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SYNTHESIS OF OIL SOLUBLE TRIARYLMETHANE AND FORMAZAN DYES

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งานวิจัยนี้ศึกษาการสังเคราะห์สีย้อมประเภทไตรแอริลมีเทนจากปฏิกิริยาควบแน่นระหว่าง เอ็น,เอ็น-ไดเอทิลแอนิลีนและแอโรแมติกอัลดีไฮด์ชนิดต่างๆ และผลของการแปรชนิดของแอโรแมติกอัลดีไฮด์ชนิดต่างๆ ที่มีต่อการเกิดปฏิกิริยา สมบัติการละลาย และสมบัติทางแสงของสีย้อมที่สังเคราะห์ได้ จากการทดลองพบว่า สีย้อมทุกตัวละลายดี และสีย้อมที่สังเคราะห์ได้ส่วนใหญ่มีสีเขียว สีย้อมไตรแอริลมีเทน10 มีความสามารถในการละลายได้ดีในน้ำมันแก๊สโซลีนและตัวทำละลายอินทรีย์อื่นๆ เมื่อนำสีย้อมไตรแอริลมีเทน10 บริสุทธิ์ซึ่งมีสีเขียวที่ระดับความเข้มข้น 12,000 ส่วนในล้านส่วน มาทดสอบความคงตัวของสีย้อมไตรแอริลมีเทนที่สังเคราะห์ได้พบว่า สามารถมีความคงตัวอยู่ในน้ำมันแก๊สโซลีนเป็นระยะเวลาไม่ต่ำกว่า 3 เดือน นอกจากนี้ยังทำการสังเคราะห์สีย้อมประเภทฟอร์มาแซนจากปฏิกิริยาควบแน่นระหว่างคาร์ดานอลและสารประกอบฟีนิลไฮดราซีน จากนั้นทำปฏิกิริยาควบคู่ระหว่างผลิตภัณฑ์ที่ได้และเกลือไดแอโซเนียมของแอโรแมติกแอมีนชนิดต่างๆ และศึกษาผลของการแปรชนิดของแอโรแมติกแอมีนชนิดต่างๆ ที่มีต่อการเกิดปฏิกิริยา สมบัติการละลาย และสมบัติทางแสงของสีย้อมที่ได้ จากการทดลองพบว่า สีย้อมทุกตัวให้การละลายที่ดีในน้ำมันเนื่องจากมีคาร์ดานอลเป็นองค์ประกอบในโมเลกุล และสีย้อมที่สังเคราะห์ได้พบว่ามีสีเหลืองและสีส้ม

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In this research, a series of triarylmethane dyes was synthesized by a condensation reaction of *N,N*-diethylaniline with various aromatic aldehydes. Effects of the aromatic aldehyde on the dye formation, solubility and photophysical behavior of the triarylmethane compounds were investigated. Most of triarylmethane dyes have good solubility property in organic solvent. The resulting triarylmethane dyes had green color. The selected triarylmethane dye **10** exhibited high solubility in gasoline and common organic solvents. The triarylmethane dye **10** at a concentration of 12,000 ppm was found to be stable in gasoline for at least 3 months. A series of formazan dyes was synthesized by a condensation reaction of cardanol with phenylhydrazine compounds, then coupling these products with diazonium salts of various aromatic amines. Effect of the solubility and photophysical behavior of the formazan compounds were investigated. In most cases, cardanol in the dye molecules was proved to be advantageous in giving dyes with satisfactory solubility in fuel. The resulting formazan dyes had yellow and orange color.

Field of Study: Petrochemistry and Polymer Science Student's Signature Waraporn. Ariyakriang
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4-23 Synthesis of compound **21**……………………………………………. 51

LIST OF ABBREVIATIONS

λ_{abs} : absorption wavelength
calcd : calculated
^{13}C-NMR : carbon-13 nuclear magnetic resonance spectroscopy
CNSL : cashew nut shell liquid
δ : chemical shift
$CHCl_3$: chloroform
J : coupling constant
ºC : degree Celsius
$CDCl_3$: deuterated chloroform
d : doublet (NMR)
dd : doublet of doublet (NMR)
g : gram (s)
Hz : hertz (s)
h : hour (s)
IR : Infrared spectroscopy
MS : mass spectrometry
MALDI-MS : matrix-assisted laser desorption ionization mass spectrometry
max : maximum
λ_{max} : maximum wavelength
CH_2Cl_2 : methylene chloride
μL : microliter (s)
mg : milligram (s)
mL : milliliter (s)
mmol : millimole (s)
ε : molar absorptivity
ε_{max} : molar absorptivity of maximum wavelength
m : multiplet (NMR)
nm : nanometer

NMR : nuclear magnetic resonance spectroscopy

obsd : observed

ppm : parts per million

^{1}H-NMR : proton nuclear magnetic resonance spectroscopy

st : stretching vibration (IR)

TEA : triethylamine

t : triplet (NMR)

UV/Vis : ultraviolet and visible spectroscopy

cm^{-1} : unit of wavenumber (IR)

CHAPTER I

INTRODUCTION

Nowadays, commercial petroleum products are visibly classified by adding coloring materials. For example, gasohol 95 is green while gasohol 91 is red. This is regulated by the government in order to avoid miss use of the fuel in different kind of engines. The commonly use of dyes are azo dyes and they are all imported.

Triarylmethane is an important class of compound which is found widely application in the chemical industry such as in textiles, paper, food, medicals, cosmetic, petroleum products, and especially as a sensitizer in solar cells for photoconductivity [1]. Malachite green is a typical example of this class [2]. Numerous methods have been developed for the synthesis of triarylmethane derivatives. The common method of triarylmethane preparation is the condensation reaction of aromatic aldehyde with *N*,*N*-diethylaniline.

Formazan dyes are colour azo compound of the general structure, RNH-N=CR'-N=NR', formed by reduction of a tetrazolium salt in the histochemical demonstration of oxidative enzymes. They have a variety of colors from dark blue to deep red to orange, depending on the original tetrazolium salt used as the substrate for the reaction.

Most of commercial triarylmethane and formazan dyes have good solubility in water but low solubility in petroleum products. By incorporation of long chain hydrocarbon in cardanol moiety, oil soluble triarylmethane and formazan dyes are expected.

Cardanol is a natural alkyl phenol obtained from cashew nut shell liquid (CNSL), which is commonly available in the southern part of Thailand. It is an inexpensive natural raw material bearing a long hydrocarbon chain, which enables the enhanced solubility in organic solvent and petroleum product. Cardanol derivatives are used in the preparation of additives for lubricants, diesel engine fuels, resin, stabilizers and antioxidants.

This research involves the synthesis of a highly oil soluble triarylmethane and formazan dyes as coloring agent for gasoline fuel by use of locally available cardanol as a solubilizing and inexpensive precursor for synthesis. The stability of the dye in the gasoline fuel will be examined to evaluate the possibility of the dyes for being used commercially.

1.1 Objectives of this research

The objectives of this research are synthesizing triarylmethane and formazan dyes from cardanol as coloring agent for petroleum products.

1.2 Scope of this research

The scope of this research covers the synthesis of triarylmethane dyes from aromatic aldehyde and *N*,*N*-diethylaniline, synthesis of formazan dyes from condensation of cardanol formaldehyde and phenylhydrazine derivatives such as 2,4-dinitrophenylhydrazine, then coupling with aromatic amine such as aniline, benzidine, *p*-phenylenediamine and 4-amino-*N*,*N*-dimethyl-anilne, as gasoline dyes. The product were characterized by spectroscopic techniques such as mass spectrometry, and FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV-visible spectroscopy. In addition, physical properties of dyed gasoline and the stability of the triarylmethane dyes in petroleum fuel were studied.

CHAPTER II
THEORY AND LITERATURE REVIEWS

THEORY

2.1 Color and UV/VIS spectroscopy [3-7]

Colorimetry involves the determination of a substance from its ability to absorb visible light. Visual colorimetric methods are based on the comparison of a colored solution of unknown concentration with one or more colored solutions of known concentration. In spectrophotometric methods, the ratio of the intensities of the incident and the transmitted beams of light is measured at a specific wavelength by means of a detector such as photocell.

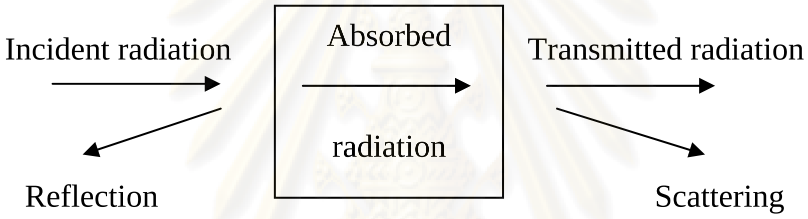


Figure 2-1 Interaction of chemical compound with light or radiation

When a continuous beam of light passes through a chemical compound, one part of the light is reflected, one part is absorbed, one part is scattered, and another part is transmitted. This last part lacks those portions of the incident light that have been absorbed or reflected and their absence will reveal on their own spectroanalytically in absorption bands. Since the reflected light has a different composition from the incident light, selective absorption of certain wavelengths of the spectrum has occurred. Whenever selective absorption occur in the visible part of the spectrum, the eye will perceive the change as an appearance of the complementary color to the colors represents by the absorbed wavelengths. The range of wavelengths, color of the corresponding light beam, and complementary colors of the various regions of the spectrum are given in table 2-1.

Table 2-1 Relation between color absorbed and color visualized.

Wavelength absorbed (nm)	Color absorbed	Color visualized
400-435	Violet	Yellow-green
435-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-blue
605-750	Red	Blue-green

The absorption of the particular part of visible region is the characteristic of its molecular structure, which depends on the structural configurations of that compound. A UV-VIS spectrophotometer is designed in order to measure the absorption of a sample at various wavelengths and plotted by a recorder to give the spectrum. The wavelength of absorption is usually reported as the maximum wavelength (λ_{max}), which is the wavelength at the highest point of the curve, while the absorption of energy is recorded as absorbance. This is shown below in the equation of Beer's law.

$$A = \varepsilon bc$$

Where A = absorbance
ε = molar absorptivity
b = cell length (cm)
c = concentration (mole/L)

It is found that the absorbance of a solution is directly proportional to the concentration. This relation is advantageous due to the quantitative analysis using a standard calibration curve, which is produced by measuring absorbance at a maximum wavelength of standard solution at various concentrations. The standard calibration curve is a plot between absorbance (y axis) and the concentration (x axis) of standard solution. When the absorbance of a sample is measured, the quantity of the sample is obtained by comparing the absorbance with a standard calibration curve.

2.2 Dye

2.2.1 Dye [8-11]

A dye may be defined as an organic compound used to impart color to other substances. It has necessarily retaining power properly on the substance to retain its color on prolonged exposure to light or to resist removal under conditions to which the substance normally is exposed.

Dyes used for coloring petroleum products, such as, gasoline, kerosene, are carried out in order to render them identifiable, and thus make difficult the possible tax evasions, which can result from utilizing said products for purpose that differ from the ones for which they are taxed. These dyes must satisfy various requirements as the following:

1. To have a high dyeing power.
2. To have a sufficient solubility in organic solvents and fuel oils.
3. To have a high diffusion index.
4. To contain little or no by-product insoluble in fuels.
5. To leave only a minimum deposit of sludge in the engines.
6. To have a proper fastness to light during storage.
7. To be compatible with additives and not cause difficulties during combustion.
8. To be brittle but no powders in the solid form.
9. To be sufficiently fluid to be solubilized in organic solvents, if it used in the form of a concentrated solution.
10. Not to be extractable from the system in which it is dissolved.

Color strength of a dye can be measured quantitatively as molar absorptivity which falls within the general ranges given below.

Table 2-2 Dye measure quantitatively as molar absorptivity.

Dye type	Molar absorptivity
Anthraquinone	5,000 – 15,000
Azo	20,000 – 40,000
Cyanine	40,000 – 80,000
Triarylmethane	40,000 – 160,000

The most precise and scientific classification of dyes is based on their chemical structure. This is the classification of interest to the research chemist and the manufacturer of dyes. The classes that are listed in the color index.

Table 2-3 Some important dyes.

Some important dyes	Uses and properties
Nitroso (quinone oxime)	For wool
Azo (aromatic and heterocyclic azo compounds)	For miscellaneous materials
Diphenylmethane (ketone imine)	For cotton, nylon and leather
Triarylmethane	For cellulose fibers
Xanthene	For paper and inks
Quinoline	For paper and wool
Thiazole	For cellulose fibers
Indamine and Indophenol	For color photography
Thiazine	For paper
Anthraquinone	For wool and silk
Indigoid	For cellulose fibers and wool

2.2.2 Triarylmethane dyes [8]

Triarylmethane dyes are basic dyes of compound which is found widely application in the chemical industry such as wool or silk, or for cotton mordanted with tannic acid. Similarly other workers have prepared electrodes using triarylmethane dyes. While others have investigated using the dyes in solar cells as sensitizers for photoconductivity [12]. From the time of their discovery in 1859 to the development of the anthraquinone vat dyes, the triarylmethane dyes were regarded highly because of their brilliant color that is not only absorb strongly some parts of the spectrum, but they reflect strongly other parts of the spectrum. They are not fast to light or washing, however, except when applied to acrylic fibers.

In their structures, the central carbon is bonded to three aromatic rings. One of which is in the quinonoid form (the chromophore). Basic Green 4 (Malachite Green, 489), the typical example of this class which used for dyeing acrylic fibers and leather and for coloring bast fibers, paper, and lacquers, is made by condensing benzaldehyde with dimethylaniline to give bis(p-dimethylaminophenyl)phenylmethane, which is known as the leuco base. Oxidation converts it to the carbinol, which also is colorless and is known as the color base or the carbinol base. Strong acids convert the color base into the colored dye.

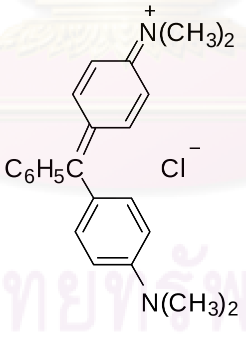


Figure 2-2 Structure of Basic Green 4 (Malachite Green)

2.2.3 Formazan [13]

Formazans are compounds which contain the characteristic chain of atoms -N=N-C=N-NH-. Such compounds form a distinct class with characteristic properties, their structures were first elucidated by Bamberger and by von Pechmann who agreed to call them formazyl compounds. The term *guanazyl* is applied to variations of this structure in which the =N-NH- group is linked to a guanyl group and not to an aryl radical (as it is in all ordinary formazans hitherto described). Such compounds are characterized by the group -N=N-C=N-NH-C (=NH)-NH_2 They are sufficiently akin to the formazans to be described in this review, but their chemistry is not extensive. Recently two further types of compounds of related structure have been described: *(a)* In one, a cholyl radical (introduced as a cholylhydrazide) replaces the aryl group normally attached to the –NH-N= system. *(b)* In the other, a diary1 carbonyl group (introduced as a diarylsemicarbazone) replaces the same aryl group.

2.3 Cashew Nut Shell Liquid (CNSL) [14-19]

The cashew tree, *Anacardium occidentable* Linn., is a native plant of Brazil and was brought to Asia and Africa by the Portuguese in the 1600’s. It was first brought into Thailand by the governor of Trang in 1901. It can be grown in all parts of Thailand especially in Songkhla, Phuket, Nakhon Sithammarat, Phung-nga, Krabi and Surat Thani. The shape of the nut is look like the kidney. The shell of the nut is grey brown in color and hard. It consists of two layers. The outer layer, which is smooth surfaced, thin and tough. The inner layer is hard. Between the two layers is a honeycomb structure which contains a phenolic material known as Cashew Nut Shell Liquid (CNSL) which is a reddish brown viscous liquid. Inside the shell is the kernel, wrapped in a thin brown skin, known as the testa.

Cashew nut shell liquid (CNSL) is obtained as a by-product from mechanical processing for edible use of cashew kernel (Anacardium occidentale L.) and is a mixture of anacardic acid **1**, cardanol **2** and smaller amounts of cardol **3** and 2-methyl-cardol **4**. Due to the easy thermal decarboxylation of anacardic acid **1**, the main component of distilled CNSL is cardanol **2** (yield up to 70–80% and purity up to 90%) as a mixture of saturated (3-n-pentadecylphenol), monoolefinic [3-(n-pentadeca-8-enyl)phenol], diolefinic [3-(n-pentadeca-8,11-dienyl)phenol], and triolefinic [3-(n-pentadeca-8,11,14-trienyl)phenol] long-chain phenols, with an average value of two double bonds per molecule. Cardol **3** and methylcardol **4** are present in smaller percentages (Figure 2-3).

Anacardic acid | Cardanol

6-pentadecenyl salicylic acid | 3-pentadecenyl phenol

2-methyl cardol | Cardol

2-methyl-5-pentadecenyl resorcinol | 5-pentadecenyl resorcinol

where n= 0, 2, 4 or 6

Figure 2-3 Chemical structure of components in natural CNSL.

Cardanol is a phenolic compound with a C_{15} aliphatic chain in the meta position, obtained from cashew nut shell liquid (CNSL). The structure and composition of cardanol is given in Figure 2-4. It is a mixture of saturated and unsaturated (mono-, di-, and tri-) compounds.

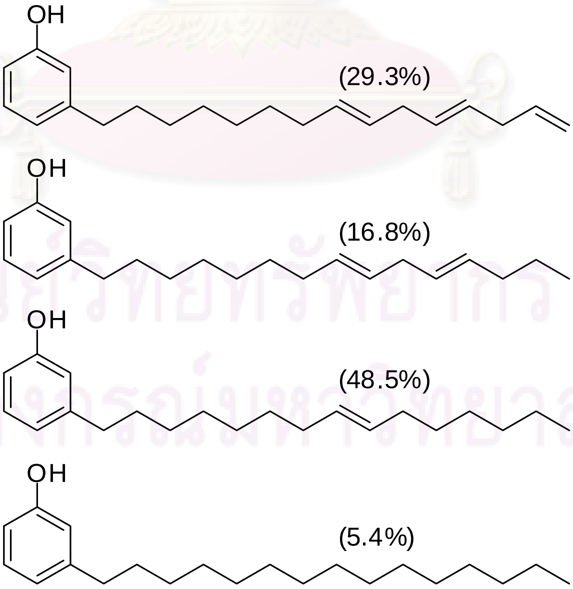


Figure 2-4 Structure and composition of cardanol.

Table 2-4 Characteristics of cardanol.

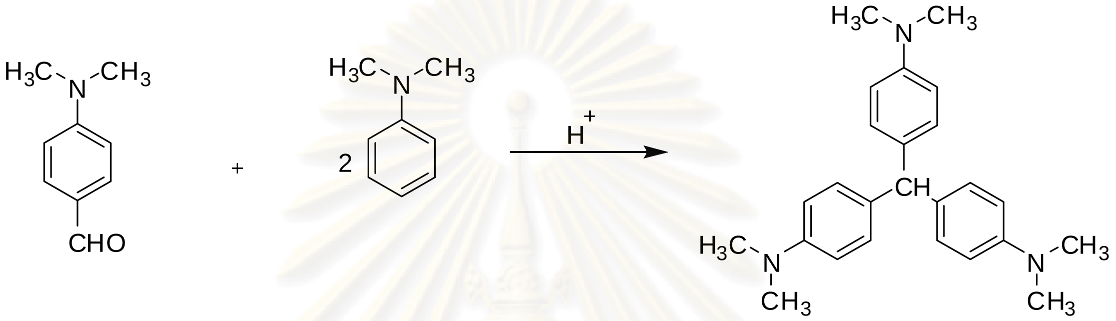
Boiling point, ^{o}C	228–235 (3.4 mmHg)
Color (Livibond, 1 cm cell) (freshly distilled)	Red (1.0–3.0) Yellow (1.5–3.5)
Viscosity, 30^{o}C (cP)	40–60
Specific gravity 30/30 ^{o}C	0.93–0.95
Volatile loss, % by wt (max)	2.0
Acid value	1.9–2.0
Iodine value (Wijs method)	210–220
Hydroxyl value	180–200

2.3.1 Uses and applications

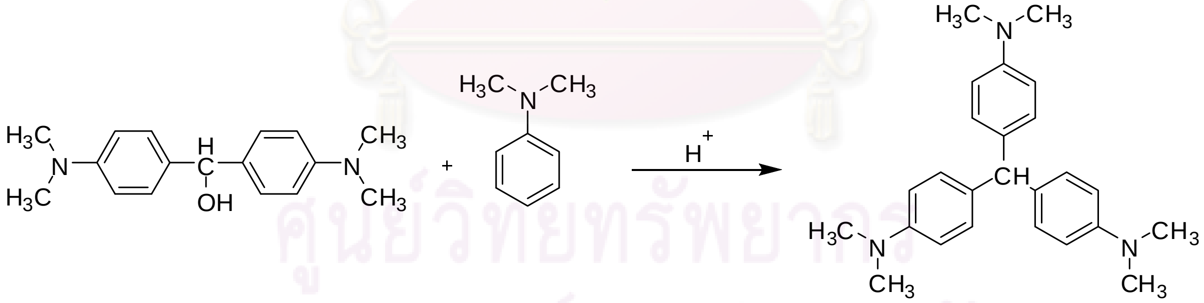
The CNSL is an undesirable by-product of the cashew kernel industry. It has become a valuable raw material in the manufacture of numerous industrial products. It is used commercially as a phenolic raw material for the manufacture of certain resins and plastics [20]. In particular, it is used as a friction modifier in the manufacture of brake linings and clutch facings because it has an excellent frictional properties [21]. It is also used in rubber compounds, where it acts as vulcanizing agents by mixing with natural rubber and other additives. The mechanical properties of the resulting rubber, such as tensile strength, hardness, elongation and rebound resilience are improved [22]. The resins from CNSL are used in laminating for papers, cloths and glass fibers, or impregnating materials where oil or acid resistance is required [23]. Furthermore, hydrogenated cardanol represented a simple and easily available entry to various derivatives useful for different purposes such as antioxidants, flame-retardants, water-proofing agents and gum inhibitors for gasoline [24]. Other applications include used in the manufacture of lacquers, paints, printing inks, electrical insulation material, impregnating materials, anti-corrosive for metals, laminates, insulating varnishes, surface coating, adhesives, insecticides and fungicides [25, 26, 27].

LITERATURE REVIEWS

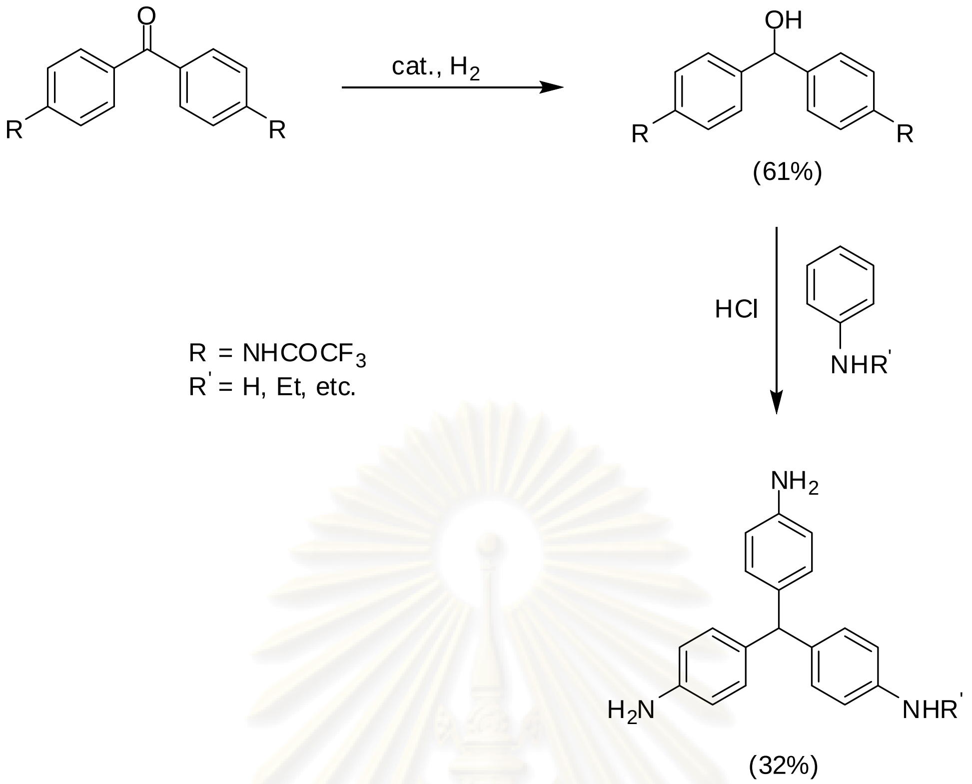
Tsujimoto et al. [28] reported two typical methods for the synthesis of triarylmethane compounds. Method A, it is generally prepared by a reacting aromatic aldehyde with a complex of a formylating agent (dimethylformamide, diethylformamide) and an acid catalyst (phosphorus oxychloride, phosphorus oxybromide, thionyl chloride) to form an aromatic aldehyde. Then, the catalyst is hydrolyzed and the reaction system is neutralized by addition of an alkaline substance.



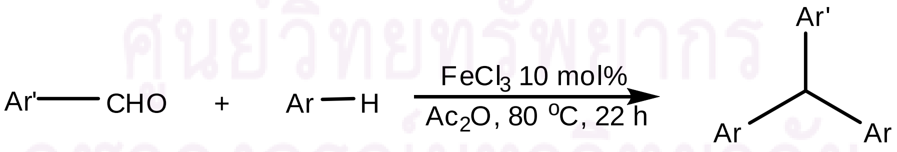
On the other hand, method B have a problem of low purity of the hydrol derivative used as the starting material. This reason makes it difficult to obtain the desired product in a highly pure form.



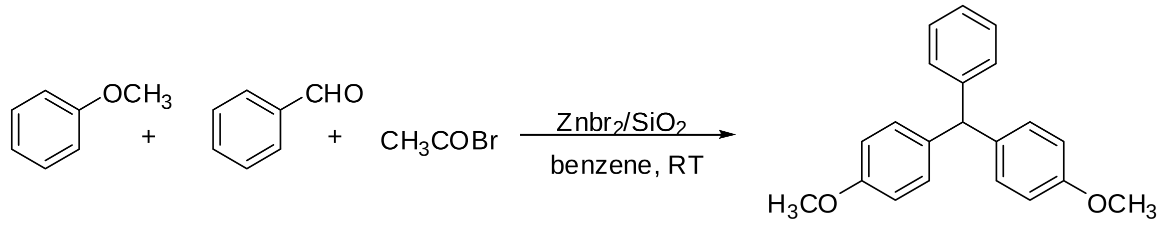
Nair et al. [29] report a facile method for the synthesis of triarylmethane by the catalytic hydrogenation of the diaryl ketone and the subsequent treatment of the carbinol with aryl amines and HCl.

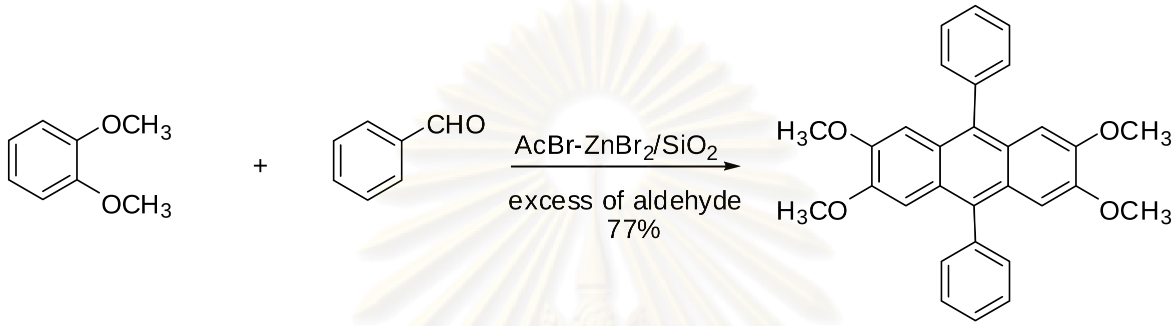


Li et al. [30] reported the synthesis of triarylmethane derivatives from aromatic aldehydes and arenes catalyzed by $FeCl_3$. This method is simple and mild reaction conditions. They found that the yield was improved when acetic anhydride was added. The reactions proceeded smoothly with both electron-rich and electron-poor aromatic aldehydes and acetylation of arenes was not observed in these reactions in the presence of acetic anhydride. Longer reaction times were required (50 h) when highly electron deficient p-nitrobenzaldehyde was used.

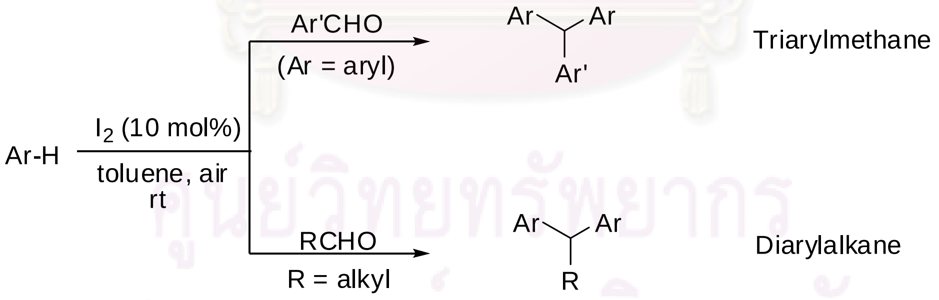


Kodomari et al. [31] reported the synthesis of triarylmethane and 9,10-diarylanthracenes which are very important compounds in pharmaceutical industry from an electron-rich arenes such as anisole, 1,2-dimethoxybenzene, 1,3,5-trimethoxybenzene, 2- and 4-methoxytoluene, and 1-methoxynaphthalene with acetyl bromide and aromatic aldehydes in the presence of $ZnBr_2/SiO_2$. This method gave the corresponding triarylmethanes in high yields under mild conditions. They found that the reaction of anisole with benzaldehyde in the presence of $ZnBr_2/SiO_2$ at room temperature did not give the products but this reaction with acetyl bromide and benzaldehyde in the presence of $ZnBr_2/SiO_2$ in the same condition gave 4,4'-dimethoxytriphenylmethane in high yield.

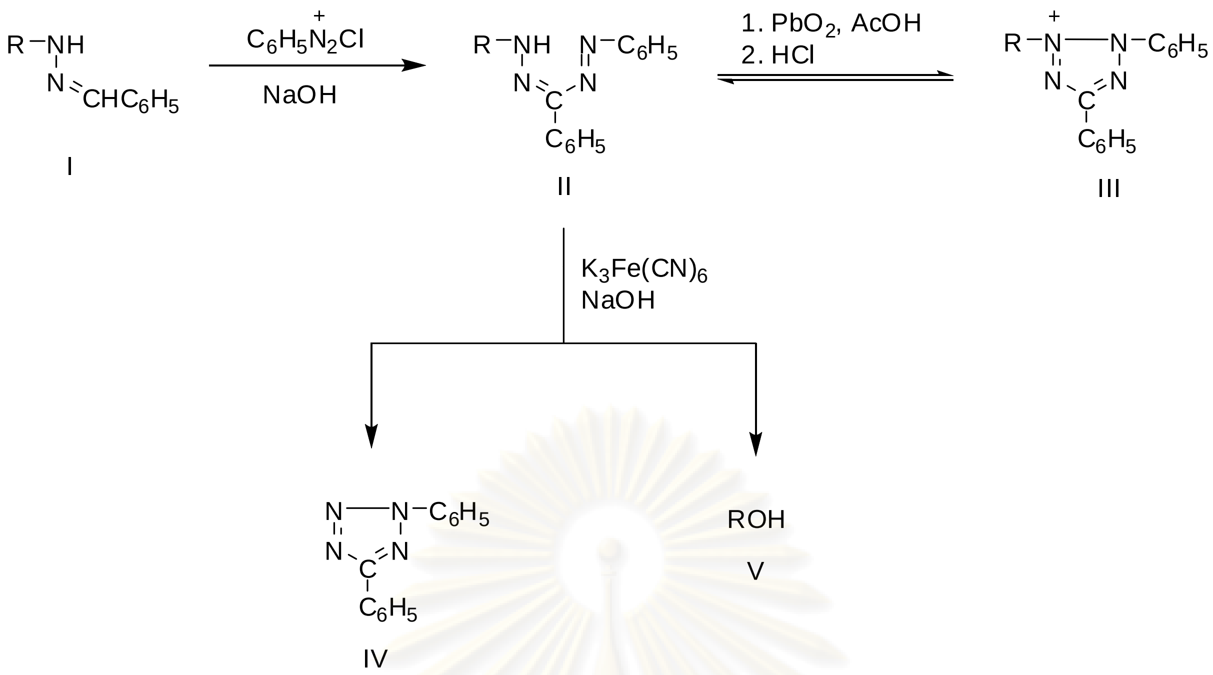




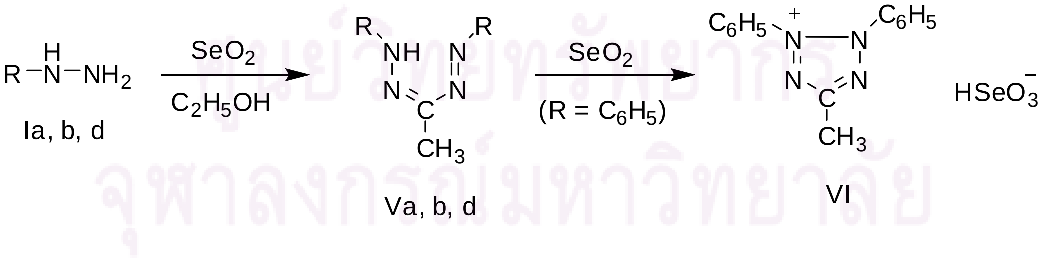
Jaratjaroonphong et al. [32] reported the synthesis of triarylmethanes and diarylalkanes from electron-rich arenes reacted with aromatic aldehydes and aliphatic aldehydes using iodine catalyzed Friedel-Crafts alkylation in high yields under mild conditions.



Shchipanov et al. [33] reported the synthesis of formazan obtained by diazo coupling of benzaldehyde (1-methyl-5-pyrazolyl)hydrazone (I) with benzenediazonium chloride which is resistant to autoxidation but under the influence of potassium ferricyanide readily undergoes destruction to give 2,5-diphenyltetrazole (IV) and 1-methyl-5-hydroxytetrazole (V). A tetrazolium salt, which was isolated in the form of the chloride (III), is obtained in good yield by oxidation of II with lead dioxide in acetic acid.

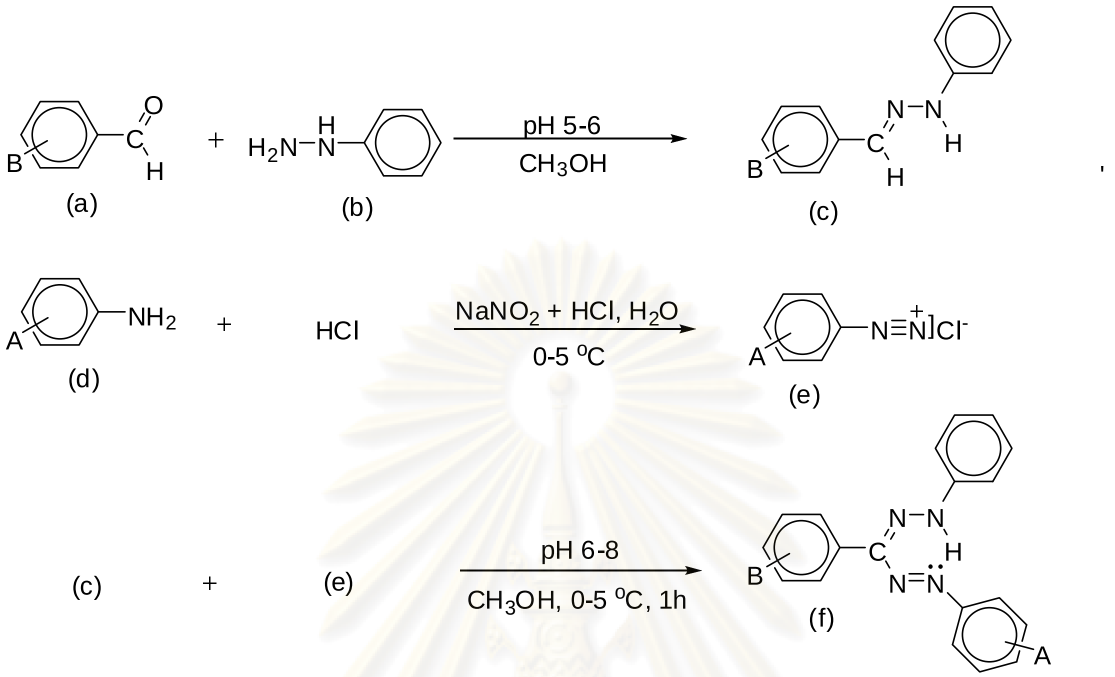


Sedov [34] reported that the oxidation of benzimidazolylhydrazines Ia, b with selenium dioxide in absolute ethanol proceeds via a different pathway. In this case symmetrical 1,5-di(2'-benzimidazolyl)-3-methylformazans (Va, b) are formed in low yields. Their structures were confirmed by comparison with compounds with known structures. Phenylhydrazine (Id), like hydrazines Ia, b, also gives symmetrical 1,5-diphenyl-2-methylformazan (Vd), althaugh in very low yield (~1%), when it is oxidized in absolute alcohol the process does not stop at this stage but proceeds further to give tetrazolium salt VI, which without isolation from the solution.



a: R = 2-benzimidazolyl, b: R = i- methy]-2-benzimidazolyl, d: R = C_6H_5

Tezcan and Uzluk [35] reported the synthesis of formazans with various substituents attached at the 1- and 3-phenyl rings which less toxic compounds for medical use by condensation of aromatic and aliphatic aldehydes with phenylhydrazine and then coupling the resulting hydrazones with diazonium salts. This method gives a low yield and the purification of the products is difficult but it has the advantage of synthesizing both symmetrical and asymmetrical formazans. The general formula is shown below:



CHAPTER III
EXPERIMENTAL

3.1 Chemicals

All chemicals were purchased from commercial sources and used as received, unless noted otherwise.

1. Cardanol : Obtained locally
2. Hydrogenated cardanol : A gift from Dr.Nantanit Wanichacheva
3. Urea : Fluka
4. Acetic acid : Merck
5. *N*,*N*-diethylaniline : Merck
6. Benzaldehyde : Merck
7. Salicylaldehyde : Fluka
8. 2-Nitrobenzaldehyde : Fluka
9. 4-Nitrobenzaldehyde : Aldrich
10. 4-Methoxybenzaldehyde : Panreac Sintesis
11. 4-(Dimethylamino)benzaldehyde : Merck
12. 2-Chlorobenzaldehyde : Fluka
13. 4-Carboxybenzaldehyde : Fluka
14. Cinnamaldehyde : Aldrich
15. Toluene : Lab Scan
16. Triethylamine : Merck
17. Tin (IV) tetrachloride : Fluka
18. Paraformaldehyde : Merck
19. Hydrochloric acid : Merck
20. Phenylhydrazine : Aldrich
21. 2,4-Dinitrophenylhydrazine : Aldrich
22. Tetrahydrofuran : Merck
23. Dioxane : Merck
24. Sodium sulfate (anhydrous) : Merck
25. Potassium hydroxide : Merck
26. Sodium nitrite : Merck
27. 4-Amino-*N*,*N*-dimethylaniline : Fluka

28. Aniline : Merck
29. Benzidine : Fluka
30. *p*-Phenylenediamine : Fluka
31. Methanol : Merck
32. Ethanol : Merck
33. Methylene chloride : Distilled from commercial grade (Lab-scan)
34. Hexane : Distilled from commercial grade (Lab-scan)
35. Ethyl acetate : Distilled from commercial grade (Lab-scan)
36. Silica gel : Merck
37. Base gasoline 91 : Veerasuwan oil refinery
38. Deuterated chloroform : Merck

3.2 Analytical instruments

FT-IR spectra were recorded on a Nicolet Fourier Transform Infrared Spectrophotometer: Impact 410 (Nicolet Instruments Technologies, Inc. WI, USA). Infrared spectra were recorded between 400 cm^{-1} to 4,000 cm^{-1} in transmittance mode.

^{1}H-NMR and ^{13}C-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) using Bruker Spectrospin AG, Switzerland and Varian Mercury NMR spectrometer (Varian Company, CA, USA) operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual $CHCl_3$ peak (7.26 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR). Coupling constants (J) are reported in Hertz (Hz).

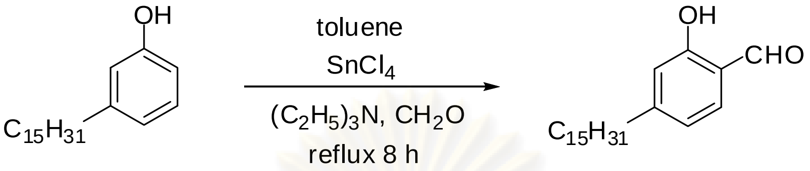
Mass spectra were obtained using matrix-assisted laser desorption ionization mass spectrometry (MALDI-TOF) by using dithranol as a matrix.

Absorption spectra and quantities of triarylmethane dyes in gasoline fuel were measured using a Hewlett-Packard 8453 spectrophotometer.

3.3 Experimental procedure

Part 1: Synthesis of hydrogenated cardanol formaldehyde

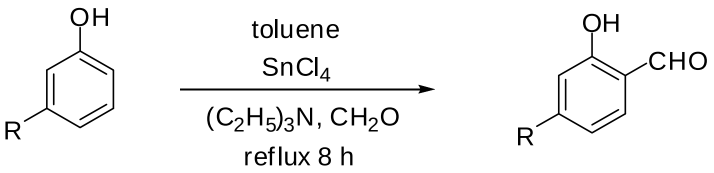
3.3.1 Condensation of hydrogenated cardanol with paraformaldehyde



Following a previously published procedure [36], to a solution of hydrogenated cardanol (3.04 g, 0.01 mol) in toluene (20 mL) was added triethylamine (0.55 mL, 0.004 mol) and tin(IV)tetrachloride (115.0 μL, 0.001 mol). The reaction mixture was stirred for 30 minutes at room temperature under N_2 and then paraformaldehyde (0.66 g, 0.02 mol) was added. The reaction mixture was heated at 100 °C for 8 h. After cooling down to room temperature, the reaction mixture was poured into water and acidified to pH 2 with hydrochloric acid. Then the aqueous layer was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated to dryness. The resulting crude product was purified by chromatography (silica, hexane) to give a white crystals, (6.53 g, 65%); ^{1}H-NMR: δ (ppm) 0.87 (t, *J* = 6.8 Hz, 3H), 1.20 – 1.70 (m, 26H), 2.61 (t, *J*= 7.6 Hz, 2H), 6.80 (s, 1H), 6.83 (d, *J*= 6.8 Hz, 1H), 7.44 (d, *J* =7.9 Hz, 1H), 9.83 (s, 1H), 11.04 (s, 1H) (**Figure A-1**); ^{13}C-NMR: δ (ppm) 14.1, 22.7, 29.2, 29.40, 29.43, 29.5, 29.63, 29.65, 29.69, 30.7, 31.9, 36.4, 117.1, 118.4, 120.5, 133.6, 153.9, 161.8, 195.8 (**Figure A-2**); IR: ν_{max} (cm^{-1}): 3184 (O-H st), 2958 (=C-H st), 2850, 2915 (C-H st), 1623, 1666 (C=C st) (**Figure A-3**).

Part 2: Synthesis of cardanol formaldehyde

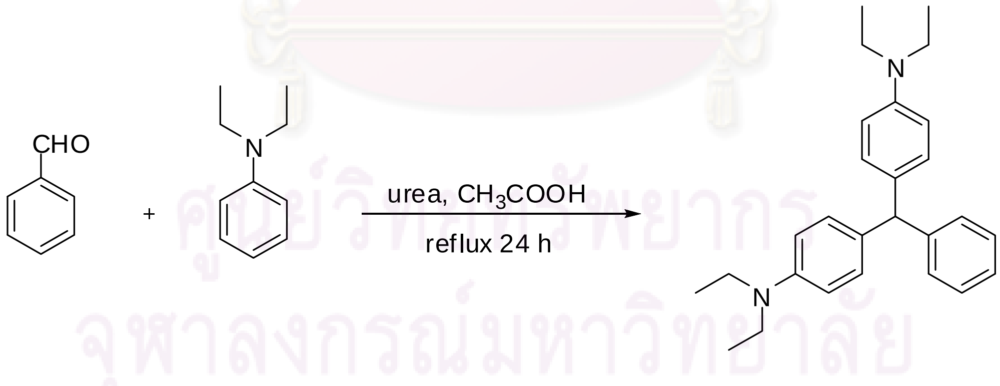
3.3.2 Condensation of cardanol with paraformaldehyde



According to the above-mentioned synthesis of hydrogenated cardanol formaldehyde, to a solution of cardanol (2.98 g, 10.00 mol) in toluene (20 mL) was added triethylamine (0.55 mL, 4.00 mmol) and tin(IV)tetrachloride (115 µL, 1.00 mmol). The reaction mixture was stirred for 30 min at room temperature under N_2 and then paraformaldehyde (0.66 g, 0.02 mol) was added. The reaction mixture was heated at 100 °C for 8 h. After cooling down to room temperature, the reaction mixture was poured into water and acidified to pH 2 with hydrochloric acid. Then the aqueous layer was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated to dryness. The resulting crude product was purified by chromatography (silica, hexane) to give a pale yellow oil**;** (2.14 g, 66%); ^{1}H-NMR: δ (ppm) 0.80 – 2.10 (m), 2.61 (t, *J*= 7.6 Hz), 2.80 (m), 5.0, 5.4, 5.8 (m), 6.79 (s), 6.83 (d, *J* =7.9 Hz), 7.44 (d, *J* =7.9 Hz), 9.83 (s), 11.04 (s) (**Figure A-4**); ^{13}C-NMR: δ (ppm) 14.1, 25.6-31.8, 36.4, 114.7, 117.0, 118.9, 120.5, 126.8, 127.7, 128.1, 129.3, 129.7, 130.0, 130.2, 133.6, 153.7, 161.9, 195.8 (**Figure A-5**); IR: ν_{max} (cm^{-1}): 3408 (O-H st), 3003(=C-H st), 2850, 2927 (C-H st), 2741 (C-OH st) 1628, 1652 (C=C st) (**Figure A-6**).

Part 3: Synthesis of triarylmethane dye

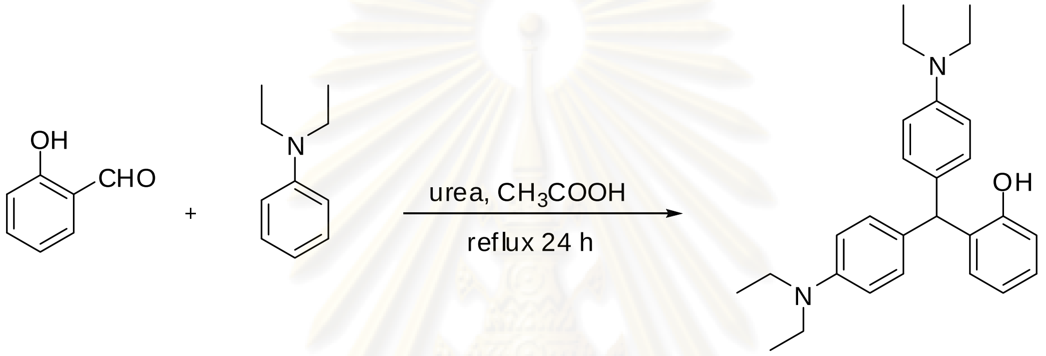
3.3.3 Triarylmethane dye 1 from benzaldehyde and *N,N*-diethylaniline



1

Following a previously published procedure [37], benzaldehyde (0.13 g, 1.21 mmol), *N,N*-diethylaniline (0.41 mL, 2.66 mmol), and urea (0.05g, 0.91 mmol) were dissolved in glacial acetic acid (6.25 mL) and then were refluxed for 24 h. The reaction mixture was evaporated and extracted with CH_2Cl_2. The organic phase was separated, dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a blue-green oil (0.12 g, 25%); ^{1}H-NMR: δ (ppm) 1.13 (t, *J* = 6.4 Hz, 12H), 3.31 (q, *J* = 7.0 Hz, 8H), 5.33 (s, 1H), 6.59 (d, *J* = 7.3 Hz, 4H), 6.95 (d, *J* = 7.7 Hz, 4H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 6.5 Hz, 2H), 7.26 (t, *J* = 6.9 Hz, 2H) (**Figure A-7**); ^{13}C-NMR: δ (ppm) 12.7, 44.4, 55.0, 111.7, 125.7, 128.0, 129.4, 130.1, 131.7, 145.8, 146.1 (**Figure A-8**); IR: ν_{max} (cm^{-1}): 2920, 2963 (C-H st), 1562, 1615 (C=C st), 1197 (C-N st) (**Figure A-9**); MALDI-MS obsd 386.710; calcd avg mass 386.572 [M = $C_{27}H_{34}N_2$] (**Figure A-10**); UV: λ_{abs} (CH_2Cl_2) 629 nm, ε (CH_2Cl_2) 7.04 (**Figure B-1**).

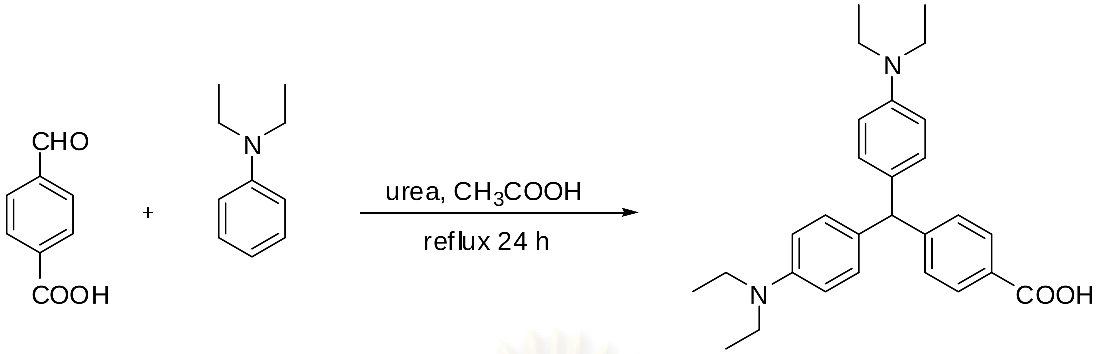
3.3.4 Triarylmethane dye 2 from salicylaldehyde and *N*,*N*-diethylaniline



2

According to the above-mentioned synthesis of compound **1** using salicylaldehyde (0.15 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a green oil (0.13 g, 27%); ^{1}H-NMR: δ (ppm) 1.15 (t, *J* = 7.0 Hz, 12H), 3.33 (q, *J* = 7.0 Hz, 8H), 4.96 (s, 1H), 5.39 (s, 1H), 6.62 (d, *J* = 8.5 Hz, 4H), 6.83-6.89 (m, 3H), 7.00 (d, *J* = 8.5 Hz, 4H), 7.14 (t, *J* = 7.4 Hz, 1H) (**Figure A-11**); ^{13}C-NMR: δ (ppm) 12.7, 44.3, 50.0, 112.0, 116.4, 120.5, 127.6, 128.9, 130.1, 130.3, 131.6, 146.7, 154.0 (**Figure A-12**); IR: ν_{max} (cm^{-1}): 3477 (O-H st), 2924, 2967 (C-H st), 1561, 1611 (C=C st), 1193 (C-N st) (**Figure A-13**); MALDI-MS obsd 402.590; calcd avg mass 402.572 [M = $C_{27}H_{34}N_2O$] (**Figure A-14)**; UV: λ_{abs} (CH_2Cl_2) 627 nm, ε (CH_2Cl_2) 15.52 (**Figure B-2**).

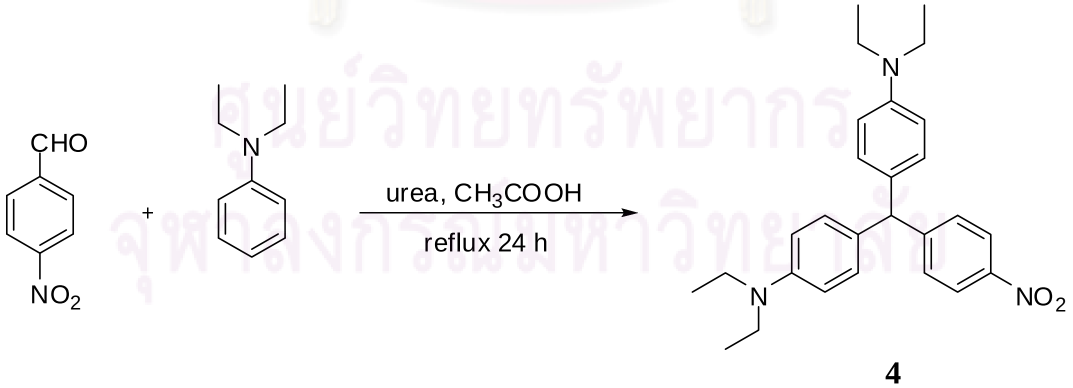
3.3.5 Triarylmethane dye 3 from 4-carboxybenzaldehyde and *N,N*-diethylaniline



3

According to the above-mentioned synthesis of compound **1** using 4-carboxybenzaldehyde (0.18 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by sonication in hexane and filter to give a green solid (0.15 g, 30%); ^{1}H-NMR: δ (ppm) 1.14 (t, *J*=7.0 Hz, 12H), 3.32 (q, *J*=6.9 Hz, 8H), 5.39 (s, 1H), 6.61 (d, *J*=6.3 Hz, 4H), 6.94 (d, *J*=8.5 Hz, 4H), 7.26 (d, *J*=8.2 Hz, 2H), 7.99 (d, *J*=8.3 Hz, 2H) (**Figure A-15**); ^{13}C-NMR: δ (ppm) 12.1, 44.1, 55.0, 112.0, 126.6, 129.5, 130.0, 130.5, 146.1, 152.0, 171.8 (**Figure A-16**); IR: ν_{max} (cm^{-1}): 3032 (=C-H st), 2930, 2964 (C-H st), 1577, 1607 (C=C st), 1441 (COOH st), 1190 (C-N st) (**Figure A-17**); MALDI-MS obsd 429.614; calcd avg mass 430.582 [M = $C_{28}H_{34}N_2O_2$] (**Figure A-18**); UV: λ_{abs} (CH_2Cl_2) 630 nm, ε (CH_2Cl_2) 941.16 (**Figure B-3**).

