CHAPTER II

EXPERIMENTAL SECTION

2.1 Synthesis of Calix[4]arene Derivatives

2.1.1 General Procedure

2.1.1.1 Analytical Instruments

Elemental analyses were analyzed on a Perkin Elmer CHON/S analyser (PE2400 series II). Mass spectra were recorded on a Bruker MALDI-TOF mass spectrometer (BIFEX) using a α-cyanocinnamic acid matrix. Melting point were obtained on an Electrothermal 9100 apparatus. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ACF 200 MHz nuclear magnetic resonance spectrometer. In all cases, samples were dissolved in deuterated chloroform and chemical shifts were recorded using a residual chloroform signal as internal reference. Assignments of ^{13}C-NMR spectra were carried out by DEPT experiments.

2.1.1.2 Meterials

Unless otherwise stated, all materials and solvents were standard analytical grade, purchased from Fluka, J.T. Baker or Merck, and used without further purification. Commercial grade solvents such as acetone, dichloromethane and methanol were distilled and stored over 4 Å molecular sieves. Chromatographic seperations were performed on silica gel column (kieselgel 60, 0.063-0.200 mm, Merck). Thin layer chromatography (TLC) were carried out using silica gel plates (kieselgel 60 F_{254}, 1 mm, Merck). All reactions were carried out under nitrogen. The synthetic procedures of 2-bromoethoxy-benzaldehyde (**1-1**)[21], 4-bromoethoxy-benzaldehyde (**1-2**)[22], 25,27-di-((2-ethoxy)benzaldehyde)-*p-tert*-butylcalix[4]arene (**2-1**)[21], 25,27-di-((4-ethoxy)benzaldehyde)-*p-tert*-butylcalix[4]arene (**2-2**)[22], 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediimine-*p-tert*-butylcalix[4]arene (**3a**)[23], 25,27-*N,N'*-di-((2-ethoxy)benzyl)propylenediimine-*p-tert*-butylcalix[4]arene (**3b**)[23], 25,27-*N,N'*-di-((2-ethoxy)benzyl)butylenediimine-*p-tert*-butylcalix[4]arene (**3c**)[23], 25,27-*N,N'*-di-((2-ethoxy)benzyl)propylenediamine-*p-tert*-butylcalix[4]arene·2HCl (**4b**)[23], 25,27-*N,N'*-di-((2-ethoxy)benzyl)butylenediamine-*p-tert*-butylcalix[4]arene·2HCl (**4c**)[23], 25,27-*N,N'*-di-((2-ethoxy)benzyl)propylenediamine-*p-tert*-butylcalix[4]arene (**5b**)[21]and 25,27-*N,N'*-di-((2-ethoxy)benzyl)butylenediamine-*p-tert*-butylcalix[4]arene (**5c**)[24] have been reported by our research group. The products were characterized by ^{1}H-NMR spectroscopy.

2.1.2 Experimental Procedure

2.1.2.1 Preperation of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p*-*tert*-butylcalix[4]arene (5a)

The synthesis of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p*-*tert*-butylcalix[4]arene·(5a) can be carried out by the following two steps.

2.1.2.1.1 Preperation of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p*-*tert*-butylcalix[4]arene·2HCl (4a)

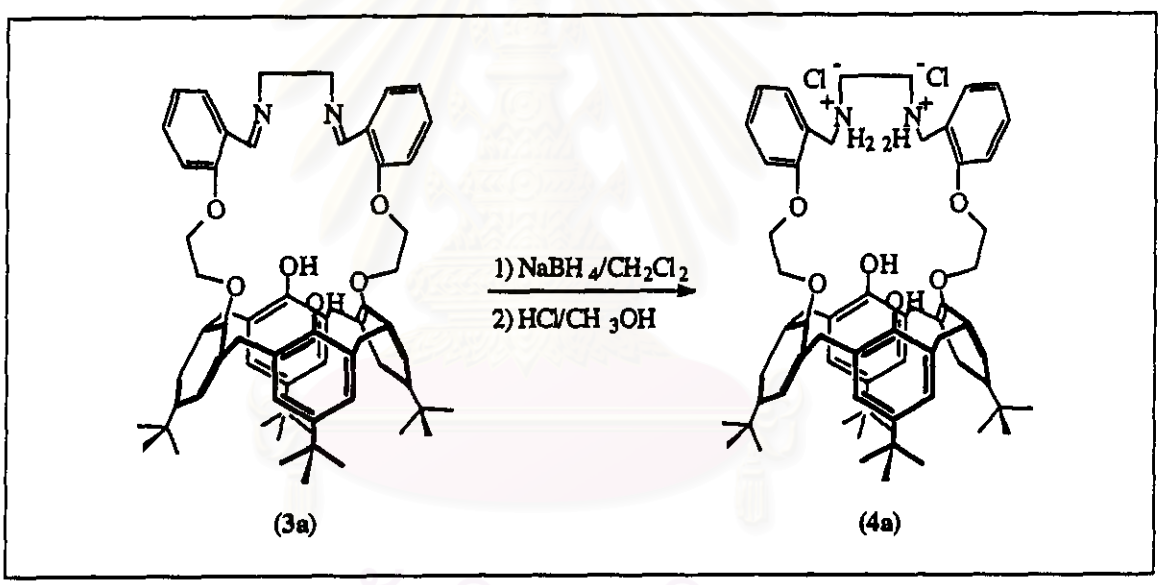


Figure 2.1. Preperation of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p*-*tert*-butylcalix[4]arene·2HCl (**4a**).

