THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Materials Engineering)

DEGREE

Materials Engineering | Materials Engineering

FIELD | **DEPARTMENT**

TITLE: Designs and Developments of Novel Ion Extraction Materials based on Supramolecular Properties of Benzoxazine Derivatives

NAME: Mr. Attaphon Kaewvilai

THIS THESIS HAS BEEN ACCEPTED BY

_____ **THESIS ADVISOR**

(Assistant Professor Apirat Laobuthee, Ph.D. **)**

_____ **THESIS CO- ADVISOR**

(Assistant Professor Nattamon Koonsaeng, Ph.D. **)**

_____ **THESIS CO- ADVISOR**

(Ms. Harittapak Kiratisaevee, Ph.D. **)**

_____ **THESIS CO- ADVISOR**

(Mr. Pittaya Takolpuckdee, Ph.D. **)**

_____ **DEPARTMENT HEAD**

(Assistant Professor Wisit Locharoenrat, M.S. **)**

APPROVED BY THE GRADUATE SCHOOL ON _____

_____ **DEAN**

(Associate Professor Gunjana Theeragool, D.Agr. **)**

THESIS

DESIGNS AND DEVELOPMENTS OF NOVEL ION EXTRACTION MATERIALS BASED ON SUPRAMOLECULAR PROPERTIES OF BENZOXAZINE DERIVATIVES

ATTAPHON KAEWVILAI

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Materials Engineering)
Graduate School, Kasetsart University
2009

Attaphon Kaewvilai 2009: Designs and Developments of Novel Ion Extraction Materials based on Supramolecular Properties of Benzoxazine Derivatives. Master of Engineering (Materials Engineering), Major Field: Materials Engineering, Department of Materials Engineering. Thesis Advisor: Assistant Professor Apirat Laobuthee, Ph.D. 60 pages.

In this present work, three types of benzoxazine supramolecules with ring closure, open ring and etherified benzoxazines were synthesized. The ring closure (**BX1-BX3**) and open ring (**BX4-BX6**) benzoxazines with linear aliphatic linkage were prepared by Mannich reaction and ring opening reaction, respectively. Both reactions were also simple and effective reactions without using any specific catalysts to produce high yield products. Additionally, we successfully prepared the etherified benzoxazine (**BX7- BX9**) via molecular design based on benzoxazine dimer structure. By using a reaction of etherification, the desired products with high yield were obtained. The all chemical structures of products were confirmed by FT-IR, ^{1}H-NMR and MS. The all products exhibited the unique property as supramolecules to interact with alkali metal ions via the molecular assembly were observed by Pedersen's technique. In this case, the results indicated that etherified benzoxazines (**BX7**, **BX8** and **BX9**) shows stoichiometrically interacted with metal ion guest as 2:1, 3:1 and 4:1, respectively.

Keywords: Supramolecule, Molecular assembly Benzoxazines, Mannich reaction, Ring opening reaction, Etherification, Pedersen's technique, stoichiometric interaction ratio.

_____ _____ ___ / ___ / ___

Student's signature Thesis Advisor's signature

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his advisor, Assistant Professor Dr. Apirat Laobuthee who always gave him intensive recommendation, constructive criticism, suggestions, constant encouragement, and inspiration.

He wants to express appreciation to all Professors at Department of Materials Engineering, Faculty of Engineering, Kasetsart University for giving him invaluable knowledge.

A deep gratitude is expressed to Assistant Professor Dr. Nattamon Koonsaeng (Department of Chemistry, Faculty of Science, Kasetsart University) for helps in NMR measurements and Assistant Professor Sawittee Rujithanaphanit (Program of Chemistry, Faculty of Science and Technology, Phranakhon Rajabhat University) who gave valuable advice, encouragement and helped in FTIR measurements.

He would like to thank all members of Laobuthee's group, Dr. Chatchai Veranitisagul, Mr. Sarawut Sangngern, Mr. Thamrong Rakthin, and staffs at Department of Materials Engineering, Faculty of Engineering, Kasetsart University for their unconditional friendship.

He also owes his thanks to many other friends whose names are not mentioned here who have helped in various ways and unconditional friendship.

Finally, he wishes to express his great appreciation and his gratitude to his mother and father for their advice, encouragement and especially financial support.

Attaphon Kaewvilai

April, 2009

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF ABBREVIATIONS

I	=	N,N-Bis(2-hydroxyl methyl benzyl)methyllamine
II	=	N,N-Bis(2-hydroxyl ethyl benzyl)methyllamine
III	=	N,N-Bis(2-hydroxyl methoxy benzyl)methyllamine
BX1	=	1,6-Bis(3'4'-dihydro-6'-methyl-2'H,1',3'-benzoxazine) hexamethylenediamine
BX2	=	1,6-Bis(3'4'-dihydro-6'-ethyl-2'H,1',3'-benzoxazine) hexamethylenediamine
BX3	=	1,6-Bis(3'4'-dihydro-6'-methoxy-2'H,1',3'-benzoxazine) hexamethylenediamine
BX4	=	N,N,N',N'-Tetrakis(2-hydroxyl methyl benzyl)hexamethylenediamine
BX5	=	N,N,N',N'-Tetrakis(2-hydroxyl ethyl benzyl)hexamethylenediamine
BX6	=	N,N,N',N'-Tetrakis (2-hydroxyl methoxy benzyl)hexamethylenediamine
BX7	=	N,N-bis[5-methyl-2-(1',3'-diethoxy-2'-propoxy) benzyl]methylamine
BX8	=	N,N-bis[5-ethyl-2-(1',3'-diethoxy-2'-propoxy) benzyl]methylamine
BX9	=	N,N-bis[5-methoxy-2-(1',3'-diethoxy-2'-propoxy) benzyl]methylamine
mL.	=	milliliter
g	=	gram
mmol	=	millimole
M	=	Molar
%	=	percentage
nm	=	nanometer
cm^{-1}	=	per centimeter

LIST OF ABBREVIATIONS (Continued)

ppm	=	part per million
δ	=	chemical shift
$\overline{\nu}$	=	wavenumber
J	=	coupling constant
s	=	singlet
d	=	doublet
t	=	triplet
q	=	quartet
m	=	multiplet
m/z	=	mass/charge
Ao	=	initial absorbance of the picrate solution
A	=	absorbance of the picrate solution after extraction with the benzoxazine derivatives

DESIGNS AND DEVELOPMENTS OF NOVEL ION EXTRACTION MATERIALS BASED ON SUPRAMOLECULAR PROPERTIES OF BENZOXAZINE DERIVATIVES

INTRODUCTION

Up to now, due to their specific interactions at the molecular level and induced property as molecular recognition, supramolecules have received much attention to develop in various structures for the preferred properties. The induced molecular interactions between supramolecules and guests to form host-guest compounds or inclusion compounds are known as non-covalent interactions or secondary forces, such as van der Waals, dipole-dipole interaction, and hydrogen bonding. Novel supramolecules with specific functional groups have been, designed and proposed in both assembly and cyclic structures (Figure 1).

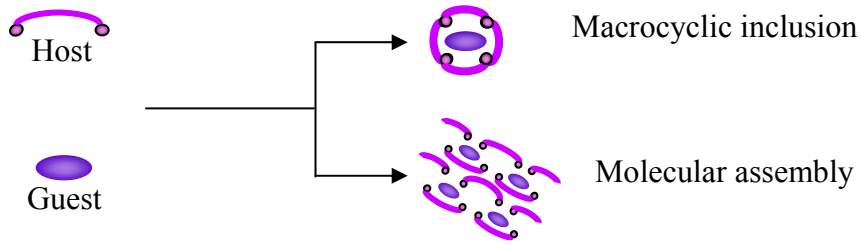


Figure 1 Type of inclusion compounds.

For the past few years, calixarenes and their various derivatives have been well-known as host compounds exhibiting the inclusion properties with various metal ions. Recently, our group has originally focused on the structure of benzoxazines which are resembled to repeating unit of calixarenes (Figure 2). Due to the interesting structure of benzoxazines which are easily controlled via the molecular designs, supramolecules based on benzoxazine structures have been proposed and synthesized to obtain a series of supramolecules as ion entrapment materials.

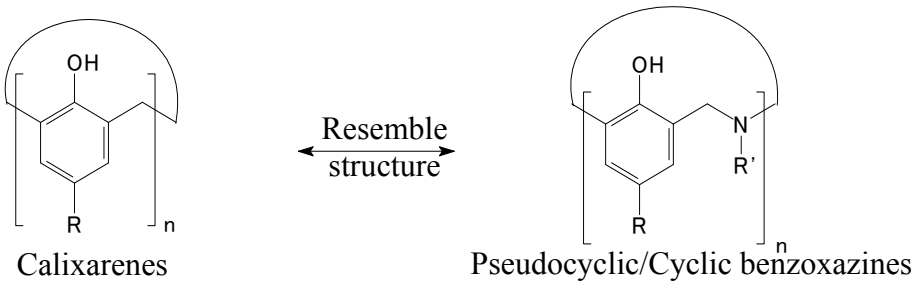


Figure 2 Repeating unit structures of benzoxazines and calixarenes.

This present work was focused on the design and synthesize of benzoxazine supramolecules by simple and effective reactions such as Mannich reaction, ring opening raction and etherification reaction. In addition, the metal ion responsive property of benzoxazines was determined by Pedersen's technique.

OBJECTIVES

1. To synthesize the benzoxazine derivatives by Mannich, ring opening and etherification reactions.
2. To study the ion extraction property of as synthesized benzoxazines by Pedersen's technique.

LITERATURE REVIEW

Host-Guest Chemistry

Host-guest phenomena were firstly reported by Michael Faraday in 1823 about the chlathrate structure of chlorine. The concept and theory of host-guest phenomena was established when C.J. Pedersen (Kroschwitz, 1995) found the inclusion between crown ether compounds and metal ions in 1960. After C.J. Pedersen, D.J. Cram, and J.M. Lehn were the 1967 Nobel Prize laureates in Chemistry, the host-guest chemistry has become advanced research themes to this present time.

For the guest molecules, they are required to fit for the size and shape to accommodate the specific properties of host cavity or channel. Polar guests are generally favored with the host cavities lined with polar groups while non polar guests are included by non polar host cavities. Concerning the size of the host cavity, most host compounds give the cavity diameters in the range of 0.4-0.8 nm. A host channel has an affinity to entrap linear guest, while a host cage is suitable for a spherical guest. The cage cavity is more stable than the channel or layer cavity (Kroschwitz *et al*., 1995).

The guest can be stabilized in the host framework with non-covalent bonding or secondary forces, such as van der Waals, ionic, hydrophilic, and hydrophobic interaction. Host-guest compounds or inclusion compounds can be explained by a model of a host concave and a guest convex relationship or lock and key model which was proposed by Fisher in 1894 as shown in Figure 3.

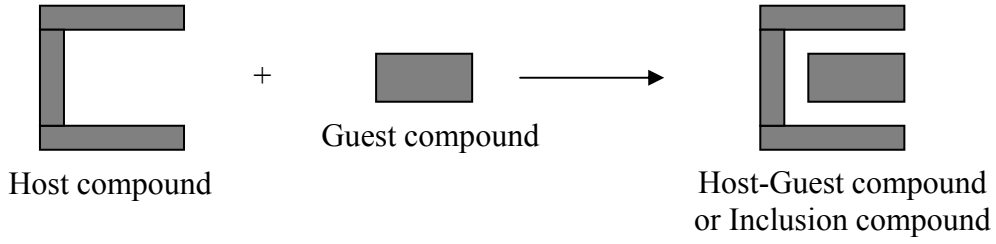


Figure 3 Model of inclusion compound (Fisher, 1894).

Well-Known Host Compounds

1. Crown compound

Crown ether macrocyclics are named by C.J. Pedersen (1967) because of its crown-like structure have methylene basic unit linked with hetero atoms such as O, N, or S as electron donor atoms in their cyclic structures. The macrocyclic polyethers having only O atoms as the electron donors are known as crown ethers (Figure 4) which azacrown ether as cyclic amino ethers where N atom substitutes for some of O atoms in crown ethers. Cyclic polyether sulfides in which S atom substitutes O atoms are called thiacrown ethers (Hiraoka, 1982).

Crown compounds show the specific property to entrap not only alkali and alkaline earth metal ions, but also some typical and transition metals through ion-dipole interaction helded by unshared pairs of electrons of O, N, and S atoms. The complexation ability depends on cavity size, donor atom, diameter, and cations. Therefore, crown ethers have been applied as phase-transfer catalyst in the organic reactions (Hiraoka, 1982). Crown ethers containing 5-10 oxygen atoms forming the complexes with Li^+, K^+, NH_4^+, etc. are reported by Izatt *et al*. (1985).

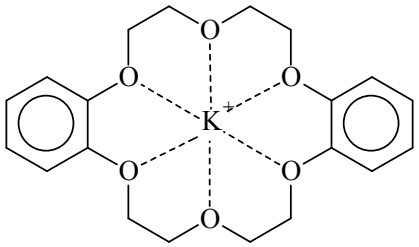


Figure 4 Inclusion of dibenzo-18-crown-6 and potassium ion.

2. Cyclodextrin

Cyclodextrins, cyclic oligosaccharides are prepared by enzymatic degradation of starch providing mainly three types of cyclodextrins, i.e., α-, β-, γ-cyclodextrins, containing 6, 7, and 8 of α-1,4-linked D-glucopyranose units, respectively (Figure 5). The circularly linked glucose units result in a molecular shape of truncated cone with an internal cavity capable for hosting organic compound guests.

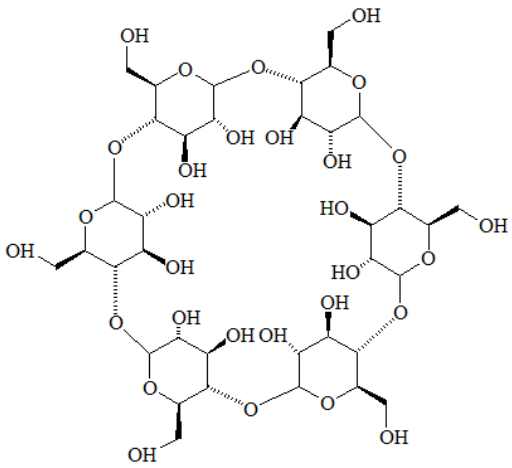


Figure 5 α-Cyclodextrin.

Hydrophilic hydroxyl groups located at the outer rim make cyclodextrin dissolve in water. The inner rim of their cavities lined by hydrogen atoms and the glycosidic oxygen bridges results in hydrophobic cavity (Chankvetadze *et al*., 1996).

Intramolecular hydrogen bonds formed between 2-hydroxy and 3-hydroxy groups of adjacent glucose units maintain the remarkably rigid structure. In addition, each D-glucose unit in cyclodextrin structure consisting of five chiral carbon atoms is a chiral macrocyclic compound. The wide range applications of cyclodextrins such as, solubilizers, diluents in pharmaceutical industries, flavor stabilizers in food industries, catalysts, and separation media in chemical industries have been found due to their properties (Chankvetadze *et al*., 1996).

3. Calixarenes

Calixarenes are interesting for host guest chemistry because of its cone- or calix-like conformation. The unique structure can be mentioned as a phenol unit linked by methylene bridges. The synthesis procedures have been improved to obtain a selective calix[4]arenes (Figure 6), calix[6]arenes, and calix[8]arenes. The compounds exhibit the specific property to include various types of organic molecules and metal ions in the cavities.

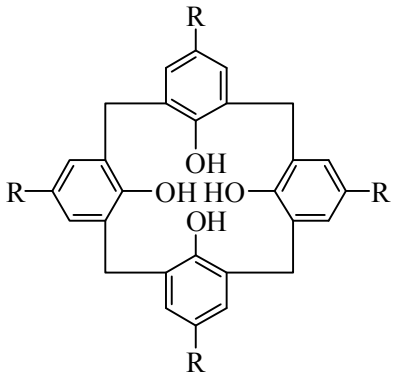


Figure 6 Calix[4]arenes.

The higher homologous (calix[6]- and calix[8]arenes) are known to be more flexible. Four possible conformations of calixarenes are reported as cone, partial cone, 1,2-alternate, and 1,3-alternate by Gutsche in 1983.

Moreover, Shinkai *et al*. (1984) proposed the sulfonate ion of calix[n]arenes to include several organic molecules and cation in aqueous solution. Ungaro, McKervy, and Change indicated a series of calixaryl esters having superb alkali metal affinity.

The Molecules and Chemistry of Benzoxazines

Benzoxazines are a type of heterocyclic compounds from the benzene and oxazine rings. Benzoxazines can be prepared by Mannich reaction form *p*-substituted phenols, formaldehyde and primary amines amine in a molar ratio of 1:2:1, respectively (Figure 7) (Holly and Cope, 1944).