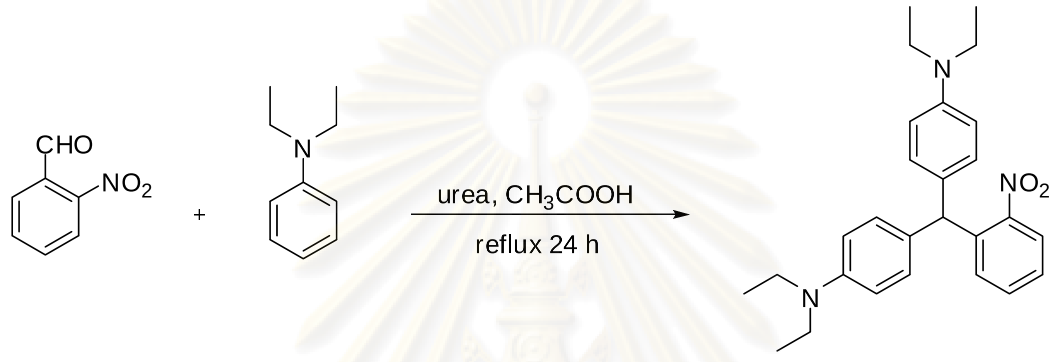
3.3.6 Triarylmethane dye 4 from 4-nitrobenzaldehyde and *N,N*-diethylaniline



4

According to the above-mentioned synthesis of compound **1** using 4-nitrobenzaldehyde (0.18 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a green oil (0.11 g, 21%); ^{1}H-NMR: δ (ppm) 1.14 (t, *J* = 7.0 Hz, 12H), 3.32 (q, *J* = 6.9 Hz, 8H), 5.40 (s, 1H), 6.60 (d, *J* = 8.3 Hz, 4H), 6.91 (d, *J* = 8.3 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H) (**Figure A-19**); ^{13}C-NMR: δ (ppm) 12.6, 44.3, 54.9, 111.7, 123.3, 129.8, 130.0, 130.1, 146.1, 146.5, 153.9 (**Figure A-20**); IR: ν_{max} (cm^{-1}): 2927, 2963 (C-H st), 1555, 1608 (C=C st), 1339 (C-NO_2), 1193 (C-N st) (**Figure A-21**); MALDI-MS obsd 431.966; calcd avg mass 431.570 [M = $C_{27}H_{33}N_3O_2$] (**Figure A-22**); UV: λ_{abs} (CH_2Cl_2) 597 nm, ε (CH_2Cl_2) 7.22 (**Figure B-4**).

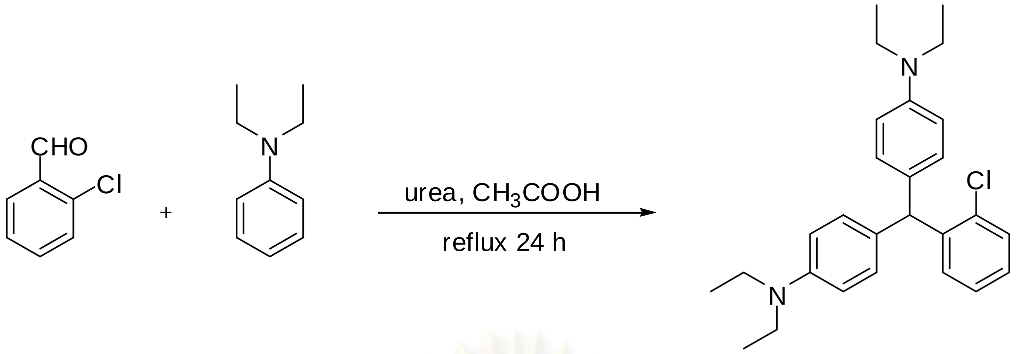
3.3.7 Triarylmethane dye 5 from 2-nitrobenzaldehyde and *N,N*-diethylaniline



5

According to the above-mentioned synthesis of compound **1** using 2-nitrobenzaldehyde (0.18 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a green oil (0.19 g, 37%); ^{1}H-NMR: δ (ppm) 1.13 (t, *J* = 7.0 Hz, 12H), 3.31 (q, *J* = 6.9 Hz, 8H), 6.02 (s, 1H), 6.58 (d, *J* = 8.4 Hz, 4H), 6.90 (d, *J* = 8.3 Hz, 4H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H) (**Figure A-23**); ^{13}C-NMR: δ (ppm) 12.6, 44.3, 49.3, 111.7, 124.3, 126.7, 129.5, 130.2, 132.01, 132.03, 140.1, 146.4, 149.9 (**Figure A-24**); IR: ν_{max} (cm^{-1}): 2927, 2967 (C-H st), 1608, 1515 (C=C st), 1353 (C-NO_2 st), 1197 (C-N st) (**Figure A-25**); MALDI-MS obsd 431.716; calcd avg mass 431.570 [M = $C_{27}H_{33}N_3O_2$] (**Figure A-26**); UV: λ_{abs} (CH_2Cl_2) 644 nm, ε (CH_2Cl_2) 30.67 (**Figure B-5**).

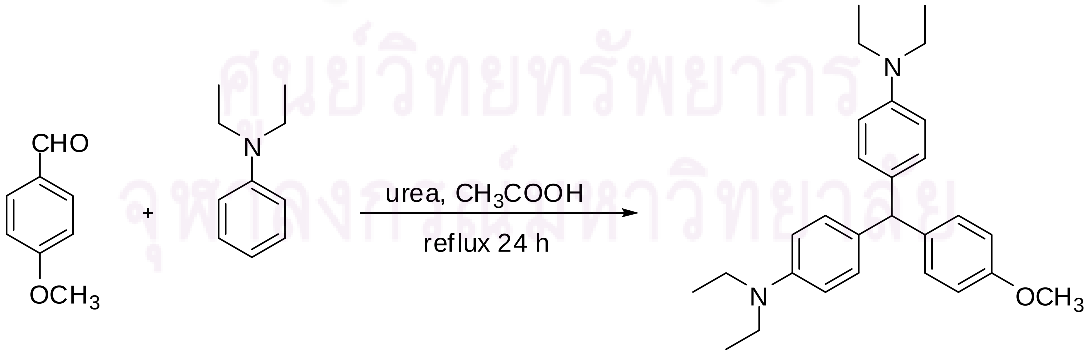
3.3.8 Triarylmethane dye 6 from 2-chlorobenzaldehyde and *N,N*-diethylaniline



6

According to the above-mentioned synthesis of compound **1** using 2-chlorobenzaldehyde (0.17 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a blue-green oil (0.18 g, 36%); ^{1}H-NMR: δ (ppm) 1.14 (t, *J* = 7.0 Hz, 12H), 3.32 (q, *J* = 7.0 Hz, 8H), 5.75 (s, 1H), 6.60 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.04-7.17 (m, 3H), 7.34 (d, *J* = 7.2 Hz, 1H) (**Figure A-27**); ^{13}C-NMR: δ (ppm) 12.7, 44.3, 51.4, 126.3, 127.1, 128.3, 129.4, 130.2, 131.1, 134.4, 143.3, 146.3 (**Figure A-28**); IR: ν_{max} (cm^{-1}): 2920, 2963 (C-H st), 1565, 1608 (C=C st), 1197 (C-N st), 692 (C-Cl st) (**Figure A-29**); MALDI-MS obsd 421.818; calcd avg mass 421.017 [M = $C_{27}H_{33}ClN_2$] (**Figure A-30**); UV: λ_{abs} (CH_2Cl_2) 643 nm, ε (CH_2Cl_2) 72.76 (**Figure B-6**).

3.3.9 Triarylmethane dye 7 from 4-methoxybenzaldehyde and *N,N*-diethylaniline

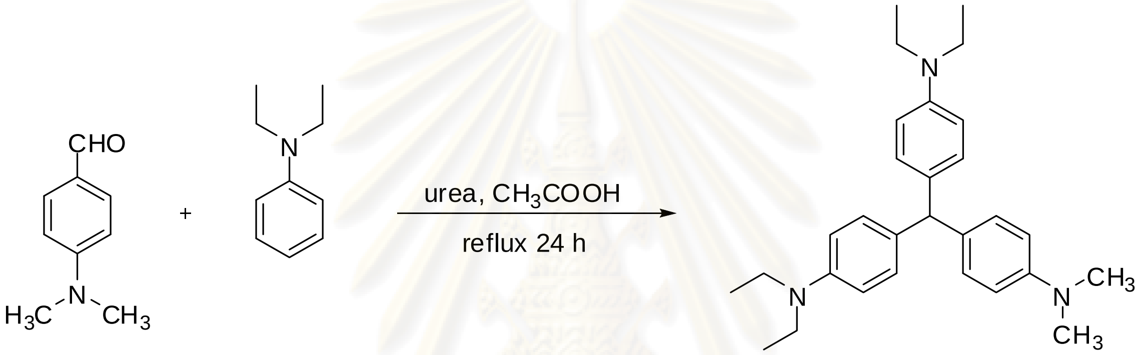


7

According to the above-mentioned synthesis of compound **1** using 4-methoxybenzaldehyde (0.16 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a green oil (0.10

g, 21%); ^{1}H-NMR: δ (ppm) 1.13 (t, *J* = 6.6 Hz, 12H), 3.31 (q, *J* = 6.8 Hz, 8H), 3.77 (s, 3H), 5.28 (s, 1H), 6.59 (d, *J* = 7.7 Hz, 4H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 4H), 7.06 (d, *J* = 7.7 Hz, 2H) (**Figure A-31**); ^{13}C-NMR: δ (ppm) 12.7, 44.3, 54.1, 55.2, 111.7, 113.4, 130.0, 130.3, 132.1, 138.0, 146.1, 157.6 (**Figure A-32**); IR: ν_{max} (cm^{-1}): 2930, 2973 (C-H st), 2831 (OCH_3) 1578, 1608 (C=C st), 1197 (C-N st) (**Figure A-33**); MALDI-MS obsd 416.535; calcd avg mass 416.598 [M = $C_{28}H_{36}N_2O$] (**Figure A-34**); UV: λ_{abs} (CH_2Cl_2) 617 nm, ε (CH_2Cl_2) 836.65 (**Figure B-7**).

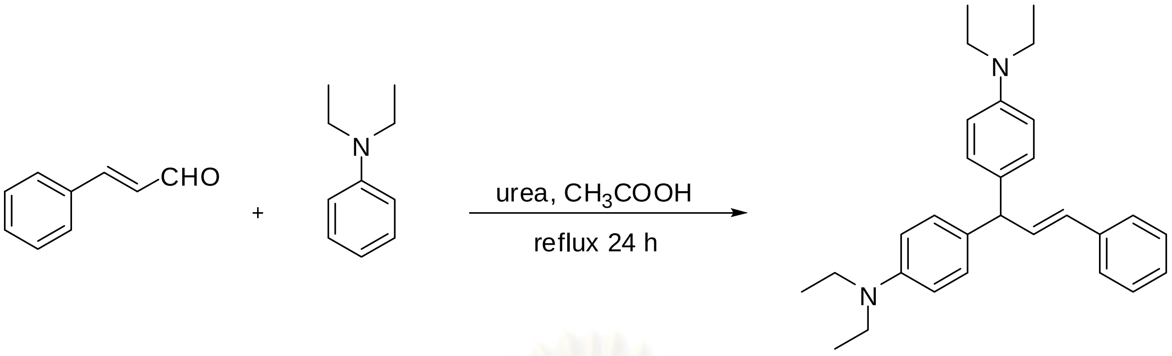
3.3.10 Triarylmethane dye 8 from 4-(dimethylamino)benzaldehyde and *N,N*-diethylaniline



8

According to the above-mentioned synthesis of compound **1** using 4-(dimethylamino)benzaldehyde (0.18 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (1:1)] to give a dark blue oil. However, the target compound could not be isolated. Due to the complication of the spectrum of the crude sample, the target compound could not be elucidated. ^{1}H-NMR spectrum of the reaction crude indicated the formation of compound **8** in the region at 1.12, 2.89, 3.30, 5.30, 6.59, 6.96, 7.05 ppm (**Figure A-35**); MALDI-MS obsd 429.903; calcd avg mass 429.640 [M = $C_{29}H_{39}N_3$] (**Figure A-36**); UV: λ_{abs} (CH_2Cl_2) 590 nm, ε (CH_2Cl_2) 176.3185 (**Figure B-8**).

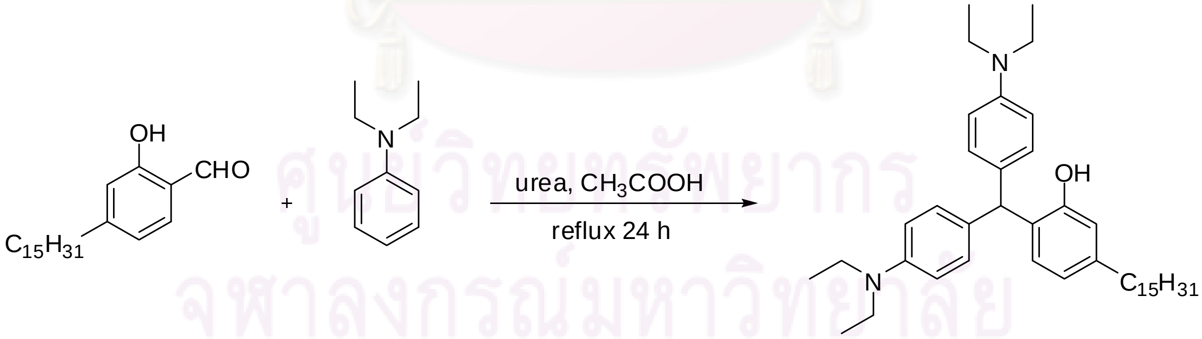
3.3.11 Triarylmethane dye 9 from cinnamaldehyde and *N,N*-diethylaniline



9

According to the above-mentioned synthesis of compound **1** using cinnamaldehyde (0.16 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (6:1)] to give a green oil, However, the target compound could not be isolated. Due to the complication of the spectrum of the crude sample, the target compound could not be elucidated. ^{1}H-NMR spectrum of the reaction crude indicated the formation of compound **9** in the region at δ 1.12, 3.30, 5.32, 6.59, 6.94, 7.06, 7.15 ppm (**Figure A-37**); MALDI-MS obsd 412.775; calcd avg mass 412.610 [M = $C_{29}H_{36}N_2$] (**Figure A-38**); UV: λ_{abs} (CH_2Cl_2) 729 nm, ε (CH_2Cl_2) 135.9571 (**Figure B-9**).

3.3.12 Triarylmethane dye 10 from hydrogenated cardanol formaldehyde and *N,N*-diethylaniline

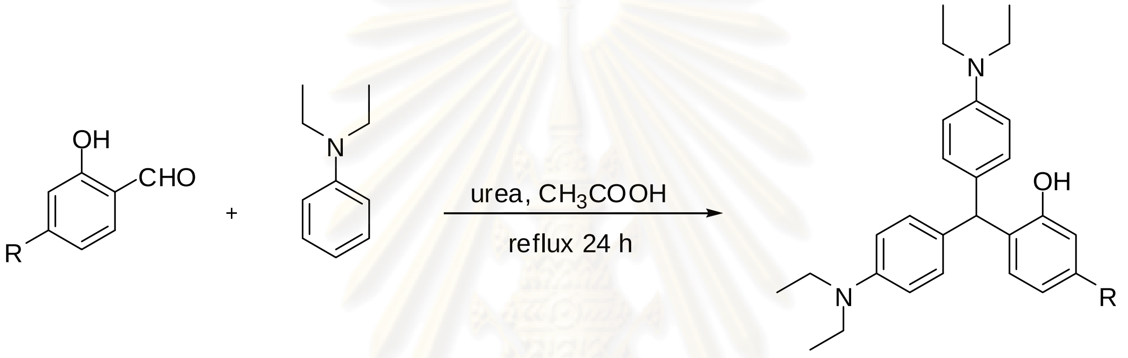


10

According to the above-mentioned synthesis of compound **1** using hydrogenated cardanol formaldehyde (0.40 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a green oil (0.30 g, 41%); ^{1}H-NMR: δ (ppm) 0.88 (t, *J* = 6.7 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 12H), 1.20-1.60 (m, 26H), 2.52 (t, *J* = 8.0 Hz, 2H), 3.32 (q, *J* = 7.0 Hz, 8H),), 4.85 (s, 1H), 5.32 (s, 1H), 6.61 (d, *J* = 8.6 Hz, 4H), 6.66 (d, *J* = 4.2 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.6

Hz, 4H) (**Figure A-39**); ^{13}C-NMR: δ (ppm) 12.6, 14.1, 22.7, 29.3, 29.4, 29.5, 29.6, 29.7, 31.2, 31.9, 35.5, 44.4, 49.8, 112.1, 116.4, 120.5, 128.2, 128.7, 129.3, 130.0, 142.7, 146.7, 153.8 (**Figure A-40**); IR: ν_{max} (cm^{-1}): 3485 (O-H st), 3016 (=C-H st), 2847, 2917 (C-H st), 1562, 1608 (C=C st), 1200 (C-N st) (**Figure A-41**); MALDI-MS obsd 612.106; calcd avg mass 612.970 [M = $C_{42}H_{64}N_2O$] (**Figure A-42**); UV: λ_{abs} (CH_2Cl_2) 624 nm, ε (CH_2Cl_2) 35.01 (**Figure B-10**).

3.3.13 Triarylmethane dye 11 from cardanol formaldehyde and *N,N*-diethylaniline

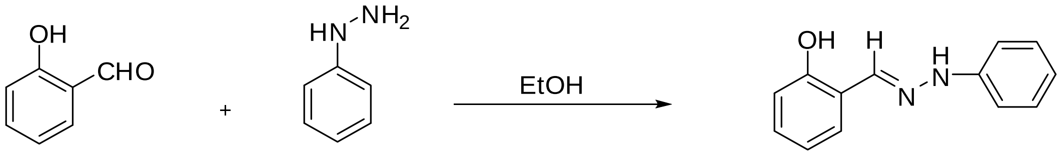


11

According to the above-mentioned synthesis of compound **1** using non-hydrogenated cardanol formaldehyde (0.40 g, 1.21 mmol) as a benzaldehyde derivative. The resulting crude product was purified by preparative TLC [hexane/ethyl acetate (5:1)] to give a green oil (0.21 g, 29%); ^{1}H-NMR: δ (ppm) 0.86-2.83 (m), 1.13 (t, *J* = 6.8 Hz), 2.52 (t, *J* = 7.7 Hz), 2.80 (m), 3.31 (q, *J* = 6.8 Hz), 4.84 (s), 4.96-5.87 (m), 6.60 (d, *J* = 8.1 Hz), 6.65 (d, *J* = 4.7 Hz), 6.74 (d, *J* = 7.5 Hz), 6.99 (d, *J* = 8.1 Hz) (**Figure A-43**); ^{13}C-NMR: δ (ppm) 12.6, 14.1, 22.8, 25.6–31.8, 35.5, 44.3, 49.8, 112.0, 114.7, 116.3, 120.5, 126.8, 127.6, 129.9, 130.5142.7, 146.6, 153.8 (**Figure A-44**); IR: ν_{max} (cm^{-1}): 3478 (O-H st), 3003 (=C-H st), 2850, 2923 (C-H st), 1569, 1612 (C=C st), 1193 (C-N st) (**Figure A-45**); MALDI-MS obsd 605.179-612.334; calcd avg mass 606.923-612.970 [M = $C_{42}H_{64-n}N_2O$; n = 0, 2, 4, 6] (**Figure A-46**); UV: λ_{abs} (CH_2Cl_2) 593 nm, ε (CH_2Cl_2) 39.27 (**Figure B-11**).

Part 4: Synthesis of formazan model

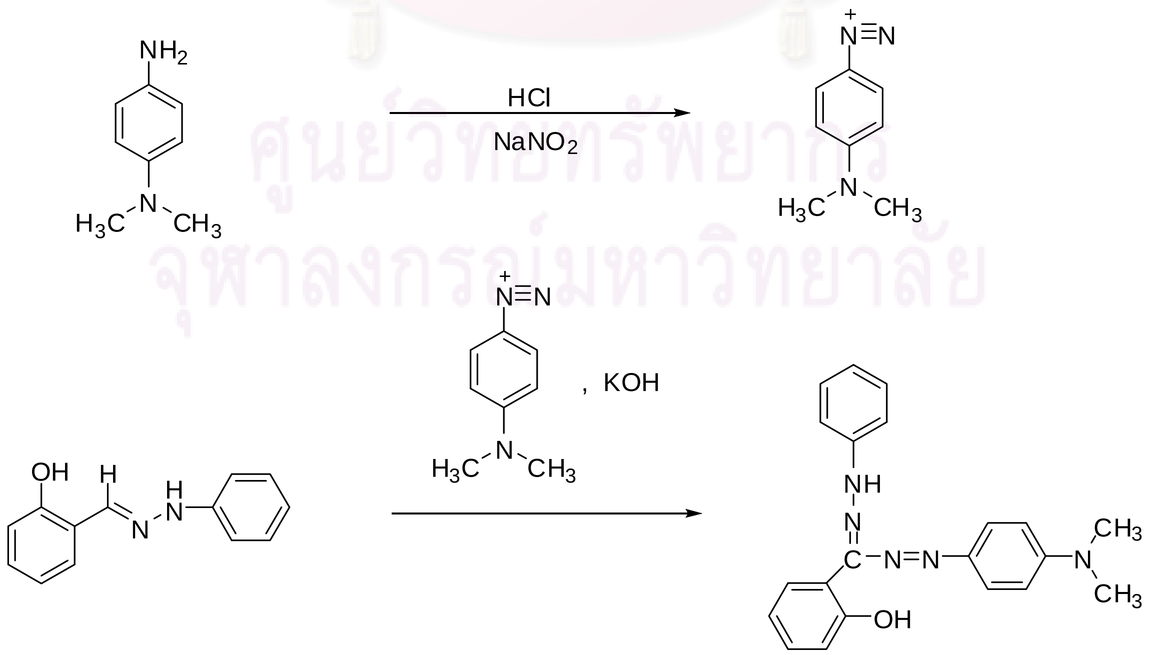
3.3.14 Synthesis of phenylhydrazone 12 from salicylaldehyde and phenylhydrazine



12

Following a previously published procedure [38], phenylhydrazine (0.27 g, 2.50 mmol) was dissolved in ethanol (5 mL) and salicylaldehyde (0.30 g, 2.50 mmol) was added in a solution. The reaction mixture was stirred at room temperature for 3 h. Then the reaction mixture was cooled and filtered. The resulting crude product was purified by tritulation with hexane to give a yellow solid (0.29 g, 55%); ^{1}H-NMR: δ (ppm) 6.89–7.02 (m, 5H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.22–7.33 (m, 3H), 7.84 (s, 1H), 10.90 (s, 1H) (**Figure A-47**); ^{13}C-NMR: δ (ppm) 112.7, 116.6, 118.5, 119.5, 120.9, 129.4, 129.6, 130.1, 141.2, 143.4, 157.1 (**Figure A-48**); IR: ν_{max} (cm^{-1}): 3286 (N-H st), 2844, 2912 (C-H st), 1589, 1601 (C=C st), 1564 (C=N st) (**Figure A-49**); MALDI-MS obsd 212.148; calcd avg mass 212.247 [M = $C_{13}H_{12}N_2O$] (**Figure A-50**).

3.3.15 Synthesis of formazan 13 from phenylhydrazone 12

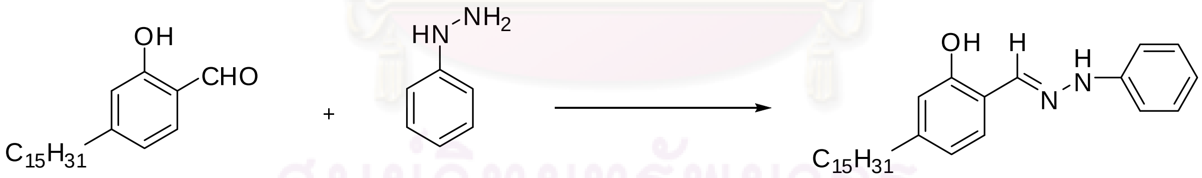


13

Following a previously published procedure [39], 4-*N*,*N*-dimethylaniline (0.02 g, 0.16 mmol) was dissolved in water (0.26 mL) and hydrochloric acid (0.10 mL). Then diazotized at 0-5 ºC with a solution of sodium nitrite (0.02 g, 0.33 mmol) in water (0.12 mL). After that the reaction mixture was added to a solution of phenylhydrazone **12** (0.07 g, 0.33 mmol) in tetrahydrofuran (2.66 mL). Then a solution of potassium hydroxide (0.20 g, 3.66 mmol) in water (0.66 mL) was added to a reaction mixture and stirred at below -2 ºC for 2 h. The reaction mixture was cooled to room temperature and diluted with water, then the precipitate was filtered. The resulting crude product was purified by preparative TLC (CH_2Cl_2) to give a dark purple solid (0.01 g, 24%); ^{1}H-NMR: δ (ppm) 3.15 (s, 6H), 6.79 (d, *J* = 9.1 Hz, 2H), 6.94 (t, *J* = 7.0 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 6.5 Hz, 1H), 11.55 (s, 1H) (**Figure A-51**); ^{13}C-NMR: δ (ppm) 40.3, 111.9, 114.2, 117.1, 119.0, 120.2, 122.9, 125.0, 127.6, 129.4, 129.6, 142.3, 142.7, 142.8, 153.2, 156.6 (**Figure A-52**); MALDI-MS obsd 358.628; calcd avg mass 359.424 [M = $C_{21}H_{21}N_5O$] (**Figure A-5**3); UV: λ_{abs} (CH_2Cl_2) 560 nm, ε (CH_2Cl_2) 191,154 (**Figure B-12**).

Part 5: Synthesis of formazan from hydrogenated cardanol formaldehyde

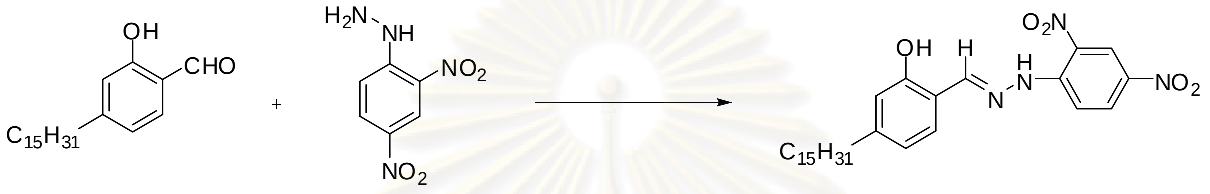
3.3.16 Synthesis of phenylhydrazone 14 from hydrogenated cardanol formaldehyde and phenylhydrazine



14

Following a previously published procedure [38], phenylhydrazine (0.07 g, 0.62 mmol) was dissolved in tetrahydrofuran (2.50 mL) and hydrogenated cardanol formaldehyde (0.21 g, 0.62 mmol) was added in a solution. The reaction mixture was stirred at room temperature for 3 h. Then the reaction mixture was cooled and filtered. The resulting crude product was purified by column chromatography on a silica gel [hexane/CH_2Cl_2 (1:1)] to give a pale yellow solid (0.23 g, 87%); ^{1}H-NMR: δ (ppm), 0.88 (t, *J* = 6.5 Hz, 3H),1.25–1.63 (m, 26H), 2.58 (t, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.83 (s, 1H), 6.91 (t, *J* = 7.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.42 (s, 1H), 7.85 (s, 1H), 10.80 (s, 1H) (**Figure A-54**); ^{13}C-NMR: δ (ppm) 14.1, 22.7, 29.7, 31.1, 31.9, 36.0, 112.6, 116.1, 116.4, 119.4, 120.7, 129.2, 129.5, 141.5, 143.6, 145.9, 157.1 (**Figure A-55**); IR: ν_{max} (cm^{-1}): 3314 (N-H st), 2844, 2912 (C-H st), 1601, 1629 (C=C st), 1558 (C=N st) (**Figure A-56**); MALDI-MS obsd 422.602; calcd avg mass 422.646 [M = $C_{28}H_{42}N_2O$] (**Figure A-57**).

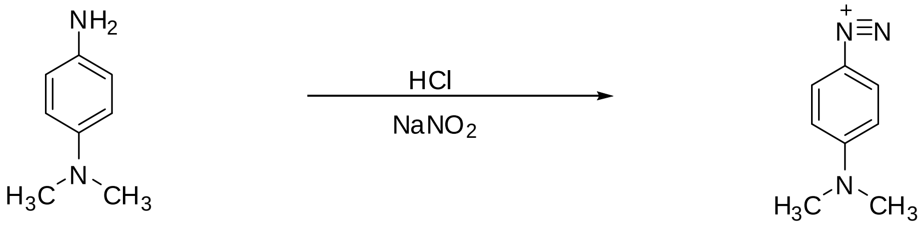
3.3.17 Synthesis of phenylhydrazone 15 from hydrogenated cardanol formaldehyde and 2,4-dinitrophenylhydrazine

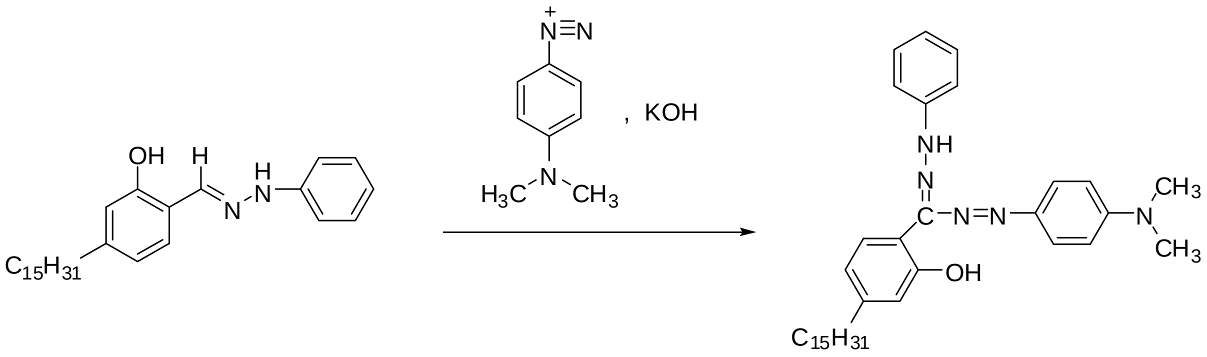


15

According to the above-mentioned synthesis of compound **14** using 2,4-dinitrophenylhydrazine (0.12 g, 0.62 mmol) as a phenylhydrazine derivative was dissolved in dioxane (2.50 mL). The resulting crude product was purified by column chromatography on a silica gel [hexane/CH_2Cl_2 (1:1)] to give an orange solid (0.12 g, 37%); ^{1}H-NMR: δ (ppm) 0.78 (t, *J* = 6.1 Hz, 3H), 1.18–1.62 (m, 26H), 2.49 (t, *J* = 7.6 Hz, 2H), 6.66 (s, 1H), 6.67 (d, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 9.6 Hz, 1H), 8.29 (d, *J* = 9.6 Hz, 1H), 8.56 (s, 1H), 8.93 (s, 1H), 9.63 (s, 1H), 11.31 (s, 1H) (**Figure A-58**); ^{13}C-NMR: δ (ppm) 13.4, 22.6, 29.3, 29.5, 29.7, 31.0, 31.9, 35.8, 115.6, 116.1, 120.1, 122.8, 129.3, 129.7, 137.9, 144.0, 147.9, 149.9, 157.8 (**Figure A-59**); IR: ν_{max} (cm^{-1}): 3270 (N-H st), 3088 (=C-H st), 2844, 2918 (C-H st), 1592, 1611 (C=C st), 1580 (C=N st) (**Figure A-60**); MALDI-MS obsd 512.595; calcd avg mass 512.641 [M = $C_{28}H_{40}N_4O_5$] (**Figure A-61**).

3.3.18 Synthesis of formazan 16 from phenylhydrazone 14 and 4-Amino-*N,N*-dimethylaniline

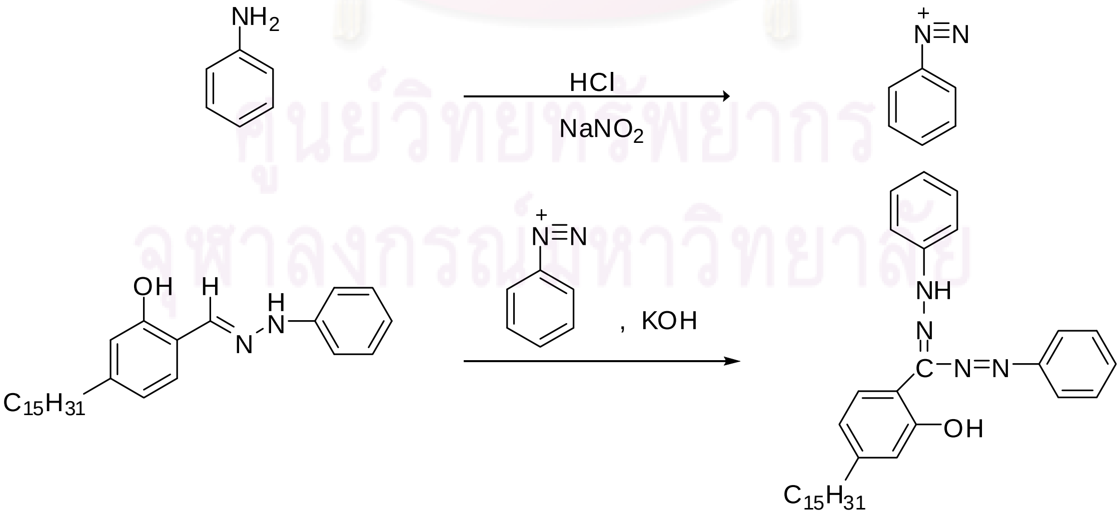




16

Following a previously published procedure [39], 4-*N,N*-dimethylaniline (0.02 g, 0.16 mmol) was dissolved in water (0.26 mL) and hydrochloric acid (0.1 mL). Then diazotized at 0-5 ºC with a solution of sodium nitrite (0.02 g, 0.33 mmol) in water (0.12 mL). After that the reaction mixture was added to a solution of phenylhydrazone **14** (0.14 g, 0.33 mmol) in tetrahydrofuran (2.66 mL). Then a solution of potassium hydroxide (0.20 g, 3.67 mmol) in water (0.66 mL) was added to a reaction mixture and stirred at below -2 ºC for 2 h. The reaction mixture was cooled to room temperature and diluted with water, then the precipitate was filtered. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (2:1)] to give a yellow solid; MALDI-MS obsd 568.178; calcd avg mass 569.823 [M = $C_{36}H_{51}N_5O$] (**Figure A-62**).

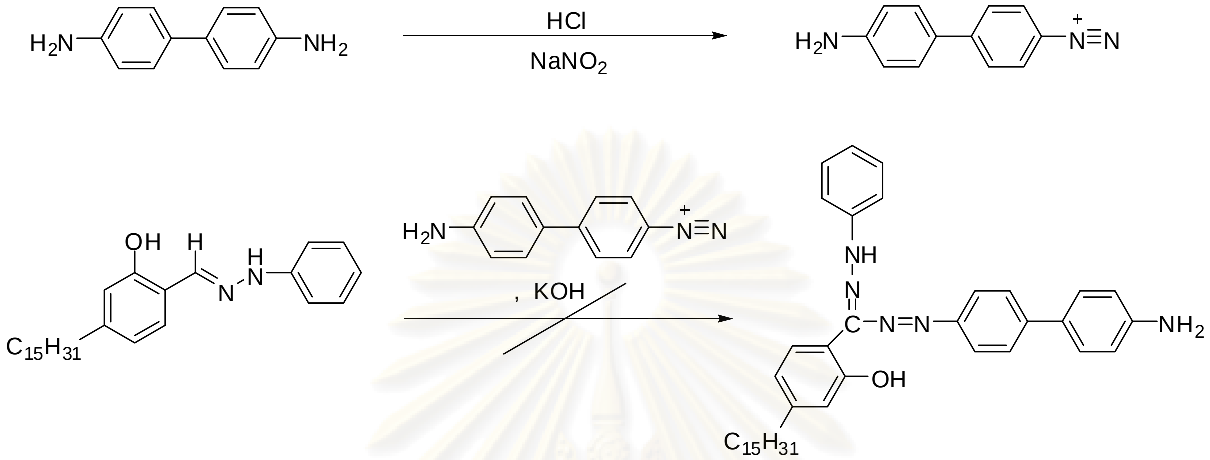
3.3.19 Synthesis of formazan 17 from phenylhydrazone 14 and aniline



17

According to the above-mentioned synthesis of compound **16** using aniline (0.01 g, 0.16 mmol) as an aromatic amine derivative. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (2:1)] to give a yellow solid; MALDI-MS obsd 525.192; calcd avg mass 526.755 [M = $C_{34}H_{46}N_4O$] (**Figure A-63**); UV: λ_{abs} (CH_2Cl_2) 339 nm, ε (CH_2Cl_2) 26,551 (**Figure B-13**).

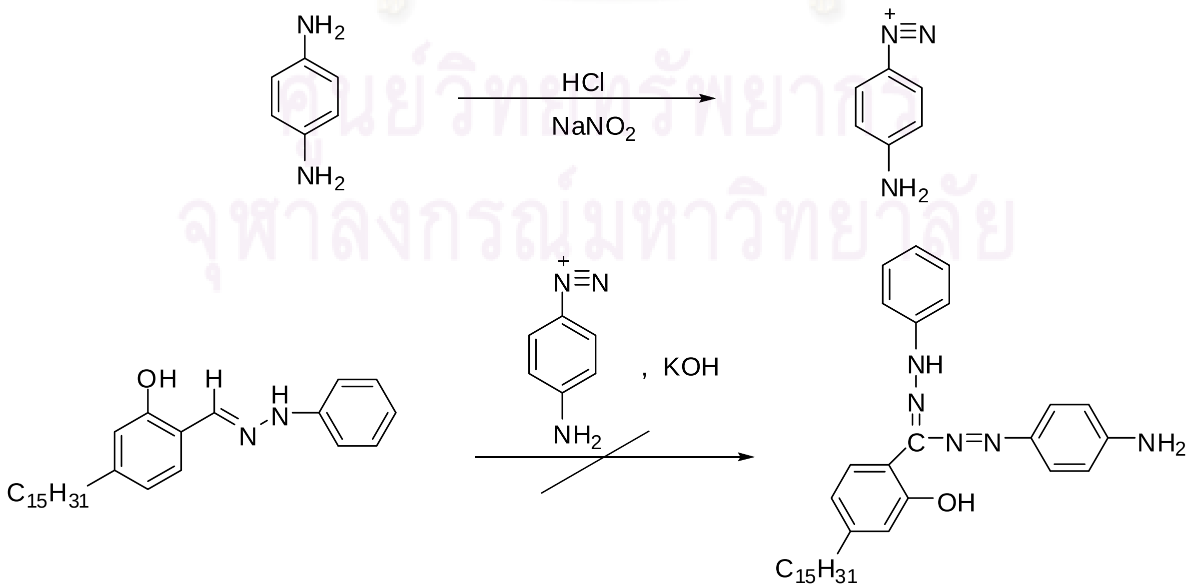
3.3.20 Synthesis of formazan 18 from phenylhydrazone 14 and benzidine



18

According to the above-mentioned synthesis of compound **16** using benzidine (0.03 g, 0.16 mmol) as an aromatic amine derivative. An attempt to coupling benzidine with phenylhydrazone **14** failed to give compound **18**.

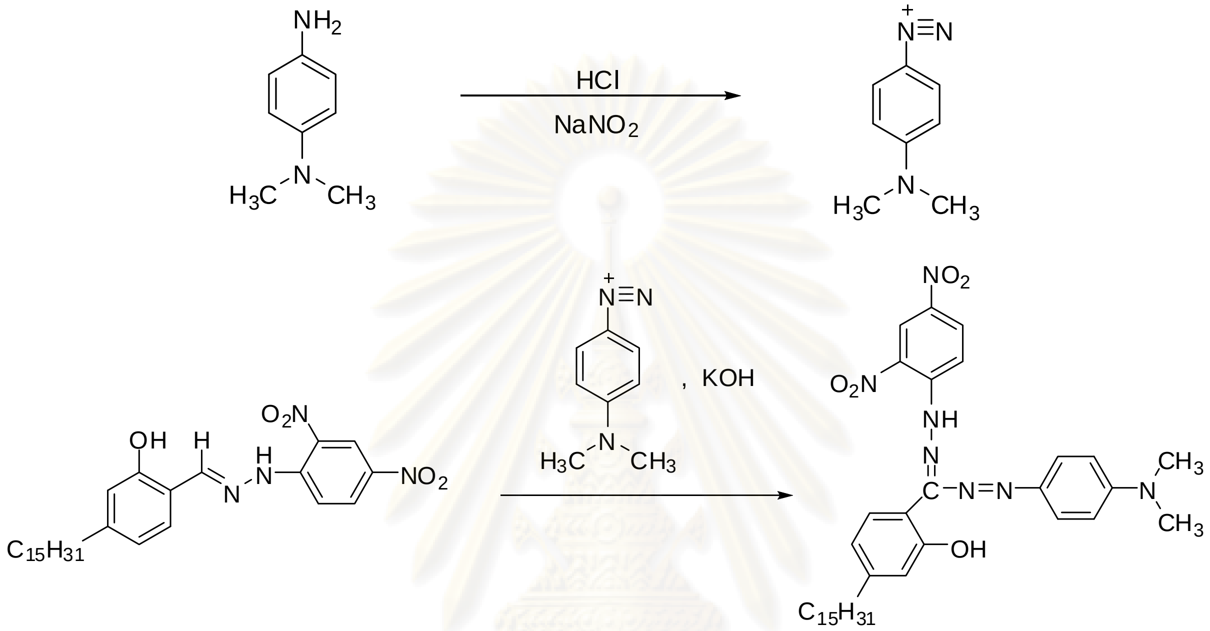
3.3.21 Synthesis of formazan 19 from phenylhydrazone 14 and *p*-phenylenediamine



19

According to the above-mentioned synthesis of compound **16** using *p*-phenylenediamine (0.02 g, 0.16 mmol) as an aromatic amine derivative. An attempt to coupling *p*-phenylenediamine with phenylhydrazone **14** failed to give compound **19**.

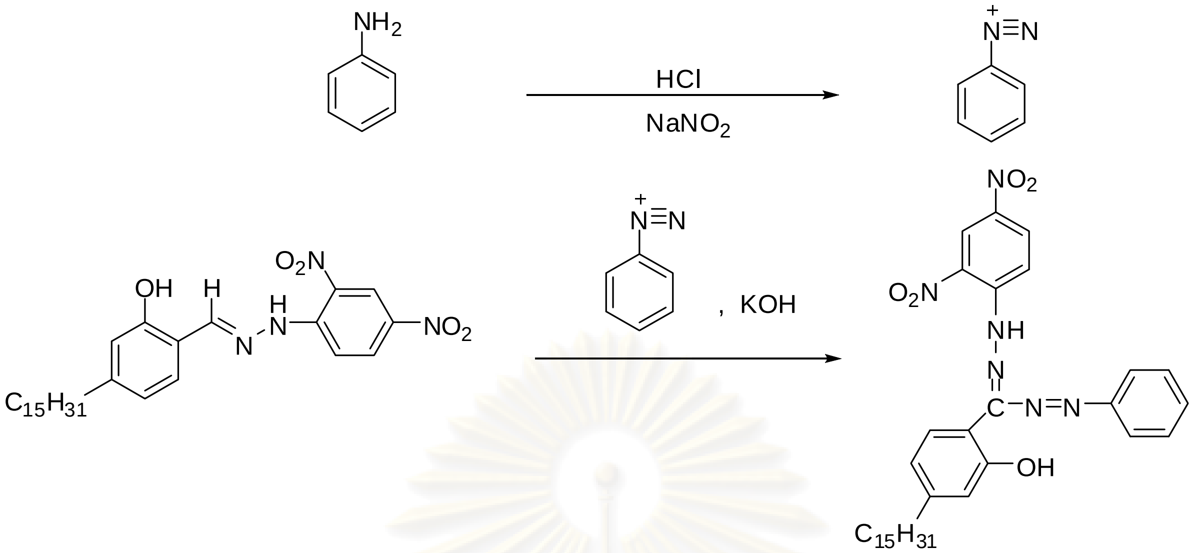
3.3.22 Synthesis of formazan 20 from phenylhydrazone 15 and 4-Amino-*N,N*-dimethylaniline



20

Following a previously published procedure [40], 4-*N,N*-dimethylaniline (0.02 g, 0.16 mmol) was dissolved in water (0.26 mL) and hydrochloric acid (0.10 mL). Then diazotized at 0-5 ºC with a solution of sodium nitrite (0.02 g, 0.33 mmol) in water (0.12 mL). After that the reaction mixture was added to a solution of phenylhydrazone **15** (0.17 g, 0.33 mmol) in tetrahydrofuran (2.66 mL). Then a solution of potassium hydroxide (0.20 g, 3.67 mmol) in water (0.66 mL) was added to a reaction mixture and stirred at below -2 ºC for 2 h. The reaction mixture was cooled to room temperature and diluted with water, then the precipitate was filtered. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (1:2)] to give an orange solid; MALDI-MS obsd 660.510; calcd avg mass 659.818 [M = $C_{36}H_{49}N_7O_5$] (**Figure A-64**); UV: λ_{abs} (CH_2Cl_2) 417 nm, ε (CH_2Cl_2) 8,475 (**Figure B-14**).

3.3.23 Synthesis of formazan 21 from phenylhydrazone 15 and aniline



21

According to the above-mentioned synthesis of compound **20** using aniline (0.01 g, 0.16 mmol) as an aromatic amine derivative. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (1:2)] to give a yellow solid; MALDI-MS obsd 617.040; calcd avg mass 616.750 [M = $C_{34}H_{44}N_6O_5$] (**Figure A-65**); UV: λ_{abs} (CH_2Cl_2) 392 nm, ε (CH_2Cl_2) 6,612 (**Figure B-15**).

Part 6: Physical property of triarylmethane dye in base gasoline

3.3.24 Preparation of stock solution of crude triarylmethane dye 10

A 10,000 ppm stock of triarylmethane dye solution was prepared by dissolving 0.2500 g of crude compound **10** in base gasoline and the volume was made up to 25 mL in a volumetric flask.

3.3.25 Quantitative determination of crude triarylmethane dye 10 in gasoline

A standard calibration curve of **10** in base gasoline was prepared at concentration of 2,000–6,000 ppm by pipetting the stock solution into a 5 mL volumetric flask and the volume was made up with base gasoline. The volume of the stock solution used to prepare each calibration solution is shown in Table 3-1.

Table 3-1 Preparation of calibration solution of crude triarylmethane dye **10** in base gasoline.

Concentration (ppm)	Volume of ppm stock solution (mL)
0	0.00
2,000	1.00
3,000	1.50
4,000	2.00
5,000	2.50
6,000	3.00

Absorption spectra of each calibration solution were recorded by a UV/Vis spectrophotometer (**Figure B-16)**. The calibration curve was plotted between absorbance (y-axis) and the concentration (x-axis) of crude triarylmethane dye **10** in base gasoline (**Figure B-17**).

3.3.26 Preparation of stock solution of pure triarylmethane dye 10

A 16,000 ppm stock of triarylmethane dye solution was prepared by dissolving 0.8000 g of compound **10** in base gasoline and the volume was made up to 50 mL in a volumetric flask.

3.3.27 Quantitative determination of pure triarylmethane dye 10 in gasoline

A standard calibration curve of **10** in base gasoline was prepared at concentration of 8,000–16,000 ppm by pipetting the stock solution into a 5 mL volumetric flask and the volume was made up with base gasoline. The volume of the stock solution used to prepare each calibration solution is shown in Table 3-2.

Table 3-2 Preparation of calibration solution of pure triarylmethane dye **10** in base gasoline.

Concentration (ppm)	Volume of 16,000 ppm stock solution (mL)
0	0.00
8,000	2.50
10,000	3.13
12,000	3.75
14,000	4.38
16,000	5.00

Absorption spectra of each calibration solution were recorded by a UV/Vis spectrophotometer (**Figure B-18**). The calibration curve was plotted between absorbance (y-axis) and the concentration (x-axis) of pure triarylmethane dye **10** in base gasoline (**Figure B-19**).

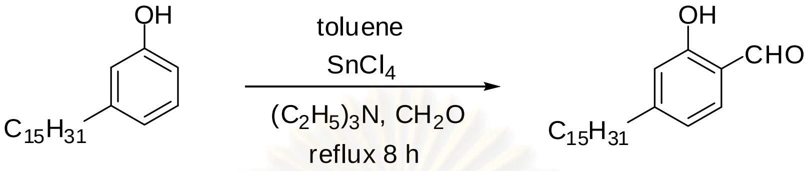
<u>Part 7: Stability test of triarylmethane dye 10 in gasoline</u>

The stability test was performed with the base gasoline dyed containing compound **10** in the concentration of 12,000 ppm on a UV-visible spectrophotometer. The three 12,000 ppm solutions of compound **10** in base gasoline were prepared by diluting the 16,000 ppm stock solution of triarylmethane dye **10** (7.5 mL) with the base gasoline to 10-mL in three volumetric flasks. A portion of each 10-mL solution (3 mL) was placed into 3 sealed vials and stored for 3 months in an ambient environment. Each solution was directly taken from the vial to the UV-visible measurement (λ_{abs} = 610 nm) after 1, 2 and 3 months. The quantity of triarylmethane dye **10** in the blended gasoline was determined by the calibration equation.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of hydrogenated cardanol formaldehyde



Scheme 4-1 Synthesis of hydrogenated cardanol formaldehyde**.**

The synthesis of hydrogenated cardanol formaldehyde was successfully performed by condensation reaction of hydrogenated cardanol with paraformaldehyde. The resulting crude product was purified by column chromatography using hexane as the solvent system, leading to white solid of hydrogenated cardanol formaldehyde in 65% yield. According to ^{1}H-NMR spectral analysis, the signal of phenolic hydroxyl proton of hydrogenated cardanol formaldehyde appeared as a singlet at δ 11.04 ppm (lit. 10.94 ppm [40], **Figure A-1** in Appendix A) indicating that the molecule bears intramolecular hydrogen bond between hydroxyl hydrogen and formyl oxygen atom.

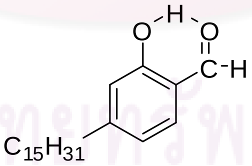
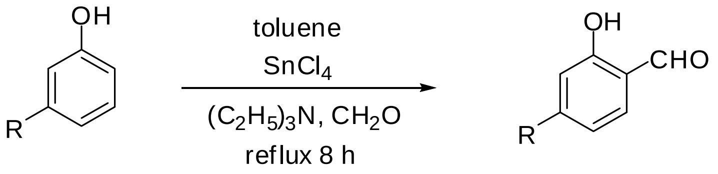


Figure 4-1 Intramolecular hydrogen bond of hydrogenated cardanol formaldehyde**.**

4.2 Synthesis of cardanol formaldehyde



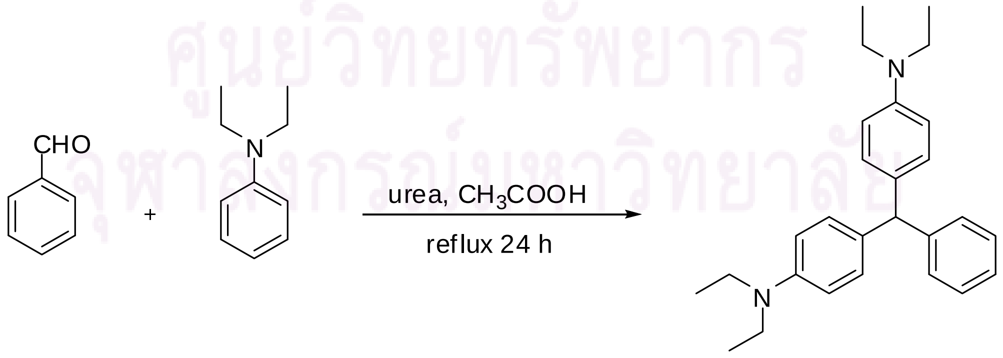
Scheme 4-2 Synthesis of cardanol formaldehyde**.**

The synthesis of cardanol formaldehyde was successfully performed by condensation reaction of cardanol with paraformaldehyde. The resulting crude product was purified by column chromatography using hexane as the solvent system, leading to pale yellow oil of cardanol formaldehyde which used as starting material to synthesized triarylmethane dye.

4.3 Synthesis of triarylmethane dye

Most of resulting dyes in this synthesis exhibited moderate solubility in common organic solvents. The presence of cardanol in molecular structure of triarylmethane dyes enhanced solubility of the dye in organic solvent and petroleum product due to the presence of a long hydrocarbon chain.

4.3.1 Triarylmethane dye 1 from benzaldehyde and *N,N*-diethylaniline

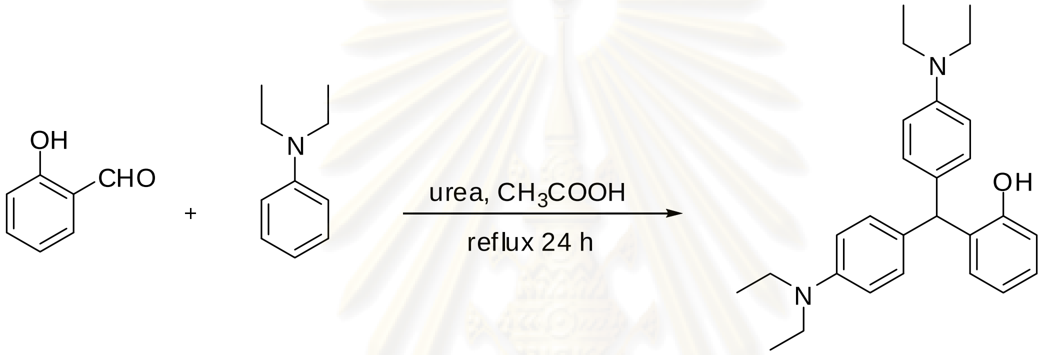


1

Scheme 4-3 Synthesis of Compound **1.**

The synthesis of compound **1** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with benzaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a blue-green oil in 25% yield (lit. 72%) [41]. The appearance of the singlet signal of –CH group at δ 5.33 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **1** by showing the molecular ion peaks at 386.710 m/z.

4.3.2 Triarylmethane dye 2 from salicylaldehyde and *N*,*N*-diethylaniline

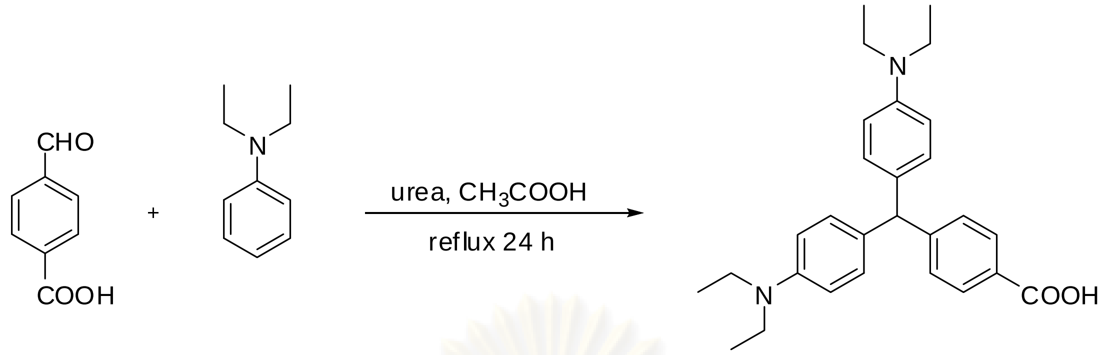


2

Scheme 4-4 Synthesis of Compound **2.**

The synthesis of compound **2** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with salicylaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a green oil in 27% yield. The appearance of the singlet signal of –CH group at δ 5.39 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **2** by showing the molecular ion peaks at 402.590 m/z.

4.3.3 Triarylmethane dye 3 from 4-carboxybenzaldehyde and *N,N*-diethylaniline

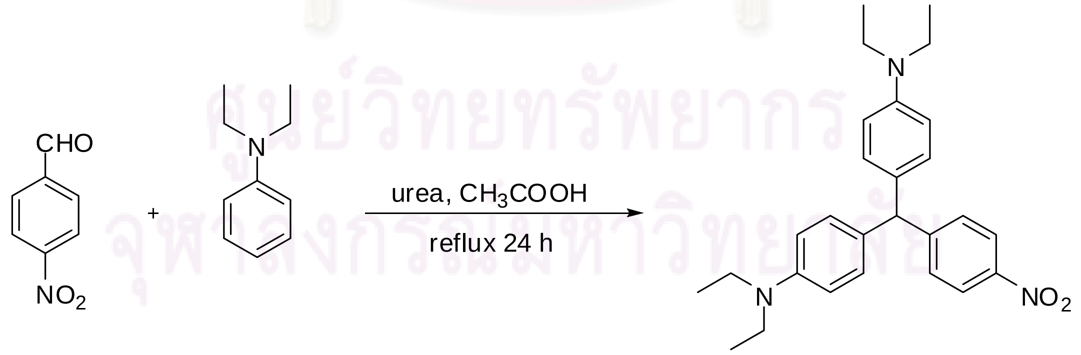


3

Scheme 4-5 Synthesis of Compound **3.**

The synthesis of compound **3** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with 4-carboxybenzaldehyde. The resulting crude product was purified by sonication in hexane and filter to give a green solid in 30% yield. The appearance of the singlet signal of –CH group at δ 5.39 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **3** by showing the molecular ion peaks at 429.614 m/z.

