

การสังเคราะห์คัลกิรි[4] อารีนสำหรับการแยกแยะใจอ่อน

นายธีรวัท ใจอ่อน



## ศูนย์วิทยทรัพยากร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
ภาควิชาเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2539

ISBN 974-633-151-5

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

# SYNTHESIS OF CALIX[4]ARENES FOR ANION SEPARATIONS

Mr. Teerapat Rojsajjakul

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science

Department of Chemistry

Graduate School

Chulalongkorn University

1996

ISBN 974-633-151-5

Copyright of Graduate School, Chulalongkorn University

**Thesis Title**                    Synthesis of Calix[4]arenes for Anion Separations  
**By**                            Mr. Teerapat Rojsajjakul  
**Department**                Chemistry  
**Thesis Advisor**              Associate Professor Ratana Magee, Ph.D.  
**Co-advisor**                  Associate Professor Sophon Roengsumran, Ph.D.

---

Accepted by the Graduate School, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree.

*Santi Thoongsuwan* ..... Dean of Graduate School  
(Associate Professor Santi Thoongsuwan, Ph.D.)

Thesis Committee

*Siri Varothai* ..... Chairman  
(Associate Professor Siri Varothai, Ph.D.)

*Ratana Magee* ..... Thesis Advisor  
(Associate Professor Ratana Magee, Ph.D.)

*Sophon Roengsumran* ..... Co-advisor  
(Associate Professor Sophon Roengsumran, Ph.D.)

*Wimonrat Trakarnpruk* ..... Member  
(Assistant Professor Wimonrat Trakarnpruk, Ph.D.)

*Warinthon Chavasiri* ..... Member  
(Assistant Professor Warinthon Chavasiri, Ph.D.)

พิมพ์ดันจับนทกด้วยวิทยานิพนธ์ภายในกรอบสีเขียวเพียงแผ่นเดียว

ชีรภัทร์ ใจน์ส์จจะกุล : การสังเคราะห์คาลิกซ์[4]อะเรนสำหรับการแยกแอนไอออน  
(SYNTHESIS OF CALIX[4]ARENES FOR ANION SEPARATIONS) อ. ที่ปรึกษา : รศ. ดร. รัตนา  
มาภี, อ. ที่ปรึกษาร่วม : รศ. ดร. ไสวณ ใจสำราญ, 147 หน้า, ISBN 974-633-151-5

สามารถเตรียมสารประกอบใหม่ 2 ตัว  $25,27-[2,2'-(1,9-(2,5,8-triammonium)nonylene)-2,2'-$   
 $diphenoxy]diphenyl]-p-tert-butylcalix[4]arene$  (5c) และ  $25,27-[2,2'-(1,9-(2,5,8-hexamethylammonium)$   
 $nonylene)-2,2'-diphenoxy]diphenyl]-p-tert-butylcalix[4]arene$  (7b) สารประกอบ (5c) เตรียมได้จากการ  
ไฮโดรเจนอ่อนนุพันธ์ฟีเบต ด้วยโซเดียมไฮไดร์ด แล้วตามด้วยการเติมกรดไฮโดรคลอริก สามารถพิสูจน์  
เอกลักษณ์ของ (5c) โดยเทคนิคทาง  $^1\text{H-NMR}$  สเปกตรอกิปี, แมสสเปกตรومetri และ การวิเคราะห์  
ปริมาณธาตุองค์ประกอบ สารประกอบ (7b) เป็นอนุพันธ์ของเมทิลแอมโมนีียมของ (5c) ซึ่งเตรียมได้โดย  
การเมทิล化ทรูปเบสของ (5c) โดยการทำปฏิกิริยาับเมทิลไอโอดีดและไดเมทิลซัลเฟต สามารถพิสูจน์  
เอกลักษณ์ของ (7b) โดยเทคนิคทาง  $^1\text{H-NMR}$  สเปกตรอกิปี และ แมสสเปกตรومetri เมื่อนำสารประกอบ  
(5c), อนุพันธ์แอมโมนีียมที่มีในตรีเจน 3 อะตอน, (7a), อนุพันธ์เมทิลที่มีในตรีเจน 2 อะตอน และ (7b),  
อนุพันธ์เมทิลที่มีในตรีเจน 3 อะตอน มาศึกษาการจับกับ ในเทρทไออกอน และ คาร์บอนเอนทไออกอน โดย  
เทคนิคทาง  $^1\text{H-NMR}$  สเปกตรอกิปี พบร่วม สารประกอบทั้งสามจับกับ คาร์บอนเอนทไออกอน ได้ดีกว่า ในเทρท  
ไออกอน และ สารประกอบ (5c) สามารถจับได้ดีกว่า สารประกอบ (7a) และ (7b) โดยการจับเป็นแบบ 1 : 1  
(LA) สารประกอบ (5c) แสดงการเลือกจดจำ คาร์บอนเอนทไออกอนได้ดีกว่าในเทρทไออกอน

