# CHAPTER IV

# EXPERIMENTAL

## 4.1 Operation and Apparatus

The preparations of ferrocenylamine and other ferrocenyl derivatives were done in inert atmosphere, prepurified nitrogen, using Schlenk technique.

## 4.2 Reagents and Solvents

All chemicals in analytical grade, were obtained from Fluka and Merck and used as received. β-Cyclodextrin (10-13 wt % $H_2O$) was dried at 110 °C for 10 hr. Diethylzinc solution was 1 M in hexane. Standard 1-phenyl-1-propanol was racemic mixture. R(-)-α-methoxy-α-trifluoromethylphenylacetic acid chloride (MTPA-Cl, R:S = 95.5:0.5) was stored at −18 °C. *n*-Butyllithium (15 % in hexane), highly flammable and air sensitive, was transferred in nitrogen atmosphere with syringe. Benzaldehyde was distilled at 60 °C by reduced pressure (10 mm. Hg)

Solvents were obtained from BDH and Carlo Erba, and dried before used. Anhydrous diethyl ether was dried in 4 Å molecular sieves. Carbon tetrachloride was predried over 4 Å molecular sieves and distilled. Pyridine was distilled with sodium hydroxide.

Tetrahydrofuran, hexane and toluene were dried with Na and benzophenone. Freshly cut sodium (1g) was added into the solvent (500 mL) and benzophenone (3g) was added. After swirling to dissolve the benzophenone, a blue colour should form at the metal surface. This localized colour will initially disappear but, on refluxing, the bulk of the solvent should gradually turned green and then blue as all of water and oxidizing impurities were removed.

## 4.3 Physical and Analytical Measurements

### 4.3.1 Nuclear Magnetic Resonance

$^1$H NMR spectra were obtained on a Bruker ACF 200 MHz at Chemistry Department, Chulalongkorn University and JMN 500 MHz at Scientific and Technological Research Equipment Centre, Chulalongkorn University. The spectra were referenced to the residual proton peaks in the deuterated solvent: deuterochloroform (7.2 ppm), dimethylsulfoxide-$d_6$ (2.6 ppm). Chemical shifts were given in parts per million (ppm) and coupling constant (J) in Hertz (Hz).

### 4.3.2 Fourier Transform Infrared Spectrometry

Fourier transform infrared spectra were recorded on Nicolet Impact 410 Spectrometer. Solid samples were examined by incorporating into a pellet of potassium bromide (KBr). For liquid samples a sodium chloride cell was used.

### 4.3.3 Ultraviolet and Visible Spectroscopy

UV-visible spectra were recorded on Milton Roy Spectronic 3000. Wavelength is in range of 400-800 nm and cell width is 1 cm.

### 4.3.4 Elemental Analyses

Elemental analyses were carried out on Perkin Elmer Elemental Analyzer 2400 CHN, by ignition combustion gas chromatography separated by frontal analysis and quantitatively detected by thermal conductivity detector. This technique was performed by Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### 4.3.5 Thermogravimetric Analyses

Thermogravimetric analyses were carried out under air atmosphere (10 mL/ min) on a Netzsch Model STA 409 C. The sample size was 10 mg. The heating rate for nonisothermal experiment was 10 °C/min to study change of mass during 20-500 °C heating. This technique was performed by Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### 4.3.6 X-Ray Powder Diffraction

X-ray powder diffraction patterns were obtained by X-ray diffractometer Model JDX-8030, Jeol, Japan. Target was Cu, voltage 45.0 kV, current 30 mA, start angle at 5 degree, stop angle was 90 degree, step angle was 0.040 degree. This technique was performed by Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### 4.3.7 GC-Mass Spectrometry

Gas chromatography was carried out on Varian, Star 3400CX and mass spectrometry was carried out on Varian, Saturn 4D by Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### 4.3.8 Melting Point

Melting points of complexes were measured in glass capillaries using Electrothermal apparatus. The uncorrected melting points were reported in degrees Celsius.

### 4.3.9 Column Chromatography

Column chromatography was used to separate the products of alkylation, and to purify ferrocenyl derivatives. The column was glass tube, 1 cm diameter and 30 cm length. Stationary phase was 70-230 mesh of silica gel or alumina.

### 4.3.10 High Performance Liquid Chromatography

High Performance Liquid Chromatography was carried out on HPLC, Diacel chiral OB column (25×0.46 cm), Ultraviolet 254 nm detector. This technique was performed by Advanced Institute of Science and Technology (JAIST), Japan.

### 4.3.11 Gas Chromatography

Pack column gas chromatography GC 9A, Shimadzu was used for the determination of product yield. The conditions are as follows:

**Column:** DC 200

**Column Temp:** 145 °C

**Detector:** Flame ionization (FID)

**Detector Temp:** 145 °C

**Injection Temp:** 220 °C

**Carrier gas:** $N_2$

**Flow rate:** 50 mL/min

Capillary column gas chromatograph GC9A, Shimadzu used for the determination of enantiomeric excess (% e.e.). The conditions are as follows:

**Column:** DB wax

**Programmed Temp:** 180 °C for 5 min, increased at 10 °C /min to 220 °C, held for 15 min

**Detector:** Flame ionization (FID)

**Detector Temp:** 250 °C

**Injection Temp:** 250 °C

**Carrier gas:** $N_2$

**Flow rate:** 70 mL/min

## 4.4 Preparations of Ferrocenylamine Derivatives

### 4.4.1 Preparation of *N, N*-Dimethylaminomethylferrocene[29] ($Fc\text{-}CH_2N(CH_3)_2$)

Ferrocene 4.00 g (0.0215 mol) was added to a well-stirred solution of 6 mL (4.49 g, 0.0439 mol) of *N, N, N', N'*-tetramethylethylenediamine, 3 mL (5.09 g, 0.0518 mol) of phosphoric acid and 35 mL of glacial acetic acid. The reaction mixture was refluxed for 4 hr under nitrogen. A dark-amber solution was allowed to cool to room temperature and was diluted with 50 mL of water. The unreacted ferrocene was removed by extracting with diethyl ether. The aqueous solution was then cooled in ice water and made alkaline by slowly added 25 g of sodium hydroxide pellet. The tertiary amine was separated from the alkaline solution as an oil in the presence of some black tar. The mixture was extracted with diethyl ether. The organic solution was dried with anhydrous sodium sulphate. *N, N*-dimethylaminomethylferrocene was obtained as a dark-red oil after the solvent was removed. The yield of product was 4.22 g (81 %)

**FTIR (NaCl):** $\nu$ **($cm^{-1}$)** 3092 (s), 2938 (s), 2858 (s), 2813 (s), 2768 (vs), 1637 (m, br), 1460 (s), 1350 (m), 1262 (m), 1226 (m), 1170 (m), 1134 (w), 1103 (m), 1020 (s), 928 (w), 818 (vs), 751 (w), 489 (s)

**$^1$H NMR ($CDCl_3$): $\delta$ (ppm)** 4.14 (s, 2H), 4.09 (s, 7H), 3.27 (s, 2H), 2.15 (s, 6H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 440 nm; $\epsilon$ = 89

### 4.4.2 Preparation of *N, N*-Dimethylaminomethylferrocene Methiodide[30] ($Fc\text{-}CH_2N(CH_3)_3I$)

To a cooled solution of 2.13 g (0.0088 mol) of *N, N*-dimethylaminomethyl ferrocene in an 10 mL of absolute methanol was added dropwise a solution of 1 mL (2.28 g, 0.0160 mol) of iodomethane in 10 mL of absolute methanol. The mixture was refluxed for 15 min, and 100 mL of diethyl ether was then added. The resulting precipitate of the product was collected on funnel, and washed with diethyl ether until

the washings were colorless. The yellow crystals of *N, N*-dimethylaminomethylferrocene methiodide were obtained in 3.24 g (96 %). Recrystallizing with acetonitrile-diethyl ether gave yellow leaflets which decomposed slowly on heating to 220 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3120 (w), 3098 (w), 3074 (w), 3064 (w), 3052 (w), 3048 (m), 2993 (w), 2968 (w), 2939 (w), 1655 (m), 1483 (m), 1472 (m), 1458 (w), 1408 (m), 1387 (m), 1243 (w), 1104 (m), 1046 (m), 1038 (w), 994 (m), 920 (m), 886 (s), 830 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 4.48 (s, 2H), 4.38 (d, 2H), 4.24 (s, 5H), 3.33 (s, 9H), 2.90 (s, 2H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 436 nm; $\epsilon$ = 134

### 4.4.3 Preparation of Ferrocenylacetonitrile[31] (Fc-$CH_2CN$)

*N, N*-Dimethylaminomethylferrocene methiodide 2.00 g (0.0052 mol) was added to potassium cyanide 1.00 g (0.0154 mol) in 50 mL absolute ethanol, and the mixture was refluxed for 4 hr. After cooling, diethyl ether was added to precipitate unchanged quaternary salt, and the mixture was filtered. The filtrate was diluted with water and the aqueous layer extracted with diethyl ether. The combined diethyl ether extracts were dried with anhydrous sodium sulphate and purified by chromatography on alumina. Evaporation of solvent resulted in yellow powder 0.53 g (45 %), mp 82 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3108 (m), 3083 (w), 2970 (w), 2929 (w), 2874 (w), 2250 (s), 1664 (m), 1470 (w), 1413 (m), 1393 (m), 1309 (w), 1265 (w), 1240 (w), 1229 (w), 1170 (w), 1111 (vs), 1040 (s), 1029 (s), 1010 (s), 901 (w), 876 (w), 835 (s), 819 (vs), 748 (w), 533 (m), 507 (m), 487 (vs)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 4.22 (s, 5H), 4.16 (t, 2H), 4.12 (s, 2H), 3.41 (s, 2H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 437 nm; $\epsilon$ = 127

### 4.4.4 Preparation of α-Methylferrocenylmethylamine ($Fc\text{-}CH_2NHCH_3$)

Methylamine 2 mL (0.0237 mol) in aqueous solution was added to a solution of *N, N*-dimethylaminomethylferrocene methiodide 2.00 g (0.0052 mol) in 20 mL of water and refluxed for 4 hr. The product was extracted with diethyl ether, dried with anhydrous sodium sulphate and purified by column chromatography on alumina. After evaporation, the product was recrystallized with hexane to give yellow crystal 0.65 g (55 %), mp 67- 68 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3439 (s, br), 2920 (s), 2850 (m), 2773 (m), 2748 (w), 2680 (w), 2520 (w), 2407 (w), 2375 (w), 1740 (w), 1638 (m, br), 1557 (m), 1510 (s), 1465 (m), 1427 (m), 1392 (m), 1342 (w), 1286 (m), 1233 (m), 1178 (w), 1103 (m), 1024 (m), 957 (w), 910 (w), 817 (m), 748 (w), 722 (w), 661 (w), 615 (w), 584 (w), 512 (m), 478 (m)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 4.18 (t, 2H), 4.11 (s, 5H), 4.09 (m, 2H), 3.46 (s, 2H), 2.80 (br), 2.43 (s, 3H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 440 nm; ∈ = 137

### 4.4.5 Preparation of Ferrocenylethylamine[32] ($Fc\text{-}CH_2CH_2NH_2$)

This preparation was modified from that in the reference 32. A solution of ferrocenylacetonitrile 1.00 g (0.0044 mol) in distilled tetrahydrofuran was added dropwise to lithium aluminium hydride 0.70 g (0.0200 mol) in the same solvent under nitrogen atmosphere. The mixture was refluxed for 2 hr. The excess of hydride was destroyed by addition of ethyl acetate and water. The mixture was filtered, extracted with diethyl ether and dried with anhydrous sodium sulphate. After evaporation red oil 0.81 g (80 %) was obtained.

