โบรมิเนชันสารแอโรแมติกโดยใช้โซเดียมโบรไมด์/ โซเดียมไฮโปคลอไรต์

นางสาวนฤมล กาเผือก

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BROMINATION OF AROMATIC COMPOUNDS USING SODIUM BROMIDE / SODIUM HYPOCHLORITE

Miss Naruemon Kapuch

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
Faculty of Science
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Thesis Advisor	Associate Professor Amorn Petsom, Ph.D.

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โซเดียมโบรไมด์/ โซเดียมไฮโปคลอไรต์ เป็นโบรมิเนตทิงและคลอริเนตทิงรีเอเจนต์ชนิดใหม่ที่มีความปลอดภัย เพื่อใช้ในปฏิกิริยาเฮโลจิเนชันของสารแอโรแมติกที่มีหมู่แทนที่เป็นหมู่ให้อิเล็กตรอน และเหมาะสมในการใช้สังเคราะห์สารในห้องปฏิบัติการ สารประกอบเฮโลจิเนตสังเคราะห์ได้จากปฏิกิริยาเฮโลจิเนชันในตัวทำละลาย 2 วัฏภาค (น้ำและตัวทำละลายอินทรีย์) ของสารแอโรแมติกกับเกลือโซเดียมโบรไมด์โดยใช้โซเดียมไฮโปคลอไรต์ในสภาวะกรดเป็นตัวออกซิไดซ์ ที่อุณหภูมิห้อง ตัวทำละลายอินทรีย์ที่เหมาะสมคือไอโซออกเทน สารแอโรแมติกที่ใช้เป็นสารตั้งต้นในปฏิกิริยา เช่น ไดฟีนิล อีเธอร์, ฟีนอล และ โทลูอีน การพิสูจน์เอกลักษณ์ของสารประกอบเฮโลจิเนตทำได้โดยใช้เทคนิคทางสเปกโทรสโกปี เช่น อินฟราเรดสเปกโทรสโกปี, นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี และ แมสสเปกโทรเมทรี สารประกอบไดฟีนิลอีเธอร์ที่สังเคราะห์ได้ที่อัตราส่วนสารตั้งต้น/ โซเดียมโบรไมด์/ โซเดียมไฮโปคลอไรต์ เป็น 1/10/16 ได้ผลิตภัณฑ์คือ พาราไดโบรโมไดฟีนิล อีเธอร์ (94%) ใช้เวลาทำปฏิกิริยา 2 ชั่วโมง สารประกอบฟีนอลที่สังเคราะห์ได้ในสภาวะมี เททระบิวทิล แอมโมเนียมเททระฟลูออโรโบเรต เป็นเฟสทรานสเฟอร์ โดยที่อัตราส่วนสารตั้งต้น/ โซเดียมโบรไมด์/ โซเดียมไฮโปคลอไรต์ เป็น 1/0/8ได้ผลิตภัณฑ์ คือ 2,4,6-ไทรคลอโรฟีนอล (87%) และที่อัตราส่วนสารตั้งต้น/ โซเดียมโบรไมด์/ โซเดียมไฮโปคลอไรต์ เป็น 1/5/8 ได้ผลิตภัณฑ์ คือ ไทรโบรโมฟีนอล (50%) ใช้เวลาทำปฏิกิริยา 2 ชั่วโมง และสารประกอบโทลูอีนที่อัตราส่วนสารตั้งต้น/ โซเดียมโบรไมด์/ โซเดียมไฮโปคลอไรต์ เป็น 1/5/8 ได้ผลิตภัณฑ์ คือ ไดโบรโมโทลูอีน (83%) ใช้เวลาทำปฏิกิริยา 4 ชั่วโมง

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต.......................................

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา...........................

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4372301123 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: BROMINATION/ AROMATIC COMPOUNDS/ SODIUM BROMIDE/ SODIUM HYPOCHLORITE

NARUEMON KAPUCH: BROMINATION OF AROMATIC COMPOUNDS USING SODIUM BROMIDE / SODIUM HYPOCHLORITE. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D. 219 pp. ISBN_______

Sodium bromide/ sodium hypochlorite are innovative and safe brominating agents for aromatic compounds that contain activating substituents. A halogenation process, in which sodium hypochlorite is utilized, was optimized on laboratory scale. Halogenated compounds were synthesized by a halogenation reaction in 2 phases (aqueous and organic solvent) of aromatic compounds such as diphenyl ether, phenol and toluene in the presence of acetic acid and sodium bromide salt/ sodium hypochlorite which was oxidizing agent with isooctane as a solvent at room temperature. Halogenated compounds were identified by spectroscopic techniques such as Infrared Spectroscopy, Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry. The bromination of diphenyl ether gave 94% *p*-dibromodiphenyl ether using mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:10:16 and reaction time for 2 hours. The halogenation of phenol in the presence of tetrabutyl ammoniumtetrafluoroborate as a phase transfer gave 87% 2,4,6-trichlorophenol using a mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:0:8 and gave 50% tribromophenol using a mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:5:8 and reaction time for 2 hours. The bromination of toluene gave 83% dibromotoluene using a mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:5:8 and reaction time for 4 hours.

Department……Petrochemistry and Polymer Science…… Student's signature……………………...

Field of study……Petrochemistry and Polymer Science…… Advisor's signature……………………..

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CONTENTS

CONTENTS (continued)

CONTENTS (continued)

CONTENTS (continued)

CONTENTS (continued)

Page

LIST OF FIGURES

LIST OF FIGURES (continued)

Page

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

Page

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

Page

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

Page

LIST OF FIGURES (continued)

Page

LIST OF TABLES

LIST OF TABLES (continued)

Page

LIST OF ABBREVIATIONS

^{13}C-NMR	Carbon-13 Nuclear Magnetic Resonance
^{o}C	degree celsius
cm^{-1}	Unit of wavenumber
d	doublet (NMR)
FT-IR	Fourier Transform Infrared Spectroscopy
g	gram (s)
Hz	Hertz
^{1}H-NMR	Proton Nuclear Magnetic Resonance
MS	Mass spectrometry
m/ z	mass to charge ratio
ml	milliliter(s)
M^{+}	Molecular ion in mass spectrum
m	multiplet (NMR)
ppm	part per million
q	quartet (NMR)
R*f*	Retardation factor in chromatography
s	singlet (NMR)
TLC	Thin Layer Chromatography
t	triplet (NMR)
δ	Unit of chemical shift

Chapter I

Introduction

1.1 Introduction

Brominated intermediates are important reactants for the functionalization of compound, such as toluene derivatives which were demonstrated in figure 1.1.

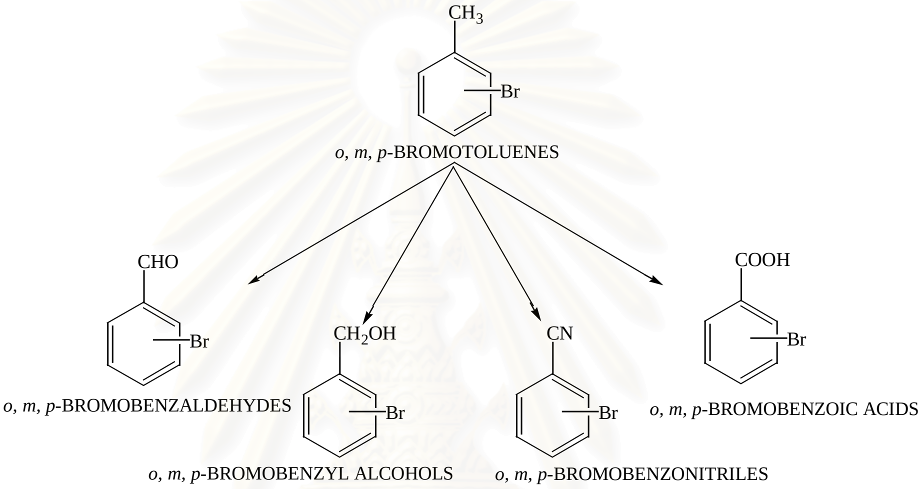


Figure 1.1 Bromotoluene products road map [1]

Halogenation reactions are widely used in the synthesis of flame retardants, pharmaceuticals, agochemicals and special chemicals.

Flame retardants are chemicals, which added to materials (*e.g.* printed circuit board resins) during or after manufacture in order to inhibit or even suppress the combustion process. The use of flame retardants in the manufacture of electronic equipments, upholstered furnitures, construction materials and textiles has been shown to save many lifes from fire. There are a number of different families of flame retardants:

- Brominated flame retardants (*e.g.* brominated diphenyl ether)
- Chlorinated flame retardants
- Phosphorous-containing flame retardants
- Nitrogen-containing flame retardants (*i.e.* Melamines)
- Inorganic flame retardants

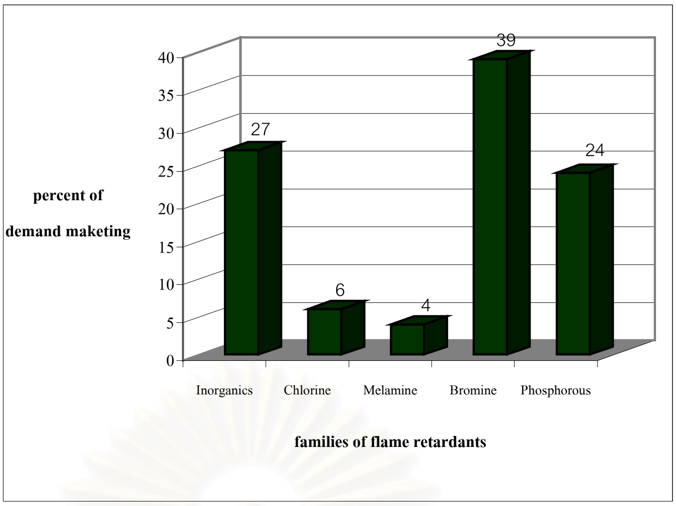


Figure 1.2 Flame retardant worldwide market [2]

The product 4,4'-dibromodiphenyl ether, a flame retardant agent useful in a variety of potential applications (*e.g.* polyesters and polystyrenes) has also been used as a processing aid in polycarbonates. The material is also useful as a reactant for producting other di-functional 4,4'-diphenyl ether derivatives such as 4,4'-dihydroxydiphenyl ether [3].

The chlorination of phenol proceeds stepwise so that six chlorophenols of commercial value are obtained which were 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. The chlorophenols of most commerical importance are 2,4-dichlorophenol, an intermediate in the manufacture of 2,4-dichlorophenoxy-acetic acid (2,4-D) and derivatives, which are selective herbicides; and pentachlorophenol (PCP), used as a wood preservative due to its fungicidal properties [4].

Both 2-chlorophenol and 4-chlorophenol are used as chemical intermediates, with the latter compound having more commercial importance. Benzyl chloride reacts with 4-chlorophenol to give 2-benzyl-4-chlorophenol, a widely used germicide. 2,4,6-Trichlorophenol is used as a wood preservative, glue preservative and bactericide, as well as in antimildew treatment for fabrics. 2,3,4,6-Tetrachlorophenol are used as a wood preservative.

A lot of approaches have been used in producing brominated intermediates but these approaches have some disadvantages, such as:

i) Using halogenated solvents for instance carbon tetrachloride (CCl_4), trichloromethane ($CHCl_3$) and dichloroethane (CH_2ClCH_2Cl)

-The elimination of these solvents is complicated.

-These solvents are poisonous to the environment.

ii) Using make it difficult to handle concentrate acid in reactions

iii) Using bromine (Br_2) that make it difficult to handle

As a result, a new chemical process for brominating aromatic compounds in order to avoid those mentioned disadvantages is still needed.

1.2 Objectives and scope of the research

1.2.1 Objectives

1. To study the new chemical process for brominating aromatic compounds using sodium bromide/ sodium hypochlorite

2. To investigate the effect of 1) solvents 2) ratio of substrate and sodium bromide/ sodium hypochlorite 3) reaction time

1.2.2 Scope of research

1. Literature survey of relevant research works
2. Synthesizing of brominated aromatic compounds using the following substrates:
    a) diphenyl ether
    b) phenol
    c) toluene
    d) linear alkyl benzene
3. Investigation of brominated aromatic compounds affected by the following parameters:
    a) solvents
    b) ratio of substrate and sodium bromide/ sodium hypochlorite
    c) reaction time
4. Summarizing of the results.

Chapter II

Theory and literature review

2.1 Halogens [5]

The halogens appear in Group VII, subgroup B, of the Periodic Table and their atoms, having seven valence electrons, combine readily with one electron to form a stable negative ion having a completed octet with a charge of minus one. In their elemental state, they exist as diatomic molecules. Fluorine has the highest electron affinity and is therefore the most reactive of the halogens; it forms fluorides with evolution of considerable energy. Iodine is the least reactive of the halogens. Free fluorine is prepared with great difficulty, while free iodine is the easiest to prepare. The relative reactivity decreases from fluorine to iodine. Thus, the halogen of lower atomic weight displaces one of higher atomic weight. As halide ions, the relative activity of the halogen in the oxidized state is the reverse of the reduced state. For example, chlorine will reduce elemental iodide dissolved in an aqueous solution of potassium iodide, while iodine will displace chlorine in potassium chlorate forming the more stable potassium iodate. Thus, iodine as the iodate is the best reducing agent in the halogen family, and chlorine as the chlorate is the best oxidizing agent. Except for fluorine, the halogens are readily oxidized in an alkaline medium.

In addition, the color of the halogens is found to deepen from fluorine to iodine, the boiling points and density increase, and the average of the properties of chlorine and iodine are approximate the properties of bromine. They form salts by direct union with metals. The binary compounds of halogens, excluding the oxides, are known as “halides” and solutions of metal halides, except for some fluorides, are soluble in water.

Table 2.1 Properties of halogens

Properties	Fluorine	Chlorine	Bromine	Iodine	Astatine
Atomic weight	19	35.46	79.92	126.92	210
Symbol	F	Cl	Br	I	At
Physical appearance	Gas	Gas	Liquid	Solid	-
Color of gas	Pale yellow	Greenish	Brownish	Violet	-
Melting point, °C	-223	-102	-7.3	113	-
Boiling point, °C	-187	-34.6	58.8	184.35	-
Specific gravity	1.08 (liq.)	1.55 (liq.)	3.19 (liq.)	4.93 (solid)	-
Atomic volume*	16.7	22.9	25.1	25.1	-
Atomic number	9	17	35	35	85

*Atomic volume = Atomic weight/ Specific gravity

2.2 Substitution in aromatic compounds [6]

There is a concentration of negative charge above and below the plane of the ring of carbon atoms of benzene due to the presence of delocalized π-orbitals. Therefore the attack of a negatively charged species of a neutral nucleophile will suffer great electrostatic repulsion and hence nucleophilic substitution will not be favoured, whereas the attack by positively charged species (electrophiles) will be facilitated. Thus electrophilic substitution is expected to be more common in the case of benzene (the representative of all the aromatic compounds) than nucleophilic substitution. However, under some special circumstances, nucleophilic and homolytic substitution reactions can also occur.

Nucleophilic substitution

$$\text{Nu:} + \text{H:C}_6\text{H}_4\text{X} \longrightarrow \text{Nu-C}_6\text{H}_4\text{-X} + \text{H}^-$$

Homolytic substitution

$$\text{R}^\bullet + \text{H:C}_6\text{H}_4\text{X} \longrightarrow \text{Nu-C}_6\text{H}_4\text{-X} + \text{H}^\bullet$$

Electrophilic substitution

$$\text{E}^+ + \text{H:C}_6\text{H}_4\text{X} \longrightarrow \text{E-C}_6\text{H}_4\text{-X} + \text{H}^+$$

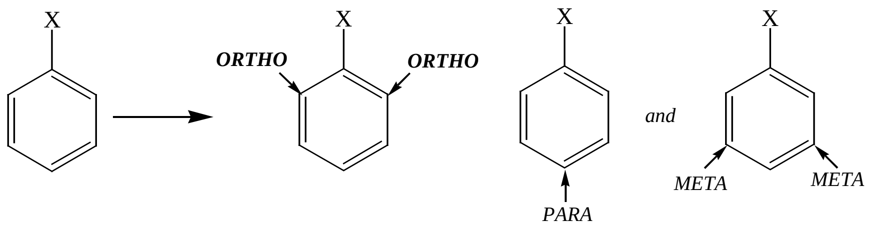
In the eletrophilic substitution, the attacking species is a positively charged ion or the positive end of a dipole or induced dipole. The leaving group must therefore, depart without the electron pair. The most common leaving group in electrophilic displacement reactions is a proton. In nucleophilic substitution, the attacking species is a negatively charged ion or a group capable of donating a pair of electrons and consequently the leaving group should also be able to accommodate the unshared pair of electrons.

2.3 Electrophilic substitution

Electrophilic substitution reactions, unlike nucleophilic substitutions, proceed by a common bimolecular mechanism, *via* the formation of an intermediate which constitutes the rate determining step. The attacking species may be produced in various ways, even for the same reaction. Again, the same reaction may produce different attacking species under different experimental conditions of temperature, concentration, catalyst, *etc*., but what is happening to the benzene ring is basically the same in all the cases. Thus in electrophilic substitutions, it is of utmost importance to indentify the actual attacking species and the mode of its formation.

2.4 Orientation and directive influence

When one group is introduced into the benzene ring, only one product is possible. When a second group is introduced, three isomers are possible, depending upon whether the incoming group goes to the *ortho*, *meta* or *para* position with respects to the substituent already present. The rate of substitution may be slower or faster than in benzene depending upon the substituent already present. Groups which increase the electron density on the benzene ring either by inductive, mesomeric or hyperconjugative effect, are said to activate the benzene nucleus. In such cases, the rate of substitution will be more than that of the corresponding substitution reaction with benzene.



Such groups direct the incoming group to the *ortho* and *para* positions. When, however, the group already present is electron withdrawing, it will deactivate the benzene nucleus and will direct the incoming group to the *meta* position. Thus some groups are meta directing while others are ortho/ para directing. Some groups, like halogens, are electron withdrawing but still are ortho/ para orienting because of their inductive effect.

Although a *meta* directing group directs the substitution to take place at the *meta* position, the *meta* product is not formed exclusively and *ortho/ para* substitution also takes place in addition to *meta* substitution. For example, in the nitration of nitrobenzene they get 93% of *m*-dinitrobenzene, 6% of *o*-dinitrobenzene and 1% *p*-dinitrobenzene. Similarly when *ortho para* directing group is present, there get small amounts of the *meta* product also. Thus the *directive influence* decides only the predominant and not the exclusive course of the reaction.

All this discussion, however, is valid only when the free energy change of the reaction is appreciably negative or the reaction is irreversible. For reversible reaction, however, thermodynamically controlled product is favoured.

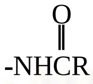
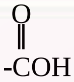
Two factors are important in deciding the stability of the intermidiate:

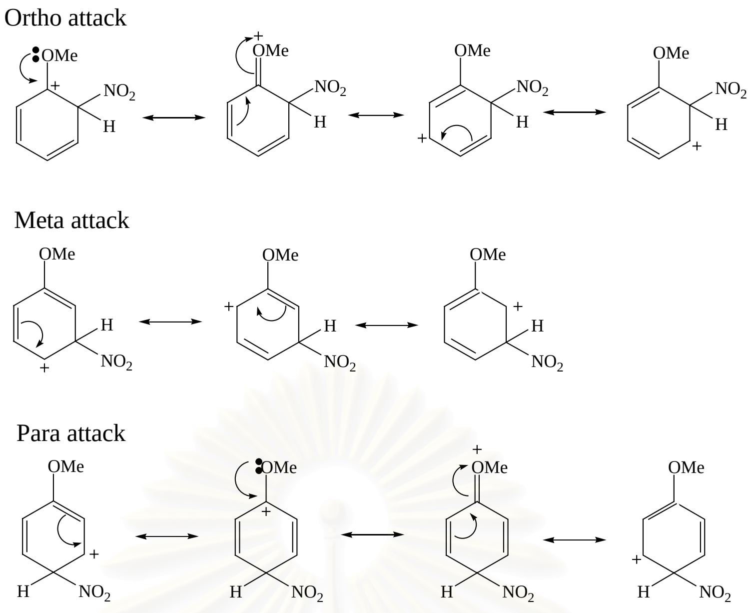
(a) Inductive effect, and

(b) Resonance or mesomeric effect of the substituent.

The three possible intermidiates expected in the nitration of anisole with a view to predict the *orientation* of the incoming group. Here the substituent already present is OMe group, which is capable of donating a pair of electrons, thereby giving four resonance forms for the *ortho/ para* transition state (intermidiate) and three resonance forms for the transition state of the *meta* product. The classification of substituents in electrophilic aromatic substitution reaction is shown in Table 2.2.

Table 2.2 Classification of substituents in electrophilic aromatic substitution reaction [7]

Effect on rate	**Substituent**		**Effect on orientation**
Very strongly activating	$-NH_2$	(amino)	Ortho, para-directing
	$-NHR$	(alkylamino)	
	$-NR_2$	(dialkylamino)	
	$-OH$	(hydroxyl)	
Strongly activating	 $-NH\overset{O}{\overset{\|}{C}}R$	(acylamino)	Ortho, para-directing
	$-OR$	(alkoxy)	
	 $-O\overset{O}{\overset{\|}{C}}R$	(acyloxy)	
Activating	$-R$	(alkyl)	Ortho, para-directing
	$-Ar$	(aryl)	
	$-CH{=}CR_2$	(alkenyl)	
Standard of comparison	$-H$	(hydrogen)	
Deactivating	$-X$ (X = F, Cl, Br, I)	(halogen)	Ortho, para-directing
	$-CH_2X$	(halomethyl)	
Strongly deactivating	 $-\overset{O}{\overset{\|}{C}}H$	(formyl)	Meta- directing
	 $-\overset{O}{\overset{\|}{C}}R$	(acyl)	
	 $-\overset{O}{\overset{\|}{C}}OH$	(carboxylic acid)	
	 $-\overset{O}{\overset{\|}{C}}OR$	(ester)	
	 $-\overset{O}{\overset{\|}{C}}Cl$	(acyl chloride)	
	$-C\equiv N$	(cyano)	
	$-SO_3H$	(sulfonic acid)	
Very strong deactivating	$-CF_3$	(trifluoromethyl)	Meta-directing
	$-NO_2$	(nitro)	



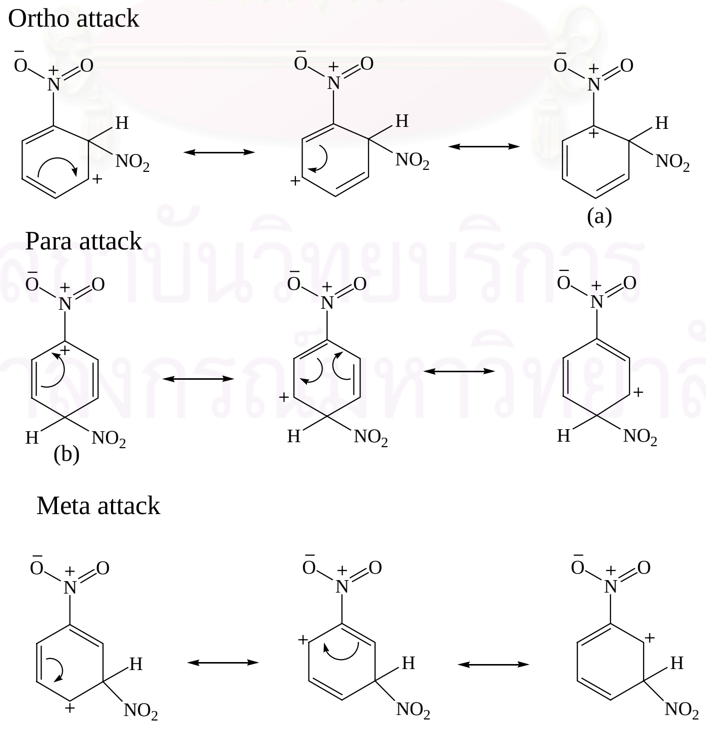
Ortho attack

Meta attack

Para attack

Thus the transition state for ortho/para substitution product is more stabilized which amount to the lowering of activation energy for the reaction leading to its formation and hence *o/p* substitution takes place preferentially.

When the group already present is *meta* directing, *i.e.* the electron withdrawing or deactivating, *e.g.*, NO_2 group, the three possible intermediates will be stabilized as shown below:



Ortho attack

Para attack

Meta attack

Each intermediate has three resonance forms but *ortho* and *para* intermediates have one canonical structure, (a) and (b), respectively, in which there is a charge separation. This will cause the *o/p* intermediate to be of higher energy than the meta intermediate, and hence meta substitution will take place predominantly.

On the basis of what we have discussed above, we can divide the groups already present in the benzene nucleus into the following three categories:

(i) Electron donating groups. These are groups which can donate a pair of electrons to the benzene ring, *e.g.*, -O-, $-NR_2$, -NRH, $-NH_2$, -OH, -OR, -NHCOR, -OCOR and halogen. It can be expected that all of these are *ortho/ para* orienting.

It is interesting to note that although Cl, Br and I are deactivating (electron withdrawing) yet they are *ortho-para* directing. The halogens in the halo-benzenes make the *ortho* and *para* intermediates more stable than the *meta* but less stable than that of the unsubstituted benzene. For other groups, the ortho and para intermediates are more stable than both of the meta and the unsubstituted benzenes.

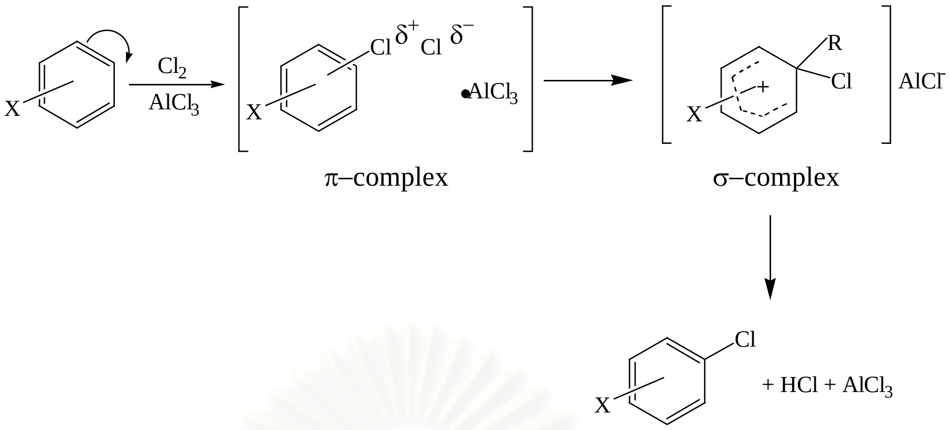
(ii) Electron withdrawing group. These are groups which are electron withdrawing, e.g. $–N^+R_3$, $-NO_2$, -CN, $-SO_3H$, -CHO, $-CO_2H$, $-CO_2R$, $-CCl_3$, $-N^+H_3$. Inductive effect of these groups causes the deactivation of benzene nucleus and predicts that all of them should be meta directing.

2.5 Halogenation

Halogenation (chlorination and bromination) takes place in the presence of catalytic amounts of Lewis acids such as $ZnCl_2$, $FeBr_3$, $AlBr_3$ etc. The function of the catalyst is to induce a small degree of polarization in the halogen molecule. The molecular halogen, usually in solution in acetone and/ or a non-polar sovent such as CCl_4 is used. Chlorine and bromine may be introduced in the gaseous form or may be generated *in situ* from and N-haloamide and acid, e.g.,

$$R_2N\text{--}Cl + HCl \longrightarrow R_2NH + Cl_2$$

Since HCl is formed as a result of the aromatic chlorination, this procedure for generating chlorine (or bromine) is a continuous one and the concentration of chlorine can thus be maintained at a desired level, according to the amount of HCl added initially. The mechanism of halogenation is illustrated by taking chlorination of benzene with chlorine in the presence of aluminium chloride:



When ferric chloride is used as a catalyst, it is added usually as iron fillings from which the metal chloride is generated *in situ*. The function of Lewis acid is to draw electrons from the halogen molecule thereby increasing its electrophilic character. It should be emphasized that the polarization influence of Lewis acid does not lead to complete ionization. More vigorous conditions for chlorination are obtained by using an acidified solution of hypochlorous acid. HOCl alone, like HNO_3, has very little action on benzene. The presence of an entity, for example a strong acid, is essential to release the highly electrophilic species Cl^+, called the *chloronium ion* just analogous to NO_2^+, the nitronium ion.

$$\text{HO-Cl-} \longrightarrow H_2O^+ \overset{\curvearrowleft}{\text{-Cl-}} \longrightarrow H_2O + Cl^+$$

The mechanism of the attack of Cl^+ on aromatic compound is exactly analogous to that of nitration.

Further support to this mechanism has been obtained by carrying out the reaction with interhalogen compound. Thus Br-Cl leads to bromination and I-Cl only to iodination, i.e. it is the less electronegative halogen atom that is introduced into the nucleus.

2.6 Sodium Hypochlorite [8], [9]

Sodium hypochlorite, a versatile and easily handled oxidizing agent, can oxidize alcohols, aldehydes, electron deficient alkenes, amines, and transition metal catalysts, reagent for *N*-chlorination, oxidative coupling and degradation reactions. Form supplied in commercially available as aqueous solutions with 5.25-12.5% available oxidant (w/v) (0.74-1.75 M). Concentration is expressed in % available chlorine, since half of chlorine in bleach is present as

NaCl. The pH of commercial bleach is typically 11-12.5, and it may be adjusted and buffered. The equilibrium composition of aqueous solutions of NaOCl is pH-dependent (eqs 1 and 2) and so pH control can be a critical consideration in many oxidation and chlorination reaction. Under strongly alkaline condition (pH > 12), OCl^- is the predominant form of positive chlorine. Because hypochlorite ion is insoluble in organic solvent, phase transfer catalysts are needed at this pH to effect oxidation reaction in biphasic media. In general, tetraalkylammonium salts have been the phase-transfer catalysts of choice for such applications. Below pH 11, the equilibrium amount of HOCl becomes significant, and this form of positive chlorine is soluble in polar organic solvent such as CH_2Cl_2. No phase-transfer catalyst is necessary to effect oxidation of substrates or catalysts dissolved in the organic phase of biphasic reactions in the pH range 10-11. Below pH 10, molecular chlorine becomes a significant component of aqueous bleach solutions, and the reactivity of these solutions can be attributed to that of Cl_2.

$$\mathbf{ClO^- + Cl^- + H_2O \rightleftharpoons Cl_2 + 2OH^-} \qquad \mathbf{(1)}$$

$$\mathbf{ClO^- + H_2O \rightleftharpoons HOCl + OH^-} \qquad \mathbf{(2)}$$

2.7 Mass spectrometry [10]

The mass spectrometer is an instrument that serves for establishment of the molecular weight and structure of organic compounds, and the identification and determination of the components of inorganic substances.

The sample is volatilized within the spectrometer and gas-phase ions formed from it are separated according to their mass/ charge (*m/z*) ratio, and are usually detected electrically. The ion-currents corresponding to the different species are amplified and either displayed on an oscilloscope or a chart-recorder, or are stored in a computer. An example of a mass spectrum thus obtained is shown in Fig. 2.1. The peak intensities are plotted as ordinates, in arbitrary units or normalized with respect to the most important peak (or some other selected peak), which is assigned a value of 100.

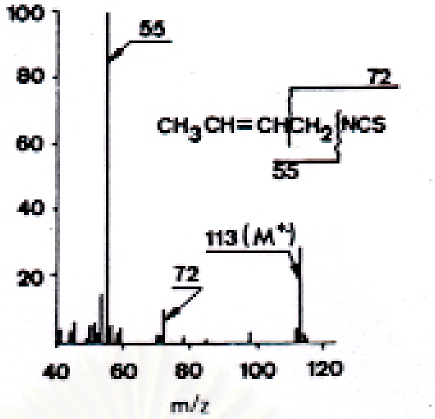


Figure 2.1 A typical mass spectrum, showing fragmentation pattern.

Isotopic analysis

Chemical elements can have several isotopes, but sometimes only one or a few of them will be stable, and for some elements none occur in nature. Thus naturally occurring oxygen contains isotope with mass numbers 16, 17 and 18, and magnesium also has three stable isotopes, with mass numbers 24, 25 and 26. An element such as chlorine, which has two stable isotopes and forms a diatomic molecule, is ionized to produce the molecular ion, the peaks will correspond to the various combinations of the isotopes. The isotopes are $^{35}\mathrm{Cl}$ (abundance 24.5%) which can combine to yield

$^{35}\mathrm{Cl}^{35}\mathrm{Cl}^{+}$	$m/z = 70$
$^{35}\mathrm{Cl}^{37}\mathrm{Cl}^{+}$	$m/z = 72$
$^{37}\mathrm{Cl}^{37}\mathrm{Cl}^{+}$	$m/z = 74$

Calculation of spectral distribution of isotopic combinations, relative masses and intensities

Chlorine as an example of an element with more than one stable isotope. The possible isotopic combinations for three chlorine atom in a compound are

$^{35}\mathrm{Cl}^{35}\mathrm{Cl}^{35}\mathrm{Cl}$ $^{35}\mathrm{Cl}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$ $^{35}\mathrm{Cl}^{37}\mathrm{Cl}^{35}\mathrm{Cl}$ $^{37}\mathrm{Cl}^{35}\mathrm{Cl}^{35}\mathrm{Cl}$
$^{35}\mathrm{Cl}^{37}\mathrm{Cl}^{37}\mathrm{Cl}$ $^{37}\mathrm{Cl}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$ $^{37}\mathrm{Cl}^{37}\mathrm{Cl}^{35}\mathrm{Cl}$ $^{37}\mathrm{Cl}^{37}\mathrm{Cl}^{37}\mathrm{Cl}$

a total of eight:

$(^{35}\mathrm{Cl}_3) + 3(^{35}\mathrm{Cl}_2{}^{37}\mathrm{Cl}) + 3(^{35}\mathrm{Cl}^{37}\mathrm{Cl}_2) + (^{37}\mathrm{Cl}_3)$

and write the binomial expansion $(a + b)^n$ when $^{35}\mathrm{Cl}$ by a and $^{37}\mathrm{Cl}$ by b

$a^3 + 3a^2b + 3ab^2 + b^3$ for $n = 3$

The table 2.3 is shown the possible peaks appearing in the mass spectrum, and their relative intensities. This example is simplified by the fact that the abundance ratio ^{35}Cl/ ^{37}Cl = 75.5/ 24.5 is approximately equal to 3.

Table 2.3 The possible peaks appearing in the mass spectrum, and their relative intensities

Binomial term	Isotope combination	mass	Relative intensity
a^3	$^{35}Cl_3$	M	$3^3 = 27$
$3a^2b$	$^{35}Cl_2{}^{37}Cl$	M + 2	$3 \times 3^2 \times 1 = 27$
$3ab^2$	$^{35}Cl^{37}Cl_2$	M + 4	$3 \times 3 \times 1^2 = 9$
b^3	$^{37}Cl_3$	M + 6	$1^3 = 1$

The appearance of the mass spectrum is shown in Figure 2.2.

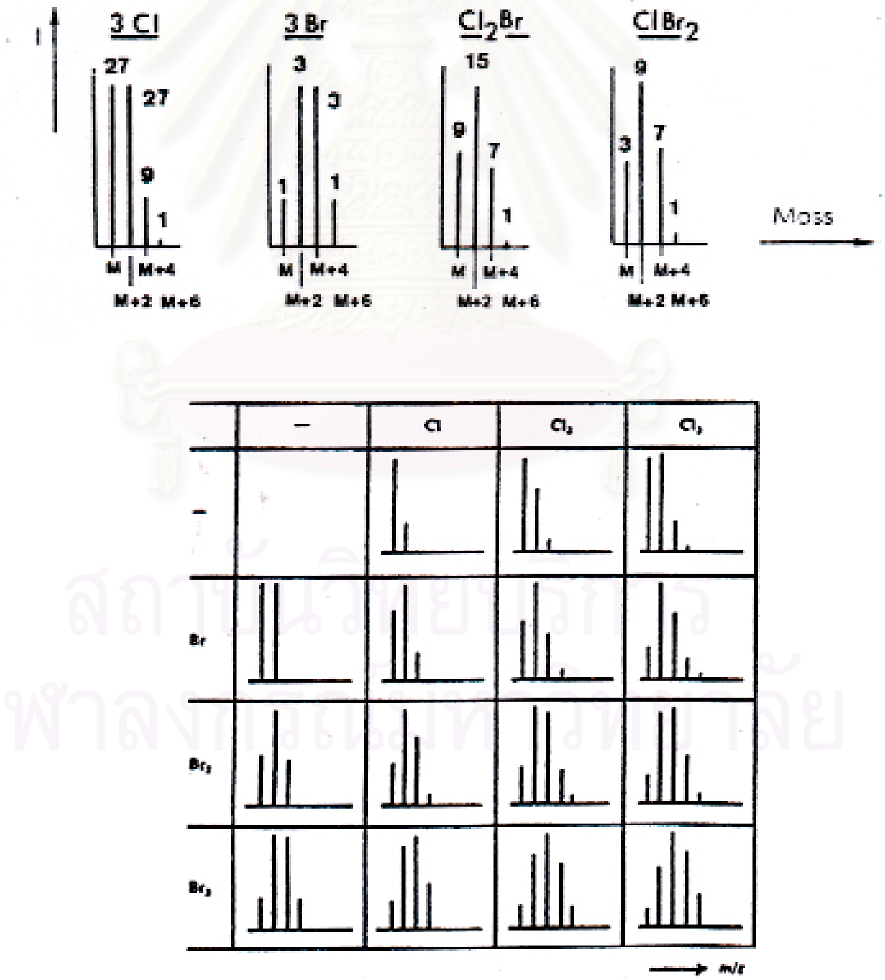


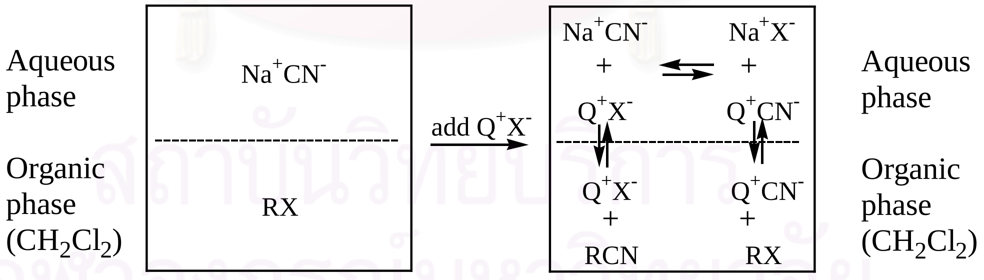
Figure 2.2 Relative intensities of peaks corresponding to different isotopic combinations.

2.8 Nucleophilic substitution reaction in nonpolar solvent using phase-transfer catalysis [11]

Nonpolar solvents such as a hydrocarbon or chlorinated hydrocarbon were seldom used for nucleophilic substituent reaction because of their inability to dissolve ionic compound. This situation has changed with the development of a procedure called ***phase-transfer catalysis***.

With phase-transfer catalysis, usually use two immiscible phase that are in contact – often an aqueous phase containing an ionic reactant and an organic phade (benzene, $CHCl_3$, etc.) containing the organic substrate. Normally the reaction of two substances in sepatate phases like this is inhibited because the reaction takes place in an aprotic medium, S_N2 reactions occur rapidly.

An example of phase-transfer catalysis is outlined in Figure 2.3. The phase-transfer catalyst, Q^+X^-, is usually a quaternary ammonium halide ($R_4N^+X^-$) such as tetrabutylammonium halide, $(CH_3CH_2CH_2CH_2)_4N^+X^-$. The phase-transfer catalyst causes the transfer of the nucleophile as an ion pair [Q^+CN^-] into the organic phase. This transfer apparently takes place because the cation (Q^+) of the ion pair, with its four alkyl groups, resembles a hydrocarbon in spite of its positive charge. It is said to be *lipophilic* – it prefers a nonpolar environment to an aqueous one. In the organic phase the nucleophile of the ion pair (CN^-) reacts with the organic substrate RX. The cation (Q^+) then migrates back into the aqueous phase to complete the cycle. This process continues until all of the nucleophile or the organic substrate has reacted.



Here no reaction takes place because the nucleophile, CN^-, cannot enter the organic phase to react with RX.

Here the phase-transfer catalyst transport the cyanide ion (as Q+CN-) into the organic phase where the reaction CN- + RX → RCN + X- takes place rapidly.

Figure 2.3 Phase-transfer catalysis of the S_N2 reaction between sodium cyanide and alkyl halide.

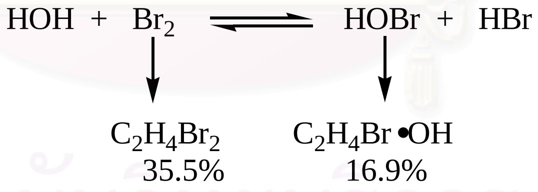
2.9 Literature reviews

Halogenation reactions are widely used in the synthesis because halogenated intermediates are important reactants for the functionalization of compound. Therefore, a lot of approaches have been reports on various chlorinated and brominated intermediates, which are listed as follow.

In 1901, Stieglitz, J. [12] proved the hypothesis of the existence of positive as well as negative ion of the chlorine and especially of the formation of positive halogen ions by hypochlorous acid which ionizes very little. It ionizes both as a weak acid, and at the same time as a weak base. The ionization of water for hypochlorous acid (for OH^- and Cl^+) was established, it involves the fact of the existence of positive chlorine ions.

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H^+} + \mathrm{OCl^-}$$
$$\mathrm{HOCl} \rightleftharpoons \mathrm{OH^-} + \mathrm{Cl^+}$$

In 1917, Read, J. et al. [13] studied the formation of hypobromous acid from bromine and water, and the consequent removal of free bromine from the sphere of the action for ethylene. They used bromine that dissolved in water for the synthesis of brominated ethylene at room temperature. The bromination of ethylene gave 37.5% of ethylene dibromide and 16.9% of ethylene bromohydrin when using mole ratio of ethylene and bromine as 1:5.



In 1925, Francis, A.W. [14] studied the relative rates of bromination with bromine water and with hypobromous acid solution. Bromine is hydrolyzed by water in two way,

$$\mathrm{Br_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{HBr} + \mathrm{HOBr} \qquad (1)$$
$$3\mathrm{Br_2} + 3\mathrm{H_2O} \rightleftharpoons 5\mathrm{HBr} + \mathrm{HBrO_3} \qquad (2)$$

In acid solution the hydrolysis is very small as shown by the constant,

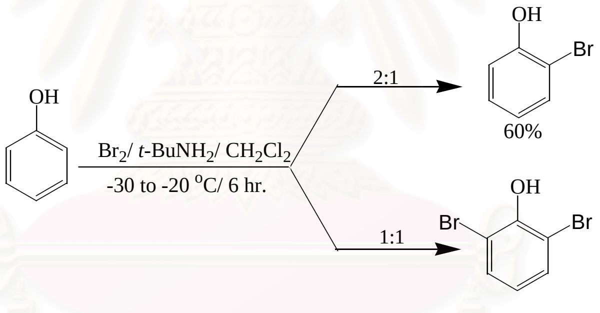
$$K_1 = \frac{(\mathrm{H^+})(\mathrm{Br^-})(\mathrm{HOBr})}{(\mathrm{Br_2})} = 5.2 \times 10^{-9} \qquad (3)$$

$$K_2 = \frac{(\mathrm{H^+})^6(\mathrm{Br^-})^5(\mathrm{OBr^-})}{(\mathrm{Br_2})^3} = 10^{-33} \qquad (4)$$

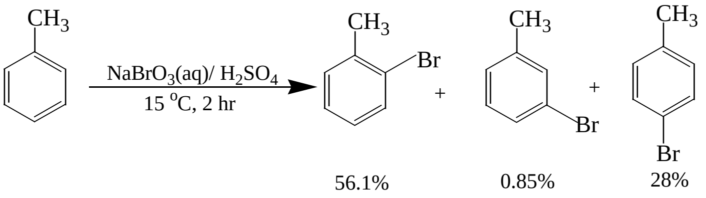
In 1954, Mare, D. L. [15] studied the velocity of the reaction between hypochlorous and aromatic compounds, such as anisole, phenol and *p*-dimethoxybenzene. The velocity coefficient was dependent on the acidity and was independent of the concentration of aromatic compound. It was concluded that the rate controlling step was the heterolytic fission of ClOH and $ClOH_2^+$. The reactions involved is shown in the scheme below:

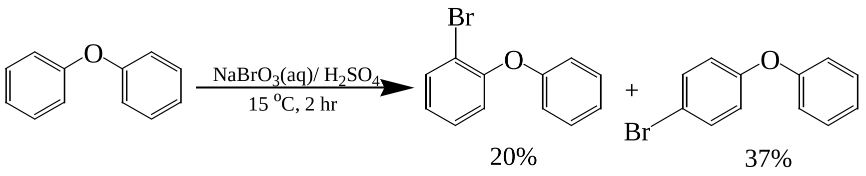
$$\begin{aligned} ClOH &\rightleftharpoons Cl^+ + OH^- \\ ClOH + H^+ &\rightleftharpoons ClOH_2^+ \\ ClOH_2^+ &\rightleftharpoons Cl^+ + OH_2 \\ Cl^+ + ArH &\longrightarrow ArCl + H^+ \end{aligned}$$

In 1967, Pearson, D.E. et al.[16] used bromine and *tert*-butylamine (Br_2/ *t*-$BuNH_2$) for synthesizing brominated phenol at –30 to –20 °C and reaction time for 6 hours. The bromination of phenol gave the ortho substitution and depended on the mole of bromine. They obtained 60% 2-bromophenol when using mole ratio of phenol and bromine as 2:1 and 87% 2,6-dibromophenol when using the mole ratio of phenol and bromine as 1:1.

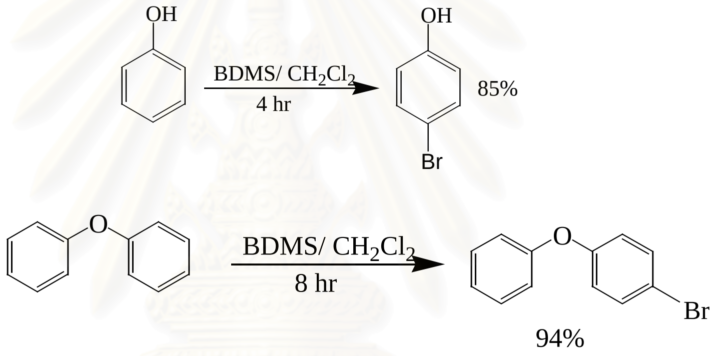


In the same year, Crump, J.W. et al. [17] used sodium bromate solution ($NaBrO_3$) and sulfuric acid (H_2SO_4) for synthesizing brominated toluene and diphenyl ether at 15 °C. They used mole ratio of substrate and $NaBrO_3$ as 1:1 and reaction time for 2 hours. The bromination of toluene gave 85% monobrominated toluene containing 56.1% 2-bromotoluene, 28% 4-bromotoluene and 0.85% 3-bromotoluene. The bromination of diphenyl ether gave 57% monobrominated diphenyl ether containing 20% 2-bromodiphenyl ether and 37% 4-bromodiphenyl ether.

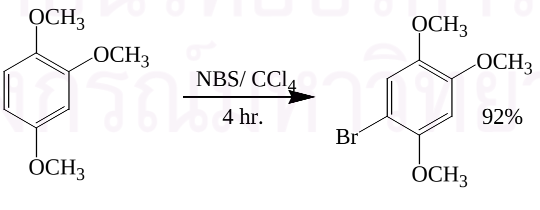




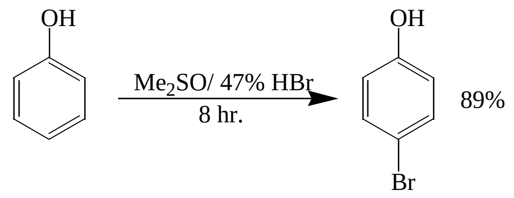
In 1986, Olah, G.A. et al. [18] used bromodimethylsulfonium bromide (BDMS) that prepared from dimethyl sulfide and bromine or chlorine for synthesizing brominated phenol and diphenyl ether at –78 to –25 °C. They used mole ratio of phenol and BDMS as 1:1.25 and reaction time for 4 hours. The bromination of phenol gave 85% 4-bromophenol. They used mole ratio of diphenyl ether and BDMS as 1:1.2 and 1:2.4 and reaction time for 8 hours. The bromination of diphenyl ether that using both of mole ratio gave 94% monobromination product as 4-bromodiphenyl ether.

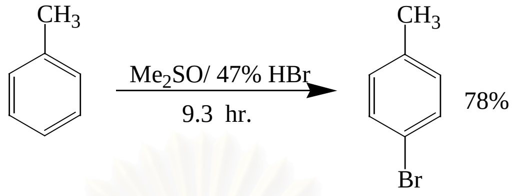


In 1995, Carreno, M.C. et al. [19] used N-bromosuccinimide (NBS) in carbon tetrachloride (CCl_4) for synthesizing of brominated aromatic derivatives. They used mole ratio of 1,2,4-trimethoxybenzene and NBS as 1:1.1 and reaction time for 4 hours. The bromination gave 92% 5-bromo-1,2,4-trimethoxybenzene.

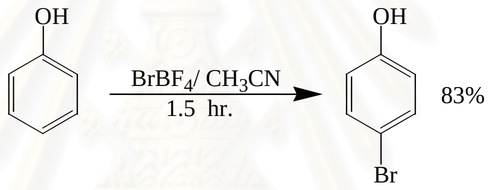


Srivatava, S.K. et el.[20] used dimethyl sulfoxide and hydrobromic acid solution (Me_2SO/ 47% HBr) for synthesizing brominated phenol and toluene. The bromination of phenol used 8 hours reaction time and obtained 89% 4-bromophenol. The bromination of toluene used 9.3 hours reaction time and obtained 78% 4-bromotoluene.

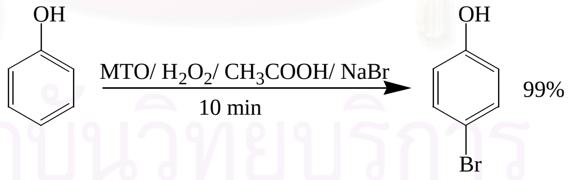




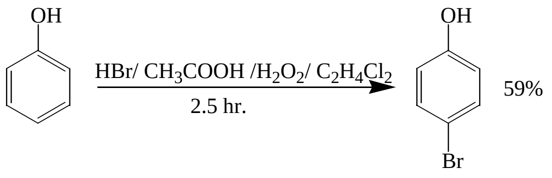
Oberhauser, T.[21] used bromonium tetrafluoroborate ($BrBF_4$) that prepared from N-bromosuccinimide (NBS) and $HBF_4 \bullet Et_2O$ in acetonitrile (CH_3CN) for synthesizing brominated phenol and reaction time for 1.5 hours. They used mole ratio of substrate and $HBF_4 \bullet Et_2O$ as 1:1.2 and obtained 83% 4-bromophenol.



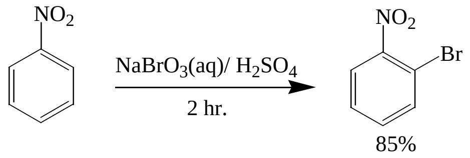
Espenson, J.H. et al.[22] used methyltrioxorhenium (MTO), hydrogen peroxide, acetic acid and sodium bromide for synthesizing of brominated phenol. They used 10 minutes reaction time and obtained 99% 4-bromophenol.



Mukhopadhyay, S. et al.[23] used hydrobromic acid ($HBr \bullet CH_3COOH$) and hydrogen peroxide in ethylene dichloride ($C_2H_4Cl_2$) for synthesizing of brominated phenol and reaction time for 2.5 hours. They used mole ratio of substrate and hydrobromic acid as 1:1.4 and obtained 59% 4-bromophenol.



Finally, Groweiss, A.[24] used sodium bromate solution ($NaBrO_3$) and sulfuric acid (H_2SO_4) for synthesizing brominated nitrobenzene and 2 hours reaction time. The mole ratio of substrate and sodium bromate as 1:1.2 was used and 85% 2-bromonitrobenzene was obtained.



Chapter III

Experimental

3.1 General methods

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck kieselgel 60 F_{254}). Column chromatography was performed on silica gel (Merck Kieselgel 60G). The FI-IR spectra were recorded on a Nicolet Fourier Transformed Infrared Spectrophotometer model Impact 410. Liquid samples were dropped on sodium chloride cells. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Bruker model ACF200 Spectrometer, which operated at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C nuclei. In all cases, samples were dissolved in deuterated chloroform and chemical shifts were recorded using a residual chloroform signal as internal reference except indication of other deuterated solvents.

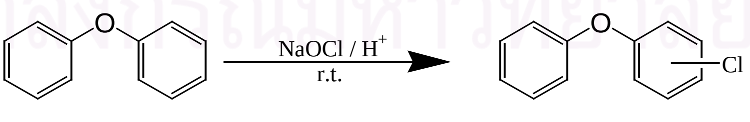
3.2 Chemicals

Linear alkylbenzenes, phenols and sodium hypochlorite were obtained from the Department of Customs. Acetic acid, diphenyl ether, toluene and isooctane were purchased from Merck. Sodium bromide was obtained from BDH. Standard analytical grade reagents were used without further purification. Commercial grade hexane were used without further purification.

3.3 Experimental Procedure

3.3.1 Bromination of aromatic substrate containing activating group

3.3.1.1 Bromination of diphenyl ether using 1/8 mole ratio of substrate and sodium hypochlorite (mixture **1D**)

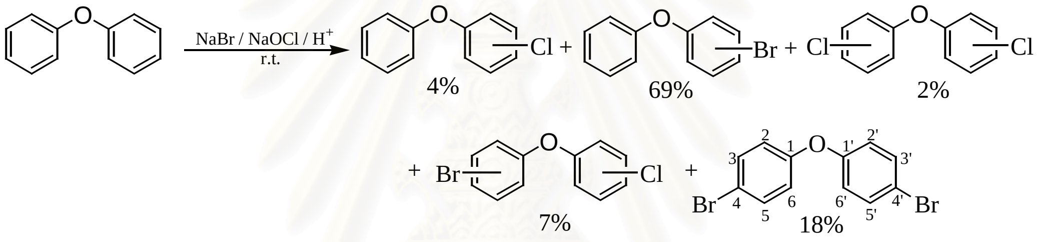


25 ml of 2M sodium hypochlorite was added in a 100 ml two-neck flask to the solution of diphenyl ether (1.02 g, 6 mmol) and 8 ml of isooctane. Then glacial acetic acid (6.0 ml) was added very slowly by dropping-funnel into the light-yellow mixture and stirred for 2 hours. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated by separating-funnel, then the yellow oil product was extracted with 5 ml of hexane (8 times) and

washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered to give an oil product. Hexane and isooctane were removed by evaporation and the product was obtained as a light-yellow liquid (0.89 g, 73%) with R_f 0.68 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 1D: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.38-7.27 (m, 4H), 7.14-6.92 (m, 5H); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 157.25, 156.88, 129.76, 127.93, 124.68, 123.22, 120.53, 118.92 (C, $C_6H_5OC_6H_4Cl$); **IR spectrum** (KBr (cm^{-1})): 3067 (CH, st (aromatic)), 1588, 1490 (C=C, st), 1239 (C-O, st); **Mass spectrum** (m/z): 204 (Int.100%, C_6H_5-O-C_6H_4Cl).

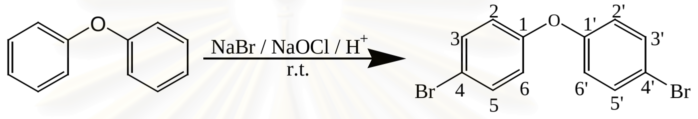
3.3.1.2 Bromination of diphenyl ether using 1/1 mole ratio of substrate and sodium bromide (mixture **2D**)



Sodium hypochlorite (10 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (0.62 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at room-temperature. A solution of diphenyl ether (1.02 g, 6 mmol) in 8 ml of isooctane was added slowly by a dropping-funnel into the light-yellow mixture. Then glacial acetic acid (4.0 ml) was added very slowly. The light-brown mixture was vigorous stirred for 2 hours, then the mixture was neutralised with 3M sodium hydroxide. The two phases were separated in separating-funnel, then the yellow oil product was extracted with 5 ml of hexane (8 times) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane and isooctane were removed by evaporation and the product was obtained as a light-yellow liquid (1.08 g, 69%) with R_f 0.80 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 2D: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.48-7.33 (m), 7.14-6.87 (m); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 156.88, 156.13, 134.05, 130.11, 129.95, 129.92, 128.84, 125.16, 123.93, 123.41, 120.61, 120.29, 119.53, 118.34, 116.41 (C, $C_6H_5OC_6H_4Cl$, $C_6H_5OC_6H_4Br$, $ClC_6H_4OC_6H_4Cl$, $ClC_6H_4OC_6H_4Br$), 156.88 (1C, C-1), 156.13 (1C, C-1’), 133.05 (2C, C-3’ and C-5’), 129.96 (2C, C-3 and C-5), 125.77 (1C, C-4), 120.76 (2C, C-2’ and C-6’), 120.39 (2C, C-2 and C-6), 116.46 (1C, C-4’); **IR spectrum (KBr, (cm^{-1})):** 3057 (CH, st (aromatic)), 1572, 1475 (C=C, st), 1239 (C-O, st); **GC-MS spectrum** 204 (t_R: 9.09, 9.34 min; $C_6H_5OC_6H_4Cl$), 248 (t_R: 10.13, 10.55 min; $C_6H_5OC_6H_4Br$), 238 (t_R: 11.43, 11.80 min; $ClC_6H_4OC_6H_4Cl$), 282 (t_R: 12.85, 13.29 min; $ClC_6H_4OC_6H_4Br$), 326 (t_R: 14.42, 15.27; $ClC_6H_4OC_6H_4Br$).

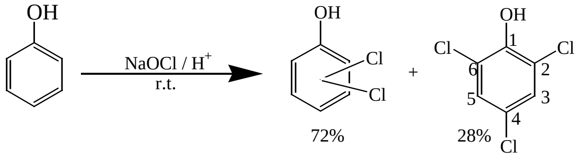
3.3.1.3 Bromination of diphenyl ether using 1/10 mole ratio of substrate and sodium bromide (mixture **3D**)



The same procedure as in the preparation of mixture 2D was followed, except 10 ml of 2M sodium hypochlorite and sodium bromide (0.62 g, 6 mmol) were substituted by 50 ml of 2M sodium hypochlorite and sodium bromide (6.2 g, 60 mmol). After the glacial acid (6.0 ml) was added very slowly, giving a deep red-brown mixture, then the procedure of mixture 2D was followed. The white solid of mixture 3D (1.83 g, 94%) was obtained with R_f 0.56 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 3D: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.41 (d, 4H, J_{H-H}= 2.41 Hz, *o*-BrOAr***H***), 6.88 (d, 4H, J_{H-H}= 2.30 Hz, *m*-BrOAr***H***); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 156.71 (2C, C-1 and C-1’) 132.88 (4C, C-2, C-6, C-2’ and C-6’), 120.61 (4C, C-3, C-5, C-3’ and C-5’), 116.24 (2C, C-4 and C-4’);
IR spectrum (KBr (cm^{-1})): 3077 (CH, st (aromatic)), 1571, 1475 (C=C, st), 1237 (C-O, st);
Mass spectrum (m/z): 326 (Int.100%, $BrC_6H_4OC_6H_4Br$); mp 53.5-54 °C.

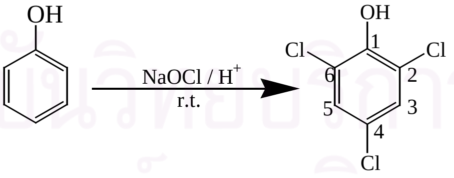
3.3.1.4 Bromination of phenol using 1/2 mole ratio of substrate and sodium hypochlorite (mixture **1P**)



Phenol (0.56 g, 6 mmol) and 10 ml of 1.2M sodium hypochlorite were added into a 100 ml two-neck flask with stirring while the reaction temperature was held at the room-temperature and 8 ml isoocatane was added. Then glacial acetic acid (2 ml) was added slowly by a dropping-funnel into the light-yellow mixture, giving an unstable white color for a while. After the color of the solution turned to light-yellow, then the mixture was vigorous stirred for 2 hours. The solution was left at room temperature until two phases were separated in a separating-funnel and the yellow oil product was extracted with 5 ml of methylene chloride (8 times) and washed 4-5 times with water until the aqueous layer was neutral. The combined organic layer was dried over sodium sulfate anhydrous and filtered. The solvent was removed by evaporation and crystalized in hexane to obtain the product as a brown solid (0.81 g, 79%) with R_f 0.52 and 0.70 (100% dichloromethane).

Characteristic data for mixture 1P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.31-7.11 (m, Ar***H***OHCl$_2$), 7.02-6.76 (m, Ar***H***OHCl$_2$), 5.62 (s, 1H, ArHO***H***Cl$_2$), 7.27 (s, 2H, *m*-Ar***H***OHCl$_3$), 5.93 (s, 1H, ArHO***H***Cl$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 147.58, 128.56, 128.52, 121.15, 117.13 (C, ArHOHCl$_2$), 147.30 (1C, C-1), 128.06 (2C, C-3 and C-5), 125.33 (1C, C-4), 121.60 (2C, C-2 and C-6), **IR spectrum** (KBr (cm^{-1})): 3698-3119 (OH, st), 3083 (CH, st (aromatic)), 1568, 1475 (C=C, st) 1330 (OH), 1219 (C-O, st); **GC-MS spectrum** (m/z): 162 (t_R: 8.95, 9.36 min; $C_6H_3Cl_2OH$), 196 (t_R: 10.99 min; $C_6H_2Cl_3OH$).

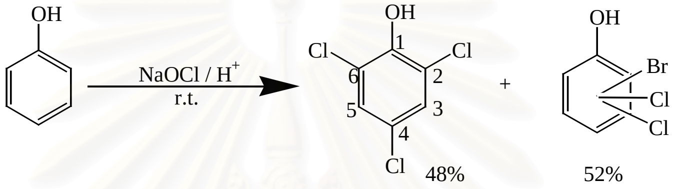
3.3.1.5 Bromination of phenol using 1/8 mole ratio of substrate and sodium hypochlorite (mixture **2P**)



The same procedure as in the preparation of mixture 1P was followed, except 10 ml of 1.2M sodium hypochlorite was substituted by 25 ml of 2M sodium hypochlorite and 8 ml isoocatane was added. After the glacial acid (4 ml) was added very slowly, giving an unstable green color for a while. After the color of the solution turned to brown, then the procedure of mixture 1P was followed. The brown-need crystal of mixture 2P (0.82 g, 70%) was obtained with R_f 0.41 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 2P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.26 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.84 (s, 1H, ArHO***H***Cl_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.87 (1C, C-1), 128.06 (2C, C-3, and C-5), 125.33 (1C, C-4), 121.58 (2C, C-2 and C-6); **IR spectrum** (KBr (cm^{-1})): 3545-3391 (OH, st), 3083 (CH, st (aromatic)), 1567, 1465 (C=C, st) 1316 (OH), 1224 (C-O, st); **Mass spectrum** (m/z): 196 (Int. 100%, $C_6H_2Cl_3OH$); mp 68.5-69 °C.

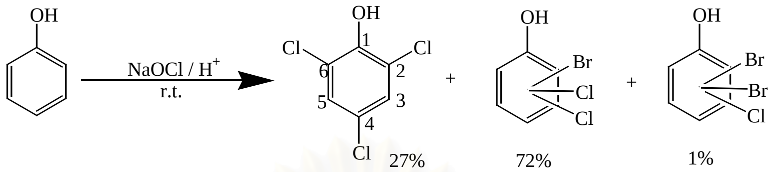
3.3.1.6 Bromination of phenol 1/1 using mole ratio of substrate and sodium bromide (mixture **3P**)



Sodium hypochlorite (10 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (0.62 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. The solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added slowly by a dropping-funnel into the light-yellow mixture, giving an unstable green color for a while. After the color of the solution turned to yellow, 8 ml of isooctane was added.). After the glacial acid (2.0 ml) was added very slowly, then the procedure of mixture 1P was followed. The white-needle crystal of mixture 3P (0.69 g, 53%) was obtained with R_f 0.44 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 3P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.26 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.84 (s, 1H, ArHO***H***Cl_3), 5.85 (s, 1H, ArHO***H***$BrCl_2$), 7.40, 7.30, 7.24 (Ar***H***$OHBrCl_2$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.87 (1C, C-1), 128.06 (2C, C-3, and C-5), 125.33 (1C, C-4), 121.58 (2C, C-2 and C-6), 147.73, 147.33, 130.91, 130.77, 128.68, 128.26, 125.78, 121.93, 121.13, 111.71, 110.30 (C, $ArHOHBrCl_2$); **IR spectrum** (KBr (cm^{-1})): 3554-3190 (OH, st), 3083 (CH, st (aromatic)), 1568, 1475 (C=C, st) 1311(OH), 1219 (C-O, st); **GC-MS spectrum** (m/z): 196 (t_R: 11.08 min; $C_6H_2Cl_3OH$), 240 (t_R: 12.06 min; $C_6H_2BrCl_2OH$).

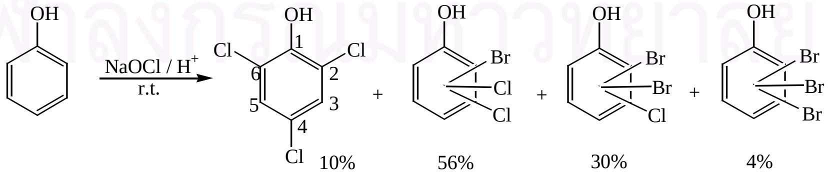
3.3.1.7 Bromination of phenol using 1/5 mole ratio of substrate and sodium bromide (mixture **4P**)



The same procedure as in the preparation of mixture 3P was followed, except 10 ml of 2M sodium hypochlorite and sodium bromide (0.62 g, 6 mmol) were substituted by 25 ml of 2M sodium hypochlorite and sodium bromide (3.1 g, 30 mmol). After that the glacial acetic acid (3 ml) was added very slowly, giving an unstable brown-green color for a while. After the color of the solution turned to yellow, then the procedure of mixture 3P was followed. The white-need crystal of mixture 4P (0.86 g, 63%) was obtained with R_f 0.44 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 4P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.26 (s, 2H, *m*-Ar***H***OHCl_3), 5.84 (s, 1H, ArHO***H***Cl_3), 7.41, 7.40, 7.31, 7.30, 7.26 (Ar***H***OHBrCl_2, Ar***H***OHBr_2Cl), 5.89 (s, 1H, ArHO***H***BrCl_2, ArHO***H***Br_2Cl); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.87 (1C, C-1), 128.07 (2C, C-3, and C-5), 125.30 (1C, C-4), 121.61 (2C, C-2 and C-6), 147.74, 147.36, 130.80, 128.68, 121.96, 121.14, 110.68, 110.42 (C, ArHOHBrCl_2, ArHOHBr_2Cl); **IR spectrum** (KBr (cm^{-1})): 3632-3380 (OH, st), 3078 (CH, st (aromatic)), 1557, 1470 (C=C, st), 11317(OH), 1219 (C-O, st); **GC-MS spectrum** (m/z): 196 (t_R: 14.30 min; $C_6H_2Cl_3OH$), 240 (t_R: 15.29 min; $C_6H_2BrCl_2OH$), 284 (t_R: 16.26 min; $C_6H_2Br_2ClOH$).

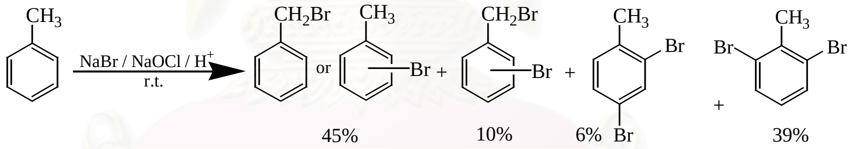
3.3.1.8 Bromination of phenol using 1/5 (mixed) mole ratio of substrate and sodium bromide (mixture **5P**)



Sodium hypochlorite (25 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (3.1 g, 30 mmol) and phenol (0.56 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at room-temperature. Then the light-yellow mixture gave an unstable brown-green color for a while. After the color of the solution turned to yellow, 8 ml of isooctane was added. After the glacial acid (3.0 ml) was added very slowly, then the procedure of mixture 3P was followed. The white-needle crystal of mixture 5P (0.84 g, 56%) was obtained with R_f 0.43 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 5P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.26 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.88 (s, 1H, ArHO***H***Cl_3), 7.57, 7.54, 7.53, 7.45, 7.44, 7.43, 7.41, 7.40, 7.39, 7.31, 7.30 (Ar***H***$OHBrCl_2$, Ar***H***$OHBr_2Cl$), 5.90 (s, ArHO***H***$BrCl_2$, ArHO***H***Br_2Cl), 7.57, 7.25 (Ar***H***$OHBr_3$), 5.84 (s, 1H, ArHO***H***Br_3);**^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 147.37 (1C, C-1), 128.09 (2C, C-3, and C-5), 125.77 (1C, C-4), 121.61 (2C, C-2 and C-6), 133.59, 131.56, 131.41, 130.93, 130.79, 128.69, 121.95, 112.21, 110.85, 104.96(C, $ArHOHBrCl_2$, $ArHOHBr_2Cl$) 148.19, 134.23, 112.69, 110.42 (C, $ArHOHBr_3$); **IR spectrum** (KBr (cm^{-1})): 3514-3229 (OH, st), 3021 (CH, st (aromatic)), 1568, 1455 (C=C, st), 1327 (OH), 1229 (C-O, st); **GC-MS spectrum** (m/z): 196 (t_R: 11.08 min; $C_6H_2Cl_3OH$), 240 (t_R: 12.05 min; $C_6H_2BrCl_2OH$), 284 (t_R: 12.99 min; $C_6H_2Br_2ClOH$), 328 (t_R: 14.14 min; $C_6H_2Br_3OH$).

3.3.1.9 Bromination of toluene using 1/1 mole ratio of substrate and sodium bromide (mixture **1T**)

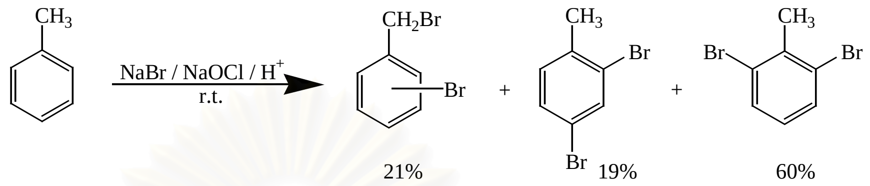


Sodium hypochlorite (10 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (0.62 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. The solution of toluene (0.56 g, 6 mmol) and 8 ml of isooctane was added slowly. Then glacial acetic acid (4.0 ml) was added. The mixture was vigorous stirred for 4 hours then the procedure of mixture 2D was followed. The yellow-brown liquid (0.34g, 27%) was obtained with R_f0.42 (100% hexane).

Characteristic data for mixture 1T: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.48-7.23 (m, Ar***H***Br, Ar***H***Br_2), 5.09, 4.57, 4.53, 4.49, 4.44, 4.43, 4.11, 4.04, 4.00, 3.96, 3.94, 3.92, 3.89, 3.88, 3.86, 2.21, 2.01, 1.92 (CH_2, CH_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 170.88, 146.21, 137.82, 135.97, 131.99, 131.27, 130.73, 129.08, 128.83, 128.61, 128.45, 128.29, 126.53, 122.48, 91.07, 66.34, 66.07 (C, ArHBr, $ArHBr_2$); **IR spectrum** (KBr (cm^1)):3033 (CH, st (aromatic)), 2943 (CH, aliphatic), 1592, 1491 (C=C, st); **GC-MS spectrum** (m/z): 170

(t_R: 11.37 min; C_7H_8Br), 248 (t_R: 13.97 min; 2, 4-dibromotoluene), 248 (t_R: 14.50 min; $C_7H_7Br_2$), 248 (t_R: 14.72 min; 2,6-dibromotoluene).

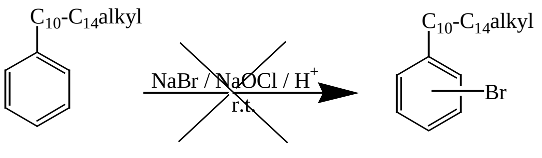
3.3.1.10 Bromination of toluene using 1/5 mole ratio of substrate and sodium bromide (mixture **2T**)



The same procedure as the preparation of mixture 1T was followed, except sodium hypochlorite (10 ml, 2M) and sodium bromide (0.62 g, 6 mmol) were substituted by sodium hypochlorite (25 ml, 2M) and sodium bromide (3.1 g, 30 mmol). The solution of toluene (0.56 g, 6 mmol) and 8 ml of isooctane was added slowly. Then glacial acetic acid (4.0 ml) was added. The mixture was vigorous stirred for 4 hours then the procedure of mixture 1T was followed. The yellow-brown liquid of mixture 2T (1.23 g, 83%) was obtained with R_f 0.46 and 0.58 (100% hexane).

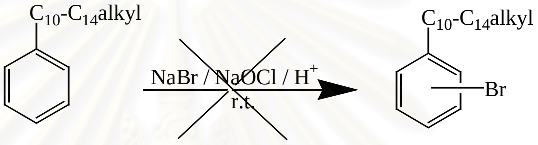
Characteristic data for mixture 2T: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.45 (d, J_{H-H}= 6.54 Hz, Ar***H***Br$_2$), 7.26-7.22 (m, Ar***H***Br$_2$), 4.59, 4.52, 4.42, 4.29, 4.14, 4.10, 4.04, 3.98, 9.90, 3.89, 3.87, 3.85, 2.16, 2.10, 2.03, 1.91, 1.34 (CH_2, CH_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.16, 136.80, 131.97, 130.72, 129.85, 128.67, 126.53, 66.05 (C, $ArHBr_2$) **IR spectrum** (KBr (cm^{-1})): 3066 (CH, st (aromatic)), 2963 (CH, aliphatic), 1594, 1481 (C=C, st); **GC-MS spectrum** (m/z): 248 (t_R: 13.97 min; 2, 4-dibromotoluene), 248 (t_R: 14.50 min; $C_7H_7Br_2$), 248 (t_R: 14.72 min; 2,6-dibromotoluene).

3.3.1.11 Bromination of linear alkyl benzene using 1/1 mole ratio of substrate and sodium bromide (mixture **1L**)



Sodium hypochlorite (10 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (0.62 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at room-temperature. The solution of linear alkyl benzene (1.5 g, 6 mmol) and 8 ml of isooctane was added slowly. Then glacial acetic acid (4.0 ml) was added very slowly. The mixture was vigorous stirred for 4 hours then the procedure of mixture 2D was followed. The obtained residue was characterized by ^{1}H-NMR spectroscopy was not observed on the ^{1}H-NMR spectrum indicated that desired product was not obtained.

3.1.1.12 Bromination of linear alkyl benzene using 1/5 mole ratio of substrate and sodium bromide (mixture **2L**)

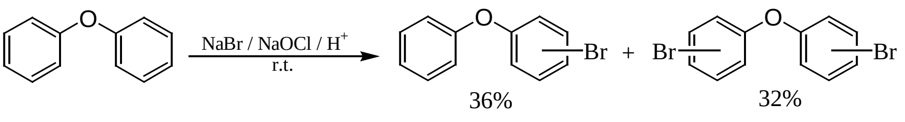


The same procedure as in the preparation of mixture 1L was followed, except 10 ml of 2M sodium hypochlorite and sodium bromide (0.62 g, 6 mmol) were substituted by 25 ml of 2M sodium hypochlorite and sodium bromide (3.1 g, 30 mmol). The solution of linear alkyl benzene (1.5 g, 6 mmol) and 8 ml of isooctane was added slowly. Then glacial acetic acid (4.0 ml) was added very slowly. The obtained residue was characterized by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum indicated that the proposed product was not obtained.

3.3.2 Bromination of aromatic substrate that containing ring activating group using phase transfer

3.3.2.1 Using tetrabutylammonium tetrafluoroborate (TBA)

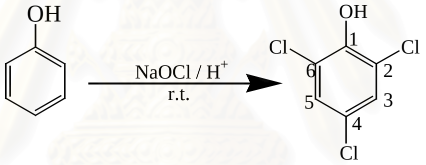
3.3.2.1.1 Bromination of diphenyl ether using 1/10 mole ratio of substrate and sodium bromide (mixture **4D**)



Sodium hypochlorite (50 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (6.2 g, 60 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. Tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was added and stirred for 30 minutes and followed by the solution of diphenyl ether (1.02 g, 6 mmol) in 8 ml of isooctane. After that the glacial acid (6 ml) was added very slowly, giving a deep red-brown mixture and stirring was continued for 2 hours, then the procedure of mixture 2D was followed. The white solid of mixture 4D (1.41 g, 64%) was obtained with R_f 0.56 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 4D: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.46-7.29 (m, Ar***H***Br, Ar***H***Br_2), 7.12-6.85 (m, Ar***H***Br, Ar***H***Br_2); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 156.93, 156.89, 123.97, 119.17, 115.90 (C, ArHBr), 157.50, 129.97, 123.44, 119.11 (C, $ArHBr_2$); **IR spectrum** (KBr (cm^{-1})): 3066 (CH, st (aromatic)), 1578, 1480 (C=C, st), 1236 (C-O, st); **GC-MS spectrum** (m/z): 248 (t_R: 11.16, 11.58 min; $C_6H_5OC_6H_4Br$), 326 (t_R: 16.31, 17.30 min; $BrC_6H_4OC_6H_4Br$).

3.3.2.1.2 Bromination of phenol using 1/8 mole ratio of substrate and sodium hypochlorite (mixture **6P**)

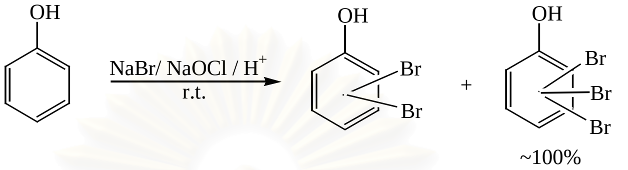


Tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) and sodium hypochlorite (25 ml, 2M) were added in a 100 ml two-neck flask with stirring for 30 minutes while the reaction temperature was held at the room-temperature and the solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added into the light-yellow mixture. The color of the mixture turned to brown, then the mixture was stirred for 15 minutes before 8 ml isooctane was added. The mixture was left to stir for 30 minute, the aqueous phase was homogeneous solution. Then glacial acetic acid (6 ml) was add slowly by a dropping-funnel into the brown mixture, giving a stable brown color, then the mixture was vigorous stirred for 2 hours. The solution was left at room temperature until two phases were separated by separating-funnel, then the yellow oil product was extracted with 5 ml of methylene chloride (8 times) and washed 4-5 times with water until the aqueous solution was neutral. The combined organic layer was dried over sodium sulfate anhydrous and filtered of to give oil product. Hexane and isooctane were removed by evaporation and the product crystalized from hexane. as brown needle crystals (1.02 g, 87%) with R_f 0.41 (ethyl acetate: hexane (20:80)).

Characteristic data for Mixture **6P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.26 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.88 (s, 1H, ArHO***H***Cl_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50

MHz): 147.37 (1C, C-1), 128.07 (2C, C-3, and C-5), 125.32 (1C, C-4), 121.60 (2C, C-2 and C-6); **IR spectrum** (KBr (cm^{-1})): 3668-3457 (OH, st), 3073 (CH, st (aromatic)), 1573, 1470 (C=C, st) 1393 (OH), 1224 (C-O, st); **Mass spectrum** (m/z): 196 (Int. 100%, $C_6H_2Cl_3OH$); mp 68.5-69 °C.

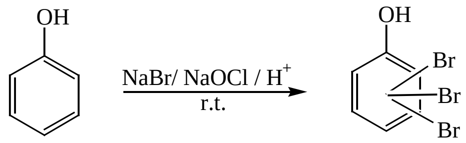
3.3.2.1.3 Bromination of phenol using 1/1 mole ratio of substrate and sodium bromide (mixture **7P**)



Sodium hypochlorite (10 ml, 2M was added into a 100 ml two-neck flask containing sodium bromide (0.62 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. Tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was added and stirred for 30 minutes. Then the solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added slowly by a dropping-funnel into the light-yellow mixture, giving an unstable green color for a while. After the color of the solution turned to yellow, then the mixture was stirred for 15 minutes before 8 ml isooctane was added. The mixture was left to stir for 30 minute, the aqueous phase was homogeneous solution. Then glacial acetic acid (4.0 ml) was added very slowly. Then light-yellow mixture was vigorous stirred for 2 hours and the solution was left at room temperature until two phases were separated by separated by separating-funnel, then the yellow oil product was extracted with 5 ml of methylene chloride (8 times) and washed 4-5 times with water until the aqueous solution was neutral. The combined organic layer was dried over sodium sulfate anhydrous and filtered of to give oil product. Hexane and isooctane were removed by evaporation and the product was obtained as white-needle crystals (0.89 g, 46%) with R_f 0.44 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture **7P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.26, 7.52 (Ar***H***OHBr$_2$Cl), 7.57 (s, Ar***H***OHBr$_3$), 7.24 (s, Ar***H***OHBr$_3$),5.89 (s, ArHO***H***Br$_2$Cl, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 148.95, 134.22, 112.68, 110.43 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3570-3411 (OH, st), 3058 (CH, st (aromatic)), 1552, 1460 (C=C, st), 1378 (OH), 1234 (C-O, st); **Mass spectrum** (m/z): 284 (Int. 0.33%, $C_6H_2Br_2ClOH$), 328 (Int. 100%, $C_6H_2Br_3OH$).

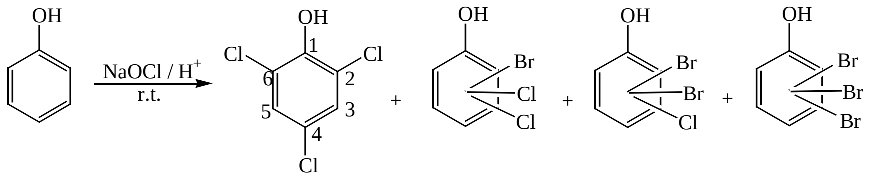
3.3.2.1.4 Bromination of phenol using 1/5 mole ratio of substrate and sodium bromide (mixture **8P**)



Sodium hypochlorite (25 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (3.1 g, 30 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. Tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was added and stirring was continued for 30 minutes. Then the solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added slowly by a dropping-funnel into the light-yellow mixture, giving a stable light-brown color. Then the mixture was stirred for 15 minutes before 8 ml isooctane was added. The mixture was left to stir for 30 minute, the aqueous phase was homogeneous solution. Then glacial acetic acid (6.0 ml) was added very slowly. The light-brown mixture was vigorous stirred for 2 hours and the solution was left at room temperature until two phases were separated by separated by separating-funnel. The yellow oil product was extracted with 5 ml of methylene chloride (8 times) and washed 4-5 times with water until the aqueous solution was neutral. The combined organic layer was dried over sodium sulfate anhydrous and filtered of to give oil product. Hexane and isooctane were removed by evaporation and the product crystalized from hexane as white-needle crystals (0.99 g, 50%) with R_f 0.44(ethyl acetate: hexane (20:80)).

Characteristic data for mixture **8P**: ^{1}H-NMR spectrum (CDCl$_3$, δ (ppm), 200 MHz): 7.58 (s, Ar***H***OHBr$_3$), 7.24 (s, Ar***H***OHBr$_3$),5.89 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** (CDCl$_3$, δ (ppm), 50 MHz): 148.95, 134.22, 112.69, 110.45 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3570-3421 (OH, st), 3073 (CH, st (aromatic)), 1593, 1460 (C=C, st) 1373 (OH), 1214 (C-O, st); **Mass spectrum** (m/z): 328 (Int. 100%, $C_6H_2Br_3OH$); mp 58-59 °C.

3.3.2.1.5 Bromination of phenol using 1/5 (mixed) mole ratio of substrate and sodium bromide (mixture **9P**)

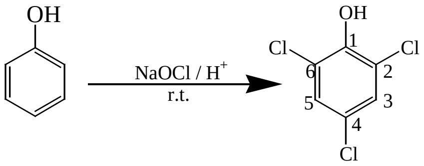


Sodium hypochlorite (25 ml, 2M) was added into a 100 ml two-neck flask containing sodium bromide (3.1 g, 30 mmol) and phenol (0.56 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. Then the light-yellow mixture, gave an unstable brown-green color for a while. After the color of the solution turned to yellow, tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was added and stirred for 30 minutes . Then 8 ml of isooctane was added. The mixture was left to stir for 30 minute, until the aqueous phase became homogeneous solution. Then glacial acetic acid (6.0 ml) was added very slowly. Then light-yellow mixture was vigorous stirred for 2 hours. The solution was left at room temperature until two phases were separated by separating-funnel, then the yellow oil product was extracted with 5 ml of methylene chloride (8 times) and washed 4-5 times with water until the aqueous solution was neutral. The combined organic layer was dried over sodium sulfate anhydrous and filtered to give oil product. Hexane and isooctane were removed by evaporation and the product crystalized from hexane. as white-needle crystals (1.00 g) with R_f 0.43 (ethyl acetate: hexane (20:80)).

Characteristic data for mixture 9P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.25 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.84 (s, 1H, ArHO***H***Cl_3), 7.55, 7.53, 7.45, 7.44, 7.41, 7.39, 7.35, 7.31, 7.30, 7.29, 7.20 (Ar***H***$OHBrCl_2$, Ar***H***$OHBr_2Cl$), 5.86 (s, ArHO***H***$BrCl_2$, ArHO***H***Br_2Cl), 7.58, 7.27 (Ar***H***$OHBr_3$), 5.74 (s, 1H, ArHO***H***Br_3);**^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 147.36 (1C, C-1), 128.07 (2C, C-3, and C-5), 125.30 (1C, C-4), 121.59 (2C, C-2 and C-6), 133.57, 131.55, 131.40, 130.92, 130.79, 128.68, 121.96, 111.69, 110.86, (C, $ArHOHCl_2Br$, $ArHOHClBr_2$) 147.75, 134.21, 112.21, 110.41 (C, $ArHOHBr_3$); **IR spectrum** (KBr (cm^{-1})): 3606-3411 (OH, st), 3073 (CH, st (aromatic)), 1562, 1470 (C=C, st), 1388 (OH), 1229 (C-O, st); **Mass spectrum** (m/z): 196 (Int. 29%, $_6H_2Cl_3OH$), 240 (Int. 100%, $C_6H_2BrCl_2OH$), 284 (Int. 70%, $C_6H_2Br_2ClOH$), 328 (Int. 13%, $C_6H_2Br_3OH$).

3.3.2.2 Using cetyl ammonium bromide (CTAB)

3.3.2.2.1 Bromination of phenol using 1/8 mole ratio of substrate and sodium hypochlorite (mixture **10P**)



The same procedure as in the preparation of Mixture **6P** was followed, except tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was substituted by cetyl ammonium bromide (0.22 g, 0.6 mmol). The brown needle crystals of mixture **10P** (0.80 g, 68%) with R_f 0.41 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for Mixture **10P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.29 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.87 (s, 1H, ArHO***H***Cl_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.92 (1C, C-1), 128.68 (2C, C-3, and C-5), 125.31 (1C, C-4), 121.60 (2C, C-2 and C-6); **IR spectrum** (KBr (cm^{-1})): 3718-3119 (OH, st), 3078 (CH, st (aromatic)), 1562, 1475 (C=C, st) 1388 (OH), 1214 (C-O, st); **Mass spectrum** (m/z): 196 (Int. 100%, $C_6H_2Cl_3OH$); mp 68-69.5 °C.

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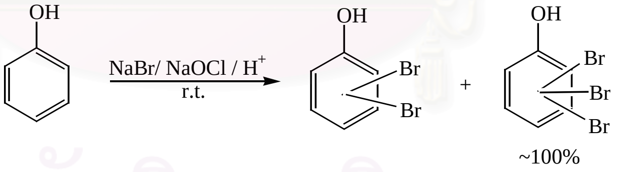
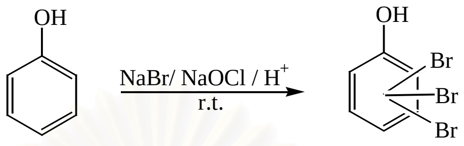
3.3.2.2.2 Bromination of phenol using 1/1 mole ratio of substrate and sodium bromide (mixture **11P**)



The same procedure as in the preparation of mixture **7P** was followed, except tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was substituted by cetyl ammonium bromide (0.22 g, 0.6 mmol). The brown solid of mixture **11P** (0.56 g, 29%) with R_f 0.44 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture **11P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.62, 7.57, 7.53, 7.44, 7.20 (Ar***H***$OHBr_2Cl$), 7.60 (s, Ar***H***$OHBr_3$), 7.24 (s, Ar***H***$OHBr_3$),5.89 (s, ArHO***H***Br_2Cl, ArHO***H***Br_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 148.96, 134.22, 112.68, 110.44 (C, $ArHOHBr_3$); **IR spectrum** (KBr (cm^{-1})): 3677-3425 (OH, st), 3073 (CH, st (aromatic)), 1547, 1460 (C=C, st), 1270 (C-O, st); **Mass spectrum** (m/z): 284 (Int. 6%, $C_6H_2Br_2ClOH$), 328 (Int. 100%, $C_6H_2Br_3OH$).

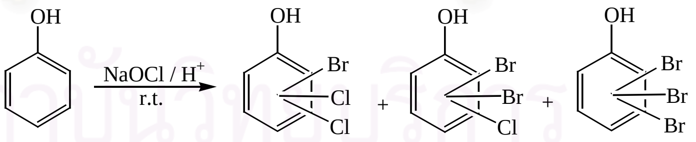
3.3.2.2.3 Bromination of phenol using 1/5 mole ratio of substrate and sodium bromide (mixture **12P**)



The same procedure as in the preparation of Mixture **8P** was followed, except tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was substituted by cetyl ammonium bromide (0.22 g, 0.6 mmol). The brown solid of mixture **12P** (0.95 g, 48%) with with R_f 0.44 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture **12P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.62 (s, Ar***H***OHBr$_3$), 7.24 (s, Ar***H***OHBr$_3$),5.28 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 148.96, 134.22, 112.69, 110.47 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3687-3411 (OH, st), 3073 (CH, st (aromatic)), 1588, 1450 (C=C, st) 1320 (OH), 1230 (C-O, st); **Mass spectrum** (m/z): 328 (Int. 100%, $C_6H_2Br_3OH$); mp 58-59 °C.