To a solution of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediimine-*p*-*tert*-butylcalix[4]arene (**3a**) (2.00 g, 2.06 mmol) in dry dichloromethane (200 mL) was added excess sodium borohydride (0.80 g, 21.15 mmol). The reaction mixture was purged with nitrogen and stirred under nitrogen atmosphere for two hours. A copious amount of water was then added to destroy excess sodium borohydride. After evaporating to dryness, the solid residue was dissolved in dichloromethane and

washed with water until the pH of the aqueous layer became neutral. The organic layer was seperated and dried over anhydrous sodium sulfate and evaporated to dryness. The solid was dissolved in a small amount of dichloromethane and acidified with HCl/CH_3OH (0.74 % V/V) until the pH of the solution reached 1. Upon reducing the volume of solvent, the reduced product was precipitated as white crystals (1.78 g, 83 %).

Characterization data for (4a) :

^{1}H-NMR spectrum ($CDCl_3$) :δ (ppm) = 9.87 (s (broad), 4H, $NH_2^+Cl^-$); 7.51 (d, 2H, $J_{H\text{-}H}$ = 6.9 Hz, H_a); 7.29 (t, 2H, $J_{H\text{-}H}$ = 7.5 Hz, H_b); 7.02, 6.65 (s, 8H, HOAr*H* and ROAr*H*), 6.96-6.83 (m, 4H, H_c and H_d); 6.71 (s, 2H, ArO*H*); 4.51 (s (broad), 4H, Ar-CH_2-NH); 4.34 (s (broad), 4H, OCH_2CH_2O); 4.22, 3.25(dd (AB system), 8H, $J_{H\text{-}H}$ =13.1 Hz, $ArCH_AH_BAr$); 3.76 (s (broad), 4H, NCH_2CH_2); 1.26, 0.84 (s, 36H, HOAr-*t*-C_4H_9 and ROAr-*t*-C_4H_9) (Figure A.1)

2.1.2.1.2 Preperation of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p-tert*-butylcalix[4]arene (5a)

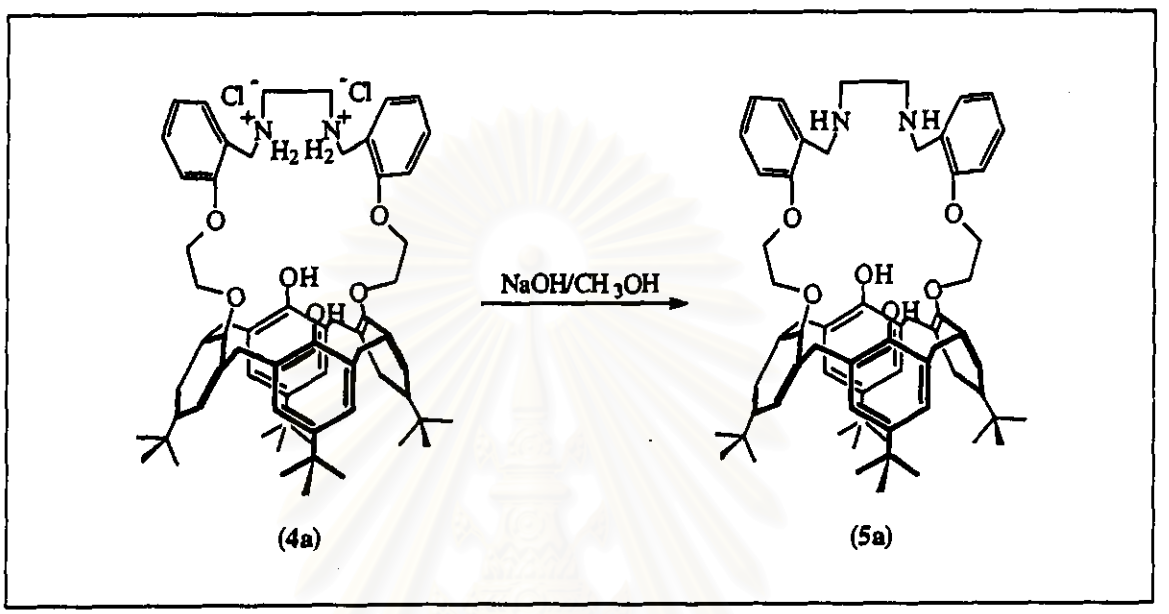


Figure 2.2. Preperation of 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p-tert*-butylcalix[4]arene (**5a**).