**FTIR (NaCl): ν ($cm^{-1}$)** 3751 (w), 3321 (m), 3091 (m), 2967 (m), 2928 (m), 2859 (m), 1651 (m), 1541 (w), 1452 (w), 1412 (w), 1378 (w), 1262 (m), 1172 (s), 1104 (s), 1025 (s), 1004 (s), 925 (w), 814 (s), 485 (s)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 4.08 (s, 5H), 4.10 (m, 4H), 3.50 (s, 2H), 2.44 (t, 4H), 2.75 (t, 2H)

### 4.4.6 Preparation of *N*, *N*-Diphenylaminomethylferrocene ($Fc\text{-}CH_2NPh_2$)

Diphenylamine 1.50 g (0.0089 mol) was added to a solution of *N*, *N*-dimethylaminomethylferrocene methiodide 2.00 g (0.0052 mol) in 20 mL of water. The mixture was refluxed for 4 hr. The product was extracted with diethyl ether, dried with anhydrous sodium sulphate. After evaporation, the dark brown oil was purified by column chromatography on alumina, using hexane as eluent. Evaporation of solvent resulted in yellow crystals 0.86 g (45 %), mp 50-51 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3093 (m), 3047 (m), 3021 (m), 1600(s), 1495 (s), 1465 (m), 1424 (m), 1362 (m), 1316 (s), 1250 (m), 1173 (m), 1111(w), 1081(w), 1040 (w), 1029 (m), 999 (w), 876 (w), 830 (w), 748 (s), 692 (s), 513 (m), 492 (m)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 7.00 (m, 10H), 4.70 (s, 2H), 4.15 (s, 2H), 4.05 (s, 2H), 3.90 (s, 5H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 435 nm; $\epsilon$ = 35

### 4.4.7 Preparation of Schiff Base Derivative[33] ($Fc\text{-}CH{=}N(CH_2)_2N{=}CH\text{-}Fc$)

This preparation was modified from that in the reference 33. Ferrocenylaldehyde 1.00 g (0.0047 mol) in 10 mL toluene was cooled and the solution of ethylenediamine 0.20 mL (0.0025 mole) in 3 mL toluene was added dropwise. The mixture was stirred for 2 hr. The resulting orange solution was evaporated to dryness, the residue was dissolved in dichloromethane. Addition of hexane resulted in an orange solid 0.86 g (82 %), mp 152 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3431 (m, br), 3111 (w), 3072 (w), 2913 (w), 2895 (w), 2858 (w), 2830 (s), 1642 (vs), 1470 (w), 1459 (w), 1410 (w), 1379 (w), 1327 (w), 1281 (m), 1249 (m), 1106 (m), 1049(m), 1012 (s), 963 (w), 820 (s), 516 (s), 488 (s)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 8.20 (s, 2H), 4.60 (t, 4H), 4.31 (t, 4H), 4.15 (s, 10H), 3.75 (s, 4H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 446 nm; $\epsilon$ = 681

### 4.4.8 Preparation of Reduced Schiff Base Derivative[33] ($Fc\text{-}CH_2NH(CH_2)_2NH\text{-}CH_2\text{-}Fc$)

This preparation was modified from that in the reference 33. Lithium aluminium hydride 0.30 g (0.0079 mol) was added to a 50 mL tetrahydrofuran solution of Schiff base derivative 1.00 g (0.0047 mol). The mixture was refluxed for 1 hr, and small amount of methanol and water added. The suspension was filtered and the pale yellow filtrate was evaporated to dryness. About 10 mL ammonia solution was added. The product was extracted with dichloromethane, dried with anhydrous sodium sulphate and evaporated. Recrystallization from dichlomethane-hexane gave yellow powder 0.75 g (75 %), mp 91 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3435 (v, br), 3098 (m), 3077 (w), 2927 (m), 2887 (m), 2857 (m), 2835 (m), 1643 (m), 1543 (w), 1463 (m), 1412 (m), 1394 (m), 1326 (w), 1262 (w), 1227 (w), 1104 (s), 1037 (m), 1028 (m), 1000 (m), 816 (s), 774 (m), 716(m)

