CHAPTER II

EXPERIMENTAL SECTION

2.1 General procedures

Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60 PF_{254}). Melting points were determined with a John-Fisher melting point apparatus and are uncorrected.

2.2 Instrumentation

The FT-IR spectra were performed on a Fourier Transform Infrared Spectrophotometer on Nicolet model Impact 410: solid samples were mixed with potassium bromide (KBr) to form pellets. The ^1H-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference on a Bruker model ACF 200 Spectrometer. Gas chromatography analysis was carried out on a Shimadzu Gas Chromatograph GC-14A instrument equipped with flame ionization detector (FID) by using N_2 as a carrier gas. UV-Vis was determined by Hewlett Packard 8452A diode array spectrophotometer. The column used for chromatography was a capillary column type of DB-wax (30 m x 0.250 mm) from J&W Scientific Company.

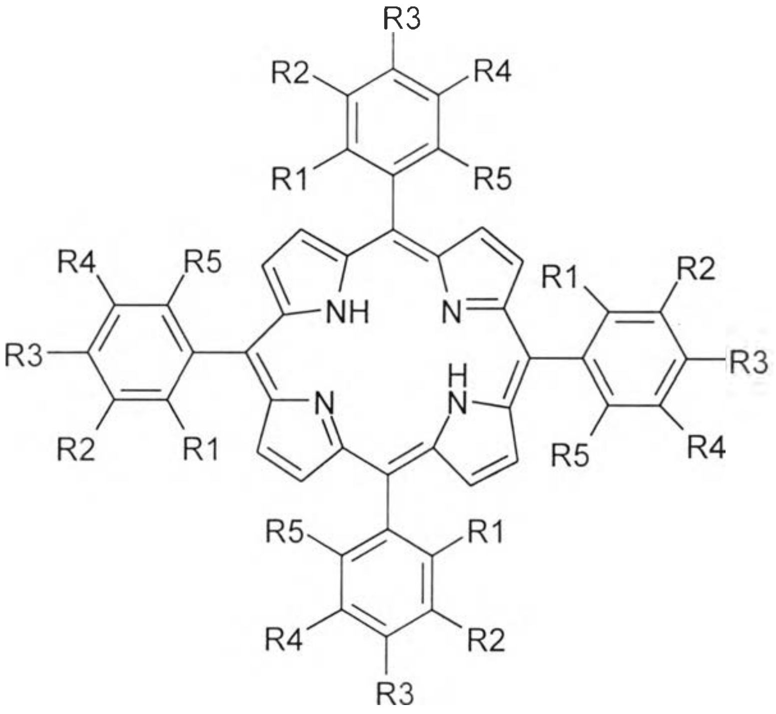
2.3 Chemicals

The reagents for synthesizing porphyrin ligands, metalloporphyrins and for oxidation reaction were purchased from Fluka and Merck chemical companies. All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades.

2.4 Syntheses

2.4.1 Syntheses of porphyrin ligands

General procedure[31]: Place 2.8 mL (0.04 mol) of freshly distilled pyrrole in a 250-mL round-bottomed flask, along with 0.04 mol of an interested aromatic aldehyde and 150 mL of glacial acetic acid or propionic acid. The mixture was refluxed for 2-3 hours. The solution was allowed to cool to room temperature, then placed the flask in an ice bath. Dark purple crystals were formed. The crystals were removed by vacuum filtration. The collected crystals were washed with ice-cold methanol and warm distilled water. Finally, the crystals were allowed to dry at room temperature. The resulting porphyrin ligands were pure enough for the subsequent metallation process. Ten synthesized porphyrin ligands **(1-10)** are depicted as shown below.