The methanolic solution (50 mL) of 25,27-*N,N'*-di-((2-ethoxy)benzyl) ethylenediamine-*p-tert*-butylcalix[4]arene·2HCl (**4a**) (2.00 g, 1.91 mmol) was neutralized by slowly adding a methanolic solution (50 mL) of sodium hydroxide (0.16 g, 4.00 mmol). The reaction was stirred for 1 hour. The solvent was subsequently removed under reduced pressure, and the residue was redissolved in dichloromethane and extracted with water until the aqueous phase contained no Cl^- ion. The organic layer was then dried over anhydrous sodium sulfate and concentrated on a rotary evaporator. Upon slowly adding methanol and water, white microcrystalline precipitated and was collected by filtration (1.23 g, 66 %, mp 154 °c).

Characterization data for (5a) :

^{1}H-NMR spectrum ($CDCl_3$) :δ (ppm) = 7.30-7.18 (m, 4H, H_a and H_b); 7.04, 6.71 (s, 8H, HOAr*H* and ROAr*H*); 6.93 (t, 2H, $J_{H\text{-}H}$ = 7.2 Hz, H_c); 6.83 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, H_d); 4.39, 3.25 (dd (AB system), 8H, $J_{H\text{-}H}$ =13.0 Hz, ArCH_AH_BAr); 4.38, 4.31 (2s (broad), 8H, OCH_2CH_2O); 3.89 (s 4H, Ar-CH_2-NH); 2.59 (s 4H, NCH_2CH_2); 1.30, 0.89 (s, 36H, HOAr-*t*-C_4H_9 and ROAr-*t*-C_4H_9) (Figure A.2)

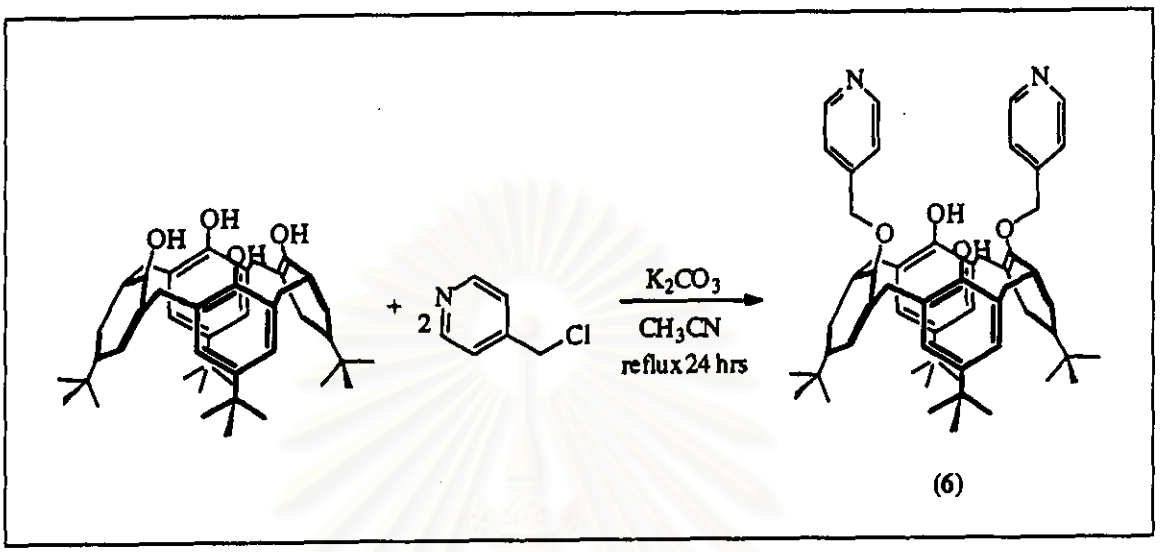
^{13}C-NMR spectrum ($CDCl_3$) :δ (DEPT) (ppm) = 30.97 (q), 31.16 (t), 31.50 (s), 31.73 (q), 33.85 (s), 47.48 (t), 48.63 (t), 66.04 (t), 74.75 (t), 110.86 (d), 120.90 (d), 125.12 (d), 125.53 (d), 127.91 (s), 128.12 (d), 128.96 (s), 130.47 (d), 132.40 (s), 141.52 (s), 146.96 (s), 149.42 (s), 150.42 (s), 156.59 (s) (Figure A.3)

MALDI-TOF MS : 973.3 m/z (Figure A.4)

Elemental analysis : *Anal Calcd.* for $C_{64}H_{80}O_6N_2$: C,78.98; H,8.28; N,2.88.

Found : C, 78.94; H, 8.22; N, 2.90.

2.1.2.2 Preperation of 25,27-di-(4-pyridylmethoxy)-*p-tert*-butylcalix[4]arene (6)



(6)

Figure 2.3. Preperation of 25,27-di-(4-pyridylmethoxy)-*p-tert*-butylcalix[4]arene (6).

