การสังเคราะห์บิสคาลิกซ์[4]เอรีน-คาลิกซ์[4]ไพร์โรลสำหรับเป็นตัวรับไอออนแพร์

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SYNTHESIS OF BIS-CALIX[4]ARENE-CALIX[4]PYRROLE AS ION PAIR RECEPTOR

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ได้ทำการสังเคราะห์บิสคาลิกซ์[4]เอรีน-คาลิกซ์[4]ไพร์โรล (**5**) คาลิกซ์[4]เอรีน-คาลิกซ์[4]ไพร์โรล (**9**) และพาราเทอร์เชียรี-บิวทิลคาลิกซ์[4]เอรีน-คาลิกซ์[4]ไพร์โรล (**10**) และ 1,3-อัลเทอร์เนท-คาลิกซ์[4]เอรีน-คาลิกซ์[4]ไพร์โรล-คราวน์-5 (**11**) สำหรับเป็นตัวรับไอออนแพร์ จากการหาโครงสร้างผลึกสาร **9** ด้วยเทคนิคเอกซ์เรย์พบว่า คาลิกซ์[4]เอรีนมีคอนฟอร์เมชันแบบโคน ส่วนคอนฟอร์เมชันของคาลิกซ์[4]ไพร์โรลเป็นแบบ 1,3-อัลเทอร์เนท การเกิดสารประกอบเชิงซ้อนของลิแกนด์ **9** และ **11** กับเกลือเตตระบิวทิลแอมโมเนียม และเกลือโพแทสเซียม ได้ศึกษาด้วยเทคนิคโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์ (เอ็นเอ็มอาร์) พบว่า ลิแกนด์ **9** จับฟลูออไรด์ได้ดีที่สุด ตามด้วยคลอไรด์ไอออน แต่ไม่เกิดสารประกอบเชิงซ้อนกับโพแทสเซียมไอออน โดยฟลูออไรด์ถูกคาลิกซ์[4]ไพร์โรลจับด้วยพันธะไฮโดรเจน ในการเกิดสารประกอบเชิงซ้อนนั้น คอนฟอร์เมชันของคาลิกซ์[4]ไพร์โรลเปลี่ยนจาก 1,3-อัลเทอร์เนทไปเป็นแบบโคน ส่วนลิแกนด์ **11** จับกับไอออนของโพแทสเซียมและฟลูออไรด์ โดยโพแทสเซียมจับกับลิแกนด์ **11** ภายในโพรงของคราวน์อีเธอร์ ในขณะที่ฟลูออไรด์ถูกจับด้วยหมู่คาลิกซ์[4]ไพร์โรล ลิแกนด์ **11** จึงจัดว่าเป็นตัวรับไอออนแพร์ ในการหาค่าคงที่การเกิดสารประกอบเชิงซ้อนของลิแกนด์ **11** กับฟลูออไรด์และคลอไรด์แอนไอออนด้วยเทคนิคโปรตรอนเอ็นเอ็มอาร์ไทเทรชัน พบว่าค่าคงที่ของการเกิดสารประกอบเชิงซ้อนเป็น 1721 และ 457 โมลาร์$^{-1}$ ตามลำดับ จากการศึกษาการเกิดสารประกอบเชิงซ้อนกับกับฟลูออไรด์ไอออนของลิแกนด์ **11** เมื่อมีโพแทสเซียมไอออนจับกับลิแกนด์อยู่ พบว่าฟลูออไรด์ไอออนถูกคาลิกซ์[4]ไพร์โรลจับไว้ด้านนอกโพรง (แบบเอกซ์โซ) แต่กรณีที่ลิแกนด์ **11** เกิดสารประกอบเชิงซ้อนกับโพแทสเซียมฟลูออไรด์ ฟลูออไรด์ไอออนเกิดสารประกอบเชิงซ้อนภายในโพรงและอยู่ใกล้กับคาลิกซ์[4]-ไพร์โรล (แบบเอนโด)

ภาควิชา เคมี.....	ลายมือชื่อนิสิต.....
สาขาวิชา เคมี.....	ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา 2547.....	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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Bis-calix[4]arene-calix[4]pyrrole (**5**), calix[4]arene-calix[4]pyrrole (**9**) and *p-tert*-butylcalix[4]arene-calix[4]pyrrole (**10**) and 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (**11**) were synthesized. Crystal structure of **9** was analyzed by X-ray crystallography which showed that calix[4]arene unit was in cone conformation while calix[4]pyrrole moiety was in 1,3-alternate form. Complexation studies of ligands **9** and **11** were carried out with tetrabutylammonium and potassium salts by ^{1}H-NMR spectroscopy. Ligand **9** formed complexes with high affinity to fluoride following by chloride ion, but could not bind potassium ion. Fluoride ion was bound to calix[4]pyrrole by using hydrogen bond. Upon complexation, the conformation of calix[4]pyrrole changed from 1,3-alternate to cone. Complexation studies of ligand **11** with potassium ion and fluoride ion was carried out which revealed that the potassium ion was bound to ligand **11** by the crown ether moiety whereas fluoride ion was complexed by calix[4]pyrrole. Thus, ligand **11** could act as an ion pair receptor. The stability constants of **11** with anions were determined by using ^{1}H-NMR titrations. It was found that the association constants of ligand **11** with fluoride and chloride ion were 1721 and 457 M^{-1}, respectively. The influence of potassium ion upon complexation of fluoride ion by ligand **11** was also studied. It was found that the fluoride ion was accommodated in an exo-fashion, whereas in the case of KF salt, fluoride was encapsulated inside cavity nearby calix[4]pyrrole unit (endo-fashion).

Department……Chemistry……..	Student's signature…….
Field of study……Chemistry……	Advisor's signature……
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Å	Angstrom
Bu_4NBr	Tetrabutylammonium bromide
Bu_4NCl	Tetrabutylammonium chloride
Bu_4NF	Tetrabutylammonium fluoride
Bu_4NI	Tetrabutylammonium iodide
°C	Degree Celcius
δ	Chemical shift
equiv.	Equivalent
g	Gram
^{1}H-NMR	Proton Nuclear Magnetic Resonance
Hz	Hertz
IR	Infared spectroscopy
J	Coupling constant
K	Kelvin
K_a	Association constant
λ	wavelength
M	Molar
MALDI-TOF	Matrix Assistance Laser Desorption/Ionization-Time of Flight
mL	Milliliter
mmol	Millimole
ppm	Part per million
RT	Room temperature
s, d, t, m	Splitting patterns of ^{1}H-NMR (singlet, doublet, triplet and multiplet)
TFA	Trifluoro acetic acid
TsCl	Toluene-4-sulfonyl chloride

CHAPTER I

INTRODUCTION

1.1 Supramolecular Chemistry

Supramolecular chemistry is one of the most popular and fastest growing areas of experimental chemistry and it seems to remain that way for the foreseeable future.[1] For many years, chemists have synthesized molecules and investigated their physical and chemical properties. The field of *supramolecular chemistry*, however, has been defined as 'chemistry beyond the molecule', and involves investigation of new molecular systems.[2] The components are held together by *intermolecular forces, not by covalent bonds*. Chemists working in this area can be thought of as architects combining individual covalently bonded molecular building blocks, designed to be held together by intermolecular forces, in order to create functional architectures. Alternatively, supramolecular chemistry is known as host-guest chemistry. The definition of supramolecular chemistry is depicted in the Figure 1.1.

Molecular Chemistry → **Supramolecular Chemistry**

Covalent bond formation ***Non-covalent bond formation***

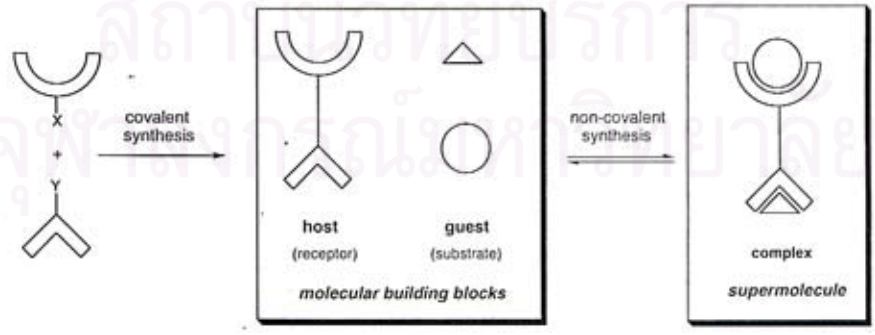


Figure 1.1 Supramolecular chemistry.[2]

Supramolecular chemistry is a highly *interdisciplinary* field of science covering the chemical, physical, and biological features of greater complexity than molecules themselves. This introduction describes a generalized approach to supramolecular science and provides an indication of the wide ranging interests of chemists working in this area. Biological systems often provide inspiration, whereas organic and inorganic chemistry are required for the synthesis of the pre-designed supramolecular components, and physical chemistry is used to fully understand their properties. Finally, a degree of technical expertise can lead to functioning devices ready for application to the real world.

In the complexation of supramolecular molecules, the glue used by supramolecular chemists to hold molecules together is non-covalent, and there are a number of such interactions that can be utilized. They include:

(i) electrostatics (ion-ion, ion-dipole and dipole-dipole);

(ii) hydrogen bonding;

(iii) π-π stacking interactions;

(iv) dispersion and induction forces (van der Waals forces);

(v) hydrophobic or solvatophobic effects.

1.2 Cation Receptors

Recognition of cation is one of the most interesting subjects in recent years. Due to various metal ions belong to metalloenzymes or it is well known that some heavy metal ions are toxic for organism, and early detection in the environment is desirable.[3]

Some of many applications of cationic receptors are to get rid of metallic pollutants in the environment and to study a metal ion playing an important role in living systems. Over the last two decades, the search for new material as chemical receptor for metal ion has been an area of rapid development. Many molecular platforms such as crown ethers[4,5], cryptands[6], cyclodextrins[7], porphyrin[8] and calixarenes[9] are used to construct well-defined structures. Especially, attention has been paid on calixarene since it has binding ability toward alkaline and alkali earth metal ions that play various important roles in biochemistry and environmental science.

1.2.1 Calixarenes

Calixarenes are cavity-shaped cyclic molecules obtained from the base-catalyzed condensation of *p-tert*-butylphenol and formaldehyde. Among calixarenes, calix[4]arene is the most interesting platform due to its ease of synthesis, functionalization, its conformations and its promise as selective complexation agents in sensors. The "beaker like shape" of calix[4]arene ("calic" means vase in Greek) can behave as platform for inclusion of guest molecule due to their flexible cavities.[10-12]

In solution, calix[4]arene exists in 4 conformations calls cone, partial cone, 1,2-alternate, and 1,3-alternate (see Figure 1.2). Each of them has its own specific properties and characteristic utilization in host-guest chemistry. Calix[4]arene is a very attractive compound that can be used as a platform for designing more sophisticated structure for binding ions and neutral molecules. [10-13]

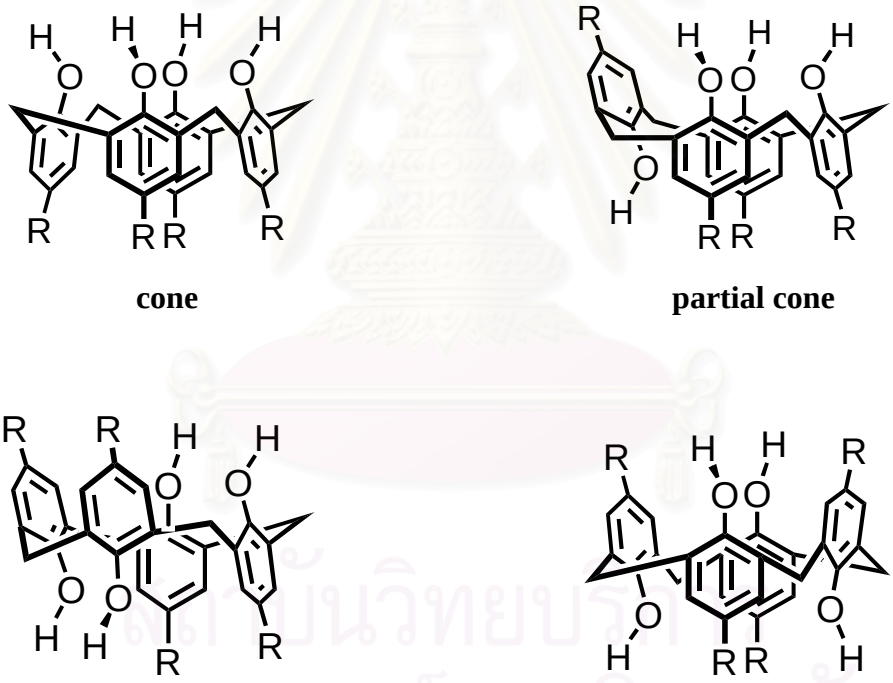


Figure 1.2 Conformations adopted by calix[4]arene.

Calix[4]arene can be fixed in one conformation when complexed with ions or neutral molecules and restricted the flipping motion of the benzene ring by functionalization with the groups bulkier than ethoxy groups at lower rim (at hydroxy positions) or bridge each benzene ring intramolecularly or intermolecularly.[14]

1.2.1.1 Calixarenes as cation binding agents

Calixarenes have been widely used in the last two decades as the building blocks for constructing the host molecules in supramolecular chemistry. When properly functionalized, calixarenes can also form complexes with cationic guest species.

An example of a cation included in a calixarene cavity is shown in Figure 1.3a, in which a caesium cation is held in the cavity of *p-tert*-butylcalix[4]arene *via* π-cation interactions (a molecule of acetonitrile is also coordinated to the metal cation). These π-cation interactions are believed to arise from favorable electrostatic interactions between the electron deficient cation and the electron rich aromatic ring. (2)

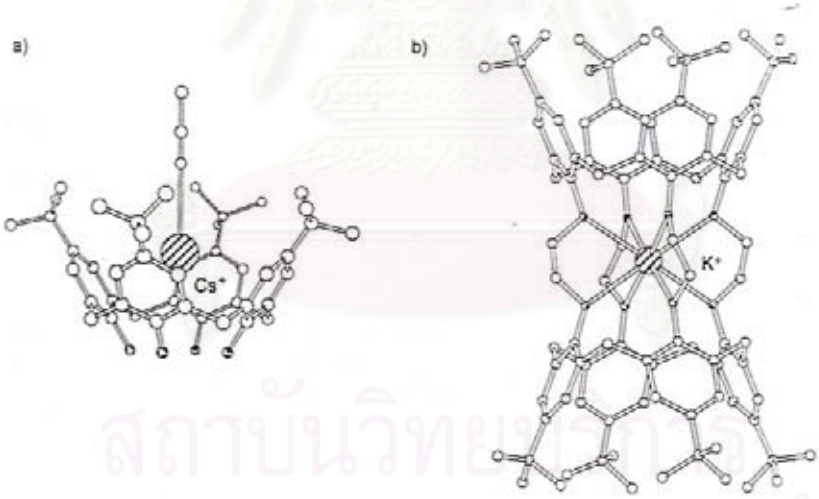


Figure 1.3 (a) A caesium cation bound in the cavity of *p-tert*-butylcalix[4]arene (with an acetonitrile molecule)[(2)] and (b) the structure of calix[4]tube-potassium complex.[(12)]

This π-cation interaction has also been used to produce a model for the selection filter present in potassium channel proteins. Calix[4]tube (Figure 1.3b) is a bis-calix[4]arene linked lower rim to lower rim *via* four ethylene bridges. Potassium cations pass through the calixarene cavity and are bound by the eight phenolic oxygens in the middle of the tube (Figure 1.4). Uptake of other group I metal cations by the tube is insignificant. [15]

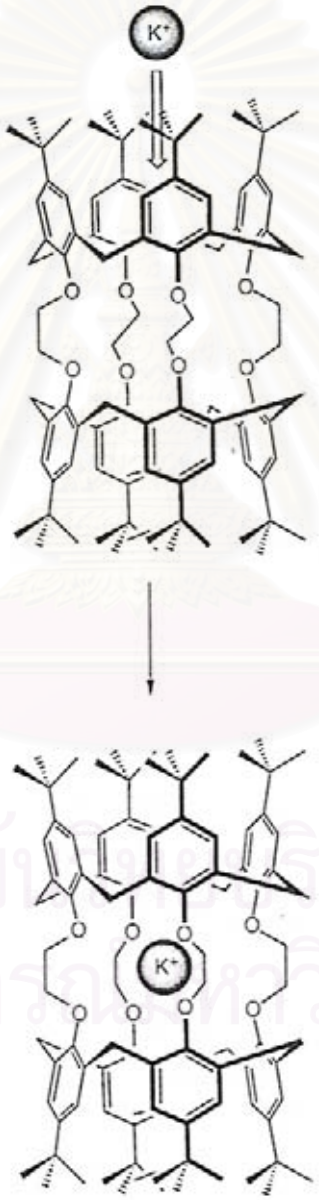


Figure 1.4 Potassium encapsulation in calix[4]tube.

1.3 Anion Receptors

The synthesis of anion receptors possessing high affinity and adequate selectivity for various targeted substrates represents an ongoing challenge in the area of supramolecular chemistry. Anion recognition is often affected by hydrogen-bonding interactions. Such interactions are weak and this is one of the reasons that anion recognition is more challenging to achieve than cation complexation.[16-17] Appreciated as being more difficult to achieve than cation recognition, this challenge continues to attract the attention of the researchers within the molecular recognition community due to the important role anions play in various biological as well as environmental systems.

Compared to relatively well-developed cation receptors[18], development of anion receptors is only emerging as a research area of significant importance.[19] The slow development of anion recognition can be related to some inherent differences between anions and cations.[20]

i) Anions are relatively large and therefore require (macrocyclic) receptors with a much larger binding site. The smallest anions, F^-, has the same ionic radius (1.33 Å) as a moderate size cation (K^+).

ii) Anions have many different shapes, e.g., spherical halides, linear SCN^-, trigonal planar NO_3^-, and tetrahedral $H_2PO_4^-$.

iii) Anions are more strongly hydrated than cations of equal size, whereas the solvation by organic solvents is generally less favorable.

iv) Several anions are presented only in a narrow pH window, e.g., $H_2PO_4^-$, and CO_3^{2-} anions in acidic and basic environment, respectively.

1.3.1 Calix[4]pyrrole

Among the various neutral anion receptors described in many literatures, calix[4]pyrroles[21], which are readily accessible from pyrrole and ketone, have been identified as one of the most attractive hosts for the binding of halide anions, especially for fluoride ions.[22-24] The crystal structure of the free macrocycle has a 1,3-alternate conformation with alternating pyrrole rings oriented ‘up’ and ‘down’ (Figure 1.6a). On binding a halide anion, however, crystallographic and NMR

spectroscopic experiments indicated that the pyrrole rings allign with all four N-H groups convergent, forming hydrogen bonds with the bound guest (Fig. 1.6 b).

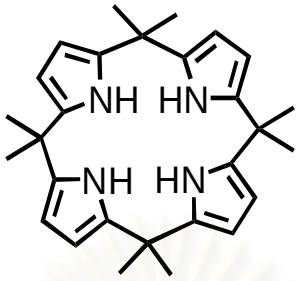
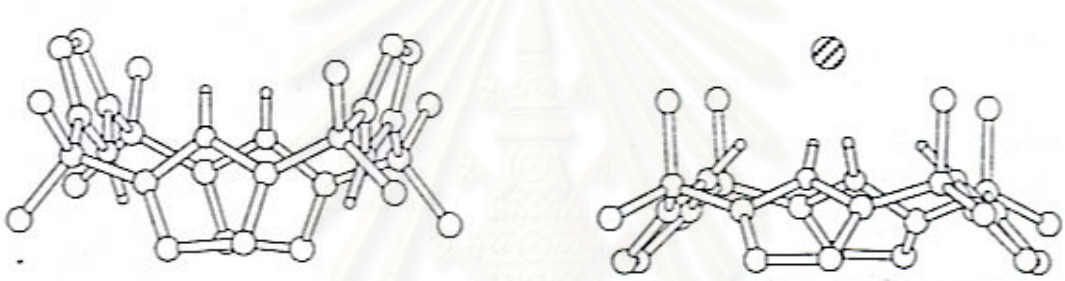


Figure 1.5 *meso*-octamethylcalix[4]pyrrole.



(a) **(b)**

Figure 1.6 Crystal of (a) free *meso*-octamethylcalix[4]pyrrole and (b) *meso*-octamethylcalix[4]pyrrole with a bound chloride anion perched above the macrocyclic plane.

Since their anion recognition characteristics were first reported by Sessler et al. in 1996,[23-29] various modifications have been made in an effort to tune the binding characteristics of the parent, acetone-derived system.

In 2002, the first example of a new class of calix[4]pyrrole bearing *trans*-substituted straps on one side of the molecule has been reported.[30] The conformation of calix[4]pyrrole bearing diester bridged strapped system is close to the asymmetric 1,3-alternate form. The strapping at the calixpyrrole increases its anion binding affinity significantly, especially for chloride anion. Its inner aromatic protons form a stronger hydrogen–binding interaction with chloride ion than fluoride ion. These

support the contention that a better match of the size between the chloride ion and the binding site defined by the presence of the strap.

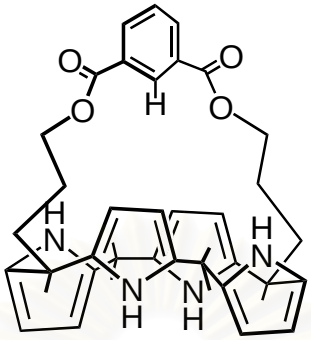
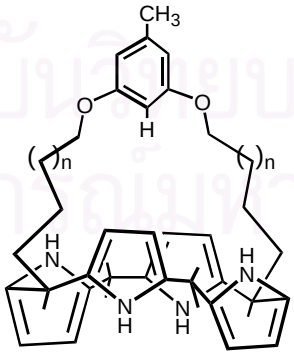


Figure 1.7 Molecular structure of the strapped calix[4]pyrrole.

A year later, three calix[4]pyrroles bearing *m*-orcinol-derived diether straps of different lengths on one side of the tetrapyrrolic core have been synthesized and characterized.[31] In its complexation studies, the largest chloride affinity was seen with the shortest strap, whereas the largest affinity for bromide anion was recorded in the case of the largest strap. Moreover, by ^{1}H NMR spectroscopic studies, it was postulated that not only cavity size per se, but also the ability of the aryl portion of the strap to serve as a CH hydrogen bond donor site are important in regulating the observed anion affinities.



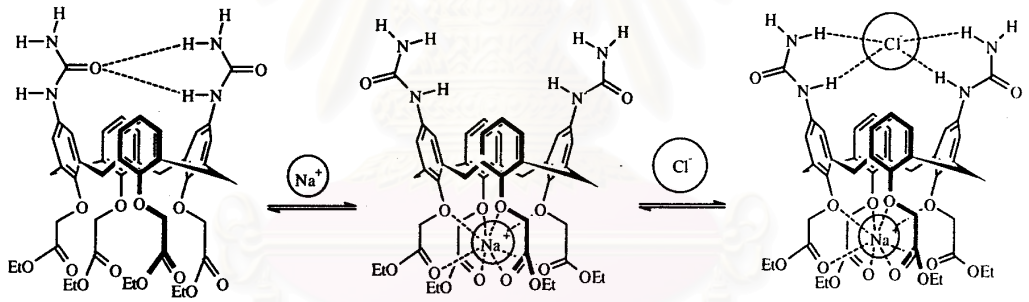
(n = 1, 2, 3)

Figure 1.8 Calixpyrroles bearing diether straps of different length.

1.4 Bifunctional receptors

Ligands which simultaneously bind cations and anions have been a topic of current interest in supramolecular chemistry. Ditopic receptors have been prepared by attaching both cation and anion binding sites on a core molecule, either a rigid framework or a non-rigid one.

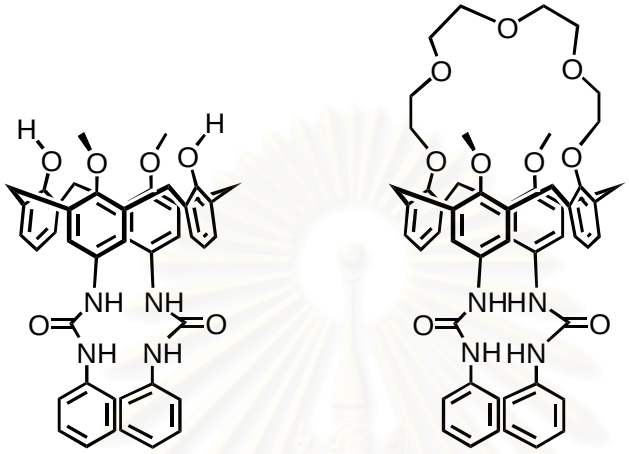
Reinhoudt and coworkers[2] have synthesized a receptor that consists of a calix[4]arene with cation binding ester groups at the lower rim and anion binding ureas groups at the upper rim. This receptor displays a very elegant ion-pair binding. In the chloroform solution, the two urea groups are hydrogen bonded together and so are not available for hydrogen bonding to any putative anionic guest species. However, when sodium cations are added, they bind the ester groups of the calixarene, causing the lower rim to contract. This force apart the urea groups at the upper rim apart which are then available for binding anionic species such as chloride anion (Figure 1.9).



A **A-Na$^+$** **A-Na$^+$-Cl$^-$**

Figure 1.9 Anion and cation coorperative binding in receptor **A**.

In 2003, Pan Tongraung and coworkers,[32] had synthesized calixarenes containing urea and crown/urea moieties **(a)** and **(b)**. It was showed that **(a)** and **(b)** formed complexes with $H_2PO_4^- > Cl^- > Br^- > NO_3^-$. However, upon addition of Na^+, compared with the former Bu_4N^+, the binding ability of **(b)** towards $H_2PO_4^-$ was increased due to ion-pair enhancement.

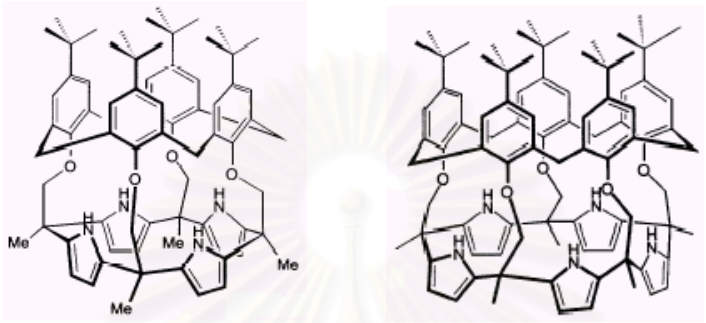


(a) **(b)**

Figure 1.10 Calixarene containing (a) urea and (b) crown urea moieties as bifunctional receptor.

In 1996, the first calix[4]arene-capped calix[4]pyrrole, calix[4]arene-calix[4]pyrrole pseudo dimer (Figure 1.11), was obtained as the result of a template mediated condensation between a keto-functionalized calixarene and pyrrole by Sessler and co-workers.[33] From its ^{1}H-NMR spectroscopic studies, this receptor contained a strong hydrogen bonding between the pyrrole NH groups and the calixarene oxygen atoms. Addition of tetrabutylammonium fluoride to the ligand solution caused no changes on the ^{1}H-NMR spectrum.

A year later, the same group[34] has achieved the first synthesis of the expanded calix[n]pyrrole, n=5. In its complexation studies with tetrabutylammomnium chloride, the calix[5]arene-calix[5]pyrrole shows a small downfield shift in the NH proton caused by weaker internal hydrogen bonding array compared with its corresponding tetrameric dimer.



(a) **(b)**

Figure 1.11 Molecular structures of calix[n]arene-calix[n]pyrrole pseudo dimer (a) n=4, (b) n=5.

In 1995, Reinhoudt[35] has reported the synthesis and complexation of large metalloreceptor (Figure 1.12) in which the active Zn-pophyrin core was covalently incorporated into a bis-calix[4]arene cavity, providing both effective shielding and encapsulation of a substrate from the environment. He has demonstrated that doubly calix[4]arene capped porphyrin was an excellent receptor for different aza-heterocycles, in addition to shielding due to the ideal combination of the properties of both building blocks.

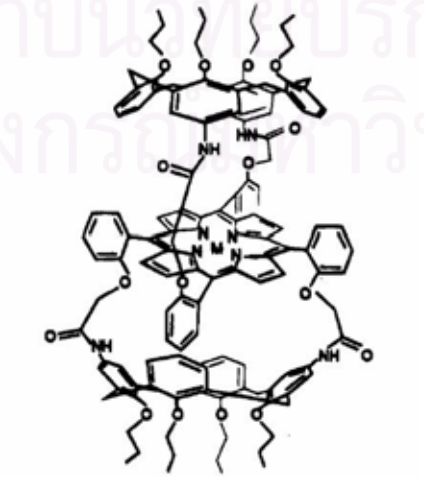


Figure 1.12 Molecular structure of bis-calix[4]arene-Zn-porphyrin.

Objectives and scope of the research

Our approach to the construction of large receptor structures is based on the proper covalent combination of different, readily available supramolecular building blocks (i.e. calixarenes, calixpyrrole) in one molecule.

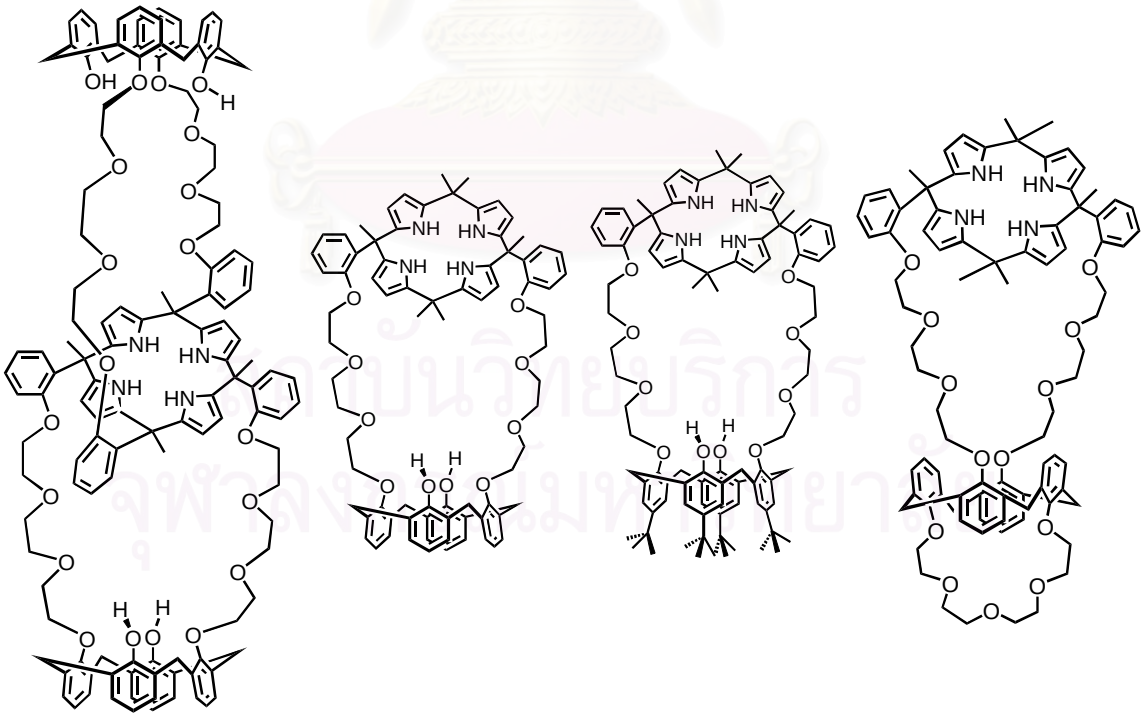
The targets of this work are to synthesize bifunctional receptor, bis(calix[4]arene)-calix[4]pyrrole **5**, and study its complexation properties.

Moreover, this work also described two more main topics:

i) The synthesis of calix[4]arene-calix[4]pyrrole **9**, *p-tert*-butylcalix[4]arene-calix[4]pyrrole **10** and 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 **11**.

ii) The binding abilities of these compounds, **9** and **11**, were investigated by ^{1}H-NMR spectroscopy.

The target molecules were shown below.



5 **9** **10** **11**

Figure 1.13 Target molecules.

CHAPTER II

EXPERIMENTAL SECTION

2.1 General Procedures

2.1.1 Analytical Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 MHz nuclear magnetic resonance spectrometer. In all cases, sample were dissolved in deuterated chloroform and chemical shifts were recorded in part per million (ppm) using a residual proton or carbon signals in deuterated solvents as internal reference. Elemental analysis were carried out on a CHNS/O analyzer (Perkin Elmer PE2400 series II). MALDI-TOF Mass spectra were recorded on a Biflex Bruker Mass spectrometer. Infrared spectra were obtained on a Nicolet Impact 410 using KBr pellet.

2.1.2 Materials

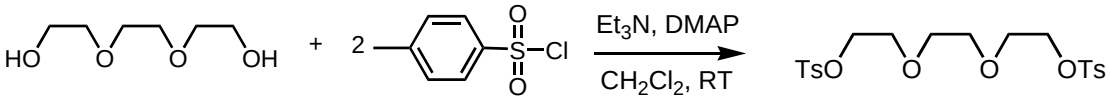
All materials were standard analytical grade, purchased from Fluka, Aldrich or Merck and used without further purification. Commercial grade solvents such as acetone, hexane, dichloromethane, methanol and ethyl acetate were distilled before used. Acetonitrile was dried over CaH_2 and freshy distilled under nitrogen prior to use.

Column chromatography was carried out using silica gel (Kieselgel 60, 0.063-0.200 mm, Merck). Thin layer chromatography (TLC) was performed on silica gel plates (Kieselgel 60 F_{254}, 1 mm, Merck).

Starting materials such as *p-tert*-butylcalix[4]arene were prepared according to the literature procedure.[36] The compounds were characterized by ^{1}H-NMR spectroscopy, infrared spectroscopy, mass spectroscopy and elemental analysis.

2.2 Synthesis

2.2.1 Preparation of triethyleneglycol ditosylate (1)

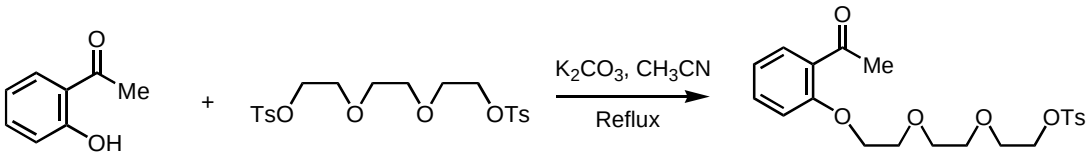


1

Into a 250 mL two-necked round bottom flask, a solution of triethyleneglycol (3 g, 28 mmol), triethylamine (11.8 mL, 85 mmol) and a catalytic amount of DMAP in 50 mL of dichloromethane was chilled to 0 ^{o}C with an ice bath. The solution of tosylchloride (11.86 g, 62 mmol) in dichloromethane (100 mL) was then added dropwise. The reaction mixture was stirred for 4 hours at room temperature under nitrogen atmosphere. After the reaction was completed, the solution of 3 M hydrochloric acid was added until the pH of the solution reached to 1 and then extracted with dichloromethane (2x50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane and methanol was added to precipitate a white solid (7.66 g, 65% yield).