**$^1H$ NMR ($CDCl_3$): δ (ppm)** 4.20 (s, 4H), 4.15 (s, 10H), 4.12 (s, 4H), 3.50 (s, 4H), 2.75 (s, 4H)

### 4.4.9 Preparation of 6-Ferrocenyl-2, 2′-Bipyridine[34] ($Fc\text{-}C_6H_5N\text{-}NC_6H_5$)

Ferrocene 1.00 g (0.0054 mol) was dissolved in 15 mL of anhydrous diethyl ether and *n*-butyllithium 5 mL (0.0080 mol) was added. The solution was stirred at room temperature for 12 hr. After that it was cooled to –70 °C (dry ice-acetone) and added 0.15 g (0.0010 mol) of 2, 2′ bipyridine. The reaction mixture was warmed up slowly to room temperature and stirred for 3 days, then hydrolyzed under aerobic condition with water. The organic layer was separated and the remaining solid was extracted with dichloromethane. The combined organic fractions were dried with anhydrous sodium sulphate and evaporated to give crude orange solid of which the composition was analyzed by TLC (hexane/diethyl ether 50:50). Ferrocene, mono and disubstituted compounds were separated by column chromatography on alumina, using hexane to elute unreacted ferrocene, diethyl ether-dichloromethane (50:50) for mono substituted compound (6-ferrocenyl-2, 2′-bipyridine) and ethyl acetate for disubstituted compound (1, 1-bis (6, (2, 2′-bipyridine) ferrocene). The monosubstituted compound

was recrystallized with diethyl ether-hexane (50:50). The yield was 0.25 g (15%). mp 243 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3440 (s), 3098 (w), 1635 (w), 1586 (s), 1489 (m), 1426 (s), 1380 (w), 1287 (w), 1162 (w), 1106 (w), 1002 (w), 1054 (w), 1028 (m), 1006 (w), 849 (w), 813 (s), 746 (w), 704 (w), 633 (w), 504 (m), 485 (m)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 8.68 (ddd, 1H), 8.57 (td, 1H), 8.21 (dd, 1H), 7.85(ddd, 1H), 7.74 (m, 1H), 7.43 (ddd, 1H), 7.31 (ddd, 1H), 5.03 (td, 2H), 4.42 (t, 2H), 4.07(s, 5H)

#### 4.4.10 2-(α,α-Diphenylhydroxymethyl)dimethylaminomethylferrocene[35]

**Fc-$CH_2$-$N(CH_3)_2$**
**C-OH-$(Ph)_2$**

A solution of 2.44 g (0.0010 mol) of *N, N*-dimethylaminomethylferrocene in 10 mL of anhydrous diethyl ether was treated dropwise over period of 10 min. with 16 mL (0.0025 mol) of *n*-butyllithium. Metallation was completed by stirring for 1 hr at room temperature. An etheral solution of benzophenone 7.30 g (0.0040 mol) was added dropwise with moderate refluxing and the product was hydrolyzed by careful addition of water after stirred for 4 hr. Separation of the organic layer was followed by extraction of remaining aqueous layer with diethyl ether. The organic fractions were added phosphoric acid (1:10) solution and the resulting acid solution was neutralized with 10% sodium carbonate with stirring. Crude product was chromatographed on alumina. Elution with dichloromethane gave 2.95 g (70 %) of 2- (α, α-diphenylhydroxy methyl) dimethylaminomethylferrocene, mp 126-127 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3450 (m, br), 3088 (m), 3067 (m), 3032 (m), 2986 (m), 2950 (m), 2817 (s), 2781 (s), 1603 (w), 1495 (s), 1460 (s), 1357 (m), 1285 (m), 1260(m), 1234 (w), 1198 (m), 1183 (m), 1152 (w), 1111 (m), 1055 (s), 1014 (s), 886 (m), 825 (s), 753 (s), 707 (s), 676 (w), 620 (w), 604 (w), 975 (w), 522 (m), 492 (m), 446 (m)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 7.60 (d, 1H), 7.20 (m, 10H), 4.10 (t, 2H), 4.00 (s, 5H), 3.80 (d, 1H), 2.65 (d, 2H), 2.00 (s, 6H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 441 nm; ∈ = 12

## 4.5 Preparations of Other Ferrocenyl Derivatives

### 4.5.1 Preparation of Acetylferrocene[36] (Fc-$COCH_3$)

Anhydrous aluminium chloride 0.50 g (0.0037 mol) in 15 mL dichloromethane was added to distilled acetyl chloride 0.25 mL (0.0037 mol) and the flask was attached a calcium chloride drying tube. After stirring, ferrocene 0.69 g. (0.0037 mol) was added. After 30 min reaction time, the reaction mixture was poured into 50 mL ice water and neutralized with 25 % sodium hydroxide solution. The neutralized solution was poured into a separatory funnel containing water. The organic layer was removed and the water layer was washed three times with small portions of dichloromethane. The combined dichloromethane fractions were dried with anhydrous sodium sulfate. The product was separated by column chromatography using dichloromethane. Acetylferrocene (0.52 g, 85 % base on reacted ferrocene) was obtained, mp 83 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3116 (w), 3094 (w), 3073 (w), 1662 (s), 1457 (m), 1412 (w), 1377 (m), 1358 (w), 1282 (s), 1103 (w), 1167 (w), 1043 (w), 1021 (w), 1005 (w), 967 (w), 894 (w), 848 (w), 826 (w), 669 (w), 623 (w), 534 (m), 501 (m), 484 (m), 464 (m)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 4.88 (s, 2H), 4.76 (d, 2H), 4.18 (s, 5H), 2.37 (s, 3H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 451 nm; $\epsilon$ = 499

