Chemical Constituents from the Leaves of *Desmos chinensis* Lour.

Tharikarn Rittiwong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemical Studies
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Thesis Title	Chemical Constituents from the Leaves of *Desmos chinensis* Lour.
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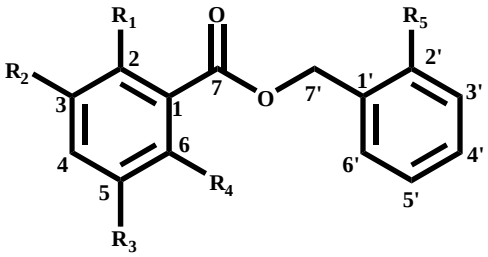
(Prof. Dr. Amornrat Phongdara)

Dean of Graduate School

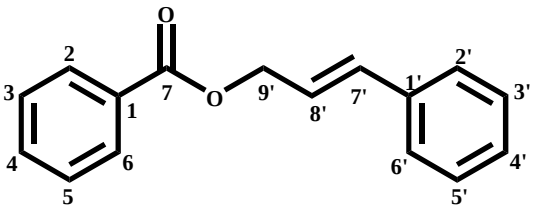
ชื่อวิทยานิพนธ์	องค์ประกอบทางเคมีจากใบสายหยุด (*Desmos chinensis* Lour.)
ผู้เขียน	นางสาวฑริกานต์ ฤทธิวงศ์
สาขาวิชา	เคมีศึกษา
ปีการศึกษา	2553

บทคัดย่อ

การศึกษาองค์ประกอบทางเคมีของส่วนสกัดหยาบไดคลอโรมีเทนจากใบสายหยุด สามารถแยกสารใหม่ได้ 4 สาร เป็นสารประกอบประเภท biflavones คือ saiyunensis A (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(5′′,7′′-dihydroxy-8′′-methylflavone) (**DC16**), saiyunensis B **(DC17)**, saiyunensis C (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(2′′,5′′,7′′-trihydroxy-8′′-methylflavanone) **(DC18)** และ saiyunensis D **(DC20)** นอกจากนี้ยังได้พบสารที่มีการรายงานมาแล้ว 16 สาร ประกอบด้วยสารประเภท benzoate esters 9 สาร คือ benzyl 2-hydroxybenzoate (**DC1**), benzyl benzoate (**DC2**), benzyl 2,6-dihydroxybenzoate (**DC3**), cinnamyl benzoate (**DC4**), benzyl 2-hydroxy-5-methoxybenzoate **(DC5)**, 2-methoxybenzyl benzoate **(DC6**), benzyl 2-hydroxy-6-methoxybenzoate **(DC7)**, benzyl 2-methoxybenzoate **(DC9)** และ benzyl 3-hydroxybenzoate **(DC14)** สารประเภท flavones 5 สาร คือ isounonal **(DC10)**, unonal **(DC11)**, 6-formyl-2,5,7-trihydroxy-8-methylflavanone **(DC12)**, desmal **(DC13)** และ matteuorien **(DC19)** สารประเภท diterpene 1 สาร คือ phytol **(DC8)** และสารประเภท อนุพันธ์ของกรดเบนโซอิก 1 สาร คือ 2-methoxybenzoic acid (**DC15**) โครงสร้างของสารประกอบเหล่านี้วิเคราะห์โดยใช้ข้อมูลทางสเปกโทรสโกปี UV IR NMR MS และเปรียบเทียบกับสารที่มีรายงานการวิจัยแล้ว



DC1: R_1 = OH	**R_2 = H**	**R_3 = H**	**R_4 = H**	**R_5 = H**
DC2: R_1 = H	**R_2 = H**	**R_3 = H**	**R_4 = H**	**R_5 = H**
DC3: R_1 = OH	**R_2 = H**	**R_3 = H**	**R_4 = OH**	**R_5 = H**
DC5: R_1 = OH	**R_2 = H**	**R_3 = OCH_3**	**R_4 = H**	**R_5 = H**
DC6: R_1 = H	**R_2 = H**	**R_3 = H**	**R_4 = H**	**R_5 = OCH_3**
DC7: R_1 = OH	**R_2 = H**	**R_3 = H**	**R_4 = OCH_3**	**R_5 = H**
DC9: R_1 = OCH_3	**R_2 = H**	**R_3 = H**	**R_4 = H**	**R_5 = H**
DC14: R_1 = H	**R_2 = OH**	**R_3 = H**	**R_4 = H**	**R_5 = H**



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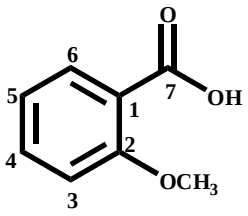

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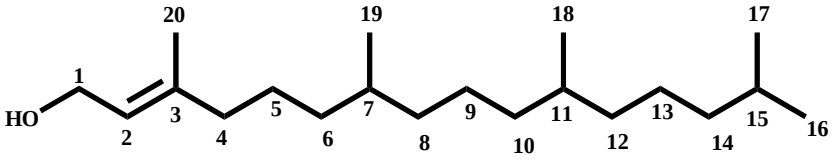