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา .....  
สาขาวิชา .....  
ปีการศึกษา .....

ลายมือชื่อนิสิต ..... วิจิตร ใจน์ส์จจะกุล  
ลายมือชื่ออาจารย์ที่ปรึกษา ..... รศ. ดร. รัตนา  
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ..... รศ. ดร. ไสวณ ใจสำราญ

# # C625045 : MAJOR CHEMISTRY

KEY WORD: CALIX[4]AREN / ANION / SEPARATION

TEERAPAT ROJSAJJAKUL : SYNTHESIS OF CALIX[4]ARENES FOR ANION SEPARATIONS :

THESIS ADVISOR : ASSOC. PROF. RATANA MAGEE, Ph. D. : THESIS CO-ADVISOR : ASSOC.

PROF. SOPHON ROENGSUMRAN, Ph. D. 147 pp. ISBN 974-633-151-5

Two novel compounds, 25,27-[2,2'-[(1,9-(2,5,8-triammonium)nonylene)-2,2'-diphenoxyl diethyl]-*p*-tert-butylcalix[4]arene (5c) and 25,27-[2,2'-[(1,9-(2,5,8-hexamethylammonium)nonylene)-2,2'-diphenoxyl diethyl]-*p*-tert-butylcalix[4]arene (7b) were synthesised. (5c) was synthesized by hydrogenation its Schiff base analog with sodium borohydride, followed by acidifying the product with hydrochloric acid to yield an ammonium derivative of *p*-tert-butylcalix[4]arene. The compound was characterized by <sup>1</sup>H-NMR spectroscopy, mass spectrometry and elemental analysis. (7b) was a methylammonium derivative of (5c), prepared by methylating the basic form of (5c) with methyl iodide and dimethyl sulfate and characterized by <sup>1</sup>H-NMR spectroscopy and mass spectrometry. Complexation studies with nitrate and carbonate ions by <sup>1</sup>H-NMR spectroscopy technique were performed on (5c) ammonium derivative of three nitrogen sites, (7a) methylated derivative of two nitrogen sites and (7b) methylated derivative of three nitrogen sites. In all cases, the extent of interaction of carbonate ion was greater than nitrate ion. The methylammonium derivatives (7a) and (7b) could bind the anions to a lesser extent than (5c). The complex was observed to be 1 : 1 type, LA. (5c) showed a recognition for carbonate over nitrate ion.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....

สาขาวิชา.....

ปีการศึกษา.....

ลายมือชื่อนิสิต.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

## **ACKNOWLEDGEMENT**



I would like to express my sincerest gratitude to Assoc. Prof. Dr. Ratana Magee and Assoc. Prof. Dr. Sophon Roengsumran for their kindness, guidance, suggestions and assistance throughout the course of this thesis. I am very obliged to Assoc. Prof. Dr. Siri Varothai, Asst. Prof. Dr. Wimonrat Trakarnpruk and Asst. Prof. Dr. Warinthon Chavasiri for their valuable suggestions as thesis examiners.

This thesis could not have been completed without the generous help of both the Supramolecular Chemistry Laboratory at Chemistry Department, Faculty of Science and the Graduate School, Chulalongkorn University by awarding scholarships.