### 4.5.2 Preparation of Ferrocenylmethylalcohol[30] (Fc-$CH_2OH$)

To 20 mL of 1 M sodium hydroxide solution was added 2.00 g (0.052 mol) of *N, N*-dimethylaminomethylferrocene methiodide, and the mixture was refluxed for 2 hr. The evolution of trimethylamine at the top of the condenser was readily detected by its odor. After cooling, the oily material was taken up in diethyl ether. The etheral solution was washed with water until neutral to litmus, and dried over anhydrous sodium sulphate. After filtering, the solvent was removed, and the residue was recrystallized

from hexane to give 0.78 g (70 %) of ferrocenylmethylalcohol as yellow needles, mp 81-82 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3236 (m, br), 3088 (w), 3077 (w), 2956 (w), 2930 (w), 2873 (w), 1646 (w), 1469 (w) 1453 (w), 1432 (w), 1410 (w), 1378 (w), 1350 (w), 1260 (w), 1236 (m), 1190 (w), 1104 (m), 1039 (vs), 1022 (m), 1012 (w), 989 (s), 923 (w), 809 (m), 516 (m), 499 (m), 478 (m)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 4.32 (d, 2H), 4.20 (d, 2H), 4.15 (s, 5H), 2.50 (s, 3H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 438 nm; ∈ = 145

### 4.5.3 Preparation of α-Hydroxyethylferrocene[37] (Fc-CH(OH)-$CH_3$)

Lithium aluminium hydride 0.20 g (0.0053 mol) was added to a solution of acetylferrocene 1.00 g (0.0044 mol) in 25 mL anhydrous diethyl ether. The mixture was refluxed for 30 min. The ethyl acetate was addded dropwise to the reaction mixture until there is no evidence of reaction. After cooling, an aqueous solution of ammonium chloride (1.10 g in 10 mL water) was added. The mixture was stirred for 15 min and filtered to remove white solid (lithium and aluminium by products). The filtrate was washed with water, dried with anhydrous sodium sulphate. Evaporation of solvent resulted in yellow solid. After recrystallizing with 80/20 (v/v) hexane/diethyl ether gave yellow needles 0.80 g (80 %), mp 72-73 °C.

**FTIR (KBr): ν ($cm^{-1}$)** 3217 (s), 3097 (m), 2975 (m), 2930 (w), 1637 (w), 1445 (w), 1410 (m), 1368 (w), 1308 (s), 1236 (m), 1099 (m), 1067 (s), 1044 (w), 1034 (w), 1002 (s), 918 (w), 868 (m), 835 (m), 807 (w), 516 (m), 481 (s)

**$^1$H NMR ($CDCl_3$): δ (ppm)** 4.52 (m, 1H), 4.25 (m, 4H), 4.21 (s, 5H),1.87 (d, 1H), 1.44 (d, 3H)

**UV-Visible Spectrum:** $\lambda_{max}$ = 444 nm; ∈ = 168

## 4.6 Preparations of β-Cyclodextrin-Ferrocenyl Derivative Inclusion Compounds

Ferrocenyl derivatives are almost insoluble in water. A cocrystallized method from aqueous solution, as is usually used with water-soluble compounds to obtain the inclusion compounds, cannot be employed. A method followed Harada,[21] adding ferrocenyl derivatives to the aqueous solution of cyclodextrin was used.

Ferrocenyl derivative (0.0010 mol) was added to an aqueous solution of β-cyclodextrin (0.0005 mol) at 60 °C with 30 min stirring. The product was filtered and washed with water to remove the remaining cyclodextrin. Ferrocenyl derivative was removed with tetrahydrofuran. The inclusion compound was recrystallized from water.

### 4.6.1 β-Cyclodextrin-*N*, *N*-Dimethylaminomethylferrocene Inclusion Compound

$C_{55}H_{87}O_{35}NFe.4H_2O$ Yellow crystal

65% yield mp 207-208 °C (decomp)

**FTIR (KBr):** ν (**cm**$^{-1}$) 3358 (br, s), 2923 (m), 2895 (w), 1637 (m), 1451 (s), 1419 (m), 1370 (m), 1333 (m), 1302 (w), 1203 (w), 1157 (s), 1102 (m), 1081 (s), 1031 (vs), 1003 (m), 943 (m), 860 (w), 756 (w), 703 (w), 605 (w), 576 (w), 529 (w)

**$^1$H NMR ($CDCl_3$):** δ **(ppm)** 5.75 (d, 7H), 5.70 (s, 7H), 4.83 (d, 7H), 4.47 (s, 7H), 4.14 (d, 2H), 4.13 (s, 5H), 4.10 (d, 2H), 3.67 (m, 21H), 3.61 (m, 7H), 3.35 (m, 7H), 3.30 (m, 7H), 3.21 (s, 2H), 2.04 (s, 6H)

**Elemental Analysis:** Calc; C, 45.55; H, 6.60

Found; C, 45.75; H, 6.38

**UV-Visible Spectrum:** $\lambda_{max}$ = 440 nm; ∈ = 86

### 4.6.2 β-Cyclodextrin-*N*, *N*-Dimethylaminomethylferrocene Methiodide Inclusion Compound

$C_{56}H_{90}NIO_{35}Fe.4H_2O$ Yellow crystal

62% yield mp 218-220 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3388 (s, br), 2928 (m), 2900 (m), 1637 (m), 1482 (w), 1473 (w), 1457 (w), 1437 (w), 1429 (w), 1414 (m), 1386 (w), 1367 (m), 1333 (m), 1302 (m), 1246 (w), 1203 (w), 1157 (s), 1102 (s), 1081 (s), 1056 (s), 1031 (s), 1003 (m), 947 (m), 882 (w), 756 (w), 615 (m), 584 (m), 538 (m), 481 (m)

**$^1$H NMR (DMSO-$d_6$): δ(ppm)** 5.75(d, 7H), 5.68 (d, 7H), 4.83 (d, 7H), 4.45 (s, 7H), 4.25 (s, 2H), 4.18 (t, 2H), 4.13 (d, 5H), 3.66 (m, 21H), 3.61 (m, 7H), 3.37 (s, 2H), 3.35 (m, 7H), 3.30 (m, 7H), 2.91 (s, 9H)