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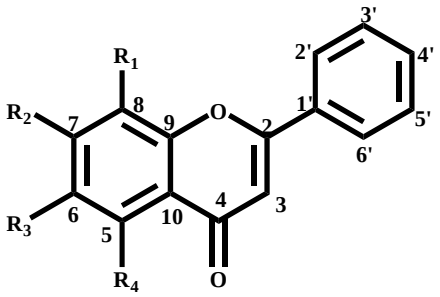

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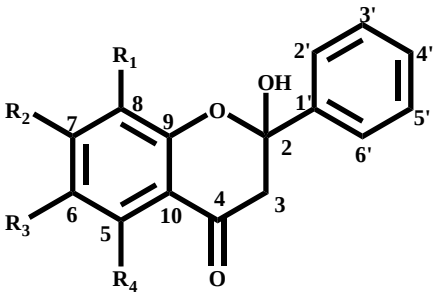
DC11: R_1 = CH_3 R_2 = OH R_3 = CHO R_4 = OH

DC19: R_1 = CH_3 R_2 = OH R_3 = CH_3 R_4 = OH



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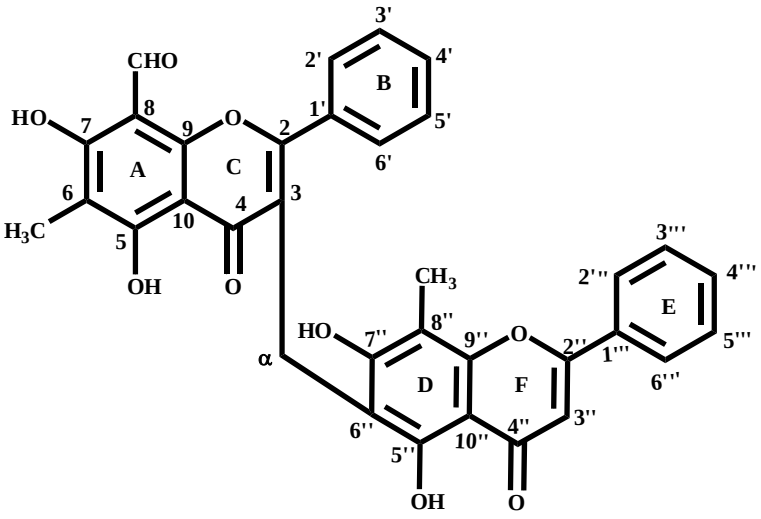
DC13: R_1 = CHO R_2 = OH R_3 = CH_3 R_4 = OH



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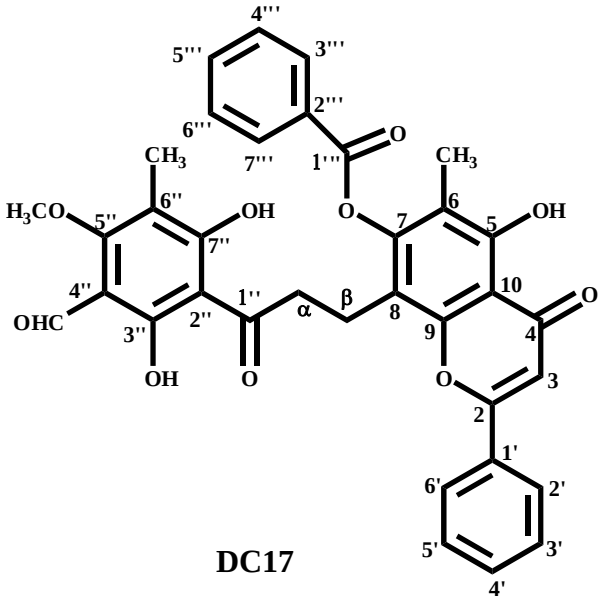

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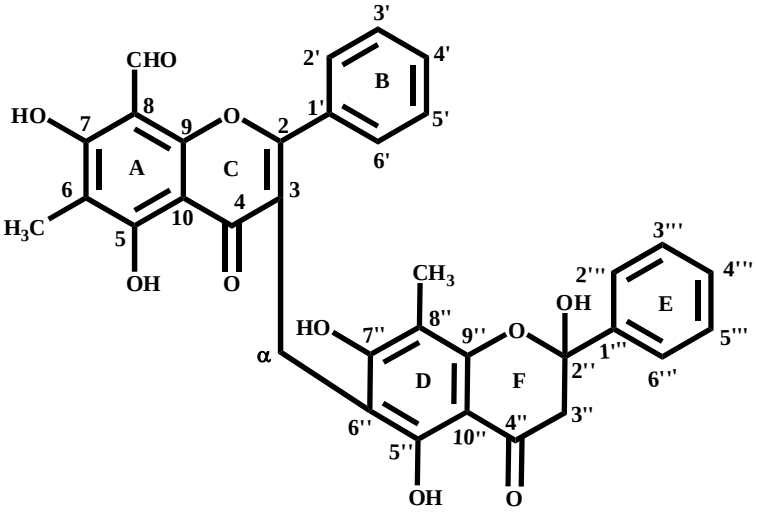