A suspension of calix[4]arene (2.00 g, 3.08 mmol) and potassium carbonate (4.25 g, 30.8 mmol) in the presence of a catalytic amount of NaI (2.30 g, 15.3 mmol) in acetonitrile (200 mL) was heated to reflux under nitrogen for 0.5 hours. The methanolic solution (50 mL) of 4-(chloromethyl)pyridine hydrochloride (1.05 g, 6.40 mmol) was subsequently added dropwise to the reaction mixture over a 15 minute period. The dark brown slurry was refluxed for an additional 24 hours. The solvent was then removed by rotary evaporator to obtain a dark brown solid (12.3 g). The residue was dissolved in CH_2Cl_2 (100 mL) and subsequently washed with 0.5 M of HCl (150 mL) and 1 M of sodium hydrogen carbonate solution (150 mL). The organic layer was then dried over anhydrous sodium sulfate and followed by concentrated under reduced pressure to afford a red brown solid (9.06 g). The solid was redissolved in a minimum amount of dichloromethane and placed on a silica gel column (100 g). Unreacted reagents were eluted with 2% acetone/dichloromethane. The desired product was eluted with 10% acetone/dichloromethane and was purified by adding diethylether to precipitate a white solid (1.13 g, 44 %, mp_{obs} 107 °c).

Characterization data for (6) :

^{1}H-NMR spectrum ($CDCl_3$) :δ (ppm) = 8.60 (d, 4H, $J_{H\text{-}H}$ = 6.1 Hz, Py-2-proton); 7.64 (d, 4H, $J_{H\text{-}H}$ = 5.9 Hz, Py-3-proton); 7.05, 6.77 (s, 8H, HOAr*H* and ROAr*H*); 6.99 (s, 2H, ArO*H*); 5.05 (s (broad), 4H, OCH_2Ar); 4.23, 3.31 (dd (AB system), 8H, $J_{H\text{-}H}$ =13.1 Hz, ArCH_AH_BAr); 1.28, 0.91 (s, 36H, HOAr-*t*-C_4H_9 and ROAr-*t*-C_4H_9) (Figure A.5)

^{13}C-NMR spectrum ($CDCl_3$) :δ (DEPT) (ppm) = 30.93 (q), 31.55 (t), 31.68 (q), 33.84 (s), 33.94 (s), 75.93 (t), 121.33 (s), 125.13 (s), 125.71 (d), 127.52 (d), 132.23 (d), 141.85 (s), 146.13 (s), 147.57 (s),149.36 (s), 150.11 (d), 150.47 (s) (Figure A.6)

MALDI-TOF MS : 830.3 m/z (Figure A.7)

Elemental analysis : *Anal Calcd.* for $C_{56}H_{66}O_4N_2$: C, 80.93; H, 8.00; N, 3.37.

Found : C, 80.60 ; H, 7.92 ; N, 3.21.

2.2 Inclusion Studies

2.2.1 General Procedure

2.2.1.1 Apparatus

One dimentional proton NMR spectra were taken on a Bruker ACF 200 MHz nuclear magnetic resomance spectrometer. Two dimentional NMR spectra, NOESY and ROESY, were recorded on a Geol 500 MHz nuclear magnetic resonance spectrometer. For anion complexation studies in case of bromide, chloride, iodide and nitrate anion, spectra were recorded in the mixture of methanol-d_4 :chloroform-d (2:1) with chemical shifts referred to a CHD_2OD signal. The other anions (carbonate, phosphate and sulfate) and neutral molecules were recorded in chloroform-d and using a residual chloroform signal as internal standard.

2.2.1.2 Chemicals

All materials and solvents were standard analytical grade purchased from BDH, Fluka, J.T. Baker and Merck, and used without further purification unless otherwise noted. Chloroform and deuterated solvents (chloroform-d and methanol-d_4) were stored over 3 Å molecular sieves. All calix[4]arene derivatives were prepared as previously described. 1,2-Dihydroxybenzene, 1,3-dihydroxybenzene and 1,4-dihydroxybenzene were purified by standard procedures[25]. Benzene-1,3-dicarboxylic acid was obtained according to the literature procedure[26].

2.2.2 Experimental Procedures

2.2.2.1 Anion Inclusion Studies of Ligands (5a), (5b) and (5c)

2.2.2.1.1 Anion Complexation with Sodium Bromide, Sodium Chloride, Sodium Iodide and Sodium Nitrate

Typically, a 0.05 M solution of a ligand (0.125 mmol) in $CDCl_3$ (2.5 mL) was prepared. To 0.2 mL of this solution in NMR tubes were added 0-4 equivalence of 0.10 M sodium salts (0.200 mmol) (Table 2.1) in CD_3OD. The spectra were then recorded every 24 hours.

