CHAPTER II

EXPERIMENTAL

2.1 General Procedures

2.1.1 Analytical Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a VARIAN 400 MHz nuclear magnetic resonance spectrometer. All chemical shifts were reported in part per million (ppm) using the residual proton or carbon signal in deuterated $CDCl_3$ as internal reference, except the NMR titration experiments were recorded in 5% CD_3CN:$CDCl_3$ and chemical shifts referred to a residue proton signal. The 2D NMR techniques such as ^1H-^1H COSY and ^1H-^{13}C HMQC have been applied to assign the structure of the receptors.

Elemental analyses were carried out on CHNS/O analyzer (Perkin Elmer PE 2400 seriesII). MALDI-TOF mass spectra were recorded on Bruker Daltonic using doubly recrystallized 2-cyano-4-hydroxy cinnamic acid (CCA) as matrix.

Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) were performed using a μ-AUTOLAB TYPE III potentiostat. All electrochemical experiments carried out with three electrode cells comprising of a working electrode, a counter electrode and a reference electrode at room temperature. The supporting electrolyte is 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in 40% CH_3CN:CH_2Cl_2. The Pt electrode with a diameter 3 mm embedded in Teflon was used as a working electrode which was polished with slurries of 0.3 μm followed with 1.0 μm alumina powder, and washed by sonication for 5 minutes in 0.05 M H_2PO_4 and subsequently with a solvent before used. The Pt electrode was used as a counter electrode. The $Ag/AgNO_3$ electrode, constructed by immersing a silver wire into a solution of 0.01 M $AgNO_3$ in 0.1 M $TBAPF_6$, was used as a reference electrode. The appropriate scan rate was found to be 100 mV/s for both cyclic voltammetry and square wave voltammetry.

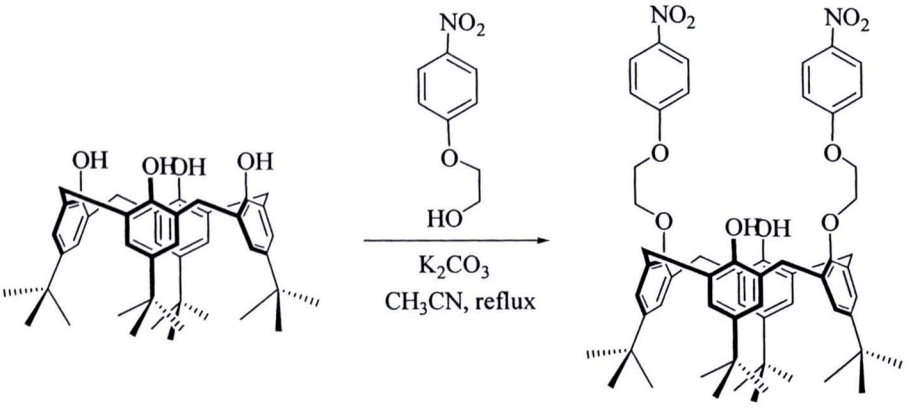
2.1.2 Materials

Unless otherwise specified, the solvents and materials were reagent grades purchased from Fluka, BDH, Aldrich, Carlo erba, Merk or Lab scan and used without further purification. Commercial grade solvents such as acetone, dichloromethane, hexane, methanol and ethyl acetate were purified by distillation before used. Acetonitrile and dichloromethane for set up the reaction were dried over calcium hydride and freshly distilled under nitrogen prior to use. DMF was dried with calcium hydride, distilled under reduced pressure and stored over molecular sieves 3 or 4 Å under nitrogen.

Column chromatography was carried out on 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), Compounds on TLC plates were detected by the UV-light. *p-tert*-Butylcalix[4]arene was prepared according to published procedures. Moreover, the ferrocene derivatives: 1,1'-diacetylferrocene and 1,1'-ferrocenedicarboxylic acid have been synthesized using the published procedure [27].

2.2 Synthesis

2.2.1 Preparation of 1a



1a

A mixture of *p-tert*-butylcalix[4]arene (1.500 g, 2.31 mmol) and K_2CO_3 (3.194 g, 23.10 mmol) in acetonitrile 60 mL was stirred at room temperature for 30 minutes under nitrogen atmosphere. 2-(4-Nitrophenoxy)ethyl 4-methylbenzenesulfonate (1.95 g, 5.78 mmol) in acetonitrile was added dropwise and the mixture was refluxed for 72 hours. Then, K_2CO_3 was removed by filtration. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 (50 mL) and stirred with 3M HCl (15 mL) for 30 minutes. The aqueous solution was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The pure product was obtained by recrystallization from CH_2Cl_2/CH_3OH as white solid (1.511 g, 67 %).

