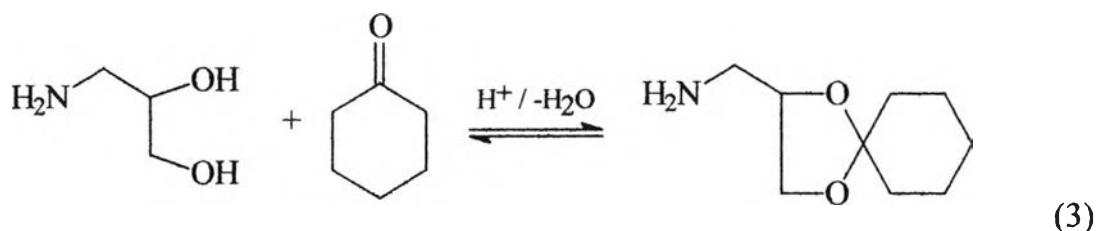


## CHAPTER IV

### RESULTS AND DISCUSSION

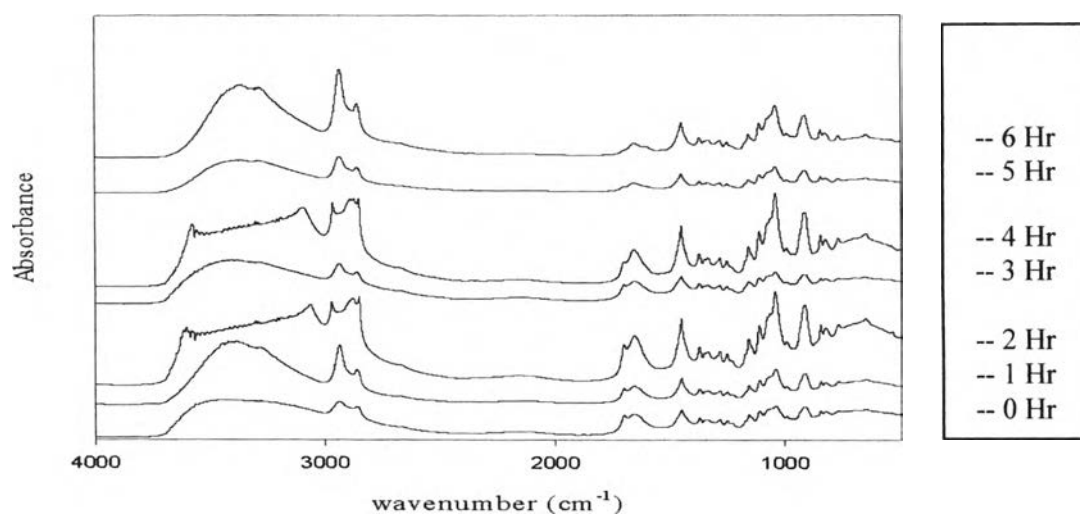
#### 4.1 Protecting Hydroxyl Groups of 3-Amino-1,2-propanediol

In this study, ketal C3 product was synthesized directly from a mixture of 3-amino-1,2-propanediol and cyclohexanone in the presence of hydrochloric acid as a catalyst. Since water generated during the equilibrium reaction hydrolyzed the product, it must be removed out from the system to push the reaction forward, as illustrated in equation 3.

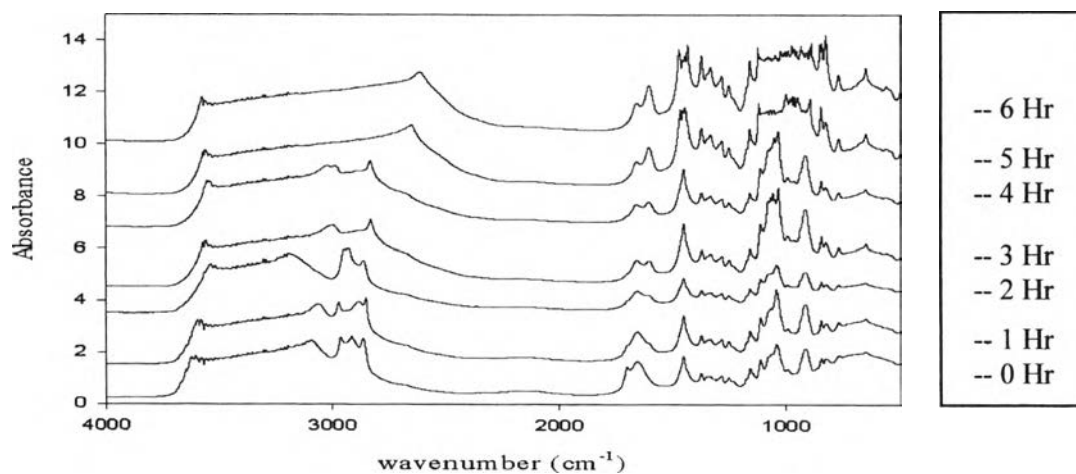


##### 4.1.1 Effect of Reaction Time and Temperature on the Ketal C3 Synthesis

The mixture of 3-amino-1,2-propanediol and cyclohexanone in the presence of hydrochloric acid was heated to 100°C and 110°C for a variation of time, 0-6 hours. Sampling of the mixture was done every hour to follow the reaction, using FTIR.



**Figure 4.1** FTIR spectra of crude product of ketal C3 at 100°C from 0-6 hours.



**Figure 4.2** FTIR spectra of crude product of ketal C3 at 110°C from 0-6 hours.

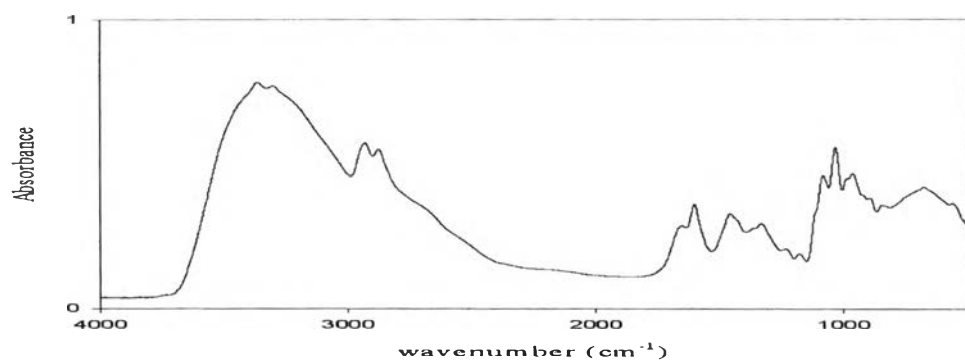
As shown in figures 4.1 and 4.2, as the reaction went on the peak at 1700  $\text{cm}^{-1}$  representing C=O in cyclohexanone was decreased whereas the peaks at 1040  $\text{cm}^{-1}$  and 910  $\text{cm}^{-1}$  representing C-O-C in ketal structure were increased. As compared to the results from both temperatures, the suitable

condition for ketal C3 synthesis is at the temperature of 110°C at 3 hours reaction time.

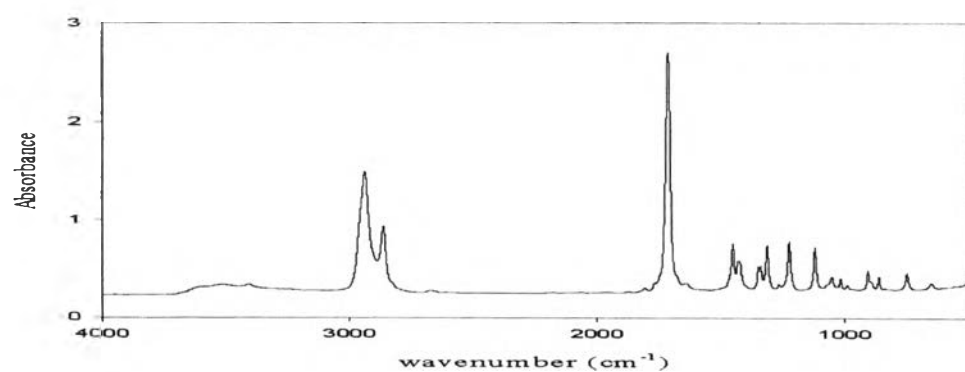
The product was separated by liquid extraction using diethyl ether. The ether layer containing the desired product was evaporated out to obtain the final product.

