CHAPTER III

EXPERIMENTAL

3.1 Materials

2,4-Dimethylphenol (99%), 4-t-butylphenol, 4-ethylphenol, sodium sulfate anhydrous, propylamine, cyclohexylamine, and methylamine (w/w 40 %) were purchased from Fluka Chemicals (Buchs, Switzerland). Calcium chloride, barium chloride two hydrates, cupric chloride two hydrates and *p*-cresol were purchased from E. Merck (Germany). Phenol, picric acid, chloroform, methanol, sodium hydroxide, and potassium hydroxide were bought from Ajax Chemicals (Australia). Dichloromethane, 1,4 dioxane, and isopropanol were purchased from Lab-scan (Thailand). Paraformaldehyde was purchased from Sigma (USA.). Diethylether was bought from Scharlau (Barcelona, Spain). All chemicals were used without purification.

3.2 Instruments

3.2.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra were obtained from a Bruker Equinox55 Spectrometer with 32 scans at a resolution of 4 cm^{-1} in the frequency range of 4,000-400 cm^{-1}. Neat technique on ZnSe cell and sample powder pressed with KBr into a pellet were used.

3.2.2 Vortex Mixer

Vigorous shaking of the mixture between organic and aqueous solution was performed using Vortex mixer; GENIE-2 Scientific Industries.

3.2.3 Ultraviolet-Visible Spectrophotometer (UV-Vis)

Picrate metal ion concentration in aqueous phase was determined by Ultraviolet-Visible Spectrophotometry, Perkin-Elmer Lamda-16 Spectrometer.

3.2.4 Nuclear Magnetic Resonance Spectrometer (NMR)

Fourier transform ^{1}H-NMR spectrometer (ACF 200 MHz of Bruker Switzerland) was used to determine the structures of the prepared compounds.

3.2.5 Mass Spectrometer (MS)

The cluster formations of benzoxazine derivatives and metals were studied by Electrospray Mass Spectrometer, PE SCIEX API III Biomolecular Mass Analyzer.

3.2.6 X-ray Powder Diffraction (XRD)

The structures of the compounds and metal complexation were studied using XRD, Rigaku RINT2000 wide-angle goniometer. The samples were observed at 2θ between 2-60° with a scan speed of 5°/min. CuKα was used as an X-ray source and operated at 40 kV and 30 mA with a Ni filter.

3.3 Methodology

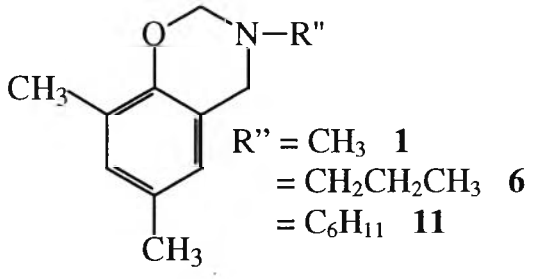
3.3.1 Preparation of benzoxazine monomer derivatives; (3,4-dihydro-3,6,8-trimethyl-2H-1,3-benzoxazine **1**, 3,4-dihydro-3,6-dimethyl-2H-1,3-benzoxazine **2**, 3,4-dihydro-6-ethyl-3-methyl-2H-1,3-benzoxazine **3**, 3,4-dihydro-6-*t*-butyl-3-methyl-2H-1,3-benzoxazine **4**, 3,4-dihydro-3-methyl-2H-1,3-benzoxazine **5**, 3,4-dihydro-6,8-dimethyl-3-propyl-2H-1,3-benzoxazine **6**, 3,4-dihydro-6-methyl-3-propyl-2H-1,3-benzoxazine **7**, 3,4-dihydro-6-ethyl-3-propyl-2H-1,3-benzoxazine **8**, 3,4-dihydro-6-*t*-butyl-3-propyl-2H-1,3-benzoxazine **9**, 3,4-dihydro-3-propyl-2H-1,3-benzoxazine **10**, 3,4-dihydro-6,8-dimethyl-3-cyclohexyl-2H-1,3-benzoxazine **11**, 3,4-dihydro-6-methyl-3-cyclohexyl-2H-1,3-benzoxazine **12**, 3,4-dihydro-6-ethyl-3-cyclohexyl-2H-1,3-benzoxazine **13**, 3,4-dihydro-6-*t*-butyl-3-cyclohexyl-2H-1,3-benzoxazine **14**, 3,4-dihydro-3-cyclohexyl-2H-1,3-benzoxazine **15**)

Benzoxazine monomers **1-15** were synthesized (Scheme 3.1) as referred to Ishida *et al.* The structures of the obtained monomers were studied by ^{1}H-NMR, FTIR, and MS.

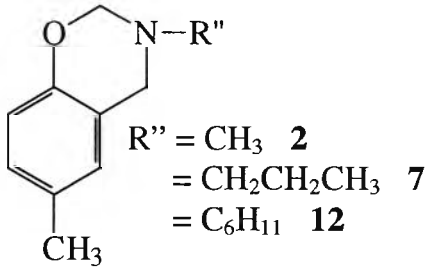
3.3.2 Preparation of the open ring benzoxazine monomers (abbreviated as benzoxazine dimers); (N,N-Bis (3,5-dimethyl-2-hydroxybenzyl) methylamine **16**, N,N-Bis (3,5-dimethyl-2-hydroxybenzyl) propylamine **17**, N,N-Bis (3,5-dimethyl-2-hydroxybenzyl) cyclohexylamine **18**, N,N-Bis (5-ethyl-2-hydroxybenzyl) methylamine **19**, N,N-Bis (5-ethyl-2-hydroxybenzyl) propylamine **20**, N,N-Bis (5-ethyl-2-hydroxybenzyl) cyclohexylamine **21**, N,N-Bis (5-methyl-2-hydroxybenzyl) methylamine **22**, N,N-Bis (5-methyl-2-hydroxybenzyl) propylamine **23**, N,N-Bis (5-methyl-2-hydroxybenzyl) cyclohexylamine **24**)

Benzoxazine monomers (**1-3**, **6-8**, and **11-13**) were reacted with the phenol derivatives (Scheme 3.2) to prepare the open ring of benzoxazine monomers to form dimers as referred to Laobuthee *et al.*

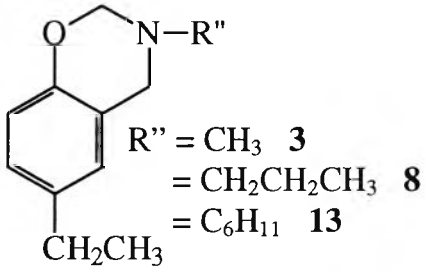
Scheme 3.1 Chemical Structures of Benzoxazine Monomers **1-15**



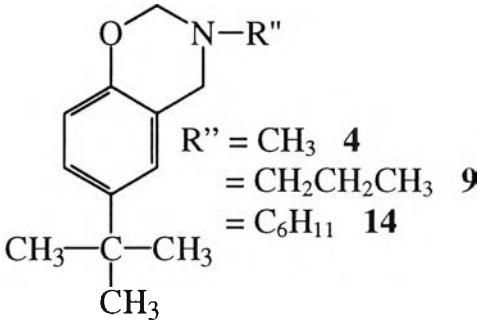
R" = CH_3 **1**
= $CH_2CH_2CH_3$ **6**
= C_6H_{11} **11**



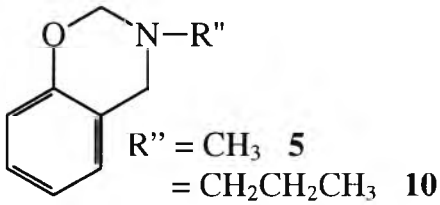
R" = CH_3 **2**
= $CH_2CH_2CH_3$ **7**
= C_6H_{11} **12**



R" = CH_3 **3**
= $CH_2CH_2CH_3$ **8**
= C_6H_{11} **13**

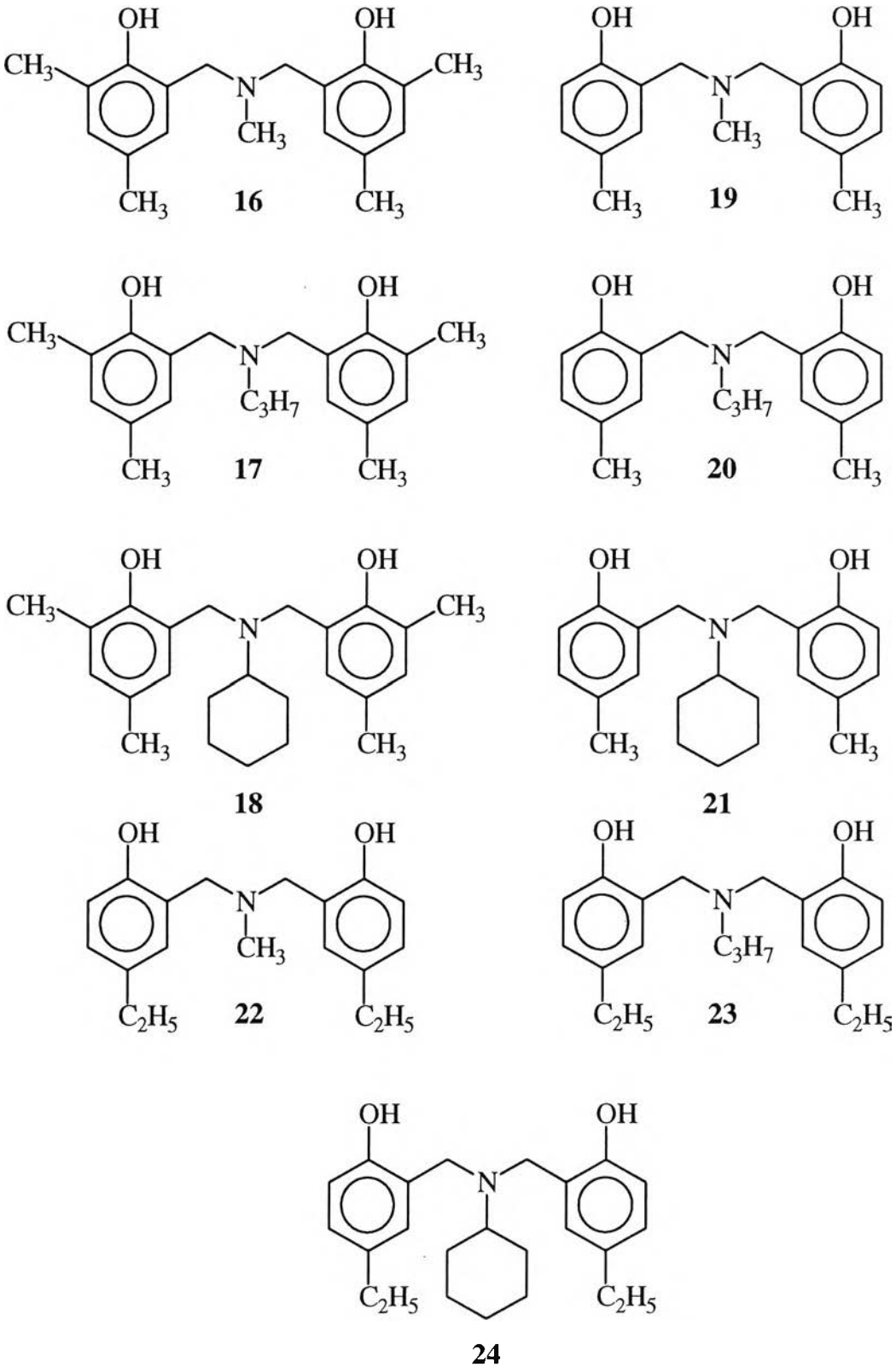


R" = CH_3 **4**
= $CH_2CH_2CH_3$ **9**
= C_6H_{11} **14**



R" = CH_3 **5**
= $CH_2CH_2CH_3$ **10**
= C_6H_{11} **15**

Scheme 3.2 Chemical structures of the open ring benzoxazine dimers **16-24**



3.3.3 Ion Interaction Properties

3.3.3.1 *Preparation of Metal Picrate Solution*

Sodium and potassium picrates were prepared by recrystallization of picric acid with NaOH and KOH, respectively, in methanol. The metal picrate was dissolved in aqueous solution at concentration $7x10^{-5}$ M and used as a metal picrate solution.

3.3.3.2 *Ion Extraction Studies*

Five mL. of picrate (concentration $7x10^{-5}$ M) and benzoxazine solution (concentration $7x10^{-5}$, $7x10^{-4}$, $3.5x10^{-3}$, and $7x10^{-3}$ M) were taken and mixed vigorously for 1 min. The mixture was left at room temperature till the aqueous and organic phases were completely separated. The decrease of picrate salt concentration in aqueous phase was determined by UV-Vis spectrophotometer at 354 nm.

3.3.4 Preparation of Dimer-Metal Complex

In order to study the complexation of benzoxazine dimer and metal, dimers **16-24** were prepared with metal in 2 types; i.e., by both blending (hereinafter abbreviated as benzoxazine dimer-metal salt-blend) and liquid-liquid extraction (hereinafter, abbreviated as benzoxazine dimer-metal salt-extract) as follows.

Benzoxazine dimer-metal salt-blends were prepared by grinding benzoxazine dimer **16-24** with metal salt. Benzoxazine dimer-metal ion-extracts were obtained from the liquid-liquid extraction. Each metal salt, i.e., $BaCl_2$, $CaCl_2$, and $CuCl_2$ was dissolved in deionized water to be $3.2x10^{-1}$ M. Each benzoxazine dimers **16-24** was dissolved in methylene chloride for $7x10^{-4}$ M. Five mL. of the salt and benzoxazine solution was mixed and shaken vigorously for a minute. The mixture was left at room temperature till

the aqueous and organic phases were separated completely. The aqueous solution was analyzed quantitatively and qualitatively for metal ion by UV/Vis. The structures of benzoxazine dimer-metal salt-blend and benzoxazine dimer-metal salt-extract were characterized by XRD, MS and FTIR.