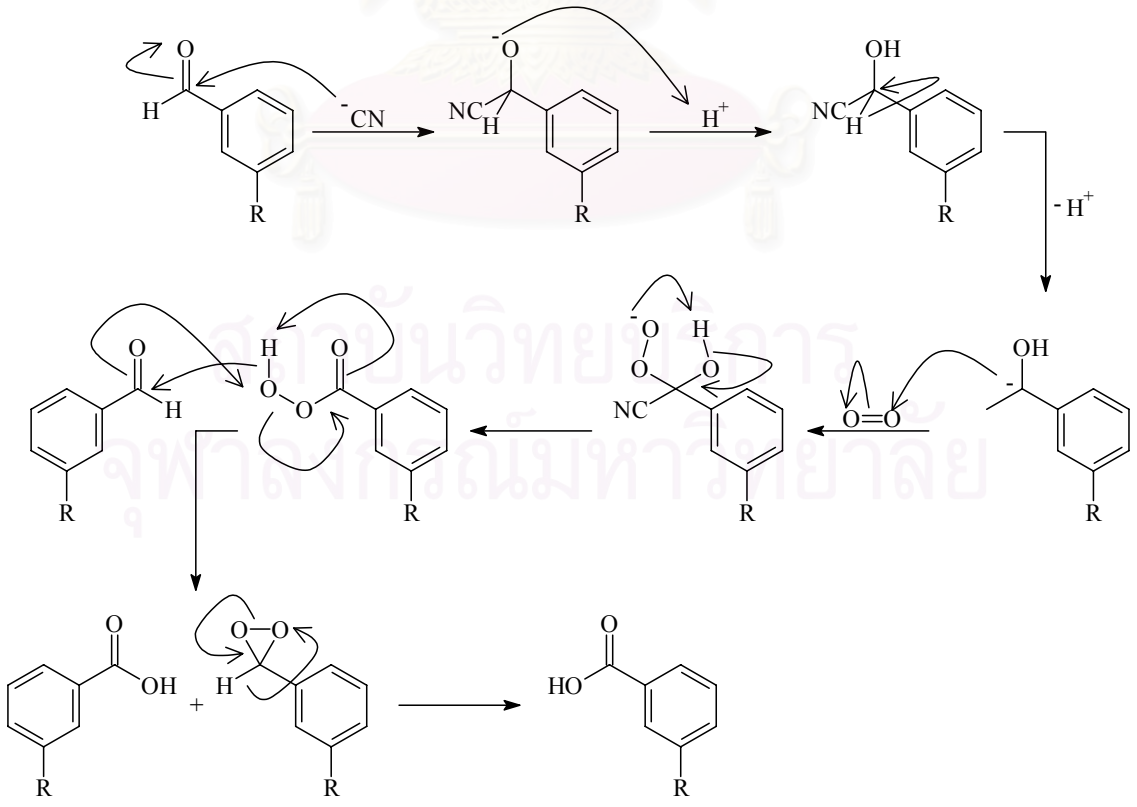
As the experiments described previously did not provide positive evidence supporting for either auto-oxidation or Cannizzaro reaction, a study of the model compound, 3-methoxybenzaldehyde was performed to acquire more information.

Using the same reaction condition as the oxidation of the bis-*m*-benzaldehyde gave the corresponding benzoin as a major product in 42% yield along with a minor oxidation product, *m*-methoxybenzoic acid, in 20% yield. In the presence of KCN, the auto-oxidation was, therefore, a competitive reaction of benzoin formation. Interestingly, the esterification of the auto-oxidation product, *m*-methoxybenzoic acid, was not observed in this reaction (**Scheme 3.1.11**).



Scheme 3.1.11: KCN catalyse benzoin coupling of 3-methoxybenzaldehyde (re-run)

According to the results described above, the proposed mechanism for the formation of mono-ester from bis-*m*-benzaldehyde was resulted from the esterification of the auto-oxidation product generated *in situ* from the bis-*m*-benzaldehyde starting material. The oxidation was catalysed by cyanide anion (**Scheme 3.1.12**) and the esterification was presumably catalysed by an acidic proton on the lower rim of *p-tert*-butylcalix[4]arene.[38]

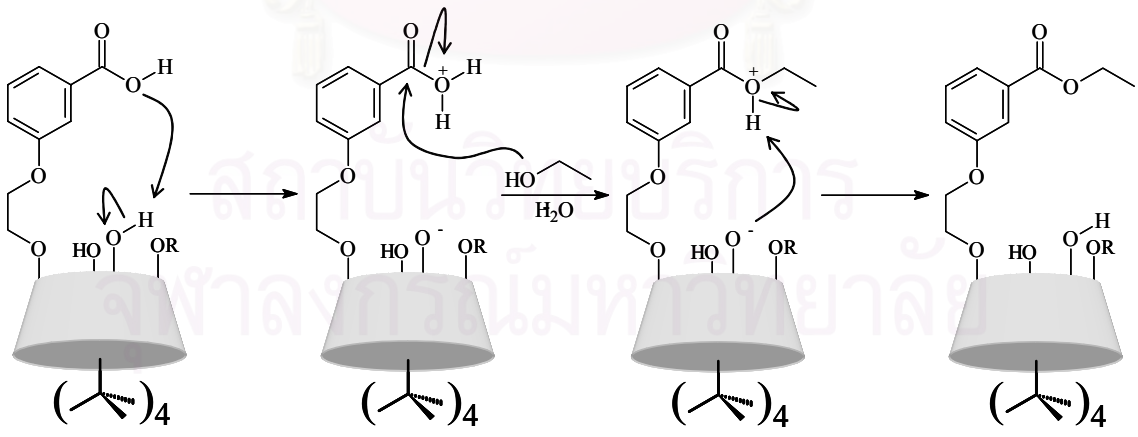


Scheme 3.1.12: Proposed mechanism for the KCN catalysed auto-oxidation

The most intriguing point of this reaction is the selectivity of the auto-oxidation step, in which only one of the two aldehyde groups was oxidised. The reason for this selectivity remains elusive. However, from the chemical structure of the bis-*m*-benzaldehyde starting materials, the phenolic OH groups of the lower rim of *p-tert*-butylcalix[4]arene should play an important role in controlling this selectivity. These phenolic OH groups may act as intramolecular hydrogen bond donors to induce a geometry that one of the aldehyde groups was hidden away from being attacked by the cyanide anion. This specific geometry of bis-*m*-benzaldehydecalix[4]arene may as well prevent the formation of the corresponding benzoin.

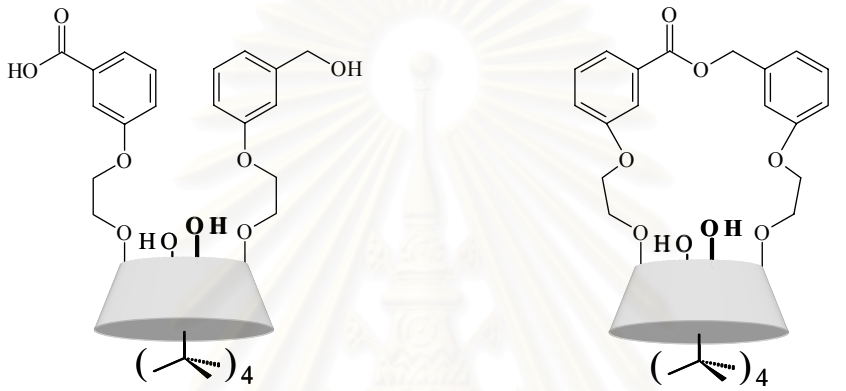
It is important to point out that this auto-oxidation reaction differs significantly from similar oxidations reported in the literature. Corey and co-workers used 5 equivalents of NaCN and 10-15 equivalents of an oxidizing agent, Ag_2O, to synthesise carboxylic acids from the corresponding conjugated aldehydes.[55] Castells and his colleagues reported ester formation using thiazolium salt or cyanide ion as a catalyst with nitrobenzene as an oxidizing agent.[56] In the present work, however, no extra oxidizing agent besides oxygen from the air was required.

Moreover, the phenolic OH groups of the lower rim of *p-tert*-butylcalix[4]arene should also responsible for the esterification process (**Scheme 3.1.13**), for the oxidation of the 3-methoxybenzaldehyde model compound, no ester product was observed.



Scheme 3.1.13: Proposed mechanism for the self-catalysed esterification

Another interesting point is the absence of esterification process in the formation of product **6** from Cannizzaro reaction. As discussed earlier in the reaction of *m*-**1**, the phenolic OH groups possibly acted as an intramolecular self catalyst to esterified the carboxylic group with ethanol solvent. But the structure of product **6** from Cannizzaro reaction contained both carboxylic and hydroxyl groups (**Figure 3.1.12**). The macrocyclic lactone was not observed in this reaction was probably due to the basicity of the reaction condition. As the excess amount of hydroxide was applied, the phenolic OH groups on calix[4]arene could be easily deprotonated.



6 **lactone** (not observed)

Figure 3.1.12: Structure of product **6** and the related macrocyclic lactone

The structure of compound **6** was confirmed by HMBC spectrum. There was no relationship between two calix[4]arene side arms. Indicating the absence of lactone structure.

In HMBC spectrum (**Figure 3.1.13**), the carboxylic carbon has no correlation to the benzylic proton. The benzylic proton is only correlated to the carbn on its own aromatic ring at position **3** and **7**.

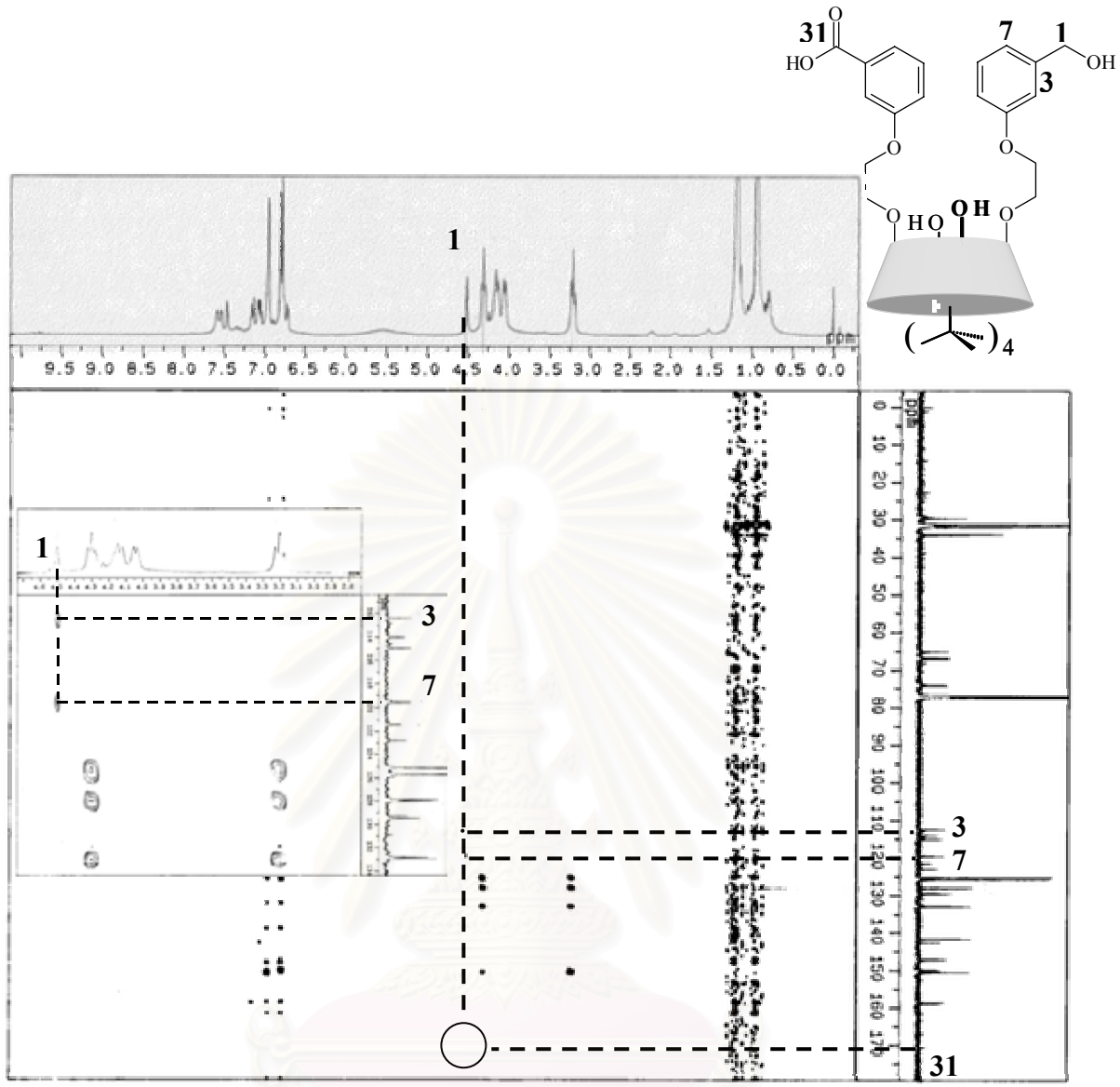


Figure 3.1.13: HMBC correlation of product **6**

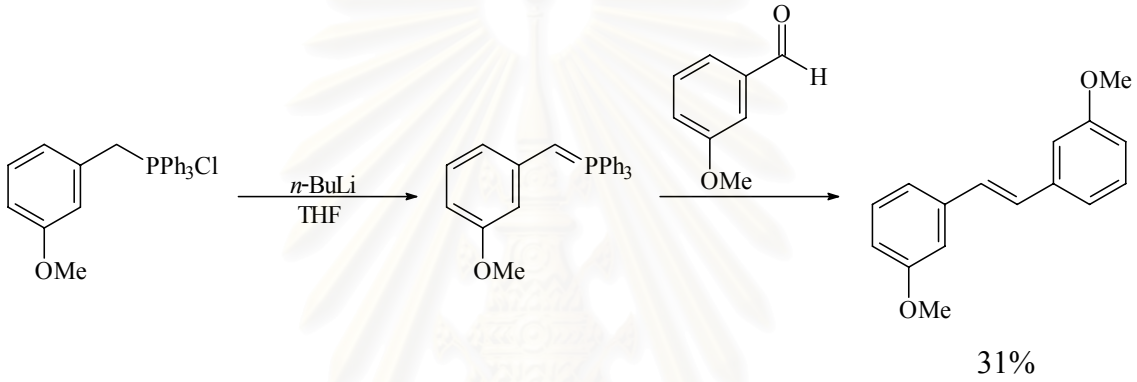
Another well known catalyst used for benzoin coupling is thiazolium family. A simple 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride was chosen to be used as a catalyst in the 3-metoxybenzaldehyde model system. Disappointingly, there was no major product observed.

Because of the failure of this benzoin method for coupling of the bis-*m*-benzaldehyde *p-tert*-butylcalix[4]arene, other approaches towards the synthesis of the desired stilbene were explored.

The most well known C=C formation from carbonyl compound is Wittig reaction.[46] Starting from 3-methoxybenzaldehyde, the aldehyde group was reduced to alcohol effectively by $NaBH_4$ in 94% yield. The resulting 3-methoxybenzyl alcohol was

subsequently converted to 3-methoxybenzyl chloride in 78% yield using PPh_3 in CCl_4. Then, the desired 3-methoxybenzyltriphenylphosphonium chloride was prepared in a very high yield (94% yield) by treating 3-methoxybenzyl chloride with PPh_3 in chloroform.

The Wittig reaction was performed by starting from generating the ylide by deprotonation of the 3-methoxybenzyltriphenylphosphonium chloride with *n*-butyl lithium. The ylide was deep red colour, so, the colour of the reaction mixture indicated the formation of the ylide. The 3-methoxybenzaldehyde was then added dropwise at 5 ^{o}C. After stirring at room temperature the expected 3,3'-dimethoxystilbene was observed on TLC (**Scheme 3.1.14**).



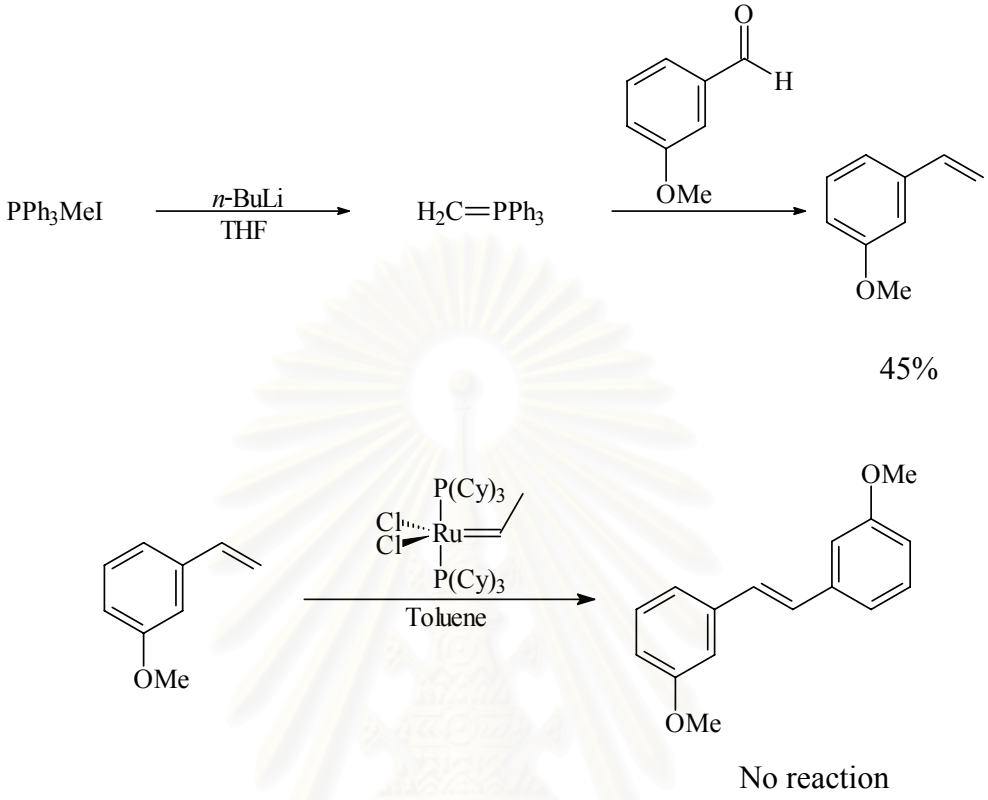
Scheme 3.1.14: Synthesis of 3,3'-dimethoxystilbene (Wittig method)

The reaction on the model compound gave low yield (31% yield) of the desired stilbene. On the calix[4]arene this reaction could be worse besides, a protecting group on one of the two aldehydes would be required in the reduction step. Thus, this approach was not so interesting to be performed directly on the bis-*m*-benzaldehydecalix[4]arene.

Another interesting C=C bond formation is the metathesis reaction using Grubb's catalyst as this approach would require a symmetrical bisstyrenecalix[4]arene derivatives.[47] The metathesis was tested on 3-methoxystyrene model compound synthesised from 3-methoxybenzaldehyde using Wittig reaction (**Scheme 3.1.16**). Several bases such as NaH/DMSO, *tert*-BuOK/THF and *n*-BuLi/THF were used. Only *n*-BuLi/THF gave the desired 3-methoxystyrene product (45% yield) while other bases did not give the desired product.

With 3-methoxy styrene in hands, the metathesis reaction was performed using Grubb's catalyst. The reaction however did not proceed even after being subjected to

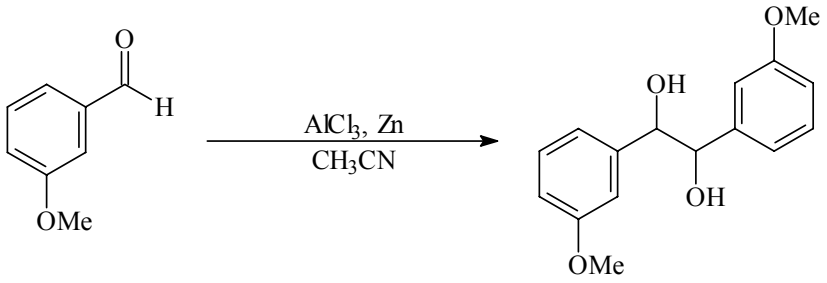
prolonged heating (**Scheme 3.1.15**). This may be due to the steric hindrance of the aryl group around the double bond.



Scheme 3.1.15: Synthesis of 3,3'-dimethoxystilbene (Grubb's method)

Dutta and Konwar reported an interesting reductive coupling two aromatic carbonyl compounds to olefins using $AlCl_3$-Zn.[48] Starting form 3-methoxybenzaldehyde, the $AlCl_3$-Zn reductive coupling was applied. The only product yielded from the coupling was a mixture of the corresponding pinacols (60% yield) 1,2-dihydroxy-1,2-di-(3,3'-methoxyphenyl)ethane (**Scheme 3.1.16**).

The pinacol products were characterised by ^1H and ^{13}C-NMR spectroscopy. All signals were spit into 2 sets of signals indicating the diastereomeric mixture. The product gave neither signal of aldehydic nor vinylic protons. The signals around 4.60 ppm suggested the existence of the protons on saturated chains adjacent to electron withdrawing groups. These ^1H-NMR signals consistent with the benzylic protons attached with the electron withdrawing OH groups in the proposed pinacol products, a diastereomeric mixture of 1,2-dihydroxy-1,2-di-(3,3'-methoxyphenyl)ethane.

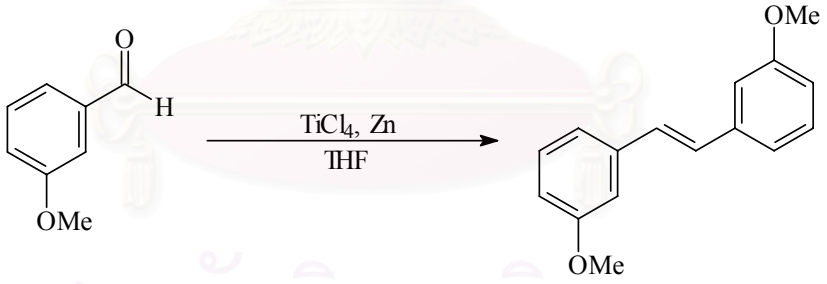


84%

Scheme 3.1.16: Reductive coupling of 3-methoxybenzaldehyde by $AlCl_3$-Zn

This pinacol-type product suggested that this $AlCl_3$-Zn reductive coupling underwent through this pinacol intermediate, as reported by Grant, Allukian and Fry in their alkyl phenyl system.[58] However, when the pinacol isolated was treated with the $AlCl_3$/Zn, again, only decomposition products were observed.

McMurry coupling[49] is another reductive coupling similar to the $AlCl_3$-Zn system. This reaction is however more difficult to handle because of the highly moisture sensitivity of $TiCl_4$. Starting from the 3-methoxybenzaldehyde, this reaction yielded the desired model compound, *trans*-3,3'-dimethoxystilbene in 84% yield (**Scheme 3.1.17**).



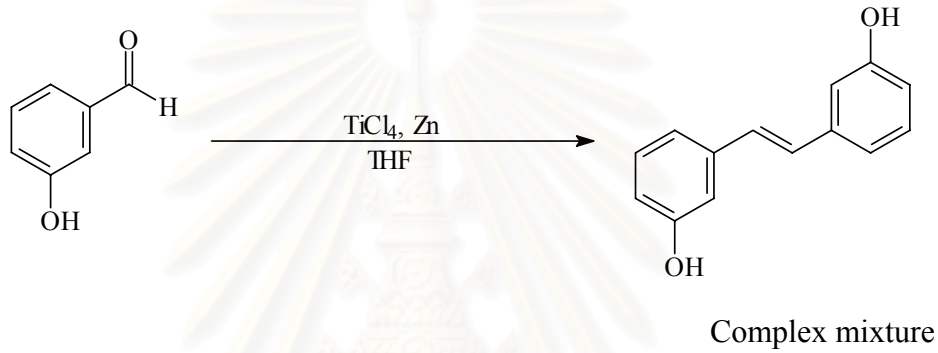
80%

Scheme 3.1.17: McMurry coupling of 3-methoxybenzaldehyde

The reaction mechanism started from the reduction of Ti(IV) to Ti(0) by activated zinc. The Ti(IV) was slowly reduced to Ti(0) which was indicated easily by the sequence of colour change of the reaction mixture. The starting Ti(IV)-THF complex was bright yellow which was gradually turned to green and finally to deep purple or black colour of Ti(0) upon refluxing with Zn powder. Then, the aldehyde was slowly added into the mixture. After refluxing for 15 hours, the reaction was cooled to room temperature and

the Ti(0) was deactivated by addition of K_2CO_3 aqueous solution. The mixture was slowly turned from grey to white or pale yellow. The complete deactivation was required in order to prevent the crude mixture turn into muddy sticky gum during washing with acetone and dichloromethane.

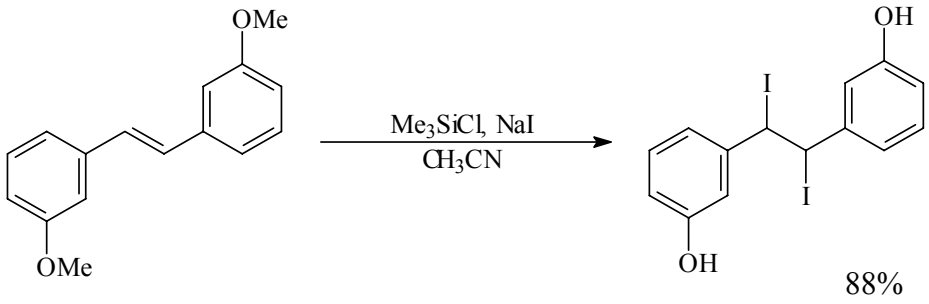
Follow the success in McMurry coupling of the 3-methoxybenzaldehyde, the same reaction was performed on 3-hydroxybenzaldehyde in order to synthesise the 3,3'-dihydroxystilbene (**Scheme 3.1.18**), but many products were observed on a TLC plate. The result suggested that the McMurry coupling may be not suitable for the molecule containing phenolic OH group.



Scheme 3.1.18: McMurry coupling of 3-hydroxybenzaldehyde

The alternative route to synthesise the 3,3'-dihydroxystilbene was the demethylation of 3,3'-dimethoxystilbene which was already obtained from McMurry coupling.

In the dark, the demethylation of 3,3'-dimethoxystilbene was performed under nitrogen atmosphere using trimethylchlorosilane and sodium iodide.[50] The reaction was quenched with water, and then aqueous NaS_2O_3. From the reaction, the only product separated was diastereomeric mixture of 1,2-diiodo-1,2-di-(3,3'-dihydroxyphenyl)ethane in 88% yield (**Scheme 3.1.19**). This product is the addition product of 3,3'-dihydroxystilbene with iodine.



Scheme 3.1.19: Demethylation of 3,3'-dimethoxystilbene

In summary, none of the other approaches, besides the direct McMurry coupling of the bisbenzaldehydecalix[4]arene derivatives, provided the desired stilbene product; however, many reactions have been learned during these attempts.

3.2 Photoisomerisation **Study**

The photoisomerisation study of the stilbene or azobenzene crown ether *p-tert*-butylcalix[4]arene was performed using a medium pressure mercury lamp. The ration of *cis/trans* isomers was determined from the integration in the ^{1}H-NMR spectra.

All the stilbene bridged calix[4]arenes synthesised did not isomerise under the room light but readily isomerised under the UV light (medium pressure mercury lamp). The photo-stationary states were observed for all isomers and the percentages of *cis*- and *trans*-isomers were determined (**Table 3.2.1**). The same photostationary state was obtained, no matter the irradiation was started from which geometrically pure forms *cis*- or *trans*.[38]

Table 3.2.1. The percentages of *cis*- and *trans*-isomers at the photostationary states

Compound	% Isomer at photostationary state	
	cis-isomer	*trans*-isomer
o-**3**	15	85
m-**3**	70	30
p-**3**	75	25
o-***4***	36	64
m-***4***	13	87

The *cis*- and *trans*-percentages for each derivative at the photostationary state were determined from the peak areas of the best resolved signals corresponding to each geometrical isomers (**Figure 3.2.1**). The signals of the similar protons in *cis*- and *trans*-forms for each isomer were used to reduce the unidentical relaxation time of the chemically inequivalent protons.

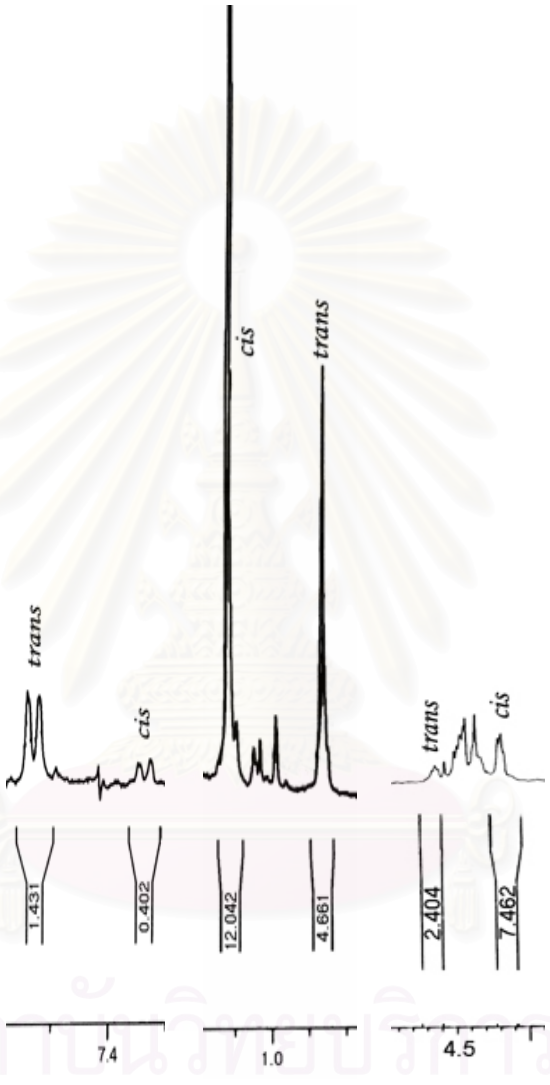


Figure 3.2.1. ^{1}H-NMR signals, (a) aromatic protons *ortho*- to vinylic carbon in *o*-**3,** (b) *t*-butyl protons in *m*-**3** and (c) ethylene glycolic protons in *p*-**3,** at the photostationary state

Unlike the stilbene derivatives, the azobenzenecalix[4]arenes isomerized even in the absence of light due to its usual thermal isomerisation of the diazo (N=N) unit. While the photosteady state of both stilbens and azobenzens under UV light could be achieved in minutes, the thermal isomerisation of the azobenzenes was much slower, taking over a

week to reach the equilibrium. Both thermal and photo isomerisations of azobenzene derivativatives produced the same final *cis:trans* ratios.

3.3 Complexation Study

All calix[4]arene analogues contain 2 pockets to hold guest molecules or ions. The first one is the electron rich oxygen pocket. All four phenolic oxygens of calix[4]arene along with the other two oxygens from ethylene bridge are positioning into an electron rich cavity containing 6 oxygen donor atoms. This pocket was designed based on the crown ether calix[4]arene host molecules for trapping a metal ion.[59]

The other possible binding pocket is inside the calix[4]arene basket. The calix[4]arene is composed of four electron rich aromatic rings facing inwards to form a π electron cavity. This π electron pocket is another interesting binding site for the cations or a molecule containing an acidic proton or an aromatic compound.[60] Basically, the *p-tert*-butylcalix[4]arene itself can complex with toluene in the crystallisation during the synthesis process of calix[4]arene. The complexation of cation and molecular compounds with the stilbene and azobenzenecalix[4]arene derivatives were studied.

3.3.1 Complexation with Metal Picrate

In 2000, Pipoosananakaton found that the *cis-o*-**4** can complex with sodium and potassium ion in picrate salts. The complexation with sodium ion also shifted the equilibrium between the two geometrical isomers towards the *cis*-form while the complexation with potassium ion shifted the equilibrium towards the *trans*-isomer.[39] With this discovery, the rest of geometrial azobenzenecalix[4]arene analogues was synthesised along with their stilbene family and their complexation ability of each isomer was investigated.

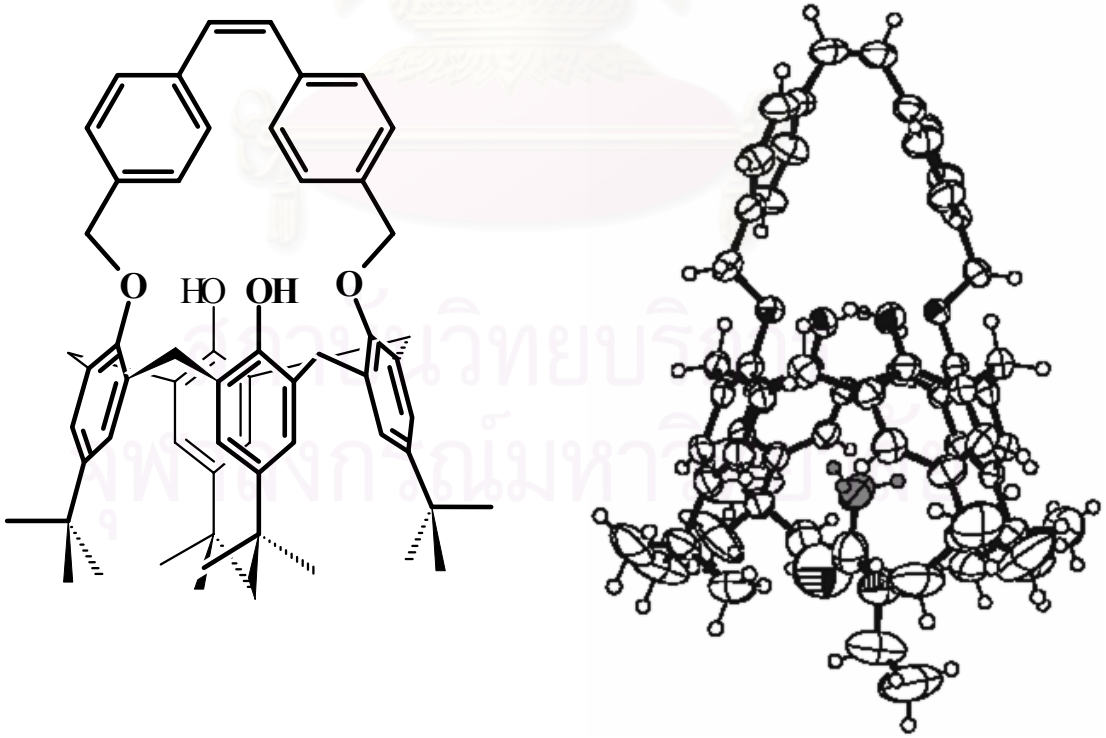
The complexation ability can be easily observed by colour changing. The chloroform-*d* solution of a host is colourless, but once the solid yellow picrate salt was dissolved, the solution turned to yellow because of the picrate counter ion. The complexation can also be investigated by ^{1}H-NMR spectroscopy by detecting the singlet picrate signal around 8 ppm.

Although *cis*-*o*-**4** and *trans*-*o*-**4** could complex with sodium and potassium ion, the stilbene analogues and the *m*-**4** derivatives did not complex with any metal ion tested, Li^+, Na^+, K^+ and Cs^+.

These results suggested that the lone pair electrons on the nitrogen atom of the azobenzene group participated in the complexation. Thus, only the *o*-azobenzene isomer**,** either *cis*-or *trans*-**,** that has at least one nitrogen lone pair electrons pointing inward the crown ether binding cavity can bind with the metal ions.