(1) $R_1 = H, R_2 = H, R_3 = H, R_4 = H, R_5 = H$

(2) $R_1 = H, R_2 = H, R_3 =$ *tert*-butyl, $R_4 = H. R_5 = H$

(3) $R_1 = H, R_2 = Cl, R_3 = H, R_4 = H, R_5 = H$

(4) $R_1 = H, R_2 = H, R_3 = Cl, R_4 = H, R_5 = H$

(5) $R_1 = H, R_2 = H, R_3 = Br, R_4 = H, R_5 = H$

(6) $R_1 = H, R_2 = H, R_3 = CH_3, R_4 = H, R_5 = H$

(7) $R_1 = H, R_2 = H, R_3 = OCH_3, R_4 = H, R_5 = H$

(8) $R_1 = H, R_2 = OCH_3, R_3 = H, R_4 = OCH_3. R_5 = H$

(9) $R_1 = H, R_2 = OCH_3, R_3 = OCH_3, R_4 = OCH_3, R_5 = H$

(10) $R_1 = OCH_3, R_2 = OCH_3, R_3 = OCH_3, R_4 = H, R_5 = H$

5,10,15,20-tetrakis-phenylporphyrin[31] **(1)**: Deep purple crystal (11%), R_f 0.70 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 512, IR (KBr, cm^{-1}): 3304, 2943, 2875, 1461, 1358, 1075, 963, 794 and 726; ^1H-NMR ($CDCl_3$) δ (ppm): 7.75 (8H, m), 7.77 (4H, m), 8.28 (8H, m) and 8.85 (8H, s).

5,10,15,20-tetrakis(4-tert-butylphenyl)-porphyrin **(2)**: Purple crystal (7%), R_f 0.69 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 421, IR (KBr, cm^{-1}): 3428, 2959, 1471, 1386, 1113, 965 and 798; ^1H-NMR ($CDCl_3$) δ (ppm): 1.60 (36H, m), 7.77 (8H, d, J = 8.23 Hz), 8.12 (8H, d, J = 8.18 Hz) and 8.86 (8H, s).

5,10,15,20-tetrakis(3-chlorophenyl)-porphyrin[32] **(3)**: Dark purple crystal (16%), R_f 0.35 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 421, IR (KBr, cm^{-1}): 3438, 3316, 2388, 1588, 1555, 1466, 1405, 1344, 972, 892, 798, 775 and 733; ^1H-NMR ($CDCl_3$) δ (ppm): 7.94 (4H, d, J = 3.75 Hz), 8.07 (4H, d, J = 7.17 Hz), 8.20 (4H, s), 8.59 (4H, s) and 8.84 (8H, s).

5,10,15,20-tetrakis(4-chlorophenyl)-porphyrin[32] **(4)**: Purple crystal (27%), R_f 0.81 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 422, IR (KBr, cm^{-1}): 3316, 1555, 1471, 1395, 1344, 1014, 960, 794 and 723; ^1H-NMR ($CDCl_3$) δ (ppm): 7.74 (8H, d, J = 4.60 Hz), 8.10 (8H, d, J = 8.33 Hz) and 8.83 (8H, s).

5,10,15,20-tetrakis(4-bromophenyl)-porphyrin **(5)**: Dark purple solid (34%), R_f 0.34 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 421, IR (KBr, cm^{-1}): 3428, 1579, 1471, 1391, 1344, 1221, 1071, 1014, 963, 791 and 725; ^1H-NMR ($CDCl_3$) δ (ppm): 7.91 (8H, d, J = 8.31 Hz), 8.04 (8H, d, J = 8.41 Hz) and 8.83 (8H, s).

5,10,15,20-tetrakis(4-methylphenyl)-porphyrin[31] **(6)**: Purple crystal (23%), R_f 0.35 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 420, IR (KBr, cm^{-1}): 3391, 3016, 2903, 1560, 1508, 1461, 1348, 1221, 1184, 1104, 960, 794 and 730; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.70 (12H, s), 7.54 (8H, d, J = 7.84 Hz), 8.09 (8H, d, J = 7.92 Hz) and 8.85 (8H, s).

5,10,15,20-tetrakis(4-methoxyphenyl)-porphyrin[31] **(7)**: Purple solid (17%), R_f 0.33 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 423, IR (KBr, cm^{-1}): 2931, 2838, 1602, 1508, 1466, 1287, 1245, 1174, 1038, 803 and 735; ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.09 (12H, t, J = 8.35 Hz), 7.28 (8H, d J = 6.98 Hz), 8.11 (8H, d, J = 4.73 Hz) and 8.85 (8H, s).

5,10,15,20-tetrakis(3,5-dimethoxyphenyl)-porphyrin **(8)**: Purple solid (17%). R_f 0.69 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 420, IR (KBr, cm^{-1}): 3447, 2931, 1598, 1456, 1414, 1202, 1160, 1061, 925, 803 and 735; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.94 (24H, t, J = 7.97 Hz), 7.29 (8H, s), 7.39 (4H, d, J = 2.32 Hz) and 8.91 (8H, s).