3.3.2.2.4 Bromination of phenol using 1/5 (mixed) mole ratio of substrate and sodium bromide (mixture **13P**)

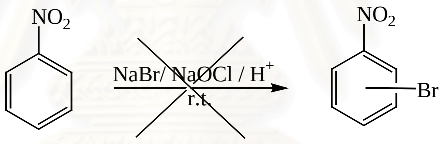


The same procedure as in the preparation of mixture **9P** was followed, except tetrabutylammonium tetrafluoroborate (0.20 g, 0.6 mmol) was substituted by cetryl ammonium bromide (0.22 g, 0.6 mmol). The brown solid of mixture **13P** (0.95g) R_f 0.43 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 13P: ^{1}H-NMR spectrum (CDCl$_3$, (ppm),200 MHz): 7.57, 7.54, 7.53, 7.48, 7.44, 7.41, 7.39, 7.35, 7.31, 7.30, 7.26, 7.22, 7.20 (Ar***H***OHBrCl$_2$, Ar***H***OH Br$_2$Cl), 5.86 (s, ArHO***H***BrCl$_2$Br, ArHO***H***Br$_2$Cl), 7.62, 7.24 (Ar***H***OHBr$_3$), 5.85 (s, 1H, ArHO***H***Br$_3$);**^{13}C-NMR spectrum** (CDCl$_3$, δ (ppm), 50 MHz): 148.14, 147.76, 147.36, 134.21, 133.57, 131.55, 131.40, 130.92, 130.79, 128.68, 128.07, 125.76, 121.95, 121.53, 121.14, 112.21, 111.69,110.85, 109.98 (C, ArHOHCl$_2$Br, ArHOHClBr$_2$) 148.53, 134.21, 112.68, 110.42 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3611-3375 (OH, st), 3073 (CH, st (aromatic)), 1557, 1460 (C=C, st), 1393 (OH), 1224 (C-O, st); **Mass spectrum** (m/z): 240 (Int. 75%, $C_6H_2BrCl_2OH$), 284 (Int. 100%, $C_6H_2Br_2ClOH$), 328 (Int. 25%, $C_6H_2Br_3OH$).

3.3.3 Bromination of aromatic substrate containing electron-withdrawing groups

3.3.3.2 Bromination of nitrobenzene using 1/1 mole ratio of substrate and sodium bromide (**mixture N1**)



The same procedure as in the preparation of mixture **2D** was followed, except nitrobenzene (0.86 g, 6 mmol) was used. The obtained residue was characterized by ^{1}H-NMR spectroscopy but the signal of aromatic proton (Ar***H***) at about 8.39-7.24 ppm was not observed in the ^{1}H-NMR spectrum indicated that the desired product was not obtained.

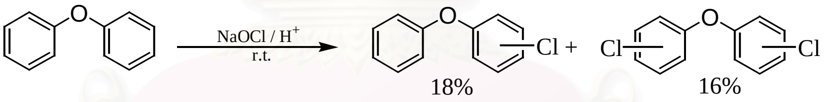
3.3.4 Effect of oil phase studies

The same procedure as in the preparation was followed and shown in Table 3.1, except 8 ml of isooctane was substituted by 20 ml of hexane.

Table 3.1 The procedure of the preparation

Substrate	Mixture	The same procedure as in the preparation was followed
Diphenyl ether	5D	1D
	6D	2D
	7D	3D
Phenol	14P	2P
	15P	3P
	16P	4P
	17P	5P
*Phenol (no oil phase)	18P	2P
Toluene	3T	1T
	4T	2T

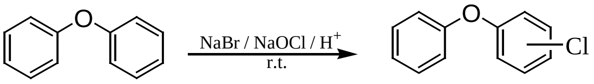
3.3.4.1 Bromination of diphenyl ether using mole ratio of substrate and sodium hypochlorite : 1/8 (mixture **5D**)



The same procedure as in the preparation of mixture **1D** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The light-yellow oil of mixture **5D** (0.76 g, 23%) with R_f 0.80 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 5D: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.42-7.31 (m), 7.16-7.01 (m); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): -; **IR spectrum (KBr, (cm^{-1})):** 3055(CH, st (aromatic)), 1588, 1487 (C=C, st), 1235 (C-O, st); **GC-MS spectrum** (m/z): 204 (t_R: 16.43, 16.63 min; $C_6H_5OC_6H_4Cl$), 238 (t_R: 17.95, 18.10, 18.32 min; $ClC_6H_4OC_6H_4Cl$).

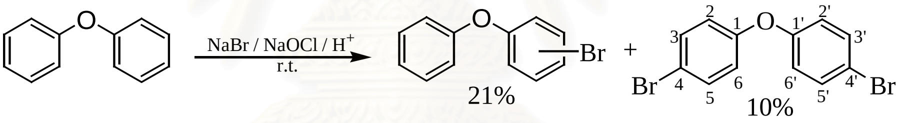
3.3.4.2 Bromination of diphenyl ether using mole ratio of substrate and sodium bromide : 1/1 (mixture **6D**)



The same procedure as in the preparation of mixture **2D** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The light-yellow oil of mixture **6D** (0.55 g, 1.5%) with R_f 0.70 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 6D: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.37-7.25 (m), 7.13-6.59 (m); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 156.96, 156.79, 130.15, 123.90, 120.28, 118.19 (C, $C_6H_5OC_6H_4Cl$); **IR spectrum** (KBr (cm^{-1})): 3072 (CH, st (aromatic)), 1588, 1491 (C=C, st), 1227 (C-O, st); **GC-MS spectrum** (m/z): 204 (t_R: 11.17 min; C_6H_5-O-C_6H_4Cl).

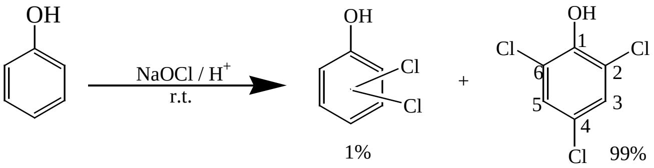
3.3.4.3 Bromination of diphenyl ether using 1/10 mole ratio of substrate and sodium bromide (mixture **7D**)



The same procedure as in the preparation of mixture **3D** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The white solid of mixture **7D** (1.22 g, 31%) with R_f 0.70 (ethyl acetate: hexane (20:80)) was obtained.

.**Characteristic data for mixture 7D: ^{1}H-NMR spectrum** ($CDCl_3$, (ppm),200 MHz): 7.46-7.25 (m), 7.13-6.49 (m); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 156.96, 156.62, 133.11, 123.98, 119.16, 115.56 (C, $C_6H_5OC_6H_4Cl$), 156.78 (2C, C-1 and C-1') 132.94 (4C, C-2, C-6, C-2' and C-6'), 120.83 (4C, C-3, C-5, C-3' and C-5'), 115.89 (2C, C-4 and C-4');
IR spectrum (KBr (cm^{-1})): 3068 (CH, st (aromatic)), 1588, 1487 (C=C, st), 1235 (C-O, st);
GC-MS spectrum (m/z): 248 (t_R: 12.68 min; C_6H_5-O-C_6H_4Br), 326 (t_R: 19.50 min; $BrC_6H_4OC_6H_4Br$).

3.3.4.4 Bromination of phenol using 1/8 mole ratio of substrate and sodium hypochlorite (mixture **14P**)



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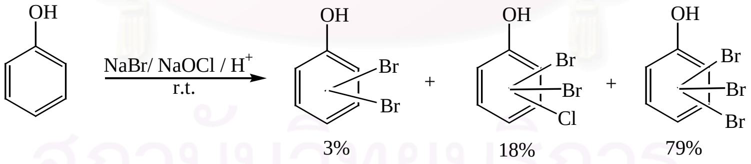
The same procedure as in the preparation of mixture **2P** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The brown needle crystal of mixture **14P** (0.71 g, 61%) with R_f 0.41 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 14P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.48, 7.56, 7.43, 7.35, 7.33, 7.31, 7.29, 7.23, 6.88, 6.87, 7.85 (Ar***H***OHCl$_2$), 5.62 (ArHO***H***Cl$_2$), 7.26 (s, 2H, *m*-Ar***H***OHCl$_3$), 5.94 (s, 1H, ArHO***H***Cl$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.93 (1C, C-1), 128.06 (2C, C-3, and C-5), 125.29 (1C, C-4), 121.26 (2C, C-2 and C-6); **IR spectrum** (KBr (cm^{-1})): 3642-3577 (OH, st), 3073 (CH, st (aromatic)), 1573, 1475 (C=C, st) 1321 (OH), 1219 (C-O, st); **GC-MS spectrum** (m/z): 162 (t_R: 5.18 min, $C_6H_3Cl_2OH$), 196 (t_R: 7.01 min; $C_6H_2Cl_3OH$).

3.3.4.5 Bromination of phenol using 1/1 mole ratio of substrate and sodium bromide (mixture **15P**)

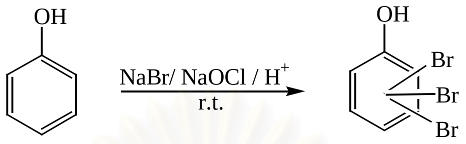


The same procedure as in the preparation of mixture **3P** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The brown solid of mixture **15P** (0.82 g, 43%) with R_f 0.44 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 15P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.77, 7.71, 7.67, 7.62, 7.53, 7.44, 7.40, 7.28, 7.20 (Ar***H***OHBr$_2$, Ar***H***OHBr$_2$Cl),), 7.62, 7.24 (Ar***H***OHBr$_3$), 5.89 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 148.95, 134.22, 112.68, 110.45 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3606-3416 (OH, st), 3073 (CH, st (aromatic)), 1552, 1455 (C=C, st) 1383 (OH), 1265 (C-O, st); **GC-MS spectrum** (m/z):

250 (t_R: 7.38, 7.67 min; $C_6H_2Br_2OH$), 284 (t_R: 9.65 min; $C_6H_2Br_2ClOH$), 328 (t_R: 10.88 min; $C_6H_2Br_3OH$).

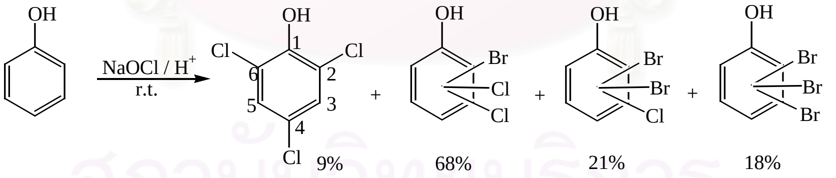
3.3.4.6 Bromination of phenol using 1/5 mole ratio of substrate and sodium bromide (mixture **16P**)



The same procedure as in the preparation of mixture **4P** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The brown solid of mixture **16P** (0.77 g, 39%) with with R_f 0.44 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture **16P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.49 (s, Ar***H***OHBr$_3$), 7.13 (s, Ar***H***OHBr$_3$),2.89 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 148.98, 134.23, 112.49, 110.49 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3570-3421 (OH, st), 3073 (CH, st (aromatic)), 1598, 1465 (C=C, st) 1328 (OH), 1245 (C-O, st); **GC-MS spectrum** (m/z): 328 (t_R: 11.41 min; $C_6H_2Br_3OH$); mp 58-59 °C.

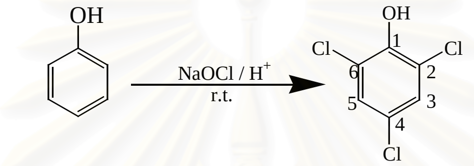
3.3.4.7 Bromination of phenol using 1/5 (mixed) mole ratio of substrate and sodium bromide (mixture **17P**)



The same procedure as in the preparation of mixture **5P** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The brown solid of mixture **17P** (0.91 g, 61%) with R_f 0.43 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 17P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.26 (s, 2H, *m*-Ar***H***OHCl$_3$), 5.86 (s, 1H, ArHO***H***Cl$_3$ 7.54, 7.53, 7.44, 7.43, 7.41, 7.40, 7.31, 7.30, 7.29 (Ar***H***OHBrCl$_2$, Ar***H***OHBr$_2$Cl), 5.86 (s, ArHO***H***BrCl$_2$, ArHO***H***Br$_2$Cl), 7.57, 7.24 (Ar***H***OHBr$_3$), 5.86 (s, 1H, ArHO***H***Br$_3$);**^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 147.93 (1C, C-1), 128.07 (2C, C-3, and C-5), 125.29 (1C, C-4), 121.54 (2C, C-2 and C-6) 147.17, 147.37, 133.58, 131.55, 131.40, 130.93, 130.79, 128.68, 128.28, 125.74, 121.97, 121.62, 121.15, 112.21, 111.69, 110.87, 109.99 (C, ArHOHBrCl$_2$, ArHOHBr$_2$Cl) 148.21, 134.21, 112.68, 110.45 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})): 3611-3406 (OH, st), 3068 (CH, st (aromatic)), 1562, 1475 (C=C, st), 1312 (OH), 1276 (C-O, st); **GC-MS spectrum** (m/z): 196 (t$_R$: 7.43 min; $C_6H_2Cl_3OH$), 240 (t$_R$: 8.72 min; $C_6H_2BrCl_2OH$), 284 (t$_R$: 9.93 min; $C_6H_2Br_2ClOH$), 328 (t$_R$: 11.14 min; $C_6H_2Br_3OH$).

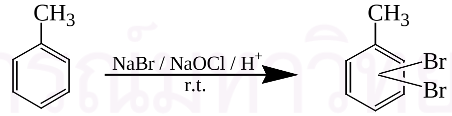
3.3.4.8 Bromination of phenol using 1/8 mole ratio of substrate and sodium hypochlorite and no oil phase (mixture **18P**)



The same procedure as in the preparation of mixture **2P** was followed, except 8 ml of isooctane was substituted by no using oil phase. The brown needle crytal of mixture **18P** (0.40 g, 34%) with R$_f$ 0.41 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 18P: ^{1}H-NMR spectrum (CDCl$_3$, (ppm),200 MHz): 7.29 (s, 2H, *m*-Ar***H***OHCl$_3$), 5.86 (s, 1H, ArHO***H***Cl$_3$); **^{13}C-NMR spectrum** (CDCl$_3$, δ (ppm), 50 MHz): 146.92 (1C, C-1), 128.08 (2C, C-3, and C-5), 125.30 (1C, C-4), 121.61 (2C, C-2 and C-6); **IR spectrum** (KBr (cm^{-1})): 3560-3396 (OH, st), 3088 (CH, st (aromatic)), 1568, 1465 (C=C, st) 1388 (OH), 1270 (C-O, st); **Mass spectrum** (m/z): 196 (Int. 100%; $C_6H_2Cl_3OH$); mp 68-69.5 ^{o}C.

3.3.4.9 Bromination of toluene using mole ratio of substrate and sodium bromide: 1/1 (mixture **3T**)

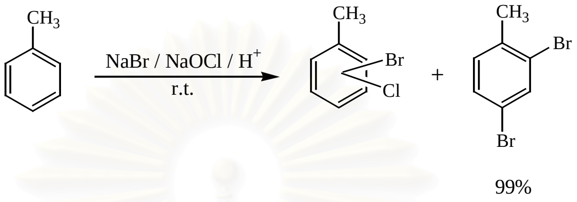


The same procedure as in the preparation of mixture **1T** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The yellow-brown oil of mixture **3T** (0.40 g, 27%) with R$_f$ 0.42 (100% hexane) was obtained.

Characteristic data for mixture 3T: ^{1}H-NMR spectrum (CDCl$_3$, (ppm),200 MHz): 7.57-7.25(m, Ar***H***Br$_2$), 6.64, 5.10, 4.69, 6.65, 4.47, 4.42, 2.79, 2.54, 2.33, 2.21, 2.09, 2.05, 2.04, 2.00, 1.91, 1.83, 1.77, 1.49, 1.46 (CH$_2$, CH$_3$); **^{13}C-NMR spectrum** (CDCl$_3$, δ (ppm), 50 MHz):

131.97, 129.85, 128.65, 128.59, 128.28, 126.49, 41.05, 29.71, 29.38, 22.71, 14.15, 1.03 (C, ArHBr, $ArHBr_2$); **IR spectrum** (KBr (cm^{1})):3068 (CH, st (aromatic)), 2916 (CH, aliphatic), 1592, 1453 (C=C, st); **GC-MS spectrum** (m/z): 248 (t_R: 13.97, 14.74 min; $C_7H_7Br_2$).

3.3.4.10 Bromination of toluene using 1/5 mole ratio of substrate and sodium bromide (mixture **4T**)



The same procedure as in the preparation of mixture **2T** was followed, except 8 ml of isooctane was substituted by 20 ml of hexane. The yellow-brown oil of mixture **4T** (0.88 g, 59%) with with R_f 0.50 (100% hexane) was obtained.

Characteristic data for mixture 4T: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.55 (d, J_{H-H}= 8.12 Hz, Ar***H***Br_2), 7.39 (d, J_{H-H}= 7.05 Hz, Ar***H***Br_2), 6.64 (CH_2, CH_3); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 141.97, 129.84, 126.56, 123.32, 41.39 (C, $ArHBr_2$); **IR spectrum** (KBr (cm^{1})):3067 (CH, st (aromatic)), 2920 (CH, aliphatic), 1577, 1487 (C=C, st); **GC-MS spectrum** (m/z): 204 (t_R: 13.11 min; C_7H_8BrCl), 248 (t_R: 13.97 min; $C_7H_7Br_2$).

3.3.5 Mole ratio of substrate and reagents

3.3.5.1 Mole ratio of diphenyl ether and sodium bromide

The same procedure as in the preparation of mixture **2D** or mixture **3D** was followed, except the amount of sodium bromide is shown in Table 3.2,

Table 3.2 Mole ratio of diphenyl ether and sodium bromide

Mixture	Mole of diphenyl ether	Mole of sodium bromide (NaBr)	Mole ratio of diphenyl ether and NaBr	Volumn of 2M sodium hypochlorite
2D	6 mmol(1.02 g)	6 mmol(0.62 g)	1:1	10
8D	6 mmol(1.02 g)	12 mmol(1.24 g)	1:2	15
9D	6 mmol(1.02 g)	24 mmol(2.50 g)	1:4	20
10D	6 mmol(1.02 g)	36 mmol(3.72 g)	1:6	30
11D	6 mmol(1.02 g)	48 mmol(4.94 g)	1:8	30
3D	6 mmol(1.02 g)	60 mmol(6.20 g)	1:10	40
12D	6 mmol(1.02 g)	72 mmol(7.40 g)	1:12	50

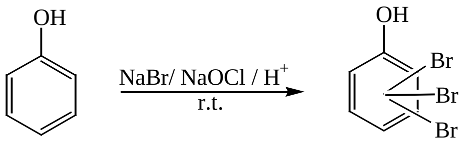
3.3.5.2 **Mole ratio of phenol and sodium hypochlorite**

The reactions were carried out by mixing the solution of phenol, sodium bromide, sodium hypochlorite, organic solvent (isooctane) and acid (glacial acetic acid) since aqueous phase and organic phase are not compatible and shown in Table 3.3, the brominations were performed by gradually adding aqueous phase into the organic phase.

Table 3.3 Mole ratio of phenol and sodium hypochlorite (Using NaBr 6 mmol)

Mixture	Mole of phenol	Mole of sodium hypochlorite (NaOCl)	Mole ratio of phenol and NaOCl	Volumn of glacial acetic acid
19P	6 mmol(0.56 g)	6 mmol	1:1	2 ml
20P	6 mmol(0.56 g)	12 mmol	1:2	2 ml
21P	6 mmol(0.56 g)	18 mmol	1:3	4 ml
22P	6 mmol(0.56 g)	24 mmol	1:4	4 ml

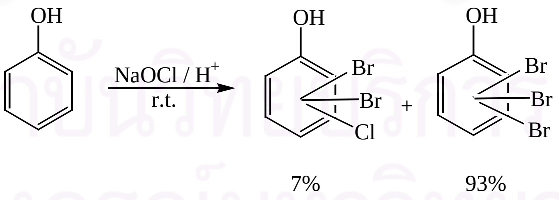
3.3.5.2.1 Bromination of phenol using 1/1 mole ratio of substrate and sodium hypochlorite (mixture **19P**)



Sodium hypochlorite (5 ml, 1.2 M), (6 mmol) was added into a 100 ml two-neck flask containing sodium bromide (0.62 g, 6 mmol) with stirring by a magnetic stirrer while the reaction temperature was held at the room-temperature. The solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added slowly by a dropping-funnel into the light-yellow mixture, giving an unstable grey-green color for a while. After the color of the solution turned to yellow, 8 ml of isooctane was added. Then glacial acetic acid (2.0 ml) was added very slowly, giving a stable red-brown color. Then mixture was vigorous stirred for 2 hours. The solution was left at room temperature until two phases were separated by separating-funnel, then the yellow oil product was extracted with 5 ml of methylene chloride (8 times) and washed 4-5 times with water until the aqueous solution was neutral. The combined organic layer was dried over sodium sulfate anhydrous and filtered of to give a oil product, hexane and isooctane were removed by the evaporation and the product crystalized from hexane. The product was obtained as a brown solid (0.24 g, 12%) with R_f 0.44(ethyl acetate: hexane (20:80)).

Characteristic data for mixture **19P**: ^{1}H-NMR spectrum ($CDCl_3$, δ (ppm), 200 MHz): 7.57 (s, Ar***H***OHBr$_3$), 7.24 (s, Ar***H***OHBr$_3$),5.88 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 148.94, 134.22, 112.69, 110.41 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})) 3580-3145 (OH, st), 3068 (CH, st (aromatic)), 1557, 1465(C=C, st) 1388 (OH), 1271 (C-O, st); **GC-MS spectrum** (m/z): 328 (t_R: 13.83 min; $C_6H_2Br_3OH$); mp 58-59 °C.

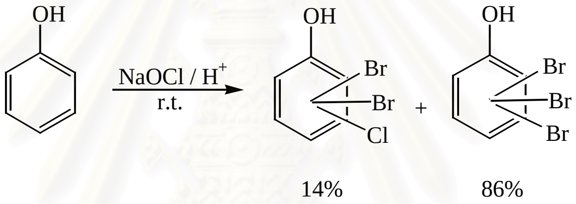
3.3.5.2.2 Bromination of phenol using 1/2 mole ratio of substrate and sodium hypochlorite (mixture **20P**)



The same procedure as in the preparation of Mixture **19P** was followed, except sodium hypochlorite (5 ml, 1.2M), (6 mmol) was substituted by sodium hypochlorite (10 ml, 1.2M), (12 mmol). The solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added into the light-yellow mixture, giving an unstable grey-red color for a while. After the color of the solution turned to yellow, 8 ml of isooctane was added. Then glacial acetic acid (2.0 ml) was added very slowly, giving a stable red-brown color. Then the procedure of mixture **19P** was followed. The brown solid of mixture **20P**(0.22 g, 11%) with R$_f$ 0.44(ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture **20P**: ^{1}H-NMR spectrum (CDCl$_3$, δ (ppm), 200 MHz): 7.62, 7.60, 7.54, 7.52, 7.44, 7.43, 6.91, 6.87, 6.75, 6.72, 6.68, 6.64 (Ar***H***OHBr$_2$Cl), 5.89 (s, 1H, ArHO***H***Br$_2$Cl), 7.57 (s, Ar***H***OHBr$_3$), 7.24 (s, Ar***H***OHBr$_3$),5.52 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** (CDCl$_3$, δ (ppm), 50 MHz): 148.94, 134.22, 112.69, 110.41 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1}))3524-3150 (OH, st), 3068 (CH, st (aromatic)), 1557, 1455 (C=C, st) 1378 (OH), 1265 (C-O, st); **GC-MS spectrum** (m/z): 284 (t$_R$: 9.74 min; $C_6H_2Br_2ClOH$), 328 (t$_R$: 10.94 min; $C_6H_2Br_3OH$).

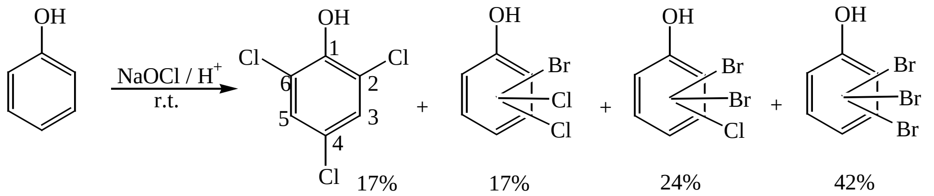
3.3.5.2.3 Bromination of phenol using 1/3 mole ratio of substrate and sodium hypochlorite (mixture **21P**)



The same procedure as in the preparation of mixture **19P** was followed, except sodium hypochlorite (5 ml, 1.2M), (6 mmol) was substituted by sodium hypochlorite (15 ml, 1.2M), (18 mmol). The solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added into the light-yellow mixture, giving an unstable grey-red color for a while. After the color of the solution turned to yellow, 8 ml of isooctane was added. Then, glacial acetic acid (4.0 ml) was added very slowly, giving a stable red-brown color. Then, the procedure of mixture **19P** was followed. The brown solid of mixture **21P** (0.46 g, 24%) with R$_f$ 0.44 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture **21P**: ^{1}H-NMR spectrum (CDCl$_3$, δ (ppm), 200 MHz): 7.62, 7.56, 7.53, 7.44, 7.43,7.40, 7.32, 7.29, 7.24, 7.17, 7.12, 7.02, 7.00, 6.85, 6.80, 6.65 (Ar***H***OHBr$_2$Cl) 5.52 (s, 1H, ArHO***H***Br$_2$Cl),7.57 (s, Ar***H***OHBr$_3$), 7.24 (s, Ar***H***OHBr$_3$),5.88 (s, 1H, ArHO***H***Br$_3$); **^{13}C-NMR spectrum** (CDCl$_3$, δ (ppm), 50 MHz): 148.20, 133.59, 131.56, 131.41 (C, ArHOHBr$_2$Cl), 148.94, 134.22, 112.69, 110.41 (C, ArHOHBr$_3$); **IR spectrum** (KBr (cm^{-1})) 3514-3165 (OH, st), 3063 (CH, st (aromatic)), 1552, 1460 (C=C, st) 1383 (OH), 1271 (C-O, st); **GC-MS spectrum** (m/z): 284 (t$_R$: 12.95 min; $C_6H_2Br_2ClOH$), 328 (t$_R$: 13.83 min; $C_6H_2Br_3OH$).

3.3.5.2.4 Bromination of phenol using 1/4 mole ratio of substrate and sodium hypochlorite (mixture **22P**)



The same procedure as in the preparation of mixture **19P** was followed, except sodium hypochlorite (5 ml, 1.2M), (6 mmol) was substituted by sodium hypochlorite (20 ml, 1.2M), (24 mmol). The solution of phenol (0.56 g, 6 mmol) in 5 ml of water was added into the light-yellow mixture, then 8 ml of isooctane was added. Then, glacial acetic acid (4.0 ml) was added very slowly, giving an unstable blue-brown color. Then, the procedure of mixture **19P** was followed. The brown solid of mixture **22P** (0.76 g, 45%) with R_f 0.43 (ethyl acetate: hexane (20:80)) was obtained.

Characteristic data for mixture 22P: ^{1}H-NMR spectrum ($CDCl_3$, (ppm),200 MHz): 7.26 (s, 2H, *m*-Ar***H***$OHCl_3$), 5.86 (s, 1H, ArHO***H***Cl_3), 7.54, 7.53, 7.44, 7.43, 7.41, 7.40, 7.31, 7.30, 7.29, 6.95, 6.91, 6.84, 6.80, 6.76, 6.74, 6.68 (Ar***H***$OHCl_2Br$, Ar***H***$OHClBr_2$), 5.52 (s, ArHO***H***$BrCl_2$, ArHO***H***Br_2Cl), 7.57, 7.24 (Ar***H***$OHBr_3$), 5.86 (s, 1H, ArHO***H***Br_3);**^{13}C-NMR spectrum** ($CDCl_3$, δ (ppm), 50 MHz): 146.89 (1C, C-1), 128.07 (2C, C-3, and C-5), 125.29 (1C, C-4), 121.58 (2C, C-2 and C-6), 148.17, 134.21, 133.58, 132.10131.55, 131.40, 130.93, 130.79, 128.68, 128.28, 122.46, 121.58, 117.45, 112.69, 112.24, 110.42, 109.96 (C, $ArHOHBrCl_2$, $ArHOHBr_2Cl$) 148.94, 134.21, 112.69, 110.42 (C, $ArHOHBr_3$); **IR spectrum** (KBr (cm^{-1})): 3687-3104 (OH, st), 3078 (CH, st (aromatic)), 1557, 1455 (C=C, st), 1388 (OH), 1271(C-O, st); **GC-MS spectrum** (m/z): 196 (t_R: 11.10 min; $C_6H_2Cl_3OH$), 240 (t_R: 12.07 min; $C_6H_2BrCl_2OH$), 284 (t_R: 12.95 min; $C_6H_2Br_2ClOH$), 328 (t_R: 13.83 min; $C_6H_2Br_3OH$).

3.4 Characterization of synthesized mixture by using instuments as follows:

1. Fourier-Transform Infrared Spectrophotometer (FT-IR)
2. ^{1}H and ^{13}C Nuclear Magnetic Resonance spectrometer (NMR)
3. Mass Spectrometry (MS)
4. Gas Chromatography-Mass Spectrometer (GC-MS)

Gas chromatograph –mass spectrometer was used to identify and quantitatively determination of the mixture. The GC-MS was performed using DB5 capillary column. The general condition can be summerized as follows:

Column : DB5 MS (30 m.)

Injection : split 1:50 250 °C

Carrier : He at 24 cm^{3}/min

Oven : 60 °C for 3 min
60 °C-220 °C at 10 °C/min
220 °C for 5 min

Chapter IV

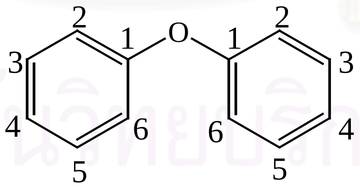
Results and discussion

The main purpose of this research focused on the new bromination of aromatic mixture in order to avoid handling liquid bromine. Sodium bromide/ sodium hypochlorite reagent was studied and utilized for the bromination process in two phase system (aqueous and organic solvent). This reagent is innovative, safe and easy to use.

4.1 Halogenation of diphenyl ether

From the literature search, it was obviously revealed that dibromodiphenyl ether could be used as the flame retardant agent useful in a variety of potential applications (e.g. polyesters and polystyrenes). In 1989, there has been reported on the approach for synthesizing dibromodiphenyl ether using liquid bromine. In this research, two reagents (sodium hypochlorite and a combination of sodium bromide / sodium hypochlorite) were used in the bromination of diphenyl ether. In approach 1, sodium hypochlorite reagent was used in the chlorination of diphenyl ether to give chlorodiphenyl ether. The other approach used sodium bromide / sodium hypochlorite reagent in the bromination of diphenyl ether to give bromodiphenyl ether and dibromodiphenyl ether.

Diphenyl ether is a colorless liquid, insoluble in water but freely soluble in organic solvent. Its structure is shown below:



The IR spectrum of diphenyl ether showed absorption peaks of =C-H stretching of aromatic at 3036 cm^{-1} (w), C=C ring stretching of aromatic at 1584 and 1484 cm^{-1} (m) and C-O stretching of alkoxy group at 1226 cm^{-1} (m). In addition, the ^{1}H-NMR spectrum of aromatic protons appear at 7.06-7.67 ppm as the multiplet signals, respectively. The ^{13}C-NMR spectrum of diphenyl ether revealed the presence of C-1 at 157.5 ppm, C-2 and C-6 at 118.7 ppm, C-3 and C-5 at 129.7 ppm and C-4 at 123.1 ppm. The mass spectrum of diphenyl ether exhibited m/z at 170, which was the molecular weight of diphenyl ether.

Table 4.1 The physical properties and %yield of diphenyl ether derivatives

Cpd	Solvent	Mole ratio			Physical properties	%Yield
		substrate	NaOCl	NaBr		
1D	isooctane	1	8	0	Light-yellow liquid	73
2D	isooctane	1	3	1	Light-yellow liquid	69
3D	isooctane	1	16	10	White solid	94
4D^{T}	isooctane	1	16	10	White liquid	64
5D	hexane	1	8	0	Light-yellow liquid	23
6D	hexane	1	3	1	Light-yellow liquid	1.5
7D	hexane	1	16	10	White liquid	31

^{T}**Added phase transfer using mole ratio of substrate and TBA : 1/0.1**

Table 4.2 The FT-IR absorption bands assignment of diphenyl ether derivatives

Cpd	Wave mumber (cm^{-1})		
	=C-H aromatic	C=C ring	C-O streching
1D	3067	1588, 1490	1239
2D	3057	1572, 1475	1239
3D	3077	1571, 1475	1237
4D	3066	1578, 1480	1236
5D	3055	1588, 1487	1235
6D	3072	1588, 1491	1227
7D	3068	1588, 1487	1235

Table 4.3 The ^{1}H-NMR spectral assignment of diphenyl ether derivatives

Cpd	Chemical shift (δ (ppm))	Multiplicity	Position of proton	Number of proton
1D	7.38-7.27	*m*	Ar*H*	4
	7.14-6.92	*m*	Ar*H*	5
2D	7.48-7.33	*m*	Ar*H*	-
	7.14-6.87	*m*	Ar*H*	-
3D	7.42-7.40	*d*	2,6,2',6'	4
	6.88-6.87	*d*	3,5,3',5'	4
4D	7.46-7.29	*m*	Ar*H*	-
	7.12-6.85	*m*	Ar*H*	-
5D	7.42-7.31	*m*	Ar*H*	-
	7.16-7.01	*m*	Ar*H*	-
6D	7.37-7.25	*m*	Ar*H*	-
	7.13-6.59	*m*	Ar*H*	-
7D	7.46-7.25	*m*	Ar*H*	-
	7.13-6.49	*m*	Ar*H*	-

Table 4.4 The ^{13}C-NMR spectral assignment of diphenyl ether derivatives

Cpd	Products	Chemical shift (δ (ppm))	Carbon assignment
1D	chlorodiphenyl ether	157.25, 156.88, 129.76, 127.93, 124.68, 123.22, 120.53, 118.92	-
2D	chlorodiphenyl ether bromodiphenyl ether dichlorodiphenyl ether bromochlorodiphenyl ether	156.88, 156.13, 134.05, 130.11, 129.95, 129.92, 128.84, 125.16, 123.93, 123.41, 120.61, 120.29, 119.53, 118.34, 116.41	-
	dibromodiphenyl ether	156.71 132.88 120.61 116.44	1,1' 2,6,2',6' 3,5,3',5' 4,4'
3D	dibromodiphenyl ether	156.01 132.87 120.61 116.24	1,1' 2,6,2',6' 3,5,3',5' 4,4'

Cpd	Products	Chemical shift (δ (ppm))	Carbon assignment
4D	diphenyl ether*	157.50	1,1’
		129.97	3,5,3’,5’
		123.44	4,4’
		119.11	2,6,2’,6’
	Bromodiphenyl ether	156.93, 156.89, 123.97, 119.17, 115.90	-
5D	diphenyl ether*	157.66	1,1’
		130.11	3,5,3’,5’
		123.54	4,4’
		119.25	2,6,2’,6’
	chlorodiphenyl ether	-	-
	dichlorodiphenyl ether	-	-
6D	diphenyl ether*	157.49	1,1’
		130.03	3,5,3’,5’
		123.47	4,4’
		119.19	2,6,2’,6’
	chlorodiphenyl ether	156.96, 156.79, 130.15 123.90, 120.28, 118.19	-
7D	diphenyl ether*	157.51	1,1’
		130.10	3,5,3’,5’
		123.10	4,4’
		120.67	2,6,2’,6’
	bromodiphenyl ether	156.96, 156.62, 133.11, 123.98, 119.16, 115.56	-
	dibromodiphenyl ether	156.78	1,1’
		132.94	2,6,2’,6’
		120.83	3,5,3’,5’
		115.89	4,4’

***substrate**

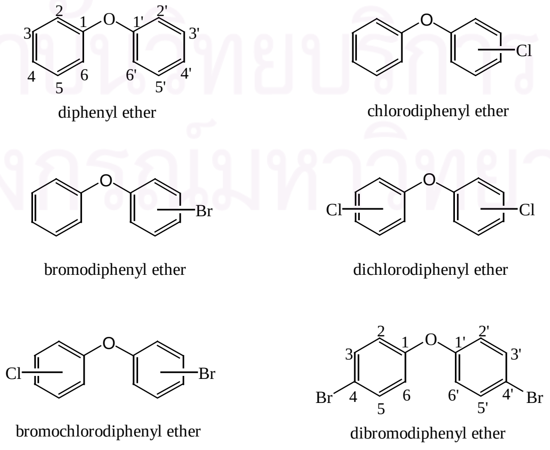


Figure 4.1 The structures of diphenyl ether mixture

Table 4.5 Simple normalisation-integrator of GC-MS or MS in the group of diphenyl ether derivatives

Mixture	**Peak**	**t_R (min)**	**Peak area**	**%Composition**	**Molecular weight**	**Relative intensities of peak**	**Products**
1D	-	-	-	-	204	3:1	chlorodiphenyl ether
2D	1	9.09	1157	0.91	204	3:1	chlorodiphenyl ether
	2	9.34	3764	2.96	204	3:1	chlorodiphenyl ether
	3	10.13	6578	5.18	248	1:1	bromodiphenyl ether
	4	10.55	81462	64.13	248	1:1	bromodiphenyl ether
	5	11.43	1076	0.85	238	9:6:1	dichlorodiphenyl ether
	6	11.80	1326	1.04	238	9:6:1	dichlorodiphenyl ether
	7	12.85	2155	1.70	282	3:4:1	bromochlorodiphenyl ether
	8	13.29	6888	5.42	282	3:4:1	bromochlorodiphenyl ether
	9	14.42	3293	2.59	326	1:2:1	dibromodiphenyl ether
	10	15.27	19323	15.21	326	1:2:1	dibromodiphenyl ether
			Total = 127,022				
3D	-	-	-	-	326	1:2:1	dibromodiphenyl ether
4D	1	7.86	25788	32.31	170	-	diphenyl ether
	2	11.16	590	0.74	248	1:1	bromodiphenyl ether
	3	11.58	28127	35.24	248	1:1	bromodiphenyl ether
	4	16.31	836	1.05	326	1:2:1	dibromodiphenyl ether
	5	17.30	24479	30.67	326	1:2:1	dibromodiphenyl ether
			Total = 79,820				
5D	1	14.98	951198	66.32	170	-	diphenyl ether
	2	16.43	85981	6.00	204	3:1	chlorodiphenyl ether
	3	16.63	164540	11.47	204	3:1	chlorodiphenyl ether
	4	17.95	15955	1.11	238	9:6:1	dichlorodiphenyl ether
	5	18.10	100684	7.02	238	9:6:1	dichlorodiphenyl ether
	6	18.32	115865	8.08	238	9:6:1	dichlorodiphenyl ether
			Total = 1,434,223				
6D	1	8.75	57312	97.30	170	-	diphenyl ether
	2	11.17	1589	2.70	204	3:1	chlorodiphenyl ether
			Total = 58,901				
7D	1	8.79	8003	69.42	170	-	diphenyl ether
	2	12.68	2400	20.82	248	1:1	bromodiphenyl ether
	3	19.50	1125	9.76	326	1:2:1	dibromodiphenyl ether
			Total = 11,528				

Table 4.6 The fragmentation ion in the MS spectra of diphenyl ether derivatives

Cdp	**Products**	**Fragmentation ion peak**	
		1	**2**
		m/z (ion)	**m/z (ion)**
1D	chlorodiphenyl ether	204 (C_6H_5-O-$C_6H_4Cl^+$)	169 (C_6H_5-O-$C_6H_4^+$)
2D	chlorodiphenyl ether	204 (C_6H_5-O-$C_6H_4Cl^+$)	169 (C_6H_5-O-$C_6H_4^+$)
	bromodiphenyl ether	248 (C_6H_5-O-$C_6H_4Br^+$)	169 (C_6H_5-O-$C_6H_4^+$)
	dichlorodiphenyl ether	238 (ClC_6H_4-O-$C_6H_4Cl^+$)	203 (C_6H_4-O-$C_6H_4Cl^+$)
	bromochlorodiphenyl ether	282 (ClC_6H_4-O-$C_6H_4Br^+$)	168 (C_6H_4-O-$C_6H_4^+$)
	dibromodiphenyl ether	326 (BrC_6H_4-O-$C_6H_4Br^+$)	168 (C_6H_4-O-$C_6H_4^+$)
3D	dibromodiphenyl ether	326 (BrC_6H_4-O-$C_6H_4Br^+$)	168 (C_6H_4-O-$C_6H_4^+$)
4D	bromodiphenyl ether	248 (C_6H_5-O-$C_6H_4Br^+$)	169 (C_6H_5-O-$C_6H_4^+$)
	dibromodiphenyl ether	326 (BrC_6H_4-O-$C_6H_4Br^+$)	168 (C_6H_4-O-$C_6H_4^+$)
5D	chlorodiphenyl ether	204 (C_6H_5-O-$C_6H_4Cl^+$)	169 (C_6H_5-O-$C_6H_4^+$)
	dichlorodiphenyl ether	238 (ClC_6H_4-O-$C_6H_4Cl^+$)	203 (C_6H_4-O-$C_6H_4Cl^+$)
6D	chlorodiphenyl ether	204 (C_6H_5-O-$C_6H_4Cl^+$)	169 (C_6H_5-O-$C_6H_4^+$)
7D	bromodiphenyl ether	248 (C_6H_5-O-$C_6H_4Br^+$)	169 (C_6H_5-O-$C_6H_4^+$)
	dibromodiphenyl ether	326 (BrC_6H_4-O-$C_6H_4Br^+$)	168 (C_6H_4-O-$C_6H_4^+$)

Bromination of diphenyl ether using sodium bromide/ sodium hypochlorite is a "**neat**" bromination technology to produce a high yield of 4,4'-dibromodiphenyl ether. Comparison of this method with the liquid bromine method [3] is shown in Table 4.7.

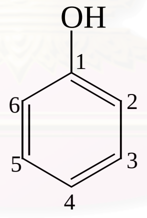
Table 4.7 Comparison of the bromination of diphenyl ether using NaBr/ NaOCl and liquid bromine

Method	**Sodium bromide/ sodium hypochlorite**	**Liquid bromine**
Temperature	Room-Temperature	60-70 ^{o}C
Reaction time	2 hours	2.5 hours
Catalyst	none	none
"Br" amount	10	2.16
Yield	94	92

4.2 Halogenation of phenol

From the literature search, it was obviously revealed that six chlorophenols of commercial value are 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. They are used as the chemical intermediate, herbicides, fungicides in the wood preservative, germicides and bactericides. In 1989, there has been reported on the approach for synthesizing 2,4,6-trichlorophenol using ortho-substitued phenol, *e.g.* 2,6-dichlorophenol reacting with gaseous chlorine, in the presence of a catalytic amount of a strong acid or Lewis acid. In this research, two reagents (sodium hypochlorite and sodium bromide / sodium hypochlorite) was used to halogenate phenol. In approach 1, using sodium hypochlorite reagent was used in the chlorination of phenol to give dichlorophenol and trichlorophenol. The other approach sodium bromide/ sodium hypochlorite reagents were used in the bromination and chlorination of phenol to give trichlorophenol, bromodichlorophenol, dibromochlorophenol and tribromophenol.

Phenol is a light-brown liquid, soluble in water, ethyl ether, ethyl alcohol, acetic acid, glycerol, liquid sulfur dioxide and benzene but less soluble in paraffin hydrocarbons. Its structure is shown below:



The IR spectrum of phenol showed absorption peaks of OH stretching of hydroxyl group at 3689-3099 cm^{-1} (m), =C-H stretching of aromatic at 3040 cm^{-1} (w), C=C ring stretching of aromatic at 1596, 1467 cm^{-1} (m), O-H bending at 1375 cm^{-1} and C-O stretching at 1239 cm^{-1}. In addition, the ^{1}H-NMR spectrum of OH proton and aromatic protons appeared at δ 5.58 ppm as the singlet signal at of 6.70-7.30 ppm as the multiplet signals, respectively. The ^{13}C-NMR spectrum of phenol revealed the presence of C-1 at 155.2 ppm, C-2 and C-6 at 115.6 ppm, C-3 and C-5 at 129.9 ppm and C-4 at 121.1 ppm. The mass spectrum of phenol exhibited m/z at 94, which was the molecular weight of phenol.

Table 4.8 The physical properties and %yield of phenolic derivatives

Cpd	Solvent	Mole ratio			Physical properties	%Yield
		substrate	NaOCl	NaBr		
1P	isooctane	1	2	0	Brown solid	79
2P	isooctane	1	8	0	Brown-needle crystal	70
3P	isooctane	1	3	1	White-needle crystal	53
4P	isooctane	1	8	5	White-needle crystal	63
5P	isooctane	1	8	5	White-needle crystal	56
6P^T	isooctane	1	8	0	Brown-needle crystal	87
7P^T	isooctane	1	3	1	White-needle crystal	~46
8P^T	isooctane	1	8	5	White-needle crystal	50
9P^T	isooctane	1	8	5	White-needle crystal	-
10P^C	isooctane	1	8	0	Brown-needle crystal	68
11P^C	isooctane	1	3	1	White-needle crystal	~29
12P^C	isooctane	1	8	5	White-needle crystal	48
13P^C	isooctane	1	8	5	White-needle crystal	-
14P	hexane	1	8	0	Brown-needle crystal	61
15P	hexane	1	3	1	Brown solid	43
16P	hexane	1	8	5	Brown solid	39
17P	hexane	1	8	5	Brown solid	61
18P	none	1	8	0	Brown needle crytal	34
19P	isooctane	1	1	1	Light-brown solid	12
20P	isooctane	1	2	1	Light-brown solid	11
21P	isooctane	1	3	1	Brown solid	24
22P	Isooctae	1	4	1	Brown solid	45

^{T}**Added phase transfer using mole ratio of substrate and TBA : 1/0.1**

^{C}**Added phase transfer using mole ratio of substrate and CTAB: 1/0.1**

Table 4.9 The FT-IR absorption bands of assignment of phenolic derivatives

Cpd	Wave mumber (cm^{-1})				
	O-H stretching	**=C-H aromatic**	**C=C ring**	**O-H bending**	**C-O streching**
1P	3698-3119	3083	1568, 1475	1330	1219
2P	3545-3391	3083	1567, 1465	1316	1224
3P	3554-3190	3083	1568, 1475	1311	1219
4P	3632-3380	3078	1557, 1470	1317	1219
5P	3514-3229	3021	1568, 1455	1327	1229
6P	3668-3457	3073	1573, 1470	1393	1224
7P	3570-3411	3058	1552, 1460	1378	1234
8P	3570-3421	3073	1593, 1460	1373	1214
9P	3606-3411	3073	1562, 1470	1388	1229
10P	3718-3119	3078	1562, 1475	1388	1214
11P	3677-3425	3073	1547, 1460	-	1270
12P	3687-3411	3073	1588, 1450	1320	1230
13P	3611-3375	3073	1557, 1460	1393	1224
14P	3642-3577	3073	1573, 1475	1321	1219
15P	3606-3416	3073	1552, 1455	1383	1265
16P	3570-3421	3073	1598, 1465	1328	1245
17P	3611-3406	3068	1562, 1475	1312	1276
18P	3560-3396	3088	1568, 1465	1388	1270
19P	3580-3145	3068	1465, 1557	1388	1271
20P	3524-3150	3068	1557, 1455	1378	1265
21P	3514-3165	3063	1552, 1460	1383	1271
22P	3687-3104	3078	1557, 1455	1388	1271

Table 4.10 The ^{1}H-NMR spectral assignment of phenolic derivatives

Cpd	Chemical shift (δ (ppm))	Multiplicity	Position of proton	Number of proton
1P	7.31-7.11	*m*	Ar*H*OHCl$_2$	-
	7.02-6.76	*m*	Ar*H*OHCl$_2$	-
	5.62	*s*	ArHO*H*Cl$_2$	1H
	7.27	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.93	*s*	ArHO*H*Cl$_3$	1H
2P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.84	*s*	ArHO*H*Cl$_3$	1H
3P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.84	*s*	ArHO*H*Cl$_3$	1H
	7.40, 7.30, 7.24	-	Ar*H*OHBrCl$_2$	-
	5.85	*s*	ArHO*H*BrCl$_2$	1H
4P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.84	*s*	ArHO*H*Cl$_3$	1H
	7.41, 7.40, 7.31, 7.30, 7.27, 7.26	-	Ar*H*OHBrCl$_2$ Ar*H*OHBr$_2$Cl	-
	5.86	*s*	ArHO*H*BrCl$_2$ ArHO*H*Br$_2$Cl	-
5P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.88	*s*	ArHO*H*Cl$_3$	1H
	7.57, 7.54, 7.53, 7.45, 7.44, 7.43, 7.41, 7.40, 7.39, 7.31, 7.30	-	Ar*H*OHBrCl$_2$ Ar*H*OHBr$_2$Cl	-
	5.90	*s*	ArHO*H*BrCl$_2$ ArHO*H*Br$_2$Cl	-
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.25	*s*	Ar*H*OHBr$_3$	-
	5.84	*s*	ArHO*H*Br$_3$	1H
6P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.88	*s*	ArHO*H*Cl$_3$	1H
7P	7.26, 7.52	-	Ar*H*OHBr$_2$Cl	-
	5.89	*s*	ArHO*H*Br$_2$Cl	1H
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.89	*s*	ArHO*H*Br$_3$	1H

Cpd	Chemical shift (δ (ppm))	Multiplicity	Position of proton	Number of proton
8P	7.58	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	7.24	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	5.89	*s*	$\mathrm{ArHO}H\mathrm{Br_3}$	1H
9P	7.25	*s*	m-$\mathrm{Ar}H\mathrm{OHCl_3}$	2H
	5.84	*s*	$\mathrm{ArHO}H\mathrm{Cl_3}$	1H
	7.55, 7.53, 7.45, 7.44, 7.43, 7.41, 7.39, 7.35, 7.31, 7.30, 7.29, 7.20	-	$\mathrm{Ar}H\mathrm{OHBrCl_2}$ $\mathrm{Ar}H\mathrm{OHBr_2Cl}$	-
	5.86	*s*	$\mathrm{ArHO}H\mathrm{BrCl_2}$ $\mathrm{ArHO}H\mathrm{Br_2Cl}$	-
	7.58	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	7.27	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	5.87	*s*	$\mathrm{ArHO}H\mathrm{Br_3}$	1H
10P	7.29	*s*	m-$\mathrm{Ar}H\mathrm{OHCl_3}$	2H
	5.87	*s*	$\mathrm{ArHO}H\mathrm{Cl_3}$	1H
11P	7.62, 7.57, 7.53, 7.44, 7.20	-	$\mathrm{Ar}H\mathrm{OHBr_2Cl}$	-
	5.89	*s*	$\mathrm{ArHO}H\mathrm{Br_2Cl}$	1H
	7.60	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	7.24	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	5.89	*s*	$\mathrm{ArHO}H\mathrm{Br_3}$	1H
12P	7.62	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	7.24	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	5.28	*s*	$\mathrm{ArHO}H\mathrm{Br_3}$	1H
13P	7.57, 7.54, 7.53, 7.48, 7.47, 7.44, 7.41, 7.39, 7.35, 7.31, 7.30, 7.26, 7.22, 7.20	-	$\mathrm{Ar}H\mathrm{OHBrCl_2}$ $\mathrm{Ar}H\mathrm{OHBr_2Cl}$	-
	5.86	*s*	$\mathrm{ArHO}H\mathrm{BrCl_2}$ $\mathrm{ArHO}H\mathrm{Br_2Cl}$	-
	7.62	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	7.24	*s*	$\mathrm{Ar}H\mathrm{OHBr_3}$	-
	5.85	*s*	$\mathrm{ArHO}H\mathrm{Br_3}$	1H
14P	7.48, 7.56, 7.43, 7.35, 7.33, 7.31, 7.29, 7.23, 6.88, 6.87, 7.85	-	$\mathrm{Ar}H\mathrm{OHCl_2}$	-
	5.62	*s*	$\mathrm{ArHO}H\mathrm{Cl_2}$	1H
	7.26	*s*	m-$\mathrm{Ar}H\mathrm{OHCl_3}$	2H
	5.94	*s*	$\mathrm{ArHO}H\mathrm{Cl_3}$	1H

Cpd	Chemical shift (δ (ppm))	Multiplicity	Position of proton	Number of proton
15P	7.77, 7.71, 7.67, 7.62, 7.53, 7.44, 7.40, 7.28, 7.20	-	Ar*H*OHBr$_2$ Ar*H*OHBr$_2$Cl	-
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.89	*s*	ArHO*H*Br$_3$	1H
16P	7.49	*s*	Ar*H*OHBr$_3$	-
	7.13	*s*	Ar*H*OHBr$_3$	-
	2.39	*s*	ArHO*H*Br$_3$	1H
17P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.86	*s*	ArHO*H*Cl$_3$	1H
	7.54, 7.53, 7.44, 7.43, 7.41, 7.40, 7.31, 7.30, 7.29	-	Ar*H*OHBrCl$_2$ Ar*H*OHBr$_2$Cl	-
	5.86	*s*	ArHO*H*BrCl$_2$ ArHO*H*Br$_2$Cl	-
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.86	*s*	ArHO*H*Br$_3$	1H
18P	7.29	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.86	*s*	ArHO*H*Cl$_3$	1H
19P	7.57	*s*	Ar*H*OHBr$_3$	1H
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.88	*s*	ArHO*H*Br$_3$	1H
20P	7.62, 7.60, 7.54, 7.52, 7.44, 7.43, 6.91, 6.87, 6.75, 6.72, 6.68, 6.64	-	Ar*H*OHBr$_2$Cl	-
	5.89	*s*	ArHO*H*Br$_2$Cl	1H
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.52	*s*	ArHO*H*Br$_3$	1H
21P	7.62, 7.56, 7.53, 7.44, 7.43,7.40, 7.32, 7.29, 7.24, 7.17, 7.12, 7.02, 7.00, 6.85, 6.80, 6.65	-	Ar*H*OHBr$_2$Cl	-
	5.52	*s*	ArHO*H*Br$_2$Cl	1H
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.88	*s*	ArHO*H*Br$_3$	1H

Cpd	Chemical shift (δ (ppm))	Multiplicity	Position of proton	Number of proton
22P	7.26	*s*	*m*-Ar*H*OHCl$_3$	2H
	5.86	*s*	ArHO*H*Cl$_3$	1H
	7.54, 7.53, 7.44, 7.43, 7.41, 7.40, 7.31, 7.30, 7.29, 6.95, 6.91, 6.84, 6.80, 6.76, 6.74, 6.68	-	Ar*H*OHBrCl$_2$ Ar*H*OHBr$_2$Cl	-
	5.52	*s*	ArHO*H*BrCl$_2$ ArHO*H*Br$_2$Cl	-
	7.57	*s*	Ar*H*OHBr$_3$	-
	7.24	*s*	Ar*H*OHBr$_3$	-
	5.86	*s*	ArHO*H*Br$_3$	1H

Table 4.11 The ^{13}C-NMR spectral assignment of phenolic derivatives

Cpd	Product	Chemical shift (δ (ppm))	Carbon assignment
1P	dichlorophenol	147.58, 128.56, 128.52, 121.15, 117.13	-
	trichlorophenol	147.30	1
		128.06	3, 5
		125.33	4
		121.60	2, 6
2P	trichlorophenol	146.87	1
		128.06	3, 5
		125.33	4
		121.58	2, 6
3P	trichlorophenol	146.87	1
		128.06	3, 5
		125.33	4
		121.58	2, 6
	bromodichlorophenol	147.73, 147.33, 130.91, 130.77, 128.68, 128.26, 125.78, 121.93, 121.13, 111.71, 110.30	-
4P	trichlorophenol	146.87	1
		128.07	3, 5
		125.30	4
		121.61	2, 6
	bromodichlorophenol dibromochlorophenol	147.74, 147.36, 130.91, 130.80, 130.78, 128.68, 121.96, 121.93, 121.14, 110.68, 110.68, 110.42, 110.38	-

Cpd	Product	Chemical shift (δ (ppm))	Carbon assignment
5P	trichlorophenol	147.37	1
		128.09	3, 5
		125.77	4
		121.61	2, 6
	bromodichlorophenol dibromochlorophenol	133.59, 131.56, 131.41, 130.93, 130.79, 128.69, 121.95, 112.21, 110.85, 109.96	-
	tribromophenol	148.19	-
		134.23	
		112.69	
		110.42	
6P	trichlorophenol	147.37	1
		128.07	3, 5
		125.32	4
		121.60	2, 6
7P	dibromochlorophenol	-	-
	tribromophenol	148.95	-
		134.22	
		112.68	
		110.43	
8P	tribromophenol	148.95	-
		134.22	
		112.69	
		110.45	
9P	trichlorophenol	147.36	1
		128.07	3, 5
		125.30	4
		121.59	2, 6
	bromodichlorophenol dibromochlorophenol	133.57, 131.55, 131.40, 130.92, 130.79, 128.68, 121.96, 111.69, 110.83	-
	tribromophenol	147.75	-
		134.21	
		112.21	
		110.41	
10P	trichlorophenol	146.92	1
		128.68	3, 5
		125.31	4
		121.61	2, 6

Cpd	Product	Chemical shift (δ (ppm))	Carbon assignment
11P	dibromochlorophenol	-	-
	tribromophenol	148.96 134.22 112.68 110.44	-
12P	tribromophenol	148.96 134.22 112.69 110.47	-
13P	dibromochlorophenol bromodichlorophenol	148.14, 147.76, 147.36, 134.21, 133.57, 131.55, 131.40, 130.92, 130.79, 128.68, 128.07, 125.76, 121.95, 121.53, 121.14, 112.21, 111.69,110.85, 109.98	-
	tribromophenol	148.53 134.21 112.68 110.42	-
14P	dichlorophenol	-	-
	trichlorophenol	146.93 128.06 125.29 121.62	1 3, 5 4 2, 6
15P	dibromophenol	-	-
	dibromochlorophenol	-	-
	tribromophenol	148.95 134.22 112.64 110.45	-
16P	tribromophenol	148.98 134.23 112.49 110.49	-

Cpd	Product	Chemical shift (δ (ppm))	Carbon assignment
17P	trichlorophenol	146.93	1
		128.07	3, 5
		125.29	4
		121.54	2, 6
	bromodichlorophenol dibromochlorophenol	147.17, 147.37, 133.58, 131.55, 131.40, 130.93, 130.79, 128.68, 128.28, 125.74, 121.97, 121.62, 121.15, 112.21, 111.69, 110.87, 109.99	-
	tribromophenol	148.21	-
		134.21	
		112.68	
		110.45	
18P	trichlorophenol	146.92	1
		128.08	3, 5
		125.30	4
		121.61	2, 6
19P	tribromophenol	148.94	-
		134.22	
		112.69	
		110.41	
20P	dibromochlorophenol	-	-
	tribromophenol	148.94	-
		134.22	
		112.69	
		110.41	
21P	dibromochlorophenol	148.20, 133.59, 131.56, 131.41	-
	tribromophenol	148.94	-
		134.22	
		112.69	
		110.41	
22P	trichlorophenol	146.89	1
		128.07	3, 5
		125.29	4
		121.58	2, 6
	bromodichlorophenol dibromochlorophenol	148.17, 134.21, 133.58, 132.10131.55, 131.40, 130.93, 130.79, 128.68, 128.28, 122.46, 121.58, 117.45, 112.69, 112.24, 110.42, 109.96	-
	tribromophenol	148.94	-
		134.21	
		112.69	
		110.42	

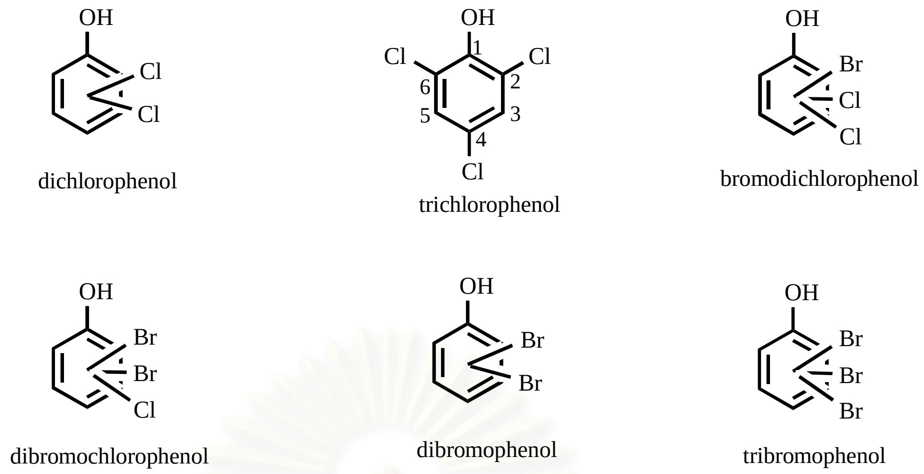


Figure 4.2 The structures of phenolic derivatives

Table 4.12 Simple normalisation-integrator of GC-MS or MS in the group of phenolic derivatives

Mixture	Peak	t_R (min)	Peak area	%composition	Molecular weight	Relative intensities of peak	Products
1P	1	8.95	55975	33.28	162	9:6:1	dichlorophenol
	2	9.36	65462	38.91	162	9:6:1	dichlorophenol
	3	10.99	46787	27.81	196	27:27:9:1	trichlorophenol
			Total = 168,224				
2P	-	-	-	-	196	27:27:9:1	trichlorophenol
3P	1	11.08	9190	48.34	196	27:27:9:1	trichlorophenol
	2	12.06	9822	51.66	240	9:15:7:1	bromodichlorophenol
			Total = 19,012				
4P	1	14.30	58146	26.69	196	27:27:9:1	trichlorophenol
	2	15.29	156694	71.92	240	9:15:7:1	bromodichlorophenol
	3	16.26	3047	1.40	284	3:7:5:1	dibromochlorophenol
			Total = 217,887				
5P	1	11.08	5522	10.62	196	27:27:9:1	trichlorophenol
	2	12.05	26384	55.78	240	9:15:7:1	bromodichlorophenol
	3	12.99	14096	29.80	284	3:7:5:1	dibromochlorophenol
	4	14.14	1799	3.80	328	3:3:1	tribromophenol
			Total = 47,301				
6P	-	-	-	-	196	27:27:9:1	trichlorophenol
7P	-	-	-	-	284	3:7:5:1	dibromochlorophenol
					328	3:3:1	tribromophenol
8P	-	-	-	-	328	3:3:1	tribromophenol

Mixture	Peak	t_R (min)	Peak area	%composition	Molecular weight	Relative intensities of peak	Products
9P	-	-	-	-	196	27:27:9:1	trichlorophenol
					240	9:15:7:1	bromodichlorophenol
					284	3:7:5:1	dibromochlorophenol
					328	3:3:1	tribromophenol
10P	-	-	-	-	196	27:27:9:1	trichlorophenol
11P	-	-	-	-	284	3:7:5:1	dibromochlorophenol
					328	3:3:1	tribromophenol
12P	-	-	-	-	328	3:3:1	tribromophenol
13P	-	-	-	-	240	9:15:7:1	bromodichlorophenol
					284	3:7:5:1	dibromochlorophenol
					328	3:3:1	tribromophenol
14P	1	5.18	1916	1.31	162	9:6:1	dichlorophenol
	2	7.01	144281	98.69	196	27:27:9:1	trichlorophenol
			Total = 146,197				
15P	1	7.38	365	0.79	250	1:2:1	dibromophenol
	2	7.67	877	1.89	250	1:2:1	dibromophenol
	3	9.65	8376	18.02	284	3:7:5:1	dibromochlorophenol
	4	10.88	36867	79.31	328	1:3:3:1	tribromophenol
			Total = 46,485				
16P	1	11.41	1424	100	328	1:3:3:1	tribromophenol
17P	1	7.43	1187	9.05	196	27:27:9:1	trichlorophenol
	2	8.72	8917	67.96	240	9:15:7:1	bromodichlorophenol
	3	9.93	2785	21.23	284	3:7:5:1	dibromochlorophenol
	4	11.14	231	1.76	328	1:3:3:1	tribromophenol
			Total = 13,120				
18P	-	-	-	-	196	27:27:9:1	trichlorophenol
19P	1	13.83	23009	100	328	1:3:3:1	tribromophenol
20P	1	9.74	1531	7.18	284	3:7:5:1	dibromochlorophenol
	2	10.94	19802	92.82	328	1:3:3:1	tribromophenol
			Total = 21,333				
21P	1	12.95	12530	14.20	284	3:7:5:1	dibromochlorophenol
	2	13.83	75759	85.80	328	1:3:3:1	tribromophenol
			Total = 88,289				
22P	1	11.10	3140	17.19	196	27:27:9:1	trichlorophenol
	2	12.07	3091	16.92	240	9:15:7:1	bromodichlorophenol
	3	12.95	4362	23.88	284	3:7:5:1	dibromochlorophenol
	4	13.83	7676	42.02	328	1:3:3:1	tribromophenol
			Total = 18,269				

Table 4.13 The fragmentation ion in the MS spectra of phenolic derivatives

Cdp	Product	Fragmentation ion peak	
		1	2
		m/z (ion)	m/z (ion)
1P	dichlorophenol	162 ($C_6H_3Cl_2OH^+$)	126 ($C_6H_3ClOH^+$)
	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
2P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
3P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
4P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
5P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
6P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
7P	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	-
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
8P	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
9P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	-
10P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
11P	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	-
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
12P	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
13P	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	-
14P	dichlorophenol	162 ($C_6H_3Cl_2OH^+$)	126 ($C_6H_3ClOH^+$)
	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)

Cdp	Product	Fragmentation ion peak	
		1	2
		m/z (ion)	m/z (ion)
15P	dibromophenol	250 ($C_6H_3Br_2OH^+$)	172 ($C_6H_3BrOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
16P	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
17P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	-
18P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
19P	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
20P	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
21P	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)
22P	trichlorophenol	196 ($C_6H_2Cl_3OH^+$)	160 ($C_6H_2Cl_2OH^+$)
	bromodichlorophenol	240 ($C_6H_2BrCl_2OH^+$)	204 ($C_6H_2BrClOH^+$)
	dibromochlorophenol	284 ($C_6H_2Br_2ClOH^+$)	204 ($C_6H_2BrClOH^+$)
	tribromophenol	328 ($C_6H_2Br_3OH^+$)	248 ($C_6H_2Br_2OH^+$)

Chlorination of phenol using sodium hypochlorite is a new chlorinating agent to produce high yield of 2,4,6-trichlorophenol. Comparison of this method with the chlorine gas method [23] is shown in Table 4.14.

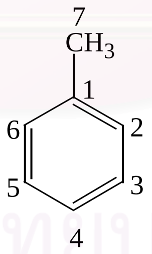
Table 4.14 Comparison of method for the chlorination of phenol

Method	**Sodium bromide/ sodium hypochlorite**	**Chlorine gas**		
Substrate	Phenol	2,6-dichlorophenol	2,6-dichlorophenol	2,6-dichlorophenol
Temperature	Room-Temperature	70 ^{o}C	70 ^{o}C	70 ^{o}C
Reaction time	2 hours	2 hours	2 hours	2 hours
Catalyst	none	none	$AlCl_3$	$FeCl_3$
“Cl” amount	8	1	1	1
Yield	87%	76%	83%	80%

4.3 Halogenation of toluene

From the literature search, it was obviously revealed that bromotoluene could be used as the important intermediates for the functionalization of toluene derivatives. In 1967 [17], there has been reported on the synthesizing of bromotoluene using sodium bromate ($NaBrO_3$) and sulfuric acid (H_2SO_4). In this research, (sodium bromide / sodium hypochlorite) combination was used in the bromination of toluene.

Toluene is a colorless liquid, insoluble in water but freely soluble in organic solvent. Its structure is shown below:



The IR spectrum of toluene showed absorption peaks of =C-H stretching of aromatic at 3071 cm^{-1} (w), CH stretching of aliphatic at 2958 cm^{-1} and C=C ring stretching of aromatic at 1602 and 1494 cm^{-1} (m). In addition, the ^{1}H-NMR spectrum of aromatic protons appeared at δ 7.32-7.15 ppm as the multiplet signals and methyl protons as the singlet signal, respectively. The ^{13}C-NMR spectrum of toluene revealed the presence of C-1 at 137.9 ppm, C-2 and C-6 at 129.2 ppm, C-3 and C-5 at 128.5 ppm, C-4 at 125.6 ppm and C-7 at 21.6 ppm. The mass spectrum of toluene exhibited at 92 m/z, which was the molecular weight of toluene.

Table 4.15 The physical properties and %yield of toluene derivatives

Cpd	**Solvent**	**Mole ratio**			**Physical properties**	**%Yield**
		substrate	**NaOCl**	**NaBr**		
1T	isooctane	1	3	1	Yellow-brown liquid	27
2T	isooctane	1	8	5	Yellow-brown liquid	83
3T	hexane	1	3	1	Yellow-brown liquid	27
4T	hexane	1	8	5	Yellow-brown liquid	59

Table 4.16 The FT-IR absorption bands assignment of toluene mixture

Cdp	**Wave mumber (cm^{-1})**		
	=C-H aromatic	**C-H aliphatic**	**C=C ring**
1T	3033	2943	1592, 1491
2T	3066	2963	1594, 1481
3T	3068	2916	1592, 1453
4T	3067	2920	1577, 1487

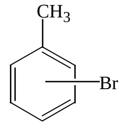
.

Table 4.17 The ^{1}H-NMR spectral assignment of toluene mixture

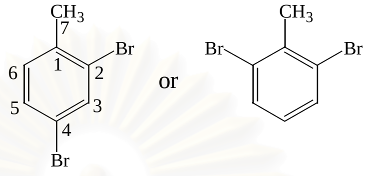
Cpd	Chemical shift (δ (ppm))	Multiplicity	Position of proton	Number of proton
1T	7.48-7.23	*m*	Ar*H*	-
	5.09, 4.57, 4.53, 4.49, 4.44, 4.43, 4.11, 4.04, 4.00, 3.96, 3.94, 3.92, 3.89, 3.88, 3.86, 2.21, 2.01, 1.92	-	CH_2 or CH_3	-
2T	7.45	*d*	Ar*H*	-
	7.26-7.22	*m*	Ar*H*	-
	4.59, 4.52, 4.42, 4.29, 4.14, 4.10, 4.04, 3.98, 9.90, 3.89, 3.87, 3.85, 2.16, 2.10, 2.03, 1.91, 1.34	-	CH_2 or CH_3	-
3T	7.57-7.25	*m*	Ar*H*	-
	6.64, 5.10, 4.69, 6.65, 4.47, 4.42, 2.79, 2.54, 2.33, 2.21, 2.09, 2.05, 2.04, 2.00, 1.91, 1.83, 1.77, 1.49, 1.46	-	CH_3	-
4T	7.55	*d*	Ar*H*	1H
	7.39	*d*	Ar*H*	2H
	6.64	-	CH_3	-

Table 4.18 The ^{13}C-NMR spectral assignment of toluene mixture

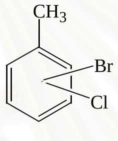
Cpd	Product	Chemical shift (δ (ppm))	Carbon assignment
1T	bromotoluene dibromotoluene	170.88, 146.21, 137.82, 135.97, 131.99, 131.27, 130.73, 129.08, 128.83, 128.61, 128.45, 128.29, 126.53, 122.48, 91.07, 66.34, 66.07	-
2T	dibromotoluene	146.16, 136.80, 131.97, 130.72, 129.85, 128.67, 126.53, 66.05	-
3T	dibromotoluene	131.97, 129.85, 128.65, 128.59, 128.28, 126.49, 41.05, 29.71, 29.38, 22.71, 14.15, 1.03	-
4T	bromochlorotoluene	-	-
	dibromotoluene	141.97	1
		129.84	3, 6
		126.56	2, 5
		123.32	4
		41.29	7



bromotoluene



dibromotoluene



bromochlorotoluene

Figure 4.3 The structures of toluene mixture

Table 4.19 Simple normalisation-integrator of GC-MS in the group of toluene derivatives

Mixture	Peak	t_R (min)	Peak area	%composition	Molecular weight	Relative intensities of peak	Product
1T	1	11.37	61061	45.37	170	1:1	bromotoluene
	2	13.97	7371	5.48	248	1:2:1	dibromotoluene
	3	14.50	13820	10.27	248	1:2:1	dibromotoluene
	4	14.72	52332	38.88	248	1:2:1	dibromotoluene
			Total = 134,584				
2T	1	13.97	5658	18.85	248	1:2:1	dibromotoluene
	2	14.50	6209	20.69	248	1:2:1	dibromotoluene
	3	14.72	18146	60.46	248	1:2:1	dibromotoluene
			Total = 30,013				
3T	1	13.97	31558	84.98	248	1:2:1	dibromotoluene
	2	14.74	5578	15.02	248	1:2:1	dibromotoluene
			Total = 37,136				
4T	1	13.11	1112	0.94	204	3:4:1	bromochlorotolene
	2	13.97	117673	99.06	248	1:2:1	dibromotoluene
			Total = 118,785				

Table 4.20 The fragmentation ion in the MS spectra of toluene derivatives

Cdp	Product	Fragmentation ion peak	
		1	2
		m/z (ion)	m/z (ion)
1T	bromotoluene	170 ($C_6H_4BrCH_3^+$)	91 ($C_6H_4CH_3^+$)
	dibromotoluene	248 ($C_6H_3Br_2CH_3^+$)	169 ($C_6H_3BrCH_3^+$)
2T	dibromotoluene	248 ($C_6H_3Br_2CH_3^+$)	169 ($C_6H_3BrCH_3^+$)
3T	dibromotoluene	248 ($C_6H_3Br_2CH_3^+$)	169 ($C_6H_3BrCH_3^+$)
4T	bromochlorotoluene	204 ($C_6H_3BrClCH_3^+$)	169 ($C_6H_3BrCH_3^+$)
	dibromotoluene	248 ($C_6H_3Br_2CH_3^+$)	169 ($C_6H_3BrCH_3^+$)

Bromination of toluene using sodium bromide/ sodium hypochlorite is a new brominating agent to produce high yield of dibromotoluene. Comparison of this method with the sodium bromate/ sulfuric acid method [17] is shown in Table 4.21.

Table 4.21 Comparison of method for the bromination of toluene

Method	Sodium bromide/ sodium hypochlorite	Sodium bromate/ sulfuric acid
Temperature	Room-Temperature	15 °C
Reaction time	4 hours	2 hours
Catalyst	none	none
“Br” amount	5	1
Product	dibromotoluene	bromotoluene
Yield	83	85

4.4 Bromination of aromatic substrate

Four aromatic substrates that containing ring activating group such as diphenyl ether, phenol, toluene and linear alkyl benzene were studied using sodium bromide/ sodium hypochloite for bromination or chlorination. The product of linear alkyl benzene could not characterise, therefore the desired product was not obtained. Diphenyl ether was brominated in high yield and specificity 4,4’-dibromodiphenyl ether (94%). In addition, sodium bromide/ sodium hypochlorite is a good halogenating agent of phenol and toluene, too.

One aromatic substrate that containing strong ring deactivating group such as nitrobenzene was studied. Sodium bromide/ sodium hypochlorite reagents can not be used to brominate this mixture.

The mechanism of Chlorinating ion

$$NaOCl \longrightarrow Na^{+} + OCl^{-}$$

$$OCl^{-} + H^{+} \longrightarrow HOCl$$

$$HOCl + H^{+} \rightleftharpoons ClOH_2^{+}$$

$$ClOH_2^{+} \rightleftharpoons Cl^{+} + H_2O$$

$$ArH + Cl^{+} \longrightarrow ArCl + H^{+}$$

The mechanism of Brominating ion

$$NaBr \longrightarrow Na^{+} + Br^{-}$$

$$Br^{-} + H^{+} \longrightarrow HBr$$

$$HOCl + HBr \longrightarrow BrCl + H_2O$$

$$Cl_2 + Br^{-} \longrightarrow BrCl + Cl^{-}$$

$$BrCl + Br^{-} \longrightarrow Br_2 + Cl^{-}$$

$$Br_2 + H_2O \rightleftharpoons HBr + HOBr$$

$$HOBr + H^{+} \rightleftharpoons BrOH_2^{+}$$

$$BrOH_2^{+} \rightleftharpoons Br^{+} + H_2O$$

Reaction in organic phase	**Reaction in aqueous phase**
$ArH + Br_2 \longrightarrow ArBr + HBr$	$ArH + Br^{+} \longrightarrow ArBr + H^{+}$

4.5 Effects of Phase-transfer catalyst

Two phase-transfer catalysts such as tetrabutylammonium tetrafluoroborate (TBA; $Bu_4N(BF_4)$) and cetyl ammonium bromide (CTAB) were studied in two phase system (aqueous and isooctane) for bromination of aromatic compound. Comparison of the reaction using phase-transfer catalyst with none is shown in Figure 4.4.

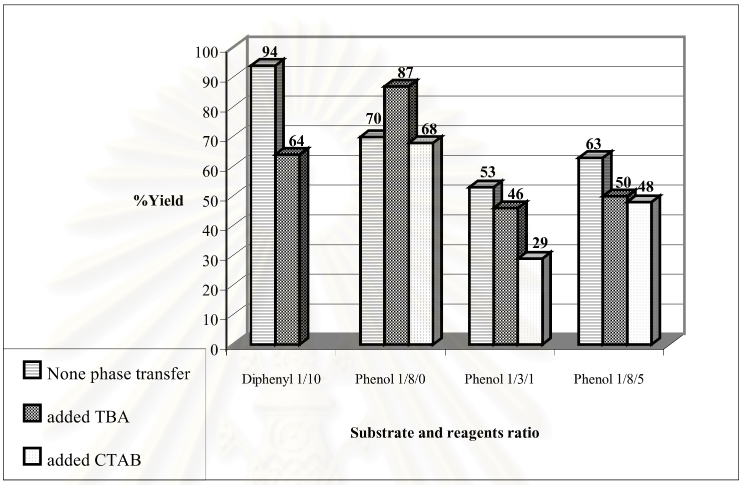


Figure 4.4 Comparison of using phase-transfer catalyst with none

The bromination of phenol using TBA as phase transfer gave high yield of product than CTAB because TBA has better water solubility than CTAB. TBA can be dispersed between aqueous phase and isooctane phase better than CTAB and can form more stable emulsions system. Increase interfacial area may lead to increase of reaction rate and increase percent yield.

4.6 Effect of oil phase studies

Two organic solvents such as isooctane and hexane were studied as are oil phase in two phases systems between aqueous and organic solvent. The comparison of %yield using isooctane and hexane as oil phase is shown in Figure 4.5.

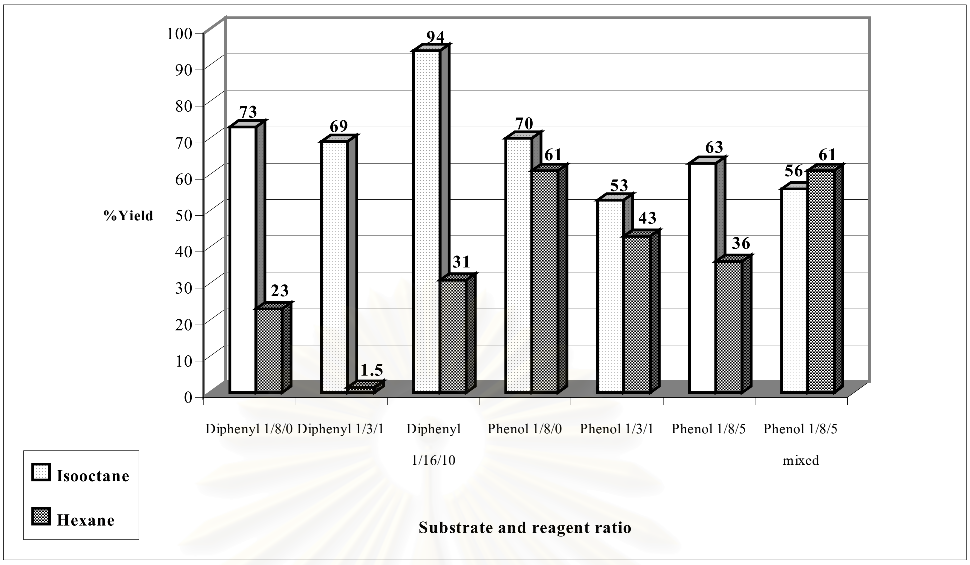


Figure 4.5 Comparison of %yield when using isooctane and hexane as oil phase

The bromination using isooctane as are oil phase gave higher yield of product than those using hexane because isooctane has lower interfacial tension, γ ,(~49 mNm^{-1}) with water than hexane (~ 51 mNm^{-1}). The lower γ may facilitate reaction between organic substrate and hydrophilic reactants at the interface. This lower γ reflects the fact that isooctane is more miscible with water than hexane.

4.7 The effect of mole ratio of diphenyl ether and sodium bromide

The bromination of diphenyl ether was studied producing 4,4’-dibromodiphenyl ether was studied as a model product. Various mole ratios of diphenyl ether and sodium bromide such as 1:1, 1:2, 1:3, …, 1:10, 1:12 were studied using isooctane as an oil phase. The ^{1}H-NMR spectra of diphenyl ether derivatives are shown in Figure 4.6.

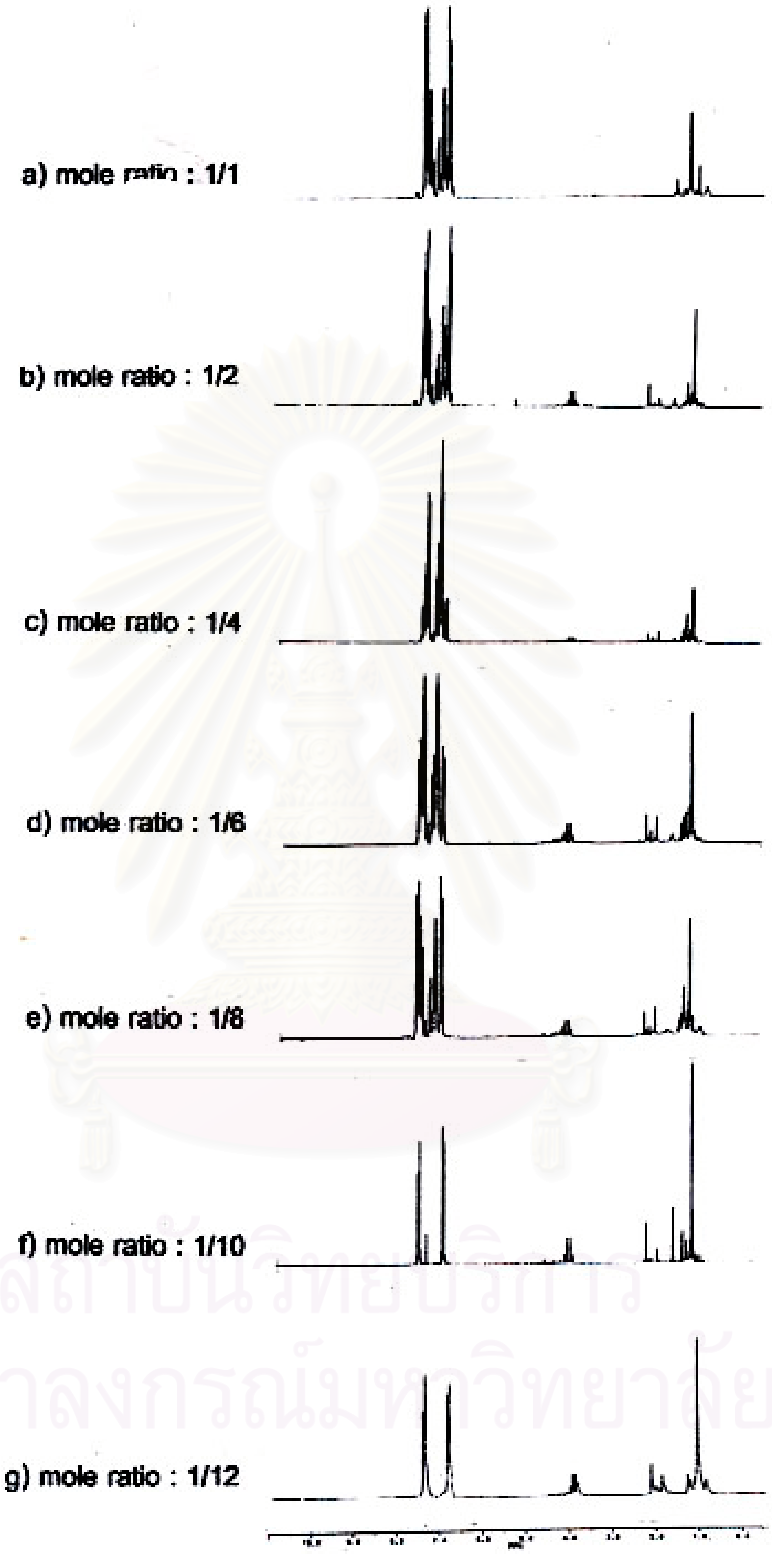


Figure 4.6. The ^{1}H-NMR spectrs of diphenyl ether derivatives

The bromination of diphenyl ether gave 4,4’-dibromodiphenyl ether by using mole ratio of substrate and sodium bromide as 1:10 and 1:12. Mole ratio as 1:10 is the best economical ratio to gave 4,4’-dibromodiphenyl ether.

4.8 The effect of mole ratio of phenol and sodium hypochlorite

The bromination of phenol producing tribromophenol as a model product was studied. Various mole ratios of phenol and sodium hypochlorite such as 1:1, 1:2, 1:3, 1:4 were studied using isooctane as oil phase and using mole ratio of phenol and sodium bromide as 1:1. The %composition of phenol mixture is shown in Figure 4.7.

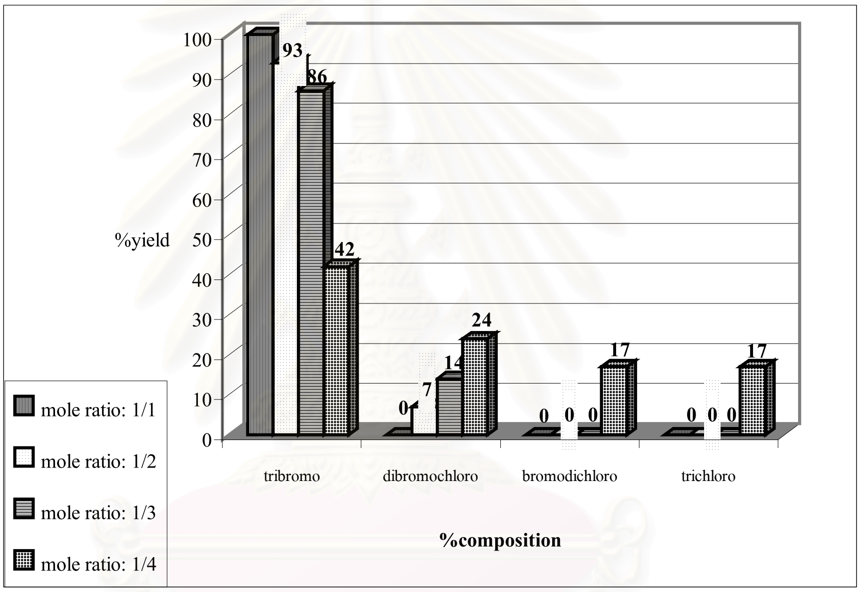


Figure 4.7 The %composition of phenolic derivatives

The bromination of phenol gave 100% of tribromophenol using the 1:1 mole ratio of substrate and sodium hypochlorite.

Chapter V

Conclusion

Sodium bromide/ sodium hypochlorite are innovative and safe brominating agents for aromatic mixture that contain activating substituents. A halogenation process, in which sodium hypochlorite is utilized, was optimized on laboratory scale and gave high yield to avoid the mentioned disadvantages (using halogenated solvents, strong condition in producting approaches and bromine (Br_2)) is still needed. Halogenated mixture were synthesized by a halogenation reaction in 2 phases (aqueous and organic solvent) of aromatic mixture such as diphenyl ether, phenol and toluene in the presence of acetic acid and a combination of sodium bromide/ sodium hypochlorite which was oxidizing agent with isooctane as a solvent at room temperature . Halogenated mixture were identified by spectroscopic techniques such as Infrared Spectroscopy, Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry.

In the approach 1 of halogenation of diphenyl ether, the chlorination using mole ratio of substrate and sodium hypochlorite as 1:8 gave chlorodiphenyl ether. The other approach, the bromination of diphenyl ether using mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:10:16 gave 94% *p*-dibromodiphenyl ether , a flame retardant agent useful in a variety of potential applications and reaction time for 2 hours.

The halogenation of phenol that added tetrabutyl ammoniumtetrafluoroborate as a phase transfer gave 87% 2,4,6-trichlorophenol used as a wood preservative, glue preservative and bactericide, as well as in antimildew treatment applications by using mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:0:8. The bromination gave 50% tribromophenol by using mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:5:8 and reaction time for 2 hours.

The bromination of toluene gave 83% dibromotoluene are important reactants for the functionalization of mixture by using mole ratio of substrate, sodium bromide and sodium hypochlorite as 1:5:8 and reaction time for 4 hours.

Two phase-transfer catalyst such as tetrabutylammonium tetrafluoroborate (TBA; (Bu_4N (BF_4)) and cetyl ammononium bromide (CTAB) were studied in two phase system (aqueous and isooctane) for bromination of aromatic compound. The bromination of phenol using TBA as phase transfer gave high yield of product than CTAB because TBA has better water solubility than CTAB. TBA can be dispersed between aqueous phase and isooctane phase better than CTAB and can form more stable emulsions system. Increase interfacial area may lead to increase of reaction rate and increase percent yield.

