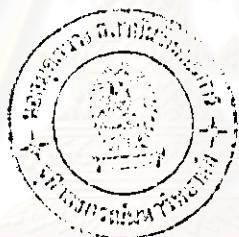


การเตรียมและประเมินคัดกรองเร่งปฐมภิจัยของอาจารย์ประจำบัณฑิต
โซนภาคตะวันออกเฉียงเหนือ

นางสาว ภาระเกต ภาควี



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาเคมี ภาควิชาเคมี

บัญชีวิทยาอ้อ อุทาองกรณ์มหาวิทยาลัย

ปีการศึกษา 2542

ISBN 974-332-910-2

บินเดินเชื่องบัณฑิตวิทยาอ้อ อุทาองกรณ์มหาวิทยาลัย

**PREPARATION AND CATALYTIC PROPERTY OF
CYCLODEXTRIN - FERROCENYLAMINE INCLUSION COMPOUNDS**

Miss Karaked Tedsree

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Chemistry

Department of Chemistry

Graduate School

Chulalongkorn University

Academic Year 1999

ISBN 974-332-910-2

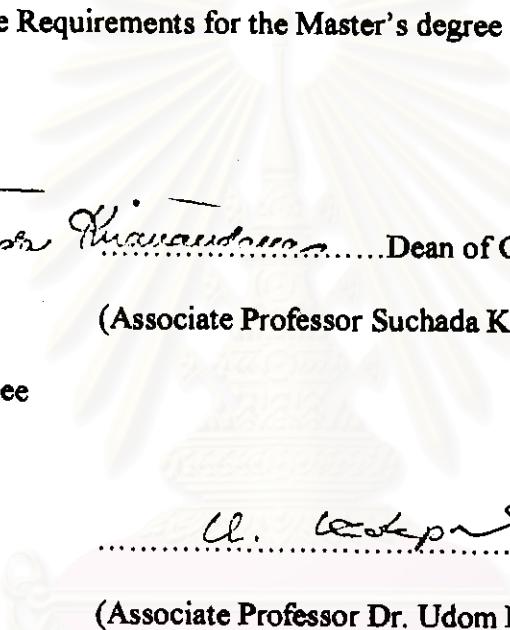
Thesis PREPARATION AND CATALYTIC PROPERTY OF
CYCLODEXTRIN-FERROCENYLAMINE INCLUSION
COMPOUNDS

By Miss Karaked Tedsree

Department Chemistry

Thesis Advisor Associate Professor Dr. Wimonrat Trakarnpruk

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


Suchada Kiranandana Dean of Graduate School

(Associate Professor Suchada Kiranandana, Ph.D.)

Thesis Committee

U. Kokpol Chairman

(Associate Professor Dr. Udom Kokpol)

W. Trakarnpruk Thesis Advisor

(Associate Professor Dr. Wimonrat Trakarnpruk)

Warinthorn Chavasiri Member

(Assistant Professor Dr. Warinthorn Chavasiri)

Orawan Sanguanruang Member

(Dr. Orawan Sanguanruang)

การระเกด เทศวิริ : การเตรียมและสมบัติการเร่งปฏิกิริยาของสารประกอบอินคุลป์ชันไนโคลเดกซ์ทรีน-เฟอร์โรซิโน่กอเม็น (PREPARATION AND CATALYTIC PROPERTY OF CYCLODEXTRIN-FERROCENYLAMINE INCLUSION COMPOUNDS) อ.ที่ปรึกษา: ดร. ดร. วินสันต์ គរការທຖກ; 162 หน้า, ISBN 974-332-910-2.

ได้เครื่องมือพันธ์เพื่อไว้ใช้นิยมอีนีน *N,N*-dimethylaminomethylferrocene, *N,N*-dimethyl-aminomethylferrocene methiodide, α -methylferrocenylmethylamine, ferrocenylethylamine, diphenylaminomethylferrocene, Schiff base derivative, reduced Schiff base derivative, 6-ferrocenyl-2, 2'-bipyridine, 2-(α, α -diphenylhydroxymethyl)dimethylaminomethylferrocene และอนุพันธ์เพื่อไว้ใช้นิยมอีนีน คือ acetylferrocene, ferrocenylmethanol และ α -hydroxyethylferrocene ตรวจพิสูจน์เอกลักษณ์ด้วยเทคนิคทางอินฟราเรดและไปร์คอนอีนอีมาร์