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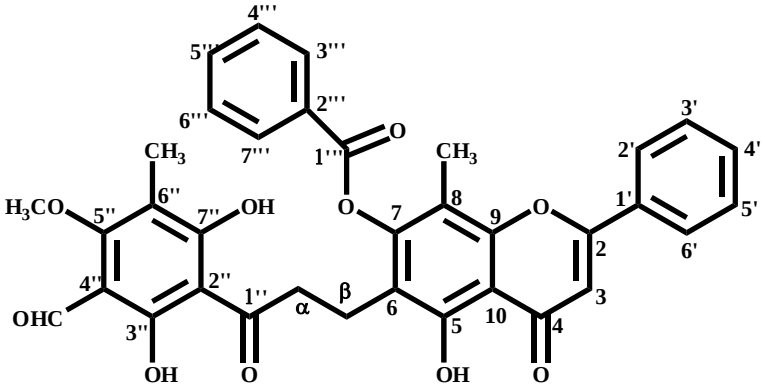
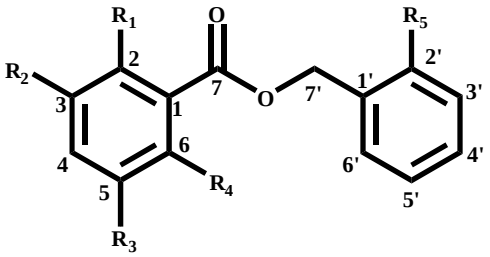


DC20

Thesis Title	Chemical Constituents from the Leaves of *Desmos chinensis* Lour.
Author	Miss Tharikarn Rittiwong
Major Program	Chemical Studies
Academic Year	2010

ABSTRACT

Investigation of the crude dichloromethane extract of the leaves of *Desmos chinensis* yielded four new biflavones: saiyunensis A (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(5′′,7′′-dihydroxy-8′′-methylflavone) (**DC16**), saiyunensis B **(DC17)** and saiyunensis C (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(2′′,5′′,7′′-trihydroxy-8′′-methylflavanone) **(DC18)** and saiyunensis D **(DC20)**, together with sixteen known compounds: nine benzoate esters: benzyl 2-hydroxybenzoate (**DC1**), benzyl benzoate (**DC2**), benzyl 2,6-dihydroxybenzoate (**DC3**), cinnamyl benzoate (**DC4**), benzyl 2-hydroxy-5-methoxybenzoate **(DC5)**, 2-methoxybenzyl benzoate **(DC6**), benzyl 2-hydroxy-6-methoxybenzoate **(DC7)**, benzyl 2-methoxybenzoate **(DC9)** and benzyl 3-hydroxybenzoate **(DC14)**, five flavones: isounonal **(DC10)**, unonal **(DC11)**, 6-formyl-2,5,7-trihydroxy-8-methylflavanone **(DC12)**, desmal **(DC13)** and matteuorien **(DC19)**, one diterpene: phytol **(DC8)** and one benzoic acid derivative: 2-methoxybenzoic acid (**DC15**). Their structures were determined on the basis of UV, IR, NMR, MS and by comparison of their spectroscopic data with those reported.



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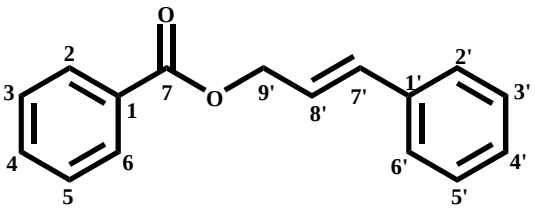

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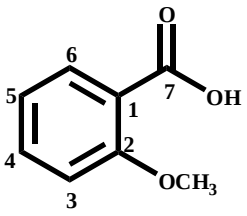

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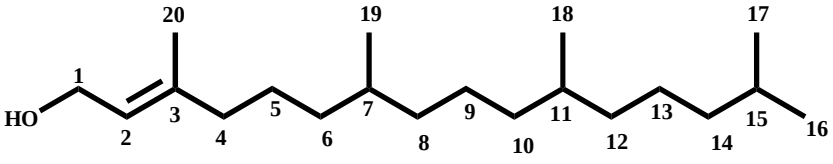

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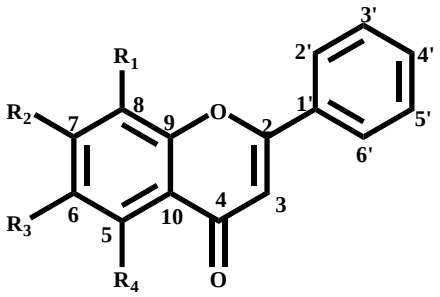