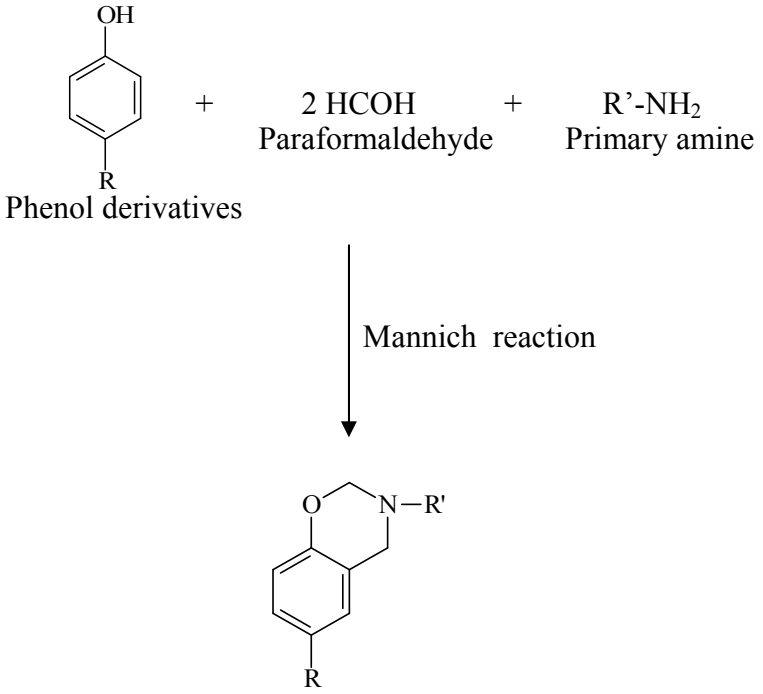


Figure 7 Synthesis pathway of 3,4-dihydro-6-alkyl-3-alkyl-2*H*-benzoxazines.

The ring opening polymerization of *p*-substituted phenol-based benzoxazines are self-terminated to the dimer level with obtain high yield (80-90%) of *N*,*N*-Bis(2-hydroxylalkylbenzyl)alkylamine derivatives. Considering the structure of these derivatives, the single crystallography analysis pointed out the unique structures with inter-and intra-molecular hydrogen bonds network to provide asymmetric reaction (Figure 8), (Laobuthee, 2003).

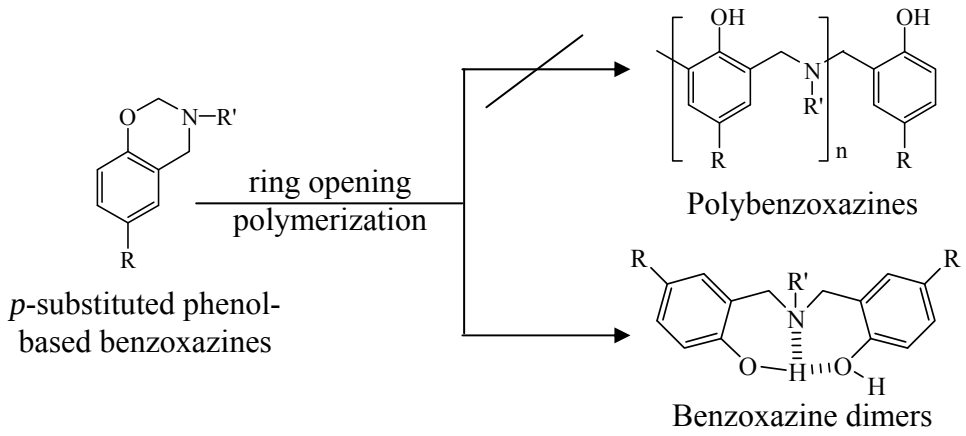


Figure 8 Ring opening polymerization of benzoxazines (Laobuthee, 2003).

According to the repeat unit of *N*,*N*-Bis(2-hydroxylalkylbenzyl)alkylamine derivative resembling to that of calixarene, this derivative can perform as host compound to accept various guest species. For example, Laobuthee *et al*., 2003 reported about the inclusion phenomena of *N*,*N*-Bis(2-hydroxylalkylbenzyl)alkylamine derivatives with alkaline picrate salts. In this research, the molecular designs and synthesis of benzoxazine derivatives for novel alkali metals extraction materials have been proposed. The ion extraction property of as synthesized compounds was studied via Pedersen's technique.

MATERIALS AND METHOD

Materials

Phenol derivatives (*p*-cresol, 4-ethyl phenol and 4-methoxy phenol), 1,6-hexamethylenediamine, methylamine (40%w/v in water), potassium hydroxide (KOH), 1,3-diethoxy-2-propanol, *p*-toluene sulfonyl chloride, cesium carbonate, paraformaldehyde, sodium hydroxide and anhydrous sodium sulfate were purchased from Fluka Chemicals (Buchs, Switzerland). 1,4-Dioxane, and diethylether were purchased from Merck. Ethanol, methanol (MeOH), methylene chloride (CH_2Cl_2), iso-propanol, acetonitrile and picric acid were the products of Ajax chemicals (Australia). All chemicals were analytical grade and used without further purification.

Infrared spectra were obtained from Fourier transform infrared spectrophotometer: Shimadzu partige 21 with 45 scans at a resolution 16 cm^{-1}. NMR spectra were taken from ^{1}H-NMR spectrometer (Varian Mercury-400 spectrometer). Mass spectra of precursors were obtained from ESI-MS (Bruker Esquire mass spectrometer). Methylene chloride was used as received for preparing the sample solutions.

Methods

1. Synthesis of benzoxazine derivatives

1.1 Synthesis of ring closure benzoxazines (**BX1 – BX3**)

The ring closure benzoxazine (**BX1 – BX3**) were prepared as shown in Figure 9. Paraformaldehyde (12.01 g, 400 mmol) was mixed with 1,6-hexamethylenediamine (11.62 g, 100 mmol) in 1,4-dioxane (100 mL) and stirred at room temperature for 30 min. The *p*-Cresol (21.42 g, 200 mmol) was then added and refluxed for 8 h. The obtained solution was collected, washed by solvent extraction (sodium hydroxide and water), dried over anhydrous sodium sulfate and removed solvent by evaporation.

Similarly, **BX2** and **BX3** were prepared as for **BX1** with the starting materials as 4-ethylphenol (24.43 g, 200 mmol) and 4-methoxyphenol (24.82 g, 200 mmol), respectively. The obtained products were characterized by FT-IR, ^{1}H-NMR, and ESI-MS spectrometer.

1.2 Synthesis of open ring benzoxazines (**BX4 – BX6**)

By ring opening reaction, **BX4** was prepared from **BX1** and *p*-cresol as shown in Figure 9. The ring closure benzoxazine (**BX1**) (19.00 g, 50 mmol) and *p*-cresol (10.81. g, 100 mmol) was mixed in 30 mL methylene chloride. The mixture was stirred at 60°C for 6 h and purified by solvent extraction (sodium hydroxide and water), dried over anhydrous sodium sulfate and removed solvent by evaporation.

Other open ring benzoxazines (**BX5** and **BX6**) were similarly prepared as for **BX4**. The starting materials as **BX2** (20.20 g, 50 mmol) and 4-ethylphenol (12.21 g, 100 mmol) were used for preparing **BX5** while **BX3** (20.60 g, 50 mmol) and 4-methoxyphenol (12.41 g, 100 mmol) were used as starting materials for **BX6**. The products were identified by FT-IR, ^{1}H NMR, and ESI-MS.

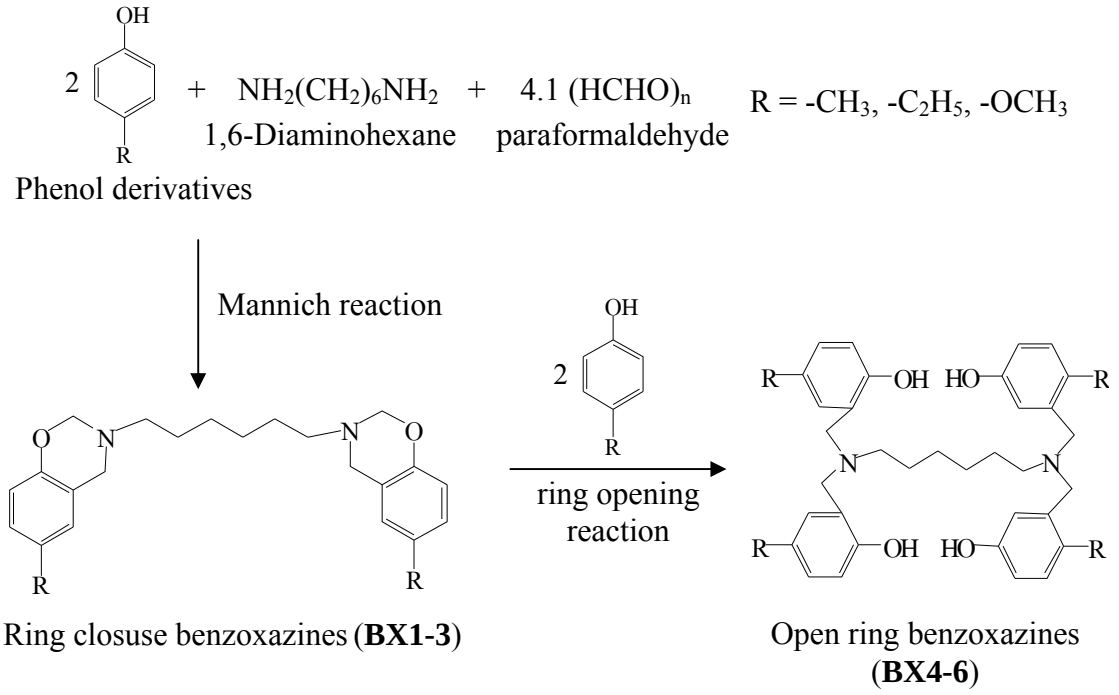


Figure 9 Synthesis pathways for ring closure and open ring benzoxazines.

1.3 Synthesis of tosylated 1,3-diethoxy-2-propanol

Tosylated 1,3-diethoxy-2-propanol (1.5 mL, 10 mmol) was dissolved in methylene chloride (50 mL) followed by the addition of NaOH (28.80 g, 20 mmol) in 20 mL water (Figure 10). The mixture was stirred vigorously at room temperature for 30 min and a solution of *p*-toluene sulfonyl chloride (1.90 g, 10 mmol) in methylene chloride (50 mL) was added dropwise for 1 h. The reaction was allowed to proceed at room temperature for 6 h. The organic phase was collected and extracted with water several times. The product was dried over sodium sulfate and the solvent was removed to obtain a white viscous product. The product obtained was characterized by FTIR.

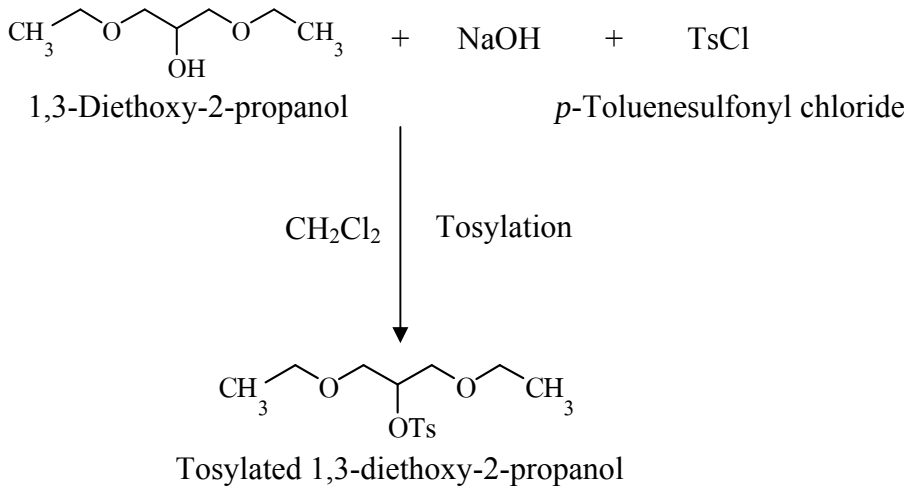


Figure 10 Preparation of tosylated 1,3-diethoxy-2-propanol by tosylation reaction.

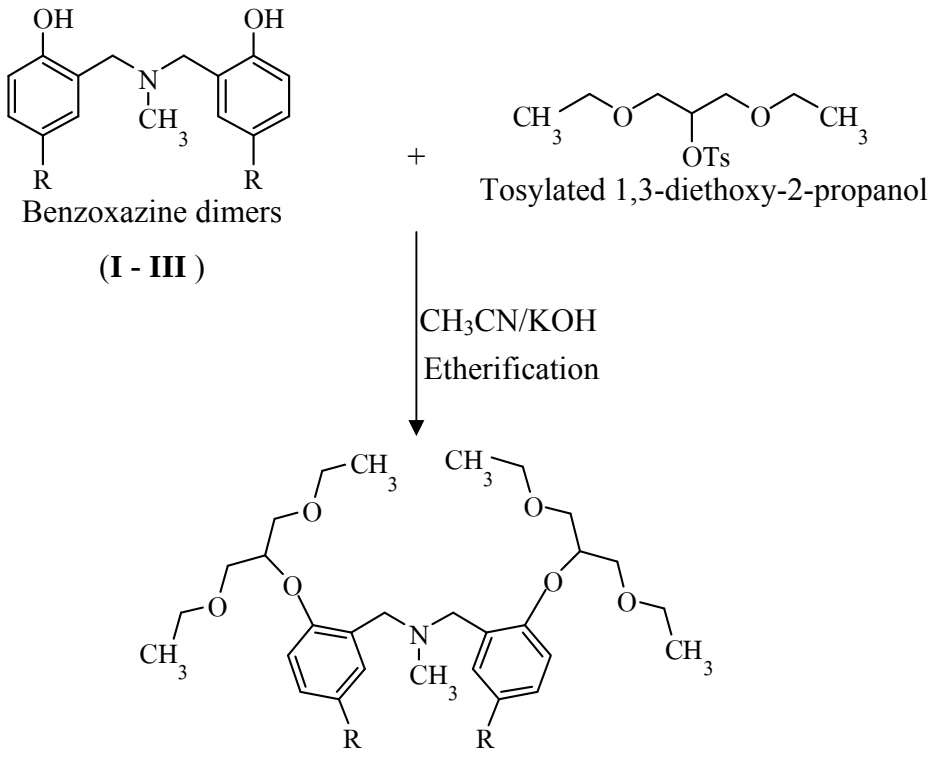
1.4 Synthesis of benzoxazine dimers (**I** – **III**)

The benzoxazine dimers (**I** – **III**) used as the starting materials for products (**BX7** – **BX9**) (Figure 7) were prepared as reported elsewhere (Laobuthee, 2002).

1.5 Synthesis of etherified benzoxazines (**BX7 – BX9**)

The products (**BX7 – BX9**) were synthesized as shown in Figure 11. Benzoxazine dimer (**I**) (5 mmol) was dissolved in acetronitrile (50 mL) followed by the addition of NaOH (20 mmol). The mixture was stirred and refluxed for 30 min and a solution of tosylated 1,3-diethoxy-2-propanol (10 mmol) in acetronitrile (50 mL) was added dropwise for 1 h. The reaction was allowed to proceed for 3 days. After that, acetonitrile was removed by vacuum distillation. The sticky yellow liquid of product dissolved in methylene chloride was washed by several times with distilled water. The product was dried over sodium sulfate and the solvent removed to obtain a product **BX7**.

Similarly, **BX8** and **BX9** were prepared as for **BX7** with the starting materials **II** and **III**, respectively. The final products are clear yellow oil. All products were characterized by FTIR, ^{1}H-NMR and ESI-MS.



N,N-bis[5-alkyl-2-(1',3'-diethoxy-2'-propoxy) benzyl]methylamine (**BX7 - BX9**)

R = -CH_3 (**I** and **BX7**), -C_2H_5 (**II** and **BX8**), and -OCH_3 (**III** and **BX9**)

Figure 11 Feasible structures of etherified benzoxazine.

2. Ion extraction property of benzoxazine derivatives

Ion extraction property of benzoxazine derivatives was determined by liquid-liquid extraction via Pedersen's technique. All benzoxazine derivatives (**BX1 – BX9**) dissolved in methylene chloride and alkali metal picrates aqueous solutions were prepared with the concentration of 7.0×10^{-5} M. Five milliliters of each solution were vigorously mixed and left at room temperature until each phase was completely separated. The concentration of metal picrates was determined by the UV-Vis spectrophotometer at λ_{max} 355 nm ($\varepsilon = 1.45 \times 10^{4}$ $M^{-1}.cm^{-1}$). The percentage extraction was calculated by the equation as follow.

$$\%\text{Extraction} = [(A_o - A) / A_o] \times 100$$

A_o = the initial absorbance of the picrate solution.
A = the absorbance of the picrate solution after extraction with the benzoxazine derivatives.

In addition, the molar ratios between the etherified benzoxazine (**BX7 – BX9**) and metal ions were confirmed by ^{1}H-NMR and ESI-MS.

RESULTS AND DISCUSSION

1. Synthesis of ring closure and open ring benzoxazines (BX1 – BX6)

Considering Figure 12 (a), **BX1** showed the oxazine peak at 1501 cm^{-1} whereas the broad peak of hydroxyl group of *p*-cresol disappeared. **BX1** was used as a starting material to react with *p*-cresol by the ring opening reaction and provided a product as **BX4**. It was found that **BX4** gave a broad peak of hydroxyl group in the region of 3200-3500 cm^{-1} and the peak of oxazine disappeared (Figure 12 (b)).

