Chemical Constituents from the Stem of *Caesalpinia pulcherrima*

Wirote Pranithanchai

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Organic Chemistry

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Thesis Title	Chemical Constituents from the Stem of *Caesalpinia pulcherrima*
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Major Program	Organic Chemistry

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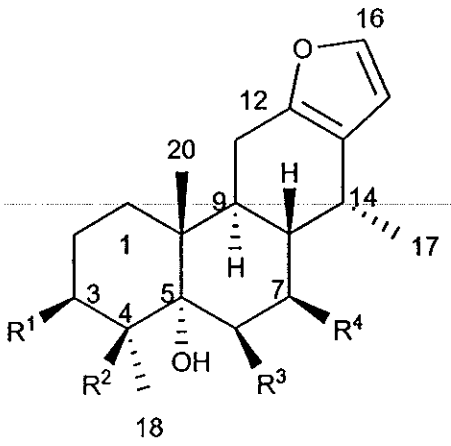
ชื่อวิทยานิพนธ์	องค์ประกอบทางเคมีจากลำต้นหางนกยูงไทย
ผู้เขียน	นายวิโรจน์ ประณิธานชัย
สาขาวิชา	เคมีอินทรีย์
ปีการศึกษา	2551

บทคัดย่อ

การศึกษาองค์ประกอบทางเคมีของส่วนสกัดเมทิลีนคลอไรด์จากลำต้นของหางนกยูงไทย สามารถแยกได้สารใหม่ประเภทไดเทอร์พีนอยด์ 6 สาร คือ pulcherrin A (**CP1**), pulcherrin B (**CP2**), pulcherrin C (**CP3**), neocaesalpin P (**CP4**), neocaesalpin Q (**CP5**) และ neocaesalpin R (**CP6**) และประเภทเฟอร์รูลิกเอสเทอร์ 1 สาร คือ tritriacontyl ferrulate (**CP15**) นอกจากนี้ยังพบสารที่มีการรายงานแล้ว 8 สาร คือ isovouacapenol C (**CP7**), 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol (**CP8**), pulcherrimin E (**CP9**), pulcherrimin C (**CP10**), α-cadinol (**CP11**), 7-hydroxycadalene (**CP12**), teucladiol (**CP13**) and bonducellin (**CP14**) โครงสร้างของสารประกอบเหล่านี้วิเคราะห์โดยใช้ข้อมูลทางสเปกโทรสโกปี



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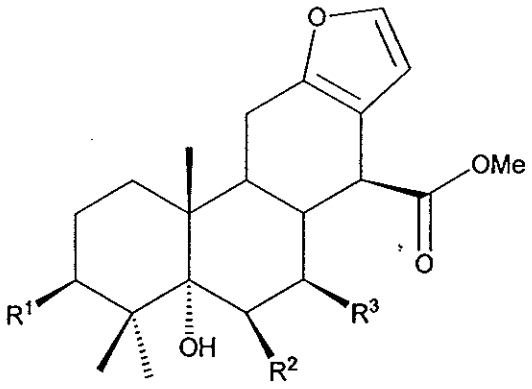
CP2 R^1 = OCOPh, R^2 = Me, R^3 = H, R^4 = OH

CP7 R^1 = H, R^2 = Me, R^3 = OCOPh, R^4 = OH

CP8 R^1 = H, R^2 = Me, R^3 = OCOCH=CHPh, R^4 = OH

CP9 R^1 = OCOPh, R^2 = COOH, R^3 = OCOPh, R^4 = OAc

CP10 R^1 = H, R^2 = COOH, R^3 = OCOPh, R^4 = OCOPh



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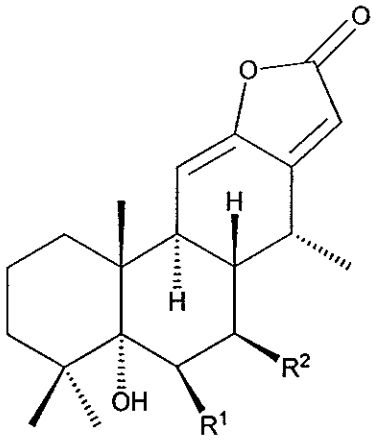

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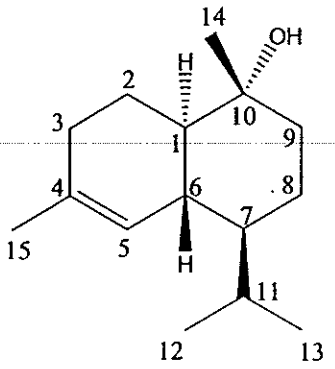

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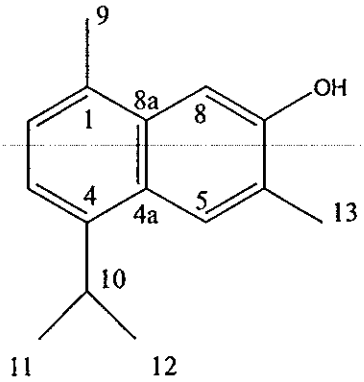

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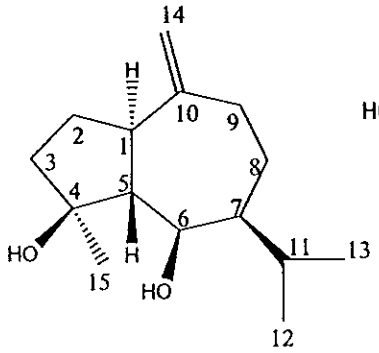

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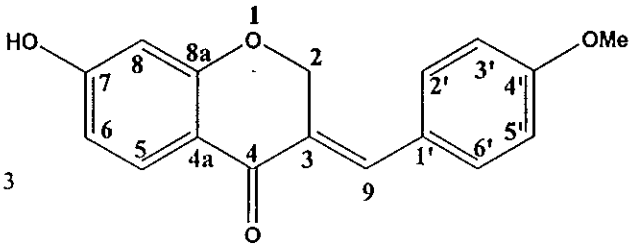

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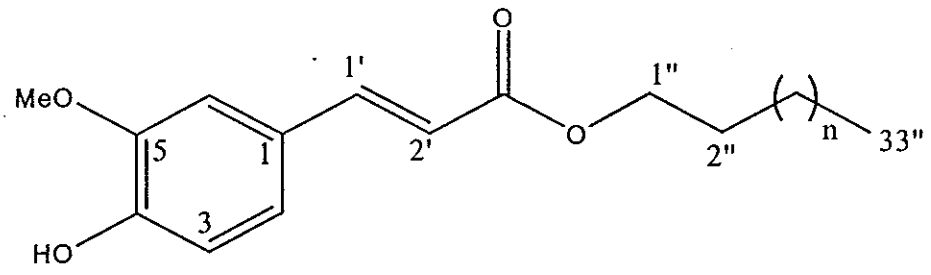

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Thesis Title	Chemical Constituents from the Stem of *Caesalpinia pulcherrima*
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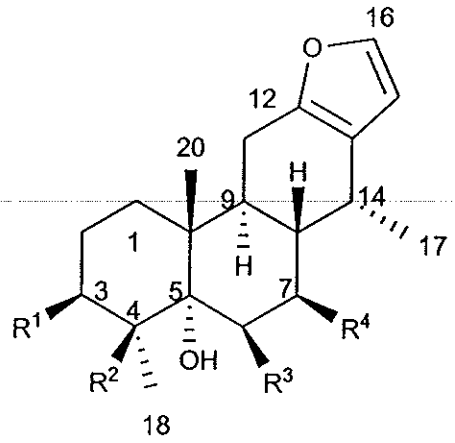
Major Program	Organic Chemistry
Academic Year	2008

ABSTRACT

Investigation of the methylene chloride extract of the stem of *Caesalpinia pulcherrima* resulted in six new cassane diterpenoids: pulcherrin A (**CP1**), pulcherrin B (**CP2**), pulcherrin C (**CP3**), neocaesalpin P (CP4), neocaesalpin Q (**CP5**) and neocaesalpin R (**CP6**) and a new ferrulic ester: tritriacontyl ferrulate (**CP15**), together with eight known compounds: isovouacapenol C (**CP7**), 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol (**CP8**), pulcherrimin E (**CP9**), pulcherrimin C (**CP10**), α-cadinol (**CP11**), 7-hydroxycadalene (**CP12**), teucladiol (**CP13**) and bonducellin (**CP14**). Their structures were elucidated on the basis of spectroscopic data.



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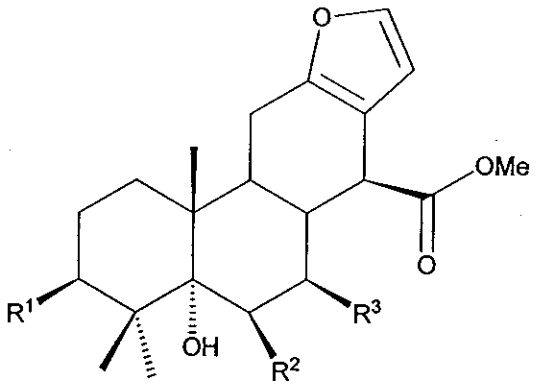

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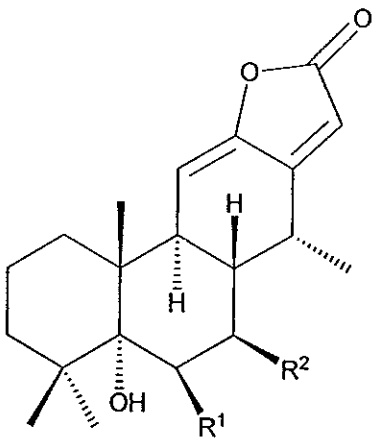
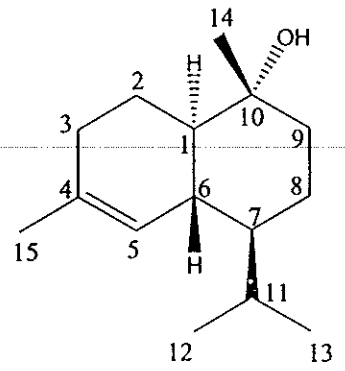


CP4 R^1 = OCOCH=CHPh, R^2 = OH

CP5 R^1 = OCOPh, R^2 = H

CP6 R^1 = OCOPh, R^2 = OH



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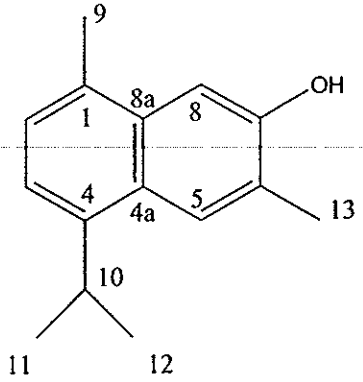

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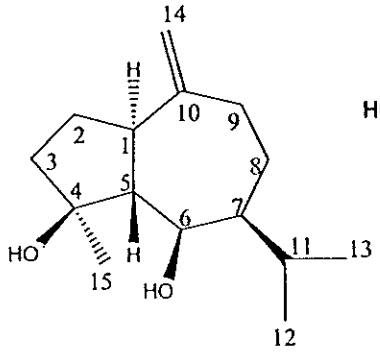

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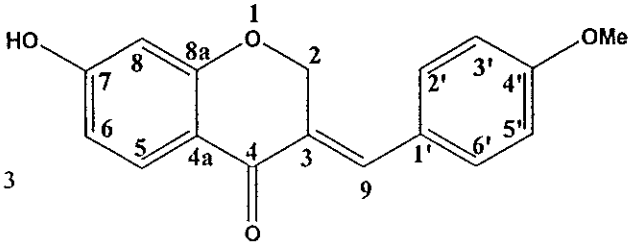

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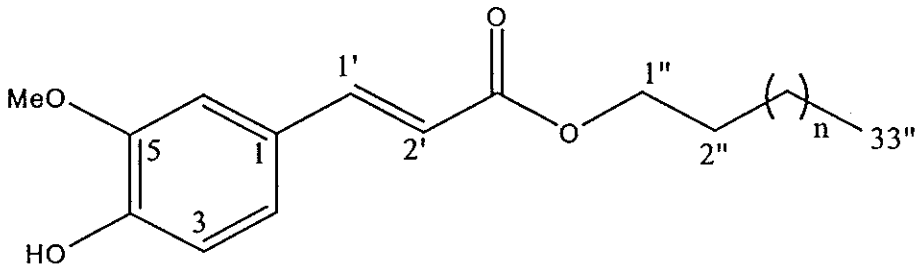

CP15

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I would like to express my appreciation to the staffs of the Department of Chemistry, Faculty of Science, Prince of Songkla University for making this thesis possible. Dr. Yaowapa Sukpondma is highly acknowledged for recording NMR spectral data.

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Wirote Pranithanchai

THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The purpose of this research is to investigate the chemical constituents of *Caesalpinia pulcherrima*. It is a part of the basic research on the utilization of the Thai medicinal plants. Chemical investigation of constituents from the stem of *C. pulcherrima* has led to isolation of seven new compounds together with eight known compounds.

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LISTS OF SCHEMES

ABBREVIATIONS AND SYMBOLS

s	=	*singlet*
d	=	*doublet*
t	=	*triplet*
q	=	*quartet*
m	=	*multiplet*
dd	=	*doublet of doublet*
dt	=	*doublet of triplet*
br s	=	*broad singlet*
R_f	=	Retention factor
g	=	gram
nm	=	nanometer
m.p.	=	melting point
cm^{-1}	=	reciprocol centimeter (wave number)
δ	=	chemical shift relative to TMS
J	=	coupling constant
$[\alpha]_D$	=	specific rotation
λ_{max}	=	maximum wavelength
ν	=	absorption frequencies
ε	=	molar extinction coefficient
m/z	=	a value of mass divided by charge
°C	=	degree celcius
MHz	=	Megahertz
ppm	=	part per million
c	=	concentration
IR	=	Infrared
UV-VIS	=	Ultraviolet-Visible
MS	=	Mass Spectroscopy
NMR	=	Nuclear Magnetic Resonance

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
CC	=	Column Chromatography
QCC	=	Quick Column Chromatography
TMS	=	tetramethylsilane
$CDCl_3$	=	deuterochloroform
CD_3OD	=	deuteromethanol

CHAPTER 1
INTRODUCTION

1.1 Introduction

Caesalpinia pulcherrima Swartz. belongs to Leguminosae - Caesalpinioideae family and, is known locally as "Hang Nok Yung Thai (หางนกยูงไทย)". Other common names for this species are Poinciana, Peacock Flower, Red Bird of Paradise, Mexican Bird of Paradise, Dwarf Poinciana, Pride of Barbados, and flamboyan-de-jardin. The Leguminosae-Caesalpinioideae family comprises about 150 genera with 2,200 species. In Thailand only 20 genera with 113 species are found, from *Caesalpinia* genus only 18 species are found. *C. pulcherrima* has been found through out Thailand.

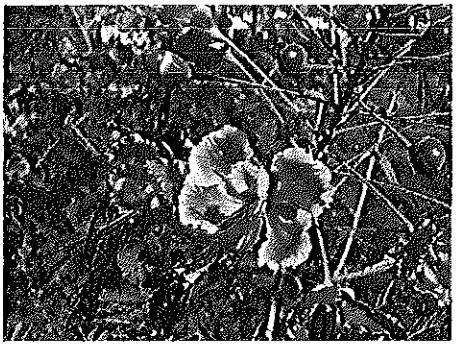
C. pulcherrima is a small sized, perennial shrub, 1-3 m tall. The leaves are bipinnate, 20-40 cm long, bearing 3-10 pairs of pinnae, each with 6-10 pair of leaflets 15-25 mm long and 10-15 mm broad. The flowers are borne in recemes up to 2 cm long which appear yellow, pink, off-white and red with yellow margins. This plant is a striking ornamental plant, widely grown in tropical gardens. It is also the national flower of the Caribbean island of Barbados, and is depicted on the Queen's personal Barbadian flag.

Several members of *Caesalpinia* genus are being used traditionally for a wide variety of ethnomedical properties (Uphof, 1968). The stem of this plant possesses interesting antitumor activities (Che *et al.*, 1986). Previous studies undertaken on *C. pulcherrima* in view of its medicinal significance have led to the isolation of several cassane-type diterpene (Ragasa *et al.*, 2002). Ester cassane-type diterpenes were found to be active against DNA repair-deficient yeast mutant (Patel *et al.*, 1997).

a. Tree

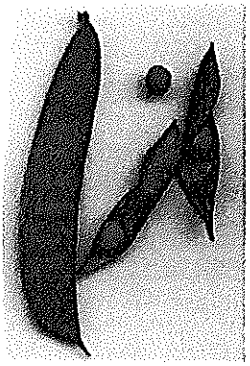
b. Leaves

c. Stem



d. Flowers

e. Fruits



f. Seeds

Figure 1 Parts of *Caesalpinia pulcherrima*

1.2 Review of literatures

Chemical constituents isolated from 18 species of the genus *Caesalpinia* were summarized by Orapun Yodsaoue in 2008 (Yodsaoue, 2008). These compounds are presented in Table 1.

Table 1 Compounds from plants of *Caesalpinia* genus

a : Benzenoids **b** : Coumarins **c** : Diterpenes
d : Flavonoids **e** : Phenylpropanoids
f : Sesquiterpenes **g** : Steroids **h** : Triterpenes

Scientific name	Investigated part	Compound	Bibliography
C. benthamiana	Root bark	Benthaminin 1, **8c** Benthaminin 2, **9c** Deoxycaesaldekarin C, **69c**	Dickson *et al.*, 2007
C. bonduc	Part not specified	Caesalpinolide A, **65c** Caesalpinolide B, **66c**	Yadav *et al.*, 2007
	Bark	Caesaldekarin J, **19c** 17-Hydroxy-campesta-4,6-dien-3-one, **151g** 13,14-*seco*-Stigmasta-5,14-dien-3α-ol, **152g** 13,14-*seco*-Stigmasta-9(11),14-Dien-3α-ol, **153g** Pipataline, **148e**	Udenigwe *et al.*, 2007
	Kernels	2-Acetoxycaesaldekarin E, **6c**	Pudhom *et al.*, 2007

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. bonduc	Kernels	Bonducellpin A, **10c** Bonducellpin B, **14c** Bonducellpin C, **11c** Bonducellpin E, **15c** Bonducellpin F, **16c** Bonducellpin G, **17c** α-Caesalpin, **26c** γ-Caesalpin, **28c** Caesalmin B, **20c** Caesalmin D, **24c** Caesalmin E, **25c** Caesalpinin C, **30c** Caesalpinin I, **39c** Caesalpinin K, **44c** Caesalpinin P, **48c** 14(17)-Dehydrocaesalpin F, **35c**	Pudhom *et al.*, 2007
C. crista	Seeds	Taepeenin J, **109c** Taepeenin K, **110c** Taepeenin L, **111c** (5α)-Vouacapa-(14),9(11)-diene, **112c** (5α,8β)-Vouacapane, **113c** (5α,6β,8β)-Vouacapan-6-ol, **114c**	Cheenpracha *et al.*, 2006
	Root	Taepeenin E, **102c** Taepeenin H, **105c**	Cheenpracha *et al.*, 2005

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. crista	Root	Taepeenin I, **106c** Vinhaticoic acid, **107c**	Cheenpracha *et al.*, 2005
	Stems	*ent*-11β-Hydroxy-rosa-5,15-diene, **70c** Methyl vinhaticoate, **108c** Nortaepeenin A, **85c** Nortaepeenin B, **86c** Taepeenin A, **98c** Taepeenin B, **99c** Taepeenin C, **100c** Taepeenin D, **101c** Taepeenin F, **103c** Taepeenin G, **104c**	Cheenpracha *et al.*, 2005
	Kernels	7-Acetoxybonducellpin C, **37c** 2-Acetoxycaesaldekarin E, **6c** 2-Acetoxy-3-deacetoxy Caesaldekarin E, **4c** 6-Acetoxy-3-deacetoxy Caesaldekarin E, **7c** Caesaldekarin E, **5c** Caesalmin B, **20c** Caesalmin C, **23c** Caesalmin E, **25c** 14(17)-Dehydrocaesalpin F, **35c**	Kalauni *et al.*, 2004

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. crista	Kernels	Caesalpinin C, **30c**	Kalauni *et al.*, 2004
		Caesalpinin E, **36c**	
		Caesalpinin MA, **49c**	
		Caesalpinin MB, **50c**	
		Caesalpinin MC, **51c**	
		Caesalpinin ME, **53c**	
		Norcaesalpinin B, **34c**	
		Norcaesalpinin MA, **81c**	
		Norcaesalpinin MB, **82c**	
		Norcaesalpinin MC, **83c**	
		7-Acetoxybonducellpin C, **37c**	Kalauni *et al.*, 2005a
		2-Acetoxycaesaldekarin E, **6c**	
		Caesaldekarin E, **5c**	
		Caesalmin C, **23c**	
		Caesalmin G, **21c**	
		β-Caesalpin, **27c**	
		Caesalpinin C, **30c**	
		Caesalpinin D, **22c**	
		Caesalpinin E, **36c**	
		Caesalpinin F, **38c**	
		Caesalpinin H, **42c**	
		Caesalpinin I, **39c**	
		Caesalpinin J, **40c**	
		Caesalpinin K, **44c**	
		Caesalpinin MF, **54c**	
		Caesalpinin MG, **55c**	

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. crista	Kernels	Caesalpinin MH, **56c** Caesalpinin MI, **57c** Caesalpinin MJ, **58c** Caesalpinin MK, **59c** Caesalpinin ML, **62c** Caesalpinin M, **47c** Caesalpinin N, **46c** Caesalpinin O, **43c** Norcaesalpinin MD, **84c**	Kalauni *et al.*, 2005a
		2-Acetoxycaesaldekarin E, **6c** Bonducellpin C, **11c** Caesaldekarin E, **5c** Caesalmin C, **23c** Caesalpinin MM, **60c** Caesalpinin MN, **61c** Caesalpinin MO, **63c** Caesalpinin MP, **64c** 1-Deacetoxy-1-oxocaesalmin C, **67c** 1-Deacetylcaesalmin C, **68c** Norcaesalpinin E, **32c**	Kalauni *et al.*, 2005b
		2-Acetoxycaesaldekarin E, **6c** 7-Acetoxybonducellpin, **37c** 2-Acetoxy-3-deacetoxycaesaldekarin E, **4c** Caesaldekarin E, **5c** Caesalmin B, **20c**	Linn *et al.*, 2005

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. crista	Kernels	Caesalmin G, **41c** Caesalpin F, **29c** Caesalpinin D, **22c** Caesalpinin E, **36c** Caesalpinin F, **38c** Caesalpinin G, **41c** 14(17)-Dehydrocaesalpin F, **35c** Norcaesalpinin A, **33c** Norcaesalpinin B, **34c** Norcaesalpinin D, **31c** Norcaesalpinin E, **32c**	Linn *et al.*, 2005
		2-Acetoxyl-3-deacetoxycaesal dekarin E, **4c** 6-Acetoxy-3-deacetoxycaesal dekarin E, **7c** Bonducellpin A, **40c** Bonducellpin B, **11c** Bonducellpin C, **14c** Caesaldekarin E, **5c** Caesalmin E, **25c** α-Caesalpin, **26c** Caesalpinin C, **30c** Caesalpinin D, **31c** Caesalpinin H, **42c** Caesalpinin I, **39c** Caesalpinin J, **40c**	Awale *et al.*, 2006

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. crista	Kernels	Caesalpinin K, **44c** Caesalpinin L, **45c** Caesalpinin M, **47c** Caesalpinin N, **46c** Caesalpinin O, **43c** Caesalpinin P, **48c** 1-Deacetoxy-1-oxocaesalmin C, **67c** Norcaesalpinin E, **32c** Norcaesalpinin F, **79c**	Awale *et al.*, 2006
	Leaves	Neocaesalpin H, **72c** Neocaesalpin I, **73c**	Kinoshita *et al.*, 2005
C. decapetala	Leaves	Caesaldecan, **18c** 4,5-Epoxy-8(14)-caryophyllene, **149f** Spathulenol, **150f** Lupeol, **154h** Squalene, **155h** *trans*-Resveratrol, **2a** Quercetin, **143d** Astragalin, **115d**	Kiem *et al.*, 2005
C. digyna	Twigs and stems roots	Bonducellin, **116d** Bergenin, **3b**	Boonsri *et al.*, 2005 Srinivasan *et al.*, 2007
C. magnifoliolata	Seeds	Caesalmin D, **24c** Caesalmin E, **25c**	Yin *et al.*, 2008

Table 1 (Continued)

Scientific name	Investigated part	Compound	Bibliography
C. magnifoliolata	Seeds	Magnicaesalpin , **71c** Neocaesalpin L, **76c** Neocaesalpin O, **79c**	Yin *et al.*, 2008
C. millettii HOOK. *et* ARN	Stems	Bonducellin, **116d** Eucomin, **126d** Intricatinol, **128d** 8-Methoxybonducellin, **127d** 8-Methoxyisobonducellin, **134d** Tamarixetin 3-*O*-(6″-*O*-*E*-caffeoyl)-*β*-D-alactopyranoside, **147d**	Chen and Yang, 2007
C. mimosoides Lamk	Part not specified	Gallic acid, **1a**	Chanwitheesuk *et al.*, 2007
C. minax	seeds	Neocaesalpin J, **74c** Neocaesalpin K, **75c** Neocaesalpin L, **76c** Neocaesalpin M, **77c** Neocaesalpin N, **78c**	Li *et al.*, 2006
C. pulcherrima	Part not specified	Bonducellin, **116d** Dihydrobonducellin, **119d** Isobonducellin, **132d** 20-Methoxybonducellin, **133d** 20-Methoxydihydrobonducellin, **120d**	Zhao *et al.*, 2004

Table 1 (Continued)

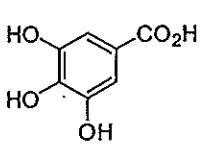
Scientific name	Investigated part	Compound	Bibliography
C. pulcherrima	Part not specified	Isobonducellin, **132d** (*E*)-7-Hydroxy-3-(4'-methoxybenzylidene)chroman-4-one, **130d** (E)-7-Hydroxy-3-(3',4',5'-trimethoxybenzylidene)chroman-4-one, **131d** (*E*)-7-Methoxy-3-(4'-methoxybenzylidene)chroman-4-one, **129d**	Maheswara *et al.*,2006
C. sappan	Heartwood	Bonducellin, **116d** Neoprotosappanin, **136d** Brazilin, **117d** 3'-Deoxysappanol, **123d** 3'-Deoxy-4-*O*-methylsappanol, **122d** 3′-Deoxysappanone B, **145d** 3'-*O*-Methylbrazilin, **118d** 4-*O*-Methylepisappanol, **135d** 4-*O*-Methylsappanol, **124d** Neosappanone A, **137d** Protosappanin A, **138d** Protosappanin A dimethyl acetal, **140d** Protosappanin B, **141d** Protosappanin C dimethyl acetal, **142d**	Nguyen *et al.*, 2004 Nguyen *et al.*, 2005

Table 1 (Continued)

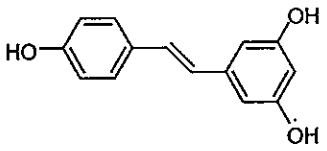
Scientific name	Investigated part	Compound	Bibliography
C. sappan	Heartwood	Protosappanin E-2, **139d** Sappanol, **121d** Sappanone B, **146d** Sappanchalcone, **144d**	Nguyen *et al.*, 2005
	Seeds	Phanginin A , **87c** Phanginin B, **88c** Phanginin C, **89c** Phanginin D, **90c** Phanginin E, **91c** Phanginin F, **92c** Phanginin G, **93c** Phanginin H, **94c** Phanginin I, **95c** Phanginin J, **96c** Phanginin K, **97c**	Yodsaoue *et al.*, 2008

Structures

a: Benzenoids

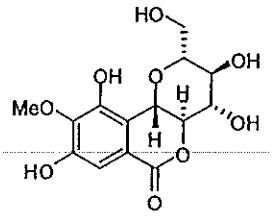


1a: Gallic acid



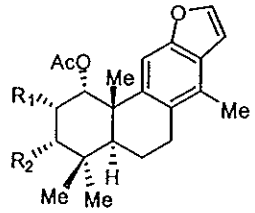
2a: *trans*-Resveratrol

b: Coumarins



3b: Bergenin

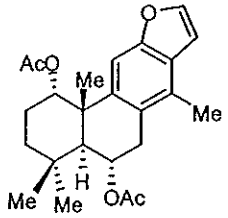
c: Diterpenes



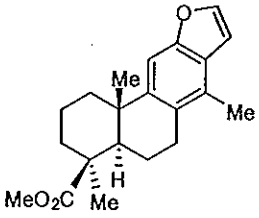
4c: R_1 = OAc, R_2 = H;
2-Acetoxy-3-deacetoxycaesaldekarin E

5c: R_1 = H, R_2 = OAc; Caesaldekarin E

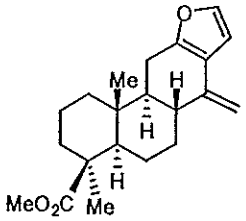
6c: R_1 = R_2 = OAc; 2-Acetoxycaesaldekarin E



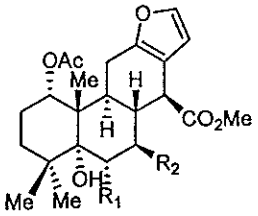
7c: 6-Acetoxy-3-deacetoxycaesaldekarin E



8c: Benthaminin 1



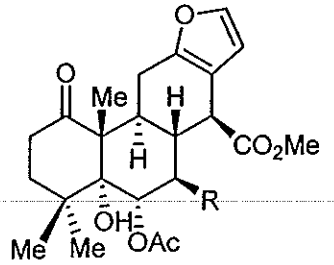
9c: Benthaminin 2



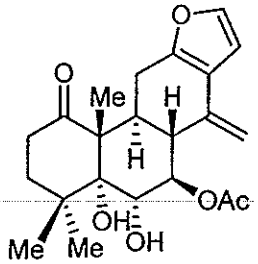
10c: R_1 = OAc, R_2 = OH; Bonducellpin A

11c: R_1 = H, R_2 = OH; Bonducellpin C

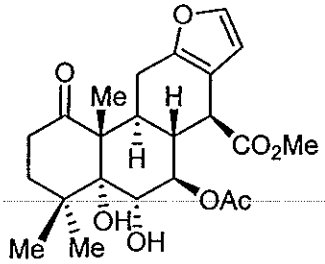
12c: R_1 = OH, R_2 = OAc; Caesalpinin M



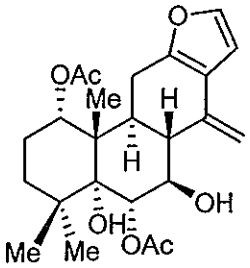
13c: R = OAc; Caesalpinin J
14c: R = OH; Bonducellpin B



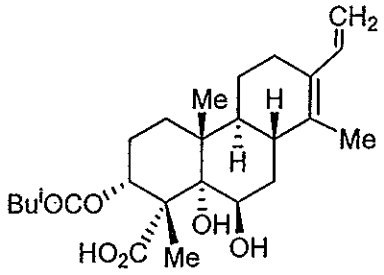
15c: Bonducellpin E



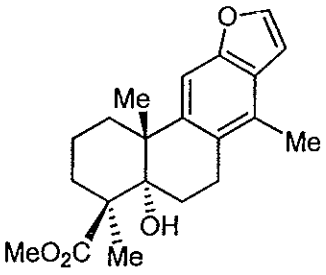
16c: Bonducellpin F



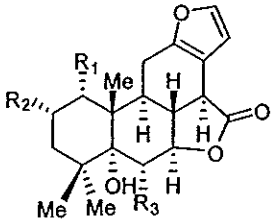
17c: Bonducellpin G



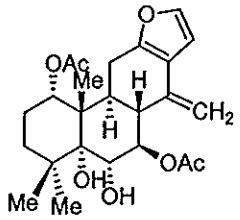
18c: Caesaldecan



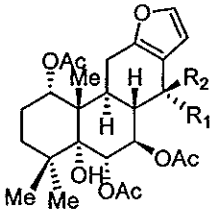
9c: Caesaldekarin J



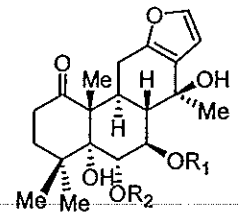
20c: R_1 = OAc, R_2 = R_3 = H; Caesalmin B
21c: R_1 = OH, R_2 = R_3 = H; Caesalmin G
22c: R_1 = R_3 = OAc, R_2 = H; Caesalpinin D



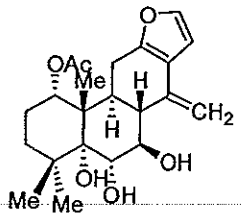
23c: Caesalmin C



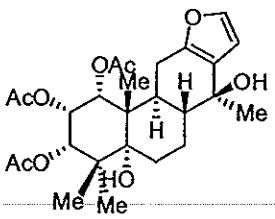
24c: R_1 = OH, R_2 = Me; Caesalmin D
25c: R_1 = Me, R_2 = OH; Caesalmin E



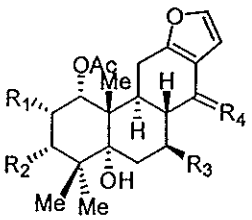
26c: R = Ac; α-Caesalpin
27c: R = H; β-Caesalpin



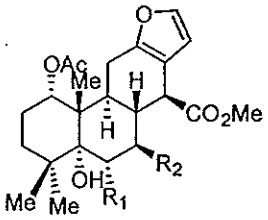
28c: γ-Caesalpin



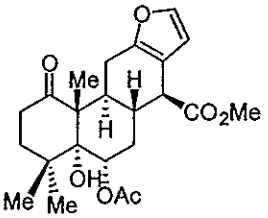
39c: Caesalpin F



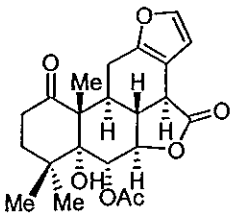
30c: $R_1 = R_3 = OH$, $R_2 = OAc$, $R_4 = CH_2$; Caesalpinin C
31c: $R_1 = R_2 = OAc$, $R_3 = H$, $R_4 = O$; Norcaesalpinin D
32c: $R_1 = R_2 = H$, $R_3 = OH$, $R_4 = O$; Norcaesalpinin E
33c: $R_1 = OAc$, $R_2 = R_3 = H$, $R_4 = O$; Norcaesalpinin A
34c: $R_1 = R_3 = H$, $R_2 = OAc$, $R_4 = O$; Norcaesalpinin B
35c: $R_1 = R_2 = OAc$, $R_3 = H$, $R_4 = CH_2$;
14(17)-Dehydrocaesalpin F



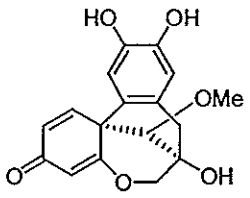
36c: $R_1 = OAc$, $R_2 = H$; Caesalpinin E
37c: $R_1 = H$, $R_2 = OAc$; 7-Acetoxybonducellpin C



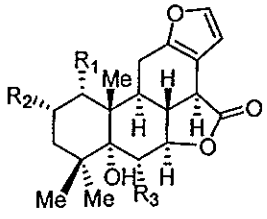
38c: Caesalpinin F



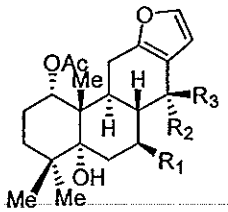
39c: Caesalpinin I



40c: Caesalpinin J



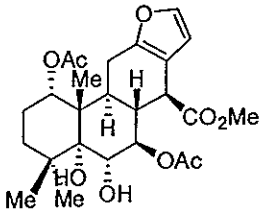
41c: $R_1 = R_2 = OAc$, $R_3 = H$; Caesalpinin G
42c: $R_1 = OH$, $R_2 = H$, $R_3 = OAc$; Caesalpinin H
43c: $R_1 = OAc$, $R_2 = H$, $R_3 = OH$; Caesalpinin O



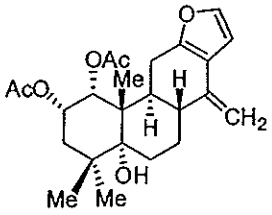
44c: R_1 = OH, R_2 = Me, R_3 = H; Caesalpinin K

45c: R_1 = OAc, R_2 = OH, R_3 = Me; Caesalpinin L

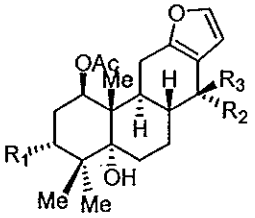
46c: R_1 = OH, R_2 = H, R_3 = CHO; Caesalpinin N



47c: Caesalpinin M

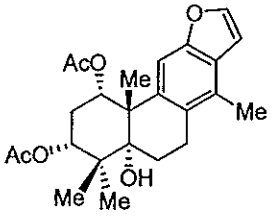


48c: Caesalpinin P

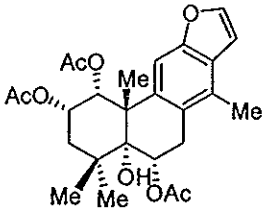


49c: R_1 = OAc, R_2 = Me, R_3 = H; Caesalpinin MA

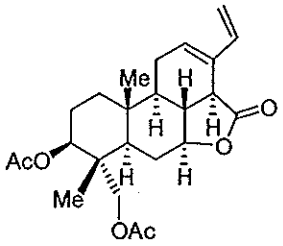
50c: R_1 = R_2 = H, R_3 = CO_2Me; Caesalpinin MB



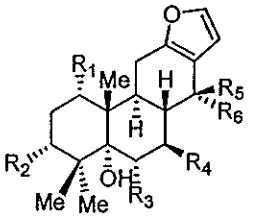
51c: Caesalpinin MC



52c: Caesalpinin MD



53c: Caesalpinin ME

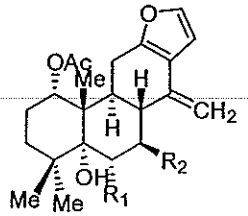


54c: R_1 = R_2 = OAc, R_3 = R_4 = R_6 = H, R_5 = CO_2Me; Caesalpinin MF

55c: R_1 = R_3 = R_4 = OAc, R_2 = R_6 = H, R_5 = CO_2Me; Caesalpinin MG

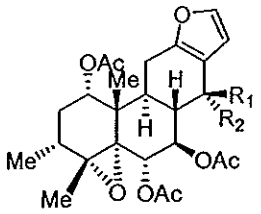
56c: R_1 = R_3 = OAc, R_2 = R_6 = H, R_4 = OH, R_5 = CO_2H; Caesalpinin MH

57c: R_1 = R_2 = R_3 = R_5 = H, R_4 = OH, R_6 = Me; Caesalpinin MI



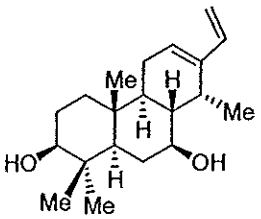
58c: R_1 = H, R_2 = OAc; Caesalpinin MJ

59c: R_1 = OAc, R_2 = H; Caesalpinin MK

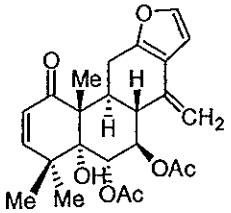


60c: R_1 = Me, R_2 = OH; Caesalpinin MM

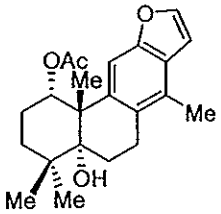
61c: R_1 = OH, R_2 = Me; Caesalpinin MN



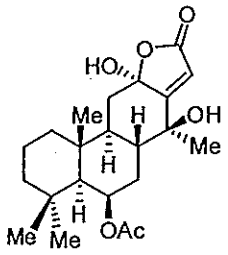
62c: Caesalpinin ML



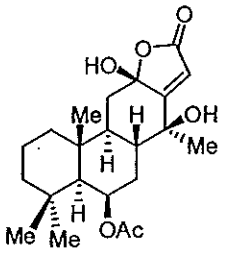
63c: Caesalpinin MO



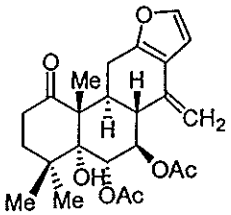
64c: Caesalpinin MP



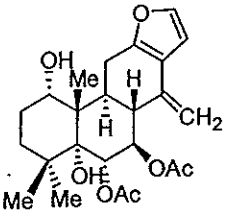
65c: Caesalpinolide A



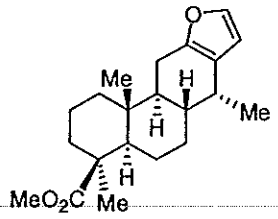
66c: Caesalpinolide B



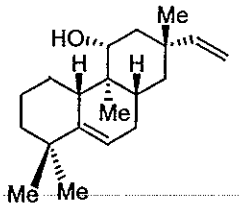
67c: 1-Deacetoxy-1-oxocaesalmin C



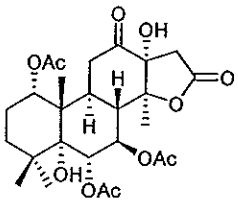
68c: 1-Deacetylcaesalmin C



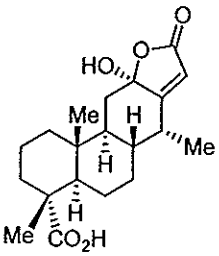
69c: Deoxycaesaldekarin C



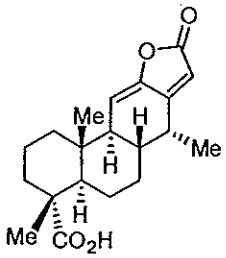
70c: *ent*-11β-Hydroxy-rosa-5,15-diene



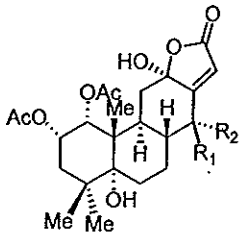
71c: Magnicaesalpin



72c: Neocaesalpin H

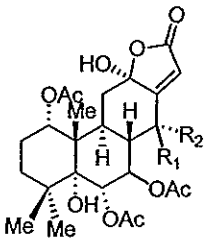


73c: Neocaesalpin I



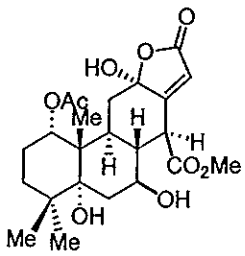
74c: R_1 = Me, R_2 = H; Neocaesalpin J

75c: R_1 = Me, R_2 = OMe; Neocaesalpin K

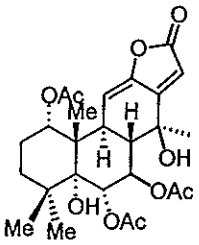


76c: R_1 = OH, R_2 = Me; Neocaesalpin L

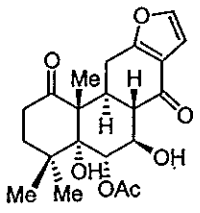
77c: R_1 = OMe, R_2 = Me; Neocaesalpin M



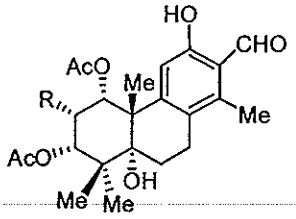
78c: Neocaesalpin N



79c: Neocaesalpin O

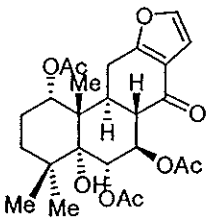


80c: Norcaesalpinin F

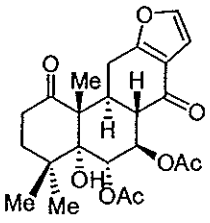


81c: R = H; Norcaesalpinin MA

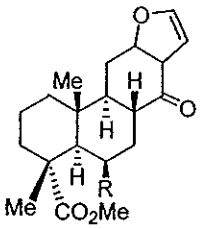
82c: R = OAc; Norcaesalpinin MB



83c: Norcaesalpinin MC

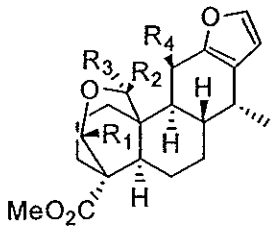


84c: Norcaesalpinin MD



85c: R = H; Nortaepeenin A

86c: R = OH; Nortaepeenin B



87c: $R_1 = R_3 = R_4 = H$, $R_2 = OH$; Phanginin A

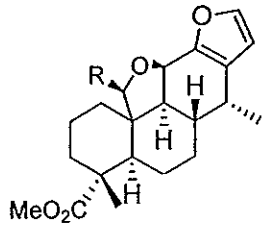
88c: $R_1 = OH$, $R_2 = R_3 = R_4 = H$; Phanginin B

89c: $R_1 = R_2 = R_4 = H$, $R_3 = OMe$; Phanginin C

90c: $R_1 = OMe$, $R_2 = R_3 = R_4 = H$; Phanginin D

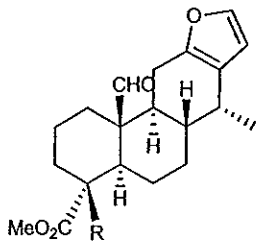
91c: $R_1 = =O$, $R_2 = R_3 = R_4 = H$; Phanginin E

92c: $R_1 = R_2 = H$, $R_3 = R_4 = OH$; Phanginin



93c: R = OH; Phanginin G

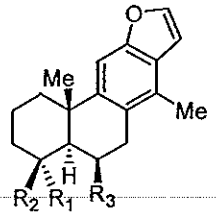
94c: R = H; Phanginin H



95c: R = Me; Phanginin I

96c: R = CHO; Phanginin J

97c: R = CO_2Me; Phanginin K



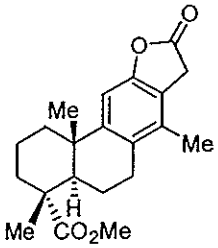
98c: $R_1 = CO_2Me$, $R_2 = Me$, $R_3 = H$; Taepeenin A

99c: $R_1 = CO_2H$, $R_2 = Me$, $R_3 = H$; Taepeenin B

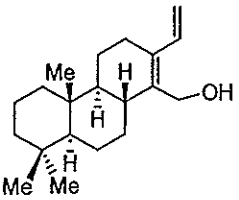
100c: $R_1 = CO_2Me$, $R_2 = Me$, $R_3 = OH$; Taepeenin C

101c: $R_1 = CO_2Me$, $R_2 = Me$, $R_3 = OAc$; Taepeenin D

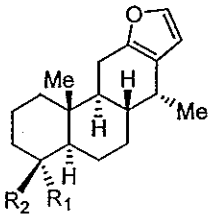
102c: $R_1 = CO_2Me$, $R_2 = CHO$, $R_3 = H$; Taepeenin E



103c: Taepeenin F



104c: Taepeenin G

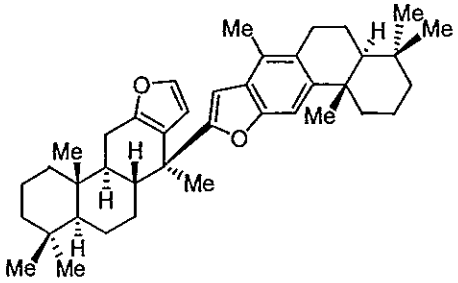


104c: $R_1 = CO_2Me$, $R_2 = CHO$; Taepeenin H

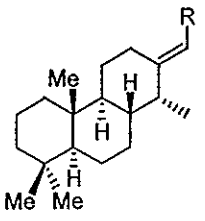
106c: $R_1 = CO_2Me$, $R_2 = CH_2OH$; Taepeenin I

107c: $R_1 = CO_2H$, $R_2 = Me$; Vinhaticoic acid

108c: $R_1 = CO_2Me$, $R_2 = Me$; Methyl vinhaticoate

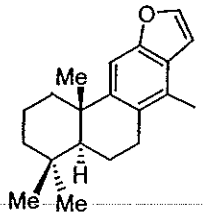


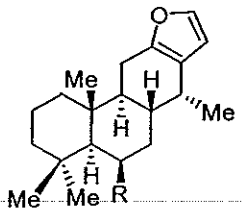
109c: Taepeenin J



110c: R = CHO; Taepeenin K

111c: R = CH_2OH; Taepeenin L

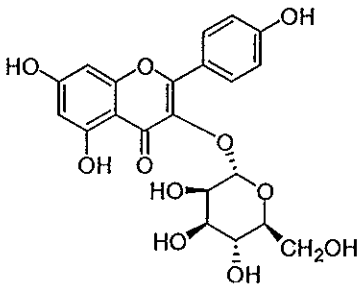


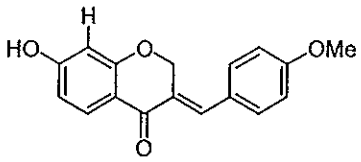


112c: (5α)-Vouacapa-8(14),9(11)-diene **113c**: R = H; (5α,8β)-Vouacapane

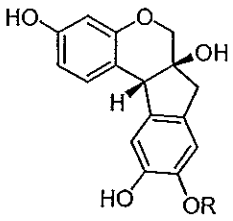
114c: R = OH; (5α,6β,8β)-Vouacapan-6-ol

d : Flavonoids



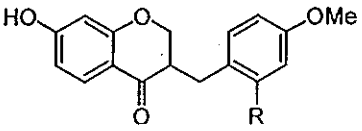


115d: Astragalin **116d**: Bonducellin



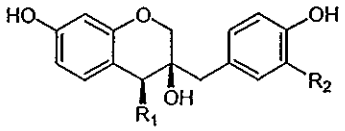
117d: R = H; Brazilin

118d: R = CH_3; 3′-*O*-Methylbrazilin



119d: R = H; Dihydrobonducellin

120d: R = CH_3; 20-Methoxydihydrobonducellin



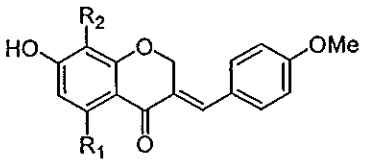
121d: $R_1 = R_2 = OH$; Sappanol

122d: R_1 = OMe, R_2 = H; 3′-Deoxy-4-*O*-methylsappanol

123d: R_1 = OH, R_2 = H; 3′-Deoxysappanol

124d: R_1 = OMe, R_2 = OH; 4-*O*-Methylsappanol

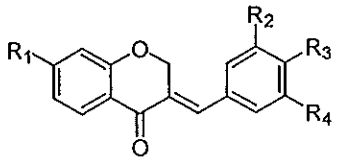
125d: R_1 = OH, R_2 = OMe; 3′-*O*-Methylsappanol



126d: R_1 = OH, R_2 = H; Eucomin

127d: R_1 = H, R_2 = OMe; 8-Methoxybonducellin

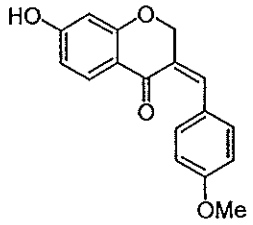
128d: R_1 = H, R_2 = OH; Intricatinol



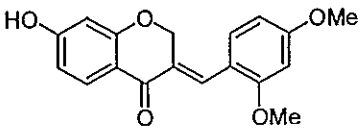
129d: R_1 = OMe, R_2 = R_4 = H, R_3 = OMe; (*E*)-7-Methoxy-3-(4'-methoxybenzylidene)chroman-4-one

130d: R_1 = OH, R_2 = R_4 = H, R_3 = OMe; (*E*)-7-Hydroxy-3-(4'-methoxybenzylidene)chroman-4-one

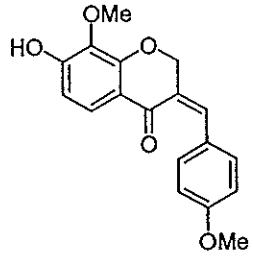
131d: R_1 = OH, R_2 = R_4 = R_3 = OMe; (*E*)-7-Hydroxy-3-(3',4',5'-trimethoxybenzylidene)chroman-4-one



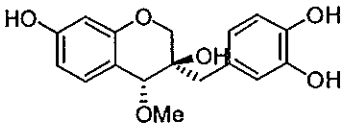
132d: Isobonducellin



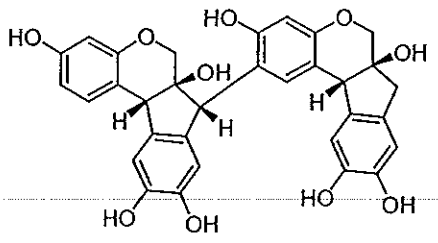
133d: 20-Methoxybonducellin



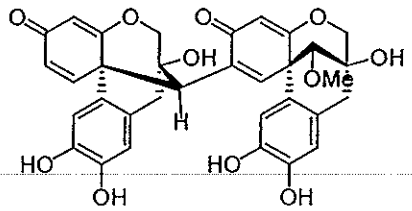
134d: 8-Methoxyisobonducellin



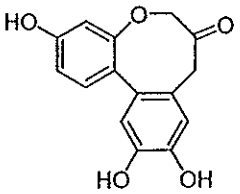
135d: 4-*O*-Methylepisappanol



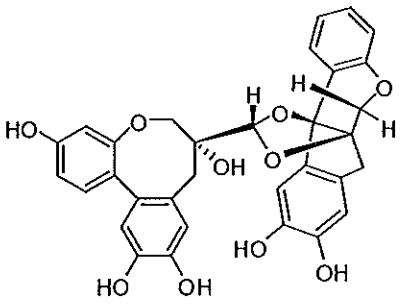
136d: Neoprotosappanin



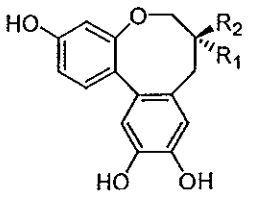
137d: Neosappanone A



138d: Protosappanin A



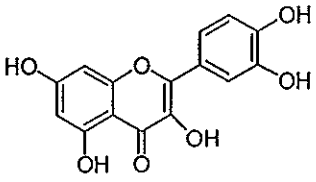
139d: Protosappanin E-2



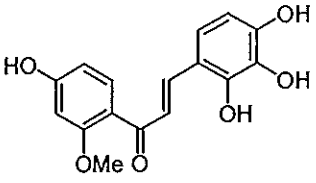
140d: $R_1 = R_2 = OMe$; Protosappanin A dimethyl acetal

141d: $R_1 = OH$, $R_2 = CH_2OH$; Protosappanin B

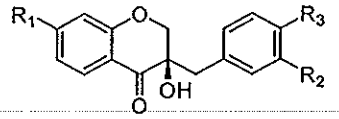
142d: $R_1 = OH$, $R_2 = CH(OCH_3)_2$;
Protosappanin C dimethyl acetal



143d: $R_1 = R_2 = R_3 = R_4 = OH$; Quercetin

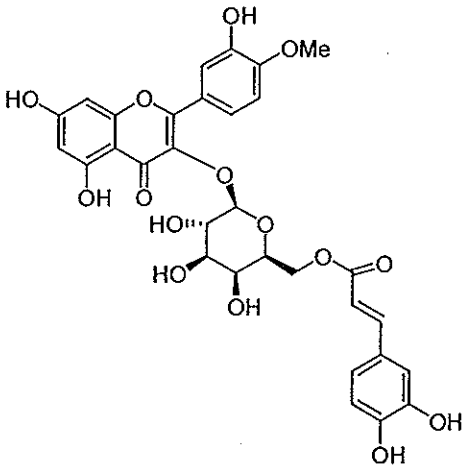


144d: $R_1 = OMe$, $R_2 = H$, $R_3 = OH$; Sappanchalcone



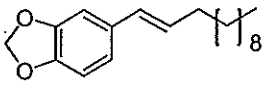
145d: $R_1 = R_3 = OMe$, $R_2 = H$; 3′-Deoxysappanone B

146d: $R_1 = R_2 = R_3 = OH$; Sappanone B



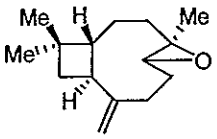
147d: Tamarixetin 3-*O*-(6″-*O*-*E*-caffeoyl)-*β*-D-alactopyranoside

e: Phenylpropanoids

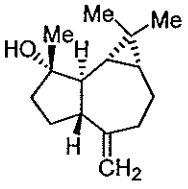


148e: Pipataline

f: Sesquiterpenes

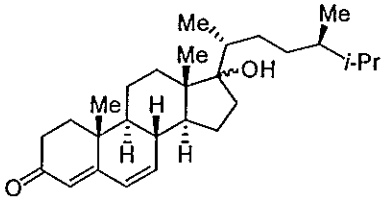


149f: 4,5-Epoxy-8(14)-caryophyllene

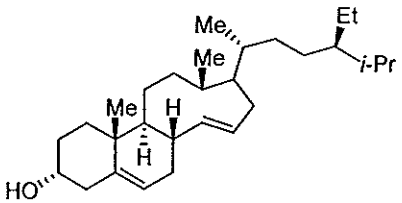


150f: Spathulenol

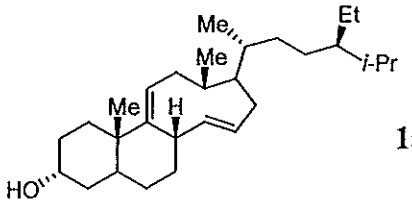
g: Steroids



151g: 17-Hydroxy-campesta-4,6-dien-3-one

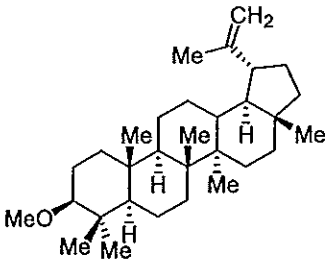


152g: 13,14-*seco*-Stigmasta-5,14-dien-3α-ol

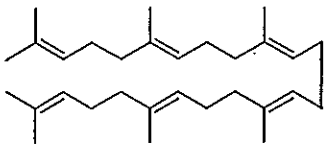


153g: 13,14-*seco*-Stigmasta-9(11),14-dien-3α-ol

h: Triterpenes



154h: Lupeol



155h: Squalene

1.3 Objective

This research involved isolation, purification and structure elucidation of chemical constituents investigated from the stem of *Caesalpinia pulcherrima.*

CHAPTER 2
EXPERIMENTAL

2.1 Instruments and chemicals

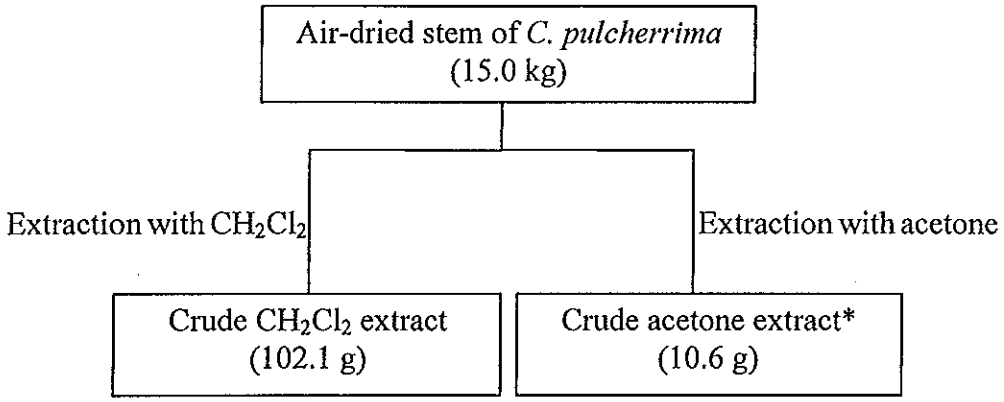
Melting point was recorded in °C on a Fisher-Johns melting point apparatus. Infrared spectra were recorded using FTS FT-IR spectrophotometer and major bands (ν) were recorded in wave number (cm^{-1}). Ultraviolet (UV) absorption spectra were recorded using a SPECORD S 100 (Analytikjena) and UV-160A spectrophotometer (SHIMADZU) and principle bands (λ_{max}) were recorded as wavelengths (nm) and log ε in chloroform and methanol solution. Nuclear magnetic resonance spectra were recorded using 300 MHz Bruker FTNMR Ultra Shield^{TM}. Spectra were recorded in deuterochloroform and deuteroacetone solution and were recorded as δ value in ppm downfield from TMS (internal standard δ 0.00). The EI-MS and ESI-TOF-MS were performed using a MAT 95 XL and Micromass LCT mass spectrometer, respectively. Optical rotation was measured in chloroform solution with sodium D line (590 nm) on an AUTOPOL^{R} II automatic polarimeter. Solvent for extraction and chromatography were distilled at their boiling point ranges prior to use except diethyl ether was analytical grade reagent. Quick column chromatography was performed on silica gel 60 GF_{254} (Merck). Column chromatography was performed on silica gel (Merck) type 100 (0.063 – 0.200).

2.2 Plant material

Stem of *Caesalpinia pulcherrima* (L.) Swartz. was collected from Songkhla province, Thailand in October 2005. Identification was made by Assoc. Prof. Dr. Kitichate Sridith, Department of Biology, Faculty of Science, Prince of Songkla University and a specimen (No. SC51) deposited at Prince of Songkla University Herbarium.

2.3 Extraction

The air-dried stem (15.0 kg) of *C. pulcherrima* was extracted with CH_2Cl_2 and acetone successively (each 2 x 2.5 L, for 5 days) at room temp. The crude extracts were evaporated under reduced pressure to afford brownish CH_2Cl_2 (102.1 g) and acetone (10.6 g) extracts, respectively. The process of extraction was shown in **Scheme 1**.

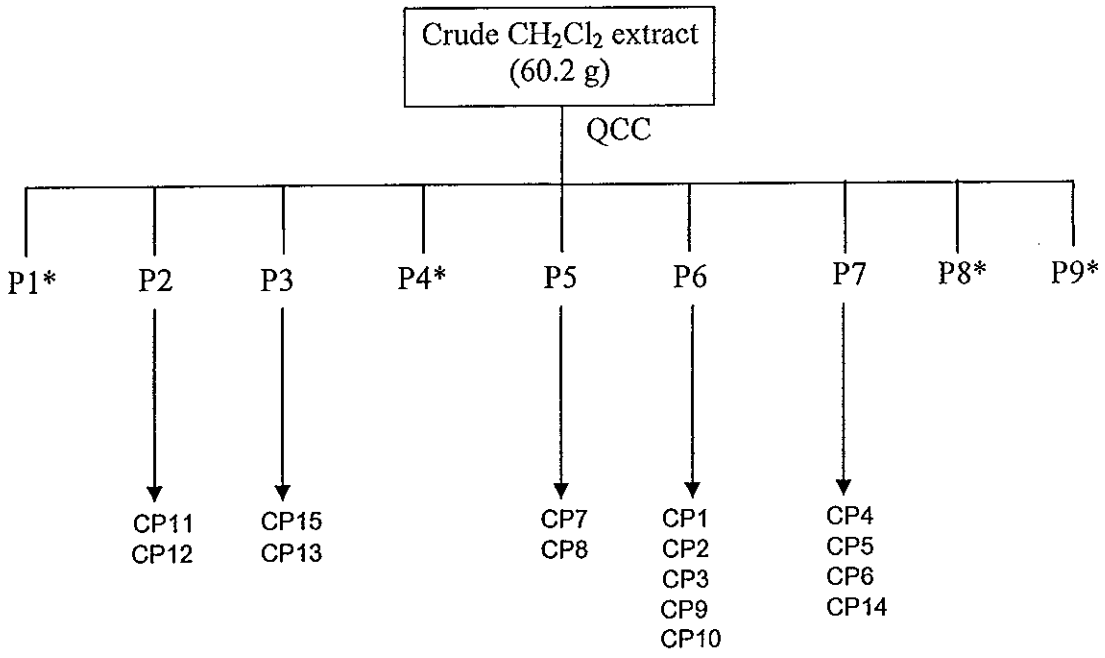


* Not further investigated

Scheme 1 Extraction of the stem of *C. pulcherrima*

2.4 Isolation and chemical investigation

2.4.1 Investigation of the crude methylene chloride extract from the stem of *C. pulcherrima*



* Not further investigated

Scheme 2 Isolation of compounds **CP1-CP15** from the stem of *C. pulcherrima*

A portion of the crude methylene chloride extract (60.2 g) was purified by QCC using hexane as eluent and increasing polarity with ethyl acetate to give nine fractions (P1-P9, **Scheme 2**).