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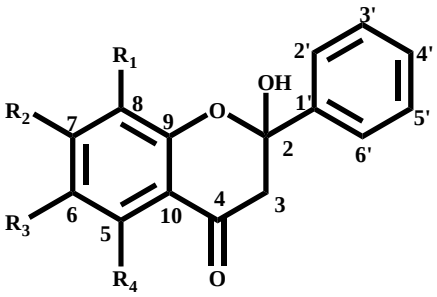

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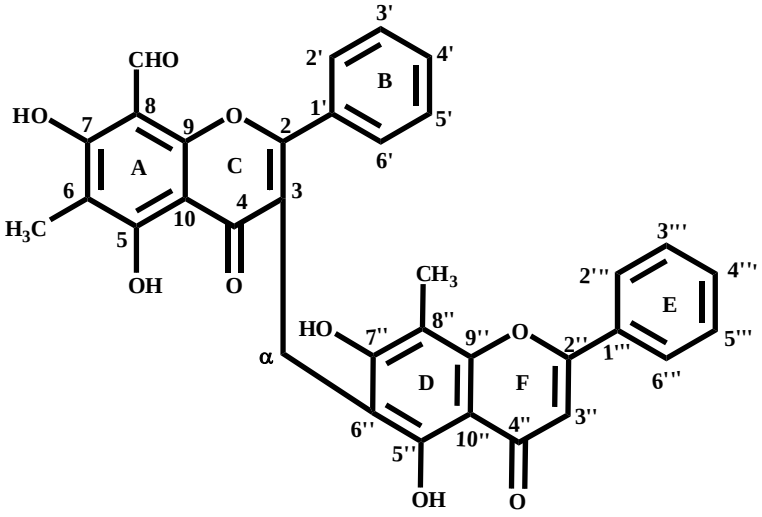

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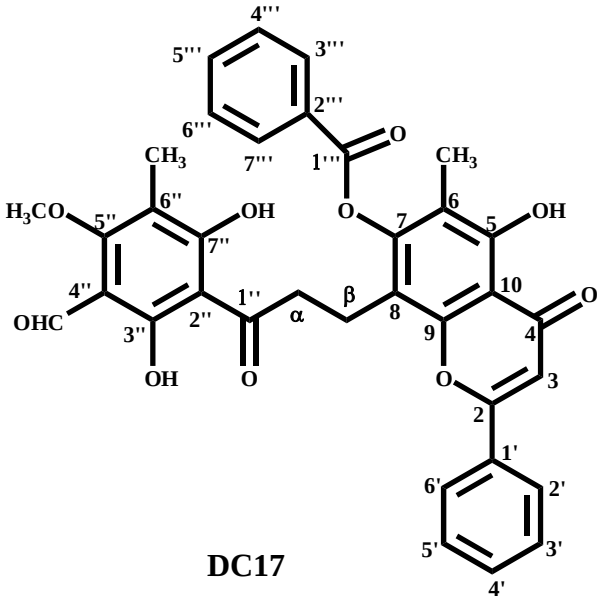

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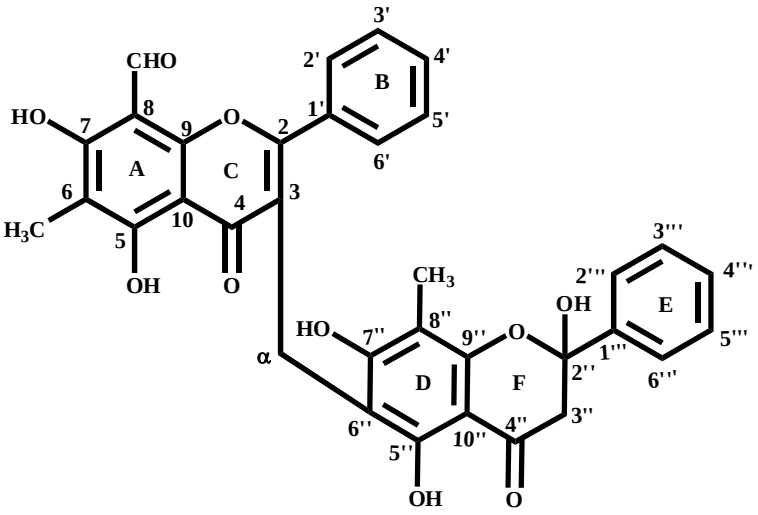

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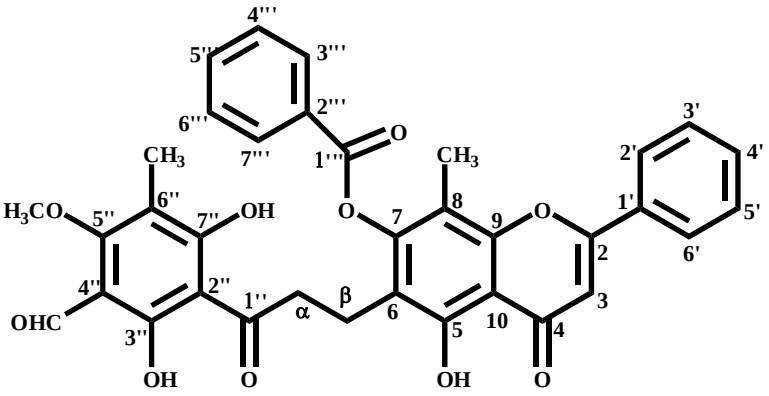

DC20

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Tharikarn Rittiwong

THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The purpose of this research is to investigate the chemical constituents from the leaves of *Desmos chinensis.* They are a part of the basic research on the Thai medicinal plants. A derivative of benzoic acid, a diterpene, nine benzoate esters, five flavones, and two biflavones were isolated from the leaves of *Desmos chinensis*.