**Elemental Analysis:** Calc; C, 42.25; H, 6.38

Found; C, 42.39; H, 6.20

**UV-Visible Spectrum:** $\lambda_{max}$ = 436 nm; $\epsilon$ = 78

### 4.6.3 β-Cyclodextrin-Ferrocenylacetonitrile Inclusion Compound

$C_{54}H_{81}O_{35}NFe.4H_2O$ Yellow crystal

61 % yield mp 198-199 °C (decomp)

**FTIR (KBr): ν($cm^{-1}$)** 3365 (s, br), 2929 (m), 2899 (m), 1644 (m), 2248 (w) 1419 (m), 1367 (m), 1337 (m), 1309 (m), 1250 (w), 1209 (w), 1167 (s), 1111 (s), 1086 (s), 1063 (s), 1029 (s), 1004 (s), 950 (m), 901 (w), 865 (w), 835 (w), 756 (m), 710 (m), 781 (m), 553 (m), 490 (m)

**$^1$H NMR (DMSO-$d_6$): δ(ppm)** 5.76 (d, 7H), 5.71 (d, 7H), 4.83 (d, 7H), 4.53 (t, 7H), 4.25 (t, 2H), 4.22 (s, 5H), 4.16 (t, 2H), 3.65 (s, 2H), 3.64 (m, 21H), 3.60 (m, 7H), 3.51 (m, 7H), 3.32 (m, 7H)

**Elemental Analysis:** Calc; C, 45.29; H, 6.26

Found; C, 45.00; H, 6.29

**UV-Visible Spectrum:** $\lambda_{max}$ = 437 nm; $\epsilon$ = 114

**4.6.4 β-Cyclodextrin-α-Methylferrocenylmethylamine Inclusion Compound**

$C_{54}H_{85}NO_{35}Fe.4H_2O$ Yellow crystal

60 % yield mp 208-210 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3375 (s, br), 2923 (m), 2894 (m), 1637 (m), 1488 (m), 1473 (w), 1458 (w), 1413 (m), 1381 (m), 1368 (m), 1333 (m), 1302 (m), 1246 (w), 1203 (w), 1157 (s), 1102 (s), 1081 (s), 1056 (s), 1031 (vs), 1009 (s), 947 (m), 937 (m), 874 (m), 756 (m), 704 (m), 578 (m), 528 (m), 481 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 5.75 (br, 7H), 5.71 (br, 7H) 4.83 (d, 7H), 4.47 (br, 7H), 4.19 (s, 2H), 4.14 (s, 5H), 4.07 (s, 2H) 3.66 (m, 21H), 3.62 (s, 2H), 3.61 (m, 7H), 3.35 (m, 7H), 3.30 (m, 7H), 2.85 (s, 1H) 2.25 (s, 3H)

**Elemental Analysis:** Calc; C, 45.16; H, 6.53

Found; C, 45.19; H, 6.50

**UV-Visible Spectrum:** $\lambda_{max}$ = 431 nm; $\epsilon$ = 121

**4.6.5 β-Cyclodextrin-Ferrocenylethylamine Inclusion Compound**

$C_{54}H_{85}NO_{35}Fe.4H_2O$ Yellow crystal

65 % yield mp 235-237 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3375 (vs, br), 2923 (m), 2894 (w) 1637 (m), 1544 (w), 1460 (w), 1413 (m), 1370 (m), 1337 (m), 1302 (m), 1260 (m), 1205 (m), 1102 (s), 1081 (s), 1057 (s), 1031 (vs), 1003 (s), 945 (m), 839 (m), 757 (m), 706 (m), 581 (m), 531 (m)

**$^1$H NMR (DMSO-$d_6$): δ(ppm)** 5.75 (d, 7H), 5.70 (d, 7H), 4.83 (d, 7H), 4.54 (t, 7H), 4.22 (s, 5H), 4.18 (m, 2H), 4.14(m, 2H), 3.64 (m, 21H); 3.62 (d, 2H), 3.52 (m, 7H), 3.46 (m, 7H), 3.35 (s, 7H), 2.70(s, 2H), 2.35(t, 2H)

**Elemental Analysis:** Calc; C, 45.16; H, 6.53

Found; C, 44.95; H, 6.62

### 4.6.6 β-Cyclodextrin-Schiff Base Derivative Inclusion Compound

$C_{108}H_{164}N_2O_{76}Fe_2.6H_2O$ Orange crystal

58 %yield mp 258-260 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3390 (s, br), 2923 (w), 2892 (w), 1685 (m), 1657 (m), 1637 (m), 1457 (w), 1412 (w), 1371 (w), 1333 (w), 1303 (w), 1244 (w), 1206 (w), 1157 (s), 1102 (s), 1086 (s), 1056 (s), 1031 (vs), 1003 (s), 942 (m), 860 (w), 835 (w), 763 (m), 707 (m), 594 (m), 589 (m), 528 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 8.30 (s, 2H), 5.74 (d, 14H), 5.70 (s, 14H), 4.83 (d, 14H), 4.82 (s, 4H), 4.68 (s, 4H), 4.47 (t, 14H), 4.31 (s, 10H), 3.66 (m, 42H), 3.58 (m, 14H), 3.35 (m, 14H), 3.30 (m, 14H)