Teerapat Rojsajjakul

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## CONTENTS

	Page
Abstract in Thai.....	iv
Abstract in English.....	v
Acknowledgement.....	vi
List of Figures.....	xii
List of Tables.....	xix
List of Schemes.....	xxi
 CHAPTER I      INTRODUCTION.....	 1
Review of Macrocyclic Compounds.....	1
Crown Ether.....	3
Mixed-donor Crown Ether.....	5
Cryptands.....	6
Cyclophanes.....	10
Cyclodextrins.....	11
Calixarene.....	13
Calix[4]arenes.....	17
Chemically Modified Calix[4]arenes for Host-guest Chemistry.....	18
Reason for Undertaking This Study.....	23
 CHAPTER II      EXPERIMENTAL.....	 24
2.1 Synthesis of Calix[4]arene Derivatives.....	24
2.1.1 Preparation of <i>p</i> - <i>tert</i> -butylcalix[4]arene (1).....	26

	Page
2.1.2 Preparation of 2[(1-formyl-2-phenyl)oxy]ethylbromide (2a).....	28
2.1.3 Preparation of 25,27-bis[2-[(1-formyl-2-phenyl) oxy]ethyl]- <i>p</i> -tert-butylcalix[4]arene (3).....	29
2.1.4 Preparation of 25,27-[2,2'-[1,1'-(1,3-propylenediimino)- 2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene (4a).....	30
2.1.5 Preparation of 25,27-[2,2'-[1,1'-(1,4-butylenediimino)- 2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene (4b).....	31
2.1.6 Preparation of 25,27-[2,2'-[(1,1'-(1,5-(3-aza)pentylene) diimino)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4] arene (4c).....	32
2.1.7 Preparation of 25,27-[2,2'-[(1,1'-(1,8-(3,6-diaza)octylene) diimino)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4] arene (4d).....	33
2.1.8 Preparation of 25,27-[2,2'-[(1,1'-(1,11-(3,6,9-triaza) undecylene)diimino)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert- butylcalix[4]arene (4e).....	34
2.1.9 Preparation of 25,27-[2,2'-[(1,7-(2,6-diammonium) heptylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix [4]arene.dichloride (5a).....	35
2.1.10 Preparation of 25,27-[2,2'-[(1,8-(2,7-diammonium) octylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix [4]arene.dichloride (5b).....	36

	Page
2.1.11 Preparation of 25,27-[2,2'-[(1,9-(2,5,8-triammonium) nonylene)-2,2'-diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix [4]arene.trichloride (5c).....	37
2.1.12 Preparation of 25,27-[2,2'-[(1,12-(2,5,8,11-tetra ammonium)dodecylene)-2,2'-diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix[4]arene.tetrachloride (5d).....	38
2.1.13 Preparation of 25,27-[2,2'-[(1,15-(2,5,8,11,14-penta ammonium)pentadecylene)-2,2'-diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix[4]arene.pentachloride (5e).....	39
2.1.14 Preparation of 25,27-[2,2'-[(1,7-(2,6-diaza)heptylene)- 2,2'-diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix[4]arene (6a).....	40
2.1.15 Preparation of 25,27-[2,2'-[(1,8-(2,7-diaza)octylene)- 2,2'-diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix[4]arene (6b).....	41
2.1.16 Preparation of 25,27-[2,2'-[(1,9-(2,5,8-triaza) nonylene)-2,2'-diphenoxyl]diethyl]- <i>p-tert</i> - butylcalix[4]arene (6c).....	42
2.1.17 Preparation of 24,26-dimethyl-25,27-[2,2'-[(1,7- (2,6-tetramethylammonium)heptylene)-2,2'- diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix[4]arene. di(hydrogensulfate) (7a).....	43
2.1.19 Preparation of 24,26-dimethyl-25,27-[2,2'-[(1,9- (2,5,8-hexamethylammonium)nonylene)-2,2'- diphenoxyl]diethyl]- <i>p-tert</i> -butylcalix[4]arene. tri(hydrogen sulfate) (7b).....	44

	Page
2.2 Complexation Study .....	45
2.2.1 Complexation study between sodium nitrate and ligand (5c).....	46
2.2.2 Complexation study between sodium carbonate and ligand (5c).....	47
2.2.3 Complexation study of sodium carbonate and sodium nitrate with ligand (5c).....	48
2.2.4 Complexation study between sodium nitrate and ligand (7a).....	49
2.2.5 Complexation study between sodium carbonate and ligand (7a).....	49
2.2.6 Complexation study between sodium nitrate and ligand (7b).....	50
2.2.7 Complexation study between sodium carbonate and ligand (7b).....	51
CHAPTER III     RESULTS AND DISCUSSION .....	52
3.1 Synthesis .....	52
3.2 Complexation Study.....	58
CHAPTER IV     CONCLUSIONS.....	83
REFERENCES.....	84