Table 2.1. Volume of a sodium salt solution and a ligand used to prepare various sodium salt : ligand ratio

Mole ratio NaBr : (5a)	Volume of (mL)		
	0.10 M Na salt in CD_3OD	0.05 M ligand in $CDCl_3$	CD_3OD
0.0 : 1.0	0.00	0.20	0.40
0.2 : 1.0	0.02	0.20	0.38
0.4 : 1.0	0.04	0.20	0.36
0.6 : 1.0	0.06	0.20	0.34
0.8 : 1.0	0.08	0.20	0.32
1.0 : 1.0	0.10	0.20	0.30
1.2 : 1.0	0.12	0.20	0.28
1.5 : 1.0	0.15	0.20	0.25
2.0 : 1.0	0.20	0.20	0.20
2.5 : 1.0	0.25	0.20	0.15
3.0 : 1.0	0.30	0.20	0.10
4.0 : 1.0	0.40	0.20	0.00

2.2.2.1.2 Anion Complexation with Sodium Carbonate, Sodium Sulfate and Sodium Phosphate

Typically, a 0.0167 M solution of a ligand (0.375 mmol) in dry $CHCl_3$ (22.5 mL) was prepared. A sodium salt (0-4 Equivalence) was added into 1.8 mL of ligand solution at various ratios (Table 2.2). The mixture was stirred at room temperature for 48 hours. Non soluble material was then separated by filtration, and the supernatant was removed solvent *in vacuo*. The residual was dissolved in $CDCl_3$ and ^{1}H-NMR spectrum were recorded.

Table 2.2. Quantity of a sodium salt and volume of a ligand solution used to prepare various sodium salt : ligand ratio

Mole ratio Na salt : (5a)	Na salt (mmol)	0.0167 M ligand in $CHCl_3$ (mL)
0.0 : 1.0	0	1.80
0.2 : 1.0	6.0×10^{-3}	1.80
0.4 : 1.0	1.1×10^{-2}	1.80
0.6 : 1.0	1.8×10^{-2}	1.80
0.8 : 1.0	2.4×10^{-2}	1.80
1.0 : 1.0	3.0×10^{-2}	1.80
1.2 : 1.0	3.6×10^{-2}	1.80
1.5 : 1.0	4.5×10^{-2}	1.80
2.0 : 1.0	6.0×10^{-2}	1.80
2.5 : 1.0	7.5×10^{-2}	1.80
3.0 : 1.0	9.0×10^{-2}	1.80
4.0 : 1.0	1.2×10^{-1}	1.80

2.2.2.2 Neutral Inclusion Studies

2.2.2.2.1 Neutral Inclusion Studies of Ligand (6) and Aldehydes (H-C=O), Compounds (2-1) and (2-2)

Typically, a 0.05 M solution of the ligand (6) (0.1039 g, 0.125 mmol) in $CDCl_3$ (2.5 mL) was prepared. To 0.2 mL of this solution in NMR tubes were added 0-4 equivalence of 0.10 M ligand (2-1) or (2-2) (0.2364 g, 0.250 mmol) (Table 2.3) in $CDCl_3$ (2.5 mL). The spectra were then recorded every 24 hours.

Table 2.3. Volume of ligand (2-1) or (2-2) and ligand (6) solution used to prepare various (2-1) or (2-2) : (6) ratio

Mole ratio (2-1) : (6)	Volume of (mL)		
	0.10 M (2-1) or (2-2) in $CDCl_3$	0.05 M (6) in $CDCl_3$	$CDCl_3$
0.0 : 1.0	0.00	0.20	0.40
0.2 : 1.0	0.02	0.20	0.38
0.4 : 1.0	0.04	0.20	0.36
0.6 : 1.0	0.06	0.20	0.34
0.8 : 1.0	0.08	0.20	0.32
1.0 : 1.0	0.10	0.20	0.30
1.2 : 1.0	0.12	0.20	0.28
1.5 : 1.0	0.15	0.20	0.25
2.0 : 1.0	0.20	0.20	0.20
2.5 : 1.0	0.25	0.20	0.15
3.0 : 1.0	0.30	0.20	0.10
4.0 : 1.0	0.40	0.20	0.00
4.0 : 0.0	0.40	-	0.20

2.2.2.2.2 Neutral Inclusion Studies between Ligand (6) and Ketones (-C=O)

A 0.05 M solution of the ligand (6) (0.1039 g, 0.125 mmol) in $CDCl_3$ (2.5 mL) was prepared. To 0.2 mL of this solution in NMR tubes were added 0-4 equivalence of 0.10 M 2,4-pentanedione (0.0250 g (0.026 mL), 0.250 mmol) (Table 2.4) in $CDCl_3$ (2.5 mL). The spectra were then recorded every 24 hours.