เครื่องมือการประกอบอินคุลป์ชันของอนุพันธ์เพื่อไว้ใช้นิยมและอนุพันธ์ชนิดอื่นๆ กับบิตาไนโคลเดกซ์ทรีน ไคลเคนอนุพันธ์เพื่อไว้ใช้นิยมลงในกระถางน้ำของบิตาไนโคลเดกซ์ทรีนที่อุณหภูมิ 60 องศาเซลเซียส ให้เป็นรู实体์ พลังไค 60-75 ครั้งพิสูจน์เอกลักษณ์ของสารประกอบอินคุลป์ชันโดยเทคนิคไปร์คอนอีนอีมาร์ อินฟราเรด และการเก็บวนรังสีอีกซ์ อัตราส่วนที่หาด้วยการวิเคราะห์ข้าวเป็น 1:1 การวิเคราะห์ทางท่อร์ไมโครวิเมตريแสดงว่าการประกอบอินคุลป์ชันเกิดขึ้นต่อความร้อน ข้อมูลทางไปร์คอนอีนอีมาร์แสดงให้เห็นว่าแรงกระทำระหว่างอนุพันธ์เพื่อไว้ใช้นิยมกับอินคุลป์ชัน คิฟเฟร์กไคแกรมของรังสีอีกซ์ของสารประกอบอินคุลป์ชันต่างจากของของสารในชุดเดียวกัน ศึกษาความสามารถในการเร่งปฏิกิริยาของอนุพันธ์เพื่อไว้ใช้นิยมอีนีนที่เตรียมได้ในแยกคิดเกร้นของเบนซอลดีไอด์ ศูนย์ไคเอ็ทิกซิงค์ ได้ผลได้ปานกลางถึงสูง (45-96%) และมีความถือใจทางอิเนนท์ไฮเมอร์ค่า ในทางตรงกันข้ามสารประกอบอินคุลป์ชันให้ผลได้ต่ำ (37-54%) และมีความถือใจทางอิเนนท์ไฮเมอร์ที่สูงกว่า

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา เศรษฐศาสตร์
สาขาวิชา เศรษฐศาสตร์
ปีการศึกษา 2542

นายมีอธิบดีนิสิต ประมาณ ๗๖๒ ตัว
นายมีอธิบดีอาจารย์ที่ปรึกษา ๑ 位
นายมีอธิบดีอาจารย์ที่ปรึกษาร่วม

3970094123 : MAJOR CHEMISTRY

KEY WORD:

β -CYCLODEXTRIN / FERROCENYLAMINE / ALKYLATION

KARAKED TEDSREE : PREPARATION AND CATALYTIC PROPERTY OF CYCLODEXTRIN-

FERROCENYLAMINE INCLUSION COMPOUNDS. THESIS ADVISOR : ASSOC. PROF. WIMONRAT

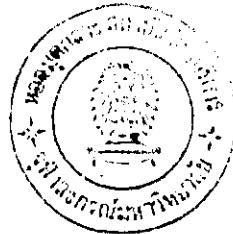
TRAKARNPRUK, Ph.D. 162 pp. ISBN 974-332-910-2.

Ferrocenylamines : *N, N*-dimethylaminomethylferrocene, *N, N*-dimethylaminomethyl ferrocene methiodide, α -methylferrocenylmethylethylamine, ferrocenylethylamine, *N, N*-diphenylamino methylferrocene, Schiff base derivative, reduced Schiff base derivative, 6-ferrocenyl-2, 2'-dipyridine, 2-(α , α -diphenylhydroxymethyl)dimethylaminomethylferrocene and other ferrocenyl derivatives: acetylferrocene, ferrocenylmethylalcohol, α -hydroxyethylferrocene were prepared and characterized by FTIR and ^1H NMR technique.

The inclusion compounds of the above complexes with β -cyclodextrin can be easily prepared 60-75 percent yields by adding ferrocenyl derivatives directly to an aqueous β -cyclodextrin solution at 60°C. The inclusion compounds were characterized by ^1H NMR, IR and X-ray diffraction techniques. Stoichiometries were determined by elemental analyses to be 1:1. Thermogravimetric analyses showed that inclusion compounds are thermally stable. ^1H NMR data indicate that the interaction between cyclodextrin and ferrocenyl derivative is a real inclusion phenomenon. X-ray diffractograms of the inclusion compounds were different from those of the corresponding mixtures. The synthesized ferrocenylamine derivatives were studied for the catalytic activity in the alkylation of benzaldehyde with diethylzinc. Moderate to high yields (45-96%) but low enantioselectivities were obtained. On the contrary, the inclusion compounds gave lower yields (37-54%) with higher enantioselectivities.