4.3.4 Triarylmethane dye 4 from 4-nitrobenzaldehyde and *N,N*-diethylaniline

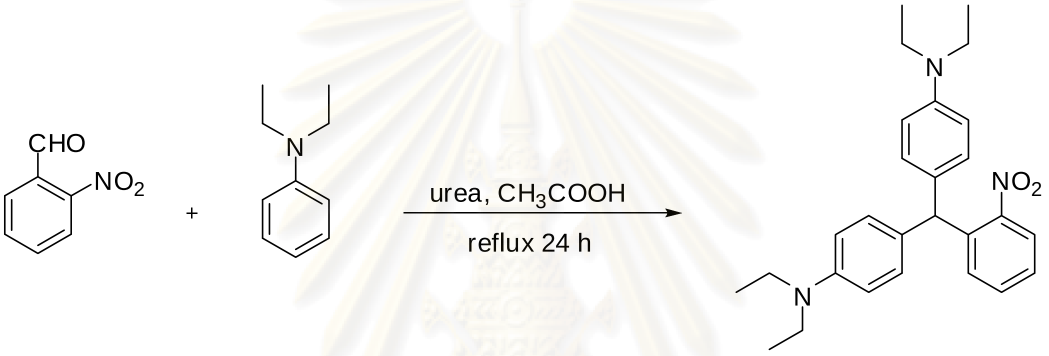


4

Scheme 4-6 Synthesis of Compound **4.**

The synthesis of compound **4** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with 4-nitrobenzaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a green oil in 21% yield (lit. 67%) [41]. The appearance of the singlet signal of –CH group at δ 5.40 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **4** by showing the molecular ion peaks at 431.966 m/z.

4.3.5 Triarylmethane dye 5 from 2-nitrobenzaldehyde and *N*,*N*-diethylaniline

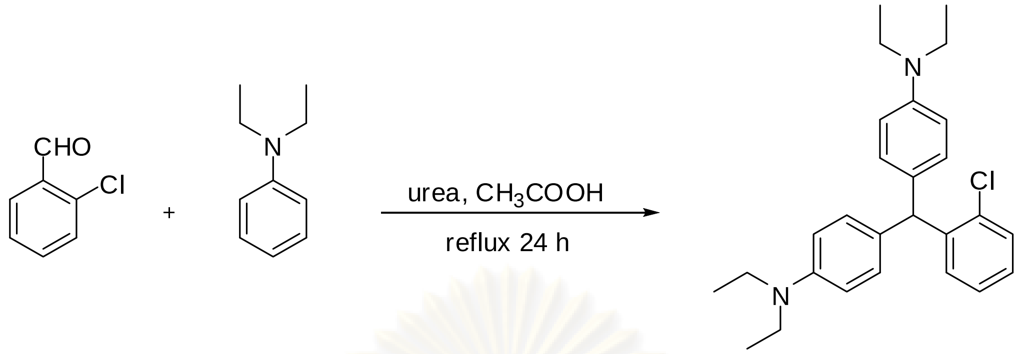


5

Scheme 4-7 Synthesis of Compound **5.**

The synthesis of compound **5** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with 2-nitrobenzaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a green oil in 37% yield (lit. 71%) [41]. The appearance of the singlet signal of –CH group at δ 6.02 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **5** by showing the molecular ion peaks at 431.716 m/z.

4.3.6 Triarylmethane dye 6 from 2-chlorobenzaldehyde and *N*,*N*-diethylaniline

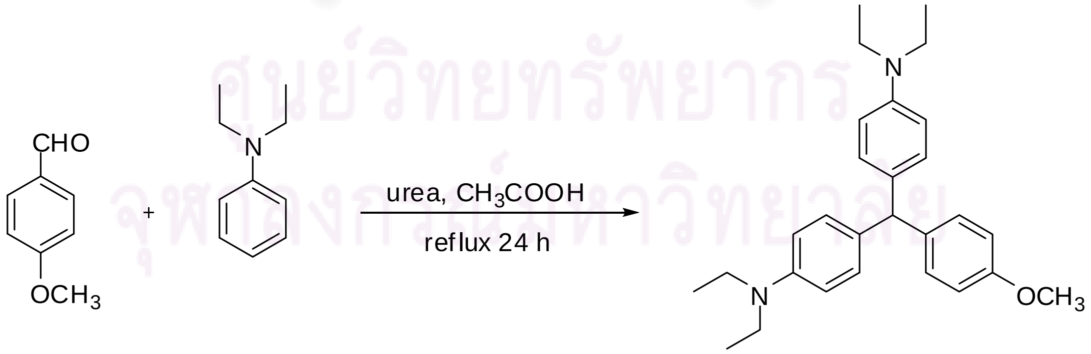


6

Scheme 4-8 Synthesis of Compound **6.**

The synthesis of compound **6** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with 2-chlorobenzaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a blue-green oil in 36% yield. The appearance of the singlet signal of –CH group at δ 5.75 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **6** by showing the molecular ion peaks at 421.818 m/z.

4.3.7 Triarylmethane dye 7 from 4-methoxybenzaldehyde and *N*,*N*-diethylaniline

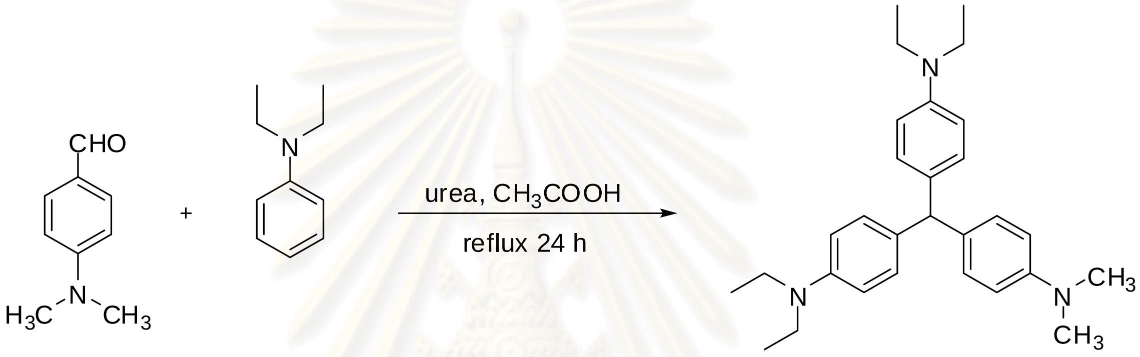


7

Scheme 4-9 Synthesis of Compound **7.**

The synthesis of compound **7** was successfully performed by condensation reaction of N,N-diethylaniline with 4-methoxybenzaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a green oil in 21% yield. The appearance of the singlet signal of –CH group at δ 5.28 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **7** by showing the molecular ion peaks at 416.535 m/z.

4.3.8 Triarylmethane dye 8 from 4-(dimethylamino)benzaldehyde and *N,N*-diethylaniline

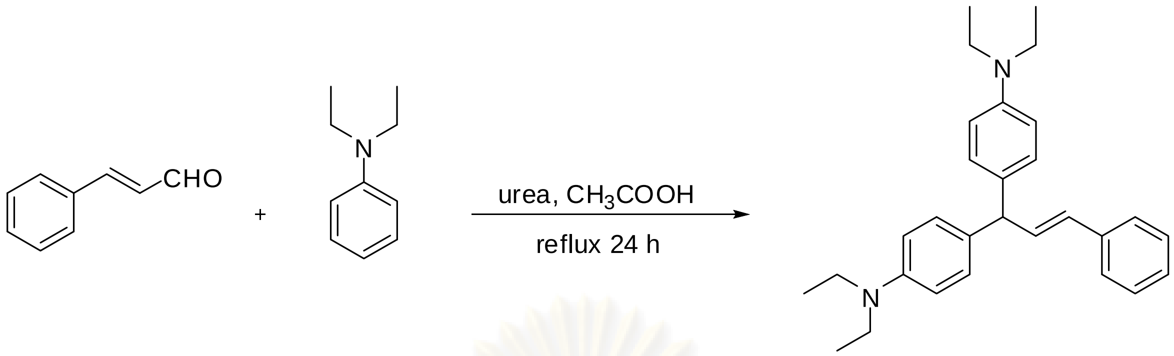


8

Scheme 4-10 Synthesis of Compound **8.**

The synthesis of compound **8** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with 4-(dimethylamino)benzaldehyde. An attempt to completely isolate the resulting dye by preparative TLC was failed. ^{1}H-NMR spectral analysis of the crude product indicated the characterize peaks of compound **8** at 1.12, 2.89, 3.30, 5.30, 6.59, 6.96, 7.05 ppm which cannot be elucidated from the other side products (**Figure A-35**). The molecular peak at m/z 429.903 in mass spectrum of the crude dye **8** as shown in **Figure A-36** indicated the formation of compound **8** and the presence of the unremovable products.

4.3.9 Triarylmethane dye 9 from cinnamaldehyde and *N,N*-diethylaniline

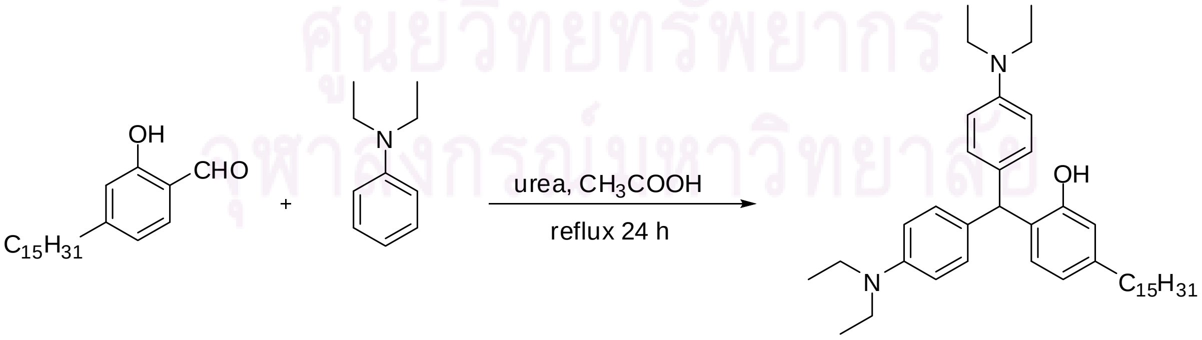


9

Scheme 4-11 Synthesis of Compound **9.**

The synthesis of compound **9** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with cinnamaldehyde. An attempt to completely isolate the resulting dye by preparative TLC was failed. ^{1}H-NMR spectral analysis of the crude product indicated the characterize peaks of compound **9** at 1.12, 3.30, 5.32, 6.59, 6.94, 7.06, 7.15 ppm which cannot be elucidated from the other side products (**Figure A-37**). The molecular peak at m/z 412.775 in mass spectrum of the crude dye **9** as shown in **Figure A-38** indicated the formation of compound **9** and the presence of the unremovable products.

4.3.10 Triarylmethane dye 10 from hydrogenated cardanol formaldehyde and *N,N*-diethylaniline

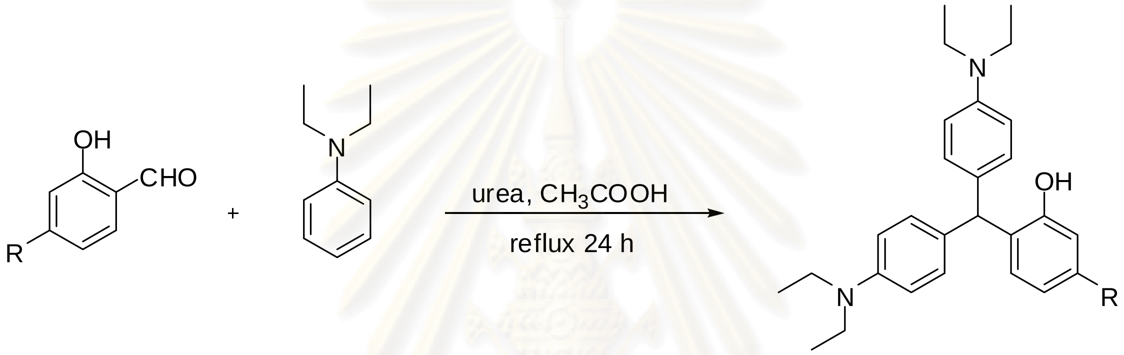


10

Scheme 4-12 Synthesis of Compound **10.**

The synthesis of compound **10** was successfully performed by condensation reaction of *N*,*N*-diethylaniline with hydrogenated cardanol formaldehyde. The resulting crude product was purified by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system to give a green oil in 41% yield. The appearance of the singlet signal of –CH group at δ 5.32 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **10** by showing the molecular ion peaks at 612.106 m/z.

4.3.11 Triarylmethane dye 11 from cardanol formaldehyde and *N,N*-diethylaniline



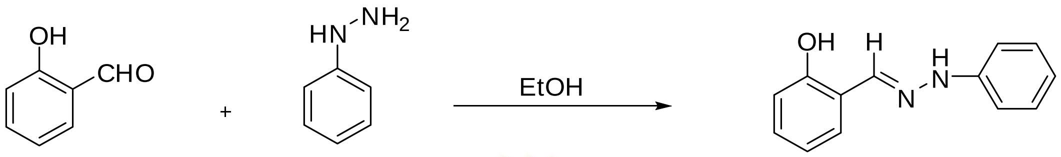
11

Scheme 4-13 Synthesis of Compound **11.**

Synthesis of compound **11** was achieved in the same manner as described in the synthesis of compound **10**, except that cardanol was used instead. Purification by preparative TLC using hexane/ethyl acetate (5:1) as a solvent system afforded compound **11** as a green oil in 29% yield. The appearance of the singlet signal of –CH group at δ 4.84 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **11** by showing the molecular ion peaks at 605.179-612.334 m/z.

4.4 Synthesis of formazan model

4.4.1 Synthesis of phenylhydrazone 12 from salicylaldehyde and phenylhydrazine

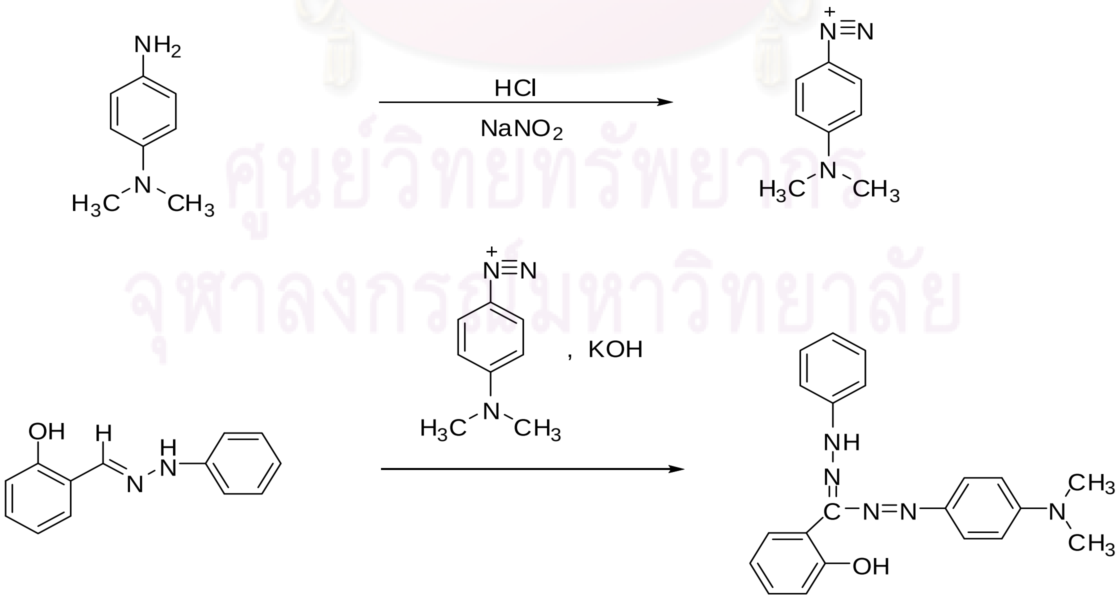


12

Scheme 4-14 Synthesis of compound **12.**

The synthesis of compound **12** was successfully performed by condensation reaction of phenylhydrazine with salicylaldehyde which was used as model. The resulting crude product was purified by tritulation with hexane to give a yellow solid in 55% yield. In the literature, benzaldehyde was used to give 92% yield [38]. The appearance of the singlet signal of -CH and -NH group at δ 7.84 and 10.90 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **12** by showing the molecular ion peaks at 212.148 m/z.

4.4.2 Synthesis of formazan 13 from phenylhydrazone 12



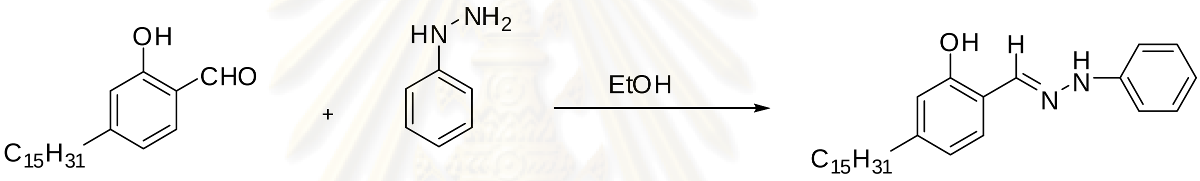
12 **13**

Scheme 4-15 Synthesis of compound **13.**

The synthesis of compound **13** was successfully performed by coupling reaction of phenylhydrazone **12** with diazonium salt of 4-amino-*N*,*N*-dimethylaniline. The resulting crude product was purified by preparative TLC (CH_2Cl_2) to give a dark purple solid in 24% yield. The disappearance of the singlet signal of –CH group at δ 7.84 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **13** by showing the molecular ion peaks at 358.628 m/z.

4.5 Synthesis of formazan from hydrogenated cardanol formaldehyde

4.5.1 Synthesis of phenylhydrazone 14 from hydrogenated cardanol formaldehyde and phenylhydrazine

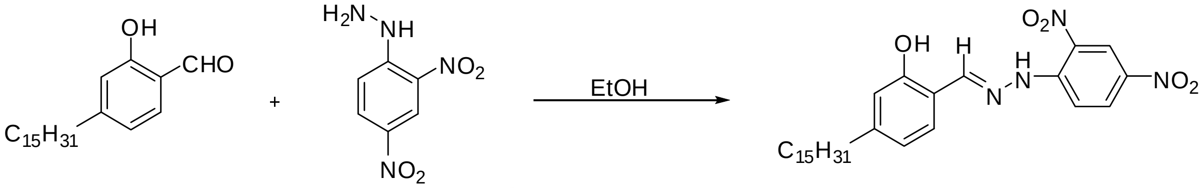


14

Scheme 4-16 Synthesis of compound **14.**

The synthesis of compound **14** was successfully performed by condensation reaction of phenylhydrazine with hydrogenated cardanol formaldehyde. The resulting crude product was purified by column chromatography using hexane/CH_2Cl_2 (1:1) as a solvent system to give a pale yellow solid in 87%. The appearance of the singlet signal of -CH and -NH group at δ 7.85 and 10.80 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **14** by showing the molecular ion peaks at 422.602 m/z.

4.5.2 Synthesis of phenylhydrazone 15 from hydrogenated cardanol formaldehyde and 2,4-dinitrophenylhydrazine

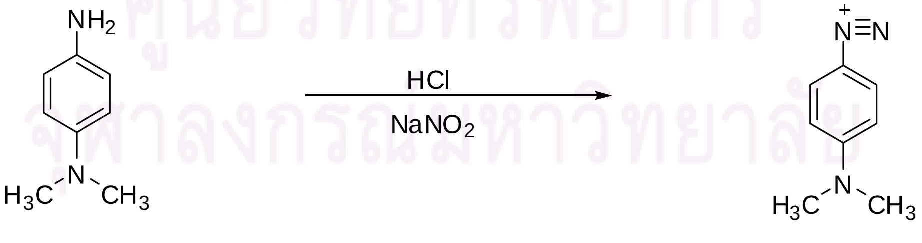


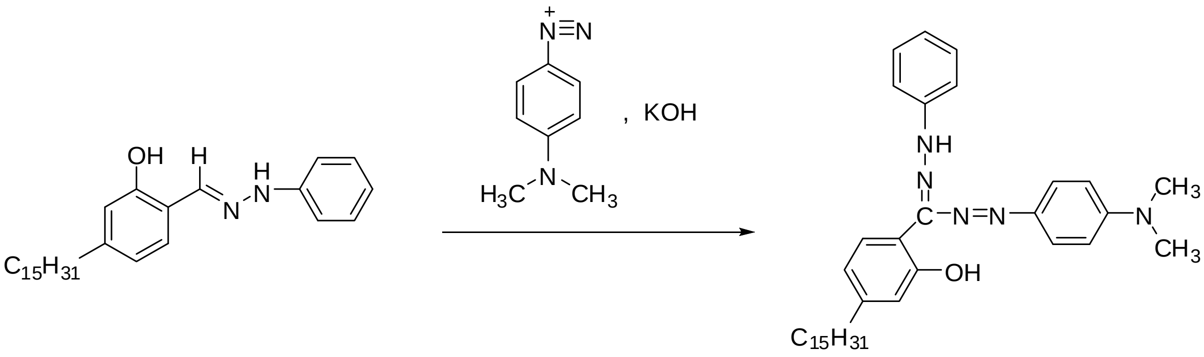
15

Scheme 4-17 Synthesis of compound **15.**

The synthesis of compound **15** was successfully performed by condensation reaction of 2,4-dinitrophenylhydrazine with hydrogenated cardanol formaldehyde. The resulting crude product was purified by column chromatography using hexane/CH_2Cl_2 (1:1) as a solvent system to give an orange solid in 37%. The appearance of the singlet signal of -CH and -NH group at δ 8.56 and 9.63 ppm in the ^{1}H–NMR spectrum indicated the completion of the reaction. Mass spectrum confirmed the formation of compound **15** by showing the molecular ion peaks at 512.595 m/z.

4.5.3 Synthesis of formazan 16 from phenylhydrazone 14 and 4-Amino-*N,N*-dimethylaniline



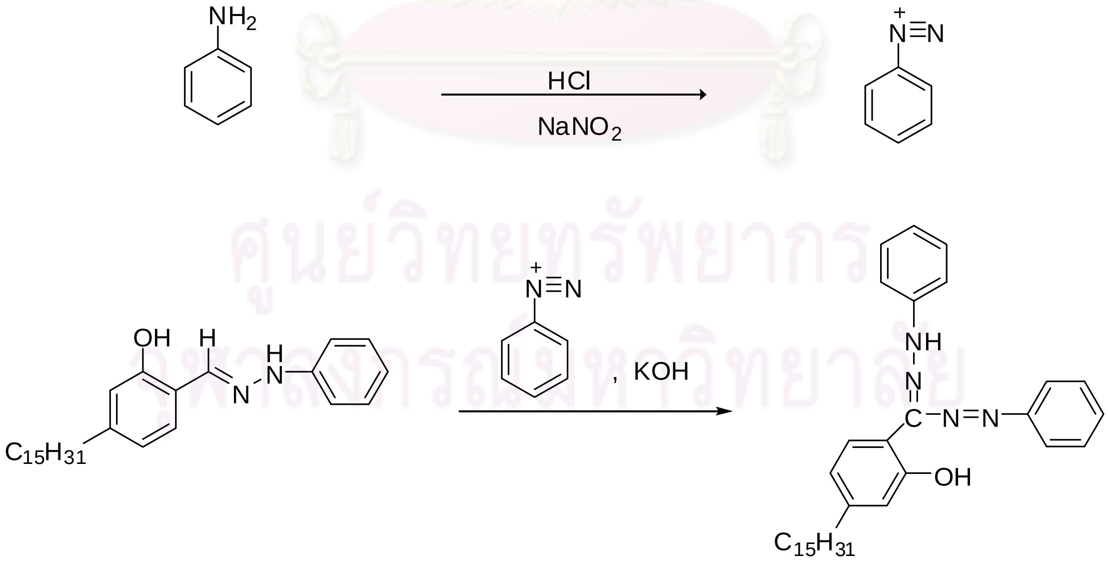


14 **16**

Scheme 4-18 Synthesis of compound **16.**

The synthesis of compound **16** was successfully performed by coupling reaction of phenylhydrazone **14** with diazonium salt of 4-amino-*N*,*N*-dimethylaniline. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (2:1)] to give a yellow solid. Mass spectrum confirmed the formation of compound **16** by showing the molecular ion peaks at 568.178 m/z.

4.5.4 Synthesis of formazan 17 from phenylhydrazone 14 and aniline

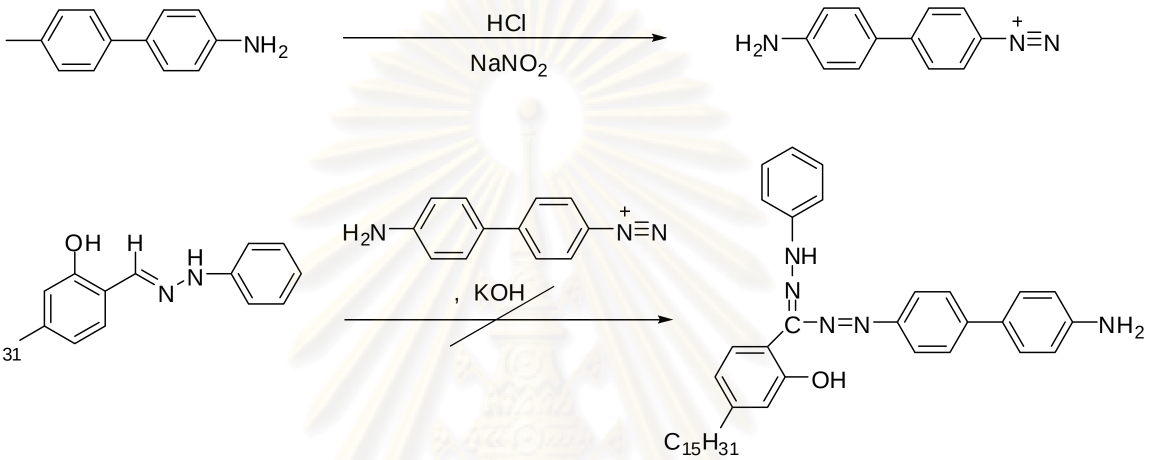


14 **17**

Scheme 4-19 Synthesis of compound **17.**

The synthesis of compound **17** was successfully performed by coupling reaction of phenylhydrazone **14** with diazonium salt of aniline. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (2:1)] to give a yellow solid. Mass spectrum confirmed the formation of compounds **17** by showing the molecular ion peaks at 525.192 m/z.

4.5.5 Synthesis of formazan 18 from phenylhydrazone 14 and benzidine

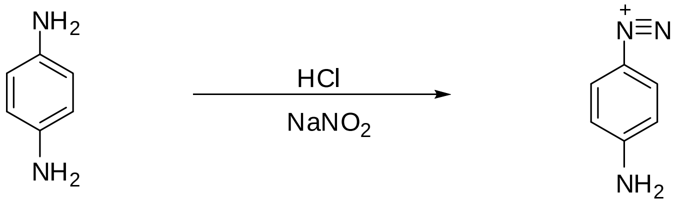


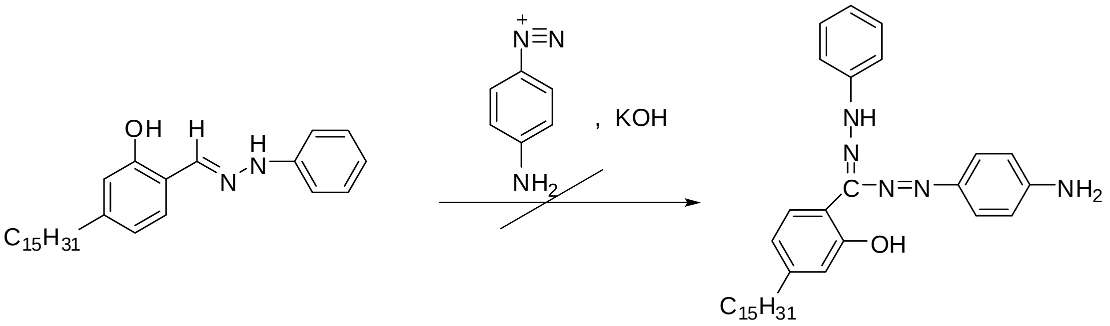
14 **18**

Scheme 4-20 Synthesis of compound **18.**

According to TLC analysis, ^{1}H-NMR and mass spectrum, an attempt to prepare formazan dye compound **18** by coupling reaction of phenylhydrazone **14** with diazonium salt of benzidine was failed. The reason of this may be due to the instability of the diazonium salt of benzidine which could undergo different type of reactions.

4.5.6 Synthesis of formazan 19 from phenylhydrazone 14 and *p*-phenylenediamine



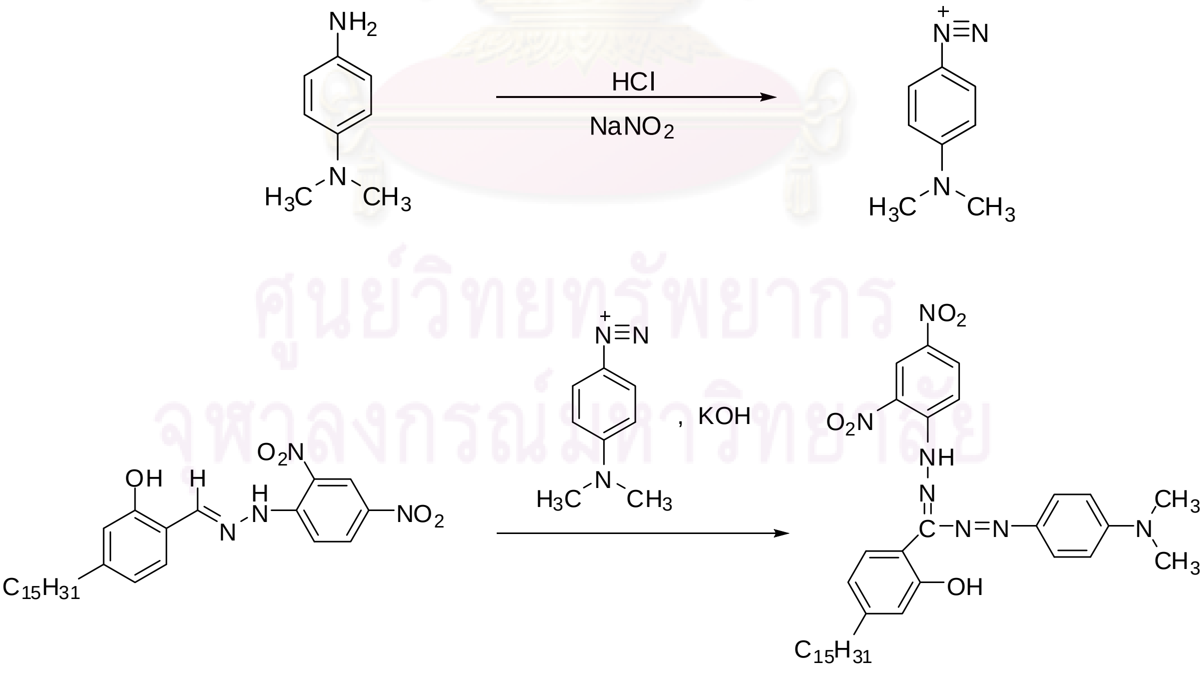


14 **19**

Scheme 4-21 Synthesis of compound **19.**

According to TLC analysis, ^{1}H-NMR and mass spectrum, an attempt to prepare formazan dye compound **19** by coupling reaction of phenylhydrazone **14** with diazonium salt of *p*-phenylenediamine was failed. The reason of this may be due to the instability of the diazonium salt of *p*-phenylenediamine which could undergo different type of reactions.

4.5.7 Synthesis of formazan 20 from phenylhydrazone 15 and 4-Amino-*N,N*-dimethylaniline

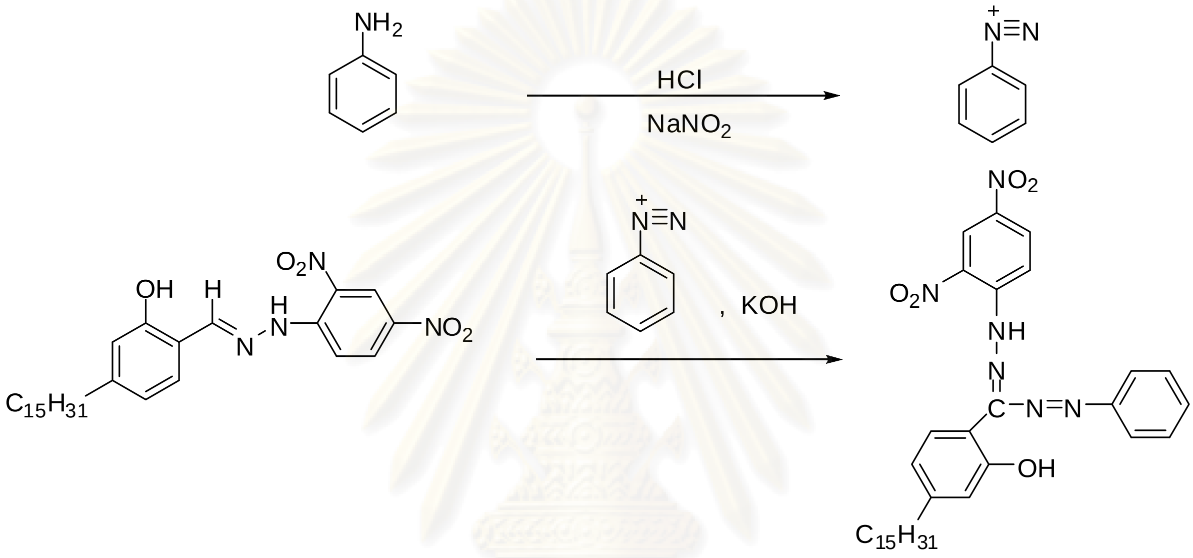


15 **20**

Scheme 4-22 Synthesis of compound **20.**

The synthesis of compound **20** was successfully performed by coupling reaction of phenylhydrazone **15** with diazonium salt of 4-amino-*N*,*N*-dimethylaniline. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (1:2)] to give an orange solid. Mass spectrum confirmed the formation of compounds **20** by showing the molecular ion peaks at 660.510 m/z.

4.5.8 Synthesis of formazan 21 from phenylhydrazone 15 and aniline



15 **21**

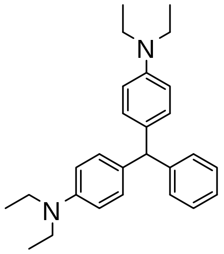
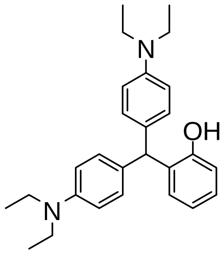
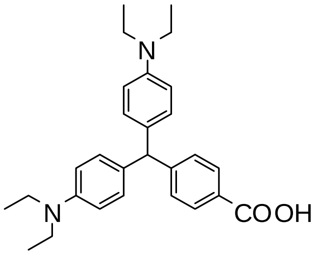
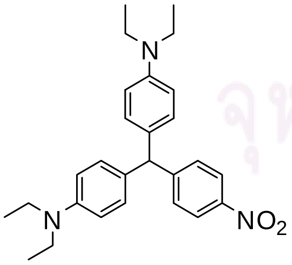
Scheme 4-23 Synthesis of compound **21.**

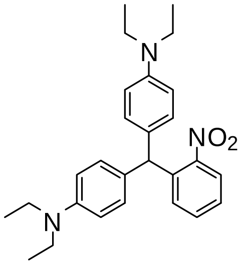
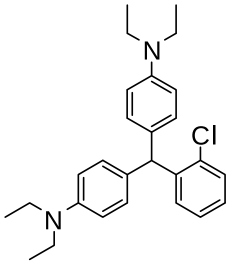
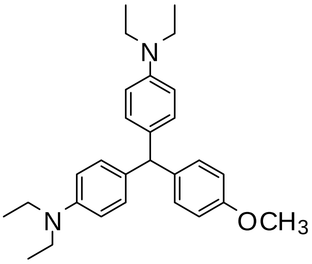
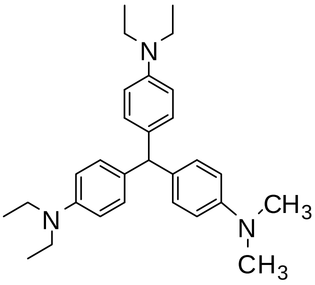
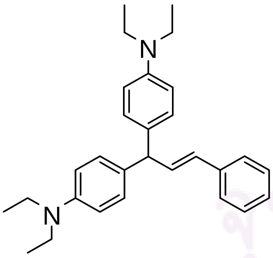
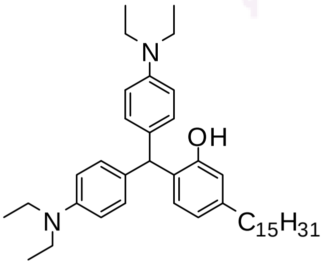
The synthesis of compound **21** was successfully performed by coupling reaction of phenylhydrazone **15** with diazonium salt of aniline. The resulting crude product was purified by preparative TLC [hexane/CH_2Cl_2 (1:2)] to give a yellow solid. Mass spectrum confirmed the formation of compounds **21** by showing the molecular ion peaks at 617.040 m/z.

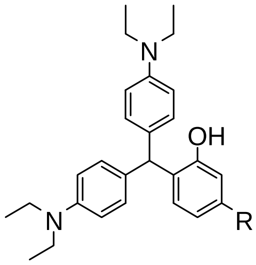
4.6 Solubility properties of triarylmethane dyes

Solubility properties of triarylmethane compounds were observed by dissolve triarylmethane compounds about 1 mg in various solvents 0.1 mL (10,000 ppm). The results are shown in table 4-1.

Table 4-1 Observed solubility of triarylmethane compounds in various solvents.

solvent **substance**	hexane	CH_2Cl_2	EtOAc	MeOH	H_2O	toluene	base gasoline
 **(1)**	×	√	√	√	×	√	√
 **(2)**	×	√	√	√	×	√	√
 **(3)**	×	√	√	√	×	×	×
 **(4)**	×	√	√	√	×	√	√

solvent **substance**	hexane	CH_2Cl_2	EtOAc	MeOH	H_2O	toluene	base gasoline
 **(5)**	×	√	√	√	×	√	√
 **(6)**	×	√	√	√	×	√	√
 **(7)**	×	√	√	√	×	√	√
 **(8)**	×	√	√	√	×	√	√
 **(9)**	×	√	√	√	×	√	√
 **(10)**	√	√	√	×	×	√	√

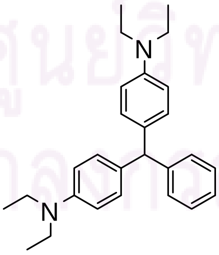
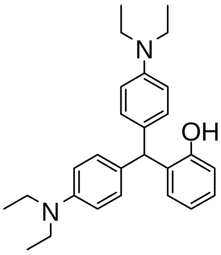
solvent / substance	hexane	CH_2Cl_2	EtOAc	MeOH	H_2O	toluene	base gasoline
 **(11)**	√	√	√	×	×	√	√

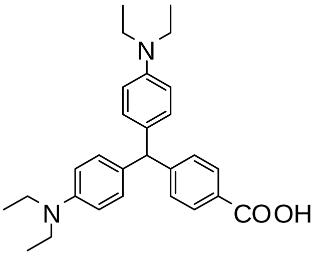
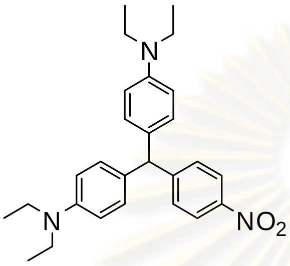
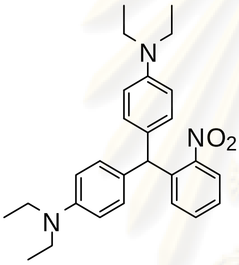
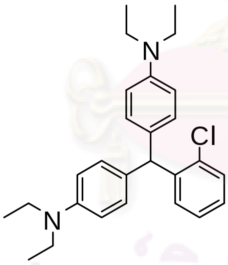
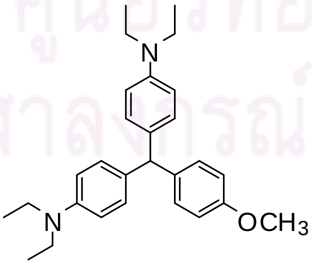
These results were shown that most of triarylmethane compounds were soluble in various solvent. Compound **1, 2, 3, 4, 5, 6, 7, 8** and **9** could not dissolve in hexane, but compound **10** and **11** could dissolve in hexane because of long chain hydrocarbon of cardanol. These compounds dissolved in base gasoline as well.

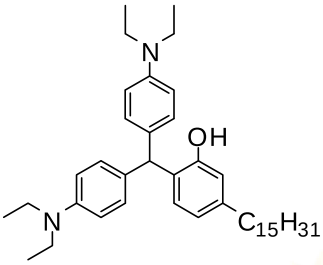
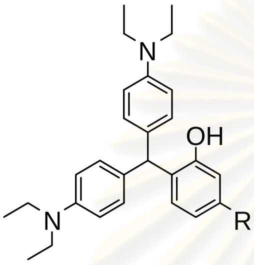
4.7 Photophysical properties of triarylmethane dyes

The photophysical properties of compounds **1**, **2**, **3**, **4**, **5**, **6**, **7**, **10** and **11** were investigated and summarized in **Table 4-2**. Compounds 8 and 9 could not be obtained in pure form, therefore they were not used in this study.

Table 4-2 Observed absorption maxima and molar absorptivities of triarylmethane compounds in CH_2Cl_2 .

compound	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)
 **(1)**	629	7.04
 **(2)**	627	15.52

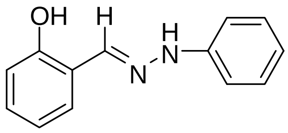
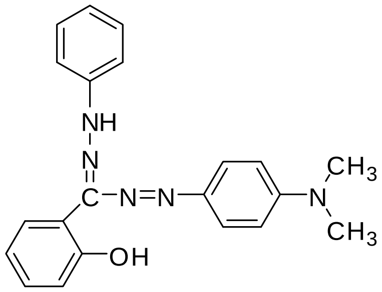
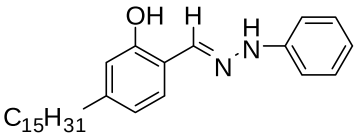
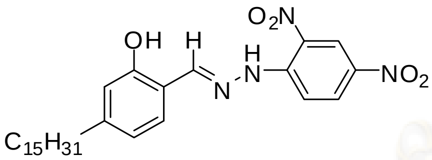
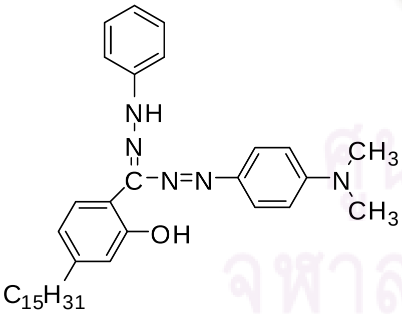
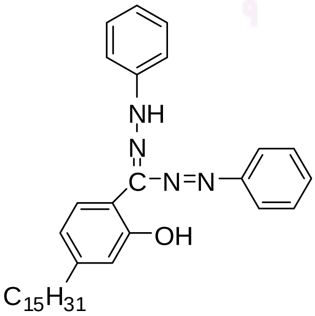
compound	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)
 **(3)**	630	941.16
 **(4)**	597	7.22
 **(5)**	644	30.67
 **(6)**	643	72.76
 **(7)**	617	836.65

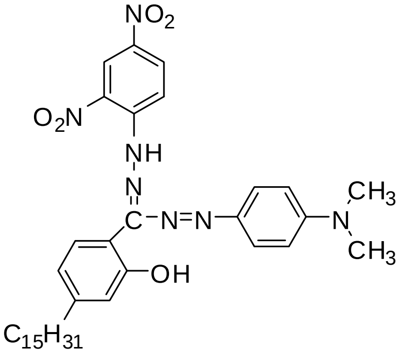
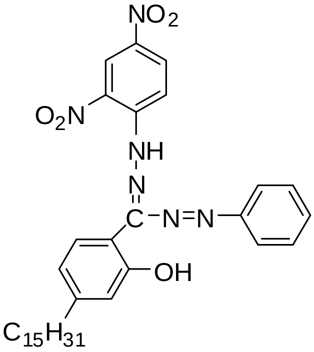
compound	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)
 **(10)**	624	35.01
 **(11)**	593	39.27

4.8 Solubility properties of phenylhydrazone and formazan dyes

Solubility properties of phenylhydrazone and formazan compounds were observed by dissolve phenylhydrazone and formazan compounds about 2 mg in various solvents 0.1 mL (20,000 ppm). The results are shown in table 4-3.

Table 4-3 Observed solubility of phenylhydrazone and formazan compounds in various solvents.

solvent **substance**	hexane	CH_2Cl_2	EtOAc	MeOH	H_2O	toluene	base gasoline
 **(12)**	×	√	√	√	×	√	√
 **(13)**	√[a]	√	√	√	×	√	√
 **(14)**	×	√	√	×	×	√	√
 **(15)**	√[a]	√	√	×	×	√	√[a]
 **(16)**	√	√	√	×	×	√	√
 **(17)**	√	√	√	×	×	√	√

solvent **substance**	hexane	CH_2Cl_2	EtOAc	MeOH	H_2O	toluene	base gasoline
 **(20)**	√[a]	√	√	×	×	√	√[a]
 **(21)**	√[a]	√	√	×	×	√	√

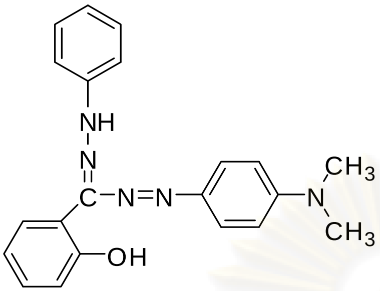
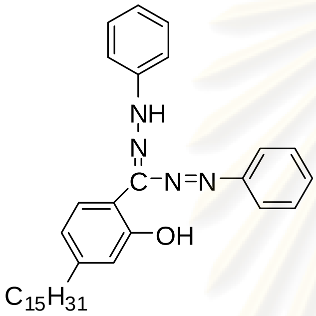
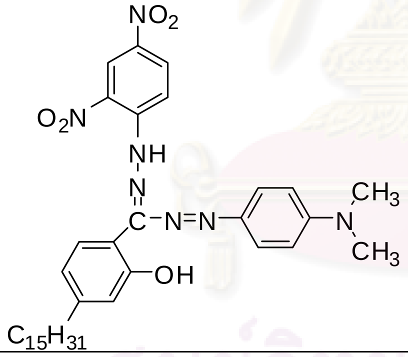
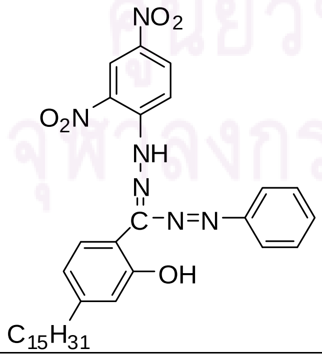
[a] Solubility was not complete.

These results were shown that most of phenylhydrazone and formazan compounds were soluble in various solvents. Compound **16** and **17** were completely soluble in hexane, but compound **20** and **21** were not completely soluble in hexane because of the polarity of nitro group in their molecules.

4.9 Photophysical properties of formazan dyes

The photophysical properties of compounds **13**, **17**, **20** and **21** were investigated and summarized in **Table 4-4**.

Table 4-4 Observed absorption maxima and molar absorptivities of formazan compounds in CH_2Cl_2.

Compound	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)
 **(13)**	560	191,154
 **(17)**	339	26,551
 **(20)**	417	8,475
 **(21)**	392	6,612

4.10 Physical properties of triarylmethane dyes in base gasoline

4.10.1 Quantitative determination of crude triarylmethane dye 10 in base gasoline

A standard calibration curve of crude triarylmethane dye **10** in base gasoline was prepared by plotting absorbance at 599 nm of a series of the solution of **10** in base gasoline with the concentration ranging from 2,000 to 6,000 ppm **(Figure B-17)**.

The standard calibration equation of crude triarylmethane dye **10** in base gasoline was found to be Y = 0.0001X with the correlation coefficient equal to 0.9997.

4.10.2 Quantitative determination of pure triarylmethane dye 10 in base gasoline

A standard calibration curve of pure triarylmethane dye **10** in base gasoline was prepared by plotting absorbance at 610 nm of a series of the solution of **10** in base gasoline with the concentration ranging from 8,000 to 16,000 ppm **(Figure B-19)**.

The standard calibration equation of pure triarylmethane dye **10** in base gasoline was found to be $Y = 2x10^{-5}X$ with the correlation coefficient equal to 0.9997. This equation was used to evaluate the stability of the triarylmethane dye **10** in gasoline fuel.

4.11 Stability test of triarylmethane dye in base gasoline

Generally, gasoline is consumed within 3 months after released to the market. Therefore, in this study, the stability test of the triarylmethane dye **10** in base gasoline was designed to be performed in a period of 3 months. The test was carried out by measuring absorbance of λ_{abs} at 610 nm of a solution of **10** in base gasoline at the concentration of 12,000 ppm after 1−3 months by using a spectrophotometer. The absorbance at 610 nm was converted into the triarylmethane dye concentration by the above-mentioned calibration equation.

Table 4-5 Concentration of compound **10** (12,000 ppm) in base gasoline.

Month	Concentration in gasoline (ppm)			
	1st	2nd	3rd	Average
1	11,995 ± 8	12,009 ± 8	12,004 ± 8	12,003 ± 8
2	11,997 ± 8	12,010 ± 8	12,008 ± 8	12,005 ± 8
3	11,997 ± 8	12,011 ± 8	12,008 ± 8	12,005 ± 8

The results shown in Table 4-5 indicated that there were no significant difference in the concentrations of triarylmethane dye in each gasoline sample throughout the period of 3 months and hence the triarylmethane dye **10** exhibited the stability for at least 3 months.

CHAPTER V

CONCLUSION

5.1 Conclusion

This research is related to the synthesis of triarylmethane and formazan dyes from cardanol which is a naturally occurring compound obtained from extraction of cashew nut shell for use as coloring agent in gasoline fuel. These triarylmethane dyes were synthesized by condensation reaction of *N*,*N*-diethylaniline with various aromatic aldehydes including benzaldehyde (compound **1**), salicylaldehyde (compound **2**), 4-carboxybenzaldehyde (compound **3**), 4-nitrobenzaldehyde (compound **4**), 2-nitrobenzaldehyde (compound **5**), 2-chlorobenzaldehyde (compound **6**), 4-methoxybenzaldehyde (compound **7**), 4-(dimethylamino)benzaldehyde (compound **8**) and cinnamaldehyde (compound **9**), hydrogenated cardanol formaldehyde (compound **10**) and cardanol formaldehyde (compound **11**). Most of dyes provided green color, only compound **8** provided blue color. Formazan dyes were synthesized by condensation reaction of hydrogenated cardanol formaldehyde with phenylhydrazine and 2,4-dinitrophenylhydrazine, then coupling the product with diazonium salt of 4-amino-*N,N*-dimethylaniline, aniline, benzidine and *p*-phenylenediamine. The formazan dyes **16, 17** and **21** provided a pale yellow color and formazan dyes **20** provided an orange color.

Among these dyes, besides the desirable green color with maximum absorption at 610 nm, triarylmethane dye **10** showed high solubility in gasoline fuel and common organic solvents. Moreover, the stability of triarylmethane dye **10** was found to be satisfactory in gasoline fuel for at least three months, but the concentration was too high. According to the above properties, it could be concluded that triarylmethane dye **10** was not suitable for being used in commercial gasoline.

5.2 Suggestion for future work

- Preparation of other triarylmethane dye from cardanol having various color.

REFERENCES

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APPENDICES

APPENDIX A

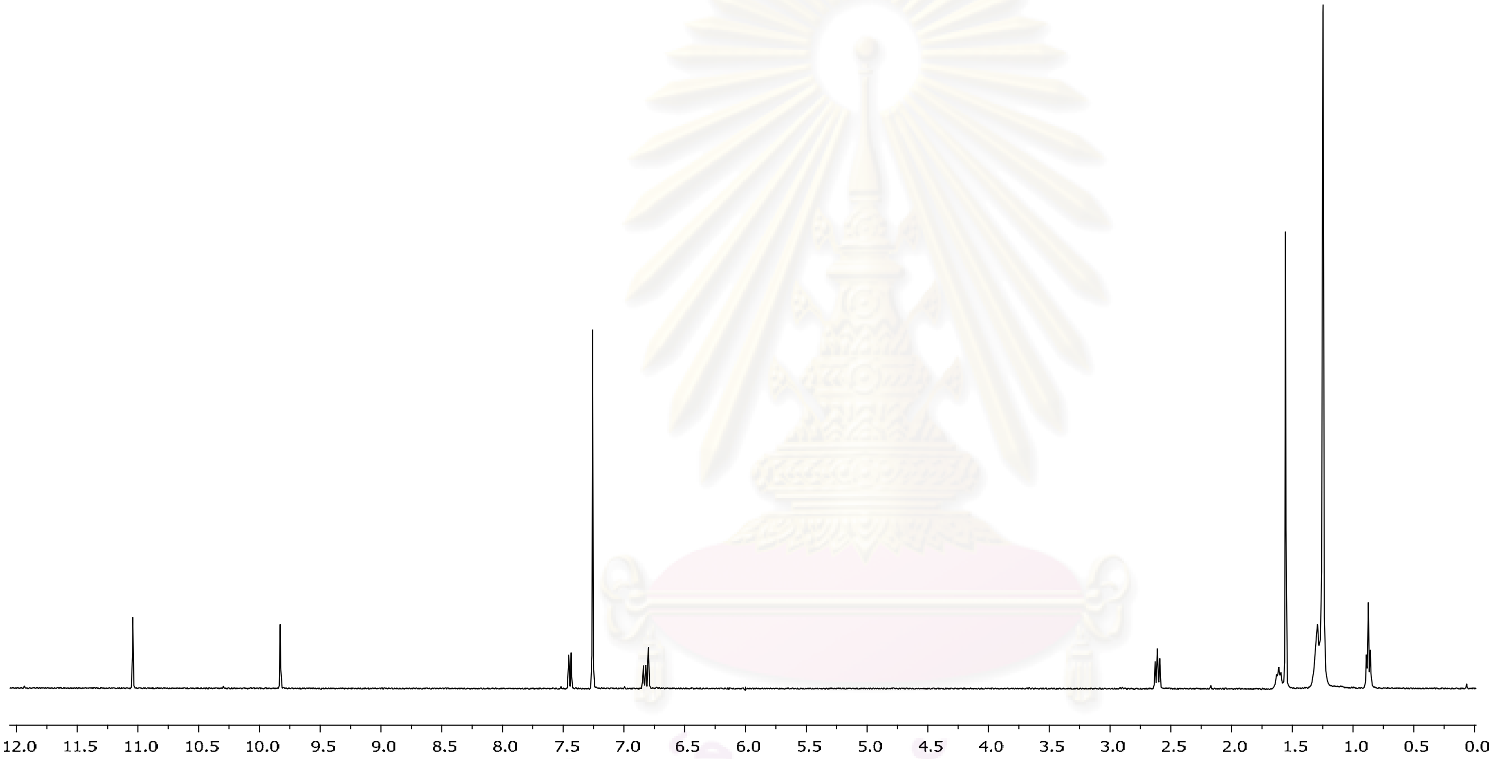


Figure A-1 ^{1}H-NMR spectrum of hydrogenated cardanol formaldehyde.