Characteristic data for (1): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.77 (d, $J_{H\text{-}H}$ = 8.2 Hz, 4H, SO_2*o*-Ar**H**), 7.32 (d, $J_{H\text{-}H}$ = 8.2 Hz, 4H, SO_2*m*-Ar**H**), 4.10 (t, $J_{H\text{-}H}$ = 4.7 Hz, 4H, OC**H**$_2$CH$_2$OCH$_2$), 3.60 (t, $J_{H\text{-}H}$ = 4.7 Hz, 4H, OCH$_2$C**H**$_2$OCH$_2$), 3.50 (s, 4H, OCH$_2$CH$_2$OC**H**$_2$), 2.42 (s, 6H, Ar-C**H**$_3$); **IR spectrum (KBr pellet (cm^{-1}))**: 2800-3000 (CH, st), 1150-1200 (C-O-C, st)

2.2.2 Preparation of 2-(8-tosyltriethyleneglycol)acetophenone (2)



1 **2**

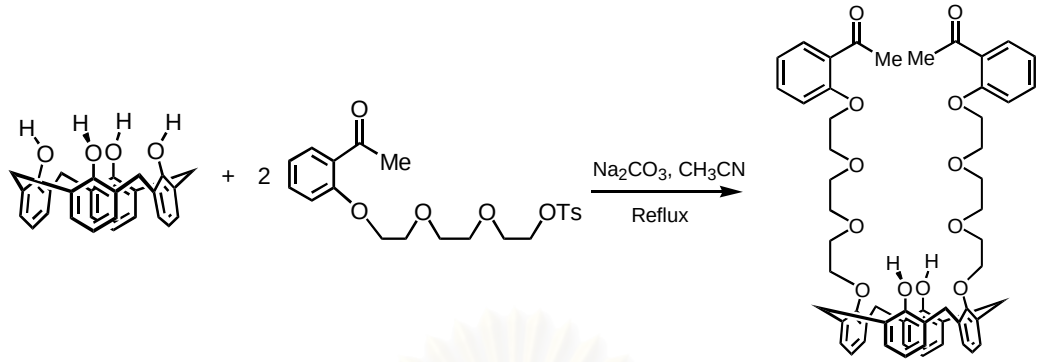
Into a 250 mL two-necked round bottom flask, 2-hydroxy acetophenone (1.36 g, 10.0 mmol) and K_2CO_3 (13.82 g, 100 mmol) were suspended in dried acetonitrile (50 mL). The mixture was stirred at room temperature under nitrogen atmosphere for 1 hour. A solution of triethyleneglycol ditosylate (**1**) (9.16 g, 20.0 mmol) in dried acetonitrile (100 mL) was then added dropwise. The reaction mixture was stirred and refluxed under nitrogen atmosphere for 18 hours. After the reaction was completed by TLC result, the solution was allowed to cool to room temperature. The solvent was then evaporated. The obtained residue was dissolved in dichloromethane (100 mL) and extracted with 3 M HCl (1x100 mL) and water (2x100 mL), respectively. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered off to give a yellow oil. Compound **2** was purified by column chromatography (silica gel, CH_2Cl_2 : EtOAc; 90:10) and obtained as a colorless oil (2.53 g, 30%).

Characteristic data for (2): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.82 (d, $J_{H\text{-}H}$ = 4 Hz, 2H, Ar_{tosyl}**H**), 7.77 (dd, $J_{H\text{-}H}$ = 1.6, 8.0 Hz, 1H, Ar**H**), 7.47 (t, $J_{H\text{-}H}$ = 2.0, 8.0 Hz, 1H, Ar**H**), 7.36 (d, $J_{H\text{-}H}$ = 4 Hz, 2H, Ar_{tosyl}**H**), 7.03 (t, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar**H**), 6.98 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar**H**), 4.25 (t, $J_{H\text{-}H}$ = 4.8 Hz, 2H, $SO_2OC\mathbf{H}_2$), 4.18 (t, $J_{H\text{-}H}$ = 4.8 Hz, 2H, $ArOC\mathbf{H}_2$), 3.91 (t, $J_{H\text{-}H}$ = 4.8 Hz, 2H, $C\mathbf{H}_2O$), 3.73-3.64 (m, 6H, $C\mathbf{H}_2O$), 2.66 (s, 3H, $COC\mathbf{H}_3$), 2.46 (s, 3H, $ArC\mathbf{H}_3$),

Elemental analysis: *Anal calcd* for $C_{21}H_{26}O_7S$: C, 59.70%; H, 6.20%

Found: C, 59.78%; H, 6.29%

2.2.3 Preparation of 1,3-calix[4]-diacetophenone (3)

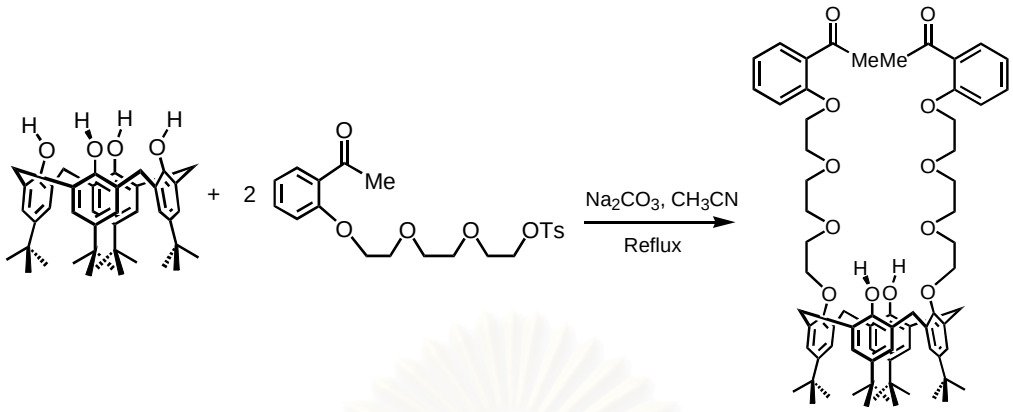


2 **3**

Into a 250 mL two-necked round bottom flask containing calix[4]arene (2.40 g, 5.66 mmol), Na_2CO_3 (6.00 g, 56.64 mmol) and acetonitrile (50 mL), a solution of 2-(triethyleneglycol tosylate) acetophenone (**2**) (4.78 g, 11.33 mmol) in acetonitrile (100 mL) was added dropwise. The reaction mixture was refluxed with stirring under nitrogen atmosphere for 7 days. After cooling to room temperature, the solvent was removed under reduced pressure to give a yellow oil. The residue was dissolved in dichloromethane (100 mL) and extracted with 3 M HCl (1x100 mL) and water (2x100 mL), respectively. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered off. The residue was dissolved in a minimum amount of dichloromethane and methanol was added to precipitate 1,3-calix[4]-diacetophenone (**3**) as a white solid (4.47 g, 85%).

Characteristic data for (3): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.78 (d, $J_{H\text{-}H}$ = 2.0 Hz, 2H, Ar**H**$COCH_3$), 7.54 (s, 2H, ArO**H**), 7.45 (dt, $J_{H\text{-}H}$ = 8.0, 2.0 Hz, 2H, Ar**H**$COCH_3$), 7.07 (d, $J_{H\text{-}H}$ = 7.6 Hz, 4H, Ar**H**OCH_2), 7.02 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, Ar**H**$COCH_3$), 6.89 (d, $J_{H\text{-}H}$ = 7.6 Hz, 4H, Ar**H**OH), 6.86 (d, $J_{H\text{-}H}$ = 8.8 Hz, 2H, Ar**H**$COCH_3$), 6.75 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, Ar**H**OCH_2), 6.67 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, Ar**H**OH), 4.43 (d, $J_{H\text{-}H}$ = 13.0 Hz, 4H, ArC**H**$_2$Ar), 4.19 (t, $J_{H\text{-}H}$ = 4.2 Hz, 4H, OC**H**$_2$), 4.08 (t, $J_{H\text{-}H}$ = 4.2 Hz, 4H, OC**H**$_2$), 3.99 (t, $J_{H\text{-}H}$ = 4.2 Hz, 4H, OC**H**$_2$), 3.90-3.89 (m, 8H, OC**H**$_2$), 3.78-3.82 (m, 4H, OC**H**$_2$), 3.36 (d, =13.0 Hz, 4H, ArC**H**$_2$Ar), 2.67 (s, 6H, ArCOC**H**$_3$); **IR spectrum (KBr, (cm^{-1}))**: 3379 (OH, st), 3024 (=C-H, st), 2916, 2875 (-C-H, st), 1674 (C=O, st), 1597, 1453, 1360 (C=C, st (aromatic)), 1242,1114 (C-C(O)-C, st), 1042 (O-C-C, st); **Elemental analysis:** *Anal calcd* for $C_{56}H_{60}O_{12}$: C, 72.71%; H, 6.54% *Found*: C, 71.72%; H, 6.41%

2.2.4 Preparation of 1,3-*p*-*tert*-butylcalix[4]-diacetophenone (4)

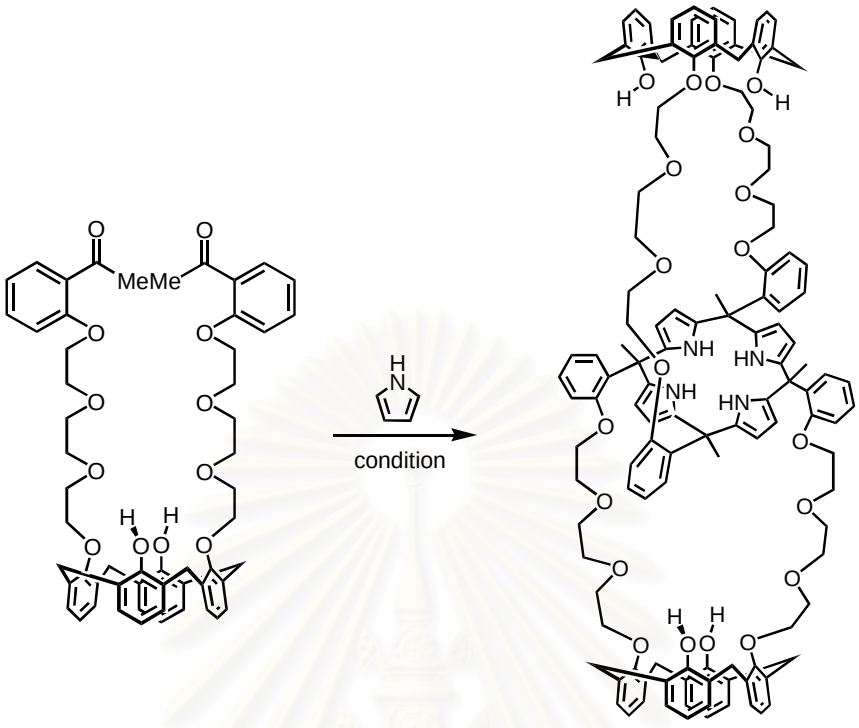


2 **4**

Into a 250 mL two-necked round bottom flask containing *p*-*tert*-calix[4]arene (1.15 g, 1.78 mmol), Na_2CO_3 (1.88 g, 17.77 mmol) and acetonitrile (100 mL), a solution of 2-(triethyleneglycol tosylate) acetophenone (**2**) (1.50 g, 3.55 mmol) in acetonitrile (100 mL) was added dropwise. The reaction mixture was refluxed with stirring under nitrogen atmosphere for 7 days. After cooling to room temperature, the solvent was removed under reduced pressure to give a yellow oil. The residue was dissolved in dichloromethane (100 mL) and extracted with 3 M HCl (1x100 mL) and water (2x100 mL), respectively. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered off. The residue was separated by column chromatography (silica gel, CH_2Cl_2 : acetone = 98 : 2) and 1,3-*p*-*tert*-butylcalix[4]-diacetophenone (**4**) was obtained as a colorless viscous oil (1.28 g, 63%).

Characteristic data for (4): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.77 (dd, $J_{H\text{-}H}$ = 7.6, 1.6 Hz, 2H, Ar**H**$COCH_3$), 7.44 (dt, $J_{H\text{-}H}$ = 8.0, 1.6 Hz, 2H, Ar**H**$COCH_3$), 7.26 (s, 2H, ArO**H**), 7.08 (s, 4H, Ar**H**OCH_2), 7.01 (t, $J_{H\text{-}H}$ = 7.2 Hz, 2H, Ar**H**$COCH_3$), 6.87 (d, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar**H**$COCH_3$), 6.80 (s, 4H, Ar**H**OH), 4.39 (d, $J_{H\text{-}H}$ = 13.0 Hz, 4H, Ar$C\mathbf{H}_2$Ar), 4.17 (t, $J_{H\text{-}H}$ = 4.0 Hz, 4H, O$C\mathbf{H}_2$), 4.10 (t, $J_{H\text{-}H}$ = 4.2 Hz, 4H, O$C\mathbf{H}_2$), 3.96 (t, $J_{H\text{-}H}$ = 4.2 Hz, 4H, O$C\mathbf{H}_2$), 3.91 (t, $J_{H\text{-}H}$ = 4.6 Hz 4H, O$C\mathbf{H}_2$), 3.84-3.88 (m, 4H, O$C\mathbf{H}_2$), 3.78-3.82 (m, 4H, O$C\mathbf{H}_2$), 3.30 (d, =13.0 Hz, 4H, Ar$C\mathbf{H}_2$Ar), 2.68 (s, 6H, ArCO$C\mathbf{H}_3$), 1.31 (s, 18H, Ar-*t*-$C_4\mathbf{H}_9$), 0.98 (s, 18H, Ar-*t*-$C_4\mathbf{H}_9$)

2.2.5 Synthesis of bis(calix[4]arene)-calix[4]pyrrole (5)

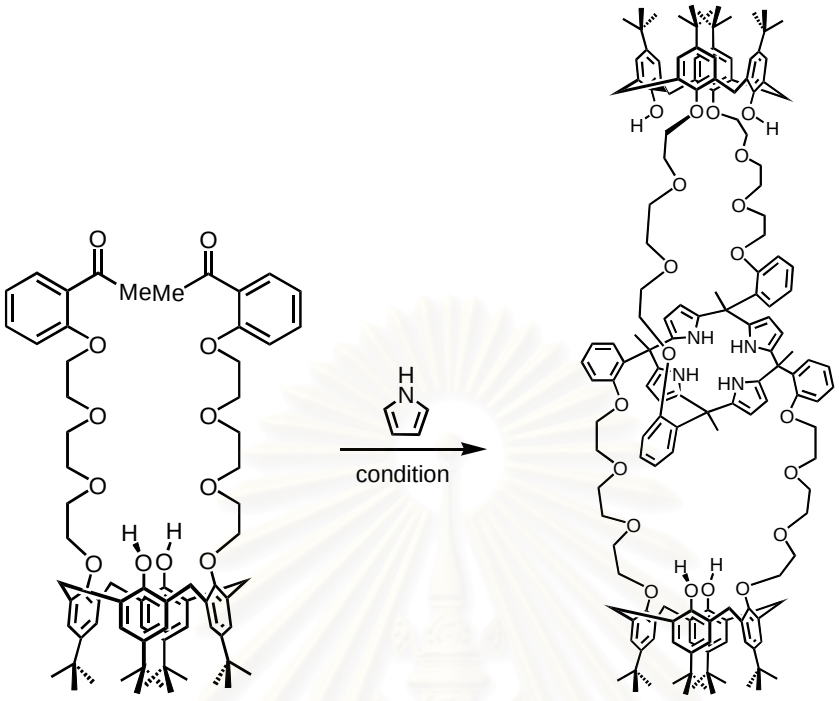


3 **5**

Conditions	Reagents and solvents	Temperature
i	$BF_3.OEt_2$, CH_2Cl_2	RT
ii	Propionic acid, NaCl, toluene	Reflux
iii	$BF_3.OEt_2$, CH_2Cl_2, $Zn(OAc)_2.2H_2O$	RT

In a 100 mL two-necked round bottom flask, 1,3-calix[4]-diacetophenone (**3**) (0.93 g, 1 mmol) and pyrrole (0.05 mL, 1 mmol), salt (NaCl in condition ii and $Zn(OAc)_2.2H_2O$ in condition iii), the acid catalysts ($BF_3.OEt_2$ in condition i and ii or propionic acid in condition iii) and the solvent 50 mL (as indicated in reaction conditions) was degassed by bubbling with nitrogen for 15 min. The solution was allowed to stir for 24 hours at conditions indicated temperature. After the reaction was complete, the reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with 0.1 M aqueous $NaHCO_3$ (2 x 100 mL) and water (2 x 100 mL), respectively. The combined organic layer were dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure. The residue was purified by column chromatography over silica gel (CH_2Cl_2: EtOAc = 95 : 5). The compound in each fraction was characterized by ^{1}H-NMR spectroscopy. The desired product (**5**) was not obtained.

2.2.6 Synthesis of bis(*p-tert*-butylcalix[4]arene)-calix[4]pyrrole (6)

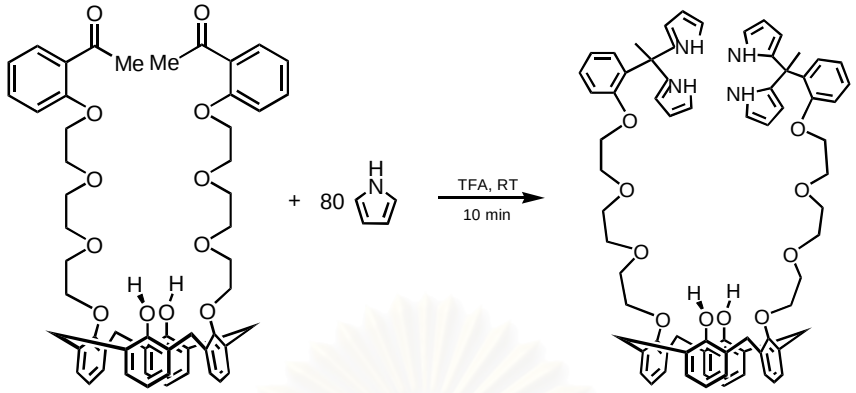


4 **6**

Conditions	Reagents and solvents	Temperature
i	TFA, CH_2Cl_2	RT
ii	Methanesulfonic acid, CH_2Cl_2	RT

In a 100 mL two-necked round bottom flask, a solution of *p-tert*-butylcalix[4]-diacetophenone (**4**) (1.15 g, 1 mmol) and pyrrole (0.05 mL, 1 mmol), the acid catalysts (TFA in condition i and methanesulfonic acid in condition ii) and the solvent 50 mL (as indicated in reaction conditions) was degassed by bubbling with nitrogen for 15 min. The solution was allowed to stir for 24 hours at conditions indicated temperature. After the reaction was complete, the reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with 0.1 M aqueous $NaHCO_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (CH_2Cl_2: EtOAc = 90 : 10). The compound in each fraction was characterized by ^{1}H-NMR spectroscopy. The desired product (**6**) was not obtained.

2.2.7 Preparation of 1,3-calix[4]-bis-dipyrroethane (7)



3 **7**

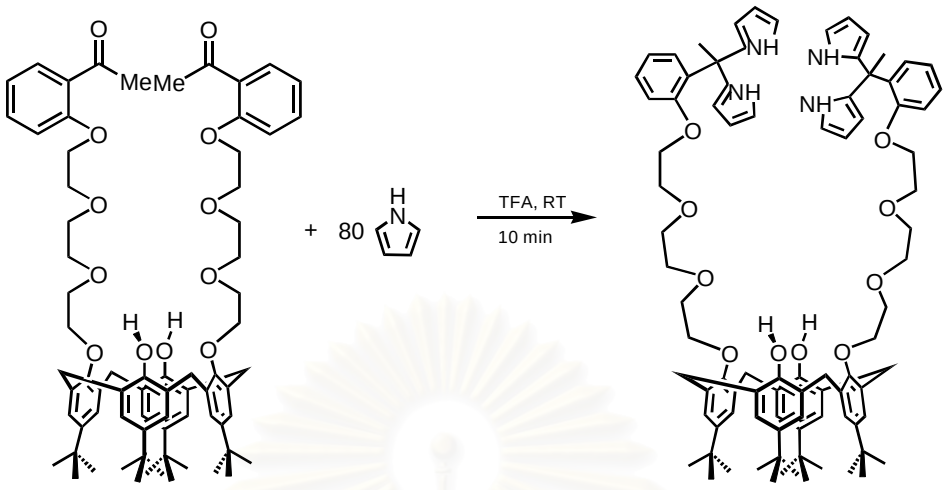
In a 100 mL two-necked round bottom flask, a solution of calix[4]-diacetophenone (**3**) (4.23 g, 4.57 mmol) in pyrrole (25.36 mL, 365.46 mmol) was degassed by bubbling with nitrogen for 15 min, and then CF_3COOH (0.07 mL, 0.91 mmol) was added. The solution was stirred for 10 min at room temperature. Then the reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with 0.1 M aqueous $NaHCO_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The obtained residue was purified by column chromatography over silica gel (CH_2Cl_2:EtOAc:NEt_3 = 95:5:1) to give 3.22 g of the 1,3-calix[4]-bis-dipyrroethane (**7**) as a tacky white solid with light brown splotches (61% yield).

Characteristic data for (7): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 8.86 (s, 4H, N**H**), 7.74 (s, 2H, ArO**H**), 7.32 (m, 2H, Ar**H**$COCH_3$), 7.22 (m, 2H, Ar**H**$COCH_3$), 7.10 (d, $J_{H\text{-}H}$ = 7.6 Hz, 4H, Ar**H**OCH_2), 6.95 (t, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar**H**$COCH_3$), 6.90 (d, $J_{H\text{-}H}$ = 8.0 Hz, 4H, Ar**H**OH), 6.75 (t, $J_{H\text{-}H}$ = 7.6 Hz, 2H, Ar**H**$COCH_3$), 6.71 (t, $J_{H\text{-}H}$ = 7.6 Hz, 4H, Ar**H**OCH_2), 6.60-6.64 (m, 4H, pyrrole-**H**), 6.09-6.13 (m, 4H, pyrrole-**H**), 5.90-5.94 (m, 4H, pyrrole-**H**), 4.44 (d, $J_{H\text{-}H}$ = 13.0 Hz, 4H, ArC**H**$_2$Ar), 4.15-4.19 (m, 4H, OC**H**$_2$), 3.96 (t, $J_{H\text{-}H}$ = 4.6 Hz, 4H, OC**H**$_2$), 3.87 (t, $J_{H\text{-}H}$ = 4.6 Hz, 4H, OC**H**$_2$), 3.78 (t, $J_{H\text{-}H}$ = 4.6 Hz, 4H, OC**H**$_2$), 3.70 (t, $J_{H\text{-}H}$ = 4.6 Hz, 4H, OC**H**$_2$), 3.39 (d, =13.0 Hz, 4H, ArC**H**$_2$Ar), 3.36 (d, $J_{H\text{-}H}$ = 4.8 Hz, 4H, OCH_2), 2.67 (s, 6H, ArCOC**H**$_3$)

Elemental analysis: *Anal calcd* for $C_{72}H_{76}N_4O_{10}$: C, 74.72%; H, 6.62%; N, 4.84%

Found: C, 73.38%; H, 6.61%; N, 4.66%

2.2.8 Preparation of 1,3-*p*-*tert*-calix[4]-bis-dipyrroethane (8)

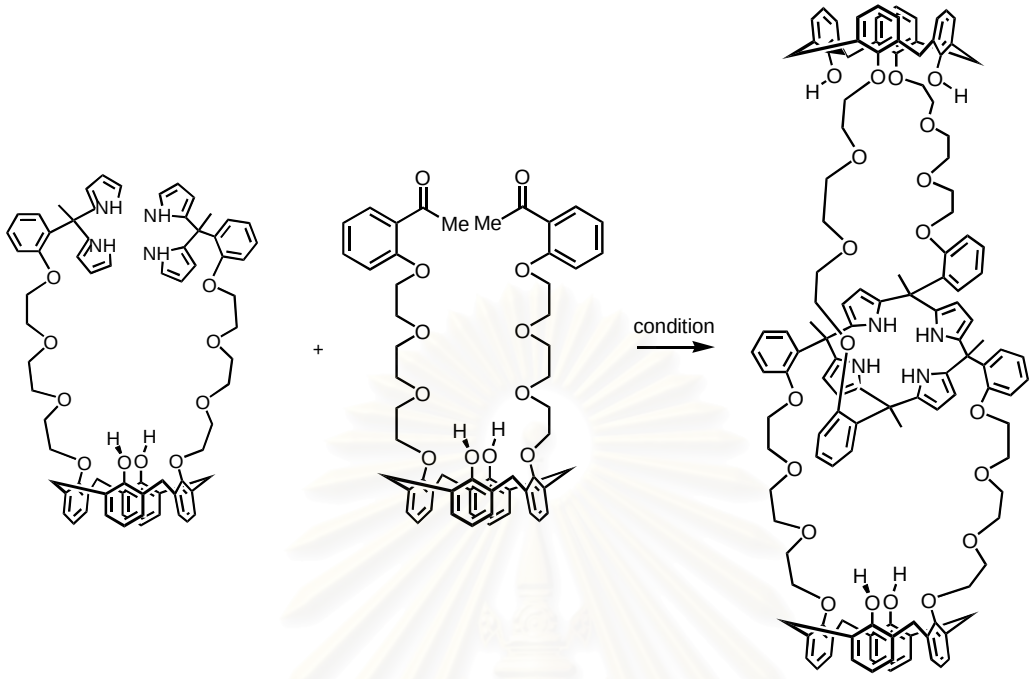


4 **8**

In a 100 mL two-necked round bottom flask, a solution of *p*-*tert*-butylcalix[4]-diacetophenone (**4**) (0.97 g, 0.84 mmol) in pyrrole (4.67 mL, 67.30 mmol) was degassed by bubbling with nitrogen for 15 min, and then CF_3COOH (0.02 mL, 0.17 mmol) was added. The solution was stirred for 10 min at room temperature, diluted with CH_2Cl_2 (100 mL), washed with 0.1 M aqueous $NaHCO_3$ (2 x 100 mL) and water (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The oily residue was purified by column chromatography over silica gel (Hexane:EtOAc:NEt_3 = 60:40:1) to give 0.41 g of the 1,3-*p*-*tert*-calix[4]-bis-dipyrroethane (**8**) as a tacky white solid with light brown splotches (35% yield).

Characteristic data for (8): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 8.91 (s, 4H, N**H**), 7.32 (d, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar**H**$COCH_3$), 7.20 (t, $J_{H\text{-}H}$ = 4.0 Hz, 2H, Ar**H**$COCH_3$), 7.19 (s, 2H, ArO**H**), 7.10 (s, 4H, Ar**H**OCH_2), 6.94 (t, $J_{H\text{-}H}$ = 7.2 Hz, 2H, Ar**H**$COCH_3$), 6.80 (s, 4H, Ar**H**OH), 6.75 (d, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar**H**$COCH_3$), 6.63 (d, $J_{H\text{-}H}$ = 1.2 Hz, 4H, pyrrole-**H**), 6.11 (t, $J_{H\text{-}H}$ = 2.6 Hz, 4H, pyrrole-**H**), 5.91 (d, $J_{H\text{-}H}$ = 1.2 Hz, 4H, pyrrole-**H**), 4.38 (d, $J_{H\text{-}H}$ = 13.0 Hz, 4H, ArC**H**$_2$Ar), 4.12 (t, $J_{H\text{-}H}$ = 4.4 Hz, 4H, OC**H**$_2$), 3.93 (t, $J_{H\text{-}H}$ = 4.8 Hz, 4H, OC**H**$_2$), 3.86 (t, $J_{H\text{-}H}$ = 4.0 Hz, 4H, OC**H**$_2$), 3.80 (t, $J_{H\text{-}H}$ = 4.0 Hz, 4H, OC**H**$_2$), 3.70 (t, $J_{H\text{-}H}$ = 4.4 Hz 4H, OC**H**$_2$), 3.37 (t, $J_{H\text{-}H}$ = 4.0 Hz, 4H, OC**H**$_2$), 3.32 (d, =13.0 Hz, 4H, ArC**H**$_2$Ar), 2.13 (s, 6H, ArCOC**H**$_3$), 1.33 (s, 18H, CH_2OAr-*t*-C_4**H**$_9$), 0.98 (s, 18H, HOAr-*t*-C_4**H**$_9$)

2.2.9 Synthesis of bis(calix[4]arene)-calix[4]pyrrole (5) *via* 1,3-calix[4]-bis-dipyrroethane (7)



7 **3** **5**

Conditions	Reagents and solvents	Temperature
i	$BF_3.OEt_2$, CH_3CN	Reflux
ii	$BF_3.OEt_2$, CH_2Cl_2	RT
iii	Propionic acid, toluene, $Zn(OAc)_2.2H_2O$	Reflux
iv	$BF_3.OEt_2$, CH_2Cl_2, Bu_4NF	RT

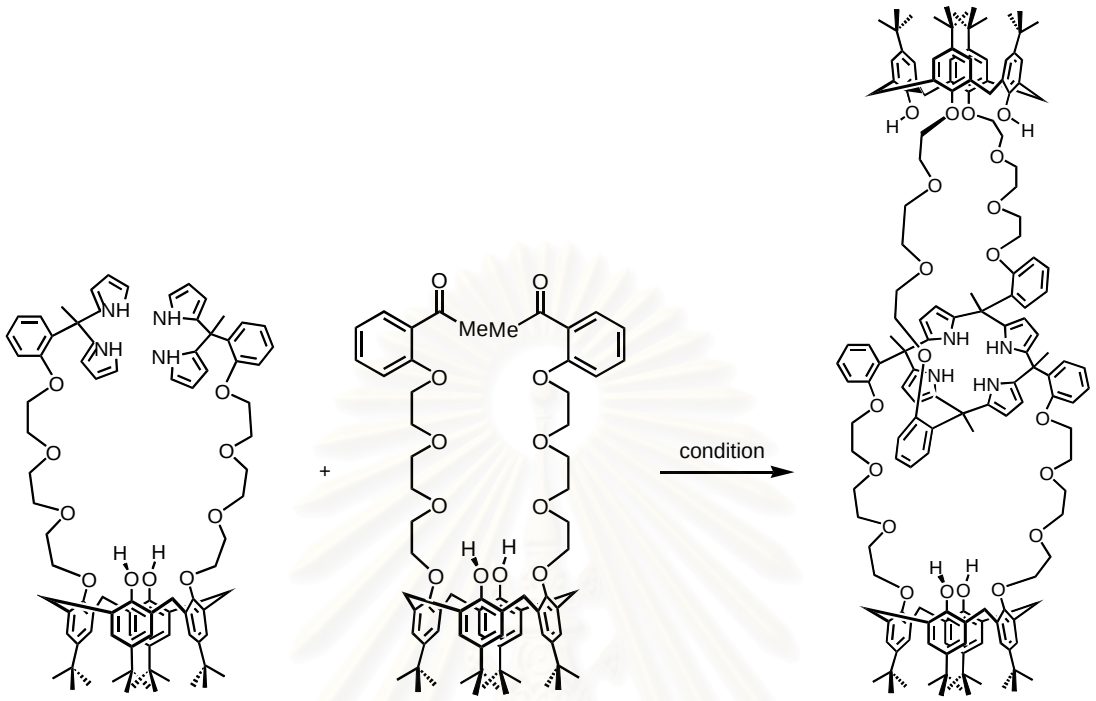
In a 100 mL two-necked round bottom flask, a solution of 1,3-calix[4]-diacetophenone (**3**) (0.93 g, 1 mmol) and 1,3-calix[4]-bis-dipyrroethane (**7**) (1.15 g, 1 mmol), salt ($Zn(OAc)_2.2H_2O$ in condition iii and Bu_4NF in condition iv), the acid catalysts ($BF_3.OEt_2$ in condition i, ii and iv or propionic acid in condition iii) and the solvent 50 mL (as indicated in reaction conditions) was degassed by bubbling with nitrogen for 15 min. The solution was allowed to stir for 24 hours at conditions indicated temperature. After the reaction was complete, the reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with 0.1 M aqueous $NaHCO_3$ (2 x 100 mL)

and water (2 x 100 mL), respectively. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (CH_2Cl_2: EtOAc = 95 : 5). The compound in each fraction was characterized by ^{1}H-NMR spectroscopy. The desired product (**5**) was obtained in condition iv as a white solid (2% yield).

Characteristic data for (5): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.90 (br, 4H, N**H**), 7.79 (s, 2H, ArO**H**), 7.64 (s, 2H, ArO**H**), 7.19 (s, 4H, Ar**H**), 7.12 (s, 4H, Ar**H**), 6.99 (d, $J_{H\text{-}H}$ = 5.6 Hz, 8H, Ar**H**), 6.81 (s, 12H, Ar**H**), 6.76 (d, $J_{H\text{-}H}$ = 6.8 Hz, 4H, Ar**H**), 6.68 (d, $J_{H\text{-}H}$ = 7.2 Hz, 4H, Ar**H**), 6.59-6.57 (m, 4H, Ar**H**), 5.82(d, $J_{H\text{-}H}$ = 13.6 Hz 4H, pyrrole-**H**), 5.56 (s, 4H, pyrrole-**H**), 4.29 (d, $J_{H\text{-}H}$ = 12.8 Hz, 8H, ArC**H**$_2$Ar), 4.10-4.05 (m, 10H, OC**H**$_2$), 3.97-3.91 (m, 12H, OC**H**$_2$), 3.77-3.66 (m, 12H, OC**H**$_2$), 3.46 (s, 2H, OC**H**$_2$), 3.35-3.28 (m, 8H, ArC**H**$_2$Ar), 3.06 (s, 12H, OC**H**$_2$), 1.97 (s, 12H, ArCC**H**$_3$)

MALDI-TOF mass (m/z) : 2044.82

2.2.10 Synthesis of bis(*p-tert*-butylcalix[4]arene)-calix[4]pyrrole (6) *via* 1,3-*p-tert*-butylcalix[4]-bis-dipyrroethane (8)

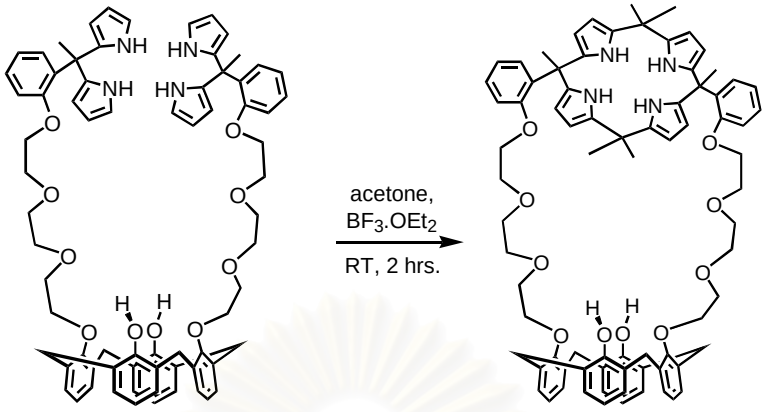


8 **4** **6**

Conditions	Reagents and solvents	Temperature
i	TFA, CH_2Cl_2	RT
ii	$BF_3.OEt_2$, CH_2Cl_2	RT

In a 100 mL two-necked round bottom flask, a solution of 1,3-*p-tert*-butylcalix[4]-diacetophenone (**4**) (1.15 g, 1 mmol) and 1,3-*p-tert*-butylcalix[4]-bis-dipyrroethane (**8**) (1.38 g, 1 mmol), the acid catalysts (TFA in condition i and $BF_3.OEt_2$ in condition ii) in 50 mL of dried dichloromethane was degassed by bubbling with nitrogen for 15 min. The solution was allowed to stir for 24 hrs at room temperature. After the reaction was complete, the reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with 0.1 M aqueous $NaHCO_3$ (2 x 100 mL) and water (2 x 100 mL), respectively. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (CH_2Cl_2: EtOAc = 95 : 5). The compound in each fraction was characterized by ^{1}H-NMR spectroscopy. The desired product (**6**) was not obtained.

2.2.11 Preparation of calix[4]arene-calix[4]pyrrole (9)



7 **9**

Into a 100 mL two-necked round bottom flask, a solution of 1,3-calix[4]-bis-dipyrroethane (**7**) (0.13 g, 0.12 mmol) in acetone (30 mL) was added with $BF_3.OEt_2$ (0.01 mL, 0.04 mmol). The solution was stirred for 2 hours at room temperature. The solvent was removed and then diluted with CH_2Cl_2 and extracted with saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography over silica gel (CH_2Cl_2 : EtOAc = 95 : 5) and recrystallized with methanol to give 0.05 g of the calix[4]arene-calix[4]pyrrole (**9**) as a white solid (37% yield).