Two organic solvents such as isooctane and hexane were studied as are oil phase in two phases systems between aqueous and organic solvent. The bromination using isooctane as are oil phase gave higher yield of product than those using hexane because isooctane has lower interfacial tension, γ ,(~49 mNm^{-1}) with water than hexane (~ 51 mNm^{-1}). The lower γ may facilitate reaction between organic substrate and hydrophilic reactants at the interface. This lower γ reflects the fact that isooctane is more miscible with water than hexane.

The bromination of diphenyl ether was studied producing 4,4'-dibromodiphenyl ether was studied as a model product. Various mole ratios of diphenyl ether and sodium bromide such as 1:1, 1:2, 1:3, …, 1:10, 1:12 were studied using isooctane as an oil phase. The bromination of diphenyl ether gave 4,4'-dibromodiphenyl ether by using mole ratio of substrate and sodium bromide as 1:10 and 1:12. Mole ratio as 1:10 is the best economical ratio to gave 4,4'-dibromodiphenyl ether.

The bromination of phenol producing tribromophenol as a model product was studied. Various mole ratios of phenol and sodium hypochlorite such as 1:1, 1:2, 1:3, 1:4 were studied using isooctane as oil phase and using mole ratio of phenol and sodium bromide as 1:1. The bromination of phenol gave 100% of tribromophenol using the 1:1 mole ratio of substrate and sodium hypochlorite.

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APPENDICES

APPENDIX A

SPECTRA OF DIPHENYL ETHER DERIVATIVES

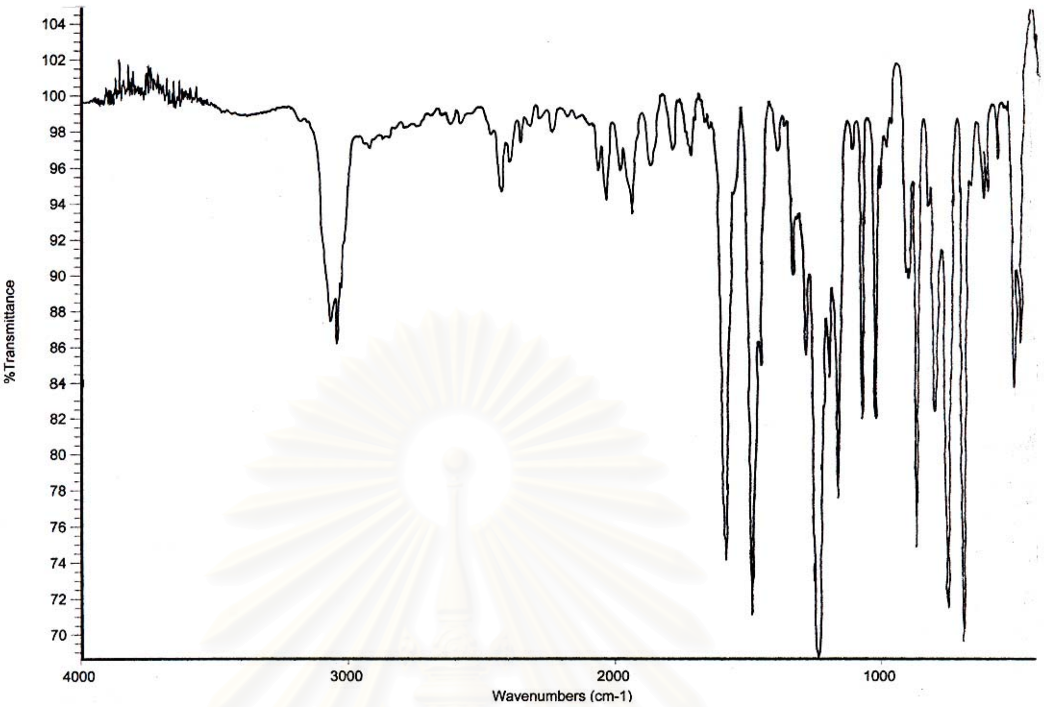

Figure A1 The FTIR spectrum of diphenyl ether

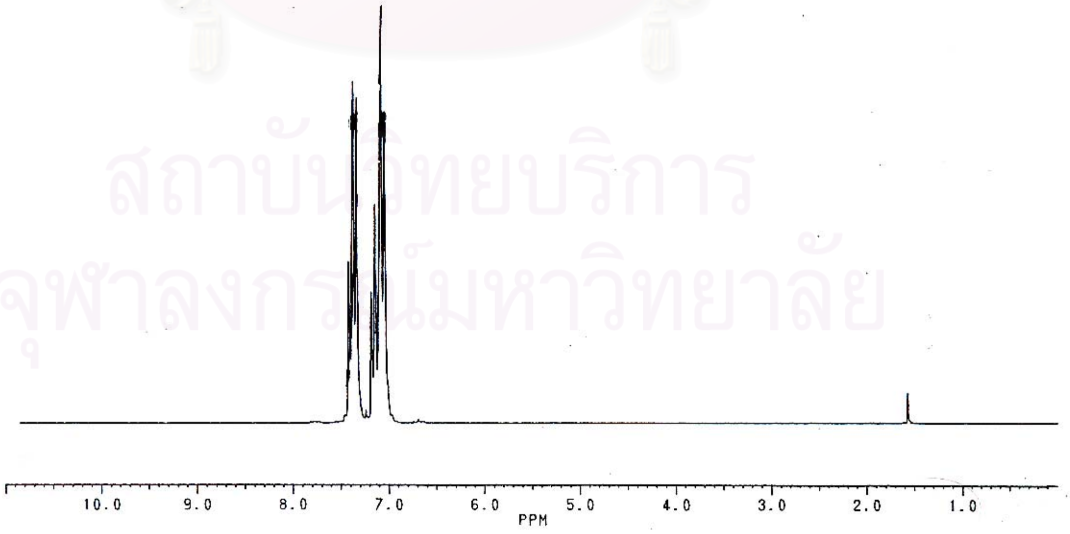

Figure A2 The ^{1}H-NMR spectrum of diphenyl ether

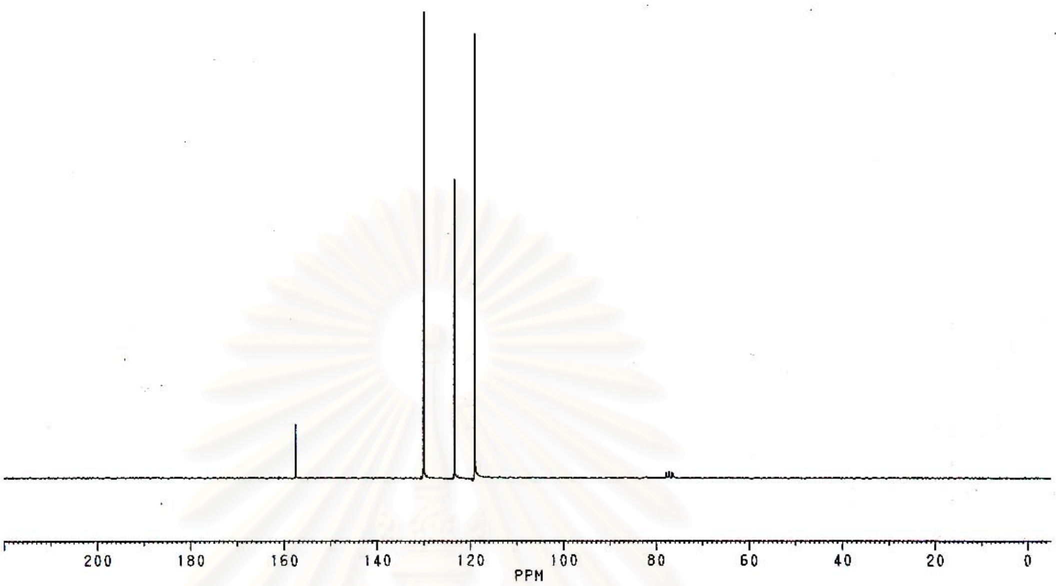

Figure A3 The ^{13}C-NMR spectrum of diphenyl ether

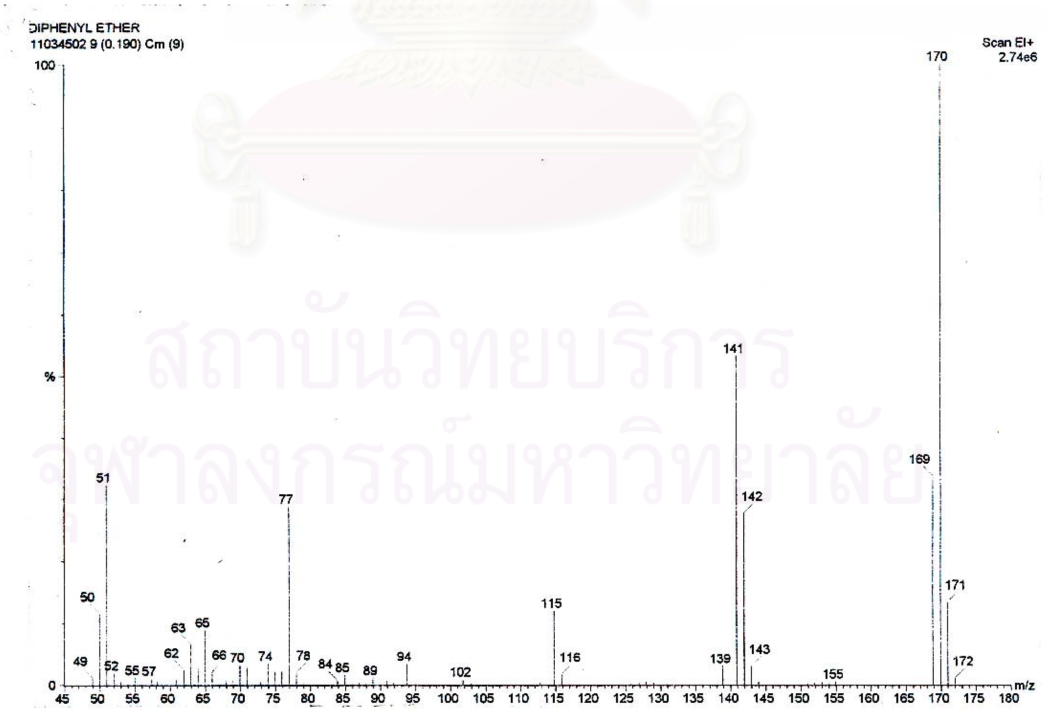

Figure A4 The mass spectrum of diphenyl ether

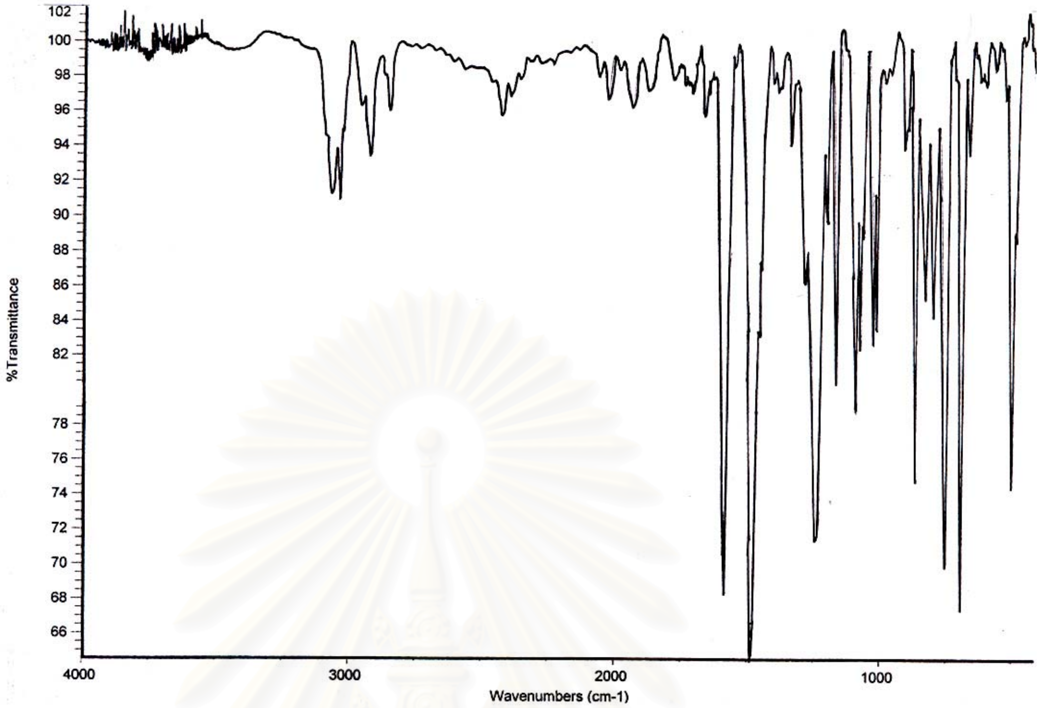

Figure A5 The FTIR spectrum of mixture1D

(using mole ratio of substrate and sodium hypochlorite: 1/8)

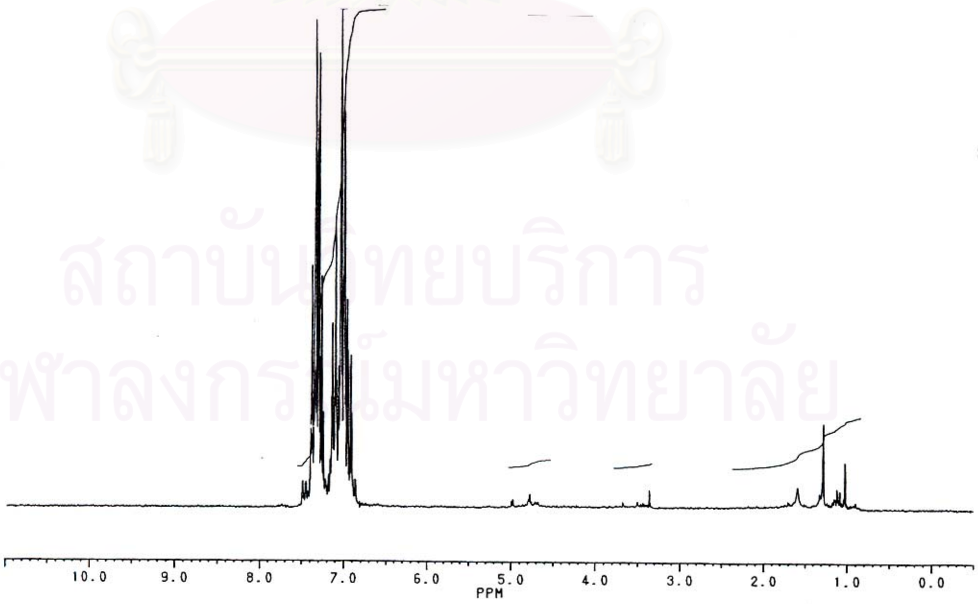

Figure A6 The ^{1}H-NMR spectrum of mixture 1D

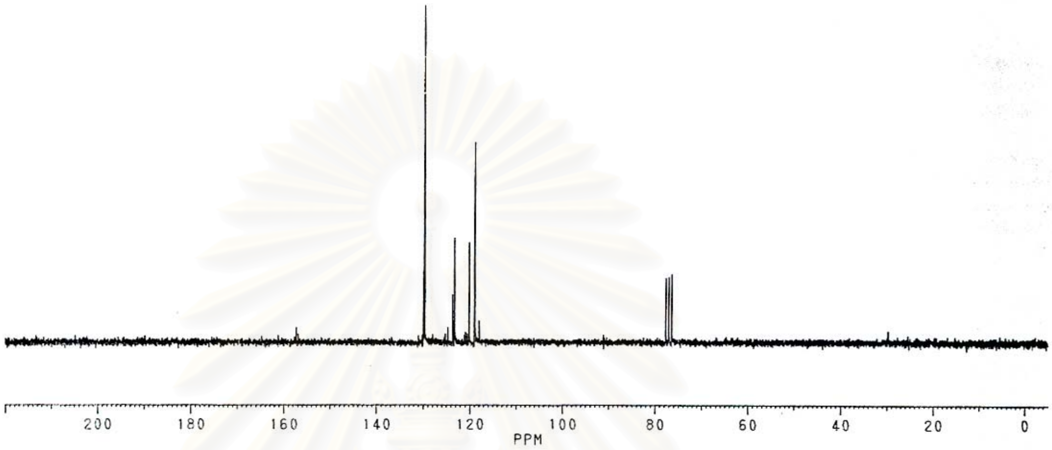

Figure A7 The ^{13}C-NMR spectrum of mixture 1D

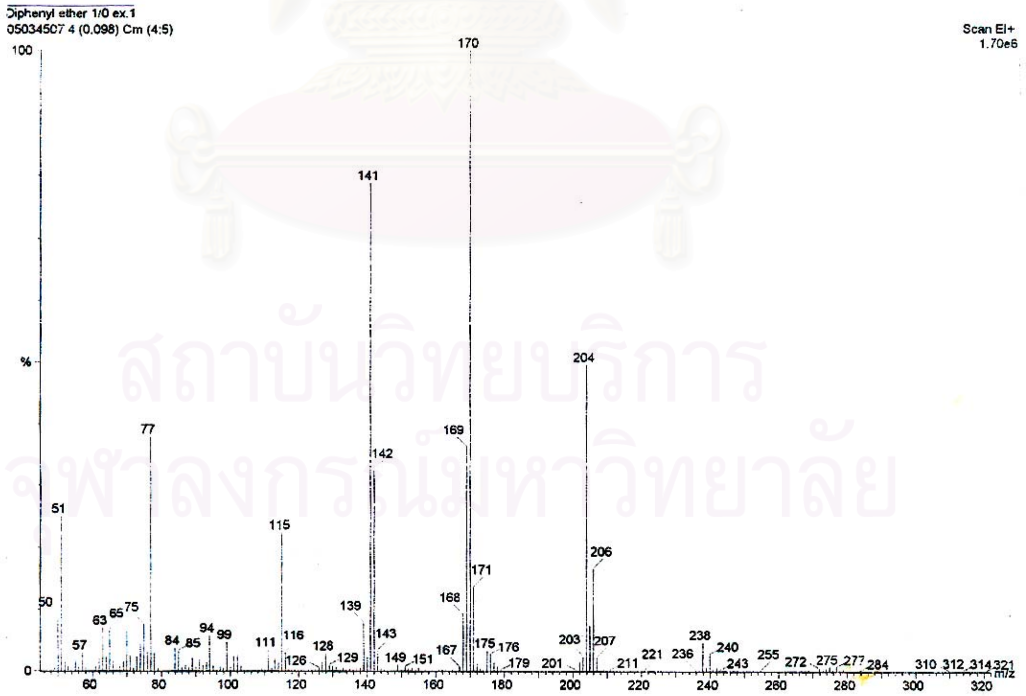

Figure A8 The mass spectrum of mixture 1D

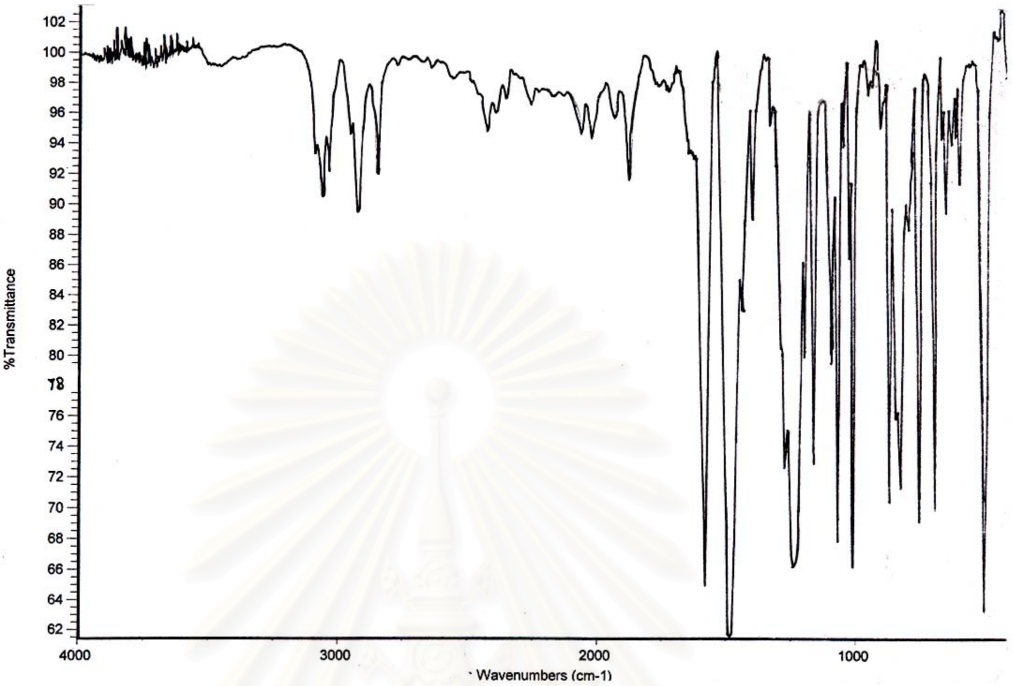

Figure A9 The FTIR spectrum of mixture 2D

(using mole ratio of substrate and sodium bromide: 1/1)

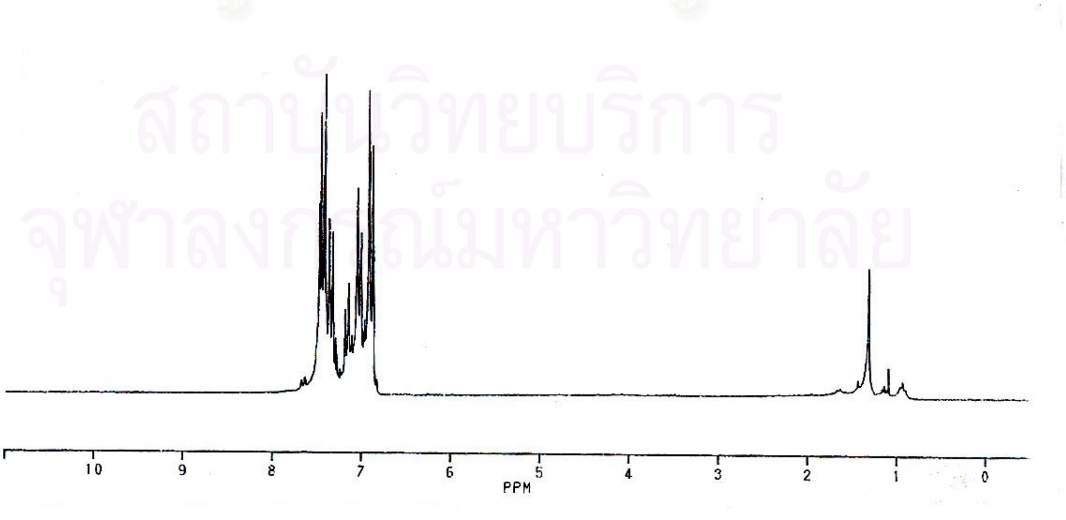

Figure A10 The ^{1}H-NMR spectrum of mixture 2D

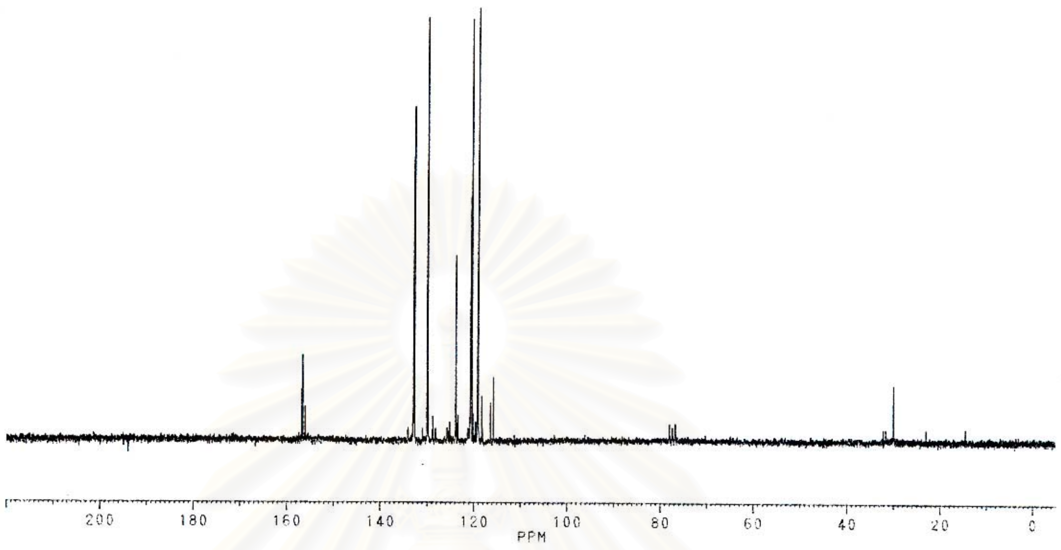

Figure A11 The ^{13}C-NMR spectrum of mixture 2D

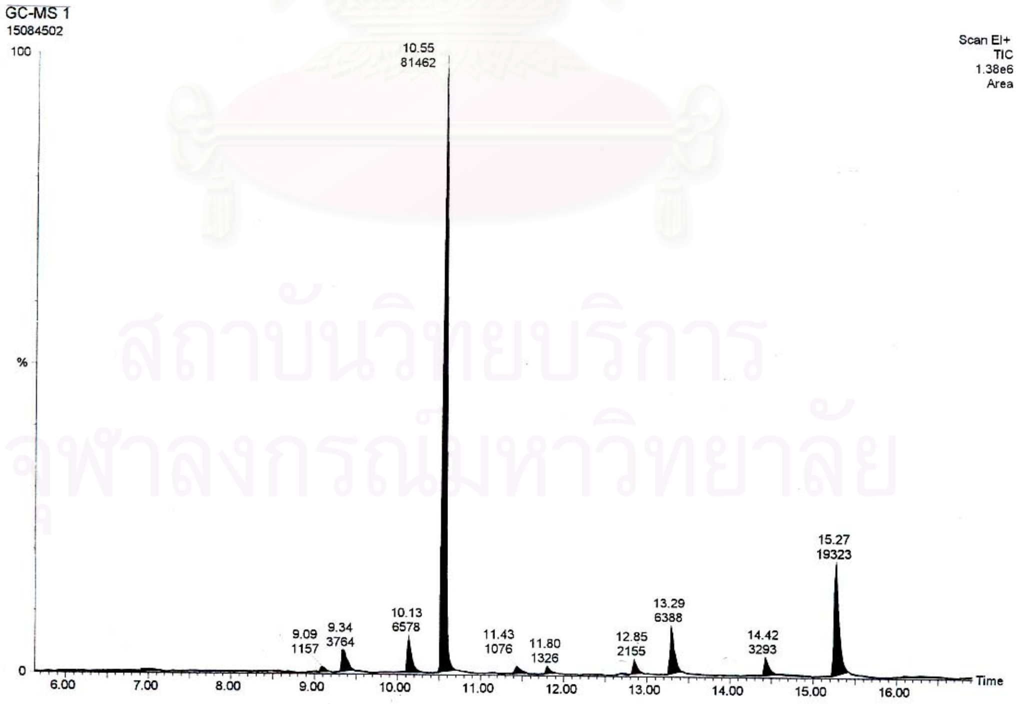

Figure A12 The gas chromatogram of mixture 2D

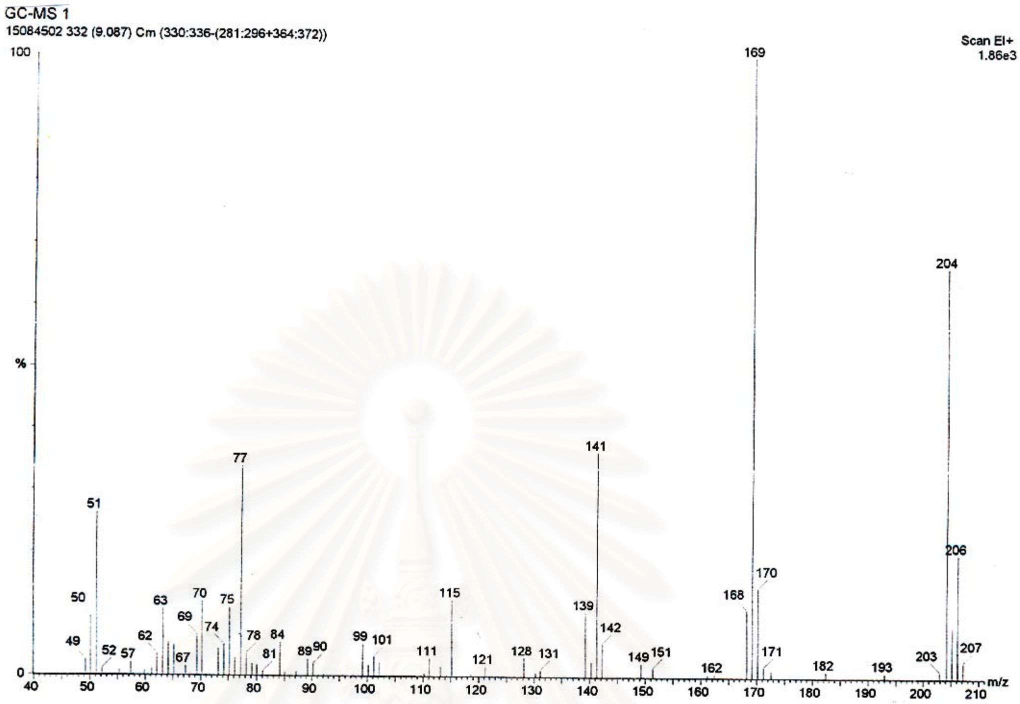

Figure A13 The mass spectrum of mixture 2D at t_R = 9.09 min

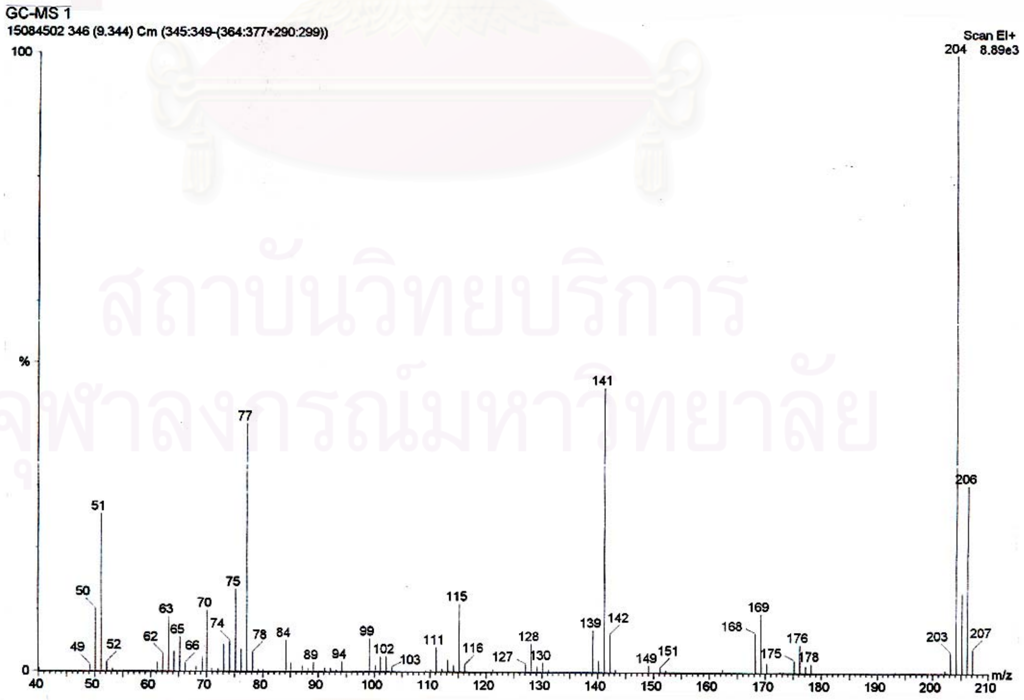

Figure A14 The mass spectrum of mixture 2D at t_R = 9.34 min

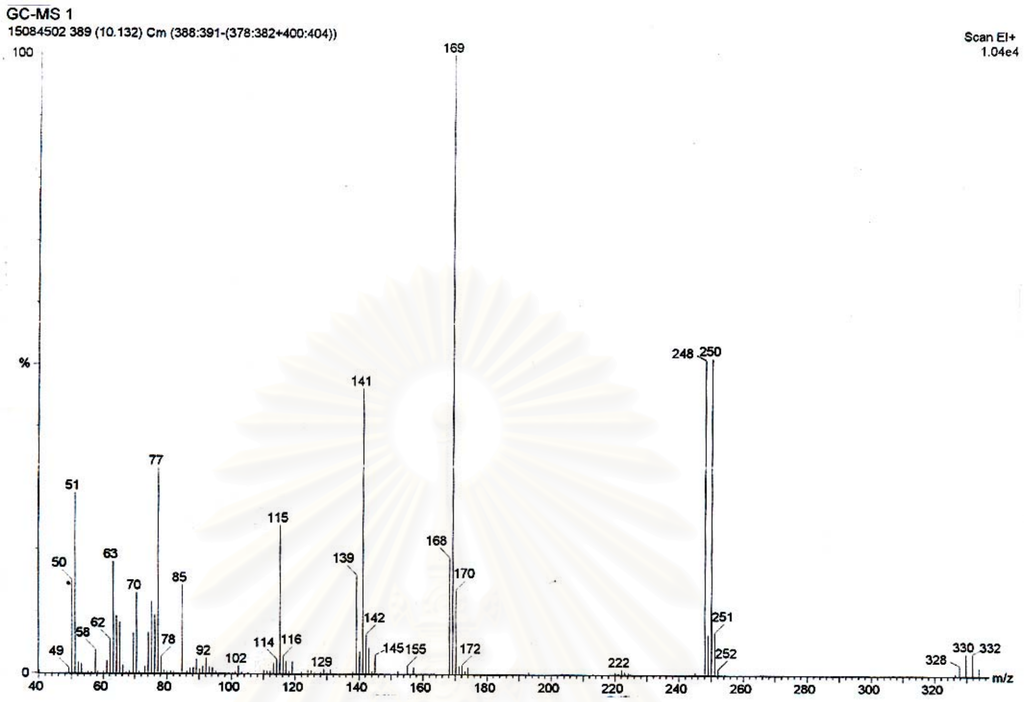

Figure A15 The mass spectrum of mixture 2D at t_R = 10.13 min

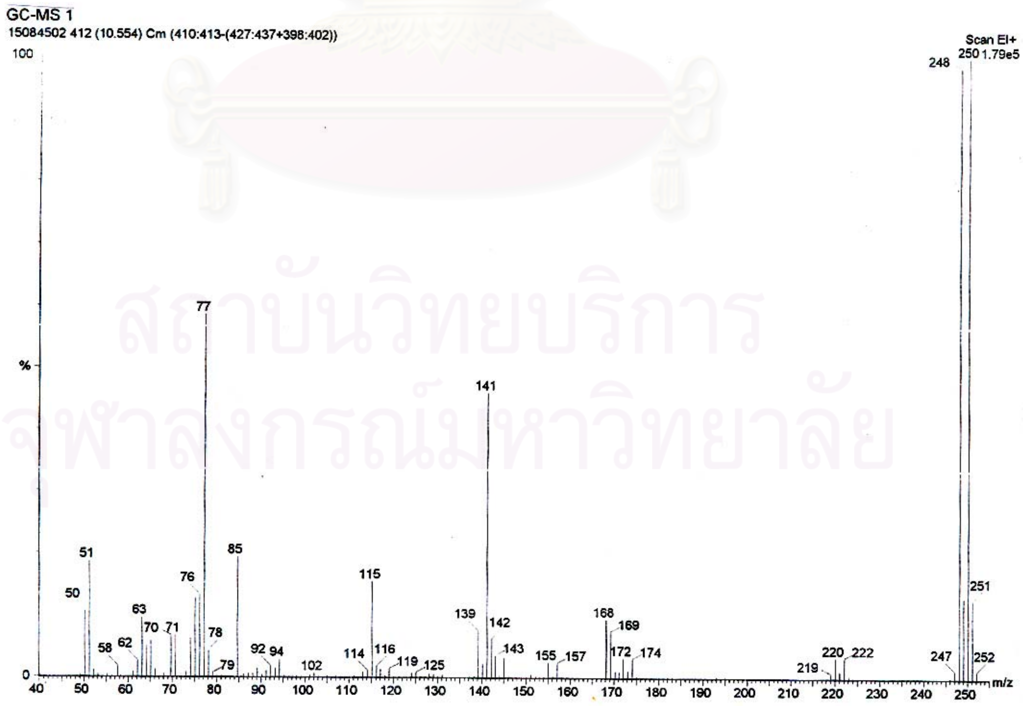

Figure A16 The mass spectrum of mixture 2D at t_R = 10.55 min

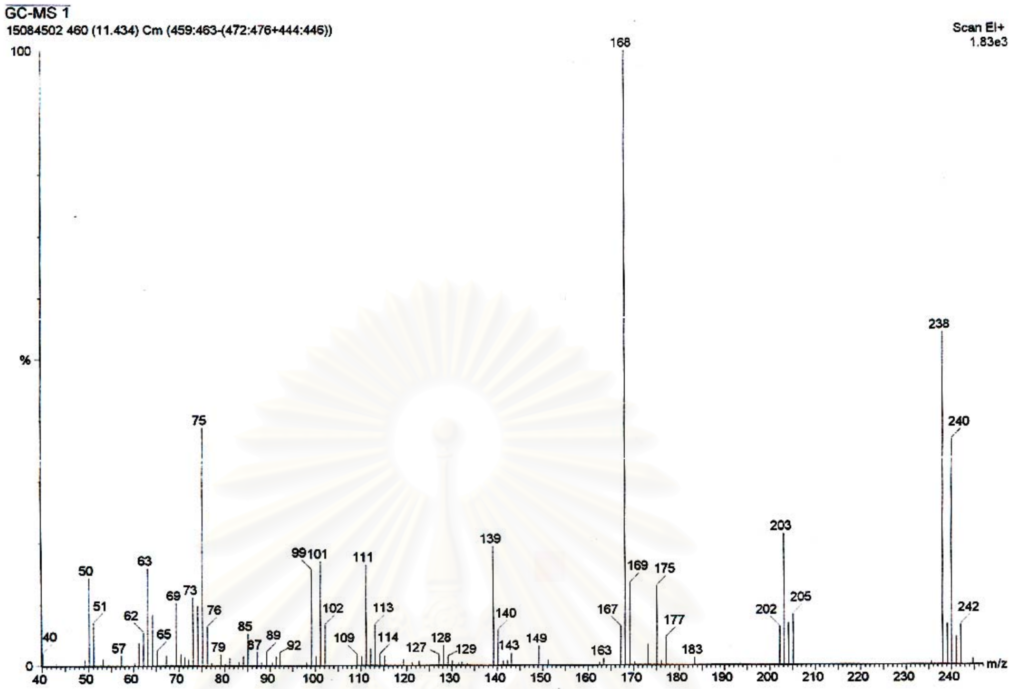

Figure A17 The mass spectrum of mixture 2D at t_R = 11.43 min

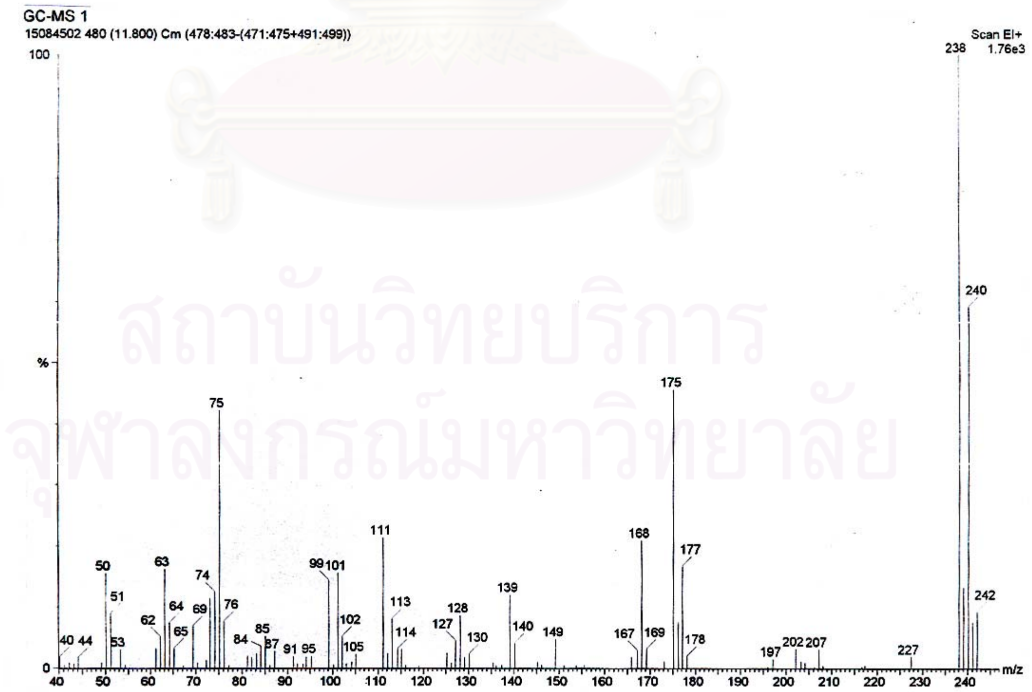

Figure A18 The mass spectrum of mixture 2D at t_R = 11.80 min

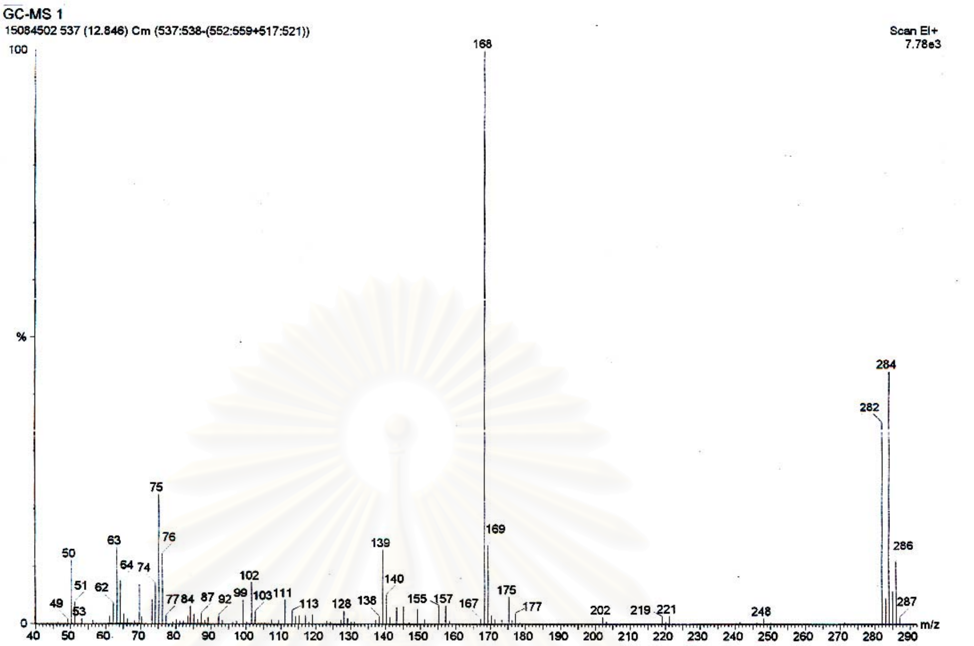

Figure A19 The mass spectrum of mixture 2D at t_R = 12.85 min

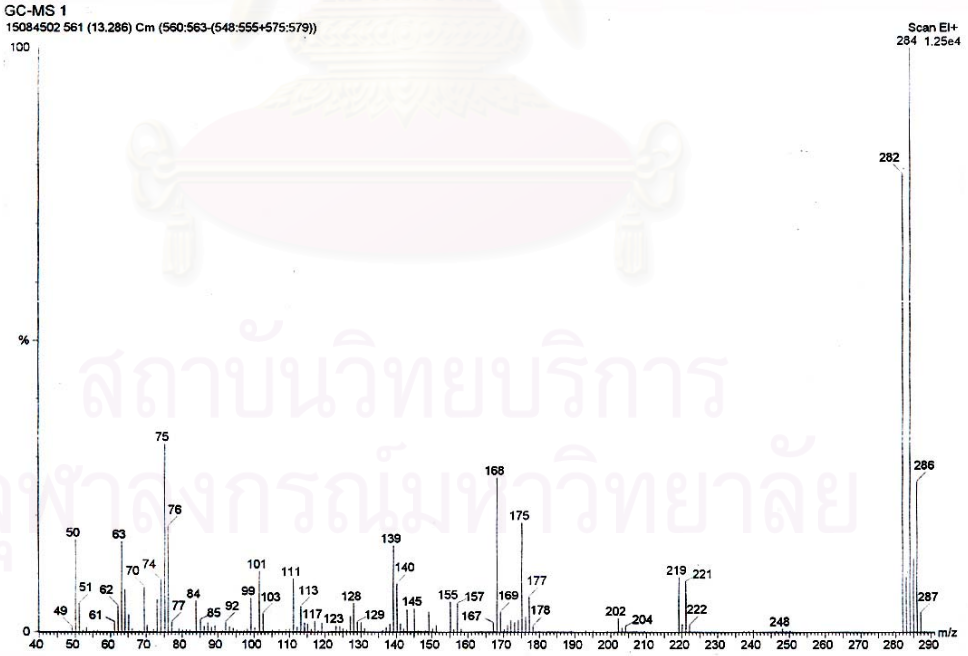

Figure A20 The mass spectrum of mixture 2D at t_R = 13.29 min

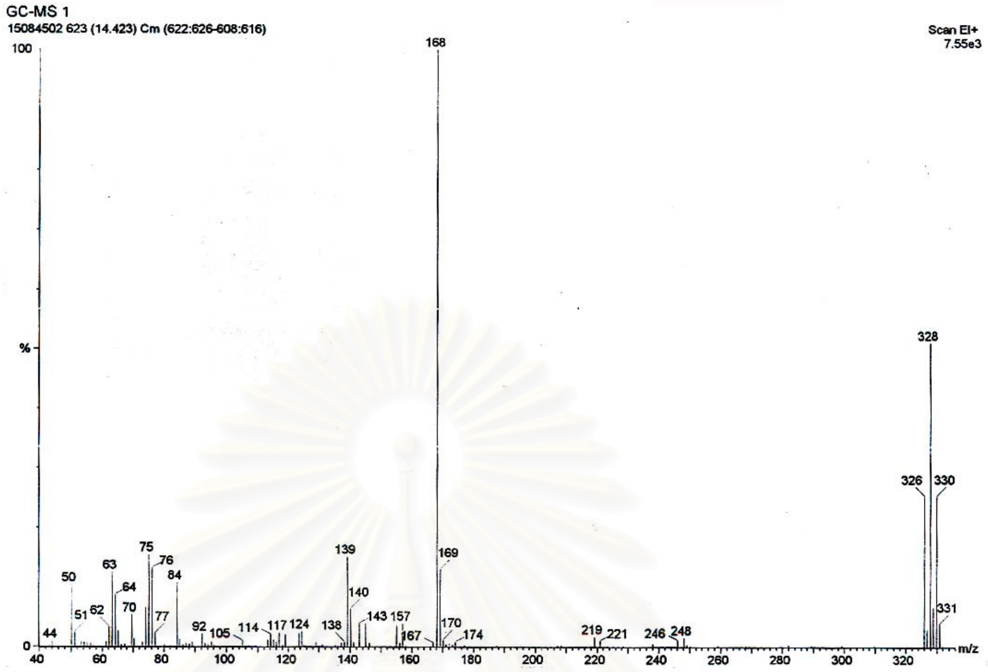

Figure 21 The mass spectrum of mixture 2D at t_R = 14.42 min

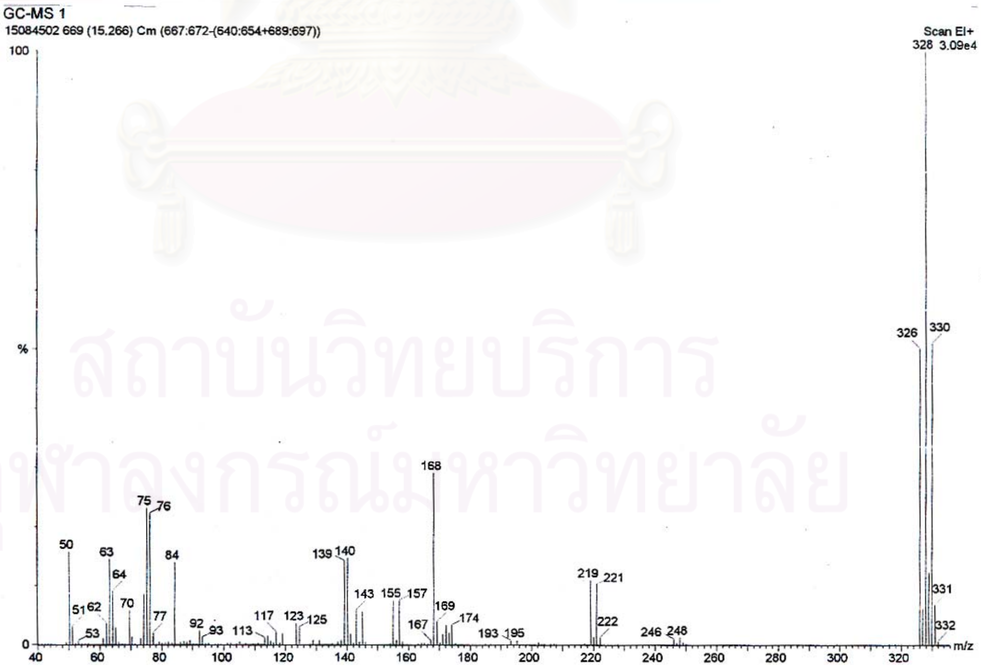

Figure A22 The mass spectrum of mixture 2D at t_R = 15.27 min

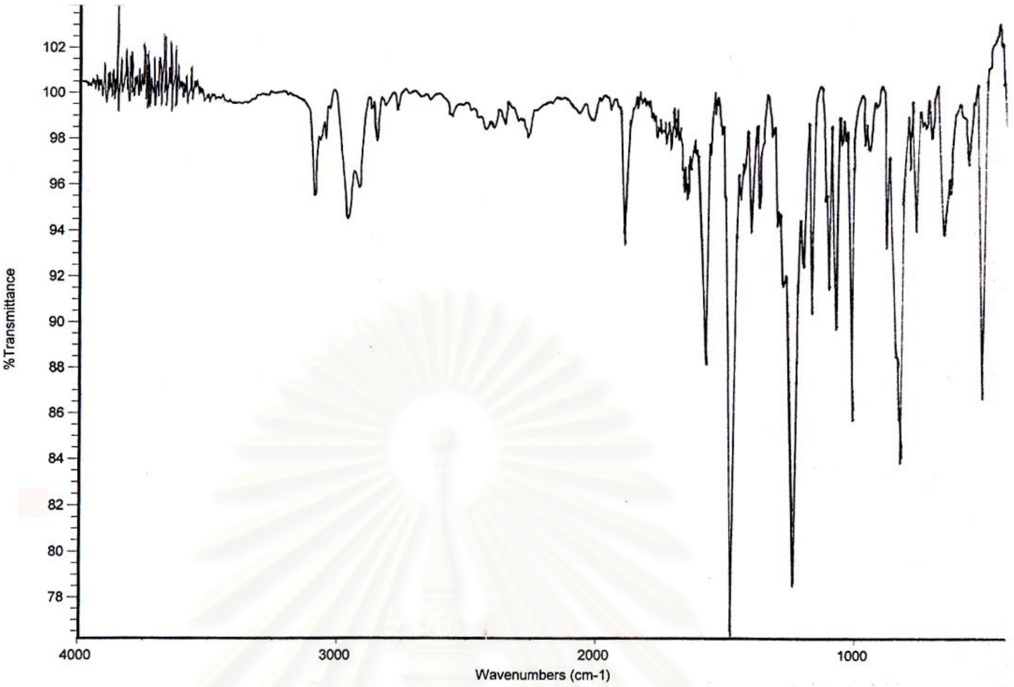

Figure A23 The FTIR spectrum of mixture 3D

(using mole ratio of substrate and sodium bromide: 1/10)

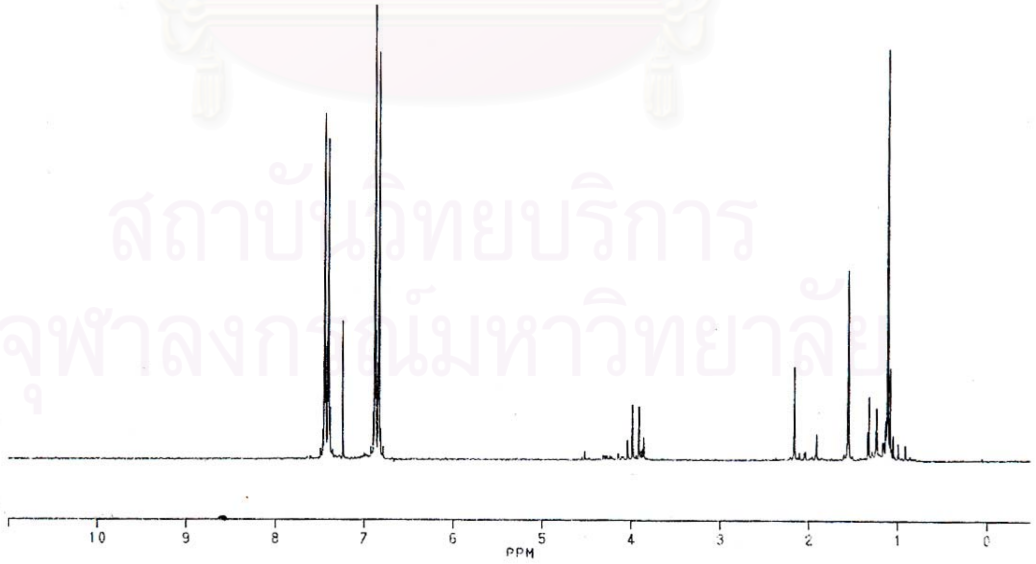

Figure A24 The ^{1}H-NMR spectrum of mixture 3D

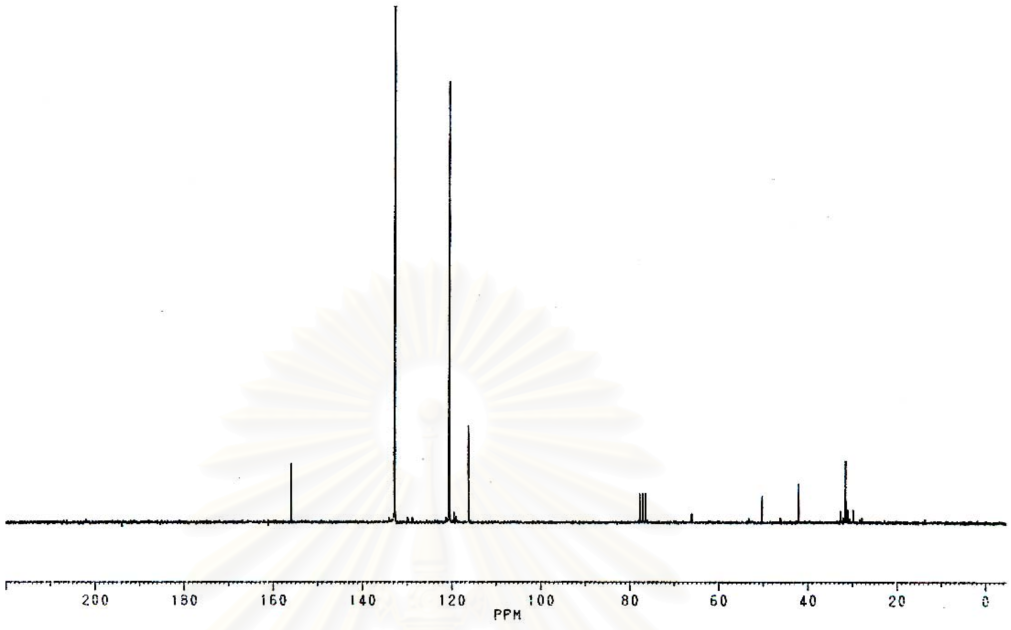

Figure A25 The ^{13}C-NMR spectrum of mixture 3D

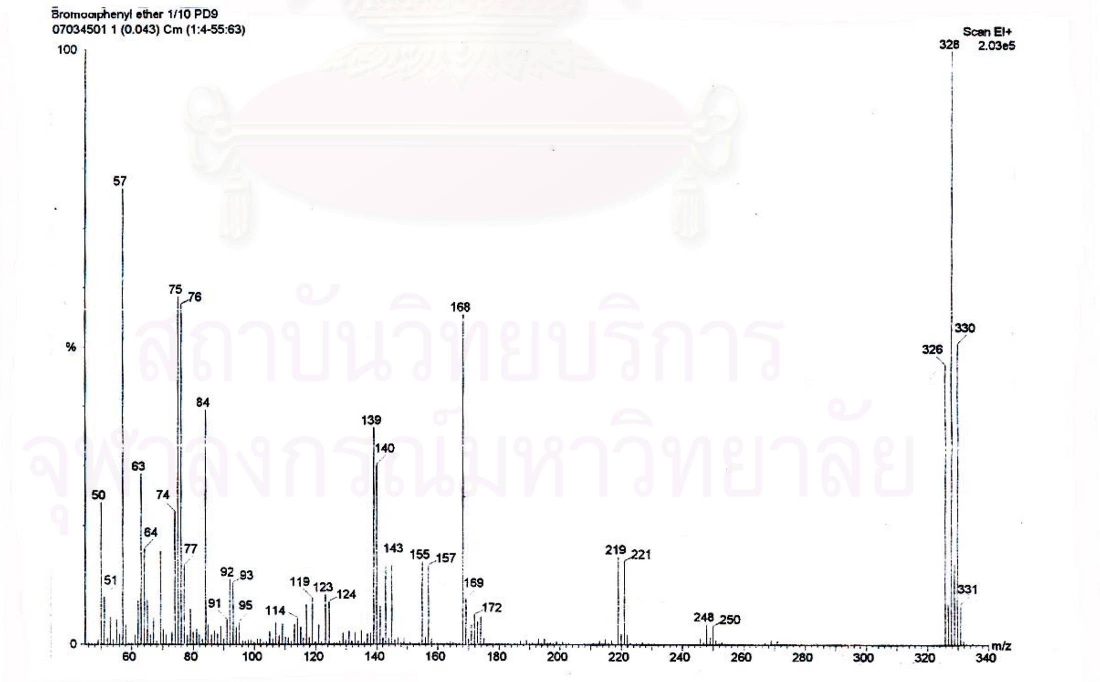

Figure A26 The mass spectrum of mixture 3D

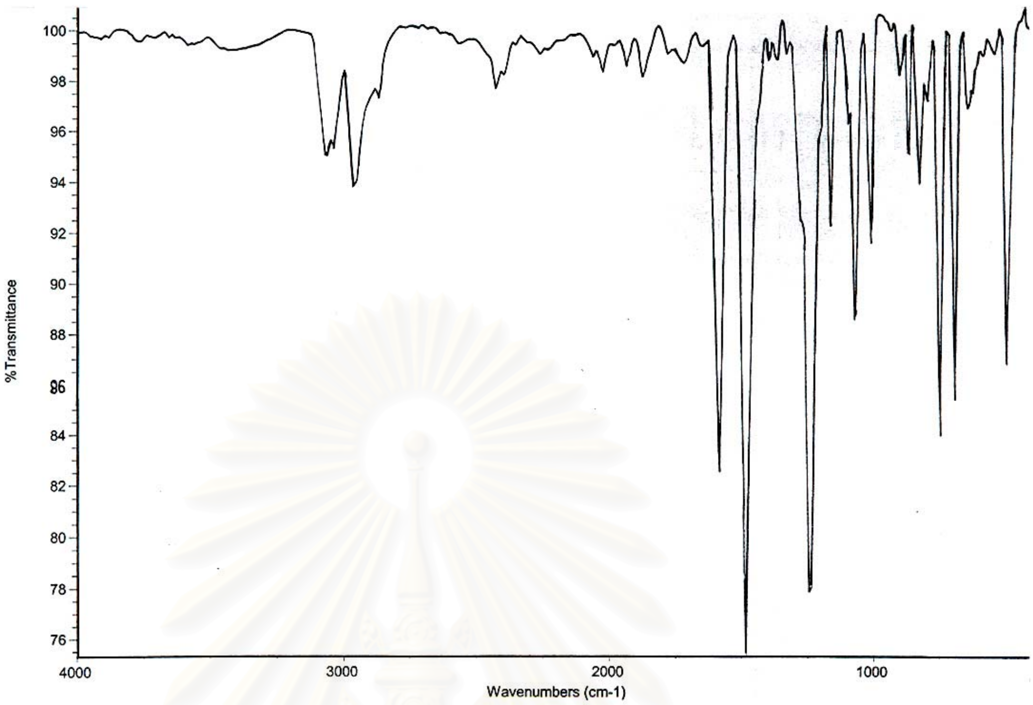

Figure A27 The FTIR spectrum of mixture 4D

(PT (TBA); using mole ratio of substrate and sodium bromide: 1/10)

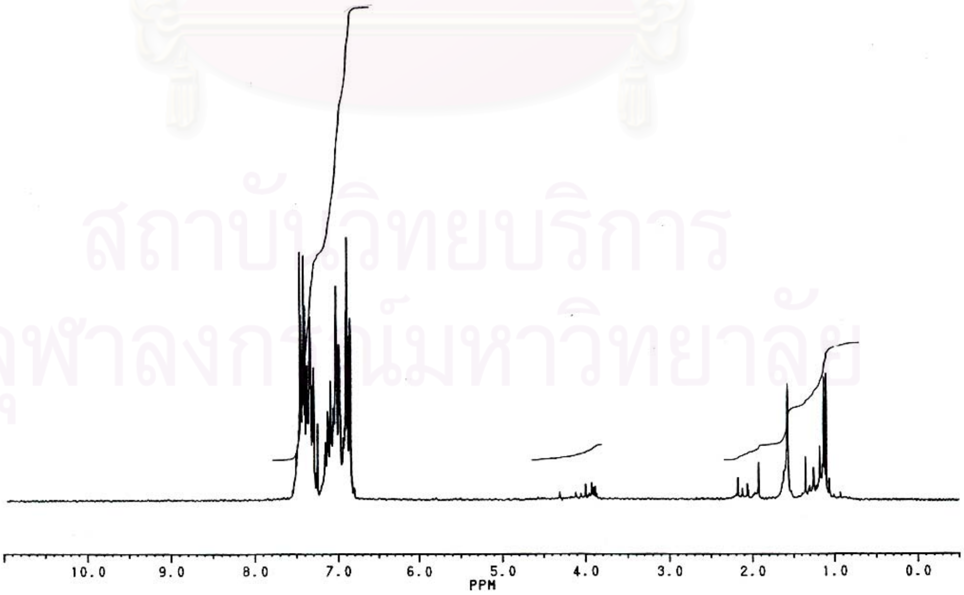

Figure A28 The ^{1}H-NMR spectrum of mixture 4D

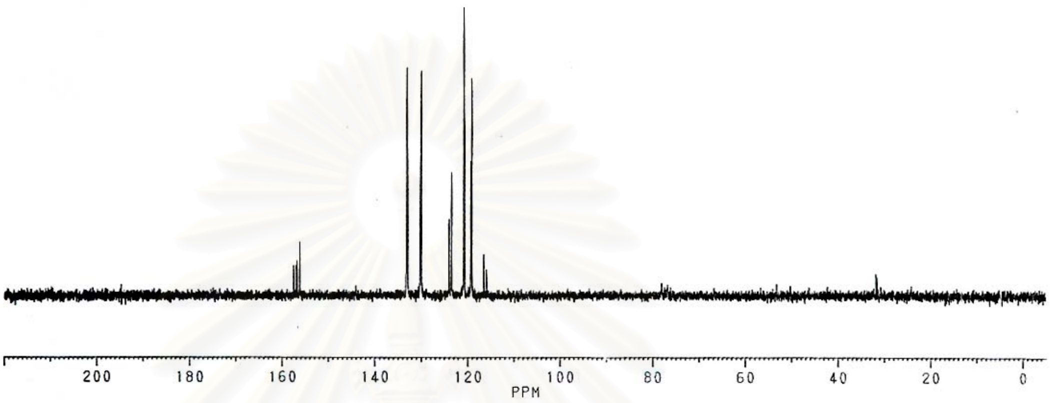

Figure A29 The ^{13}C-NMR spectrum of mixture 4D

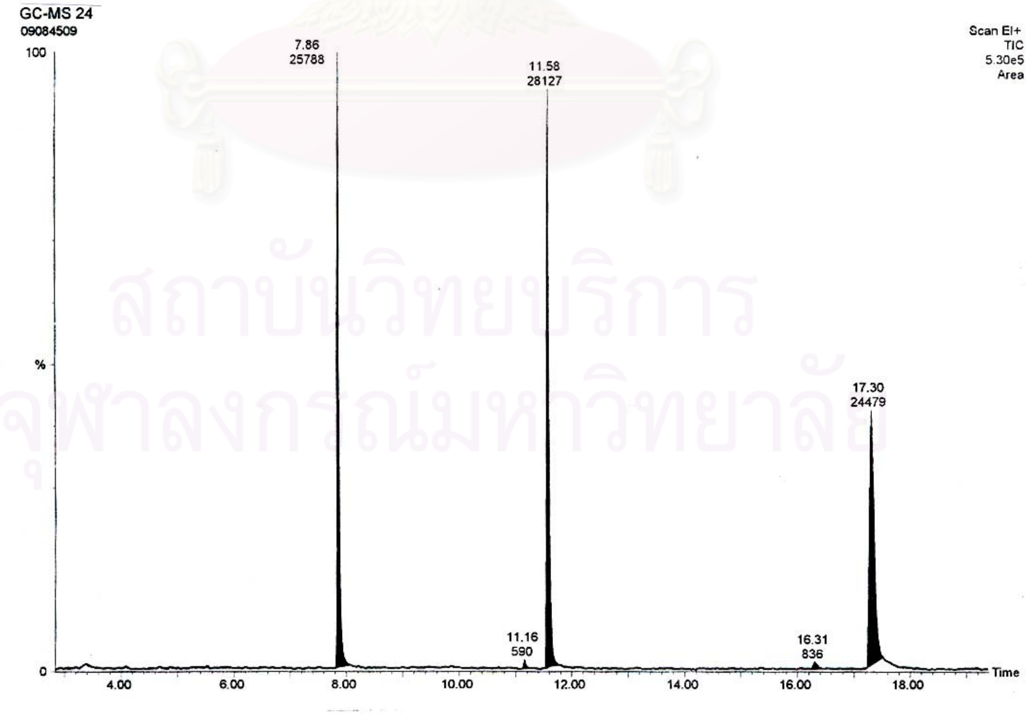

Figure A30 The gas chromatogram of mixture 4D

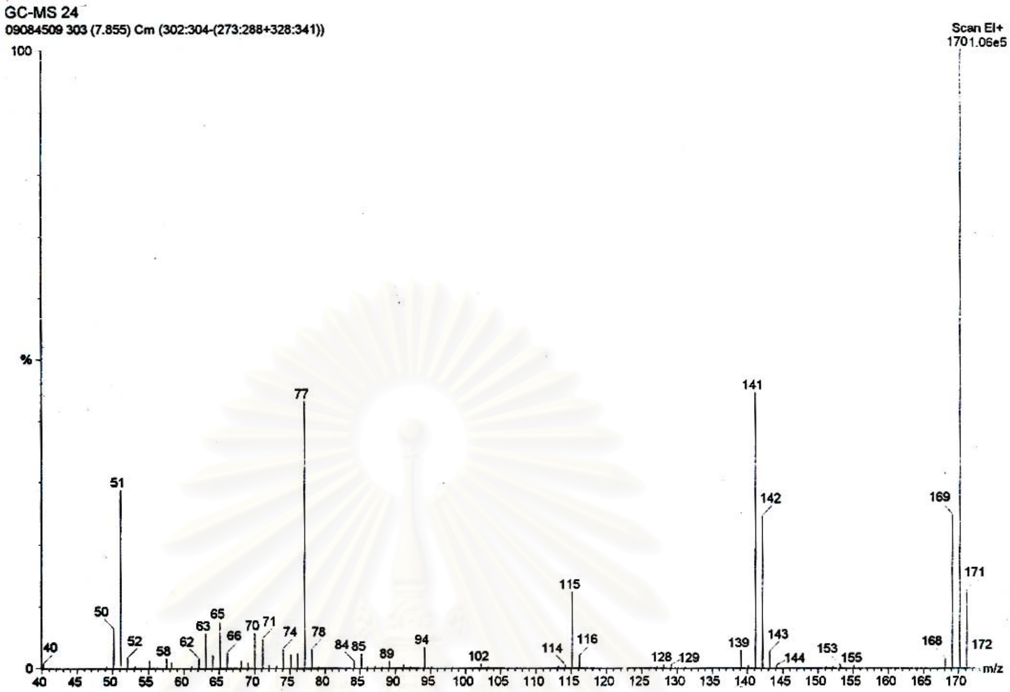

Figure A31 The mass spectrum of mixture 4D at t_R = 7.86 min

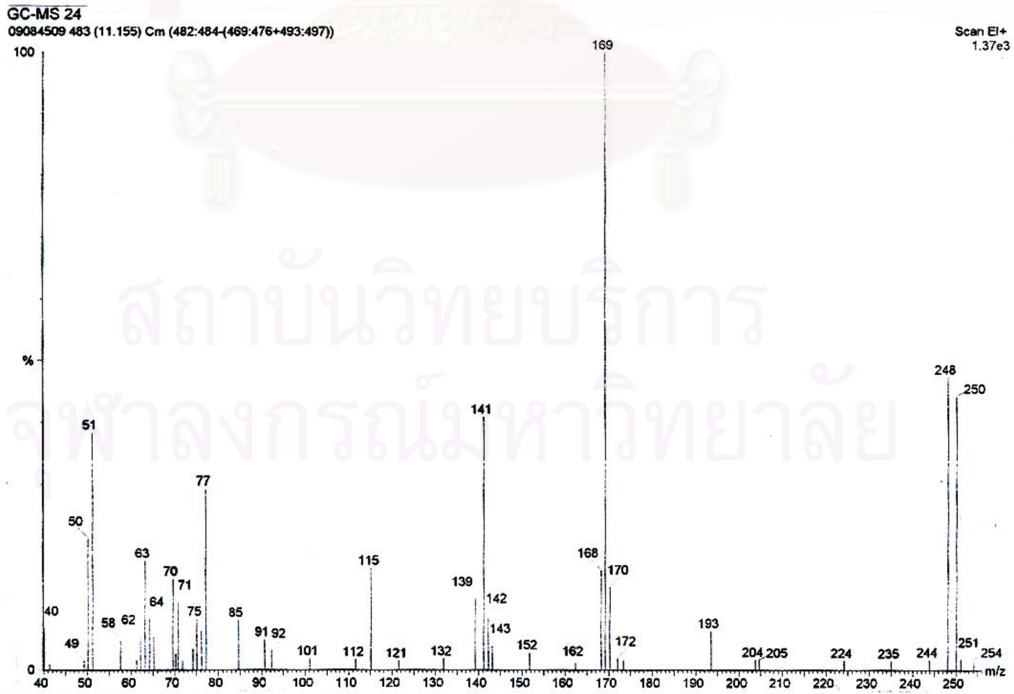

Figure A32 The mass spectrum of mixture 4D at t_R = 11.16 min

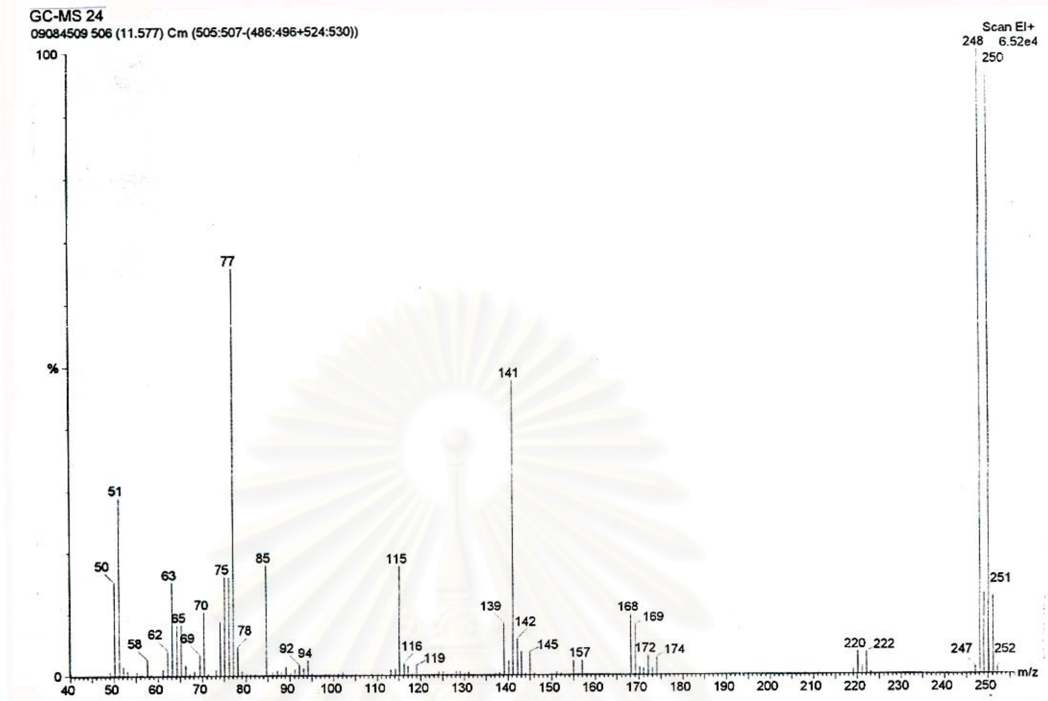

Figure A33 The mass spectrum of mixture 4D at t_R = 11.58 min

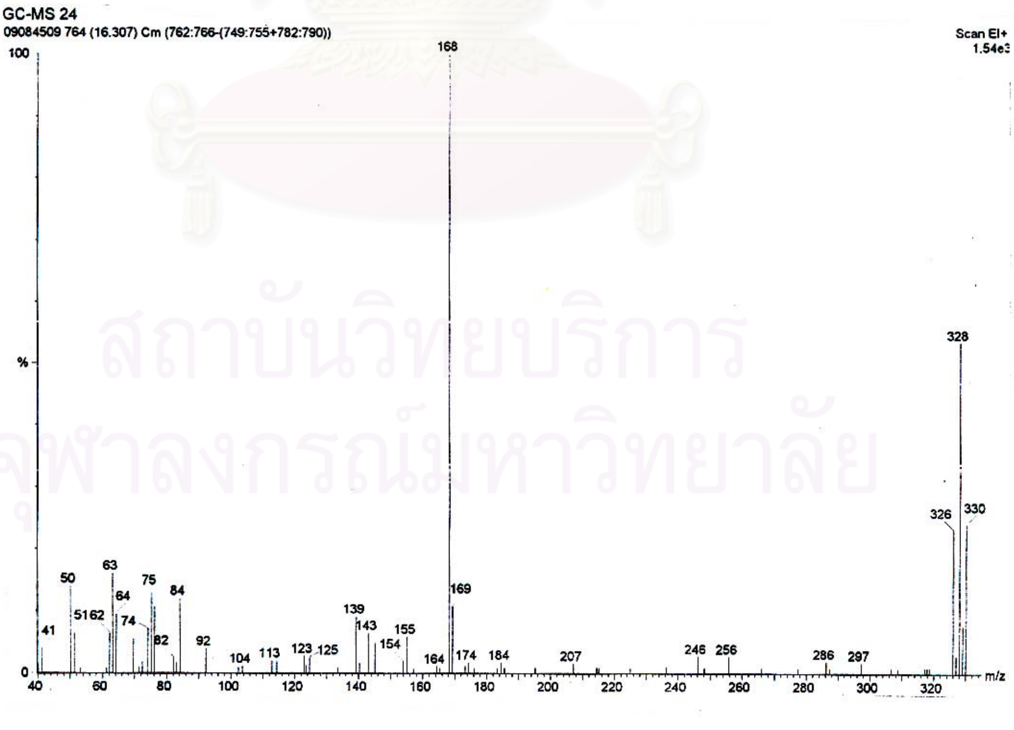

Figure A34 The mass spectrum of mixture 4D at t_R = 16.31 min

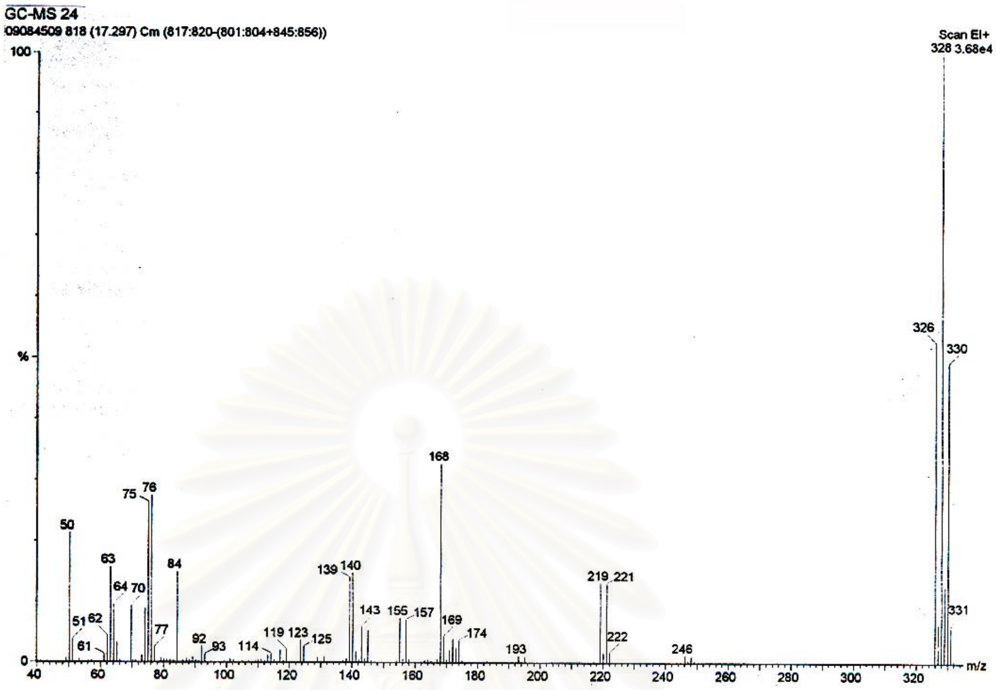

Figure A35 The mass spectrum of mixture 4D at t_R = 17.30 min

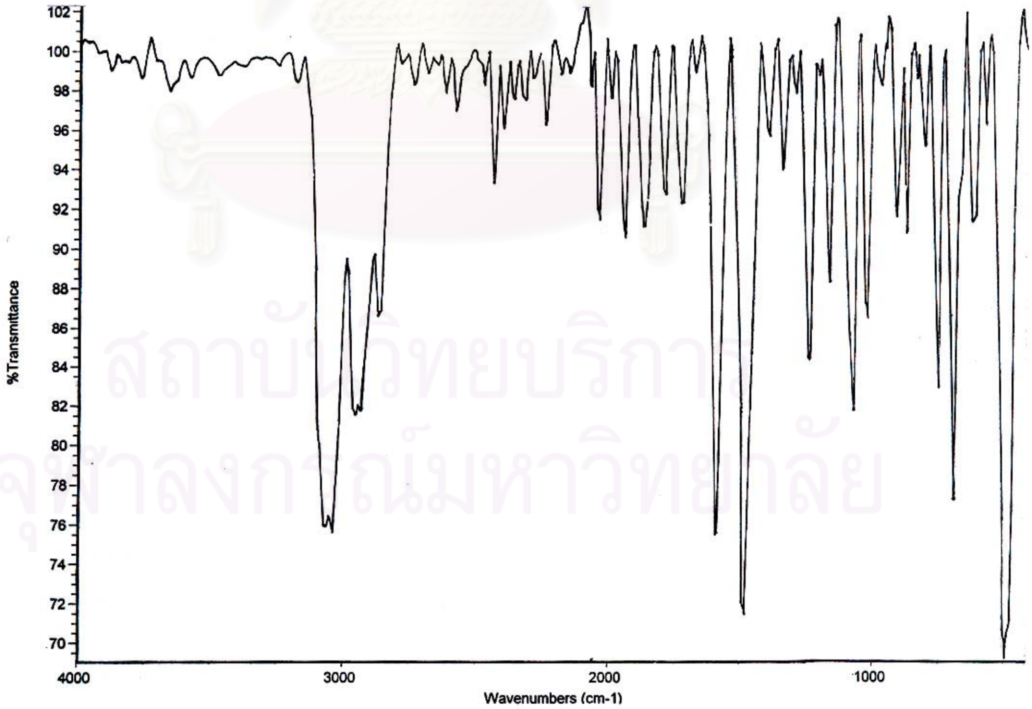

Figure A36 The FTIR spectrum of mixture 5D

(haxane; using mole ratio of substrate and sodium hypochlorite: 1/8)

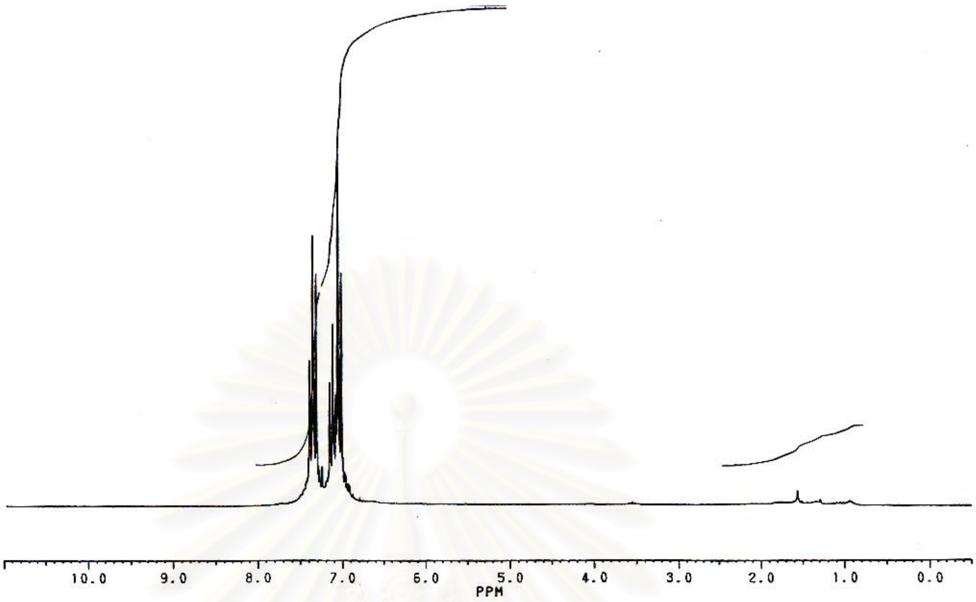

Figure A37 The ^{1}H-NMR spectrum of mixture 5D

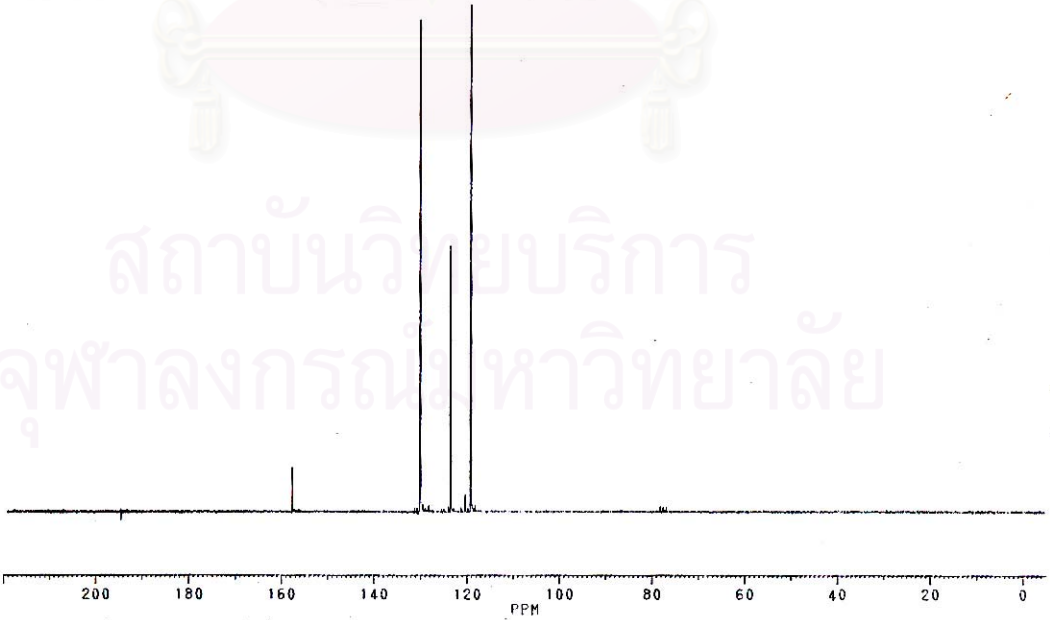

Figure A38 The ^{13}C-NMR spectrum of mixture 5D

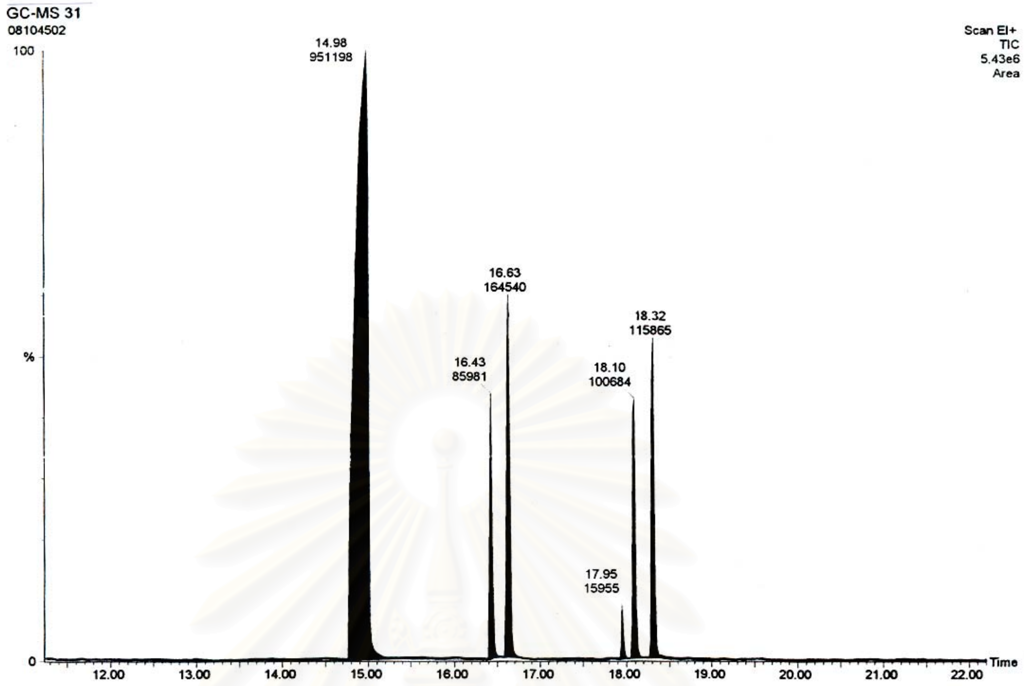

Figure A39 The gas chromatogram of mixture 5D

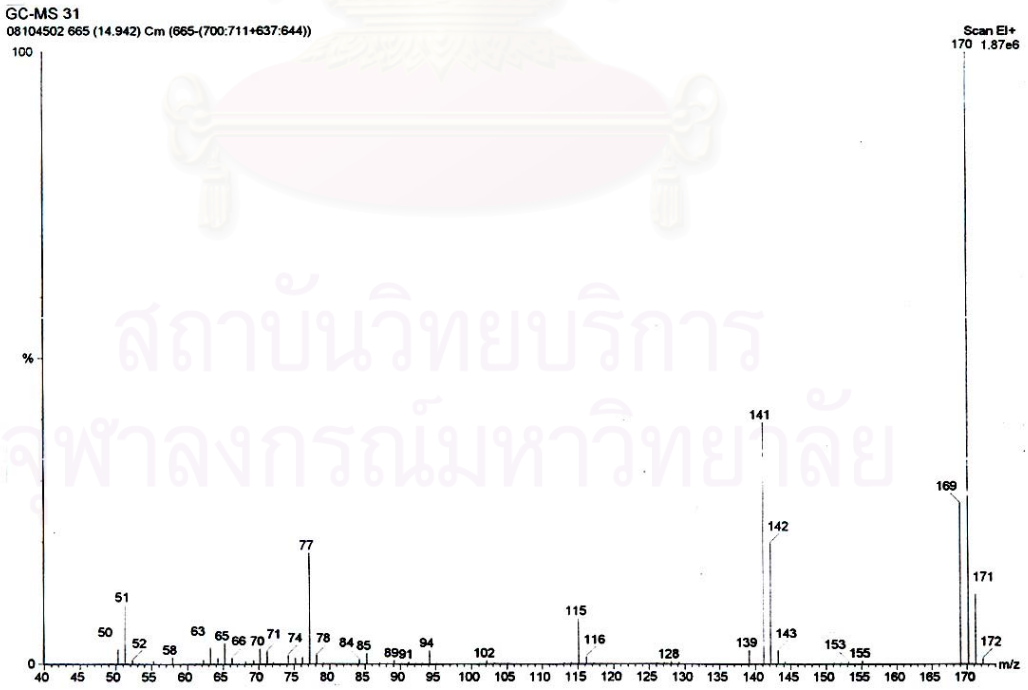

Figure A40 The mass spectrum of mixture 5D at t_R = 14.98 min

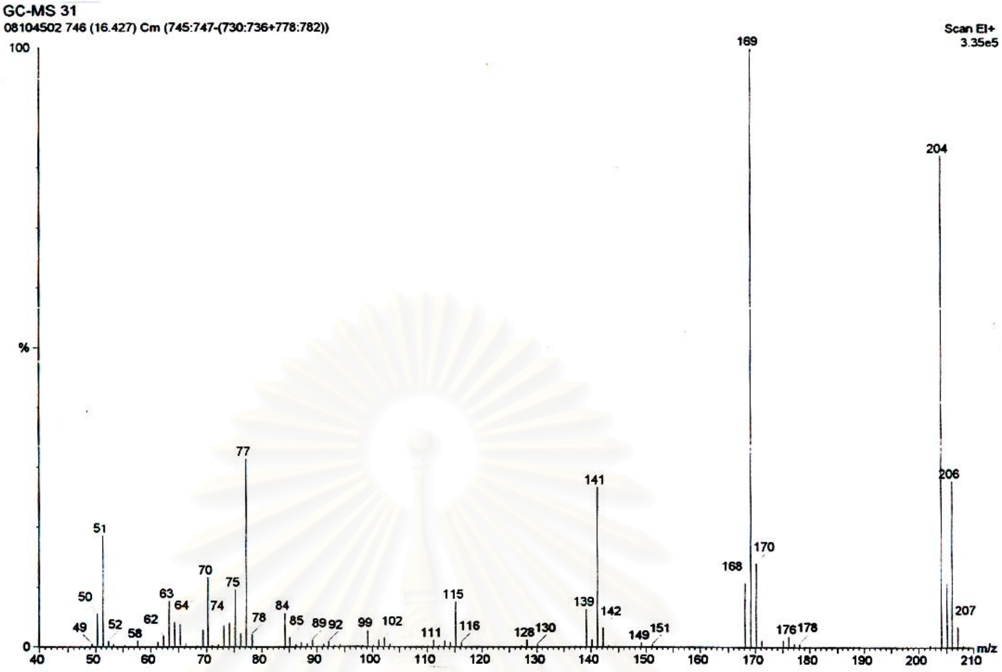

Figure A41 The mass spectrum of mixture 5D at t_R = 16.43 min

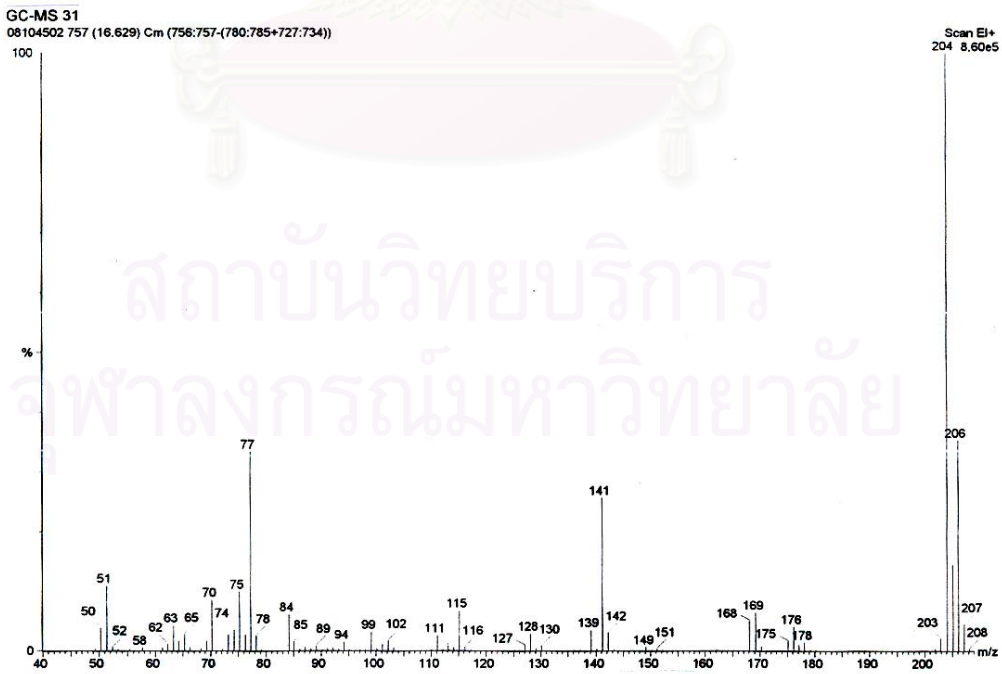

Figure A42 The mass spectrum of mixture 5D at t_R = 16.63 min

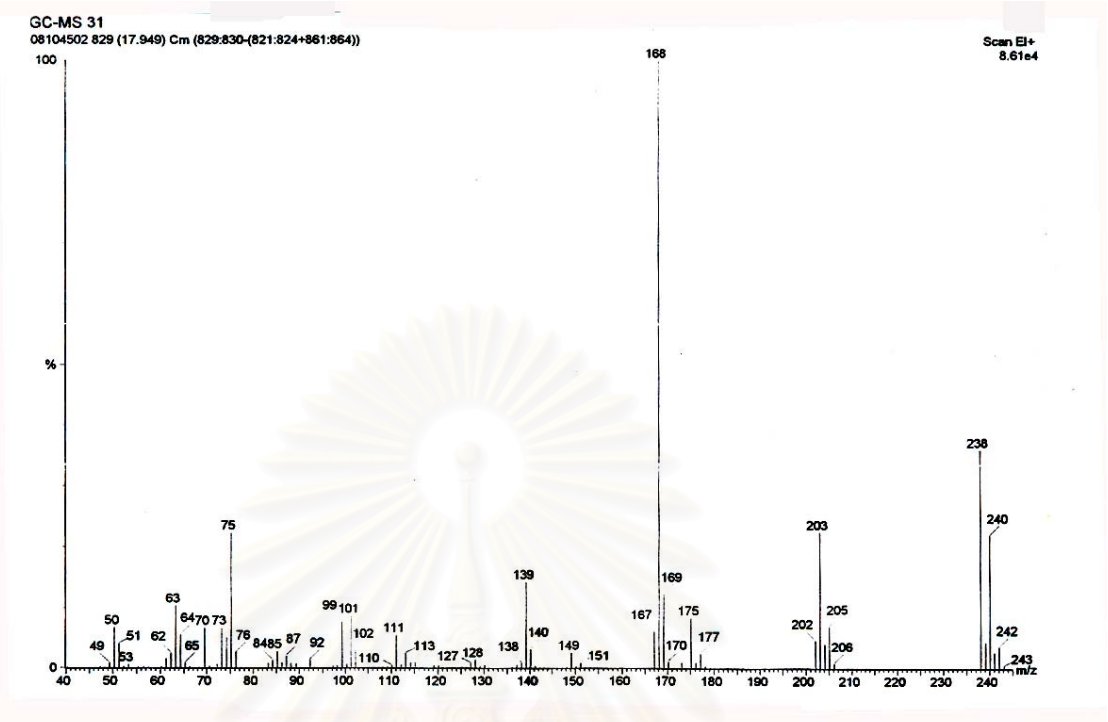

Figure A43 The mass spectrum of mixture 5D at t_R = 17.95 min

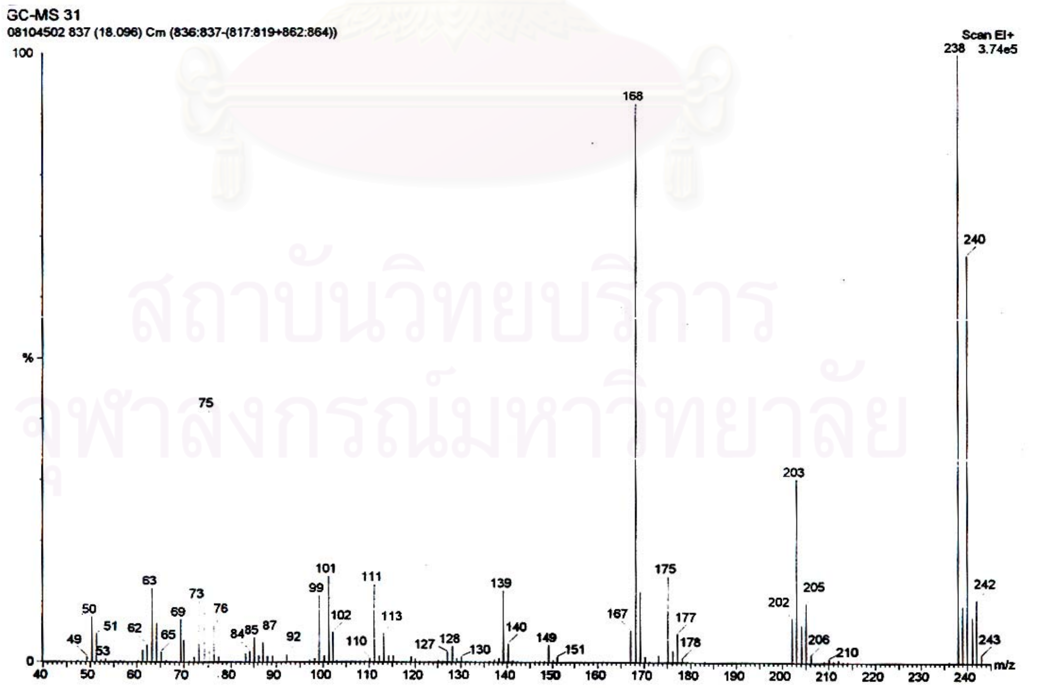

Figure A44 The mass spectrum of mixture 5D at t_R = 18.10 min

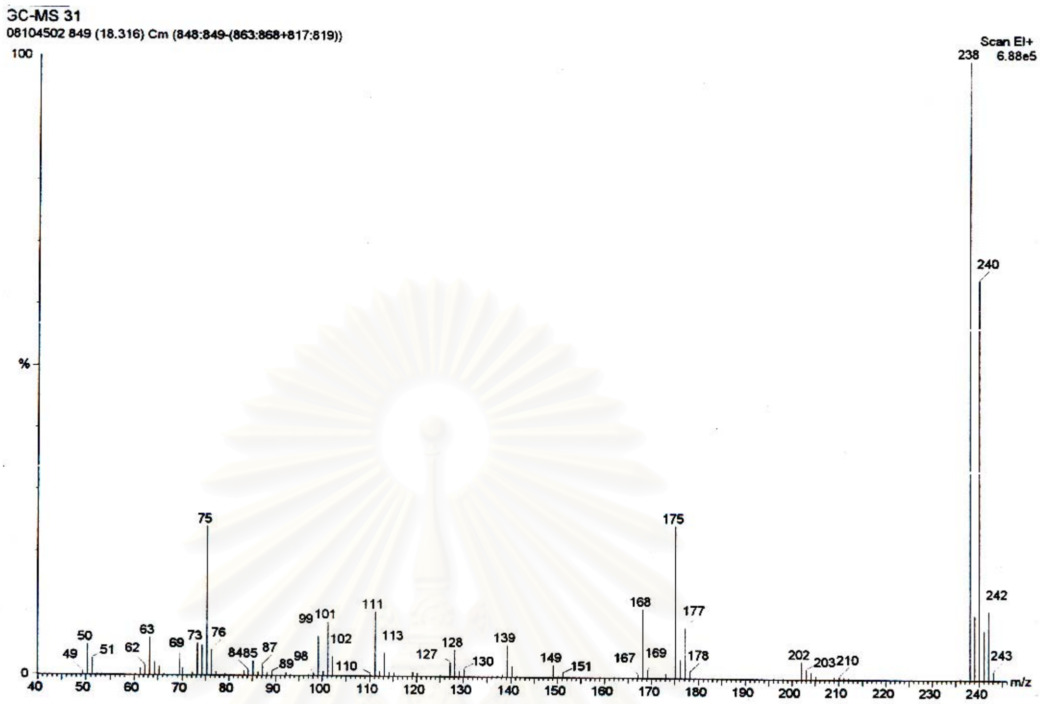

Figure A45 The mass spectrum of mixture 5D at t_R = 18.32 min

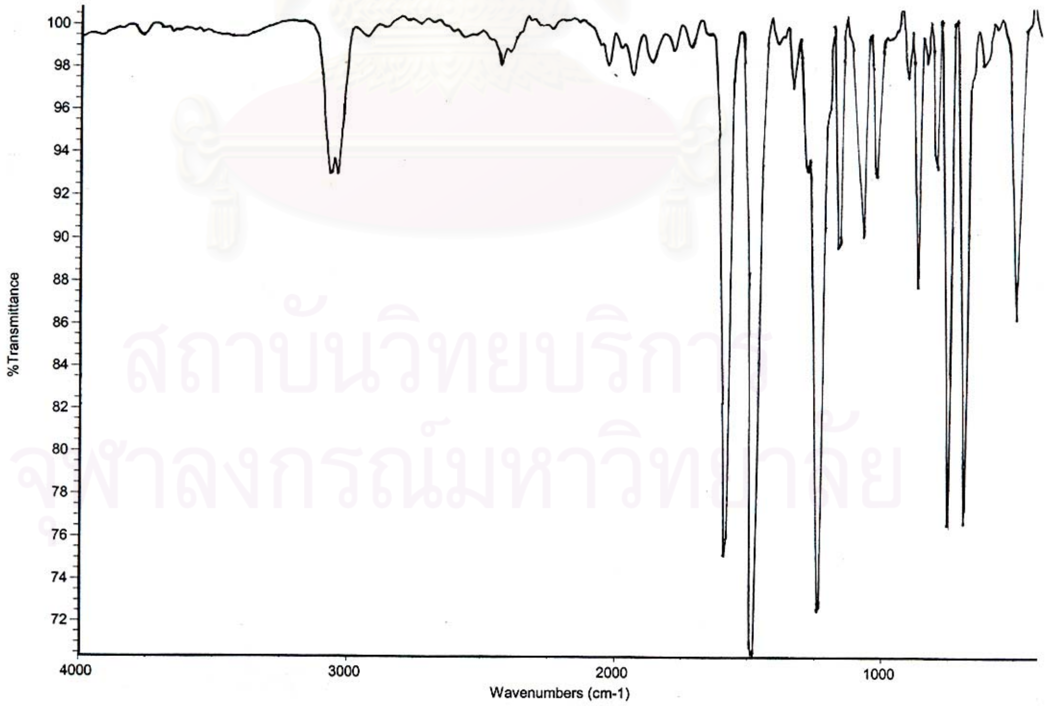

Figure A46 The FTIR spectrum of mixture 6D

(haxane; using mole ratio of substrate and sodium bromide: 1/1)

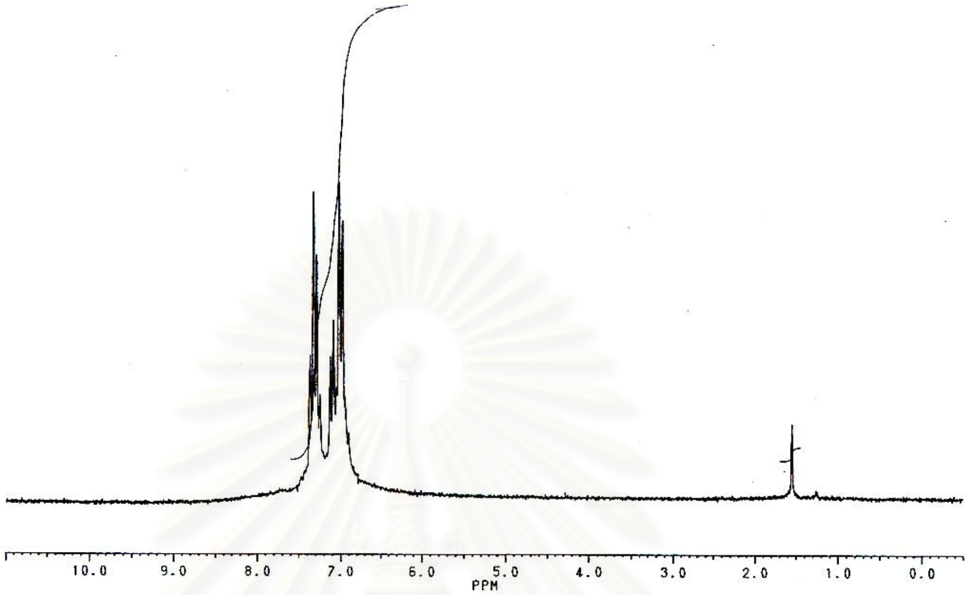

Figure A47 The ^{1}H-NMR spectrum of mixture 6D

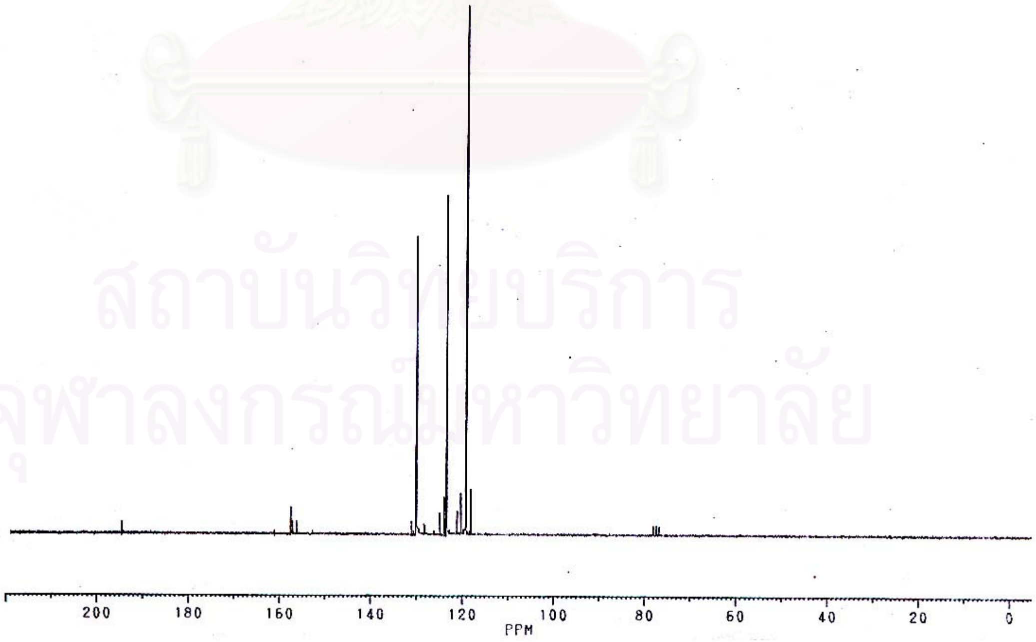

Figure A48 The ^{13}C-NMR spectrum of mixture 6D

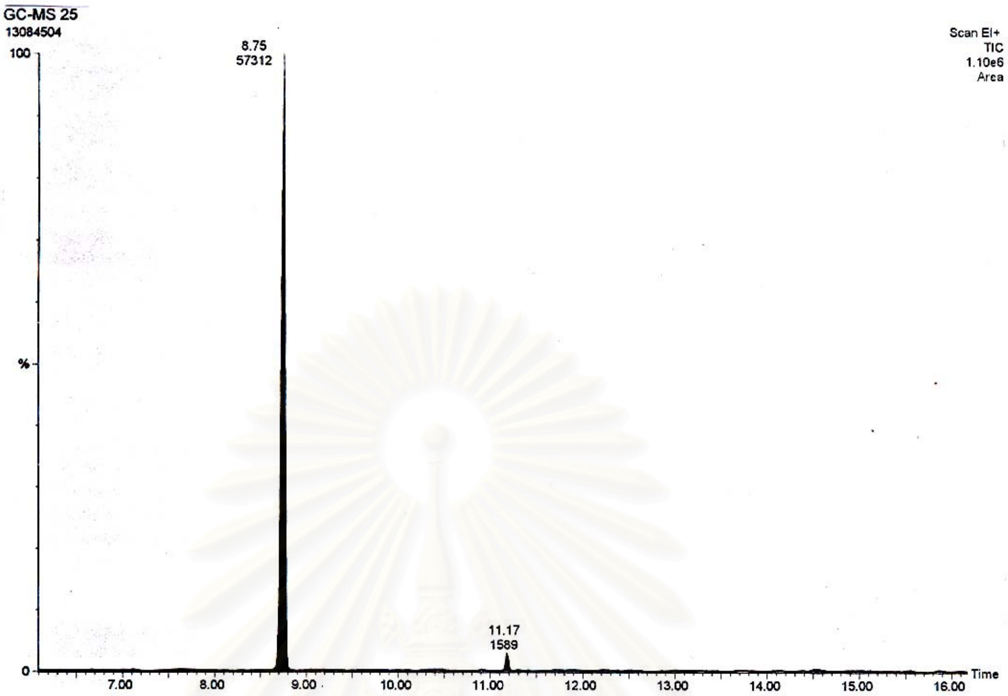

Figure A49 The gas chromatogram of mixture 6D

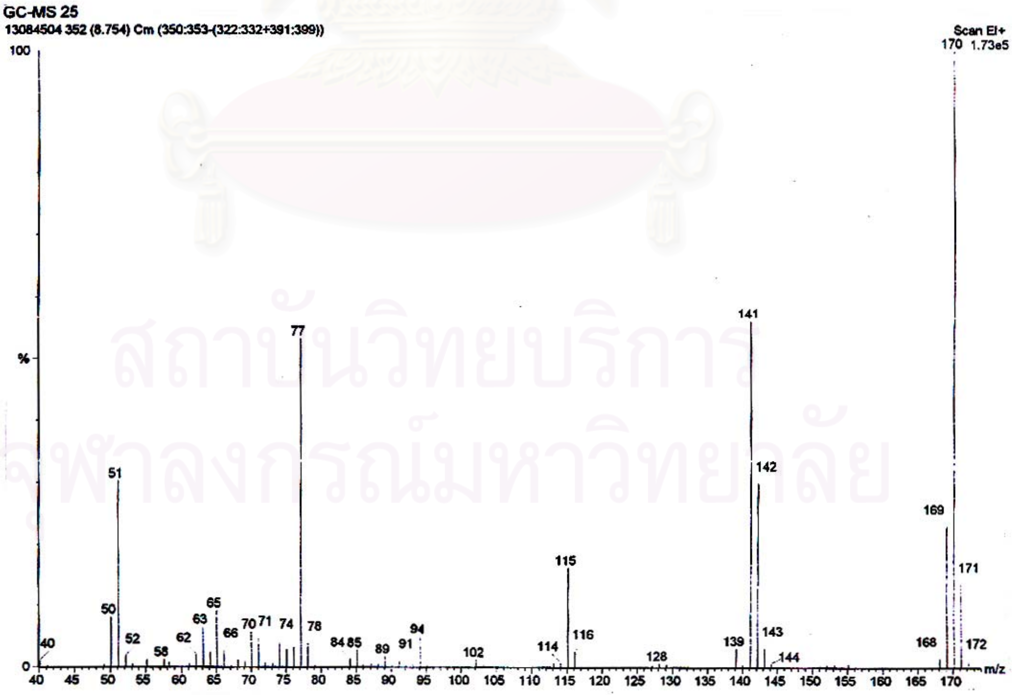

Figure A50 The mass spectrum of mixture 6D at t_R = 8.75 min

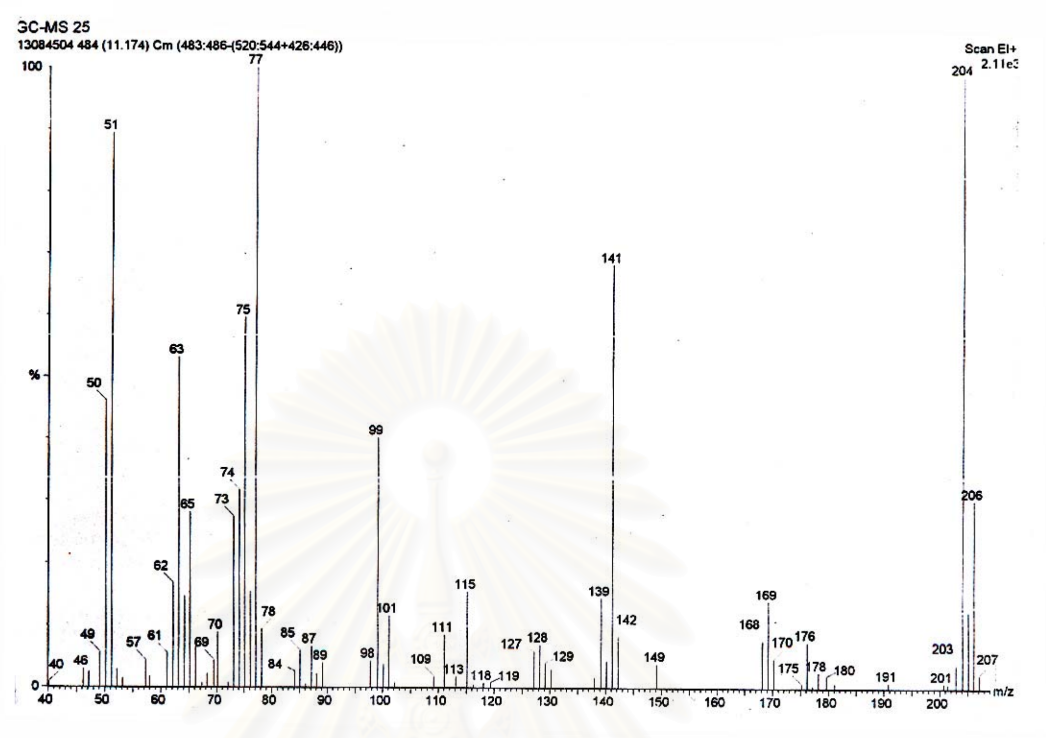

Figure A51 The mass spectrum of mixture 6D at t_R = 11.17 min

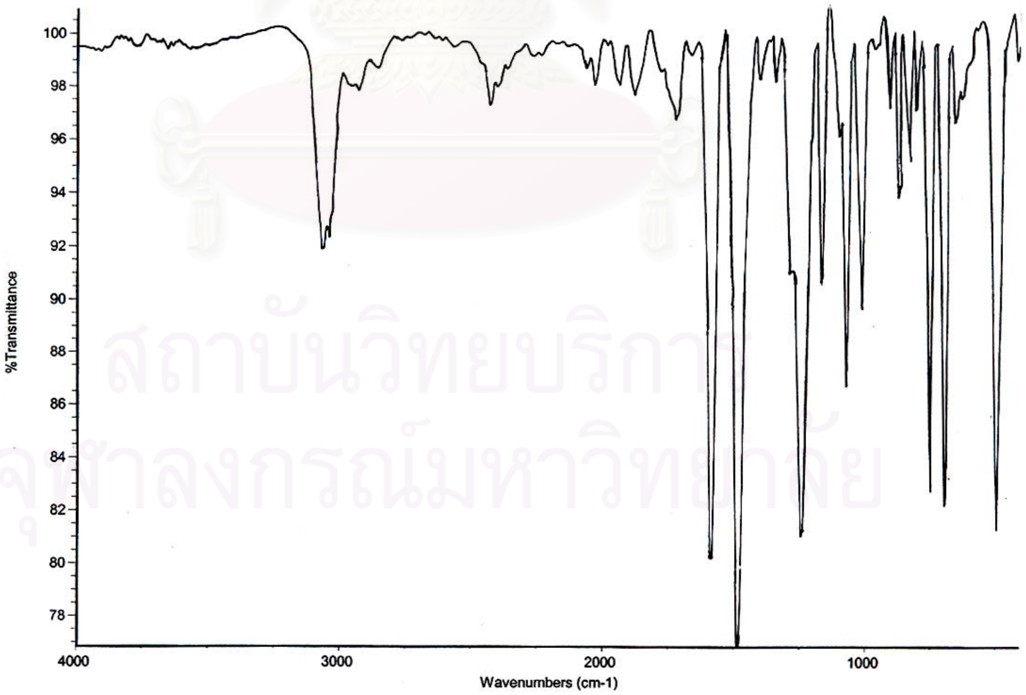

Figure A52 The FTIR spectrum of mixture 7D

(haxane; using mole ratio of substrate and sodium bromide: 1/10)

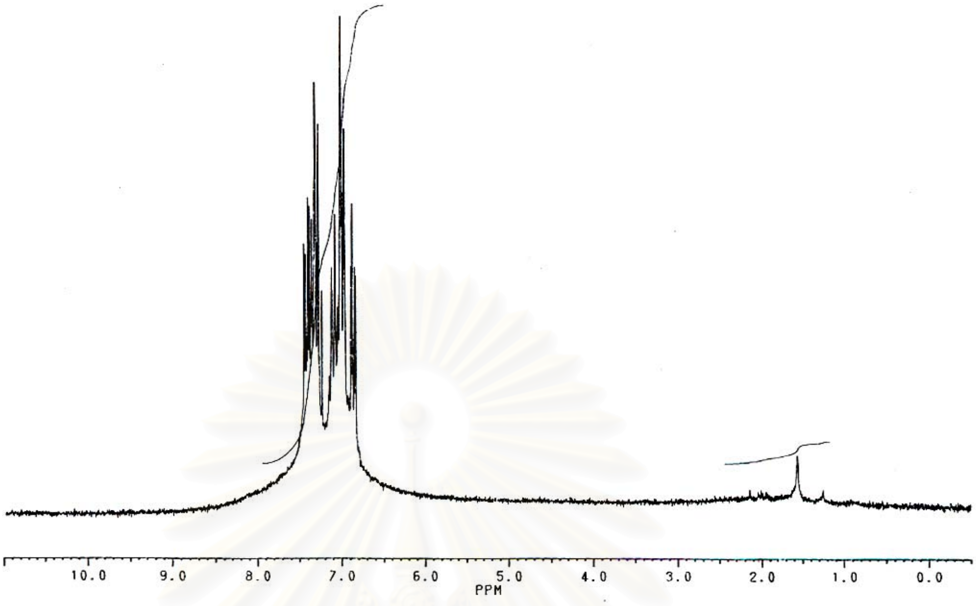

Figure A53 The ^{1}H-NMR spectrum of mixture 7D

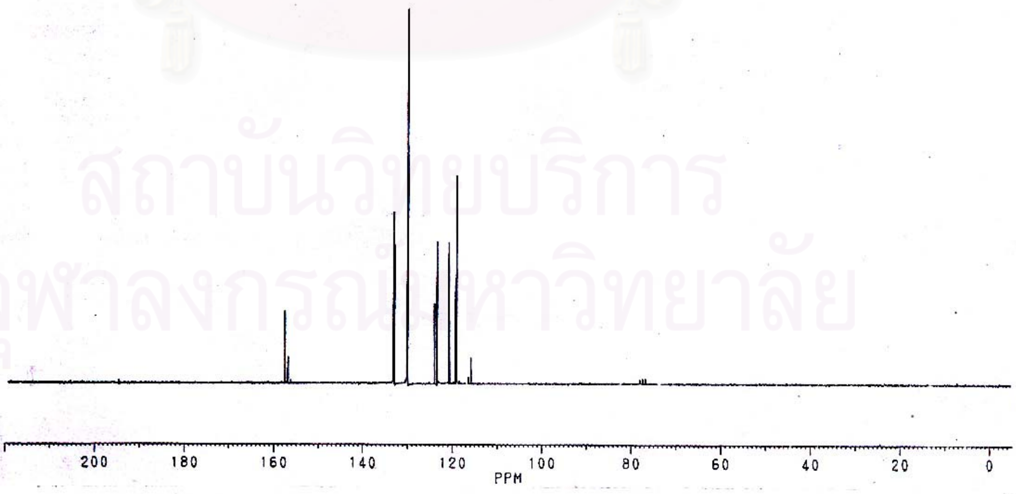

Figure A54 The ^{13}C-NMR spectrum of mixture 7D

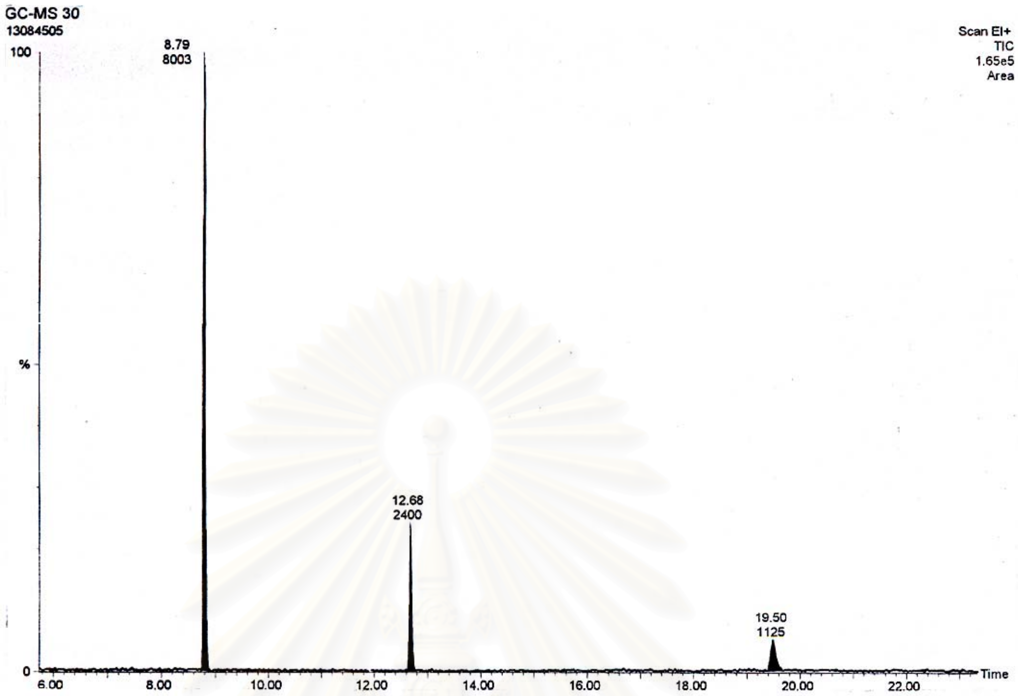

Figure A55 The gas chromatogram of mixture 7D

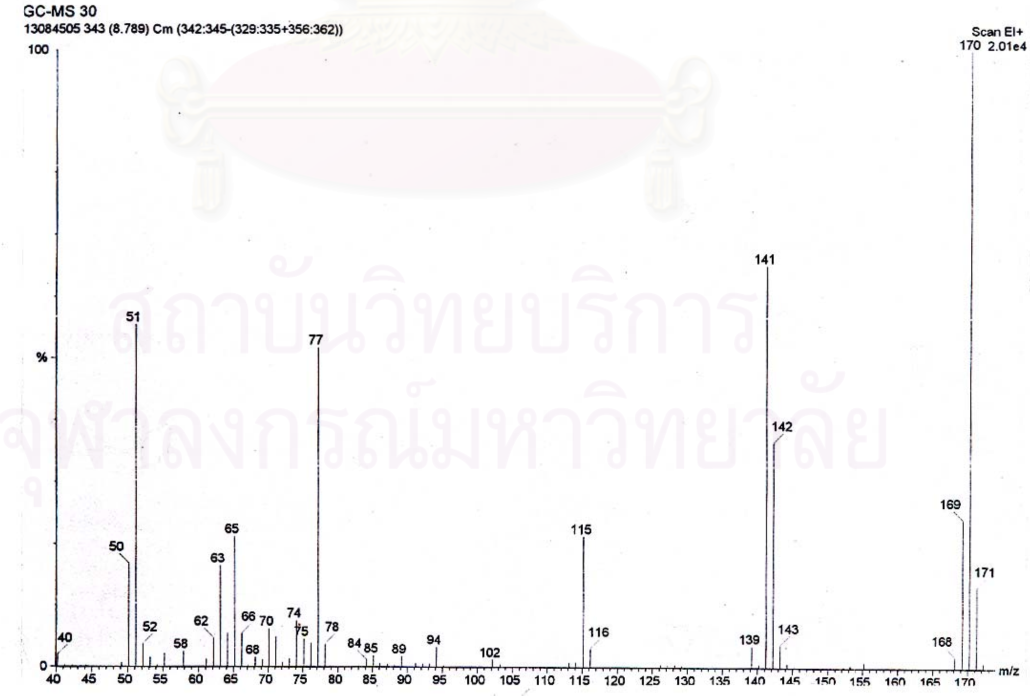

Figure A56 The mass spectrum of mixture 7D at t_R = 8.79 min

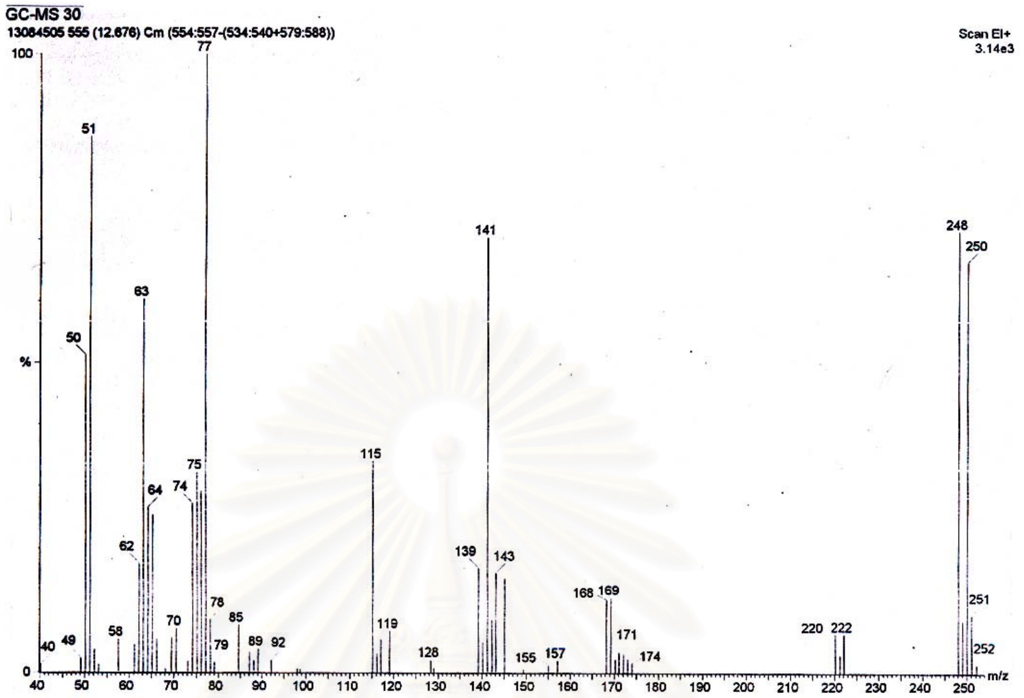

Figure A57 The mass spectrum of mixture 7D at t_R = 12.68 min

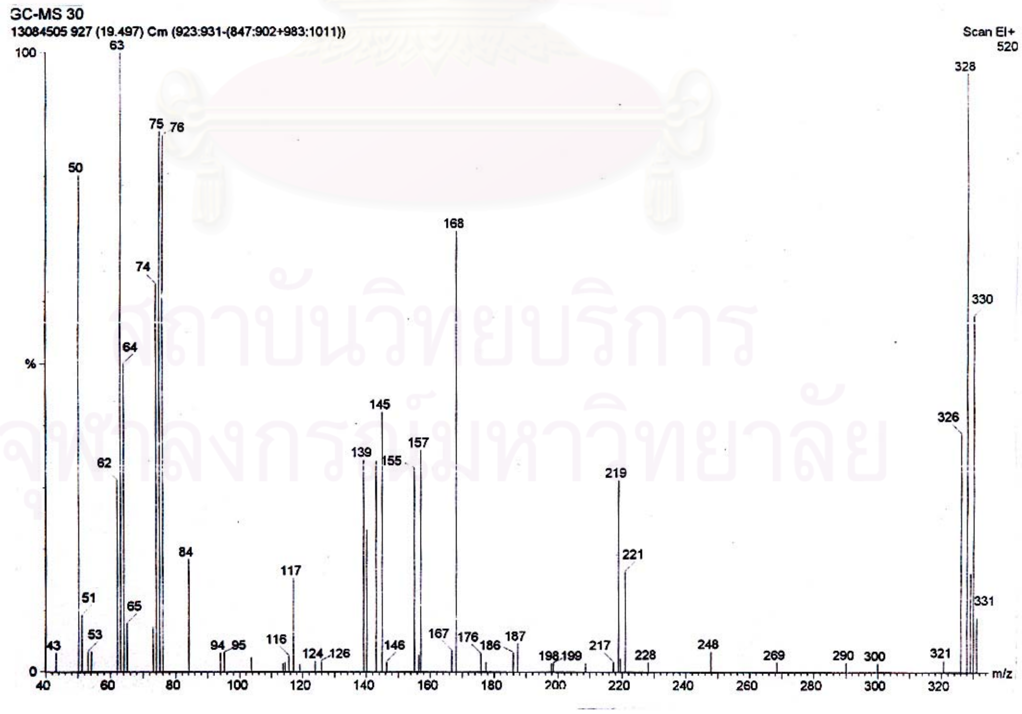

Figure A58 The mass spectrum of mixture 7D at t_R = 19.50 min

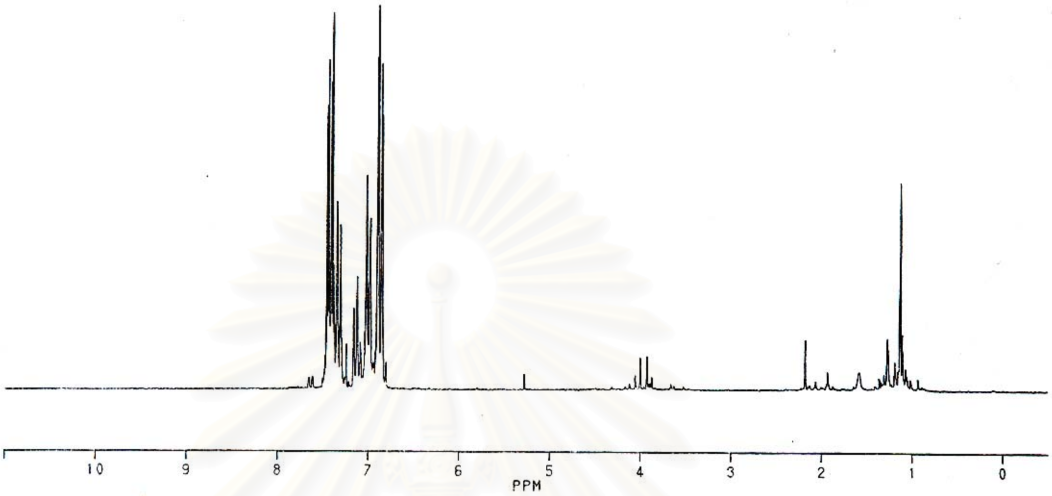

Figure A59 The ^{1}H-NMR spectrum of mixture 8D

(using mole ratio of substrate and sodium bromide: 1/2)

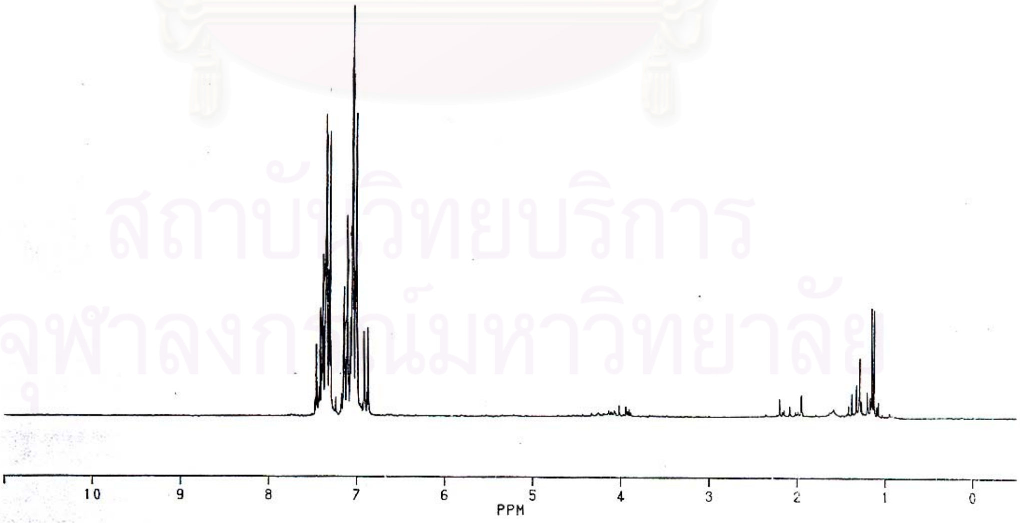

Figure A60 The ^{1}H-NMR spectrum of mixture 9D

(using mole ratio of substrate and sodium bromide: 1/4)

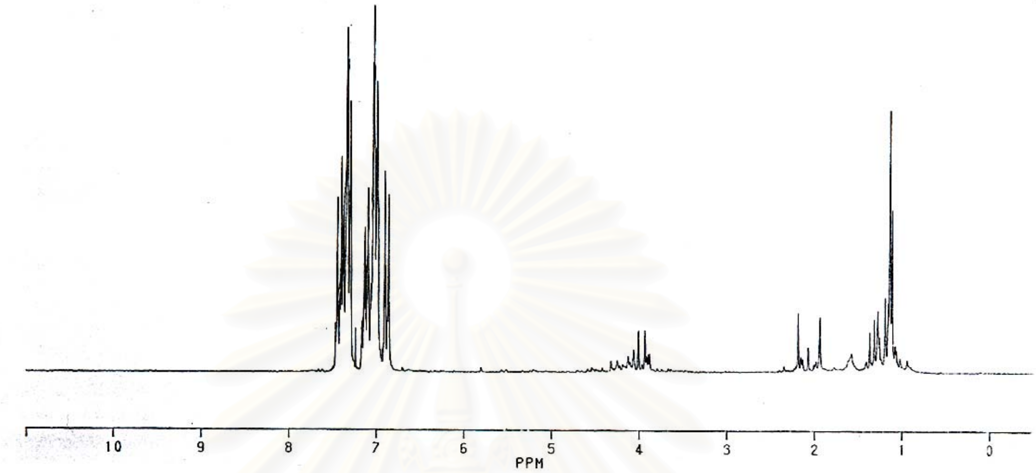

Figure A61 The ^{1}H-NMR spectrum of mixture 10D

(using mole ratio of substrate and sodium bromide: 1/6)

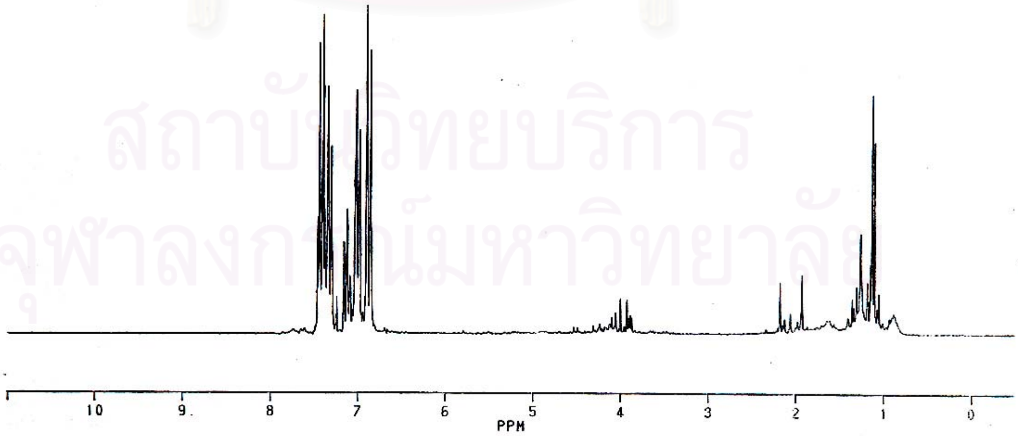

Figure A62 The ^{1}H-NMR spectrum of mixture 11D

(using mole ratio of substrate and sodium bromide: 1/8)

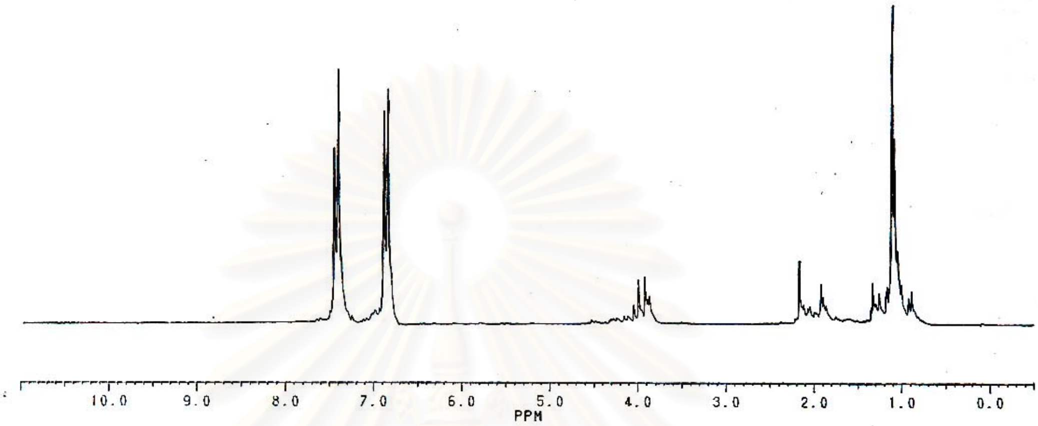

Figure A63 The ^{1}H-NMR spectrum of mixture 12D

(using mole ratio of substrate and sodium bromide: 1/12)

APPENDIX B

SPECTRA OF PHENOL DERIVATIVES

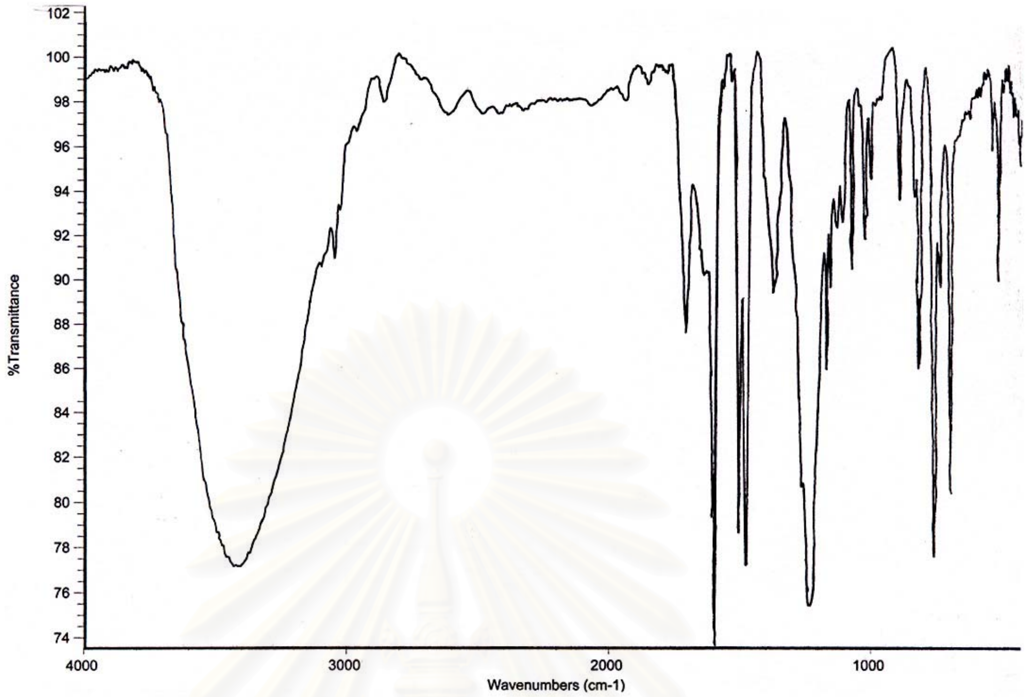

Figure B1 The FTIR spectrum of phenol

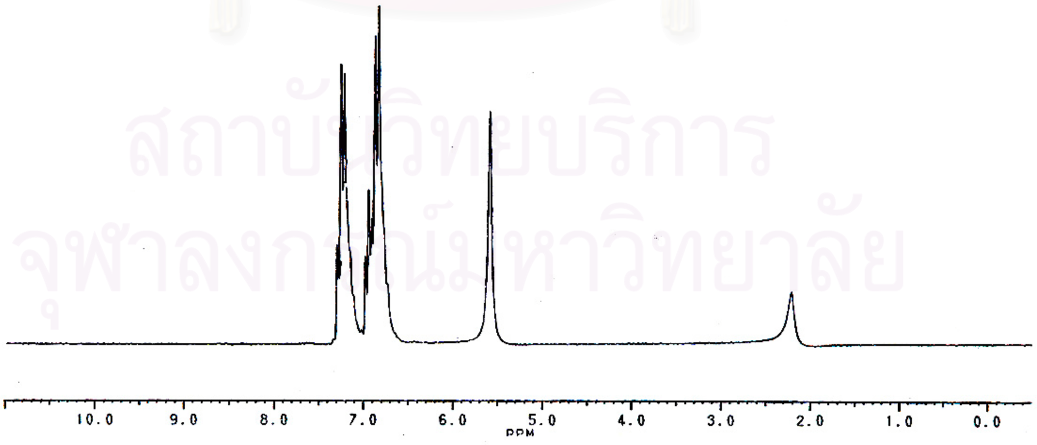

Figure B2 The ^{1}H-NMR spectrum of phenol

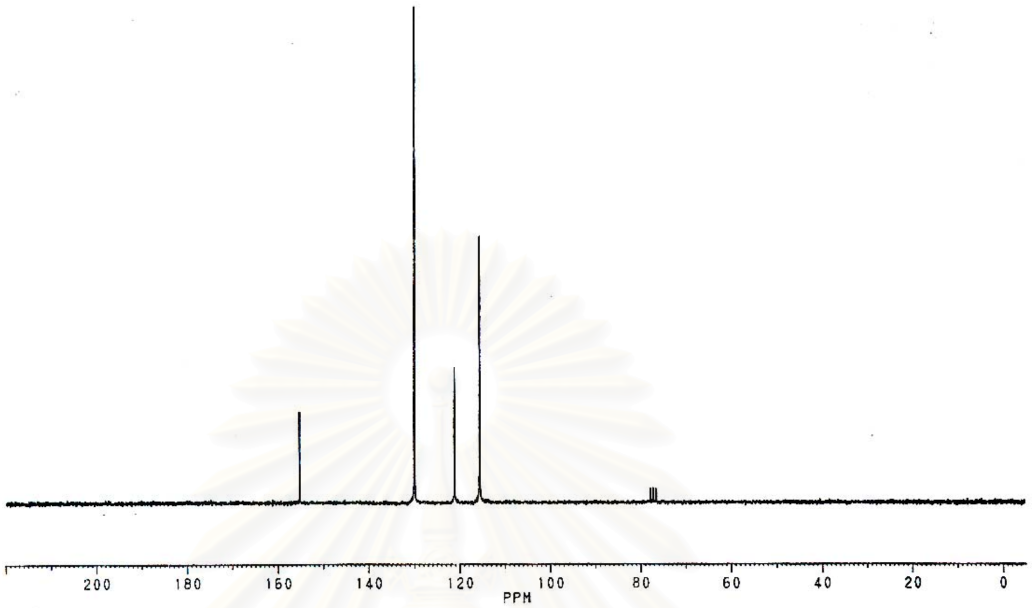

Figure B3 The ^{13}C-NMR spectrum of phenol

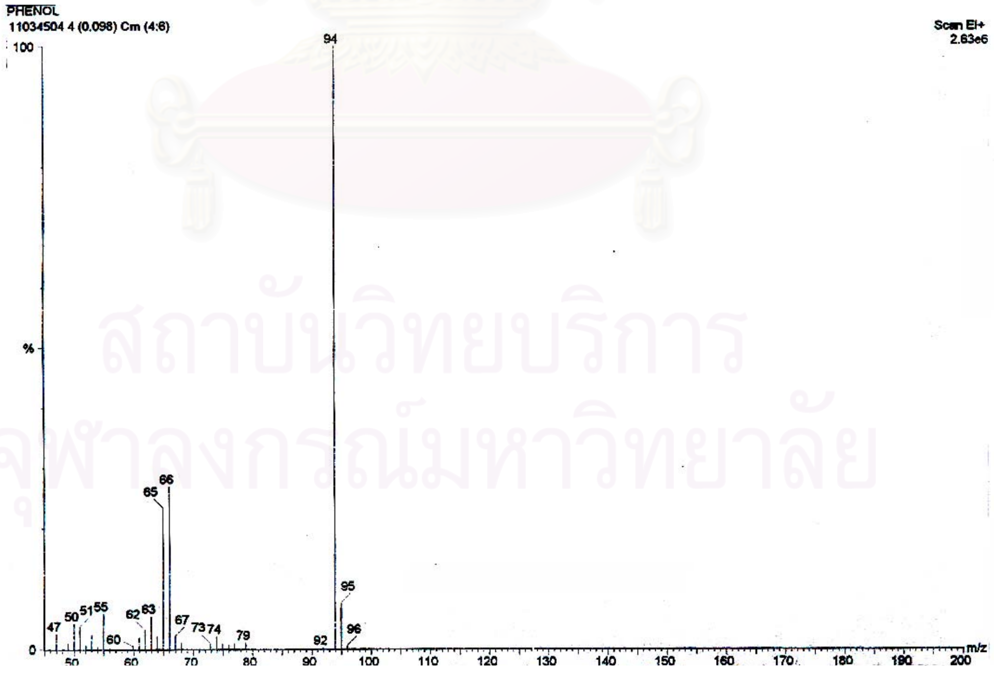

Figure B4 The mass spectrum of phenol

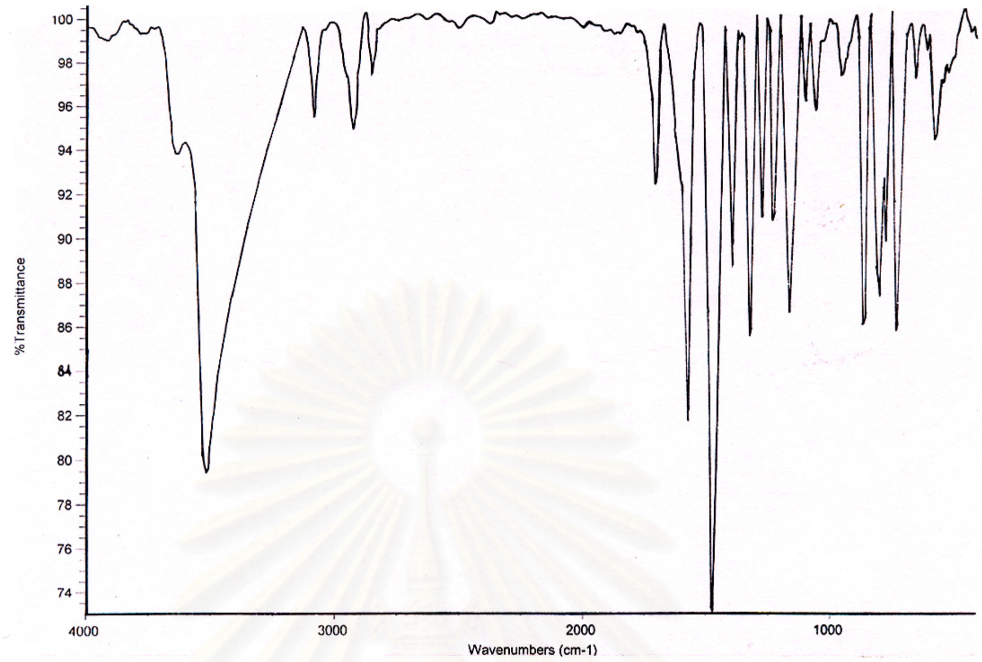

Figure B5 The FTIR spectrum of mixture 1P

(using mole ratio of substrate and sodium hypochlorite: 1/2)

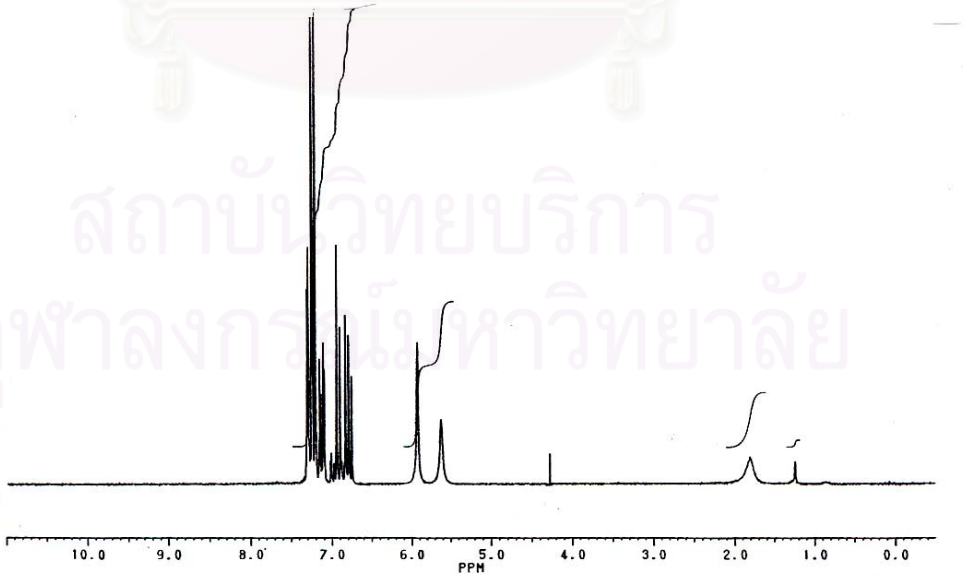

Figure B6 The ^{1}H-NMR spectrum of mixture 1P

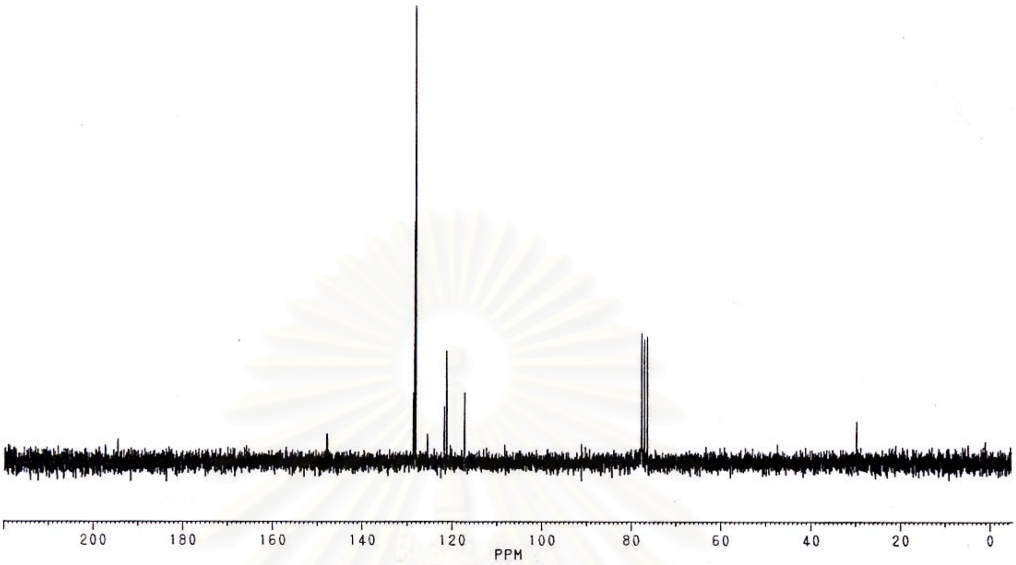

Figure B7 The ^{13}C-NMR spectrum of mixture 1P

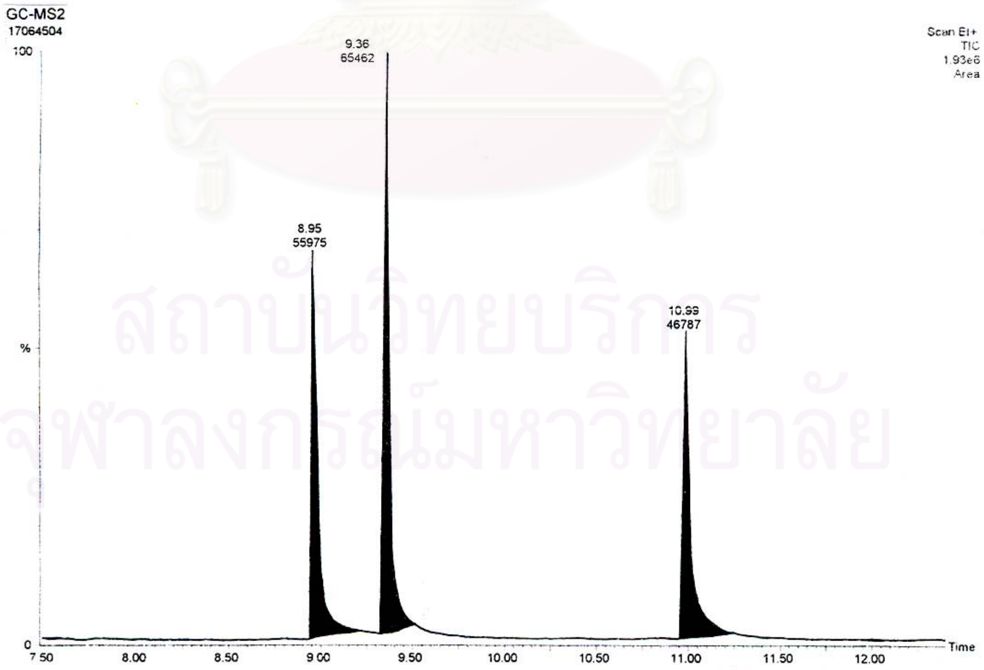

Figure B8 The gas chromatogram of mixture 1P

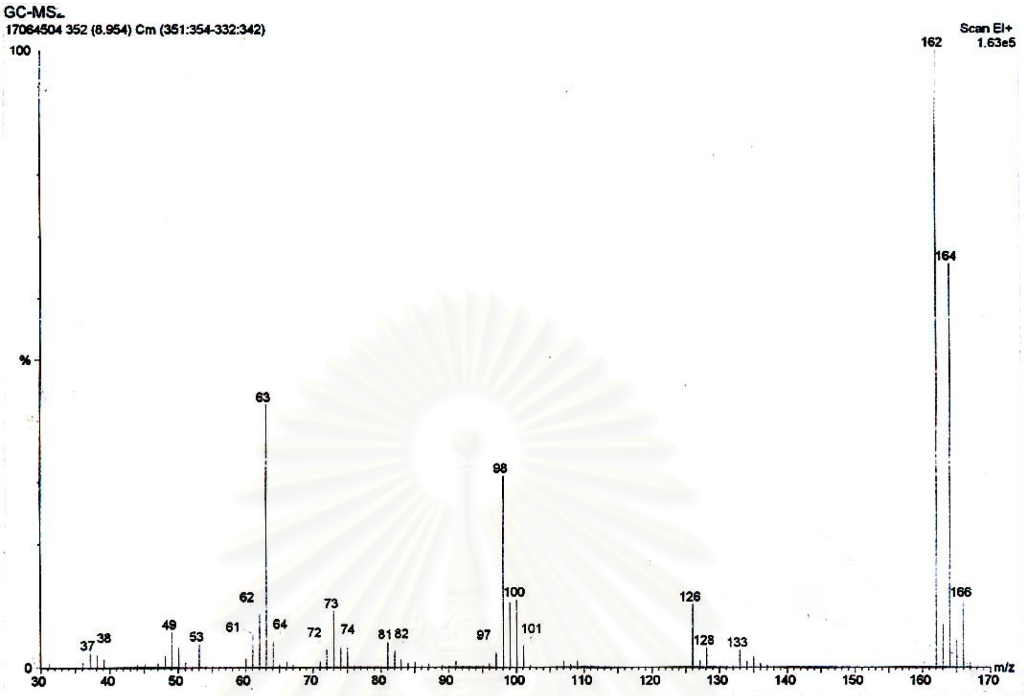

Figure B9 The mass spectrum of mixture 1P at t_R = 8.95 min

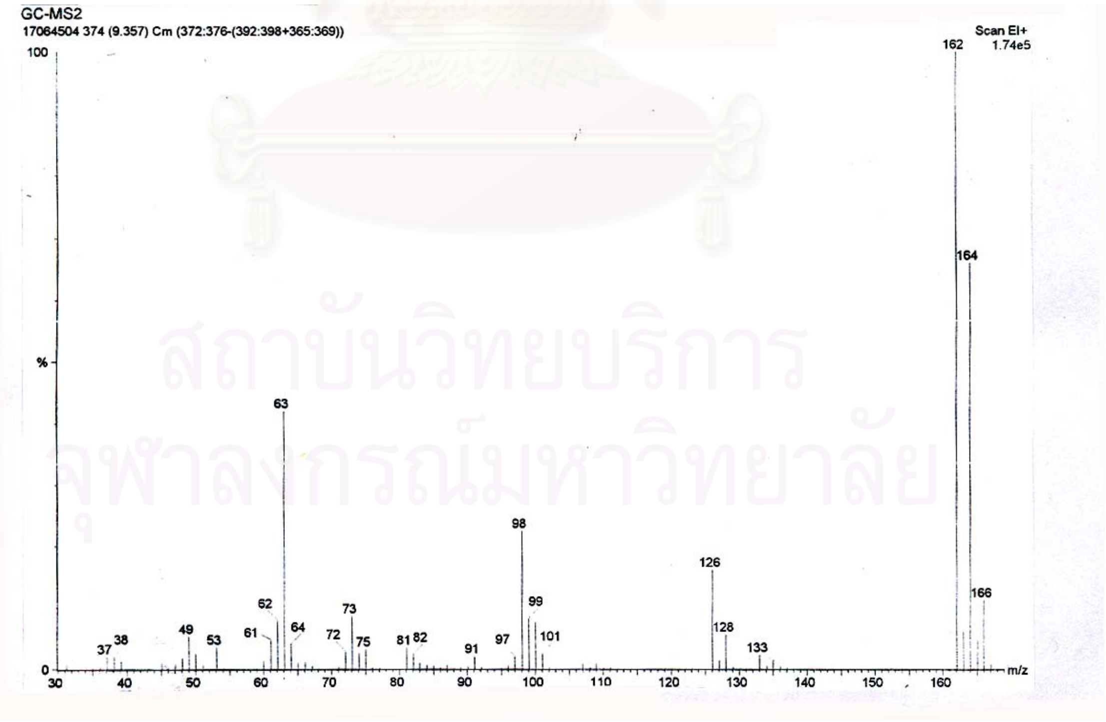

Figure B10 The mass spectrum of mixture 1P at t_R = 9.36 min

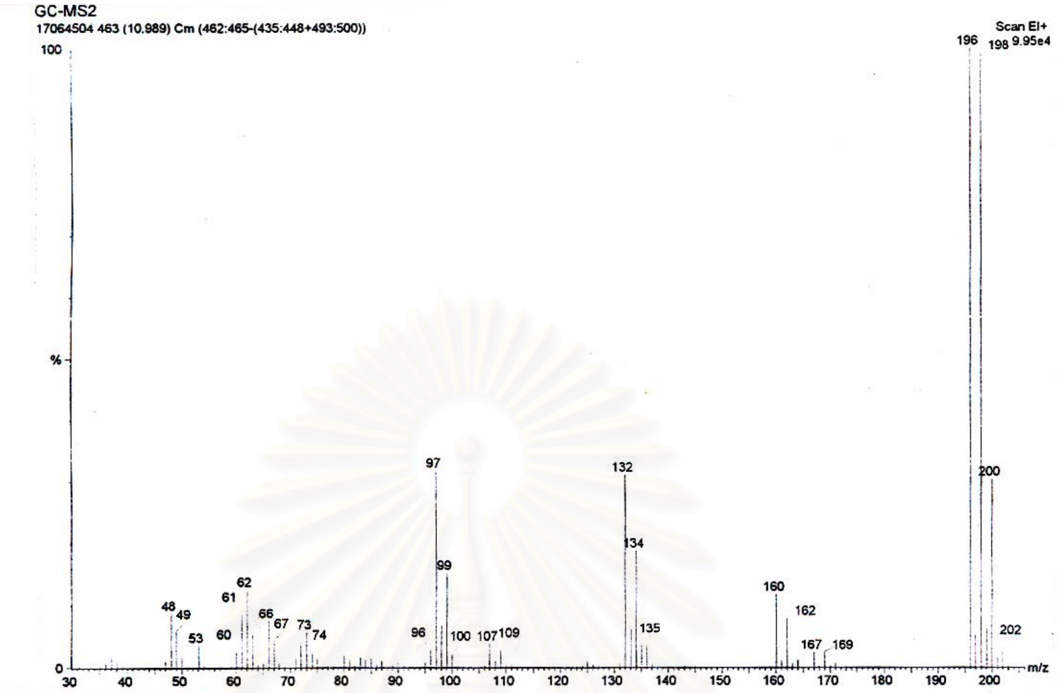

Figure B11 The mass spectrum of mixture 1P at t_R = 10.99 min

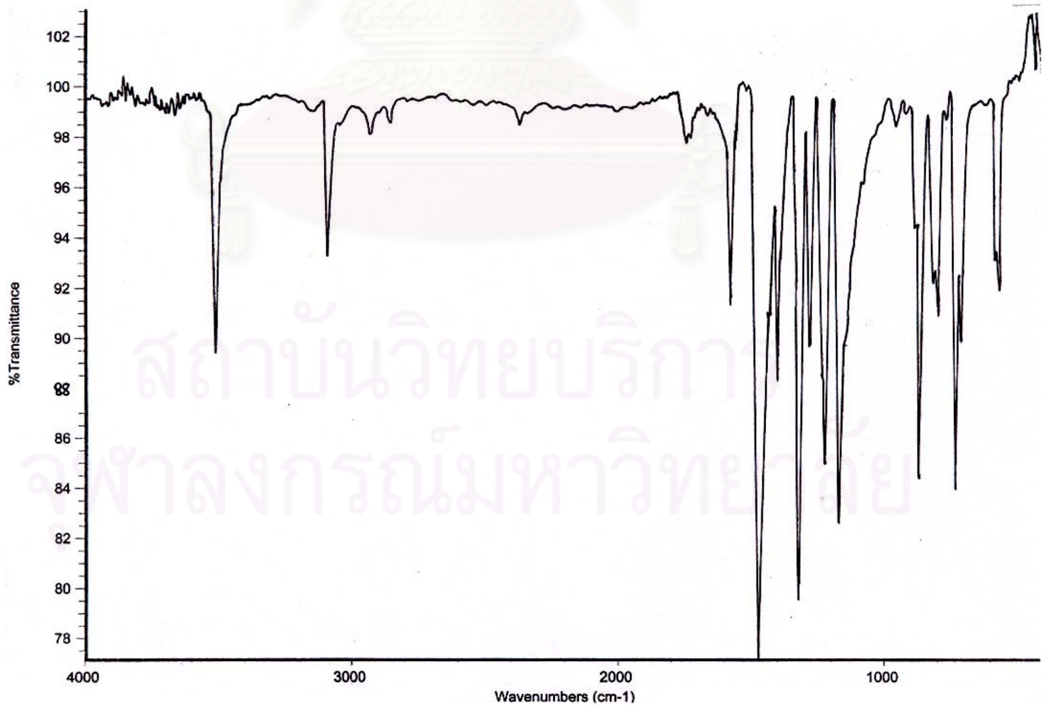

Figure B12 The FTIR spectrum of mixture 2P

(using mole ratio of substrate and sodium hypochlorite: 1/8)

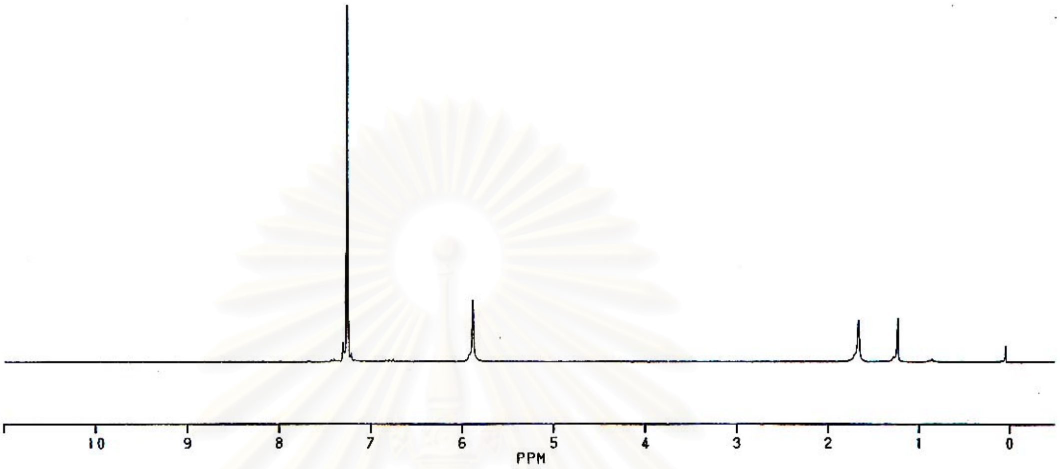

Figure B13 The ^{1}H-NMR spectrum of mixture 2P

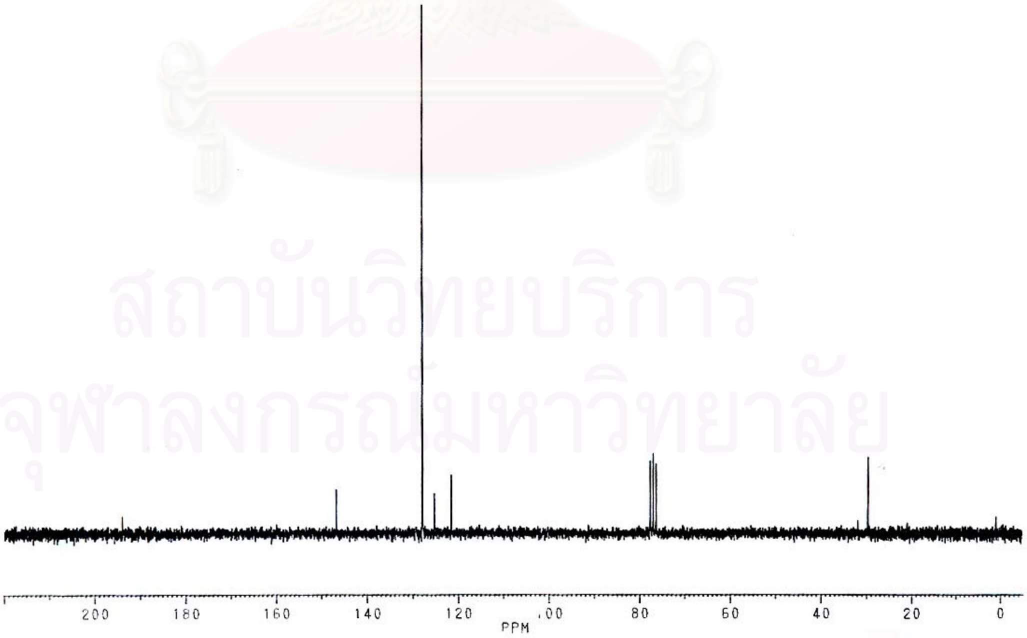

Figure B14 The ^{13}C-NMR spectrum of mixture 2P

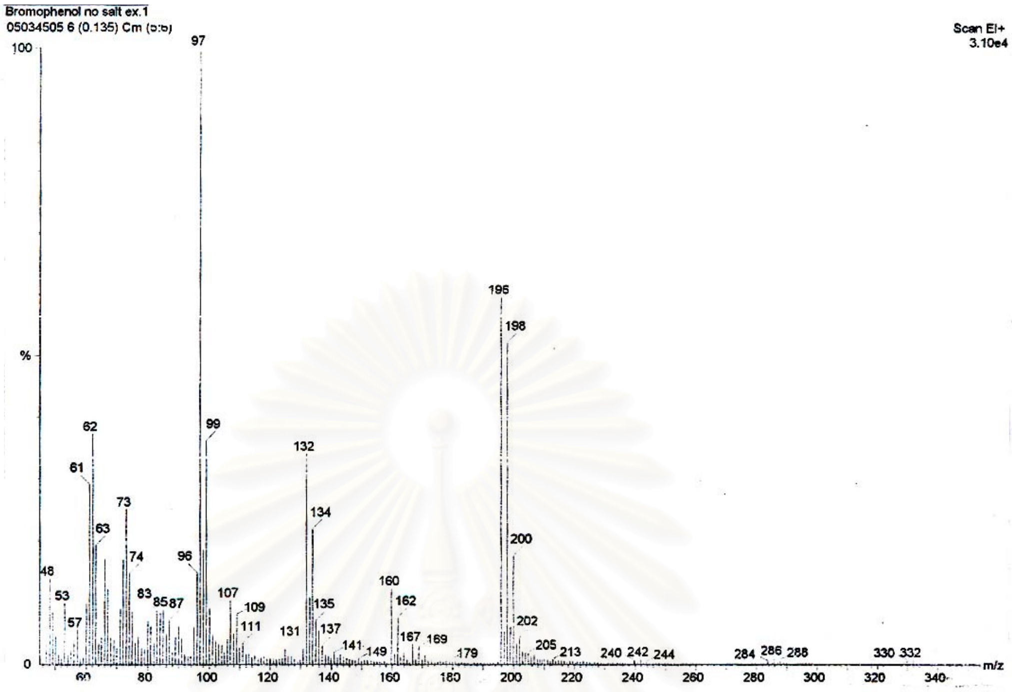

Figure B15 The mass spectrum of mixture 2P

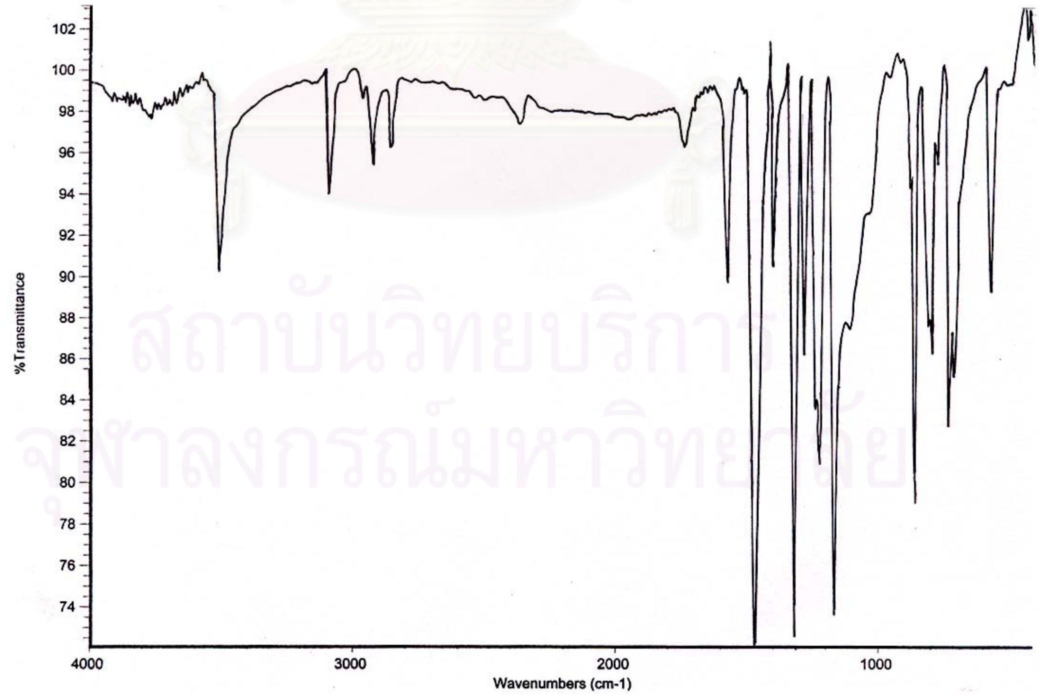

Figure B16 The FTIR spectrum of mixture 3P

(using mole ratio of substrate and sodium bromide: 1/1)

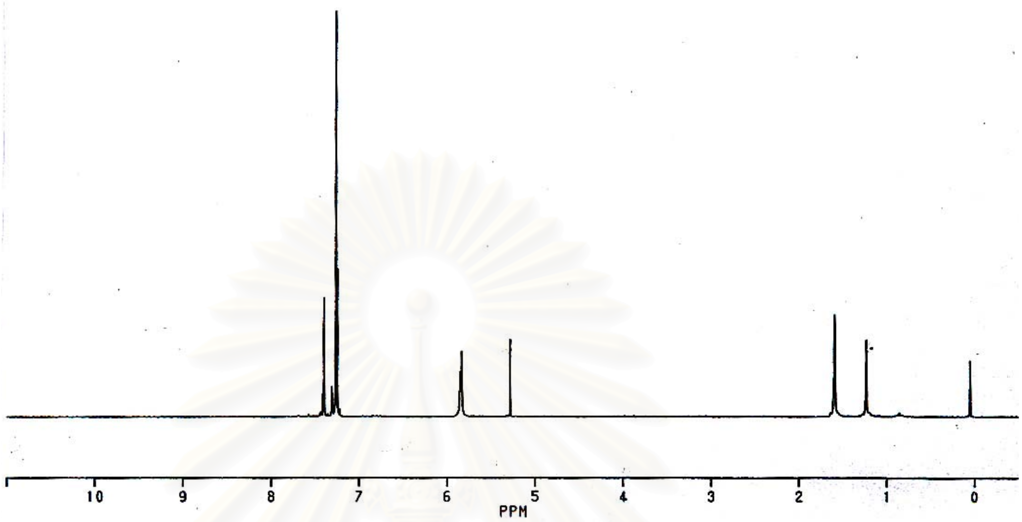

Figure B17 The ^{1}H-NMR spectrum of mixture 3P

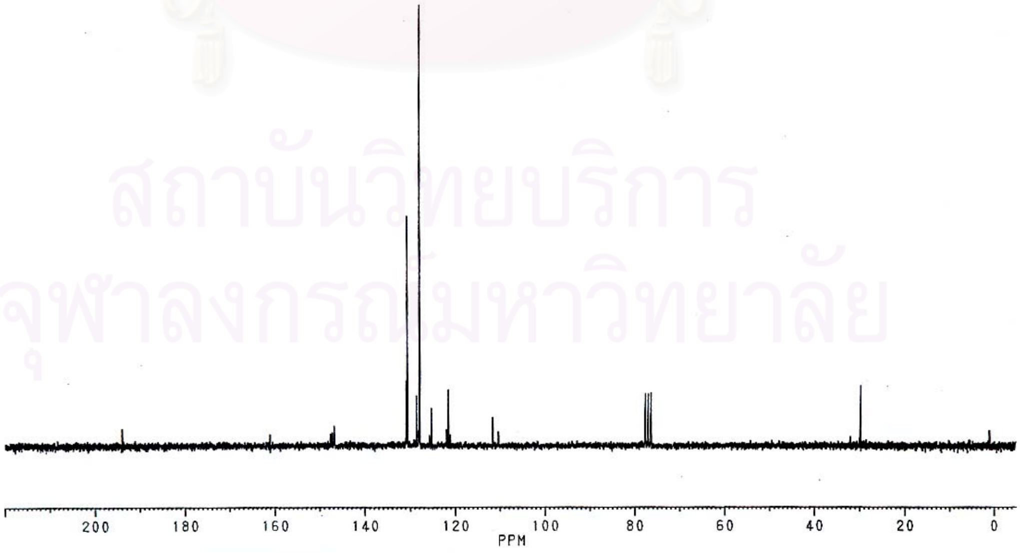

Figure B18 The ^{13}C-NMR spectrum of mixture 3P

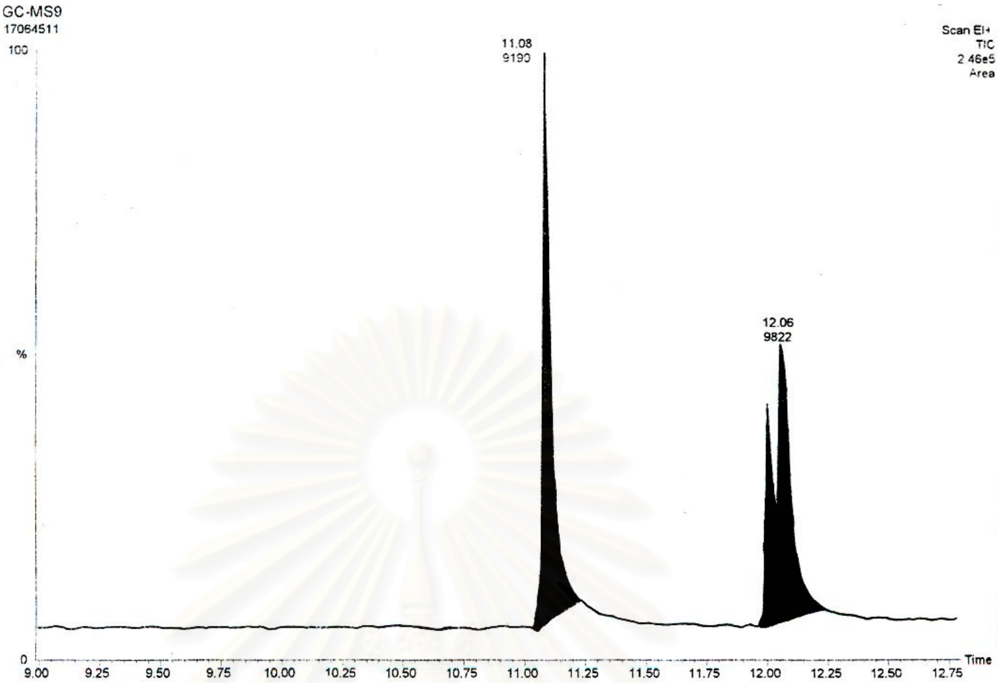

Figure B19 The gas chromatogram of mixture 3P

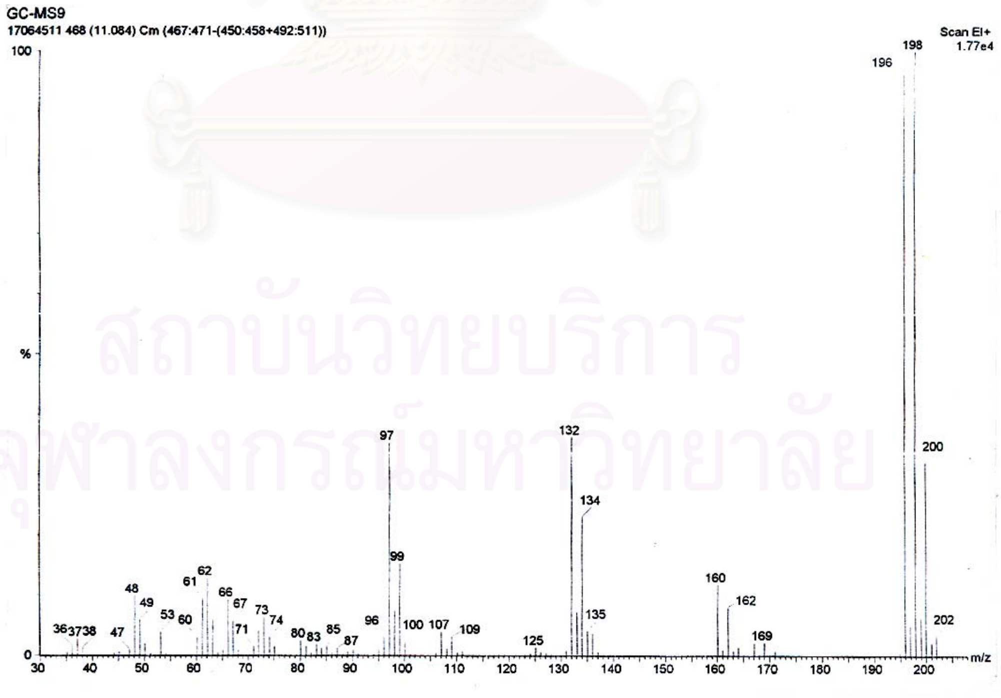

Figure B20 The mass spectrum of mixture 3P at t_R = 11.08 min

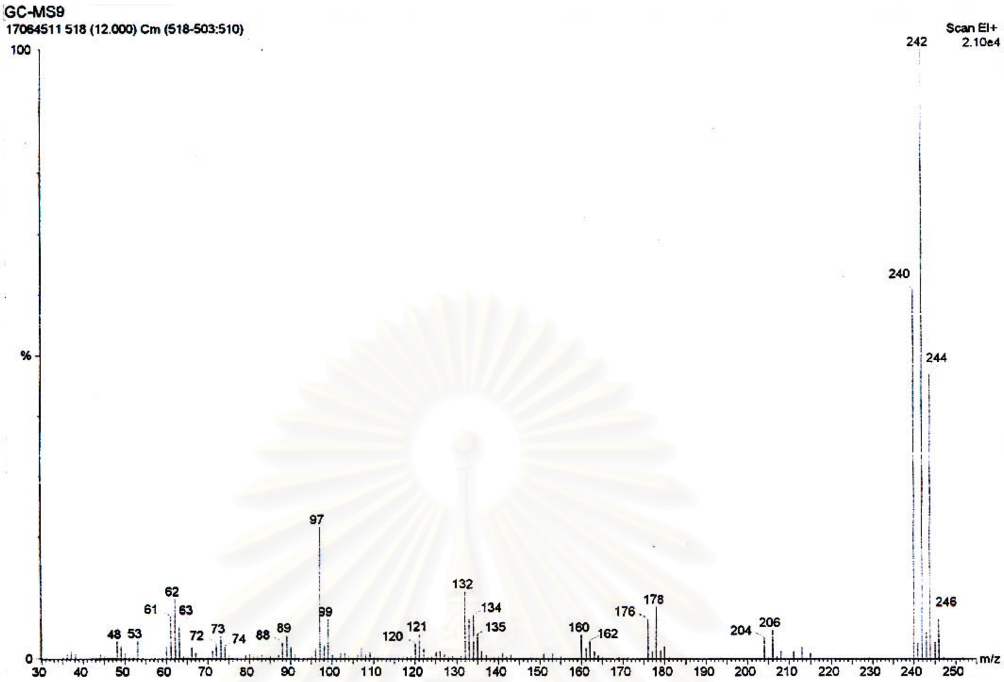

Figure B21 The mass spectrum of mixture 3P at t_R = 12.00 min

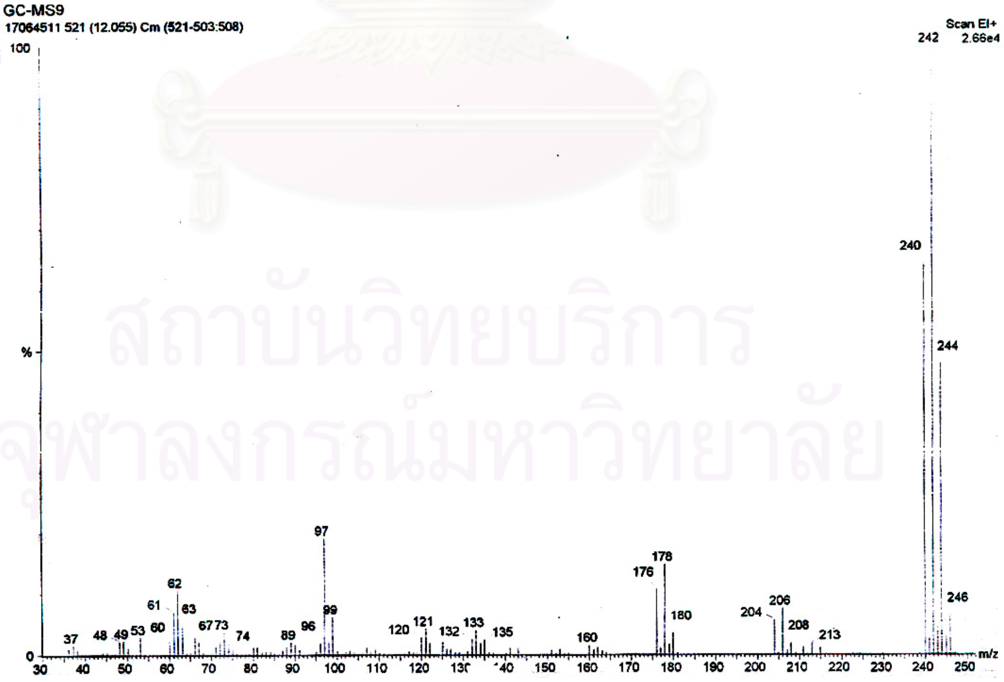

Figure B22 The mass spectrum of mixture 3P at t_R = 12.06 min

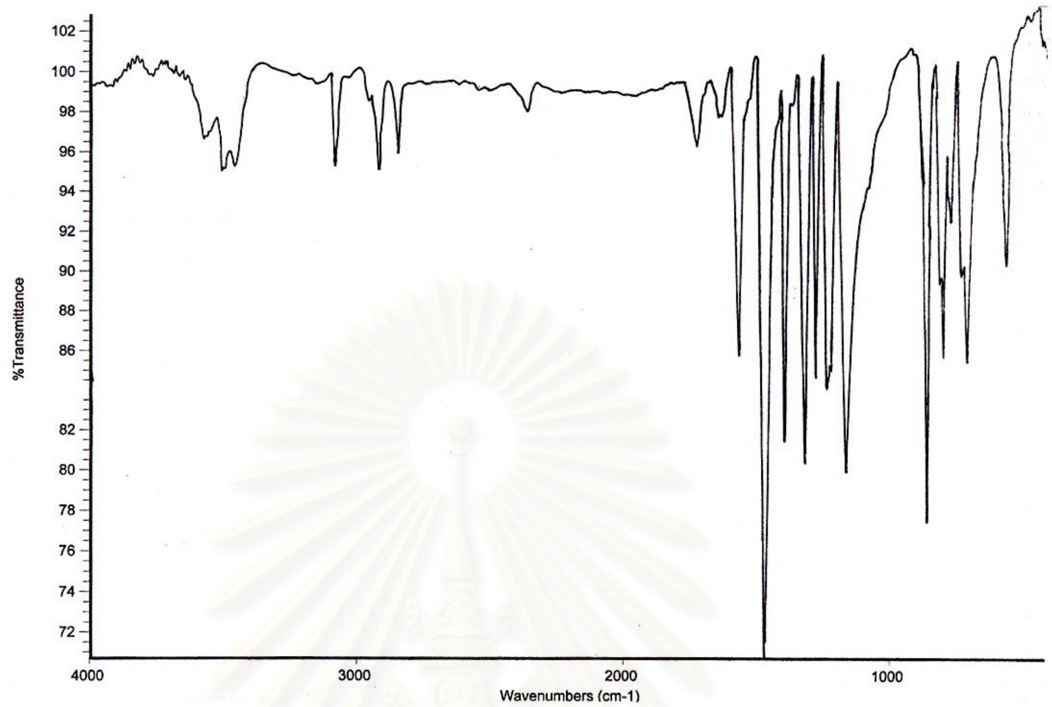

Figure B23 The FTIR spectrum of mixture 4P

(using mole ratio of substrate and sodium bromide: 1/5)

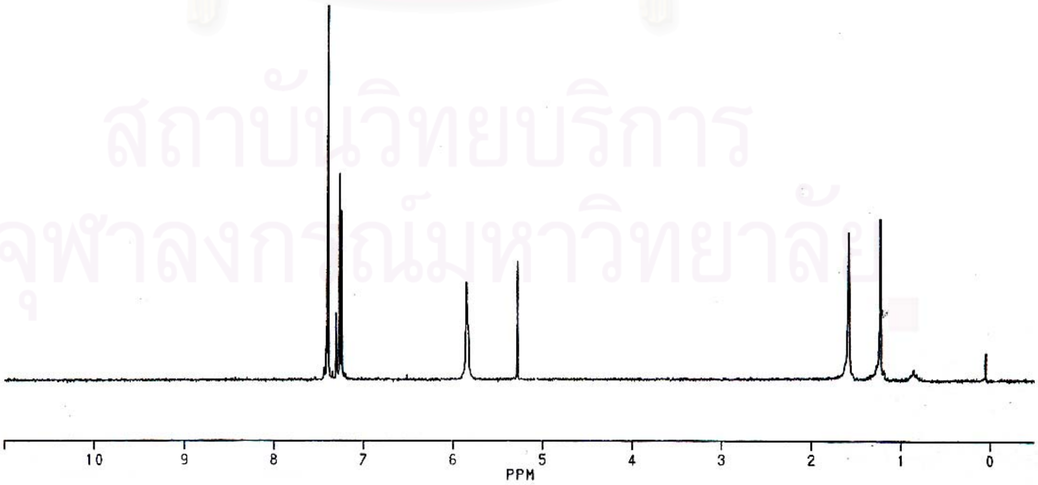

Figure B24 The ^{1}H-NMR spectrum of mixture 4P

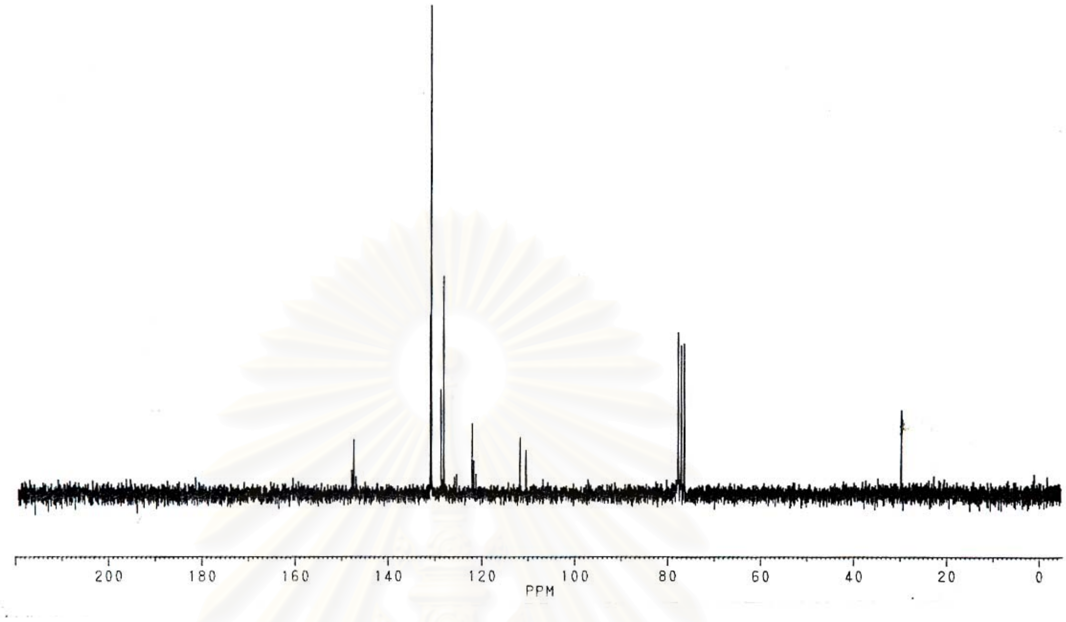

Figure B25 The ^{13}C-NMR spectrum of mixture 4P

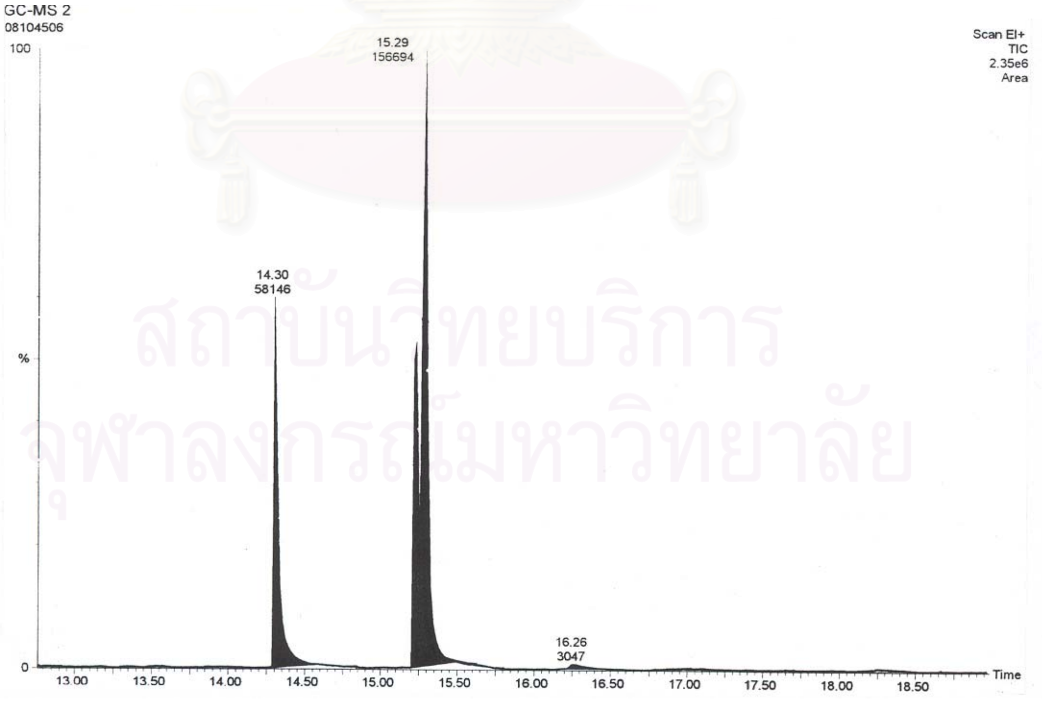

Figure B26 The gas chromatogram of mixture 4P

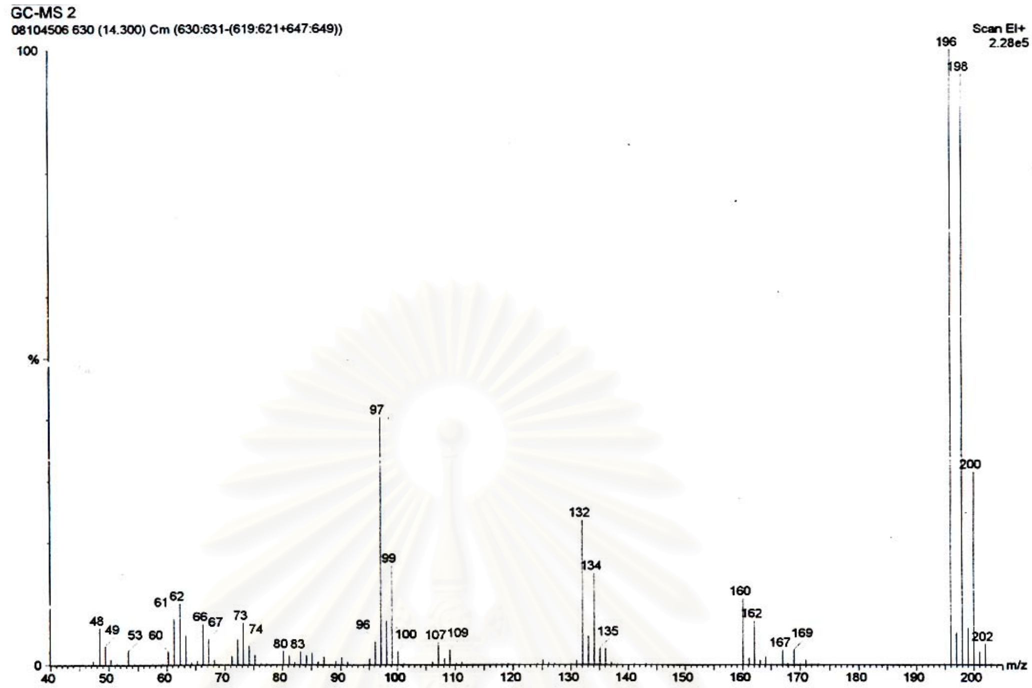

Figure B27 The mass spectrum of mixture 4P at t_R = 14.30 min

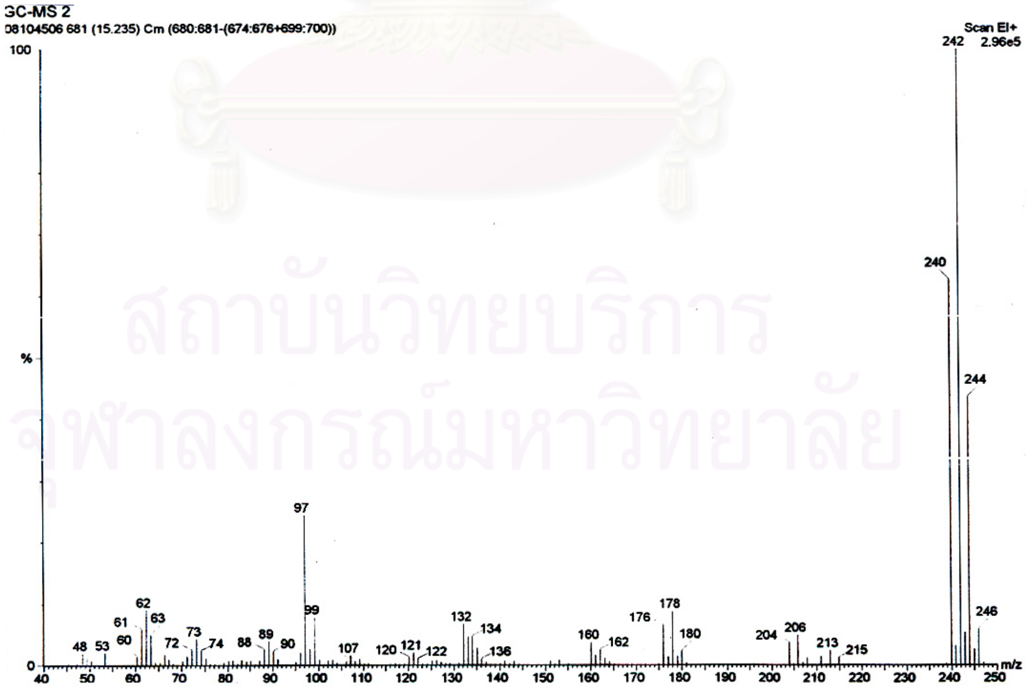

Figure B28 The mass spectrum of mixture 4P at t_R = 15.24 min

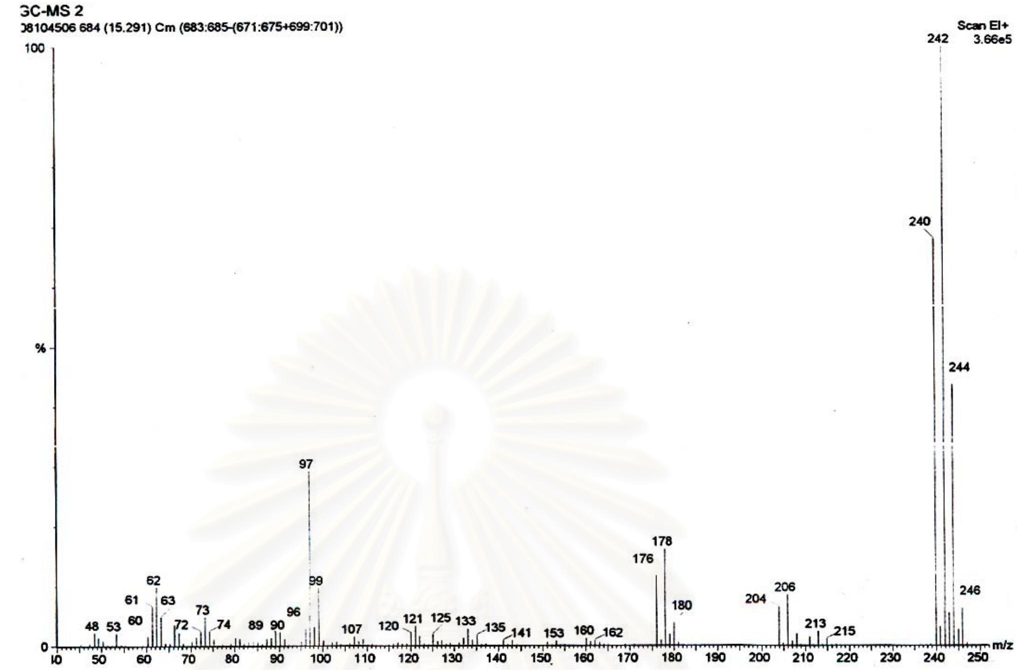

Figure B29 The mass spectrum of mixture 4P at t_R = 15.30 min

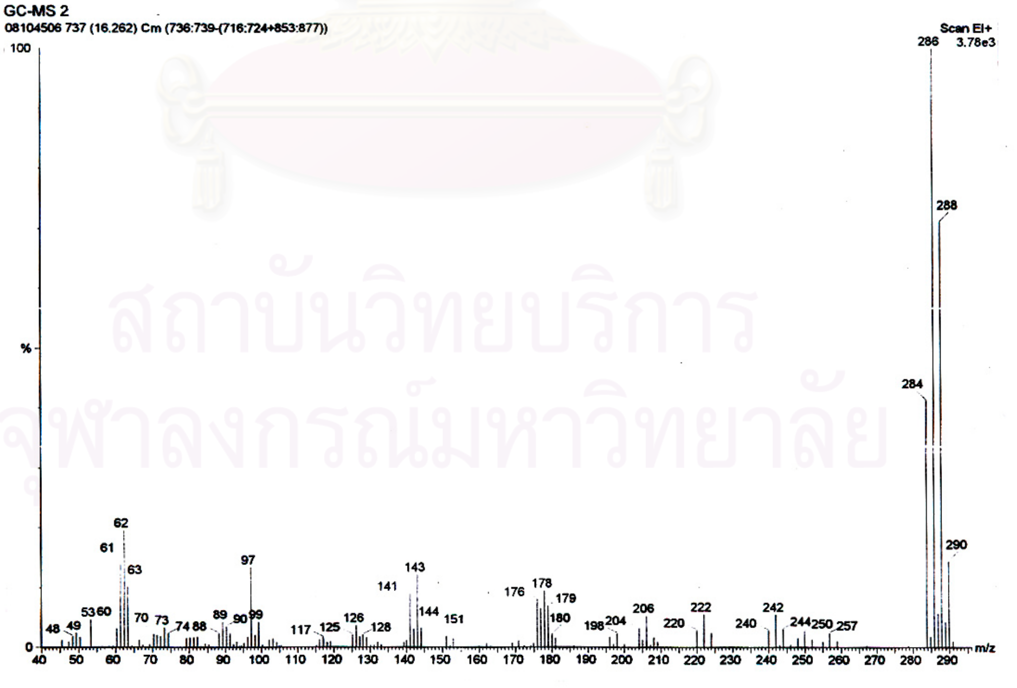

Figure B30 The mass spectrum of mixture 4P at t_R = 16.26 min

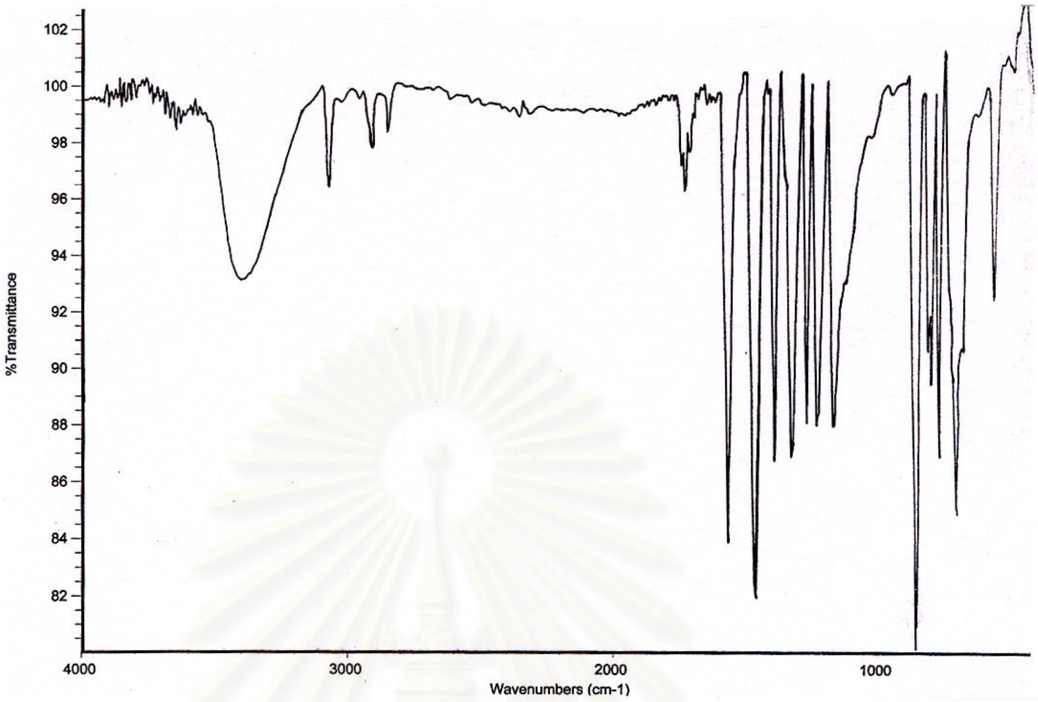

Figure B31 The FTIR spectrum of mixture 5P

(using mole ratio of substrate and sodium bromide: 1/5 mixed)

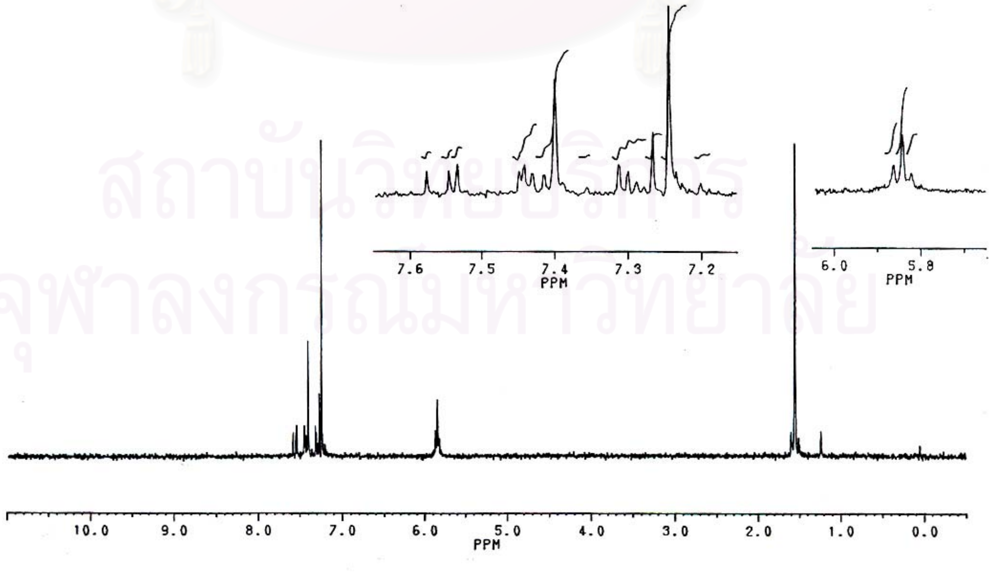

Figure B32 The ^{1}H-NMR spectrum of mixture 5P

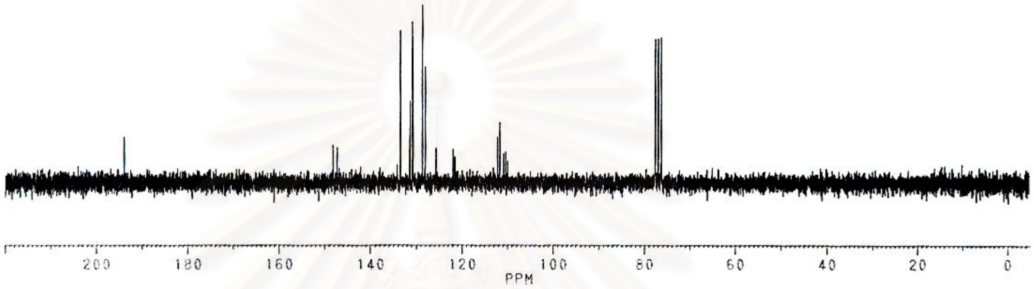

Figure B33 The ^{13}C-NMR spectrum of mixture 5P

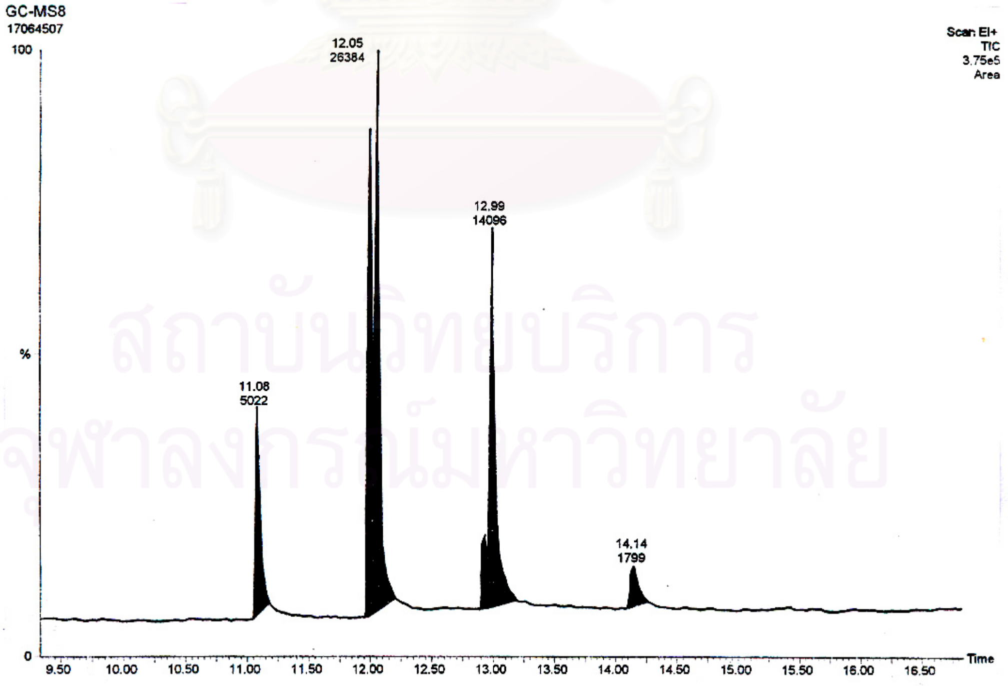

Figure B34 The gas chromatogram of mixture 5P

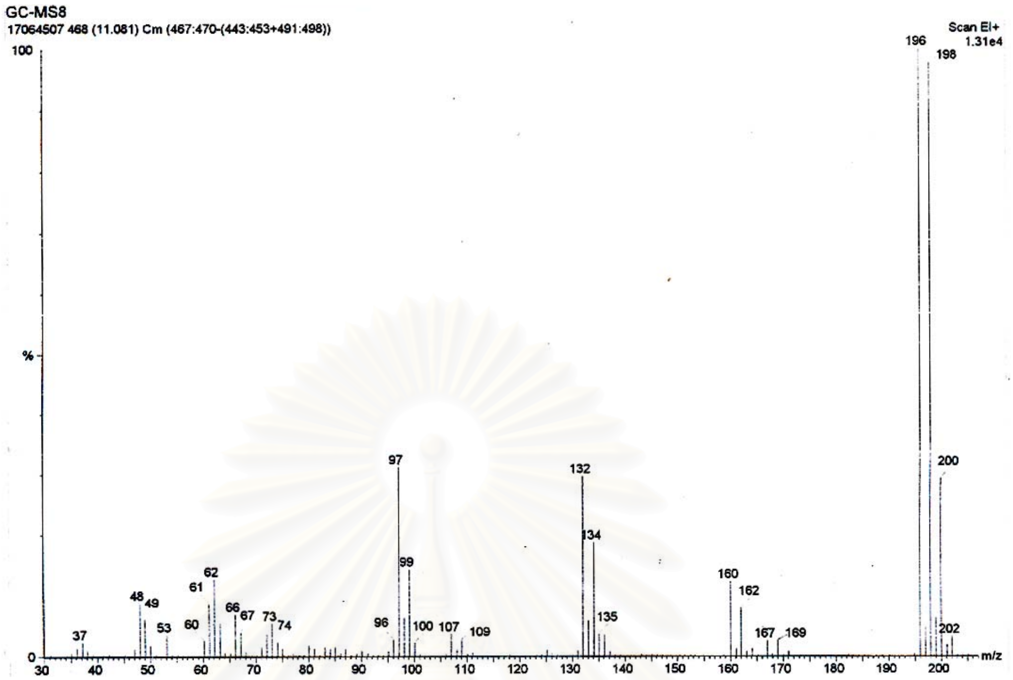

Figure B35 The mass spectrum of mixture 5P at t_R = 11.08 min

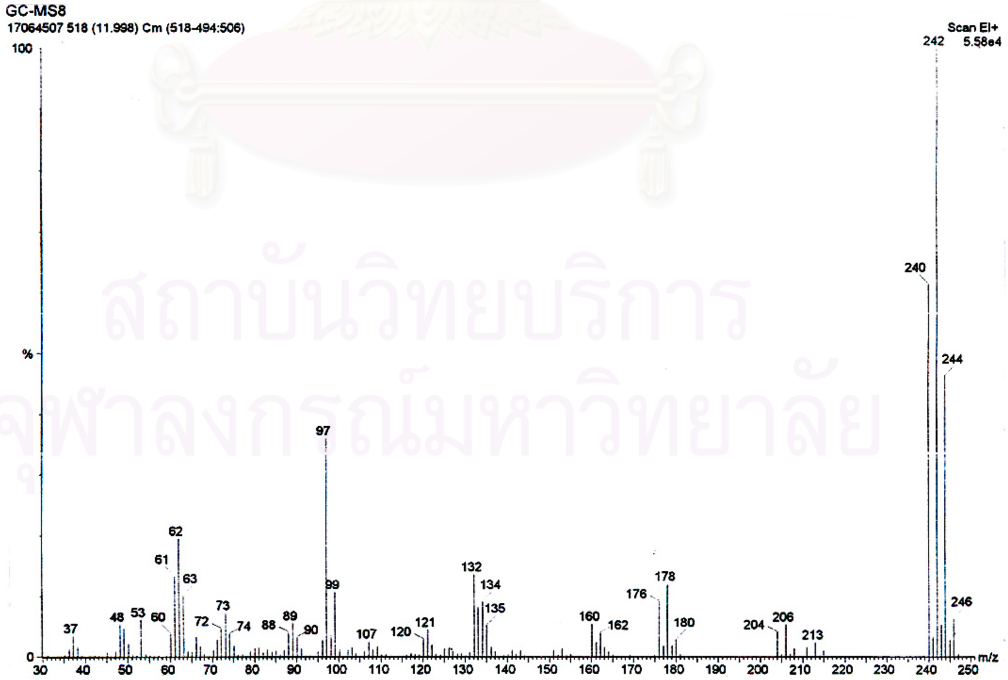

Figure B36 The mass spectrum of mixture 5P at t_R = 12.00 min

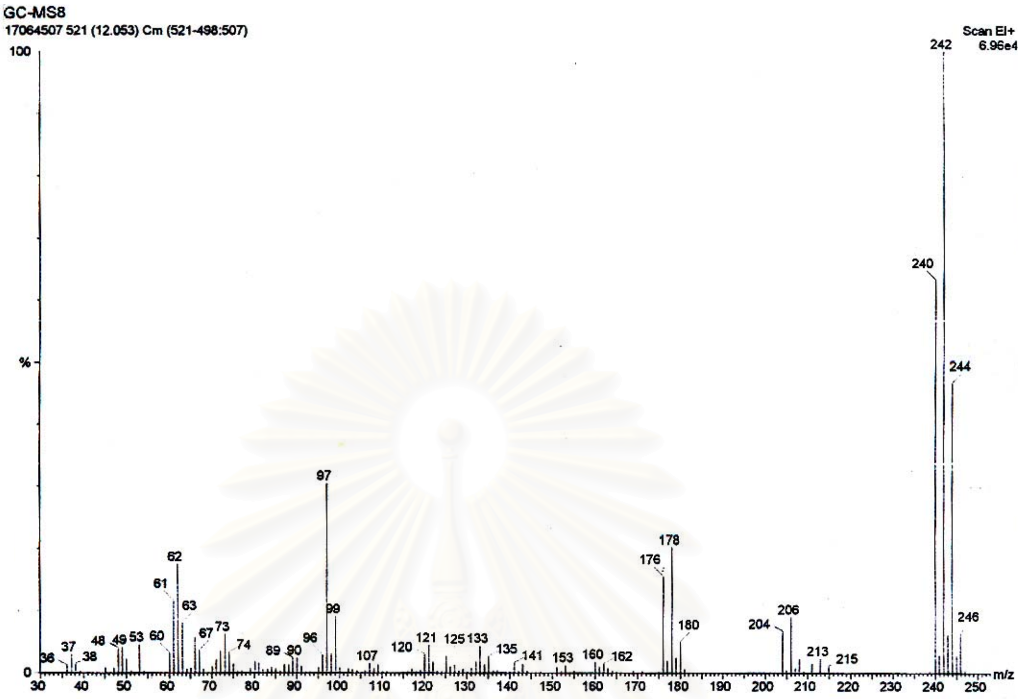

Figure B37 The mass spectrum of mixture 5P at t_R = 12.05 min

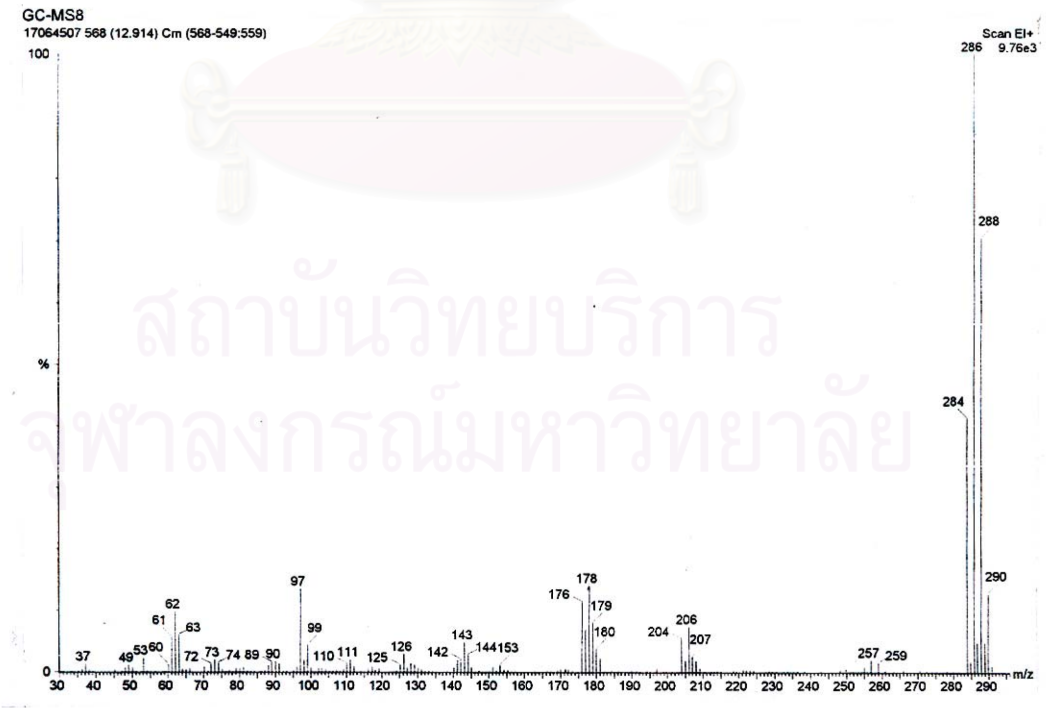

Figure B38 The mass spectrum of mixture 5P at t_R = 12.91 min

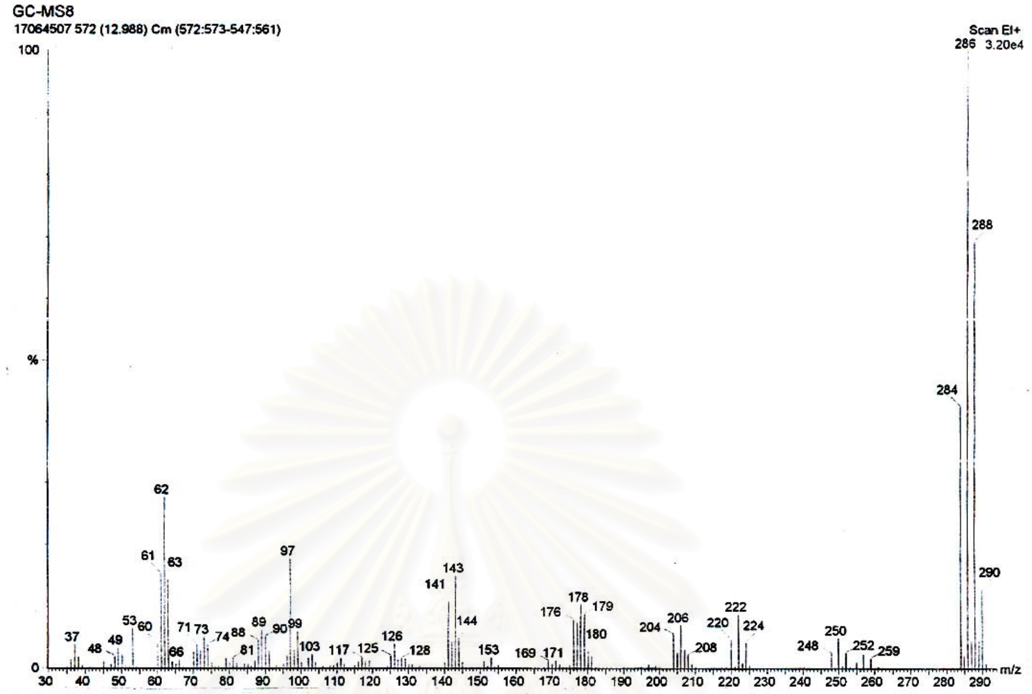

Figure B39 The mass spectrum of mixture 5P at t_R = 12.99 min

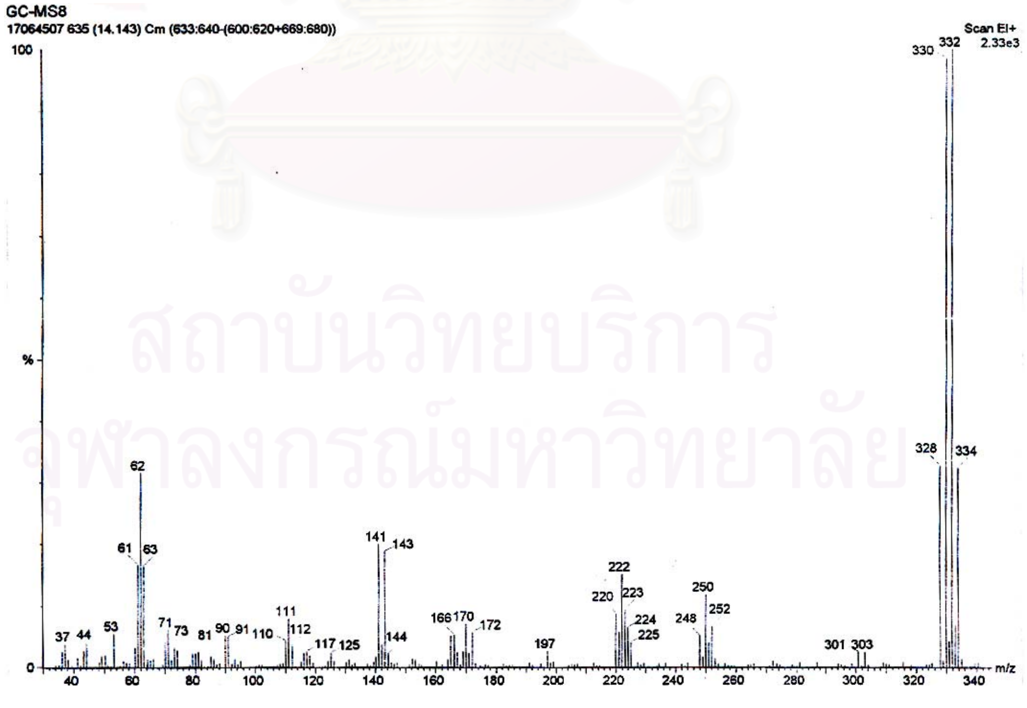

Figure B40 The mass spectrum of mixture 5P at t_R = 14.14 min

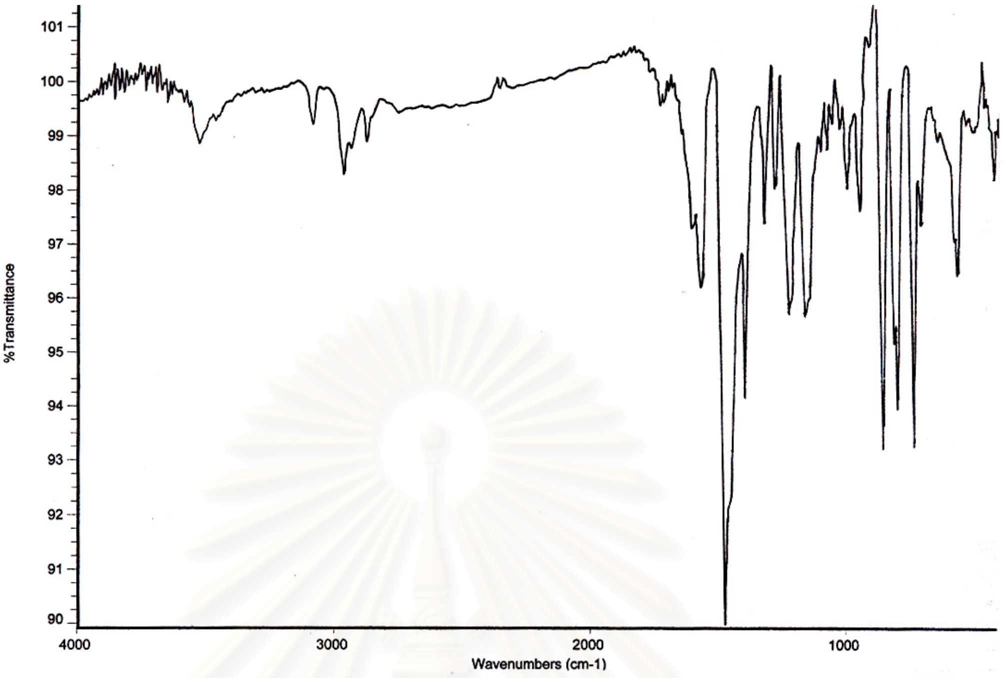

Figure B41 The FTIR spectrum of mixture 6P

(PT (TBA); using mole ratio of substrate and sodium hypochlorite: 1/8)

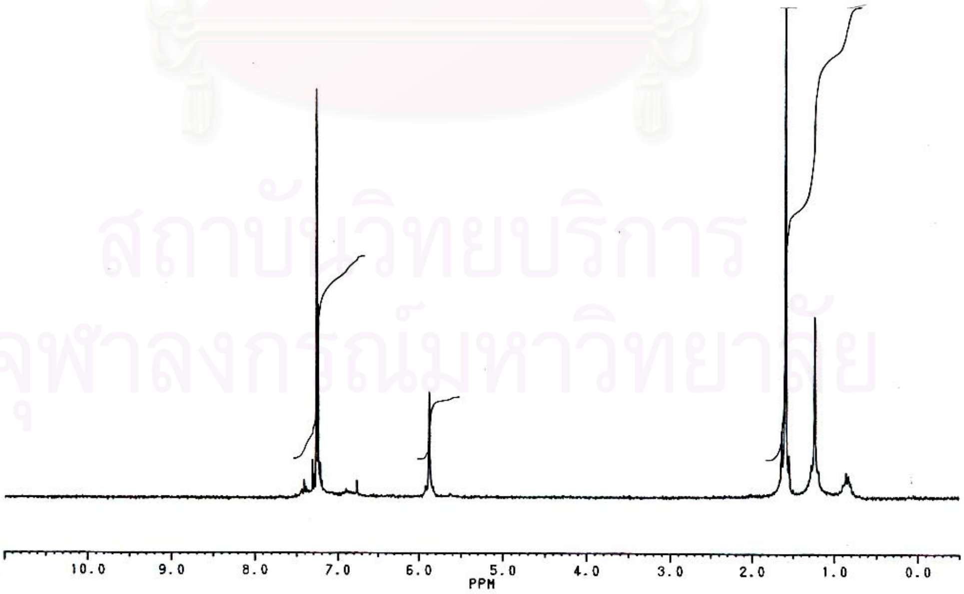

Figure B42 The ^{1}H-NMR spectrum of mixture 6P

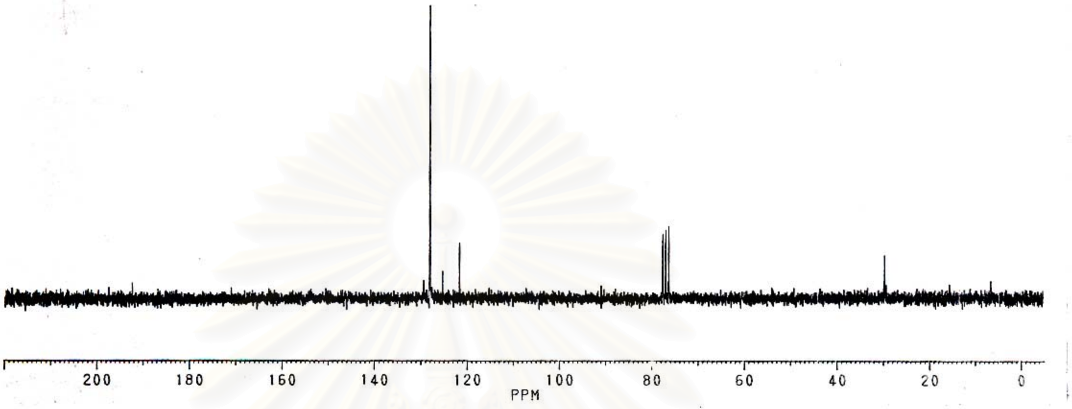

Figure B43 The ^{13}C-NMR spectrum of mixture 6P

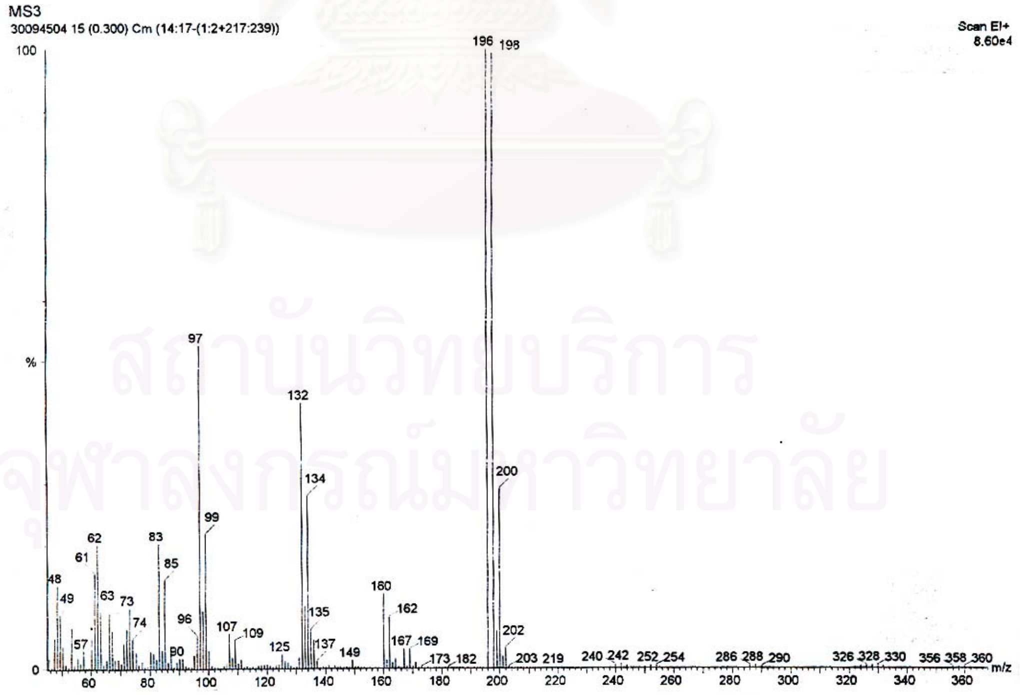

Figure B44 The mass spectrum of mixture 6P

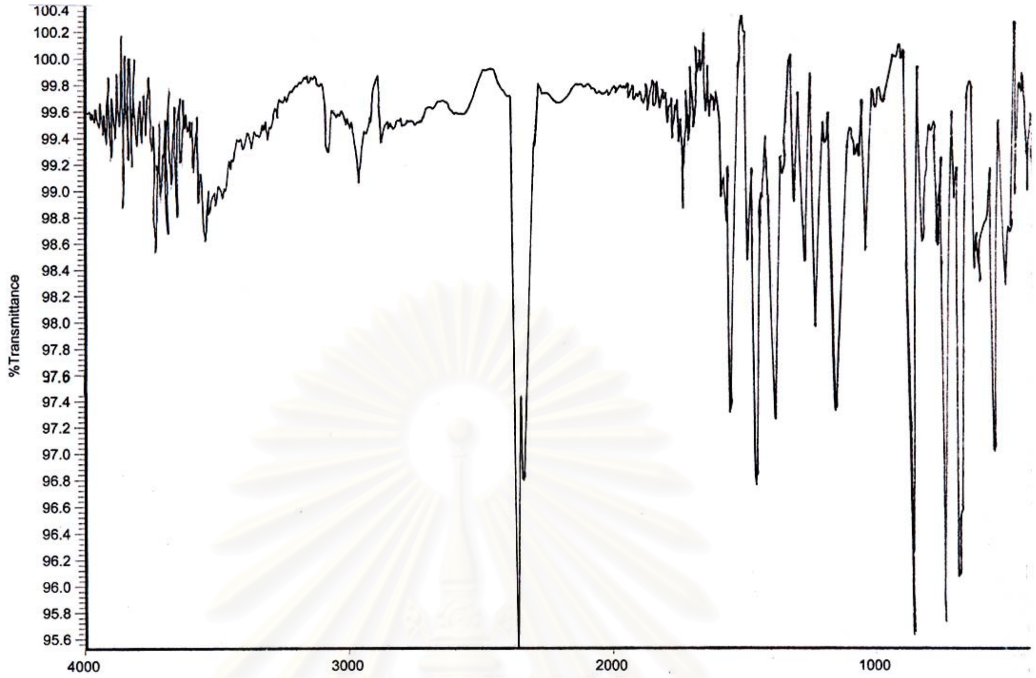

Figure B45 The FTIR spectrum of mixture 7P

(PT (TBA); using mole ratio of substrate and sodium bromide: 1/1

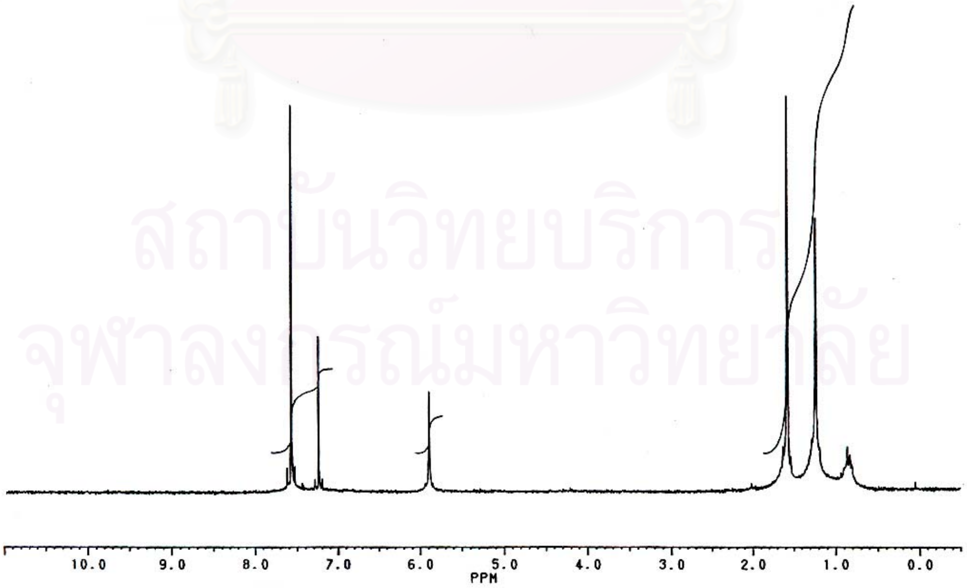

Figure B46 The ^{1}H-NMR spectrum of mixture 7P

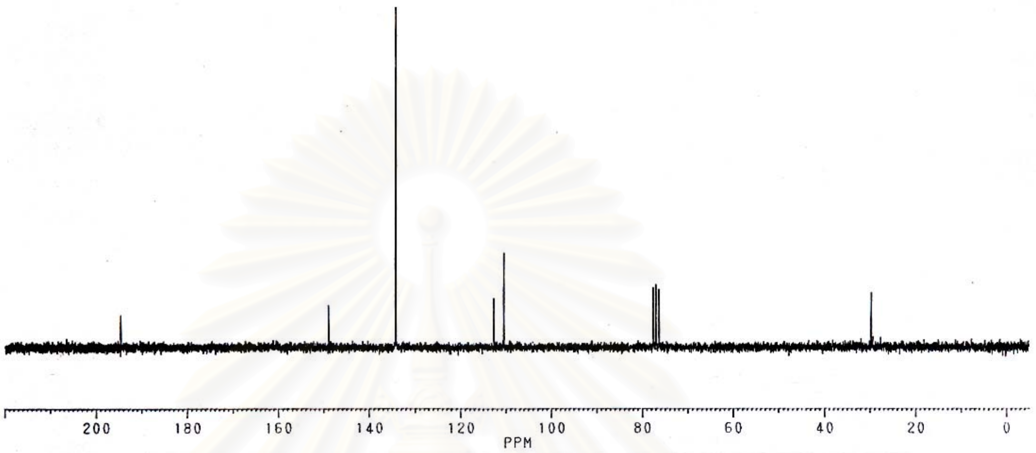

Figure B47 The ^{13}C-NMR spectrum of mixture 7P

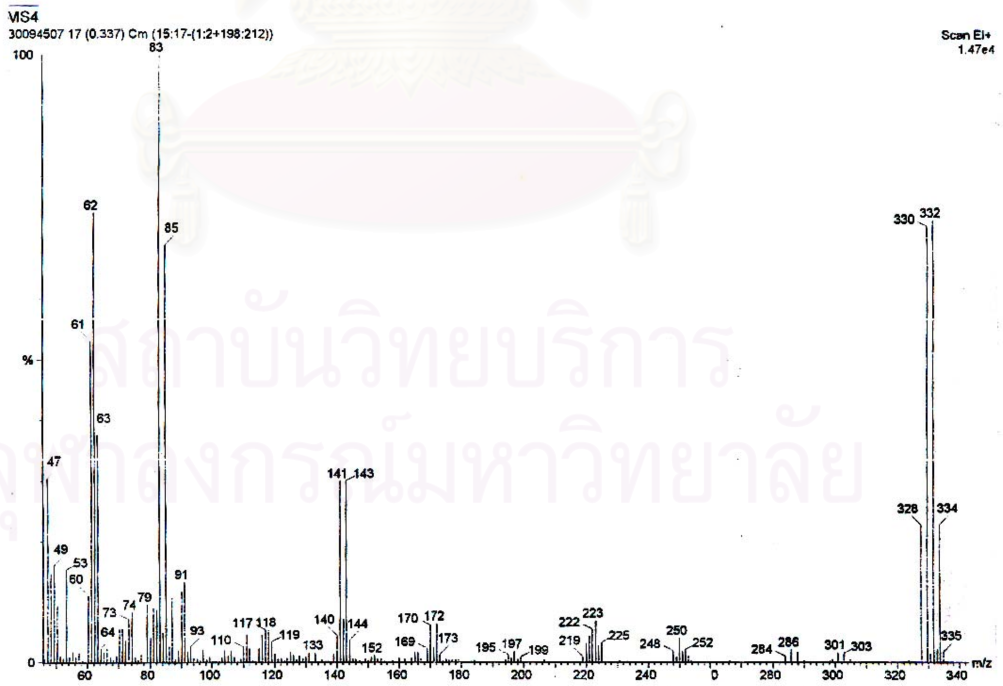

Figure B48 The mass spectrum of mixture 7P

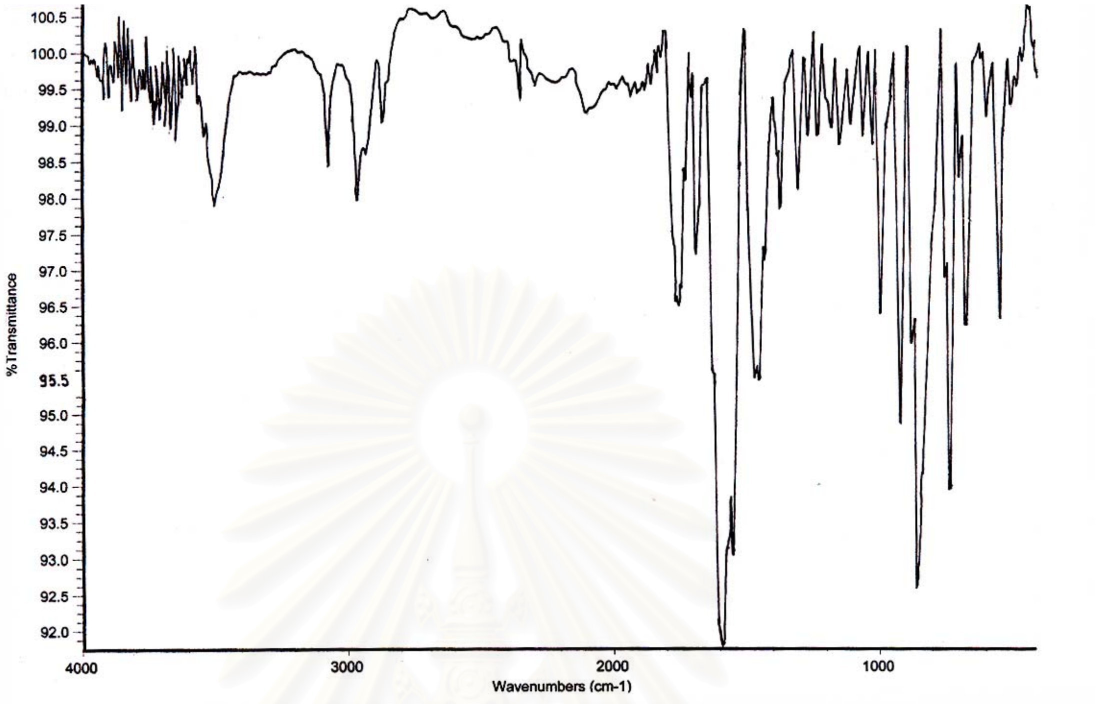

Figure B49 The FTIR spectrum of mixture 8P

(PT (TBA); using mole ratio of substrate and sodium bromide: 1/5)

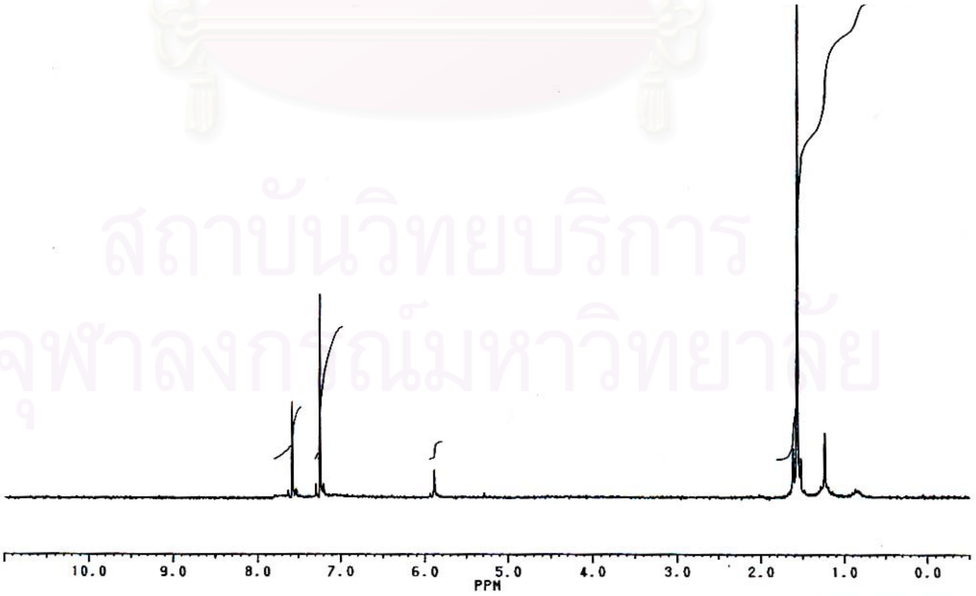

Figure B50 The ^{1}H-NMR spectrum of mixture 8P

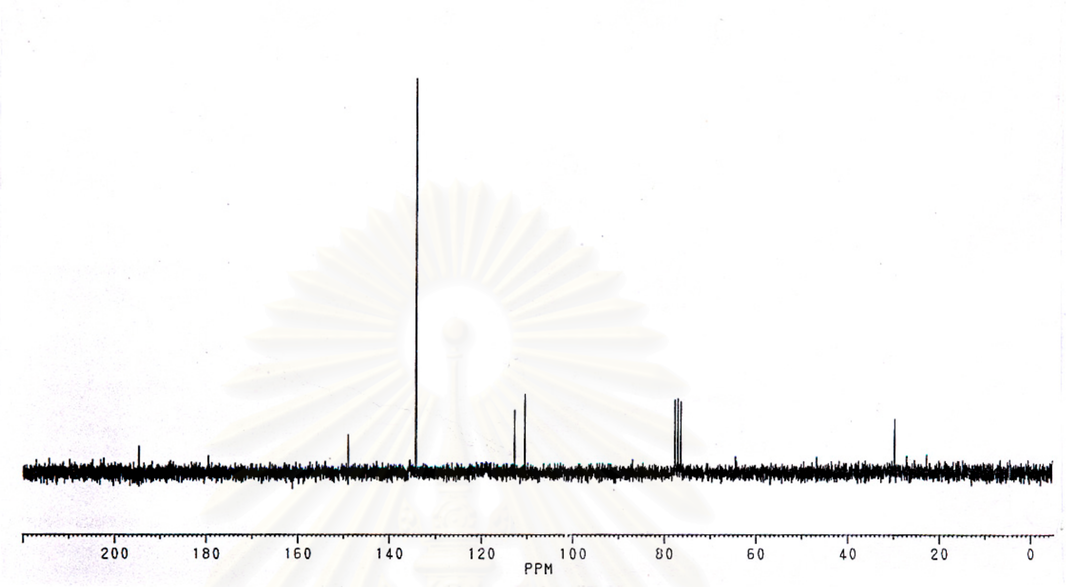

Figure B51 The ^{13}C-NMR spectrum of mixture 8P

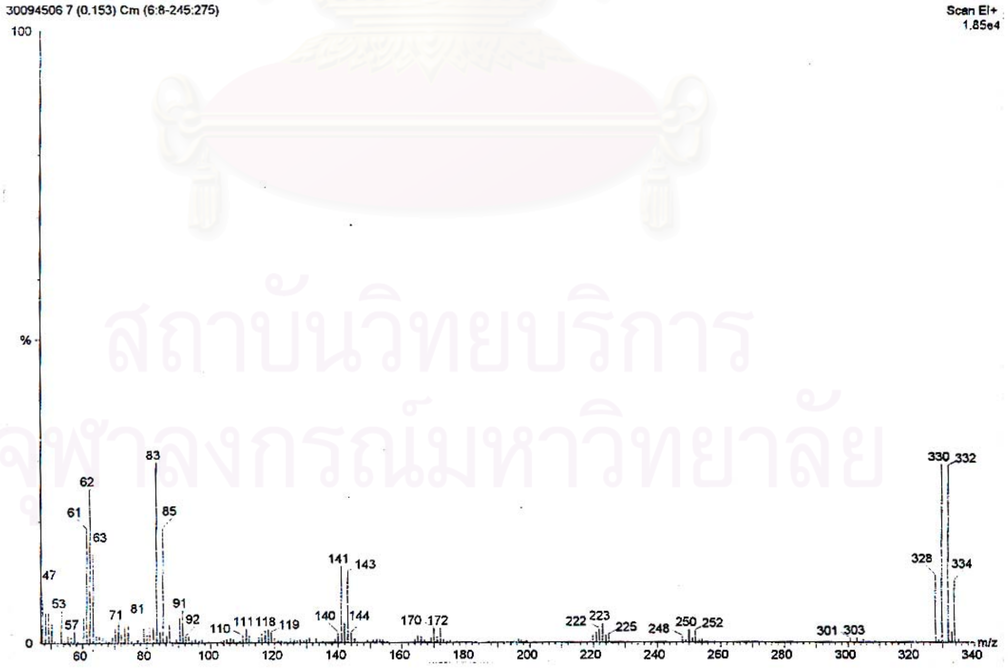

Figure B52 The mass spectrum of mixture 8P

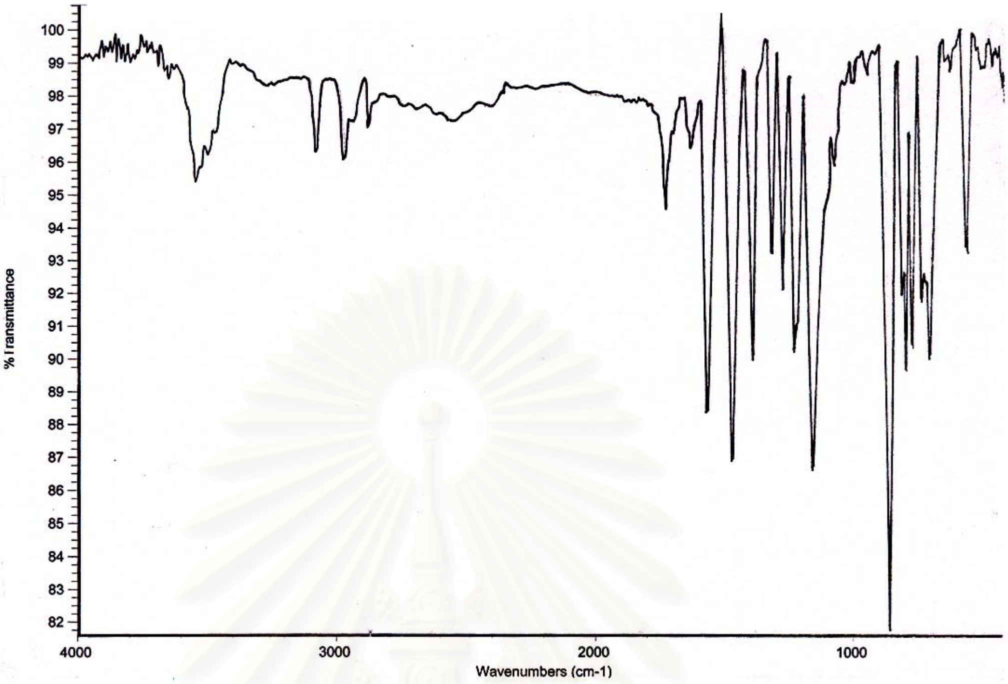

Figure B53 The FTIR spectrum of mixture 9P

(PT (TBA); using mole ratio of substrate and sodium bromide: 1/5 mixed)

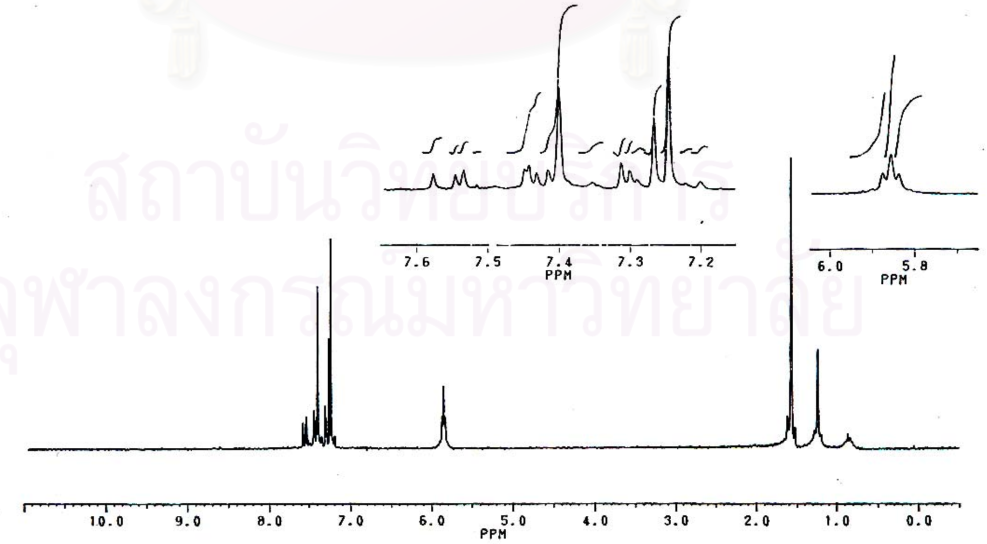

Figure B54 The ^{1}H-NMR spectrum of mixture 9P

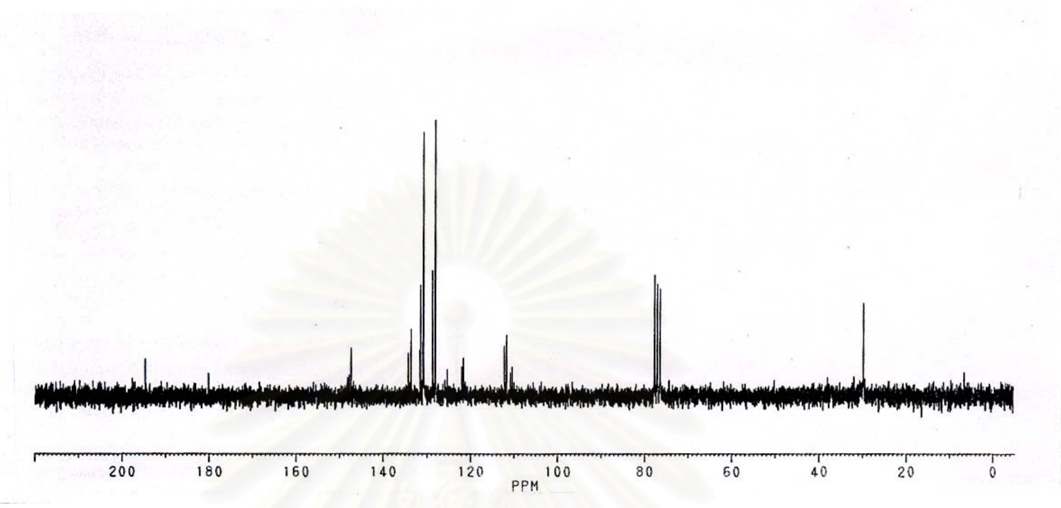

Figure B55 The ^{13}C-NMR spectrum of mixture 9P

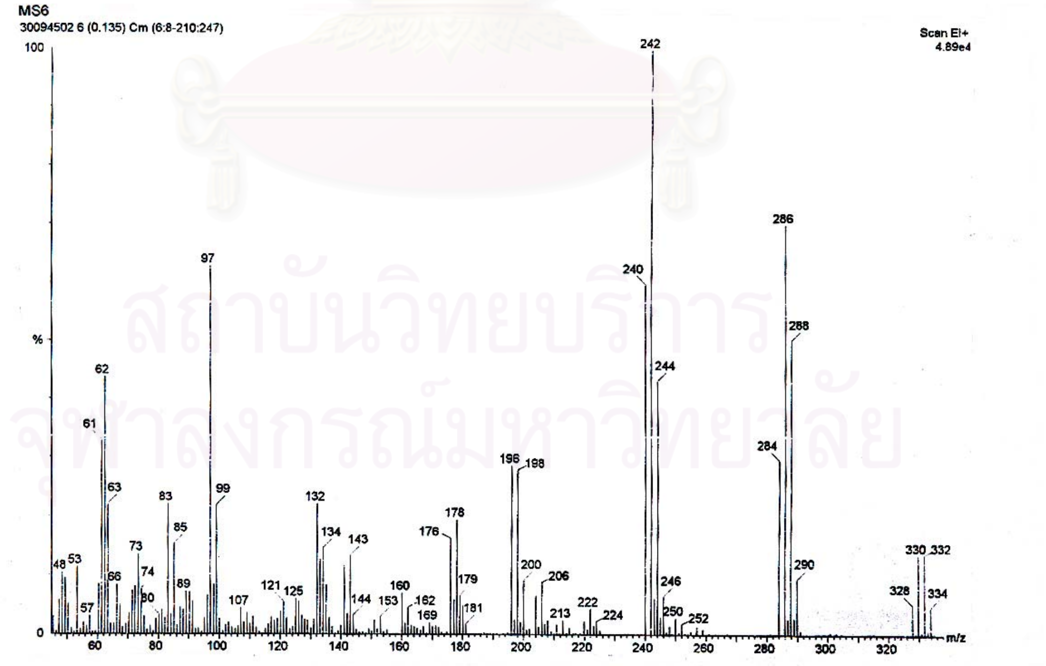

Figure B56 The mass spectrum of mixture 9P

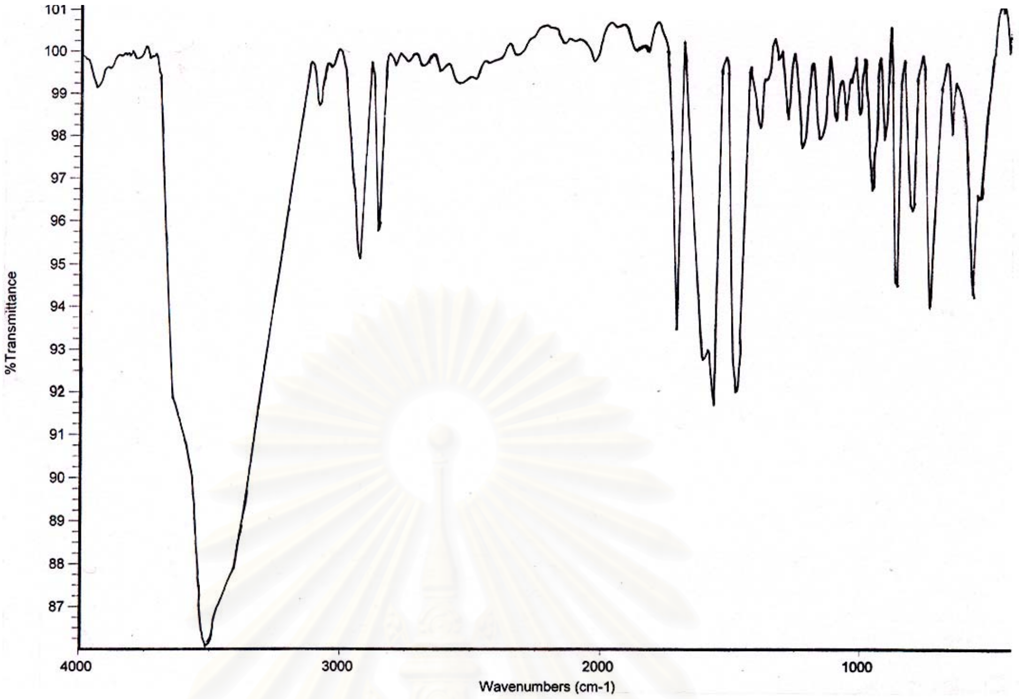

Figure B57 The FTIR spectrum of mixture 10P

(PT (CTAB); using mole ratio of substrate and sodium hypochlorite: 1/8)

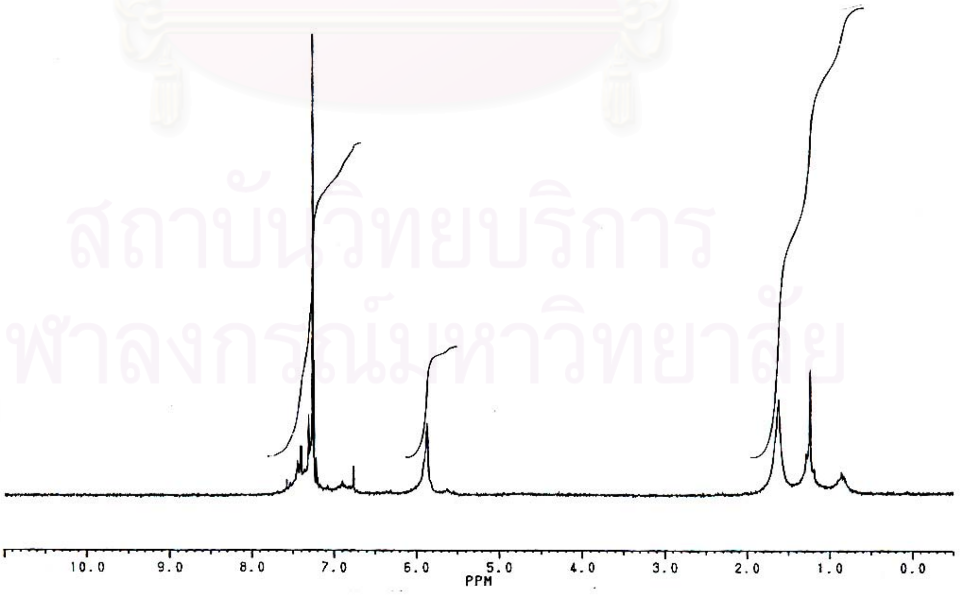

Figure B58 The ^{1}H-NMR spectrum of mixture 10P

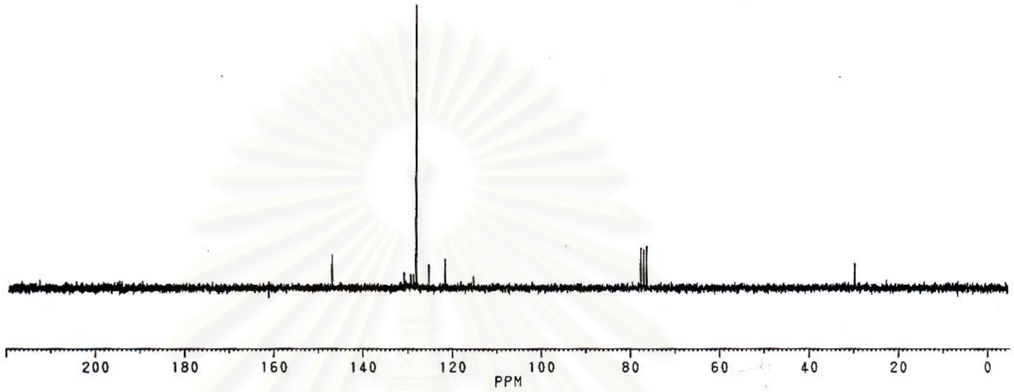

Figure B59 The ^{13}C-NMR spectrum of mixture 10P

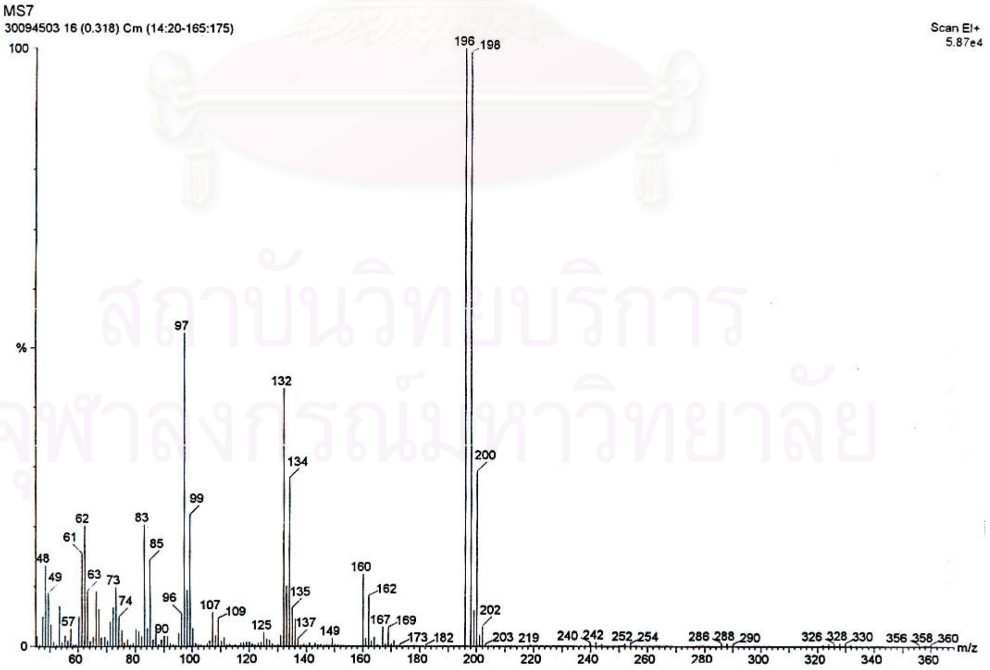

Figure B60 The mass spectrum of mixture 10P

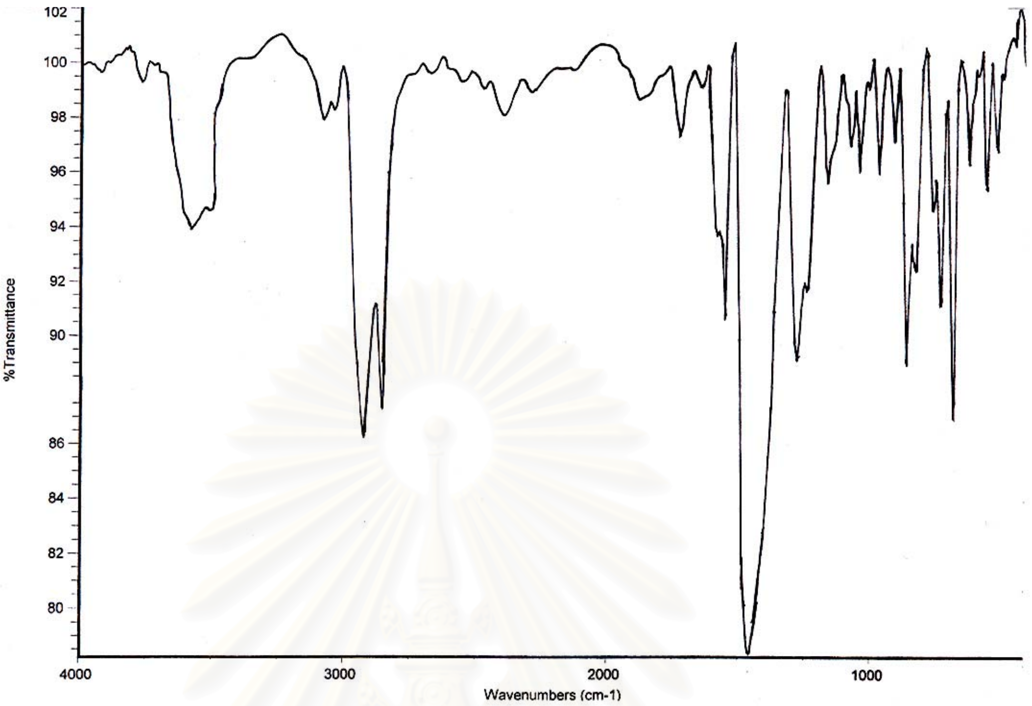

Figure B61 The FTIR spectrum of mixture 11P

(PT (CTAB); using mole ratio of substrate and sodium bromide: 1/1)

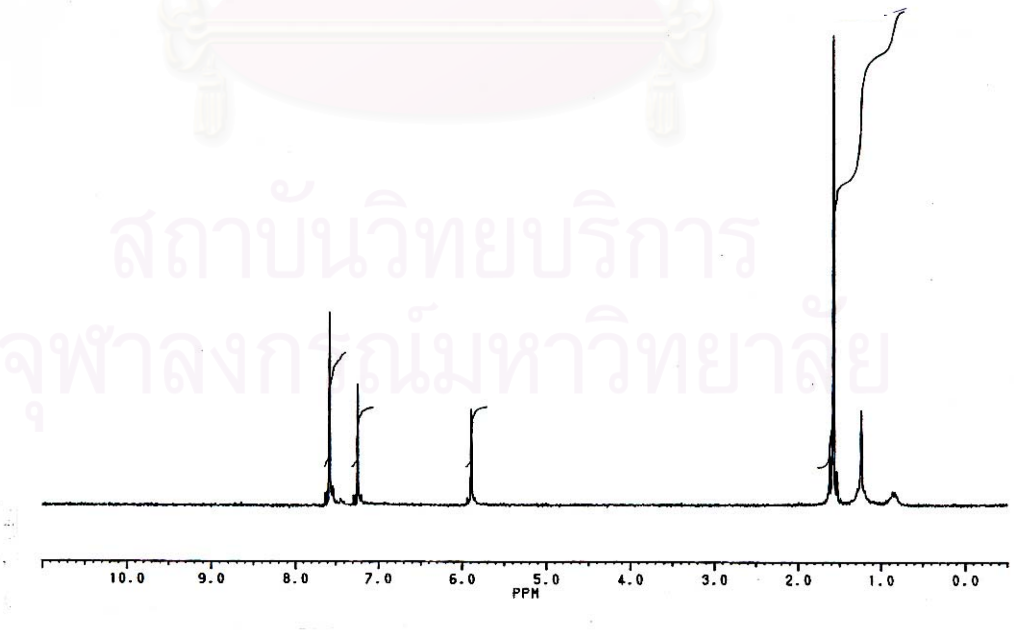

Figure B62 The ^{1}H-NMR spectrum of mixture 11P

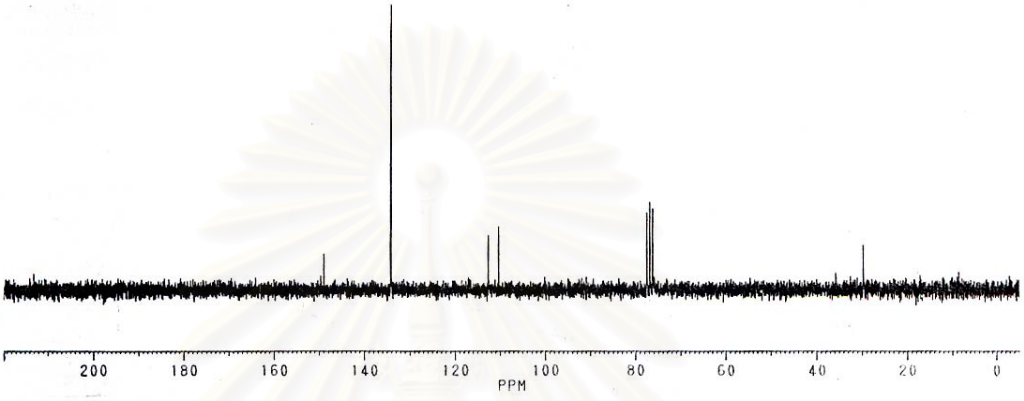

Figure B63 The ^{13}C-NMR spectrum of mixture 11P

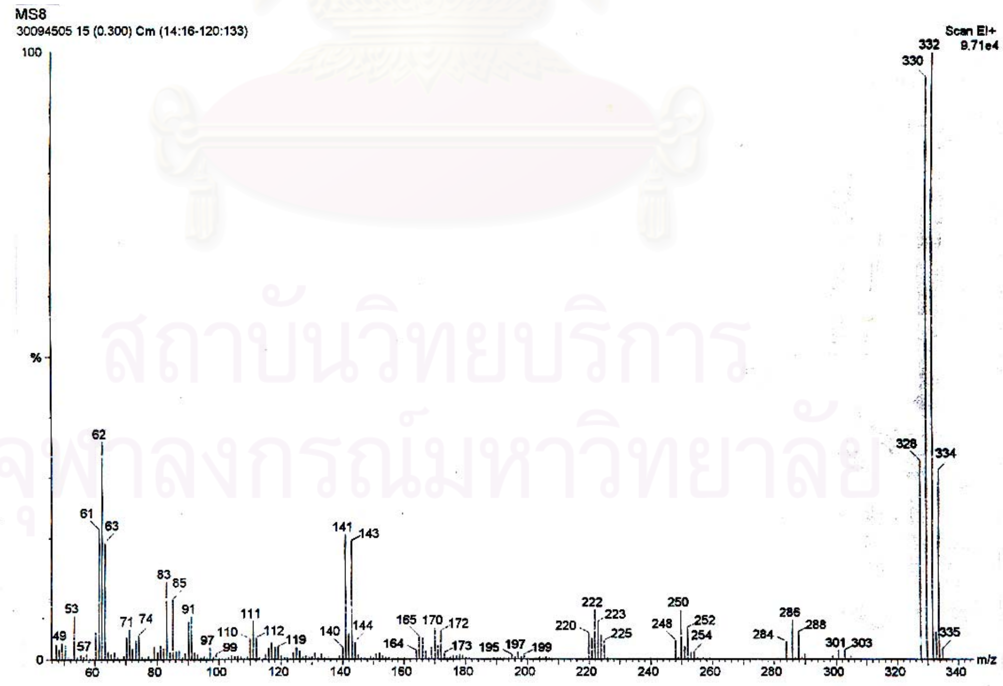

Figure B64 The mass spectrum of mixture 11P

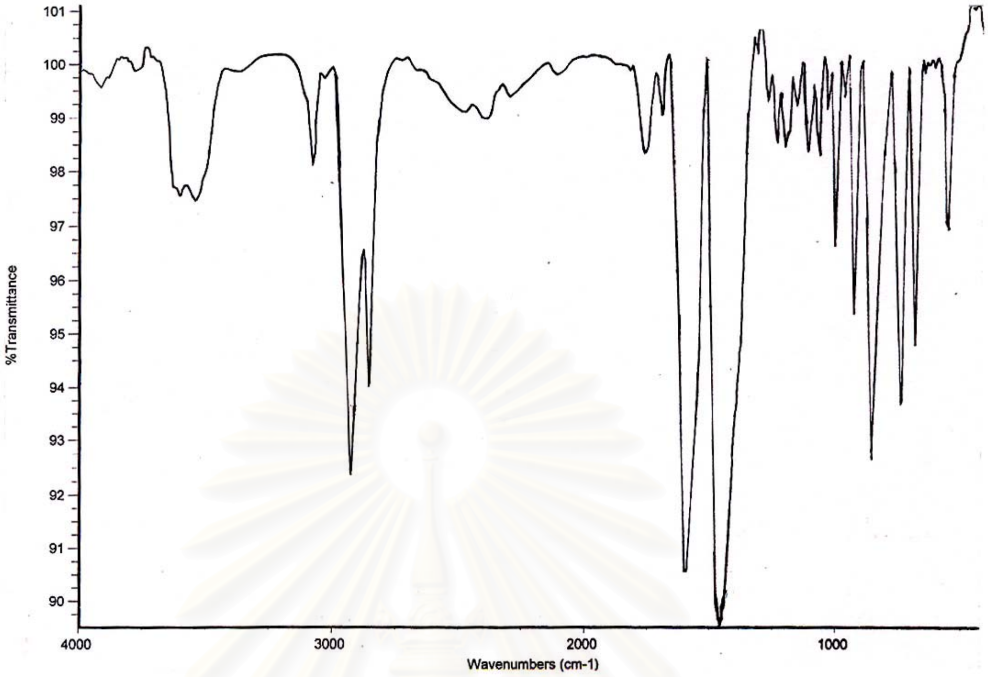

Figure B65 The FTIR spectrum of mixture 12P

(PT (CTAB); using mole ratio of substrate and sodium bromide: 1/5)

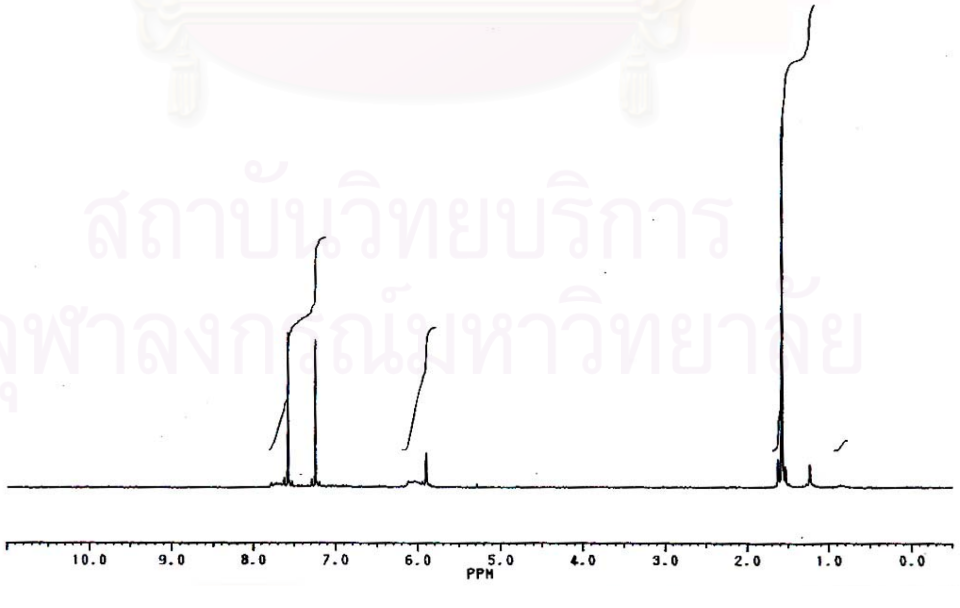

Figure B66 The ^{1}H-NMR spectrum of mixture 12P

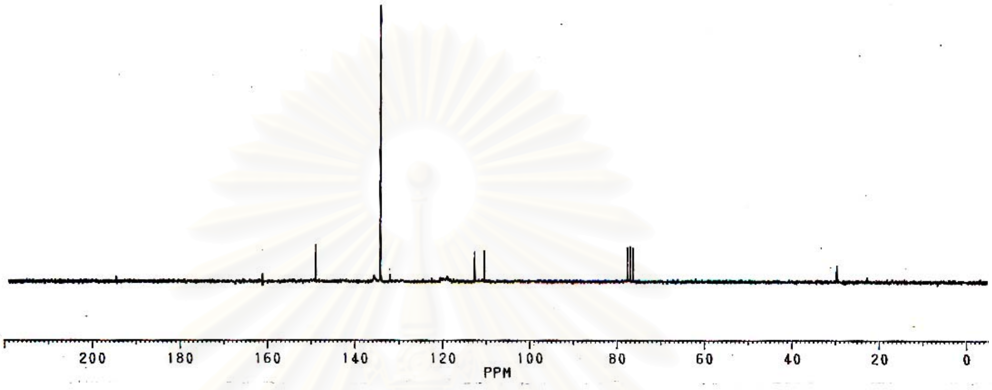

Figure B67 The ^{13}C-NMR spectrum of mixture 12P

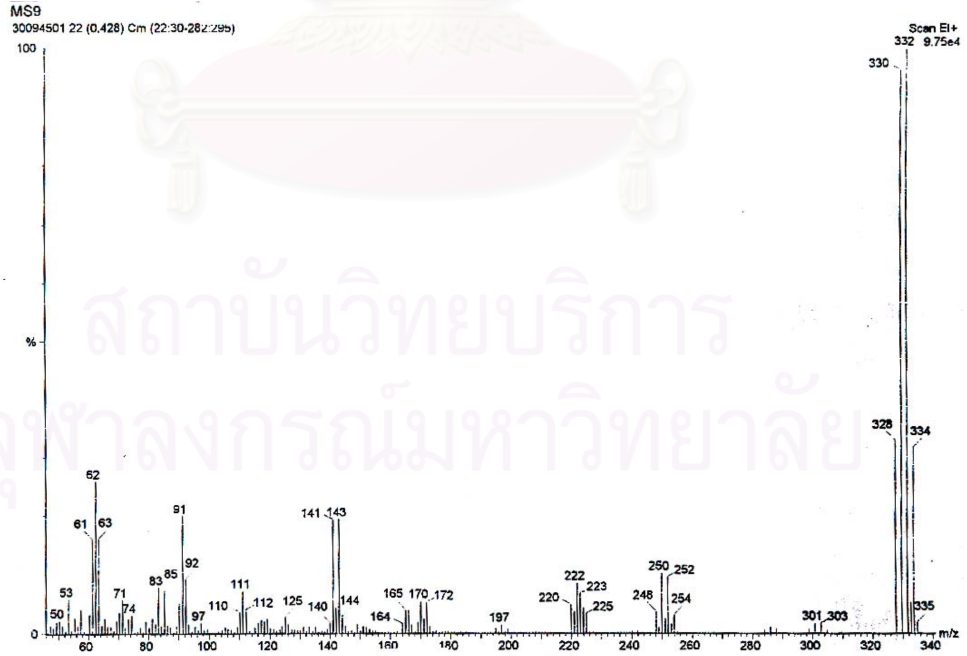

Figure B68 The mass spectrum of mixture 12P

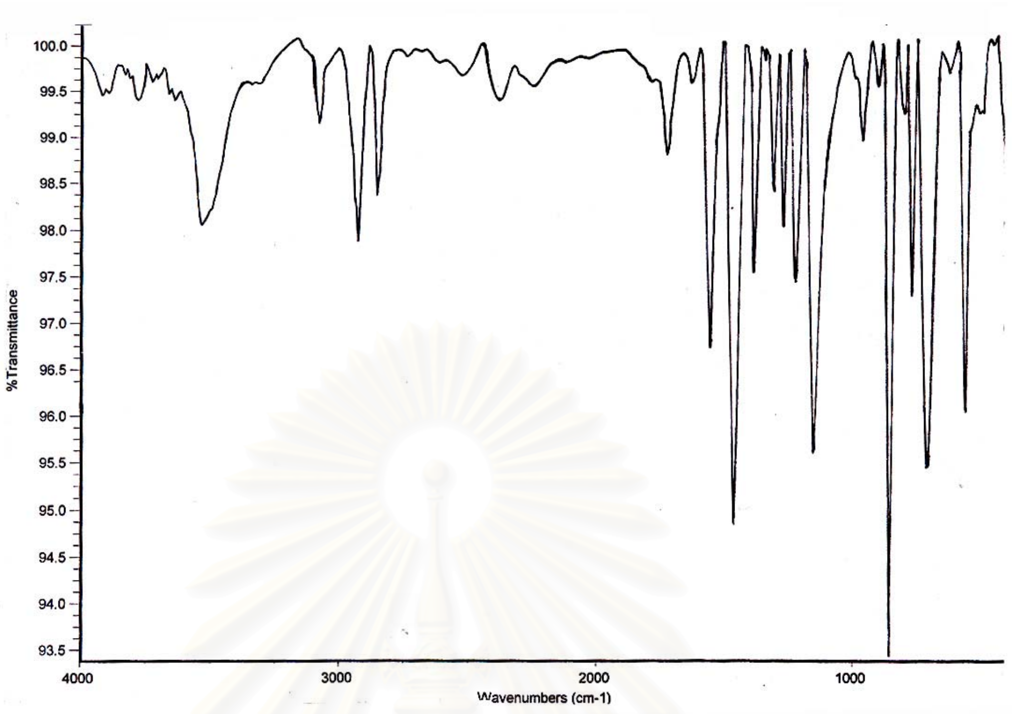

Figure B69 The FTIR spectrum of mixture 13P

(PT (CTAB); using mole ratio of substrate and sodium bromide: 1/5 mixed)

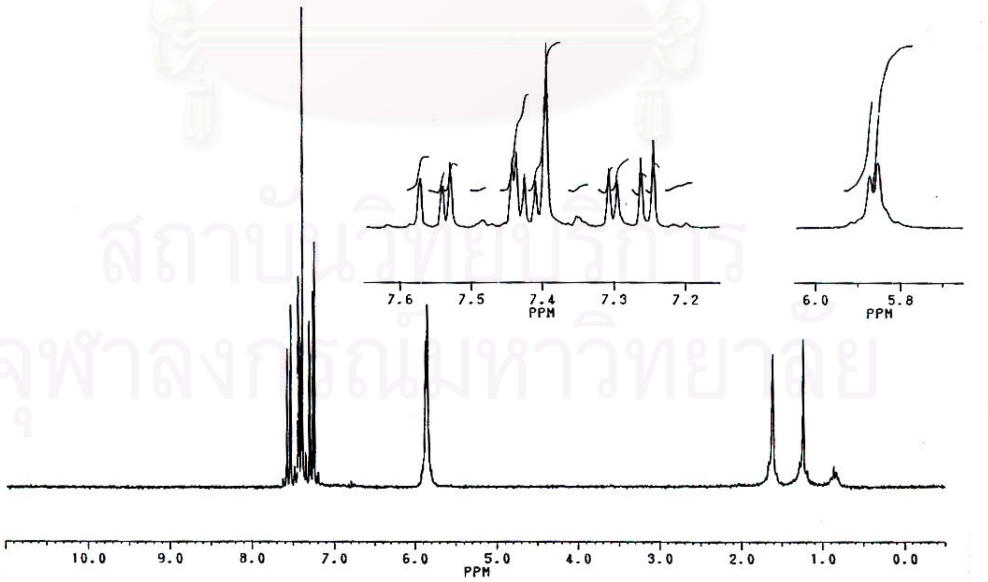

Figure B70 The ^{1}H-NMR spectrum of mixture 13P

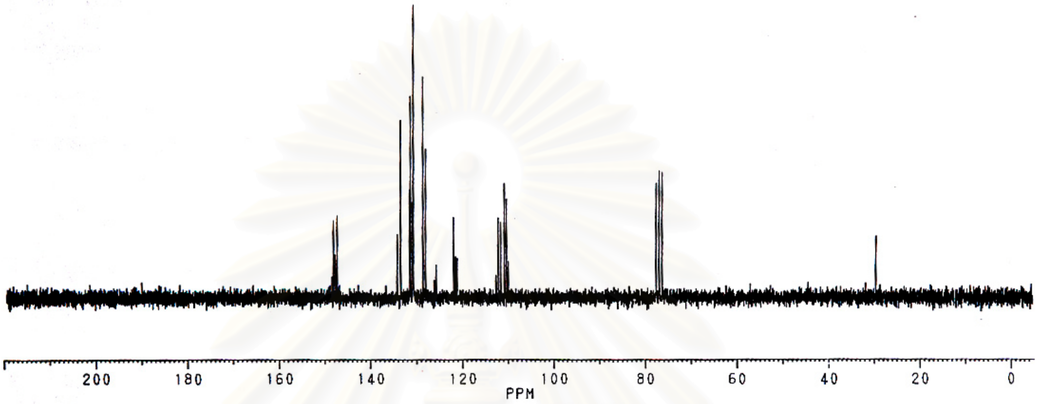

Figure B71 The ^{13}C-NMR spectrum of mixture 13P

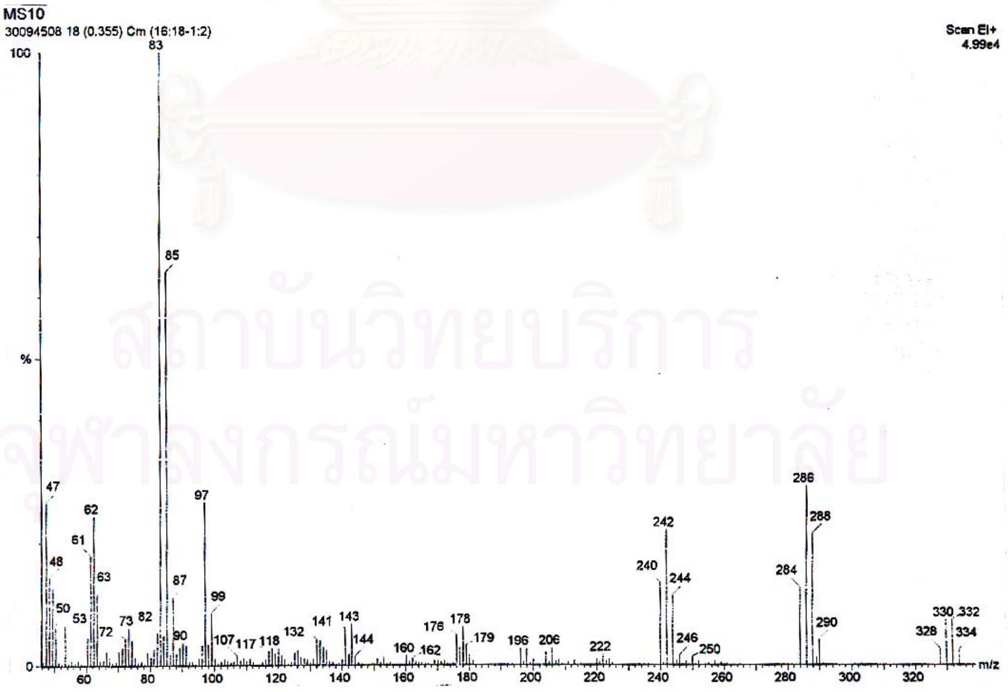

Figure B72 The mass spectrum of mixture 13P

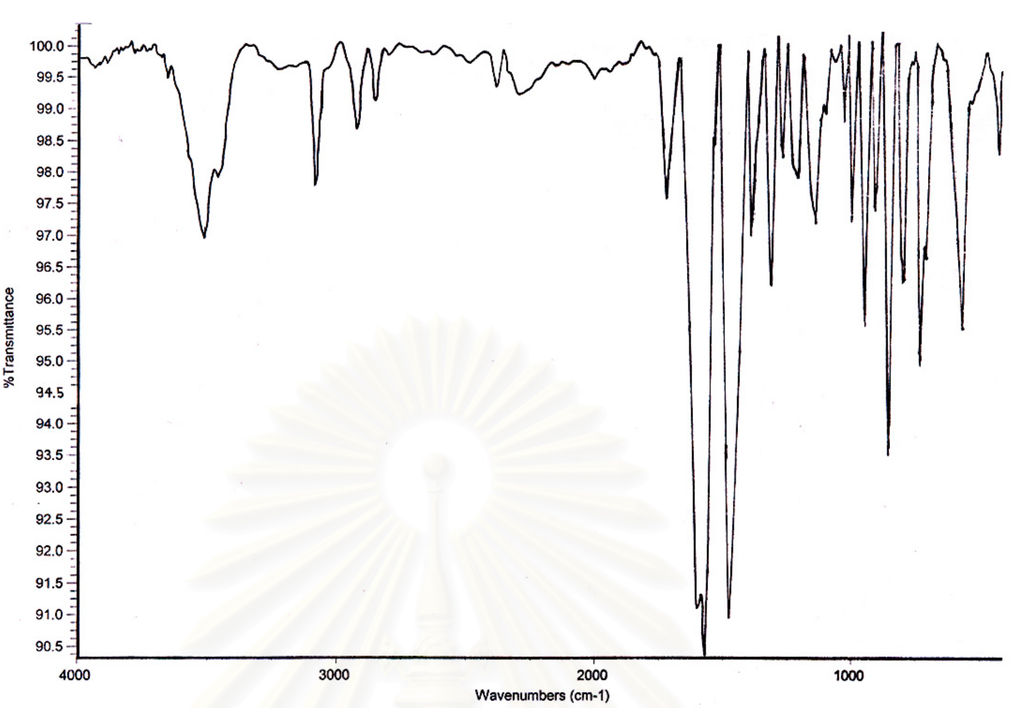

Figure B73 The FTIR spectrum of mixture 14P

(haxane; using mole ratio of substrate and sodium hypochlorite: 1/8)

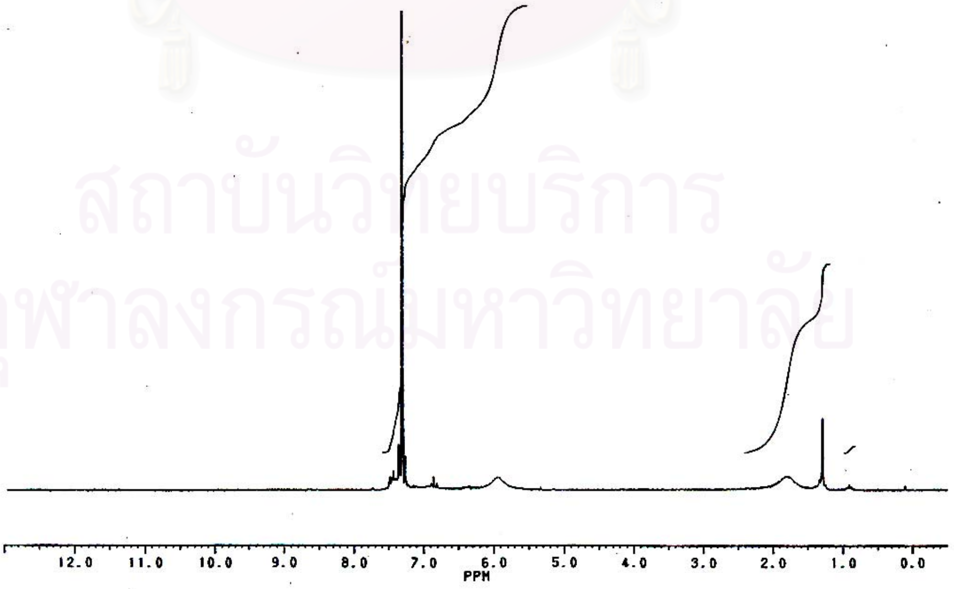

Figure B74 The ^{1}H-NMR spectrum of mixture 14P

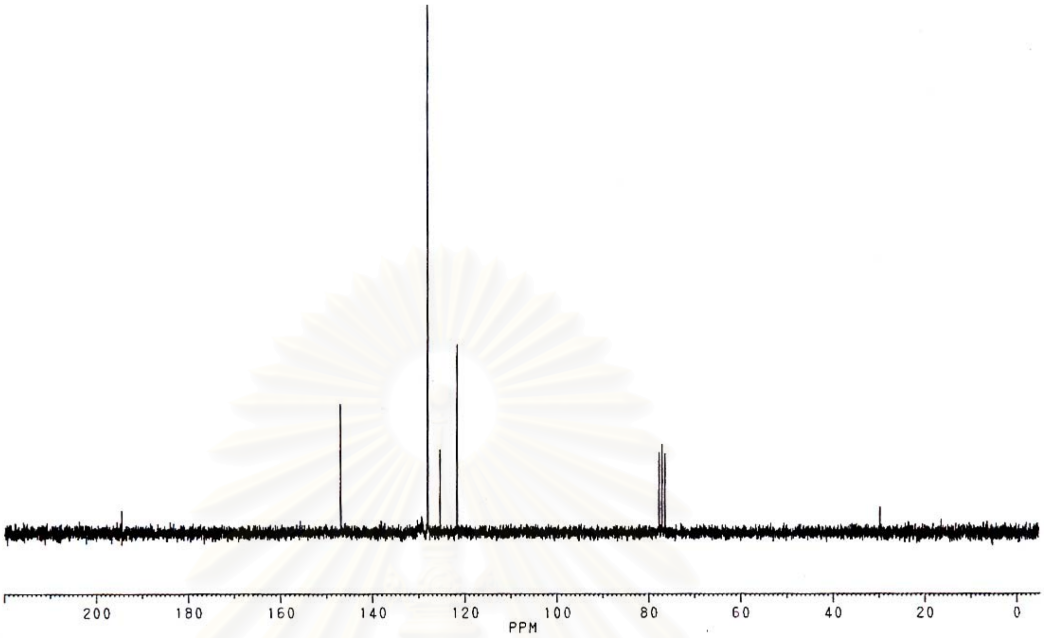

Figure B75 The ^{13}C-NMR spectrum of mixture 14P

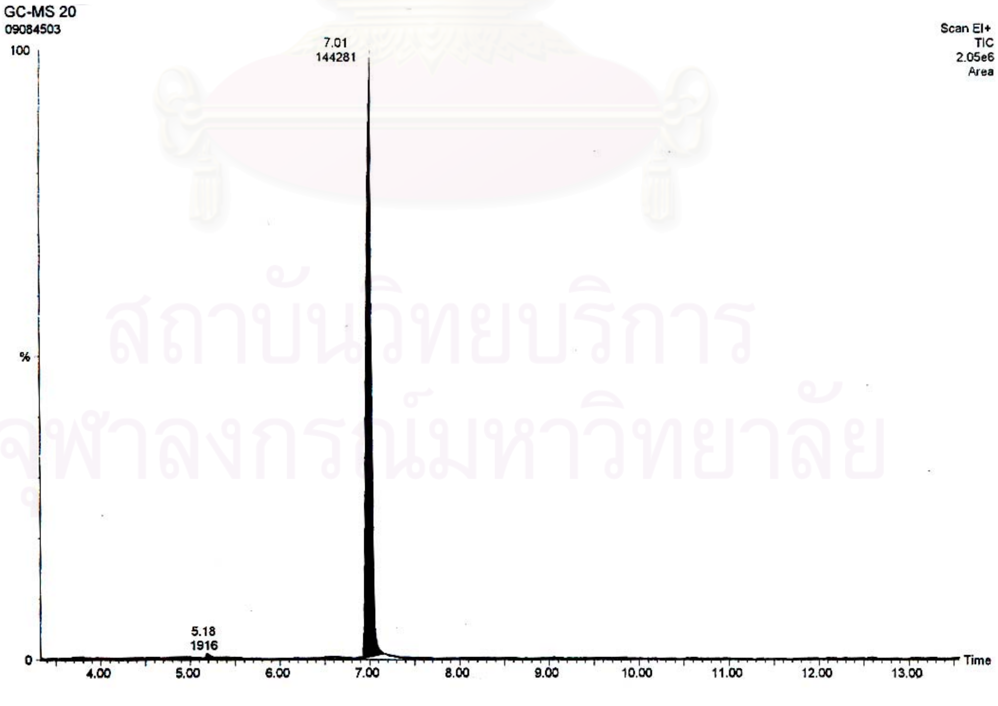

Figure B76 The gas chromatogram of mixture 14P

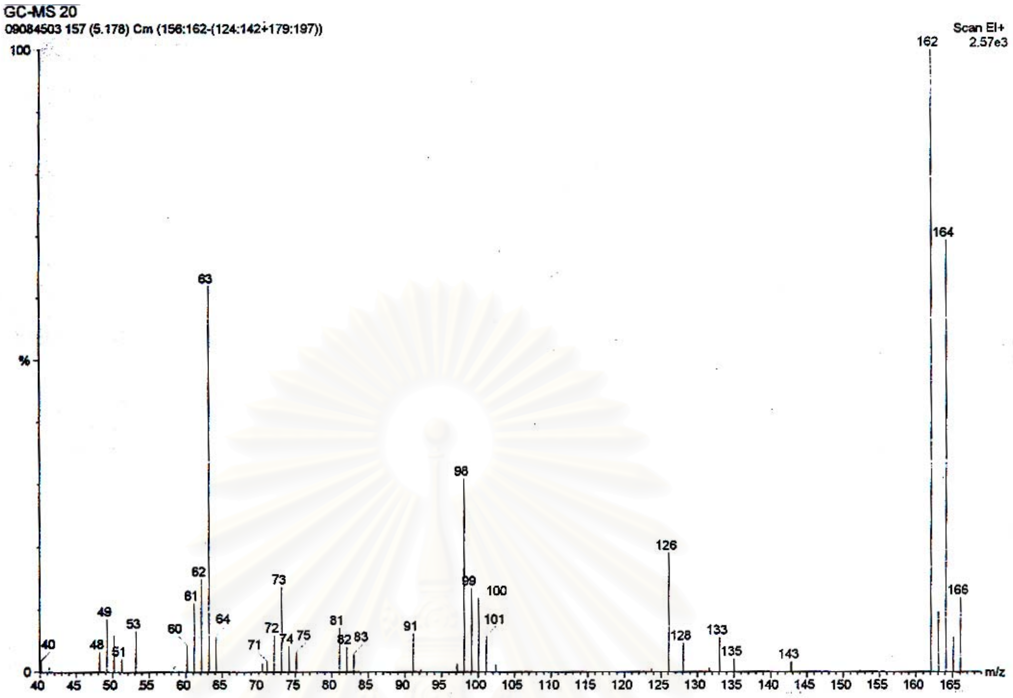

Figure B77 The mass spectrum of mixture 14P at t_R = 5.18 min

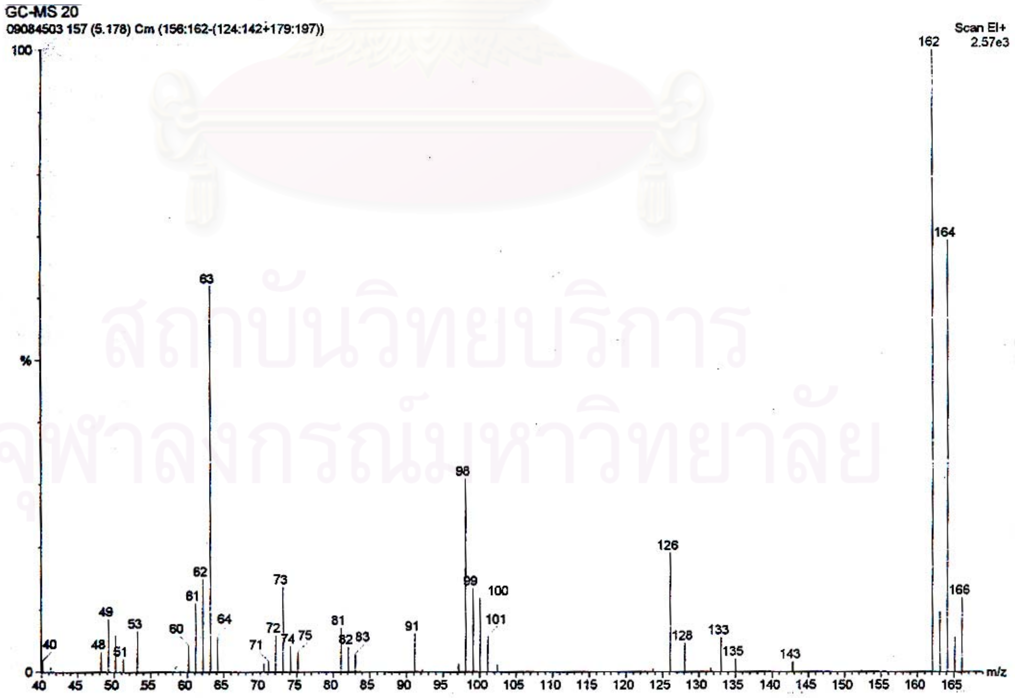

Figure B78 The mass spectrum of mixture 14P at t_R = 7.01 min

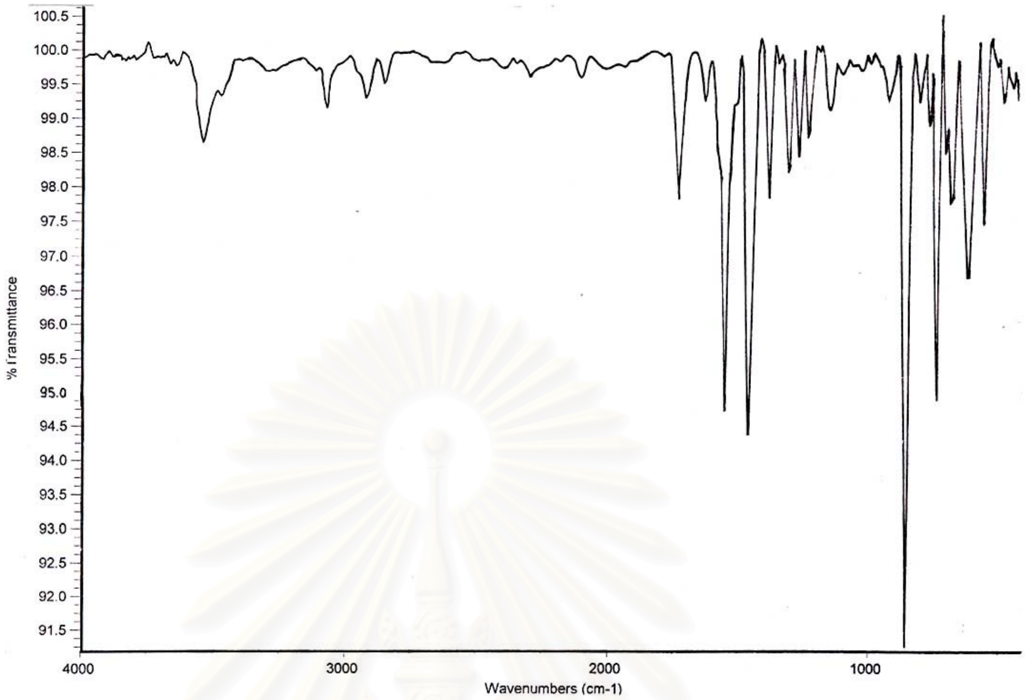

Figure B79 The FTIR spectrum of mixture 15P

(haxane; using mole ratio of substrate and sodium bromide: 1/1)

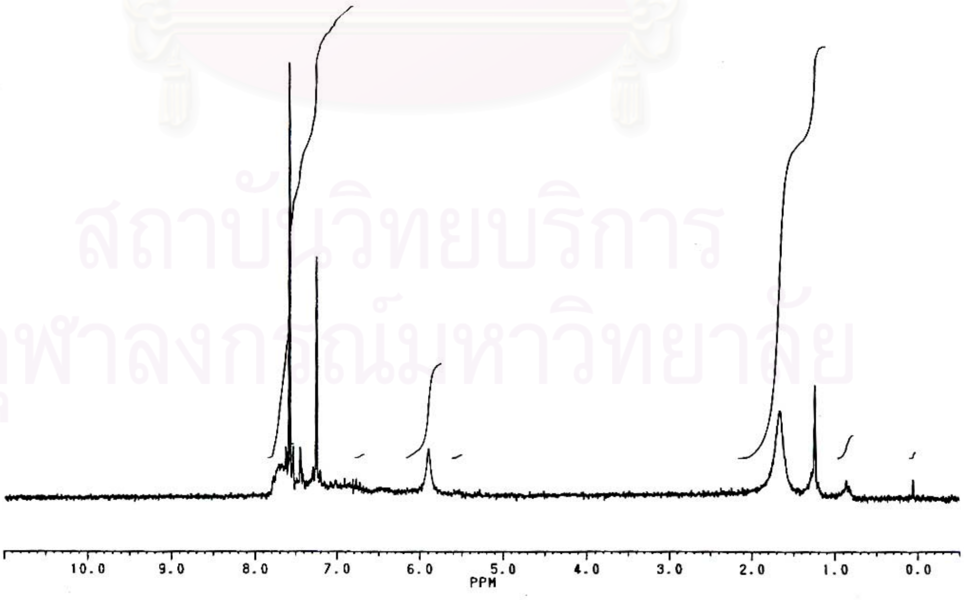

Figure B80 The ^{1}H-NMR spectrum of mixture 15P

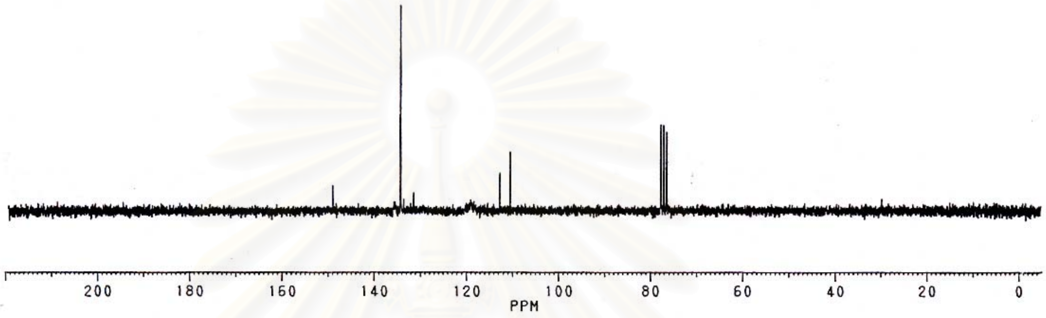

Figure B81 The ^{13}C-NMR spectrum of mixture 15P

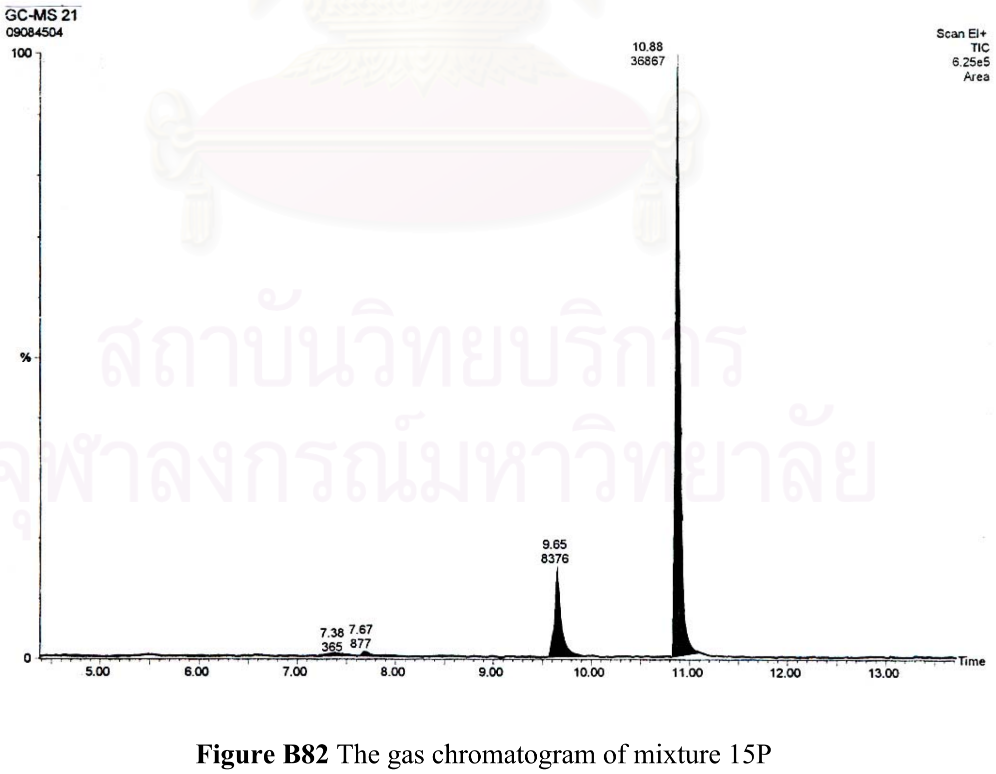

Figure B82 The gas chromatogram of mixture 15P

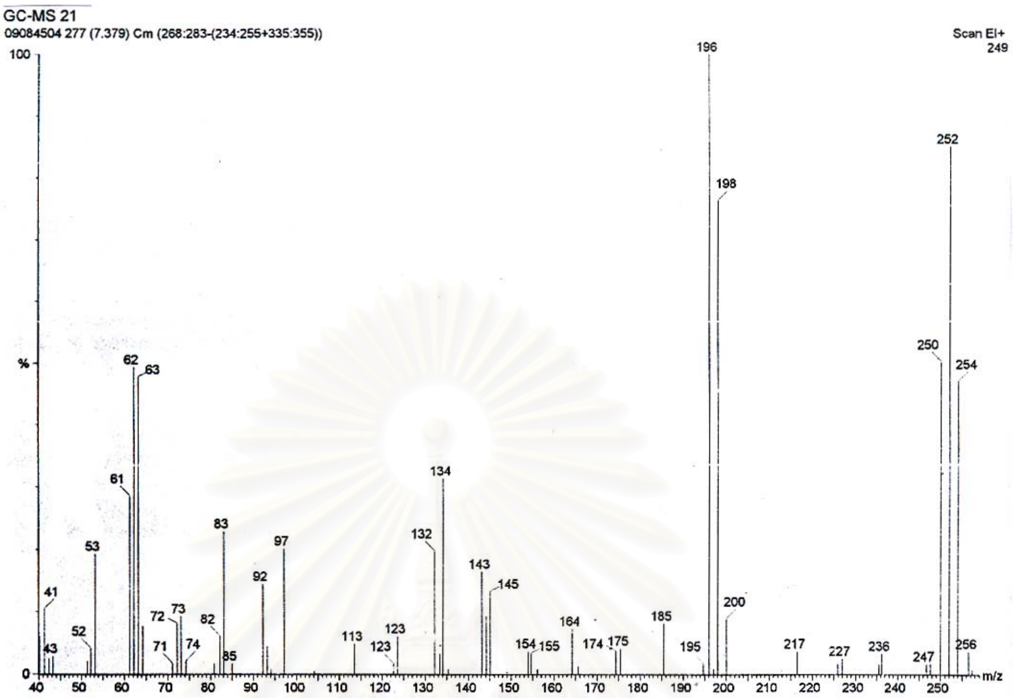

Figure B83 The mass spectrum of mixture 15P at t_R = 7.38 min

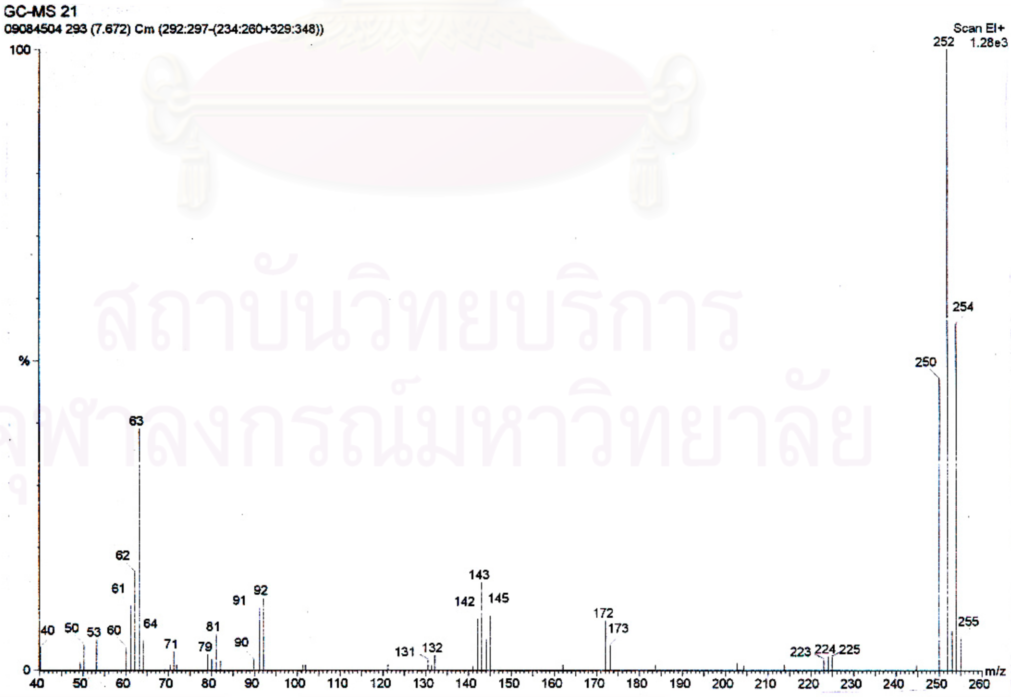

Figure B84 The mass spectrum of mixture 15P at t_R = 7.67 min

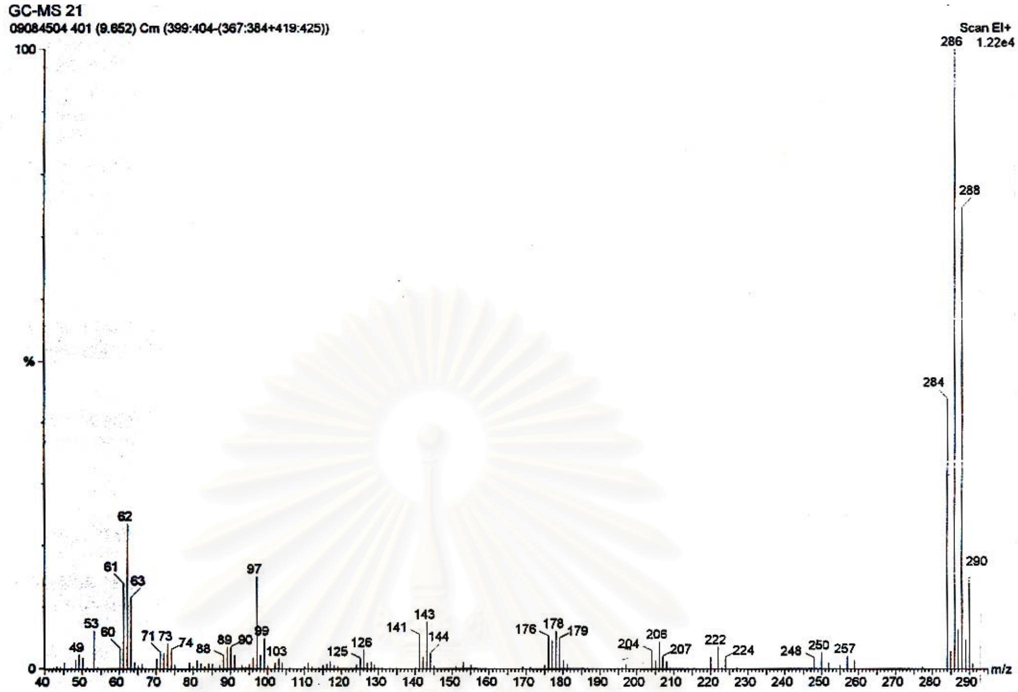

Figure B85 The mass spectrum of mixture 15P at t_R = 9.65 min

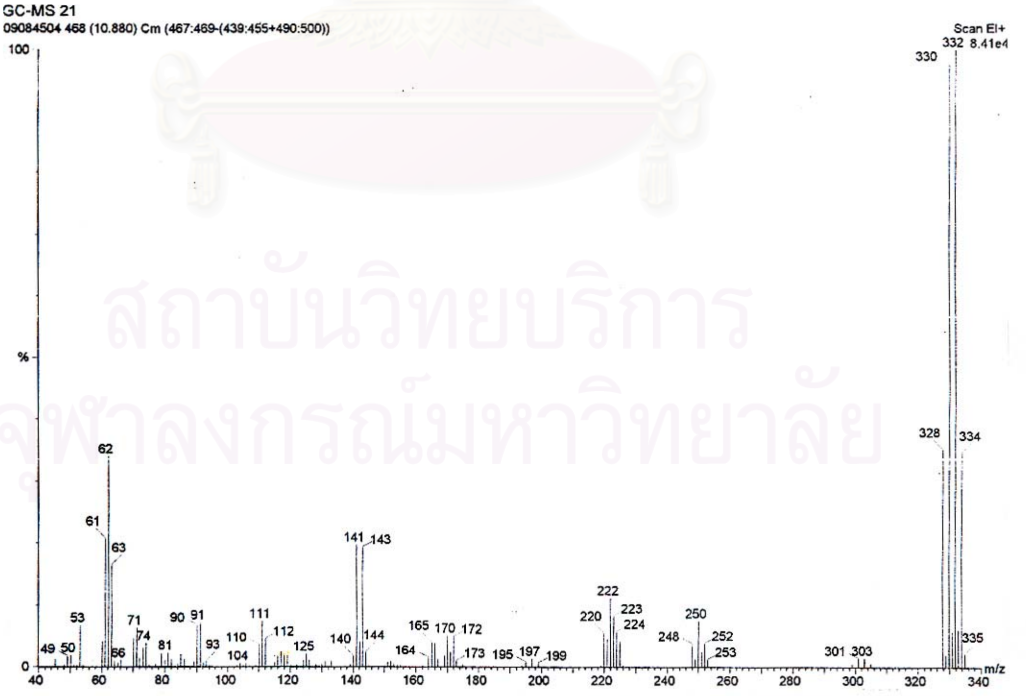

Figure B86 The mass spectrum of mixture 15P at t_R = 10.88 min

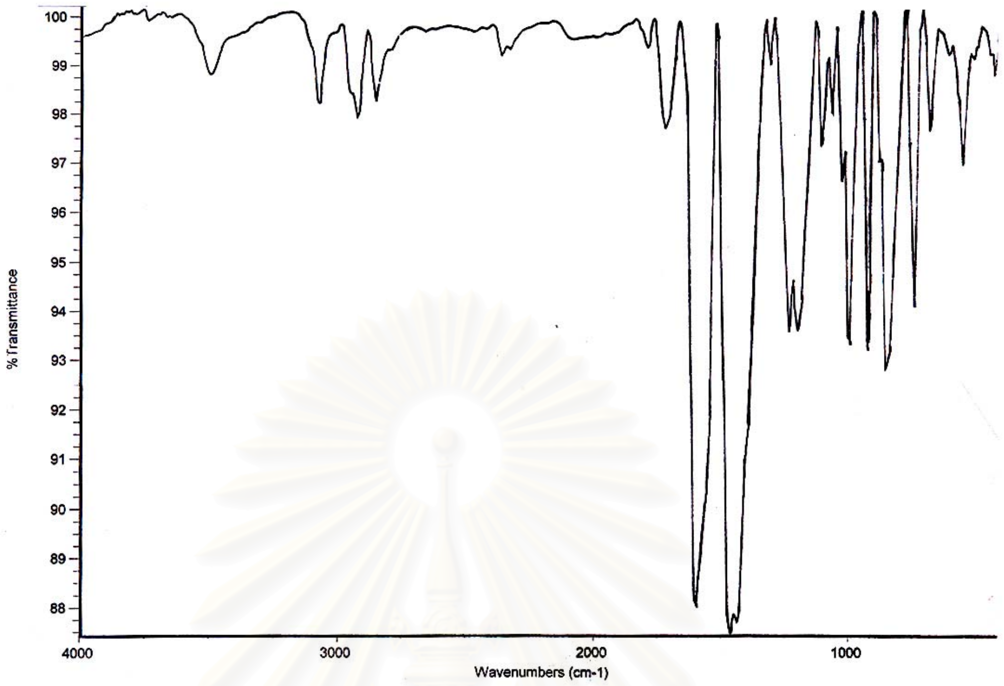

Figure B87 The FTIR spectrum of mixture 16P

(haxane; using mole ratio of substrate and sodium bromide: 1/5)

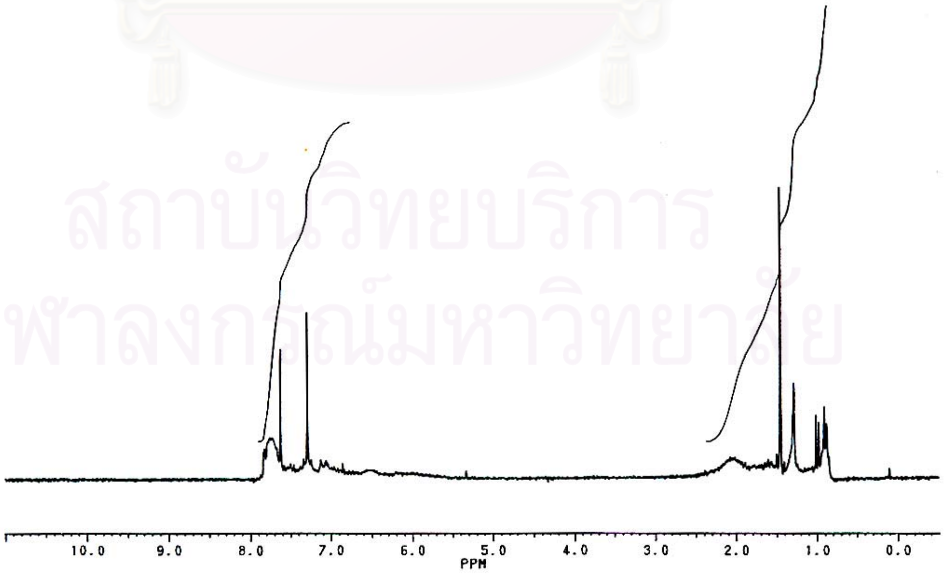

Figure B88 The ^{1}H-NMR spectrum of mixture 16P

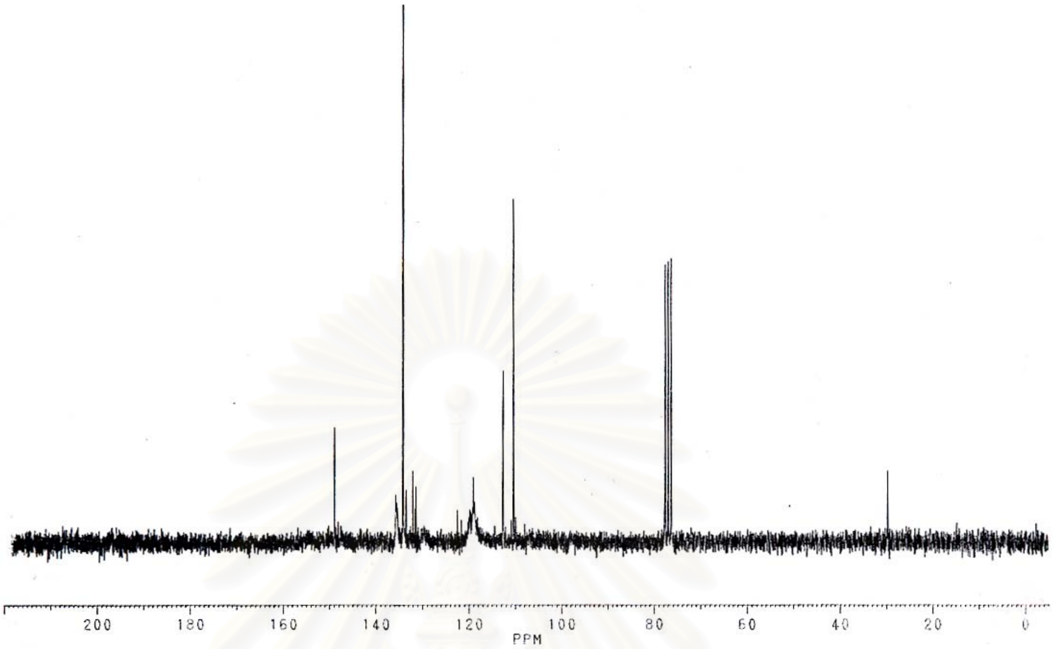

Figure B89 The ^{13}C-NMR spectrum of mixture 16P

Figure B90 The gas chromatogram of mixture 16P

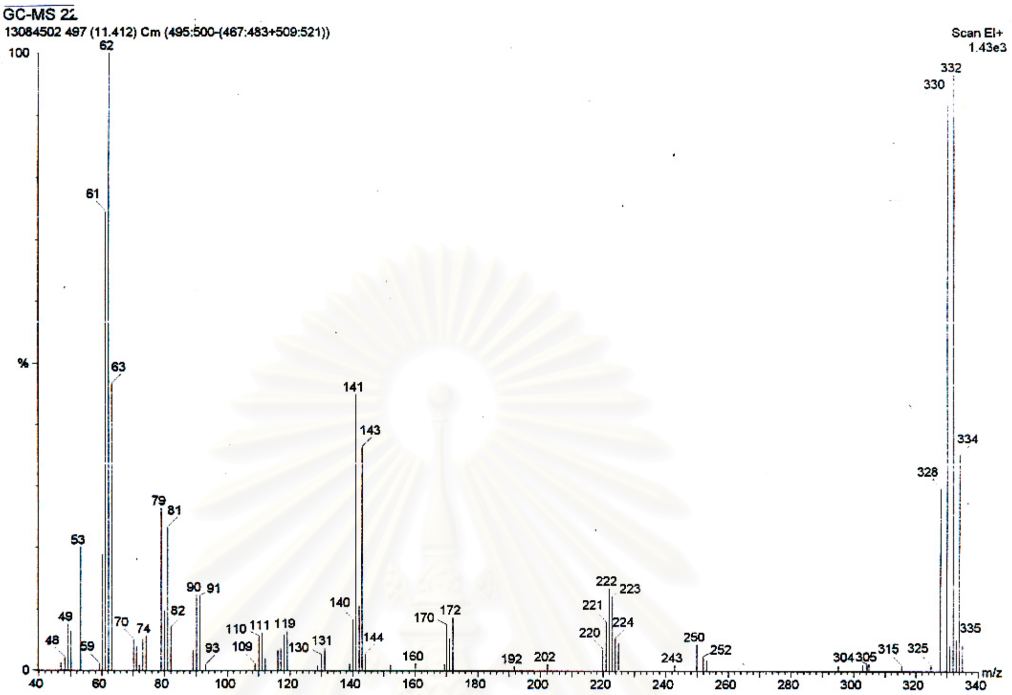

Figure B91 The mass spectrum of mixture 16P at t_R = 11.41 min

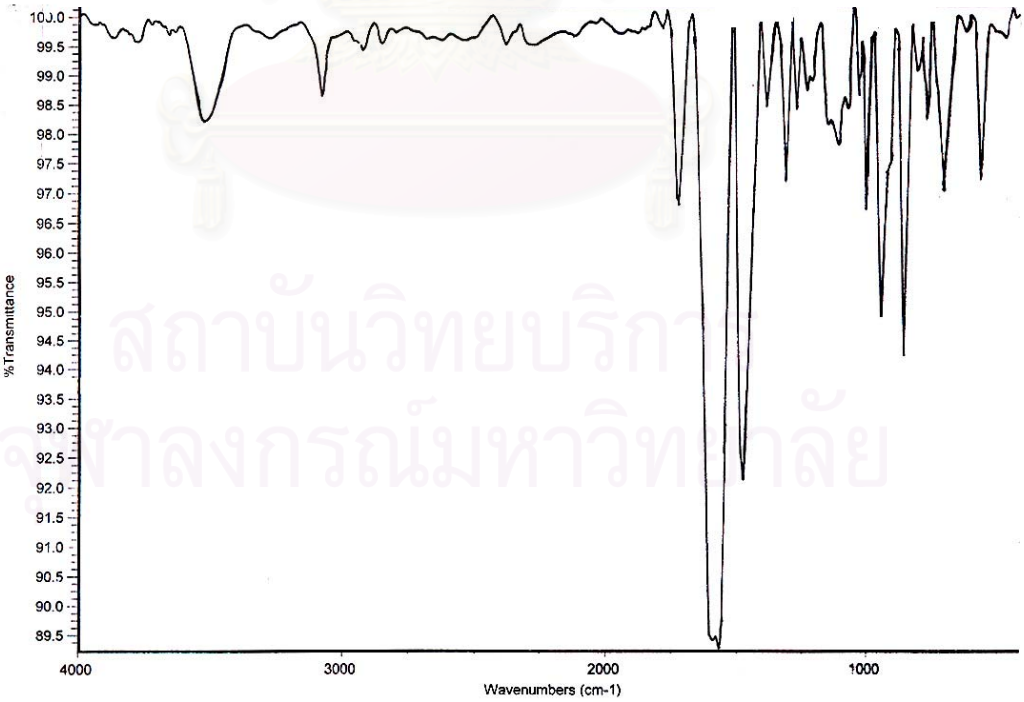

Figure B92 The FTIR spectrum of mixture 17P

(haxane; using mole ratio of substrate and sodium bromide: 1/5 mixed)

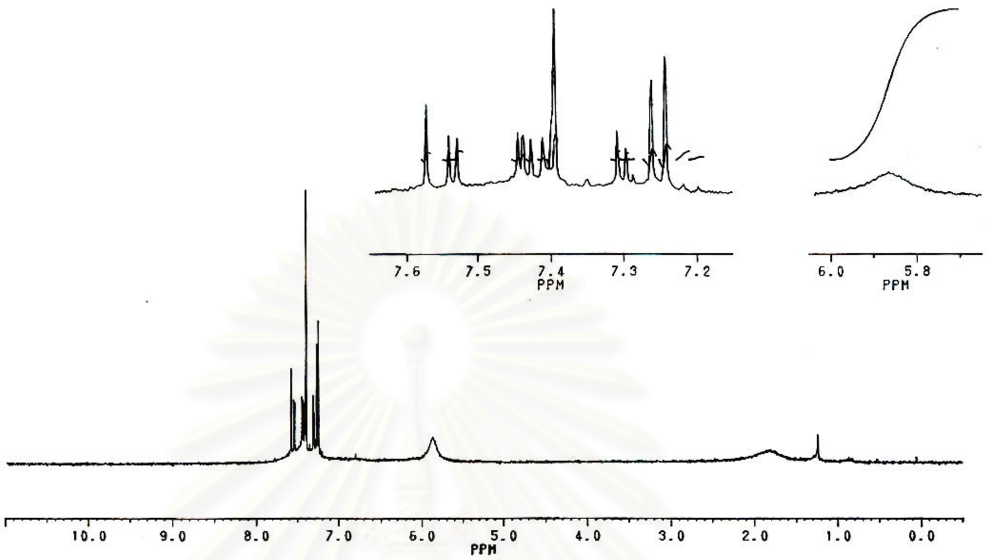

Figure B93 The ^{1}H-NMR spectrum of mixture 17P

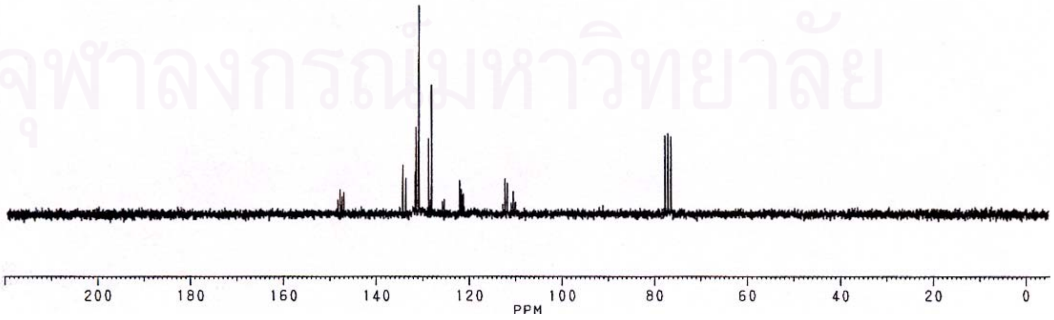

Figure B94 ^{13}C-NMR spectrum of mixture 17P

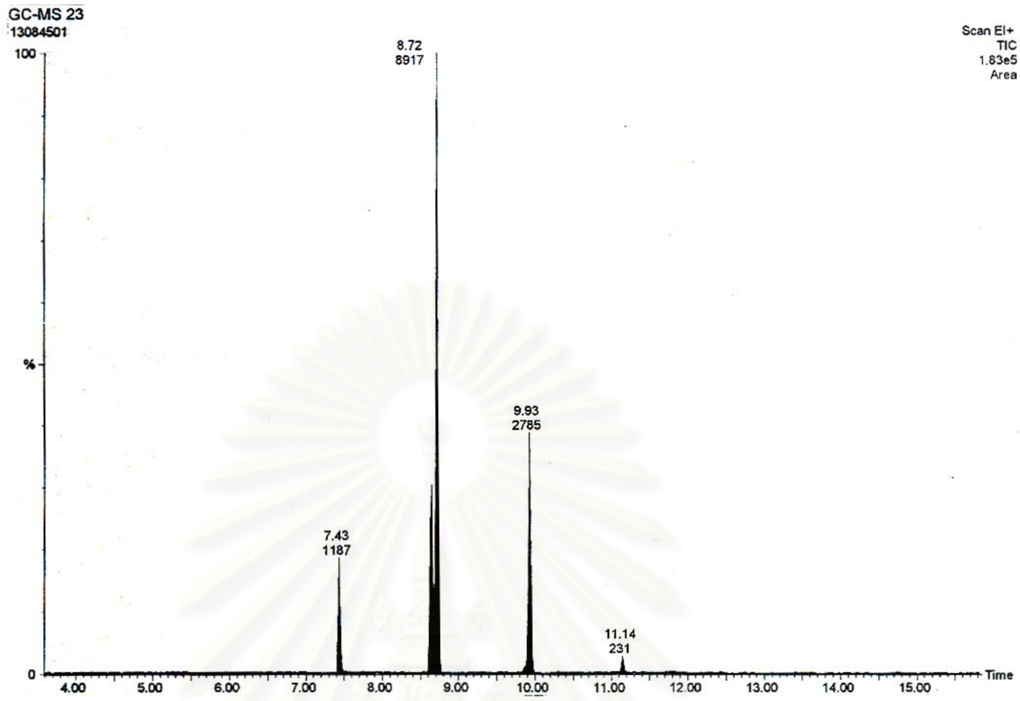

Figure B95 The gas chromatogram of mixture 17P

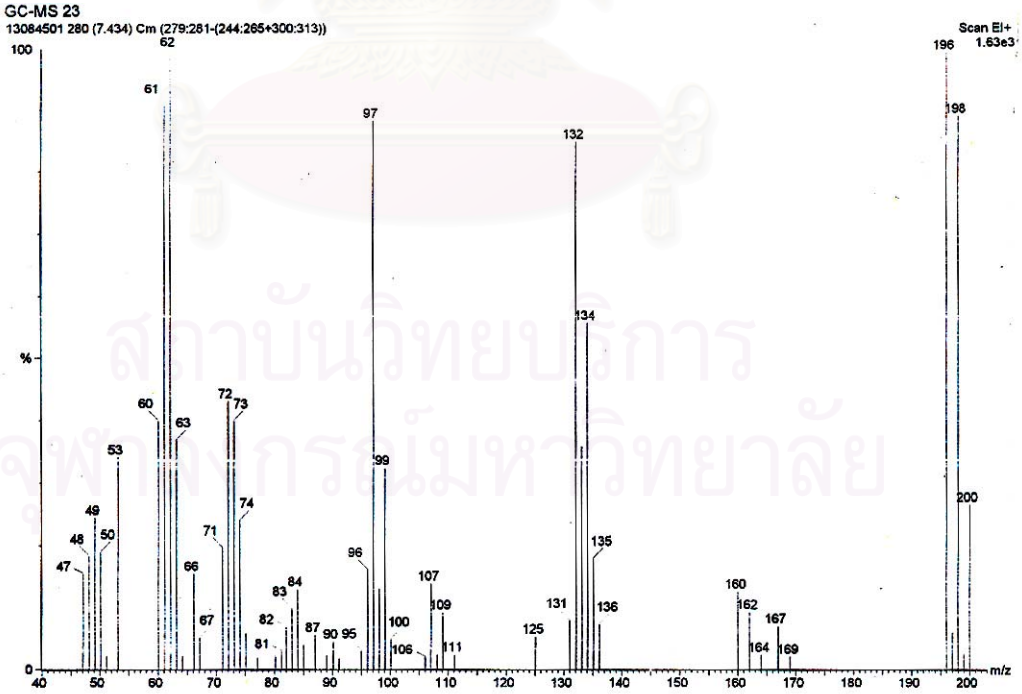

Figure B96 The mass spectrum of mixture 17P at t_R = 7.43 min

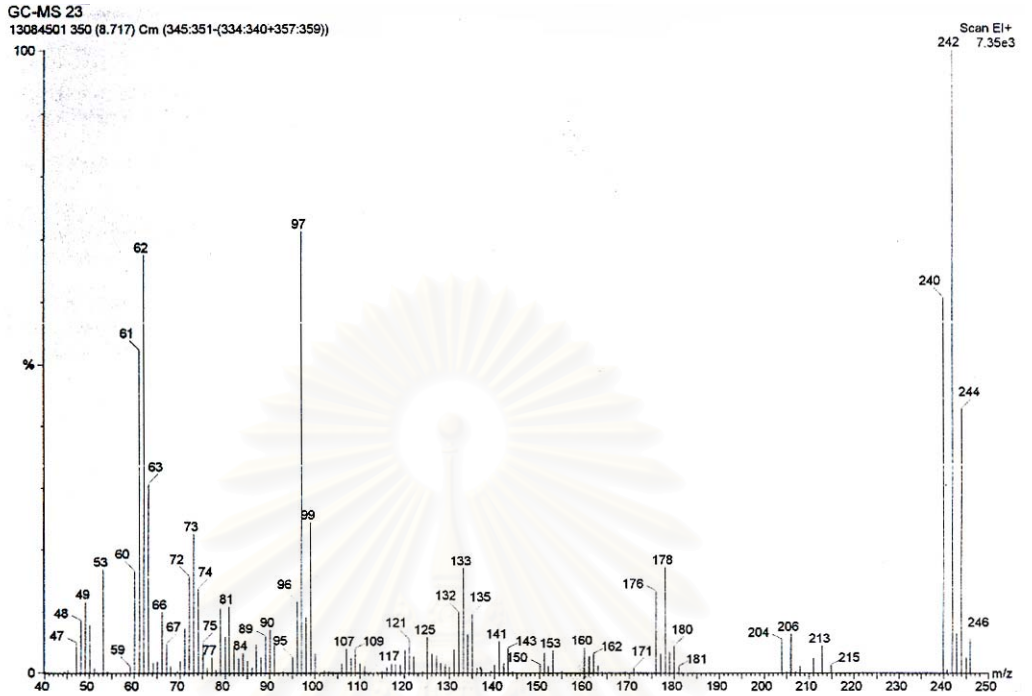

Figure B97 The mass spectrum of mixture 17P at t_R = 8.72 min

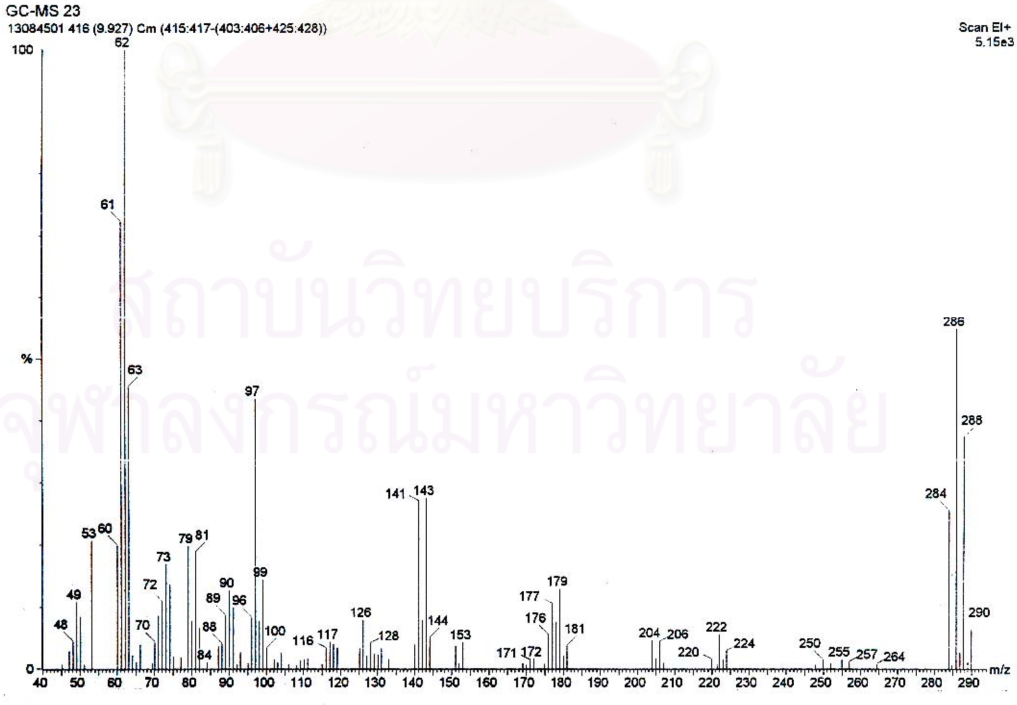

Figure B98 The mass spectrum of mixture 17P at t_R = 9.93 min

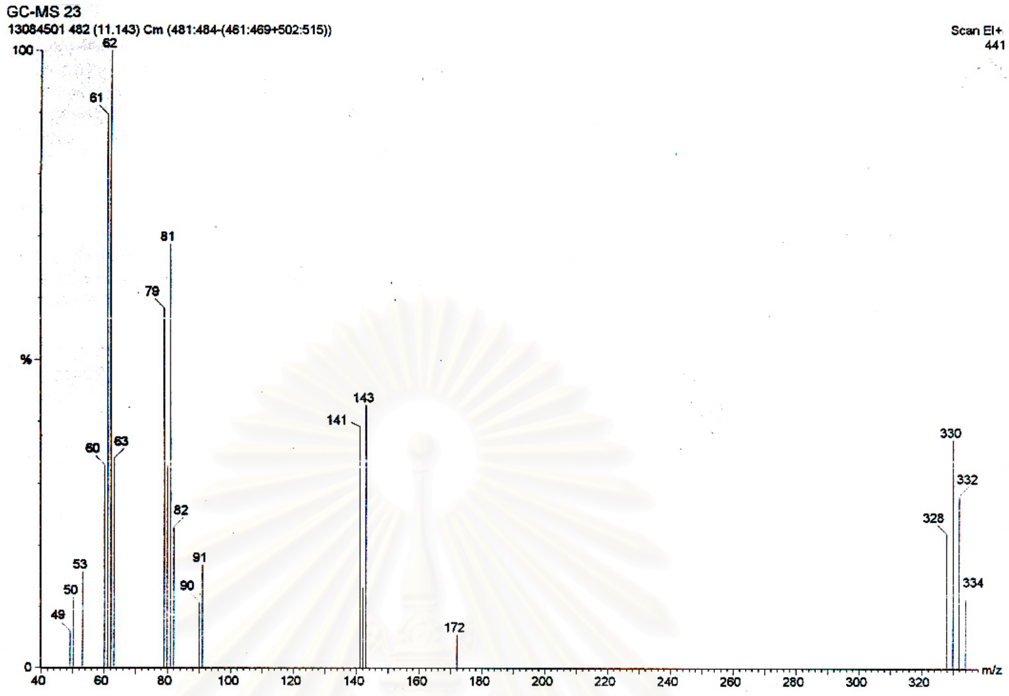

Figure B99 The mass spectrum of mixture 17P at t_R = 11.14 min

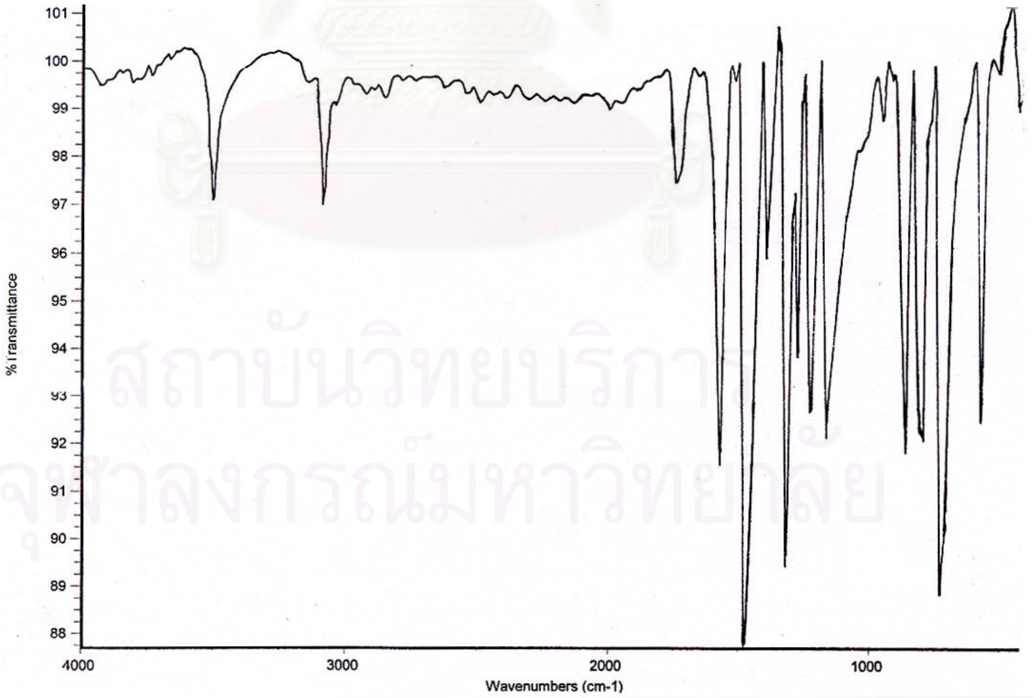

Figure B100 The FTIR spectrum of mixture 18P

(no organic solvent; using mole ratio of substrate and sodium hypochlorite: 1/8)

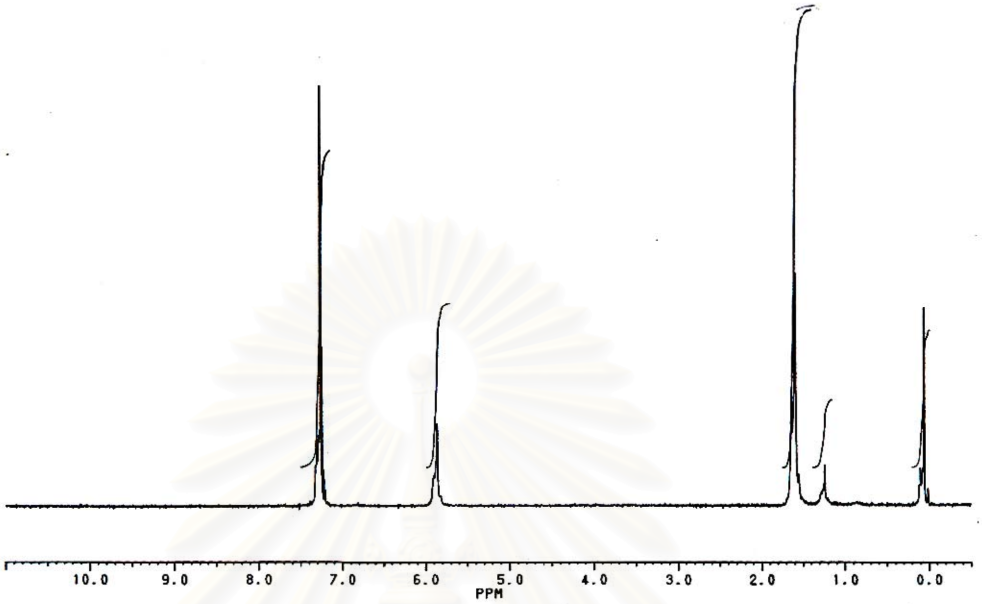

Figure B101 The ^{1}H-NMR spectrum of mixture 18P

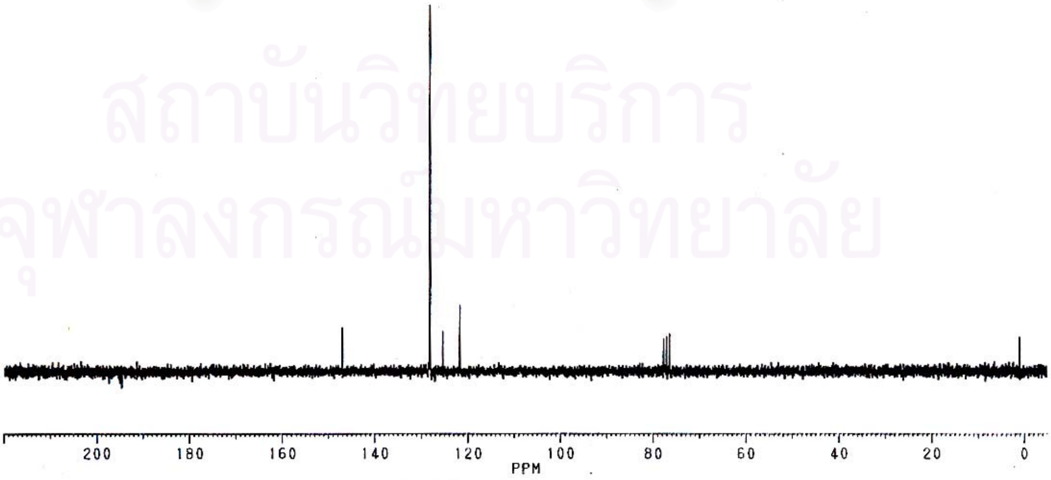

Figure A102 The ^{13}C-NMR spectrum of mixture 18P

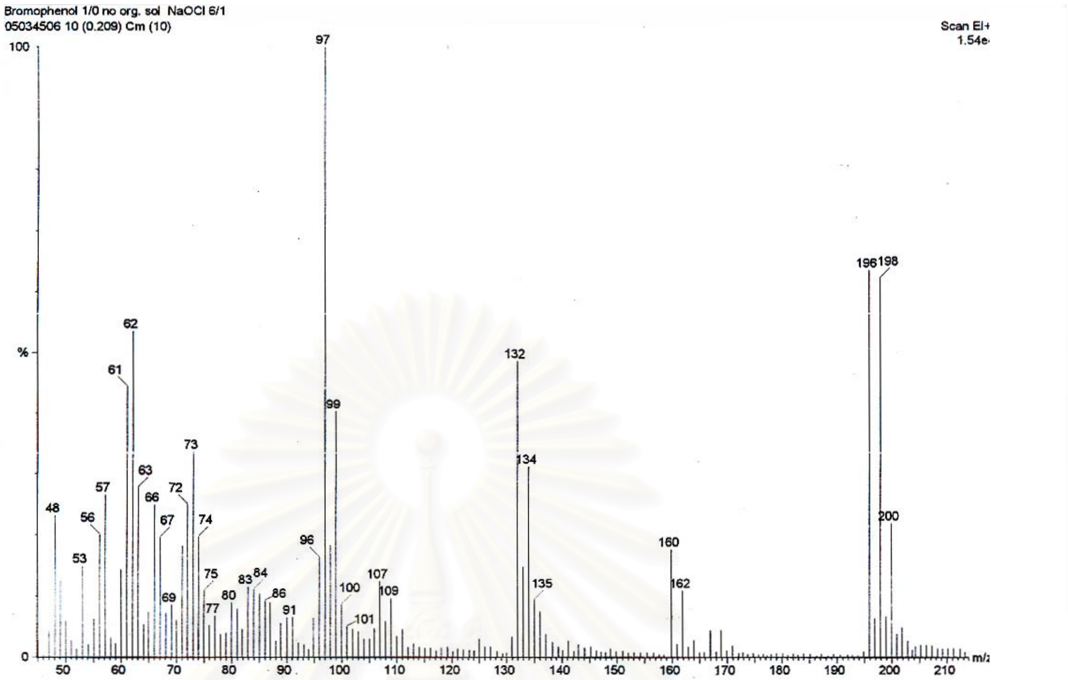

Figure B103 The mass spectrum of mixture 18P

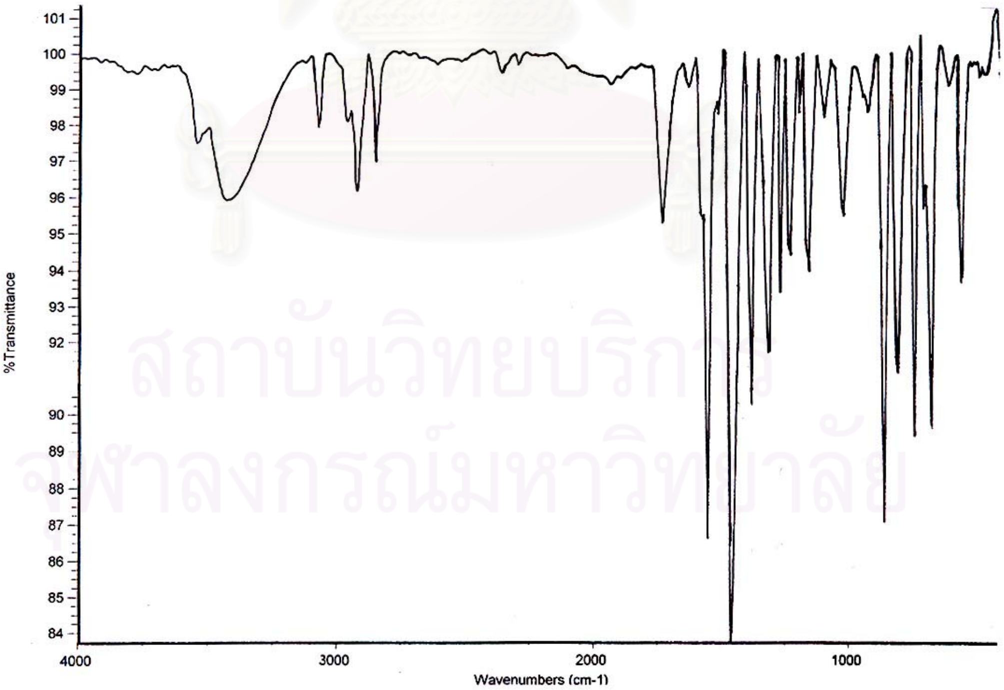

Figure B104 The FTIR spectrum of mixture 19P

(using mole ratio of substrate and sodium hypochlorite: 1/1)