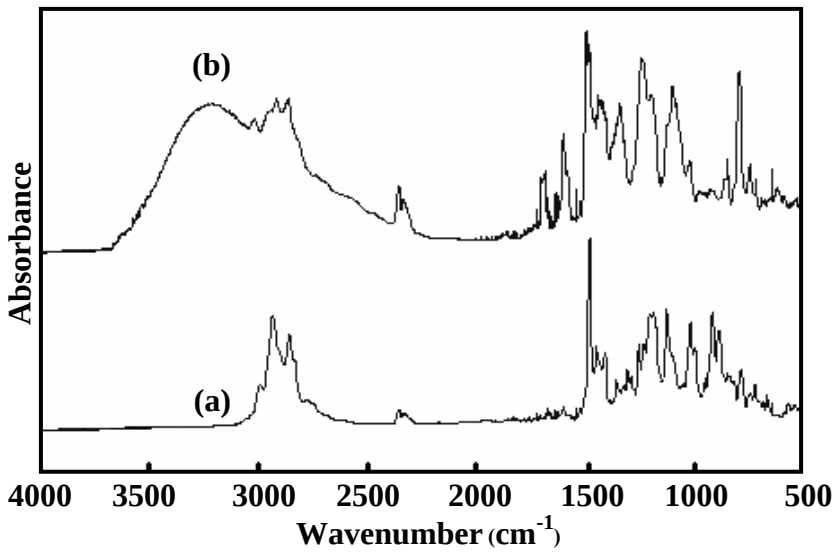


Figure 12 FTIR spectrum of (a) **BX1** and (b) **BX4**.

^{1}H NMR was used to determine the structures of products. **BX1** exhibited two characteristic peaks of methylene protons (N-CH_2-O and N-CH_2-Ar) at 4.81 and 3.93 ppm while **BX4** showed only one characteristic peak of proton belonging to aza-methylene linkage (CH_2-N-) at 3.65 ppm (Figures 13 and 14).

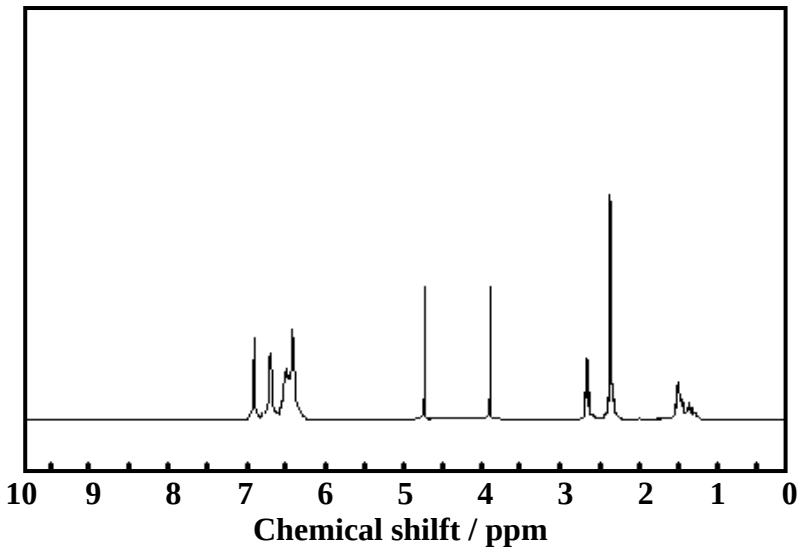


Figure 13 ^{1}H-NMR spectrum of **BX1**.

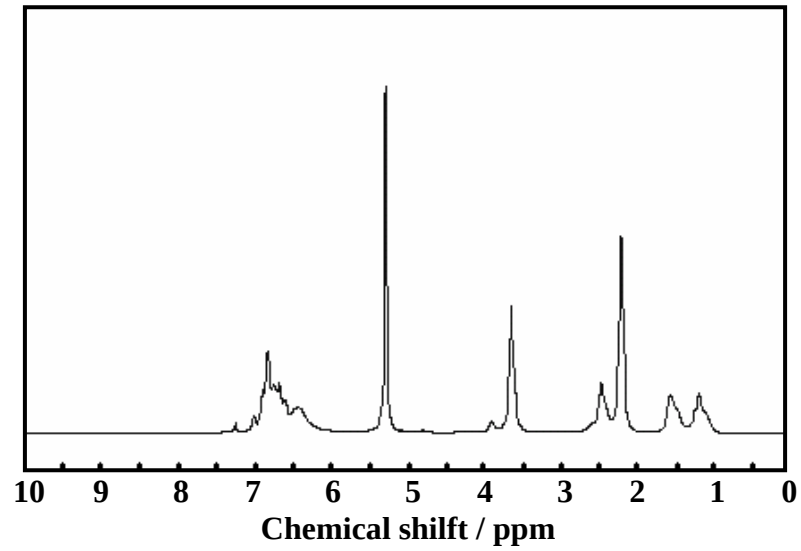


Figure 14 ^{1}H-NMR spectrum of **BX4**.

Figures 15 and 16 show the molecular ion peaks at m/z = 381 and 597 corresponding to the molecular weights of **BX1** and **BX4**, respectively.

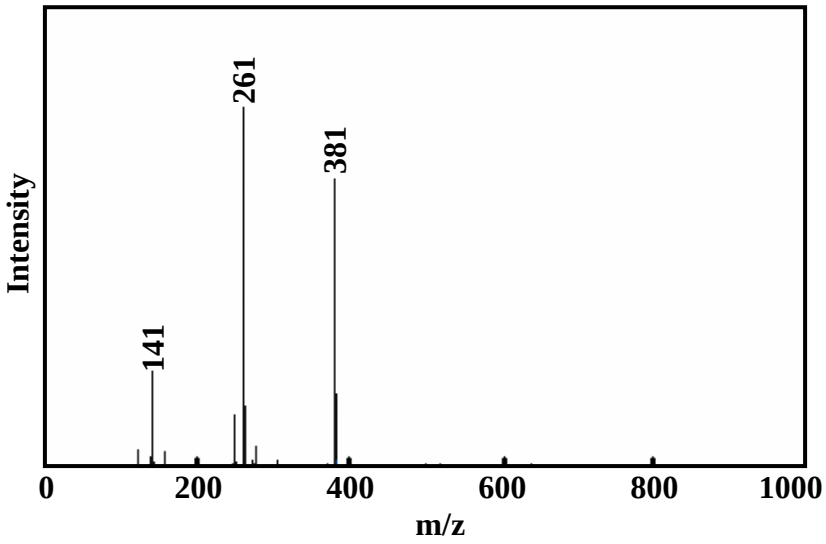


Figure 15 ESI-MS spectrum of **BX1**.

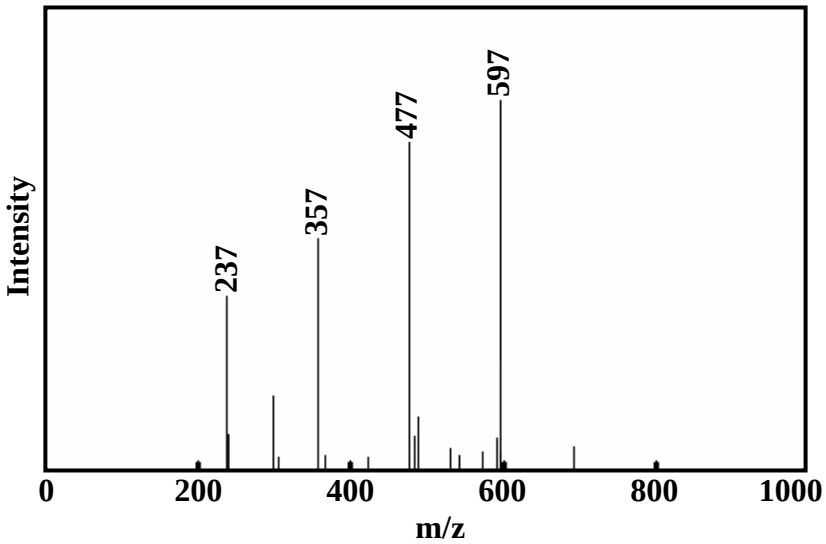


Figure 16 ESI-MS spectrum of **BX4**.

Similarly, the ring closure benzoxazines (**BX2** and **BX3**) and the open ring benzoxazines (**BX5** and **BX6**) were characterized as **BX1** and **BX4.** The results confirm the successful in the preparation of the ring closure and the open ring benzoxazines via Mannich and ring opening reactions.

The results of structure characterization of **BX1** - **BX6** were presented as follows.

BX1: FTIR (KBr, cm^{-1}): 1501 (vs, oxazine), 2932 (s, C-H-stretching), 1247 (C-N-C stretching Aromatic). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 1.34 (8H, m, J_1 = 7.86 Hz, J_2 = 6.20 Hz, -N- CH_2- **CH_2-CH_2**), 2.35 (3H, s, Ar-**CH_3**), 2.56 (4H, t, J_1 = 7.86 Hz, -N- **CH_2**-CH_2-CH_2), 3.93 (4H, s, -N-**CH_2**-Ar), 4.81 (4H, s, -N-**CH_2**-O), 6.66 (2H, J_3 = 7.56 Hz, Ar–**H**), 6.72 (2H, Ar–**H**), 6.91 (2H, J_3 = 7.56 Hz, Ar–**H**). ESI-MS (m/z): 381 (M+1).

BX2: FTIR (KBr, cm^{-1}): 1485 (vs, oxazine), 2857 (s, C-H-stretching), 1247 (C-N-C-stretching). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 1.19 (6H, t, J_1 = 9.92 Hz, Ar-CH_2-**CH_3**), (4H, t, J_2 = 6.20 Hz, -N- CH_2- CH_2-**CH_2**), 1.40 (4H, m, J_2 = 6.20 Hz, -N- CH_2- **CH_2**-CH_2), 2.56 (4H, t, J_2 = 4.45 Hz, -N- **CH_2**-CH_2-CH_2), (4H, q, J_1 = 9.92 Hz, Ar-**CH_2**-CH_3) , 3.85 (4H,-N-**CH_2**-Ar), 4.80 (4H,-N-**CH_2**-O), 6.74 (2H, J_3 = 8.39 Hz, Ar–**H**) , 6.86 (2H, Ar–**H**), 7.04 (2H, J_3 = 8.39 Hz, Ar–**H**). ESI-MS (m/z): 409 (M+1).

BX3: FTIR (KBr, cm^{-1}): 1485 (vs, oxazine), 2857 (s, C-H-stretching), 1247 (C-N-C-stretching). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 1.29 (4H, t, J_1 = 4.45 Hz, -N-CH_2- CH_2-**CH_2**), 1.40 (4H, m, J_1 = 4.45 Hz, -N-CH_2-**CH_2**-CH_2), 2.66 (4H, t, J_1 = 4.45 Hz, -N-**CH_2**-CH_2-CH_2), 3.68 (6H, Ar-O-CH_3), 3.89 (4H, -N-**CH_2**-Ar), 4.73 (4H,-N-**CH_2**-O), 6.44 (2H, J_2 = 4.45 Hz, Ar–**H**) , 6.58 (2H, Ar–**H**), 6.64 (2H, J_2 = 4.45 Hz, Ar–**H**). ESI-MS (m/z): 409 (M+1).

BX4: FTIR (KBr, cm^{-1}): 2919 (OH-stretching), 2932 (s, C-H-stretching), 1247 (C-N-C stretching). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ_H 1.190 (4H, t, J_1 = 8.24 Hz, N-CH_2-CH_2 -**CH_2**), 1.571 (4H, m, J_1 = 8.24 Hz, N-CH_2-**CH_2** -CH_2), 2.216 (12H, s, Ar-**CH_3**), 2.466 (4H, t, J_1 = 8.24 Hz, N-**CH_2**-CH_2-CH_2), 3.646 (4H, s, Ar-**CH_2**-N), 5.288 (4H, s, Ar-**OH**), 6.683 (4H, d, J_2 = 8.11 Hz, Ar-**H**), 6.830 (4H, s, Ar-**H**), 6.883 (4H, d, J_2 = 8.11 Hz, Ar-**H**). ESI-MS (m/z): 597 (M+1).

BX5: FTIR (KBr, cm^{-1}): 3102 (OH-stretching), 2969 (s, C-H-stretching), 1253 (C-N-C stretching). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ_H 1.077 (12H, t, J_1 = 7.61 Hz, Ar-CH_2-**CH_3**), 1.105 (4H, t, J_2 = 8.24 Hz, N-CH_2-CH_2 -**CH_2**), 1.571 (4H, m, J_2 = 8.24 Hz, N-CH_2-**CH_2** -CH_2), 2.216 (12H, s, J_1 = 7.61 Hz, Ar-**CH_2**CH_3), 2.466 (4H, t, J_2 = 8.24 Hz, N-**CH_2** CH_2), 3.598 (4H, s, Ar-**CH_2**-N), 5.288 (4H, s, Ar-**OH**), 6.666 (4H, d, J_3 = 8.094 Hz, Ar-**H**), 6.782 (4H, s, Ar-**H**), 6.845 (4H, d, J_3 = 8.094 Hz, Ar-**H**) . ESI-MS (m/z): 653 (M+1).

BX6: FTIR (KBr, cm^{-1}): 3357 (OH-stretching), 2935 (s, C-H-stretching), 1227 (C-N-C stretching). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ_H 1.165 (4H, t, J_1 = 8.917 Hz, N-CH_2-CH_2 -**CH_2**), 1.530 (4H, m, J_1 = 8.917 Hz, N-CH_2-**CH_2** -CH_2), 2.444 (4H, t, J_1 = 8.917 Hz, N-**CH_2** CH_2), 3.685 (12H, s, Ar-O-**CH_3**), 3.705 (4H, s, Ar-**CH_2**-N), 5.273 (4H, s, Ar-**OH**), 6.599 (4H, d, J_2 = 6.175 Hz, Ar-**H**), 6.830 (4H, s, Ar-**H**), 6.883 (4H, d, J_2 = 6.175 Hz, Ar-**H**). ESI-MS (m/z): 661 (M+1).

2. Synthesis of etherified benzoxazine (BX7-BX9)

FTIR spectra of benzoxazine dimer (**I**) and etherified benzoxazine (**BX7**) in the 4000-500 cm^{-1} range are compared in Figure 13. From evidence of the crystal structure of **I**, the peak positions at 3298, 1483 and 1199 cm^{-1} were assigned to be hydroxyl groups, tri-substituted benzene, and C-N-C stretching, respectively (Figure 17 (a)). The peaks referred to hydroxyl groups were not observed in (**BX7**). However, the ether functional group, wave number = 1117 cm^{-1}, was found (Figure 17 (b)), indicating that the etherified dimer had been successfully prepared. There were no significant shifts in tri-substituted benzene (1499 cm^{-1}) or C-N-C stretching vibration (1200 cm^{-1}). This suggested that **I** was only changed in the functional group from the phenol to ether, while the backbone structure of product belonging to that of dimer still remained.

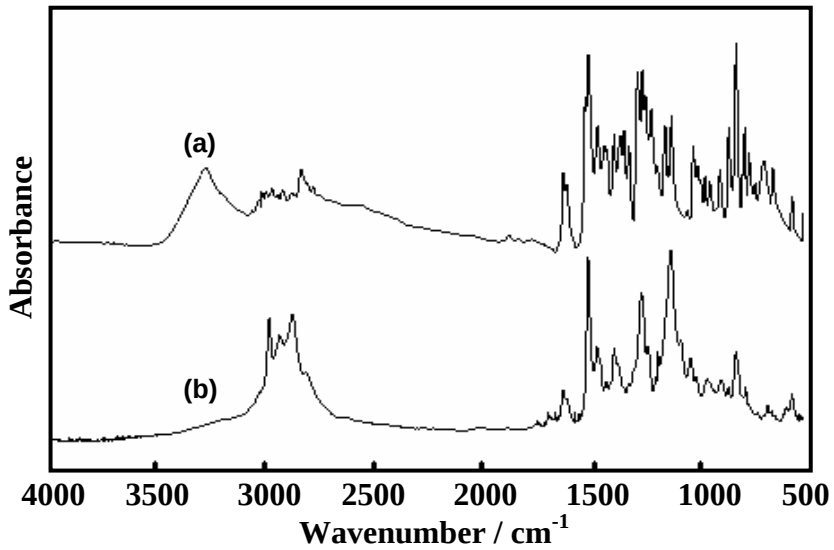


Figure 17. FTIR spectra of (a) **I** and (b) **BX7**.

Similar to **BX7, BX8** and **BX9** did not provide the hydroxyl group peaks in FTIR spectra. Both compounds exhibited the peak positions of tri-substituted benzene, C-N-C stretching vibration and C-O-C around 1497, 1200, and 1114 cm^{-1}, respectively. These frequencies are not significantly different from **BX7**.

^{1}H-NMR spectrum (Figure 18) of **BX7** showed the multiplex peak of methine protons (-CH-) at δH = 4.44 ppm which was not observed in **I**. In addition, methylene protons of aza-linkage were singlet at chemical shift of 3.66 ppm, indicating that two symmetric hydroxyl groups of **I** were completely substituted by tosylated-1,3-diethoxy-2-propanol and yielded the symmetrical structure of etherifeid benzoxazine (**BX7**). The data of the ^{1}H-NMR spectra (in $CDCl_3$) obtained for **BX8** and **BX9**. Both products, **BX8** and **BX9**, were clarified as products with symmetrical structures as **BX7**.