**Elemental analysis:** Calc; C, 44.33; H, 6.06

Found; C, 44.21; H, 6.27

**UV-Visible Spectrum:** $\lambda_{max}$ = 458 nm; ε = 1107

### 4.6.7 β-Cyclodextrin-Reduced Schiff Base Derivative Inclusion Compound

$C_{108}H_{168}N_2O_{76}Fe_2.6H_2O$ Yellow crystal

62 % yield mp 245-247 °C (decomp)

**FTIR (KBr):ν ($cm^{-1}$)** 3375 (vs, br), 2923 (m), 2896 (m), 1637 (m), 1546 (w), 1448 (m), 1414 (m), 1370 (m), 1332 (m), 1306 (w), 1203 (w), 1157 (s), 1102 (m), 1081 (s), 1031 (s), 945 (w), 757 (w), 706(w), 581 (m), 531 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 5.72 (br, 28H), 4.83 (d, 14H), 4.45 (br, 14H), 4.17 (d, 4H), 4.13 (s, 5H), 4.05 (s, 4H), 3.65 (m, 42H), 3.61 (m, 14H), 3.35 (m, 14H), 3.49 (s, 4H), 3.30 (m, 14H), 2.75 (s, 6H)

**Elemental analysis:** Calc; C, 44.27; H, 6.19

Found; C, 44.10; H, 6.30

### 4.6.8 β-Cyclodextrin-Acetylferrocene Inclusion Compound

$C_{54}H_{82}O_{36}Fe.3H_2O$ Orange crystal

70 % yield mp 244-247 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3356 (s, br), 2923 (m), 2895 (m), 1672 (m), 1655 (m), 1637 (w), 1413 (w), 1382 (w), 1371 (w), 1332 (w), 1303 (w), 1275 (W), 1245 (w), 1205 (w), 1157 (m), 1104 (m), 1081 (s), 1057 (s), 1031 (vs), 1004 (m), 947 (m), 939 (w), 859 (w), 703 (w), 574 (w), 528 (w), 491 (w)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 5.72 (d, 7H), 5.67 (d, 7H) 4.83 (d, 7H), 4.78 (t, 2H), 4.56 (t, 2H), 4.45 (t, 7H), 4.24 (s, 5H), 3.65 (m, 21H), 3.60 (m, 7H), 3.35 (m, 7H), 3.30 (m, 7H), 2.35 (s, 3H)

**Elemental Analysis:** Calc ; C, 45.77; H, 6.26

Found ; C, 45.58; H, 6.30

**UV-Visible Spectrum:** $\lambda_{max}$ = 451 nm; ∈ = 415

### 4.6.9 β-Cyclodextrin-Ferrocenylaldehyde Inclusion Compound

$C_{53}H_{80}O_{36}Fe.3H_2O$ Orange crystal

75% yield mp 228-230 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3375 (s, br), 2923 (m), 2900 (m), 1683 (m), 1462(w) 1659 (m), 1637 (m), 1414 (m), 1372 (m), 1333 (m), 1303 (m), 1248 (m), 1204 (w), 1157 (s), 1105 (s), 1081 (s), 1056 (vs), 1031 (m), 1004 (s), 946 (m), 939 (m), 834 (w), 755 (w), 703 (w), 610 (w), 578 (w)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 9.90 (s, 1H), 5.71 (d, 7H), 5.67 (d, 7H), 4.83 (d, 7H), 4.82 (d, 2H), 4.68 (t, 2H), 4.45 (t, 7H), 4.31 (s, 5H), 3.65 (m, 21H), 3.60 (m, 7H), 3.35 (m, 7H), 3.30 (m, 7H)

**Elemental Analysis:** Calc; C, 45.57; H, 6.18

Found; C, 45.38; H, 5.80

**UV-Visible Spectrum:** $\lambda_{max}$ = 457 nm; ∈ = 522

### 4.6.10 β-Cyclodextrin-Ferrocenylmethylalcohol Inclusion Compound

$C_{53}H_{82}O_{36}Fe.4H_2O$ Yellow crystal

63% yield mp 221-222 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3365 (s, br), 2925 (m), 2896 (m), 1637 (m), 1414 (m), 1374 (m), 1332 (m), 1303 (w), 1242 (w), 1204 (w), 1156 (s), 1104 (s), 1004 (s), 1081 (s), 1031 (vs), 940 (m), 859 (w), 832 (w), 756 (m), 703 (m), 605 (m), 578 (m), 528 (m), 484 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 5.76 (br, 7H), 5.71 (d, 7H), 4.83 (d, 7H), 4.55 (t, 7H), 4.20 (m, 2H), 4.14 (d, 5H), 4.09 (t, 2H), 3.65 (m, 21H), 3.54 (m, 7H), 3.49 (m, 7H), 3.35 (m, 7H), 2.09 (s, 3H)

**Elemental analysis:** Calc; C, 44.73; H, 6.37

Found; C, 44.38; H, 6.29

**UV-Visible Spectrum:** $\lambda_{max}$ = 438 nm; ∈ = 110

### 4.6.11 β-Cyclodextrin-α-Hydroxyethylferrocene Inclusion Compound

$C_{54}H_{84}O_{36}Fe.4H_2O$ Yellow crystal

65 % yield mp 222-223 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3375 (s, br) 2929 (m), 2899 (m), 1644 (m), 1419 (m), 1367 (m), 1337 (m), 1306 (m), 1250 (w), 1209 (w), 1157 (s), 1081 (s), 1031 (vs), 947 (m), 871 (w), 825 (w), 758 (m), 707 (m), 604 (m), 584 (m), 528 (m), 481 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 5.74 (br, 7H), 5.69 (d, 7H), 4.81 (d, 7H), 4.55 (s, 1H), 4.53 (t, 7H), 4.23-4.13 (m, 2H), 4.11 (s, 5H), 4.08-4.04 (m, 2H), 3.64 (m, 21H), 3.53 (s, 7H), 3.48 (m, 7H), 3.32 (m, 7H), 2.30 (s, 3H), 1.56 (d, 3H)

**Elemental Analysis:** Calc; C, 45.13, H, 6.45

Found; C, 45.13, H, 6.30

**UV-Visible Spectrum:** $\lambda_{max}$ = 444 nm; ∈ = 129

## 4.7 Preparations of β-Cyclodextrin-Organic Compound inclusion compounds

Benzaldehyde and 1-phenyl-1-propanol were prepared inclusion compounds by the same method of ferrocenyl derivatives.

