CHAPTER III
EXPERIMENTAL

3.1 Materials

2,4-Dimethylphenol was purchased from Merck Millipore. Formaldehyde solution was purchased from RCI Labscan, Thailand. Propargylamine, terephthaloyl chloride and sodium hydroxide were purchased from Sigma Aldrich. Deuterated chloroform ($CDCl_3$) and deuterium oxide (D_2O) were purchased from Sigma Aldrich. Sodium hydroxide and sodium sulphate anhydrous were purchased from Ajax Finechem. Dichloromethane, isopropanol, 1,4-dioxane and acetone were purchased from RCI Labscan,, Thailand.

3.2 Instruments

Chemical structure Structure was analyzed by Bruker ultrashield plus 500 MHz Proton nuclear magnetic resonance spectra (^{1}H-NMR). Fourier transform infrared spectra (FTIR) was recorded by Nicolet Nexus 670 FT-IR spectrometer. Mass spectroscopy was analyzed by Bruker a micrOTOF electrospray ionization mass spectrome-ter (ESI-MS).

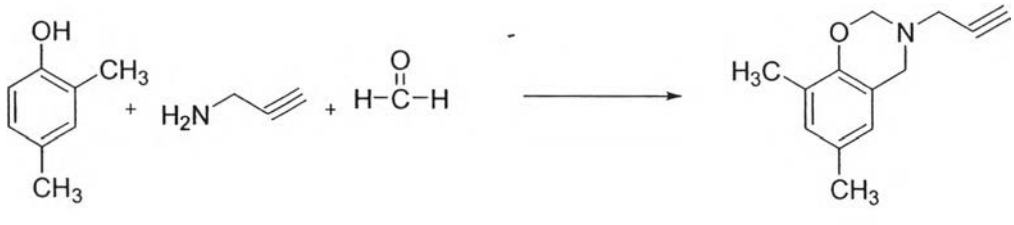
3.3 Methodology

3.3.1 Preparation of Benzoxazine

3.3.1.1 Preparation of Benzoxazine Monomer

Propargylamine (0.54 mL, 0.01 mol, 1.0 eq.) and formaldehyde solution 30-40% w/w (3.06 mL, 0.04 mol, 4.0 eq.) were dissolved in 20 mL of dioxane and stirred while being chilled in an ice bath for 30 min. 2,4-Dimethylphenol (1.20 mL, 0.01 mol, 1.0 eq.) was added into the reaction mixture and stirred for further 12 hr. under reflux conditions (Scheme 3.1). The reaction was followed by thin layer chromatography (TLC) and FT-IR spectroscopy (FT-IR). After cooling the solvent was removed under reduced pressure to obtain the crude product. This highly viscous liquid was solubilized in 20 mL of diethylether, washed three times with 0.5 M sodium hydroxide (NaOH), four times with distillated water and finally the organic layer was dried over sodium sulfate anhydrous. The solvent was removed to obtain the **1**.

Scheme 3.1

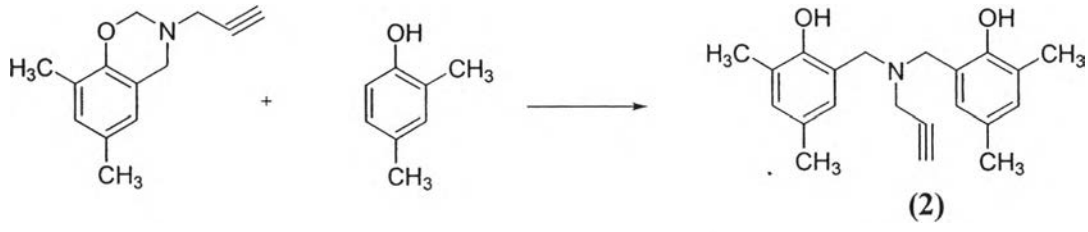


(1)

3.3.1.2 Preparation of Benzoxazine Dimer

1 (2.01 g, 0.01 mol, 1.0 eq.) and 2,4-dimethylphenol (1.20 mL, 0.01 mol, 1.0 eq.) was solubilized in 20 mL of dioxane and refluxed for 20 hr. (Scheme 3.2). The reaction was followed by TLC and ^{1}H-NMR. The solvent was removed under reduced pressure and the crude product was crystallized in a 1:1 isopropanol/chloroform mixture to obtain a colorless crystalline product , **2**.

Scheme 3.2



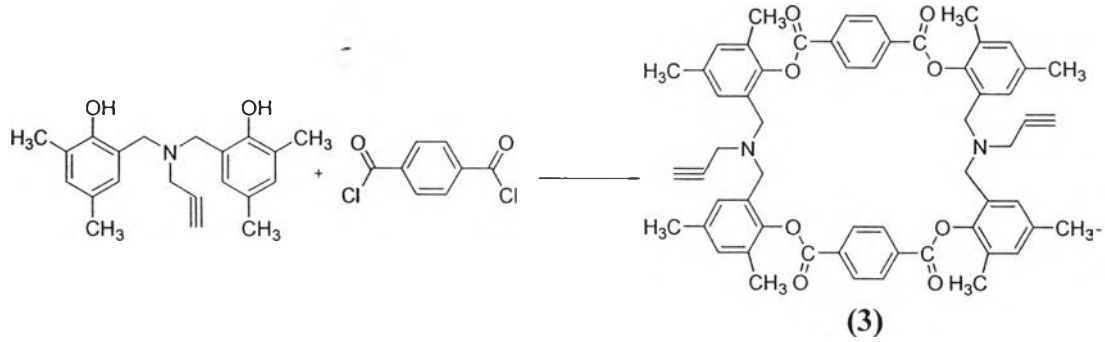
(2)

3.3.2. Preparation of Macrocyclic Benzoxazine

3.3.2.1 Interfacial Polycondensation

The macrocyclic benzoxazine was prepared by interfacial polycondensation. A 0.15 M solution of **2** in water in the presence of NaOH, and a 0.15 M solution of terephthaloyl dichloride in dichloromethane in separate syringes were added dropwisely into the mixture of dichloromethane (35 mL), water (10 mL) and hexadecyltrimethylammonium bromide, and stirred at room temperature for 7 days. The solution obtained was washed with distilled water several times. The solvent was removed under reduced pressure to obtain the crude product. The product obtained was further purified by column chromatography.

Scheme 3.3



(3)

3.3.3. Preparation of 1,4-diazidobutane

Dibromobutane (0.6 mL, 0.007 mol) and sodium azide (0.81g, 0.013 mol) were dissolved in 10 mL of DMF and stirred at 80 °C for 24 hr. After cooled to room temperature, 5 mL of water was added to the reaction. The solution obtained was extracted with 30 mL of diethyl ether. The organic layer was washed with 4%

NaCl solution for four times and dried with sodium sulfate anhydrous. After filtration and solvent evaporation, 1,4-diazidobutane was obtained as a colourless liquid.

Scheme 3.4

3.3.4. Preparation of Molecular Necklace

3 (0.070 mg, 0.07mol) was dissolved in DMF (5 ml) containing CuI/pyridine complex under nitrogen atmosphere at room temperature for a half hour. 1,4-Diazidobutane(9.8 mg,0.007 mol) was added into solution mixture and stirred further for 24 hr. The solution obtained was poured into water for purification. The precipitates were washed by distilled water several times

3.4 Characterization

Compound **(1)** – **(3)** were confirmed by a Bruker Fourier transform infrared (FTIR) spectrometer in the range 4000 - 650 cm^{-1} at a resolution of 2 cm^{-1}, a Bruker Avance nuclear magnetic resonance (NMR) spectrometer (Germany) operating at Larmor frequencies of 500.13 MHz which used $CDCl_3$ as a solvent, and a Bruker Daltonic Micro-TOF mass spectrometer (ESI-TOF) in positive ion mode.