	Page
APPENDIXES.....	87
CURRICULUM VITAE.....	147



## LIST OF FIGURES

	Page
Figure 1.1 Examples of crown ethers.....	3
Figure 1.2 X-ray structure of the RbNCS complex of dibenzo-18-crown-6.....	4
Figure 1.3 The complexation between other guest molecules with crown ethers.....	4
Figure 1.4 Examples of mixed-donor crown ethers.....	5
Figure 1.5 The representative parent series of cryptands.....	6
Figure 1.6 Examples of macrotricyclic cryptands.....	7
Figure 1.7 Structure of the Rb <sup>+</sup> complex of cryptand 1:1:1.....	8
Figure 1.8 The complexation between water molecule and anion with protonated cryptands.....	9
Figure 1.9 The complexation between azide anion with cryptand.....	9
Figure 1.10 The derivative of cyclophane.....	10
Figure 1.11 An example of the derivatives of cyclodextrins.....	11
Figure 1.12 The $\beta$ -cyclodextrin derivative adduct.....	12
Figure 1.13 The hydrolysis of esters by the nickel derivative.....	12
Figure 1.14 Example of duplex cyclodextrin.....	13
Figure 1.15 General formula of calixarenes.....	14
Figure 1.16 Products of basic condensation of <i>p</i> - <i>tert</i> -butylphenol with formaldehyde.....	16
Figure 1.17 The conformations of calix[4]arenes.....	17
Figure 1.18 Chemical modification of calix[4]arenes at the 1,3-dihydroxyl group at lower rim.....	18

	Page
Figure 1.19 Calix[4]arene-crown-5.....	19
Figure 1.20 Schiff base <i>p</i> - <i>tert</i> -butylcalix[4]arenes .....	20
Figure 1.21 Calix salophane crown ethers.....	21
Figure 1.22 Double-calix-crown.....	21
Figure 1.23 A novel neutral fluoride anion selective <i>bis</i> -calix[4]arene receptor.....	22
Figure A.1 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of <i>p</i> - <i>tert</i> -butylcalix[4]arene(1).....	88
Figure A.2 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 2[(1-formyl-2-phenyl)oxy] ethylbromide (2a).....	89
Figure A.3 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 2,2'-(1,1'-dioxyethane) bisbenzaldehyde (2b).....	90
Figure A.4 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 25,27-bis[2[1-formyl-2- phenyl)oxy]ethyl]- <i>p</i> - <i>tert</i> -butylcalix[4]arene (3).....	91
Figure A.5 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 25,27-[2,2'-(1,1'- (1,3-propylenediiimino)-2,2'-diphenoxyl]diethyl]- <i>p</i> - <i>tert</i> -butylcalix[4]arene (4a).....	92
Figure A.6 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 25,27-[2,2'-(1,1'- (1,4-butylenediiimino)-2,2'-diphenoxyl]diethyl]- <i>p</i> - <i>tert</i> -butylcalix[4]arene (4b).....	93
Figure A.7 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 25,27-[2,2'-(1,1'- (1,5-(3-aza)pentylene)diimino)-2,2'-diphenoxyl]diethyl]- <i>p</i> - <i>tert</i> -butylcalix[4]arene (4c).....	94
Figure A.8 $^1\text{H-NMR}(\text{CDCl}_3)$ spectrum of 25,27-[2,2'-(1,1'-(1,8- (3,6-diaza)octylene)diimino)-2,2'-diphenoxyl]diethyl]- <i>p</i> - <i>tert</i> -butylcalix[4]arene (4d).....	95

	Page
Figure A.9 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,1'-(1,11-(3,6,9-triaza)undecylene)diimino)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene (4e).....	96
Figure A.10 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,7-(2,6-diammonium)heptylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene.dichloride (5a).....	97
Figure A.11 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,8-(2,7-diammonium)octylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene.dichloride (5b).....	98
Figure A.12 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,9-(2,5,8-triammonium)nonylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene.trichloride (5c).....	99
Figure A.13 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,12-(2,5,8,11-tetraammonium)dodecylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene.tetrachloride (5d).....	100
Figure A.14 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,15-(2,5,8,11,14-pentaammonium)pentadecylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene.pentachloride (5e).....	101
Figure A.15 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,7-(2,6-diaza)heptylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene (6a).....	102
Figure A.16 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,8-(2,7-diaza)octylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene (6b).....	103
Figure A.17 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 25,27-[2,2'-[(1,9-(2,5,8-triaza)nonylene)-2,2'-diphenoxyl]diethyl]- <i>p</i> -tert-butylcalix[4]arene (6c).....	104