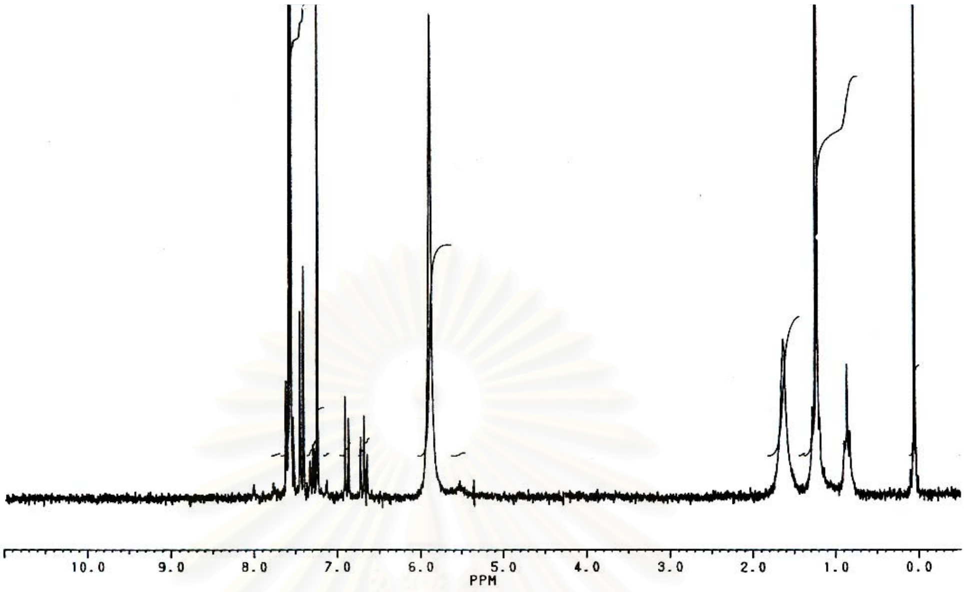

Figure B105 The ^{1}H-NMR spectrum of mixture 19P

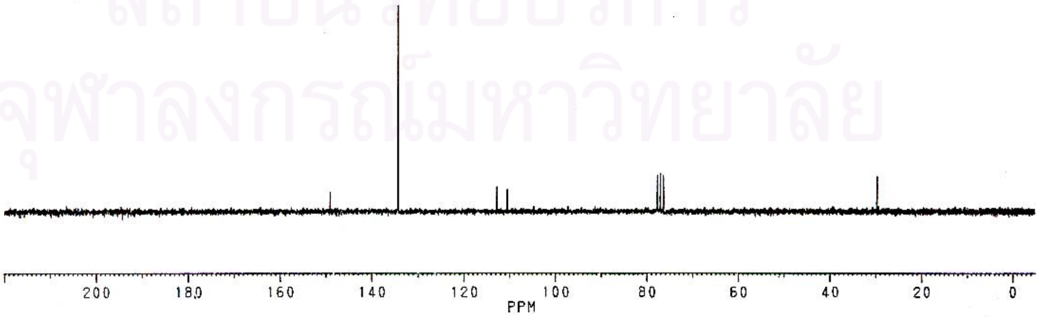

Figure B106 ^{13}C-NMR spectrum of mixture 19P

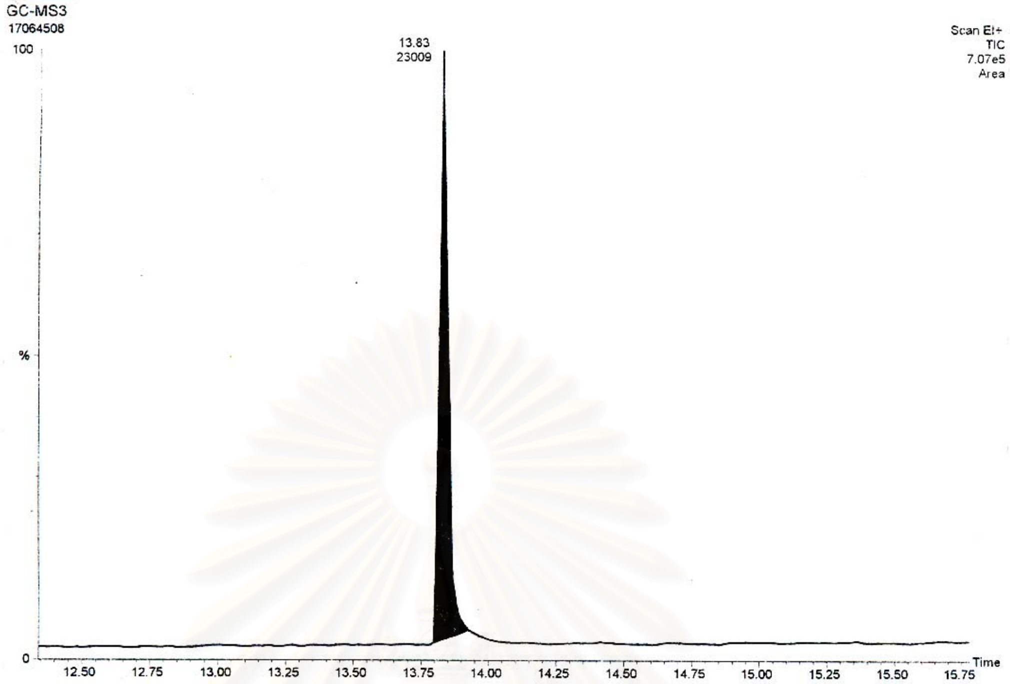

Figure B107 The gas chromatogram of mixture 19P

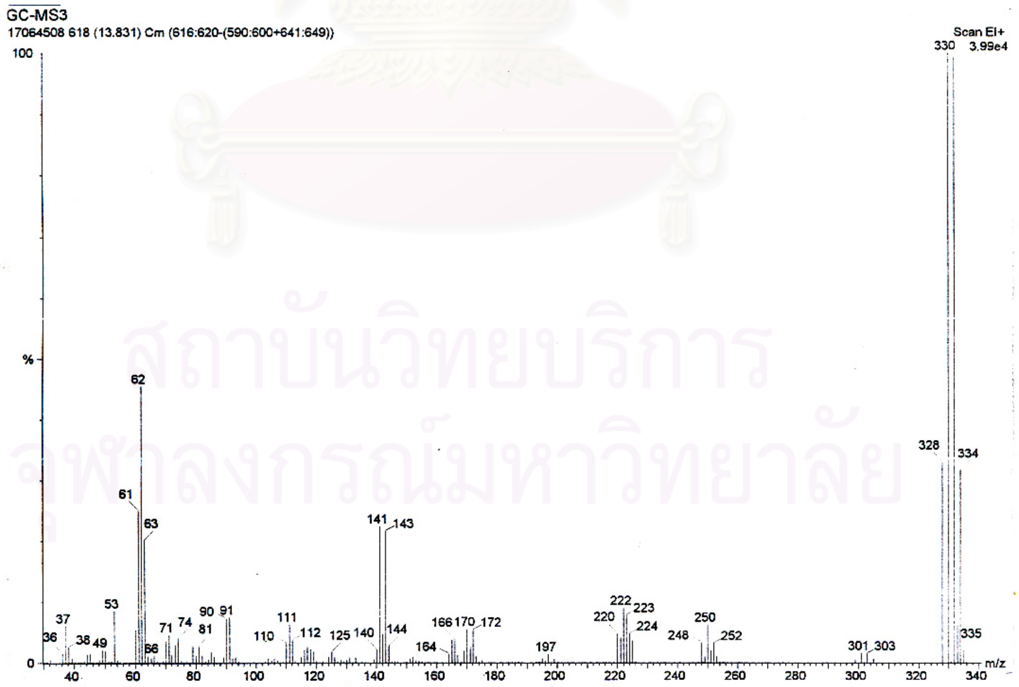

Figure B108 The mass spectrum of mixture 19P at t_R = 13.83 min

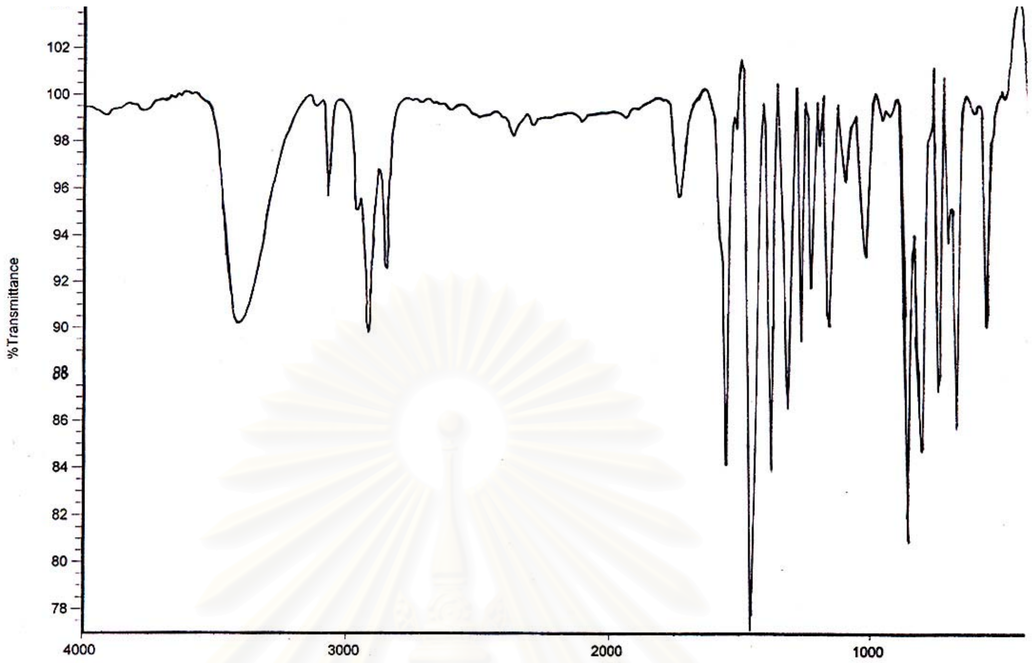

Figure B109 The FTIR spectrum of mixture 20P

(using mole ratio of substrate and sodium hypochlorite: 1/2)

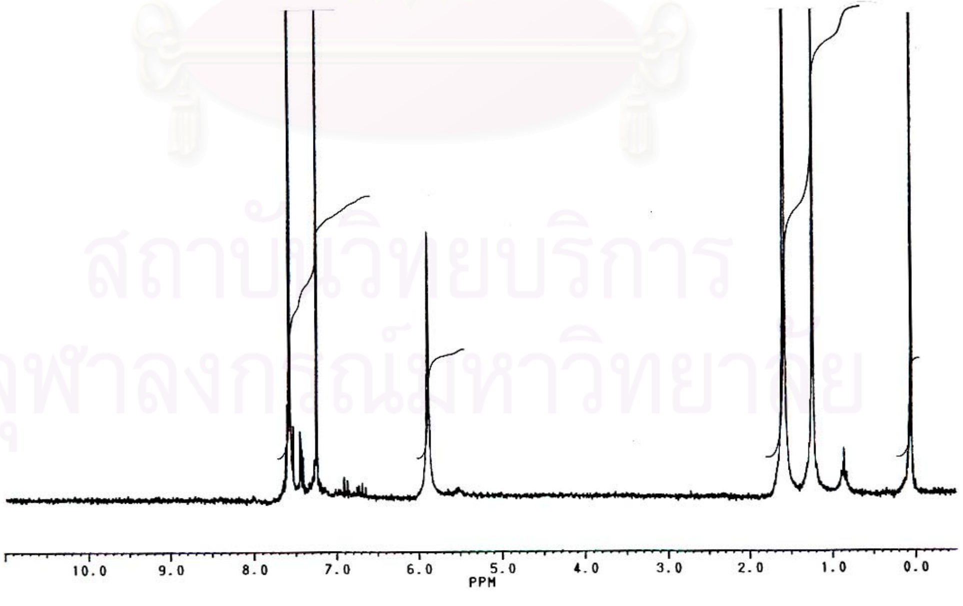

Figure B110 The ^{1}H-NMR spectrum of mixture 20P

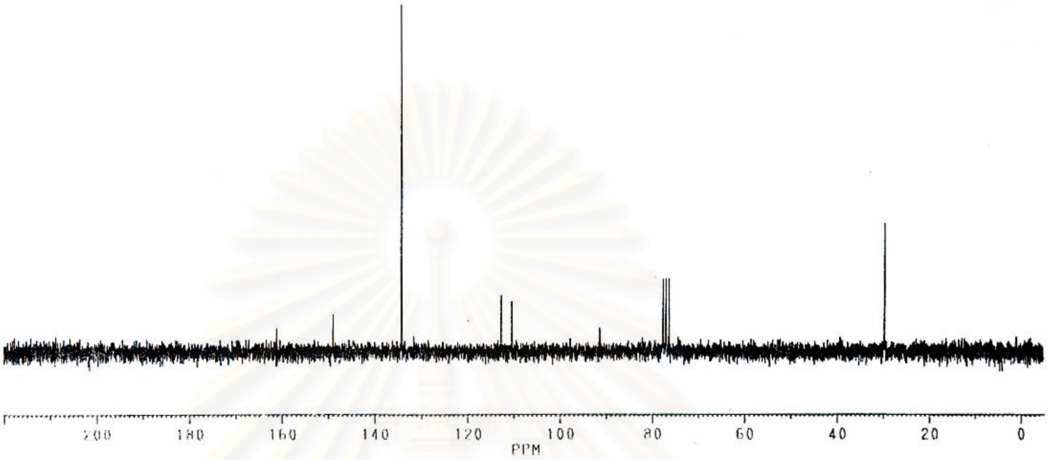

Figure B111 ^{13}C-NMR spectrum of mixture 20P

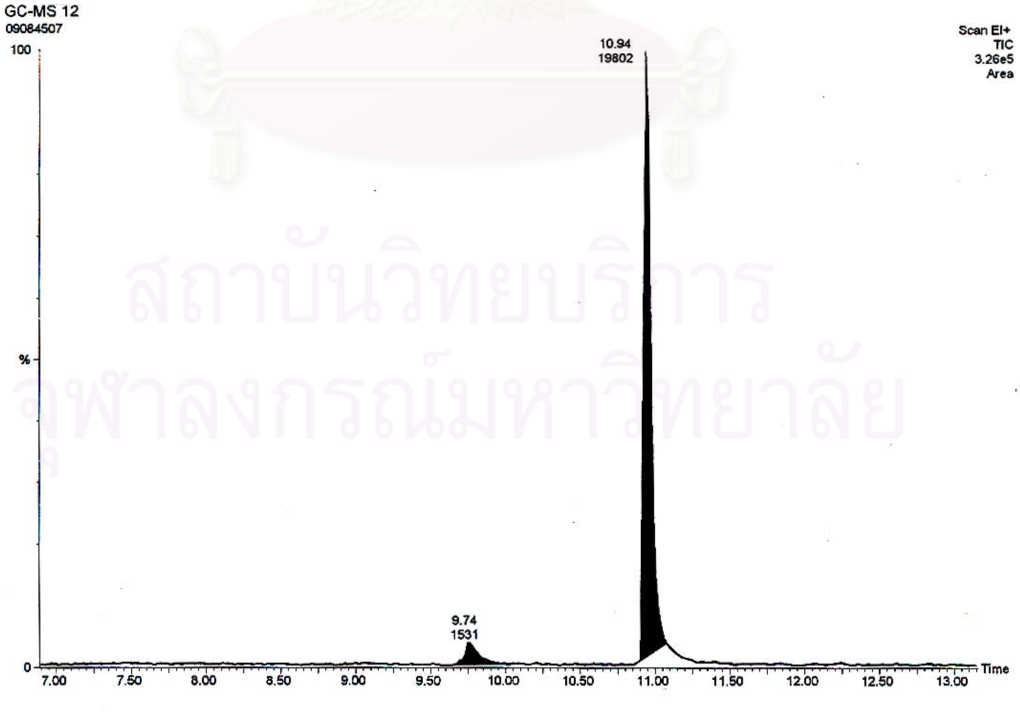

Figure B112 The gas chromatogram of mixture 20P

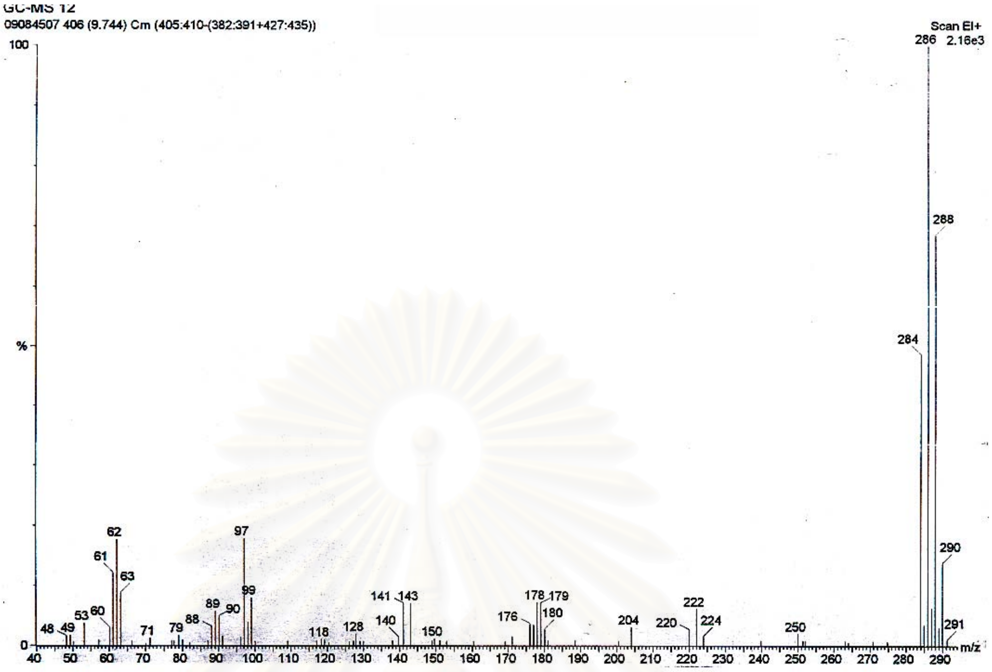

Figure B113 The mass spectrum of mixture 20P at t_R = 9.74 min

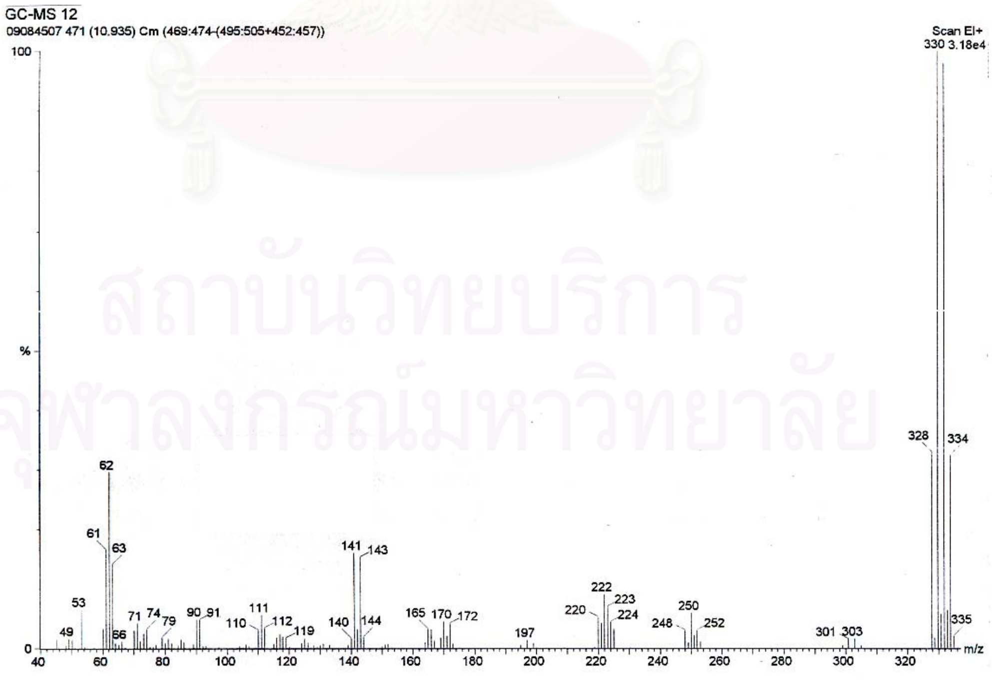

Figure B114 The mass spectrum of mixture 20P at t_R = 10.94 min

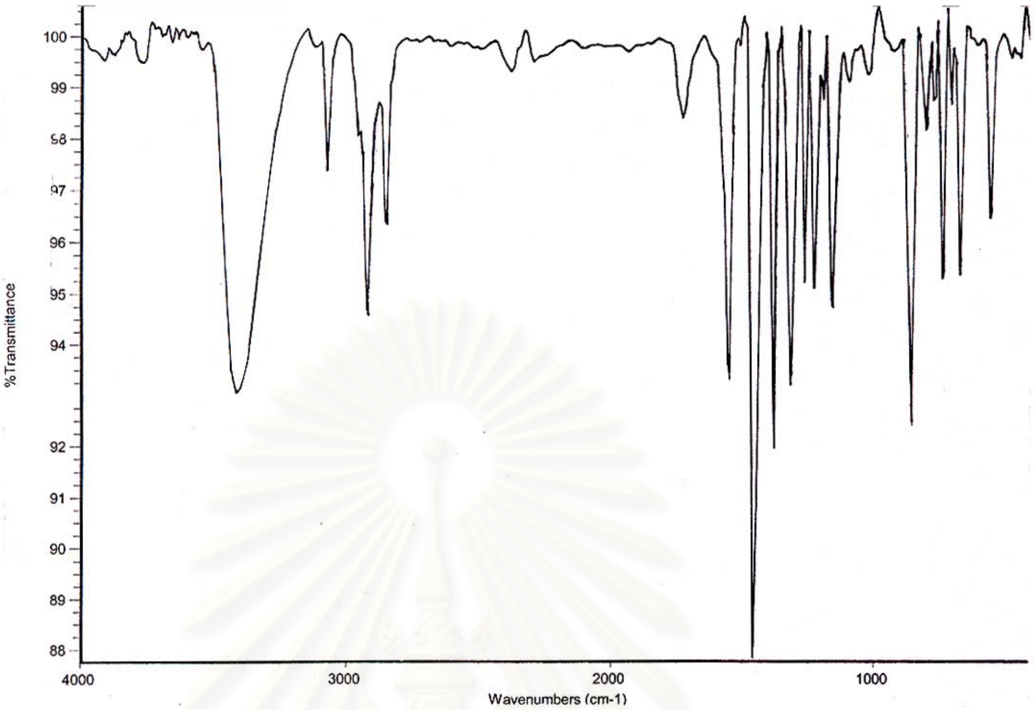

Figure B115 The FTIR spectrum of mixture 21P

(using mole ratio of substrate and sodium hypochlorite: 1/3)

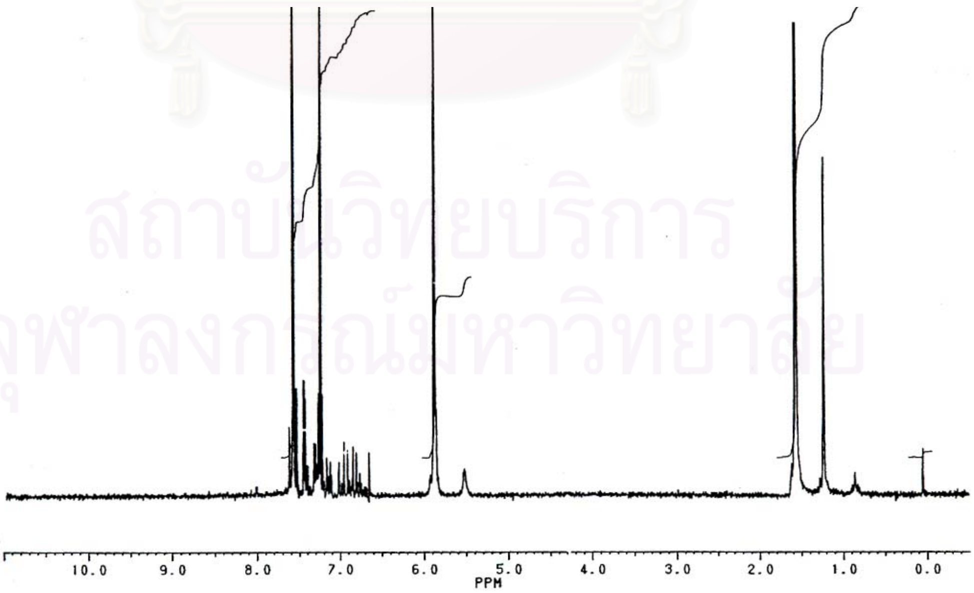

Figure B116 The ^{1}H-NMR spectrum of mixture 21P

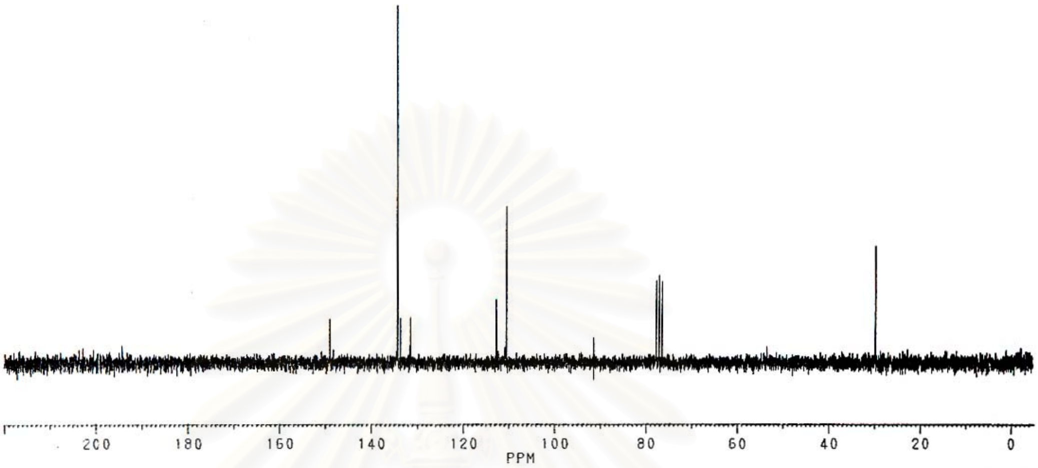

Figure B117 The ^{13}C-NMR spectrum of mixture 21P

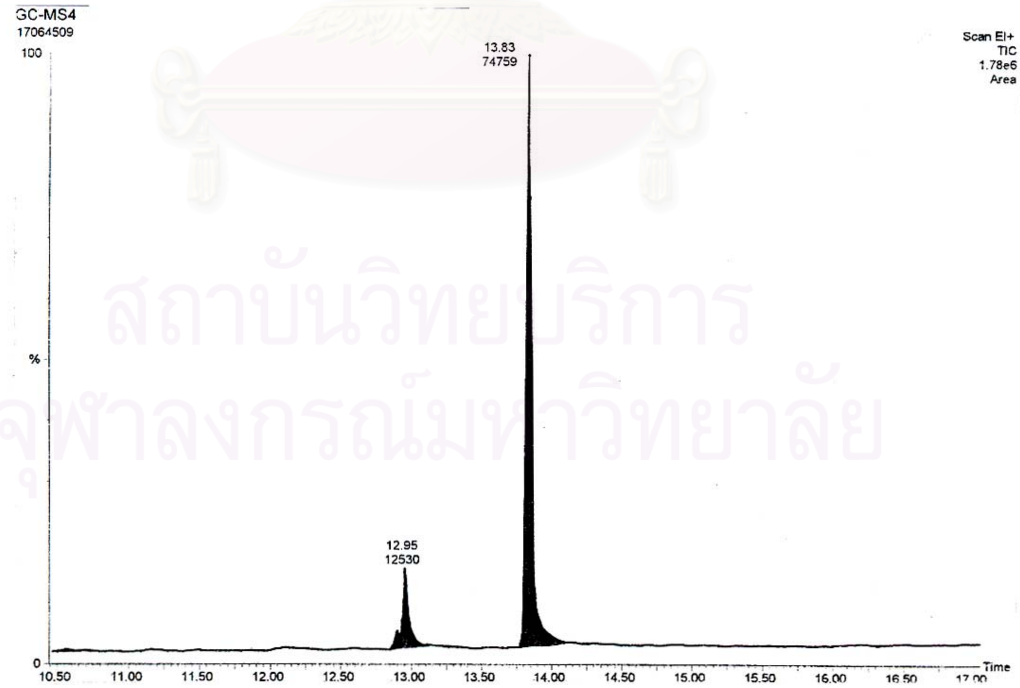

Figure B118 The gas chromatogram of mixture 21P

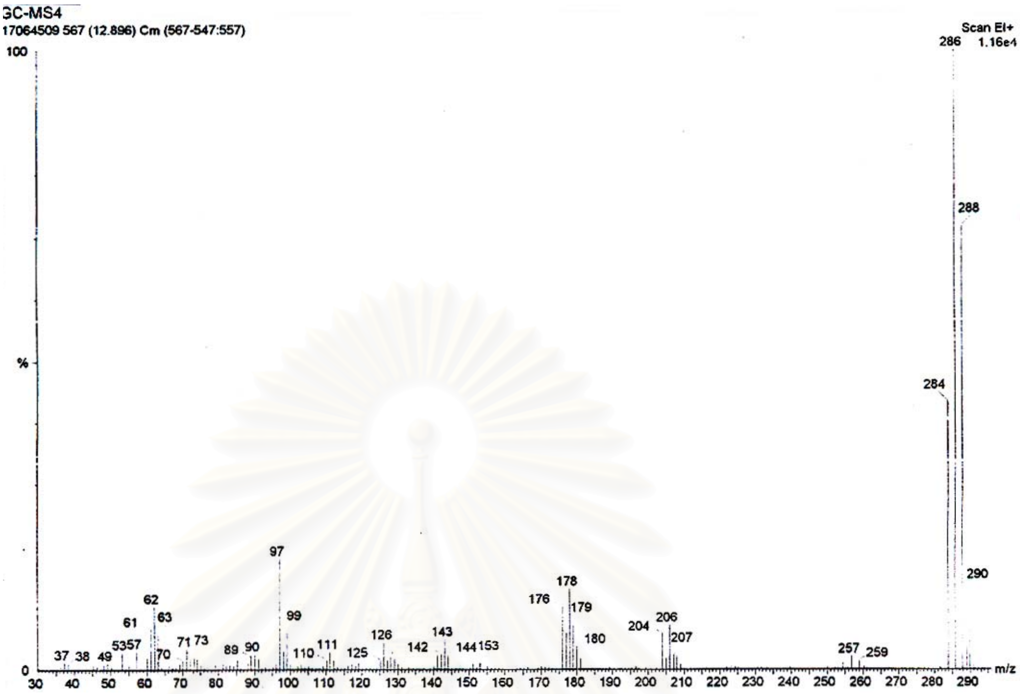

Figure B119 The mass spectrum of mixture 21P at t_R = 12.90 min

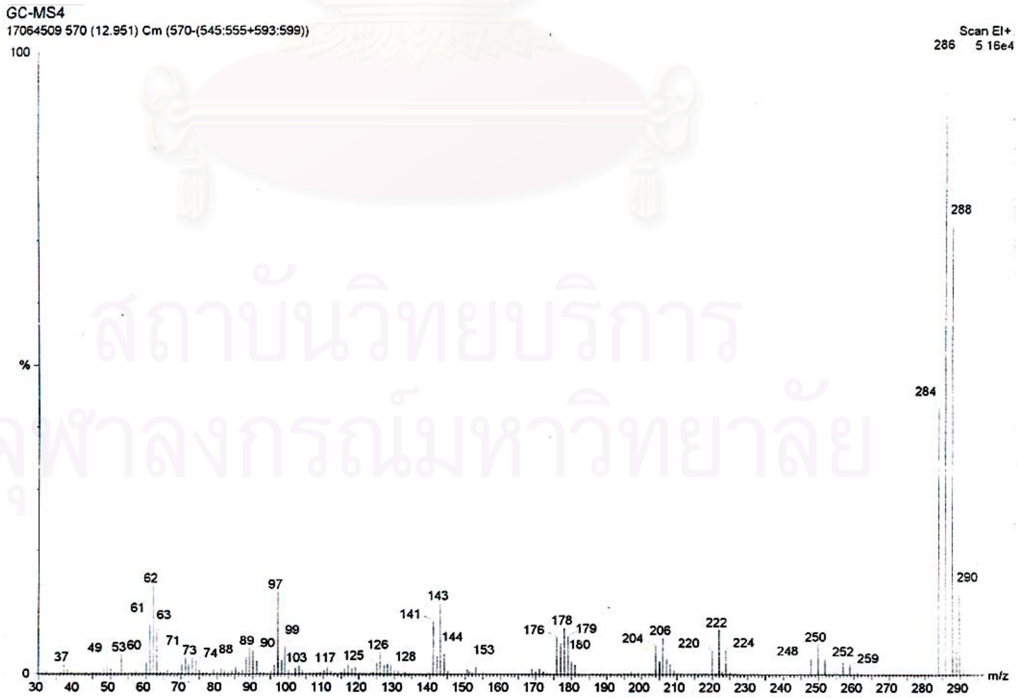

Figure B120 The mass spectrum of mixture 21P at t_R = 12.95 min

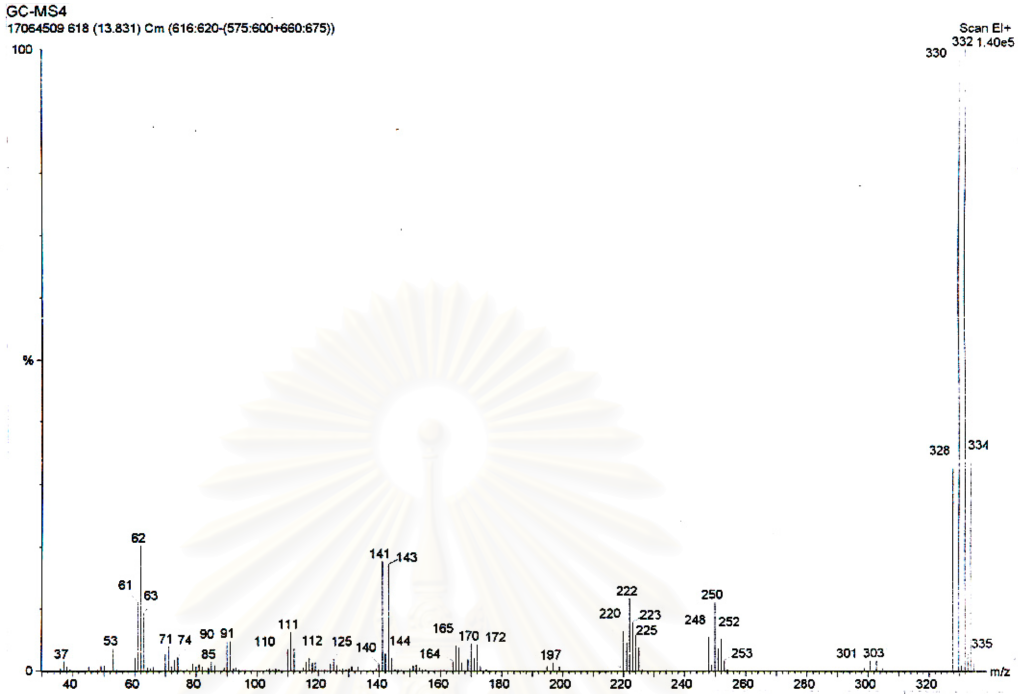

Figure B121 The mass spectrum of mixture 21P at t_R = 13.83 min

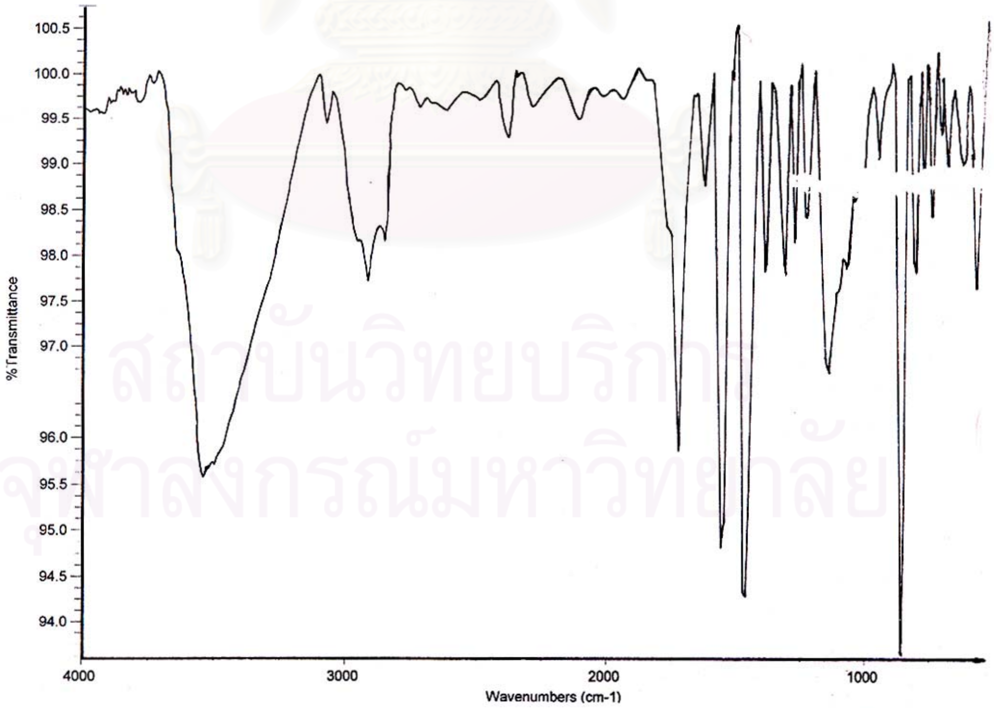

Figure B122 The FTIR spectrum of mixture 22P

(using mole ratio of substrate and sodium hypochlorite: 1/4)

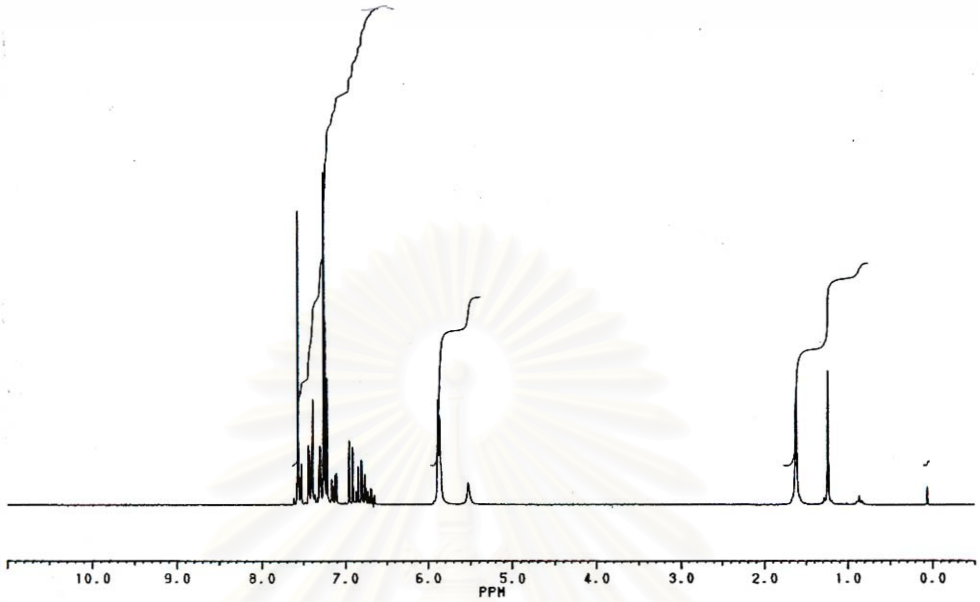

Figure B123 The ^{1}H-NMR spectrum of mixture 22P

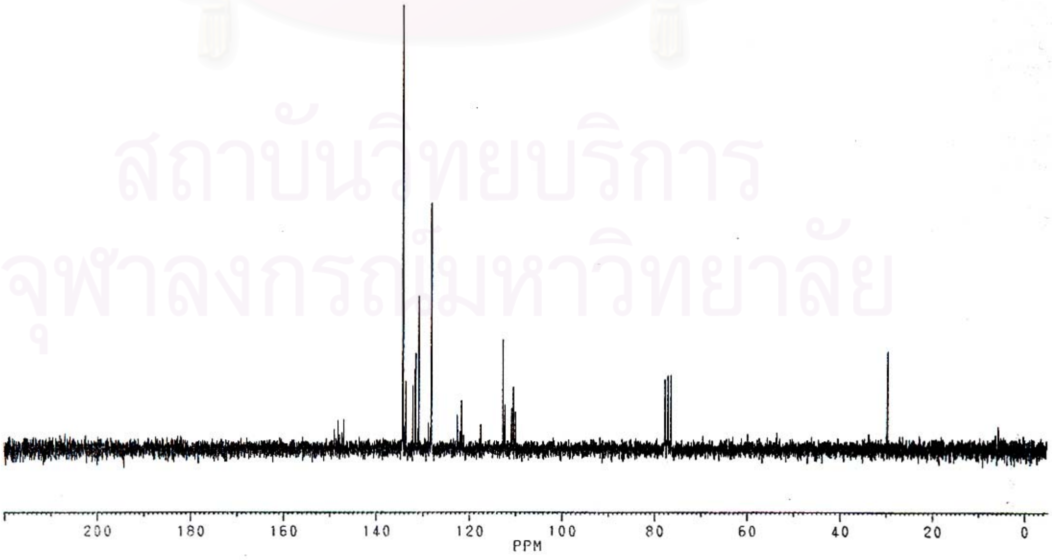

Figure B124 The ^{13}C-NMR spectrum of mixture 22P

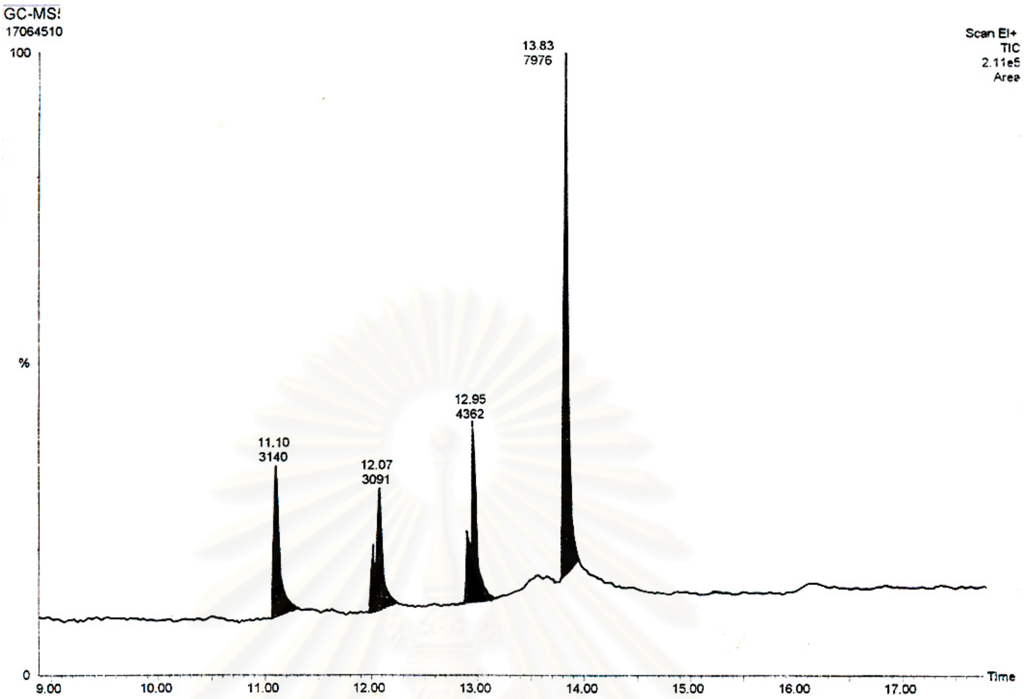

Figure B125 The gas chromatogram of mixture 22P

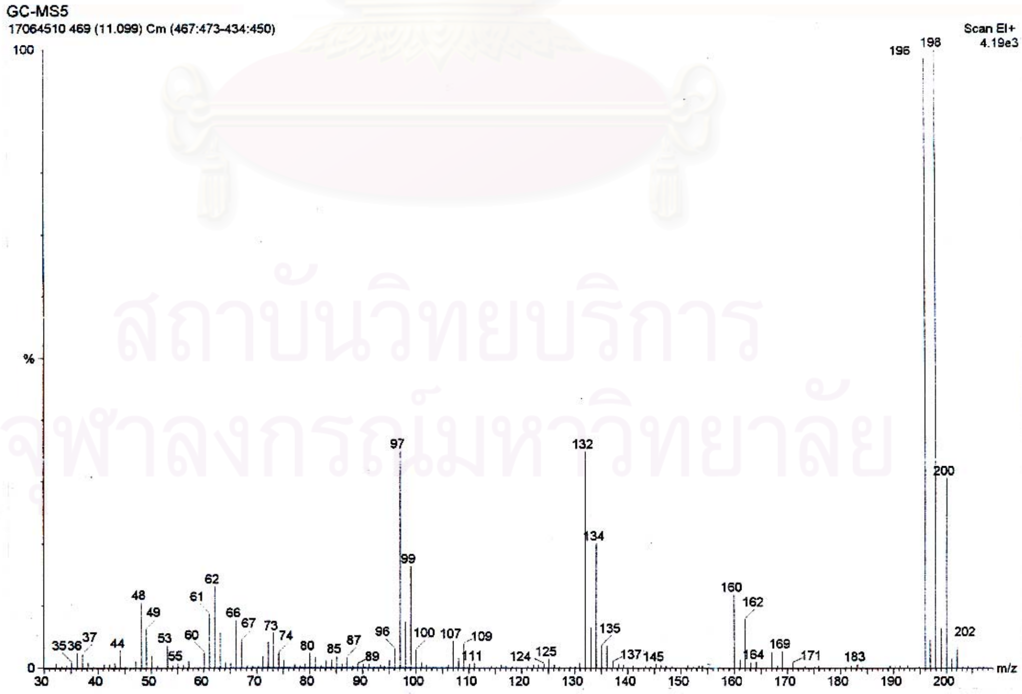

Figure B126 The mass spectrum of mixture 22P at t_R = 11.10 min

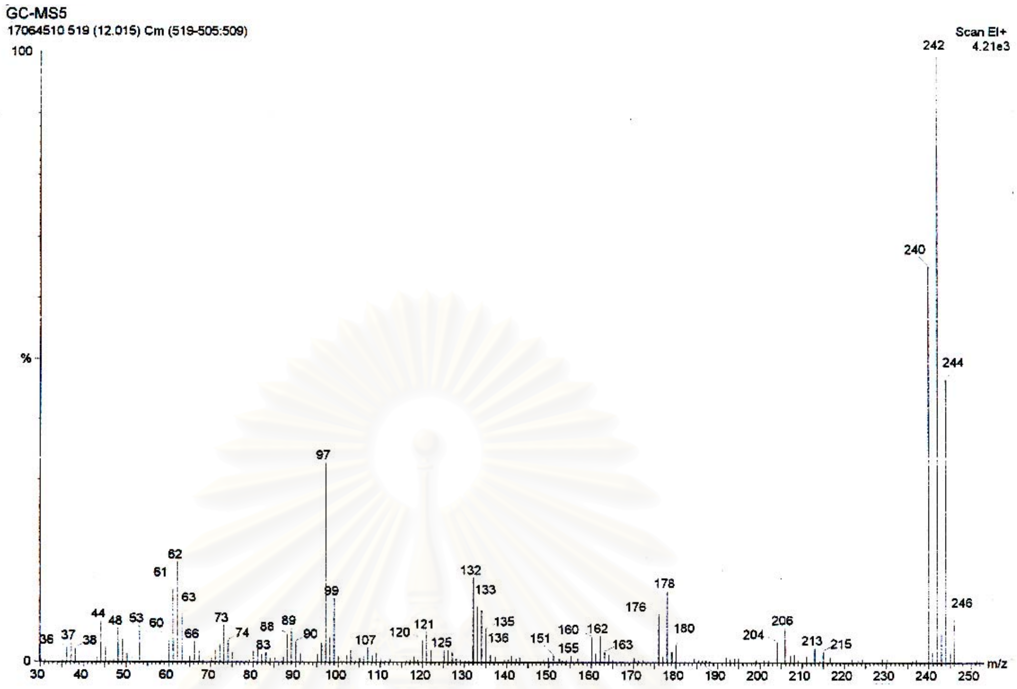

Figure B127 The mass spectrum of mixture 22P at t_R = 12.02 min

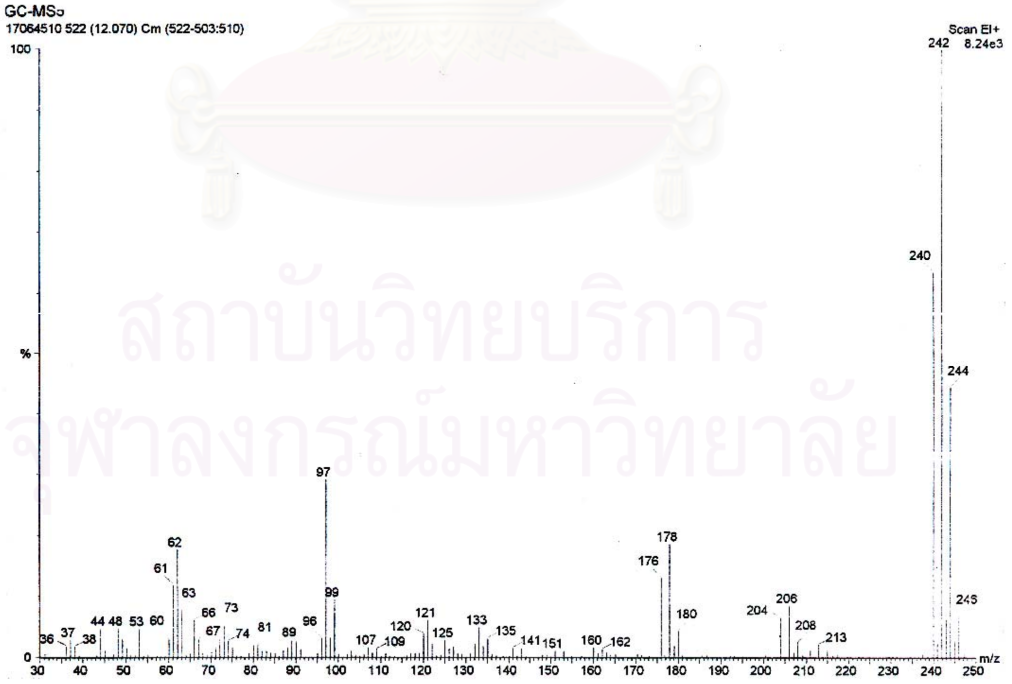

Figure B128 The mass spectrum of mixture 22P at t_R = 12.07 min

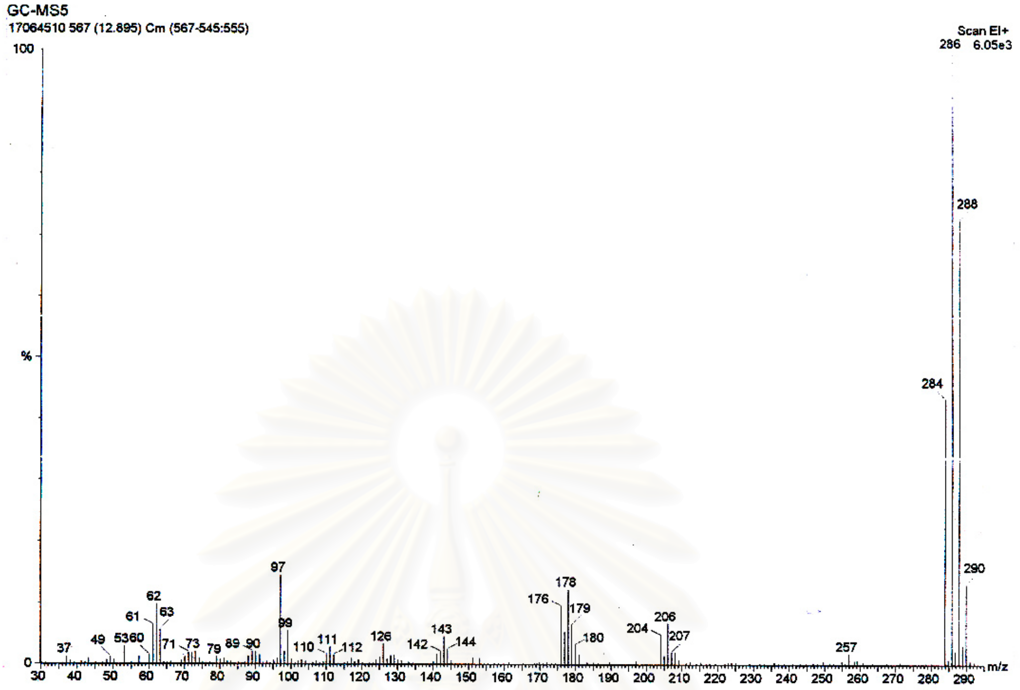

Figure B129 The mass spectrum of mixture 22P at t_R = 12.90 min

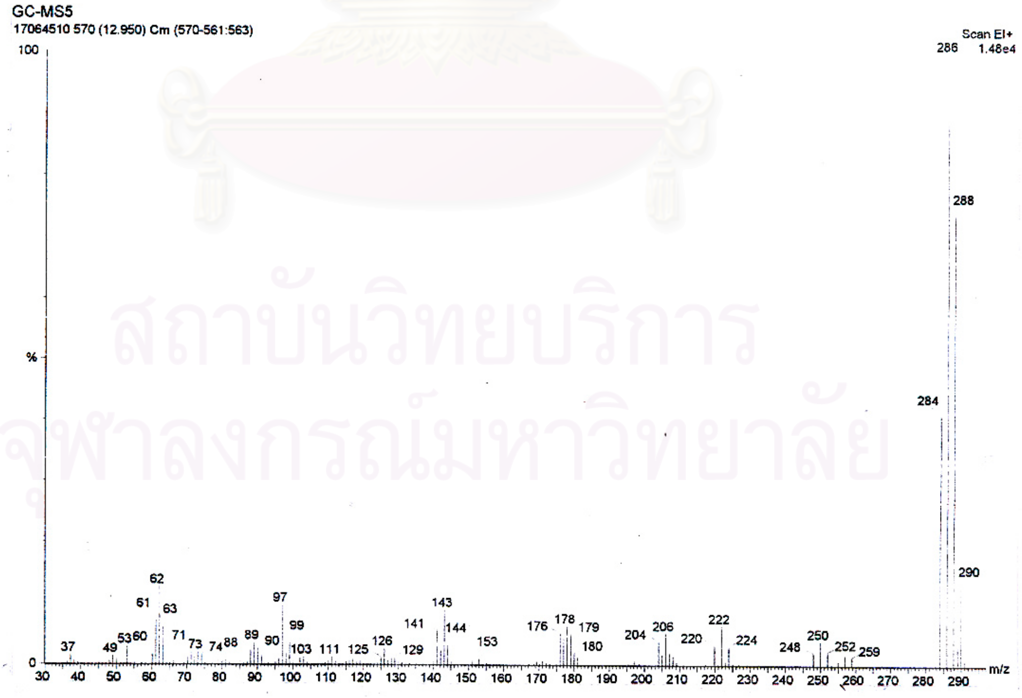

Figure B130 The mass spectrum of mixture 22P at t_R = 12.95 min

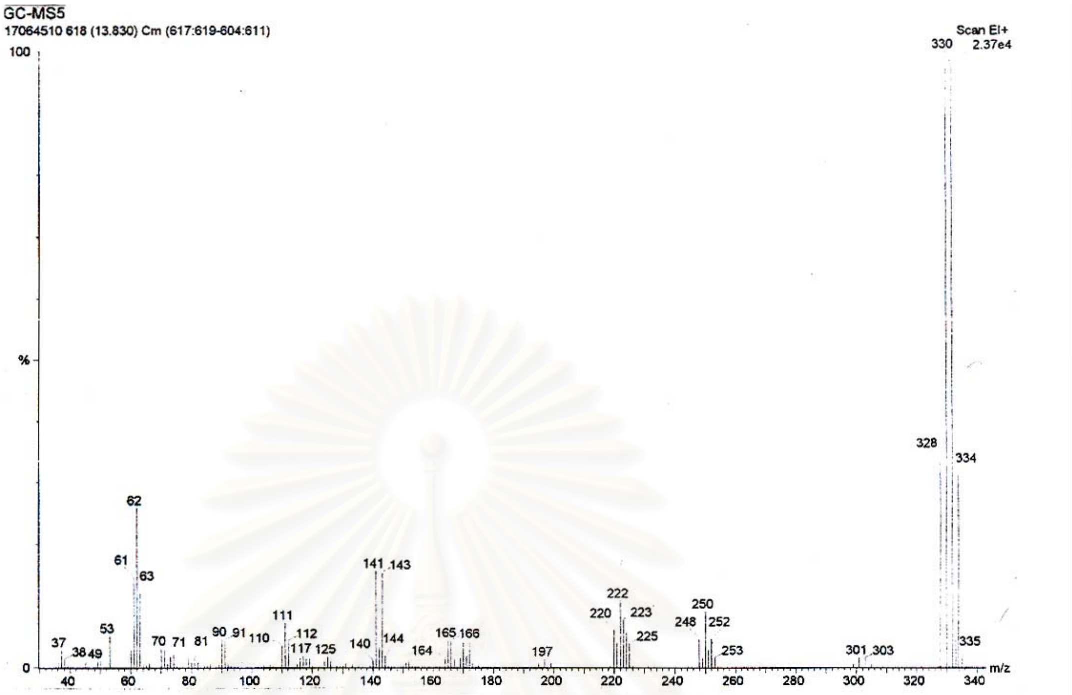

Figure B131 The mass spectrum of mixture 22P at t_R = 13.83 min

APPENDIX C

SPECTRA OF TOLUENE DERIVATIVES

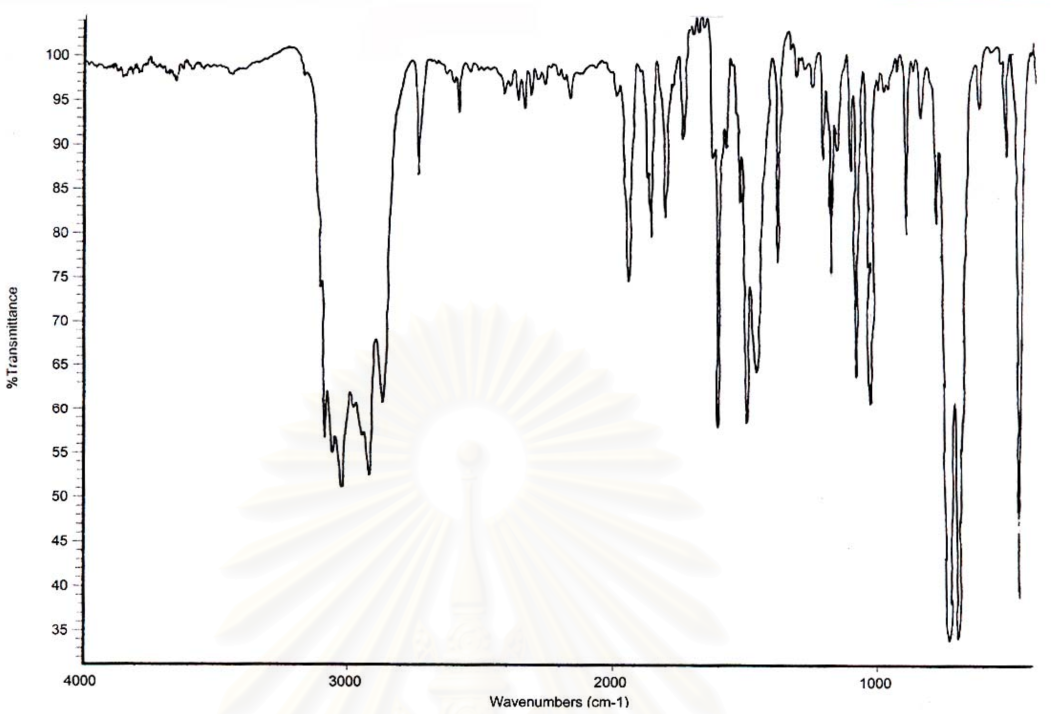

Figure C1 The FTIR spectrum of toluene

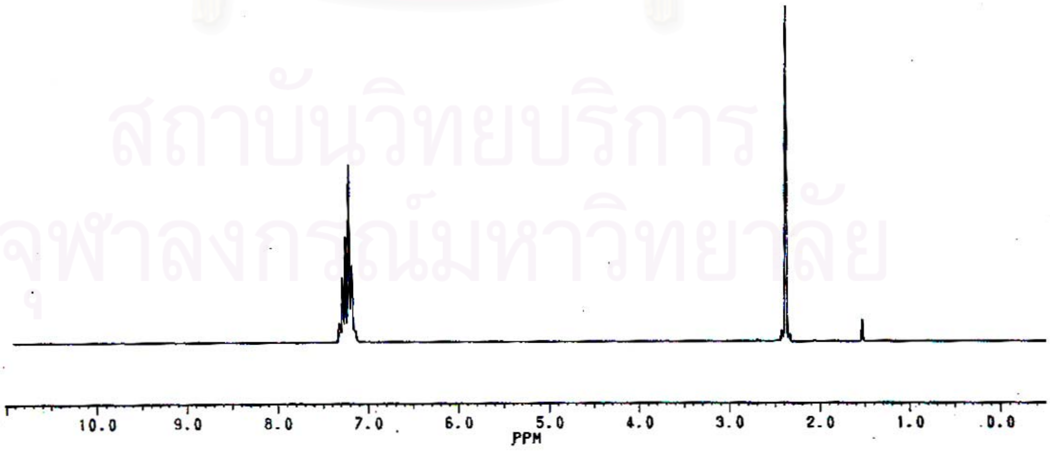

Figure C2 The ^{1}H-NMR spectrum of toluene

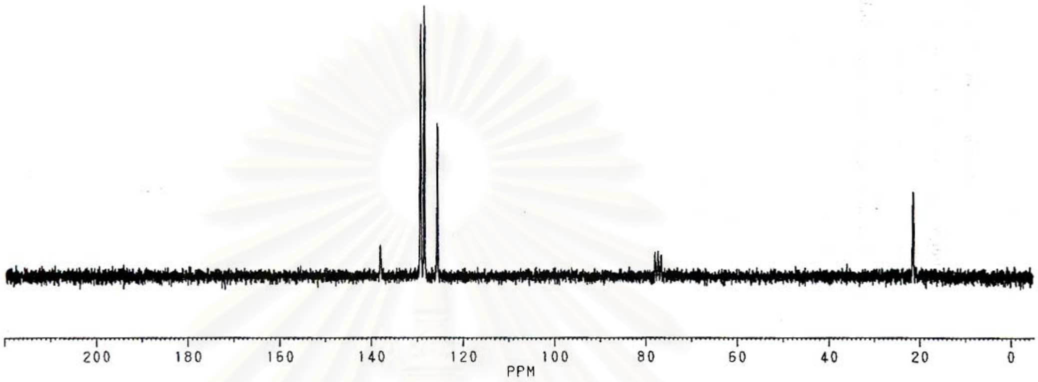

Figure C3 The ^{13}C-NMR spectrum of toluene

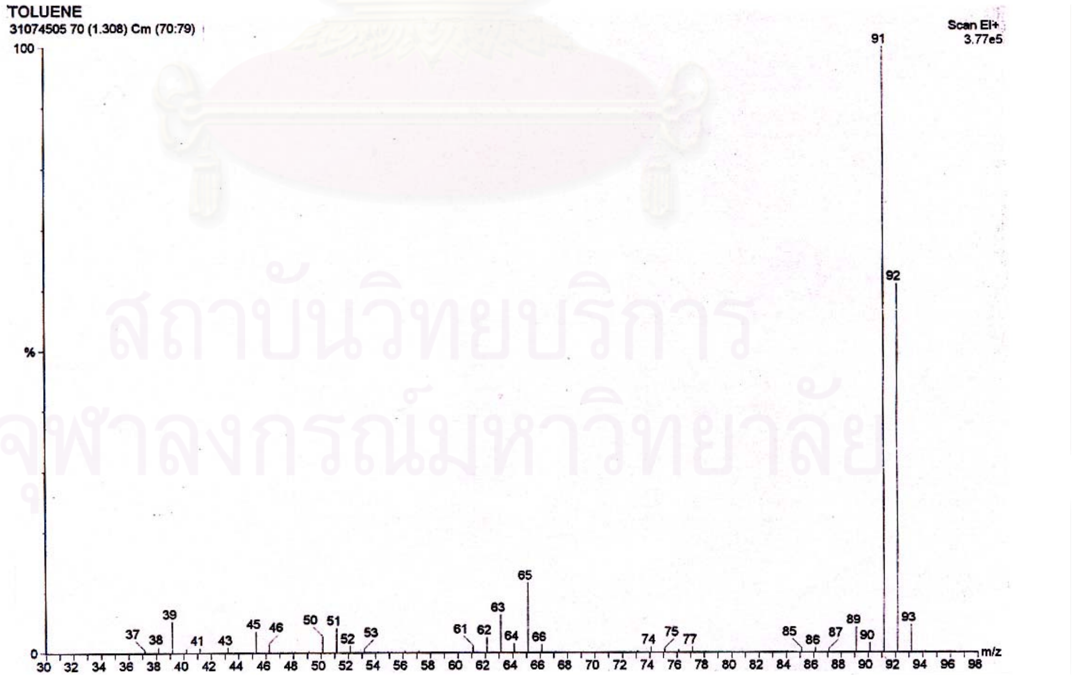

Figure C4 The mass spectrum of toluene

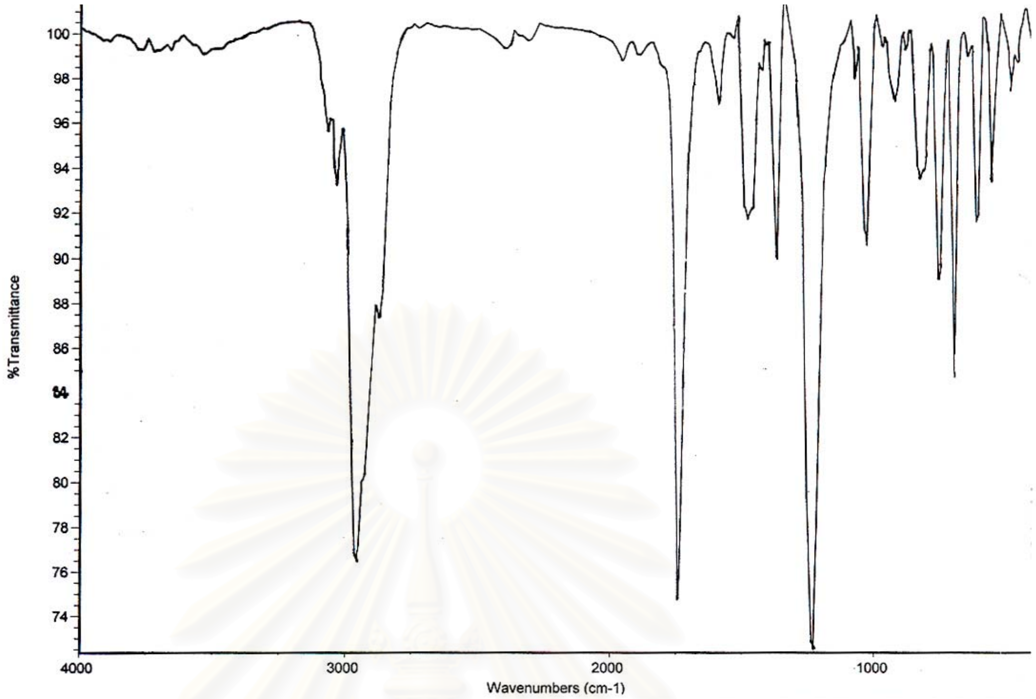

Figure C5 The FTIR spectrum of mixture 1T

(using mole ratio of substrate and sodium bromide: 1/1)

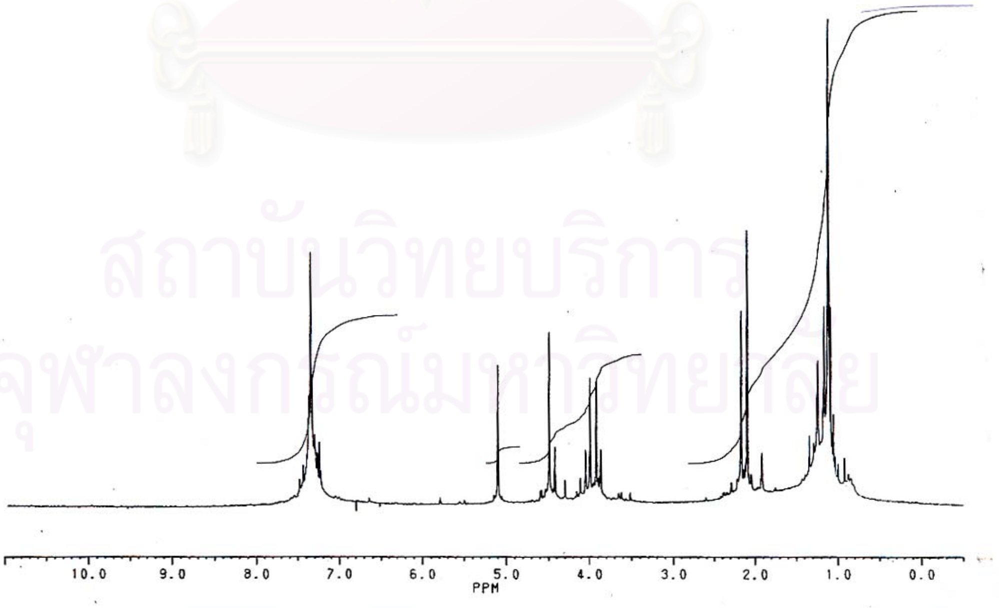

Figure C6 The ^{1}H-NMR spectrum of mixture 1T

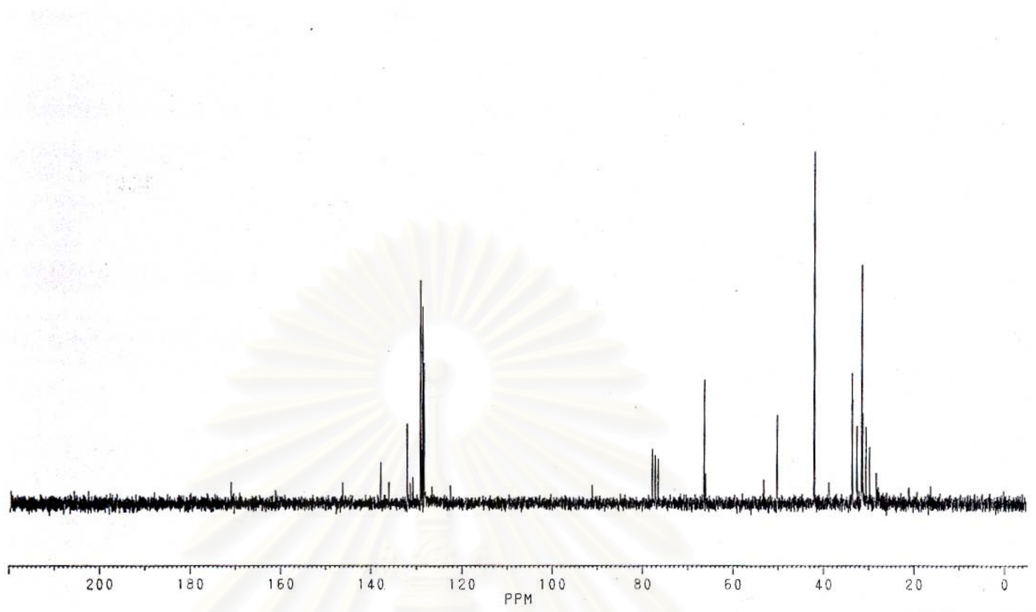

Figure C7 The ^{13}C-NMR spectrum of mixture 1T

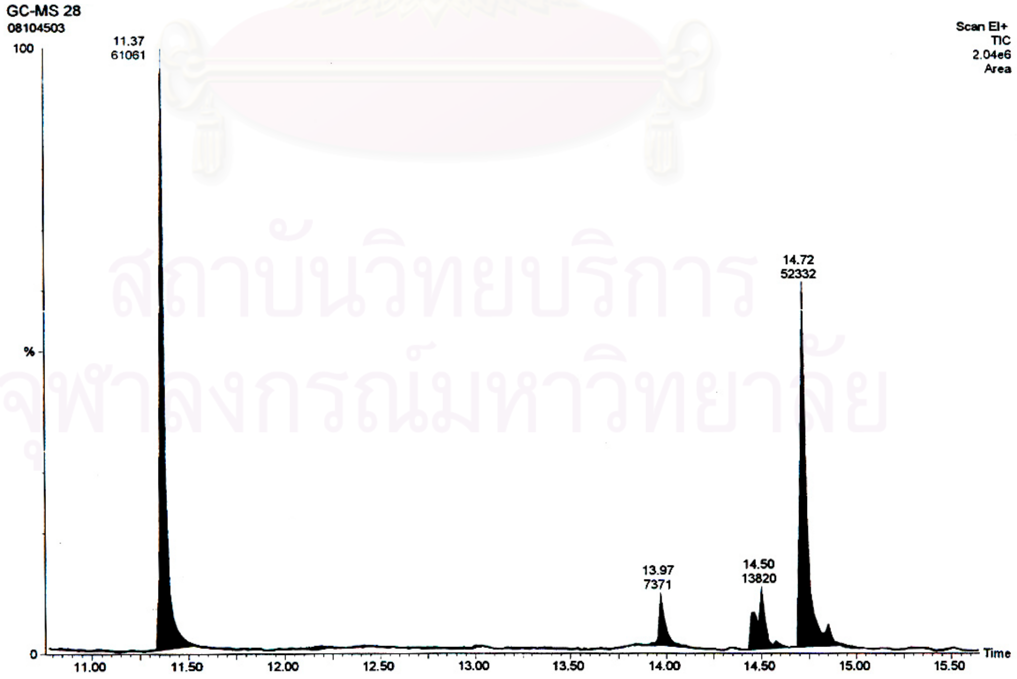

Figure C8 The gas chromatogram of mixture 1T

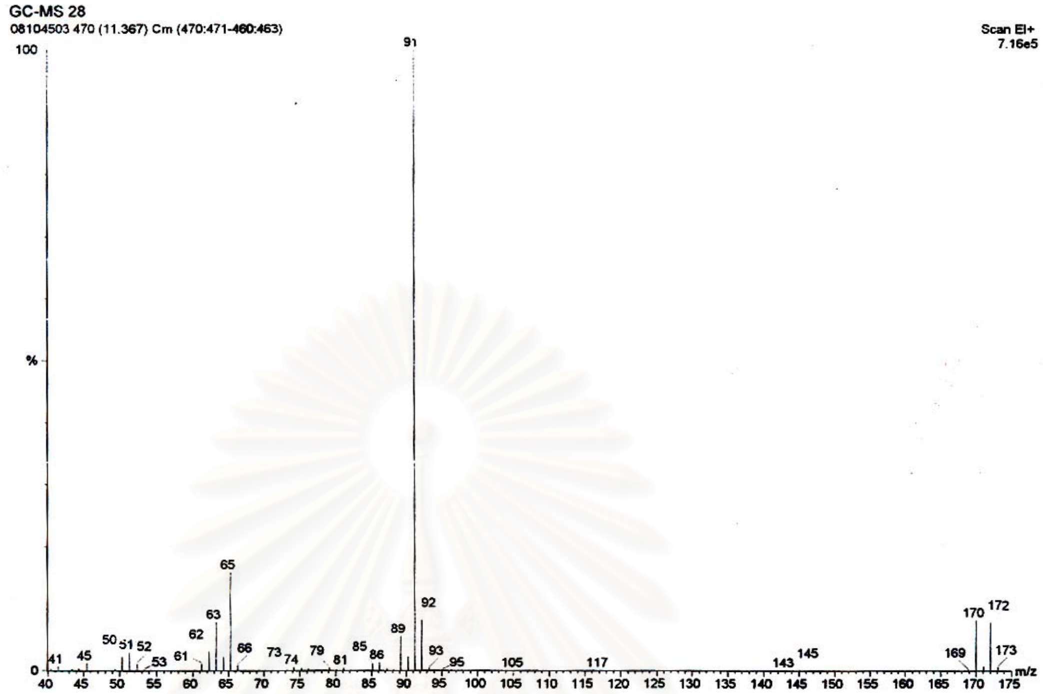

Figure C9 The mass spectrum of mixture 1T at t_R = 11.37 min

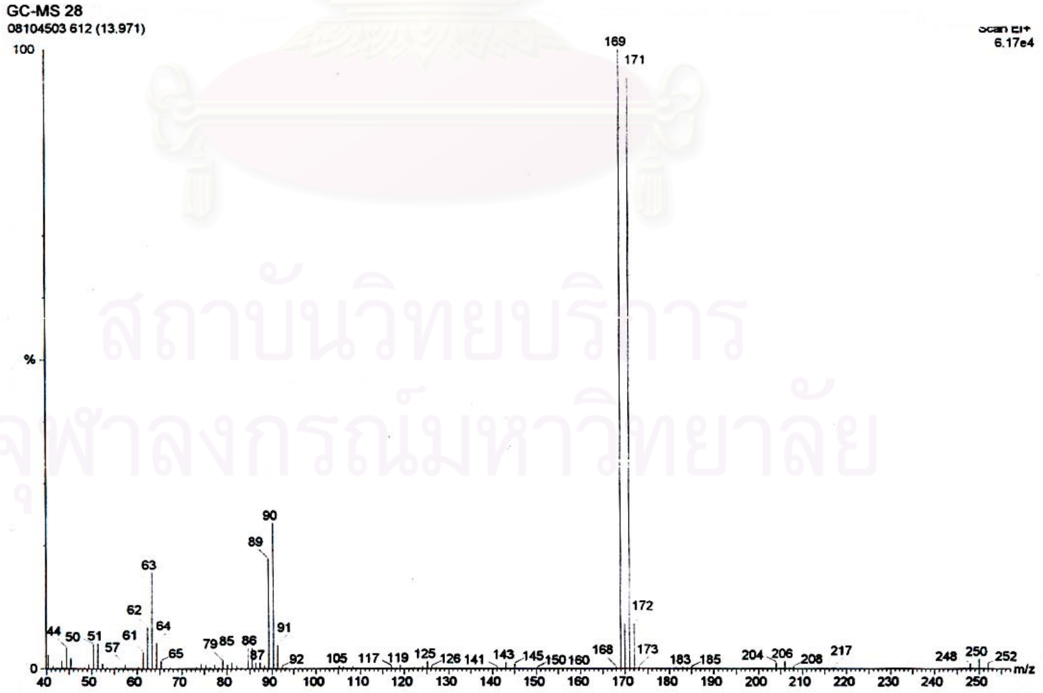

Figure C10 The mass spectrum of mixture 1T at t_R = 13.97 min

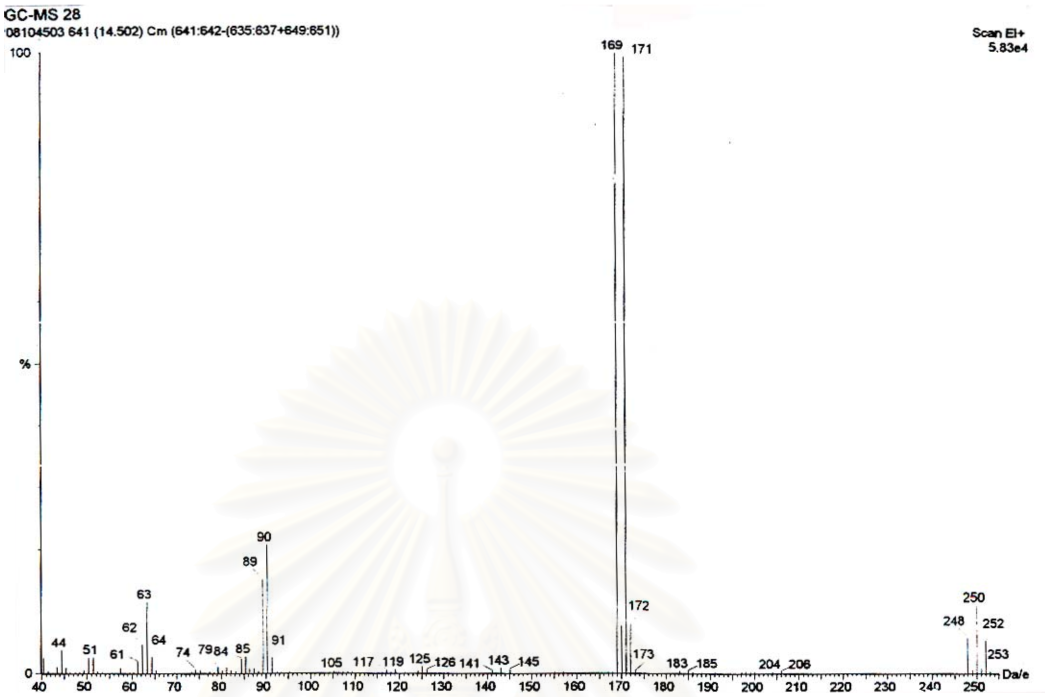

Figure C11 The mass spectrum of mixture 1T at t_R = 14.50 min

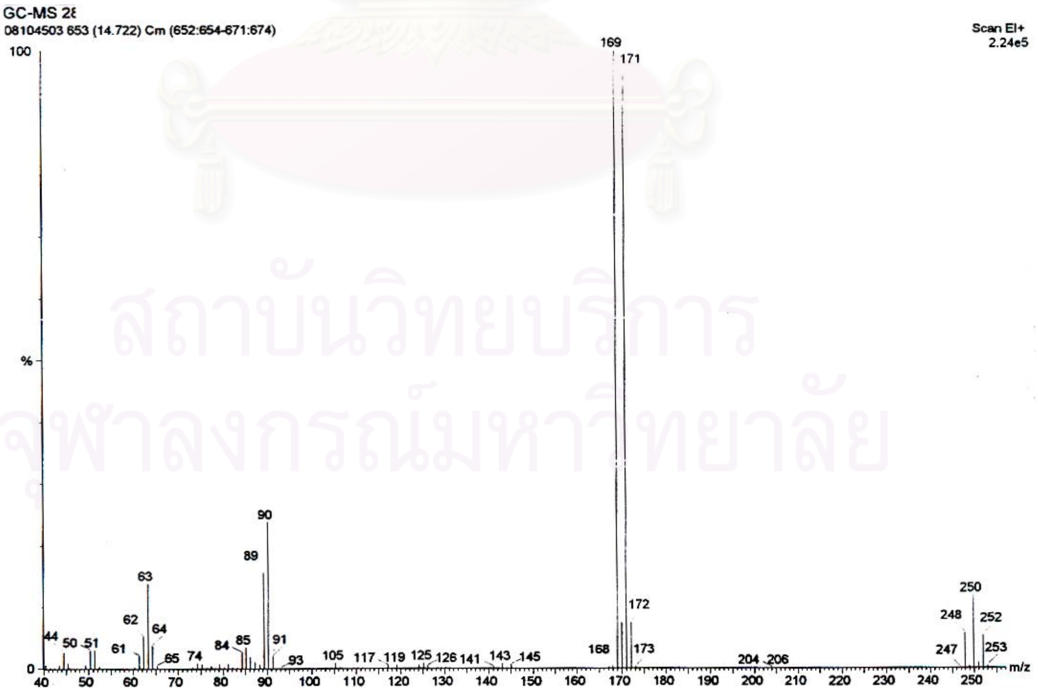

Figure C12 The mass spectrum of mixture 1T at t_R = 14.72 min

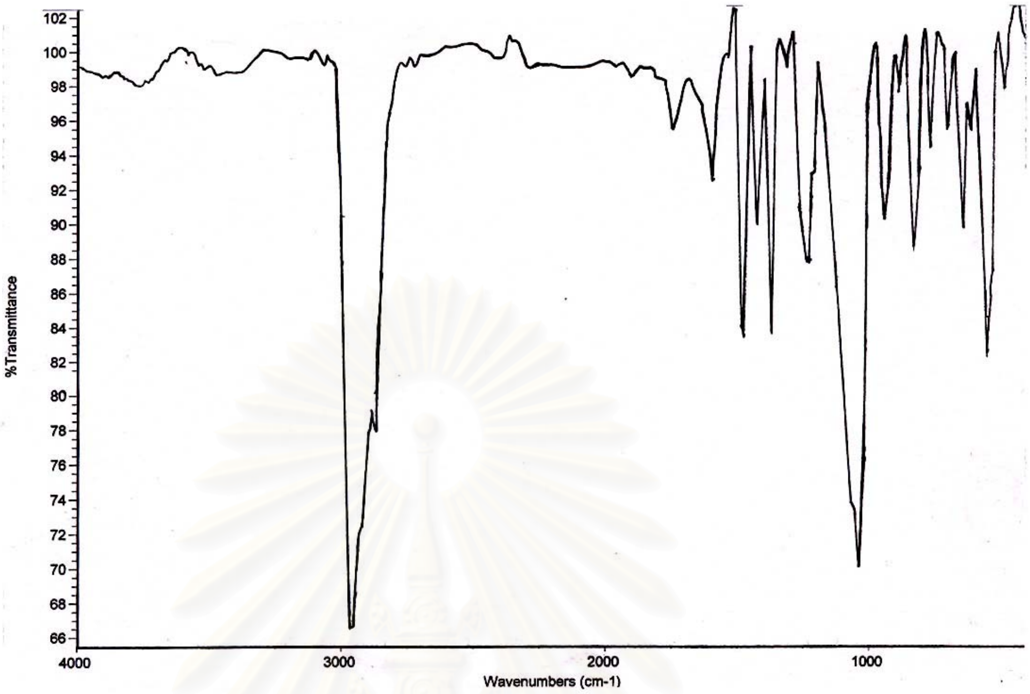

Figure C13 The FTIR spectrum of mixture 2T

(using mole ratio of substrate and sodium bromide: 1/5)

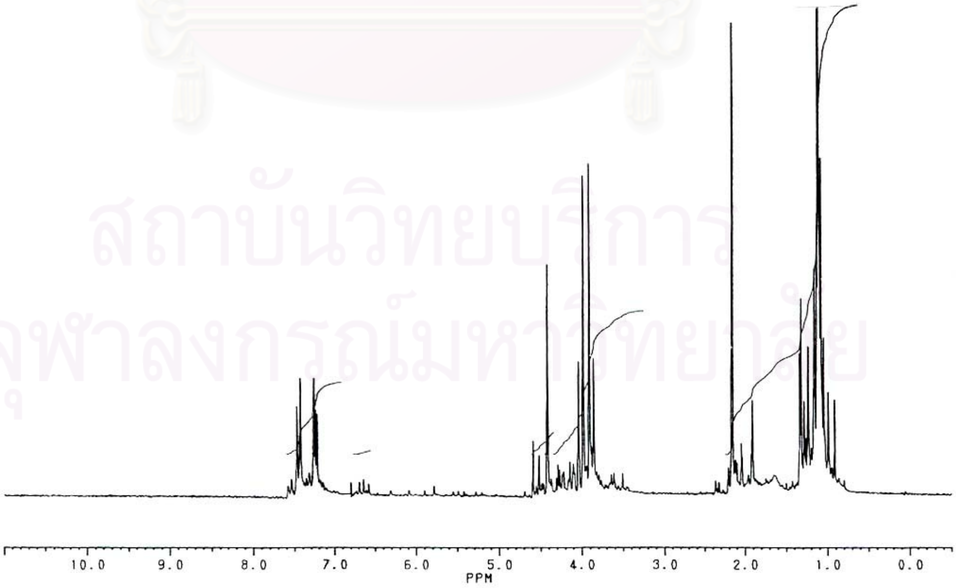

Figure C14 The ^{1}H-NMR spectrum of mixture 2T

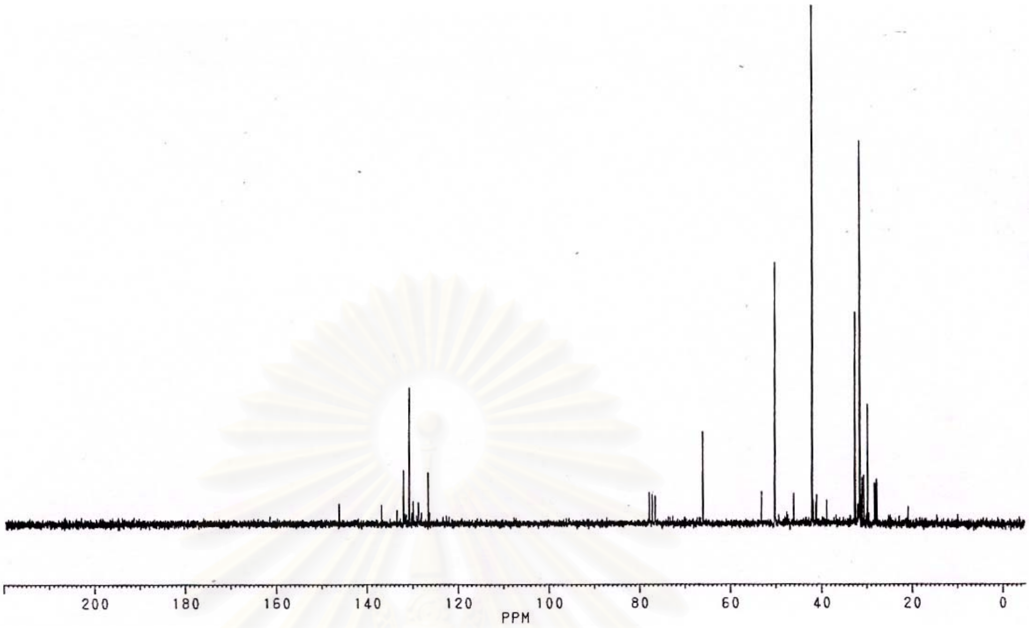

Figure C15 The ^{13}C-NMR spectrum of mixture 2T

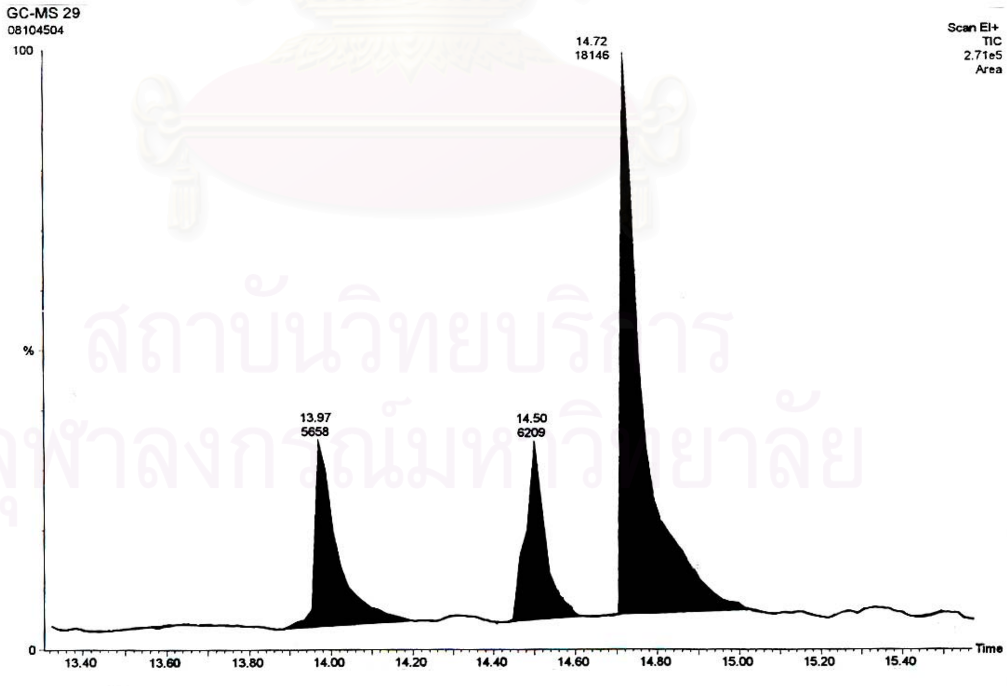

Figure C16 The gas chromatogram of mixture 2T

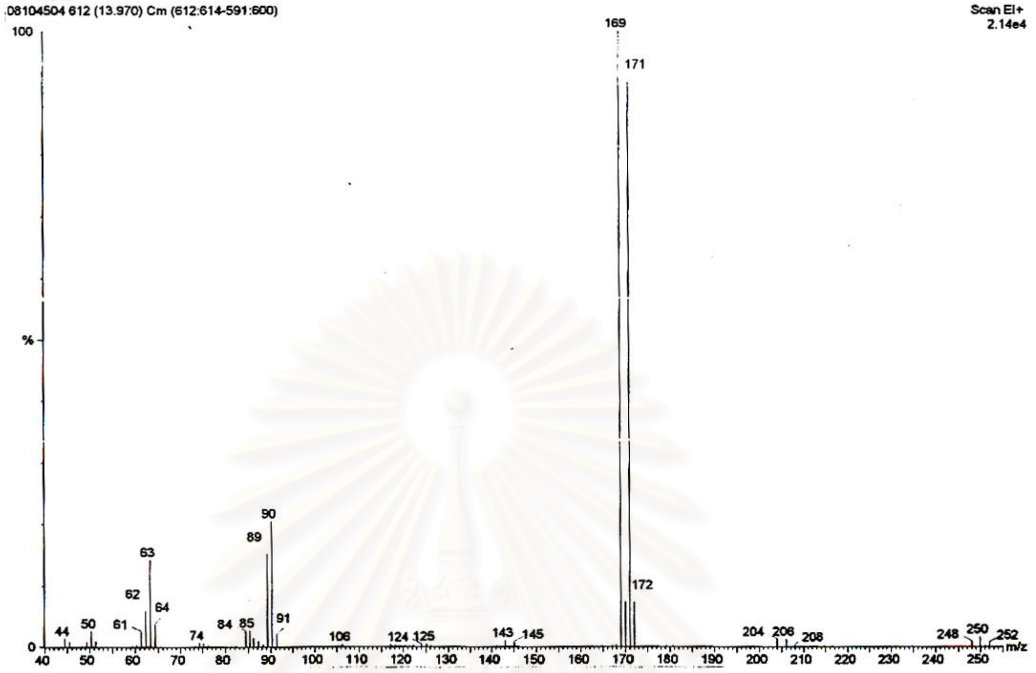

Figure C17 The mass spectrum of mixture 2T at t_R = 13.97 min

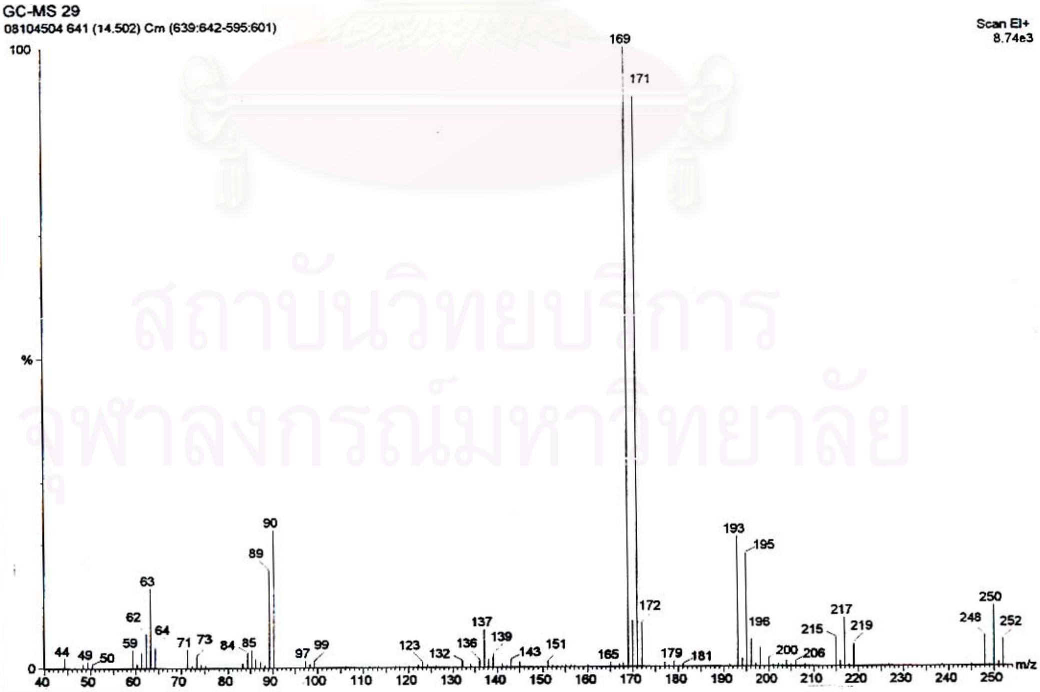

Figure C18 The mass spectrum of mixture 2T at t_R = 14.50 min

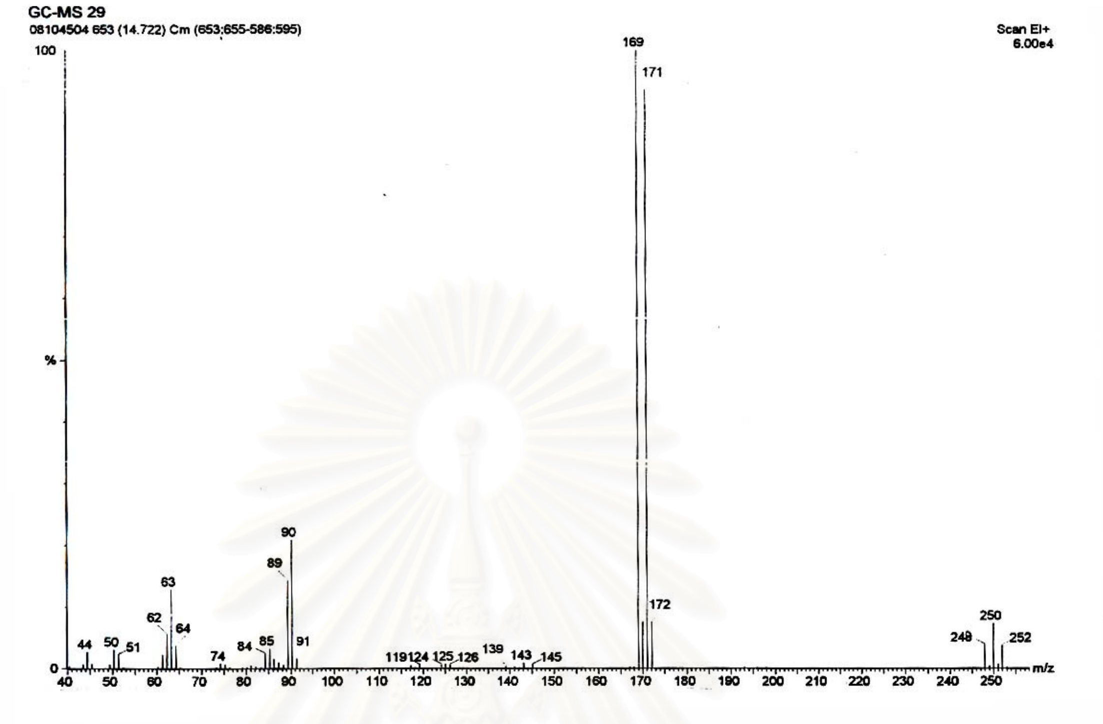

Figure C19 The mass spectrum of mixture 2T at t_R = 14.72 min

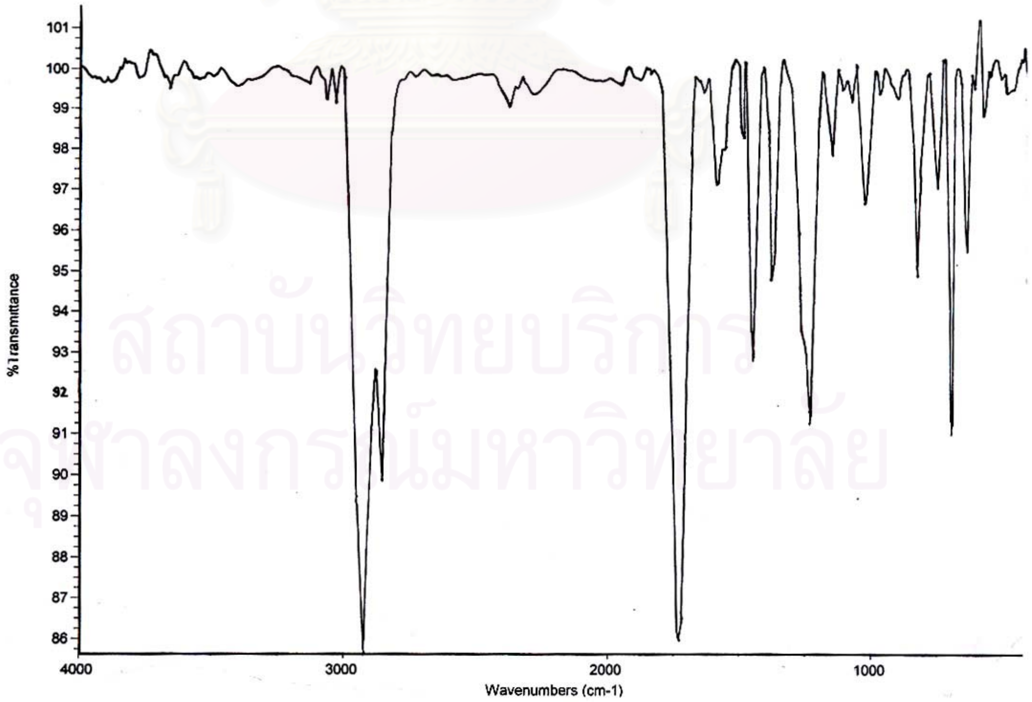

Figure C20 The FTIR spectrum of mixture 3T

(hexane; using mole ratio of substrate and sodium bromide: 1/1)

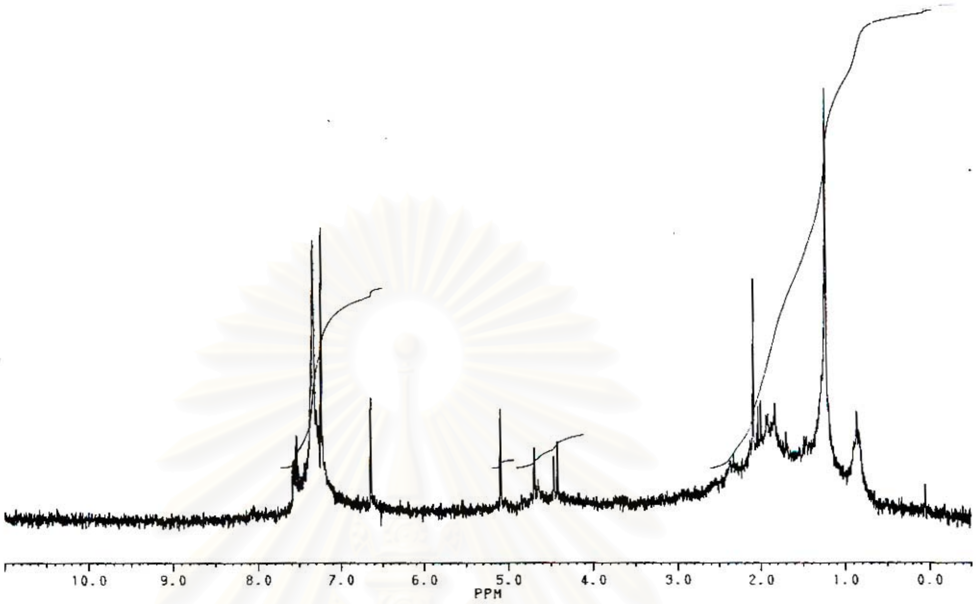

Figure C21 The ^{1}H-NMR spectrum of mixture 3T

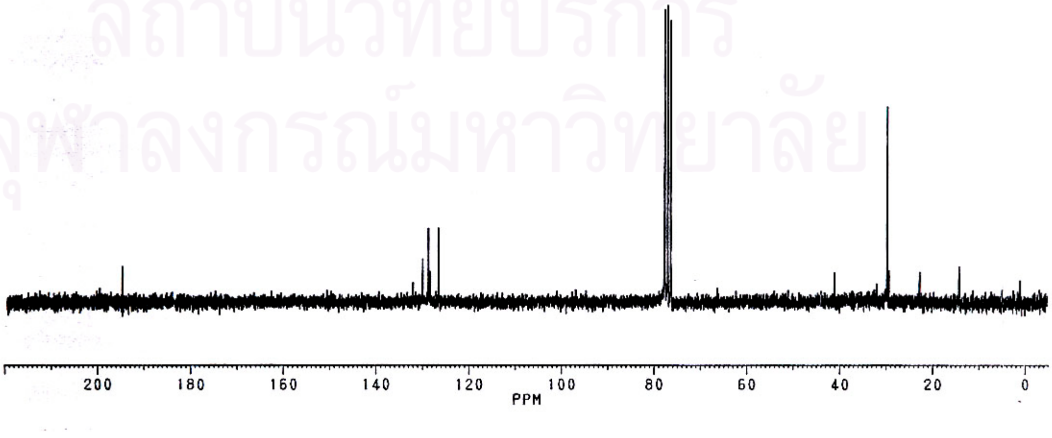

Figure C22 The ^{13}C-NMR spectrum of mixture 3T

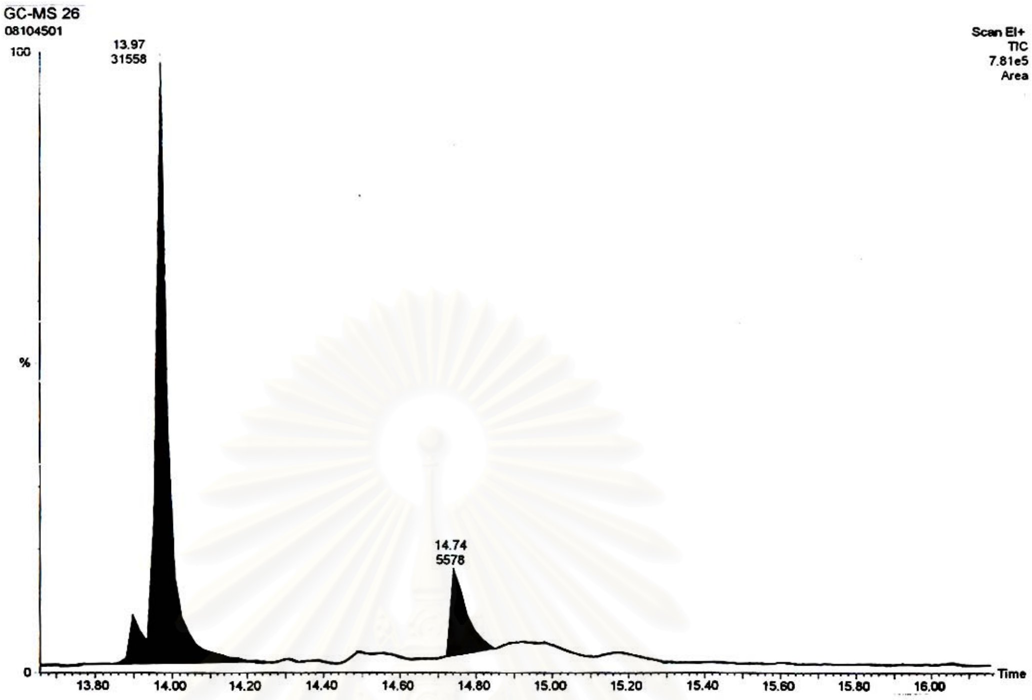

Figure C23 The gas chromatogram of mixture 3T

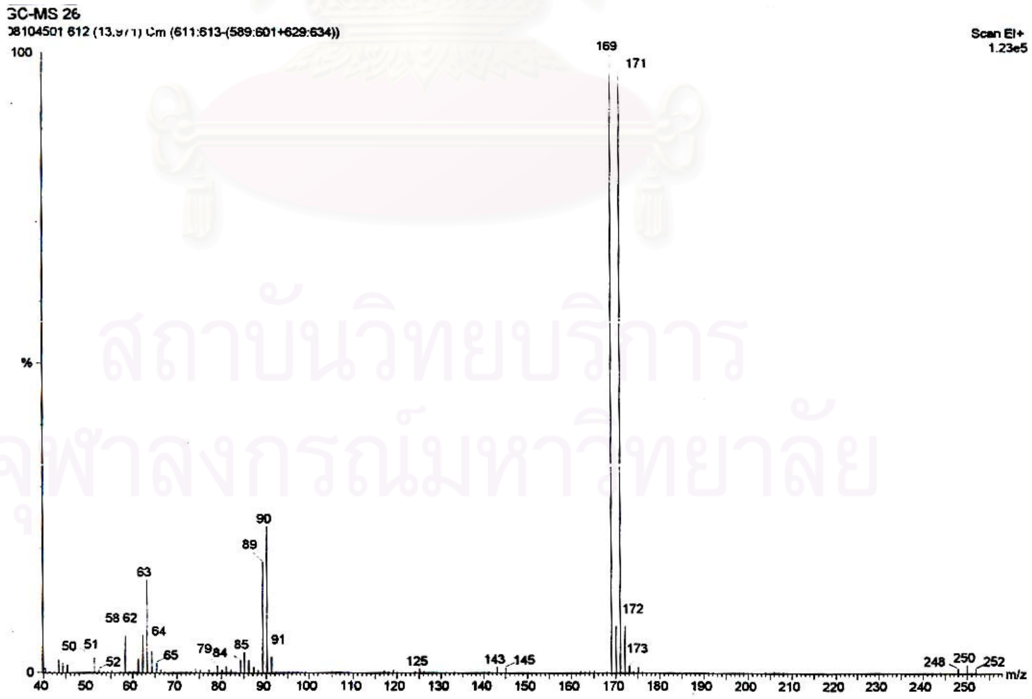

Figure C24 The mass spectrum of mixture 3T at t_R = 13.97 min

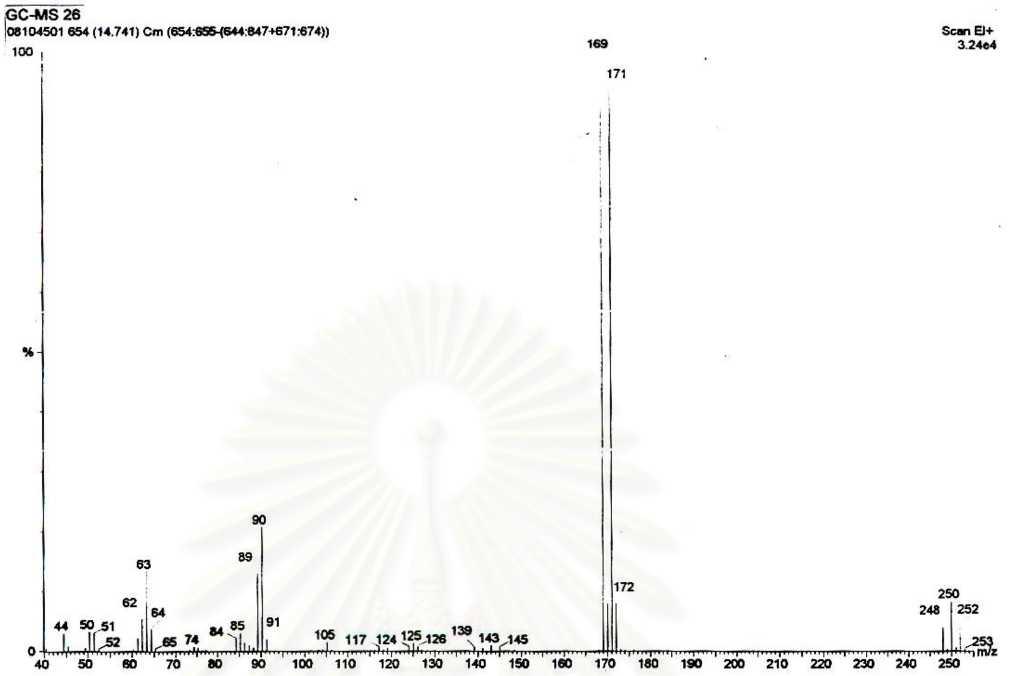

Figure C25 The mass spectrum of mixture 3T at t_R = 14.74 min

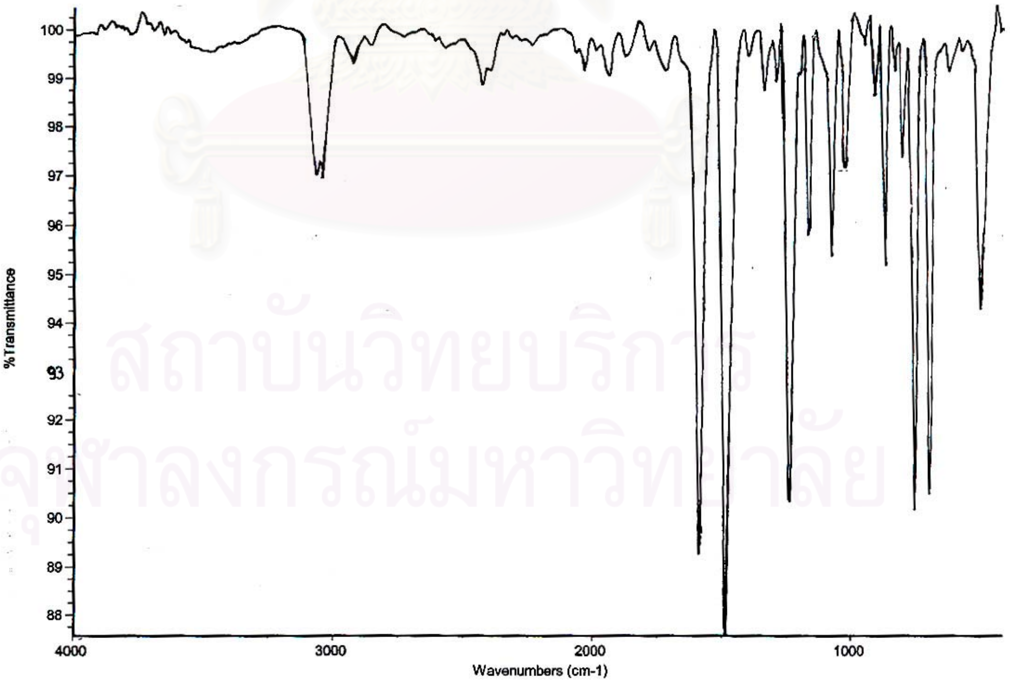

Figure C26 The FTIR spectrum of mixture 4T

(hexane; using mole ratio of substrate and sodium bromide: 1/5)

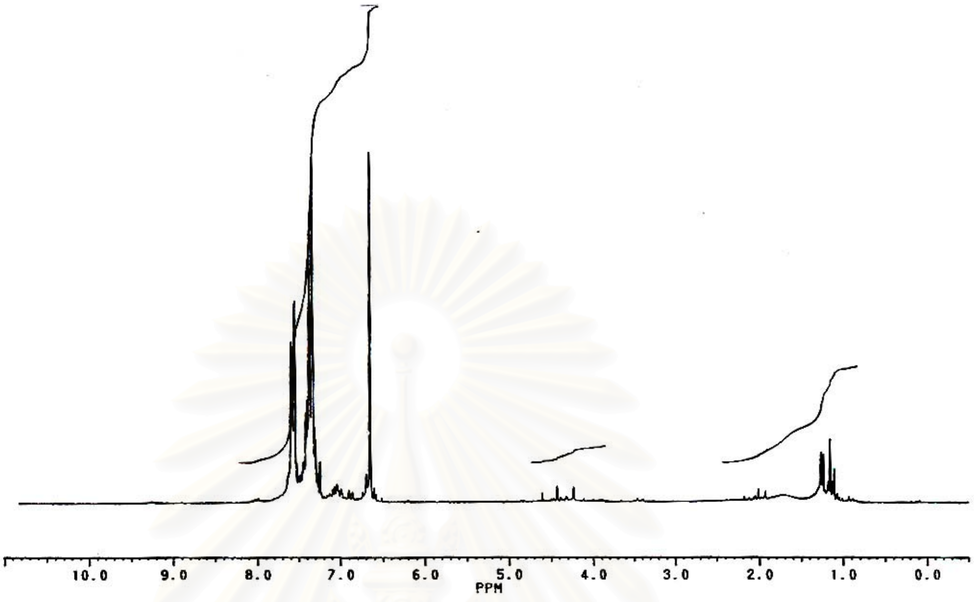

Figure C27 The ^{1}H-NMR spectrum of mixture 4T

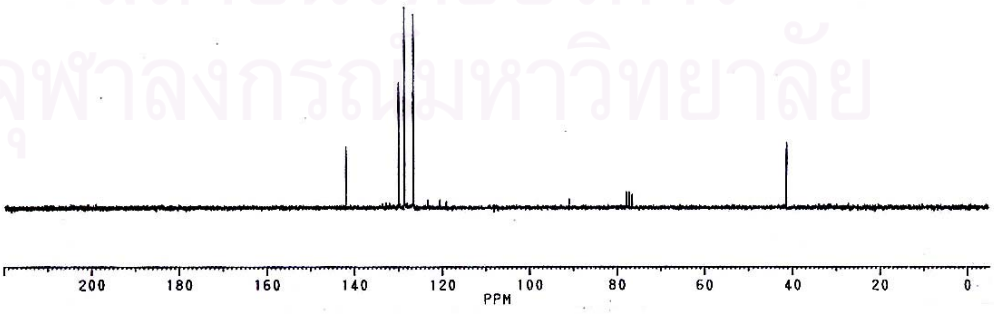

Figure C28 The ^{13}C-NMR spectrum of mixture 4T

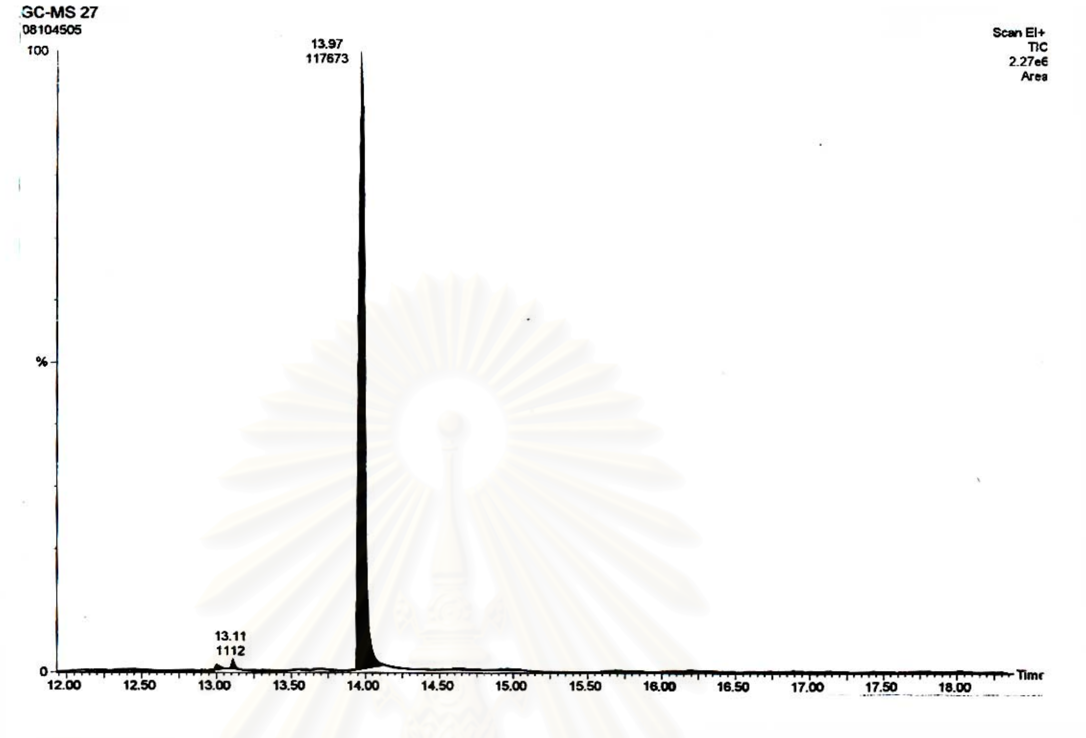

Figure C29 The gas chromatogram of mixture 4T

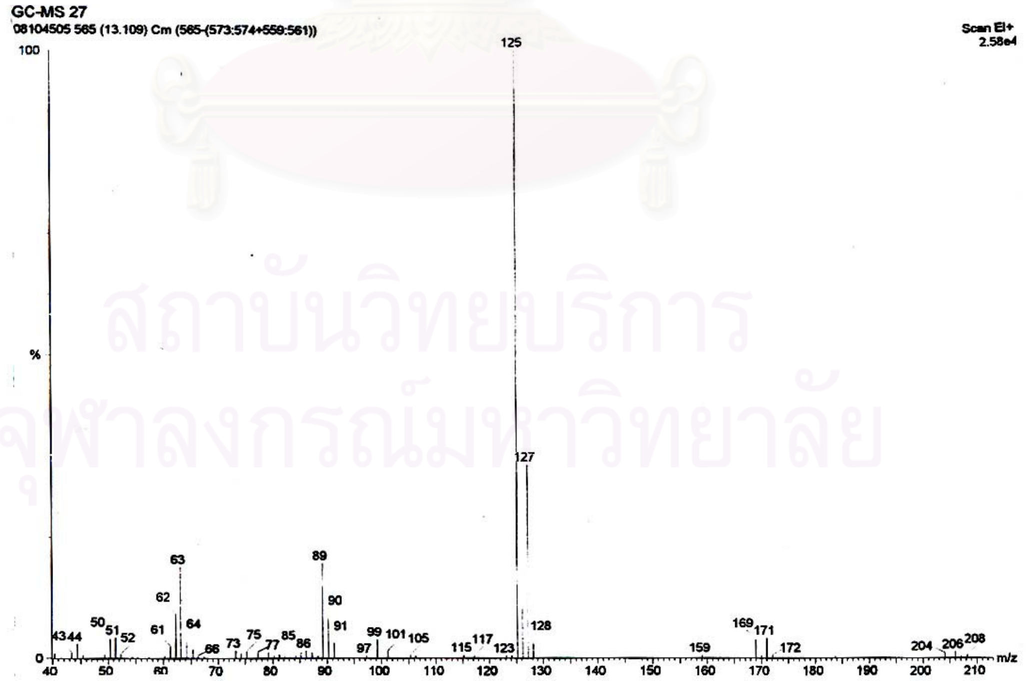

Figure C30 The mass spectrum of mixture 4T at t_R = 13.11 min

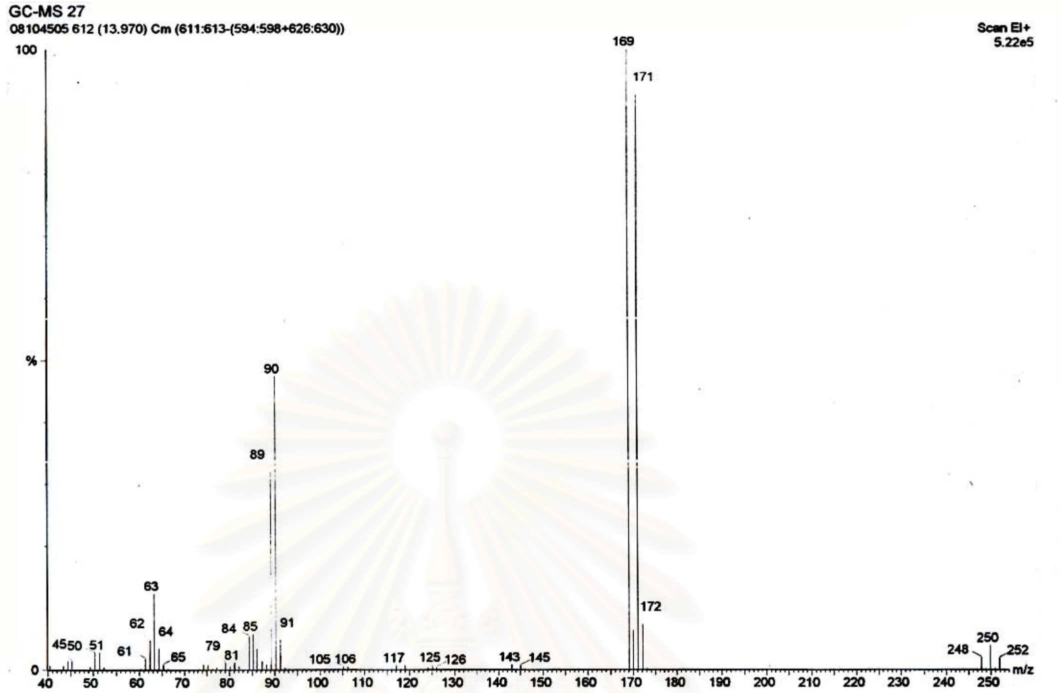

Figure C31 The mass spectrum of mixture 4T at t_R = 13.97 min

APPENDIX D

SPECTRA OF LINEAR ALKYL BENZENE DERIVATIVES

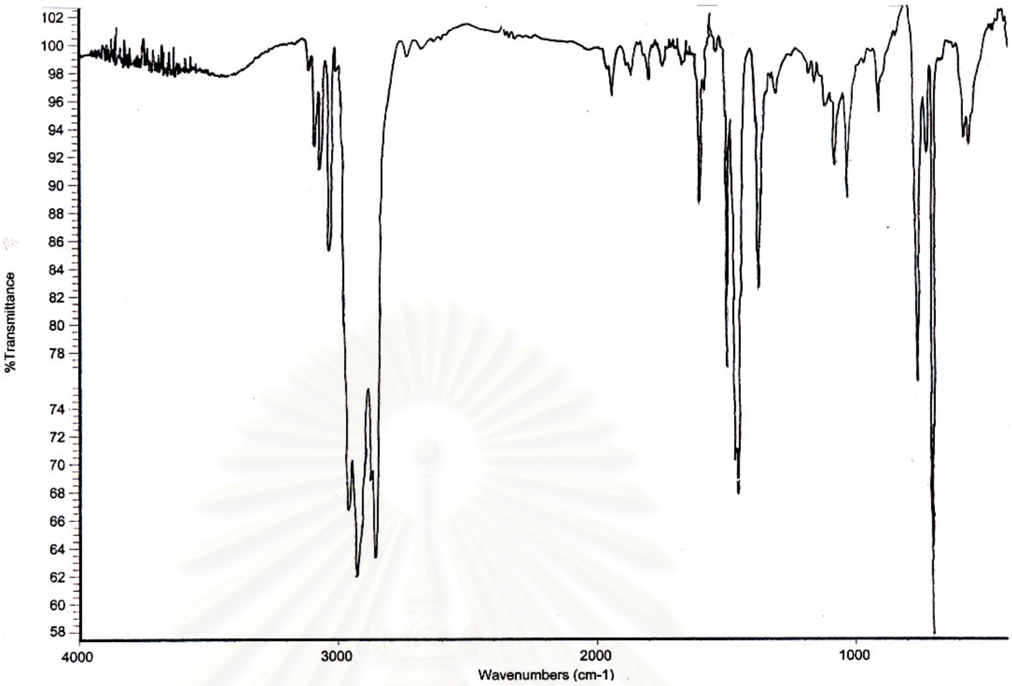

Figure D1 The FTIR spectrum of linear alkyl benzene

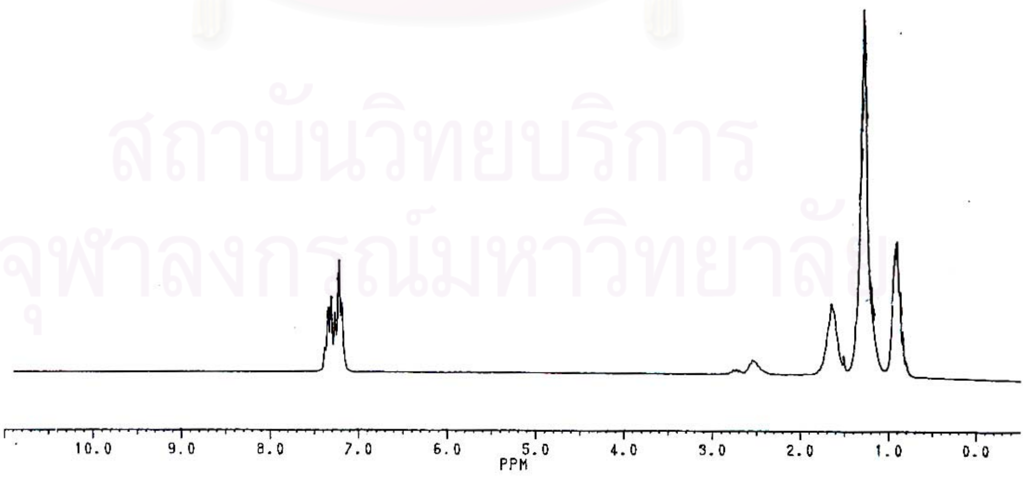

Figure D2 The ^{1}H-NMR spectrum of linear alkyl benzene

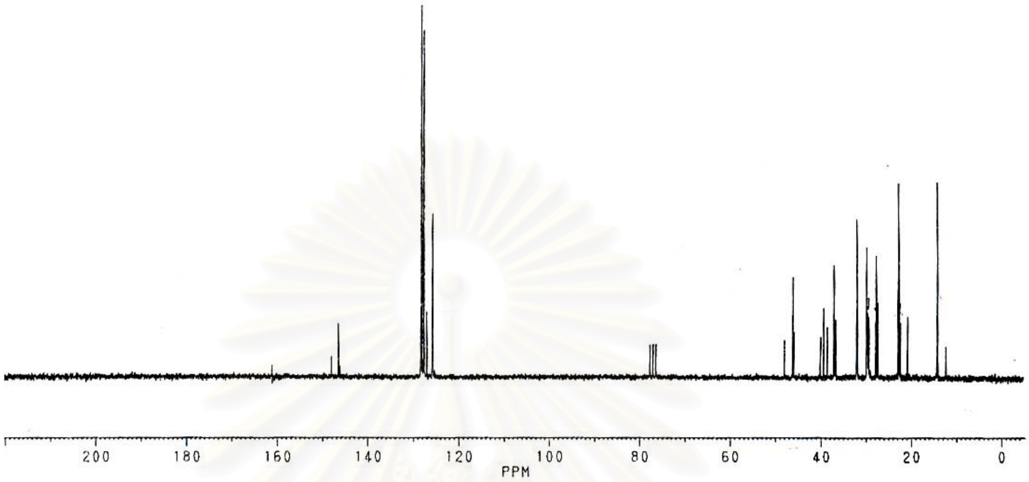

Figure D3 The ^{13}C-NMR spectrum of linear alkyl benzene

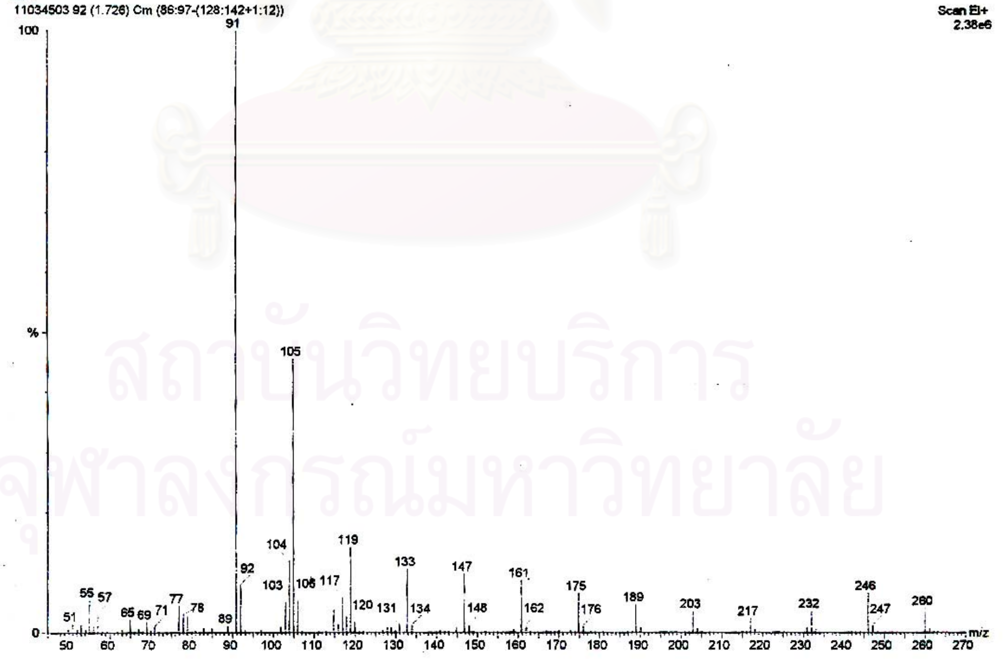

Figure D4 The mass spectrum of linear alkyl benzene

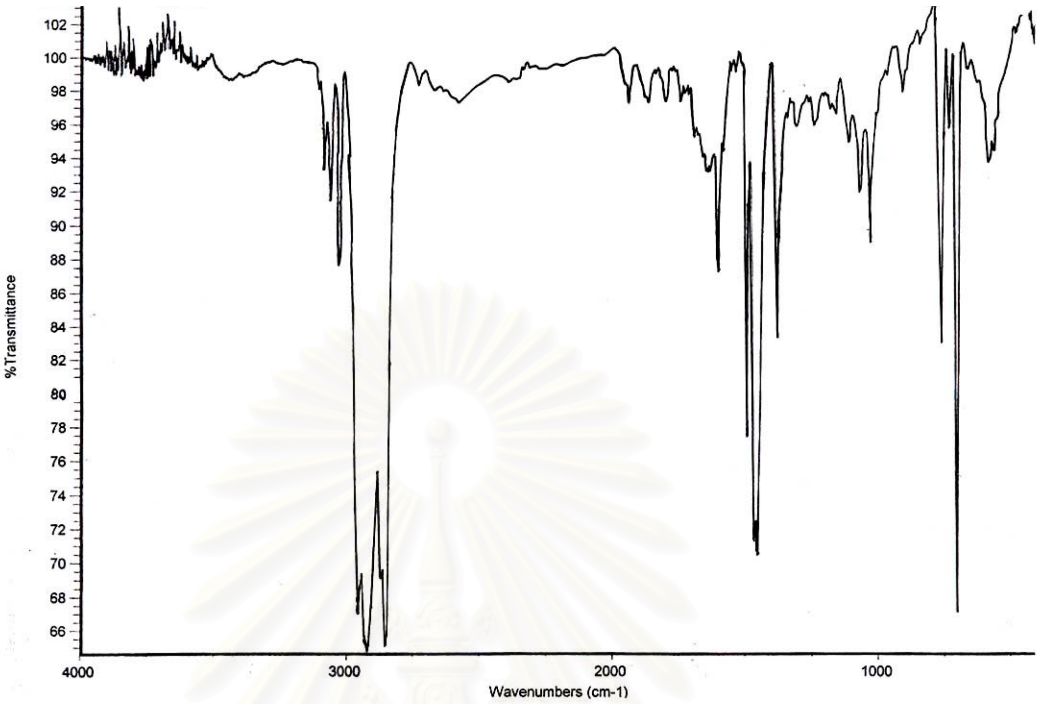

Figure D5 The FTIR spectrum of mixture 1L

(using mole ratio of substrate and sodium bromide: 1/1)

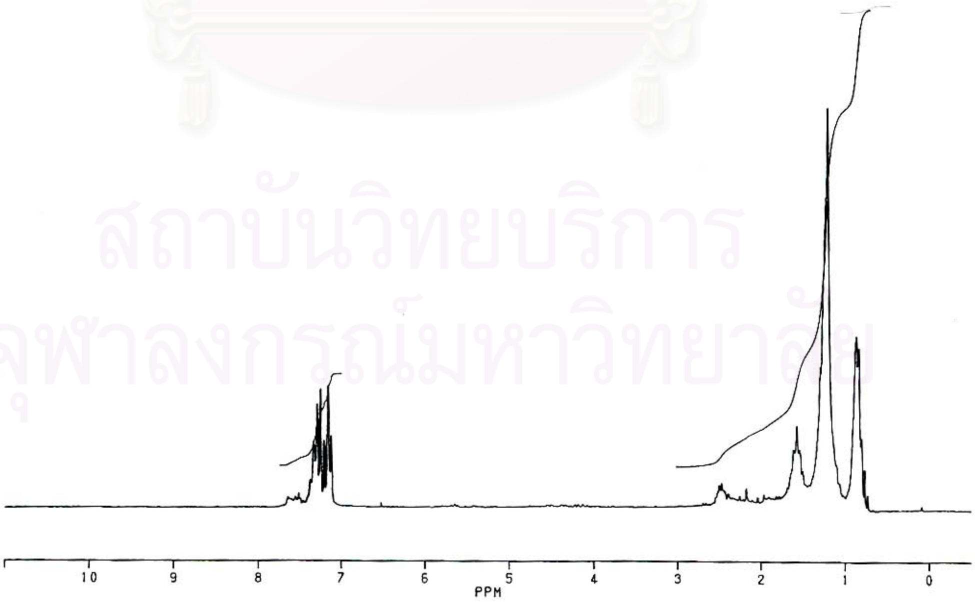

Figure D6 The ^{1}H-NMR spectrum of mixture 1L

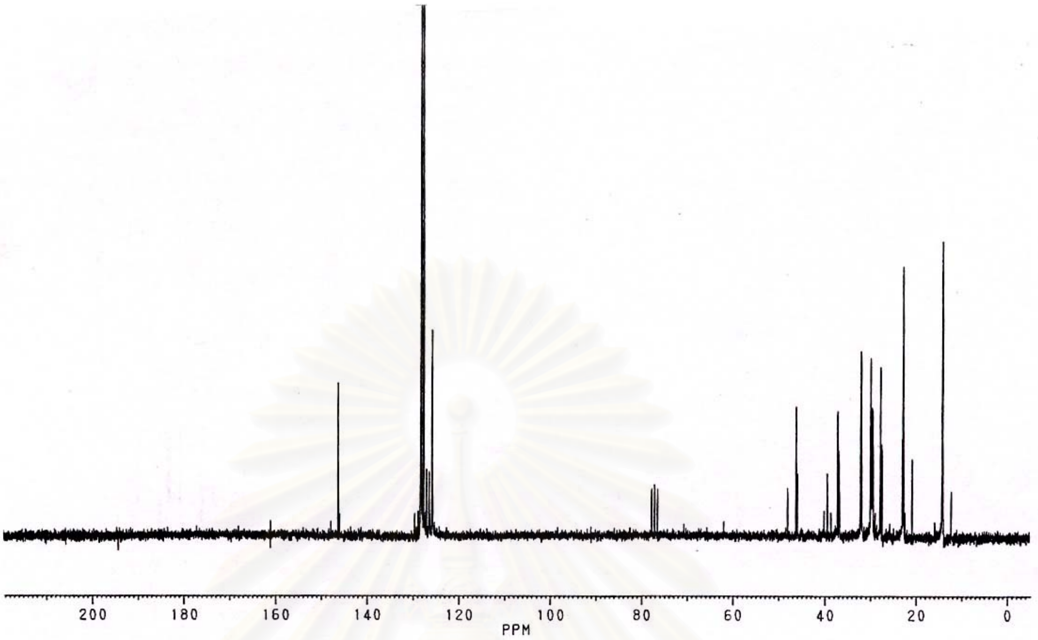

Figure D7 The ^{13}C-NMR spectrum of mixture 1L

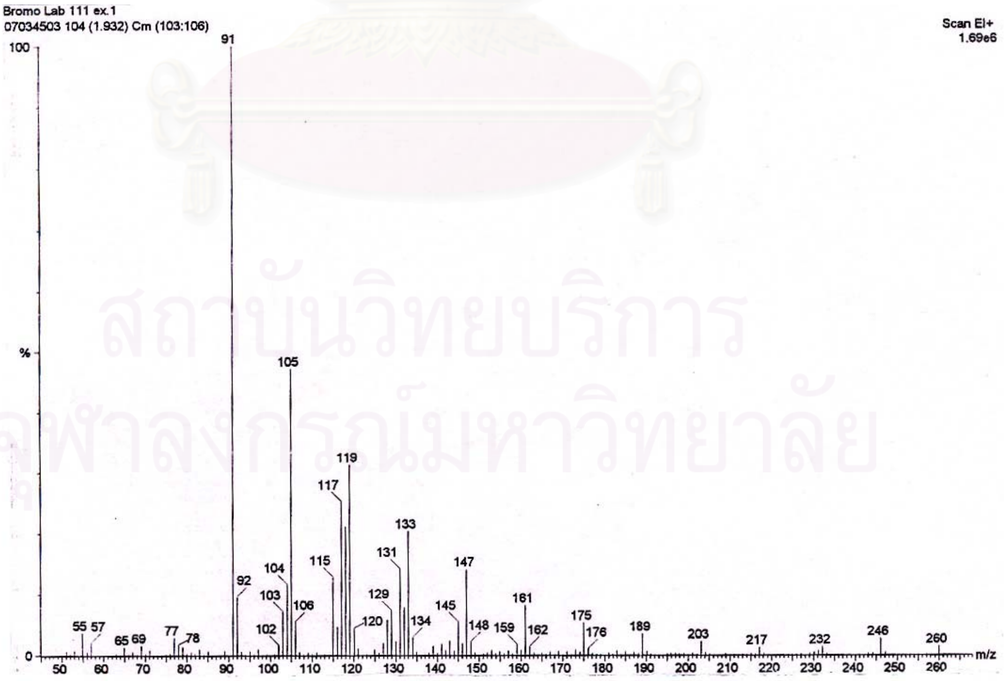

Figure D8 The mass spectrum of mixture 1L

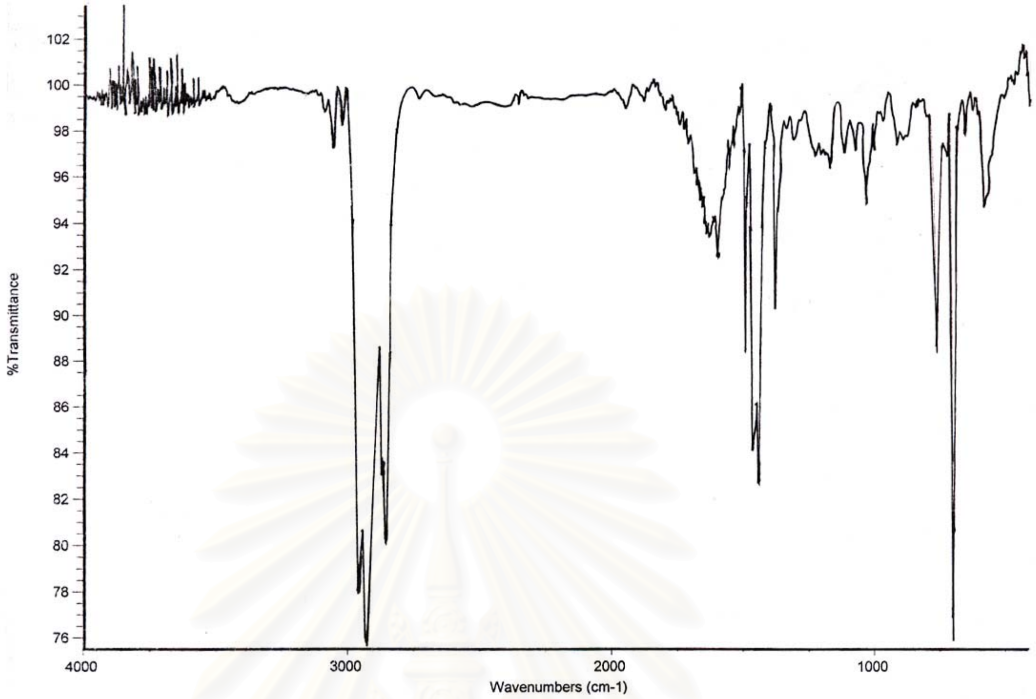

Figure D9 The FTIR spectrum of mixture 2L

(using mole ratio of substrate and sodium bromide: 1/5)

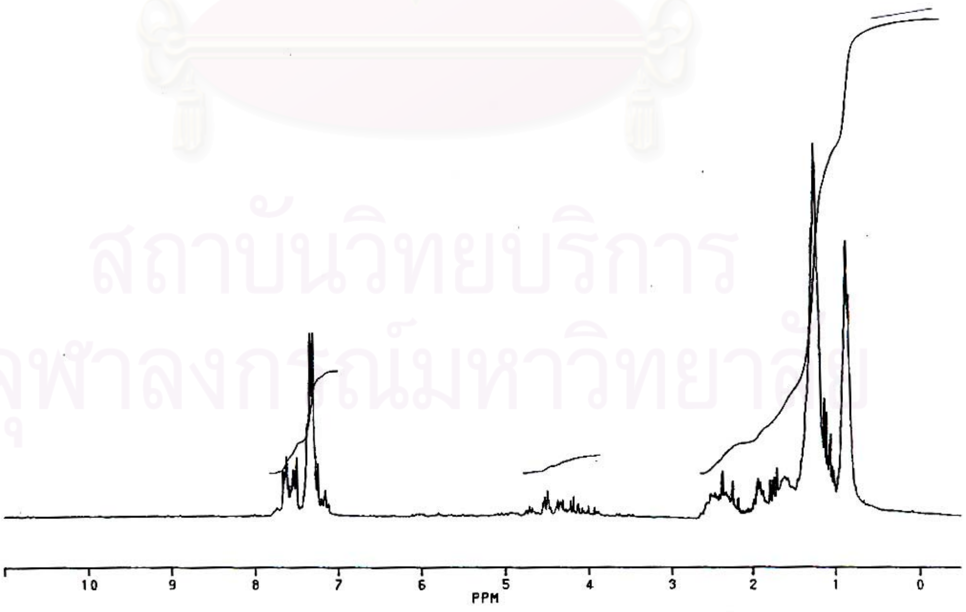

Figure D10 The ^{1}H-NMR spectrum of mixture 2L

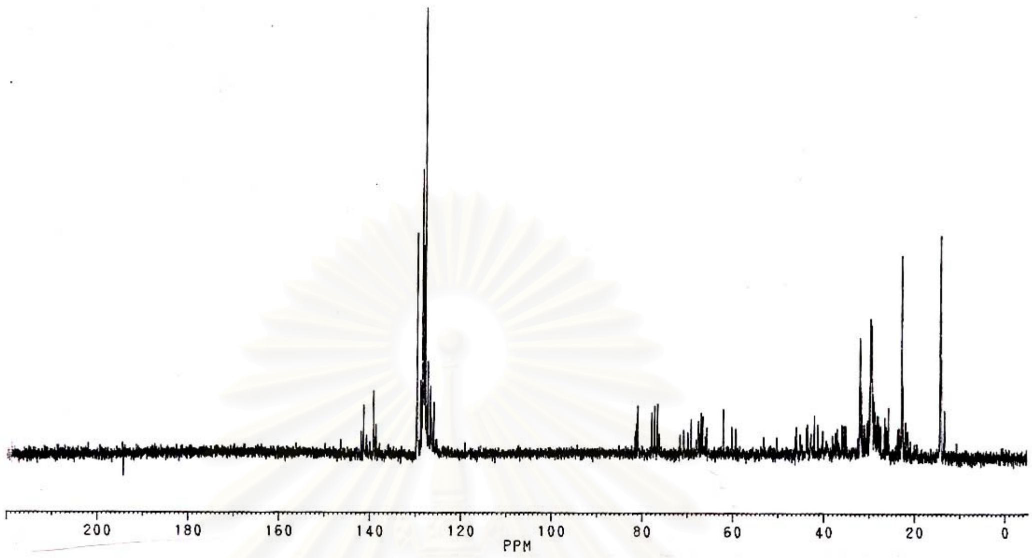

Figure D11 The ^{13}C-NMR spectrum of mixture 2L

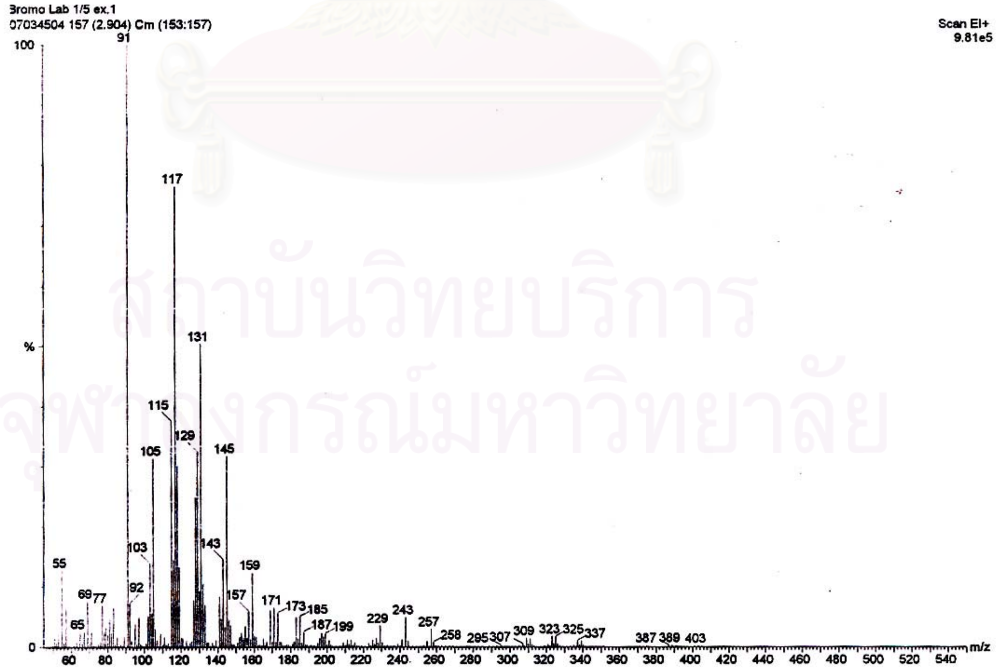

Figure D12 The mass spectrum of mixture 2L

APPENDIX E

SPECTRA OF NITROBENZENE COMPOUND, SOLVENTS AND PHASE TRANSFERS

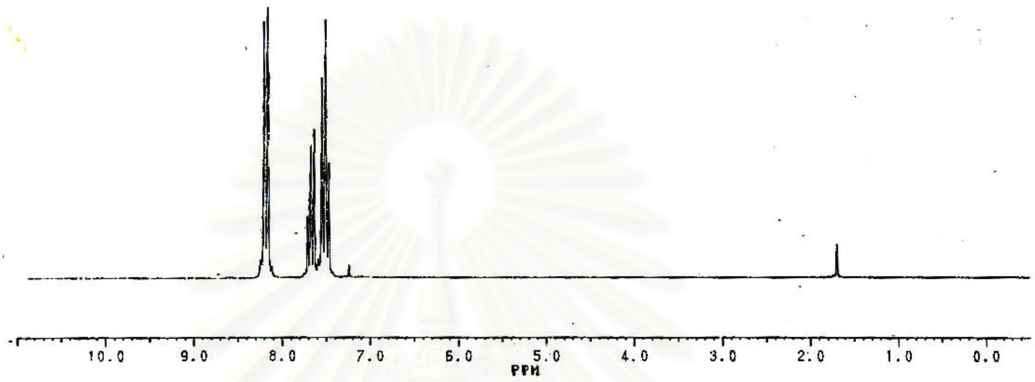

Figure E1 The ^{1}H-NMR spectrum of nitrobenzene

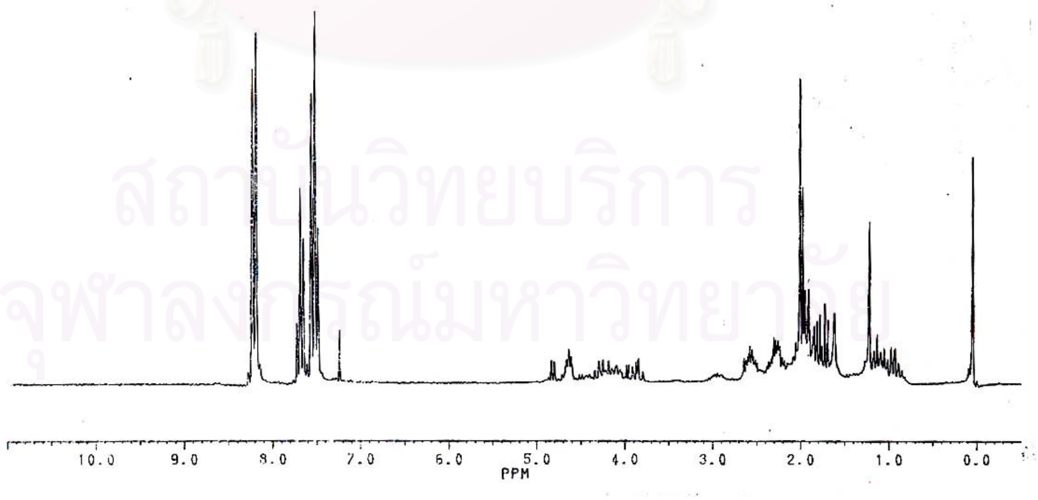

Figure E2 The ^{1}H-NMR spectrum of mixture 1N

(using mole ratio of substrate and sodium bromide: 1/5)

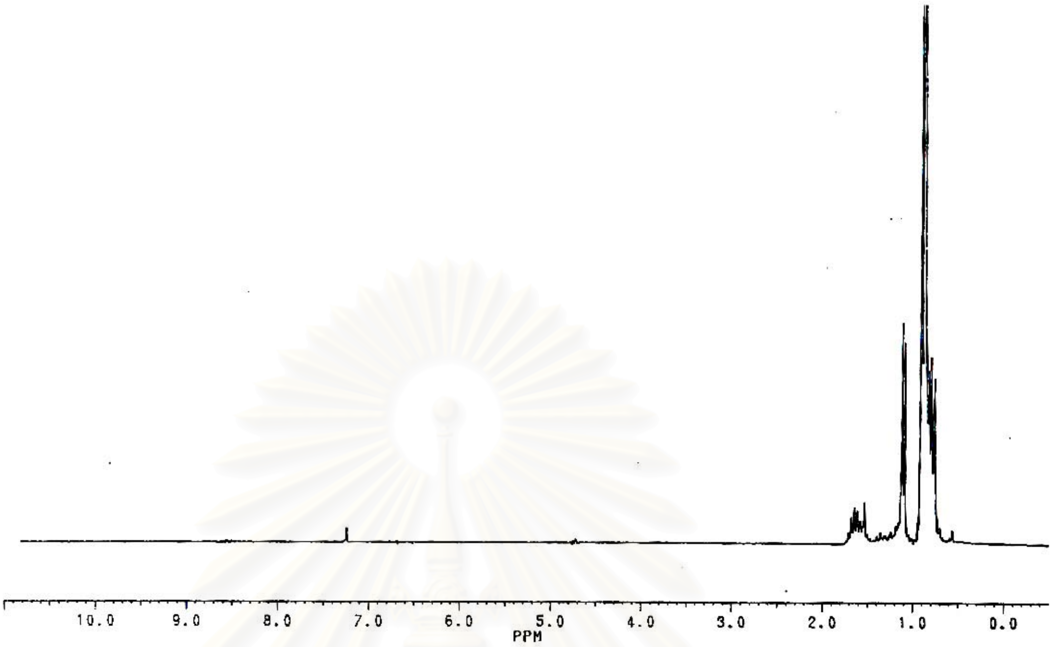

Figure E3 The ^{1}H-NMR spectrum of isooctane

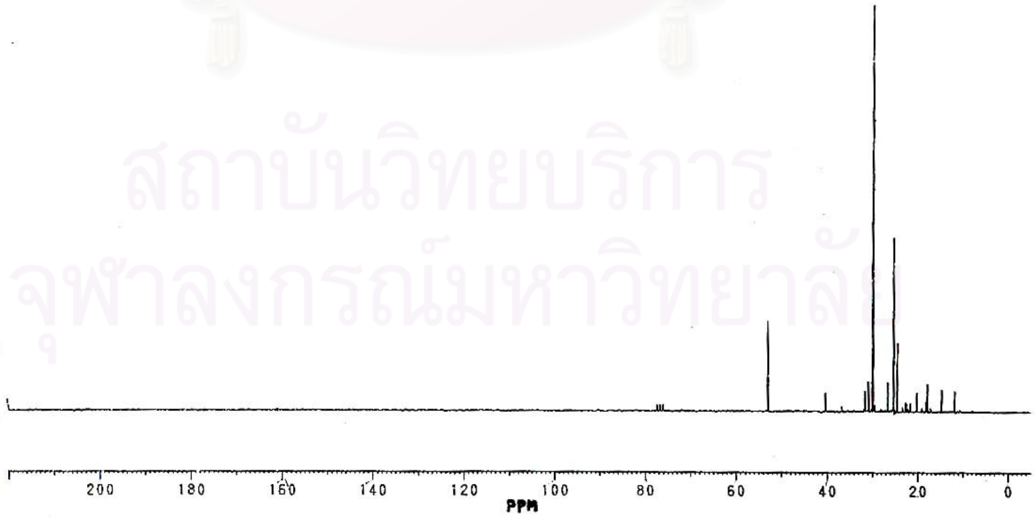

Figure E4 The ^{13}C-NMR spectrum of isooctane

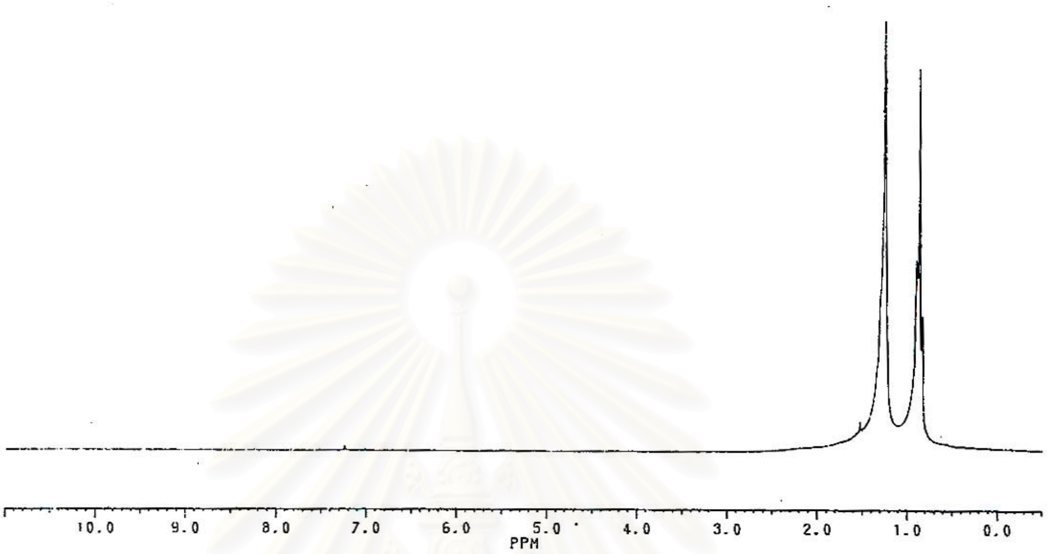

Figure E5 The ^{1}H-NMR spectrum of hexane

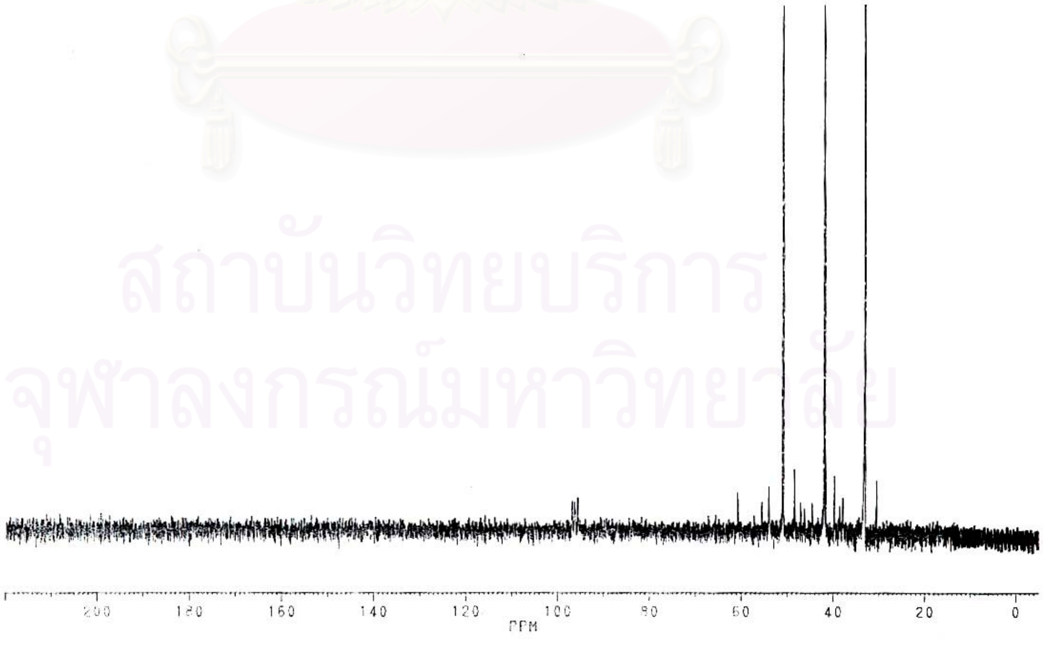

Figure E6 The ^{13}C-NMR spectrum of hexane

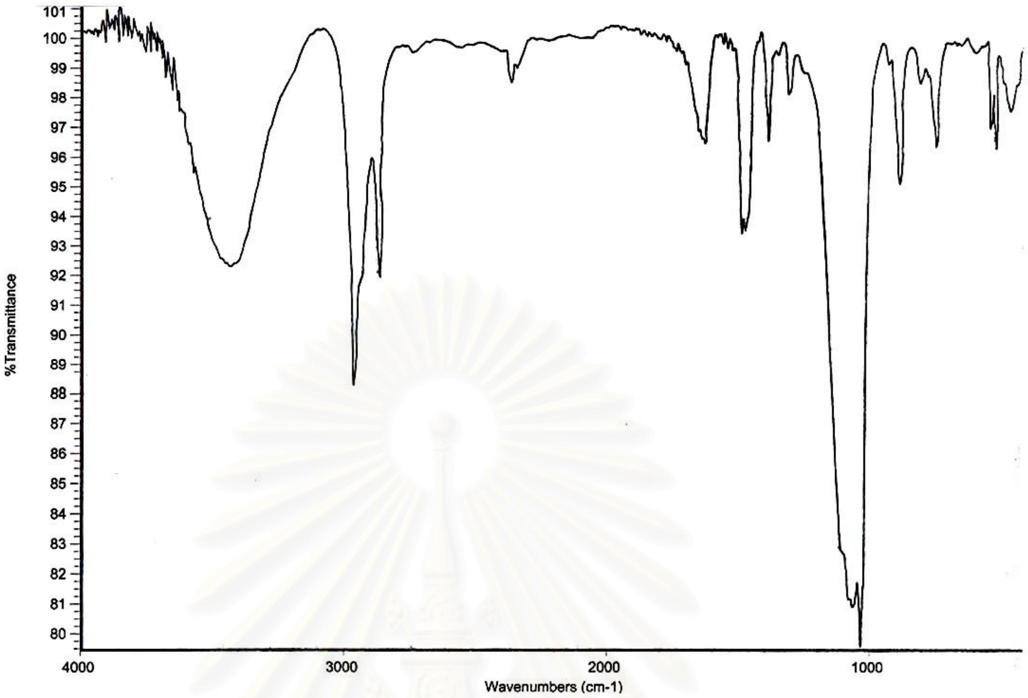

Figure E7 The FTIR spectrum of tetrabutyl ammoniumtetrafluoroborate (TBA)

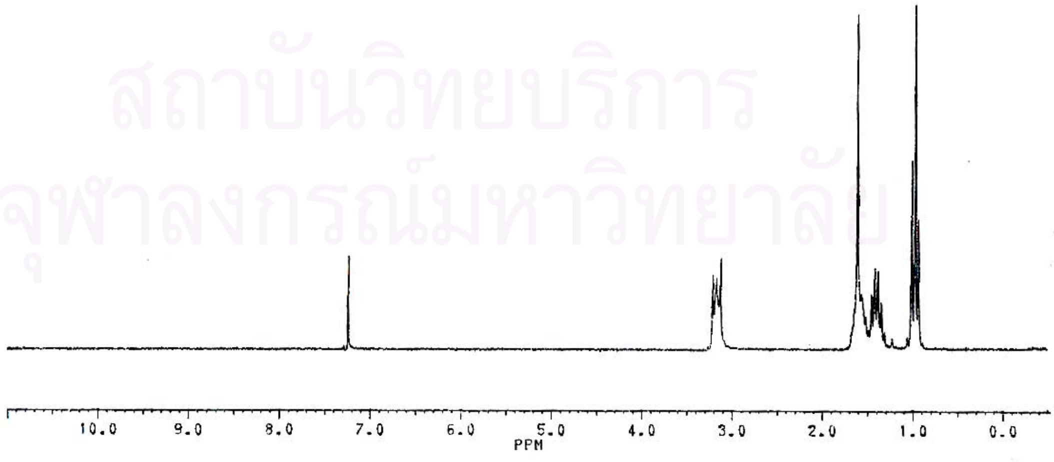

Figure E8 The ^{1}H-NMR spectrum of TBA

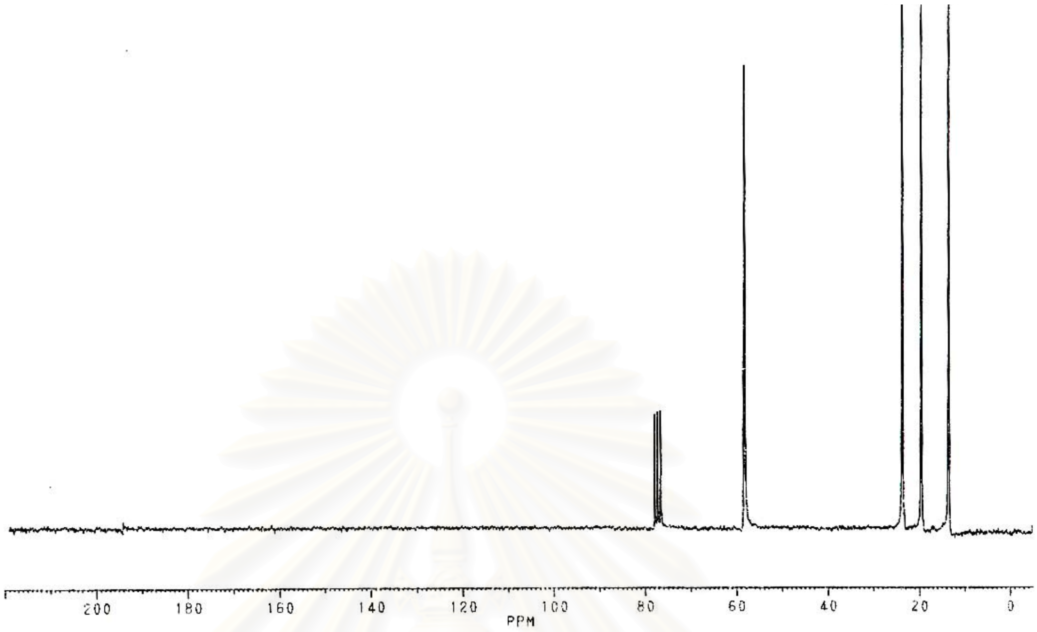

Figure E9 The ^{13}C-NMR spectrum of TBA

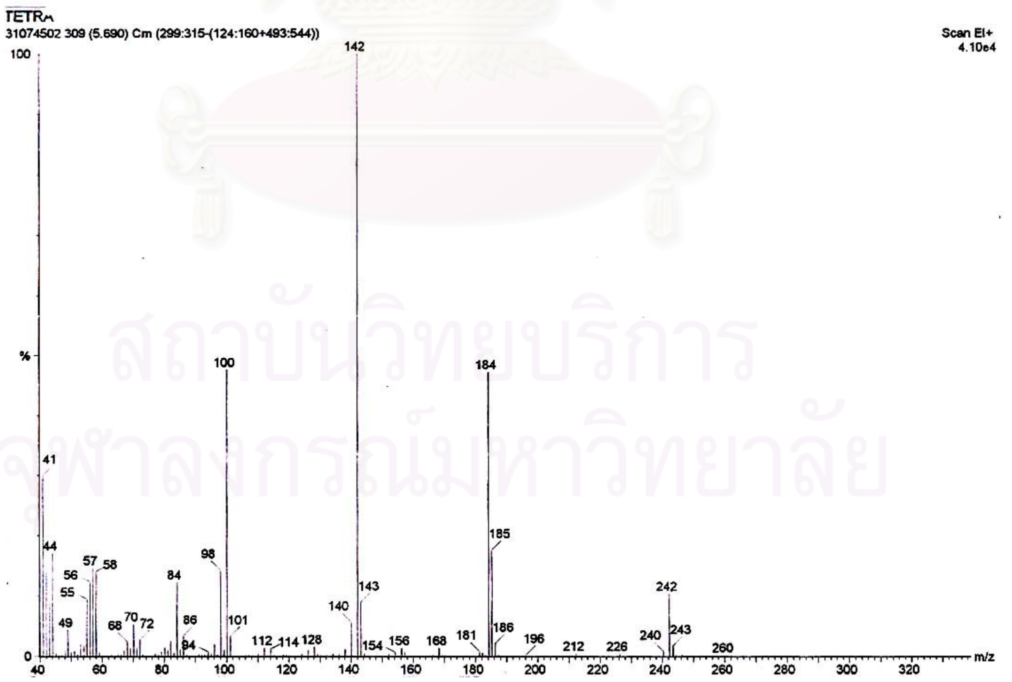

Figure E10 The mass spectrum of TBA

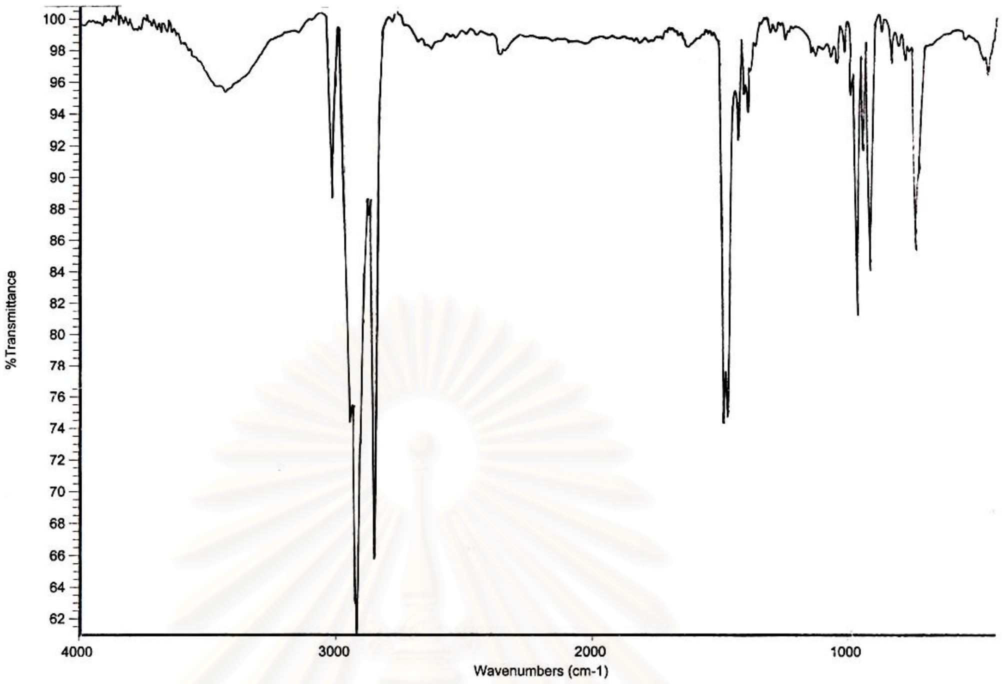

Figure E11 The FTIR spectrum of N-cetyl-N,N,N-trimethyl-ammonium bromide (CTAB)

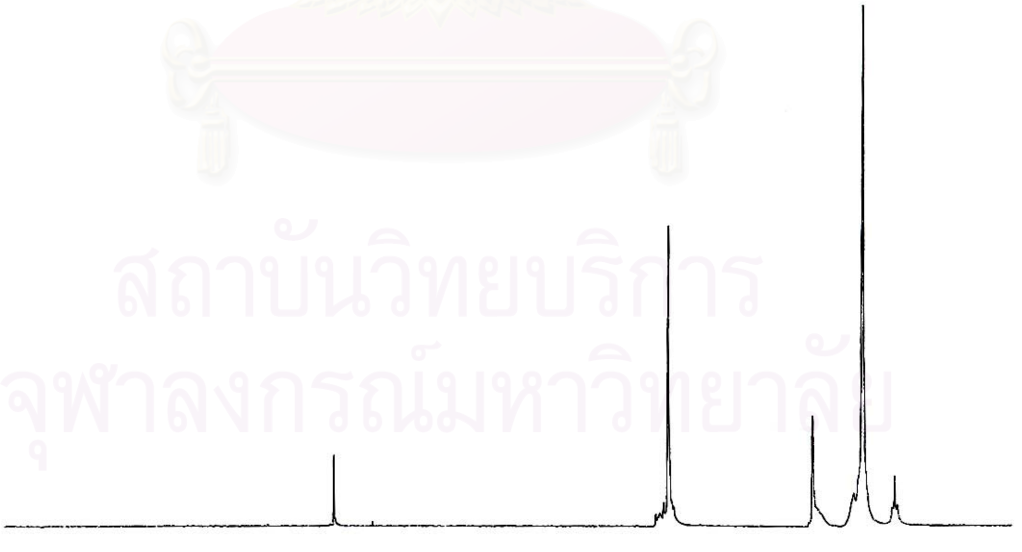

Figure E12 The ^{1}H-NMR spectrum of CTAB

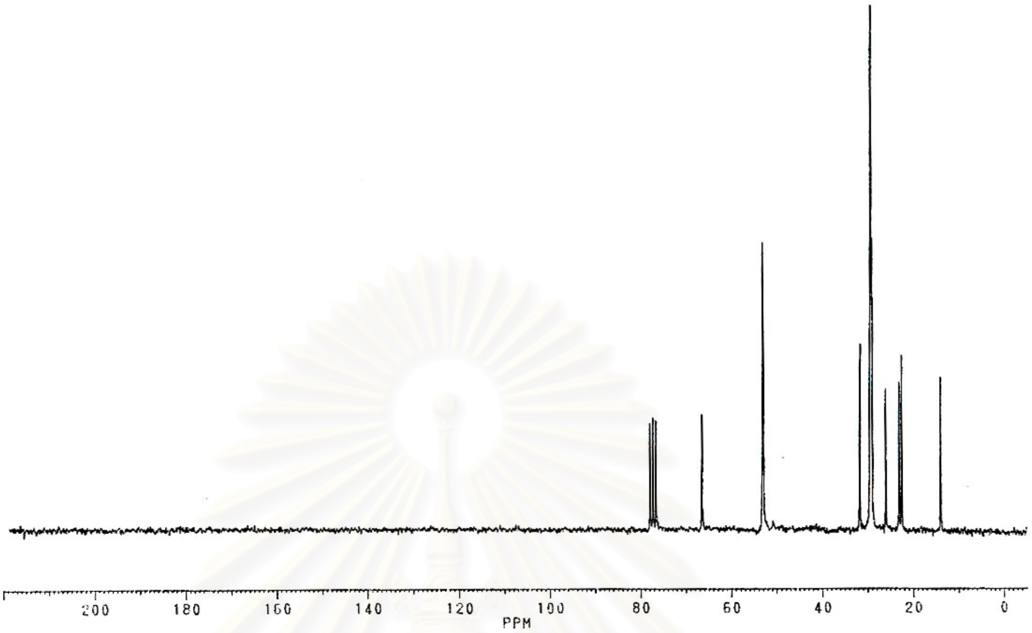

Figure E13 The ^{13}C-NMR spectrum of CTAB

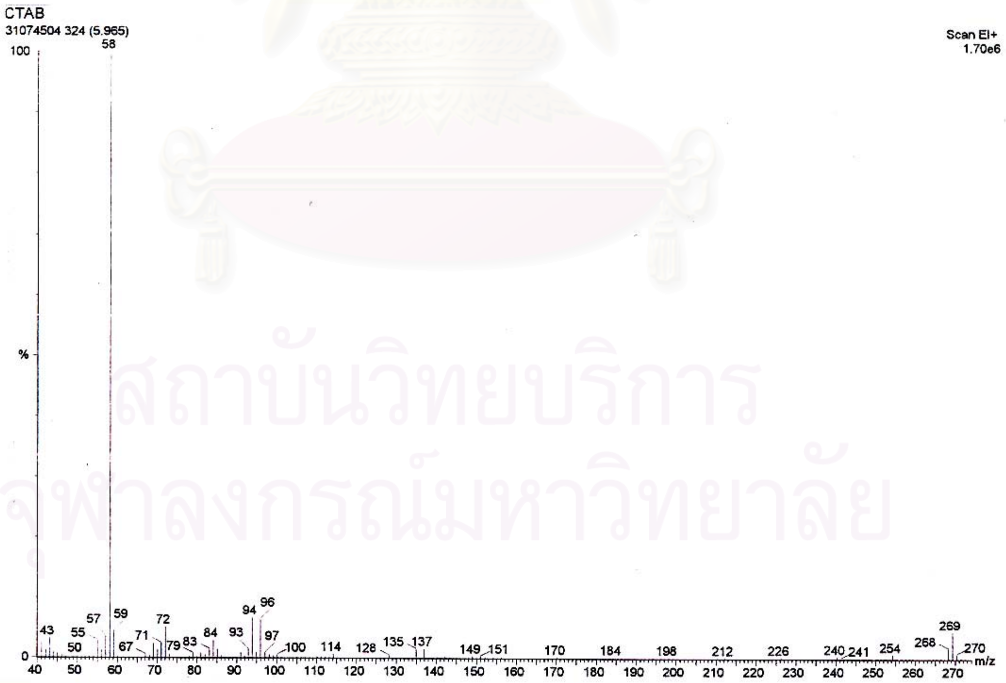

Figure E14 The mass spectrum of CTAB

APPENDIX F

% YIELD DATA OF COMPOUNDS

Table F.1 % Yield data of compound

Mixture	Weight of Mixture (g)	Molecular weight of product	Ratio of composition	Total mole $(*10^{-3})$	%Yield
1D	0.89	204	1.000	4.36	73
2D	1.08	204 248 238 282 326	0.039 0.693 0.019 0.071 0.178	4.15	69
3D	1.83	326	1.000	5.61	94
4D	1.41	170* 248 326	0.323* 0.360 0.317	3.86	64
5D	0.76	170* 204 238	0.663* 0.175 0.162	1.37	23
6D	0.55	170* 204	0.973* 0.027	0.09	1.5
7D	1.22	170* 248 326	0.694* 0.208 0.097	1.86	31
1P	0.81	162 196	0.722 0.278	4.72	79
2P	0.82	196	1.000	4.18	70
3P	0.69	196 240	0.483 0.517	3.15	53
4P	0.86	196 240 284	0.267 0.719 0.014	3.76	63
5P	0.84	196 240 284 328	0.106 0.558 0.298 0.038	3.34	56
6P	1.02	196	1.000	5.20	87

Mixture	Weight of Mixture (g)	Molecular weight of product	Ratio of composition	Total mole ($*10^{-3}$)	%Yield
7P	0.89	284	-	-	~46
		328	~1.000	2.71	
8P	0.99	328	1.000	3.02	50
9P	1.00	196	-		
		240			
		284			
		328			
10P	0.80	196	1.000	4.08	68
11P	0.56	284	-	-	29
		328	~1.000	1.71	
12P	0.95	328	1.000	2.90	48
13P	0.95	240	-		
		284			
		328			
14P	0.71	162	0.013	3.63	61
		196	0.987		
15P	0.82	250	0.027	2.58	43
		284	0.180		
		328	0.793		
16P	0.77	328	1.000	2.35	39
17P	0.91	196	0.091	3.68	61
		240	0.680		
		284	0.212		
		328	0.018		
18P	0.40	196	1.000	2.04	34
19P	0.24	328	1.000	0.73	12
20P	0.22	284	0.072	0.68	11
		328	0.928		
21P	0.46	284	0.142	1.43	24
		328	0.858		

Mixture	Weight of Mixture (g)	Molecular weight of product	Ratio of composition	Total mole (*10^{-3})	%Yield
22P	0.76	196 240 284 328	0.172 0.169 0.239 0.420	2.72	45
1T	0.34	170 248	0.454 0.546	1.60	27
2T	1.23	248	1.000	4.96	83
3T	0.40	248	1.000	1.61	27
4T	0.88	204 248	0.009 0.991	3.55	59

Total mole = Weight of mixture / Σ (Molecular weight of product * Ratio of composition)

%Yield = (Total mole / 0.006) * 100

VITA

Naruemon Kapuch was born on November 30, 1977 in Bangkok, Thailand. She received her Bachelor's Degree of Science in Chemistry, Chulalongkorn University in 1999. She continued her master's Degree of Science in Petrochemistry and Polymer Science, Faculty of Science at Chulalongkorn University in 2000 and finished in 2003.