CHAPTER II
EXPERIMENTAL

2.1 General Procedure

Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected.

Spectrometers: FTIR spectra were recorded on a Fourier Transformed Infrared Spectrophotometer model Impact 410, solid samples were incorporated to potassium bromide to form a pellet. ^{1}H and ^{13}C NMR spectra were performed in deuterated chloroform, dimethylsulfoxide-d_6 or deuterium oxide with tetramethylsilane (TMS) as an internal reference on Fourier Transformed Nuclear Magnetic Resonance Spectrometer of Bruker, model AC-F200 and a Joel, model JNM-A500. Mass spectrometry (MS) analysis was conducted on Fisson Instrument Model Trio 2000 and Model Saturn 4D.

Chromatography: thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF_{254}). Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G) and flash chromatography was performed on silica gel (40 μm average particle diameter). Gas chromatography analysis was carried out on a Shimadzu Gas Chromatograph GC-9A and GC-7AG, GC-star 3400(GC-MS) instrument equipped with flame ionization detector with N_2 as a carrier gas. The columns used for chromatography were Carbowax 20M and DB-5MS(GCMS).

Elemental Analysis (EA) was carried out on a Perkin Elmer PE 2400 Series II : option CHN and gas chromatographically separated by frontal analysis quantitatively detected by thermal conductivity detector.

2.2 Chemicals

All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades.

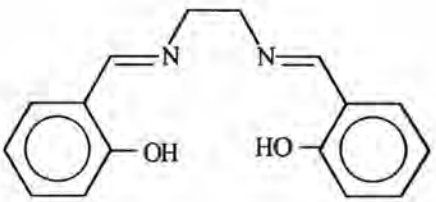
The reagents for synthesizing the Schiff's base ligands, metal Schiff's base complexes and all alkenes were purchased from Fluka chemical company and were used without further purification.

Merck's silica gel 60 G Art 7734 (70-230 mesh) were used as adsorbents for column chromatography.

2.3 Syntheses

2.3.1 Schiff's Base Ligands

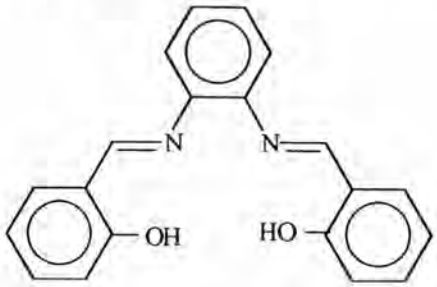
***Bis*(salicylaldehyde) *N, N'*-ethylenediimine[58] (salen)**



(1)

'Salen **(1)**' was prepared by slowly adding ethylenediamine 5.00 mL (0.06 mol) to salicylaldehyde 18.30 mL (0.15 mol) which was being stirred at room temperature. The yellow precipitate occurred immediately and recrystallized by 95% ethanol. Bright yellow crystals 15.67 g (97 % yield) were obtained; m. p. 124-125 °C; R_f 0.74 (silica gel: dichloromethane); IR (KBr): 3500(w), 3010-3050(w), 2870-2950(w), 1750-2000(w), 1640(s), 1450-1600(s), 1280(s) and 1170(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.84 (s, 4H), 6.83 (dt, J = 7.48, 1.22 Hz, 2H), 6.93 (d, J = 8.24 Hz, 2H), 7.18 (dd, J = 7.78, 1.53 Hz, 2H), 7.26 (dt, J = 7.78, 1.53 Hz, 2H), 8.29 (s, 2H) and 13.2 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 59.5 (2C), 116.8 (2C), 118.5 (2 x 2C), 131.4 (2C), 132.2 (2C), 160.9 (2C) and 166.3 (2C).

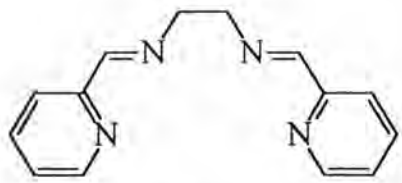
***Bis*(salicylaldehyde) *N, N'-o*-phenylenediimine[59] (salophen)**



(2)

'Salophen **(2)**' was prepared by slowly adding salicylaldehyde 7.00 mL (0.07 mol) to a solution of *o*-phenylenediamine 3.00 g (0.03 mol) in 50 mL methanol which was being stirred at room temperature. The orange precipitate was recrystallized from acetone. Orange needle crystals 7.74 g (82 % yield) were obtained; m. p. 164-165 °C; R_f 0.80 (silica gel: dichloromethane); IR (KBr): 3500(w), 3050(w), 2870-2950(w), 1630(s), 1560-1485(s), 1275(s) and 1190(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.85 (t, J = 7.32 Hz, 2H), 7.02 (d, J = 13.24 Hz, 2H), 7.20 (m, 4H), 7.31 (m, 2H), 7.35 (m, 2H), 8.60 (s, 2H) and 13.0 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 117.5 (2C), 118.9 (2C), 119.1 (2C), 119.6 (2C), 127.7 (2C), 132.3 (2C), 133.3 (2C), 142.4 (2C), 161.3 (2C) and 163.6 (2C).