### 4.7.1 β-Cyclodextrin-Benzaldehyde Inclusion Compound

$C_{49}H_{70}O_{36}.6H_2O$ White crystal

70 % yield mp 278-280 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 3370 (s, br), 2929 (m), 1705 (m), 1644 (m), 1589 (w), 1413 (m), 1372 (m), 1337 (m), 1311 (m), 1250 (w), 1209 (w), 1163 (s), 1101 (s), 1086 (s), 1065 (s), 1034 (vs), 1009 (s), 947 (m), 866 (w), 835 (w), 753 (m), 712 (m), 686 (m), 656 (m), 609 (m), 584 (m), 533 (m), 476 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 10.02 (s, 1H), 7.93 (m, 2H), 7.72 (m, 1H), 7.61 (t, 1H), 7.46 (t, 1H), 5.72 (d, 7H), 5.68 (d, 7H), 4.83 (d, 7H), 4.45 (t, 7H), 3.64 (m, 21H), 3.59 (m, 7H), 3.35(m, 7H), 3.30 (m, 7H)

### 4.7.2 β-Cyclodextrin-1-Phenyl-1-Propanol Inclusion Compound

$C_{51}H_{82}O_{36}.6H_2O$ White crystal

65% yield mp 288-290 °C (decomp)

**FTIR (KBr): ν ($cm^{-1}$)** 2385 (s, br), 2929 (m), 1644 (m), 1454 (m), 1419 (m), 1367 (m), 1301 (m), 1250 (w), 1209 (w), 1163 (s), 1106 (s), 1086 (s), 1029 (s), 1009 (s), 947 (m), 866 (w), 763 (m), 707 (m), 615 (m), 584 (m), 533 (m)

**$^1$H NMR (DMSO-$d_6$): δ (ppm)** 7.78 (m, 1H), 7.74 (m, 1H), 7.62 (m, 2H), 7.48 (m, 1H), 5.77 ( br, 7H), 5.72 (s, 7H), 4.83 (d, 7H), 4.77 (s, 2H), 4.57 (t, 7H), 3.58 (m, 21H), 3.54 (m, 7H), 3.35 (m, 7H), 2.09 (s, 5H)

## 4.8 Alkylation of Benzaldehyde with Diethylzinc

### 4.8.1 Alkylation Reaction

A 250 mL flask equipped with a septum and a magnetic bar and purged with nitrogen, was charged with benzaldehyde (0.0010 mol), catalyst (%mol) and 5 mL of solvent. Diethylzinc 2 mL (0.0020 mol) was injected through the septum. After being stirring, the reaction was quenched with cooled 1 M hydrochloric acid (for basic reaction), with saturated sodium bicarbonate or 1% ammonium hydroxide (for acid reaction). The resulting mixture was extracted with diethyl ether. The combined organic extracts were washed with saturated brine, and dried over anhydrous sodium sulphate. Purification by chromatography on silica gel by eluting with diethyl ether:hexane (1:4) affords 1-phenyl-1-propanol of which the quality was determined by gas chromatography.

### 4.8.2 Determination of Correction Factor for Gas Chromatography

Determination of correction factor was done as follows:

1. Pipet 0.10 mL 1-phenyl-1-propanol into a round bottom flask and add 5 mL hexane, stir the solution.

2. Pipet 0.10 mL benzyl alcohol into a 25 mL volumetric flask and make volume with absolute ethanol. Pipet 5.00 mL of this solution into a solution in number 1, stir the solution, worked up with 1 M hydrochloric acid, washed with sodium chloride and dry with anhydrous sodium sulphate. 1.00 mL of cyclohexanol was added as internal standard.

3. Determine quantity of 1-phenyl-1-propanol by gas chromatography.

4. Calculate correction factor

### 4.8.3 Some Effects on % Yield of Alkylation Product

Determine % yield of alkylation product by varying some factors: mole ratio of benzaldehyde/diethylzinc, solvent, temperature and reaction time. The optimum condition was chosen for catalytic activity test of ferrocenyl derivatives and its inclusion in alkylation reaction.

## 4.9 Preparation of Diastereomeric Esters

The reaction was carried out in a dry small test tube fitted in a Schlenk flask. The reagents were injected via syringe into the test tube in the following order: dry pyridine 300 μl, R(-)-MTPA-Cl 26 μl (0.14 mmol), carbon tetrachloride 300 μl and 1-phenyl-1-propanol 13 μl (0.0100 mol). The reaction mixture was then shaken and allowed to stand at room temperature until the reaction was complete as evidenced by no more formation of crystalline pyridine hydrochloride. After reaction was complete, diethyl ether was added, washed (with cold 1 M hydrochloric acid, saturated sodium sulphate, and saturated sodium chloride solution), and dried with anhydrous sodium sulphate.