Table 2.4. Volume of 2,4-pentanedione and ligand (6) solution used to prepare various 2,4-pentanedione : (6) ratio

Mole ratio Neutral : (6)	Volume of (mL)		
	0.10 M neutral in $CDCl_3$	0.05 M (6) in $CDCl_3$	$CDCl_3$
0.0 : 1.0	0.00	0.20	0.40
0.2 : 1.0	0.02	0.20	0.38
0.4 : 1.0	0.04	0.20	0.36
0.6 : 1.0	0.06	0.20	0.34
0.8 : 1.0	0.08	0.20	0.32
1.0 : 1.0	0.10	0.20	0.30
1.2 : 1.0	0.12	0.20	0.28
1.5 : 1.0	0.15	0.20	0.25
2.0 : 1.0	0.20	0.20	0.20
2.5 : 1.0	0.25	0.20	0.15
3.0 : 1.0	0.30	0.20	0.10
4.0 : 1.0	0.40	0.20	0.00
4.0 : 0.0	0.40	-	0.20

2.2.2.2.3 Neutral Inclusion Studies between Ligand (6) and Amines ($-NH_2$)

2.2.2.2.3.1 Complexation Studies between Ligand (6) and 1,2-Diaminoethane

A 0.05 M solution of the ligand (6) (0.1039 g, 0.125 mmol) in $CDCl_3$ (2.5 mL) was prepared. To 0.2 mL of this solution in NMR tubes were added 0-4 equivalence of 0.10 M 1,2-diaminoethane (0.0150 g (0.017 mL), 0.250 mmol) (Table 2.5) in $CDCl_3$ (2.5 mL). The spectra were recorded every 24 hours.

Table 2.5. Volume of 1,2-diaminoethane and ligand (6) solution used to prepare various 1,2-diaminoethane : (6) ratio

Mole ratio neutral : (6)	Volume of (mL)		
	0.10 M neutral in $CDCl_3$	0.05 M (6) in $CDCl_3$	$CDCl_3$
0.0 : 1.0	0.00	0.20	0.40
0.2 : 1.0	0.02	0.20	0.38
0.4 : 1.0	0.04	0.20	0.36
0.6 : 1.0	0.06	0.20	0.34
0.8 : 1.0	0.08	0.20	0.32
1.0 : 1.0	0.10	0.20	0.30
1.2 : 1.0	0.12	0.20	0.28
1.5 : 1.0	0.15	0.20	0.25
2.0 : 1.0	0.20	0.20	0.20
2.5 : 1.0	0.25	0.20	0.15
3.0 : 1.0	0.30	0.20	0.10
4.0 : 1.0	0.40	0.20	0.00
4.0 : 0.0	0.40	-	0.20

2.2.2.2.3.2 Complexation Studies between Ligand (6) and 2,6-Diaminopyridine

A 0.05 M solution of the ligand (**6**) (0.1039 g, 0.125 mmol) in $CDCl_3$ (2.5 mL) was prepared. 2,6-Diaminopyridine (0-4 Equivalent) was brought into the NMR tubes containing 0.2 mL of a ligand (**6**) solution (Table 2.6). The ^{1}H-NMR spectra were recorded every 24 hours.

Table 2.6. Quantity of 2,6-diaminopyrodine and volume of ligand (**6**) solution used to prepare various 2,6-diaminopyrodine : (**6**) ratio

Mole ratio neutral : (**6**)	Quantity of		
	Neutral (g)	0.05 M (**6**) in $CDCl_3$ (mL)	$CDCl_3$ (mL)
0.0 : 1.0	0.0000	0.20	0.40
0.5 : 1.0	0.0005	0.20	0.40
1.0 : 1.0	0.0011	0.20	0.40
1.5 : 1.0	0.0016	0.20	0.40
2.0 : 1.0	0.0022	0.20	0.40
2.5 : 1.0	0.0027	0.20	0.40
3.0 : 1.0	0.0033	0.20	0.40
4.0 : 1.0	0.0044	0.20	0.40
4.0 : 0.0	0.0044	-	0.60

2.2.2.2.4 Neutral Inclusion Studies between Ligand (6) and Alcohols (-OH)

2.2.2.2.4.1 Complexation Studies between Ligand (6) and 1,2-Dihydroxybenzene (Catechol)

In case of 0-4 equivalents, a 0.05 M solution of the ligand (6) (0.1039 g, 0.125 mmol) in $CDCl_3$ (2.5 mL) was prepared. To 0.2 mL of this solution in NMR tubes were added 0-4 equivalence of 0.10 M 1,2-dihydroxybenzene (0.0275 g, 0 250 mmol) (Table 2.7) in $CDCl_3$ (2.5 mL). The spectra were recorded every 24 hours (Figure B.1-B.17).