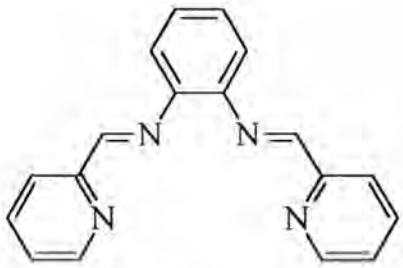
Bis (pyridinyl)-_N, N'_-ethylenediimine[60] (pyren)



(3)

15 g of pyridine-2-carboxaldehyde (0.16 mol) dissolved in 50 mL of absolute EtOH was mixed with ethylenediamine 6.67 mL (0.08 mol), whereupon a considerable amount of heat was evolved. After standing for 30 minutes, the solvent was removed by warming to about 60 °C under vacuum. As the last of the solvent was removed, the product solidified as a tan wax-like cake. It was recovered by extracting into several 100-150 mL portions of hot, low boiling petroleum ether, from which it was crystallized on cooling. Recrystallization from petroleum ether gave a product melting at 67-68 °C (lit.[60] m. p. 67-68 °C). Light yellow crystals 4.03 g (21% yield) were obtained; R_f 0.5 (silica gel: ethyl acetate); IR (KBr): 3010-3050(w), 2870-2950(w), 1645(s), 1595(s), 1420-1580(s) and 1330(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.07 (s, 4H), 7.29 (ddd, J = 7.48, 4.88, 1.22 Hz, 2H), 7.72 (dt, J = 7.63, 1.53 Hz, 2H), 7.98 (d, J = 2.06 Hz, 2H), 8.43 (s, 2H) and 8.62 (d, J = 4.58 Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 66.2 (2C), 121.3 (2C), 124.7 (2C), 136.4 (2C), 149.3 (2C), 154.3 (2C) and 163.3 (2C).

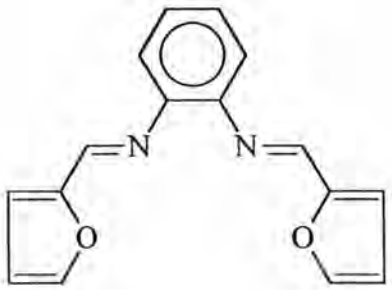
***Bis* (pyridinyl)-*N, N'*-phenylenediimine[61] (pyrophen)**



(4)

This ligand was prepared employing the similar method to that described for pyren using *o*-aminobenzene 8.10 g (0.08 mol) and pyridinaldehyde 15 g (0.16 mol). The yellow crystals 2.38 g (10 % yield) were obtained; m. p. 98-100 °C (lit.[61] m. p. 98-100 °C); R_f 0.30 (silica gel: dichloromethane); IR (KBr): 3060-3006(w), 2950-2900(w), 1630(w), 1590(s), 1560-1400(s) and 1170(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.29 (s, 2H), 6.90 (d, J = 7.93 Hz, 1H), 7.13 (dd, J = 7.33, 4.88 Hz, 1H), 7.29 (m, 3H), 7.37 (d, J = 7.94 Hz, 1H), 7.48 (dt, J = 7.63, 1.83 Hz, 1H) 7.83 (dt, J = 7.63, 1.83 Hz, 1H); 7.86 (d, J = 7.93 Hz, 1H), 8.48 (d, J = 8.24 Hz, 1H) and 8.57 (t, J = 5.94 Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 51.1 (2C), 110.8 (1C), 120.1 (1C), 120.9 (1C), 122.2 (1C), 122.9 (1C), 123.7 (1C), 123.8 (1C), 124.5 (1C), 136.8 (2C), 142.6 (1C), 148.6 (1C), 149.1 (1C), 149.8 (1C), 150.3 (1C) and 157.4 (1C).

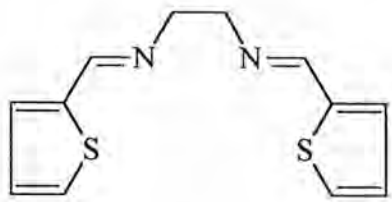
***N, N'*-difurfurylidenephenylenediamine[62] (fufuren-*O*-phen)**



(5)

To a solution of *o*-diaminobenzene 5.4 g (0.05 mol) in dry methanol (25 mL) was added furfural 9.6 g (0.10 mol). The reaction mixture was stirred at room temperature for 2 hours. The solvent was evaporated *in vacuo* and the residue was washed with petroleum ether to afford the ligand 0.54 g (5 % yield); m. p. 96-98 °C (lit[62] m. p. 97-98 °C); R_f 0.67 (silica gel: dichloromethane); IR (KBr): 3090-3140(w), 2950(w), 1605(s), 1430-1515(s), 1170(s) and 1150(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.63 (s, 2H), 6.23 (dd, J = 2.69, 0.62 Hz, 1H), 6.27 (dd, J = 3.36, 1.83 Hz, 1H), 6.60 (dd, J = 3.66, 1.83 Hz, 1H), 7.22 (dd, J = 3.52, 0.61 Hz, 1H), 7.29 (m, 2H), 7.32 (dd, J=1.83, 0.92 Hz, 1H); 7.49 (m, 1H), 7.64 (dd, J = 1.68, 0.61 Hz, 1H) and 7.78 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 41.6 (2C), 108.3 (1C), 109.9 (1C), 110.5 (1C), 112.0 (1C), 112.9 (1C), 119.8 (1C), 122.9 (1C), 123.2 (1C), 135.5 (1C), 142.6 (1C), 142.9 (1C), 143.9 (1C), 145.4 (1C) and 149.6 (1C).