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LIST OF ILLUSTRATIONS (Continued)

LIST OF ABBREVIATIONS AND SYMBOLS

s	=	singlet
d	=	doublet
t	=	triplet
m	=	multiplet
dd	=	doublet of doublet
ddd	=	doublet of doublet of doublet
dt	=	doublet of triplet
g	=	gram
nm	=	nanometer
mp	=	melting point
cm^{-1}	=	reciprocal 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

LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

UV	=	Ultraviolet
MS	=	Mass Spectroscopy
EIMS	=	Electron Impact Mass Spectroscopy
NMR	=	Nuclear Magnetic Resonance
1D NMR	=	One Dimensional Nuclear Magnetic Resonance
2D NMR	=	Two Dimensional Nuclear Magnetic Resonance
COSY	=	Correlation Spectroscopy
DEPT	=	Distortionless Enhancement by Polarization Transfer
HMBC	=	Heteronuclear Multiple Bond Correlation
HMQC	=	Heteronuclear Multiple Quantum Coherence
NOESY	=	Nuclear Overhauser Effect Spectrosopy
CC	=	Column Chromatography
QCC	=	Quick Column Chromatography
PLC	=	Preparative Thin Layer Chromatography
TLC	=	Thin Layer Chromatography
TMS	=	tetramethylsilane
$CDCl_3$	=	deuterochloroform
DMSO-d_6	=	dimethylsulfoxide-d_6

CHAPTER 1
INTRODUCTION

1.1 Introduction

Desmos chinensis Lour. is the plant in the Annonaceae family, which is locally known as "สายหยุด". The tree is a climbing shrub with straggling branches, up to 5 meters tall, flowers are greenish-yellow. The petals arrange in 6 layers. Young flowers are green and inconspicuous. Only mature yellow flowers have strong lemon-like fruity scent can be detected at a distance, especially in the evening. When the flower fades, the petals turn to rusty-red and then drop. The aggregate fruits like bead bracelet and the ripe are glittering black that contain 2-5 seeds. The flowers open between April and July and fruit can be observed from June to March of the following year. The plant *Desmos chinensis* is distributed widely in Asia and northern Australia (Frodin *et al*., 1990). This plant has been used as a folk medicine for treatment of malaria, parturition and vertigo (Rahman *et al*., 2003). In Thailand it is used traditionally to treat pyretic and dysentery (Kummee *et al*., 2008). The extracted oil from flowers is used as cardiotonic, antipyretic and vertiginous relieving. The stem and root are used to relief the drug addict by vapor exposing.

According to Smitinand (2001), there are five species of genus *Desmos* found in Thailand as follows.

1. *D. chinensis*
2. *D. cochinchinensis*
3. *D. crinitus*
4. *D. dumosus*
5. *D. macrocarpus*

The leaf extract of this plant contains flavonoids such as flavones, chalcones and flavanones (Rahman *et al*., 2003). This plant exhibited antibacterial activity against *S. aureus*, *Bacillus cereus*, *B. subtilis*, *Salmonella typh*i A, *Shigella boydii*, *Shigella shiga* and *S. sonnei* at concentration of 400 μg/disc (Qais *et al*., 1996),

cytotoxicity (Nakanishi *et al*., 1965) and tyrosine kinase enzyme inhibitory properties (Kakeya *et al*., 1993).