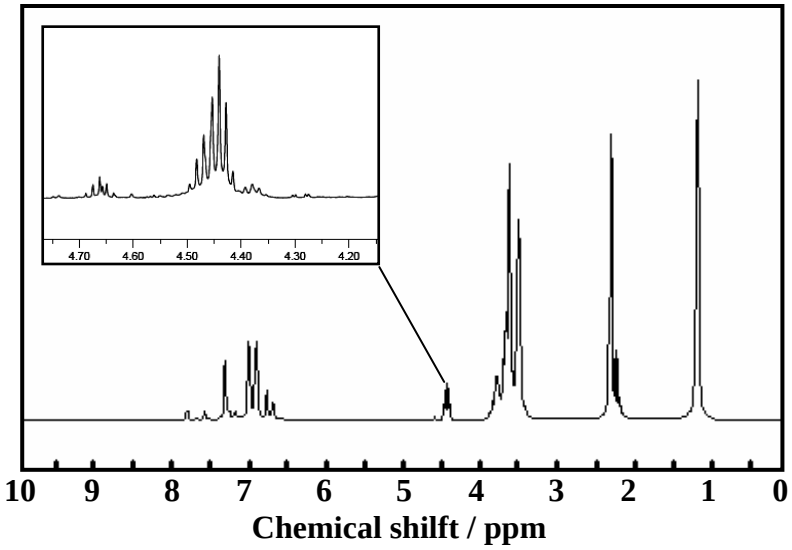


Figure 18 ^{1}H-NMR spectrum of **BX7**.

The results of mass/charge were determined by ESI mode mass spectrometer. Figure 19 shows the mass spectrum of **BX7**. The protonated **BX7** (m/z = 532) closely agreed with the calculated molecular weight of 531 in symmetric structure. This indicated that the etherification had completely occurred on both hydroxyl groups of benzoxazine dimer and resulted in etherified benzoxazines (**BX7**). Similarly, the structures of **BX8** and **BX9** were also symmetric as confirmed by m/z results and the corresponding calculated molecular weight of structure.

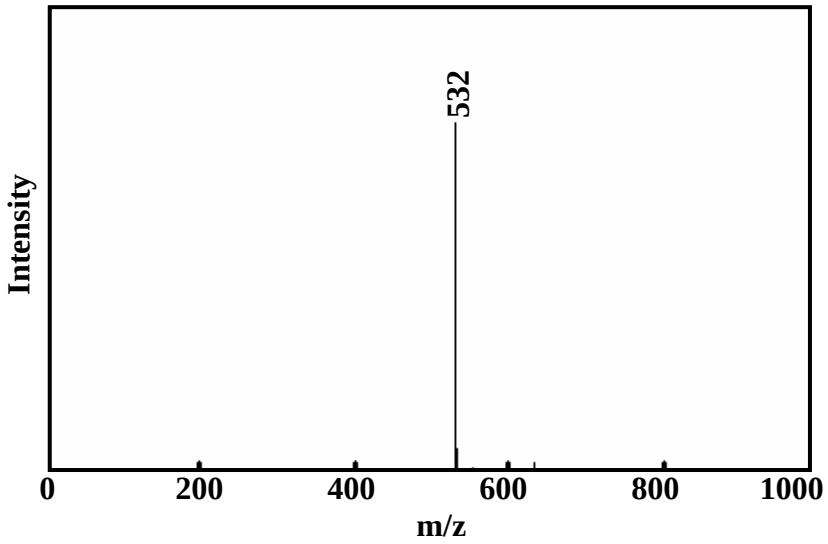


Figure 19 ESI-MS spectrum of **BX7**.

The results of structure characterization of **BX7 - BX9** were exhibited as follows.

BX7: FTIR (KBr, cm^{-1}): 1499 (tri-substituted benzene), 1200 (C-N-C stretching), 1117 (C-O-C). ^{1}H-NMR (200 MHz, $CDCl_3$, ppm):δ_H 1.158 (12H, t, J_1 = 6.59 Hz, O-CH_2-**CH_3**), 2.288 (9H, s, N-**CH_3** and Ar-**CH_3**), 3.501 (8H, q, J_1 = 6.59 Hz, O-**CH_2**-CH_3), 3.618 (8H, d, J_2 = 4.99 Hz, -**CH_2**-CH-**CH_2**-), 3.660 (4H, s, Ar-**CH_2**-N), 4.441 (2H, t, J_2 = 4.99 Hz, -CH_2-**CH**-CH_2-), 6.781 (2H, d, J_3 = 6.59 Hz, Ar-**H**), 6.918 (2H, s, Ar-**H**), 7.022 (2H, d, J_3 = 6.59 Hz, Ar-**H**). ESI-MS (m/z): 532 (M+1).

BX8: FTIR (KBr, cm^{-1}): 1497 (tri-substituted benzene), 1200 (C-N-C stretching), 1114 (C-O-C).^{1}H-NMR (200 MHz, $CDCl_3$, ppm):δ_H 1.086 (6H, t, J_2 = 5.19 Hz, Ar-CH_2-**CH_3**), 1.140 (12H, t, J_1 = 6.59 Hz, O-CH_2-**CH_3**), 2.252 (3H, s, N-**CH_3**), 2.515 (4H, q, J_2 = 4.99 Hz, Ar-**CH_2**-CH_3), 3.425 (8H, q, J_1 = 6.59 Hz, O-**CH_2**-CH_3), 3.545 (8H, d, J_3 = 5.19 Hz, -**CH_2**-CH-**CH_2**-), 3.641 (4H, s, Ar-**CH_2**-N), 4.377 (2H, t, J_3 = 4.99 Hz, -CH_2-**CH**-CH_2-), 6.665 (2H, d, J_4 = 6.59 Hz, Ar-**H**), 6.869 (2H, s, Ar-**H**), 6.973 (2H, d, J_4 = 6.59 Hz, Ar-**H**). ESI-MS (m/z): 560 (M+1).

BX9: FTIR (KBr, cm^{-1}): 1497 (tri-substituted benzene), 1200 (C-N-C stretching), 1115 (C-O-C). ^{1}H-NMR (200 MHz, $CDCl_3$, ppm):δ_H 1.098 (12H, t, J_1 = 6.58 Hz, O-CH_2-**CH_3**), 2.204 (3H, s, N-**CH_3**), 3.435 (8H, q, J_1 = 6.58 Hz, O-**CH_2**-CH_3), 3.541 (8H, d, J_2 = 4.99 Hz, -**CH_2**-CH-**CH_2**-), 3.623 (4H, s, Ar-**CH_2**-N), 3.684 (6H, s, Ar-O-**CH_3**), 4.273 (2H, t, J_2 = 4.99 Hz, -CH_2-**CH**-CH_2-), 6.733 (2H, d, J_3 = 6.59 Hz, Ar-**H**), 6.888 (2H, s, Ar-**H**), 7.080 (2H, d, J_3 = 6.59 Hz, Ar-**H**) . ESI-MS (m/z): 564 (M+1).

3. Ion extraction property

4.1 Ion extraction property of ring closure and open ring benzoxazines (**BX1 – BX6**)

Pedersen's technique was used to study the interactions between benzoxazines and alkali metal ions. **BX1**, **BX4** and Na^+ picrate provided the maximum absorption peaks at 263, 285 and 356 nm, respectively, whereas the maximum absorption of complexes of **BX1**-Na^+ picrate and **BX4**-Na^+ picrate were found at 333 and 342 nm, respectively (Figure 20). The results implied that the ring closure and the open ring benzoxazines interacted metal ions.

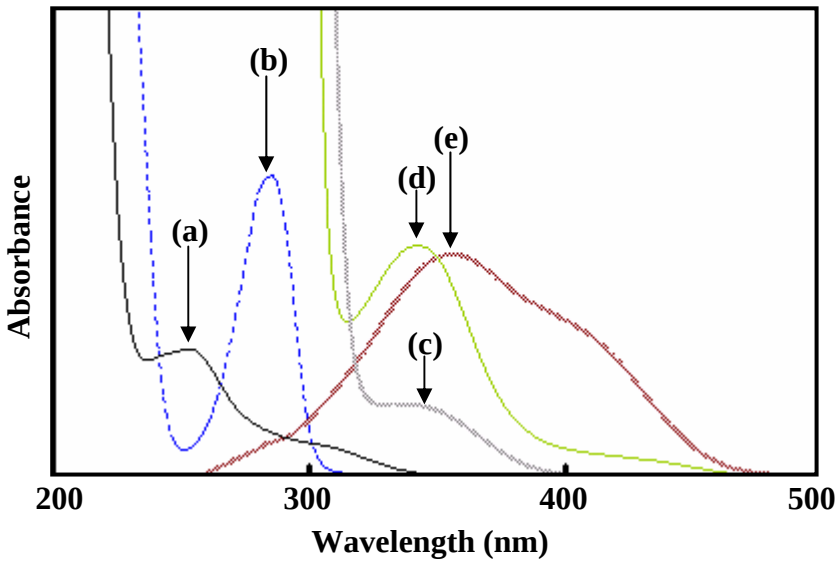


Figure 20 UV-Vis spectra of (a) **BX1**, (b) **BX4**, (c) **BX1**- Na^+ picrate complex, (d) **BX4**- Na^+ picrate complex, and (e) Na^+ picrate.

The extracted organic phase was qualitatively collected and measured by UV-Vis. Figure 20 shows the absorption spectra of **BX1**, **BX4**, Na^+-picrate, and **BX1, BX4** in Na^+-picrate solution. The peak shift implied the complex formation between **BX1, BX4** and Na^+-picrate. The maximum wavelengths of complexes formed between , **BX1-BX9** with Na^+, K^+, and Cs^+ picrates are summarized in Table 1.

Table 1 Peak positions of maximum absorbances of products (**BX1** – **BX6**) and product (**BX1** – **BX6**) -alkali metal ion complexes.

λ_{max} of Guest (Na^+, K^+ and Cs^+) is 355.00 nm

Host	**λ_{max} of product (nm)**	**λ_{max} of Complex (nm)**		
		Na^+	**K^+**	**Cs^+**
BX1	263.00	333.00	333.00	332.50
BX2	263.50	330.00	330.00	330.00
BX3	265.00	346.00	346.00	346.50
BX4	285.00	342.00	342.50	342.50
BX5	290.00	343.50	343.00	343.00
BX6	295.00	345.00	345.00	345.00

The ion extraction percentages of sodium, potassium and cesium picrates with ring closure and open ring benzoxazines (**BX1** – **BX6**) were shown in Figures 21 and 22. For all alkali metal ions, it was found that the ion extraction ability for the ring closure benzoxazines, **BX1** – **BX3** was not significant (Figure 21). When the equimolar concentrations ($7.0x10^{-5}$ M) of benzoxazines and metal picrates were applied, the ring closure benzoxazines (**BX1** – **BX3**) show approximately 2-10% extraction for metal ions. These obtained ring closure benzoxazines obviously perform the ion extraction abilities at ten times lower concentration of metal picrate solution ($7.0x10^{-5}$ M) as compared to those previously reported for ring closure benzoxazines which showed [1-2] the ion extraction abilities at $7.0x10^{-4}$ M.

In the case of ring opening benzoxazines, especially, **BX4** and **BX5**, the ion extraction abilities were significant (>15%) as shown in Figure 22. However, **BX6** showed slightly extraction ability (<10%), although it has another source of electrons as the methoxy group at the para-position of benzene to interact with metal ion. It implied that the structures of the open ring benzoxazines might influence to the molecular assembly formation to interact with metal ions. Consequently, **BX4** formed the suitable cavity for Na^+ and K^+ ions while **BX5** provided the cavity only for Na^+ ion.

Considering the electron withdrawing and electron donating groups of the substituted group on the para-position of benzene, they might affect to electron density in the structures of open ring benzoxazines to interact with metal ions. Methoxy group is an electron withdrawing group while methyl and ethyl groups are electron donating groups. Therefore, the electron density of **BX6** might be decreased whereas that of **BX4** and **BX5** might be increased. The methoxy group of **BX6** did not enhance the ion extraction ability while methyl of **BX4** and ethyl groups of **BX5** provided the significant extraction abilities.

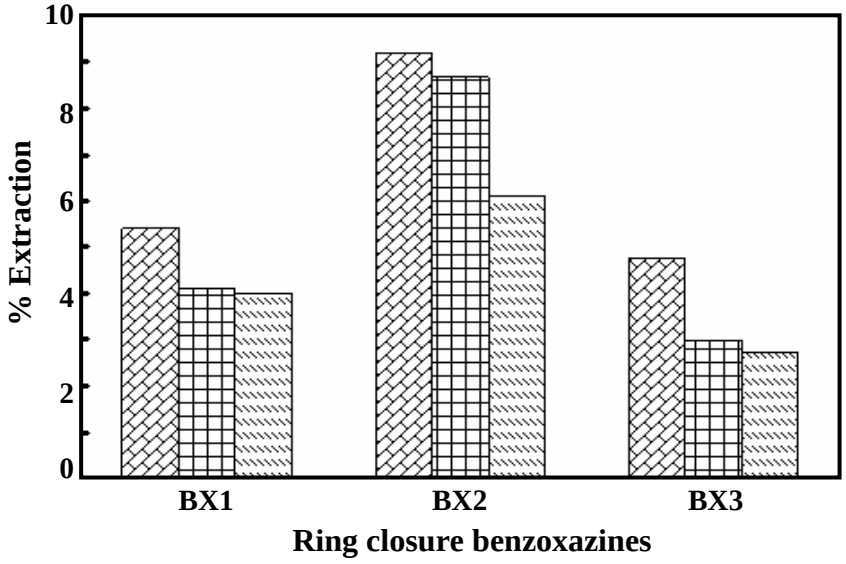


Figure 21 Extraction percentages of sodium picrate (▨) potassium picrate (▦) and cesium picrate (▧) in water at 25°C at equimolar concentration (7.0×10^{-5} M) of benzoxazines and metal picrates: ring closure benzoxazines

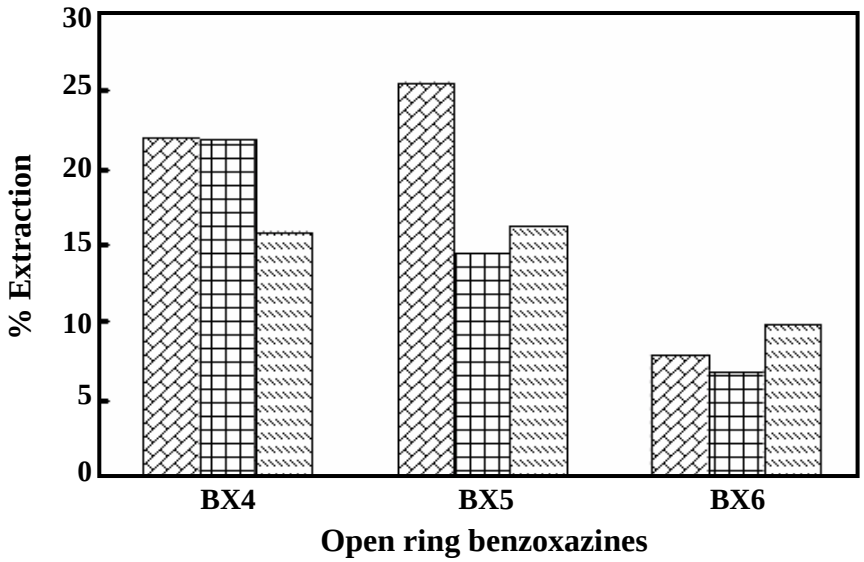


Figure 22 Extraction percentages of sodium picrate (▨) potassium picrate (⊞) and cesium picrate (▧) in water at 25°C at equimolar concentration (7.0 x 10^{-5} M) of benzoxazines and metal picrates: open ring benzoxazines.

4.2 Ion extraction property of etherified benzoxazines (**BX7 – BX9**)

To identify the ion extraction ability of products (**BX7** – **BX9**), Pedersen's technique was applied by using the equimolar concentrations of benzoxazine derivatives and alkali metal picrates under extraction condition at 25°C

The extracted organic phase was qualitatively collected and measured by UV-Vis. Figure 23 shows the absorption spectra of **BX7**, Na^+-picrate, and **BX7** in Na^+-picrate solution. The peak shift implied the complex formation between **BX7** and Na^+-picrate. The maximum wavelengths of complexes formed between, **BX8** and **BX9** with Na^+, K^+, and Cs^+ picrates are summarized in Table 2.

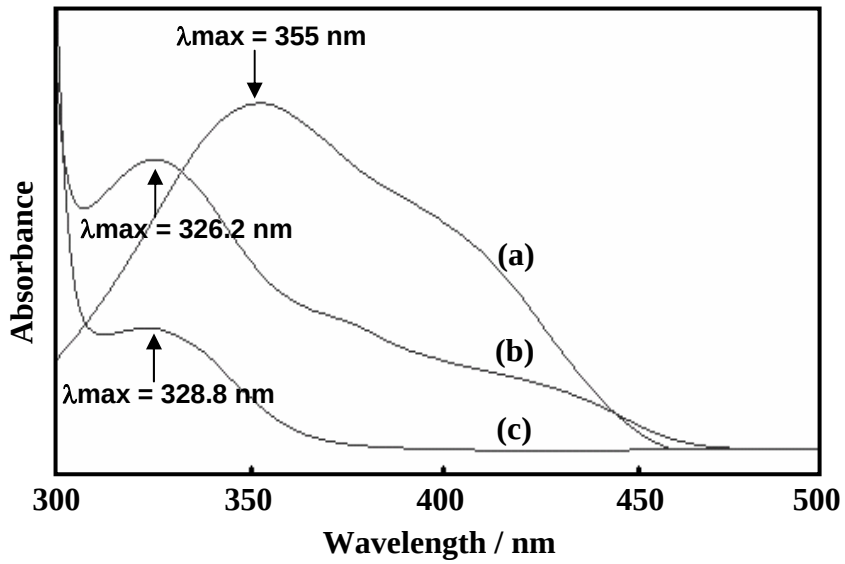


Figure 23 UV spectra of (a) Na^+-picrate (b) **BX7** and (c) the complex of **BX7** and Na^+ picrate.

Table 2 Peak positions of maximum absorbances of etherified benzoxazines and etherified benzoxazine-alkali metal ion complexes.

λ_{max} of Guest (Na^+, K^+ and Cs^+) is 355.00 nm

Host	λ_{max} of Host (nm)	λ_{max} of Host-Guest Complex (nm)		
		Na^+	K^+	Cs^+
BX7	326.20	328.80	328.80	328.40
BX8	326.80	372.20	372.80	372.40
BX9	326.40	360.60	360.40	360.40

Although the original benzoxazine dimers exhibited a supramolecular property, the ion extraction ability at the equimolar concentrations of dimers and metal ions ($7x10^{-5}$ M) was not significant. It is a fact that molecular hydrogen bonds generated in the dimer structure obstruct the ion extraction ability of the original benzoxazine dimers. In addition, two other effects on ion extraction ability of the original benzoxazine dimers were found to be the substituted groups on hydroxyl groups or on benzene rings.

In this present work, by using tosylated 1,3-diethoxy propanol reacted with benzoxazine dimers, the elimination of hydrogen bonds together with an increase in hydrophilicity and lone pair electrons of benzoxazine dimers was carried out. The efficiency of metal ion interaction was evaluated from the aqueous phase by measuring the absorbance before and after extraction to calculate the percentage of ion extraction. Figure 24 summarizes the ion extraction percentage of etherified benzoxazines (**BX7** – **BX9**) and alkali metal ions (Na^+, K^+ and Cs^+ picrates).

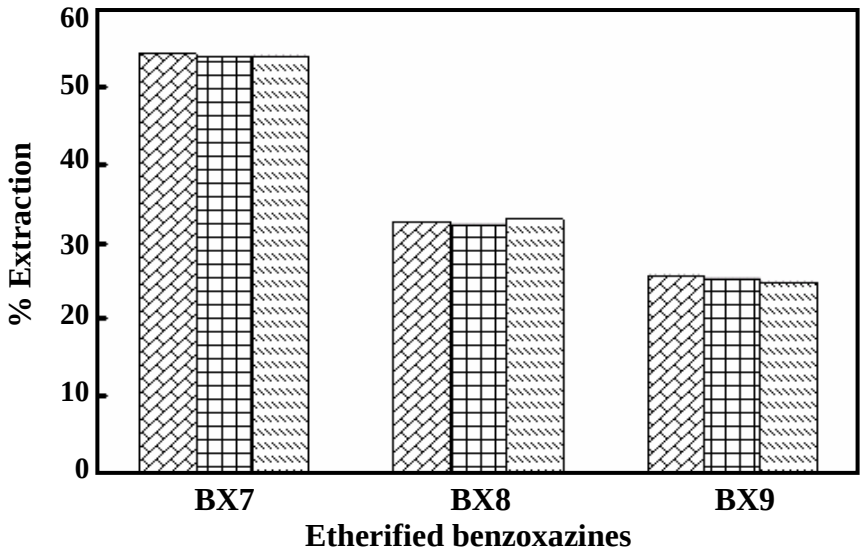


Figure 24 Extraction percentages of sodium picrate (▨) potassium picrate (⊞) and cesium picrate (▧) in water at 25°C at equimolar concentration (7.0 x 10^{-5} M) of benzoxazines and metal picrates: etherified benzoxazines

Etherified benzoxazines (**BX7**–**BX9**), consequently, provide high sensitivity and ion extraction ability at equimolar concentration of benzoxazines and ions ($7x10^{-5}$ M) as shown in Figure 24. However, all etherified benzoxazines (**BX7**–**BX9**) showed no selectivity on each alkali ion guest, Na^+, K^+ and Cs^+. It might be the fact that the interaction between dimers and metal ions was induced by the molecular assembly and dimer molecules provide the flexible structure for all types of metal ions to be allowed in the channel.

These results provide us information on how ion extraction ability changes when the hydrogen bond was eliminated and structures of dimers were modified.

It is conceivable that substituted groups in the benzene ring might be one reason for the ion extraction ability of etherified benzoxazines. Due to the additional lone pair electrons from the oxygen atom belonging to methoxy group, the -OCH_3 substituted group at the para-position in benzene ring of **BX9** was expected to provide much higher ion extraction ability than that of –CH_3 in **BX7** and –C_2H_5 in **BX8**. The results, however, are the opposite. The results in Figure 20 show that **BX7** provided the highest extraction ability to all metal ions (~50%); while that of **BX9** had the lowest efficiency (~25%). **BX7** with a methyl substituted group might form a loosely assembled structure, and have a favorable space to interact with metal ions.

The results imply that the difference in ion extraction might be due to the structure of etherified benzoxazines and the molecular assembly formation, although etherified benzoxazines (**BX7**-**BX9**) showed no ion selectivity.

4.2.1 Stoichiometry of etherified benzoxazines-ion interaction

As this was the first time to study the interaction of benzoxazines based dimer with metal ions via the molecular assembly, the stoichiometric ratio of each etherified benzoxazines (**BX7** – **BX9**) to Na^+, K^+ and Cs^+ was determined. By using the equimolar concentrations ($7x10^{-5}$ M) of benzoxazines and metal species, the percentage of ion extraction determined by Pedersen's technique was used to calculate the molar ratios of etherified benzoxazines to metal ion. The different stoichiometric ratios of each etherified benzoxazine-ion interaction were found and are presented in Table 3.

The **BX7**, **BX8**, and **BX9** provided the 50%, 30%, and 25% extraction abilities, respectively; their complexations were, therefore, confirmed by ^{1}H-NMR spectroscopy.

Table 3 Host-Guest ratios of etherified benzoxazines with alkali metal ions.

Host	Host-Guest ratio		
	Na+	**K+**	**Cs+**
BX7	2:1	2:1	2:1
BX8	3:1	3:1	3:1
BX9	4:1	4:1	4:1

4.2.2 Ion interaction studies by ^{1}H-NMR

^{1}H-NMR is an effective method to qualitatively and quantitatively study the inclusion phenomena. By solid-liquid extraction, an excess amount of solid potassium picrate was added into the solutions of **BX7**, **BX8**, and **BX9** in $CDCl_3$. Dissolution of picrate salt turns colorless $CDCl_3$ to yellow. The peak shifts in ^{1}H-NMR spectra provide useful information of complexation while the integration ratios between picrate protons and protons of etherified benzoxazine can be used to evaluate the host-guest ratio. Thus, the picrate peak at 8.8 ppm will be observed whenever the host-metal complexes are formed.

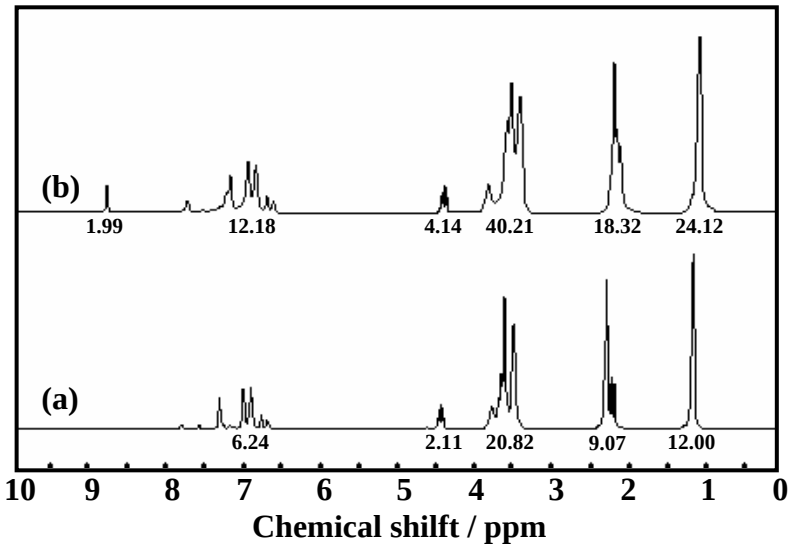


Figure 25 ^{1}H-NMR spectra of (a) **BX7** and (b) the complex between **BX7** and potassium picrate.

Figures 25 and 26 (a) clarify that chemical shifts of **BX7** changed after extraction with potassium picrate, especially, methyl protons of aza group ($-NCH_3$), methylene protons of aza-methylene linkage ($-CH_2-N-$), and protons of 1,3-diethoxy-2-propoxy groups. This implies that **BX7** interacts with K^+ ion via the lone pair electrons of nitrogen and oxygen atoms. In addition, the results indicate that K^+ ion sit in the upper rim of **BX7**on complexation. The integration ratio of picrate and methine protons was investigated to determine the host-guest ratio. **BX7** showed a host-guest ratio of 2:1 for K^+ ions as corresponded to the results from liquid-liquid extraction.

In the case of **BX9**, the peaks of methyl protons belonging to N-CH3 and methylene linkage ($-CH_2-N-$) were obviously shifted (Figure 26 (b)) while the protons of 1,3-diethoxy-2-propoxy groups were slightly changed. This hints at the possibility that the interaction between **BX9** and K^+ ion is only induced at nitrogen atom. In addition, it was found that the peak of methoxy protons was insignificantly moved after extraction. This suggests that the methoxy groups at para-positions of aromatic rings might not enhance the extraction ability of **BX9**. Thus, **BX9** provides the highest host-guest ratio (4:1) as compared to **BX7** (2:1) and **BX8** (3:1).

It is important to note that the ion extraction ability depends on the original structures of benzoxazine dimers (**BX7**– **BX9**) even if the modifications are done with the same procedure.

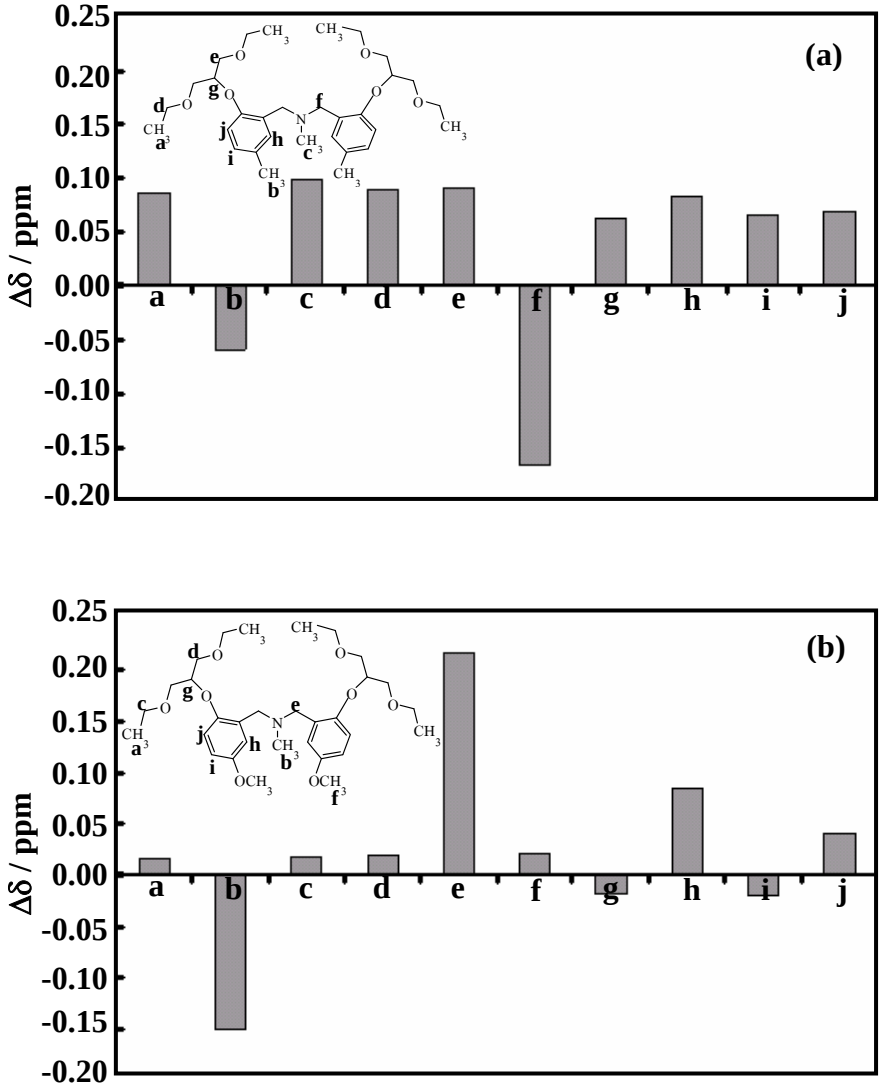


Figure 26 Δδ of (a) the complex of **BX7** with K^+ picrate and (b) the complex of **BX9** with K^+ picrate.

4.2.3 Ion interaction studies by ESI-MS

To study the host-guest compounds formation via molecular assembly, electrospray ionization mass spectroscopy (ESI-MS) was applied as seen in the complexation of macrolides. The complex between **BX7** and K^+ was, therefore, elucidated by ESI-MS. Figure 27 shows the parent peak (M+1) at m/z = 1102 which is equal to the molecular weight of the complex between two molecules of **BX7** and one K+ ion. The result implies that **BX7** forms an assembly structure with the host-guest ratio of 2:1 as corresponding to the results from liquid-liquid extraction and ^{1}H-NMR.

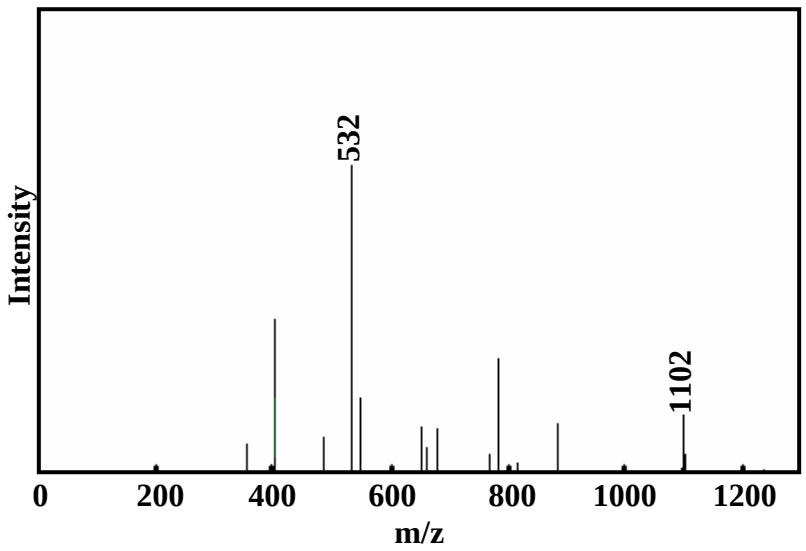


Figure 27 ESI-MS spectrum of the complex between **BX7** and potassium ion.

CONCLUSIONS

Benzoxazine supramolecular structures with linear aliphatic linkage were successfully prepared via Mannich and ring opening reactions. These simple reactions were effective for synthesizing the ring closure and ring opening benzoxazines via molecular designs and provided the high yield products without using any specific catalyst. The ring closure and open ring benzoxazines were interacted with metal ions via molecular assembly. By using Mannich reaction and molecular designs, the novel ring closure supramolecular benzoxazines with alkali ion extraction abilities were successfully prepared. These ring closure benzoxazines were used as starting materials for synthesizing the novel open ring supramolecular benzoxazines. By UV-Vis studies, it was indicated that the structures of open ring benzoxazines affected to their molecular assembly formation and ion extraction abilities.

In addition, we successfully prepared the novel benzoxazine derivatives (**BX7 – BX9**) via molecular design based on benzoxazine dimer structure. By using a simple and effective reaction of etherification, the desired products with high yield were obtained. The products exhibited the unique property as supramolecules to interact with alkali metal ions. Additionally, this present work gives us lead to achieve well-defined benzoxazine derivative products exhibiting the stoichiometric interaction with metal ions.

LITERATURE CITED

Arduni, A., A. Pochini, S. Reverberi and R. Ungaro. 1986. The preparation and properties of a new lipophilic sodium selective ether ester ligand derived from p-t-butylcalix[4]arene. **Tetrahedron.** 42: 2089-2100.

Baoming, J. 1998. The inclusion behavior of benzo-15-crown-5 with hydrate transition metal picrate. **Chemistry Letters.** 17: 4327-4330.

Böhmer, V. 1995. Calixarenes, macrocycles with (almost) unlimited possibilities. **Angewandte Chemie International Edition.** 34: 713-745.

Chankvetadze, B., G. Endresz and G. Blaschke. 1996. Charged cyclodextrin derivatives as chiral selectors in capillary electrophoresis. **Chemical Society Reviews.** 141-153

Chirachanchai, S., A. Laobuthee and H. Ishida. 1999. A Novel Ion Extraction Material Using Host-Guest Properties of Oligobenzoxazine Local structure and Benzoxazine Monomer Molecular Assembly. **Journal Applied Polymer Sciences.** 77: 2561-2568

Chirachanchai, S., A. Laobuthee, H. Ishida and K. Tashiro. 2000. Self-Terminated of Benzoxazine Ring Opening Polymerization and Generation of Asymmetric Typed Monooxazine-benzoxazine Dimer. **26th Congress on Science and Technology of Thailand.** 737.

Chirachanchai, S., S. Phongtamrug and A. Laobuthee. 2003. A simple, effective and selective synthesis route without template effect (Part II) for [2+2] difunctional 28-membered macrocyclic ethers based on benzoxazine dimers and its inclusion phenomena with metal ions. **Chemistry Letters.** 32: 432-433.

Chirachanchai, S., S. Phongtamrug and A. Laobuthee. 2008. Self termination of ring opening reaction of *p*-substituted phenol-based benzoxazines: An obstructive effect via intramolecular hydrogen bond. **Journal of Heterocyclic Chemistry.** (In press).

Dobrawa, R. and F. Würthner. 2005. Metallosupramolecular approach toward functional coordination polymers. **John Wiley & Son**, **Ltd**. 43: 4981-4995.

Fischer, E. 1894. Einfluss der Configuration auf die Wirkung der Enzym. **Berichte der Deutschen Chemischen Gesellschaft**. 27: 713-745.

Ganem, B. and Y.-T. Li. 1991. Detection of noncovalent receptor-ligand complexes by mass spectrometry. **Journal of American Chemical Society.** 113: 6294-6296.

Gutscher, D. 1983. Calixarenes. **Accounts of Chemical Research.** 16: 161-170.

Hiraoka, M. 1982. Crown Compounds: Their Characteristics and Applications. **Elsevier Science & Technology.** 275.

Ho-Dong Kim. and H. Ishida. 2003. Model Compound Study on the Network Structure of Polybenzoxazine. **Macromolecules.** 36: 8320-8329.

Ishida, H. and C.M. Krus. 1998. Synthesis and Charcterization of Structurally Uniform Model Oligomer of Polybenzoxazine. **Macromolecules.** 31: 2409-2418.

Izatt, R. M., J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen. 1985. Thermodynamic and kinetic data for cation-macrocycle interaction. **Chemical Reviews.** 85: 271-339.

Jonathan, W.S. and L.A. Jerry. 2000. Supramolecular Chemistry. **John Wiley & Son**, **Ltd.** New York, 4-5, 88-94, 98-99, 107-109.

Kroschwitz, J.I. and Howegrant, M. (Eds.). 1995. Inclusion compounds. **Encyclopedia of Chemical Technology.** 14: 122-154.

Laobuthee, A. 2002. Molecular designs and development of mono-substituted phenol-based benzoxazines: a controlled structure at molecular level and their unique supramolecular chemistry. Ph. D. **Thesis in Polymer Science, The Petroleum and Petrochemical College**, Chulalongkorn University, Bangkok, Thailand.

Laobuthee, A. 2004. Effect of Benzoxazine Rings and Electron Donor Group of Benzoxazine Dimer, Esterified Benzoxazine Dimer and Macrocyclic onto Inclusion Phenomena with Metal Picrate. **International of Materials and Structural Reliability.** 2: 135-147.

Laobuthee, A., B. Pulpoka and S. Chirachanchai. 2001. Synthesis of Macrocyclic Compound from Benzoxazine Dimer Derivatives. **27th Congress on Science and Technology of Thailand.** 920.

Laobuthee, A., H. Ishida and S. Chirachanchai. 2003. Metal ion guest responsive benzoxazine dimers and inclusion phenomena of cyclic derivatives**. Journal of Inclusion Phenomena and Macrocyclic Chemistry.** 47: 179-185.

Laobuthee, A., S. Chirachanchai., H. Ishida and K. Tashiro. 2001. Asymmetric mono-oxazine: an inevitable product from Mannich reaction of benzoxazine dimers. **Journal of American Chemical Society.** 123: 9947-9955.

Miyata, M., M. Shibakami, S. Chirachanchai, K. Takemoto, N. Kasai and K. Miki. 1990. Guest-responsive structural changes in cholic acid intercalation crystals. **Nature.** 343: 446-447.

Nakano, K., K. Sada and M. Miyata. 1996. Novel additive effect of inclusion crystals on polymorphs–cholic acid crystals having different hydrogen-bonded networks with the same organic guest. **Chemical Communications.** 989-990.

Pacharaprakiti, R. 2001. Molecular design of benzoxazines an approach for inclusion compounds. MS. D. **Thesis in Polymer Science, The Petroleum and Petrochemical College**, Chulalongkorn University, Bangkok, Thailand.

Pedersen, C. J. 1967. Cyclic polyethers and their complexes with metal salts. **Journal of American Chemical Society.** 89: 7017-7036.

Pedersen, C. J. and H. K. Frensdorff. 1972. Macrocyclic Polyethers and Their Complexes. **Angewandte Chemie International Edition.** Int. Ed. Engl. 11: 16-25.

Rungsimanon, T. 2008. Development of *N*,*N*-Bis(2-hydroxyalkylbenzyl)alkyllamine derivatives to crown ethers based macrocycles. Ph. D. **Thesis in Polymer Science, The Petroleum and Petrochemical College**, Chulalongkorn University, Bangkok, Thailand.

Rungsimanon, T., A. Laobuthee and S. Chirachanchai. 2008. [1+1] and [2+2] crown ethers derived from *N*,*N*-Bis(2-hydroxyalkylbenzyl)alkyllamine and their inclusion phenomena with metal ions. **Journal of Inclusion Phenomena and Macrocyclic Chemistry**. (In press).

Shinkai, S. 1993. Calixarenes: the third generation of supramolecules. **Tetrahedron.** 49, 8933-8968.

Siripattanasarakit, W. 1997. A novel type of ion extraction material using host – guest properties of polybenzoxazine local strucyure. MS. D. **Thesis in Polymer Science, The Petroleum and Petrochemical College**, Chulalongkorn University, Bangkok, Thailand.

Sone, T., Y. Ohba and H. Yamazaki. 1989. Inclusion Properties of Acyclic p-Substituted Phenol–Formaldehyde Oligomers. **Bulletin of the Chemical Society of Japan.** 62: 1111.

Yamagishi, T., K. Tani, H. Ishida and Y. Nakamoto. 1994. Linear all-ortho oligomers of phenol-formaldehyde resins. **Polymer Bulletin.** 33: 281.

.

APPENDIX

Appendix Table 1 Peak positions of maximum absorbances of alkali metal picrate.

No.	λ_{max} of metal picrates (nm)		
	Na^+	K^+	Cs^+
1	355.00	355.00	355.00
2	355.00	355.00	355.00
3	355.00	355.00	355.00
mean	**355.00**	**355.00**	**355.00**

Appendix Table 2 Absorbances of alkali metal picrate at wavelength 355.00 nm.

No.	Initial absorbance of metal picrates (A_o)		
	Na^+	K^+	Cs^+
1	0.997	0.996	0.995
2	0.994	0.995	0.998
3	0.995	0.995	0.994
mean	**0.995**	**0.995**	**0.996**

Appendix Table 3 The percentage extraction of **BX1 - BX9** and sodium picrate.

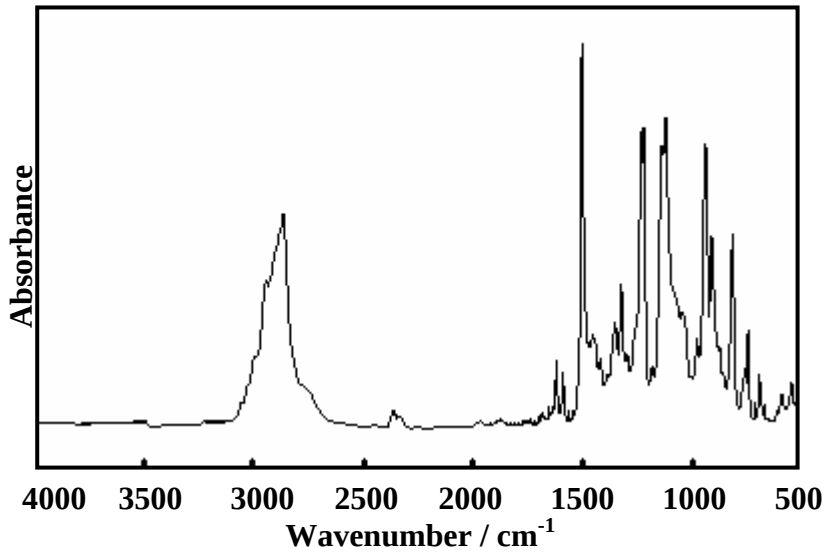
Type of Host	Absorbance of Na^+ picrate after extraction (A)				% Extraction
	1	**2**	**3**	**mean**	
BX1	0.940	0.943	0.947	**0.943**	**5.23**
BX2	0.900	0.904	0.907	**0.903**	**9.25**
BX3	0.950	0.944	0.947	**0.947**	**4.82**
BX4	0.771	0.780	0.777	**0.776**	**22.01**
BX5	0.745	0.743	0.747	**0.745**	**25.13**
BX6	0.898	0.921	0.854	**0.915**	**8.04**
BX7	0.449	0.453	0.458	**0.453**	**54.44**
BX8	0.675	0.671	0.668	**0.671**	**32.53**
BX9	0.727	0.749	0.745	**0.740**	**25.59**

Appendix Table 4 The percentage extraction of **BX1 - BX9** and potassium picrate.

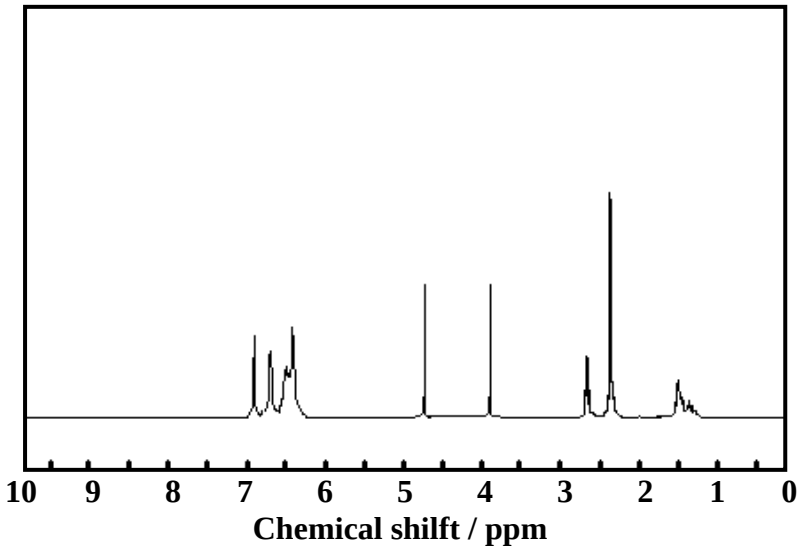
Type of Host	Absorbance of K^+ picrate after extraction (A)				% Extraction
	1	**2**	**3**	**mean**	
BX1	0.952	0.958	0.955	**0.955**	**4.02**
BX2	0.909	0.912	0.904	**0.908**	**8.74**
BX3	0.967	0.963	0.968	**0.965**	**3.01**
BX4	0.781	0.776	0.777	**0.778**	**21.81**
BX5	0.850	0.845	0.855	**0.850**	**14.57**
BX6	0.926	0.927	0.927	**0.926**	**6.93**
BX7	0.461	0.461	0.453	**0.458**	**53.94**
BX8	0.679	0.677	0.669	**0.675**	**32.16**
BX9	0.736	0.748	0.751	**0.745**	**25.13**

Appendix Table 5 The percentage extraction of **BX1 - BX9** and cesium picrate.

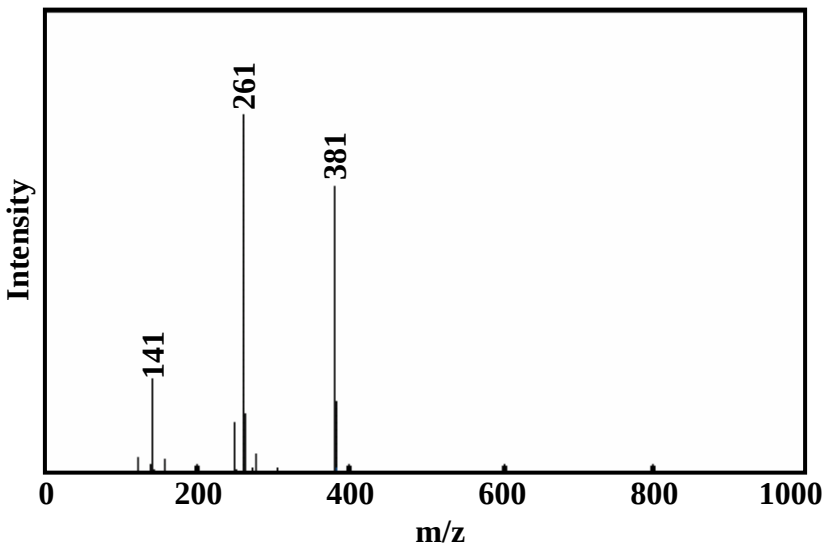
Type of Host	Absorbance of Cs^+ picrate after extraction (A)				% Extraction
	1	2	3	mean	
BX1	0.957	0.956	0.957	**0.956**	**4.02**
BX2	0.933	0.934	0.935	**0.934**	**6.22**
BX3	0.973	0.960	0.963	**0.965**	**3.11**
BX4	0.835	0.839	0.833	**0.836**	**15.97**
BX5	0.823	0.831	0.798	**0.817**	**17.97**
BX6	0.895	0.893	0.898	**0.895**	**10.14**
BX7	0.449	0.473	0.451	**0.458**	**54.05**
BX8	0.661	0.669	0.673	**0.668**	**32.97**
BX9	0.752	0.755	0.743	**0.750**	**24.70**



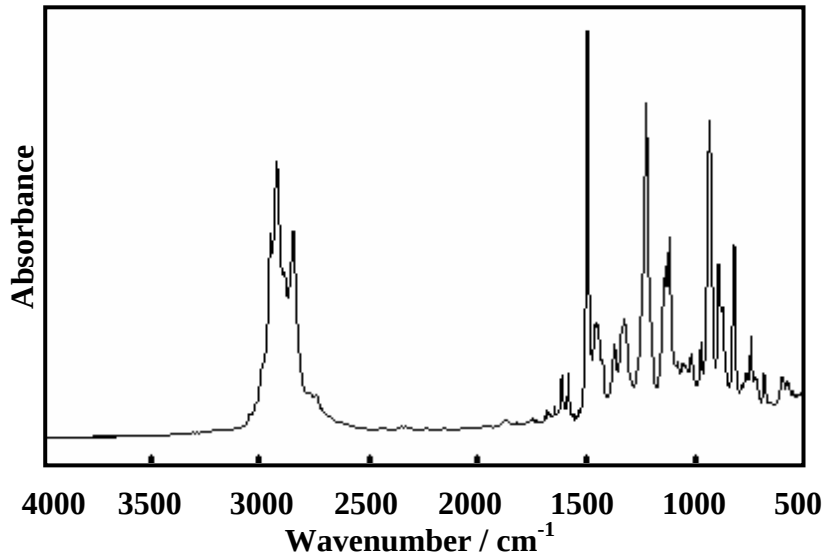
Appendix Figure 1 FTIR spectrum of **BX1**.



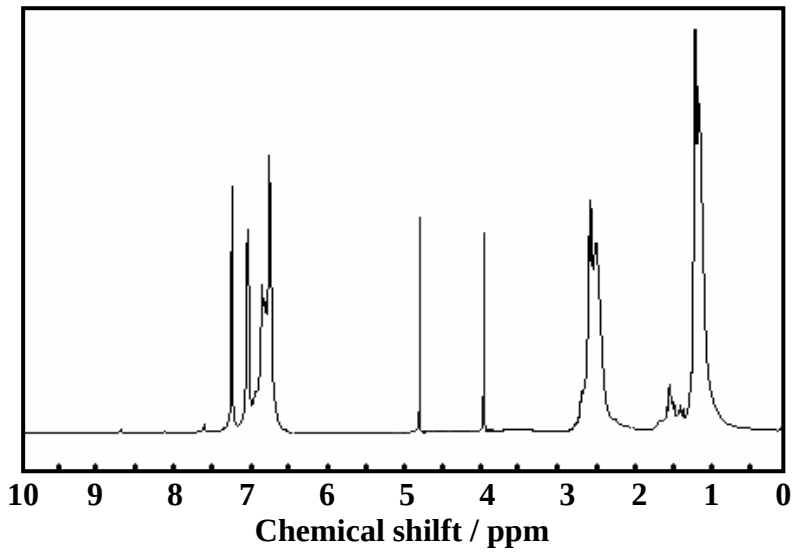
Appendix Figure 2 ^{1}H-NMR spectrum of **BX1**.