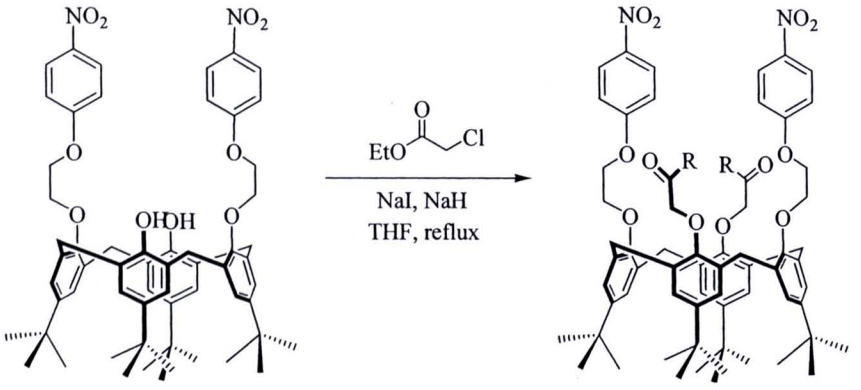
Characterization data for 1a

^{1}H-NMR spectrum (400 MHz, CDCl3, ppm): δ 0.97 (s, $(CH_3)_3$CArOR, 18H), 1.28 (s, $(CH_3)_3$CArOH, 18H), 3.31 and 4.32 (dd, $J_{H\text{-}H}$= 13.0 Hz, ArCH_ACH_BAr, AB system, 8H), 4.31 (d, $J_{H\text{-}H}$= 7.2 Hz , RCH_2OAr(calix), 4H), 4.51 Hz, RCH_2OArNO_2, 4H), 6.82 (s, Ar*H*OR, 4H), 7.00 (d, $J_{H\text{-}H}$= 9.6 Hz , *m*-Ar*H*, 4H), 7.36 (d, $J_{H\text{-}H}$= 052 (s, Ar*H*OH, 4H), 7.10 (s, -O*H*, 2H), 8.20 (d, $J_{H\text{-}H}$= 9.2 Hz, *o*-Ar*H*, 4H). ^{13}C-NMR spectrum (100 MHz, $CDCl_3$, ppm): δ 166.7, 153.6, 150.5, 145.0, 135.7, 131.0, 128.7, 118.0, 77.0, 70.6, 37.5, 34.7.

Elemental analysis: Anal. Calcd. For $C_{60}H_{70}O_{10}N_2$: C, 73.58; H, 7.21; N, 2.86, found: C, 73.72; H, 7.20; N, 2.85

ESI mass: calcd: 979.22; found 1,017.207 [M + K^+].

2.2.2 Preparation of 1b



1a **1b**

A mixture of compound **1a** (0.500 g, 0.511 mmol) and NaH (0.245 g, 10.21 mmol) in THF 40 mL was stirred at room temperature for 30 minutes under nitrogen atmosphere. Then, chloroethylacetate (0.38 mL, 3.56 mmol) and NaI was added and the mixture was refluxed for 12 hours. Cold water was added to the solution and stirred for 30 minutes. The solvent was evaporated under reduced pressure. CH_2Cl_2 (50 mL) and water (30 mL) were added to the residue and the aqueous solution was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The pure product was obtained by recrystallization from CH_2Cl_2/CH_3OH. (yield 0.411 g, 72%)