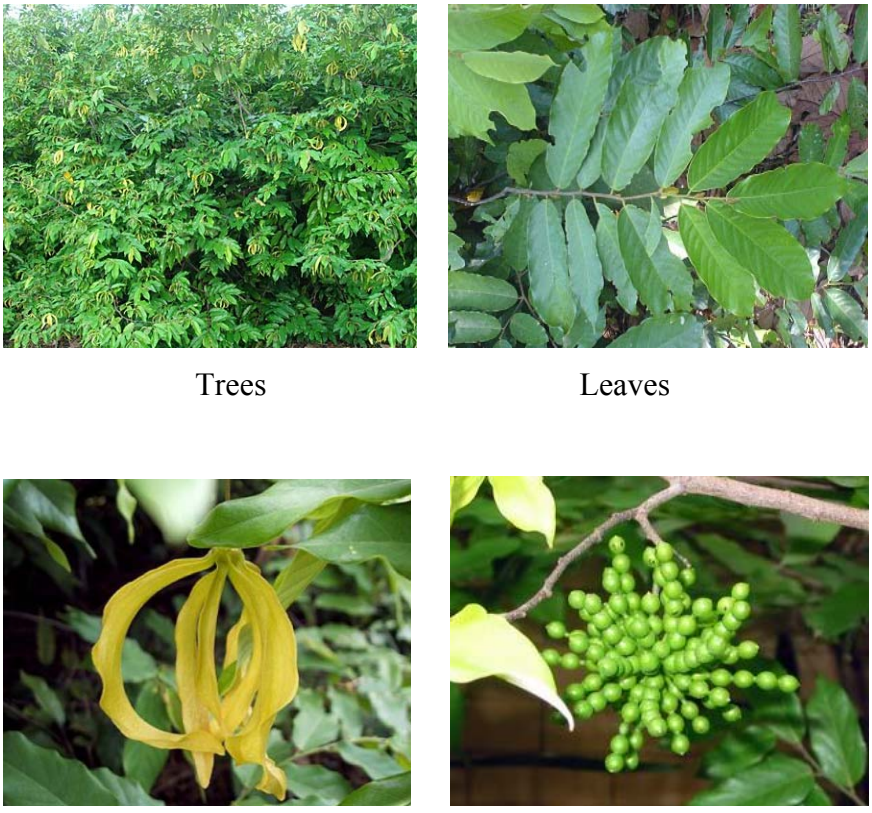


Figure 1 Different parts of *Desmos chinensis* Lour.

1.2 Review of Literatures

The chemical constituents isolated from the eight species of *Desmos* spp. were summarized in **Table 1**. Information obtained from SciFinder Scholar copyright in 2010 will be presented and classified into groups: Acids, Alkaloids, Chalcones, Esters Flavonoids, Steroids and Triterpenoids.

1.2.1 The Biological Activity of *D. chinensis*

The compounds isolated from *D. chinensis* have been investigated for biological activity. For example, negletein, 2′,3′-dihydroxy-4′,6′-dimethoxydihydrochalcone and 2-methoxybenzyl benzoate isolated from leaves of *D.*

chinensis showed the inhibitory activity against nuclear factor of activated T cells (NFAT) transcription factor with IC_{50} values of 3.89 ± 0.39 μM, 9.77 ± 0.26 μM and 28.4 ± 2.62 μM, respectively (Kiem *et al*., 2005), 8-formyl-2,5,7-trihydroxy-6-methylflavone was an anticancer agent and inhibited tyrosine kinase with IC_{50} of 0.85 μg/mL (Umezawa *et al*., 1994), 2-methoxy-3-methyl-4,6-dihydroxy-5-(3′-hydroxy) cinnamoylbenzaldehyde and lawinal demonstrated potent anti-HIV activity with EC_{50} values of 0.022 and 2.30 μg/mL and therapeutic indexes of 489 and 45.2, respectively (Wu *et al*., 2003).

Table 1 Compounds from plants of *Desmos* species.

a. Acids
b. Alkaloids
c. Chalcones
d. Esters
e. Flavonoids
f. Steroids
g. Triterpenoids

Scientific name	Part	Compounds	Bibliography
D. chinensis	Root	Desmethoxymatteucinol, **e1**	Zhao *et al*., 1992
		4,7-Dihydroxy-5-methoxy-6-methyl-8-formylflavane, **e2**	
		Benzoic acid, **a2**	Wu *et al*., 2000
		Desmethoxymatteucinol-7-methyl ether, **e3**	
		Negletein, **e4**	
		Unonal, **e5**	
		β-Sitosterol, **f2**	
		Stigmasterol, **f3**	
	Seed	Allantonic acid, **a1**	Ju *et al*., 1999
		Daucosterol, **f1**	
		Desmosal, **e6**	
		Desmosflavone, **e7**	
		Isounonal, **e8**	
		Lawinal, **e9**	
		Stearic acid, **a3**	

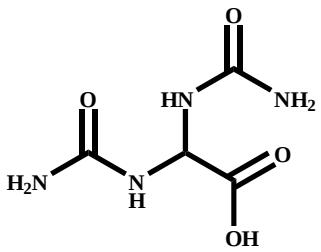
Scientific name	Part	Compounds	Bibliography
D. chinensis		Succinic acid, **a4**	
		β-Sitosterol, **f2**	
		Unonal, **e5**	
	Leaves	2',4'-Dihydroxy-3'-(2,6-dihydroxybenzyl)-6'-methoxychalcone, **c1**	Rahman *et al*., 2003
		Uvaretin, **c2**	
		Isoouvaretin, **c3**	
		Astillbin, **e10**	Shi *et al*., 2003
		Eucryphin, **e11**	
		Negletein, **e4**	
		Mosloflavone, **e12**	
		Astillbin, **e10**	Kiem *et al*., 2005
		2',3'-Dihydroxy-4',6'-dimethoxydihydrochalcone, **c4**	
		5,6-Dihydroxy-7-methoxy-dihydroflavone, **e13**	
		2-Methoxybenzyl benzoate, **d1**	
		Negletein, **e4**	
		Quercitrin, **e14**	
	Branch	Mosloflavone, **e12**	Liu *et al*., 2004
		Negletein, **e4**	
		Oxoanolobin, **b1**	
		β-Sitosterol, **f2**	
		3,9,11-Trimethoxy-1,2-methylenedioxyloxoaporphine, **b2**	
D. cochinchinensis	Root	Desmethoxymatteucinol, **e1**	Wu *et al*., 1994
		Desmosflavone, **e7**	
		β-Sitosterol, **f2**	