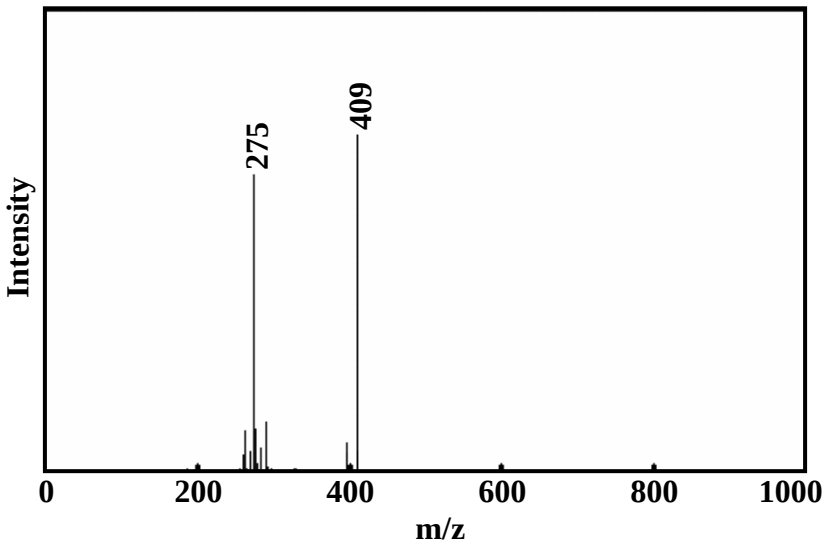
Appendix Figure 3 ESI-MS spectrum of **BX1**.



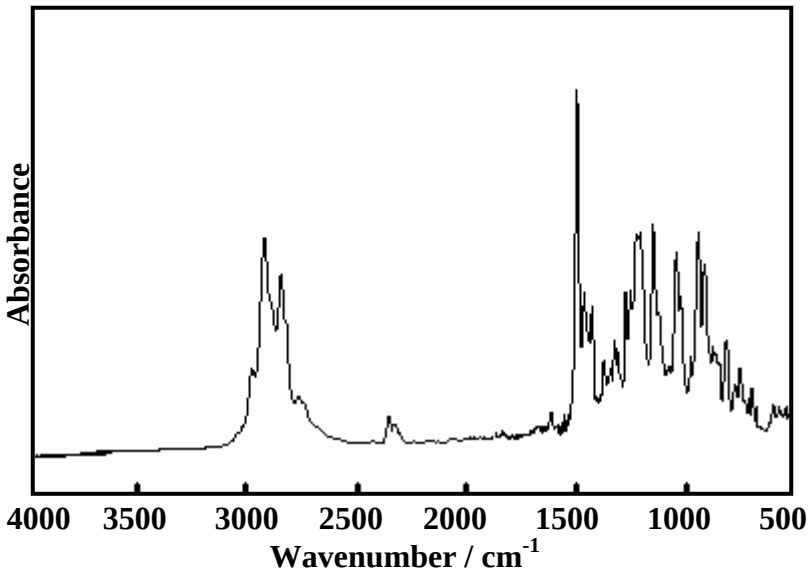
Appendix Figure 4 FTIR spectrum of **BX2**.



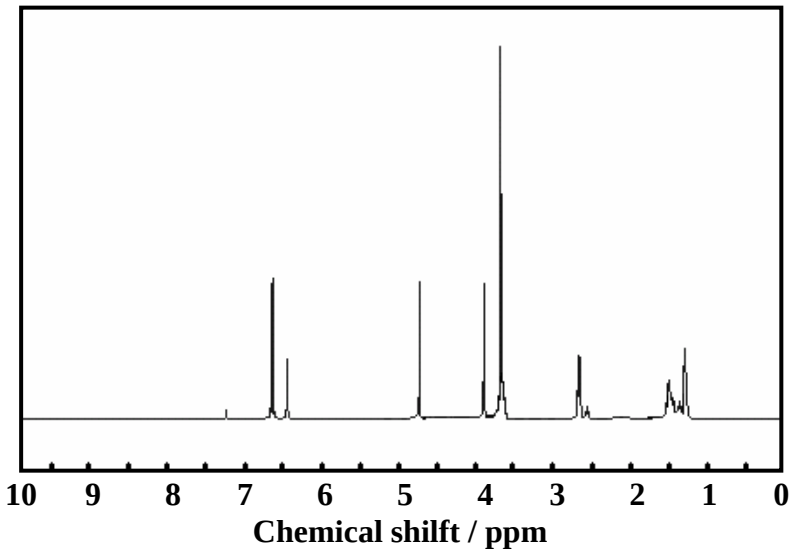
Appendix Figure 5 ^{1}H-NMR spectrum of **BX2**.



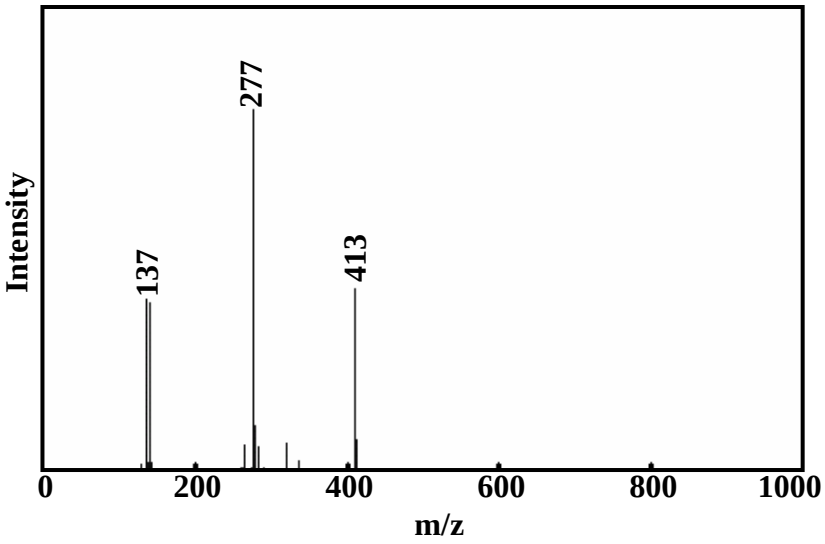
Appendix Figure 6 ESI-MS spectrum of **BX2**.



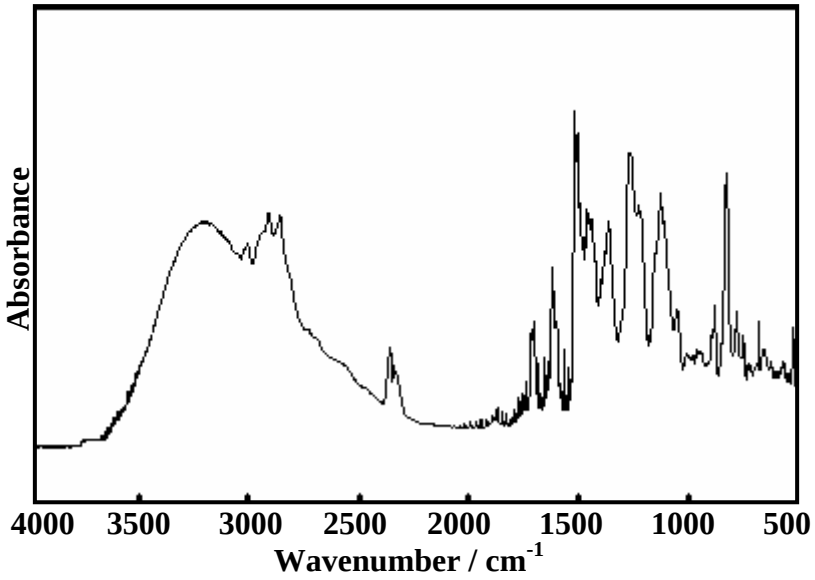
Appendix Figure 7 FTIR spectrum of **BX3**.



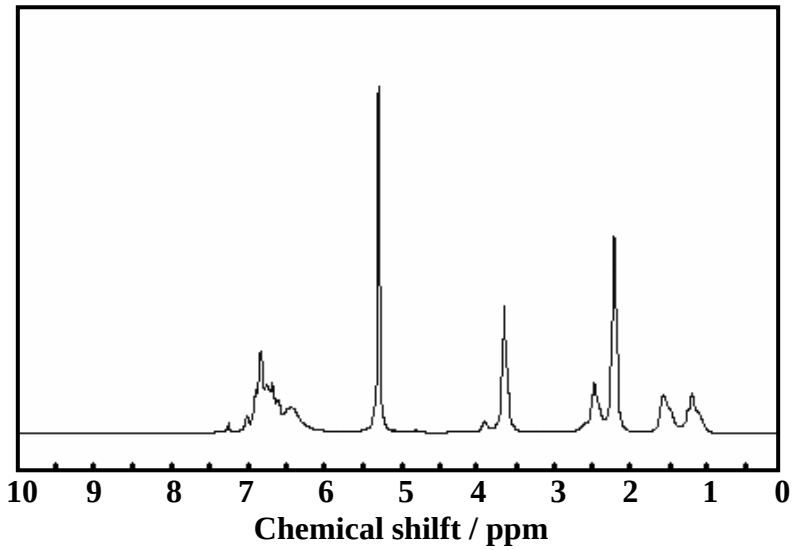
Appendix Figure 8 ^{1}H-NMR spectrum of **BX3**.



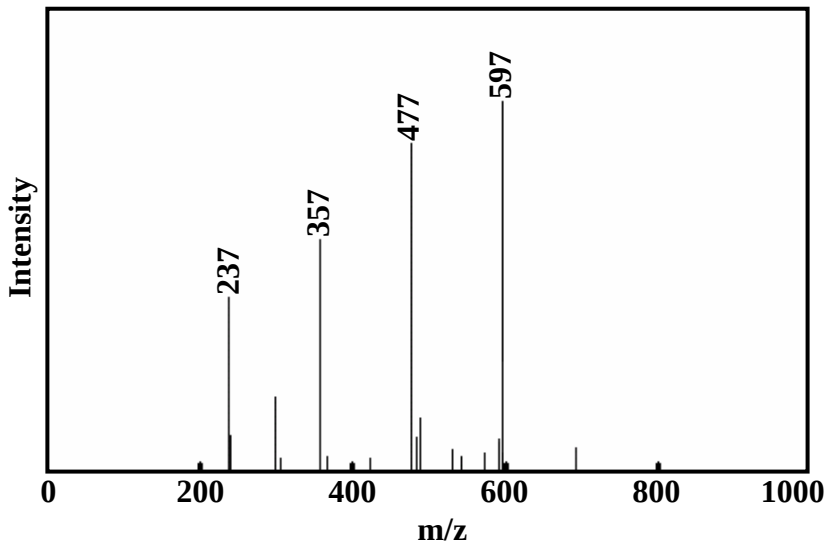
Appendix Figure 9 ESI-MS spectrum of **BX3**.



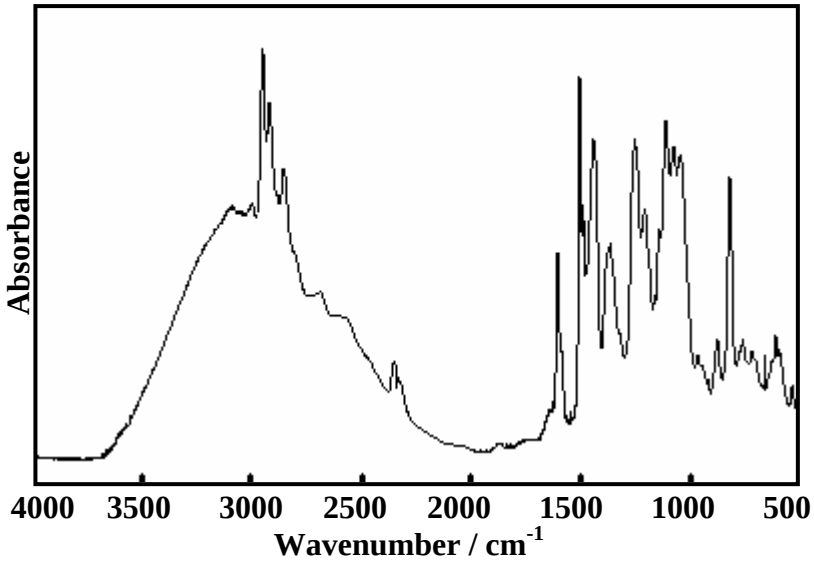
Appendix Figure 10 FTIR spectrum of **BX4**.



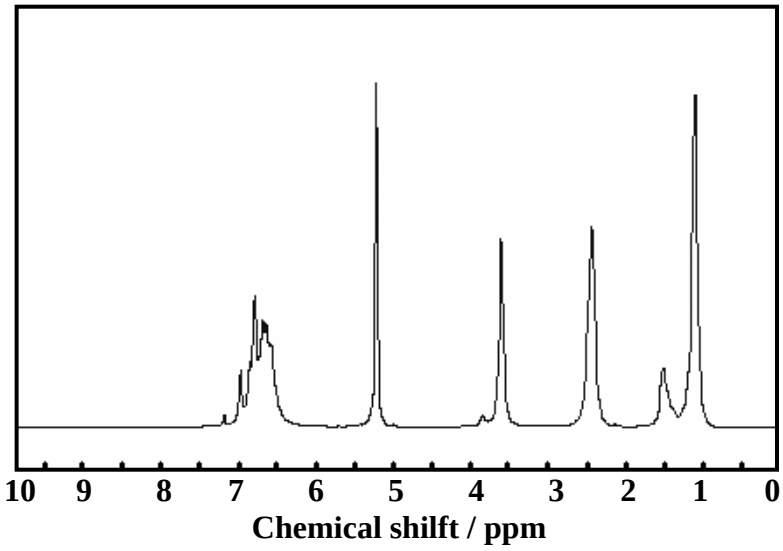
Appendix Figure 11 ^{1}H-NMR spectrum of **BX4**.



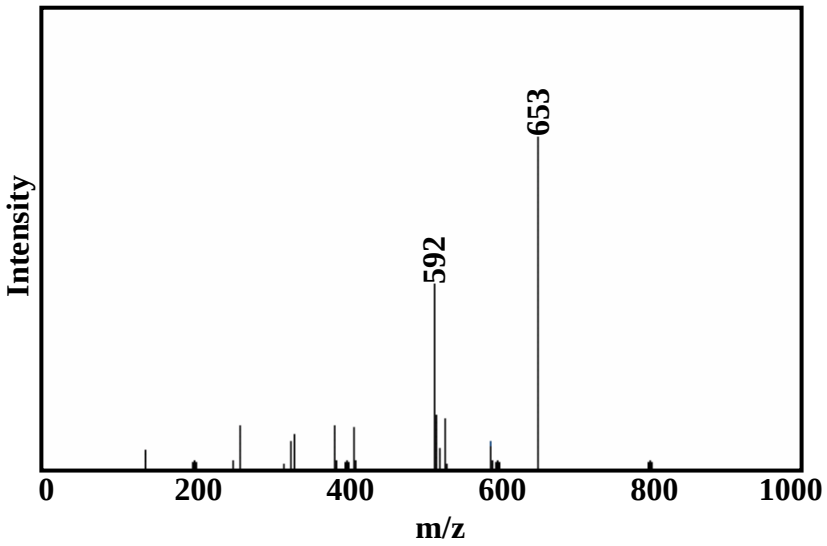
Appendix Figure 12 ESI-MS spectrum of **BX4**.



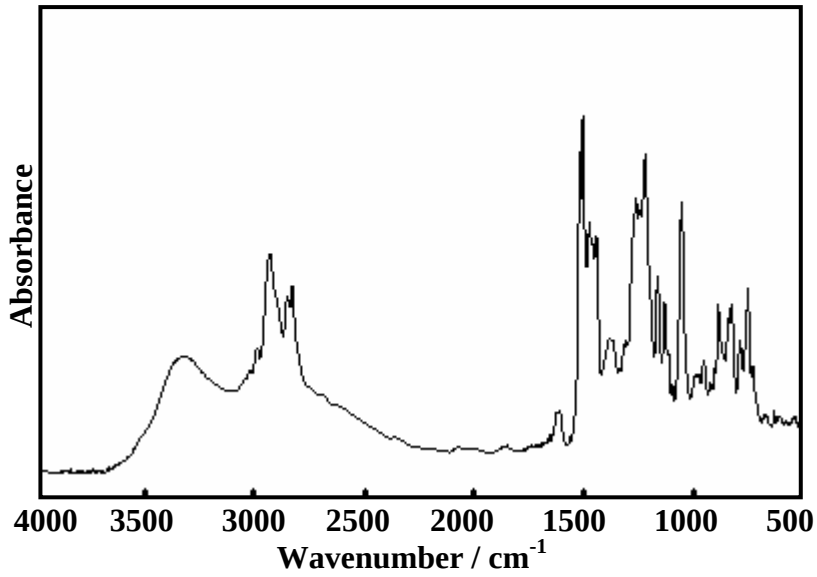
Appendix Figure 13 FTIR spectrum of **BX5**.