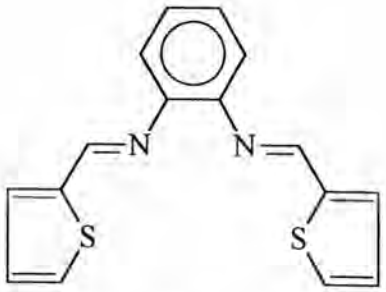
***Bis* (2-thiophenealdehyde) *N, N'*-ethylenediimine[63] (thiophen)**



(6)

'Thiophen **(6)**' was attained by reacting 2-thiophenealdehyde 5.6 g (0.05 mol) and ethylenediamine 1.5 g (0.025 mol). A small amount of 95 % ethyl alcohol was used as solvent. The white solid was filtered on a buchner funnel and washed with several portions of distilled water-ethanol solution and dried at room temperature, the white crystals 3.56 g (57 % yield) were obtained; m. p. 90-91 °C (lit.[63] m. p. 90-92 °C); R_f 0.60 (silica gel: ethanol); IR (KBr) 3050-3090(w), 2850-2920(w), 1640(s), 1430-1460(s) and 1220(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.90 (s, 4H), 7.03 (t, J = 4.42 Hz, 2H), 7.24 (d, J = 3.66 Hz, 2H), 7.36 (d, J = 5.19 Hz, 2H) and 8.34 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 60.9 (2C), 127.3 (2C), 128.7 (2C), 130.5 (2C), 142.3 (1C) and 156.0 (2C).

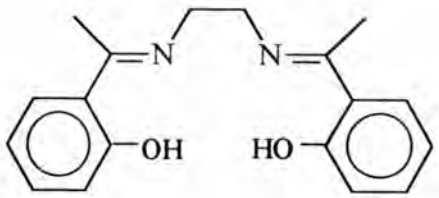
N, N'-1, 2-phenylene *bis* (2-thenylideneimine)[64] (thiophen-*o*-phen)



(7)

o-Phenylenediamine 2.7 g (0.05 mol) in ethanol (30 mL) was added to thiophen-2-aldehyde 5.6 g (0.05 mol) to give a dark green solution which was then heated on the steam-bath for 30 min, whereupon the colour changed to red. The reaction mixture was cooled and the clear red solution was decanted from a small amount of brown oil and filtered. The filtrate on standing overnight deposited yellow needles of the Schiff's base 4.56 g (62 % yield); m. p. 148-149 °C (lit.[64] m. p. 148 °C); R_f 0.68 (silica gel: ethanol); IR (KBr) 3090-3050(w), 2950(w), 1630(w) and 1225(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.70 (s, 2H), 6.86 (dd, J = 3.36, 1.22 Hz, 1H), 6.94 (t, J = 4.43 Hz, 1H), 7.13 (t, J = 4.27 Hz, 1H), 7.23 (dd, J = 4.89, 1.23 Hz, 1H), 7.29 (m, 2H), 7.37 (dd, J = 7.32, 1.22 Hz, 1H); 7.47 (dd, J = 3.82, 1.22 Hz, 1H), 7.51 (dd, J = 5.03, 1.22 Hz, 1H) and 7.83 (dd, J = 6.87, 1.83 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 44.0 (1C), 109.9 (1C), 119.9 (1C), 123.0 (1C), 123.3 (1C), 125.2 (1C), 125.4 (1C), 127.2 (1C), 127.9 (1C), 128.0 (1C), 128.9 (1C), 131.8 (1C), 135.8 (1C), 138.8 (1C), 143.0 (1C) and 147.6 (1C).

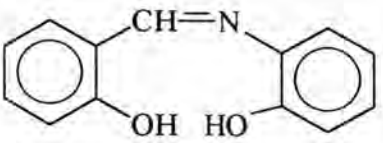
***Bis*(2-hydroxyacetophenone) *N, N'*-ethylenediimine (Me salen)**



(8)

'Me salen **(8)**' was prepared utilizing the same methodology as that used for the preparation of salen by employing ethylenediamine 4.17 mL (0.05 mol) and 2-hydroxyacetophenone 13.62 g (0.10 mol). The yellow needle crystals 11.97 g (81 % yield) were obtained; m. p. 200-1 °C; R_f 0.70 (silica gel: dichloromethane); IR (KBr) 3500(w), 3010-3050(w), 3080(w), 2870-2950(w), 1800-2000(w), 1620(s), 1450-1600(s), 1220(s) and 1180(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.37 (s, OH), 3.97 (s, 4H), 6.78 (dt, J = 7.70, 1.28 Hz, 2H), 6.91 (dd, J = 8.55, 1.28 Hz, 2H), 7.27 (dt, J = 7.91, 1.28 Hz, 2H), 7.52 (dd, J = 7.91, 1.50 Hz, 2H) and 15.80 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 14.7 (2C), 50.2 (2C), 117.4 (2C), 118.5 (2C), 119.4 (2C), 128.1 (2C), 132.4 (2C), 163.1 (2C) and 172.7 (2C).