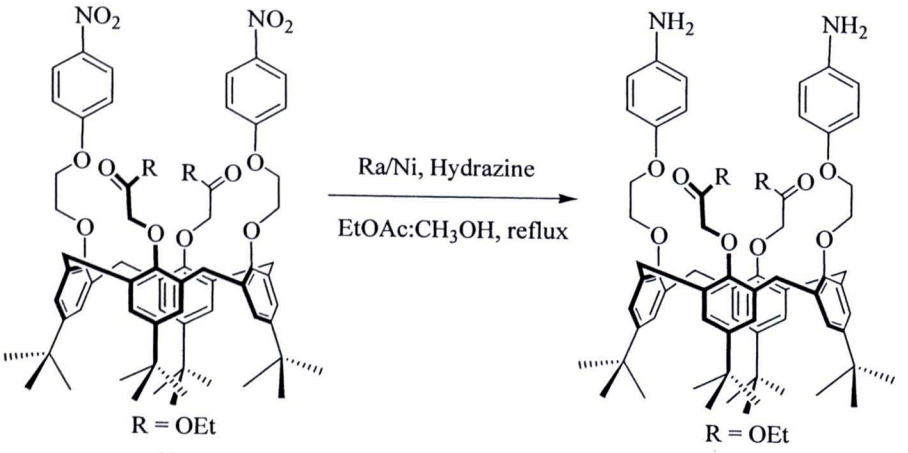
Characterization data for 1b

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 0.91 (s, $(CH_3)_3CArOCH_2CH_2OArNO_2$, 18H), 1.21 (t, J_{H-H}= 7.2 Hz, CH_3CH_2OCOR, 6H), 1.25 (s, $(CH_3)_3CArOCH_2COOR$, 18H), 3.17 and 4.51 (dd, J_{H-H}= 12.8 Hz, $ArCH_ACH_BAr$, AB system, 8H), 4.13 (q, J_{H-H} = 7.1 Hz, CH_3CH_2O-, 4H), 4.38 (s, -OCH_2COOR, 4H), 4.61 (t, J_{H-H} = 5.4 Hz, RCH_2OAr(calix), 4H), 4.71 (t, J_{H-H}= 5.4 Hz, RCH_2OArNO_2, 4H), 6.59 (s, $ArHOCH_2CH_2OArNO_2$, 4H), 7.01 (s, $ArHOCH_2COOR$, 4H), 7.01 (d, J_{H-H}= 8.8 Hz, *m*-Ar*H*, 4H), 8.16 (d, J_{H-H}= 9.6 Hz , *o*-Ar*H*, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 172.9, 167.3, 157.3, 155.2, 148.6, 144.5, 137.7, 135.3, 128.9, 117.9, 75.1, 71.9, 63.9, 37.3, 34.6, 17.4.

Elemental analysis: Anal. Calcd. For $C_{68}H_{82}O_{14}N_2$: C, 70.92; H, 7.18; N, 2.43, found: C, 70.97; H, 7.07; N, 2.47

ESI mass: calcd: 1151.40; found 1173.400 [M + Na^+].

2.2.3 Preparation of 1c

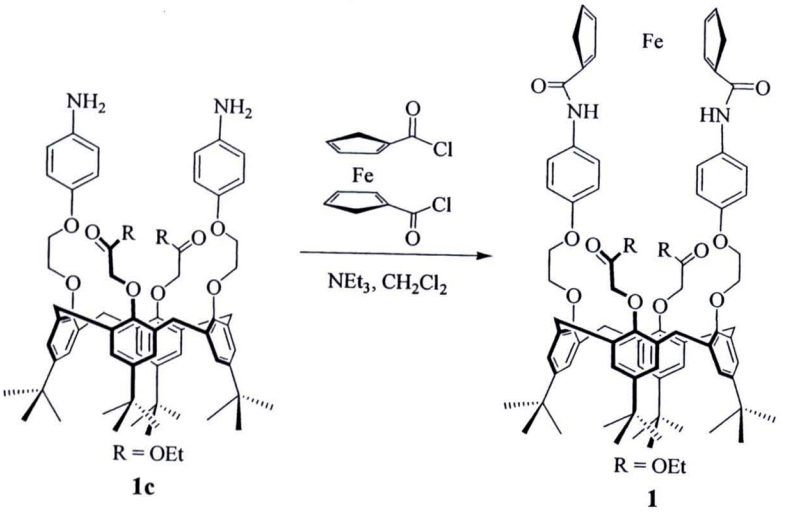


Raney nickel (0.394 g, 6.80 mmol) was added to the solution of compound **1b** (0.761 g, 0.68 mmol) in 30 mL of ethyl acetate and 22 mL of methanol under nitrogen atmosphere. Hydrazine (1.91 mL, 40.81 mmole) was added and the reaction was refluxed for 2 hours. The suspension was filtered and washed with methanol. The filtrate was then evaporated to dryness under reduced pressure. The residue was taken up with CH_2Cl_2 (50 mL) and extracted with water. The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give compound **1c** as yellow solid (0.563 g, 90%). Compound **1c** was used immediately for further reaction.