5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)-porphyrin[32,33] **(9)**: Purple needle crystal (32%), R_f 0.30 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 420, IR (KBr, cm^{-1}): 3447, 3308, 2933, 1579, 1504, 1461, 1406, 1356, 1236, 1122, 1005, 925, 803 and 726; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.98 (24H, d, J = 8.35 Hz), 4.19 (12H, s), 7.48 (8H, d, J = 7.44 Hz) and 8.97 (8H, s).

5,10,15,20-tetrakis(2,3,4-trimethoxyphenyl)-porphyrin **(10)**: Purple solid (15%), R_f 0.34 (hexane : dichloromethane; 3 : 2). UV (λ_{max}, nm): 422, IR (KBr, cm^{-1}): 3466, 2931, 1598, 1466, 1409, 1348, 1296, 1235, 1104, 1005, 902, 794 and 738; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.55 (12H, s), 3.24 (12H, m), 4.12 (12H, m), 7.29 (4H, s), 7.75 (4H, s) and 8.81 (8H, s).

2.4.2 Syntheses of metalloporphyrins

General procedure[34]: Dissolve 1.82 mmol of an interested transition metal salt (*e.g.* $CuCl_2.2H_2O$) in DMF. Then, a solution of transition metal salt was added to a solution of porphyrin ligand in 70 mL of DMF. The mixture was heated to 80 °C at least for 3 hours using an oil bath. After that, the mixture was allowed to cool to room temperature and added an equal volume of water. The crystals were removed by vacuum filtration.

Meso-tetraphenylporphyrin copper(II) complex[35] **(11)**: Red solid (69%), R_f 0.74 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 538, IR (KBr, cm^{-1}): 2963, 2856, 1438, 1348, 1075, 1009, 796, 742 and 695.

Meso-tetraphenylporphyrin nickel(II) complex **(12)**: Purple solid (56%), R_f 0.75 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 525, IR (KBr, cm^{-1}): 2919, 2853, 1583, 1547, 1475, 1352, 1020 and 794.

Meso-tetraphenylporphyrin cobalt(II) complex **(13)**: Brown solid (80%), R_f 0.75 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 524, IR (KBr, cm^{-1}): 2909, 2848, 1378, 1352, 1071, 1004, 794, 748 and 702.

Meso-tetraphenylporphyrin manganese(II) complex[32] **(14)**: Greenish black solid (56%), R_f 0.24 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 523, IR (KBr, cm^{-1}): 3016, 1598, 1442, 1381, 1344, 1202, 1179, 1075, 1019, 805, 751 and 702.

Meso-tetraphenylporphyrin iron(II) complex **(15)**: Dark blue solid (75%), R_f 0.74 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 394, IR (KBr, cm^{-1}): 1593, 1475, 1450, 1393, 1184, 1071, 1004, 968 and 805.

Meso-tetraphenylporphyrin iron(III) chloride complex[32,36] **(16)**: Dark blue solid (79%), R_f 0.75 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 418, IR (KBr, cm^{-1}): 1591, 1470, 1440, 1388, 968 and 805.

Meso-tetraphenylporphyrin zinc(II) complex[37] **(17)**: Dark blue solid (69%), R_f 0.75 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 418, IR (KBr, cm^{-1}): 2909, 1600, 1461, 1343, 1202, 1179, 1071, 1004, 794 and 750.

Tetra(4-tert-butylphenyl)-porphyrin iron(II) complex **(18)**: Dark blue solid (79%), R_f 0.31 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 421, IR (KBr, cm^{-1}): 3419, 2950, 1475, 1386, 1113, 967, 801 and 733.

Tetra(3-chlorophenyl)-porphyrin iron(II) complex[32] **(19)**: Dark blue solid (46%), R_f 0.31 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 416, IR (KBr, cm^{-1}): 3419, 1588, 1560, 1466, 1381, 1094, 979, 895, 803 and 730.

Tetra(4-chlorophenyl)-porphyrin iron(II) complex[32] **(20)**: Dark blue solid (88%), R_f 0.31 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 420, IR (KBr, cm^{-1}): 3438, 1475, 1391, 1089, 960, 803 and 733.