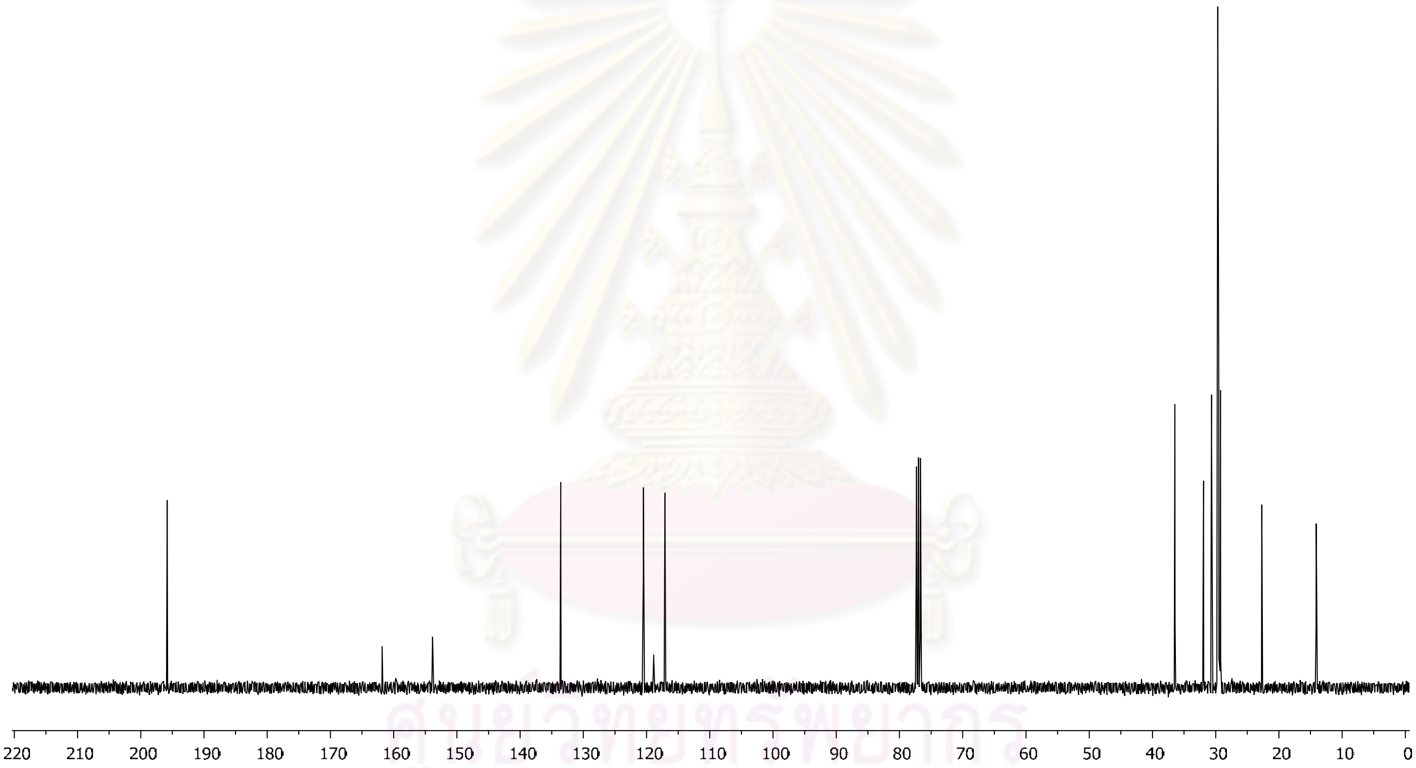


Figure A-2 ^{13}C-NMR spectrum of hydrogenated cardanol formaldehyde.

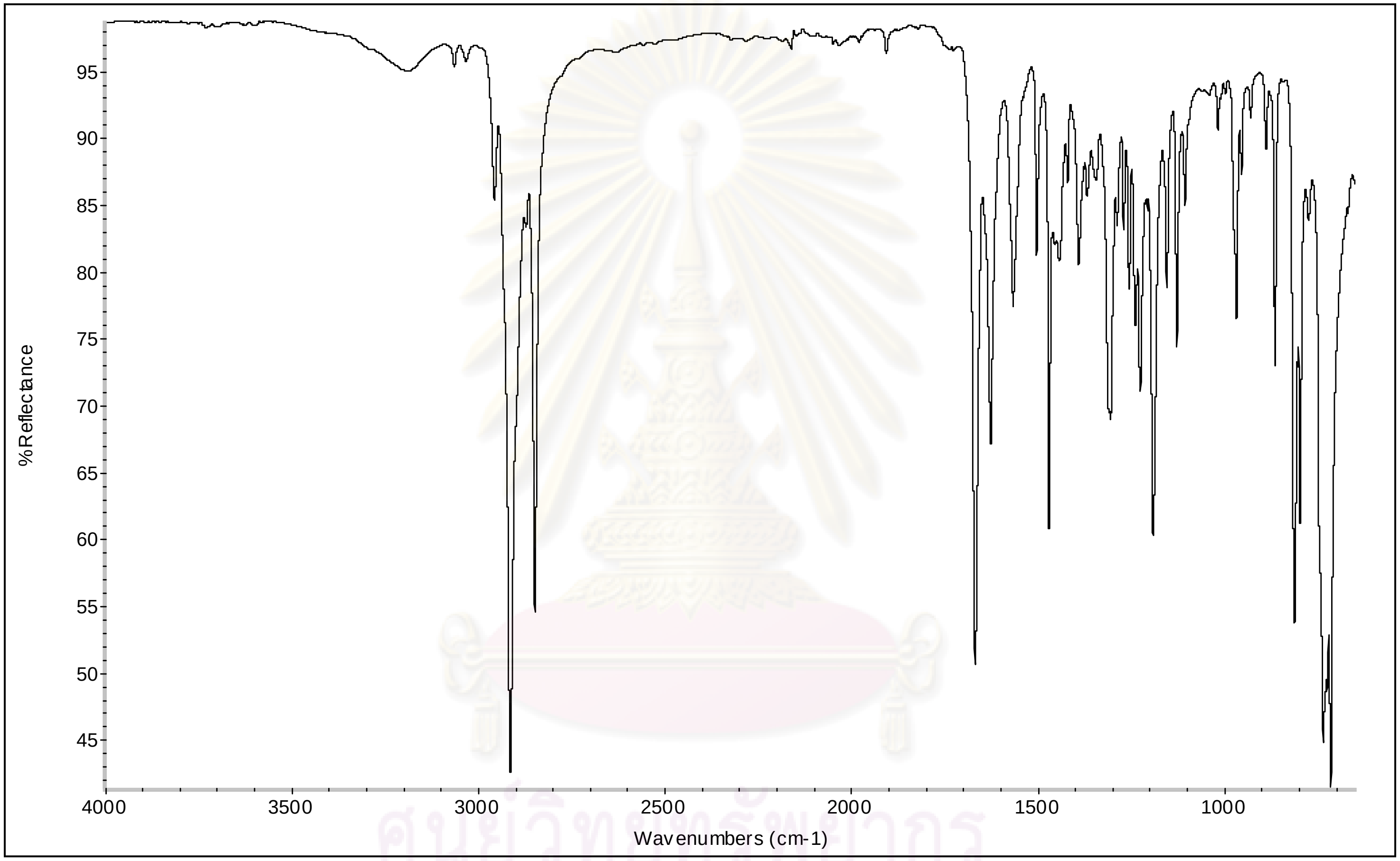


Figure A-3 IR spectrum of hydrogenated cardanol formaldehyde.

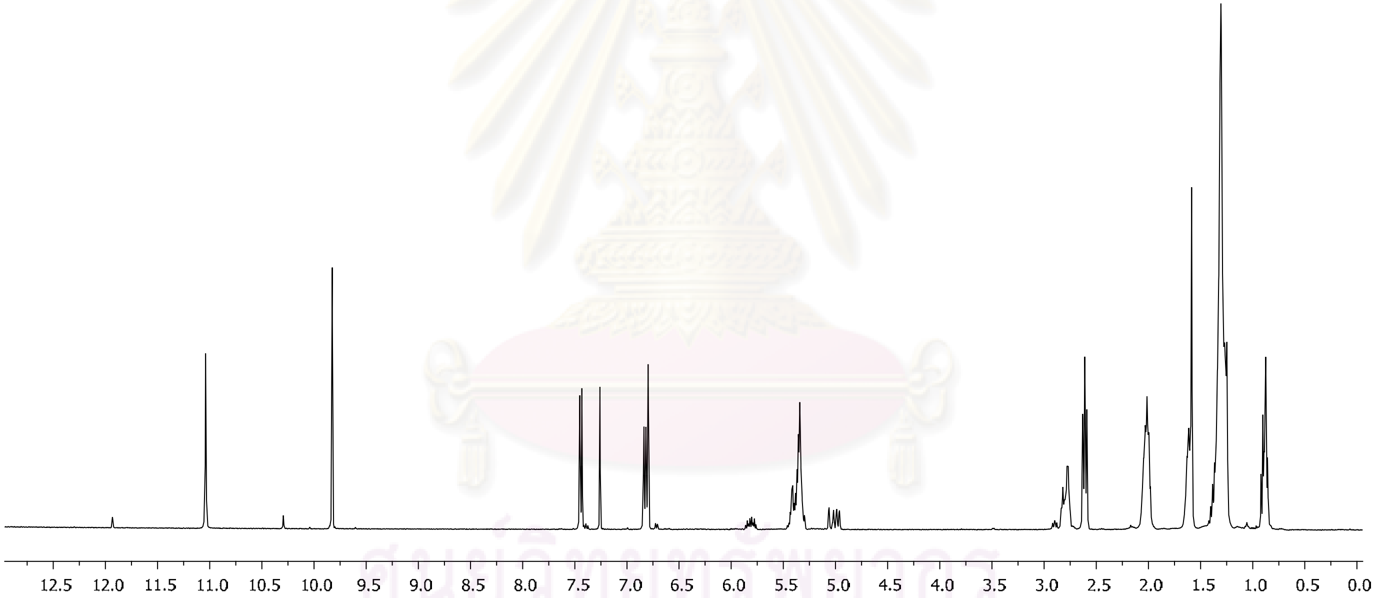


Figure A-4 ^{1}H-NMR spectrum of cardanol formaldehyde.

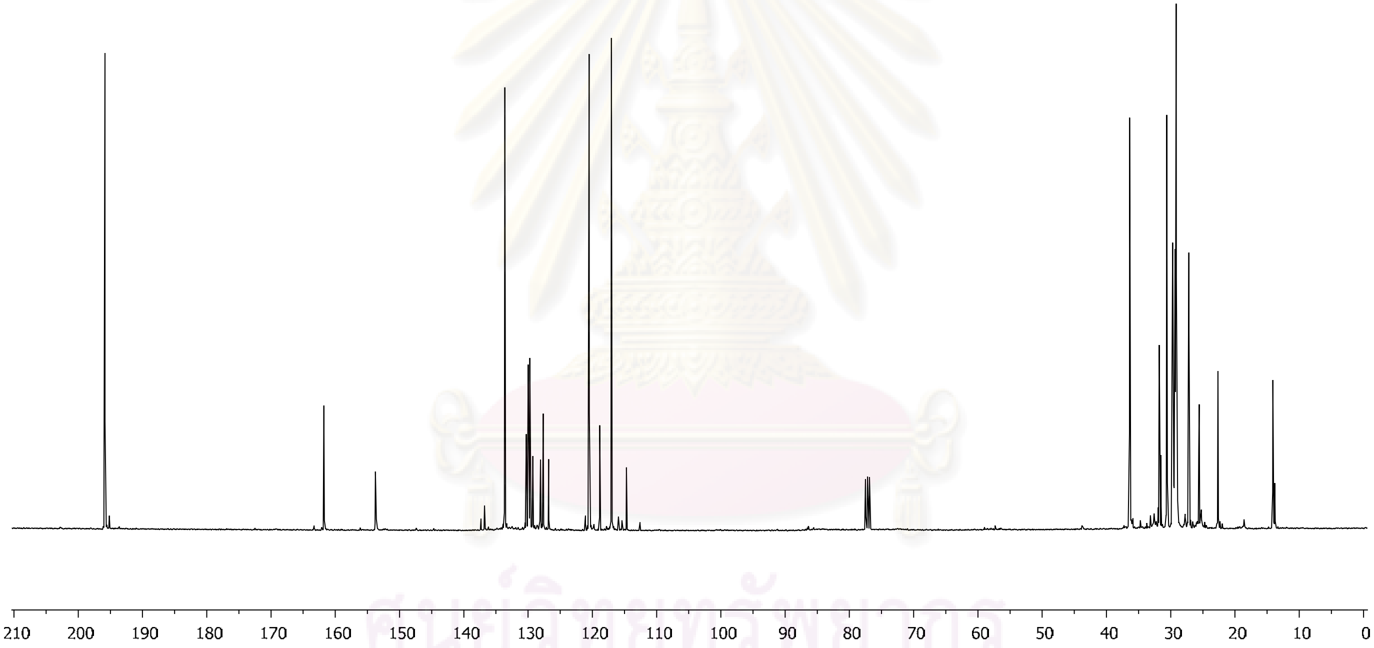


Figure A-5 ^{13}C-NMR spectrum of cardanol formaldehyde.

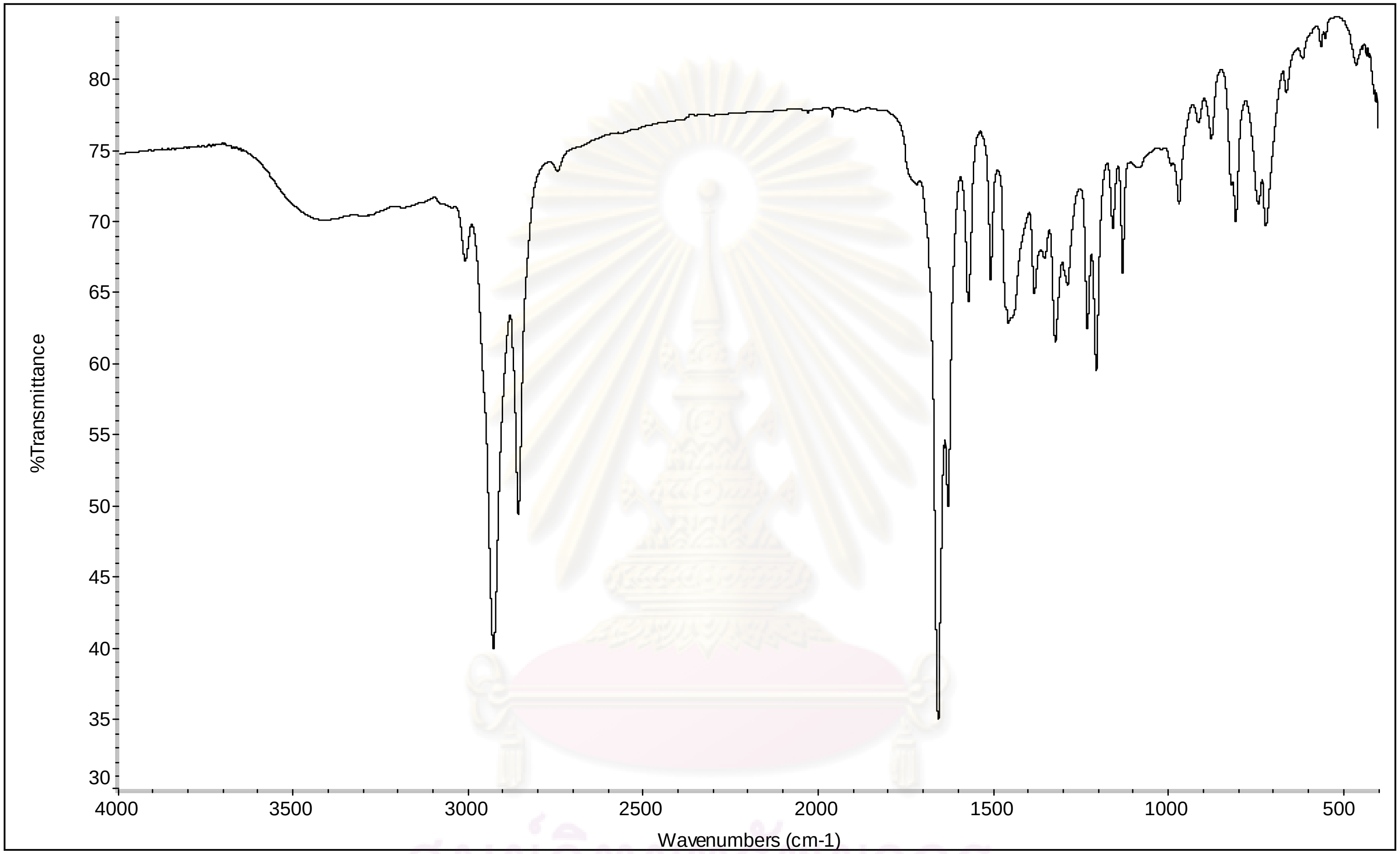


Figure A-6 IR spectrum of cardanol formaldehyde.

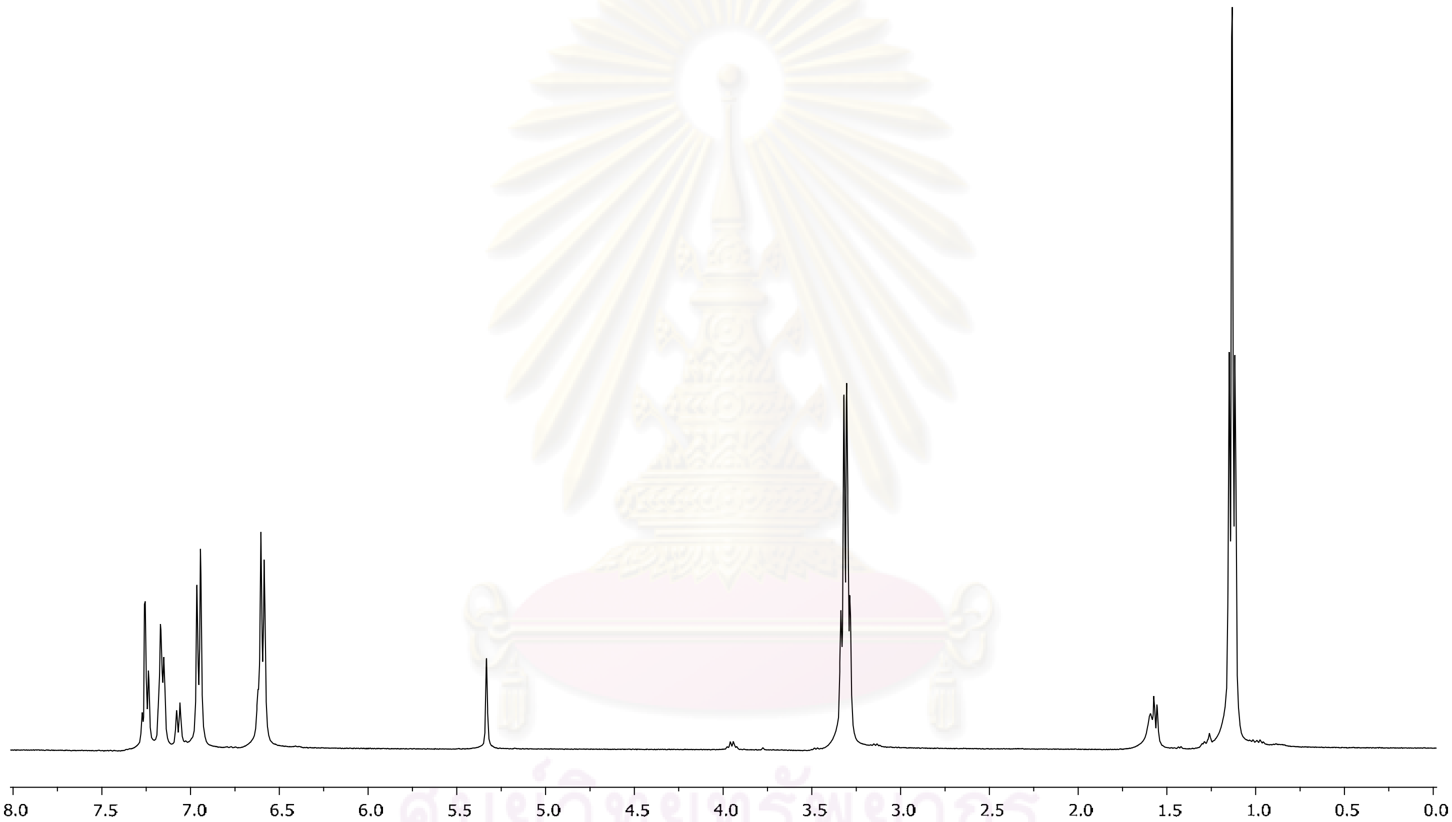


Figure A-7 ^{1}H-NMR spectrum of Compound **1**.

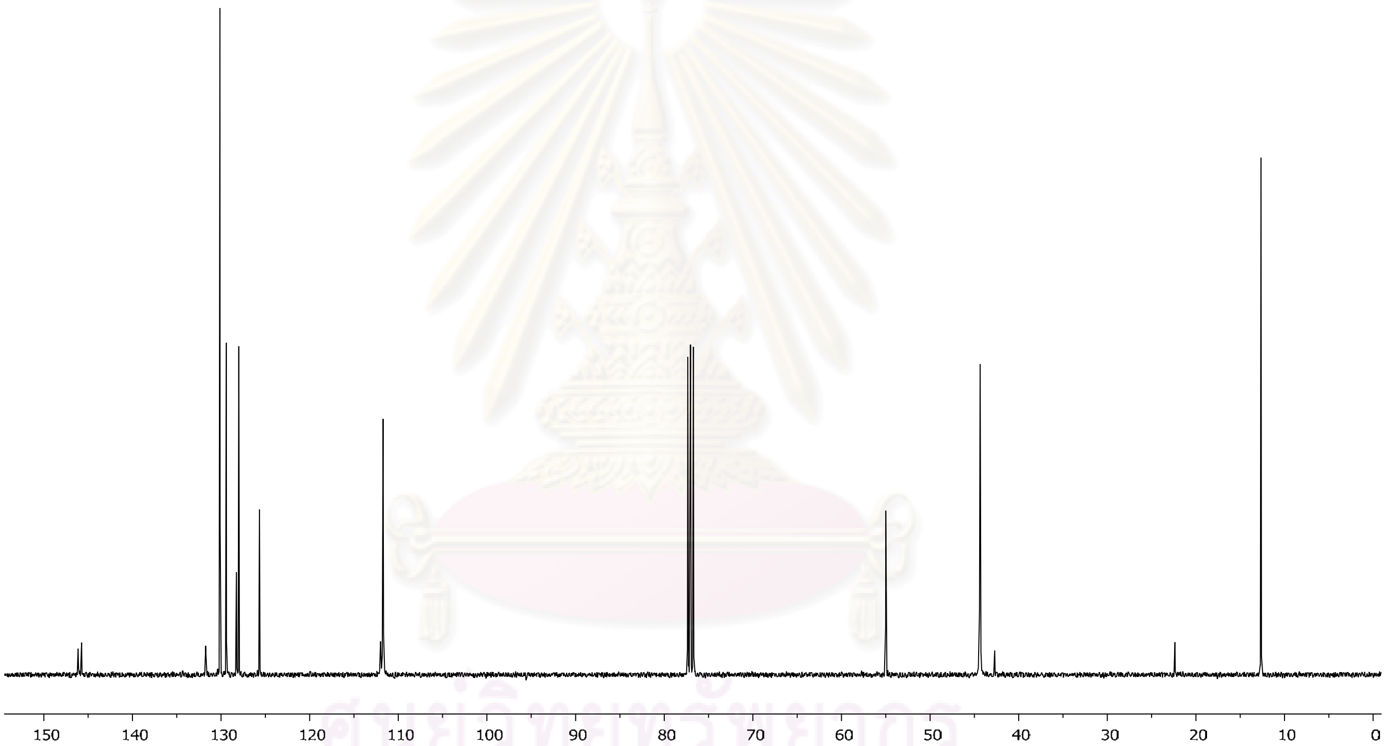


Figure A-8 ^{13}C-NMR spectrum of Compound **1**

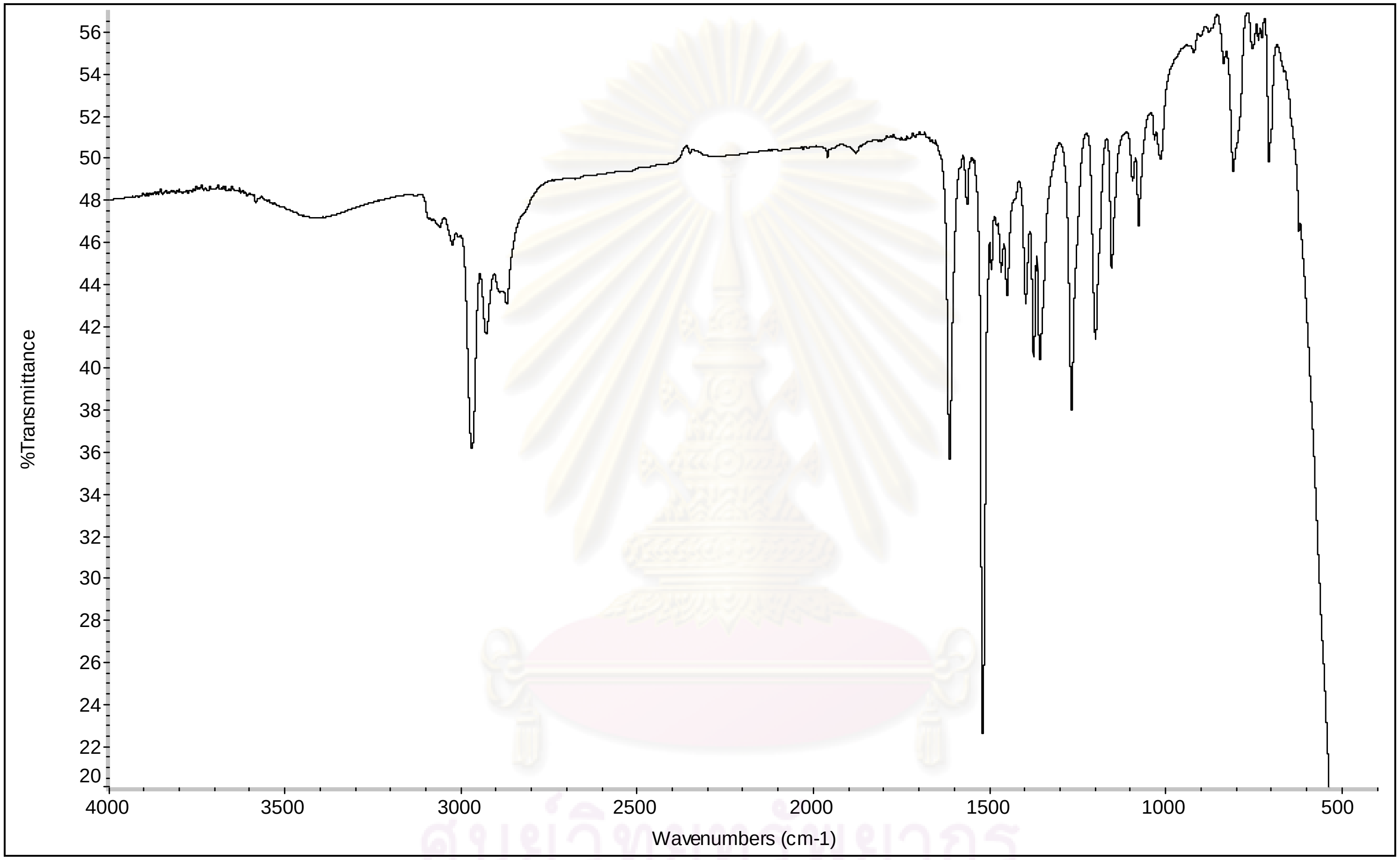


Figure A-9 IR spectrum of Compound **1**.

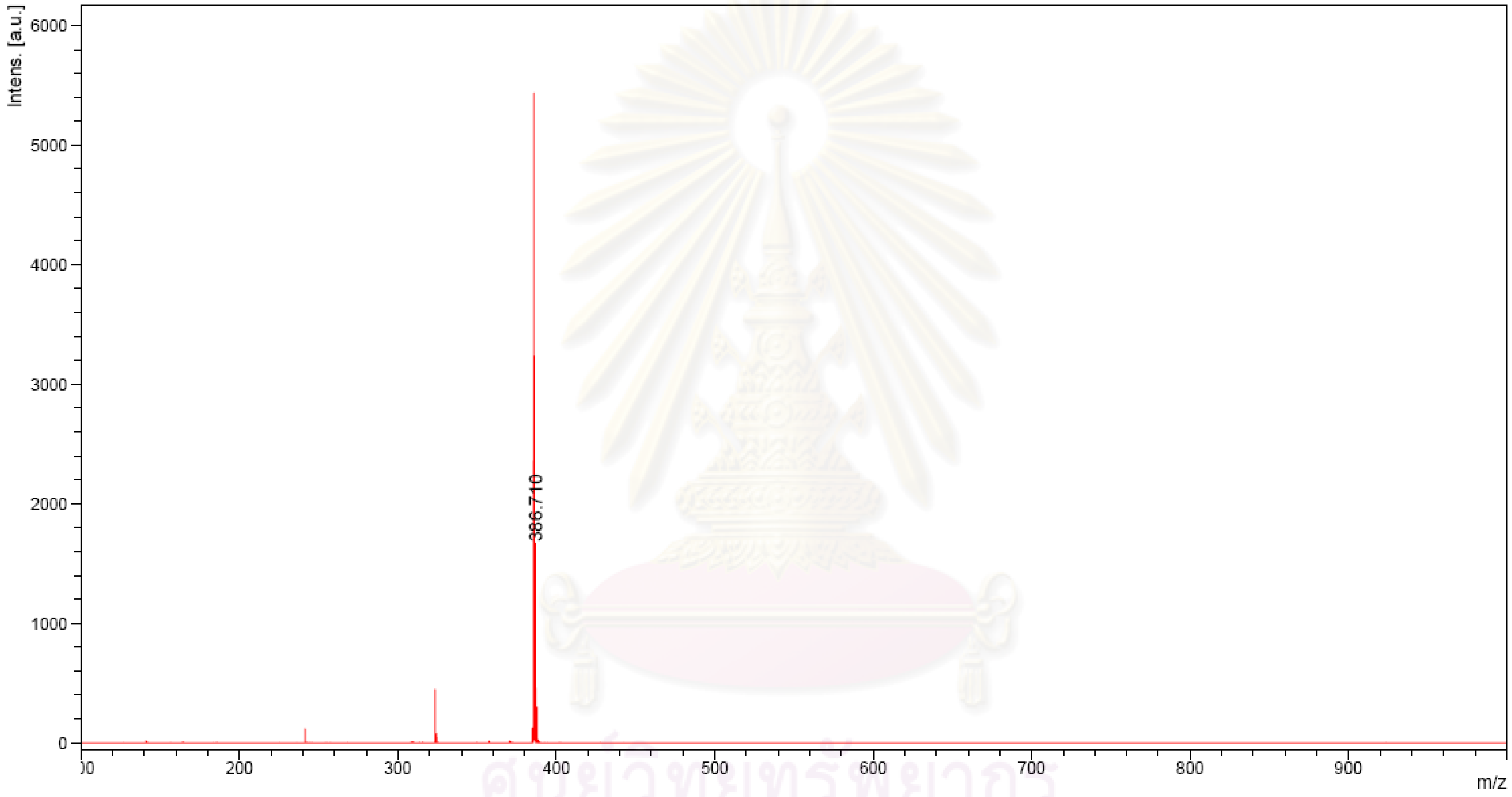


Figure A-10 Mass spectrum of Compound **1**.

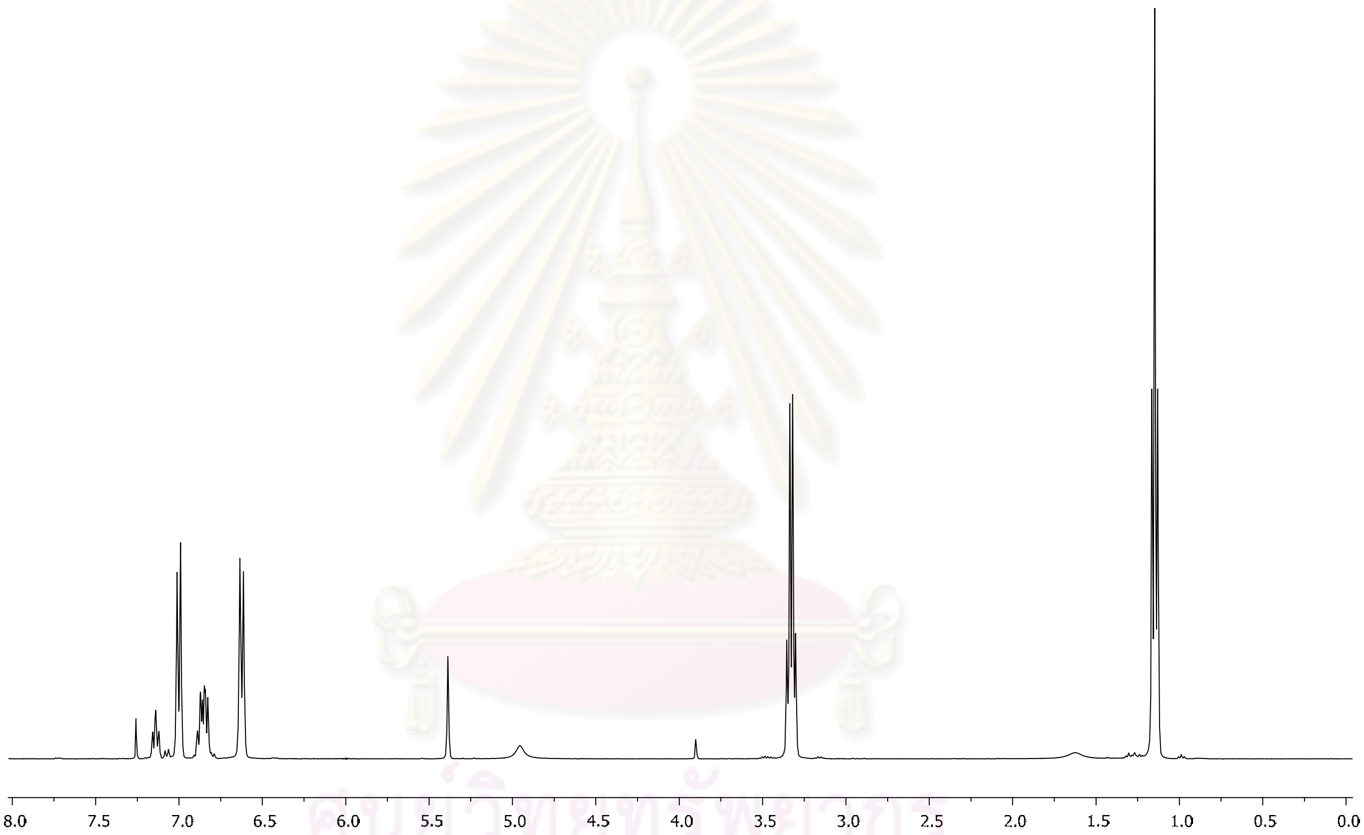


Figure A-11 ^{1}H-NMR spectrum of Compound **2**.

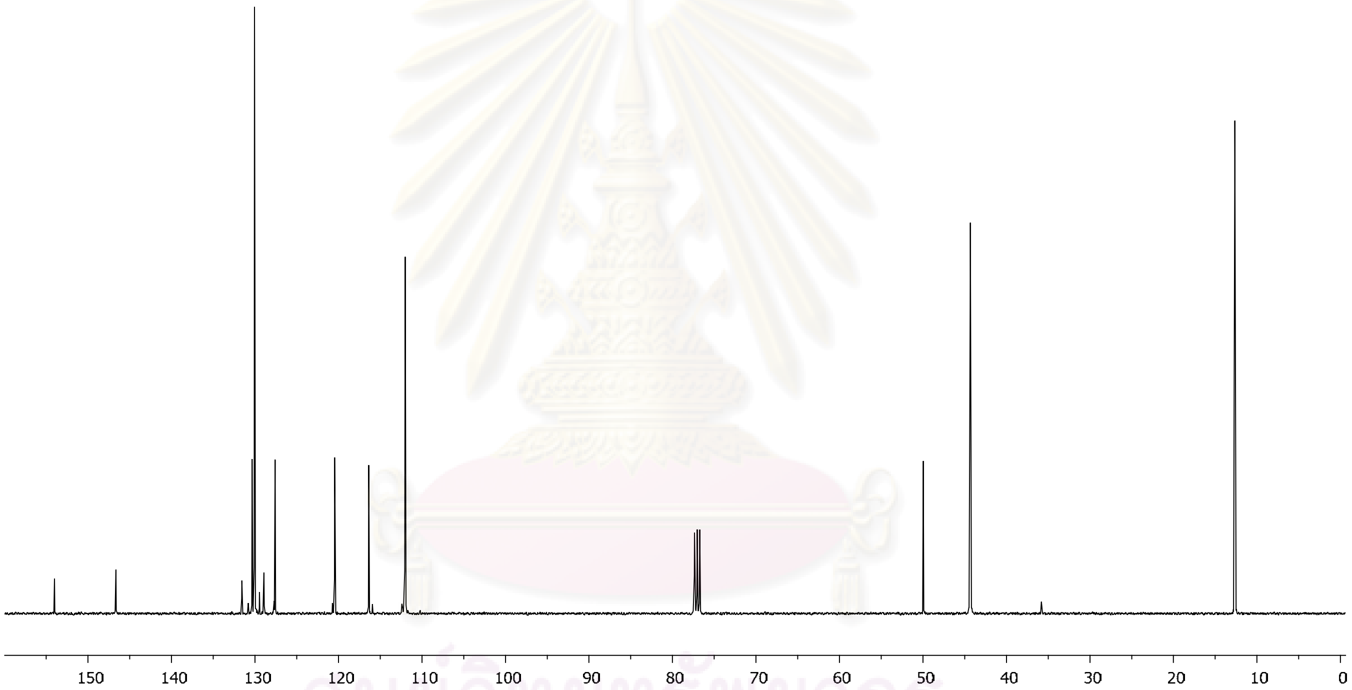


Figure A-12 ^{13}C-NMR spectrum of Compound **2**.

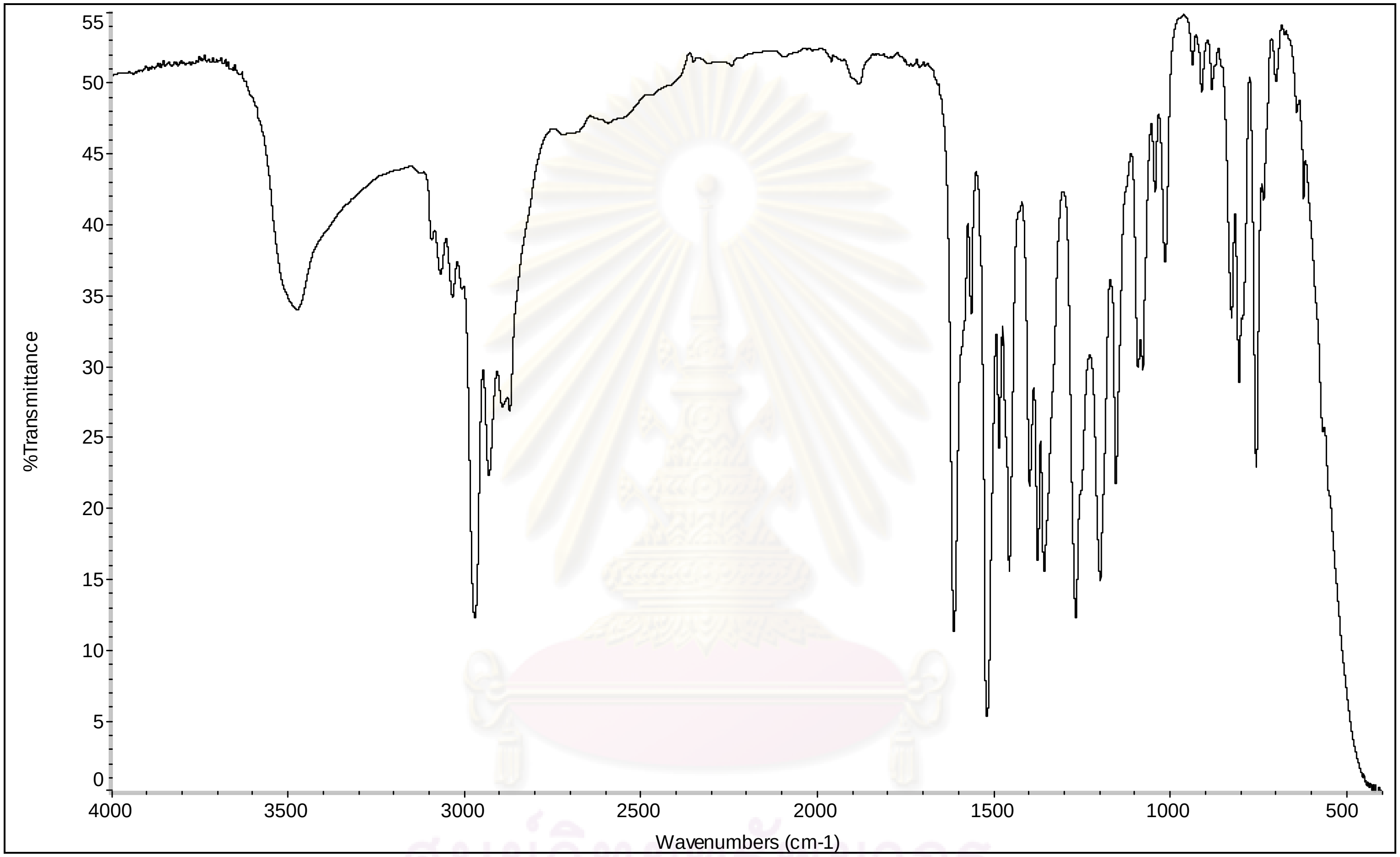


Figure A-13 IR spectrum of Compound **2**.

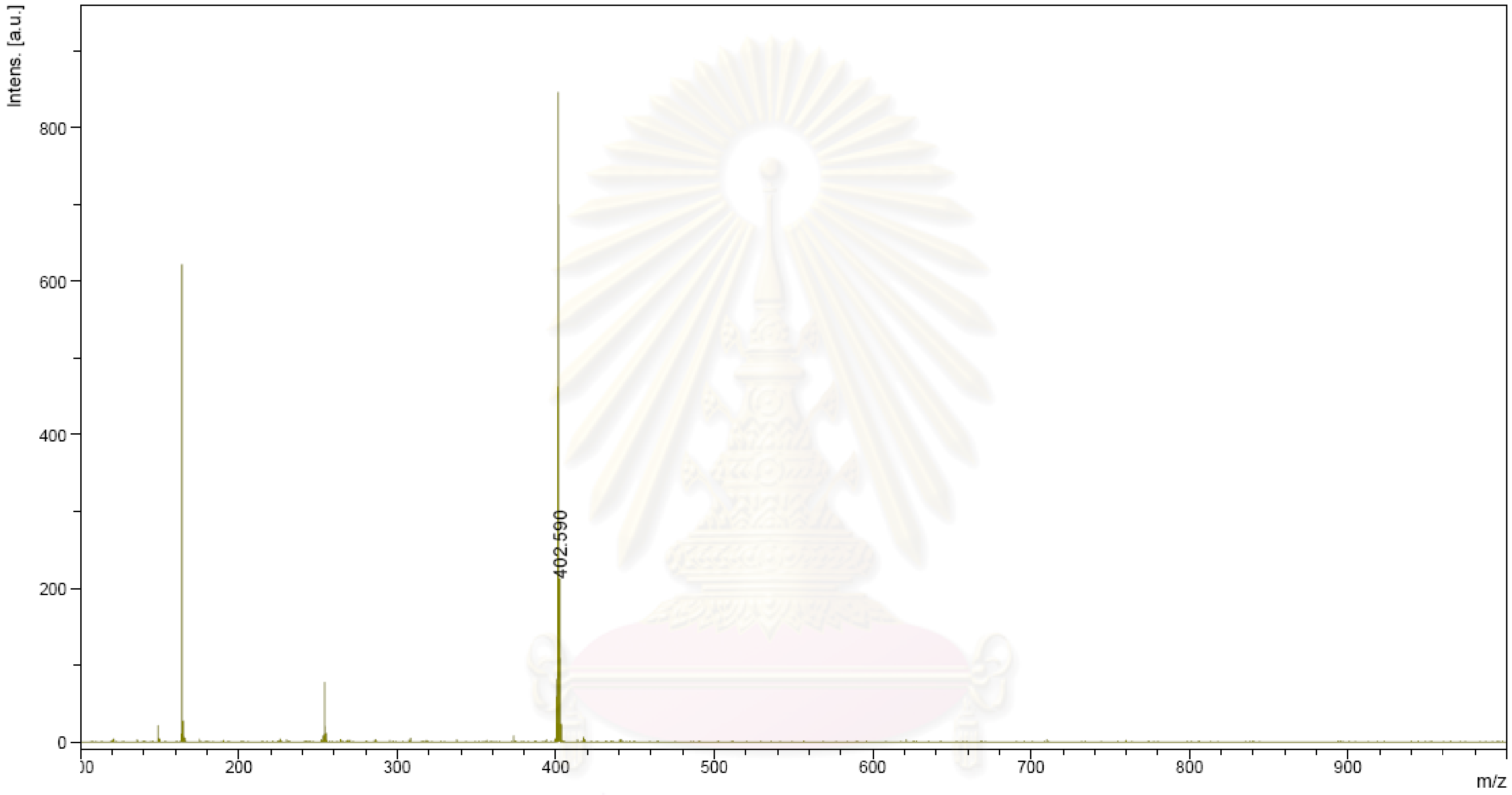


Figure A-14 Mass spectrum of Compound **2**.

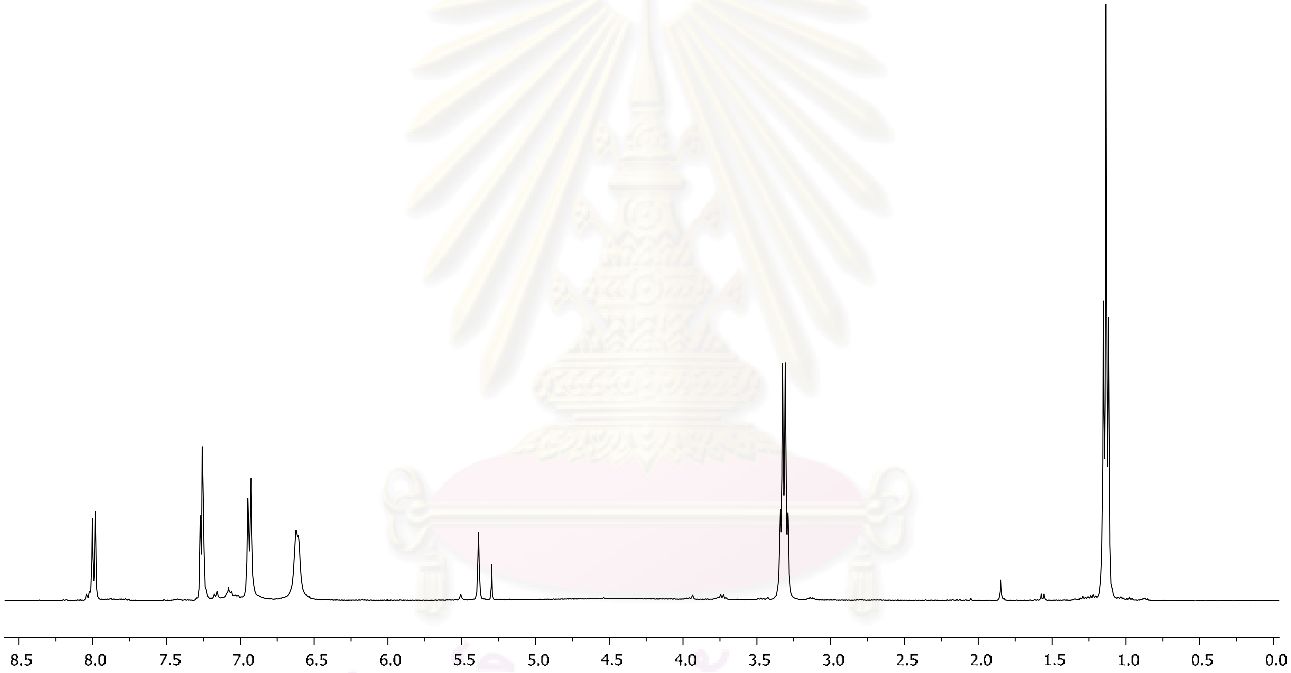


Figure A-15 ^{1}H-NMR spectrum of Compound **3**.

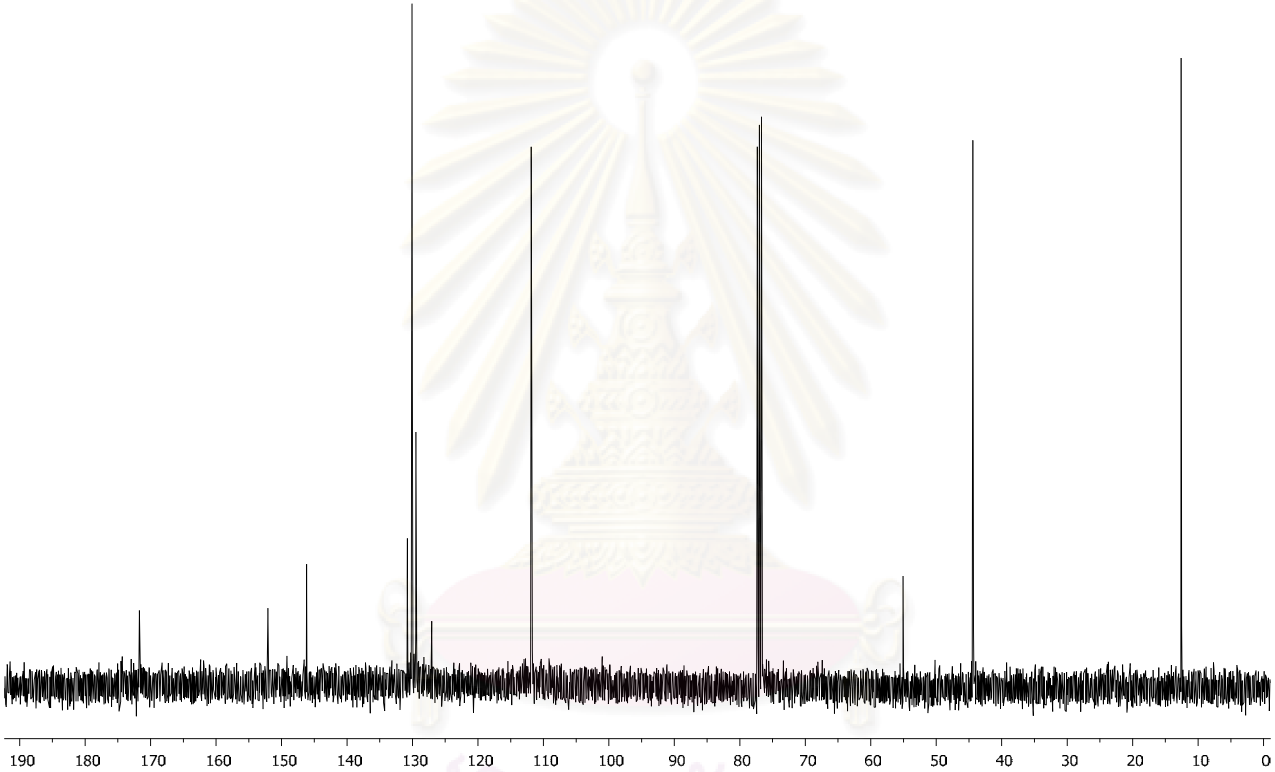


Figure A-16 ^{13}C-NMR spectrum of Compound **3**.

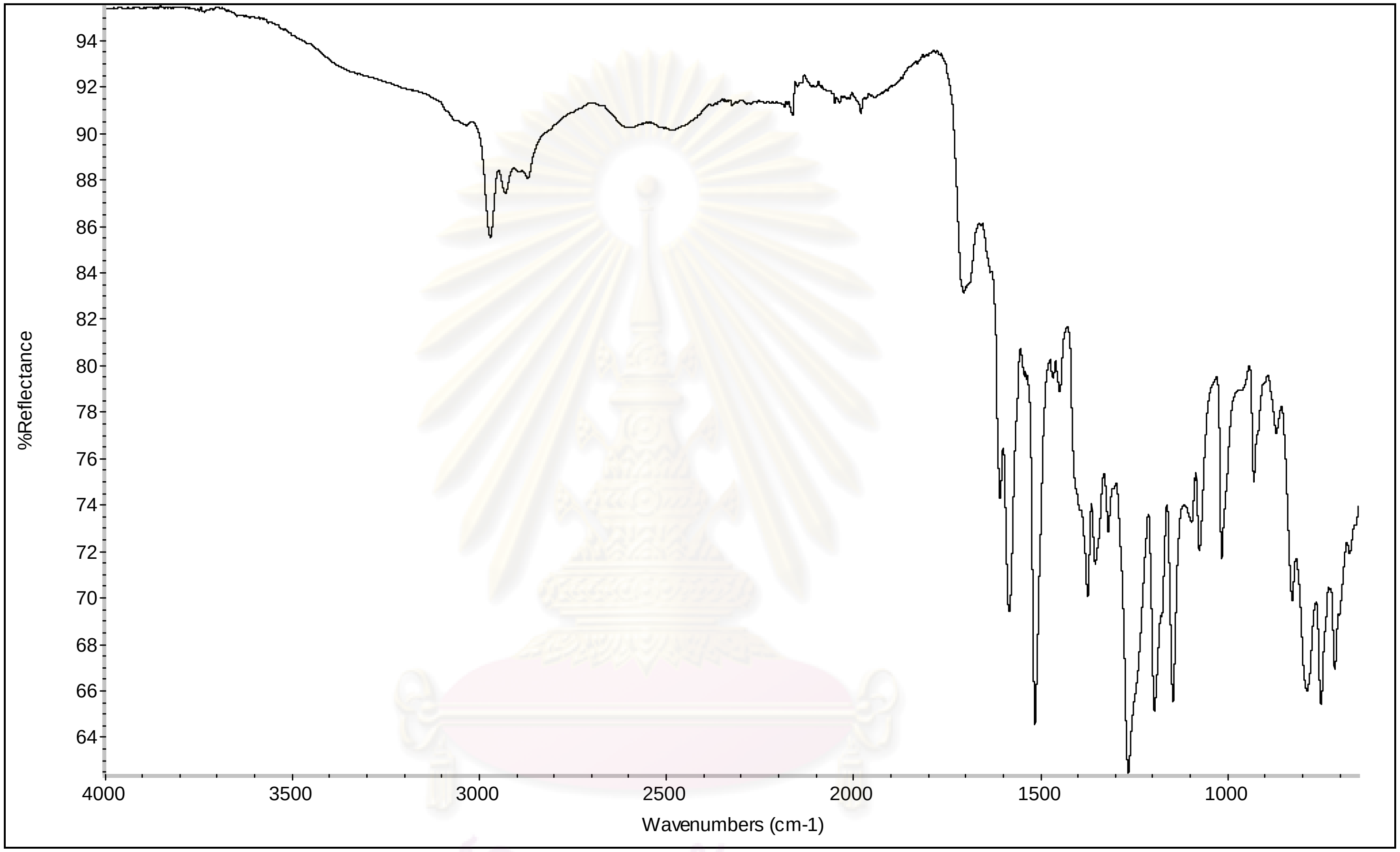


Figure A-17 IR spectrum of Compound **3**.