	Page
Figure A.18 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 24,26-dimethyl-25,27-[2,2'-[(1,7-(2,6-tetramethylammonium)heptylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene di(hydrogensulfate) (7a).....	105
Figure A.19 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of 24,26-dimethyl-25,27-[2,2'-[(1,8-(2,5,8-hexamethylammonium)nonylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene.tri(hydrogensulfate) (7b).....	106
Figure A.20 Mass spectrum ( $\text{EI}^+$ ) of <i>p</i> -tert-butylcalix[4]arene (1).....	107
Figure A.21 Mass spectrum ( $\text{FAB}^+$ ) of 25,27-[2,2'-[(1,1'-(1,5-(3-aza-pentylene)diimino)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene (4c).....	108
Figure A.22 Mass spectrum ( $\text{FAB}^+$ ) of 25,27-[2,2'-[(1,9-(2,5,8-triammonium)nonylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene.trichloride (5c).....	109
Figure A.23 Mass spectrum ( $\text{FAB}^+$ ) of 25,27-[2,2'-[(1,9-(2,5,8-triaza)nonylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene (6c).....	110
Figure A.24 Mass spectrum ( $\text{FAB}^+$ ) of 24,26-dimethyl-25,27-[2,2'-[(1,9-(2,5,8,9-hexamethyammonium)nonylene)-2,2'-diphenoxy]diethyl]- <i>p</i> -tert-butylcalix[4]arene.tri(hydrogensulfate) (7b).....	111
Figure A.25 Plot between mole ratios (A :L) and $\Delta\text{Hz}$ of $\text{CH}_2\text{-NH}_2^+ \text{-CH}_2$ protons of complexation between ligand (5c) with $\text{NaNO}_3$ .....	112

	Page
Figure A.26 Plot between mole ratios (A : L) and $\Delta\text{Hz}$ of Ar-CH <sub>2</sub> -NH <sub>2</sub> <sup>+</sup> -CH <sub>2</sub> protons of complexation between ligand (5c) with NaNO <sub>3</sub> .....	113
Figure A.27 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 0.0 : 1.0.....	114
Figure A.28 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 0.5 : 1.0.....	115
Figure A.29 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 1.0 : 1.0.....	116
Figure A.30 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 1.5 : 1.0.....	117
Figure A.31 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 2.0 : 1.0.....	118
Figure A.32 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 2.5 : 1.0.....	119
Figure A.33 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 3.0 : 1.0.....	120
Figure A.34 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 3.5 : 1.0.....	121
Figure A.35 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 4.0 : 1.0.....	122
Figure A.36 Plot between mole ratios, (A : L) and $\Delta\text{Hz}$ of CH <sub>2</sub> -NH <sub>2</sub> <sup>+</sup> -CH <sub>2</sub> protons of complexation between ligand (5c) with Na <sub>2</sub> CO <sub>3</sub> .....	123

	Page
Figure A.37 Plot between mole ratios, (A : L) and $\Delta\text{Hz}$ of Ar-CH <sub>2</sub> -NH <sub>2</sub> <sup>+</sup> -CH <sub>2</sub> protons of complexation between ligand (5c) with Na <sub>2</sub> CO <sub>3</sub> .....	124
Figure A.38 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 0.0 : 1.0.....	125
Figure A.39 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 0.5 : 1.0.....	126
Figure A.40 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 1.0 : 1.0.....	127
Figure A.41 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 1.5 : 1.0.....	128
Figure A.42 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 2.0 : 1.0.....	129
Figure A.43 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 2.5 : 1.0.....	130
Figure A.44 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 3.0 : 1.0.....	131
Figure A.45 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 3.5 : 1.0.....	132
Figure A.46 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) mole ratio (A : L) 4.0 : 1.0.....	133
Figures A.47 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between sodium nitrate and ligand (5c) mole ratio (A : L) 1: 1.....	134
Figure A.48 <sup>1</sup> H-NMR (CDCl <sub>3</sub> ) spectrum of complexation between Na <sub>2</sub> CO <sub>3</sub> and ligand (5c) nitrate ion solution (A <sub>2</sub> : L : A <sub>1</sub> = 1 : 1 : 1) .....	135

