การสังเคราะห์อนุพันธ์ของ 6–เอ็น-เพนทาเดซิล–8–ไฮดรอกซีควิโนลีน

นางสาวสุวิมล วงศ์เลิศวิศวกร

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SYNTHESIS OF 6-*N*-PENTADECYL-8-HYDROXYQUINOLINE FROM CARDANOL

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Field of Study	Petrochemistry and Polymer Science
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สุวิมล วงศ์เลิศวิศวกร : การสังเคราะห์ 6-เอ็น-เพนทาเดซิล-8-ไฮดรอกซีควิโนลีนจากคาร์ดานอล. (SYNTHESIS OF 6-*N*-PENTADECYL-8-HYDROXYQUINOLINE FROM CARDANOL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. อมร เพชรสม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ. ดร.พัชณิตา ธรรมยงค์กิจ, 89 หน้า.

ได้สังเคราะห์สารทำเครื่องหมายชนิดเรืองแสงสำหรับน้ำมันดีเซล จากอนุพันธ์ของคาร์ดานอล ซึ่งสกัดได้จากเปลือกเม็ดมะม่วงหิมพานต์ โดยสังเคราะห์ 8-ไฮดรอกซีควิโนลีน เพื่อใช้เป็นสารต้นแบบในการสังเคราะห์ 6-เอ็น-เพนทาเดซิล-8-ไฮดรอกซีควิโนลีน จากคาร์ดานอล พบว่าสาร 6-เอ็น-เพนทาเดซิล-8-ไฮดรอกซีควิโนลีน ที่ได้ สามารถละลายได้ดีในน้ำมันดีเซลและสารละลายอินทรีย์อื่นๆ แต่เมื่อนำไปเติมในน้ำมันดีเซลที่ระดับความเข้มข้น 2 ถึง 5 ส่วนในล้านส่วน พบว่า ไม่สามารถใช้เป็นสารทำเครื่องหมายเรืองแสงในน้ำมันได้ เนื่องจากเกิดการเควนชิง กับ น้ำมันดีเซล แต่เมื่อนำ 6-เอ็น-เพนทาเดซิล-8-ไฮดรอกซีควิโนลีน ใช้เป็นรีเอเจนต์สำหรับจับไอออนของโลหะโครเมียม (III) ในน้ำ แล้วสกัดแยกสารประกอบเชิงซ้อนของโลหะโครเมียม (III) กับ 6-เอ็น-เพนทาเดซิล-8-ไฮดรอกซีควิโนลีน ด้วยคลอโรฟอร์มแล้วนำไปตรวจสอบด้วยเทคนิคยูวี–วิสิเบิล สเปกโตรสโคปีที่ความยาวคลื่น 407 นาโนเมตร พบว่า6-เอ็น-เพนทาเดซิล-8-ไฮดรอกซีควิโนลีน สามารถใช้เป็นรีเอเจนต์สำหรับตรวจวิเคราะห์ปริมาณไอออนของโครเมียม (III) โดยเทคนิคทางแสงยูวี–วิสิเบิล ได้ใกล้เคียงกับ 8-ไฮดรอกซีควิโนลีนต้นแบบทุกประการ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต สุวิมล วงศ์เลิศวิศวกร

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SUWIMOL WONGLERTWISAWAKORN : SYNTHESIS OF 6-*N*-PENTADECYL-8-HYDROXYQUINOLINE FROM CARDANOL. ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., CO–ADVISOR: ASST. PROF. PATCHANITA THAMYONGKIT, Dr.rer.nat., 89 pp.

In this research, the fluorescence marker for diesel oil was synthesized from cardanol, which was obtained from cashew nut shell liquid. The synthesis of 8-hydroxyquinoline was performed as a model synthetic pathway for the synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline from cardanol. The resulting 6-*n*-pentadecyl-8-hydroxyquinoline (**8**) exhibited high solubility in diesel fuel and common organic solvents. When added into diesel fuel at the concentration of 2–5 ppm, compound **8** could not be applied as fluorescence marker in diesel fuel due to the quenching phenomenon with diesel fuel. However, compound **8** was used as chelating agent for chromium (III) ions in water. Complex of Cr (III) with compound **8** was extracted with chloroform and detected by UV-Vis spectroscopy at λ_{max} 407 nm. It was found that compound **8** could be used as a reagent for quantitative determination of chromium (III) ion by using UV-Vis technique in a similar manner as that using 8-hydroxyquinoline.

Field of Study: Petrochemistry and Polymer science Student's Signature: Suwimol W.

Academic Year: .....2008..... Advisor's Signature: .....

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

br	:	broad
^{13}C-NMR	:	carbon-13 nuclear magnetic resonance spectroscopy
CNSL	:	cashew nut shell liquid
cP	:	centipoise
δ	:	chemical shift
$CHCl_3$	:	chloroform
J	:	coupling constant
^{o}C	:	degree celcius
$CDCl_3$	:	deuterated chloroform
d	:	doublet (NMR)
dd	:	doublet of doublet (NMR)
λ_{em}	:	emission wavelength
eq	:	equivalent (s)
EtOH	:	ethanol
EtOAc	:	ethyl acetate
λ_{ex}	:	excitation wavelength
g	:	gram (s)
Hz	:	hertz (s)
h	:	hour (s)
IR	:	infrared spectroscopy
^{1}H-NMR	:	proton nuclear magnetic resonance spectroscopy
m/z	:	mass per charge ratio
MS	:	mass spectroscopy
max	:	maximum
λ_{max}	:	maximum wavelength
m.p.	:	melting point
MeOH	:	methanol
CH_2Cl_2	:	methylene chloride
mg	:	milligram (s)

mL	:	milliliter (s)
mM	:	millimolar (s)
mmol	:	millimole (s)
min	:	minute
M	:	molar (s)
m	:	multiplet (NMR)
nm	:	nanometer
NMR	:	nuclear magnetic resonance spectroscopy
ppm	:	parts per million
rt	:	room temperature
s	:	singlet (NMR)
st	:	stretching vibration (IR)
TLC	:	thin layer chromatography
THF	:	tetrahydrofuran
t	:	triplet (NMR)
UV-Vis	:	ultraviolet visible spectrometry
cm^{-1}	:	unit of wavenumber (IR)

CHAPTER I
INTRODUCTION

At present a large amount of petroleum fuel oil is consumed in many countries. Petroleum imports are at record levels in the world, and will continue to rise as domestic supplies of oil shrink. Our transportation sector relies almost exclusively on petroleum as a source of energy. This is due to the high level of demand for gasoline and diesel fuel. One of the solutions to these problems is to use biodiesel (alone, or blended with conventional petrodiesel) in unmodified diesel-engine vehicles instead of pure diesel fuel oil. In the process of biodiesel production, we receive by-product via the transesterification of vegetable oil or animal fat is obtained as a glycerol. This has led to an excess of crude glycerol in the market. The challenge investigates the feasibility of manufacturing value-added chemicals from glycerol.

The thesis presents the way to add value of excess crude glycerol, which is to use it as reagent for synthesis of a 8-hydroxyquinoline derivative. 8-hydroxyquinoline compound is widely used as chelating agent for extracting metal ions from waste water. There are methods for extracting metal ions such as, precipitation and liquid-liquid extraction technique. Because of the determination of metal ions at trace level is very important in context of environmental protection in many industry such as, pottery and porcelain industry, paper mills industry, fertilizers and petroleum refining industry.

8-hydroxyquinoline has a structure which is suitable for photometric investigation, and the stability constants for cationic chelates are very high [1,2]. Because of good chelating complexation with many cationics, 8-hydroxyquinoline has special photophysical properties and has been used in many fields. In recent years, 8-hydroxyquinoine is used as a parent compound to make drugs (especially anti-malarial medicines) and fungicides [3]; while 8-hydroxyquinoline is used as a biological marker [4]; 8-hydroxyquinoline is used as a precipitating agent or chelating agent to separate metals from water [5,6]. However, a major concern of the use of 8-hydroxyquinoline in such applications is its low solubility due to high tendency of high-polar molecule.

To enhance solubility of resulting, the use of cardanol is introduced into its 6-alkyl-8-hydroxyquinoline in this work. Cardanol is a natural alkyl phenol obtained by vacuum distillation of cashew nut shell liquid (CNSL). Cardanol derivatives represent a simple for the preparation of additives for lubricants, diesel engine fuels, poor point depressant, flame retardants, resin, inks hydrorepellents, stabilizers and antioxidants.

This research involves the synthesis of a highly oil soluble 8-hydroxyquinoline as fluorescent marker in diesel as well as cheating agent for chromium ion in waste water by liquid-liquid extraction from the naturally occurring cardanol derivatives.

The quantitative determination of chromium (III) in water solution by using UV-Vis spectroscopy are also investigated.

1.1 The objective of this research

The objectives of this research are synthesizing 6-*n*-pentadecyl-8-hydroxyquinoline from cardanol as fluorescent marker in diesel and as chelating agent for chromium (III) ion and evaluating its performance.

1.2 The scope of this research

The scope of this research covers the synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline from cardanol via nitro and amino derivative. The amino derivative was then condensed with glycerol in the Skraup synthesis to give 6-*n*-pentadecyl-8-hydroxyquinoline. The product was fully characterized by spectroscopic techniques such as mass spectrometry, and FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis and Fluorescence spectroscopy, In addition, the quantitative determination of chromium (III) in water solution by using UV-Vis spectroscopy were also investigated.

CHAPTER II
THEORY AND LITERATURE REVIEWS

THEORY

2.1 UV-Vis Spectroscopy [7–9]

Molecular ultraviolet/visible absorption spectroscopy is used primarily for quantitative analysis and is probably more widely used in chemical and clinical laboratories all in the world than any tools for determining the structure of inorganic and organic compounds. In addition, it is now assuming a role in quantitative analysis, particularly for determining environmental pollutants. Absorption of ultraviolet and visible radiation by molecules occurs in one or more electronic absorption bands, each of which is made up of numerous closely packed but discrete lines. Each line arises from the transition of an electron from the ground state to one of the many vibrational and rotational energy states associated with each excited electronic energy state. Because there are so many of these vibrational and rotational states and because their energies differ only slightly, the number of lines contained in the typical band is large and their displacement from one another minute.

The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, b, and the concentration, c, of the absorbing species. Beer's Law states that

$$A = -\log_{10}(I/I_0) = \epsilon \cdot c \cdot L$$

where A is the measured absorbance

I_0 is the intensity of the incident light at a given wavelength

I is the transmitted intensity

L is the path length through the sample

c is the concentration of the absorbing species, for each species and wavelength

ε is a constant known as the molar absorptivity or extinction coefficient

This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure, and has units of $1 / M * cm$ or often $AU / M * cm$. The absorbance and extinction ε are sometimes defined in terms of the natural logarithm instead of the base-10 logarithm.

2.1.1 Absorption by organic compounds

The wavelength region of absorption in organic molecules are 180 to 780 nm results from interactions between photons and those electrons that either participate directly in bond formation or are localized about such atoms as oxygen, nitrogen, and the halogens. Unsaturated organic function groups which absorb in ultraviolet or visible regions are known as chromophores. The position and peak intensity both are influenced by solvent effects as well as other structural details of the molecule. Moreover, conjugation between two (or more) chromophores tends to cause shifts in peak maxima to longer wavelengths. Finally, vibrational effects broaden absorption peaks in the ultraviolet and visible regions, which often make precise determination of a maximum difficult.

Saturated organic compounds containing heteroatoms (such as oxygen, nitrogen and halogens) contain nonbonding electrons that can be excited by radiation in the 170 to 250 nm range. Some of these compounds are used as solvents, such as alcohols and ether, and their absorption leads to lower cutoff spectral limits of 180 to 200 nm.

2.1.2 Absorption by inorganic species

The ions and complexes of elements in the first two transition series absorb broad bands of visible radiation in at least one of their oxidation states and are, as a consequence, colored. Here, absorption involves transitions between filled and unfilled *d*-orbitals with energies which depend on the ligands bonded to metal ions. The energy differences between these *d*-orbitals depend on the position of the periodic table, oxidation state, and the nature of the ligand bonded to it.

2.2 Fluorescence [10–12]

Fluorescence is analytically important emission process in which atoms or molecules are excited by the absorption of electromagnetic radiation. The excited

species then relax to the ground state, giving up their excess energy as photons. In this chapter we consider applications of molecular fluorescence. Fluorescence is a member of the ubiquitous luminescence family of processes in which susceptible molecules emit light from electronically excited states created by either a physical (for example, absorption of light), mechanical (friction), or chemical mechanism. Fluorescence is the property of some atoms and molecules to absorb light at a particular wavelength and to subsequently emit light of longer wavelength after a brief interval, termed the fluorescence lifetime, as shown below in **Figure 2-1**.

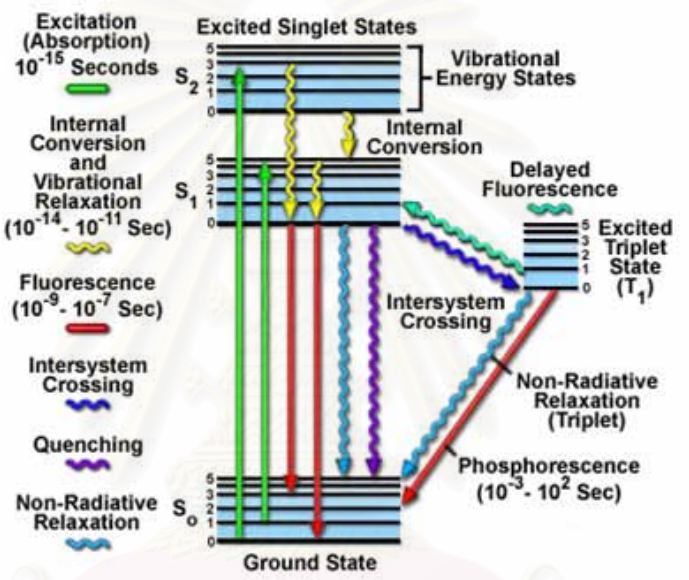


Figure 2-1 Transition giving rise to absorption and fluorescence emission spectra [9].

Excitation can result in the molecule reaching any of the vibrational sub-levels associated with each electronic state. Since the energy is absorbed as discrete quanta, this should result in a series of distinct absorption bands. However, the simple diagram above neglects the rotational levels associated with each vibrational level and which normally increase the number of possible absorption bands to such an extent that it becomes impossible to resolve individual transitions.

Therefore, most compounds have broad absorption spectra except for those where rotational levels are restricted (for example, planar, aromatic compounds).

Having absorbed energy and reached one of the higher vibrational levels of an excited state, the molecule rapidly loses its excess of vibrational energy by collision

and falls to the lowest vibrational level of the excited state. In addition, almost all molecules occupying an electronic state higher than the second undergo internal conversion and pass from the lowest vibrational level of the upper state to a higher vibrational level of a lower excited state which has the same energy. From there the molecules again lose energy until the lowest vibrational level of the first excited state is reached.

From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. If this process takes place for all the molecules that absorbed light, then the quantum efficiency of the solution will be a maximum and unity. However, other route is followed the quantum efficiency will be less than one and may even be almost zero.

One transition, that is from the lowest vibrational level in the ground electronic state to the lowest vibrational level in the first excited state, the 0 – 0 transitions, is common to both the absorption and emission phenomena, whereas all other absorption transitions require more energy than any transition in the fluorescence emission. Therefore we can expect the emission spectrum to overlap the absorption spectrum at the wavelength corresponding to the 0 – 0 transitions and the rest of the emission spectrum to be of lower energy, or longer wavelength

In practice, the 0–0 transitions in the absorption and emission spectra rarely coincide exactly. The absorption of energy to produce the first excited state does not perturb the shape of the molecule greatly and this means that the distribution of vibrational levels is very similar in both the ground and first excited states. The energy differences between the bands in the emission spectrum will be similar to those in the absorption spectrum and frequently the emission spectrum will be approximate to a mirror image of the absorption spectrum. Since the emission of fluorescence always takes place from the lowest vibrational level of the first excited state, the shape of the emission spectrum is always the same, despite changing the wavelength of exciting light. A plot of emission against wavelength for any given excitation wavelength is known as the emission spectrum. If the wavelength of the exciting light is changed and the emission from the sample is plotted against the wavelength of exciting light, the result is known as the excitation spectrum. Furthermore, if the intensity of exciting light is kept constant as its wavelength is changed, the plot of emission against exciting wavelength is known as the corrected excitation spectrum. The quantum efficiency of most complex molecules is

independent of the wavelength of exciting light and the emission will be directly related to the molecular extinction coefficient of the compound; in other words, the corrected excitation spectrum of a substance will be the same as its absorption spectrum.

2.2.1 Fluorescent structure [7]

Compounds containing aromatic rings give the most intense and most useful molecular fluorescence emission. The aliphatic and alicyclic carbonyl compounds as well as highly conjugated double–bonded structures also fluorescence, their numbers are small in comparison with the number of fluorescent compounds which have aromatic systems. Most unsubstitued aromatic hydrocarbons fluoresce in solution, with the quantum efficiency increasing with the number of rings and their degree of condensation. The heterocyclics, such as pyridine, furan, thiophene, and pyrrole, do not exhibit molecular fluorescence, but fused–ring structures containing these rings often do. Substituted groups on an aromatic ring cause shift in the wavelength of absorption maxima and corresponding change in the fluorescence peaks. In addition, substitution frequently affects the fluorescence efficiency.

2.2.2 The Effect of structural rigidity

It is found experimentally that fluorescence is particularly favored in rigid molecules. For example, under similar conditions of measurement, the quantum efficiency of fluorine is nearly 1.0 whereas that of biphenyl is about 0.2. The difference in behavior appears to be largely a result of the increased rigidity furnished by the bridging methylene group in fluorine. This rigidity lowers the rate of nonradiative relaxation to the point where relaxation by fluorescence has time to occur. Many similar examples can be cited. The influence of rigidity has also been invoked to account for the increase in fluorescence of organic chelating agents when they are complexed with a metal ion. For example, the fluorescence intensity of 8-quinolinol is much less than that of the zinc complex.

2.2.3 Temperature and solvent effects

In most molecules, the quantum efficiency of fluorescence decreases with increasing temperature because the increased frequency of collision at elevated

temperatures improves the probability of collisional relaxation. A decrease in solvent viscosity leads to the same result.

nonfluorescing **fluorescing**

Figure 2-2 Effect of rigidity on fluorescence [7].

2.2.4 Applications of fluorescence methods

Fluorescence methods are generally methods which based upon absorption because the sensitivity of the former can use enhanced either by increasing the power of the excitation beam or amplifying the detector signal. Neither of these options improves the sensitivity of methods based upon absorption, however, increasing the amplification of the detector signal affects the two measured quantities in an identical way and leads to no improvement.

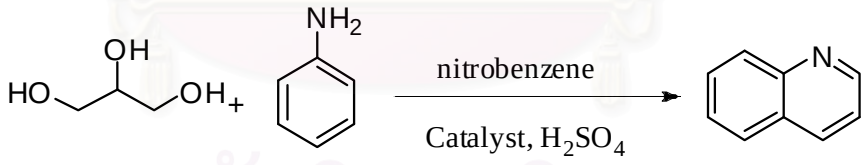
2.2.5 Methods for inorganic species [13]

Inorganic fluorometric methods are of two types. Direct methods are based upon the reaction of the analyte with a chelating agent to form a complex that fluoresces. In contrast, indirect methods depend on the quenching, of fluorescence of reagent as a result of its reaction with the analyte. Quenching used primarily for the determination of anions. The most successful fluorometric reagents for the determination of cations are aromatic compounds with two or more donor functional groups that permit chelate formation with the metal ion. A typical example is 8-quinolinol. The most of these reagents with the cation are extracted into a solution of the reagent in an immiscible organic solvent, such as chloroform. The fluorescence of the organic solvent is then measured. Nonradiative relaxation of transition–metal chelates is so efficient that most transition metals absorb in the ultraviolet or visible region, whereas nontransition metal ion do not. In this reason, fluorometry often complements ultraviolet/visible spectrophotometry as a method for the determination of cations.

2.3 8-hydroyquinoline [14,15]

8-hydroyquinoline, is an aromatic nitrogen compound characterized by a double-ring structure contains a benzene fused to pyridine at two adjacent carbon atoms. (Pyridine is a ring structure compound of five carbon atoms with a nitrogen atom). Quinoline itself is the simplest member of the quinoline. It is a hygroscopic, yellowish oily liquid; slightly soluble in water, soluble alcohol, ether, carbon disulfide and readily in many organic solvents. Quinoline can be prepared from aniline with acrolein under heated sulfuric acid (Skraup synthesis). Various quinoline compounds can be prepared by Skraup synthesis series of different oxidizing agents. Quinoline family compounds are widely used as a parent compound to make drugs (especially anti-malarial medicines), fungicides, biocides, alkaloids, dyes, rubber chemicals and flavoring agents. Hydroxyquinoline at 8- position is used as a bacteriostatic and fungistatic agent. It is used in preparing antiseptics, deodorants, antiperspirants, and fungicides. The sulfate salt of 8-hydroxyquinoline is used as a complexing agent for pharmaceuticals. 8-hydroxyquinoline is used as a precipitating agent or chelating agent to separate metals. It is also used in formulating anti-dandruff agents for shampoo.

2.3.1 8-hydroxyquinoline synthesis [16-18]



Scheme 2-1 Synthesis of quinoline.

Quinoline can be prepared by heating a mixture of aniline, glycerol, and sulfuric acid alone or with an oxidizing agent like nitrobenzene, arsenic acid, ferric oxide, and vanadic acid. With the use of nitrobenzene, the reaction, according to the original method, takes place with extreme violence. The procedure followed here gives higher yields than those obtained with the ferric oxide method and is the most satisfactory for the preparation of quinoline, but its homologs are preferably prepared by the use of arsenic acid because of the somewhat greater yields. The violence of the original nitrobenzene method may also be moderated by the use of acetic or boric

acid. Copper sulfate has been used as a catalyst in the Skraup synthesis, and the iron salt of *m*-nitrobenzenesulfonic acid has been employed as the oxidizing agent. Preliminary experiments on the boric acid method showed that the reaction runs smoothly but gives yields somewhat lower than those reported.

In the Skraup synthesis of quinoline the principal difficulty has always been the violence with which the reaction generally takes place; it occasionally proceeds relatively smoothly, but in the majority of cases gets beyond control, with consequent loss of material through the condenser. By the addition of ferrous sulfate, which appears to function as an oxygen carrier, the reaction is extended over a longer period of time. It is thus possible to work with much larger quantities of material when ferrous sulfate is employed.

In a number of experiments, the glycerol used contained an appreciable amount of water. Under these conditions, the yield of product is much lower. "Dynamite" glycerol containing less than one-half per cent of water is best employed; glycerol contains 5 per cent of water and usually gives lower yields.

It is important that the materials should be added in the correct order; should the sulfuric acid be added before the ferrous sulfate, the reaction may start at once. It is also important to mix the materials well before applying heat; the aniline sulfate should have dissolved almost completely, and the ferrous sulfate should be distributed throughout the solution. To avoid danger of overheating, it is well to apply the flame away from the center of the flask where any solids would be liable to congregate.

Much time can be saved by the use of the steam distillation, especially when large quantities have to be handled. The above directions avoid the use of extraction methods, which not only consume more time but may lead to appreciable losses of material. The percentage yields have been based on the amount of aniline taken. It would probably be more legitimate to base the calculation on the amounts of aniline taken and of nitrobenzene not recovered, since undoubtedly the latter is reduced to aniline during the course of the reaction. If this is done, the yield is found to be only 55 to 60 per cent of the calculated amount.

2.4 Cashew Nut Shell Liquid (CNSL) [19]

Cashew nut shell liquid (CNSL) is the international name of the alkylphenolic oil that present in nearly 25–30% of the total cashew nut weight inside the spongy

mesocarp of the shell (*Anacardium occidentale* L.). It occurs as a reddish brown viscous liquid in the soft honeycomb structure of the shell of cashew nut. CNSL is obtained as a by-product from mechanical processing for edible use of the cashew kernel. Since worldwide cashew nut production is presently estimated to be 1,200,000 tons per annum, the availability of CNSL ranges between 300,000–360,000 tons per annum.

CNSL is essentially a mixture of phenolics extracted from the shells of the cashew nut and is good natural alternatives to petrochemically derived phenol, a product whose price inherently linked to the fickle oil price and availability of fossil fuels. The major component of CNSL, depending slightly on the geographical location of the tree, is anacardic acid. It breaks down to give cardanol, which is essentially a phenol. Selected physical and chemical properties are shown in **Table 2-2** [20].

Table 2-2 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

2.4.1 Extracting process of CNSL [21]

Traditionally, Indian processors of cashew nuts roast them in an open perforated drum. CNSL either leaks away or is burnt in the fire. With increase in the price of CNSL, many refined extraction techniques have come into vogue.

Hot oil bath method

This is the most common method for commercial extraction. The raw nuts are passed through a bath of hot CNSL (180 - 200^{o}C) itself, when the outer part of the shell burst open and releases CNSL (50% recovery). Another 20% could be extracted

by passing the spent shells through an expeller and the rest by solvent extraction techniques.

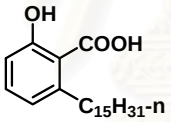
Expeller method

Some factories introduce manually operated cutting machines in which shell of lightly roasted nuts are cut, keeping the kernel intact. The shells are then fed to an expeller to recover 90% of the oil.

Klin method

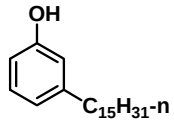
The nuts are shelled after sun drying or after drum roasting. The liquid is obtained however, crude is contaminated.

CNSL, extracted with low boiling petroleum ether, contains about 90% anacardic acid and about 10% cardol. On distillation, CNSL gives the pale yellow phenolic derivative cardanol. The chemical structures of major compounds in natural CNSL are shown in Scheme 2-11. The side chain exists in saturated (n=0), monoene (n=2), diene (n=4), and triene (n=6) that form with *cis* configuration.



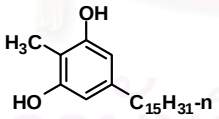
Anacardic acid

6-entadecenyl salicylic acid



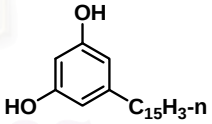
Cardanol

3-pentadecenyl phenol



2-methyl cardol

2-methyl-5-pentadecenyl resorcinol



Cardol

5-pentadecenyl resorcinol

where n= 0, 2, 4 or 6

Figure 2-3 Chemical structure of major compounds in natural CNSL.

2.4.2 Uses and applications

The CNSL is an undesirable by-product of the cashew kernel industry. This is an effective replacement of source and expensive petrochemicals. CNSL is described

often a versatile industrial raw material. It has wide application in the manufacture of numerous industrial products.

The CNSL of the cashew kernel or nutmeat is important in economic. In its natural state, it serves as a protection to the kernel against insect attack. If used in combination with kerosene or diesel oil, it is an effective insecticide against mosquito larvae [22]. Made into a varnish it is a preservation of wooden floors and fine carved wood, protecting from insect destruction [23]. For many years, fishermen have used the liquid to waterproof and preserve their fishnets, fishings lines and boats [24].

With recent advances in chemical technology, the CNSL is finding many new industrial applications. It is used commercially as a phenolic raw material for the manufacture of certain resin and plastics [25]. In particular, it is used as a friction modifier in the manufacture of brake linings and clutch facings. It has the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer [26]. It is also used in rubber compounds, where its acts as reinforcing fillers, which tensile strength, hardness and abrasion resistance are improved [27]. The resins from CNSL are used in laminating for papers, cloth and glass fibers, or impregnating materials where oil or acid resistance is required [28]. Other uses include the manufacture of lacquers, paints, printing inks, electrical insulation material, anti-corrosive for metals, water proofing compounds and adhesives [29].

2.5 Sources of industrial water pollution [30, 31]

In addition to its function in carrying off sewage produced by workers, water plays two main roles in manufacturing industries. It may serve as a source or sink for heat or it may be directly involved in some chemical process as a reactant, product or solvent. Table 2-1 has already made the distinction between cooling and process water use in industry. It is an important one because cooling water contains far fewer impurities in most cases, and usually is not treated. Among these are acid mine drainage and thermal pollution control, effluent from petroleum refining and oil spills, radioactive materials, solids and acid resulting from air pollution control, spent pickle liquor and other effluents associated with steel production, and contamination from other metals processing. Sulfuric acid is widely used in a great many chemical processes as well as in the manufacture of rubber and plastics. Spent solution must be

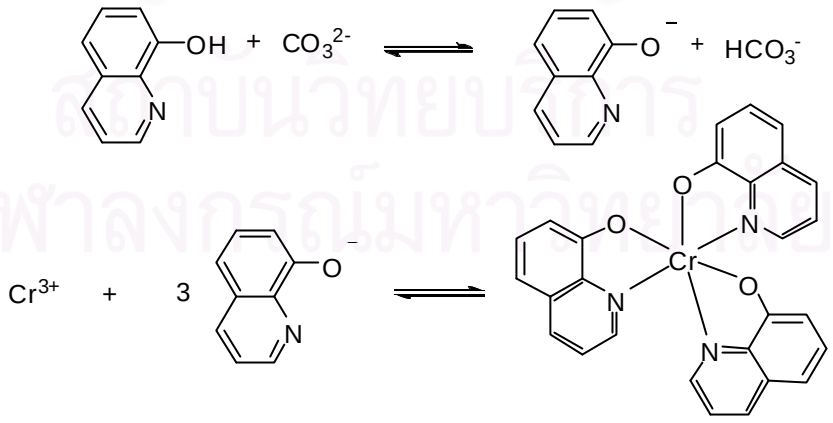
neutralized or recycled as in the case of pickle liquor. The same is true of sodium hydroxide (caustic) used in vegetable processing. Food processing also releases high concentrations of BOD from of objectionable materials such as entrails, grease and fat, which degrade slowly. Processing of natural textile fibers requires alkaline solutions and may lead to emission of impurities.

From all of these examples of industrial water pollution two–heavy metals and pulp and paper. Small quantities of a variety of metals are released by almost every industry. Since many of them are toxic and relatively little is known about their cycling in the biosphere, they constitute a very real problem. The pulp and paper industry uses more process water than any other in the United states, and its emissions often occur in otherwise unspoiled areas of natural beauty. It is hoped that the reader will be able to generalize from specific details on these two types of water pollution to others which have received less than complete treatment herein.

Table 2–1 Occurrence of metals or their compounds in effluents from various industries [31]

Industry	Metals																					
	Al	Ag	As	Au	Ba	Be	Bi	Cd	Co	Cr	Cu	Fe	Hg	In	Mn	Mo	Pb	Ni	Sb	Ti	U	Zn
Mining operations and ore processing	x		x					x					x		x	x	x				x	
Metallurgy and electroplating		x	x			x	x	x		x	x		x	x			x	x				x
Chemical industries	x		x		x			x		x	x	x	x				x				x	x
Dyes and pigments	x		x					x			x	x					x			x		
Ink manufacturing									x		x	x	x					x				
Pottery and porcelain			x							x									x		x	
Alloys						x								x								
Paint					x					x							x			x		x
Photography		x		x				x		x						x	x				x	
Glass			x		x				x									x		x		
Paper mills	x									x	x		x				x	x		x		
Leather tanning	x		x		x					x	x	x	x									x
Pharmaceuticals	x										x	x	x									
Textiles	x		x		x			x			x	x	x				x	x	x			
Nuclear technology						x		x						x							x	
Fertilizers	x		x					x		x	x	x	x		x		x	x				x
Chrolo–alkali production	x		x					x		x		x	x				x					x
Petroleum refining	x		x					x		x	x	x					x	x				x

The heavy metals which in industrial processes is illustrated nicely by Table 2–1. The every type of process involves release of least trace quantities of half a dozen or more metals in one form or another. Some techniques are available for removal of heavy metals from industrial effluents. Adjustments of pH can cause heavy metals to precipitate because many of their hydroxide has a good insoluble. Lime or limestone is often used for this purpose. The difficulty of hydroxide precipitation is problem of separating metals since many hydroxides are hydrophilic. This makes the complete removal of water rather difficult. If the metal to be recovered is valuable, electrodeposition techniques may be used to obtain it in pure form. A dilute solution may be concentrated by evaporation and then placed in an electrolytic cell. Scrap iron or shredded tin cans may be used to treat effluents containing metal ions such as Ni^{2+} and Cu^{2+} which are more easily reduced than Fe^{2+} or Fe^{3+}. Another important means of removing metals from fairly concentrated solutions is solvent extraction. It depends on the formation of chelate compounds between the metal ions and negatively charged ligands. When neutral compounds are formed they are usually soluble in nonpolar solvents which are immiscible with water. The metals may be transfer into the organic phase and removed from the water. Some common sequestering agents are ethylenediaminetetraacetic acid (EDTA), 8-quinolinol (8-hydroxyquinoline or oxine), nitrilotriacetic acid (NTA), and acetylacetone. As an example of the solvent extraction process, the following equations describe the reactions involved in the sequestration of chromium (III) by 8-hydroxyquinoline:



$$Cr(oxine)_3\,(aq) \rightleftharpoons Cr(oxine)_3\,(nonpolar\ solvent)$$

Scheme 2-2 Equation of chelation between chromium (III) and 8-hydroxyquinoline.

In addition to the methods just enumerated, ultrafiltration, ion exchange, activated carbon adsorption, and other techniques are often applied to industrial waste.

2.6 Literature reviews

J. S. Kim *et al.* [32]

Kim *et al.* studied the determination of water content in aprotic organic solvents which used 8-hydroxyquinoline derivative as base fluorescent probe.

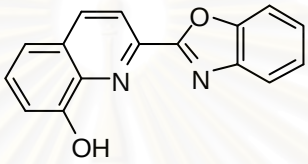


Figure 2–4 Structure of 8-hydroxyquinoline derivative (**i**).

8-hydroxyquinoline based benzoxazole derivative (**i**) was prepared by reaction between 8-hydroxy-2quinolinecarboxylic acid and 2-aminophenol in the present of polyphosphoric acid as catalyst at 150 ºC for 24 h under N_2 atmosphere. In this paper, they report the behavior of 8-hydroxyquinoline derivative (**i**) in florescence property for the determination of water content in aprotic organic solvents such as THF, dioxane and acetronitrile. Among the tested solvent, the highest sensitivity was observed for THF. Detection limits were found to be in between THF (0.006%) and dioxane (0.05%) that imply the fact that the compound may utilized for determination of water composition. The fluorescence was effectively quenched with small changes by specific solvent effects with water molecules. They concluded that 8-hydroxyquinoline derivative (**i**) may be used as chemosensing for probing of water content in aprotic organic solvents.

M. D. Prat *et al.* [6]

Prat *et al.* studied the fluorescence characteristics of chelating complex of 8-hydoxyquinoline and many metal ions, such as Al^{3+}, Ga^{3+}, Zn^{2+}, In^{3+} and Be^{2+} in many types of surfactant solution, for example cationic surfactant, anionic surfactant and nonionic surfactant. The chelating studies were observed in micellar media compared with hydroorganic solvent (MeOH). The result indicated that, Zn-(8-

hydroxyquinoline)$_2$ complex gave low fluorescence in anionic sodium lauryl sulfate media (anionic surfactant),which is the most difference other metal complexes.

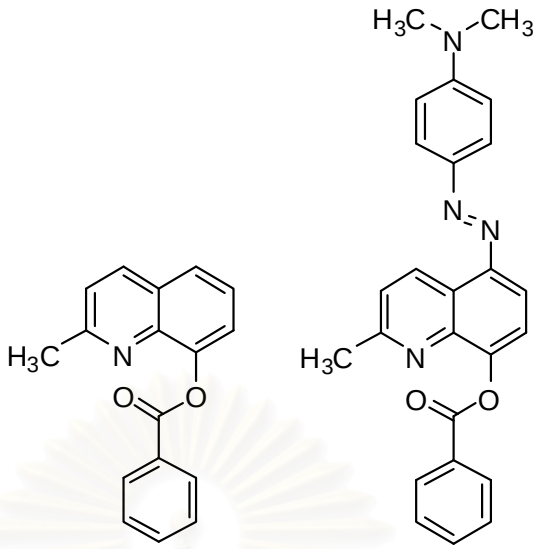
The results concluded that, the chemosensors give both photo-induced proton transfer (PPT) and photo-induced electron transfer (PET) which led to fluorescent quenching of the molecule. The result from x-ray crystal structure found that, the proton shift concomitant with complex formation between metals and chemosensor, inhibits the quenching of molecule.

K. Fujinaka. *et al.* [34]

In this paper, the authors developed the method for liquid-liquid extraction, which use hydrophilic solvents such as methanol. The combination of tetrahydrofuran and WOSEP (oil–water separator) which made by fibrous polypropylene was subjected to an extraction of complexation between 8-hydroxyquinoline and alkaline earth metals. It was found that, this method was useful to extract the alkaline earth metals other than Mg^{2+}, Ca^{2+} and Sr^{2+} in range of pH 11.2–13.9 and 10.6–13.9 with an extractability of more than 90%. It was reported that Mg^{2+}, Ca^{2+} and Sr^{2+}could be extracted at pH 10.8, 11 and 11.3. This method can extract alkaline earth metals in the form of hydrated 8-quinolinolato complexes.

Y-F. Cheng. *et al.* [35]

Cheng *et al* synthesized azo 8-hydroxyquinoline benzoate (**6**) in order to use as a new chemosensors for metal ions. They studied the effective of complexation of transition metals such as Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} Ni^{2+}, Co^{2+}, Cr^{2+}, Pb^{2+} Zn^{2+} and Ag^{+} and alkaline metals such as Na^{+}, K^{+} and Ca^{2+} in acetonitrile.



ii iii

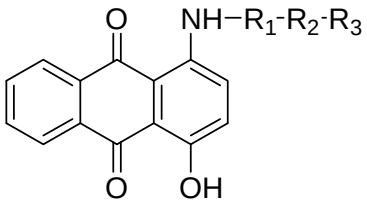
Figure 2–5 Molecular structure of new chemosensors **ii** and **iii**.

The results concluded that, compound **ii** was more distinguish color than compound **ii**. The compound **iii** gave difference selectivity, which gave out the chromogenic ability in the following order: Hg^{2+} > Cu^{2+}> Zn^{2+}, Cd^{2+} Ni^{2+}, Co^{2+}, Cr^{2+}, Pb^{2+} Zn^{2+}, Ag^{+}, Na^{+}, K^{+} and Ca^{2+} in acetonitrile.

Finally, the presence of transition metal ions Hg^{2+} or Cu^{2+} developed a selective chromogenic chemosensor because Hg^{2+} or Cu^{2+} complex was distinguished from other metal ions by the neked eye. The process recognition of Hg^{2+} gave rise to the obvious color change from yellow to red. The recognition process of Cu^{2+} consisted of two processes, and the color changed from yellow to pale red, then back to colorless. Such a design strategy would develop for metal ions as chemosensors.

Friswell, M.R. *et al.* [36]

Reported the synthesis of tagging markers with the following formula:

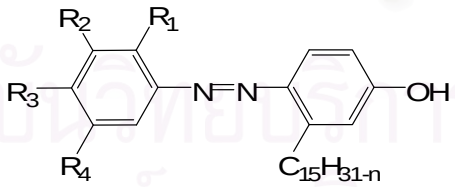


where R_1 is C_1-C_6 alkyl, and R_2 and R_3 are nothing or O-(C_1-C_3 alkyl)

These markers, which are known as “marker purple” were prepared by reaction of quinizarin, reduced quinizarin or mixture of quinizarin and reduced quinizarin with the amine formula, H_2N-$R_1R_2R_3$, wherein R_1, R_2 and R_3 are as define above. These compounds have purple colors but in the range from about 1-100 ppm, the markers impart little visible color to the petroluem products. The markers were detected in the petroleum products by the extraction with a reagent comprising water, a strong base and preferably a water soluble oxygenated cosolvent or a water-soluble amine cosolvent. This reagent causes the markers to react and produces a clearly defined color that allow the identification of petroleum products.

Suwanprasop, S. *et al.* [37]

Synthesized petroleum marker dyes from cardanol and aniline derivatives. The general formula is shown as follows:



where n = 0, 2, 4, 6; R_1 is H, NO_2, Cl, CH_3 or OCH_3; R_2 and R_3 are H, NO_2, Cl or CH_3 and R_4 is H or NO_2.

These monoazo dyes were prepared by coupling reaction of the diazonium salt of an aniline derivative with non-hydrogenated cardanol. Aniline derivatives in this study include aniline, 4-nitroaniline, 3-nitroaniline, 2-nitroaniline, 4-chloroaniline, 3-chloroaniline, 2-chloroaniline, 2-chloro-4-nitroaniline, 2-chloro-5-nitroaniline, 4-

chloro-2-nitroaniline, 4-chloro-3-nitroaniline, 4-methylaniline, 3-methylaniline, 2-methylaniline and 2-methoxy-4-nitroaniline. The synthetic compounds showed potential to be applied as marker for the commercial fuel oil such as gasoline and high-speed diesel fuel. These markers provided invisible color in gasoline and diesel fuel at 2–5 ppm, but gave visible color when extracted by 50% v/v 1,2-diaminoethane in a 1:1 v/v solution of ethane-1,2-diol:methanol. The marker dyes did not exhibit significant effects on the physical properties of fuel oil and were found to be stable in fuel oil for at least three months.

CHAPTER III
EXPERIMENTAL

3.1 Chemicals

1. Hydrogenated cardanol : A gift from Dr.Nantanit Wanichacheva
2. Sodium sulfate (anhydrous) : Merck
3. Triethylamine : Merck
4. Nitrogen gas : TIG
5. Methylene chloride : Distilled from commercial grade
6. Hexane : Distilled from commercial grade
7. Ethyl acetate : Distilled from commercial grade
8. Sodium chloride : Merck
9. Glycerol : Lab-scan
10. Sodium nitrite : Merck
11. Hydrazine hydrate : Aldrich
12. Oxalic acid : Fluka
13. Formic acid : Merck
14. Zinc dust : Fluka
15. Sulfuric acid : Merck
16. Sodium 3-nitrobenzensulfonate : Merck
17. Silica gel : Merck
18. Ammonium hydroxide solution : Merck
19. Chromic (III) nitrate standard solution : BDH chemicals Ltd.
20. Acetone : Merck
21. Chloroform : Merck
22. Tetrahydrofuran : Merck
23. Copper nitrite hexahydrate : Aldrich
24. Methanol : Merck
25. Glacial acetic acid : Merck
26. *p*-Toluenesulfonic : Fluka
27. Fuming nitric acid : Merck

3.2 Analytical instruments

Melting points were determined with a Stuart Scientific Melting Point SMP1 (Bibby Sterlin Ltd., Staffordshire, UK).

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 Varian Mercury NMR spectrometer operated at 400.00 MHz for ^{1}H and 100.00 MHz for ^{13}C nuclei (Varian Company, CA, USA). The chemical shifts (δ) were 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). The coupling constants (*J*) were reported in Hertz (Hz).

Mass spectra were recorded on Mass Spectrometer: Waters Micromass Quatto micro API ESCi (Waters, MA, USA.). Samples were dissolved in ethyl acetate and 50 μL was directly injected into Mass Spectrometer (Compound **6a**, **7** and **8**), and mass spectra of the 8–hydroxyquinoline derivative were recorded by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS).

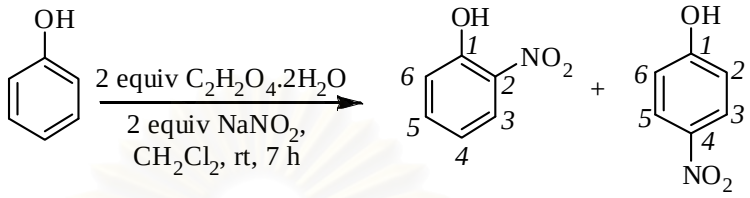
Absorption spectra and quantities of chromium complex in $CHCl_3$ were measured using a Perkin-Elmer (Lamda 2) UV/Vis spectrophotometer.

Fluorescence spectra were recorded on a Perkin Elmer LS 50 luminescence spectrophotometer. Wavelength was in the range of 400-800 nm and cell width was 1 cm.

3.3 Experimental procedure

Part 1: Synthesis of 8-hydroxyquinoline

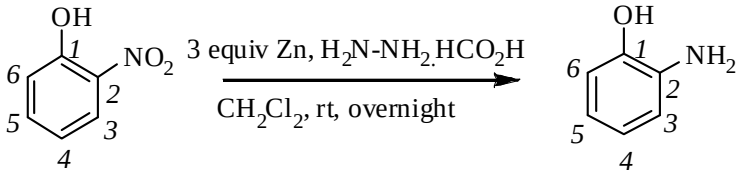
3.3.1 Synthesis of 2-nitrophenol (2a)



1 **2a** **2b**

Following a known procedure [38]**,** to a magnetically stirred solution of phenol (0.094 g, 1.0 mmol), oxalic acid (0.25 g, 2.0 mmol) and wet SiO_2 (2.0 g, 1:1 w/w in H_2O) in CH_2Cl_2 (20.0 mL), $NaNO_2$ (0.13 g, 2.0 mmol,) was added with vigorous stirring at room temperature. The reaction was completed after 7 h (monitored by TLC, CH_2Cl_2). The solvent was evaporated and the resulting mixture was mixed with silica gel. The resulting residue was chromatographed on a silica gel column eluted with dichloromethane to give 2-nitrophenol (**2a**) as bright yellow crystals (0.04 g, 29%). ^{1}H-NMR: δ (ppm) 6.94 (t, J=8.4, 1H, H_4), 7.10 (dd, J=8.5 Hz, 0.9 Hz, 1H, H_6), 7.53 (t, 8.6 Hz, 1H, H_5), 8.03 (dd, J=8.6 Hz, 1.5 Hz, 1H, H_3), 10.55 (s, 1H, *OH*), (**Figure A–1**); ^{13}C-NMR δ (ppm) 115.8(C_4), 119.9(C_6), 120.1(C_5), 125.1(C_3), 137.9(C_2), 155.2(C_1), (**Figure A–2**); and (**2b**) as red brown solid (0.09 g, 54%). ^{1}H-NMR: δ (ppm) 6.93 (d, J=8.7 Hz, 2H, H_2, H_6), 8.15 (d, J=8.7 Hz, 1H, H_3, H_5), (**Figure A–3**); ^{13}C-NMR: δ (ppm) 124.5(C_2), 124.5(C_6), 128.0(C_3),128(C_5), 142.0(C_4), 162.5(C_1), (**Figure A–4**).

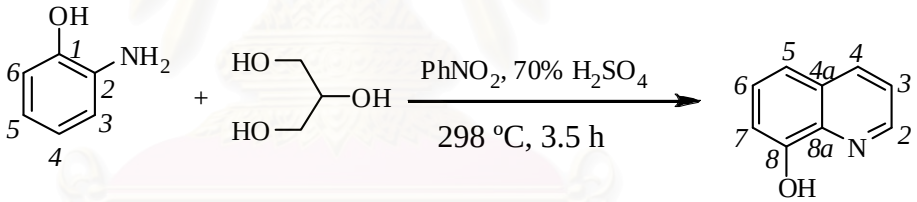
3.3.2 Synthesis of 2-aminophenol (3)



2a **3**

Following a known procedure [39], hydrazinium monoformate was freshly prepared by mixing equimolar amount of hydrazine hydrate and 85% formic acid in an ice–water bath slowly. The resulting solution (2.0 mL) was added into a suspension of compound **2a** (0.14 g, 1.0 mmol) and zinc dust (0.20 g, 3.0 mmol) in dichloromethane (50 mL) under nitrogen atmosphere at room temperature for 14 h. The organic layer was concentrated under reduced pressure and the residue was dissolved in ethyl acetate. The solution was washed with a saturated sodium chloride solution to remove the remaining hydrazinium monoformate. The organic layer was dried with Na_2SO_4, concentrated and purified by column chromatography (silica, CH_2Cl_2 + 1% TEA and then CH_2Cl_2:hexane (1:2) + 1% TEA), to obtain 2-aminophenol (**3**) as a yellow brown solid (0.04 g, 36%). ^{1}H-NMR: δ (ppm) 6.52 (s, 1H, H_5), 6.57–6.67 (m, 2H, H_4, H_6), 6.72 (d, J=7.3 Hz, 1H, H_3), (**Figure A–5**); ^{13}C-NMR: δ (ppm) 115.4(C_6), 117.8(C_3), 121.5(C_4), 130.8(C_2), 137.5(C_5), 142.5(C_1), (**Figure A–6**).

3.3.3 Synthesis of 8-hydroxyquinoline (4)



3 **4**

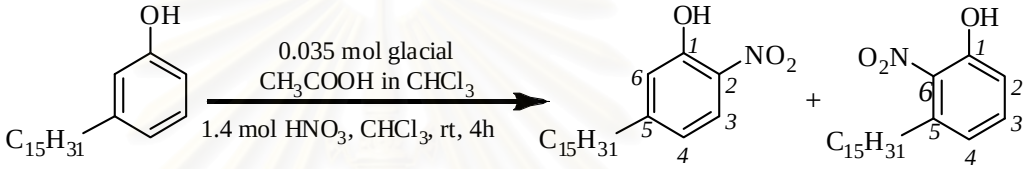
Following a published procedure [40], a mixture of H_2SO_4 (0.59 g, 6.0 mmol), H_2O (0.25 mL, 10 mmol), sodium 3-nitrobenzensulfonate (0.28 g, 10 mmol), glycerol (0.33 g, 10 mmol) and compound **3** (0.11 g, 1.0 mmol) was heated until it became homogenous. The mixture was stirred and heated slowly until boiled. This was continued at 298 °C for 3.5 h. After cooling down to room temperature, the reaction mixture was poured into water and adjusted to pH 8 with concentrate NH_4OH. The solution was purified by distillation. Compound **4** was obtained by filtration, which gave a white yellow crystals (0.05 g, 33%). ^{1}H-NMR: δ (ppm) 7.20 (d, J=7.6 Hz, 1H, H_7), 7.32 (d, J=8.2 Hz, 1H, H_3), 7.40–7.48 (m, 2H, H_6, H_5) 8.13 (d, J=8.3 Hz, 1H, H_4), 8.79 (d, J=3.9 Hz, 1H, H_2), (**Figure A**–7); ^{13}C-NMR: δ (ppm) 111.3(C_7), 116.3(C_5), 121.8(C_{4a}), 128.4(C_3), 135.5(C_4), 137.1(C_6), 143.0(C_{8a}), 147.0(C_2),

151.8(C_8), (**Figure A–8**); IR ν_{max}Ø 3324 (O – H st), 2919 (C – H st) cm^{-1}, (**Figure A–9**)

Part 2 Synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline from hydrogenated cardanol

3.3.4. Synthesis of 5-*n*-pentadecyl-2-nitrophenol (6a)

3.3.4.1 Synthesis of 5-*n*-pentadecyl-2-nitrophenol (6a) using fuming nitric acid and glacial acetic acid

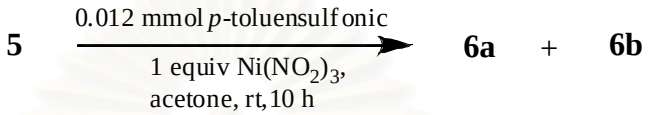


5 **6a** **6b**

Following a known procedure [41]**,** to a stirred solution of glacial acetic acid (2.0 mL, 35 mmol) and hydrogenated cardanol (**5**) (0.31 g, 1.0 mmol) in chloroform (4.0 mL), a stoichiometric amount of fuming nitric acid (0.08 mL, 1.4 mol) in glacial acetic acid (1.6 mL, 3.5 mmol) was added dropwise over 30 min at room temperature. After stirring for 4 h, a reaction mixture was dried over anhydrous sodium sulfate and solvent was evaporated under reduced pressure. After removal of solvent, the resulting residue was chromatographed on a silica gel column eluted with dichloromethane:hexane (1:3) to give 5-*n*-pentadecyl-2-nitrophenol (**6a**) as bright yellow crystals (0.05 g, 15 %). m.p. 43.4–44.2 ºC. ^{1}H-NMR: δ (ppm) 0.87 (t, *J*=6.8 Hz, 3H, CH_3), 1.19–18.38 (m, 24H, CH_2), 1.51–1.65 (m, 2H, ArCH_2CH_2), 2.62 (t, *J*=7.6 Hz, 2H, ArCH_2), 6.80 (dd, *J*=8.8 Hz, 1.6 Hz, 1H, H_4), 6.94 (d, *J*=1.6 Hz, 1H, H_6), 7.99 (d, *J*=8.8 Hz, 1H, H_3), 10.61(s, 1H, *OH*), (**Figure A–10**); ^{13}C-NMR: δ (ppm) 14.5, 23.1, 27.3, 29.3, 29.5, 29.6, 29.7, 29.8, 29.9, 30.1, 30.8, 32.3, 36.4, 119.1(C_f), 120.9(C_4), 125.0(C_5), 131.8(C_2), 154.6(C_3), 155.2(C_1), (**Figure A–11**); IR ν_{max}Ø cm^{-1} 3292 (O – H st), 2917 (C – H st), 1582 (N – O st), 1333 (N – O st), (**Figure A–12**) ESI-MS obsd 349.5580, calcd 349.5442 [M=$C_{21}H_{35}NO_3$], (**Figure A–13**), 3-*n*-pentadecyl-2-nitrophenol (**6b**) as bright yellow crystals (0.02 g, 6.0%). m.p. 50.0–51.7 ºC. ^{1}H-NMR: δ (ppm) 0.87 (t, *J*=6.7 Hz, 3H, CH_3), 1.20–1.45 (m, 24H, CH_2),

1.52–1.64 (m, 2H, $ArCH_2CH_2$), 2.90 (t, *J*=8.0 Hz, 2H, $ArCH_2$), 6.82 (d, *J*=7.4 Hz, 1H, H_4), 6.98 (dd, *J*=8.0 Hz, 0.9 Hz, 1H, H_6), 7.38 (t, *J*=8.0 Hz, 1H, H_5), 9.94 (s, 1H, *OH*), (**Figure A–14**); ^{13}C-NMR: δ (ppm) 14.3, 22.9, 27.1, 29.4, 29.5 29.6, 29.8, 29.9, 30.4, 30.8, 32.2, 34.7, 117.2(C_6), 123.0(C_4), 134.7(C_5), 135.5(C_3), 140.7(C_2), 154.5(C_1), (**Figure A-15**).

3.3.4.2 Synthesis of 5-*n*-pentadecyl-2-nitrophenol (6a) using $Ni(NO_3)_2{\cdot}6H_2O$ and *p*-toluenesulfonic acid



Following a published procedure [42]**,** to a vigorously stirred solution of **5** (0.31 g, 1.0 mmol) and *p*-toluenesulfonic (23 mg, 1.2 μmol) in acetone (15 mL), $Ni(NO_3)_2{\cdot}6H_2O$ (0.29 g, 1.0 mmol) was then added and the mixture was heated at 56 °C for 30 min. A reaction mixture was stirred at room temperature overnight. After that, the solvent was evaporated and the resulting crude product was purified in the similar manner as that described in method A to give compound **6a** in (0.11 g, 30%) yield, 3-*n*-pentadecyl-2-nitrophenol (**6b**) as bright yellow crystals (0.12 g, 33%). The characterization data were consistent with those obtained from method A.

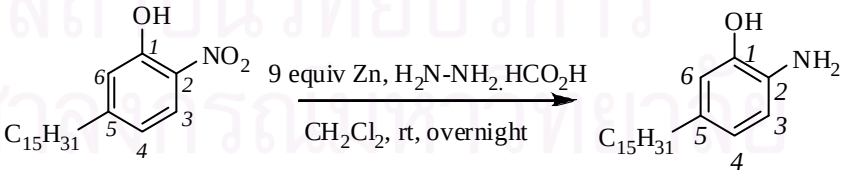
3.3.4.3 Synthesis of 5-*n*-pentadecyl-2-nitrophenol (6a) using $C_2H_2O_4{\cdot}2H_2O/NaNO_2$

6c

Following a known procedure [38], to a magnetically stirred solution of (**5**) (0.30 g, 1.0 mmol), oxalic acid (0.25 g, 2.0 mmol) and wet SiO_2 (2.0 g, 1:1 w/w in H_2O) in CH_2Cl_2 (20 mL), $NaNO_2$ (0.14 g, 2.0 mmol) was added with vigorous stirring at room temperature. The reaction was completed after 4 h. (monitored by TLC, CH_2Cl_2). The solvent was evaporated and the resulting mixture was mixed with silica gel. The resulting residue was chromatographed on a silica gel column eluted with

CH_2Cl_2:hexane (1:3) to give 5-*n*-pentadecyl-2-nitrophenol (**6a**) as bright yellow crystals (0.10 g, 27%). m.p. 43.4–44.2 ºC. ^{1}H-NMR: δ (ppm) 0.87 (t, *J*=6.8 Hz, 3H, CH_3), 1.19–1.38 (m, 24H, CH_2), 1.51–1.65 (m, 2H, $ArCH_2CH_2$), 2.62 (t, *J*=7.6 Hz, 2H, $ArCH_2$), 6.80 (dd, *J*=8.8 Hz, 1.6 Hz, 1H, H_4), 6.94 (d, *J*=1.6 Hz, 1H, H_6), 7.99 (d, *J*=8.8 Hz, 1H, H_3), 10.61(s, 1H, *OH*), (**Figure A–10**); ^{13}C-NMR: δ (ppm) 14.5, 23.1, 27.3, 29.3, 29.5, 29.6, 29.7, 29.8, 29.9, 30.1, 30.8, 32.3, 36.4, 119.1(C_6), 120.9(C_4), 125.0(C_5), 131.8(C_2), 154.6(C_3), 155.2(C_1), (**Figure A–11**); IR ν_{max}Ø cm^{-1} 3292 (O – H st), 2917 (C – H st), 1582 (N – O st), 1333 (N – O st), (**Figure A–12**) ESI-MS obsd 349.5580, calcd 349.5442 [M=$C_{21}H_{35}NO_3$], (**Figure A–13**), 3-*n*-pentadecyl-2-nitrophenol (**6b**) as bright yellow crystals (0.05 g, 14%). m.p. 50.0–51.7 ºC. ^{1}H-NMR: δ (ppm) 0.87 (t, *J*=6.7 Hz, 3H, CH_3), 1.20–1.45 (m, 24H, CH_2), 1.52–1.64 (m, 2H, $ArCH_2CH_2$), 2.90 (t, *J*=8.0 Hz, 2H, $ArCH_2$), 6.82 (d, *J*=7.4 Hz, 1H, H_4), 6.98 (dd, *J*=8.0 Hz, 0.9 Hz, 1H, H_6), 7.38 (t, *J*=8.0 Hz ,1H, H_5), 9.94 (s, 1H, *OH*), (**Figure A–14**); ^{13}C-NMR: δ (ppm) 14.3, 22.9, 27.1, 29.4, 29.5 29.6, 29.8, 29.9, 30.4, 30.8, 32.2, 34.7, 117.2(C_6), 123.0(C_4), 134.7(C_5), 135.5(C_3), 140.7(C_2), 154.5(C_1), (**Figure A-15**), 3-*n*-pentadecyl-4-nitrophenol (**6c**) as a brown solid (0.14 g, 39%) m.p. 70.0-71.4 ºC. ^{1}H-NMR: δ (ppm) 0.87 (t, *J*=6.7 Hz, 3H, CH_3), 1.21–1.40 (m, 24H, CH_2), 1.58–1.68 (m, 2H, $ArCH_2CH_2$), 2.89 (t, *J*=8.0 Hz 2H, $ArCH_2$), 6.71–6.78 (m, 2H, H_2, H_6), 7.97 (d, *J*=9.6 Hz, 1H, H_3), (**Figure A**-16); ^{13}C-NMR: δ (ppm) 14.1, 22.6, 29.4, 29.5, 29.6, 29.7, 29.8, 30.5, 31.9, 33.9, 113.6(C_6), 118.1(C_2), 128.0(C_5), 141.8(C_3), 142.0(C_4), 160.0(C_1), (**Figure A**-17).

3.3.5 Synthesis of 5-*n*-pentadecyl-2-aminophenol (**7**)

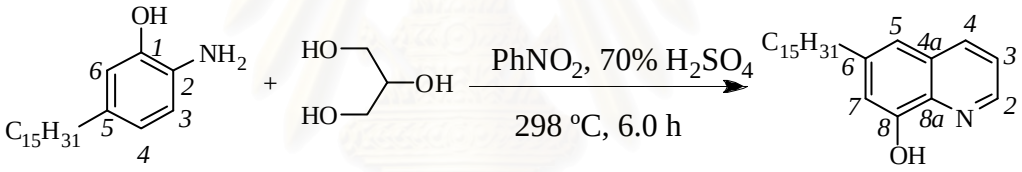


6a **7**

Following a known procedure [39], hydrazinium monoformate was freshly prepared by slowly mixing equimolar amount of hydrazine hydrate and 85% formic acid in an ice–water bath. The resulting solution (6.0 mL) was added into a suspension of compound **6a** (0.35 g, 1.0 mmol) and zinc dust (0.59 g, 9.0 mmol) in dichloromethane (50 mL) under nitrogen atmosphere at room temperature for 14 h.

The organic layer was concentrated under reduced pressure and the residue was dissolved in ethyl acetate. The solution was washed with a saturated sodium chloride solution to remove the remaining hydrazinium monoformate. The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography (silica, CH_2Cl_2 + 1% TEA, to obtain 5-*n*-pentadecyl-2-aminophenol (**7**) as a yellow brown solid (0.25 g, 90%). m.p. 114.1–115.4 ºC. ^{1}H-NMR: δ (ppm) 0.87 (t, *J*=6.7 Hz, 3H, CH_3), 1.21–1.28 (m, 24H, CH_2), 1.57–1.60 (m, 2H, $ArCH_2CH_2$), 2.45 (t, *J*=7.6 Hz, 2H, $ArCH_2$), 6.58–6.60 (m, 2H, H_3, H_6), 6.69 (d, *J*=8.2 Hz, 1H, H_4), (**Figure A–18**); ^{13}C-NMR: δ (ppm) 7.8, 14.2, 22.7, 29.2, 29.3, 29.5, 29.6, 29.7, 29.8, 31.7, 31.9, 35.2, 52.8, 115.5(C_6), 117.3(C_3), 120.7(C_4), 131.6(C_2), 135.1(C_5), 144.7(C_1), (**Figure A–19**); IR ν_{max}Ø cm^{-1} 3377 (N – H st), 3302 (O – H st), 2919(C – H st), (**Figure A–20**); HR–ESI–MS obsd 320.2900, calcd 320.2948 [$(M+H)^+$; M=$C_{21}H_{38}NO$], (**Figure A–21**).

3.3.6 Synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline (**8**)



7 **8**

Following a published procedure [40], a mixture of H_2SO_4 (0.59 g, 6.0 mmol), H_2O (0.25 mL, 10 mmol), sodium 3-nitrobenzensulfonate (0.28 g, 1.0 mmol), glycerol (4.00 g, 40 mmol) and compound **7** (0.32 g, 1.0 mmol) was heated until it became homogenous. The mixture was stirred and heated slowly until boiled. This was continued at 298 ^{o}C for 3.5 h. After cooling down to room temperature, the reaction mixture was poured into water and adjusted to pH 8 with concentrate NH_4OH. The solution was extracted with ethyl acetate. The organic phase was separated, dried over anhydrous sodium sulfate, filtered and concentrated to dryness. The resulting crude product was purified by chromatography (silica, ethyl acetate + 1% TEA) to give brown crystals (0.24 g, 71%). m.p. 68.0-69.0 ºC. ^{1}H-NMR: δ (ppm) 0.81 (t, *J*=5.9 Hz, 3H, CH_3), 1.18–1.25 (m, 24H, CH_2), 1.54–1.63 (m, 2H, $ArCH_2CH_2$), 2.45 (t, *J*=7.6 Hz, 2H, $ArCH_2$), 6.99 (s, 1H, H_7), 7.04 (s, 1H, H_5), 7.33 (m, 1H, H_4) 8.05 (d, *J*=8.3 Hz, 1H, H_7), 8.63 (d, *J*=3.9 Hz, 1H, H_3), (**Figure A–22**), ^{13}C-NMR: δ (ppm) 14.1, 22.7, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.1, 31.9, 36.5, 111.3(C_7), 116.3(C_5),

121.8(C_{4a}), 128.4(C_3), 135.5(C_4), 137.1(C_6), 143.0(C_{8a}), 147.0(C_2), 151.8(C_8), (**Figure A–23**); IR ν_{max}Ø cm^{-1} 3324 (O – H st), 2919 (C – H st), (**Figure 24**); ESI-MS obsd 356.2885, calcd 356.2948 [$(M+H)^+$; M=$C_{24}H_{38}NO$], (**Figure A–25**).

3.4 UV−Vis properties of compound 4 and compound 8

UV−Vis properties of 8-hydroxyquinoline and 6-*n*-pentadecyl-8-hydroxyquinoline were studied by using solvent such as CH_2Cl_2, THF and $CHCl_3$. The results were used in the study of fluorescent properties.

3.5 Fluorescent properties of compound 4, compound 8 and diesel fuel oil

Fluorescent properties of 8-hydroxyquinoline, 6-*n*-pentadecyl-8-hydroxyquinoline and diesel fuel oil were studied by using CH_2Cl_2 as solvent and the measuring parameters for fluorescent measurement were set as the followings:

- The wavelength of the excitation monochromator (λ_{ex}) was set at 241, 315, 382 and 600 nm.
- The response was set for one second.
- The photomultiplier tube voltage level (PMT Grain) was set at a medium level.
- The spectrum bandwidth of the emission monochromator (EM SBW) was set at 5.
- The spectrum bandwidth of the excitation monochromator (EM SBW) was set at 5.

Ideally, the useful fluorescent markers in the practice should have adequate solubility in diesel fuel, and strong intensity of fluorescent in the range of 400-800 nm, and the emission wavelength of fluorescent marker should not be interfered with the emission wavelength of diesel fuel. These markers should give the emission level when added to diesel fuel at extremely low levels, e.g. 1 ppm or less [43].

3.6 Use of compound 4 for determination of chromium (III) in water [44]

The method was developed for extraction of chromium (III) by compound **4**, from the mother-liquor. The colorimetric estimation of the extracted solution was carried out at 417 nm by UV/Vis spectrophotometer.

3.6.1 Preparation of chromium (III) solution

The chromic (III) nitrate standard solution (19.2 mmol/L) for atomic absorption spectroscopy was pipetted (520 μL) into the volumetric flack (10 mL). The solution was made up to volume by water. The standard solution contained 0.1 mM of chromium (III).

3.6.2 Preparation of stock solution of compound 4

A solution of compound **4** (0.51 g, 3.5mmol) in glacial acetic acid (2.9 mL, 2.0 M) was placed into beaker 12 mL of THF, and then neutralized with ammonium hydroxide, until precipitate was produced. The volume was made up with THF to 25 mL.

3.6.3 Preparation of stock solution (104 ppm) of chromium (III) complex

The solution of chromium (III), (1.0 mM, 10 mL), was taken into a 50 mL beaker. The stock solution of compound **4** (5 mL) was added into it and the mixture was heated on the hot plate at 40–50 ^{o}C for 5 minutes. The resulting solution was diluted with THF (5 mL) and the heating was continued for 10 minutes, after which it was cooled to room temperature. The whole mixture was transferred into a 100 mL separating funnel then $CHCl_3$ (10 mL) and saturated NaCl solution (20 mL) were added. After shaking, the organic layer was collected in the same beaker and $CHCl_3$ (5 mL) was added again. The process was repeated 2–3 times until complete removal of chromium complex ensured. The combined organic phase was dried over anhydrous sodium sulphate (4 g) and then waited for 10 minutes. The solution was transferred into a 50 mL volumetric flask where the volume was made up by $CHCl_3$.

3.6.4 Quantitative determination of chromium (III) complex

Quantitative determination of chromium (III) complex was carried out by a UV/Vis spectrophotometer at wavelength 417 nm. A standard calibration curve of chromium (III) complex was prepared as in **Table 3–1**.

Table 3–1 Volume of the stock solution (104 ppm) used to prepare 0-80 ppm chromium complex

Concentration (ppm)	Volume of 104 ppm stock solution (mL)
0.0	0.0
5.0	0.48
10	0.97
20	1.9
30	2.9
50	4.8
80	7.7

3.7 Use of compound 8 for determination of chromium (III) in water

The method was developed for extraction of chromium (III) by compound **8**, from the mother-liquor. The colorimetric estimation of extracted solution was carried out at 407 nm by UV/Vis spectrophotometer.

3.7.1 Preparation of chromium (III) solution

The chromic (III) nitrate standard solution (19.2 mmol/L) for atomic absorption spectroscopy was pipetted (256 μL) into the volumetric flack (10 mL). The solution was made up to volume by water. The standard solution contained 0.5 mM of chromium (III).

3.7.2 Preparation of stock solution of compound 8

A solution of compound **4** (0.04 g, 0.1 mmol) in glacial acetic acid (2.9 mL, 2.0 M) was placed into15 mL of MeOH, and then neutralized with ammonium hydroxide until precipitate was produced. Volume was made up with MeOH to 50 mL.

3.7.3 Preparation of stock solution (520 ppm) of chromium (III) complex

The solution of chromium (III), (0.5. mM, 10 mL), was taken into a 50 mL beaker. The stock solution of compound **8** (5 mL) was added into it and the mixture was heated on the hot plate at 40–50 ^{o}C for 5 minutes. The resulting solution was diluted with MeOH (5 mL) and the heating was continued for 10 minutes, after which it was cooled to room temperature. The whole mixture was transferred into a 100 mL separating funnel then $CHCl_3$ (10 mL) and saturated NaCl solution (20 mL) were added. After shaking, the organic layer was collected in the same beaker and $CHCl_3$ (5 mL) was added again. The process was repeated 2–3 times until complete removal of chromium complex ensured. The combined organic phase was dried over anhydrous sodium sulphate (4 g) and then waited for 10 minutes. The solution was transferred into a 50 mL volumetric flask where the volume was made up with $CHCl_3$.

3.7.4 Quantitative determination of chromium (III) complex

Quantitative determination of chromium (III) complex was carried out by a UV/Vis spectrophotometer at wavelength 407 nm. A standard calibration curve of chromium (III) complex was prepared as in **Table 3–2**.

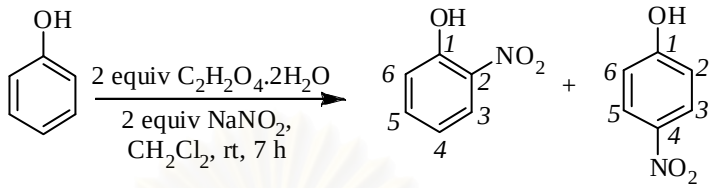
Table 3-2 The volume of the stock solution (520 ppm) used to prepare 0-520 ppm chromium complex

Concentration (ppm)	Volume of 104 ppm stock solution (mL)
0	0.00
20	0.380
50	0.960
150	2.90
200	3.84
300	5.76
400	7.70
520	10.0

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of ortho and para-nitrophenol



1 **2a** **2b**

Scheme 4-1 Synthesis of *o*-nitrophenol (2-nitophenol).

In this study, phenol was used as a model because cardanol had the core structure similar to that of phenol. This model was used to study the pattern of ^{1}H-NMR spectrum, ^{13}C-NMR spectrum and IR spectrum for cardanol in the next step. From ^{1}H-NMR spectrum (**Figure A-1**), a characteristic signal of –OH group of compound **2a** appeared at δ 10.55 while compound **2b** was not found. The proton had deshield effect from intramolecular hydrogen bonding between –H of hydroxyl group and =O of nitro group, as shown in **Figure 4-1**. From ^{13}C-NMR spectrum (**Figure A-2**), the characteristic signal of carbon bearing –OH group was found at δ 155 and $–NO_2$ group at δ 134. The %yield of compound **2a** and **2b** were shown in **Table 4-1**.

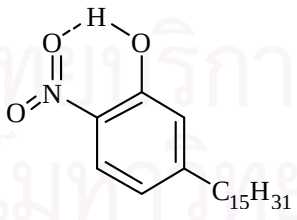


Figure 4-1 Intramolecular hydrogen bonding of compound **2a**.

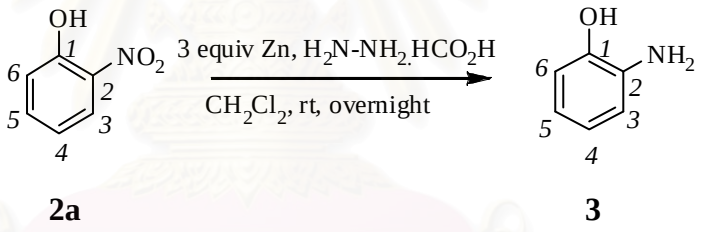
Table 4-1 Various conditions for the synthesis of compound **2a**

reactant (mmol)	mol ratio of nitrating agent*	%yield		
		2a	**2b**	**all**
1 (M)	1	27.4	34.0	61.4
1 (M)	2	28.8	54.3	83.1

* nitrating agents = $C_2H_2O_4 \cdot 2H_2O$, $NaNO_2$ in CH_2Cl_2

From these experiments, the suitable condition for synthesis of compound **2a** (Model) was condition 2 which used 1:2 ratio of reactant and nitrating agent. The reaction proceeded at room temperature under mild conditions and gave compound **2a** in 29% and compound **2b** in 54%.

4.2 Synthesis of ortho-aminophenol

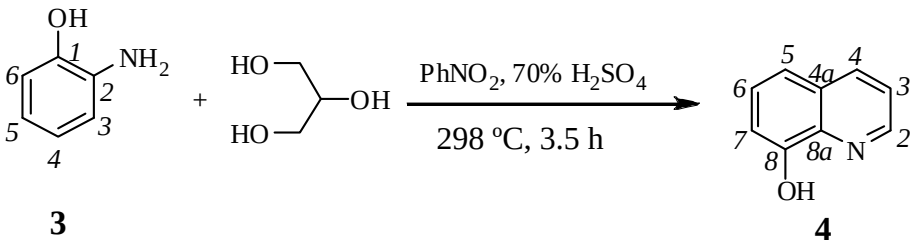


2a **3**

Scheme 4-2 Synthesis of *o*-aminophenol (2-aminophenol).

In this study, zinc dust and hydrazinium monoformate were used as a reducing agent to convert nitro compound to amino compound in nitrogen atmosphere at room temperature, with 1:3 mole ratio of reactant and reagent. The method gave compound **3** in 36%. From the NMR-spectra, the ^{1}H-NMR-spectra was the same as that of the commercial product. The ^{1}H-NMR-spectra in **Figure A-5** indicated that a characteristic signal of intramolecular hydrogen bonding disappeared.

4.3 Synthesis of 8-hydroxyquinoline

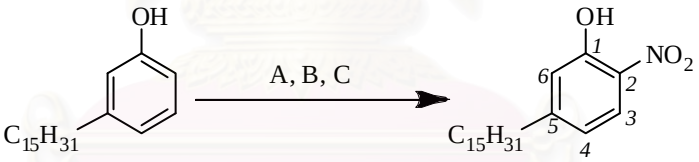


3 **4**

Scheme 4-3 Synthesis of 8-hydroxyquinoline.

In this study, the reaction consisted of compound **3** with glycerol in nitrobenzene as a solvent and 70% sulfuric acid as catalyst. The purification of product was distilled by steam distillation. The method gave compound **4** in 33%. Compound **4** could be distilled with steam because compound **4** formed hydrogen bond with water and volatiled with steam.

4.4 Synthesis of 5-*n*-pentadecyl-2-nitrophenol (6a)



5 **6a**

Scheme 4-4 Synthesis of 5-*n*-pentadecyl-2-nitrophenol (**6a**).

The nitration of cardanol and 3–*n*–pentadecylphenol were carried out using various reagents as shown in **Table 4–2**.

Table 4-2 Nitration of 3-*n*-pentadecylphenol by various methods

Method	**Condition**	**Time (h)**	**%yield**		
			6a	**6b**	**all**
A	Fuming HNO_3, glacial CH_3COOH**,** chloroform	4	15	7	22
B	$Ni(NO_3)_2 \cdot 6H_2O$, *p*-TSA**,** acetone	10	30	24	54
C	$NaNO_2$, $C_2H_2O_4 \cdot 2H_2O$, wet SiO_2, THF	5	35	14	49

According to the result in **Table 4-2**, method C gave the highest yield. Therefore, method C was chosen for nitration of 3-*n*-pentadecylphenol.

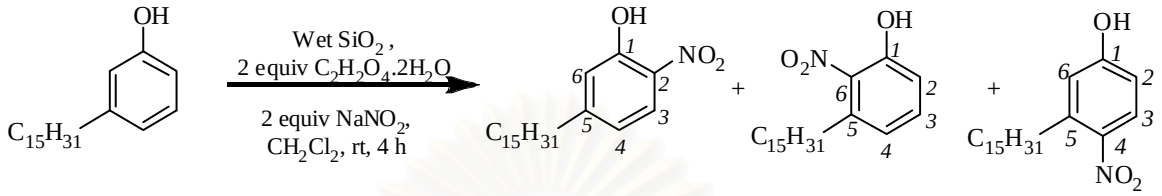
Table 4-3 Nitration of cardanol and 3-*n*-pentadecylphenol by various nitrating agents

Method	**%yield**	
	2–nitrocardanol	**5–*n*–pentadecyl–2–nitrophenol (6a)**
A	9	15
B	23	30
C	25	35

In this work, a mononitration of cardanol which gave moderate yield of *o*-nitrocardanol (**6a**) was described. A comparison between the use of hydrogenated cardanol and that of cardanol as a starting material was made to study the effect of double bond in an alkyl chain. The results in **Table 4-3** showed that the nitration of hydrogenated cardanol gave better yield than that of cardanol. It was likely that the

presence of double bonds in the cardanol alkyl chain gave rise to the side products and, hence, reduced the yield.

4.4.1 Optimization for the synthesis of 5-*n*-pentadecyl-2-nitrophenol (6a) by method C



5 **6a** **6b** **6c**

Scheme 4-5 The synthesis of 5-*n*-pentadecyl-2-nitrophenol (**6**) by method C.

The optimization to synthesize 6a using method C was carried out which consisted of the hydrogenated cardanol, $C_2H_2O_4 \cdot 2H_2O$ and $NaNO_2$ as nitrating agent, SiO_2 as solid support, and water as medium for $C_2H_2O_4 \cdot 2H_2O$ and $NaNO_2$. The mole ratio between reactant and reagents, solvent and time were varied. The total results of various conditions were reported in **Table 4–4**.

4.4.2 Effect of the mole ratio between 3-*n*-pentadecyl-phenol and nitrating agents

In this nitration step, the effect of mole ratio between reactant and nitrating agent in the same condition was observed. It was found that, the suitable ratio of reactant: reagents are 1:2 because this ratio gave the highest yield.

4.4.3 Effect of solvent type

In this step, type of solvents was investigated. It was found that, at 12 h, mole ratio 1:2, CH_2Cl_2 gave compound **6a** in 27%. Therefore, CH_2Cl_2 was chosen for this reaction. However, effect of polar solvent and non polar solvent was also studied and the result is shown in **Table 4-4**.

4.4.4 Effect of time

It was found that, the mole ratio of 1:2 in CH_2Cl_2 gave total yield of 79-82 % in 4 h. to 12 h. The suitable time for the reaction was 4 h.

Table 4-4 Various conditions for the synthesis of nitro compounds **6a**-**6c**

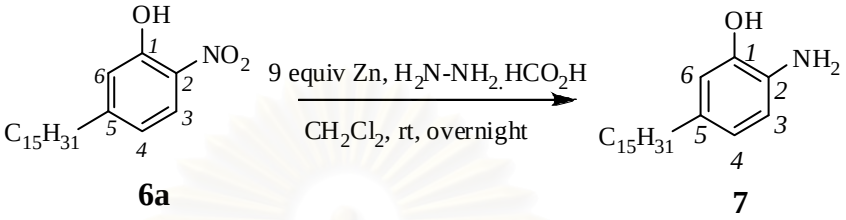
entry	mole ratio reactant : nitrating agent*	SiO_2	Solvent	time (h)	%yield			
					6a	6b	6c	all
1	1:1	2 g	CH_2Cl_2	4	20.0	16.2	36.0	72.2
2	1:2	2 g	CH_2Cl_2	4	26.7	13.5	38.5	78.7
3	1:2	2 g	THF	4	6.8	35.9	14.9	57.6
4	1:1	2 g	CH_2Cl_2	5	25.2	15.9	36.1	77.2
5	1:2	2 g	CH_2Cl_2	5	26.5	15.5	39.7	81.7
6	1:2	2 g	THF	5	34.9	14.3	40.5	89.7
7	1:1	2 g	CH_2Cl_2	6	23.9	14.6	39.2	77.7
8	1:2	10 g	CH_2Cl_2	6	24.2	15.4	40.1	79.7
9	1:2	2 g	THF	6	25.9	15.8	38.9	80.6
10	1:1	2 g	CH_2Cl_2	12	19	14.9	41.4	75.3
11	1:2	2g	CH_2Cl_2	12	26.9	9.3	44.3	80.5
12	1:2	2g	THF	12	18.8	13.8	43.6	76.2
13	5:10	10 g	CH_2Cl_2	12	31.7	16.7	39.9	88.3

* nitrating agent = $C_2H_2O_4{\cdot}2H_2O$ and $NaNO_2$

From **Table 4–4** and entries 10–11, the synthesis of **6a** was successfully performed by using $C_2H_2O_4{\cdot}2H_2O$, $NaNO_2$ as nitrating agents in mole ratio of 1:2 and wet SiO_2 as solid support in CH_2Cl_2, affording 5-*n*-pentadecyl-2-nitrophenol (**6a**) in 27% yield, 3-*n*-pentadecyl-2-nitrophenol (**6b**) in 16%, and 3-*n*-pentadecyl-4-nitrophenol (**6c**) in 40%. However, when THF was used as solvent in the same condition at 5 h, the

highest yield of compound **6a** was obtained at 35%yield, the same yield of compound **6b** at 14%, and compound **6c** at 41% and the results were shown in **Table 4-4**.

4.5 Synthesis of 5-*n*-pentadecyl-2-aminophenol (7)



6a **7**

Scheme 4-6 Synthesis of 5-*n*-pentadecyl-2-aminophenol.

Table 4-5 Condition for the synthesis of compound **7**

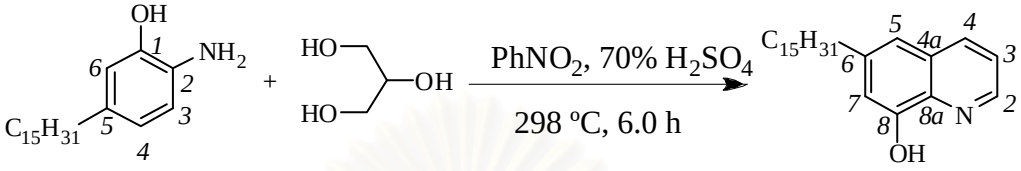
entry	mole ratio of reactant:reducing agent*	%yield
1	1:1	6.0
2	1:2	24
3	1:3	33
4	1:6	50
5	1:9	90

* =hydrazinium monoformate (hydrazine hydrate + formic acid 85%, in 1:1 equal mol)

In this study, the reduction of compound **6a** in the presence of zinc dust and hydrazinium monoformate was completed in 14 h. which the mole ratio of compound **6a** and reducing agent as 1:9 at room temperature. The progress of reaction was monitored by TLC. The reaction gave compound **7** in 90% which was characterized by ^{1}H-NMR, ^{13}C-NMR, IR spectra and ESI-MS mass spectra. In ^{1}H-NMR, the difference between compound **6a** and compound **7** was that the peak at δ (ppm) = 10.61 (1H, s, *OH*) from intramolecular hydrogen bonding of compound **6a** disappeared in ^{1}H-NMR spectra of compound **7**. In addition peaks at δ 6.80, 6.94 and 7.99 were shifted to 6.58–6.60 and 6.69, respectively. In conclusion, the reduction of compound 7 could be achieved by

using zinc dust instead of platinum or palladium, without affecting the reduction of any substituents [37].

4.6 Synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline (8)



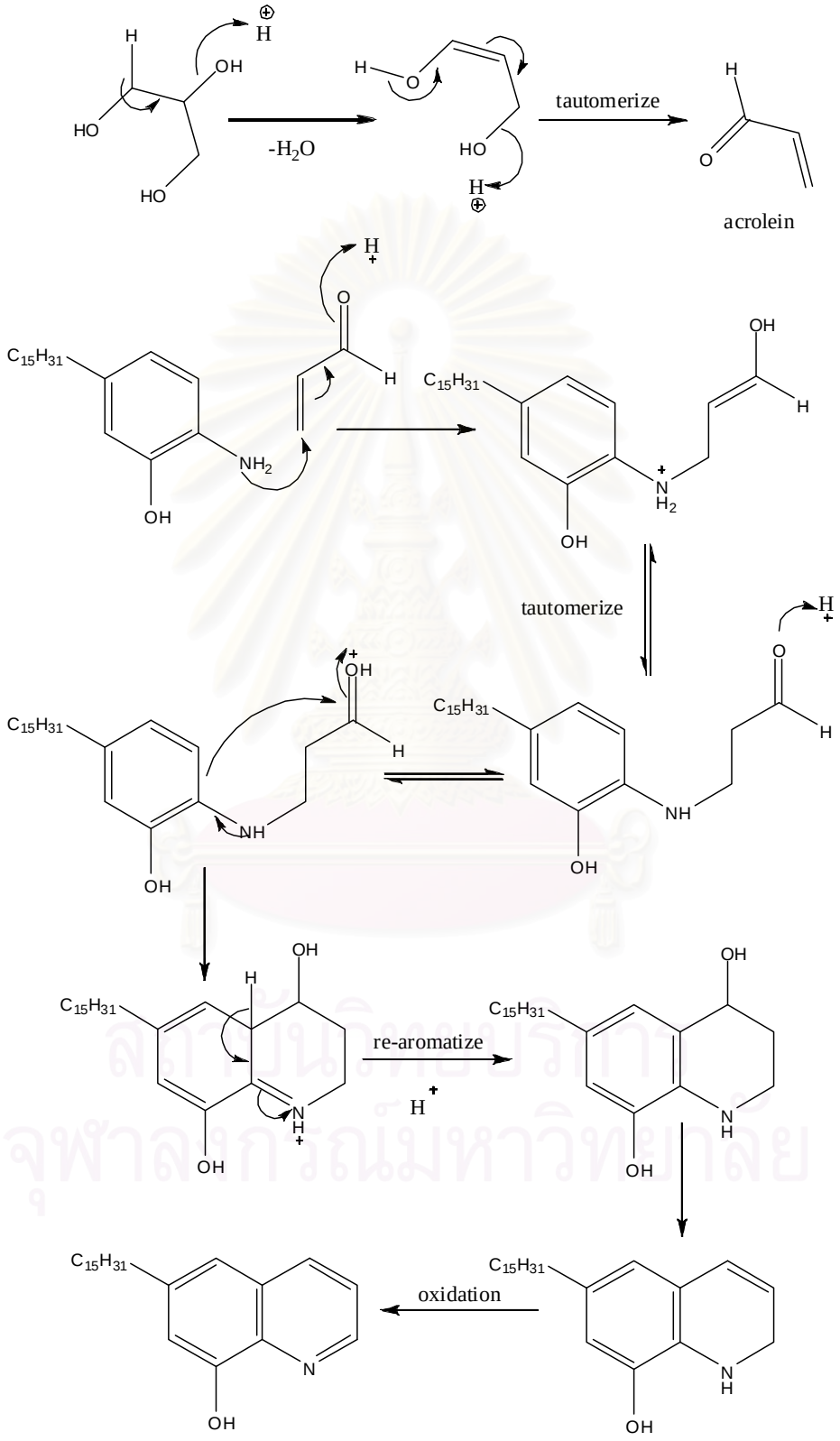
7 **8**

Scheme 4-7 Synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline.

Table 4-5 Condition for the synthesis of compound **8**

entry	sulfuric acid	glycerol (mole)	time	%yield
1	70%	20	3.5	42
2	70%	40	6.0	71
3	50%	20	3.5	22
4	98%	20	3.5	-

In this study, the synthesis of 6-*n*-pentadecyl-8-hydroxyquinoline was achieved by the Skraup synthesis which started with 5-*n*-pentadecyl-2-aminophenol (**7**) and glycerol in nitrobenzene compound as a solvent and 70% sulfuric acid. The purification of product was carried out by column chromatography. The procedure gave compound 8 in 71%. The proposed mechanism for the synthesis of compound **8** was shown in **Scheme 4-8** [44]. It was found that concentration sulfuric acid (98%) caused the destruction of alkyl side chain, and Friedel-Craft reaction was the side reaction [45].



Scheme 4-8 Proposed the mechanism of the 6-*n*-pentadecyl-8-hydroxyquinoline.

Compound **8** was synthesized under the optimized condition to improve the yield up to 71%. From ^{1}H-NMR spectrum, the pattern of ^{1}H-NMR-spectrum was similar to that of commercial product. (**Figure A-15**).

4.7 UV–Vis and fluorescent properties of 8-hydroxyquinoline and 6-*n*-pentadecyl-8-hydroxyquinoline

The λ_{max} of compound **8** was 341 nm, while compound **4** had λ_{max} at 315 nm. In addition, the presence of 6-*n*-pentadecyl-8-hydroxyquinoline was confirmed by the presence of the similar peak at 241 nm in UV-Vis spectrum which was the same as the 8-hydroxyquinoline. This peak was the secondary principle absorption bands of 8-hydroxyquinoline compounds. It is more intense and sharper in the range of 237 to 247 nm. (**Figure B-1**).

Fluorescent properties of 8-hydroxyquinoline and 6-*n*-pentadecyl-8-hydroxyquinoline were shown in **Table 4-9**.

The excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of 8-hydroxyquinoline (**4**), 6-*n*-pentadecyl–8–hydroxyquinoline (**8**) and unmarked diesel fuel in dichloromethane were shown in **Figure B-5** and **B-6,** respectively. These spectra indicated that the excitation at 315 and 382 nm were interfered with the emission of diesel fuel. In addition, the decreasing intensity of diesel fuel when added compound (**8**) was also observed. Therefore, compound 8 was not suitable to be used as a marker in diesel fuel.

Table 4-6. The summarized excitation wavelength (λ_{ex} nm) and emission wavelength (λ_{em}, nm) of compound (**4**) and compound (**8**) in CH_2Cl_2

compound	Excitation (nm)	Emission (nm)
8-hydroxyquinoline, compound (**4**)	241	-
	315	-
	382	510
	600	-
6-*n*-pentadecyl-8-hydroxyquinoline, compound (**8**)	241	-
	315	-
	382	440
	600	-
Diesel fuel oil	241	-
	315	380
	382	419
	600	-
Diesel + compound (**8**)	241	-
	315	376
	382	419
	600	-

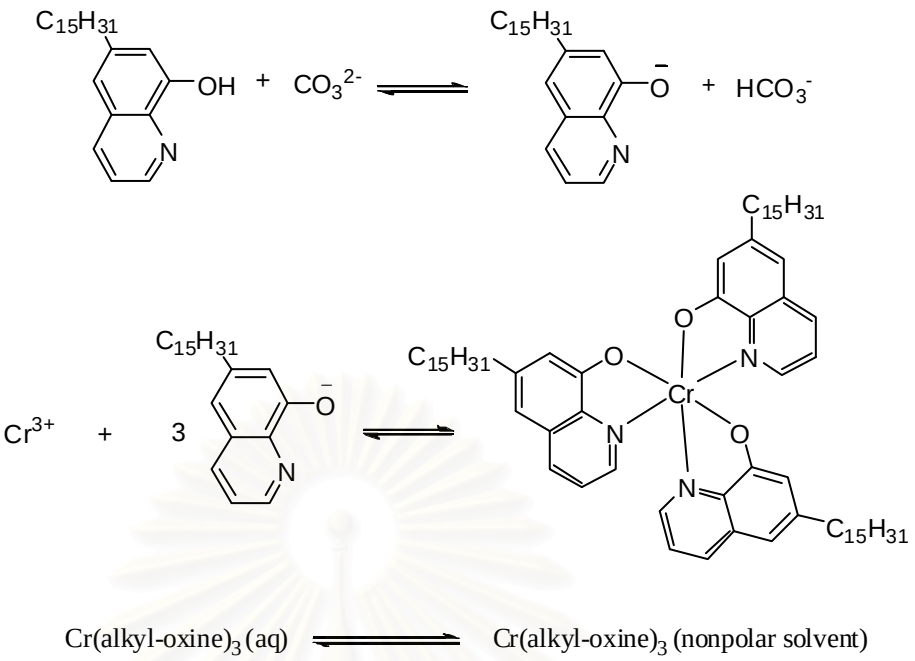
4.7.1 Quenching of fluorescent marker in diesel

From the UV-Vis spectra at excitation wavelength at 315 nm in **Figure B-5**, the intensity of diesel peak + 6-*n*-pentadecyl-8-hydroxyquinoline (**8**) was decreased when compared with intensity of diesel peak. The same situation was taken place at excitation wavelength at 382 nm in **Figure B-6** and Cu-8-hydroxyquinoline complex in diesel oil in **Figure B-7**. The decreasing of intensity was called quenching which had many types. In this case, the static quenching was assumed. The static quenching was the case when

quencher formed a complex with analyte, which gave non-fluorescence or low-fluorescence. Because of the composition of diesel fuel contained the aromatic compounds, hydrocarbon compounds thus it was expected that aromatic molecules formed complexes with compound **8**. It was reported that the alkane solution promoted the dimer formation of 8-hydroxyquinoline [46], which gave the low quantum yield as shown in **Figure B-8** and **Figure B-9**. In addition, the similar behavior of 7-hydroxyquinoline in benzene was also reported [46].

4.8 Chelating agent properties of 8-hydroxyquinoline (compound 4) and 6-*n*-pentadecyl-8-hydroxyquinoline (compound 8)

In order to find another application of 8-hydroxyquinoline, chelating property of 8-hydroxyquinoline was investigated. Generally, 8-hydroxyquinoline is the name most frequently used in the analytical literature; the trivial name oxine is very convenient, particularly for the description of the chelate compounds, which may be called oxinated. Information about chelate compounds of oxine with group IV element is complete. The only divalent ion of this group that certainly forms the normal oxinate is divalent lead. The only simple chelate compound obtainable is chromic (III) oxinated, as shown in **Scheme 4-9**.



Scheme 4-9 The complexation of 6-*n*-pentadecyl-8-hydroxyquinoline and chromium (III).

The procedure of examine the Cr (III) was followed by a known procedure [41]. It was found that 8-hydroxyquinoline model could form complex with Cr (III) in THF as shown in **Figure B-10**, the complex was extracted with $CHCl_3$ and measured by UV-Vis spectroscopy at 417 nm. This procedure was applied for 6-*n*-alkyl-8-hydroxyquinoline (compound **8**), using MeOH as solvent. Therefore, the mixture was extracted with $CHCl_3$ and was measured by UV-Vis spectroscopy at λ_{max} 407 nm. The UV-Vis spectra as shown in **Figure B-12**.

4.9 Quantitative determination of chromium (III) complex

4.9.1 Quantitative determination of chromium (III) oxinated complex

A standard calibration curve of chromium (III) oxinated in chloroform was prepared by plotting absorbance at 417 nm of series of the solution of chromic oxinated complex in chloroform with the concentration ranging from 0 to 104 ppm (**Figure B-11**).

The standard calibration equation of chromic oxinated complex in chloroform was found to be Y = 0.006X with the correlation coefficient equal to 0.9995. This equation was used to evaluate chromium (III) ions.

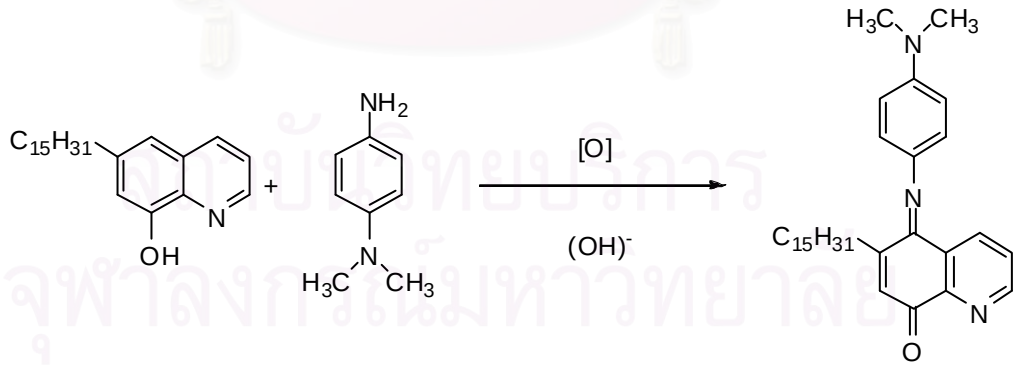
4.9.2 Quantitative determination of chromium (III) 6-alkyl-oxinated complex

A standard calibration curve of chromium (III) oxinate in chloroform was prepared by plotting absorbance at 407 nm of series of the solution of chromic 6-alkyl-oxinate complex in chloroform with the concentration ranging from 0 to 520 ppm (**Figure B-13**).

The standard calibration equation of chromic 6-alkyl-oxinate complex in chloroform was found to be Y = 0.001X with the correlation coefficient equal to 0.9986. This equation was used to evaluate chromium (III) ions.

4.10 Future work

Even though, compound **8** could not be used as fluorescent marker in diesel oil, it may be possible to be used as marker and detected via indoaniline reaction [2] as shown in **Scheme 4-10**.



9

Scheme 4-10 The indoaniline reaction of compound **8**.

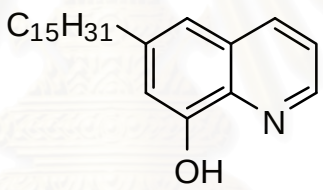
Oxidation with potassium dichromate of compound **8** and *N, N* – dimethyl–*p* – phenylenediamine gave a blue compound **9**. Thus the detail of this reaction should be studied in more detail.

CHAPTER V

CONCLUSION

The synthesis of 8-hydroxyquinoline model had been successfully performed by using 2-aminophenol as starting material reacted with glycerol in 70% H_2SO_4 containing 3-nitrobenzensulfonic acid sodium salt as solvent. The reaction was refluxed for 6 h. followed by adjusting pH with NH_4OH. The desired 6-*n*-pentadecyl-8-hydroxyquinoline was performed followed a model synthetic pathway in the synthesis of 8-hydroxyquinoline from cardanol.

The synthesis started from the nitration of hydrogenated cardanol and reduction of the nitro group 6-*n*-pentadecyl-8-hydroxyquinoline. The product (**8**) was successfully prepared from the Skraup synthesis of the aniline precursor and glycerol under catalysis of 70% H_2SO_4 in 71 % yield.



As expected, compound **8** showed high solubility in common organic solvents and diesel due to the presence of long alkyl chain. The fluorescent emission of compound **8** was indistinguishable from diesel fuel when added at the concentration of 5-10 ppm. At this concentration, compound **8** exhibited an obvious fluorescence (440 nm) in the same range of diesel fuel (419 nm) and compound **8** was quenching in this range. However, 6-*n*-pentadecyl-8-hydroxyquinoline could be used as chelating agent for a simple UV-Vis spectroscopy method for the determination of Cr (III) ions. The 6-*n*-pentadecyl-8-hydroyquuinoline reagent was chelated with Cr (III) to form Cr-(6-alkyl-8-hydroxyquinoline)$_3$ complex, which was extracted with $CHCl_3$ and measured at 407 nm. According to above properties, it was concluded that compound **8** was suitable for being a chelating agent for chromium (III) in water.

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APPENDICES

APPENDIX A

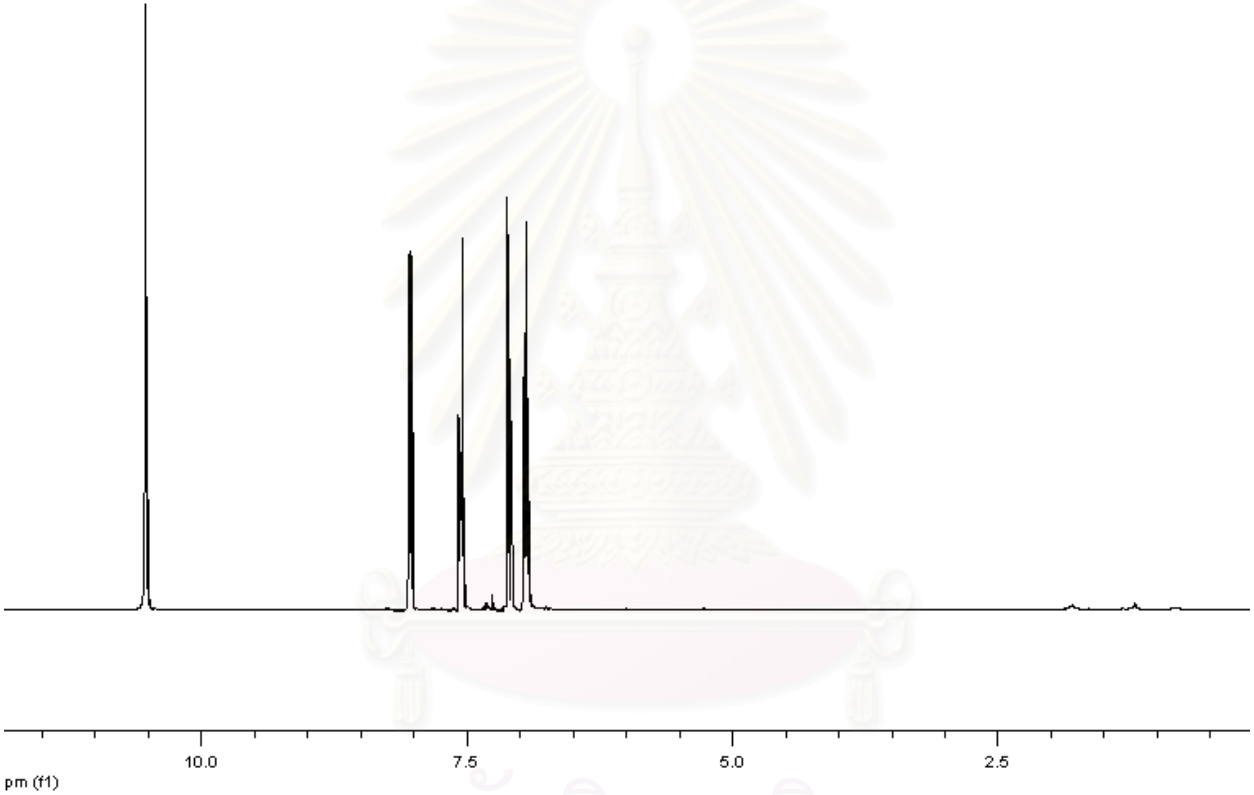

Figure A-1 ^{1}H-NMR spectrum of 2-nitrophenol (compound **2a**).

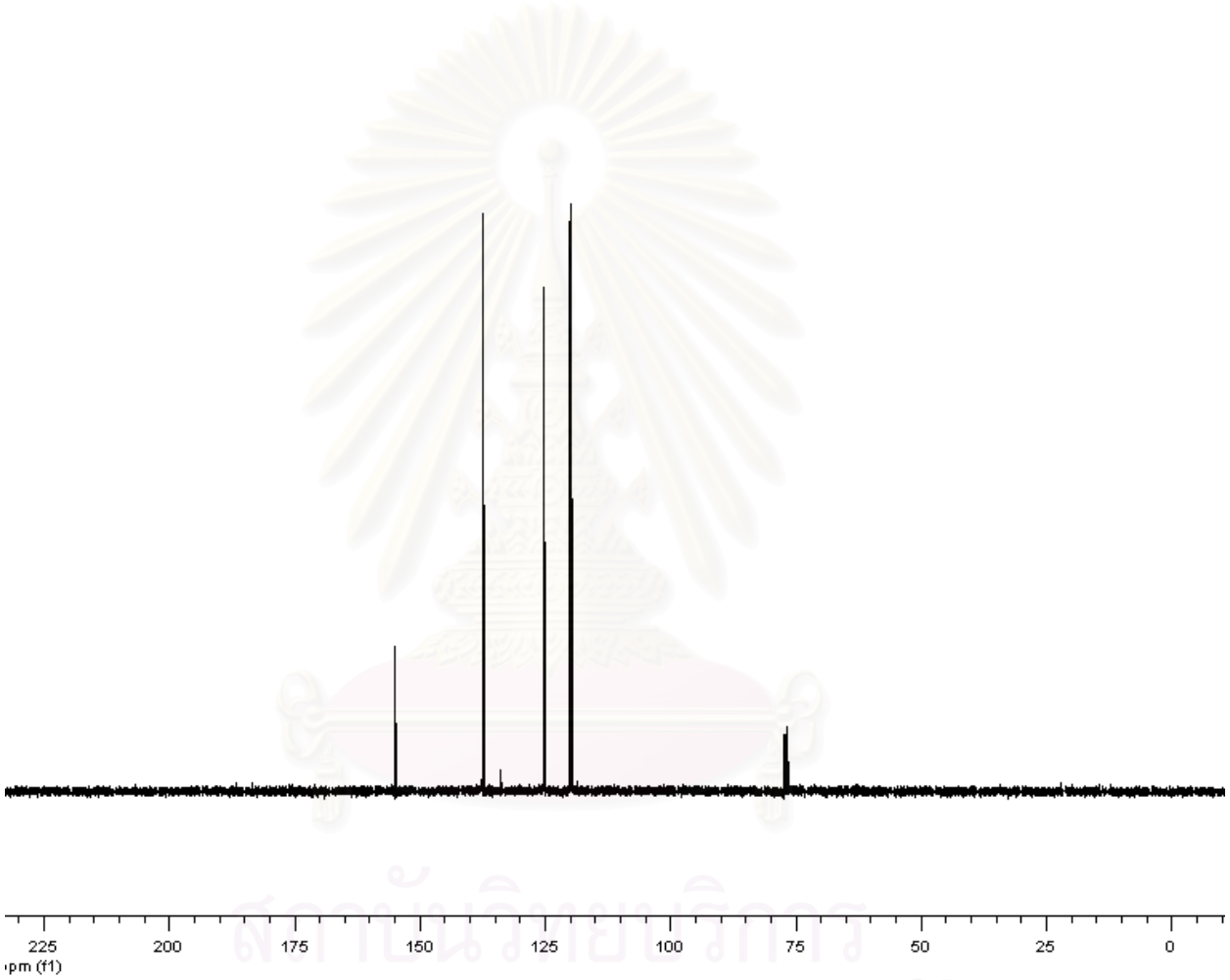

Figure A-2 ^{13}C-NMR spectrum 2-nitrophenol (compound **2a**).

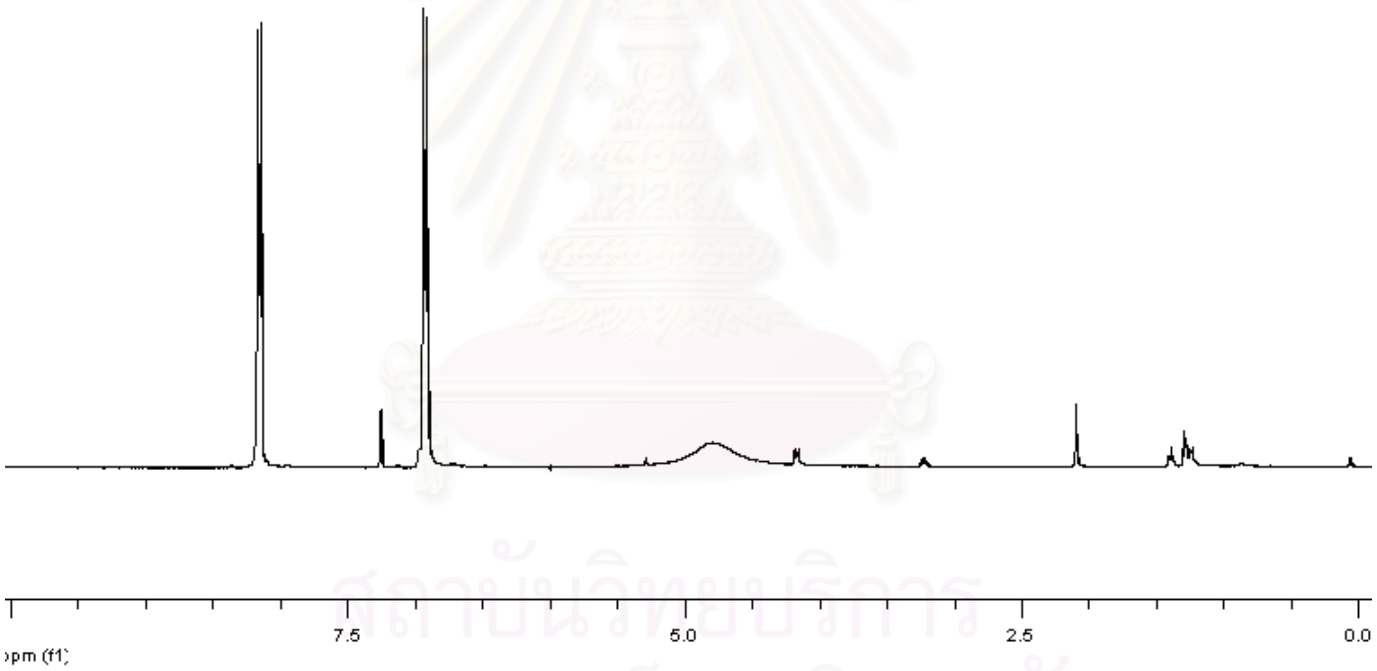

Figure A-3 ^{1}H-NMR spectrum of 4-nitrophenol (compound **2b**).

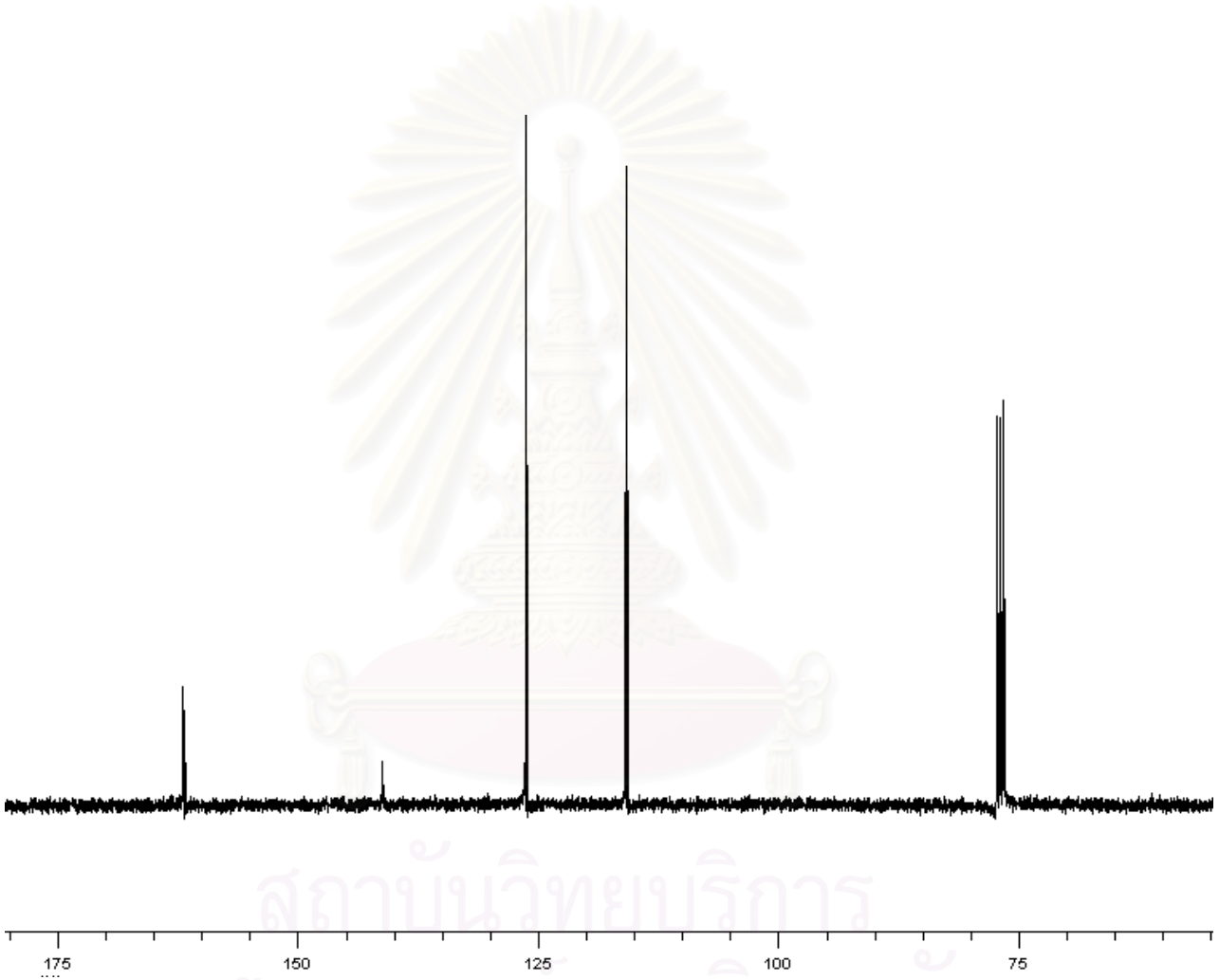

Figure A-4 ^{13}C-NMR spectrum of 4-nitrophenol (compound **2b**).

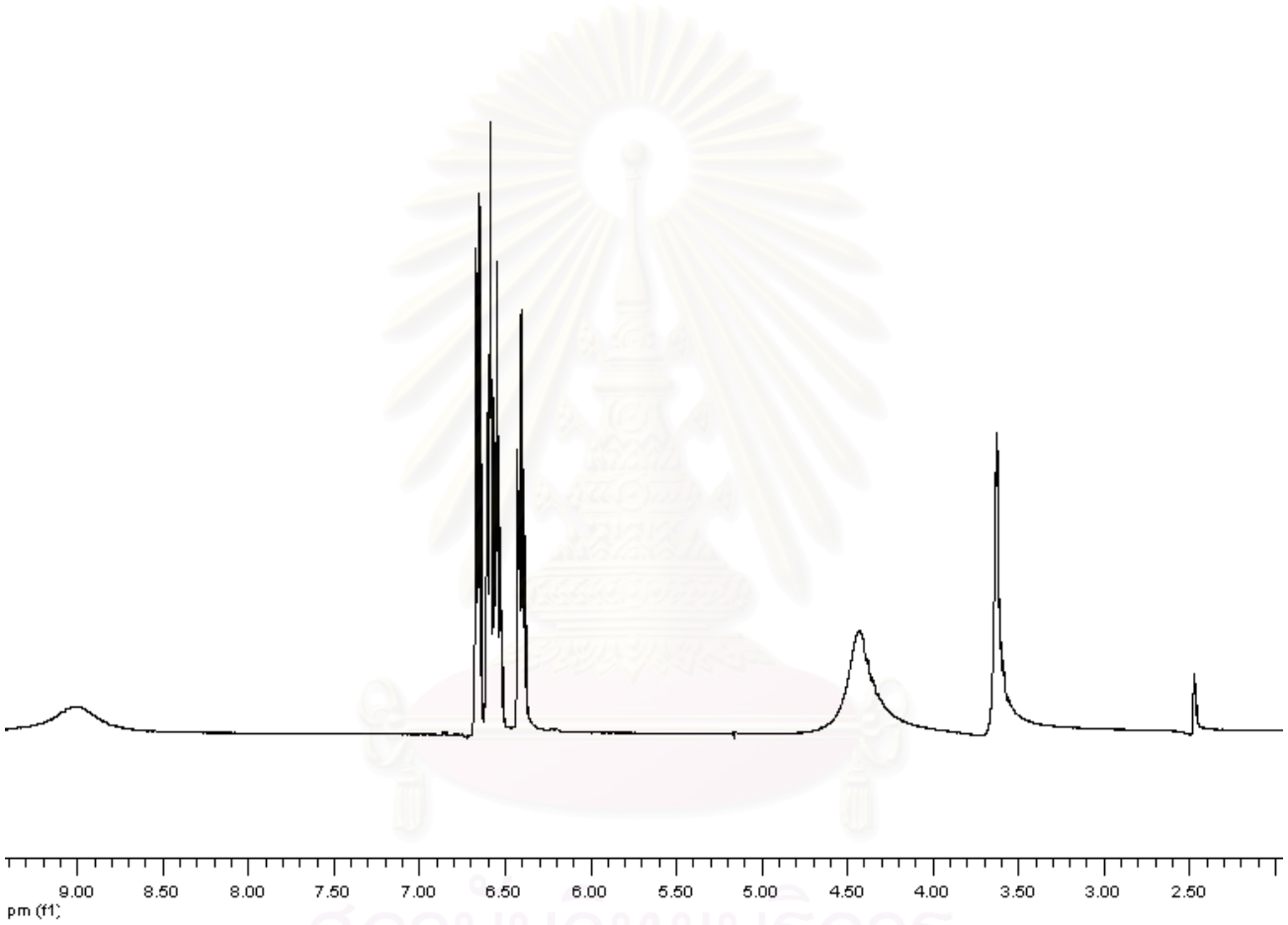

Figure A-5 ^{1}H-NMR spectrum of 2-aminophenol (compound **3**).

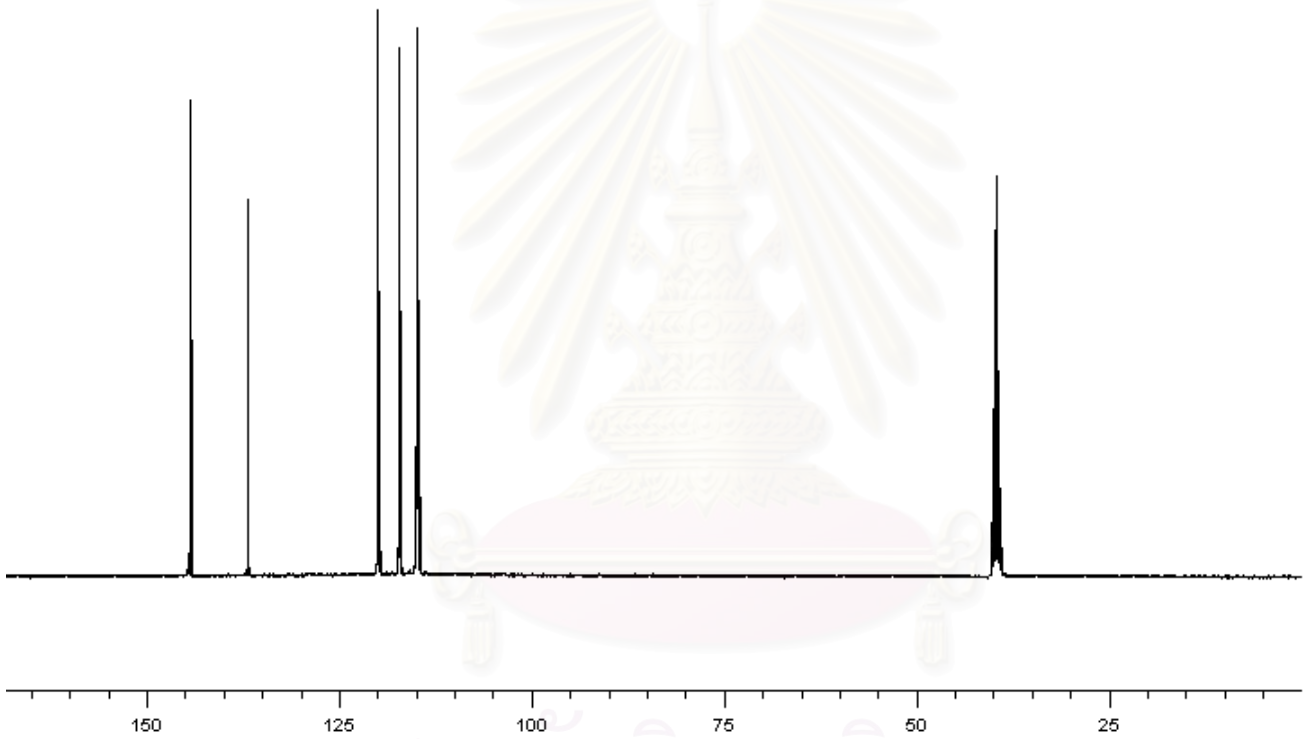

Figure A-6 ^{13}C-NMR spectrum of 2-aminophenol (compound **3**).

61

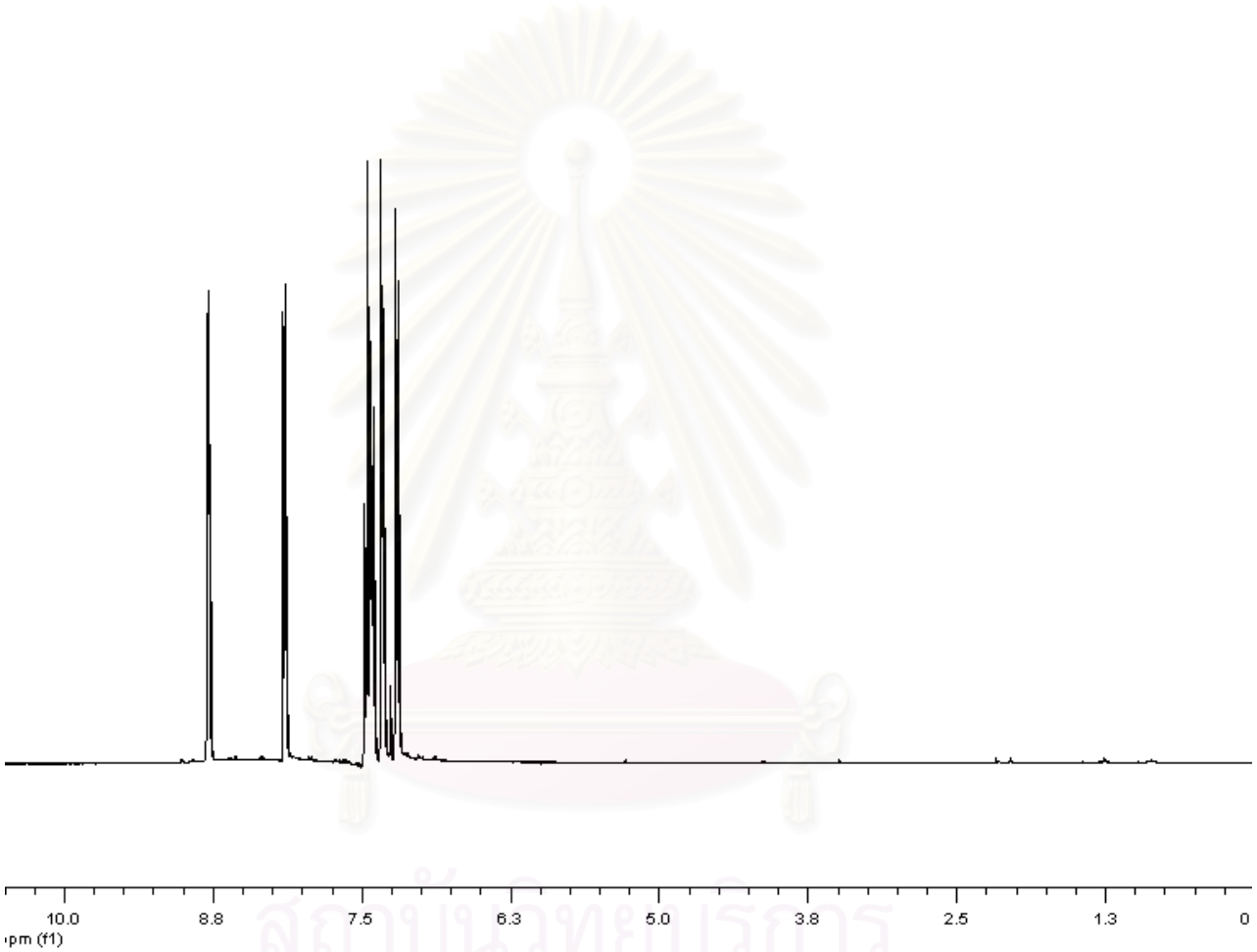

Figure A-7 ^{1}H-NMR spectrum of 8-hydroxyquinoline (compound **4**).

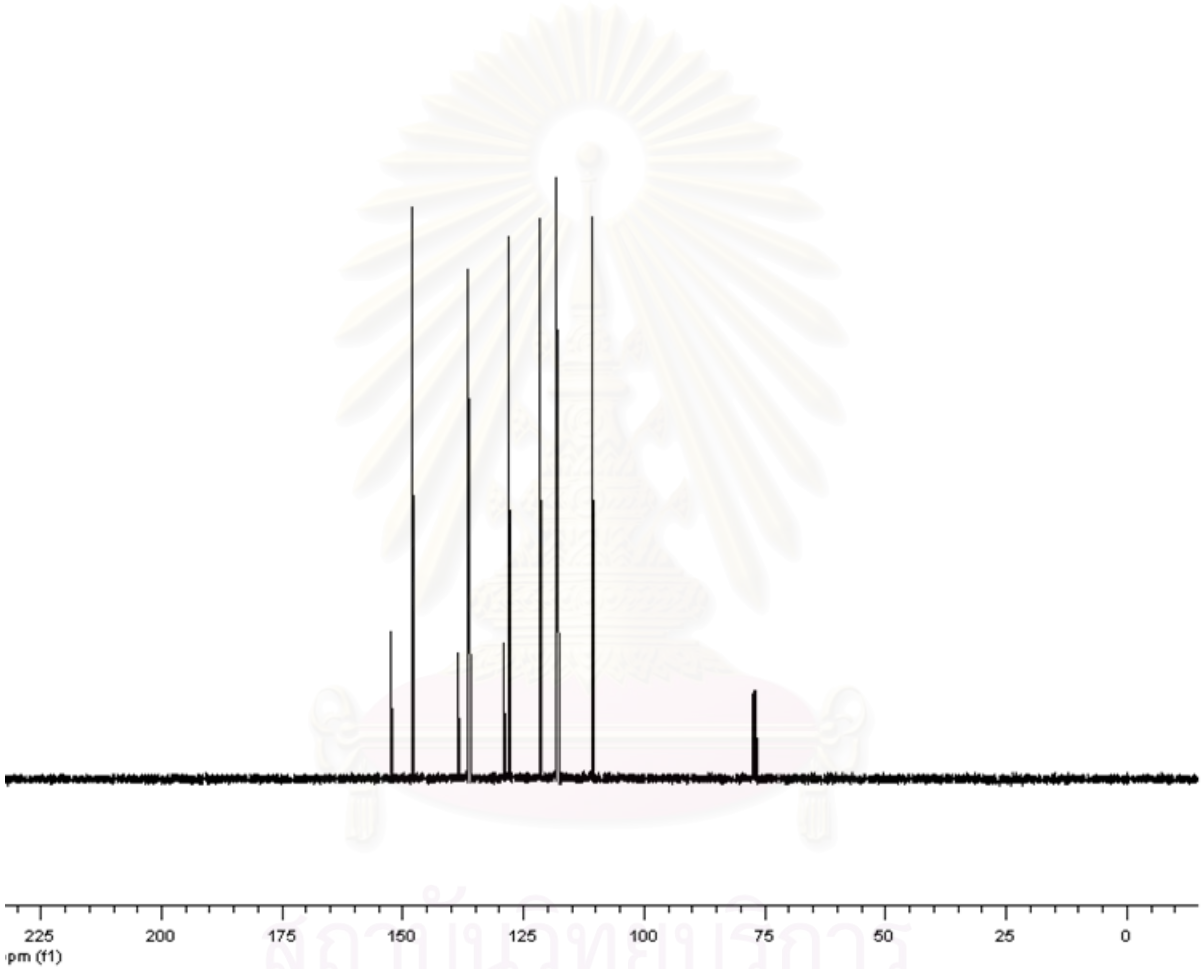

Figure A-8 ^{13}C-NMR spectrum of 8-hydroxyquinoline (compound **4**).

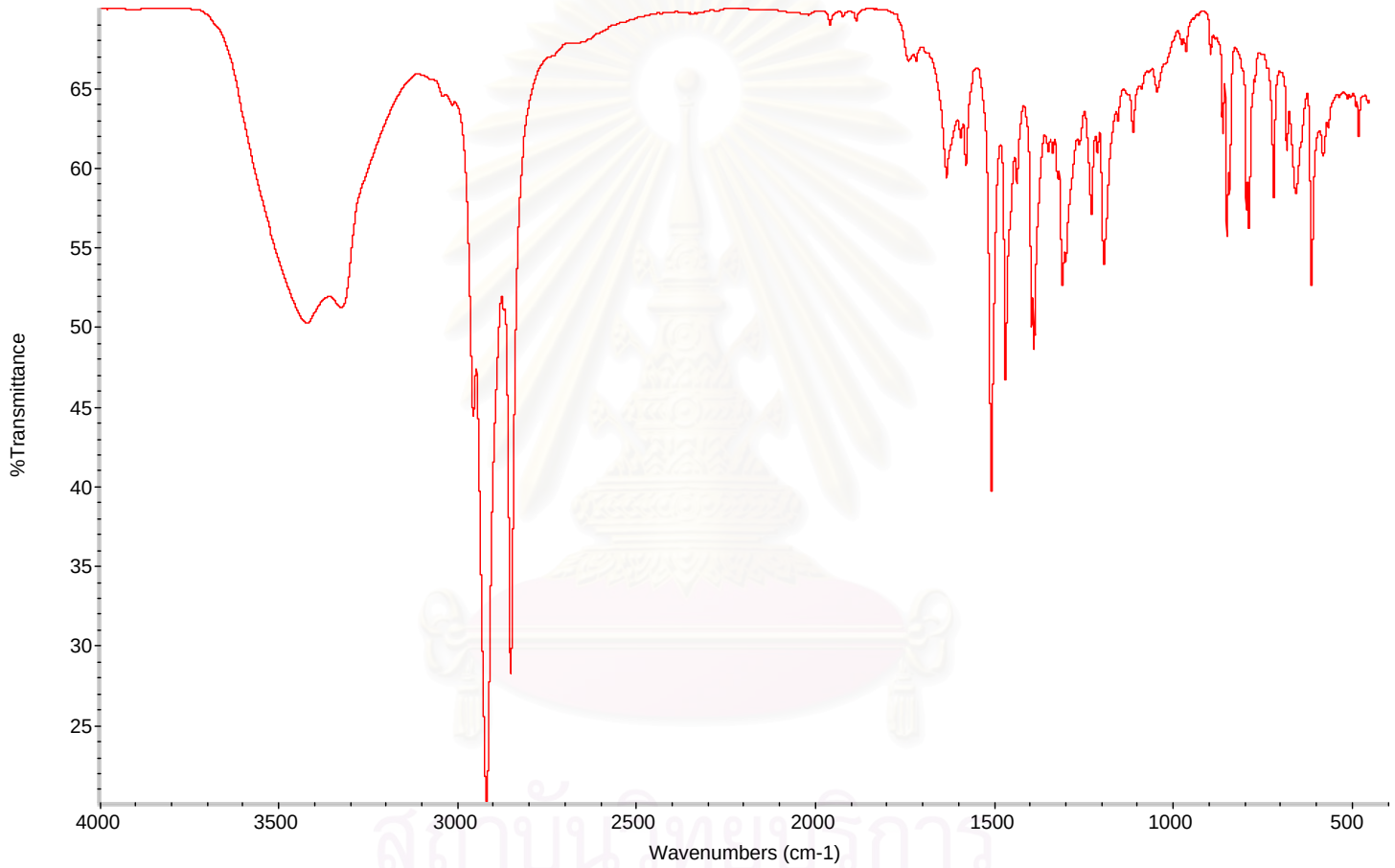

Figure A-9 IR spectrum spectrum of 8-hydroxyquinoline (compound **4**).

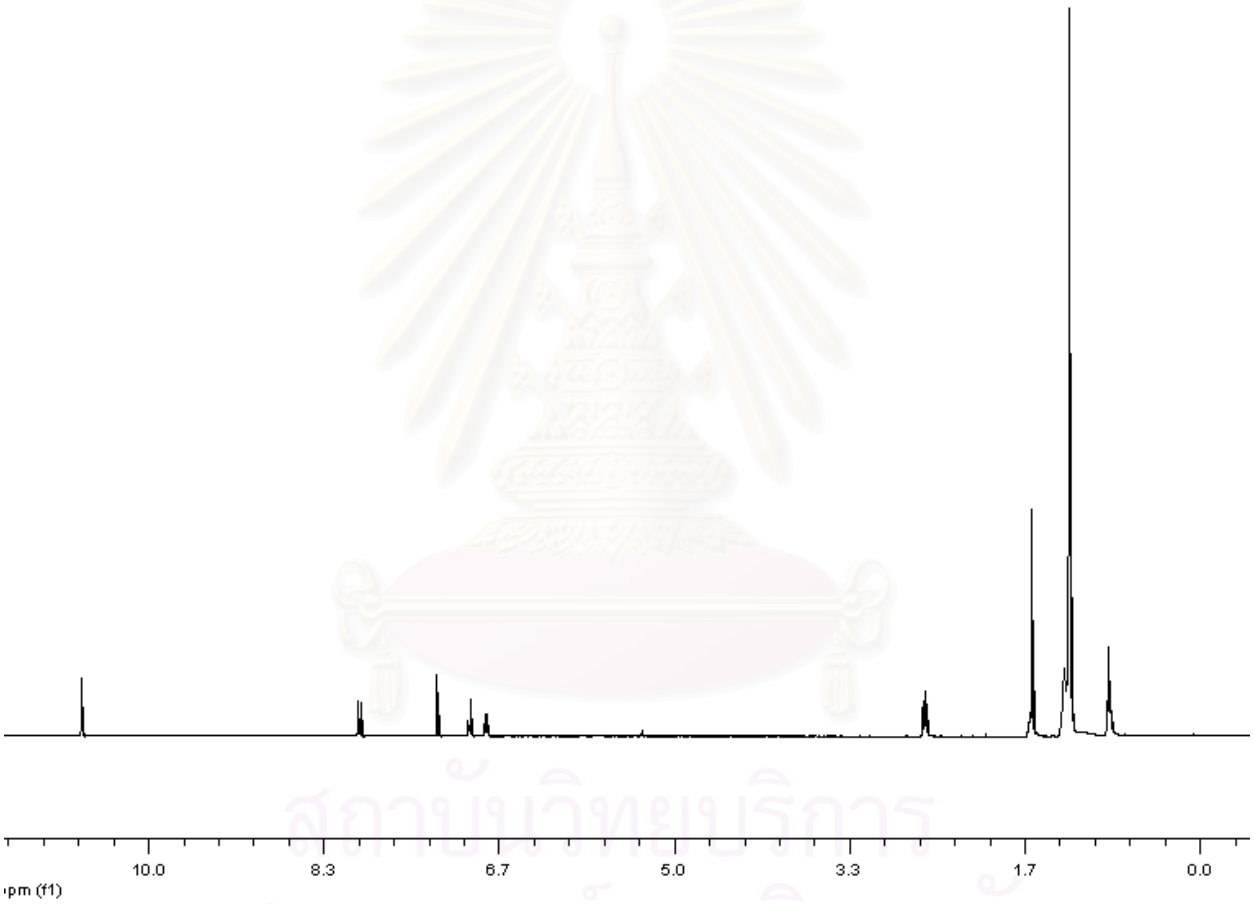

Figure A-10 ^{1}H-NMR spectrum of 5-*n*-pentadecyl-2-nitrophenol (compound **6a**).

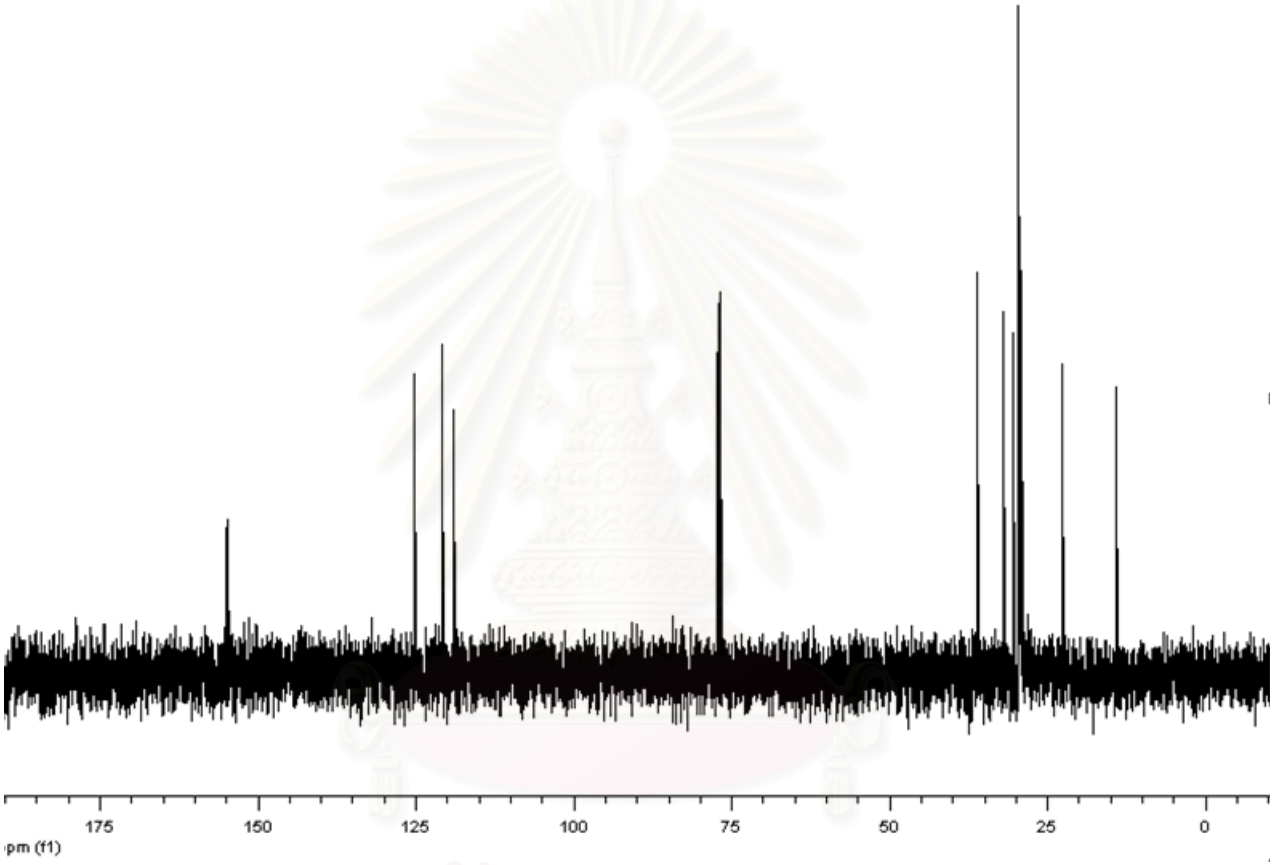

Figure A-11 ^{13}C-NMR spectrum of 5-*n*-pentadecyl-2-nitrophenol (compound **6a**).

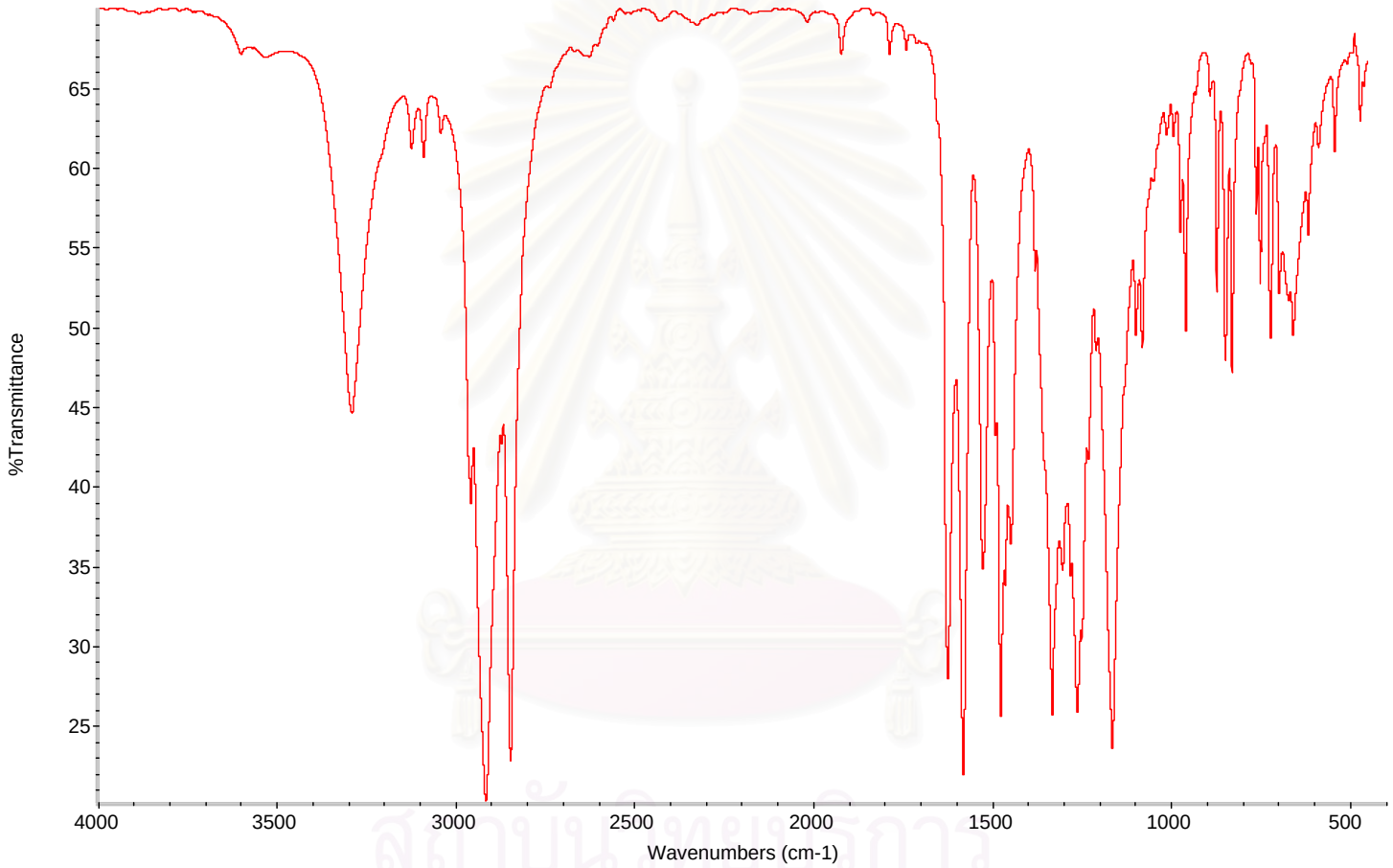

Figure A-12 IR spectrum of 5-*n*-pentadecyl-2-nitrophenol (compound **6a**).

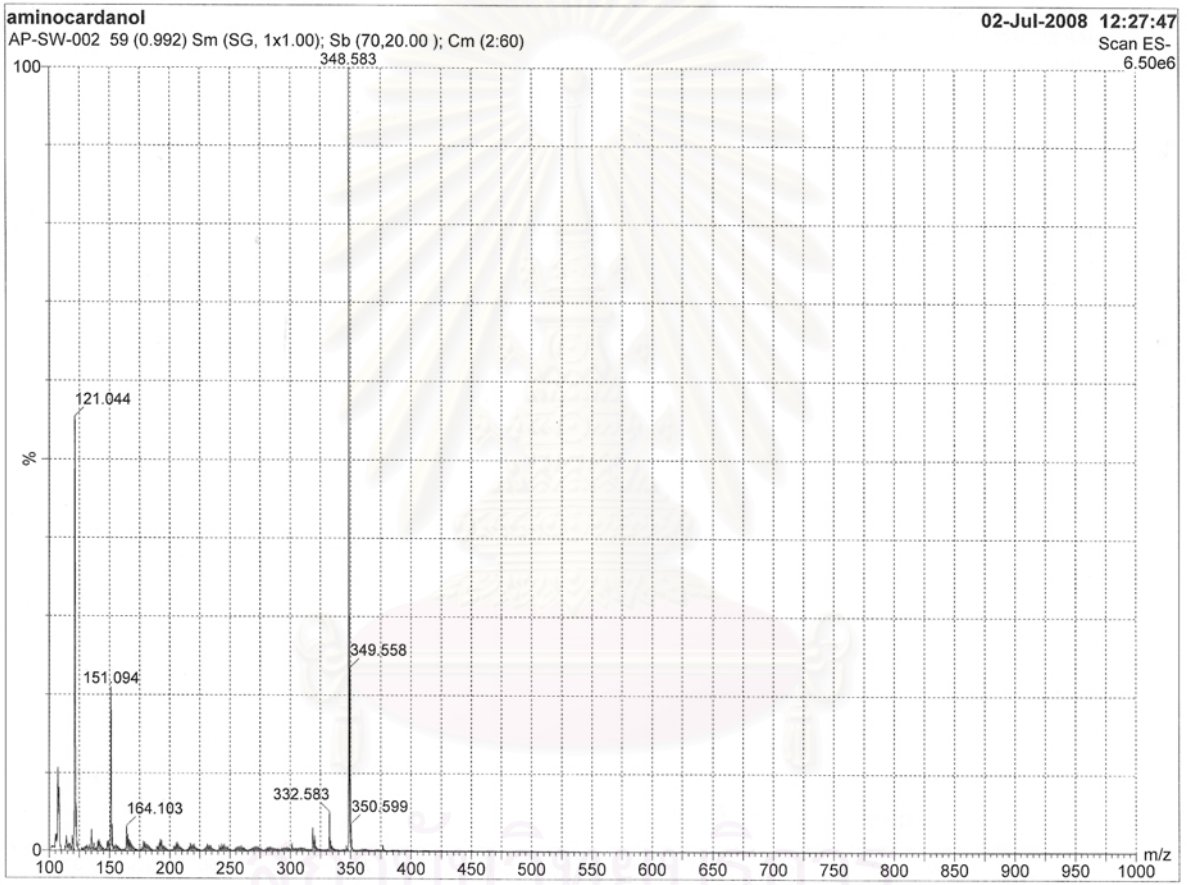

Figure A-13 Mass spectrum of 5-*n*-pentadecyl-2-nitrophenol (compound **6a**).

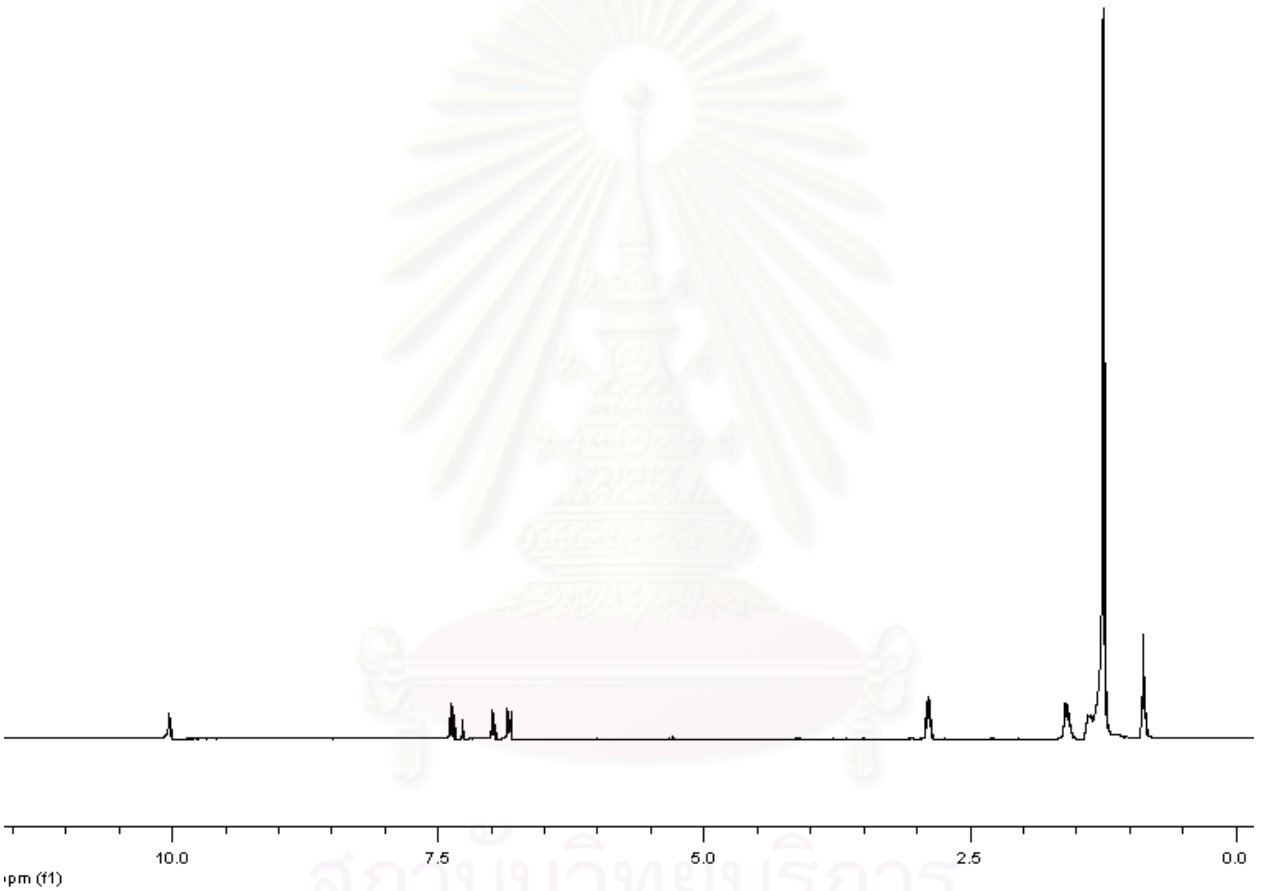

Figure A-14 ^{1}H-NMR spectrum of 3-*n*-pentadecyl-2-nitrophenol (compound **6b**).

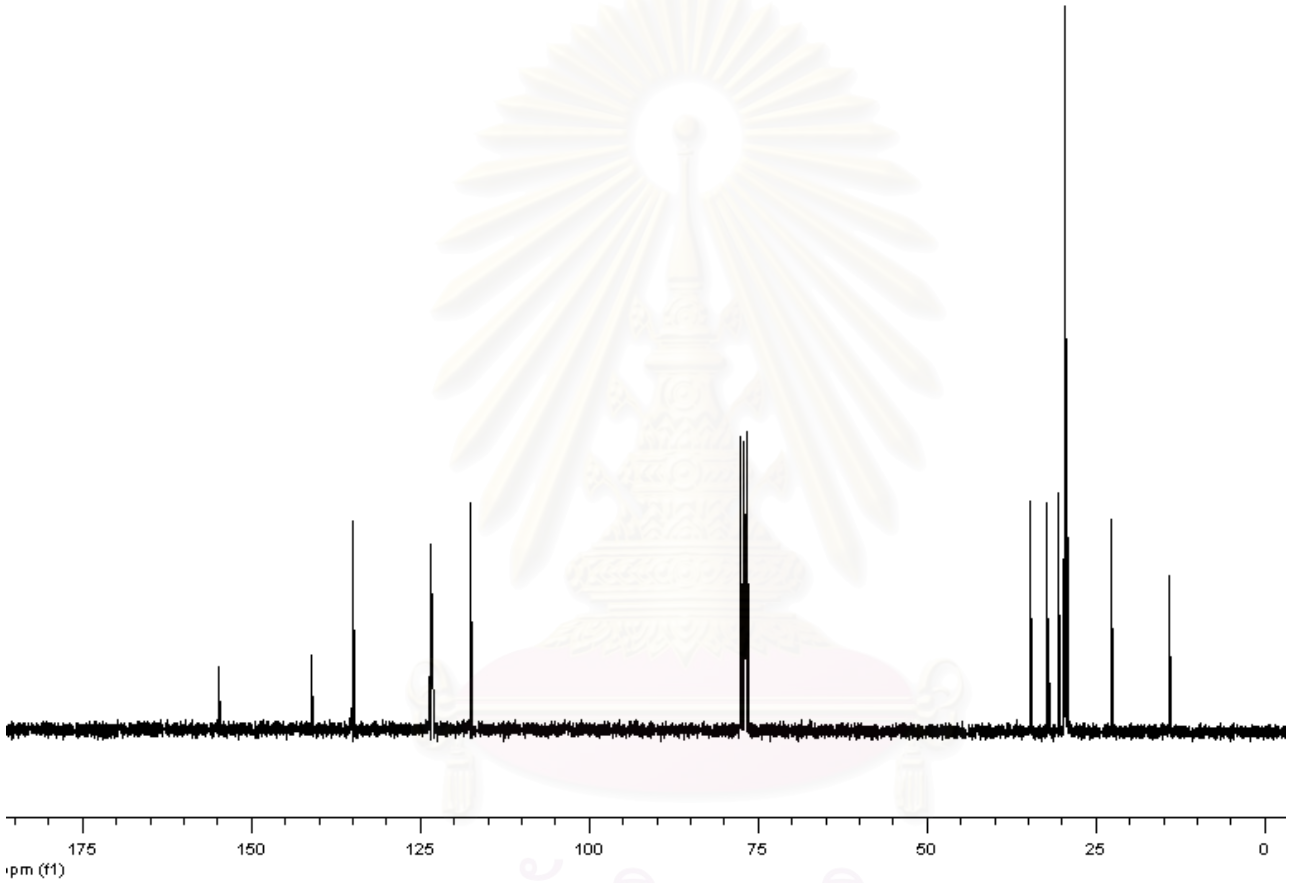

Figure A-15 ^{13}C-NMR spectrum of 3-*n*-pentadecyl-2-nitrophenol (compound **6b**).

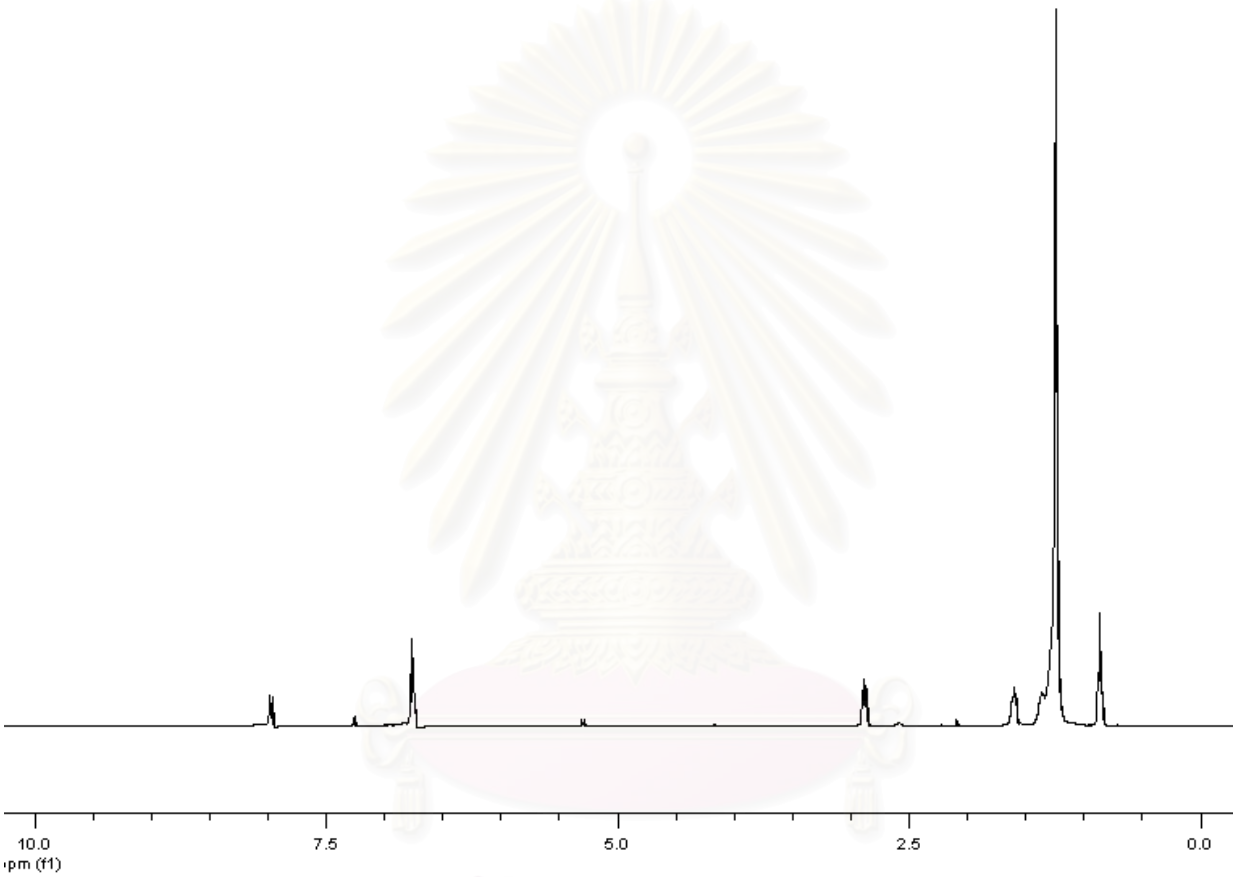

Figure A-16 ^{1}H-NMR spectrum of 3-*n*-pentadecyl-4-nitrophenol (compound **6c**).

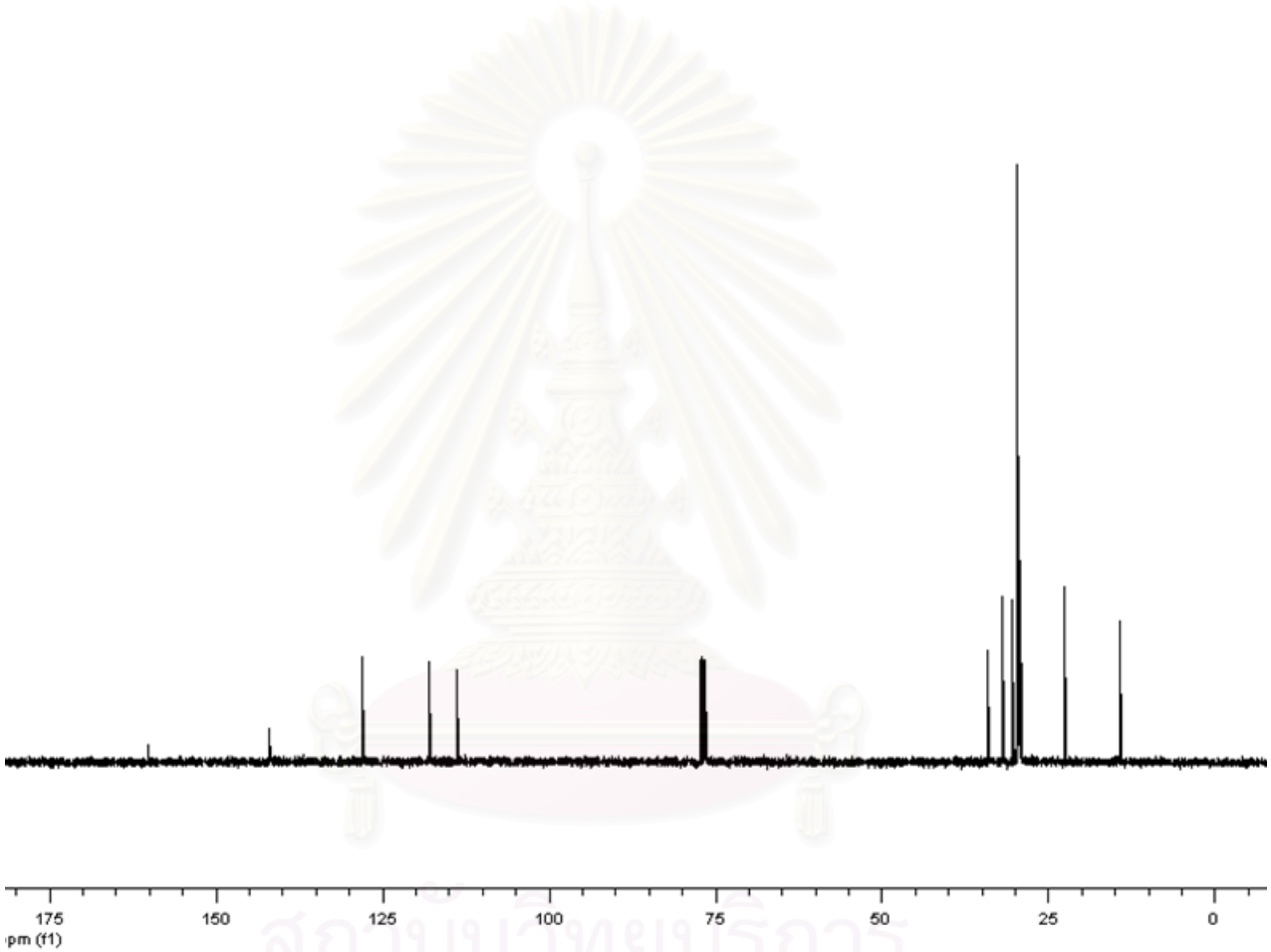

Figure A-17 ^{13}C-NMR spectrum of 3-*n*-pentadecyl-4-nitrophenol (compound **6c**).

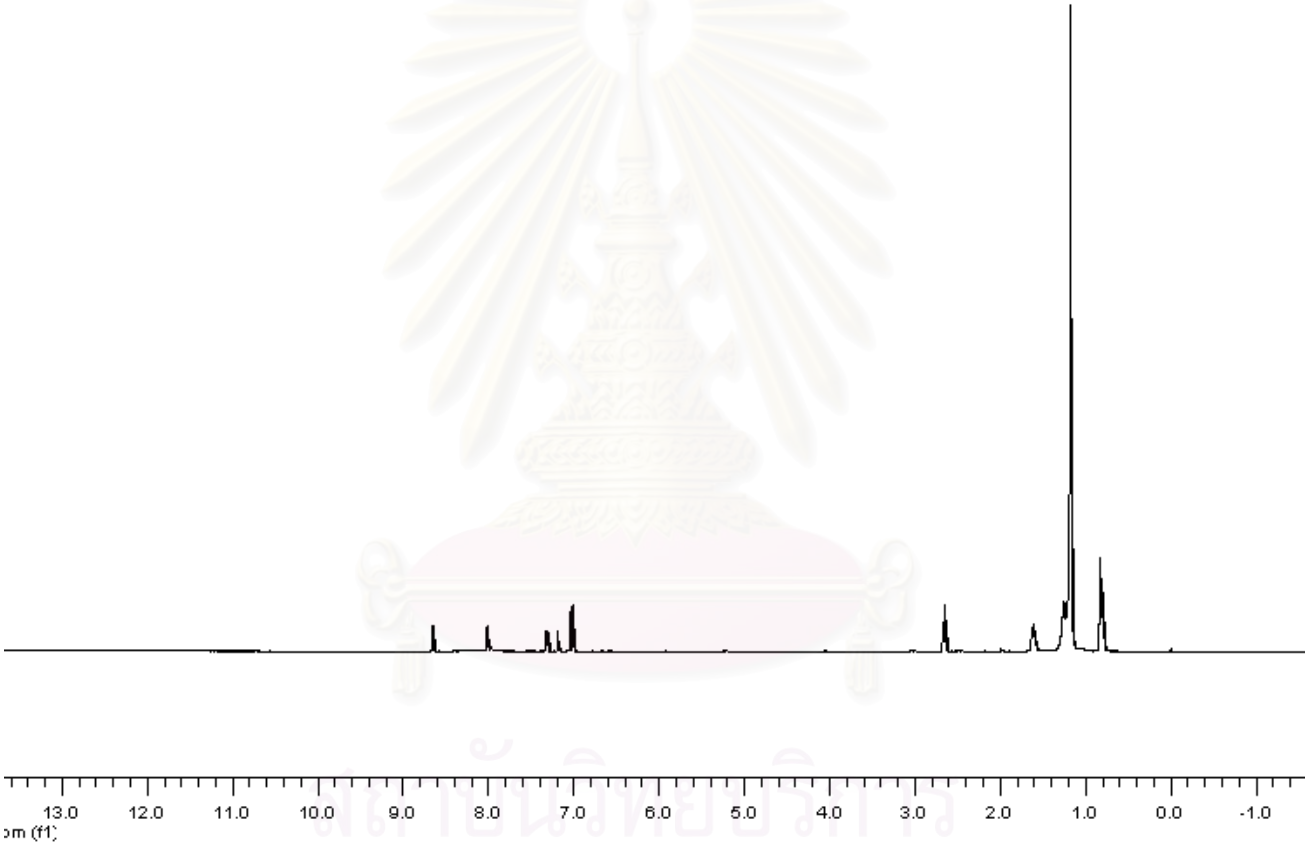

Figure A-18 ^{1}H-NMR spectrum of 5-*n*-pentadecyl-2-aminophenol (compound **7**).

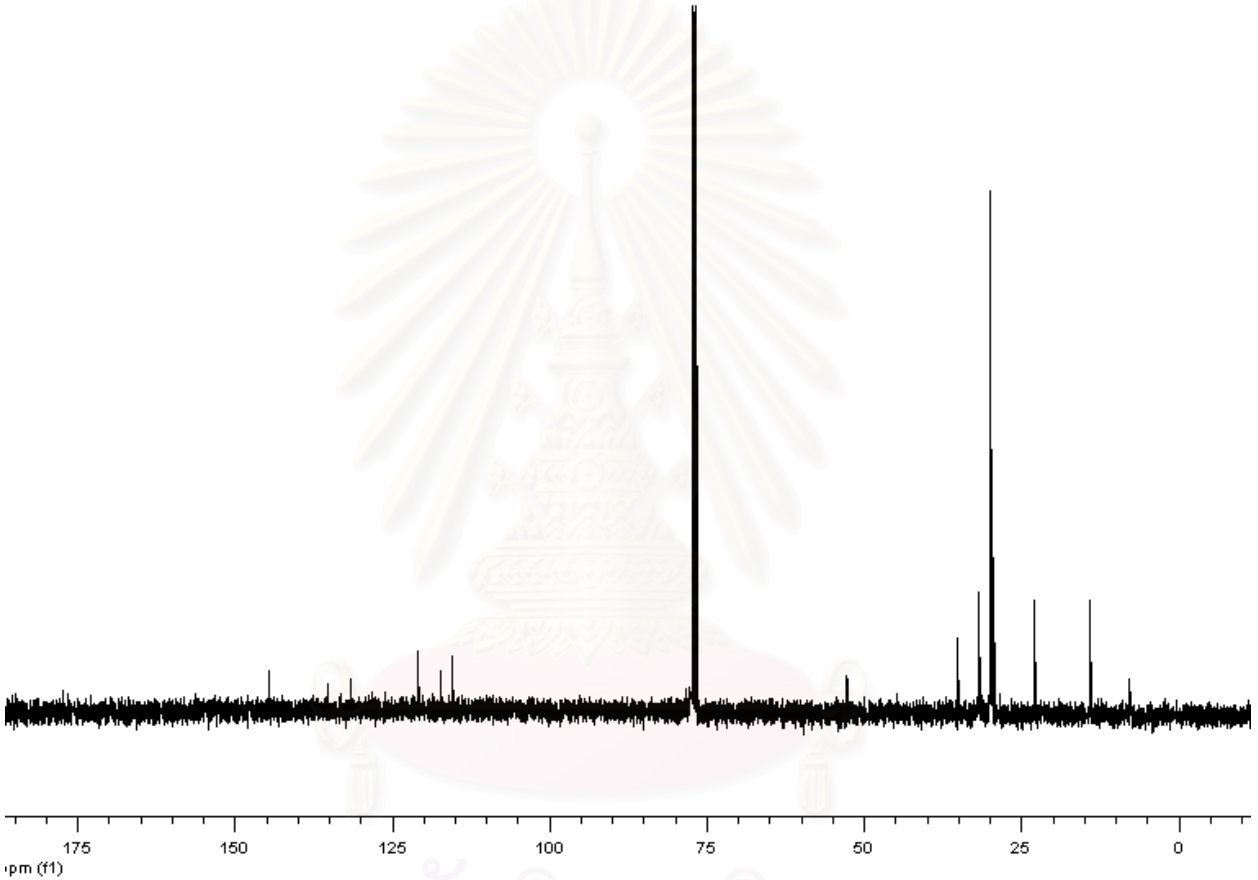

Figure A-19 ^{13}C-NMR spectrum of 5-*n*-pentadecyl-2-aminophenol (compound **7**).

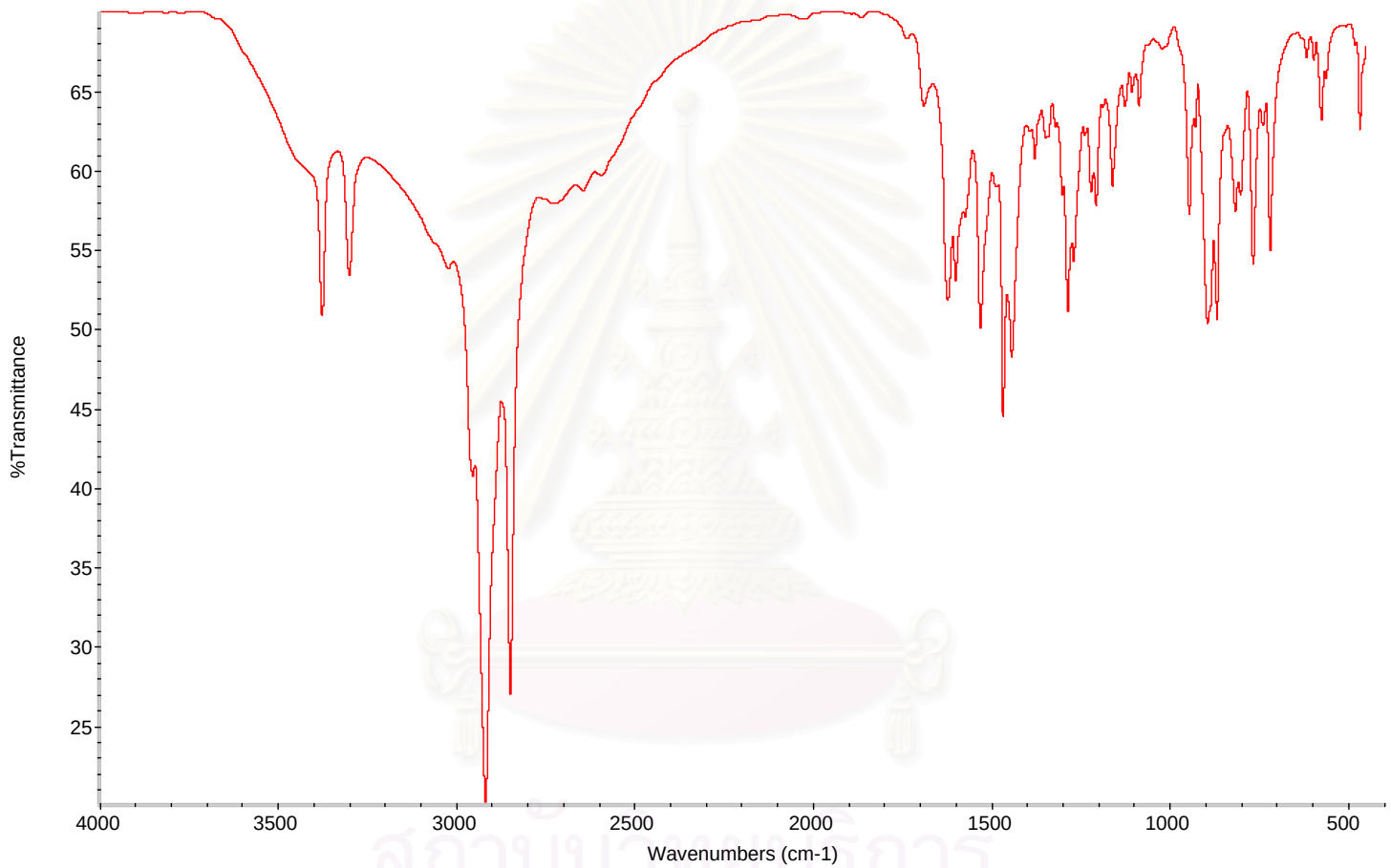

Figure A-20 IR spectrum of 5-*n*-pentadecyl-2-aminophenol (compound **7**).

Mass Spectrum List Report

Analysis Info

Analysis Name	6-penta.d	Acquisition Date	12/3/2008 9:32:26 AM
Method	TMall17NOV08.m	Operator	Administrator
Sample Name	6-pentadecylquinolin-8-ol	Instrument	micrOTOF 72
	6-pentadecylquinolin-8-ol		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	150.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	200.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

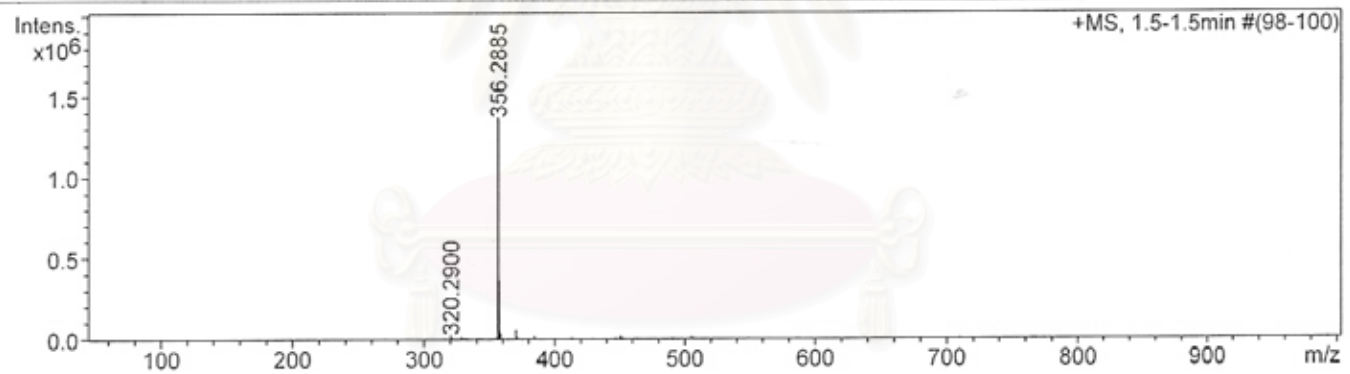

Figure A-21 Mass spectrum of 5-*n*-pentadecyl-2-aminophenol (compound **7**).

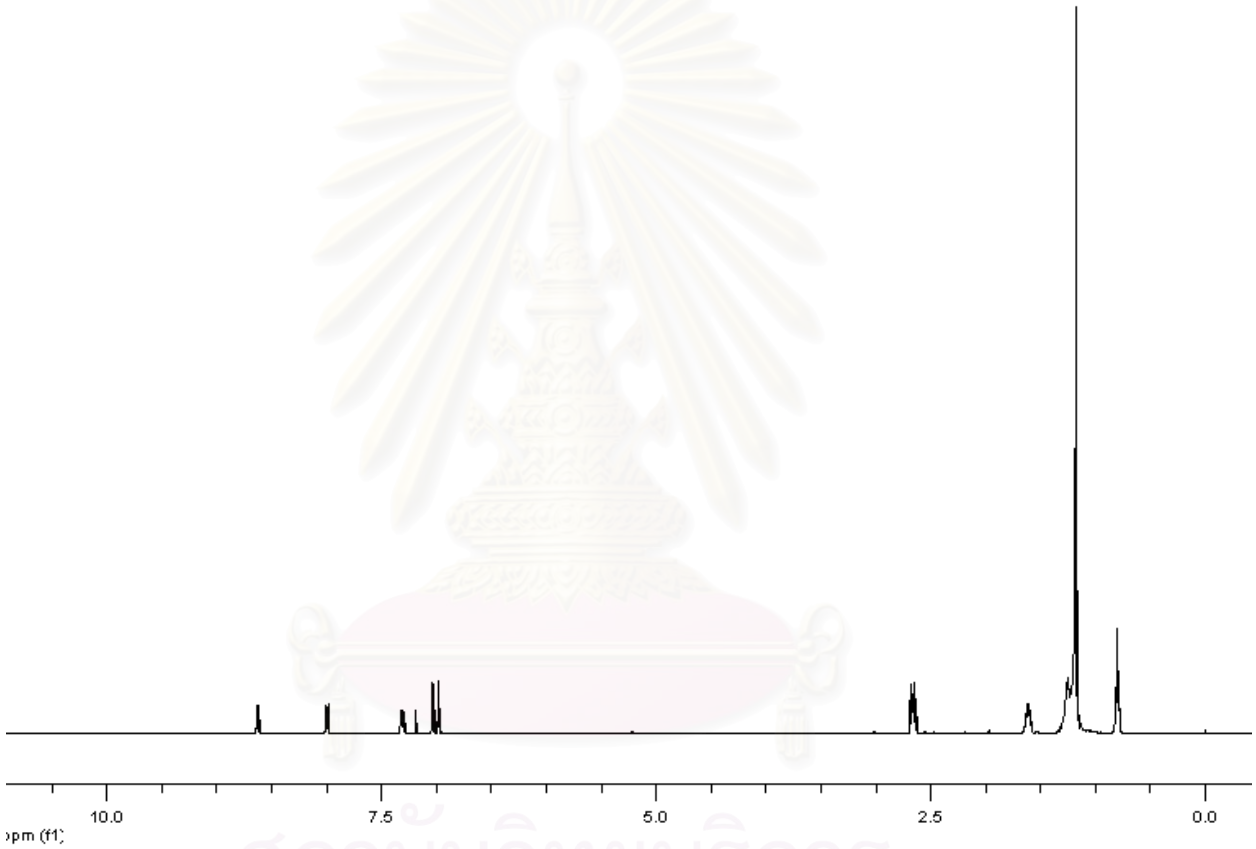

Figure A-22 ^{1}H-NMR spectrum of 6-*n*-pentadecyl-8-hydroxyquinoline (compound **8**).

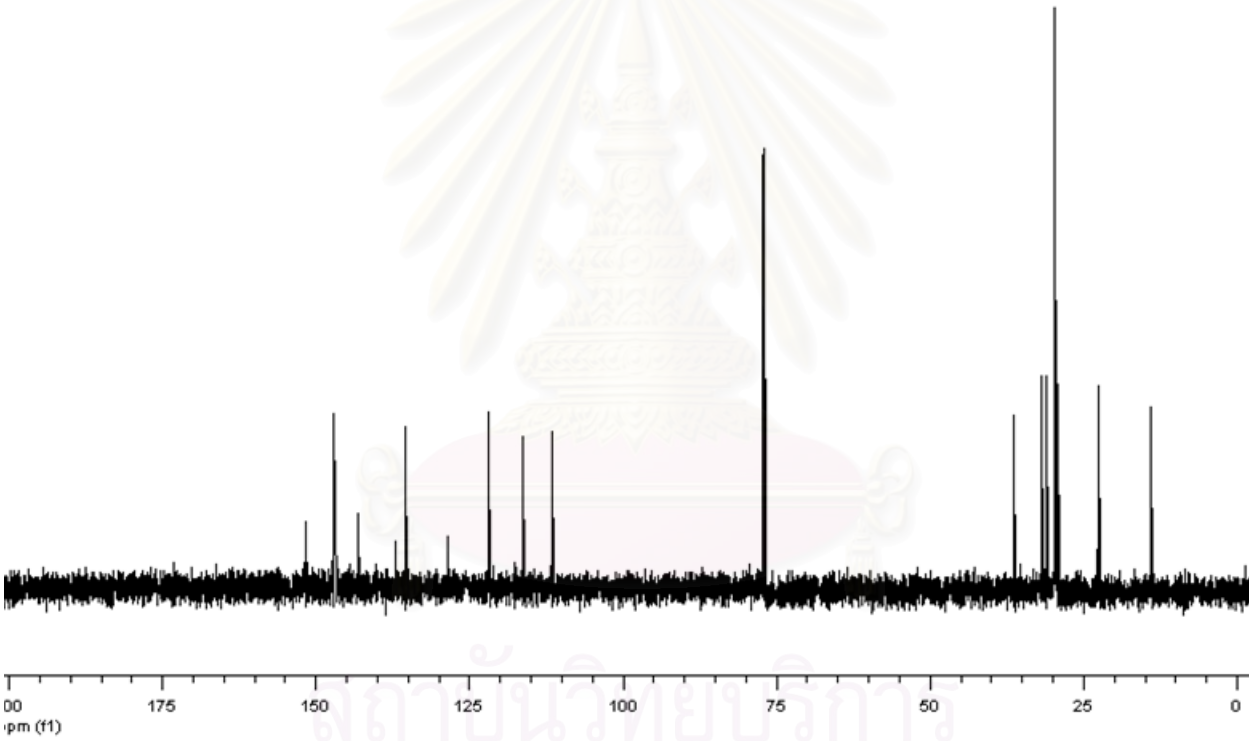

Figure A-23 ^{13}C-NMR spectrum of 6-*n*-pentadecyl-8-hydroxyquinoline (compound **8**).

Figure A-24 IR spectrum spectrum of 6-*n*-pentadecyl-8-hydroxyquinoline (compound **8**).

Mass Spectrum List Report

Analysis Info

Analysis Name	6-penta.d	Acquisition Date	12/3/2008 9:32:26 AM
Method	TMall17NOV08.m	Operator	Administrator
Sample Name	6-pentadecylquinolin-8-ol	Instrument	micrOTOF 72
	6-pentadecylquinolin-8-ol		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	150.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	200.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

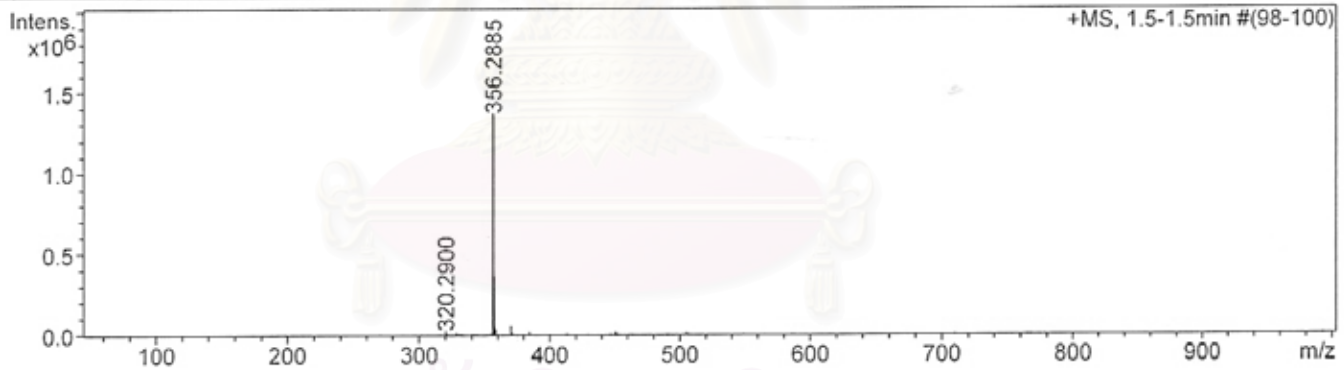

Figure A-25 Mass spectrum of 6-*n*-pentadecyl-8-hydroxyquinoline (compound **8**).

APPENDIX B

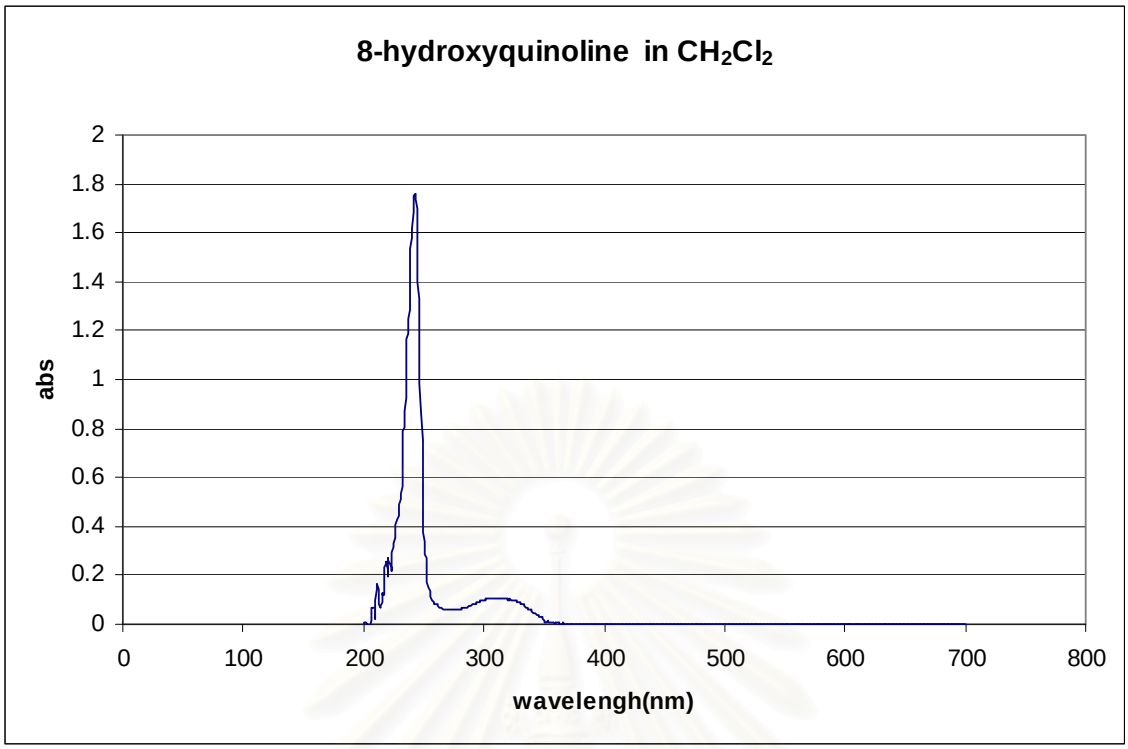

Figure B-1 Absorption spectrum of compound **4** in CH_2Cl_2.

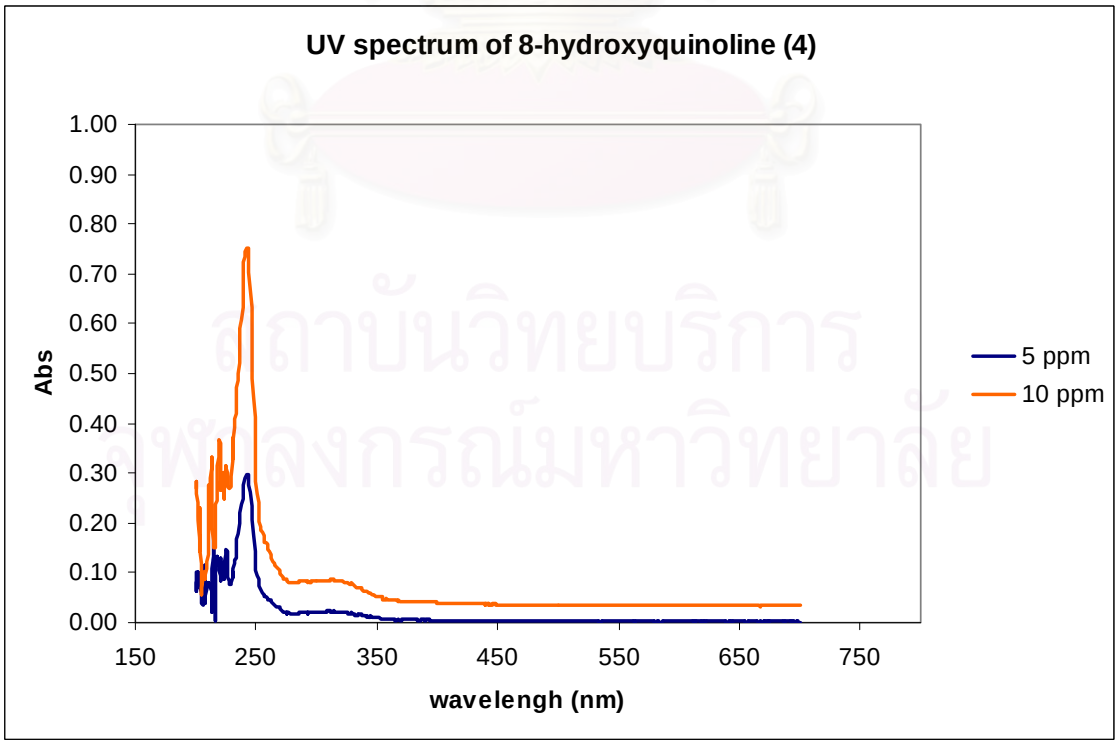

Figure B-2 Absorption spectra of compound **4** in $CHCl_3$ in 5 and 10 ppm.

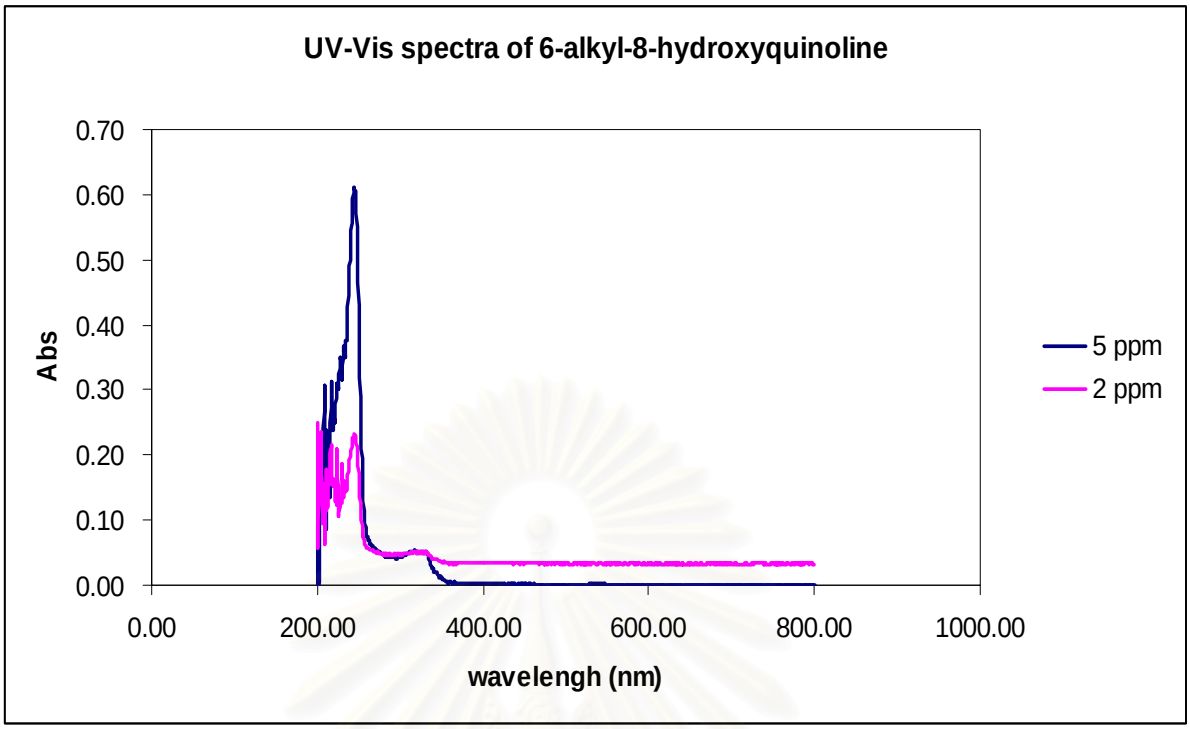

Figure B-3 Absorption spectra of compound **8** in CH_2Cl_2 in 2 and 5 ppm.

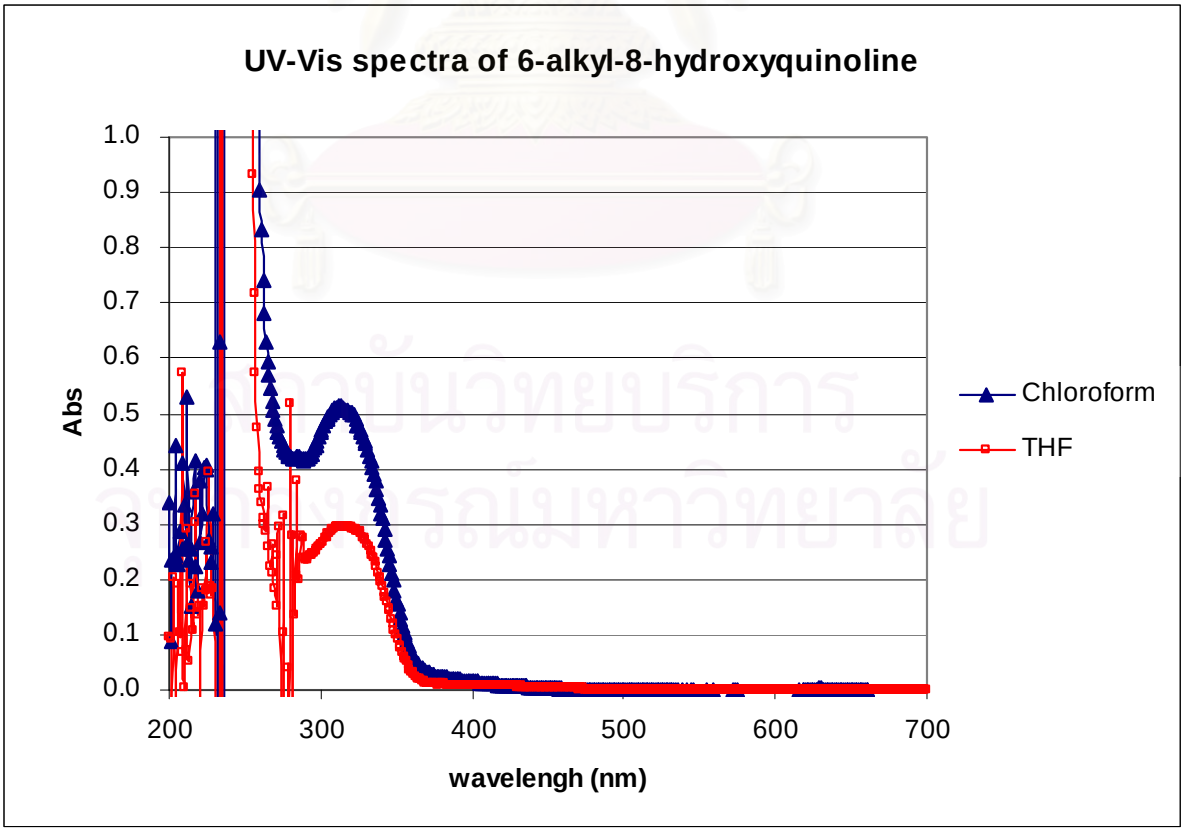

Figure B-4 Absorption spectra of compound **8** in $CHCl_3$ and THF.

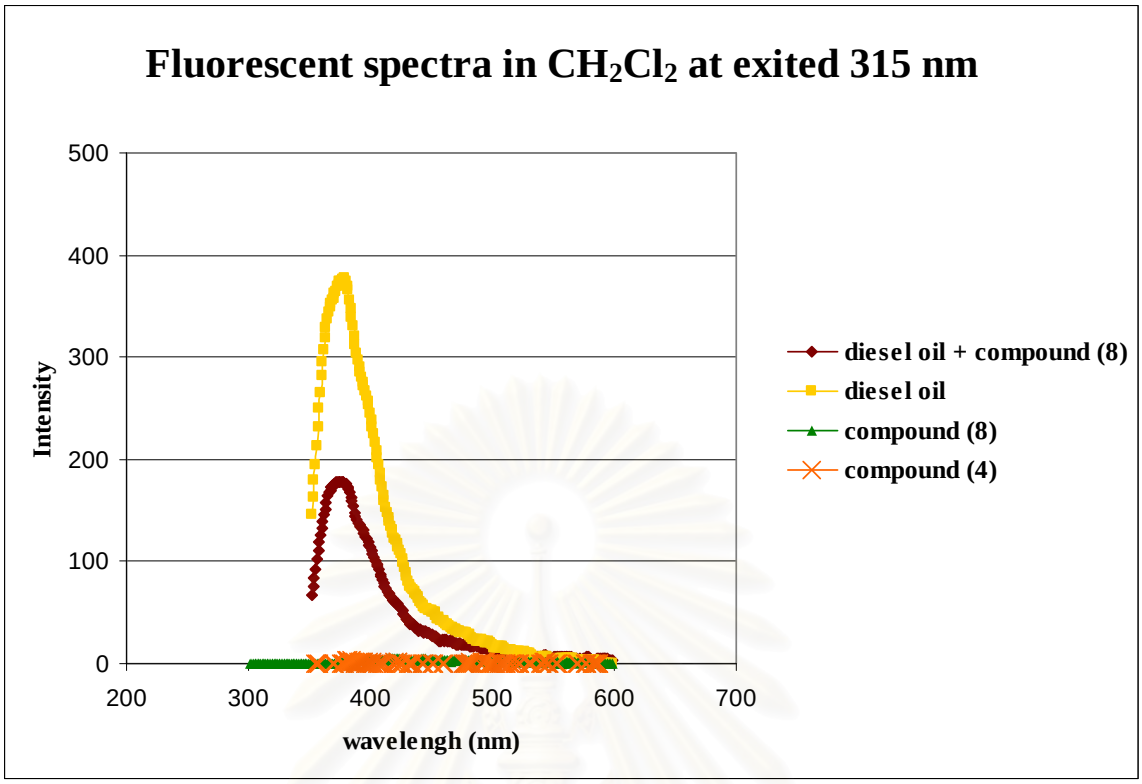

Figure B-5 Fluorescent spectra in CH_2Cl_2 at 315 nm.

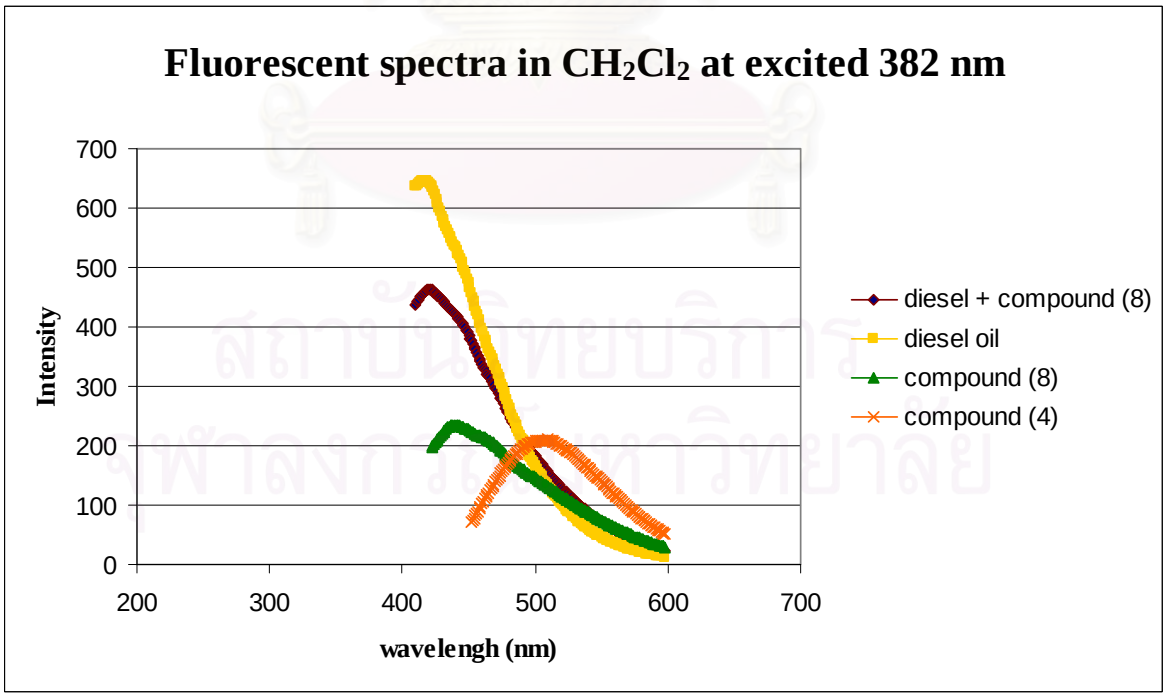

Figure B-6 Fluorescent spectra in CH_2Cl_2 at 382 nm.

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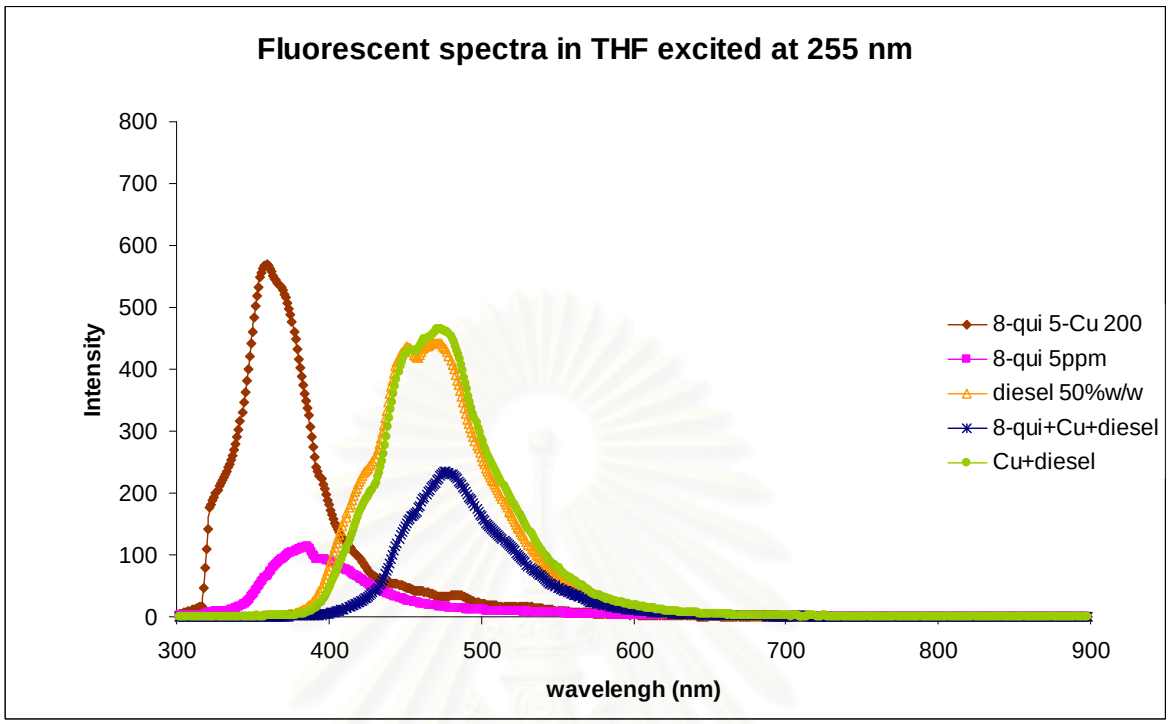

Figure B-7 Fluorescent spectra of Cu -compound **4** complex in THF with diesel fuel oil.

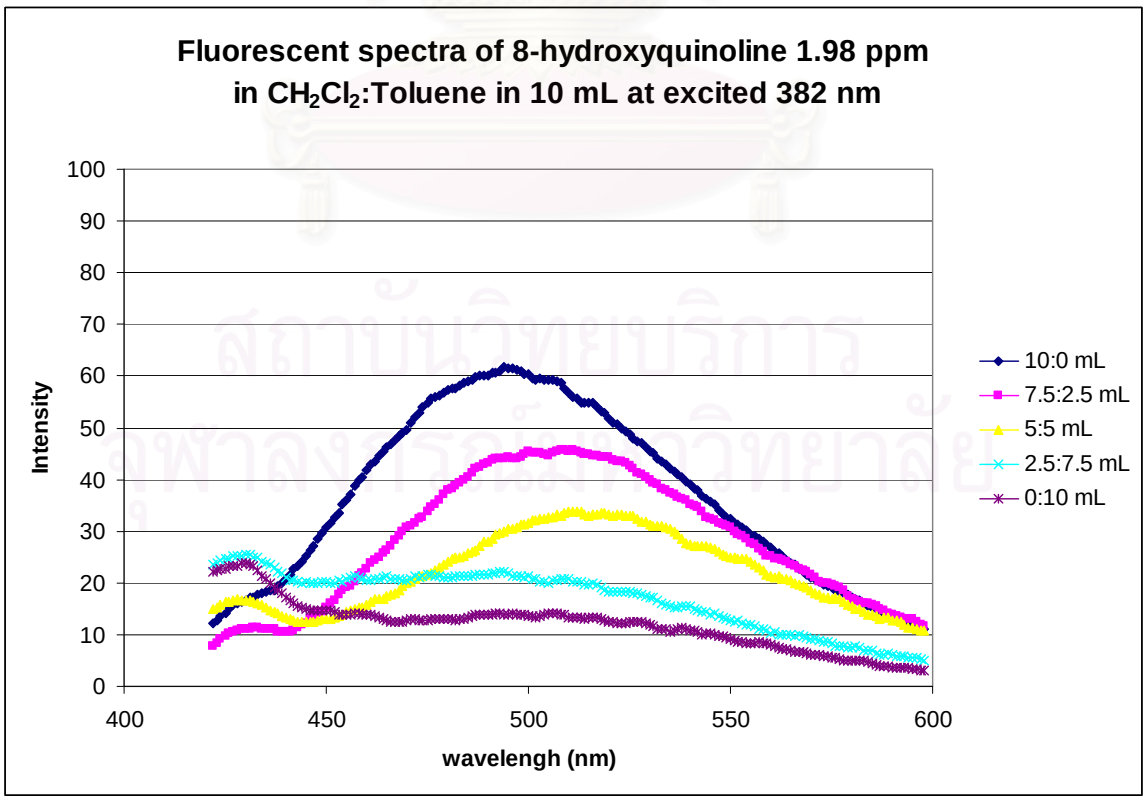

Figure B-8 Fluorescent spectra in CH_2Cl_2:toluene excited at 382 nm.

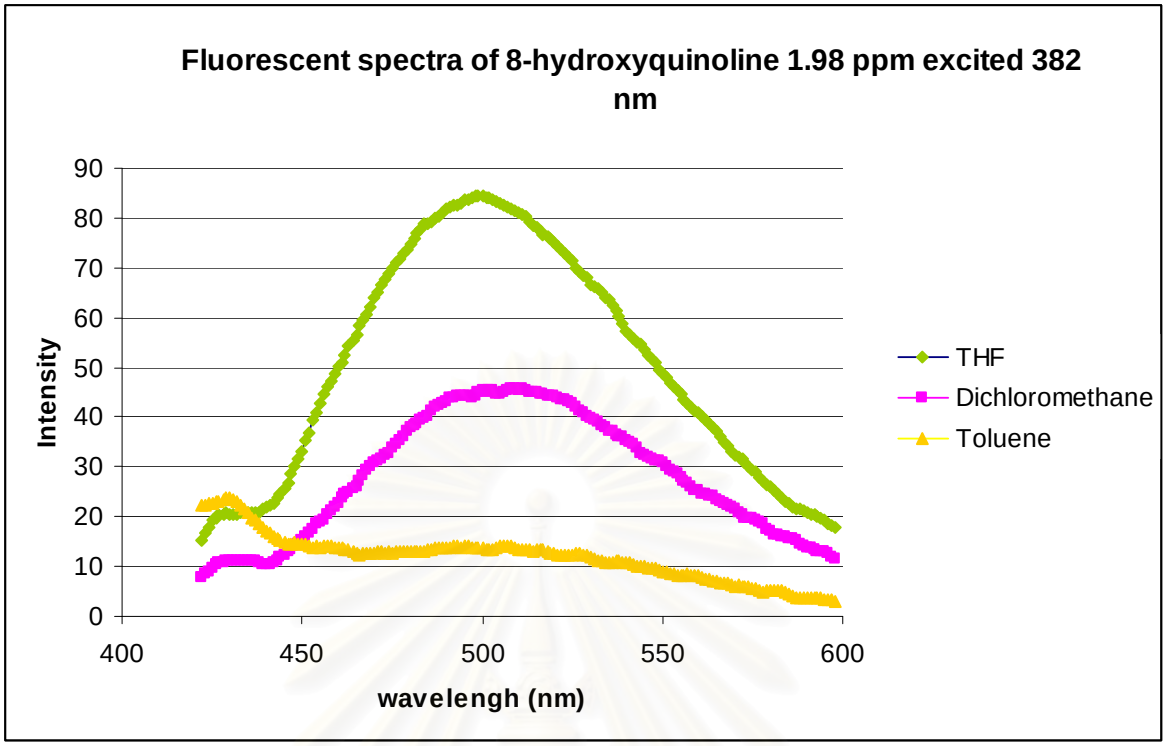

Figure B-9 Fluorescent spectra in THF, CH_2Cl_2, and toluene excited at 382 nm.

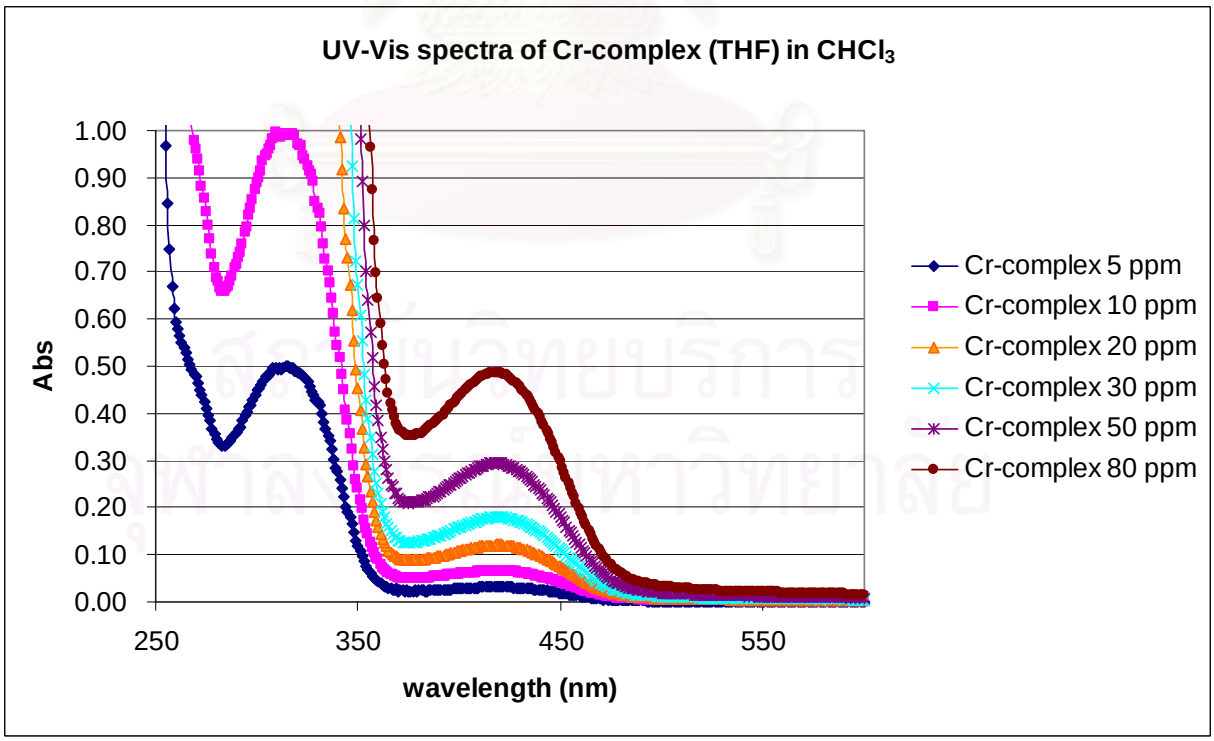

Figure B-10 Absorption spectra of Cr (III) with compound **4** complex in $CHCl_3$.

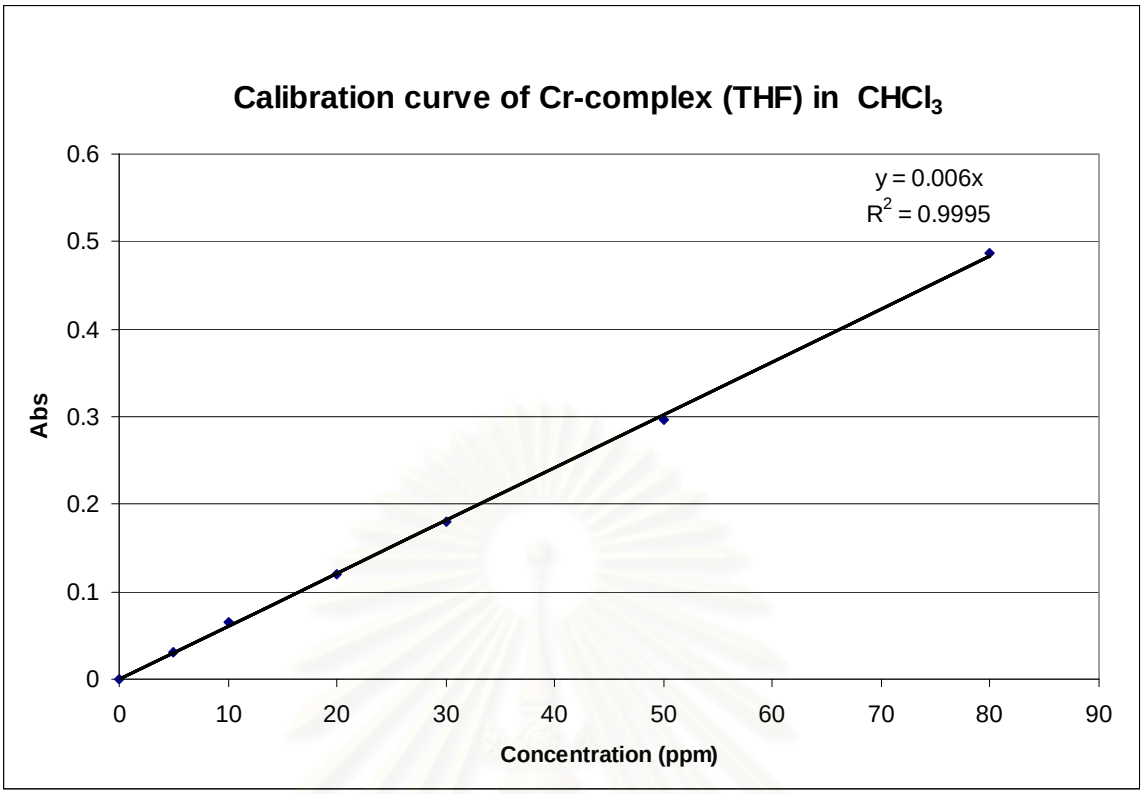

Figure B-11 The calibration curve for the quantitative determinations of Cr (III) with compound **4** complex in THF, extracted with $CHCl_3$ (λ_{max} = 417 nm).

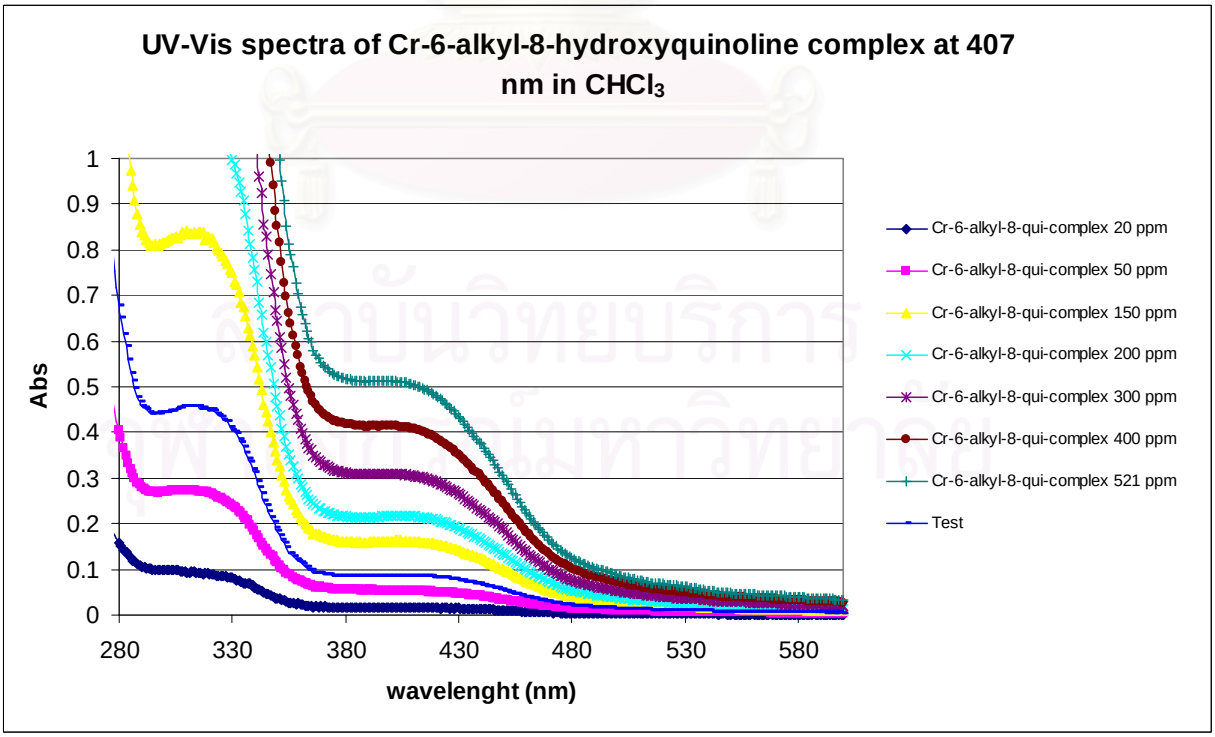

Figure B-12 Absorption spectra of Cr (III) with compound **8** complex in $CHCl_3$.

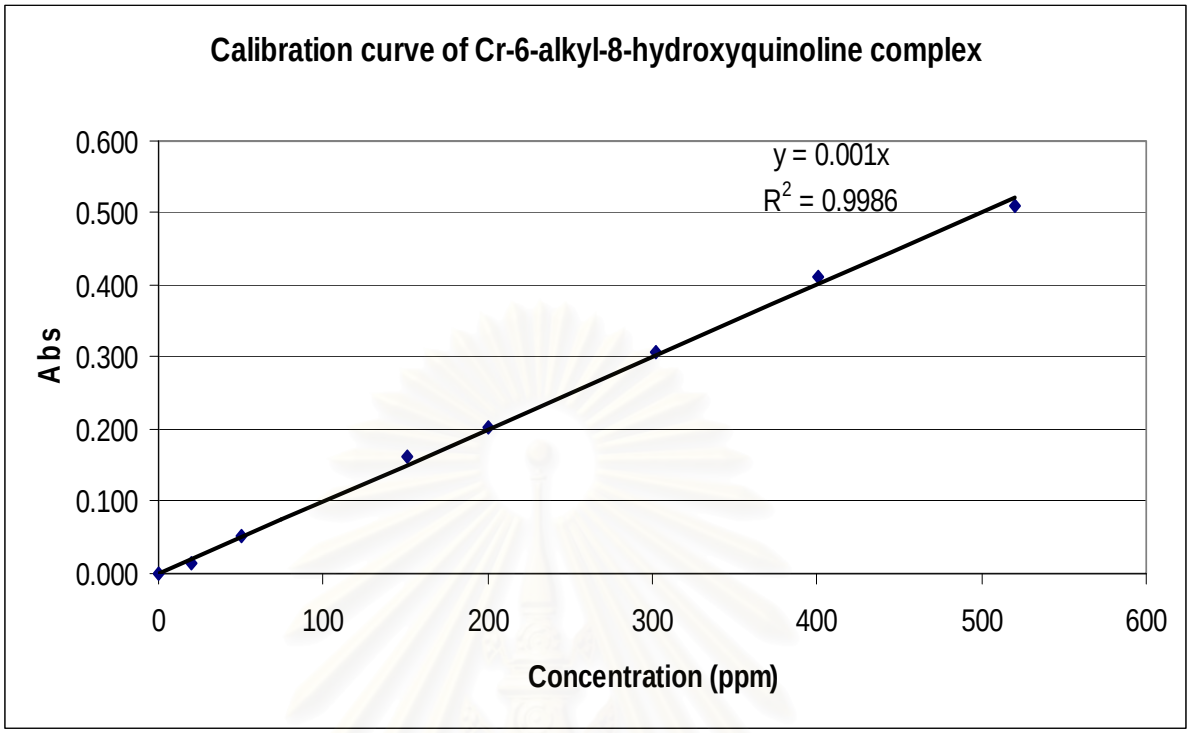

Figure B-13 The calibration curve for the quantitative determinations of Cr (III) with compound **8** complex in THF, extracted with $CHCl_3$ (λ_{max} = 407 nm).

VITA

Miss Suwimol Wonglertwisawakorn was born on November 27, 1982 in Bangkok province, Thailand. She got a Bachelor's Degree of Chemistry from Chulalongkorn University in 2006. Then, she was admitted into a Master Degree program in Petrochemistry and Polymer Science, Chulalongkorn University in 2007 and completed the program in 2008.