Characterization data for 1c

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 1.04 (s, $(CH_3)_3CArOCH_2CH_2OArNH_2$, 18H), 1.13 (s, $(CH_3)_3CArOCH_2COOR$, 18H), 1.19 (t, J_{H-H}= 7.2 Hz, CH_3CH_2OCOR, 6H), 3.17 and 4.68 (dd, J_{H-H}= 12.8 Hz , $ArCH_2$ CH_ACH_BAr, AB system, 8H), 4.11 (q, J_{H-H}= 7.2 Hz, CH_3CH_2O-, 4H), 4.39 (s, -OCH_2CH_2-, 8H), 4.62 (s, -OCH_2COOR, 4H), 6.61, 6.78 (d, J_{H-H}= 8.8 Hz, $ArHNH_2$, 8H), 6.74, 6.84 (s, ArH in calix, 8H).

2.2.4 Preparation of 1



Under nitrogen atmosphere, ferrocene acid chloride (prepared from ferrocene dicarboxylic acid 0.200 g, 0.73 mmol) in 20 mL of dry CH_2Cl_2 was transferred via a cannula to a stirred solution of compound **1c** (0.670 g, 0.73 mmol) and triethylamine (0.25 mL, 1.82 mmol) in 200 mL of CH_2Cl_2. The reaction was stirred for 3 hours at room temperature under nitrogen atmosphere. Water was then added, and the organic layer was separated and washed with water. The organic was dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 20% hexane in ethylacetate) to give compound **1** as a orange solid (0.100 g, 12%).

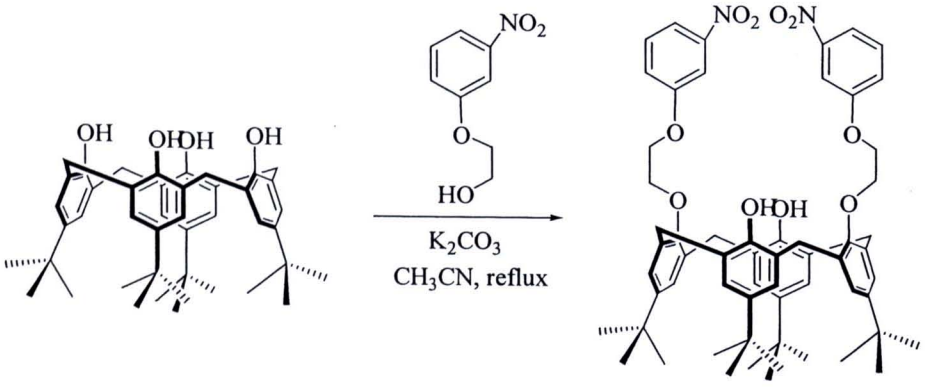
Characterization data for 1

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 0.99 (s, $(CH_3)_3CArOCH_2CH_2OAr$, 18H), 1.19 (s, $(CH_3)_3CArOCH_2COOR$, 18H), 1.28 (t, J_{H-H}= 7.2 Hz, CH_3CH_2OCOR, 6H), 3.24 and 4.65 (dd, J_{H-H}= 12.8 Hz, $ArCH_2Ar$, AB system, 8H), 4.20 (q, J_{H-H}= 7.1 Hz, CH_3CH_2O-, 4H), 4.39 (s, -OCH_2CH_2O-, 8H), 4.46 (s, -OCH_2COOR, 4H), 4.69, 4.89 (s, C_5H_4-(ferrocene), 8H), 6.75, 7.21 (d, J_{H-H}= 8.8 Hz ,Ar*H*NHCOR, 8H), 6.68, 6.95 (s, Ar*H* in calix, 8H), 7.37 (s, RN*H*COR, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 170.2, 166.8, 155.6, 154.1, 152.3, 145.1, 134.3, 132.7, 130.7, 125.1, 122.0, 114.0, 79.2, 71.3, 69.7, 60.9, 34.0, 31.3, 14.4.

Elemental analysis: Anal. Calcd. For $C_{80}H_{92}FeO_{12}N_2$: C, 72.26; H, 6.98; N, 2.11, found: C, 72.24; H, 6.97; N, 2.15

ESI mass: calcd: 1329.46; found 1351.452 [M + Na^+].