Table 2.7. Volume of 1,2-dihydroxybenzene and ligand (6) solution used to prepare various 1,2-dihydroxybenzene : (6) ratio

Mole ratio Neutral : (6)	Volume of (mL)		
	0.10 M neutral in $CDCl_3$	0.05 M (6) in $CDCl_3$	$CDCl_3$
0.0 : 1.0	0.00	0.20	0.40
0.2 : 1.0	0.02	0.20	0.38
0.4 : 1.0	0.04	0.20	0.36
0.6 : 1.0	0.06	0.20	0.34
0.8 : 1.0	0.08	0.20	0.32
1.0 : 1.0	0.10	0.20	0.30
1.2 : 1.0	0.12	0.20	0.28
1.5 : 1.0	0.15	0.20	0.25
1.8 : 1.0	0.18	0.20	0.22
2.0 : 1.0	0.20	0.20	0.20
2.2 : 1.0	0.22	0.20	0.18
2.5 : 1.0	0.25	0.20	0.15
2.8 : 1.0	0.28	0.20	0.12
3.0 : 1.0	0.30	0.20	0.10
3.2 : 1.0	0.32	0.20	0.08
4.0 : 1.0	0.40	0.20	0.00
4.0 : 0.0	0.40	-	0.20

In case of 5-10 equivalents, a 0.05 M solution of the ligand (**6**) (0.0623 g, 0.0750 mmol) in $CDCl_3$ (1.5 mL) was prepared. 1,2-Dihydroxybenzene (0-4 Equivalent) was brought into the NMR tubes containing 0.2 mL of ligand (**6**) solution (Table 2.8). The ^{1}H-NMR spectra were recorded every 24 hours (Figure B.18-B.23).

Table 2.8. Quantity of 1,2-dihydroxybenzene and volume of ligand (**6**) solution used to prepare various 1,2-dihydroxybenzene : (**6**) ratio

Mole ratio Neutral : (**6**)	Quantity of		
	Neutral (g)	0.05 M (**6**) in $CDCl_3$ (mL)	$CDCl_3$ (mL)
5.0 : 1.0	0.0055	0.20	0.40
6.0 : 1.0	0.0066	0.20	0.40
7.0 : 1.0	0.0077	0.20	0.40
8.0 : 1.0	0.0088	0.20	0.40
9.0 : 1.0	0.0099	0.20	0.40
10.0 : 1.0	0.0110	0.20	0.40

The chemical shifts of the signals were followed and plot against the equivalents of added guest.

2.2.2.2.4.2 Complexation Studies between Ligand (6) and 1,3-Dihydroxybenzene or 1,4-Dihydroxybenzene

Typically, a 0.05 M solution of the ligand (**6**) (0.0707 g, 0.0851 mmol) in $CDCl_3$ (1.7 mL) was prepared. 1,3-Dihydroxybenzene or 1,4-dihydroxybenzene (0-4 Equivalent) was brought into the NMR tubes containing 0.2 mL of ligand (**6**) solution (Table 2.9). The ^{1}H-NMR spectra were recorded every 24 hours (Figure B.24-B.32). The chemical shifts of the signals were followed and plot against the equivalent of added guest. The association constant was determined using the iteration method[27].

Table 2.9. Quantity of 1,3-dihydroxybenzene and volume of ligand (**6**) solution used to prepare various 1,3-dihydroxybenzene : (**6**) ratio

Mole ratio Neutral : (**6**)	Quantity of		
	Neutral (g)	0.05 M (**6**) in $CDCl_3$ (mL)	$CDCl_3$ (mL)
0.0 : 1.0	0.00000	0.20	0.40
0.5 : 1.0	0.00055	0.20	0.40
1.0 : 1.0	0.00110	0.20	0.40
1.5 : 1.0	0.00165	0.20	0.40
2.0 : 1.0	0.00220	0.20	0.40
2.5 : 1.0	0.00275	0.20	0.40
3.0 : 1.0	0.00330	0.20	0.40
4.0 : 1.0	0.00440	0.20	0.40
4.0 : 0.0	0.00440	-	0.60

2.2.2.2.5 Neutral Inclusion Studies between Ligand (6) and Benzene Dicarboxylic Acids (O=C-OH)

Typically, a 0.05 M solution of the ligand (**6**) (0.0707 g, 0.0851 mmol) in $CDCl_3$ (1.7 mL) was prepared. Benzene dicarboxylic acid (0-4 Equivalent) was brought into the NMR tubes containing 0.2 mL of ligand (**6**) solution (Table 2.10). The ^{1}H-NMR spectra were recorded every 24 hours (Figure B.33-B.40). The chemical shifts of the signals were followed and plot against the equivalent of added guest. The association constant was determined using the iteration method[27].