The FTIR spectrum of ketal C3 product is shown in figure 4.3. It shows the band at 3376-3287  $\text{cm}^{-1}$  corresponding to the  $-\text{NH}_2$  stretching, whereas 2935-2859  $\text{cm}^{-1}$  refers to the C-H stretching. The peaks at 1043 and 911  $\text{cm}^{-1}$  are assigned to C-O-C in ketal structure.

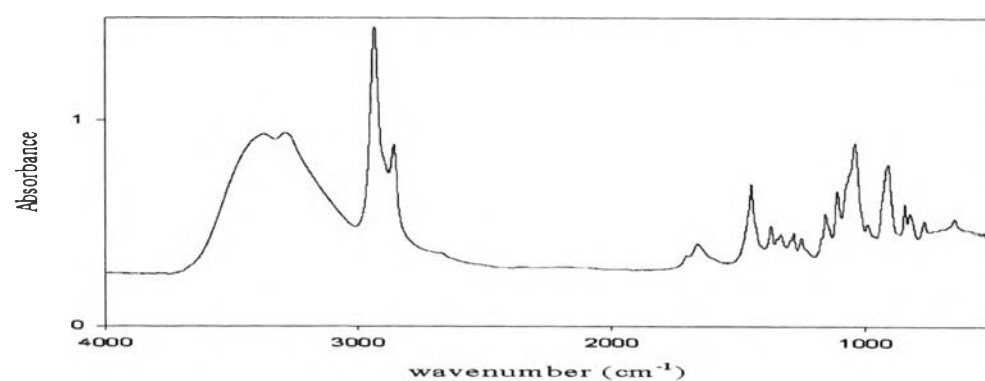
The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of ketal C3 are shown in figures 4.4 and 4.5, respectively.



(a)



(b)



(c)

**Figure 4.3** FTIR spectra of (a) 3-amino-1,2-propanediol, (b) cyclohexanone, and (c) ketal C3 product.

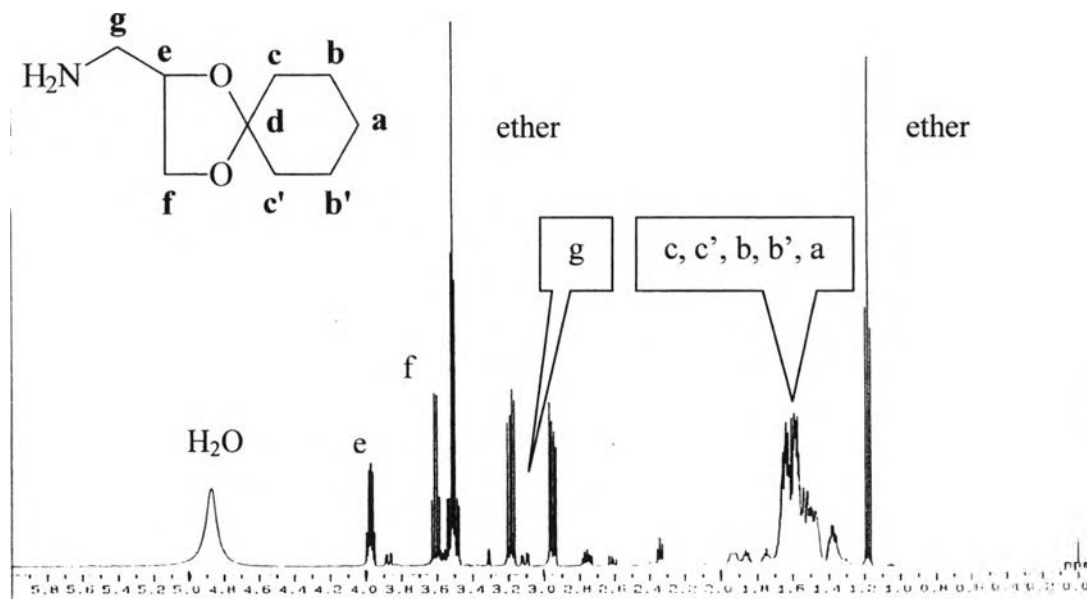


Figure 4.4  $^1\text{H-NMR}$  of ketal C3.

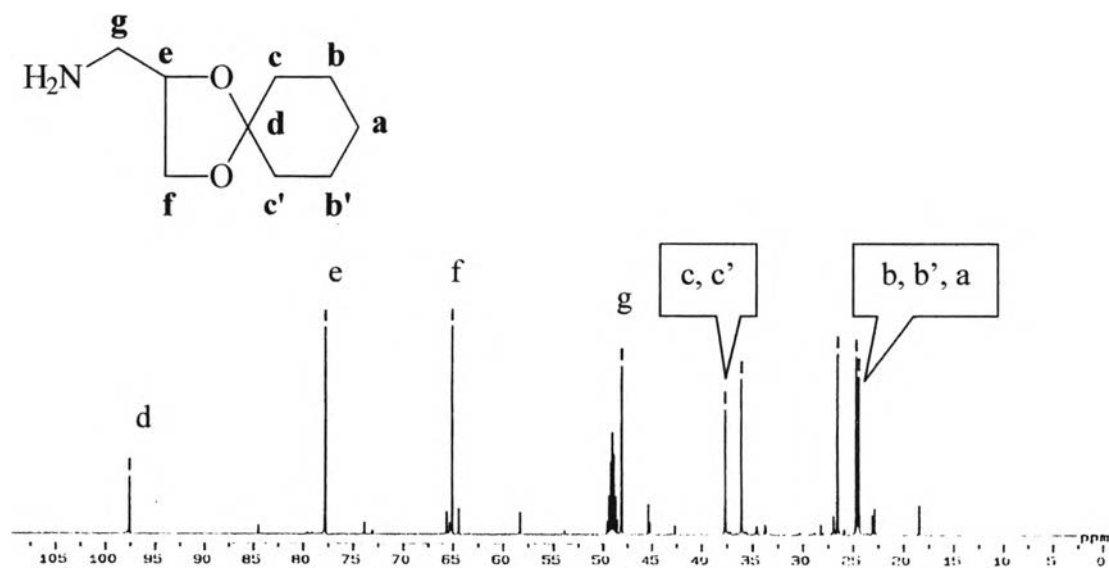
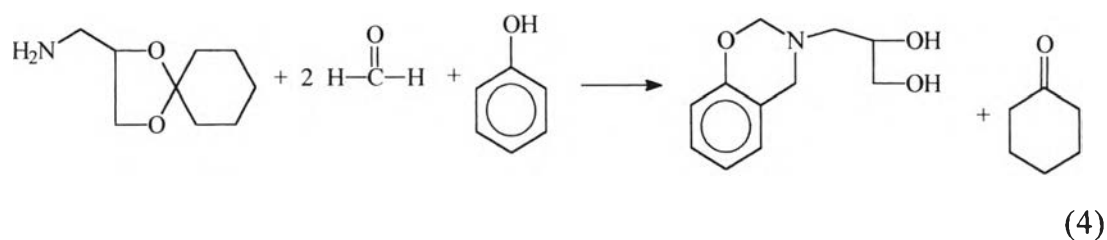


Figure 4.5  $^{13}\text{C-NMR}$  of ketal C3.