2.2.5 Preparation of 2a



2a

A mixture of *p-tert*-butylcalix[4]arene (1.536 g, 2.37 mmol) and Na_2CO_3 (2.502 g, 23.60 mmol) in acetonitrile 60 mL was stirred at room temperature for 30 minutes under nitrogen atmosphere. 2-(3-Nitrophenoxy)ethyl4-methylbenzenesulfonate (2.00 g, 5.93 mmol) in acetonitrile was added dropwise and the mixture was refluxed for 72 hours. Then, Na_2CO_3 was removed by filtration. The filtrate was evaporated and the residue was dissolved in CH_2Cl_2 (50 mL) and stirred with 3M HCl (15 mL) for 30 minutes. The aqueous solution was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on a silica gel column using 30% hexane/CH_2Cl_2 as eluent. Recrystalization from CH_2Cl_2/CH_3OH gave compound **2a** as white solid (1.44 g, 62%).

Characterization data for 2a

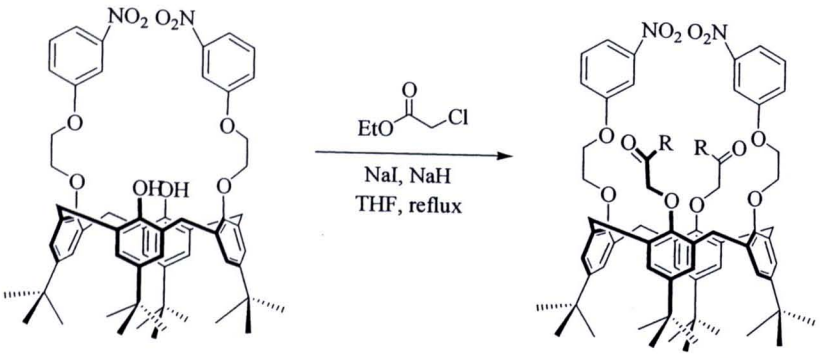
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, ppm): δ 0.99 (s, $(CH_3)_3$CArOR, 18H), 1.28 (s, $(CH_3)_3$CArOH, 18H), 3.31 and 4.36 (dd, $J_{H\text{-}H}$= 13.0 Hz, ArCH_ACH_BAr, AB system, 8H), 4.35 (s, RCH_2OAr(calix), 4H), 4.38 (s, RCH_2OArNO_2, 4H), 6.84 (s, Ar*H*OR , 4H), 7.05 (s, Ar*H*OH , 4H), 7.24 (d, $J_{H\text{-}H}$= 20.8 Hz, *p*-Ar*H*NO_2, 2H), 7.41 (t, $J_{H\text{-}H}$= 8.0 Hz, *m*-Ar*H*NO_2, 2H), 7.76 (s, *o*-Ar*H*NO_2, 2H), 7.81 (t, $J_{H\text{-}H}$= 8.8 Hz, *o*-Ar*H*NO_2, 2H).

^{13}C-NMR spectrum (100 MHz, $CDCl_3$, ppm): δ 162.3, 153.7, 150.5, 144.9, 135.9, 133.3, 131.0, 129.0, 125.4, 119.0, 112.3, 77.1, 70.5, 37.0, 34.7.

Elemental analysis: Anal. Calcd. For $C_{60}H_{70}O_{10}N_2$: C, 73.58; H, 7.21; N, 2.86, found: C, 73.59; H, 7.25; N, 2.85

ESI mass: calcd: 979.22; found 1017.324 [M + K^+].

2.2.6 Preparation of 2b



2a **2b**

A mixture of compound **2a** (0.500 g, 0.511 mmol) and NaH (0.245 g, 10.21 mmol) in THF 40 mL was stirred at room temperature for 30 minutes under nitrogen atmosphere. Then, chloroethylacetate (0.38 mL, 3.56 mmole) and NaI was added and the mixture was refluxed for 12 hours. Cold water was added to the solution and stirred for 30 minutes. The solvent was evaporated under reduced pressure. Dichloromethane (50 mL) and water (30 mL) were added to the residue and the aqueous solution was extracted with dichloromethane and the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The pure product was obtained by column chromatography using 10% ethyl acetate in CH_2Cl_2 as eluent. Recrystallization from CH_2Cl_2/CH_3OH yielded **2b** as a white solid (0.14 g, 24%).