ภาควิชา.....	เคมี	ลายมือชื่อนิสิต.....	_____
สาขาวิชา.....	เคมี	ลายมือชื่ออาจารย์ที่ปรึกษา.....	_____ ✓
ปีการศึกษา.....	2542	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....	_____

ACKNOWLEDGEMENT



The author wishes to express her deepest appreciation to her advisor, Associate Professor Dr. Wimonrat Trakarnpruk, for her assistance and encouragement throughout the course of this research, as well as personal friendship during her graduate study. She also would like to thank the members of her thesis committee, Associate Professor Dr. Udom Kokpol, Assistant Professor Dr. Warinthorn Chaovasiri and Dr. Orawan Sanguanruang for valuable discussion and advice. She would like to thank the lecturers and financial support from Department of Chemistry, Faculty of Science, Chulalongkorn University. Moreover, she thanks the staffs of the Scientific and Technology Research Equipment Centre, Chulalongkorn University for sample analysis. She would like to thank Dr. Ichijo Imae; Research Associate at Japan Advanced Institute of Science and Technology (JAIST), Japan for his help in high performance liquid chromatography.

She also would like to express her deepest gratitude to her parent for their great support and encouragement throughout the course of her education and finally she thanks all her friends for their friendships and help during her graduate study.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
Abstract in Thai.....	iv
Abstract in English.....	v
Acknowledgement.....	vi
List of Abbreviations.....	xiii
List of Figures.....	xiv
List of Schemes.....	xix
List of Tables.....	xxi
Chapter I Introduction.....	1
Chapter II Theory.....	3
2.1 Ferrocene.....	3
2.2 Cyclodextrins.....	4
2.3 Inclusion Compounds.....	8
2.4 Organozinc Chemistry.....	11
2.5 Enantioselectivity.....	12
2.6 Determination of Optical Purity.....	12
Chapter III Literature Reviews.....	14
3.1 Inclusion.....	14
3.2 Asymmetric Alkylation.....	19
Chapter IV Experimental.....	22
4.1 Operation and Apparatus.....	22
4.2 Reagents and Solvents.....	22
4.3 Physical and Analytical Measurements.....	23
4.3.1 Nuclear Magnetic Resonance.....	23
4.3.2 Fourier Transform Infrared Spectrometry.....	23
4.3.3 Ultraviolet and Visible Spectroscopy.....	23
4.3.4 Elemental Analyses.....	23

	Page
4.3.5 Thermogravimetric Analyses.....	24
4.3.6 X-Ray Powder Diffraction.....	24
4.3.7 GC-Mass Spectrometry.....	24
4.3.8 Melting Point.....	24
4.3.9 Column Chromatography.....	24
4.3.10 High Performance Liquid Chromatography.....	25
4.3.11 Gas Chromatography.....	25
4.4 Preparation of Ferrocenylamine Derivatives.....	26
4.4.1 Preparation of <i>N, N</i> -Dimethylaminomethylferrocene.....	26
4.4.2 Preparation of <i>N, N</i> -Dimethylaminomethylferrocene Methiodide	26
4.4.3 Preparation of Ferrocenylacetonitrile.....	27
4.4.4 Preparation of α -Methylferrocenylmethylamine.....	28
4.4.5 Preparation of Ferrocenylethylamine.....	28
4.4.6 Preparation of <i>N, N</i> -Diphenylaminomethylferrocene.....	29
4.4.7 Preparation of Schiff Base Derivative.....	29
4.4.8 Preparation of Reduced Schiff Base Derivative.....	30
4.4.9 Preparation of 6-Ferrocenyl-2, 2'-Bipyridine.....	30
4.4.10 2-(α , α -Diphenylhydroxymethyl)dimethylamino methylferrocene.....	31
4.5 Preparation of Other Ferrocenyl Derivatives.....	32
4.5.1 Preparation of Acetylferrocene.....	32
4.5.2 Preparation of Ferrocenylmethylalcohol.....	32
4.5.3 Preparation of α -Hydroxyethylferrocene.....	33
4.6 Preparation of β -Cyclodextrin-Ferrocenyl Derivative Inclusion Compounds.....	34
4.6.1 β -Cyclodextrin- <i>N, N</i> -Dimethylaminomethylferrocene Inclusion Compound.....	34

