

## CHAPTER II

### EXPERIMENTAL SECTION

#### 2.1 General procedures

Chromatography: Thin layer chromatography (TLC) was carried out on aluminium sheet precoated with silica gel (Merck Kieselgel 60 PF<sub>254</sub>). Column chromatography was carried out on silica gel (Merck Kieselgel 60, 70-230 mesh). Melting points were measured with a Fisher-John melting point apparatus and are uncorrected.

#### 2.2 Instrumentation

Spectrometers : FT-IR spectra were recorded on a Fourier Transform Infrared Spectrophotometer on Nicolet model Impact 410: solid samples were mixed with potassium bromide (KBr) to form pellets. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained in deuterated chloroform (CDCl<sub>3</sub>) or deuterated dimethylsulfoxide (DMSO-*d*<sub>6</sub>) with tetramethylsilane (TMS) as an internal reference on Fourier Transform Nuclear Magnetic Resonance Spectrometer of Bruker model AC-F200. Gas chromatography analysis was carried out on a Shimadzu Gas chromatograph GC-14A instrument equipped with flame ionization detector (FID) with nitrogen as a carrier gas. The column used for chromatography was a capillary column type of DB-wax (30 m x 0.250 mm) from J&W Scientific Company. UV-Vis spectrum was determined by Hewlett Packard 8452A diode array spectrophotometer.

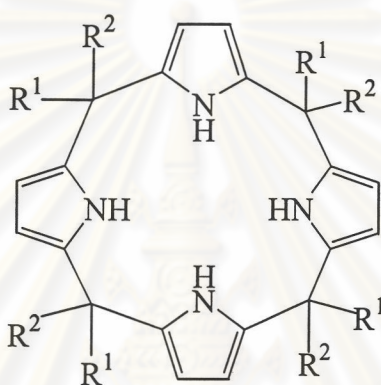
#### 2.3 Chemicals

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 calix[4]pyrrole ligands, cobalt calix[4]pyrrole complexes and all alkenes were purchased from Fluka chemical company and were used without further purification.

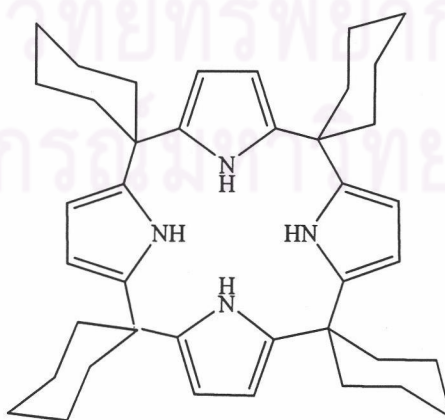
## 2.4 Syntheses

### 2.4.1 Syntheses of calix[4]pyrrole ligands (*meso*-octaalkylporphyrinogen).

General procedure<sup>60</sup> : Methanesulfonic acid (7% mol-equi) was slowly added to a solution of an interested ketone (1 mol-equi) and pyrrole (1 mol-equi) in ethanol. The mixture was allowed to reflux with stirring for 4 hours and then cooled in freezer, the white solid precipitated. The precipitate was filtered off and recrystallized by ethanol or an appropriate solvent. The resulting calix[4]pyrrole ligands were pure enough for the subsequent metallation process. Six synthesized calix[4]pyrrole ligands (1-6) are depicted as shown below.



- (1)  $R^1, R^2 = \text{Me}$
- (2)  $R^1, R^2 = \text{Et}$
- (4)  $R^1 = \text{Me}, R^2 = 4\text{-methoxyphenyl}$
- (5)  $R^1 = \text{Me}, R^2 = \text{C}_6\text{H}_5$
- (6)  $R^1, R^2 = \text{C}_6\text{H}_5$



(3)

*meso-Octamethyl calix[4]pyrrole*<sup>60</sup> (**1**): White crystal (65%),  $R_f$  0.55 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 220 °C (lit<sup>60</sup> 221°C), IR (KBr,  $\text{cm}^{-1}$ ): 3437 (s), 2978 (s), 1640 (m), 1451 (m), and 1272 (m); <sup>1</sup>H-NMR (**Fig. 1**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.01 (4H, bs), 5.88 (8H, d,  $J = 2.6$  Hz) and 1.49 (24H, s); <sup>13</sup>C-NMR (**Fig. 2**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 138.5 (8C), 102.7 (8C), 35.2 (4C) and 29.1 (8C).

*meso-Octaethyl-calix[4]pyrrole*<sup>60</sup> (**2**): White crystal (59%),  $R_f$  0.86 (hexane : ethyl acetate; 9 : 1), m.p. 119-220 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3454 (s), 2979 (s), 1644 (m), 1498 (m) and 1235 (m); <sup>1</sup>H-NMR (**Fig. 3**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.00 (4H, s), 5.86 (8H, d,  $J = 2.6$  Hz), 1.73 (16H, m) and 0.56 (24H, t,  $J = 14.6$  Hz); <sup>13</sup>C-NMR (**Fig. 4**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 135.9 (8C), 42.9 (4C), 29.0 (8C) and 8.0 (8C).

*Tetraspirohexyl-calix[4]pyrrole*<sup>65</sup> (**3**): White solid (85%),  $R_f$  0.85 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 268-269 °C (lit<sup>65</sup> 270-271°C), IR (KBr,  $\text{cm}^{-1}$ ): 3446 (s), 2931 (s), 2856 (m), 1630 (s) and 1451 (m); <sup>1</sup>H-NMR (**Fig. 5**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.04 (4H, bs), 5.87 (8H, s), 1.88 (16H, m) and 1.42 (24H, m); <sup>13</sup>C-NMR (**Fig. 6**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 136.4 (8C), 103.4 (8C), 39.6 (4C), 37.1 (8C), 26.0 (4C) and 22.7 (8C).

Isomers of *meso-tetrakis(4-methoxyphenyl)-tetramethyl-calix[4]pyrrole*<sup>65, 67</sup> (**4**): Brown crystal (92%),  $R_f$  0.44 (hexane : ethyl acetate; 8 : 2), m.p. 121-122 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3431 (s), 2970 (s), 2832 (m), 1608 (s), 1456 (s), and 1250 (s); <sup>1</sup>H-NMR (**Fig. 7**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.53 (4H, s), 6.92-7.15 (8H, m), 6.50-6.85 (8H, m), 5.66-5.92 (8H, m), 3.78 (12H, m) and 1.85 (12H, m); <sup>13</sup>C-NMR (**Fig. 8**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 157.5 (4C), 139.4 (4C), 136.8 (8C), 128.3 (8C), 113.0 (8C), 105.5 (8C), 55.0 (4C), 43.6 (4C) and 17.8 (4C).

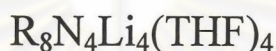
Isomers of *meso-tetramethyl-tetraphenyl-calix[4]pyrrole*<sup>66</sup> (**5**): Brown crystal (52%),  $R_f$  0.54 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 296-297 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3428 (s), 2968 (s), 1635 (m), 1489 (m) and 1121 (m); <sup>1</sup>H-NMR (**Fig. 9**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.46 (4H, bs), 7.27-7.07 (20H, m), 5.62-5.94 (8H, m) and 1.93 (12H, m); <sup>13</sup>C-NMR (**Fig. 10**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 147.7 (20C), 136.8 (4C), 136.5 (4C), 126.5-127.9 (8C), 105.9 (8C), 44.7 (4C) and 29.0 (4C).

Isomers of *meso-octaphenyl-calix[4]pyrrole*<sup>68</sup> (**6**): White solid (45%),  $R_f$  0.48 (hexane : ethylacetate; 8 : 2), m.p. 193-195 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3418 (s), 1545 (m), 1484 (m) and 1225 (m); <sup>1</sup>H-NMR (**Fig. 11**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.91 (4H, bs), 6.72-7.27 (40H, m), 6.16 (4H, m) and 5.96 (4H, m); <sup>13</sup>C-NMR (**Fig. 12**) ( $\text{CDCl}_3$ ,  $\delta$  (ppm)):

146.0 (8C), 135.3 (8C), 129.2 (16C), 127.8 (8C), 126.7 (16C), 109.6 (4C), 108.0 (4C) and 44.4 (4C).

#### 2.4.2 Syntheses of tetrapolyanions.

General procedure<sup>60</sup> : BuLi in hexane (4 mol-equi) was added dropwise to THF solution of an interested calix[4]pyrrole ligand (1 mol-equi). The mixture was refluxed at 50°C for 1 hour until gas evolution stopped. The solution was evaporated to dryness and the white residue was dissolved in hexane to afford a white suspension which was filtered off, washed with hexane and dried. A polyanion is depicted as shown below.



- (7)  $\text{R}^1, \text{R}^2 = \text{Me}$   
 (8)  $\text{R}^1, \text{R}^2 = \text{Et}$   
 (9)  $\text{R} = \text{cyclohexyl}$   
 (10)  $\text{R}^1 = \text{Me}, \text{R}^2 = 4\text{-methoxyphenyl}$   
 (11)  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{C}_6\text{H}_5$   
 (12)  $\text{R}^1, \text{R}^2 = \text{C}_6\text{H}_5$

*Lithium of meso-octamethyl-calix[4]pyrrole tetraanion*<sup>60,61</sup>(7): Yellow solid (73%),  $R_f$  0.52 (hexane : ethyl acetate; 8 : 2), m.p. 245 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3104 (m), 2965 (s), 2868 (w), 1787 (m), 1680 (s), 1419 (s) and 1244 (s);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 6.00 (8H, s), 4.29 (16H, bs, THF), 1.48 (24H, s) and 1.21 (16H, m, THF).

*Lithium of meso-octaethyl-calix[4]pyrrole tetraanion*<sup>60</sup> (8): Yellow solid (71%),  $R_f$  0.83 (hexane : ethyl acetate; 9 : 1), m.p. 257 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3124 (w), 2937 (w), 2844 (w), 1575 (s), 1431 (m) and 1203 (w);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 6.00 (8H, s), 4.73 (16H, br, THF), 1.83 (16H, m), 1.20 (16H, m, THF) and 0.74 (24H, t,  $J = 14.8$  Hz).

*Lithium of tetraspirohexyl-calix[4]pyrrole tetraanion*<sup>60</sup> (9): Light brown solid (81%),  $R_f$  0.84 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 259°C, IR (KBr,  $\text{cm}^{-1}$ ): 3108 (m), 2919 (s), 2842 (s), 1567 (m), 1444 (m) and 1291 (m);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 5.93 (8H, s), 4.70 (16H, br, THF), 1.42-1.91 (40H, m) and 1.21 (16H, m, THF)

*Lithium of meso-tetrakis(4-methoxyphenyl)-tetramethyl-calix[4]pyrrole tetraanion*<sup>60</sup> (10): Dark gold crystal (79%),  $R_f$  0.45 (hexane : ethyl acetate; 8 : 2), m.p. 112 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3090 (w), 2631 (w), 1607 (w), 1456(m) and 1250 (m);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 6.93-7.15 (8H, m), 6.64-6.78 (8H, m), 5.78-5.90 (8H, m), 3.77 (12H, m), 4.68 (16H, br, THF), 1.86 (12H, m) and 1.75 (16H, br, THF).

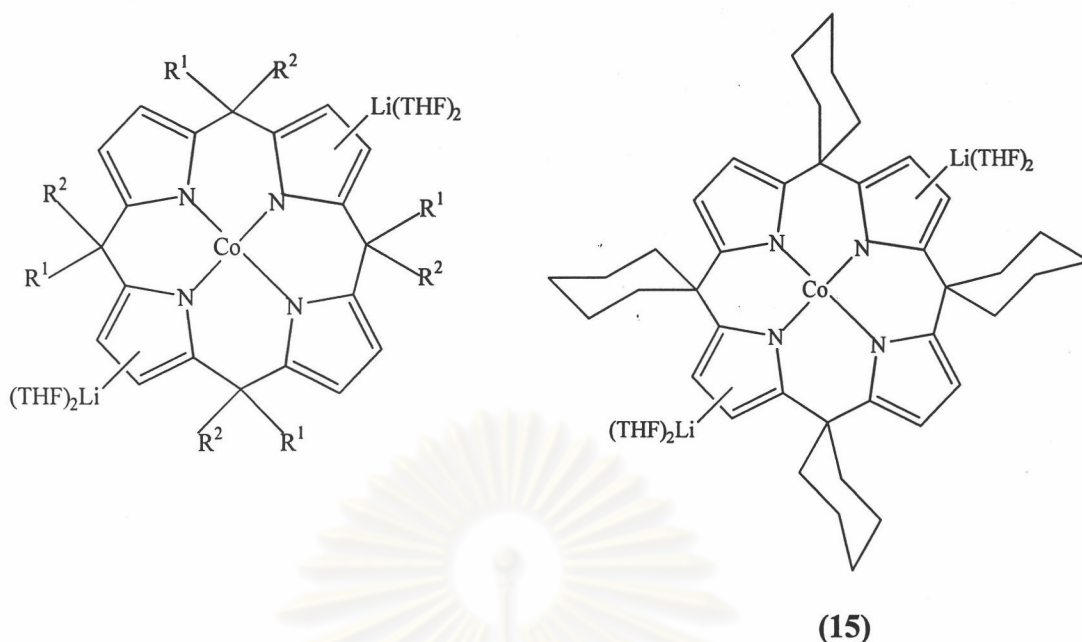
*Lithium of meso-tetramethyl-tetraphenyl-calix[4]pyrrole tetraanion*<sup>60</sup> (11): Dark brown crystal (65%),  $R_f$  0.51 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 131 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3043 (s), 2968 (m), 1574 (s), 1489 (s) and 1028 (m);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.28-7.02 (20H, m), 5.65-5.92 (8H, m), 3.75 (16H, m, THF) 1.89 (12H, bs) and 1.42 (16H, m, THF).

*Lithium of meso-octaphenyl-calix[4]pyrrole tetraanion*<sup>60</sup>(12): Bright purple solid (61%),  $R_f$  0.47 (hexane : ethyl acetate; 8 : 2), m.p. 215 °C, IR (KBr,  $\text{cm}^{-1}$ ): 3090 (w), 1588 (w), 1489 (w) and 1235 (m);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 6.71-7.28 (40H, m), 6.17 (4H, m), 5.97 (4H, m), 3.76 (16H, m, THF) and 1.84 (16H, m, THF).

### 2.4.3 Syntheses of cobalt calix[4]pyrrole

General procedure<sup>69</sup> : Dissolve 4.06 mmol of an interested polyanion followed by the addition of  $\text{CoCl}_2(\text{THF}_{1.5})$  3.38 mmol in toluene 120 mL. Then, a dark-black mixture was stirred at room temperature for 2 days. Removal of LiCl by filtration and standing of the filtrate overnight at  $-20^\circ\text{C}$  furnished desired calix[4]pyrrole complex.

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- (13)  $R^1, R^2 = \text{Me}$   
 (14)  $R^1, R^2 = \text{Et}$   
 (16)  $R^1 = \text{Me}, R^2 = 4\text{-methoxyphenyl}$   
 (17)  $R^1 = \text{Me}, R^2 = \text{C}_6\text{H}_5$   
 (18)  $R^1, R^2 = \text{C}_6\text{H}_5$

*Dilithium-tetrakis(tetrahydrofuran)- $\alpha, \beta, \gamma, \delta$ -octamethyl-calix[4]pyrrole cobalt(II) complex (13)*: Bright orange solid (49%),  $R_f$  0.48 (hexane : ethyl acetate; 8 : 2), m.p. 140°C, UV ( $\lambda_{\text{max}}$ , nm): 288, IR (KBr,  $\text{cm}^{-1}$ ): 2968 (s), 1705 (s), 1470 (m) and 1244 (m).

*Dilithium-tetrakis(tetrahydrofuran)- $\alpha, \beta, \gamma, \delta$ -octaethyl-calix[4]pyrrole cobalt(II) complex (14)*: Deep yellow solid (46%),  $R_f$  0.47 (hexane : ethyl acetate; 9 : 1), m.p. 151°C, UV ( $\lambda_{\text{max}}$ , nm): 289, IR (KBr,  $\text{cm}^{-1}$ ): 3109 (s), 2921 (s), 1644 (w), 1494 (w) and 1229 (w).

*Dilithium-tetrakis(tetrahydrofuran)- $\alpha, \beta, \gamma, \delta$ -tetraspirohexyl-calix[4]pyrrole cobalt(II) complex (15)*: Deep gray solid (79%),  $R_f$  0.84 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 230°C, UV ( $\lambda_{\text{max}}$ , nm): 287, IR (KBr,  $\text{cm}^{-1}$ ): 2931 (s), 1705 (w), 1635 (m) and 1447 (m).

*Dilithium-tetrakis(tetrahydrofuran)- $\alpha, \beta, \gamma, \delta$ -tetrakis(4-methoxyphenyl)-tetramethyl-calix[4]pyrrole cobalt(II) complex (16)*: Deep brown crystal (88%),

$R_f$  0.43 (hexane : ethyl acetate; 8 : 2), m.p. 116-117 °C, UV ( $\lambda_{\max}$ , nm): 289, IR (KBr,  $\text{cm}^{-1}$ ): 2959 (w), 1724 (s), 1672 (m), 1597 (s) and 1254 (s).

*Dilithium-tetrakis(tetrahydrofuran)- $\alpha, \beta, \gamma, \delta$ -tetramethyl-tetraphenyl-calix[4]pyrrole cobalt(II) complex (17)*: Deep brown crystal (89%),  $R_f$  0.43 (hexane : ethyl acetate; 9.5 : 0.5), m.p. 141 °C, UV ( $\lambda_{\max}$ , nm): 275, IR (KBr,  $\text{cm}^{-1}$ ): 2978 (w), 1644 (s), 1489 (m), 1442 (m) and 1216.

*Dilithium-tetrakis(tetrahydrofuran)- $\alpha, \beta, \gamma, \delta$ -octaphenyl-calix[4]pyrrole cobalt(II) complex (18)*: Deep gray solid (41%),  $R_f$  0.51 (hexane : ethyl acetate; 8 : 2), m.p. 225 °C, UV ( $\lambda_{\max}$ , nm): 278, IR (KBr,  $\text{cm}^{-1}$ ): 3370 (s), 1598 (m), 1490 (m) and 1403 (m).

The examination of each cobalt(II) calix[4]pyrrole with six various ligands by UV-Vis and IR revealed results in good agreement with those cited in previous literature.<sup>69</sup>

#### 2.4.4 Syntheses of authentic specimen

A general method for preparing authentic epoxide was performed following standard literature methods, with purification being conducted by column chromatography (silica gel, appropriate eluent). A solution of equimolar amounts of an interested alkene in 35 mL of methylene chloride at 0° C was reacted with 70% meta chloroperoxybenzoic acid (*m*-CPBA) 1.2 mol equiv relative to the olefin. Upon stirring the solution for 1 hour, the resulting mixture was monitored by TLC analysis prior to ethereal workup and excess peracid was destroyed with 5 mL of 10% sodium sulfite solution. The methylene chloride solution was then washed carefully with 50 mL of saturated sodium bicarbonate solution ( $\text{NaHCO}_3$ ), the organic layer was separated, and the aqueous layer was washed twice with methylene chloride, combined the organic layer, washed with brine, and dried over anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ).

*$\alpha$ -Methylstyrene oxide*<sup>17</sup> (19): Colorless liquid,  $R_f$  0.47 ( $\text{CH}_2\text{Cl}_2$ ); <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 7.23-7.42 (5H, m), 2.98 (1H, d,  $J = 5.4$  Hz), 2.82 (1H, d,  $J = 5.4$  Hz) and 1.73 (3H, s).

*trans*-2-Hexeneoxide-1-ol (**20**): Colorless liquid,  $R_f$  0.44 ( $\text{CH}_2\text{Cl}_2$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 3.52-3.82 (2H, dd,  $J = 2.2, 1.9$  Hz), 3.53 (1H, m), 3.48 (1H, d,  $J = 3.4$  Hz), 2.84 (1H, m), 1.26-1.51 (4H, m), and 0.86 (3H, t,  $J = 7.0$  Hz).

1,2-Epoxy-4-vinylcyclohexane<sup>11</sup> (**21**): Colorless liquid,  $R_f$  0.49 (hexane : ethyl acetate; 9 : 1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 5.68 (1H, m), 4.87-4.95 (2H, m), 3.11-3.16 (2H, m) and 1.21-2.40 (7H, m).

Mixtures of *cis*-, *trans*- of *R*-(+)-limonene oxide<sup>11</sup> (**22**): Colorless liquid,  $R_f$  0.63 (hexane : ethyl acetate; 9 : 1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 4.71 (1H, s), 4.65 (1H, s), 2.97-2.99 (1H, t,  $J = 9.2$  Hz), 1.50-2.15 (10H, m) and 1.24 (3H, m).

Mixtures of *cis*-, *trans*- of *S*-(-)-limonene oxide<sup>11</sup> (**23**): Colorless liquid,  $R_f$  0.67 (hexane : ethyl acetate; 9 : 1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 4.69 (1H, d,  $J = 1.4$  Hz), 4.64 (1H, d,  $J = 0.9$  Hz), 3.01 (1H, t,  $J = 9.6$  Hz), 1.59-2.04 (10H, m) and 1.34 (3H, m).

5,6-Epoxy- $\gamma$ -terpinene oxide (**24**): Colorless liquid,  $R_f$  0.51 (hexane : ethyl acetate; 9 : 1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 5.44 (1H, t,  $J = 1.4$  Hz), 3.09 (1H, t,  $J = 6.8$  Hz), 2.61 (4H, d,  $J = 3.9$  Hz), 2.25 (1H, m), 1.67 (3H, s) and 1.02 (6H, d,  $J = 5.6$  Hz).

## 2.5. General procedure for the epoxidation of alkenes

All reactions were carried out at room temperature. Alkene (5 mmol), 2-ethylbutyraldehyde (10 mmol) and cobalt calix[4]pyrrole complex (0.05 mmol) were well-mixed in toluene or acetonitrile in a round bottom flask, fitted with an oxygen balloon, resulting in a yellow solution. The mixture was stirred for 24 hr at room temperature. After the reaction was proceeded for a designed period of time, 1 mL of the mildly basic reaction was taken and extracted with diethyl ether. The combined extracts were washed with saturated solution of  $\text{NaHCO}_3$  and brine, respectively. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and analyzed by GC with the addition of an exact amount of a known concentration of an appropriate internal standard.



## 2.6 Effect of cobalt calix[4]pyrrole complex, $\text{CoCl}_2$ and $\text{Co}(\text{acac})_2$ on reactivity of cyclohexene epoxidation

Cobalt(II) calix[4]pyrrole complex **14**,  $\text{CoCl}_2$  and  $\text{Co}(\text{acac})_2$  were employed as a catalyst in cyclohexene epoxidation reaction using reaction conditions described in general procedure.

## 2.7 Study on the optimum conditions for the epoxidation of cyclohexene and other alkenes

### 2.7.1 Effect of ligands of cobalt calix[4]pyrrole complexes

According to the general epoxidation procedure, equimolar amount (0.05 mmol) of cobalt(II) calix[4]pyrrole complexes, **13-18** was used as a catalyst and cyclohexene (5 mmol) was used as a substrate in normal epoxidation reaction.

### 2.7.2 Effect of solvents

The epoxidation of alkene was carried out according to the general procedure, but various solvents, namely *N,N*-dimethylformamide (DMF),  $\text{CH}_2\text{Cl}_2$ , toluene, acetonitrile, tetrahydrofuran (THF) and 1,2-dichloroethane were utilized.

### 2.7.3 Effect of the amount of solvent

The epoxidation reaction of cyclohexene was carried out according to the general procedure, but the amount of acetonitrile was changed to 10, 15, 25, 30, 36, and 45 mL.

### 2.7.4 Effect of the oxidants

The epoxidation reaction was carried out as described earlier except for that hydrogenperoxide ( $\text{H}_2\text{O}_2$ ) 30% in water, *tert*-butylhydroperoxide (TBHP) 70% in water were used instead of 2-ethylbutyraldehyde/  $\text{O}_2$ .

### 2.7.5 Effect of the amount of 2-ethylbutyraldehyde on the epoxidation reaction of cyclohexene

The epoxidation reaction was carried out in the similar fashion to that previously described, but using cobalt(II) calix[4]pyrrole complex **16** as a catalyst and different amount of 2-ethylbutyraldehyde was varied (0, 10, 15, 20 and 30 mmol).

## 2.8 Applications of developed epoxidation reaction for other alkenes

Cobalt(II) calix[4]pyrrole complex **16** was employed as a catalyst in the epoxidation of other alkenes, namely cyclohexene, 1-dodecene,  $\alpha$ -methylstyrene, styrene, *trans*-2-hexen-1-ol, 4-vinylcyclohexene and monoterpenes such as  $\alpha$ -terpinene,  $\gamma$ -terpinene. In addition, *R*-(+)-limonene, and *S*-(-)-limonene were selected for the study on the regioselectivity of this developed epoxidation reaction.

### 2.8.1 Regioselectivity study of 4-vinylcyclohexene

The epoxidation of 4-vinylcyclohexene was carried out in the same way to the general procedure and 2-ethylbutyraldehyde/O<sub>2</sub> and *m*-CPBA was used as an oxidizing agent.

### 2.9 Effect of the amount of 2-ethylbutyraldehyde on the epoxidation reaction of alkenes

The epoxidation reaction was performed in the similar manner to the general procedure but exercising 1-dodecene,  $\alpha$ -methyl styrene and styrene as substrate and toluene as solvent instead of cyclohexene, respectively, In addition, the amount of oxidant was varied in the range of 0, 10, 15 and 20 mmol.

### 2.10 Comparative kinetic study of the epoxidation of cyclohexene and 1-dodecene

Following to the general epoxidation procedure, the epoxidation of cyclohexene and 1-dodecene as substrate utilizing cobalt calix[4]pyrrole complex **16** as a catalyst was carried out. At different reaction time proceeded (1, 3, 5, 7, 10, 13, 18, 21, 24 and 36 hrs), an aliquot from the reaction mixture was taken, worked up and analyzed by GC.

### 2.11 Competitive studies on the oxidation of alkenes and saturated hydrocarbon

Following the general epoxidation procedure, cyclohexene was used as a substrate in the competition reaction between the epoxidation of cyclohexene and other alkenes or that between the epoxidation of cyclohexene and the oxidation of saturated hydrocarbon.

### 2.12 Effect of the radical inhibitor in the epoxidation of alkene

The epoxidation was performed in similar manner to general procedure while pyridine 0.5 mL was added to prove the mechanistic study of the epoxidation of alkene.



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