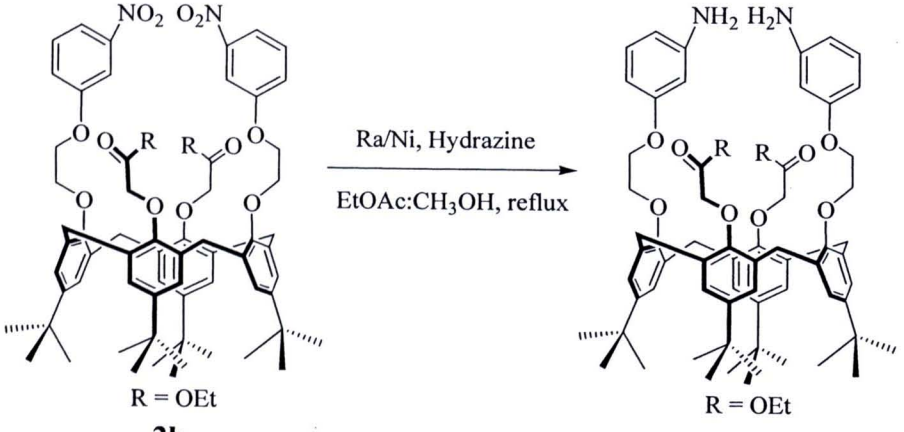
Characterization data for 2b

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 0.94 (s, $(CH_3)_3CArOCH_2CH_2OArNO_2$, 18H), 1.17 (t, J_{H-H}= 7.2 Hz, CH_3CH_2OCOR, 6H), 1.25 (s, $(CH_3)_3CArOCH_2COOR$, 18H), 3.17 and 4.58 (dd, J_{H-H}= 12.8 Hz, $ArCH_ACH_BAr$, AB system, 8H), 4.10 (q, J_{H-H} = 6.8 Hz, CH_3CH_2O-, 4H), 4.47 (s, RCH_2OAr(calix), 4H), 4.55(s, RCH_2OArNO_2, 4H), 4.67 (s, $-OCH_2COOR$, 4H), 6.63 (s, $ArHOCH_2CH_2OArNO_2$, 4H), 6.96 (s, $ArHOCH_2COOR$, 4H), 7.23 (d, J_{H-H}= 8.8 Hz, *p*-ArHNO2, 2H), 7.37 (t, J_{H-H}= 8.4 Hz, *m*-ArHNO2, 2H), 7.78 (s, *o*-$ArHNO_2$, 4H). ^{13}C-NMR spectrum (100 MHz, $CDCl_3$, ppm): δ 173.0, 162.8, 157.1, 155.5, 152.3, 148.5, 137.5, 135.8, 132.9, 125.0, 118.7, 112.2, 75.3, 71.7, 63.8, 37.4, 34.5, 17.4.

Elemental analysis: Anal. Calcd. For $C_{68}H_{82}O_{14}N_2$: C, 70.92; H, 7.18; N, 2.43, found: C, 70.52; H, 7.10; N, 2.44

ESI mass: calcd: 1151.40; found 1,173.426 [M + Na^+].

2.2.7 Preparation of 2c

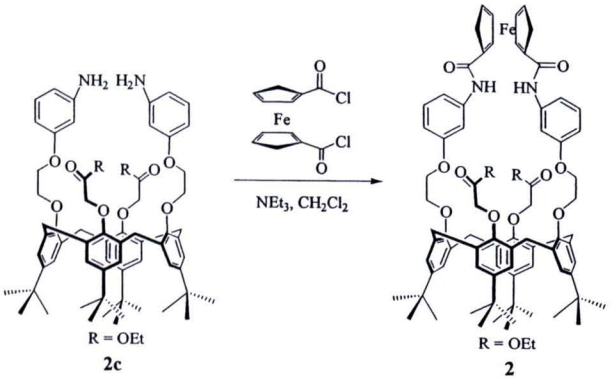


Raney nickel (0.394 g, 6.80 mmol) was added to the solution of compound **2b** (0.761 g, 0.68 mmol) in 30 mL of ethyl acetate and 22 mL of methanol under nitrogen atmosphere. Hydrazine (1.91 mL, 40.81 mmol) was added. The mixture was refluxed for 2 hours. The suspension was filtered and washed with methanol. The filtrate was then evaporated to dryness under reduced pressure. The residue was taken up with dichloromethane (50 mL) and extracted with water. The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give compound **5c** which was used immediately for further reaction. (0.67 g, 92%)

Characterization data for 2c

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 0.97 (s, $(CH_3)_3CArOCH_2CH_2OArNH_2$, 18H), 1.18 (s, $(CH_3)_3CArOCH_2COOR$, 18H), 1.33 (t, $J_{H\text{-}H}$= 6.0 Hz, CH_3CH_2OCOR, 6H), 3.17 and 4.64 (dd, $J_{H\text{-}H}$= 12.8 Hz , $ArCH_2$ CH_ACH_BAr, AB system, 8H), 4.13 (q, $J_{H\text{-}H}$= 7.2 Hz, CH_3CH_2O-, 4H), 4.46 (s, -OCH_2CH_2-, 8H), 4.54 (s, -OCH_2COOR, 4H), 6.32, 6.26 (m, $ArHNH_2$, 8H), 6.66, 6.91 (s, ArH in calix, 8H).