	Page
4.6.2 β -Cyclodextrin- <i>N,N</i> -Dimethylaminomethylferrocene Methiodide Inclusion Compound.....	35
4.6.3 β -Cyclodextrin-Ferrocenylacetonitrile Inclusion Compound.....	35
4.6.4 β -Cyclodextrin- α -Methylferrocenylmethylamine Inclusion Compound.....	36
4.6.5 β -Cyclodextrin-Ferrocenylethylamine Inclusion Compound.....	36
4.6.6 β -Cyclodextrin-Schiff Base Derivative Inclusion Compound.....	37
4.6.7 β -Cyclodextrin-Reduced Schiff Base Derivative Inclusion Compound.....	37
4.6.8 β -Cyclodextrin-Acetylferrocene Inclusion Compound.....	38
4.6.9 β -Cyclodextrin-Ferrocenylaldehyde Inclusion Compound...	38
4.6.10 β -Cyclodextrin-Ferrocenylmethanol Inclusion Compound.....	39
4.6.11 β -Cyclodextrin- α -Hydroxyethylferrocene Inclusion Compound.....	39
4.7 Preparation of β -Cyclodextrin-Organic Compound Inclusion Compounds.....	40
4.7.1 β -Cyclodextrin-Benzaldehyde Inclusion Compound.....	40
4.7.2 β -Cyclodextrin-1-Phenyl-1-Propanol Inclusion Compound.....	40
4.8 Alkylation of Benzaldehyde with Diethylzinc.....	41
4.8.1 Alkylation Reaction.....	41
4.8.2 Determination of Correction Factor for Gas Chromatography.....	41

	Page
4.8.3 Some Effects on % Yield of Alkylation Product.....	42
4.9 Preparation of Diastereomeric Esters.....	42
Chapter 5 Results and Discussion.....	43
5.1 Preparations of Ferrocenyl Derivatives.....	43
5.1.1 Ferrocenylamine Derivatives.....	43
5.1.2 Schiff Base and Reduced Derivatives.....	47
5.1.3 Lithiation of Ferrocene.....	51
5.1.4 Other Ferrocenyl Derivatives.....	58
5.1.4.1 Acetylferrocene.....	58
5.1.4.2 Ferrocenylmethylalcohol.....	58
5.1.4.3 α -Hydroxyethylferrocene.....	59
5.2 Properties of Inclusion Compounds.....	62
5.2.1 Thermogravimetric Analysis.....	62
5.2.2 Elemental Analysis.....	64
5.3 Characterization of β -Cyclodextrin by NMR Technique.....	66
5.4 Characterization of β -Cyclodextrin-Ferrocenyl Derivative Inclusion Compounds by NMR Technique.....	69
5.5 Characterization of Inclusion Compounds by NMR Technique..	70
5.5.1 β -Cyclodextrin- <i>N,N</i> -Dimethylaminomethylferrocene Inclusion Compound.....	70
5.5.2 β -Cyclodextrin- <i>N,N</i> -Dimethylaminomethylferrocene Methiodide Inclusion Compound.....	74
5.5.3 β -Cyclodextrin- α -Methylferrocenylmethylamine Inclusion Compound.....	77
5.5.4 β -Cyclodextrin-Ferrocenylethylamine Inclusion Compound.....	80
5.5.5 β -Cyclodextrin-Schiff Base Derivative Inclusion Compound.....	83

	Page
5.5.6 β-Cyclodextrin-Reduced Schiff Base Derivative Inclusion Compound.....	86
5.5.7 β-Cyclodextrin-Acetylferrocene Inclusion Compound and β-Cyclodextrin-Ferrocenylaldehyde Inclusion Compound.....	89
5.5.8 β-Cyclodextrin-Ferrocenylmethylalcohol Inclusion Compound and β-Cyclodextrin-α-Hydroxyethylferrocene Inclusion Compound	94
5.6 Characterization of β-Cyclodextrin by FTIR Technique.....	99
5.7 Characterization of Inclusion Compounds by FTIR Technique... 100	
5.8 Characterization of Inclusion Compounds by X-ray Powder Diffraction.....	116
5.9 Ultraviolet-Visible Absorption Spectroscopy.....	121
5.10 Alkylation of Benzaldehyde with Diethylzinc.....	122
5.11 Determination of % Yield.....	124
5.11.1 Alkylation Product Yield.....	124
5.11.2 Correction Factor.....	124
5.12 Some Effects on % Yield of Alkylation Reaction.....	126
5.12.1 Mole Ratio of Benzaldehyde:Diethylzinc	126
5.12.2 Solvent, Temperature and Time.....	127
5.12.3 Mol % of Catalyst.....	129
5.12.4 Types of Catalysts.....	131
5.13 Enantioselectivity.....	135
5.13.1 Determination of Enantioselectivity by Gas Chromatography.....	135
5.13.2 Determination of Enantioselectivity by ^1H NMR Technique.....	141