Tetra(4-bromophenyl)-porphyrin iron(II) complex **(21)**: Dark blue solid (33%), R_f 0.35 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 421, IR (KBr, cm^{-1}): 3428, 1475, 1381, 1071, 1014, 960, 796 and 733.

Tetra(4-methylphenyl)-porphyrin iron(II) complex **(22)**: Dark blue solid (63%), R_f 0.31 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 423, IR (KBr, cm^{-1}): 3428, 1466, 1381, 1108, 965, 798 and 742.

Tetra(4-methoxyphenyl)-porphyrin iron(II) complex[32] **(23)**: Dark blue solid (65%), R_f 0.33 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 421. IR (KBr, cm^{-1}): 2931, 2838, 1602, 1508, 1466, 1287, 1249, 1174, 1113, 1038, 963, 841, 805 and 738.

Tetra(3,5-dimethoxyphenyl)-porphyrin iron(II) complex **(24)**: Dark blue solid (69%), R_f 0.34 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 420. IR (KBr, cm^{-1}): 3438, 1602, 1461, 1353, 1207, 1155, 1066 and 801.

Tetra(3,4,5-trimethoxyphenyl)-porphyrin iron(II) complex[32] **(25)**: Purple plate solid (85%), R_f 0.41 (hexane : dichloromethane; 4 : 1). UV (λ_{max}, nm): 422, IR (KBr, cm^{-1}): 2943, 1581, 1500, 1462, 1406, 1350, 1237, 1125, 1000, 937, 812 and 725.

Tetra(2,3,4-trimethoxyphenyl)-porphyrin iron(II) complex **(26)**: Purple solid (85%), R_f 0.36 (hexane : dichloromethane; 6 : 4). UV (λ_{max}, nm): 422. IR (KBr, cm^{-1}): 3447, 2931, 1598, 1461, 1409, 1344, 1296, 1235, 1104, 974, 902, 796 and 742.

2.4.3 Syntheses of authentic specimen

2.4.3.1 Syntheses of 2-, 3- and 4-*tert*-butylcyclohexanol

General procedure[38]: Sodium borohydride 10 mmol was added over a period of 5 min to stirred solution of 20 mmol of interested ketone in 50 mL of ethanol. The reaction mixture was stirred for 2 hours at room temperature, then 10 mL of water was added. The mixture was extracted three times with 10 mL of ether. The combined organic phases were washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was evaporated and the residue was collected in vacuum desiccator.

2-tert-Butylcyclohexanol **(27)**: Liquid, colorless. IR (KBr, cm^{-1}): 3409, 2931, 1475, 1061 and 967; ^{1}H-NMR (CDCl$_3$) δ (ppm): 1.14-1.18 (9H, m), 1.45-1.49 (9H, m), 3.46 (1H, s) and 4.22 (1H, s).

3-tert-Butylcyclohexanol **(28)**: Liquid, colorless. IR (KBr, cm^{-1}): 3294, 2936, 2869, 1467, 1365 and 1070; ^{1}H-NMR (CDCl$_3$) δ (ppm): 0.77-1.16 (9H, m), 1.67-1.98 (9H, m), 3.46 (1H, s) and 4.38 (1H, s).

4-tert-Butylcyclohexanol **(29)**: White solid, mp. 60 ^{0}C. IR (KBr, cm^{-1}): 3288, 2941, 2856, 1452, 1376 and 1066; ^{1}H-NMR (CDCl$_3$) δ (ppm): 0.83-1.21 (9H, m), 1.74-2.00 (9H, m), 3.49 (1H, m) and 4.00 (1H, m).

2.4.3.2 Syntheses of 2- and 3-pentanol

2- and 3- Pentanol were prepared using reaction conditions described in the general procedure, but ketone was changed to 2- and 3-pentanone.

2-Pentanol **(30)**: Liquid, colorless. IR (KBr, cm^{-1}): 3350, 2966, 2935, 2887, 1464, 1371 and 1107; ^{1}H-NMR (CDCl$_3$) δ (ppm): 0.82 (3H, t, J = 5.40 Hz), 1.05 (3H, t, J = 3.80 Hz), 1.26 (2H, t, J = 6.34 Hz), 3.39 (1H, dd, J = 4.95, 1.01 Hz) and 3.79 (2H, s).