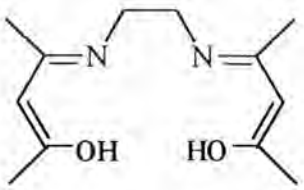
_N_-Salicylalidene-2-aminophenol[65] (salop)



(9)

The solution of 2-aminophenol 10.92 g (0.10 mol) in ethanol was slowly added to salicylaldehyde 11.21 g (0.10 mol). The red precipitate obtained was recrystallized by 95% ethanol to afford red needle 15.11 g (79 % yield); m. p. 189-190 °C; R_f 0.64 (silica gel: dichloromethane); IR (KBr): 3500(w), 3050(w), 1640(s), 1460-1600(s), 1280(s) and 1150(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.79 (s, 1H), 6.95-7.09 (m, 4H), 7.15 (dd, J = 7.79, 1.53 Hz, 1H), 7.22 (dt, J = 7.94, 1.53 Hz, 1H), 7.40-7.45 (m, 2H), 8.69 (s, 1H) and 12.25 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 115.9 (1C), 117.3 (1C), 118.3 (1C), 119.3 (1C), 119.6 (1C), 121.0 (1C), 128.8 (1C), 132.7 (1C), 133.7 (1C), 135.8 (1C), 149.9 (1C), 160.6 (1C) and 164.0 (1C).

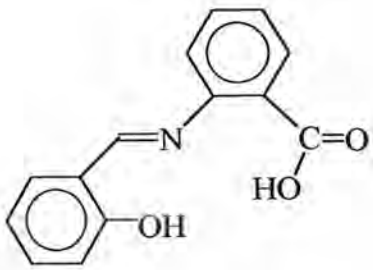
N, N'-Ethylene-*bis* (acetylacetoneiminate)[66] (acen)



(10)

Ethylenediamine 3 g (0.05 mol) was added to acetylacetone 10.02 g (0.10 mol) slowly. The obtained solution was heated and stirred for 10 min, whereupon the white solid occurred. The precipitate was recrystallized by 50 % hexane-dichloromethane to give clear white crytals; m.p. 111-3 °C (lit[66] m. p. 113 °C); R_f 0.58 (silica gel: ethanol); IR (KBr): 3500(w), 3100-3200(w), 2900-3000(w), 1600-1650(b), 1280-1300(b) and 1100(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.91 (s, 6H), 2.00 (s, 6H), 3.42 (d, J = 6.40 Hz, 4H), 5.00 (s, 2H) and 10.90 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 18.6 (2C), 28.8 (2C), 43.5 (2C), 96.1 (2C), 162.7 (2C) and 195.5 (2C).

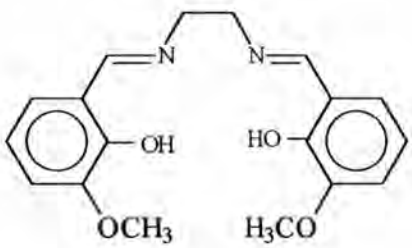
_N_-Salicylalidene-_o_-aminobenzoic acid[65] (saloa)



(11)

The solution of anthranilic acid 13.71 g (0.10 mol) in ethanol was added to salicylaldehyde 11.21 g (0.10 mol) slowly. The solution was heated and red precipitate was recrystallized by ethanol. Red crystals 12.31 g (57 % yield) were obtained; m. p. 203-5 °C; R_f 0.73 (silica gel: ethanol); IR (KBr): 3500(w), 3050-3100(w), 1620(s), 1460-1580(s), 1240(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.50 (s, 1H), 6.66 (dd, J = 8.54, 0.91 Hz, 1H), 6.67 (dd, J = 8.53, 1.22 Hz, 1H), 6.99 (d, J = 8.85 Hz, 1H), 7.03 (dd, J = 7.33, 0.92 Hz, 1H), 7.30 (dt, J = 7.78, 1.52 Hz, 1H) 7.52 (dt, J = 7.64, 1.83 Hz, 1H); 7.56 (dd, J = 7.78, 1.53 Hz, 1H), 7.90 (dd, J = 8.39, 1.83 Hz, 1H), 9.90 (s, 1H) and 11.00 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 114.5 (1C), 116.3 (1C), 117.2 (1C), 119.0 (2C), 119.4 (1C), 130.4 (1C), 131.1 (1C), 133.6 (1C), 136.4 (1C), 151.5 (1C), 160.7 (1C), 169.6 (1C) and 191.8 (1C).

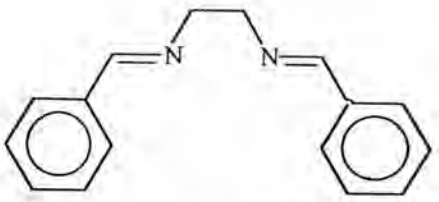
***Bis* (*o*-vanillin*) N, N'*-ethylenediimine[67] (salen OMe)**



(12)

Ethylenediamine 3 g (0.05 mol) was slowly added to a solution of *o*-vanillin 15.22 g (0.10 mol) in ethanol (40 mL). The precipitate was isolated and recrystallized from ethanol to give yellow needle 13.14 g (97 % yield); m. p. 163-5 °C (lit.[67] m. p. 163-5 °C); R_f 0.58 (silica gel: dichloromethane); IR (KBr): 3500(w), 3050(w), 2840-2990(w), 1630(s), 1465(s), 1255(s) and 1080(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.88 (s, 6H), 3.94 (s, 4H), 6.77 (t, J = 7.63 Hz, 2H), 6.84 (dd, J = 7.94, 1.53 Hz, 2H), 6.90 (dd, J = 7.94, 1.52 Hz, 2H), 8.32 (s, 2H) and 13.55 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 56.0 (2C), 59.4 (2C), 114.1 (2C), 118.0 (2C), 118.4 (2C), 123.1 (2C), 148.3 (2C), 151.4 (2C) and 166.6 (2C).