2.2.8 Preparation of 2



Under nitrogen atmosphere, ferrocene acid chloride (prepared from ferrocene dicarboxylic acid 0.200 g, 0.73 mmol) in 20 mL of dry dichloromethane was transferred via a cannula to a stirred solution of compound **2c** (0.670 g, 0.73 mmol) and triethylamine (0.25 mL, 1.82 mmol) in 200 mL of dichloromethane. The reaction was stirred for 3 hours at room temperature under nitrogen atmosphere. Water was then added, and the organic layer was separated and washed with water. The organic was dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using 20% hexane in ethyl acetate as eluent to give compound **2** as an orange solid (0.117 g, 14%).

Characterization data for 2

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 0.81 (s, $(CH_3)_3CArOCH_2CH_2OAr$, 18H), 1.09 (t, J_{H-H}= 6.8 Hz, CH_3CH_2OCOR, 6H), 1.30 (s, $(CH_3)_3CArOCH_2COOR$, 18H), 3.14 and 4.53 (dd, J_{H-H}= 12.8 Hz , $ArCH_2Ar$, AB system, 8H), 3.96 (q, J_{H-H}= 7.2Hz, CH_3CH_2O-, 4H), 4.37 (s, RCH_2OAr(calix), 4H), 4.47, 4.68 (s, C_5H_4-(ferrocene), 8H) 4.64 (s, -OCH_2R, 8H), 6.48 (s, Ar*H*OCH_2CH_2OArNH , 4H), 6.63 (d, J_{H-H}= 8.0 Hz, *p*-Ar*H*NH, 2H), 7.08 (s, Ar*H*OCH_2COOR, 4H), 7.18 (t, J_{H-H}= 8.0 Hz, *m*-Ar*H*NH, 2H), 7.28 and 7.72 (s, *o*-Ar*H*NH, 4H), 8.77 (t, J_{H-H}= 6.4 Hz, ArN*H*, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 170.5, 170.0, 169.0, 159.8, 155.5, 152.2, 144.8, 139.7, 135.1, 131.7, 129.5, 125.6, 124.9, 112.3, 111.6, 105.3, 79.0, 73.2, 71.9, 71.0, 68.8, 60.6, 51.2, 33.8, 31.1, 13.9.

Elemental analysis: Anal. Calcd. For $C_{80}H_{92}FeO_{12}N_2$: C, 72.26; H, 6.98; N, 2.11, found: C, 72.25; H, 6.94; N, 2.14

ESI mass: calcd: 1329.46; found 1351.187 [M + Na^+].

2.3 Binding Studies by NMR Titrations

2.3.1 Anion Binding Studies of Receptors 1 and 2

Typically, a 0.005 M solution of a receptor ($2.5x10^{-6}$ mole) in 5% CD_3CN:$CDCl_3$ 0.5 mL was prepared in a NMR tube. A 0.05 M stock solution of various anionic guests such as benzoate, acetate, dihydrogenphosphate, chloride, bromide and iodide (as tetrabutylammonium salts) in 5% CD_3CN:$CDCl_3$ was prepared in a small vial. The solution of guest molecules was added into NMR tubes according to the ratio shown in Table 2.1.

2.3.2 Cation Binding Studies of Receptors 1 and 2

Typically, a 0.005 M solution of a receptor ($2.5x10^{-6}$ mole) in 5% CD_3CN:$CDCl_3$ 0.5 mL was prepared in a NMR tube. A 0.05 M stock solution of cationic guests, sodium and potassium ions (as hexafluorophosphate salts), in 5% CD_3CN:$CDCl_3$ was prepared in a small vial. The solution of guest molecules was added into NMR tubes according to the ratio shown in Table 2.1.