	Page
5.13.3 Determination of Enantioselectivity by High Performance Liquid Chromatography.....	144
Chapter VI Conclusion	145
References.....	147
Appendix A.....	149
Appendix B.....	153
Appendix C.....	158
Vita.....	162

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

$^{\circ}\text{C}$	degree Celcius
cm^{-1}	unit of wavenumber
mL	millilitre
hr	hour
$^1\text{H NMR}$	Proton nuclear magnetic resonance
δ	chemical shift (ppm)
J	coupling constant (Hz)
s	singlet
d	doublet
t	triplet
m	multiplet
dd	doublets of doublet
ddd	doublets of doublets of doublet
td	triplets of doublet
CDCl_3	deuterochoroform
DMSO-d_6	methyl sulfoxide-d ₆
ppm	parts per million
FTIR	Fourier transform infrared
br	broad (IR)
s	strong (IR)
m	medium (IR)
w	weak (IR)
UV-vis	Ultraviolet-visible
ν_{max}	wavelength at maximum absorption
ϵ	molar absorptivity
m/z	mass per charge
Fc	ferrocene
CD	cyclodextrin

LIST OF FIGURES

Figure		Page
2.1	Structures of ferrocene.....	3
2.2	Structures of α -, β - and γ -cyclodextrins.....	5
2.3	X-ray structure of α -cyclodextrin.....	6
2.4	Characteristic structural features of cyclodextrin.....	7
2.5	Geometries of dimethylzinc.....	11
3.1	p-Nitrophenyl ferroceneacrylate ester.....	15
3.2	Proposed structures for ferrocene- α , - β and γ -cyclodextrin inclusion compounds.....	15
3.3	Thermogravimetric analysis of a) β -cyclodextrin-ferrocene inclusion compound b) mixture of the β -cyclodextrin and ferrocene c) ferrocene.....	16
3.4	Absorption spectra of a) β -cyclodextrin-ferrocene b) γ -cyclodextrin-ferrocene.....	17
3.5	A view based on X-ray crystallographic data of the α -cyclodextrin ferrocene (2:1) inclusion compound, along a local twofold axis through the iron atom.....	18
3.6	β -Secondary amino alcohol catalysts a) <i>endo</i> -3-amino- <i>endo</i> -2-hydroxybornane b) <i>exo</i> -3-amino- <i>exo</i> -2-hydroxybornane.....	19
3.7	Proposed mechanism for enantioselective alkylation of diethylzinc to aldehyde.....	20
5.1	^1H NMR spectrum of Schiff base derivative.....	48
5.2	^1H NMR spectrum of reduced Schiff base derivative.....	48
5.3	Coordination of ferrocenylbipyridine and metal.....	51
5.4	^1H NMR spectrum of 6-ferrocenyl-2, 2'-bipyridine.....	53
5.5	FTIR spectrum of 6-ferrocenyl-2, 2'-bipyridine.....	54

Figure	Page
5.6 FTIR spectrum of 2-(α , α -diphenylhydroxymethyl) dimethylamino methylferrocene.....	56
5.7 ^1H NMR spectrum of 2-(α , α -diphenylhydroxymethyl) dimethyl aminomethylferrocene.....	56
5.8 Thermogravimetric analysis of a) cyclodextrin b) α -methyl ferrocenylmethylamine c) mixture d) β -cyclodextrin- α -methyl ferrocenylmethylamine inclusion compound	63
5.9 ^1H NMR spectrum of β -cyclodextrin.....	69
5.10 Anisotropic effect of cyclopentadienyl ring.....	70
5.11 Anisotropic effect of cyclopentadienyl rings to H(3) and H(5) of β -cyclodextrin.....	68
5.12 Ferrocene in cyclodextrin with interaction sites of proton observable by ^1H NMR.....	69
5.13 ^1H NMR spectrum of β -cyclodextrin <i>N,N</i> -dimethylaminomethyl ferrocene inclusion compound.....	72
5.14 ^1H NMR spectrum of β -cyclodextrin <i>N,N</i> -dimethylaminomethyl ferrocene methiodide inclusion compound.....	75
5.15 ^1H NMR spectrum of β -cyclodextrin- α -methylferrocenylmethyl amine inclusion compound.....	78
5.16 ^1H NMR spectrum of β -cyclodextrin-ferrocenylethylamine inclusion compound.....	81
5.17 ^1H NMR spectrum of β -cyclodextrin-Schiff base inclusion.....	84
5.18 ^1H NMR spectrum of β -cyclodextrin-reduced Schiff base derivative inclusion compound.....	87
5.19 ^1H NMR spectrum of β -cyclodextrin-acetylferrocene inclusion compound.....	90
5.20 ^1H NMR spectrum of β -cyclodextrin-ferrocenylaldehyde inclusion compound.....	92