***Bis* (benzaldehyde) *N, N'*-ethylenediimine[68] (bzen)**



(13)

Ethylenediamine 4.17 mL (0.05 mol) was added to benzaldehyde 10.61 g (0.10 mol) slowly. The derived solution was heated and stirred until pale yellow solid occurred. Precipitate was filtered off and recrystallized from 50% methanol to produce yellow crystals 9.38 g (84 % yield); m. p. 48-50 °C; R_f 0.50 (silica gel: dichloromethane); IR (KBr): 3020-3090(w), 2850-2950(w), 1640(s), 1450-1580(s) and 1280(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.97 (s, 4H), 3.35-7.40 (m, 6H), 7.67-7.71 (m, 4H) and 8.28 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 61.6 (2C), 128.0 (4C), 128.5 (4C), 130.6 (2C), 136.1 (2C) and 162.6 (2C).

2.3.2 Metal Complexes

Preparation of Chromium Complexes and Chromium Schiff's Base Complexes

- ***Tris* (salicylaldehydato) chromium (III)**[69] [$Cr(sal)_3$]

Chromium (III) chloride hexahydrate 5.32 g (0.02 mol) and urea 40 g (1.5 mol) were dissolved in water 200 mL. The mixture was warmed for 15 min on the steam-bath. Salicylaldehyde 14.7 g (0.12 mol) in methanol 50 mL was then added and a dark orange-red oil was separated. The mixture was kept at 50°C for 16 hr. On cooling in ice bath, the oil was solidified and the crude product after filtration was recrystallized from methanol, yielding 4.0 g (48 % yield) of complex, m. p. 215-6 °C (lit[69] m. p. 215-6 °C). Elemental analysis found C, 60.46; H, 3.90 %; Calc. for $C_{21}H_{15}CrO_6$: C, 60.70; H, 3.60 %. The brown-yellow complex was readily soluble in benzene and chloroform and moderately soluble in methanol and ethanol.

- ***N*-(*p*-Toluene) salicylaldiminatochromium (III)**[69] [$Cr(sal\text{-}p\text{-}tolylen)_3$]

Tris (salicylaldehydato) chromium (III) 0.525 g (1.25 mmol) was dissolved in benzene 15 mL. The *p*-aminotoluene in 5-10 % excess was added and the mixture was refluxed for 6 hr. The solution was filtered and then concentrated, light petroleum ether was then added to produce precipitate. The product was recrystallized from benzene-light petroleum ether to give yellow-orange microcrystalline complexes 0.23 g (27 % yield), m. p. 201 °C (lit[69] m. p. 201 °C).

- ***Bis* (*N*-α-aminoethylsalicylaldiminato) chromium (III) iodide**[69]

[$Cr(salen)_2I$]

Tris (salicylaldehyde) chromium (III) 0.54 g (1.25 mmol) and ethylenediamine 2.0 g (0.033 mol) were well-mixed in methanol 20 mL and then refluxed for 30 min. The hot solution was filtered. Sodium iodide was added to this warm solution and the mixture was carefully evaporated until crystals

appeared upon cooling. The products were recrystallized from ethanol to obtain brown-red plates 0.32 g (4 % yield).

- [Cr(III)(salen)(H_2O)$_2$]Cl[70]

To a solution of chromium (III) chloride hexahydrate 26.65 g (0.1 mol) in ethylene glycol-water-methanol (1:1:3, 300 mL) were added salicylaldehyde 24.42 g (0.2 mol) and ethylenediamine 6.01 g (0.1 mol). After the mixture was heated at about 110 °C for about 30 min, sodium carbonate (0.06 mol) was added in small portions to the solution, followed by refluxing of the solution for about 3 to 4 hr. On concentrating the solution, a reddish brown precipitate was obtained. The precipitate was recrystallized from 80% methanol to give reddish orange crystals of the desired complex 19.6 g (50 % yield). Elemental analysis found: C, 49.05; H, 5.03; N, 6.82 %; Calc. for $C_{16}H_{18}N_2O_4CrCl$: C, 49.30; H, 4.65; N, 7.19 %. The crystals are highly soluble in methanol and ethanol, fairly soluble in water, and almost insoluble in benzene and diethyl ether.

- [Cr(III)(salen)(H_2O)$_2$]NO_3. 2H_2O

Bis (salicylaldehyde) *N*, *N'*-ethylenediimine 2.7 g (0.01 mol) was dissolved in EtOH 50 mL at 60 °C. After stirring the solution until homogeneity was obtained, chromium(III) nitrate nonahydrate 4.0 g (0.01 mol) dissolved in water was dropped slowly. The solution was stirred at 60 °C under vacuum. The concentrated solution on standing overnight deposited brown precipitate which was further recrystallized by 50 % EtOH to obtain brown needle crystals 3.1 g (65 % yield). Elemental analysis found: C, 44.96; H, 5.21; N, 9.22 %; Calc. for $C_{18}H_{22}N_3O_9Cr$: C, 42.48; H, 4.90; N, 9.29 %. The crystals are highly soluble in water and fairly soluble in ethanol.