Scientific name	Part	Compounds	Bibliography
		Unonal, **e5** Desmosflavone, **e7**	Wu *et al*., 1997
D. dasymachalus	Leaves	Dasymachaline, **b3** Dicentrinone, **b4**	Chan *et al*., 1986
D. dumosus	Root	Benzoic acid, **a2** Desmethoxymatteucinol-7-methyl ether, **e3** Desmethoxymatteucinol, **e1** 5,7-Dihydroxy-8-formyl-6-methylflavanone, **e15** Lawinal, **e9** β-Sitosterol, **f2** Stigmasterol, **f3**	Wu *et al*., 1997
		Desmethoxymatteucinol-7-methyl ether, **e3** 2-Methoxy-3-methyl-4,6-dihydroxy-5-(3′-hydroxy)cinnamoylbenzaldehyde, **c5** Mosloflavone, **e12** Negletein, **e4** Stigmast-4-ene-3,6-dione, **f4** Stigmastane-3,6-dione, **f5**	Wu *et al*., 1999
		5-Hydroxy-7-one-6,8,8-trimethylflavone, **e16**	Wu *et al*., 2001
		Lawinal, **e9** 2-Methoxy-3-methyl-4,6-dihydroxy-5-(3′-hydroxy)cinnamoylbenzaldehyde, **c5**	Wu *et al*., 2005

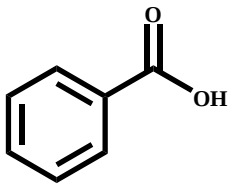
Scientific name	Part	Compounds	Bibliography
	Bark Leaves and Stem bark	Desmosine, **b5** Asimilobine, **b6** Discretamine, **b7** 3-Hydroxynornuciferine, **b8** Liriodenine, **b9** 5-Hydroxy-6,7-dimethoxyflavone, **e17** 5-Hydroxy-7,8-dimethoxyflavone, **e18** Lysicamine, **b10** *O*-Methylisopiline, **b11** *O*-Methylmoschatoline, **b12** Nornuciferine, **b13** Pronuciferine, **b14** Stepharine, **b15**	Sulaiman *et al*., 1998 Sulaiman *et al*., 2003
D. grandifolius	Root	Benzoic acid, **a2** Desmethoxymatteucinol, **e1** Desmosal, **e6** Lawinal, **e9** β-Sitosterol, **f2** Stigmasterol, **f3**	Wu *et al*., 2000
D. longiflorus	Stem bark	15a-Hydroxy-24-methylenelanosta-7,9(11)-dien-3-one, **g1** Antherospermidine, **b16** Discretamine, **b7** Lanuginosine, **b17** Liriodenine, **b9** Xylopine, **b18**	Connolly *et al*., 1994 Hossain *et al*., 1995

Scientific name	Part	Compounds	Bibliography
D. rostrata	Stem bark	Desmorostratine, **b19** Discretine-*N*-oxide, **b20** Discretine, **b21** Dehydrodiscretine, **b22** Pseudocolumbamine, **b23** Predicentrine, **b24** Aristolactam AII, **b25**	Nguyen *et al*., 2008
D. tiebaghiensis	Twigs and Leaves	Anonaine, **b26** Asimilobine, **b27** Boldine, **b28** Discretamine, **b7** Glaziovine, **b29** Isoboldine, **b30** Laurotetanine, **b31** *N*-Methyllaurotetanine, **b32** *N*-Methylcoclaurine, **b33** Norushinsunine, **b34** Pallidine, **b35** Reticuline, **b36** Stepholidine, **b37**	Leboeuf *et al*., 1982
D. yunnanensis	-	Anonaine, **b26** Demethylcorydalmine, **b38** 5,6-Dimethoxy-2,2-dimethyl-1-(4-hydroxybenzyl)-1,2,3,4-tetrahydroisoquinoline chloride, **b39** *N*-Methylisococlaurine, **b40** Isococlaurine, **b41** Spinosine, **b42**	Luo *et al*., 2000