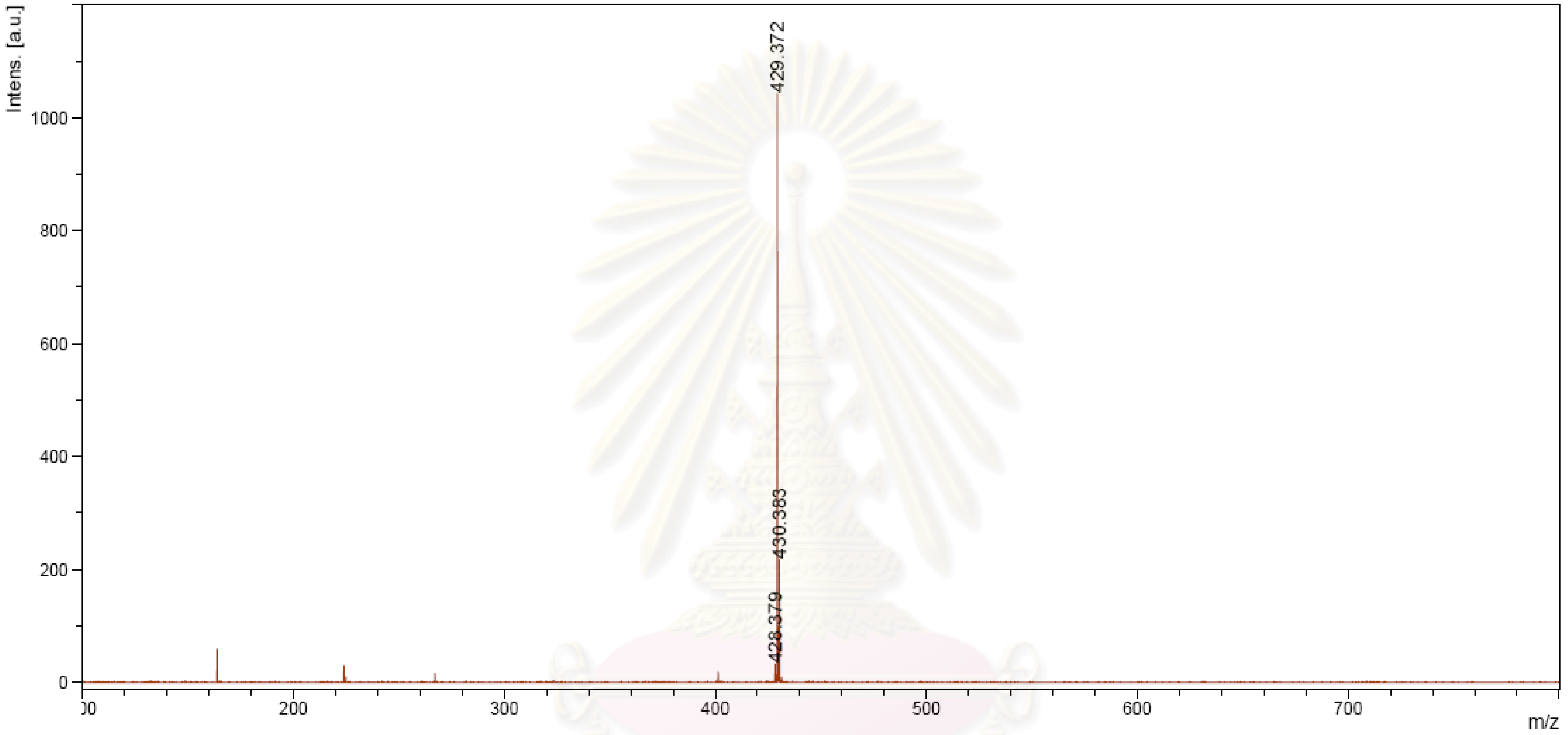


Figure A-18 Mass spectrum of Compound **3**.

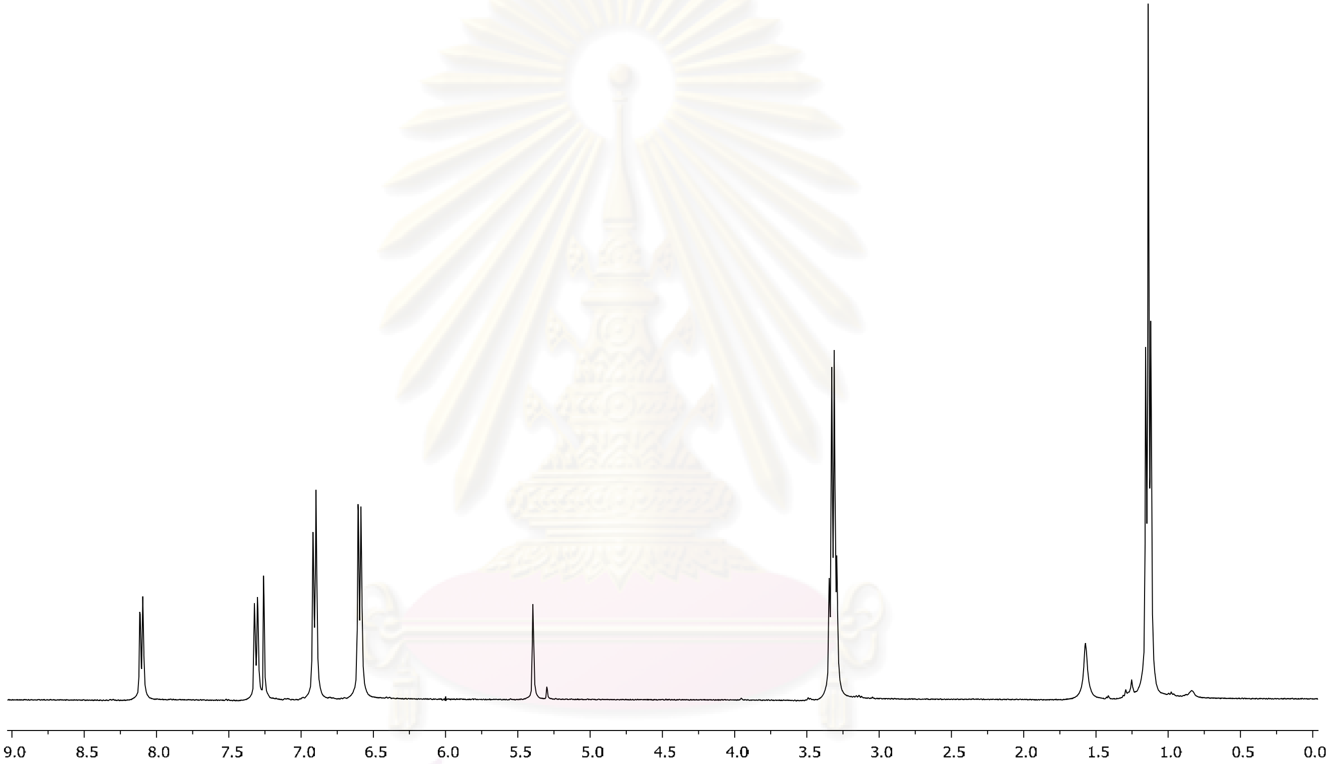


Figure A-19 ^{1}H-NMR spectrum of Compound **4**.

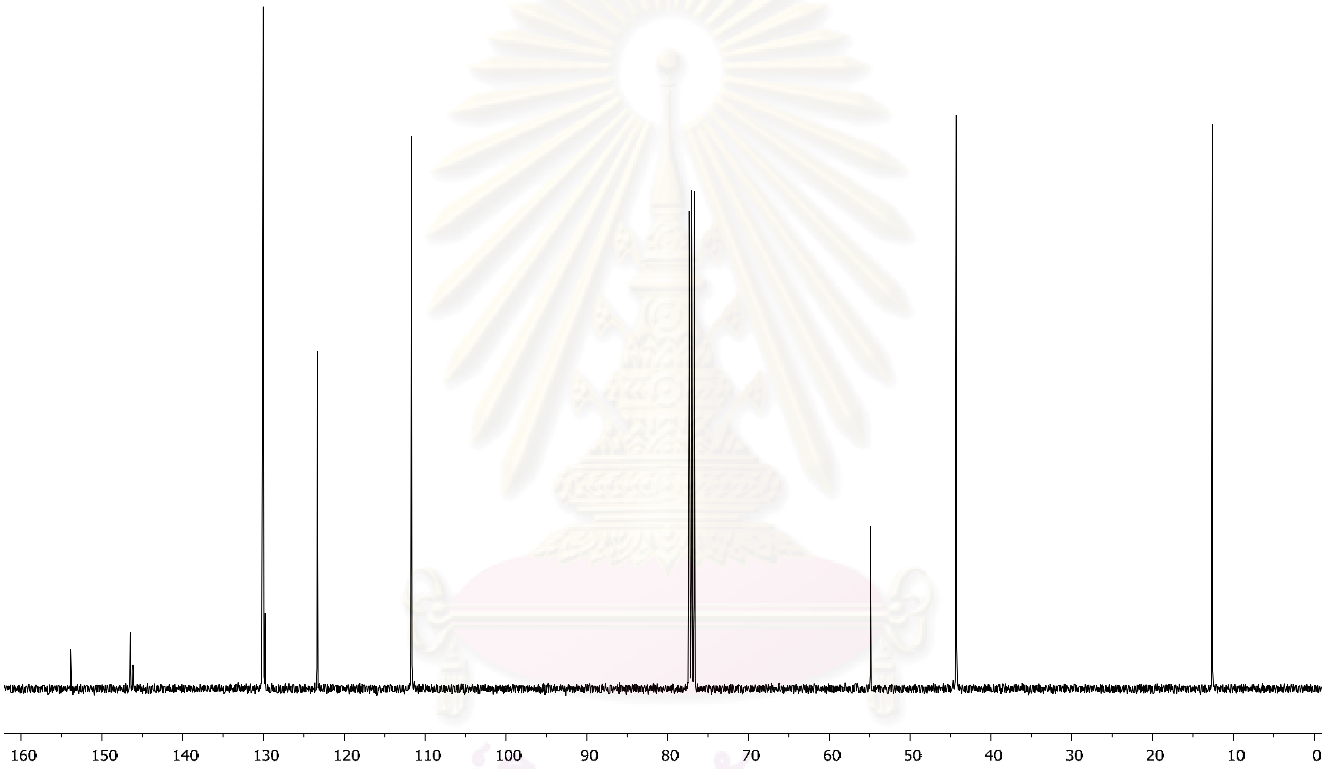
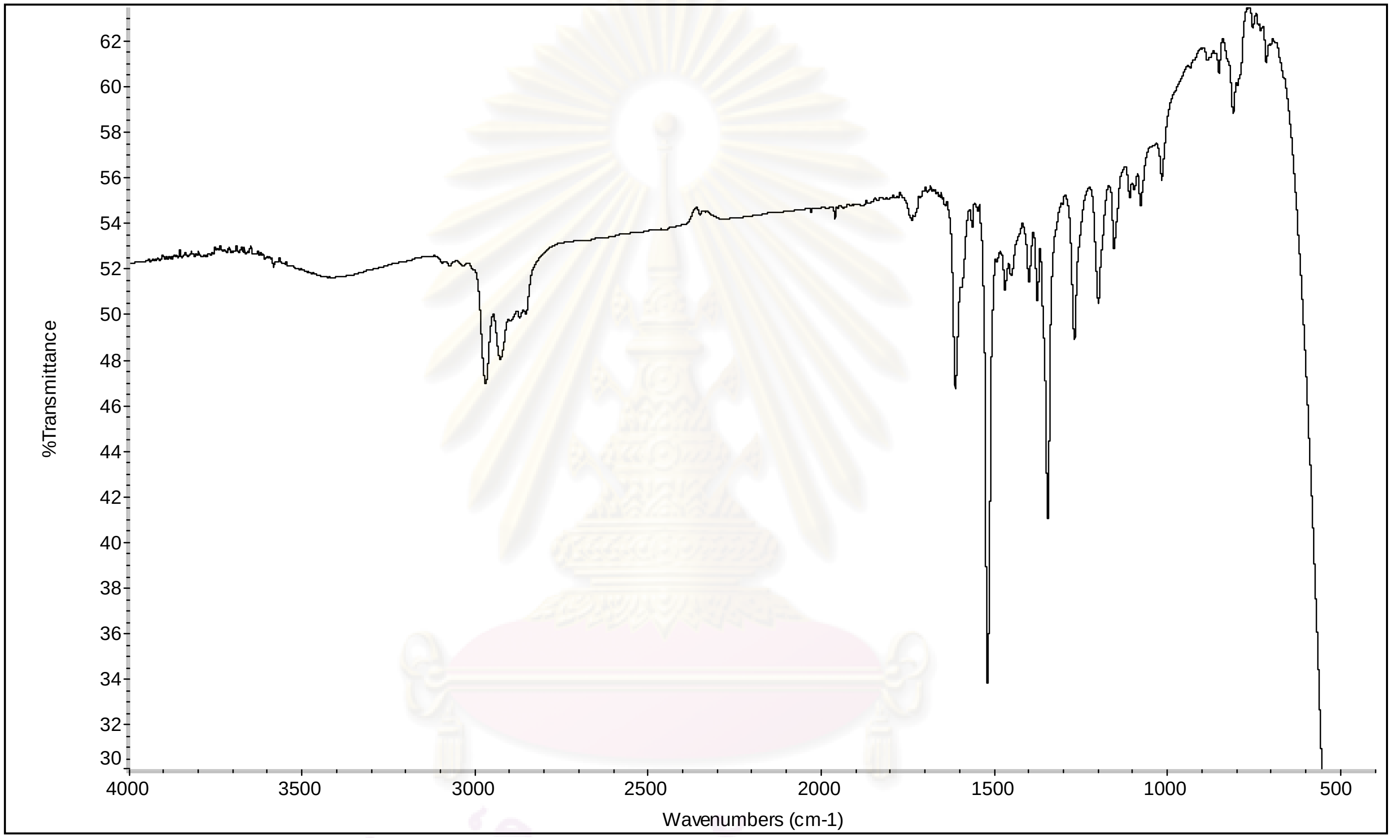


Figure A-20 ^{13}C-NMR spectrum of Compound **4**.



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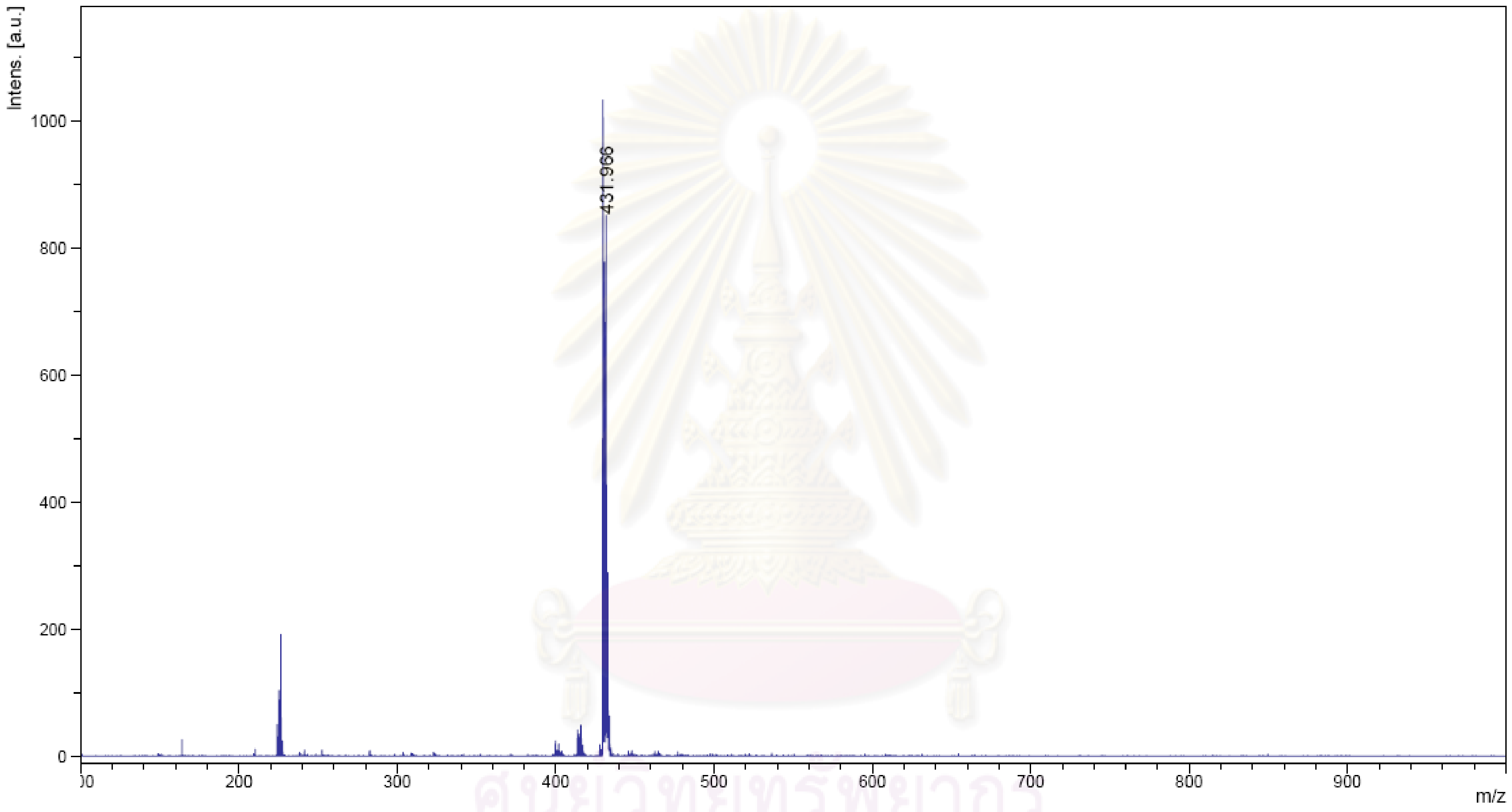
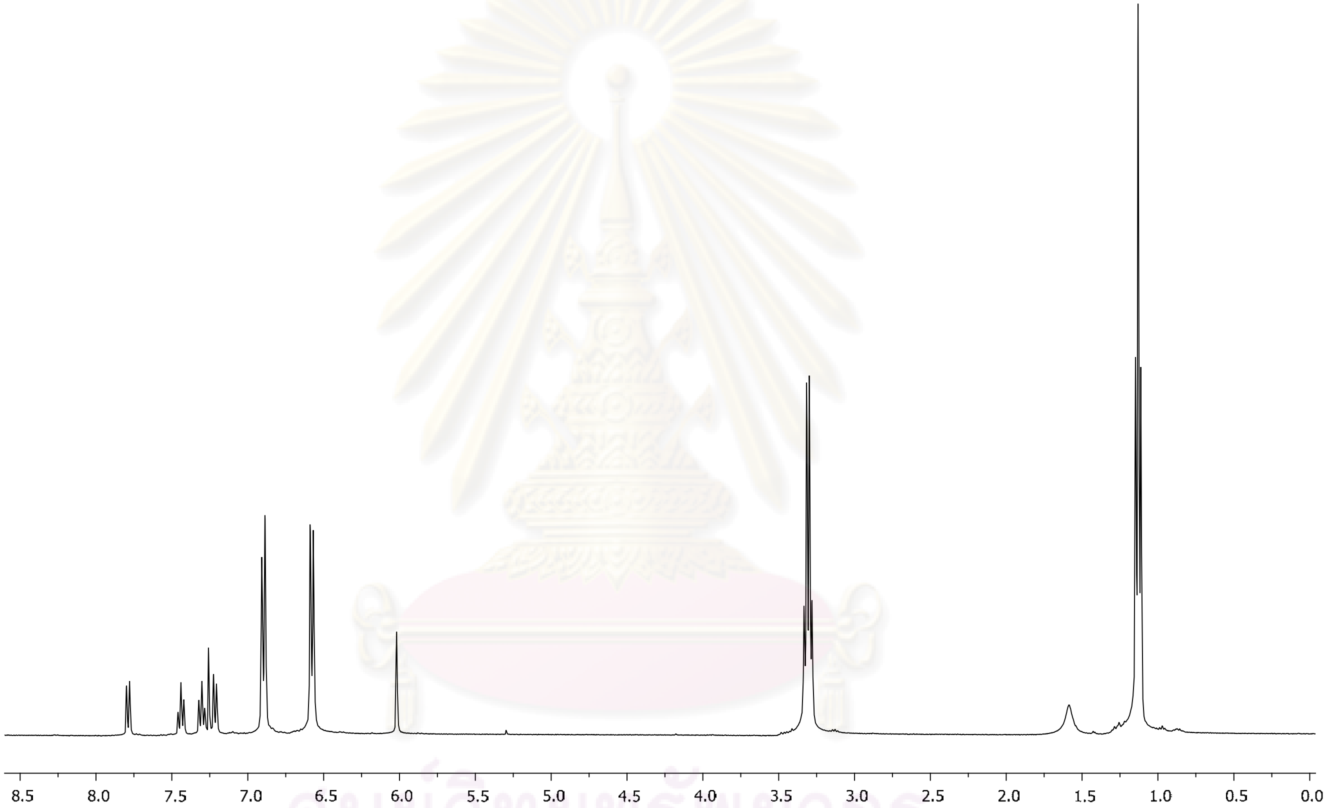


Figure A-22 Mass spectrum of Compound **4**.



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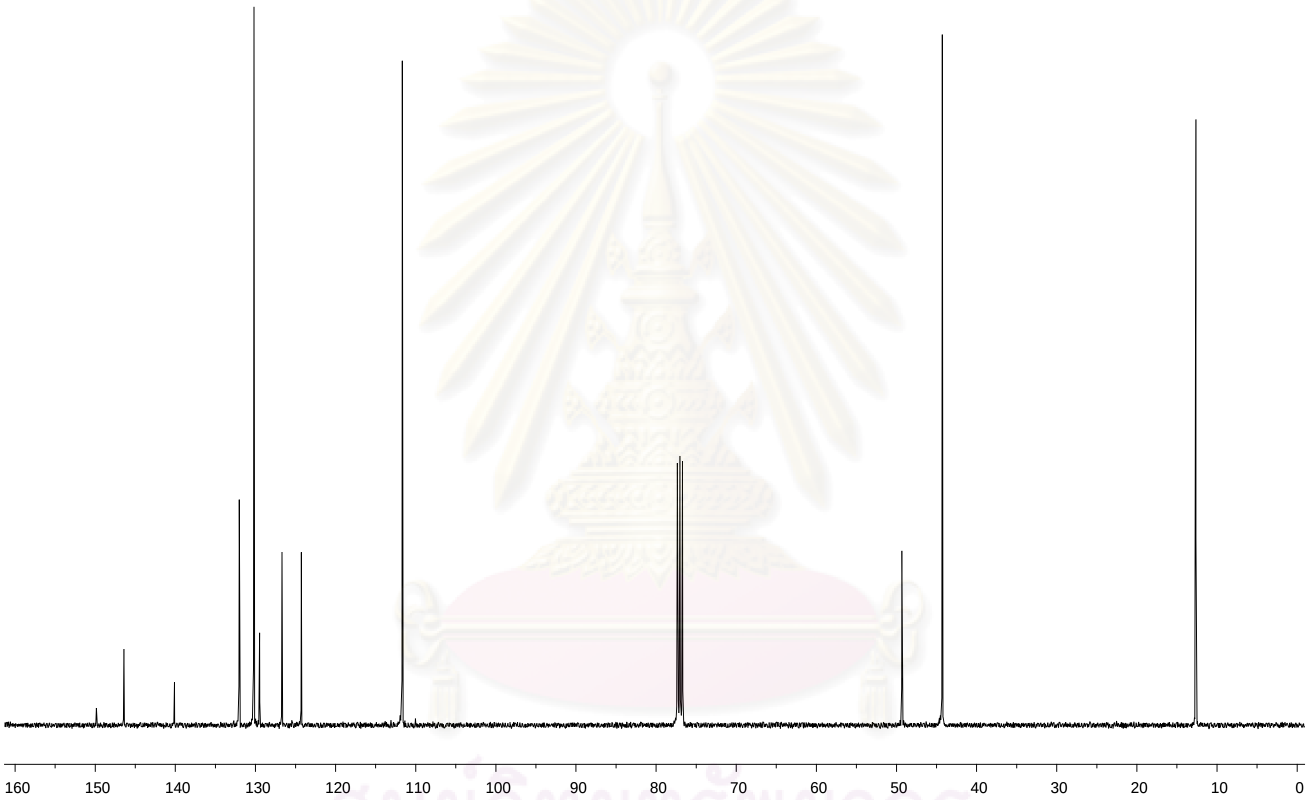
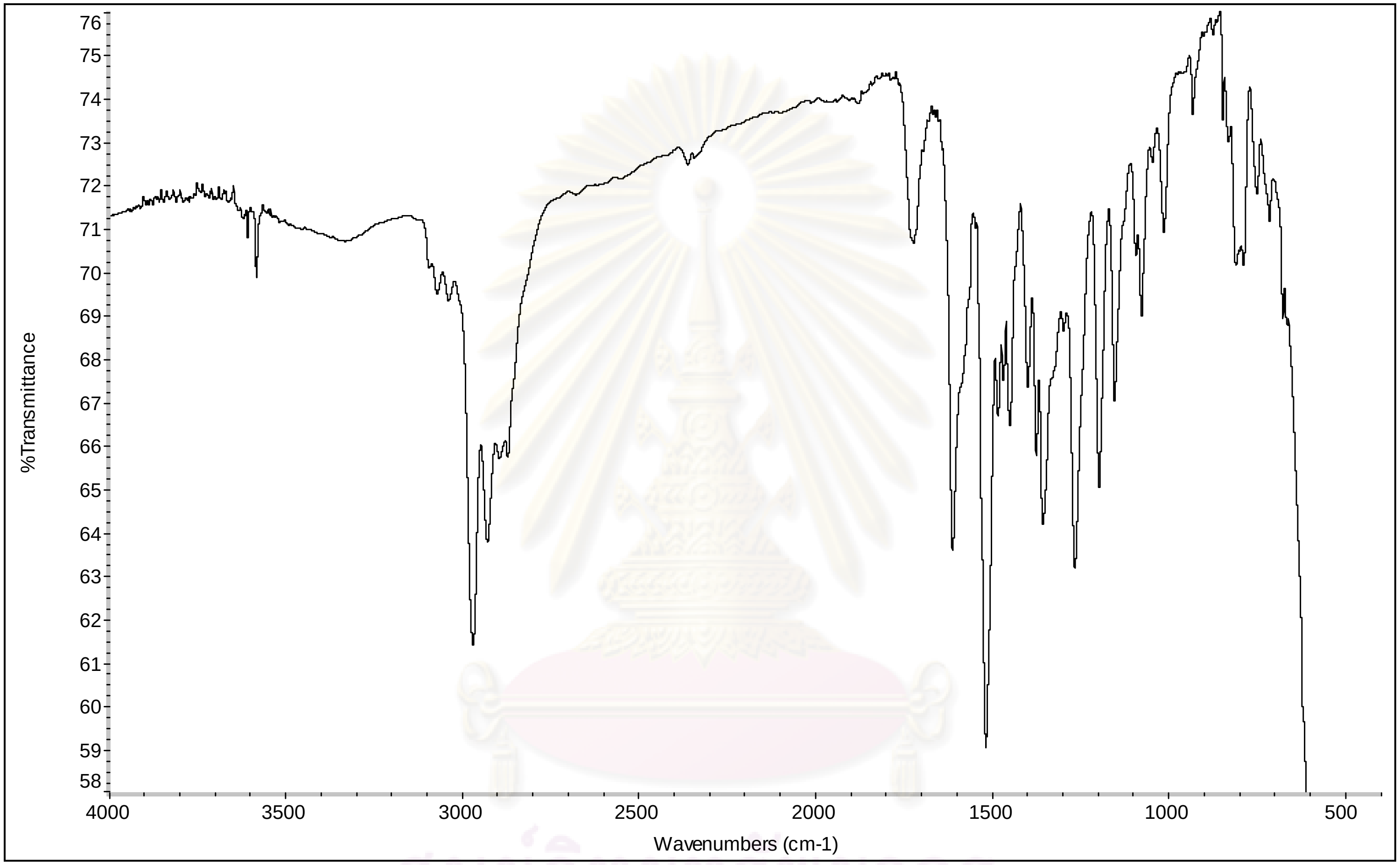


Figure A-24 ^{13}C-NMR spectrum of Compound **5**.



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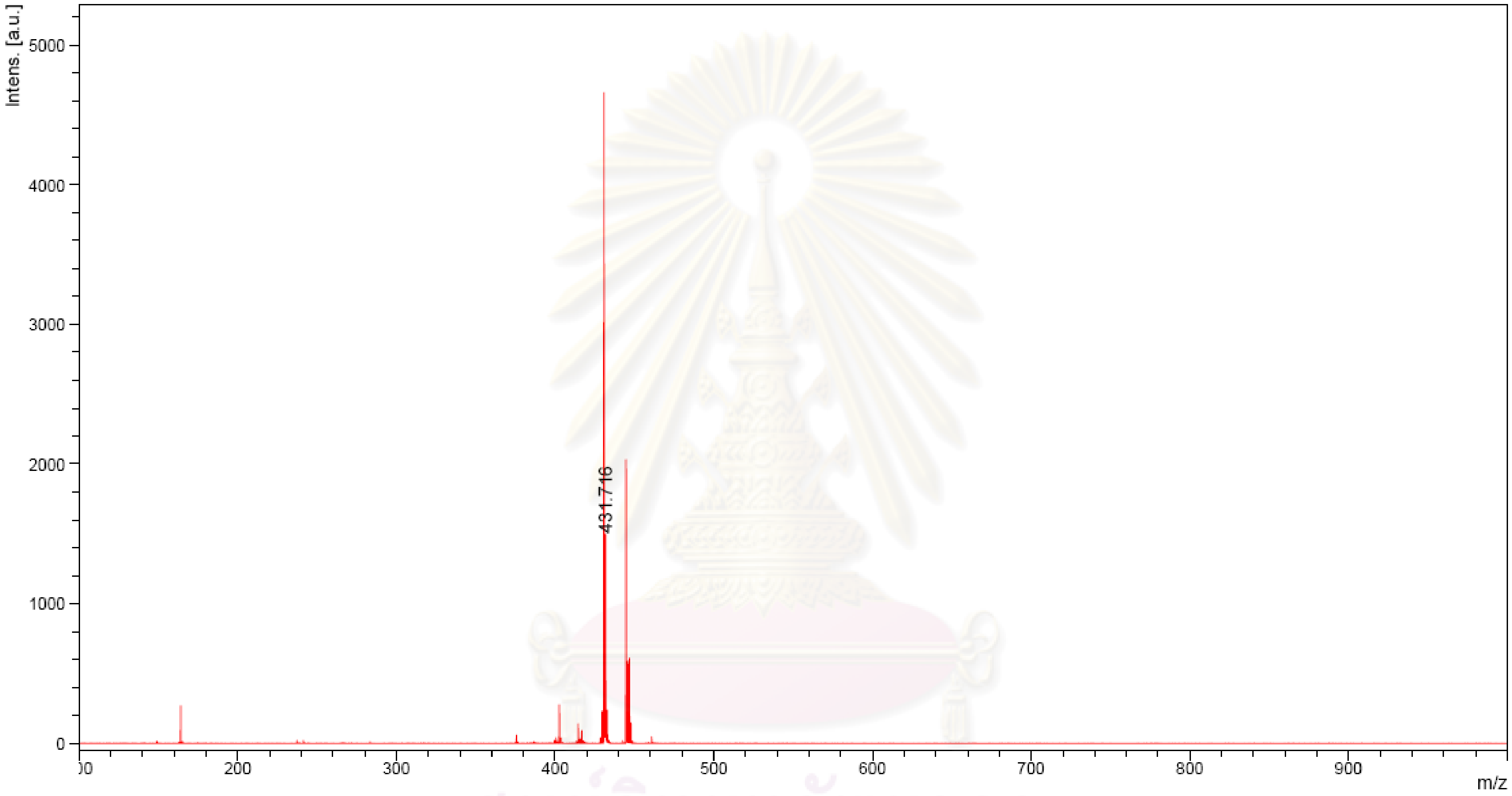

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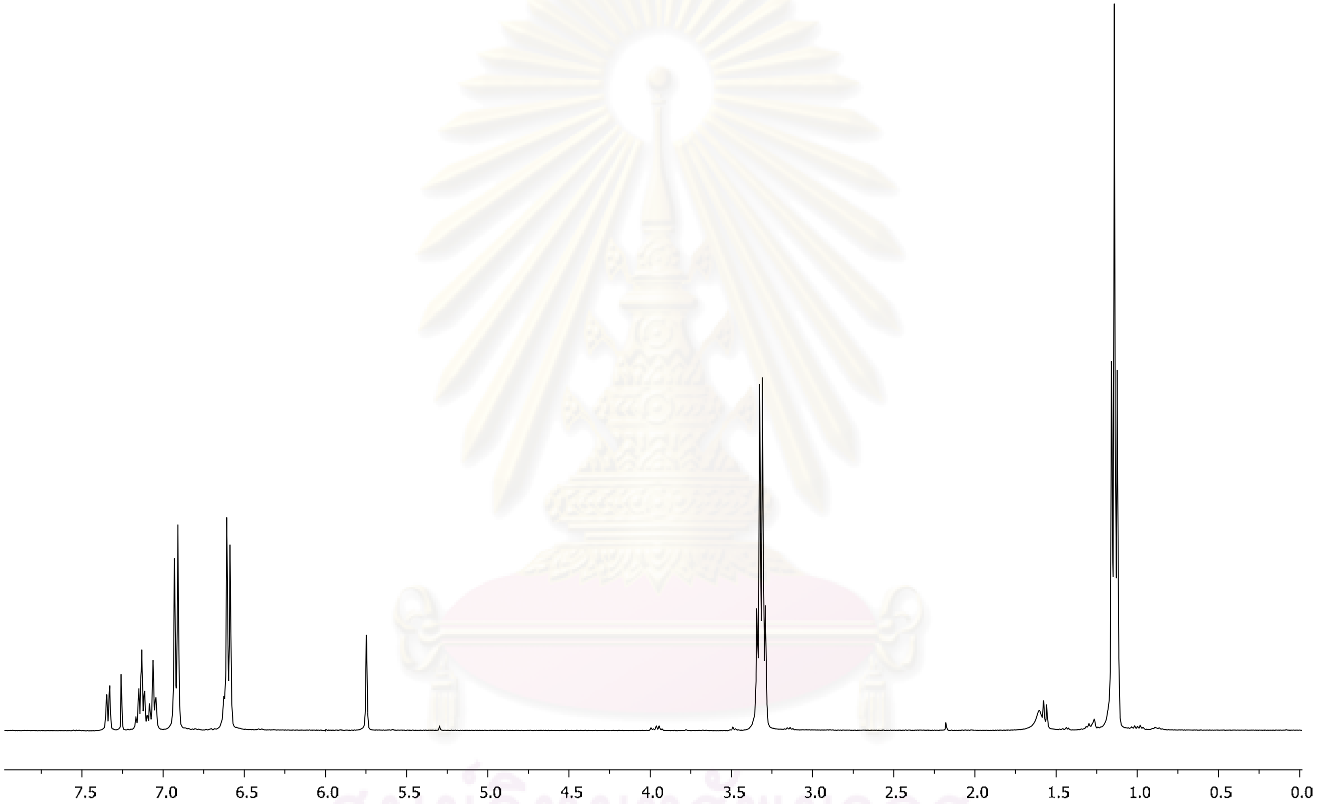
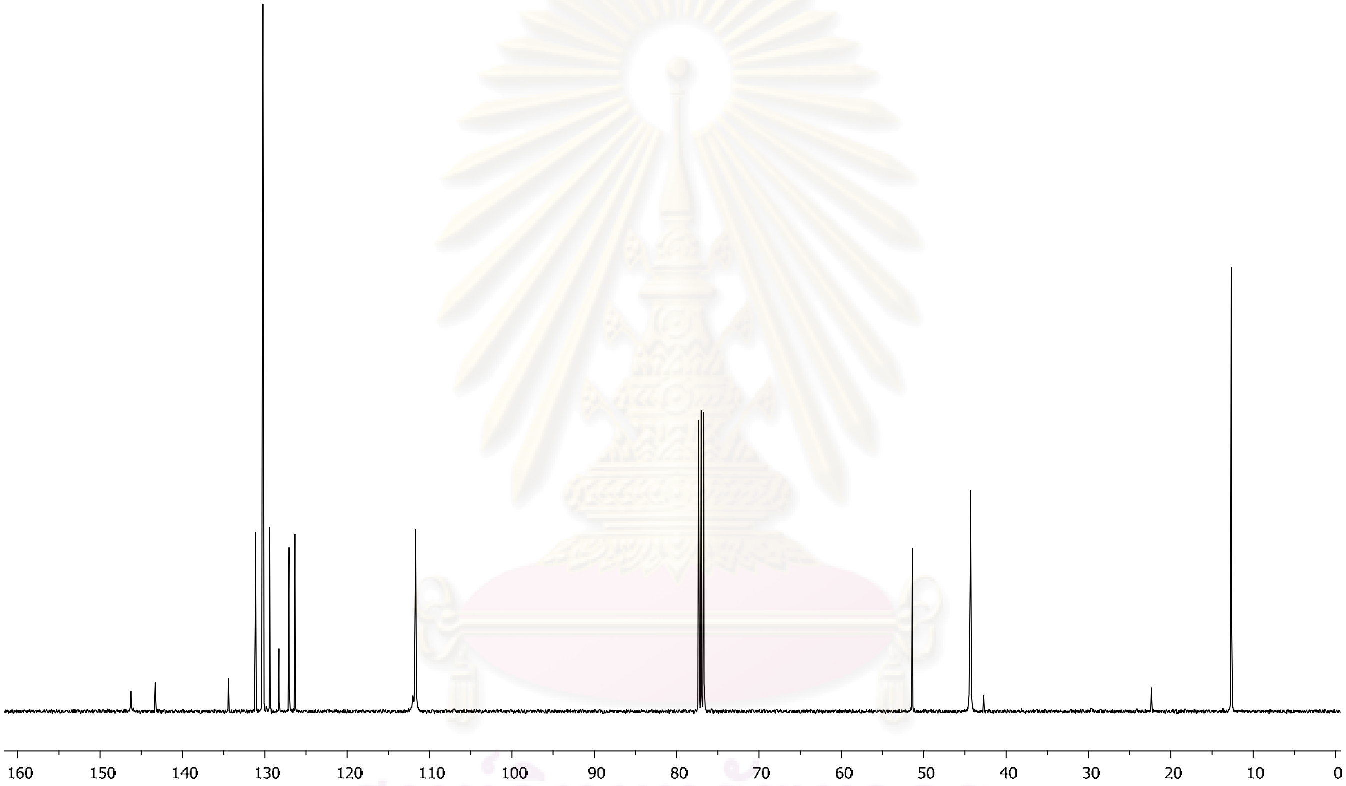


Figure A-27 ^{1}H-NMR spectrum of Compound **6**



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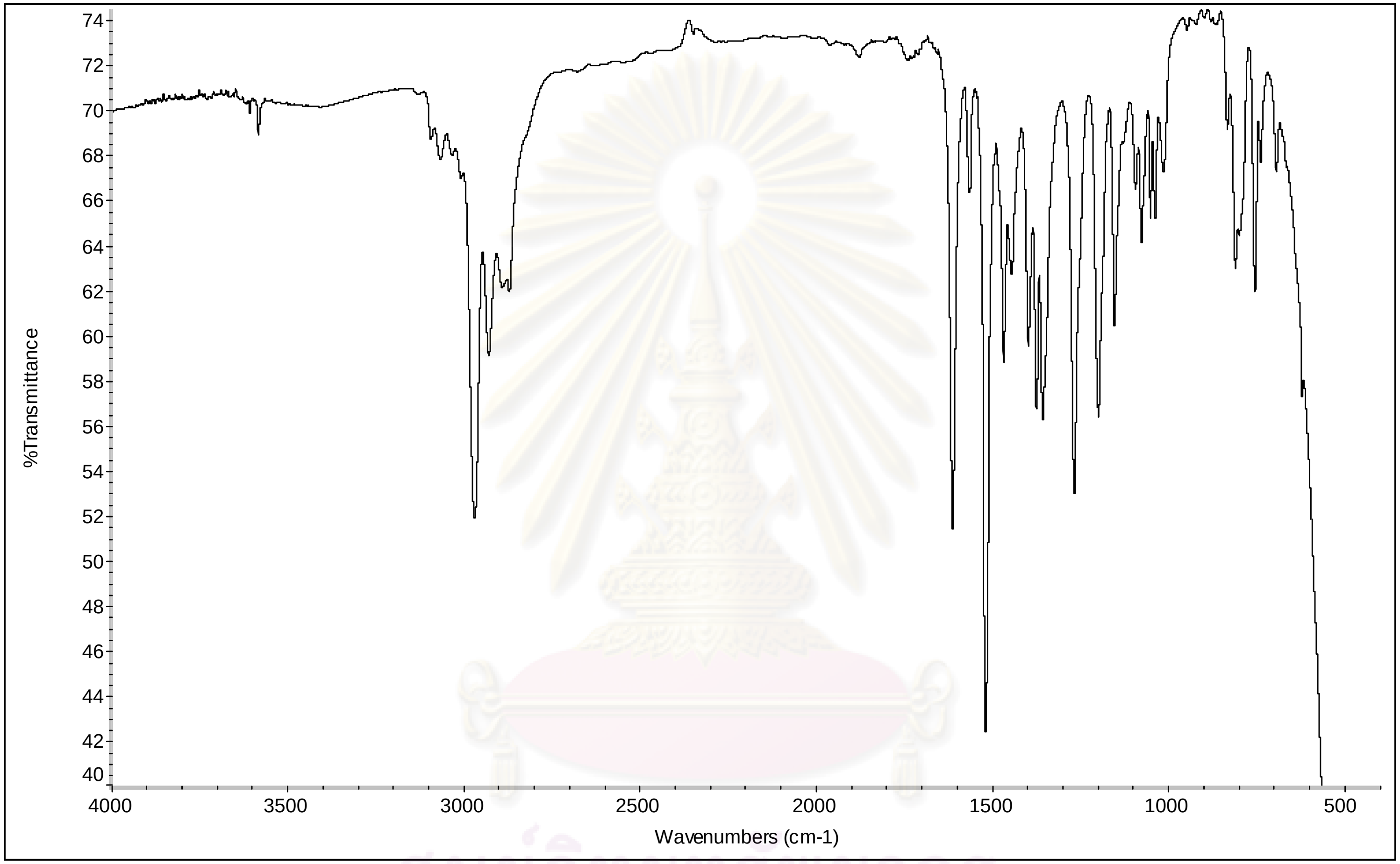

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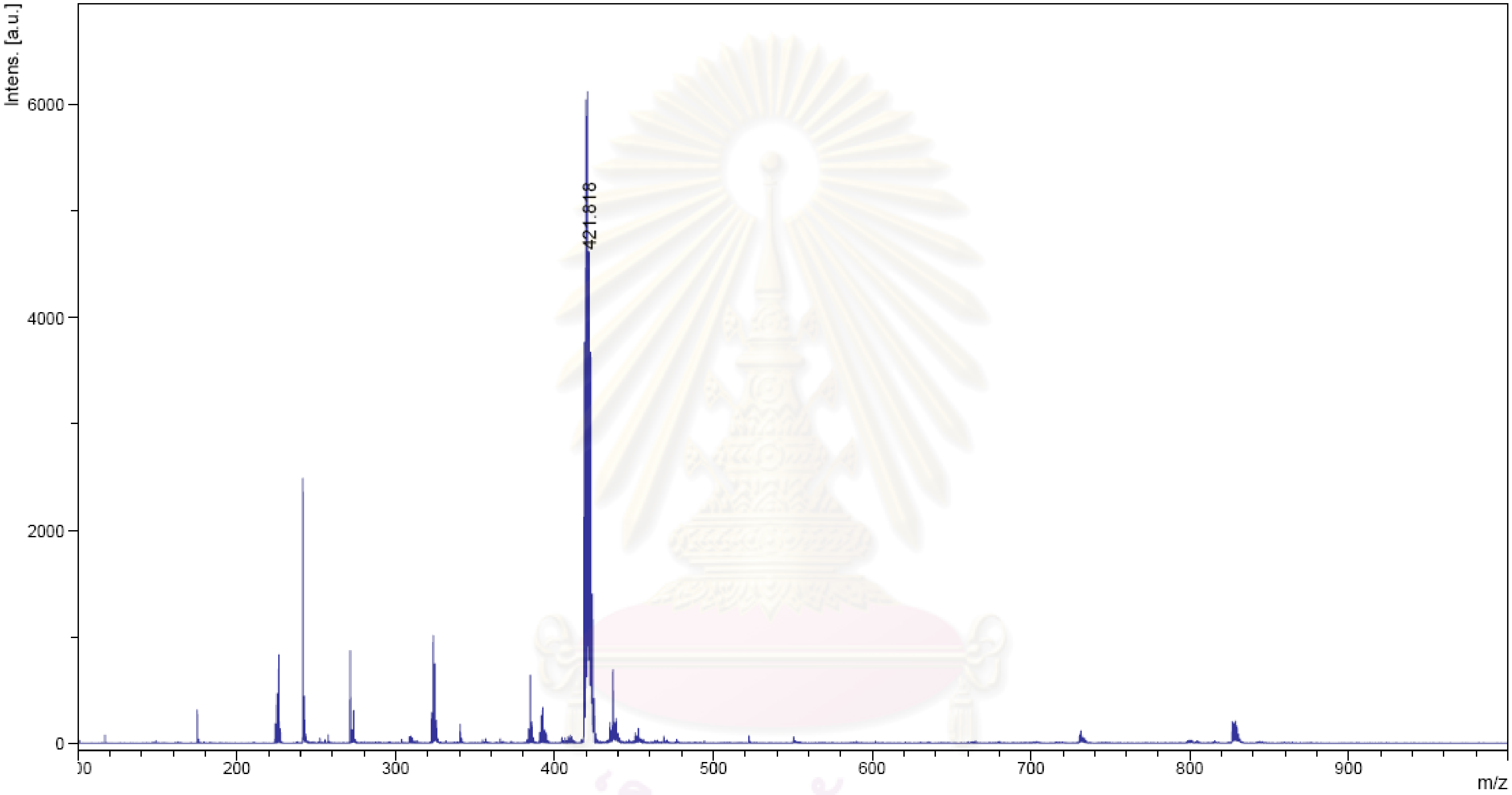

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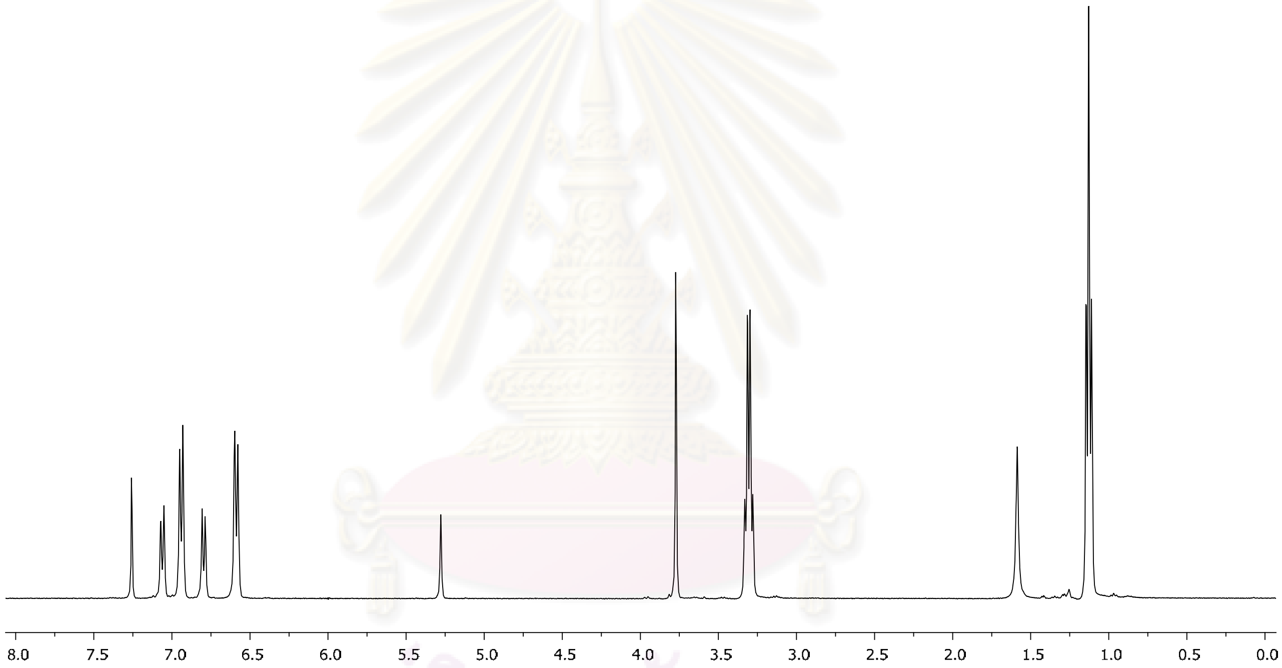

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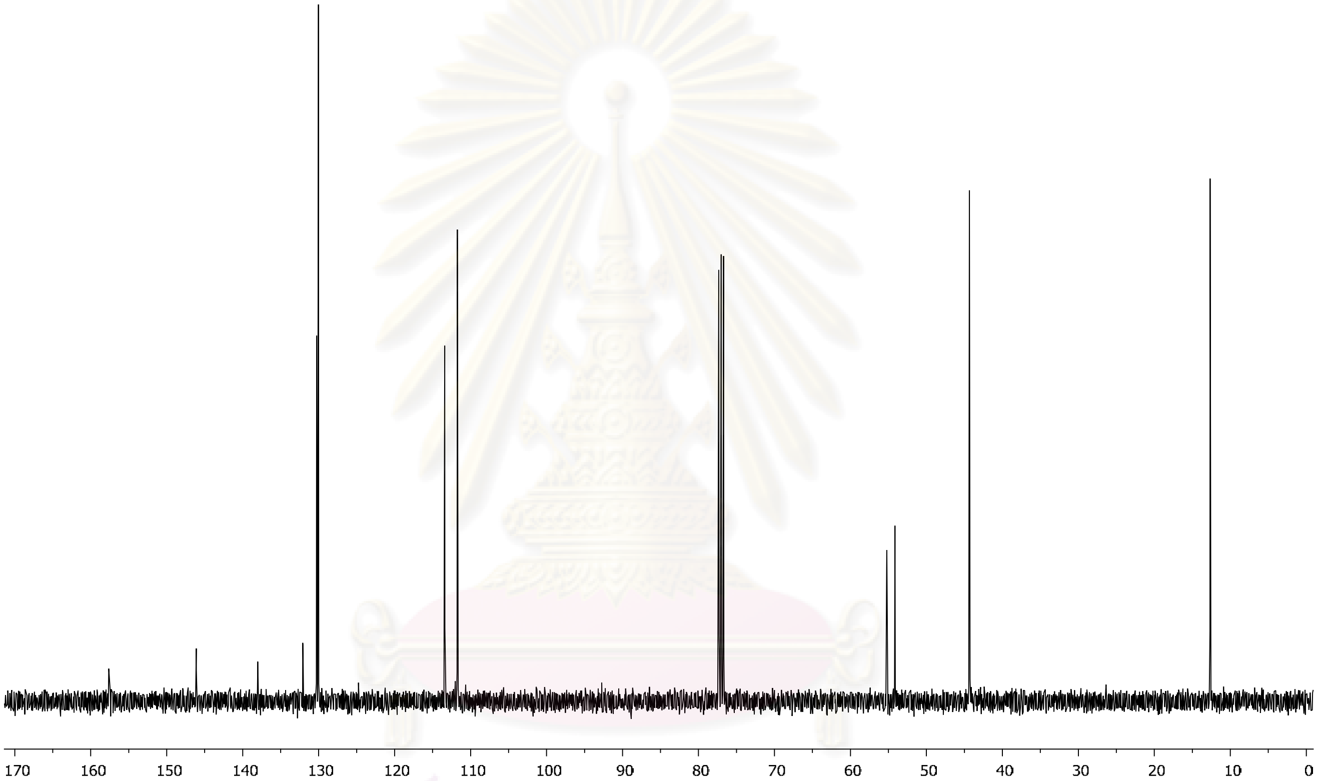

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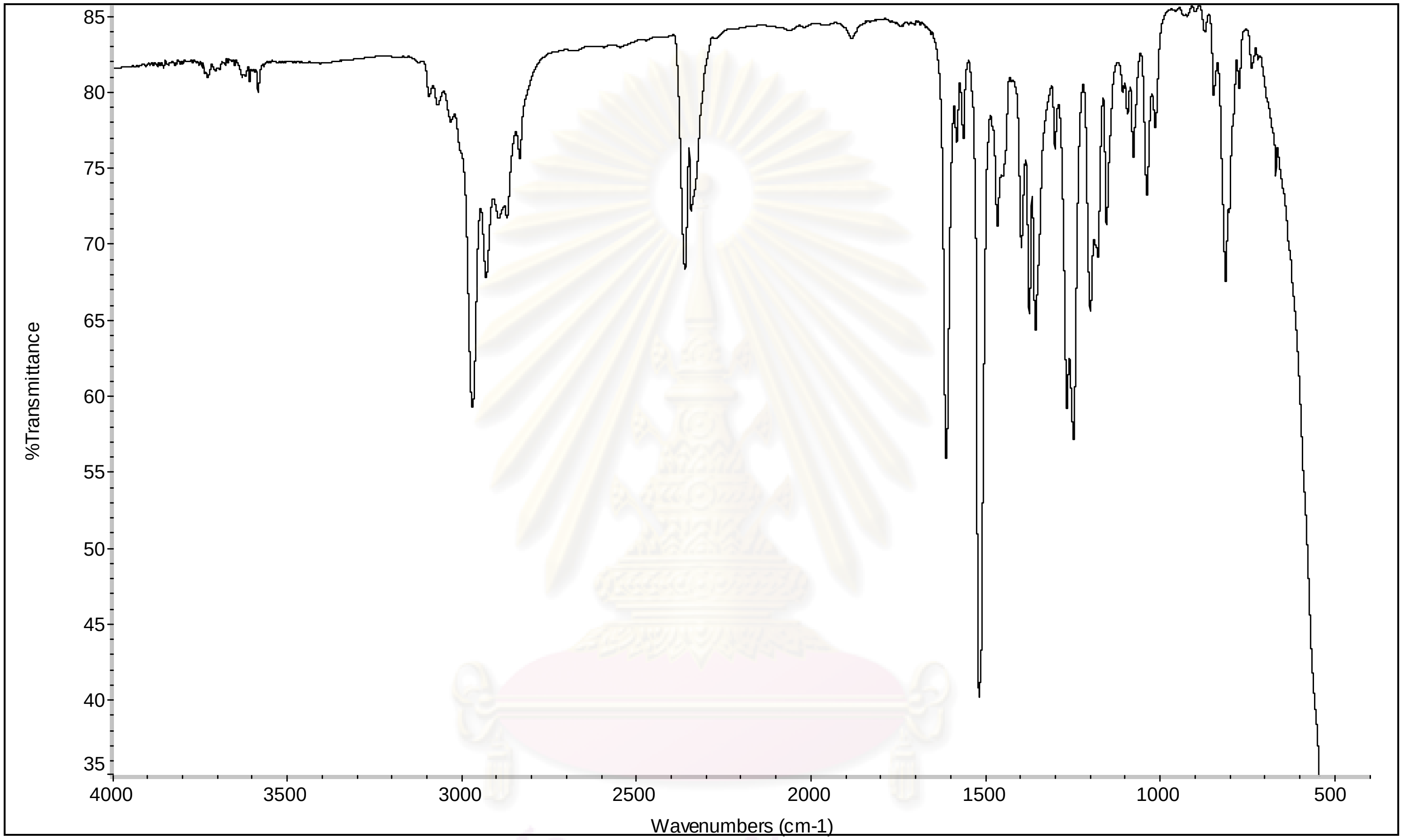

