การสังเคราะห์และการใช้สีย้อมประเภทแซนทีนเป็นสารทำเครื่องหมายในน้ำมันดีเซล

นายภัททวัฒน์ มณีวัฒนภิญโญ

SYNTHESIS AND UTILIZATION OF XANTHENE DYES

AS DIESEL MARKERS

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ภัทราวัฒน์ มณีวัฒนภิญโญ : การสังเคราะห์และการใช้สีย้อมประเภทแซนทีนเป็นสารทำเครื่องหมายในน้ำมันดีเซล (SYNTHESIS AND UTILIZATION OF XANTHENE DYES AS DIESEL MARKERS) อ.ที่ปรึกษา : รศ.ดร. อมร เพชรสม; 122 หน้า, ISBN 974-17-3147-7

ได้สังเคราะห์สีย้อมประเภทแซนทีน เพื่อนำมาเป็นสารทำเครื่องหมายในน้ำมันดีเซล สามารถจำแนกได้เป็น 2 กลุ่มดังนี้ กลุ่มแรกคือ กลุ่มอนุพันธ์ไฮดรอกซิล ซึ่งได้เพิ่มความสามารถการละลายในน้ำมันดีเซลในรูปสารประกอบอีเทอร์ และสารประกอบเอสเทอร์-อีเทอร์ กลุ่มที่สอง คือ กลุ่มอนุพันธ์อะมิโน ซึ่งเตรียมได้จากสารประกอบไดคลอโร โดยการทำปฏิกิริยากันของกลุ่ม ไฮดรอกซิลกับสารประกอบอนุพันธ์เอมีน สารทำเครื่องหมายที่ถูกสังเคราะห์ขึ้นเหล่านี้จะถูกเติมลง ในน้ำมันดีเซลที่ระดับความเข้มข้น 300 ถึง 900 ในล้านส่วน และสามารถตรวจวัดได้โดยเทคนิค แยกบนแผ่นทินเลเยอร์โครมาโทกราฟีในสภาวะตัวทำละลายผสมที่เหมาะสม รวมทั้งทำการ วิเคราะห์หาปริมาณสีย้อมที่ได้เป็นสารทำเครื่องหมายด้วยเครื่องสเปกโทรฟลูออโรมิเตอร์ ผลจาก การทดสอบสมบัติทางกายภาพของน้ำมันดีเซลด้วยวิธี ASTM พบว่าน้ำมันดีเซลที่เติมสารทำ เครื่องหมายมีคุณสมบัติไม่แตกต่างจากน้ำมันดีเซลที่ไม่เติมสารทำเครื่องหมาย นอกจากนี้ยังพบ ว่าสารทำเครื่องหมายที่สังเคราะห์ได้มีความคงตัวในน้ำมันดีเซลเป็นระยะเวลาไม่น้อยกว่า 3 เดือน

หลักสูตร.......ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...... ลายมือชื่อนิสิต...
สาขาวิชา.......ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...... ลายมือชื่ออาจารย์ที่ปรึกษา...............................
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PATTWAT MANEEWATTANAPINYO : SYNTHESIS AND UTILIZATION OF XANTHENE DYES AS DIESEL MAKERS. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., 122 PAGES. ISBN 974-17-3147-7

Synthetic xanthene dyes for marker in diesel could be classified into two groups. The first group is the hydroxyl derivative with increasing dissolvability in diesel oil by ether and ester-ether groups. The second group is the amino derivative which was obtained from dichloro compound by a reaction of hydroxyl group with amines. These synthetic marker dyes were added into diesel at concentrated levels of 300 to 900 ppm, and their presence could be separated and detected by separation on TLC plate in suitable solvent mixture. Quantitative measurement was carried out using spectrofluorometer. The testing results of fuel properties using the ASTM test methods revealed that the physical properties of the marked diesel were similar to those of the unmarked diesel oil. Moreover, those synthetic marker dyes were found to be stable in diesel oil for at least three months.

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

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ABBREVIATIONS

ASTM	=	American Society for Testing and Materials
API	=	American Petroleum Institute
^{13}C-NMR	=	Carbon-13 Nuclear Magnetic Resonance
cSt	=	Centistroke
CFR	=	Cooperative Fuel Research Council
°C	=	Degree Celcius
°F	=	Degree Fahrenheit
^{1}H-NMR	=	Proton Nuclear Magnetic Resonance
ml	=	Millilitre
Sp.Gr.	=	Specific Gravity
cm^{-1}	=	Unit of wave number
%wt	=	Percent by weight
%yield	=	Percent yield

CHAPTER I

INTRODUCTION

1.1 Introduction

For along time, a large quantity of fuel have been consumed in many countries and at the same time the government encountered many problems such as smuggling diesel from abroad into the country, mixing of organic solvents in gasoline which affected the octane number, and avoidance to pay fuel tax in higher rate by using fuels in different purposes for example; using diesel, which is used for fishery, in vehicles. These causes made the government lose many revenues and consumers have to use low-quality gasoline. For these reasons, it is essential to develop the methods of marking and identifying petroleum products so as to distinguish a variety of fuel available in the market.

A solution to these problems is the addition of marker into fuel in order to differentiate specific brands of fuel and classifying the type of fuel and petroleum products. This solution can be done by extracting the marker with suitable solvents and detect the color change which depended on the structure of markers. Therefore, this research was planned to synthesize xanthene dyes as marker in fuel in order to solve the problem of adulteration in fuel.

Marker is a chemical substance which was added into petroleum products for identifying the products by simple chemical analysis. Markers are added into petroleum products in order to prevent evading a fuel tax. At the beginning, marker is a radioactive substance which can be analyzed by special instrument. Quinizarin is a good marker but it can dissolve in solvent and extract less than other chemicals. Later, azo dyes are utilized as marker and they gave good color by pH change [1,2].

Xanthene dyes are compounds which are widely utilized as marker because it can be fluoresced [3,4]. In 1996, Smith had synthesized xanthene dyes which has hydroxyl group and derivative of hydroxyl group, by esterification with organic anhydride or organic halide, which have alkyl group (number of carbon 1-18 carbons). The markers were added into fuel and after extraction with strong base such as ammonium hydroxide, they gave strongly fluorescence [5]. In 1997, Michael had developed an extract system (quaternary alkyl ammonium base such as tetraethylamonium hydroxide) for xanthene dyes markers. The fluorescent colors depended on the type of base and solvent mixture such as green, purple and red [6].

Xanthene dyes are classified into amino group, Rhodime B, hydroxyl group, Fluorescein, and functional, which have both of hydroxyl and amino group, is Chromgen Red B (The range is yellow to purple).

This research planned to synthesize xanthene dyes containing hydroxyl group by the reaction of phthalic anhydride and resorcinol. After that the product were

esterified or etherified for better soluble in diesel oil. To synthesize the amino derivatives of xanthene dyes the hydroxyl group was changed to dichlorofluorescein and then reacted with aliphatic amine or aromatic amine [7,8]. Afterwards the marker was added into diesel oil and their performance were evaluated.

The objective of this research

1. To synthesize of xanthene dyes for use as markers in diesel.
2. Qualitative and quantitative analysis of markers after adding into diesel, including stability of marker in diesel.

The scope of this research

1. Literature review.
2. Synthesis of xanthene dyes (hydroxyl group) and characterized by spectroscopic techniques such as FT-IR and NMR.
3. Synthesis of markers from xanthene dyes (hydroxyl group).
4. Synthesis of amino derivative of xanthene dyes from the reaction between hydroxyl group and aliphatic amine or aromatic amine for marker dyes.
5. Investigation of the fluorescent property of marker dyes.

6. Study the effect of marker dyes on the physical properties of dyed fuels such as pour point, flash point, etc.

7. Discussion and conclusion.

CHAPTER II

THEORETICAL

2.1 Color of organic compounds [9]

Color vision is based on a variety of physical, chemical, physiological and psychological processes. That part of the electromagnetic spectrum visible to man is the range of wavelengths between 400 and 700 nm. Light can be absorbed completely, partly or not at all by gases, liquids or solids. That part which is not absorbed can be reflected at the surface or solids or transmitted through gases, liquids or glassy solids. The light which is emitted from a light source and the reflected or transmitted light reach the retina in the human eye. There, the light with wavelengths between 400 and 700 nm initiates a photochemical reaction, and subsequently a series of light-independent reactions in the visual pigment take phase. By a transfer of information between the eye and the brain, this process results in visual perception.

If electromagnetic rays, whose energy distribution in the visible range corresponds to that of sunlight on earth, reach a solid which reflect all visible light in a diffuse way and with complete reflectance, it appears to the human eye as white. On the other hand, if the solid absorbs all light, we recognize it as black. If it absorbs a constant fraction of light in the whole range between 400 and 700 nm it appears gray. White, gray and black are called achromatic colors.

They are characterized by a constant absorption in the range between 400 and 700 nm. In contrast to achromatic colors, solids having chromatic colors show

one or more bands; i.e. absorption maxima and minima in the visible spectrum. If an absorption band is located in the short wavelength part of the visible spectrum (400-430 nm), that part of the incoming light will be absorbed. The rest of the spectrum will be reflected and the solid will appear yellow to the eye. Analogously, absorption bands at 430-480 nm, 480-550 nm, 550-600 nm and 600-700 nm yield solids which to the eye appear orange, red, violet and blue, respectively. Solids which look green are characterized by two absorption maxima at 400-450 nm and 580-700 nm. A qualitative inspection does not allow one to decide whether a green color originates from one dye with two absorption maxima, or from a mixture of a blue and a yellow dye.
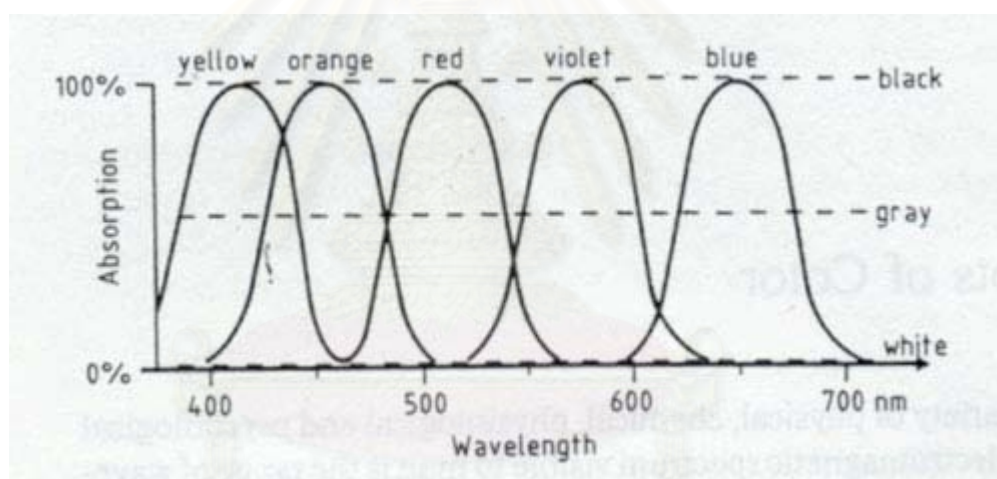
Figure 2-1: Schematic representation of the light absorption of colored solids.

The absorption spectra of such related dyes are normally found to vary. From both the scientific and technological points of view it is interesting to examine how such structural differences influence the spectrum. The changes in position and intensity of the bands are described qualitatively as indicated in figure 2-2. Shifts of the absorption maximum to longer and shorter wavelengths, respectively, are called bathochromic and hypsochromic shifts. An increase and a decrease in the magnitude

of the extinction coefficient (absorption) are termed hyperchromic and hypochromic

charges, respectively.
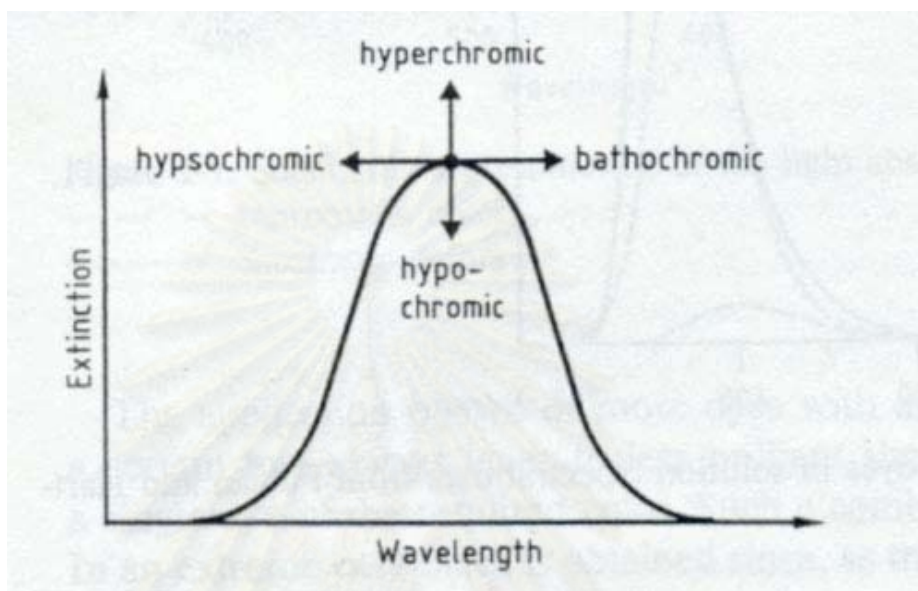
Figure 2-2: Scheme of designations for wavelength shifts and changes of extinction of absorption bands.

2.2 Dyes and Marker [3,24]

2.2.1 Dyes

Dyes are intensely colored substances that can be used to produce a significant

degree of coloration when dispersed in, or reacted with, other materials by a process

which, at least temporarily, destroys the crystal structure of the substance. This latter

point distinguishes dyes from pigments which are almost always applied in an

aggregated or crystalline-insoluble from. Modern dyes are products of synthetic

organic chemistry. To be of commercial interest, dyes must have high color intensity and produce dyeing of some permanence. The degree of permanence required varies with the end use of the dyed material.

All molecules absorb energy over various parts of the electromagnetic spectrum. The characteristic of dye molecules is they absorb radiation strongly in the visible region, which extends from 4000 – 7000 angstroms. Only organic molecules of considerable complexity which contain extensive conjugation systems linked to electron withdrawing and attracting groups give sufficient absorption (tinctorial value) in the visible region to be useful as dyes. The shade and fastness of a given dye may vary depending on the substrate, due to different interactions of the molecular orbitals of the dyes with the substrate, and the ease with which the dye may dissipate its absorbed energy to its environment without itself decomposing.

The manufacture and use of dyes is an important part of modern technology, Because of the variety of materials that must be dyed in a complete spectrum of hues, manufacturers now offer many hundreds of distinctly different dyes. An understanding of the chemistry of these dyes requires that they were classified in some way. From the viewpoint of the dyer, they are best classified according to application method. The dye manufacturer, on the other hand, prefers to classify dyes according to chemical type.

The properties of dyes may be classified as application properties and end-use properties. Applications properties include solubility, affinity, and dyeing rate. End-use properties include hue, and fastness to degrading influences such as light, washing, heat (sublimation), and bleaching. Dyes are selected for acceptable end-use properties at minimum expense. Involved application procedures are used only when necessary to achieve unusually good results.

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

Table 2-1 : Dye measure quantitatively as molar absorptivity.

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

It is obvious from the list above that many basic dyes have about 10 –20 times the color value of the anthraquinone types. Unfortunately, light fastness is in the reverse order, the anthraquinones being used where maximum durability to light is needed. The challenge to the dye chemist or engineer is to increase the color strength of the light-fast dyes or to improve the fastness of the high absorption dyes.

Of the many thousands of dyes which have been synthesized in laboratories, about 3500 have had actual commercial use. These have been indexed in several compilations. For the convenience of the dye, dyes are classified according to application method. The best classification method available is that used in the color index. The Society of Dyers and Colorist (England) and the American Association of Textile Chemists and Colorists give each dye an individual five-digit number as identification regardless of the specific manufacturer. Although some of the earliest dyes have common names with general usage, commercial dyes are sold under a large number of names, many of which relate to the some material.

Chemical structure. The most precise and scientific classification of dyes is based upon their chemical structure. This is the classification of interest to the

research chemist and the manufacturer of dyes. The classes that are listed in the color

index.

Table 2-2 : Some important dyes.

Some Important dyes	Uses and properties
Nitroso (quinone oxime)	For wool
Nitro (o-and p-nitrophenols and o- and p- nitroamines)	For cellulose acetate and nylon
Azo (aromatic and heterocyclic azo compounds)	For miscellaneous materials
Azoic	For textile fibers
Stilbene	For textiles and paper
Diphenylmethane (ketone imine)	For cotton, nylon and leather
Triarylmethane	For cellulose fibers
Xanthene	For paper and inks
Acridine	For bast fibers
Quinoline	For paper and wool
Methine and Polymethine	For photography
Thiazole	For cellulose fibers
Indamine and Indophenol	For color photography
Azine	For mordanted cotton
Oxazine	For leather
Thiazine	For paper
Sulfur	For cellulose fibers
Lactone	For chromemordanted wool
Amino ketone and Hydroxyl ketone	For cellulose fibers
Anthraquinone	For wool and silk

Some Important dyes	Uses and properties
Indigoid	For cellulose fibers and wool
Phthalocyanine	As a pigment; good fastness

2.2.2 Xanthene dyes [4,10]

Xanthene dyes are those containing the xathylium or dibenzo-γ-pyran nucleus as the chromphore with amino or hydroxyl groups meta to the oxygen as the common substituents.

xanthylium   xanthene
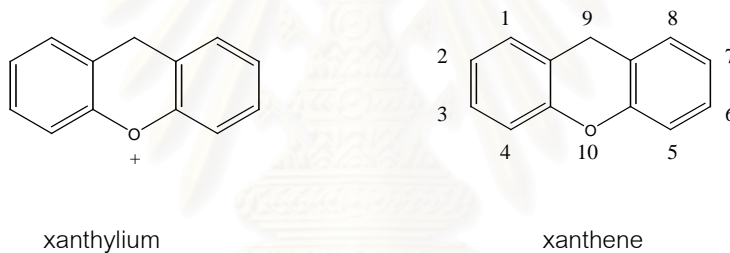
The xanthenes are characterized by pure, brilliant hues and by fluorescence. They range in shade from yellow to violet.

In general xanthene dyes are cationic (basic) dyes [11]. The class, however, comprises acid- and spirit-soluble dyes an mordant colors and lakes. The fluoresceins, which contain carboxyl and phenolic hydroxyl groups, are acid dyes. Acid xanthene dyes are obtained also by the introduction of the sulfonic groups. Esterification of the carboxyl group yields spirit-soluble dyes. Introduction of o-dihydroxybenzene or salicylic acid moieties give mordant dyes. Lakes are obtained by precipitation of hydroxyl-or carboxyl-containing dyes with salts of metals, such as lead or aluminum.

Xanthene dyes can be conveniently classified into three main groups: Those containing hydroxyl groups e.g. Fluorescein; those containing both amino and hydroxyl groups e.g. Chromogen Red B; and those containing amino groups e.g. Rhodamine B.

Xanthene dyes, like their close relative the triphenyl methanes, are cationic resonance hybrid.
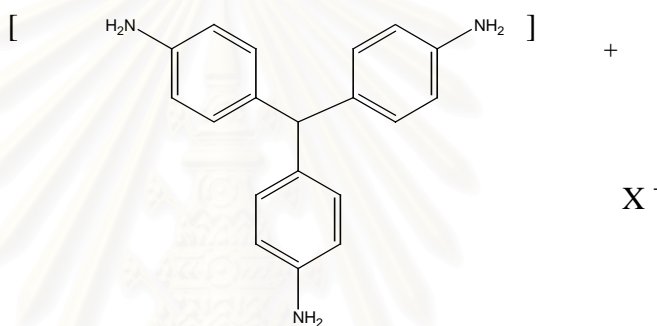
Parasaniline (a triphenylmethane)

Most xanthene dyes are fluorescent. The oxygen atom, in heterocyclie systems, and ortho-para directing are know to contribute to fluorescence. Generally they are also fugitive to light, as are many cationic dyes. Although no direct correlation has been established between fluorescence and light fastness, many fluorescent dyes have poor light fastness. However, a connection has been demonstrated by Rath and Brielmaier who increased the light fastness of fluorescent dyeing by pretreatment of the fiber with fluorescent quenching substances.

2.2.3 Marker [12]

"A Marker" is defined herein as a substance which can be dissolved in a liquid to be identified in visually undetectable quantities, and then subsequently detected by performing a simple chemical or physical test on the tagged liquid. Markers that have been proposed in crude radioactive substances, fluorescent substances, and a variety of lightly colored or virtually colorless compounds which react with selected agents to provide intensely colored derivatives. Radioactive markers, in particular, have not gained wide acceptance due to the necessity for special equipment and handling measures to prevent harmful physiological disturbances to personnel.

2.3 Fluorescence and Phosphorescence

A molecule or ion in an exited state can lose the absorbed energy in the following ways : (a) radiationless transitions, such as internal conversion or intersystem crossing (macroscopically observable by heat formation), (b) emission of radiation (fluorescence and phosphorescence) and (c) photochemical reactions.

Processes of type (a) and (b) are represented schematically in the so-called Jablonski diagram, which is a scheme of the essential levels: In figure 2-3 the lowest vibrational energy levels of electronic states are indicated by thick horizontal lines; other horizontal lines represent associated vibrational levels. A molecule (or ion) in the ground state S_0 will be brought to an excited singlet state, either S_1 or S_2 (or higher stated S_j), by absorption of light. Radiationless transitions are shown by wavy lines in the Jablonski diagram. Vibrational deactivation (vertical wavy lines) leads to the lowest vibrational level of the respective excited singlet electronic state or to lower

singlet states. Intersystem crossing (horizontal wavy line) leads to triplet states. Emission of radiation from the lowest vibrational level of the excited state S_1 to any of the vibrational levels of the ground state is called fluorescence. Emission of radiation from the lowest triplet state T_1 to the ground state is called phosphorescence.

Photochemical reactions (e.g. rearrangements, dissociations, dimerizations, photoadditions, reactions with neighboring particles etc.) generally occur in triplet states which have lifetimes between 100 ns and 10 ns. The lifetime of excited singlet states (1 to 100 ns) is normally too short for chemical reactions to take place.

With the exception of phosphorescence all radiation processes are vary fast. First order rate constants for these processes have the following orders of magnitude : Light absorption 10^{15} s^{-1}, Vibrational relaxation $\geq 10^{12}$ s^{-1}, Fluorescence 10^{16} to 10^{9} s^{-1}, Intersystem crossing 10^{-1} to 10^{5} s^{-1} and Phosphorescence 10^{-2} to 10^{4} s^{-1}

As seen from figure 2-3, absorption normally occurs from the lowest vibrational level of the electronic ground state and leads to one of the vibrational levels of an electronic excited state. Fluorescence generally takes place from the lowest vibrational level of the first excited state $(S_1)^*$ and results in the particle dropping to one the vibrational levels of the ground state. The fluorescence spectrum, in ideal cases, is there fore a mirror image of the absorption spectrum, but shifted to longer wavelengths (Stokes rule).

*An exception is azulene where fluorescence starts from S_2
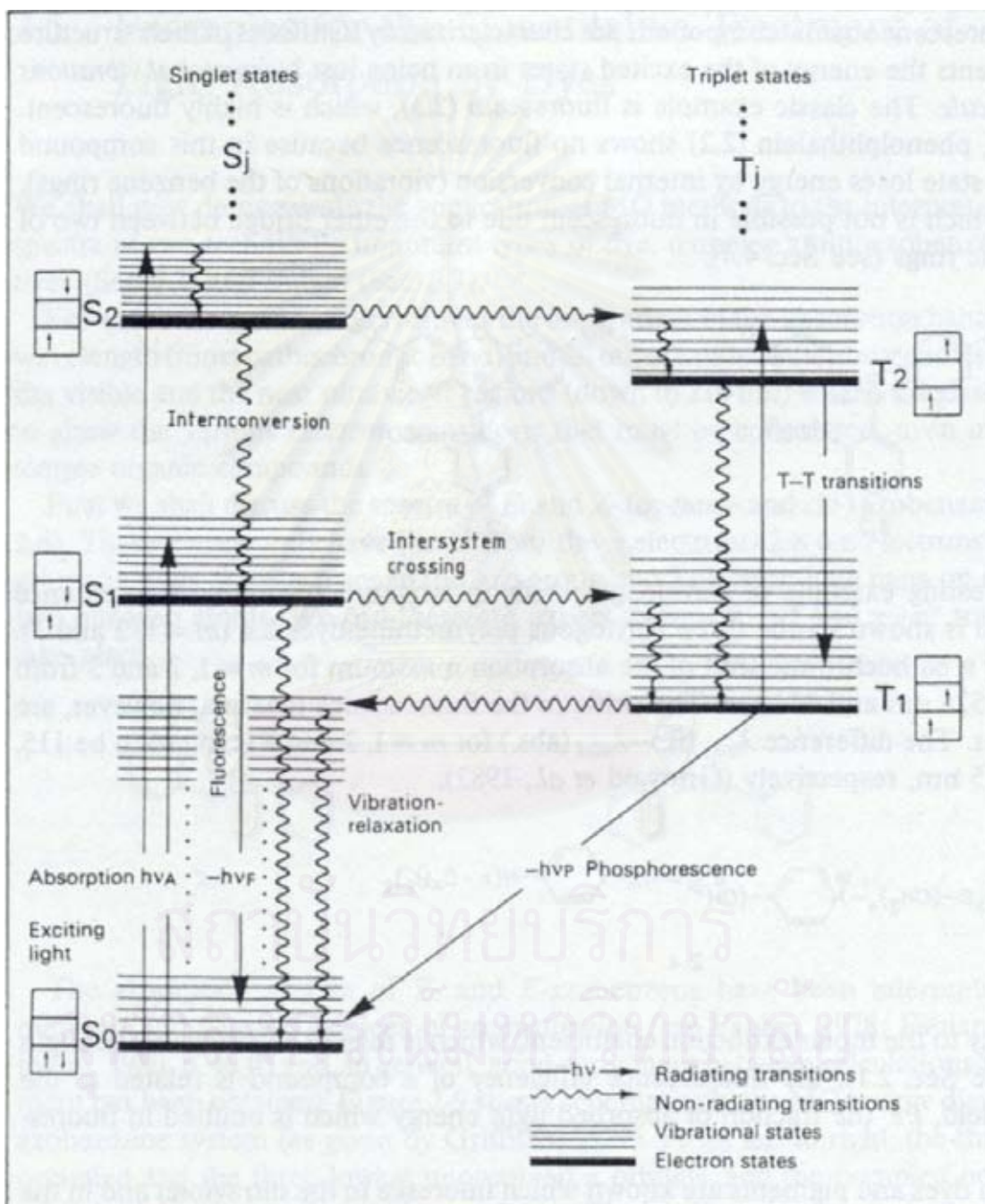
Figure 2-3 : Jablonski scheme

In order to display phosphorescence, molecules primarily excited to the S_1 singlet state must convert to the lowest level of their triplet manifold (T_1) by the radiation less process of intersystem crossing. From T_1 they can slowly emit radiation (phosphorescence), or they can return to the S_0 level without emission by intersystem crossing. Phophorescence spectra are also usually shifted bathochromically, but more so than observed in fluorescence. The reason for this is that the energy of the triplet level T_1 is usually below that of the singlet S_1. Therefore, phosphorescence takes place at higher wavelengths than fluorescence.
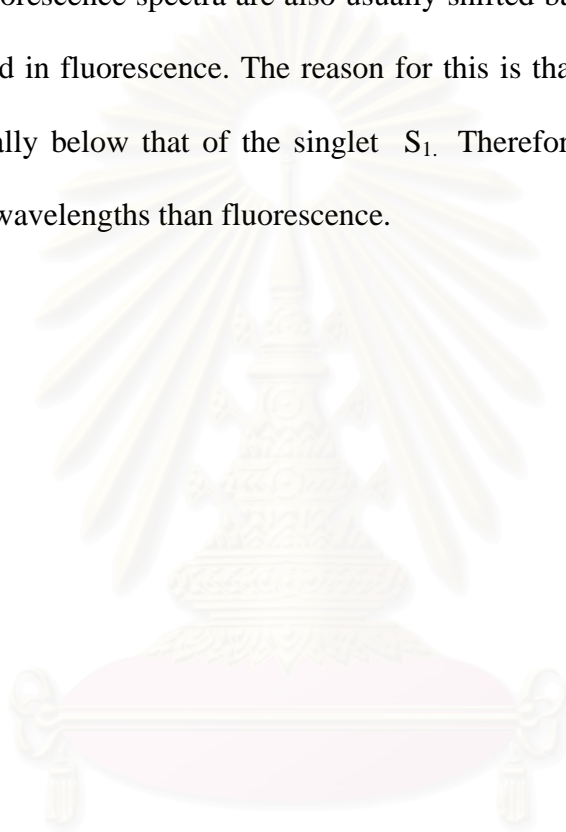
2.4 Literature reviews

In 1999, Friswell, M.R. *et al*. synthesized silent fluorescent petroleum markers having the following formula [12]:
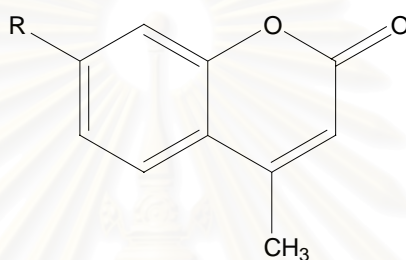
Where R is selected from a linear or branched C_1-C_{18} alkylcarboxyl radical.

These compounds are synthesized from esterification reaction between an appropriate linear or branched C_1-C_{18} alkylcarboxylic acid or acid halide, and 7-hydroxy-4-methylcoumarin. These makers are used for tagging petroleum product at levels of about 0.25 ppm to 100 ppm. They may be detected in the product by extraction with an alkali aqueous solution which produces strongly fluorescence.

In 1999, Smith, M. J. and Desai, B. synthesized colorless petroleum markers, which is a derivative of isobenzofuranone and marked in petroleum products, have the general formula [13]:
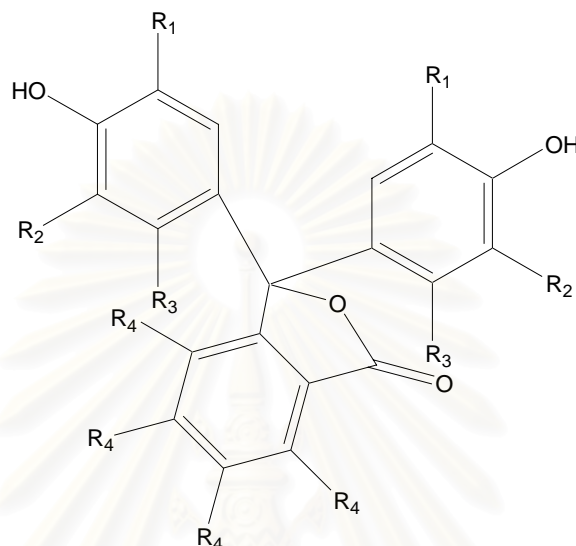
Where R_1 is C_1-C_{18} alkyl or alkoxy group; R_2 and R_3 are hydrogen, alkyl group, alkoxy group, or part of naphthalene rings system; R_4 is any combination of bromine, or hydrogen.

The marker compounds are synthesized by condensation of phthalic acid or anhydride with 2-alkylphenol or 1-naphthol. Because these markers are colorless in petroleum products, their presence are detected by reacting them with a basic developing reagent such as an alkali metal hydroxide solution. The marker will undergo chromophoric reaction, and produces color in an extracted phase.

In 1996, Smith, M. J. synthesized fluorescent petroleum markers until got colorless compounds, which developed fluorescence when extracted with an appropriate basic solution, for marking petroleum fuels. These markers, which are the derivatives of 2(3H)furanone, have the general formula [5]:
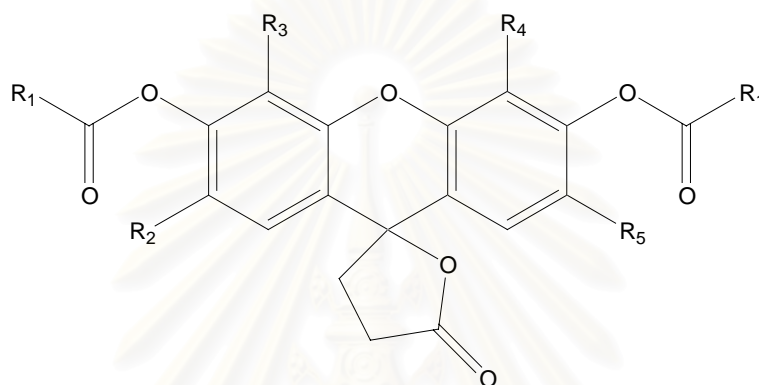
Where R_1 is C_1-C_{18} alkyl group or an aryl group; R_2, R_3, R_4 and R_5 are hydrogen, chlorine, bromine or C_1-C_{12} alkyl group.

These markers are synthesized by converting 2(3H)furanone to an organic diesters to eliminate any tendency to partition into water. The diester may be derived from an organic acid, its anhydride or halide containing from one to eighteen carbon atoms. The ester markers can be added to any liquid petroleum product, and can be detected by reacting them with the developing reagent. Example of the developing reagents are an aqueous solution of alkali metal hydroxide, and aqueous solution of the quaternary ammonium hydroxide. The base will hydrolyze the esters and prompt formation of a highly fluorescent dianion, which may be variously colored.

In 1977, Smith, M.J. developed system for base reactable petroleum fuels makers, which are the derivatives of 2(3H)furanone, have the general formula [6]:
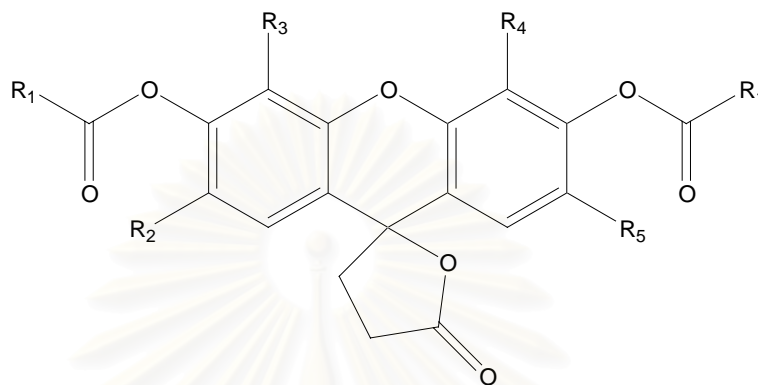
Where in R_1 is C_1-C_{18} alkyl group or an aryl group; R_2, R_3, R_4 and R_5 are hydrogen, chlorine, bromine or C_1-C_{12} alkyl group.

The present invention includes compositions for and methods of detecting or developing base reactable fuel markers. Developing agents of its present invention contain quaternary or tetra alkyl ammonium base of the following formula:
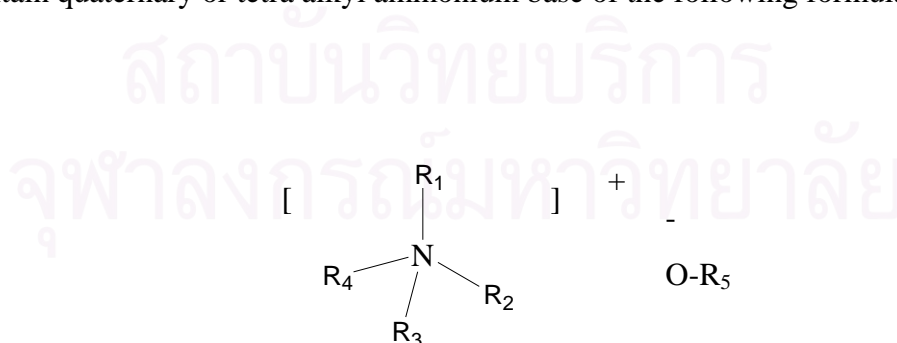
Where R_1, R_2, R_3 and R_4 are the same or different alkyl or benzyl groups and R_5 is hydrogen or an alkyl group.

Marker in fuel is developed as quaternary alkyl ammonium base such as tetraethyl ammonium hydroxide and extracted by solvent mixture between aprotic solvent and aromatic solvent such as formamide benzyl alcohol. These markers are synthesized by converting 2(3H)Furanone to an organic diesters by the reaction of alcohols with organic anhydride or organic halide. After extraction, color of the extractant is varied up to the type of solvents and markers, e.g. green, violet, and red.

CHAPTER III

EXPERIMENTAL

3.1 Materials

Phthalic anhydride, resorcinol, 1-bromodecane, phosphoric acid, toluene, phosphorus pentachloride, hydrochloric acid and zinc(II)chloride were purchased from Fluka. Carbon tetrachloride, sodium hydroxide, acetone, ethyl acetate, hexane, chloroform, methanol, aniline, ether and dichlorometane were from Merck. Nitrogen gas was obtained from Thai industrial gas.

3.2 Instruments

The infrared spectra were recorded on a Nicolet Fourier Tranform Infrared spectrophotometer model Impact 410. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Bruker model ACF200 spectrometer, which operated at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C nuclei. The fluorescence was recorded on a Jasco model FP-777 spectrofluorometer.

The quantities of marker dyes in fuel oils were measured using a Jasco model FP-777 spectrofluorometer. The kinematic viscosities of dyed and undyed diesel fuels were obtained with a Cannon automatic viscometer. Flash point (Pensky-Martens) of dyed and undyed diesel fuels were measured using an ISL (PMFP93) automatic flash point tester, while the pour points of dyed and undyed diesel fuels were recorded on an ISL(CPP92) automatic pour point tester. Sulfur contents in dyed and undyed diesel

fuels were determined using an Outokumpu (X-MET820) automatic sulfur content. The distillation of dyed and undyed diesel fuels were carried out with an Herzog (MP626) automatic distillation apparatus.

3.3 Experimental

3.3.1 Synthesis

3.3.1.1 Xanthene dyes (Hydroxyl group)

3.3.1.1.1 3',6'-dihydroxyfluoran (Compound **1a**) [14]
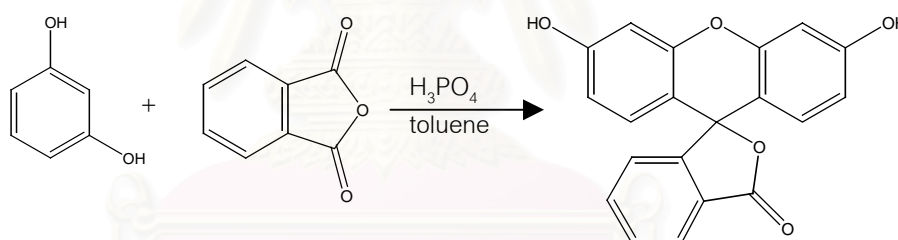
A mixture of phthalic anhydride (5.00 g, 0.03 mol), resorcinol (7.43 g, 0.06 mol), phosphoric acid (3 ml) and toluene (50 ml) was heated until boiling under reflux for 5 hours to give a reddish insoluble mass in toluene. The toluene was removed and the residue was dissolved in dilute aqueous sodium hydroxide, filtered and added to dilute (1:1) hydrochloric acid solution. This process was repeated twice and finally 3',6'-dihydroxyfluoran was dried at 100 ℃. Alternatively, it has been crystallized from acetone by allowing the solution to evaporate at 37 ℃ in an open beaker or from ethanol and dried in a vacuum oven. The reddish solid (8.40 g, 74 % yield) with m.p. 380 ℃ was obtained.

3.3.1.1.2   6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (Compound 2a) [15]
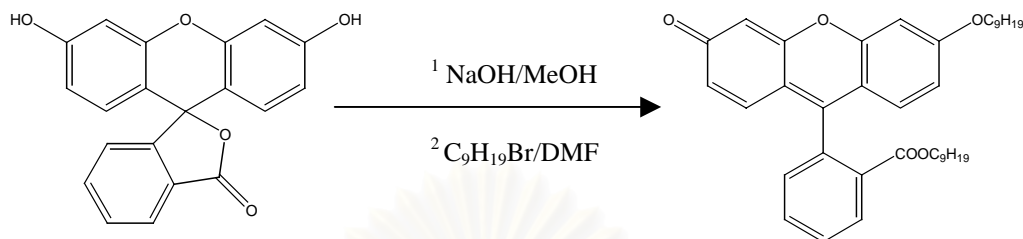
Preparation of 3', 6'-dihydroxyfluoran disodium salt by adding 2 g of 3',6'-dihydroxyfluoran (compound **1a**) into 0.50 g (0.01 mol) of sodium hydroxide in 15 ml methanol and stirred for 1 hour. Then, added 4.6 ml (0.02 mol) of bromononane in 50 ml of dimethylformamide and heated with stirring at 120 ℃ for 6 hours. This mixture was extracted with 200 ml of ethyl acetate, and the two phases were separated in a separatory funnel. The reddish liquid product was washed 4-5 times with cold water. Then the solvent was removed by vacuum to obtain crude product. This product was purified by column chromatography, which was eluted by a mixture of hexane-ethyl acetate (3:2) to obtain reddish liquid (2.49 g, 71% yield) with R_f 0.4 (hexane: ethyl acetate (3:2)).

3.3.1.1.3 3'-hydroxy-6'-nonyloxyfluoran (Compound 3a) [15]
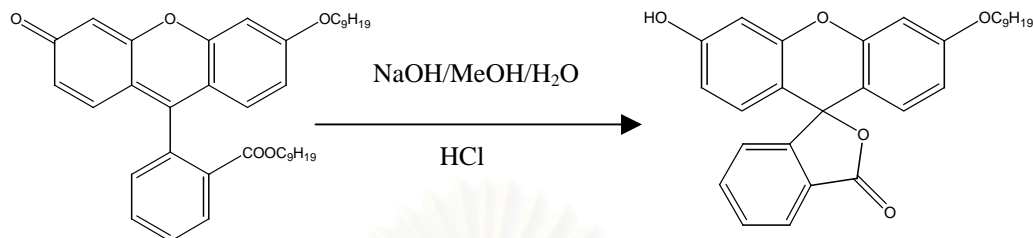
Compound **2a** was hydrolyzed to provide nonyl substituted by adding 2 g of compound 2a into 4% of sodium hydroxide in the mixture of methanol-water (MeOH/H$_2$O; (3:1), v/v) and stirred at room temperature for 4 hours. Then diluted hydrochloric acid was added. This mixture was extracted with 200 ml of ethyl acetate, and the two phases were separated in a separatory funnel. The reddish liquid oil was washed 4-5 times with water. The reddish oil was stripped to remove solvent by vacuum. This product was purified by column chromatography and eluted with a mixture of hexane-ethyl acetate (3:2) to obtain reddish oil (1.10 g, 70 % yield) with R$_f$ 0.8 (hexane: ethyl acetate (3:2)).

3.3.1.2 Xanthene dyes (Amino group)

3.3.1.2.1 3',6'-dichlorofluoran (Compound 1b)
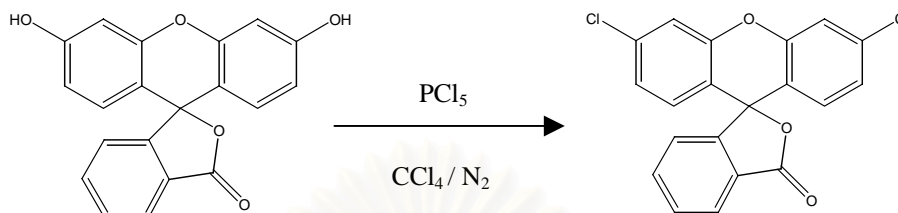
Compound **1a** (2 g) was added into 50 ml of carbon tetrachloride and 1.25 g of phosphorus pentachloride in a round bottom flask equipped with calcium chloride guarded condenser. The mixture was heated under nitrogen atmosphere until refluxed at 80 ºC for 24 hours. The reaction mixture was sampled and analyzed by thin layer chromatography. The product was separated as a yellow solution which was then vacuum stripped to remove solvent. The product was 3',6'-dichlorofluoran (1.71g, 77 %, m.p. 318 ºC).

3.3.1.2.2 *p*-nitro-linear alkylbenzene (Compound 2b)
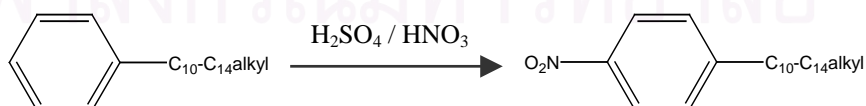
Concentrated sulfuric acid (10 g, 5.46 ml) was added in portions to concentrated nitric acid (6.3 g, 4.15 ml, 0.1 mol) with vigorous stirring and cooling. Linear alkylbenzene (10 g, 0.04 mol) was added very slowly into the above mixed acid where the reaction temperature was held at 50 ºC. The mixture was continually stirred for another 1 hour. This mixture was diluted with 200 ml of cold water and collected. The unreacted linear alkylbenzene was removed by column chromatography eluted with hexane. The product (8.97 g, 76 %yield) was yellow liquid with R_f 0.58 (hexane: dichloromethane, 1:1).

3.2.1.2.3 *p*-linear alkylaniline (Compound 3b) [16]
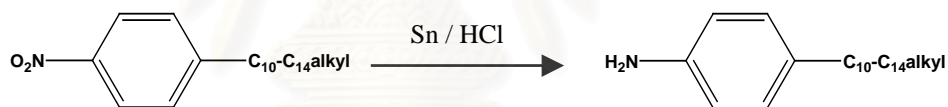
A mixture of *p*-nitro-linear alkylbenzene (5.8 g, 0.02 mol) and tin powder (5.93 g, 0.05 mol), which was placed in a flask equipped with a reflux condenser, was stirred and then 1.25 ml of concentrated hydrochloric acid was added through round-bottom, three-neck flask. This reaction is exothermic, so the flask was dipped into a cold water bath to control the temperature. When the initial reaction had subsided, another 1.25 ml of acid was poured down the round-bottom, three-neck flask. The mixture was continually stirred and cooled again. This manner was proceeded until all 11.25 ml of acid had been added and heating was continued under reflux for an hour. The above mixture was cooled to room temperature and a solution

of 9 g of sodium hydroxide in 15 ml of water was gradually added with cooling. An oily liquid product was dried and the hexane was removed by evaporation. The product (4.24 g, 81 % yield) was colorless liquid with R_f 0.37 (hexane:dichloromethane, 1:1).

3.3.1.2.4 *p*-linear alkylanilinefluorescein (Compound 4b)

3',6'-Dichlorofluoran (1.1 g, 0.003 mole) was dissolved in 500 ml of dimethylformamide and 2.5 g of calcium oxide, then stirred and 0.82 g of zinc chloride, 1.56 g of compound **3b** was added into the mixture while the reaction temperature was held at 140-150 ℃. The crude product was purified by column chromatography, which was eluted with a mixture of hexane-ethylacetate (3:2).

3.3.1.2.5 cyclohexylaminefluorescein (Compound 5b)

The same procedure was used in the preparation of 3.3.1.2.4 (compound 4b), except that the compound **3b** was replaced by 0.59 g of cyclohexyl amine.

3.3.1.2.6 isopropylaminefluorescein (Compound 6b)

The procedure of 3.3.1.2.4 (compound **4b**) was repeated except that the compound 3b was replaced by 0.61 g of isopropylamine.

3.3.1.2.7 diisoamylaminefluorescein (Compound 7b)

The same procedure as the preparation of 3.3.1.2.4 (compound **4b**) was followed, except that the compound **3b** was replaced by 0.94 g of diisoamyl amine.

3.3.1.2.8 anilinefluorescein (Compound 8b)

The preparation of 3.3.1.2.4 (compound **4b**) was instead of aniline (0.56 g, 0.55 mole) in a similar manner.

3.3.1.2.9 *N*-cyclohexylanilinefluorescein (Compound 9b)

This compound was prepared in a similar manner to the preparation of 3.3.1.2.4 (compound **4b**), except that the compound 3b was replaced by 1.05 g of *N*-cyclohexylaniline.

3.3.1.2.10 4-cyclohexylanilinefluorescein (Compound 10b)

This procedure were similar with the preparation of 3.3.1.2.4 (compound **4b**), except the compound **3b** was replaced by 1.05 g of 4-cyclo-hexylaniline.

3.3.2   Preparation of stock solution of marker dyes

Each synthetic xanthene dye was prepared by weighing 0.05 g of product and put into 50 ml volumetric flask, then diluted and made up the volume with diesel. Each 1000 ppm marker dyes in diesel was obtained.

3.3.3   Detection of marker dyes

The method for detection of marker dyes which added into diesel could be detected in petroleum products by thin layer chromatography (TLC), the spots of marker dyes have been identified on TLC by inspecting the TLC under long-wavelength (365 nm) Ultraviolet lamp.

Diesel containing 300-900 ppm of xanthene dyes was used for the determination of suitable condition. The marked diesels were prepared by weighing 0.05 g of 1000 ppm stock marker dyes solution into 50 ml volumetric flask make up with undyed diesel.

3.3.3.1 The type of developing solvent.

Spot the marker dyes diesel (2 μl) on the thin layer chromatography (TLC : silica gels 60). Then took the spotted marker dyes diesel to develop in chamber containing developing solvent saturated with the volatile of developing solvent. After that mixed solvents include dichlorometane, hexane and ethyl acetate for developing solvent were used, then detected by using the ultraviolet lamp.

3.3.3.2 The ratio of developing solvent.

Find the best solvent mixture for developing and varied the solvent mixture (from 3.3.3.1) which gave the best resolution and detected by ultraviolet lamp.

3.3.4 Effect of marker dyes on the physical properties of diesel fuels.

The physical properties of dyed and undyed diesel were studied according to the ASTM methods described in table 3-1.

Table 3-1: The ASTM testing methods of dyed and undyed diesel.

Test items	Test methods ASTM
API gravity @60 F	D 1298
Specific gravity @ 15.6/15.6 C	D 1298
Calculated cetane index	D 976
Kinematic viscosity @ 40 C, cst	D 445
Pour point, °C	D 97
Flash point, °C	D 93
Sulfur content, %wt	D 4294
Distillation	D 86
Total acid number, mg KOH/g	D 974
Color	D 1500

3.3.5 Quantitative determination of marker dyes in dyed diesel.

The method for quantitative determination of marker dyes which added into diesel could be made by using spectrofluorometer. The standard calibration curve of marker dyes in diesel was prepared at concentrations from 100 to 900 ppm of marker dye by the following procedure.

The stock marker dye solution (1,000 ppm) was pipetted into a 50 ml volumetric flask, and made up with undyed diesel. The volume of the stock solution for each concentration is shown in table 3-2.

Table 3-2 : The volume of the stock solution (1,000 ppm) for each 100-900 ppm concentration.

Concentration (ppm)	Volume of 1,000 ppm stock solution (ml)
100	5
300	15
500	25
700	35
900	45

The dyed diesel was drawn off for recording in a spectrofluorometer at its λ_{ex} and λ_{em}. The calibration curve was a plot between intensity and the concentration of marker dyes in diesel.

3.3.6 Stability of marker dyes in dyed diesel.

The dyed diesel of 300-900 ppm concentration of marker dyes were prepared and stored for 3 months. The quantity of marker dyes contained in diesel was measured by spectrofluorometer.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization and physical properties

Characterization of 3', 6'-dihydroxyfluoran

3', 6'-Dihydroxyfluoran, which was prepared in 74 % yield from condensation of phthalic anhydride with resorcinol was a reddish solid, soluble in ethyl acetate and acetone, m.p. 380 ℃ .The structure is shown below:
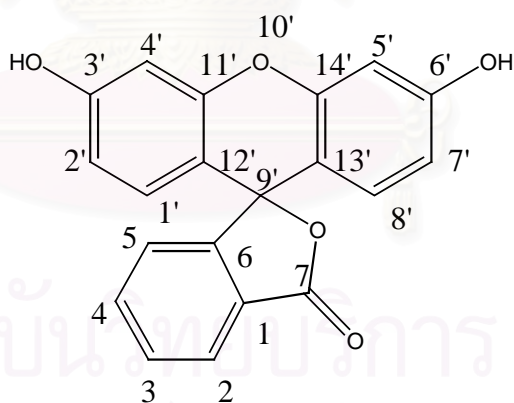
The FT-IR spectrum of 3', 6'-dihydroxyfluoran (Fig 4–1) showed the important absorptions at 3370 cm^{-1} (O-H stretching of phenol), 3011 cm^{-1} (=C-H stretching of aromatic), 1700 cm^{-1} (C=O stretching of ester), 1597and1465 cm^{-1} (C=C ring stretching of aromatic) and 1363 cm^{-1} (OH bending of phenol).

The ^{1}H-NMR spectrum of 3', 6'-dihydroxyfluoran (Fig 4–2) showed the signals at 6.53-7.97 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–1.

Table 4–1: The ^{1}H-NMR spectrum assignment of 3', 6'-dihydroxyfluoran.

Proton position	Chemical shift (ppm), J(Hz)
2	7.97; 1H; d; 7.3
3	7.71; 1H; t; 5.9
4	7.76; 1H; t; 5.1
5	7.22; 1H; d; 7.2
1', 8'	6.53; 2H; s
2', 7'	6.53; 2H; s
4', 5'	6.65; 2H; s

The ^{13}C-NMR spectrum of 3', 6'-dihydroxyfluoran (Fig 4-3) could be assigned as shown in Table 4-2. Its spectrum showed carbon signals which were aromatic carbons at 112.6–159.5 ppm, and the signal at 168.7 ppm was carboxyl carbon.

Table 4–2: The ^{13}C-NMR spectrum assignment of 3', 6'-dihydroxyfluoran.

Carbon position	Carbon type [*]	Chemical shift (ppm)	Literature [**] (ppm)
1	C	126.1	126.2
2	CH	124.6	124.5
3	CH	130.1	129.9
4	CH	135.5	135.4
5	CH	123.9	123.9
6	C	152.4	152.4
7	C	168.7	168.6
1', 8'	CH	128.9	128.9
2', 7'	CH	112.6	112.6
3', 6'	C	159.5	159.5
4', 5'	CH	102.2	102.3
9'	C	83.1	83.5
11', 14'	C	151.9	151.9
12', 13'	C	109.5	109.7

[*] It was determined by DEPT spectra as shown in Fig 4-4 and 4-5.
[**] The position of carbon of 3',6'-dihydroxyfluoran was referred by Integrated Spectral Data Base System for Organic Compounds (SDBS).

The mass spectrum of 3', 6'-dihydroxyfluoran (Fig 4-6) showed the molecular ion at 332 Da.

Characterization of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate

6-(3'-Carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate was prepared from refluxing 3', 6'-dihydroxyfluoran disodium with bromononane in 71% as a reddish liquid, soluble in organic solvents. The structure is shown below.
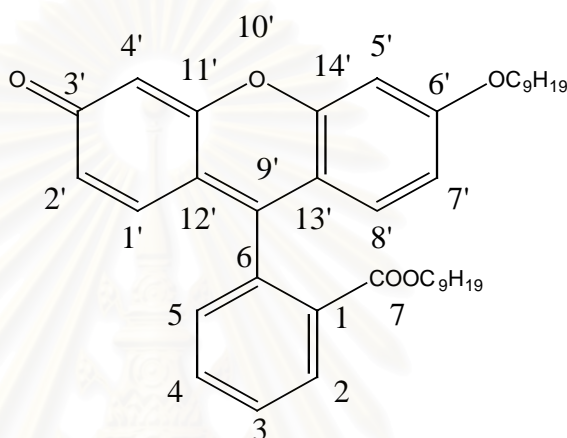
The FT-IR spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (Fig 4-7) showed the important absorptions at 3020 cm^{-1} (=C-H stretching of aromatic), 2950 cm^{-1} (C-H stretching of aliphatic), 1720 cm^{-1} (C=O stretching of ester), 1460and1600 cm^{-1} (C=C ring stretching of aromatic), 1379 cm^{-1} (C-H stretching of methyl group), 1110and 1270 cm^{-1} (C-O-C stretching vibration).

The ^{1}H-NMR spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (Fig 4–8) showed the signals at 6.53-7.98 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–3.

Table 4–3: The ^{1}H-NMR spectrum assignment of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate.

Proton position	Chemical shift (ppm), J(Hz)
2	7.98; 1H; d; 6.1
3	7.57; 1H; t; 5.7
4	7.60; 1H; t; 3.7
5	7.11; 1H; d; 6.7
1'	6.53-6.71; 1H; m
2'	6.53-6.71; 1H; m
4'	6.53; 1H; s
5'	6.57; 1H; s
7'	6.53-6.71; 1H; m
8'	6.53-6.71; 1H; m

The ^{13}C-NMR spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (Fig 4-9) could be assigned as shown in Table 4-4. Its spectrum showed carbon signals which were aromatic carbons at 100.8-165.5 ppm.

Table 4–4: The ^{13}C-NMR spectrum assignment of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate.

Carbon position	Carbon type [*]	Chemical shift (ppm)
1	C	126.1
2	CH	125.0
3	CH	131.1
4	CH	134.2
5	CH	124.0
6	C	153.1
7	C	169.7
1'	CH	133.0
2'	CH	127.6
3'	C	187.7
4'	CH	101.3
5'	CH	100.8
6'	C	165.9
7'	CH	108.0
8'	CH	129.2
9'	C	140.8
11'	C	165.5
12'	C	113.9
13'	C	112.4
14'	C	152.5

* It was determined by DEPT spectra as shown in Fig 4-10 and 4-11.

Characterization of 3'-hydroxy-6'-nonyloxyfluoran

The hydrolysis of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate to give 3'-hydroxy-6'-nonyloxyfluoran was carried out in sodium hydroxide solution. The product is a reddish oil, soluble in organic solvents. The yield of product was 70%. The structure is shown below.
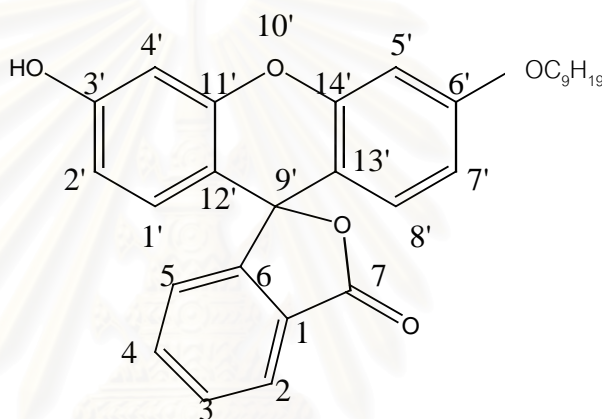
The FT-IR spectrum of 3'-hydroxy-6'-nonyloxyfluoran (Fig 4-12) showed the important absorptions at 3350 cm^{-1} (O-H stretching of phenol), 3010 cm^{-1} (=C-H stretching of aromatic), 2953 cm^{-1} (C-H stretching of aliphatic), 1740 cm^{-1} (C=O stretching of ester), 1467 and 1590 cm^{-1} (C=C ring stretching of aromatic), 1375 cm^{-1} (C-H stretching of methyl group), 1350 cm^{-1} (OH bending of phenol) and 1250 cm^{-1} (C-O-C stretching vibration).

The ^{1}H-NMR spectrum of 3'-hydroxy-6'-nonyloxyfluoran (Fig 4-13) showed the signals at 6.55-8.01 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–5.

Table 4–5: The ^{1}H-NMR spectrum assignment of 3'-hydroxy-6'-nonyloxyfluoran.

Proton position	Chemical shift (ppm), J(Hz)
2	8.01; 1H; d; 1.6
3	7.59; 1H; t; 3.3
4	7.62; 1H; t; 1.1
5	7.13; 1H; d; 1.8
1'	6.55-6.68; 1H; m
2'	6.55-6.68; 1H; m
4'	6.65; 1H; s
5'	6.74; 1H; s
7'	6.55-6.68; 1H; m
8'	6.55-6.68; 1H; m

The ^{13}C-NMR spectrum of 3'-hydroxy-6'-nonyloxyfluoran (Fig 4–14) could be assigned as shown in Table 4-6. Its spectrum showed carbon signals which were aromatic carbons at 101.3-152.9 ppm.

Table 4–6: The ^{13}C-NMR spectrum assignment of 3'-hydroxy-6'-nonyloxyfluoran.

Carbon position	Carbon type [*]	Chemical shift (ppm)
1	C	126.7
2	CH	125.1
3	CH	129.7
4	CH	135.2
5	CH	124.1
6	C	152.9
7	C	170.5
1'	CH	129.1
2'	CH	112.6
3'	C	160.9
4'	CH	103.1
5'	CH	101.3
6'	C	158.7
7'	CH	112.1
8'	CH	128.9
9'	C	85.7
11'	C	152.6
12'	C	110.6
13'	C	110.5
14'	C	152.4

* It was determined by DEPT spectra as shown in Fig 4-15 and 4-16.

Characterization of 3', 6'-dichlorofluoran

        3', 6'-Dichlorofluoran is made from the reaction of 3',6'-hydroxyfluoran with phosphorus pentachloride in 77% yield, m.p. 318 °C. The structure is shown below:
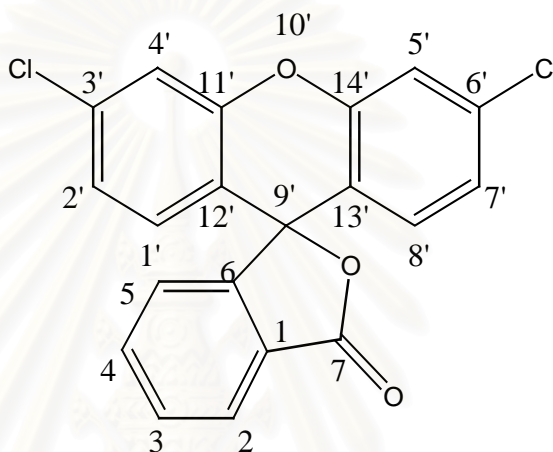
        The FT-IR spectrum of 3', 6'-dichlorofluoran (Fig 4–17) showed the important absorptions at 3016 cm^{-1} (=C-H stretching of aromatic), 1649 cm^{-1} (C=O stretching of ester), 1603 and 1465 cm^{-1} (C=C ring stretching of aromatic), 1240 cm^{-1} (C-O-C stretching vibration) and 1168 cm^{-1} (C-Cl stretching vibration of C-Cl bond).

The ^{1}H-NMR spectrum of 3', 6'-dichlorofluoran (Fig 4-18) showed the signals at 6.74-8.03 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–7.

Table 4–7: The ^{1}H-NMR spectrum assignment of 3', 6'-dichlorofluoran.

Proton position	Chemical shift (ppm), J(Hz)
2	8.03; 1H; d; 6.4
3	7.58; 1H; t; 6.3
4	7.64; 1H; t; 8.5
5	7.11; 1H; d; 7.7
1', 8'	7.02; 2H; d; 8.5
2', 7'	6.74; 2H; d; 8.5
4', 5'	7.30; 2H; s

The ^{13}C-NMR spectrum of 3', 6'-dichlorofluoran (Fig 4-19) could be assigned as shown in Table 4-8. Its spectrum showed carbon signals which were aromatic carbons at 123.7 –157.0 ppm, the signal at 168.9 ppm was carbonyl.

Table 4–8: The ^{13}C-NMR spectrum assignment of 3', 6'-dichlorofluoran.

Carbon position	Carbon type [*]	Chemical shift (ppm)
1	C	125.8
2	CH	125.4
3	CH	130.2
4	CH	135.4
5	CH	123.7
6	C	152.8
7	C	168.9
1', 8'	CH	129.0
2', 7'	CH	124.6
3', 6'	C	151.1
4', 5'	CH	117.4
9'	C	81.1
11', 14'	C	157.0
12', 13'	C	136.3

[*] It was determined by DEPT spectra as shown in Fig 4-20 and 4-21.

The mass spectrum of 3', 6'-dichlorofluoran (Fig 4-22) showed the molecular ion at 369 Da.

Characterization of *p*-nitro-linear alkylbenzene

    The nitration of linear alkylbenzene gave *p*-nitro-linear alkylbenzene. The product is a colorless liquid, insoluble in water but freely soluble in alcohol and organic solvents. The yield of product was 76%. The structure is shown below:
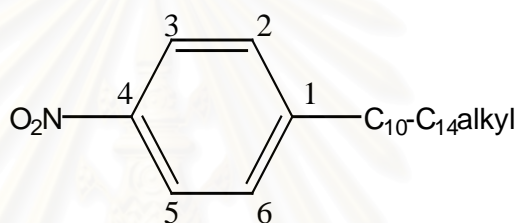
    The FT-IR spectrum of *p*-nitro-linear alkylbenzene (Fig 4–23) showed the important absorptions at 3080 cm^{-1} (=C-H stretching of aromatic), 2930 cm^{-1} (C-H stretching of aliphatic), 1530 cm^{-1} (N=O asymmetric stretching of nitrogroup), 1469 and 1607 cm^{-1} (C=C ring stretching of aromatic), and 1348 cm^{-1} (N=O symmetric stretching of nitrogroup).

The ^{1}H-NMR spectrum of *p*-nitro-linear alkylbenzene (Fig 4–24) showed the signals at 7.25-8.10 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–9.

Table 4–9: The ^{1}H-NMR spectrum assignment of *p*-nitro-linear alkylbenzene.

Proton position	Chemical shift (ppm), *J*(Hz)
2, 6	7.25; 2H; d; 8.8
3, 5	8.10; 2H; d; 8.8

The ^{13}C-NMR spectrum of *p*-nitro-linear alkylbenzene (Fig 4–25) could be assigned as shown in Table 4-10. Its spectrum showed carbon signals which were aromatic carbons at 123.5-154.6 ppm.

Table 4–10: The ^{13}C-NMR spectrum assignment of *p*-nitro-linear alkylbenzene

Carbon position	Chemical shift (ppm)
1	146.5
2	128.4
3	123.5
4	154.6
5	123.5
6	128.4

Characterization of *p*-linear alkylaniline

The reduction of *p*-nitro-linear alkylbenzene with tin powder in hydrochloric gave *p*-linear alkylaniline as a colorless liquid, insoluble in water but freely soluble in alcohol and organic solvents. The yield of product was 81%. The structure is shown below:
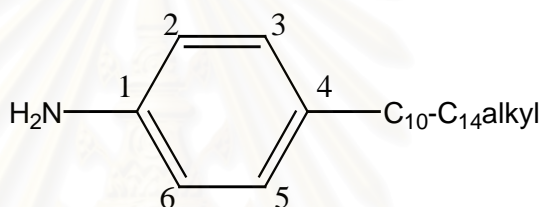
The FT-IR spectrum of *p*-linear alkylaniline (Fig 4-26) showed the important absorptions at 3469 and 3390 cm^{-1} (N-H stretching of primary amine), 3021 cm^{-1} (=C-H stretching of aromatic), 2920 cm^{-1} (C-H stretching of aliphatic), 1625 cm^{-1} (N-H bending of primary amine), 1467, 1515 and 1601 cm^{-1} (C=C ring stretching of aromatic), 1460 cm^{-1} (C-H stretching of methylene group), 1372 cm^{-1} (C-H stretching of methyl group) and 1270 cm^{-1} (C-N stretching of primary aromatic amine).

The ^{1}H-NMR spectrum of *p*-linear alkylaniline (Fig 4–27) showed the signals at 6.62-6.94 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–11.

Table 4–11: The ^{1}H-NMR spectrum assignment of *p*-linear alkylaniline.

Proton position	Chemical shift (ppm), *J*(Hz)
2, 6	6.62; 2H; d; 8.3
3, 5	6.94; 2H; d; 8.3

The ^{13}C-NMR spectrum of *p*-linear alkylaniline (Fig 4-28) could be assigned as shown in Table 4-12. Its spectrum showed carbon signals which were aromatic carbons at 115.3-144.0 ppm.

Table 4–12: The ^{13}C-NMR spectrum assignment of *p*-linear alkylaniline.

Carbon position	Chemical shift (ppm)
1	144.0
2	115.3
3	128.4
4	127.7
5	128.4
6	115.3

The reaction of calcium oxide and 3',6'-dichlorofluoran in dimethylformamide with zinc chloride and amines gave only 3',6'-bis(dimethylamino)-fluoran.

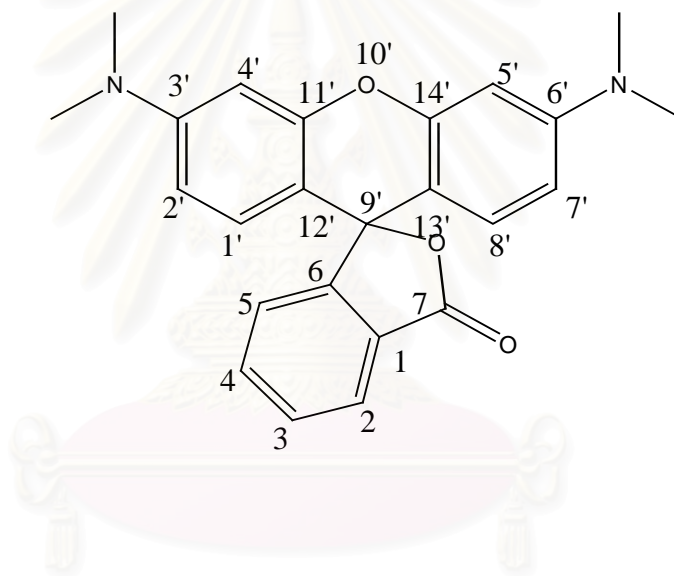The possible mechanism is showed below:
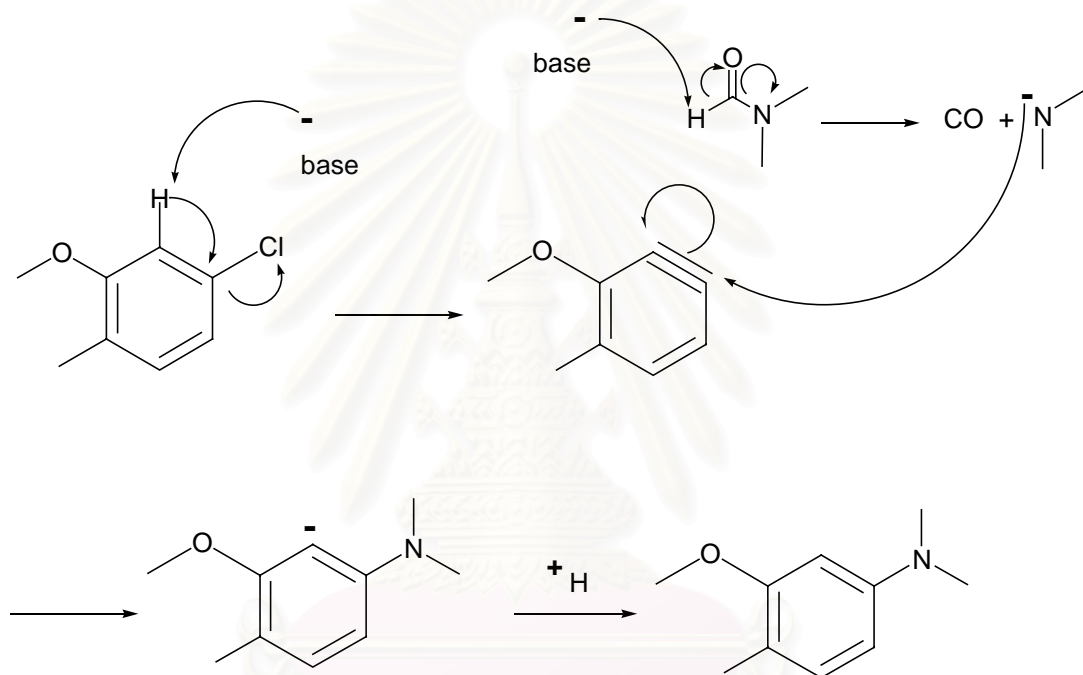
Characterization of 3', 6'-bis(dimethylamino)-fluoran

        3', 6'-bis(Dimethylamino)-fluoran was prepared from the reaction of with 3', 6'-dichlorofluoran with calcium oxide and dimethylformamide in 69% yield as a bright yellow solid, soluble in dichloromethane, chloroform and organic solvents. The structure is shown below:

The FT-IR spectrum of 3', 6'-bis(dimethylamino)-fluoran (Fig 4–29) showed the important absorptions at 3016 cm^{-1} (=C-H stretching of aromatic), 1708 cm^{-1} (C=O stretching of ester), 1600 and 1400 cm^{-1} (C=C ring stretching of aromatic), 1291 cm^{-1} (C-N stretching vibration of amine), 1240 and 1105 cm^{-1} (C-O-C stretching vibration).

The ^{1}H-NMR spectrum of 3', 6'-bis(dimethylamino)-fluoran (Fig 4–30) showed the signals at 6.38-8.18 ppm, which were the signals of aromatic protons. It could be assigned as shown in Table 4–13.

Table 4–13: The ^{1}H-NMR spectrum assignment of 3', 6'-bis(dimethylamino)-fluoran.

Proton position	Chemical shift (ppm), J(Hz)
2	8.18; 1H; d; 8.5
3	7.25; 1H; t; 10.9
4	8.16; 1H; t; 2.5
5	8.07; 1H; d; 9.0
1', 8'	7.30; 2H; d; 13.9
2', 7'	6.66; 2H; d; 6.7
4', 5'	6.38; 2H; s
methyl	3.06; 12H; s

The ^{13}C-NMR spectrum of 3',6'-bis(dimethylamino)-fluoran (Fig 4–31) could be assigned as shown in Table 4–14. Its spectrum showed carbon signals which were aromatic carbons at 96.7–158.2 ppm.

Table 4–14: The ^{13}C-NMR spectrum assignment of 3', 6'-bis(dimethylamino)-fluoran.

Carbon position	Carbon type [*]	Chemical shift (ppm)
1	C	111.4
2	CH	117.4
3	CH	109.5
4	CH	127.9
5	CH	109.8
6	C	156.2
7	C	174.9
1', 8'	CH	127.9
2', 7'	CH	124.1
3', 6'	C	154.9
4', 5'	CH	96.7
9'	C	77.5
11', 14'	C	158.2
12', 13'	C	120.8
methyl	CH$_3$	40.2

* It was determined by DEPT spectra as shown in Fig 4-32 and 4-33.

4.2 Results for the detection of marker dyes in fuels.

The type of developing solvents and conditions with good separation of the marker dyed diesel and diesel were studied. The results are shown in Table 4-15.

Table 4–15: Type of developing solvent system and retardation factor.

Type of developing solvent system	Retardation factor (R_f)				
	Spot of additive in diesel	Spot of markers			
		Compound 2a	Compound 3a	Compound 1b	Compound B
Methylenechloride : hexane (1:4)	0.543	-	-	-	-
Methylenechloride : hexane (2:3)	0.671	-	-	-	0.057
Methylenechloride : hexane (3:2)	0.714	-	-	-	0.114
Methylenechloride : hexane (4:1)	0.743	-	-	0.029	0.200
Methylenechloride: ethyl acetate (1:4)	0.629	0.771	0.714	0.757	0.714
Methylenechloride: ethyl acetate (2:3)	0.657	0.829	0.729	0.771	0.771
Methylenechloride: ethyl acetate (3:2)	0.866	0.829	0.729	0.786	0.800
Methylenechloride: ethyl acetate (4:1)	0.866	0.571	0.514	0.800	0.826
Ethyl acetate : hexane (1:4)	0.629	0.086	0.057	0.100	0.200
Ethyl acetate : hexane (2:3)	**0.714**	**0.400**	**0.229**	**0.314**	**0.371**
Ethyl acetate : hexane (3:2)	**0.714**	**0.657**	**0.543**	**0.571**	**0.600**
Ethyl acetate : hexane (4:1)	0.866	0.800	0.686	0.571	0.714

From Table 4-15, the solvent mixtures which was used to differentiate between marker dyed diesel and diesel are presented. The solvents used as developing solvents were methylenechloride, hexane, ethyl acetate and combination there off.

There were used as solvent mixtures, such as methylenechloride:hexane, methylenechloride: ethyl acetate and ethyl acetate:hexane. The ratio of solvent mixtures were varied for better separation between each marker dyed diesel and diesel.

Table 4–16 indicated the retardation factor of each marker for different developing solvent systems and found the ratio of ethyl acetate: hexane at 2.4:2.6 gave the best separation of each marker.

Table 4–16: Ratio of developing solvent system and retardation factor.

Ratio of developing solvent system	Retardation factor (R_f)				
	Spot of additive in diesel	Spot of markers			
		Compound 2a	Compound 3a	Compound 1b	Compound B
Ethyl acetate : hexane (2.1: 2.9)	0.714	0.429	0.286	0.371	0.371
Ethyl acetate : hexane (2.2 : 2.8)	0.714	0.457	0.371	0.371	0.429
Ethyl acetate : hexane (2.3 : 2.7)	0.714	0.486	0.371	0.429	0.714
Ethyl acetate : hexane (2.4 : 2.6)	**0.714**	**0.543**	**0.386**	**0.547**	**0.571**
Ethyl acetate : hexane (2.5 : 2.5)	0.714	0.571	0.400	0.547	0.571
Ethyl acetate : hexane (2.6 : 2.4)	0.714	0.600	0.429	0.547	0.571
Ethyl acetate : hexane (2.7 : 2.3)	0.714	0.600	0.457	0.486	0.600
Ethyl acetate : hexane (2.8 : 2.2)	0.714	0.629	0.486	0.514	0.600
Ethyl acetate : hexane (2.9 : 2.1)	0.714	0.657	0.514	0.543	0.600

These marker dyes could be detected on thin layer chromatography (TLC) using (ethyl acetate: hexane; 2.4: 2.6) as developing solvent. The marker dyed diesel and diesel have been identified on TLC under ultraviolet lamp (365 nm). The detection of marker dyed diesel and diesel were shown below.
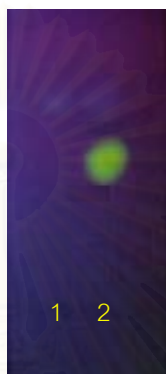
Fig 4–34: The detection of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (2a: lane 2) in diesel comparing without marker dyed diesel (lane 1).

Fig 4–35: The detection of 3'-hydroxy-6'-nonyloxyfluoran (3a: lane 2) in diesel comparing without marker dyed diesel (lane 1).
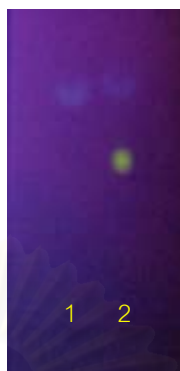
Fig 4–36: The detection of 3', 6'-dichlorofluoran (1b : lane2) in diesel comparing without marker dyed diesel (lane 1).

Fig 4–37: The detection of 3', 6'-bis(dimethylamino)-fluoran(B: lane 2) in diesel comparing without marker dyed diesel (lane 1).

Fig 4–38: The detection of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (2a:lane2), 3'-hydroxy-6'-nonyloxyfluoran (3a:lane3), 3',6'-dichlorofluoran (1b:lane 4) and 3',6'-bis(dimethylamino)-fluoran (B:lane 5) in diesel comparing without marker dyed diesel (lane 1).

The exitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of each marker (Fig 4-39 to 4-48) is shown in Table 4–17.

Table 4–17: The color, exitation wavelength and emission wavelength of marker dyes.

Marker dyes	color	exitation wavelength (λ_{ex} ; nm)	emission wavelength (λ_{em} ; nm)
1a	strong green fluorescence	437.5	487.0
2a	strong green fluorescence	452.0	509.0
3a	strong green fluorescence	352.0	424.0
1b	yellow fluorescence	365.0	421.5
B	blue fluorescence	303.5	434.0

4.3 Effect of marker dyes on the physical properties of dyed diesel.

Diesel containing 1000 ppm of 3', 6'-dichlorofluoran was used for physical properties testing, using the ASTM methods. The physical properties of the dyed and undyed diesel were compared. The results are shown in Table 4–18.

Table 4-18: The effects of marker dye on the physical properties of dyed and undyed diesel.

Test items	ASTM	limit	Result	
			dyed	undyed
API gravity @60 °F	D 1298	report	37.9	37.9
Specific gravity@ 15.6/15.6 °C	D 1298	report	0.8353	0.8353
Calculated cetane index	D 976	47 min	53.5	53.0
Kinematic viscosity @ 40 °C, cSt	D 445	1.8-4.1	3.0	3.1
Pour point, °C	D 97	10	+1	+1
Flash point, °C	D 93	52	68	71
Sulfur content, %wt	D 4294	0.05	0.05	0.05
Distillation (Correct Temp.)	D 86			
IBP, °C		report	171	176
10% rec., °C		report	205	204
50% rec., °C		report	275	271
90% rec., °C		357max	354	352
Total acid number, mg KOH/g	D 974	-	0.008	0.008
Color	D 1500	2.0max	<0.7	<0.7

The physical properties of dyed diesel were not significatly different from undyed diesel (table 4-18). Both dyed and undyed diesel provided similar specific gravity, calculated cetane index, pour point, flash point, distillation properties and colors. The results revealed this compound did not have effect on the physical properties of diesel, therefore it is possible to use this marker dye as the marker in diesel.

4.4 Quantitative determinations of marker dyes in dyed diesel.

The standard calibration curve of marker dyes in diesel was prepared by adding marker dyes at different concentration into diesel. The standard calibration curve was plotted between intensity and concentration of marker dyes in diesel.

The standard calibration curve equations of marker dyes in diesel are shown in Table 4-19 and the standard calibration curve of marker dyes are shown in the Appendix section (Fig 4-49 to 4-52).

Table 4–19: The calibration equation for quantitative determinations of marker dyes in dyed diesel.

Marker dyes	Standard calibration equation	Correlation coefficient (r)
2a	$Y = 0.2627 X + 5.505$	0.998
3a	$Y = 0.7701 X + 36.405$	1.000
1b	$Y = 0.9689 X + 66.13$	1.000
B	$Y = 0.3615 X - 15$	0.999

The measuring parameters were set on the following.

- The wavelength of the excitation monochromator (λ_{ex}) at was set 365 nm.

- The response was set for one second.

- The photomultiplier tube votage level (PMT Gain) was set at medium.

- The spectrum bandwidth of the emission monochromator (Em SBW) was set at 1.5.

- The spectrum bandwidth of the excitation monochromator (Ex SBW) was set at 10.

The wavelength of the emission monochromator (λ_{em}) of each substance was set at 424, 509, 421.5 and 434 nm which corresponded to compound 2a, 3a, 1b and B.

Because of the possible interference from diesel fuel, compound 2a, 3a were added at concentrated levels of 500 ppm, 1b was added at concentrated levels of 300 ppm and B was added at concentrated levels of 900 ppm in order to make intensity of synthetic marker dyes more intense than the intensity of diesel.

4.5 Stability of marker dyes in dyed diesel.

The stability of marker dyes in diesel was studied by monitoring the quantities of marker dyes in diesel for 3 months using spectrofluorometer. The marker dyes which were used are 2a, 3a, 1b and B in diesel. The results are shown in Table 4–20 to 4-23.

Table 4-20: The stability of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate (2a; 500 ppm) in diesel.

Month.	Concentration in diesel (ppm)		
	1st	2nd	Average
1	500.5	500.2	500.4 ± 0.3
2	500.2	500.2	500.2 ± 0.2
3	500.2	500.2	500.2 ± 0.2

Table 4-21:The stability of 3'-hydroxy-6'-nonyloxyfluoran (3a; 500 ppm) in diesel.

Month.	Concentration in diesel (ppm)		
	1st	2nd	Average
1	499.0	500.1	499.6 ± 0.5
2	500.1	499.9	500.0 ± 0.1
3	500.1	500.1	500.1 ± 0.1

Table 4-22:The stability of 3', 6'-dichlorofluoran (1b; 300 ppm) in diesel.

Month.	Concentration in diesel (ppm)		
	1st	2nd	Average
1	300.0	300.1	300.1 ± 0.1
2	300.0	300.0	300.0 ± 0.1
3	300.0	300.0	300.0 ± 0.1

Table4 -23:The stability of 3', 6'-bis(dimethylamino)-fluoran (B; 900 ppm) in diesel.

Month.	Concentration in diesel (ppm)		
	1st	2nd	Average
1	900.1	899.9	900.0 ± 0.1
2	900.1	900.1	900.1 ± 0.1
3	900.1	900.1	900.1 ± 0.1

From Tables 4–20 to 4-23, found that the concentration of marker dyes in diesel was not different from the original value. The results indicated that the marker dyes has stability at least for 3 months. Generally, diesel is consumed within 3 months after released to the market. Therefore it was possible that the marker dyes could be used to mark diesel fuel.

CHAPTER V

CONCLUSION

The xanthene dyes, which were synthesized to evaluate as marker dyes in diesel, were divided into two groups which were hydroxyl group and amino group. The hydroxyl group which was obtained from condensation product between phthalic anhydride and resorcinol was reacted with alkyl halide such as bromononane to form ester-ether and ether derivatives in order to increase its solubility. The amino group was obtained from the reaction between hydroxyl group and phosphorus pentachloride to form dichloro compound which subsequently reacted with amino group containing compounds such as aniline, linear alkylaniline and cyclohexylamine. These synthetic marker dyes were 2a, 3a, 1b and B. These synthetic marker dyes were invisible in diesel but they could be detected by spotting 2 μl sample on TLC plate and using suitable developing solvent to develop the plate. The suitable developing solvent was 48% ethyl acetate in hexane and the presence of marker was detected under ultraviolet light (365nm). The quantification was determined using spectrofluorometer. Compound 2a and 3a were used at 500 ppm, compound 1b was used at 300 ppm while compound B was needed to add into diesel at concentration of 900 ppm. The physical properties of diesel oil which was tested according to ASTM method revealed that they were unaffected with the presence of marker dye up to at least three months.

Suggestion for further studies:

1. The synthesis of amino xanthene dyes needs to be explored in order to find a better way to prepare this group of dyes.

2. The excitation of marker dyes in this study is partially overlap to that of diesel fuel, therefore another group of fluorescent dyes should be investigated to avoid interference from fluorescence of diesel fuel.
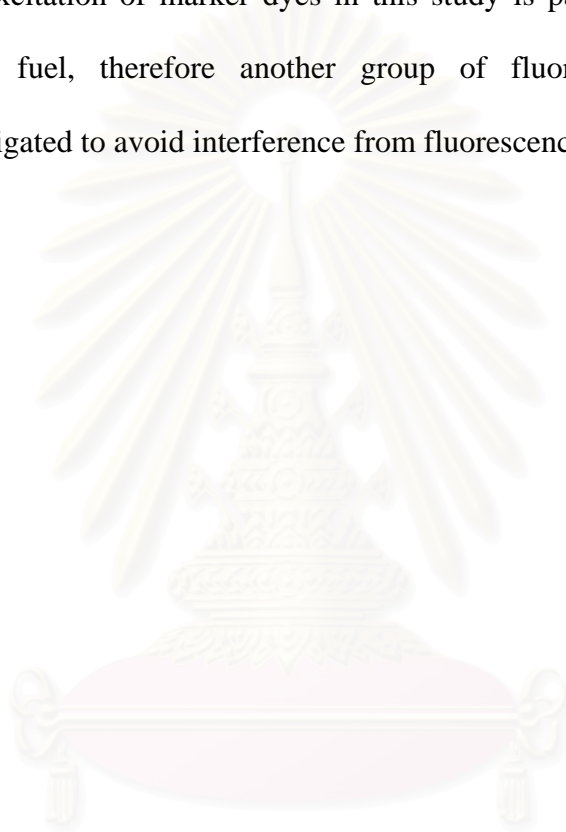
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APPENDICES
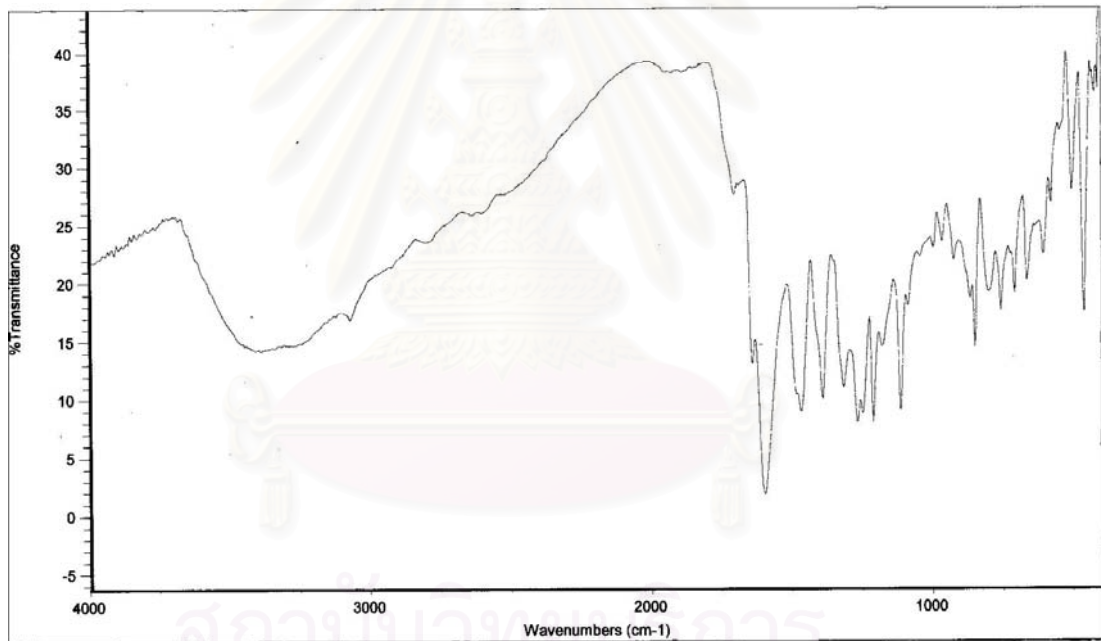
Fig.4-1 The FT-IR spectrum of 3', 6'-dihydroxyfluoran
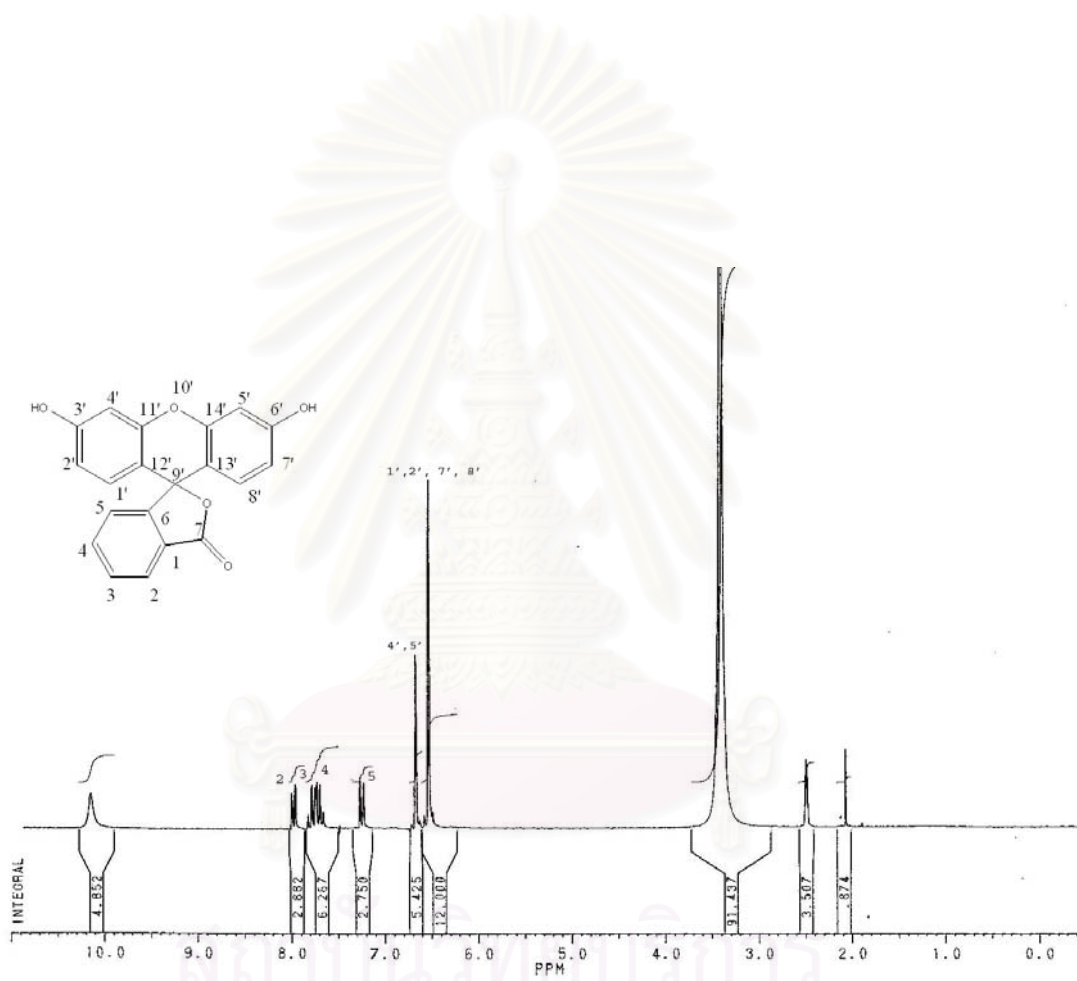
Fig. 4-2 The ^{1}H-NMR spectrum of 3', 6'-dihydroxyfluoran
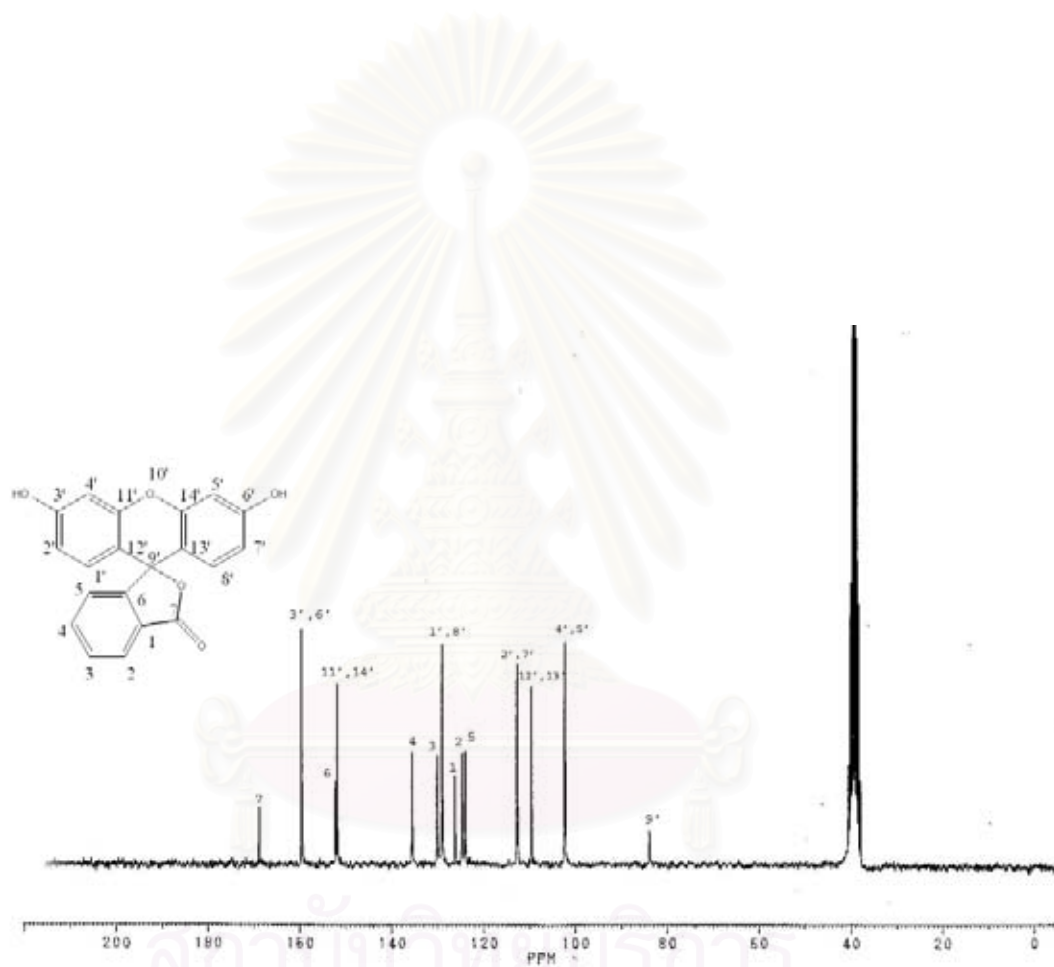
Fig. 4-3 The ^{13}C-NMR spectrum of 3', 6'-dihydroxyfluoran
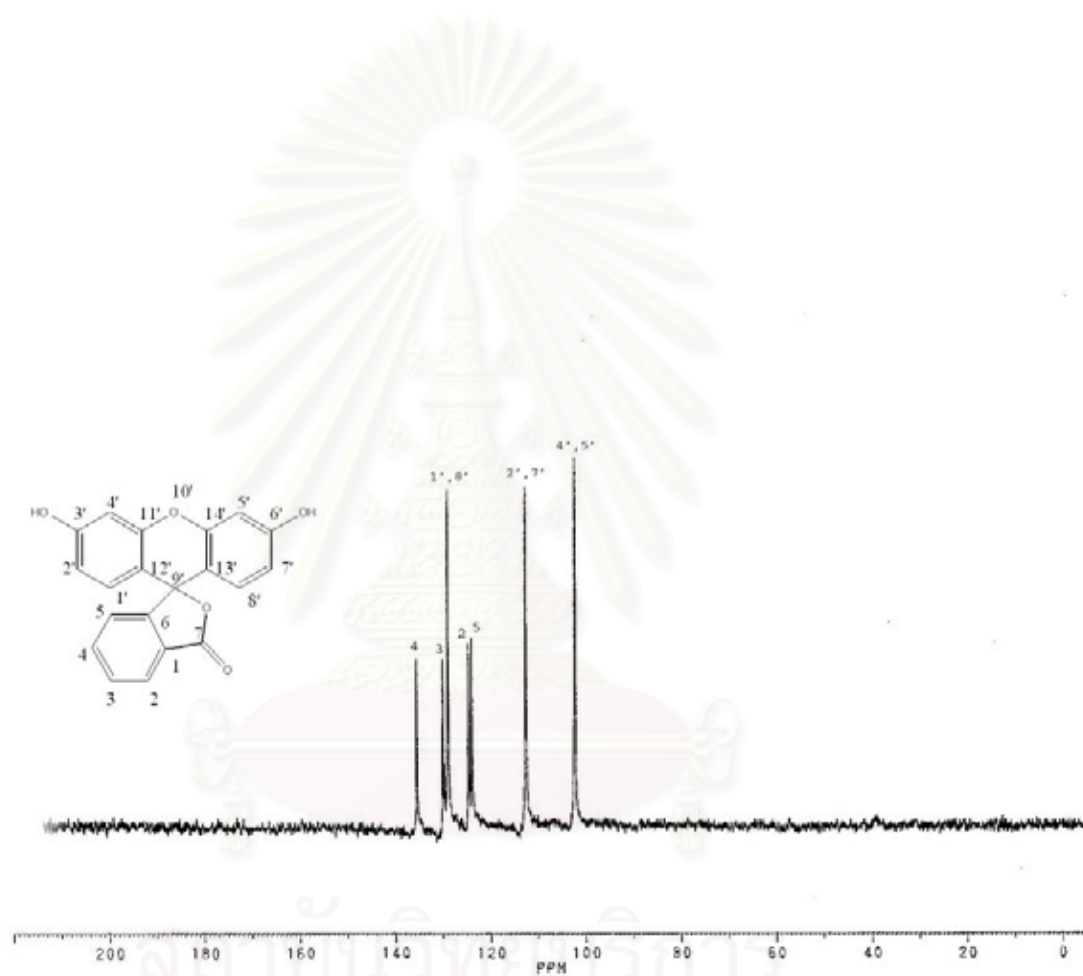
Fig. 4-4 The DEPT135 spectrum of 3', 6'-dihydroxyfluoran
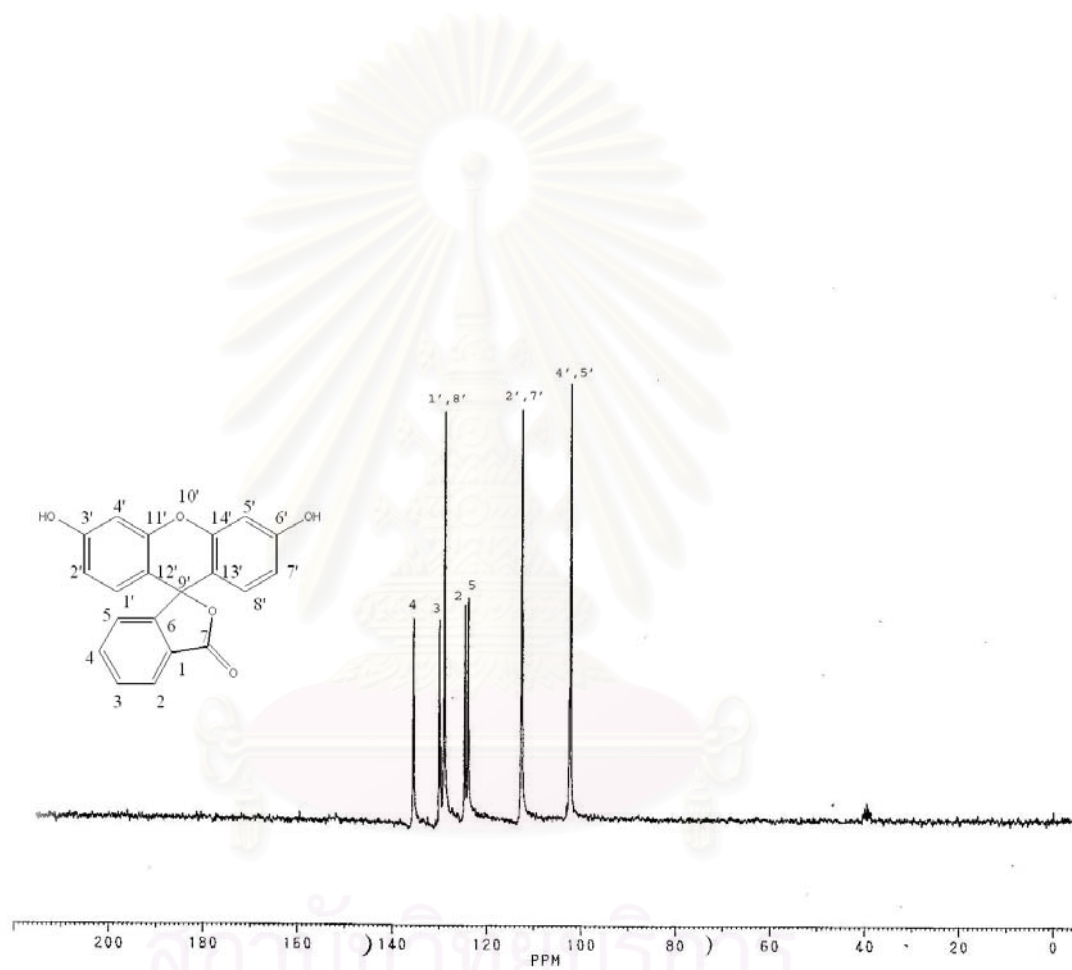
Fig. 4-5 The DEPT 90 spectrum of 3', 6'-dihydroxyfluoran
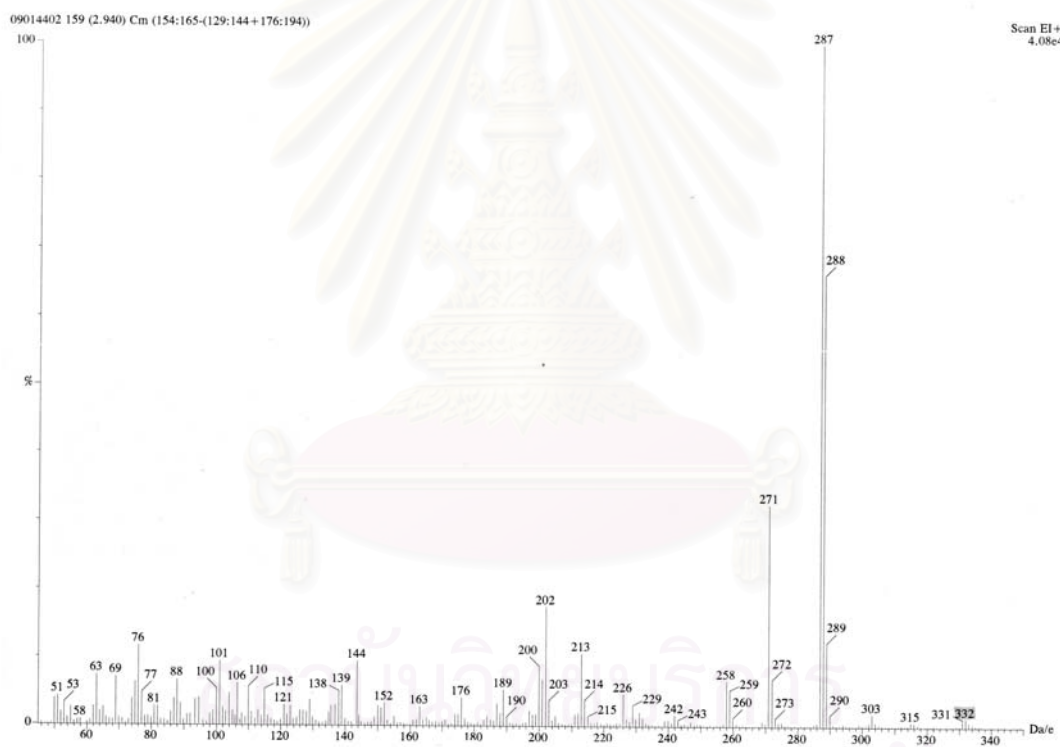
Fig.4-6 Mass spectrum of 3', 6'-dihydroxyfluoran

Fig.4-7 The FT-IR spectrum spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate
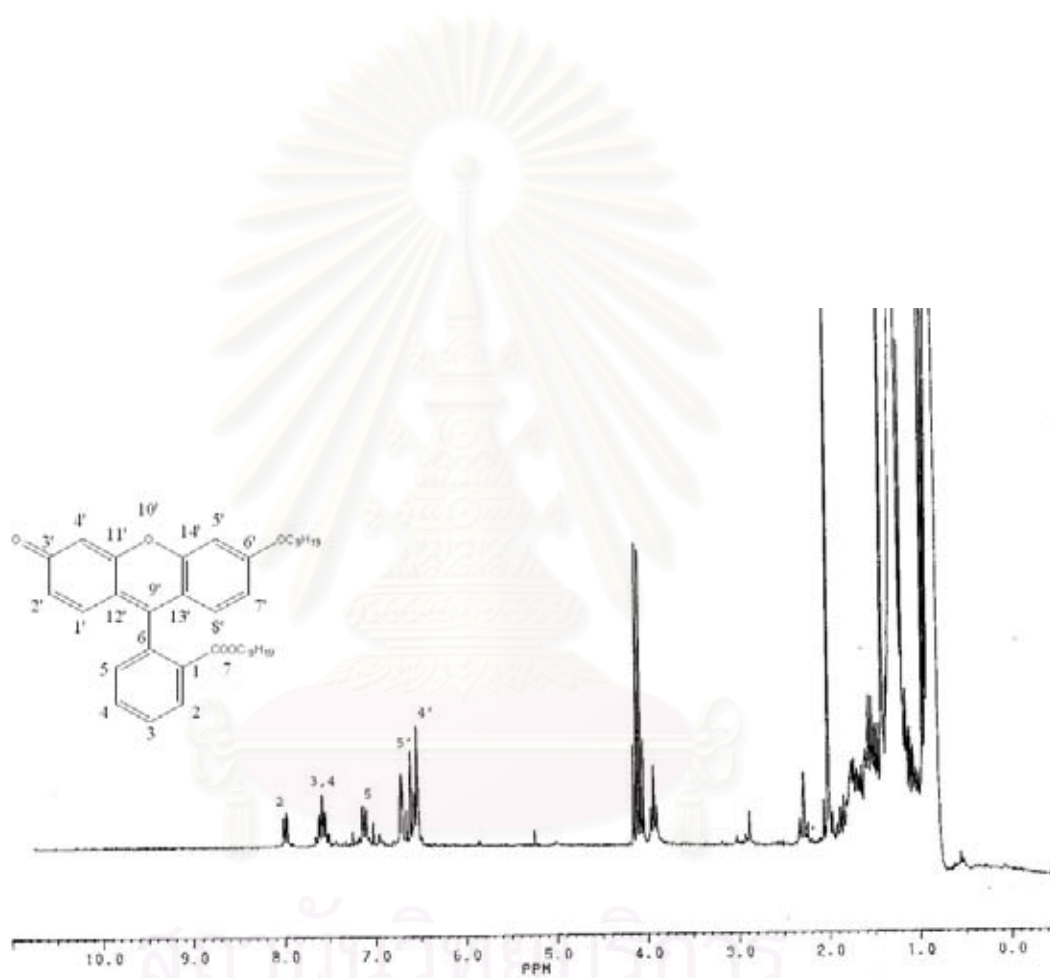
Fig.4-8 The ^{1}H-NMR spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-
nonyl benzoate
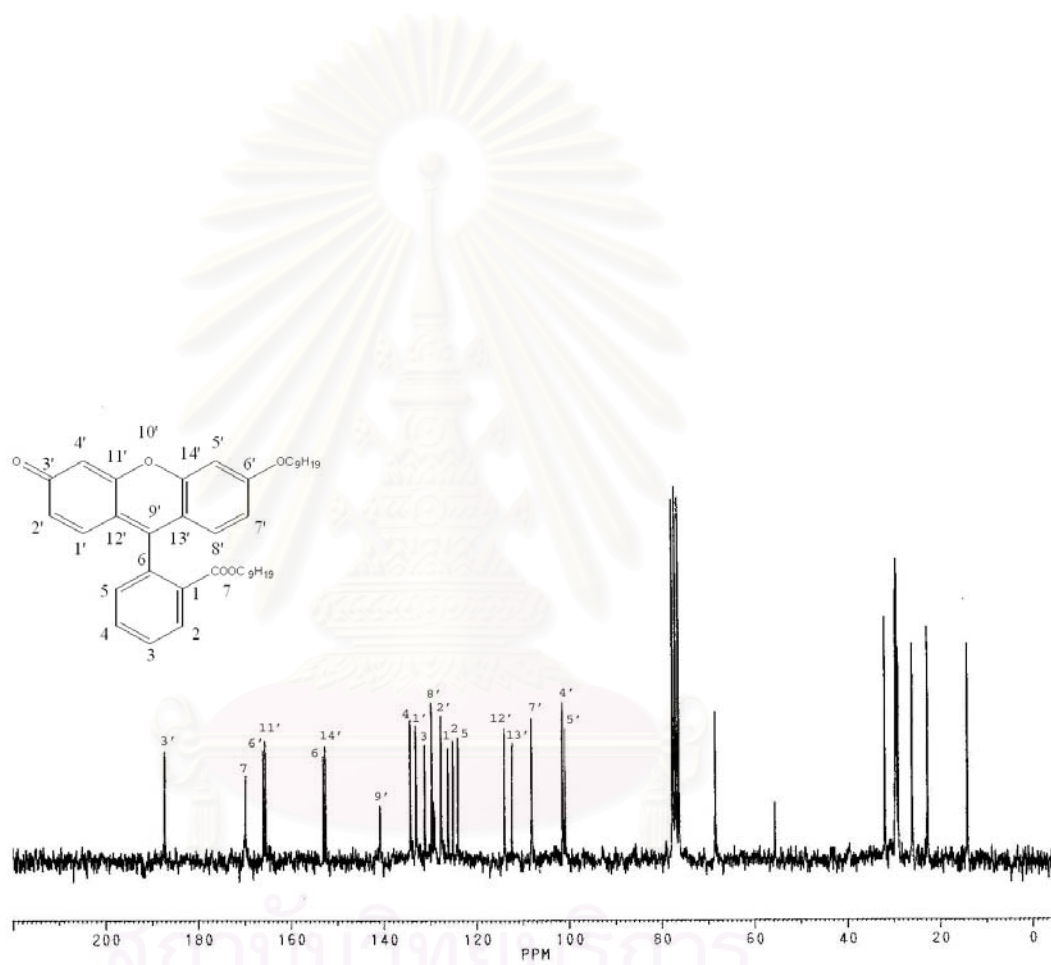
Fig.4-9 The ^{13}C-NMR spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate
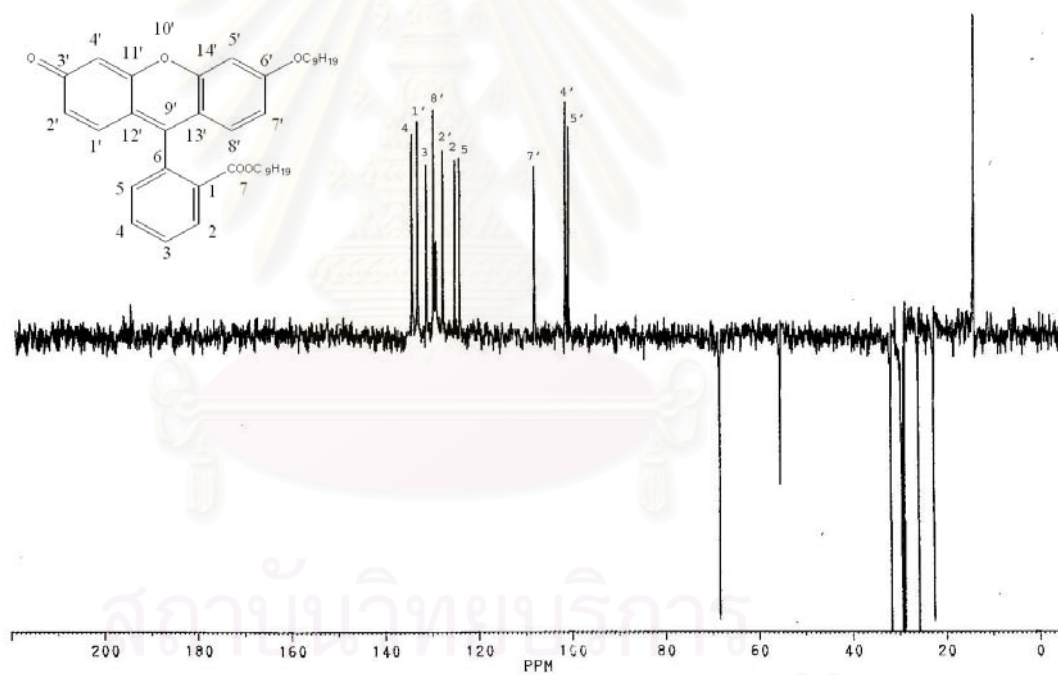
Fig.4-10 The DEPT 135 spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate
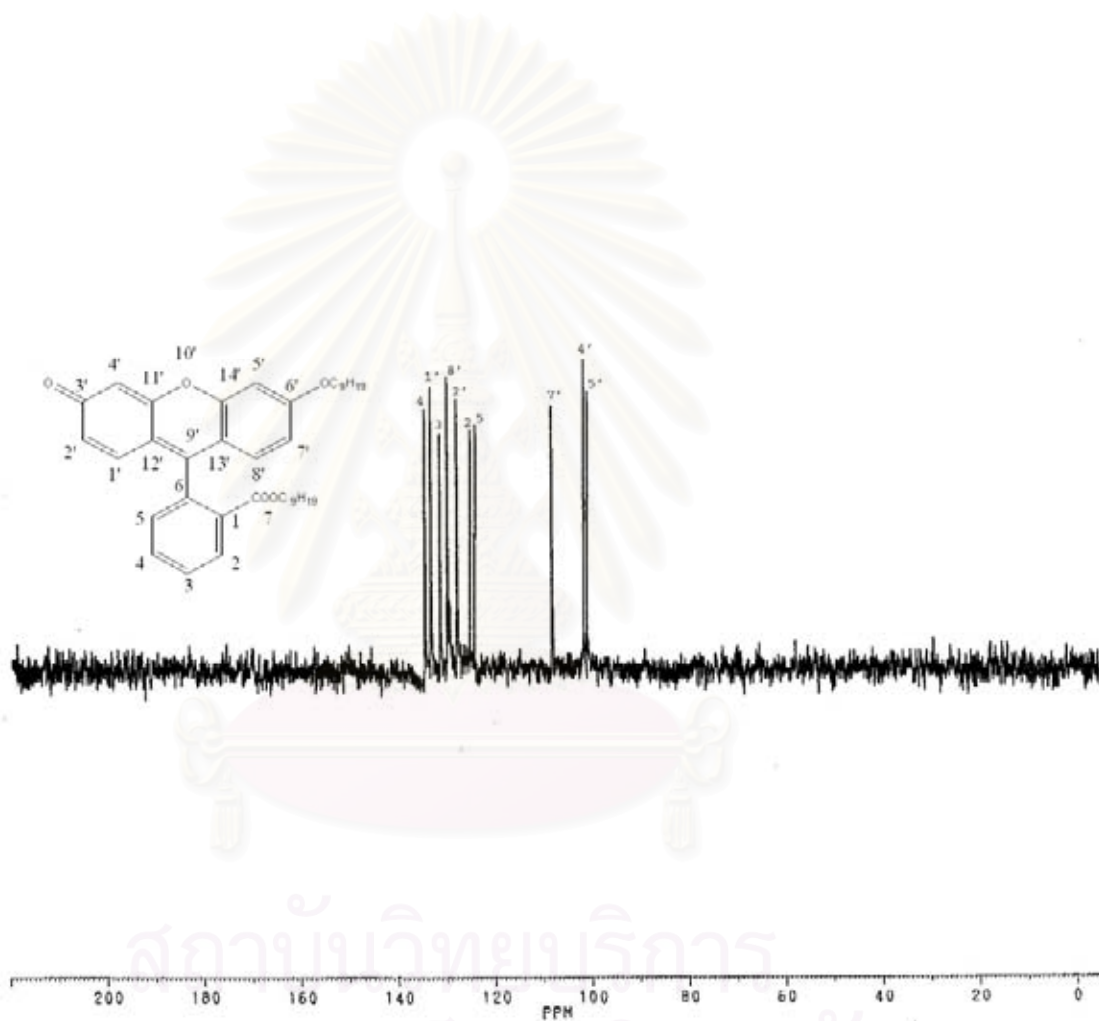
Fig.4-11 The DEPT 90 spectrum of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate
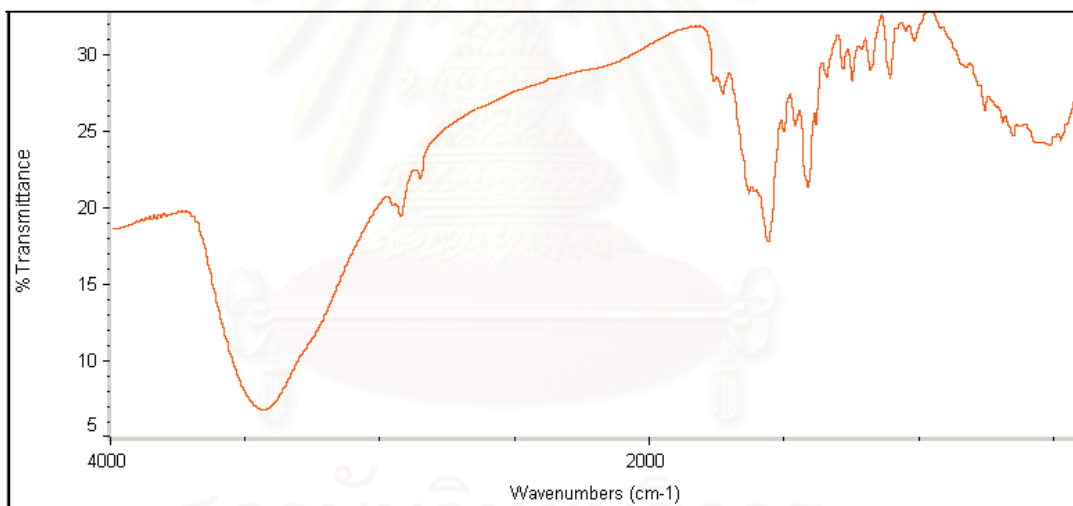
Fig.4-12 The FT-IR spectrum of 3'-hydroxy-6'-nonyloxyfluoran
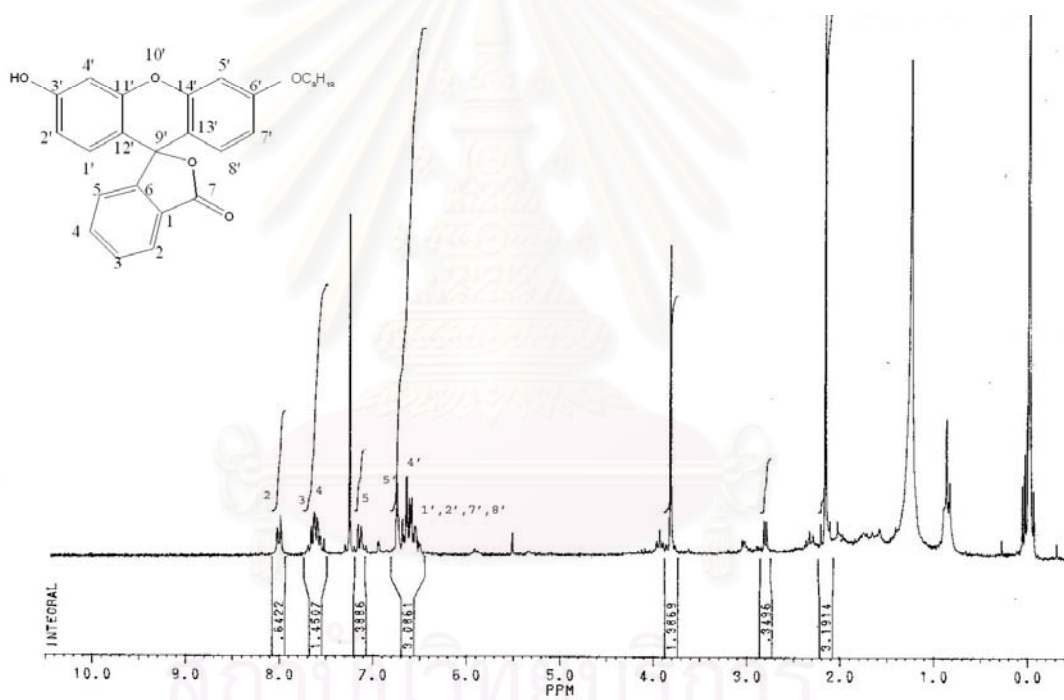
Fig.4-13 The ^{1}H-NMR spectrum of 3'-hydroxy-6'-nonyloxyfluoran
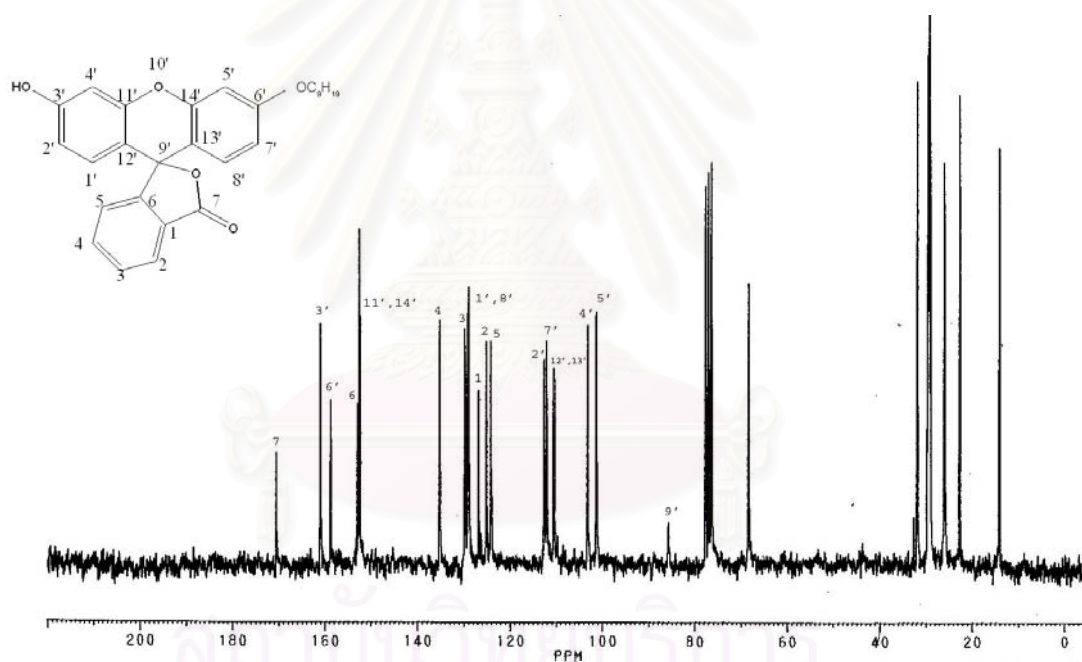
Fig.4-14 The ^{13}C-NMR spectrum of 3'-hydroxy-6'-nonyloxyfluoran
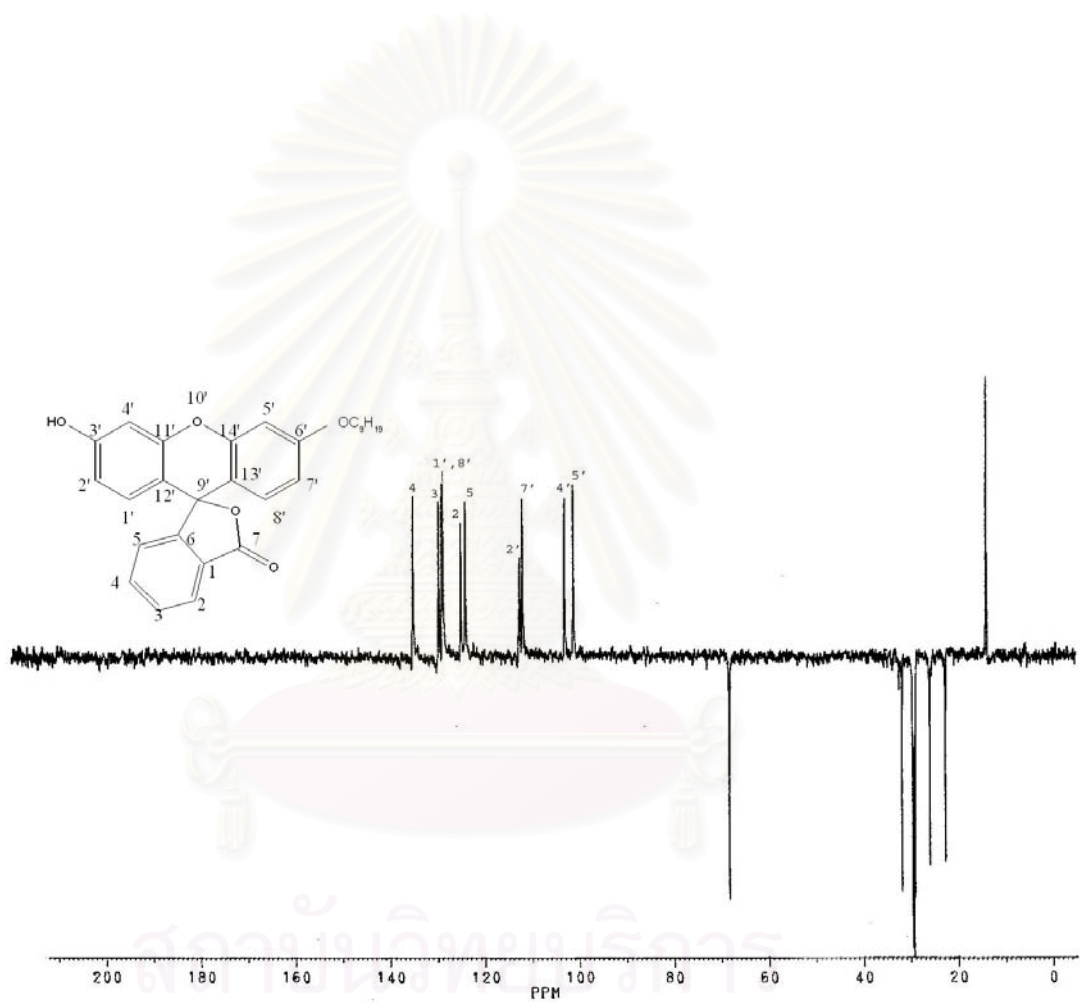
Fig.4-15 The DEPT135 spectrum of 3'-hydroxy-6'-nonyloxyfluoran
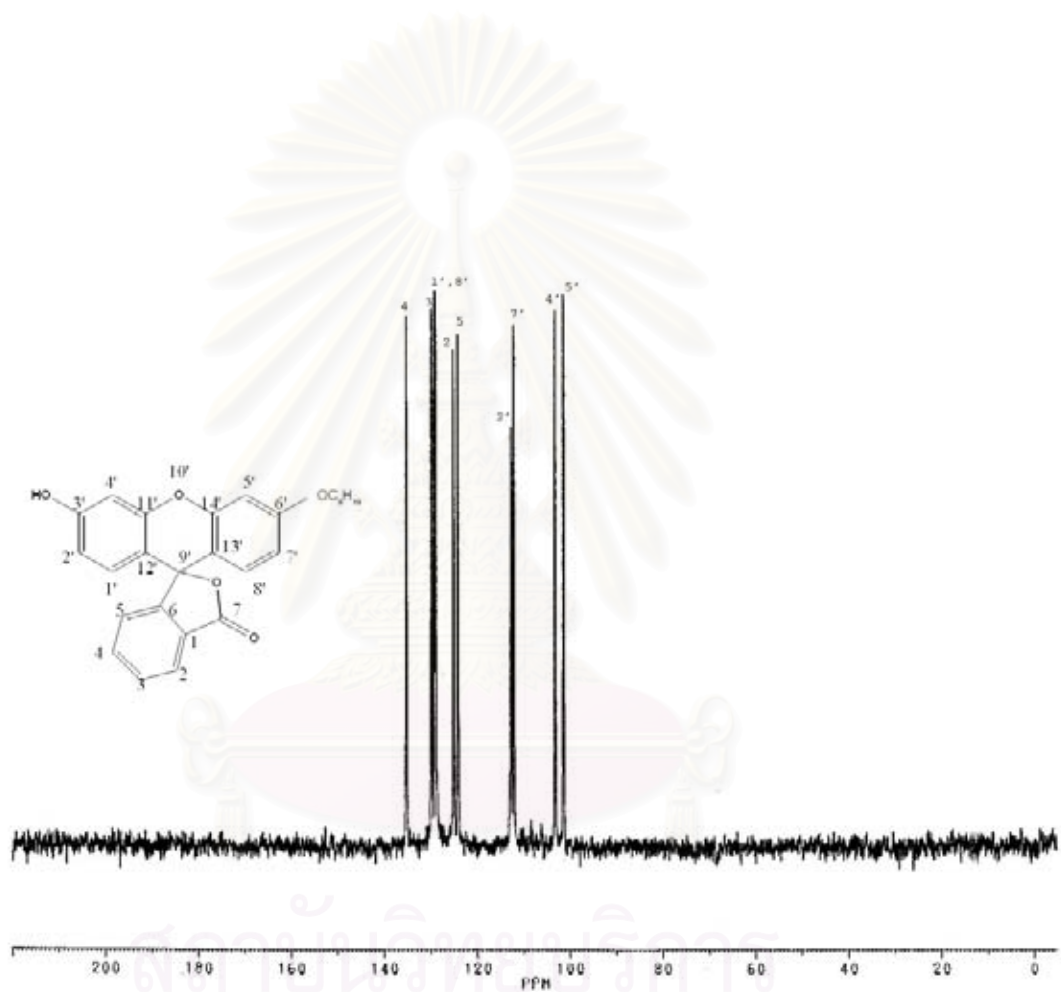
Fig.4-16 The DEPT90 spectrum of 3'-hydroxy-6'-nonyloxyfluoran
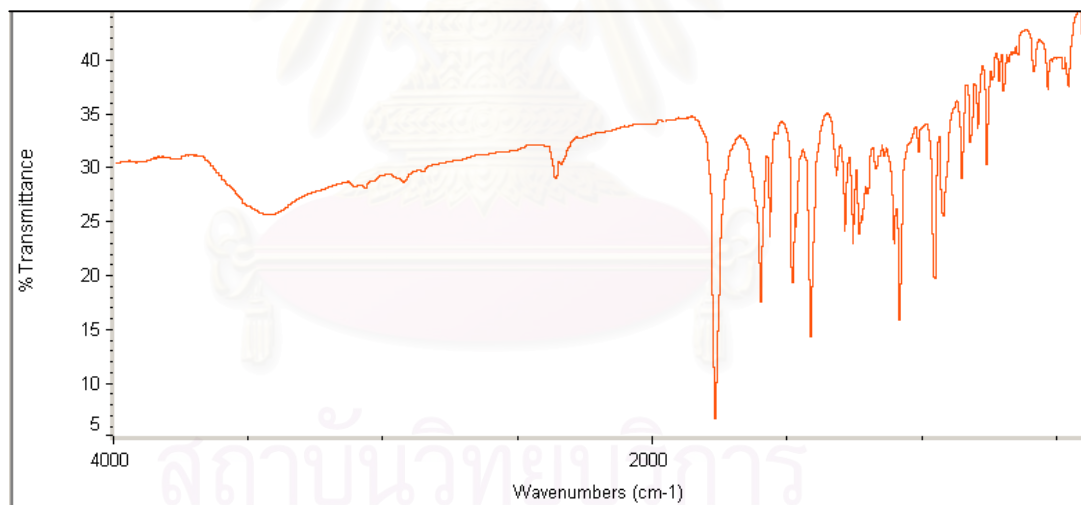
Fig.4-17 The FT-IR spectrum of 3',6'-dichlorofluoran
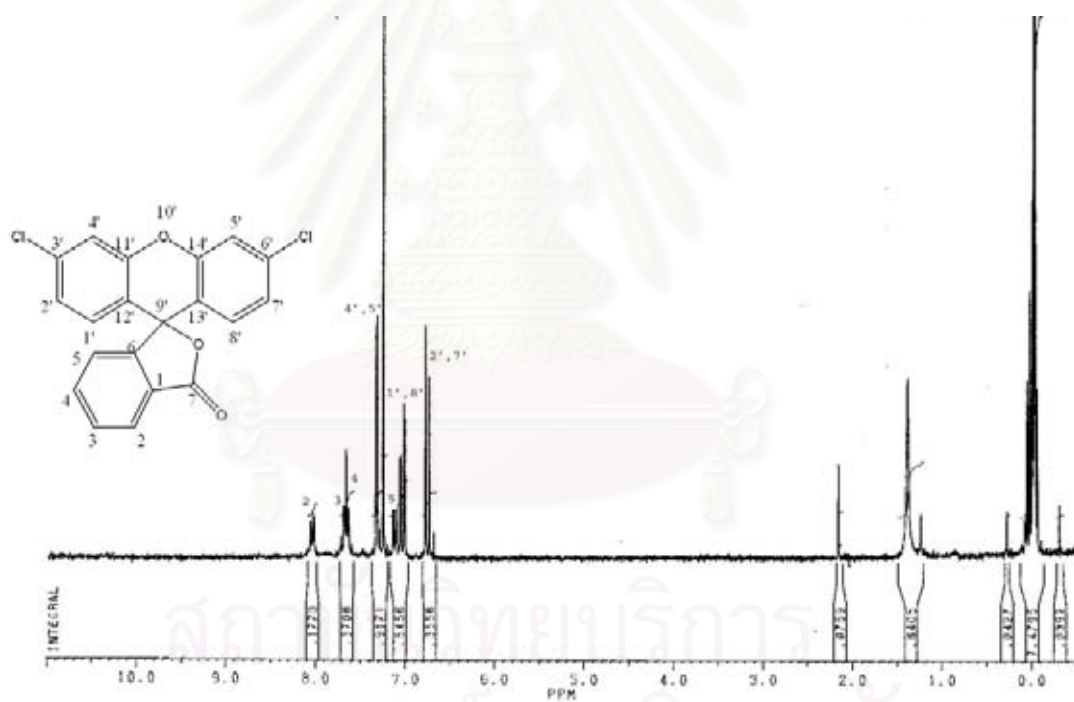
Fig.4-18 The ^{1}H-NMR spectrum of 3', 6'-dichlorofluoran
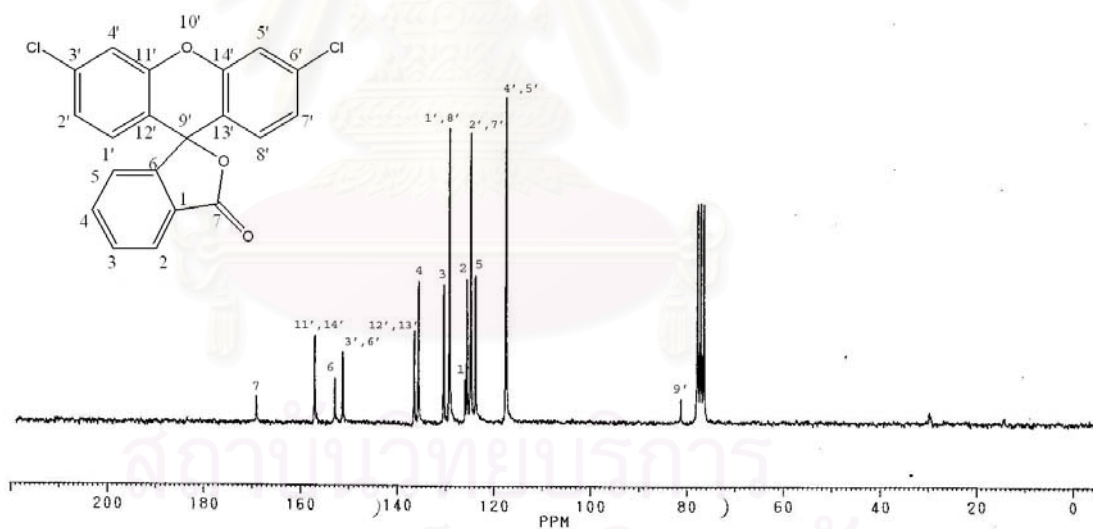
Fig. 4-19 The ^{13}C-NMR spectrum of 3', 6'-dichlorofluoran
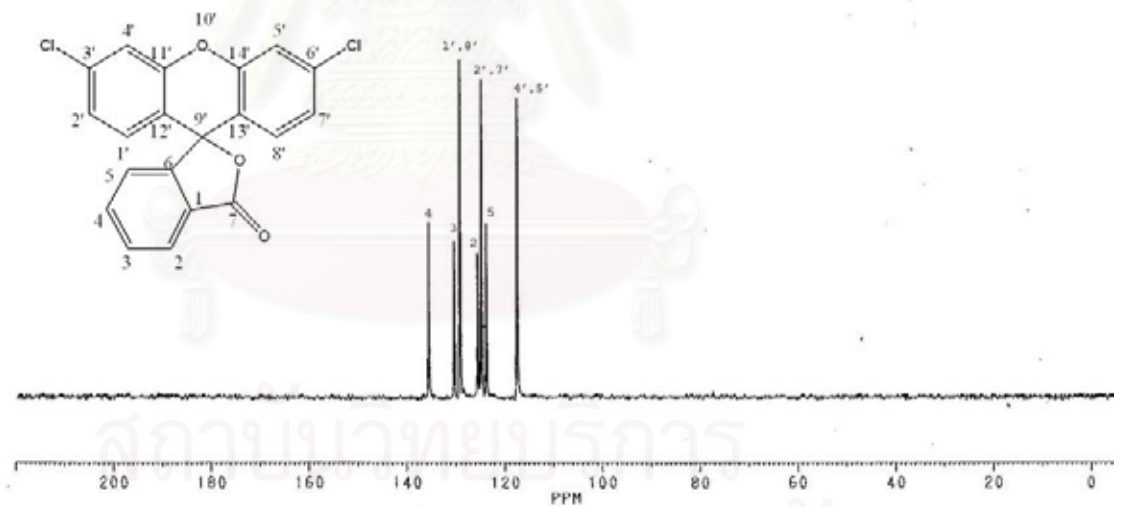
Fig. 4-20 The DEPT 135 spectrum of 3', 6'-dichlorofluoran
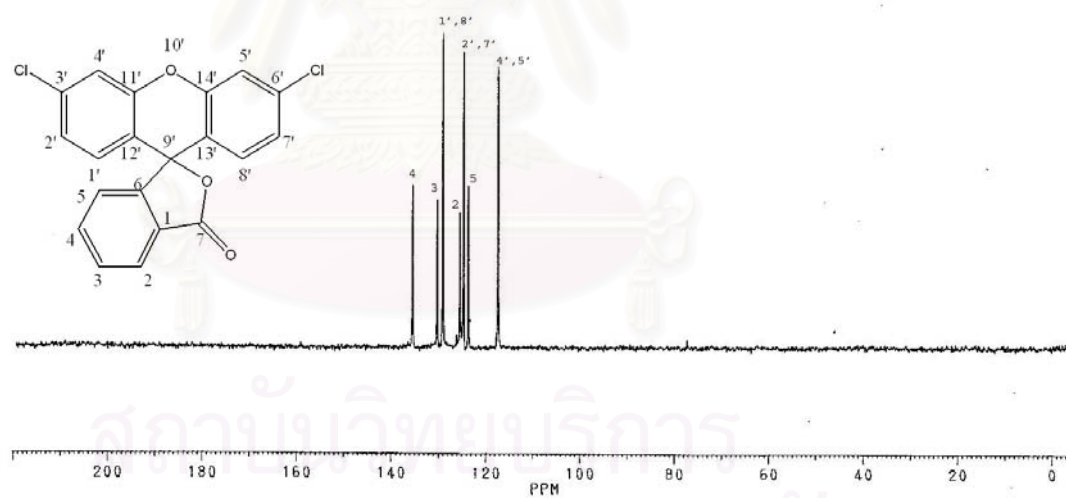
Fig. 4-21 The DEPT 90 spectrum of 3', 6'-dichlorofluoran
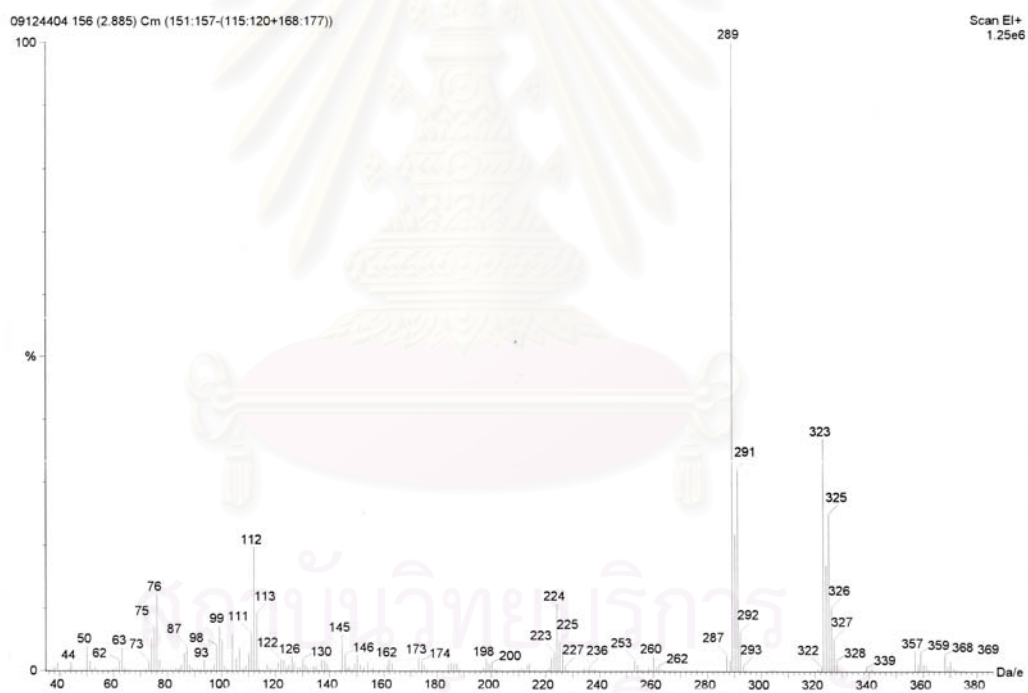
Fig.4-22 Mass spectrum of 3', 6'-dichlorofluoran
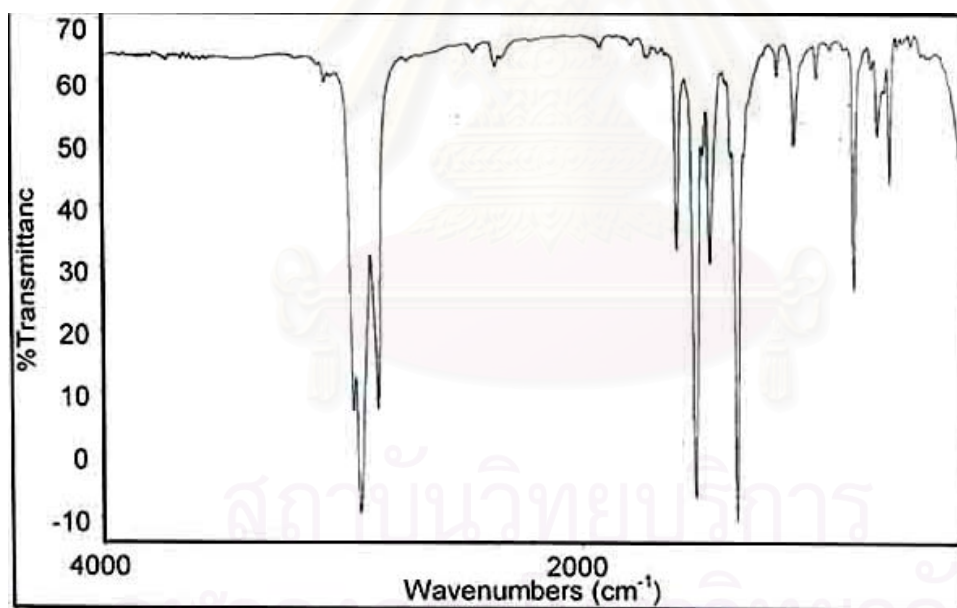
Fig.4-23 The FT-IR spectrum of *p*-nitro-linear alkylbenzene
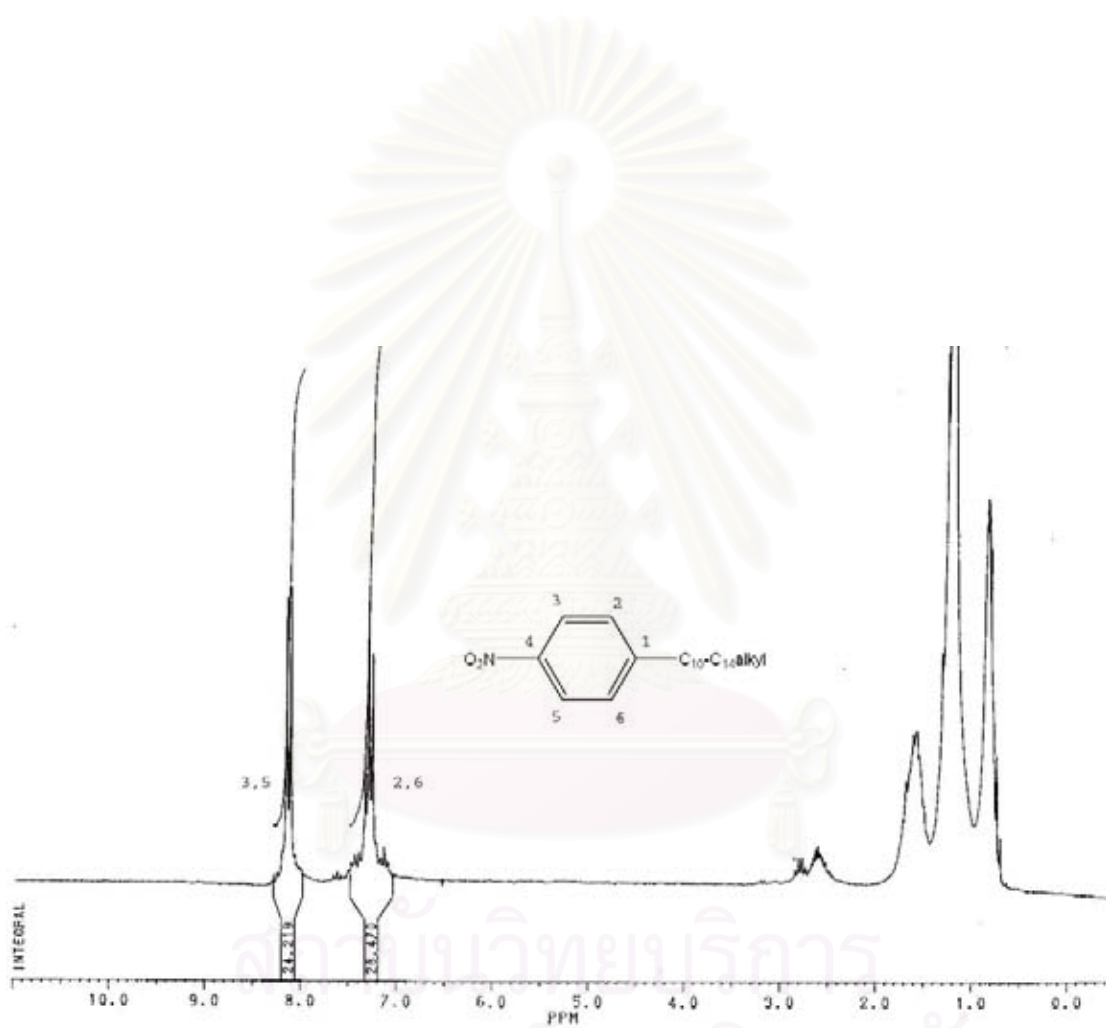
Fig.4-24 The ^{1}H-NMR spectrum of *p*-nitro-linear alkylbenzene
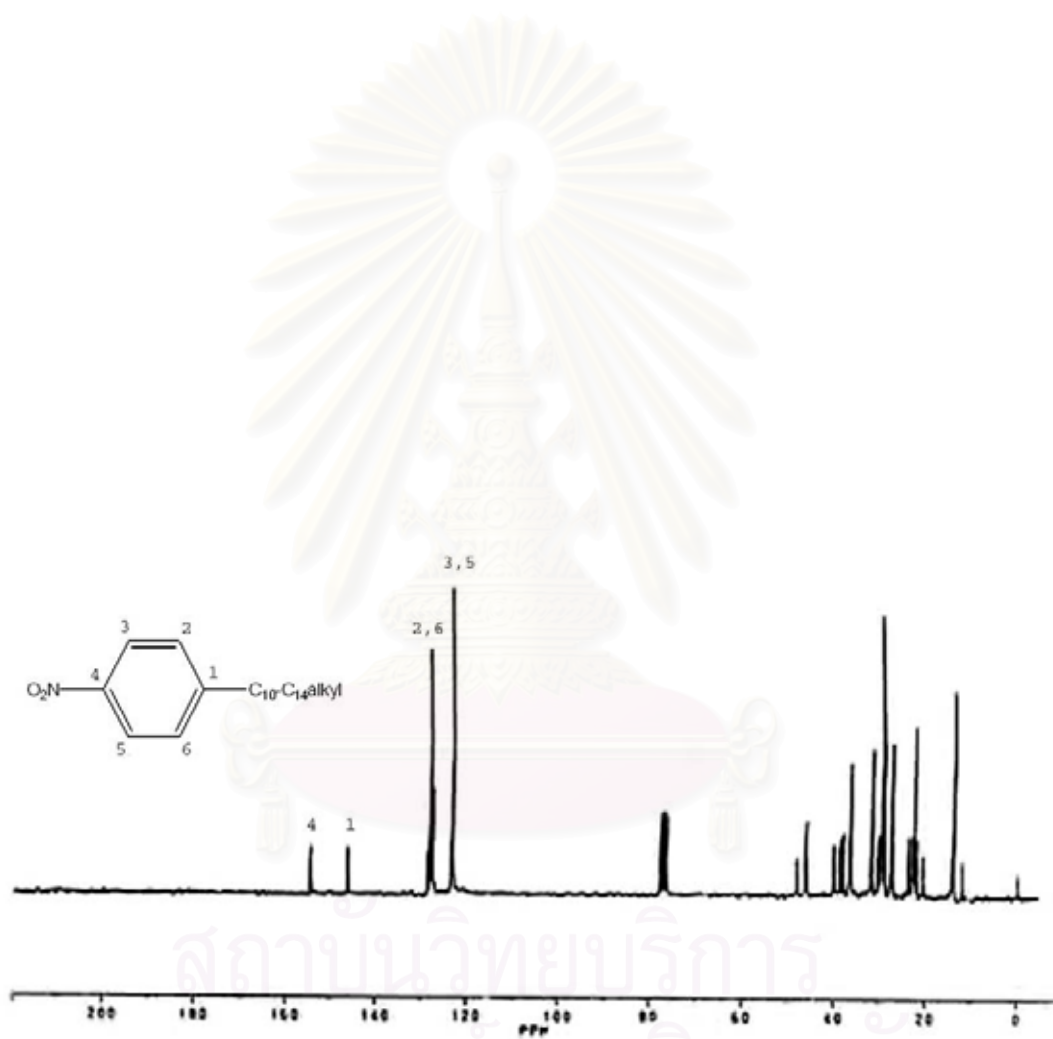
Fig.4-25 The ^{13}C-NMR spectrum of *p*-nitro-linear alkylbenzene
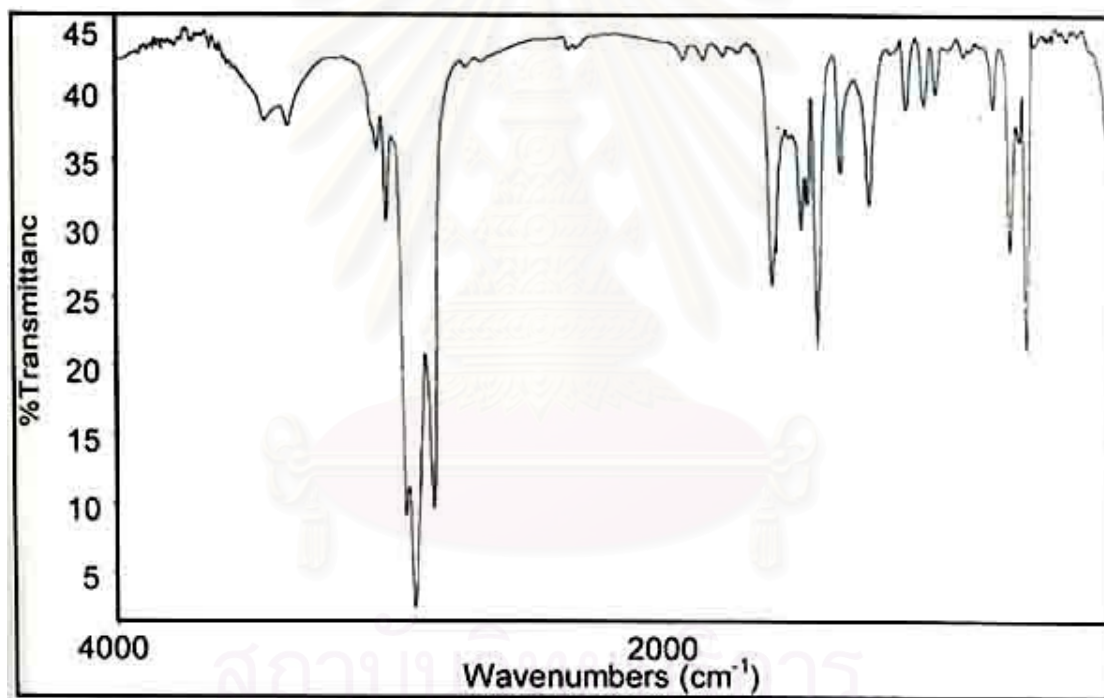
Fig.4-26 The FT-IR spectrum of *p*-linear alkylaniline
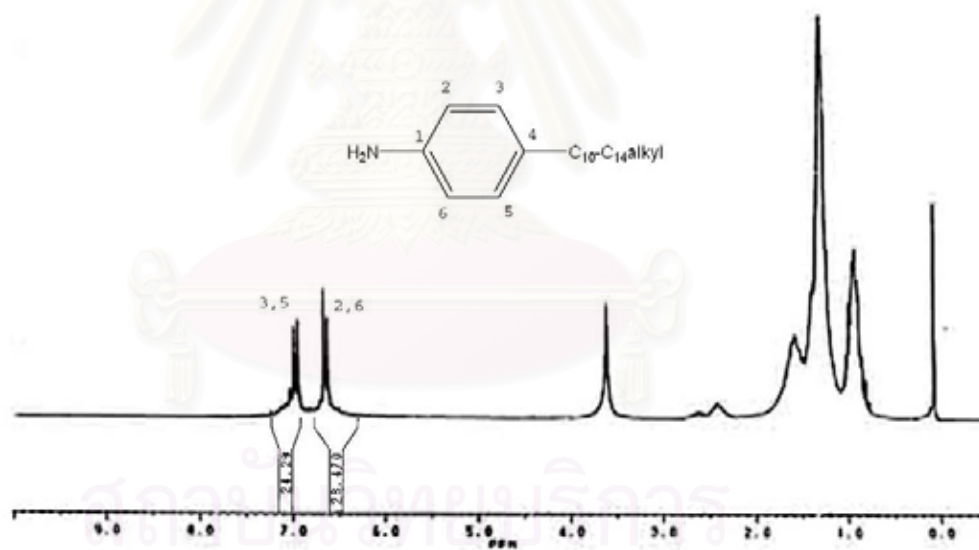
Fig.4-27 The ^{1}H-NMR spectrum of *p*-linear alkylaniline
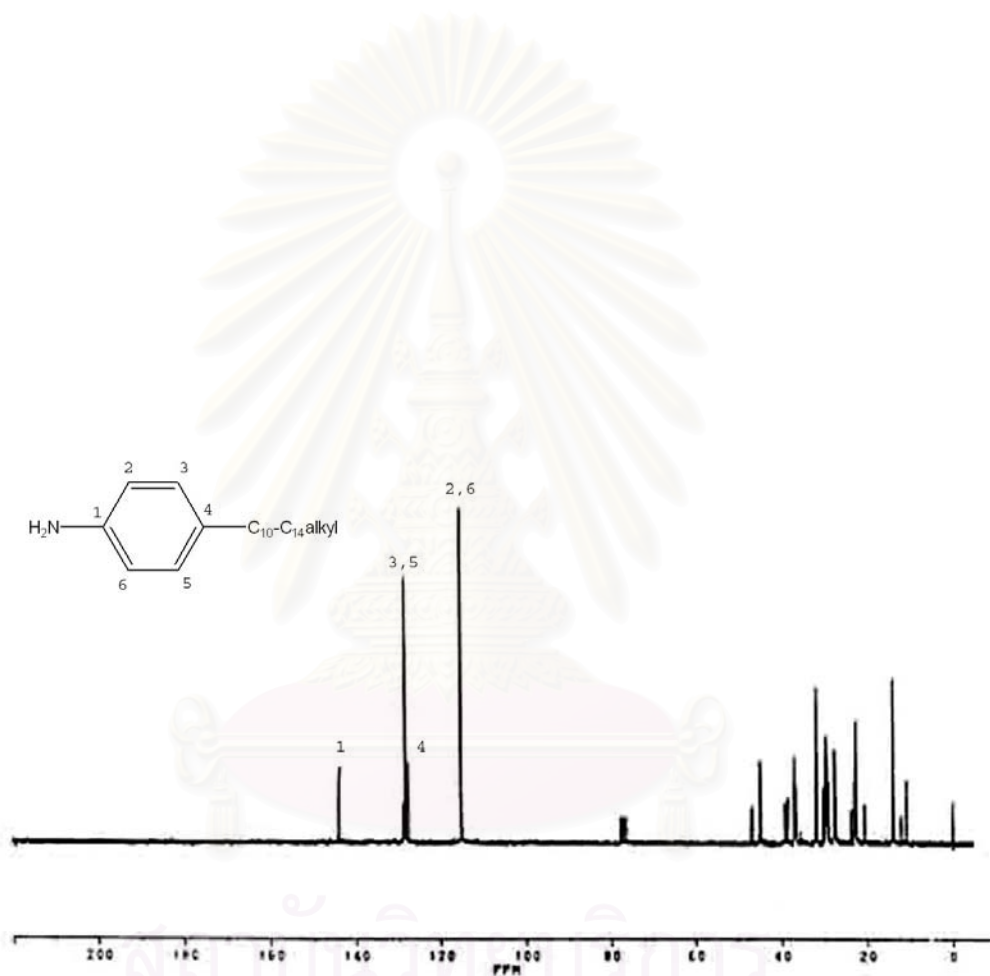
Fig.4-28 The ^{13}C-NMR spectrum of *p*-linear alkylaniline
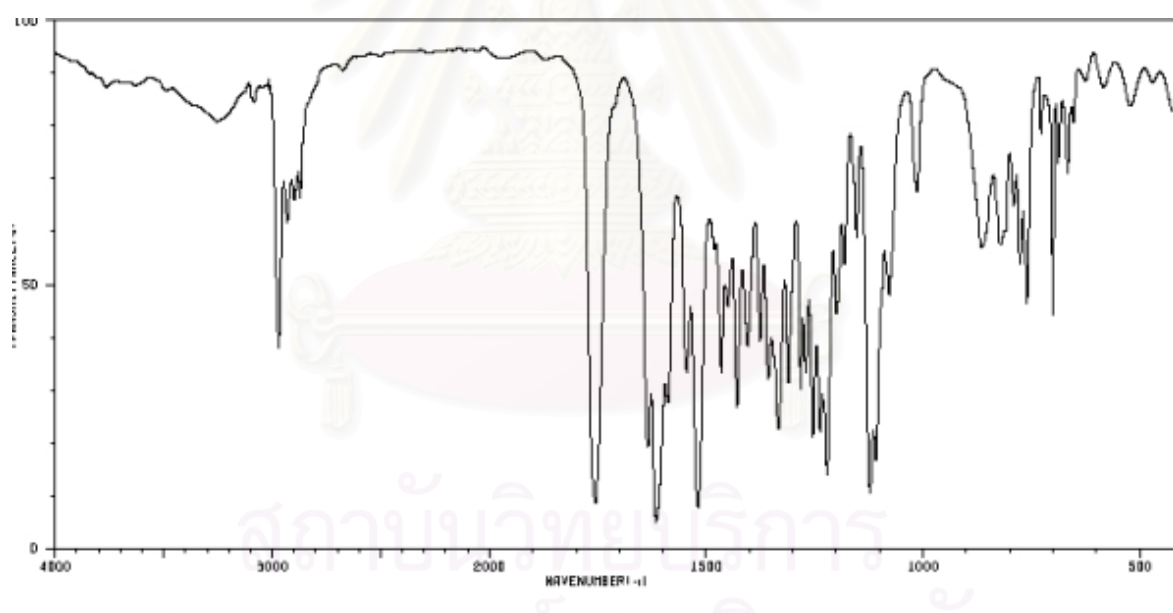
Fig.4-29 The FT-IR spectrum of 3', 6'-bis(dimethylamino)-fluoran
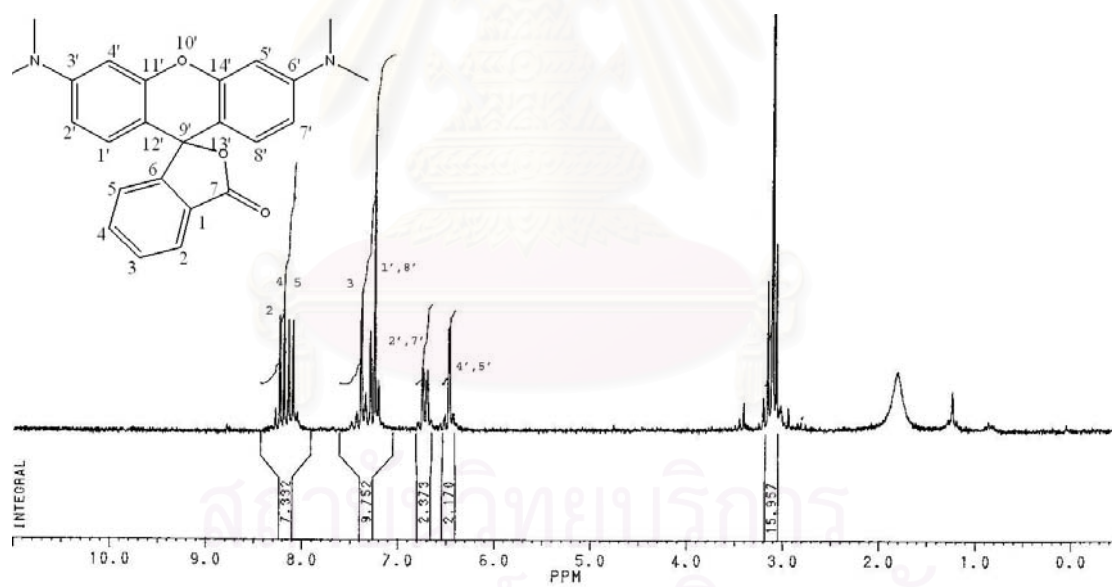
Fig.4-30 The ^{1}H-NMR spectrum of 3', 6'-bis(dimethylamino)-fluoran
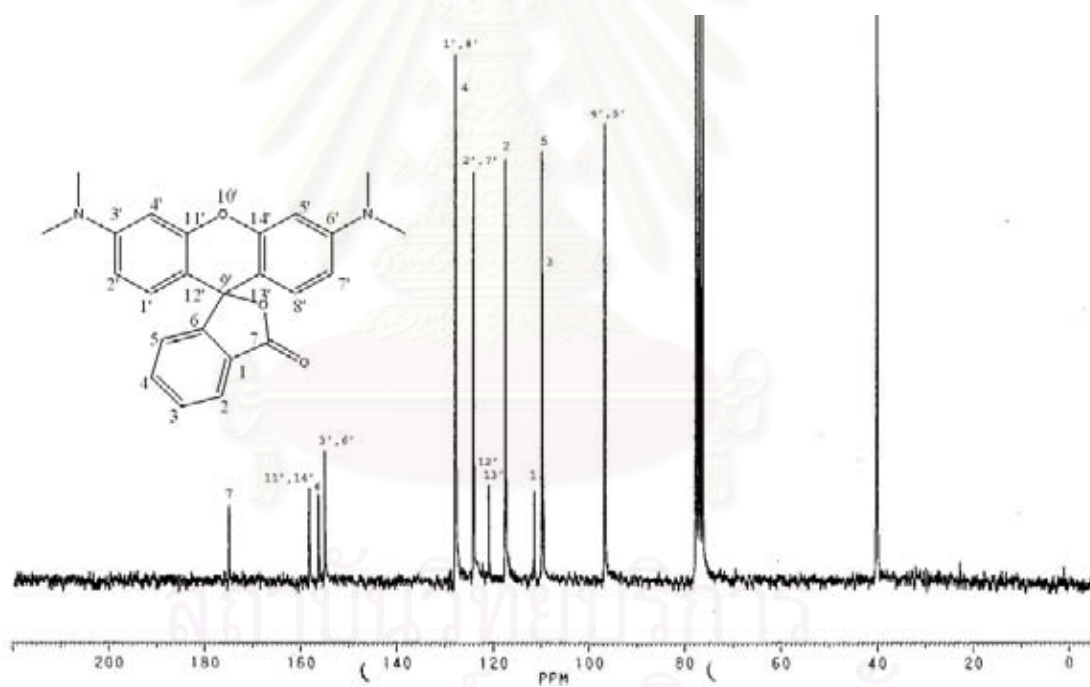
Fig. 4-31 The ^{13}C-NMR spectrum of 3', 6'-bis(dimethylamino)-fluoran
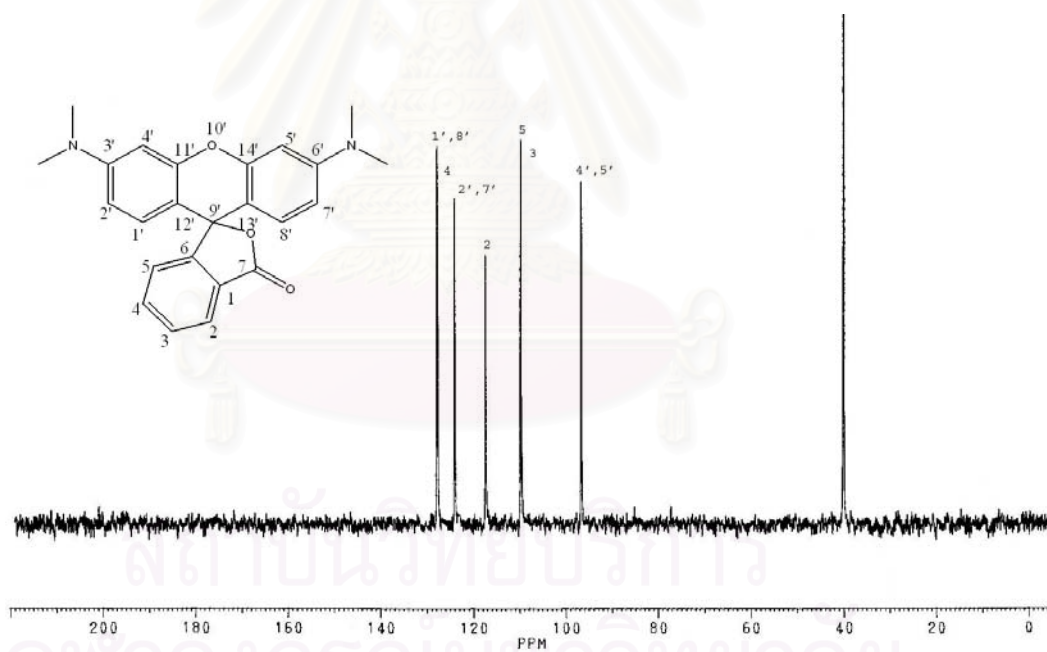
Fig. 4-32 The DEPT135 spectrum of 3', 6'-bis(dimethylamino)-fluoran
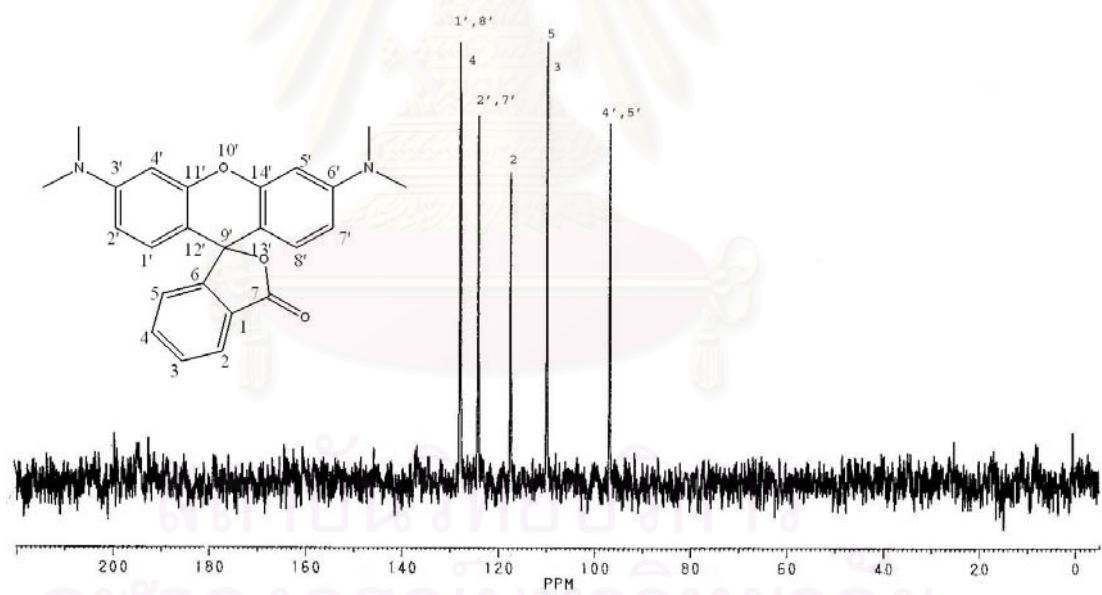
Fig. 4-33 The DEPT 90 spectrum of 3', 6'-bis(dimethylamino)-fluoran
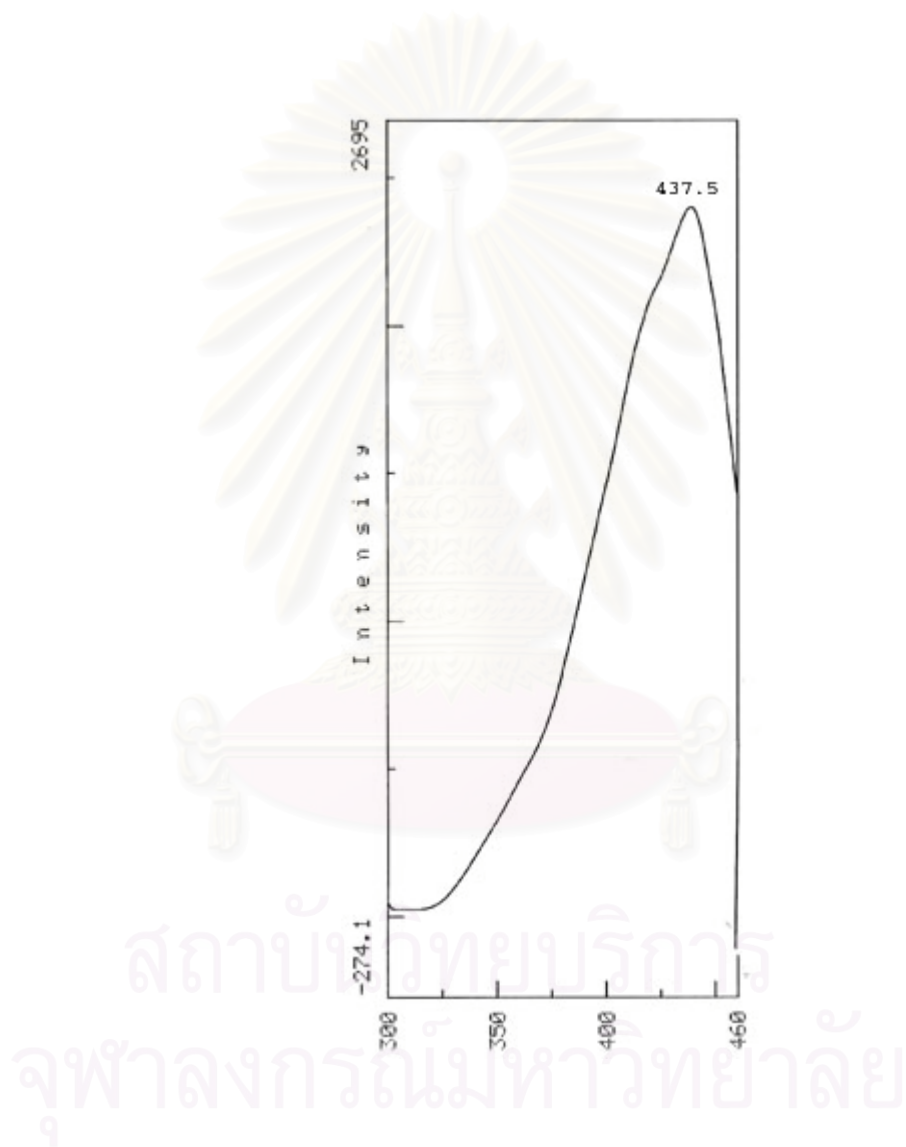
Fig.4-39 Exitation wavelength of 3', 6'-dihydroxyfluoran
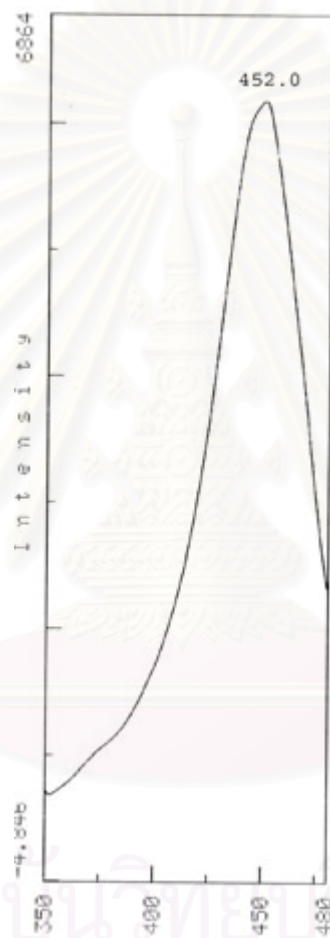
Fig.4-40 Exitation wavelength of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate

Fig.4-41 Exitation wavelength of 3'-hydroxy-6'-nonyloxyfluoran
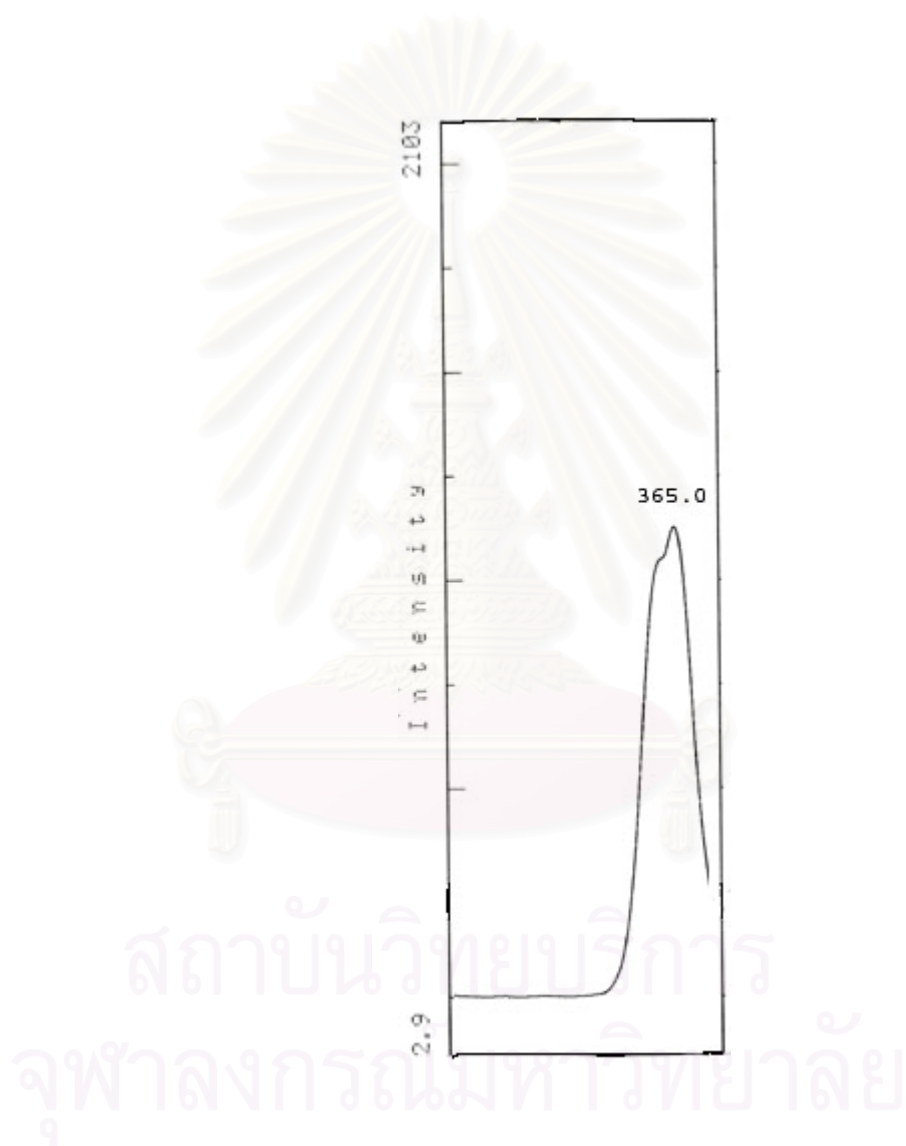
Fig.4-42 Exitation wavelength of 3', 6'-dichlorofluoran
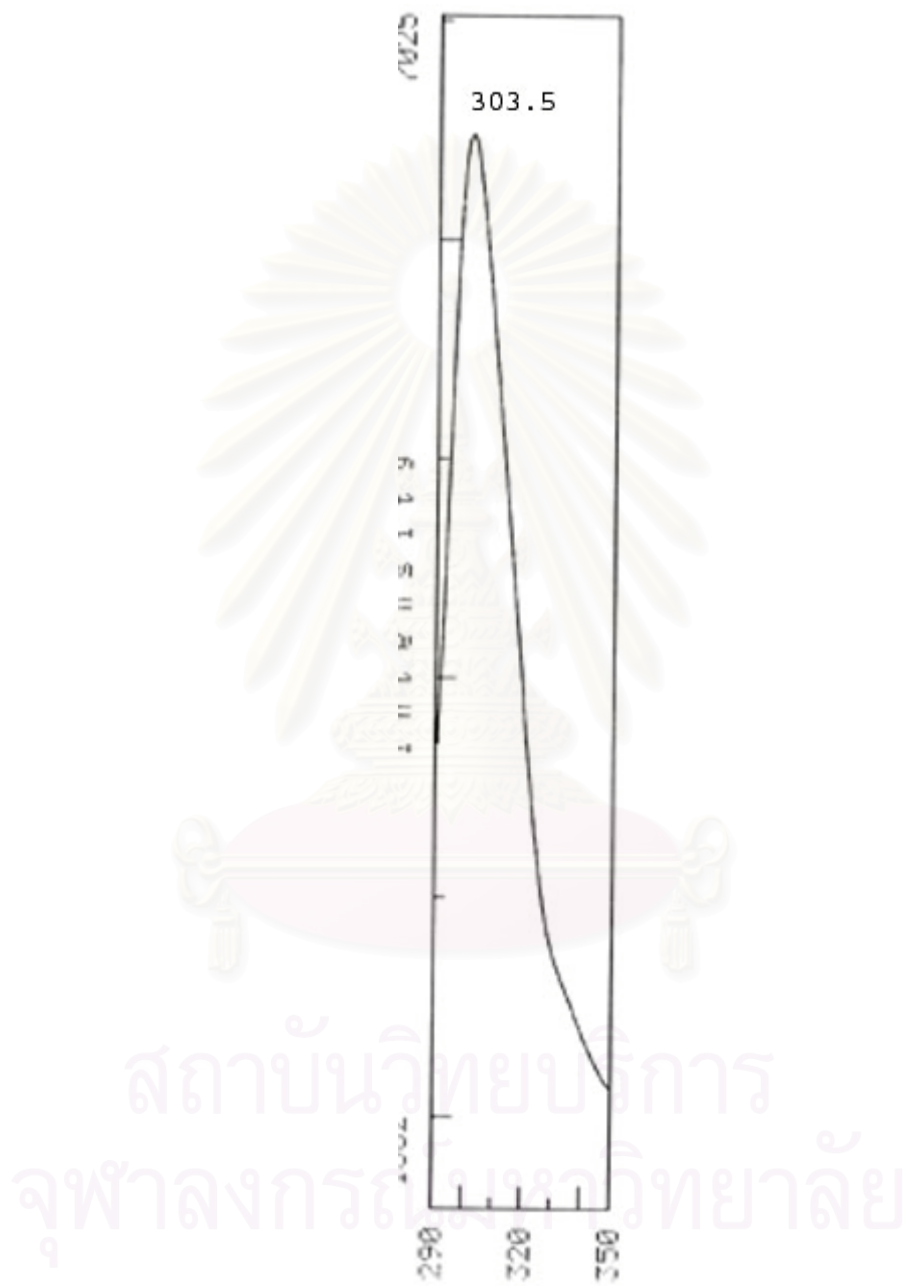
Fig.4-43 Exitation wavelength of 3', 6'-bis(dimethylamino)-fluoran

Fig.4-44 Emission wavelength of 3', 6'-dihydroxyfluoran
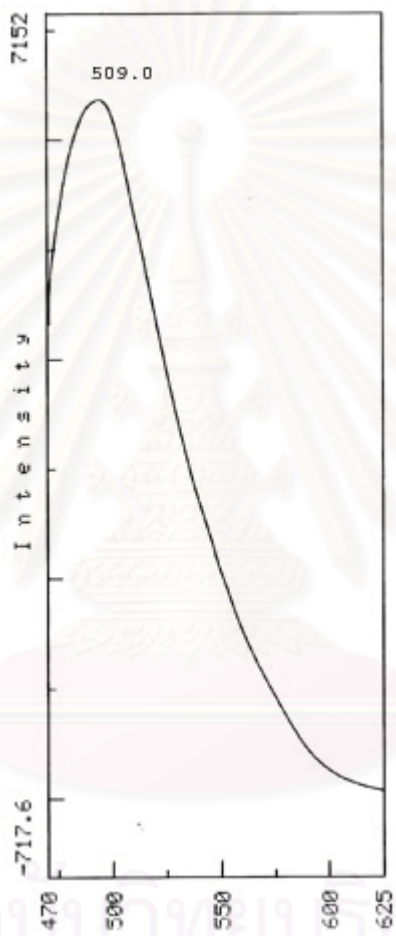
Fig.4-45 Emission wavelength of 6-(3'-carbony-6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate

Fig.4-46 Emission wavelength of 3'-hydroxy-6'-nonyloxyfluoran
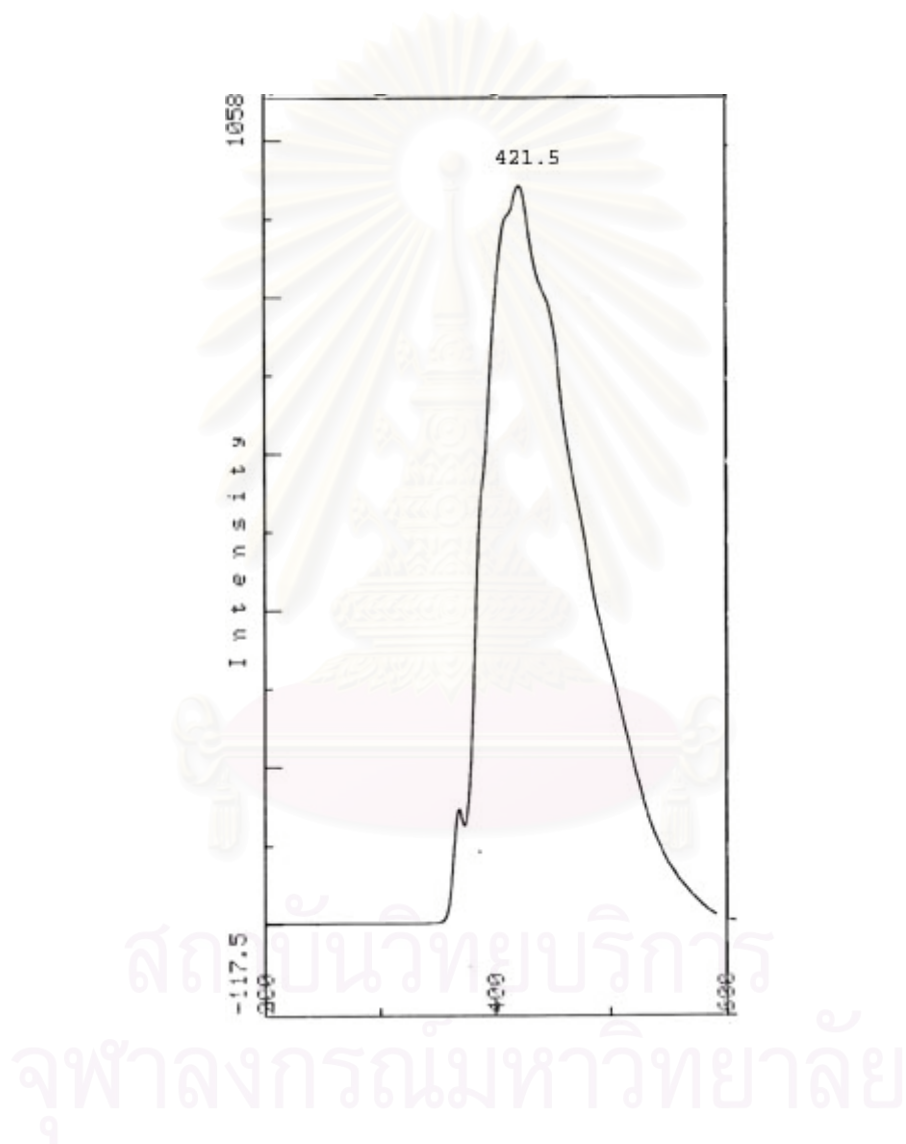
Fig.4-47 Emission wavelength of 3', 6'-dichlorofluoran
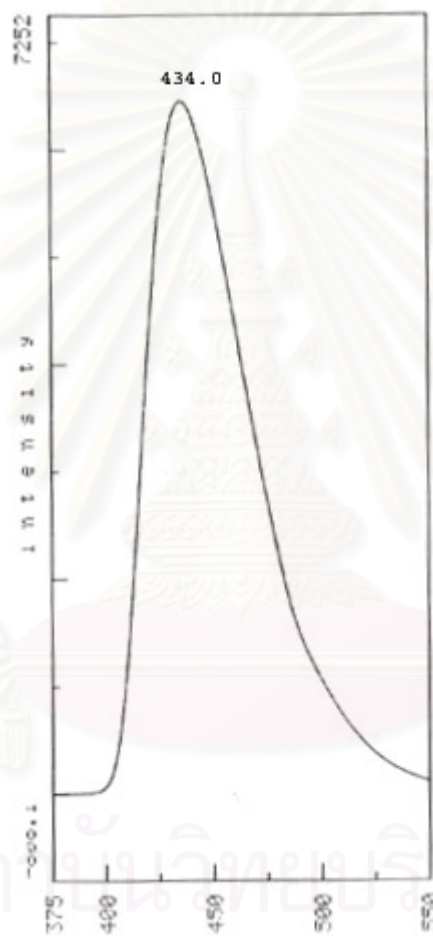
Fig.4-48 Emission wavelength of 3', 6'-bis(dimethylamino)-fluoran
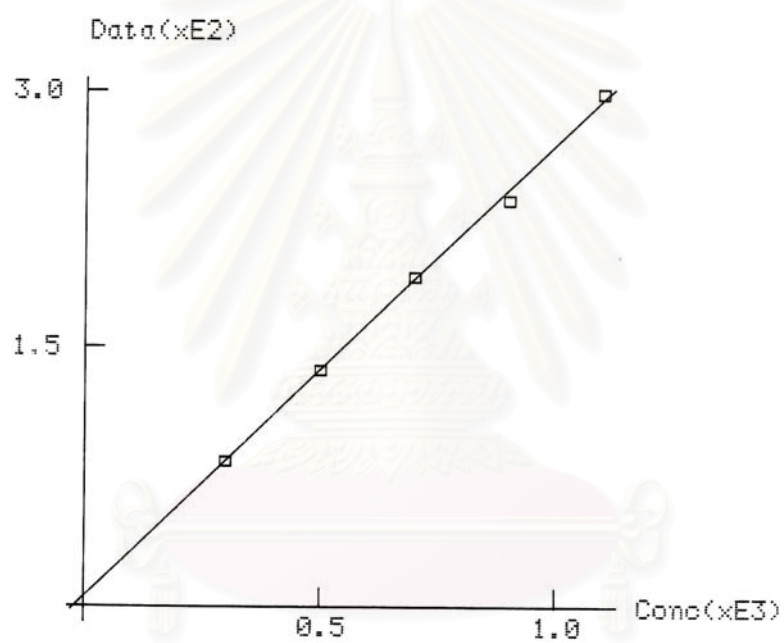
Fig.4-49 The calibration curve for the quantitative determinations of 6-(3'-carbony-
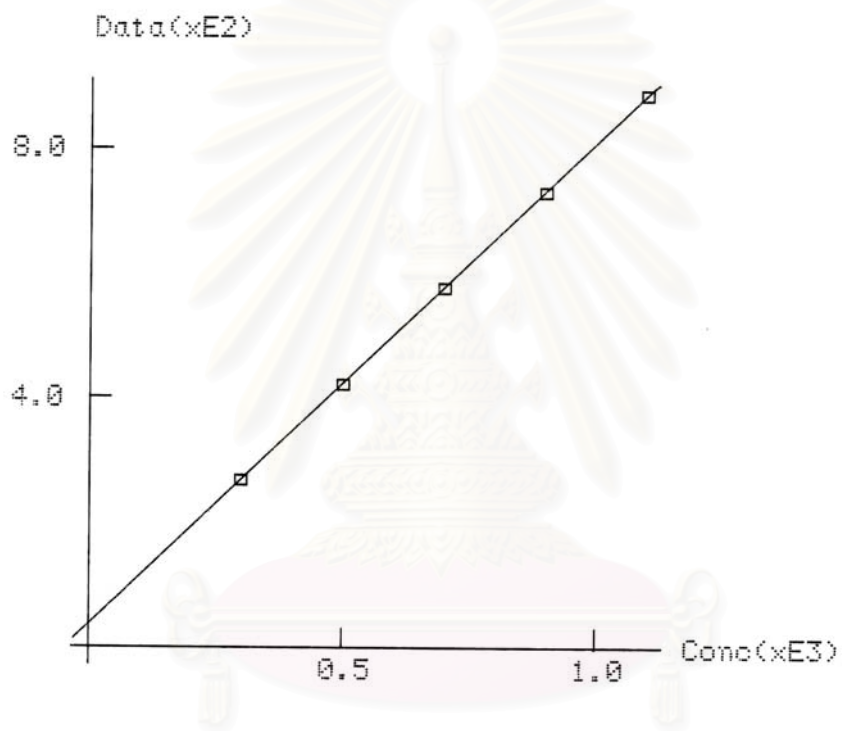6'-nonyloxy-xanthen-9'-yl)-nonyl benzoate

Fig.4-50 The calibration curve for the quantitative determinations of 3'-hydroxy-6'-nonyloxyfluoran
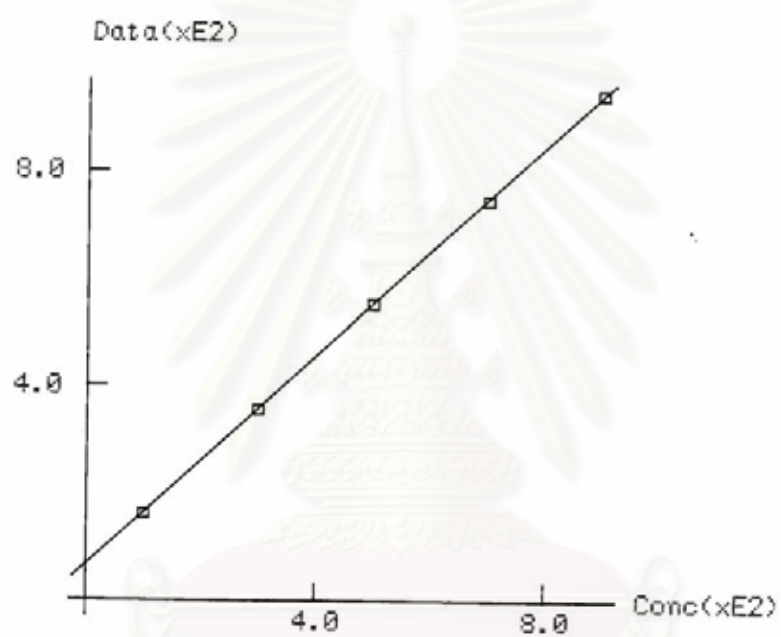
Fig.4-51 The calibration curve for the quantitative determinations of 3',6'-dichlorofluoran
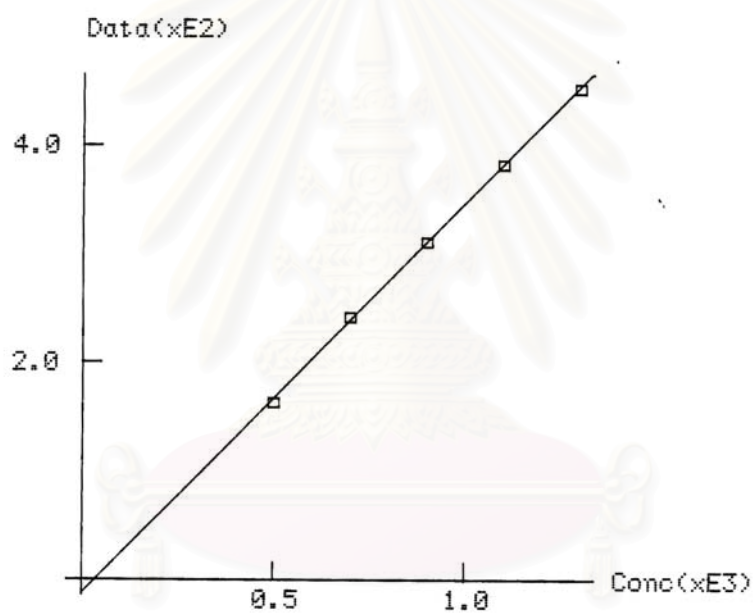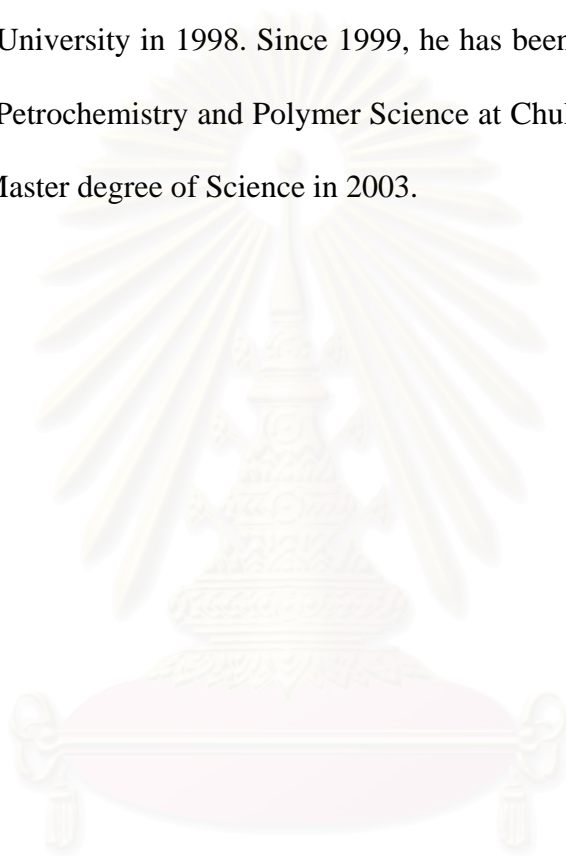
Fig.4-52 The calibration curve for the quantitative determinations of 3',6'-bis(dimethylamino)-fluoran

VITA

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