Figure	Page
5.21 ^1H NMR spectrum of β -cyclodextrin-ferrocenylmethylalcohol inclusion compound.....	95
5.22 ^1H NMR spectrum of β -cyclodextrin- α -hydroxyferrocenyl methyl alcohol inclusion compound.....	97
5.23 FTIR spectrum of β -cyclodextrin.....	99
5.24 FTIR spectrum of N, N -dimethylaminomethylferrocene.....	106
5.25 FTIR spectrum of β -cyclodextrin- N, N -dimethylaminomethyl ferrocene inclusion compound.....	106
5.26 FTIR spectrum of N, N -dimethylaminomethylferrocene methiodide.....	107
5.27 FTIR spectrum of β -cyclodextrin N, N -dimethylaminomethyl ferrocene methiodide inclusion compound.....	107
5.28 FTIR spectrum of α -methylferrocenylmethylamine.....	108
5.29 FTIR spectrum of β -cyclodextrin- α -methylferrocenylmethyl amine inclusion compound.....	108
5.30 FTIR spectrum of ferrocenylethylamine.....	109
5.31 FTIR spectrum β -cyclodextrin-ferrocenylethylamine inclusion compound.....	109
5.32 FTIR spectrum of Schiff base derivative.....	110
5.33 FTIR spectrum of β -cyclodextrin-Schiff base derivative inclusion compound.....	110
5.34 FTIR spectrum of reduced Schiff base derivative.....	111
5.35 FTIR spectrum of β -cyclodextrin-reduced Schiff base derivative inclusion compound.....	111
5.36 FTIR spectrum of acetylferrocene.....	112
5.37 FTIR spectrum of β -cyclodextrin-acetylferrocene inclusion compound.....	112
5.38 FTIR spectrum of ferrocenylaldehyde.....	113

Figure	Page
5.39 FTIR spectrum of β -cyclodextrin-ferrocenylaldehyde inclusion compound.....	113
5.40 FTIR spectrum of ferrocenylmethylalcohol.....	114
5.41 FTIR spectrum of β -cyclodextrin-ferrocenylmethylalcohol inclusion compound.....	114
5.42 FTIR spectrum of α -hydroxyethylferrocene.....	115
5.43 FTIR spectrum of β -cyclodextrin- α -hydroxyferrocenylmethyl alcohol inclusion compound.....	115
5.44 X-ray diffraction patterns of a) β -cyclodextrin b) <i>N,N</i> -dimethyl aminomethylferrocene methiodide c) mixture d) inclusion compound	117
5.45 X-ray diffraction patterns of a) β -cyclodextrin b) α -methylferrocenylmethylamine c) mixture d) inclusion compound.....	118
5.46 X-ray diffraction patterns of a) β -cyclodextrin b) Schiff base derivative c) mixture d) inclusion compound.....	119
5.47 X-ray diffraction patterns of a) β -cyclodextrin b) reduced Schiff base derivative c) mixture d) inclusion compound.....	120
5.48 Chromatogram of product from ethylation.....	122
5.49 Gas chromatogram of alkylation product and internal standard.....	124
5.50 Graph plotted between % yield and time of <i>N,N</i> - dimethylamino methylferrocene	129
5.51 Graph plotted between % yield and time of β -cyclodextrin.....	130
5.52 Graph plotted between % yield and time of β -cyclodextrin- <i>N,N</i> - dimethylaminomethylferrocene.....	130
5.53 Binding of diethylzinc to hydroxyl group.....	132
5.54 Chromatogram of R and S products of alkylation after derivatized with R(-)MTPA-Cl.....	136
5.55 Mass spectra of MTPA-ester.....	137
5.56 Chromatogram of derivatization showing peaks.....	139