VO(IV) salen, Ni(II) salen, Cr(III) salen.NO_3, Cu(II) salen, Fe(II) salen, Co(II) salen and Mn(II) salen were kindly provided from Miss Duangamol Nuntasri.[71] Each metal salen complexes were synthesized employing different methods which were described below.

- VO(IV) salen[72]

The complex $VO(acac)_2$ 4.35 g (16.40 mmol) was added to acetonitrile 150 mL and the mixture heated to reflux and filtered hot leaving a small residue. Salen 5.07 g (16.40 mmol) was added to the hot fitrate using a Soxhlet extractor. The mixture was kept at reflux temperature for 30 min, then cooled. After 1 day the green needle of VO salen 2.52 g (46 % yield) were filtered off, washed with cold acetonitrile and diethyl ether, and dried *in vacuo*, m. p. 168 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2900 (w) (ν (C-H aliphatic)) and 1620 (s) (ν (C=N)).

- Co(II) salen and Ni(II) salen[73]

Bis(salicylaldehyde) *N, N'*-ethylenediimine 2.7 g (0.01 mol) was dissolved in ethanol 50 mL at 70 °C. After stirring the solution until homogeneity, metal(II) acetate (0.01 mol) dissolved in ethanol was dropped slowly and refluxed for 1 hr. Precipitrate of metal salen complexes had occurred. The products were filtered and washed with cold ethanol.

Co(II) salen: yield 62 %, m. p. 228 °C (d); IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2900 (w) (ν (C-H aliphatic)) and 1640 (ms) (ν (C=N)).

Ni(II) salen: yield 98 %, m. p. 141 °C (d); IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2920 (w) (ν (C-H aliphatic)) and 1610 (ms) (ν (C=N)).

- Cu(II) salen and Mn(II) salen[73]

Bis (salicylaldehyde) *N, N'*-ethylenediimine 2.7 g (0.01 mol) was dissolved in *N, N'*-dimethylformamide (DMF) 30 mL at 60 °C. After stirring the solution until homogeneity, metal(II) acetate (0.01 mol) dissolved in DMF was dropped slowly and precipitation of metal salen complexes had occurred. The products were filtered and washed with acetone.

Cu(II) salen: 91 % yield; m. p. 296 °C (d); IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3015 (w) (ν (C-H aromatic)), 2940 (w) (ν (C-H aliphatic)) and 1620 (s) (ν (C=N)).

Mn(II) salen: yield 92 %, m. p. 95 °C (d); IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3060 (w) (ν (C-H aromatic)), 2900 (w) (ν (C-H aliphatic)) and 1620 (ms) (ν (C=N)).

- **Cr(III) salen.NO_3**

This complex was firstly prepared in this work by employing a similar method to that described for Co(II) salen by using salen 2.7 g (0.01 mol) and chromium(III) nitrate nonahydrate (0.01 mol) and recrystallized by 95 % ethanol-dichlorometbane; the pale orange solid was obtained 1.05 g (33 % yield); m. p. 187-189 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2900 (w) (ν (C-H aliphatic)), 1750 (s) (ν (NO_3) and 1600 (ms) (ν (C=N)).

- **Fe(II) salen**[73]

This complex was prepared employing the similar method to that described for Co(II) salen by using salen 2.7 g (0.01 mol) and iron (II) sulfrate (0.01 mol) and recrystallized by 95 % ethanol-dichloromethane. The dark brown of Fe(II) salen 0.5 g was obtained (18 % yield); m. p. 198-200 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2920 (w) (ν (C-H aliphatic)) and 1620 (s) (ν (C=N)).

- **Co(II) salophen and Mn(II) salophen**

These complexes were prepared utilizing the same methodology as that described for the preparation of Co(II) salen using salophen 3.2 g (0.01 mol) and metal(II) acetate (0.01 mole).

The brown powder of Co(II) salophen 1.10 g was obtained (29 % yield); m. p. 165 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2950 (w) (ν (C-H aliphatic)) and 1610 (s) (ν (C=N)).

The yellow powder of Mn(II) salophen 1.90 g was obtained (51 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2950 (w) (ν (C-H aliphatic)) and 1605 (s) (ν (C=N)).

- **Co(II) (Me salen), Co(II) salop, Co(II) (salen OMe), Mn(II) (Me salen), Mn(II) salop and Mn(II) (salen OMe)**

The general procedure for the preparation of the following metal complexes are described as follows: an ethanol (80 mL; 95 %) solution of ligand (10 mmol) was mixed with an aqueous (80 mL) solution of MX (10 mmol) and then a solution (42 mL) of $CH_3COONa.3H_2O$ (30 mmol) was added and refluxed for 2-3 hr. After that the solution was cooled for overnight and metal Schiff's base complexes were obtained.