3.3.2 Complexation with Neutral Molecules

In 2003, Lhoták P. and co-workers found that their *p*-*cis*-stilbenecalix[4]arene with shorter methylene linker in stead of the ethylene glycol chain (**Figuer 3.3.1**) in this research can complex with some molecular compounds such as acetonitrile, acetone and malononitrile.(52) With this interesting report, complexation of the synthesised stilbene family with molecular compounds was investigated with ^{1}H-NMR spectroscopy. The magnetic environment of certain protons in the free and complexed guest molecule is difference and this can lead to the difference in the chemical shift of the guest molecule.



Free host Complexed with ethyl acetate

Figure 3.3.1: Structure of Lhoták's stilbene and its complex

The guest molecules investigated were acetonitrile, nitromethane, chloroform, acetone, ethyl acetate, propagyl bromide and DMSO all of which contain weak acidic proton. Another class of guest molecules was benzene derivatives, benzene, toluene and *p*-nitrotoluene.

Interestingly, from ^{1}H-NMR spectra, not all stilbenecalix[4]arenes could complex with these neutral molecules but only *cis*- and *trans-ortho*- isomers and *cis-meta*- isomer (**Table 3.3.1** and **Figure 3.3.2**). Thus, only the *meta*- isomer displayed the switchable binding to the molecular compounds. Due to photo-isomerisable properties of the stilbene derivative, if one geometry can complex with the guest whilst the other cannot, this molecule is promising to be used as a photoswitchable host molecule for the complexation. Another interesting point is the selectivity towards the guest. Only nitromethane and acetonitrile can complex with the appropriate host molecule. This selectivity may stem from both acidity of the protons and also the geometry of the guest molecules. With this selectivity, the selective separation and sensor application could be developed.

Table 3.3.1: The chemical shift change of guest proton

Guest	Chemical shift of free guest (ppm)	Δδ of guest in present of host molecule (ppm)				
		cis-*o*-**3**	*trans*-*o*-**3**	*cis*-*m*-**3**	*trans*-*m*-**3**	*cis*-*p*-**3**
CH_3CN	2.011	***0.406***	***0.433***	***0.461***	0.006	0.083
CH_3NO_2	4.330	***0.219***	***0.205***	***0.417***	0.005	0.041
Acetone	2.173	0.006	0.007	0.022	0.000	0.001
EtOAc	1.292	0.037	0.039	0.045	0.034	0.034
	2.080	0.035	0.035	0.036	0.034	0.034
	4.154	0.036	0.036	0.040	0.034	0.034
DMSO	2.682	0.062	0.057	0.030	0.054	0.053
Propagyl bromide	3.879	0.004	0.010	0.000	0.004	-0.003
	2.526	0.000	0.004	0.007	-0.003	-0.007
Toluene (methyl)	2.355	0.000	0.000	0.023	0.000	-0.001
p-Nitrotoluene	2.469	0.017	0.022	0.010	0.003	0.004

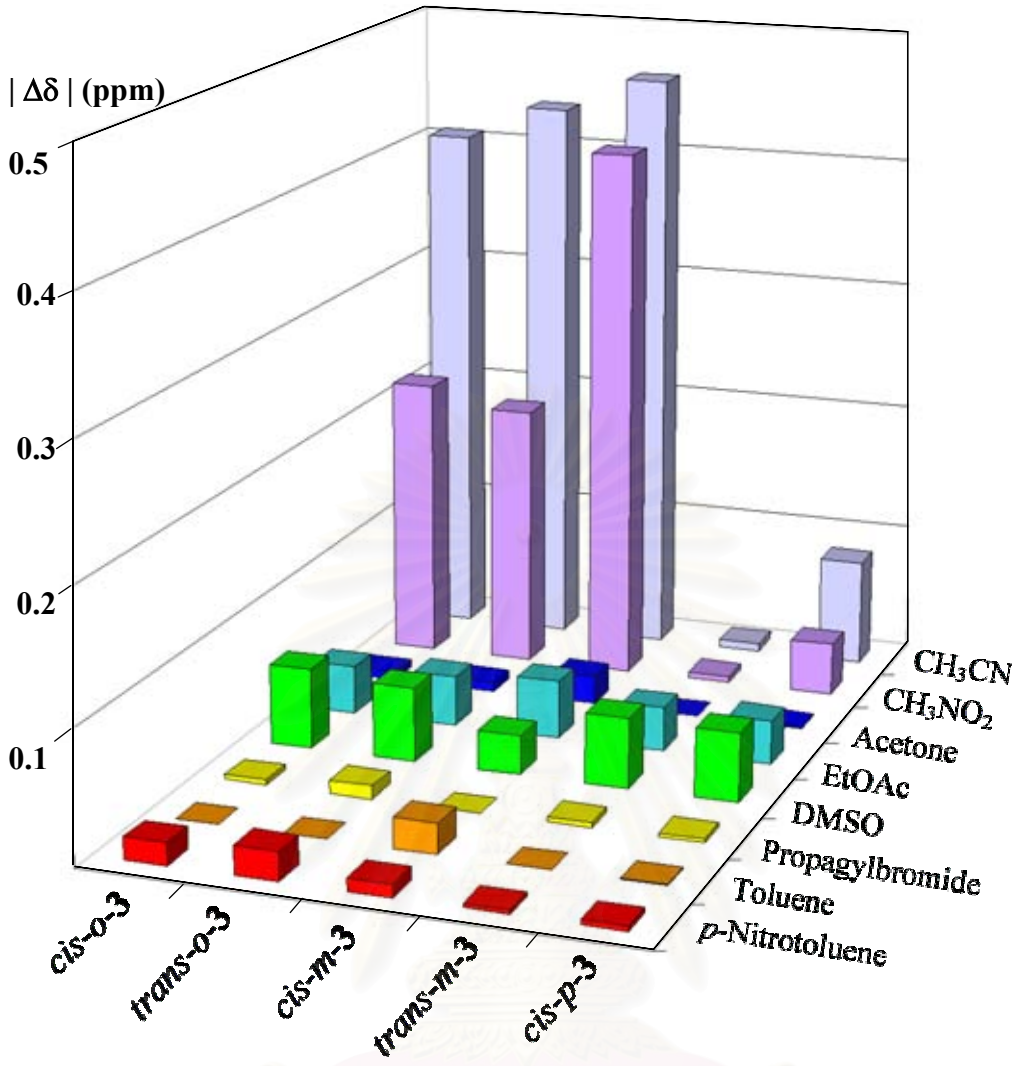


Figure 3.3.2: | Δδ | of CH_3 group in guest molecule after addition into host solution

The complexed host molecule showed variation in the shift of the chemical shift values of protons (**Figure 3.3.3**). This variation suggests the interaction between guest and host molecule. The greatest shift was observed for the signal calix[4]arene protons implying that the guest molecules were located inside the calix[4]arene π-cavity.

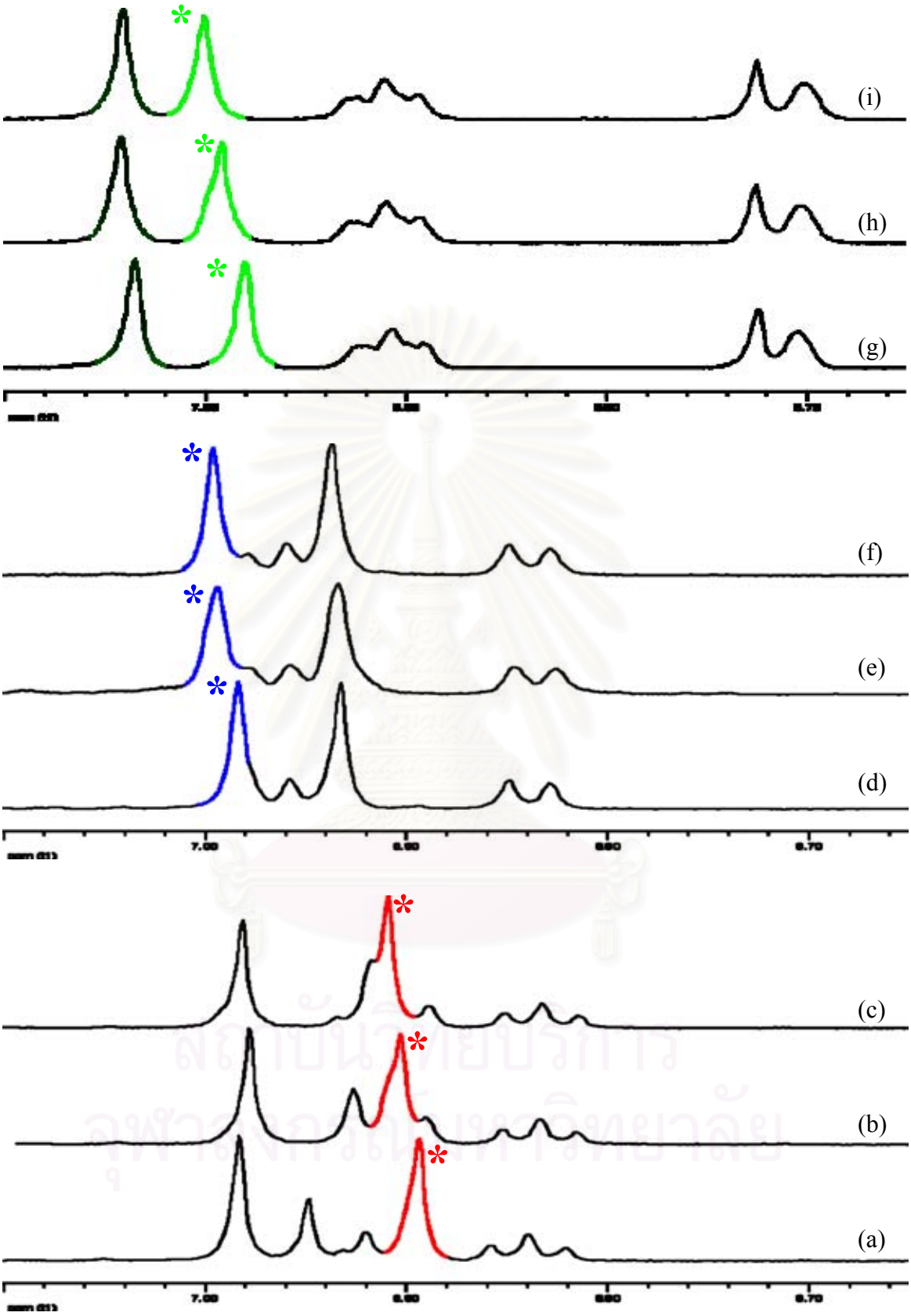


Figure 3.3.3: ^{1}H-NMR spectra of host and 1:1 mixture of host and guest: (a) *cis-o*-**3** (b) *cis-o*-**3** : CH_3NO_2 (c) *cis-o*-**3** : CH_3CN (d) *trans-o*-**3** (e) *trans-o*-**3** : CH_3NO_2 (f) *trans-o*-**3** : CH_3CN (g) *cis-m*-**3** (h) *cis-m*-**3** : CH_3NO_2 (i) *cis-m*-**3** : CH_3CN

3.3.3 Determination of complexation constant by NMR Titration

The ^{1}H-NMR signals of the complexed guest and the free guest were observed as one set indicating the faster exchange rate (k_1 and k_{-1}) comparing to the ^{1}H-NMR time scale.

$$H + G \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

The host to guest ratio in the complex formation was determined by utilising a Job's plot. The plotting was coordinated by the guest to host mole ratio (x value) and the $\Delta\delta(1\text{-}x)$. With the x value ran between 0 to 1, the $\Delta\delta(1\text{-}x)$ was achieved at x value equal to 0.5. This indicates the 1 to 1 ratio of guest to host complex (**Figure 3.3.4**). The result is in good agreement with the X-ray structure of ethyl acetate inclusion complex with *trans-o*-**4** and Lhoták's stilbene, which show that the calix[4]arene cavity can accommodate only one guest molecule.

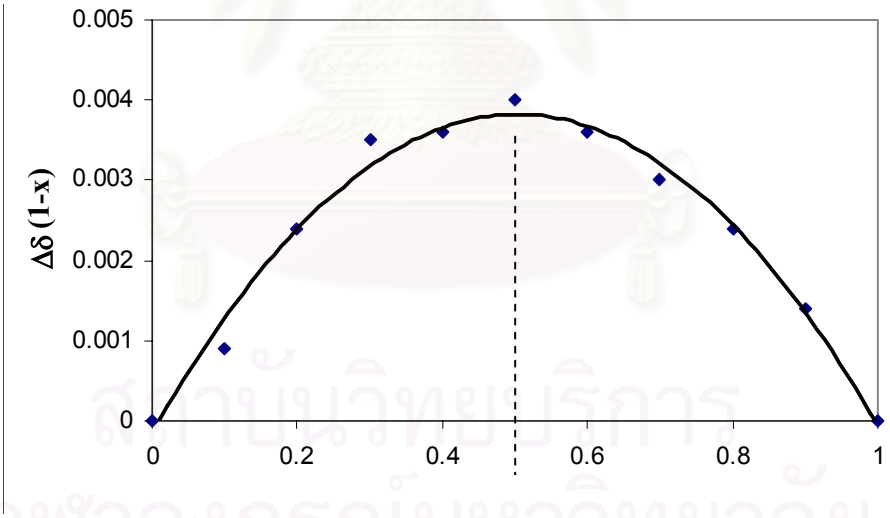


Figure 3.3.4: Job's plot of CH_3CN : *cis-m*-stilbenecalix[4]arene complex

The complexation constant of each complex was determined by the ^{1}H-NMR titration. The chemical shifts of host and guest mixture in $CDCl_3$, with varied guest concentration were collected. The $\Delta\delta$ values were determined and plotted against the guest to host mole ratio (**Figure 3.3.5** and **Figure 3.3.6**).

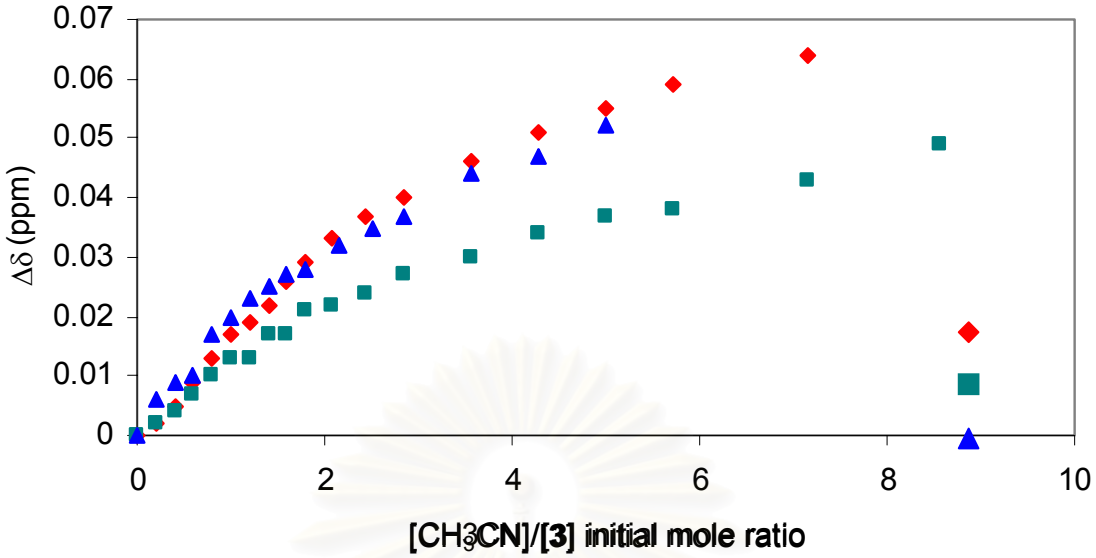


Figure 3.3.5: Titration plot of the molecular complexes: a) CH_3CN : *cis-o*-**3** b) CH_3CN : *trans-o*-**3** c) CH_3CN : *cis-m*-**3**

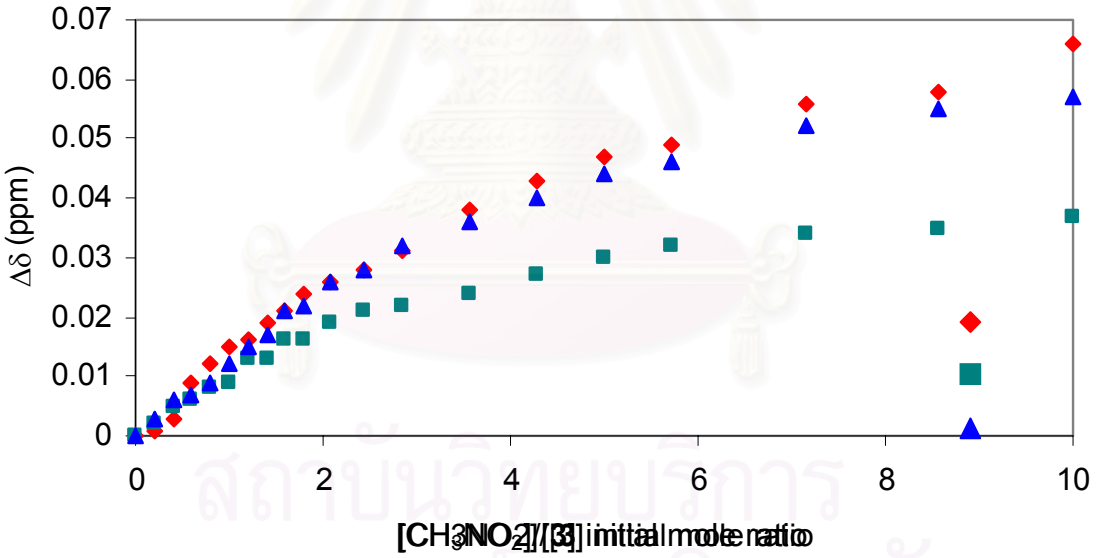


Figure 3.3.6: Titration plot of the molecular complexes: a) CH_3NO_2 : *cis-o*-**3** b) CH_3NO_2 : *trans-o*-**3** c) CH_3NO_2 : *cis-m*-**3**

The complexation constant for the 1:1 complexes were calculated from the EQNMR simulating program,[53] using the ^{1}H-NMR signals, which have the highest Δδ value to minimise the experimental error from the chemical shift reading. These selected signals are the aromatic protons adjacent to the *tert*-butyl group of calix[4]arene.

Table 3.3.2: The complexation constants of stilbenecalix[4]arenes with some neutral molecules

Host	Selected signal (ppm)	$K_{eq(CH3CN)}$ (M)	Error (%)	$K_{eq(CH3NO2)}$ (M)	Error (%)
o-cis-**3**	6.89	57	7	38	10
o-trans-**3**	6.98	57	3	74	9
m-cis-**3**	6.98	58	3	45	10

Comparing to the work reported by Lhoták and co-workers,[52] they also found a weak binding affinity of a similar host with acetonitrile, acetone and chloroacetonitrile. The binding affinity with acetonitrile of *cis-o*-**3**, *trans-o*-**3** and *cis-m*-**3** are three times higher than that Lhoták's stilbene (**Table 3.3.3**).

Table 3.3.3: The complexation constants of Lhoták's stilbene with some neutral molecules[52]

Guest	K_{eq}
CH_3CN	19
Acetone	4
EtOAc	0
$NCCH_2CN$	113
$ClCH_2CN$	19

3.4 Photoswitchability complexation study

Due to the difference of complexation property of *cis*- and *trans-m*-stilbenecalix[4]arene, the photo-induced catching and releasing process was investigated in 1:1 of host:guest mixture.

The guest molecule was released from the starting pure *cis*-isomer after irradiation to the photostationary state (**Figure 3.4.1** and **Table 3.4.1**). The release was determined to be about 30%. This 30% release is equal to the percentage of the *trans*-isomer in photostationary state as found in **Section 3.2**. The result was a direct evidence for photoswitchable complexation of *m*-stilbenecalix[4]arene.

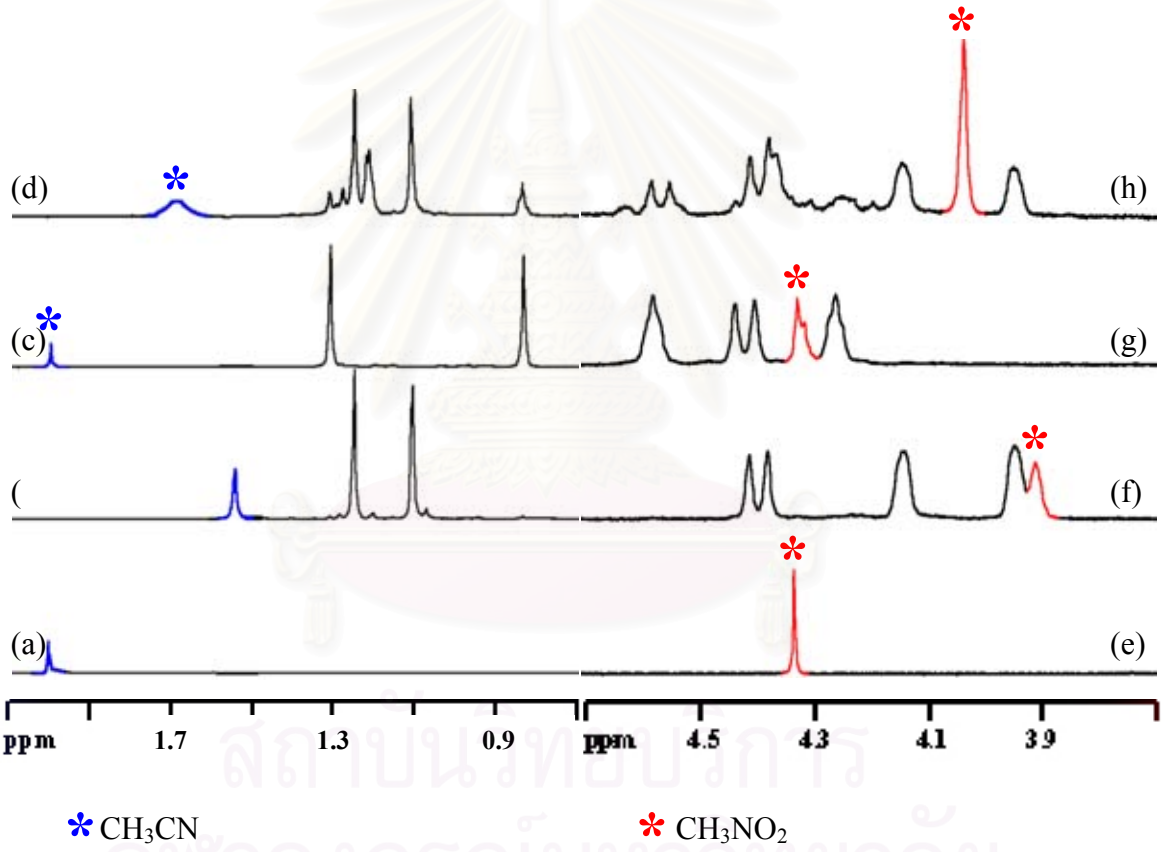


Figure 3.4.1: ^{1}H-NMR spectra 1:1 mixture of host and guest: (a) CH_3CN (b) *cis-m*-**3** : CH_3CN (c) *trans-m*-**3** : CH_3CN (d) photostationary state *o*-**3** : CH_3CN (e) CH_3NO_2 (f) *cis-m*-**3** : CH_3NO_2 (g) *trans-m*-**3** : CH_3 NO_2 (h) photostationary state *o*-**3** : CH_3 NO_2

Table 3.4.1: The Δδ of guest molecules at initial and at photostationary state (p.s.)

	Δδ CH_3CN (ppm)		Δδ CH_3NO_2 (ppm)	
	initial	p.s.	initial	p.s.
*cis-m-***3**	0.461	0.320	0.417	0.295
*trans-m-***3**	0.006	0.320	0.005	0.295

The methyl proton of free CH_3CN and CH_3NO_2 were observed at 2.011 and 4.330 ppm respectively. As CH_3CN was complexed with *cis-m-***3**, the signal of methyl proton was shifted upfield by 0.461 ppm to 1.550 ppm.

The *trans-m-***3** hardly shifted the signal of CH_3CN for only 0.006 ppm to 2.005 ppm. After irradiation, the mix hosts shifted the CH_3CN signal for 0.320 ppm. This is 0.141 ppm different from CH_3CN in pure *cis*-isomer and 0.318 ppm different from CH_3CN in pure *trans*-isomer that represent 70:30 of *cis*-: *trans*-ratio.

The *trans-m-***3** hardly shifted the signal of CH_3NO_2 for only 0.005 ppm to 4.325 ppm. After irradiation, the mix hosts shifted the CH_3NO_2 signal for 0.295 ppm. This is 0.122 ppm different from CH_3 NO_2 in pure *cis*-isomer and 0.290 ppm different from CH_3 NO_2 in pure *trans*-isomer that also represent 70:30 of *cis*-: *trans*-ratio.

According to the 70% *cis:trans* ratio in the photostationary state calculated from the peak area in **Table 3.2.1**, the 70% *cis*-isomer in photostationary state solution gave 70% *cis-m-***3** / CH_3CN and 70% *cis-m-***3** / CH_3NO_2 complex straight forward. This imply directly to the photo-switchable complex between *m-***3** with both CH_3CN and CH_3NO_2. Moreover, this also imply to the stability of the stilbene-bridged calix[4]arene that the complexation could not switch the *cis*-, *trans*-isomer of the stilbene bridge as the metal ion complexation can switch the structure of azobenzene bridge on the *o-***4**.

CHAPTER IV

CONCLUSION

Five stilbene-bridged calix[4]arene derivatives (**3**) were synthesised by McMurry coupling. The assignment of geometrical isomers was based primarily on ^{1}H-NMR and UV-Vis spectroscopy using both *cis*- and *trans*-stilbene as references. The assignment was also confirmed with the X-ray structure of *cis*-*o*-**3**. The coupling yielded the *cis*- in preference to the *trans*-isomer. This is probably due to the limited orientation of the transition state.

The azobenzene-bridged calix[4]arene derivatives (**4**) were synthesised by a reductive coupling with zinc. The high-pressure method increased the yield of the coupling products significantly. The geomety of the azobenzene derivatives was elucidated by X-ray crystallography. Only the *trans*-isomer can be obtained from the reaction due to the instability of the *cis*-isomer and also the thermal isomerisation properties of the azobenzene. The *para* analogues seemed to be unstable and cannot be obtained from the reaction.

Both stilbene and azobenzene-bridge were isomerised under UV light and reached the photo-stationary state no matter the irradiation starting from which geometrical isomer.

Whilst the *o*-**4** complexed with both sodium and potassium picrate, the *m*-**4** and all stilbene derivatives **3** cannot complex with metal picrate under the experimental condition. This indicates the participation of the electron pair of the azobenzene nitrogen in the *ortho* isomer which directly pointed into the crown ether pocket.

Even though the stilbene analogues did not complex with metal picrates, but some guest molecules could be trapped in the π cavity of the calix[4]arene ring of some stilbene derivatives. Two neutral molecules; nitromethane and acetonitrile, among 8 investigated neutral molecules, were able to complex with *o*-**3** and *m*-**3**. Interestingly, while both *cis*- and *trans*-isomer of *o*-**3**, only the *cis*-isomer of *m*-**3**, can bind with both CH_3CN and CH_3NO_2.

In photoisomerisation study of the *m*-**3** complex, the *cis*-: *trans*-ratio in photostationary state was equal to the “complexed : free” ratio of guest molecule in the

same photo-stationary state. The photostationary state of the complex system had the same *cis*-: *trans*-ratio as the photostationary state of the free host system.

The ***m*-1** underwent an unusual selective oxidation–esterification when treated with 0.20 equivalent of KCN. Only one benzaldehyde groups was oxidised and esterified. This selectivity may be due to hydrogen bonding of benzaldehyde with phenolic OH group in calix[4]arene ring. Further more, the oxidation product was spontaneously esterified with the alcohol used as a solvent. This esterification can not be found in simple model molecule implying an intramolecular acid catalysis by the phenolic OH group on calix[4]arene ring.

The suggestions for future works

The suggested future works should be focused on

1. Synthesis switchable stilbene bridged calix[4]arene containing longer ethylene glycol chain to improve the cation complexation ability.
2. Extend the complexation study to wider range of organic guests.
3. Crystallisation the host-guest complexes for structural determination with X-ray.
4. Derivatisation of the host molecule by attaching a proper receptor group for complexation of biologically interesting compounds such as proteins and nucleic acids.