## 4.2 Synthesis of Benzoxazine from Ketal C3.

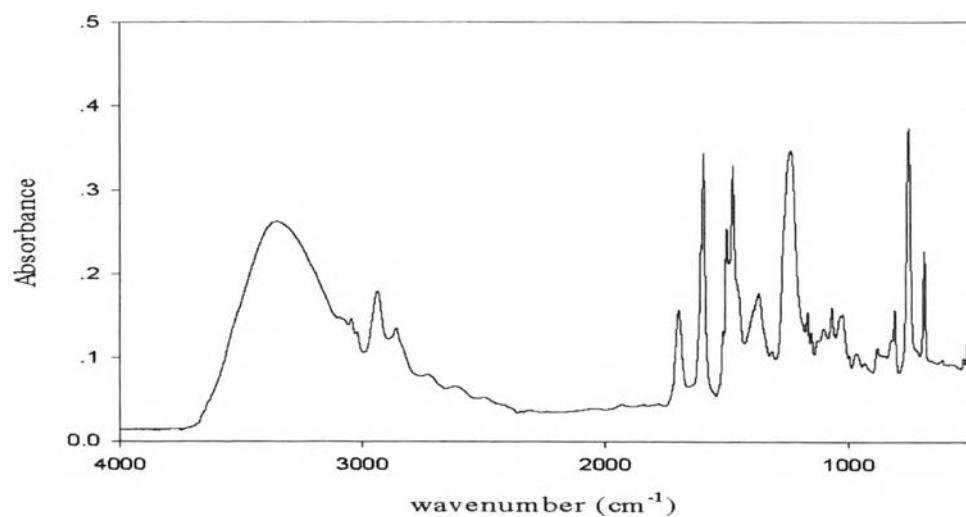
In this study, benzoxazine C3 product was synthesized directly from a mixture of ketal C3, formaldehyde and phenol, as illustrated in equation (4).



This reaction gave cyclohexanone, protecting agent, as a by-product, due to phenol acting as acid catalyst in the decomposition of ketal structure. In addition, the decomposition of ketal occurs easier when the reaction was heated to form benzoxazine.

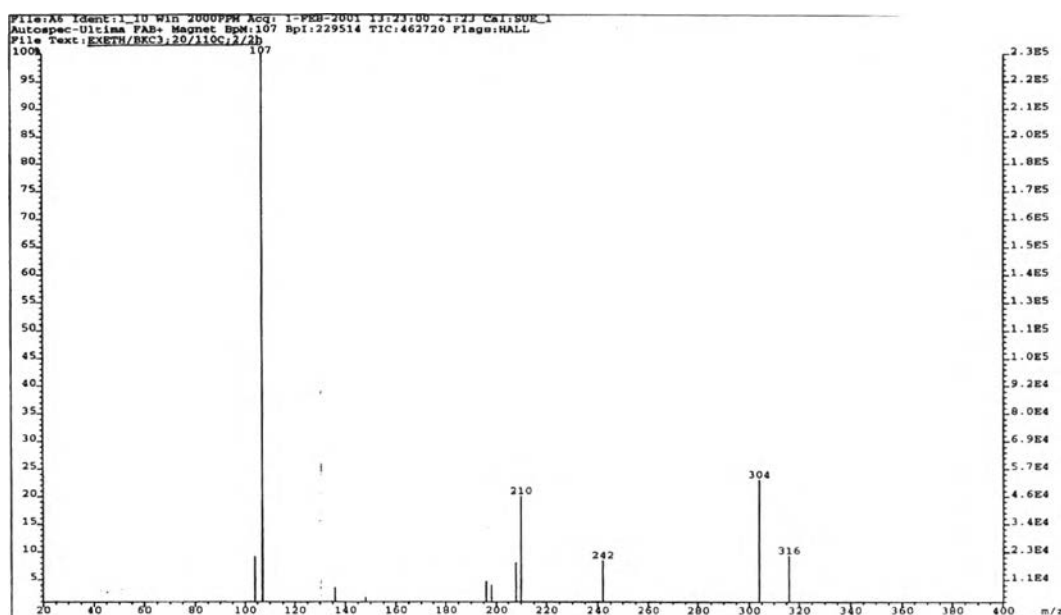
The product was separated by liquid extraction using ether and 1N NaOH solution. Further separation was done by neutralizing the NaOH layer and then ether was again used in liquid extraction. The ether layer was separated and evaporated out to obtain the final product.

Figure 4.6 shows FTIR spectrum of the as-synthesized benzoxazine C3. The peak at  $1503\text{ cm}^{-1}$  represents the di-substituted benzene ring-mode in the oxazine structure, while the peak at  $1475\text{ cm}^{-1}$  represents the di-substituted benzene ring-mode in the ortho-substituted (methylene-amine-methylene bridge) phenolic structure formed by the reaction between the oxazine ring and the free ortho position of phenol. Moreover, the bands at  $755$  and  $693\text{ cm}^{-1}$  represent the 1,2-disubstituted benzene ring in the benzoxazine structures.



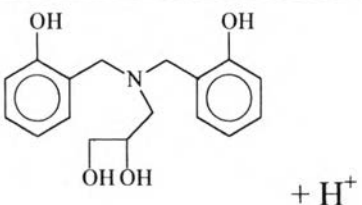
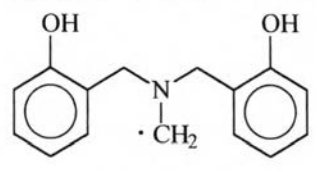
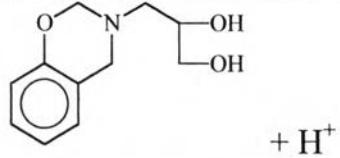
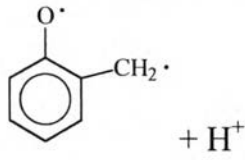
**Figure 4.6** FTIR spectrum of benzoxazine C3.

Figure 4.7 illustrates the mass spectrum of benzoxazine C3. The fragmentation of the product is shown in table 4.1.



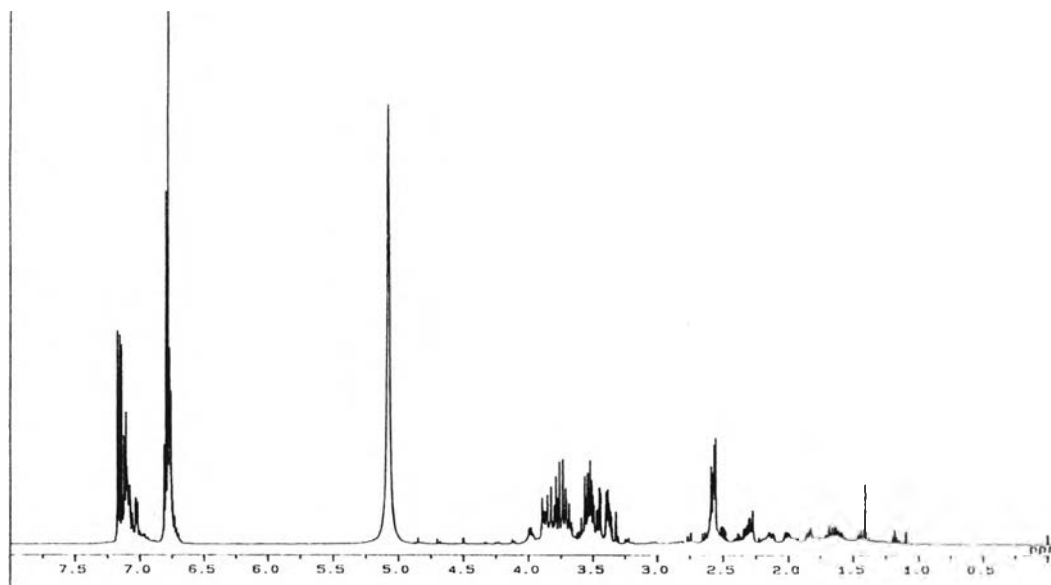
**Figure 4.7** The mass spectrum of benzoxazine C3.