2.3.3 Simultaneous Cation and Anion Binding Studies of 1 and 2

Typically, a 0.005 M solution of a receptor ($2.5x10^{-6}$ mole) and a cationic guest molecule ($3.0x10^{-6}$ mole) in 5% CD_3CN:$CDCl_3$ 0.5 mL was prepared in a NMR tube. A 0.05 M stock solution of anionic guest molecules in 5% CD_3CN:$CDCl_3$ was prepared in a small vial. The solution of anionic guest molecules was added into NMR tubes according to the ratio shown in Table 2.1.

Table 2.1 Volume and concentration of guest solution which have been used in the NMR titration.

Mole ratio Guest : Receptor	*Added volume of 0.05 M of guest solution (μL)*	*Concentration of a guest molecule(M)*	*Concentration of a receptor (M)*
0.0 : 1.0	0	0.00000	0.00500
0.1 : 1.0	5	0.00050	0.00495
0.2 : 1.0	5	0.00098	0.00490
0.3 : 1.0	5	0.00146	0.00485

0.4 : 1.0	5	0.00192	0.00481
0.5 : 1.0	5	0.00238	0.00476
0.6 : 1.0	5	0.00283	0.00472
0.7 : 1.0	5	0.00327	0.00467
0.8 : 1.0	5	0.00370	0.00463
0.9 : 1.0	5	0.00413	0.00459
1.0 : 1.0	5	0.00455	0.00455
1.2 : 1.0	10	0.00536	0.00446
1.4 : 1.0	10	0.00614	0.00439
1.6 : 1.0	10	0.00690	0.00431
1.8 : 1.0	10	0.00763	0.00424
2.0 : 1.0	10	0.00833	0.00417
3.0 : 1.0	50	0.01154	0.00385
4.0 : 1.0	50	0.01429	0.00357

2.4 Electrochemical Studies

2.4.1 Anion Binding Studies of Receptors 1 and 2

Typically, a 0.005 M solution of a receptor ($2.5x10^{-5}$ mole) in 5 mL of supporting electrolyte (0.1 M $TBAPF_6$ in 40% CH_3CN:CH_2Cl_2) was prepared. A 0.50 M stock solution of anionic guests was prepared in the supporting electrolyte solution. Upon titration, the solution of anionic guests was added into the solution of the receptor following the ratio shown in the Table 2.2.

2.4.2 Cation Binding Studies of Receptors 1 and 2

Typically, a 0.005 M solution of a receptor ($2.5x10^{-5}$ mole) in 5 mL of supporting electrolyte (0.1 M $TBAPF_6$ in 40% CH_3CN:CH_2Cl_2) was prepared. A 0.50 M stock solution of metal salts, $NaClO_4$ and KPF_6, was prepared in the supporting electrolyte solution. Upon titration, the solution of metal salts was added into the solution of the receptor following the ratio shown in the Table 2.2.

2.4.3 Simultaneous Cation and Anion Binding Studies of Receptors 1 and 2

Typically, a 0.005 M solution of a receptor ($2.5x10^{-5}$ mole) and cationic guest ($3.0x10^{-5}$ mole) in 5 mL of supporting electrolyte (0.1 M $TBAPF_6$ in 40% CH_3CN:CH_2Cl_2) was prepared. A 0.50 M stock solution of anionic guests in the supporting electrolyte solution was prepared. Upon titration, the solution of anionic guests was added into the solution of the receptor following the ratio shown in the Table 2.2

Table 2.2 Volume and concentration of guest solution which have been used in the CV titration.

Mole ratio Guest : Receptor	*Added volume of 0.50 M of guest solution (μL)*	*Concentration of a guest molecule(M)*	*Concentration of a receptor (M)*
0.0 : 1.0	0	0.00000	0.00500
0.1 : 1.0	5	0.00050	0.00500
0.2 : 1.0	5	0.00100	0.00499
0.3 : 1.0	5	0.00150	0.00499
0.4 : 1.0	5	0.00199	0.00498
0.5 : 1.0	5	0.00249	0.00498
0.6 : 1.0	5	0.00298	0.00497
0.7 : 1.0	5	0.00348	0.00497
0.8 : 1.0	5	0.00397	0.00496
0.9 : 1.0	5	0.00446	0.00496
1.0 : 1.0	5	0.00495	0.00495
1.2 : 1.0	10	0.00593	0.00494
1.4 : 1.0	10	0.00690	0.00493
1.6 : 1.0	10	0.00787	0.00492
1.8 : 1.0	10	0.00884	0.00491
2.0 : 1.0	10	0.00980	0.00490
3.0 : 1.0	50	0.01456	0.00485
4.0 : 1.0	50	0.01923	0.00481