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APPENDIX A

NMR SPECTRA

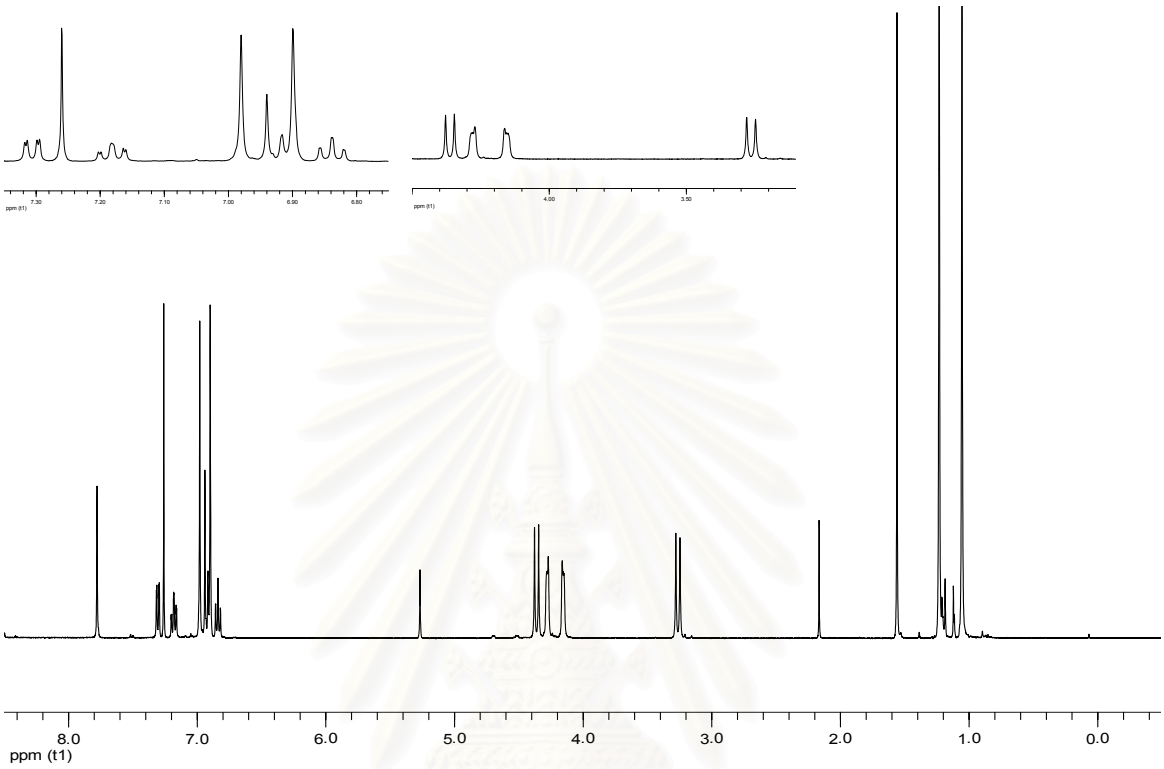


Figure A1: ^{1}H-NMR Spectrum of *cis*-*o*-**3**

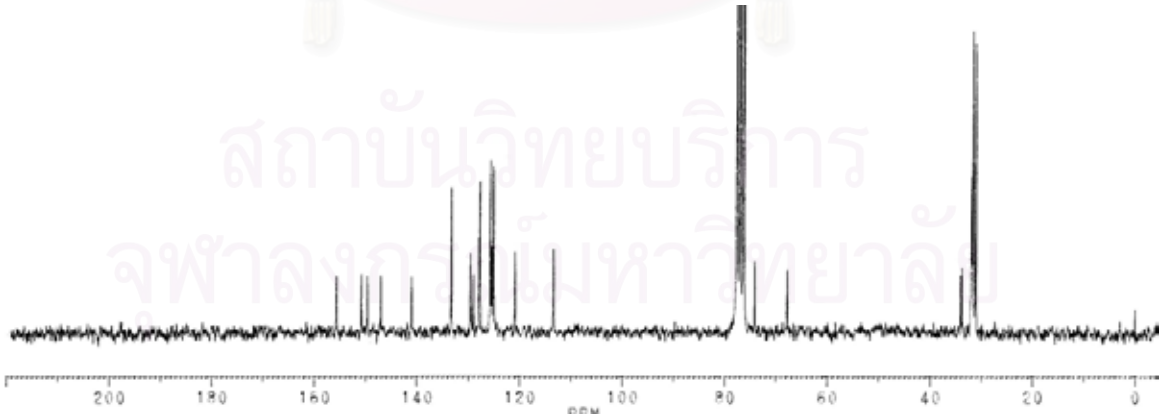


Figure A2: ^{13}C-NMR Spectrum of *cis*-*o*-**3**

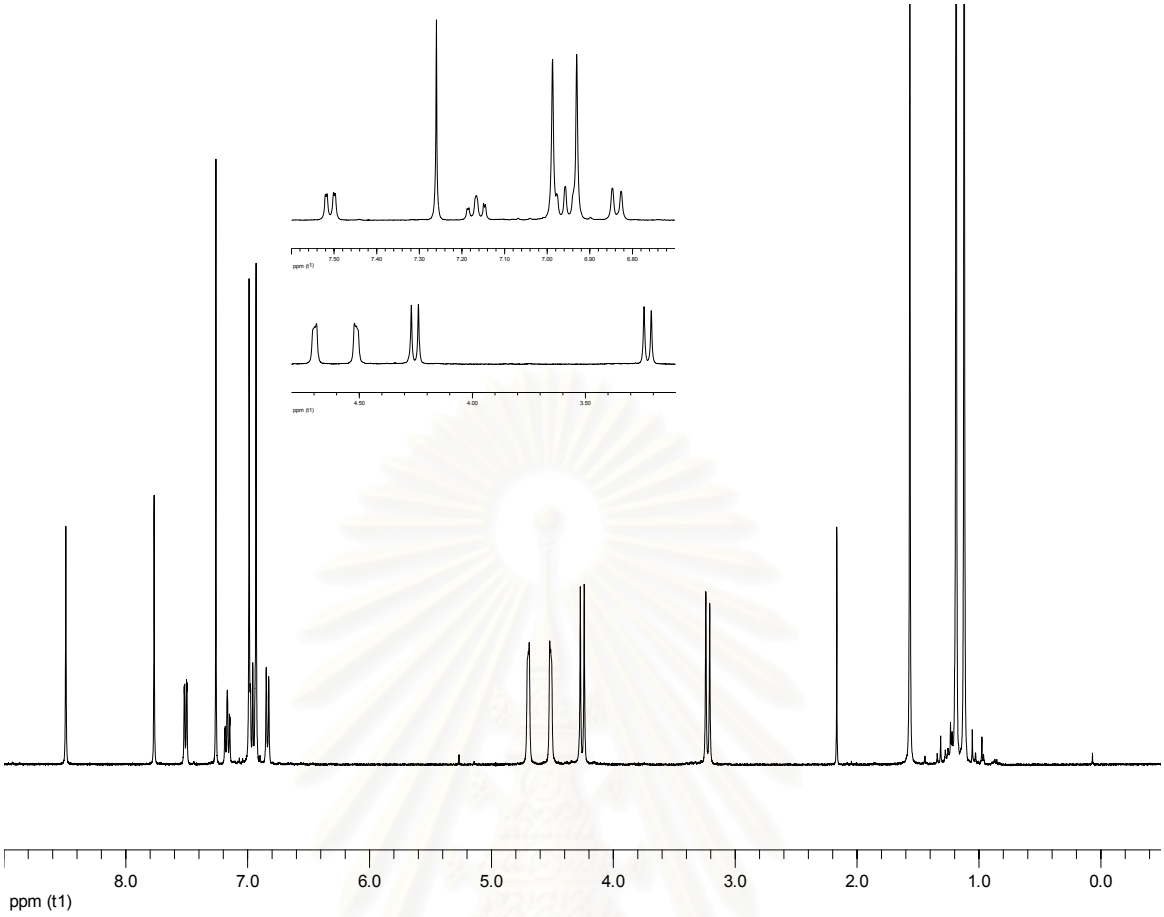


Figure A3: ^{1}H-NMR Spectrum of *trans*-*o*-**3**

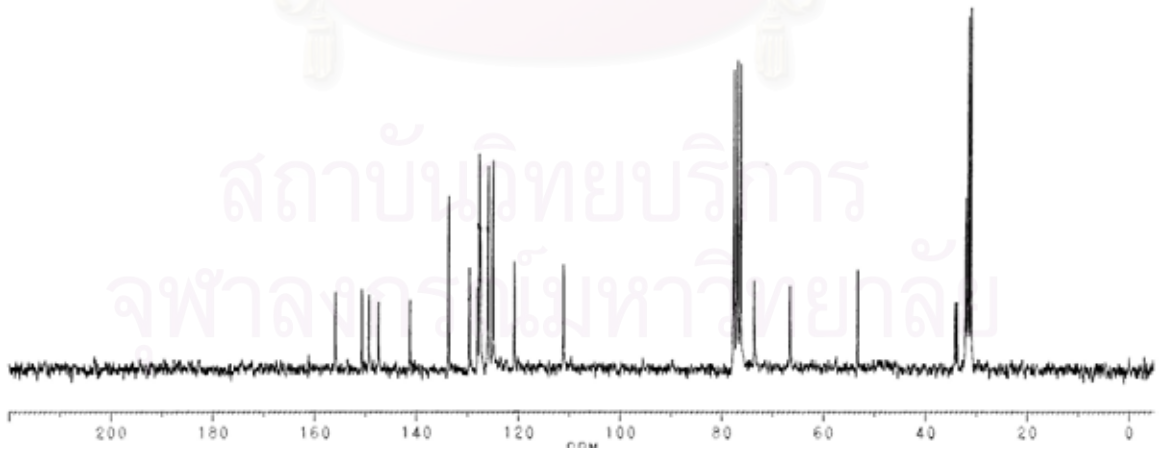


Figure A4: ^{13}C-NMR Spectrum of *trans*-*o*-**3**

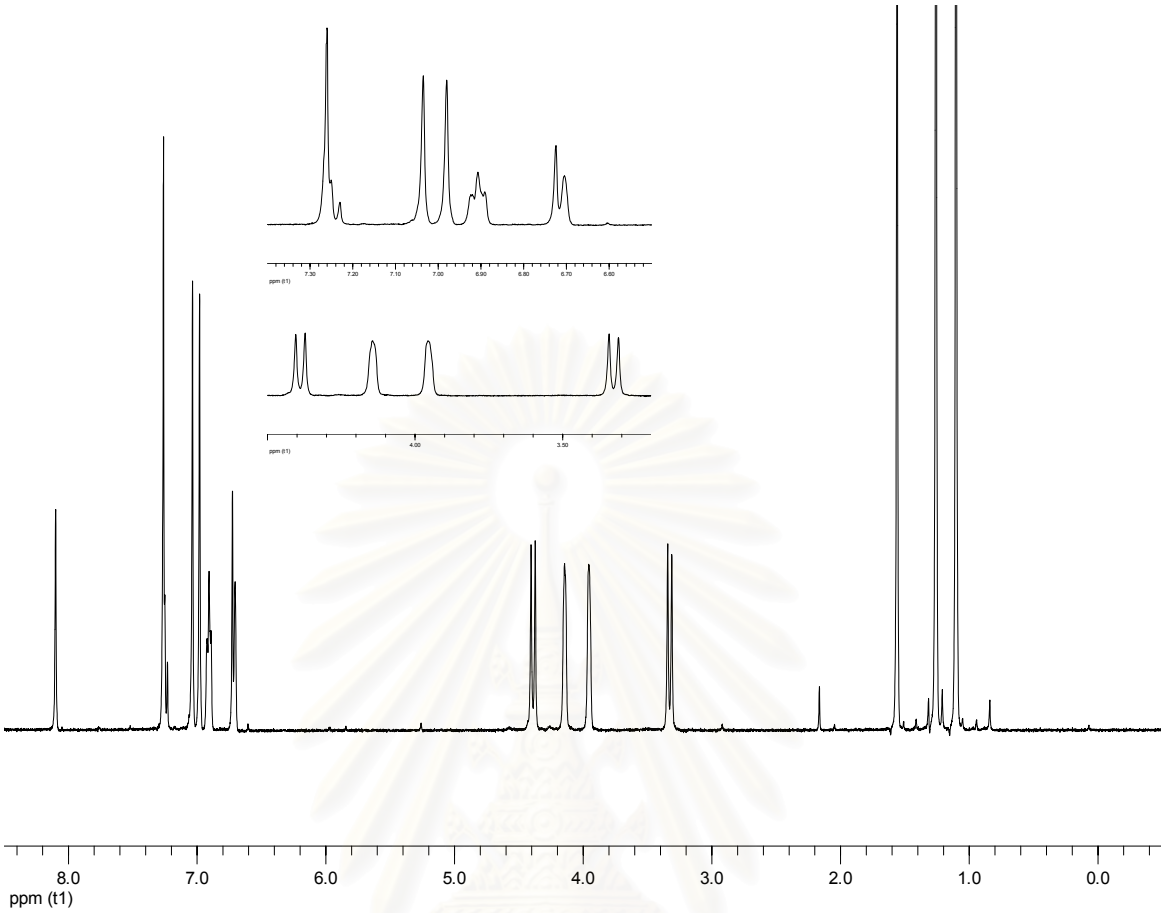


Figure A5: ^{1}H-NMR Spectrum of *cis*-*m*-**3**

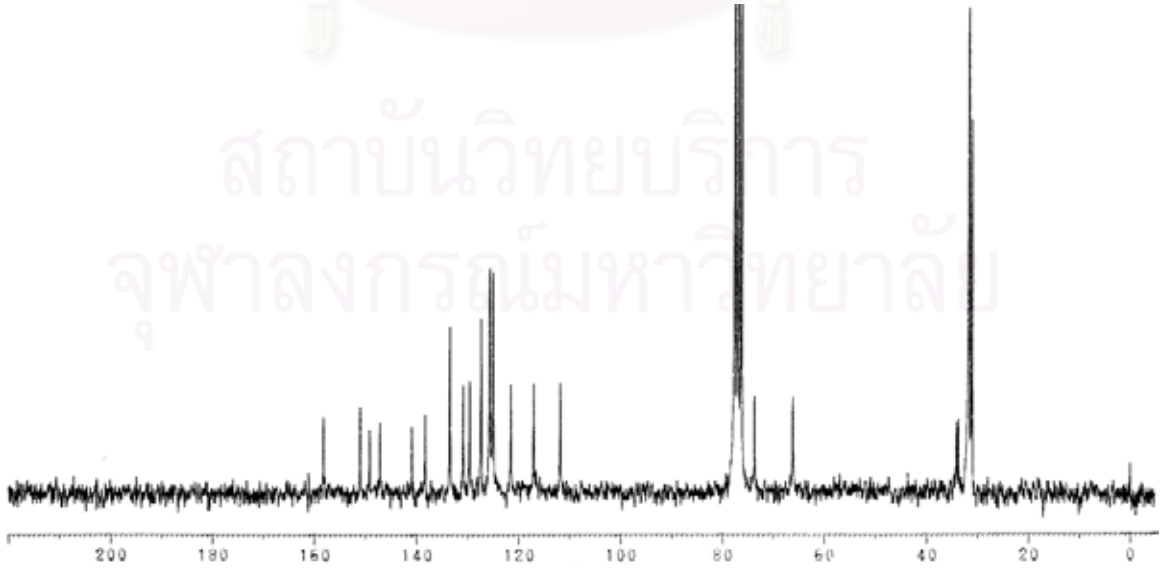


Figure A6: ^{13}C-NMR Spectrum of *cis*-*m*-**3**

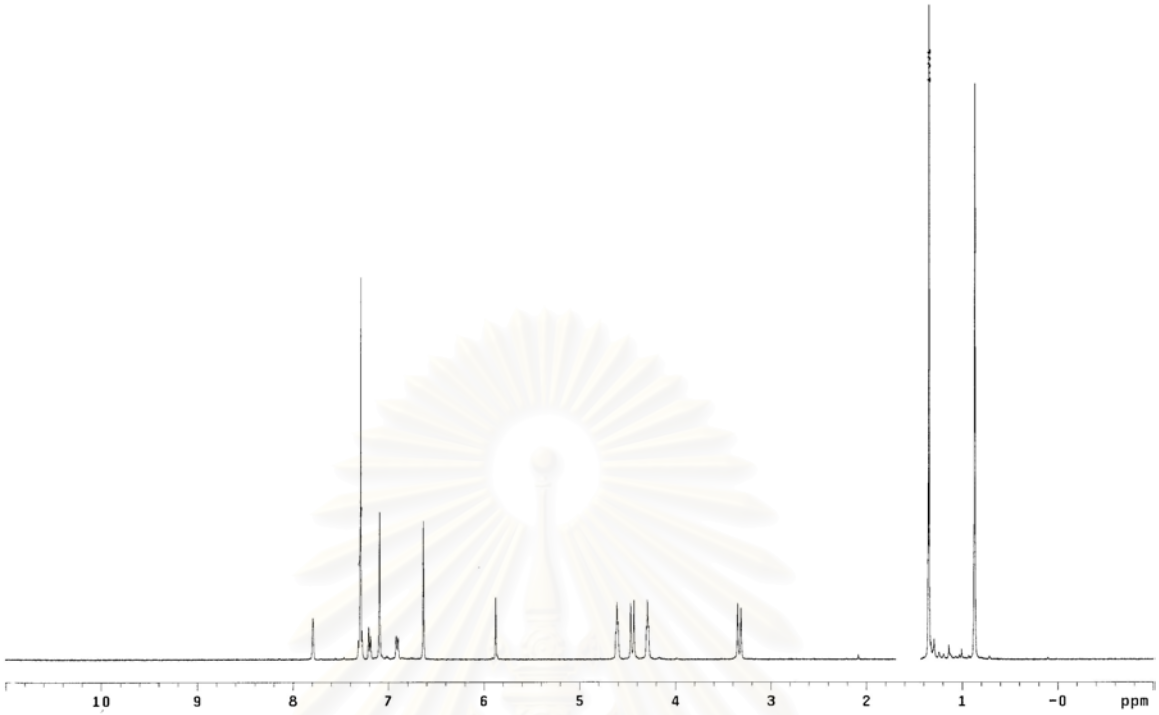


Figure A7: ^{1}H-NMR Spectrum of *trans-m*-**3**

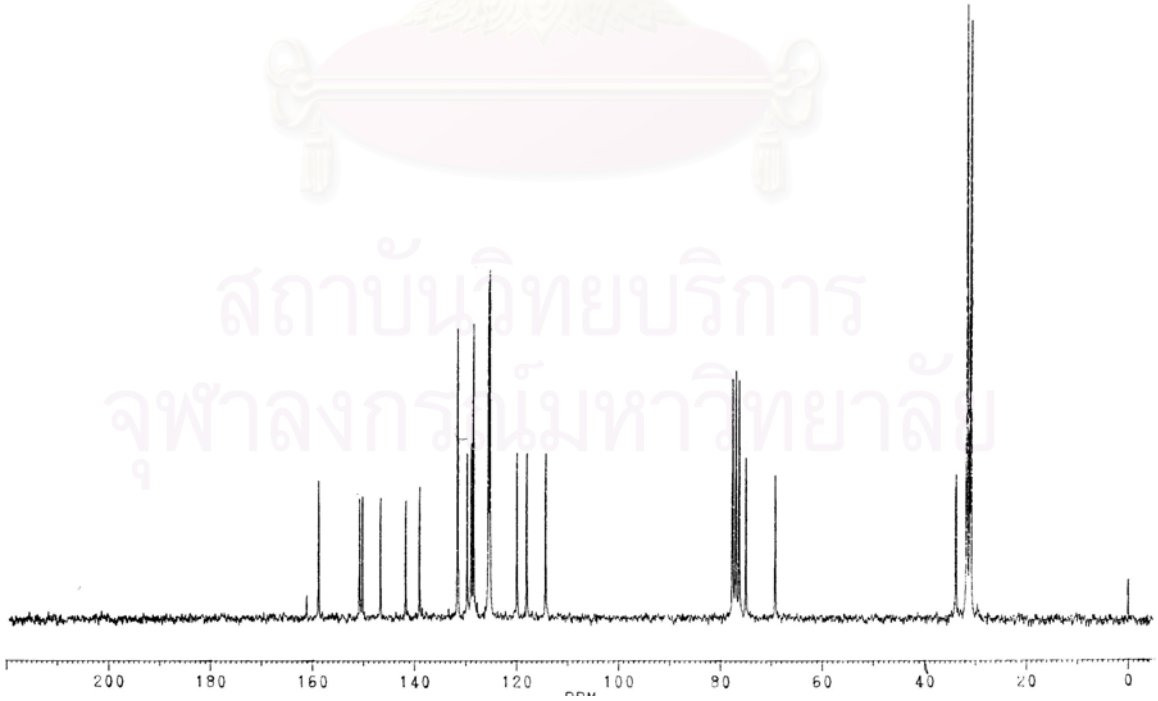


Figure A8: ^{13}C-NMR Spectrum of *trans-m*-**3**

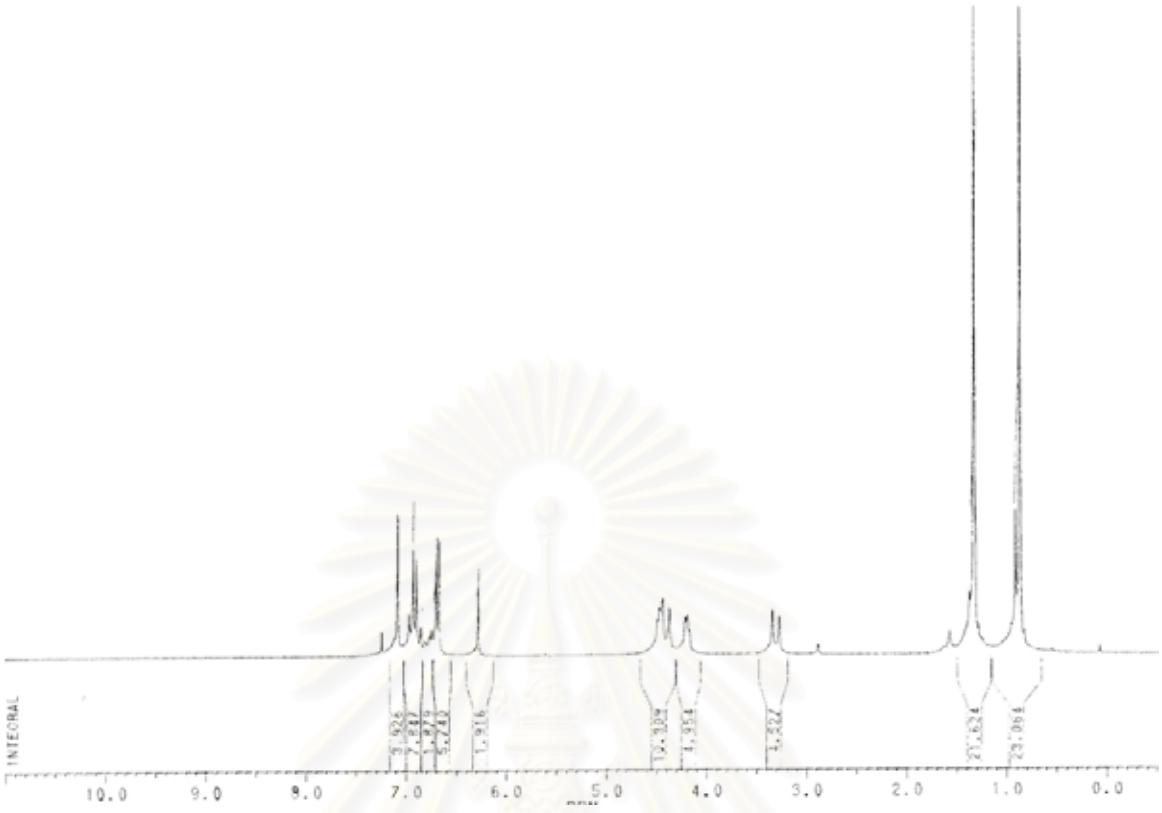


Figure A9: ^{1}H-NMR Spectrum of *cis-p*-**3**

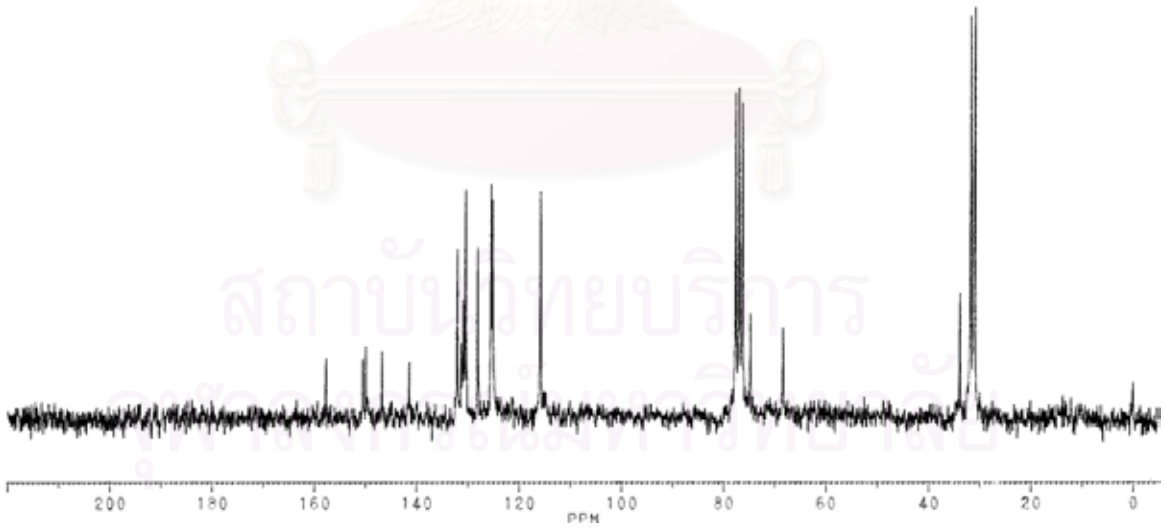


Figure A10: ^{13}C-NMR Spectrum of *cis-p*-**3**

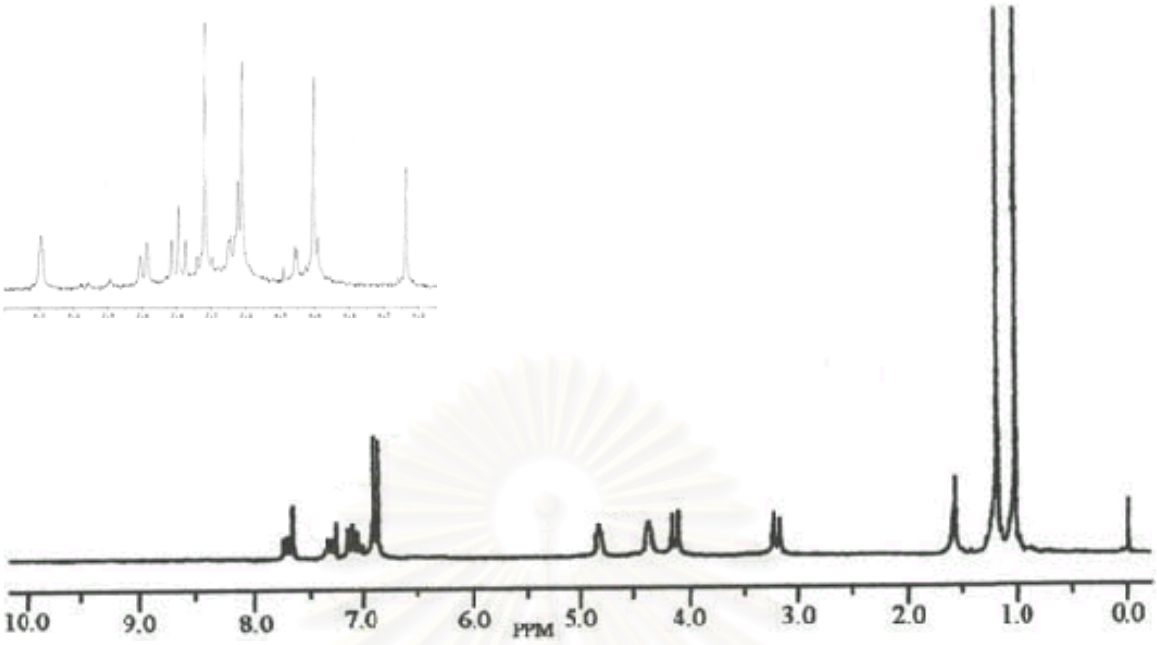


Figure A11: ^{1}H-NMR Spectrum of *trans*-*m*-**4**

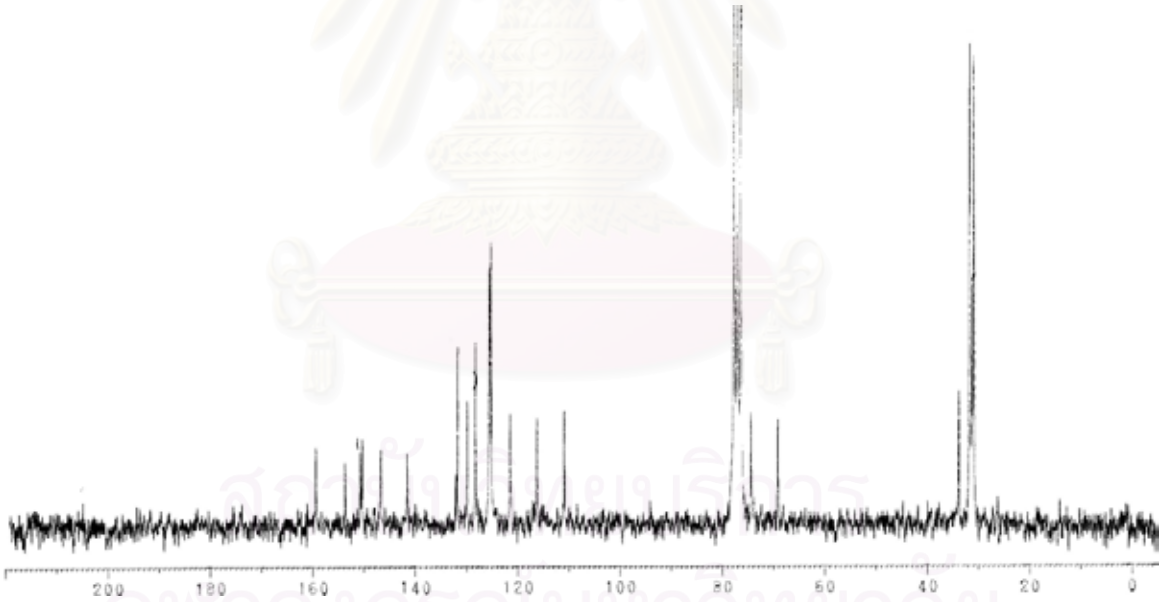


Figure A12: ^{13}C-NMR Spectrum of *trans*-*m*-**4**

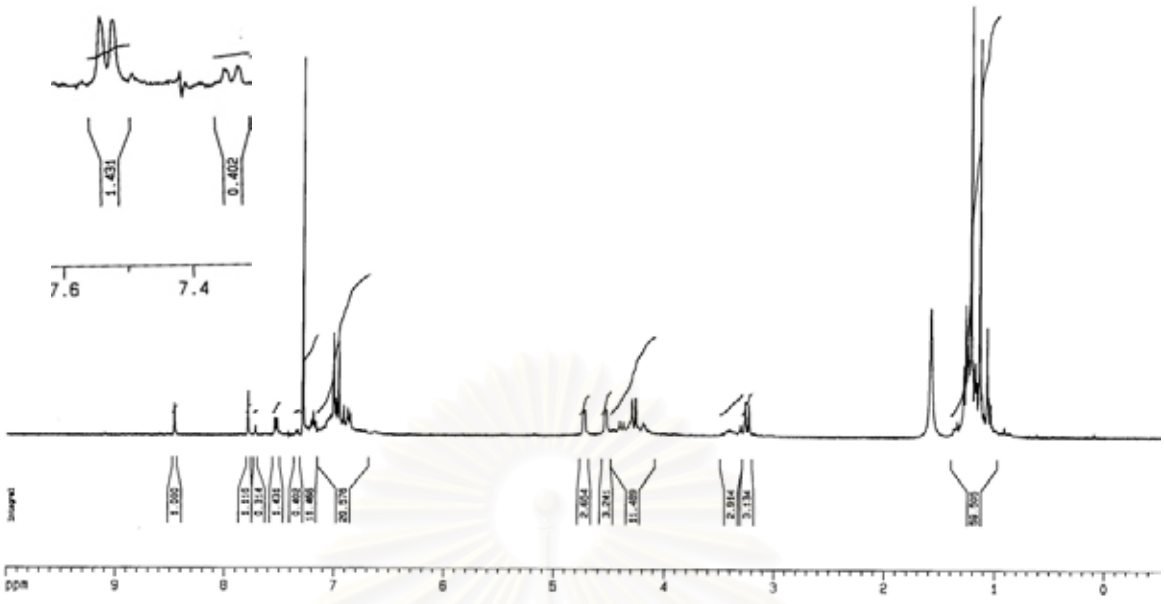


Figure A13: ^{1}H-NMR Spectrum of *o*-**3** at Photostationary State

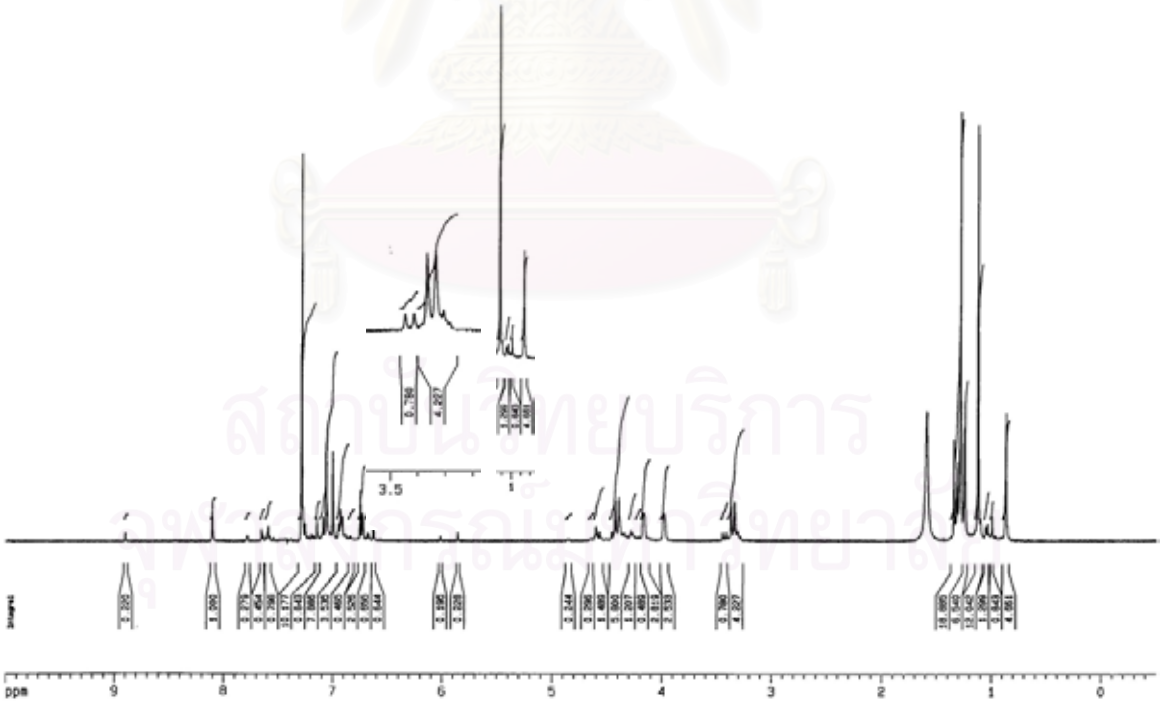


Figure A14: ^{1}H-NMR Spectrum of *m*-**3** at Photostationary State

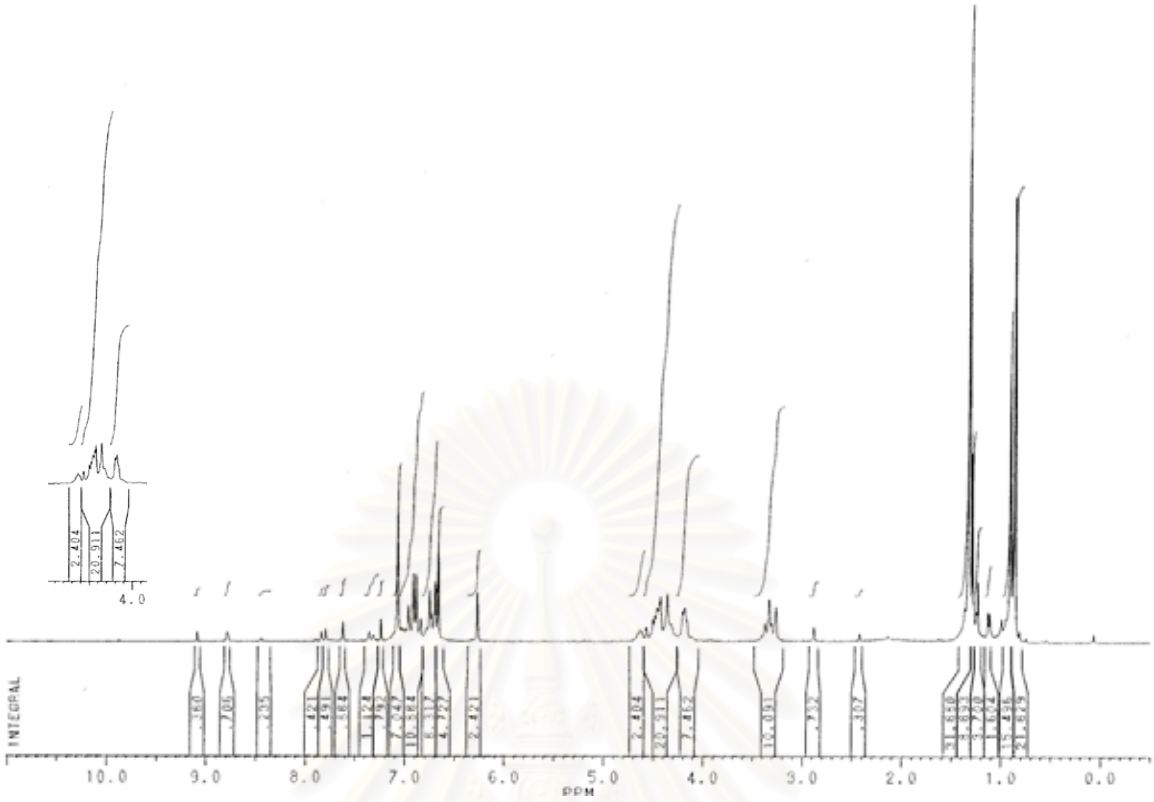


Figure A15: ^{1}H-NMR Spectrum of *p*-**3** at Photostationary State

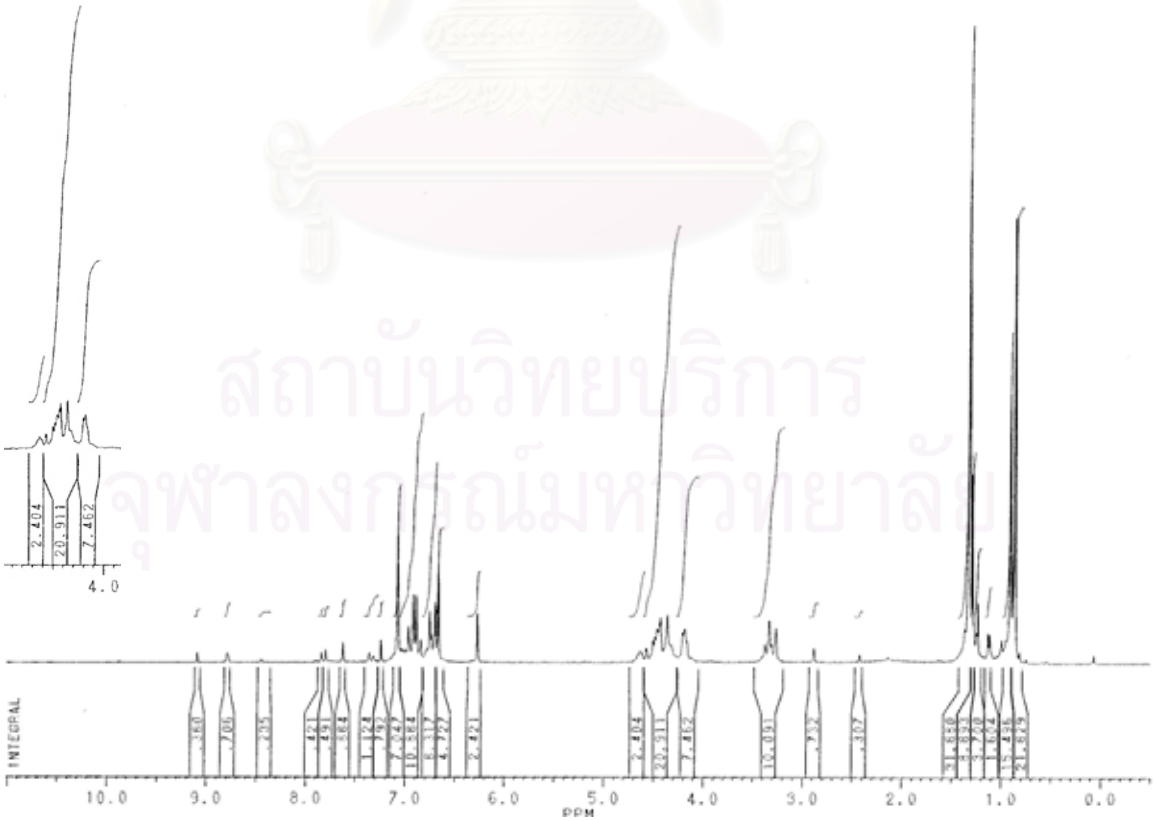