**Table 4.1** The proposed structure and fragmentation of products.

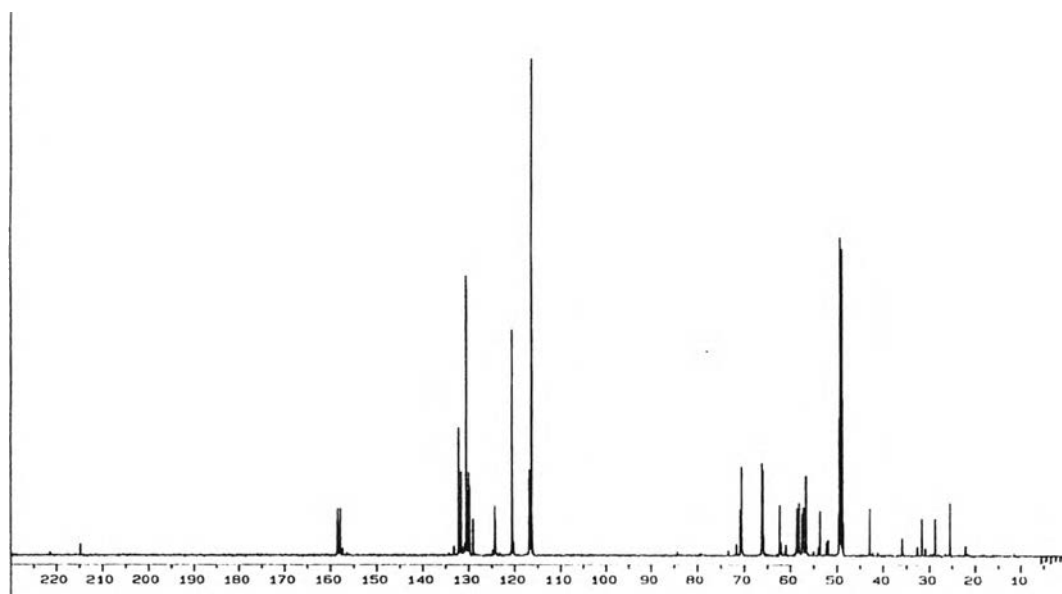
m/e	Intensities	Propose structure
304	23.08	
242	8.51	
210	20.05	
107	100	

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of benzoxazine C3 are shown in figures 4.8 and 4.9, respectively.





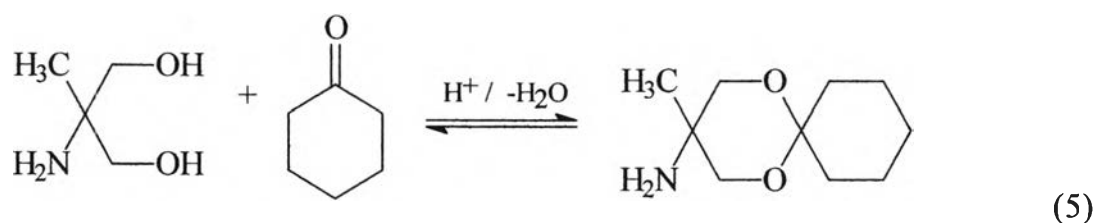
**Figure 4.8** <sup>1</sup>H-NMR spectrum of benzoxazine C3.



**Figure 4.9** <sup>13</sup>C-NMR spectrum of benzoxazine C3.

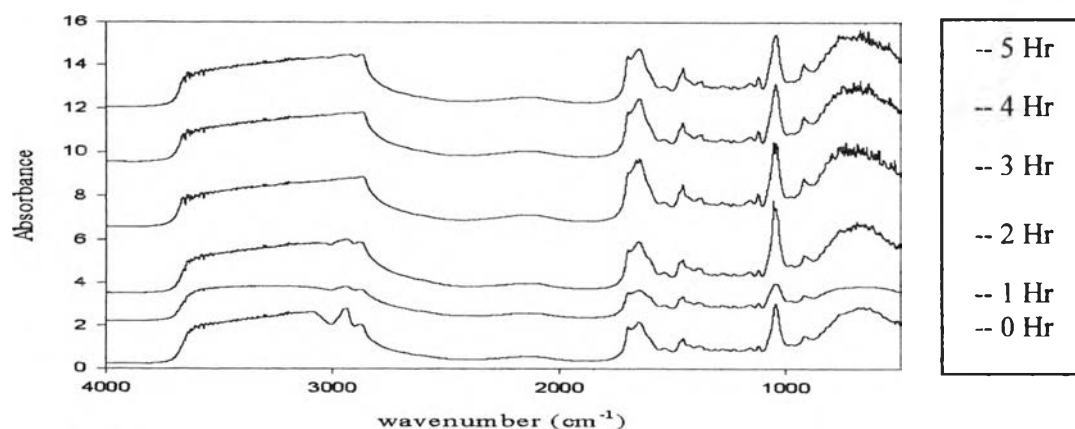
### 4.3 Protecting Hydroxyl Groups of 2-Amino-2-methyl-1,3-propanediol

In this study, ketal C4 product was synthesized directly from a mixture of 2-amino-2-methyl-1,3-propanediol and cyclohexanone in the presence of hydrochloric acid as a catalyst. Since water produced during the equilibrium reaction hydrolyzed the product, it must be removed out from the system to push the reaction forward, as illustrated in equation (5).

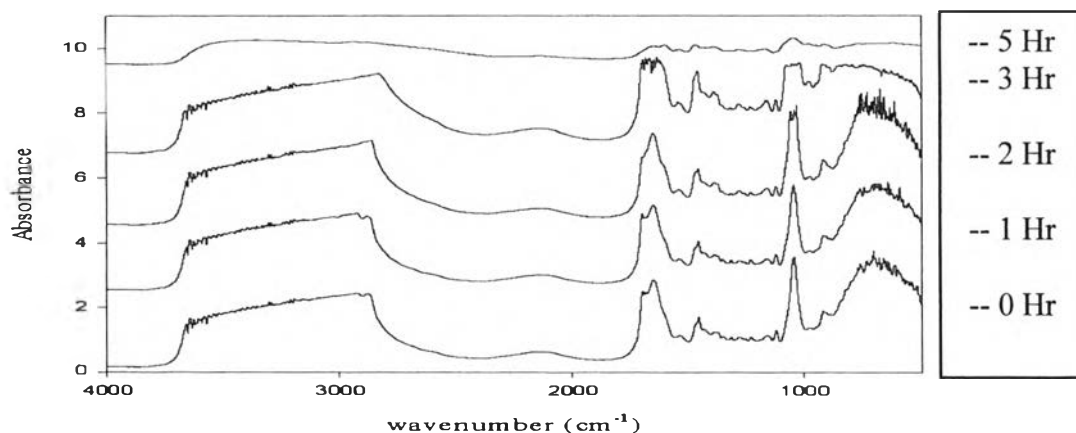


#### 4.3.1 Effect of Reaction Time and Temperature on the Ketal C4 Synthesis

The mixture of 2-amino-2-methyl-1,3-propanediol and cyclohexanone in the presence of hydrochloric acid was heated to 100°C and 110°C for a variation of time, 0-5 hours. Sampling of the mixture was done every hour to follow the reaction, using FTIR.