	Page
Figure A.49 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between ligand (5c), $\text{NaNO}_3$ and $\text{Na}_2\text{CO}_3$ ( $L : \text{A}_1 : \text{A}_2 = 1 : 1 : 1$ ) .....	136
Figure A.50 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{NaNO}_3$ and ligand (7a) mole ratio ( $A : L$ ) 0 : 1.....	137
Figure A.51 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{NaNO}_3$ and ligand (7a) mole ratio ( $A : L$ ) 1 : 1.....	138
Figure A.52 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{NaNO}_3$ and ligand (7a) mole ratio ( $A : L$ ) 4 : 1.....	139
Figure A.53 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{Na}_2\text{CO}_3$ and ligand (7a) mole ratio ( $A : L$ ) 1 : 1.....	140
Figure A.54 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{Na}_2\text{CO}_3$ and ligand (7a) mole ratio ( $A : L$ ) 4 : 1.....	141
Figure A.55 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{NaNO}_3$ and ligand (7b) mole ratio ( $A : L$ ) 0 : 1.....	142
Figure A.56 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{NaNO}_3$ and ligand (7b) mole ratio ( $A : L$ ) 1 : 1.....	143
Figure A.57 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{NaNO}_3$ and ligand (7b) mole ratio ( $A : L$ ) 4 : 1.....	144
Figure A.58 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{Na}_2\text{CO}_3$ and ligand (7b) mole ratio ( $A : L$ ) 1 : 1.....	145
Figure A.59 $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) spectrum of complexation between $\text{Na}_2\text{CO}_3$ and ligand (7b) mole ratio ( $A : L$ ) 4 : 1.....	146

## LIST OF TABLES

Table	Page
1.1 Representative parent series of cryptands.....	6
1.2 Comparison of three representative host molecules.....	15
2.2.1 Ratios of sodium nitrate to ligand (5c) in dichloromethane.....	46
2.2.2 Ratios of sodium carbonate to ligand (5c) in dichloromethane.....	47
2.2.4 Ratios of sodium nitrate to ligand (7a) in methanol.....	49
2.2.5 Ratios of sodium carbonate to ligand (7a) in methanol.....	50
2.2.6 Ratios of sodium nitrate to ligand (7b) in dichloromethane.....	51
2.2.7 Ratios of sodium carbonate to ligand (7b) in dichloromethane.....	51
3.1 $^1\text{H-NMR}$ analysis of (1).....	61
3.2 $^1\text{H-NMR}$ analysis of (2a).....	61
3.3 $^1\text{H-NMR}$ analysis of (2b).....	62
3.4 $^1\text{H-NMR}$ analysis of (3).....	63
3.5 $^1\text{H-NMR}$ analysis of (4a).....	64
3.6 $^1\text{H-NMR}$ analysis of (4b).....	65
3.7 $^1\text{H-NMR}$ analysis of (4c).....	66
3.8 $^1\text{H-NMR}$ analysis of (4d).....	67
3.9 $^1\text{H-NMR}$ analysis of (4e).....	67
3.10 $^1\text{H-NMR}$ analysis of (5a).....	68
3.11 $^1\text{H-NMR}$ analysis of (5b).....	69
3.12 $^1\text{H-NMR}$ analysis of (5c).....	70
3.13 $^1\text{H-NMR}$ analysis of (5d).....	71
3.14 $^1\text{H-NMR}$ analysis of (5e).....	72
3.15 $^1\text{H-NMR}$ analysis of (6a).....	73
3.16 $^1\text{H-NMR}$ analysis of (6b).....	74
3.17 $^1\text{H-NMR}$ analysis of (6c).....	75

Table	Page
3.18 $^1\text{H}$ -NMR analysis of (7a).....	76
3.19 $^1\text{H}$ -NMR analysis of (7b).....	77



## **LIST OF SCHEMES**

	Page
Scheme I .....	78
Scheme II .....	79
Scheme III .....	80
Scheme IV .....	81
Scheme V .....	82

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย