

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Chemical reagents were purchased from the following companies. Paraformaldehyde and fumed silica (particle diameter = 0.007 μm) were from Sigma (U.S.A). Diethyl ether was purchased from Schalau (Barcelona, Spain). Cyclohexylamine, formic acid, sodium formate anhydrous, 3-amino-propyltriethoxysilane and sodium sulfate anhydrous were purchased from Fluka Chemicals (Buchs, Switzerland). 1,4-dioxane and 2-propanol were received from Lab-Scan (Thailand). *p*-Cresol was purchased from E. Merck (Germany). Methanol, xylene, ethanol, and lead (II) chloride were obtained from BDH Laboratories Pools (England). Manganese (II) chloride was from Carlo ERBA (France). Chloroform, potassium hydrogen phthalate, potassium dihydrogen phthalate, zinc (II) chloride, cadmium (II) chloride, ammonium chloride and ammonium hydroxide were obtained from Ajax Chemicals (Australia). Acetic acid, sodium acetate and tetrahydrofuran were purchased from J.T Baker (U.S.A). All reagents were used as received and all solvents were stocked over 0.4 nm molecular sieve before use.

3.2 Instruments and Equipment

3.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

Fourier transform infrared (FTIR) spectra were taken at a resolution 4 cm^{-1} in the frequency range of 4000-400 cm^{-1} . Two techniques were used on ZnSe plate and KBr pellet.

3.2.2 Proton Nuclear Magnetic Resonance Spectrometer ($^1\text{H-NMR}$) and NOESY $^1\text{H-NMR}$

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) and correlation spectroscopy were obtained from Fourier transform $^1\text{H-NMR}$ and NOESY $^1\text{H-NMR}$ (Varian INITY plus 600). Samples were dissolved in deuterated chloroform with tetramethylsilane used as an internal standard.

3.2.3 Elemental Analysis

The percent elements were obtained from (Yanako CHN Corder MT-3, MT-5) with the combustion temperature 975°C , under He gas at flow rate 20 mL/min.

3.2.4 Vortex Mixer

Vigorous shaking of the organic-aqueous mixture and treated silica-aqueous mixture were performed using Vortex mixer (GENIE-2, Scientific Industries).

3.2.5 Atomic Absorption Spectrophotometer

Metal ion concentration in aqueous phase of both experiments (ion extraction ability of **2** and **3**) was determined using an atomic absorption spectrometer (Varian Spectra AA-300). The hollow cathode lamps used were; manganese cathode lamp for manganese, lead cathode lamp for lead, cadmium cathode lamp for cadmium, and zinc cathode lamp for zinc. Ion solution standard was prepared according to the analytical method of Varian machine.

3.2.6 pH meter

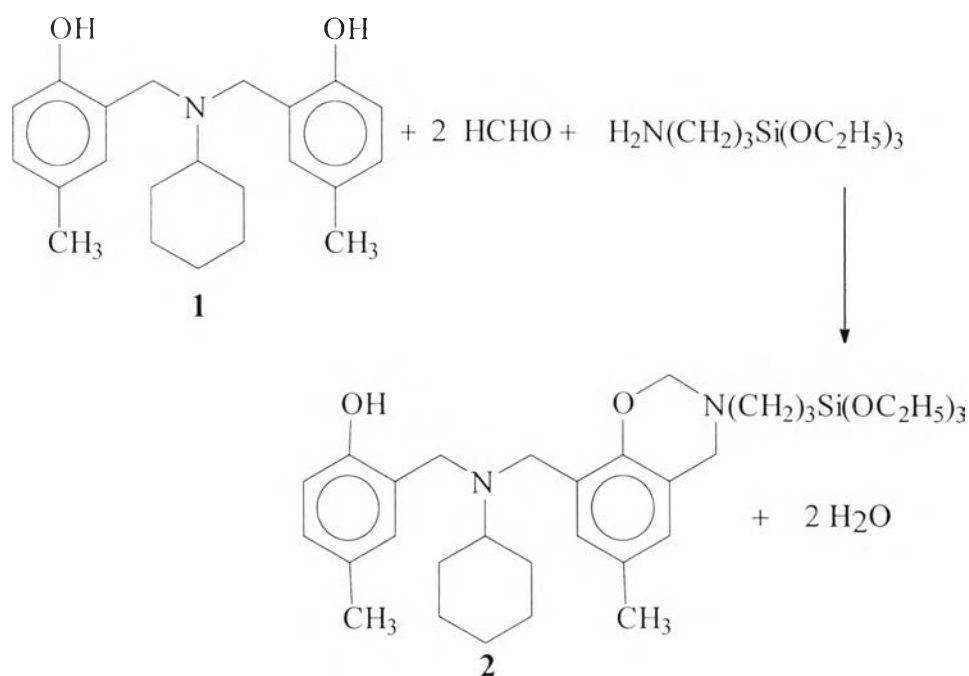
Each pH value of buffer solution was measured using pH meter ORION Model 420 A.

3.3 Methodology

3.3.1 Preparation of Silylbenzoxazine; 3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylamino-methyl]-2H-1,3-benzoxazine **2**

The procedure in preparation is shown in Scheme 3.1.

Scheme 3.1 Preparation of 3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylamino-methyl]-2H-1,3-benzoxazine **2**



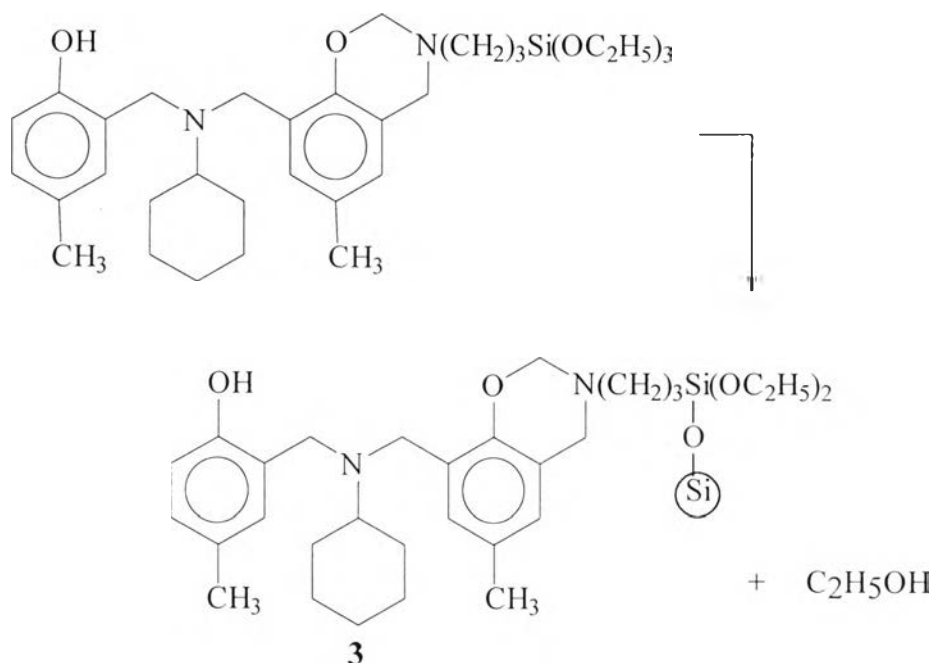
Compound **1** was used as a precursor to prepare 3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylaminomethyl]-2H-1,3-benzoxazine **2**. Paraformaldehyde 0.60 g (20 mmol) was dissolved in 5 mL CHCl₃, followed by adding 3-aminopropyltriethoxysilane 2.22 g (10 mmol) which was diluted by 3 mL CHCl₃. The mixture was heated and stirred for 10 minutes, followed by

adding compound **1** (3.39 g), which was dissolved in 20 mL CHCl₃. The reaction was refluxed continuously for 6 h and confirmed by thin layer chromatography using the mobile phase CHCl₃: CH₃OH mixture (19:1, v/v). After drying by sodium sulfate anhydrous, the solvent was evaporated. The crude product was purified by a silica gel column using CHCl₃: CH₃OH mixture (19:1; v/v) as a mobile phase. The product was collected. After the solvent was evaporated to obtain clear yellowish liquid, the product was characterized by FTIR, ¹H-NMR and NOESY-NMR.

3.3.2 Preparation of Silica-Silylbenzoxazine: 3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylamino-methyl]-2H-1,3-benzoxazine **3**

3,4-Dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylaminomethyl]-2H-1,3-benzoxazine **2**, 4.5 g (7.7 mmol) was mixed with fumed silica 1g in 5 mL of xylene. The mixture was refluxed in oil bath under N₂ for 24 h to get yellowish silica. The obtained product was washed thoroughly by xylene to eliminate the excess **2** on silica surface. The product was washed with ethanol to remove xylene, followed by THF to exclude the physisorbed silane on silica surface. The obtained compound was washed by ether and dried under pressure at 40°C for 2 h to get compound **3** (Scheme 3.2). The obtained product was characterized by FTIR and EA.

Scheme 3.2 Preparation of silica-3,4-dihydro-3-triethoxysilyl-n-propyl-6-methyl-8-[(2'-hydroxy-5'-methylbenzyl)cyclohexylamino methyl]-2H-1,3-benzoxazine **3**



3.4 Ion Extraction Studies

Ion entrapment property was studied by using Pedersen's technique (Pedersen, 1968), for **2** and **3**. Chloride salts of zinc, cadmium, manganese, and lead were used as metal ions. 1×10^{-4} M metal ion was dissolved in various buffer solutions. The buffer solutions were pH 3.4 (formic acid / sodium formate buffer), pH 4.6 and 5.1 (acetic acid / sodium acetate buffer), pH 7.01 and 8.1 (KH_2PO_4 / K_2HPO_4 buffer), pH 9.0, 10.0, and 10.9 (ammonium hydroxide / ammonium chloride buffer). Compound **2** was dissolved in chloroform for 0.01 M, 0.1 M, 0.2 M and 0.3 M.

Ion extraction was studied by the following procedures. Twelve mL of aqueous ion metal salt solution and 5 mL of **2** solution was vigorously shaken for 1 minute at room temperature and allowed phase separation completely.

The aqueous phase was taken to determine the metal ion concentration by atomic absorption spectrophotometer.

The ion extraction ability of **3** was as follows. Twelve mL of buffer ion solution was mixed with 0.05 g of silane-treated silica monooxazine dimer, after shaking 1 minute at room temperature. The mixture was allowed for phase separation at room temperature. The aqueous phase was taken to determine the ion concentration by atomic absorption spectrophotometer.