The green needles of Co(II) (Me salen) were obtained 1.98 g (56 % yield); m. p. 260 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2950 (w) (ν (C-H aliphatic)), 1620 (b) (ν (CO_2^-)) and 1610 (s) (ν (C=N)). Elemental analysis found C, 52.14; H, 5.13; N, 5.23 %; Calc. for $Co(C_{18}H_{18}N_2O_2)(CH_3CO_2)_3$: C, 54.35; H, 5.13; N, 5.28 %.

The yellow powder of Co(II) salop was obtained 2.16 g (80 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2950 (w) (ν (C-H aliphatic)) and 1605 (s) (ν (C=N)). Elemental analysis found C, 58.04; H, 3.11; N, 5.13 %; Calc. for $Co(C_{13}H_9NO_2)$: C, 57.59; H, 3.35; N, 5.17 %.

The gold solid of Co(II) (salen OMe) was obtained 1.48 g (45 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3050 (w) (ν (C-H aromatic)), 2900-2950 (w) (ν (C-H aliphatic)), 1650 (b) (ν (CO_2^-) and 1610 (s) (ν (C=N)). Elemental analysis found C, 53.63; H, 4.99; N, 6.95 %; Calc. for $Co(C_{16}H_{18}N_2O_4)(CH_3CO_2)$: C, 51.44; H, 5.04; N, 6.67 %.

The dark brown of Mn(II) (Me salen) 1.16 g was obtained (33 % yield); m. p. 200 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2900 (w) (ν (C-H aliphatic)), 1610 (s) (ν (C=N)) and 1600 (b) (ν (CO_2^-)).

The yellow solid of Mn(II) salop 1.31 g was obtained (49 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2950 (w) (ν (C-H aliphatic)) and 1605 (s) (ν (C=N)). Elemental analysis found C, 55.11; H, 3.06; N, 4.92 %; Calc. for $Mn(C_{13}H_9NO_2)$: C, 58.67; H, 3.41; N, 5.26 %.

The dark brown of Mn(II) (salen OMe) 1.20 g was obtained (36 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3020 (w) (ν (C-H aromatic)), 2900 (w) (ν (C-H aliphatic)), 1630 (b) (ν (CO_2^-) and 1605 (s) (ν (C=N)). Elemental analysis found C, 50.62; H, 5.40; N, 6.21 %; Calc. for $Co(C_{16}H_{18}N_2O_4)(CH_3CO_2)_2$: C, 50.54; H, 5.09; N, 5.89 %.

- **Cr(III) salophen.NO_3, Cr(III) (Me salen).NO_3, Cr(III) acen.NO_3 and Cr(III) (salen OMe).NO_3**

The Schiff's base ligand (10 mmol) was dissolved in 100 mL ethanol at 70 °C. Cr(III) nitrate nonahydrate (10 mmol) dissolved in ethanol was dropped slowly and refluxed for 2-3 hr. The solvent was removed under vacuum. The concentrating solution was standing overnight, the precipitation of metal Schiff's base complexes occurred.

The dark brown of Cr(III) salophen.NO_3 0.12 g was obtained (3 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (w, b) (ν (O-H)), 3050 (w) (ν (C-H aromatic)), 2950-2920 (w) (ν (C-H aliphatic)) and 1610 (s) (ν (C=N)).

The dark brown of Cr(III) (Me salen).NO_3 0.19 g was obtained (6 % yield); m. p. 123 °C; IR (KBr, cm^{-1}): 3100-3200 (w) (ν (C-H aromatic)), 2850-2950 (w) (ν (C-H aliphatic)), 1750 (s) (ν (NO_3)) and 1610 (ms) (ν (C=N)).

The white plates of Cr(III) acen.NO_3 1.10 g was obtained (42 % yield); m. p. 185 °C; IR (KBr, cm^{-1}): 3500 (b) (ν (O-H)), 3070 (w) (ν (C-H aromatic)), 2910-2990 (w) (ν (C-H aliphatic)) and 1620 (s) (ν (C=N)).

The red brown of Cr(III) (salen OMe).NO_3 1.27 g was obtained (40 % yield); m. p. >300 °C; IR (KBr, cm^{-1}): 3500 (b) (ν (O-H)), 3050 (w) (ν (C-H aromatic)), 2920 (w) (ν (C-H aliphatic)) and 1620 (s) (ν (C=N)). Elemental analysis

found C, 37.38; H, 4.22; N, 10.84 %; Calc. for $Cr(C_{16}H_{18}N_2O_4)(NO_3)_2.2H_2O$: C, 37.38; H, 4.31; N, 10.90 %.

2.4 The General Procedure for the Epoxidation of Alkenes

An acetonitrile (30 mL) solution composing of alkene (5 mmol), aldehyde (isobutyraldehyde 10 mmol) and metal Schiff's base complex (0.2 mmol) in a round bottle flask was fitted with a balloon filled with oxygen. The mixture was stirred for 24 hr at room temperature. After the reaction was finished, 1 mL of the reaction mixture was taken and extracted with diethyl ether. The combined extracts were washed with saturated solution of $NaHCO_3$ and brine, respectively. The organic layer was dried over anhydrous Na_2SO_4 and analyzed by GLC with the addition of an exact amount of an appropriate internal standard.

2.5 Study on the Optimum Conditions for the Epoxidation of Cyclohexene and Other Alkenes

Effects of Metal salen : VO(IV) salen, Ni(II) salen, Cr(III) salen.NO_3, Cu(II) salen, Fe(II) salen, Co(II) salen and Mn(II) salen

The epoxidation reaction was carried out in the same manner as previously described employing seven metal salen complexes: VO(IV) salen, Ni(II) salen, Cr(III) salen.NO_3, Cu(II) salen, Fe(II) salen, Co(II) salen and Mn(II) salen as catalyst.

Effects of the Amount of Isobutyraldehyde

The epoxidation reaction was carried out in the similar fashion to that previously described, but using Cr(III) salen.NO_3 as catalyst and different amount of isobutyraldehyde was varied (0, 15 and 20 mmol).

Effects of Reaction Atmosphere: Oxygen, Nitrogen and Air

The epoxidation reaction was carried out in the same manner as aforementioned, but nitrogen and air were used instead of an oxygen atmosphere.

Effects of Aldehyde:

The epoxidation reaction was carried as dercribed earlier except for that 2-ethylbutyraldehyde, butyraldehyde, benzaldehyde, *p*-anisaldehyde and cyclohexanecarboxzaldehyde were used to replace isobutyraldehyde.

Effects of Solvent:

The epoxidation reaction was carried out in the same manner as previously described except for that chloroform and 1,2-dichloroethane were employed instead of acetonitrile.

Effect of the Amount of Catalyst (Cr(III) Salen.NO_3)

The epoxidation reaction was carried out as previously described but the amount of catalyst was varied (0, 0.05, 0.10 and 0.20 mmol).

2.6 Comparative Kinetic Study of the Epoxidation of Cyclohexene Catalyzed by Cr(III) salen.NO_3 and Co(II) salen

The general epoxidation procedure utilizing Cr(III) salen.NO_3 or Co(II) salen as catalyst was carried out. At different reaction times proceeded, an aliquot (1, 2, 4, 6, 8 and 9.5 hr) (1.0 mL) of the reaction mixture was taken, worked up and analyzed by GLC.

2.7 Competitive Studies on the Oxidation of Cyclohexene, γ-Terpinene and Cyclohexanol

Following the general epoxidation procedure, equimolar amount (5 mmol) of cyclohexene and γ-terpinene or cyclohexene and cyclohexanol were used as competitive substrates in the reaction. Competition between the epoxidation of cyclohexene and the aromatization of γ-terpinene or that between the epoxidation of cyclohexene and the oxidation of cyclohexanol were compared.

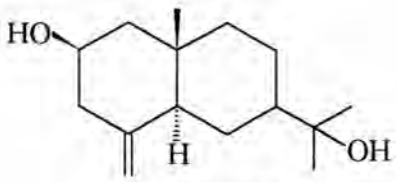
2.8 Chemoselectivity Study

Following the general epoxidation procedure, ethanol 5, 10 and 20 mmol were added as co-substrate to the optimum epoxidation conditions of cyclohexene.

2.9 Epoxidation of Other Alkenes and Application to Natural Products

Other alkenes, namely cyclooctene, 1-dodecene, styrene, α-methylstyrene and 1-methylcyclohexene and natural products containing double bonds namely, α-terpinene, γ-terpinene, (+)-valencene and pterocarpol were selected for the study on the regioselectivity of this developed epoxidation reaction utilizing the optimum conditions for cyclohexene. The specified reaction time was varied from one substrate to another.

2.10 Separation of Pterocarpol from *Pterocarpus macrocarpus*



pterocarpol

2.75 Kg of dried heartwoods of *Pterocarpus macrocarpus* were extracted with hexane at room temperature for 7 days. The solution was filtered and the solvent was removed by simple distillation. The filtrate on standing overnight deposited orange precipitate which was then filtered and recrystallized by 50 % hexane : ethyl acetate to yield a pale yellow solid. This solid 1.95 g was recrystallized by hot hexane to gain white needle of pterocarpol 0.435 g (1.58×10^{-4} % yield), m. p. 100-2 °C (lit[74] m. p. 104-105 °C); R_f 0.46 (silica gel : ethylacetate); IR (KBr): 3340 (b) (ν (O-H), 2850-2966 (s) (C-H aliphatic), 1644 (s) (ν (exomethylene group)), 1045-1385 (s) (ν (C=C)), 1045 (s) (ν (C-O)) and 890 (s) (bending of oxomethylene group) cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 0.70 (s, $-CH_3$), 1.07-1.43 (m, 5H), 1.21 (s, 2 x $-CH_3$), 1.55-1.85 (m, 7H), 1.97 (t, J = 11.6 Hz, 1H), 2.65 (ddd, J = 12.21, 5.19, 2.14 Hz, -OH), 3.86 (m, 1H), 4.56 (d, J = 1.53 Hz, -OH), 4.56 (d, J = 1.53 Hz, $=CH_2$) and 4.83 (d, J = 1.52 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ (ppm): 17.2 (1C), 21.9 (1C), 24.6 (1C), 27.1 (1C), 27.3 (1C), 35.2 (-$\overset{|}{C}$-), 40.7 (1C), 46.4 (1C), 49.0 (1C), 49.2 (1C), 50.9 (1C), 67.9 (-$\overset{|}{C}$H-OH), 72.8 (-$\overset{|}{C}$-OH), 108.0 ($=CH_2$) and 147.8 (-$\overset{|}{C}$=).