3-Pentanol **(31)**: Liquid, colorless. IR (KBr, cm^{-1}): 3287, 2965, 2945, 2920, 1457, 1375 and 1106; ^{1}H-NMR (CDCl$_3$) δ (ppm): 0.82 (6H, t, J = 7.49 Hz), 1.29 (4H, s), 3.20 (1H, s) and 3.48 (1H, q, J = 6.88, 3.06 Hz).

2.5 Oxidation of saturated hydrocarbons catalyzed by metal porphyrin complexes

Various factors affecting the oxidation reaction of cyclohexane involved temperature, reaction media, oxidants and additives were thoroughly examined. In addition, various saturated hydrocarbons were selected as a probe to study regioselectivity of this developed oxidation system.

General procedure for the oxidation of cyclohexane

Catalyst (0.25 mmol), cyclohexane (30 mmol), zinc grit (20 mmol), acetic acid (2.3 mL) and pyridine (28 mL) were placed in an Erlenmeyer flask. The mixture was stirred continuously for 24 hours at room temperature and atmospheric pressure. After the reaction was proceeded for a designed period of time, 1 mL of the reaction mixture was taken, acidified with cold 25% H_2SO_4 and extracted with diethyl ether. The combined extracts were washed with saturated solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4 anhydrous and analyzed by GC with the addition of an exact amount of an appropriate internal standard. Each experiment was repeated two times.

2.6 Effect of metal porphyrin complexes on cyclohexane oxidation

2.6.1 Effect of metal porphyrin complexes

The oxidation reaction of cyclohexane was carried out using reaction conditions described in the general procedure, but using different metal porphyrin complexes **11-17** as a catalyst.

2.6.2 Effect of porphyrin ligands

According to the general oxidation procedure, equimolar amount (0.25 mmol) of iron (II) porphyrin complexes, **18-26** was used as a catalyst and cyclohexane (30 mmol) was used as a substrate in the normal oxidation reaction.

2.7 Optimum conditions study for saturated hydrocarbon oxidation

2.7.1 Effect of reaction media

2.7.1.1 Oxidation of cyclohexane using pyridine and acetonitrile as solvent

The oxidation reaction of cyclohexane was carried out in the same fashion as described in general procedure, but the solvent of the reaction was changed to pyridine and acetonitrile with a ratio of 28.0:0, 21.0:7.0, 14.0: 14.0, 7.0:21.0 and 0:28.0.

2.7.1.2 Oxidation of cyclohexane using various solvents

The oxidation reaction of cyclohexane was carried out according to the general procedure. Various solvents (acetonitrile, acetone, dichloromethane, iso-octane and *tert*-butanol) were employed to replace pyridine.

2.7.2 Effect of the oxidants

The oxidation reaction of cyclohexane was carried out in the same manner as previously described, with the different oxidants (2-ethyl butyraldehyde/O_2, hydrogen peroxide and *tert*-butylhydroperoxide).

2.7.3 Effect of the additives

The oxidation reaction of cyclohexane was carried out as that described in the general procedure. Ascorbic acid, triphenylphosphine (PPh_3), carbon tetrachloride (CCl_4) and imidazole were separately added to the oxidation reaction to observe the effect of additives.

2.8 Kinetic study on the reaction rate of cyclohexane oxidation

The general oxidation procedure of cyclohexane using $FeCl_2.4H_2O$, and metal porphyrin complexes **15** and **25** as catalysts was carried out. At different reaction time proceeded (30, 60, 120, 240, 360 and 480 min), an aliquot from the reaction mixture was taken, worked up and analyzed by GC.

2.9 Comparative study on relative reactivity of cycloalkane in oxidation reactions

Two competitive cycloalkanes; with equimolar amount of cyclohexane and either cyclopentane, cycloheptane, cyclooctane or cyclododecane were oxidized respectively employing the general oxidation procedure.

2.10 Regioselectivity study on the oxidation reaction of other saturated hydrocarbons

Iron (II) porphyrin complex **25** was employed as a catalyst in *tert*-butylcyclohexane and *n*-pentane oxidation using reaction conditions described in the general procedure.