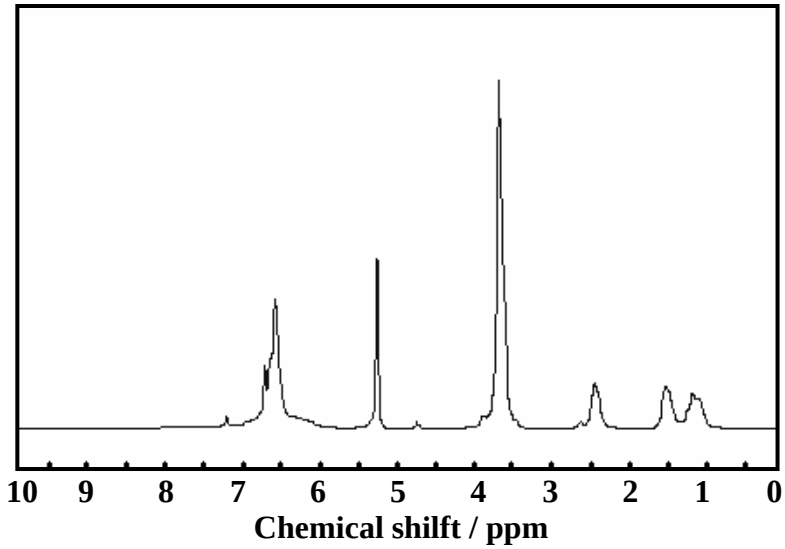
Appendix Figure 14 ^{1}H-NMR spectrum of **BX5**.



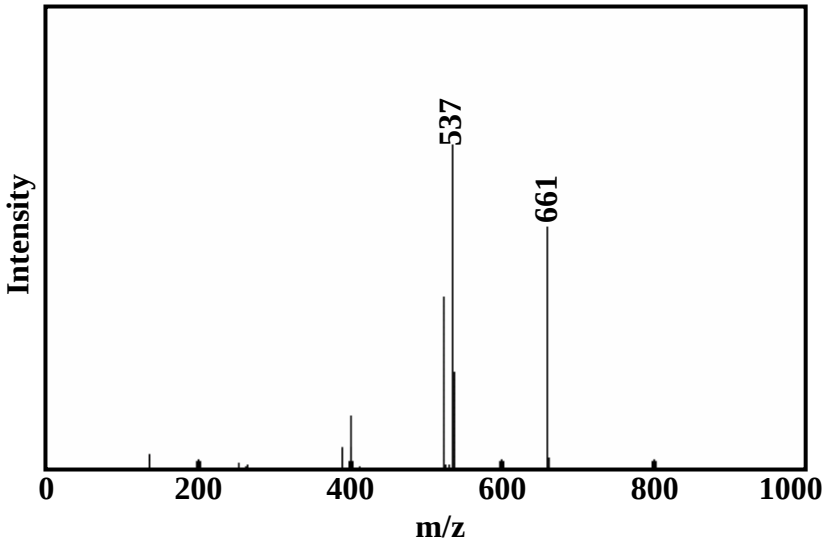
Appendix Figure 15 ESI-MS spectrum of **BX5**.



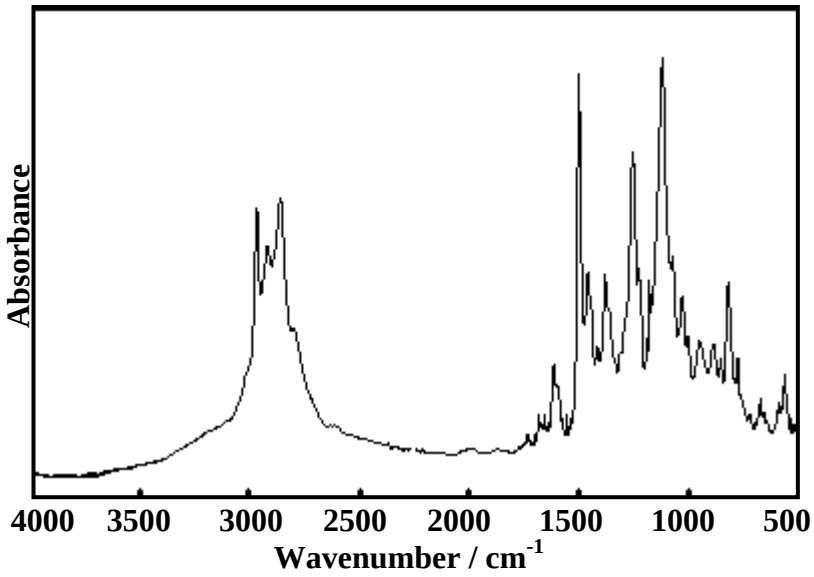
Appendix Figure 16 FTIR spectrum of **BX6**.



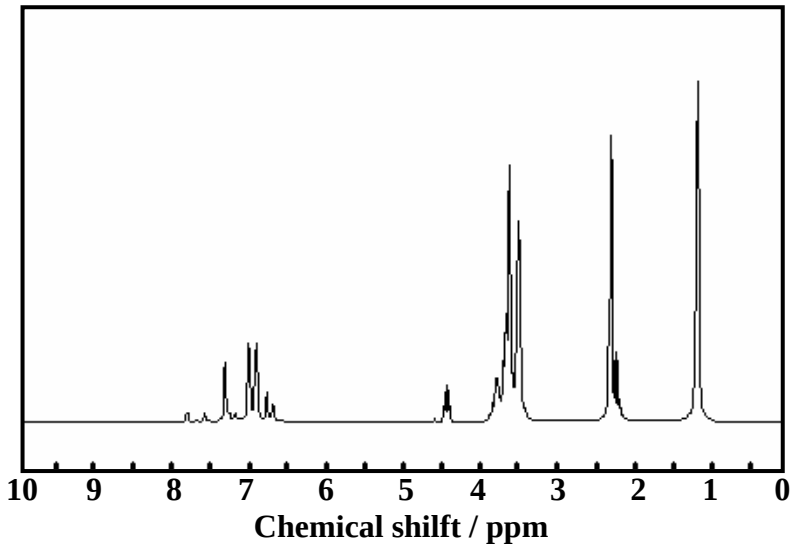
Appendix Figure 17 ^{1}H-NMR spectrum of **BX6**.



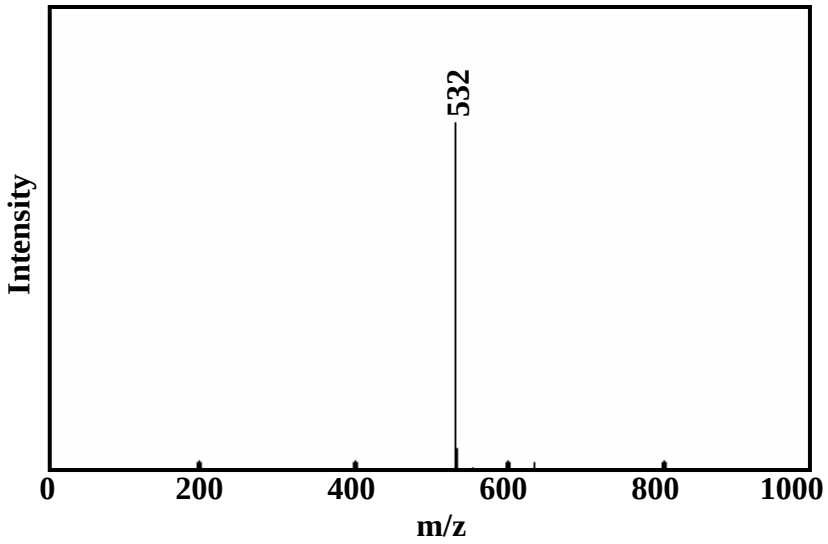
Appendix Figure 18 ESI-MS spectrum of **BX6**.



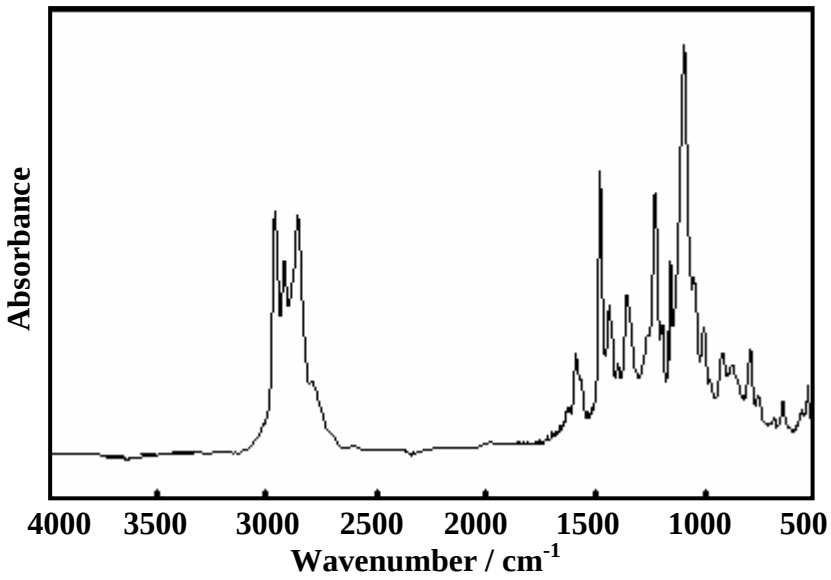
Appendix Figure 19 FTIR spectrum of **BX7**.



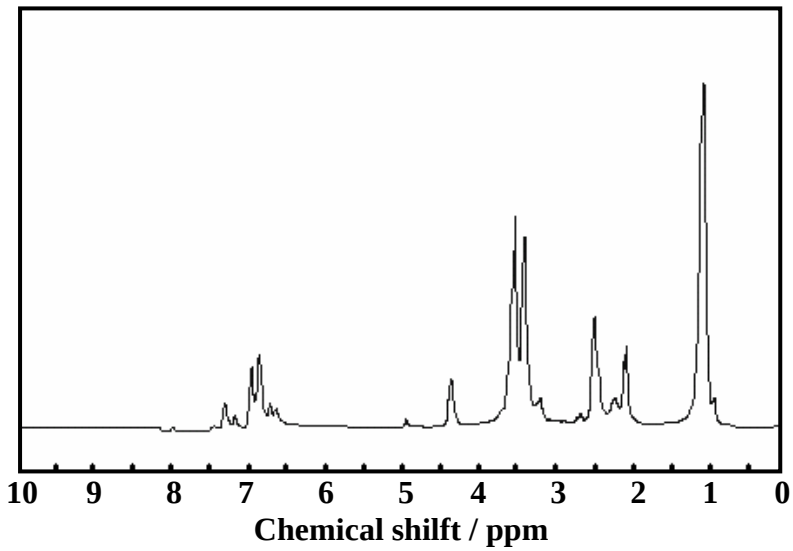
Appendix Figure 20 ^{1}H-NMR spectrum of **BX7**.



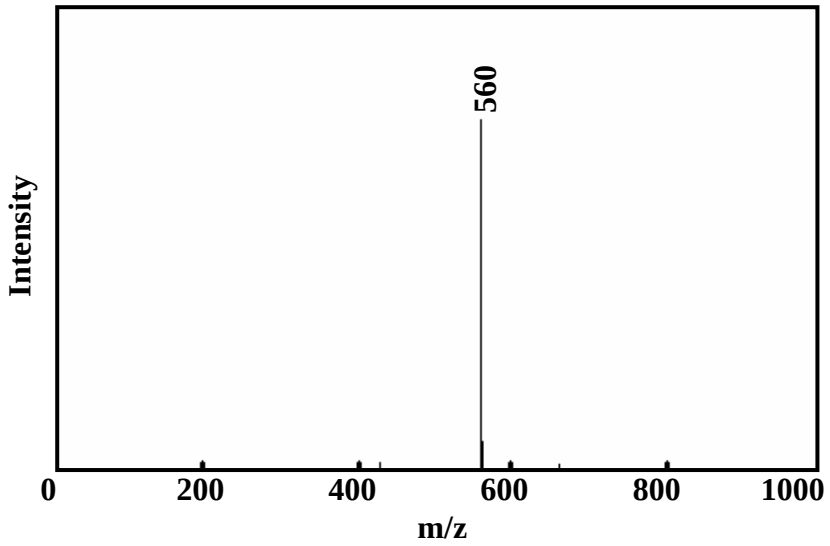
Appendix Figure 21 ESI-MS spectrum of **BX7**.



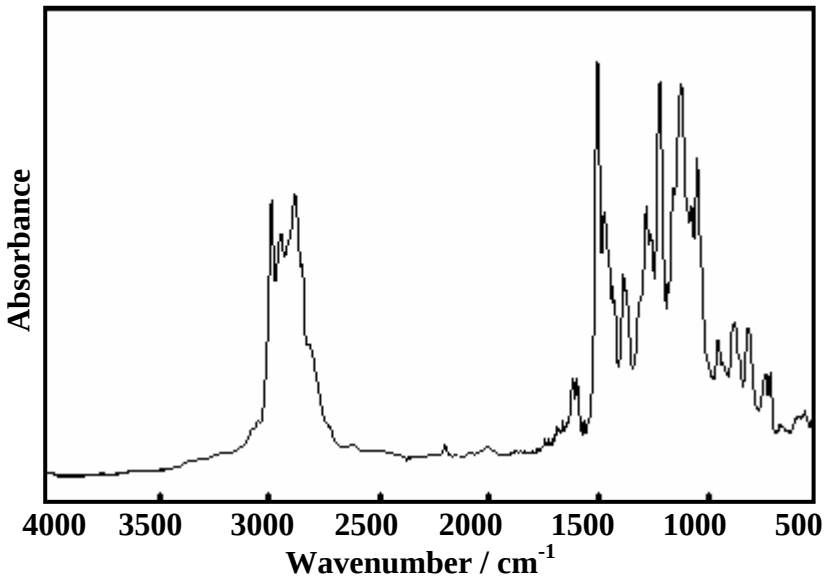
Appendix Figure 22 FTIR spectrum of **BX8**.



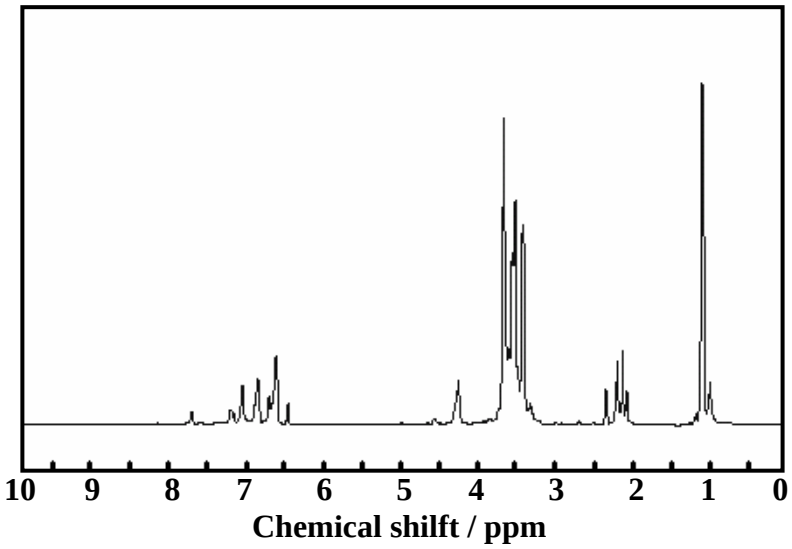
Appendix Figure 23 ^{1}H-NMR spectrum of **BX8**.



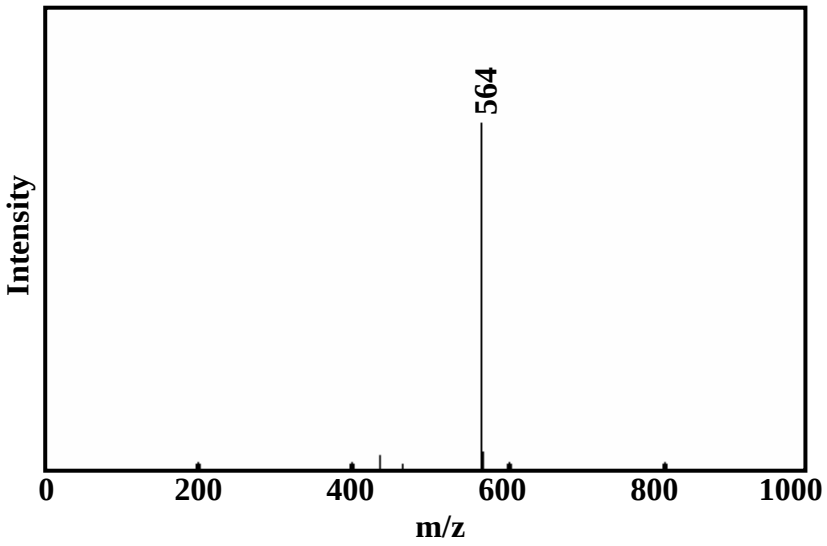
Appendix Figure 24 ESI-MS spectrum of **BX8**.



Appendix Figure 25 FTIR spectrum of **BX9**.



Appendix Figure 26 ^{1}H-NMR spectrum of **BX9**.



Appendix Figure 27 ESI-MS spectrum of **BX9**.

CIRRICULUM VITAE

NAME : Mr. Attaphon Kaewvilai

BIRTH DATE : April 17, 1984

BIRTH PLACE : Bangkok, Thailand

EDUCATION :

YEAR	ISTITUTE	DEGREE/DIPLOMA
2007	Phranakhon Rajabhat University	B.Sc. (Chemistry)

POSITION/TITLE : Postgraduated student

WORK PLACE : Department of Materials Engineering
Faculty of Engineering, Kasetsart University