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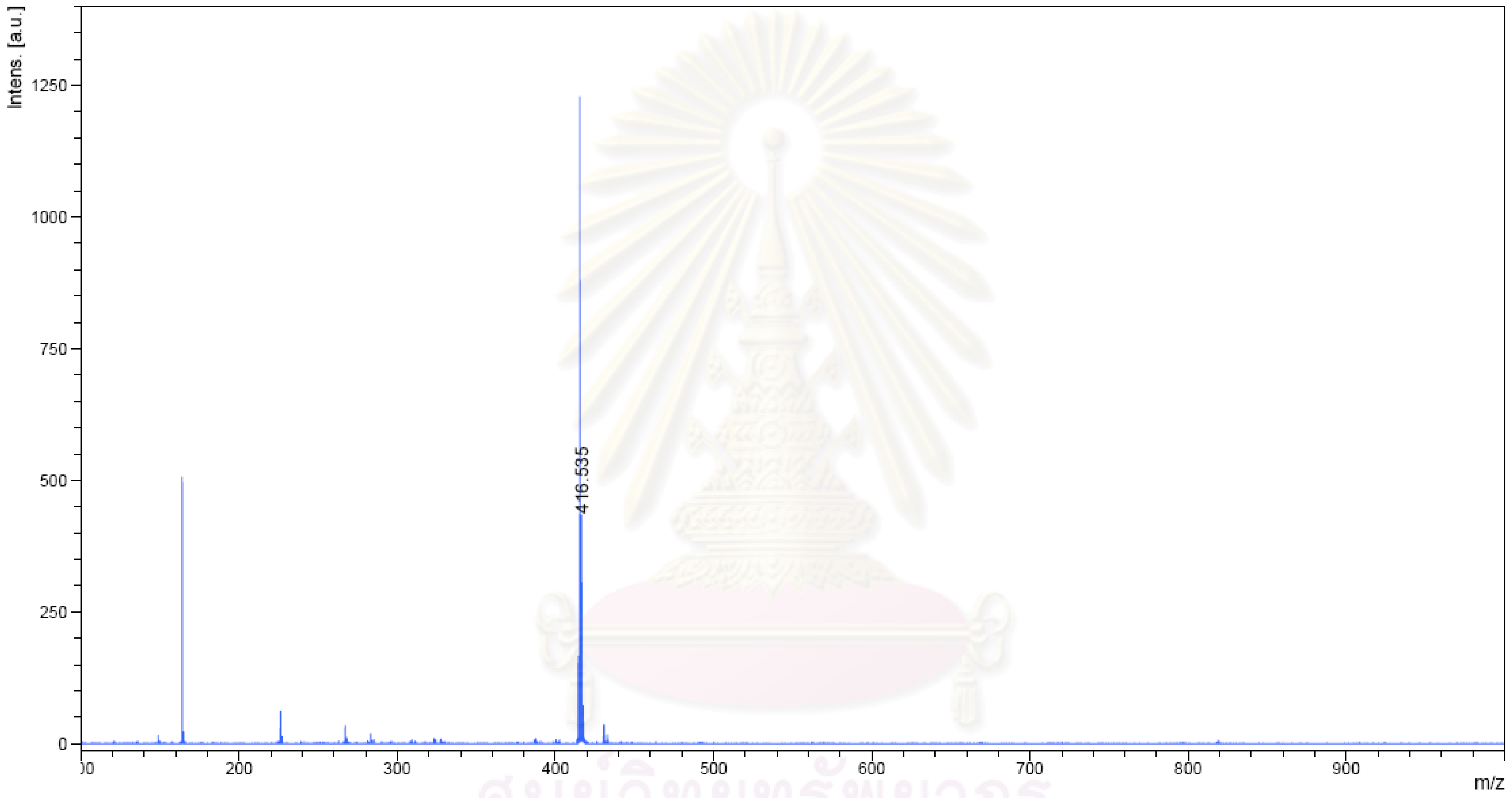

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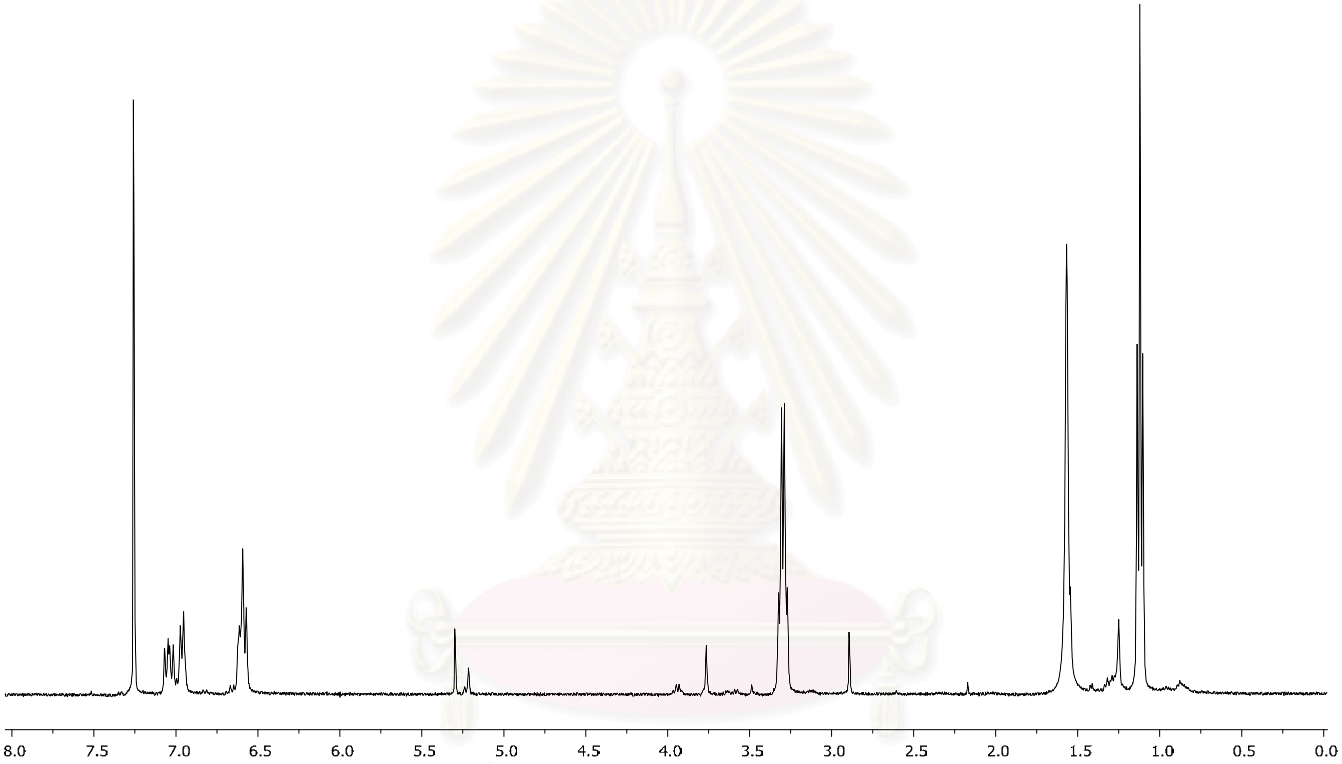

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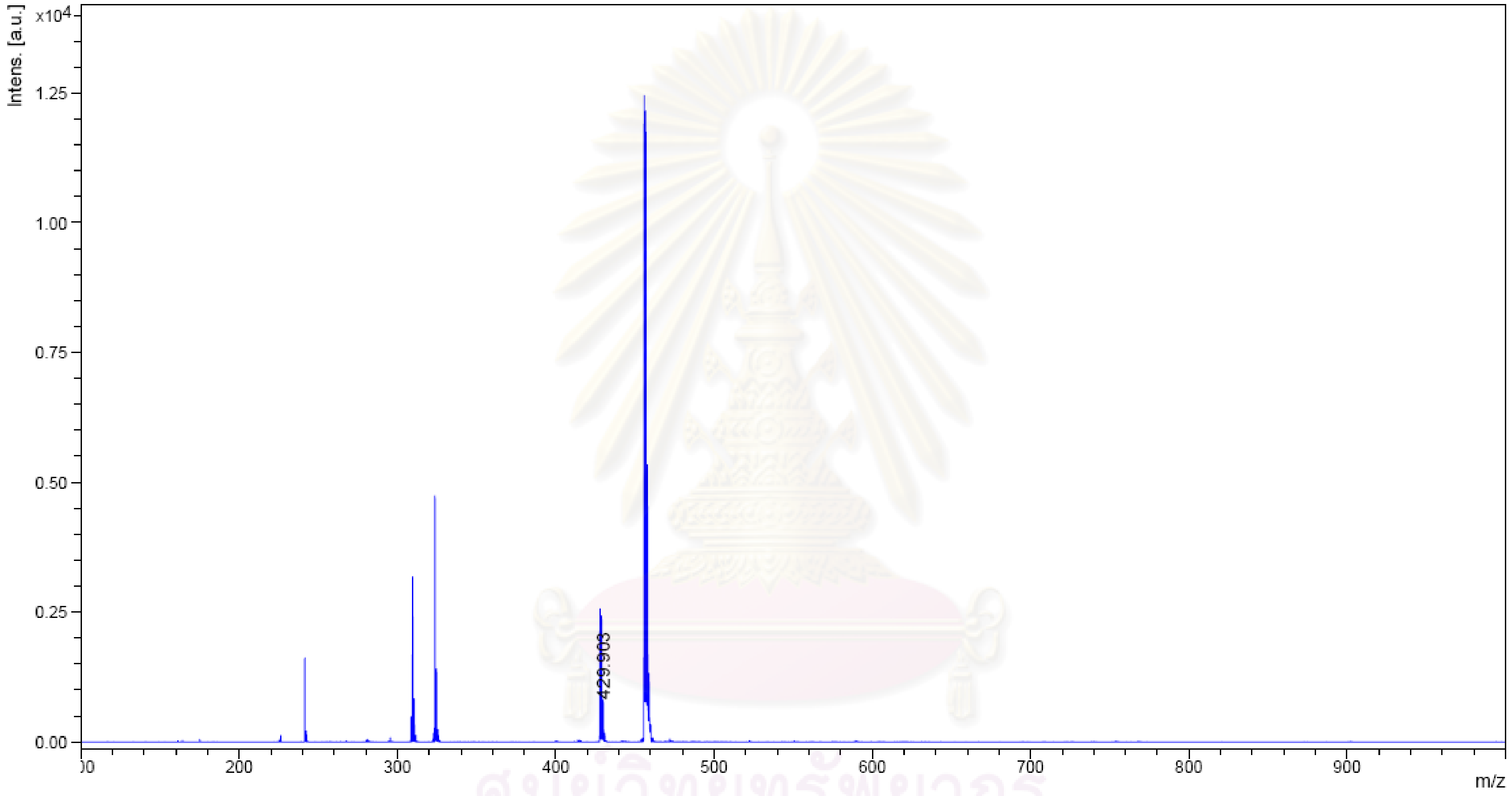

Figure A-36 Mass spectrum of Compound **8**.

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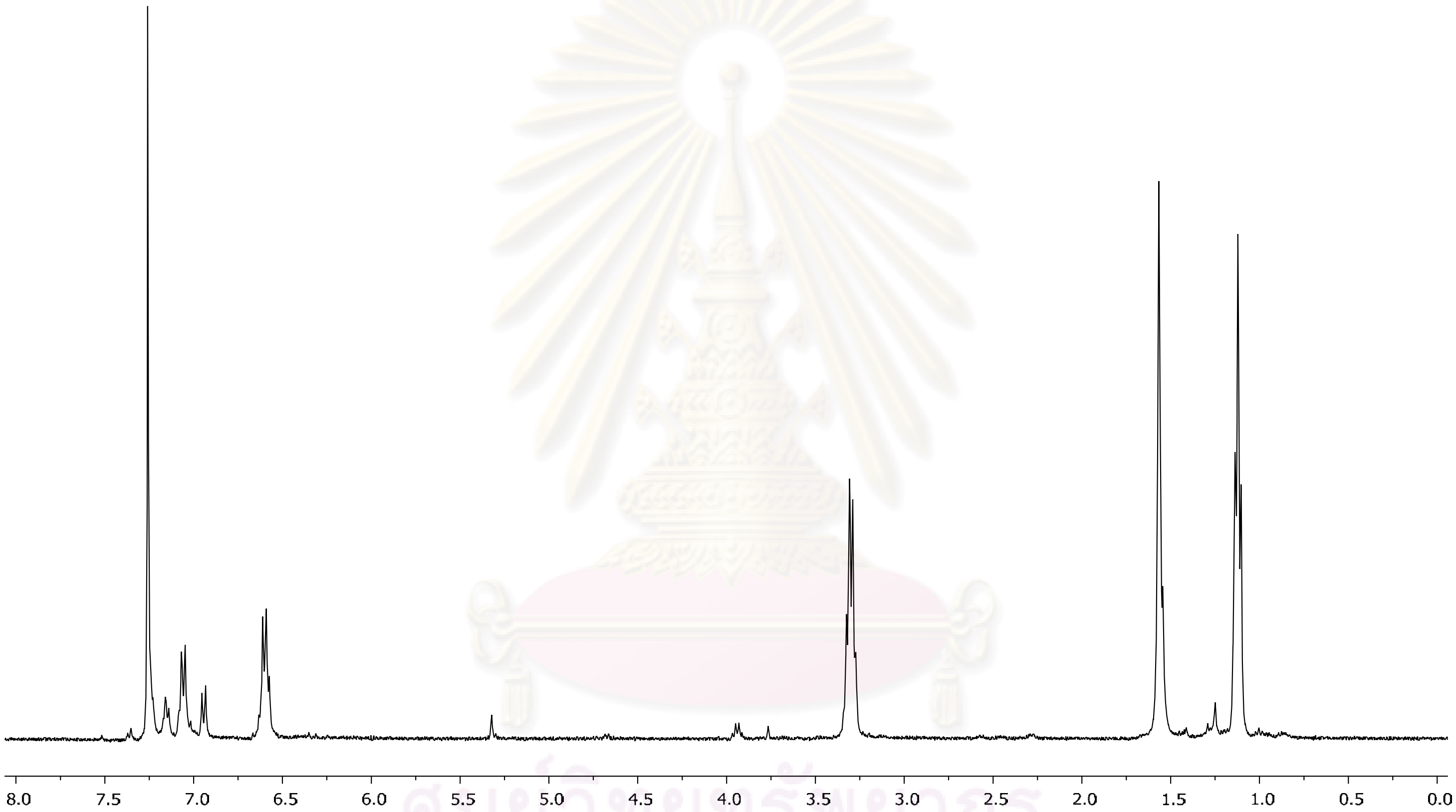

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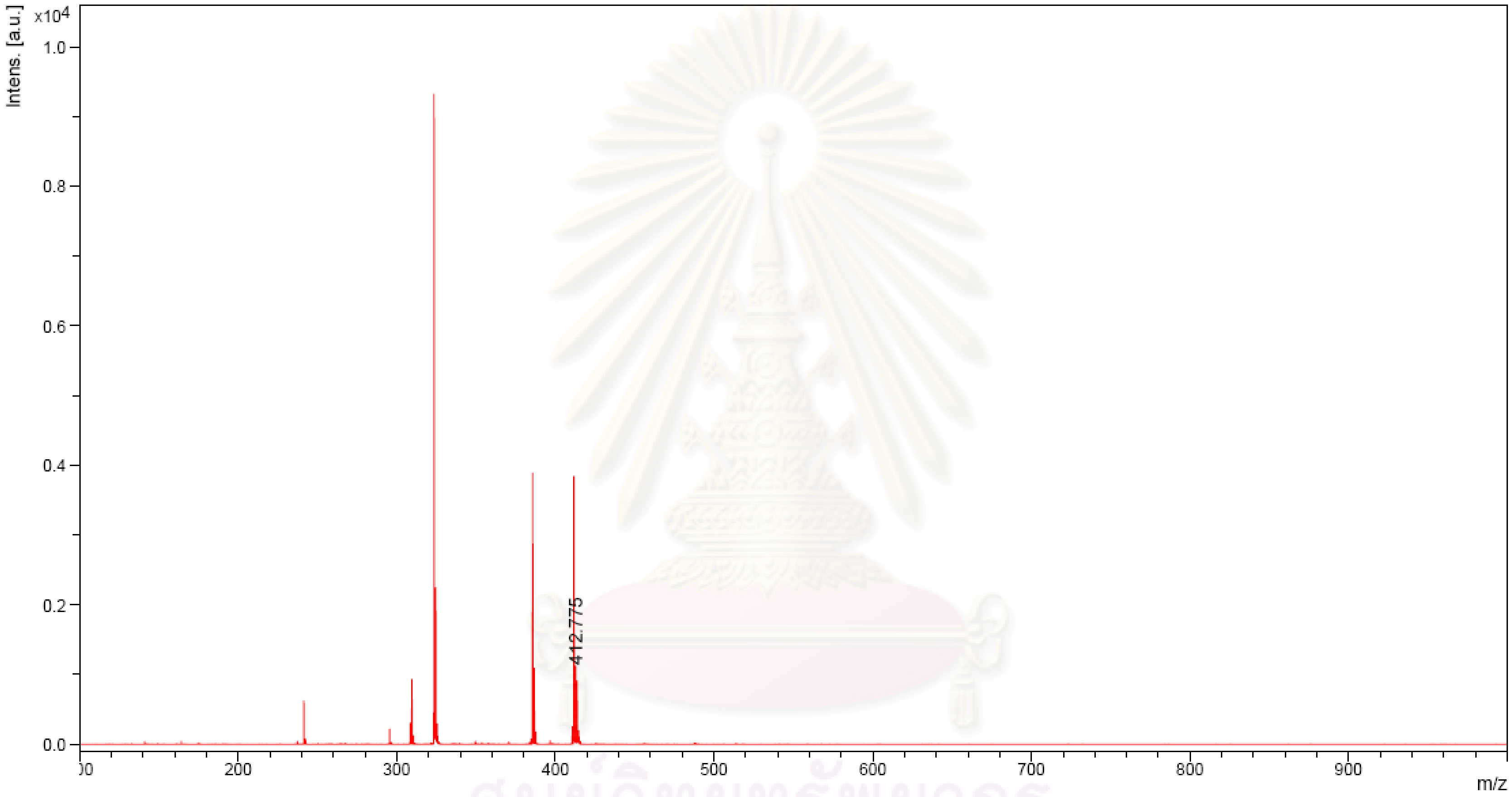

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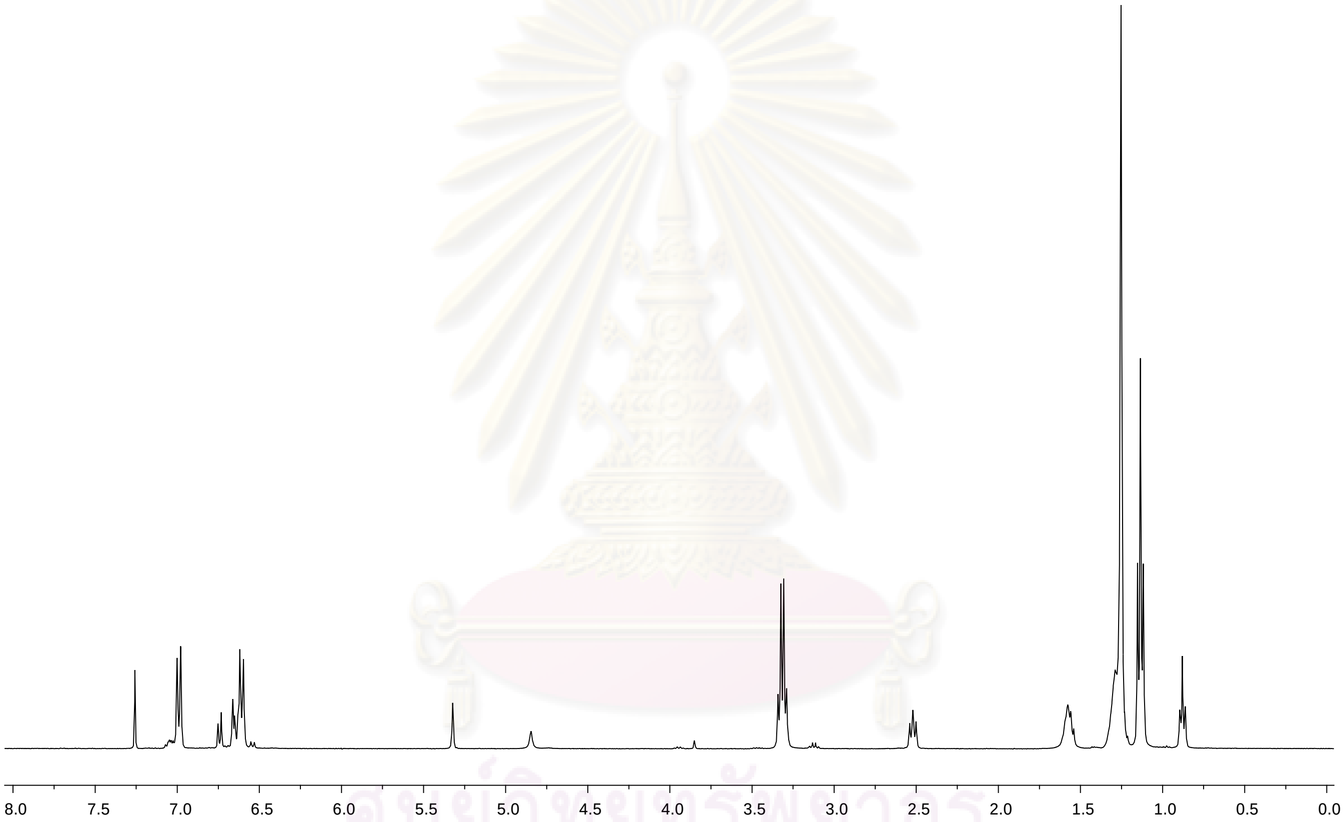

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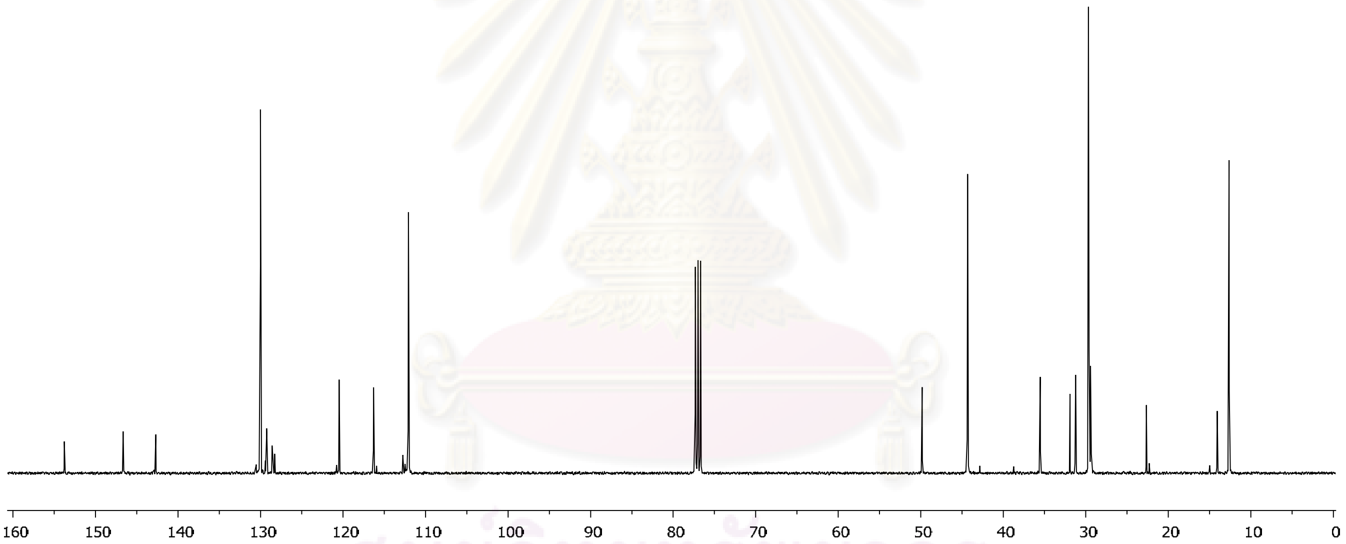

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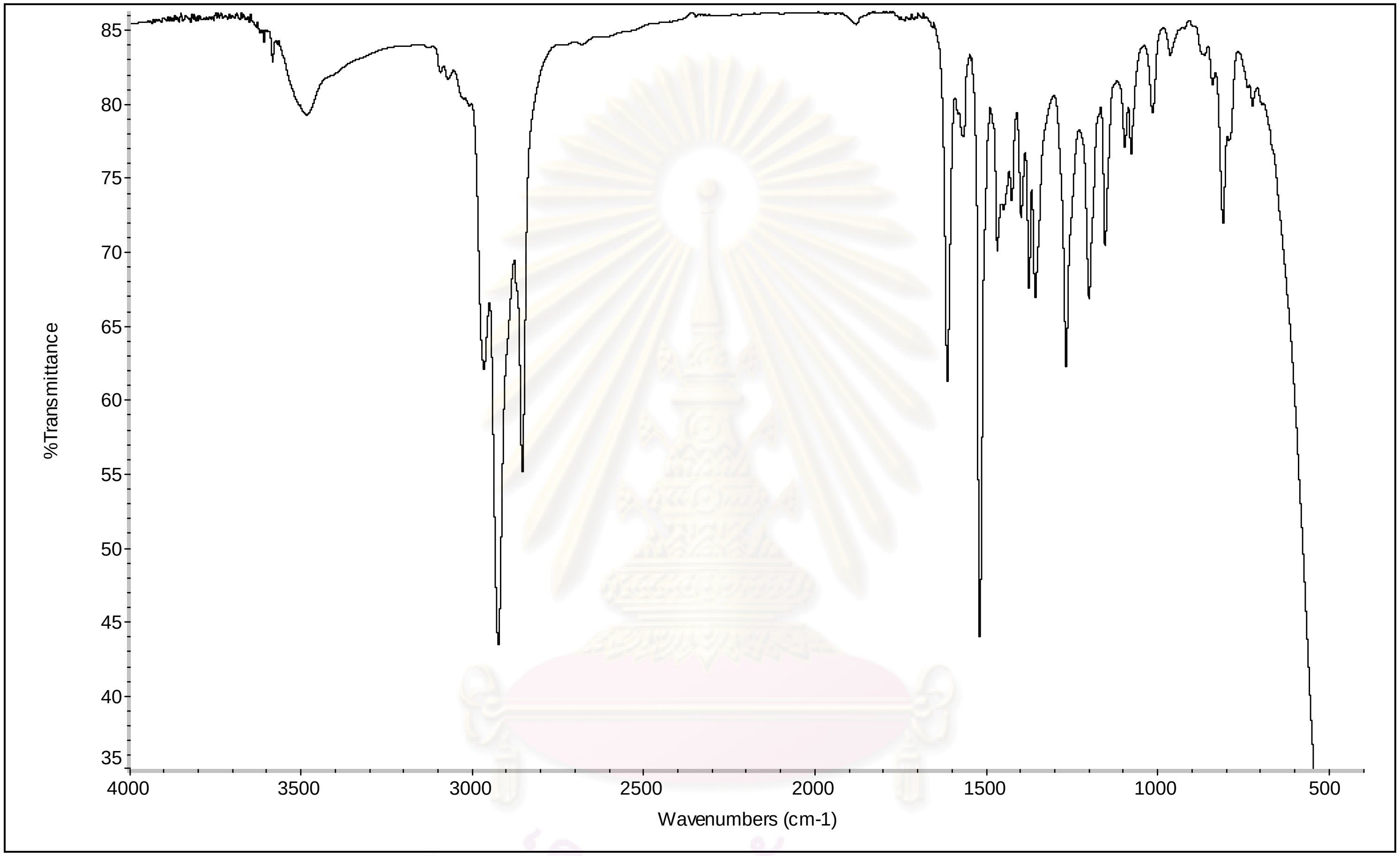

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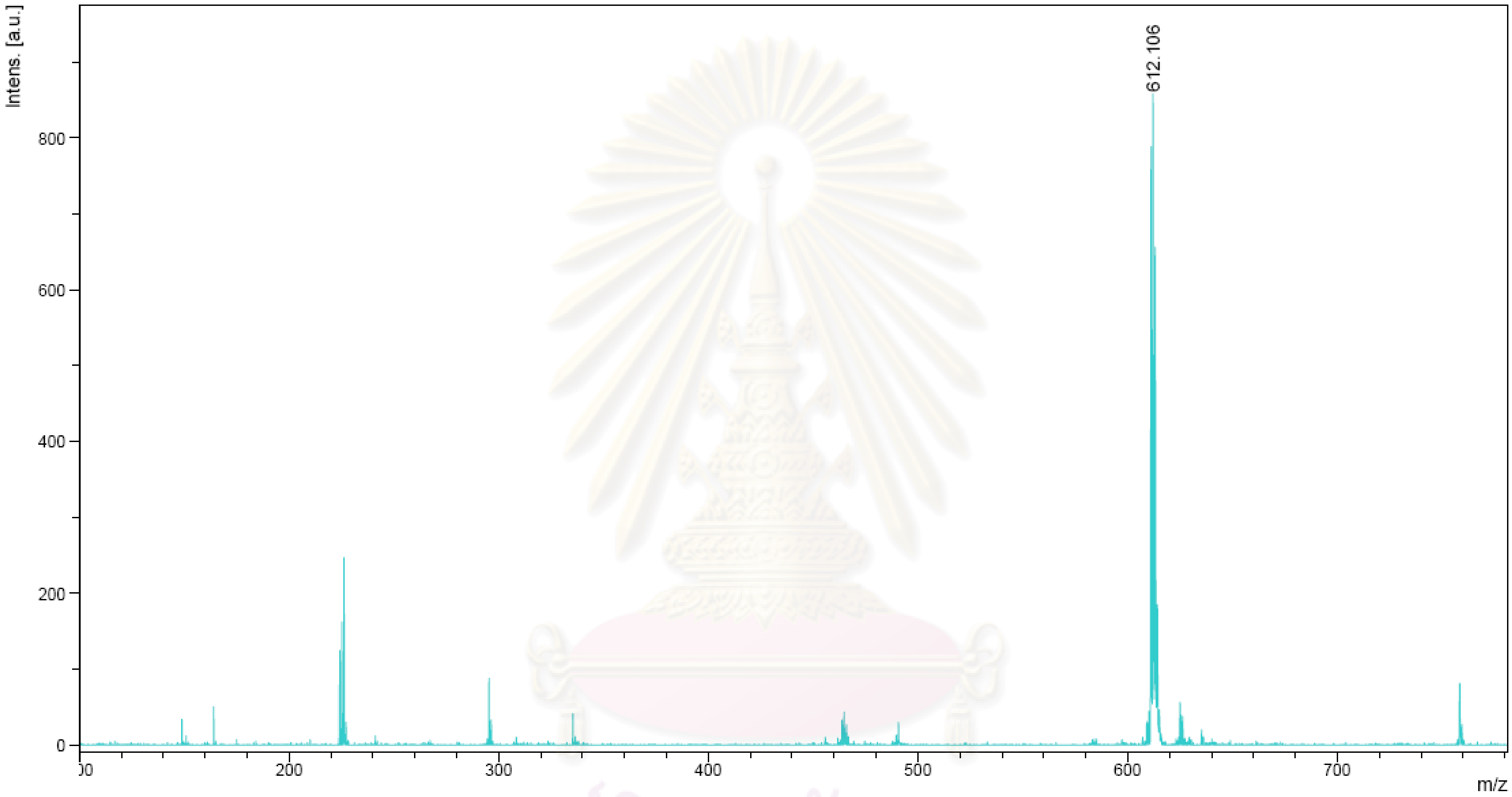

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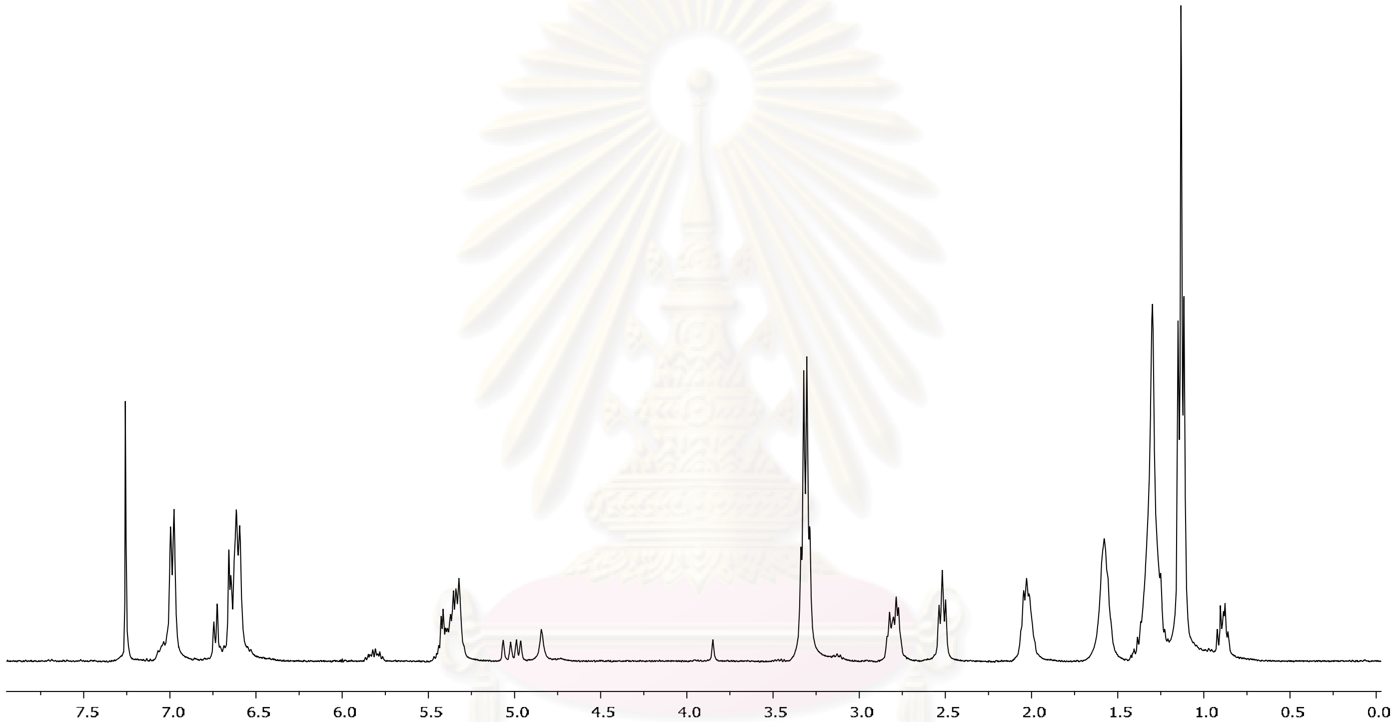

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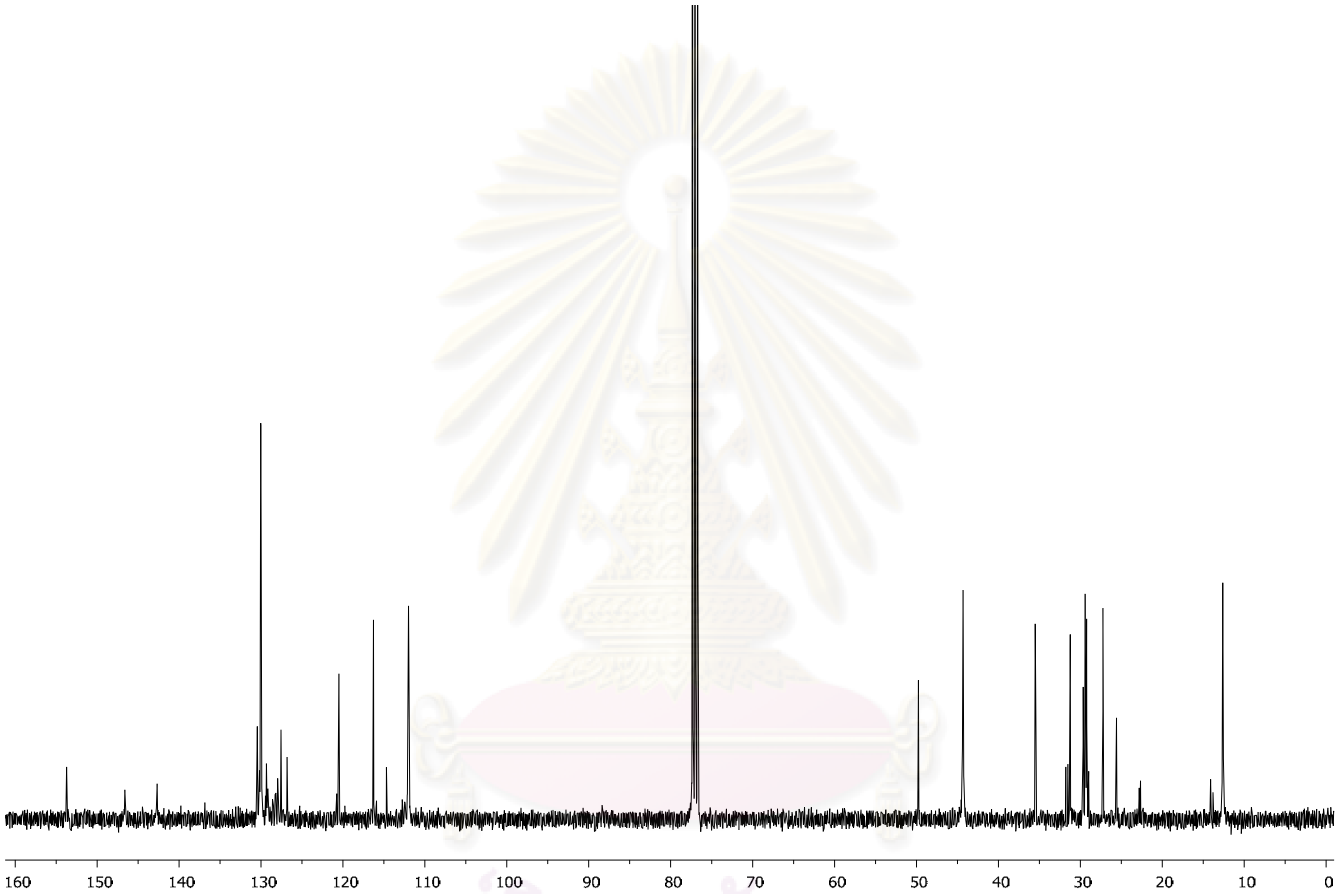

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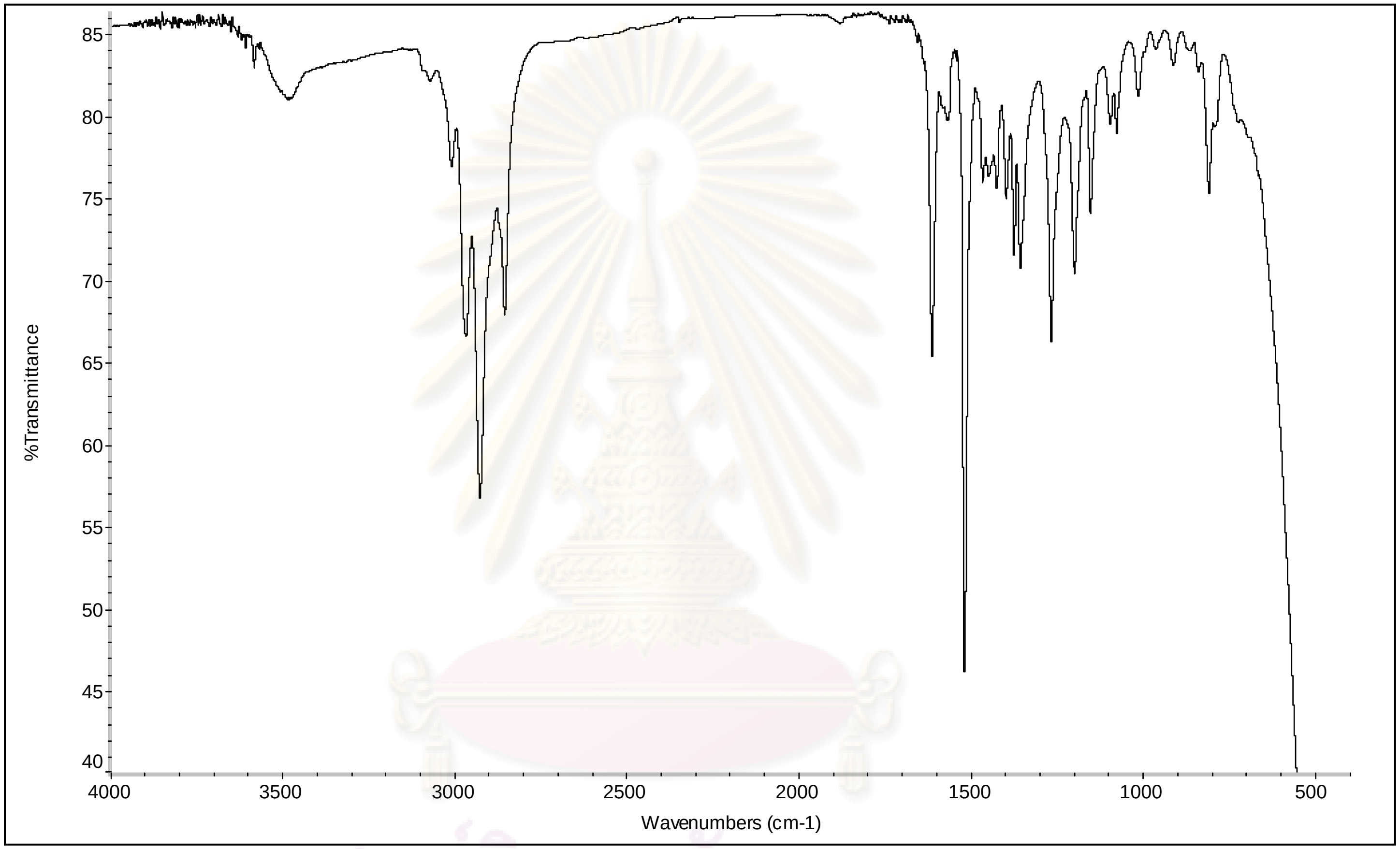

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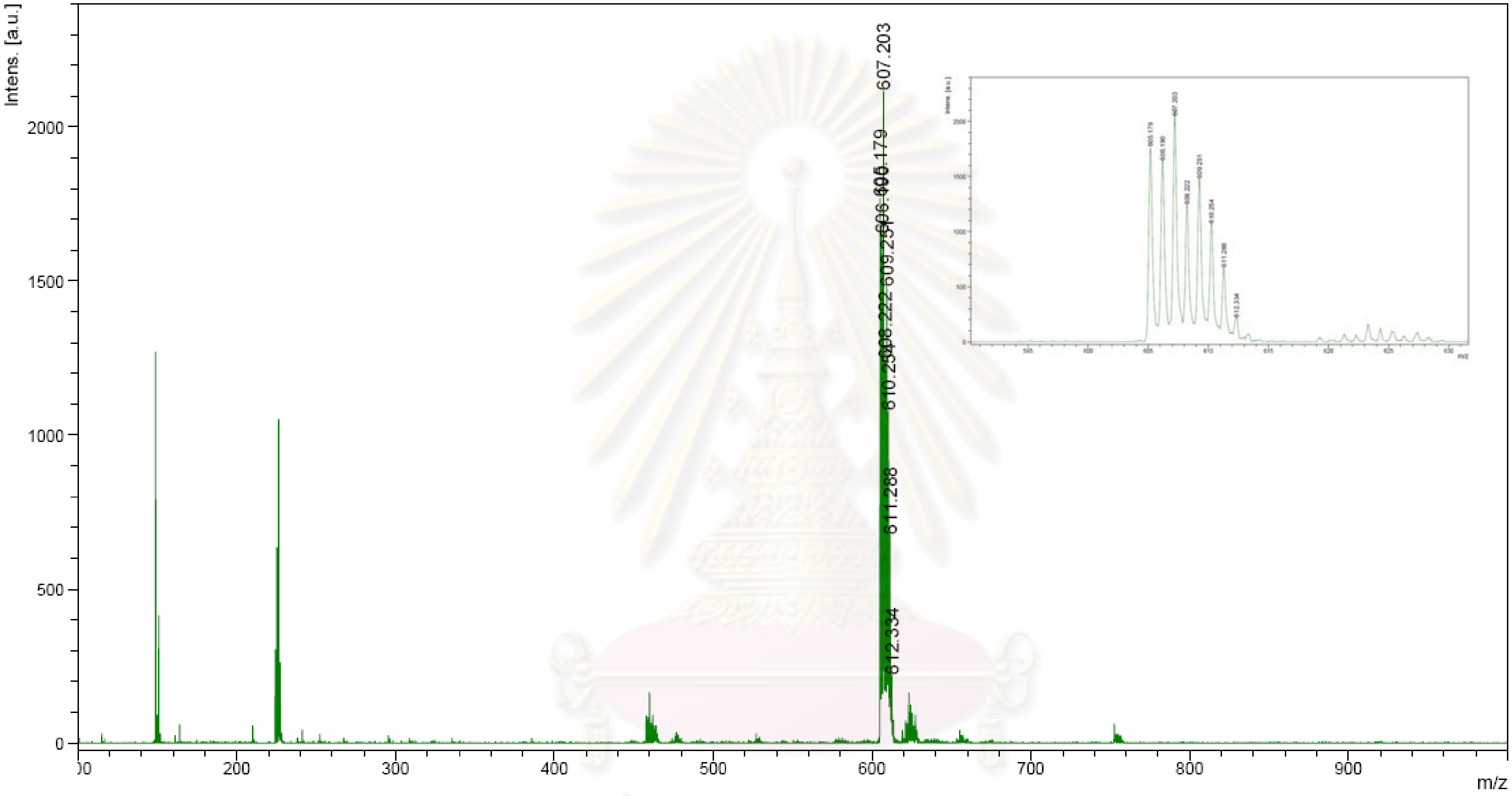

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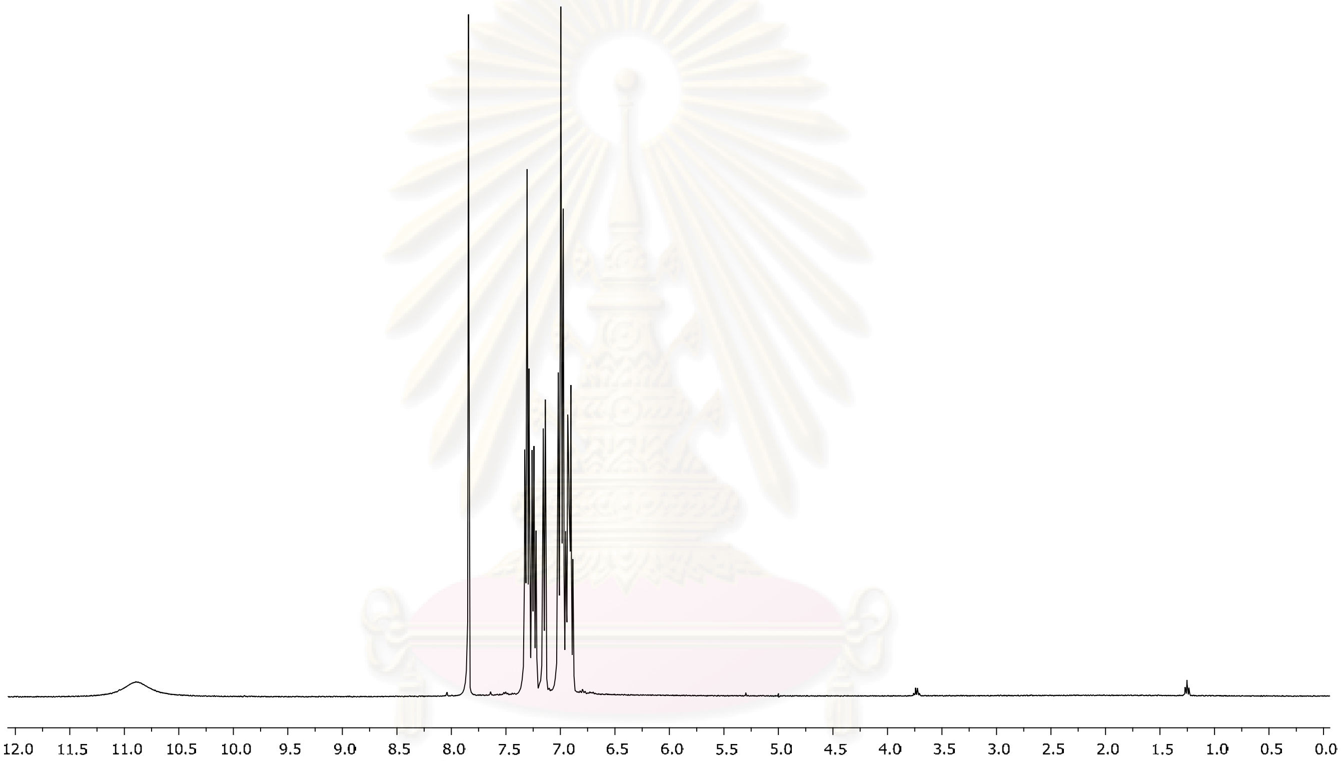

Figure A-47 ^{1}H-NMR spectrum of compound **12**.

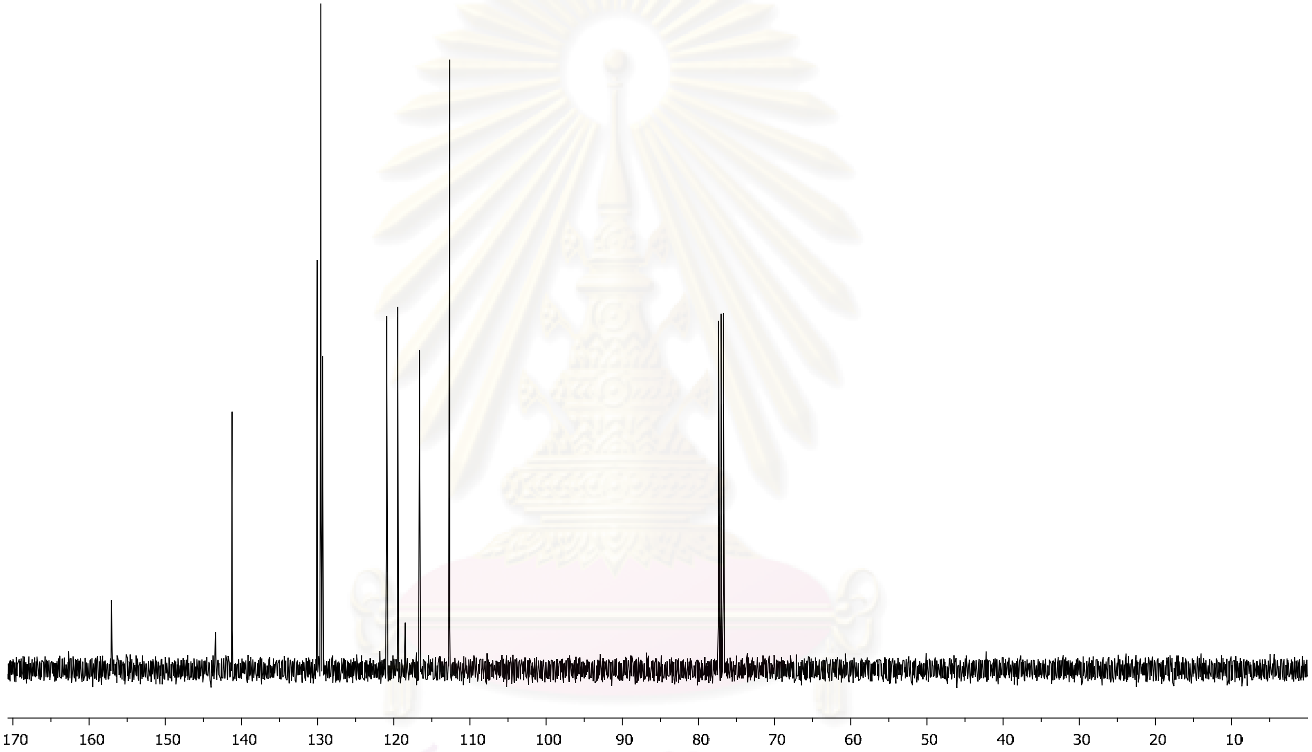

Figure A-48 ^{13}C-NMR spectrum of compound **12**.

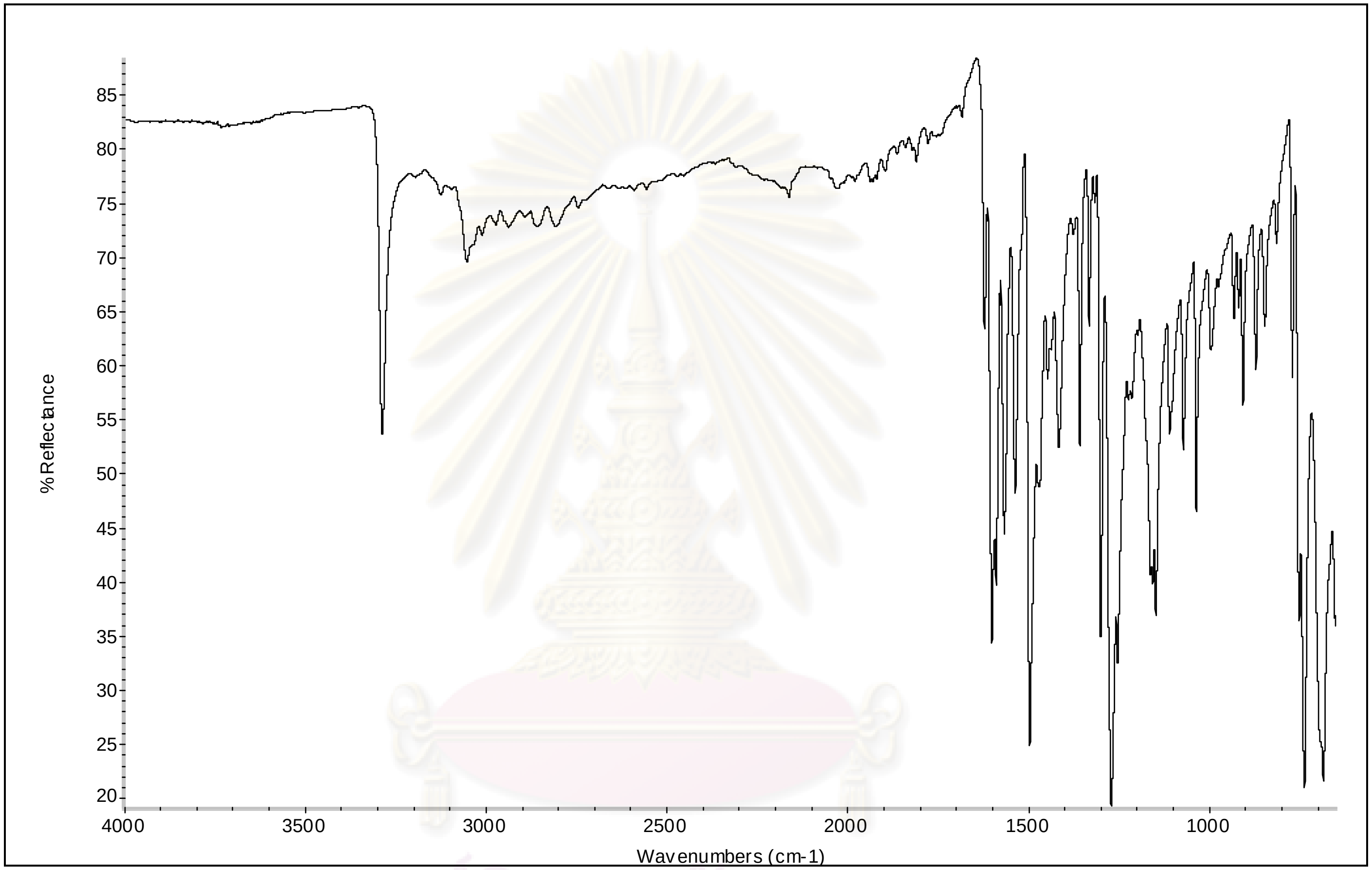

Figure A-49 IR spectrum of compound **12**.

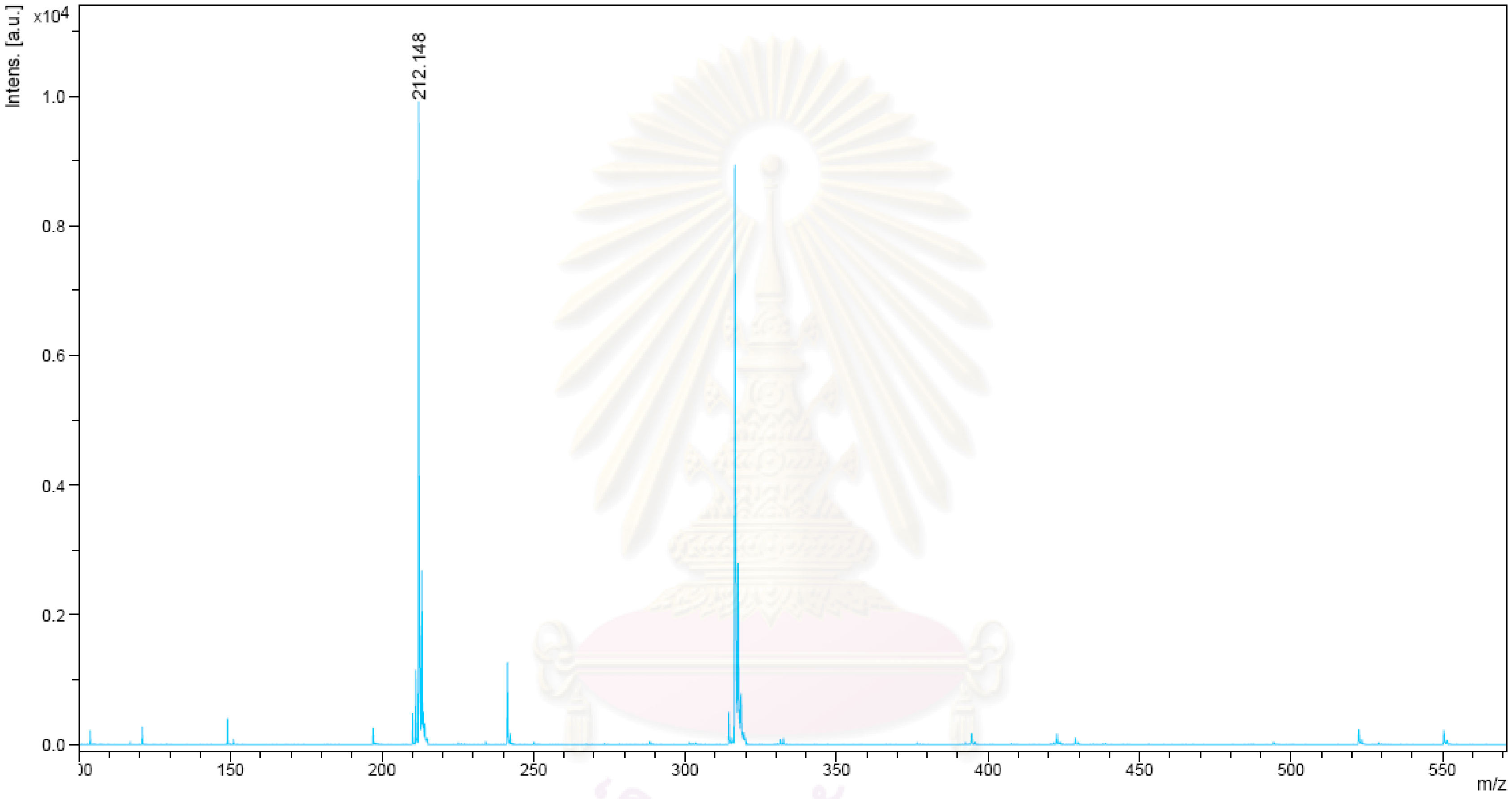

Figure A-50 Mass spectrum of compound **12**.

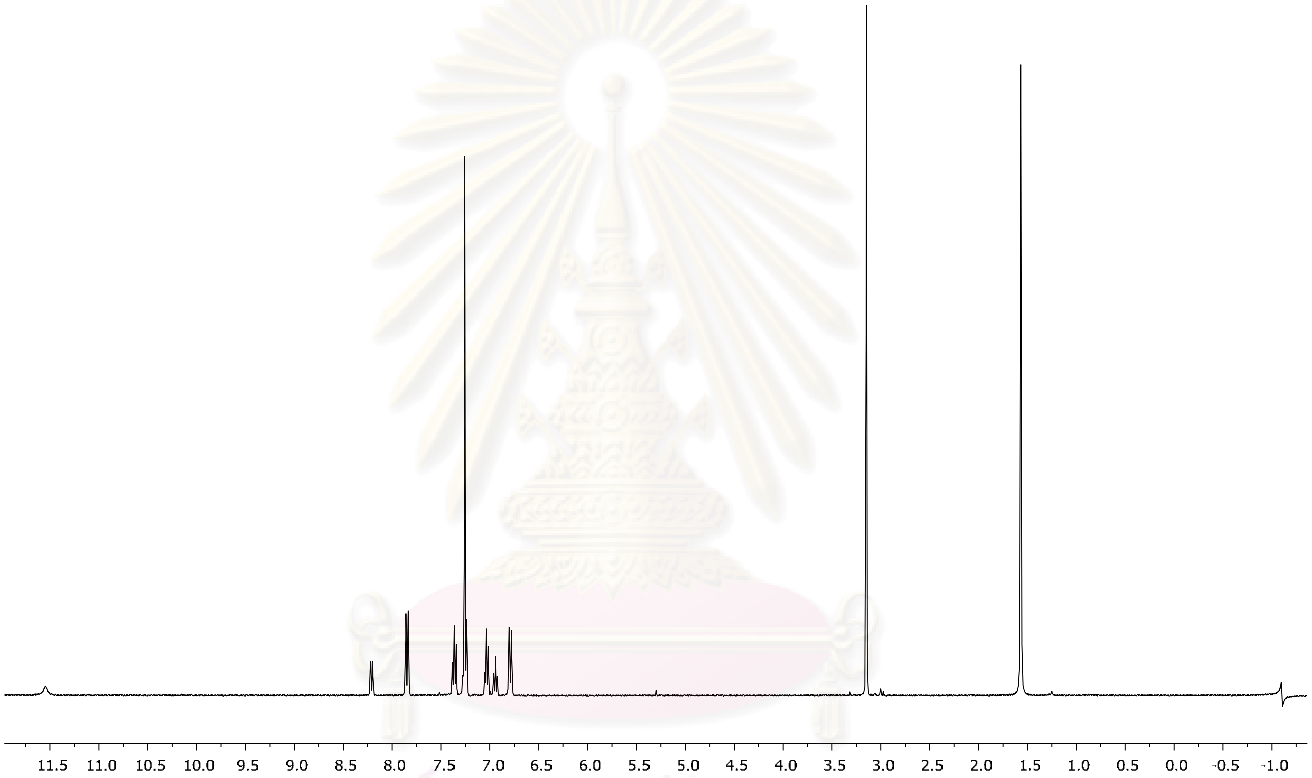

Figure A-51 ^{1}H-NMR spectrum of compound **13**.

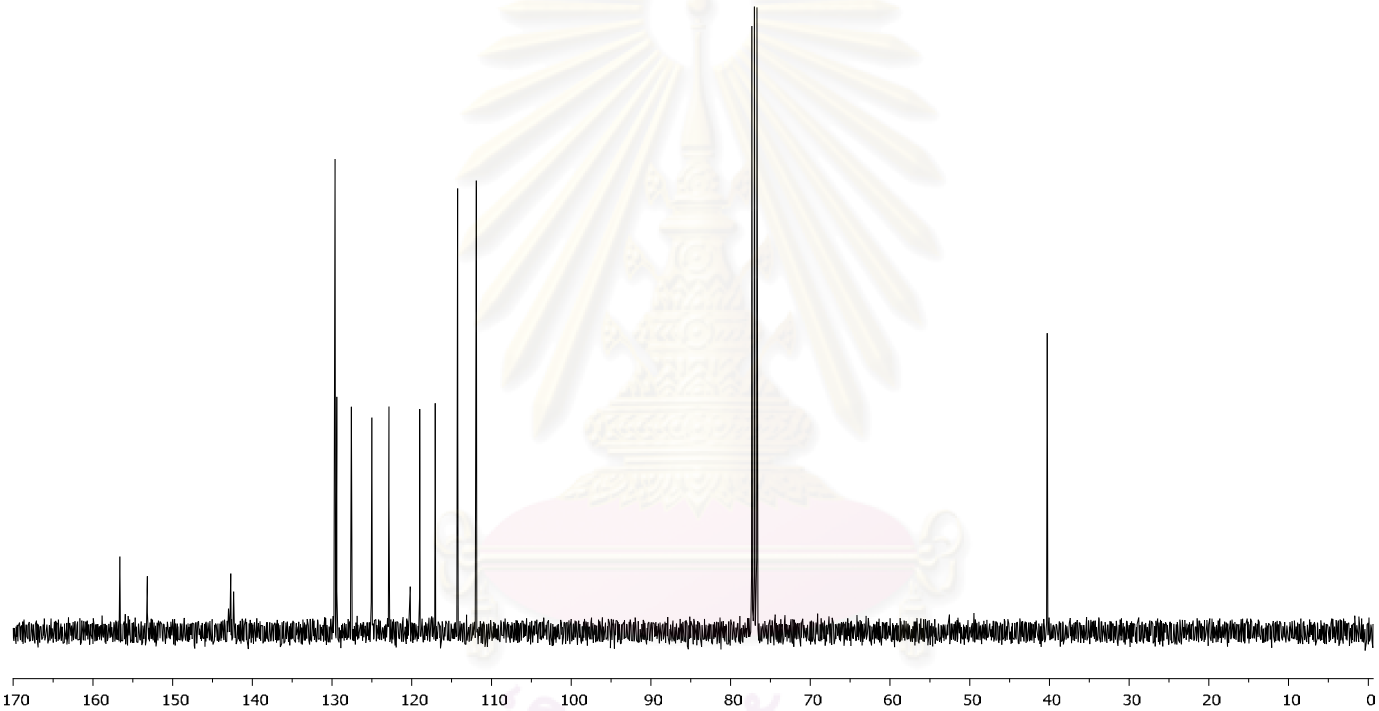

Figure A-52 ^{13}C-NMR spectrum of compound **13**.

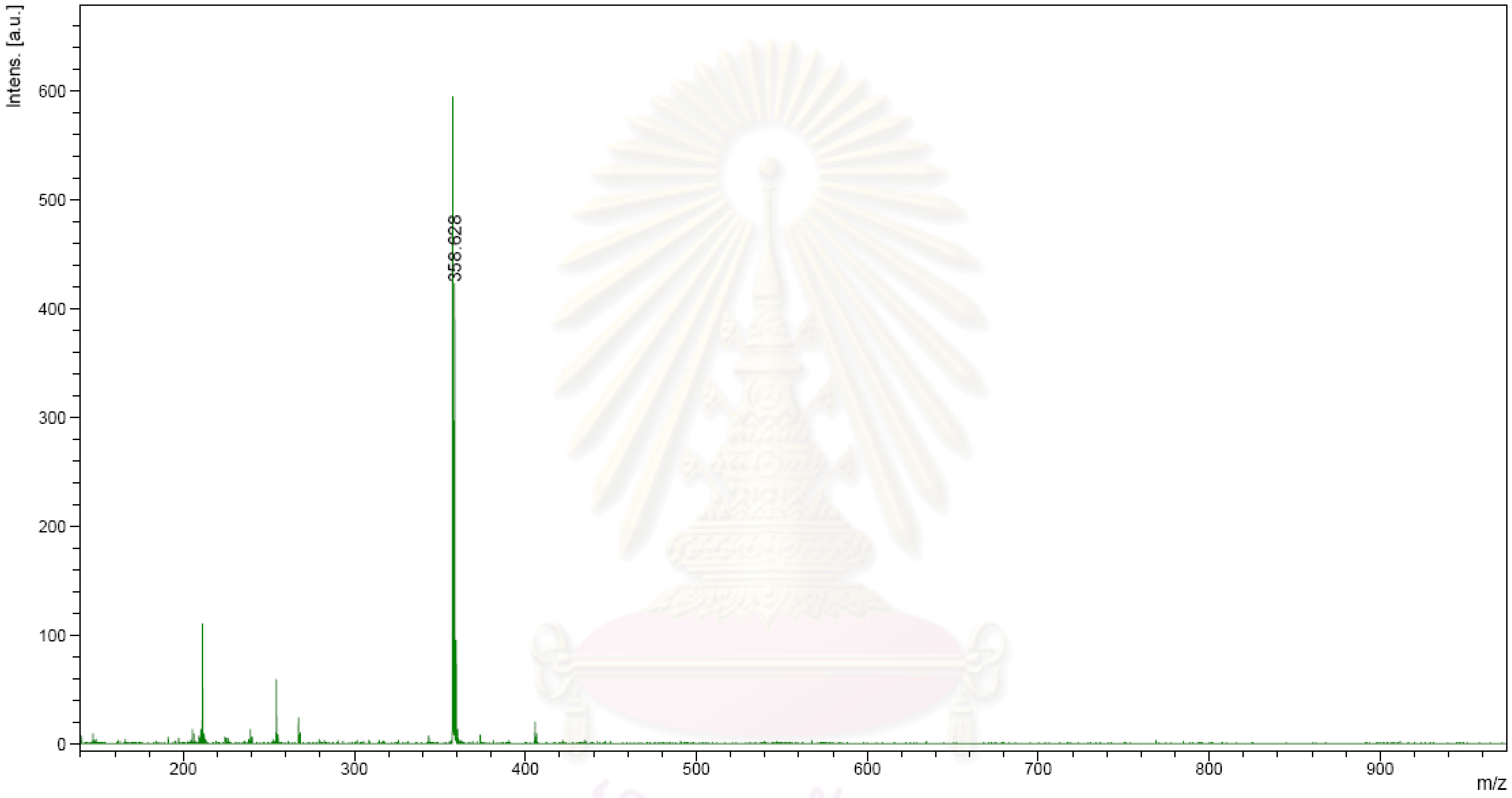

Figure A-53 Mass spectrum of compound **13**.

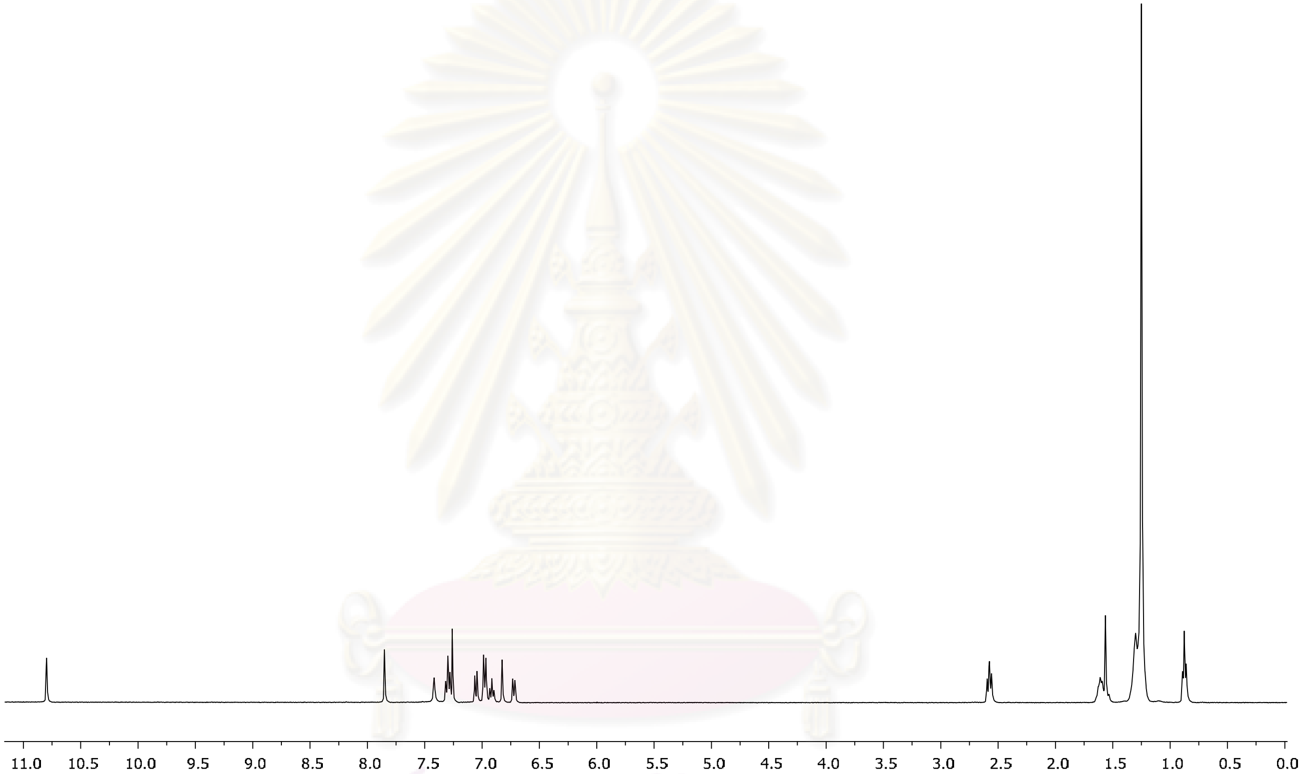

Figure A-54 ^{1}H-NMR spectrum of compound **14**.

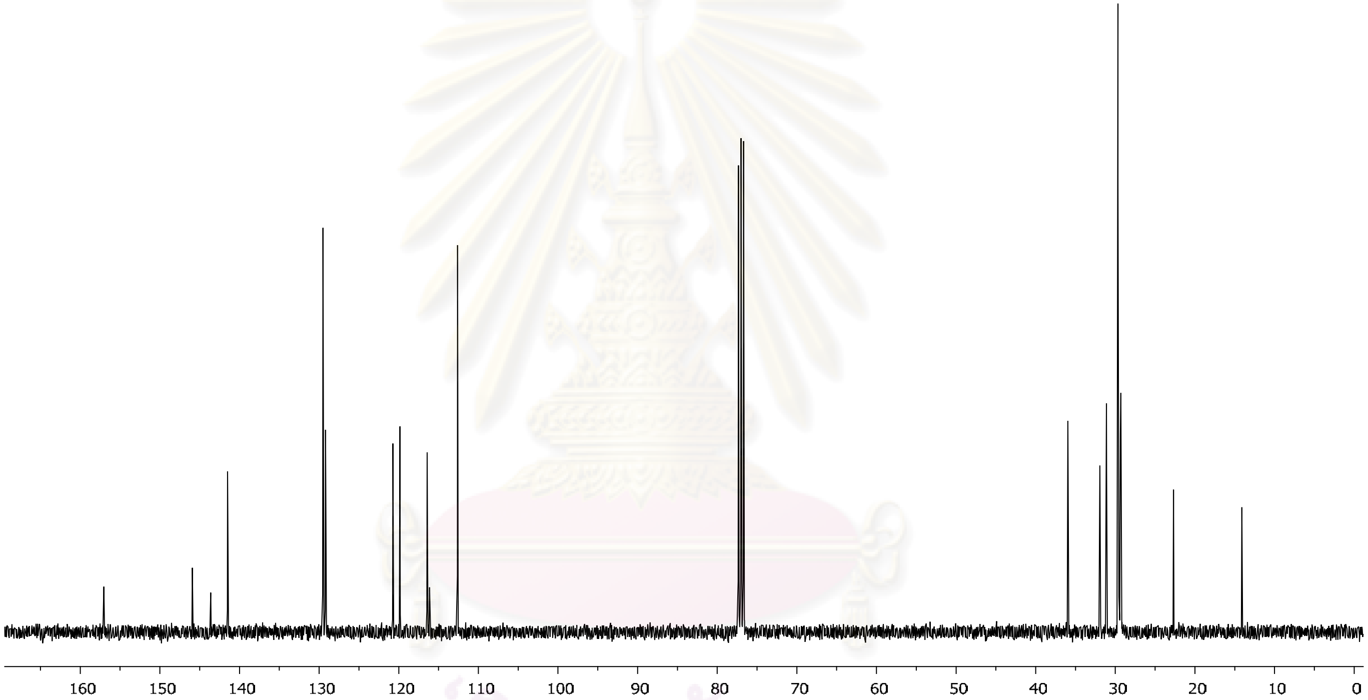

Figure A-55 ^{13}C-NMR spectrum compound **14**.

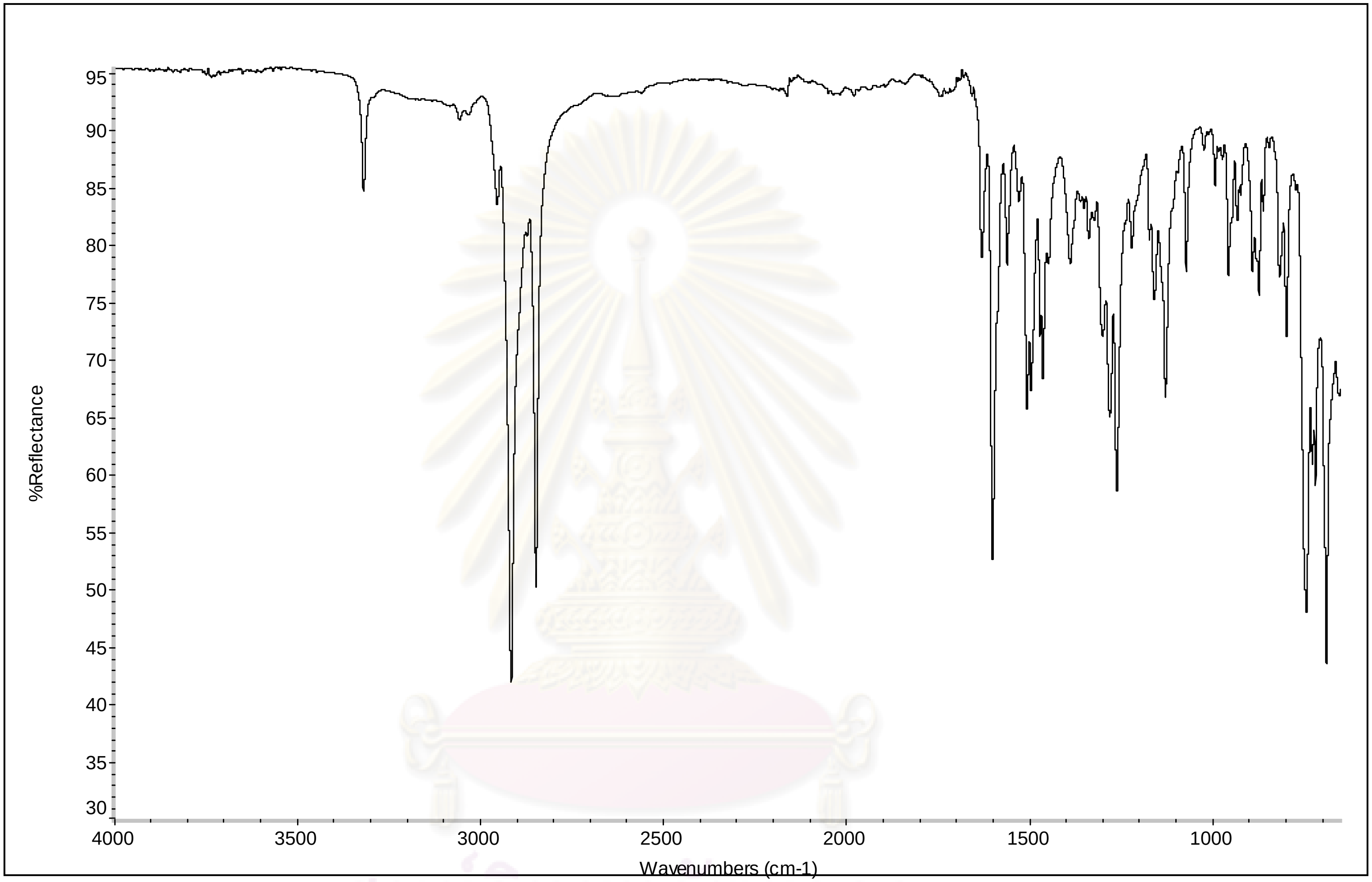

Figure **A-56** IR spectrum of compound **14**.

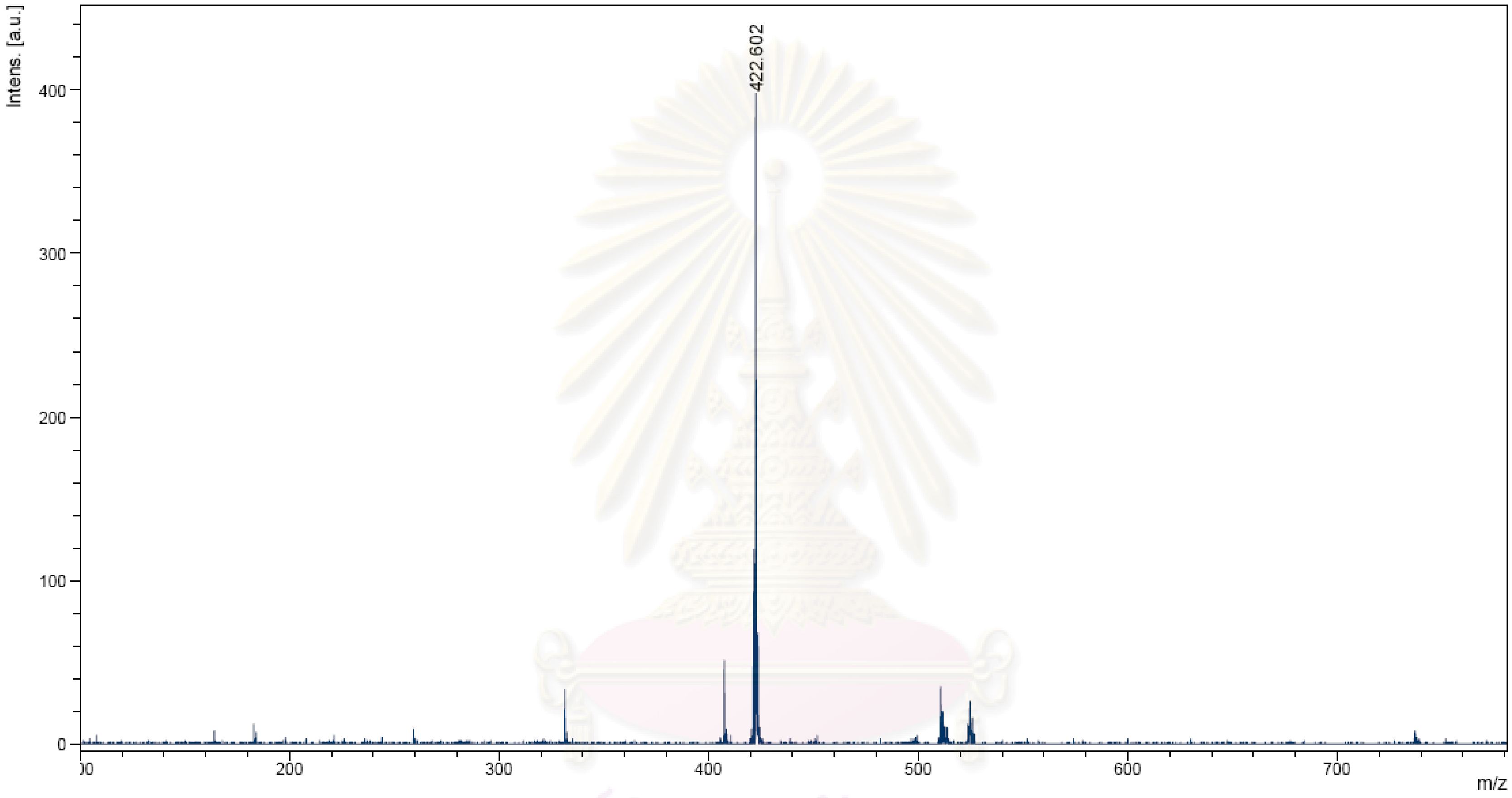

Figure A-57 Mass spectrum of compound **14.**

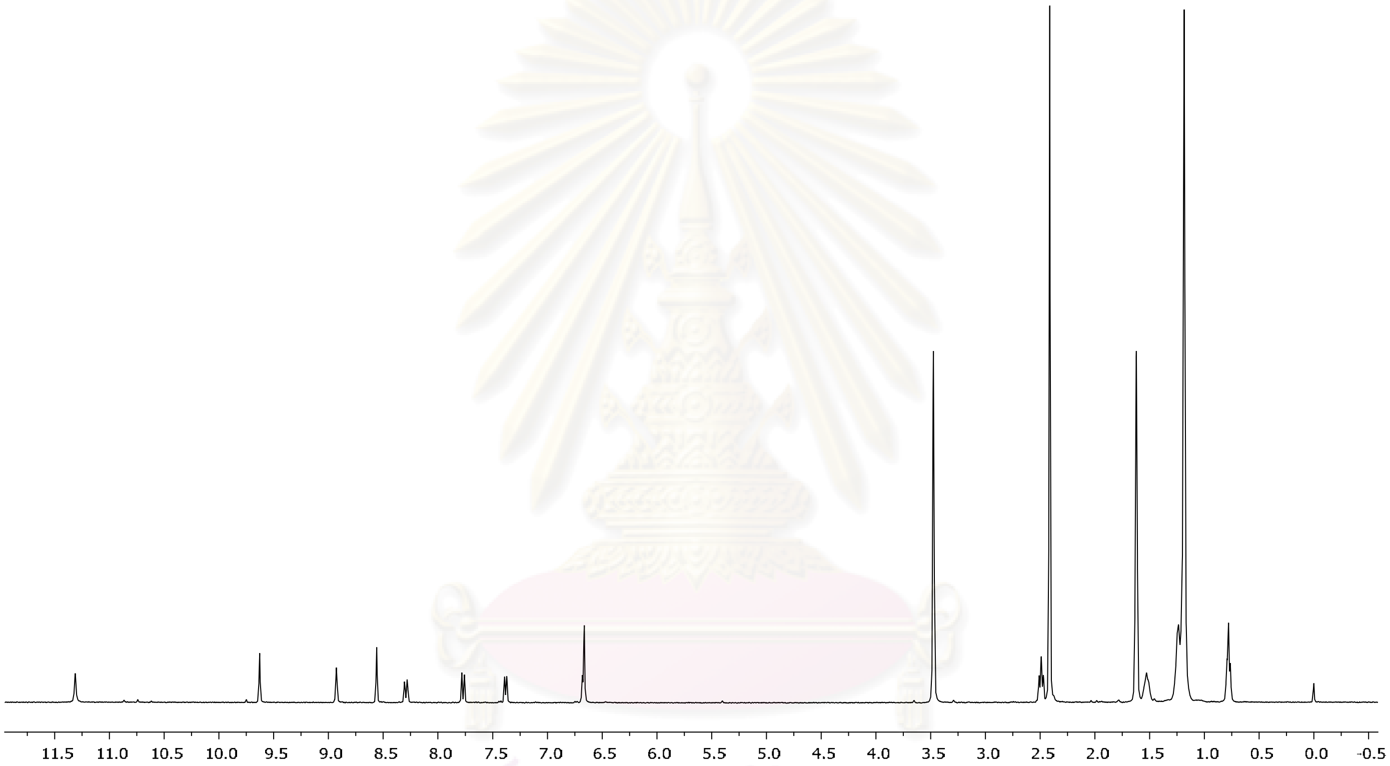

Figure A-58 ^{1}H-NMR spectrum of compound **15**.

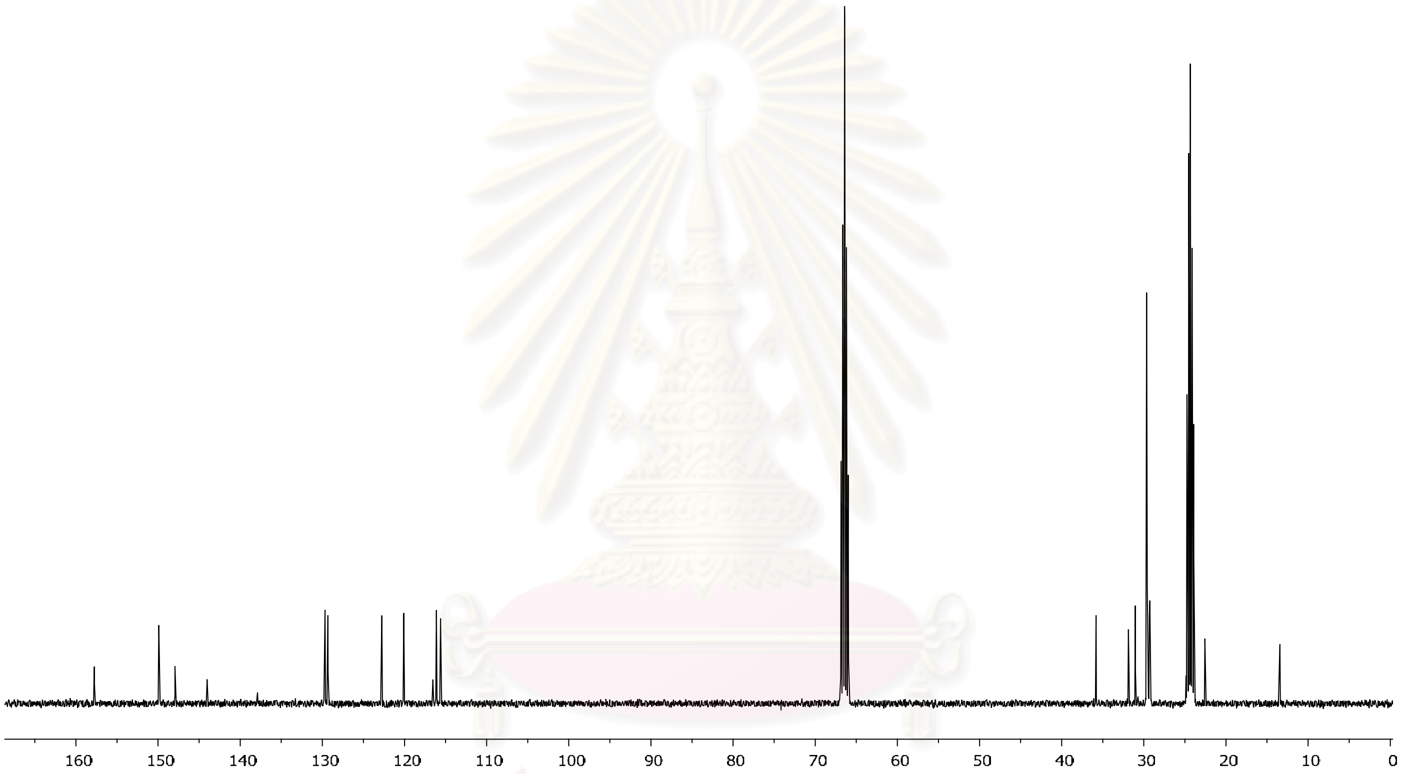

Figure A-59 ^{13}C-NMR spectrum of compound **15.**

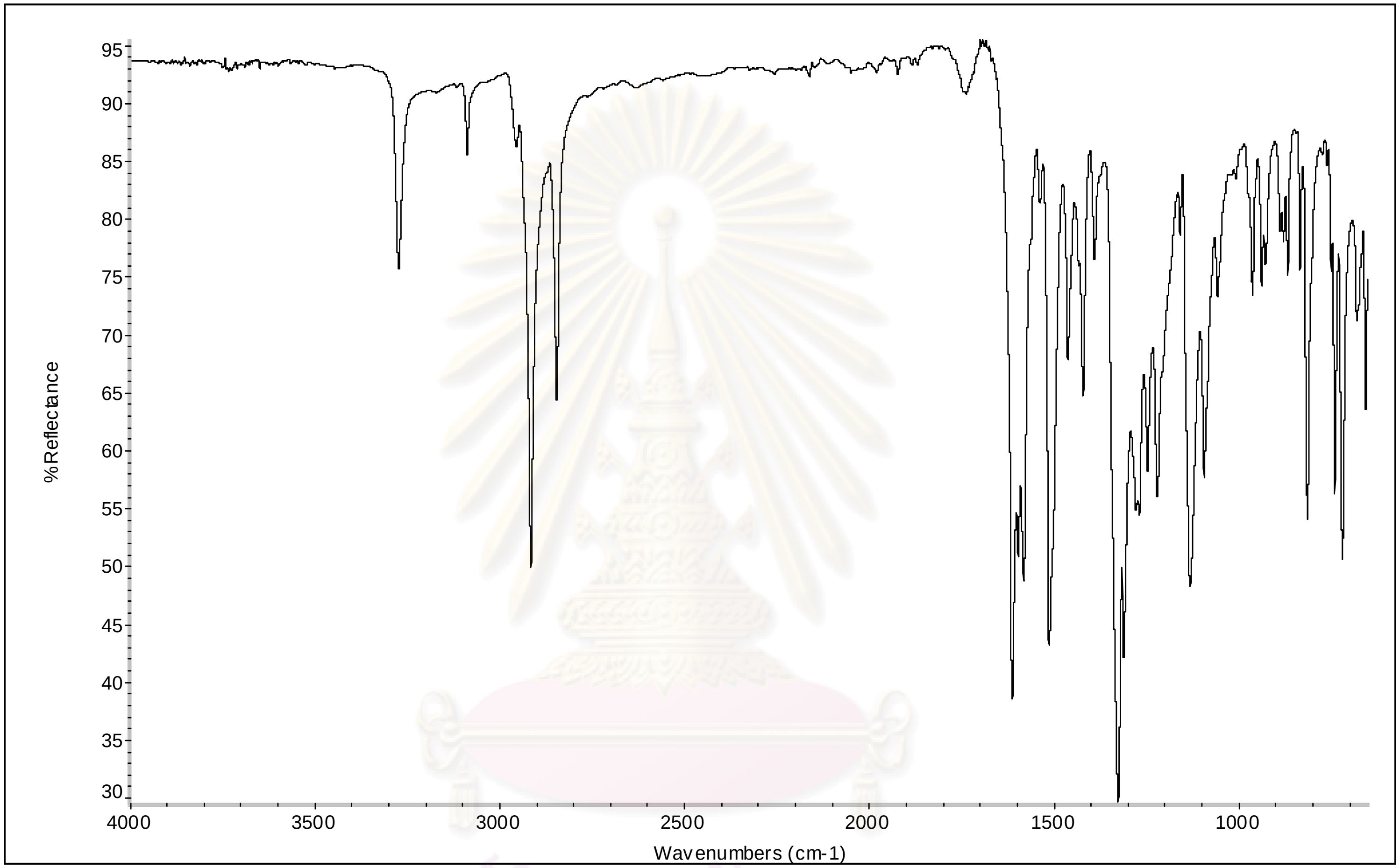

Figure A-60 IR spectrum of compound **15**.

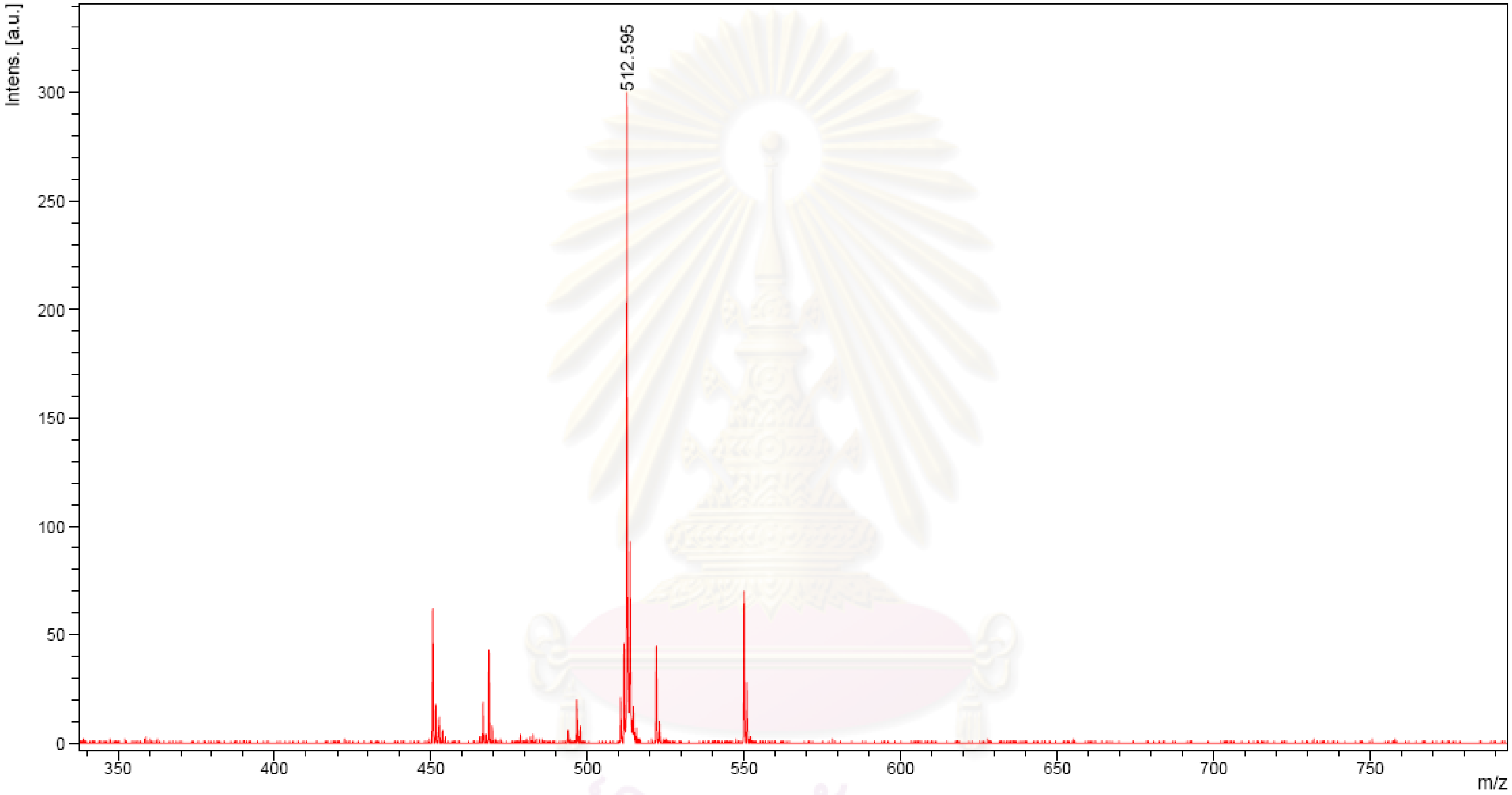

Figure A-61 Mass spectrum of compound **15**.

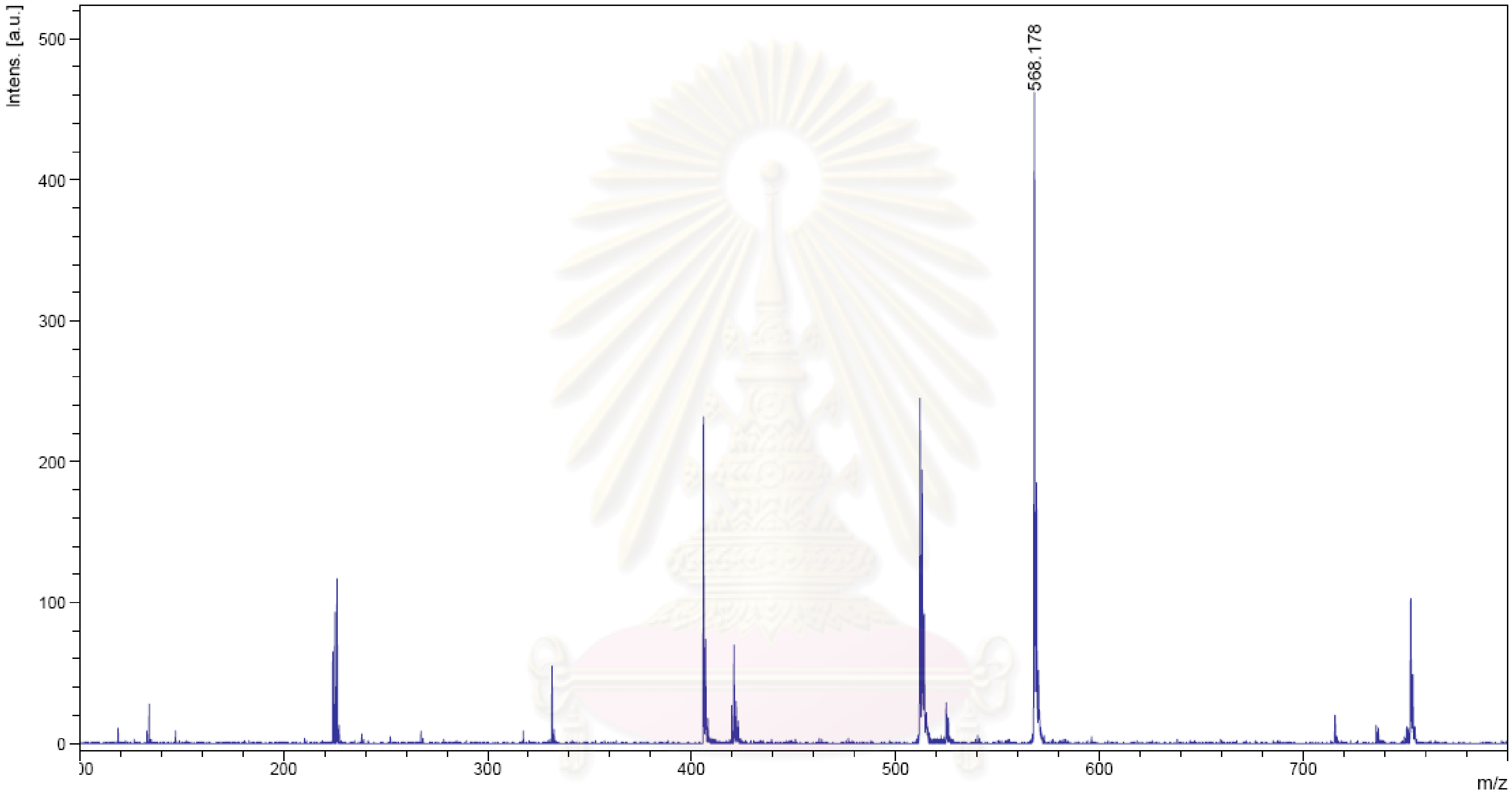

Figure A-62 Mass spectrum of compound **16**.

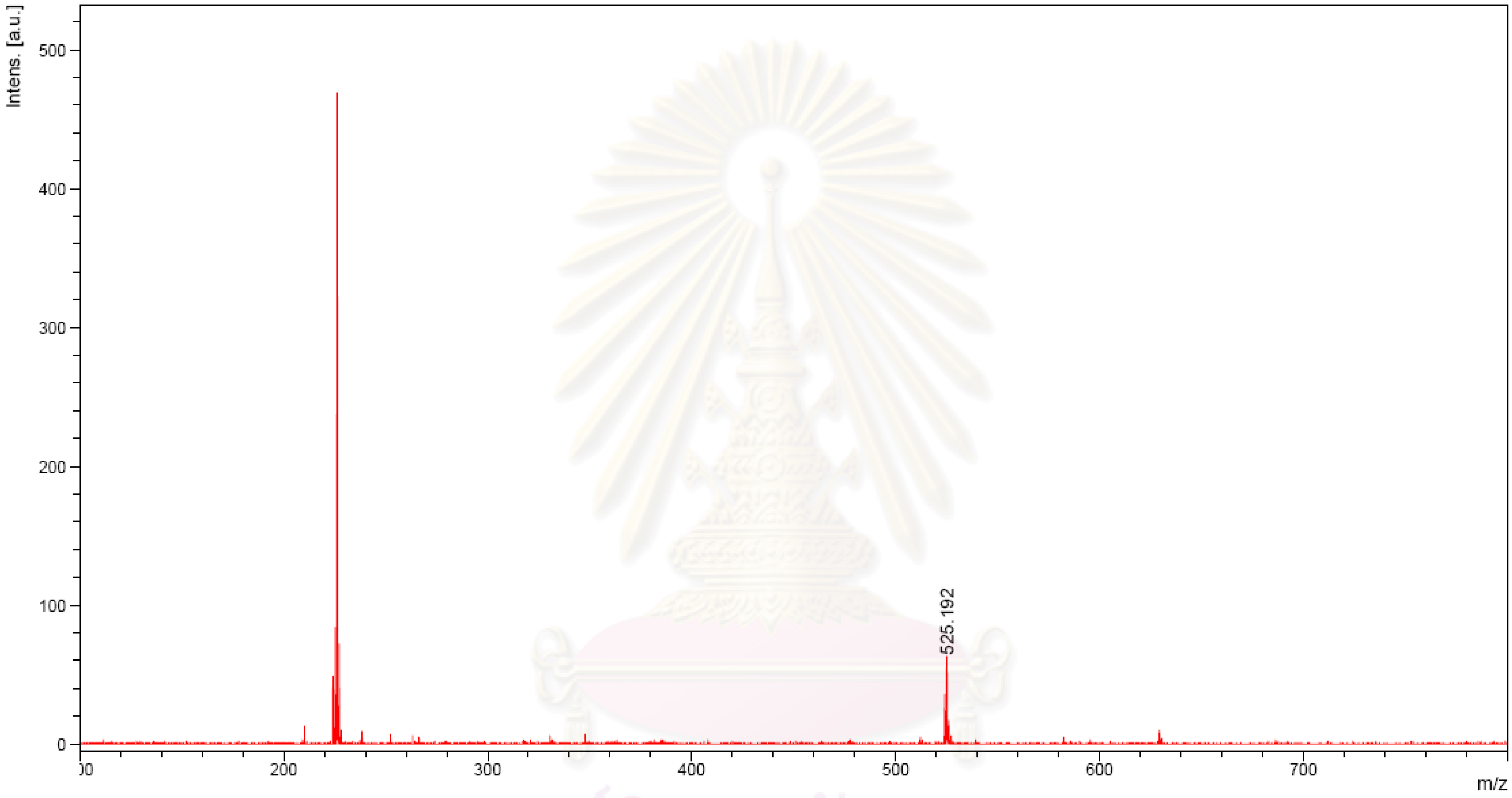

Figure A-63 Mass spectrum of compound 17.

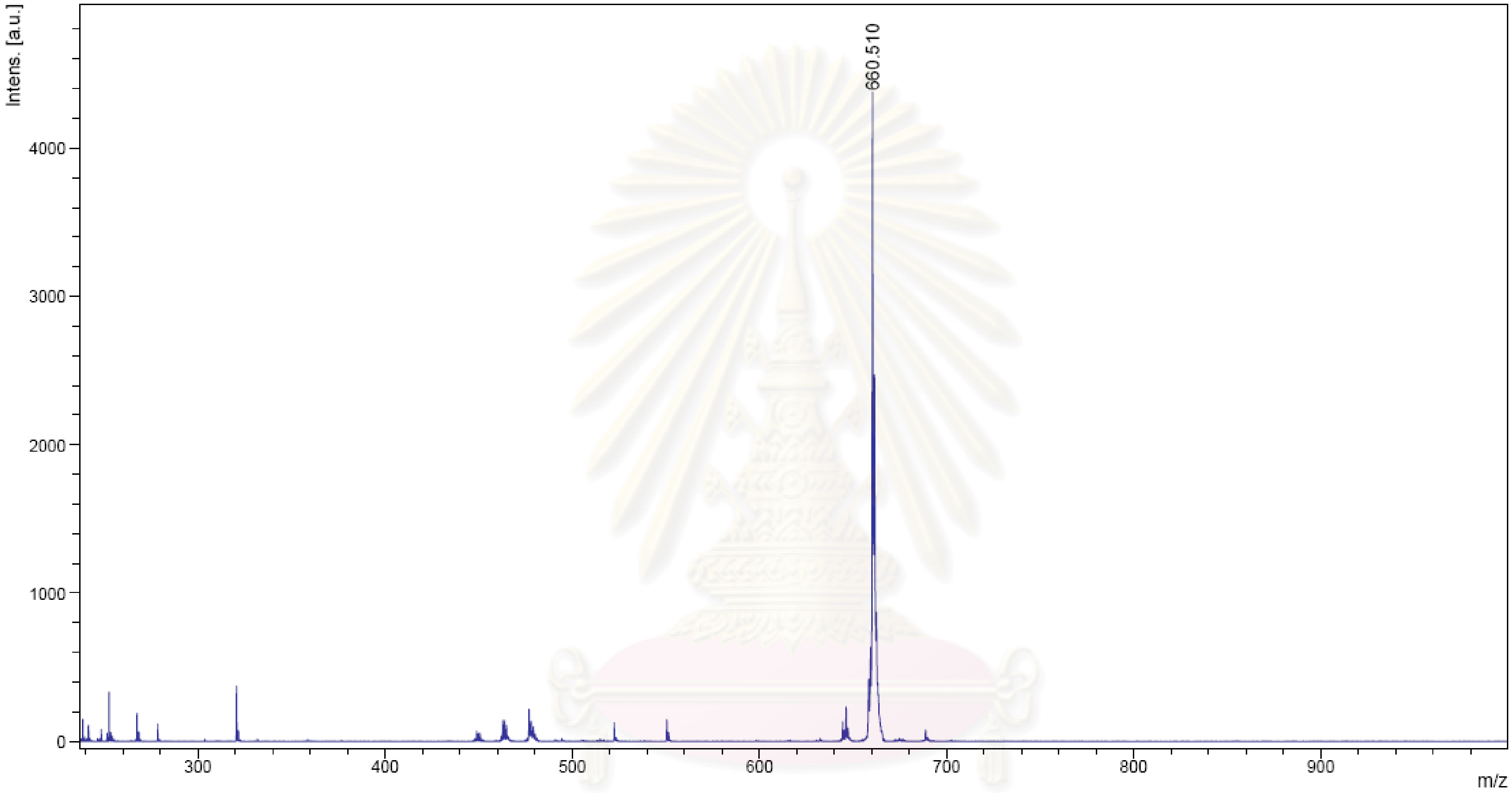

Figure A-64 Mass spectrum of compound **20**.

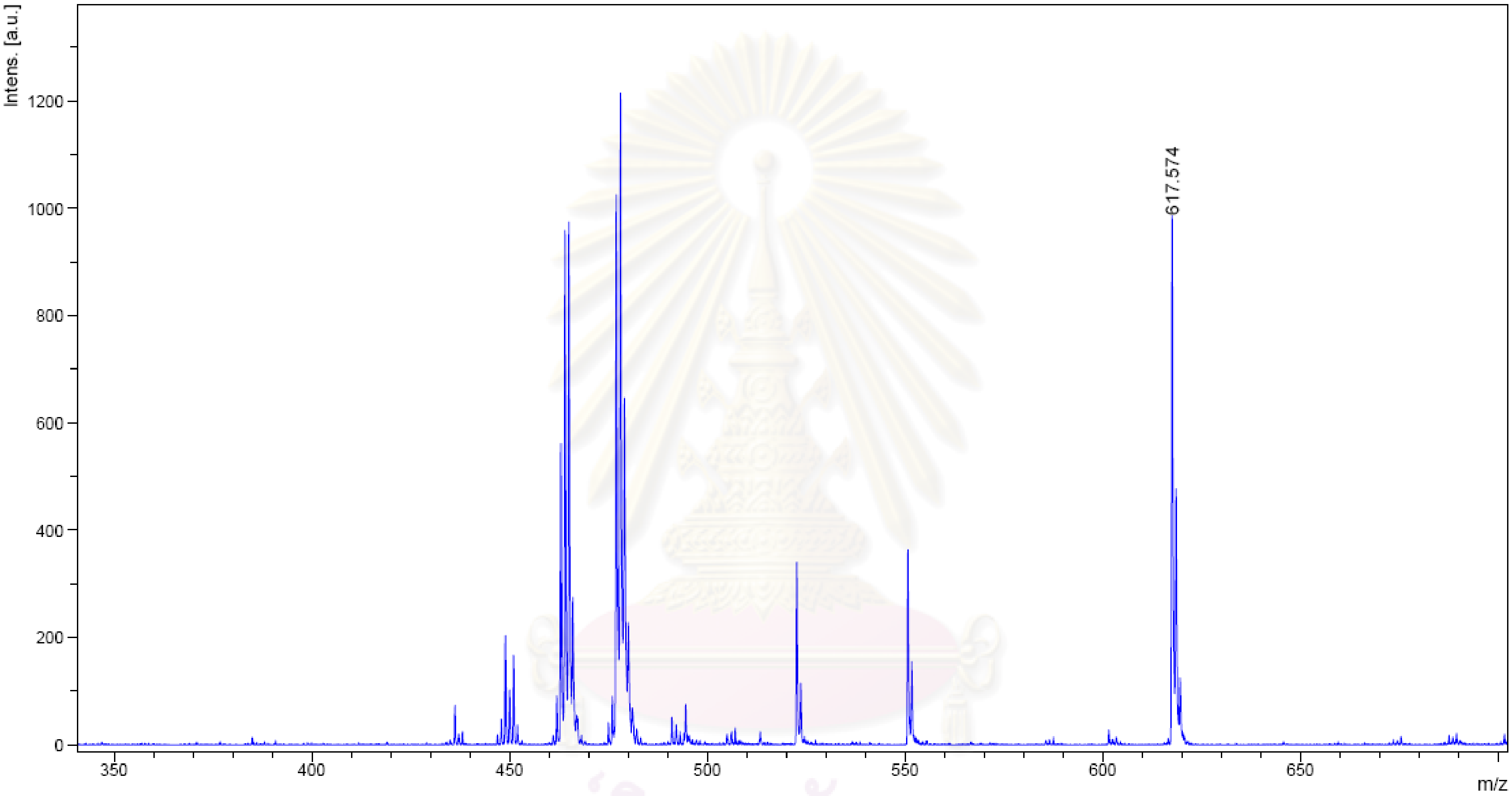

Figure A-65 Mass spectrum of compound **21**.

APPENDIX B

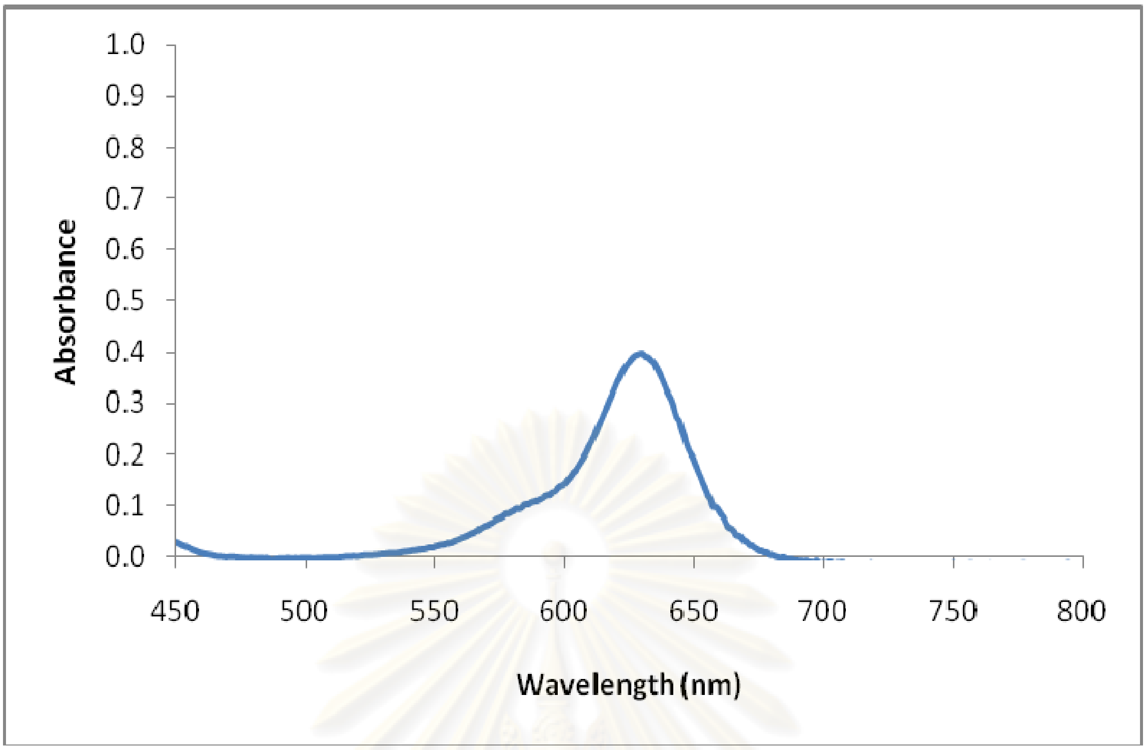

Figure B-1 Absorption spectrum of compound **1** in CH_2Cl_2.

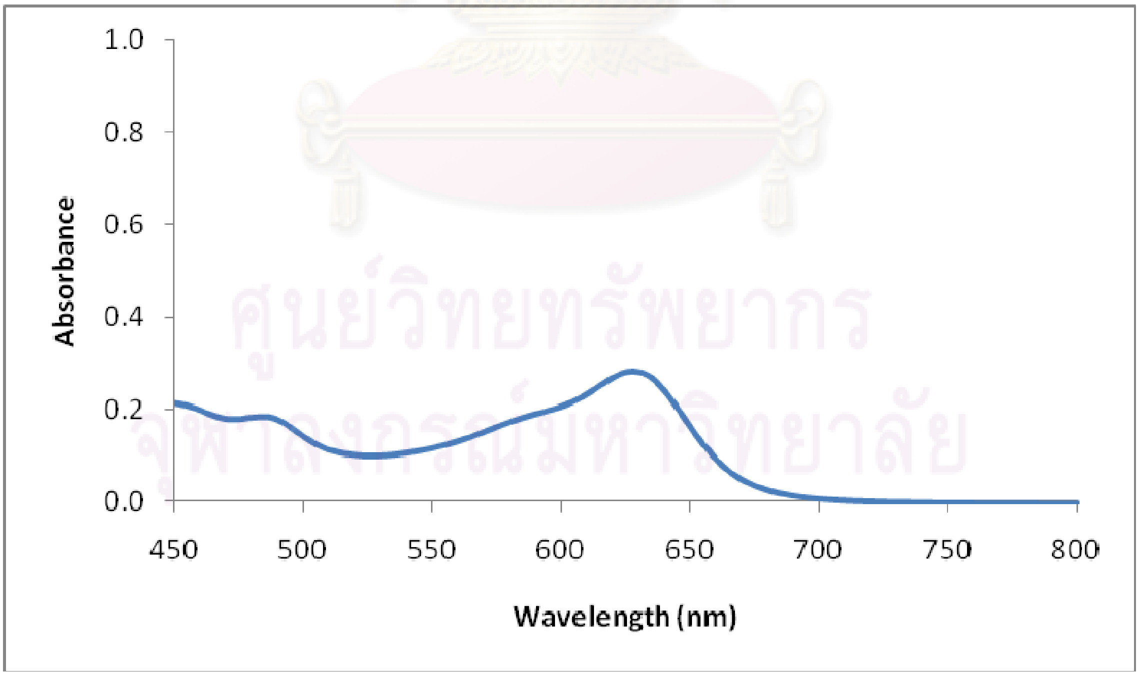

Figure B-2 Absorption spectrum of compound **2** in CH_2Cl_2.

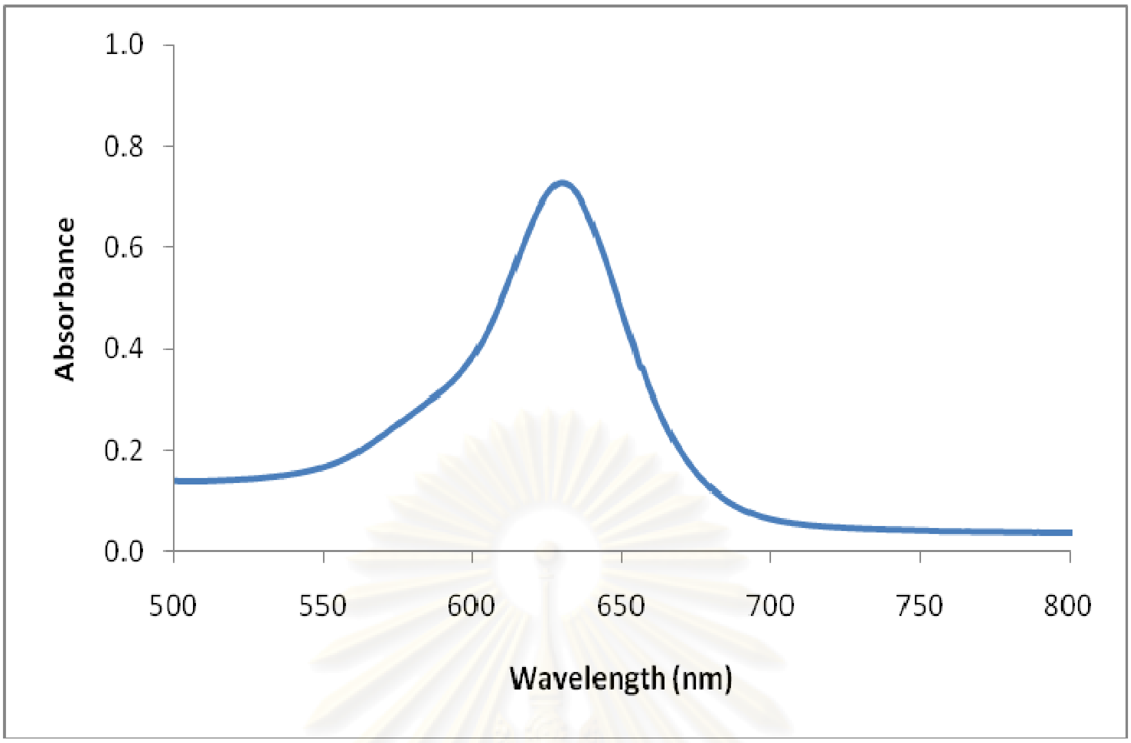

Figure B-3 Absorption spectrum of compound **3** in CH_2Cl_2.

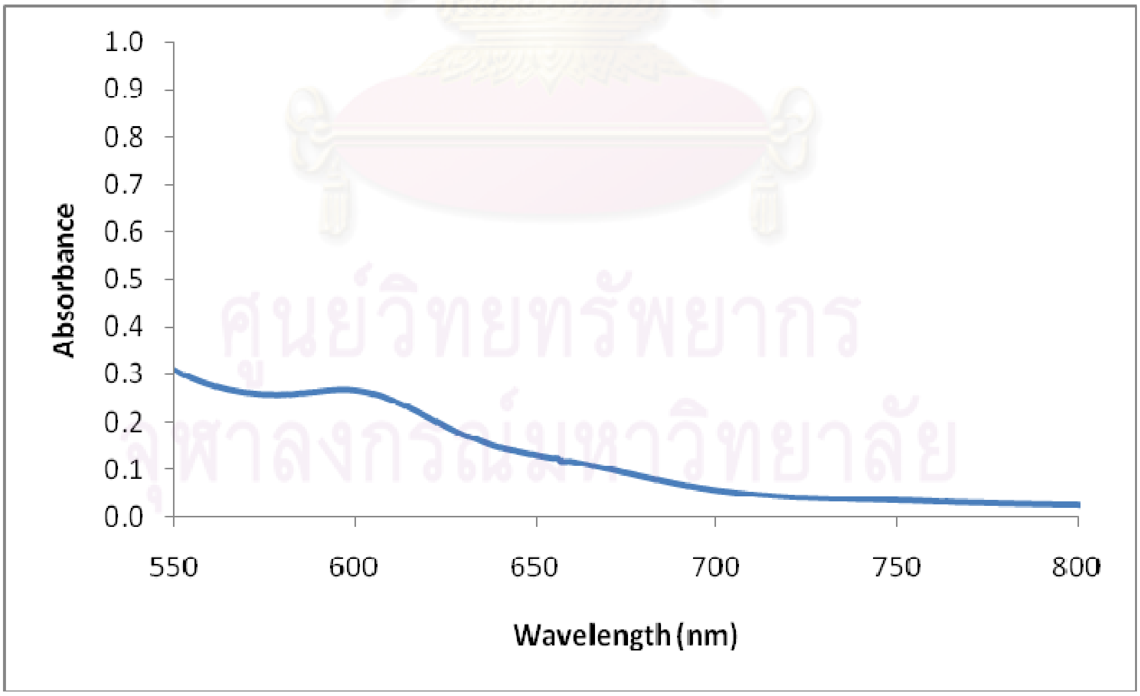

Figure B-4 Absorption spectrum of compound **4** in CH_2Cl_2.

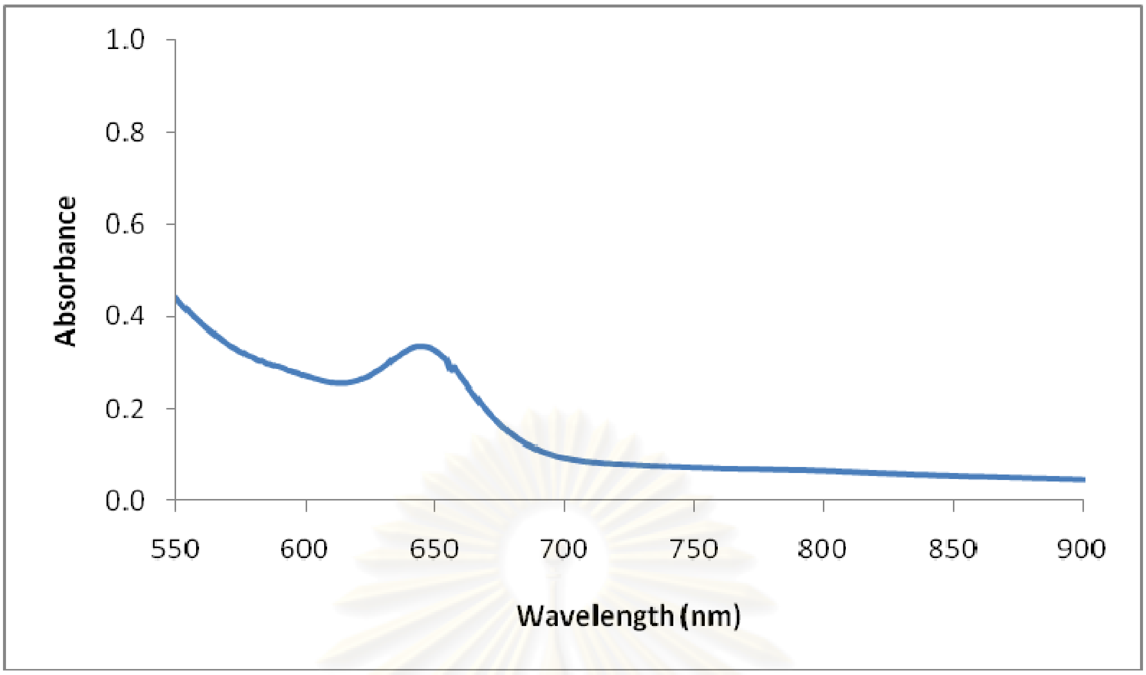

Figure B-5 Absorption spectrum of compound **5** in CH_2Cl_2.

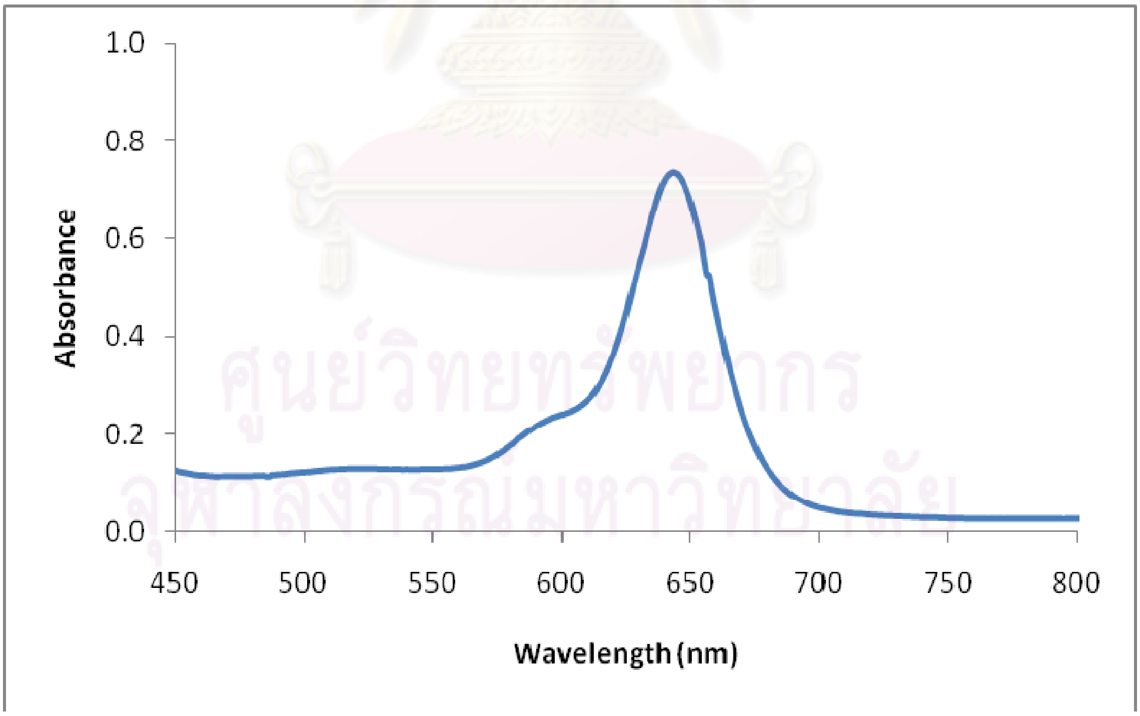

Figure B-6 Absorption spectrum of compound **6** in CH_2Cl_2.

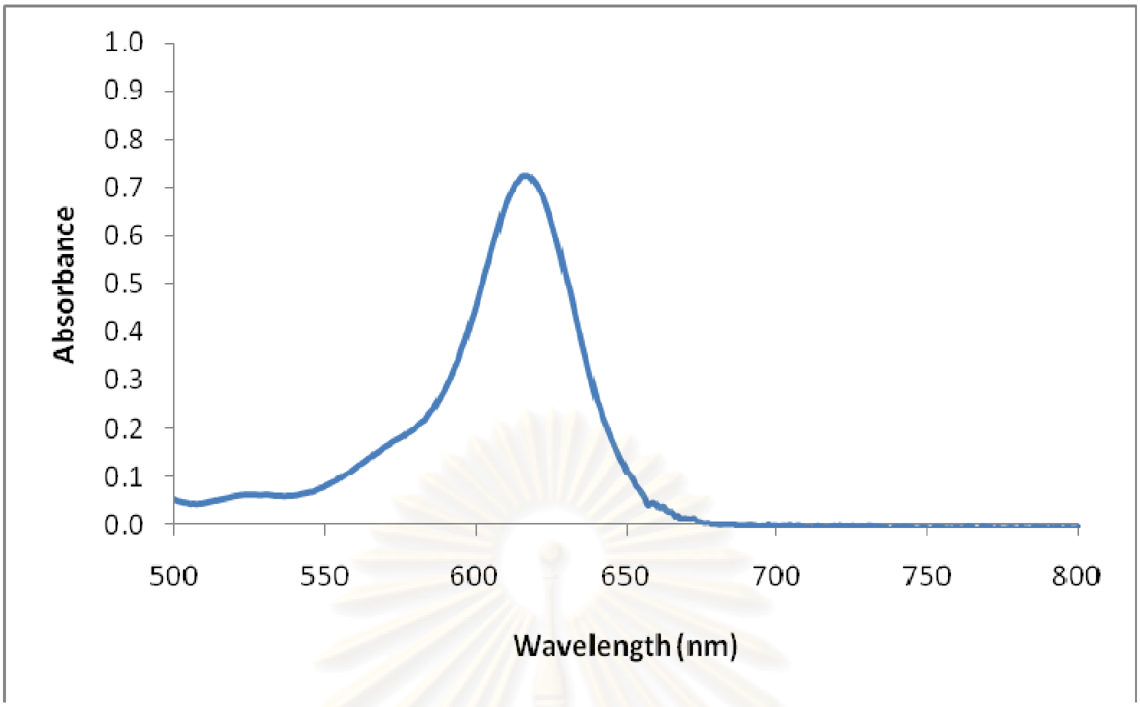

Figure B-7 Absorption spectrum of compound **7** in CH_2Cl_2.

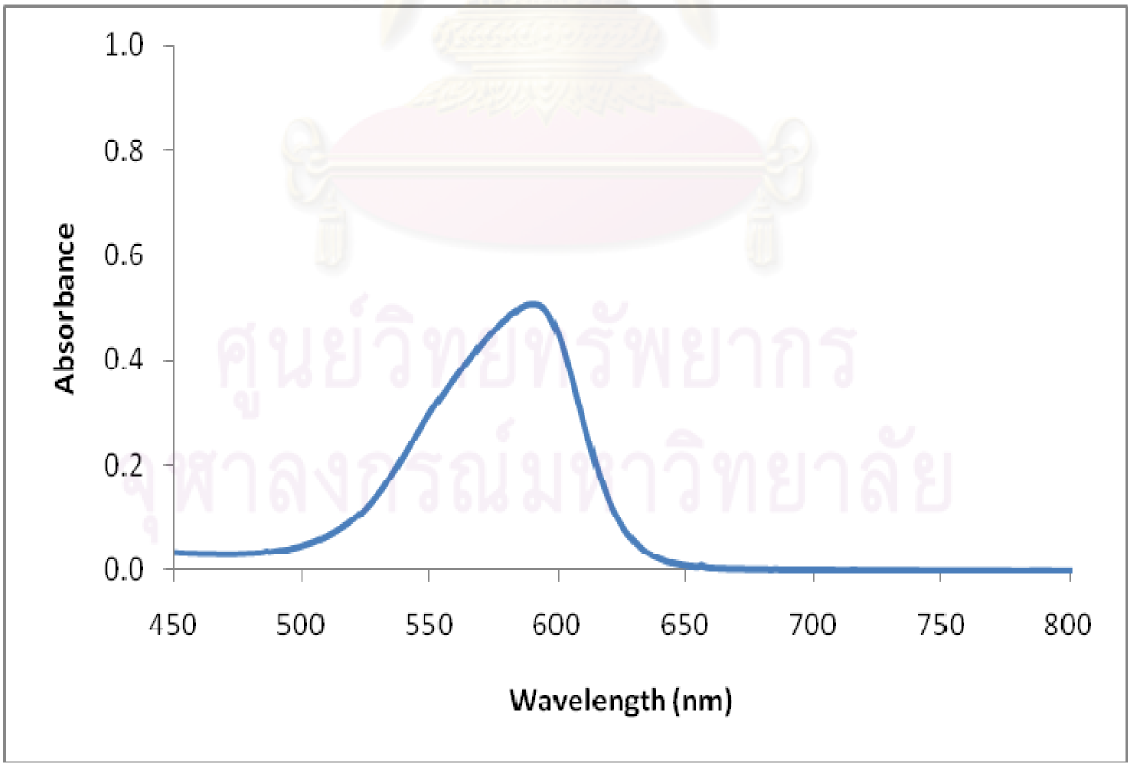

Figure B-8 Absorption spectrum of compound **8** in CH_2Cl_2.

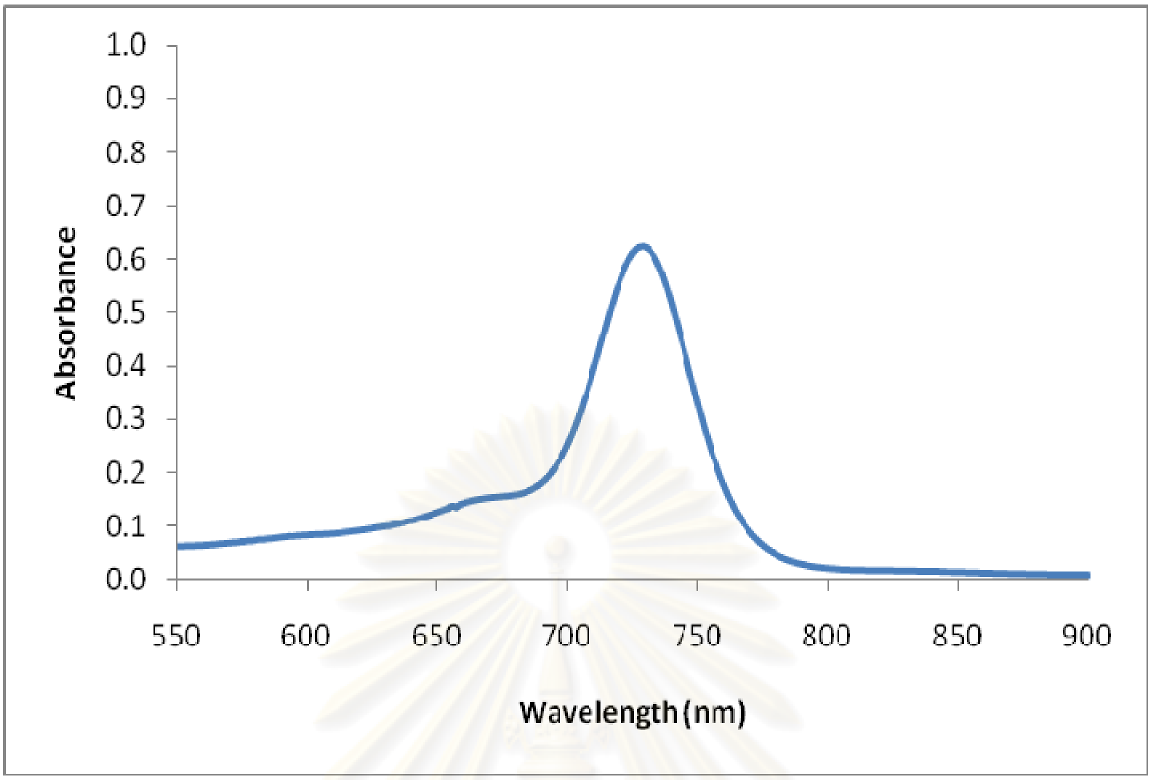

Figure B-9 Absorption spectrum of compound **9** in CH_2Cl_2.

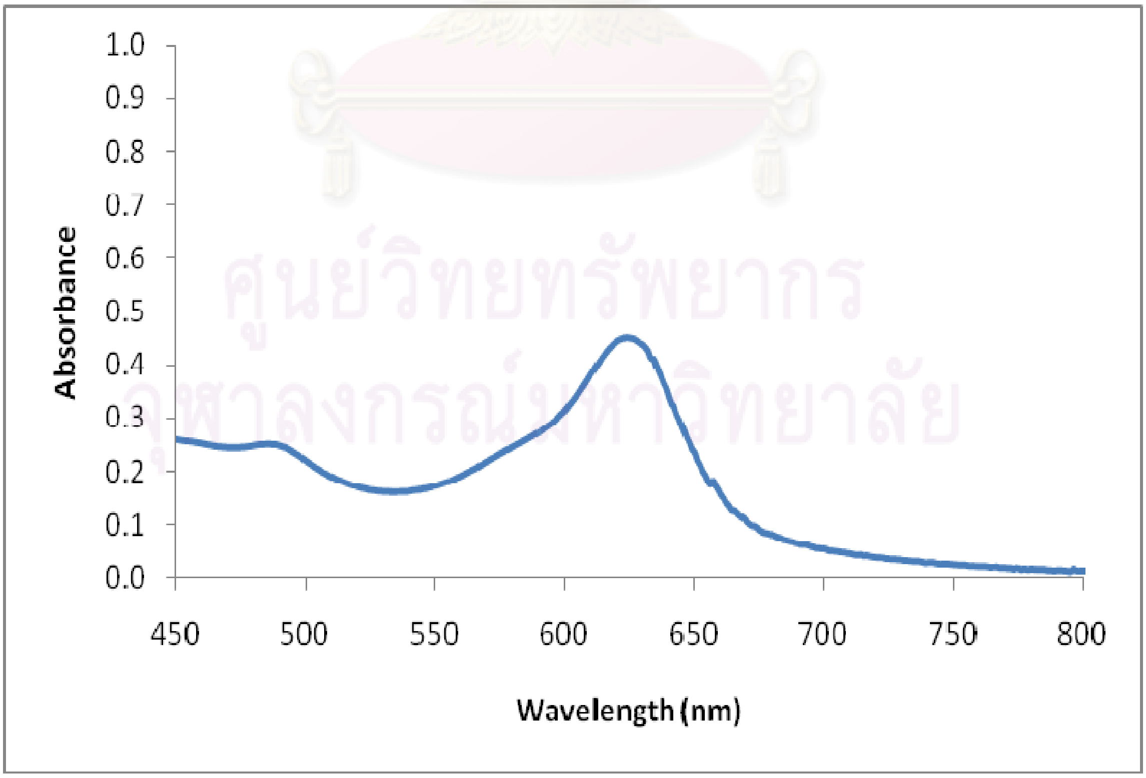

Figure B-10 Absorption spectrum of compound **10** in CH_2Cl_2.

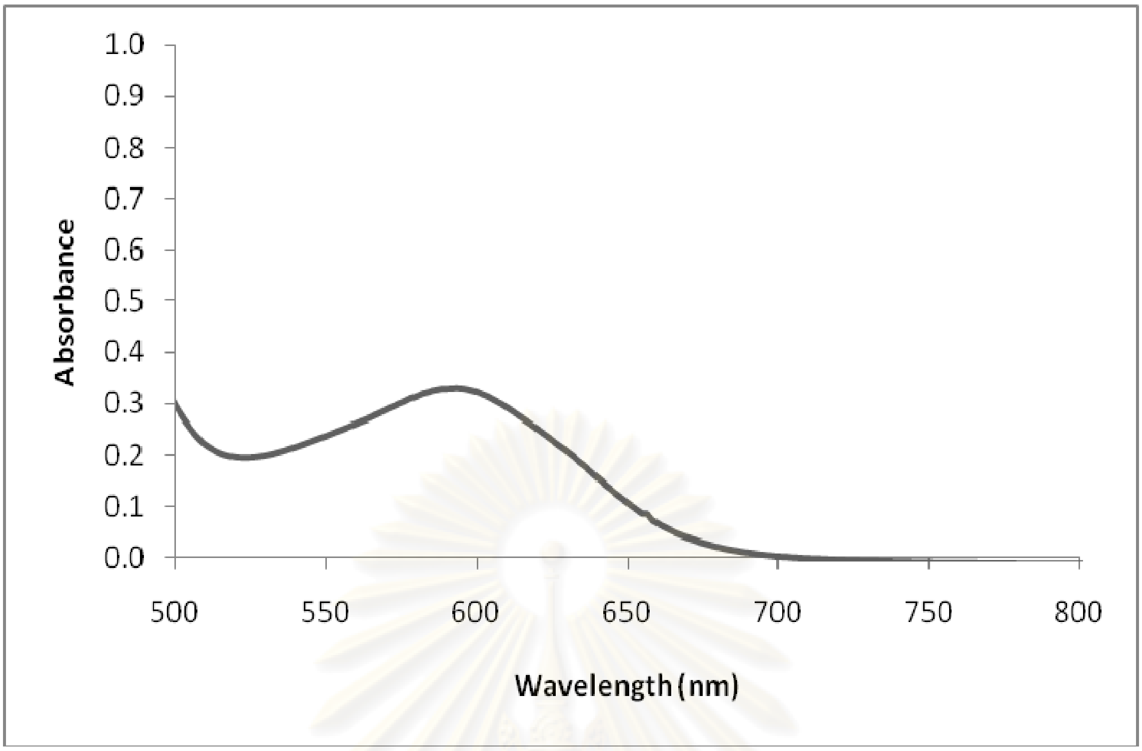

Figure B-11 Absorption spectrum of compound **11** in CH_2Cl_2.

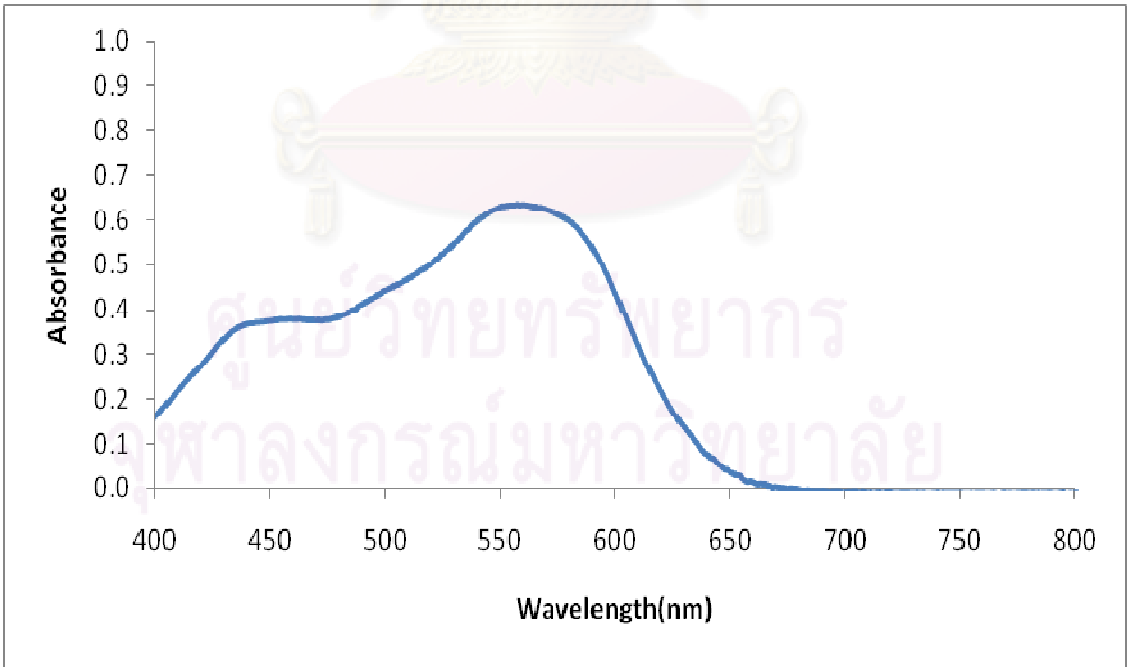

Figure B-12 Absorption spectrum of compound **13** in CH_2Cl_2.

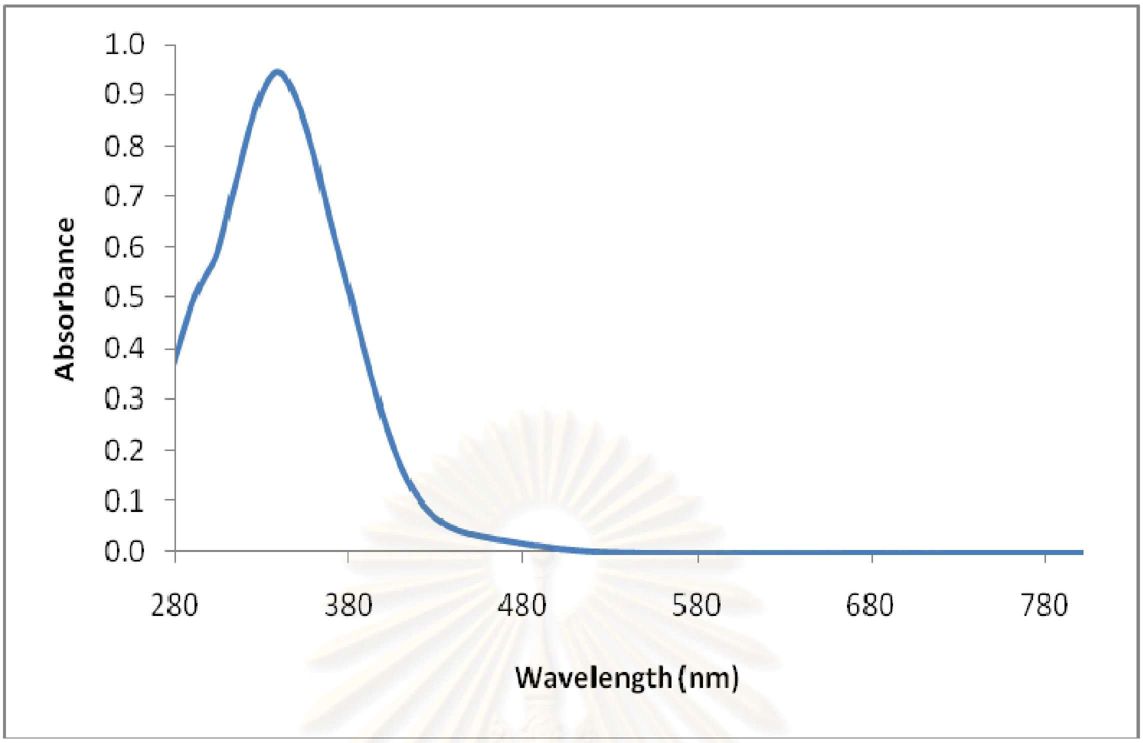

Figure B-13 Absorption spectrum of compound **17** in CH_2Cl_2.

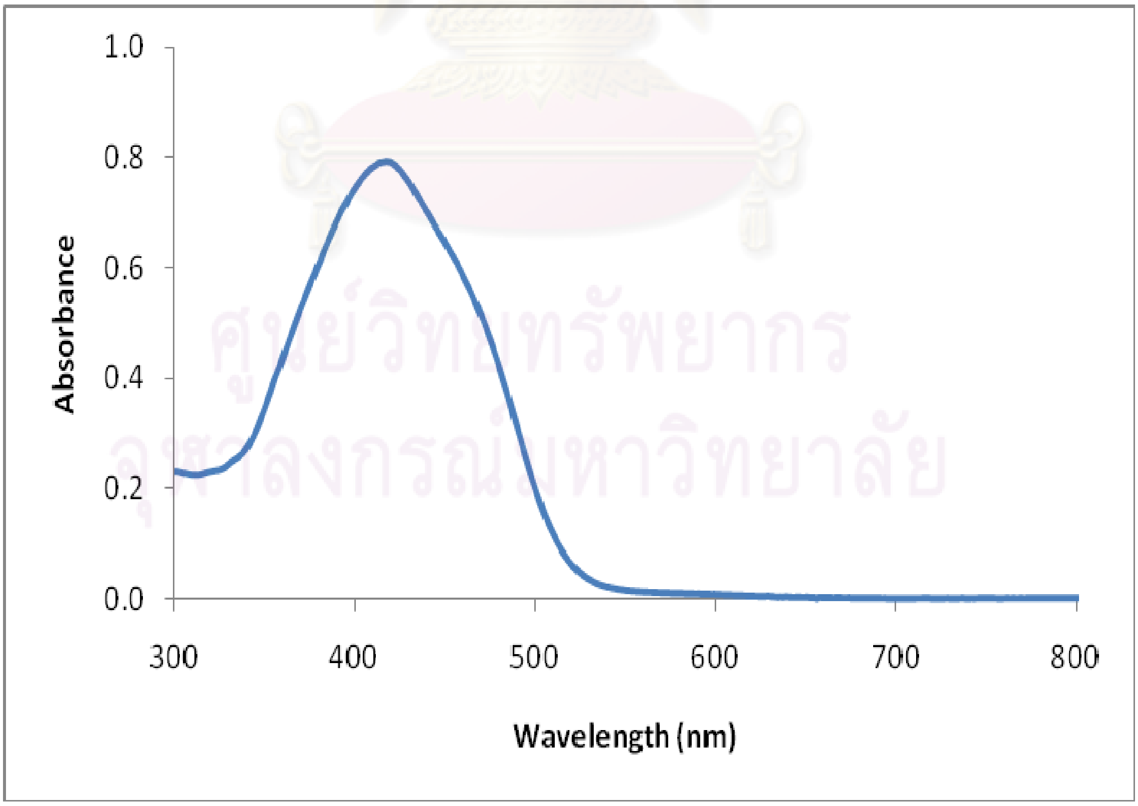

Figure B-14 Absorption spectrum of compound **20** in CH_2Cl_2.

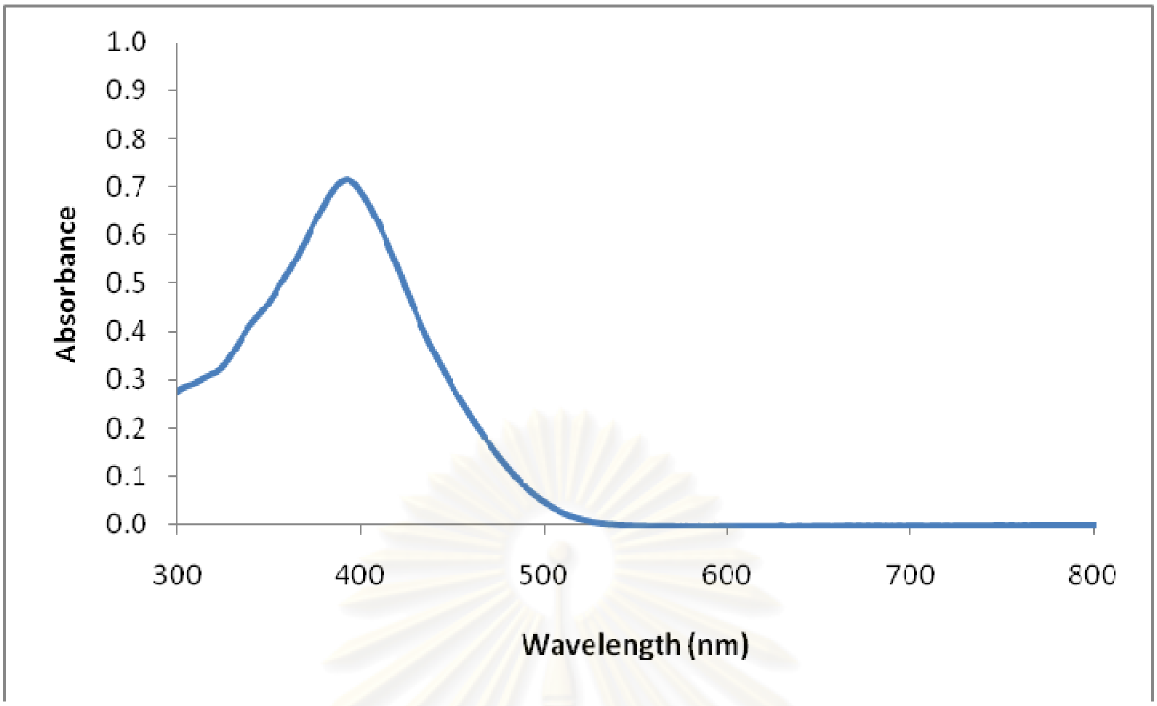

Figure B-15 Absorption spectrum of compound **21** in CH_2Cl_2.

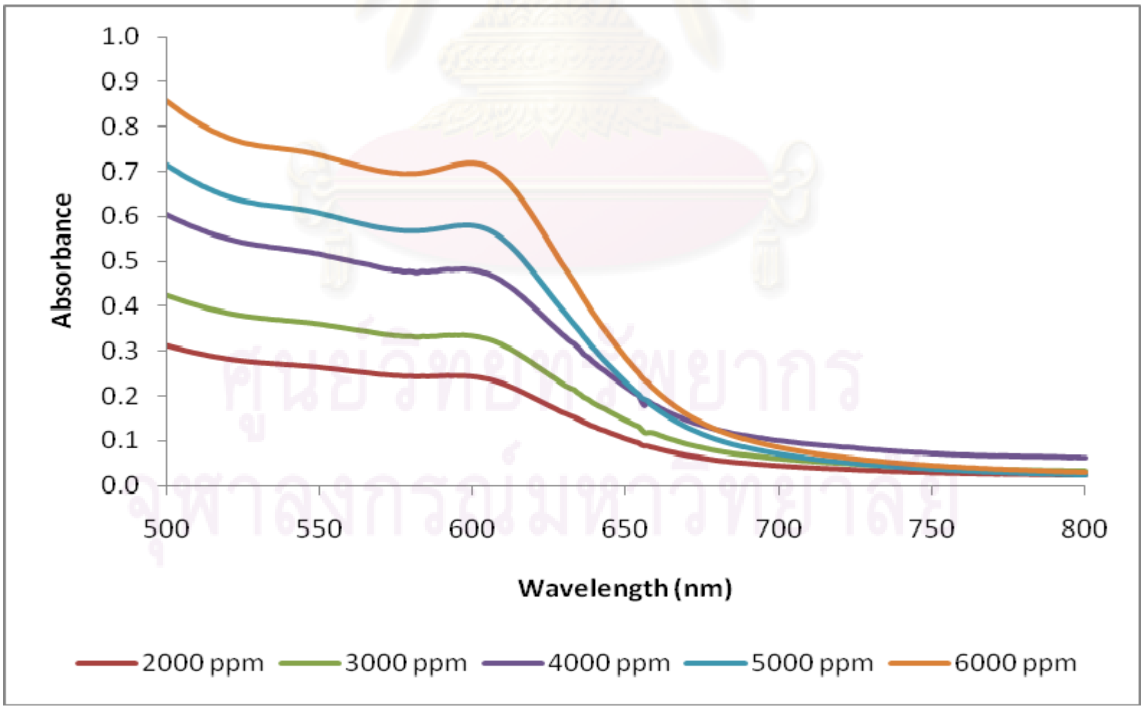

Figure B-16 Absorption spectrum of crude compound **10** in base gasoline at 2,000, 3,000, 4,000, 5,000 and 6,000 ppm (λ_{abs} = 599 nm).

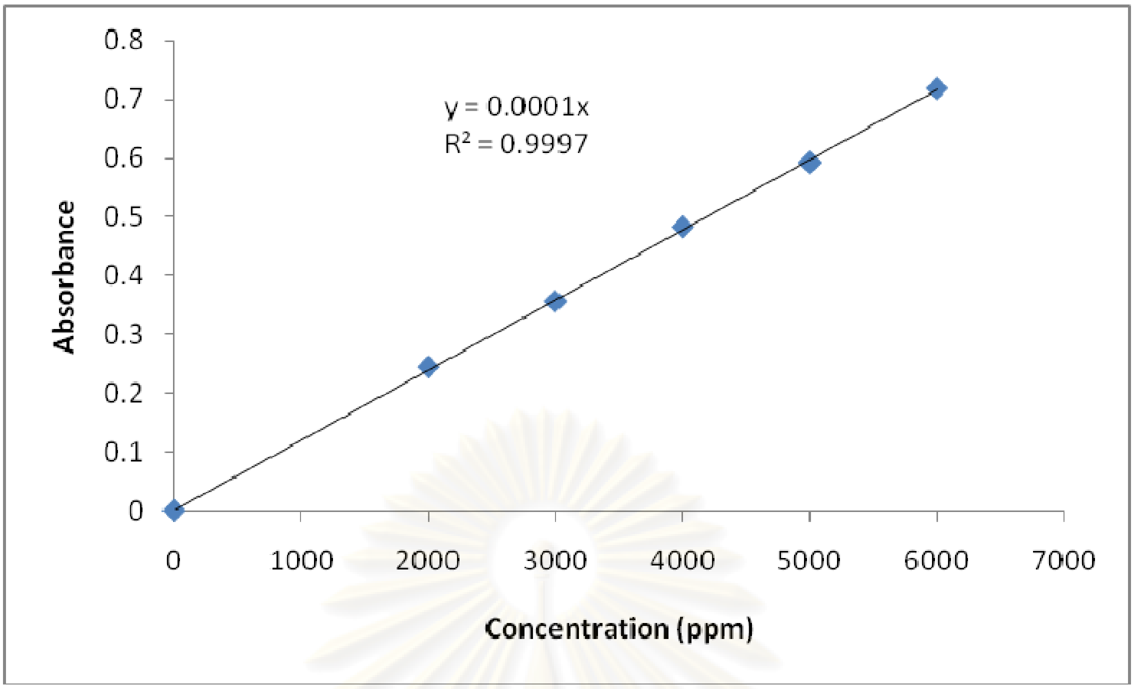

Figure B-17 Calibration curve for the quantitative determination of crude compound **10** in base gasoline (λ_{abs} = 599 nm).

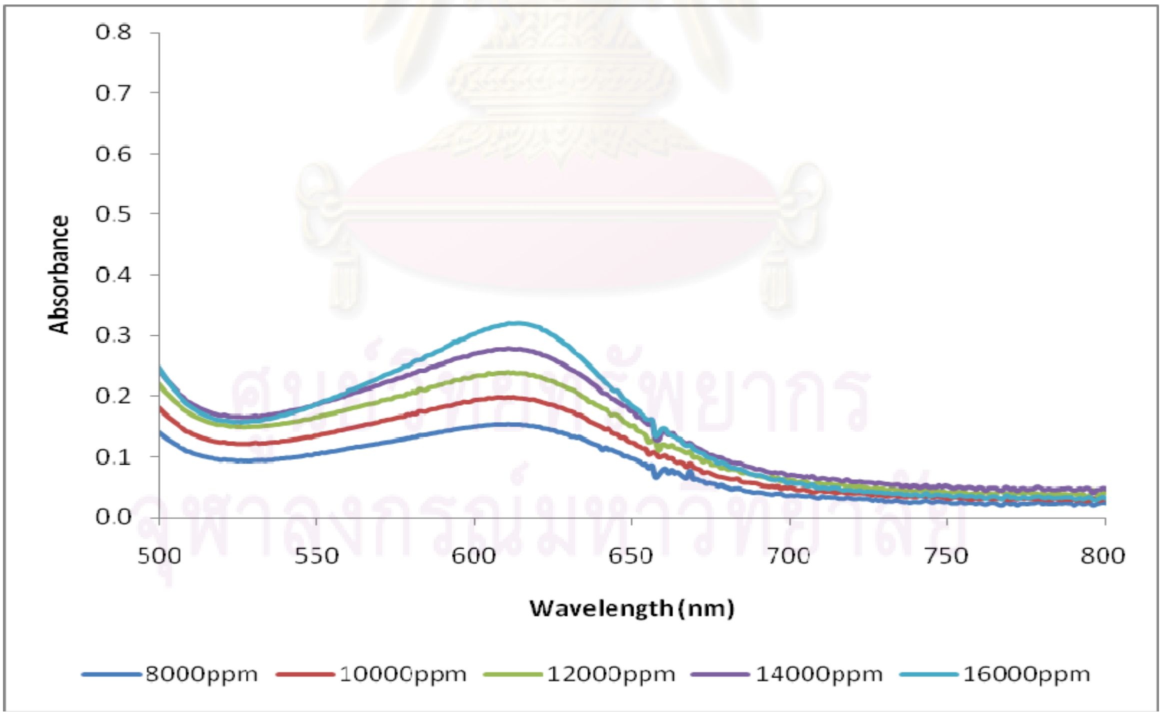

Figure B-18 Absorption spectrum of compound **10** in base gasoline at 8,000, 10,000, 12,000, 14,000 and 16,000 ppm (λ_{abs} = 610 nm).

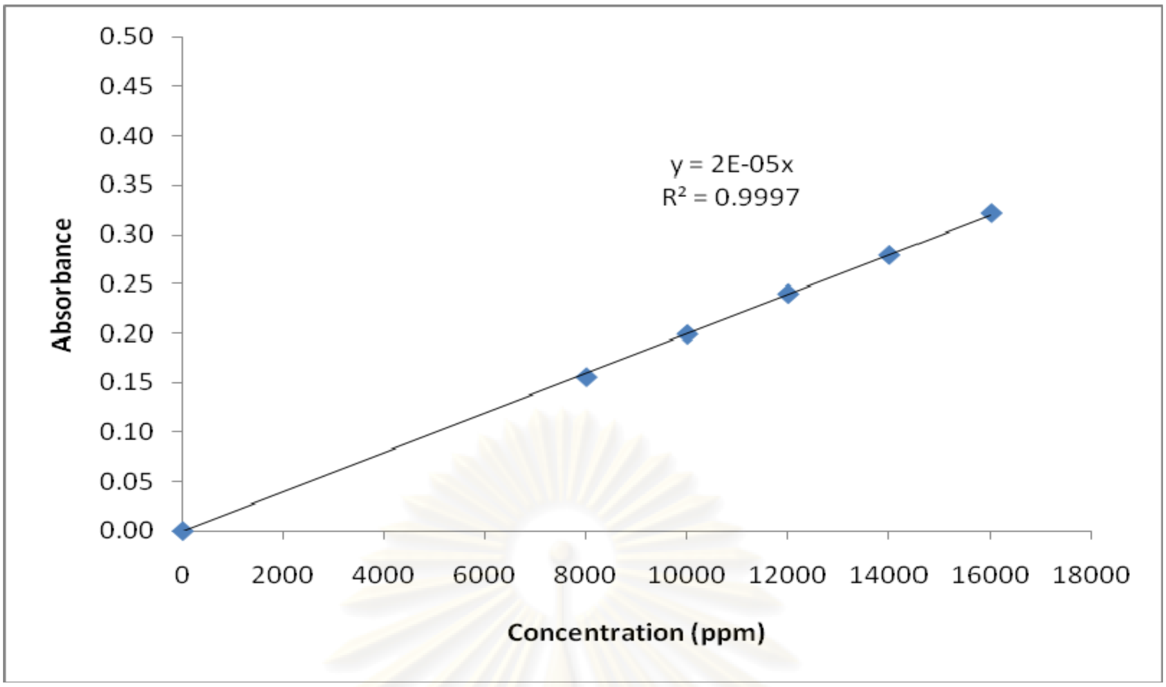

Figure B-19 Calibration curve for the quantitative determination of compound **10** in base gasoline (λ_{abs} = 610 nm).

VITA

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