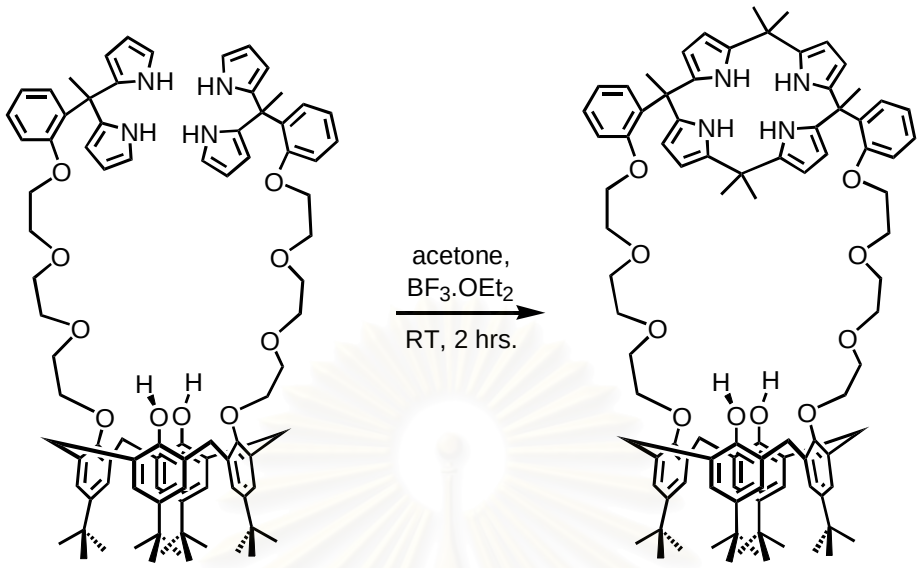
Characteristic data for (9): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.91 (s, 2H, ArO**H**), 7.98 (s(br), 4H, N**H**), 7.23 (t, J_{H-H} = 8.4 Hz, 2H, Ar**H**), 7.08 (d, J_{H-H} = 7.6 Hz, 4H, Ar**H**), 6.94 (d, J_{H-H} = 7.6 Hz, 8H, Ar**H**), 6.85 (d, J_{H-H} = 8.0 Hz, 2H, Ar**H**), 6.78 (t, J_{H-H} = 7.6 Hz, 2H, Ar**H**), 6.68 (t, J_{H-H} = 7.6 Hz, 2H, Ar**H**), 5.91 (s, 4H, pyrrole-**H**), 5.67 (s(br), 4H, pyrrole-**H**), 4.40 (d, J_{H-H} = 13.0 Hz, 4H, ArC**H**$_2$Ar), 4.20 (t, J_{H-H} = 4.8 Hz, 4H, OC**H**$_2$), 4.09 (t, J_{H-H} = 5.0 Hz, 4H, OC**H**$_2$), 3.89 (t, J_{H-H} = 4.6 Hz, 4H, OC**H**$_2$), 3.83 (s, 4H, OC**H**$_2$), 3.57 (s, 4H, OC**H**$_2$), 3.39 (d, J_{H-H} =13.0 Hz, 4H, ArC**H**$_2$Ar), 3.13 (s, 4H, OC**H**$_2$), 2.09 (s, 6H, ArCC**H**$_3$), 1.55 (s, 12H, (C**H**$_3$)$_2$CPy$_2$);); **IR spectrum (KBr, (cm^{-1}))**: 3404 (OH, st), 3363 (NH, st), 3024 (=C-H, st), 2963, 2922, 2865 (-C-H, st), 1571, 1453, 1355 (C=C, st (aromatic)), 1119 (O-C-C, st)

Elemental analysis: *Anal calcd* for $C_{78}H_{84}N_4O_{10}$: C, 75.70%; H, 6.84%; N, 4.53%

Found: C, 75.65%; H, 6.73%; N, 4.56%

MALDI-TOF mass (m/z) [M+Na$^+$] : 1259.65

2.2.12 Preparation of *p-tert*-calix[4]arene-calix[4]pyrrole (10)

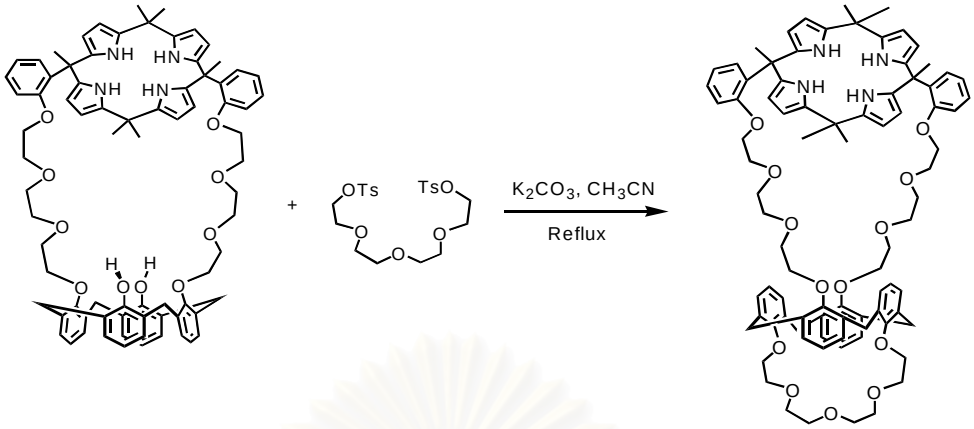


8 **10**

Into a 100 mL two-necked round bottom flask, a solution of 1,3-*p-tert*-calix[4]-bis-dipyrromethane (**8**) (0.14 g, 0.10 mmol) in acetone (30 mL) was added with $BF_3.OEt_2$ (0.01 mL, 0.03 mmol). The solution was stirred for 2 hours at room temperature. The solvent was removed and then diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography over silica gel (CH_2Cl_2 : EtOAc = 94 : 6) to give 0.05 g of the *p-tert*-calix[4]arene-calix[4]pyrrole (**10**) as a light brown solid (33% yield).

Characteristic data for (10): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.42 (s, 2H, ArO**H**), 7.23 (t, $J_{H\text{-}H}$ = 8.4 Hz, 2H, Ar**H**), 7.07 (s, 4H, Ar**H**), 6.92 (t, $J_{H\text{-}H}$ = 7.2 Hz, 4H, Ar**H**), 6.86 (s, 2H, Ar**H**), 6.85 (s, 4H, Ar**H**), 5.91 (s, 4H, pyrrole-**H**), 5.67 (s(br), 4H, pyrrole-**H**), 4.36 (d, $J_{H\text{-}H}$ = 13.0 Hz, 4H, ArC**H**$_2$Ar), 4.17 (t, $J_{H\text{-}H}$ = 3.6 Hz, 4H, OC**H**$_2$), 4.06 (t, $J_{H\text{-}H}$ = 4.8 Hz, 4H, OC**H**$_2$), 3.87 (s, 4H, OC**H**$_2$), 3.83 (s, 4H, OC**H**$_2$), 3.54 (s, 4H, OC**H**$_2$), 3.33 (d, $J_{H\text{-}H}$ =13.0 Hz, 4H, ArC**H**$_2$Ar), 3.13 (s, 4H, OC**H**$_2$), 2.08 (s, 6H, ArCC**H**$_3$), 1.55 (s, 12H, (C**H**$_3$)$_2$CPy$_2$), 1.32 (s, 18H, CH_2OAr-*t*-C_4**H**$_9$), 1.01 (s, 18H, HOAr-*t*-C_4**H**$_9$)

2.2.13 Preparation of 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (11)



9 **11**

Into a 250 mL two-necked round bottom flask, calix[4]arene-calix[4]pyrrole (**9**) (0.30 g, 0.24 mmol) and K_2CO_3 (0.33 g, 2.40 mmol) were suspended in dried acetonitrile (50 mL). The reaction mixture was stirred at room temperature under nitrogen for 1 hour. A solution of tetraethyleneglycol ditosylate (0.12 g, 0.24 mmol) in dried acetonitrile (50 mL) was added dropwise. The reaction mixture was stirred and refluxed under nitrogen atmosphere for 3 days. After the reaction was completed, the solution was allowed to cool to room temperature. The solvent was then removed. The obtained residue was dissolved in CH_2Cl_2 (100 mL) and extracted with 3 M HCl (1x100 mL) and water (2x100 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The obtained residue was purified by column chromatography (silica gel, CH_2Cl_2:MeOH; 94:6) to obtain 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (**11**) as a white solid (0.23 g, 68 %).

Characteristic data for (11): ^{1}H NMR spectrum ($CDCl_3$, δ(ppm), 400 MHz): 7.96 (br, 4H, N**H**), 7.24 (t, $J_{H\text{-}H}$ = 8.0 Hz, 2H, Ar**H**), 7.11 (dd, $J_{H\text{-}H}$ = 8.0, 8.0 Hz, 8H, Ar**H**), 6.92 (m, 10H, Ar**H**), 5.95 (s, 4H, pyrrole-**H**), 5.71 (s(br), 4H, pyrrole-**H**), 3.90 (s(br), 12H, C**H**$_2$), 3.58-3.62 (m, 12H, C**H**$_2$), 3.41-3.45 (m, 12H, C**H**$_2$), 3.12-3.16 (m, 8H, C**H**$_2$), 3.02-3.05 (m, 4H, C**H**$_2$), 2.10 (s, 6H, ArCC**H**$_3$), 1.57 (s, 12H, (C**H**$_3$)$_2$CPy$_2$); **IR spectrum (KBr, (cm^{-1}))**: 3404 (NH, st), 3101, 3060 (=C-H, st), 2963, 2922, 2865 (-C-H, st), 1576, 1453, 1360 (C=C, st (aromatic)), 1129 (O-C-C, st)

Elemental analysis: *Anal calcd* for $C_{86}H_{98}N_4O_{13}$: C, 74.01%; H, 7.08%; N, 4.01%

Found: C, 73.77%; H, 7.22%; N, 4.05%

2.3 X-ray crystallography

The crystal of **9** was mounted on the end of a hollow glass fiber approximately parallel to the long dimension of the crystal using cyanoacrylate glue. Preliminary examination and data collection were performed using MoK_α X-radiation (λ = 0.71073 Å) on Bruker IIX SMART area detector diffractometer. The program used to solve the structure was SHELX 97. Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were in calculated positions and their parameter fixed during the refinement. Crystallographic parameters for **9** are described in Table 2.1.

Table 2.1. Crystal data and structure refinement details for compound **9**.

Empirical formula	$C_{78}H_{84}N_4O_{10}$
Formula weight	1237.08
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 18.7183(9) Å α = 90 deg. b = 19.1141(9) Å β = 96.4980(10) deg. c = 19.5849(9) Å γ = 90 deg.
Volume	6962.1(6) $Å^3$
Z, Calculated density	4, 1.213 g/cm^3

Table 2.1. (continued) Crystal data and structure refinement details for compound **9**.

Absorption coefficient	0.082 mm^{-1}
F(000)	2712
Theta range for data collection	1.43 to 25.00 deg.
Limiting indices	-22<=h<=22, -22<=k<=22, -23<=l<=23
Reflections collected / unique	66336 / 12256 [*R*(int) = 0.1010]
Completeness to theta = 25.00	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12256 / 0 / 870
Goodness-of-fit on F^2	1.052
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.1080, wR2 = 0.2995
R indices (all data)	R1 = 0.1908, wR2 = 0.3664
Extinction coefficient	0.0038(8)

2.4 Complexation studies

2.4.1 Complexation studies of ligand 9 with potassium and tetrabutylammonium salts

Typically, an excess (10 equiv.) of potassium or tetrabutylammonium salts were added into NMR tubes. A solution of 0.01 M of ligand **9** (0.055 mmol) in a mixture of 1:9 of $CDCl_3$: CD_3CN (v/v) (5.5 mL) was prepared and 0.5 mL of this solution was added in each NMR tube (Table 2.2). The ^{1}H-NMR spectra were recorded after addition and every 24 hours until the complexation reached to the equilibrium.

Table 2.2 The amount of various salts used in complexation studies with ligand **9**.

Salts	Weight of salts (g)
KF	0.00349
KCl	0.00447
KBr	0.00714
KI	0.00996
KH_2PO_4	0.00817
KPF_6	0.01104
NBu_4F	0.01893
NBu_4Cl	0.01668
NBu_4Br	0.01934
NBu_4I	0.02216

2.4.2 Complexation study of ligand 9 with potassium picrate

Typically, excess potassium picrate (0.01603 g, $5x10^{-5}$ mol) and ligand **9** (0.00619 g, 0.005 mmol) was added directly into NMR tube. The $CDCl_3$ 0.5 mL was added into NMR tube. The ^{1}H-NMR spectra were recorded after addition and every 24 hours until the complexation reached to the equilibrium.

2.4.3 Complexation studies of ligand 11 with potassium and tetrabutylammonium salts

Typically, excess potassium or tetrabutylammonium salts were brought into NMR tubes. A solution of 0.01 M of ligand **11** (0.055 mmol) in CD_3CN (5.5 mL) was prepared and 0.5 mL of this solution was added in each NMR tube (same as ligand **9** in Table 2.2). The ^{1}H-NMR spectra were recorded after addition and every 24 hours until the complexation reached to the equilibrium.

2.4.4 Complexation study of ligand 11 with potassium picrate

Typically, excess potassium picrate (0.01603 g, $5x10^{-5}$ mol) and ligand **11** (0.00698 g, 0.005 mmol) was added directly into NMR tube. The $CDCl_3$ 0.5 mL was added into NMR tube. The ^{1}H-NMR spectra were recorded after addition and every 24 hours until the complexation reached to the equilibrium.

2.4.5 ^{1}H-NMR titration of ligand 9 with Bu_4NF

A 0.005 M solution of ligand **9** (0.00309 g, 2.5 x 10^{-6} mol) in a mixture of 1:9 of $CDCl_3$: CD_3CN (v/v) (0.5 mL) was prepared in an NMR tube. A solution of 0.05 M of Bu_4NF in CD_3CN (0.25 mL) was prepared in a vial and added directly into the NMR tube by a microsyringe to obtain the guest : host ratios as shown in Table 2.3. The ^{1}H-NMR spectra were recorded after each addition.

Table 2.3 The amount of solution of guest used to prepare various guest : ligand **9** ratios

Ratio of cation:ligand	Volume of added cation (μL)	[ligand]	[cation]
0.0:1.0	0	0.00050	0
0.1:1.0	5	0.00495	0.00049
0.2:1.0	5	0.00490	0.00098
0.3:1.0	5	0.00485	0.00146
0.4:1.0	5	0.00481	0.00192
0.5:1.0	5	0.00476	0.00238
0.6:1.0	5	0.00472	0.00283
0.7:1.0	5	0.00467	0.00327
0.8:1.0	5	0.00463	0.00370
0.9:1.0	5	0.00459	0.00413
1.0:1.0	5	0.00454	0.00454
1.2:1.0	10	0.00446	0.00536
1.4:1.0	10	0.00439	0.00614
1.6:1.0	10	0.00431	0.00689
1.8:1.0	10	0.00424	0.00763
2.0:1.0	10	0.00417	0.00833
3.0:1.0	50	0.00385	0.01154
4.0:1.0	50	0.00357	0.01429

2.4.6 ^{1}H-NMR titration of ligand 11 with Bu_4NF

A 0.005 M solution of ligand **11** (0.00349 g, 2.5 x 10^{-6} mol) in CD_3CN (0.5 mL) was prepared in an NMR tube. A solution of 0.05 M of Bu_4NF in CD_3CN (0.25 mL) was prepared in a vial and added directly into the NMR tube by a microsyringe to obtain the guest : host ratios as shown in Table 2.3. The ^{1}H-NMR spectra were recorded after each addition.

2.4.7 ^{1}H-NMR titration of ligand 11 with Bu_4NCl

A 0.005 M solution of ligand **11** (0.00349 g, 2.5 x 10^{-6} mol) in CD_3CN (0.5 mL) was prepared in an NMR tube. A solution of 0.05 M of Bu_4NCl in CD_3CN (0.25 mL) was prepared in a vial and added directly into the NMR tube by a microsyringe to obtain the guest : host ratios as shown in Table 2.3. The ^{1}H-NMR spectra were recorded after each addition.

2.4.8 ^{1}H-NMR titration of ligand 11 in the presence of 2 equivalents of KPF_6 with Bu_4NF

The titration experiment was carried out by addition 2 equivalents of KPF_6 (0.00092 g, 5x10^{-6} mol) and ligand **11** (0.00349 g, 2.5 x 10^{-6} mol) in CD_3CN (0.5 mL) in the NMR tube. A solution of 0.05 M of Bu_4NF in CD_3CN (0.25 mL) was prepared in a vial and added directly into the NMR tube by a microsyringe to obtain the guest : host ratios as shown in Table 2.3. The ^{1}H-NMR spectra were recorded after each addition.

2.4.9 Complexation study of ligand 11 in the presence of Bu_4NF with Bu_4NCl.

The complexation experiment was carried out by addition 4 equivalents of Bu_4NCl directly to the solution of ligand **11** in the presence of 4 equivalents of Bu_4NF (from section 2.4.6). The ^{1}H-NMR spectrum was recorded after addition.

2.4.10 Complexation study of ligand 11 in the presence of Bu_4NCl with Bu_4NF.

The complexation experiment was carried out by addition 4 equivalents of Bu_4NF directly to the solution of ligand **11** in the presence of 4 equivalents of Bu_4NCl (from section 2.4.7). The ^{1}H-NMR spectrum was recorded after addition.

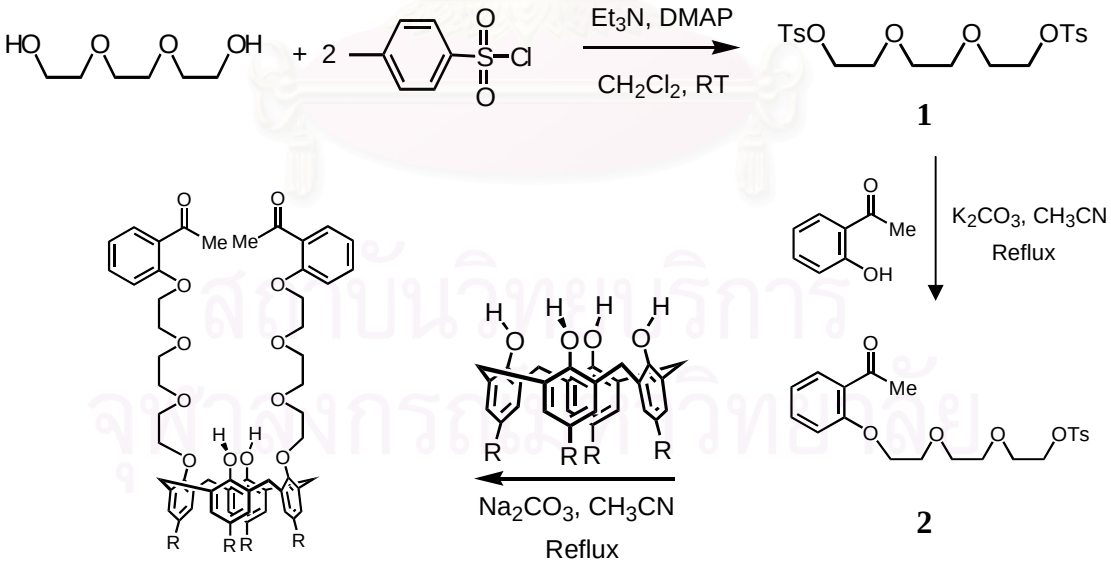
CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis and characterization of calix[4]arene-calix[4]pyrrole derivatives and 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5.

3.1.1 Synthesis and characterization of 1,3-calix[4]-diacetophenone (3) and 1,3-*p*-*tert*-butylcalix[4]arene-diacetophenone (4)

The synthetic pathway of 1,3-calix[4]-diacetophenone **3** and 1,3-*p*-*tert*-butylcalix[4]arene-diacetophenone **4** (Scheme 3.1) started with a preparation of triethylene glycol ditosylate **1** by tosylation of triethylene glycol in the presence of triethylamine as base and a catalytic amount of DMAP in dichloromethane at room temperature for 4 hours. A white solid of compound **1** was obtained in 82% yield by precipitating with methanol. The ^{1}H-NMR spectrum of compound **1** showed the characteristic peaks of tosyl groups; a singlet of C**H**$_3$ at 2.42 ppm and two doublets of Ar**H** at 7.77 and 7.32 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 8.2 Hz).



Scheme 3.1 Synthetic pathway of 1,3-calix[4]-diacetophenone **3** and 1,3-*p*-*tert*-butylcalix[4]-diacetophenone **4**.

The nucleophilic substitution reaction of 2-hydroxy acetophenone with triethylene glycol ditosylate **1** using excess K_2CO_3 as base in acetonitrile provided 2-(8-tosyltriethyleneglycol)acetophenone **2** as a yellow oil (30% yield). The ^{1}H-NMR spectrum of **2** showed the characteristic peaks of tosyl groups; a singlet of C**H**$_3$ at 2.46 ppm and two doublets of Ar**H** at 7.82 and 7.36 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 4.0 Hz), and the characteristic peaks of the acetophenone unit, a singlet of C**H**$_3$ at 2.66 ppm, two doublets of Ar**H** at 7.77 and 6.98 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz) and two triplets of Ar**H** at 7.47 and 7.03 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz).

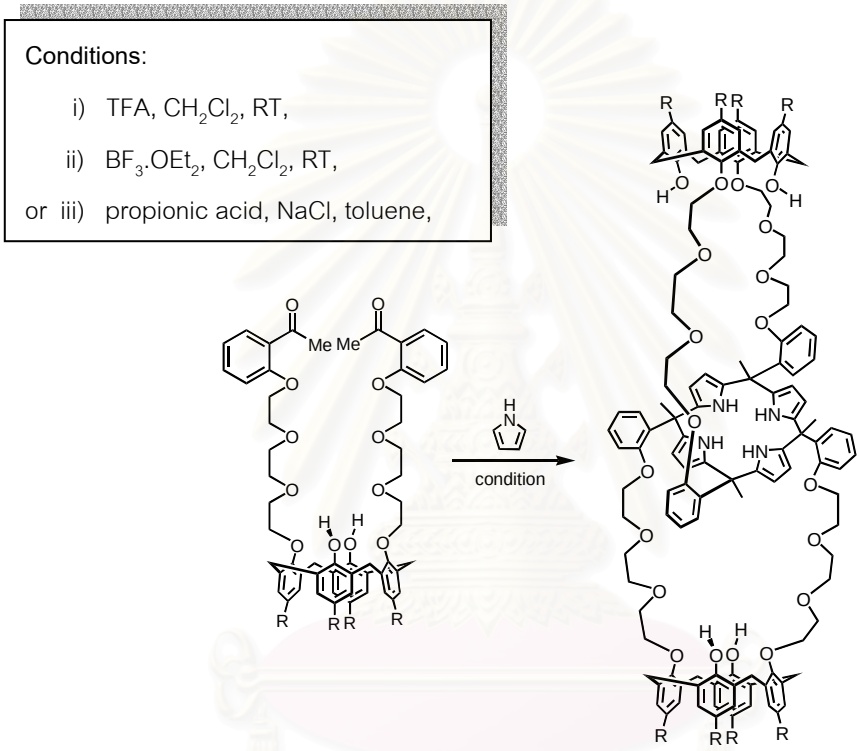
A condensation of 2 equiv. of 2-(8-tosyltriethyleneglycol)acetophenone **2** with calix[4]arene was carried out by using K_2CO_3 as a base in acetonitrile for 7 days. A white solid of compound **3** was obtained in 85% yield by precipitation with methanol in dichloromethane. From the ^{1}H-NMR spectrum, the substitution occurred in distal manner due to the presence of only **AB**-system of ArC**H**$_2$Ar as two doublets at 3.36 and 4.43 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 13.0 Hz). These two doublets also indicated that compound **3** exists in cone conformation. The elemental analysis was in accordance with the structure of **3**.

A condensation of 2 equiv. of 2-(8-tosyltriethyleneglycol)acetophenone **2** with *p-tert*-butylcalix[4]arene was carried out by using K_2CO_3 as base in acetonitrile for 7 days. Compound **4** was separated by column chromatography to afford a colorless viscous oil (63%). The ^{1}H-NMR spectrum of compound **4** showed two doublets of ArC**H**$_2$Ar of calix[4]arene at 3.30 and 4.39 ppm with $\boldsymbol{J}_{H\text{-}H}$ = 13.0 Hz. This indicated that compound **4** presented in a cone conformation.

3.1.2 Synthesis and characterization of bis(calix[4]arene)-calix[4]pyrrole (5) and bis(*p-tert*-butylcalix[4]arene)-calix[4]pyrrole (6)

The synthesis of bis(calix[4]arene)-calix[4]pyrrole **5** and its derivative **6**, were carried out into two pathways as shown in Scheme 3.2 and 3.3.

Pathway I (*via* direct condensation)



3:R=H **5:**R=H

4:R=*t*-butyl **6:**R=*t*-butyl

Scheme 3.2 Synthetic pathway I of bis(calix[4]arene)-calix[4]pyrrole **5** and bis(*p-tert*-butylcalix[4]arene)-calix[4]pyrrole **6**.

At the beginning, we tried to synthesize compound **5** by the direct condensation between the diketone derivative **3** and pyrrole in the presence of TFA in dried CH_2Cl_2 for 24 hours. After purification by column chromatography, the compounds in each fraction were characterized by ^{1}H-NMR spectroscopy and the results indicated that the desired product **5** was not obtained.

The results from ^{1}H-NMR spectrum indicates that the ring cyclization of calix[4]pyrrole was not completed due to the presence of three characteristic peaks of *β*-pyrrolic protons in the form of dipyrroethane, multiplet at 5.92, 6.11 and 6.62 ppm, respectively.

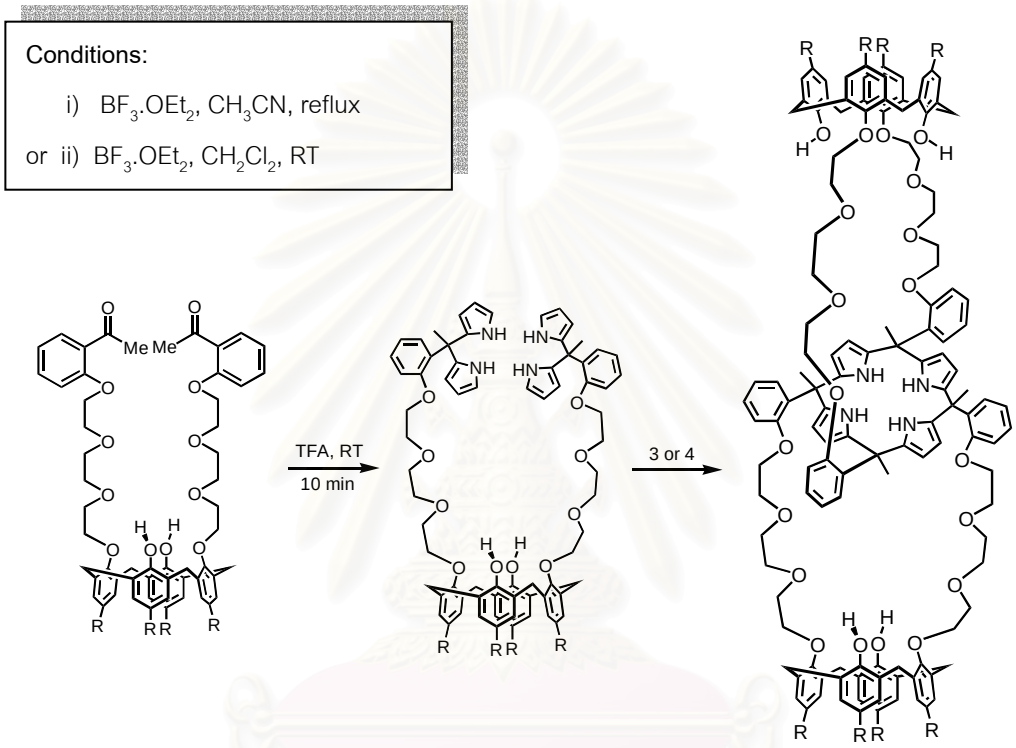
Changes of the acid and solvent were tried. The systems of $BF_3.OEt_2$ in dried CH_2Cl_2 or propionic acid in refluxing toluene were used. After purified by column chromatography, the obtained compound was characterized by ^{1}H-NMR spectroscopy and the result demonstrated that the desired product was not obtained.

The way to synthesize compound **6** was treated identically as for **5**, by starting with the condensation of 1,3-*p*-*tert*-butylcalix[4]-diacetophenone **4** with pyrrole in the presence of TFA in dried CH_2Cl_2 or methanesulfonic acid in dried CH_2Cl_2. After purified by column chromatography, the obtained compound was characterized by ^{1}H-NMR spectroscopy and the result indicated that the desired product was not obtained.

In summary, the syntheses of bis(calix[4]arene)-calix[4]pyrrole **5** or its analogue **6** by coupling of 2 equiv. of the diketone **3** or **4** with 4 equiv. of pyrrole were not successful.

Pathway II (*via* bis-dipyrroethane)

From the failure of the coupling reaction by the pathway I, a new pathway was used. Scheme 3.3 showed the pathway II for synthesizing bis(calix[4]arene)-calix[4]pyrrole **5** and its analogue **6**.



3:R=H **7:**R=H **5:**R=H

4:R=*t*-butyl **8:**R=*t*-butyl **6:**R=*t*-butyl

Scheme 3.3 Synthetic pathway II of bis(calix[4]arene)-calix[4]pyrrole **5** and bis(*p*-*tert*-butylcalix[4]arene)-calix[4]pyrrole **6**.

In order to generate a calix[4]pyrrole unit at the center of the molecule, *trans*-substituted calixpyrrole can be prepared by condensation of dipyrroethane with ketone.[37]

The synthetic pathway II started with the synthesis of 1,3-calix[4]arene-bis-dipyrroethane **7** by treating 1,3-calix[4]-diacetophenone **3** with (40 times excess) pyrrole in a presence of catalytic amount of trifluoroacetic acid for 10 minutes

according to conventional procedure.[37] The obtained residue was isolated by column chromatography on silica (dichloromethane/ethyl acetate/triethylamine = 80/20/1). Compound **7** was obtained as a tacky white solid with light brown splotches in 61% yield. The ^{1}H-NMR spectrum of **7** showed the characteristic peaks of NH pyrrole as a singlet at 8.86 ppm and three multiplets of the β-pyrrolic protons of the dipyrroethane at 6.62, 6.11 and 5.92 ppm, respectively. On the other hand, elemental analysis was not in good agreement with the structure due to its unstability at room temperature.

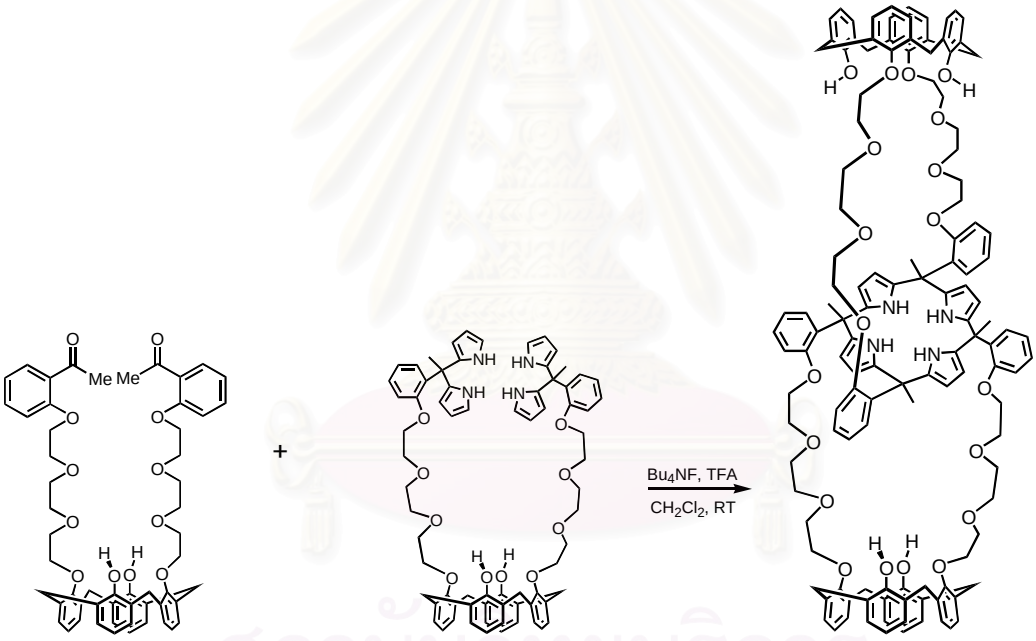
The synthesis of 1,3-*p*-*tert*-butylcalix[4]-bis-dipyrroethane **8** was treated identically as for **7** by treating 1,3-*p*-*tert*-butylcalix[4]-diacetophenone **4** with (40 times excess) pyrrole in a presence of catalytic amount of trifluoroacetic acid for 10 minutes. The obtained residue was isolated by column chromatography on silica (hexane/ethyl acetate/triethylamine = 60/40/1). Compound **8** was obtained as a tacky white solid with light brown splotches in 35% yield. The ^{1}H-NMR spectrum of **8** showed the characteristic peaks of NH pyrrole as a singlet at 8.91 ppm and three multiplets of the β-pyrrolic protons of the dipyrroethane at 6.63, 6.11 and 5.91 ppm, respectively.

The 1,3-calix[4]-bis-dipyrroethane **7** was coupled with the ketone derivative **3** in dried CH_2Cl_2 in the presence of $BF_3.OEt_2$ or in the CH_3CN with $BF_3.OEt_2$ under reflux condition. The obtained residue were then purified and characterized by ^{1}H-NMR spectroscopy and the results indicated that the desired product **5** was not obtained.

The 1,3-calix[4]-bis-dipyrroethane **8** was coupled with the ketone derivative **4** in dried CH_2Cl_2 in the presence of TFA or in dried CH_2Cl_2 with $BF_3.OEt_2$ under room temperature. The obtained residue were then purified and characterized by ^{1}H-NMR spectroscopy and the results indicated that the desired product **6** was not obtained.

Pathway III

As it is well known that calix[4]pyrrole can bind selectively with F^- ion,[22-23] then, the tetrabutylammonium fluoride salt was selected to be a template in the ketone-dipyrroethane condensation. After the reaction was completed by TLC analysis, the residue was purified by column chromatography (silica, CH_2Cl_2:EtOAC = 95:5) resulting a white solid (2% yield). The ^{1}H-NMR spectrum of bis(calix[4]arene)-calix[4]pyrrole **5** showed the signal of NH protons at 7.90 ppm and the doublet and singlet peak of *β*-pyrrolic protons at 5.82 and 5.56 ppm, respectively. These results indicated the calix[4]pyrrole unit was generated. MALDI-TOF mass spectra also supported the presence of **5** by showing an intense line at m/z 2044.82 corresponding to the calculated molecular weight of **5**.

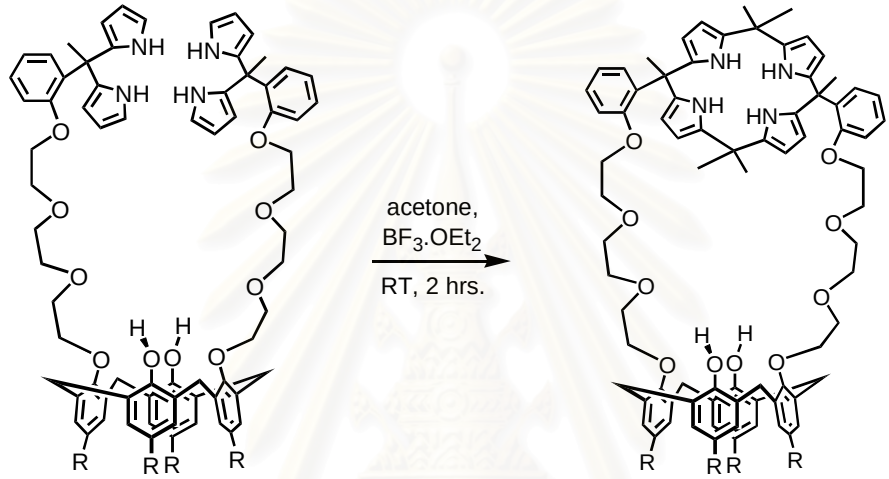


3 **7** **5**

Scheme 3.4 Synthetic pathway III of bis(calix[4]arene)-calix[4]pyrrole **5** using Bu_4NF as a template .