Table 2.10. Quantity of benzene dicarboxylic acid and volume of ligand (**6**) solution used to prepare various benzene dicarboxylic acid : (**6**) ratio

Mole ratio neutral : (**6**)	Quantity of		
	Neutral (g)	0.05 M (**6**) in $CDCl_3$ (mL)	$CDCl_3$ (mL)
0.0 : 1.0	0.00000	0.20	0.40
0.5 : 1.0	0.00083	0.20	0.40
1.0 : 1.0	0.00166	0.20	0.40
1.5 : 1.0	0.00249	0.20	0.40
2.0 : 1.0	0.00332	0.20	0.40
2.5 : 1.0	0.00415	0.20	0.40
3.0 : 1.0	0.00498	0.20	0.40
4.0 : 1.0	0.00665	0.20	0.40
4.0 : 0.0	0.00665	-	0.60

2.2.2.2.6 Competition Studies

2.2.2.2.6.1 Competition Studies between 1,2-Dihydroxybenzene and 1,3-Dihydroxybenzene with Ligand (6)

A 0.05 M solution of ligand (6) (0.0707 g, 0.0851 mmol) and a 0.10 M solution of 1,2-dihydroxybenzene (0.0275 g, 0 250 mmol) in $CDCl_3$ (1.7 and 2.5 mL, respectively) were prepared. A 0.2 mL of the prepared ligand (6) solution was mixed with 1,2-dihydroxybenzene solution and then added the of solid 1,3-dihydroxybenzene (Table 2.11). The ^{1}H-NMR spectra were recorded every 24 hours (Figure B.41-B.49). The chemical shifts of the mixture were compared to the known chemical shifts of (6)·catechol and (6)·resorcinol.

Table 2.11. Quantity of 1,2-dihydroxybenzene (7), 1,3-dihydroxybenzene (8) and ligand (6) solution used to prepare various (7) : (8) : (6) ratio

Mole ratio (7) : (8) : (6)	Quantity of			
	0.10 M of (7) (mL)	(8) (g)	0.05 M (6) in $CDCl_3$ (mL)	$CDCl_3$ (mL)
0.0 : 0.0 : 1.0	0.00	0.00000	0.20	0.40
0.5 : 0.5 : 1.0	0.05	0.00055	0.20	0.35
1.0 : 1.0 : 1.0	0.10	0.00110	0.20	0.30
1.5 : 1.5 : 1.0	0.15	0.00165	0.20	0.25
2.0 : 2.0 : 1.0	0.20	0.00220	0.20	0.20
2.5 : 2.5 : 1.0	0.25	0.00275	0.20	0.15
3.0 : 3.0 : 1.0	0.30	0.00330	0.20	0.10
4.0 : 4.0 : 1.0	0.40	0.00440	0.20	0.00
4.0 : 4.0 : 0.0	0.40	0.00440	-	0.20

2.2.2.2.6.2 Competition Studies between 1,2-Dihydroxybenzene and Benzene-1,2-Dicarboxylic Acid with Ligand (6)

A 0.05 M solution of ligand (6) (0.0707 g, 0.0851 mmol) and a 0.10 M solution of 1,2-dihydroxybenzene (0.0275 g, 0 250 mmol) in $CDCl_3$ (1.7 and 2.5 mL, respectively) were prepared. A 0.2 mL of the prepared ligand (6) solution was mixed with 1,2-dihydroxybenzene solution and then added the of solid benzene-1,2-dicarboxylic acid (Table 2.12). The ^{1}H-NMR spectra were recorded every 24 hours (Figure B.50-B.57). The chemical shifts of the mixture were compared to the known chemical shifts of (6)·catechol and (6)·phthalic acid.

Table 2.12. Quantity of 1,2-dihydroxybenzene (7), benzene-1,2-dicarboxylic acid (9) and ligand (6) solution used to prepare various (7) : (9) : (6) ratio

Mole ratio (7) : (9) : (6)	Quantity of			
	0.10 M of (7) (mL)	(9) (g)	0.05 M (6) in $CDCl_3$ (mL)	$CDCl_3$ (mL)
0.0 : 0.0 : 1.0	0.00	0.00000	0.20	0.40
0.5 : 0.5 : 1.0	0.05	0.00083	0.20	0.35
1.0 : 1.0 : 1.0	0.10	0.00166	0.20	0.30
1.5 : 1.5 : 1.0	0.15	0.00249	0.20	0.25
2.0 : 2.0 : 1.0	0.20	0.00332	0.20	0.20
2.5 : 2.5 : 1.0	0.25	0.00415	0.20	0.15
3.0 : 3.0 : 1.0	0.30	0.00498	0.20	0.10
4.0 : 4.0 : 1.0	0.40	0.00665	0.20	0.00
4.0 : 4.0 : 0.0	0.40	0.00665	-	0.20

2.2.2.2.7 Two Dimentional NMR Spectroscopy

Ligand (**6**), 1,2-dihydroxybenzene:(**6**) complexes (2:1 and 4:1), 1,3-dihydroxybenzene:(**6**) complex (1:1) and a benzene-1,2-dicarboxylic acid:(**6**) complex (1:1) were taken to investigate the structure of the complexes using two dimentonal NMR spectroscopy (NOESY and ROESY) (Figure B.58-B.67).

2.3 Theoretical Studies

Quantum calculations using molecular mechanic method (MM^+) were performed to obtain gas phase structures of ligand (**6**) which was also referred to the results from 2D-NMR spectra. An empirical method, PM3, was used to calculate the structures of benzene dialcohols and benzene dicarboxylic acids.