Figure A16: ^{1}H-NMR Spectrum of *m*-**4** at Photostationary State

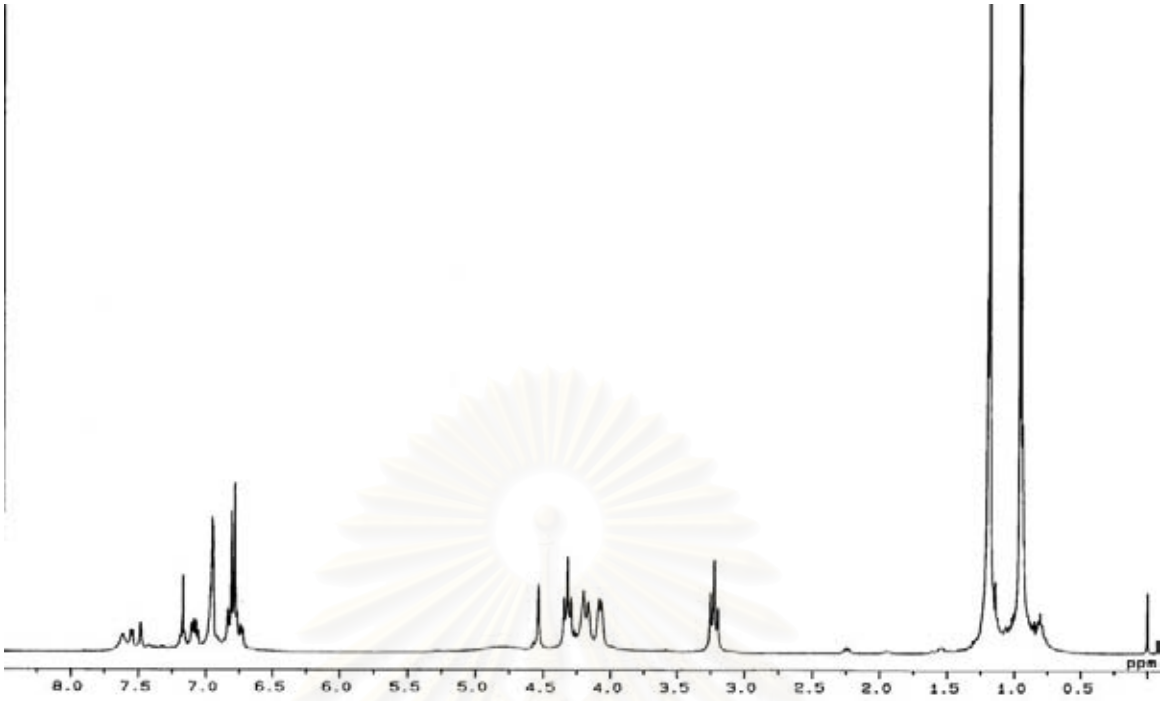


Figure A17: ^{1}H-NMR Spectrum of **6**

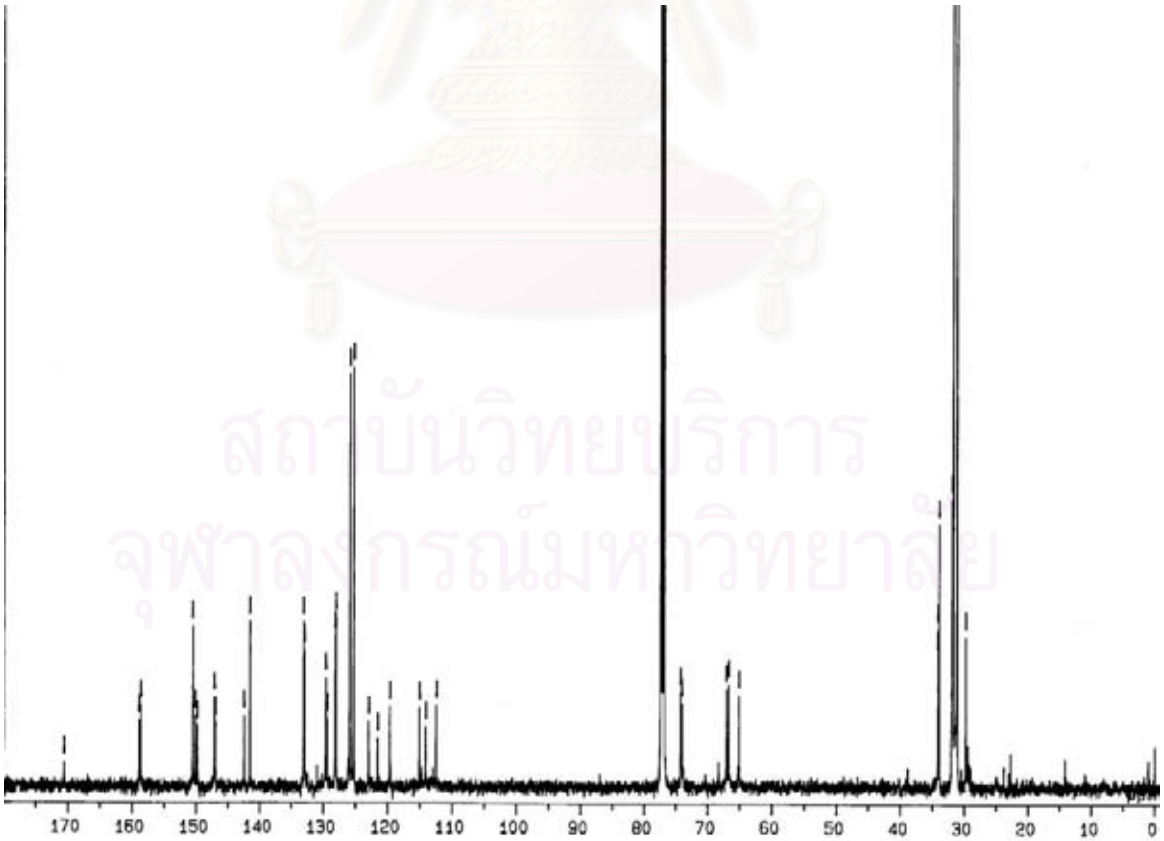


Figure A18: ^{13}C-NMR Spectrum of **6**

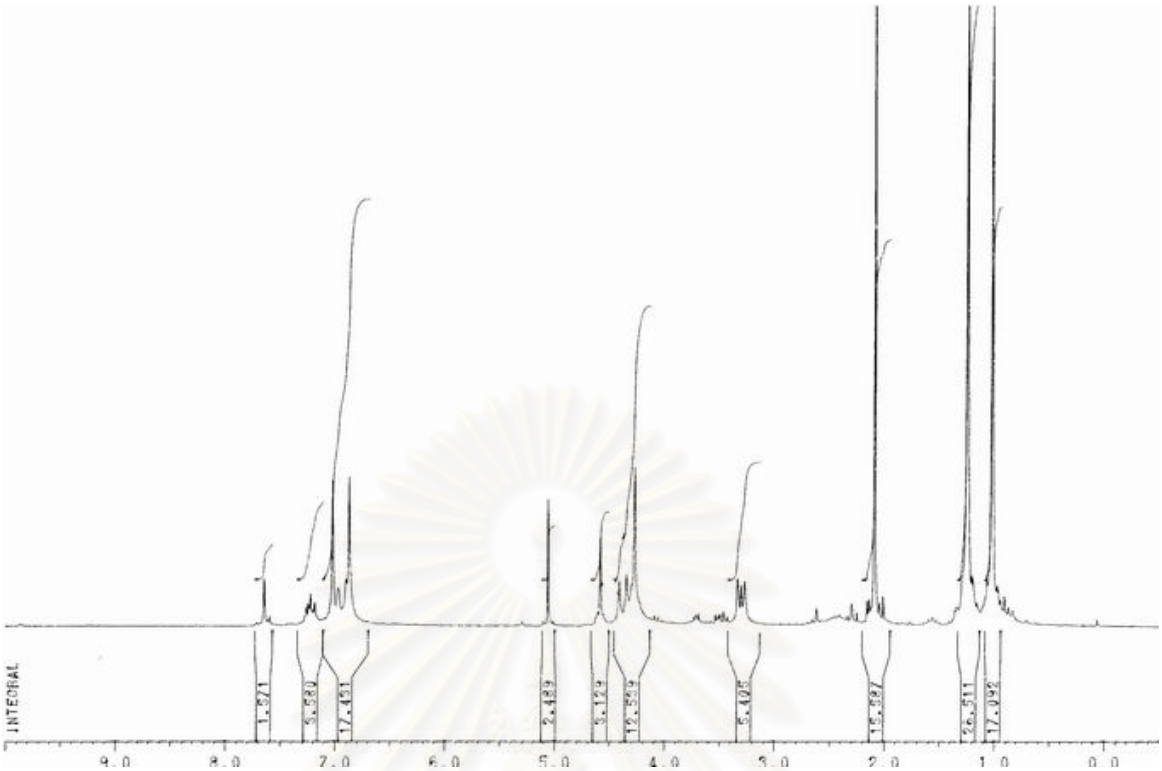


Figure A19: ^{1}H-NMR Spectrum of **7**

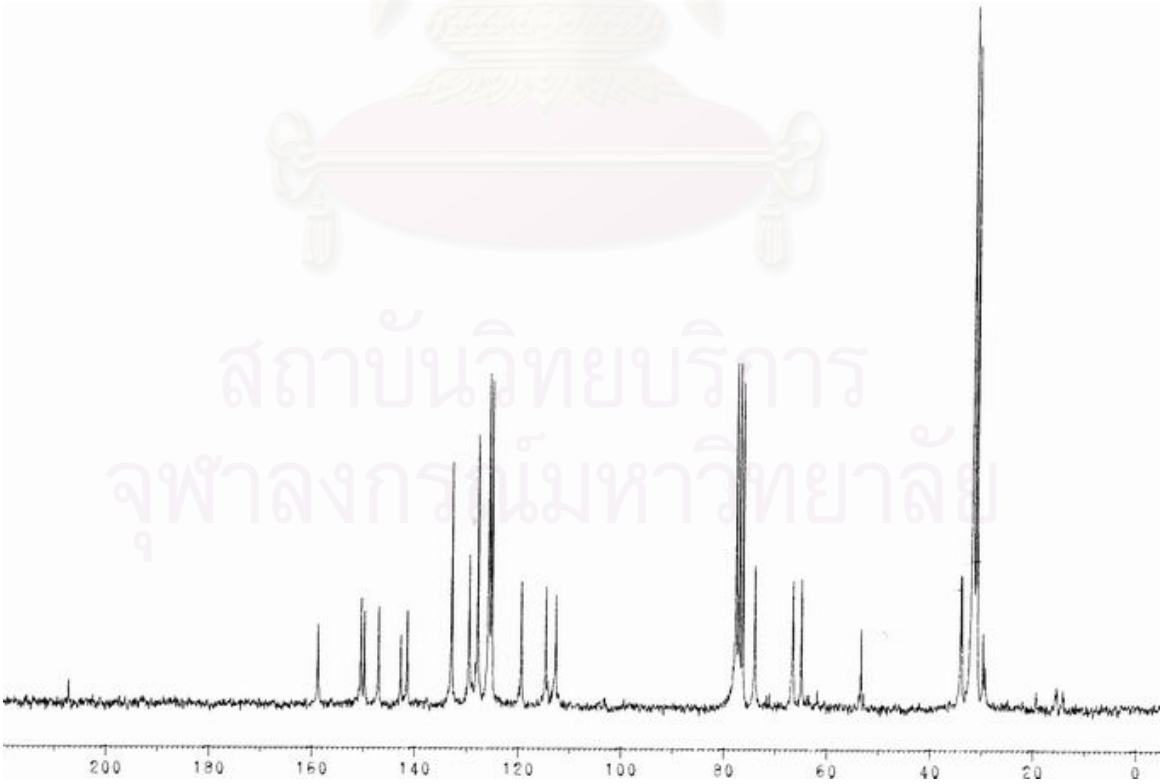


Figure A20: ^{13}C-NMR Spectrum of **7**

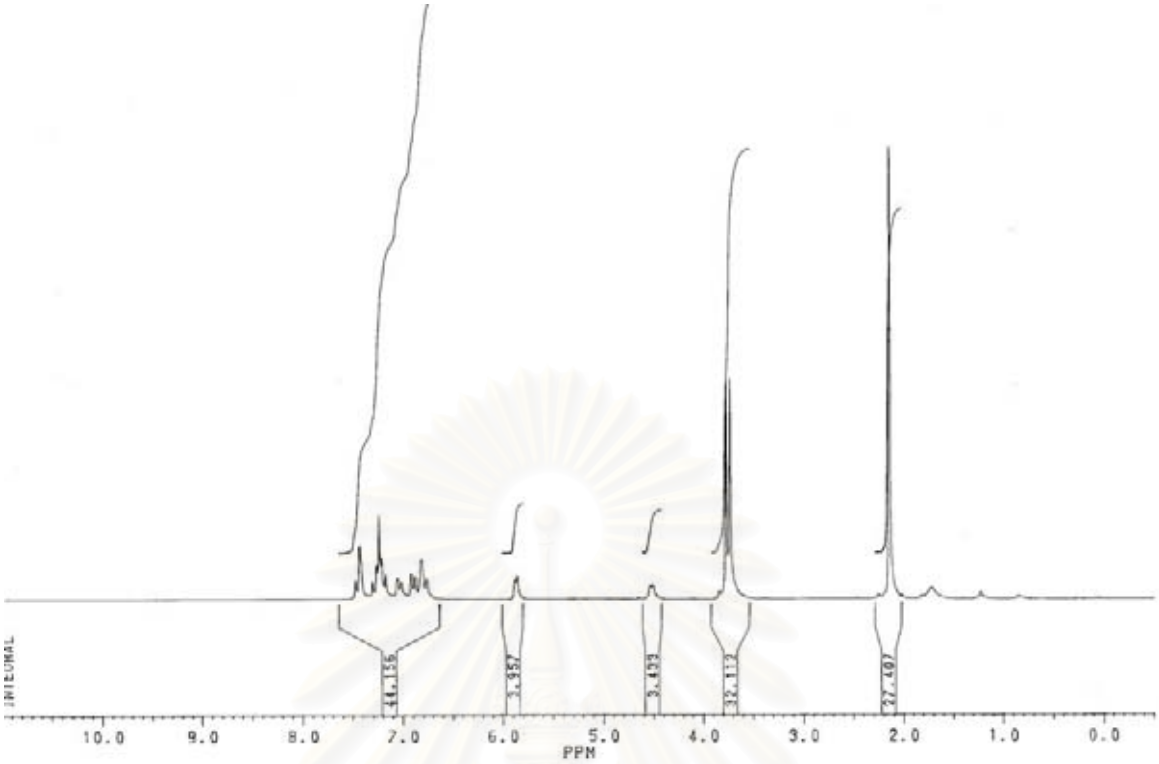


Figure A21: ^{1}H-NMR Spectrum of 3,3'-Dimethoxybenzoin

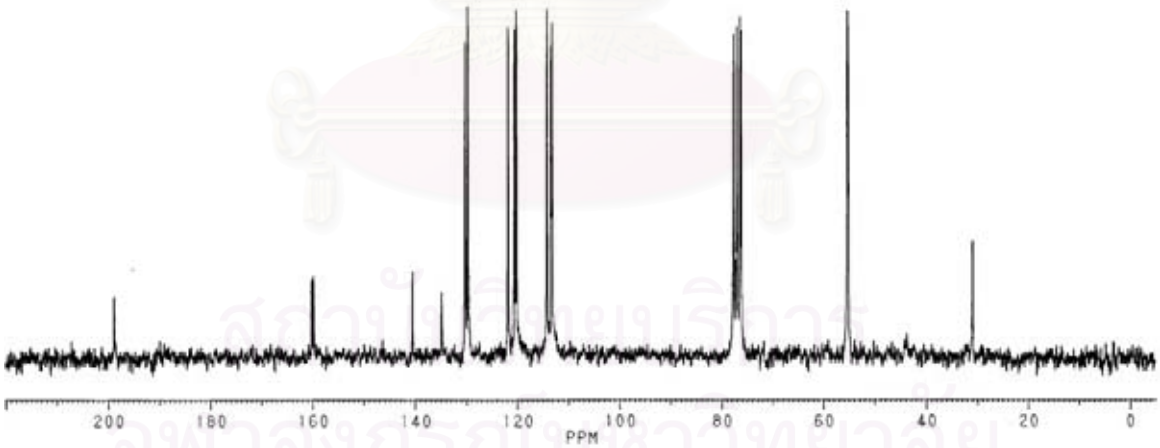


Figure A22: ^{13}C-NMR Spectrum of 3,3'-Dimethoxybenzoin

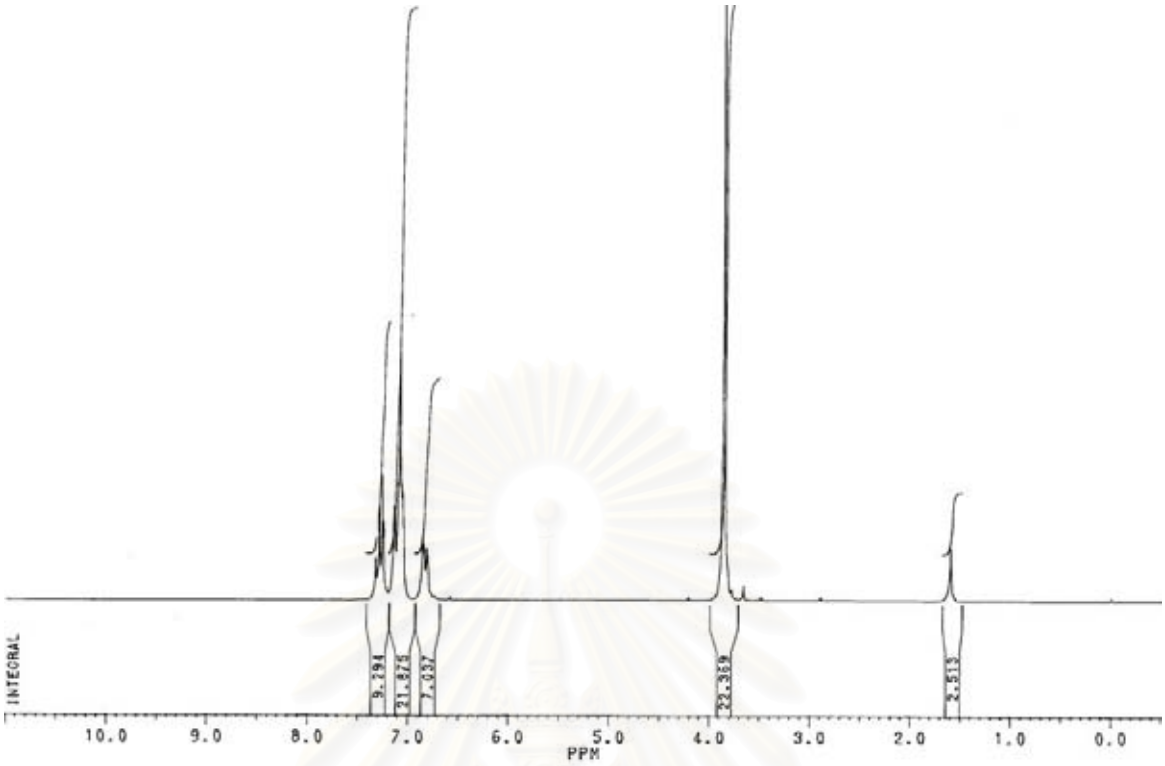


Figure A23: ^{1}H-NMR Spectrum of *trans*-3,3'-Dimethoxystilbene

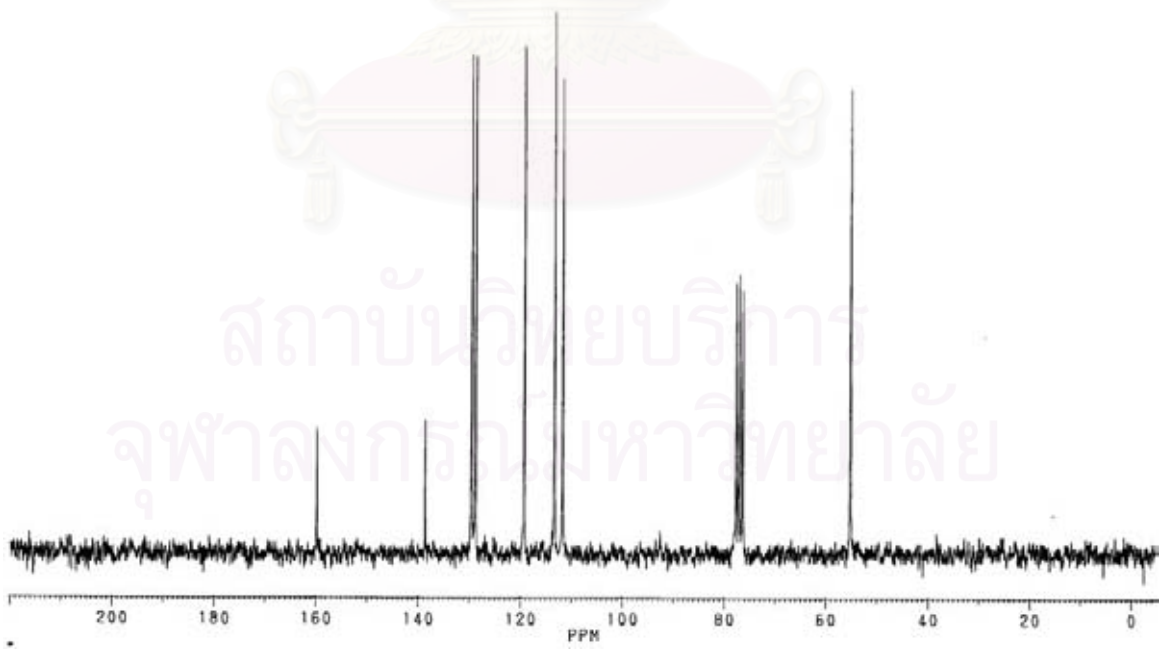


Figure A24: ^{13}C-NMR Spectrum of *trans*-3,3'-Dimethoxystilbene

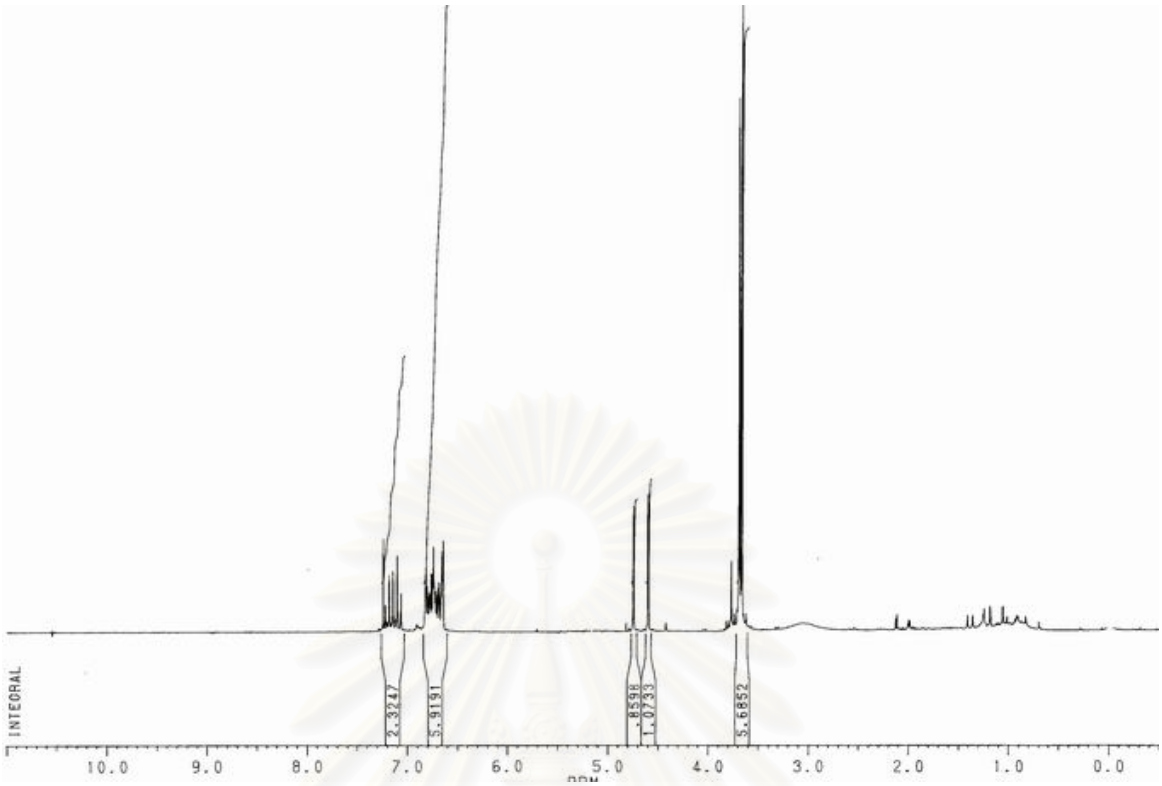


Figure A25: ^{1}H-NMR Spectrum of Diastereomeric Mixture of 3,3'-Dimethoxypinacol

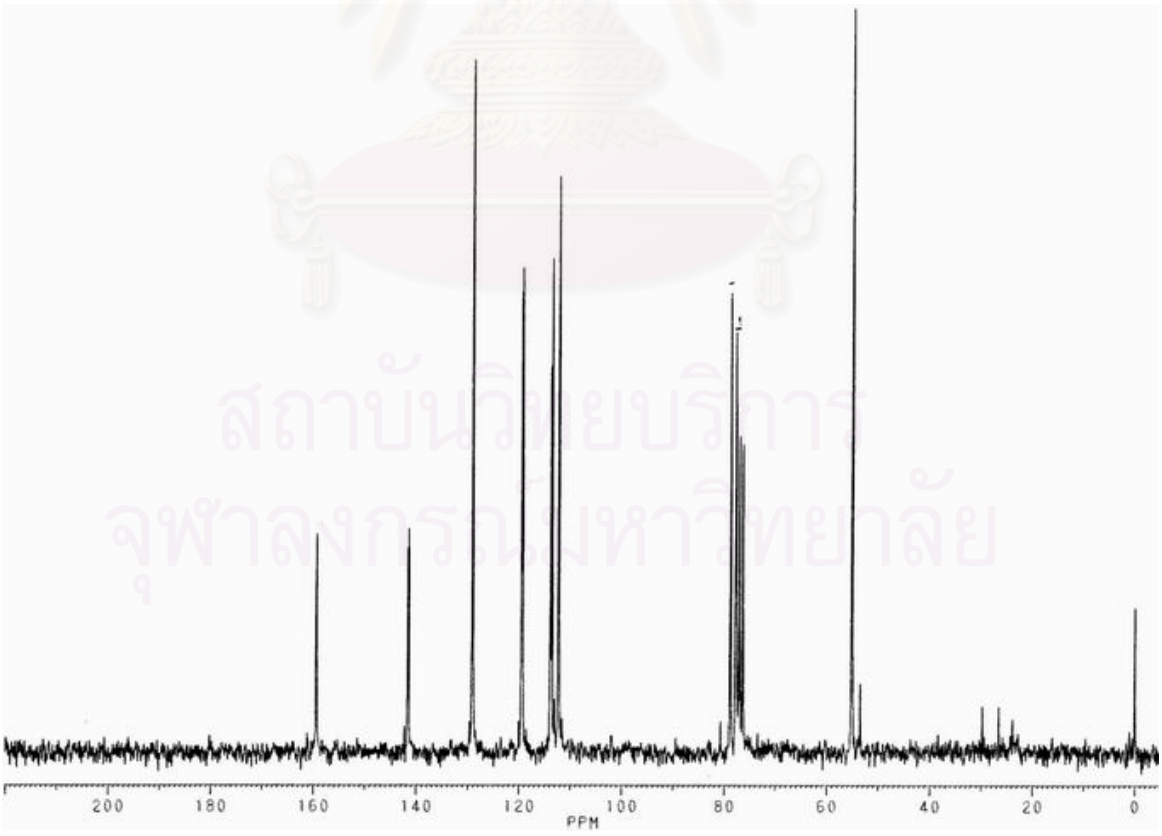


Figure A26: ^{13}C-NMR Spectrum of Diastereomeric Mixture of 3,3'-Dimethoxypinacol

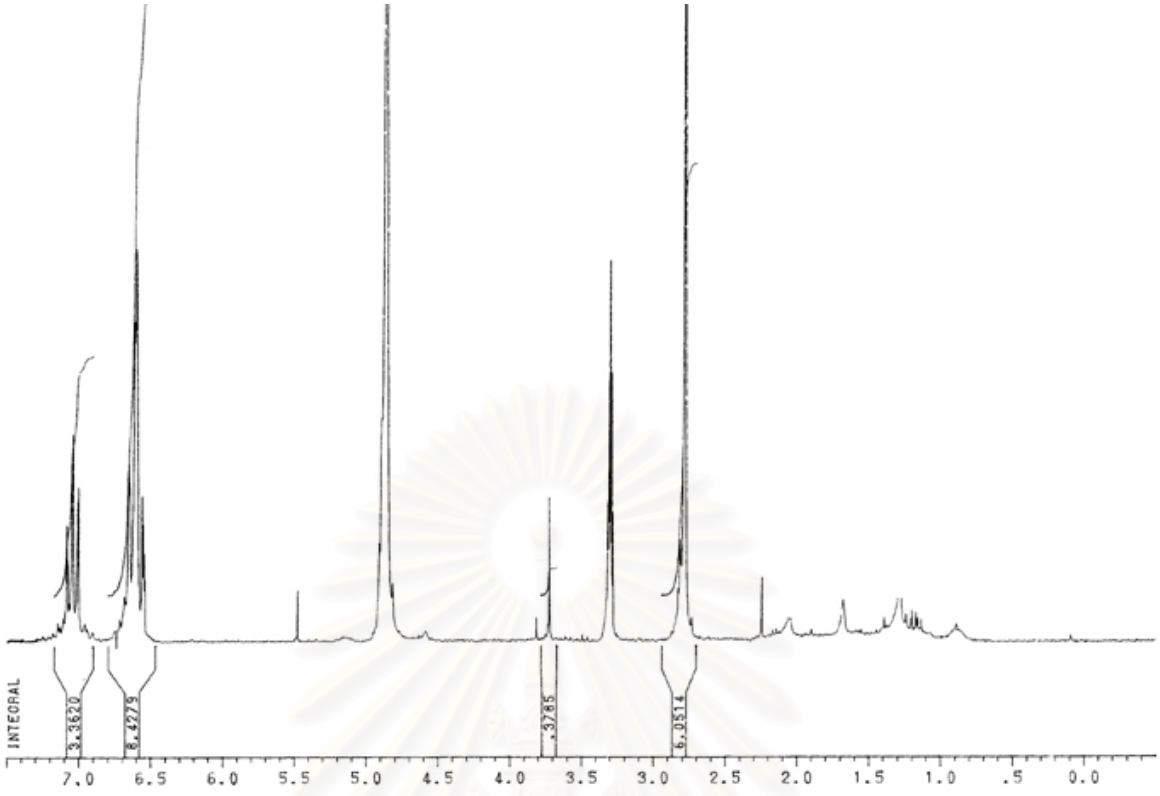


Figure A27: ^{1}H-NMR Spectrum of Diastereomeric Mixture of 1,2-Diiodo-1,2-di-(3,3'-dihydroxyphenyl)ethane

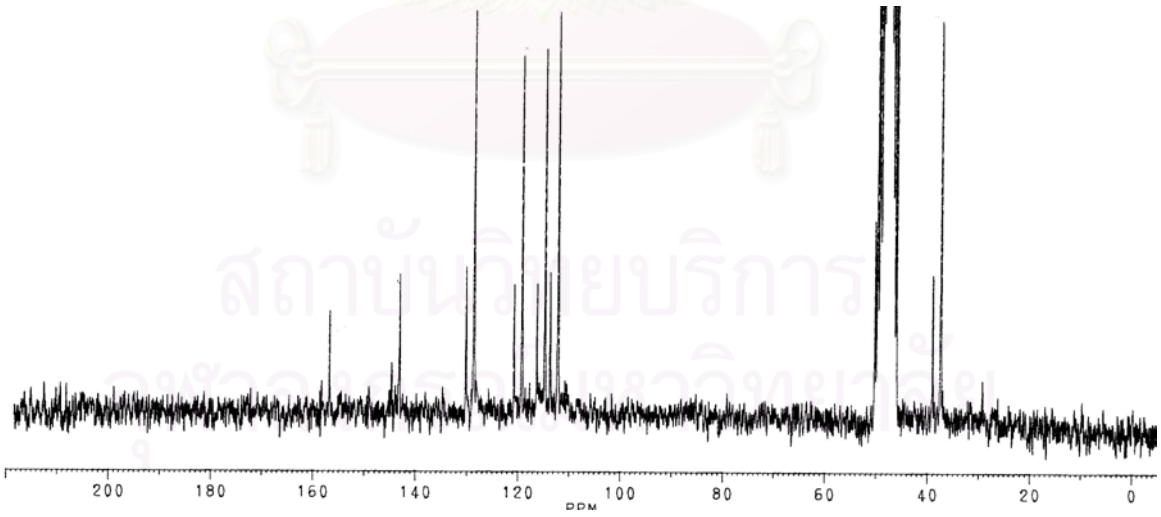
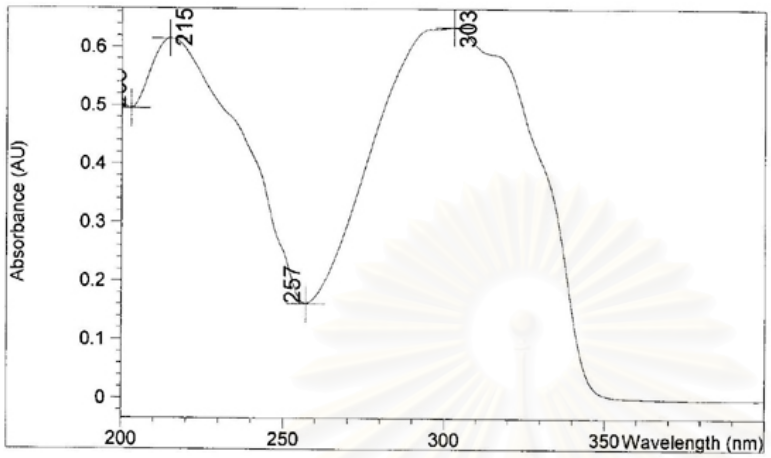


Figure A28: ^{13}C-NMR Spectrum of Diastereomeric Mixture of 1,2-Diiodo-1,2-di-(3,3'-dihydroxyphenyl)ethane

APPENDIX B

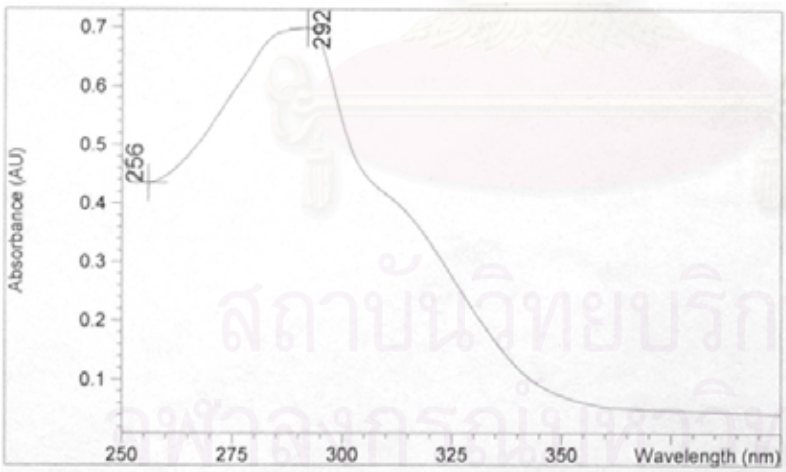
UV-VIS SPECTRA



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1		303.0	0.63481	257.0	0.16144
1		215.0	0.61504	203.0	0.49441
1		***	***	***	***

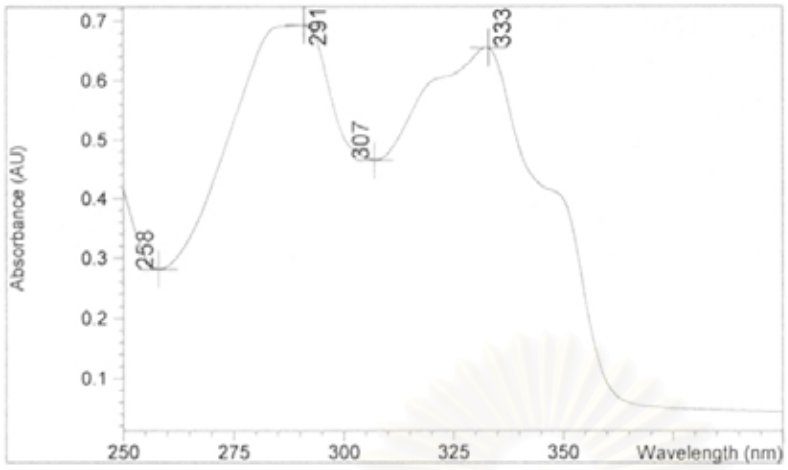
Figure B1: UV-Vis Spectrum of *trans*-3,3'-Dimethoxybenzoin



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1	cis-o-OH CS	292.0	0.69815	256.0	0.43512
1		***	***	***	***
1		***	***	***	***

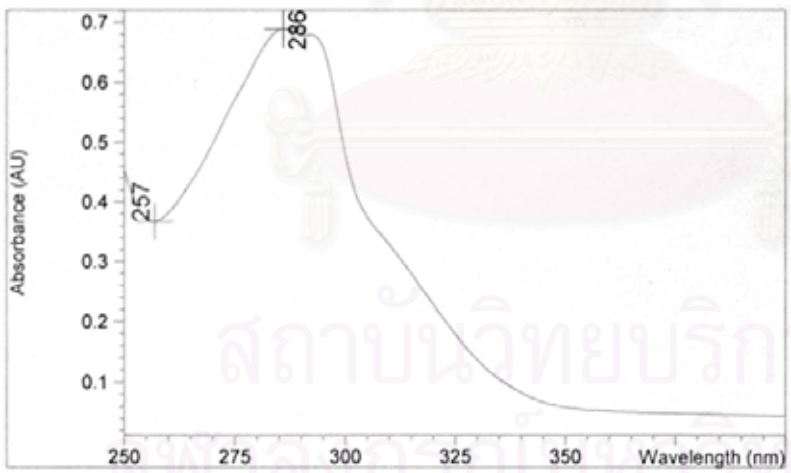
Figure B2: UV-Vis Spectrum of *cis*-*o*-**3** (36 μM)



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1		291.0	0.69228	258.0	0.28077
1		333.0	0.65517	307.0	0.46562
1		***	***	***	***

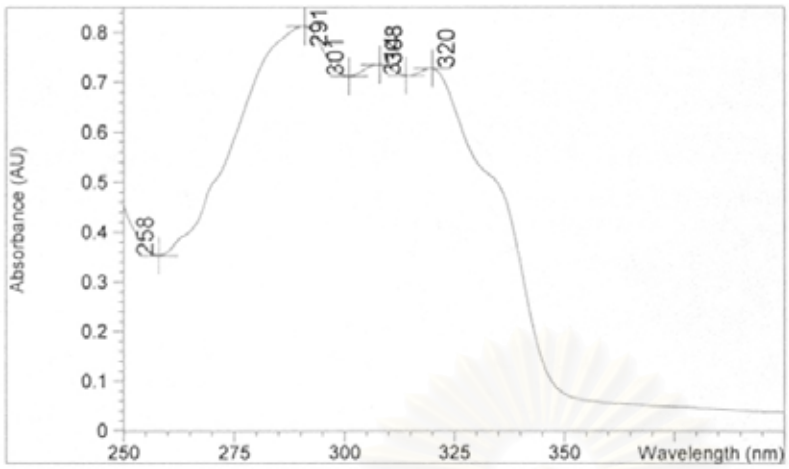
Figure B3: UV-Vis Spectrum of *trans-o*-**3** (23 μM)



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1		286.0	0.68838	257.0	0.3673E
1		***	***	***	***
1		***	***	***	***

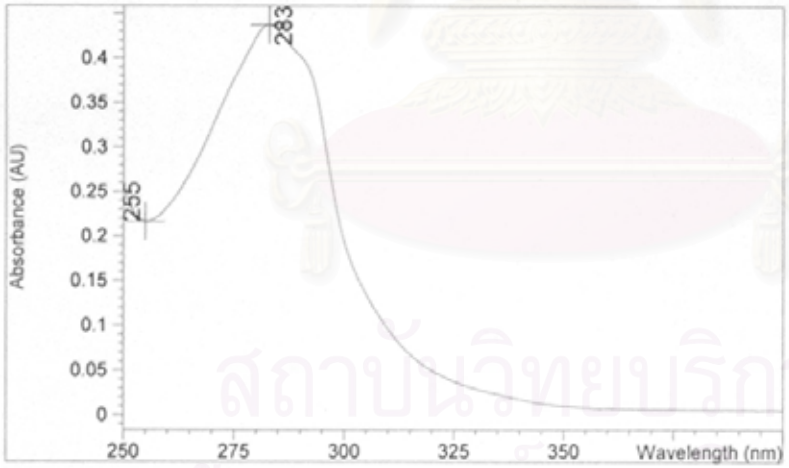
Figure B4: UV-Vis Spectrum of *cis-m*-**3** (33 μM)



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1	m-OH CS 3E-5 M	291.0	0.81269	258.0	0.3533
1	m-OH CS 3E-5 M	308.0	0.73516	301.0	0.7118
1	m-OH CS 3E-5 M	320.0	0.72814	314.0	0.7138

Figure B5: UV-Vis Spectrum of *trans-m*-**3** (30 μM)



Sample/Result Table

#	Name	Peaks(nm)	Abs(AU)	Valleys(nm)	Abs(AU)
1		283.0	0.43708	255.0	0.2164
1		***	***	***	***
1		***	***	***	***

Figure B6: UV-Vis Spectrum of *cis-p*-**3** (26 μM)

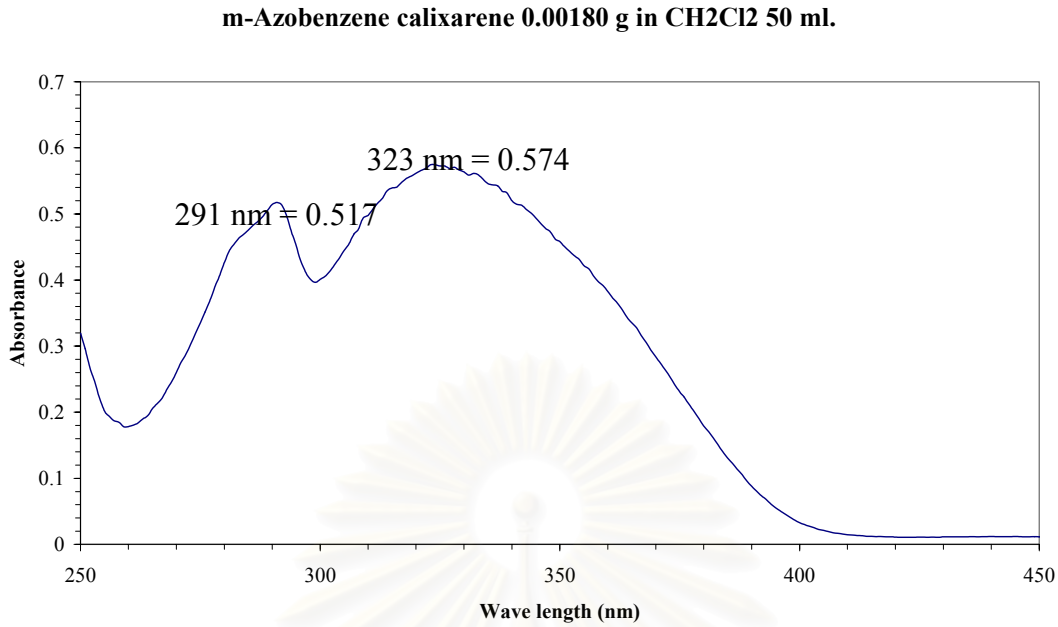


Figure B7: UV-Vis Spectrum of *cis*-*m*-**4** (39 μM)

APPENDIX C

X-RAY DATA

1. X-Ray Data of *cis-o*-3 (CCDC249144)

Empirical formula	$C_{63}H_{74}Cl_2O_6$	
Formula weight	998.12	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 20.7486(5) Å	α = 90.00°
	b = 12.3713(4) Å	β = 109.373(2)°
	c = 19.5738(8) Å	γ = 90.00°
Volume	5480.8(3) Å^3	
Z	4	
Density (calculated)	1.210 Mg / m^3	
Absorption coefficient	0.169 mm^{-1}	
F(000)	2136	
Crystal	colourless block	
Crystal size	0.24 x 0.18 x 0.12 mm^3	
θ range for data collection	1.0 – 27.48°	
Index ranges	$-26 \le h \le 26$, $-14 \le k \le 16$, $-28 \le l \le 29$	
Reflections collected	32983	
Independent reflections	12074 [R_{int} = 0.0700]	
Completeness to θ = 27.52°	96.0 %	
Max. and min. transmission	0.9800 and 0.9605	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12074 / 6 / 728	
Goodness-of-fit on F^2	1.006	
Final R indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0931, *wR2* = 0.2492	
R indices (all data)	*R1* = 0.1700, *wR2* = 0.3186	
Extinction coefficient	0.0093(19)	
Largest diff. peak and hole	0.975 and –0.588 e Å^{-3}	

List of Bond lengths (Å):

C1 C2 1.383(5)
C1 C6 1.391(5)
C1 O1 1.412(5)
C2 C3 1.395(6)
C2 C44 1.508(5)
C3 C4 1.387(5)
C3 H3 0.9500
C4 C5 1.385(6)
C4 C7 1.537(6)
C5 C6 1.396(6)
C5 H5 0.9500
C6 C11 1.521(6)
C7 C8 1.506(7)
C7 C9 1.524(7)
C7 C10 1.562(7)
C8 H8A 0.9800
C8 H8B 0.9800
C8 H8C 0.9800
C9 H9A 0.9800
C9 H9B 0.9800
C9 H9C 0.9800
C10 H10A 0.9800
C10 H10B 0.9800
C10 H10C 0.9800
C11 C12 1.532(5)
C11 H11A 0.9900
C11 H11B 0.9900
C12 C17 1.382(5)
C12 C13 1.390(5)
C13 C14 1.392(5)
C13 H13 0.9500
C14 C15 1.395(5)
C14 C18 1.540(5)
C15 C16 1.391(5)
C15 H15 0.9500
C16 C17 1.404(5)
C16 C22 1.519(5)
C17 O2 1.371(4)
C18 C21 1.506(6)
C18 C19 1.521(6)
C18 C20 1.519(6)
C19 H19A 0.9800
C19 H19B 0.9800
C19 H19C 0.9800
C20 H20A 0.9800
C20 H20B 0.9800
C20 H20C 0.9800
C21 H21A 0.9800
C21 H21B 0.9800
C21 H21C 0.9800
C22 C23 1.525(5)
C22 H22A 0.9900
C22 H22B 0.9900
C23 C24 1.380(6)
C23 C28 1.405(5)
C24 C25 1.403(6)
C24 H24 0.9500
C25 C26 1.399(5)
C25 C29 1.530(6)
C26 C27 1.395(6)
C26 H26 0.9500
C27 C28 1.392(6)
C27 C33 1.518(5)
C28 O3' 1.02(4)
C28 O3 1.464(17)
C29 C32 1.527(6)
C29 C30 1.528(6)
C29 C31 1.535(6)
C30 H30A 0.9800
C30 H30B 0.9800
C30 H30C 0.9800
C31 H31A 0.9800
C31 H31B 0.9800
C31 H31C 0.9800
C32 H32A 0.9800
C32 H32B 0.9800
C32 H32C 0.9800
C33 C34 1.519(5)
C33 H33A 0.9900
C33 H33B 0.9900
C34 C35 1.390(5)
C34 C39 1.398(5)
C35 C36 1.392(5)
C35 H35 0.9500
C36 C37 1.392(5)
C36 C40 1.532(5)
C37 C38 1.392(5)
C37 H37 0.9500
C38 C39 1.402(5)
C38 C44 1.527(5)
C39 O4 1.358(4)
C40 C43' 1.453(18)
C40 C41 1.481(9)

C40 C42 1.509(8)
C40 C43 1.563(8)
C40 C41' 1.586(15)
C40 C42' 1.633(17)
C41 H41A 0.9800
C41 H41B 0.9800
C41 H41C 0.9800
C42 H42A 0.9800
C42 H42B 0.9800
C42 H42C 0.9800
C43 H43A 0.9800
C43 H43B 0.9800
C43 H43C 0.9800
C41' H41D 0.9800
C41' H41E 0.9800
C41' H41F 0.9800
C42' H42D 0.9800
C42' H42E 0.9800
C42' H42F 0.9800
C43' H43D 0.9800
C43' H43E 0.9800
C43' H43F 0.9800
C44 H44A 0.9900
C44 H44B 0.9900
C45 O1 1.437(4)
C45 C46 1.480(6)
C45 H45A 0.9900
C45 H45B 0.9900
C46 O5 1.422(5)
C46 H46A 0.9900
C46 H46B 0.9900
C47 C48 1.377(6)
C47 O5 1.382(5)
C47 C52 1.398(6)
C48 C49 1.367(6)
C48 H48 0.9500
C49 C50 1.391(7)
C49 H49 0.9500
C50 C51 1.390(6)
C50 H50 0.9500
C51 C52 1.384(6)
C51 H51 0.9500
C52 C53 1.477(5)
C53 C54 1.334(6)
C53 H53 0.9500
C54 C55 1.463(5)
C54 H54 0.9500
C55 C56 1.396(5)
C55 C60 1.405(5)
C56 C57 1.357(7)
C56 H56 0.9500
C57 C58 1.347(9)
C57 H57 0.9500
C58 C59 1.403(8)
C58 H58 0.9500
C59 C60 1.379(6)
C59 H59 0.9500
C60 O6 1.347(5)
C61 O6 1.418(10)
C61 C62 1.430(19)
C61 H61A 0.9900
C61 H61B 0.9900
C62 O3 1.566(15)
C62 H62A 0.9900
C62 H62B 0.9900
C61' O6 1.506(6)
C61' C62' 1.527(13)
C61' H61C 0.9900
C61' H61D 0.9900
C62' O3' 1.63(4)
C62' H62C 0.9900
C62' H62D 0.9900
O2 H2 0.8400
O4 H4 0.8400
Cl1 C01 1.678(7)
Cl2 Cl2' 1.084(18)
Cl2 C01 1.761(7)
C01 H01A 0.9900
C01 H01B 0.9900

List of Bond angles (deg):

C2 C1 C6 122.9(4)
C2 C1 O1 118.5(3)
C6 C1 O1 118.6(3)
C1 C2 C3 117.5(3)
C1 C2 C44 122.4(4)
C3 C2 C44 120.2(4)
C4 C3 C2 122.2(4)
C4 C3 H3 118.9
C2 C3 H3 118.9
C5 C4 C3 117.6(4)
C5 C4 C7 120.1(4)
C3 C4 C7 122.3(4)
C4 C5 C6 122.8(4)
C4 C5 H5 118.6
C6 C5 H5 118.6
C1 C6 C5 116.7(4)
C1 C6 C11 123.0(4)
C5 C6 C11 120.2(3)
C8 C7 C9 112.0(5)
C8 C7 C4 111.0(4)
C9 C7 C4 110.3(4)
C8 C7 C10 104.7(4)
C9 C7 C10 105.0(5)
C4 C7 C10 113.5(4)
C7 C8 H8A 109.5
C7 C8 H8B 109.5
H8A C8 H8B 109.5
C7 C8 H8C 109.5
H8A C8 H8C 109.5
H8B C8 H8C 109.5
C7 C9 H9A 109.5
C7 C9 H9B 109.5
H9A C9 H9B 109.5
C7 C9 H9C 109.5
H9A C9 H9C 109.5
H9B C9 H9C 109.5
C7 C10 H10A 109.5
C7 C10 H10B 109.5
H10A C10 H10B 109.5
C7 C10 H10C 109.5
H10A C10 H10C 109.5
H10B C10 H10C 109.5
C6 C11 C12 111.1(3)
C6 C11 H11A 109.4
C12 C11 H11A 109.4
C6 C11 H11B 109.4
C12 C11 H11B 109.4
H11A C11 H11B 108.0
C17 C12 C13 119.2(3)
C17 C12 C11 120.9(3)
C13 C12 C11 119.7(3)
C14 C13 C12 122.7(3)
C14 C13 H13 118.6
C12 C13 H13 118.6
C13 C14 C15 116.6(3)
C13 C14 C18 123.1(3)
C15 C14 C18 120.2(3)
C16 C15 C14 122.5(3)
C16 C15 H15 118.8
C14 C15 H15 118.8
C15 C16 C17 118.8(3)
C15 C16 C22 119.1(3)
C17 C16 C22 122.1(3)
O2 C17 C12 117.0(3)
O2 C17 C16 122.9(3)
C12 C17 C16 120.2(3)
C21 C18 C19 107.9(4)
C21 C18 C20 110.9(4)
C19 C18 C20 107.7(4)
C21 C18 C14 112.2(3)
C19 C18 C14 109.7(3)
C20 C18 C14 108.3(3)
C18 C19 H19A 109.5
C18 C19 H19B 109.5
H19A C19 H19B 109.5
C18 C19 H19C 109.5
H19A C19 H19C 109.5
H19B C19 H19C 109.5
C18 C20 H20A 109.5
C18 C20 H20B 109.5
H20A C20 H20B 109.5
C18 C20 H20C 109.5
H20A C20 H20C 109.5
H20B C20 H20C 109.5
C18 C21 H21A 109.5
C18 C21 H21B 109.5
H21A C21 H21B 109.5
C18 C21 H21C 109.5
H21A C21 H21C 109.5
H21B C21 H21C 109.5
C16 C22 C23 112.1(3)
C16 C22 H22A 109.2
C23 C22 H22A 109.2

C16 C22 H22B 109.2
C23 C22 H22B 109.2
H22A C22 H22B 107.9
C24 C23 C28 118.5(4)
C24 C23 C22 120.2(3)
C28 C23 C22 121.2(4)
C23 C24 C25 122.9(3)
C23 C24 H24 118.5
C25 C24 H24 118.5
C26 C25 C24 116.2(4)
C26 C25 C29 123.6(4)
C24 C25 C29 120.2(3)
C25 C26 C27 123.2(4)
C25 C26 H26 118.4
C27 C26 H26 118.4
C28 C27 C26 118.0(3)
C28 C27 C33 123.5(4)
C26 C27 C33 118.4(4)
O3' C28 C27 111.3(19)
O3' C28 C23 126.5(17)
C27 C28 C23 121.0(4)
O3' C28 O3 17.0(18)
C27 C28 O3 120.8(4)
C23 C28 O3 118.1(4)
C32 C29 C25 112.3(3)
C32 C29 C30 109.3(4)
C25 C29 C30 109.5(3)
C32 C29 C31 107.1(3)
C25 C29 C31 108.7(4)
C30 C29 C31 109.9(4)
C29 C30 H30A 109.5
C29 C30 H30B 109.5
H30A C30 H30B 109.5
C29 C30 H30C 109.5
H30A C30 H30C 109.5
H30B C30 H30C 109.5
C29 C31 H31A 109.5
C29 C31 H31B 109.5
H31A C31 H31B 109.5
C29 C31 H31C 109.5
H31A C31 H31C 109.5
H31B C31 H31C 109.5
C29 C32 H32A 109.5
C29 C32 H32B 109.5
H32A C32 H32B 109.5
C29 C32 H32C 109.5
H32A C32 H32C 109.5
H32B C32 H32C 109.5
C27 C33 C34 110.8(3)
C27 C33 H33A 109.5
C34 C33 H33A 109.5
C27 C33 H33B 109.5
C34 C33 H33B 109.5
H33A C33 H33B 108.1
C35 C34 C39 118.9(3)
C35 C34 C33 121.6(3)
C39 C34 C33 119.4(3)
C36 C35 C34 123.0(3)
C36 C35 H35 118.5
C34 C35 H35 118.5
C35 C36 C37 116.1(3)
C35 C36 C40 122.9(3)
C37 C36 C40 121.0(3)
C38 C37 C36 123.6(3)
C38 C37 H37 118.2
C36 C37 H37 118.2
C37 C38 C39 118.0(3)
C37 C38 C44 120.1(3)
C39 C38 C44 121.9(3)
O4 C39 C34 116.0(3)
O4 C39 C38 123.6(3)
C34 C39 C38 120.4(3)
C43' C40 C41 128.0(8)
C43' C40 C42 61.9(13)
C41 C40 C42 109.4(7)
C43' C40 C36 117.3(7)
C41 C40 C36 113.7(4)
C42 C40 C36 109.8(4)
C43' C40 C43 44.0(10)
C41 C40 C43 109.1(7)
C42 C40 C43 105.5(6)
C36 C40 C43 109.1(4)
C43' C40 C41' 115.6(15)
C41 C40 C41' 32.2(9)
C42 C40 C41' 134.5(10)
C36 C40 C41' 109.9(7)
C43 C40 C41' 81.3(14)
C43' C40 C42' 106.2(14)
C41 C40 C42' 66.6(10)
C42 C40 C42' 48.7(7)
C36 C40 C42' 107.2(7)
C43 C40 C42' 141.4(8)
C41' C40 C42' 98.4(15)
C40 C41 H41A 109.5
C40 C41 H41B 109.5
C40 C41 H41C 109.5
C40 C42 H42A 109.5
C40 C42 H42B 109.5
C40 C42 H42C 109.5

C40 C43 H43A 109.5
C40 C43 H43B 109.5
C40 C43 H43C 109.5
C40 C41' H41D 109.5
C40 C41' H41E 109.4
H41D C41' H41E 109.5
C40 C41' H41F 109.5
H41D C41' H41F 109.5
H41E C41' H41F 109.5
C40 C42' H42D 109.5
C40 C42' H42E 109.5
H42D C42' H42E 109.5
C40 C42' H42F 109.5
H42D C42' H42F 109.5
H42E C42' H42F 109.5
C40 C43' H43D 109.5
C40 C43' H43E 109.5
H43D C43' H43E 109.5
C40 C43' H43F 109.5
H43D C43' H43F 109.5
H43E C43' H43F 109.5
C2 C44 C38 114.5(3)
C2 C44 H44A 108.7
C38 C44 H44A 108.6
C2 C44 H44B 108.6
C38 C44 H44B 108.6
H44A C44 H44B 107.6
O1 C45 C46 107.7(3)
O1 C45 H45A 110.2
C46 C45 H45A 110.2
O1 C45 H45B 110.2
C46 C45 H45B 110.2
H45A C45 H45B 108.5
O5 C46 C45 107.9(3)
O5 C46 H46A 110.1
C45 C46 H46A 110.1
O5 C46 H46B 110.1
C45 C46 H46B 110.1
H46A C46 H46B 108.4
C48 C47 O5 123.1(4)
C48 C47 C52 121.0(4)
O5 C47 C52 115.9(3)
C49 C48 C47 121.2(4)
C49 C48 H48 119.4
C47 C48 H48 119.4
C48 C49 C50 119.2(4)
C48 C49 H49 120.4
C50 C49 H49 120.4
C51 C50 C49 119.4(4)
C51 C50 H50 120.3
C49 C50 H50 120.3
C52 C51 C50 121.9(5)
C52 C51 H51 119.1
C50 C51 H51 119.1
C51 C52 C47 117.3(4)
C51 C52 C53 121.9(4)
C47 C52 C53 120.8(4)
C54 C53 C52 127.7(4)
C54 C53 H53 116.2
C52 C53 H53 116.2
C53 C54 C55 129.5(4)
C53 C54 H54 115.3
C55 C54 H54 115.3
C56 C55 C60 117.8(4)
C56 C55 C54 119.5(4)
C60 C55 C54 122.7(3)
C57 C56 C55 121.8(5)
C57 C56 H56 119.1
C55 C56 H56 119.1
C58 C57 C56 121.1(5)
C58 C57 H57 119.4
C56 C57 H57 119.4
C57 C58 C59 118.9(5)
C57 C58 H58 120.6
C59 C58 H58 120.6
C60 C59 C58 121.3(5)
C60 C59 H59 119.4
C58 C59 H59 119.4
O6 C60 C59 125.3(4)
O6 C60 C55 115.7(3)
C59 C60 C55 119.0(4)
O6 C61 C62 107.2(11)
O6 C61 H61A 110.3
C62 C61 H61A 110.3
O6 C61 H61B 110.3
C62 C61 H61B 110.3
H61A C61 H61B 108.5
C61 C62 O3 98.8(13)
C61 C62 H62A 112.0
O3 C62 H62A 112.0
C61 C62 H62B 112.0
O3 C62 H62B 112.0
H62A C62 H62B 109.7
O6 C61' C62' 101.6(6)
O6 C61' H61C 111.4
C62' C61' H61C 111.4
O6 C61' H61D 111.4
C62' C61' H61D 111.4
H61C C61' H61D 109.3

C61' C62' O3' 95.5(14)	C28 O3 C62 97.8(13)	Cl1 C01 Cl2 112.7(4)
C61' C62' H62C 112.6	C28 O3' C62' 146.9(17)	Cl1 C01 H01A 109.1
O3' C62' H62C 112.6	C39 O4 H4 109.5	Cl2 C01 H01A 109.0
C61' C62' H62D 112.6	C47 O5 C46 117.2(3)	Cl1 C01 H01B 109.0
O3' C62' H62D 112.6	C60 O6 C61 137.6(5)	Cl2 C01 H01B 109.1
H62C C62' H62D 110.1	C60 O6 C61' 108.7(4)	H01A C01 H01B 107.8
C1 O1 C45 114.8(3)	C61 O6 C61' 42.5(4)	
C17 O2 H2 109.5	Cl2' Cl2 C01 64.3(7)	

Special details: The asymmetric unit contains a disordered molecule of dichloromethane and exhibits conformational disorder in one of the lower rim cage arms and rotational disorder in one of the tertiary butyl groups.

Diffractometer: Nonius KappaCCD area detector (ϕ scans and ω scans to fill asymmetric unit sphere).

Structure solution: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473).

Structure refinement: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Supplementary data have been deposited with the CCDC in CIF format with the deposition number CCDC249144.

SHELXL-97 programs were used for structure solution and refinement. 32983 reflections collected, 12074 independent [R(int) = 0.0700], giving R_1 = 0.0931 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and wR_2 = 0.3186 for all data. The max. and min. residual electron densities on the final difference Fourier map were 0.975 and –0.588eÅ^{-3}, respectively.

2. X-Ray Data of *trans-m*-3 (CCDC249145)

Empirical formula	$C_{60}H_{70}N_2O_6$	
Formula weight	915.18	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 11.8283(3) Å	α = 82.2330(10)°
	b = 12.7292(4) Å	β = 74.9430(10)°
	c = 19.5738(8) Å	γ = 66.7110(10)°
Volume	2612.32(15) Å^3	
Z	2	
Density (calculated)	1.163 Mg / m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	984	
Crystal	Block; Dark Orange	
Crystal size	0.40 x 0.20 x 0.15 mm^3	
θ range for data collection	3.05 – 27.52°	
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-25 \le l \le 25$	
Reflections collected	39735	
Independent reflections	11605 [R_{int} = 0.1407]	
Completeness to θ = 27.52°	96.4 %	
Max. and min. transmission	0.9890 and 0.9710	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11605 / 0 / 618	
Goodness-of-fit on F^2	1.029	
Final R indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0777, *wR2* = 0.1831	
R indices (all data)	*R1* = 0.1404, *wR2* = 0.2157	
Extinction coefficient	0.020(2)	
Largest diff. peak and hole	0.801 and –0.556 e Å^{-3}	

List of Bond lengths (Å):

C17 C15 1.552(6)	C10 C19 1.511(4)	C27 H27C 0.9800
C17 H17A 0.9800	C11 C12 1.395(4)	C28 H28A 0.9800
C17 H17B 0.9800	C11 H11 0.9500	C28 H28B 0.9800
C17 H17C 0.9800	C12 C13 1.394(4)	C28 H28C 0.9800
C18 C15 1.503(5)	C12 C15 1.530(4)	C29 H29A 0.9800
C18 H18A 0.9800	C13 C14 1.389(4)	C29 H29B 0.9800
C18 H18B 0.9800	C13 H13 0.9500	C29 H29C 0.9800
C18 H18C 0.9800	C14 C52 1.523(4)	C30 C31 1.519(4)
C1 C6 1.368(4)	C15 C16 1.500(5)	C30 H30A 0.9900
C1 C2 1.403(4)	C16 H16A 0.9800	C30 H30B 0.9900
C1 H1 0.9500	C16 H16B 0.9800	C31 C36 1.384(4)
C2 C3 1.391(4)	C16 H16C 0.9800	C31 C32 1.406(4)
C2 H2 0.9500	C19 C20 1.517(4)	C32 C33 1.393(4)
C3 C4 1.384(4)	C19 H19A 0.9900	C32 O5 1.395(3)
C3 H3 0.9500	C19 H19B 0.9900	C33 C34 1.395(4)
C4 O1 1.378(3)	C20 C21 1.390(4)	C33 C41 1.518(4)
C4 C5 1.381(4)	C20 C25 1.392(4)	C34 C35 1.395(4)
C5 C6 1.397(4)	C21 O3 1.378(3)	C34 H34 0.9500
C5 H5 0.9500	C21 C22 1.396(4)	C35 C36 1.401(4)
C6 N1 1.474(4)	C22 C23 1.391(4)	C35 C37 1.533(4)
C7 O1 1.434(4)	C22 C30 1.515(4)	C36 H36 0.9500
C7 C8 1.502(5)	C23 C24 1.393(4)	C37 C39 1.511(4)
C7 H7A 0.9900	C23 H23 0.9500	C37 C38 1.526(5)
C7 H7B 0.9900	C24 C25 1.394(4)	C37 C40 1.540(4)
C8 O2 1.427(4)	C24 C26 1.534(4)	C38 H38A 0.9800
C8 H8A 0.9900	C25 H25 0.9500	C38 H38B 0.9800
C8 H8B 0.9900	C26 C27 1.521(4)	C38 H38C 0.9800
C9 C14 1.396(4)	C26 C29 1.522(4)	C39 H39A 0.9800
C9 C10 1.397(4)	C26 C28 1.534(5)	C39 H39B 0.9800
C9 O2 1.399(3)	C27 H27A 0.9800	C39 H39C 0.9800
C10 C11 1.384(4)	C27 H27B 0.9800	C40 H40A 0.9800

C40 H40B 0.9800
C40 H40C 0.9800
C41 C42 1.523(4)
C41 H41A 0.9900
C41 H41B 0.9900
C42 C47 1.395(4)
C42 C43 1.396(4)
C43 O4 1.374(3)
C43 C44 1.402(4)
C44 C45 1.387(4)
C44 C52 1.514(4)
C45 C46 1.390(4)
C45 H45 0.9500
C46 C47 1.404(4)
C46 C48 1.535(4)
C47 H47 0.9500
C48 C51 1.531(4)
C48 C49 1.532(4)
C48 C50 1.538(4)
C49 H49A 0.9800
C49 H49B 0.9800
C49 H49C 0.9800
C50 H50A 0.9800
C50 H50B 0.9800
C50 H50C 0.9800
C51 H51A 0.9800
C51 H51B 0.9800
C51 H51C 0.9800
C52 H52A 0.9900
C52 H52B 0.9900
C53 O5 1.446(3)
C53 C54 1.497(4)
C53 H53A 0.9900
C53 H53B 0.9900
C54 O6 1.444(3)
C54 H54A 0.9900
C54 H54B 0.9900
C55 O6 1.372(3)
C55 C60 1.378(4)
C55 C56 1.398(4)
C56 C57 1.378(4)
C56 H56 0.9500
C57 C58 1.366(4)
C57 H57 0.9500
C58 C59 1.380(4)
C58 H58 0.9500
C59 C60 1.404(4)
C59 N2 1.439(4)
C60 H60 0.9500
N1 N2 1.234(3)
O3 H3A 0.8400
O4 H4 0.8400

List of Bond angles (deg):

C15 C17 H17A 109.5
C15 C17 H17B 109.5
H17A C17 H17B 109.5
C15 C17 H17C 109.5
H17A C17 H17C 109.5
H17B C17 H17C 109.5
C15 C18 H18A 109.5
C15 C18 H18B 109.5
H18A C18 H18B 109.5
C15 C18 H18C 109.5
H18A C18 H18C 109.5
H18B C18 H18C 109.5
C6 C1 C2 119.2(3)
C6 C1 H1 120.4
C2 C1 H1 120.4
C3 C2 C1 120.3(3)
C3 C2 H2 119.8
C1 C2 H2 119.8
C4 C3 C2 119.1(3)
C4 C3 H3 120.4
C2 C3 H3 120.4
O1 C4 C5 123.5(3)
O1 C4 C3 115.3(3)
C5 C4 C3 121.2(3)
C4 C5 C6 118.9(3)
C4 C5 H5 120.6
C6 C5 H5 120.6
C1 C6 C5 121.2(3)
C1 C6 N1 126.5(3)
C5 C6 N1 112.3(3)
O1 C7 C8 113.2(3)
O1 C7 H7A 108.9
C8 C7 H7A 108.9
O1 C7 H7B 108.9
C8 C7 H7B 108.9
H7A C7 H7B 107.8

O2 C8 C7 111.9(3)
O2 C8 H8A 109.2
C7 C8 H8A 109.2
O2 C8 H8B 109.2
C7 C8 H8B 109.2
H8A C8 H8B 107.9
C14 C9 C10 120.7(3)
C14 C9 O2 119.6(2)
C10 C9 O2 119.6(2)
C11 C10 C9 118.5(3)
C11 C10 C19 119.3(2)
C9 C10 C19 122.0(3)
C10 C11 C12 122.5(3)
C10 C11 H11 118.8
C12 C11 H11 118.8
C13 C12 C11 116.9(3)
C13 C12 C15 123.0(3)
C11 C12 C15 120.1(3)
C14 C13 C12 122.6(3)
C14 C13 H13 118.7
C12 C13 H13 118.7
C13 C14 C9 118.2(2)
C13 C14 C52 119.6(2)
C9 C14 C52 122.0(3)
C16 C15 C18 112.8(4)
C16 C15 C12 109.4(3)
C18 C15 C12 113.1(3)
C16 C15 C17 106.3(4)
C18 C15 C17 105.3(3)
C12 C15 C17 109.6(3)
C15 C16 H16A 109.5
C15 C16 H16B 109.5
H16A C16 H16B 109.5
C15 C16 H16C 109.5
H16A C16 H16C 109.5
H16B C16 H16C 109.5
C10 C19 C20 111.5(2)
C10 C19 H19A 109.3
C20 C19 H19A 109.3
C10 C19 H19B 109.3
C20 C19 H19B 109.3
H19A C19 H19B 108.0
C21 C20 C25 118.3(2)
C21 C20 C19 119.9(2)
C25 C20 C19 121.8(2)
O3 C21 C20 120.6(2)
O3 C21 C22 117.8(2)
C20 C21 C22 121.5(2)
C23 C22 C21 118.0(2)
C23 C22 C30 121.9(2)
C21 C22 C30 120.1(2)
C22 C23 C24 122.6(2)
C22 C23 H23 118.7
C24 C23 H23 118.7
C23 C24 C25 117.1(2)
C23 C24 C26 120.1(2)
C25 C24 C26 122.8(2)
C20 C25 C24 122.4(2)
C20 C25 H25 118.8
C24 C25 H25 118.8
C27 C26 C29 109.4(3)
C27 C26 C28 108.4(3)
C29 C26 C28 107.6(3)
C27 C26 C24 109.4(2)
C29 C26 C24 112.5(2)
C28 C26 C24 109.3(2)
C26 C27 H27A 109.5
C26 C27 H27B 109.5
H27A C27 H27B 109.5
C26 C27 H27C 109.5
H27A C27 H27C 109.5
H27B C27 H27C 109.5
C26 C28 H28A 109.5
C26 C28 H28B 109.5
H28A C28 H28B 109.5
C26 C28 H28C 109.5
H28A C28 H28C 109.5
H28B C28 H28C 109.5
C26 C29 H29A 109.5
C26 C29 H29B 109.5
H29A C29 H29B 109.5
C26 C29 H29C 109.5
H29A C29 H29C 109.5
H29B C29 H29C 109.5
C22 C30 C31 113.2(2)
C22 C30 H30A 108.9
C31 C30 H30A 108.9
C22 C30 H30B 108.9
C31 C30 H30B 108.9
H30A C30 H30B 107.7
C36 C31 C32 117.5(2)
C36 C31 C30 120.7(2)
C32 C31 C30 121.7(2)
C33 C32 O5 118.0(2)
C33 C32 C31 121.7(3)
O5 C32 C31 120.2(2)
C32 C33 C34 118.0(2)
C32 C33 C41 121.1(2)
C34 C33 C41 120.8(2)

C35 C34 C33 122.7(2)
C35 C34 H34 118.6
C33 C34 H34 118.6
C34 C35 C36 116.6(3)
C34 C35 C37 123.0(2)
C36 C35 C37 120.4(2)
C31 C36 C35 123.4(2)
C31 C36 H36 118.3
C35 C36 H36 118.3
C39 C37 C38 109.6(3)
C39 C37 C35 112.4(2)
C38 C37 C35 109.5(2)
C39 C37 C40 107.1(3)
C38 C37 C40 108.0(3)
C35 C37 C40 110.2(2)
C37 C38 H38A 109.5
C37 C38 H38B 109.5
H38A C38 H38B 109.5
C37 C38 H38C 109.5
H38A C38 H38C 109.5
H38B C38 H38C 109.5
C37 C39 H39A 109.5
C37 C39 H39B 109.5
H39A C39 H39B 109.5
C37 C39 H39C 109.5
H39A C39 H39C 109.5
H39B C39 H39C 109.5
C37 C40 H40A 109.5
C37 C40 H40B 109.5
H40A C40 H40B 109.5
C37 C40 H40C 109.5
H40A C40 H40C 109.5
H40B C40 H40C 109.5
C33 C41 C42 113.1(2)
C33 C41 H41A 109.0
C42 C41 H41A 109.0
C33 C41 H41B 109.0
C42 C41 H41B 109.0
H41A C41 H41B 107.8
C47 C42 C43 118.2(2)
C47 C42 C41 119.3(2)
C43 C42 C41 122.4(2)
O4 C43 C42 123.5(2)
O4 C43 C44 115.7(2)
C42 C43 C44 120.8(2)
C45 C44 C43 118.7(2)
C45 C44 C52 120.7(2)
C43 C44 C52 120.1(2)
C44 C45 C46 122.8(2)
C44 C45 H45 118.6
C46 C45 H45 118.6
C45 C46 C47 116.6(2)
C45 C46 C48 122.1(2)
C47 C46 C48 121.3(2)
C42 C47 C46 122.8(2)
C42 C47 H47 118.6
C46 C47 H47 118.6
C51 C48 C49 107.5(3)
C51 C48 C46 111.1(2)
C49 C48 C46 110.8(2)
C51 C48 C50 109.4(2)
C49 C48 C50 109.0(2)
C46 C48 C50 109.0(2)
C48 C49 H49A 109.5
C48 C49 H49B 109.5
H49A C49 H49B 109.5
C48 C49 H49C 109.5
H49A C49 H49C 109.5
H49B C49 H49C 109.5
C48 C50 H50A 109.5
C48 C50 H50B 109.5
H50A C50 H50B 109.5
C48 C50 H50C 109.5
H50A C50 H50C 109.5
H50B C50 H50C 109.5
C48 C51 H51A 109.5
C48 C51 H51B 109.5
H51A C51 H51B 109.5
C48 C51 H51C 109.5
H51A C51 H51C 109.5
H51B C51 H51C 109.5
C44 C52 C14 108.6(2)
C44 C52 H52A 110.0
C14 C52 H52A 110.0
C44 C52 H52B 110.0
C14 C52 H52B 110.0
H52A C52 H52B 108.4
O5 C53 C54 110.3(2)
O5 C53 H53A 109.6
C54 C53 H53A 109.6
O5 C53 H53B 109.6
C54 C53 H53B 109.6
H53A C53 H53B 108.1
O6 C54 C53 108.8(2)
O6 C54 H54A 109.9
C53 C54 H54A 109.9
O6 C54 H54B 109.9
C53 C54 H54B 109.9
H54A C54 H54B 108.3

O6 C55 C60 124.3(3)	C57 C58 C59 119.3(3)	N2 N1 C6 113.5(2)
O6 C55 C56 115.9(2)	C57 C58 H58 120.3	N1 N2 C59 111.4(3)
C60 C55 C56 119.6(3)	C59 C58 H58 120.3	C4 O1 C7 119.4(2)
C57 C56 C55 120.2(3)	C58 C59 C60 121.0(3)	C9 O2 C8 111.3(2)
C57 C56 H56 119.9	C58 C59 N2 115.5(3)	C21 O3 H3A 109.5
C55 C56 H56 119.9	C60 C59 N2 123.6(3)	C43 O4 H4 109.5
C58 C57 C56 120.9(3)	C55 C60 C59 119.0(3)	C32 O5 C53 115.08(19)
C58 C57 H57 119.5	C55 C60 H60 120.5	C55 O6 C54 119.3(2)
C56 C57 H57 119.5	C59 C60 H60 120.5	

Special details: All H atom fixed at idealized positions, with a riding model and fixed thermal parameters (U_{ij} = 1.2*U*ij (eq) for the atom to which they are bonded) used for subsequent refinements.

Diffractometer: Nonius KappaCCD area detector (ϕ scans and ω scans to fill asymmetric unit sphere).

Structure solution: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473).

Structure refinement: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Supplementary data have been deposited with the CCDC in CIF format with the deposition number CCDC249145.

APPENDIX D

NMR TITRATION

Table D1: NMR Titration of *cis*-*o*-**3** with CH_3CN

[*cis*-*o*-**3**] initial = 4.29 mM, 0.70 mL
[CH_3CN] stock solution = 85.7 mM

V_G (μL)	n_G (μmol)	[G] (mM)	n_H (μmol)	[H] (mM)	[G]/[H]	Δδ at ppm (ppm)		
						1	2	average
0	0.00	0.00	3.00	4.29	0.00	6.892	6.893	6.893
7	0.60	0.85	3.00	4.24	0.20	6.894	6.896	6.895
14	1.20	1.68	3.00	4.20	0.40	6.897	6.899	6.898
21	1.80	2.50	3.00	4.16	0.60	6.903	6.900	6.902
28	2.40	3.30	3.00	4.12	0.80	6.905	6.906	6.906
35	3.00	4.08	3.00	4.08	1.00	6.909	6.910	6.910
42	3.60	4.85	3.00	4.04	1.20	6.913	6.911	6.912
49	4.20	5.61	3.00	4.01	1.40	6.914	6.916	6.915
56	4.80	6.35	3.00	3.97	1.60	6.919	6.919	6.919
63	5.40	7.08	3.00	3.93	1.80	6.921	6.923	6.922
73	6.26	8.10	3.00	3.88	2.09	6.927	6.924	6.926
85	7.29	9.28	3.00	3.82	2.43	6.931	6.929	6.930
100	8.57	10.72	3.00	3.75	2.86	6.931	6.934	6.933
125	10.72	12.99	3.00	3.64	3.57	6.937	6.941	6.939
150	12.86	15.13	3.00	3.53	4.29	6.942	6.946	6.944
175	15.00	17.14	3.00	3.43	5.00	6.946	6.950	6.948
200	17.14	19.05	3.00	3.33	5.72	6.949	6.954	6.952
250	21.43	22.56	3.00	3.16	7.14	6.955	6.959	6.957

G = CH_3CN H = *cis*-*o*-**3** *n* = mole V = addition volumn

Table D2: NMR Titration of *trans-o*-**3** with CH_3CN

[*trans-o*-**3**] initial = 4.29 mM, 0.70 mL
[CH_3CN] stock solution = 85.7 mM

V_G (μL)	n_G (μmol)	[G] (mM)	n_H (μmol)	[H] (mM)	[G]/[H]	Δδ at ppm (ppm)		
						1	2	average
0	0.00	0.00	3.00	4.29	0.00	6.983	6.983	6.983
7	0.60	0.85	3.00	4.24	0.20	6.984	6.985	6.985
14	1.20	1.68	3.00	4.20	0.40	6.987	6.987	6.987
21	1.80	2.50	3.00	4.16	0.60	6.999	6.989	6.990
28	2.40	3.30	3.00	4.12	0.80	6.993	6.992	6.993
35	3.00	4.08	3.00	4.08	1.00	6.996	6.995	6.996
42	3.60	4.85	3.00	4.04	1.20	6.996	6.996	6.996
49	4.20	5.61	3.00	4.01	1.40	7.000	6.999	7.000
56	4.80	6.35	3.00	3.97	1.60	6.99	7.001	7.000
63	5.40	7.08	3.00	3.93	1.80	7.003	7.004	7.004
73	6.26	8.10	3.00	3.88	2.09	7.003	7.006	7.005
85	7.29	9.28	3.00	3.82	2.43	7.005	7.008	7.007
100	8.57	10.72	3.00	3.75	2.86	7.009	7.011	7.010
125	10.72	12.99	3.00	3.64	3.57	7.011	7.015	7.013
150	12.86	15.13	3.00	3.53	4.29	7.016	7.018	7.017
175	15.00	17.14	3.00	3.43	5.00	7.019	7.022	7.020
200	17.14	19.05	3.00	3.33	5.72	7.021	7.021	7.021
250	21.43	22.56	3.00	3.16	7.14	7.026	7.026	7.026
300	25.72	25.72	3.00	3.00	8.57	7.032	7.031	7.032

G = CH_3CN H = *trans-o*-**3** *n* = mole V = addition volumn

Table D3: NMR Titration of *cis-m*-**3** with CH_3CN

[*cis-m*-**3**] initial = 4.29 mM, 0.70 mL
[CH_3CN] stock solution = 42.9 mM

V_G (μL)	n_G (μmol)	[G] (mM)	n_H (μmol)	[H] (mM)	[G]/[H]	Δδ at ppm (ppm)		
						1	2	average
0	0.00	0.00	3.00	4.29	0.00	6.980	6.981	6.981
14	0.60	0.84	3.00	4.20	0.20	6.987	6.987	6.987
28	1.20	1.65	3.00	4.12	0.40	6.991	6.989	6.990
42	1.80	2.43	3.00	4.04	0.60	6.991	6.991	6.991
56	2.40	3.17	3.00	3.97	0.80	6.999	6.996	6.998
70	3.00	3.90	3.00	3.90	1.00	7.002	7.000	7.001
84	3.60	4.59	3.00	3.83	1.20	7.004	7.003	7.004
98	4.20	5.26	3.00	3.75	1.40	7.006	7.0005	7.006
112	4.80	5.91	3.00	3.69	1.60	7.009	7.007	7.008
126	5.40	6.54	3.00	3.63	1.80	7.010	7.018	7.019
150	6.43	7.56	3.00	3.53	2.14	7.014	7.011	7.013
175	7.50	8.57	3.00	3.43	2.50	7.016	7.015	7.016
200	8.57	9.52	3.00	3.33	2.86	7.018	7.017	7.018
250	10.71	11.28	3.00	3.16	3.57	7.025	7.024	7.025
300	12.86	12.86	3.00	3.00	4.29	7.029	7.026	7.028
350	15.00	14.29	3.00	2.86	5.00	7.032	7.034	7.033

G = CH_3CN H = *cis-m*-**3** *n* = mole V = addition volumn

Table D4: NMR Titration of *cis*-*o*-**3** with CH_3NO_2

[*cis*-*o*-**3**] initial = 4.29 mM, 0.70 mL
[CH_3 NO_2] stock solution = 85.7 mM

V_G (μL)	n_G (μmol)	[G] (mM)	n_H (μmol)	[H] (mM)	[G]/[H]	Δδ at ppm (ppm)		
						1	2	average
0	0.00	0.00	3.00	4.29	0.00	6.892	6.892	6.892
7	0.60	0.85	3.00	4.24	0.20	6.893	6.893	6.893
14	1.20	1.68	3.00	4.20	0.40	6.896	6.894	6.895
21	1.80	2.50	3.00	4.16	0.60	6.899	6.902	6.901
28	2.40	3.30	3.00	4.12	0.80	6.902	6.905	6.904
35	3.00	4.08	3.00	4.08	1.00	6.906	6.907	6.907
42	3.60	4.85	3.00	4.04	1.20	6.907	6.908	6.908
49	4.20	5.61	3.00	4.01	1.40	6.911	6.911	6.911
56	4.80	6.35	3.00	3.97	1.60	6.912	6.914	6.913
63	5.40	7.08	3.00	3.93	1.80	6.915	6.917	6.916
73	6.26	8.10	3.00	3.88	2.09	6.919	6.917	6.918
85	7.29	9.28	3.00	3.82	2.43	6.922	6.919	6.920
100	8.57	10.72	3.00	3.75	2.86	6.924	6.921	6.923
125	10.72	12.99	3.00	3.64	3.57	6.928	6.931	6.930
150	12.86	15.13	3.00	3.53	4.29	6.936	6.934	6.935
175	15.00	17.14	3.00	3.43	5.00	6.940	6.936	6.939
200	17.14	19.05	3.00	3.33	5.72	6.942	6.939	6.941
250	21.43	22.56	3.00	3.16	7.14	6.949	6.946	6.948
300	25.72	25.72	3.00	3.00	8.57	6.950	6.949	6.950
350	30.00	28.57	3.00	8.57	10.00	6.958	6.958	6.958

G = CH_3 NO_2 H = *cis*-*o*-**3** *n* = mole V = addition volumn

Table D5: NMR Titration of *trans-o*-**3** with $CH_3 NO_2$

[*trans-o*-**3**] initial = 4.29 mM, 0.70 mL
[$CH_3 NO_2$] stock solution = 85.7 mM

V_G (μL)	n_G (μmol)	[G] (mM)	n_H (μmol)	[H] (mM)	[G]/[H]	Δδ at ppm (ppm)		
						1	2	average
0	0.00	0.00	3.00	4.29	0.00	6.985	6.985	6.985
7	0.60	0.85	3.00	4.24	0.20	6.985	6.987	6.986
14	1.20	1.68	3.00	4.20	0.40	6.988	6.990	6.989
21	1.80	2.50	3.00	4.16	0.60	6.999	6.991	6.991
28	2.40	3.30	3.00	4.12	0.80	6.992	6.994	6.993
35	3.00	4.08	3.00	4.08	1.00	6.995	6.993	6.994
42	3.60	4.85	3.00	4.04	1.20	6.997	6.999	6.998
49	4.20	5.61	3.00	4.01	1.40	6.998	6.998	6.998
56	4.80	6.35	3.00	3.97	1.60	7.000	7.001	7.001
63	5.40	7.08	3.00	3.93	1.80	7.002	7.000	7.001
73	6.26	8.10	3.00	3.88	2.09	7.004	7.003	7.004
85	7.29	9.28	3.00	3.82	2.43	7.006	7.006	7.006
100	8.57	10.72	3.00	3.75	2.86	7.007	7.006	7.007
125	10.72	12.99	3.00	3.64	3.57	7.011	7.018	7.019
150	12.86	15.13	3.00	3.53	4.29	7.012	7.012	7.012
175	15.00	17.14	3.00	3.43	5.00	7.017	7.013	7.015
200	17.14	19.05	3.00	3.33	5.72	7.019	7.015	7.017
250	21.43	22.56	3.00	3.16	7.14	7.021	7.017	7.019
300	25.72	25.72	3.00	3.00	8.57	7.022	7.018	7.020
350	30.00	28.57	3.00	8.57	10.00	7.024	7.022	7.02

G = $CH_3 NO_2$ H = *trans-o*-**3** *n* = mole V = addition volumn

Table D6: NMR Titration of *cis-m*-**3** with $CH_3 NO_2$

[*cis-m*-**3**] initial = 4.29 mM, 0.70 mL
[$CH_3 NO_2$] stock solution = 85.7 mM

V_G (μL)	n_G (μmol)	[G] (mM)	n_H (μmol)	[H] (mM)	[G]/[H]	Δδ at ppm (ppm)		
						1	2	average
0	0.00	0.00	3.00	4.29	0.00	6.980	6.980	6.980
7	0.60	0.85	3.00	4.24	0.20	6.982	6.983	6.983
14	1.20	1.68	3.00	4.20	0.40	6.985	6.986	6.986
21	1.80	2.50	3.00	4.16	0.60	6.986	6.988	6.987
28	2.40	3.30	3.00	4.12	0.80	6.991	6.987	6.989
35	3.00	4.08	3.00	4.08	1.00	6.993	6.991	6.992
42	3.60	4.85	3.00	4.04	1.20	6.996	6.994	6.995
49	4.20	5.61	3.00	4.01	1.40	6.997	6.997	6.997
56	4.80	6.35	3.00	3.97	1.60	7.001	7.000	7.001
63	5.40	7.08	3.00	3.93	1.80	7.003	7.001	7.002
73	6.26	8.10	3.00	3.88	2.09	7.005	7.007	7.006
85	7.29	9.28	3.00	3.82	2.43	7.008	7.008	7.008
100	8.57	10.72	3.00	3.75	2.86	7.011	7.012	7.012
125	10.72	12.99	3.00	3.64	3.57	7.016	7.015	7.016
150	12.86	15.13	3.00	3.53	4.29	7.019	7.020	7.020
175	15.00	17.14	3.00	3.43	5.00	7.024	7.024	7.024
200	17.14	19.05	3.00	3.33	5.72	7.026	7.025	7.026
250	21.43	22.56	3.00	3.16	7.14	7.032	7.032	7.032
300	25.72	25.72	3.00	3.00	8.57	7.035	7.034	7.035
350	30.00	28.57	3.00	8.57	10.00	7.038	7.036	7.037

G = $CH_3 NO_2$ H = *cis-m*-**3** *n* = mole V = addition volumn

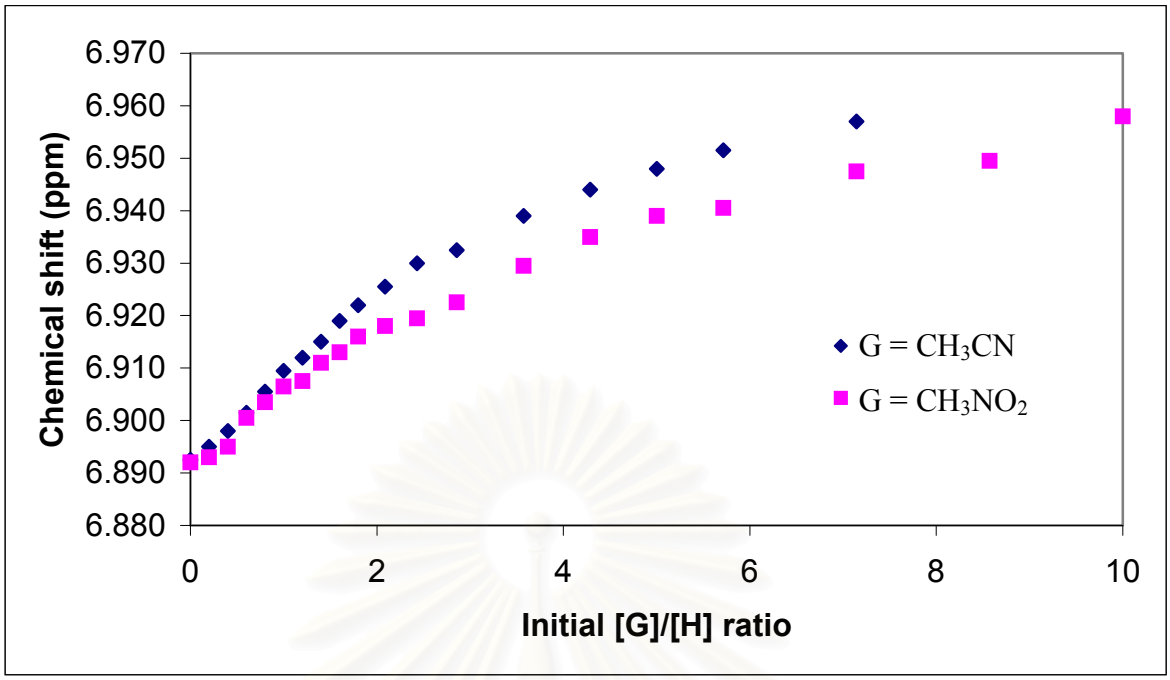


Figure D1: Comparative NMR Titration Curve of *cis*-*o*-**3** with CH_3CN and CH_3NO_2

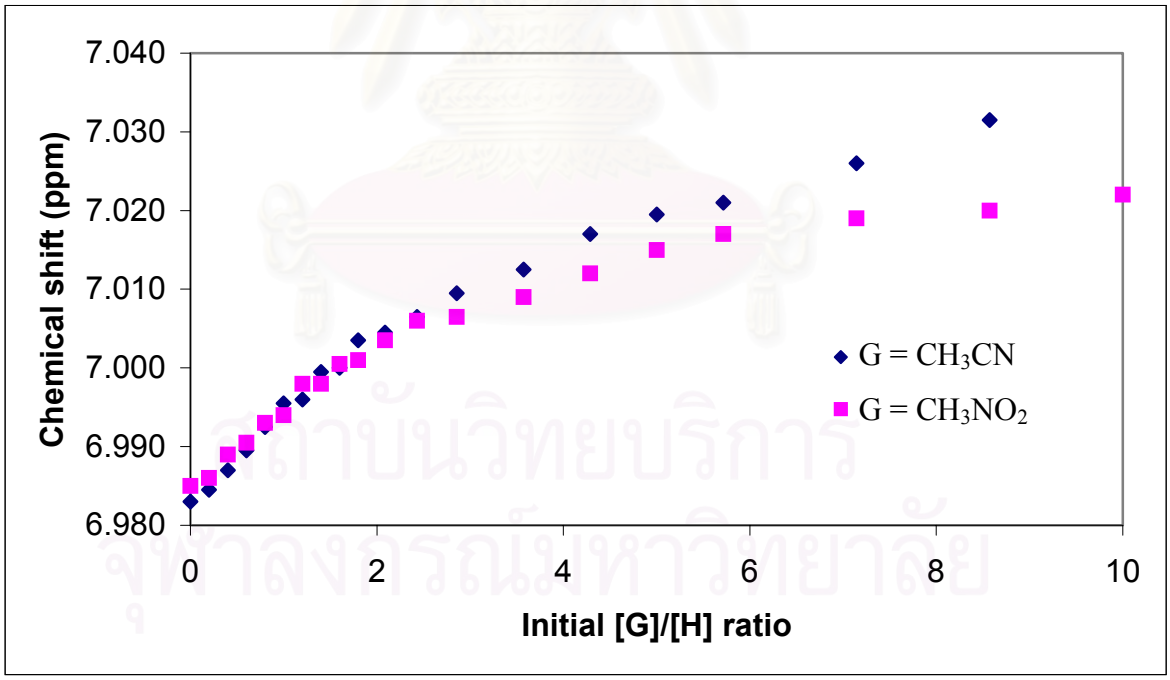


Figure D2: Comparative NMR Titration Curve of *trans*-*o*-**3** with CH_3CN and CH_3NO_2

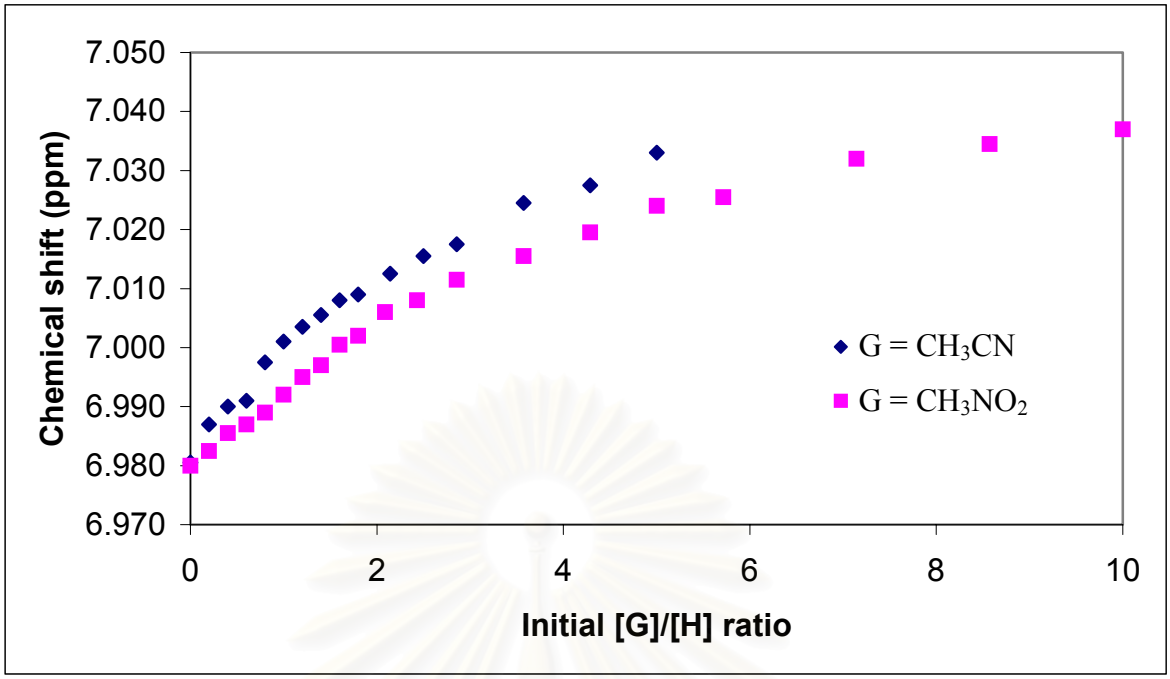


Figure D3: Comparative NMR Titration Curve of *cis*-*m*-**3** with CH_3CN and CH_3NO_2

APPENDIX E

REPRINTS

1. Sukwattanasinitt, M.; Rojanathanes, R.; Jiwpanich, S.; Tuntulani, T.; Ruangpornvisuti, V. Selective oxidation of 25,27-bis-(3-formylphenoxylethylene)-*p*-*tert*-butylcalix[4]arene, *Science Asia* **2002**, *28*, 25-28.
2. Sukwattanasinitt, M.; Rojanathanes, R.; Tuntulani, T.; Sritana-Anant, Y.; Ruangpornvisuti V. Synthesis of stilbene crown ether *p*-*tert*-butylcalix[4]arenes *Tetrahedron Lett.* **2001**, *42(31)*, 5291-5293.
3. Rojanathanes, R.; Pipoosananakaton, B.; Tuntulani, T.; Bhanthumnavin, W.; Orton, J. B.; Cole, S. J.; Hursthouse, M. B.; Grossel, M. C.; Sukwattanasinitt, M. Comparative study of azobenzene and stilbene bridged crown ether *p*-*tert*-butyl-calix[4]arene *Tetrahedron* **2004**, submitted.

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Selective Oxidation of 25,27-Bis-(3-formylphenoxylethoxy)-*p*-*tert*-butylcalix[4]arene

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ABSTRACT Reaction of 25,27-bis-(3-formylphenoxyethoxy)-*p*-*tert*-butylcalix[4]arene (1) with 20% mole of KCN in ethanol and *i*-propanol yielded monoethylester (2) (50%) and monoisopropylester (3) (15%). Compound 1 was not oxidized by air in the absence of KCN under reflux. The Cannizzaro reaction of 1 in ethanol using KOH gave bis-alcohol (4), acid-alcohol (5).

KEYWORDS: calix, oxidation, aldehyde, ester, cyanide.

INTRODUCTION

Owing to its pre-organized structure, calix[4] arene has become one of the most popular molecular platforms for synthesis of highly selective receptors for molecular and ionic guests.[1] The simplicity of structural modification on the lower rim of calix[4]arene has furnished a variety of calix[4]arene derivatives.[2-6] Recently the derivatives containing multiple benzaldehyde groups have been demonstrated to be useful for syntheses of several host molecules with selective binding properties.[7-10]

We are currently interested in preparation of functional supermolecules from the bisaldehyde derivatives. During this investigation, a serendipitously selective oxidation reaction of calix[4]arene containing two aromatic aldehydic functional groups was encountered. This reaction presents an unprecedented cyanide-catalyzed autoxidation of aldehyde and a new convenient route to unsymmetrical substituted calix[4]arenes. We report here a study of this selective oxidation and full characterization of its product.

The simple calixarene derivatization using the template method always yields 1,3-alternate or tri-substituted calixarenes. Syntheses of mono substituted or different substituted calixarenes is a drawback of this template method. Using this oxidation, the symmetry of the molecule can be destroyed easier. This is an alternative route to successive preparation of unsymmetrical calixarene derivatives, which can be further functionalized to chiral host molecules. From unsymmetrical di-substituted calixarenes, a simple methylation of a phenolic group on the lower rim will form unsymmetrical tri-substituted calixarenes, which are chiral molecules. These chiral molecules can be used as chiral hosts for some chiral recognition processes. Therefore, this oxidation will be a useful technique, as it aids in synthesizing this type of chiral calixarenes.

MATERIALS AND METHODS

All reagents were purchased from Fluka® (Buch, Switzerland) and Merck®(Darmstadt, Germany). Solvents such as acetonitrile, methylene chloride and alcohols were reagent grade stored over molecular sieves. In anhydrous reactions, solvents were dried by standard procedures and distilled before use.[16] For extraction and chromatography, solvents were commercial grade and were distilled prior to use.

The melting points were determined using an Electrothermal 900 melting point apparatus (Electrothermal Engineering, Essex, UK). Elemental analyses were performed on Perkin-Elmer PE 2400 Series II (Perkin-Elmer, Massachusetts, USA). Infrared photometry experiments were done on a Nicolet Impact 410 FT-IR (Thermo Nicolet, Wisconsin, USA), using thin film samples prepared from solutions in methylene chloride on KBr windows. Mass analyses were carried out on a FISONS VG TRIO 2000 mass spectrometer (Fisons, Sussex, UK). The NMR spectra were acquired on a Bruker ACF 200 NMR (Bruker, Fällanden, Switzerland), using $CDCl_3$ as a solvent.

Bisaldehyde (1). In a 1 L, 2-necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser, *p*-*tert*-butylcalix[4]arene (7.8 mmol, 5.00 g) and K_2CO_3 (57.9 mmol, 8.00 g) were suspended in CH_3CN (300 mL). The mixture was

stirred for 30 minutes at ambient temperature and 3-(2-bromoethoxy)-benzaldehyde (17.5 mmol, 4.00 g) was then added dropwise. The mixture was refluxed for 60 hours and then allowed to cool to ambient temperature. The mixture was filtered and washed with acetone and CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and then extracted with aqueous HCl (2 M). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was crystallized in CH_2Cl_2/CH_3OH yielding the desired product as a white solid (4.7 mmol, 4.42 g, 60%): mp (decompose) = 184.8-185.3ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H), 1.27 (s, 18H), 3.32 (d, 4H, J = 13.0 Hz), 4.3-4.4 (m, 12H), 6.85 (s, 4H), 7.04 (s, 4H) 7.20–7.45 (m, 8H), 9.93 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.1, 31.7, 33.8, 34.0, 66.9, 73.7, 113.4, 122.4, 123.6, 125.2, 125.7, 127.8, 130.2, 132.8, 137.8, 141.5, 147.1, 149.7, 150.5, 159.2, 192.1; IR (neat) ν_{max} 3336 (phenolic O-H stretching), 3050, 2958, 2869 (aldehydic C-H stretching), 2731 (aldehydic C-H stretching), 1697 (aldehydic C=O stretching), 1597, 1485, 1450, 1265 cm^{-1}; Anal. Calcd for $C_{62}H_{72}O_8$: C, 78.78; H, 7.68; Found: C, 76.80; H, 7.95.

Ethylester-aldehyde (2). In a 100 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser, 1 (0.6 mmol, 0.50 g) and KCN (0.15 mmol, 0.01 g) were dissolved in 95% ethanol (20 mL). The mixture was refluxed for 24 hours and then allowed to cool to ambient temperature. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and then extracted with aqueous HCl (2 M). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was crystallized in CH_2Cl_2/CH_3OH yielding the product 2 as a white solid (0.3 mmol, 0.25 g., 50%): mp(decompose) = 133-134ºC.; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.03 (s, 18H), 1.30 (s, 18H), 1.40 (t, 3H, J = 8.0 Hz), 3.34 (d, 4H, J = 12.0 Hz), 4.34-4.43 (m, 14H), 6.88 (s, 4H), 7.07 (s, 4H), 7.18 (d, 1H, J = 8.0 Hz), 7.25 (d, 1H, J = 8.0 Hz), 7.35 (t, 1H, J = 8.0 Hz), 7.43-7.50 (m, 5H), 7.61 (d, 1H, J = 4.0 Hz), 7.67 (s, 1H), 9.92 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 14.2, 31.0, 31.6, 31.7, 33.8, 34.0, 53.2, 61.0, 66.8, 66.9, 73.7, 113.7, 114.8, 120.3, 122.2, 122.3, 123.3, 125.1, 125.7, 127.7, 129.4, 130.1, 131.7, 132.8, 137.7, 141.4, 147.1, 149.7, 150.4, 158.5, 159.1, 166.4, 192.1; IR (KBr pellet) ν_{max} 3363 (Ar-OH), 3047, 2958, 2870 (aldehydic C-H stretching), 2727 (aldehydic C-H stretching), 1716 (carboxylate C=O stretching), 1701 (aldehydic C=O stretching), 1589, 1485, 1446, 1277, 1200 cm^{-1}; Anal. Calcd for $C_{64}H_{76}O_9$: C, 77.70; H, 7.74; Found: C, 77.80; H, 7.77.

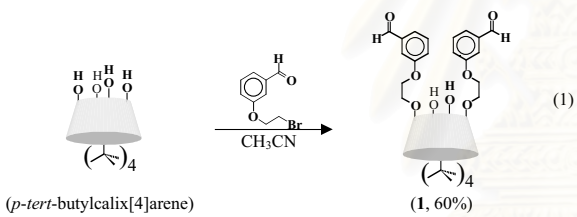
i-Propylester-aldehyde (3). In a 100 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser, 1 (0.6 mmol, 0.50 g) and KCN (0.15 mmol, 0.01 g) were dissolved in 95% *i*-propanol (20 mL). The mixture was refluxed for 24 hours and then allowed to cool to ambient temperature. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and then extracted with aqueous HCl (2 M). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was crystallized in CH_2Cl_2/CH_3OH yielding the product 3 as a white solid (0.1 mmol, 0.09 g, 15%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H), 1.25 (s, 18H), 1.33 (d, 6H, J = 6.0 Hz), 3.29 (d, 4H, J = 13.0 Hz), 4.09-4.41 (m, 14H), 6.84 (s, 4H), 7.02 (s, 4H), 7.20-7.43 (m, 8H), 7.55 (s, 1H), 7.62 (d, 1H, J = 7.5 Hz), 9.92 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.9, 31.1, 31.3, 31.7, 33.8, 34.0, 66.8, 68.5, 73.7, 113.7, 114.9, 120.2, 122.2, 122.3, 123.3, 125.2, 125.7, 127.8, 129.4, 130.1, 132.2, 137.7, 141.4, 147.1, 149.7, 150.6, 158.5, 159.2, 165.9, 192.1; Anal Calcd for $C_{65}H_{78}O_9 \bullet CH_2Cl_2$: C, 72.84; H, 7.41; Found: C, 73.25; H, 7.55.

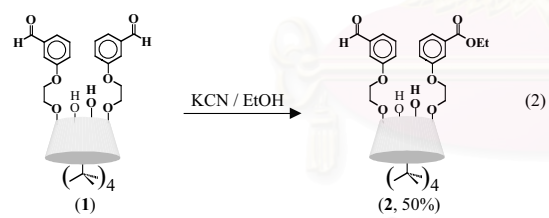
Cannizzaro reaction of the bisaldehyde (1). In a 100 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser, 1 (0.6 mmol, 0.50 g) and KOH (3.6 mmol, 0.20 g) were dissolved in 95% ethanol (15 mL). The mixture was refluxed for 24 hours and then allowed to cool to ambient temperature. The solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and then extracted with aqueous HCl (2 M). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The products were isolated by column chromatography (silica gel 60, Merck®) using EtOAc/CH_2Cl_2 (20/80) as an eluent yielding two products as white solids. The first product is the bisalcohol (4) (0.09 mmol, 0.08 g, 16%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H), 1.25 (s, 18H), 3.29 (d, 4H, J = 13.0 Hz), 4.30-4.40 (m, 12H), 4.60 (s, 4H), 6.84-7.02 (m, 16H), 7.20-7.29 (m, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 30.9, 31.1, 31.7, 33.8, 34.0, 64.9, 66.6, 74.0, 112.7, 114.6, 119.4, 125.2, 125.7, 129.5, 132.9, 141.5, 142.7, 147.1, 149.9, 150.5, 158.8. The other product is

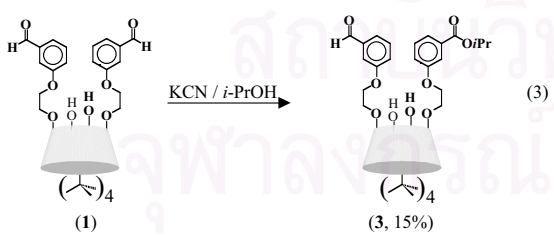
the alcohol-acid (5) (0.02 mmol, 0.02 g, 4%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 18H), 1.03 (s, 18H), 1.24 (s, 36), 3.30 (dd, 4H, J = 13, 6.5 Hz), 4.20 – 4.42 (m, 14H), 4.66 (s, 1H), 7.05–7.11 (m, 4H), 9.88 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.1, 31.7, 33.8, 34.0, 65.1, 66.6, 67.0, 74.1, 74.1, 112.8, 114.4, 114.8, 119.6, 121.9, 122.9, 125.1, 125.7, 127.9, 129.5, 130.9, 132.8, 141.5, 142.2, 147.0, 147.0, 150.0, 150.0, 150.5, 158.7, 158.6, 170.0.

Results and Discussion

During our attempt to prepare benzoin derivative of calix[4]arene from the reaction of 25,27-bis-(3-formylphenoxyethoxy)-*p*-*tert*-butylcalix[4]arene 1, which was synthesized according to the literature procedure (eq 1),[11, 12] with 20% mole of KCN in ethanol, we observed a single product on TLC (eq 2). The product was isolated by recrystallization in methanol/CH_2Cl_2 to give a white crystalline material. The ^{1}H NMR and ^{13}C NMR spectra of the isolated material suggested that it was not the expected benzoin but the monoethyl ester 2 (50%). All the signals in ^{1}H NMR and ^{13}C NMR can be assigned corresponding to the proposed structure of the product with the aid of 2-D NMR spectroscopy, COSY, NOESY and HMBC.





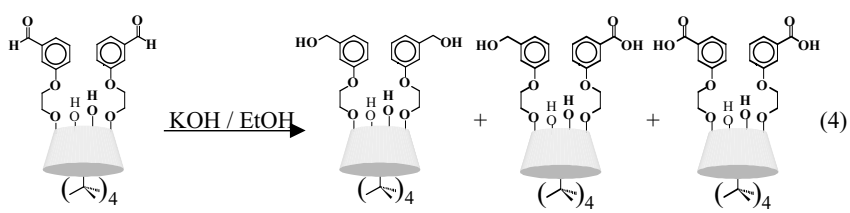


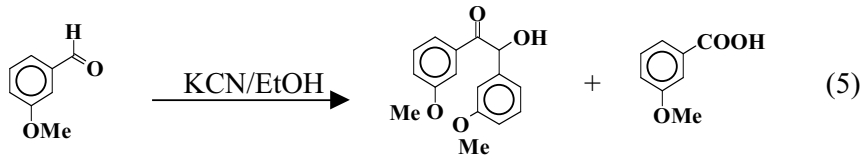
The mono-*i*-propyl ester 3 was synthesized through the reaction of KCN and aldehyde 1 in *i*-propanol (eq 3). As the product is unpredicted and the reaction showed rather unusual selectivity, we decided to investigate this reaction in further detail.

Two mechanistically different types of reactions, Cannizzaro reaction and autoxidation, may be responsible for the formation of the observed product. When the autoxidation reaction of 1 was performed in the present of air but without KCN, the TLC trace did not show any product but only the unreacted starting material, even after 5 days of reflux. The results indicated that the autoxidation of 1 did not proceed without KCN. The Cannizzaro reaction of bisaldehyde 1 was performed in ethanol using KOH yielding two products as white solids (eq 4). The first product is the bisalcohol 4 and the second isolated product is the alcohol-acid 5. The observation of the bisalcohol 4 suggested that there should be another product, the biscarboxylic acid 6. However, an attempt in to isolate 6 was not successful. As this reaction did not produce the aldehyde-ester 2, the Cannizzaro reaction could not account for the formation of the product 2 and 3 from 1.

As the experiments described previously did not provide any positive evidence supporting for either autoxidation or Cannizzaro reaction, a study of the model compound, *m*-anisaldehyde was initiated to acquire more information.

The reaction of *m*-anisaldehyde with 20% mole of KCN in ethanol, using the same reaction condition as the oxidation of the bisaldehyde 1 gave the corresponding benzoin 7 as a major product along with a minor oxidation product, *m*-methoxybenzoic acid 8 (eq 5). In the presence of KCN, the autoxidation is, therefore, a competitive reaction of benzoin





(**7**, 42%) (**8**, 20%)

formation. Interestingly, esterification of the autoxidation product 8 was not observed in this reaction.

According to the results described above, we proposed a mechanism of the formation of product 2 from 1 as a result of esterification of the autoxidation product of 1. The oxidation was catalyzed by cyanide anion and the esterification was presumably catalyzed by an acidic proton on the lower rim of *p-tert*-butylcalix[4]arene. The most intriguing point of this reaction is the selectivity of the autoxidation step, in which only one of the two aldehyde groups was oxidized. The reason for this selectivity remains elusive to us. We however suspect that it had something to do with the phenolic OH groups of the lower rim of *p-tert*-butylcalix[4] arene. These phenolic OH groups may act as intramolecular hydrogen bond donors to induce a geometry that protects one of the aldehyde groups from the attack of the cyanide anion. This unique geometry of bisaldehyde calixarene 1 may also prevent the formation of the corresponding benzoin from the reaction of 1.

It is important to point out that this autoxidation reaction differs significantly from similar oxidations reported in the literature. Corey and coworkers used 5 equivalents of NaCN and 10-15 equivalents of oxidizing agent, Ag_2O, to synthesize carboxylic acids from the corresponding conjugated aldehydes.[13, 14] Castells and his colleagues reported ester formation by using thiazolium salt or cyanide ion as a catalyst with nitrobenzene as an oxidizing agent.[15] In our reaction, however, no external oxidizing agent besides oxygen from air was required. We are now working toward a synthesis of chiral calixarenes using this selective autoxidation reaction.

Acknowledgements

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TETRAHEDRON LETTERS

Synthesis of stilbene crown ether *p*-*tert*-butylcalix[4]arenes

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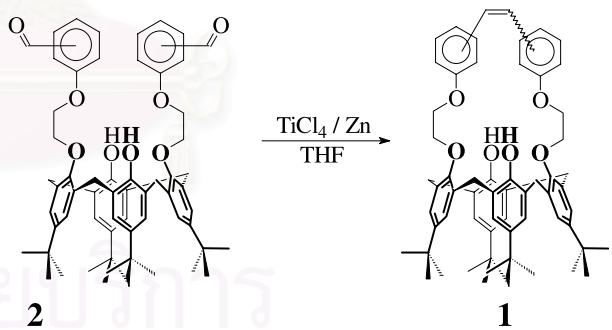
Abstract—Photo-switchable calixarene crown ether derivatives were synthesized in order to control the ring sizes and shapes of ionophores by isomerization between two different geometrical isomers. Five stilbene crown ether calix[4]arenes were prepared via McMurry coupling of the corresponding bisbenzaldehyde–calix[4]arene derivatives. The coupling reactions yielded both *cis*- and *trans*-stilbenes from *o*- and *m*-bisbenzaldehydes while only the *cis*-isomer was obtained from the reaction of the *p*-isomer. Unlike diazobenzene analogues, the stilbene crown ether calix[4]arene derivatives did not undergo thermal isomerization. Nevertheless, the isomerization of all synthesized stilbene crown ether calix[4]arenes can be photochemically induced.

Recently, supramolecular chemistry has become one of the most dynamic fields in chemistry. The molecular architecture required for selective recognition of molecules or ions by shape and size is one of the key points of interest in this subject.[1] The crown ether family is well known as ionophores.[2] In 1980, Shinkai and his colleagues synthesized an azobenzene containing crown ether to be used as a switchable alkali ion receptor.[3] The azobenzene moiety isomerized from the *trans*- to the *cis*-isomer upon irradiation, while the more sterically hindered *cis*-isomer converted back to the *trans*-isomer in the dark. The *cis*-isomer suitably bound K^+, Rb^+, and Cs^+ but the *trans*-isomer preferred to bind Li^+ and Na^+. An azobenzene-containing cryptand was also later synthesized by this group.[4] The switching of this cryptand from the *trans*- to the *cis*-isomer resulted in ring expansion that altered its binding preference from Na^+ to K^+.

Owing to its pre-organized structure, calix[4]arene is currently a popular molecular platform for designing highly selective receptors.[5] Several isomerizable azobenzene crown ether calix[4]arenes have been prepared and studied.[6–8] Although the *cis*- and *trans*-isomers of these azobenzene derivatives display different selectivity in binding alkali metal ions, their thermal isomerization has prevented them from being good candidates for controllable molecular photo-switches. Unlike azobenzenes, the stilbene analogues have been found not to undergo thermal isomerization[9] and thus are more promising as switching units for molecular photo-switches.

The *p*-*tert*-butylcalix[4]arene derivatives containing multiple benzaldehyde groups have been demonstrated



Scheme 1.

Table 1. Yields and *cis*:*trans* ratios of the products from the coupling reactions

Compound	Yield (%)		*cis*:*trans* ratio
	cis	*trans*	
o-**1**	57	10	85:15
m-**1**	20	8	73:27
p-**1**	51	0	100:0

* Corresponding author.

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to be useful for syntheses of several selective host molecules.[10,11] We report herein syntheses of stilbene crown ether *p-tert*-butylcalix[4]arenes from *p-tert*-butylcalix[4]arene derivatives containing two benzaldehyde groups.

Three regioisomers, *o*-, *m*- and *p*-stilbene crown ether *p-tert*-butylcalix[4]arenes (**1**) were synthesized from McMurry coupling[12,13] of the corresponding bisbenzaldehydes (**2**) (Scheme 1). The bisbenzaldehydes were prepared by nucleophilic substitution reactions between *p-tert*-butylcalix[4]arene and the corresponding (2-bromoethoxy)benzaldehydes.[10,11]

The *m*-stilbene derivatives were prepared under modified McMurry conditions.[12,13] The *m*-bisbenzaldehyde reaction yielded 28% of the stilbene (*m*-**1**) and 20% of the corresponding pinacol by-product. The reaction of the *o*- and *p*-bisbenzaldehydes gave higher yields of stilbenes (*o*-**1** and *p*-**1**), 67% and 51%, respectively, and no pinacol by-product. Both *cis*- and *trans*-stilbenes were obtained from the coupling reaction of *o*- and *m*-bisbenzaldehydes but only the *cis*-stilbene was obtained from the *p*-isomer (Table 1). The assignment of *cis*- and *trans*-geometries was based on ^{1}H NMR and UV–vis spectra. The *cis*-geometry was assigned to the isomer possessing lower chemical shift values for the vinylic protons relative to the chemical shifts observed for unsubstituted stilbene (Table 2). This assignment is consistent with the data from UV–vis spectra that showed shorter λ_{max} and lower extinction coefficients for all *cis*-isomers (Table 3).

Table 2. Chemical shifts of the vinylic protons of the stilbene products and stilbene in ($CDCl_3$)

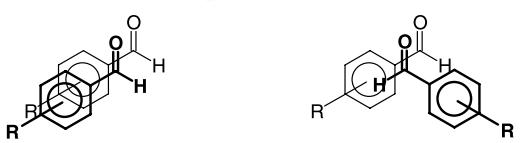
Compound	^{1}H NMR (ppm)	
	cis-isomer	*trans*-isomer
o-**1**	7.25	7.74
m-**1**	6.71	7.24
p-**1**	6.68	–
Stilbene[a]	6.57	7.15

[a] Measured in methanol.

Table 3. λ_{max} and extinction coefficient (ε) of the stilbene products and stilbene (in CH_2Cl_2)

Compound	*cis*-isomer		*trans*-isomer	
	λ_{max} (nm)	ε (cm^{-1} M^{-1})	λ_{max} (nm)	ε (cm^{-1} M^{-1})
o-**1**	292	19321	291	30106
			333	28492
m-**1**	286	20955	291	27488
			308	24866
			320	24629
p-**1**	283	16632	n.a.	n.a.
Stilbene[a]	223	20600	227	21000
	276	10900	294	33200
			307	32100

[a] Measured in methanol.



erythro *threo*

Figure 1. Proposed orientations of the two benzaldehyde groups that would lead to the formation of *cis*- and *trans*-products.

The predominant formation of the *cis*- over *trans*-products in this coupling reaction suggests that the pre-organized structure of the starting bisbenzaldehyde *p-tert*-butylcalix[4]arene may play an important role in controlling the geometry of the product. The shorter ethylene glycol linkages over the small and rigid lower rim of the *p-tert*-butylcalix[4]arene are less likely to allow the *threo* orientation of the two benzaldehyde moieties (Fig. 1) resulting in less *trans*-product. The situation becomes more obvious for the coupling of the *p*-bisbenzaldehyde in which the *threo*-like orientation would be most difficult to form and no *trans*-isomer was observed.

As predicted, all the stilbene crown ether *p-tert*-butylcalix[4]arenes synthesized did not isomerize under room light but readily isomerized under UV light. The photostationary states were observed for all isomers. We are currently studying the photo-switchable properties of these stilbene crown ether *p-tert*-butylcalix[4]arenes and their metal ions binding properties and will report the results in due course.

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13. $TiCl_4$ (3.17 mmol, 0.60 g) was charged into a two-necked, round-bottomed flask under a nitrogen atmosphere. Anhydrous THF (30 mL) was added dropwise and activated Zn powder (6.35 mmol, 0.41 g) was added cautiously. After 1 h reflux, the bisbenzaldehyde (1.06 mmol, 1.00 g) in THF (10 mL) was added dropwise. The mixture was refluxed for an additional 15 h and was then allowed to cool to room temperature. A solution of K_2CO_3 (15% w/v) was added to quench the excess $TiCl_4$. The precipitate was filtered off over Celite and washed with acetone and CH_2Cl_2. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 and then extracted with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product, which was purified by column chromatography using 5% ethyl acetate in hexane as eluent. The *cis*- and *trans*-isomers can be separated (*cis*-isomers have a higher R_f value).

   cis-o-**1**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.03 (s, 18 $C(CH_3)_3$), 1.22 (s, 18 $C(CH_3)_3$), 3.25 (d, 4 Ar_2CH_2, J= 13.0), 4.16 (broad, 4 OCH_2), 4.26 (broad, 4 OCH_2), 4.35 (d, 4 Ar_2CH_2, J=13.0), 6.83 (t, 2 stilbene-ArH, J=7.5), 6.88 (d, 2 stilbene-ArH, J=7.5), 6.90 (s, 4 calix-ArH), 6.97 (s, 4 calix-ArH), 7.17 (t, 2 stilbene-ArH, J=7.5), 7.25 (s, 2 CH=CH), 7.29 (d, 2 stilbene-ArH, J=7.5), 7.70 (s, 2 OH). Anal. calcd for $C_{62}H_{72}O_6 \cdot CH_2Cl_2$: C, 75.88; H, 7.38. Found: C, 76.12; H, 7.25.

   trans-o-**1**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.06 (s, 18 $C(CH_3)_3$), 1.18 (s, 18 $C(CH_3)_3$), 3.21 (d, 4 Ar_2CH_2, J= 12.5), 4.23 (d, 4 Ar_2CH_2, J=12.5), 4.51 (broad, 4 OCH_2), 4.68 (broad, 4 OCH_2), 6.82 (d, 2 stilbene-ArH, J=8.0), 6.93 (m, 4 calix-ArH and 2 stilbene-ArH), 6.97 (s, 4 calix-ArH), 7.15 (t, 2 stilbene-ArH, J=8.0), 7.50 (d, 2 stilbene-ArH, J=8.0), 7.74 (s, 2 CH=CH), 8.43 (s, 2 OH). Anal. calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95. Found: C, 81.41; H, 7.94.

   cis-m-**1**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.09 (s, 18 $C(CH_3)_3$), 1.25 (s, 18 $C(CH_3)_3$), 3.32 (d, 4 Ar_2CH_2, J= 12.5), 3.94 (broad, 4 OCH_2), 4.12 (broad, 4 OCH_2), 4.38 (d, 4 Ar_2CH_2, J=12.5), 6.69 (broad, 2 stilbene-ArH), 6.71 (s, 2 CH=CH), 6.89 (m, 4 stilbene-ArH), 6.97 (s, 4 calix-ArH), 7.02 (s, 4 calix-ArH), 7.24 (t, 2 stilbene-ArH, J=8.5), 8.08 (s, 2 OH). Anal. calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95. Found: C, 81.48; H, 7.92.

   trans-m-**1**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83 (s, 18 $C(CH_3)_3$), 1.31 (s, 18 $C(CH_3)_3$), 3.29 (d, 4 Ar_2CH_2, J= 13.5), 4.25 (t, 4 OCH_2, J=5.0), 4.41 (d, 4 Ar_2CH_2, J=13.5), 4.57 (t, 4 OCH_2, J=5.0), 5.84 (s, 2 OH), 6.60 (s, 4 calix-ArH), 6.87 (t, 2 stilbene-ArH, J=8.5), 7.06 (s, 4 calix-ArH), 7.14 (d, 2 stilbene-ArH, J=7.5), 7.24 (s, 2 CH=CH), 7.25 (t, 2 stilbene-ArH, J=7.5), 7.74 (s, 2 stilbene-ArH). Anal. calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95. Found: C, 81.59; H, 8.00.

   cis-p-**1**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85 (s, 18 $C(CH_3)_3$), 1.31 (s, 18 $C(CH_3)_3$), 3.28 (d, 4 Ar_2CH_2, J= 13.5), 4.17 (t, 4 OCH_2, J=4.0), 4.38 (d, 4 Ar_2CH_2, J=13.5), 4.45 (t, 4 OCH_2, J=4.0), 6.29 (s, 2 OH), 6.66 (s, 4 calix-ArH), 6.68 (s, 2 CH=CH), 6.85 (d, 4 stilbene-ArH, J=9.0 Hz), 6.93 (d, 4 stilbene-ArH, J=9.0), 7.06 (s, 4 calix-ArH). Anal. calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95. Found: C, 81.57; H, 8.14.

Graphical Abstract

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Comparative Study of Azobenzene and Stilbene Bridged Crown Ether *p-tert*-Butylcalix[4]arene

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Rojrit Rojanathanes, Bongkot Pipoosananakaton, Thawatchai Tuntulani, Worawan Bhanthumnavin, James B. Orton, Simon J. Cole, Michael B. Hursthouse, Martin C. Grossel and Mongkol Sukwattanasinitt*
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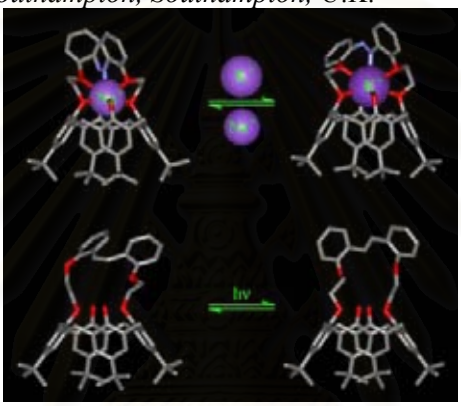

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TETRAHEDRON

Comparative study of azobenzene and stilbene bridged crown ether *p-tert*-butylcalix[4]arene

Rojrit Rojanathanes,[a] Bongkot Pipoosananakaton,[a] Thawatchai Tuntulani,[a] Worawan Bhanthumnavin,[a] James B. Orton,[b] Simon J. Cole,[b] Michael B. Hursthouse,[b] Martin C. Grossel[b] and Mongkol Sukwattanasinitt[a,*]

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Abstract— Photo-switchable calixarenes consisting of a stilbene or azobenzene bridge, across the narrow rim as a switching unit, were synthesized through reductive coupling of *o*-, *m*- and *p*-bisbenzaldehyde and bisnitrobenzene substituted calix[4]arene. Both *cis*- and *trans*-stilbenes were produced from the reductive coupling of the *o*- and *m*-bisbenzaldehyde with *cis* isomer being predominant for both regioisomers while the coupling of *p*-bisbenzaldehyde gave only *cis* product. On the other hand, the only isolable product obtained from the reductive coupling of bis-*o*- and bis-*m*-nitrobenzene was the corresponding *trans*-azobenzene and the coupling product from bis-*p*-nitrobenzene was not stable. All the synthesized compounds showed photostationary state of their *cis-trans* isomerization. The complexation with alkali metal ion was observed for only the o-azobenzene derivative suggesting that the lone pair of N-atom in the azo bridge participateed in the complexation.

1. Introduction

On a cell membrane, there are plenty of specific receptors that control the diffusion of molecules or ions in and out of the cell such as, potassium channel,[1] maltoporin[2] and sucroporin,[3] which control the diffusion of potassium ion, maltose and sucrose respectively. To specifically bind with each molecular or ionic guest, the shape and size of these receptors have to precisely fit with the preferred guest only. An extraordinary natural molecule that is always chosen as an example of a receptor due to its extremely high specificity binding, is valicomycin, which can bind specifically with potassium ions.[4,5] This cyclic molecule is composed of numerous oxygen donor atoms forming a nice pocket that fits perfectly with a potassium ion.

Aspiring to control the nature or at least understand nature, chemists have tried to design and synthesize synthetic molecules to function as ones arbitrarily desired. Crown ether family is an appealing group, which has been developed as a mimicked valicomycin to entrap the desired ion using the high electron density pocket of donor atoms.[6] The crown ether based ion receptors have been exploited extensively. Synthetic cation channels containing crown ether rings, called hydraphiles, have been published.[7] These hydraphile channels can kill *Escherichia coli* bacteria effectively via incorporating into the surface membrane disturbing sodium ion transport rate across the bacteria cell membrane.

Beside the donor atoms themselves, the pre-organized structure of the binding pocket is also a vital factor of binding properties. Calix[4]arene has become one of the most interesting platform to construct a selective receptor molecule due to its four pre-organized structures; cone, partial-cone, 1,2 alternating-cone and 1,3 alternating-cone.[8] The very first application of this well-ordered molecule as a cation receptor is calix[4]arene crown ether, which can be used to catch cesium ion for its perfectly fitted size.[9] Many receptors developed nowadays are calixarene-based receptors. But there is a crucial drawback of such a perfect fit host-guess pairs. The stronger the binding, the more difficult to regenerate the receptor back after its application, a proper attachment of a molecular switching unit to the receptor molecule should overcome this

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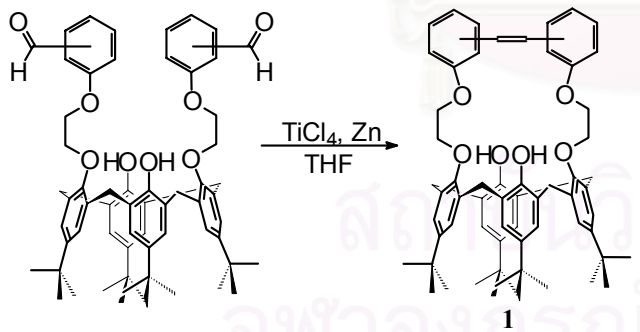
problem. There are many switching systems available, but among them, photo-switching mode is one of the most easy-to-operate systems.[10] Azobenzene and stilbene are widely used due to their facile *cis-trans* photoisomerization property.[11] Additionally, another appealing advantage potentially gained from switchable receptors is amphiphilic-binding property may be achieved.[12-13] During isomerization the binding cavity is altered and the binding property is then switched. They may switch from binding to unbinding or they may also switch from binding one ion to another ion. These are, actually, due to the transition in sizes and shapes of the binding pockets before and after isomerization.

We report herein the synthesis of two series of photoswitchable calix[4]arene derivatives. One series contain stilbene and the others contain azobenzene switching unit as a bridge across the narrow rim of the calixarene platform. Photoisomerization and complexation properties of the synthesized compounds are also compared.

2. Results and discussion

2.1. Synthesis

Three positional isomers, *o*-, *m*- and *p*-stilbene crown ether *p-tert*-butylcalix[4]arenes (1) were synthesized from the corresponding bisbenzaldehydes by the McMurry coupling (**Scheme 1**).[14,15] The bisbenzaldehydes were prepared from the corresponding (2-bromoethoxy)benzaldehydes by nucleophilic substitution of *p-tert*-butylcalix[4]arene with the corresponding (2-bromoethoxy)benzaldehyde.



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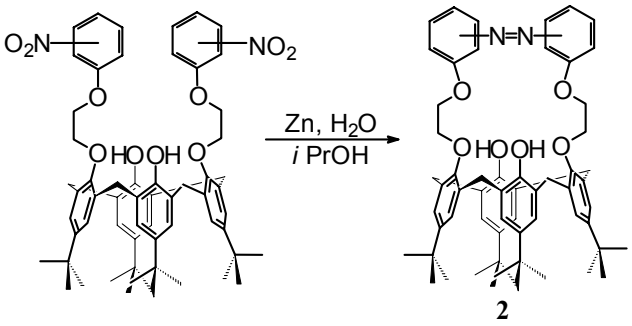
Scheme 1. Synthesis of stilbene crown ether calixarenes

Analogously, all isomers of azobenzene crown ether calixarenes (2) were synthesized from a reductive coupling of the corresponding bisnitrobenzenes (**Scheme 2**). The bisnitrobenzenes were prepared by nucleophilic substitution of the corresponding (2-bromoethoxy)nitrobenzene analogues.[12]



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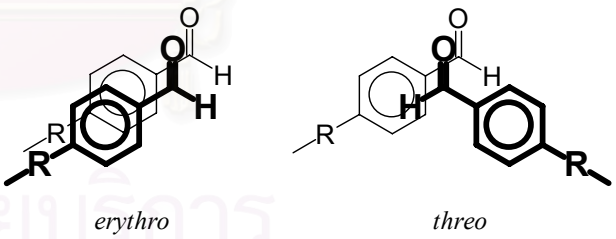
Scheme 2. Synthesis of azobenzene crown ether calixarenes

The *m*-stilbene derivatives were prepared under a modified McMurry condition to give both *cis*- and *trans*-stilbenes in 28% total yield (**Table 1**). This reaction also gave 20% of the corresponding pinacol byproduct. The coupling reaction of the *o*- and *p*-bisbenzaldehydes gave higher yields of stilbenes (*o*-1 and *p*-1), 67% and 51%, respectively, without observable pinacol. Both *cis*- and *trans*-stilbenes were obtained from the coupling reaction of *o*- and *m*-bisbenzaldehydes but the coupling of the *p*-isomer gave only *cis*-stilbene. IT is important to note here that McMurry coupling proceeded successfully despite the presence of phenolic O H groups in the starting materials.

The predominant formation of the *cis* over *trans* products in the McMurry couplin g reaction suggests that the pre-organized structure of the starting bisb enzaldehyde *p-tert*-butylcalix[4]arene may play an important role in controlling the geometry of the products. The shorter ethylene glycol linkages over the small and rigid lower rim of the *p-tert*-butylcalix[4]arene are less likely to allow the *threo* orientation of the two benzaldehyde moieties (**Figure 1**) resulting in no formation of the *trans*-product.



erythro *threo*

Figure 1. The proposed orientations, erythro and threo, of the two benzaldehyde groups that would lead to the formation of *cis* and *trans* products

In the synthesis of *o*-azobenzene crown ether calixarene in ambient pressure, only *trans* isomer was isolated in 8% yield. The *cis* isomer could not be obtained in a pure form due to its rapid thermal isomerization. The *m*-isomer gave higher yield of the azobenzene product compared to the *o*-isomer because the high-pressure method was applied (**Table 1**). The *p*-isomer however seemed to be unstable as the color of the terminated reaction solution changed rapidly from bright orange to dark brown upon exposure to air and moisture and no desired product could be isolated.

Table 1. Products from the synthesis of stilbene and azobenzene crown ether calixarenes

Products	% Yield	
	cis	*trans*
o-1	57	10
m-1	20	8
p-1	51	0
o-2	0	8
m-2	0	59[a]
p-2	0	0

[a]via high-pressure method

Table 2. ^{1}H NMR (in $CDCl_3$) and electronic absorption (in CH_2Cl_2) data of the synthesized stilbene-calix derivatives in comparison with stilbene

Compound	δ for vinylic proton (ppm)	λ_{max} (nm)	ε (cm^{-1} M^{-1})
cis-o-1	7.25	292	19321
trans-o-1	7.74	291	30106
		333	28492
cis-m-1	6.71	286	20955
trans-m-1	7.24	291	27488
		308	24866
		320	24629
cis-p-1	6.68	283	16632
cis-stilbene	6.57	223	20600
		276	10900
trans-stilbene	7.15	227	21000
		294	33200
		307	32100

2.2. Characterization of products

All *cis*- and *trans*-stilbene derivatives possess C_2 axis, the coupling between two vinylic protons in ^{1}H-NMR, which would normally be used for distinguishing between *cis* and *trans* isomers, does not exist. The assignment of *cis* and *trans* geometries was thus initially based on the chemical shift of vinylic protons and the UV-Vis absorption using the parent *cis* and *trans* unsubstituted stilbenes as references. According to the chemical shifts observed for unsubstituted stilbenes, the *cis* geometry was assigned to the isomer possessing vinylic protons with the lower chemical shift values (**Table 2**). This assignment is consistent with the data from UV-Vis spectra that showed shorter λ_{max} and lower extinction coefficients for all *cis* isomers.

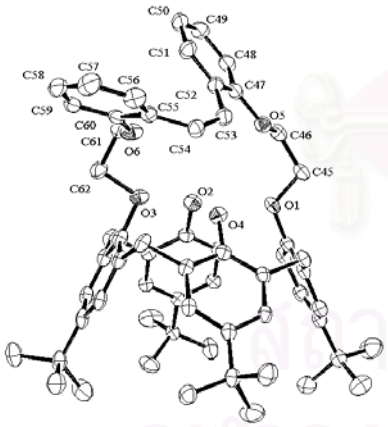


Figure 2. X-ray crystallographic structure of *cis-o*-1

The structural assignments were confirmed by X-ray crystallography. The proposed *cis-o*-**1** was successfully crystallized as a single crystal (**Figure 2**). The X-ray data was in agreement with the proposed structure.

In the synthesis of azobenzene derivatives, only one product was isolated for each regioisomer, *o*-2 and *m*-2. Since only one stereoisomer of each azobenzene derivative is available and the nitrogen contains no proton to be observed by ^{1}H-NMR, the assignment of *cis* and *trans* geometry was only possible through X-ray crystalography. Fortunately, both azobenzene derivatives (*o*-2 and *m*-2) could be crystallized into single crystals suitable for X-ray crystallography. The X-ray structure of these azobenzene derivatives revealed that both compounds were the *trans* isomers (**Figure 3**).

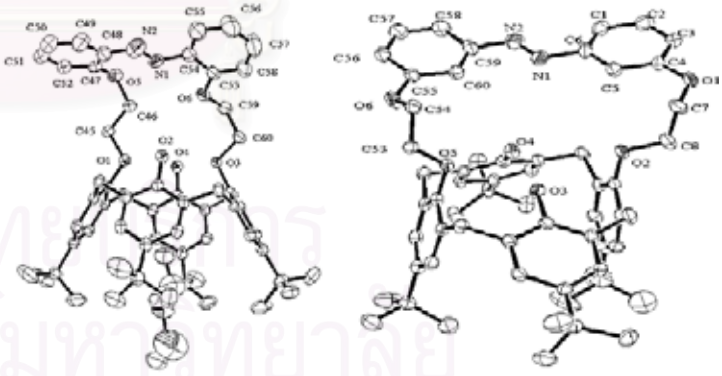


Figure 3. X-ray crystallographic structure of *trans-o*-2•$CH_3CO_2CH_2CH_3$ and *trans-m*-2

2.3. Isomerization study

All the stilbene crown ether *p-tert*-butylcalix[4]arenes synthesized did not isomerize under room light but readily isomerized under the UV light (medium pressure mercury lamp). The *cis* and *trans* percentages for each derivative at the photostationary state were determined by ^{1}H NMR spectroscopy using the ratio of the peak areas of the best

resolved signals corresponding to each geometrical isomer (**Figure 4**).

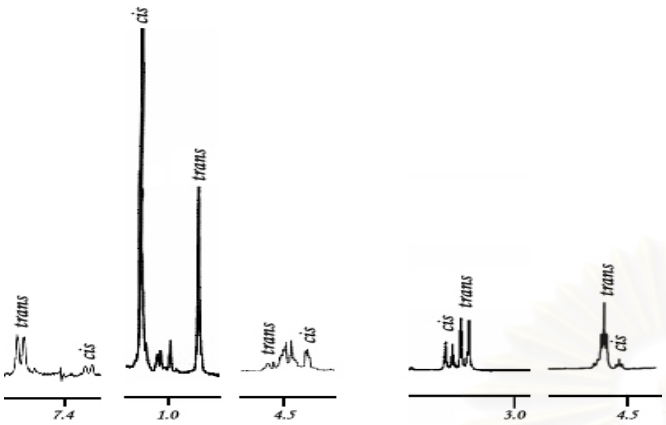


Figure 4. ^{1}H NMR signals used for calculation of *cis/trans* ratio at the photostationary state, (a) aromatic protons *ortho* to vinylic carbon in *o*-1, (b) *t*-butyl protons in *m*-1, (c) ethylene glycolic protons in *p*-1, at the photostationary state (d) methylene bridge protons in *o*-2 and (e) ethylene glycolic protons in *m*-2.

The signals of the same type of protons in *cis* and *trans* forms of each regioisomer, aromatic protons *ortho* to vinylic carbon for *o*-**1**, *t*-butyl protons for *m*-**1**, ethylene glycolic protons for *p*-**1**, methylene bridge protons in *o*-**2** and ethylene glycolic protons for *m*-**2**, were selected for the ratio calculation. The photo-stationary states were observed for all isomers and the percentages of *cis* and *trans* isomers were obtained from ^{1}H NMR (**Table 3**).

Table 3. The percentages of *cis* and *trans* isomers at the photostationary states

Compound	% Isomer at photostationary state	
	cis	*trans*
o-**1**	15	85
m-**1**	70	30
p-**1**	75	25
o-**2**	36	64
m-**2**	13	87

For stilbene derivatives, the same photostationary state was reached, no matter the isomerization started from which geometrically pure isomer, *cis* or *trans*. But in the case of azobenzene analogues, the irradiation was performed only on the available *trans* isomer.

Unlike the stilbene derivatives, the azobenzene calixarenes isomerized even in the absence of light due to the usual thermal isomerization of the diazo (N=N) unit.[16] While the photoisomerization of both stilbenes and azobenzenes under a medium pressure Hg lamp took minutes, the thermal isomerization of the azobenzenes was much slower, taking over a week to reach the equilibrium. Both thermal and photoisomerizations of azobenzene derivativatives produced the same final *cis*:*trans* product ratios implying that, under our experimental condition, the product ratio in photoizomerization directly associated to the relative thermal stability of each isomer.

2.4. Complexation study

Picrate salt extraction was chosen for the complexation study. The complexation can be observed through various means, color change, ^{1}H-NMR and UV-Vis spectroscopy. To our surprise, from the complexation study with ^{1}H NMR of all the compounds synthesized, only *o*-**2** complexed with sodium and potassium picrate (**Figure 5**) while the other derivatives showed no observable complexation.

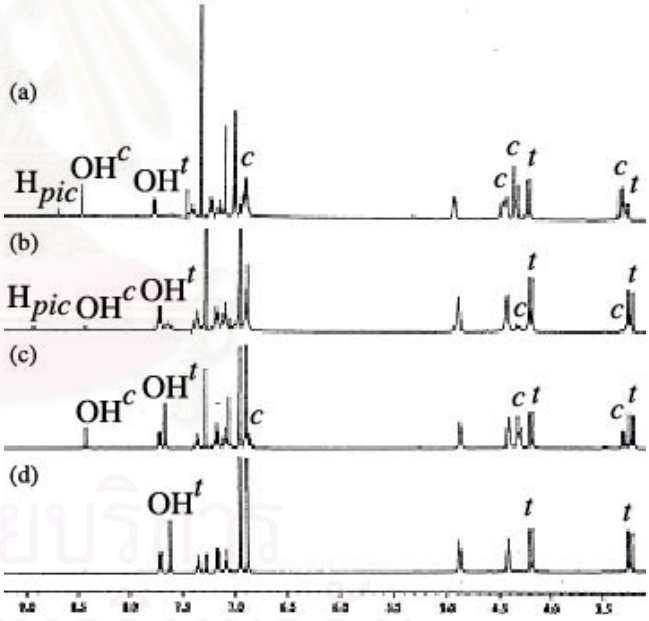
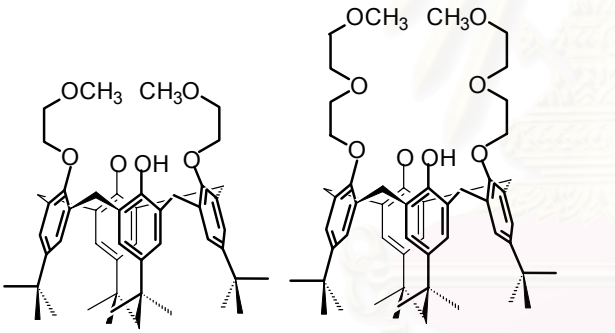


Figure 5. ^{1}H NMR spectra of (a) *trans*-*o*-**2** (b) *cis*- and *trans*-*o*-**2** at the photostationary state (c) *o*-**2** with potassium picrate and (d) *o*-**2** with sodium picrate. (*pic* = picrate, *c* = *cis*, *t* = *trans*)

The complexation results suggested that the lone pair electrons on nitrogen of the diazo group participated in the binding with the metal ions. Thus, only the *o*-**2**, which possesses at least one nitrogen lone pair of electorons pointing inward the crown ether biding cavity, can form a host-guest complex. It is also interesting to point out here that the complexation of *o*-**2** with Na^+ and K^+ ion shifted the thermal equilibrium between *cis* and *trans* isomers to

opposite directions. The complexation with K^+ resulted in the equilibrium shift toward the *trans* isomer (compare **Figure 5c** with **5b**) while the complexation with Na^+ moved the equilibrium toward the *cis* isomer (compare **Figure 5d** with **5b**).

Unfortunately, we have not been able to crystallize the *o*-**2** metal complex as a single crystal to confirm our hypothesis about the participation of the nitrogen lone pair in the complexation. We however studied the complexation of the model compounds, calixarene derivatives **3** and **4** with sodium and potassium picrates. When solid sodium (or potassium) picrate was added to the colorless solution of **4** in CH_2Cl_2, the solution turned yellow and the UV-Vis spectrum showed strong absorption band of the picrate ion around 375 nm (**Figure 6**), although it was barely detected in ^{1}H-NMR. The mixture of **3** and sodium (or potassium) picrate in CH_2Cl_2, on the other hand, showed no absorption band of picrate anion. The results indicated that while compound **4** which contains eight oxygen donor atoms complexed with sodium and potassium ions, compound **3** which contains only six oxygen donor atoms complexed with neither ions. The results thus supported our hypothesis that six etherial oxygen donor atoms in this calixarene based system were not sufficient for the biding of alkali metal ions.



3 **4**

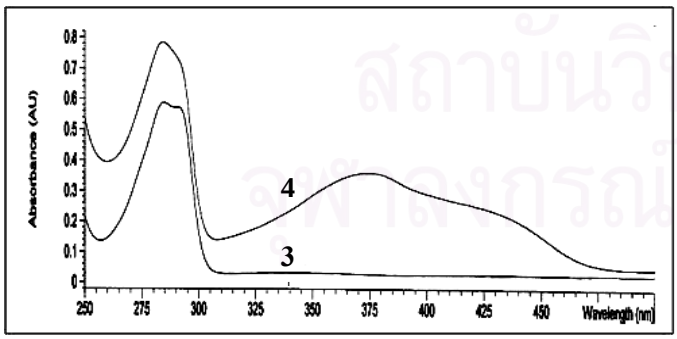


Figure 6. UV-Vis spectra of **3** and **4** in CH_2Cl_2 in the presence of sodium picrate salt added as a solid.

3. Conclusion

We have successfully synthesized and fully characterized two series of photoswitchable calix[4]arene containing different regioisomers of stilbene and azobenzene bridges. The *cis-trans* isomerization study indicated that the stilbene derivatives isomerized only under UV irradiation while the azobenzene derivatives underwent either thermal isomerization or photoisomerization. Only the *o*-azobenzene derivative showed complexation with sodium and potassium ions presumably due to the participation of the nitrogen atom of the diazo group in the coordination to the ions. The results represent a rare example of the coordination of the nonpolar diazo nitrogen to an alkali ion. The complexation also induced the thermal equilibrium shift between *cis* and *trans* isomers of the azobenzenes. The finding in this work will lead to new design and synthesis of more effective photoswitchable ionophores for sodium and potassium ions.

4. Experimental section

4.1. Synthesis of bis-benzaldehyde

In a 1 L, two-necked, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser, *p-tert*-butyl-calix[4]arene (7.8 mmol, 5.00 g) and K_2CO_3 (57.9 mmol, 8.00 g) were dissolved in CH_3CN (300 mL). The mixture was stirred for 30 minutes at room temperature and (2-bromoethoxy)-benzaldehyde (17.5 mmol, 4.00 g) was then added dropwise. The mixture was refluxed for 60 hours and then allowed to cool to room temperature. The mixture was filtered and washed with acetone and CH_2Cl_2. The filtrate was combined and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and then extracted with aqueous HCl (2 M, 4 x 25 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by crystallization in CH_2Cl_2/CH_3OH yielding a white solid as the product.

o-isomer (5.5 mmol, 5.16 g., 70%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H), 1.24 (s, 18H), 3.29 (d, 4H, J = 13.0 Hz), 4.29 (d, 4H, J = 13.0 Hz), 4.38-4.40 (m, 8H), 6.85 (s, 4H), 7.00 (s, 4H) 6.94–7.04 (m, 4H), 7.50 (s, 4H), 7.45-7.55 (m, 2H), 7.82 (dd, 2H, J = 7.5, 2.0 Hz), 10.48 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.1, 31.7, 31.8, 33.8, 34.0, 67.5, 73.6, 112.4, 121.0, 125.2, 125.2, 125.8, 127.7, 128.2, 132.6, 135.8, 141.7, 147.3, 149.8 ,150.3, 160.8, 190.2.

m-isomer (4.7 mmol, 4.42 g., 60%): mp (decompose) = 184.8-185.3ºC; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 18H), 1.27 (s, 18H), 3.32 (d, 4H, J = 13.0 Hz), 4.30-4.40 (m, 12H), 6.85 (s, 4H), 7.04 (s, 4H) 7.20–7.45 (m, 8H), 9.93 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.1, 31.7, 31.7, 33.8, 34.0, 66.9, 73.7, 113.4, 122.4, 123.6, 125.2, 125.7, 127.8, 130.2, 132.8, 137.8, 141.5, 147.1, 149.7, 150.5, 159.2, 192.1; IR (neat) ν_{max} 3336 (phenolic O-H stretching), 3050, 2958, 2869 (aldehydic C-H stretching), 2731 (aldehydic C-H stretching), 1697 (aldehydic C=O stretching), 1597, 1485, 1450, 1265 cm^{-1}; Anal. Calcd for $C_{62}H_{72}O_8$: C, 78.78; H, 7.68; Found: C, 76.80; H, 7.95.

p-isomer (4.3 mmol, 4.05 g., 55%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18 (s, 18H), 1.50 (s, 18H), 3.49 (d, 4H, J = 13.0 Hz), 4.80-4.52 (m, 8H), 4.54 (d, 4H, J = 13.0 Hz), 7.02 (s, 4H), 7.19 (d, 4H, J = 8.5 Hz), 7.24 (s, 4H), 7.42 (s, 2H), 10.06 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.0, 31.5, 31.7, 33.8, 34.0, 66.9, 73.5, 115.1, 125.2, 125.7, 127.8, 130.2, 131.9, 132.6, 141.6, 147.2, 149.6, 150.4, 163.5, 190.8.

4.2. Synthesis of bis-nitrobenzene

In a 500 mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser, a mixture of potassium carbonate (0.43 mmol, 6.0 g), (2-bromoethoxy)nitrobenzene (40.64 mmol, 10.0 g)and *p-tert*-butyl calyx[4]arene (18.85 mmol, 8.0 g) were stirred in CH_3CN (200 mL). The mixture was kept stirring at reflux temperature overnight. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH2Cl2 (150 mL) and then extracted with water for several times. The combinded organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was further purified crystallisation using CH_2Cl_2 / MeOH solvent system. The purified product was obtained as a yellow crystal.

o-isomer (12.44 mmol, 12.2 g., 66%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99 (s, 18H), 1.26 (s, 18H), 3.31 (d, 4H, J = 13.0 Hz), 4.33 (s, 8H), 4.35 (d, 4H, J = 13.0 Hz), 6.85 (s, 4H), 7.03 (s, 4H), 7.24 (ddd, 2H, J = 8.0, 2.0, 1.0 Hz), 7.35 (s, 2H), 7.40 (t, 2H, J = 8.0 Hz), 7.74 (t, 2H, 2.0 Hz), 7.81 (ddd, 2H, 8.0, 2.0, 1.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.1, 31.7, 31.7, 33.9, 34.0, 67.4, 73.4, 109.1, 116.2, 122.2, 125.2, 125.8, 127.8, 130.0, 132.8, 141.8, 147.5, 149.1, 149.5, 150.3, 159.1; Anal. Calcd for $C_{60}H_{70}N_2O_{10}$: C, 73.60; H, 7.21; N, 2.386; Found: C, 73.62; H, 7.27; N, 2.73: mp. = 205-207^{o}C.

m-isomer (13.28 mmol, 13.0 g., 70%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99 (s, 18H), 1.26 (s, 18H), 3.31 (d, 4H, J = 13.0 Hz), 4.33 (s, 8H), 4.35 (d, 4H, J = 13.0 Hz), 6.85 (s, 4H), 7.03 (s, 4H), 7.24 (ddd, 2H, J = 8.0, 2.0, 1.0 Hz), 7.35 (s, 2H), 7.40 (t, 2H, J = 8.0 Hz), 7.74 (t, 2H, 2.0 Hz), 7.81 (ddd, 2H, 8.0, 2.0, 1.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.1, 31.7, 31.7, 33.9, 34.0, 67.4, 73.4, 109.1, 116.2, 122.2, 125.2, 125.8, 127.8, 130.0, 132.8, 141.8, 147.5, 149.1, 149.5, 150.3, 159.1.

p-isomer (15.1 mmol, 14.8 g., 80%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (s, 18H), 1.27 (s, 18H), 3.30 (d, 4H, J = 13.0 Hz), 4.31 (s, 8H), 4.35 (d, 4H, J = 13.0 Hz), 6.80 (s, 4H), 6.98 (d, 4H, J = 9.0 Hz), 7.05 (s, 4H), 7.07 (s, 2H), 8.18 (d, 4H, J = 9.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.0, 31.5, 31.7, 33.9, 34.0, 67.4, 73.5, 114.8, 125.2, 125.7, 125.9, 127.7, 132.5, 141.8, 141.8, 147.3, 149.4, 150.4, 163.5.

4.3. Synthesis of 1

Typically, $TiCl_4$ (3.17 mmol, 0.60 g) was charged into a two-necked, round-bottomed flask under a N_2 atmosphere. Anhydrous THF (30 mL) was added dropwise and activated Zn powder (6.35 mmol, 0.41 g) was added cautiously. After 1 h reflux, the bisbenzaldehyde (1.06 mmol, 1.00 g) in THF (10 mL) was added dropwise. The mixture was refluxed for additional 15 h and it was allowed to cool to room temperature. A solution of K_2CO_3 (15% w/v) was added to quench the excess $TiCl_4$. The precipitate was filtered over celite and washed with acetone and CH_2Cl_2. The filtrate was evaporated to give the residue which was dissolved in CH_2Cl_2 (20 mL) and then extracted with water (3 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product. The *cis* and *trans* isomers was separated by column chromatography using 5% ethyl acetate in hexane as eluent (*cis* isomers have a higher R_f value).

cis-o-1 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.03 (s, 18 C(C$\underline{H}_3$)$_3$), 1.22 (s, 18 C(C$\underline{H}_3$)$_3$), 3.25 (d, 4 Ar$_2$C$\underline{H}_2$, *J* = 13.0), 4.16 (broad, 4 OC$\underline{H}_2$), 4.26 (broad, 4 OC$\underline{H}_2$), 4.35 (d, 4 Ar$_2$C$\underline{H}_2$, *J* = 13.0), 6.83 (t, 2 stilbene-Ar$\underline{H}$, *J* = 7.5), 6.88 (d, 2 stilbene-Ar$\underline{H}$, *J* = 7.5), 6.90 (s, 4 calix-Ar$\underline{H}$), 6.97 (s, 4 calix-Ar$\underline{H}$), 7.17 (t, 2 stilbene-Ar$\underline{H}$, *J* = 7.5), 7.25 (s, 2 C$\underline{H}$=C$\underline{H}$), 7.29 (d, 2 stilbene-Ar$\underline{H}$, *J* = 7.5), 7.70 (s, 2 O$\underline{H}$) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.1 (6 C(C$\underline{H}_3$)$_3$), 31.7 (6 C(C$\underline{H}_3$)$_3$), 31.9 (4 Ar$_2$C$\underline{H}_2$), 33.8 (2 $\underline{C}$(CH$_3$)$_3$), 34.0 (2 $\underline{C}$(CH3)3), 67.8 (2 OC$\underline{H}_2$), 74.1 (2 OC$\underline{H}_2$), 113.4 (2 stilbene-Ar$\underline{C}$), 120.8 (2 stilbene-Ar$\underline{C}$), 125.1 (4 calix-Ar$\underline{C}$), 125.4 (2 C$\underline{H}$=C$\underline{H}$), 125.7 (4 calix-Ar$\underline{C}$), 127.7 (4 calix-Ar$\underline{C}$), 127.9 (2 stilbene-Ar$\underline{C}$), 129.0 (2 stilbene-Ar$\underline{C}$), 129.5 (2 stilbene-Ar$\underline{C}$), 133.3 (4 stilbene-Ar$\underline{C}$), 141.0 (2 calix-Ar$\underline{C}$), 147.0 (2 calix-Ar$\underline{C}$), 149.6 (2 calix-Ar$\underline{C}$), 150.8 (2calix-Ar$\underline{C}$), 155.7 (2 stilbene-Ar$\underline{C}$); Anal. Calcd for $C_{62}H_{72}O_6$•CH_2Cl_2: C, 75.88; H, 7.38; Found: C, 76.12; H, 7.25: mp. = 292-294^{o}C (decomposed).

trans-o-1 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (s, 18 C(C$\underline{H}_3$)$_3$), 1.18 (s, 18 C(C$\underline{H}_3$)$_3$), 3.21 (d, 4 Ar$_2$C$\underline{H}_2$, *J* = 12.5), 4.23 (d, 4 Ar$_2$C$\underline{H}_2$, *J* = 12.5), 4.51 (broad, 4 OC$\underline{H}_2$), 4.68 (broad, 4 OC$\underline{H}_2$), 6.82 (d, 2 stilbene-Ar$\underline{H}$, *J* = 8.0), 6.93 (m, 4 calix-Ar$\underline{H}$ & 2 stilbene-Ar$\underline{H}$), 6.97 (s, 4 calix-Ar$\underline{H}$), 7.15 (t, 2 stilbene-Ar$\underline{H}$, *J* = 8.0), 7.50 (d, 2 stilbene-Ar$\underline{H}$, *J* = 8.0), 7.74 (s, 2 C$\underline{H}$=C$\underline{H}$), 8.43 (s, 2 O$\underline{H}$) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.2 (6 C($\underline{C}$H$_3$)$_3$), 31.6 (6 C($\underline{C}$H$_3$)$_3$), 32.1 (4 Ar$_2$$\underline{C}H_2$), 33.8 (2 $\underline{C}$(CH$_3$)$_3$), 34.1 (2 $\underline{C}$(CH3)3), 66.6 (2 O$\underline{C}$H$_2$), 73.6 (2 O$\underline{C}$H$_2$), 111.1 (2 stilbene-Ar$\underline{C}$), 120.8 (2 stilbene-Ar$\underline{C}$), 125.0 (4 calix-Ar$\underline{C}$), 125.9 (4 calix-Ar$\underline{C}$), 127.5 (4 calix-Ar$\underline{C}$), 127.5 (2 C$\underline{H}$=C$\underline{H}$), 127.7 (2 stilbene-Ar$\underline{C}$), 128.0 (2 stilbene-Ar$\underline{C}$), 129.6 (2 stilbene-Ar$\underline{C}$), 133.7 (4 calix-Ar$\underline{C}$), 141.2 (2 calix-Ar$\underline{C}$), 147.4 (2 calix-Ar$\underline{C}$), 149.3 (2 calix-Ar$\underline{C}$), 150.7 (2 calix-Ar$\underline{C}$), 155.9 (2 stilbene-Ar$\underline{C}$); Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.41; H, 7.94: mp. = 278-280^{o}C (decomposed).

cis-m-1 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (s, 18 C(C$\underline{H}_3$)$_3$), 1.25 (s, 18 C(C$\underline{H}_3$)$_3$), 3.32 (d, 4 Ar$_2$C$\underline{H}_2$, *J* = 12.5), 3.94 (broad, 4 OC$\underline{H}_2$), 4.12 (broad, 4 OC$\underline{H}_2$), 4.38 (d,

4 $Ar_2C\underline{H}_2$, J = 12.5), 6.69 (broad, 2 stilbene-Ar$\underline{H}$), 6.71 (s, 2 C$\underline{H}$=C$\underline{H}$), 6.89 (m, 4 stilbene-Ar$\underline{H}$), 6.97 (s, 4 calix-Ar$\underline{H}$), 7.02 (s, 4 calix-Ar$\underline{H}$), 7.24 (t, 2 stilbene-Ar$\underline{H}$, J = 8.5), 8.08 (s, 2 O$\underline{H}$) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.2 (6 C($\underline{C}H_3)_3$), 31.7 (6 C($\underline{C}H_3)_3$), 31.7 (4 $Ar_2\underline{C}H_2$), 33.8 (2 $\underline{C}(CH_3)_3$), 34.1 (2 $\underline{C}$(CH3)3), 66.2 (2 O$\underline{C}H_2$), 73.7 (2 O$\underline{C}H_2$), 111.8 (2 stilbene-Ar$\underline{C}$), 117.0 (2 stilbene-Ar$\underline{C}$), 121.5 (2 stilbene-Ar$\underline{C}$), 125.0 (4 calix-Ar$\underline{C}$), 125.7 (4 calix-Ar$\underline{C}$), 127.3 (4 calix-Ar$\underline{C}$), 129.6 (2 $\underline{C}$H=$\underline{C}$H), 130.9 (2 stilbene-Ar$\underline{C}$), 133.5 (4 calix-Ar$\underline{C}$), 138.3 (2 stilbene-Ar$\underline{C}$), 140.9 (2 calix-Ar$\underline{C}$), 147.2 (2 calix-Ar$\underline{C}$), 149.2 (2 calix-Ar$\underline{C}$), 151.1 (2 calix-Ar$\underline{C}$), 158.2 (2 stilbene-Ar$\underline{C}$); Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.48; H, 7.92: mp. = 264-265 ºC.

trans-m-1 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (s, 18 C($C\underline{H}_3)_3$), 1.31 (s, 18 C($C\underline{H}_3)_3$), 3.29 (d, 4 $Ar_2C\underline{H}_2$, J = 13.5), 4.25 (t, 4 O$C\underline{H}_2$, J = 5.0), 4.41 (d, 4 $Ar_2C\underline{H}_2$, J = 13.5), 4.57 (t, 4 O$C\underline{H}_2$, J = 5.0), 5.84 (s, 2 O$\underline{H}$), 6.60 (s, 4 calix-Ar$\underline{H}$), 6.87 (t, 2 stilbene-Ar$\underline{H}$, J = 8.5), 7.06 (s, 4 calix-Ar$\underline{H}$), 7.14 (d, 2 stilbene-Ar$\underline{H}$, J = 7.5), 7.24 (s, 2 C$\underline{H}$=C$\underline{H}$), 7.25 (t, 2 stilbene-Ar$\underline{H}$, J = 7.5), 7.74 (s, 2 stilbene-Ar$\underline{H}$) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 30.8 (6 C($\underline{C}H_3)_3$), 31.2 (4 $Ar_2\underline{C}H_2$), 31.7 (6 C($\underline{C}H_3)_3$), 33.8 (2 $\underline{C}(CH_3)_3$), 33.9 (2 $\underline{C}$(CH3)3), 69.3 (2 O$\underline{C}H_2$), 75.0 (2 O$\underline{C}H_2$), 114.3 (2 stilbene-Ar$\underline{C}$), 118.0 (2 stilbene-Ar$\underline{C}$), 119.9 (2 stilbene-Ar$\underline{C}$), 125.3 (4 calix-Ar$\underline{C}$), 125.4 (4 calix-Ar$\underline{C}$), 128.5 (4 calix-Ar$\underline{C}$), 128.9 (2 $\underline{C}$H=$\underline{C}$H), 129.8 (2 stilbene-Ar$\underline{C}$), 131.6 (4 calix-Ar$\underline{C}$), 139.1 (2 stilbene-Ar$\underline{C}$), 141.8 (2 calix-Ar$\underline{C}$), 146.7 (2 calix-Ar$\underline{C}$), 150.3 (2 calix-Ar$\underline{C}$), 150.8 (2 calix-Ar$\underline{C}$), 158.8 (2 stilbene-Ar$\underline{C}$) ; Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.59; H, 8.00: mp. = 281-283ºC (decomposed).

cis-p-1 ; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85 (s, 18 C($C\underline{H}_3)_3$), 1.31 (s, 18 C($C\underline{H}_3)_3$), 3.28 (d, 4 $Ar_2C\underline{H}_2$, J = 13.5), 4.17 (t, 4 O$C\underline{H}_2$, J = 4.0), 4.38 (d, 4 $Ar_2C\underline{H}_2$, J = 13.5), 4.45 (t, 4 O$C\underline{H}_2$, J = 4.0), 6.29 (s, 2 O$\underline{H}$), 6.66 (s, 4 calix-Ar$\underline{H}$), 6.68 (s, 2 C$\underline{H}$=C$\underline{H}$), 6.85 (d, 4 stilbene-Ar$\underline{H}$, J = 9.0 Hz), 6.93 (d, 4 stilbene-Ar$\underline{H}$, J = 9.0), 7.06 (s, 4 calix-Ar$\underline{H}$) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.0 (6 C($\underline{C}H_3)_3$), 31.1 (4 $Ar_2\underline{C}H_2$), 31.8 (6 C($\underline{C}H_3)_3$), 33.8 (2 $\underline{C}(CH_3)_3$), 33.8 (2 $\underline{C}$(CH3)3), 68.4 (2 O$\underline{C}H_2$), 74.8 (2 O$\underline{C}H_2$), 115.8 (4 stilbene-Ar$\underline{C}$), 125.2 (4 calix-Ar$\underline{C}$), 125.4 (4 calix-Ar$\underline{C}$), 128.1 (4 calix-Ar$\underline{C}$), 130.4 (4 stilbene-Ar$\underline{C}$), 130.8 (2 $\underline{C}$H=$\underline{C}$H), 131.3 (2 stilbene-Ar$\underline{C}$), 132.0 (4 calix-Ar$\underline{C}$), 141.4 (2 calix-Ar$\underline{C}$), 146.8 (2 calix-Ar$\underline{C}$), 149.9 (2 calix-Ar$\underline{C}$), 150.5 (2 calix-Ar$\underline{C}$), 157.7 (2 stilbene-Ar$\underline{C}$); Anal. Calcd for $C_{62}H_{72}O_6$: C, 81.54; H, 7.95; Found: C, 81.57; H, 8.14: mp. = 290-291 ºC (decomposed).

4.4. Synthesis of 2

Ambient pressure method: In a 50 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser, a mixture of bis-nitrobenzene, (0.71 mmol, 0.70 g) in isopropanol (8 mL), sodium hydroxide (7.0 mmol, 0.28g) in water (4mL) and zinc (3.06 mmol, 0.20 g) was stirred. The mixture was refluxed under nitrogen atmosphere for 48 hours and it was then allowed to cool to room temperature. The mixture was filtered off and washed with CH_2Cl_2. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 and then extracted with 2M HCl (2x20 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product, which was purified by column chromatography using 15% ethyl acetate in hexane as eluent. The *trans* isomers was collected and crystallized in CH_2Cl_2/CH_3OH mixture to give orange crystals.

High pressure method: In a 100 mL high-pressure glass tube equipped with pressure gauge and a magnetic bar, a mixture of bis-nitrobenzene, (0.71 mmol, 0.70 g) in isopropanol (8 mL), sodium hydroxide (7.0 mmol, 0.28g) in water (4mL) and zinc (3.06 mmol, 0.20 g) was added and stirred. The reaction was operated under 3 atm nitrogen atmosphere for overnight at 130 ºC and it was then allowed to cool to room temperature. The mixture was filtered off and washed with CH_2Cl_2. The filtrate was evaporated to give the residue which was dissolved in CH_2Cl_2 and then extracted with 2M HCl (2x20 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed to give the crude product, which was purified by column chromatography using 5% ethyl acetate in hexane as eluent. The *trans* isomers was separated and crystallized in CH_2Cl_2/CH_3OH mixture to give orange crystals.

trans-o-2 : ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 18 C($C\underline{H}_3)_3$), 1.20 (s, 18 C($C\underline{H}_3)_3$), 3.20 (d, 4 $Ar_2C\underline{H}_2$, J = 13.0), 4.15 (d, 4 $Ar_2C\underline{H}_2$, J = 13.0), 4.38 (br t, 4 O$C\underline{H}_2$), 4.84 (br t, 4 O$C\underline{H}_2$), 6.86 (s, 4 calix-Ar$\underline{H}$), 6.92 (s, 4 calix-Ar$\underline{H}$), 7.08 (d, 2 azobenzene-Ar$\underline{H}$, J = 6.0), 7.16 (d, 2 azobenzene-Ar$\underline{H}$, J = 8.0), 7.34 (t, 2 azobenzene-Ar$\underline{H}$, J = 6.0), 7.61 (s, 2 O$\underline{H}$), 7.70 (d, 2 azobenzene-Ar$\underline{H}$, J = 8.0) ; Anal. Calcd for $C_{60}H_{70}N_2O_6$: C, 78.74; H, 7.71; N, 3.06 Found: C, 77.21; H, 7.51, N 2.72 mp: 195-197 ºC (decomposed).

trans-m-2 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (s, 18 C($C\underline{H}_3)_3$), 1.28 (s, 18 C($C\underline{H}_3)_3$), 3.26 (d, 4 $Ar_2C\underline{H}_2$, J = 13.0), 4.38 (t, 4 O$C\underline{H}_2$, J = 5.0) , 4.34 (d, 4 $Ar_2C\underline{H}_2$, J = 13.0), 4.66 (t, 4 O$C\underline{H}_2$, J = 5.0) , 6.07 (s, 2 O$\underline{H}$) , 6.61 (s, 4 calix-Ar$\underline{H}$), 7.03 (s, 4 calix-Ar$\underline{H}$), 7.08 (d, 2 azobenzene-Ar$\underline{H}$, J = 8.0), 7.39 (t, 2 azobenzene-Ar$\underline{H}$, J = 8.0), 7.60 (d, 2 azobenzene-Ar$\underline{H}$, J = 8.0) , 8.19 (s, 2 azobenzene-Ar$\underline{H}$) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 30.9 (6 C($\underline{C}H_3)_3$), 31.2 (4 $Ar_2\underline{C}H_2$), 31.7 (6 C($\underline{C}H_3)_3$), 33.8 (2 $\underline{C}(CH_3)_3$), 33.8 (2 $\underline{C}$(CH3)3), 69.1 (2 O$\underline{C}H_2$), 74.4 (2 O$\underline{C}H_2$), 110.9 (2 azobnzene-Ar$\underline{C}$), 116.2 (2 azobnzene-Ar$\underline{C}$), 121.4 (2 azobnzene-Ar$\underline{C}$), 125.2 (4 calix-Ar$\underline{C}$), 125.5 (4 calix-Ar$\underline{C}$), 128.2 (4 calix-Ar$\underline{C}$), 129.8 (2 azobnzene-Ar$\underline{C}$), 131.7 (4 calix-Ar$\underline{C}$), 141.6 (2 calix-Ar$\underline{C}$), 146.7 (2 calix-Ar$\underline{C}$), 150.4 (2 calix-Ar$\underline{C}$), 150.7 (2 calix-Ar$\underline{C}$), 153.7 (2 azobnzene-Ar$\underline{C}$), 159.4 (2 stilbene-Ar$\underline{C}$); Anal. Calcd for $C_{60}H_{70}N_2O_6$: C, 78.74; H, 7.71; N, 3.06 Found: C, 78.41; H, 7.78, N 3.01 mp: 351-352ºC.

4.5. Complexation study

For the 1H NMR study, the studied calixarene derivative (10 mg) was dissolved in $CDCl_3$ (0.7 mL) in an NMR tube and the ^{1}H NMR spectrum was collected. Sodium or

potassium picrate (20 mg) was added as a solid into the solution. The mixture was sonicated for 1 hour before the spectrum was collected again. The color would turn to deep yellow and a singlet signal of the aromatic picrate proton could be observed around 9.0 ppm if complexation had taken place. If the signal was not observed by ^{1}H NMR, the results was confirmed by UV-Vis which was the cases for compounds **4** that the complexation was clearly observed in UV-Vis spectra but barely seen from the ^{1}H-NMR spectra.

4.6. Isomerization study

The studied compound was dissolved in $CDCl_3$ at 0.0060 molar and into an NMR tube. Using a Hanovia 450 W medium pressure murcury lamp equipped with a cooling jacket, the sample was irradiated at 30 cm away from the lamp for a specific period of time. The ^{1}H NMR was checked. Once the NMR spectra were unchanged, the *cis*:*trans* ratio of that specific analogue was determined by NMR integration of a selected signal.

5. Crystallographic data

5.1. *cis-o*-1

$C_{63}H_{74}Cl_2O_6$, Monoclinic, space group $P2_1/c$, a = 20.7486(5), b = 12.3713(4), c = 22.6335(5)Å, β = 109.373(2)°, U = 5480.8(3)Å^3, D_c = 1.210Mg m^{-3}, Z = 4, T = 120(2) K, colourless block, 0.24 x 0.18 x 0.12 mm^3. Data collection was carried out using a Bruker-Nonius KappaCCD area detector and SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement. 32983 reflections collected, 12074 independent [R(int) = 0.0700], giving R_1 = 0.0931 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and wR_2 = 0.3186 for all data. The max. and min. residual electron densities on the final difference Fourier map were 0.975 and –0.588eÅ^{-3}, respectively. The asymmetric unit contains a disordered molecule of dichloromethane and exhibits conformational disorder in one of the lower rim cage arms and rotational disorder in one of the tertiary butyl groups. Supplementary data have been deposited with the CCDC in CIF format with the deposition number CCDC249144.

5.2. *trans-o*-2

$C_{64}H_{78}N_2O_8$, Monoclinic, space group Cc, a = 15.1260(3), b = 31.1347(3), c = 12.6692(3)Å, β = 98.4970(10)°, U = 5900.99(19)Å^3, D_c = 1.129Mg m^{-3}, Z = 4, T = 293(2) K, dark-orange block, 0.60 x 0.30 x 0.30 mm^3. Data collection was carried out using a Bruker SmartCCD detector and SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement. 21046 reflections collected, 14604 independent [R(int) = 0.0190], giving R_1 = 0.0731 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and wR_2 = 0.1982 for all data. The max. and min. residual electron densities on the final difference Fourier map were 0.225 and –0.211eÅ^{-3}, respectively. Supplementary data have been deposited with the CCDC in CIF format with the deposition number CCDC137509.

5.3. *trans-m*-2

$C_{60}H_{70}N_2O_6$, Triclinic, space group P-1, a = 11.8283(3), b = 12.7292(4), c = 19.5738(8)Å, α = 82.2330(10)°, β = 74.9430(10)°, γ = 66.7110(10)°, U = 2612.32(15)Å^3, D_c = 1.163Mg m^{-3}, Z = 2, T = 120(2) K, dark-orange block, 0.40 x 0.20 x 0.15 mm^3. Data collection was carried out using a Bruker-Nonius KappaCCD area detector and SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement. 39735 reflections collected, 11605 independent [R(int) = 0.1407], giving R_1 = 0.0777 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and wR_2 = 0.2157 for all data. The max. and min. residual electron densities on the final difference Fourier map were 0.801 and –0.556eÅ^{-3}, respectively. Supplementary data have been deposited with the CCDC in CIF format with the deposition number CCDC249145.

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Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.

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