Fraction P2 (2.7g) was further purified by QCC with EtOAc-hexane (1:19, v/v) to give seven subfractions (P2a-P2g). Subfraction P2b (80.5 mg) was separated by CC with EtOAc-hexane (1:19, v/v) to give CP**11** (10.2 mg). Subfraction P2c (50.8 mg) was purified by CC with EtOAc-hexane (1:13, v/v) to give CP**12** (1.5 mg).

Fraction P3 (1.5 g) was separated by QCC using hexane as eluent and increasing polarity with acetone to afford four subfractions (P3a-P3d). Subfraction P3a (640.9 mg) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to afford five subfractions (P3a1-P3a5). Subfraction P3a1 (80.5 mg) was separated by QCC with EtOAc-hexane (1:9, v/v) to give CP**15** (6.2 mg).Subfraction P3b (751.0 mg) was subjected to QCC using hexane as eluent and increasing polarity with EtOAc to afford four subfractions (P3b1-P3b4). Subfraction P3b2 (30.2 mg) was separated by CC with EtOAc-CH_2Cl_2-hexane (5:13:15, v/v) to give CP**13** (3.0 mg).

Fraction P5 (3.5 g) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to afford six subfractions (P5a-P5f). Subfraction P5e (760.5 mg) was separated by CC with EtOAc-hexane (3:17, v/v) to afford CP**7** (48.3 mg) and CP**8** (6.4 mg).

Fraction P6 (3.1 g) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to give eight subfractions (P6a-P6h). Subfraction P6f (1.3 g) was separated by QCC using hexane as eluent and increasing polarity with EtOAc to afford six subfractions (P6f1-P6f6). Subfraction P6f2 (501.8 mg) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to give CP**1** (10.2 mg). Subfraction P6f4 (85.1 mg) was subjected to CC with EtOAc-CH_2Cl_2-hexane (1:2:17, v/v) to afford CP**2** (3.5 mg). Subfraction P6f5 (177.1 mg) was separated by CC with EtOAc-CH_2Cl_2-hexane (1:2:17, v/v) to afford CP**9** (4.5 mg). Subfraction P6f6 (85.9 mg) was purified by CC with EtOAc-hexane (1:3, v/v) to afford CP**10** (3.4 mg). Subfraction P6g (480.7 mg) was separated by QCC using hexane as eluent and increasing polarity with EtOAc to afford four subfractions (P6g1-P6g4). Subfraction P6g3 (79.1 mg) was separated to CC with EtOAc-CH_2Cl_2-hexane (1:2:17, v/v) to afford CP**3** (8.2 mg).

Fraction P7 (1.2 g) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to afford six subfractions (P7a-P7f). Subfraction P7a (50.8 mg) was separated by CC with EtOAc-hexane (1:4, v/v) to afford CP**6** (1.5 mg). Subfraction P7c (380.4 mg) was purified by CC with acetone-hexane (3:17, v/v) and followed by prep TLC with acetone-hexane (1:4, v/v) to give CP**5** (1.5 mg), and CP**4** (2.3 mg). Subfraction P7e (111.6 mg) was separated by CC with EtOAc-hexane (1:4, v/v) to afford CP**14** (8.0 mg)

Compound CP1: White powder; m.p. 125-127 °C; $[\alpha]^{26}_D$ + 10.4° ($CHCl_3$; *c* 0.51); UV (MeOH) λ_{max} (log ε): 216 (3.63) and 277 (3.64) nm; IR (neat) υ_{max}: 3467, 2914, 2847, 2361, 2335, 1700, 1279, 1170, 1046, 997, 757, 667 cm^{-1}; HREIMS: *m/z* $[M]^+$ 464.2573 (calcd for $C_{29}H_{36}O_5$, 464.2563); ^1H ($CDCl_3$, 300 MHz), see **Table 2**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 2**.

Compound CP2: Amorphous solid; $[\alpha]^{26}_D$ + 10.9° ($CHCl_3$; *c* 0.18); UV (MeOH) λ_{max} (log ε): 226 (4.21) and 273 (3.63) nm; IR (neat) υ_{max}: 3400, 2930, 2863, 2361, 2335, 1713, 1702, 1276, 1114, 1067, 1023, 770, 711, 667cm^{-1}; HREIMS: *m/z* $[M]^+$ 438.2407 (calcd for $C_{27}H_{34}O_5$, 438.2406); ^1H NMR ($CDCl_3$, 300 MHz), see **Table 3**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 3**.

Compound CP3: White powder; m.p. 180-182 °C; $[\alpha]^{26}_D$ + 13.9° ($CHCl_3$; *c* 0.41); UV (MeOH) λ_{max} (log ε): 226 (3.98) and 273 (3.17) nm; IR (neat) υ_{max}: 3509, 2930, 2863, 1715, 1276, 1157, 1114, 1026, 760, 711, 667cm^{-1}; HREIMS: *m/z* $[M]^+$ 540.2383 (calcd for $C_{30}H_{36}O_9$, 540.2359); ^1H NMR ($CDCl_3$, 300 MHz), see **Table 4**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 4**.

Compound CP4: Amorphous solid; $[\alpha]^{26}_D$ + 89.3° ($CHCl_3$; *c* 0.12); UV (MeOH) λ_{max} (log ε): 216 (4.39) and 279 (4.67) nm; IR (neat) υ_{max}: 3338, 2919, 2852, 2356, 2341, 1746, 1702, 1449, 1274, 767, 667cm^{-1}; HREIMS: *m/z* $[M\text{-}H_2O]^+$ 460.2225 (calcd for $C_{29}H_{32}O_5$, 460.2250); ^1H NMR ($CDCl_3$, 300 MHz), see **Table 5**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 5**.

Compound CP5: White powder, m.p. 250-252 °C; $[\alpha]^{26}_D$ + 25.8° ($CHCl_3$; *c* 0.08); UV (MeOH) λ_{max} (log ε): 230 (3.96) and 280 (3.93) nm; IR (neat) υ_{max}: 3524, 2935, 2356, 1749, 1713, 1452, 1271, 1108, 1067, 990, 757, 711, 667 cm^{-1}; HREIMS: *m/z* $[M\text{-}H_2O]^+$ 428.2154 (calcd for $C_{27}H_{30}O_4$, 418.2144); ^1H NMR ($CDCl_3$, 300 MHz), see **Table 6**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 6**.

Compound CP6: Amorphous solid; $[\alpha]^{26}_D$ + 33.3° ($CHCl_3$; *c* 0.08); UV (MeOH) λ_{max} (log ε): 227 (3.86) and 280 (3.79) nm; IR (neat) υ_{max}: 3478, 2925,

2852, 2356, 2335, 1777, 1746, 1710, 1456, 1271, 767, 667 cm^{-1}; HREIMS: *m/z* $[M]^+$ 452.2219 (calcd for $C_{27}H_{32}O_6$, 452.2199). ; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 7**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 7**.

Compound CP7: Amorphous solid; $[\alpha]^{26}_D$: -25.0° (*c* = 0.85, $CHCl_3$); UV (MeOH) λ_{max} (log ε): 280 (3.94) nm; IR (neat) υ_{max}: 3482, 1709, 1276, 1176, 1126, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 8**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 8**.

Compound CP8: Amorphous solid; $[\alpha]^{26}_D$: + 70° (*c* = 0.39, $CHCl_3$); UV (MeOH) λ_{max} (log ε): 220 (4.47) nm; IR (neat) υ_{max}: 3580, 2935, 1717, 1711, 1642, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 10**; ^{13}C NMR ($CDCl_3$, 75 MHz), see Table **Table 10**.

Compound CP9: Amorphous solid; mp: 222-224 °C; $[\alpha]^{26}_D$: + 30.7° (*c* = 0.29, $CHCl_3$); UV (MeOH) λ_{max} (log ε): 226 (3.94) nm, 273 (3.92), 281 (3.84) nm; IR (neat) υ_{max}: 3446, 2929, 1723, 1275, 769, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 10**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 10**.

Compound CP10: Amorphous solid; $[\alpha]^{30}_D$: + 72.2° (*c* = 0.28, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 226 (3.94), 272 (3.92), 281 (3.87) nm; IR (neat) υ_{max}: 3446, 2929, 1728, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 11**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 11**.

Compound CP11: Amorphous solid; $[\alpha]^{26}_D$: - 30.1° (*c* = 0.90, $CHCl_3$); IR (neat) υ_{max}: 3361, 2952, 1640, 1448, 1367 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 12**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 12.**

Compound CP12: Viscous oil; UV (MeOH) λ_{max} (log ε): 225 (4.81), 235 (4.83), 276 (3.87), 286 (3.92), 299 (3.94), nm; IR (neat) υ_{max}: 3328, 2952, 2863, 1623, 1439, 1362, 1236, 1155, 1129, 1041, 853 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 14**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 13.**

Compound CP13: Viscous oil; $[\alpha]^{26}_{D}$: + 2.9° (*c* = 0.18, $CHCl_3$); IR (neat) υ_{max}: 3400, 3080, 2960, 2930, 2870, 1640, 1465, 1385, 1370, 1150, 1060, 970, 885 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 14**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 14.**

Compound CP14: yellow crystal; UV (MeOH) λ_{max} (log ε): 317 (4.12), 357 (4.20) nm; IR (neat) υ_{max}: 3439, 2929, 2857, 1655, 1462, 1373, 1166, cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), see **Table 15**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 15.**

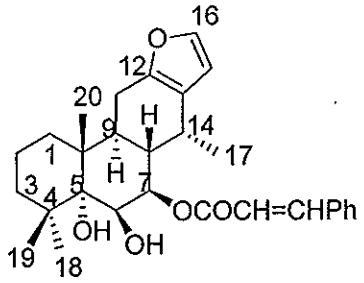
Compound CP15: Viscous oil; UV (MeOH) λ_{max} (log ε): 234, 297, 325 nm; IR (neat) υ_{max}: 3375, 1695, 1635 cm^{-1}; EIMS: *m/z* $[M-1]^+$ 655.6 (calcd for $C_{43}H_{76}O_4$, 655.6); ^1H NMR ($CDCl_3$, 300 MHz), see **Table 16**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 16.**

CHAPTER 3
RESULTS AND DISCUSSION

3.1 Structural elucidation of compounds from the stem of *C. pulcherrima*

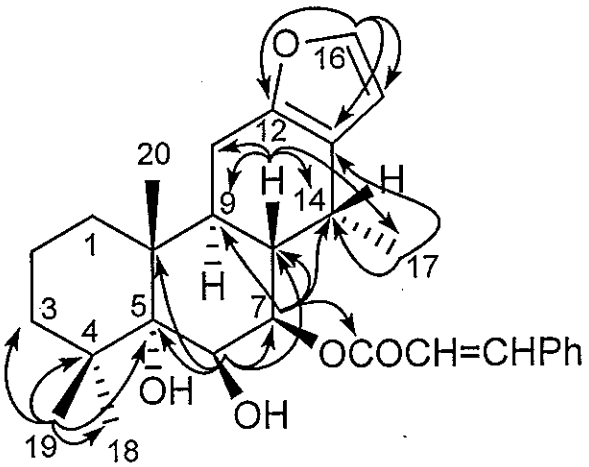
A portion of CH_2Cl_2 extract (60.2 g) of the stem of *C. pulcherrima* was subjected to chromatography to give new cassane-type diterpenes, **CP1-CP6** and a new ferrulic ester, **CP15** and eight known compounds **CP7-CP14**. The basic skeleton of compounds **CP1-CP10** was identified to be cassane diterpene on the basis of their IR and UV spectroscopic data and a positive Ehrlich test (Kuroda *et al.*, 2004). The UV absorptions of **CP1-CP3** (λ_{max} 211-225 nm) were characteristic of a furano cassane-type diterpene (Cheenpracha et al., 2005 and 2006), whereas the structures **CP4-CP6** showed absorption bands of an α,β-butenolide ring conjugated with an extra double bond (λ_{max} 279-280 nm) (Kinoshita *et al.*, 2000 and 2005). In addition, the IR spectrum of all new compounds displayed carbonyl ester functionality (1700-1777 cm^{-1}).

3.1.1 Compound CP1



Compound **CP1** was obtained as white powder with the molecular formula of $C_{29}H_{36}O_5$ on the basis of molecular ion peak $[M]^+$ at *m/z* 464.2573 in the HREIMS. The ^1H NMR spectral data (**Table 2**) supported a cassane-type furanoditerpenoid framework (Cheenpracha *et al.*, 2005 and 2006; McPherson *et al.*, 1986; Patil *et al.*, 1997; Ragasa *et al.*, 2002; Roach *et al.*, 2003; Yodsaoue *et al.*, 2008). Three tertiary methyl groups resonated at δ 1.04 (Me-19), 1.39 (Me-20), and

1.47 (Me-18) and one secondary methyl group resonated at δ 1.02 (*d*, J = 6.9 Hz, Me-17). A 2,3-disubstituted furan ring was evident from the resonances at δ 6.19 (*d*, J = 1.8 Hz, H-15) and δ 7.23 (*d*, J = 1.8 Hz, H-16). Signals of a hydroxyl proton at δ 1.97 (*d*, J = 2.1 Hz) and two oxymethine protons at δ 4.32 (*dd*, J = 3.6, 2.1 Hz) and 5.58 (*dd*, J = 11.1, 3.6 Hz) were displayed. These two oxymethine protons were assigned as H-6 and H-7, respectively due to HMBC correlation of the former proton to C-5 (δ 77.8), C-7 (δ 75.0), C-8 (δ 35.2) and C-10 (δ 40.7) and COSY correlation to H-7. The remaining ^{1}H NMR signals were those of a *trans*-cinnamoyl side chain displayed as two doublets at δ 6.51 and 7.75 (J = 15.9 Hz, H-2' and H-3', respectively), together with multiplet signals of aromatic protons betweens 7.41-7.55, whose location was placed at C-7 due to HMBC correlation of H-7 (δ 5.58) to a carbonyl carbon of a cinnamate ester group (δ 166.0). NOESY cross peaks of H-7 with H-6, H-9 and Me-17 indicated that these protons were on the same side of the molecule. The proton H-8 showed cross peaks with H-14 and Me-20 but no cross peak with H-7 and H-9, thus H-8, H-14 and Me-20 were on the same side but opposite side with H-6, H-7, H-9 and Me-17. The small vicinal coupling constant of H-6 and H-7 (3.6 Hz) supported their α-orientations. In addition, hydrolysis of compound **CP1** under methanolic K_2CO_3 afforded the parent alcohol, whose spectroscopic data were identical to those of 6β-hydroxyisovoucapenol C (Roach *et al.*, 2003). Therefore, **CP1** was 6β-hydroxy-7β-cinnamoyloxyvoaucapen-5α-ol, a new compound (Pranithanchai *et al.*, 2009) and was named as pulcherrin A.

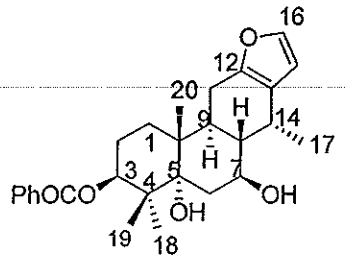


Selected HMBC correlation of **CP1**

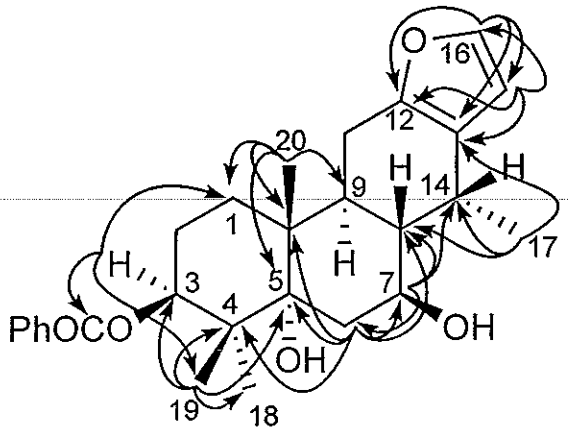
Table 2 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP1**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.43 (m), 1.54 (m)	35.2	CH_2	10
2	1.50 (m), 1.67 (m)	18.2	CH_2	10
3	1.17 (m), 1.67 (m)	37.6	CH_2	5
4	-	39.2	C	-
5	-	77.8	C	-
6	4.32 (dd, *J* = 3.6, 2.1)	71.5	CH	5, 7, 8, 10
7	5.58 (dd, *J* = 11.1, 3.6)	75.0	CH	8, 9, 14, 1′
8	2.31 (td, *J* = 11.1, 4.8)	35.2	CH	9, 11, 14, 17
9	2.49 (m)	37.3	CH	7, 8, 10, 11, 20
10	-	40.7	C	-
11	2.53 (m)	21.8	CH_2	8, 9, 12, 13
12	-	149.5	C	-
13	-	121.7	C	-
14	2.86 (qd, *J* = 6.9, 4.8)	27.6	CH	8, 9, 12, 13, 17
15	6.19 (d, *J* = 1.8)	109.5	CH	12, 13
16	7.23 (d, *J* = 1.8)	140.5	CH	12, 13, 15
17	1.02 (d, *J* = 6.9)	17.2	CH_3	8, 13, 14
18	1.47 (s)	27.8	CH_3	3, 4, 5, 19
19	1.04 (s)	25.5	CH_3	3, 4, 5, 18
20	1.39 (s)	17.4	CH_3	-
1′	-	166.0	C	-
2′	6.51 (d, *J* = 15.9)	117.8	CH	1′, 3′
3′	7.75 (d, *J* = 15.9)	145.6	CH	1′, 2′, 4′, 5′
4′	-	134.2	C	-
5′/9′	7.55 (m)	128.2	CH	4′
6′/8′	7.41 (m)	129.0	CH	4′, 5′
7′	7.41 (m)	130.5	CH	5′
6-OH	1.97 (d, *J* = 2.1)	-	-	5, 6

3.1.2 Compound CP2



Compound **CP2**, $[M]^+$ *m/z* 438.2407 ($C_{27}H_{34}O_5$) by HREIMS, showed related ^1H and ^{13}C NMR spectral data (**Table 3**) to those of **CP1**. The signals of an oxymethine proton (δ 5.30, *dd*, J = 11.5, 5.0 Hz, H-3) and methylene protons (δ 1.86, *dd*, J = 13.0, 11.0 Hz and 2.05, *dd*, J = 13.0, 5.5 Hz, 2H-6) in **CP2** replaced the methylene protons (δ 1.67 and 1.17, 2H-3) and an oxymethine proton (δ 4.32, H-6) in **CP1**. In addition, the signals of a cinnamoyloxy moiety [δ 6.51 (*d*, J = 15.9 Hz, H-2'), 7.75 (*d*, J = 15.9 Hz, H-3') and 7.41-7.55] in **CP1** were replaced by a benzoate ester group resonating between δ 7.45-8.04, whose location was placed at C-3 due to HMBC correlation of H-3 (δ 5.30) to the carbonyl carbon of benzoate ester group (δ 166.2). The proton H-3 was assigned to be axially oriented from the small and large vicinal coupling constants ($J_{3ax,2eq}$ = 5.0 Hz, $J_{3ax,2ax}$ = 11.5 Hz). The oxymethine H-7 at δ 4.12 (*dt*, J = 11.0, 5.5 Hz) was deduced to be axially oriented from two large vicinal coupling constants ($J_{7ax,6ax}$ = 11.0 Hz and $J_{7ax,8ax}$ = 11.0 Hz) and small vicinal coupling constant ($J_{7ax,6eq}$ = 5.5 Hz). It was further supported by NOESY correlations of H-7 with Me-17 and H-6α but no cross peak with H-6β, H-8 and H-14. From these data, the protons H-3 and H-7 were located on the same side. Thus, **CP2** was assigned to be 3β-benzoyloxy-7β-hydroxyvoaucapen-5α-ol, a new compound (Pranithanchai *et al.*, 2009) and was named as pulcherrin B.



Selected HMBC correlation of **CP2**

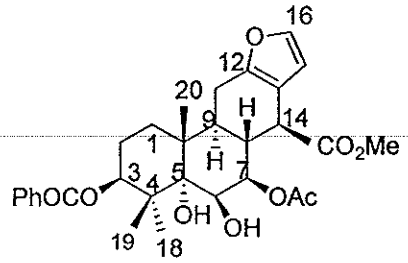
Table 3 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP2**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.51 (m), 1.77 (m)	31.0	CH_2	2, 3, 20
2	1.80 (m), 1.92 (m)	23.8	CH_2	3, 4, 10
3	5.30 (dd, *J* = 11.5 , 5.0)	77.3	CH	1, 4, 18, 19, 1′
4	-	43.5	C	-
5	-	79.9	C	-
6	1.86 (dd, *J* = 13.0, 11.0)	35.9	CH_2	4, 5, 7, 8, 10
	2.05 (dd, *J* = 13.0, 5.5)			
7	4.12 (dt, *J* = 11.0, 5.5)	68.1	CH	6, 8, 14
8	1.74 (td, *J* = 11.0, 7.0)	42.8	CH	6, 9, 11, 14, 17
9	2.46 (m)	36.7	CH	1, 8, 10, 11, 14, 20
10	-	40.9	C	-
11	2.43 (m)	22.5	CH_2	8, 9, 10, 12, 13, 15
	2.53 (dd, *J* = 13.5, 5.0)			
12	-	149.1	C	-
13	-	121.9	C	-
14	3.09 (quint, *J* = 7.0)	27.4	CH	8, 9, 12, 13, 15, 17
15	6.22 (d, *J* = 2.0)	109.7	CH	12, 13, 16
16	7.25 (d, *J* = 2.0)	140.7	CH	12, 13, 15

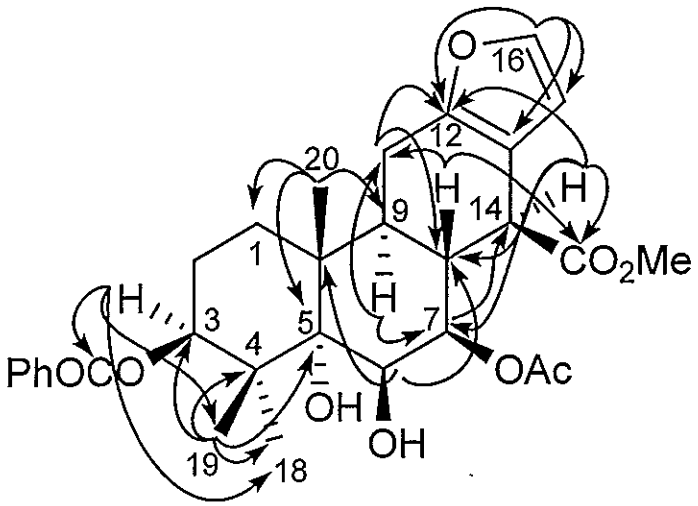
Table 3 (continued)

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
17	1.10 (d, *J* = 7.0)	17.1	CH_3	8, 13, 14
18	1.08 (s)	23.1	CH_3	3, 4, 5, 19
19	1.26 (s)	19.7	CH_3	3, 4, 5, 18
20	1.18 (s)	17.5	CH_3	1, 5, 9, 10
1′	-	166.2	C	-
2′	-	130.8	C	-
3′/7′	8.04 (dd, *J* = 7.5, 1.0)	129.5	CH	1′, 5′
4′/6′	6.51 (t, *J* = 7.5)	128.4	CH	2′
5′	7.57 (tt, *J* = 7.5, 1.0)	140.7	CH	3′, 7′

3.1.3 Compound CP3



Compound **CP3**, with the molecular formula $C_{30}H_{36}O_9$ by HERIMS, had the ^1H and ^{13}C NMR (**Table 4**) spectra related to **CP2** except at C-6 and C-17, where signals of the methylene protons at δ 1.86 and 2.05 on C-6 and a secondary methyl at δ 1.10 (Me-17) in **CP2** were replaced by those of an oxymethine proton at δ 4.15 (*d*, J = 3.3 Hz) and a methyl ester at δ 3.75, respectively in **CP3**. Besides **CP3** displayed an additional O-acetyl group as a ^1H NMR singlet signal at δ_H 2.06 : δ_C 21.0 and a carbonyl carbon at δ_C 170.2. In addition, H-14 (δ 3.38, *d*, J = 8.7 Hz) showed HMBC correlations to the ester carbonyl carbon at δ 174.9, supporting the placement of a methyl ester at C-14. The proton H-14 was in an axial position due to a large vicinal coupling constant ($J_{14ax,8ax}$ = 8.7 Hz) and NOESY cross peaks of H-14 with H-7 and H-9 but not with H-8. Thus, **CP3** was deduced to be 3β-benzoyloxy-6β-hydroxy-7β-acetoxy-17β-methoxycarbonylvoaucapen-5α-ol, a new compound (Pranithanchai *et al.*, 2009) and was named as pulcherrin C.

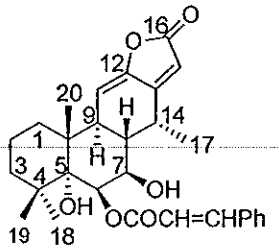


Selected HMBC correlation of **CP3**

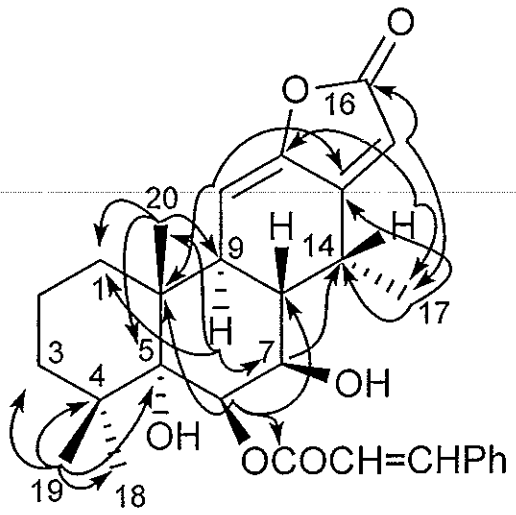
Table 4 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP3**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.46 (m), 1.89 (m)	32.7	CH_2	2, 3, 5,10
2	1.84 (m), 1.94 (m)	23.9	CH_2	1, 4, 10
3	5.31 (m)	78.8	CH	18, 19, 1′
4	-	44.2	C	-
5	-	77.0	C	-
6	4.15 (d, *J* = 3.3)	72.3	CH	7, 8, 9, 10
7	5.33 (dd, *J* = 11.4, 3.3)	78.8	CH	8, 14, 1″
8	2.76 (td, *J* = 11.4, 8.7)	34.3	CH	7, 9, 11, 14, 17
9	2.41 (m)	41.3	CH	7, 8, 10, 11
10	-	40.9	C	-
11	2.56 (brd, *J* = 8.1)	21.3	CH_2	8, 9, 12, 13
12	-	150.8	C	-
13	-	112.7	C	-
14	3.38 (d, *J* = 8.7)	45.1	CH	7, 8, 12, 13, 17
15	6.13 (d, *J* = 1.5)	108.3	CH	12, 13
16	7.24 (d, *J* = 1.5)	141.4	CH	12, 13, 15
17	-	174.9	C	-
18	1.61 (s)	19.6	CH_3	3, 4, 5, 19
19	1.08 (s)	22.6	CH_3	3, 4, 5, 18
20	1.50 (s)	16.6	CH_3	1, 5, 9, 10
1′	-	166.2	C	-
2′	-	130.8	C	-
3′/7′	8.05 (d, *J* = 7.5)	129.6	CH	1′, 5′
4′/6′	7.24 (t, *J* = 7.5)	128.4	CH	2′, 5′
5′	7.57 (t, *J* = 7.5)	132.9	CH	3′, 7′
1″	-	170.2	C	-
$OCOCH_3$	2.06 (s)	21.0	CH_3	1″
CO_2CH_3	3.75 (s)	52.1	CH_3	17

3.1.4 Compound CP4



Compound **CP4**, its molecular formula was deduced as $C_{29}H_{34}O_6$ from the HREIMS (*m/z* 460.2225, $[M-H_2O]^+$). The UV absorption maximum at 279 nm and IR absorption at 1746 cm^{-1} suggested an *α,β*-butenolide ring conjugated with an extra double bond similar to that found in neocaesalpin D (Kinoshita *et al.*, 2000) and I (Kinoshita *et al.*, 2005) previously isolated from the genus *Caesalpinia*. The ^1H NMR (**Table 5**) spectrum of **CP4** displayed a singlet and a broad singlet at δ 5.68 (H-15) and 5.70 (H-11), respectively instead of the doublet signals associated with a 2,3-disubstituted furan as in **CP1-CP3**. There were resonances for three tertiary methyl groups at *δ* 0.99 (Me-18), 1.09 (Me-19) and 1.32 (Me-20), a secondary methyl group at *δ* 1.10 (*d*, *J* = 7.5 Hz, Me-17) and two oxymethine protons at *δ* 4.33 (*dd*, *J* = 11.5, 4.0 Hz, H-7) and 5.56 (*d*, *J* = 4.0 Hz, H-6). The *trans*-cinnamoyloxy side chain was displayed as two doublets at *δ* 6.38 and 7.64 (*J* = 16.0 Hz) and aromatic-proton signals betweens 7.31-7.45 whose location was placed at C-6 due to HMBC correlation of H-6 (*δ* 5.56) with the cinnamate carbonyl carbon at *δ* 167.5. NOESY cross peaks of H-7 with H-6 and Me-17 and between H-9 and H-7 suggested that these protons lay on the same side. In addition, the small coupling constant (4.0 Hz) supported the orientation at C-6 and C-7. From these data, **CP4** was deduced to be 6*β*-cinnamoyloxy-11,13(15)-diene-5*α*,7*β*-dihydroxycassan-12,16-olide, a new compound (Pranithanchai *et al.*, 2009) and was named as neocaesalpin P.



Selective HMBC correlation of **CP4**

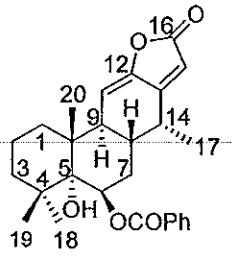
Table 5 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP4**

Position	**δ_H (mult, *J*, Hz)**	**δ_C**	**DEPT**	**HMBC**
1	1.51 (m)	33.1	CH_2	2,10
2	1.50 (m), 1.68 (m)	17.9	CH_2	4
3	1.07 (m), 1.67 (m)	37.7	CH_2	1, 2
4	-	39.2	C	-
5	-	77.9	C	-
6	5.56 (d, J = 4.0)	73.8	CH	5, 7, 8, 10, 1′
7	4.33 (dd, J = 11.5, 4.0)	67.6	CH	6, 8, 14
8	2.10 (td, J = 11.5, 4.5)	39.1	CH	6, 7, 9, 11, 14, 15, 17
9	2.90 (dt, J = 11.5)	40.6	CH	1, 7, 8, 10, 11, 12, 20
10	-	41.3	C	-
11	5.70 (brs)	111.6	CH	10, 12, 13
12	-	150.4	C	-
13	-	161.3	C	-
14	3.30 (qd, J = 7.5, 4.5)	28.4	CH	8, 9, 12, 13, 15, 17
15	5.68 (s)	110.9	CH	8, 16, 17

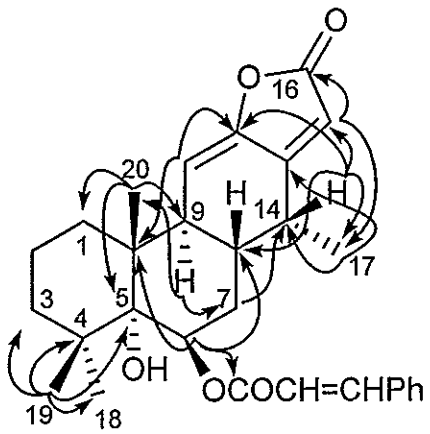
Table 5 (continued)

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
16	-	170.6	C	-
17	1.10 (d, *J* = 7.5)	14.2	CH_3	8, 13, 14
18	0.99 (s)	27.3	CH_3	3, 4, 5, 19
19	1.09 (s)	24.8	CH_3	3, 4, 5, 18
20	1.32 (s)	17.9	CH_3	1, 5, 9, 10
1′	-	167.5	C	-
2′	6.38 (d, *J* = 16.0)	117.5	CH	1′, 3′, 4′
3′	7.64 (d, *J* = 16.0)	146.5	CH	1′, 2′, 4′, 5′, 9′
4′	-	134.0	C	-
5′/9′	7.45 (dd, *J* = 7.25, 2.5)	128.3	CH	4′, 6′, 8′
6′/8′	7.32 (m)	129.0	CH	4′
7′	7.31 (m)	130.8	CH	6′, 8′

3.1.5 Compound CP5



Compound **CP5**, $C_{27}H_{32}O_5$, displayed related ^1H and ^{13}C NMR data (**Table 6**) to those of **CP4.** The differences were shown as the replacement of an oxymethine proton H-7 at δ 4.33 in **CP4** with methylene protons at δ 1.50 (*m*, H-7_{eq}) and 2.30 (td, J = 13.8, 3.6 Hz, H-7_{ax}) in **CP5**. The cinnamoyloxy side chain in **CP4** was replaced with a benzoyloxy side chain in **CP5**, whose location at C-6 was supported by HMBC correlation of H-6 (δ 5.44) with benzoate carbonyl carbon at δ 165.6. The relative configuration was characterized by NOESY correlations, the protons H-6 and H-7_{ax} were located on the same side due to cross peaks of H-7_{ax} with H-6 and Me-17, of H-7_{eq} with H-8 and of H-8 with H-14 and Me-20. In addition the small vicinal coupling constant ($J_{6eq,7ax}$, $J_{6eq,7eq}$ = 3.6 Hz) supported the equatorial orientation of H-6. Therefore, **CP5** was assigned as 6β-benzoyloxy-11,13(15)-diene-5α-hydroxycassan-12,16-olide, a new compound (Pranithanchai *et al.*, 2009) and was named as neocaesalpin Q.

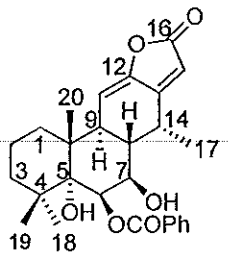


Selective HMBC correlation of **CP5**

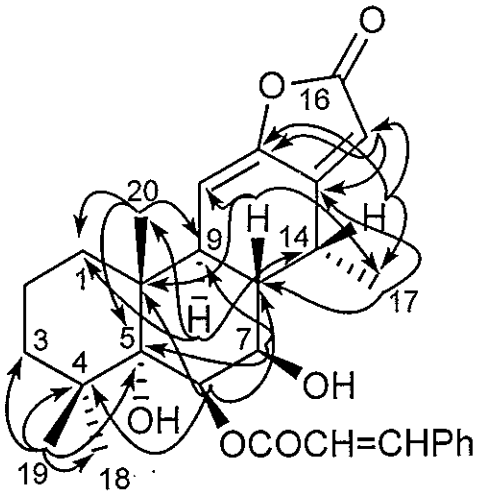
Table 6 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP5**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.62 (m), 1.64 (m)	33.2	CH_2	2, 10
2	1.52 (m), 1.54 (m)	18.0	CH_2	4
3	1.09 (m), 1.69 (m)	38.0	CH_2	2, 1
4	-	38.9	C	-
5	-	77.2	C	-
6	5.44 (t, J = 3.6)	72,5	CH	5, 7, 8, 10, 1′
7	1.50 (m)	30.9	CH_2	6, 8, 14
	2.30 (td, J = 13.8, 3.6)			
8	2.15 (tt, J = 10.2, 3.6)	33.1	CH	7, 9, 1113, 14, 17
9	2.90 (brd, J = 10.2, 3.6)	41.8	CH	7, 8, 10, 11, 12, 20
10	-	41.5	C	-
11	5.75 brs	112.3	CH	10, 12
12	-	150.2	C	-
13	-	161.3	C	-
14	2.73 (qd, J = 7.2, 3.6)	33.3	CH	8, 9, 12, 13, 15, 17
15	5.66 (s)	110.0	CH	16, 17
16	-	170.1	C	-
17	1.03 (d, J = 7.2)	14.6	CH_3	8, 13, 14
18	0.94 (s)	27.2	CH_3	3, 4, 5, 19
19	1.14 (s)	25.3	CH_3	3, 4, 5, 18
20	1.42 (s)	18.1	CH_3	1, 5, 9, 10
1′	-	165.6	C	-
2′	-	130.1	C	-
3′/7′	7.95 (dd, J = 7.5, 1.5)	129.7	CH	2′, 4′
4′/6′	7.39 (dt, J = 7.5, 1.5)	128.7	CH	2′
5′	7.52 (tt, J = 7.5, 1.5)	133.3	CH	4′,6′

3.1.6 Compound CP6



Compound **CP6**, $C_{27}H_{32}O_6$, displayed similar ^{1}H and ^{13}C NMR data (**Table 7**) to those of **CP5** except at C-7 where methylene protons at δ 1.50 (m) and 2.30 (td, J = 13.8, 3.6 Hz) in **CP5** were replaced by an oxymethine proton at δ 4.38 (dd, J = 11.5, 4.0 Hz) in **CP6**. The NOESY cross peaks of H-7 with H-6 and Me-17 supported the *cis*-configuration of H-6 and H-7. Therefore, **CP6** was assigned as 6β-benzoyloxy-11,13(15)-diene-5α,7β-dihydroxycassan-12,16-olide, a new compound (Pranithanchai *et al.*, 2009) and was named as neocaesalpin R,

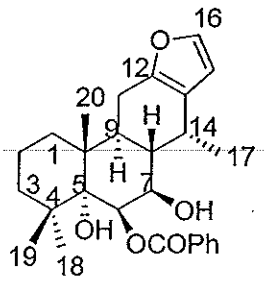


Selected HMBC correlation for compound **CP6**

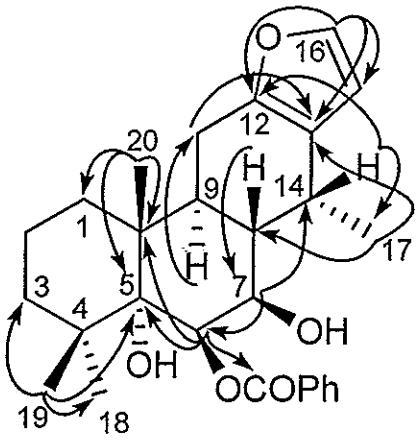
Table 7 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP6**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.52 (m), 1.59 (m)	33.2	CH_2	2, 10
2	1.34 (m), 1.53 (m)	17.0	CH_2	4
3	1.15 (m), 1.65 (m)	37.7	CH_2	2, 1
4	-	39.1	C	-
5	-	78.1	C	-
6	5.70 (d, J = 4.0)	74.1	CH	5, 7, 8, 10, 1′
7	4.38 (dd, J = 11.5, 4.0)	67.9	CH	6, 8, 14
8	2.12 (td, J = 11.5, 4.0)	39.3	CH	7, 9, 1113, 14, 17
9	2.92 (brd, J = 11.0)	40.5	CH	7, 8, 10, 11, 12, 20
10	-	41.3	C	-
11	5.72 brs	111.0	CH	10, 12
12	-	150.4	C	-
13	-	161.0	C	-
14	3.30 (qd, J = 7.5, 4.5)	28.4	CH	8, 9, 12, 13, 15, 17
15	5.70 (s)	110.4	CH	16, 17
16	-	170.3	C	-
17	1.07 (d, J = 7.0)	14.2	CH_3	8, 13, 14
18	1.00 (s)	27.2	CH_3	3, 4, 5, 19
19	1.07 (s)	24.9	CH_3	3, 4, 5, 18
20	1.41 (s)	18.0	CH_3	1, 5, 9, 10
1′	-	167.3	C	-
2′	-	129.2	C	-
3′/7′	7.96 (d, J = 7.5)	129.9	CH	2′, 4′
4′/6′	7.40 (t, J = 7.2)	128.7	CH	2′
5′	7.53 (t, J = 7.5)	133.5	CH	4′,6′

3.1.7 Compound CP7



Compound **CP7** was isolated as amorphous solid. The ^{1}H and ^{13}C NMR spectral data (**Table 8**) of **CP7** were similar to those of **CP1**. The signals of a cinnamoyloxy moiety [δ 6.51 (*d*, J = 15.9 Hz, H-2'), 7.75 (*d*, J = 15.9 Hz, H-3') and 7.41-7.55] in **1** were replaced by a benzoate ester group resonating between δ 7.44-8.05, whose location was placed at C-6 due to HMBC correlation of H-6 (δ 5.83) to the carbonyl carbon of benzoate ester group (δ 167.3). The oxymethine H-7 at δ 4.41 (*dd*, J = 11.1, 4.2 Hz) was deduced to be axially oriented from large vicinal coupling constants ($J_{7ax,8ax}$ = 11.1 Hz) and small vicinal coupling constant ($J_{7ax,6eq}$ = 4.2 Hz). It was further supported by NOESY correlations of H-7 with Me-17, H-6 and H-9 but no cross peak with Me-20, H-8 and H-14. From these data, the protons H-6 and H-7 were located on the same side. Thus, **CP7** was assigned to be isovouacapenol C (Ragasa *et al.*, 2002).



Selected HMBC correlation for compound **CP7**

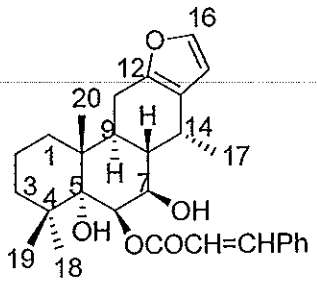
Table 8 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP7**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.47 (m), 1.57 (m)	34.9	CH_2	-
2	1.50 (m), 1.74 (m)	18.1	CH_2	-
3	1.14 (m), 1.70 (m)	37.7	CH_2	-
4	-	39.2	C	-
5	-	77.8	C	-
6	5.83 (d, J = 4.2)	74.1	CH	5, 7, 8, 10, 1′
7	4.41 (dd, J = 11.1, 4.2)	69.0	CH	6, 8, 14
8	2.02 (m)	38.2	CH	7, 9, 14
9	2.46 (m)	37.1	CH	10, 11
10	-	40.9	C	-
11	2.56 (m)	21.7	CH_2	9, 12, 13
12	-	149.2	C	-
13	-	121.9	C	-
14	3.02 (m)	27.3	CH	9, 12, 13, 15, 17
15	6.19 (d, J = 1.4)	109.7	CH	12, 13, 16
16	7.24 (d, J = 1.4)	140.5	CH	12, 13, 15
17	1.05 (d, J = 6.9)	17.1	CH_3	8, 13, 14
18	1.12 (s)	27.8	CH_3	3, 5, 19
19	1.16 (s)	25.5	CH_3	3, 5, 18
20	1.52 (s)	17.6	CH_3	1, 5, 10
1′	-	167.3	C	-
2′	-	129.9	C	-
3′/7′	8.04 (d, J = 7.5)	129.9	CH	2′, 5′
4′/6′	7.43 (t, J = 7.5)	128.5	CH	5′
5′	7.55 (t, J = 7.5)	133.2	CH	3′

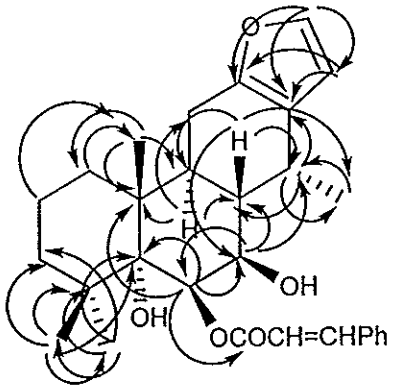
Table 9 Comparison of ^{1}H NMR and ^{13}C NMR spectral data of compounds **CP7** and isovouacapenol C (**R**, recorded in $CDCl_3$)

Position	CP7		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
1	1.47 (m), 1.57 (m)	34.9	1.49 (m), 1.54 (m)	35.1
2	1.50 (m), 1.74 (m)	18.1	1.56 (m), 1.70 (m)	18.1
3	1.14 (m), 1.70 (m)	37.7	1.18 (m), 1.67 (m)	37.8
4	-	39.2	-	39.3
5	-	77.8	-	77.9
6	5.83 (d, J = 4.2)	74.1	5.81 (d, J = 4.1)	74.7
7	4.41 (dd, J = 11.1, 4.2)	69.0	4.41 (dd, J = 11.0, 4.1)	69.3
			1.57 (s, OH)	
8	2.02 (m)	38.2	2.02 (m)	38.1
9	2.46 (m)	37.1	2.43 (m)	37.2
10	-	40.9	-	41.0
11	2.56 (m)	21.7	2.57 (m)	21.8
12	-	149.2	-	149.2
13	-	121.9	-	122.0
14	3.02 (m)	27.3	3.04 (m)	27.3
15	6.19 (d, J = 1.4)	109.7	6.20 (d, J = 1.9)	109.7
16	7.24 (d, J = 1.4)	140.5	7.24 (d, J = 1.9)	140.5
17	1.05 (d, J = 6.9)	17.1	1.09 (d, J = 6.8)	17.1
18	1.12 (s)	27.8	1.12 (s)	17.6
19	1.16 (s)	25.5	1.18 (s)	25.5
20	1.52 (s)	17.6	1.54 (s)	27.3
1′	-	167.3	-	167.2
2′	-	129.9	-	130.0
3′/7′	8.04 (d, J = 7.5)	129.9	8.05 (m)	129.9
4′/6′	7.43 (t, J = 7.5)	128.5	7.45 (m)	128.6
5′	7.55 (t, J = 7.5)	133.2	7.57 (m)	133.2

3.1.8 Compound CP8



Compound **CP8** was isolated as amorphous solid. The ^{1}H and ^{13}C NMR spectral data (**Table 10**) of **CP8** were similar to those of **CP7**, except that the benzoate ester side chain in **CP7** was replaced with a cinnamoyloxy side chain in **CP8**, whose location at C-6 was supported by HMBC correlation of H-6 (δ 5.65) with cinnamoate carbonyl carbon at δ 167.4. The NOESY cross peaks of H-7 with H-6 and Me-17 supported the *cis*-configuration of H-6 and H-7. Therefore, **CP8** was assigned as 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol (McPherson *et al.*, 1986).



Selected HMBC correlation for compound **CP8**

Table 10 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP8**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.51 (m), 1.47 (m)	35.0	CH_2	20
2	1.70 (m), 1.58 (m)	18.1	CH_2	20
3	1.68 (m), 1.18 (m)	37.8	CH_2	-
4	-	39.3	C	-
5	-	77.8	C	-
6	5.65 (d, J = 4.2)	73.5	CH	5, 7, 10, 1′
7	4.38 (dd, J = 11.1, 4.2)	69.2	CH	6, 8, 14
8	1.98 (dt, J = 11.1, 5.1)	37.9	CH	7, 9, 14, 17
9	2.43 (m)	37.2	CH	8, 10, 11
10	-	41.1	C	-
11	2.54 (brd, J = 8.4)	21.8	CH_2	-
12	-	149.2	C	-
13	-	122.0	C	-
14	3.05 (brquint, J = 6.9)	27.3	CH	8, 13, 17
15	6.20 (d, J = 1.7)	109.7	CH	12, 13
16	7.23 (d, J = 1.7)	140.5	CH	12, 13, 15
17	1.08 (d, J = 6.9)	17.3	CH_3	14
18	1.09 (s)	27.8	CH_3	3, 4, 5, 19
19	1.21 (s)	25.5	CH_3	3, 4, 5, 18
20	1.45 (s)	17.2	CH_3	1, 9, 10
1′	-	167.4	C	-
2′	6.44 (d, J = 15.9)	118.0	CH	1′, 4′
3′	7.72 (d, J = 15.9)	146.0	CH	1′, 4′
4′	-	134.2	C	-
5′/9′	7.52 (m)	128.9	CH	3′, 7′
6′/8′	7.39 (m)	128.3	CH	4′
7′	7.39 (m)	130.6	CH	5′

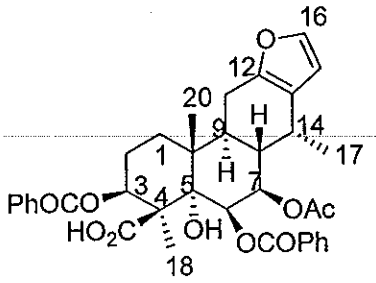
Table 11 Comparison of ^{1}H NMR and ^{13}C NMR spectral data of compounds **CP8** and 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol (**R**, recorded in $CDCl_3$)

Position	CP8		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
1	1.47 (m), 1.51 (m)	35.0	1.17 (brd), 1.68 (brd)	35.0
2	1.58 (m), 1.70 (m)	18.1	1.54 (brd), 1.65 (brd)	18.1
3	1.18 (m), 1.68 (m)	37.8	1.54 (brd), 1.76 (brd)	37.8
4	-	39.3	-	39.3
5	-	77.8	1.80, (s, OH)	76.8
6	5.65 (d, J = 4.2)	73.5	5.65 (d, J = 4.0)	73.6
7	4.38 (dd, J = 11.1, 4.2)	69.2	4.38 (dd, J = 11.0, 3.5)	69.2
8	1.98 (dt, J = 11.1, 5.1)	37.9	1.98 (ddd, J = 12.0, 11.0, 5.0)	37.9
9	2.43 (m)	37.2	2.45 (dt, J = 12.0, 9.0)	37.2
10	-	41.1	-	41.1
11	2.54 (brd, J = 8.4)	21.8	2.54 (brd, J = 9.0)	21.8
12	-	149.2	-	149.2
13	-	122.0	-	122.0
14	3.05 (brquint, J = 6.9)	27.3	3.05 (dq, J = 7.0, 6.0)	27.3
15	6.20 (d, J = 1.7)	109.7	6.20 (d, J = 2.0)	109.7
16	7.23 (d, J = 1.7)	140.5	7.23 (d, J = 2.0)	140.5
17	1.08 (d, J = 6.9)	17.3	1.07 (d, J = 7.0)	17.3
18	1.09 (s)	27.8	1.09 (s)	27.7
19	1.21 (s)	25.5	1.21 (s)	25.5
20	1.45 (s)	17.2	1.45 (s)	17.1
1′	-	167.4	-	167.4
2′	6.44 (d, J = 15.9)	118.0	6.44 (d, J = 16.0)	118.0
3′	7.72 (d, J = 15.9)	146.0	7.72 (d, J = 16.0)	145.9
4′	-	134.2	-	134.2
5′/9′	7.52 (m)	128.9	7.53 (m)	128.9
6′/8′	7.39 (m)	128.3	7.38 (m)	128.2

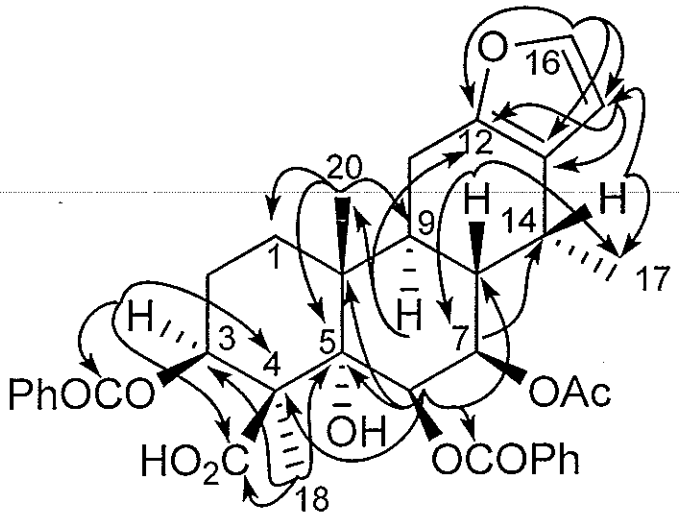
Table 11 (continued)

Position	**CP8**		**R**	
	δ_H (mult, *J*, Hz)	**δ_C**	**δ_H (mult, *J*, Hz)**	**δ_C**
7′	7.39 (m)	130.6	7.38 (m)	130.5

3.1.9 Compound CP9



Compound **CP9** was isolated as amorphous solid. The ^{1}H and ^{13}C NMR spectral data (**Table 12**) of **CP9** were related to those of **CP2**. The signals of methylene protons (δ 1.86, *dd*, J = 13.0, 11.0 Hz and 2.05, *dd*, J = 13.0, 5.5 Hz, 2H-6) and oxymethine H-7 at δ 4.12 (*dt*, J = 11.0, 5.5 Hz) in **CP2** were replaced by two oxymethine protons (δ 5.96, *d*, J = 3.9 Hz and 5.49, *dd*, J = 11.4, 3.9 Hz). The signal of methyl carbon at δ 19.7 in **CP2** was replaced by a carbonyl carbon of carboxylic group at δ 177.0. In addition , signals of two benzoate ester group were displayed between δ 7.43-7.93 and an acetoxy methyl group at δ 1.95, whose locations were placed at C-3, C-6 and C-7, respectively due to HMBC correlations of H-3 (δ 5.33) to the carbonyl carbon of benzoate ester group (δ 165.9), of H-6 (δ 5.96) to the carbonyl carbon of benzoate ester group (δ 165.8) and of H-7 (δ 5.49) and acetoxy methyl (δ 1.95) to the carbonyl carbon of acetyl ester group (δ 171.3). The proton H-3 was assigned to be axially oriented from the small and large vicinal coupling constants ($J_{3ax,2eq}$ = 4.8 Hz, $J_{3ax,2ax}$ = 12.3 Hz). The oxymethine H-7 at δ 5.49 (*dd*, J = 11.4, 3.9 Hz) was deduced to be axially oriented from large vicinal coupling constants ($J_{7ax,8ax}$ = 11.4 Hz) and small vicinal coupling constant ($J_{7ax,6eq}$ = 3.9 Hz). It was further supported by NOESY correlations of H-3 with Me-18 and H-7 with Me-17, H-9 and H-6 but no cross peak with Me-20, and H-8. From these data, the protons H-3 and Me-18, H-6 and H-7 were located on the same side. Thus, compound **CP9** was assigned to be pulcherrimin E (Roach *et al.*, 2003).



Selected HMBC correlation for compound **CP9**

Table 12 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP9**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	2.03 (m), 1.68 (m)	32.9	CH_2	2, 10
2	2.58 (m), 1.92 (m)	24.3	CH_2	1, 3, 10
3	5.33 (dd, *J* = 12.3, 4.8)	77.0	CH_2	2, 4, 19, 1′
4	-	53.5	C	-
5	-	79.4	C	-
6	5.96 (d, *J* = 3.9)	68.9	CH	4, 5, 7, 8, 10, 1″
7	5.49 (dd, *J* = 11.4, 3.9)	71.2	CH	8, 14, 1‴
8	2.29 (dt, *J* = 11.4, 3.8)	35.2	CH	7, 9, 17
9	2.61 (m)	36.9	CH	11, 12, 20
10	-	41.6	C	-
11	2.67 (m), 2.65 (m)	22.2	CH_2	9, 10, 13
12	-	148.8	C	-
13	-	121.4	C	-
14	2.82 (quint, *J* = 6.9)	27.3	CH	8, 9, 13, 15, 17
15	6.19 (d, *J* = 1.8)	109.5	CH	12, 13

Table 12 (continued)

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
16	7.26 (d, *J* = 1.8)	140.9	CH	12, 13, 15
17	0.98 (d, *J* = 6.9)	17.1	CH_3	8, 14
18	1.25 (s)	19.9	CH_3	3, 4, 19
19	-	177.0	C	-
20	1.61 (s)	17.2	CH_3	1, 5, 9, 10
1′	-	165.9	C	-
2′	-	130.2	C	-
3′/7′	7.90 (d, *J* = 7.5)	129.6	CH	1′, 2′, 5′
4′/6′	7.22 (t, *J* = 7.5)	128.5	CH	-
5′	7.54 (t, *J* = 7.5)	133.1	CH	4′
1″	-	165.8	C	-
2″	-	130.0	C	-
3″/7″	7.93 (d, *J* = 7.5)	129.4	CH	1″, 2″, 5″
4″	7.29 (t, *J* = 7.5)	128.3	CH	2″
5″	7.49 (t, *J* = 7.5)	133.2	CH	3″
1‴	-	171.3	C	-
$OCOCH_3$	1.95 (s)	20.9	CH_3	1‴

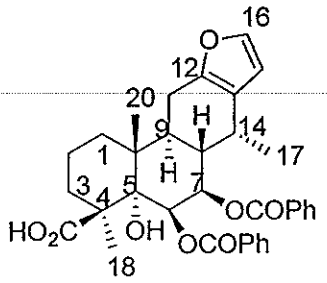
Table 13 Comparison of ^{1}H NMR and ^{13}C NMR spectral data of compounds **CP9** and pulcherrimin E (**R**, recorded in $CDCl_3$)

Position	CP9		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
1	1.68 (m), 2.03 (m)	32.9	1.68 (dd, *J* = 13.2, 3.8)	32.9
			2.02 (dd, *J* = 13.2, 3.8)	
2	1.92 (m), 2.58 (m)	24.3	1.93 (m), 2.61 (m)	24.3
3	5.33 (dd, *J* = 12.3, 4.8)	77.0	5.33 (dd, *J* = 12.2, 4.9)	77.0
4	-	53.5	-	53.4
5	-	79.4	-	79.4
6	5.96 (d, *J* = 3.9)	68.9	5.95 (d, *J* = 4.0)	69.0
7	5.49 (dd, *J* = 11.4, 3.9)	71.2	5.50 (dd, *J* = 11.7, 4.0)	71.0
8	2.29 (dt, *J* = 11.4, 3.8)	35.2	2.29 (dt, *J* = 11.7, 5.0)	35.2
9	2.61 (m)	36.9	2.58 (m)	36.9
10	-	41.6	-	41.6
11	2.65 (m), 2.67 (m)	22.2	2.62 (m), 2.66 (m)	22.2
12	-	148.8	-	148.7
13	-	121.4	-	121.4
14	2.82 (brquint, *J* = 6.9)	27.3	2.82 (dq, *J* = 7.0, 5.0)	27.3
15	6.19 (d, *J* = 1.8)	109.5	6.18 (d, *J* = 1.9)	109.5
16	7.26 (d, *J* = 1.8)	140.9	7.27 (d, *J* = 1.9)	140.9
17	0.98 (d, *J* = 6.9)	17.1	0.99 (d, *J* = 7.0)	17.1
18	1.25 (s)	19.9	1.28 (s)	19.9
19	-	177.0	-	176.4
20	1.61 (s)	17.2	1.62 (s)	17.2
1′	-	165.9	-	162.1
2′	-	130.2	-	130.0
3′/7′	7.90 (d, *J* = 7.5)	129.6	7.96 (dd, *J* = 8.5, 1.1)	129.6
4′/6′	7.22 (t, *J* = 7.5)	128.5	7.39 (dd, *J* = 8.5, 8.5)	128.5
5′	7.54 (t, *J* = 7.5)	133.1	7.56 (tm, *J* = 8.5)	133.2
1″	-	165.8	-	162.1

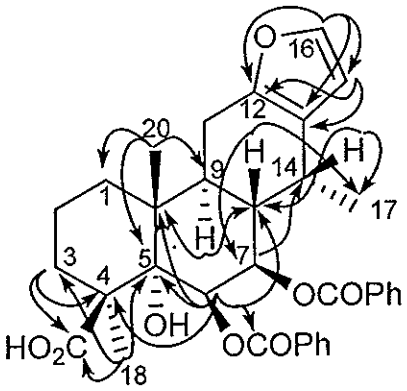
Table 13 (continued)

Position	CP9		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
2″	-	130.0	-	130.2
3″/7″	7.93 (d, *J* = 7.5)	129.4	7.91 (dd, *J* = 8.4, 1.3)	129.4
4″	7.29 (t, *J* = 7.5)	128.3	7.24 (dd, *J* = 8.4, 8.4)	128.6
5″	7.49 (t, *J* = 7.5)	133.2	7.46 (tm, *J* = 8.4)	133.1
1‴	-	171.3	-	171.2
$OCOCH_3$	1.95 (s)	20.9	1.95 (s)	20.9

3.1.10 Compound CP10



Compound **CP10** was isolated as amorphous solid. The ^{1}H and ^{13}C NMR spectral data (**Table 14**) of **CP10** were related to those of **CP9,** except that the signals of acetoxy methyl ester (δ_H 1.95, δ_C 171.3 and 20.9) in **CP9** were replaced by the methylene protons (δ 1.85, *m* and 1.53, *m*) in **CP10**. Two benzoate ester groups resonating between δ 7.29-7.78 were placed at C-6 and C-7 due to HMBC correlation of H-6 at δ 6.09 (*d*, J = 3.6 Hz) to the carbonyl carbon of benzoate ester group (δ 165.6) and H-7 at δ 5.78 (*dd*, J = 10.8, 3.6 Hz) to the carbonyl carbon of benzoate ester group (δ 166.1). Therefore, **CP10** was assigned as pulcherrimin C (Patil et al., 1997).



Selected HMBC correlation for compound **CP10**

Table 14 ^{1}H and ^{13}C NMR, DEPT and HMBC spectral data of compound **CP10**

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.74 (m), 1.58 (m)	34.7	CH_2	10
2	2.02 (m), 1.46 (m)	18.7	CH_2	5, 10
3	1.85 (m), 1.53 (m)	33.6	CH_2	4, 19
4	-	48.9	C	-
5	-	77.9	C	-
6	6.09 (d, J = 3.6)	69.0	CH	4, 5, 7, 8, 10, 1′
7	5.78 (dd, J = 10.8, 3.6)	72.3	CH	6, 8, 14, 1″
8	2.45 (dt, J = 11.7, 4.8)	35.7	CH	7, 9, 14, 17
9	2.53 (m)	37.4	CH	8, 10
10	-	41.6	C	-
11	2.70 (m), 2.60 (m)	22.3	CH_2	8, 9, 10, 13
12	-	149.1	C	-
13	-	121.4	C	-
14	2.87 (m)	27.4	CH	8, 9, 12, 13, 17
15	6.14 (d, J = 1.8)	109.5	CH	12, 13
16	7.23 (d, J = 1.8)	140.8	CH	12, 13, 15
17	1.00 (d, J = 6.9)	17.1	CH_3	8, 14
18	1.20 (s)	24.2	CH_3	3, 4, 5, 19
19	-	180.0	C	-
20	1.40 (s)	17.7	CH_3	1, 5, 9, 10
1′	-	165.6	C	-
2′	-	130.1	C	-
3′/7′	7.78 (d, J = 7.2)	129.6	CH	1′, 5′
4′/6′	7.36 (t, J = 7.2)	128.3	CH	2′
5′	7.50 (m)	132.6	CH	3′, 7′
1″	-	166.1	C	-
2″	-	130.0	C	-
3″/7″	7.81 (d, J = 7.5)	129.5	CH	1″, 5″
4″/6″	7.29 (t, J = 7.5)	128.1	CH	2″

Table 14 (continued)

Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
5″	7.49 (m)	132.8	CH	3″, 7″

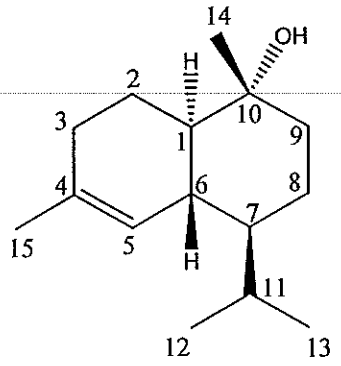
Table 15 Comparison of ^{1}H NMR and ^{13}C NMR spectral data of compounds **CP10** and pulcherrimin C (**R**, recorded in $CDCl_3$)

Position	CP8		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
1	1.58 (m), 1.74 (m)	34.7	1.53 (m), 1.70 (m)	34.6
2	1.46 (m), 2.02 (m)	18.7	1.44 (m), 1.93 (m)	18.7
3	1.53 (m), 1.85 (m)	33.6	1.55 (m), 1.76 (m)	33.4
4	-	48.9	-	49.0
5	-	77.9	-	77.8
6	6.09 (d, J = 3.6)	69.0	6.05 (d, J = 3.7)	68.9
7	5.78 (dd, J = 10.8, 3.6)	72.3	5.76 (dd, J = 11.1, 3.7)	72.4
8	2.45 (dt, J = 11.7, 4.8)	35.7	2.44 (ddd, J = 12.0, 11.1, 5.0)	35.6
9	2.53 (m)	37.4	2.52 (m)	37.3
10	-	41.6	-	41.5
11	2.60 (m), 2.70 (m)	22.3	2.63 (m), 2.67 (m)	22.2
12	-	149.1	-	149.1
13	-	121.4	-	121.4
14	2.87 (m)	27.4	2.86 (dq, J = 7.0, 5.0)	27.4
15	6.14 (d, J = 1.8)	109.5	6.14 (d, J = 1.8)	109.5
16	7.23 (d, J = 1.8)	140.8	7.24 (d, J = 1.8)	140.8
17	1.00 (d, J = 6.9)	17.1	1.00 (d, J = 7.0)	17.1
18	1.20 (s)	24.2	1.12 (s)	24.2
19	-	180.0	-	181.6
20	1.40 (s)	17.7	1.35 (s)	17.8
1′	-	165.6	-	165.6
2′	-	130.1	-	130.5
3′/7′	7.78 (d, J = 7.2)	129.6	7.76 (dd, J = 8.4, 1.3)	129.5
4′/6′	7.36 (t, J = 7.2)	128.3	7.36 (dd, J = 8.4, 8.4)	128.3
5′	7.50 (m)	132.6	7.50 (tm, J = 8.4)	132.6
1″	-	166.1	-	166.2

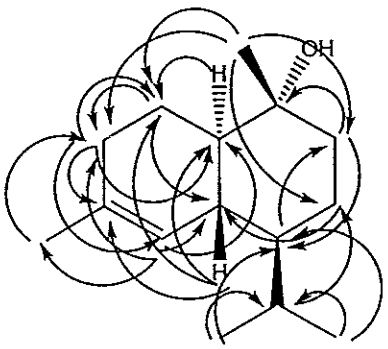
Table 15 (continued)

Position	CP9		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
2″	-	130.0	-	129.9
3″/7″	7.81 (d, *J* = 7.5)	129.5	7.78 (dd, *J* = 8.4, 1.3)	129.6
4″	7.29 (t, *J* = 7.5)	128.1	7.28 (dd, *J* = 8.4, 8.4)	128.1
5″	7.49 (m)	132.8	7.48 (tm, *J* = 8.4)	132.9

3.1.11 Compound CP11



Compound **CP11** was obtained as viscous oil, it exhibited hydroxyl (3361 cm^{-1}), and an olefinic group (1640 cm^{-1}). The ^{1}H NMR spectrum of **CP11** (**Table 16**) showed signals for an isopropyl group at δ 0.89, 0.84 (3H each, *d*, $J = 6.9$ Hz) and 1.98 (1H, m, H-12), a three-proton singlet at δ 1.20 for a methyl attached to a quaternary carbon bearing hydroxyl group, a trisubstituted olefinic proton at δ 5.56 (1H, m, H-5) and a methyl group at 1.65 (brs). The ^{13}C-NMR spectrum (**Table 16**) exhibited 15 carbon signals for four CH_3, four CH_2, two olefinic carbons, four CH, and one C. It can be proposed to be a cadinane-type sesquiterpene. The ^{1}H-^{1}H correlated spectroscopy (COSY) of **CP11** displayed the connectivity of H-5 to H-6, which was also coupled to H-1 (δ 1.53, m) and H-7 (δ 1.28, m). The NOESY cross peak of H-6 with CH_3-15, CH_3-13 and CH_3-14 and no cross peak with H-1 supported the *trans*-fused ring of **CP11**. From this data, **CP13** was assigned as α-cadinol (Kuo *et al.*, 2003).

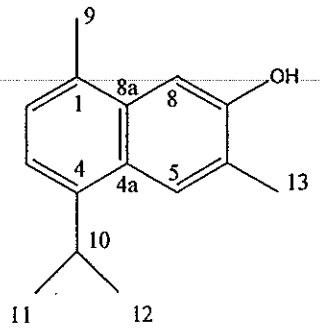


Selected HMBC correlation for compound **CP11**

Table 16 ^{1}H, ^{13}C NMR, DEPT and HMBC spectral data of compound **CP11**

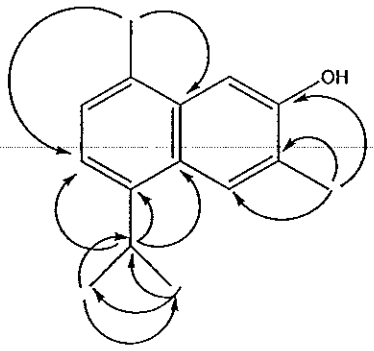
Position	δ_H (mult, *J*, Hz)	δ_C	DEPT	HMBC
1	1.53 (m)	46.1	CH	2
2	1.60 (m), 1.54 (m)	21.0	CH_2	3, 6
3	1.99 (m), 1.95 (m)	31.3	CH_2	1, 2, 4, 5
4	-	133.5	C	-
5	5.56 (m)	124.8	CH	1, 3, 6, 11
6	2.26 (m)	34.5	CH	1, 2, 4
7	1.28 (m)	43.6	CH	9
8	1.40 (m), 1.34 (m)	19.4	CH_2	6
9	1.51 (m), 1.37 (m)	34.6	CH_2	7, 10
10	-	72.4	C	-
11	1.98 (m)	26.7	CH	8, 13
12	0.89 (d, $J = 6.9$)	21.6	CH_3	7, 11
13	0.84 (d, $J = 6.9$)	21.6	CH_3	7, 11
14	1.20 (s)	29.3	CH_3	1, 2, 8, 9
15	1.65 (brs)	23.6	CH_3	3

3.1.12 Compound CP12



CP12 was obtained as viscous oil. The UV spectrum exhibited the absorption bands at 225, 235, 276, 286 and 299 nm. The IR spectrum indicated the presence of hydroxyl functionality (3328 cm^{-1}).

The ^{1}H NMR spectrum of **CP12** (**Table 17**) displayed two *ortho*-coupled of aromatic protons at δ 7.13 (d, J = 7.5 Hz, H-3) and 7.19 (d, J = 7.5 Hz, H-2). Two singlet signals of aromatic protons at δ 7.89 (*s*, H-5) and 7.25 (s, H-8), suggesting that they were *para* to each other. This was confirmed by HMBC spectrum, which showed the low-field proton (H-5) correlated with the methyl carbon at δ 16.8 (4-Me) and carbon at δ 142.2 (C-4) and the upfield proton (H-8) correlated with carbon at δ 130.1 (C-1), 126.9 (C-4a) and 125.1 (C-6). In addition, the presence of two methyl groups (δ 2.47 and 2.56) and one isopropyl moiety [δ 1.37, (6H, d, 6.6 Hz) and 3.67, (1H, sept)] was evident by ^{1}H and ^{13}C NMR signals (**Table 17**), establishing the cadinane skeleton. The methyl group at δ 2.47 was placed at C-6 because of HMBC correlations to C-5 (δ 125.6), C-6 (δ 125.1) and C-7 (δ 152.1) and the methyl at δ 2.56 was placed at C-1 due to HMBC correlations to C-2 (δ 126.2) and C-8a (δ 133.1). Finally, the isopropyl group was placed to C-4, judging from HMBC correlations of its methine proton δ 3.67 (*sept*, 6.6 Hz) with C-3 (119.1), C-4 (142.2) and C-4a (126.9). Thus, **CP12** was identified as 7-hydroxycadinane (Lindgren *et al.*, 1968)

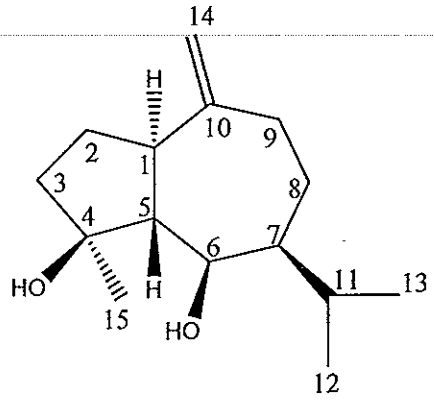


Selected HMBC correlation for compound **CP12**

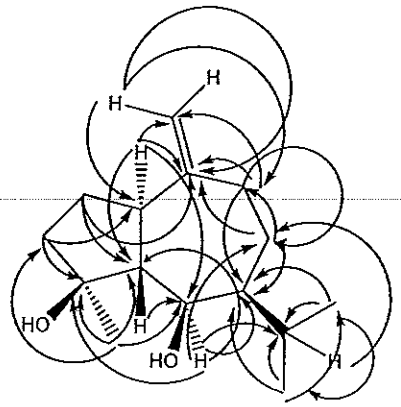
Table 17 ^{1}H, ^{13}C NMR, DEPT and HMBC spectral data of compound **CP12**

Position	**δ_H (mult, *J*, Hz)**	**δ_C**	**DEPT**	**HMBC**
1	-	130.1	C	-
2	7.19 (d, $J = 7.5$)	126.2	CH	3, 4, 8a, 9
3	7.13 (d, $J = 7.5$)	119.1	CH	1, 4a, 9, 10
4	-	142,2	C	-
4a	-	126.9	C	-
5	7.89 (s)	125.6	CH	13, 4, 8a
6	-	125.1	C	-
7	-	152.1	C	-
8	7.25 (s)	106.9	CH	4a, 6, 13
8a	-	133.1	C	-
9	2.56 (s)	19.5	CH_3	3, 8a
10	3.67 (sept)	28.4	CH	3, 4, 4a
11	1.37 (d, $J = 6.6$)	23.7	CH_3	4, 10, 12
12	1.37 (d, $J = 6.6$)	23.7	CH_3	4, 10, 11
13	2.47 (s)	16.8	CH_3	5, 6, 7

3.1.13 Compound CP13



Compound **CP13** was isolated as a colorless viscous oil. It exhibited hydroxyl (3400 cm^{-1}), and double bond (1640 cm^{-1}) absorptions in the IR spectrum. The ^1H NMR spectral data of **CP13** (**Table 18**) showed signals with a guaiane sesquiterpene hydrocarbon skeleton possessing an isopropyl group at δ 1.03, 0.96 (3H each, *d*, J = 6.6 Hz) and 1.70 (1H, m, H-11), 10(14)-exocyclic methylene at δ 4.76 (*brs*, 1H) and δ 4.73 (*brs*, 1H); δ_C 152.5 and 108.1, a tertiary methyl group at C-4 position (δ_C 80.8), a 3H singlet signal at δ 1.31 and an oxymethine proton at δ_H 4.08 : δ_C 72.6. The proton H-5 was assigned to be axially oriented from the two large vicinal coupling constants ($J_{5ax,1ax}$ = 11.7 Hz, $J_{5ax,6ax}$ = 9.3 Hz). The NOESY correlations of H-1 with Me-15 and H-7 but no cross peak with H-5, of H-6 and Me-15 and H-7 but no cross peak with Me-12 and Me-13. These data supported the *trans*-fused ring and the protons H-1, H-6, H-7 and Me-15 were located on the same side. Therefore, **CP13** was assigned as teucladiol (Bruno *et al.*, 1993).



Selected HMBC correlation for compound **CP13**

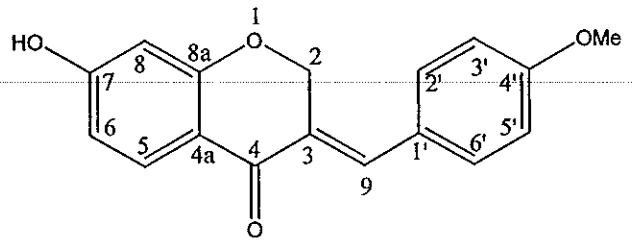
Table 18 ^{1}H, ^{13}C NMR, DEPT and HMBC spectral data of compound **CP13**

Position	**δ_H (mult, *J*, Hz)**	**δ_C**	**DEPT**	**HMBC**
1	2.37 (m)	42.8	CH	5, 6, 10, 14
2	1.86 (m), 1.74 (m)	27.3	CH_2	5, 10
3	1.88 (m), 1.72 (m)	40.5	CH_2	1, 4
4	-	80.8	C	-
5	1.90 (dd, J = 11.7, 9.3)	59.5	CH	6
6	4.08 (dd, J = 9.3, 3.6)	72.6	CH	4, 5, 7, 8, 11
7	1.26 (m)	48.5	CH	11
8	1.67 (m), 1.59 (m)	23.1	CH_2	7, 9, 10
9	2.56 (dt, J = 14.1, 6.6)	35.5	CH_2	1, 7, 8, 10, 14
	2.14 (dt, J = 14.1, 7.2)			
10	-	152.5	C	-
11	1.70 (m)	28.9	CH	8
12	1.03 (d, J = 6.6)	21.6	CH_3	7, 11, 13
13	0.96 (d, J = 6.6)	21.6	CH_3	7, 11, 12
14A	4.73 (brs)	108.1	CH_2	1, 9, 10
14B	4.76 (brs)			
15	1.31 (s)	24.0	CH_3	3, 4, 5, 6

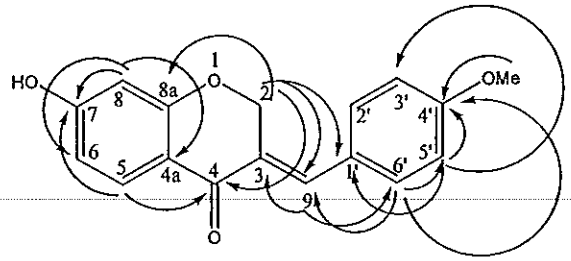
Table 19 Comparison of ^{1}H NMR and ^{13}C NMR spectral data of compounds **CP13** and teucladiol (**R**, recorded in $CDCl_3$)

Position	CP13		R	
	δ_H (mult, *J*, Hz)	δ_C	δ_H (mult, *J*, Hz)	δ_C
1	2.37 (m)	42.8	-	42.8
2	1.86 (m), 1.74 (m)	27.3	-	27.3
3	1.88 (m), 1.72 (m)	40.5	-	40.6
4	-	80.8	-	80.8
5	1.90 (dd, *J* = 11.7, 9.3)	59.5	1.88 (dd, *J* = 11.6, 9.6)	59.5
6	4.08 (dd, *J* = 9.3, 3.6)	72.6	4.09 (dd, *J* = 9.6, 3.9)	72.6
7	1.26 (m)	48.5	-	48.5
8	1.67 (m), 1.59 (m)	23.1	-	24.0
9	2.14 (dt, *J* = 14.4, 7.2)	35.5	2.14 (dt, *J* = 14.4, 7.2)	35.5
	2.56 (dt, *J* = 14.4, 7.3)		2.56 (dt, *J* = 14.4, 7.3)	
10	-	152.5	-	152.5
11	1.70 (m)	28.9	-	29.0
12	1.03 (d, *J* = 6.6)	21.6	1.03 (d, *J* = 6.6)	21.5
13	0.96 (d, *J* = 6.6)	21.6	0.97 (d, *J* = 6.6)	21.6
14A	4.73 (brs)	108.1	4.73 (d, *J* = 1.0)	108.1
14B	4.76 (brs)		4.76 (d, *J* = 0.7)	
15	1.31 (s)	24.0	1.31 (s)	23.2

3.1.14 Compound CP14



Compound **CP14** was obtained as a yellow crystal, m.p. = 158 °C. The UV spectrum exhibited the absorption bands at 317 and 357 nm. The IR spectrum showed the absorption bands of a free hydroxyl and carbonyl groups at 3439 cm^{-1}, 1655 cm^{-1} respectively. It implied that the main skeleton of compound **CP14** is a homoisoflavone type (McPherson *et al.*, 1983). The ^1H NMR spectral data of **3** showed the signals of aromatic protons on ring A at δ 7.87 (d, J = 8.7 Hz, H-5), 6.56 (dd, J = 8.7, 2.4 Hz, H-6) and 6.36 (d, J = 2.4 Hz, H-8). In the HMBC spectrum, an aromatic proton at δ_H 7.87 (d, J = 8.7 Hz, H-5) showed ^3J correlation to δ_c 164.8 (C-7), suggesting that the hydroxyl group was attached at C-7. Moreover, two sets signal of *p*-disubstituted aromatic protons on ring C were shown at δ 7.28 (d, J = 8.7 Hz, H-2′ and H-6′) and 6.99 (d, J = 8.7 Hz, H-3′ and H-5′). In the HMBC spectrum, the aromatic proton at δ_H 7.28 (d, J = 8.7 Hz, H-2′ and H-6′) showed ^3J correlation to δ_c 160.6, while the methoxy proton resonanced at δ 3.87 (*s*) also showed correlation to δ_c 160.6, implying that the methoxy group was attached at C-4′ of ring C. In the COSY spectrum of compound **CP14**, the methine proton at δ_H 7.78 was coupled with the methylene proton resonanced at δ_H 5.34, whose signals were assigned to C-9 and C-2 respectively. The geometry of C-3 and C-9 double bond was assigned as a trans-trisubstituted alkene. The HMBC data of compound **CP14** were summarized in **Table 20**. Therefore, compound **CP14** was deduced as Bonducellin (McPherson *et al.*, 1983)



Selected HMBC correlation for compound **CP14**

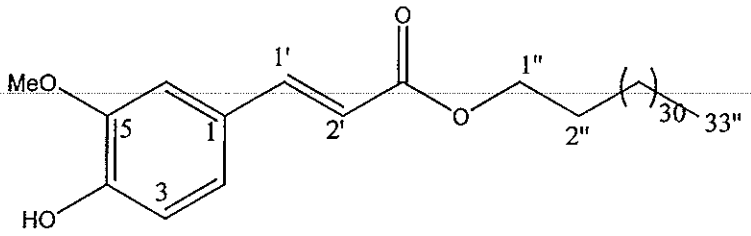
Table 20 ^{1}H, ^{13}C NMR, DEPT and HMBC spectral data of compound **CP14**

Position	**δ_H (mult, *J*, Hz)**	**δ_C**	**DEPT**	**HMBC**
2	5.34 (d, J = 1.8)	67.8	CH_2	3, 4, 8a, 9
3	-	129.0	C	-
4	-	181.7	C	2, 3, 4a, 5, 8a, 9
4a	-	114.8	C	-
5	7.87 (d, J = 8.7)	129.8	CH	4, 6, 7, 8
6	6.56 (dd, J = 8.7, 2.4)	111.2	CH	4a, 7, 8
7	-	164.8	C	-
8	6.36 (d, J = 2.4)	102.7	CH	4, 4a, 6, 7, 8a
8a	-	163.2	C	-
9	7.78 (brs)	136.8	CH	2, 3, 4, 1′, 2′, 6′
1′	-	127.1	C	-
2′/6′	7.28 (d, J = 8.7)	131.9	CH	9, 1′, 3′, 4′, 6′
3′/5′	6.99 (d, J = 8.7)	114.2	CH	4′
4′	-	160.6	C	-
OMe	3.78 (s)	55.3	CH_3	1′, 3′, 4′, 6′

Table 21 Comparison of ^{1}H NMR spectral data of compounds **CP14** (recorded in $CDCl_3$+CD_3OD) and bonducellin (**R**, recorded in acetone-d_6)

Position	CP8	R
	δ_H (mult, *J*, Hz)	δ_H (mult, *J*, Hz)
2	5.34 (d, *J* = 1.8)	5.39 (d, *J* = 1.8)
3	-	-
4	-	-
4a	-	-
5	7.87 (d, *J* = 8.7)	7.83 (d, *J* = 8.5)
6	6.56 (dd, *J* = 8.7, 2.4)	6.60 (dd, *J* = 8.7, 2.2)
7	-	-
8	6.36 (d, *J* = 2.4)	6.38 (d, *J* = 2.2)
8a	-	-
9	7.78 (brs)	7.70 (t, *J* = 1.9)
1′	-	-
2′/6′	7.28 (d, *J* = 8.7)	7.40 (d, *J* = 8.9)
3′/5′	6.99 (d, *J* = 8.7)	7.03 (d, *J* = 8.9)
4′	-	-
OMe	3.78 (s)	3.87 (s)
7-OH	-	3.31 (brs)

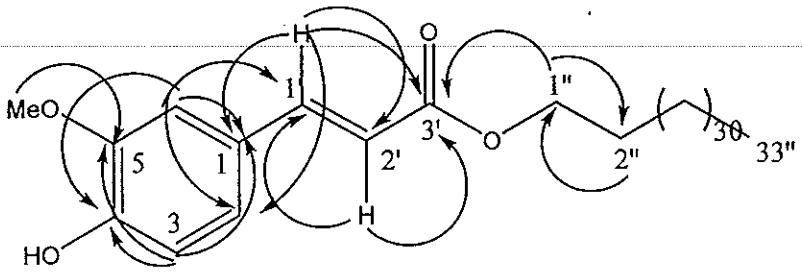
3.1.15 Compound CP15



Compound **CP15** was isolated as a colorless viscous oil, It exhibited hydroxyl (3375 cm^{-1}), conjugated ester (1695 cm^{-1}) and double bond (1635 cm^{-1}) absorptions in the IR spectrum. The UV spectrum showed absorption bands at λ_{max} : 234, 297 and 325 nm, again suggesting the presence of conjugation in the molecule. Its molecular formula, $C_{43}H_{76}O_4$ ($[M-1]^+$ 655.6 calcd 655.6), was deduced by EI mass spectrum.

In the ^1H NMR spectral data of **CP15** (Table 22), the presence of a *trans* double bond was evidenced by two doublet signals at δ 6.29 and 7.61 ppm with a coupling constant of 15.9 Hz. ^1H NMR signals at δ 6.92 (d, J = 8.4 Hz), δ 7.08 (dd, J = 8.4 and 1.8 Hz) and δ 7.04 (d, J = 1.8 Hz) established the presence of three aromatic protons with *ortho*, ortho/meta and meta coupling, respectively. The presence of one methoxyl group was also shown by a three-proton singlet at δ 3.93 ppm. Furthermore, the calculated MW of 655.6 was in agreement with molecular formula, $C_{38}H_{66}O_4$ as deduced by EI mass spectrum. The ^1H NMR spectrum showed signals of methylene protons at δ 4.19 (H_2-1″), a triplet at δ 0.88 (H_3-33″), and a broad signal at δ 1.12-1.14 which could be deduced from molecular formula to be those of 60H. Therefore, compound **CP15** should be a long chain ester of ferulic acid. The ^{13}C NMR spectral data of **CP15** showed signals at δ 167.4 (C-3′) due to the carbonyl group of an ester function and δ 144.6 (C-1′) and δ 115.7 (C-2′) due to a side chain C-C double bond. Further confirmation of this skeleton came from the mass spectrum of **CP15** which showed, besides the molecular ion, significant fragment peak at *m/z* ion 177 and 194, both being characteristic of a methoxy and hydroxyl substituted cinnamic moiety. HMBC correlations were summarized in

Table 22. On the basis of its spectroscopic data, Compound **CP15** was suggested to be tritriacontyl ferrulate, a new compound.



Selected HMBC correlation for compound **CP15**

Table 22 ^{1}H, ^{13}C NMR, DEPT and HMBC spectral data of compound **CP15**

Position	**δ_H (mult, *J*, Hz)**	**δ_C**	**DEPT**	**HMBC**
1	-	127.1	C	-
2	7.08 (dd, *J* = 8.4, 1.8)	123.0	CH	6
3	6.92 (d, *J* = 8.4)	114.7	CH	1, 4, 5
4	-	147.9	C	-
5	-	146.8	C	-
6	7.04 (d, *J* = 1.8)	109.3	CH	1, 2, 4, 1′
1′	7.61 (d, *J* = 15.9)	144.6	CH	1, 2, 2′, 3′
2′	6.29 (d, *J* = 15.9)	115.7	CH	1′, 3′
3′	-	167.4	C	-
1″	4.19 (t, *J* = 8.4)	64.6	CH_2	3′, 2″
2″	1.70 (m)	26.0	CH_2	1″
33″	0.88 (t, *J* = 6.3)	14.1	CH_3	-
OMe	3.93	55.9	CH_3	5

CHAPTER 4
CONCLUSION

Six new cassane diterpenoids: pulcherrin A (**CP1**), pulcherrin B (**CP2**), pulcherrin C (**CP3**), neocaesalpin P (**CP4**), neocaesalpin Q (**CP5**) and neocaesalpin R (**CP6**) and a new ferrulic ester: tritriacontyl ferrulate (**CP15**), together with eight known compounds: isovouacapenol C (**CP7**), 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol (**CP8**), pulcherrimin E (**CP9**), pulcherrimin C (**CP10**), α-cadinol (**CP11**), 7-hydroxycadalene (**CP12**), teucladiol (**CP13**) and bonducellin (**CP14**) were isolated from the stem of *Caesalpinia pulcherrima*. Their structures were elucidated on the basis of spectroscopic techniques.

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APPENDIX

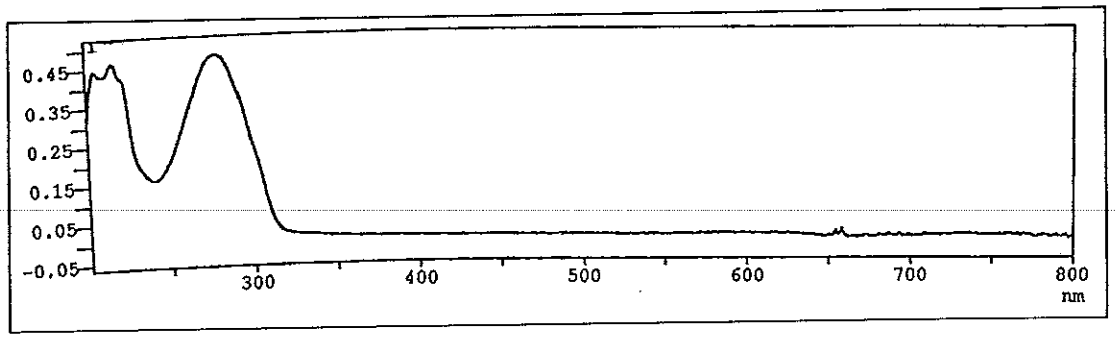

Figure 2 UV (MeOH) spectrum of compound **CP1**

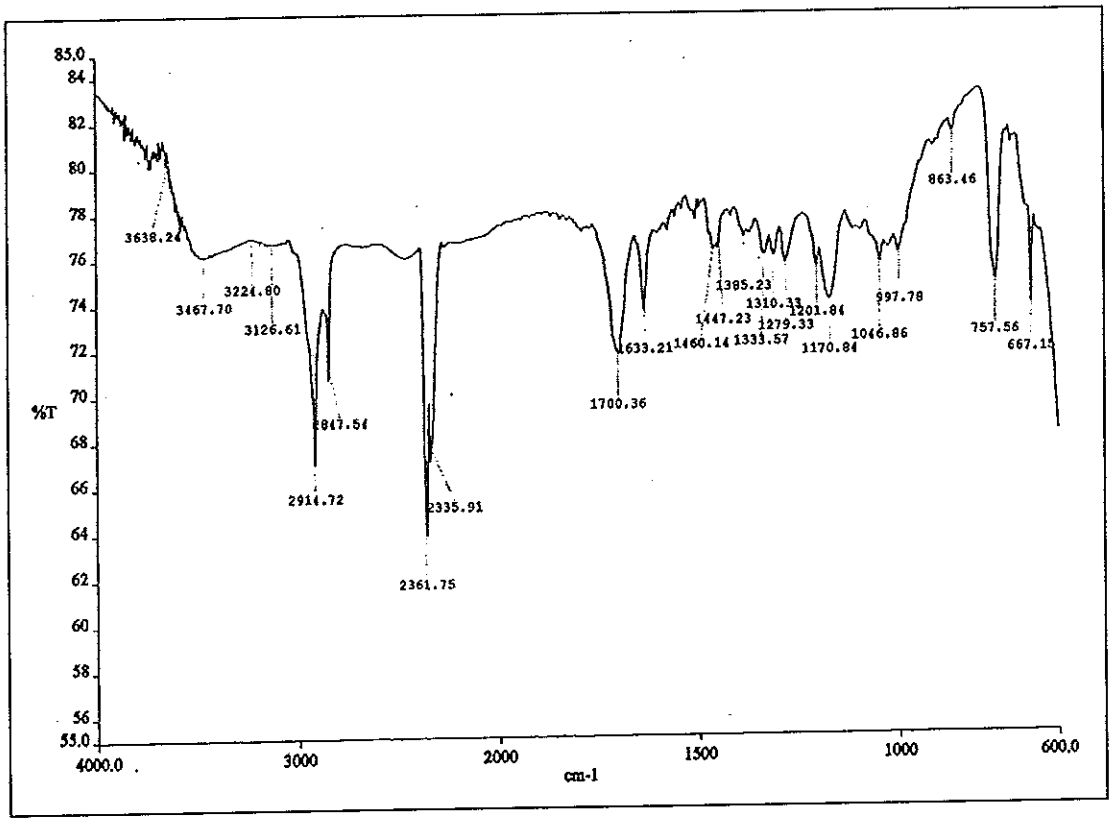

Figure 3 IR (neat) spectrum of compound **CP1**

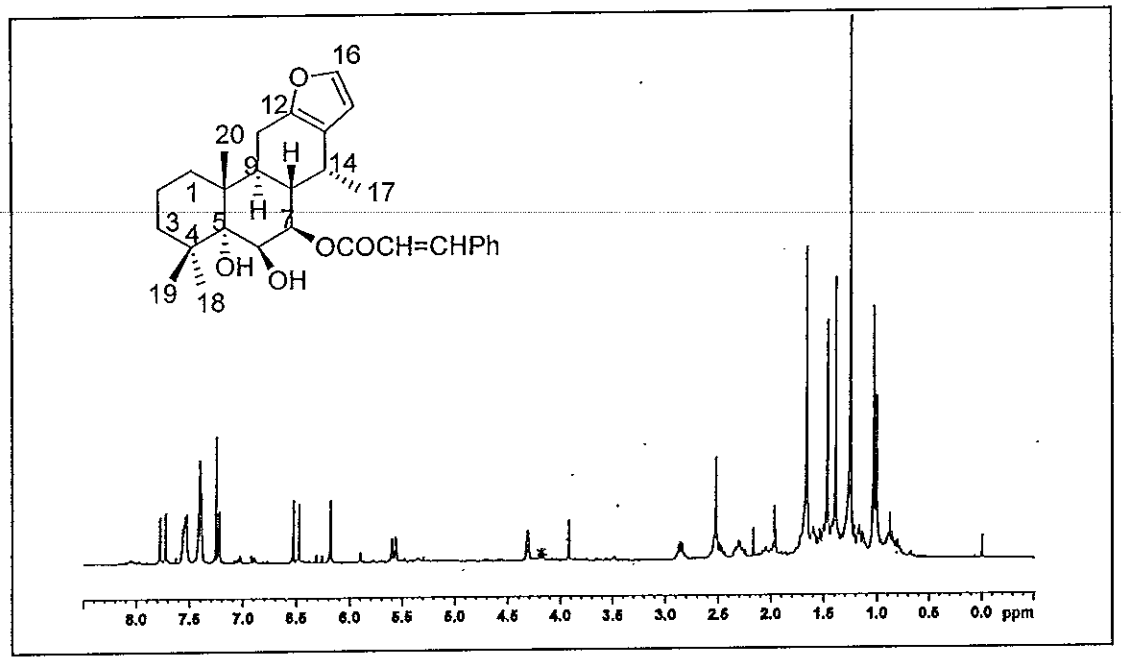

Figure 4 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP1**

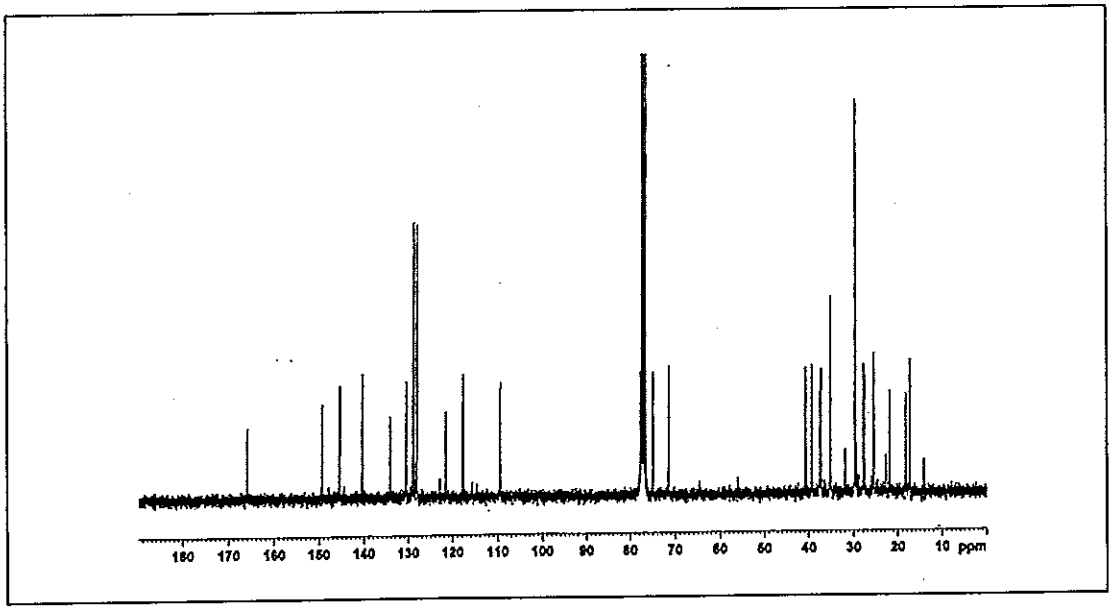

Figure 5 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP1**

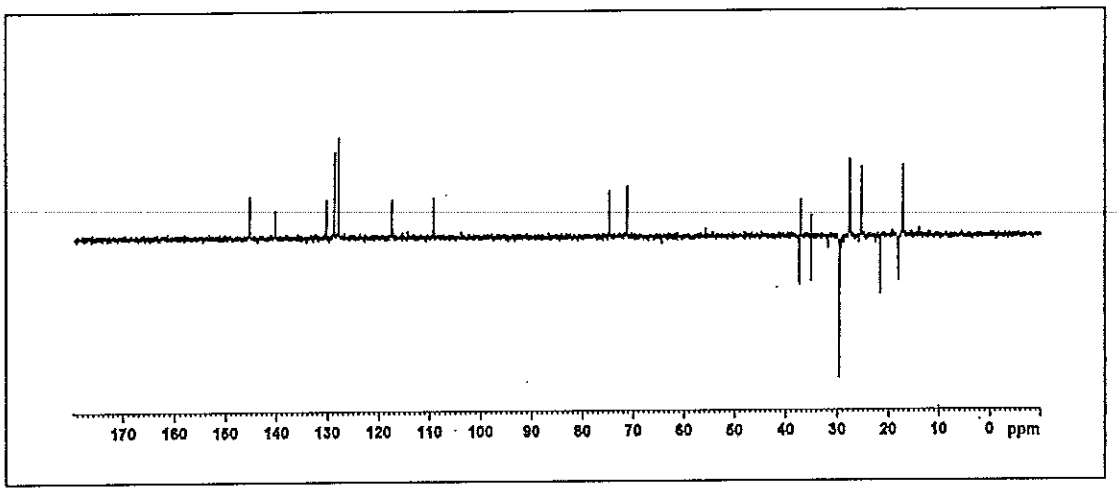

Figure 6 DEPT 135° ($CDCl_3$) spectrum of compound **CP1**

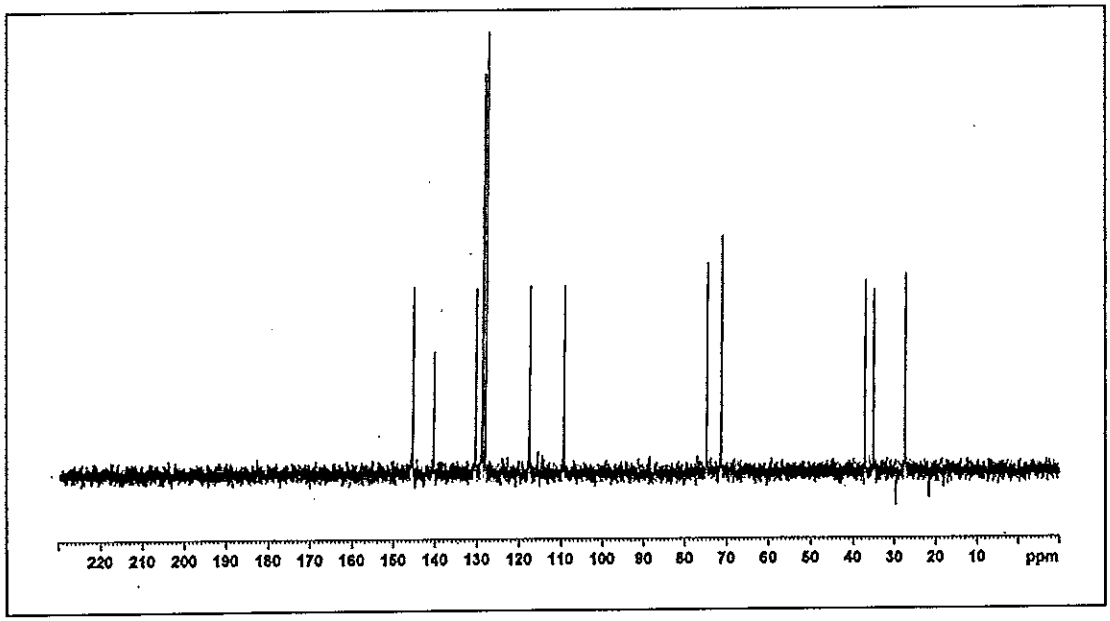

Figure 7 DEPT 90° ($CDCl_3$) spectrum of compound **CP1**

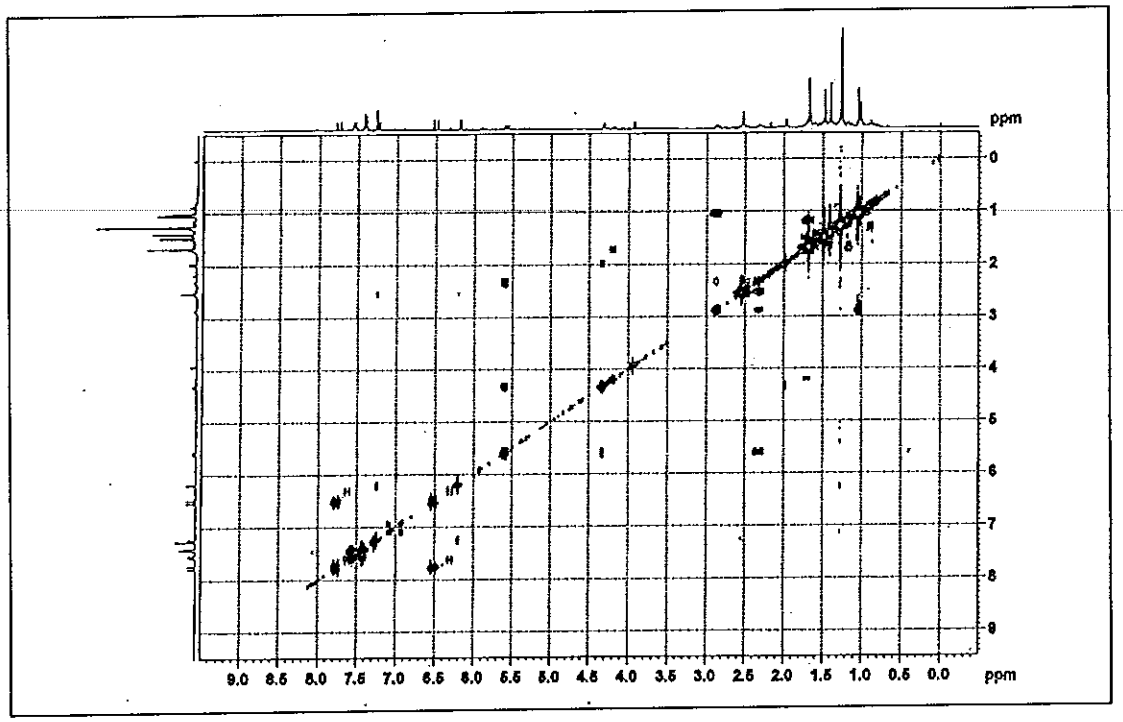

Figure 8 2D COSY ($CDCl_3$) spectrum of compound **CP1**

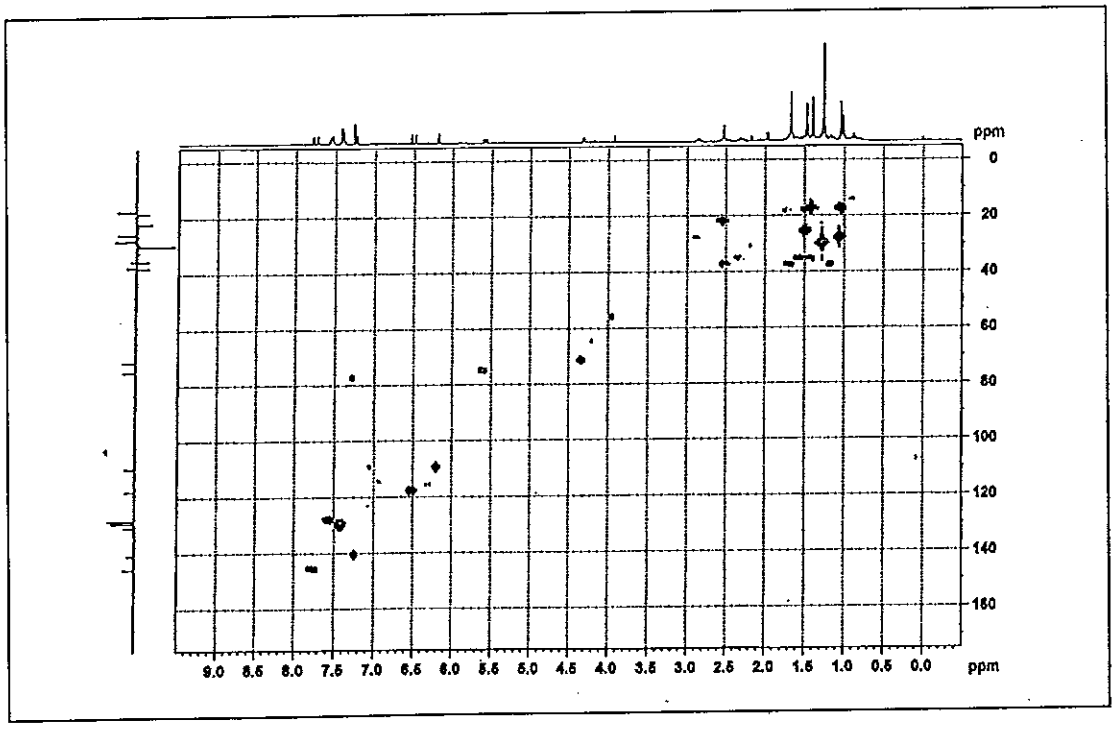

Figure 9 2D HMQC ($CDCl_3$) spectrum of compound **CP1**

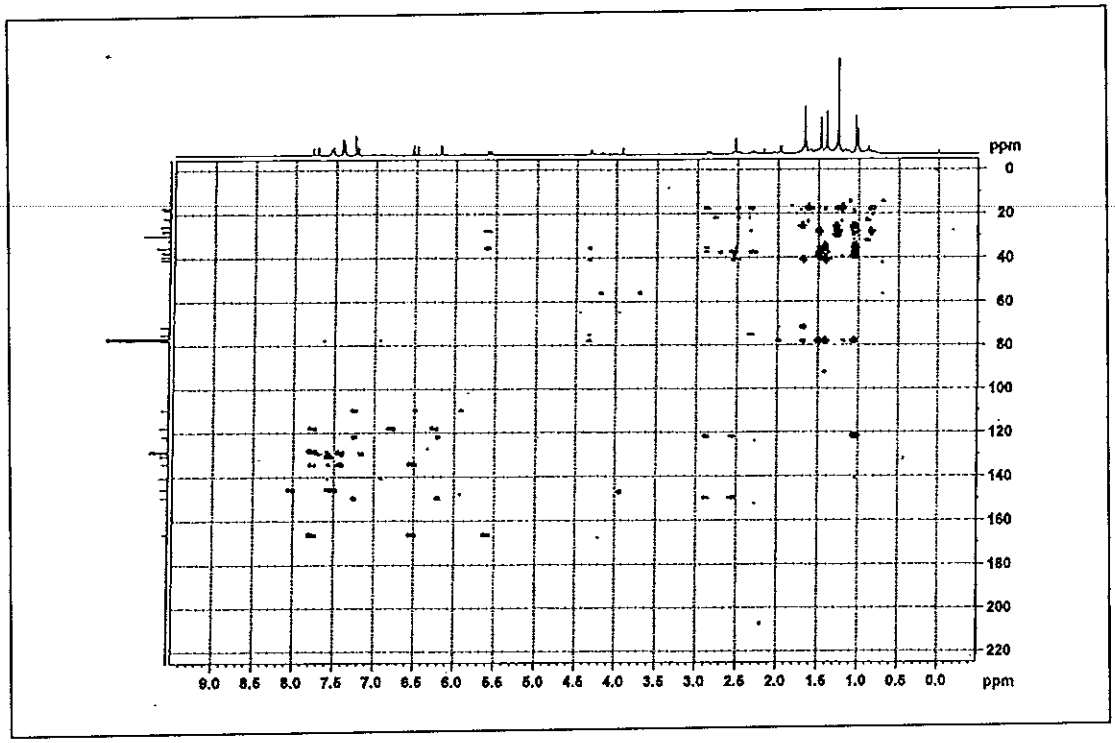

Figure 10 2D HMBC ($CDCl_3$) spectrum of compound **CP1**

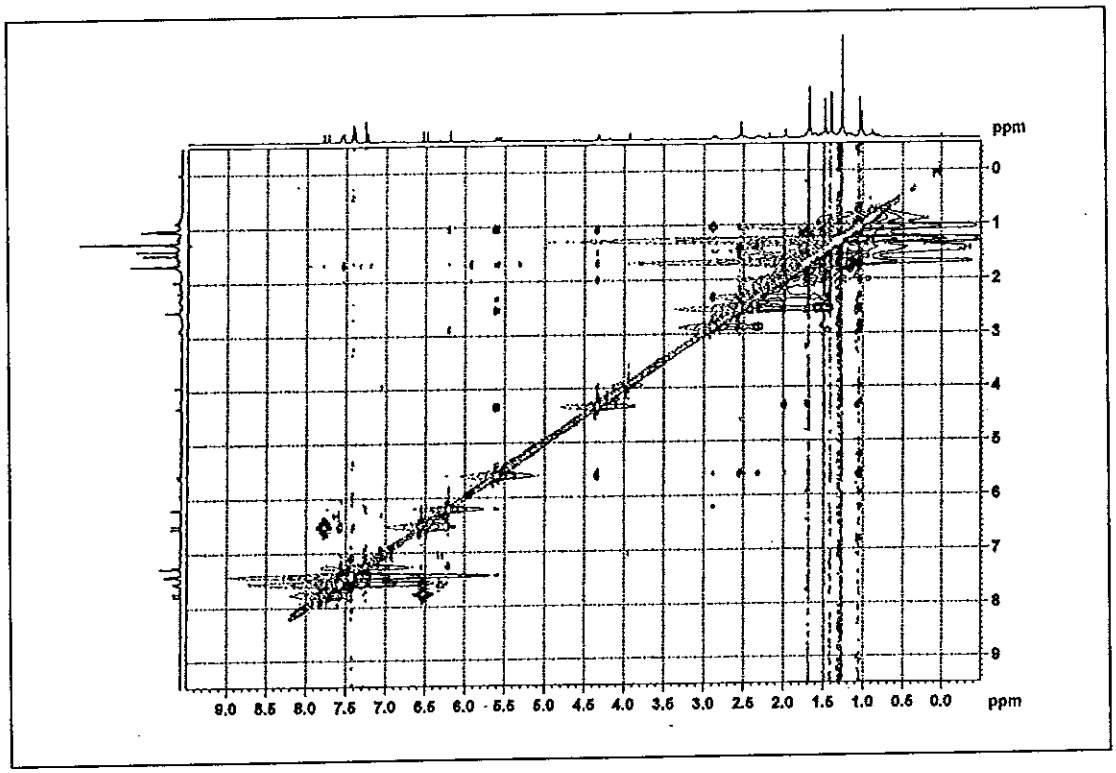

Figure 11 2D NOESY ($CDCl_3$) spectrum of compound **CP1**

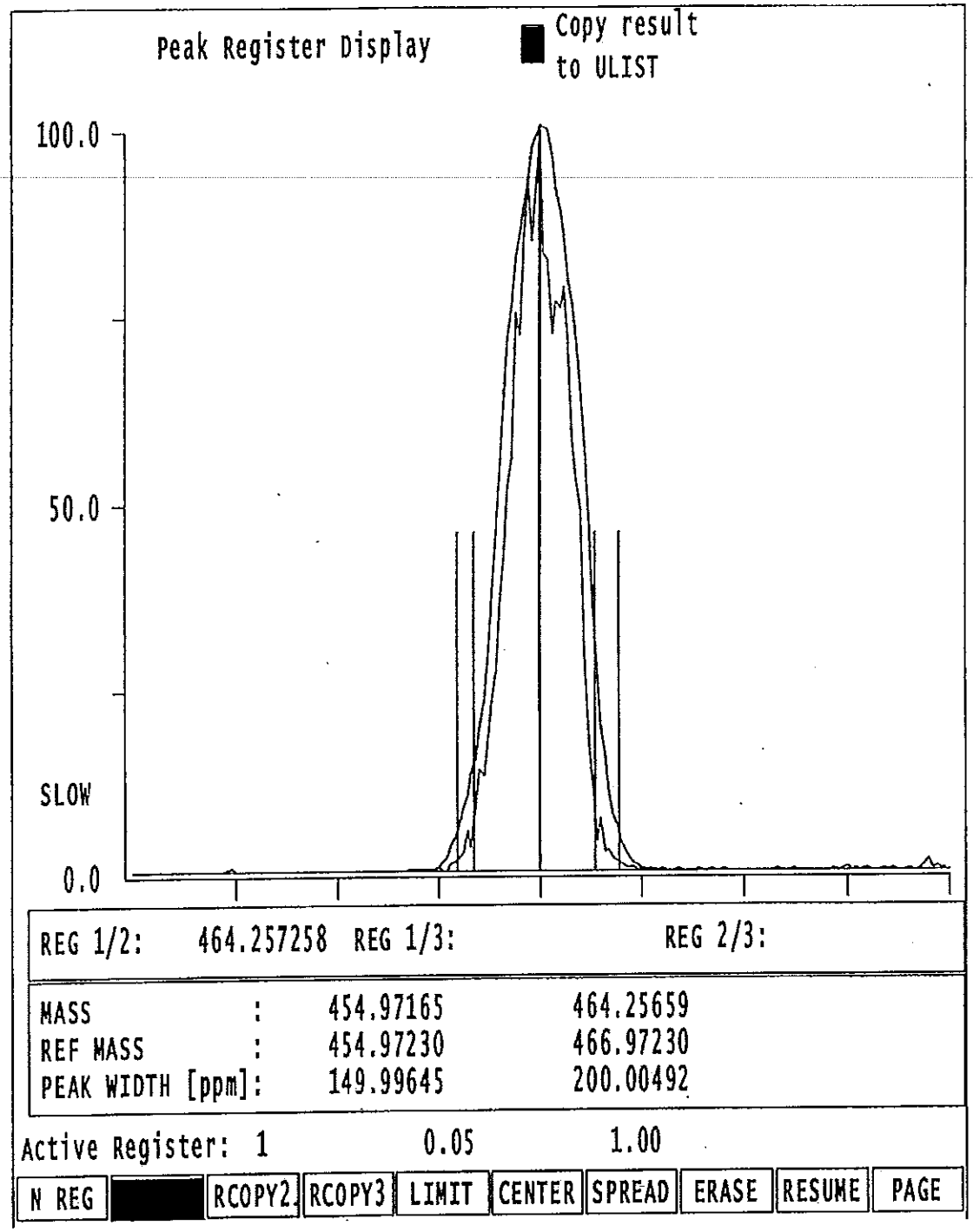

Figure 12 HREIMS spectrum of compound **CP1**

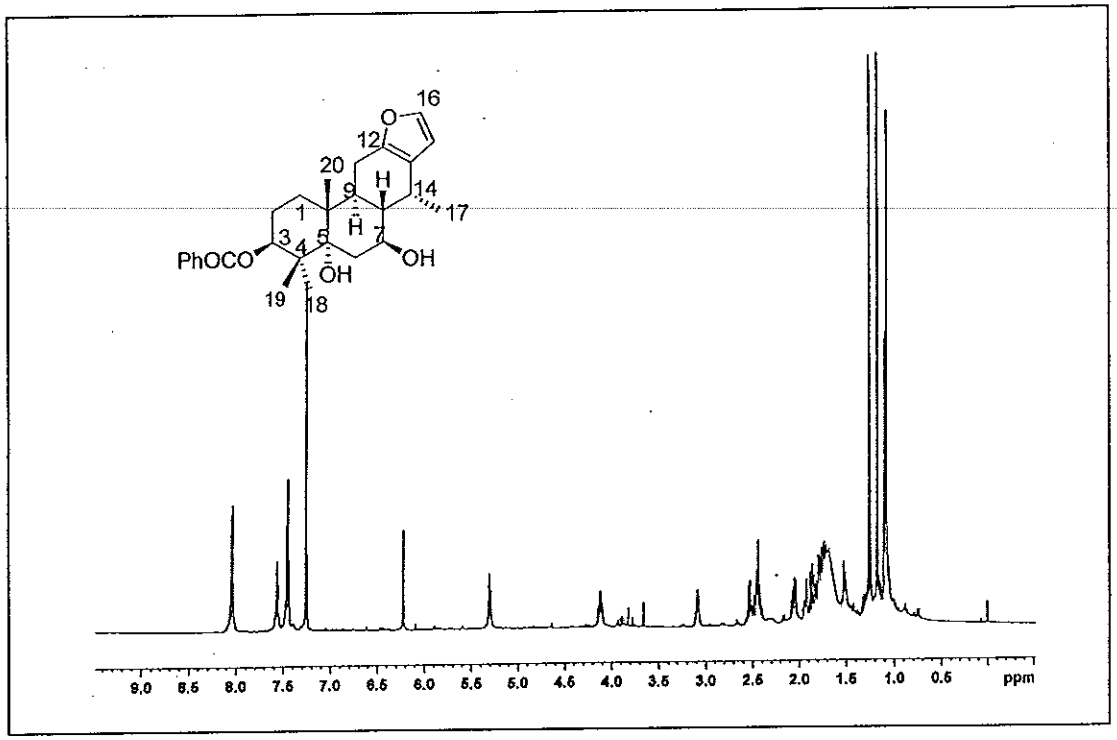

Figure 13 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP2**

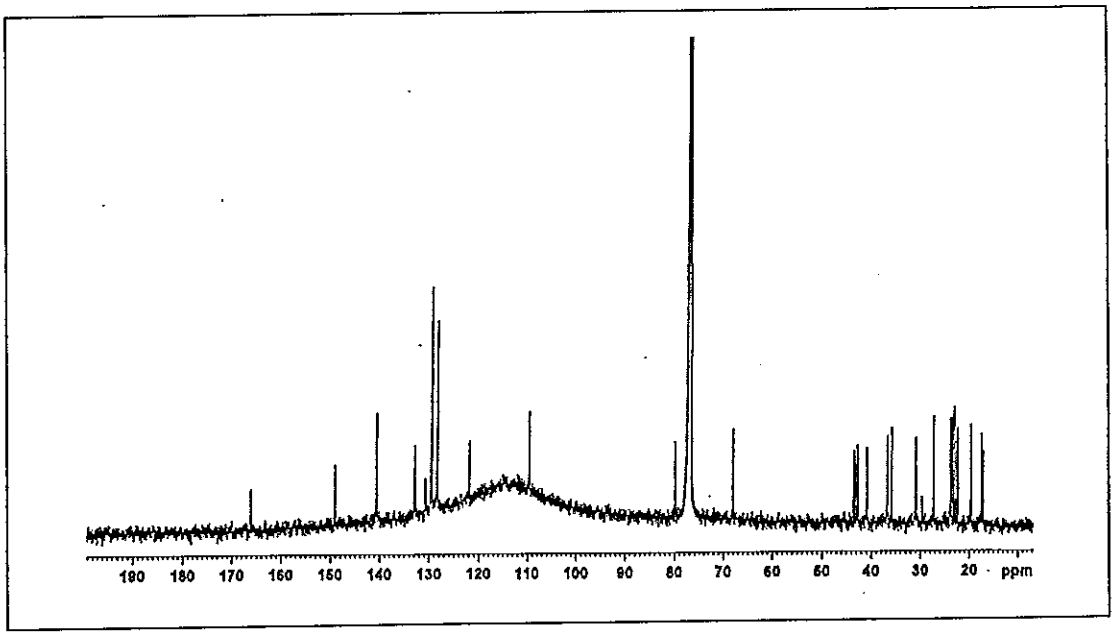

Figure 14 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP2**

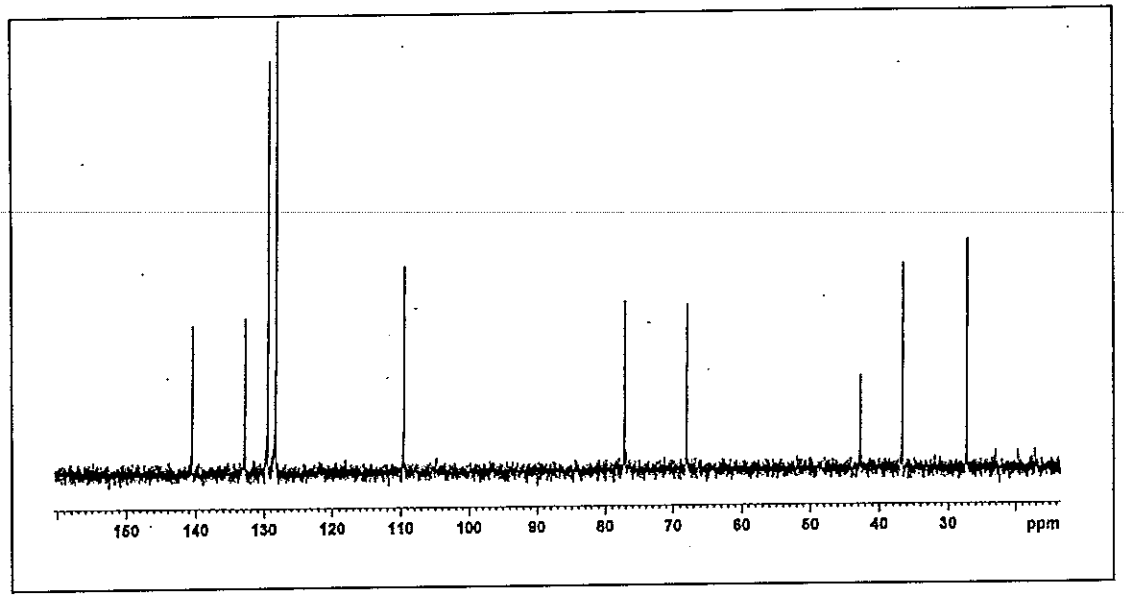

Figure 15 DEPT 90° ($CDCl_3$) spectrum of compound **CP2**

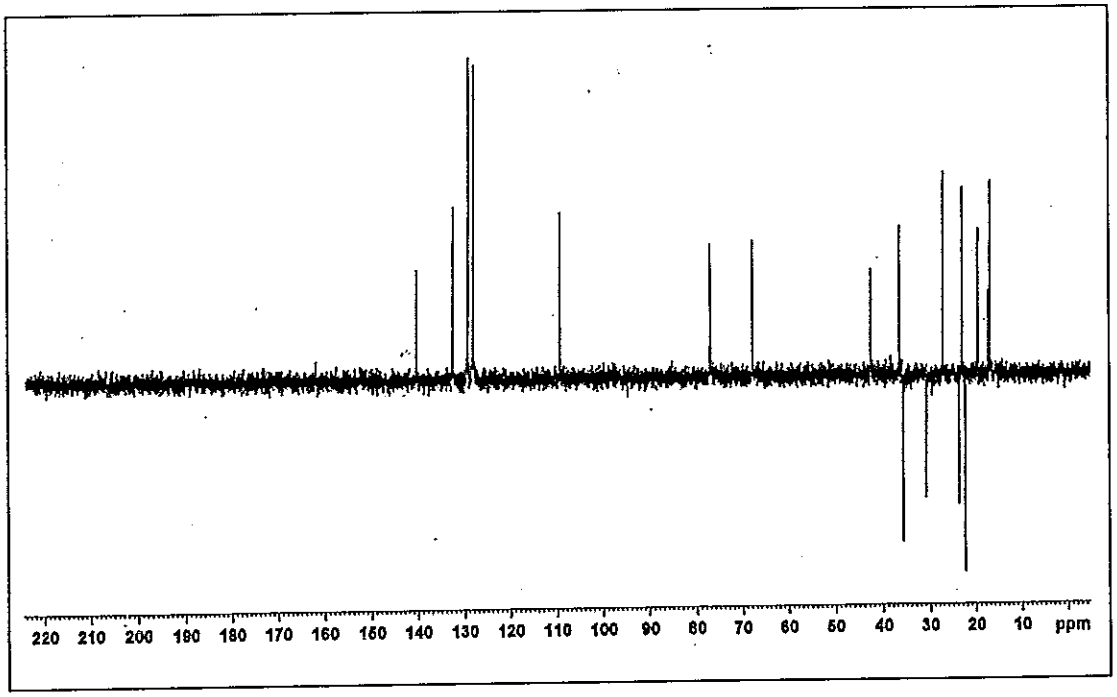

Figure 16 DEPT 135° ($CDCl_3$) spectrum of compound **CP2**

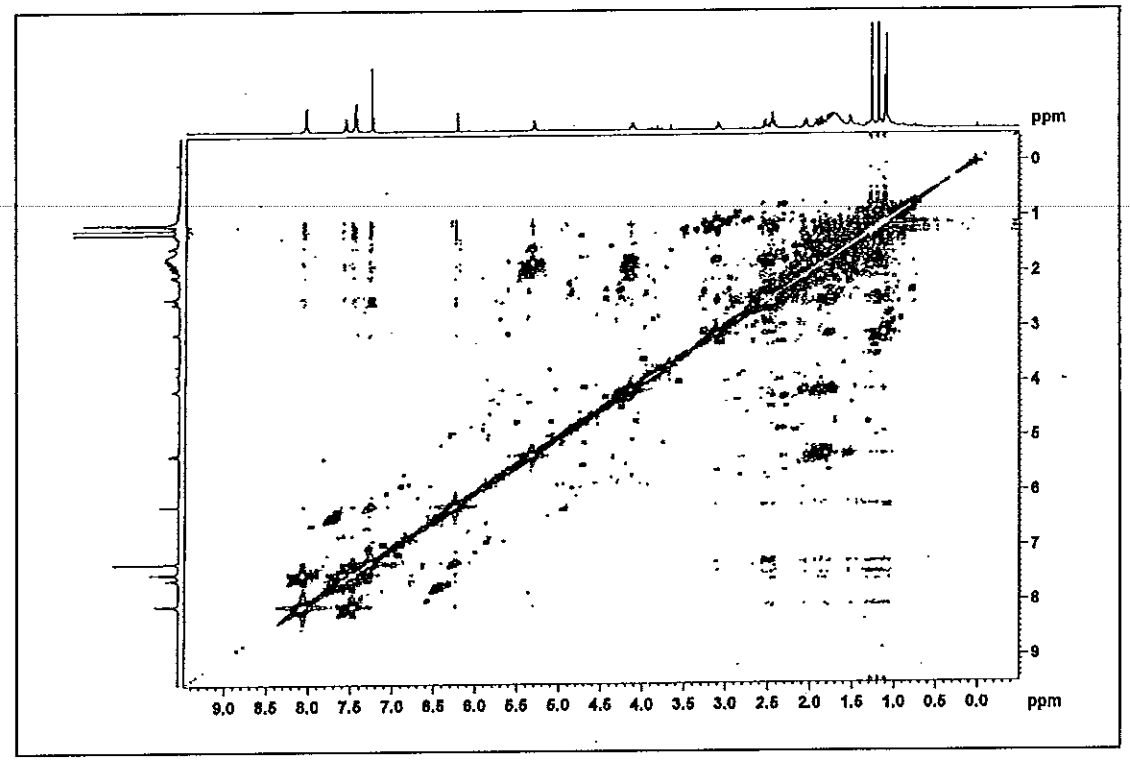

Figure 17 2D COSY ($CDCl_3$) spectrum of compound **CP2**

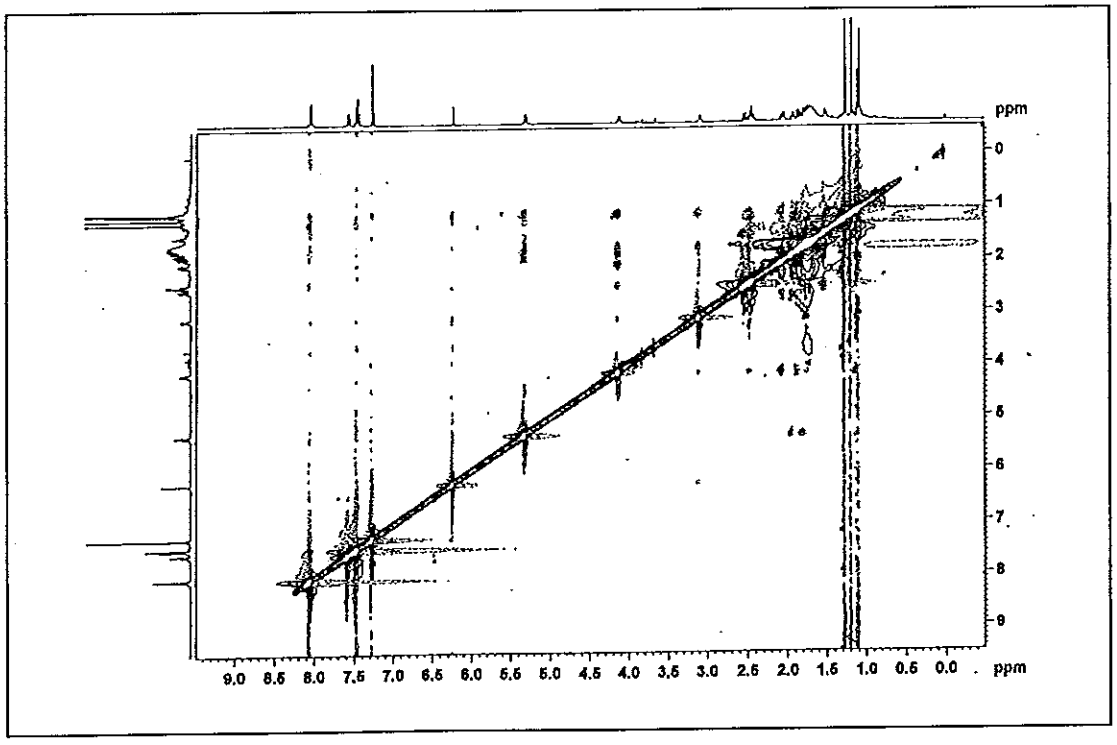

Figure 18 2D NOESY ($CDCl_3$) spectrum of compound **CP2**

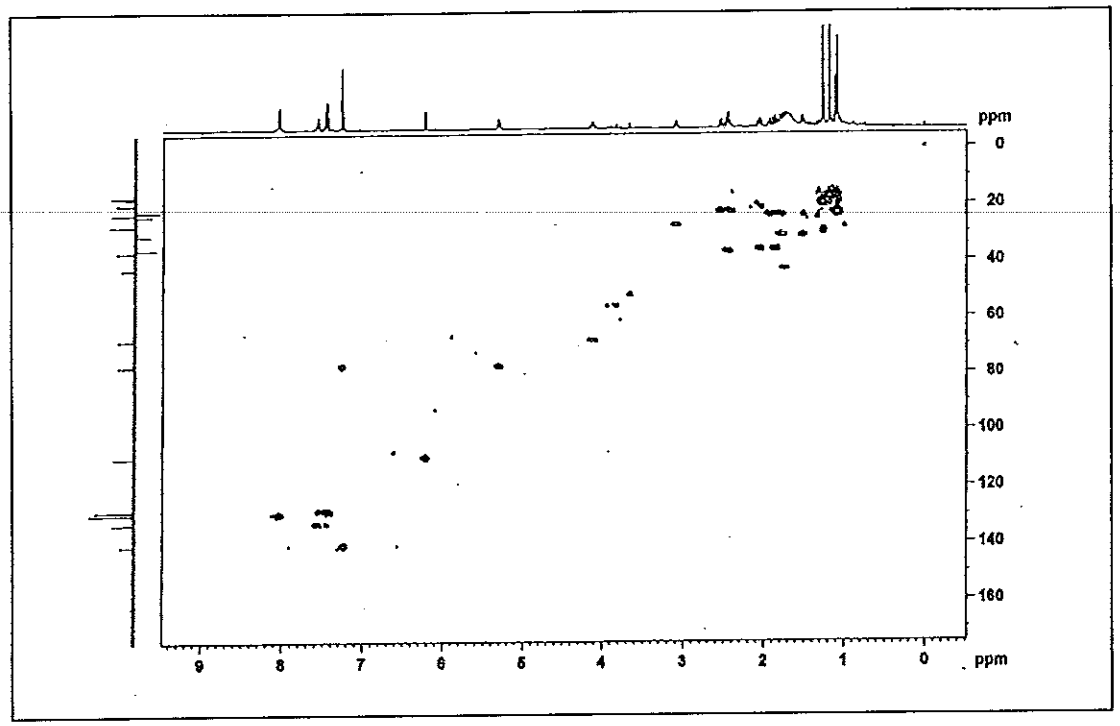

Figure 19 2D HMQC ($CDCl_3$) spectrum of compound **CP2**

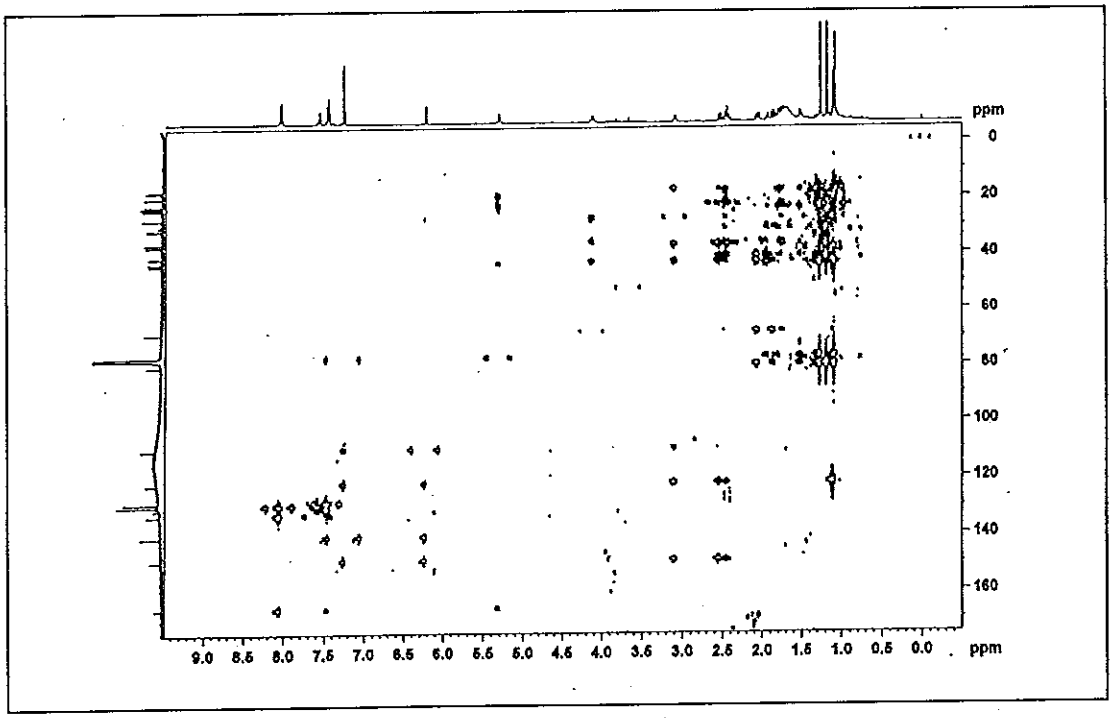

Figure 20 2D HMBC ($CDCl_3$) spectrum of compound **CP2**

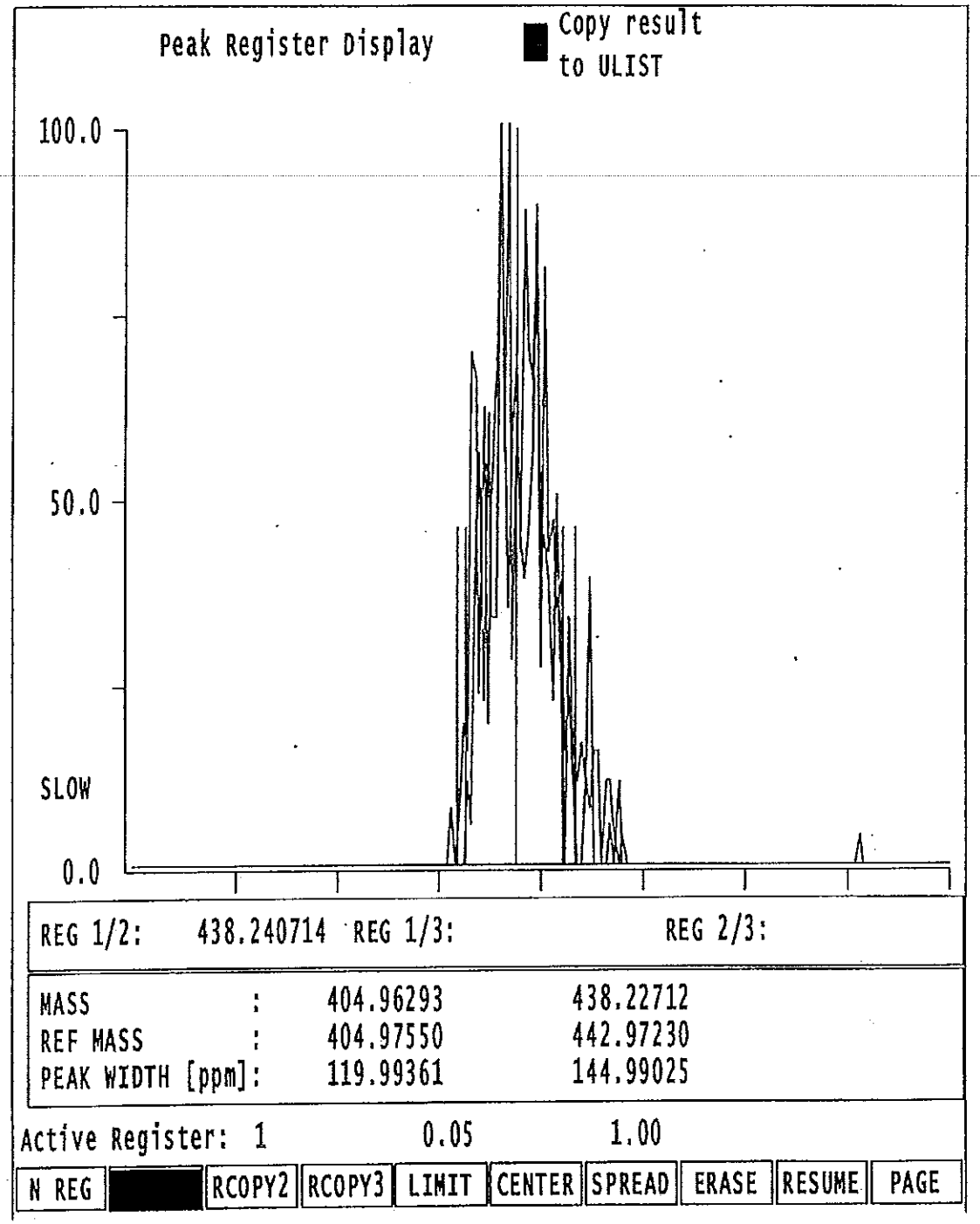

Figure 21 HREIMS spectrum of compound **CP2**

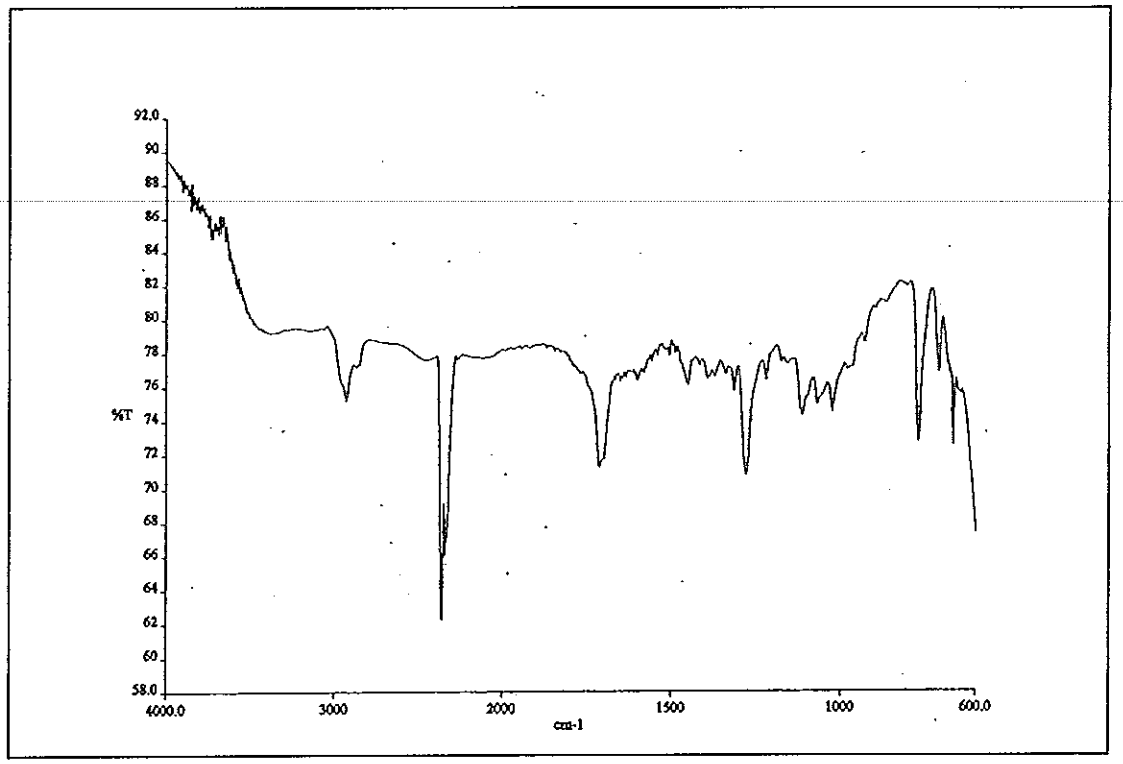

Figure 22 IR (neat) spectrum of compound **CP3**

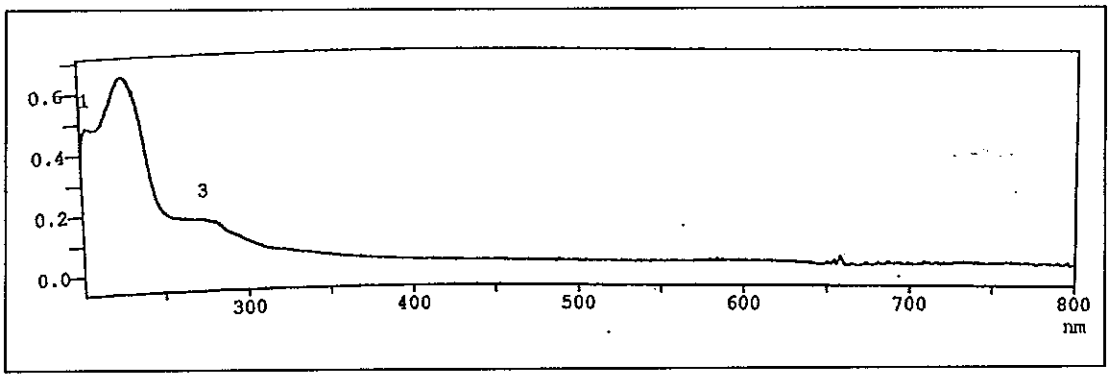

Figure 23 UV (MeOH) spectrum of compound **CP3**

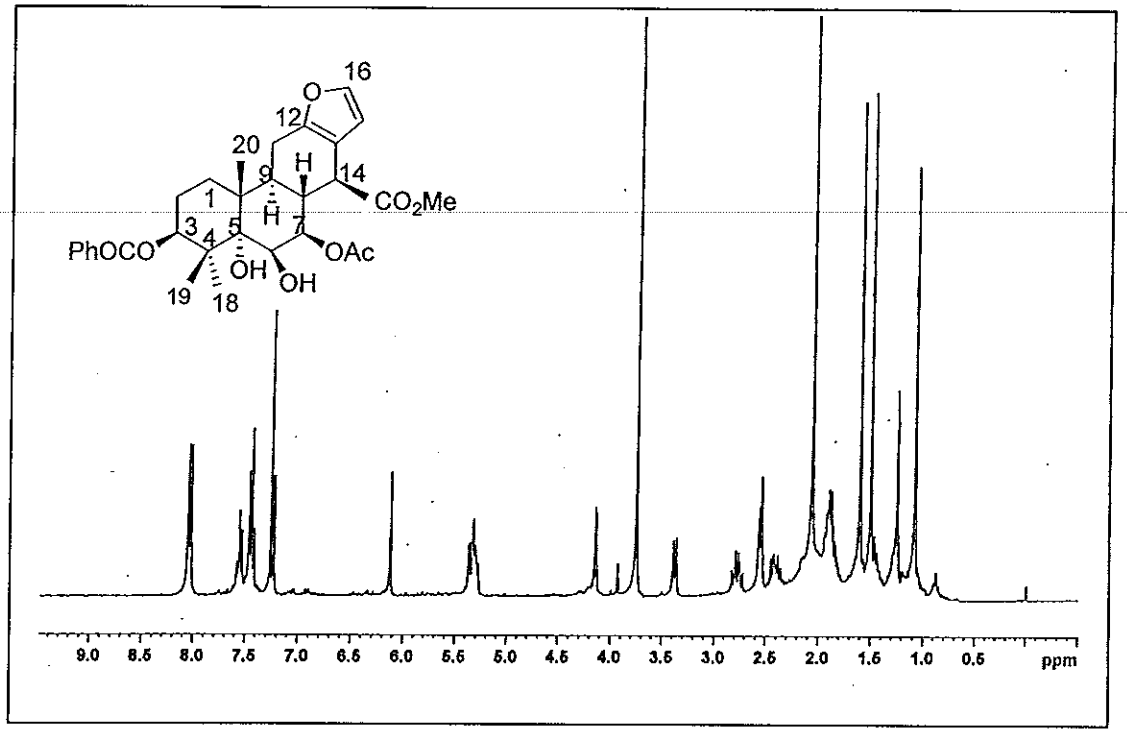

Figure 24 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP3**

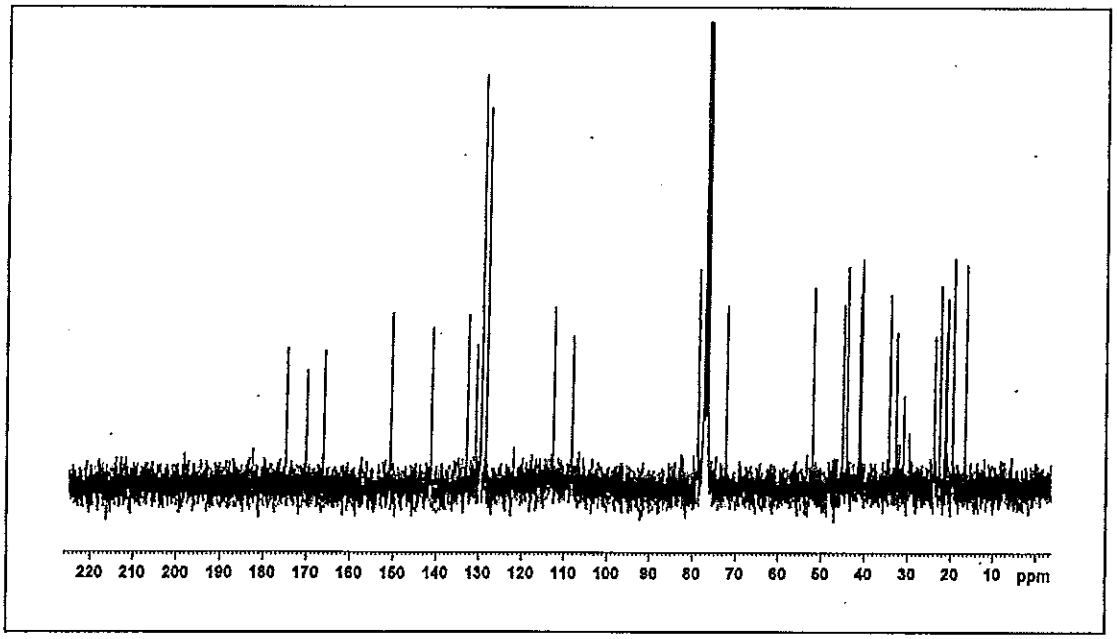

Figure 25 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP3**

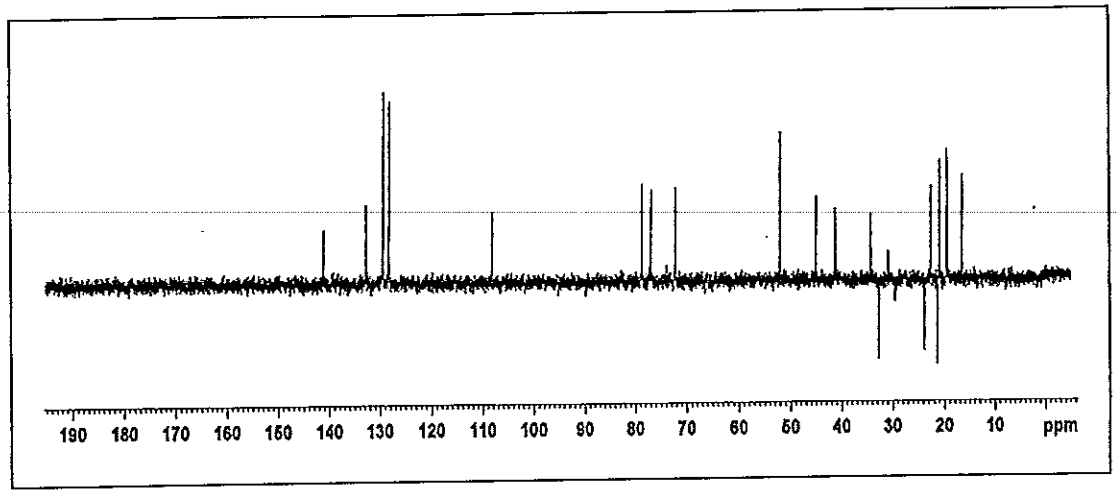

Figure 26 DEPT 135° ($CDCl_3$) spectrum of compound **CP3**

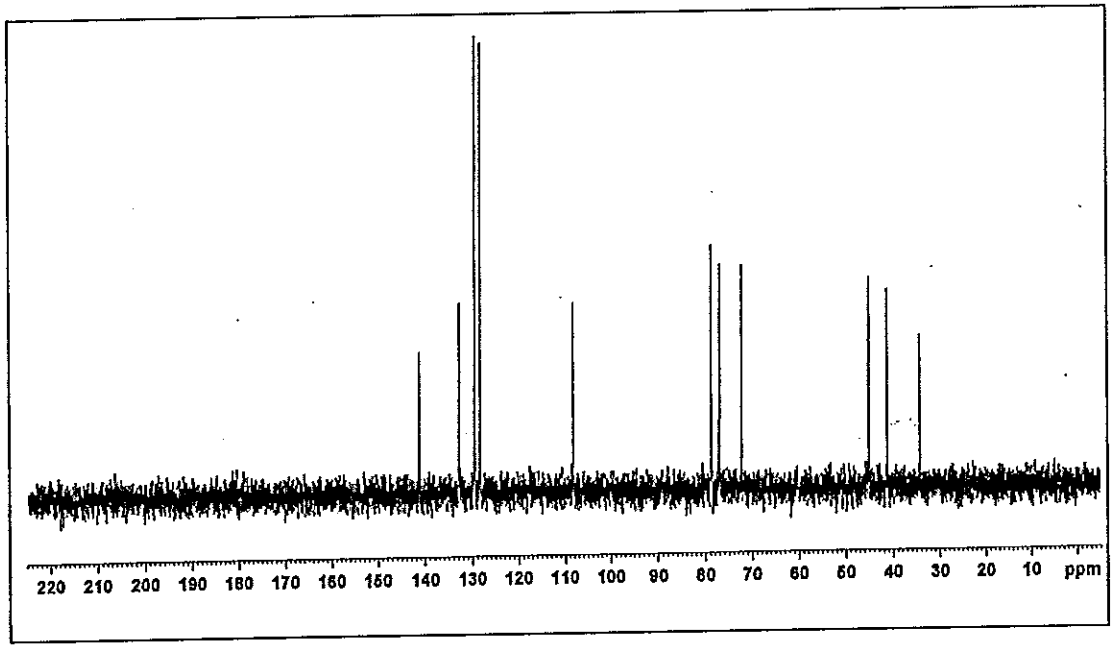

Figure 27 DEPT 90° ($CDCl_3$) spectrum of compound **CP3**

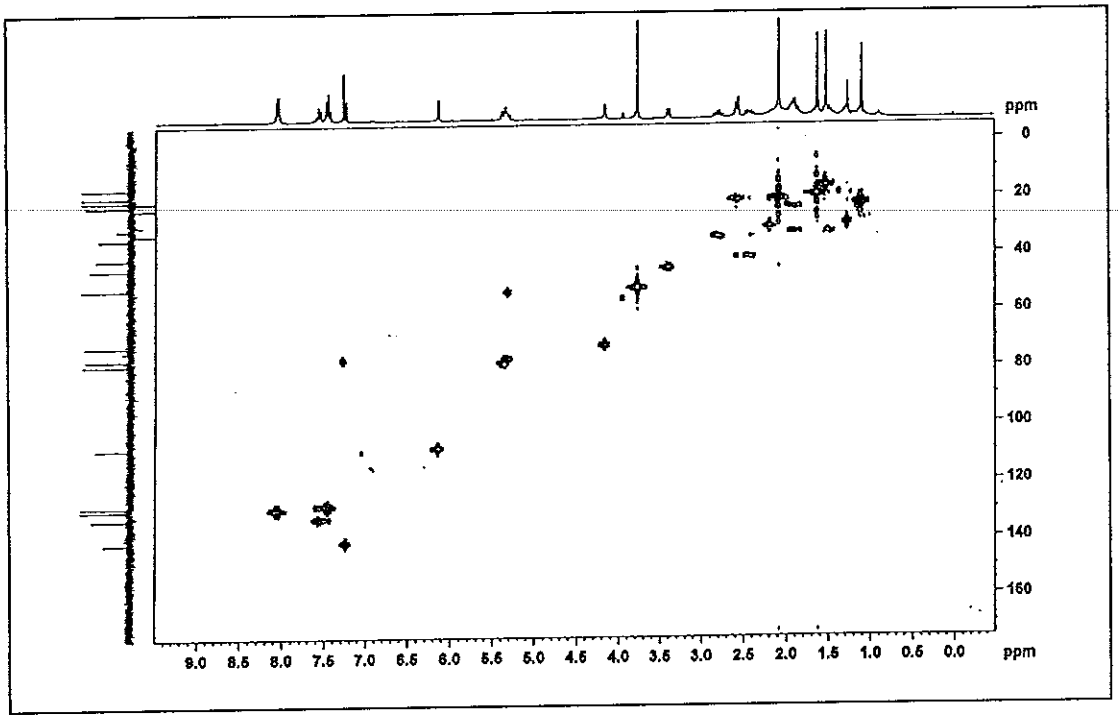

Figure 28 2D HMQC ($CDCl_3$) spectrum of compound **CP3**

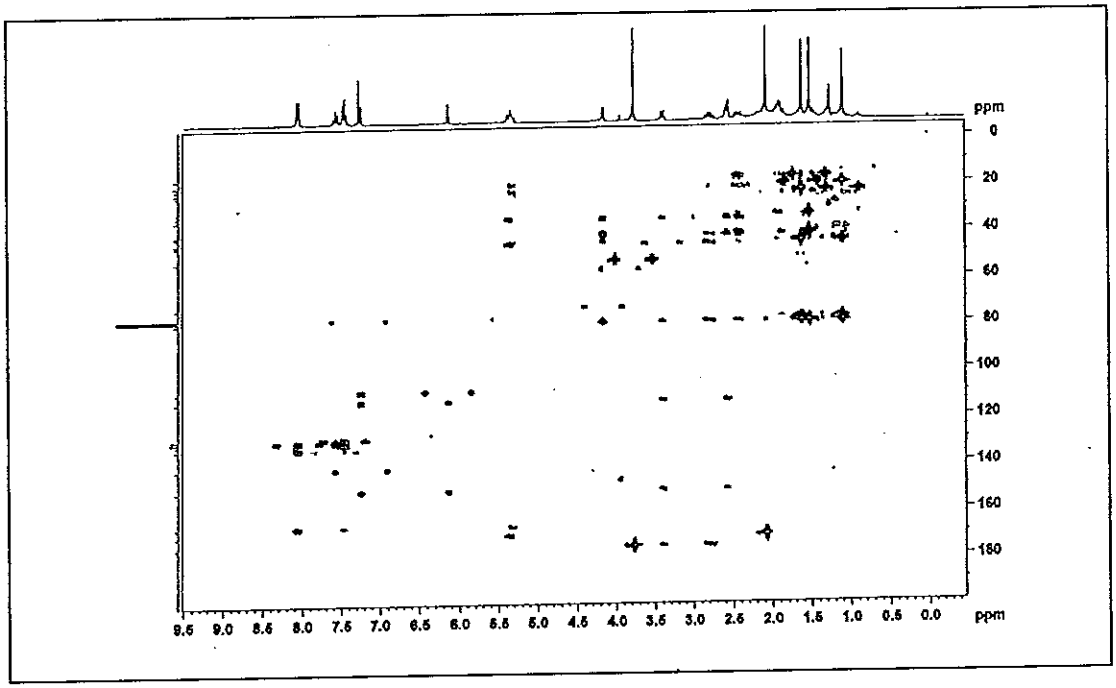

Figure 29 2D HMBC ($CDCl_3$) spectrum of compound **CP3**

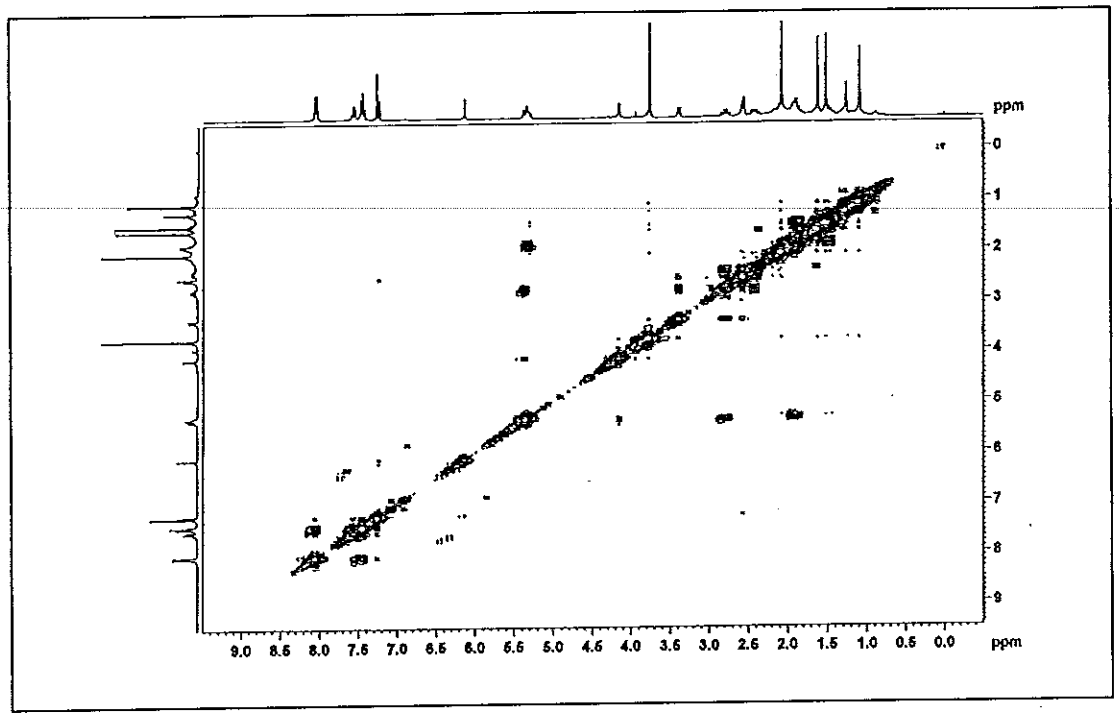

Figure 30 2D COSY ($CDCl_3$) spectrum of compound **CP3**

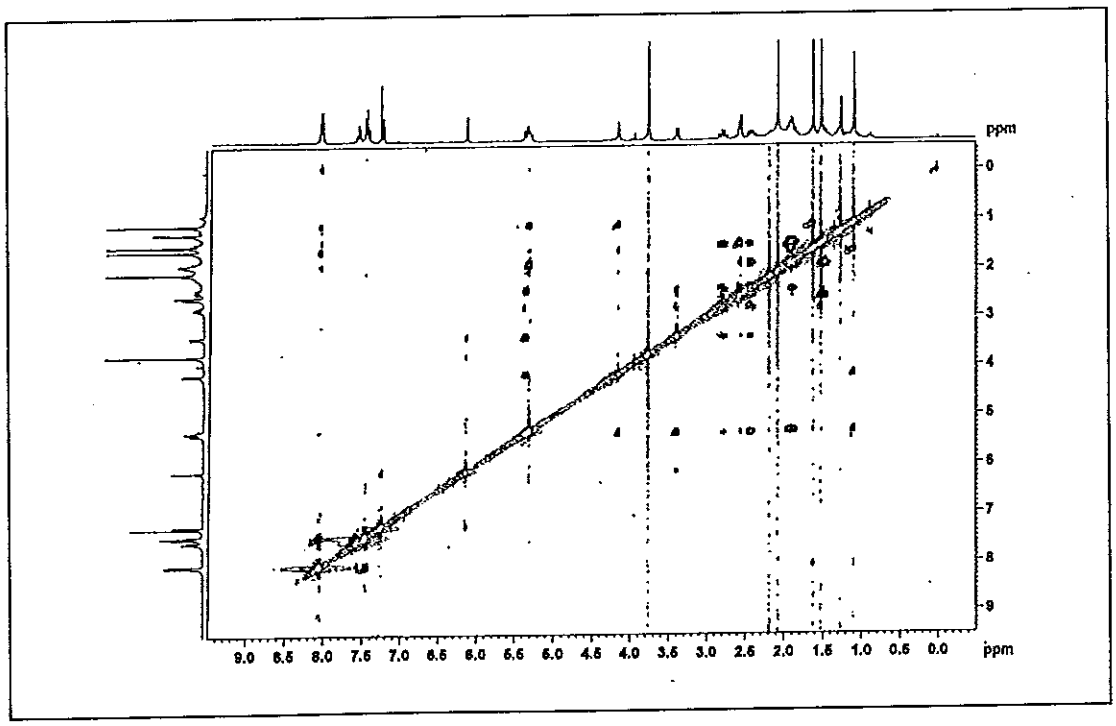

Figure 31 2D NOESY ($CDCl_3$) spectrum of compound **CP3**

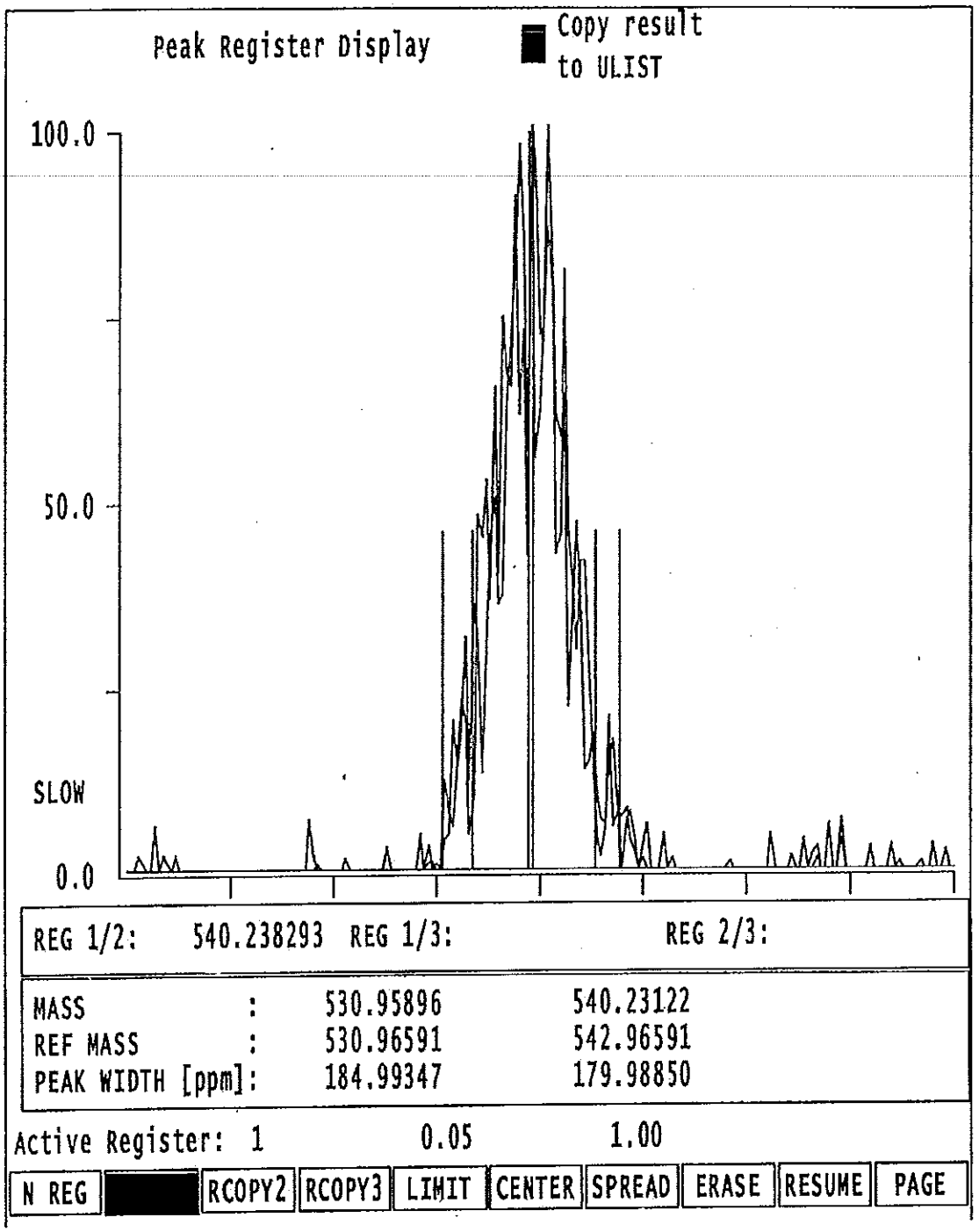

Figure 32 HREIMS spectrum of compound **CP3**

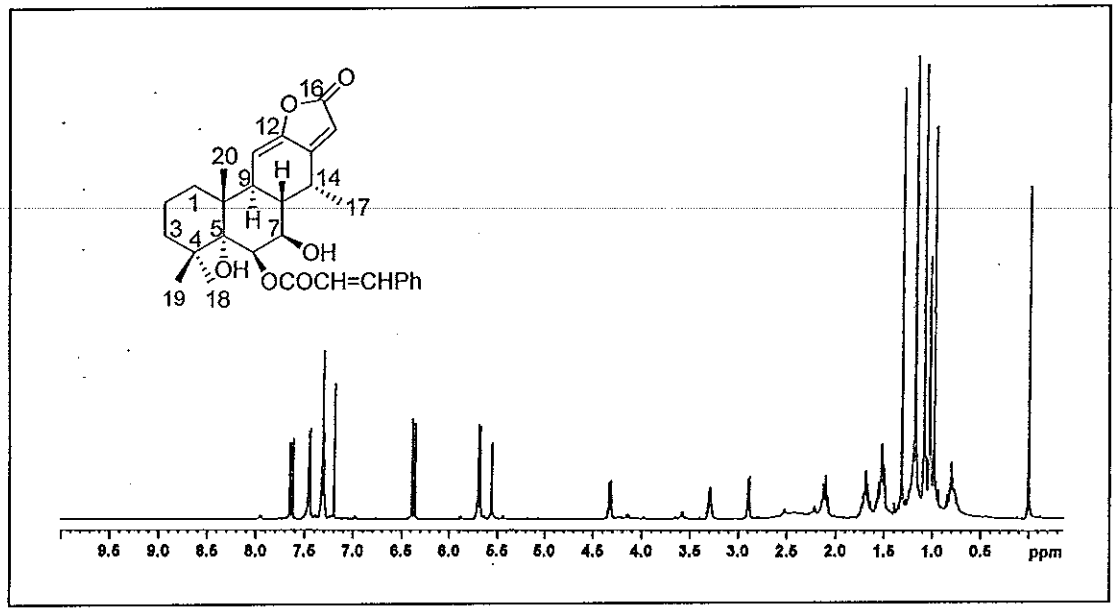

Figure 33 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of compound **CP4**

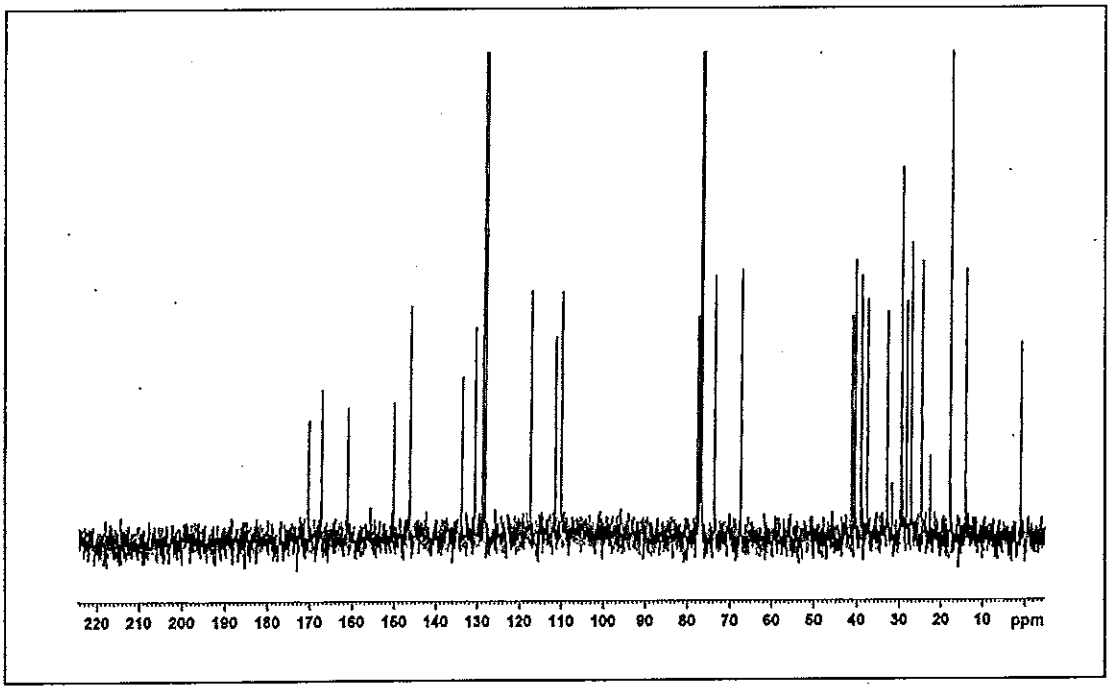

Figure 34 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of compound **CP4**

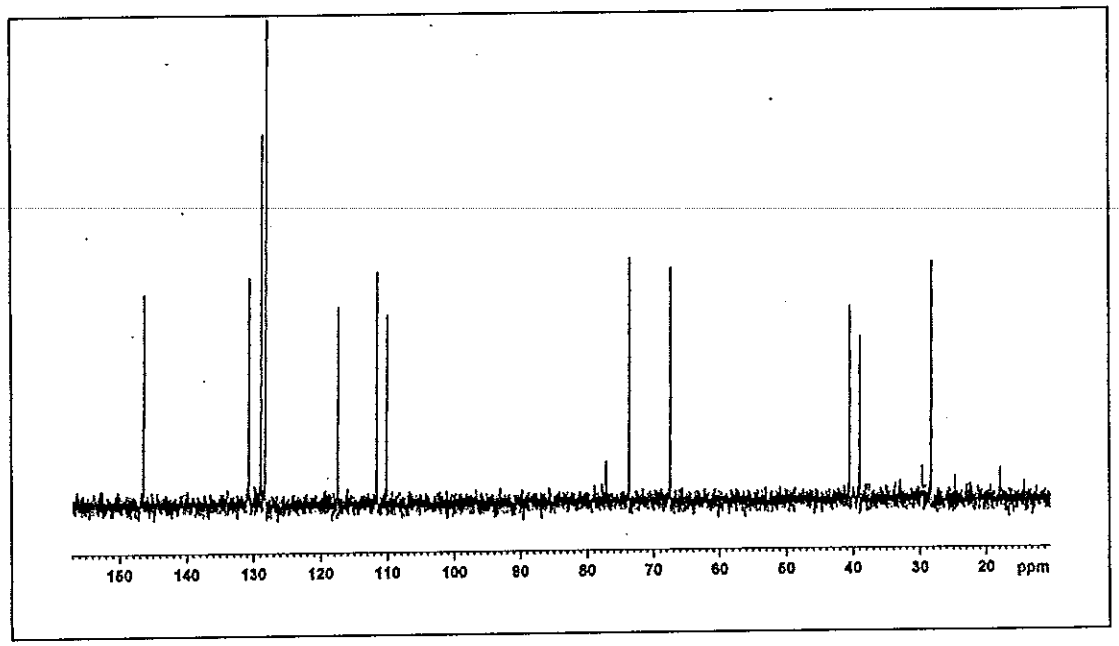

Figure 35 DEPT 90° ($CDCl_3$) spectrum of compound **CP4**

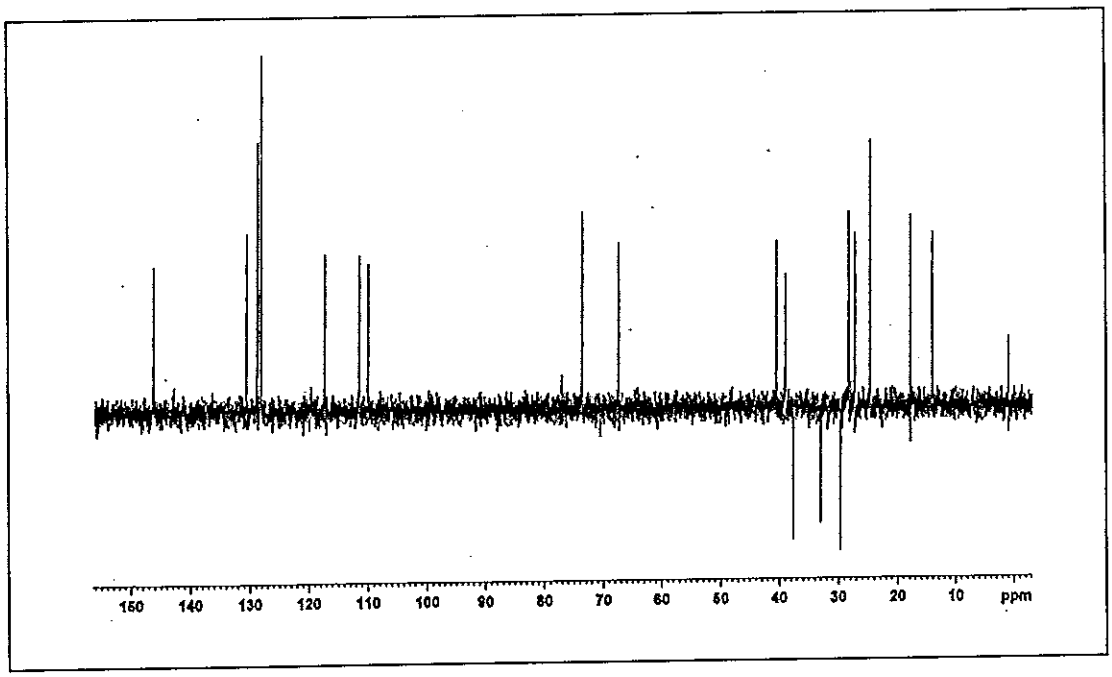

Figure 36 DEPT 135° ($CDCl_3$) spectrum of compound **CP4**

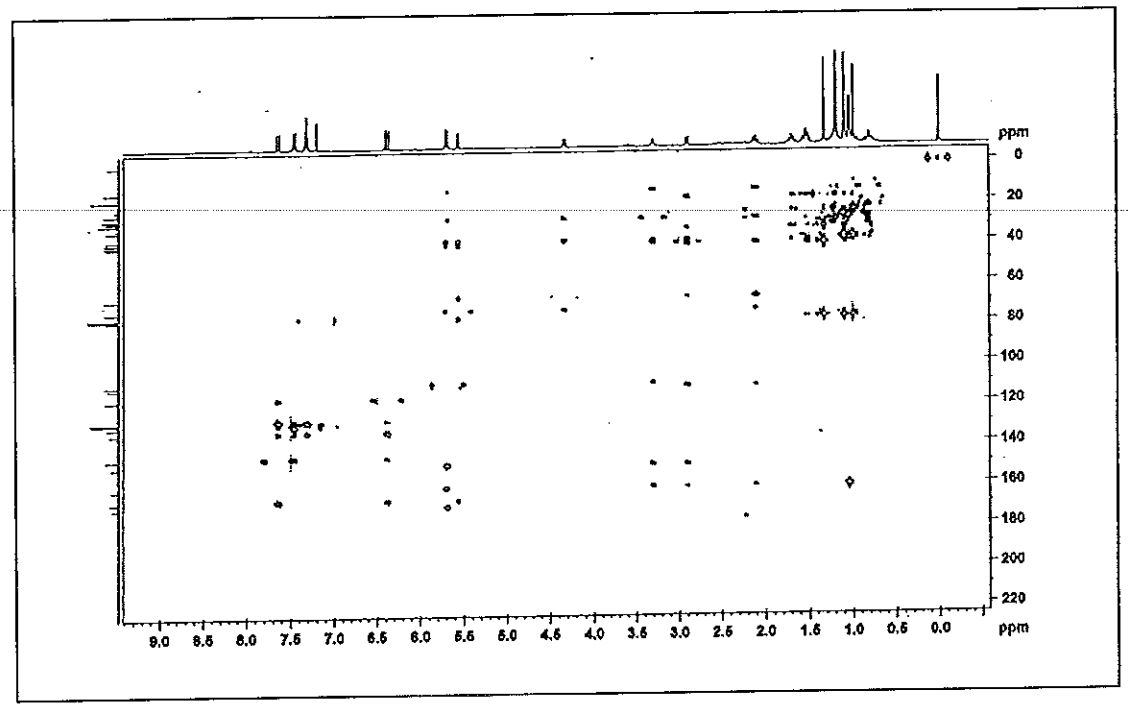

Figure 37 2D HMBC ($CDCl_3$) spectrum of compound **CP4**

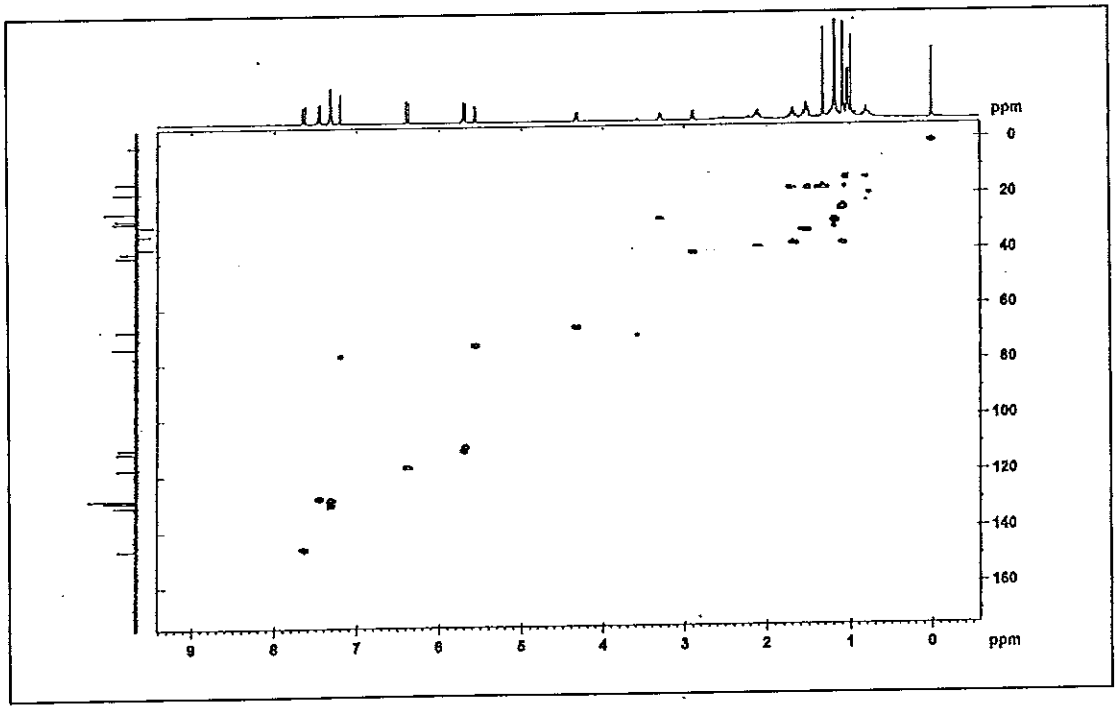

Figure 38 2D HMQC ($CDCl_3$) of compound **CP4**

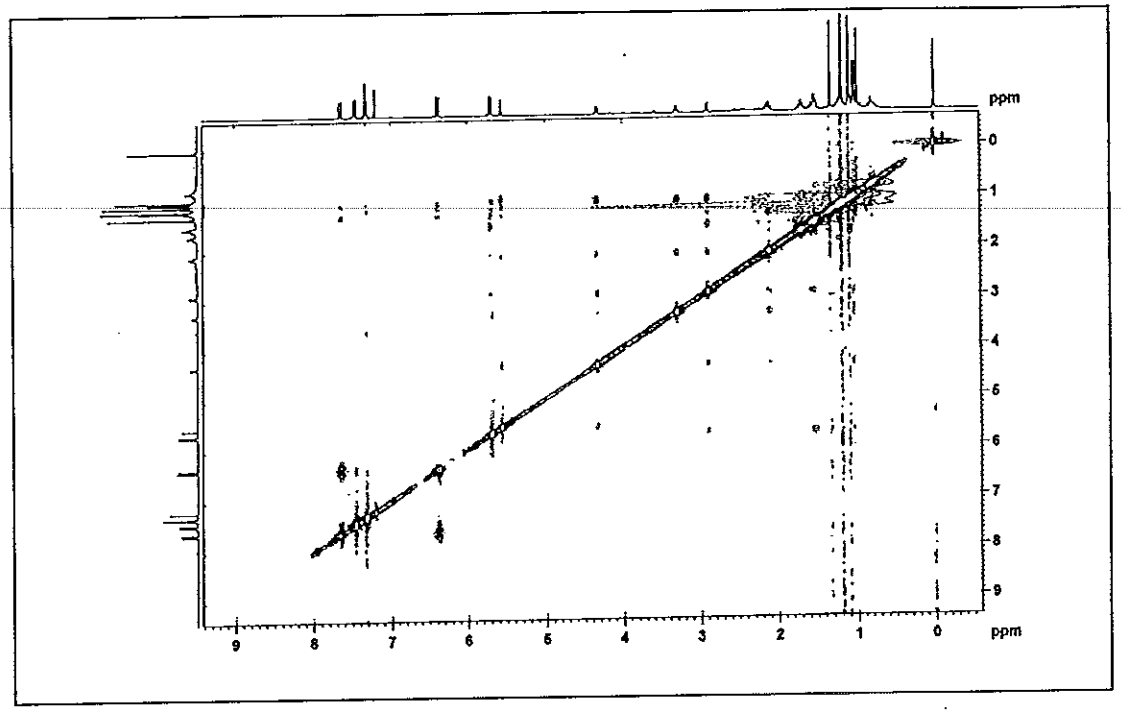

Figure 39 2D NOESY ($CDCl_3$) spectrum of compound **CP4**

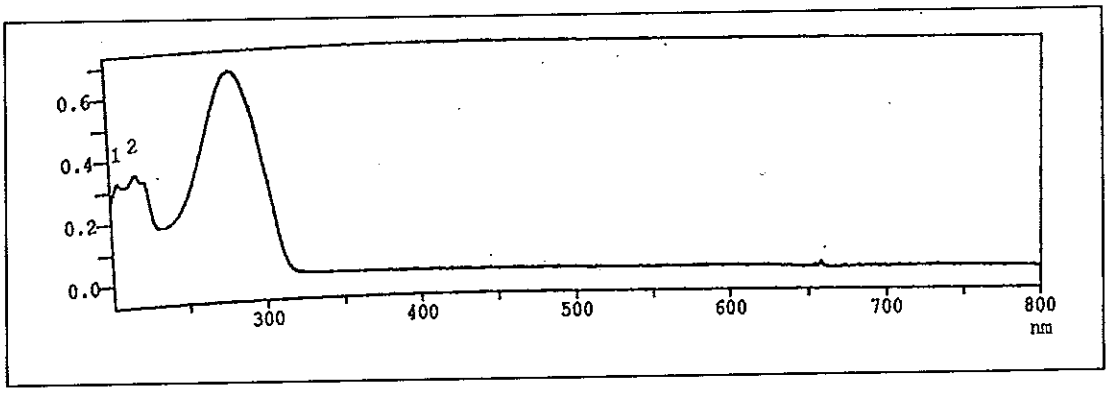

Figure 40 UV (MeOH) spectrum of compound **CP4**

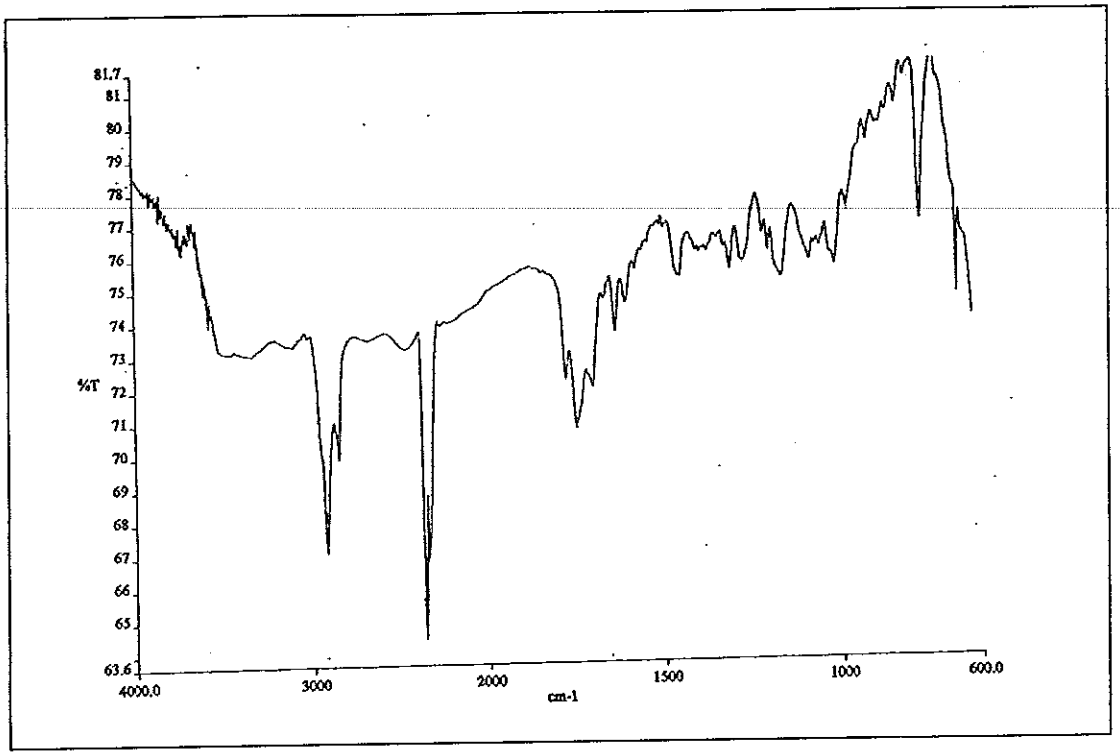

Figure 41 IR (neat) spectrum of compound **CP4**

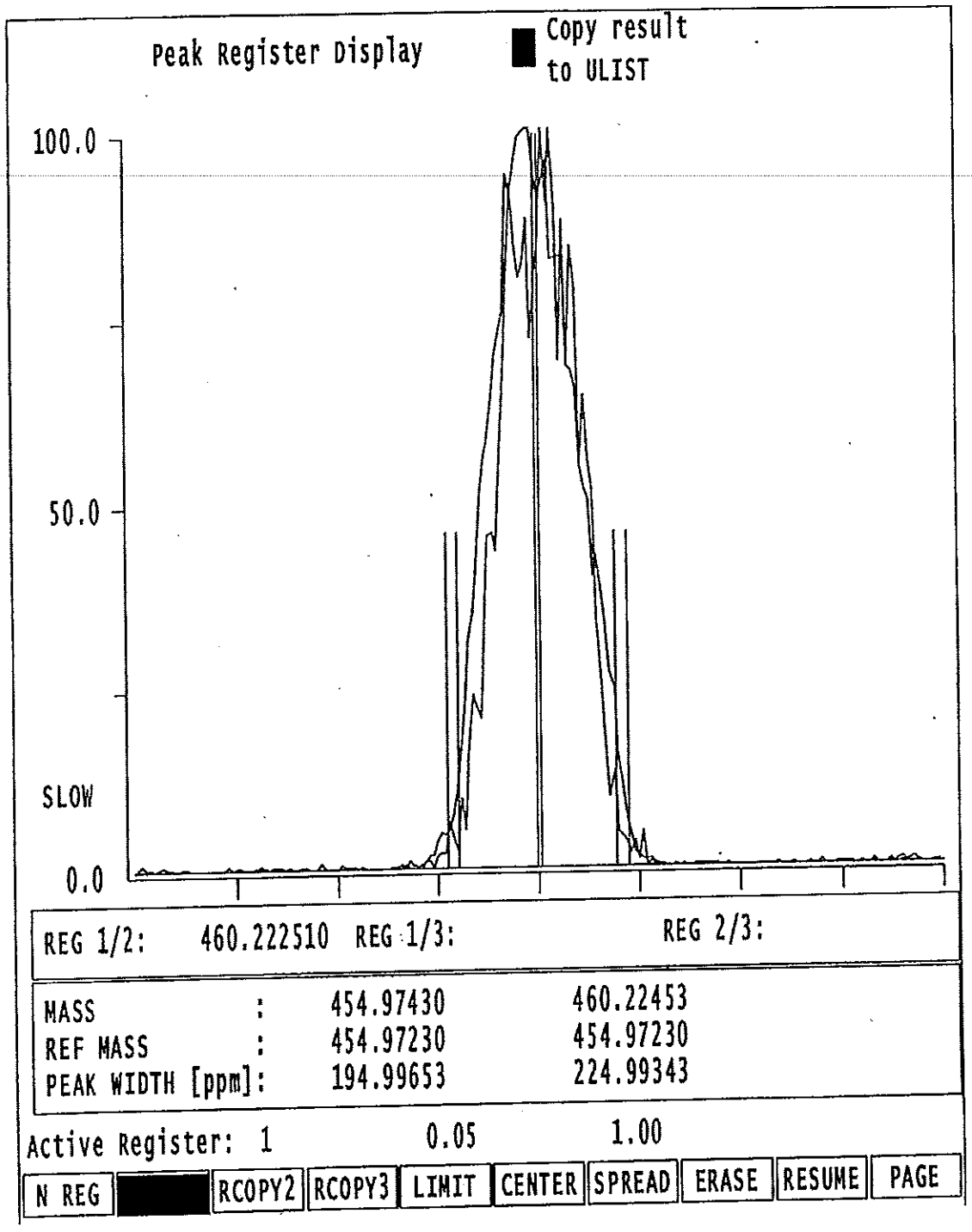

Figure 42 HREIMS spectrum of compound **CP4**

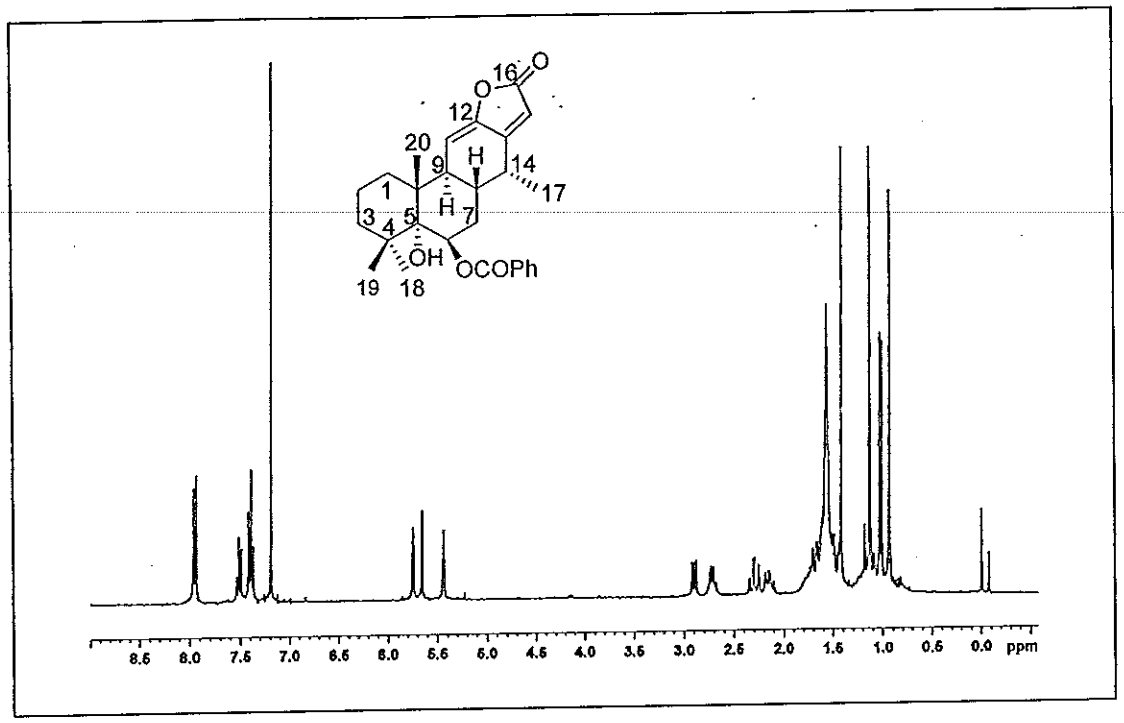

Figure 43 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP5**

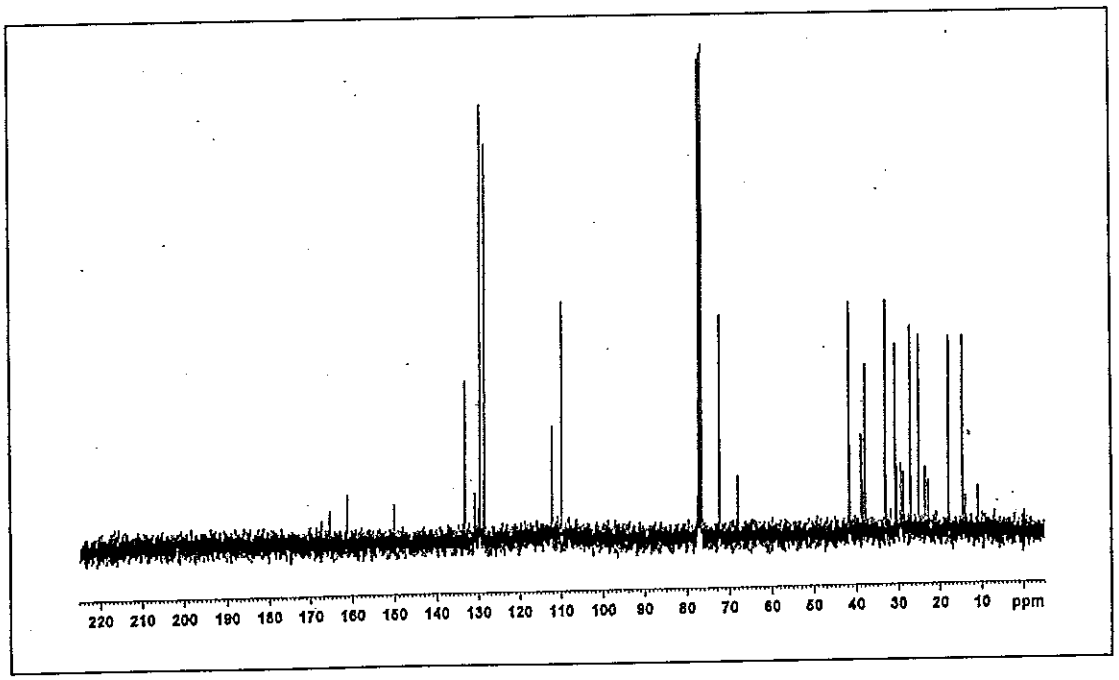

Figure 44 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP5**

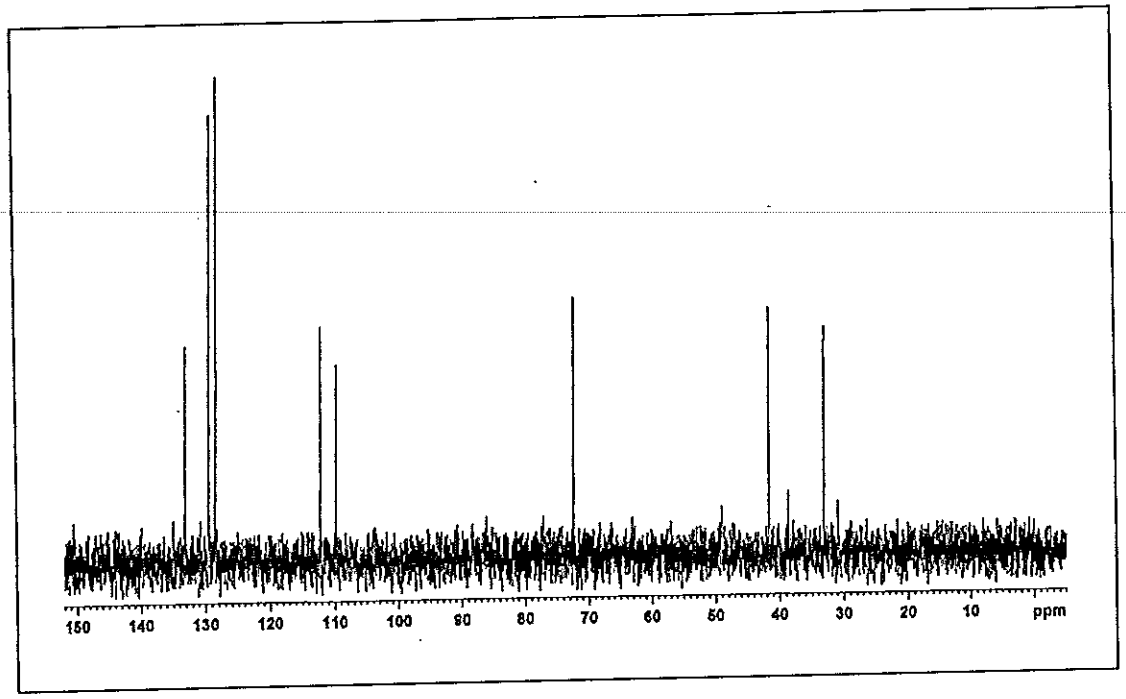

Figure 45 DEPT 90° ($CDCl_3$) spectrum of compound **CP5**

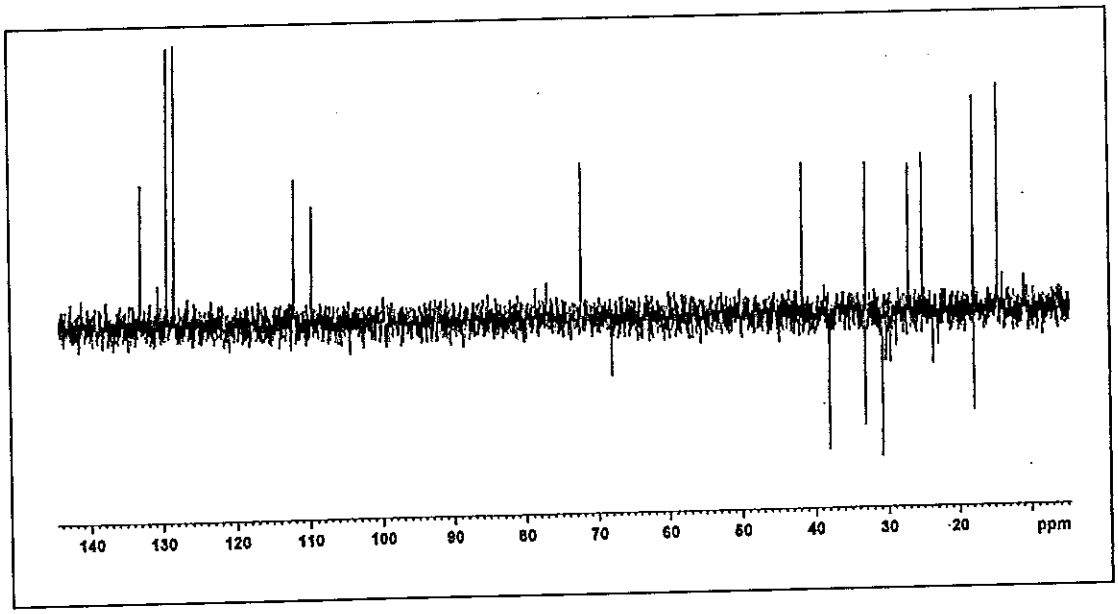

Figure 46 DEPT 135° ($CDCl_3$) spectrum of compound **CP5**

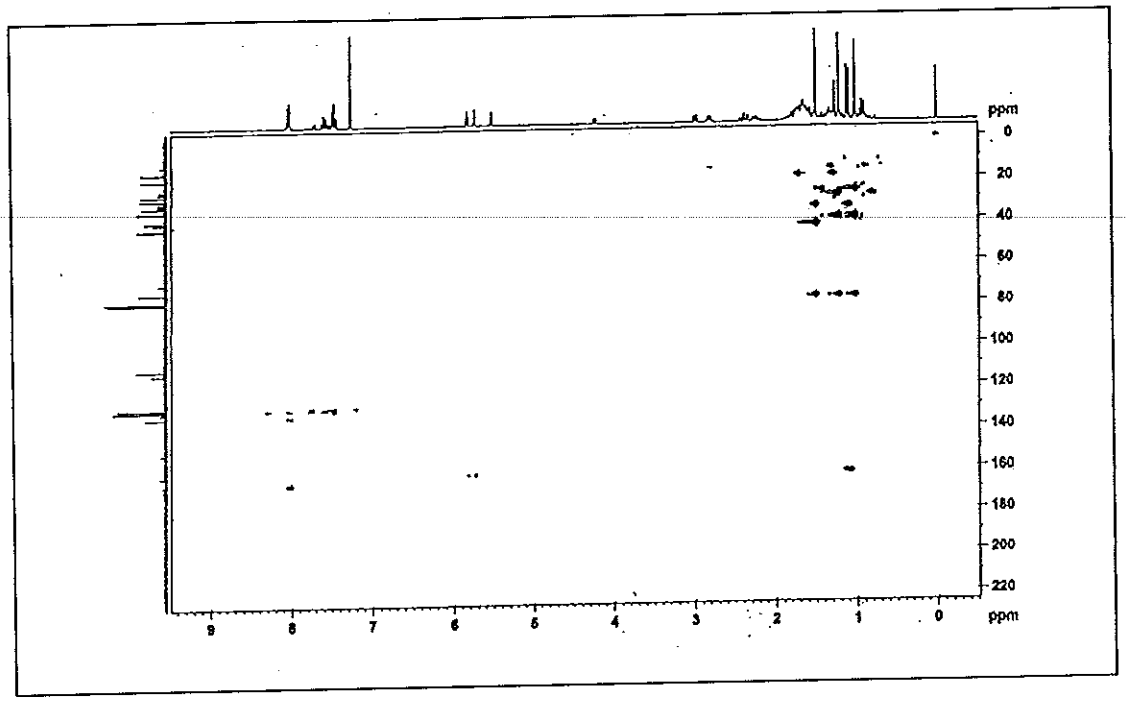

Figure 47 2D HMBC ($CDCl_3$) spectrum of compound **CP5**

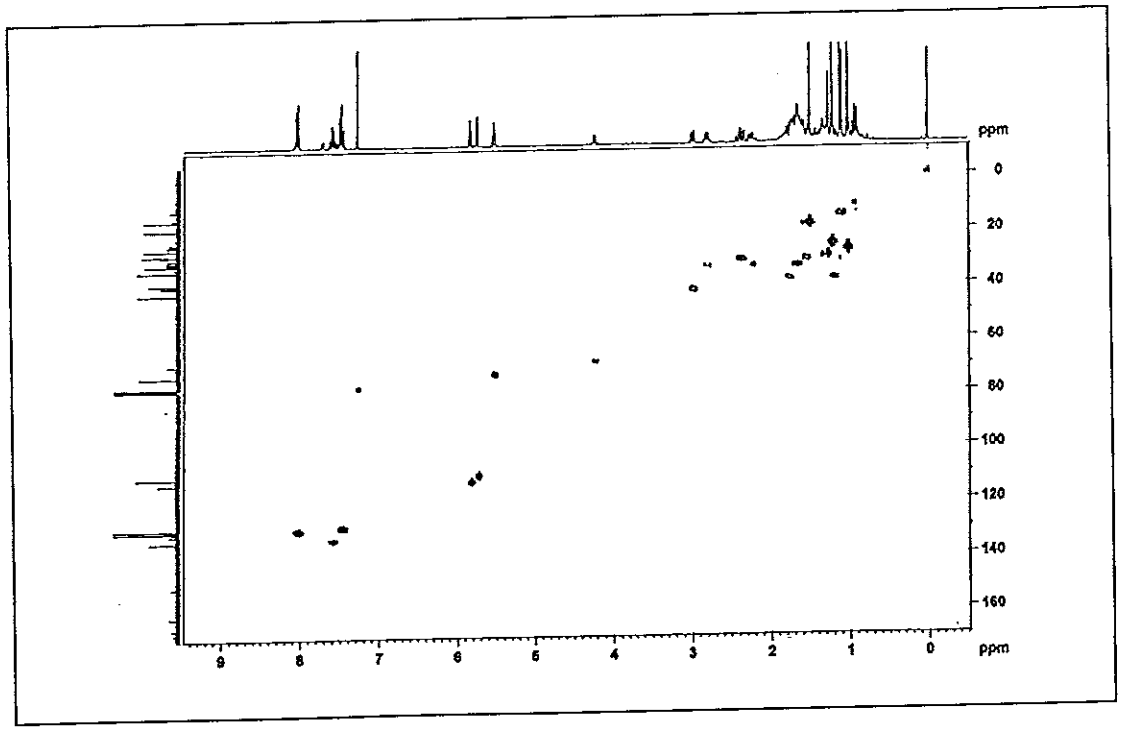

Figure 48 2D HMQC ($CDCl_3$) spectrum of compound **CP5**

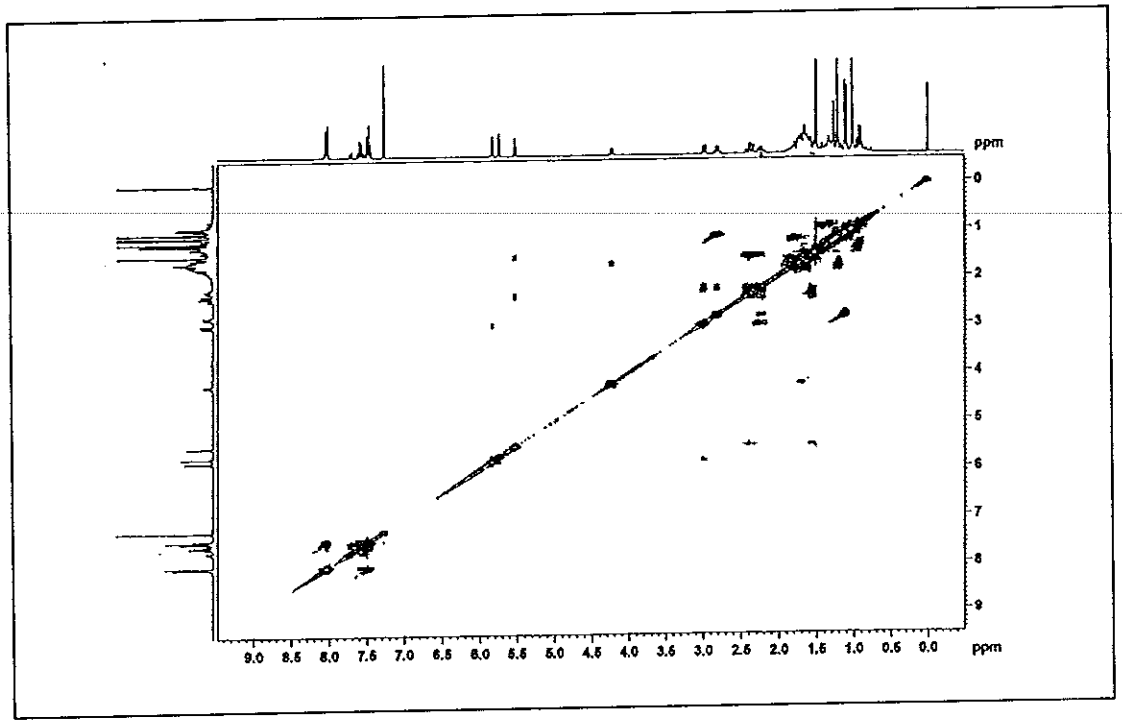

Figure 49 2D COSY ($CDCl_3$) spectrum of compound **CP5**

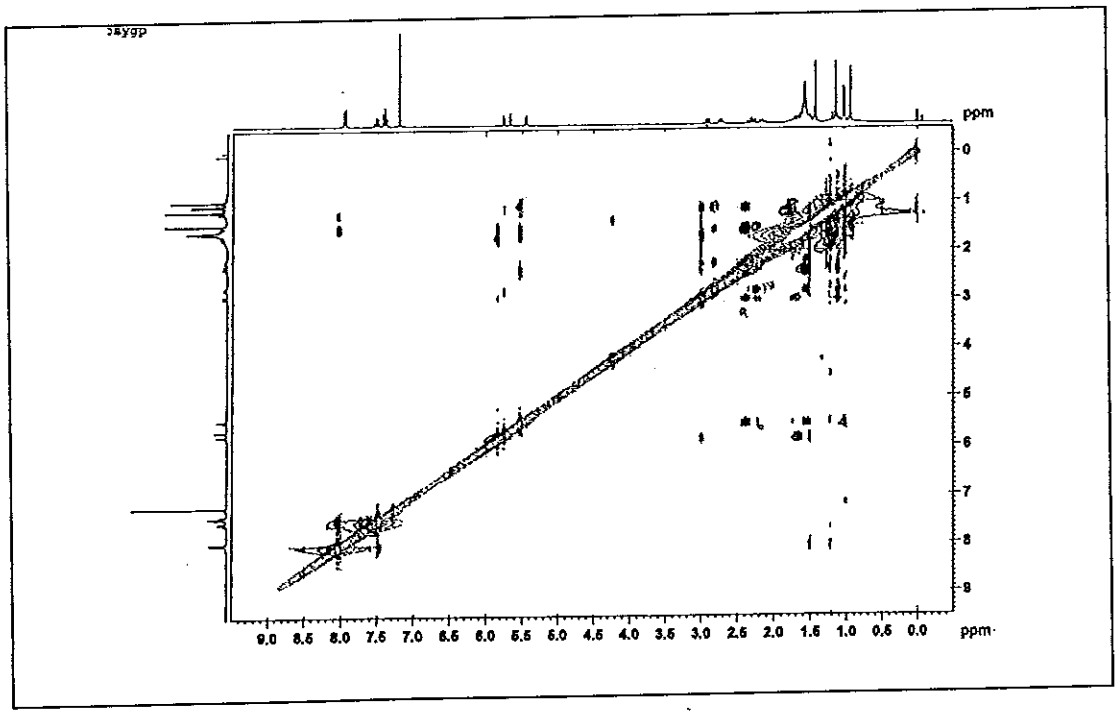

Figure 50 2D NOESY ($CDCl_3$) spectrum of compound **CP5**

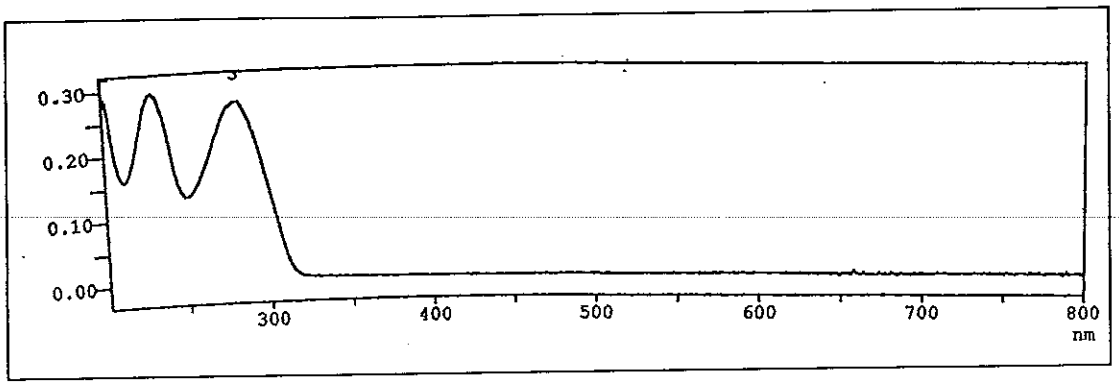

Figure 51 UV (MeOH) spectrum of compound **CP5**

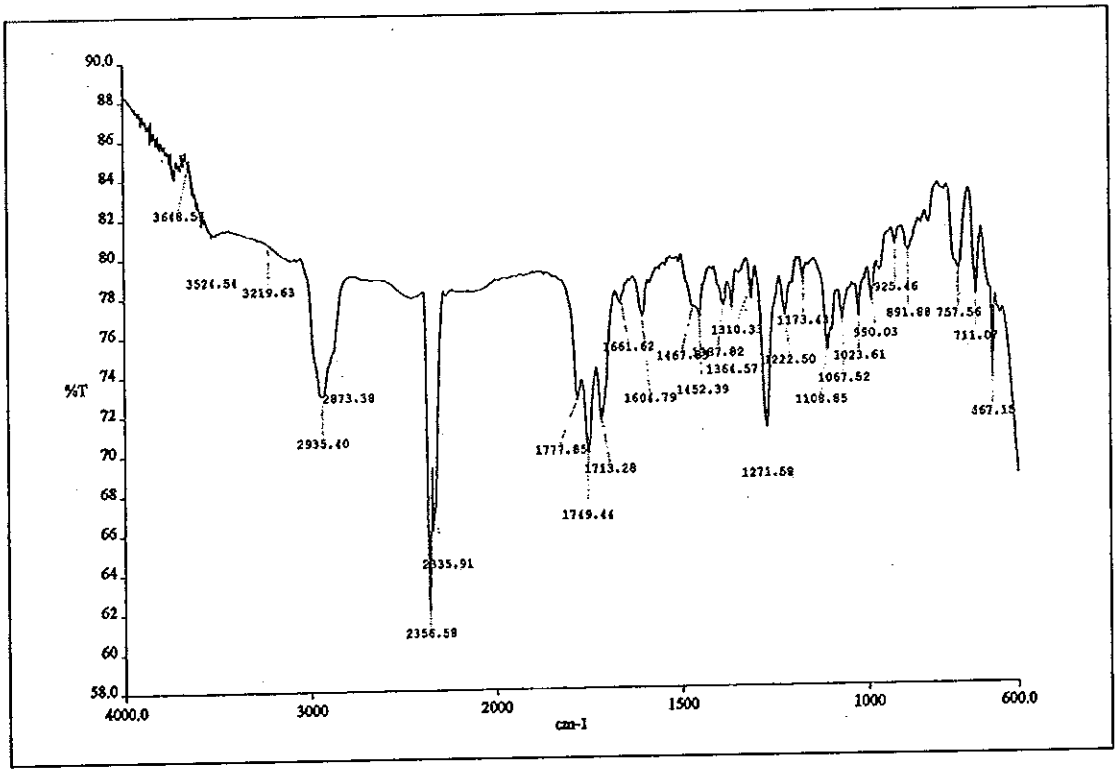

Figure 52 IR (neat) spectrum of compound **CP5**

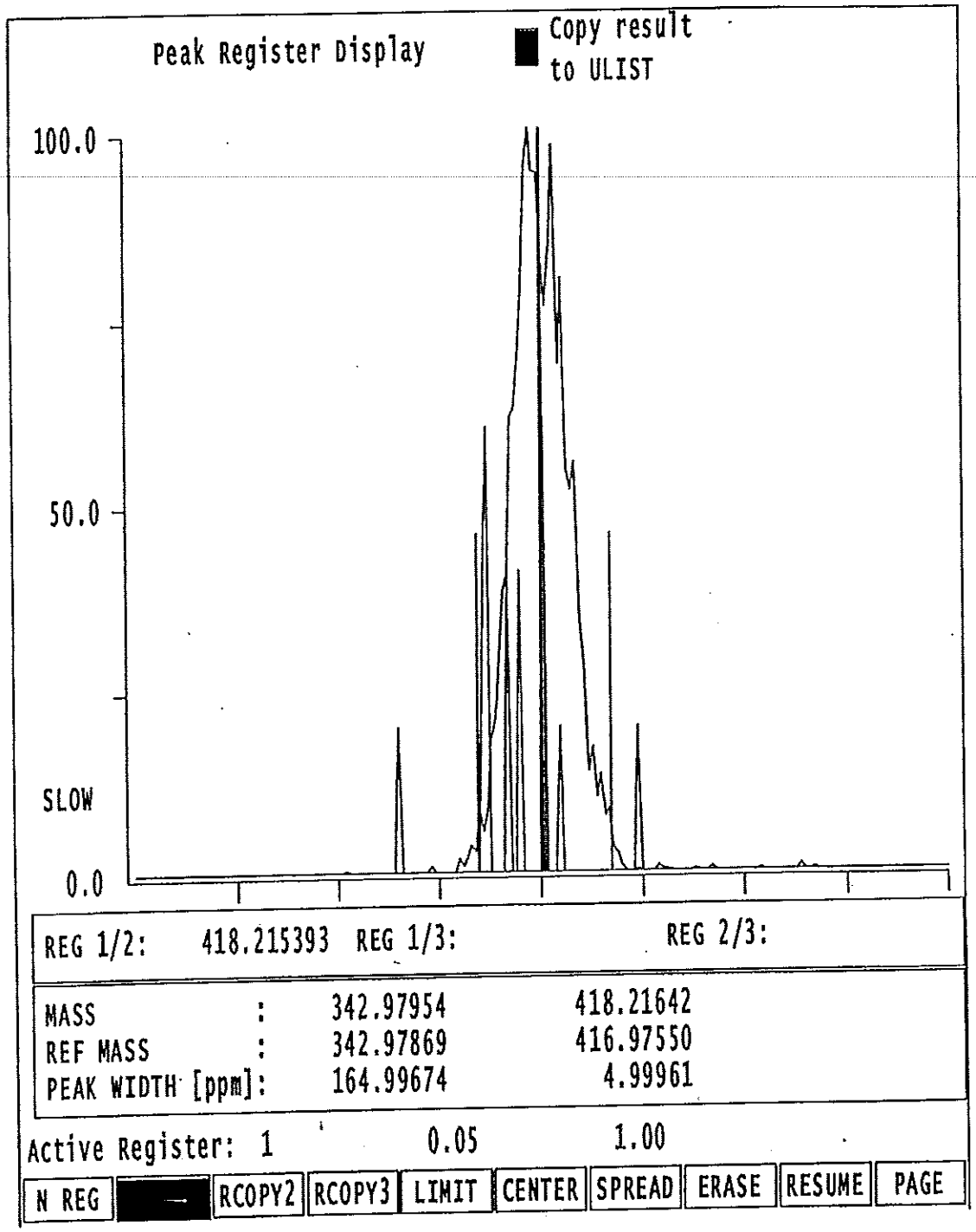

Figure 53 HRIMS spectrum of compound **CP5**

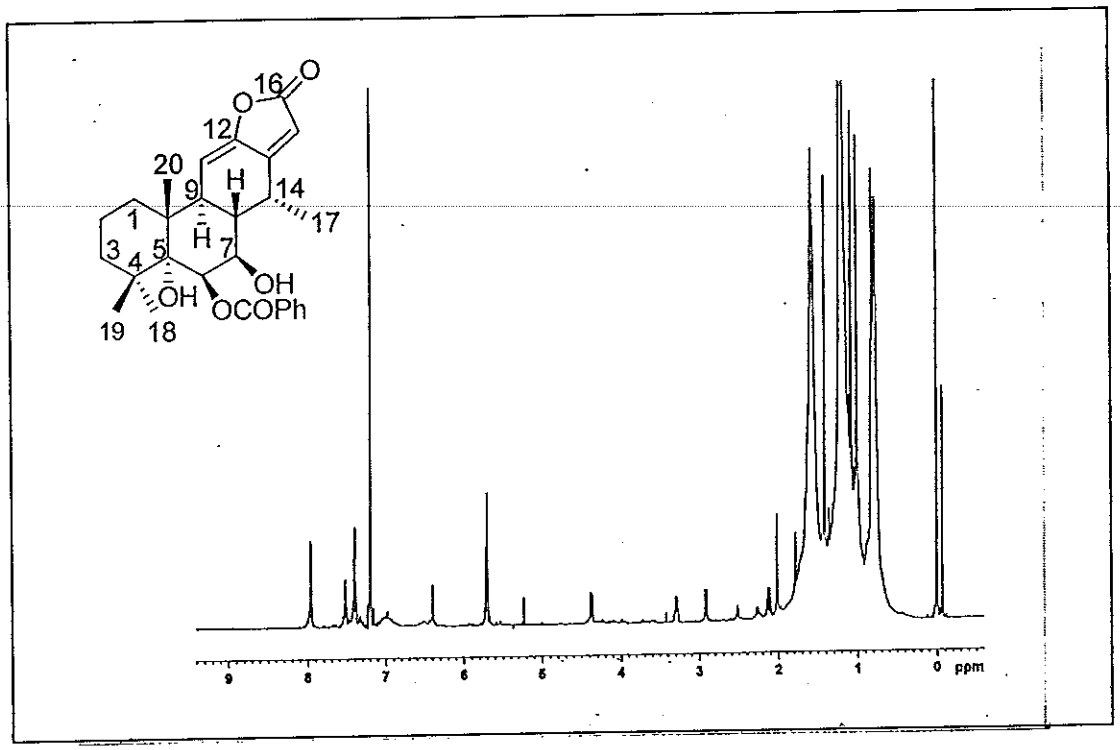

Figure 54 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of compound **CP6**

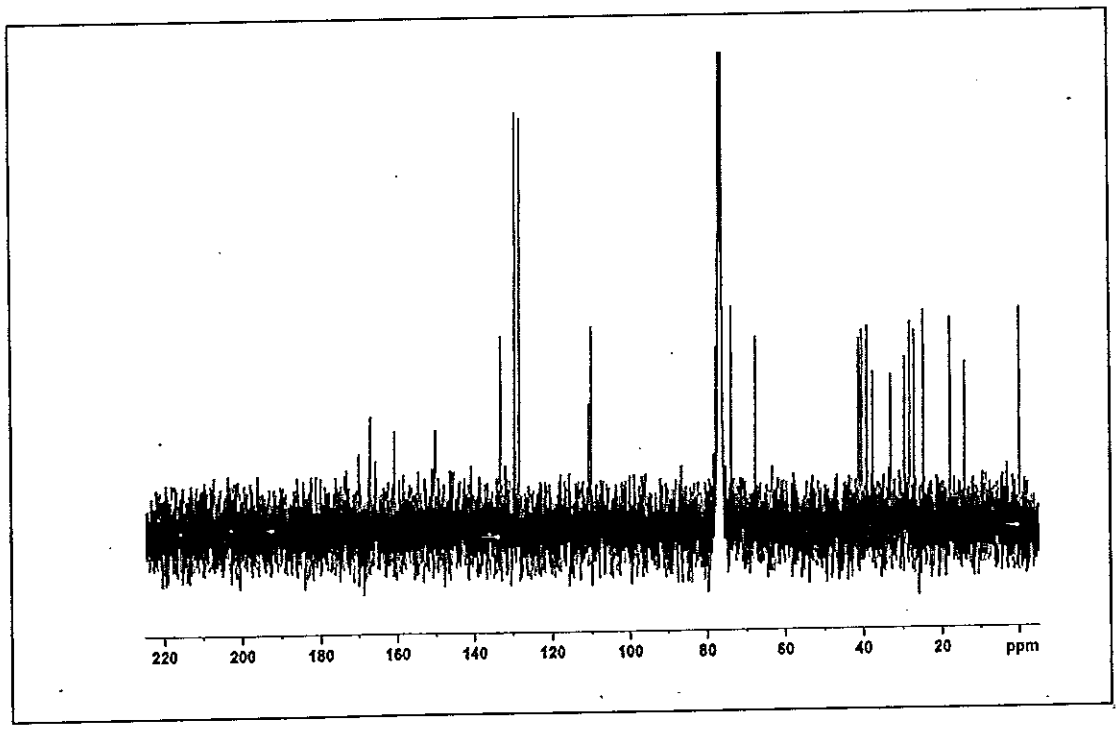

Figure 55 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of compound **CP6**

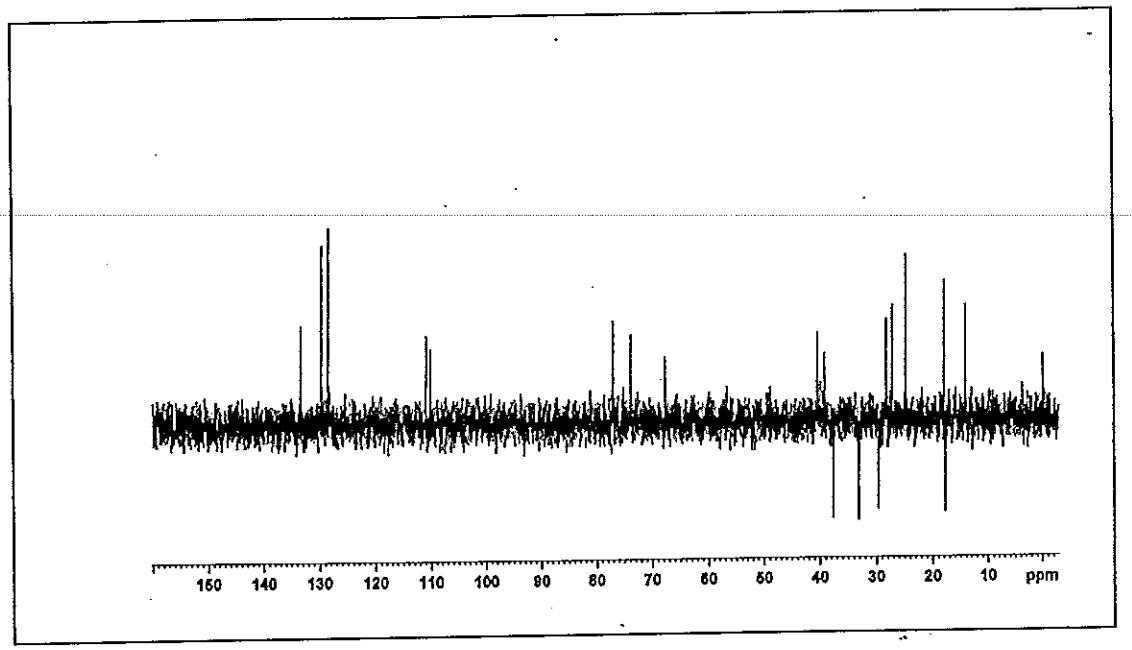

Figure 56 DEPT 135° ($CDCl_3$) spectrum of compound **CP6**

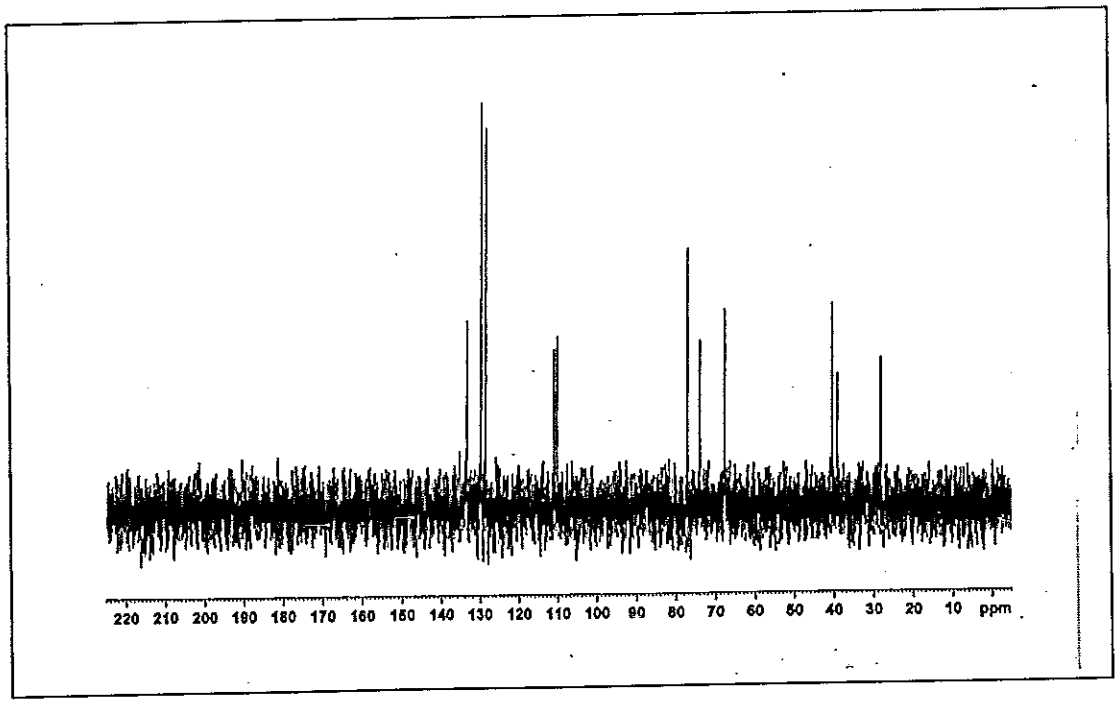

Figure 57 DEPT 90° ($CDCl_3$) spectrum of compound **CP6**

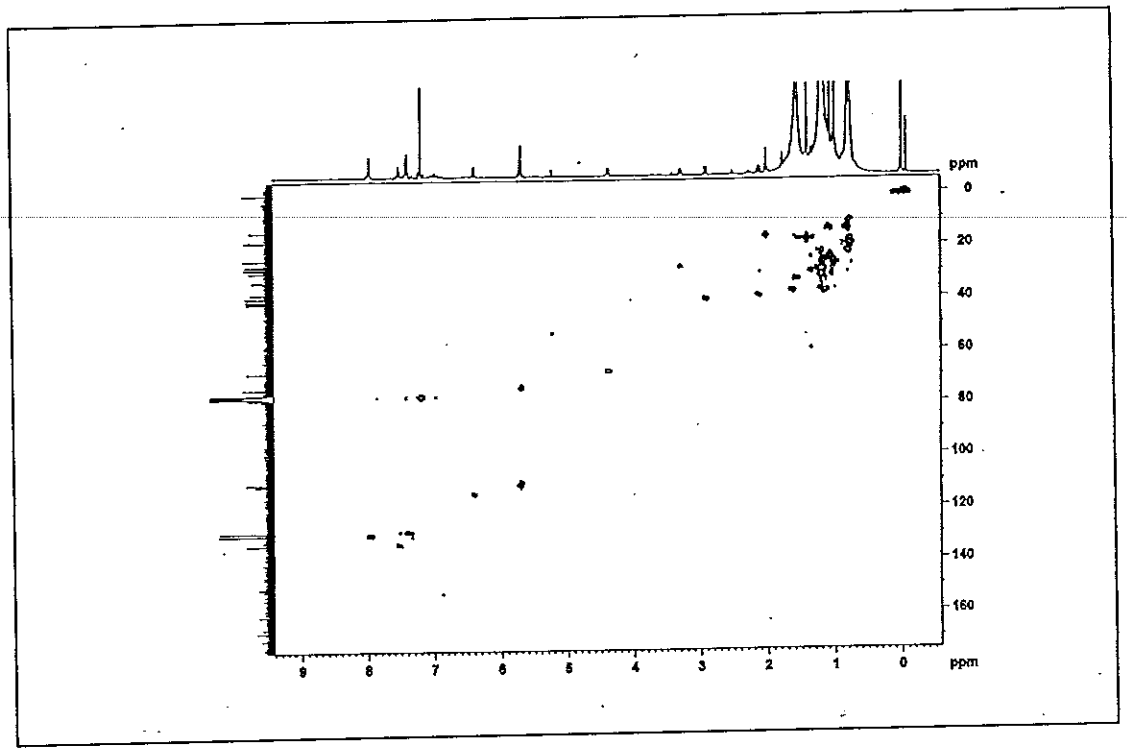

Figure 58 2D HMQC ($CDCl_3$) spectrum of compound **CP6**

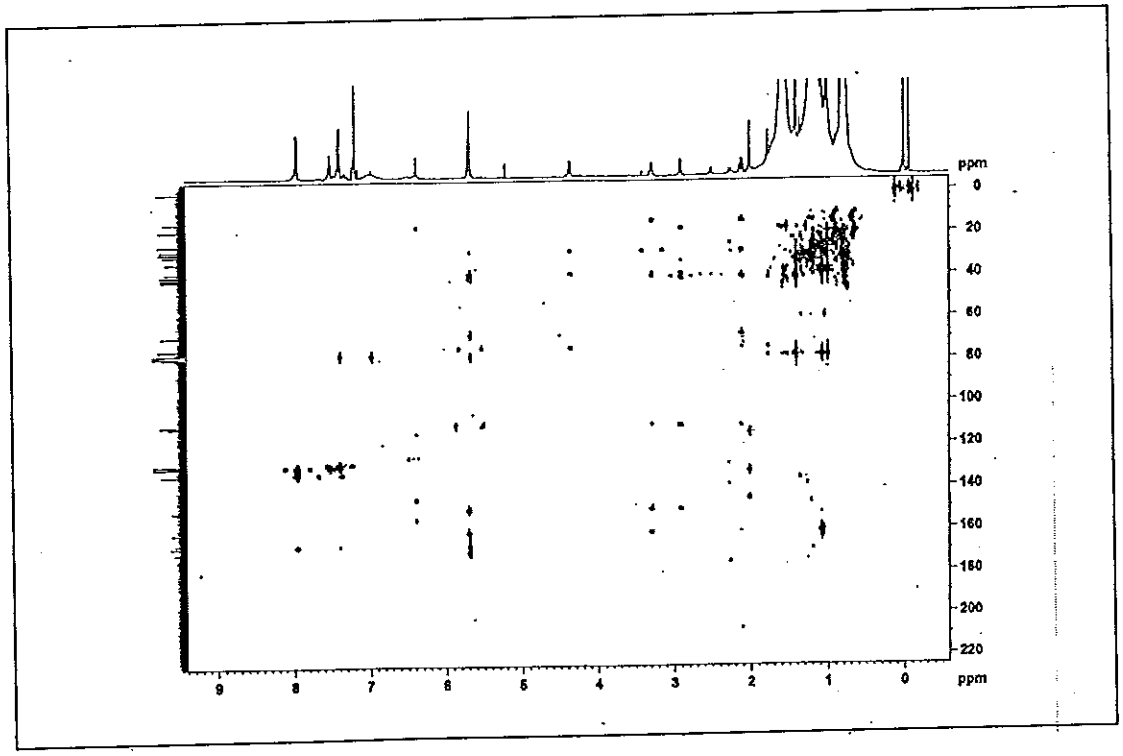

Figure 59 2D HMBC ($CDCl_3$) spectrum of compound **CP6**

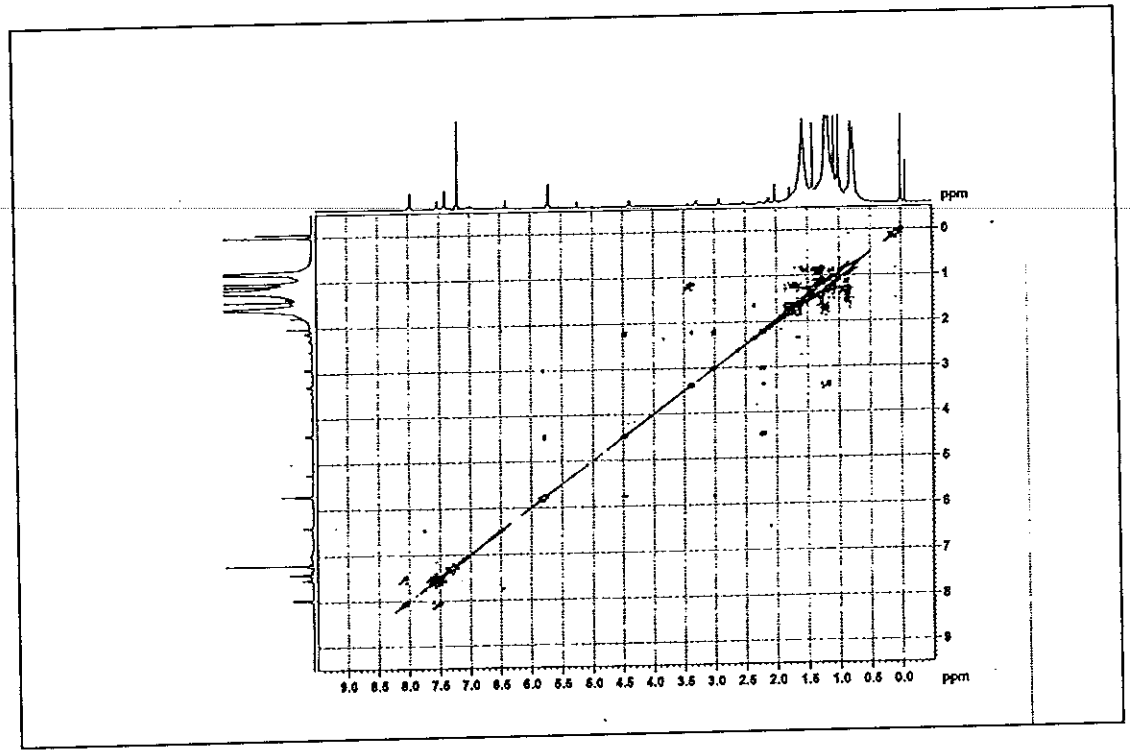

Figure 60 2D COSY ($CDCl_3$) spectrum of compound **CP6**

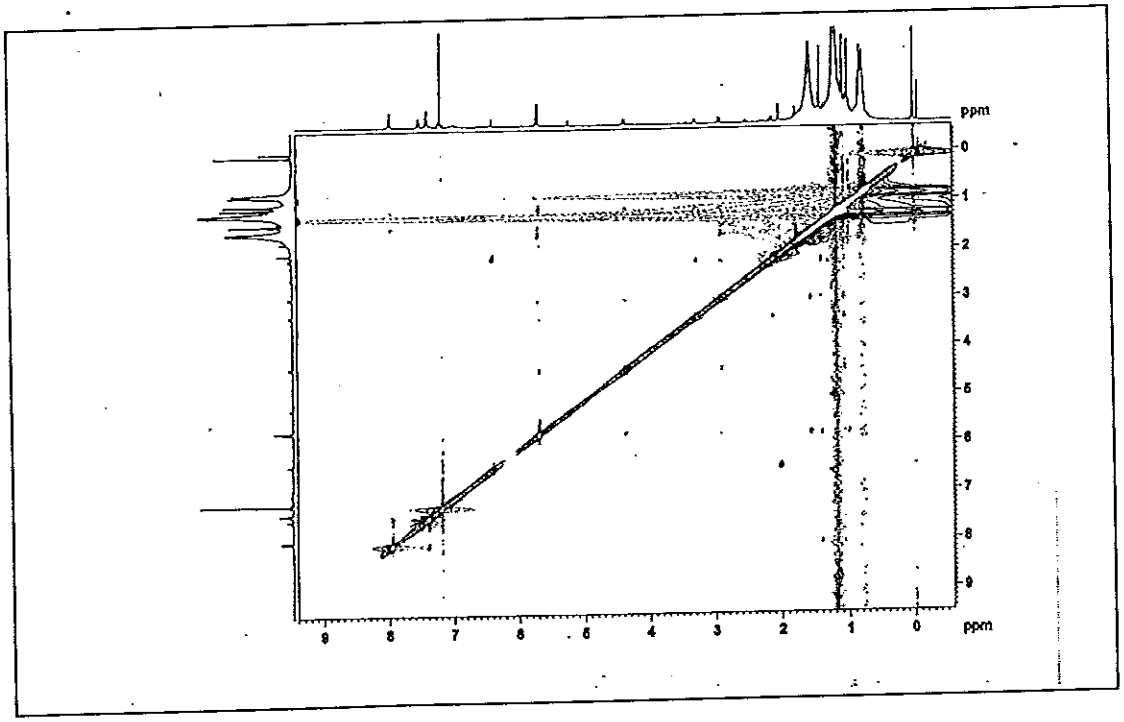

Figure 61 2D NOESY ($CDCl_3$) spectrum of compound **CP6**

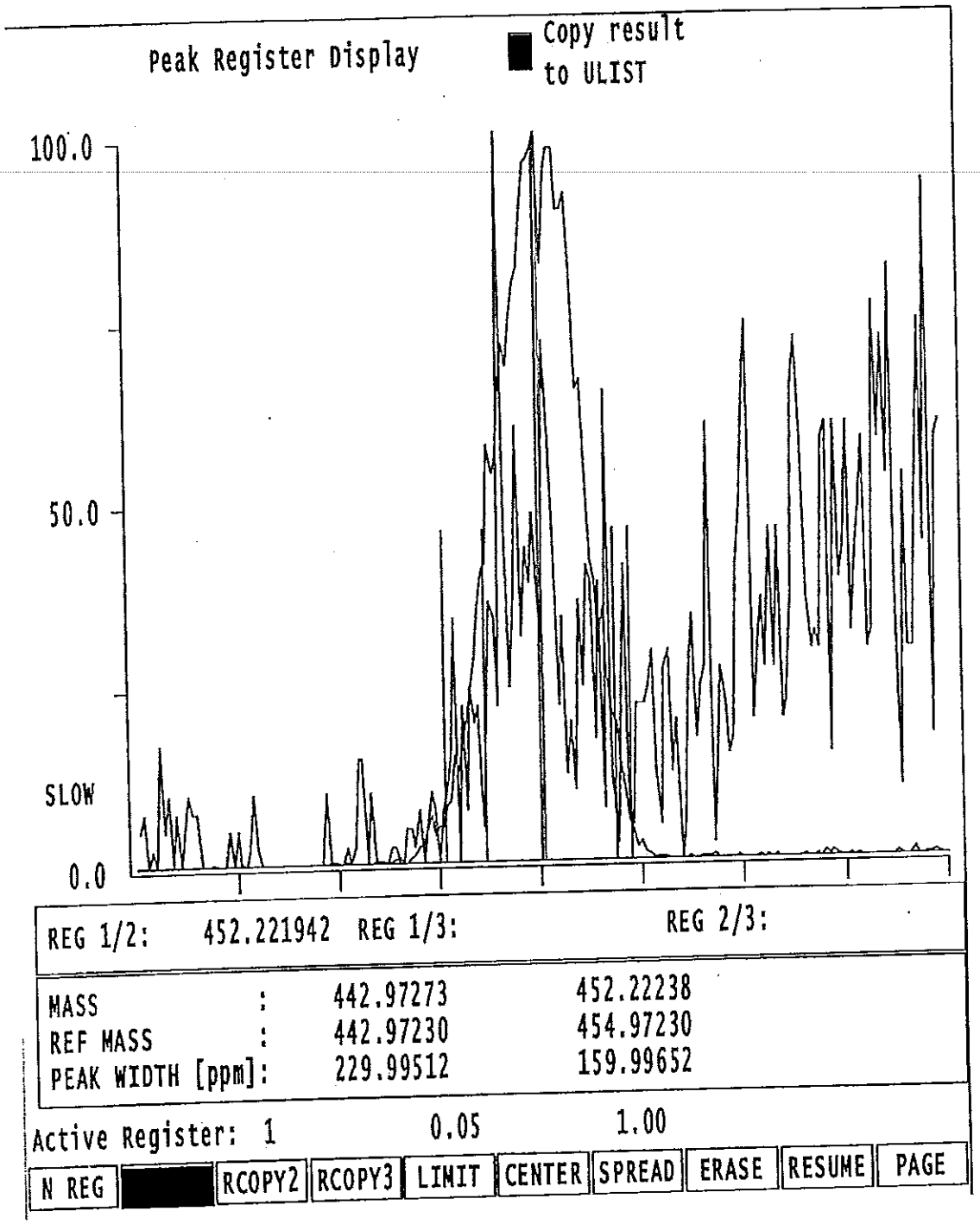

Figure 62 HRIMS spectrum of compound **CP6**

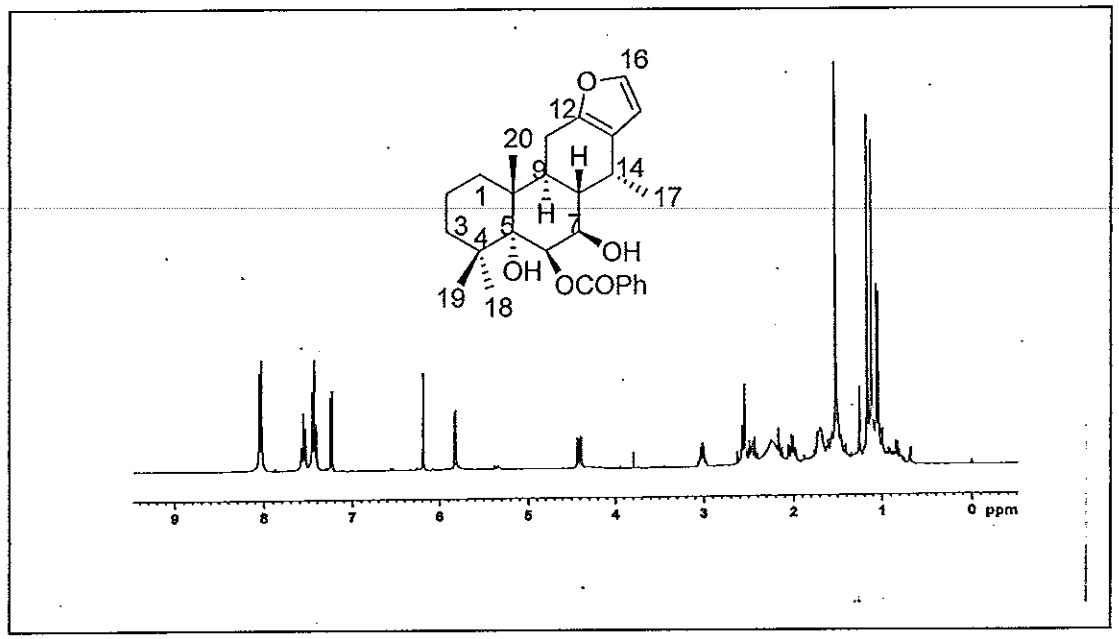

Figure 63 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP7**

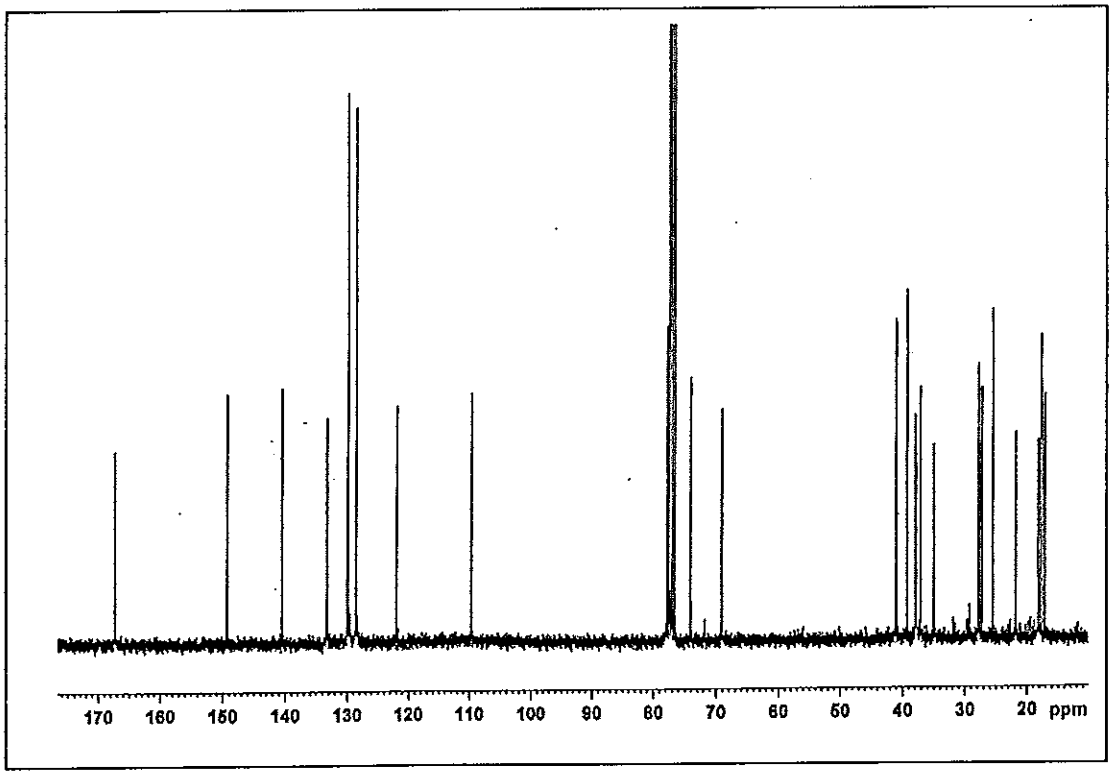

Figure 64 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP7**

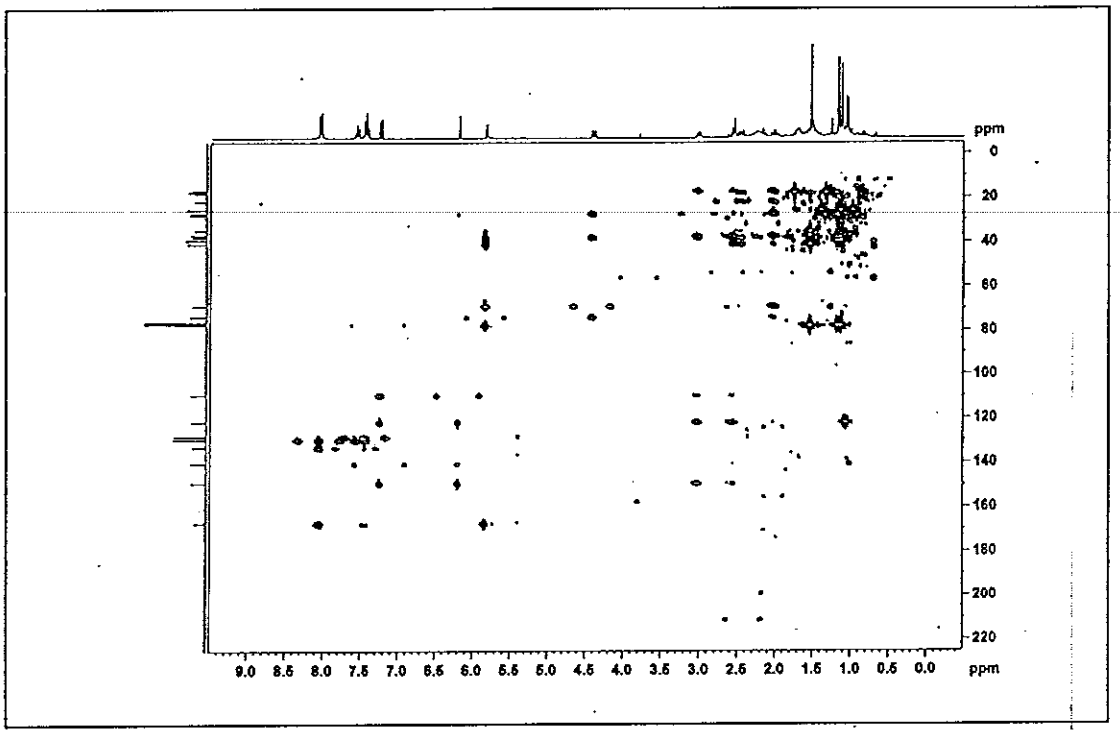

Figure 65 2D HMBC ($CDCl_3$) spectrum of compound **CP7**

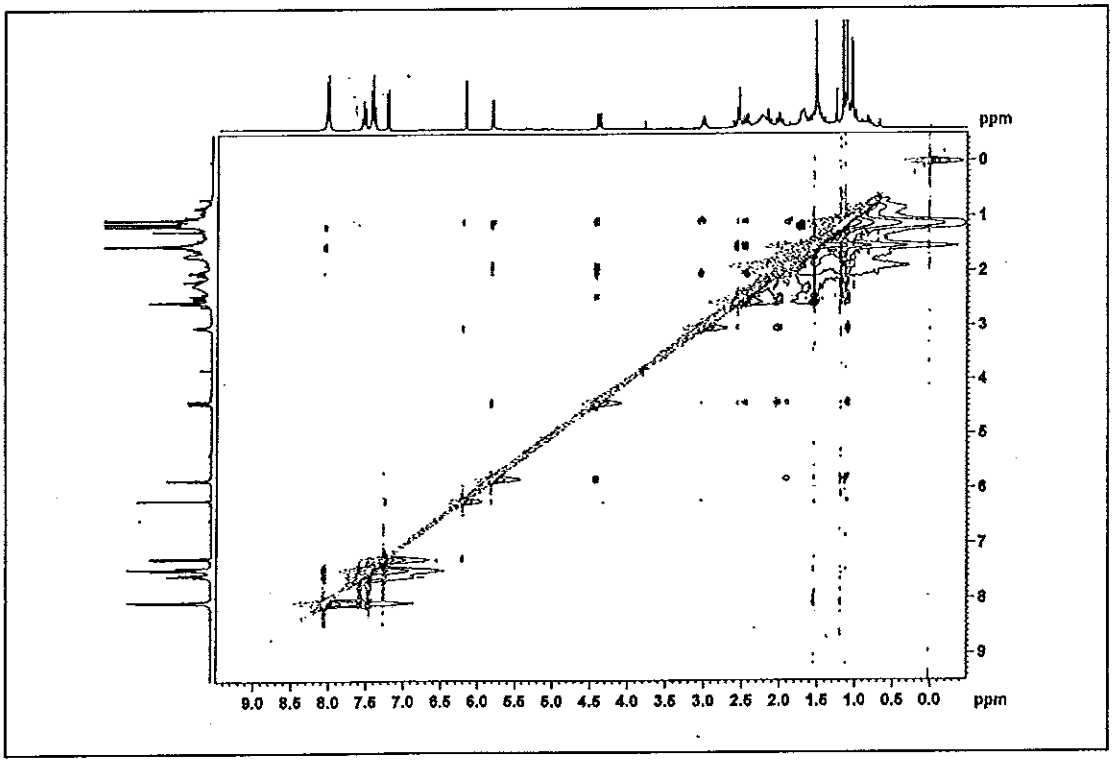

Figure 66 2D NOESY ($CDCl_3$) spectrum of compound **CP7**

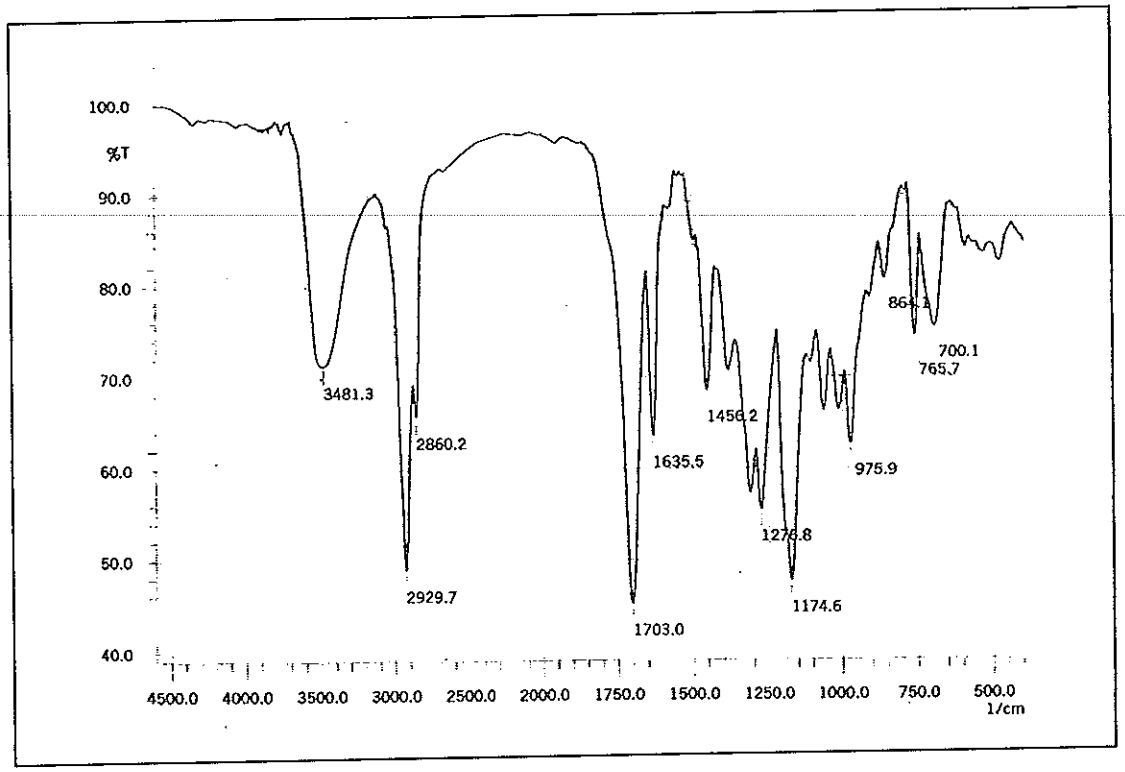

Figure 67 IR (neat) spectrum of compound **CP7**

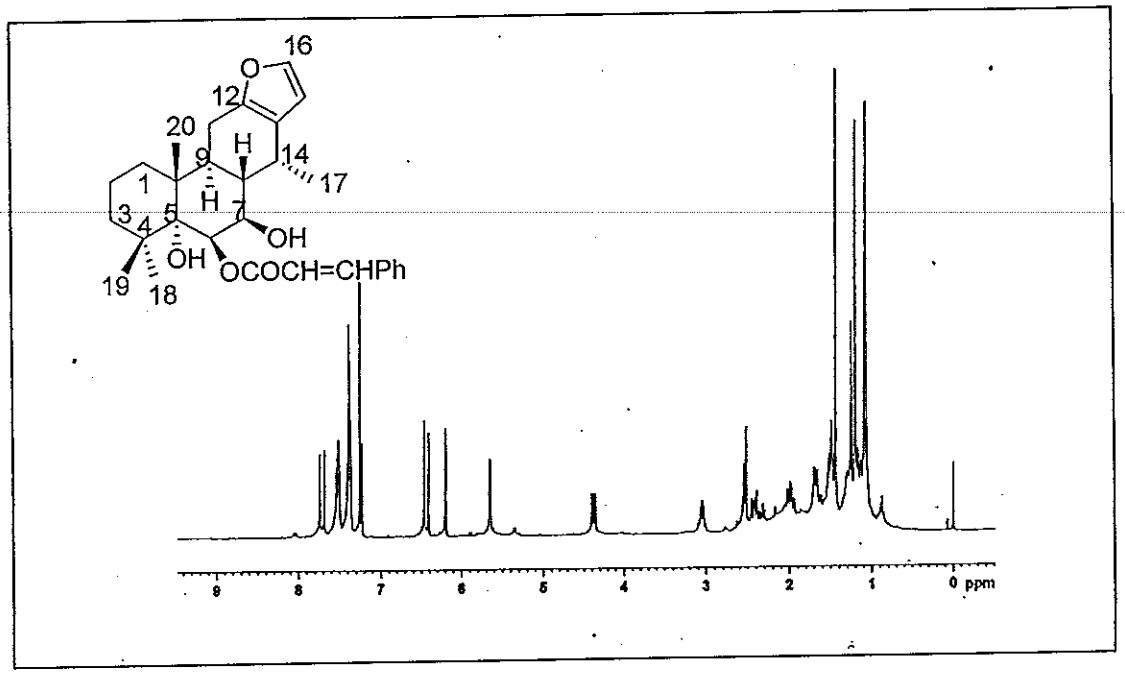

Figure 68 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP8**

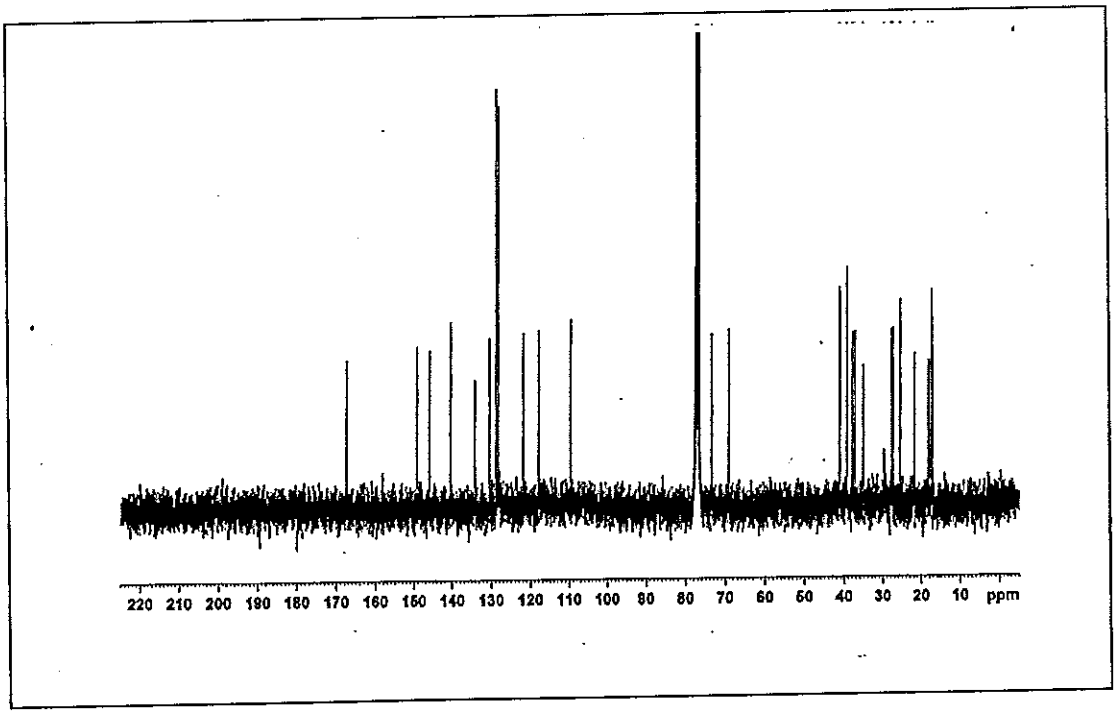

Figure 69 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP8**

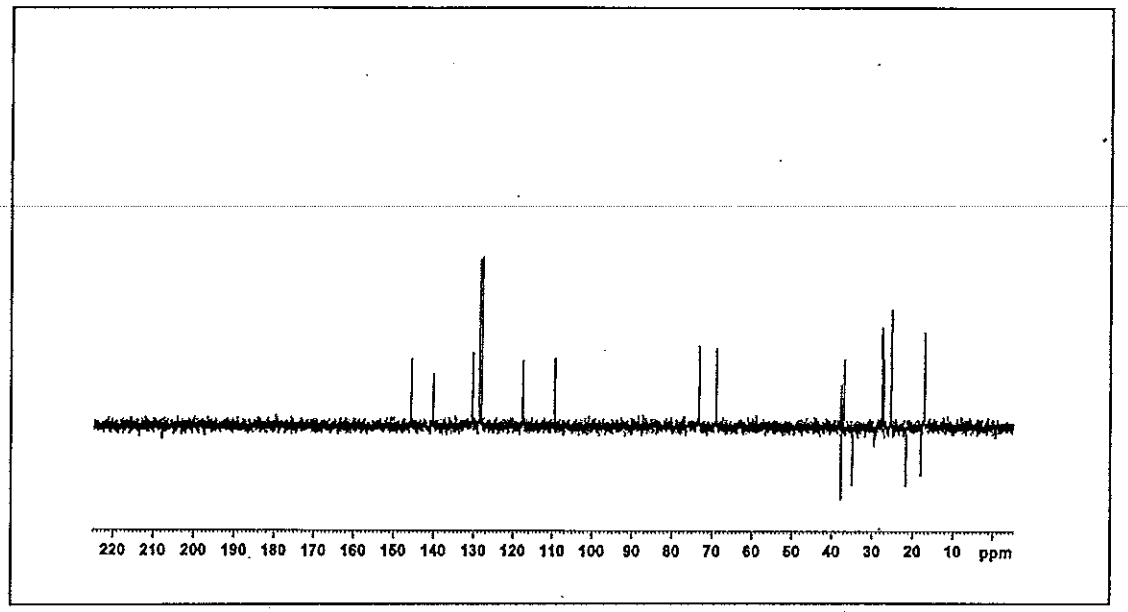

Figure 70 DEPT 135° ($CDCl_3$) spectrum of compound **CP8**

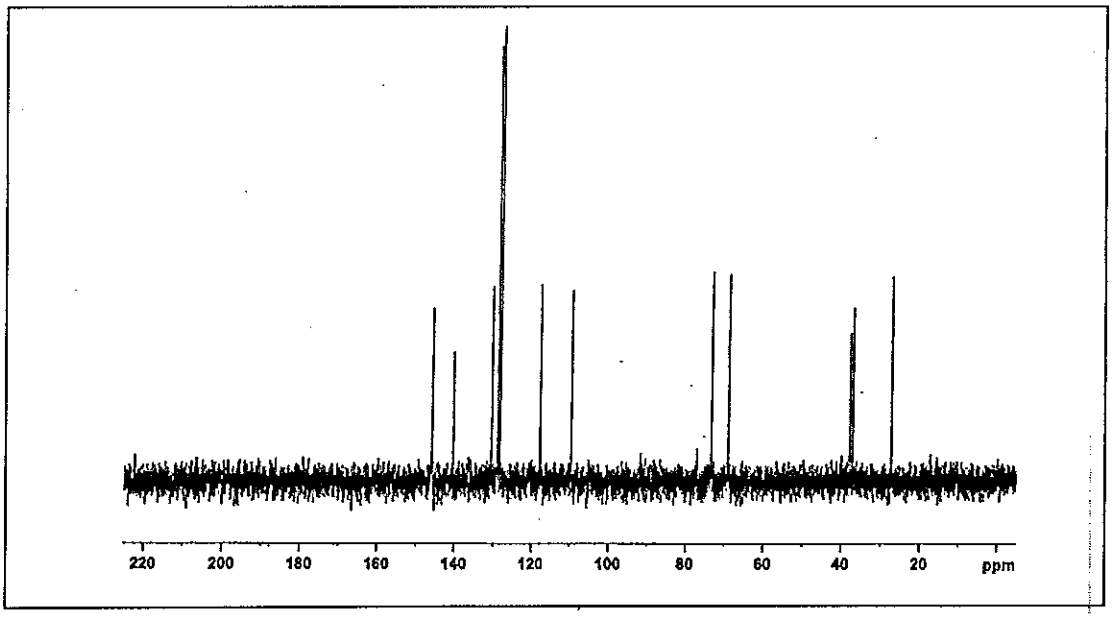

Figure 71 DEPT 90° ($CDCl_3$) spectrum of compound **CP8**

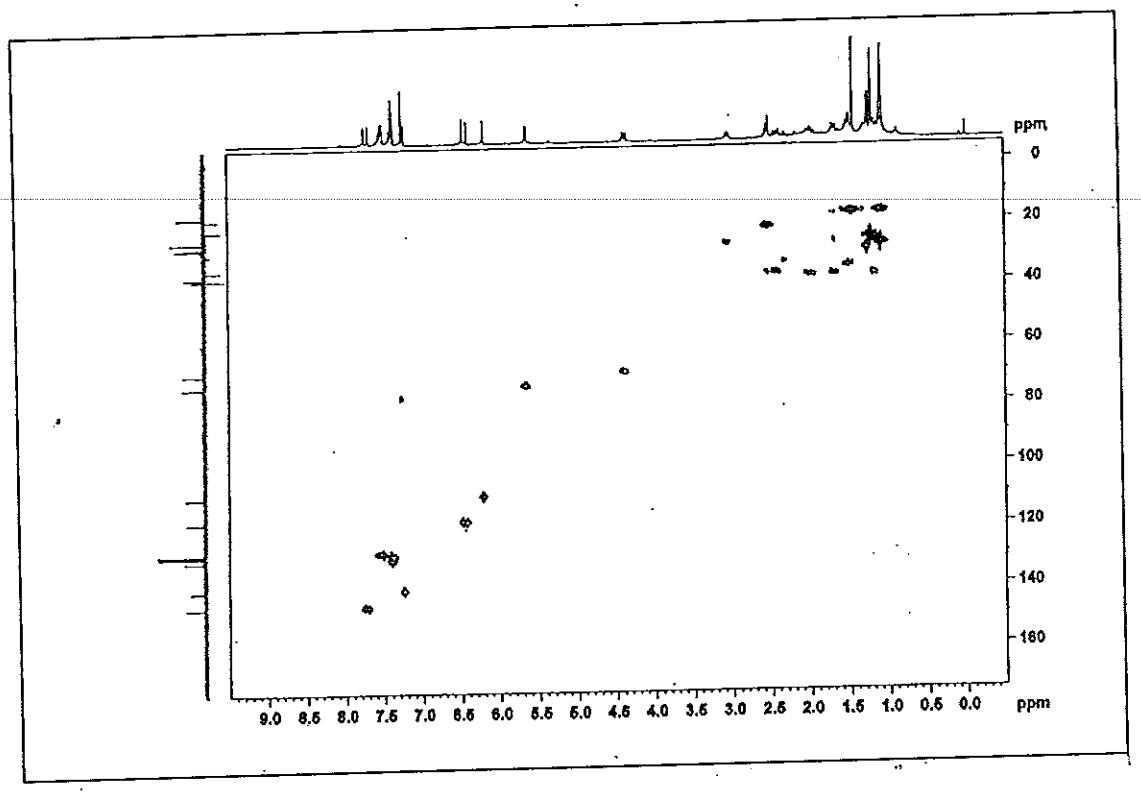

Figure 72 2D HMQC ($CDCl_3$) spectrum of compound **CP8**

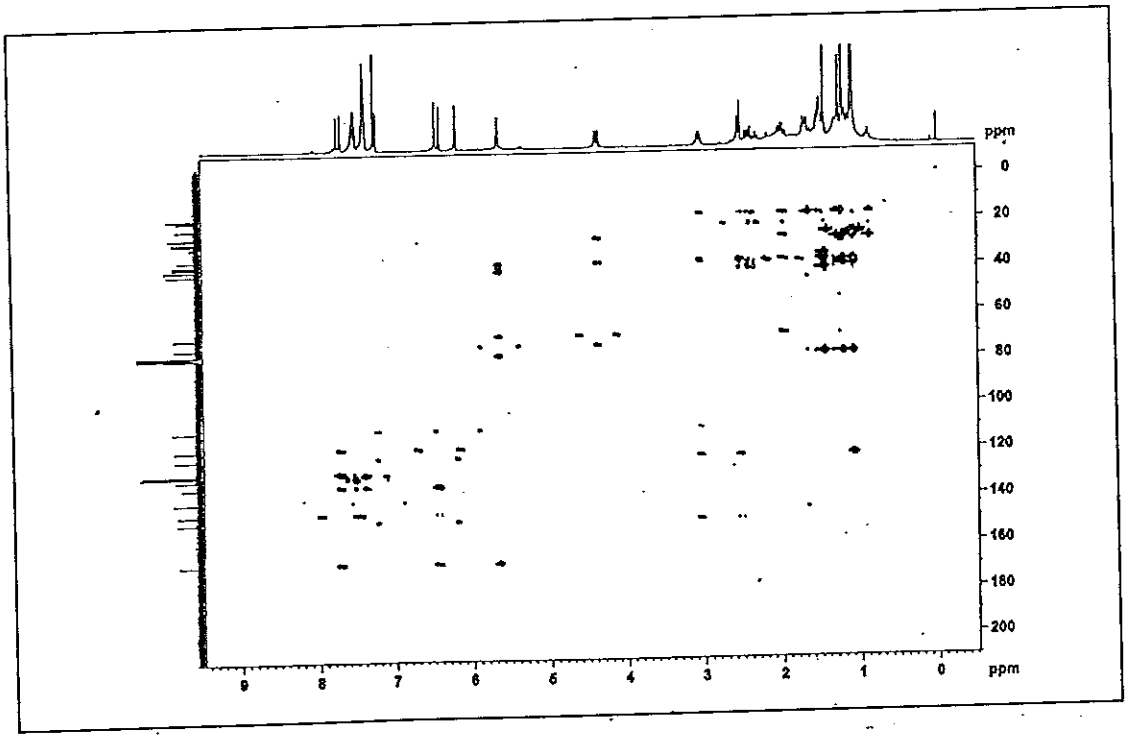

Figure 73 2D HMBC ($CDCl_3$) spectrum of compound **CP8**

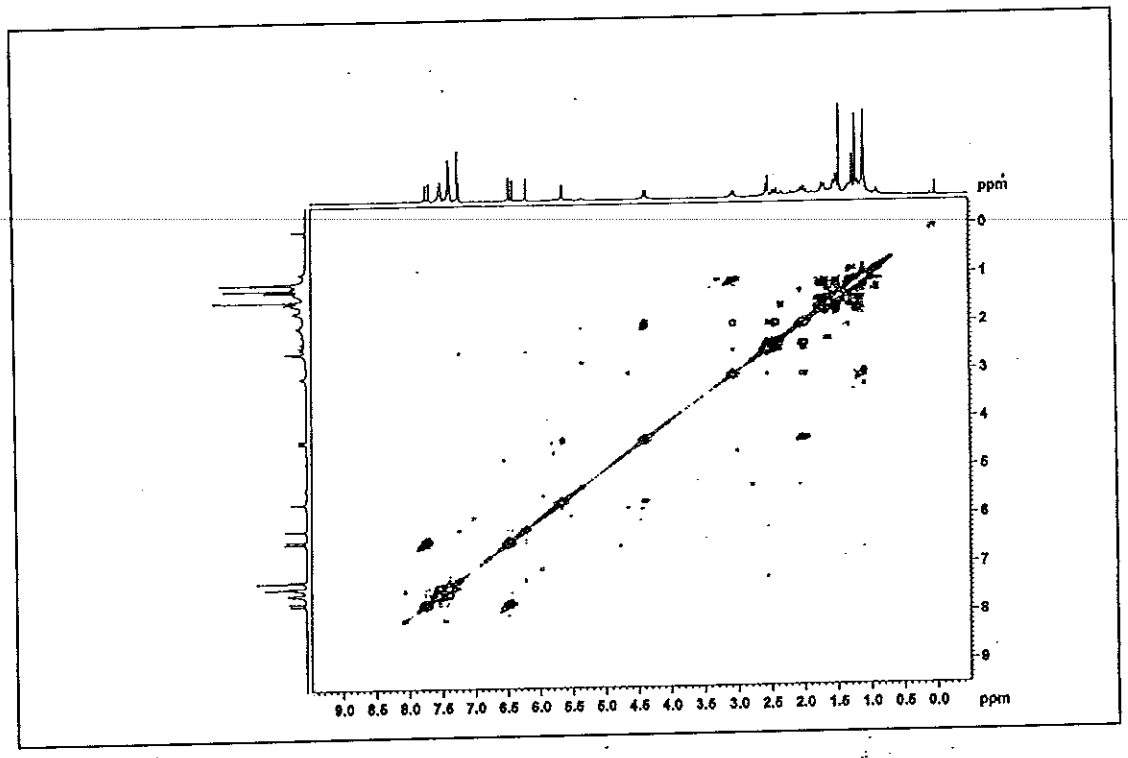

Figure 74 2D COSY ($CDCl_3$) spectrum of compound **CP8**

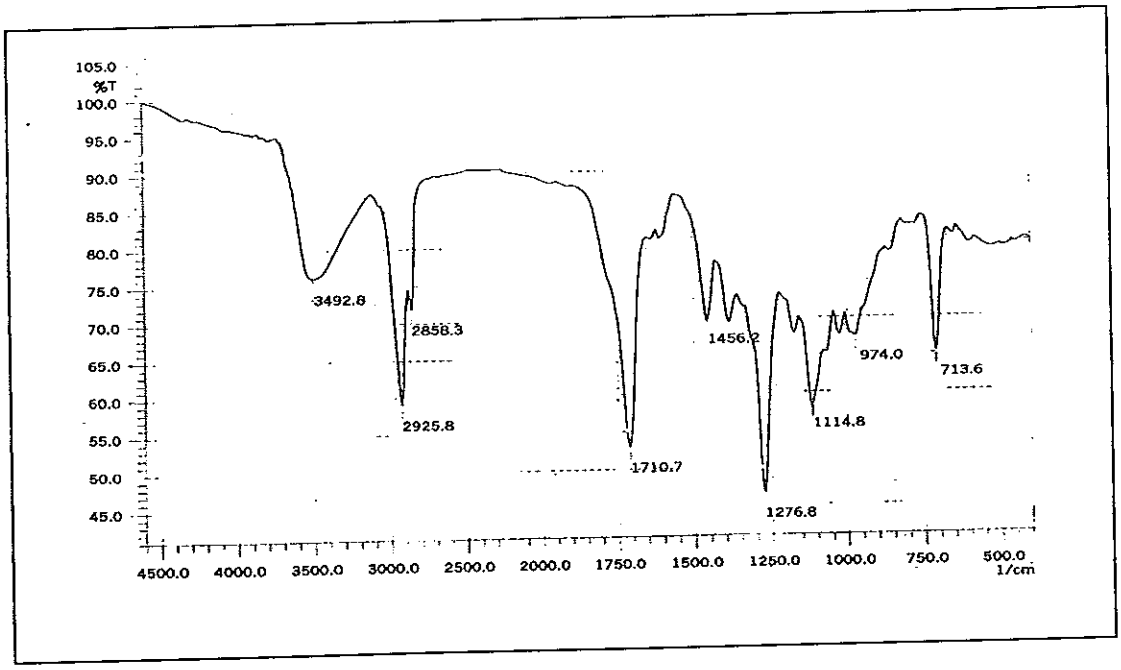

Figure 75 IR (neat) spectrum of compound **CP8**

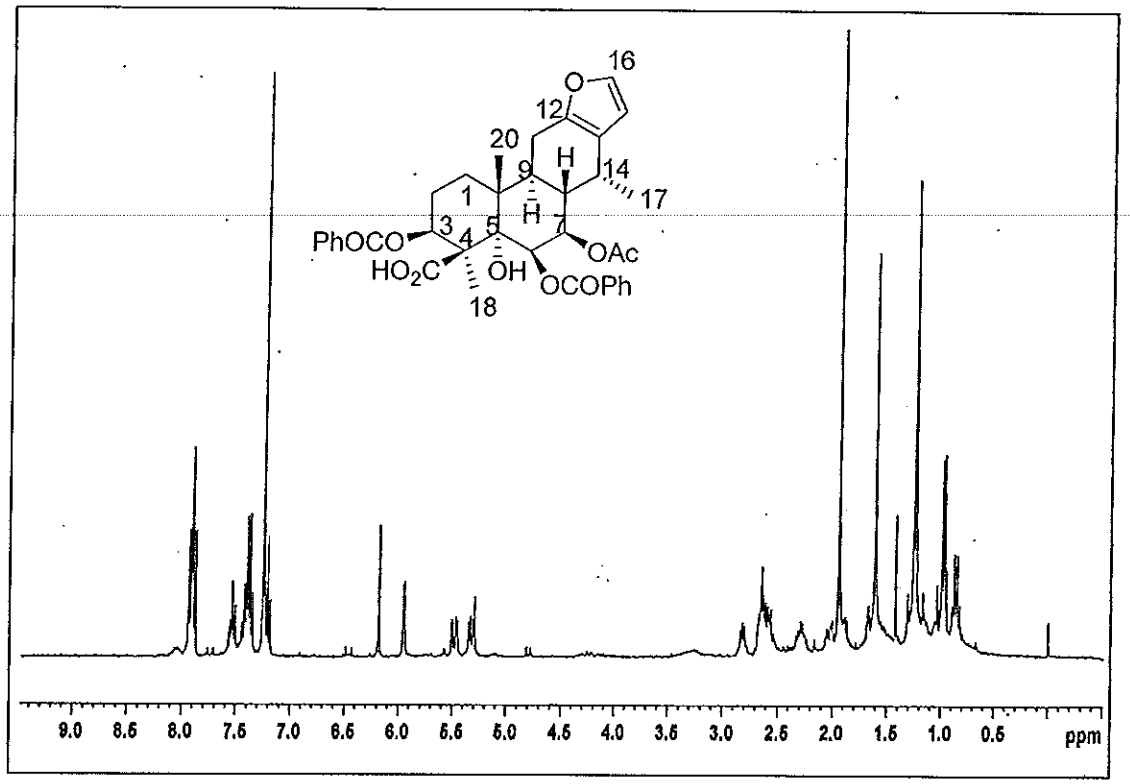

Figure 76 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP9**

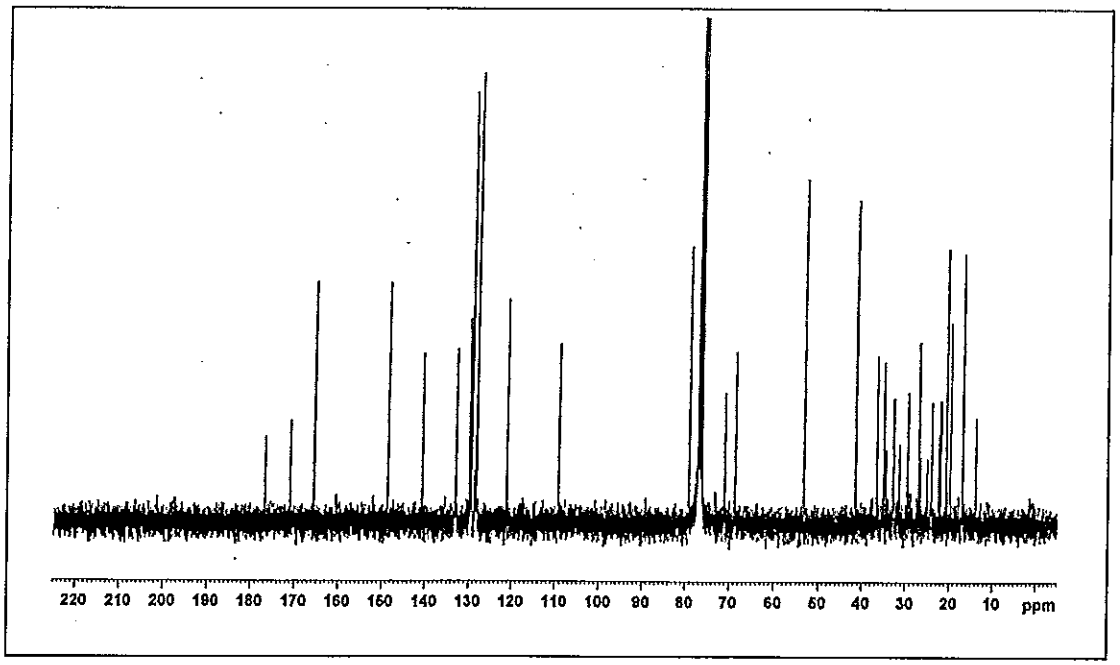

Figure 77 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP9**

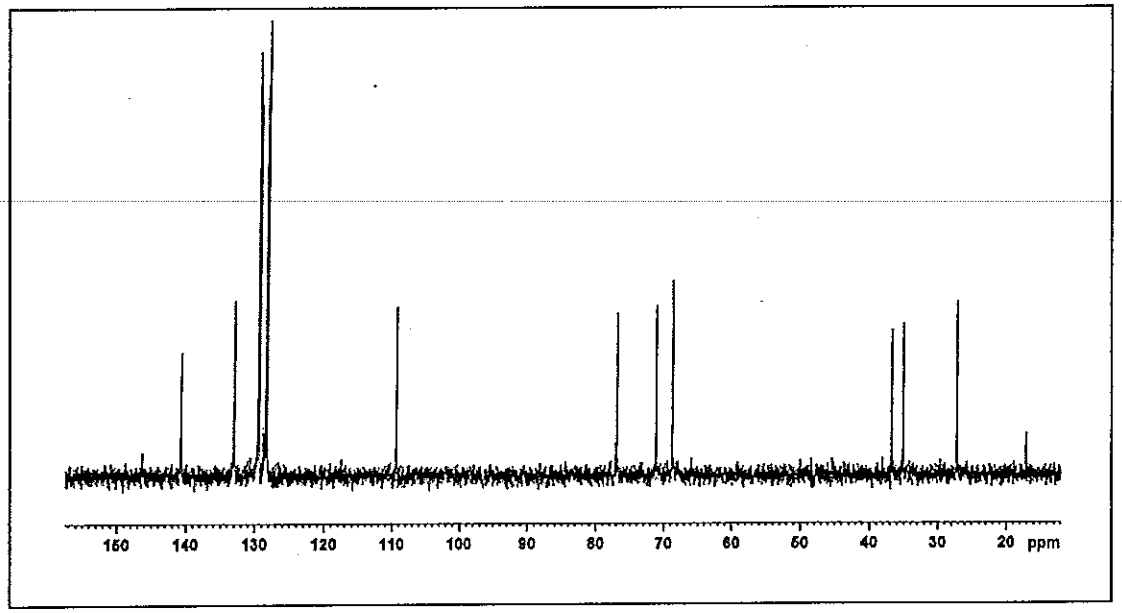

Figure 78 DEPT 90° ($CDCl_3$) spectrum of compound **CP9**

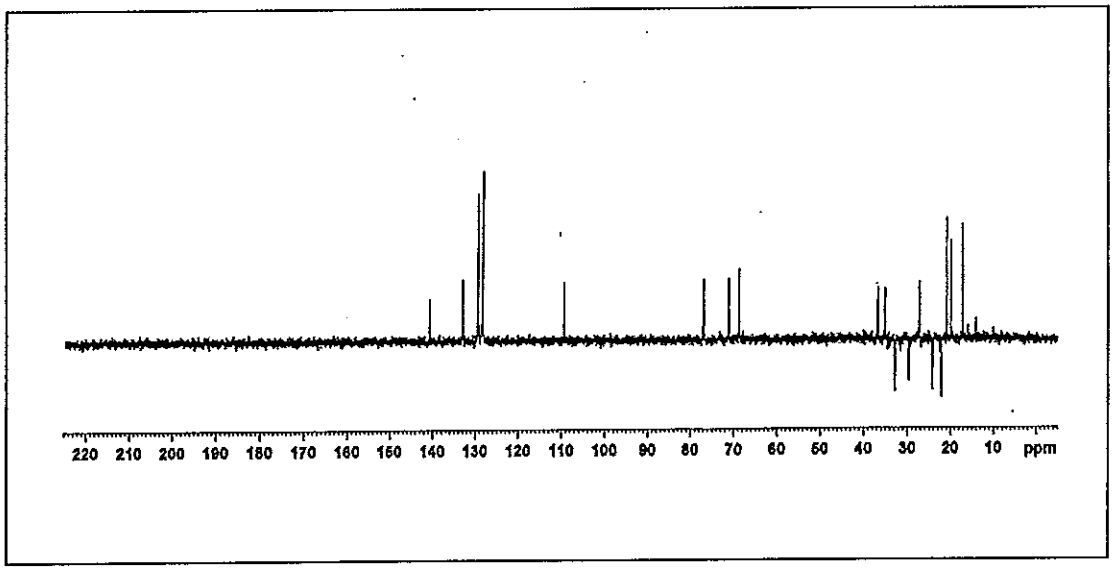

Figure 79 DEPT 135° ($CDCl_3$) spectrum of compound **CP9**

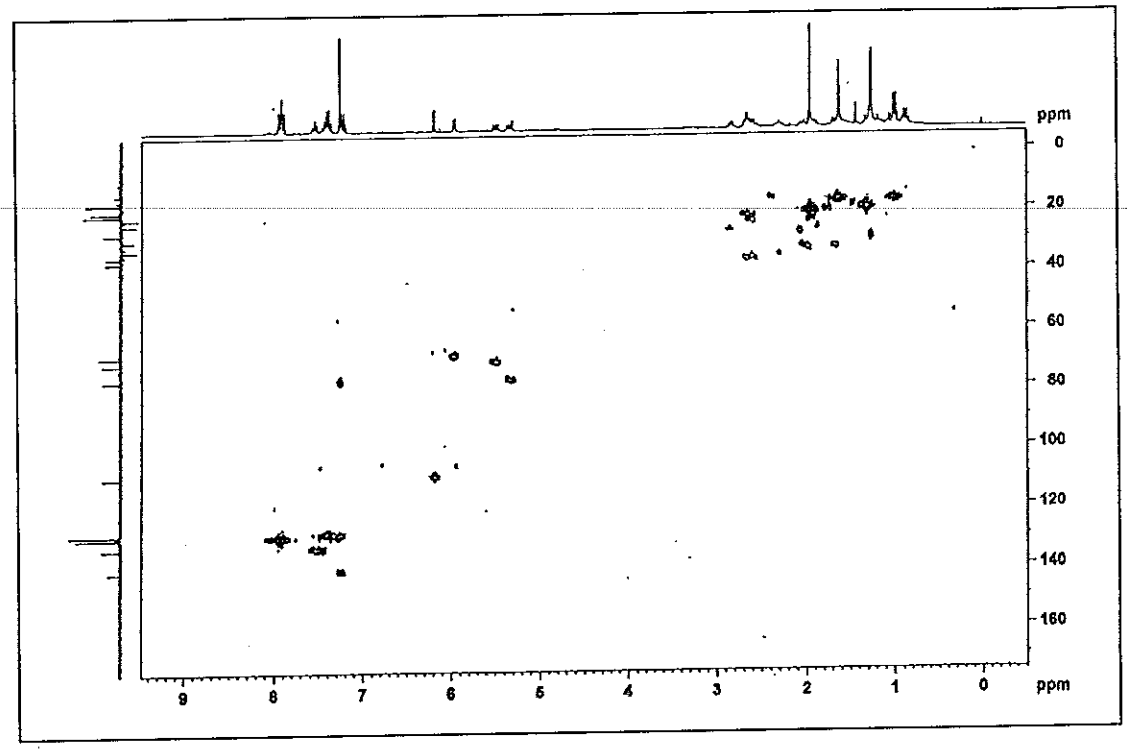

Figure 80 2D HMQC ($CDCl_3$) spectrum of compound **CP9**

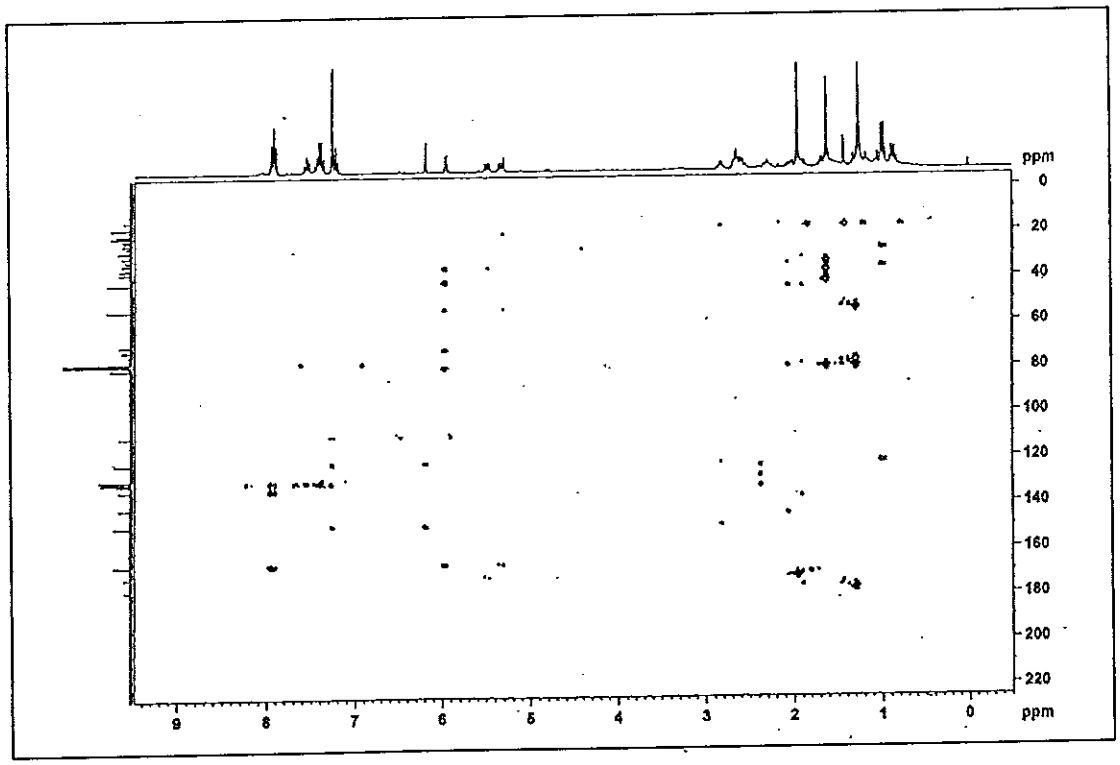

Figure 81 2D HMBC ($CDCl_3$) spectrum of compound **CP9**

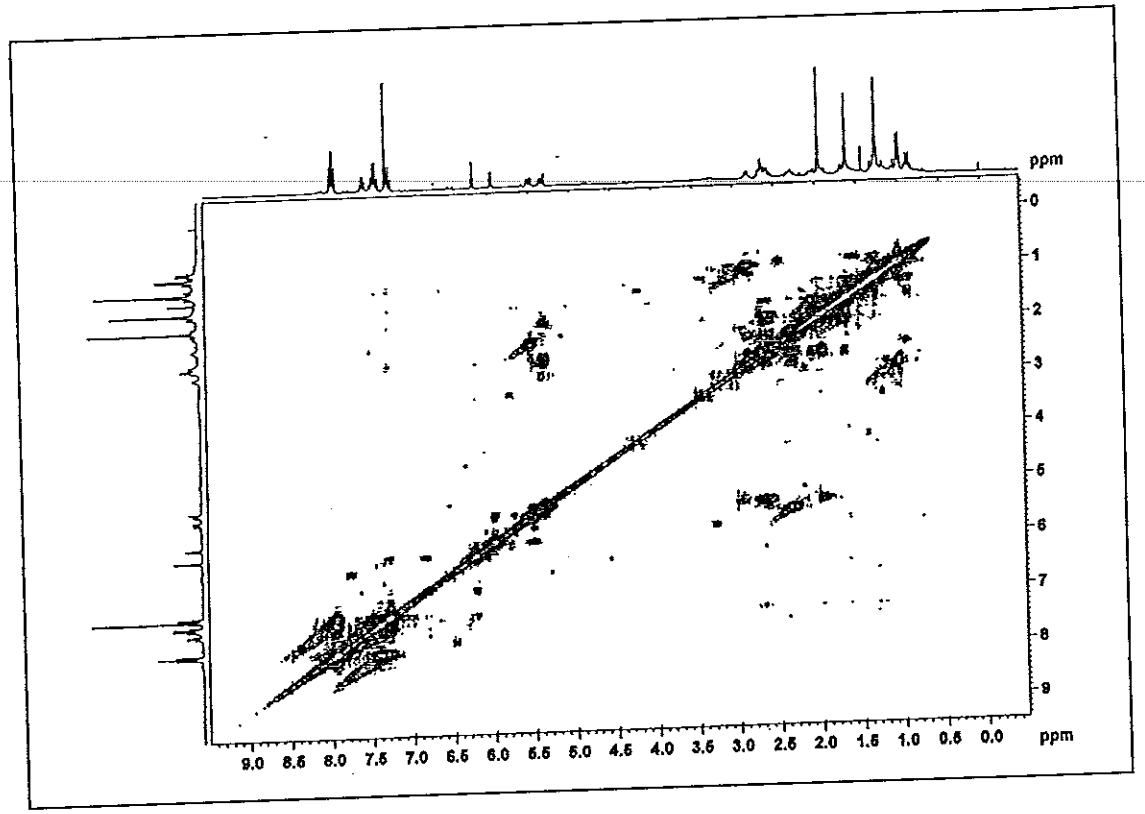

Figure 82 2D COSY ($CDCl_3$) spectrum of compound **CP9**

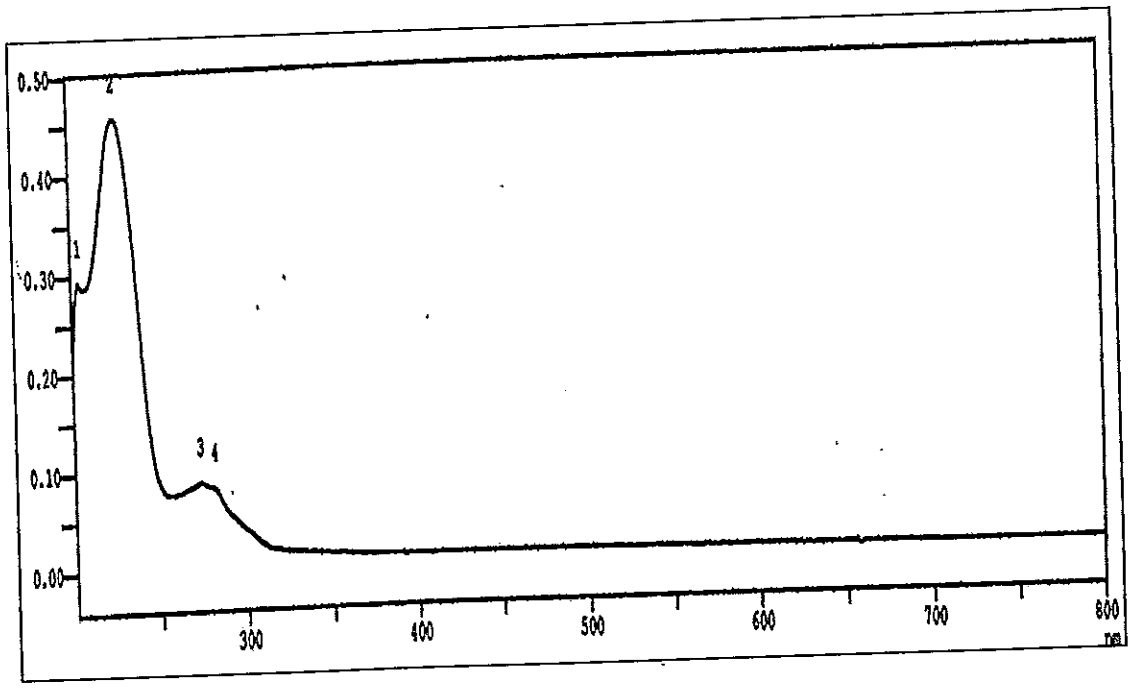

Figure 83 UV (MeOH) spectrum of compound **CP9**

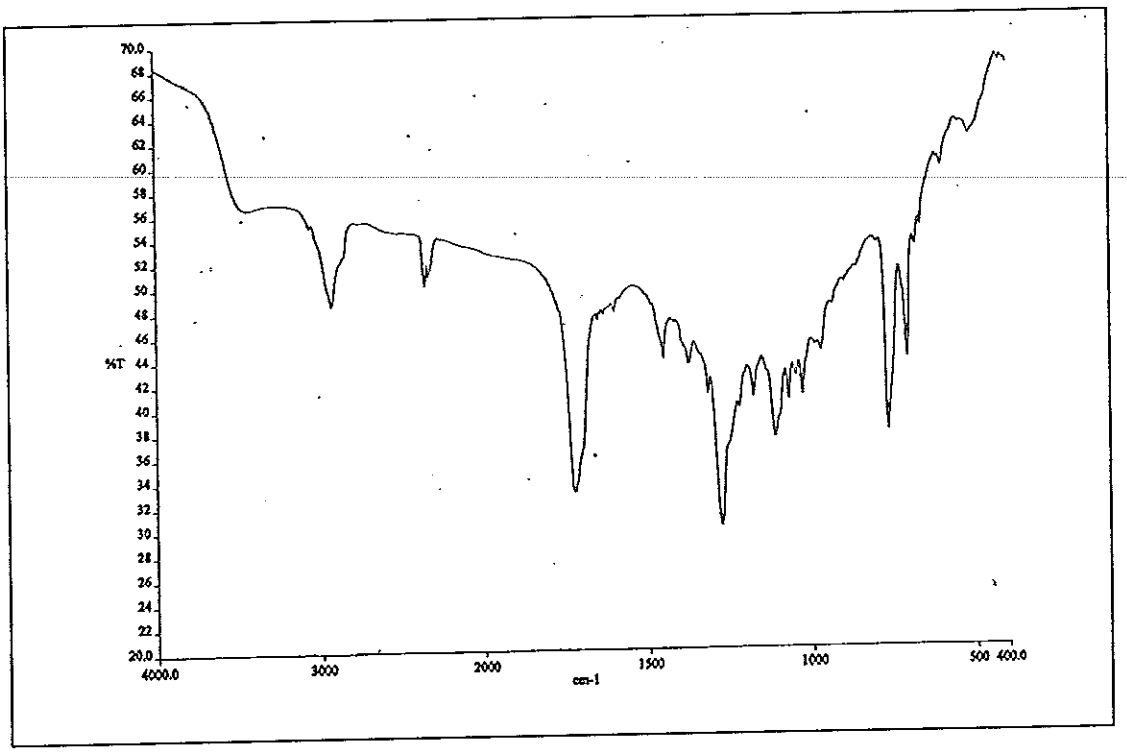

Figure 84 IR (neat) spectrum of compound **CP9**

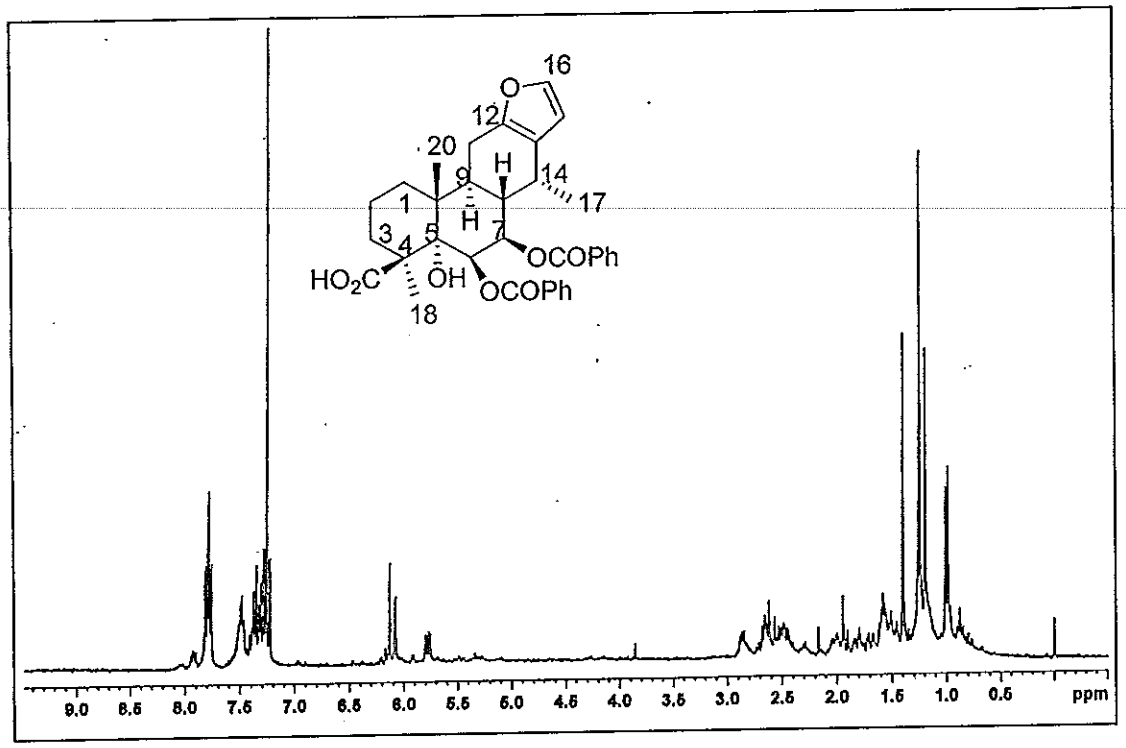

Figure 85 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP10**

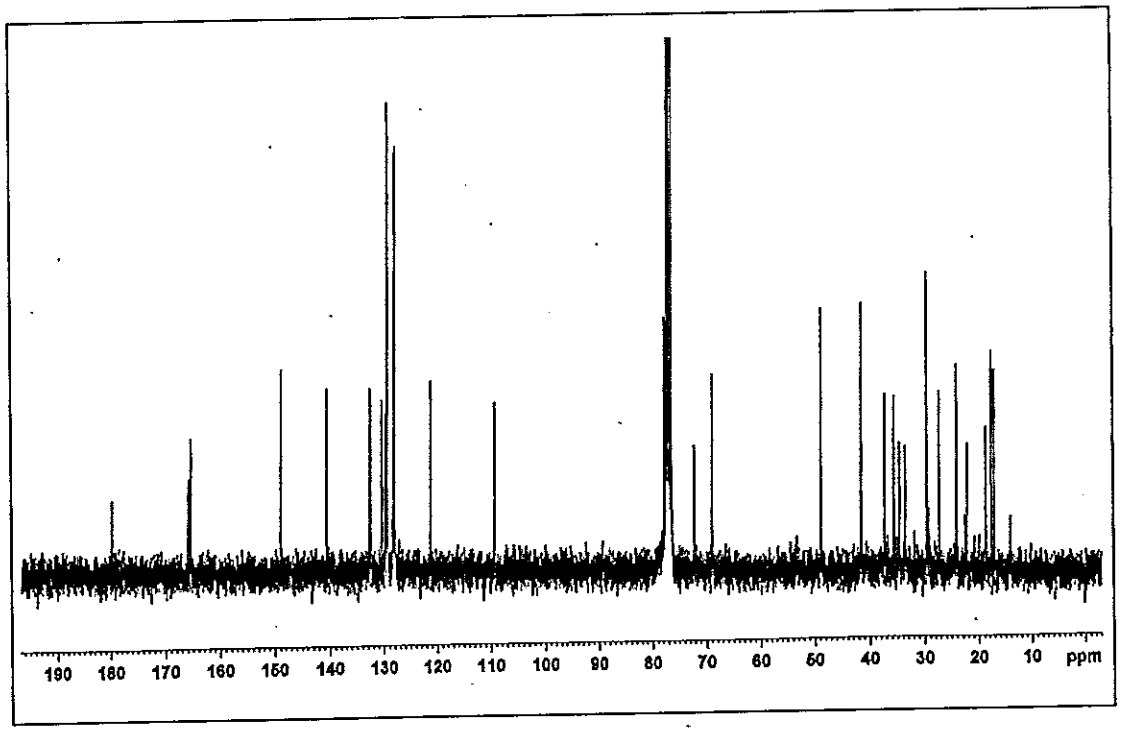

Figure 86 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP10**

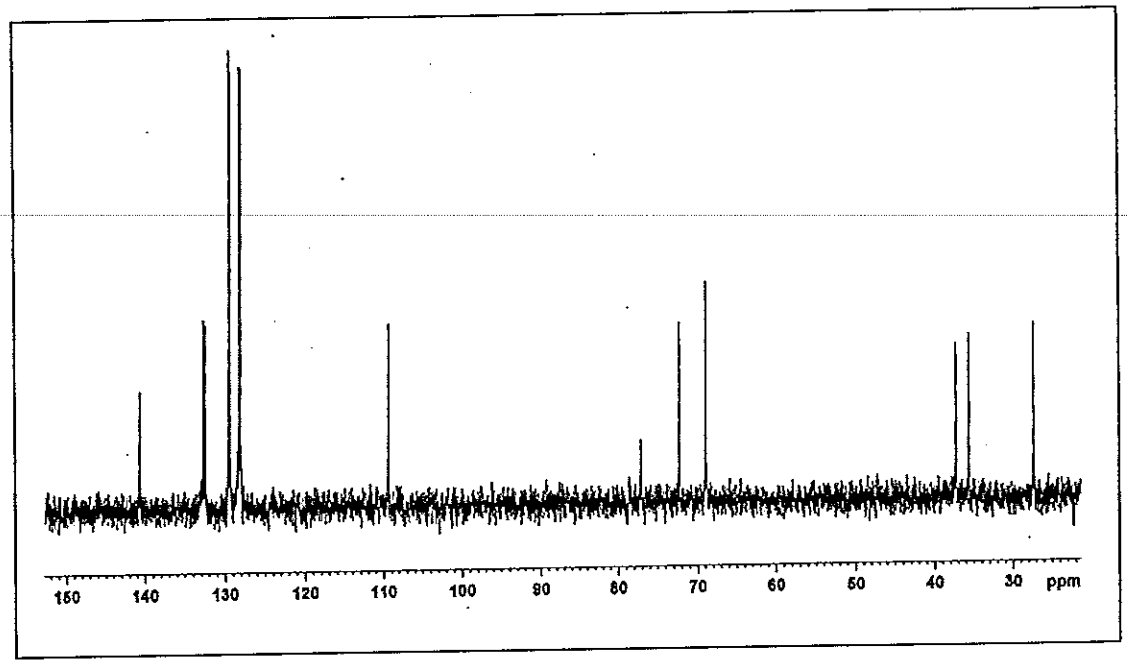

Figure 87 DEPT 90° ($CDCl_3$) spectrum of compound **CP10**

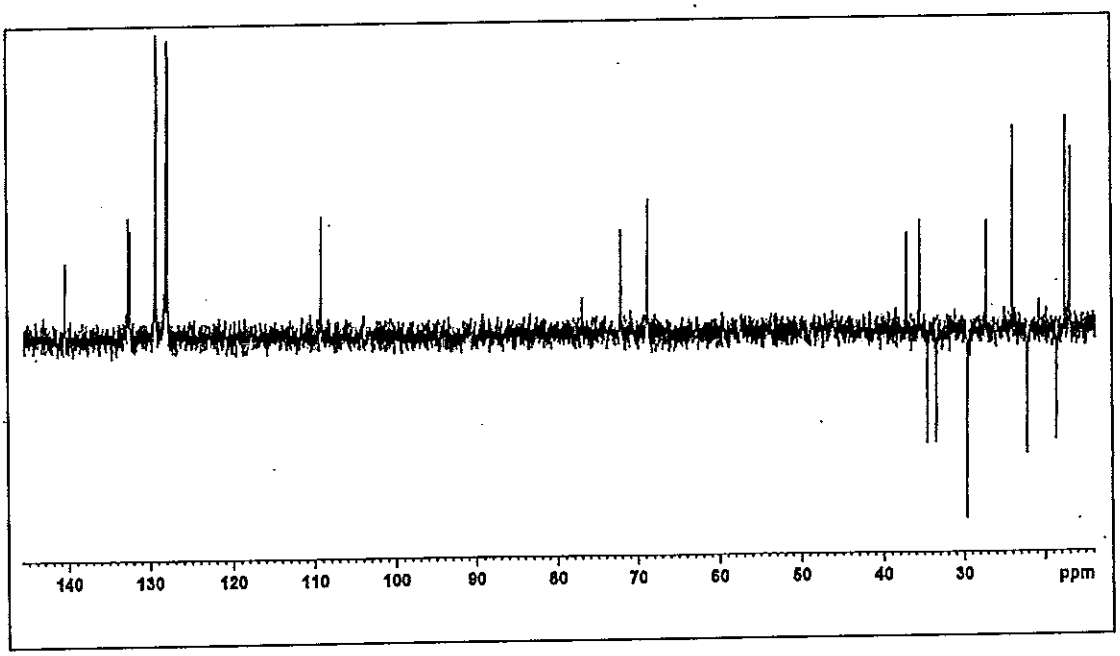

Figure 88 DEPT 135° ($CDCl_3$) spectrum of compound **CP10**

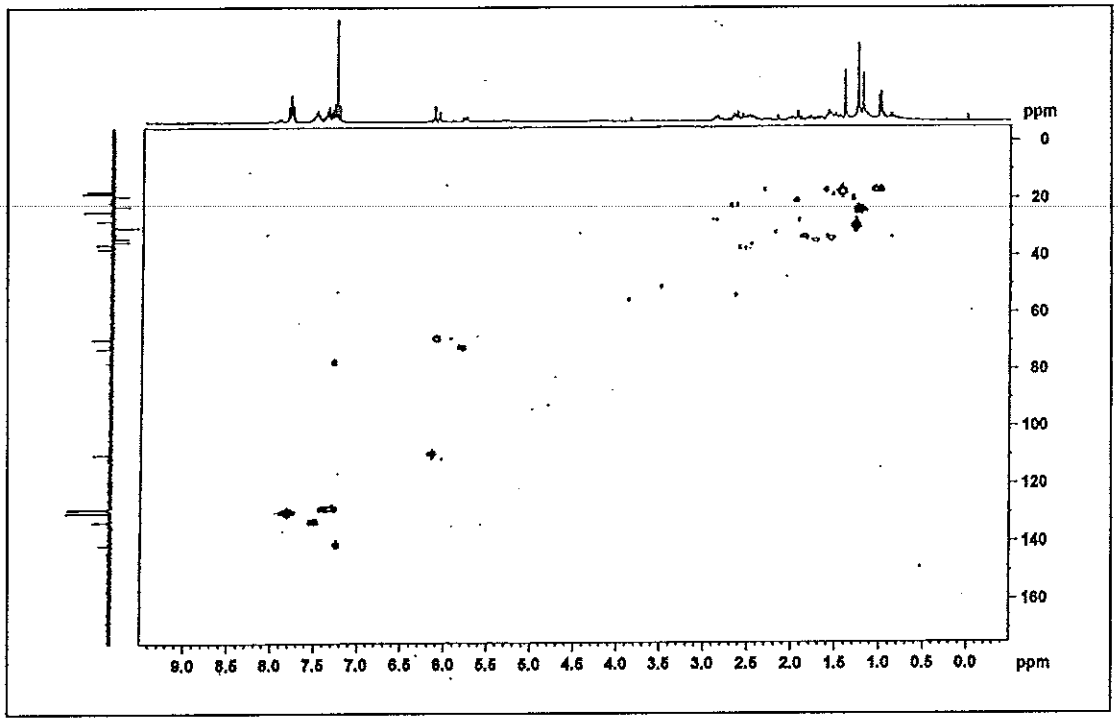

Figure 89 2D HMQC ($CDCl_3$) spectrum of compound **CP10**

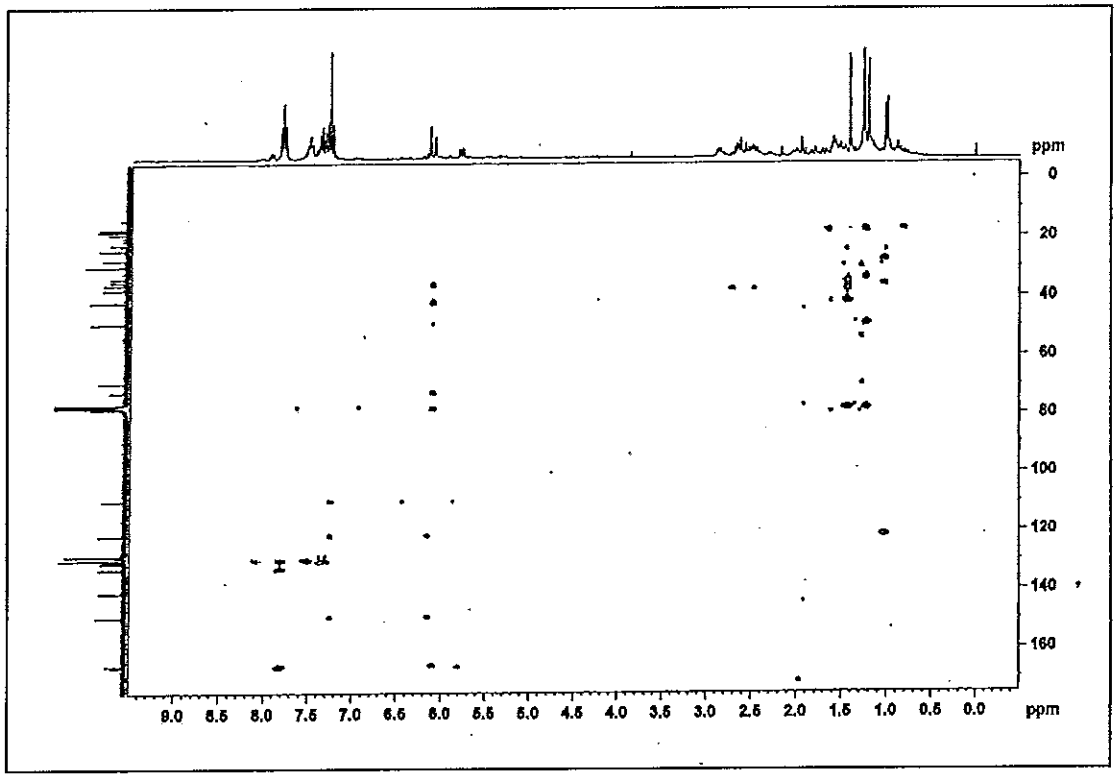

Figure 90 2D HMBC ($CDCl_3$) spectrum of compound **CP10**

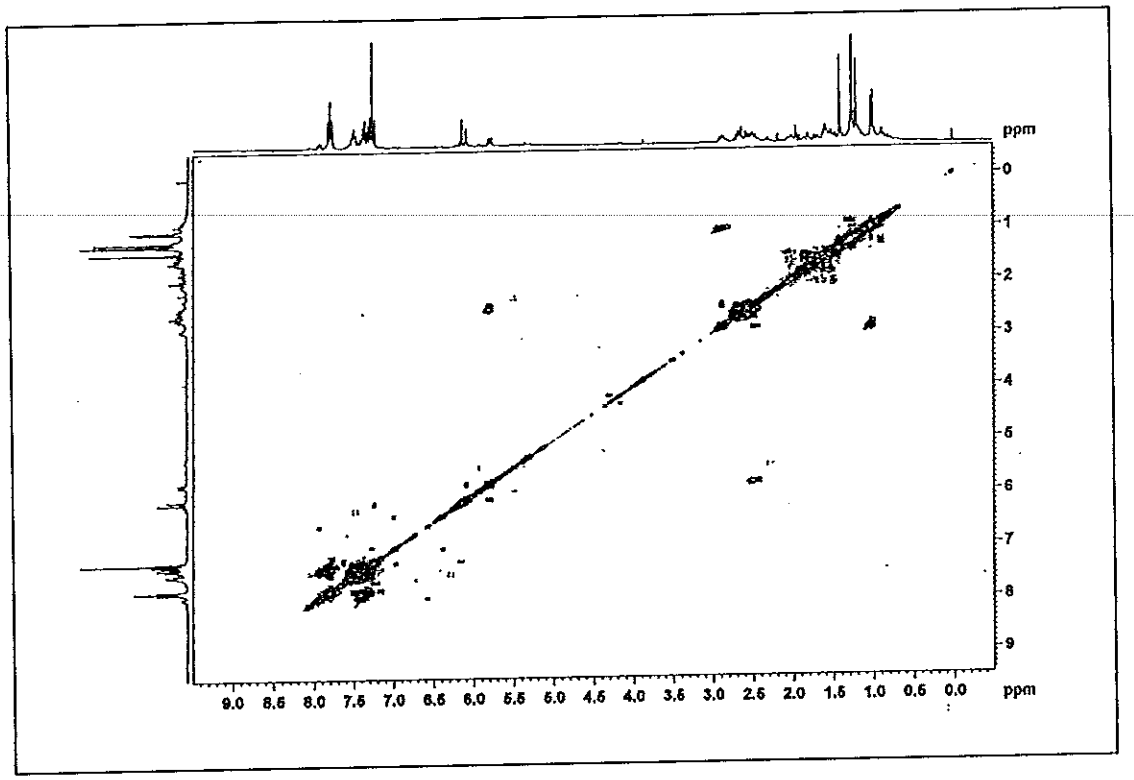

Figure 91 2D COSY ($CDCl_3$) spectrum of compound **CP10**

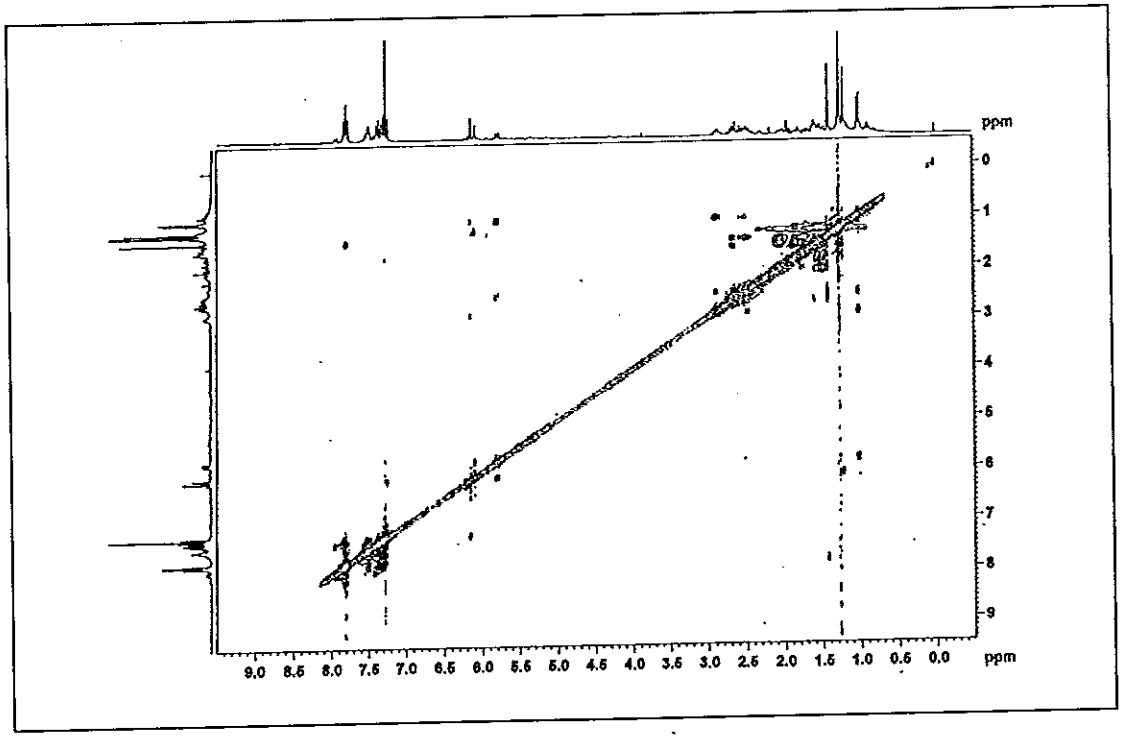

Figure 92 2D NOESY ($CDCl_3$) spectrum of compound **CP10**

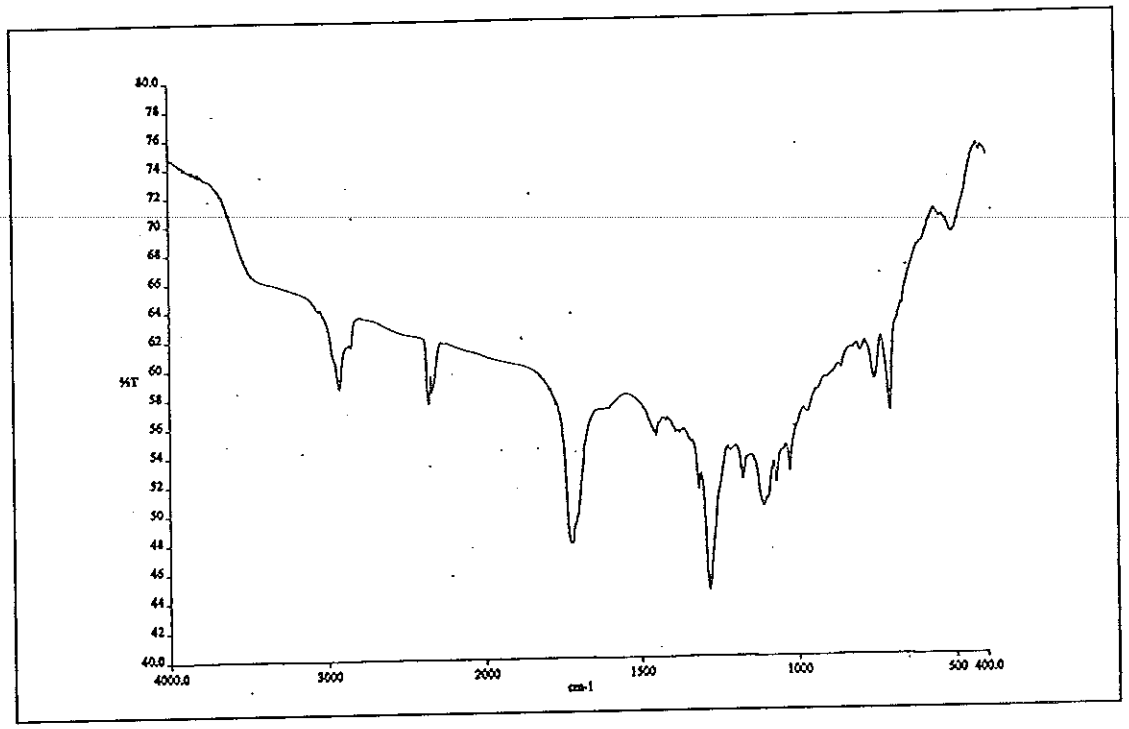

Figure 93 IR (neat) spectrum of compound **CP10**

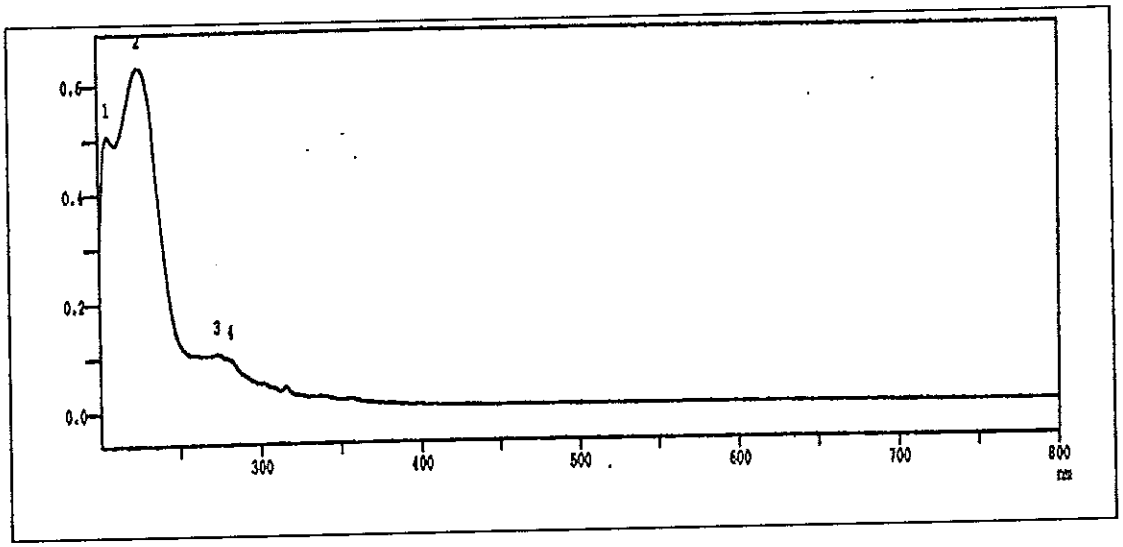

Figure 94 UV (MeOH) spectrum of compound **CP10**

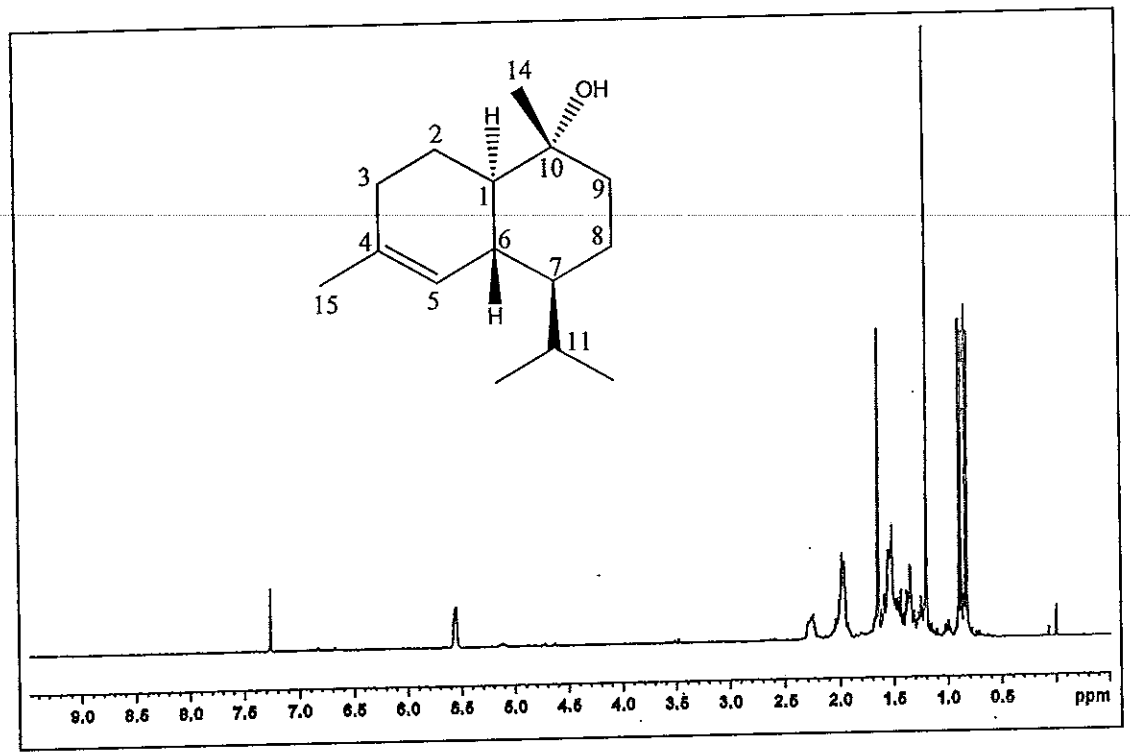

Figure 95 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP11**

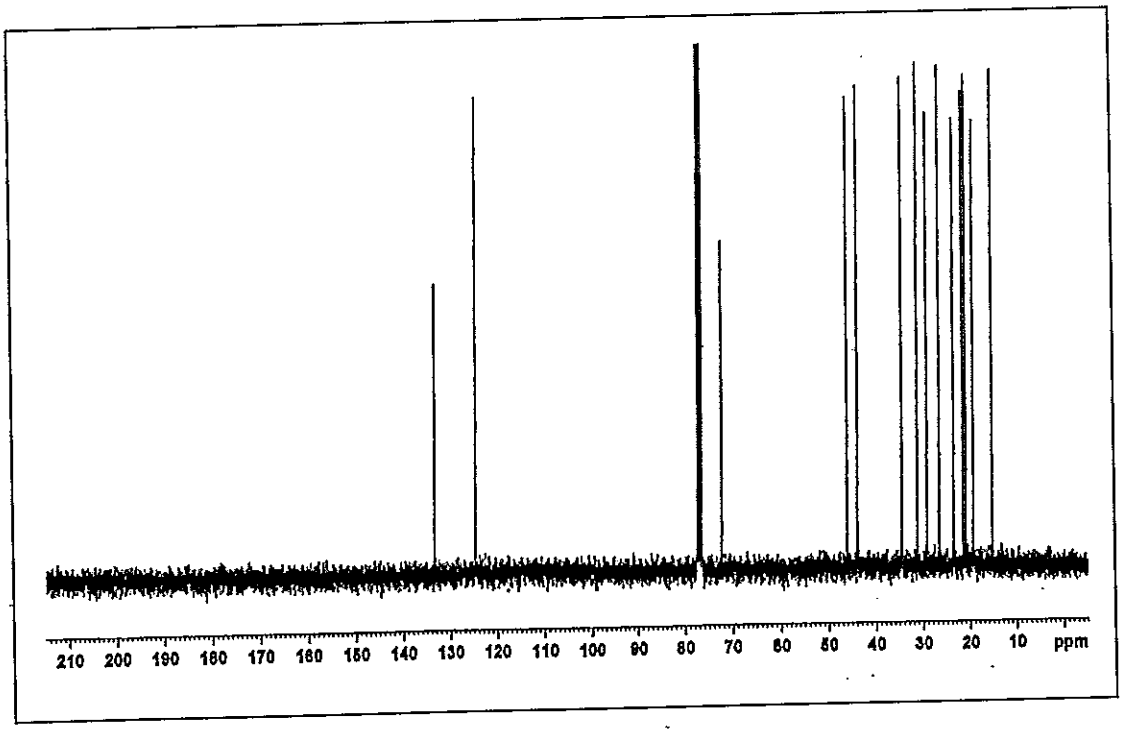

Figure 96 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP11**

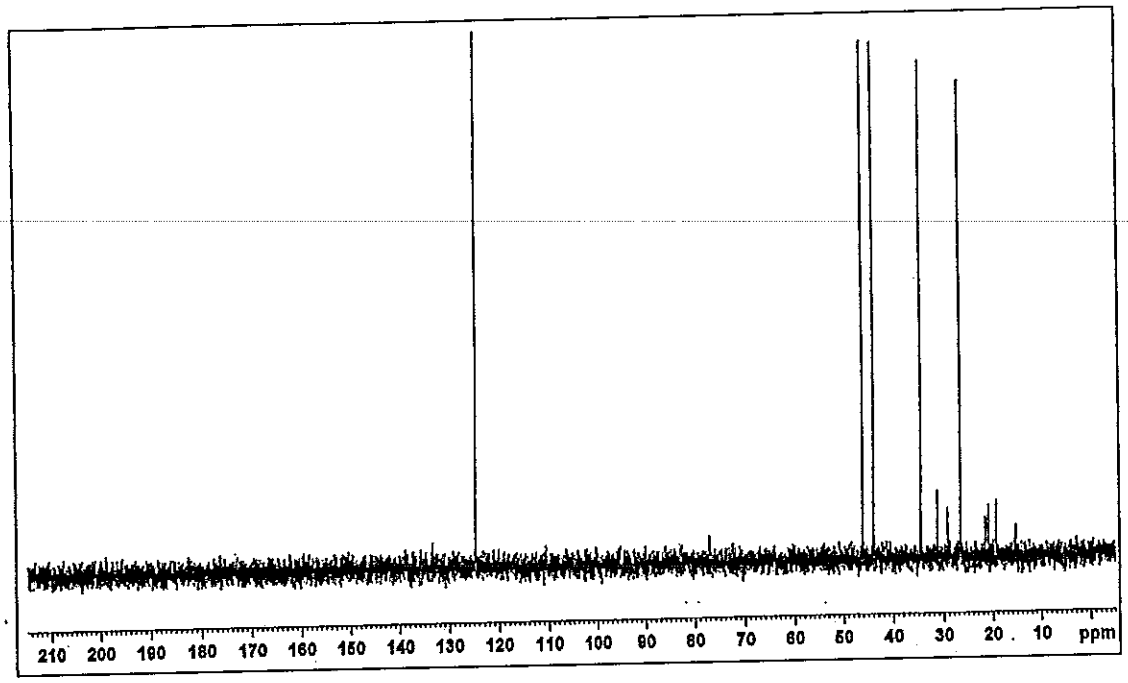

Figure 97 DEPT 90° ($CDCl_3$) spectrum of compound **CP11**

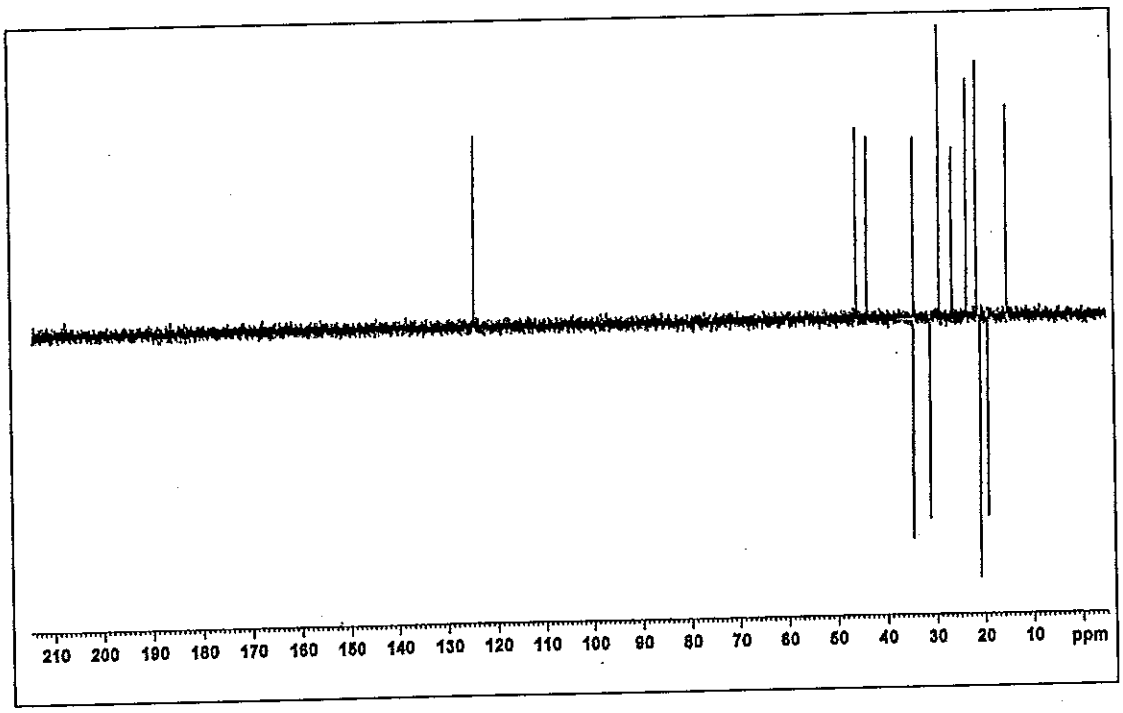

Figure 98 DEPT 135° ($CDCl_3$) spectrum of compound **CP11**

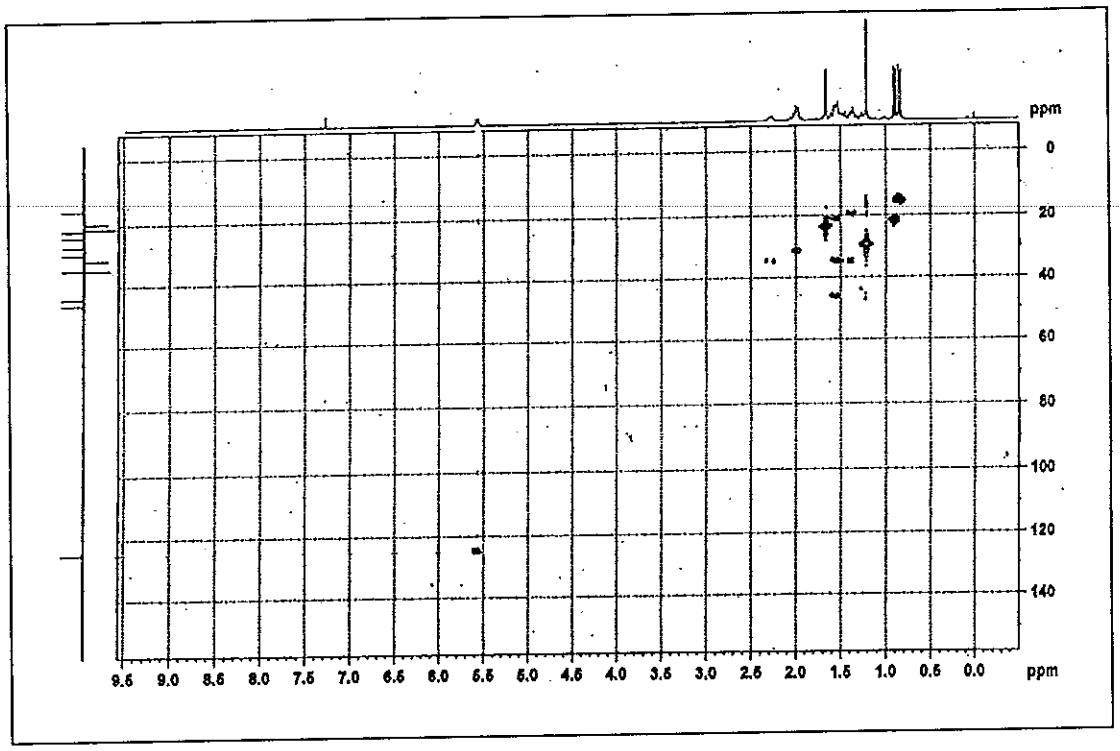

Figure 99 2D COSY ($CDCl_3$) spectrum of compound **CP11**

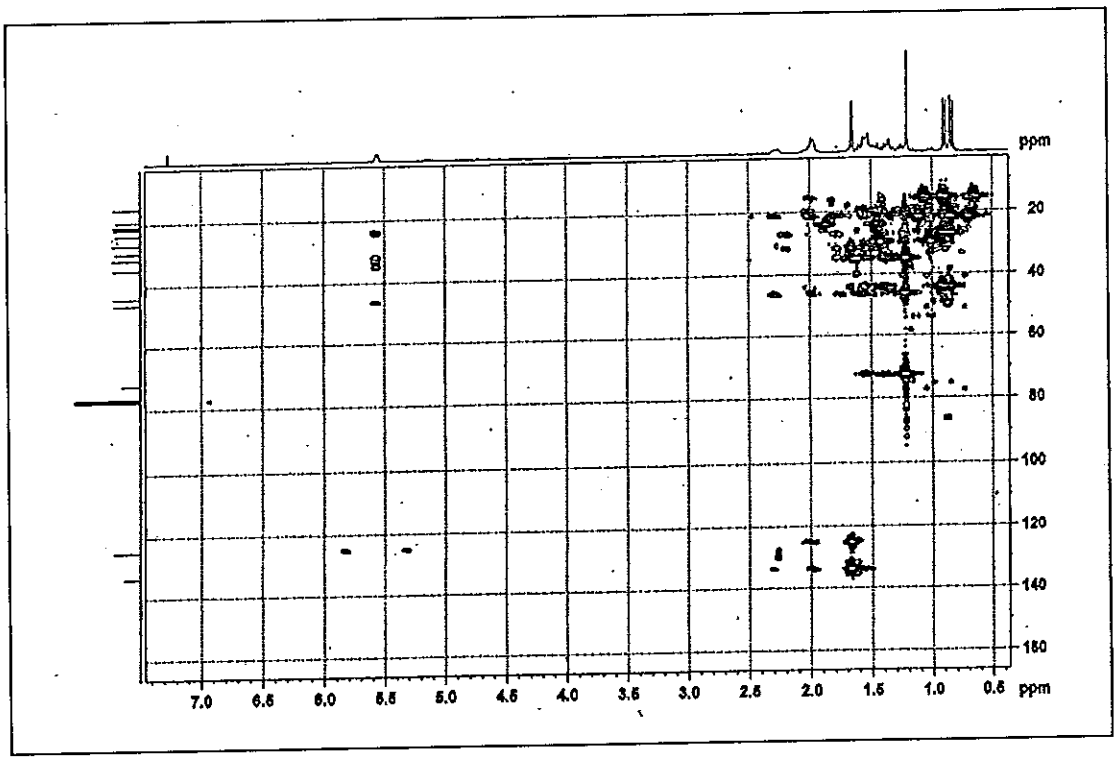

Figure 100 2D HMBC ($CDCl_3$) spectrum of compound **CP11**

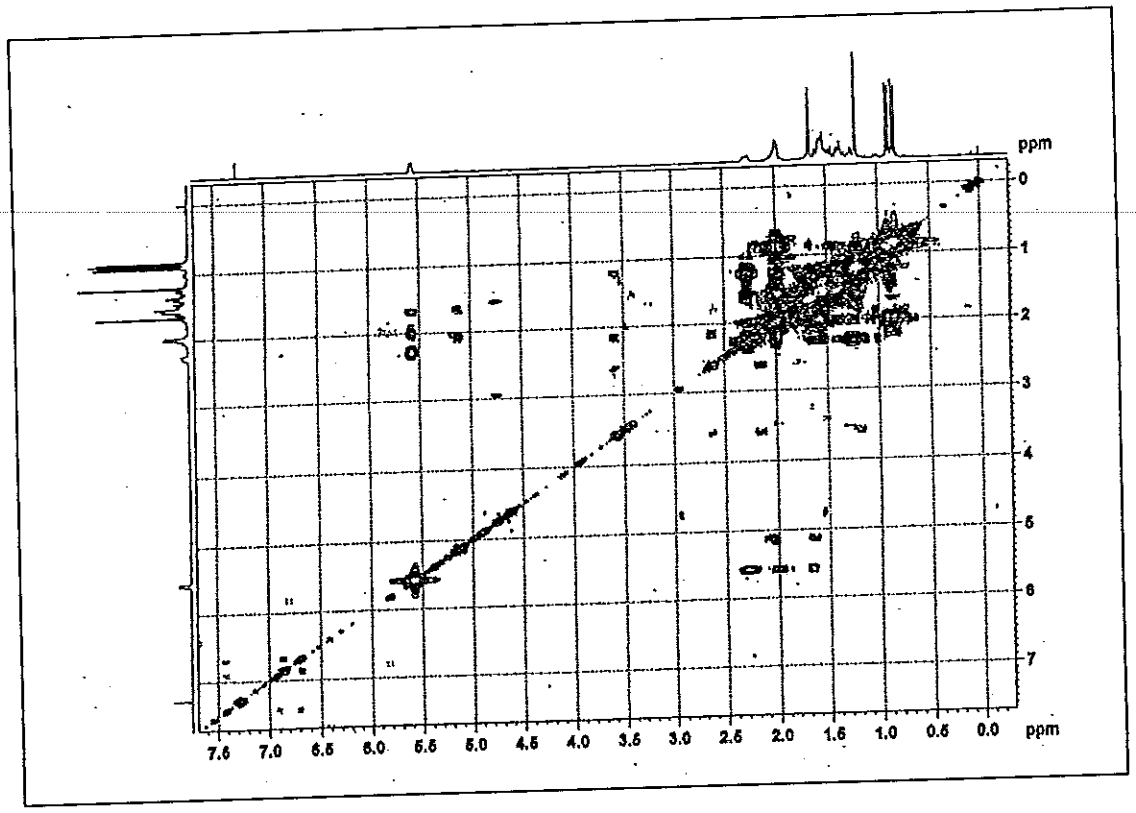

Figure 101 2D COSY ($CDCl_3$) spectrum of compound **CP11**

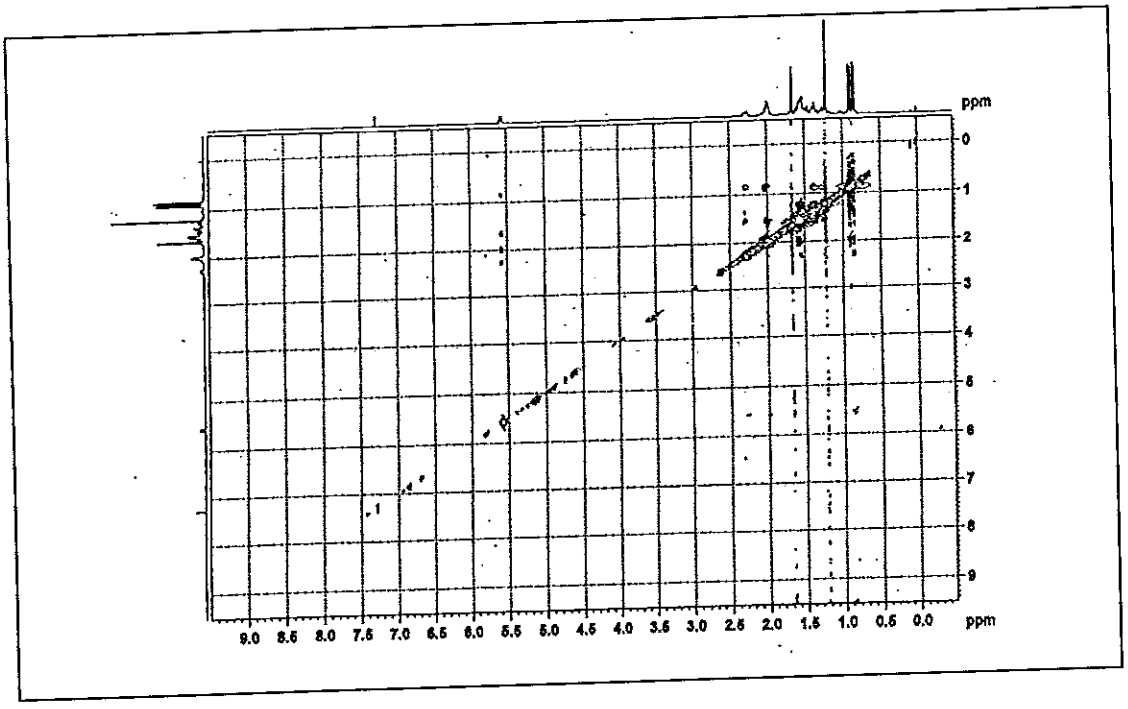

Figure 102 2D NOESY ($CDCl_3$) spectrum of compound **CP11**

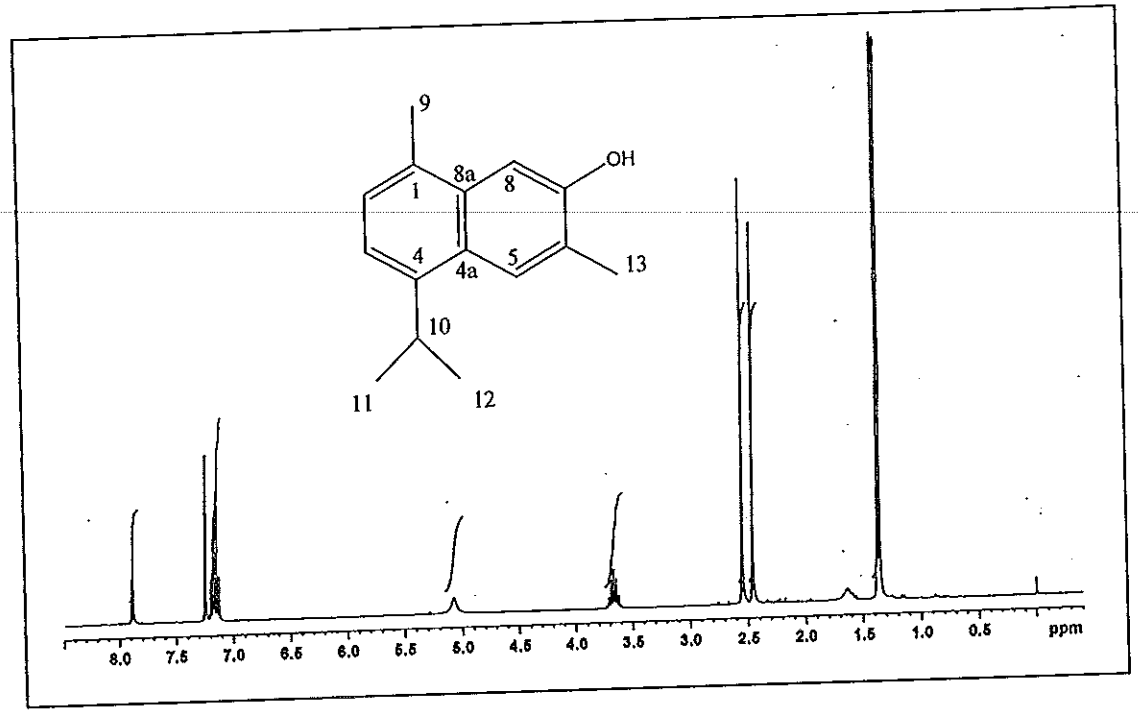

Figure 103 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP12**

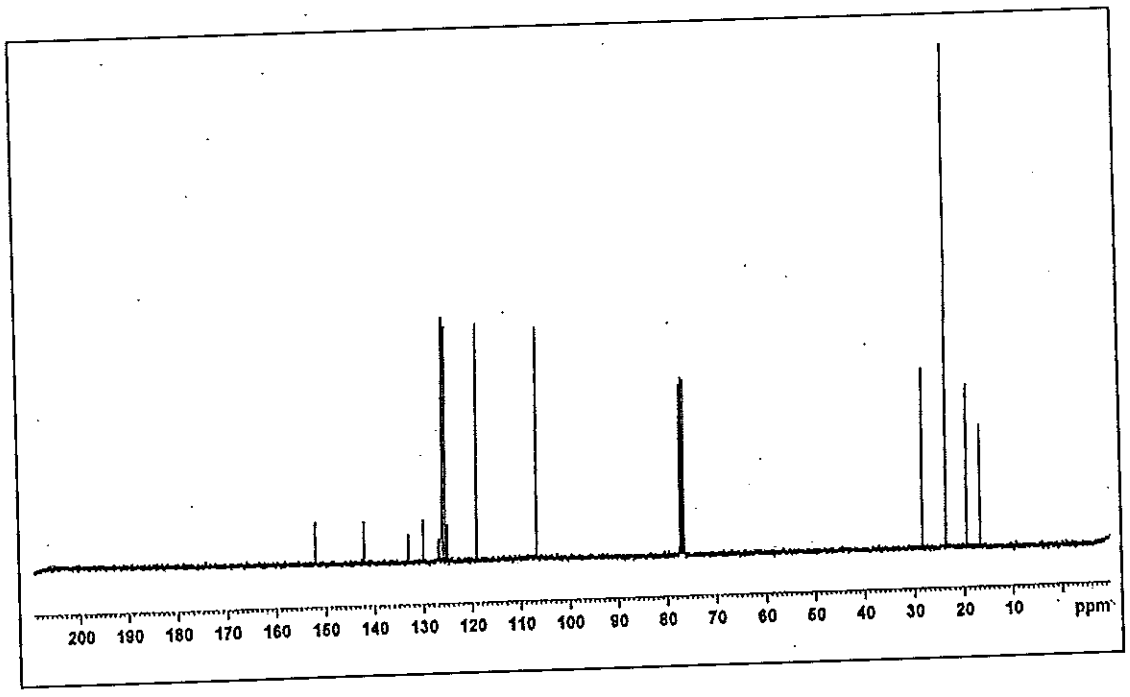

Figure 104 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP12**

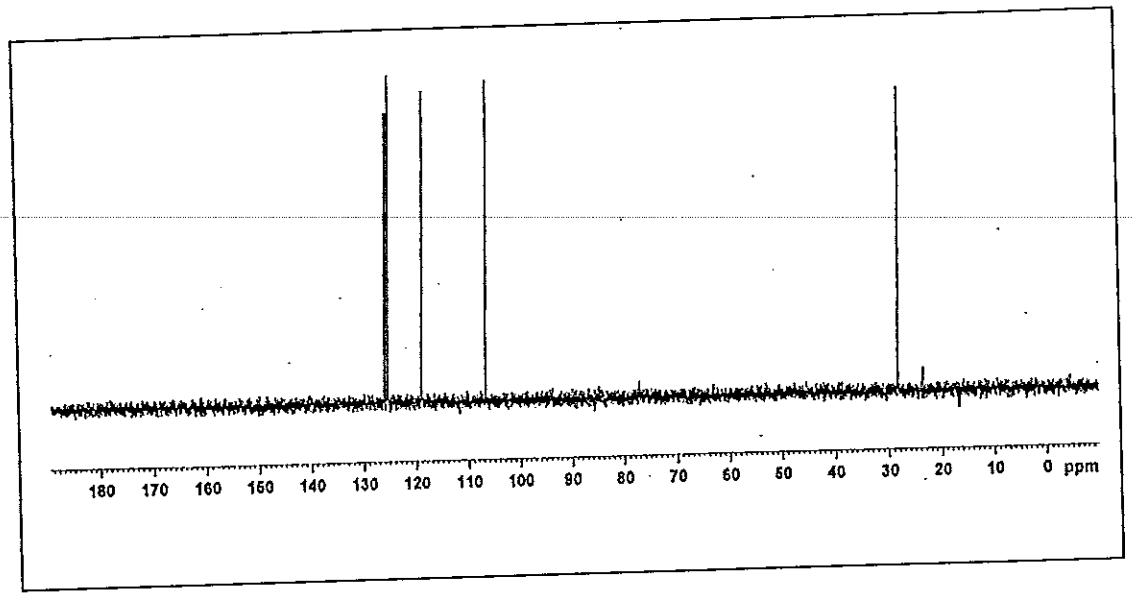

Figure 105 DEPT 90° ($CDCl_3$) spectrum of compound **CP12**

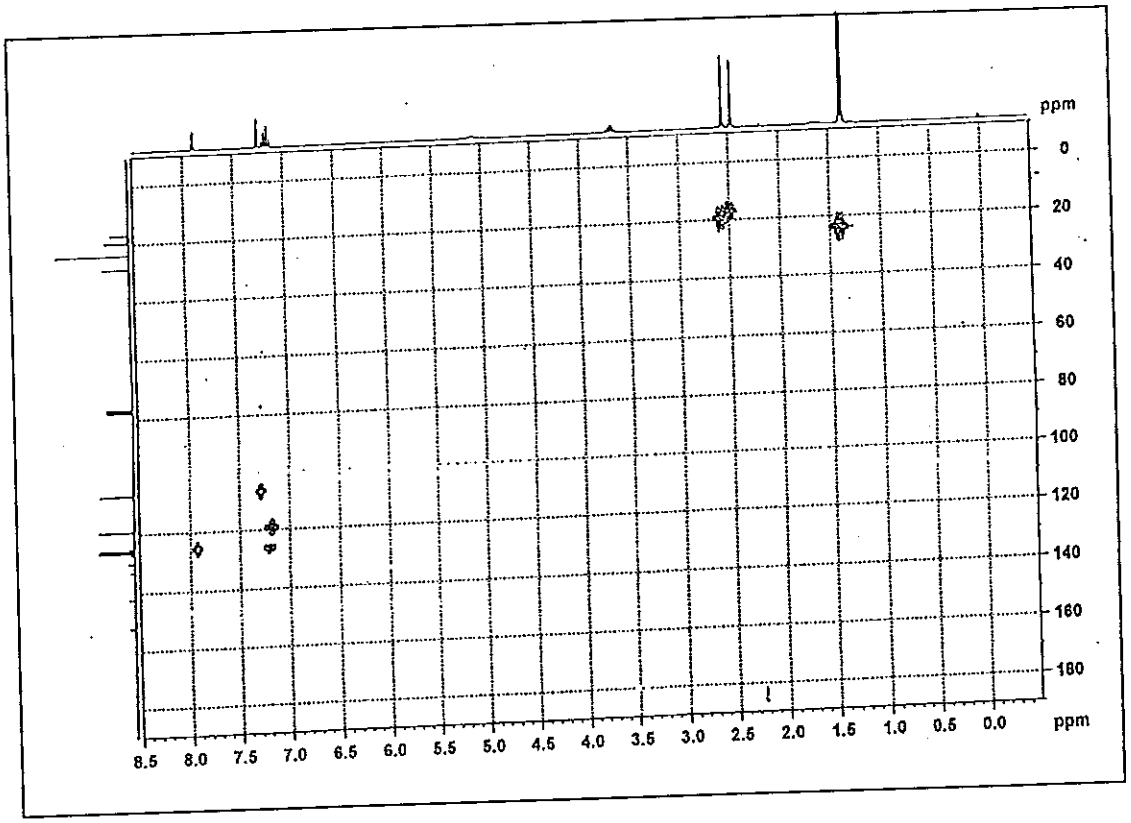

Figure 106 2D HMQC ($CDCl_3$) spectrum of compound **CP12**

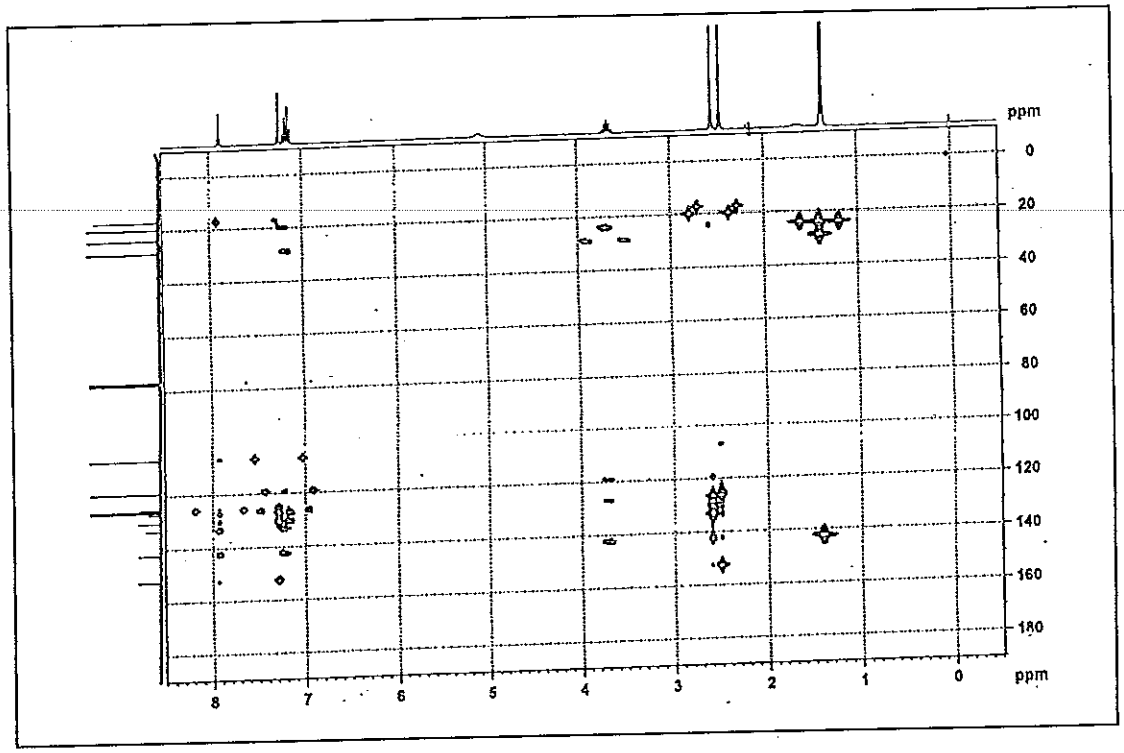

Figure 107 2D HMBC ($CDCl_3$) spectrum of compound **CP12**

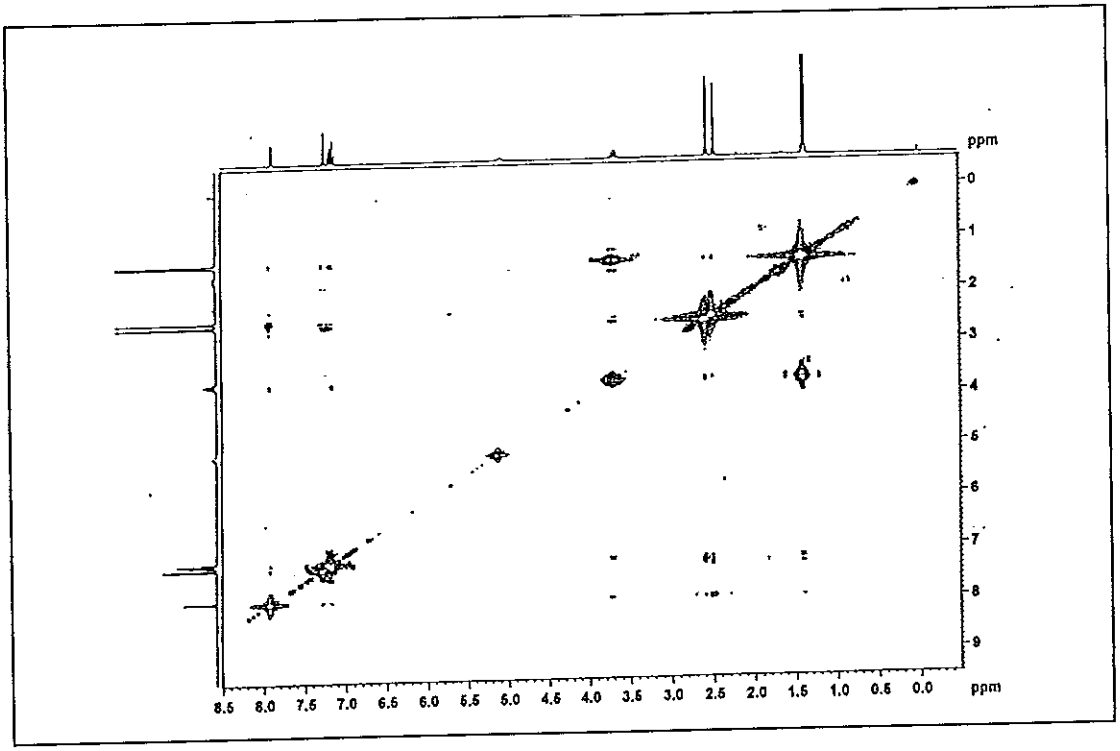

Figure 108 2D COSY ($CDCl_3$) spectrum of compound **CP12**

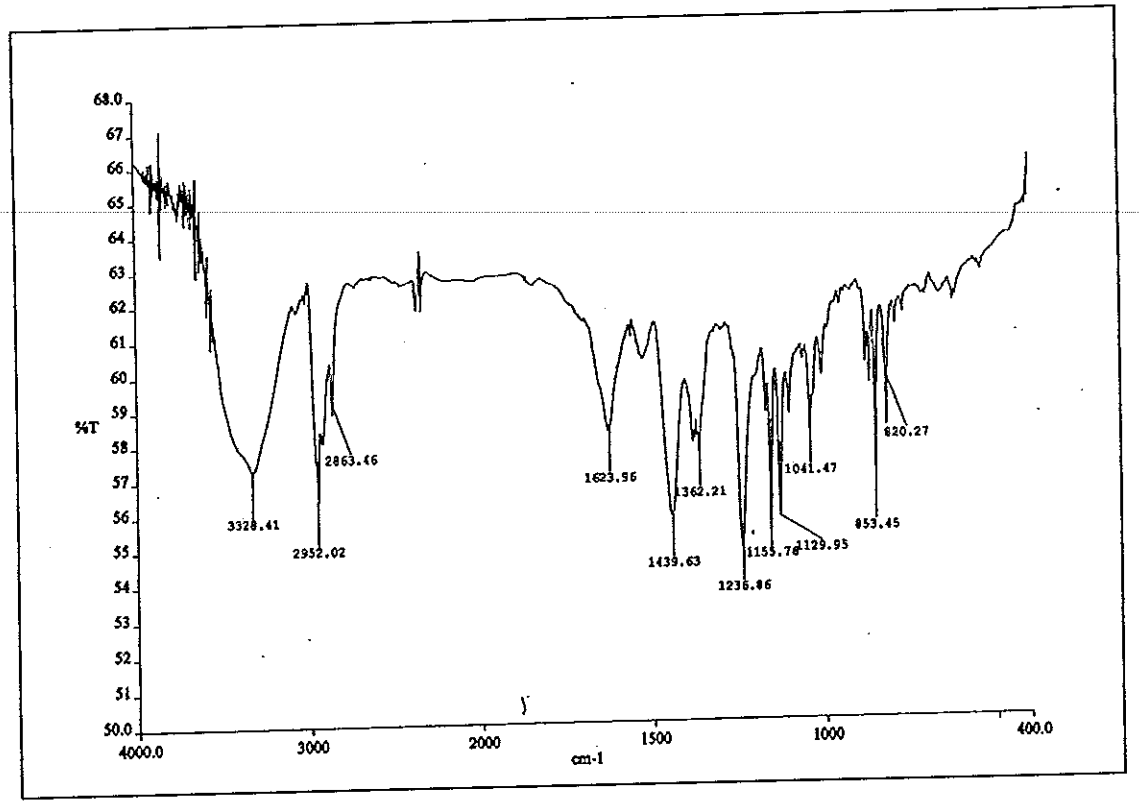

Figure 109 IR (neat) spectrum of compound **CP12**

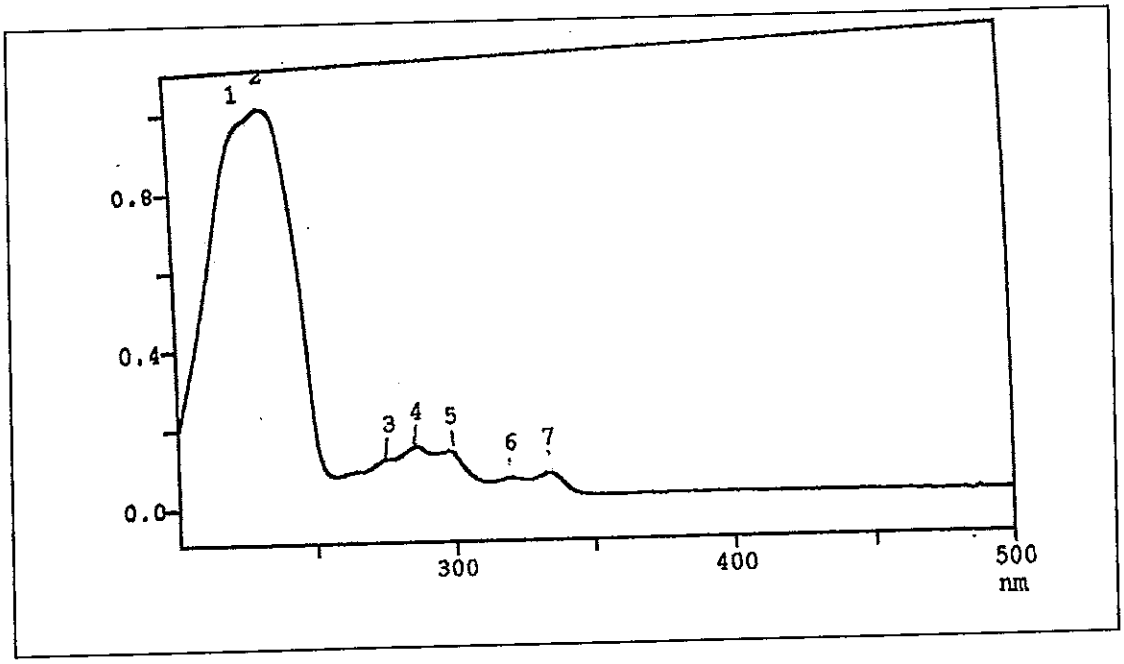

Figure 110 UV (MeOH) spectrum of compound **CP12**

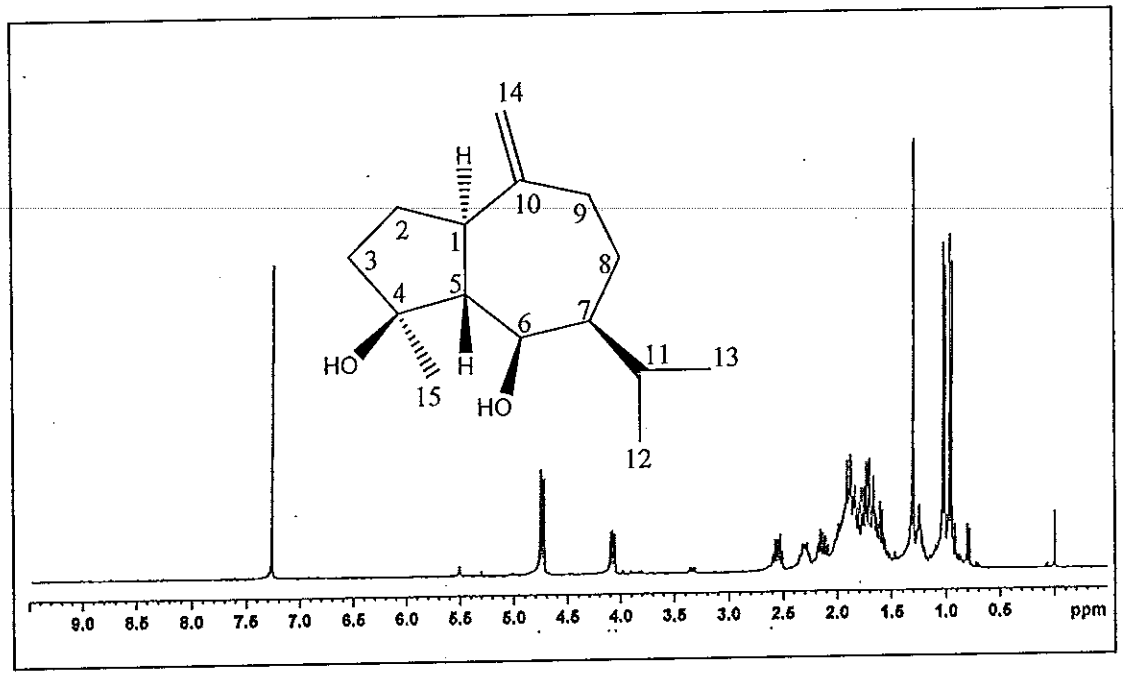

Figure 111 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP13**

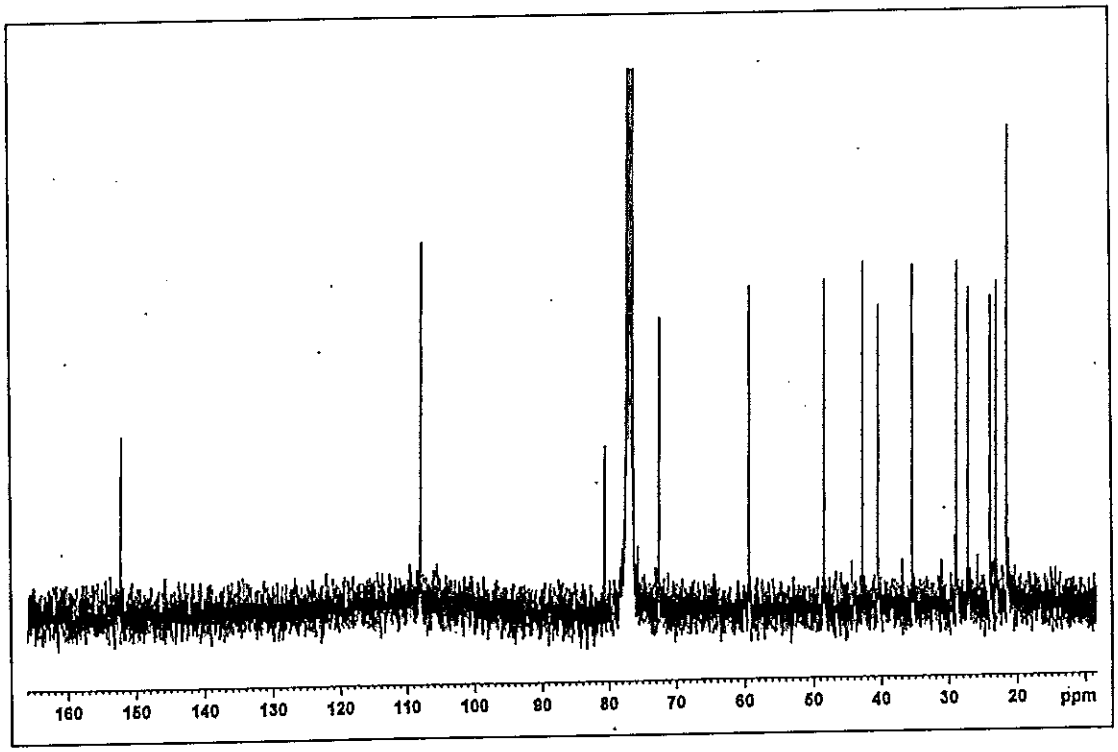

Figure 112 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP13**

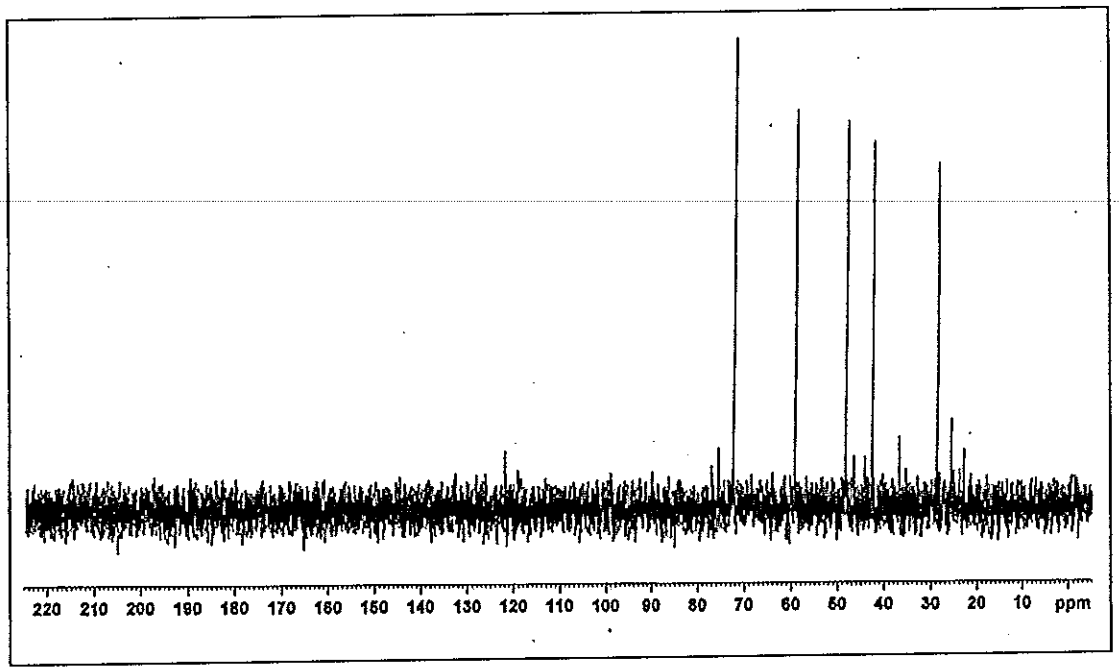

Figure 113 DEPT 90° ($CDCl_3$) spectrum of compound **CP13**

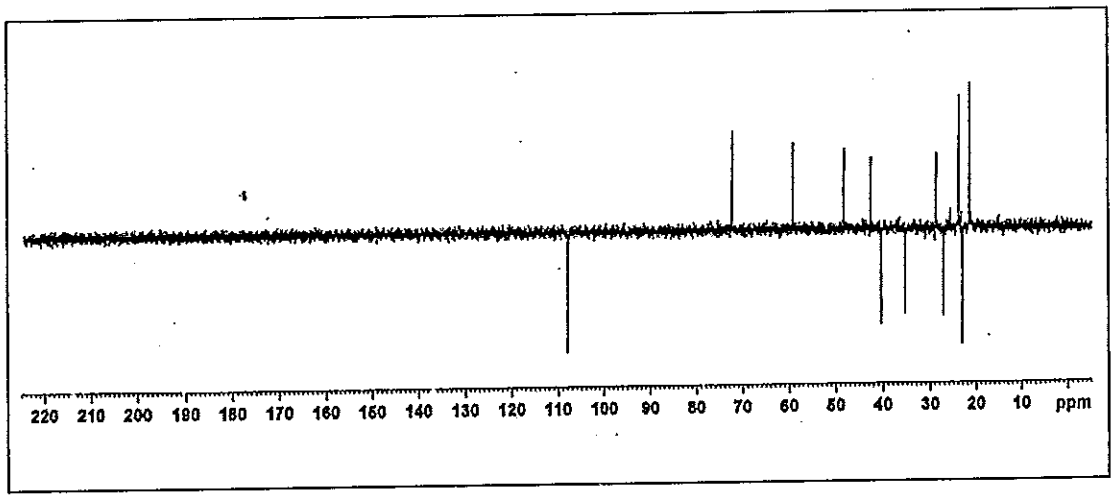

Figure 114 DEPT 135° ($CDCl_3$) spectrum of compound **CP13**

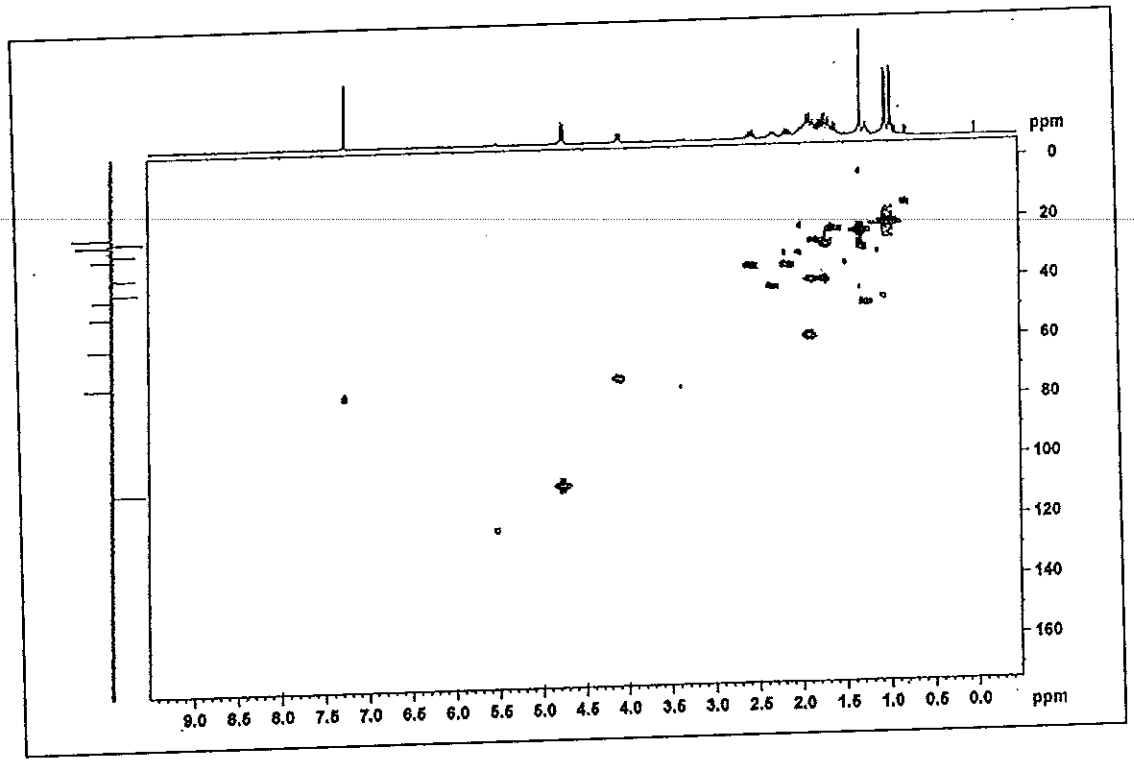

Figure 115 2D HMQC ($CDCl_3$) spectrum of compound **CP13**

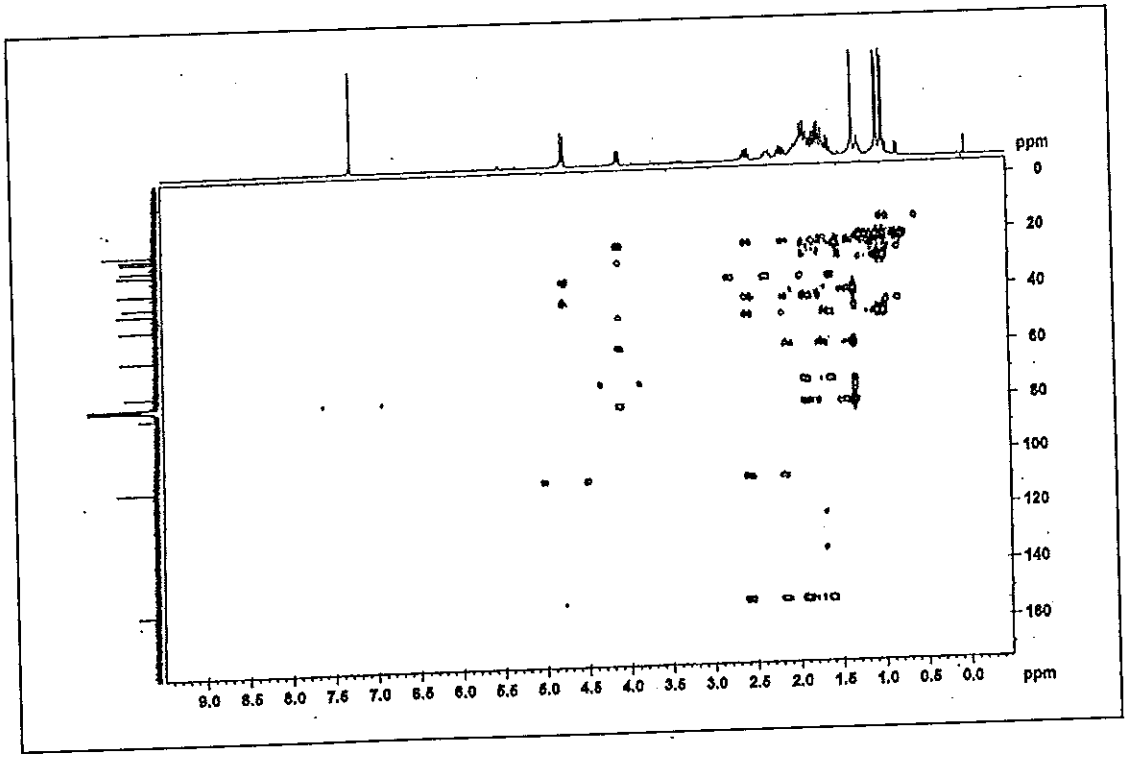

Figure 116 2D HMBC ($CDCl_3$) spectrum of compound **CP13**

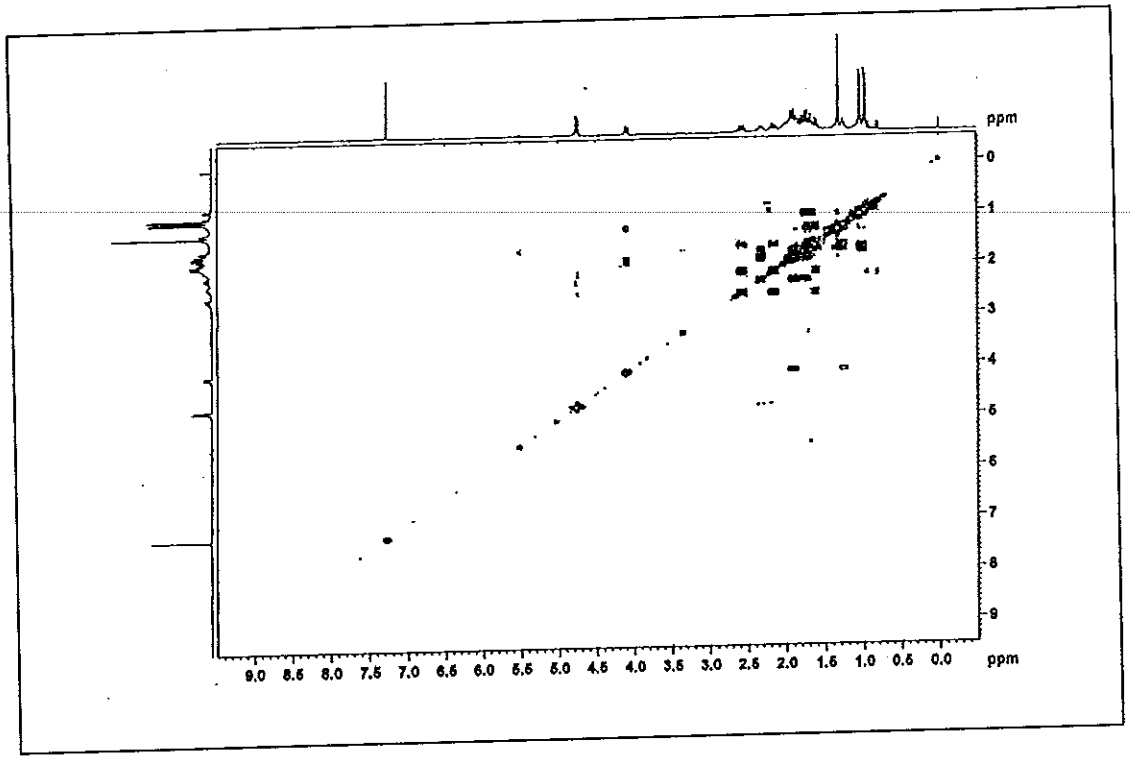

Figure 117 2D COSY ($CDCl_3$) spectrum of compound **CP13**

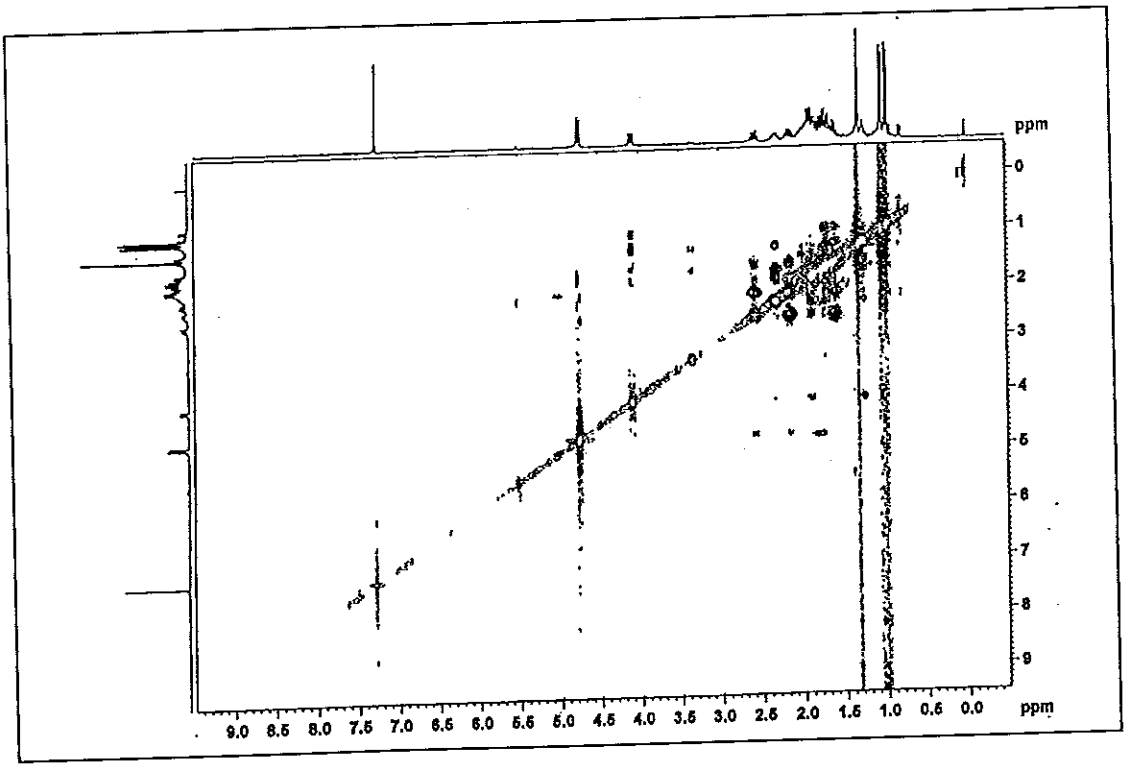

Figure 118 2D NOESY ($CDCl_3$) spectrum of compound **CP13**

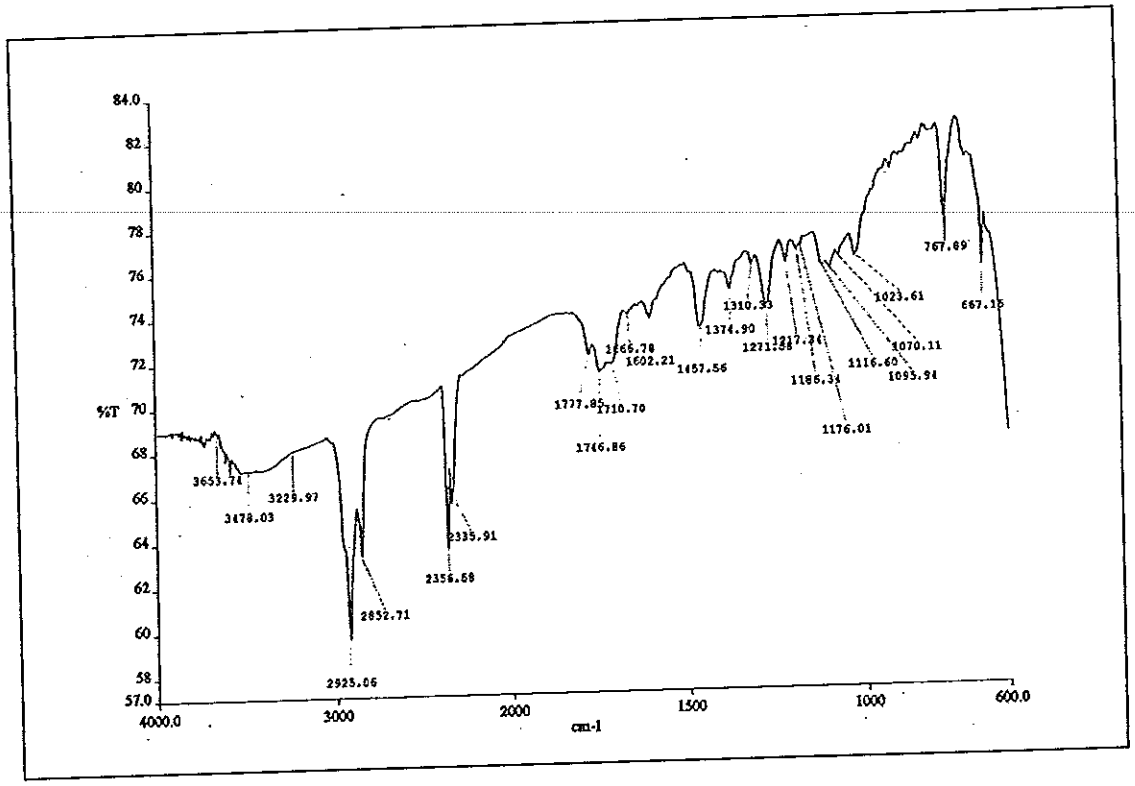

Figure 119 IR (neat) spectrum of compound **CP13**

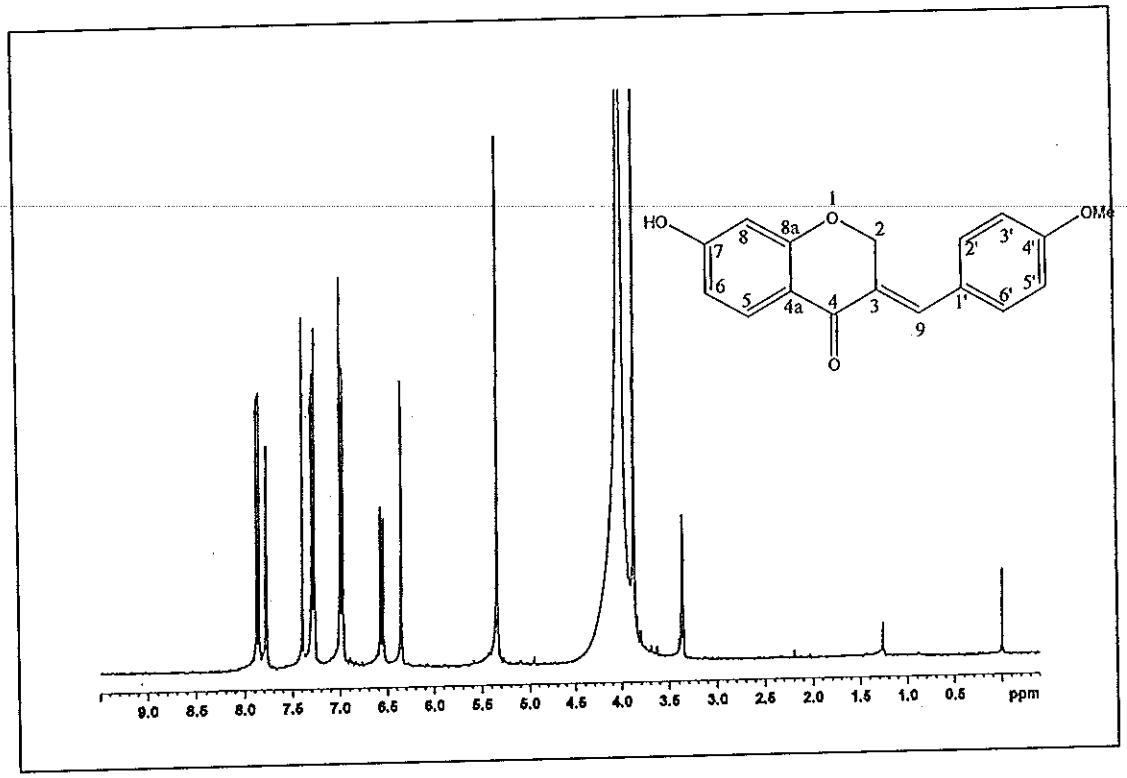

Figure 120 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

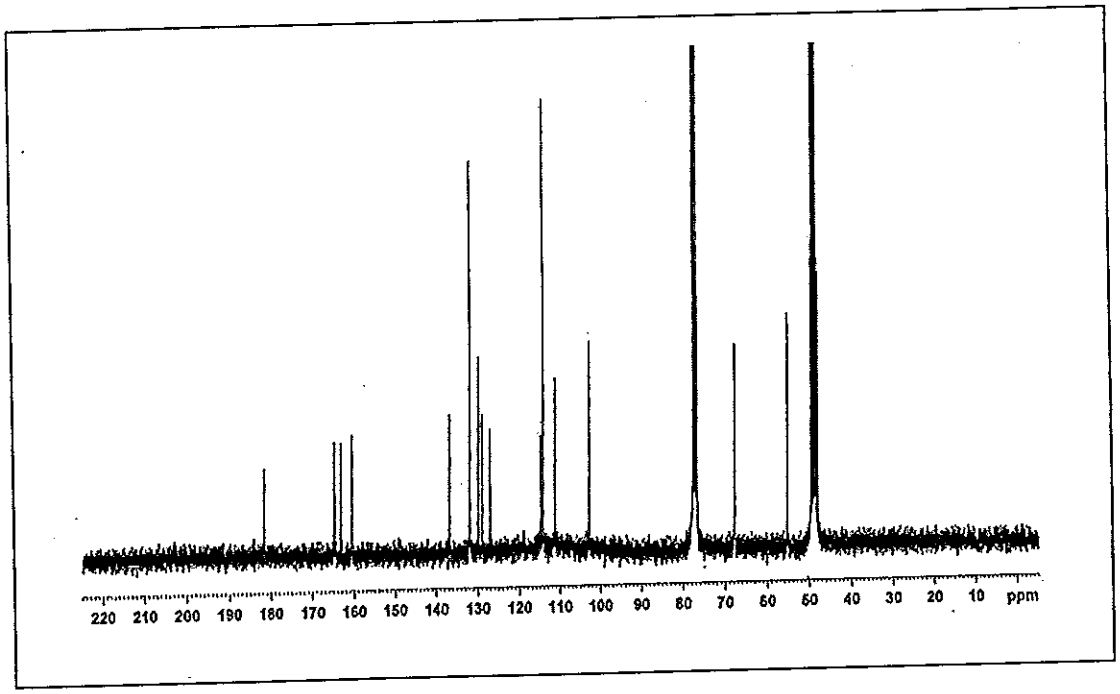

Figure 121 ^{13}C NMR (75 MHz) ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

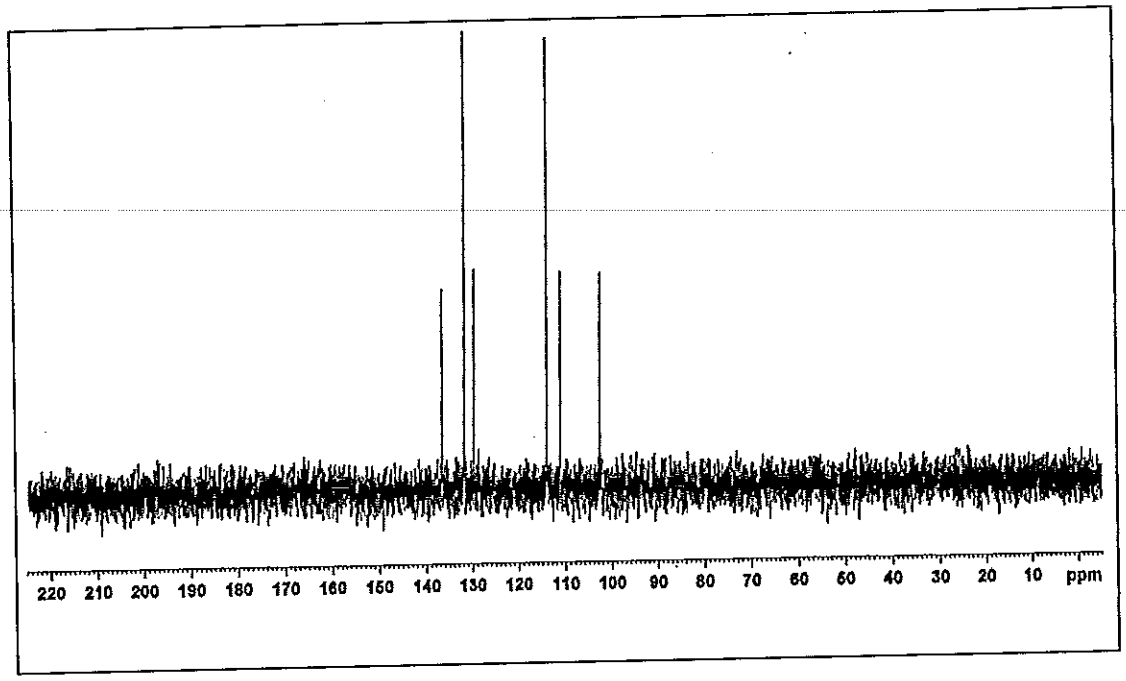

Figure 122 DEPT 90° ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

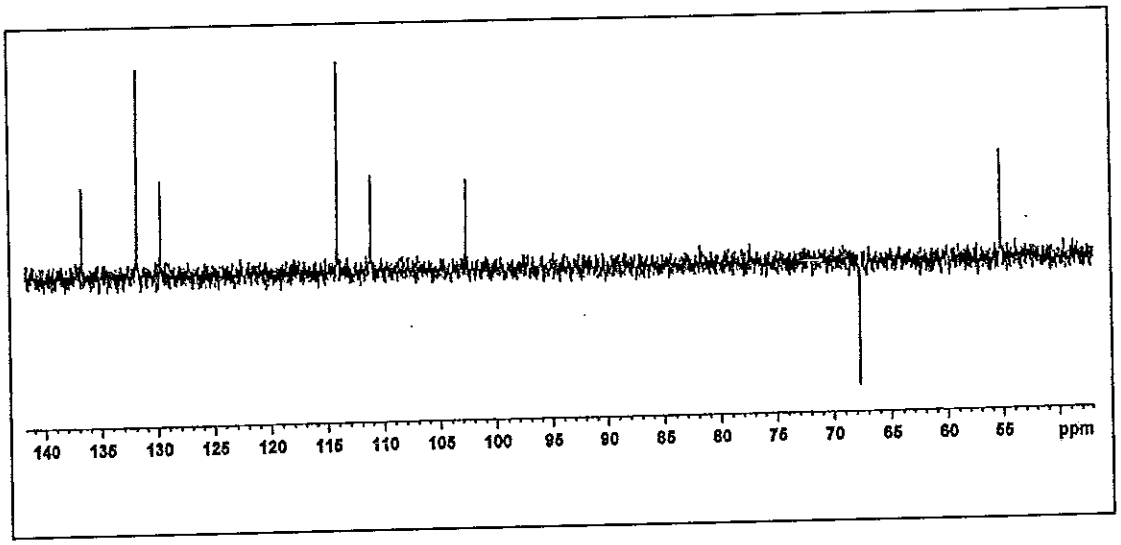

Figure 123 DEPT 135° ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

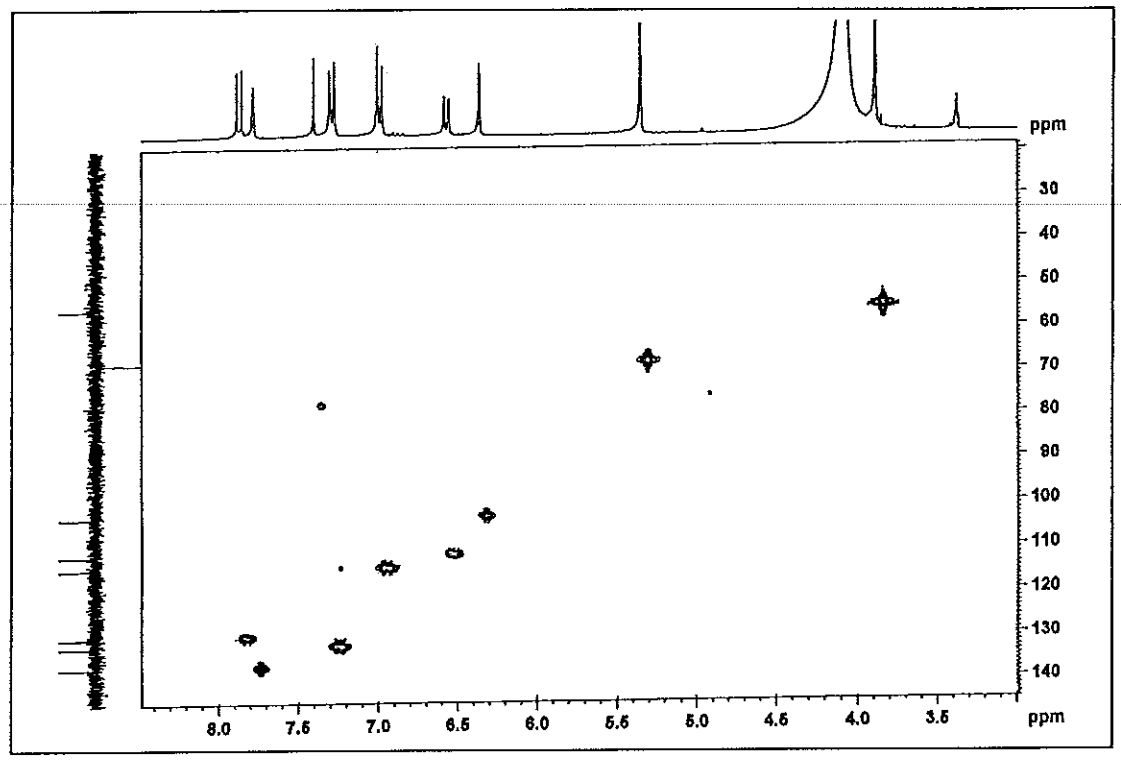

Figure 124 2D HMQC ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

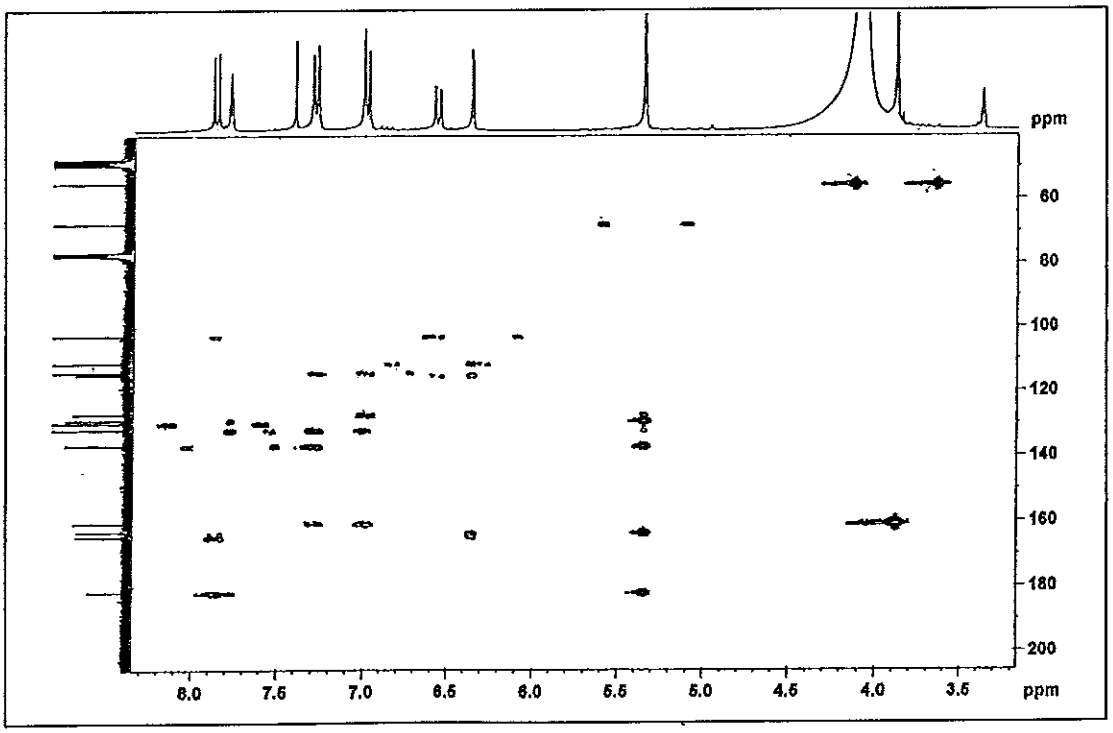

Figure 125 2D HMBC ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

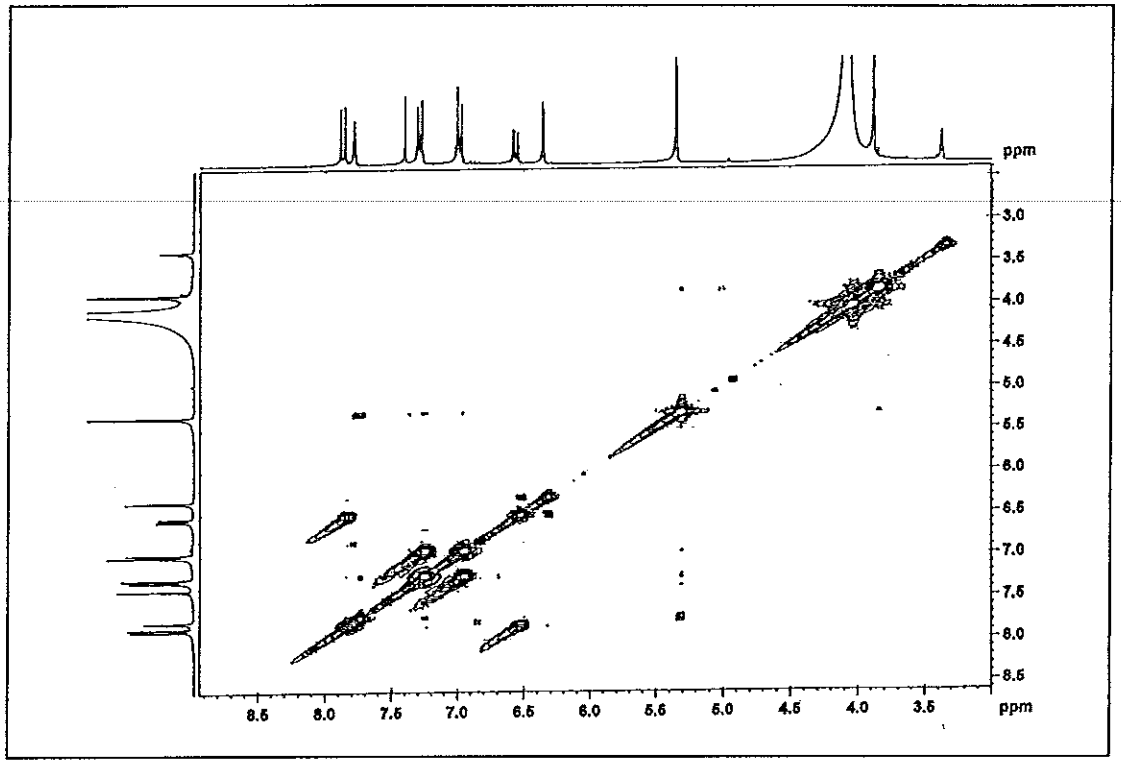

Figure 126 2D COSY ($CDCl_3$+CD_3OD) spectrum of compound **CP14**

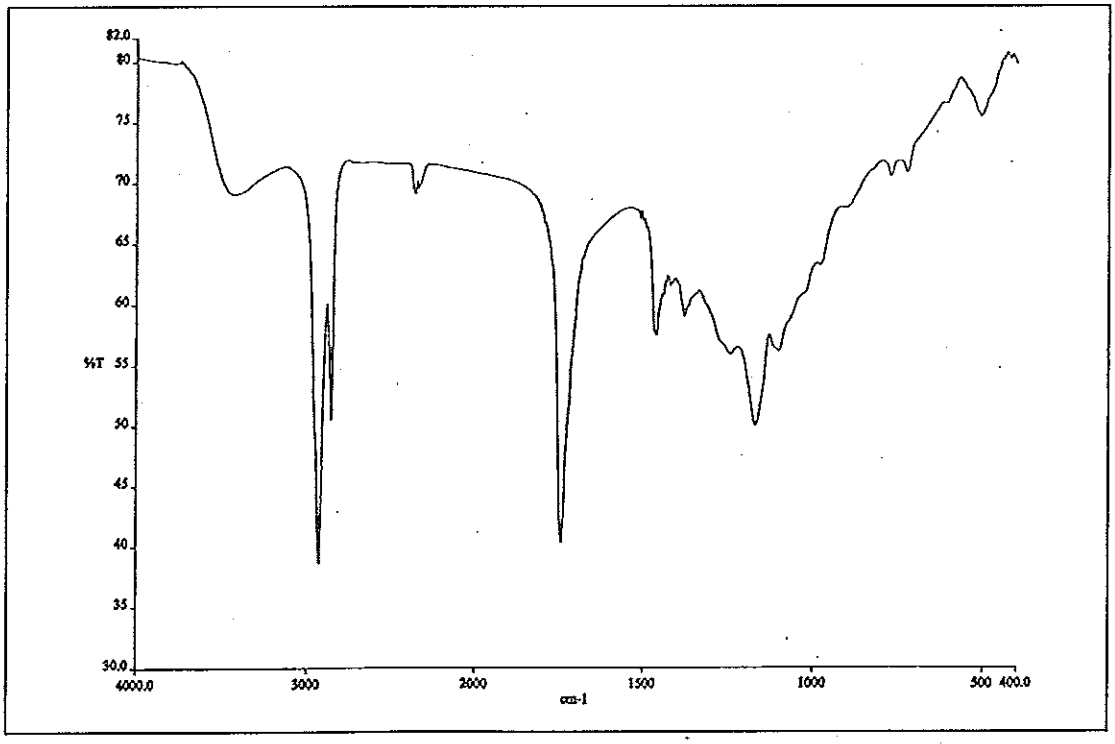

Figure 127 IR (neat) spectrum of compound **CP14**

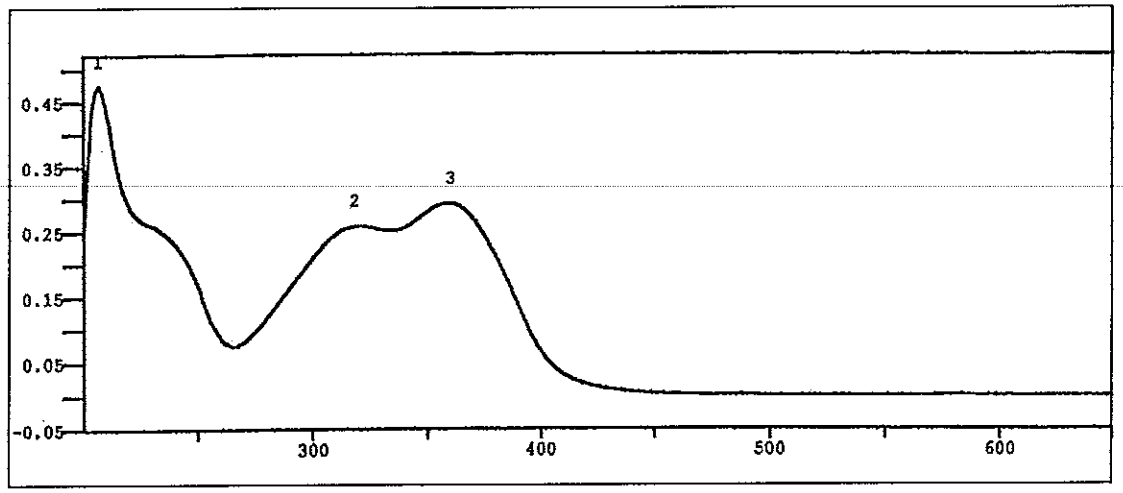

Figure 128 UV (MeOH) spectrum of compound **CP14**

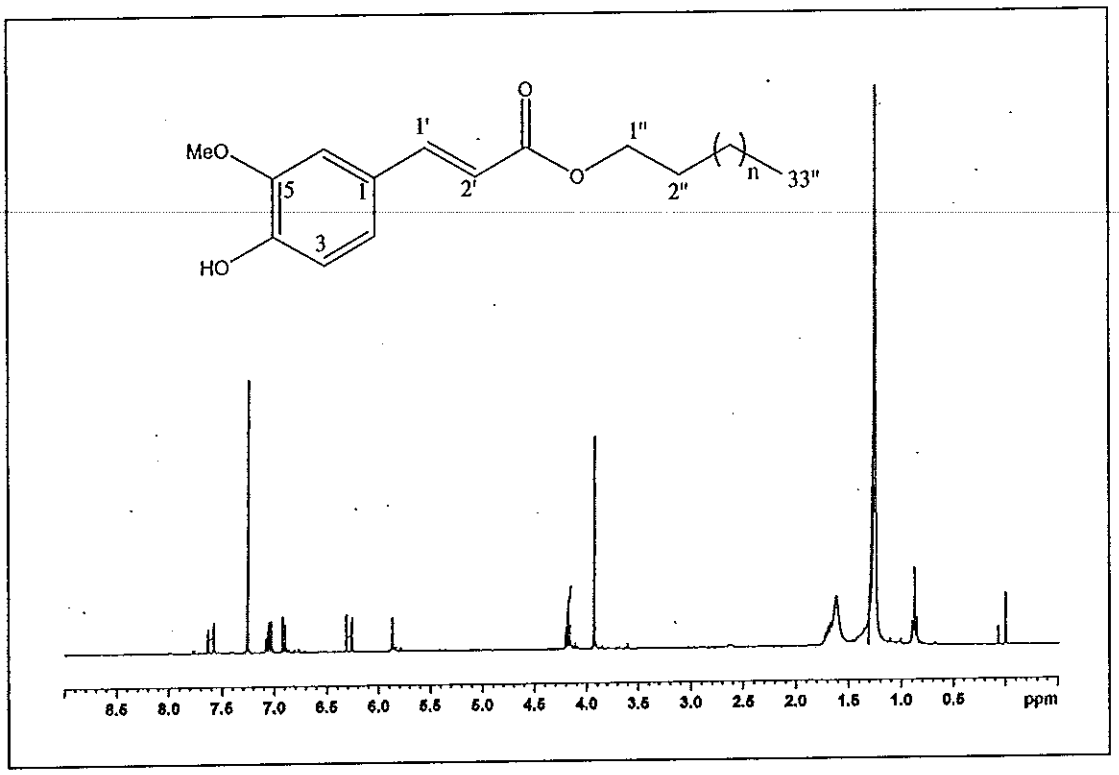

Figure 129 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of compound **CP15**

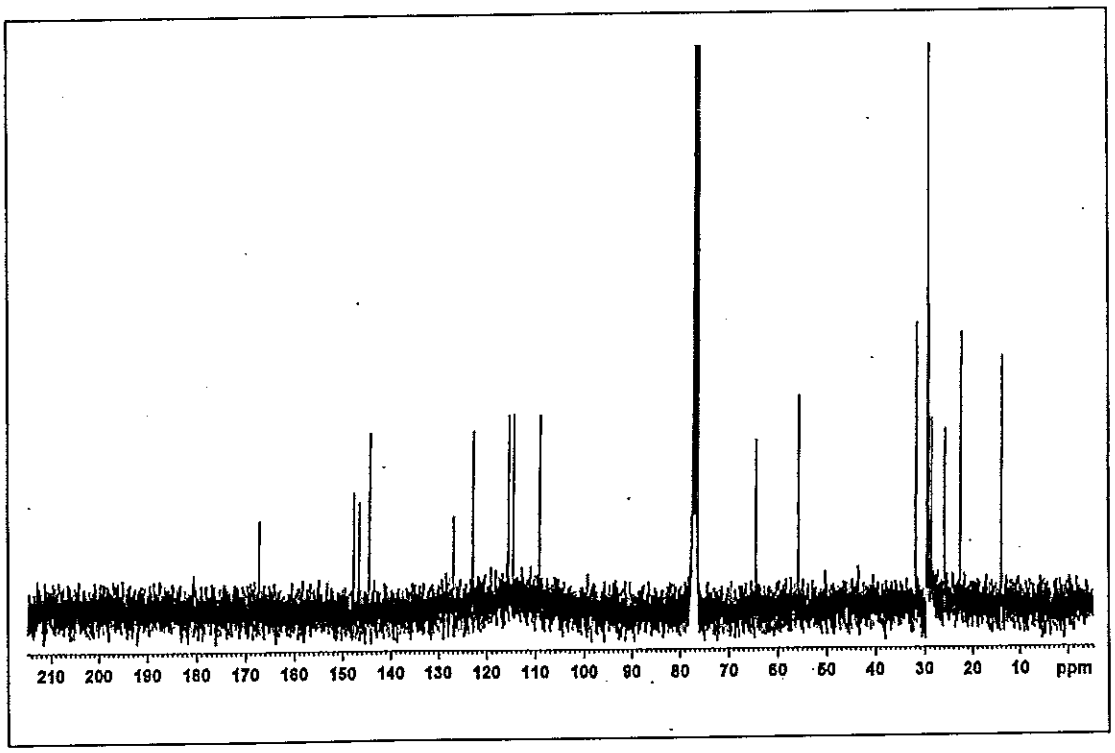

Figure 130 ^{13}C NMR (75 MHz) ($CDCl_3$) spectrum of compound **CP15**

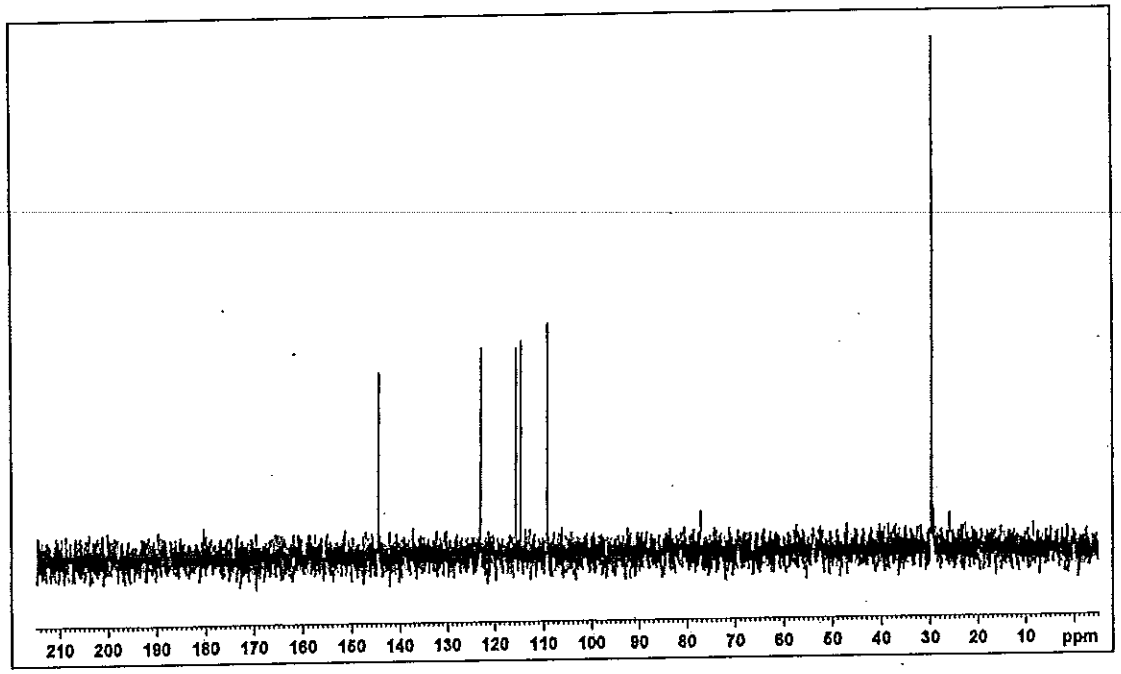

Figure 131 DEPT 90° ($CDCl_3$) spectrum of compound **CP15**

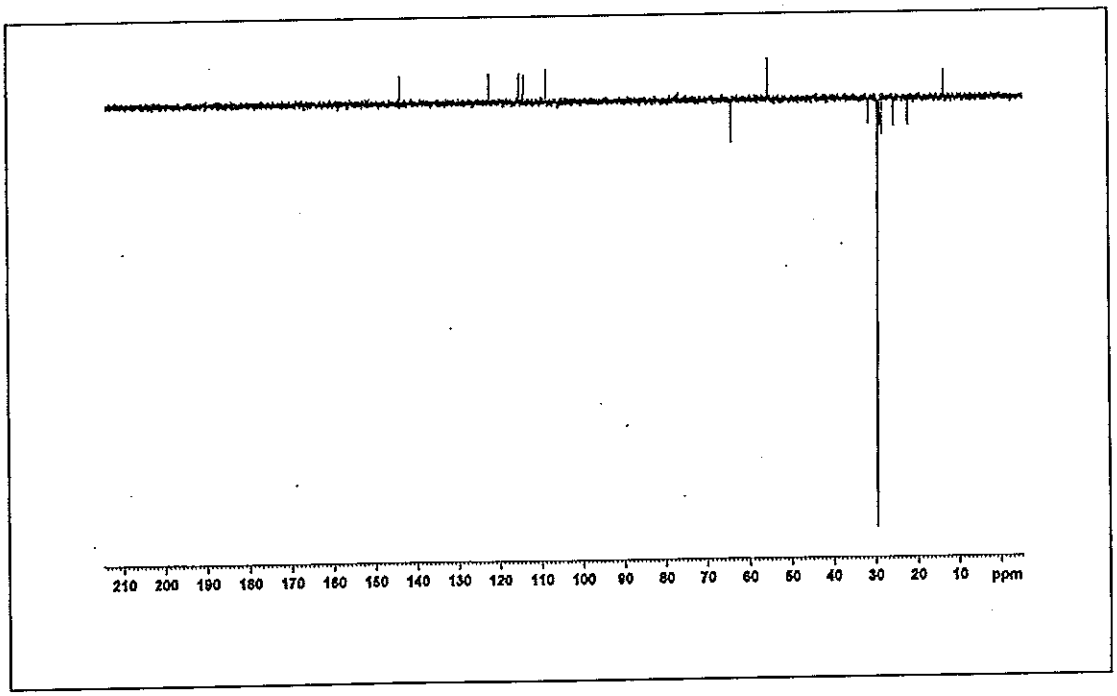

Figure 132 DEPT 135° ($CDCl_3$) spectrum of compound **CP15**

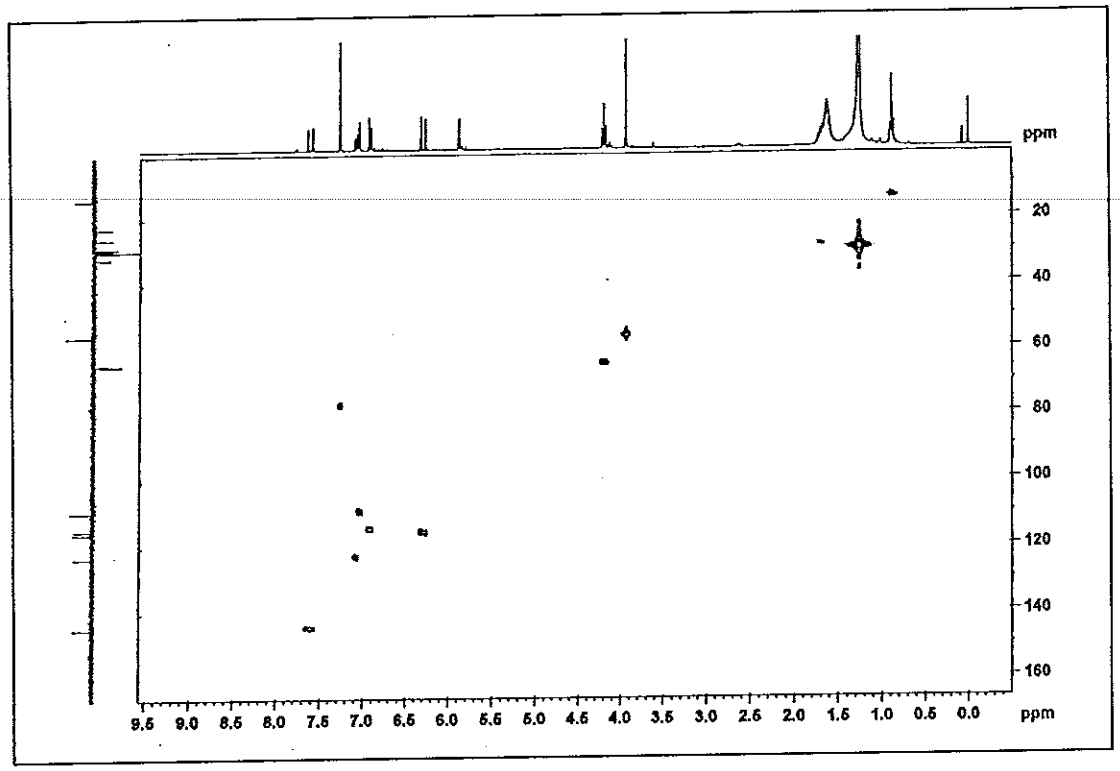

Figure 133 2D HMQC ($CDCl_3$) spectrum of compound **CP15**

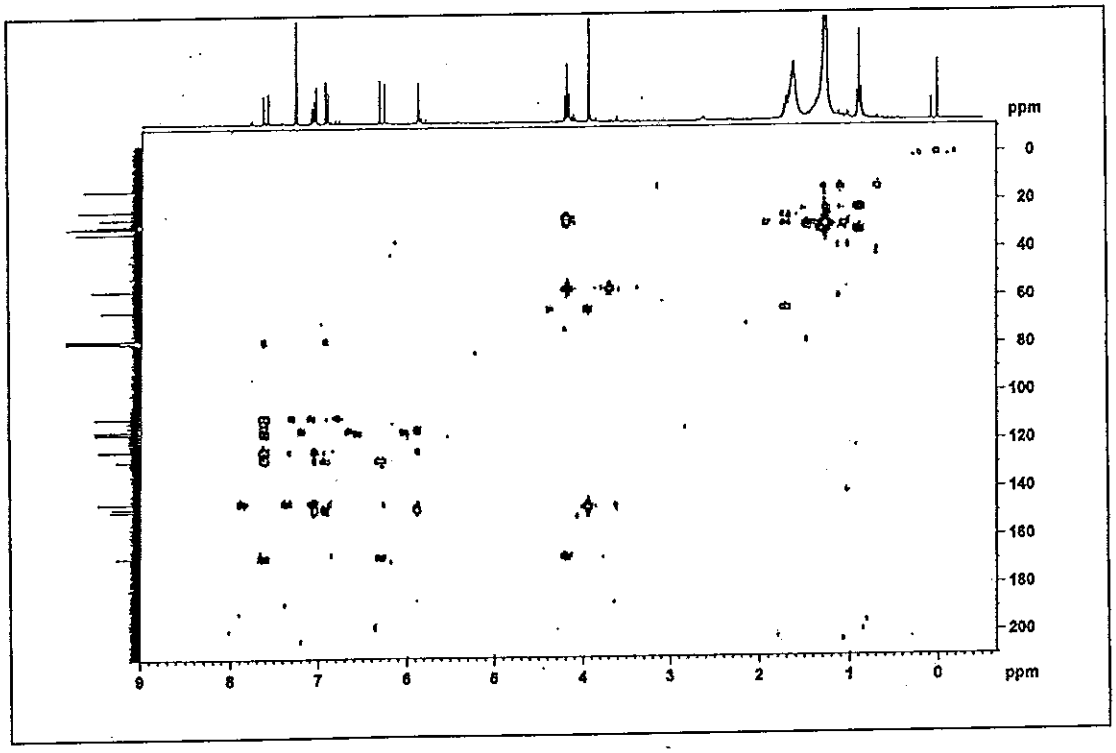

Figure 134 2D HMBC ($CDCl_3$) spectrum of compound **CP15**

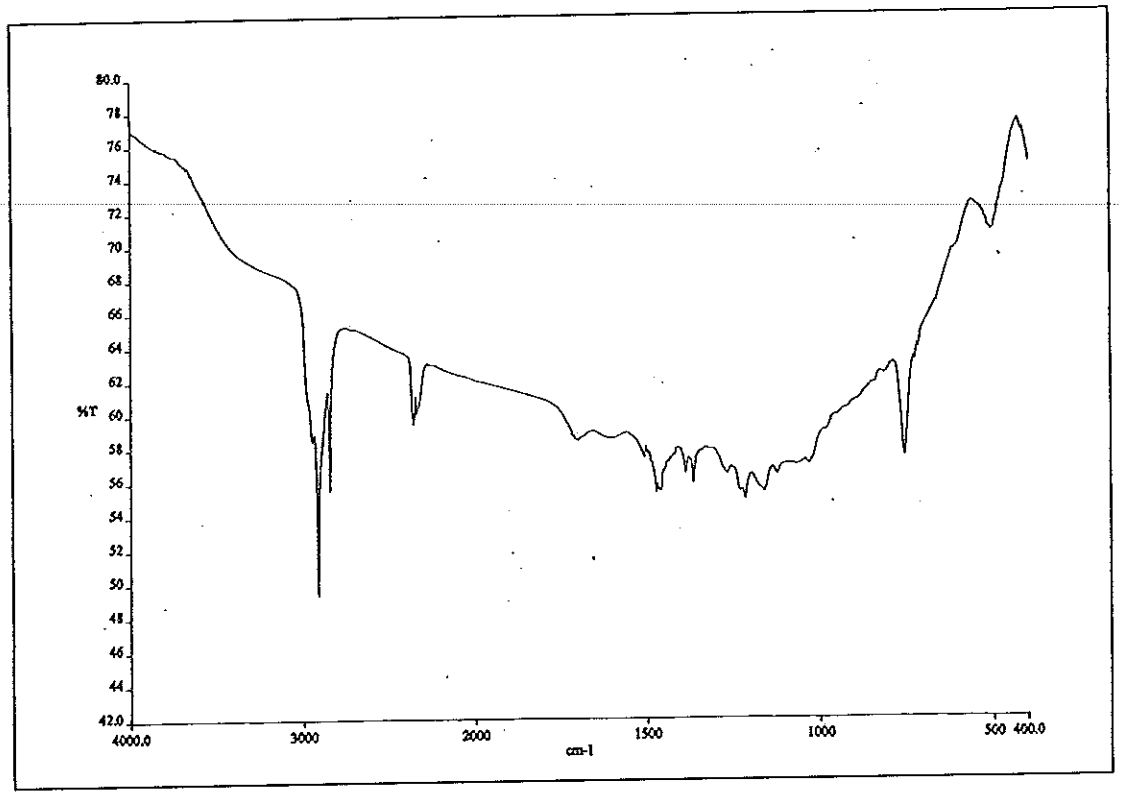

Figure 135 IR (neat) spectrum of compound **CP15**

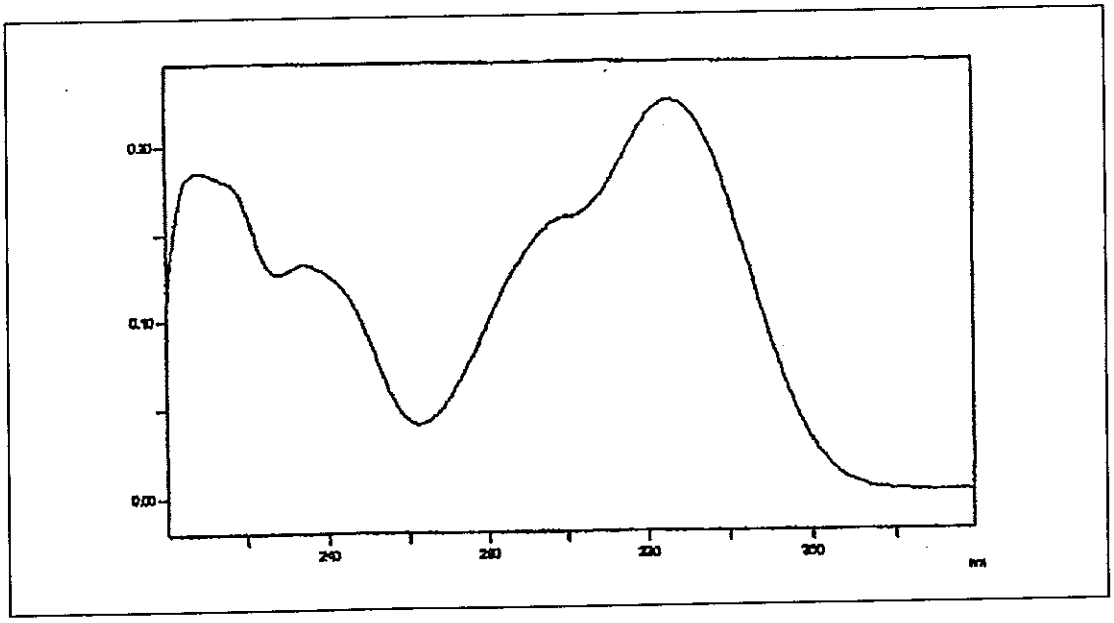

Figure 136 UV (MeOH) spectrum of compound **CP15**

VITAE

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Educational Attainment

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Bachelor of Science (Chemistry)	Rajabhat Suratthani University	2003

Scholarship Awards during Enrolment

Scholarship was awarded by the Center for Innovation in Chemistry: Postgraduate Education and Research Program in Chemistry (PERCH-CIC).

List of Publication and Proceedings

Publication

Wirote, P., Karalai, C., Subhadhirasakul, S., Ponglimanont, C. and Chantrapromma, S. (2009). Cassane diterpenoids from the stem of *Caesalpinia pulcherrima.* Phytochemisty 70, 300-304.

Proceedings

1. **Wirote, P.**, Karalai, C. and Subhadhirasakul, S. Chemical constituents from the stem of *Caesalpinia pulcherrima.*: PERCH-CIC Congress V. Jomtein Palm Beach, Pattaya, Chonburi, Thailand. 6-9 May 2007. (Poster)
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