Figure	Page
5.57 ^1H NMR spectrum of R and S products of alkylation after derivatized with R(-)MTPA-Cl.....	142
1a ^1H NMR spectrum of β -cyclodextrin-benzaldehyde inclusion compound.....	150
2a ^1H NMR spectrum of β -cyclodextrin-1-phenyl-1-propanol inclusion compound.....	152
1b UV-visible spectra of a) N, N -dimethylaminomethylferrocene b) β -cyclodextrin- N, N -dimethylaminomethylferrocene inclusion compound.....	153
2b UV-visible spectra of a) N, N -dimethylaminomethylferrocene methiodide b) β -cyclodextrin- N, N dimethylaminomethyl ferrocene inclusion compound.....	154
3b UV-visible spectra of a) α -methylferrocenylmethylamine methiodide b) β -cyclodextrin- N, N dimethylaminomethyl ferrocene inclusion compound.....	154
4b UV-visible spectra of a) Schiff base derivative b) β -cyclodextrin-Schiff base derivative inclusion compound.....	155
5b UV-visible spectra of a) reduced Schiff base derivative b) β -cyclodextrin-reduced Schiff base derivative inclusion compound.....	155
6b UV-visible spectra of a) acetylferrocene b) β -cyclodextrin-acetyl ferrocene inclusion compound.....	156
7b UV-visible spectra of a) ferrocenylaldehyde b) β -cyclodextrin-ferrocenylaldehyde inclusion compound.....	156
8b UV-visible spectra of a) ferrocenylmethylalcohol b) β -cyclodextrin-ferrocenylmethylalcohol inclusion compound.....	157
9b UV-visible spectra of a) α -hydroxyethylferrocene b) β -cyclodextrin- α -hydroxyethylferrocene inclusion compound.....	157

LIST OF SCHEMES

Scheme		Page
2.1	Esterification of chiral alcohol with MTPA-Cl.....	13
3.1	Substrate binding into the cavity of the cyclodextrin.....	14
3.2	Reduction of β -cyclodextrin-ferrocenylketones.....	17
3.3	Asymmetric aldol condensation of acetylferrocene with benzaldehyde via the formation of the β -cyclodextrin inclusion compound.....	18
3.4	Alkylation of diethylzinc with (-)-DAIB catalyst.....	19
3.5	Asymmetric alkylation of aldehyde with 1, 2-disubstituted ferrocenyl aminoalcohol catalysts.....	20
3.6	Ethylation of aldehyde with ferrocenylselenium-based enantioselective catalysts.....	21
5.1	Preparation of ferrocenylamine derivatives.....	44
5.2	Condensation of ferrocenylaldehyde with ethylenediamine and reduction with LiAlH ₄	47
5.3	Preparation of 6- ferrocenyl-2, 2'-bipyridine.....	51
5.4	Preparation of 2-(α , α -diphenylhydroxymethyl) dimethylamino methylferrocene.....	55
5.5	Preparation of acetylferrocene.....	58
5.6	Preparation of ferrocenylmethylalcohol.....	58
5.7	Preparation of α -hydroxyethylferrocene.....	59
5.8	Inclusion compound β -Cyclodextrin-ferrocene derivatives	62
5.9	Ethylation of benzaldehyde with diethylzinc.....	122
5.10	Benzyl alcohol formation.....	123
5.11	Reaction of diethylzinc with oxygen.....	123
5.12	Self catalytic reaction of benzaldehyde to 1-phenyl-1-propanol.....	126
5.13	Resonance stabilization of amine.....	132

Scheme	Page
5.14 Two diastereomers of MTPA-ester.....	135
5.15 Fragments of MTPA-ester.....	138
5.16 MTPA-anhydride formation.....	139
5.17 Proposed mechanism of alkylation with <i>N,N</i> -dimethylaminomethyl ferrocene inclusion compound catalyst.....	141
5.18 The influence of the phenyl ring on ^1H NMR signals of two diastereomeric esters of R(-)MTPA-Cl.....	143

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

Table		Page
2.1	Some parameters describing the macrocyclic conformation of cyclodextrins.....	7
2.2	Some physical properties and characteristics of various cyclodextrins.....	8
5.1	^1H NMR data of ferrocenylamine derivatives.....	45
5.2	FTIR data of ferrocenylamine derivatives.....	46
5.3	^1H NMR data of Schiff base derivative.....	49
5.4	^1H NMR data of reduced Schiff base derivative.....	49
5.5	FTIR data of Schiff base derivative.....	50
5.6	FTIR data of reduced Schiff base derivative.....	50
5.7	^1H NMR data of 6-ferrocenyl-2, 2'-bipyridine.....	52
5.8	FTIR data of 6-ferrocenyl-2, 2'-bipyridine.....	54
5.9	FTIR data of 2-(α , α -diphenylhydroxymethyl)dimethylamino methylferrocene.....	56
5.10	^1H NMR data of 2-(α , α -diphenylhydroxymethyl)dimethylamino methylferrocene.....	57
5.11	^1H NMR data of ferrocenyl derivatives.....	60
5.12	FTIR data of ferrocenyl derivatives.....	61
5.13	Characterization of ferrocenylamine inclusion compounds.....	65
5.14	Characterization of ferrocenyl derivative inclusion compounds.....	65
5.15	^1H NMR data of β -cyclodextrin.....	66
5.16	^1H NMR data of β -cyclodextrin- <i>N</i> , <i>N</i> -dimethylaminomethyl ferrocene inclusion compound.....	73
5.17	^1H NMR data of β -cyclodextrin- <i>N</i> , <i>N</i> -dimethylaminomethyl ferrocene methiodide inclusion compound.....	76
5.18	^1H NMR data of β -cyclodextrin- α -methylferrocenylmethyl amine inclusion compound.....	79