**Figure 4.10** FTIR spectra of the crude product of ketal C4 at 100°C from 0-5 hours.



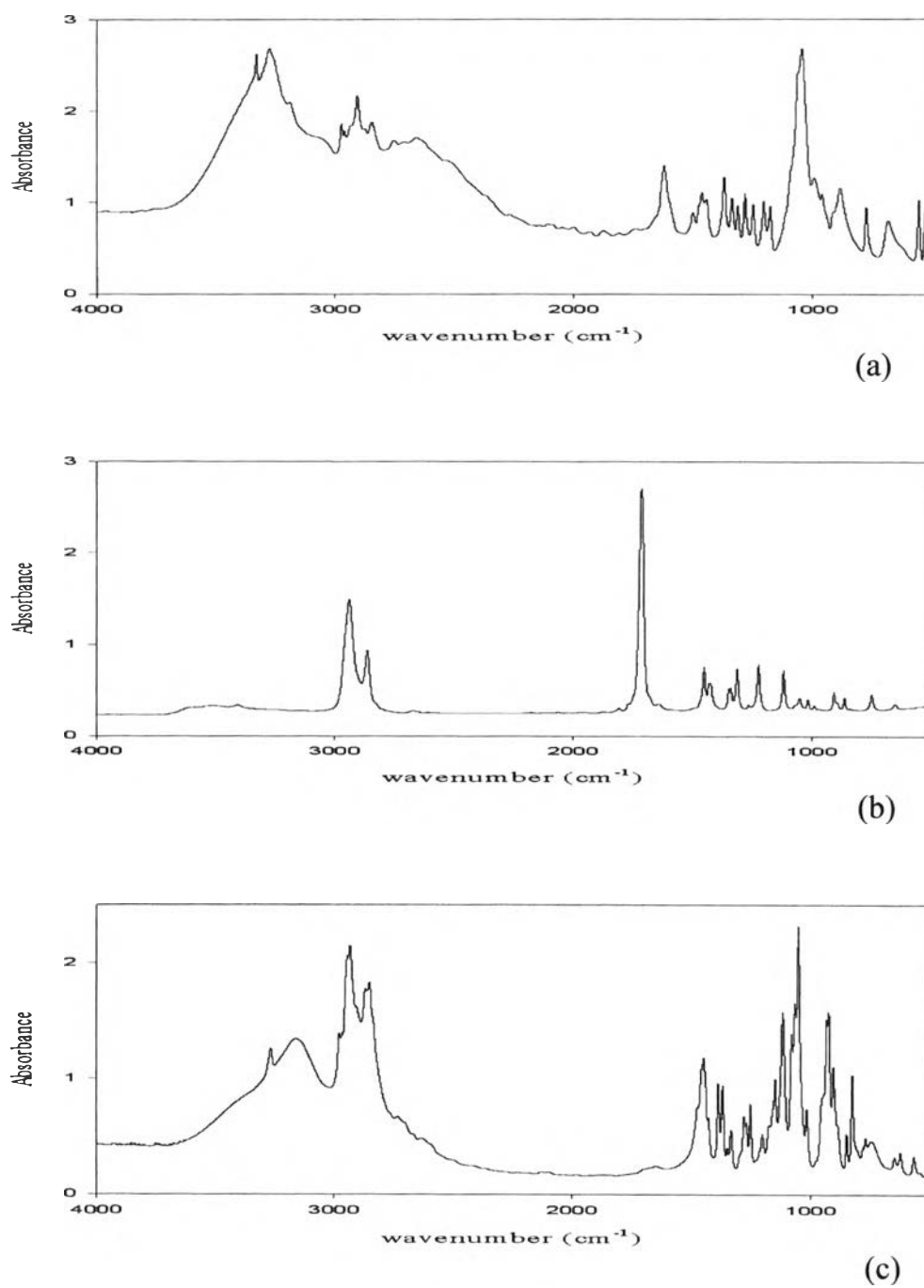
**Figure 4.11** FTIR spectra of the crude product ketal C4 at 110°C from 0-5 hours.

From FTIR spectra in figures 4.10 and 4.11, as the reaction went on, the peak at  $1693\text{ cm}^{-1}$  representing C=O in cyclohexanone was decreased whereas the peaks at  $1044\text{ cm}^{-1}$  and  $915\text{ cm}^{-1}$  representing C-O-C in ketal structure were increased. As compared with the results from both temperatures, the suitable condition for ketal C4 synthesis is at temperature  $100^{\circ}\text{C}$  for 2 hours.

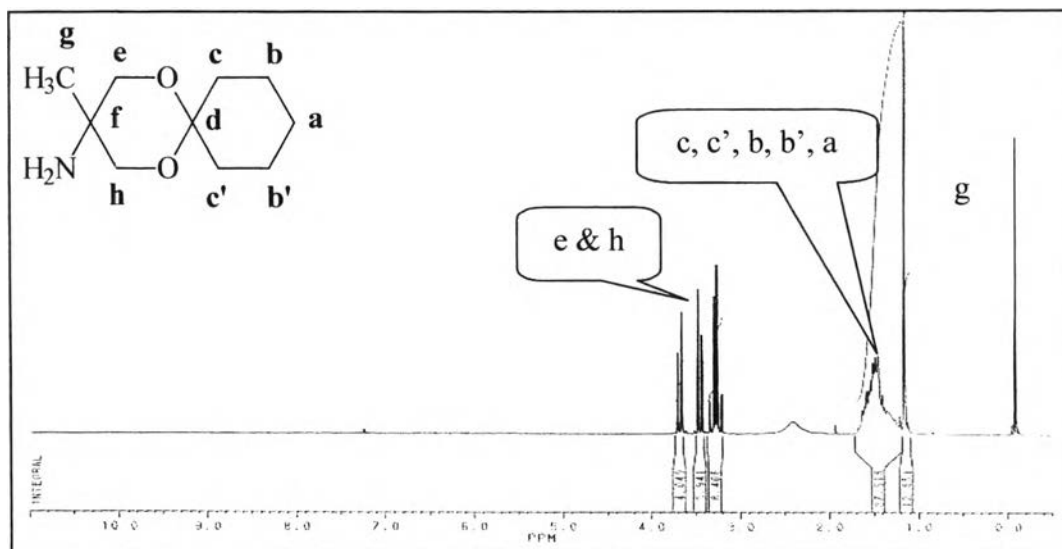
The product was separated by using column chromatography packed with silica gel as a stationary phase and a mixture of acetonitrile and methanol was used as a mobile phase. The solvents in the selected fractions were evaporated out to obtain powder product.

Figure 4.12 shows a broad band at  $3274\text{-}3165\text{ cm}^{-1}$  corresponding to  $\text{-NH}_2$  stretching, whereas, the band at  $2933\text{-}2860\text{ cm}^{-1}$  results from C-H stretching. The C-O-C structure in ketal structure is assigned by the bands at  $1046$  and  $927\text{ cm}^{-1}$ .

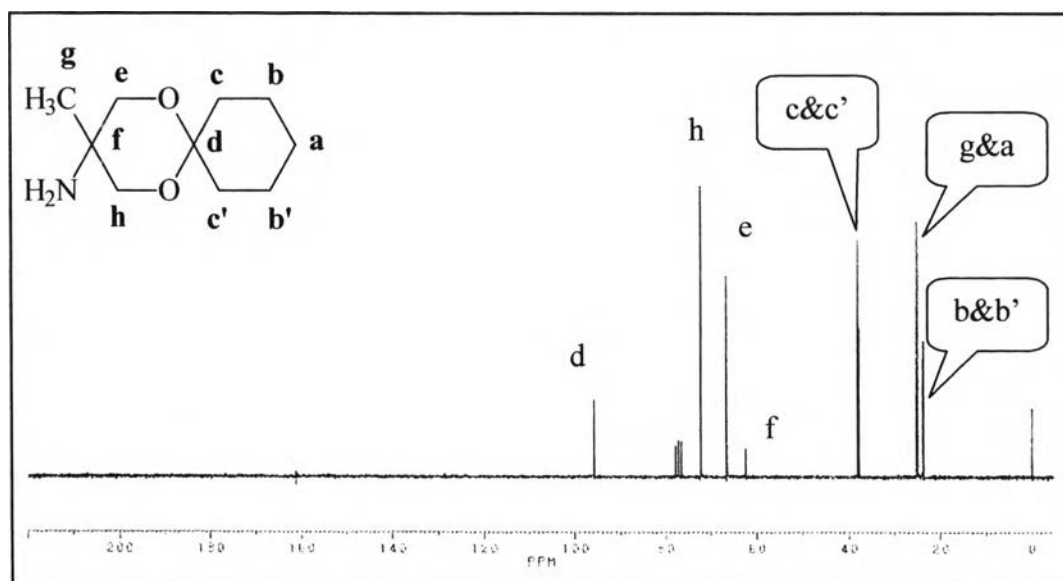
The spectra of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR of ketal C4 are shown in figures 4.13 and 4.14, respectively.



**Figure 4.12** FTIR spectra of (a) 2-amino-2-methyl-1,3-propanediol, (b) cyclohexanone, and (c) ketal C4 product.



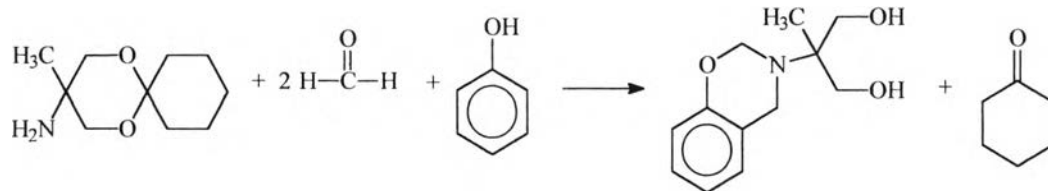
**Figure 4.13**  $^1\text{H}$ -NMR of ketal C4.



**Figure 4.14**  $^{13}\text{C}$ -NMR of ketal C4.

#### 4.4 Synthesis of Benzoxazine from Ketal C4.

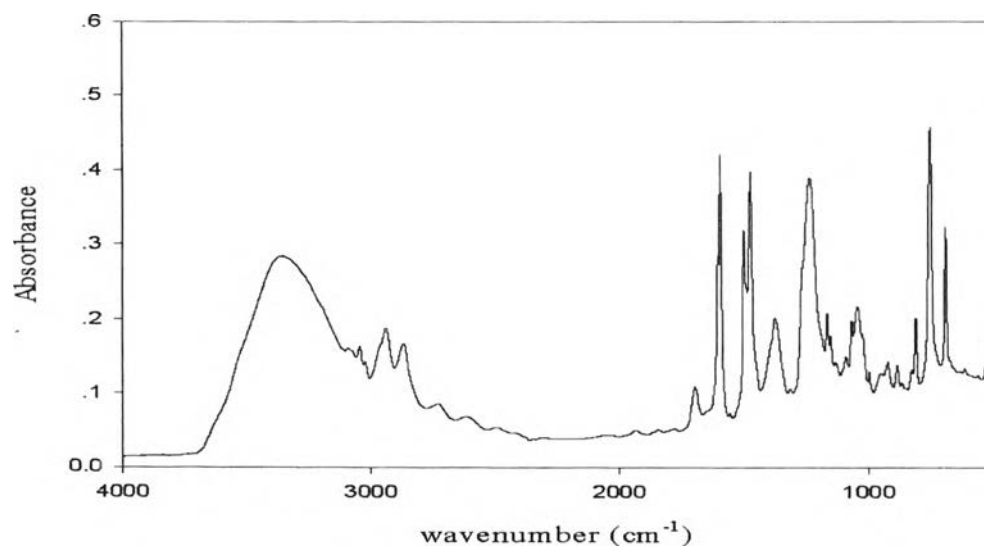
In this study, benzoxazine C4 product was synthesized directly from a mixture of ketal C4, formaldehyde and phenol, as illustrated in equation 6.



This reaction gave cyclohexanone, the protecting agent, as a by-product due to the decomposition of ketal structure since phenol acted as acid catalyst and the reaction was heated.

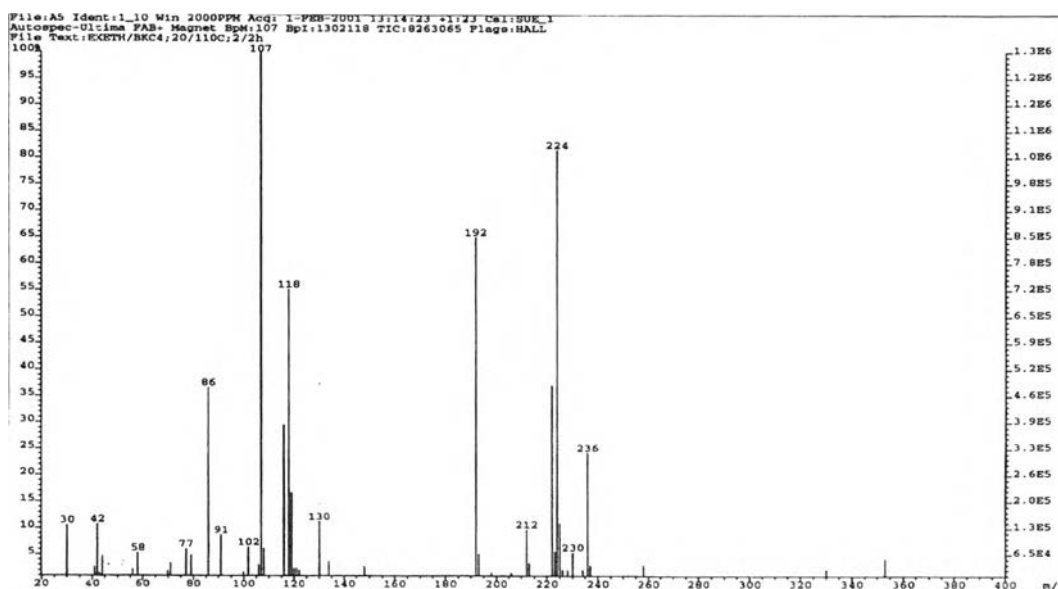
The product was separated by liquid extraction using ether and 1N NaOH solution. Further separation was done by neutralizing the NaOH layer and then ether was used in liquid extraction. The ether layer was selected and evaporated out to obtain the final product.

Fig 4.15 shows FTIR spectrum of the as-synthesized benzoxazine C4. The peak at  $1500\text{ cm}^{-1}$  represents the di-substituted benzene ring-mode in the oxazine structure, while the peak at  $1475\text{ cm}^{-1}$  represents the di-substituted benzene ring-mode in the ortho-substituted (methylene-amine-methylene bridge) phenolic structure formed by the reaction between the oxazine ring and the free ortho position of phenol. Moreover, the bands at  $755$  and  $692\text{ cm}^{-1}$  represent the 1,2-disubstituted benzene ring in the benzoxazine structures.



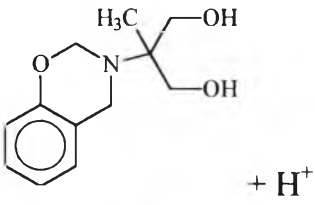
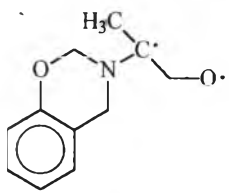
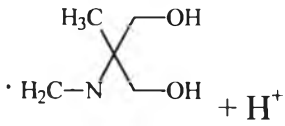
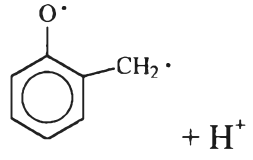
**Figure 4.15** FTIR spectrum of benzoxazine C4.

Figure 4.16 illustrates the mass spectrum of benzoxazine C4. The fragmentation of the product is shown in table 4.2.



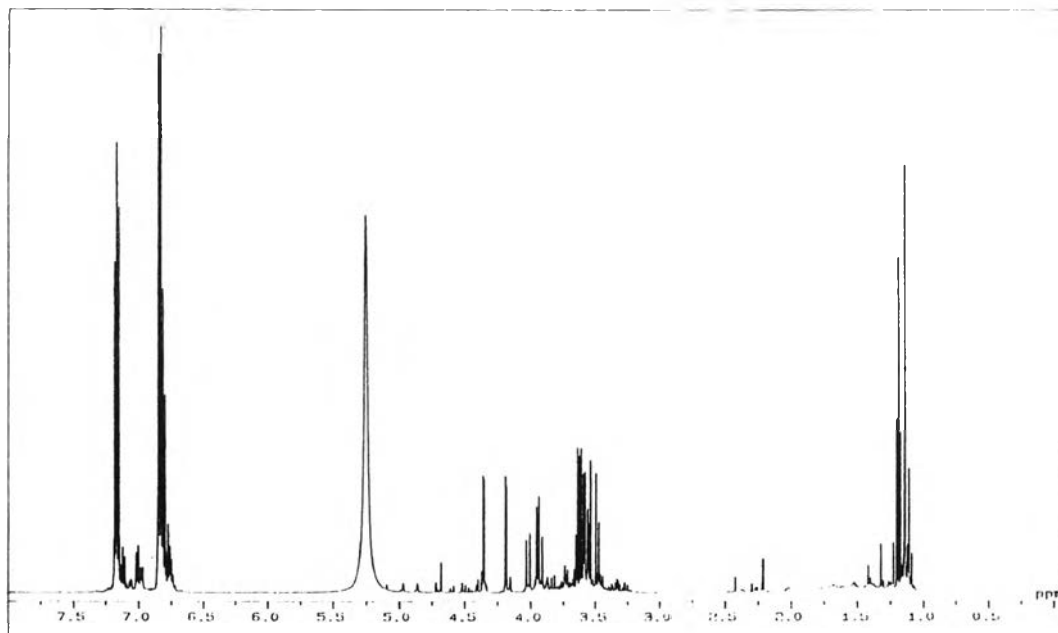
**Figure 4.16** The mass spectrum of benzoxazine C4.

**Table 4.2** The proposed structure and fragmentations of the product.

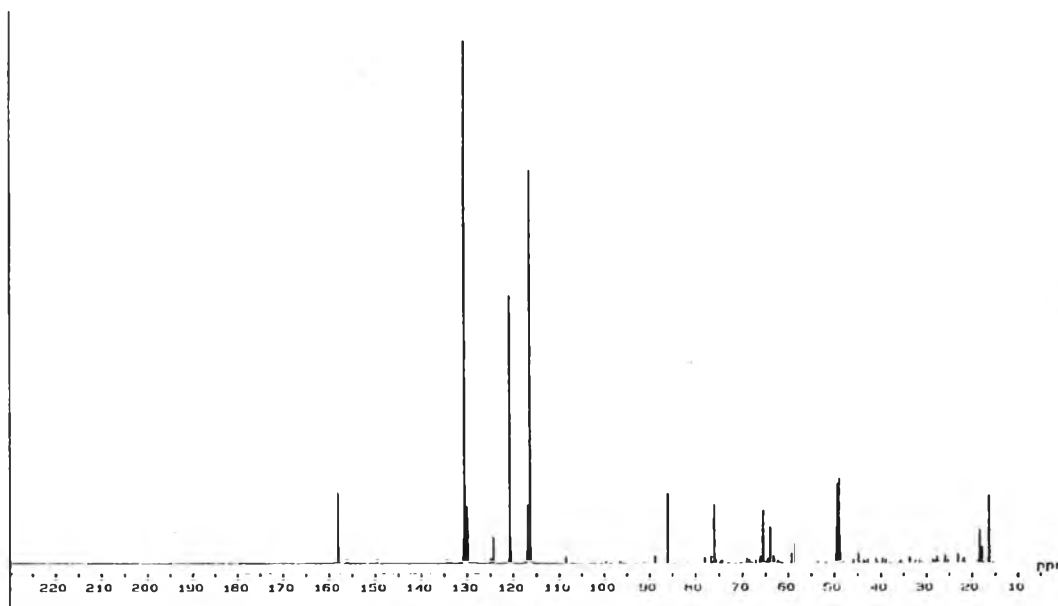
m/e	Intensities	Proposed structure
224	81.43	 + H <sup>+</sup>
192	65.00	
118	55.13	 + H <sup>+</sup>
107	100	 + H <sup>+</sup>

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of benzoxazine C4 are shown in figures 4.17 and 4.18, respectively.





**Figure 4.17**  $^1\text{H-NMR}$  of benzoxazine C4.



**Figure 4.18**  $^{13}\text{C-NMR}$  of benzoxazine C4.

#### 4.5 Synthesis of Spirosilicate/benzoxazine C3 Comonomer

In this study, spiro-silicate/benzoxazine C3 product was synthesized directly from a mixture of aminospirosilicate C3, paraformaldehyde and phenol, as illustrated in equation 7.

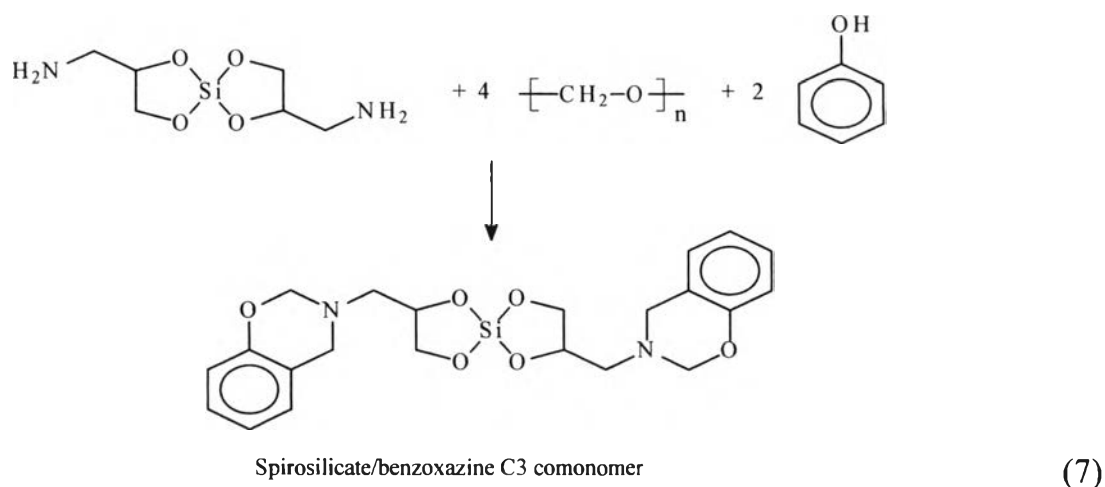
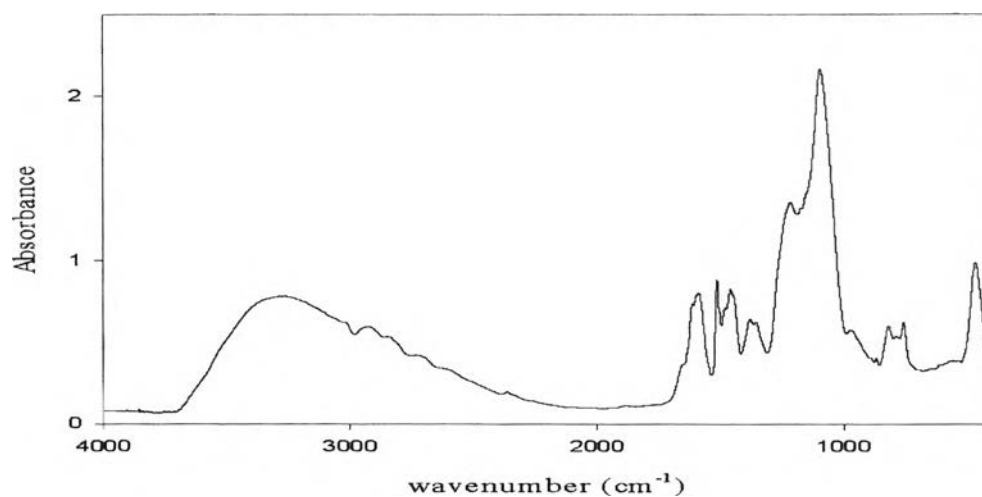
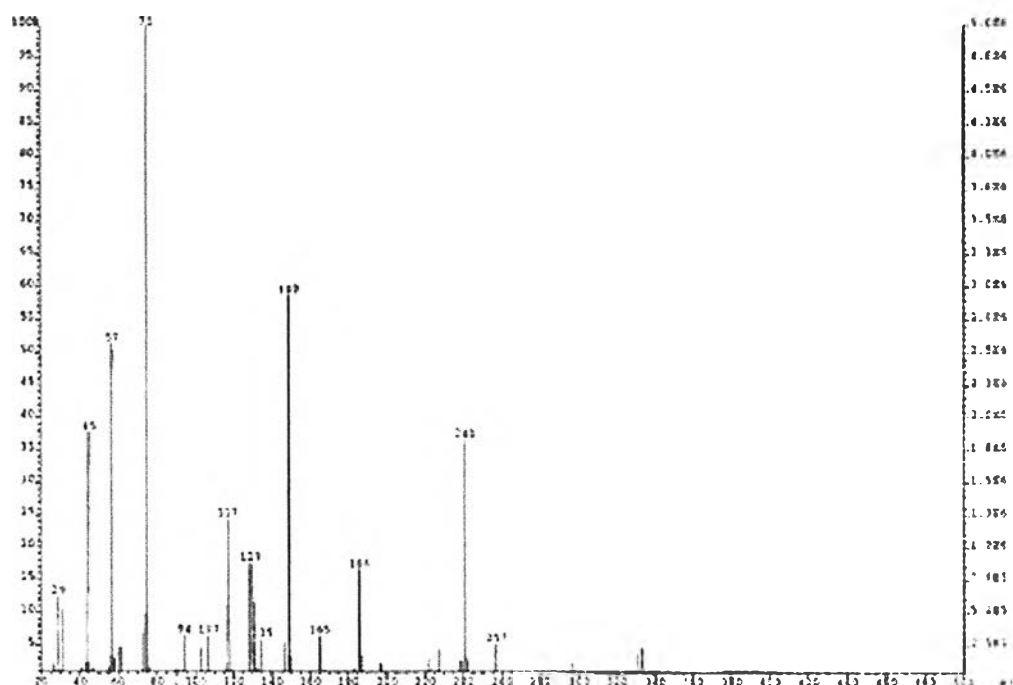


Figure 4.19 shows FTIR spectrum of the spiro-silicate/benzoxazine C3 comonomer. The peak at  $1511\text{ cm}^{-1}$  represents the oxazine ring structure. The band at  $1092\text{-}1214\text{ cm}^{-1}$  represents the Si-O and Si-O-C peaks. The peak at  $759\text{ cm}^{-1}$  refers to the benzene ring in the comonomer structure. By comparing the intensities of oxazine ring to the Si-O and Si-O-C peaks, it was found that the product was not pure. It may contain silica, the starting material, and need to be purified.



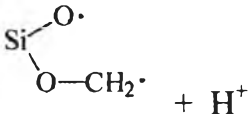
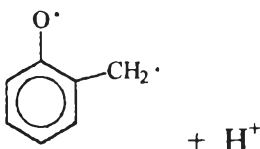
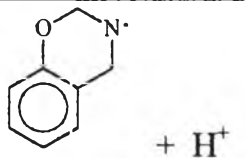
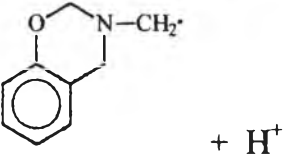
**Figure 4.19** FTIR spectrum of spirosilicate/benzoxazine C3 comonomer.

The mass spectrum of spirosilicate/benzoxazine C3 comonomer is illustrated in figure 4.20. The fragmentation of the product is shown in table 4.3.



**Figure 4.20** The mass spectrum of spirosilicate/benzoxazine C3 comonomer.

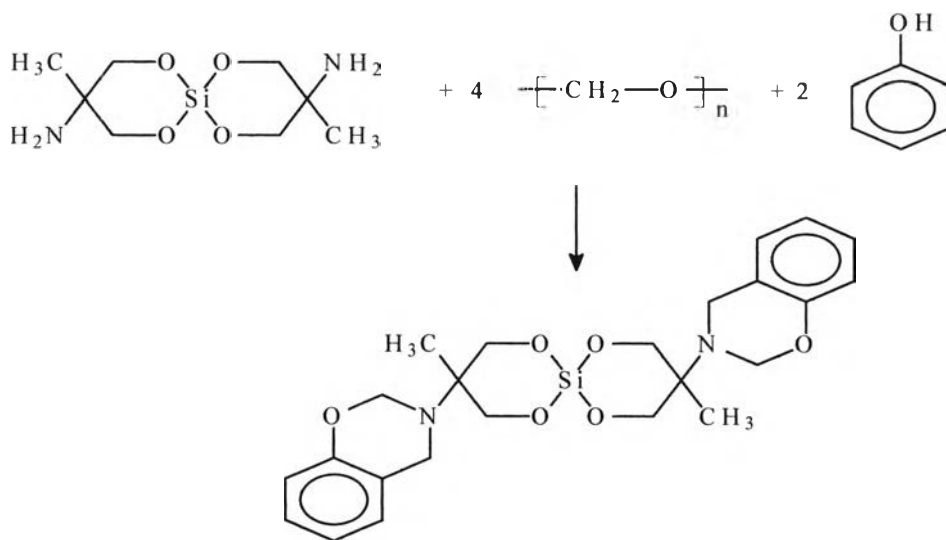
**Table 4.3** The proposed structure and fragmentations of the product.

M/e	Intensities	Proposed structure
45	37.86	Si-O + H <sup>+</sup>
75	100	 $\text{Si-O}\cdot$ $\text{O-CH}_2\cdot$ + H <sup>+</sup>
107	6.43	 $\text{O}\cdot$ $\text{CH}_2\cdot$ + H <sup>+</sup>
135	5.94	 $\text{N}\cdot$ + H <sup>+</sup>
149	58.76	 $\text{N-CH}_2\cdot$ + H <sup>+</sup>

The mass spectrum of spiro-silicate/benzoxazine C3 comonomer, as can be seen in figure 4.20, shows the fragmentations of the spiro-silicate and benzoxazine parts.

#### 4.6 Synthesis of Spiro-silicate/benzoxazine C4 Comonomer

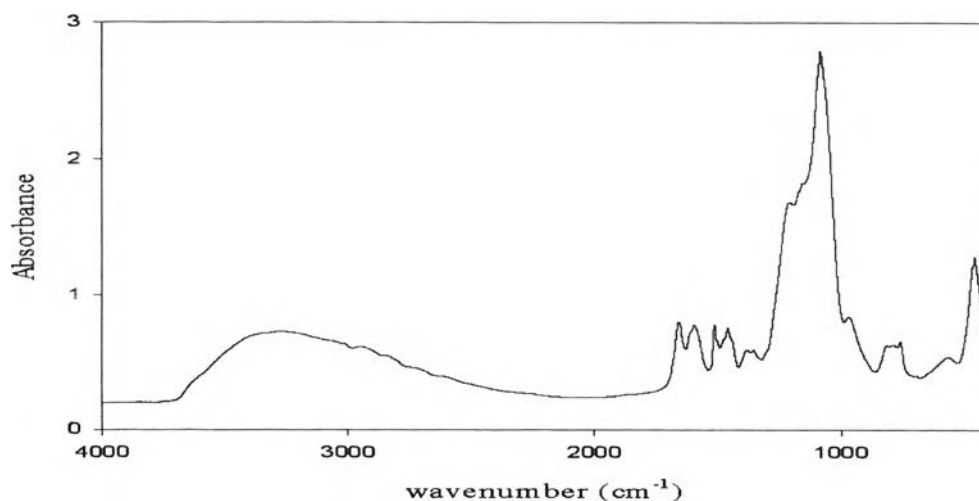
In this study, spiro-silicate/benzoxazine C4 comonomer was synthesized directly from a mixture of aminospiro-silicate C4, paraformaldehyde and phenol, as illustrated in equation 8.



Spirosilicate/benzoxazine C4

(8)

Figure 4.21 shows FTIR spectrum of the spirosilicate/benzoxazine C4 comonomer. The peak at  $1511\text{ cm}^{-1}$  represents the oxazine ring structure. The band at  $1092\text{-}1214\text{ cm}^{-1}$  represents the Si-O and Si-O-C peaks. The peak at  $759\text{ cm}^{-1}$  refers to the benzene ring in the comonomer structure. By comparing the intensities of oxazine ring to Si-O and Si-O-C peaks, it was found that the product was not pure. It again may contain silica, the starting material, and need to be purified.



**Figure 4.21** FTIR spectrum of spirosilicate/benzoxazine C4 comonomer.