3.1.3 Synthesis and characterization of calix[4]arene-calix[4]pyrrole (9) and *p-tert*-butylcalix[4]arene-calix[4]pyrrole (10)

Due to the highly selective anion binding of calix[4]pyrrole[38-42] and its easy modification of calix[4]arene to obtain a specific conformer and selective cation binding ability, the calix[4]arene-calix[4]pyrrole (**9**) and *p-tert*-butylcalix[4]arene-calix[4]pyrrole (**10**) were synthesized to serve as the intermediates to further modification as depicted in Scheme 3.5.



7:R=H **9:**R=H

8:R=*t*-butyl **10:**R=*t*-butyl

Scheme 3.5 The synthesis of calix[4]arene-calix[4]pyrrole **9**.

The synthesis of compound **9** was accomplished by the condensation of 1,3-calix[4]-bis-dipyrroethane **7** with acetone in the presence of $BF_3.OEt_2$ at room temperature for 2 hours. The compound **9** was separated by column chromatography and recrystallized with methanol afford a light brown solid (37%). The ^{1}H-NMR spectrum showed a broad signal of NH at 8.04 ppm, the singlet signal of OH at 7.91 ppm and two singet peaks of β-pyrrolic protons at 5.92 and 5.68 ppm. Calix[4]arene exists in cone conformation due to a doublet signal of ArC**H**$_2$Ar of calix[4]arene at 3.39 and 4.40 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 13.0 Hz). MALDI-TOF MS supported the structure of desired product **9** showing an intense line at m/z 1259.65 [M+Na$^+$] and the elemental analysis result was in good agreement with the proposed structure.

The synthesis of compound **10** was accomplished by the condensation of 1,3-*p-tert*-butylcalix[4]-bis-dipyrroethane **8** with acetone in the presence of $BF_3.OEt_2$ at room temperature for 2 hours. Compound **10** was separated by column chromatography to afford a light brown solid (33%). The ^{1}H-NMR spectrum shows the broad signal of NH at 8.04 ppm, the singlet signal of OH at 7.23 ppm and two singlet peaks of β-pyrrolic protons at 5.91 and 5.67 ppm. Calix[4]arene exists in cone conformation due to a doublet signal of ArC**H**$_2$Ar of calix[4]arene at 3.33 and 4.36 ppm ($\boldsymbol{J}_{H\text{-}H}$ = 13.0 Hz).

3.1.4 Synthesis and characterization of 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (11)

Bridging of compound **9** was accomplished by the reaction with tetraethylene glycol ditosylate in an excess of K_2CO_3 in refluxing acetonitrile for 3 days. The compound **11** was separated by column chromatography as a white solid (68%). It existed in 1,3-alternate conformation due to the disappearance of **AB**-system of ArC**H**$_2$Ar of calix[4]arene at 3.39 and 4.40 ppm and the appearance of a singlet in multiplet of ArC**H**$_2$Ar of calix[4]arene at 3.90 ppm on the ^{1}H-NMR spectrum. Besides this, the spectrum also shows the disappearance of a singlet of ArO**H** protons at 7.91 ppm. The ditosylate derivative of glycolic chain was bridged at 1,3-position of calix[4]arene to provide crown ether loop. The elemental analysis was in good agreement with the structure of compound **11**.

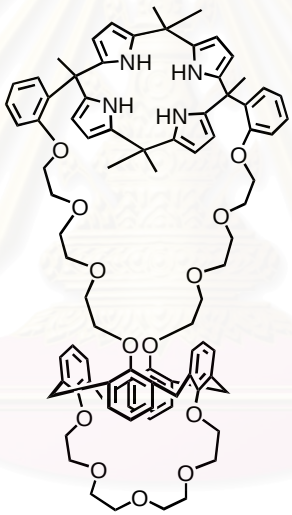


Figure 3.2 The structure of 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 **11**.

3.2 X-ray study

The solid structure of compound **9** (Figure 3.3) was determined by X-ray crystallography. The phenyl rings of the calix[4]arene unit are in a pinched cone conformation due to strong H-bonding between O(6)-H(200) to O(7) and O(5)-H(201) to O(4) of the calix[4]arene unit. In addition, at the calix[4]pyrrole moiety, the H-bonding between pyrrole N(2)-H(2) to O(10) of the glycolic chain were also observed. Conversely to calix[4]arene, the calix[4]pyrrole unit adopted in a 1,3-alternate conformation. Interestingly, one of the aromatic rings connected to the calix[4]pyrrole unit oriented up the plane, while the other oriented down. This probably resulted from a strong hydrogen bonding of pyrrolic N-H to oxygen of glycolic chain which led the calix[4]pyrrole to bend down to calix[4]arene unit and destroy the symmetry of the molecule. The bond lengths and bond angles of **9** are shown in Appendix B.

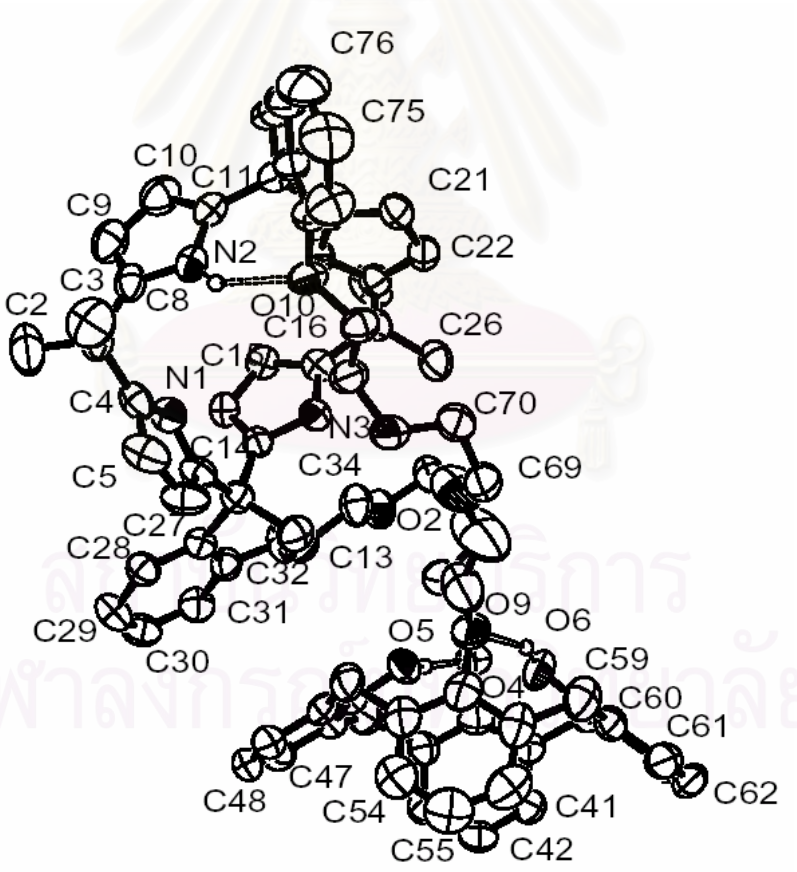


Figure 3.3 ORTEP representation of crystal structure of **9**.

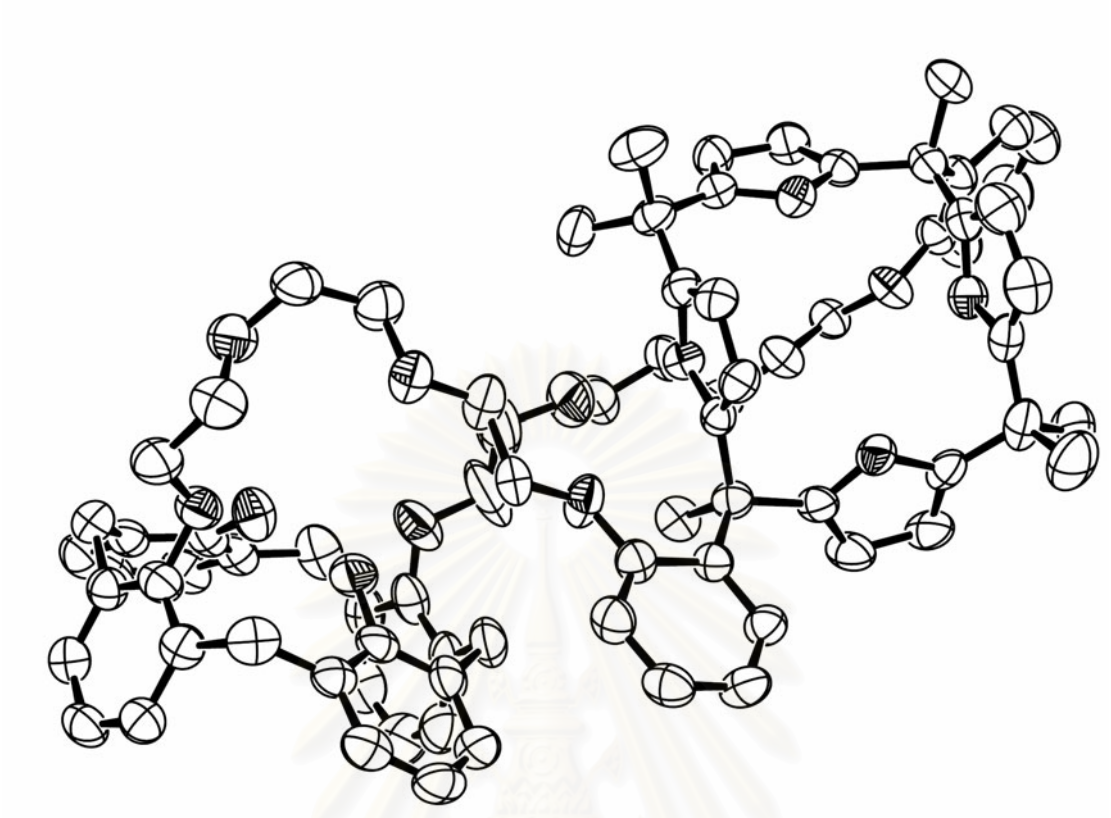


Figure 3.3 (continued) ORTEP representation of crystal structure of **9**.

3.3 Anion and cation complexation studies

Ligand **9** contains the binding sites for both cation and anion. It is composed of glycol linkages which have oxygen donor atoms for binding alkaline ions. In addition, it contained the calix[4]pyrrole moiety connected to the glycol linkages which was designed for anion binding site *via* hydrogen bonding interactions. Interactions between anions and the ligand were studied employing tetrabutylammonium and potassium salts.

3.3.1 Complexation studies of ligand 9 towards tetrabutylammonium salts

The tetrabutylammonium salts of various anions (i.e., F^-, Cl^-, Br^- and I^-) were weighted in each NMR tubes. The ^{1}H-NMR spectra were recorded after addition of a mixture of 1:9 $CDCl_3/CD_3CN$ (v/v) solution of the ligand **9** and every 24 hours. The inclusion of an anion by the ligand can be monitored by observing a singlet peak of NH-pyrrole protons around 8-13 ppm.

Upon addition of the solution of ligand **9** to Bu_4NF in the NMR tube, the signal of NH pyrrole protons at 8.15 ppm in ^{1}H-NMR spectra (Figure 3.4) shifted downfield dramatically to 12.50 ppm. The small downfield shifts for the protons of phenyl rings were observed, which may be attributed to the increasing of electron density in phenyl rings due to the presence of anion. Apparently, the two singlet of CH pyrrole protons at 5.94 and 5.69 ppm of the free ligand became a broad signal at 5.69 ppm in the complex. Morever, the signal of glycol linkage at 4.08 ppm shifted upfield to 3.89 ppm and broadened.

In the case of complexation with Bu_4NCl, the NH protons of the calix[4]pyrrole unit of the ligand showed a small downfield shift from 8.15 to 8.26 ppm. In contrast to the complexation with Bu_4NF, the β-pyrrolic signals displacement was not observed and the other peaks did not show any change upon complexation.

When the solution of **9** was added to the excess of Bu_4NBr or Bu_4NI, no displacement of signals in the ^{1}H-NMR spectrum was observed. The results showed that Br^- and I^- could not form complex with ligand **9**.

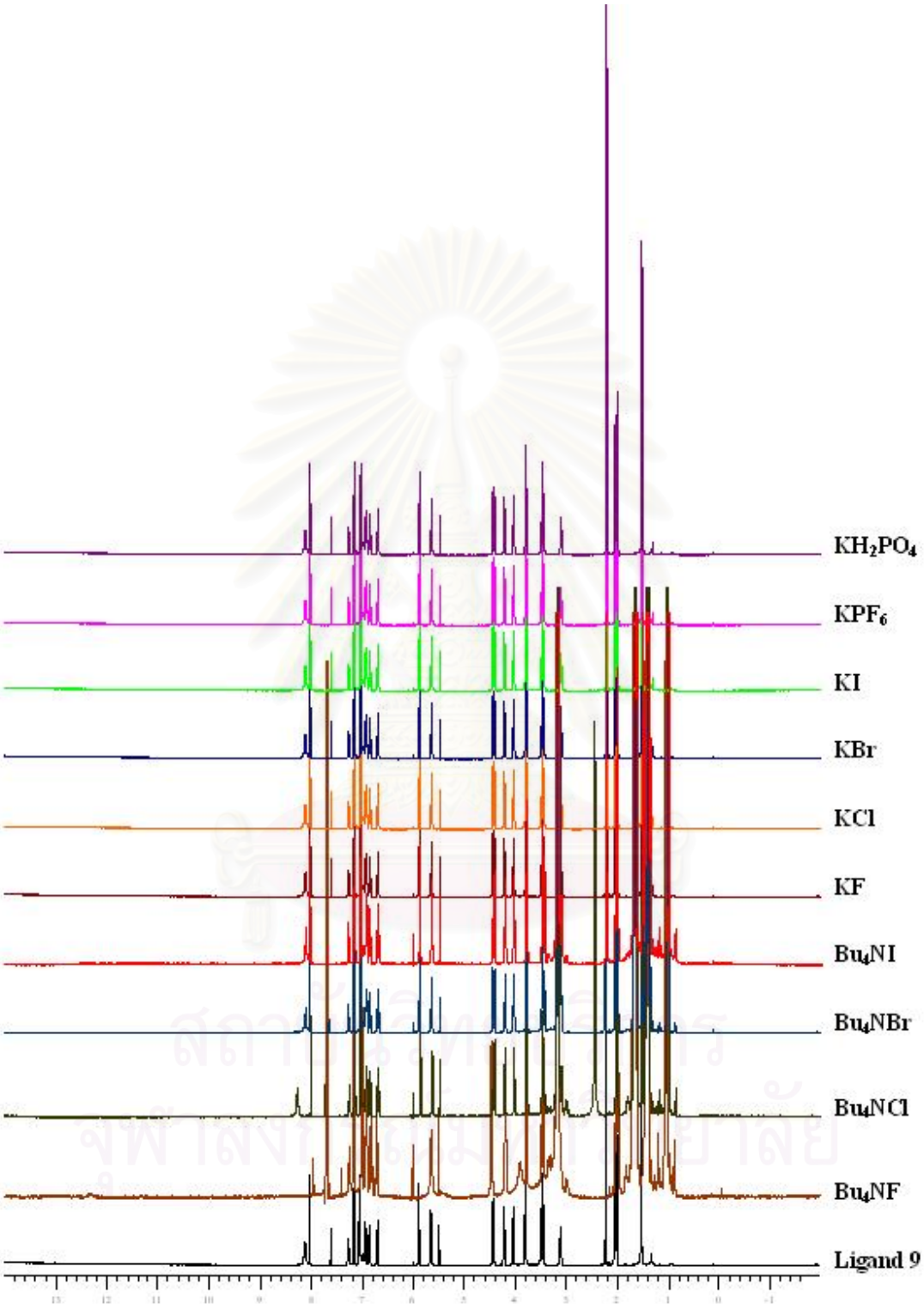


Figure 3.4 The ^{1}H-NMR spectra of **9** with various salts in a mixture of 1:9 $CDCl_3$:CD_3CN (v/v).

Considering the complexation of the ligand **9** with Bu_4NF or Bu_4NCl, the NH signal shifted downfield dramatically upon complexation with Bu_4NF, but showed a slightly shift upon complexation with Bu_4NCl. This result implied that the hydrogen bonding interaction between fluoride ion and calix[4]pyrrole moiety was stronger than that of chloride ion. In addition, the *β*-pyrrolic signals of the free ligand became a broad signal upon complexation with Bu_4NF, but did not change upon complexation with Bu_4NCl. This may indicate that the conformation of the calix[4]pyrrole moiety changed from 1,3-alternate to the cone conformation upon complexation with Bu_4NF which was also in agreement with the strong interaction provided by four pyrrolic NH protons. In the case of complexation with Bu_4NCl, chloride ion was bound by calix[4]pyrrole moiety in a 1,3-alternate conformation.

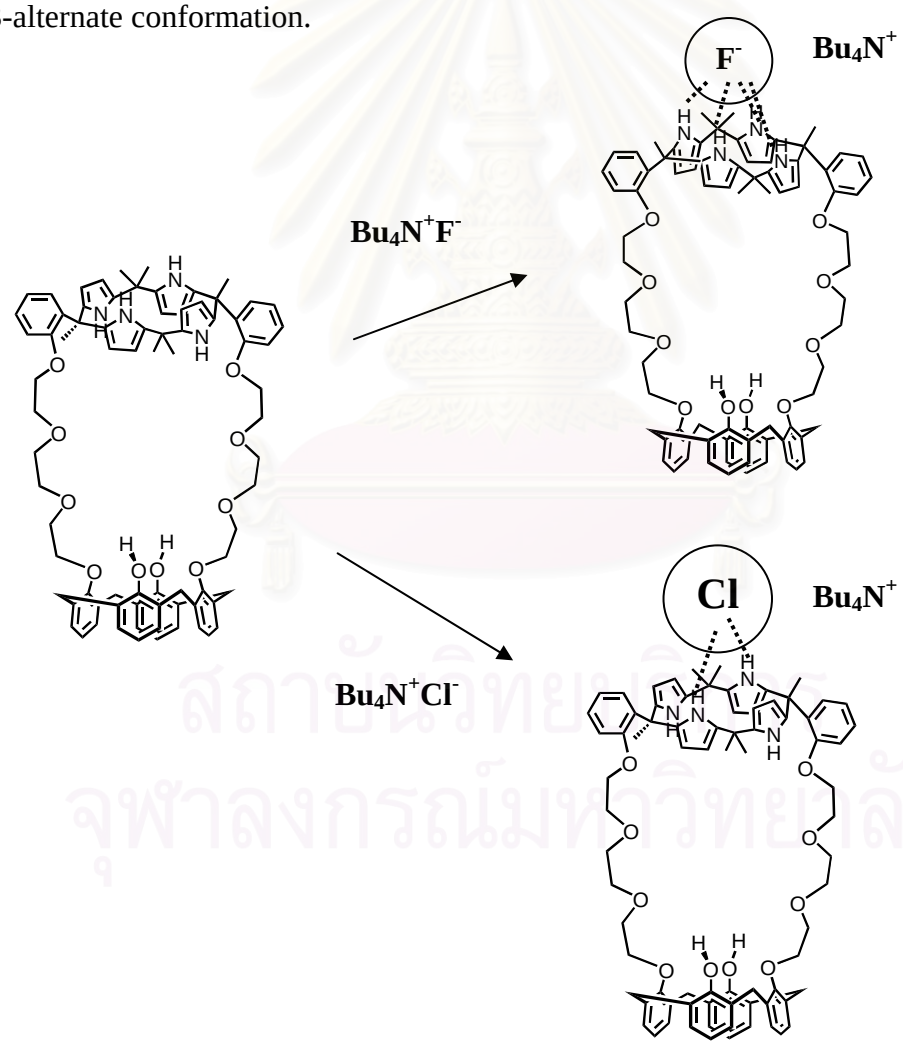


Figure 3.5 The complexation of ligand **9** towards Bu_4NF and Bu_4NCl.

In summary, the fluoride anion showed the greatest binding ability with calix[4]pyrrole moiety with 1,3-alternate-to-cone conformation change following by chloride anion with no change in conformation. This results corresponded to complexation behavior of anion binding of calix[4]pyrrole-parent system.[25]

However, in the case of Bu_4NF, the complex was observed which indicated that calix[4]pyrrole unit could accommodated F^- when tetrabutylammonium ion acted as a counter cation. These can be explained by the complex occurred in an exo-fashion (Figure 3.6) which made cation located outside the cavity. In addition, the cation solvation also played an important role in complexation in which the tetrabutylammonium ion could be solvated by CD_3CN and $CDCl_3$ easier than the potassium ion.

3.3.2 Complexation studies of ligand 9 towards potassium salts

Ligand **9** was also studied the complexation whether it can act as a heteroditopic receptor. Various potassium salts, (i.e., KF, KCl, KBr, KI, KH_2PO_4, KPF_6), were chosen to study in a mixture of 1:9 $CDCl_3/CD_3CN$ (v/v) of ligand **9**. In the case of potassium picrate, the complexation was carried out by using $CDCl_3$ as solvent. The ^{1}H-NMR spectra were recorded after the addition of the solution of the ligand and every 24 hours.

Upon addition of the mixture solution of ligand **9** to excess KF salt in the NMR tube. No displacement of signals observed in the ^{1}H-NMR spectrum (Figure 3.4). This indicated that the complexation did not occur.

When the solution of ligand **9** was added into excess KCl, KBr, KI, KH_2PO_4 and KPF_6 in the NMR tube, there was no significant shift of any peaks observed. This implied that no complexation occurred.

In the case of potassium picrate, when the solution of **9** in $CDCl_3$ was added to excess potassium picrate in the NMR tube, the solution did not turn to yellow at all. Accordingly, no signal displacement was observed in the ^{1}H-NMR spectrum (Figure 3.6). This implied that an inclusion of potassium picrate by ligand **9** was not occured.

From the complexation studies with tetrabutylammonium and potassium fluoride, it can be concluded that calix[4]arene-calix[4]pyrrole **9** cannot act as ion pair receptor

because ligand **9** could not bind K^+ with its glycol chains as seen in the case of complexations of ligand **9** with KPF_6 and potassium picrate. This might be due to the cavity was too large for potassium ion to accommodate. Besides this, the calix[4]pyrrole moiety could no longer bind F^- when there was potassium ion as a counter ion.

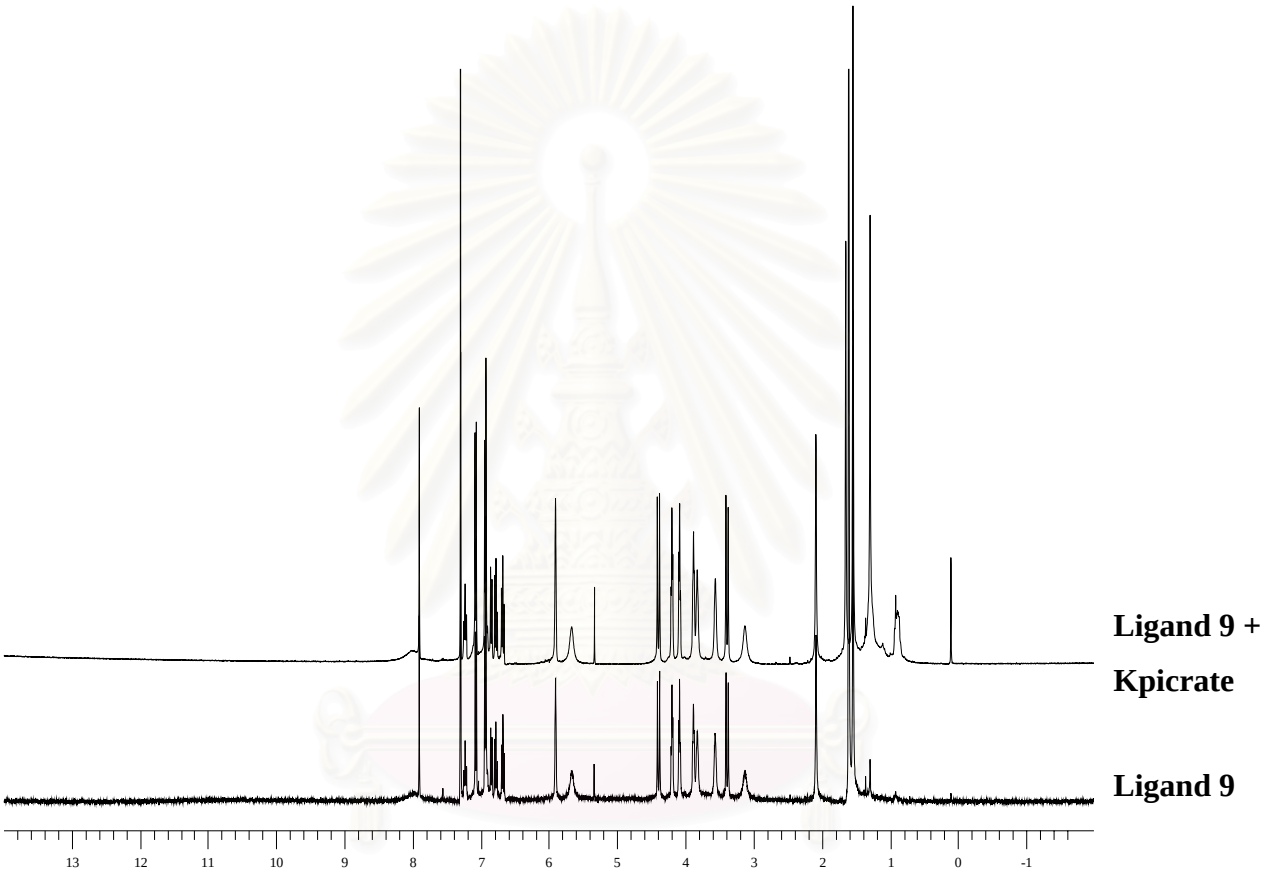


Figure 3.6 The ^{1}H-NMR spectra of **9** with potassium picrate in $CDCl_3$.

3.3.3 Complexation studies of ligand 11 towards tetrabutylammonium salts

Ligand **11** is composed of the binding sites for both cations and anions. It contains crown ether loop which has oxygen donor atoms and suitable cavity size for binding potassium ion.[43] In addition, the calix[4]pyrrole moiety connected to calix[4]arene platform by the glycol linkages is suitable for binding anions.

Upon addition of the CD_3CN solution of ligand **11** to excess Bu_4NF in the NMR tube, the signal of NH pyrrole protons at 8.15 ppm in ^{1}H-NMR spectrum of ligand **11** shifted downfield dramatically to 12.48 ppm (Figure 3.7). The signal of aromatic protons at 7.02 ppm of the free ligand showed a slightly upfield shift to 6.94 ppm. Surprisingly, the two singlet of CH pyrrole protons at 5.94 and 5.69 ppm of the free ligand shifted towards each other and coalesced to a broad signal at 5.69 ppm in the ^{1}H-NMR spectrum of the complex. In addition, the signal of the glycol linkage at 3.84 ppm shifted downfield to 3.69 ppm for the complex. These results indicated that fluoride anion was bound by the pyrrolic NH protons *via* hydrogen bond.

In the case of complexation with excess Bu_4NCl, the NH protons of the calix[4]pyrrole unit of the ligand **11** also shifted downfield from 8.15 to 9.40 ppm. In contrast to the complexation with Bu_4NF, the β-pyrrolic signals displacement was not observed and the other signals did not show any significant change upon complexation.

Upon addition of the solution of the ligand to Bu_4NBr, no chemical shift displacement in the ^{1}H-NMR spectrum was observed. The result showed that Br^- cannot form a complex with **11**.

Upon addition of the solution of the ligand to Bu_4NI, the signal displacement of NMR spectra cannot be observed in the ^{1}H-NMR spectrum. The result showed that I^- cannot form a complex with **11**.

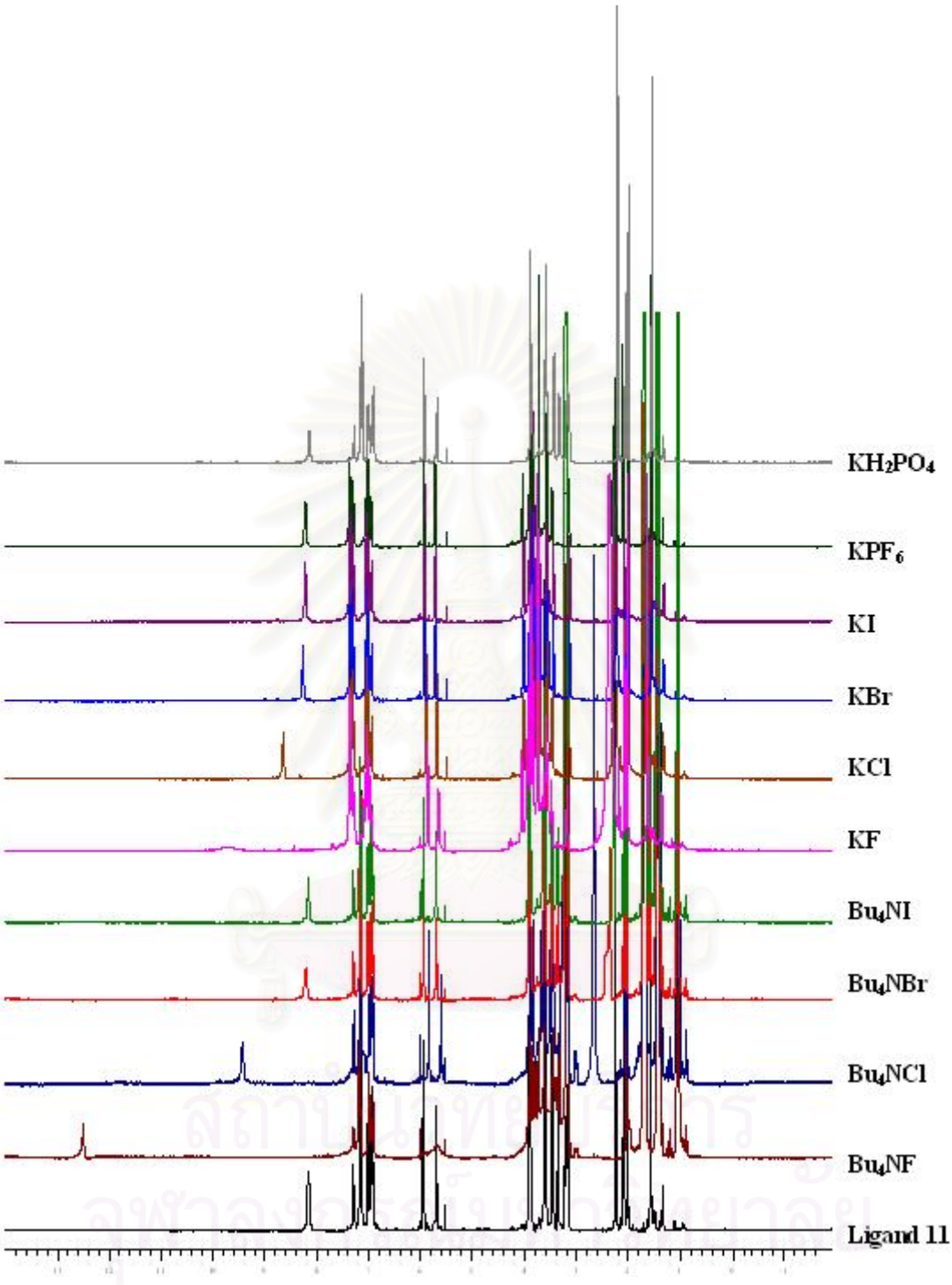


Figure 3.7 The ^{1}H-NMR spectra of **11** with various salts in CD_3CN.

In summary, fluoride anion showed the greatest binding ability with the cone conformation of calix[4]pyrrole moiety following by chloride anion in a 1,3-alternate conformation. The results corresponded to the anion binding ability of the ligand **9** (section 3.3.1) and the calix[4]pyrrole-parent system.[25] On the other hand, other anions (i.e., Br^-, I^-) cannot bind the ligand **11** due to the too large size of the anions to the calix[4]pyrrole moiety.

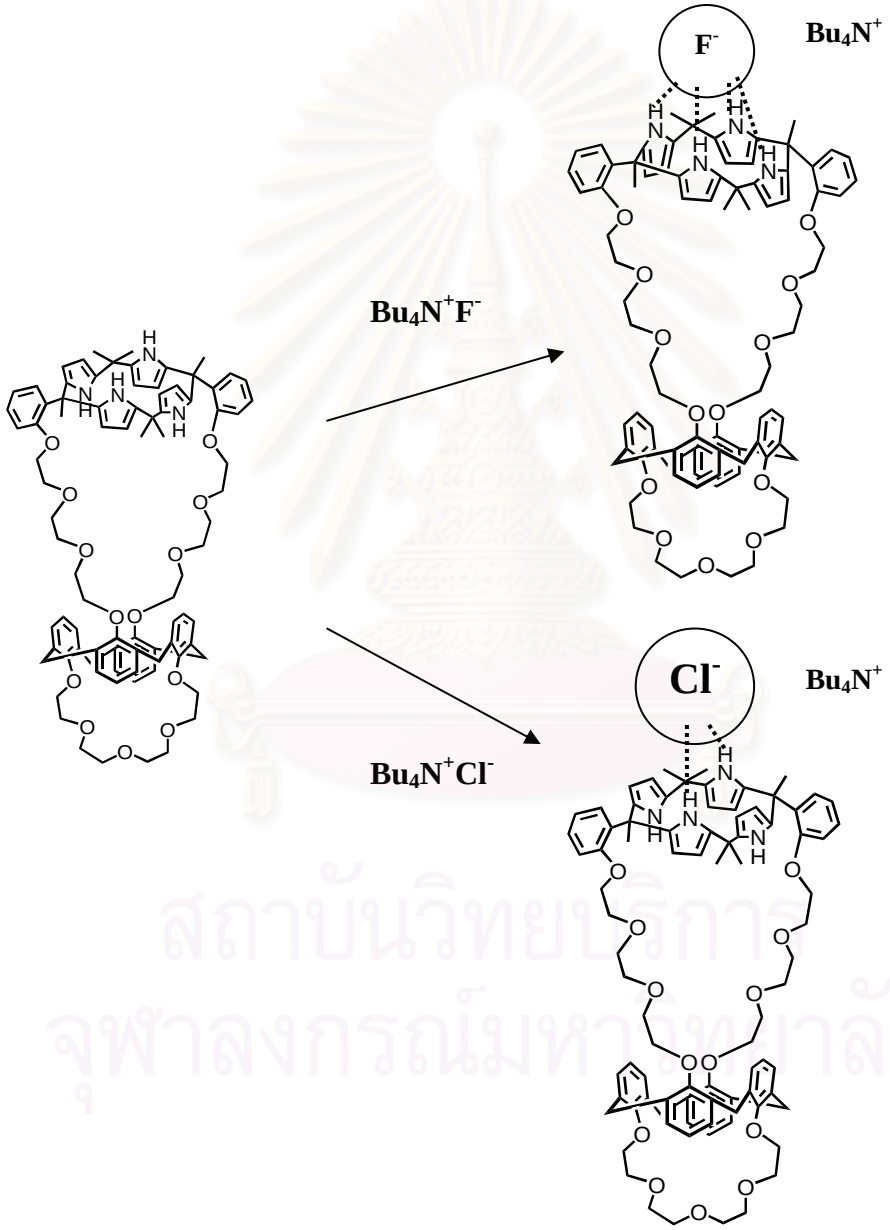


Figure 3.8 The proposed structure of ligand **11** upon complexation.

3.3.4 Complexation studies of ligand 11 towards potassium salts

In order to study an ion-pair complexation of **11**, various potassium salts, (i.e., KF, KCl, KBr, KI, KH_2PO_4, KPF_6), were therefore chosen to study in CD_3CN, while potassium picrate was studied in $CDCl_3$. The ^{1}H-NMR spectra were recorded after the addition of the solution of the ligand and every 24 hours.

Upon addition of the CD_3CN solution of the ligand **11** to excess KF salt in the NMR tube, the KF slowly dissolved in CD_3CN solution of the ligand **11**. The signal of pyrrolic NH migrated from 8.15 ppm to a broad signal at 9.82 ppm corresponding to the formation of fluoride complexes with a slow exchange complexation compared to the NMR timescale (Figure 3.7 and 3.9). The complexation reached equillibrium after 2 weeks. In contrast to the broad singlet of β-pyrrolic protons upon complexation with Bu_4NF, the β-pyrrolic protons still showed the two singlet signals but shifted from 5.94 and 5.69 ppm to 5.82 and 5.58 ppm, respectively. These results implied that F^- ion was bound to the calix[4]pyrrole moiety in a different conformer as previously discussed in the complexation with Bu_4NF (section 3.3.1 and 3.3.3).

Comparing to the complexation with Bu_4NF, the NH signal showed more dramatically downfield shift than that of KF. This result implied that, in the case of Bu_4NF, the hydrogen bonding interaction between fluoride ion and calix[4]pyrrole moiety was stronger than that of KF. In addition, the β-pyrrolic signals of the free ligand became a broad signal upon complexation with Bu_4NF, but still showed two singlet signals upon complexation with KF. This may implied that there was no conformation change of the calix[4]pyrrole moiety upon complexation with KF.

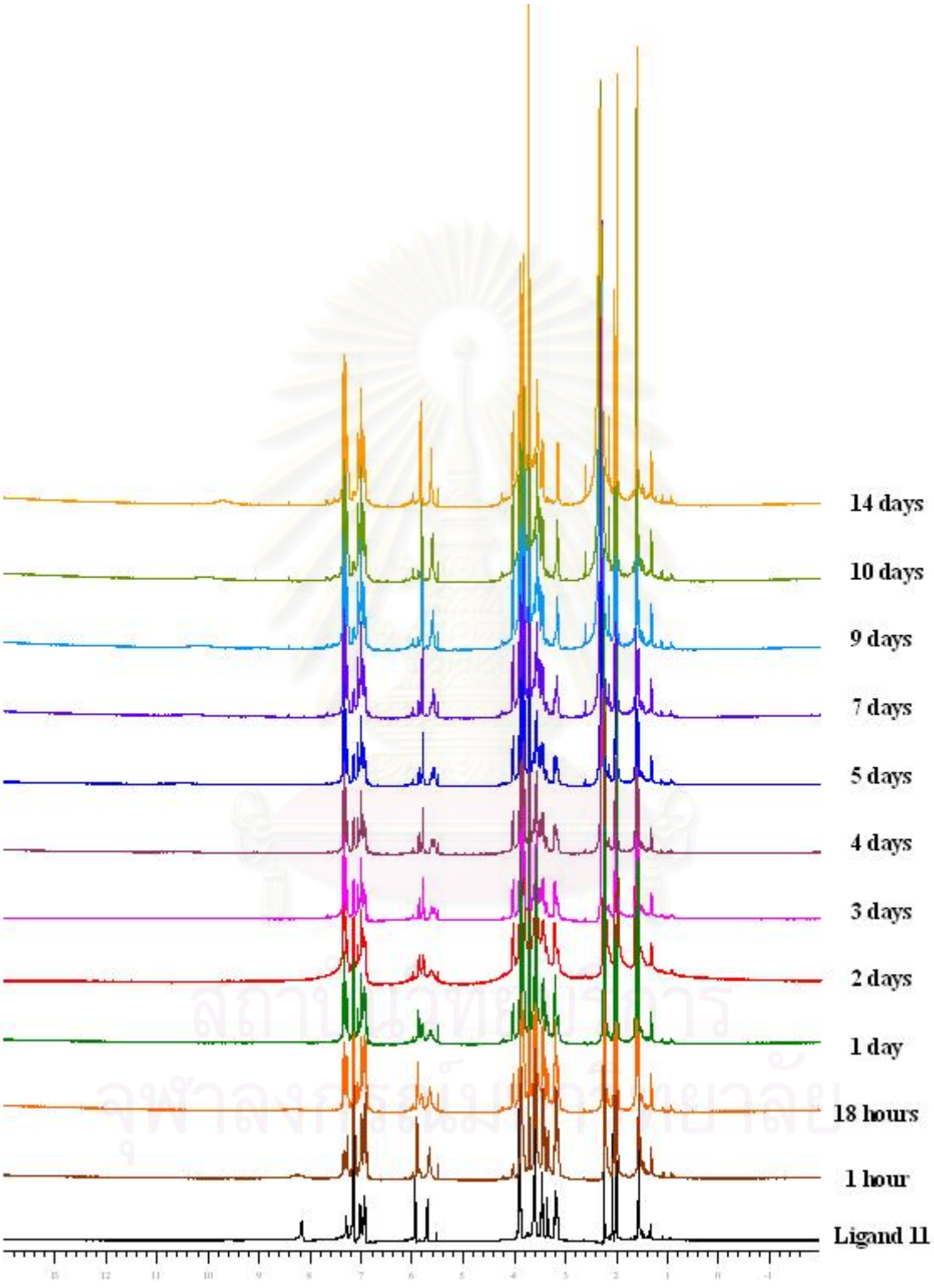


Figure 3.9 The ^{1}H-NMR spectra of **11** with KF in CD_3CN.

Furthermore, the signals of glycolic chain of the crown ether loop at 3.22 and 3.38 ppm disappeared and the new signals at 3.78 and 4.09 ppm were found. The doublet of the aromatic protons of the calix[4]arene unit at 7.17 ppm disappeared and the new signals at 7.01 and 7.38 ppm were found instead. These results suggested that K^+ ion was encapsulated into the crown cavity. These evidence implied that the fluoride ion might be encapsulated inside the calix[4]pyrrole containing cavity of **11** to act as ion pair guest which could avoid charge separation. These results led us to propose the structure of ligand **11** upon complexation with KF as depicted in Figure 3.10.

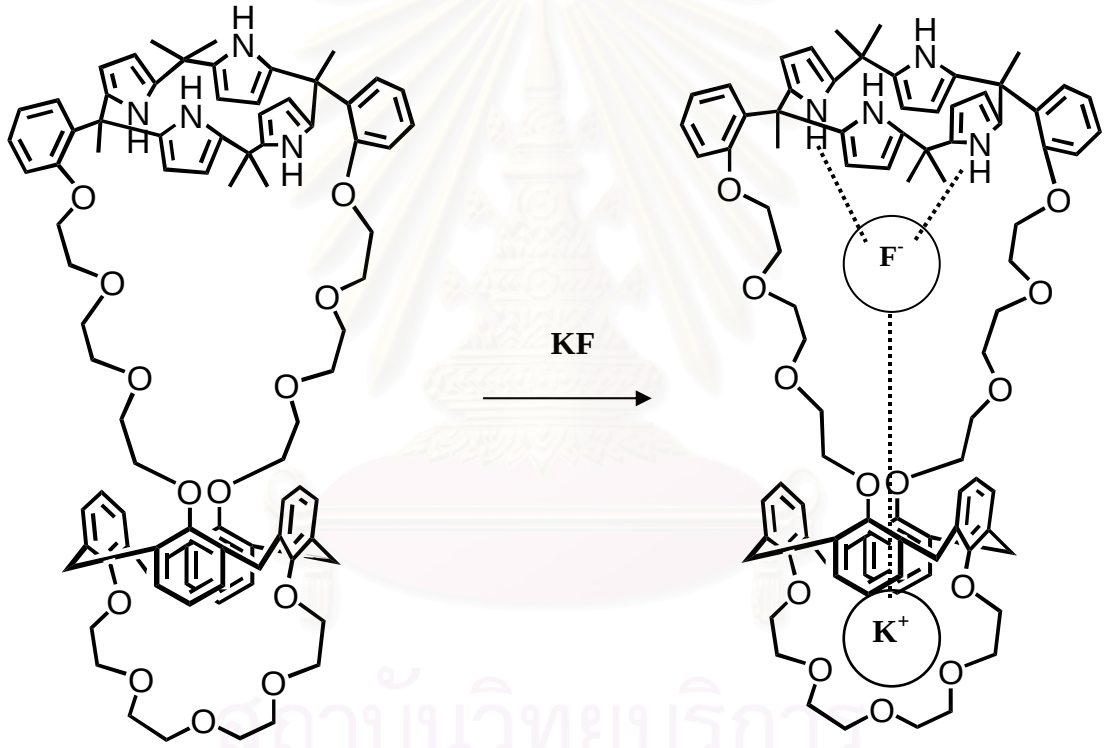


Figure 3.10 Proposed structure of ligand **11** with KF.

When the CD_3CN solution of **11** was added to the excess of KCl, the signals of pyrrolic NH of free ligand at 8.15 ppm slowly decreased while a new singlet at 8.49 ppm appeared and increased slowly (Figure 3.7 and 3.11). This implied that the complex formed with a slow process comparing to the NMR timescale. The complexation reached equillibrium within 4 days. Comparing to the complextion with KF, the singlet of pyrrolic NH and two singlet signals of β-pyrrolic protons of KCl complex showed less change than in KF complex. This may imply that the interaction between F^- ion and calix[4]pyrrole was stronger than that of Cl^- ion. Considering the crown cavity, the signal of glycolic chain of crown ether loop at 3.22 and 3.38 ppm disappeared and the new signals at 3.78 and 4.09 ppm were found. The doublet of the aromatic protons of the calix[4]arene unit at 7.17 ppm disappeared and the new signals at 7.01 and 7.38 ppm were found instead. These results indicated that potassium cation was accommodated in the crown cavity.

In accordance with KCl, upon addition of the CD_3CN solution of ligand **11** to excess KBr, the two singlet signals of β-pyrrolic protons did not show any change after complexation on the ^{1}H-NMR spectra (Figure 3.7 and 3.12). The signal of glycolic chain of crown ether loop at 3.22 and 3.38 ppm disappeared and the new signals at 3.78 and 4.09 ppm were found. The doublet of the aromatic protons of the calix[4]arene unit at 7.17 ppm disappeared and the new signals at 7.01 and 7.38 ppm were found instead. Whereas the signals of pyrrolic NH appeared at 8.15 ppm and 8.24 ppm. The complexation reached equillibrium within 2 days. These results also indicated that potassium cation located in the crown loop and bromide was slightly bound by calix[4]pyrrole moiety in a 1,3-alternate conformation.

In the case of KI, the changes of aromatic peaks at about 6.80-7.50 ppm and the glycolic peaks of crown moiety at 3.00-4.20 ppm were also the same as found in case of KCl and KBr complexes (Figure 3.7 and 3.13). These results also indicated that potassium cation was encapsulated in the crown cavity. The NH pyrrolic protons showed a very small downfield shift from 8.15 to 8.21 ppm which indicated that I^- ion may act only as a counter ion and may be not bound by calix[4]pyrrole moiety. The complexation was completed within 18 hours.

When the CD_3CN solution of **11** was added to the excess of KPF_6, the complexation was completed immediately upon addition of ligand. The ^{1}H-NMR spectra, Figure 3.7, showed that the only signals of the aromatic protons at about 6.80-7.50 ppm and the glycolic peaks of crown moiety at 3.00-4.20 ppm were changed. No signal displacement of NH peak was observed. From these results suggested that the potassium cation was complexed in the crown cavity.

Interestingly, upon addition of KH_2PO_4 to the solution, no signal displacement was observed in the ^{1}H-NMR spectrum (Figure 3.7). These results showed that **11** could not complex KH_2PO_4. This might be attributed to the strong ion pair effect of K^+ and $H_2PO_4^-$ over complexation with the ligand **11**.

With potassium picrate, the complexation with ligand **11** was studied employing CD_3Cl due to this salt is not soluble in CD_3Cl without complexation. The solution of **11** in $CDCl_3$ was added to potassium picrate in an NMR tube and the solution turned yellow immediately. This indication implied that potassium picrate was complexed by the ligand **11**. From ^{1}H-NMR spectra (Figure 3.14), a singlet of picrate protons appeared at 8.80 ppm and an upfield shift of glycolic protons of the crown unit from a multiplet at 3.7-3.9 ppm to a singlet at 3.99 ppm was also observed. The integration ratio between picrate protons and aromatic protons of the ligand indicated the formation of a 1:1 complex after 3 days. These results led us to conclude that only crown-5 cavity could accommodate the potassium ion.

In conclusion, calix[4]arene-calix[4]pyrrole-crown-5 **11** could act as an ion pair receptor. This ligand could bind K^+ with oxygen donor atom in the crown ether loop, not in the triethylene glycol linkage as we could see from the complexation of ligand **11** with potassium picrate and KPF_6. The host **11** showed a strong interaction with F^- over Cl^-, Br^- and I^-. In the case of $H_2PO_4^-$, no complexation between ligand **11** and $H_2PO_4^-$ occurred. In the case of potassium picrate, potassium cation resided in the crown ether loop.

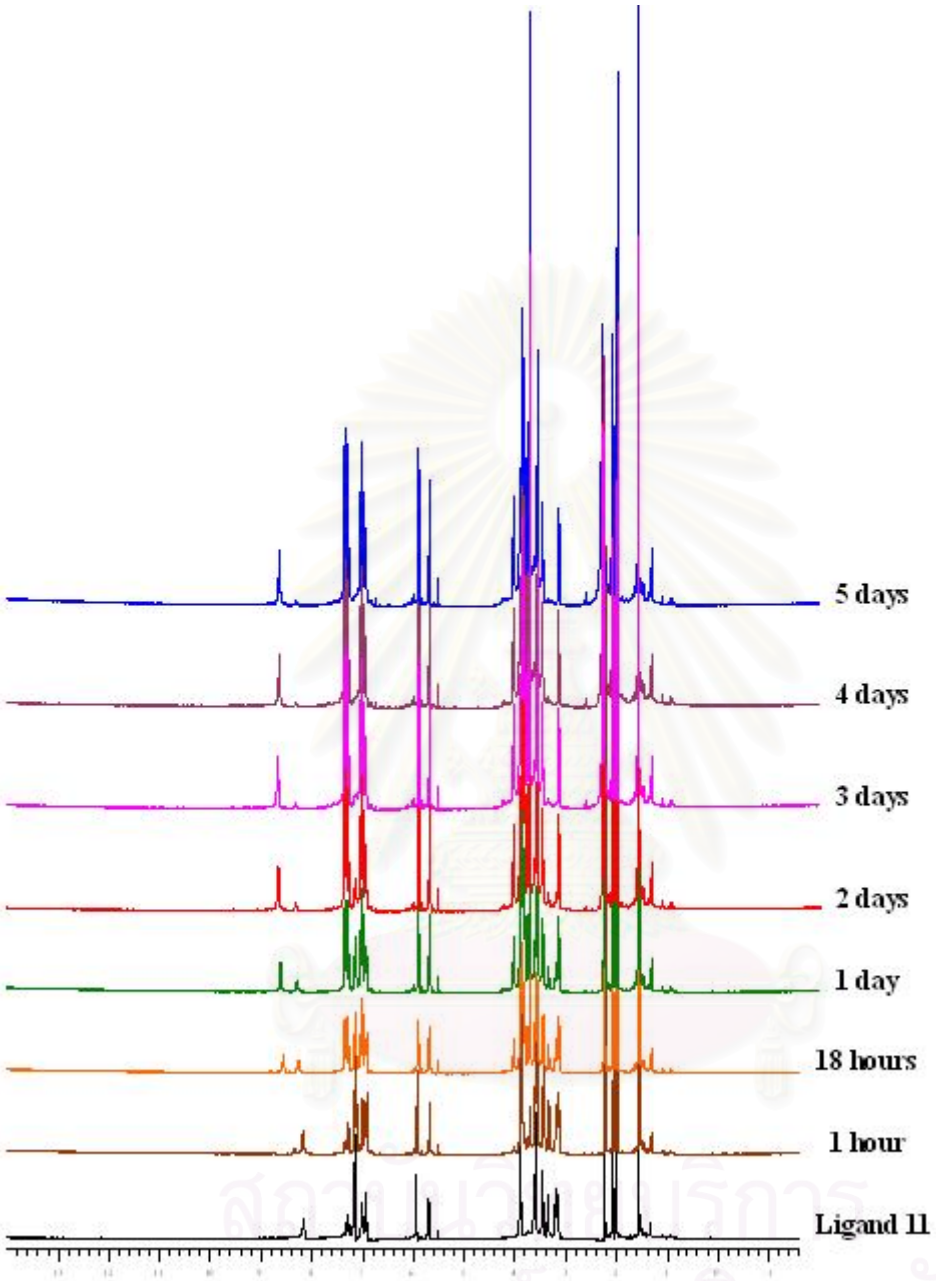


Figure 3.11 The ^{1}H-NMR spectra of **11** with KCl in CD_3CN**.**

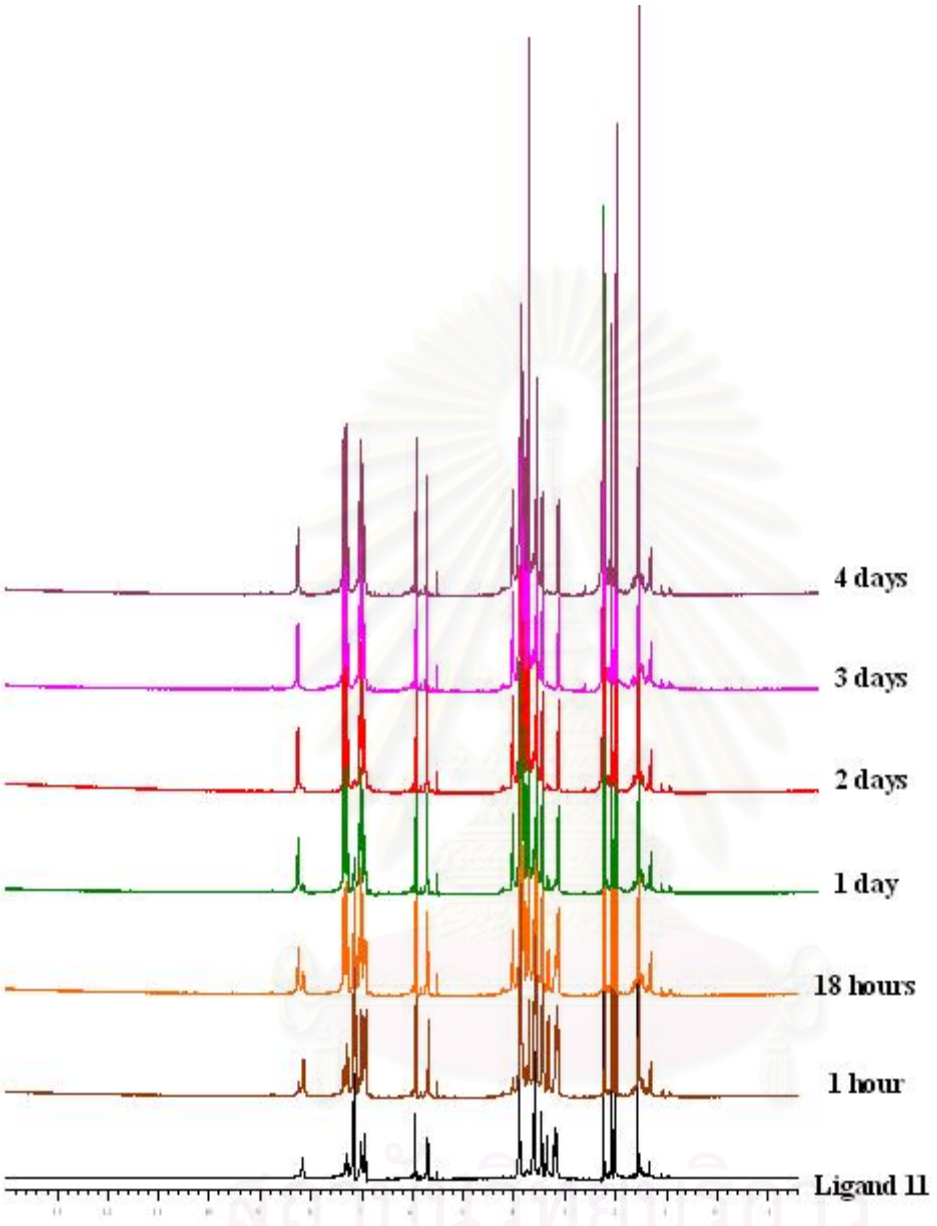


Figure 3.12 The ^{1}H-NMR spectra of **11** with KBr in CD_3CN.

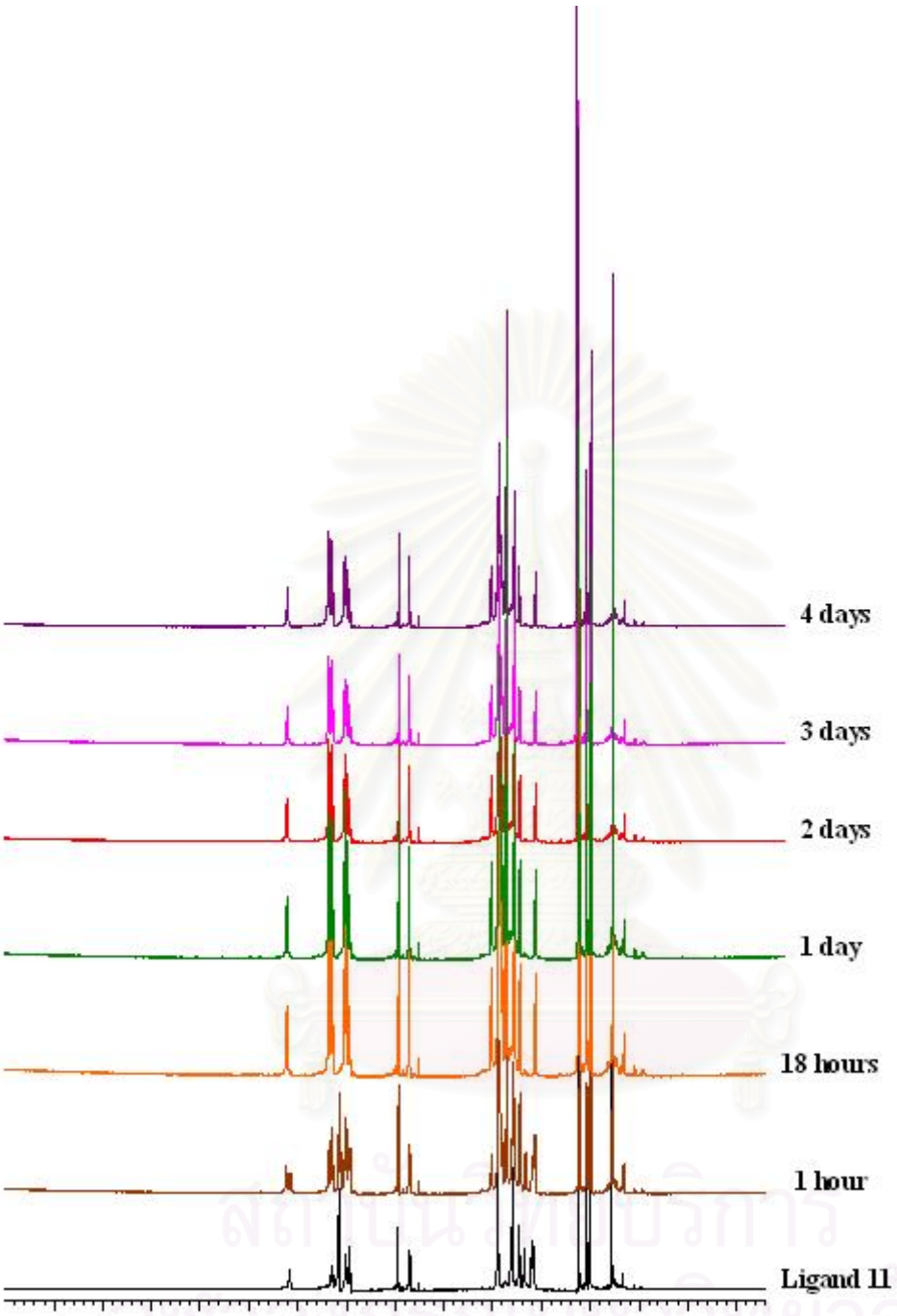


Figure 3.13 The ^{1}H-NMR spectra of **11** with KI in CD_3CN**.**

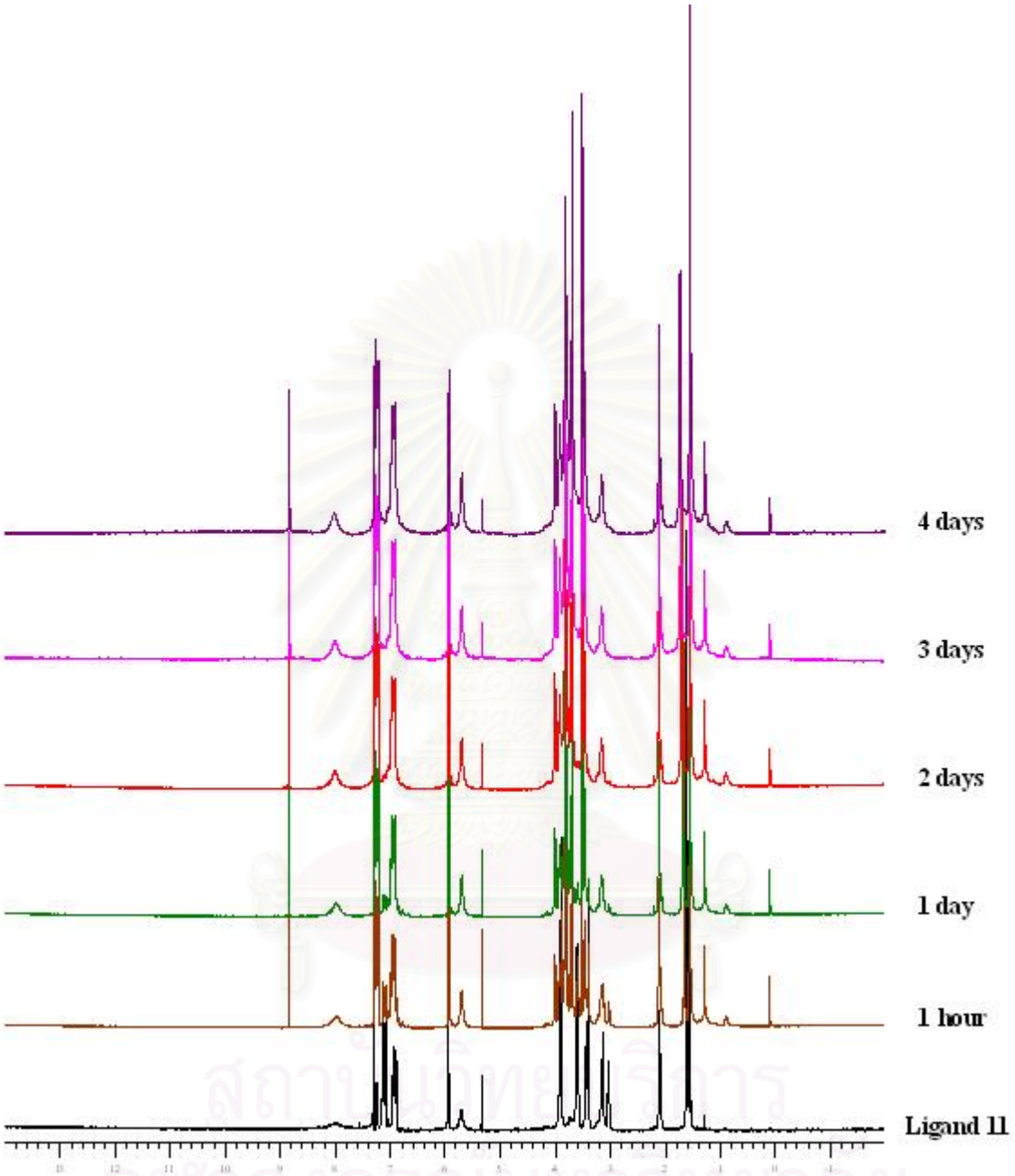


Figure 3.14 The ^{1}H-NMR spectra of **11** with potassium picrate in $CDCl_3$.

3.4 Complexation studies by ^{1}H-NMR titration

3.4.1 Complexation titration of ligand 9 towards tetrabutylammonium fluoride

^{1}H-NMR titration experiments of **9** towards Bu_4NF was performed in a 1:9 mixture of $CDCl_3$ and CD_3CN (v/v) and the ^{1}H-NMR spectra were shown in Figure 3.15. Upon each addition of fluoride anion to the solution of **9**, the signal of pyrrolic NH of free ligand at 8.15 ppm slowly decreased and disappeared after addition of 0.5 equiv. of anion while a new singlet at 12.49 ppm appeared and increased slowly after addition of 3.0 equiv. of anion. As a result, the association constant cannot be calculated. The results suggested that **9** bound fluoride anion with a strong hydrogen bonding interaction with a slow exchange complexation compared to the NMR timescale and their complexation led to the change in conformation of calix[4]pyrole moiety from 1,3-alternate to the cone conformation.

3.4.2 Complexation titration of ligand 11 towards tetrabutylammonium fluoride

Upon addition of a solution of Bu_4NF to the solution of ligand **11**, the signal of NH protons at 8.15 ppm in ^{1}H-NMR spectra (Figure 3.16) decreased slowly and the new NH signal at 12.48 ppm increased significantly. In addition, the characteristic peaks of CH pyrrole protons at 5.94 and 5.69 ppm migrated towards each other and coalesced to a singlet peak at 5.69 ppm. These suggested that **11** bound fluoride anion with a strong hydrogen bonding interaction and their complexation led to the change in conformation of calix[4]pyrole moiety from 1,3-alternate to cone conformation. The association constant with fluoride anion was 1721 M^{-1}.

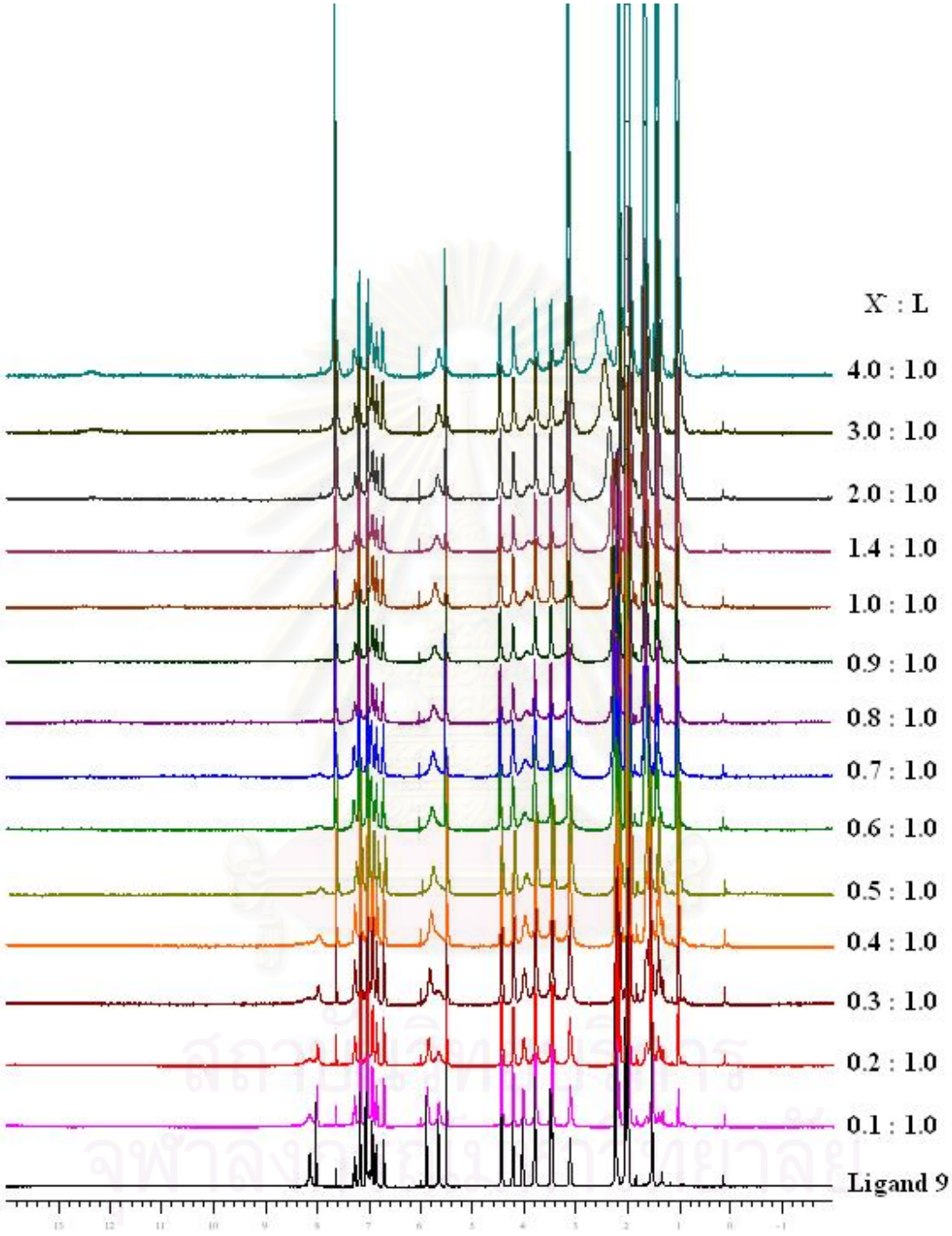


Figure 3.15 The ^{1}H-NMR spectra of titration of **9** with $Bu_4N^+F^-$ in a mixture of 1:9 $CDCl_3$:CD_3CN (v/v).

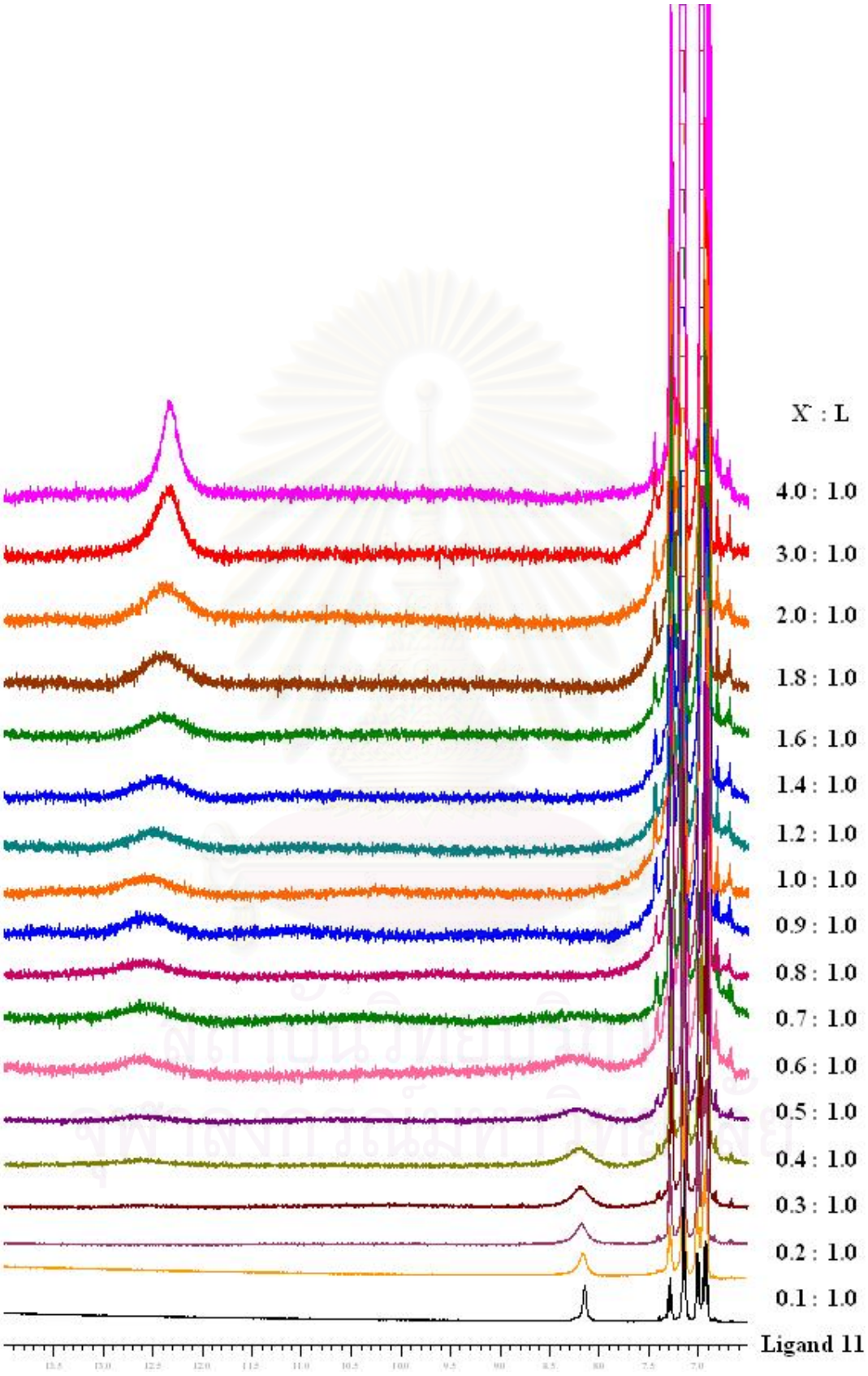


Figure 3.16 The ^{1}H-NMR spectra of **11** with various equiv. of $Bu_4N^+F^-$ in CD_3CN.

3.4.3 Complexation titration of ligand 11 towards tetrabutylammonium chloride

Upon addition of Bu_4NCl to the solution of **11**, the signals of NH pyrrole migrated from 8.15 ppm to 8.36 ppm as in Figure 3.17. The chemical shift displacements of NH signal (δ) were collected in Table 3.1.

Table 3.1 The chemical shifts of NH protons of **11** upon addition of chloride anion.

Equivalents of chroride ion	Chemical shifts	
	δ (ppm)	Δδ (ppm)
0.00	8.146	0.000
0.10	8.164	0.018
0.20	8.181	0.035
0.30	8.196	0.050
0.40	8.210	0.064
0.50	8.228	0.082
0.60	8.236	0.090
0.70	8.238	0.092
0.80	8.249	0.103
0.90	8.259	0.113
1.00	8.273	0.127
1.20	8.295	0.149
1.40	8.312	0.166
1.60	8.328	0.182
1.80	8.346	0.200
2.00	8.358	0.212

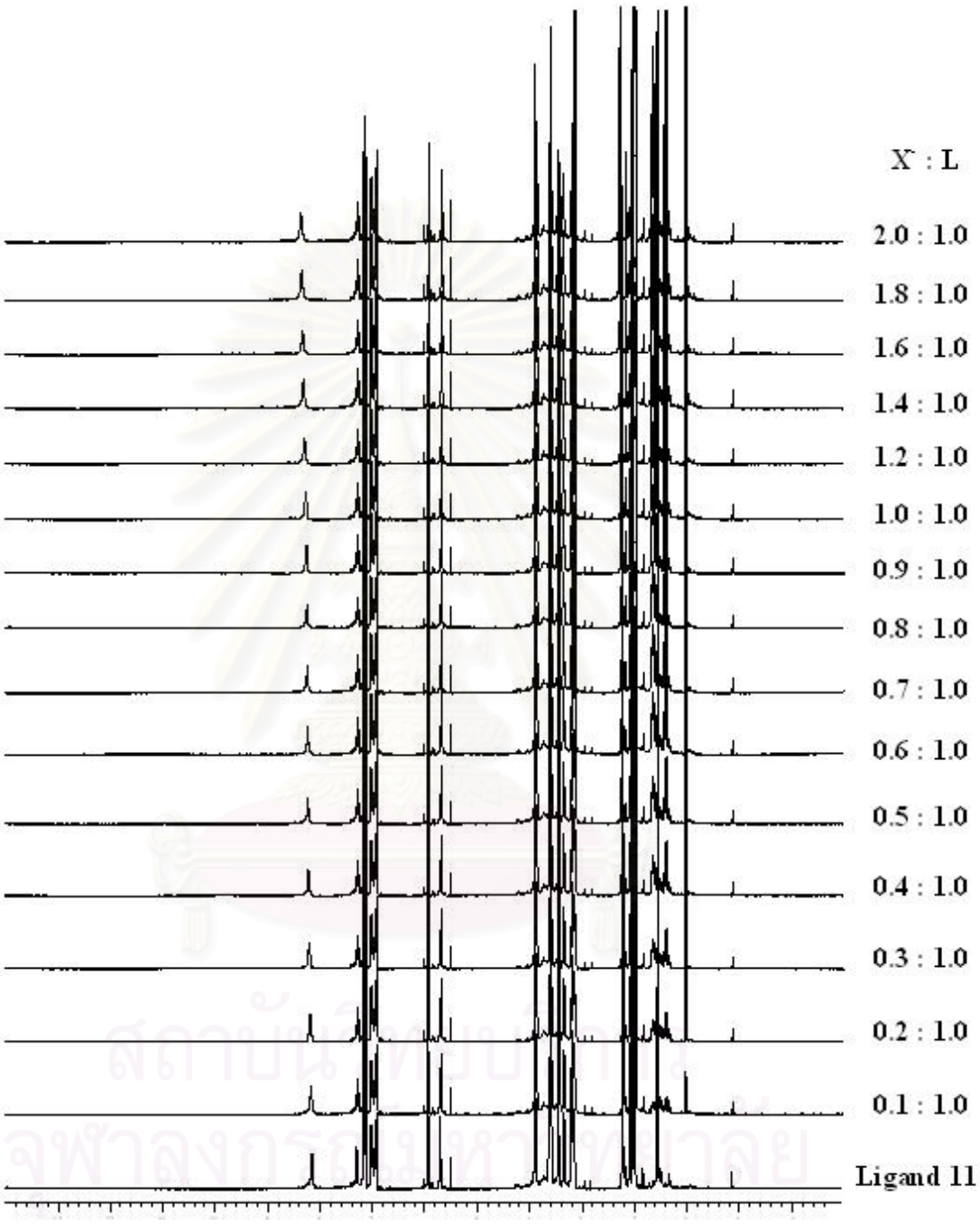


Figure 3.17 The ^{1}H-NMR spectra of **11** with various equiv. of $Bu_4N^+Cl^-$ in CD_3CN.

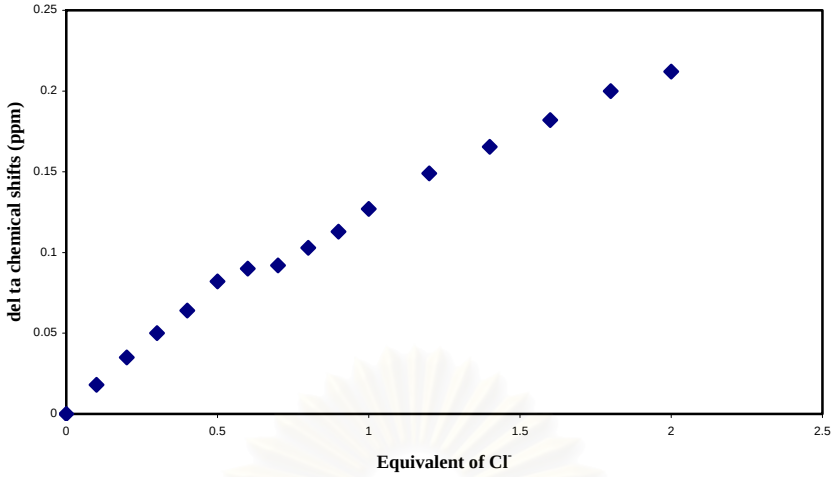


Figure 3.18 The ^{1}H-NMR titration curve of ligand **11** towards chloride anion in CD_3CN on the chemical shift of NH protons.

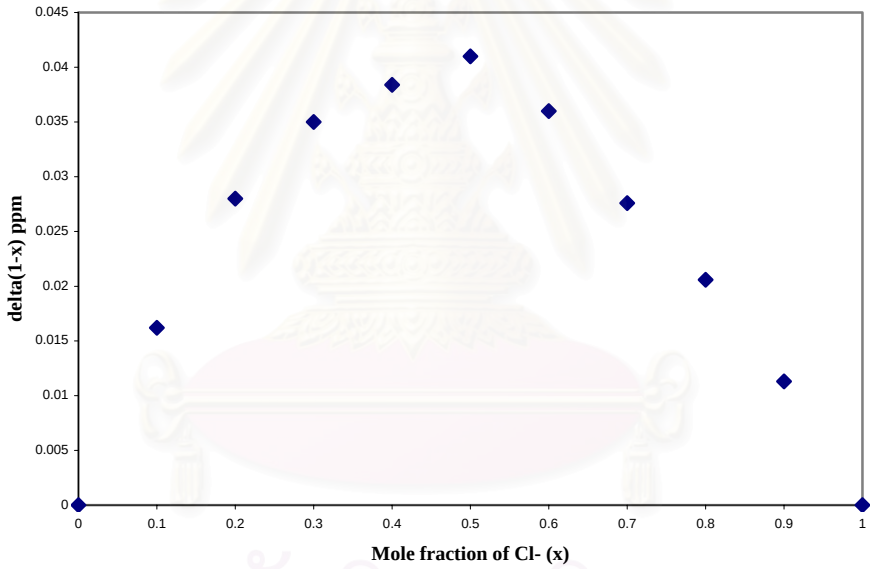


Figure 3.19 Job's plot of the complexation of ligand **11** towards chloride anion in CD_3CN on the chemical shift of NH protons.

Plot of $\Delta\delta$ against equivalents of fluoride ion was shown in Figure 3.18. The association constant was calculated by EQNMR program.[44]

The Job's plot of **11**.Cl^- was symmetric and showed a maximum at the mole fraction of guest being 0.5, which indicated a 1:1 guest-host stoichiometry as shown in Figure 3.19. The association constant with chloride anion determined by using EQNMR program was 457 M^{-1}.

3.4.4 The complexation titration of ligand 11 in the presence of potassium ion towards fluoride ion

As Ligand **11** had a crown-5 cavity which was selective towards K^+, thus, it was interesting to investigate the effect of K^+ on anion binding ability of ligand **11**. ^{1}H-NMR titration experiment of ligand **11** in the presence of 2 equivalents of KPF_6 to form complex **11**.K^+ was carried out.

From ^{1}H-NMR spectra Figure 3.20, upon addition of 0-1 equiv. of Bu_4NF into a solution of complexes **11**.KPF_6, the displacement of NH protons signal was not observed. This suggested that the complexation of **11** with F^- was not occurred. But obviously, the NH signal showed a slightly downfield shift after addition 1.0-2.0 equiv. of Bu_4NF. This result indicateed that the F^- bound ligand **11** and the change in conformation of calixpyrrole moiety was not occurred which confirmed by the coalesce of two sharp singlets of β-pyrrolic protons at 5.93 and 5.72 ppm. Furthermore, the changes of signals in the NMR spectra were also observed after addition of 2.0-4.0 equiv. of Bu_4NF. The signal of pyrrolic NH of free ligand at 8.28 ppm slowly decreased and disappeared after addition 2.2 equiv. of anion while a new singlet at 12.49 ppm appeared and increased slowly after addition 3.0 equiv. of anion. As a similar result as section 3.4.1, the association constant cannot be calculated. In addition, the characteristic peaks of CH pyrrole protons at 5.94 and 5.69 ppm migrated towards each other and coalesced to a singlet peak at 5.69 ppm. Moreover, the slightly shift of glycolic regions at 3.25-3.42 ppm were also observed in the spectra.

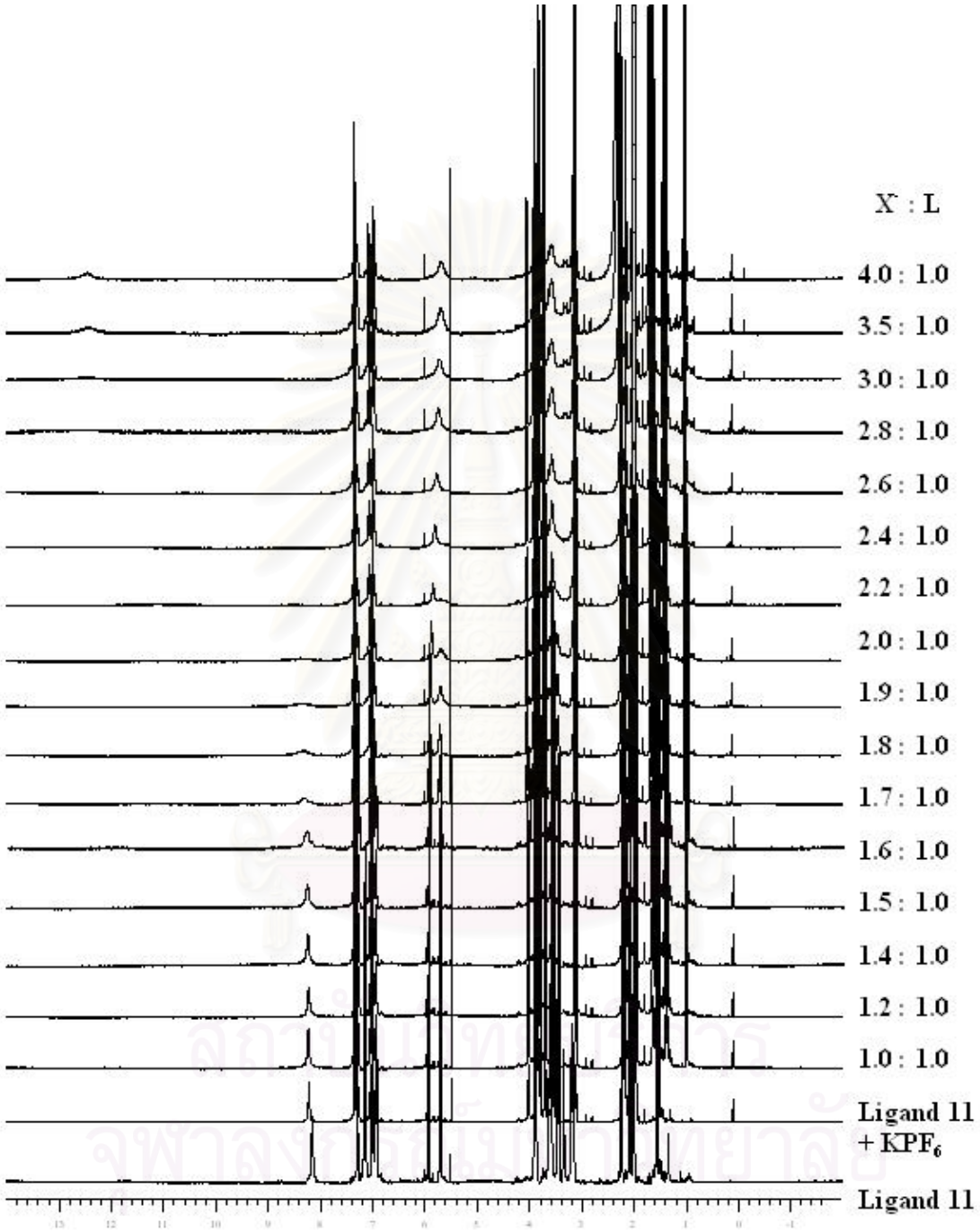


Figure 3.20 The ^{1}H-NMR spectra of titration of **11** in the presence of 2 equiv. of KPF_6 with various equiv. of $Bu_4N^+F^-$ in CD_3CN.

These indications suggested that **11** bound fluoride anion with a strong hydrogen bonding interaction and their complexation led to the change in conformation of calix[4]pyrole moiety from 1,3-alternate to cone as we have seen in the complexation of **11** with Bu_4NF. The F^- ion complexation accompanying by the conformation change occurred after 1 equivalent of Bu_4NF was added which indicated that potassium ion had a negative allosteric effect to fluoride complexation. By comparison of ^{1}H-NMR spectrum of complex between ligand **11** and KF, it was formed that the ^{1}H-NMR spectrum of complex of ligand **11** with Bu_4NF in the presence with KPF_6 was different. This led us to conclude that the fluoride ion location was different. In the case of KF complex, F^- ion might be complexed inside cavity nearby calix[4]pyrrole unit (endo-complex) whereas, in the case of Bu_4NF complex in the presence of KPF_6, F^- ion was accommodated in an exo-fashion (as shown in Figure 3.18).

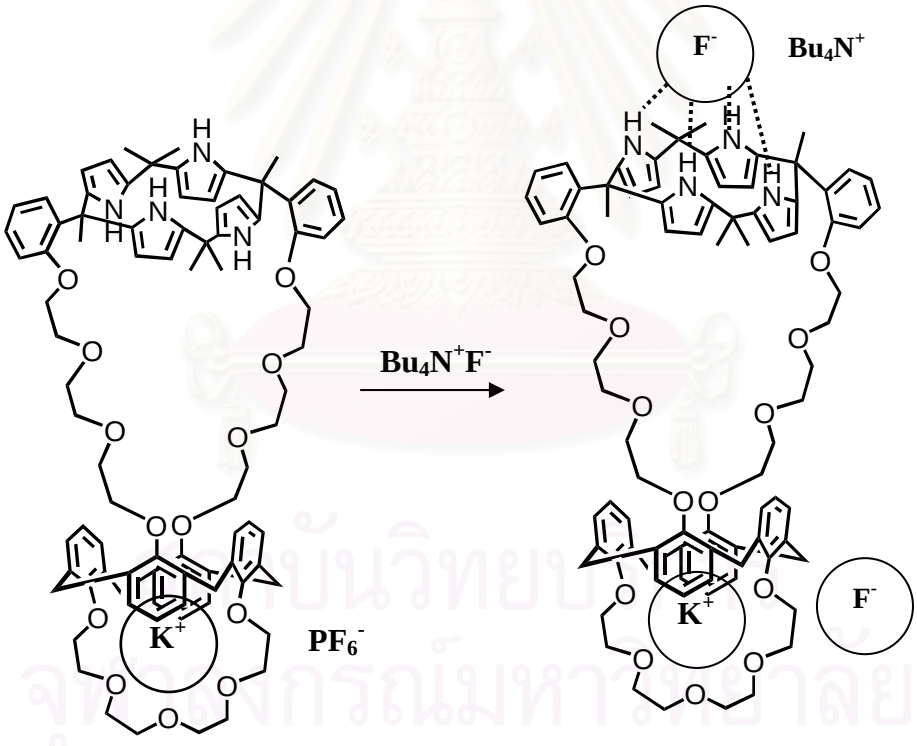


Figure 3.21 The proposed complex structure of ligand **11** with Bu_4NF in the presence of KPF_6.

3.5 Selective binding studies

3.5.1 Complexation study of ligand 11 in the presence of Bu_4NF towards Bu_4NCl

Upon addition of Bu_4NCl to the solution of ligand **11** in the presence of Bu_4NF, no signal displacement in the spectra was observed (Figure 3.22). The result implied that ligand **11** did not bind chloride anion in the presence of fluoride anion.

3.5.2 Complexation study of ligand 11 in the presence of Bu_4NCl towards Bu_4NF

Upon addition of Bu_4NF to the solution of ligand **11** in the presence of Bu_4NCl, the pyrrolic NH peak at 8.45 ppm showed a strong downfield shift to 12.48 ppm (Figure 3.23). The two singlet peaks of β-pyrrolic protons at 5.94 and 5.69 ppm also became a broadened peak at 5.69 ppm. These results were similar to the complexation of ligand **11** with Bu_4NF.

In summary, it can be concluded that ligand **11** prefer to bind fluoride anion over the other putative anion which are in accordance with the fluoride selective binding as discussed in the former section.

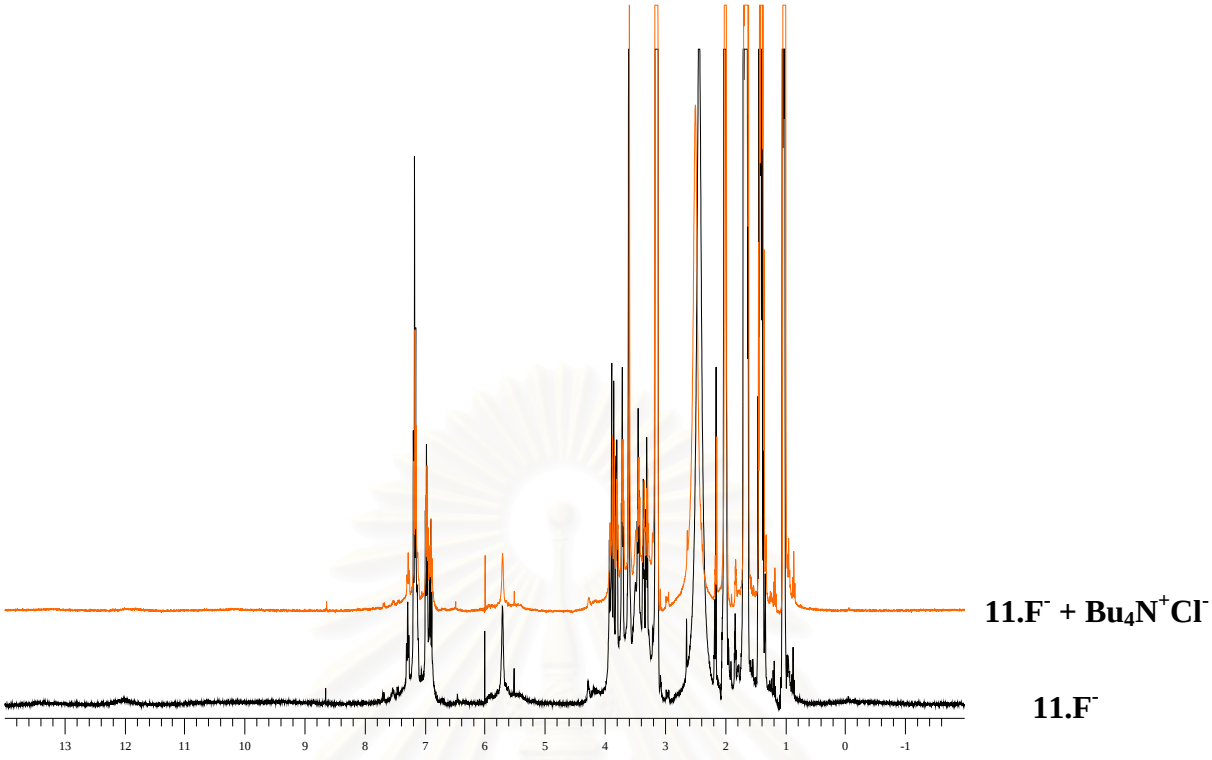


Figure 3.22 The ^{1}H-NMR spectra of complexation study of **11.F^{-}** with Bu_4NCl.

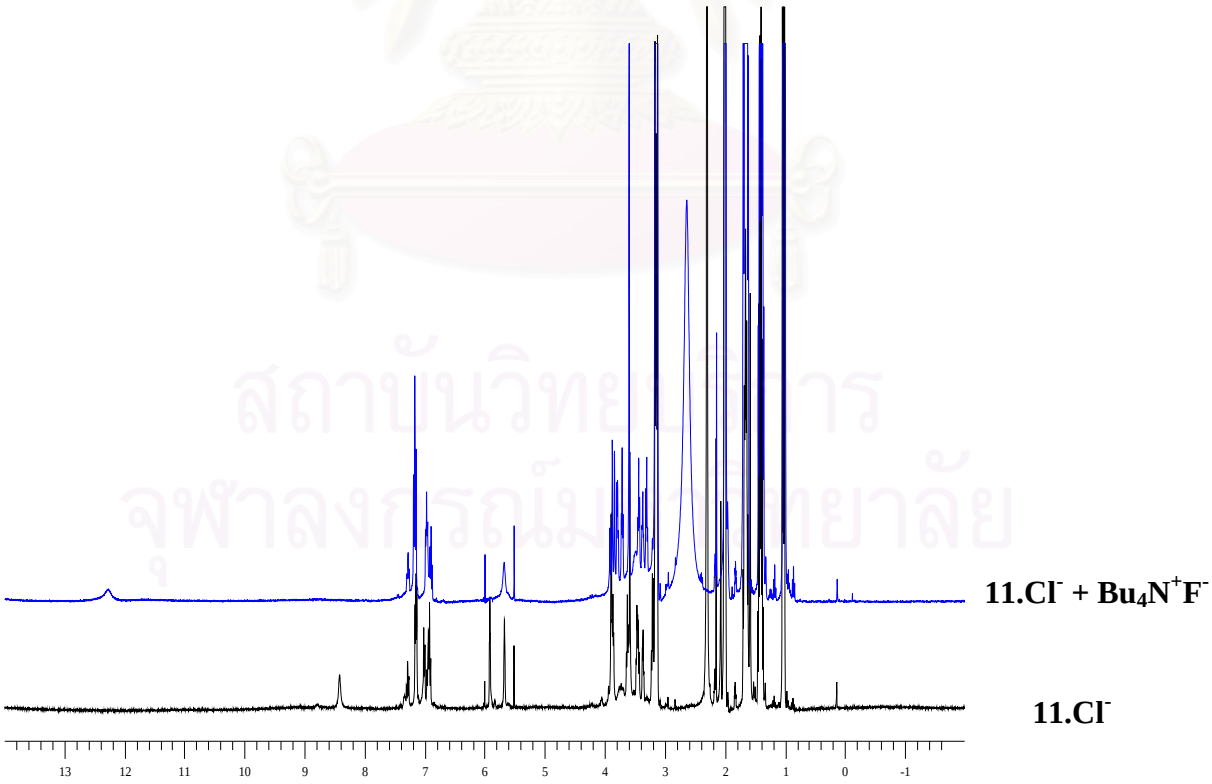


Figure 3.23 The ^{1}H-NMR spectra of complexation study of **11.Cl^{-}** with Bu_4NF.

CHAPTER IV

CONCLUSION

The ligands, bis(calix[4]arene)-calix[4]pyrrole (**5**), calix[4]arene-calix[4]pyrrole (**9**), *p-tert*-butylcalix[4]arene-calix[4]pyrrole (**10**) and 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (**11**) have been synthesized.

The synthetic pathway started with a condensation of 2-(triethyleneglycol tosylate) acetophenone (**2**) with calix[4]arene to afford 1,3-calix[4]-diacetophenone (**3**) in 82% yield. The condensation of diketone **3** with pyrrole afforded 1,3-calix[4]-bis-dipyrroethane (**7**) with 61%yield. The coupling of **3** and **7** in dried dichloromethane using Bu_4NF as a template and *TFA* as a catalyst affforded bis(calix[4]arene)-calix[4]pyrrole (**5**) in 2% yield.

In case of calix[4]arene-calix[4]pyrrole (**9**), the cyclization of 1,3-calix-[4]-bis–dipyrroethane (**7**) with excess acetone yielded calix[4]arene-calix[4]pyrrole (**9**) in 37%.

The analogue of **9**, *p-tert*-butylcalix[4]arene-calix[4]pyrrole (**10**), was also synthesized by starting with the synthesis of 1,3-*p-tert*-butylcalix[4]-diacetophenone (**4**) (63%). The condensation of **4** with pyrrole provided 1,3-*p-tert*-butylcalix[4]-bis-dipyrroethane (**8**) (35%). When dipyrroethane **8** was treated with an excess acetone in the presence of $BF_3.OEt_2$ gave **10** in 33% yield.

The synthesis of 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (**11**), was accomplished by bridging **9** with tetraethyleneglycol ditosylate to obtain **11** in 68% yield.

The solid structure of **9** was determined by X-ray crystallography. The calix[4]arene unit was in a pinched cone conformation stabilized by two O-H of calix[4]arene unit. In contrast to calix[4]arene, the calix[4]pyrrole unit adopted in a 1,3-alternate conformation. Interestingly, one of the phenyl units connected to the calix[4]pyrrole unit oriented up the plane, while the other oriented down. This probably resulted from a strong hydrogen bonding of pyrrolic N-H to oxygen of glycolic chain which led calix[4]pyrrole to bend down to calix[4]arene unit and destroy the symmetry of the molecule.

The complexation studies of the synthesized ligands **9** and **11** were carried out with tetrabutylammonium and potassium salts by ^{1}H-NMR spectroscopy.

From the complexation with tetrabutylammonium and potassium fluoride study, calix[4]arene-calix[4]pyrrole (**9**) could not act as ion pair receptor because ligand **9** could not bind K^+ with its glycol chains as seen in the case of complexations of ligand **9** with KPF_6 and potassium picrate. This might be come from that the cavity was not fit for potassium ion. Besides this, the calix[4]pyrrole moiety could not bind F^- when there was potassium ion as a counter ion.

However, in the case of Bu_4NF, the complex was observed which indicated that calix[4]pyrrole unit could accommodated F^- when tetrabutylammonium ion acted as a counter cation. These could be explained by the complex occurred in an exo-fashion which made cation located outside the cavity.

In the case of complexation with NBu_4Cl, These results indicated that chloride was bound by calix[4]pyrrole moiety in 1,3-alternate conformation.

Ligand **11** can act as an ion pair receptor. The potassium ion resided in the crown ether loop. Moreover, it interacted with F^- stronger than other putative anionic guests (*viz*. Cl^-, Br^-, I^-, $H_2PO_4^-$ and PF_6^-). These may be due to the ability of fluoride anion that can form a strong hydrogen bond with calix[4]pyrrole.

In the case of complexation with potassium salts, the anions located in calix[4]pyrrole containing cavity of **11** (endo complex) to compensate the charge separation and no conformation change of calix[4]pyrrole occurred.

However, in the case of complexation with tetrabutylammonium salts, the anions were bound by calix[4]pyrrole unit and the 1,3-alternate-to-cone conformation change of calix[4]pyrrole was observed in the case of fluoride ion.

The binding affinity study was found that the association constants of ligand **11** with fluoride anion and chloride anion were 1721 and 457 M^{-1}, respectively when using tetrabutylammonium ion as counter ion.

The suggestion for future work:

Future works should be focused on;

1. Complexation studies of the synthesized ligand **9** with RbF, CsF and titration study of ligand **11** in the presence of Bu_4NF with KPF_6 by ^{1}H-NMR spectroscopy.
2. Complexation studies of the synthesized ligand **9** and **11** with potassium ion using UV-visible spectroscopy.
3. X-ray crystallographic studies of the synthesized ligand **9** and **11** and their complexes, which will provide more precise informations.
4. Complexation studies of the synthesized ligand **5** and **10** with various salts by ^{1}H-NMR spectroscopy.

REFERENCES

1. Bianchi, A., Bowman-James, K., García-España, E., Eds.; *Supramolecular Chemistry of Anion*; Wiley-VCH: New York. **1997**.
2. Beer, P. D.; Gale, P. A.; Smith, D. K. *Supramolecular Chemistry*; Oxford University Press. **1999**.
3. Valeur, B.; Leray, I. *Coord. Chem. Rev*. **2000**, 205, 3-40.
4. Perderson, C. J. *J. Am. Soc*. **1967**, *87*, 7017.
5. *Crown Compound* : *Their Characteristic and Application*, Kodansh Ltd. Tokyo, **1982**, 53.
6. Dietrich, B.; Lehn, J.-M.; Sauvage, J.-P. *Tetrahedron Lett*. **1969**, 2885.
7. Stoddart, J. F. *Angew. Chem., Int. Ed. Engl*. **1992**, *31*, 846.
8. Kobayashi, N.; Mizuno, K.; Osa, T. A. *Inorganica Chimica Acta* **1994**, 224, 1.
9. Pochini, A.; Ungaro, R. *"Calixarenes and Related Hosts"* – Comprehensive Supramolecular Chemistry, Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vogtle, F. (Executive Eds.), Elsevier, **1996**, 524.
10. Böhmer,V. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 713.
11. Pochini, A.; Ungaro, R. *"Calixarenes and Related Hosts" – Comprehensive Supramolecular Chemistry*, Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F. (Executive Eds.), Elsevier, **1996**, 524.
12. Iqbal, M.; Mangifico, T.; Gutsh, C. D.; *Tetrahedral Lett*. **1987**, *42*, 8917.
13. Gutsch, C. D. *"Calixarene"-Monographs in Supramolecular Chemistry*, J. F. Stoddart (Ed), The Royal society of Chemistry, Cambridge, **1989**, 36.
14. Shinkai, S.; *Tetrahedron*, **1993**, *40*, 8933.
15. Schmitt, P.; Beer, P. D.; Drew, M. G. B.; Sheen, P. D. *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, *17*, 1840.
16. Sessler, J. L.; Gebauer, A.; Gale, P. A. *Gazz. Chim. Ital*. **1997**, *127*, 723.
17. Sessler, J. L.; Anzenbacher Jr. P.; Jursikova, K.; Miyaji, H.; Genge, J. W.; Tvermoes, N. A.; Allen, W. E.; Shriver, J. A. *Pure Appl. Chem*. **1998**, *70*, 2401.
18. de Silva, S. A.; Zavaleta, A.; Baron, D. E.; allam, O.; Isidor, E. V.; Kashimura, N.; Percapio, J. M. *Tetrahedral Lett*, **1997**, *38*, 2237.
19. Antonisse, M. G. M.; Reinhoudt, D. N. *Chem Commun*. **1998**, 443.

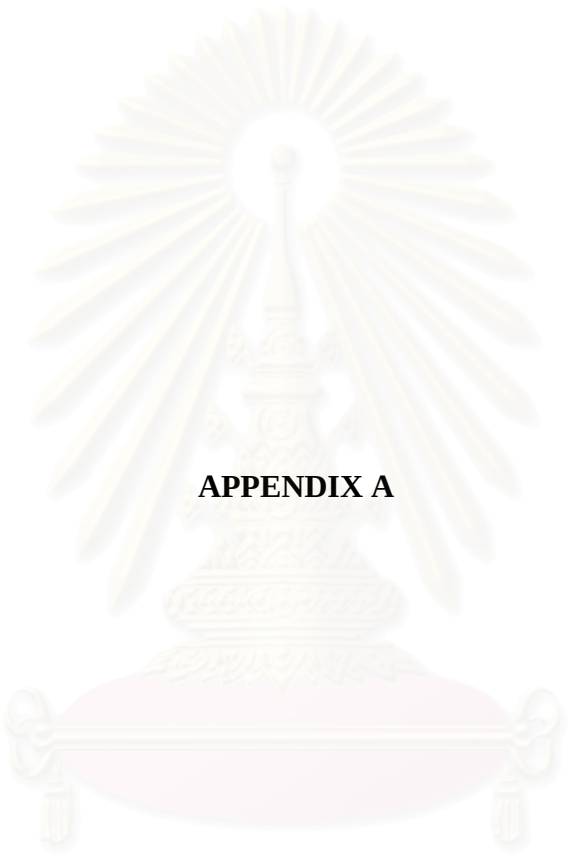
20. Atwood, J. L.; Steed, J. W. *"Supramolecular Chemisty of Anions"*, (Eds. A. Biachi, K. Bowman-James, E. García-España). Wiley-VCH, New York, 1997, 148 pp.
21. Bayer, A., *Ber. Dtsch. Chem. Ges.* **1886**, 19, 2184.
22. Gale, P. A.; Anzenbacher Jr., P.; Sessler, J. L. *Coord. Chem. Rev*. **2001**, *222*, 57.
23. Sessler, J. L.; Gale, P. A. in *The Porphyrin Handbook*, *Vol. 6* (EDS.: Kadish, K. M.; Smith, K. M.; Guilard, R.) Academic Press, Sandiego, **2000**, chap.45.
24. Sessler, J. L.; Anzenbacher Jr. P.; Mitaji, H.; Jursikova, K.; Bleasdale, E. R.; Gale. P. A. *Ind. Eng. Chem. Res*. **2000**, *39*, 3471.
25. Gale, P. A.; Sessler, J. L.; Kral, V.; Lynch, V. *J. Am. Chem. Soc*. **1996**, *118*, 5140.
26. Sessler, J. L.; Gale, P. A.; Genge, J. W. *Chem. Eur. J*. 1998, 4, 1095.
27. Sessler, J. L.; Genge, J. W.; Gale, P. A.; Kral, V. *ACS Symp. Series*. **2000**, 757. (*Calixarenes for Separations*) 238.
28. Gale, P. A.; Anzenbacher Jr. P.; Sessler, J. L. *Coord. Chem. Rev*. **2001**, *222*, 57.
29. Bucher, C.; Zimmerman, R. S.; Lynch, V.; Sessler, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 9716.
30. Yoon, D. W.; Hwang, H.; Lee, C. H. *Angew. Chem. Int. Ed*. **2002**, *41*, *10*, 1757.
31. Lee, C. H.; Na, H. K.; Yoon, D. W.; Won, D. H.; Cho, W. S.; Lynch, V. M.; Shevchuk S. V.; Sessler, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 7301.
32. Tongraung, P.; Chantarasiri, N.; Tuntulani, T. *Tetrahedron Lett*. **2003**, *44*, 29.
33. Gale, P. A.; Sessler, J. L.; Lynch, V.; Sansom, P. I. *Tetrahedron Lett.* **1996**, *37*, *44*, 7881.
34. Gale, P. A.; Genge, J. W.; Kral, V.; McKervey, M. A.; Sessler, J. L.; Walker, A. *Tetrahedron Lett.* **1997**, *38*, *49*, 8443.
35. Rudkevich, D. M.; Verboom, W; Reinhoudt, D. N. *J. Org. Chem*. **1995**, *60*, 6585.
36. Gutche, C. D.; Iqbal, M. *p-tert*-butylcalixarene *Org. Synth*. **1990**, *68*, 234.
37. Lee, C. H.; Lindsey, J. S. *Tetrahedron*. **1994**, *50*, *39*, 11427.
38. Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem. Int. Ed*. **2000**, *39*, 1777.
39. Anzenbacher Jr., P.; Jursikova, K.; Shriver, J. A.; Miyaji, H.; Lynch, V. M.; Sessler, J. L.; Gale, P. A. *J. Org.Chem*. **2000**, *65*, 7641.
40. Gale, P. A.; Twyman, L. J.; Handlin, C. T.; Sessler, J. L. *Chem. Commun*. **1999**, 1851.
41. Anzenbacher Jr., P.; Jursikova, K.; Sessler, J. L. *J. Am. Chem. Soc*. **2000**, *122*, 9350.

42. Miyaji, H.; Anzenbacher Jr., P.; Sessler, J. L.; Bleasdale, E. R.; Gale, P. A. *Chem. Commun*. **1999**, 1723.

43. Kim, J. S.; Rim, J. A.; Shon, O. J.; Noh, K. H.; Kim, E. H.; Cheong, C.; Vicens, J. *J. Incl. Phenom*. **2002**, **43**, 51.

44. Hynes, M. J. *J. Chem. Soc., Dalton Trans*. **1993**, *2*, 311.

APPENDICES



APPENDIX A

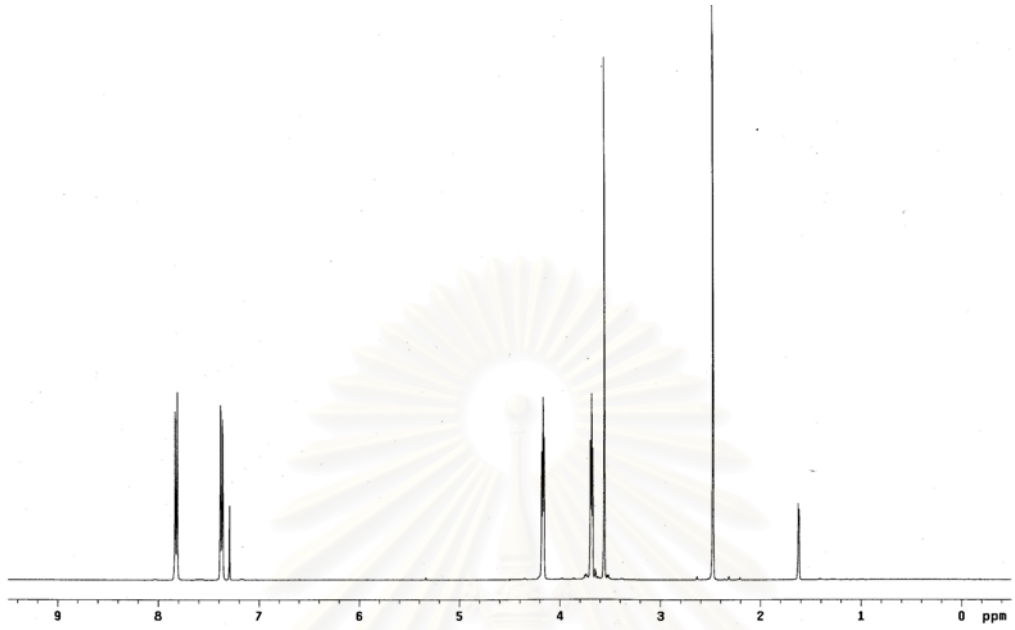


Figure A.1 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of triethyleneglycol ditosylate (**1**).

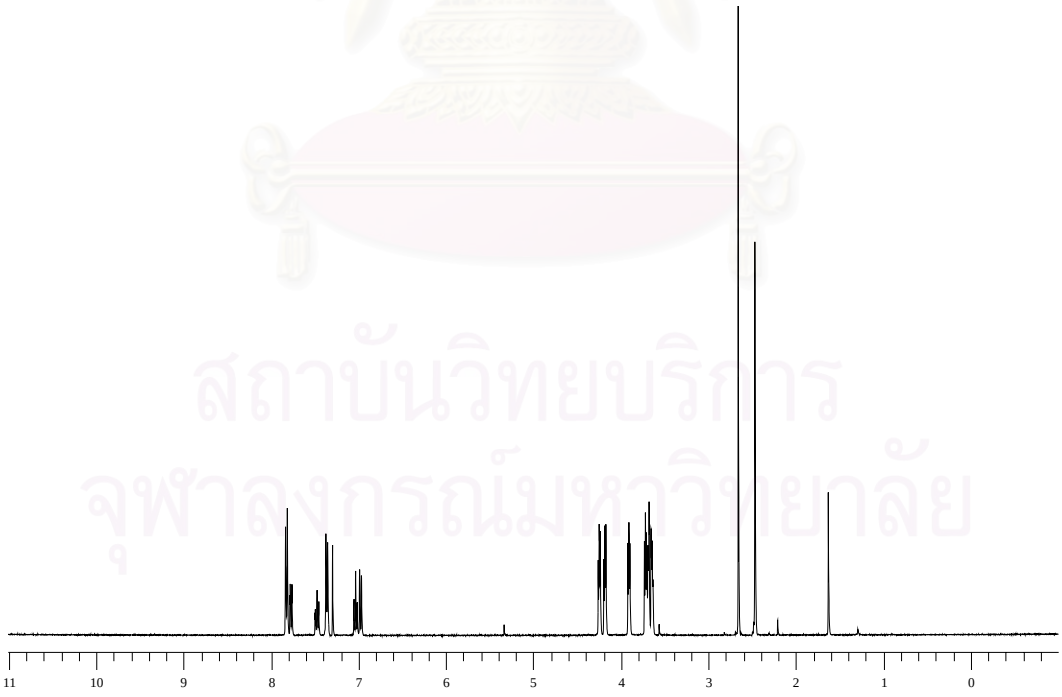


Figure A.2 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of 2-(8-tosyltriethyleneglycol) acetophenone (**2**).

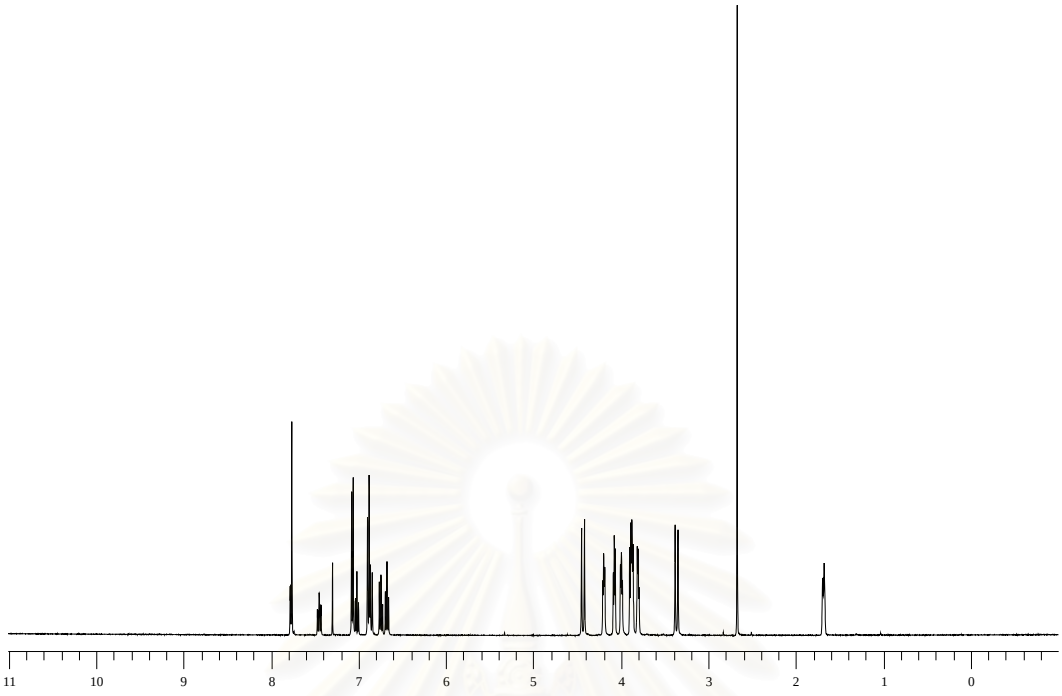


Figure A.3 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of 1,3-calix[4]-diacetophenone (**3**).

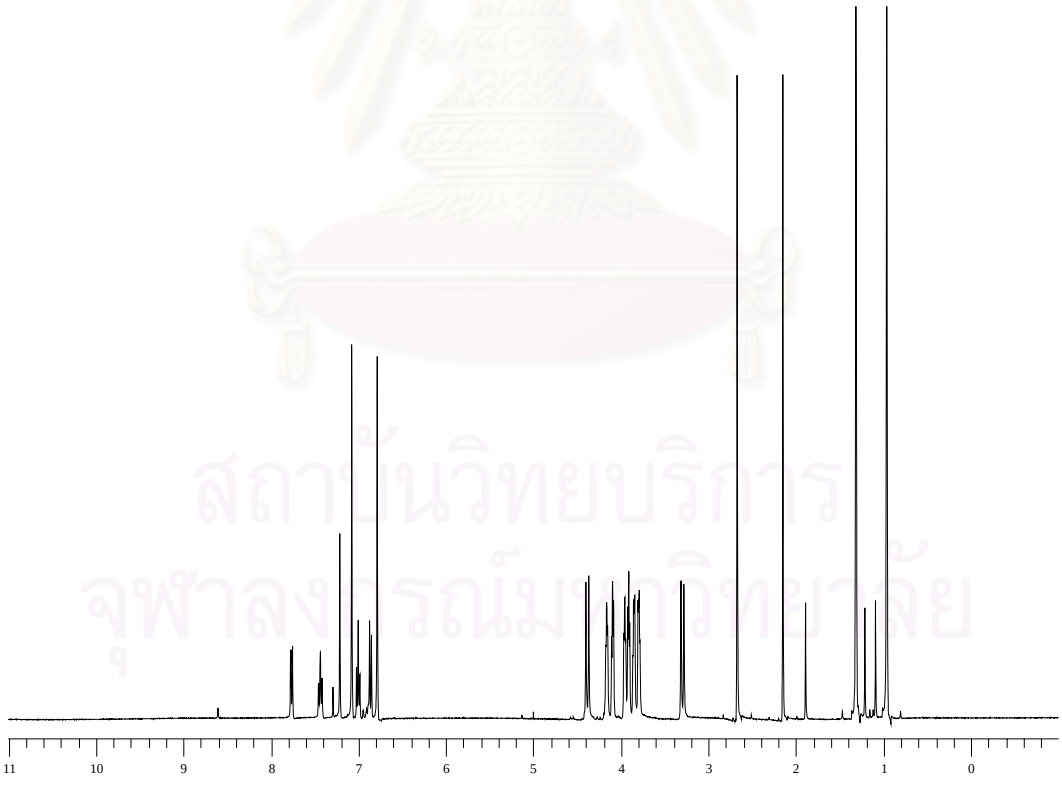


Figure A.4 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of 1,3-*p*-*tert*-butylcalix[4]-diacetophenone (**4**).

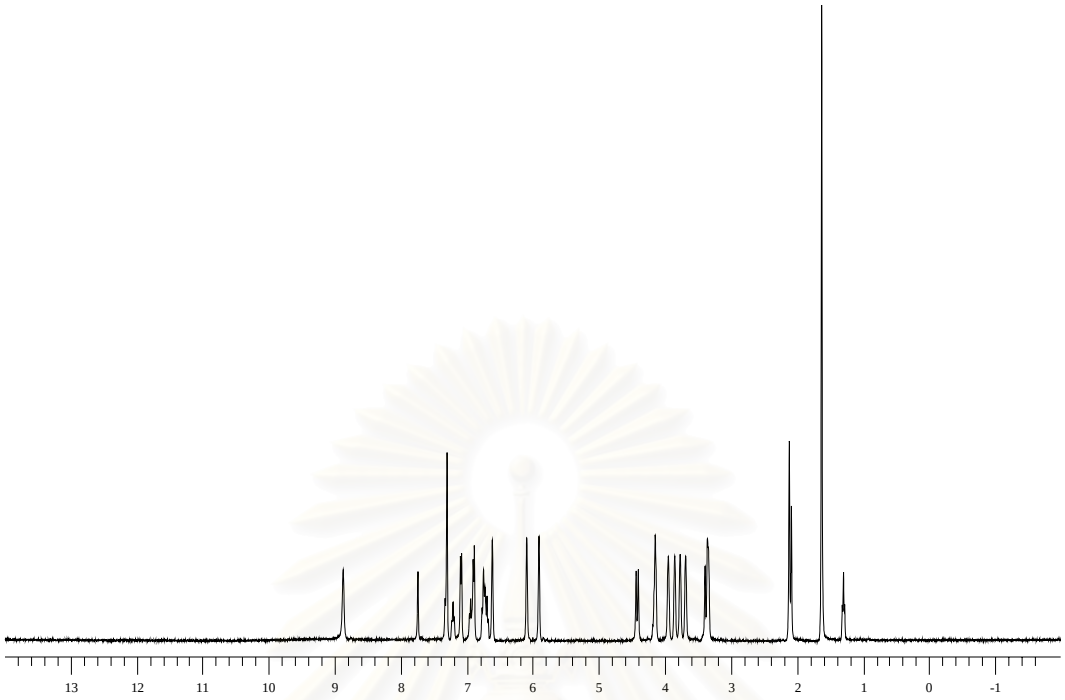


Figure A.5 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of 1,3-calix[4]-bis-dipyrroethane (**7**).

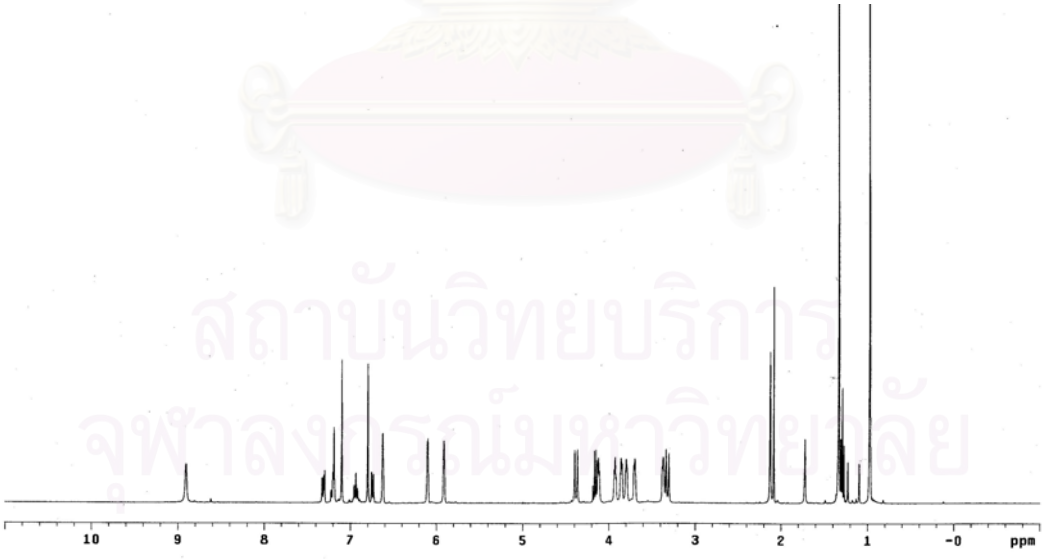


Figure A.6 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of 1,3-*p*-*tert*-butylcalix[4]-bis-dipyrroethane (**8**).

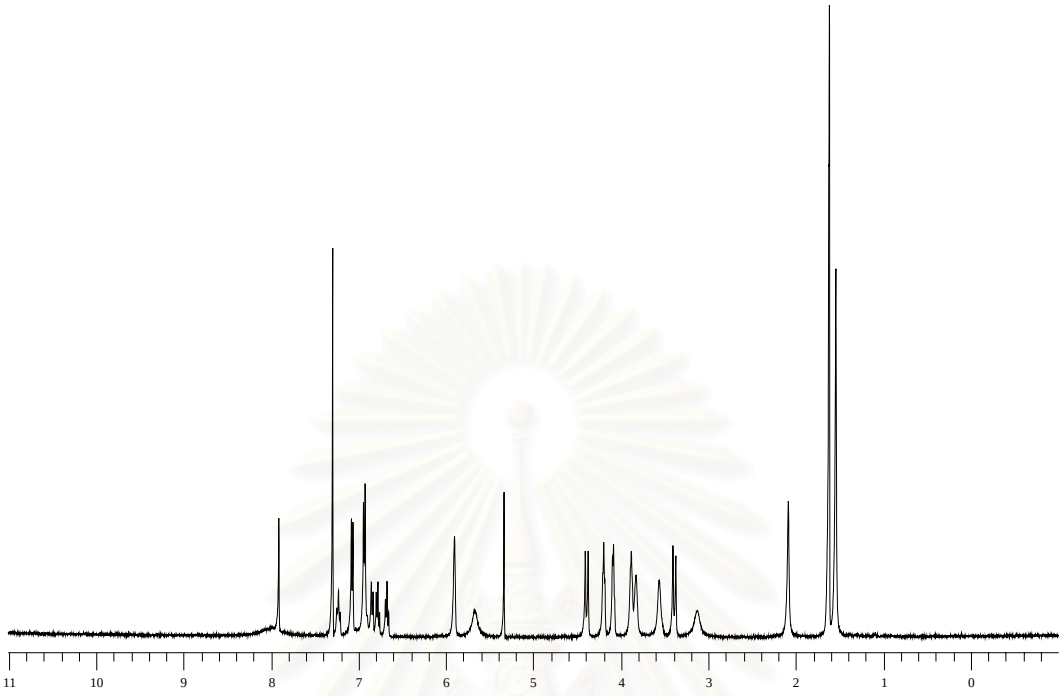


Figure A.7 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of calix[4]arene-calix[4]pyrrole (**9**).

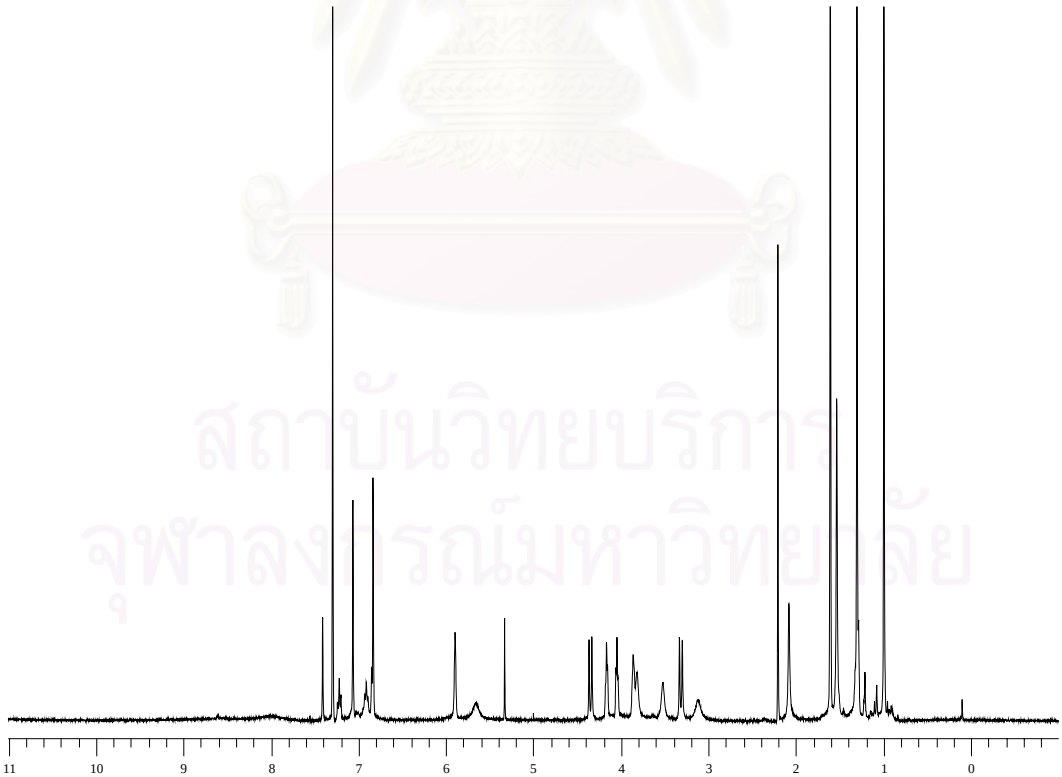


Figure A.8 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of *p-tert*-butylcalix[4]arene-calix[4]pyrrole (**10**).

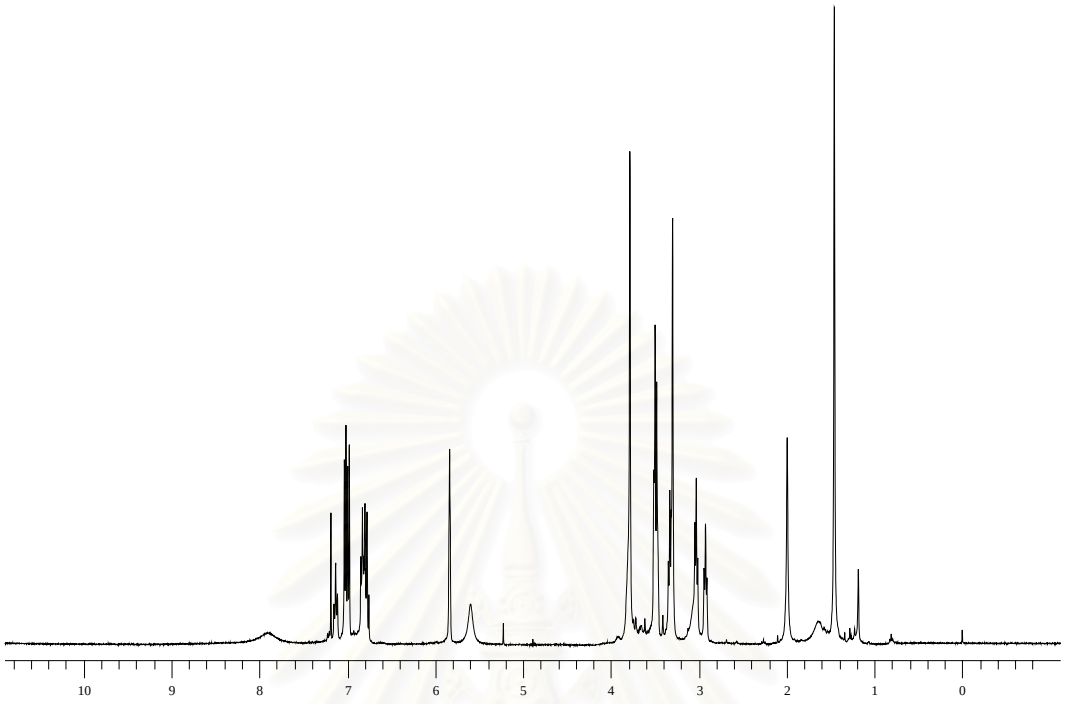


Figure A.9 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (**11**).

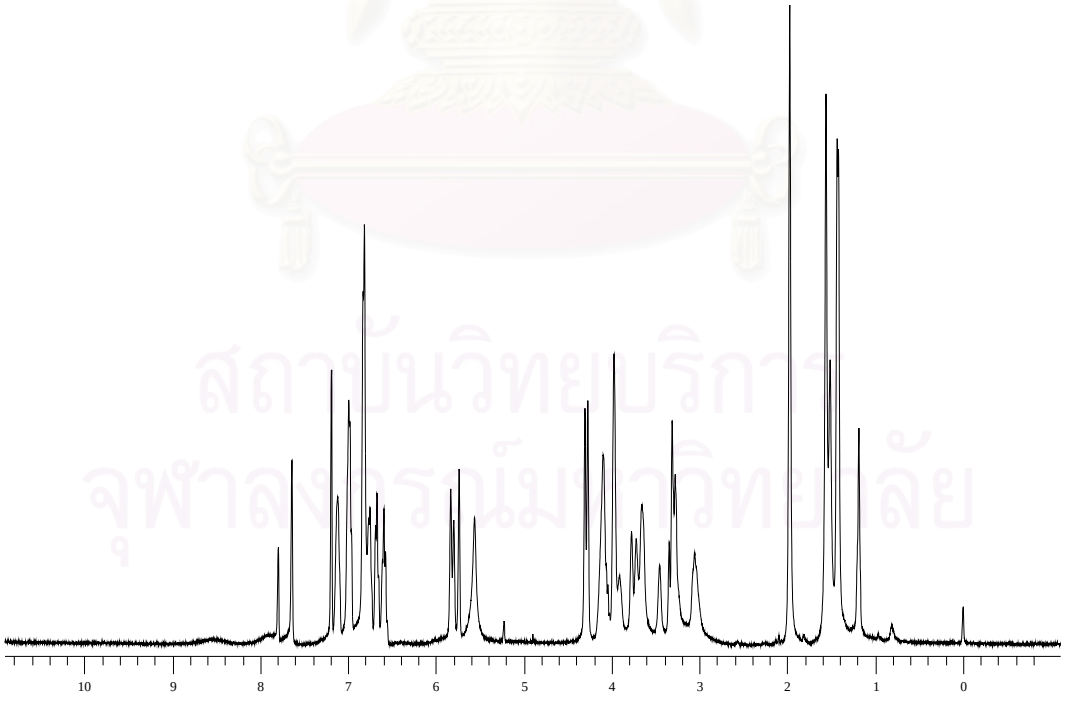


Figure A.10 ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of bis(calix[4]arene)-calix[4]pyrrole (**5**).

APPENDIX B

Table B.1 Bond lengths [Å] for **9**.

Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
C(1)-C(4)	1.501(9)	C(20)-N(4)	1.373(7)
C(1)-C(8)	1.523(9)	C(21)-C(22)	1.409(9)
C(1)-C(3)	1.532(9)	C(22)-C(23)	1.369(8)
C(1)-C(2)	1.543(9)	C(23)-N(4)	1.374(7)
C(4)-C(5)	1.354(9)	C(23)-C(24)	1.518(8)
C(4)-N(1)	1.388(7)	C(24)-C(25)	1.520(9)
C(5)-C(6)	1.407(9)	C(24)-C(26)	1.552(9)
C(6)-C(7)	1.357(8)	C(27)-C(28)	1.384(8)
C(7)-N(1)	1.353(7)	C(27)-C(32)	1.413(8)
C(7)-C(12)	1.518(8)	C(28)-C(29)	1.386(8)
C(8)-C(9)	1.351(9)	C(29)-C(30)	1.370(9)
C(8)-N(2)	1.363(7)	C(30)-C(31)	1.392(9)
C(9)-C(10)	1.432(10)	C(31)-C(32)	1.368(8)
C(10)-C(11)	1.358(9)	C(32)-O(1)	1.370(7)
C(11)-N(2)	1.371(8)	C(33)-O(1)	1.409(7)
C(11)-C(18)	1.517(9)	C(33)-C(34)	1.508(9)
C(12)-C(14)	1.525(8)	C(34)-O(2)	1.400(7)
C(12)-C(13)	1.542(8)	C(35)-O(2)	1.417(7)
C(12)-C(27)	1.556(8)	C(35)-C(36)	1.472(10)
C(14)-C(15)	1.362(8)	C(36)-O(3)	1.430(8)
C(14)-N(3)	1.366(7)	C(37)-O(3)	1.397(8)
C(15)-C(16)	1.411(8)	C(37)-C(38)	1.491(10)
C(16)-C(17)	1.355(8)	C(38)-O(4)	1.442(8)
C(17)-N(3)	1.388(7)	C(39)-C(40)	1.377(9)
C(17)-C(24)	1.512(8)	C(39)-C(44)	1.380(9)
C(18)-C(20)	1.527(8)	C(39)-O(4)	1.408(7)
C(18)-C(19)	1.536(9)	C(40)-C(41)	1.381(9)
C(18)-C(78)	1.555(9)	C(40)-C(66)	1.528(9)
C(20)-C(21)	1.360(8)	C(41)-C(42)	1.378(9)

Table B.1 (continued) Bond lengths [Å] for **9**.

Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
C(42)-C(43)	1.391(9)	C(60)-C(61)	1.398(9)
C(43)-C(44)	1.393(9)	C(61)-C(62)	1.366(10)
C(44)-C(45)	1.535(9)	C(62)-C(63)	1.363(10)
C(45)-C(46)	1.493(9)	C(63)-C(64)	1.403(9)
C(46)-C(47)	1.387(9)	C(64)-C(65)	1.404(9)
C(46)-C(51)	1.401(9)	C(64)-C(66)	1.505(9)
C(47)-C(48)	1.379(9)	C(65)-O(6)	1.368(7)
C(48)-C(49)	1.385(10)	C(67)-C(68)	1.214(15)
C(49)-C(50)	1.386(9)	C(67)-O(7)	1.466(12)
C(50)-C(51)	1.401(9)	C(68)-O(8)	1.389(11)
C(50)-C(52)	1.489(9)	C(69)-O(8)	1.419(10)
C(51)-O(5)	1.372(7)	C(69)-C(70)	1.468(9)
C(52)-C(53)	1.515(10)	C(70)-O(9)	1.397(8)
C(53)-C(54)	1.373(11)	C(71)-O(9)	1.420(7)
C(53)-C(58)	1.405(10)	C(71)-C(72)	1.500(8)
C(54)-C(55)	1.365(11)	C(72)-O(10)	1.441(7)
C(55)-C(56)	1.365(12)	C(73)-O(10)	1.377(7)
C(56)-C(57)	1.404(11)	C(73)-C(78)	1.382(9)
C(57)-C(58)	1.392(10)	C(73)-C(74)	1.382(9)
C(57)-C(59)	1.525(10)	C(74)-C(75)	1.382(11)
C(58)-O(7)	1.378(9)	C(75)-C(76)	1.370(12)
C(59)-C(60)	1.514(10)	C(76)-C(77)	1.362(11)
C(60)-C(65)	1.395(9)	C(77)-C(78)	1.405(9)

Table B.2 Angles [deg] for **9**.

Atoms	Angles (deg)	Atoms	Angles (deg)
C(4)-C(1)-C(8)	111.7(5)	C(15)-C(14)-C(12)	130.0(5)
C(4)-C(1)-C(3)	109.1(6)	N(3)-C(14)-C(12)	122.2(5)
C(8)-C(1)-C(3)	108.0(6)	C(14)-C(15)-C(16)	107.2(5)
C(4)-C(1)-C(2)	109.5(6)	C(17)-C(16)-C(15)	108.9(5)
C(8)-C(1)-C(2)	110.1(6)	C(16)-C(17)-N(3)	106.4(5)
C(3)-C(1)-C(2)	108.4(6)	C(16)-C(17)-C(24)	131.7(6)
C(5)-C(4)-N(1)	105.5(6)	N(3)-C(17)-C(24)	121.6(5)
C(5)-C(4)-C(1)	131.8(6)	C(11)-C(18)-C(20)	112.4(5)
N(1)-C(4)-C(1)	122.6(6)	C(11)-C(18)-C(19)	107.2(5)
C(4)-C(5)-C(6)	108.6(6)	C(20)-C(18)-C(19)	106.1(5)
C(7)-C(6)-C(5)	108.1(6)	C(11)-C(18)-C(78)	111.4(5)
N(1)-C(7)-C(6)	106.7(5)	C(20)-C(18)-C(78)	108.7(5)
N(1)-C(7)-C(12)	122.6(5)	C(19)-C(18)-C(78)	111.0(5)
C(6)-C(7)-C(12)	130.7(6)	C(21)-C(20)-N(4)	107.1(5)
C(9)-C(8)-N(2)	106.8(6)	C(21)-C(20)-C(18)	131.8(5)
C(9)-C(8)-C(1)	133.4(6)	N(4)-C(20)-C(18)	120.8(5)
N(2)-C(8)-C(1)	119.6(6)	C(20)-C(21)-C(22)	107.9(6)
C(8)-C(9)-C(10)	107.7(6)	C(23)-C(22)-C(21)	108.2(6)
C(11)-C(10)-C(9)	107.9(6)	C(22)-C(23)-N(4)	106.4(5)
C(10)-C(11)-N(2)	106.1(6)	C(22)-C(23)-C(24)	132.8(6)
C(10)-C(11)-C(18)	131.1(6)	N(4)-C(23)-C(24)	120.7(5)
N(2)-C(11)-C(18)	122.8(5)	C(17)-C(24)-C(23)	109.7(5)
C(7)-C(12)-C(14)	107.7(5)	C(17)-C(24)-C(25)	109.7(5)
C(7)-C(12)-C(13)	108.0(5)	C(23)-C(24)-C(25)	108.7(5)
C(14)-C(12)-C(13)	112.3(5)	C(17)-C(24)-C(26)	111.5(5)
C(7)-C(12)-C(27)	112.9(5)	C(23)-C(24)-C(26)	109.5(5)
C(14)-C(12)-C(27)	109.5(4)	C(25)-C(24)-C(26)	107.6(6)
C(13)-C(12)-C(27)	106.4(5)	C(28)-C(27)-C(32)	116.9(5)
C(15)-C(14)-N(3)	107.7(5)	C(28)-C(27)-C(12)	122.4(5)

Table B.2 (continue) Angles [deg] for **9**.

Atoms	Angles (deg)	Atoms	Angles (deg)
C(32)-C(27)-C(12)	120.5(5)	C(32)-C(27)-C(12)	120.5(5)
C(27)-C(28)-C(29)	121.7(6)	C(27)-C(28)-C(29)	121.7(6)
C(30)-C(29)-C(28)	119.8(6)	C(30)-C(29)-C(28)	119.8(6)
C(29)-C(30)-C(31)	120.5(6)	C(29)-C(30)-C(31)	120.5(6)
C(32)-C(31)-C(30)	119.1(6)	C(32)-C(31)-C(30)	119.1(6)
C(31)-C(32)-O(1)	122.2(6)	C(31)-C(32)-O(1)	122.2(6)
C(31)-C(32)-C(27)	122.0(6)	C(31)-C(32)-C(27)	122.0(6)
O(1)-C(32)-C(27)	115.7(5)	O(1)-C(32)-C(27)	115.7(5)
O(1)-C(33)-C(34)	105.2(5)	O(1)-C(33)-C(34)	105.2(5)
O(2)-C(34)-C(33)	109.1(5)	O(2)-C(34)-C(33)	109.1(5)
O(2)-C(35)-C(36)	110.5(6)	O(2)-C(35)-C(36)	110.5(6)
O(3)-C(36)-C(35)	112.9(6)	O(3)-C(36)-C(35)	112.9(6)
O(3)-C(37)-C(38)	109.3(6)	O(3)-C(37)-C(38)	109.3(6)
O(4)-C(38)-C(37)	109.4(6)	O(4)-C(38)-C(37)	109.4(6)
C(40)-C(39)-C(44)	123.3(6)	C(40)-C(39)-C(44)	123.3(6)
C(40)-C(39)-O(4)	119.5(6)	C(40)-C(39)-O(4)	119.5(6)
C(44)-C(39)-O(4)	117.2(6)	C(44)-C(39)-O(4)	117.2(6)
C(39)-C(40)-C(41)	117.6(6)	C(39)-C(40)-C(41)	117.6(6)
C(39)-C(40)-C(66)	122.2(6)	C(39)-C(40)-C(66)	122.2(6)
C(41)-C(40)-C(66)	120.3(6)	C(41)-C(40)-C(66)	120.3(6)
C(42)-C(41)-C(40)	120.8(6)	C(42)-C(41)-C(40)	120.8(6)
C(41)-C(42)-C(43)	120.8(6)	C(41)-C(42)-C(43)	120.8(6)
C(42)-C(43)-C(44)	119.2(6)	C(42)-C(43)-C(44)	119.2(6)
C(39)-C(44)-C(43)	118.2(6)	C(39)-C(44)-C(43)	118.2(6)
C(39)-C(44)-C(45)	122.1(6)	C(39)-C(44)-C(45)	122.1(6)
C(43)-C(44)-C(45)	119.7(6)	C(43)-C(44)-C(45)	119.7(6)
C(46)-C(45)-C(44)	113.7(5)	C(46)-C(45)-C(44)	113.7(5)

Table B.2 (continued) Angles [deg] for **9**.

Atoms	Angles (deg)	Atoms	Angles (deg)
C(60)-C(65)-C(64)	122.3(6)	C(73)-C(78)-C(77)	115.8(6)
C(64)-C(66)-C(40)	112.1(5)	C(73)-C(78)-C(18)	122.6(5)
C(68)-C(67)-O(7)	121.4(14)	C(77)-C(78)-C(18)	121.5(6)
C(67)-C(68)-O(8)	119.5(12)	C(7)-N(1)-C(4)	111.1(5)
O(8)-C(69)-C(70)	107.5(7)	C(8)-N(2)-C(11)	111.5(5)
O(9)-C(70)-C(69)	108.9(6)	C(14)-N(3)-C(17)	109.8(5)
O(9)-C(71)-C(72)	114.1(5)	C(20)-N(4)-C(23)	110.3(5)
O(10)-C(72)-C(71)	103.4(5)	C(32)-O(1)-C(33)	119.6(5)
O(10)-C(73)-C(78)	116.3(5)	C(34)-O(2)-C(35)	111.5(5)
O(10)-C(73)-C(74)	120.7(6)	C(37)-O(3)-C(36)	112.2(5)
C(78)-C(73)-C(74)	122.9(6)	C(39)-O(4)-C(38)	112.4(5)
C(73)-C(74)-C(75)	118.8(8)	C(58)-O(7)-C(67)	110.8(8)
C(76)-C(75)-C(74)	119.8(8)	C(68)-O(8)-C(69)	119.2(10)
C(77)-C(76)-C(75)	120.5(7)	C(70)-O(9)-C(71)	115.2(5)
C(76)-C(77)-C(78)	122.0(8)	C(73)-O(10)-C(72)	119.8(4)

Symmetry transformations used to generate equivalent atoms:

Table B.3. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
C(1)	2667(4)	6462(3)	-1381(3)	60(2)
C(2)	2264(5)	6892(5)	-1971(4)	91(3)
C(3)	2530(5)	5684(4)	-1532(4)	86(2)
C(4)	3458(4)	6604(3)	-1347(3)	51(2)
C(5)	3990(4)	6279(3)	-1639(3)	66(2)
C(6)	4637(4)	6643(3)	-1458(4)	64(2)
C(7)	4496(3)	7190(3)	-1053(3)	47(2)
C(8)	2377(3)	6634(3)	-705(3)	51(2)
C(9)	1843(4)	7054(4)	-536(4)	68(2)
C(10)	1776(4)	6947(4)	178(4)	69(2)
C(11)	2272(3)	6464(3)	421(3)	49(2)
C(12)	4994(3)	7740(3)	-698(3)	45(1)
C(13)	5721(3)	7387(3)	-464(3)	56(2)
C(14)	4636(3)	8030(3)	-96(3)	40(1)
C(15)	4101(3)	8513(3)	-88(3)	46(1)
C(16)	3936(3)	8562(3)	595(3)	47(2)
C(17)	4369(3)	8119(3)	993(3)	45(1)
C(18)	2435(3)	6141(3)	1129(3)	51(2)
C(19)	1831(3)	6364(4)	1552(4)	69(2)
C(20)	3132(3)	6420(3)	1514(3)	45(1)
C(21)	3559(3)	6175(3)	2070(3)	56(2)
C(22)	4103(3)	6673(3)	2248(3)	54(2)
C(23)	4002(3)	7219(3)	1794(3)	46(1)
C(24)	4386(3)	7913(3)	1740(3)	51(2)
C(25)	4004(5)	8466(4)	2124(4)	76(2)
C(26)	5168(4)	7853(4)	2094(3)	68(2)
C(27)	5155(3)	8349(3)	-1185(3)	42(1)

Table B.3. (continued) Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
C(28)	4981(3)	8315(3)	-1890(3)	49(2)
C(29)	5170(4)	8843(3)	-2320(3)	59(2)
C(30)	5542(4)	9415(3)	-2048(4)	60(2)
C(31)	5721(3)	9475(3)	-1341(3)	55(2)
C(32)	5543(3)	8944(3)	-923(3)	49(2)
C(33)	5960(3)	9576(3)	105(3)	51(2)
C(34)	5974(4)	9422(4)	862(3)	67(2)
C(35)	6261(4)	9895(4)	1954(3)	67(2)
C(36)	6564(3)	10509(4)	2337(4)	65(2)
C(37)	7433(4)	11053(4)	1742(4)	72(2)
C(38)	8218(4)	11080(4)	1676(4)	70(2)
C(39)	9038(3)	10553(3)	996(3)	54(2)
C(40)	9706(3)	10367(3)	1311(3)	50(2)
C(41)	10293(4)	10500(3)	962(3)	58(2)
C(42)	10206(4)	10793(3)	316(4)	61(2)
C(43)	9524(4)	10947(3)	-8(4)	61(2)
C(44)	8926(3)	10816(3)	336(3)	53(2)
C(45)	8168(4)	10932(4)	-35(3)	63(2)
C(46)	7933(3)	10376(3)	-547(3)	50(2)
C(47)	7827(3)	10530(4)	-1243(4)	58(2)
C(48)	7628(4)	10026(4)	-1731(3)	65(2)
C(49)	7527(4)	9344(4)	-1525(3)	64(2)
C(50)	7609(3)	9158(4)	-836(3)	56(2)
C(51)	7807(3)	9685(4)	-354(3)	51(2)
C(52)	7487(4)	8428(4)	-611(4)	70(2)
C(53)	8173(4)	8027(3)	-394(4)	65(2)

Table B.3. (continued) Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
C(54)	8643(5)	7859(4)	-858(4)	76(2)
C(55)	9285(5)	7542(4)	-651(5)	89(3)
C(56)	9502(5)	7415(4)	27(5)	82(2)
C(57)	9044(4)	7571(3)	526(4)	68(2)
C(58)	8371(4)	7846(3)	297(4)	64(2)
C(59)	9278(4)	7482(4)	1293(4)	78(2)
C(60)	9791(4)	8044(3)	1593(3)	58(2)
C(61)	10504(4)	7881(4)	1826(4)	68(2)
C(62)	10973(4)	8370(4)	2122(4)	71(2)
C(63)	10747(4)	9044(4)	2178(3)	67(2)
C(64)	10041(3)	9255(3)	1958(3)	53(2)
C(65)	9569(3)	8733(4)	1675(3)	54(2)
C(66)	9806(4)	10004(4)	2011(3)	61(2)
C(67)	7395(6)	7371(9)	789(6)	190(8)
C(68)	7043(8)	7285(9)	1266(6)	185(7)
C(69)	6529(4)	6120(5)	1234(4)	81(2)
C(70)	5811(4)	5810(4)	1240(4)	67(2)
C(71)	4685(3)	5907(3)	551(4)	59(2)
C(72)	4322(3)	5249(3)	746(3)	52(2)
C(73)	3065(3)	4991(3)	857(3)	51(2)
C(74)	3132(4)	4270(3)	856(4)	72(2)
C(75)	2582(6)	3868(4)	1063(5)	94(3)
C(76)	1983(5)	4186(5)	1261(5)	88(3)
C(77)	1934(4)	4897(4)	1276(4)	70(2)
C(78)	2485(3)	5330(3)	1087(3)	51(2)
N(1)	3783(3)	7171(2)	-994(2)	50(1)
N(2)	2636(3)	6284(3)	-122(3)	53(1)

Table B.3. (continued) Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
N(3)	4800(3)	7789(2)	559(2)	44(1)
N(4)	3404(3)	7057(2)	1350(2)	46(1)
O(1)	5747(2)	8944(2)	-229(2)	63(1)
O(2)	6207(2)	10019(2)	1237(2)	62(1)
O(1W)	5285(3)	9336(4)	3702(3)	109(2)
O(3)	7313(2)	10605(3)	2282(2)	70(1)
O(2W)	8996(6)	5509(4)	601(4)	117(3)
O(4)	8428(2)	10452(2)	1344(2)	59(1)
O(5)	7858(2)	9481(3)	321(2)	63(1)
O(6)	8873(2)	8941(3)	1498(3)	67(1)
O(7)	7899(3)	7957(3)	777(3)	81(2)
O(8)	6440(4)	6857(3)	1181(3)	103(2)
O(9)	5444(2)	5853(3)	579(2)	65(1)
O(10)	3568(2)	5408(2)	596(2)	55(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table B.4. Anisotropic displacement parameters (A^2 x 10^3) for **9**.

	U11	U22	U33	U23	U13	U12
C(1)	65(4)	55(4)	56(4)	2(3)	-14(3)	-13(3)
C(2)	99(6)	103(6)	64(5)	12(4)	-22(5)	-2(5)
C(3)	96(6)	68(5)	91(6)	-24(4)	-1(5)	-29(4)
C(4)	72(4)	43(3)	36(3)	-3(3)	1(3)	-15(3)
C(5)	95(6)	50(4)	57(4)	-20(3)	27(4)	-23(4)
C(6)	73(5)	54(4)	72(5)	-17(3)	34(4)	-10(4)
C(7)	59(4)	38(3)	45(3)	-2(3)	15(3)	-11(3)
C(8)	52(4)	47(4)	52(4)	3(3)	-11(3)	-11(3)
C(9)	61(4)	54(4)	84(5)	11(4)	-8(4)	9(3)
C(10)	56(4)	63(4)	88(6)	5(4)	8(4)	8(4)
C(11)	39(3)	49(4)	58(4)	-3(3)	0(3)	-2(3)
C(12)	49(4)	43(3)	45(3)	-2(3)	8(3)	2(3)
C(13)	54(4)	48(4)	67(4)	5(3)	6(3)	7(3)
C(14)	43(3)	36(3)	39(3)	1(2)	1(2)	-8(3)
C(15)	51(4)	43(3)	43(3)	0(3)	-3(3)	4(3)
C(16)	52(4)	37(3)	53(4)	-6(3)	6(3)	6(3)
C(17)	54(4)	37(3)	45(3)	-6(3)	6(3)	-5(3)
C(18)	41(3)	58(4)	56(4)	1(3)	7(3)	-4(3)
C(19)	44(4)	85(5)	81(5)	-4(4)	17(3)	-1(4)
C(20)	45(3)	44(3)	49(4)	2(3)	10(3)	-3(3)
C(21)	59(4)	56(4)	52(4)	13(3)	4(3)	-2(3)
C(22)	51(4)	59(4)	50(4)	7(3)	-1(3)	-3(3)
C(23)	48(4)	48(4)	41(3)	-4(3)	7(3)	0(3)
C(24)	68(4)	42(3)	43(3)	-5(3)	10(3)	-4(3)
C(25)	113(6)	60(4)	56(4)	-12(4)	23(4)	2(4)

Table B.4. (continued) Anisotropic displacement parameters (A^2 x 10^3) for **9**.

	U11	U22	U33	U23	U13	U12
C(26)	74(5)	72(5)	53(4)	-1(3)	-11(3)	-20(4)
C(27)	46(3)	36(3)	45(3)	1(3)	7(3)	-1(3)
C(28)	55(4)	47(4)	46(4)	-3(3)	7(3)	-2(3)
C(29)	83(5)	53(4)	43(4)	1(3)	12(3)	-2(3)
C(30)	69(4)	49(4)	65(5)	8(3)	22(4)	-6(3)
C(31)	61(4)	42(4)	62(4)	4(3)	6(3)	-9(3)
C(32)	48(4)	49(4)	50(4)	6(3)	0(3)	-2(3)
C(33)	40(3)	47(4)	64(4)	-2(3)	-4(3)	-8(3)
C(34)	76(5)	59(4)	61(4)	-3(3)	-13(4)	-10(4)
C(35)	76(5)	70(5)	52(4)	9(3)	-1(4)	-6(4)
C(36)	51(4)	87(5)	57(4)	0(4)	9(3)	9(4)
C(37)	77(5)	56(4)	86(5)	1(4)	19(4)	8(4)
C(38)	71(5)	67(5)	76(5)	-14(4)	24(4)	-1(4)
C(39)	54(4)	48(4)	62(4)	-1(3)	17(3)	-4(3)
C(40)	52(4)	47(3)	52(4)	1(3)	3(3)	-3(3)
C(41)	52(4)	58(4)	62(4)	-2(3)	1(3)	-4(3)
C(42)	62(4)	51(4)	72(5)	4(3)	20(4)	-13(3)
C(43)	64(5)	57(4)	60(4)	3(3)	8(4)	-8(3)
C(44)	59(4)	44(4)	55(4)	5(3)	5(3)	0(3)
C(45)	64(4)	62(4)	63(4)	7(3)	8(3)	13(3)
C(46)	37(3)	61(4)	51(4)	5(3)	7(3)	8(3)
C(47)	48(4)	65(4)	63(4)	15(4)	9(3)	8(3)
C(48)	57(4)	92(6)	46(4)	18(4)	6(3)	8(4)
C(49)	56(4)	87(5)	50(4)	0(4)	5(3)	-4(4)
C(50)	35(3)	72(4)	59(4)	5(3)	-3(3)	-9(3)

Table B.4. (continued) Anisotropic displacement parameters ($A^2 \times 10^3$) for **9**.

	U11	U22	U33	U23	U13	U12
C(51)	30(3)	78(5)	45(4)	14(3)	3(3)	2(3)
C(52)	54(4)	86(5)	66(5)	15(4)	-12(3)	-26(4)
C(53)	65(5)	54(4)	73(5)	7(4)	-8(4)	-26(4)
C(54)	85(6)	67(5)	76(5)	-10(4)	3(5)	-13(4)
C(55)	103(7)	66(5)	100(7)	-15(5)	20(6)	6(5)
C(56)	74(5)	52(4)	119(8)	-1(5)	8(5)	6(4)
C(57)	70(5)	42(4)	86(5)	10(4)	-14(4)	-8(3)
C(58)	57(4)	47(4)	85(5)	10(4)	-3(4)	-18(3)
C(59)	73(5)	57(4)	99(6)	29(4)	-6(4)	-3(4)
C(60)	57(4)	57(4)	59(4)	20(3)	5(3)	-2(3)
C(61)	63(5)	60(4)	83(5)	23(4)	15(4)	7(4)
C(62)	42(4)	82(6)	88(6)	29(4)	7(4)	5(4)
C(63)	55(4)	81(5)	62(4)	20(4)	-1(3)	-15(4)
C(64)	50(4)	63(4)	45(4)	13(3)	6(3)	-5(3)
C(65)	46(4)	64(4)	52(4)	17(3)	2(3)	-5(3)
C(66)	62(4)	71(5)	51(4)	-6(3)	4(3)	-7(4)
C(67)	97(8)	350(20)	107(8)	102(11)	-40(6)	-141(11)
C(68)	183(13)	259(17)	107(9)	33(10)	-9(9)	-164(13)
C(69)	60(5)	108(7)	73(5)	28(5)	-4(4)	-20(4)
C(70)	66(5)	62(4)	72(5)	22(4)	5(4)	-13(4)
C(71)	46(4)	62(4)	71(4)	10(3)	12(3)	2(3)
C(72)	48(4)	47(4)	61(4)	0(3)	10(3)	2(3)
C(73)	47(4)	50(4)	56(4)	7(3)	8(3)	-7(3)
C(74)	77(5)	46(4)	94(6)	3(4)	13(4)	-8(4)
C(75)	114(7)	53(5)	114(7)	11(5)	10(6)	-27(5)

Table B.4. (continued) Anisotropic displacement parameters ($A^2 \times 10^3$) for **9**.

	U11	U22	U33	U23	U13	U12
C(76)	87(6)	72(6)	109(7)	13(5)	21(5)	-29(5)
C(77)	61(4)	77(5)	71(5)	3(4)	12(4)	-20(4)
C(78)	48(4)	50(4)	54(4)	6(3)	4(3)	-15(3)
N(1)	56(3)	45(3)	47(3)	-9(2)	6(2)	-6(2)
N(2)	43(3)	60(3)	54(3)	4(3)	-3(2)	6(2)
N(3)	50(3)	36(3)	45(3)	2(2)	6(2)	2(2)
N(4)	50(3)	42(3)	44(3)	4(2)	-1(2)	4(2)
O(1)	81(3)	49(3)	54(3)	2(2)	-15(2)	-18(2)
O(2)	72(3)	54(3)	57(3)	0(2)	-8(2)	-7(2)
O(1W)	62(3)	137(5)	121(5)	18(4)	-24(3)	-5(3)
O(3)	55(3)	92(4)	60(3)	5(3)	0(2)	2(3)
O(2W)	141(9)	84(5)	117(6)	16(4)	-25(7)	-15(7)
O(4)	55(3)	59(3)	63(3)	-1(2)	15(2)	-2(2)
O(5)	67(3)	72(3)	51(3)	15(2)	5(2)	-7(2)
O(6)	49(3)	64(3)	83(3)	12(3)	-12(2)	4(2)
O(7)	56(3)	92(4)	92(4)	37(3)	6(3)	-18(3)
O(8)	125(5)	89(4)	94(4)	7(3)	13(4)	-62(4)
O(9)	53(3)	84(3)	58(3)	0(2)	10(2)	-11(2)
O(10)	43(2)	50(2)	74(3)	13(2)	14(2)	3(2)

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

Table B.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(2A)	2368	7380	-1899	137
H(2B)	1756	6816	-1981	137
H(2C)	2418	6747	-2400	137
H(3A)	2703	5565	-1960	129
H(3B)	2023	5592	-1562	129
H(3C)	2777	5409	-1169	129
H(5)	3936	5882	-1914	79
H(6)	5083	6529	-1593	77
H(9)	1569	7357	-830	81
H(10)	1450	7170	430	83
H(13A)	6024	7708	-187	84
H(13B)	5951	7258	-860	84
H(13C)	5643	6976	-201	84
H(15)	3886	8763	-464	56
H(16)	3587	8851	748	57
H(19A)	1855	6860	1628	103
H(19B)	1887	6126	1987	103
H(19C)	1374	6246	1307	103
H(21)	3501	5753	2295	67
H(22)	4468	6637	2610	64
H(25A)	4242	8908	2092	114
H(25B)	4016	8333	2598	114
H(25C)	3514	8505	1923	114

Table B.5. (continued) Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(26A)	5424	7508	1860	101
H(26B)	5161	7716	2565	101
H(26C)	5404	8297	2076	101
H(28)	4730	7929	-2080	59
H(29)	5045	8810	-2792	71
H(30)	5676	9765	-2338	72
H(31)	5958	9870	-1155	66
H(33A)	5619	9946	-32	62
H(33B)	6431	9718	-3	62
H(34A)	5497	9291	965	80
H(34B)	6298	9035	987	80
H(35A)	6566	9491	2068	80
H(35B)	5788	9793	2087	80
H(36A)	6305	10924	2164	78
H(36B)	6495	10457	2817	78
H(37A)	7259	11519	1832	86
H(37B)	7174	10886	1317	86
H(38A)	8324	11486	1408	84
H(38B)	8487	11121	2128	84
H(41)	10752	10390	1166	69
H(42)	10608	10890	93	73
H(43)	9468	11134	-449	73
H(45A)	7829	10953	304	75
H(45B)	8156	11380	-269	75

Table B.5. (continued) Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(47)	7894	10987	-1384	70
H(48)	7561	10144	-2195	78
H(49)	7401	9003	-1855	77
H(52A)	7213	8179	-985	84
H(52B)	7200	8441	-228	84
H(54)	8523	7962	-1321	91
H(55)	9581	7409	-979	107
H(56)	9954	7225	158	98
H(59A)	8855	7484	1536	93
H(59B)	9509	7029	1368	93
H(61)	10665	7425	1779	82
H(62)	11442	8245	2284	85
H(63)	11074	9376	2369	80
H(66A)	10164	10256	2314	74
H(66B)	9356	10018	2213	74
H(67A)	7058	7407	376	228
H(67B)	7669	6945	746	228
H(68A)	6887	7742	1405	222
H(68B)	7363	7099	1647	222
H(69A)	6831	6002	1653	97
H(69B)	6754	5944	847	97
H(70A)	5855	5325	1383	80
H(70B)	5547	6059	1562	80

Table B.5. (continued) Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(71A)	4492	6037	88	71
H(71B)	4569	6280	856	71
H(72A)	4456	4855	475	62
H(72B)	4444	5143	1230	62
H(74)	3541	4060	719	86
H(75)	2619	3383	1069	113
H(76)	1606	3915	1386	106
H(77)	1524	5101	1416	83
H(1)	3561	7470	-767	59
H(2)	2983	5988	-99	63
H(3)	5122	7479	685	52
H(4)	3225	7319	1016	55
H(100)	8570(20)	5550(20)	580(20)	0(12)
H(101)	9370(20)	5490(30)	720(20)	0(12)
H(200)	8510(50)	8540(50)	1390(40)	110(30)
H(201)	8060(60)	9980(60)	680(60)	160(40)

Table B.6. Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.86	1.99	2.697(6)	139.4	N2-H2...O10
0.72(4)	2.54(5)	2.878(10)	112(5)	O2W-H101...O1W_$1
1.03(9)	1.92(9)	2.877(7)	153(7)	O6-H200...O7
1.21(12)	1.67(12)	2.847(6)	161(9)	O5-H201...O4

APPENDIX C

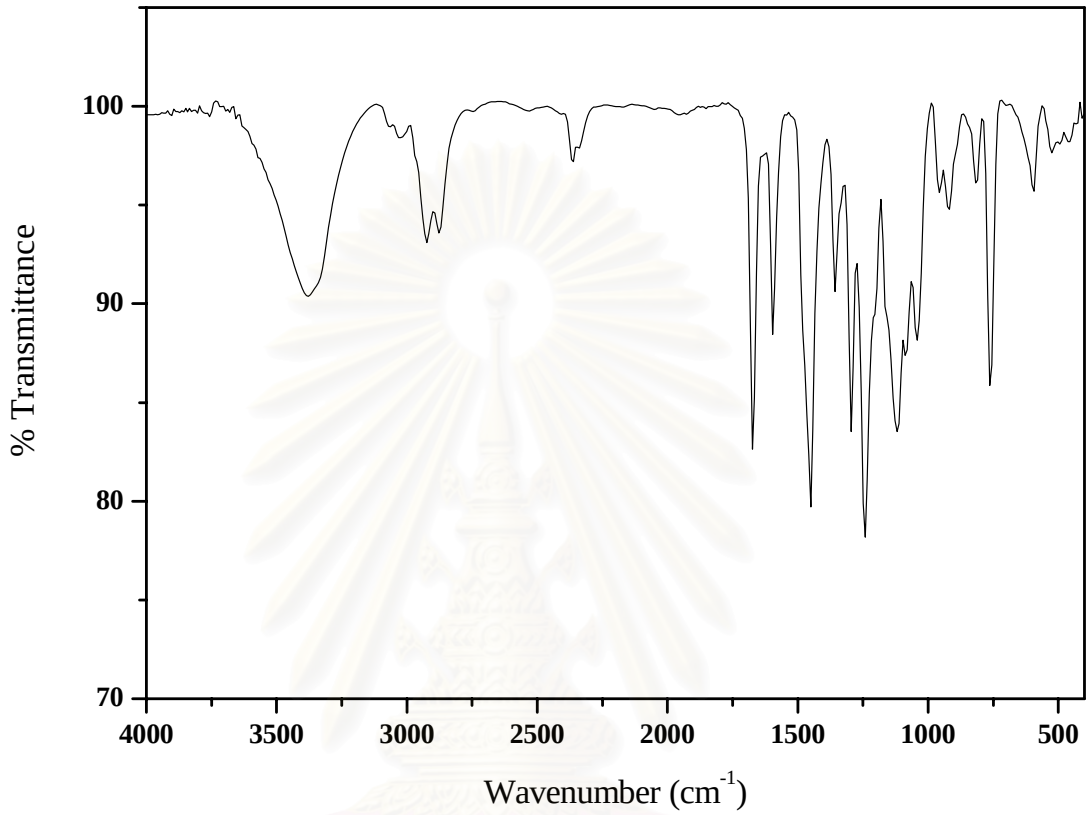


Figure C.1 IR spectrum of 1,3-calix[4]-diacetophenone (**3**).

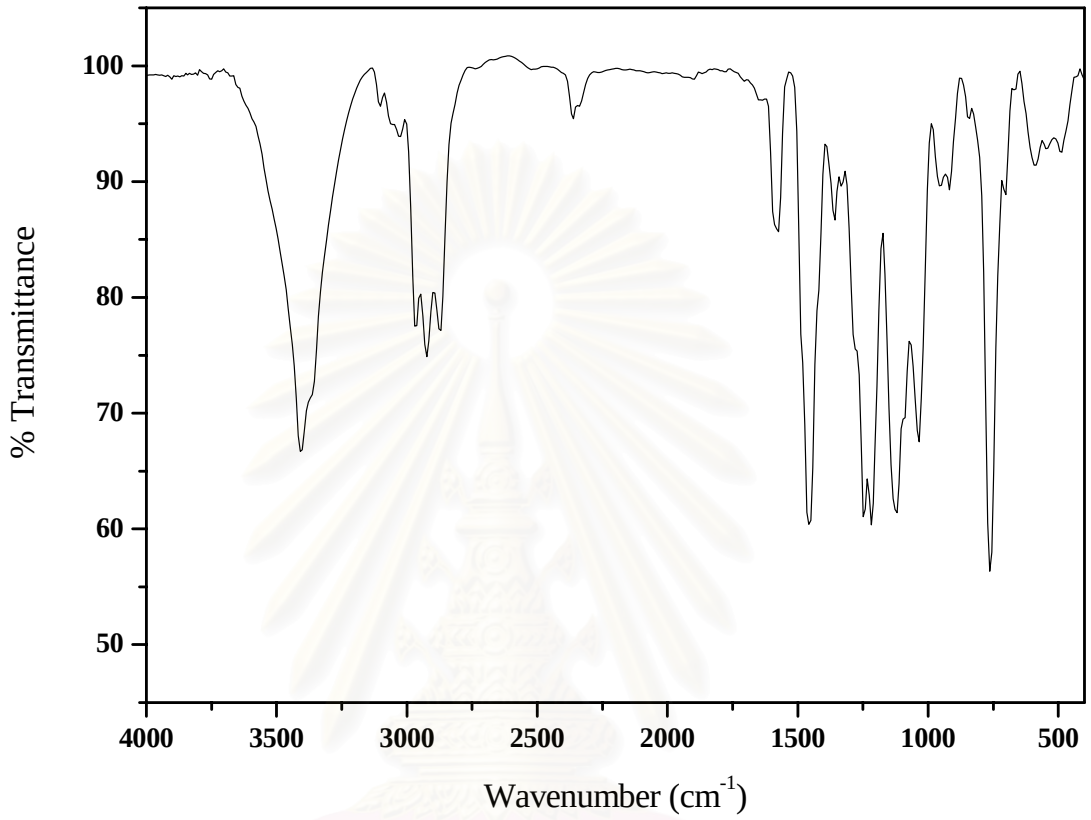


Figure C.2 IR spectrum of calix[4]arene-calix[4]pyrrole (**9**).

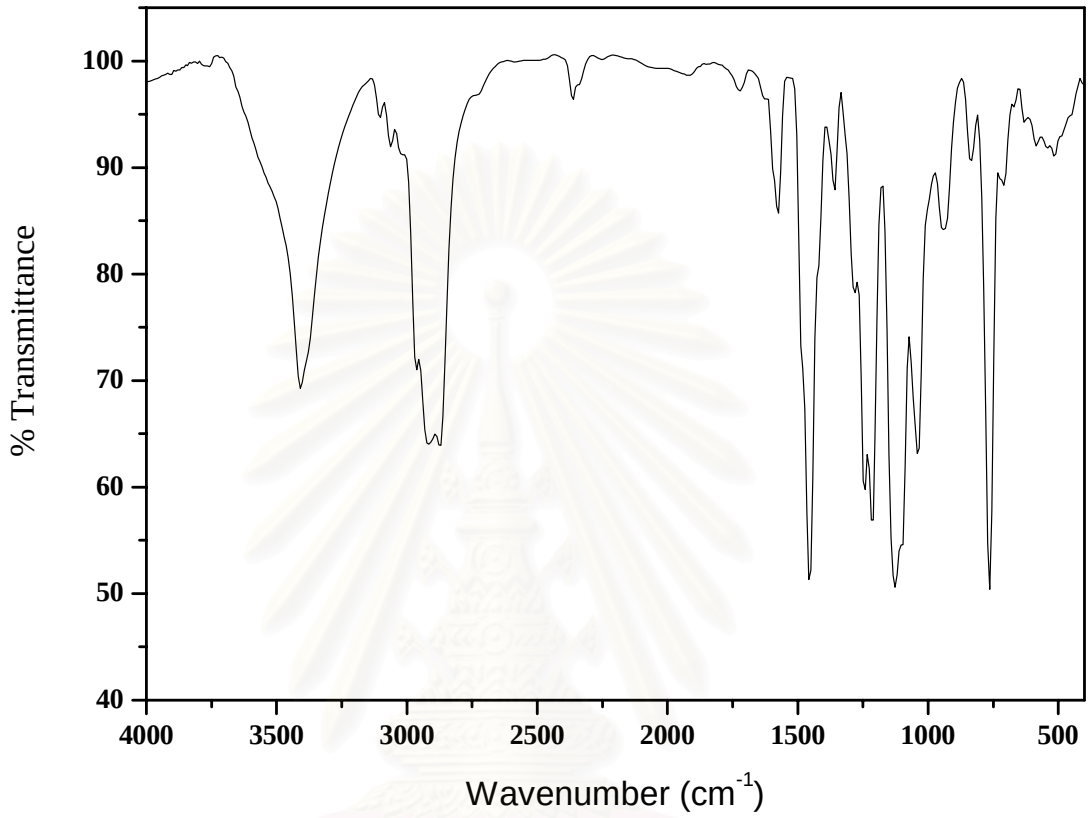


Figure C.3 IR spectrum of 1,3-alternate-calix[4]arene-calix[4]pyrrole-crown-5 (**11**).

APPENDIX D

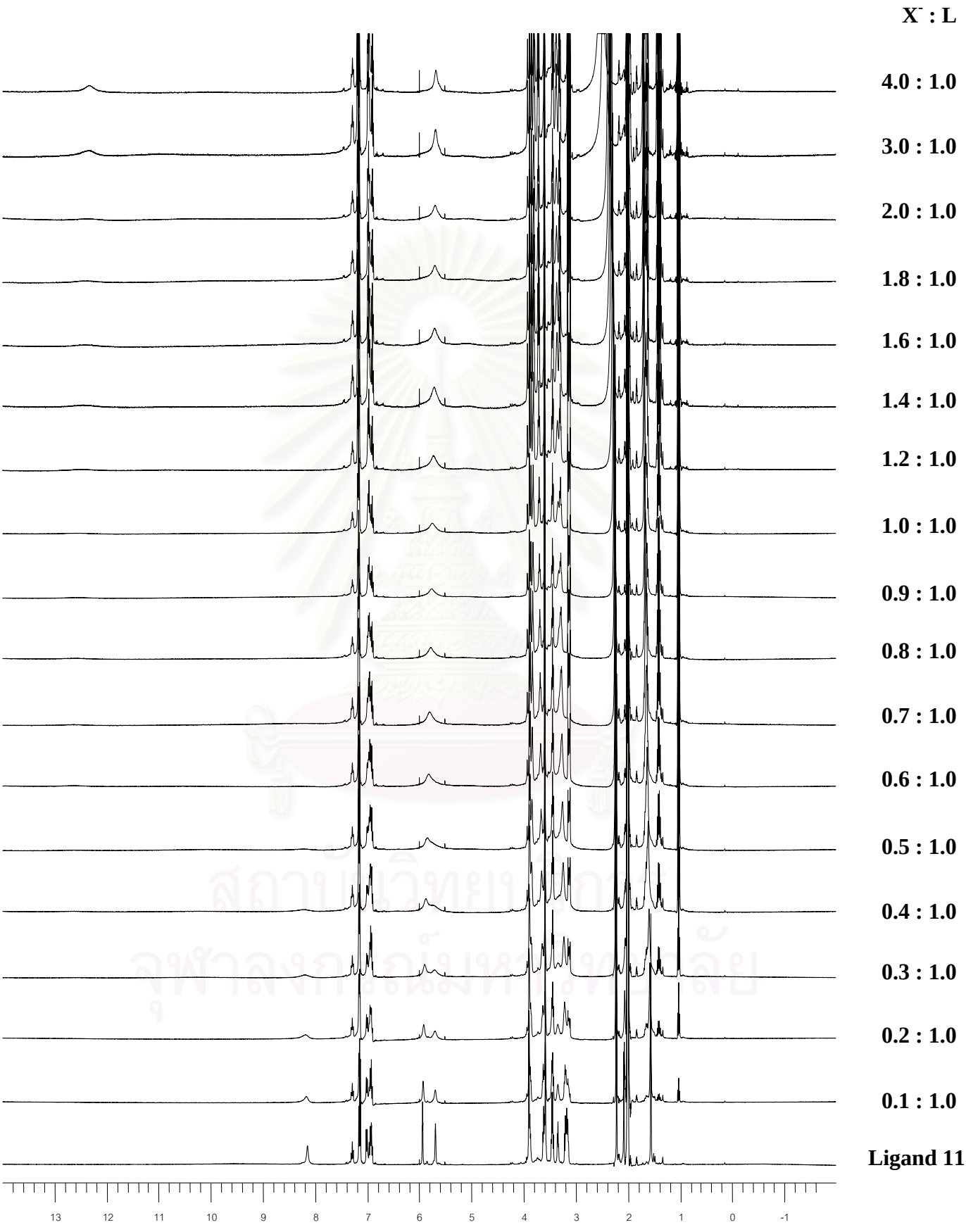


Figure D.1 ^{1}H-NMR titration of ligand **11** with Bu_4NF.

VITAE

Mr. Songtham Ruangchaithaweesuk was born on October 27, 1980 in Ratchaburi, Thailand. He graduated with a high school diploma from Debsirin School, Bangkok in 1996. He received his Bachelor's degree of Science in Chemistry from Chulalongkorn University in 2000. Since 2001, he has been a graduate student at the Department of Chemistry, Chulalongkorn University and become a member of the Supramolecular Chemistry Research Unit under Supervision of Assistance Professor Dr. Thawatchai Tuntulani and Assistance Professor Dr. Buncha Pulpoka. He finished his Master's degree of Science in the academic year 2004.