Table		Page
5.19	^1H NMR data of β-cyclodextrin-ferrocenylethylamine inclusion compound.....	82
5.20	^1H NMR data of β-cyclodextrin-Schiff base derivative inclusion compound.....	85
5.21	^1H NMR data of β-cyclodextrin-reduced Schiff base derivative inclusion compound.....	88
5.22	^1H NMR data of β-cyclodextrin-acetylferrocene inclusion compound.....	91
5.23	^1H NMR data of β-cyclodextrin-ferrocenylaldehyde inclusion compound.....	93
5.24	^1H NMR data of β-cyclodextrin-ferrocenylmethylalcohol inclusion compound.....	96
5.25	^1H NMR data of β-cyclodextrin-α-hydroxyethylferrocene inclusion compound.....	98
5.26	FTIR data of β-cyclodextrin.....	99
5.27	FTIR data of β-cyclodextrin-<i>N,N</i>-dimethylaminomethylferrocene inclusion compound.....	100
5.28	FTIR data of β-cyclodextrin-<i>N,N</i>-dimethylaminomethyl ferrocene methiodide inclusion compound.....	101
5.29	FTIR data of β-cyclodextrin-α-methylferrocenylmethylamine inclusion compound.....	101
5.30	FTIR data of β-cyclodextrin-ferrocenylethylamine inclusion compound.....	102
5.31	FTIR data of β-cyclodextrin-Schiff base derivative inclusion compound.....	102
5.32	FTIR data of β-cyclodextrin-reduced Schiff base derivative inclusion compound.....	103

Table		Page
5.33	FTIR data of β -cyclodextrin-acetylferrocene inclusion compound	103
5.34	FTIR data of β -cyclodextrin-ferrocenylaldehyde inclusion compound.....	104
5.35	FTIR data of β -cyclodextrin-ferrocenylmethylalcohol inclusion compound.....	104
5.36	FTIR data of β -cyclodextrin- α -hydroxyethylferrocene inclusion compound.....	105
5.37	Effect of mole ratio of benzaldehyde to diethylzinc on % yield	126
5.38	Effect of solvent on % yield.....	127
5.39	Effect of temperature on % yield.....	128
5.40	Benzyl alcohol formation with temperature.....	128
5.41	Effect of time on % yield.....	128
5.42	Effect of mol % of catalyst on % yield.....	129
5.43	Effect of ferrocenylamine derivative catalysts on % yield.....	131
5.44	pK _b of ferrocenylamine derivatives.....	132
5.45	Effect of ferrocenylalcohol catalysts on % yield.....	133
5.46	Effect of carbonylferrocene catalysts on % yield.....	134
5.47	Enantioselectivity of catalysts by gas chromatography.....	140
5.48	¹ H NMR chemical shift of diastereomeric ester.....	141
5.49	Enantioselectivity of catalyst by high performance liquid chromatography.....	144
1a	¹ H NMR data of β -cyclodextrin-benzaldehyde inclusion compound	149
2a	¹ H NMR data of β -cyclodextrin-1-phenyl-1-propanol inclusion compound.....	151
1c	Angle (2 θ) in X-ray diffraction patterns of <i>N,N</i> -dimethyamino methylferrocene methiodide inclusion compound and the corresponding mixture.....	158

Table		Page
2c	Angle (2θ) in X-ray diffraction patterns of α -methylaminomethyl ferrocene inclusion compound and the corresponding mixture.....	159
3c	Angle (2θ) in X-ray diffraction patterns of Schiff base derivative inclusion compound and the corresponding mixture.....	160
4c	Angle (2θ) in X-ray diffraction patterns of reduced Schiff base derivative inclusion compound and the corresponding mixture.....	161



**สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย**