

**Chemical Constituents from the Stem Bark of  
*Fagraea fragrans* Roxb.**

**Kaodeeya Kaikaew**

**A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Chemical Studies  
Prince of Songkla University**

**2010**

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**Thesis Title**                      Chemical Constituents from the Stem Bark of  
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**Author**                              Miss Kaodeeya Kaikaew  
**Major Program**                    Chemical Studies

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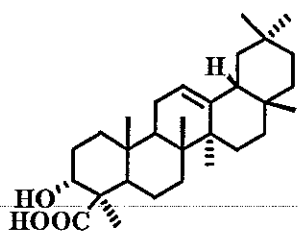
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ชื่อวิทยานิพนธ์	องค์ประกอบทางเคมีจากเปลือกต้นกันเกรา ( <i>Fagraea fragrans</i> Roxb.)
ผู้เขียน	นางสาวคอดีษฐ์ ไก่แก้ว
สาขาวิชา	เคมีศึกษา
ปีการศึกษา	2553

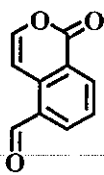
### บทคัดย่อ

การศึกษากองค์ประกอบทางเคมีในส่วนสกัดหยาบไดคลอโรมีเทนของเปลือกต้นกันเกรา แยกสารได้ 15 สาร ประกอบด้วยสารกลุ่ม triterpenes 2 สาร คือ  $\alpha$ -boswellic acid (KF1),  $\beta$ -boswellic acid (KF3), secoridoides 3 สาร: 1-oxo-1*H*-isochromene-5-carbaldehyde (KF2), gentiogenol (KF4), fagraldehyde (KF8), benzene derivatives 3 สาร คือ syringaldehyde (KF5), 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid octacosyl ester (KF6), 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid 30-oxo-triacontyl ester (KF7), iridoides 1 สาร คือ angelone (KF9), lignans 6 สาร คือ eudesmin (KF10), monomethylpinoresinol (KF11), medioresinol (KF12), pinorisinol (KF13), syringaresinol (KF14), 3,6-bis-(4-hydroxy-3,5-dimethoxyphenyl)-tetrahydro-furo[3,4-*c*]furan-1-one (KF15), KF2 และ KF15 เป็นสารใหม่, KF8 เป็น สารที่เคยมีรายงานในส่วนนี้แล้ว, KF1-KF9, KF10-KF15 เป็นสารที่แยกได้ครั้งแรกจากพืชชนิดนี้

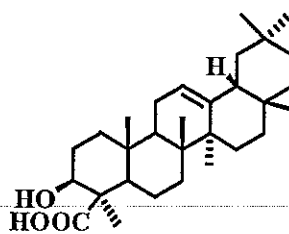
โครงสร้างของสารประกอบเหล่านี้วิเคราะห์โดยใช้ข้อมูลทางสเปกโทรสโกปี UV IR NMR MS และเปรียบเทียบกับสารที่มีรายงานการวิจัยแล้ว



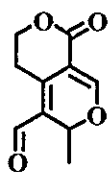
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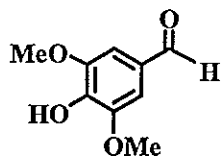
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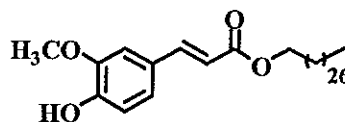
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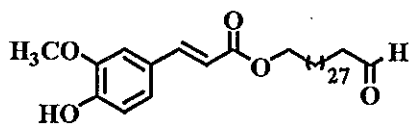
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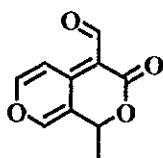
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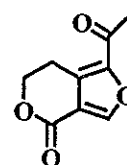
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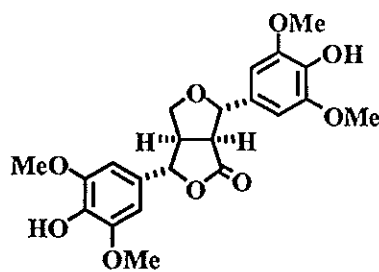
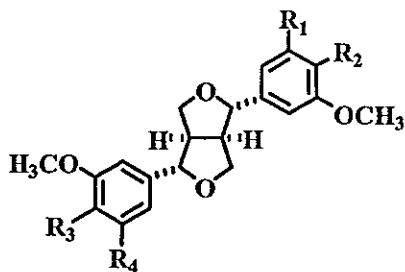
KF7



KF8



KF9



KF15

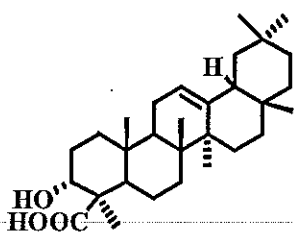
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
KF10:	H	OCH <sub>3</sub>	OCH <sub>3</sub>	H
KF11:	H	OH	OCH <sub>3</sub>	H
KF12:	OCH <sub>3</sub>	OH	OH	H
KF13:	H	OH	OH	H
KF14:	OCH <sub>3</sub>	OH	OH	OCH <sub>3</sub>

<b>Thesis Title</b>	Chemical Constituents from the Stem barks of <i>Fagraea fragrans</i> Roxb.
<b>Author</b>	Miss Kaodeeya Kaikaew
<b>Major Program</b>	Chemical Studies
<b>Academic Year</b>	2010

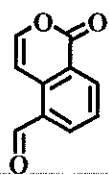
### ABSTRACT

Investigation of the chemical constituents in the dichlorometane extract of the stem bark of *Fagraea fragrans* Roxb. resulted in the isolation of 15 compounds, comprising of two triterpenes:  $\alpha$ -boswellic acid (KF1),  $\beta$ -boswellic acid (KF3), three secoiridoides: 1-oxo-1*H*-isochromene-5-carbaldehyde (KF2), gentiogenol (KF4), fagraldehyde (KF8), three benzene derivatives: syringaldehyde (KF5), 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid octacosyl ester (KF6), 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid 30-oxo-triacontyl ester (KF7), one iridoide: angelone (KF9), six lignans: eudesmin (KF10), monomethylpinoresinol (KF11), medioresinol (KF12), pinorisinol (KF13), syringaresinol (KF14), 3,6-bis-(4-hydroxy-3,5-dimethoxy-phenyl)-tetrahydro-furo[3,4-*c*]furan-1-one (KF15). KF2 and KF15 are new compounds. KF8 was previously isolated from the bark of this plant. KF1-KF7, KF9-KF15 were first isolated from this plant.

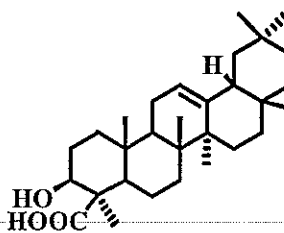
Their structures were determined on the basis of UV, IR, NMR, MS and by comparison of their spectroscopic data with those reported.



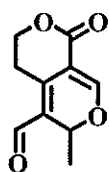
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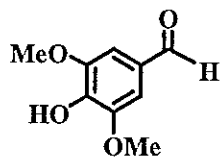
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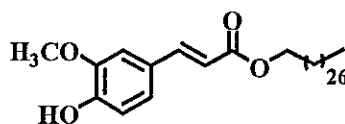
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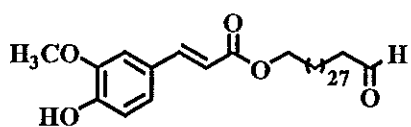
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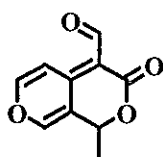
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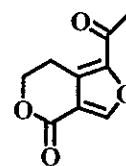
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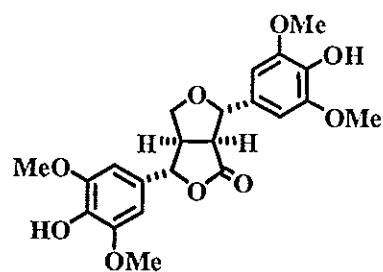
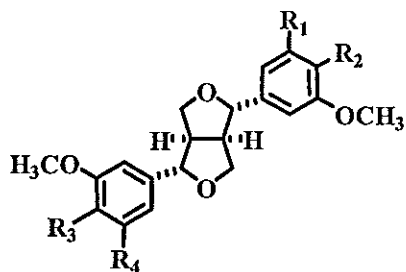
KF7



KF8



KF9



KF15

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
<b>KF10:</b>	H	OCH <sub>3</sub>	OCH <sub>3</sub>	H
<b>KF11:</b>	H	OH	OCH <sub>3</sub>	H
<b>KF12:</b>	OCH <sub>3</sub>	OH	OH	H
<b>KF13:</b>	H	OH	OH	H
<b>KF14:</b>	OCH <sub>3</sub>	OH	OH	OCH <sub>3</sub>

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Kaodeeya Kaikaew

## THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The purpose of this research is to investigate the chemical constituents of *Fagraea fragrans* Roxb.. It is a part of the basic research on the utilization of Thai medicinal plants. Two triterpenes, three secoiridoides, three benzene derivatives, one iridoide and six lignans were isolated from the stem barks of *Fagraea fragrans* Roxb..



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## LIST OF ABBREVIATIONS AND SYMBOLS

<i>s</i>	=	singlet
<i>d</i>	=	doublet
<i>t</i>	=	triplet
<i>q</i>	=	quartet
<i>m</i>	=	multiplet
<i>dd</i>	=	doublet of doublet
<i>dt</i>	=	doublet of triplet
<i>br s</i>	=	broad singlet
<i>br d</i>	=	broad doublet
<i>g</i>	=	gram
nm	=	nanometer
mp	=	melting point
cm <sup>-1</sup>	=	reciprocal centimeter (wave number)
$\delta$	=	chemical shift relative to TMS
<i>J</i>	=	coupling constant
[ $\alpha$ ] <sub>D</sub>	=	specific rotation
$\lambda_{\max}$	=	maximum wavelength
$\nu$	=	absorption frequencies
$\epsilon$	=	molar extinction coefficient
<i>m/z</i>	=	a value of mass divided by charge
°C	=	degree celcius
MHz	=	Megahertz
ppm	=	part per million
<i>c</i>	=	concentration
IR	=	Infrared
UV	=	Ultraviolet
MS	=	Mass Spectroscopy
EIMS	=	Electron Impact Mass Spectroscopy
NMR	=	Nuclear Magnetic Resonance
1D NMR	=	One Dimensional Nuclear Magnetic Resonance

## LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

2D NMR	=	Two Dimensional Nuclear Magnetic Resonance
COSY	=	Correlation Spectroscopy
DEPT	=	Distortionless Enhancement by Polarization Transfer
HMBC	=	Heteronuclear Multiple Bond Correlation
HMQC	=	Heteronuclear Multiple Quantum Coherence
NOESY	=	Nuclear Overhauser Effect Spectroscopy
CC	=	Column Chromatography
QCC	=	Quick Column Chromatography
PLC	=	Preparative Thin Layer Chromatography
TLC	=	Thin Layer Chromatography
TMS	=	tetramethylsilane
CDCl <sub>3</sub>	=	deuteriochloroform
CD <sub>3</sub> OD	=	deuteromethanol

## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

The genus *Fagraea* comprises a diverse group of trees, shrubs, scrambling lianas, and epiphytic stranglers that are found in forest gaps, forest edges, along stream beds in wet tropical forests, and less commonly in mesic forests, savannas, and mangrove swamps. This genus is comprised of approximately 177 species, the center of *Fagraea* genus diversity is Malaysia and Papuasia. This genus is also indigenous to Ceylon, India, southeastern Asia to southern China, Hainan and Taiwan, northern Australia, New Caledonia, and throughout the Pacific Islands from the Marianas to the Marquesas (Motley, 2004). Several species of *Fagraea* are used in traditional medicine such as the floral fragrance of flowers of *F. berteriana* is considered useful for aroma therapy. In Melanesia, an infusion of the leaves, inner bark and roots of *F. berteriana* is used to treat asthma and diabetes (Weiner, 1970). The root decoction was also used to reduce irritation and inflammation of the genitals (Cambie and Ash, 1994). The wood of *F. gracilipes* is especially preferred for underwater use in wharf piles. The heated leaves of *F. schlechteri* are applied to wounds, bruises, and boils. The macerated leaves are used to stop menstrual bleeding and as a purgative, a leaf infusion is poured into the ear to fight infection and is given orally to children to stimulate growth (Rageau, 1973). The leaves of *F. maingayi* are applied to boils (Perry, 1980), and the leaves of *F. bodenii* are chewed with salt to reduce the swelling of the spleen brought on by malarial infections (Woodley and Thredgold, 1991). The leaves of *F. blumei* and *F. obovata* are grated to make an infusion taken to reduce headaches and fever (Burkill, 1966). The *F. auriculata* bark is used to treat ulcers (Perry, 1980) and the fruit latex makes an adhesive or glue (Burkill, 1966) that is used to trap birds and insects (Leenhouts, 1963). Leaves and fruits of *F. fragrans* are used to treat fever. The decoction of the bark is used to treat malaria in India, Cambodia, and Malaysia and as a febrifuge in Philippines. The decoction of twigs and leaves is



used to control dysentery in Malaysia and Cambodia (Perry, 1980). This suggests that *Fagraea* genus has been widely used by many cultures for a long time.

A group of plants with such a rich herbal history should be scrutinized more closely by phytochemists to determine if there are any untapped resources of potential uses in medicine. An anti-inflammatory effect which is well documented in the ethnobotanical literature, is one. This may be conferred by secoiridoid compounds (Jensen and Schripsema, 2002). The history of herbal medicine can be seen that the plants in the genus *Fagraea* have medical benefits which are considered as interesting drugs. In Thailand, eight species of *Fagraea*: *F. acuminatissima* Merr. ขุนไทร, *F. auriculata* Jack ขุนไทร, *F. carnososa* Jack เข็มแดง, *F. ceilanica* Thunb. โขดแดง, *F. crenulata* Maingay ex C. B. Clarke ขุนไทร, *F. fragrans* กัญชง, *F. racemosa* Jack ตะเคียนเต่า, *F. tubulosa* Blume ขุนไทร, are widely distributed (Samitinand, 2544).

*Fagraea fragrans* (กัญชง) is a species that has been used as herbal medicines for some diseases such as blood tonic, skin blister, malaria, asthma, cough, hemorrhoids, suffocate, maintenance spleen, expel, anemia, disability, etc. There are a few reports on the chemical constituents from *F. fragrans*. It thus prompted us to study the chemical constituents of this species and expected to find new compounds that might show interestingly biological activity and pharmacological or it can be the basic information that will lead to research and development in the future.

## 1.2 Review of Literatures

### 1.2.1 The Chemical Constituents and Biological Activity of *Fagraea* genus

Several of compounds have been reported in the *Fagraea* genus (Genteanaceae), such as iridoids, secoiridoids, alkaloids, lignans, phenylpropanoides, steroids and triterpenes.

Secoiridoids are common compounds in Gentianales. Previously, several known secoiridoids have been described in *Fagraea* genus such as gentiopicroside, sweroside and swertiamarin, and a new secoiridoid aglycone named fagraldehyde,

isolated from the dichlorometane extract of the bark of *F. fragrans*. Fagraldehyde appears to be the first naturally occurring monoterpene product possessing this kind of bicyclic skeleton.

The secoiridoide compounds isolated from *Fragraea* genus have been investigated for biological activity such as, fagraldehyde were tested in vitro against *Plasmodium falciparum*, was weakly active, exhibiting an IC<sub>50</sub> value of  $W2 = 22.4 \pm 1.8 \mu\text{g/mL}$  (Jonville *et al.*, 2008). The secoiridoide glycosides, sweroside and swertiamarin were active against a number of bacterial species. Both sweroside and swertiamarin exhibited antibacterial activity against *Bacillus cereus*, *Bacillus subtilis*, *Citrobacter freundii* and *Escherichia coli*. While swertiamarin inhibited the growth of *Proteus mirabilis* and *Serratia marcescens*, sweroside was active against *Staphylococcus epidermidis* (Kumarasamy *et al.*, 2003).

Four new iridoid glucosides, named blumeosides A-D, were isolated from the methanol extract of the stem bark of *F. blumei*. Blumeosides inhibited bleaching of crocin induced by alkoxy radicals. Blumeosides A and D also demonstrated scavenging properties towards the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) radical in TLC autograph and spectrophotometric assays.

The major alkaloid of the leaves and fruits of *F. fragrans* was 4-(2-hydroxyethyl)-5-vinylnicotinic acid lactone, identical with gentianine, this compound show analgesic activity. The alkaloid content of the plant showed marked seasonal variation. The yield of alkaloid from the leaves was highest at the beginning of the flowering season (Wan Alfred *et al.*, 1972).

A series of phenylpropanoid components: *trans*-3,4-dimethoxycinnamyl alcohol, *trans*-3,4-dimethoxycinnamyl acetate, *trans*-3,4-dimethoxycinnamaldehyde and *trans*-coniferyl alcohol were isolated from the flower of *F. berteriana*, three compounds from the heartwood of *F. gracilipes*: methyl *p*-coumarate, methyl caffeate, methyl sinapate and one compound is 1,3-propanediol was isolated from the bark of *F. racemosa*.

The lignans compounds: (+)-pinoresinol, (+)-epipinoresinol, (+)-lariciresinol, (+)-isolariciresinol, and phenols such as syringaldehyde and 7,8-dihydro-7-oxyconiferyl alcohol were isolated from the *F. racemosa* Jack ex Wall., a medicinal

plant from Borneo, using a bioassay of the relaxation effect on neopinephrine (NE)-induced contraction in rat aortic strips. The plant extract also exhibited analgesic properties in the acetic acid-induced writhing and tail pressure tests in mice, with the activity being concentrated in the lignan fraction. (+)-Pinoresinol showed analgesic effect on writhing symptoms in mice which were dose dependent, and produced local anesthesia in guinea pigs (Okuyama *et al.*, 1995).

Five new compounds were isolated from the heartwood of the *F. gracilipes*. The new compounds were identified as methyl syringate  $\alpha$ -L-rhamnoside, (Z)-5-ethylidene-3,4,5,6-tetrahydro-*cis*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one, (Z)-5-ethylidene-3,4,5,6-tetrahydro-*trans*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one, 3-*O*-sinapoyl D-glucose and 3'-*O*-sinapoyl sweroside. A new flavone glycoside, fagovatin was isolated from *F. obovata*.

In addition, the woods of many *Fagraea* species have a turpentine or oily smell when cut (Peters, 1995). The wax layer immediately under the surface of the fruit of *F. borneensis* was found to consist of *cis*-polyisoprene (rubber) and of esters of triterpineols (mainly lupeol) and fatty acids. The essential oil was isolated from the white flowers of *F. berteriana* were identified as (*E*)- $\beta$ -ocimene, methyl benzoate, benzyl acetate, methyl salicylate, benzyl benzoate, myristic acid and benzyl salicylate.

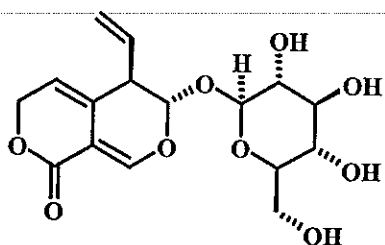
The chemical constituents isolated from the *Fagraea* genus were summarized in Table 2 (The literature survey from SciFinder Scholar database).



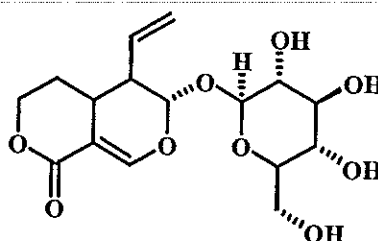
Table 1 (continued)

Scientific name (Investigated part)	Compounds/Structures	Bibliography
<p><i>F. gracilipes</i> Wood</p>	<p>3-[3-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propenoate] D-glucose, <b>19</b></p> <p>5-Ethenyl-4,4<math>\alpha</math>,5,6-tetrahydro-6-[[3-O-[3-(4-hydroxy-3,5dimethoxyphenyl)-1-oxo-2-propenyl]-<math>\beta</math>-D-glucopyranosyl]oxy]-1<i>H</i>,3<i>H</i>-pyrano[3,4-<i>c</i>]pyran-1-one, <b>20</b></p> <p>Methyl sinapate, <b>14</b></p> <p>Methyl <i>p</i>-coumarate, <b>15</b></p> <p>Methyl caffeate, <b>16</b></p> <p>5-Ethylidene-4,5,6,8-tetrahydro-6,8-dimethoxy1<i>H</i>,3<i>H</i>-pyrano[3,4-<i>c</i>]pyran-1-one, <b>5</b></p> <p>1,2:5,6-Bis-<i>O</i>-(1-methylethylidene)-3-(4-hydroxy-3,5-dimethoxyphenyl)-2-propenoate <math>\alpha</math>-D-glucofuranose, <b>18</b></p>	<p>Richard <i>et al.</i>, 1990</p>
<p><i>F. obovata</i> Leave</p>	<p>Fagovatin, <b>25</b></p>	<p>Qasim <i>et al.</i>, 1987</p>
<p><i>F. boneensis</i> Fruit</p>	<p>(+)-Lupeol, <b>26</b></p>	<p>Van Die <i>et al.</i>, 1957</p>
<p><i>F. blumei</i> Bark</p>	<p>Blumeoside A, <b>6</b></p> <p>Blumeoside B, <b>7</b></p> <p>Blumeoside C, <b>8</b></p> <p>Blumeoside D, <b>9</b></p>	<p>Muriel <i>et al.</i>, 1997</p>

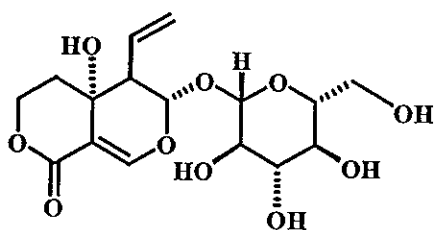
## Secoiridoids



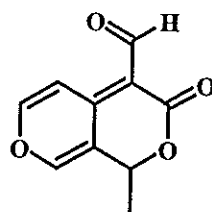
1: Gentiopicroside



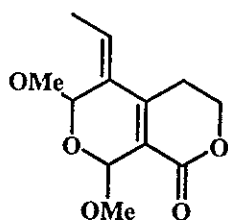
2: Sweroside



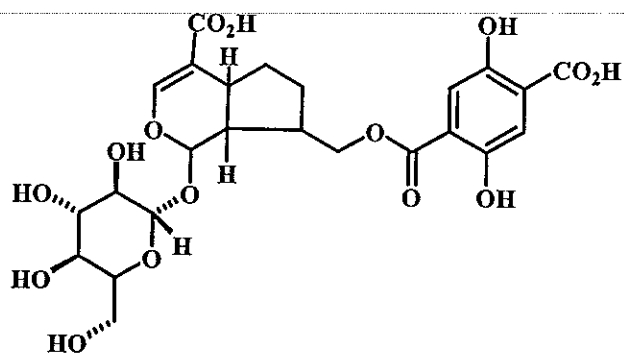
3: Swertiamarin



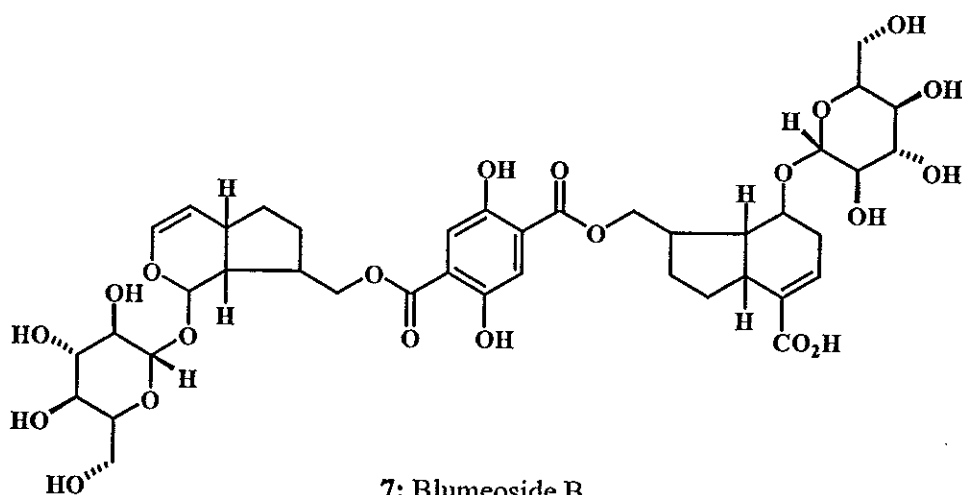
4: Fagraldehyde

5: 5-Ethylidene-4,5,6,8-tetrahydro-6,8-dimethoxy-1*H*,3*H*-pyrano[3,4-*c*]pyran-1-one

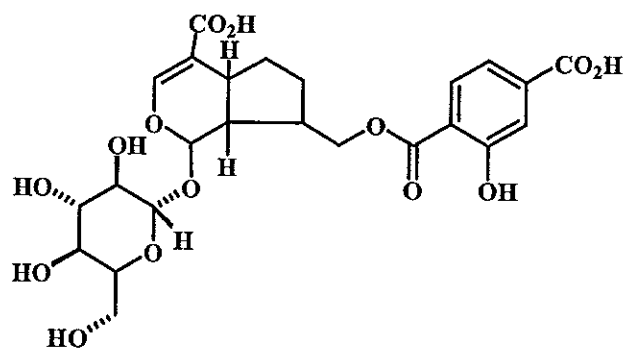
## Iridoid glucosides



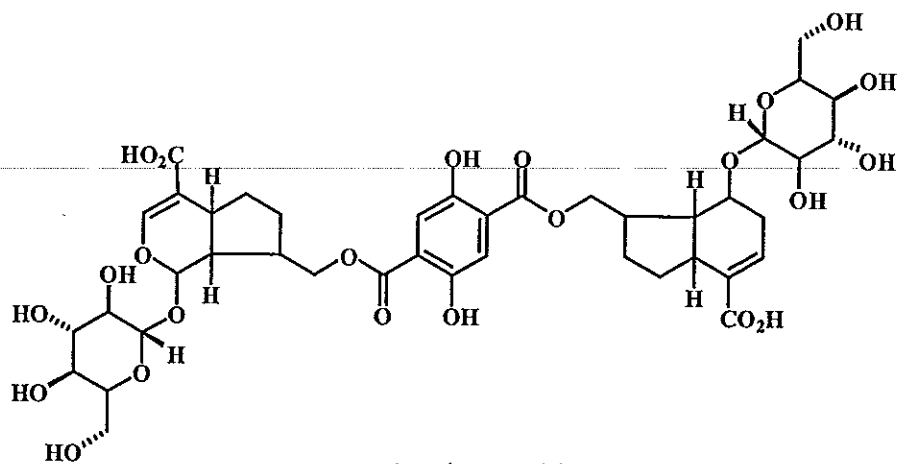
6: Blumeoside A



7: Blumeoside B

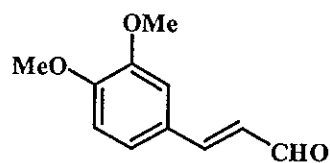
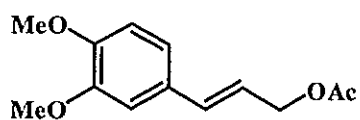
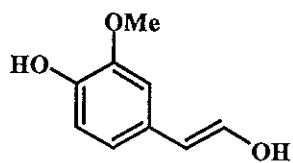
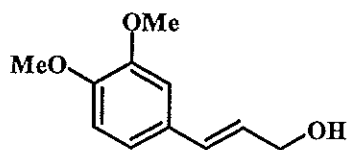
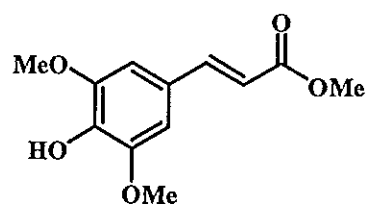


8: Blumeoside C

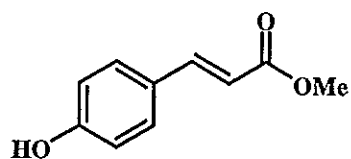


9: Blumeoside D

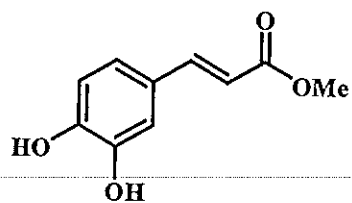
### Phenyl propanoids

10: *trans*-3,4-Dimethoxy  
cinnamaldehyde11: *trans*-3,4-Dimethoxy  
cinnamyl acetate12: *trans*-Coniferyl alcohol13: *trans*-3,4-Dimethoxy  
cinnamyl alcohol

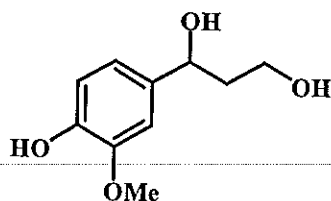
14: Methyl sinapate

15: Methyl *p*-coumarate

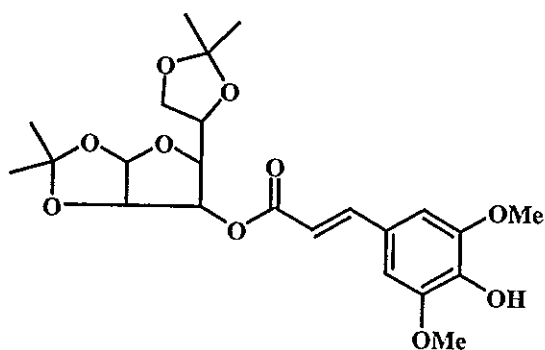
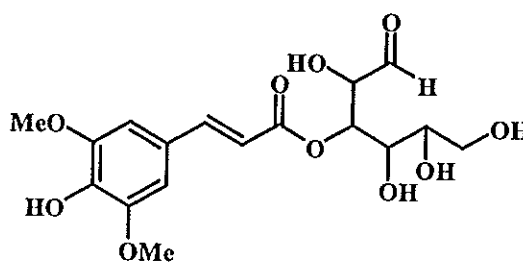
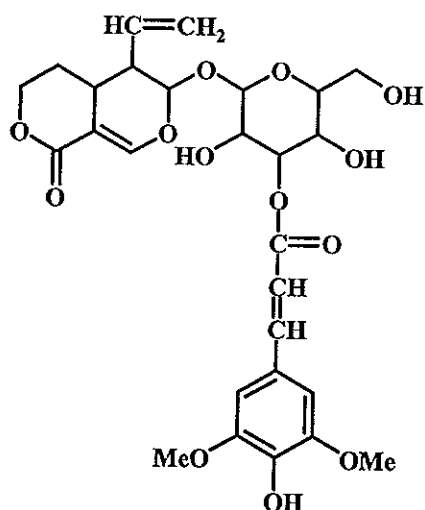




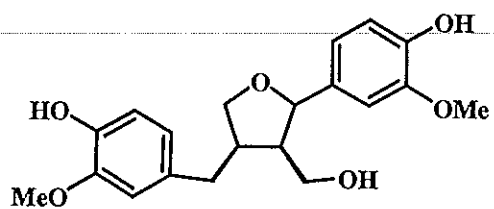
16: Methyl caffeate

17: 1-(4-Hydroxy-3-methoxyphenyl)-  
1,3-propanediol

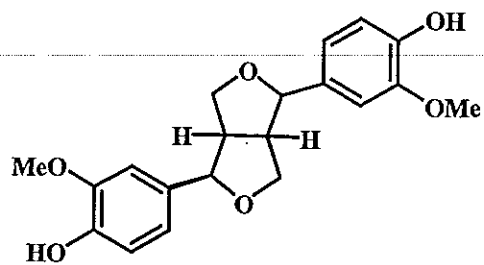
### Phenyl propanoid glycosides

18: 1,2:5,6-Bis-*O*-(1-methyl  
ethylidene)-3-(4-hydroxy-  
3,5-dimethoxy phenyl)-2-  
propenoate- $\alpha$ -D-glucofuranose19: 3-[3-(4-Hydroxy-3,5-  
dimethoxyphenyl)-  
2-propenoate] D-glucose20: 5-Ethenyl-4,4*a*,5,6-tetrahydro-6-[[3-*O*-  
[3-(4-hydroxy-3,5-dimethoxyphenyl)-1-  
oxo-2-propenyl]- $\beta$ -D-glucopyranosyl]  
oxy]-1*H*,3*H*-pyrano[3,4-*c*]pyran-1-one

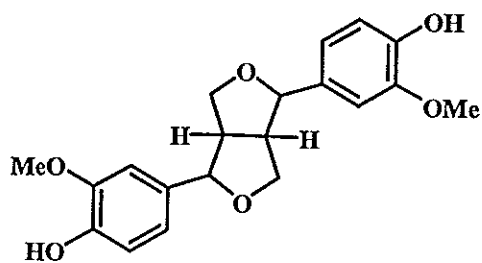
## Lignans



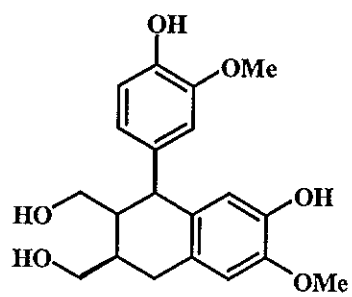
21: (+)-Lariciresinol



22: (+)-Epipinoresinol

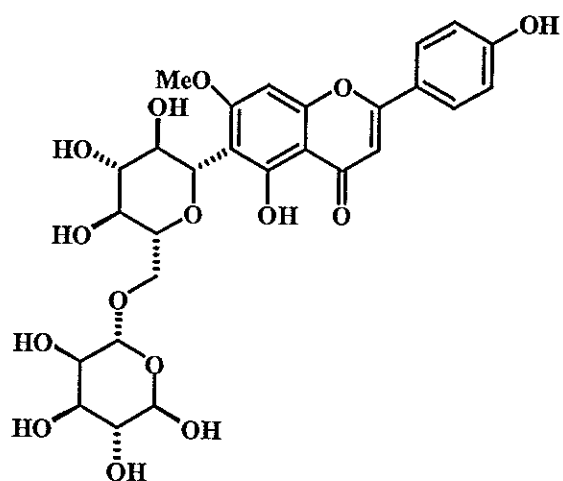


23: (+)-Pinoresinol

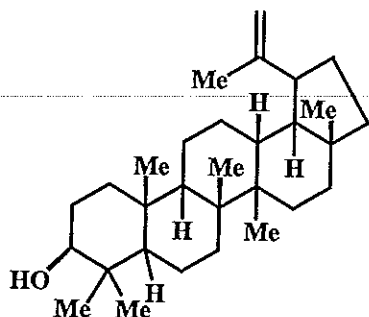


24: (+)-Isolariciresinol

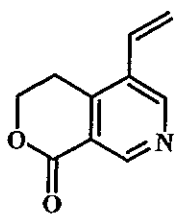
## Flavone glucosides



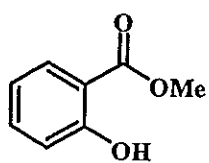
25: Fagovatin

**Terpinoids**

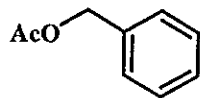
26: (+)-Lupeol

**Alkaloids**

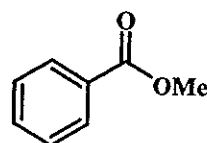
27: Gentianine

**Benzoic acid derivatives**

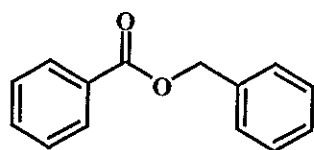
28: Methyl salicylate



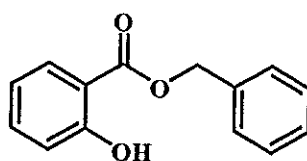
29: Benzyl acetate



30: Methyl benzoate

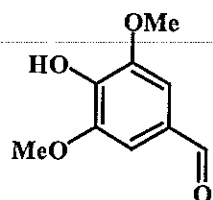


31: Benzyl benzoate

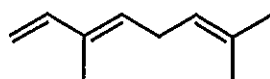


32: Benzyl salicylate

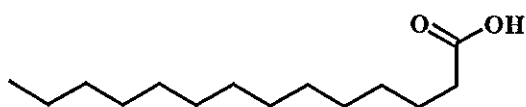
## Others



33: Syringaldehyde



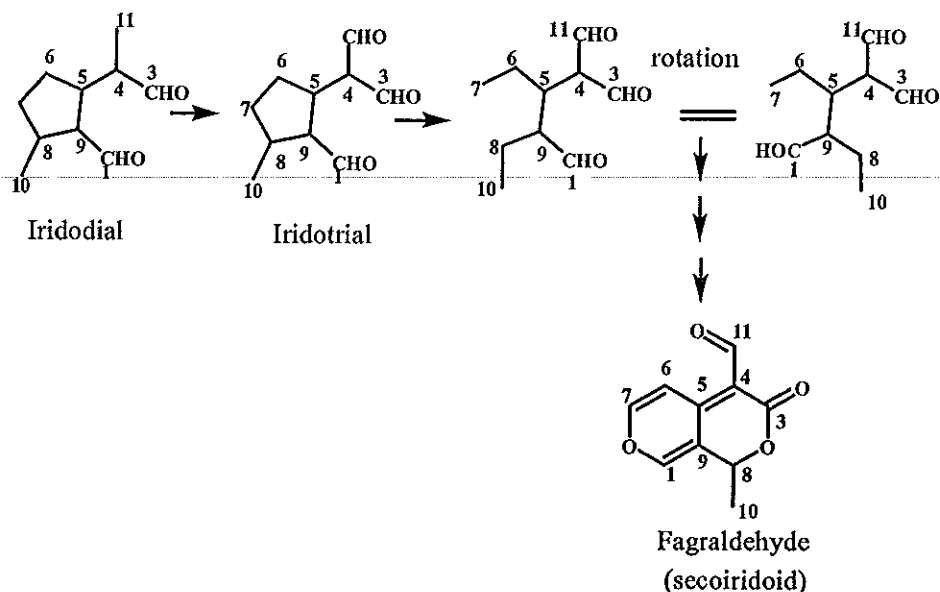
34: (*E*)- $\beta$ -Ocimene



35: Tetradecanoic acid

### 1.2.2 Biogenetic pathway of some secoiridoide

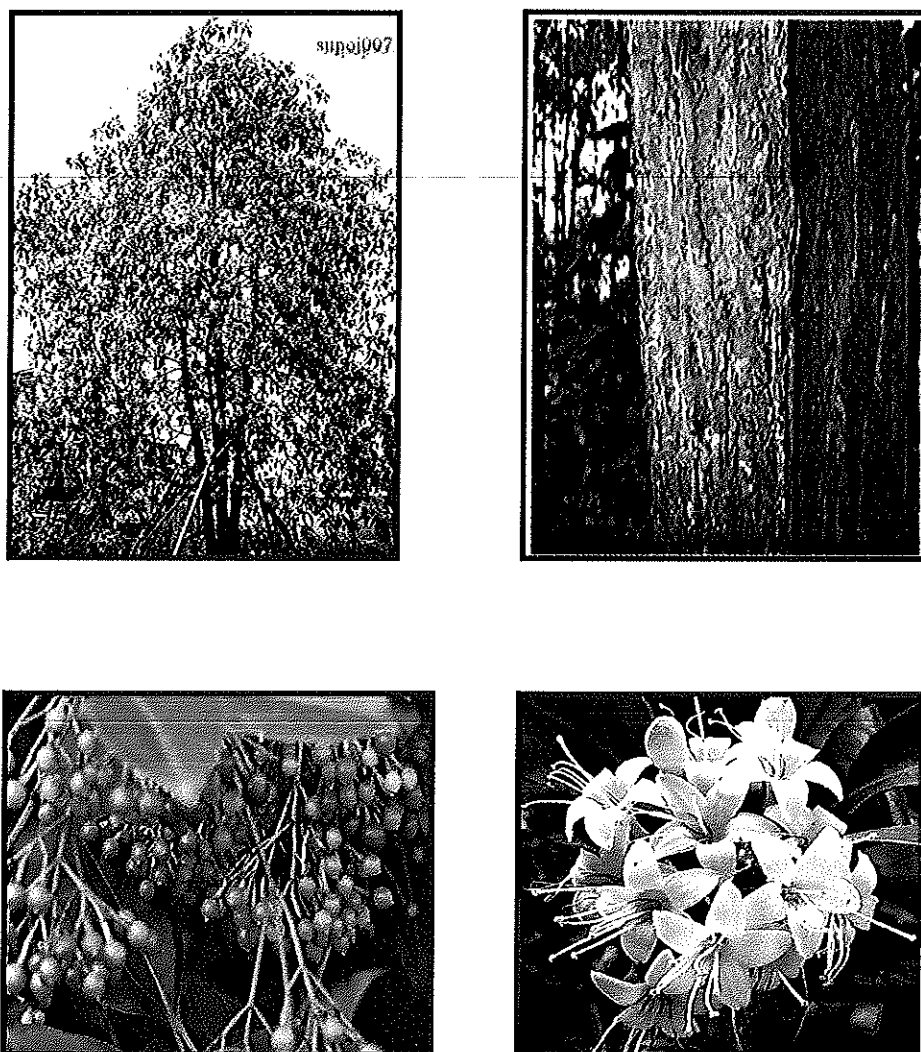
Jonville and coworker who isolated a secoiridoide named fagraldehyde from this *F. fragrans* has proposed a possible biogenetic pathway of fagraldehyde as shown in **Scheme 1** (Jonville *et al.*, 2008). Fagraldehyde should derive directly from the cleavage of iridotrial rather than from loganin, which is considered to be the common precursor. The C<sub>7</sub>-C<sub>8</sub> oxidative cleavage, in fact, appears in the cyclopentane ring for both fagraldehyde putative biosynthesis and the known secoiridoid biogenesis. Nevertheless, for most of the iridoids, glycosylation and oxidation of iridodial lead to loganoside formation, with cleavage following this formation. The putative biosynthesis process should involve direct C<sub>7</sub>-C<sub>8</sub> cleavage of iridotrial, allowing rotation about the C<sub>5</sub>-C<sub>9</sub> bond. Sequential cyclization, oxidation, and dehydration reactions should lead to the lactone and pyran rings of fagraldehyde.



**Scheme 1** Hypothesis for the conversion of iridodial into fagraldehyde.

### 1.2.3 *Fagraea fragrans* Roxb.

*Fagraea fragrans* Roxb. (Gentainaceae) is a large evergreen tree that grows up to 10–25 meter in open and swampy lowland forests and is distributed in an area that stretches from Birmania to Indomalaysia and found wild in the southern part of Thailand. The timber is a heavy, durable hardwood that is often used locally in construction and furniture. Its trunk is dark brown, with deeply fissured bark, looking somewhat like a bitter gourd. Its leaves are simple leaf, light green and oval in shape wide 2.5–3.5 cm., length 8–11 cm., Its yellowish flowers have a distinct fragrance and the fruits of the tree are simple fruit which is round and small about 6 mm, bitter tasting red berries, which are eaten by birds and fruit bats. The seed is very small. *F. fragrans* Roxb. are known as *F. cochinchinensis*, *Cyrtophyllum giganteum*, and *Cyrtophyllum peregrinum* (Struwe *et al.*, 2002). Other common names: Buabua (Fiji Islands), Urung (Philippines), Temasuk (Sabah), Tatrao, Trai (Cambodia), Tam Sao, Kan-Krao (Thailand), Tembesu (Indonesia), Anan, Ananma (Burma).



**Figure 1** *Fagraea fragrans* Roxb.

### 1.3 Objective

The objective of this work was to investigate the chemical constituents from the stem bark of *F. fragrans* Roxb..

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 Instruments and Chemicals

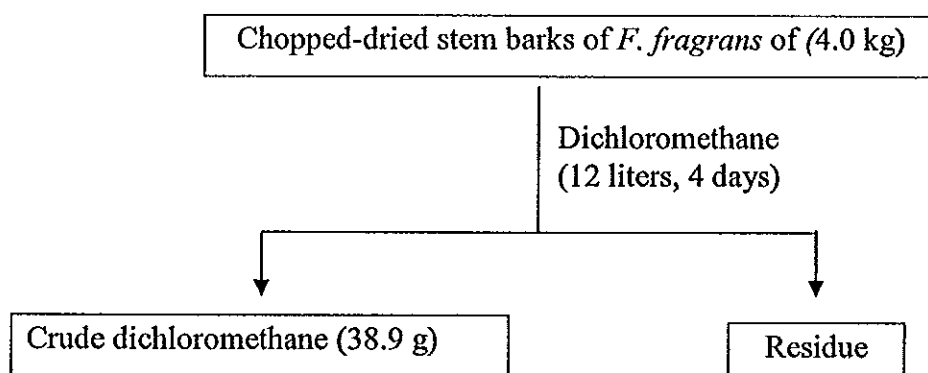
Column chromatography was performed by using silica gel 60 (230-400 Mesh ASTM, Merck) or silica gel 100 (70-230 Mesh ASTM, Merck) or Sephadex<sup>TM</sup> LH-20 (Amersham Biosciences, Sweden). For thin-layer chromatography (TLC), aluminum sheets of silica gel 60 F<sub>254</sub> (20×20 cm, layer thickness 0.2 mm, Merck) were used for analytical purposes and the compounds were visualized under ultraviolet light. Solvents for extraction and chromatography were distilled at their boiling ranges prior to use. Melting point was recorded in °C on a digital Electrothermal 9100 Melting Point Apparatus. Ultraviolet spectra were measured with a UV-160A spectrophotometer (SHIMADZU) and principle bands ( $\lambda_{\max}$ ) were recorded as wavelengths (nm) and log  $\epsilon$  in methanol solution. The optical rotation  $[\alpha]_D$  was measured in chloroform and methanol solution with Sodium D line (590 nm) on a JASCO P-1020 digital polarimeter. Infrared spectra (IR) were obtained on a Perkin-Elmer 783 FTS165 FT-IR spectrophotometer and were recorded in wave number ( $\text{cm}^{-1}$ ). <sup>1</sup>H and <sup>13</sup>C-Nuclear magnetic resonance spectra were recorded on a FT-NMR Bruker Ultra Shield<sup>TM</sup> 300 and 500 MHz spectrometer at Department of Chemistry, Faculty of Science, Prince of Songkla University. Spectra were recorded in deuteriochloroform as  $\delta$  value in ppm down field from TMS (internal standard  $\delta$  0.00) and coupling constant ( $J$ ) are expressed in hertz. EI and HREI mass spectra were measured on MAT 95 XL Mass spectrometer at Scientific Equipment Center, Prince of Songkla University.

## 2.2 Plant material

The barks of *F. fragrans* (Gentianaceae) were collected from Amphur Bangkan, Nakhon si thammarat Province in the Southern part of Thailand, on May, 2008. Identification was made by Mr. Ponlawat Pattarakulpisutti, Department of Biology, Faculty of Science, Prince of Songkla University. The specimen (K. kaikaew 01) has been deposited in the Herbarium of Department of Biology, Faculty of Science, Prince of Songkla University, Thailand. The different parts of the plant were air-dried at room temperature, with no direct sunlight.

## 2.3 Extraction and Isolation

Chopped-dried barks of *F. fragrans* (4.0 kg) were immersed in dichloromethane at room temperature (each extract time of 4 days). After removal of solvents, a dark brown gum of dichloromethane extract (38.9 g) was obtained. The process of extraction was shown in Scheme 2.

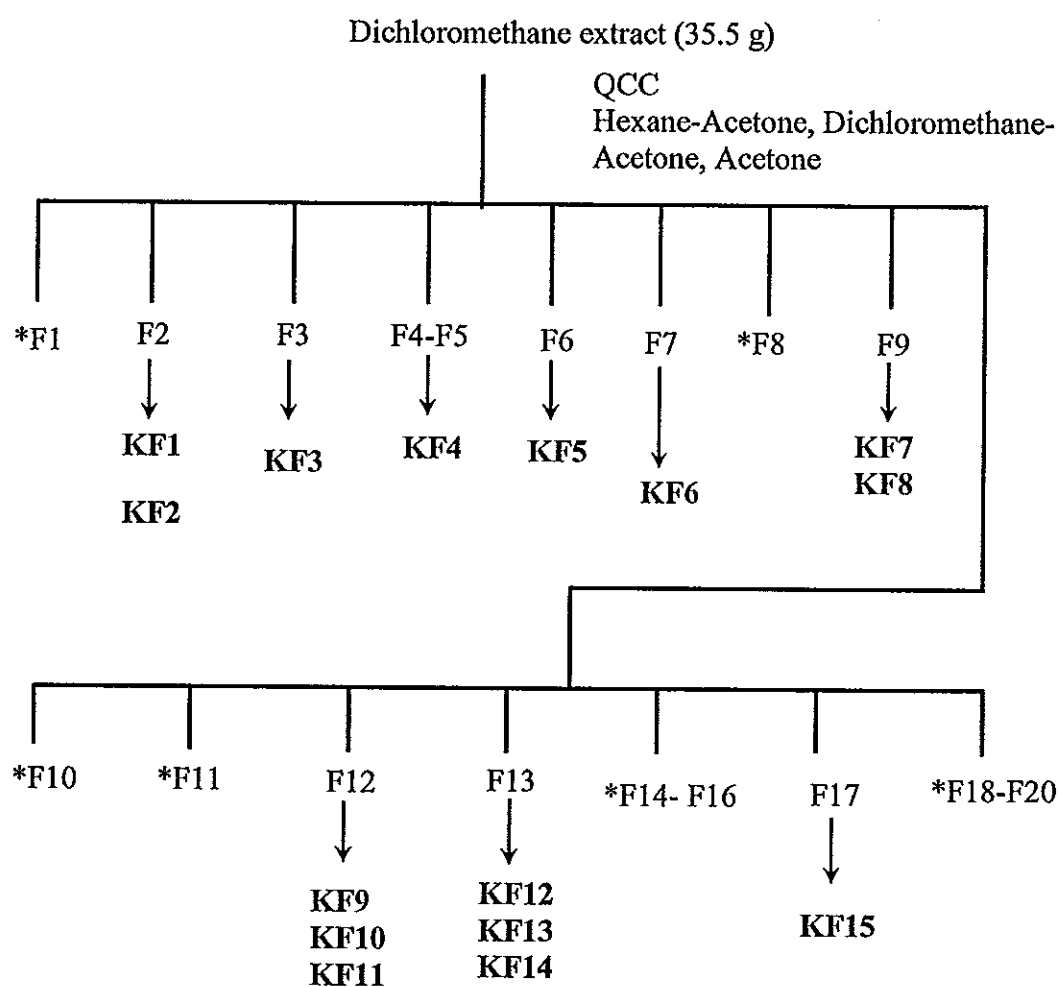


**Scheme 2** Extraction of the crude extracts from the stem barks of *F. fragrans*



### 2.3.1 Purification of dichloromethane extract

The dichloromethane extract (35.5g) was separated by quick column chromatography over silica gel 60H using gradient solvent systems of hexane-acetone, dichloromethane-acetone and acetone as eluents. On the basis of their TLC characteristics, the fractions which contained the same major components were combined to give fractions F1-F20 (Table 3). Further purification of subfractions gave fifteen pure compounds (Scheme 3).



\* No further investigation

**Scheme 3** Isolation of compounds **KF1-KF15** from dichloromethane extract

**Table 2** Physical characteristic and weight of the fractions from dichloromethane extract

<b>Fractions</b>	<b>Weight (g)</b>	<b>Physical characteristic</b>
F1	5.8726	brown viscous liquid
F2	0.8356	yellow liquid mixed with white solid
F3	0.5957	yellow viscous liquid
F4	0.5614	yellow viscous liquid
F5	0.1082	brown viscous liquid
F6	0.5528	brown viscous liquid
F7	2.1675	dark brown viscous liquid
F8	0.8969	dark brown viscous liquid
F9	2.2791	dark brown viscous liquid
F10	3.0144	dark brown solid
F11	1.6216	dark brown viscous liquid
F12	2.1363	dark brown viscous liquid
F13	1.6426	dark brown solid
F14	1.0928	dark brown solid
F15	1.2183	dark brown solid
F16	1.5774	dark brown solid
F17	1.0020	dark brown solid
F 18	1.6546	dark brown solid
F19	2.2713	dark brown solid
F20	2.6081	dark brown solid

Fraction F2 (0.8356 g) was further purified by column chromatography over silica gel and eluted with a gradient of hexane-acetone (95:5) to hexane-acetone (70:30) to give seven fractions (F2A- F2G). Subfraction F2A was further purified by crystallization from hexane-acetone to afford a white solid of **KF1** (80 mg) upon standing at room temperature. Subfraction F2G (0.0864 g) was rechromatographed on column chromatography and eluted with hexane-acetone (9:1) to give a colorless solid of **KF2** (5.5 mg).

Fraction F3 (0.5957 g) was further purified by column chromatography over silica gel and eluted with a gradient of hexane-acetone (9:1) to hexane-acetone (50:50) to give seven fractions (F3A-F3G). Subfraction F3B gave a white solid of **KF3** (2.5 mg).

Fraction F4 (0.5614 g) which contained one major component was further purified by crystallization from hexane-acetone to give **KF4** (90.0 mg) as a yellow solid of upon standing at room temperature.

Fraction F6 (0.5528 g) was further purified by column chromatography over silica gel and eluted with a mixed solvent of hexane-acetone (9:1) to give fractions F6A-F6G. Subfraction F6A (0.0329 g) was rechromatographed on column chromatography and eluted with a mixed solvent of hexane-acetone (9:1) to give a colorless solid of **KF5** (11.8 mg).

Fraction F7 (2.1675 g), was further purified by column chromatography over silica gel and eluted with a step gradient of hexane-dichloromethane-acetone (8:1:1), dichloromethane-acetone and acetone to give sixteen fractions (F7A-F7P). Subfraction F7F (0.1808 g) was rechromatographed on column chromatography and eluted with a mixed solvent of hexane-dichloromethane-acetone (7:2:1) to give five fraction (F7F1- F7F5). Subfraction F7F3 was a colorless solid of **KF6** (7.8 mg).

Fraction F9 (2.2791 g) was further purified by column chromatography over silica gel and eluted with a gradient of hexane-dichloromethane (1:1), dichloromethane and dichloromethane-methanol to give eight fractions (F9A-F9H). Subfraction F9A (0.350 g) was rechromatographed on column chromatography and eluted with a gradient of hexane-acetone (9:1) to hexane-acetone (3:7) to give a white solid of **KF7** (4.9 mg). Subfraction F9G (0.550 g) was rechromatographed on column

chromatography and eluted with a mixed solvent of dichloromethane-acetone (9:1) to give a yellow solid of **KF8** (8.8 mg).

Fraction F12 (2.1363 g) was subjected to column chromatography over silica gel and eluted with mixed solvent of hexane-dichloromethane-acetone (3:1.5:0.5) to give fractions F12A-F12L. Subfraction F12A (0.430 g) was rechromatographed on column chromatography and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1:1) to afford a yellow solid of **KF9** (12.6 mg). Subfraction F12F (120.2 mg) was further purified by column chromatography on silica gel using hexane:dichloromethane:acetone (7:2:1) as an eluent to give a colorless solid of **KF10** (16.2 mg) and brown gum of **KF11** (8.8 mg).

Fraction F13 (1.6426 g) was chromatographed on sephadex LH<sup>TM</sup> 20 and eluted with dichloromethane:methanol (9:1) to obtain fractions F13A-F13E. Subfraction F13C (0.4542 g) was further purified by column chromatography on silica gel 100 using hexane:dichloromethane:acetone (3:1:1) as an eluent to give a white solid of **KF12** (5.6 mg) and brown gum **KF13** (12.6 mg). Subfraction F13E was rechromatographed on column chromatography and eluted with a mixed solvent of hexane-dichloromethane-acetone (3:1.5:0.5) to give a brown gum of **KF14** (18.8 mg).

Fraction F17 (1.0025 g) was chromatographed on sephadex LH<sup>TM</sup> 20 and eluted with dichloromethane-methanol (1:1) solvent system. Subfractions that contained similar components were combined to give thirteen fractions (F17A-F17M). Subfraction F17G (0.324 g) was rechromatographed on column chromatography by sephadex LH<sup>TM</sup> 20 and eluted with dichloromethane-methanol (2:1) solvent system to give six fractions (F17G1-F17G6). Subfraction F17G4 (95 mg) was further purified by column chromatography on silica gel 100 using hexane-dichloromethane-acetone (2:2:1) as an eluent to give four fraction (F17G41-F17G44). Subfraction F17G43 (16.0 mg) was further purified on preparative TLC and eluted with hexane-dichloromethane-acetone (2:2:1) to give yellow viscous liquid of **KF15** (3.3 mg).

**KF1:**  $\alpha$ -boswellic acid, white solid, m.p. 328-330 °C;  $[\alpha]_D^{26} = +80.8^\circ$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 219 (3.47); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3415 (O-H stretching), 1686 (C=O stretching). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see Table 4.

**KF2:** 1-oxo-1*H*-isochromene-5-carbaldehyde, white solid, m.p. 155-156 °C; UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 225 (3.53), 243 (3.96), 265 (3.65), and 274 (3.62); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 1717, 1690 (C=O stretching). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see Table 5.

**KF3:**  $\beta$ -boswellic acid, white solid, m.p. 324-326 °C;  $[\alpha]_D^{26} = -60.8^\circ$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 210 (3.44); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3415 (O-H stretching), 1686 (C=O stretching). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see Table 6.

**KF4:** gentiogenol, yellow solid, m.p. 123-125 °C;  $[\alpha]_D^{26} = -1.2^\circ$  ( $c = 0.16$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 227 (3.87), 274 (3.66); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 1719 (C=C), 1638 (C=O stretching), 1113 (C-O). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see Table 7.

**KF5:** syringaldehyde, white solid, m.p. 100-102 °C; UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 230 (4.34), 308 (4.33); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3274 (O-H stretching) and 1670 (C=O stretching). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see Table 8.

**KF6:** 3-(4-hydroxy-3-methoxyphenyl)-acrylic acid octacosyl ester, white solid; UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 246 (3.10), 295 (3.14), 328 (3.3); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3418 (O-H stretching), 1705 (C=C), 1601, (C=O stretching) and 1515, 1159, 758 (aromatics). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see Table 9.

**KF7:** 3-(4-hydroxy-3-methoxyphenyl)-acrylic acid 30-oxo-triacontyl ester, white solid; IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3020 (O-H stretching), 1716(C=C) 1603, (C=O stretching) and 1515, 780 (aromatics). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 10**.

**KF8:** fagraldehyde, yellow solid;  $[\alpha]_{\text{D}}^{26} = -10^\circ$  ( $c = 0.01$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 368 (3.45) 241 (3.27) 205 (3.2); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 1664 and 1624  $\text{cm}^{-1}$  (C=O stretching), 1127 (C-O). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 11**.

**KF9:** angelone, white solid; m.p. 148-149; UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 221 (3.67), 250 (3.91), 268 (3.90); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 1670 and 1727  $\text{cm}^{-1}$  (C=O stretching), 1109, 1018 (C-O). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 12**.

**KF10:** eudesmin, colorless solid, m.p. 102-104  $^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{26} = +60^\circ$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 240 (4.28), 277 (4.12); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 1592, 1514, 811, 761 (aromatics), 1026 (C-O). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 13**.

**KF11:** monomethylpinoresinol,  $[\alpha]_{\text{D}}^{26} = +43.5^\circ$  ( $c = 0.1$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 232 (4.31), 278 (3.82); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3400 (O-H stretching), 1602, 1515, 784 (aromatics), 1026 (C-O). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 14**.

**KF12:** medioresinol, a white solid, m.p. 100-102 $^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{26} = +15^\circ$  ( $c = 0.05$ ,  $\text{CHCl}_3$ ). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 15**.

**KF13:** pinorisinol, brown gum,  $[\alpha]_D^{26} = +85.5^\circ$  ( $c = 0.2$ , MeOH). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 16**.

**KF14:** syringaresinol, brown gum  $[\alpha]_D^{26} = +50^\circ$  ( $c = 0.1$ ,  $\text{CHCl}_3$ ); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3396 (O-H stretching), 1514, 1456, 757 (aromatics). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 17**.

**KF15:** 3,6-Bis-(4-hydroxy-3,5-dimethoxy-phenyl)-tetrahydro-furo[3,4-*c*]furan-1-one, yellow viscous liquid,  $[\alpha]_D^{26} = +12^\circ$  ( $c = 0.1$ ,  $\text{CHCl}_3$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 222.91 (4.4), 272.63 (3.8); IR (Neat)  $\nu$  ( $\text{cm}^{-1}$ ): 3416 (C=O stretching), 1637 (O-H stretching), 1522, 1339, 834, 753 (aromatics). For  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm) and  $^{13}\text{C-NMR}$  75 MHz ( $\text{CDCl}_3$ )  $\delta$  (ppm): spectral data, see **Table 18**.

## CHAPTER 3

### RESULTS AND DISCUSSION

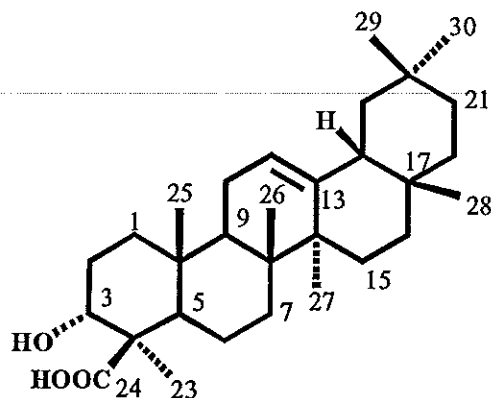
#### 3.1 Structural Determination

The stem bark of *F. fragrans* Roxb. was extracted with dichloromethane. Separation of dichloromethane extract by column chromatography produced fifteen compounds. They were identified as  $\alpha$ -boswellic acid (KF1), 1-oxo-1*H*-isochromene-5-carbaldehyde (KF2),  $\beta$ -boswellic acid (KF3), gentiogenol (KF4), syringaldehyde (KF5), 3-(4-hydroxy-3-methoxyphenyl)-acrylic acid octacosyl ester (KF6), 3-(4-hydroxy-3-methoxyphenyl)-acrylic acid 30-oxo-triacontyl ester (KF7), fagraldehyde (KF8), angelone (KF9), eudesmin (KF10), monomethylpinoresinol (KF11), medioresinol (KF12), pinorisinol (KF13), syringaresinol (KF14), 3,6-bis-(4-hydroxy-3,5-dimethoxyphenyl)-tetrahydro-furo[3,4-*c*]furan-1-one (KF15).

Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data:  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, DEPT 135°, DEPT 90°, HMQC, HMBC, COSY and NOESY. Mass spectra were determined for the new compounds: (KF15), and the physical data of the known compounds were also compared with the reported values.

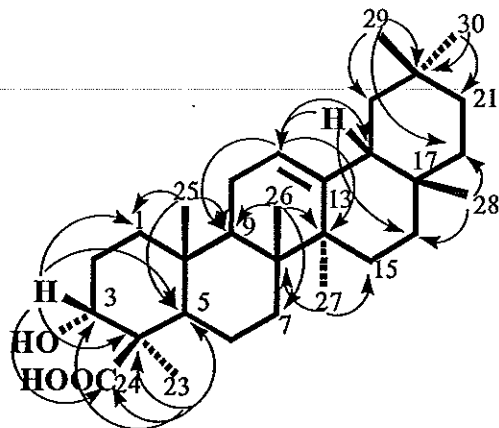


**KF1: 3 $\alpha$ -Hydroxy-olean-12-en-24-oic acid ( $\alpha$ -boswellic acid)**



**KF1** was obtained as a white solid, m.p. 328-330 °C. The IR spectrum showed absorption bands of a hydroxyl group at 3415  $\text{cm}^{-1}$  and a carbonyl group at 1686  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectral data showed characteristics of olean triterpenes as seven methyl singlet signals at  $\delta$  1.36 (H-23),  $\delta$  0.89 (H-25),  $\delta$  1.01 (H-26),  $\delta$  1.17 (H-27),  $\delta$  0.85 (H-28),  $\delta$  0.88 (H-29),  $\delta$  0.88 (H-30), an oxymethine proton at  $\delta$  4.09 (*t*,  $J = 2.4$  Hz, H-3) and olefinic proton at  $\delta$  5.20 (*t*,  $J = 3.6$  Hz, H-12). The  $^{13}\text{C}$  NMR spectrum data showed thirty carbons signals, which corresponded to seven methyl, ten methylenes, five methines, seven quaternary carbons and one carboxylic acid. The HMBC correlations of oxymethine proton H-3 ( $\delta$  4.09) to C-4 ( $\delta$  47.4), C-1 ( $\delta$  33.7), C-24 ( $\delta$  183.5) and C-23 ( $\delta$  24.2), and of methyl protons H-23 ( $\delta$  1.36) to C-4 ( $\delta$  47.4), C-3 ( $\delta$  70.8) and C-24 ( $\delta$  183.5) indicated that the oxymethine proton located at C-3. Consequently, the carboxyl group was placed at C-4. The position of the hydroxyl group at C-3 was determined through HMBC experiment, which the oxymethine proton signal at  $\delta$  4.09 (H-3) showed  $^2J_{\text{C-H}}$  correlations with C-2 ( $\delta$  26.2) and C-4 ( $\delta$  47.4) and  $^3J_{\text{C-H}}$  correlations with C-1 ( $\delta$  33.7), C-5 ( $\delta$  49.1) and C-23 ( $\delta$  24.2), C-24 ( $\delta$  183.5). The configuration of the hydroxyl group at C-3 was assigned to be  $\alpha$  on the basis of the absence of interactions between H-3 and H-5 on NOESY experiment and the absence of diaxial spin-spin coupling shown by the small  $J$  values which indicated an equatorial position for H-3 on the  $\beta$ -face and an axially orientation for the hydroxyl group on the  $\alpha$ -face. On comparison of their physical and spectral data

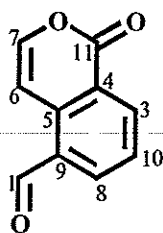
with those reported, the propose structure of **KF1** was 3 $\alpha$ -hydroxy-olean-12-en-24-oic acid (Culioli *et al.*, 2003).



Major HMBC of **KF1**

Table 3 NMR spectral data of KF1

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-type)	HMBC
1	1.44 ( <i>m</i> ), 1.29 ( <i>m</i> )	33.7 (CH <sub>2</sub> )	C-3, C-9, C-5
2	2.22 ( <i>m</i> ), 1.58 ( <i>m</i> )	26.2 (CH <sub>2</sub> )	C-4, C-5, C-10
3	4.09 ( <i>t</i> , <i>J</i> = 2.4 Hz)	70.8 (CH)	C-1, C-4, C-24
4	-	47.4 (C)	-
5	1.48 ( <i>m</i> )	49.1 (CH)	C-3, C-4, C-7
6	1.88 ( <i>m</i> ), 1.73 ( <i>m</i> )	19.7 (CH <sub>2</sub> )	C-8, C-10, C-4
7	1.52 ( <i>m</i> ), 1.40 ( <i>m</i> )	32.8 (CH <sub>2</sub> )	C-9, C-5
8	-	39.8 (C)	-
9	1.67 ( <i>m</i> )	46.8 (CH)	C-25, C-11, C-26
10	-	37.6 (C)	-
11	1.89 ( <i>m</i> )	23.5 (CH <sub>2</sub> )	C-13, C-9, C-8
12	5.20 ( <i>t</i> , <i>J</i> = 3.6 Hz)	121.8 (CH)	C-14, C-9, C-18
13	-	145.1 (C)	-
14	-	41.9 (C)	-
15	1.78 ( <i>m</i> ), 1.09 ( <i>m</i> )	26.0 (CH <sub>2</sub> )	C-14, C-17, C-27
16	2.03 ( <i>m</i> ), 0.81 ( <i>m</i> )	26.9 (CH <sub>2</sub> )	C-18, C-17, C-15
17	-	32.5 (C)	-
18	1.96 ( <i>m</i> )	47.3 (CH)	C-13, C-19, C-16
19	1.71 ( <i>m</i> ), 1.00 ( <i>m</i> )	46.8 (CH <sub>2</sub> )	C-30, C-18
20	-	31.1 (C)	-
21	1.40 ( <i>m</i> ), 1.14 ( <i>m</i> )	34.8 (CH <sub>2</sub> )	C-22, C-29
22	1.44 ( <i>m</i> ), 1.25 ( <i>m</i> )	37.1 (CH <sub>2</sub> )	C-21, C-28
23	1.36 ( <i>s</i> )	24.2 (CH <sub>3</sub> )	C-4, C-5, C-3
24	-	183.5 (C)	-
25	0.89 ( <i>s</i> )	13.1 (CH <sub>3</sub> )	C-1, C-9, C-5
26	1.01 ( <i>s</i> )	16.7 (CH <sub>3</sub> )	C-9, C-7, C-14
27	1.17 ( <i>s</i> )	25.9 (CH <sub>3</sub> )	C-8, C-14, C-15
28	0.85 ( <i>s</i> )	28.4 (CH <sub>3</sub> )	C-16, C-18, C-17, C-22
29	0.88 ( <i>s</i> )	33.4 (CH <sub>3</sub> )	C-20, C-21
30	0.88 ( <i>s</i> )	23.7 (CH <sub>3</sub> )	C-20, C-19

**KF2: 1-oxo-1*H*-Isochromene-5-carbaldehyde**

**KF2** was obtained as a white solid, m.p. 155-156 °C. The UV spectrum exhibited absorption maxima at 225, 243, 265, and 274 nm. The IR spectrum showed the absorption bands due to lactone at 1717  $\text{cm}^{-1}$  and aldehyde at 1690  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed the resonances of aromatic protons as AMB pattern at  $\delta$  8.57 (*dd*,  $J = 7.8, 1.2$  Hz, H-3),  $\delta$  7.72 (*t*,  $J = 7.8$  Hz, H-10) and  $\delta$  8.20 (*dd*,  $J = 7.8, 1.2$  Hz, H-8), indicating the presence of a 1,2,3-trisubstituted benzene ring. The spectrum further show a sharp singlet signal of aldehyde proton at  $\delta$  10.26 (H-1) and doublet signals of olefinic protons H-6 at  $\delta$  7.84 and H-7 at  $\delta$  7.41 ( $J = 6.0$  Hz). The  $^{13}\text{C}$  NMR spectrum indicated the presence of carbonyl carbon at  $\delta$  160.0 (C-11), aldehyde carbon at  $\delta$  191.2 (C-1), five methine carbons at  $\delta$  140.7, 103.2, 147.4, 135.4 and 128.2 (C-3, C-6, C-7, C-8, C-10), respectively and three quaternary carbons of a 1,2,3-trisubstituted benzene ring at  $\delta$  125.0, 135.4, 135.5 (C-4, C-5, C-9), respectively. The HMBC correlations of H-3 to C-11, C-8, C-5 and C-9 and aldehyde proton (H-1) to C-8, and C-5 confirmed the position of the lactone and aldehyde moieties. The correlations of H-8 to C-3, C-5 and C-10 and H-10 to C-4, C-9, C-8 confirmed the position of H-8 and H-10 at C-8 and C-10, respectively. Compound **KF2** therefore was identified as 1-oxo-1*H*-isochromene-5-carbaldehyde. It was a new compound.

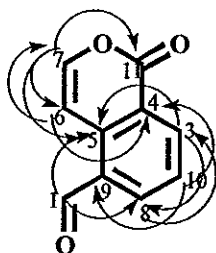
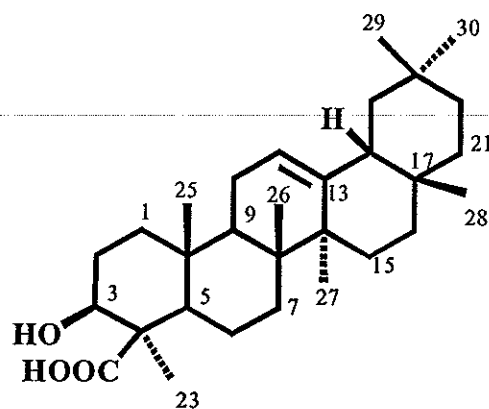
Major HMBC of **KF2**

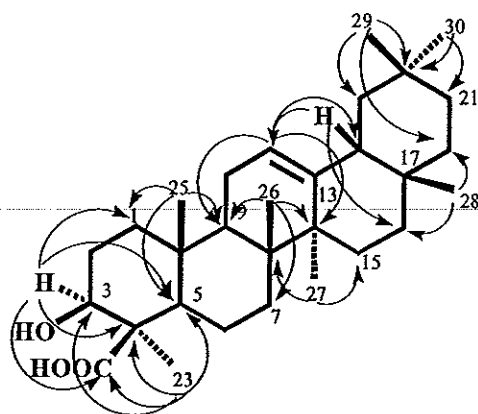
Table 4 NMR spectral data of KF2

Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1	10.26 ( <i>s</i> )	191.2 (CHO)	C-9, C-8, C-5
3	8.57 ( <i>dd</i> , $J = 7.8, 1.2$ Hz)	140.7 (CH)	C-8, C-11, C-5
4	-	125.0 (C)	-
5	-	135.5 (C)	-
6	7.84 ( <i>d</i> , $J = 6.0$ Hz)	103.2 (CH)	C-7, C-4
7	7.41 ( <i>d</i> , 6.0 Hz)	147.4 (CH)	C-6, C-5, C-11
8	8.20 ( <i>dd</i> , $J = 7.8, 1.2$ Hz)	135.4 (CH)	C-9, C-3, C1, C-9, C-5
9	-	135.5 (C)	-
10	7.72 ( <i>t</i> , $J = 7.8$ Hz)	128.2 (CH)	C-4, C-9
11	-	160.0 (C=O)	-

**KF3: 3 $\beta$ -Hydroxy-olean-12-en-24-oic acid ( $\beta$ -boswellic acid)**



**KF3** was obtained as a white solid m.p.254-255 °C. The IR spectrum showed absorption band of a hydroxyl group at 3415  $\text{cm}^{-1}$  and a carbonyl group at 1686  $\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed characteristic signals due to the olean triterpenes structure. The  $^1\text{H}$  NMR spectrum showed the resonances of seven methyl singlet signals at  $\delta$  1.49 (H-23),  $\delta$  1.09 (H-25),  $\delta$  1.04 (H-26),  $\delta$  1.14 (H-27),  $\delta$  0.83 (H-28),  $\delta$  0.87 (H-29),  $\delta$  0.87 (H-30), an oxymethine proton at  $\delta$  4.39 (*dd*,  $J = 4.2, 7.8$  Hz, H-3) and olefinic proton at  $\delta$  5.20 (*t*,  $J = 3.6$  Hz, H-12). The  $^1\text{H}$  NMR spectrum further showed the presence of the doublet of doublet splitting pattern together with coupling constant of H-3 with  $J_{ax-ax} = 7.8$  Hz and  $J_{ax-eq} = 4.2$  Hz indicated an axial ( $\alpha$ ) orientation of H-3. The  $^{13}\text{C}$  NMR spectrum data showed thirty carbons signals, which corresponded to seven methyl, ten methylenes, five methines seven quaternary carbons and one carboxylic acid. The HMBC correlations of oxymethine proton H-3 ( $\delta$  4.39) to C-4 ( $\delta$  55.3), C-1 ( $\delta$  33.4), C-24 ( $\delta$  175.6) and C-23 ( $\delta$  23.0) and of methyl proton H-23 ( $\delta$  1.49) to C-4 ( $\delta$  55.3), C-3 ( $\delta$  77.3) and C-24 ( $\delta$  175.6) indicated that the oxymethine proton located at C-3. Consequently, the carboxyl group was placed at C-4. On comparison of their physical and spectral data with those reported, the propose structure of **KF3** was 3 $\beta$ -hydroxy-olean-12-en-24-oic acid (Culioli *et al.*, 2003).



Major HMBC of KF3

Table 5 NMR spectral data of KF3

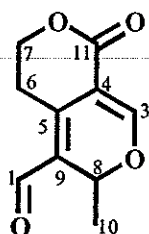
Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-type)	HMBC
1	1.40 ( <i>m</i> )	33.4 (CH <sub>2</sub> )	C-3, C-9, C-5
2	1.98 ( <i>m</i> )	23.7 (CH <sub>2</sub> )	C-4, C-5, C-10
3	4.39 ( <i>dd</i> , $J = 4.2, 7.8$ Hz)	77.3 (CH)	C-1, C-4, C-24
4	-	55.3 (C)	-
5	1.06 ( <i>m</i> )	52.7 (CH)	C-3, C-4, C-7
6	1.85 ( <i>m</i> ), 1.70 ( <i>m</i> )	19.2 (CH <sub>2</sub> )	C-8, C-10, C-4
7	1.52 ( <i>m</i> ), 1.38 ( <i>m</i> )	32.2 (CH <sub>2</sub> )	C-9, C-5
8	-	40.0 (C)	-
9	1.57 ( <i>m</i> )	45.1 (CH)	C-25, C-11, C-26
10	-	36.4 (C)	-
11	1.93 ( <i>m</i> )	23.7 (CH <sub>2</sub> )	C-13, C-9, C-8
12	5.20 ( <i>t</i> , $J = 3.6$ Hz)	121.5 (CH)	C-14, C-9, C-18
13	-	145.4 (C)	-
14	-	41.9 (C)	-
15	1.77 ( <i>m</i> ), 0.97 ( <i>m</i> )	26.0 (CH <sub>2</sub> )	C-14, C-17, C-27
16	1.99 ( <i>m</i> ), 0.80 ( <i>m</i> )	26.9 (CH <sub>2</sub> )	C-18, C-17, C-15
17	-	32.5 (C)	-

Table 5 (continued)

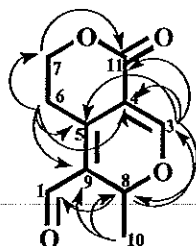
Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-type)	HMBC
18	1.96 ( <i>m</i> )	47.3 (CH)	C-13, C-19, C-16
19	1.70 ( <i>m</i> ), 1.01 ( <i>m</i> )	46.8 (CH <sub>2</sub> )	C-30, C-18
20	-	31.1 (C)	-
21	1.35 ( <i>m</i> ), 0.98 ( <i>m</i> )	35.6 (CH <sub>2</sub> )	C-22, C-29
22	1.44 ( <i>m</i> ), 1.22 ( <i>m</i> )	37.0 (CH <sub>2</sub> )	C-21, C-28
23	1.49 ( <i>s</i> )	23.0 (CH <sub>3</sub> )	C-4, C-5, C-3
24	-	175.6 (C)	-
25	1.09 ( <i>s</i> )	12.6 (CH <sub>3</sub> )	C-1, C-9, C-5
26	1.04 ( <i>s</i> )	17.0 (CH <sub>3</sub> )	C-9, C-7, C-14
27	1.14 ( <i>s</i> )	26.0 (CH <sub>3</sub> )	C-8, C-14, C-15
28	0.83 ( <i>s</i> )	28.4 (CH <sub>3</sub> )	C-16, C-18, C-17, C-22
29	0.87 ( <i>s</i> )	34.7 (CH <sub>3</sub> )	C-20, C-21
30	0.87 ( <i>s</i> )	23.8 (CH <sub>3</sub> )	C-20, C-19



**KF4: 3-Methyl-8-oxo-5,6-dihydro-3*H*,8*H*-pyrano[3,4-*c*]pyran-4-carbaldehyde (Gentiogenol)**



**KF4** was obtained as a yellow solid, m.p. 123-125 °C. The UV spectrum exhibited absorption maxima at 227 and 274 nm. The IR spectrum showed the absorption bands of carbonyl stretching at 1638  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed signal of aldehyde proton at  $\delta$  9.85 (H-1), two oxymethine protons at  $\delta$  7.91 (H-3) and  $\delta$  5.60 (H-8, *q*,  $J = 6.6$  Hz), methyl protons at  $\delta$  1.37 (H-10, *d*,  $J = 6.6$  Hz) oxymethylene protons at  $\delta$  4.38 (H-7) and methylene protons at  $\delta$  3.06 (H $_{\alpha}$ -6, H $_{\beta}$ -6). The  $^{13}\text{C}$  NMR spectrum indicated the presence of two methylene carbons at  $\delta$  22.8 (C-6),  $\delta$  65.2, (C-7) and two methine carbons at  $\delta$  163.2 (C-3),  $\delta$  73.3 (C-8), two carbonyl carbons resonance at  $\delta$  185.6 (C-1) and  $\delta$  163.3 (C-11), three quaternary carbons at  $\delta$  104.1, 142.6, 120.4 (C-4, C-5, C-9), and a methyl carbon resonance at  $\delta$  19.9 (C-10). The HMBC correlations of the methyl protons to C-8 ( $\delta$  73.3), C-9, ( $\delta$  120.4) and aldehyde proton (H-1) to C-5, C-8, C-9, indicated that the methyl group was nearby the aldehyde moiety rather than a lactone ring. The HMBC correlations of H-8 to C-9, C-3, C-5, and C-10 confirmed the position of H-8 and methyl substitution at C-8. **KF4** therefore was identified as 3-methyl-8-oxo-5,6-dihydro-3*H*,8*H*-pyrano[3,4-*c*]pyran-4-carbaldehyde after comparison of the data with those reported previously (Van der Sluis *et al.*, 1983).

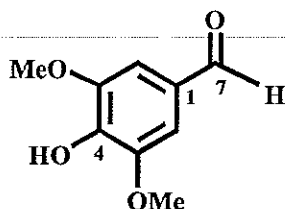


Major HMBC of KF4

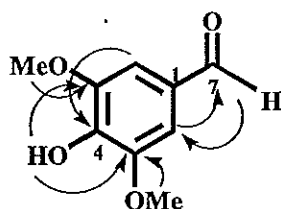
Table 6 NMR spectral data of KF4

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
1	9.85 ( <i>s</i> )	185.6 (CHO)	C-8, C-9
3	7.91 ( <i>s</i> )	163.2 (CH)	C-4, C-5, C-8, C-11
4	-	104.1 (C)	-
5	-	142.6 (C)	-
6	3.06 ( <i>m</i> )	22.8 (CH <sub>2</sub> )	C-4, C-5, C-9, C-7
7	4.38 ( <i>m</i> )	65.2 (CH <sub>2</sub> )	C-5, C-6, C-11
8	5.60 ( <i>q</i> , $J = 6.6$ Hz)	73.3 (CH)	C-3, C-5, C-9
9	-	120.4 (C)	-
10	1.37 ( <i>d</i> , $J = 6.6$ Hz)	19.9 (CH <sub>3</sub> )	C-8, C-9
11	-	163.3 (C)	-

**KF5: 4-Hydroxy-3,5-dimethoxybenzaldehyde**  
(Syringaldehyde)



**KF5** was obtained as a white solid, m.p.100-102 °C. The UV spectrum showed absorption bands at  $\lambda_{\max}$  230 and 308 nm, indicating the presence of a benzene chromophore. The IR spectrum exhibited absorption bands at 3367  $\text{cm}^{-1}$  and 1684  $\text{cm}^{-1}$  for hydroxyl and carbonyl groups, respectively. The  $^1\text{H}$  NMR spectrum showed the resonances of a 1,3,4,5-tetrasubstituted benzene ring at  $\delta$  7.15 (2H, s, H-2/H-6). The substituent groups of benzene rings were assigned for two methoxy groups, hydroxyl group and formyl group which resonated at  $\delta$  3.97,  $\delta$  6.03 and  $\delta$  9.86, respectively. The  $^{13}\text{C}$  NMR spectrum showed two methoxy carbon at  $\delta$  56.5 (3-OCH<sub>3</sub>/5-OCH<sub>3</sub>) two methine carbons at  $\delta$  106.7 (C-2/C-6) four quaternary carbons at  $\delta$  128.5, 140.9, 147.4 (C-1, C-4, C-3/5) respectively and one aldehyde carbon at  $\delta$  190.6 (C-7). The HMBC correlation of the formyl group to C-1, C-6, and H-2/H-6 to C-1, C-4, C-3 and C-5 confirmed the position of formyl group at C-1 and the correlation of hydroxyl proton to C-3 and C-5 confirmed the position of hydroxyl group at C-4. The structure of **KF5** was assigned as 4-hydroxy-3,5-dimethoxybenzaldehyde (Okuyama *et al.*, 1995).

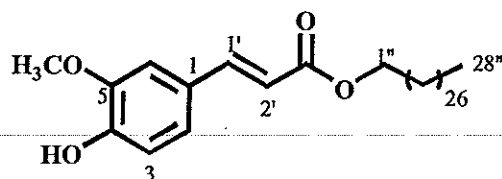


Major HMBC of **KF5**

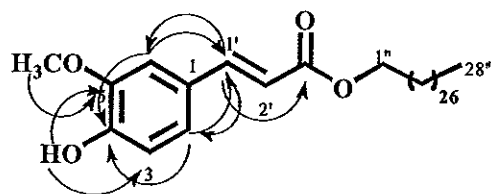
Table 7 NMR spectral data of KF5 (CDCl<sub>3</sub>)

Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1	-	128.5 (C)	-
2/6	7.15 ( <i>s</i> )	106.7 (CH)	C-3, C-4, C-7
3/5	-	147.4 (C)	-
4-OH	-	140.9 (C)	-
CHO	9.86 ( <i>s</i> )	190.6 (CHO)	C-1, C-6
OH	6.03 ( <i>brs</i> )	-	C-3, C-5
3/5-OCH <sub>3</sub>	3.97 ( <i>s</i> )	56.5 (OCH <sub>3</sub> )	C-3, C-5

**KF6: 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid octacosyl ester**



**KF6** is a white solid, the UV spectrum exhibited absorption maxima at 246, 295, and 328 nm, suggesting the presence of conjugation in the molecule. The IR spectrum showed the absorption bands of aromatic ring at 1601, 1515  $\text{cm}^{-1}$ , hydroxyl at 3418  $\text{cm}^{-1}$  and conjugated ester at 1705  $\text{cm}^{-1}$ . The molecular ion at  $m/z$  586.9 corresponding to a molecular formula of  $\text{C}_{38}\text{H}_{66}\text{O}_4$ . The  $^1\text{H}$  NMR spectrum showed the resonances of aromatic protons as an ABM pattern at  $\delta$  7.07 (H-2, *dd*,  $J = 8.1, 1.8$  Hz), 6.92 (H-3 *d*,  $J = 8.1$  Hz), and 7.05 (H-6, *d*,  $J = 1.8$  Hz) indicating the presence of 1,2,4-trisubstituted benzene rings. The substituent groups of benzene rings were assigned for the methoxy group and hydroxy group which resonated at  $\delta$  3.93 and 5.83. The HMBC correlations of 5-OCH<sub>3</sub> ( $\delta$  3.93) and H-3 ( $\delta$  6.92) to C-5 (146.8), 4-OH ( $\delta$  5.83) and H-6 ( $\delta$  7.05) to C-4 ( $\delta$  147.9), and C-5 confirmed the positions of methoxy group and hydroxy group at C-5 and C-4, respectively. The spectrum further showed the resonances of *trans* double bond by two doublet signals at  $\delta$  7.62 (H-1') and  $\delta$  6.30 (H-2') with a coupling constant of 15.9 Hz, the triplet signals of methylene protons at  $\delta$  4.19 (H-1'', *t*,  $J = 6.9$  Hz), broad multiplet signals at  $\delta$  1.70 (H-2'') triplet signals of methyl proton at  $\delta$  0.88 (*t*,  $J = 6.3$  Hz). The  $^{13}\text{C}$  NMR spectral data showed the signals at  $\delta$  167.4 (C-3') due to the carbonyl group of an ester function and  $\delta$  144.6 (C-1') and  $\delta$  115.7 (C-2') due to a side chain C-C double bond. The mass spectroscopy showed the fragment ion at  $m/z$  393.0 which was in agreement with 28 methylene groups. Therefore, **KF6** should be a long chain ester of ferulic acid. **KF6** was assigned as 3-(4-hydroxy-3-methoxyphenyl)-acrylic acid octacosyl ester (Pranithanchai *et al.*, 2009).

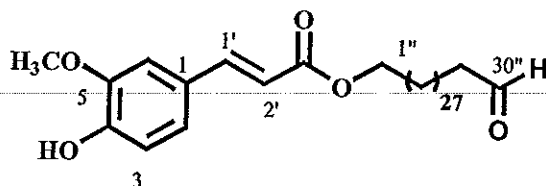


## Major HMBC of KF6

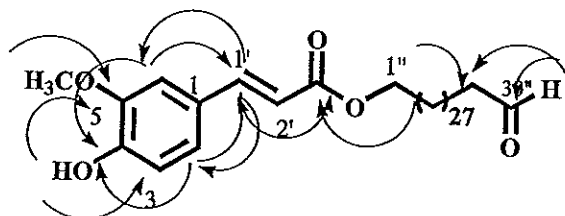
Table 8 NMR spectral data of KF6

Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1	-	127.4 (C)	-
2	7.07 ( <i>dd</i> , $J = 8.1, 1.8$ Hz)	123.0 (CH)	C-6, C-1', C-4
3	6.92 ( <i>d</i> , $J = 8.1$ Hz)	114.7 (CH)	C-1, C-4, C-5
4	-	147.9 (C)	-
5	-	146.8 (C)	-
6	7.05 ( <i>d</i> , $J = 1.8$ Hz)	109.3 (CH)	C-2, C-4, C-1'
1'	7.62 ( <i>d</i> , $J = 15.9$ Hz)	144.6 (CH)	C-1, C-2, C-6, C-3'
2'	6.30 ( <i>d</i> , $J = 15.9$ Hz)	115.7 (CH)	C-1', C-3', C-1
3'	-	167.4 (C=O)	-
1''	4.19 ( <i>t</i> , $J = 6.9$ Hz)	64.6 (CH <sub>2</sub> )	C-3', C-2''
2''	1.7 ( <i>m</i> )	26.0 (CH <sub>2</sub> )	C-1''
28''	0.88 ( <i>t</i> , $J = 6.3$ Hz)	14.1 (CH <sub>3</sub> )	-
5-OCH <sub>3</sub>	3.93 ( <i>s</i> )	55.9 (OCH <sub>3</sub> )	C-5
4-OH	5.83 ( <i>s</i> )	-	C-5, C-3

**KF7: 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid 30-oxo-triacontyl ester**



KF7 was obtained as white solid. The UV spectrum exhibited absorption maxima at 234, 297, and 325 nm, again suggesting the presence of conjugation in the molecule. The IR spectrum showed the absorption bands of aromatic ring at  $1635\text{ cm}^{-1}$ , hydroxyl at  $3375\text{ cm}^{-1}$ , conjugated ester at  $1695\text{ cm}^{-1}$  and aldehyde group at  $1603\text{ cm}^{-1}$ . The molecular ion at  $m/z$  628.9 corresponding to a molecular formula of  $\text{C}_{40}\text{H}_{68}\text{O}_5$ . The  $^1\text{H}$  NMR spectrum showed the resonances of aromatic protons as an ABM pattern at  $\delta$  7.09 (H-2, *dd*,  $J = 8.1, 1.8\text{ Hz}$ ),  $\delta$  6.92 (H-3, *d*,  $J = 8.1\text{ Hz}$ ),  $\delta$  7.05, (H-6, *d*,  $J = 1.8\text{ Hz}$ ), indicating the presence of 1,2,4-trisubstituted benzene rings. Its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were similar pattern to those of KF6 except for the replacement of the triplet signal of methyl protons ( $\delta$  0.88) by aldehyde proton resonances at  $\delta$  9.78 and the absence of methyl carbon resonances at  $\delta$  26.0. The  $^1\text{H}$  NMR spectrum showed the resonances of triplet signals of methylene proton at  $\delta$  2.43 (*t*,  $J = 7.2\text{ Hz}$ ) and a broad signal at  $\delta$  1.13. The mass spectroscopy showed the fragment ion at  $m/z$  434.0 which was in agreement with 29 methylene groups. Therefore, KF7 should be a long chain ester as 3-(4-Hydroxy-3-methoxyphenyl)-acrylic acid 30-oxo-triacontyl ester (Pranithanchai *et al.*, 2009).



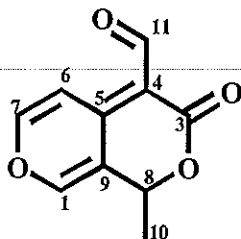
Major HMBC of KF7

Table 9 NMR spectral data of KF7

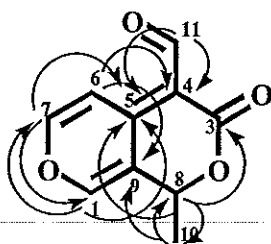
Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1	-	127.4 (C)	-
2	7.09 ( <i>dd</i> , $J = 8.1, 1.8$ Hz)	123.3 (CH)	C-6, C-1', C-4,
3	6.92 ( <i>d</i> , $J = 8.1$ Hz)	114.9 (CH)	C-1, C-4, C-5
4	-	148.1 (C)	-
5	-	146.9 (C)	-
6	7.05 ( <i>d</i> , $J = 1.8$ Hz)	109.5 (CH)	C-2, C-4, C-1'
1'	7.62 ( <i>d</i> , $J = 16.8$ Hz)	145.0 (CH)	C-1, C-2, C-6, C-3'
2'	6.30 ( <i>d</i> , $J = 16.8$ Hz)	115.8 (CH)	C-1', C-3', C-1
3'	-	167.6 (C)	-
1''	4.19 ( <i>t</i> , $J = 6.6$ Hz)	60.8 (CH <sub>2</sub> )	C-3', C-2''
29''	2.43 ( <i>t</i> , 7.2 Hz)	42.8 (CH <sub>2</sub> )	-
5-OCH <sub>3</sub>	3.94 ( <i>s</i> )	56.1 (C)	C-5
CHO	9.78 ( <i>s</i> )	203.2 (C)	C-29''



**KF8: 1-Methyl-3-oxo-1*H*,3*H*-pyrano[3,4-*c*]pyran-4-carbaldehyde  
(Fagraldehyde)**



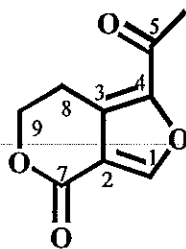
**KF8** was obtained as a yellow solid, m.p. 130-132 °C,  $[\alpha]_{\text{D}}^{26} = -10^{\circ}$  ( $c$  0.01,  $\text{CHCl}_3$ ). The UV spectrum exhibited absorption maxima at 368, 241, 205 nm indicated a highly conjugated chromophore. The IR spectrum showed the absorption bands of C=O stretching at 1664 and 1624  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed signal of aldehyded proton at  $\delta$  10.21 (H-11), three olefinic protons at  $\delta$  8.36 (H-6,  $d$ ,  $J = 5.7$  Hz), 7.63, (H-7,  $d$ ,  $J = 5.7$  Hz), 7.61, (H-1,  $d$ ,  $J = 1.5$  Hz), an oxymethine proton at  $\delta$  5.26, (H-8,  $qd$ ,  $J = 6.6, 1.5$  Hz), a methyl protons at  $\delta$  1.67 (H-10,  $d$ ,  $J = 6.6$  Hz). The  $^{13}\text{C}$  NMR spectrum showed signals of one methyl carbons at  $\delta$  20.4 (C-10), four methine carbons at  $\delta$  146.8 (C-1),  $\delta$  109.1 (C-6),  $\delta$  153.2 (C-7),  $\delta$  70.4 (C-8), and four quaternary carbons at  $\delta$  165.7 (C-3),  $\delta$  104.2 (C-4),  $\delta$  144.9 (C-5),  $\delta$  121.1 (C-9). The HMBC correlations of H-11 to C-3, C-4 and C-5 confirmed the position of the lactone and aldehyde moieties. The correlations of H-8 to C-9, C-3, C-5, and C-10 and methyl group to C-8 confirmed the position of H-8 and methyl substitution at C-8. **KF8** was then proposed as 1-methyl-3-oxo-1*H*,3*H*-pyrano[3,4-*c*]pyran-4-carbaldehyde which known as fagraldehyde (Jonville *et al.*, 2008). In the literature that fagraldehyde was reported to be a racemic with optical rotation value of  $[\alpha]_{\text{D}}^{25} = 0^{\circ}$  while **KF8** showed the optical rotation value of  $[\alpha]_{\text{D}}^{26} = -10^{\circ}$  ( $c$  0.01,  $\text{CHCl}_3$ ). It was indicated that **KF8** that we obtained was a mixture which the major component was levo-isomer.



## Major HMBC of KF8

Table 10 NMR spectral data of KF8

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
1	7.61 ( <i>d</i> , $J = 1.5$ Hz)	146.8 (CH)	C-5, C-7, C-8, C-9
3	-	165.7 (C)	-
4	-	104.2 (C)	-
5	-	144.9 (C)	-
6	8.36 ( <i>d</i> , $J = 5.7$ Hz)	109.1 (CH)	C-4, C-5, C-7, C-9
7	7.63 ( <i>d</i> , $J = 5.7$ Hz)	153.2 (CH)	C-5, C-6, C-1
8	5.26 ( <i>qd</i> , $J = 6.6, 1.5$ Hz)	70.4 (CH)	C-9, C-3, C-5, C-10
9	-	121.1 (C)	-
10	1.67 ( <i>d</i> , $J = 6.6$ Hz)	20.4 (CH <sub>3</sub> )	C-8, C-9
11	10.21 ( <i>s</i> )	190.6 (OCH)	C-4, C-3, C-5, C-11

**KF9: 1-Acetyl-6,7-dihydro-furo[3,4-*c*]pyran-4-one (Angelone)**

**KF9** was obtained as a white solid, m.p. 148-149. The UV spectrum exhibited absorption maxima at 221, 250, and 268 nm. The IR spectrum showed the absorption bands of carbonyl stretching at 1670 and 1727  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed signals of two sets of methylene proton at  $\delta$  3.21 (H-8, *t*,  $J = 6.0$  Hz) and  $\delta$  4.52 (H-9, *t*,  $J = 6.0$  Hz). An olefinic proton of furan ring was shown at  $\delta$  8.14 (H-1, *s*). The present of an acyl group was indicated from the proton resonance of methyl protons at  $\delta$  2.52 (*s*). The  $^{13}\text{C}$  NMR spectrum showed two carbonyl carbons (C-5, C-7,  $\delta$  188.3, 160.8), three quaternary carbons (C-2, C-3, C-4,  $\delta$  117.6, 128.3, 147.4), one methine carbon (C-1,  $\delta$  148.2), two methylene carbons (C-8, C-9,  $\delta$  21.3, 68.5) and one methyl carbon (C-6,  $\delta$  26.8). The HMBC correlations of H-1 to C-7, C-3, C-4, of H-8 to C-3, C-7 and of H-9 to C-8, C-3, C-4, confirmed the position of protons at C-1, C-8 and C-9, respectively. **KF9** was then assigned to be 1-acetyl-6,7-dihydro-furo[3,4-*c*]pyran-4-one which was known as angelone (Mulholland *et al.*, 2006).

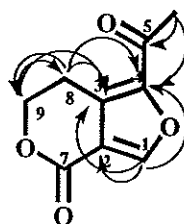
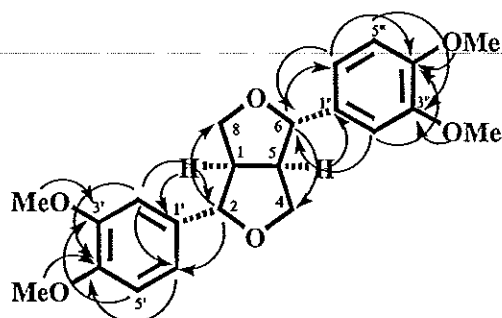
Major HMBC of **KF9**

Table 11 NMR spectral data of KF9

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
1	8.14 ( <i>s</i> )	148.2 (CH)	C-2, C-3, C-4
2	-	117.6 (C)	-
3	-	128.3 (C)	-
4	-	147.4 (C)	-
5	-	188.3 (C=O)	-
6	2.52 ( <i>s</i> )	26.8 (CH <sub>3</sub> )	C-5, C-4
7	-	160.8 (C=O)	-
8	3.21 ( <i>t</i> , $J = 6.0$ Hz)	21.3 (CH <sub>2</sub> )	C-9, C-3, C-4
9	4.52 ( <i>t</i> , $J = 6.0$ Hz)	68.5 (CH <sub>2</sub> )	C-8, C-3, C-7

149.2). This compound was identified as 1,4-bis-(3,4-dimethoxyphenyl)-tetrahydrofuro[3,4-*c*]furan (Latip *et al.*, 1999).

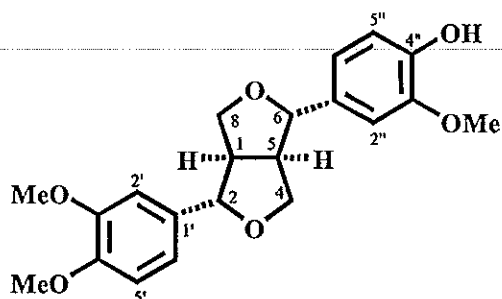


Major HMBC of KF10

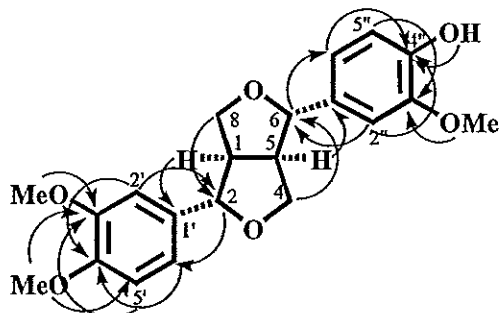
Table 12 NMR spectral data of KF10

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
1/5	3.12 ( <i>m</i> )	54.2 (CH)	C-2, C-5, C-6, C-8, C-1''
2/6	4.76 ( <i>d</i> , $J = 4.2$ Hz)	85.8 (CH)	C-1, C-8, C-1'', C-2''
4 <sub>a</sub> /8 <sub>a</sub>	3.90 ( <i>m</i> )	71.2 (CH <sub>2</sub> )	C-1, C-6,
4 <sub>e</sub> /8 <sub>e</sub>	4.26 ( <i>dd</i> , $J = 6.9, 9.0$ Hz)	71.2 (CH <sub>2</sub> )	C-1, C-2, C-5, C-6
1'/1''	-	133.6 (C)	-
2'/2''	6.91 ( <i>d</i> , $J = 1.5$ Hz)	109.3 (CH)	C-6, C-1', C-6', C-4'
3'/3''	-	148.6 (C)	-
4'/4''	-	149.2 (C)	-
5'/5''	6.83 ( <i>d</i> , $J = 8.1$ Hz)	111.1 (CH)	C-1', C-6', C3', C-4', C-6
6'/6''	6.87 ( <i>dd</i> , $J = 8.1, 1.5$ Hz)	118.3 (CH)	C-6, C-1', C-2', C-4', C-5'
3'/3''-OCH <sub>3</sub>	3.90 ( <i>s</i> )	55.9 (2×OCH <sub>3</sub> )	C-3'/3''
4'/4''-OCH <sub>3</sub>	3.88 ( <i>s</i> )	55.9 (2×OCH <sub>3</sub> )	C-4'/4''

**KF11: 5-[4-(3,4-Dimethoxyphenyl)-tetrahydro-furo[3,4-c]furan-1-yl]-2-methoxyphenol (Monomethylpinoresinol)**



KF11 was obtained as brown gum. The  $^1\text{H}$  NMR spectrum showed the resonances of aromatic protons H-2'/H-2'' ( $\delta$  6.88/6.85, *d*,  $J = 1.5$  Hz), H-5'/H-5'' ( $\delta$  6.86/6.83, *d*,  $J = 8.1$  Hz), H-6'/H-6'' ( $\delta$  6.92/6.91, *dd*,  $J = 8.1, 1.5$  Hz), methine protons H-1/H-5 ( $\delta$  3.12, *m*), benzylic oxymethine protons H-2/H-6 ( $\delta$  4.76, *m*), oxygenated methylene protons H<sub>e</sub>-4/H<sub>e</sub>-8 ( $\delta$  4.26, *dd*,  $J = 2.1, 9.0$  Hz) and H<sub>a</sub>-4/H<sub>a</sub>-8 ( $\delta$  3.90, *m*), and methoxy protons 3'/4'-OCH<sub>3</sub>, 3''-OCH<sub>3</sub> ( $\delta$  3.91, 3.89) as for KF10 with the replacement of a singlet signal of methoxy protons  $\delta$  3.88, (4''-OCH<sub>3</sub>) by hydroxyl proton resonances at  $\delta$  5.70 (4''-OH). The HMBC correlations of hydroxy protons ( $\delta$  5.70) to C-4'' ( $\delta$  145.4), C-3'' ( $\delta$  149.4), C-5'' ( $\delta$  114.8), and of H-2'' ( $\delta$  6.85) to C-4'' ( $\delta$  145.4), C-3'' ( $\delta$  149.4) indicated that the hydroxy group located at C-4''. Consequently, the methoxyl group was placed at C-3''. This compound was known as 5-[4-(3,4-dimethoxyphenyl)-tetrahydro-furo[3,4-c]furan-1-yl]-2-methoxyphenol (Miyachi *et al.*, 1997).

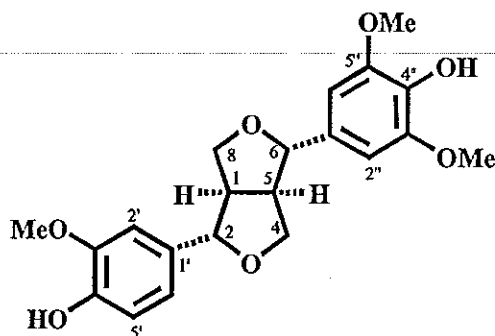


Major HMBC of KF11

Table 13 NMR spectral data of KF11

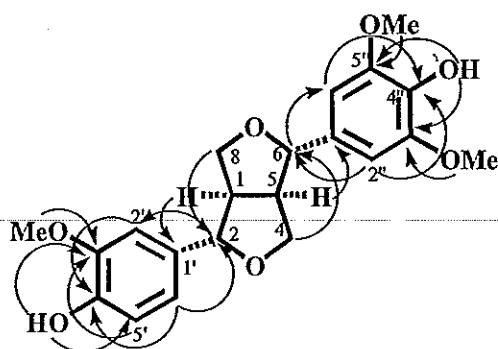
Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1/5	3.12 ( <i>m</i> )	54.3 (CH)	C-2, C-5, C-6, C-8, C-1''
2/6	4.76 ( <i>m</i> )	86.0/85.9 (CH)	C-1, C-8, C-1'', C-2''
4 <sub>a</sub> /8 <sub>a</sub>	3.90 ( <i>m</i> )	71.9/71.8 (CH <sub>2</sub> )	C-1, C-6,
4 <sub>e</sub> /8 <sub>e</sub>	4.26 ( <i>dd</i> , <i>J</i> = 2.1, 9.0 Hz)	71.9/71.8 (CH <sub>2</sub> )	C-1, C-2, C-5, C-6
1'/1''	-	133.7/133.1 (CH)	-
2'	6.88 ( <i>d</i> , <i>J</i> = 1.5 Hz)	108.8 (CH)	C-6, C-1', C-6', C-4'
3'	-	146.9 (C)	-
4'	-	148.8 (C)	-
5'	6.86 ( <i>d</i> , <i>J</i> = 8.1 Hz)	111.2 (CH)	C-1', C-6', C-3', C-4', C-6
6'	6.92 ( <i>dd</i> , <i>J</i> = 8.1, 1.5 Hz)	118.43 (CH)	C-6, C-1', C-2', C-4', C-5'
2''	6.85 ( <i>d</i> , <i>J</i> = 1.5 Hz)	109.4 (CH)	C-2, C-1'', C-6'', C-4''
3''	-	149.4 (C)	-
4''	-	145.4 (C)	-
5''	6.83 ( <i>d</i> , <i>J</i> = 8.1 Hz)	114.8 (CH)	C-1'', C-6'', C-3'', C-4'', C-2
6''	6.91 ( <i>dd</i> , <i>J</i> = 8.1, 1.5 Hz)	119.1 (CH)	C-2, C-1'', C-2'', C-4'', C-5''
3'-OCH <sub>3</sub>	3.91 ( <i>s</i> )	56.1 (CH <sub>3</sub> )	C-3'/ C-3''
4'-OH	-	-	C-4'/C-4'', C-5'/C-5''
4'-OCH <sub>3</sub>	3.89 ( <i>s</i> )	56.1 (CH <sub>3</sub> )	C-4'
5'-OCH <sub>3</sub>	3.91 ( <i>s</i> )	56.1 (CH <sub>3</sub> )	C-5'
4''-OH	5.70 ( <i>s</i> )	-	C-5'', C-3''
3''-OCH <sub>3</sub>	3.89 ( <i>s</i> )	54.3 (C)	C-3''

**KF12: 2,6-Dimethoxy-4-[tetrahydro-4-(4-hydroxy-3-methoxyphenyl)-1*H*,3*H*-furo[3,4-*c*]furan-1-yl]phenol (Medioresinol)**



KF12 was obtained as a white solid. The  $^1\text{H}$  NMR spectrum showed the resonances of aromatic protons H-2''/H-6'' ( $\delta$  6.59, *s*), H-2' ( $\delta$  6.90, *d*,  $J = 1.5$  Hz), H-5' ( $\delta$  6.92, *d*,  $J = 8.1$  Hz), H-6' ( $\delta$  6.84, *dd*,  $J = 8.1, 1.5$  Hz), methine protons H-1/H-5 ( $\delta$  5.41/5.44), benzylic oxymethine protons H-2/H-6 ( $\delta$  4.72/4.75), oxygenated methylene protons H<sub>e</sub>-4/H<sub>e</sub>-8 ( $\delta$  4.27) and H<sub>a</sub>-4/H<sub>a</sub>-8 ( $\delta$  3.87). A 1,2,4-trisubstituted benzene rings was indicated from the resonances at  $\delta$  6.92 (H-5', *d*,  $J = 8.1$  Hz), 6.84, (H-6', *dd*,  $J = 8.1, 1.5$  Hz) and 6.90, (H-2', *d*,  $J = 1.5$  Hz) while a 1,2,3,5-tetrasubstituted benzene rings was suggested from the resonances at  $\delta$  6.59. Two methoxyl groups resonated at  $\delta$  3.91 were assigned for C-3'' and C-5'' where as two hydroxyl group and a methoxyl group resonated at  $\delta$  5.50,  $\delta$  5.60 and  $\delta$  3.92 were assigned for C-4'', C-4' and C-3', respectively. The HMBC correlations of 3'-OCH<sub>3</sub> ( $\delta$  3.92) and H-5' ( $\delta$  6.92) to C-3' ( $\delta$  147.1) and correlations of 4'-OH ( $\delta$  5.60), H-2' ( $\delta$  6.90) and H-6' ( $\delta$  6.84) to C-4' ( $\delta$  145.4), confirmed the position of 3'-OCH<sub>3</sub> and 4'-OH at C-3' and C-4', respectively. The correlations of 4''-OH ( $\delta$  5.50) to C-4'' ( $\delta$  134.0), C-3'' ( $\delta$  147.1), C-5'' ( $\delta$  147.1) and of H-2''/H-6'' ( $\delta$  6.59) to C-4'' ( $\delta$  134.0), indicated that the hydroxyl group located at C-4''. Consequently, two methoxyl groups was placed at C-3'', C-5'', respectively. This compound was 2,6-dimethoxy-4-[tetrahydro-4-(4-hydroxy-3-methoxyphenyl)-1*H*,3*H*-furo[3,4-*c*]furan-1-yl]phenol (Ando *et al.*, 2007).



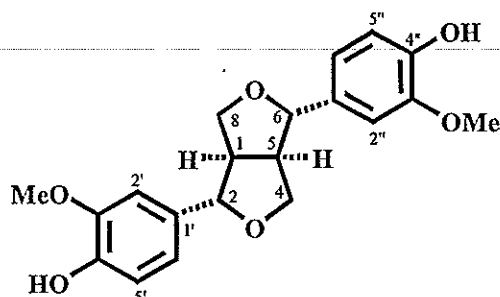


Major HMBC of KF12

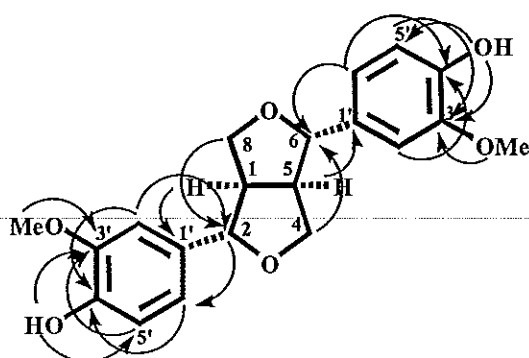
Table 14 NMR spectral data of KF12

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
1/5	3.11 ( <i>m</i> )	54.1/54.4 (CH)	C-2, C-5, C-6, C-8, C-1''
2/6	4.72/4.75 ( <i>d</i> , $J = 4.5$ Hz)	85.8/86.1 (CH)	C-1, C-8, C-1'', C-2''
4 <sub>a</sub> /8 <sub>a</sub>	3.87 ( <i>m</i> )	71.9/71.6 (CH <sub>2</sub> )	C-1, C-6,
4 <sub>e</sub> /8 <sub>e</sub>	4.27 ( <i>m</i> )	71.9 (CH <sub>2</sub> )	C-1, C-2, C-5, C-6
1'/1''	-	132.0/133.0 (C)	-
2'	6.90 ( <i>d</i> , $J = 1.5$ Hz)	108.0 (CH)	C-2, C-1', C-6', C-4'
3'	-	147.1 (CH)	-
4'	-	145.4 (CH)	-
5'	6.92 ( <i>d</i> , $J = 8.1$ Hz)	114.3 (CH)	C-1', C-6', C-3', C-4', C-2
6'	6.84 ( <i>dd</i> , $J = 8.1, 1.5$ Hz)	118.9 (CH)	C-2, C-1', C-2', C-4', C-5'
2''/6''	6.59 ( <i>s</i> )	102.7 (CH)	C-6, C-1'', C-6'', C-4''
3''	-	147.1 (C)	-
4''	-	134.0 (C)	-
5''	-	147.1 (C)	C-1'', C-6'', C-3'', C-4'', C-6
3''/5''-OCH <sub>3</sub>	3.91 ( <i>s</i> )	56.4 (CH <sub>3</sub> )	C-3'', C-5''
4''-OH	5.50 ( <i>s</i> )	-	C-3'', C-5''
4'-OH	5.60 ( <i>s</i> )	-	C-3', C-5'
3'-OCH <sub>3</sub>	3.92 ( <i>s</i> )	56.0 (CH <sub>3</sub> )	C-3'

**KF13: 4,4'-(Tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diyl)bis-2-methoxyphenol  
(Pinorisinol)**



KF13 was obtained as brown gum. The  $^1\text{H}$  NMR spectrum showed the resonances of aromatic protons H-2'/H-2'' ( $\delta$  6.89, *d*,  $J = 1.5$  Hz), H-5'/H-5'' ( $\delta$  6.92, *d*,  $J = 8.1$  Hz), H-6'/H-6'' ( $\delta$  6.85, *dd*,  $J = 8.1, 1.5$  Hz), methine protons H-1/H-5 ( $\delta$  3.13), benzylic oxymethine protons H-2/H-6 ( $\delta$  4.76, *d*,  $J = 4.2$  Hz), oxygenated methylene protons H<sub>e</sub>-4/H<sub>e</sub>-8 ( $\delta$  4.27, *m*) and H<sub>a</sub>-4/H<sub>a</sub>-8 ( $\delta$  3.90, *m*), methoxy protons 3'/3''-OCH<sub>3</sub> ( $\delta$  3.89) and hydroxyl protons 4'/4''-OH ( $\delta$  5.89). Its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were similar to those of KF10 except for the replacement of the singlet signal of two equivalence methoxyl protons 4'/4''-OCH<sub>3</sub> ( $\delta$  3.88) by two equivalence hydroxyl proton resonances at  $\delta$  5.89 (4'/4''-OH) as well as the absence of two methoxy carbon resonances at  $\delta$  55.9. The  $^3J$  HMBC correlations of 3'/3''-OCH<sub>3</sub> ( $\delta$  3.89) and H-5'/H-5'' ( $\delta$  6.92) to C-3'/C-3'' ( $\delta$  146.8), and correlations of 4'/4''-OH ( $\delta$  5.89), H-6'/H-6'' ( $\delta$  6.85) and H-2'/H-2'' ( $\delta$  6.89) to C-4'/C-4'' ( $\delta$  145.3) confirmed the position of methoxyl group at C-3'/C-3'' and hydroxyl group at C-4'/C-4'', respectively. This compound was known as 4,4'-(tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diyl)bis-2-methoxyphenol (Lin-gen *et al.*, 1982).

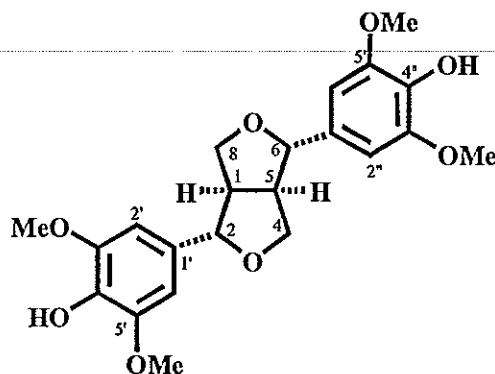


Major HMBC of KF13

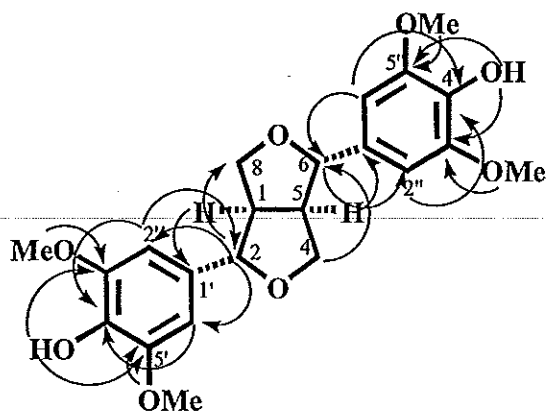
Table 15 NMR spectral data of KF13

Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1/5	3.13 ( <i>m</i> )	54.1 (CH)	C-2, C-5, C-6, C-8, C-1''
2/6	4.76 ( <i>d</i> , $J = 4.2$ Hz)	85.9 (CH)	C-1, C-8, C-1'', C-2''
4 <sub>a</sub> /8 <sub>a</sub>	3.90 ( <i>m</i> )	71.7 (CH <sub>2</sub> )	C-1, C-6
4 <sub>b</sub> /8 <sub>c</sub>	4.27 ( <i>m</i> )	71.7 (CH <sub>2</sub> )	C-1, C-2, C-5, C-6
1'/1''	-	132.9 (C)	-
2'/2''	6.89 ( <i>d</i> , $J = 1.5$ Hz)	108.8 (CH)	C-6, C-1', C-6', C-4'
3'/3''	-	146.8 (C)	-
4'/4''	-	145.3 (C)	-
5'/5''	6.92 ( <i>d</i> , $J = 8.1$ Hz)	114.4 (CH)	C-1', C-6', C-3', C-4', C-6
6'/6''	6.85 ( <i>dd</i> , $J = 8.1, 1.5$ Hz)	119.0 (CH)	C-6, C-1', C-2', C-4', C-5'
3'/3''-OCH <sub>3</sub>	3.89 ( <i>s</i> )	56.0 (OCH <sub>3</sub> )	C-3'
4'/4''-OH	5.89 ( <i>br s</i> )	-	C-4', C-3', C-5'

**KF14: 4,4'-(Tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diyl)bis-2,6-dimethoxyphenol (Syringaresinol)**



**KF14** was obtained as brown gum. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed characteristic signals due to the symmetrical dibenzylfurofuran type lignin structure. The  $^1\text{H}$  NMR spectrum showed the resonances of methine protons H-1/H-5 ( $\delta$  3.12, *m*), benzylic oxymethine protons H-2/H-6 ( $\delta$  4.75), oxygenated methylene protons H<sub>c</sub>-4/H<sub>c</sub>-8 ( $\delta$  4.30) and H<sub>a</sub>-4/H<sub>a</sub>-8 ( $\delta$  3.94) as for (**KF10**) and (**KF13**). The phenyl rings were suggested to be 1,2,3,5-tetrasubstituted benzene ring due to the resonance of *meta*-protons at  $\delta$  6.60 (H-2'/H-2'', H-6'/H-6''). The methoxy protons resonated at  $\delta$  3.91 (3'/3''-OCH<sub>3</sub>, 5'/5''-OCH<sub>3</sub>) and hydroxyl protons resonated at  $\delta$  5.53 (4'/4''-OH) were assigned for 3'/3'', 5'/5''-OCH<sub>3</sub> and 4'/4''-OH. The NOE experiment by irradiation at the resonances of H-2'/H-2''/H-6'/H-6' ( $\delta$  6.60) enhancing the resonances of methoxyl group confirmed the positions of OCH<sub>3</sub> at C-3'/C-3'', C-5'/C-5'' ( $\delta$  147.2). This compound was identical to 4,4'-(tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diyl)bis-2,6-dimethoxyphenol (Lin-gen *et al.*, 1982).

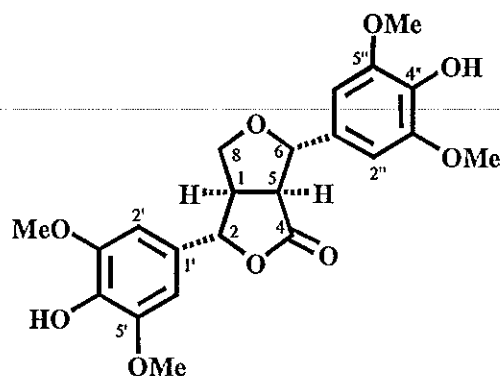


Major HMBC of KF14

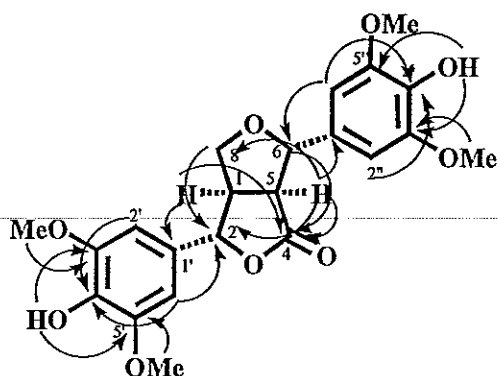
Table 16 NMR spectral data of KF14

Position	$\delta_H$ (multiplicity)	$\delta_C$ (C-Type)	HMBC
1/5	3.12 ( <i>m</i> )	54.4 (CH)	C-2, C-5, C-6, C-8, C-1''
2/6	4.75 ( <i>d</i> , $J = 4.2$ Hz)	86.1 (CH)	C-1, C-8, C-1'', C-2''
4 <sub>a</sub> /8 <sub>a</sub>	3.94 ( <i>m</i> )	71.8 (CH <sub>2</sub> )	C-1, C-6
4 <sub>b</sub> /8 <sub>c</sub>	4.30 ( <i>m</i> )	71.8 (CH <sub>2</sub> )	C-1, C-2, C-5, C-6
1'/1''	-	132.1 (C)	-
2'/2''	6.60 ( <i>s</i> )	102.7 (CH)	C-6, C-1', C-6', C-4'
3'/3''	-	147.2 (C)	-
4'/4''	-	134.3 (C)	-
5'/5''	-	147.2 (CH)	C-1', C-6', C-3', C-4', C-6
6'/6''	6.60 ( <i>s</i> )	102.8 (CH)	C-6, C-1', C-2', C-4', C-5'
3'/3'', 5'/5''-OCH <sub>3</sub>	3.91 ( <i>s</i> )	56.4 (4×OCH <sub>3</sub> )	C-3'/3'', 5'/5''
4'/4''-OH	5.53 ( <i>br s</i> )	-	C-4'/4''

**KF15: 3,6-Bis-(4-hydroxy-3,5-dimethoxyphenyl)-tetrahydro-furo[3,4-*c*]  
furan-1-one**



**KF15** was obtained as yellow viscous liquid. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed characteristic signals due to the dibenzylfurofuran type lignan structure. The  $^1\text{H}$  NMR showed the resonances of methine protons at  $\delta$  3.25 (H-1, *m*),  $\delta$  3.44 (H-5, *dd*,  $J = 3.9, 4.2$  Hz), benzylic oxymethine protons at  $\delta$  5.32 (H-2, *d*,  $J = 3.6$  Hz), 5.33 (H-6, *d*,  $J = 3.9$  Hz), oxygenated methylene protons at  $\delta$  4.07 (H<sub>a</sub>-8, *dd*,  $J = 9.6, 9.3$  Hz), 4.40 (H<sub>e</sub>-8, *dd*,  $J = 9.6, 9.3$  Hz). Two phenyl rings were suggested to be 1,2,3,5-tetrasubstituted benzene ring due to the resonance of *meta*-protons at  $\delta$  6.62 (H-2'/H-6') and  $\delta$  6.64, (H-2''/H-6''). The methoxy protons resonated at  $\delta$  3.90 (3'/3''-OCH<sub>3</sub>) and  $\delta$  3.91 (5'/5''-OCH<sub>3</sub>) and hydroxyl protons resonated at  $\delta$  5.57 (4'-OH) and  $\delta$  5.50 (4''-OH) were assigned for 3'/3'', 5'/5''-OCH<sub>3</sub> and 4'/4''-OH. The NOE experiment by irradiation at the resonances of H-2'/H-6' ( $\delta$  6.62), H-2''/H-6'' ( $\delta$  6.64), enhancing the resonances of methoxyl group confirmed the positions of OCH<sub>3</sub> at C-3'/C-3'', C-5'/C-5''. The HMBC correlations of H-5 to C-1' ( $\delta$  130.3), C-4 ( $\delta$  176.8), C-2 ( $\delta$  84.6), C-6 ( $\delta$  83.4), and C-8 ( $\delta$  72.9) as well as that of H-2'/H-6' to C-2 ( $\delta$  84.6), C-1' ( $\delta$  131.6), and C-4' ( $\delta$  135.2) and of H-2''/H-6'' to C-6 ( $\delta$  83.4), C-1'' ( $\delta$  130.3), C-4'' ( $\delta$  134.4), indicated that the furan ring and benzene ring were linked to each other C-2 and C-1', C-6 and C-1''. The resonance of ester carbonyl was shown at  $\delta$  176.8 (C-4) and in HMBC experiment, it showed correlation to H-6, the butyrolectone moiety then was assigned. A molecular ion in the HREI-MS at  $m/z$  432.1415 which corresponded to a molecular formula of C<sub>22</sub>H<sub>24</sub>O<sub>9</sub> confirmed that **KF15** was 3,6-bis-(4-hydroxy-3,5-dimethoxyphenyl)-tetrahydro-furo[3,4-*c*]furan-1-one. It was a new compound.



Major HMBC of KF15

Table 17 NMR spectral data of KF15

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
1	3.25 ( <i>m</i> )	50.2 (CH)	C-2, C-5, C-6, C-8, C-1'
2	5.32 ( <i>d</i> , $J = 3.6$ Hz)	84.6 (CH)	C-4, C-5, C-8, C-1', C-2'
5	3.44 ( <i>dd</i> , $J = 3.9, 4.2$ Hz)	53.5 (CH)	C-1'', C-4, C-2, C-6, C-8
4	-	176.80 (C)	-
6	5.33 ( <i>d</i> , $J = 3.9$ Hz)	83.4 (CH)	C-4, C-1, C-8, C-1'', C-2''
8 <sub>a</sub>	4.07 ( <i>dd</i> , $J = 9.6, 9.3$ Hz)	72.9 (CH <sub>2</sub> )	C-1, C-5, C-2, C-6
8 <sub>e</sub>	4.40 ( <i>dd</i> , $J = 9.6, 9.3$ Hz)	72.9 (CH <sub>2</sub> )	C-2, C-5, C-6
1'	-	131.6 (C)	-
2'/6'	6.62 ( <i>s</i> )	102.1 (CH)	C-1', C-4', C-3', C-6
3'	-	148.7 (C)	-
4'	-	135.2 (C)	-
5'	-	147.3 (C)	-
1''	-	130.3 (C)	-
2''/6''	6.64 ( <i>s</i> )	102.0 (CH)	C-2, C-1'', C-3'', C-4''
3''	-	147.5 (C)	-
4''	-	134.4 (C)	-
5''	-	147.4 (C)	-
3'-OCH <sub>3</sub>	3.90 ( <i>s</i> )	55.1 (OCH <sub>3</sub> )	C-3'

Table 17 (continued)

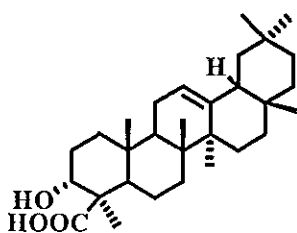
Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)	HMBC
4'-OH	5.57 ( <i>s</i> )	-	C-3', C-4'
5'-OCH <sub>3</sub>	3.91 ( <i>s</i> )	53.5 (OCH <sub>3</sub> )	C-5'
3''-OCH <sub>3</sub>	3.90 ( <i>s</i> )	55.1 (OCH <sub>3</sub> )	C-3''
4''-OH	5.50 ( <i>s</i> )	-	C-3'', C-4''
5''-OCH <sub>3</sub>	3.91 ( <i>s</i> )	53.5 (OCH <sub>3</sub> )	C-5''



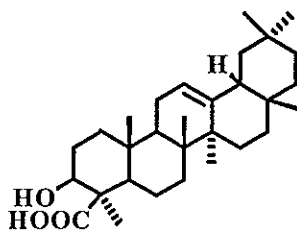
## Conclusion

Investigation of the chemical constituents of the dichloromethane extract from the stem bark of *Fagraea fragrans* Roxb. led to the isolation of five types of compounds including two triterpenes: **KF1**, **KF3**, three secoiridoides: **KF2**, **KF4**, **KF8**, three benzene derivatives: **KF5**, **KF6**, **KF7**, one iridoides: **KF9**, six lignans: **KF10-KF15**. Compounds **KF1-KF7**, **KF9-KF15** were obtained for the first time from this plant. Since this type of compound has been reported to have anti-inflammatory activity and anti oxidant, further study on the antibacterial activity and cytotoxicity activity of the isolated compounds should be performed.

## Triterpenoids

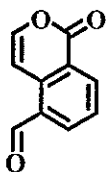


**KF1:**  $\alpha$ -boswellic acid

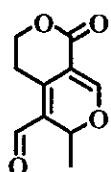


**KF3:**  $\beta$ -boswellic acid

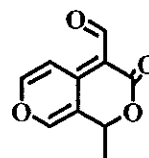
## Secoiridoides



**KF2:** 1-oxo-1*H*-isochromene-5-carbaldehyde

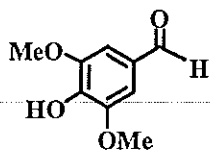


**KF4:** gentiogenol

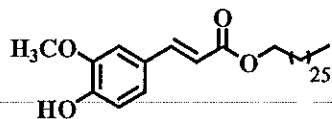
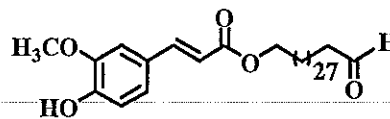


**KF8:** fagraldehyde

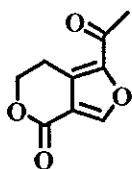
## Benzene derivatives



KF5: syringaldehyde

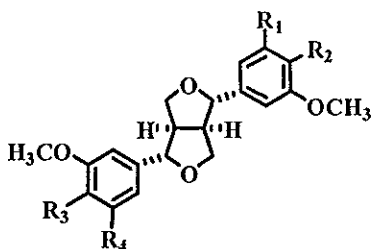
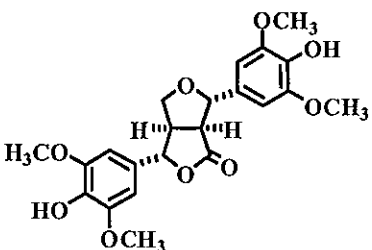
KF6: 3-(4-hydroxy-3-methoxy  
phenyl)-acrylic acid  
octacosyl esterKF7: 3-(4-hydroxy-3-methoxy  
phenyl)-acrylic acid  
30-oxo-triacontyl ester

## Iridoides



KF9: angelone

## Lignans

KF10:  $R_1, R_4 = H, R_2, R_3 = OCH_3$ : eudesminKF11:  $R_1, R_4 = H, R_2 = OH, R_3 = OCH_3$ : monomethylpinoresinolKF12:  $R_1 = OCH_3, R_2, R_3 = OH, R_4 = H$ : medioresinolKF13:  $R_1, R_4 = H, R_2, R_3 = OH$ : pinoresinolKF14:  $R_1, R_4 = OCH_3, R_2, R_3 = OH$ : syringaresinolKF15: 3,6-bis-(4-hydroxy-3,5-dimethoxyphenyl)-  
tetrahydro-furo[3,4-c]furan-1-one

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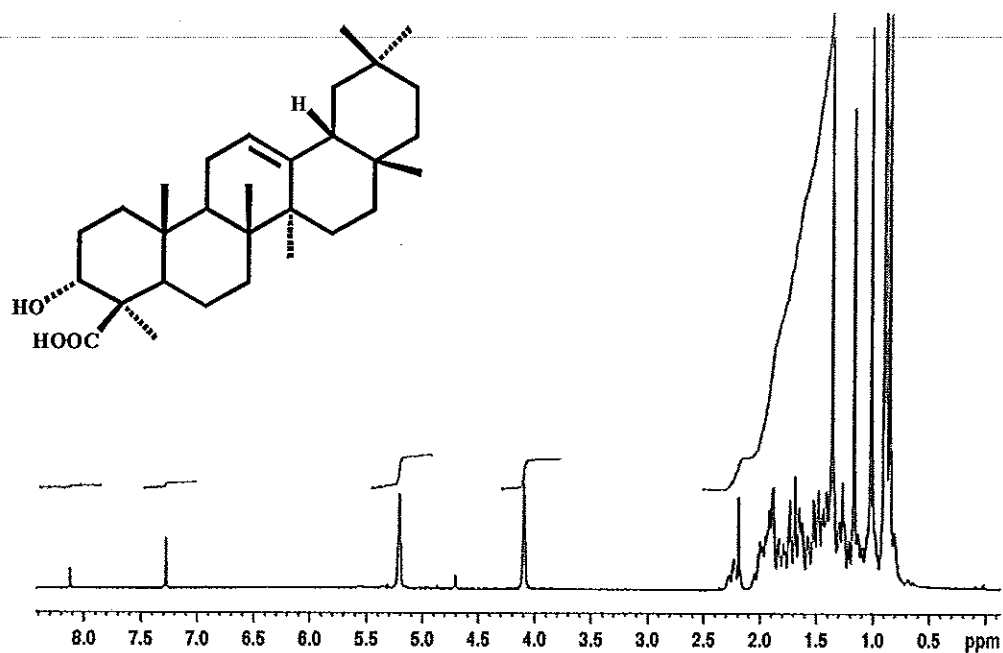
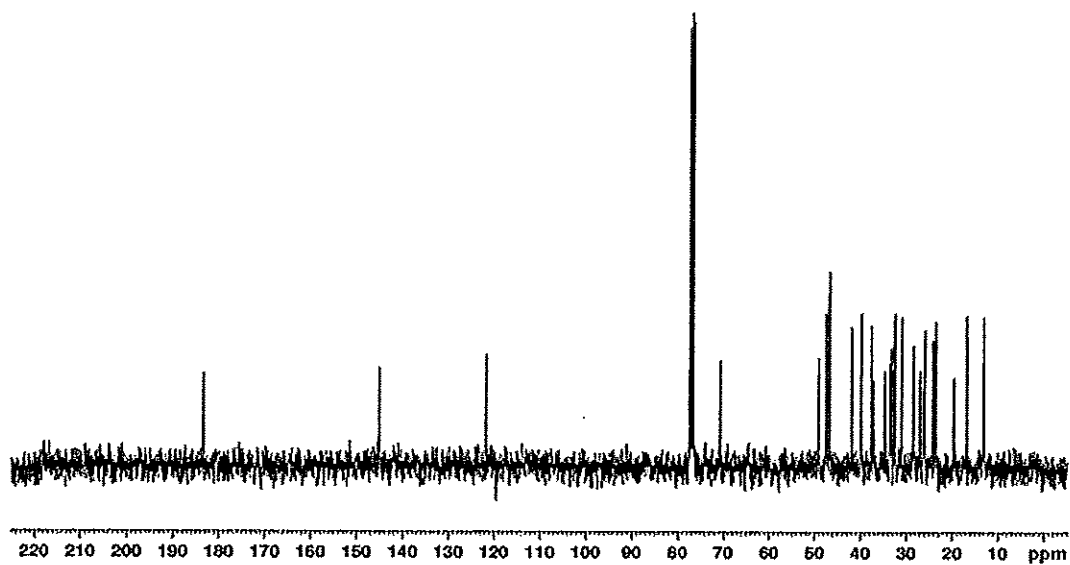
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**APPENDIX**

## 1. Spectrum of compounds KF1-KF15

Figure A-1  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF1Figure A-2  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF1



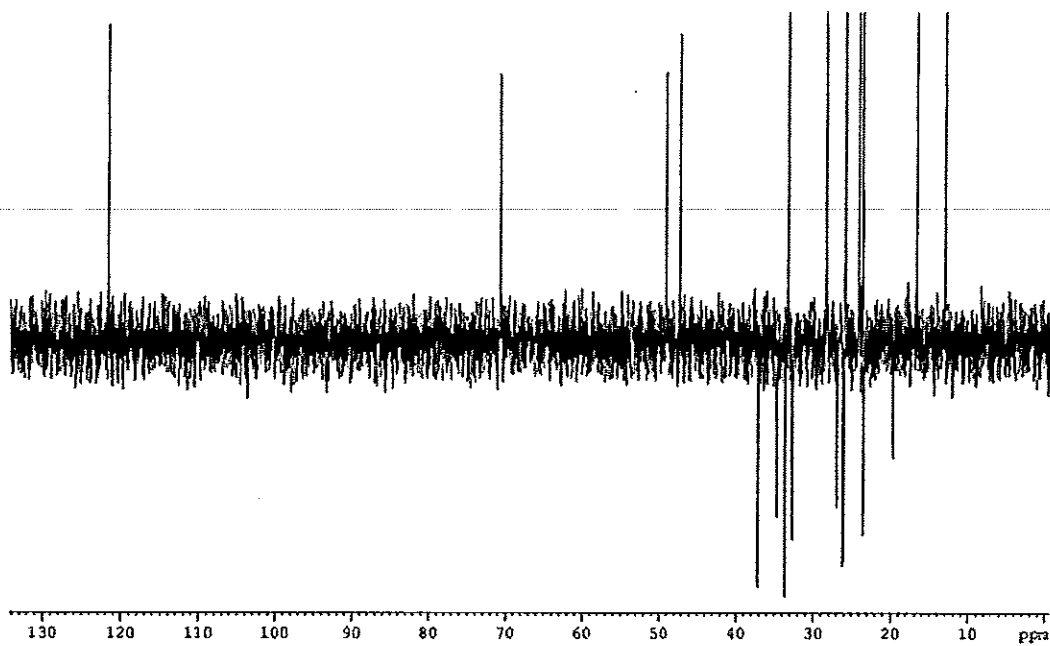


Figure A-3 DEPT 135° (CDCl<sub>3</sub>) spectrum of KF1

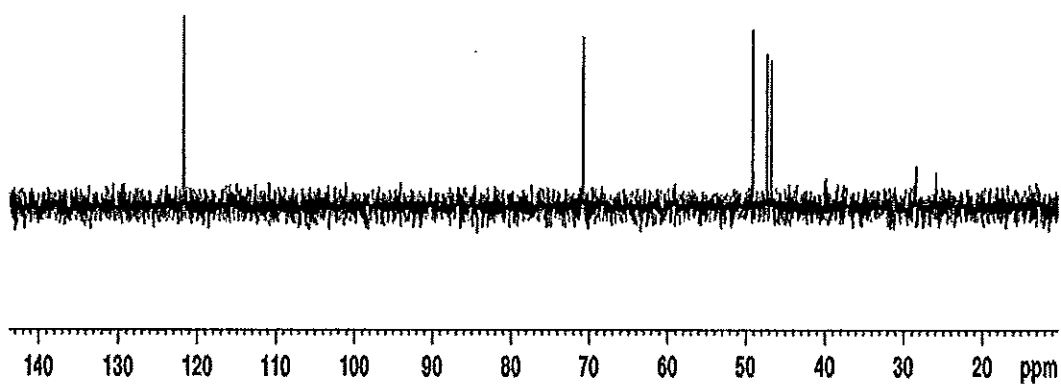


Figure A-4 DEPT 90° (CDCl<sub>3</sub>) spectrum of KF1

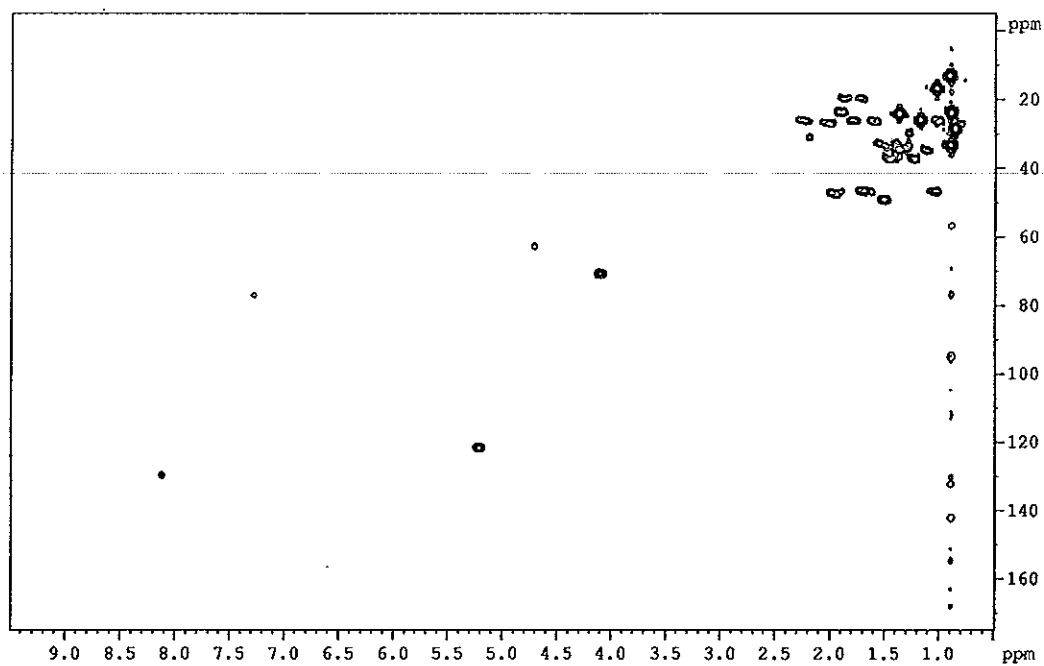


Figure A-5 2D HMQC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF1

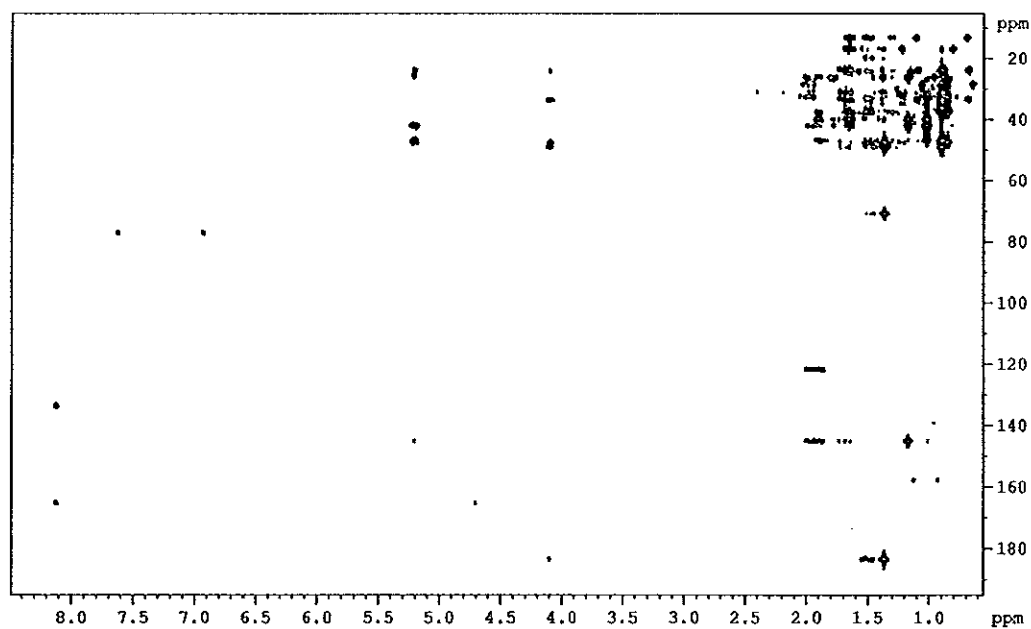


Figure A-6 2D HMBC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF1

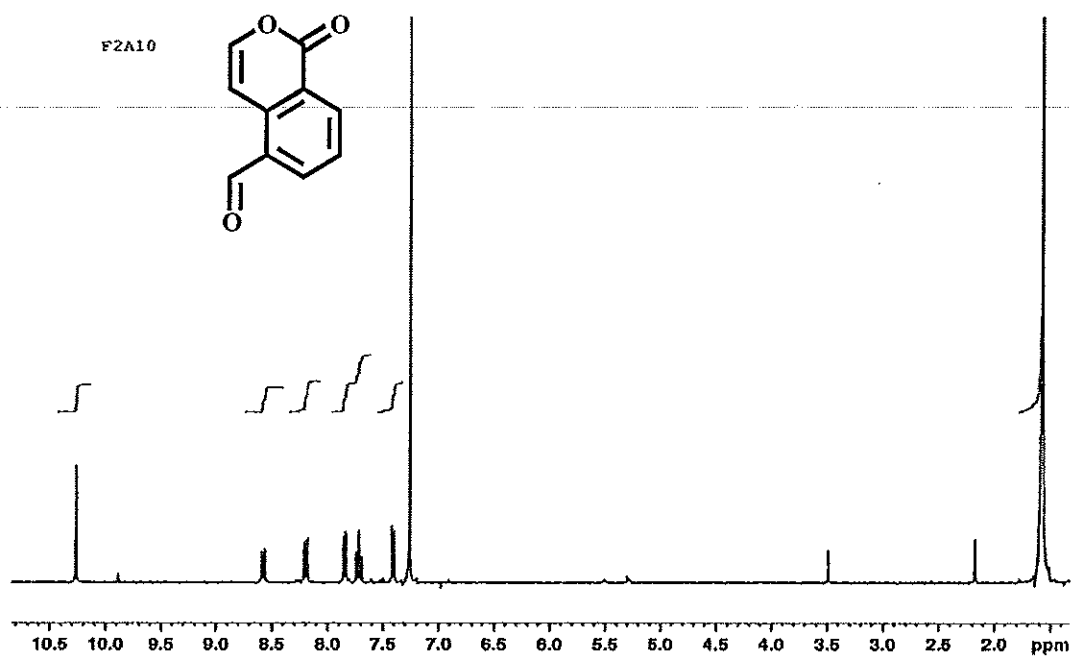


Figure A-7  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF2

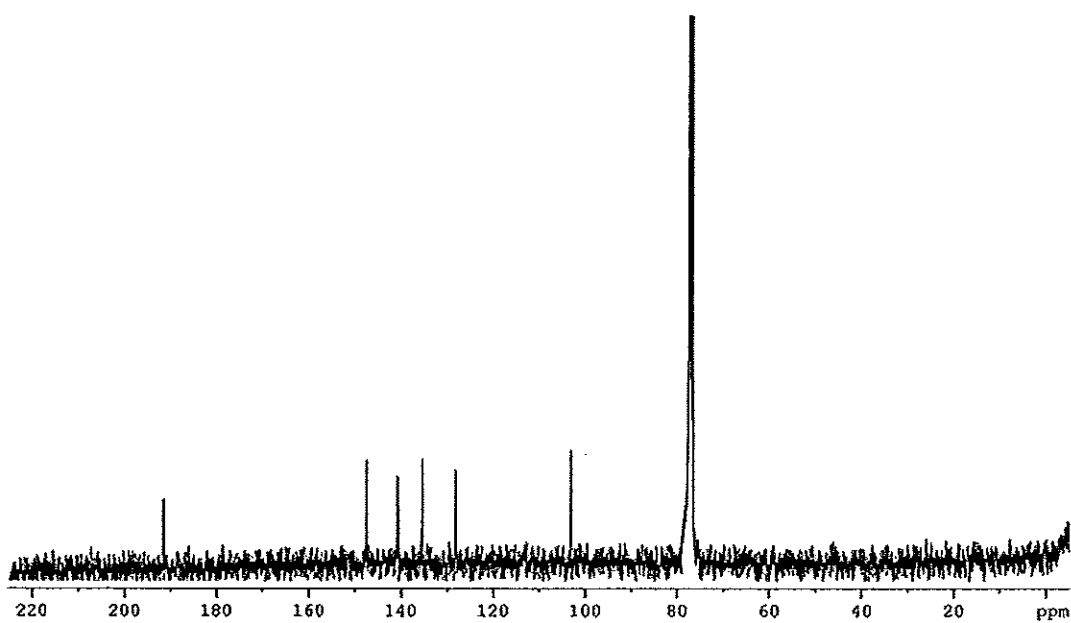


Figure A-8  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF2

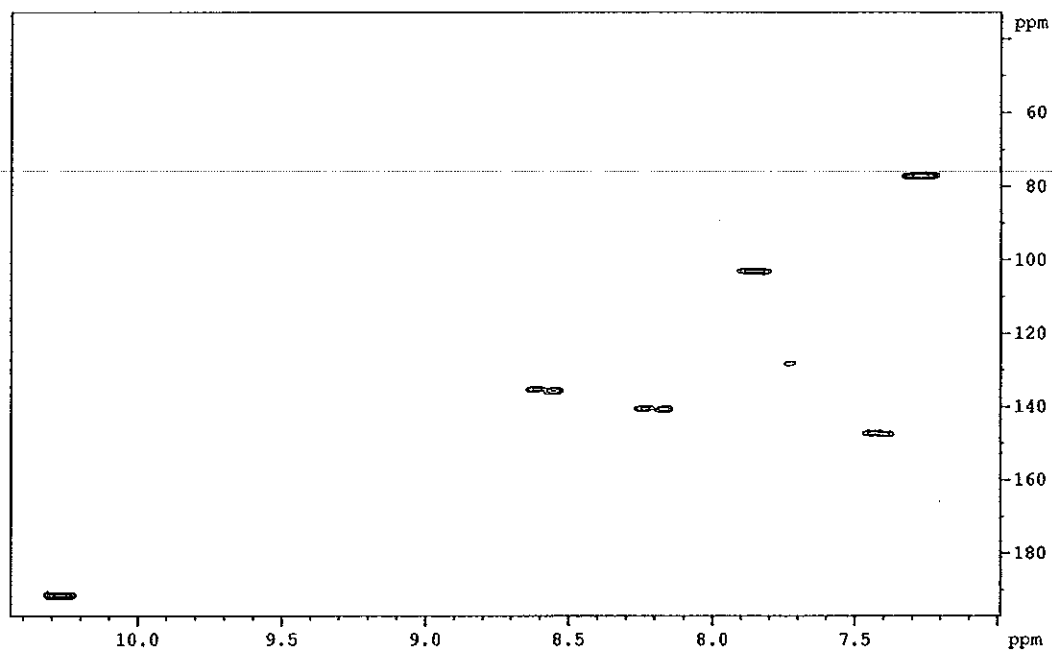


Figure A-9 2D HMQC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF2

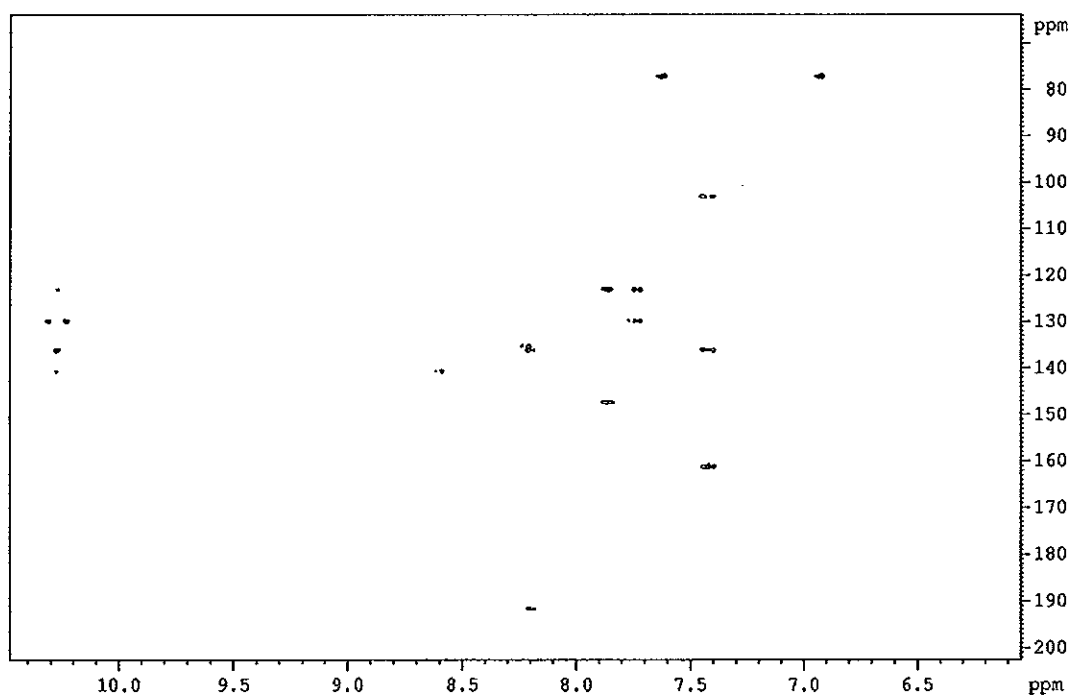


Figure A-10 2D HMBC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF2

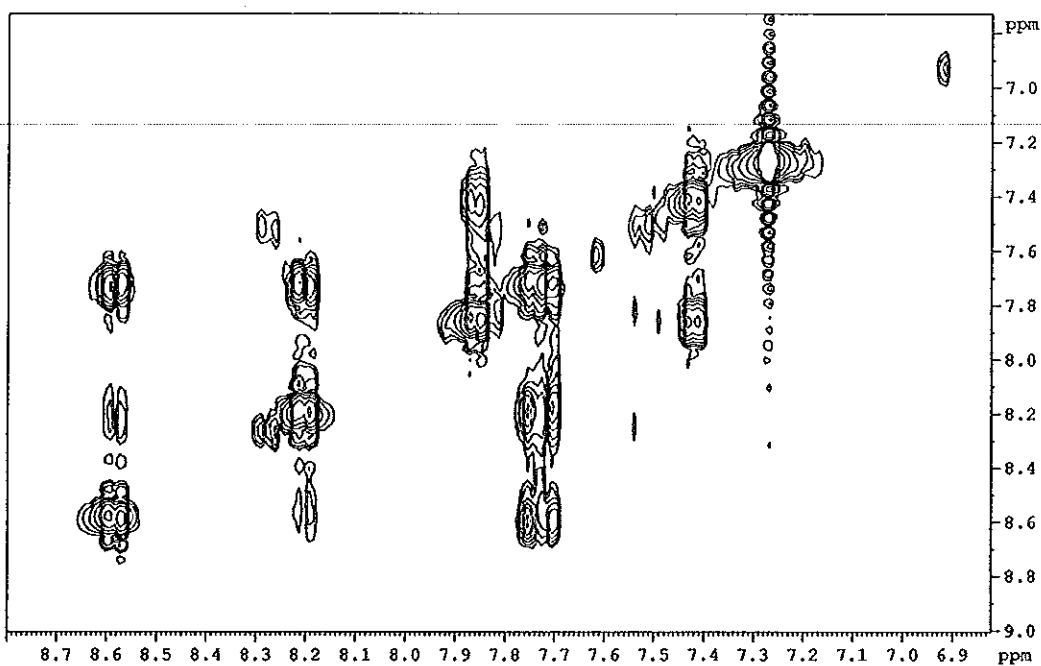


Figure A-11  $^1\text{H}$ - $^1\text{H}$  COSY ( $\text{CDCl}_3$ ) spectrum of KF2

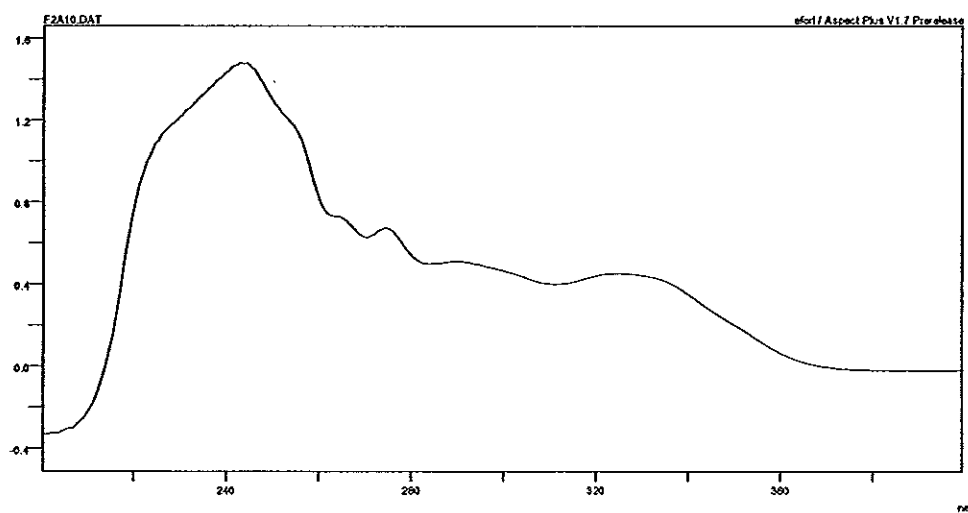


Figure A-12 UV (MeOH) spectrum of KF2

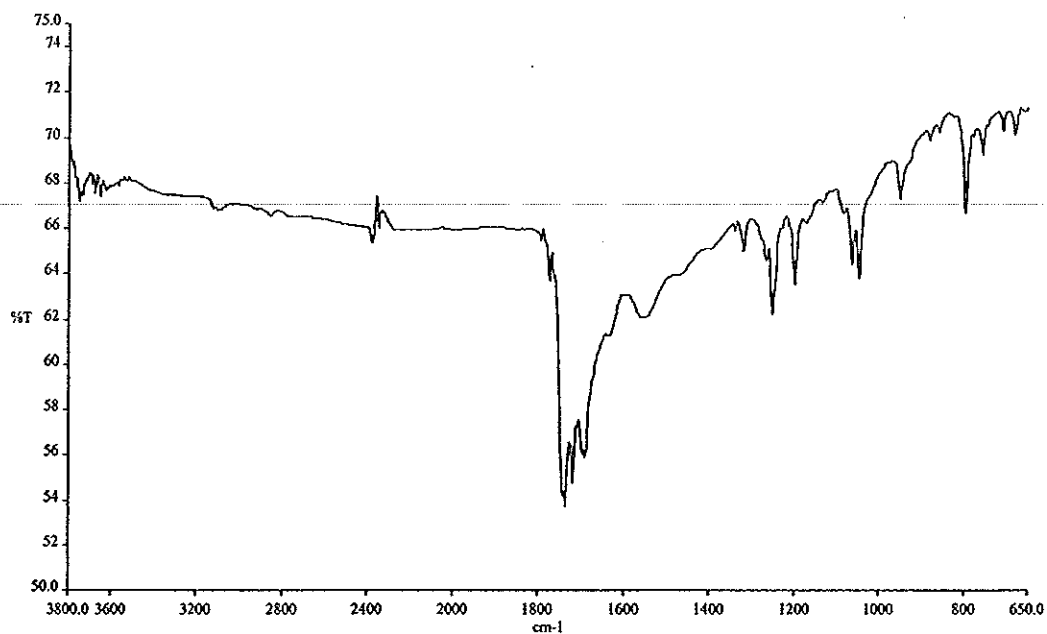


Figure A-13 IR (neat) spectrum of KF2

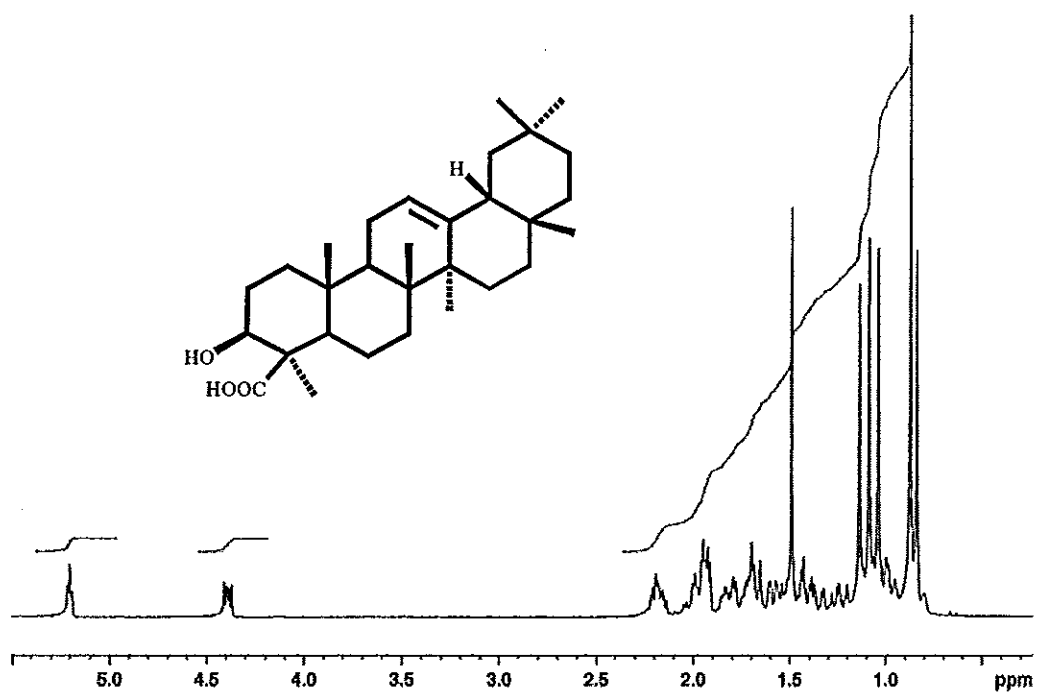


Figure A-14 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF3

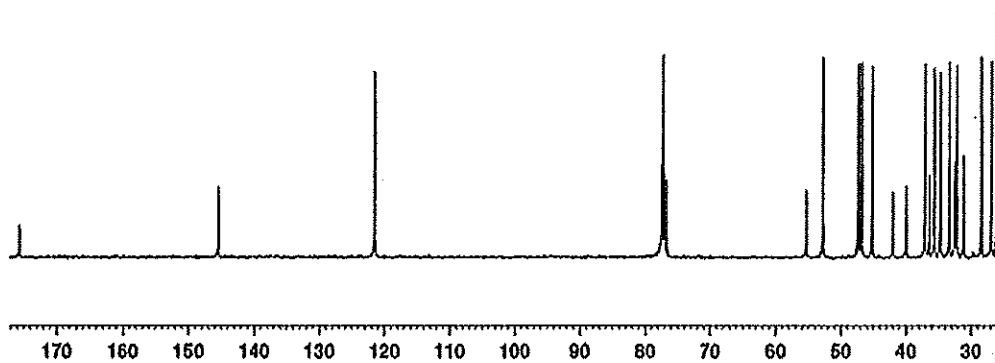


Figure A-15  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF3

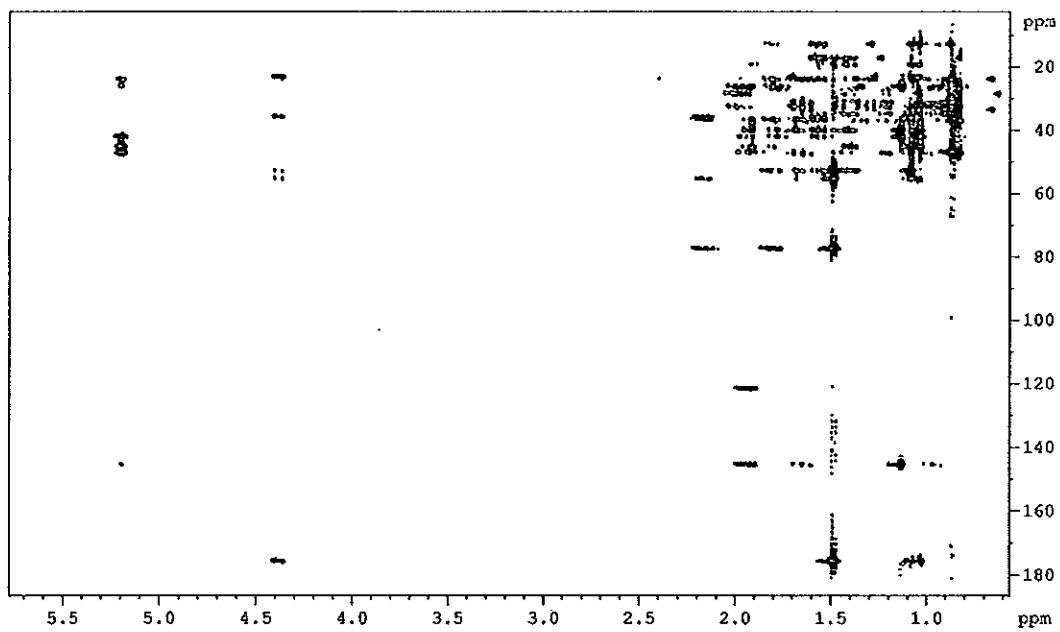


Figure A-16 2D HMBC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF3

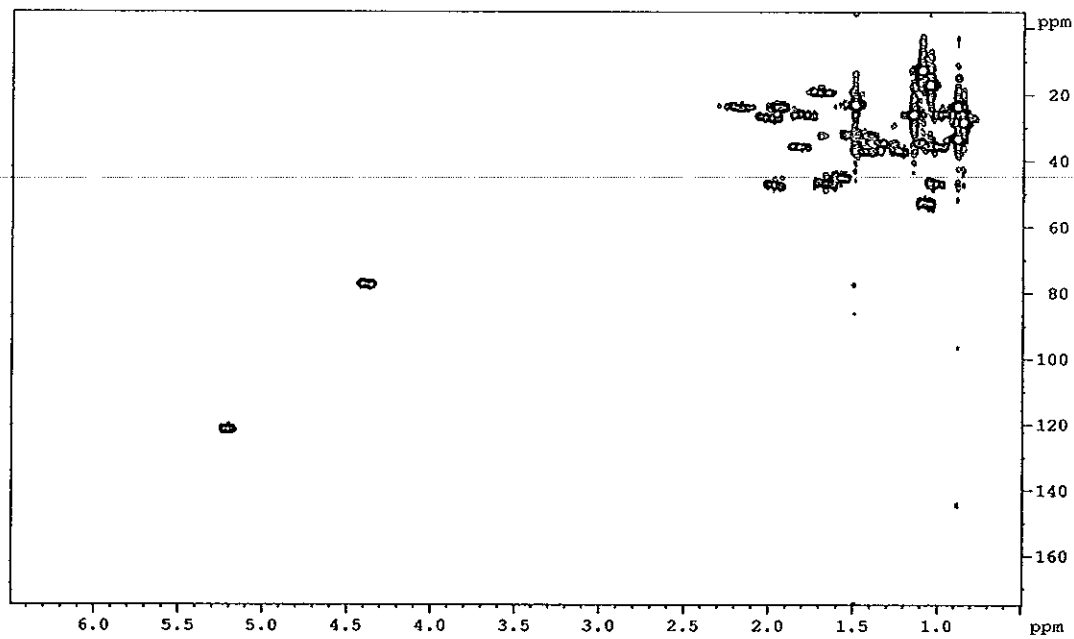


Figure A-17 2D HMQC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF3

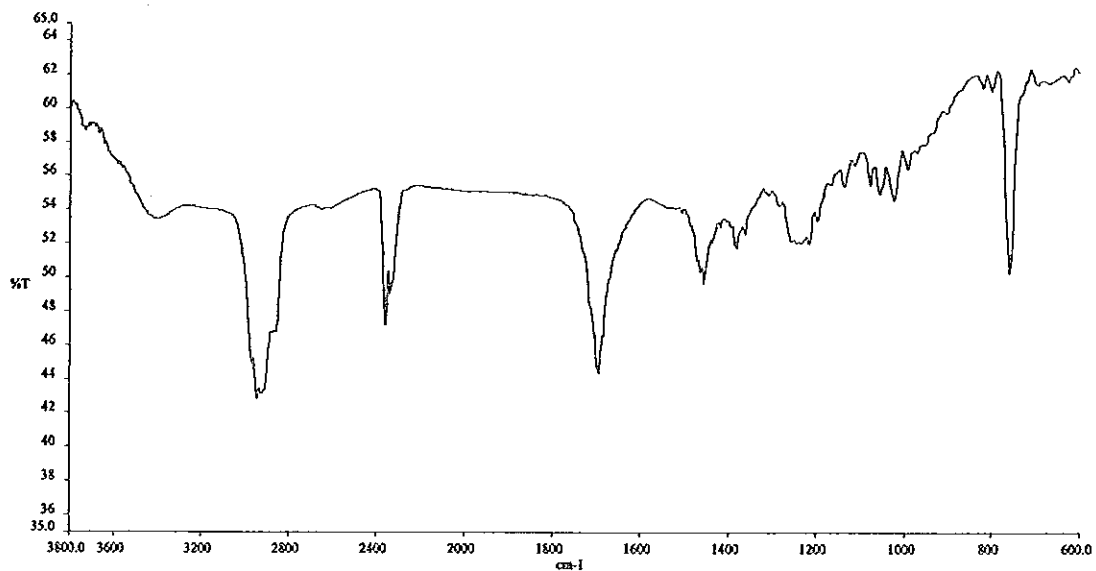


Figure A-18 IR (neat) spectrum of KF3



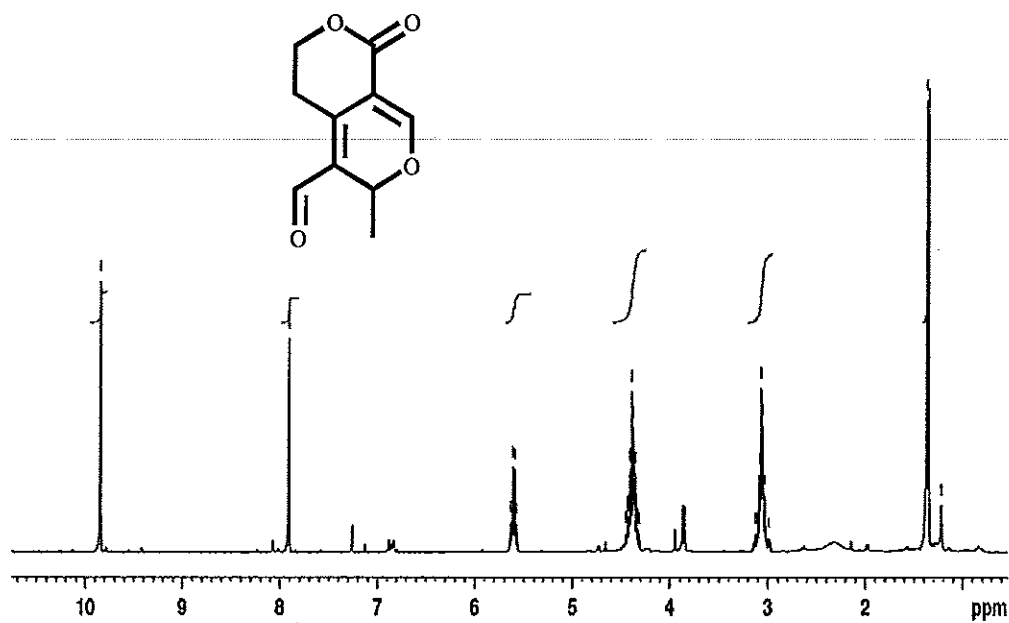


Figure A-19  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF4

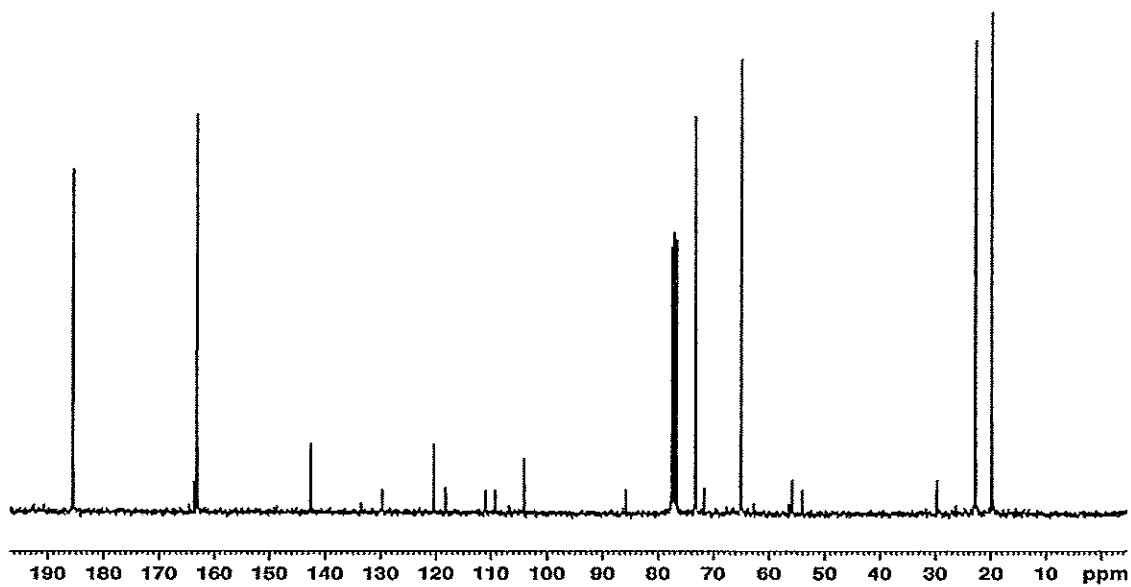


Figure A-20  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF4

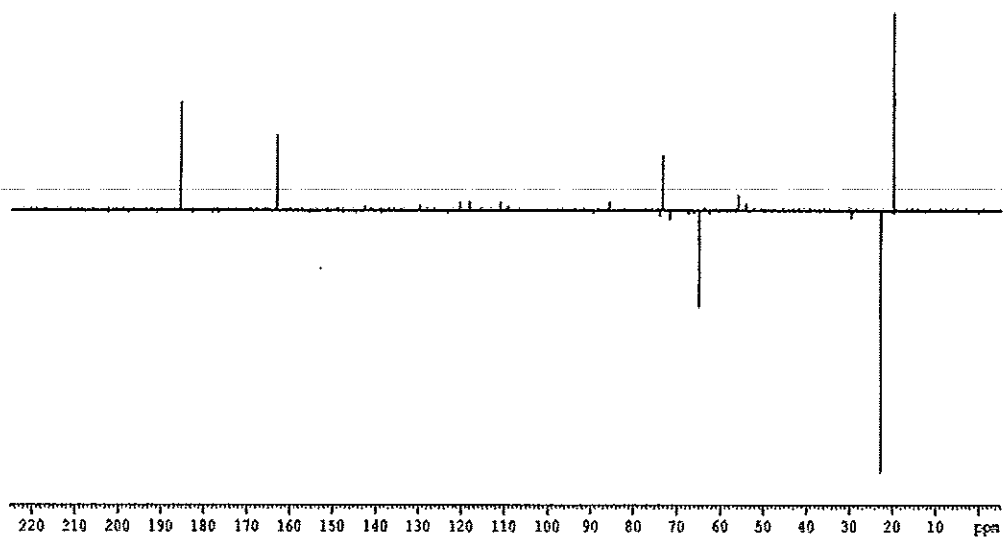


Figure A-21 DEPT 135° (CDCl<sub>3</sub>) spectrum of KF4

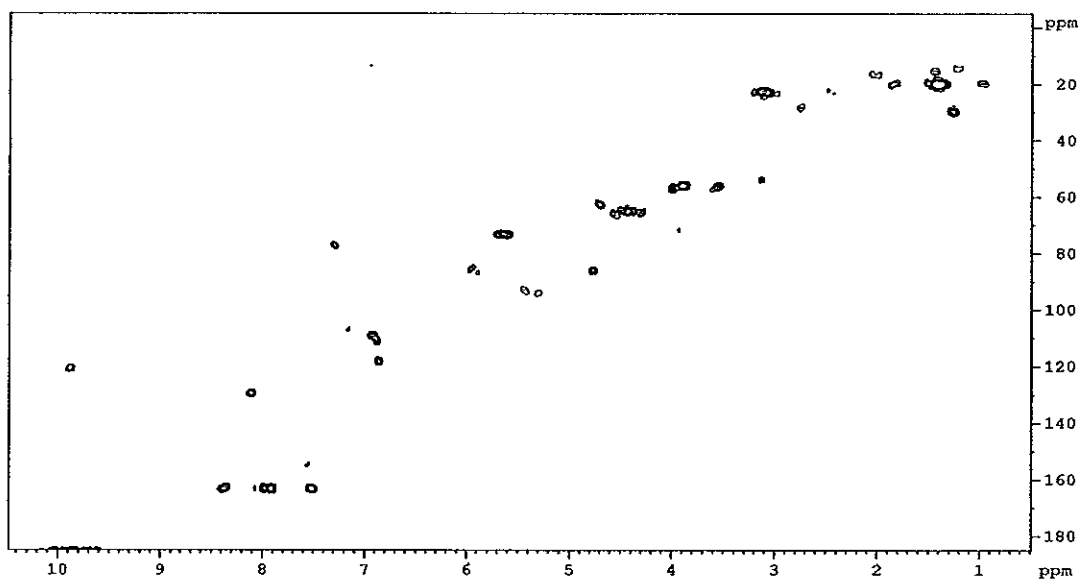


Figure A-22 2D HMQC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF4

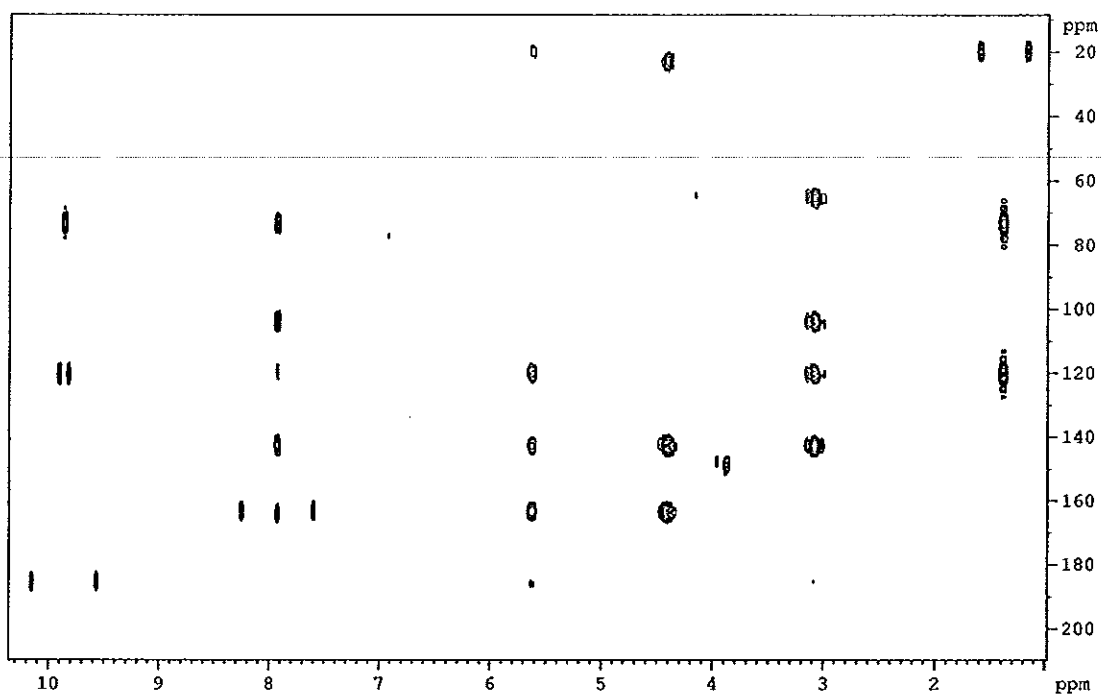


Figure A-23 2D HMBC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF4

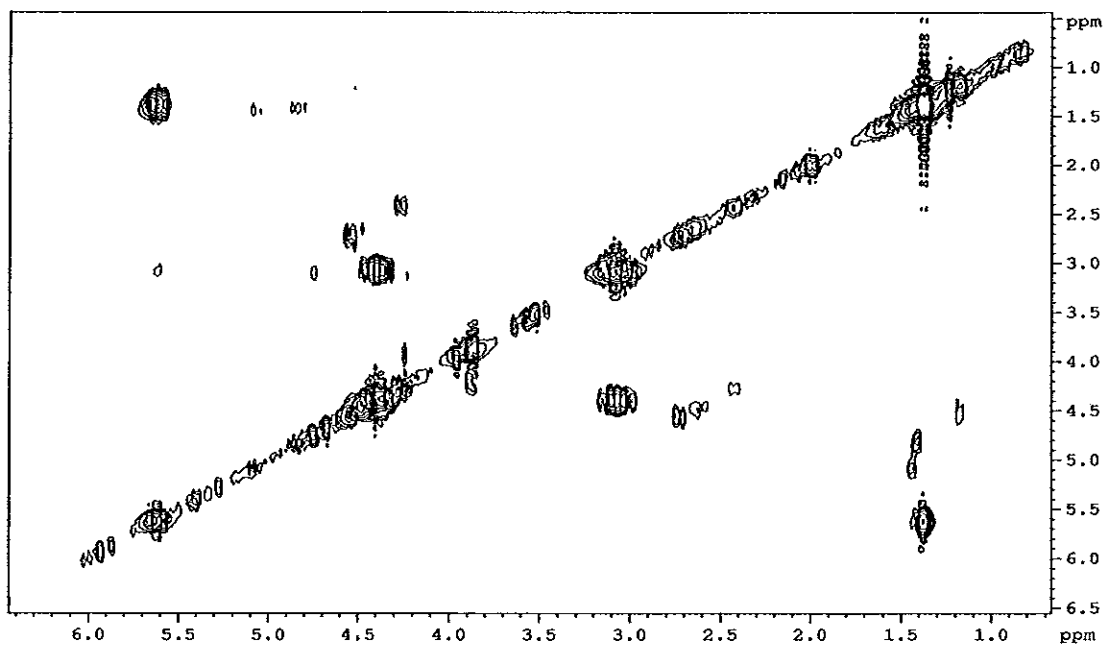


Figure A-24  $^1\text{H}$ - $^1\text{H}$  COSY ( $\text{CDCl}_3$ ) spectrum of KF4

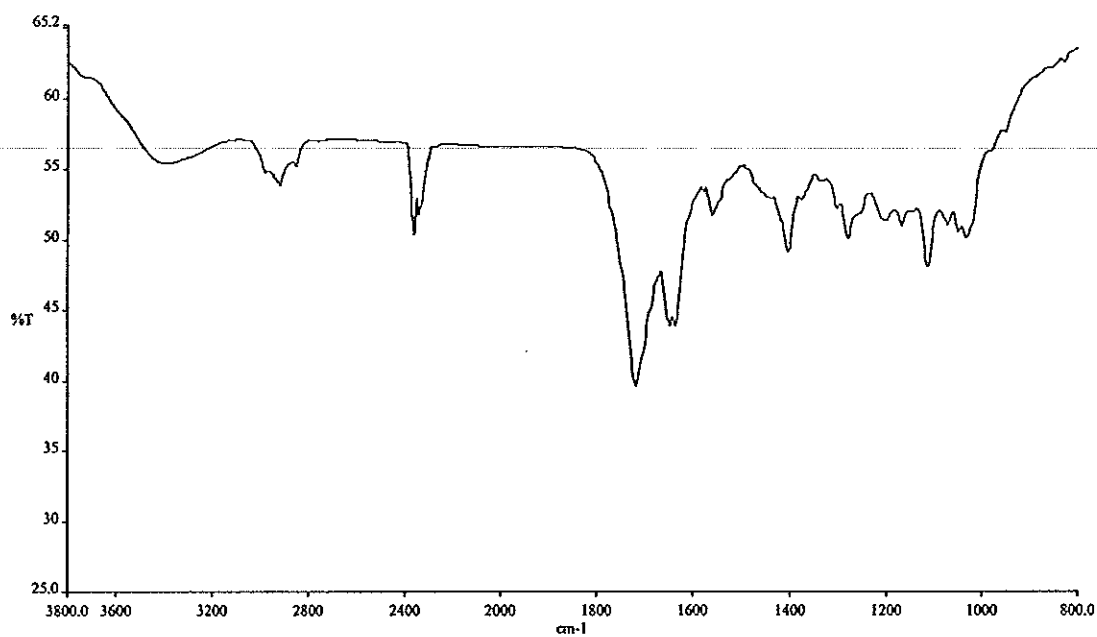


Figure A-25 IR (neat) spectrum of KF4

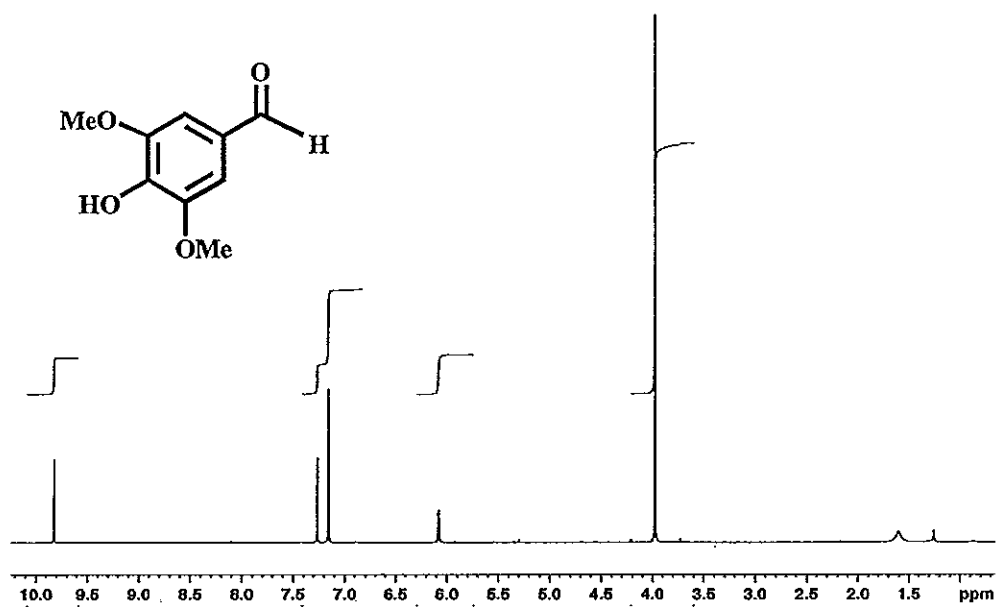


Figure A-26 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF5

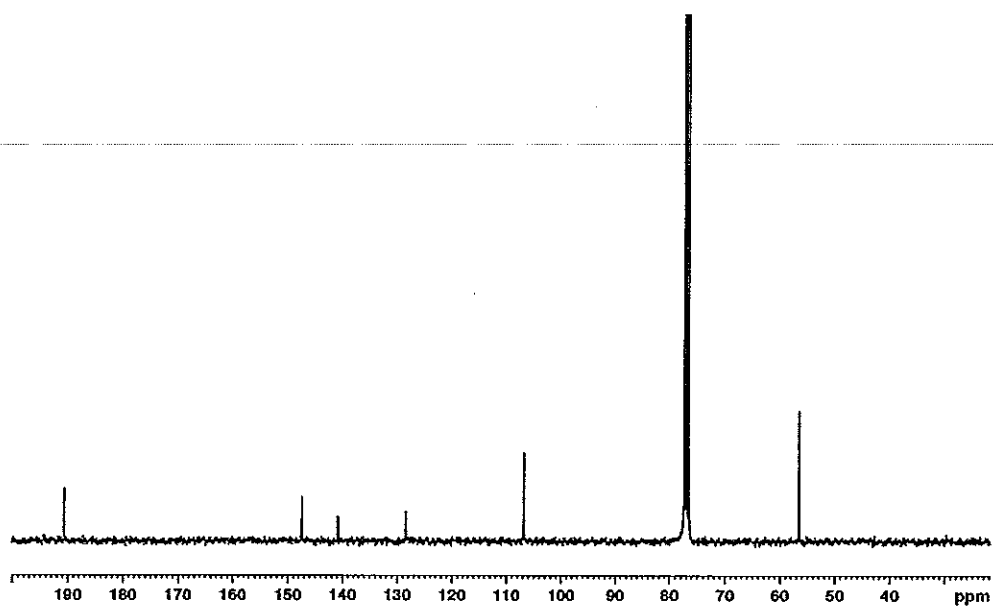


Figure A-27  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF5

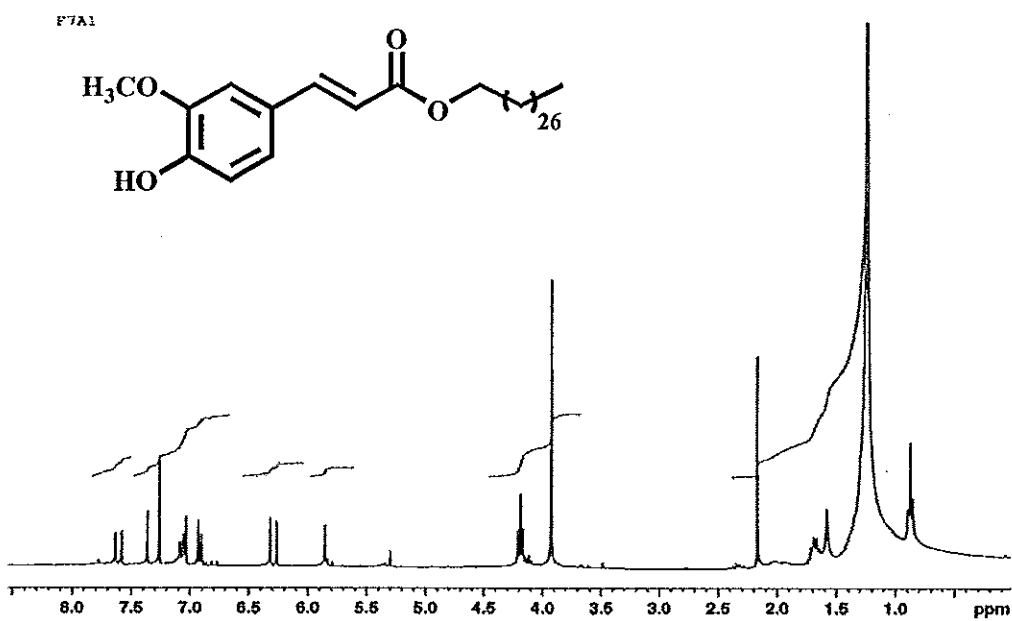


Figure A-28  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF6

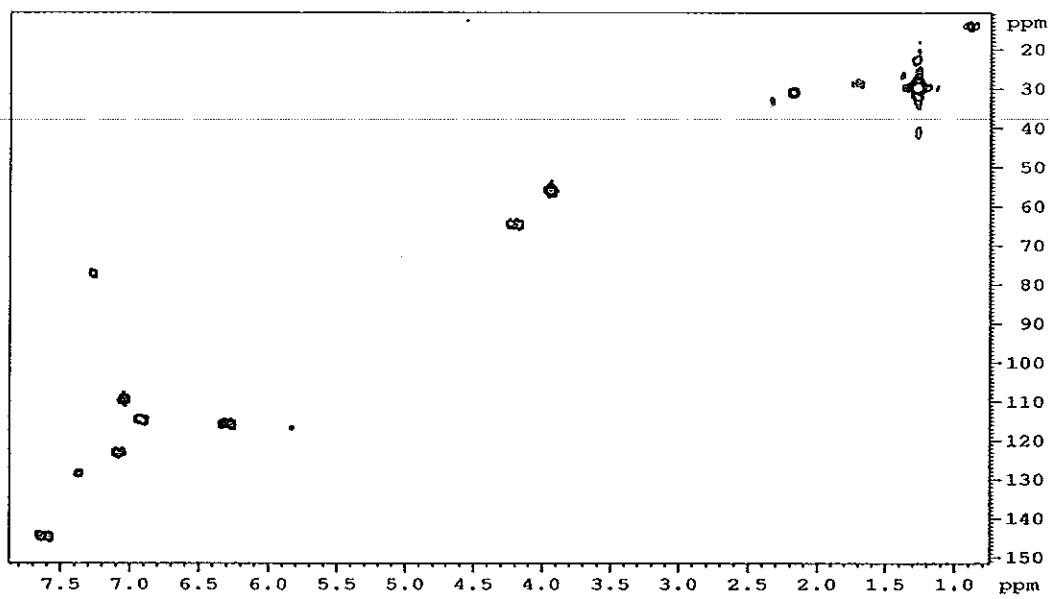


Figure A-29 2D HMQC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF6

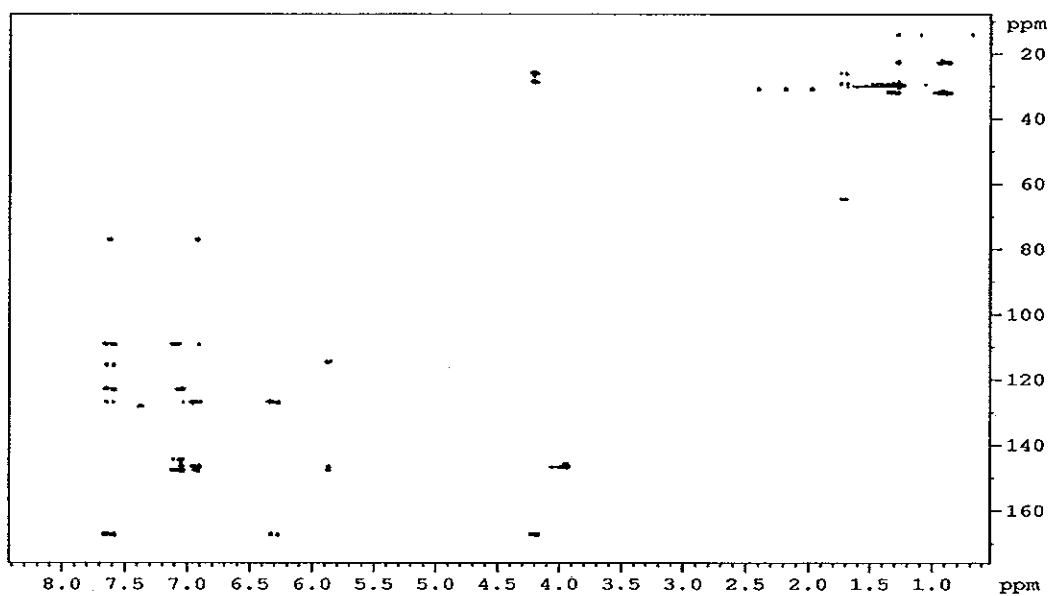


Figure A-30 2D HMQC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF6

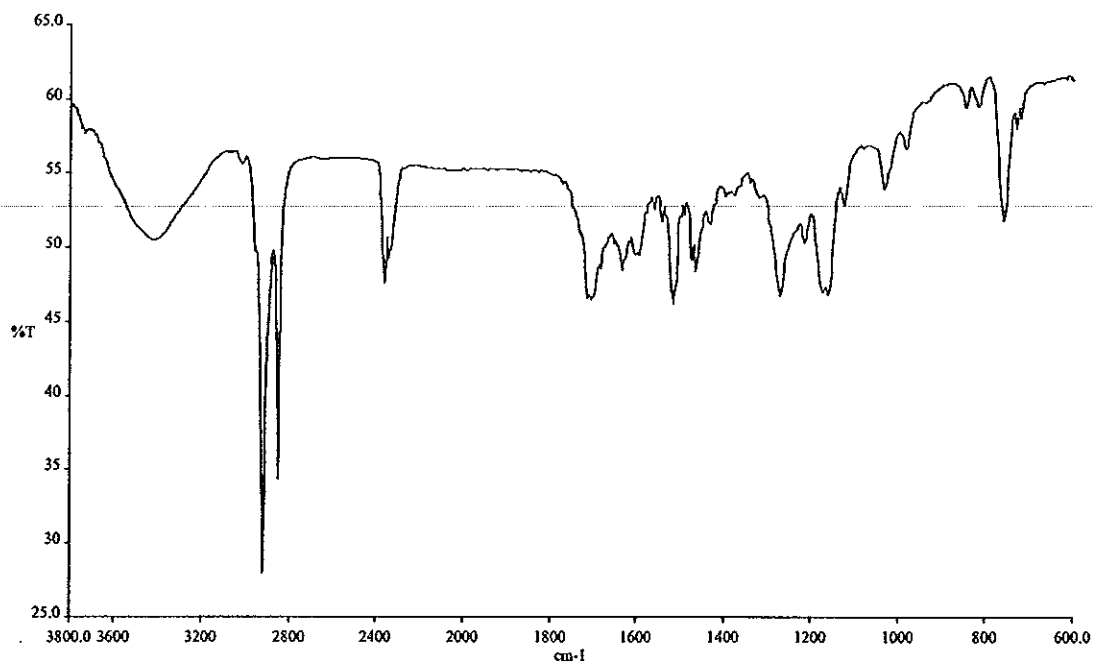


Figure A-31 IR (neat) spectrum of KF6

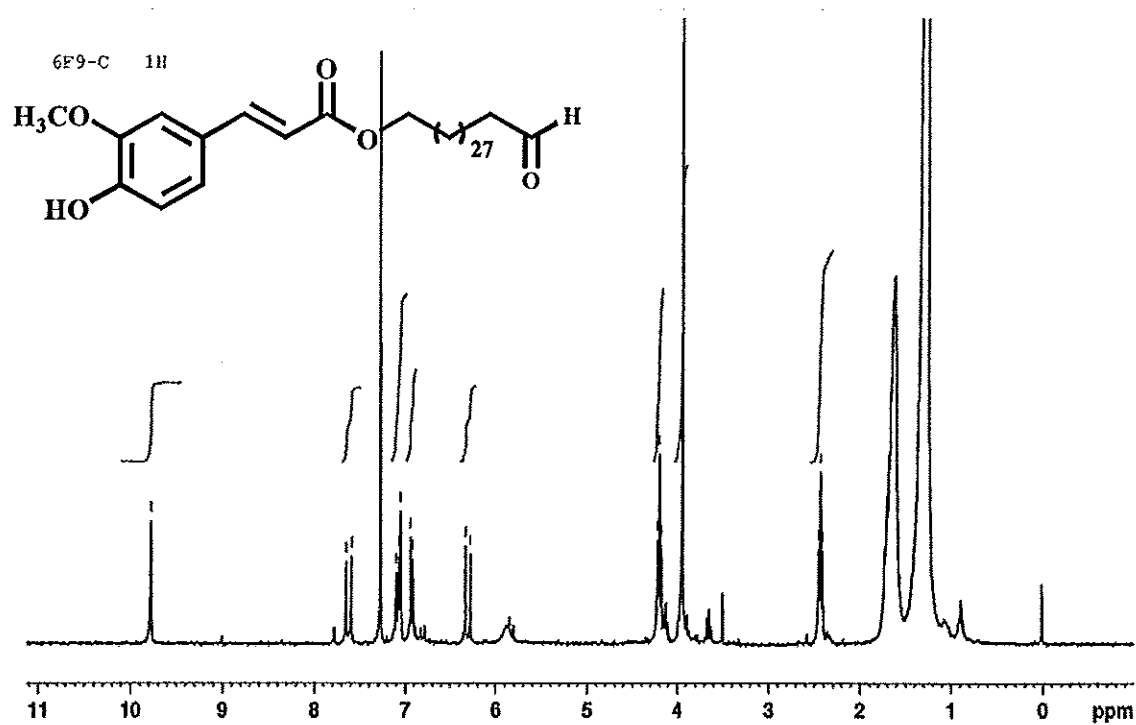


Figure A-32 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF7

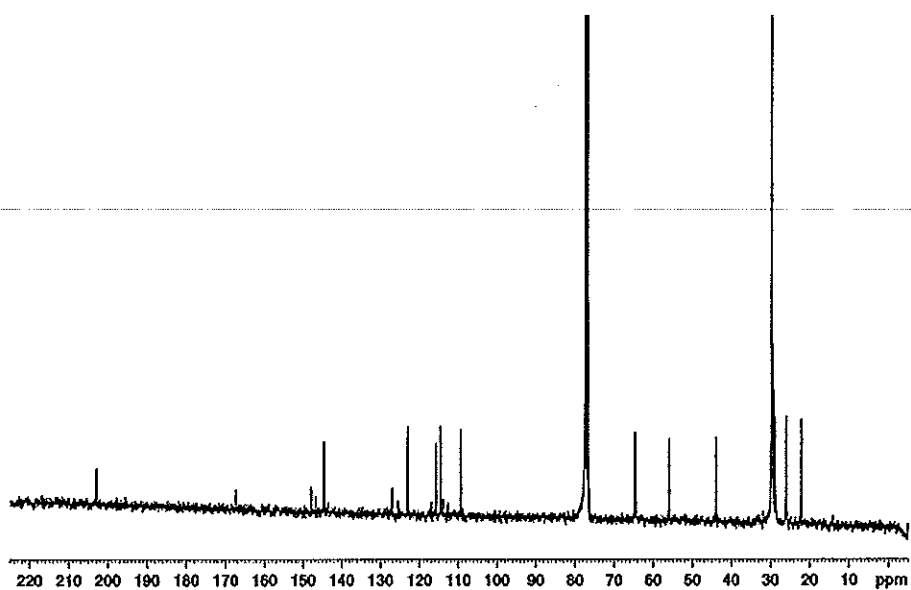


Figure A-33  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF6

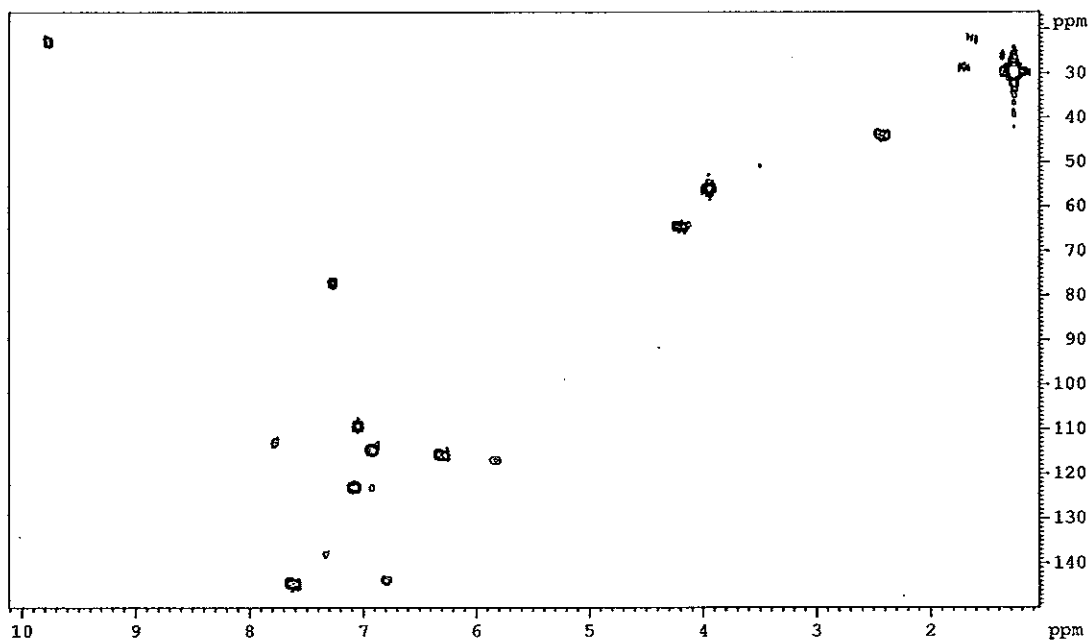


Figure A-34 2D HMQC ( $\text{CDCl}_3$ ) spectrum of KF7



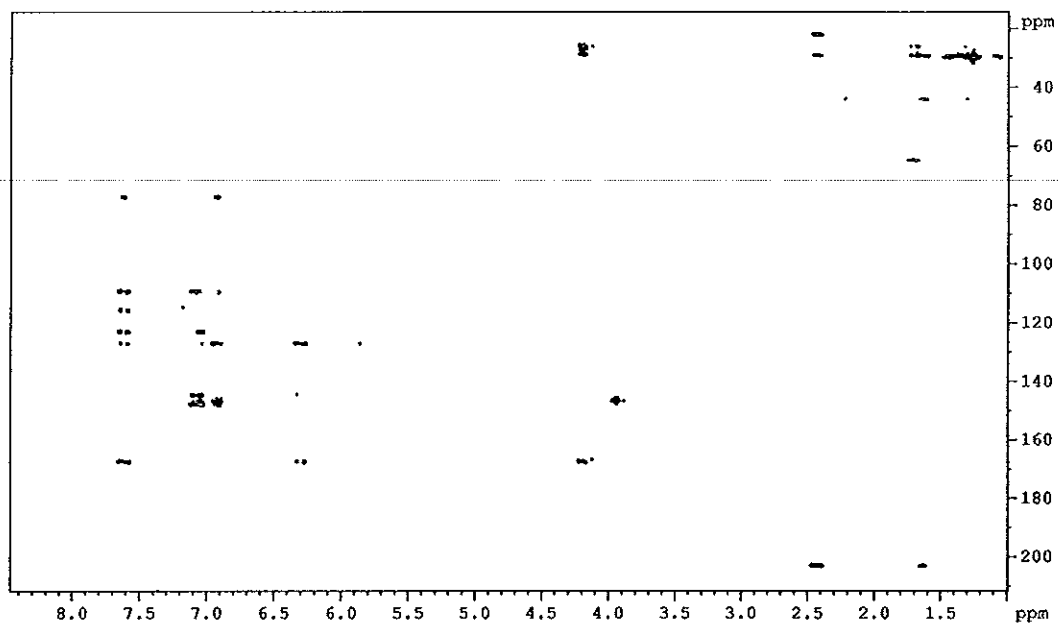


Figure A-35 2D HMBC ( $\text{CDCl}_3$ ) spectrum of KF7

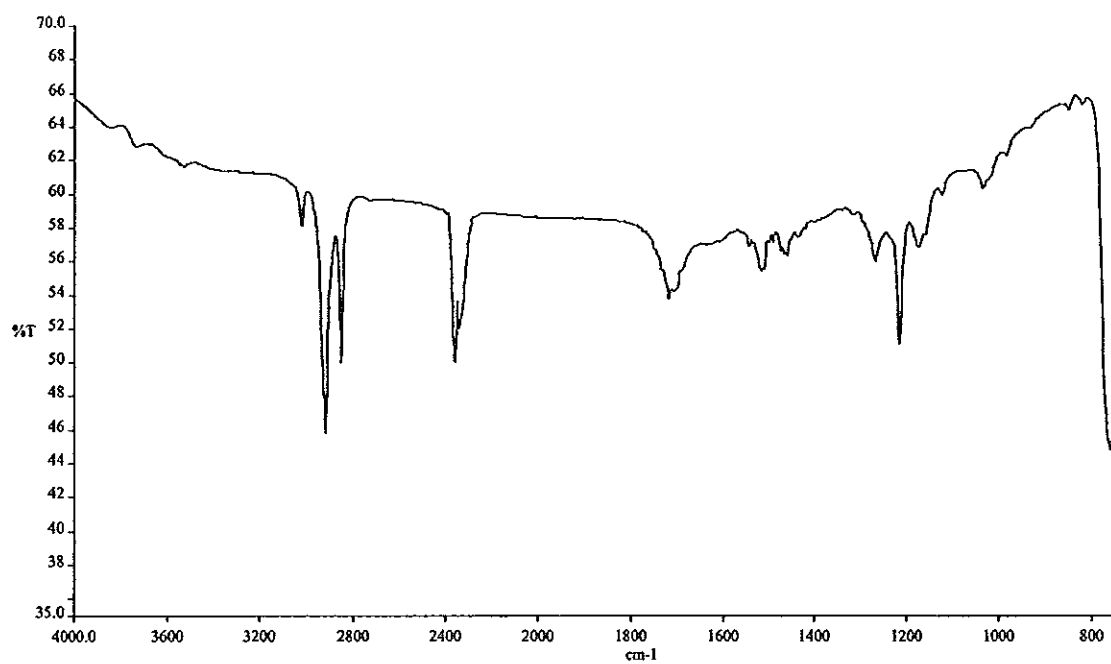


Figure A-36 IR (neat) spectrum of KF7

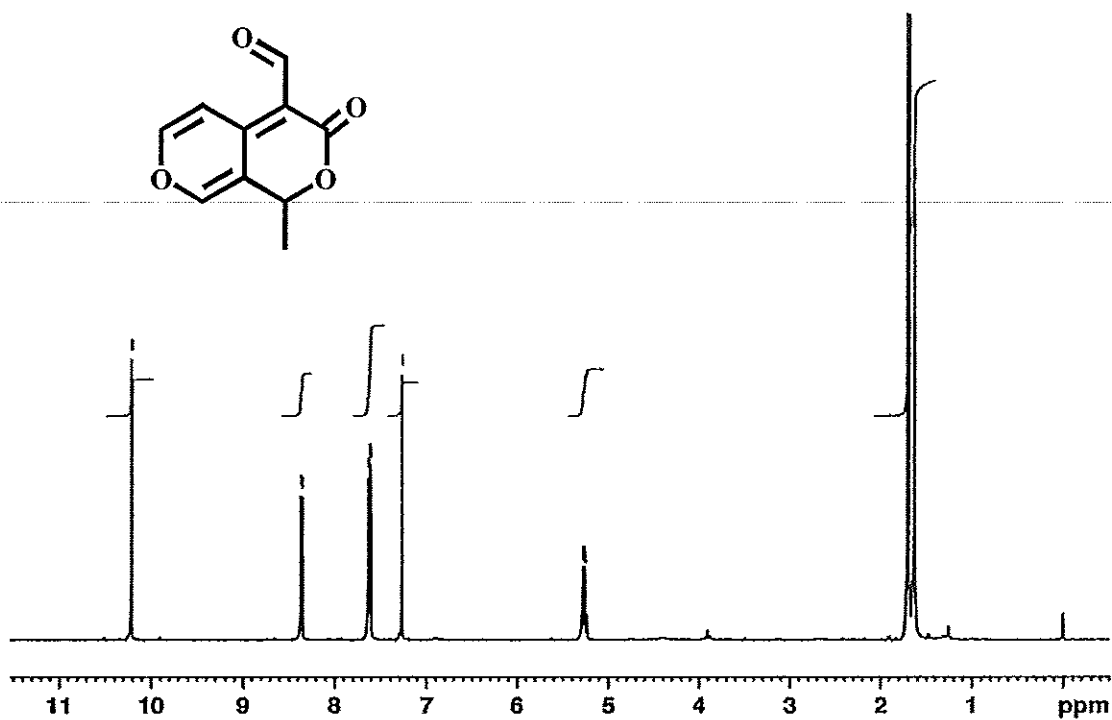


Figure A-37  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF8

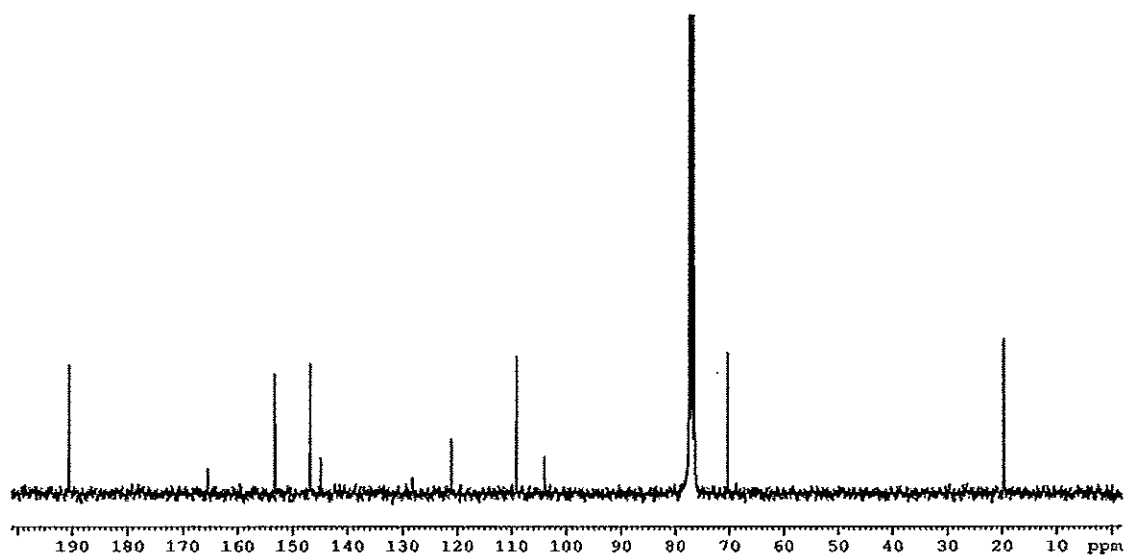


Figure A-38  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF8

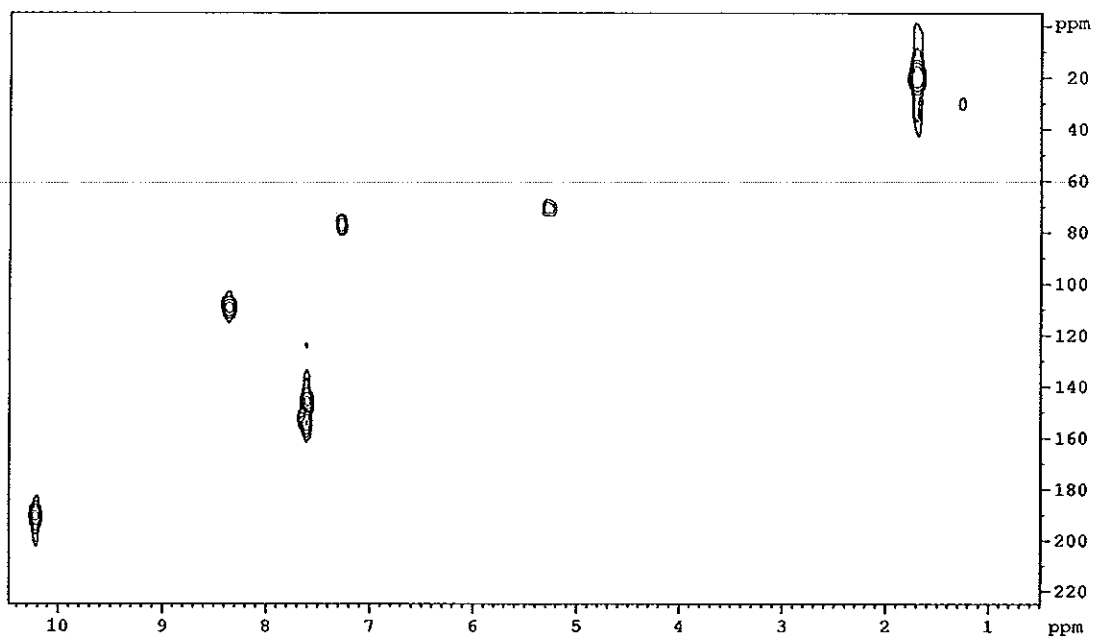


Figure A-39 2D HMQC (CDCl<sub>3</sub>) spectrum of KF8

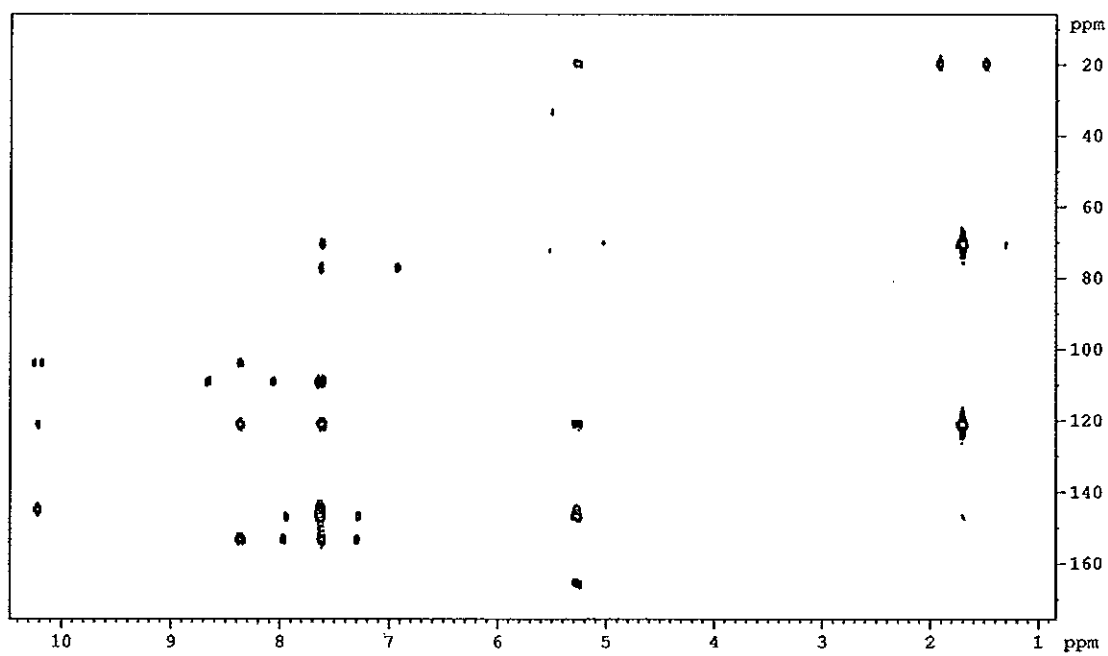


Figure A-40 2D HMBC (CDCl<sub>3</sub>) spectrum of KF8

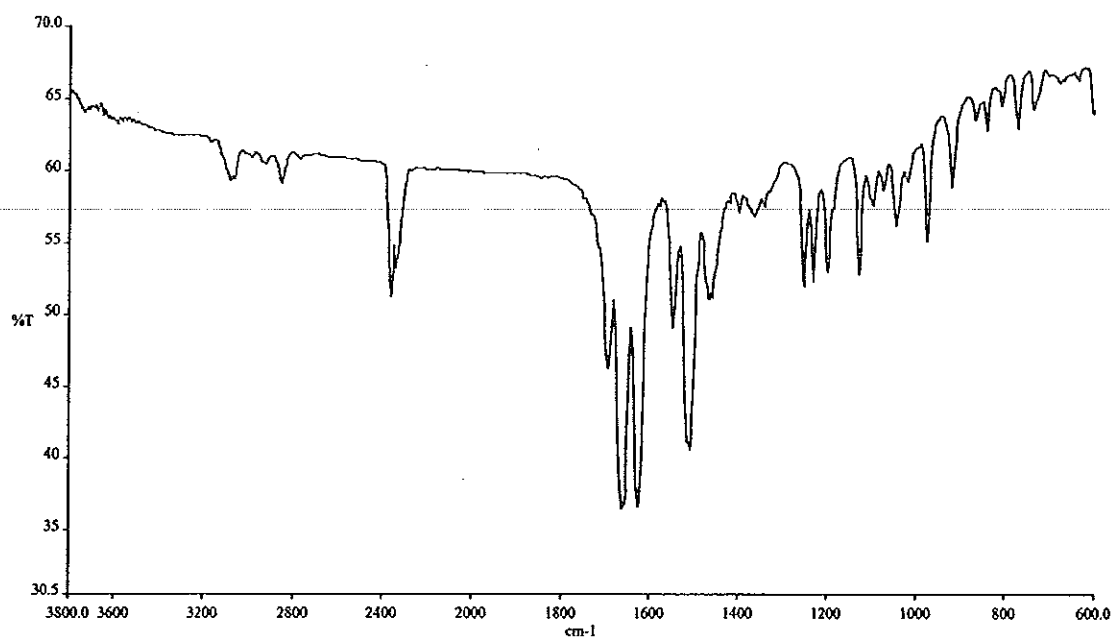


Figure A-41 IR (neat) spectrum of KF8

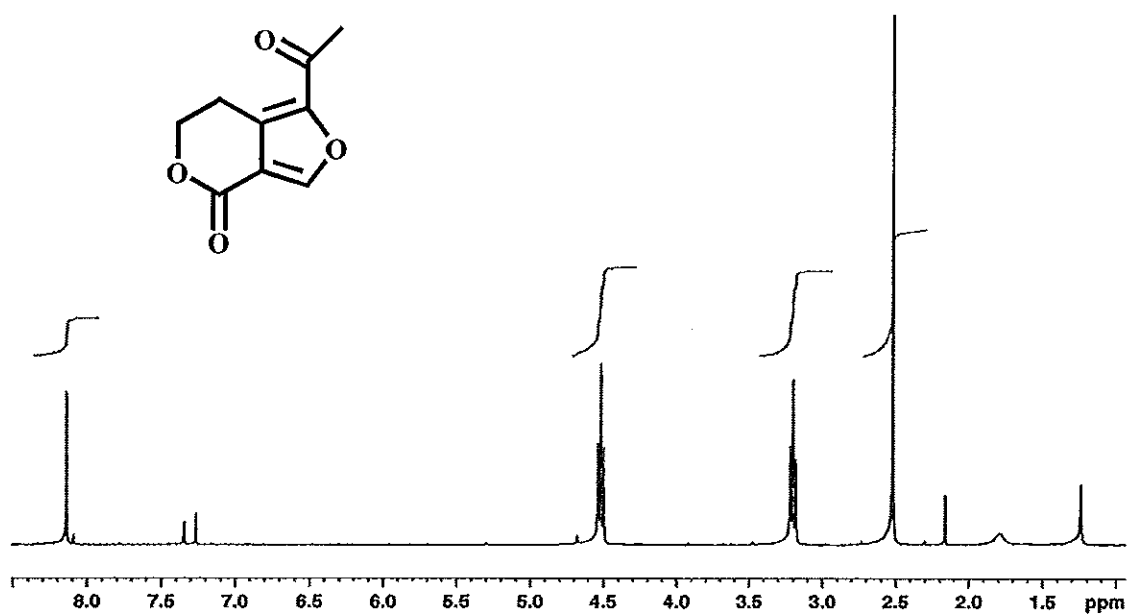


Figure A-42 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF9

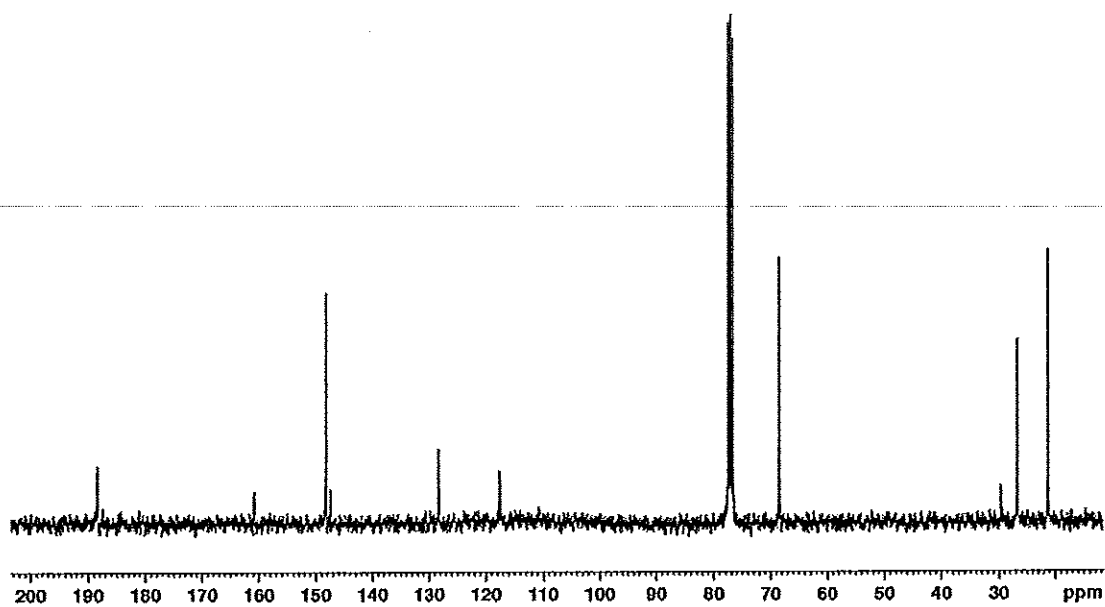


Figure A-43  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF9

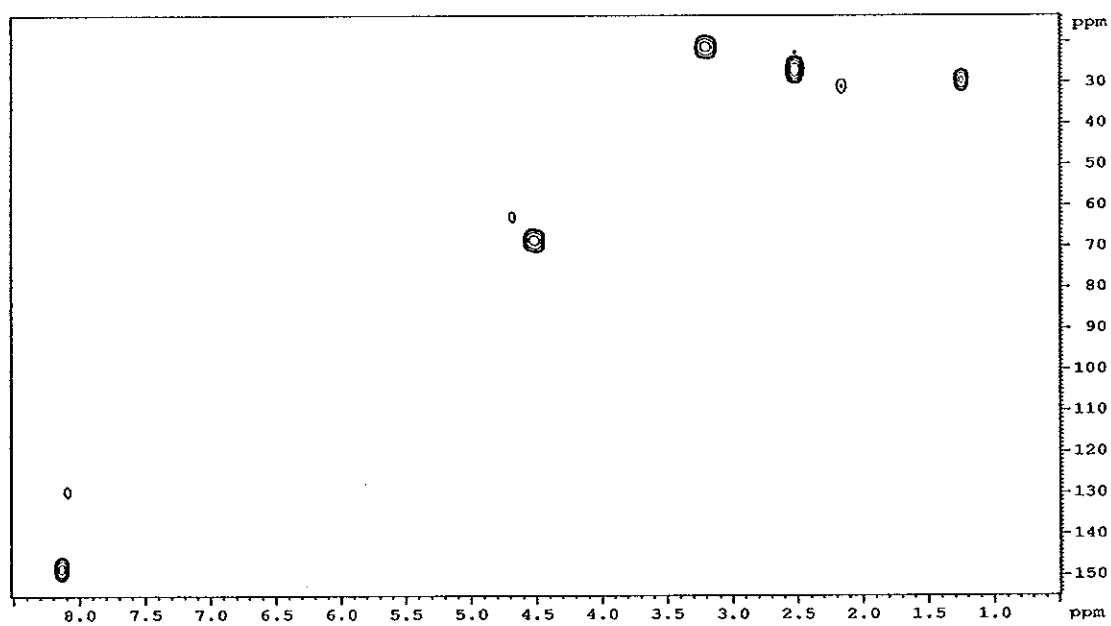


Figure A-44 2D HMQC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF9

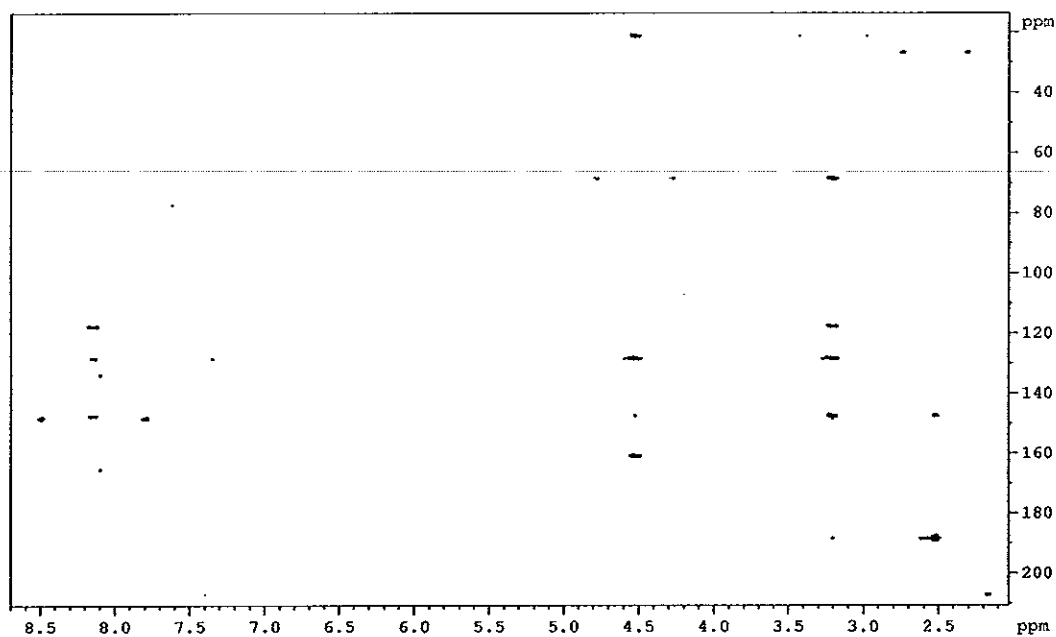


Figure A-45 2D HMBC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF9

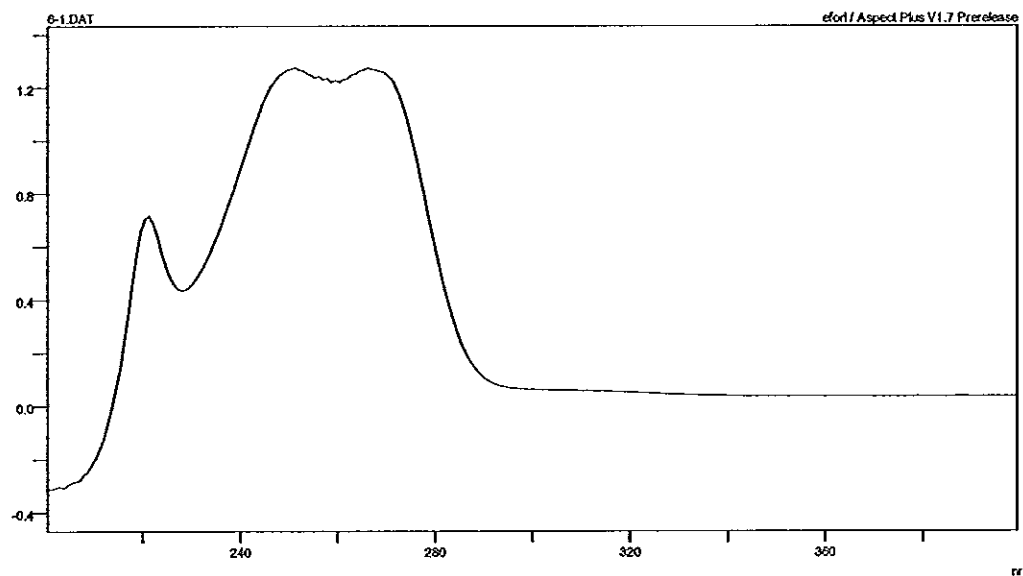


Figure A-46 UV (MeOH) spectrum of KF9

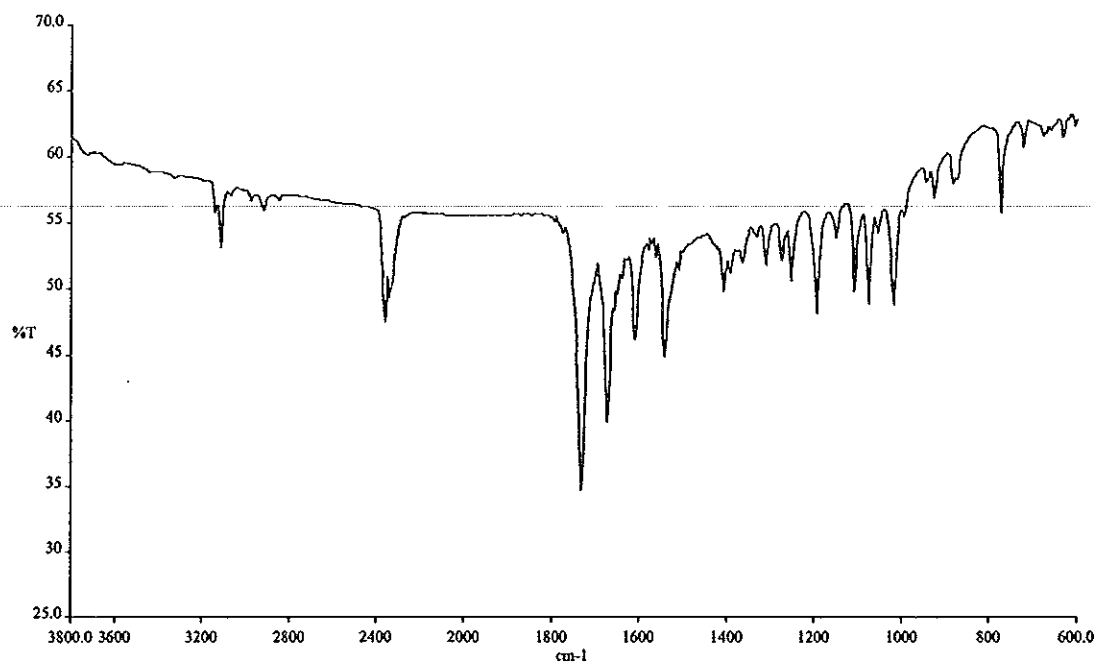


Figure A-47 IR (neat) spectrum of KF9

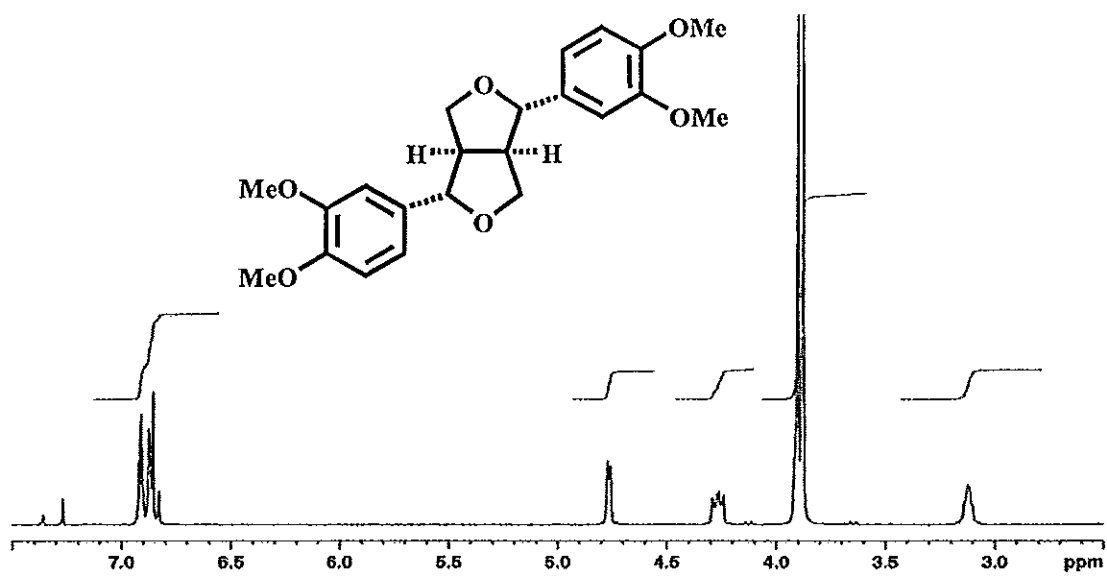


Figure A-48 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF10

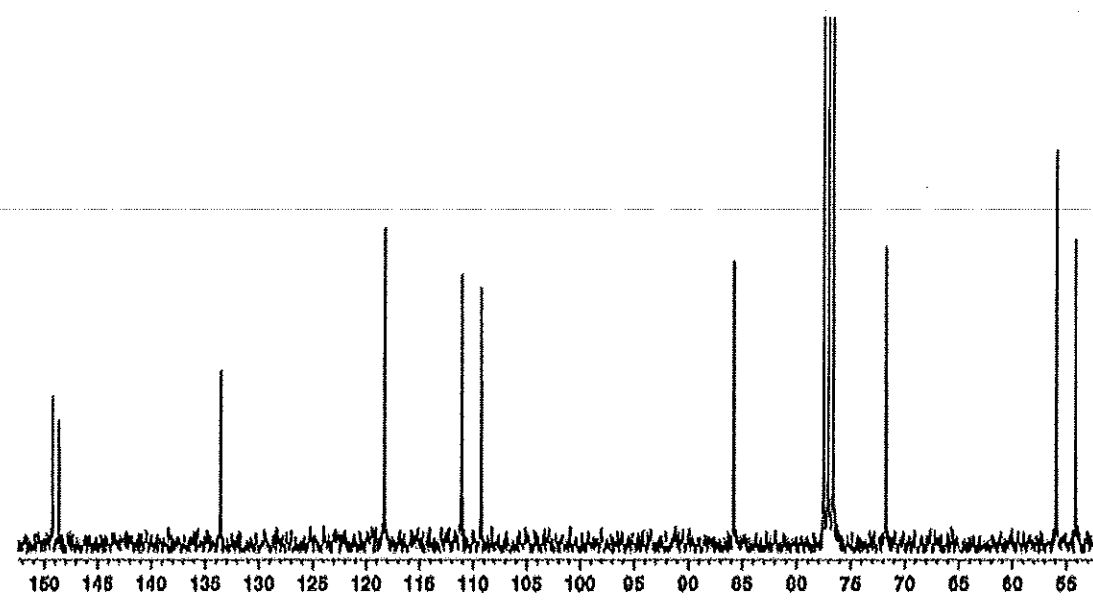


Figure A-49  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF10

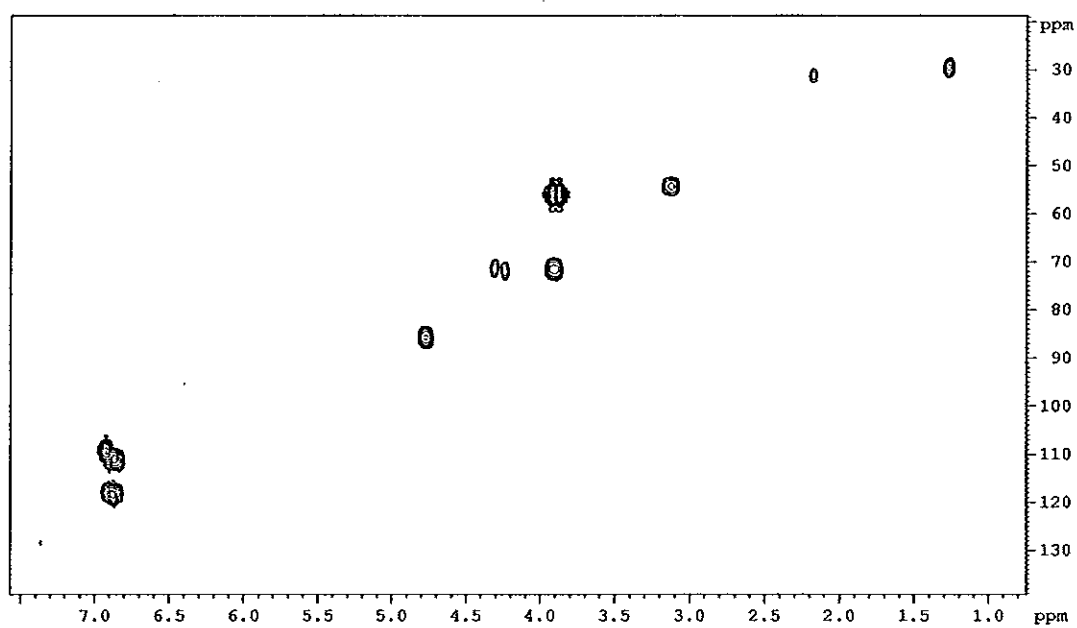


Figure A-50 2D HMQC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF10



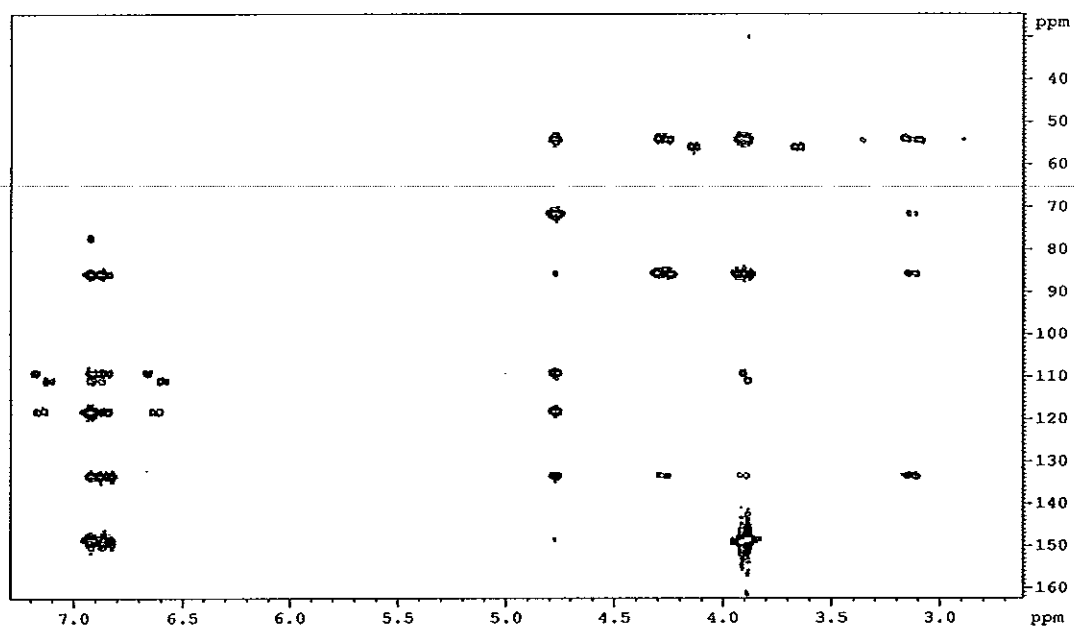


Figure A-51 2D HMBC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF10

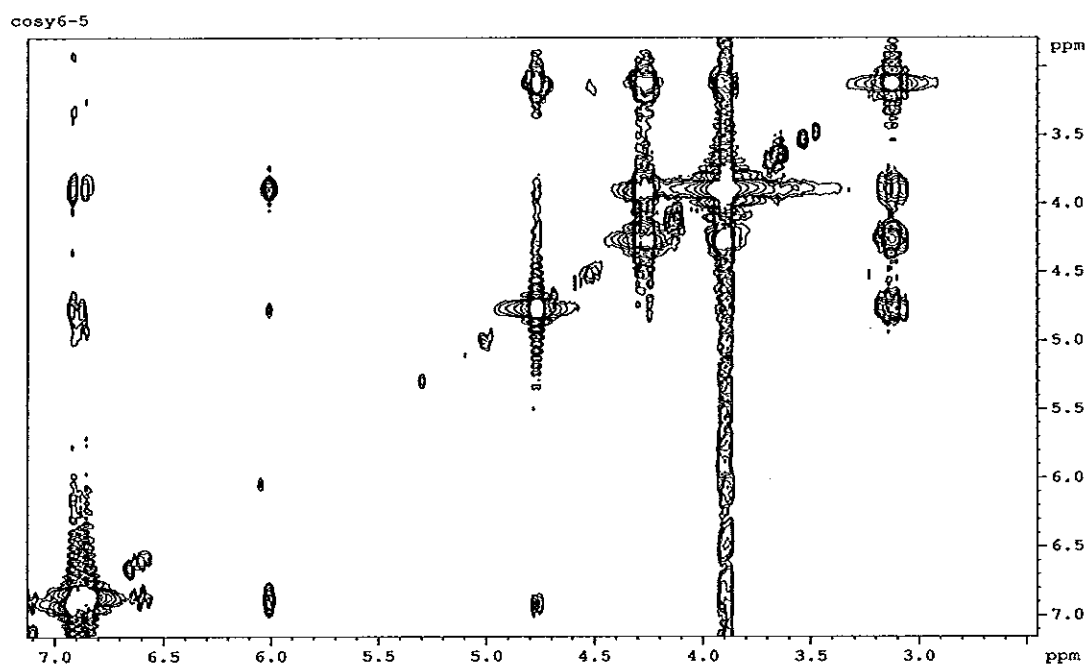


Figure A-52  $^1\text{H}$ - $^1\text{H}$  COSY ( $\text{CDCl}_3$ ) spectrum of KF10

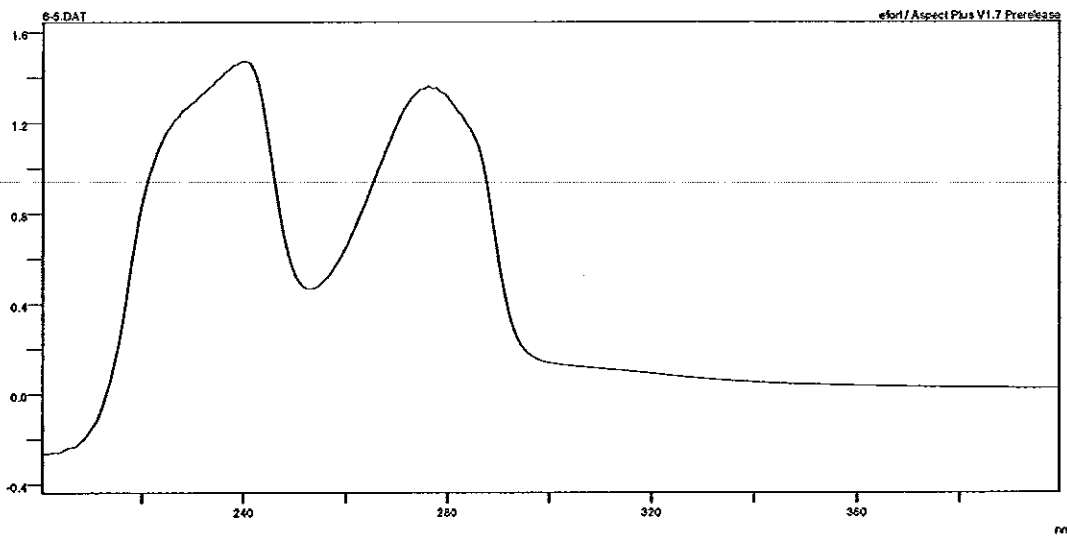


Figure A-53 UV (MeOH) spectrum of KF10

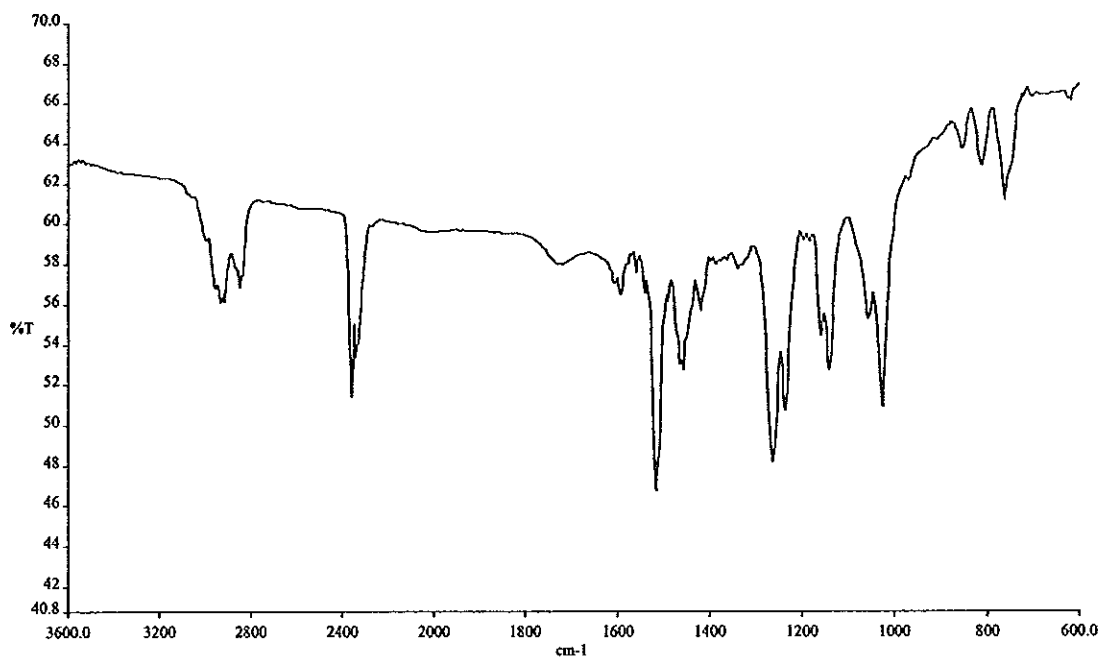


Figure A-54 IR (neat) spectrum of KF10

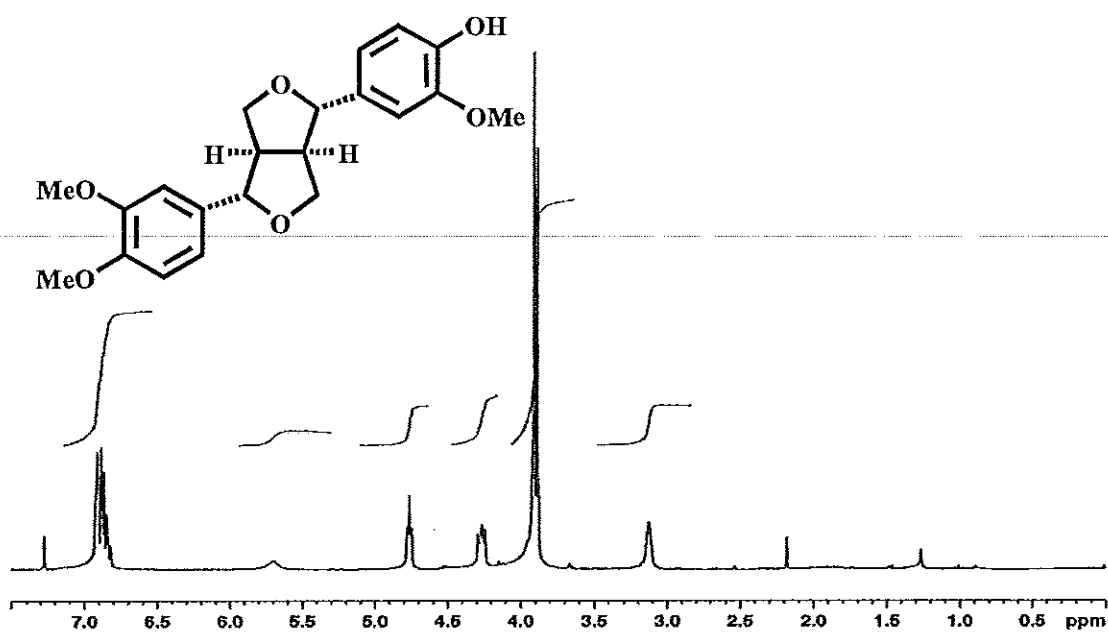


Figure A-55  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF11

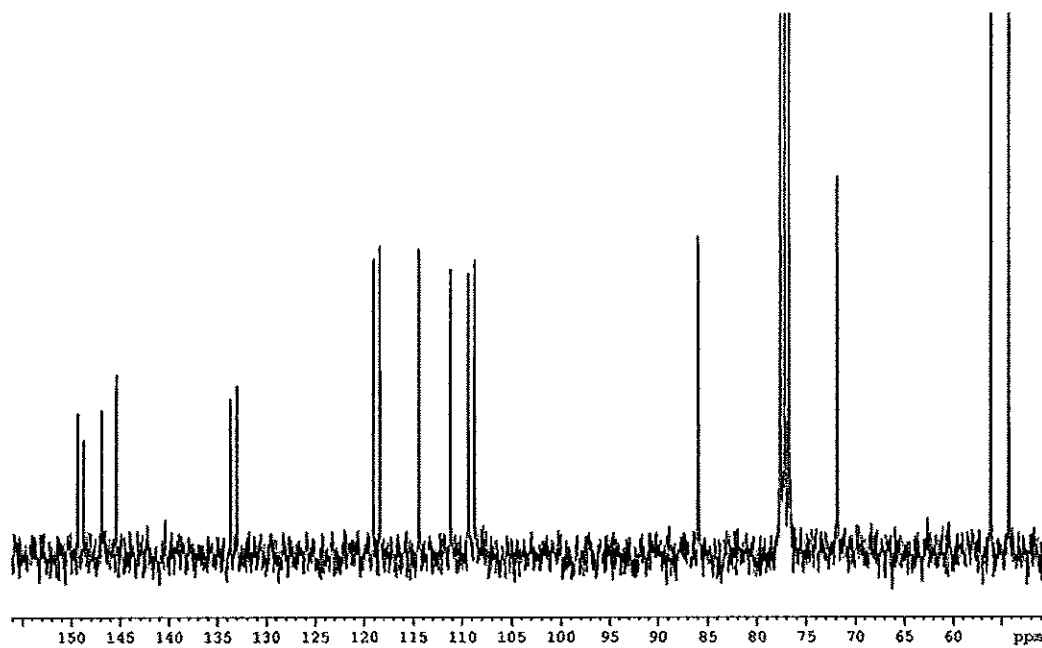


Figure A-56  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF11

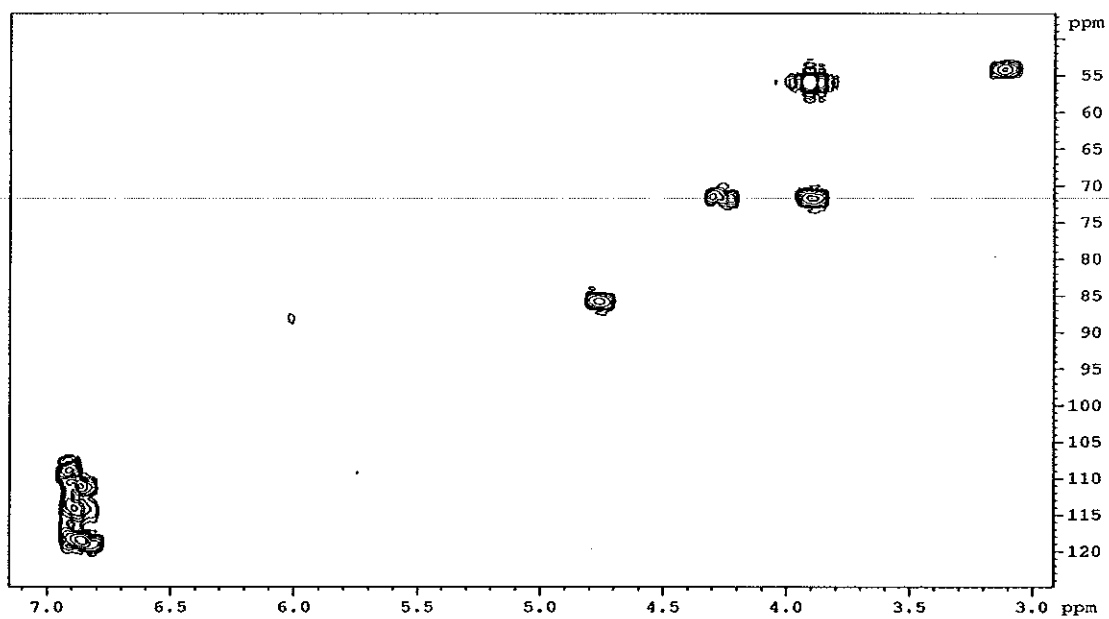


Figure A-57 2D HMQC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF11

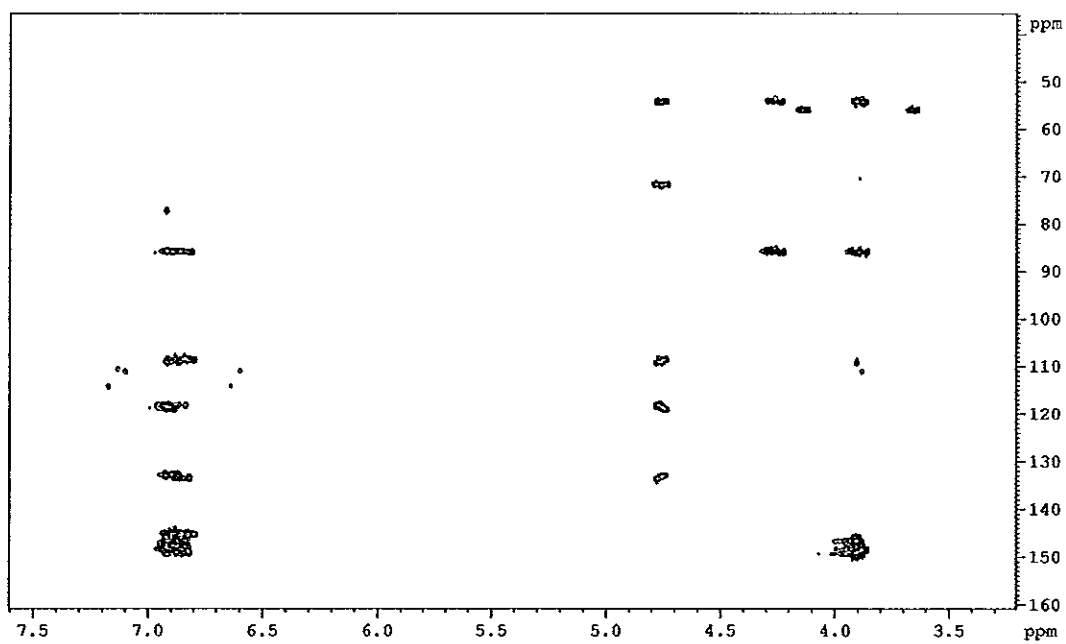
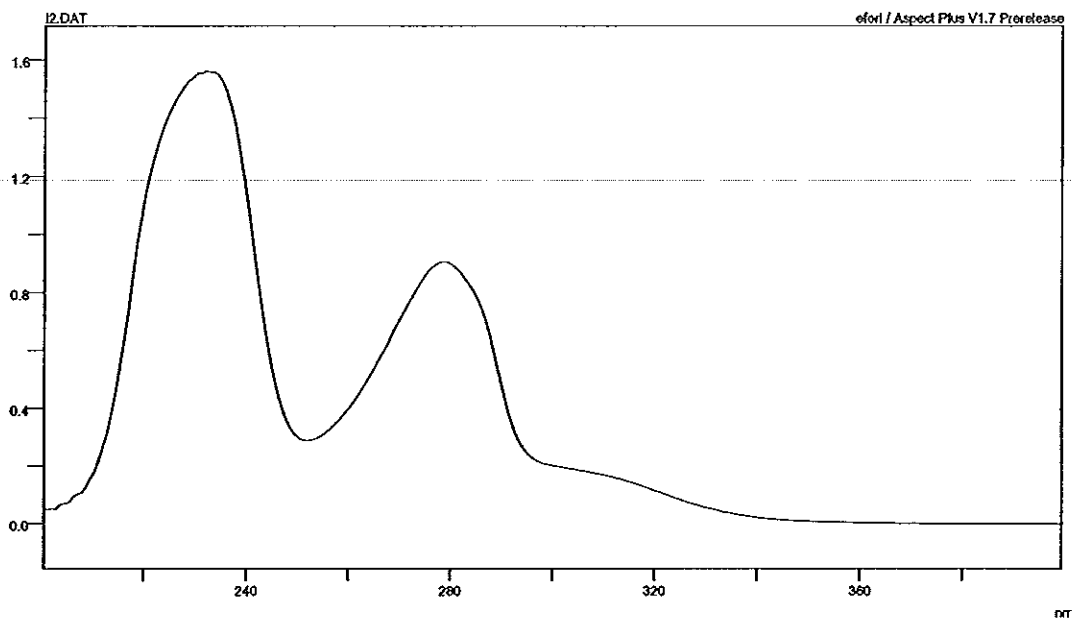
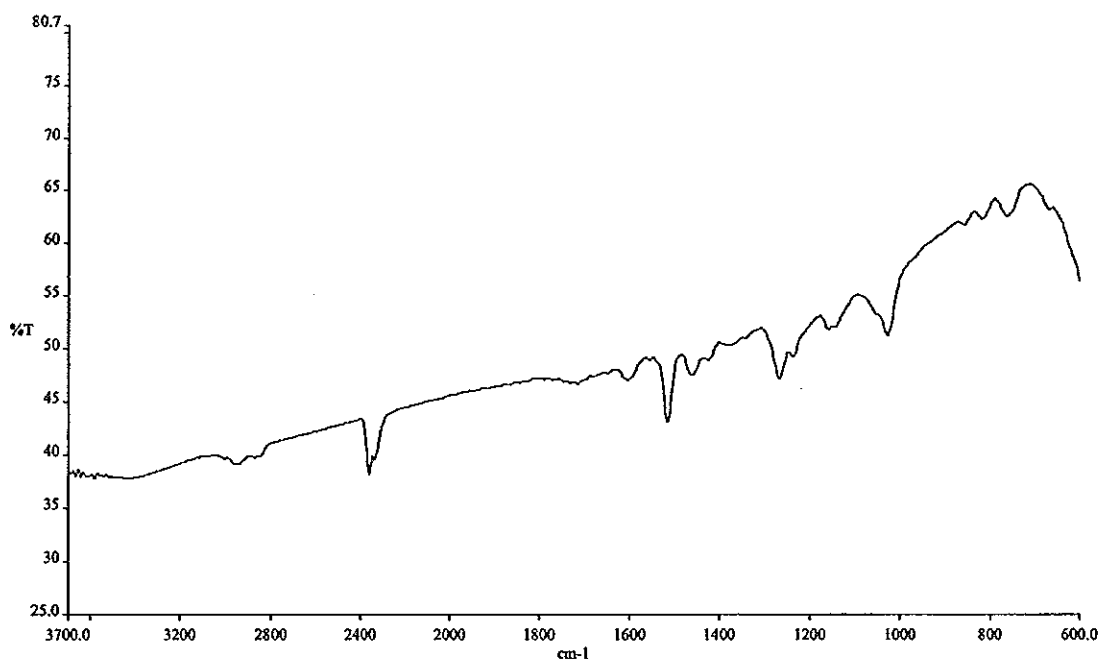


Figure A-58 2D HMBC (300 MHz) (CDCl<sub>3</sub>) spectrum of KF11



**Figure A-59** UV (MeOH) spectrum of KF11



**Figure A-60** IR (neat) spectrum of KF11

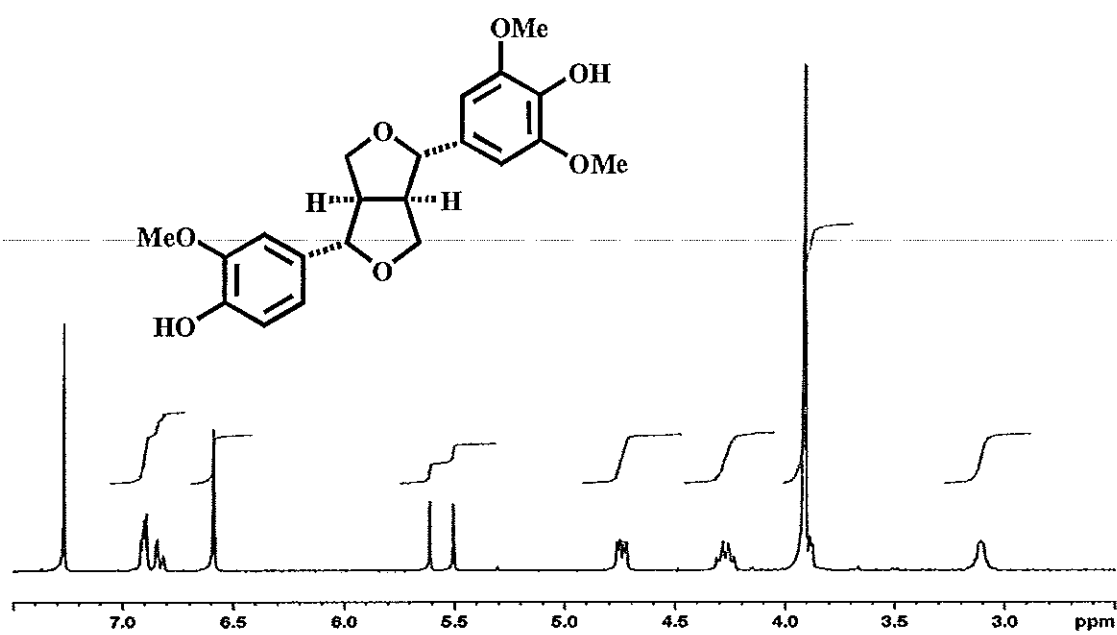


Figure A-61 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF12

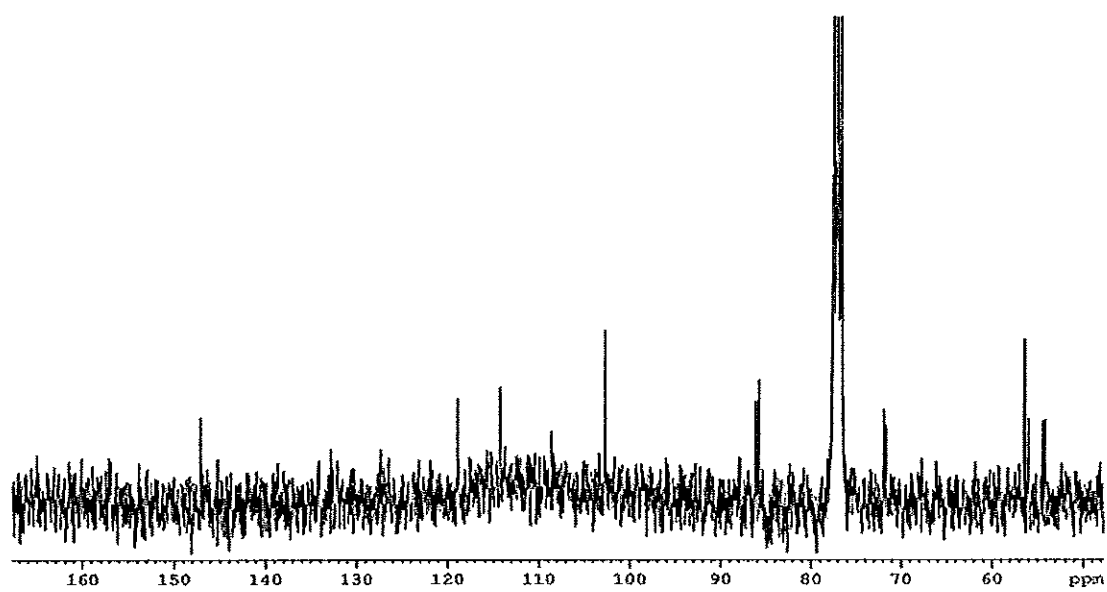


Figure A-62 <sup>13</sup>C NMR (75 MHz) (CDCl<sub>3</sub>) spectrum of KF12

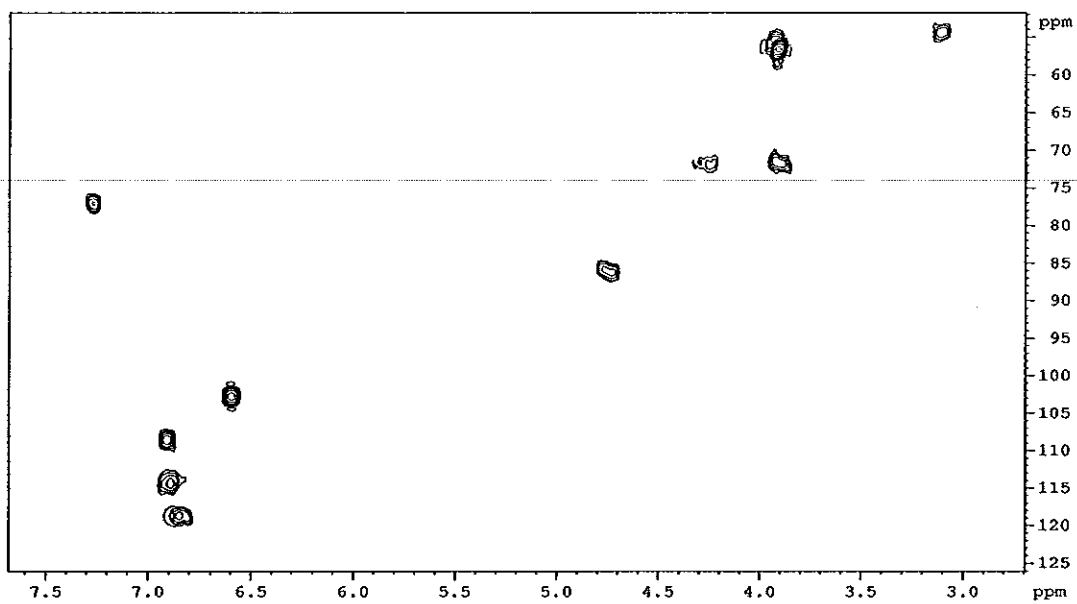


Figure A-63 2D HMQC (CDCl<sub>3</sub>) spectrum of KF12

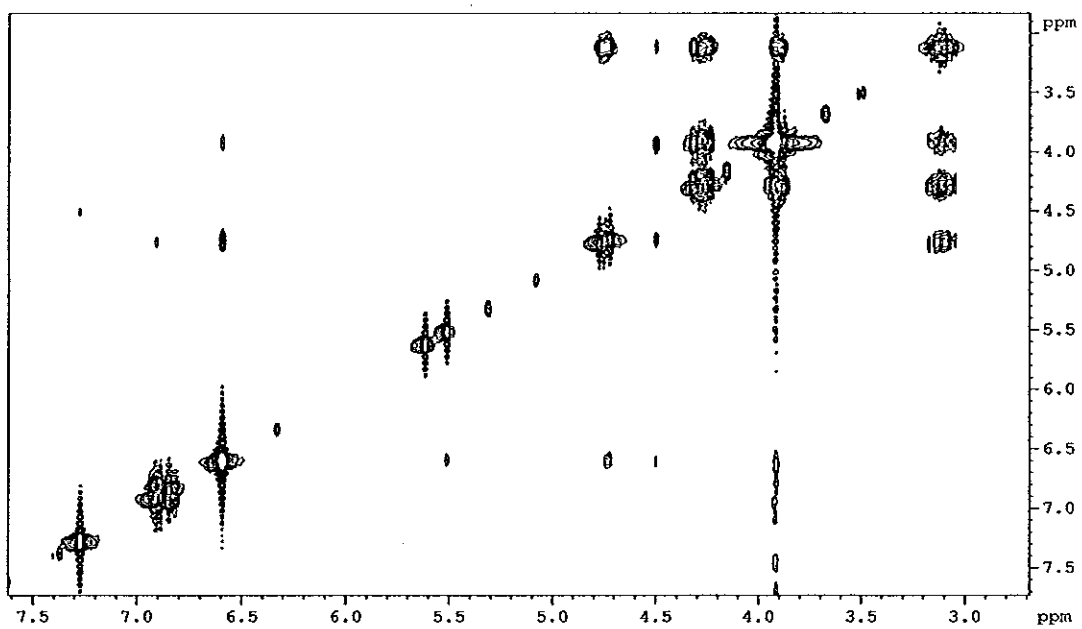


Figure A-64 <sup>1</sup>H-<sup>1</sup>H COSY (CDCl<sub>3</sub>) spectrum of KF12

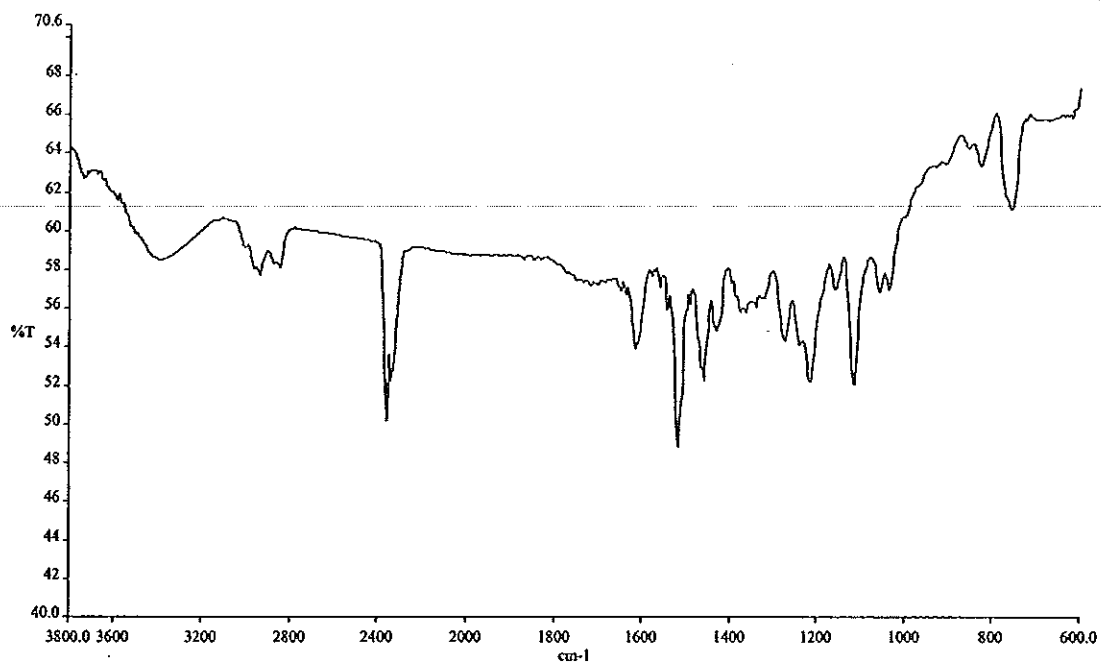


Figure A-65 IR (neat) spectrum of KF12

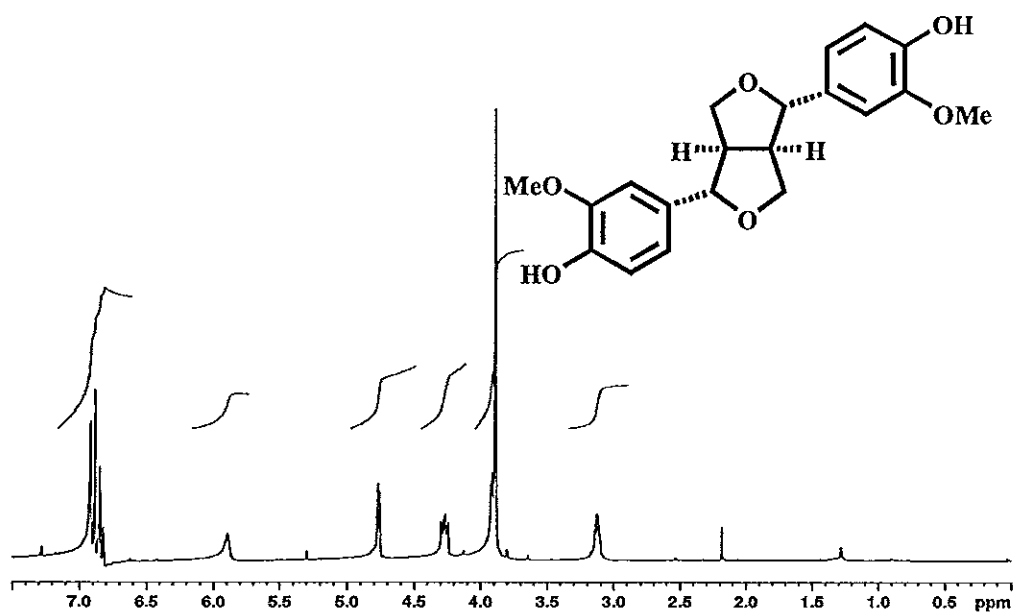


Figure A-66 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF13



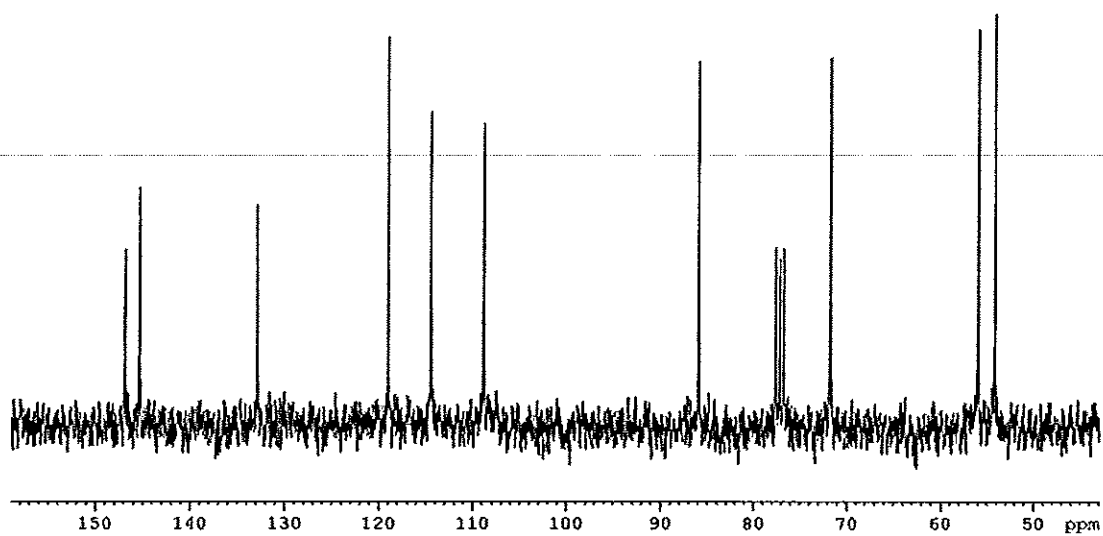


Figure A-67  $^{13}\text{C}$  NMR (75 MHz) ( $\text{CDCl}_3$ ) spectrum of KF12

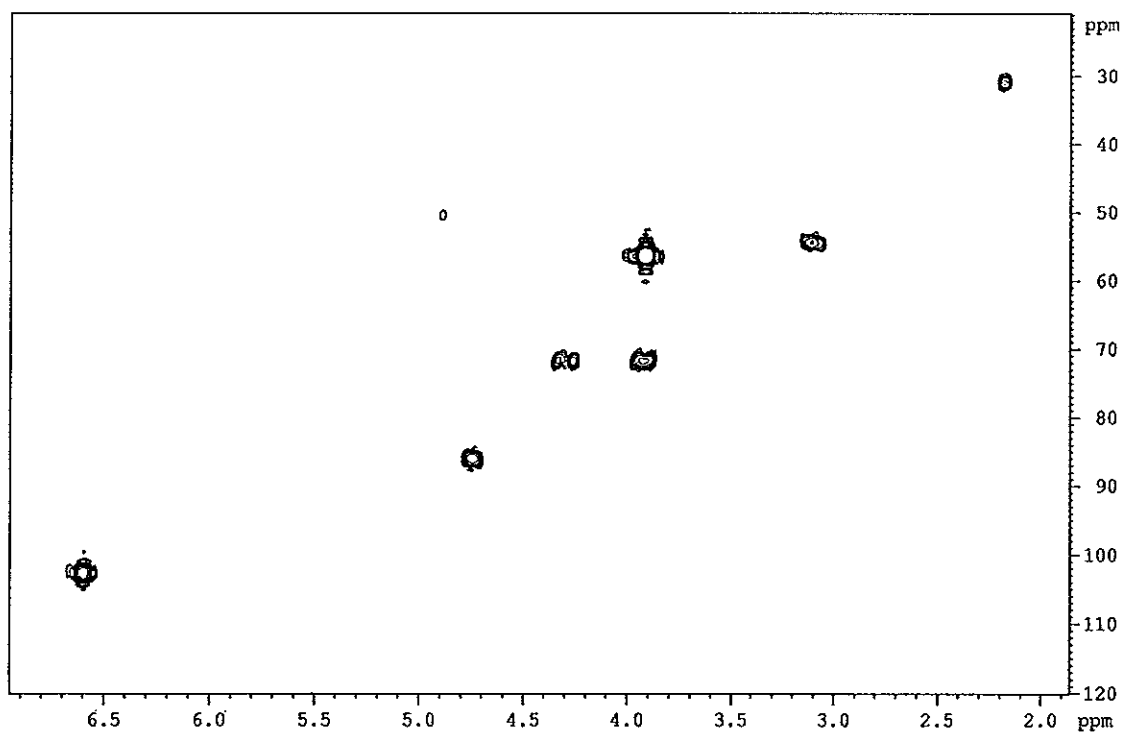


Figure A-68 2D HMQC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF13

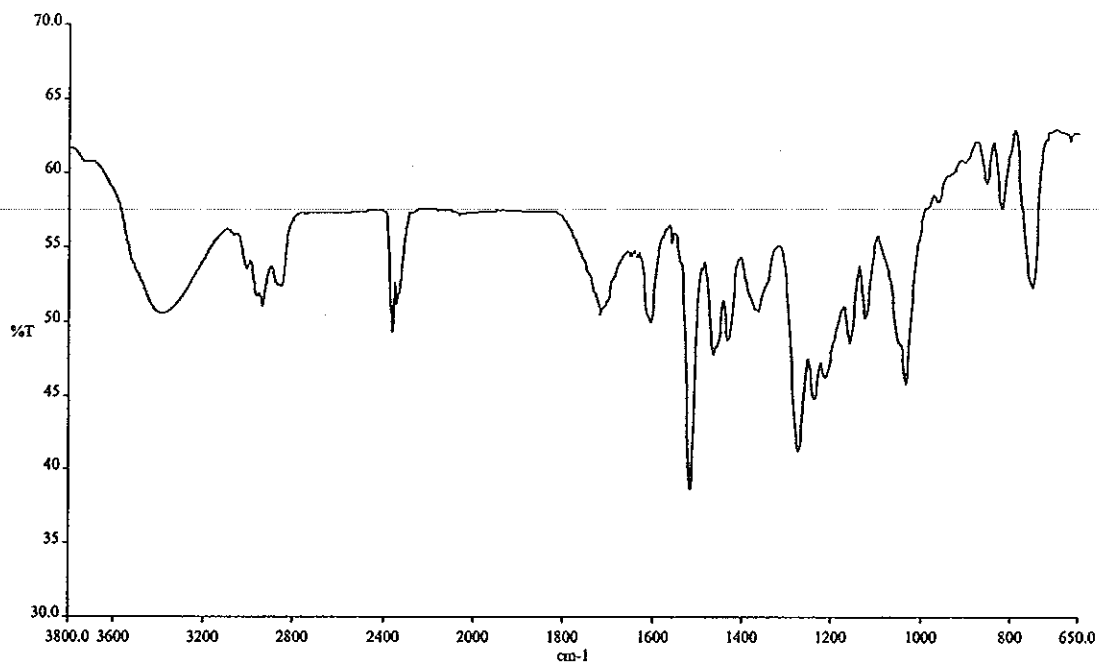


Figure A-69 IR (neat) spectrum of KF13

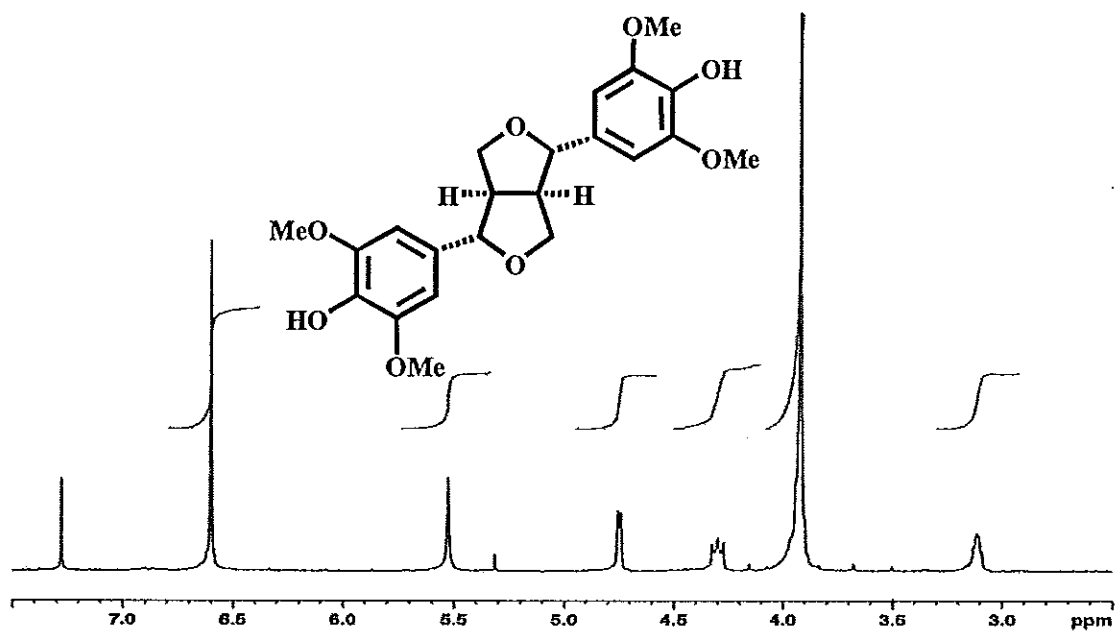


Figure A-70 <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>) spectrum of KF14

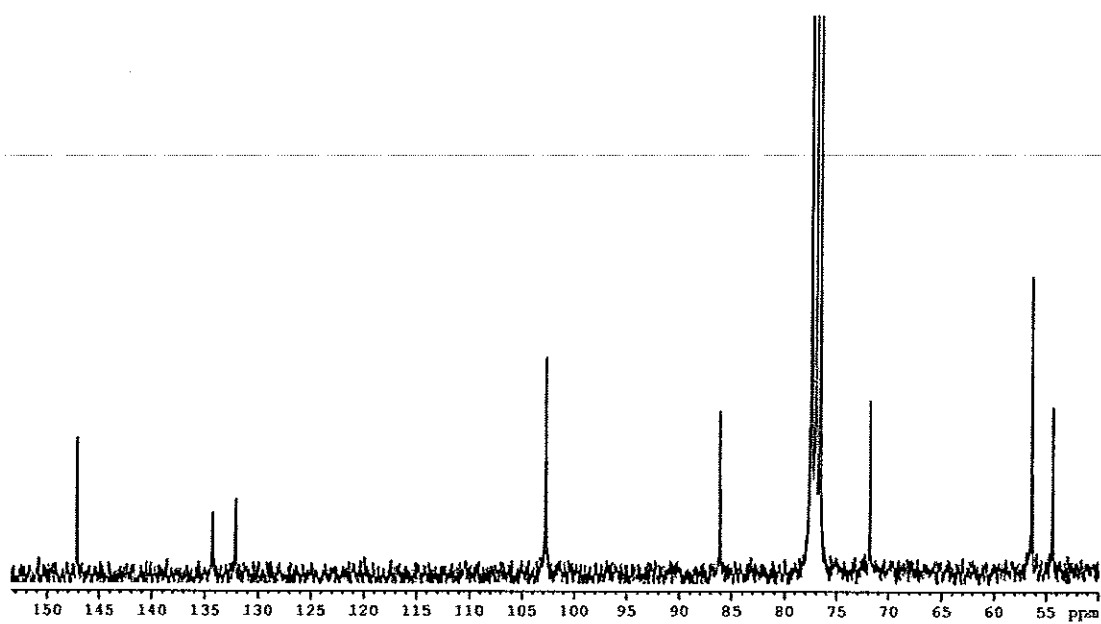


Figure A-71  $^{13}\text{C}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF14

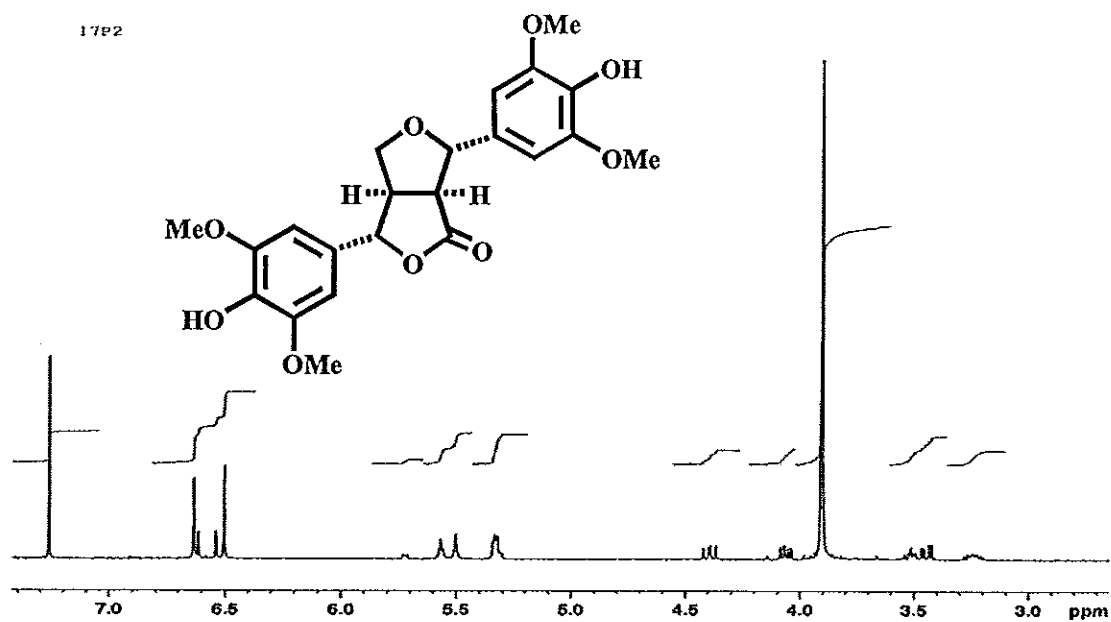


Figure A-72  $^1\text{H}$  NMR (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF15

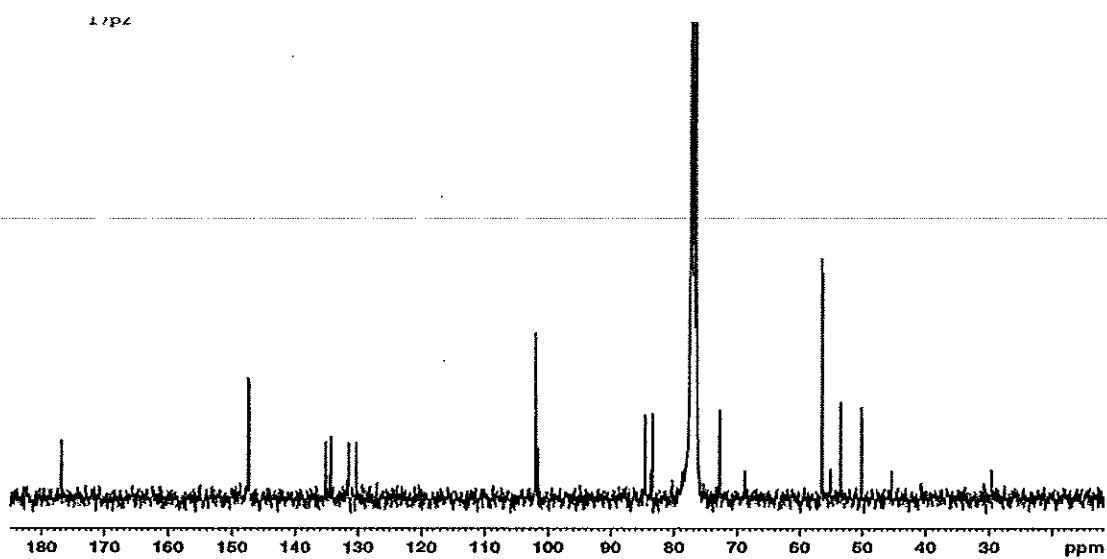


Figure A-73 <sup>13</sup>C NMR (75MHz) (CDCl<sub>3</sub>) spectrum of KF15

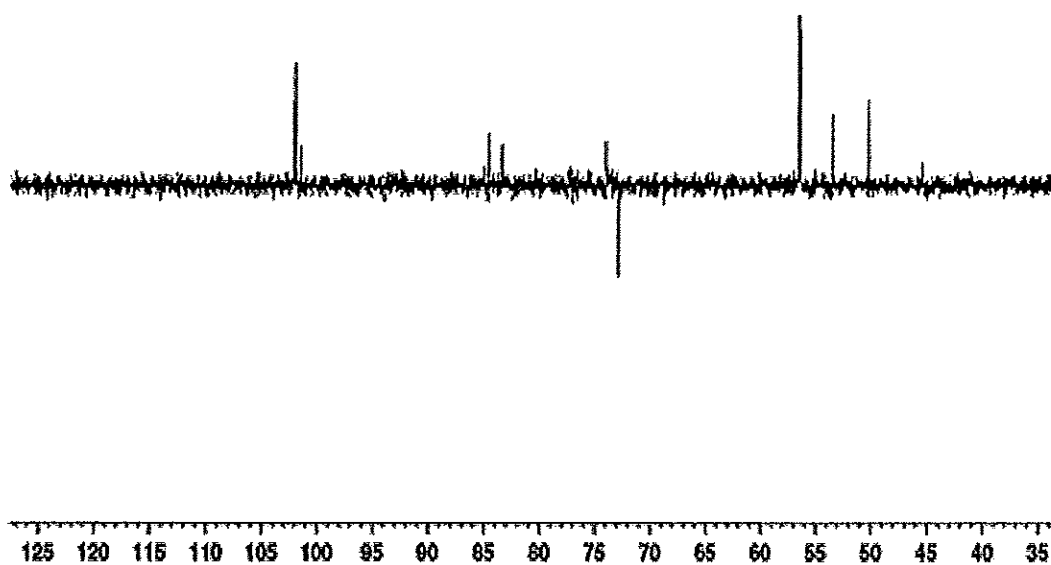


Figure A-74 DEPT 135° (CDCl<sub>3</sub>) spectrum of KF15

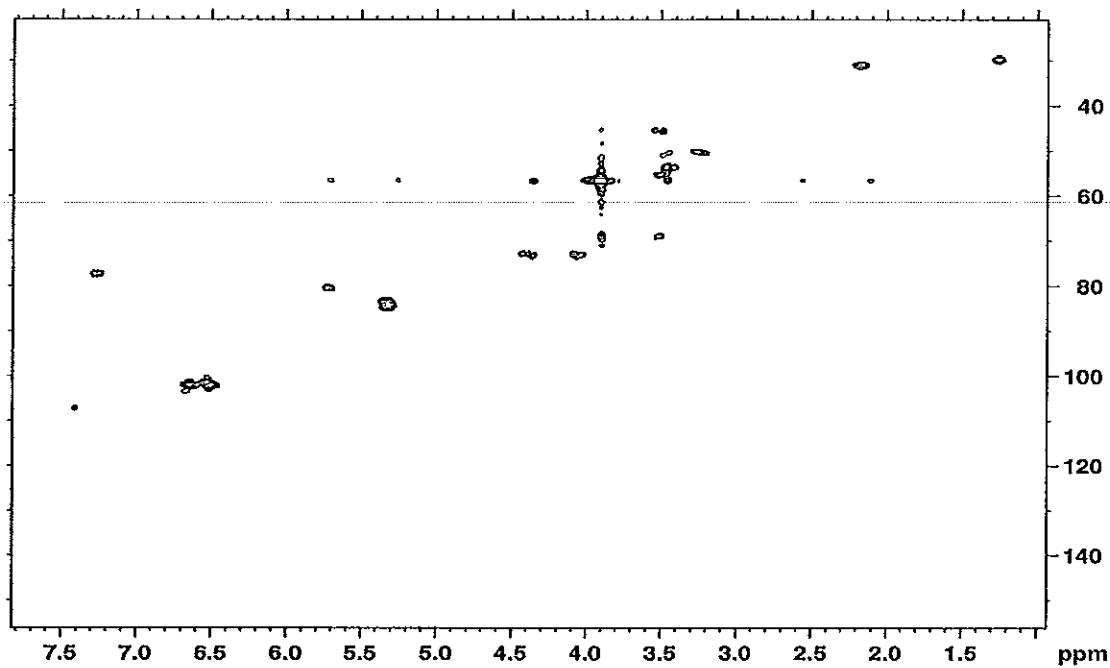


Figure A-75 2D HMQC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF15

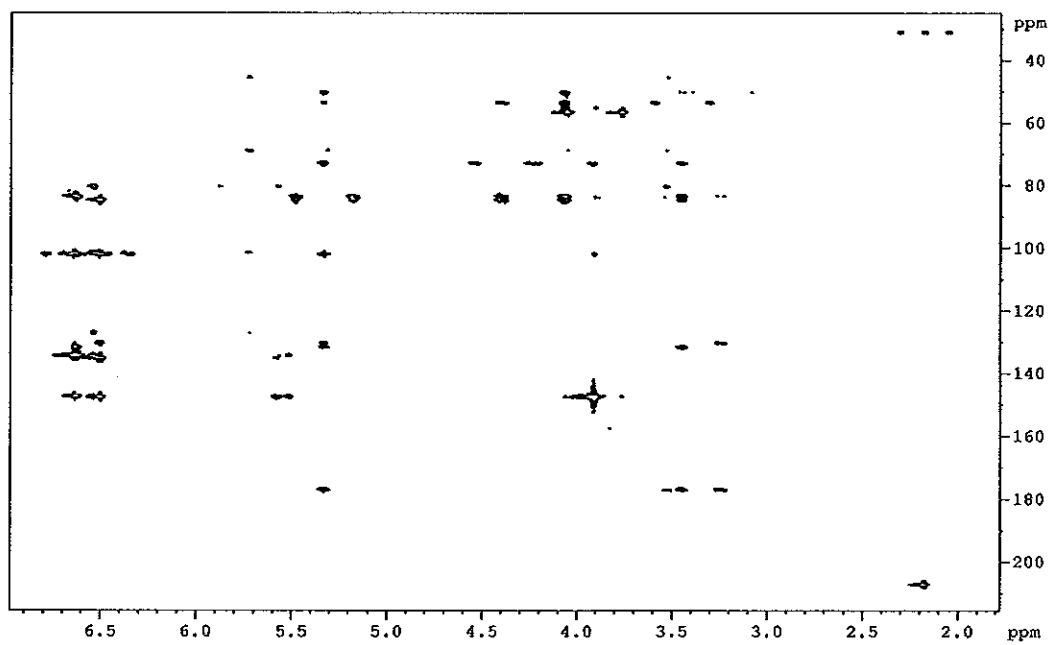


Figure A-76 2D HMBC (300 MHz) ( $\text{CDCl}_3$ ) spectrum of KF15

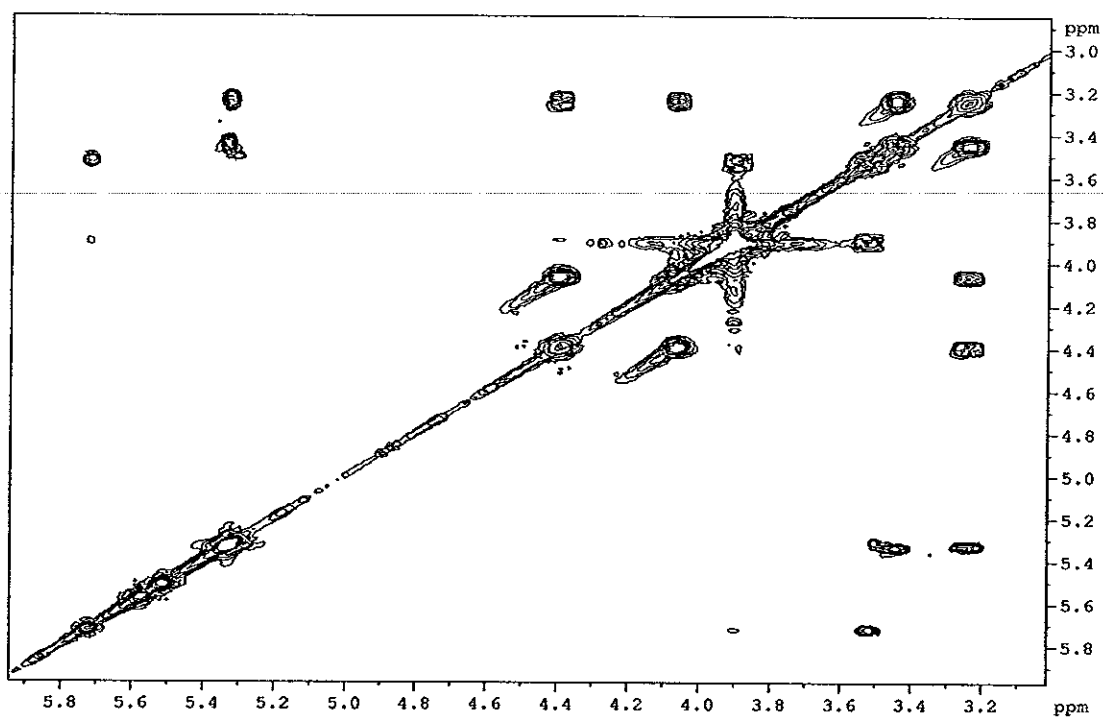


Figure A-77  $^1\text{H}$ - $^1\text{H}$  COSY ( $\text{CDCl}_3$ ) spectrum of KF15

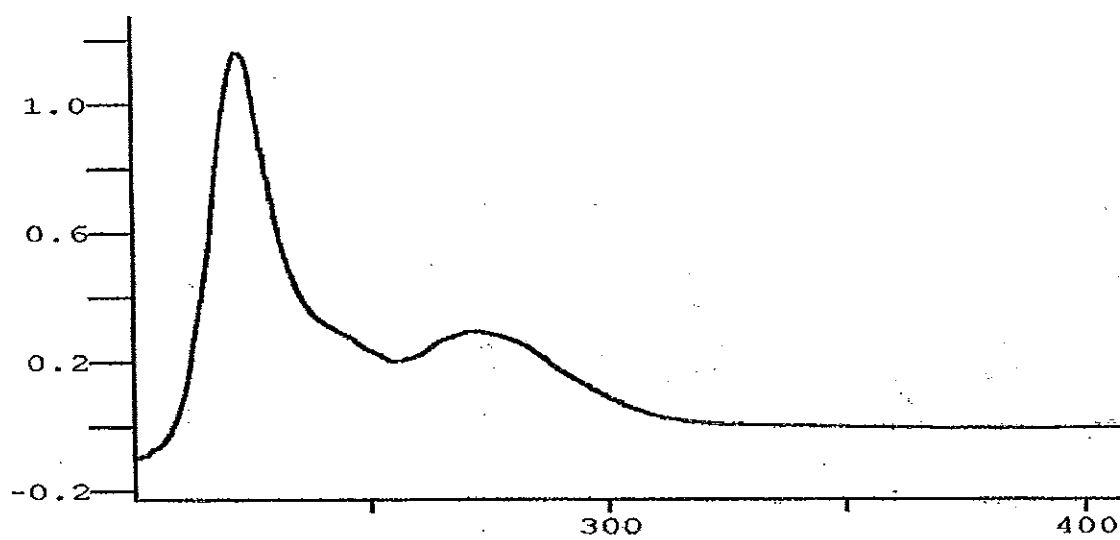


Figure A-78 UV (MeOH) spectrum of KF15

2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of known compounds from literaturesTable A-1  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of  $\alpha$ -Boswellic acid\* (Culioli *et al.*, 2003)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-type)
1	1.45 ( <i>m</i> ), 1.29 ( <i>m</i> )	33.6 (CH <sub>2</sub> )
2	2.22 ( <i>m</i> ), 1.59 ( <i>m</i> )	26.2 (CH <sub>2</sub> )
3	4.08 ( <i>t</i> , $J = 2.5$ Hz)	70.8 (CH)
4	-	47.4 (C)
5	1.49 ( <i>m</i> )	49.1 (CH)
6	1.85 ( <i>m</i> ), 1.70 ( <i>m</i> )	19.7 (CH <sub>2</sub> )
7	1.52 ( <i>m</i> ), 1.37 ( <i>m</i> )	32.7 (CH <sub>2</sub> )
8	-	39.8 (C)
9	1.66 ( <i>m</i> )	46.7 (CH)
10	-	37.6 (C)
11	1.88 ( <i>m</i> )	23.5 (CH <sub>2</sub> )
12	5.19 ( <i>t</i> , $J = 3.5$ Hz)	121.7 (CH)
13	-	145.1 (C)
14	-	41.9 (C)
15	1.77 ( <i>m</i> ), 1.00 ( <i>m</i> )	26.0 (CH <sub>2</sub> )
16	2.00 ( <i>m</i> ), 0.81 ( <i>m</i> )	26.9 (CH <sub>2</sub> )
17	-	32.5 (C)
18	1.96 ( <i>m</i> )	47.3 (CH)
19	1.70 ( <i>m</i> ), 1.02 ( <i>m</i> )	46.7 (CH <sub>2</sub> )
20	-	31.1 (C)
21	1.33 ( <i>m</i> ), 1.10 ( <i>m</i> )	34.7 (CH <sub>2</sub> )
22	1.44 ( <i>m</i> ), 1.22 ( <i>m</i> )	37.1 (CH <sub>2</sub> )
23	1.35 ( <i>s</i> )	24.2 (CH <sub>3</sub> )
24	-	183.2 (C)
25	0.89 ( <i>s</i> )	13.1 (CH <sub>3</sub> )
26	1.00 ( <i>s</i> )	16.7 (CH <sub>3</sub> )
27	1.15 ( <i>s</i> )	25.9 (CH <sub>3</sub> )

\*recorded in CDCl<sub>3</sub>

Table A-1 (Continued)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-type)
28	0.84 (s)	28.4 (CH <sub>3</sub> )
29	0.87 (s)	33.3 (CH <sub>3</sub> )
30	0.87 (s)	23.7 (CH <sub>3</sub> )

Table A-2 <sup>1</sup>H and <sup>13</sup>C NMR spectral data of Gentiogenol (Van der Sluis *et al.*, 1983)

position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)
1	9.88 (s)	185.7 (OCH)
2	7.95 (s)	163.3 (CH)
3	-	103.9 (C)
4	-	142.7 (C)
5	3.09 ( <i>t</i> *, <i>J</i> = 4.9 Hz)	22.6 (CH <sub>2</sub> )
6	4.43 ( <i>t</i> *, <i>J</i> = 4.9 Hz)	65.1 (CH <sub>2</sub> )
7	5.64 ( <i>q</i> , <i>J</i> = 6.5 Hz)	73.1 (CH)
8	-	120.2 (C)
9	1.39 ( <i>d</i> , <i>J</i> = 6.5 Hz)	19.8(CH <sub>3</sub> )
10	-	163.9 (C)

Note: NMR spectral data of gentiogenol in CDCl<sub>3</sub> at 90 MHz

\* = At 300 MHz <sup>1</sup>H NMR spectrum the signals of H-6 and H-7 occur as multiples



Table A-3  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of Fagraldehyde\* (Jonville *et al.*, 2008)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)
1	7.61 ( <i>d</i> , $J = 1.4$ Hz)	146.9 (CH)
2	-	165.6 (C)
3	-	104.0 (C)
4	-	145.0 (C)
5	8.37 ( <i>d</i> , $J = 5.7$ Hz)	109.2 (CH)
6	7.63 ( <i>d</i> , $J = 5.7$ Hz)	153.4 (CH)
7	5.27 ( <i>qd</i> , $J = 6.6, 1.4$ Hz)	70.5 (CH)
8	-	121.2 (C)
9	1.70 ( <i>d</i> , $J = 6.5$ Hz)	19.8 (CH <sub>3</sub> )
10	10.22 ( <i>s</i> )	190.8 (CHO)

\*recorded in CDCl<sub>3</sub> at 500 MHz

Table A-4  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of Angelone\* (Mulholland *et al.*, 2006)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)
1	8.12 ( <i>s</i> )	148.2 (CH)
2	-	117.6 (C)
3	-	128.3 (C)
4	-	147.4 (C)
5	-	188.3 (C=O)
6	2.50 ( <i>s</i> )	26.8 (CH <sub>3</sub> )
7	-	160.8 (C=O)
8	3.19 ( <i>t</i> , $J = 6.0$ Hz)	21.3 (CH <sub>2</sub> )
9	4.50 ( <i>t</i> , $J = 6.0$ Hz)	68.5 (CH <sub>2</sub> )

\*recorded in CDCl<sub>3</sub>

**Table A-5**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of **Eudesmin\*** (Latip *et al.*, 1999)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)
1/5	3.12 ( <i>m</i> )	54.0 (CH)
2/6	4.76 ( <i>d</i> , $J = 4.0$ Hz)	85.5 (CH)
4 <sub>e</sub> /8 <sub>e</sub>	4.26 ( <i>dd</i> , $J = 7.0, 9.0$ Hz)	71.5 (CH <sub>2</sub> )
4 <sub>a</sub> /8 <sub>a</sub>	3.86-3.96 ( <i>m</i> )	71.5 (CH <sub>2</sub> )
1'/1''	-	133.3 (C)
2'/2'', 5'/5'', 6'/6''	6.84-6.92 (Ar, <i>m</i> )	109.5, 110.9, 118.5 (CH)
3'/3''	-	148.9 (C)
4'/4''	-	149.4 (C)
3'/3''-OCH <sub>3</sub>	3.90 ( <i>s</i> )	55.2 (2×OCH <sub>3</sub> )
4'/4''-OCH <sub>3</sub>	3.86 ( <i>s</i> )	55.2 (2×OCH <sub>3</sub> )

\*recorded in CDCl<sub>3</sub>**Table A-6**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of **Pinorisinol\*** (Latip *et al.*, 1999.)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)
1/5	3.06 ( <i>m</i> )	54.0 (CH)
2/6	4.77 (2H, <i>d</i> , $J = 4.5$ Hz,)	85.5 (CH)
4 <sub>e</sub> /8 <sub>e</sub>	4.27 (2H, <i>m</i> )	71.7 (CH <sub>2</sub> )
4 <sub>a</sub> /8 <sub>a</sub>	3.91 (2H, <i>m</i> )	71.7 (CH <sub>2</sub> )
1'/1''	-	133.0 (C)
2'/2''	6.88 ( <i>d</i> , $J = 1.5$ Hz)	108.8 (CH)
3'/3''	-	146.7 (C)
4'/4''	-	145.3 (C)
5'/5''	6.90 ( <i>d</i> , $J = 8.1$ Hz)	114.3 (CH)
6'/6''	6.85 ( <i>dd</i> , 8.1, 1.5)	119.0 (CH)
3'/3''-OCH <sub>3</sub>	3.89 ( <i>s</i> )	56.0
4'/4''-OH	5.89 ( <i>bs</i> )	-

\*recorded in CDCl<sub>3</sub>

**Table A-7**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of Syringaresinol\* (Lin-gen *et al.*, 1982)

Position	$\delta_{\text{H}}$ (multiplicity)	$\delta_{\text{C}}$ (C-Type)
1/5	3.15 ( <i>m</i> )	49.5 (CH)
2/6	4.78 ( <i>d</i> , $J = 4.0$ Hz)	84.1 (CH)
4 <sub>e</sub> /8 <sub>e</sub>	4.31 ( <i>m</i> )	68.7 (CH <sub>2</sub> )
4 <sub>a</sub> /8 <sub>a</sub>	3.95( <i>m</i> )	68.7 (CH <sub>2</sub> )
1'/1''	-	130.0 (C)
2'/2'', 6'/6''	6.62 ( <i>s</i> )	103.0 (CH)
3'/3'', 5'/5''	-	147.0 (C)
4'/4''	-	133.8 (C)
3'/3'',5'/5''-OCH <sub>3</sub>	3.91 (6H, <i>s</i> )	56.3 (4×OCH <sub>3</sub> )
4'/4''-OH	5.62 (2H, <i>bs</i> )	-

\*recorded in CDCl<sub>3</sub>

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**Scholarship Awards during Enrolment**

Center for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education

**List of Publication and Proceedings**

Kaodeeya Kaikaew and Wilawan Mahabusarakam. "Furofuran lignans from the stem bark of *Fagraea fragrans* Roxb." BioScience for the Future 2010, The 60<sup>th</sup> Anniversary of His Majesty the King's Accession to the Throne International Convention Center, Prince of Songkla University, Thailand, 7 October 2010 (Oral presentation).