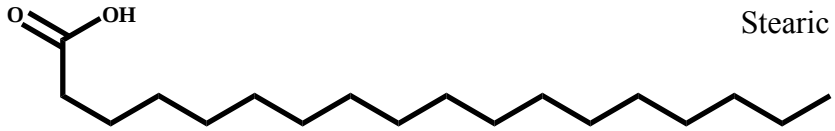
a. Acids



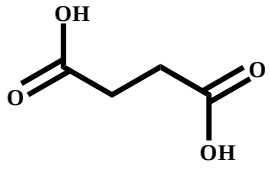
Allantoic acid, **a1**



Benzoic acid, **a2**

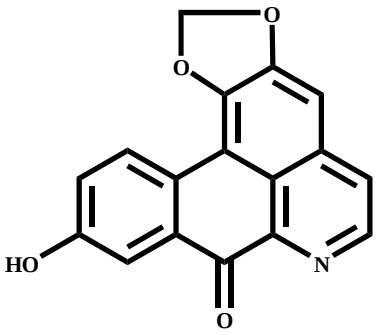


Stearic acid, **a3**

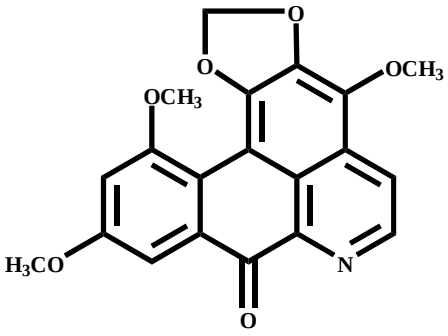


Succinic acid, **a4**

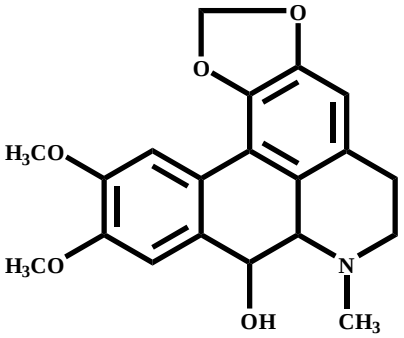
b. Alkaloids



Oxoanolobin, **b1**



3,9,11-Trimethoxy-1,2-methylenedioxyloxoaporphine , **b2**



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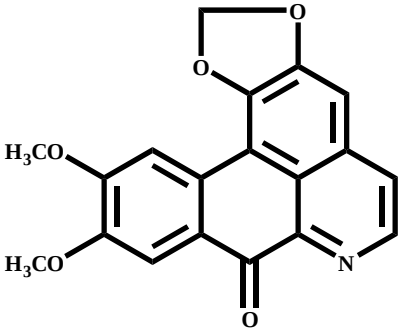

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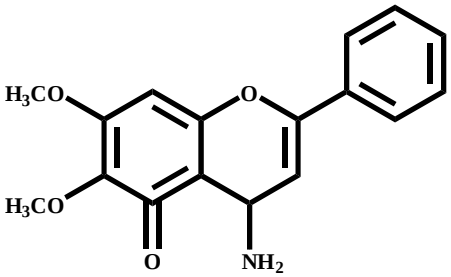

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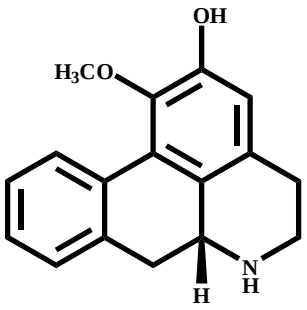
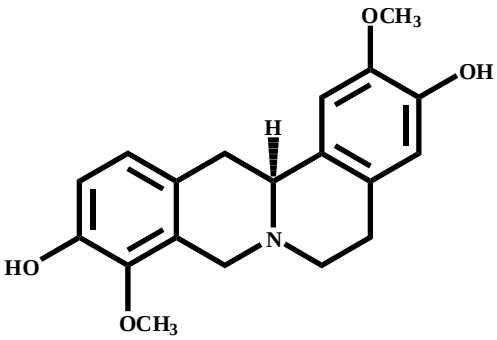


Asimilobine, **b6**



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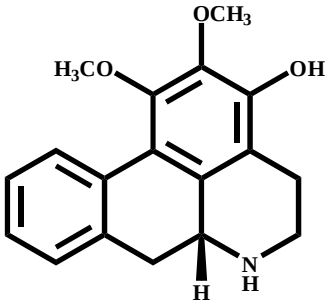
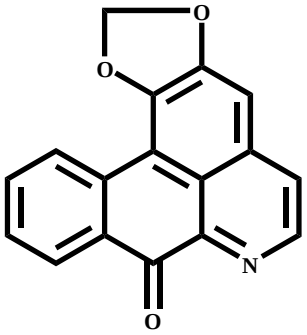


3-Hydroxynornuciferine,

b8



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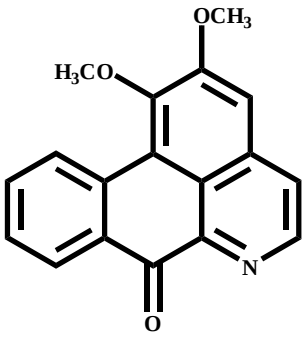

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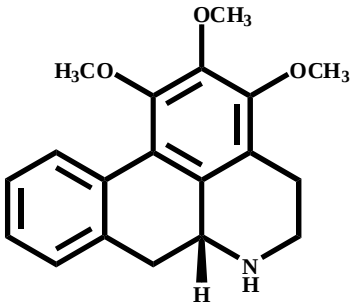
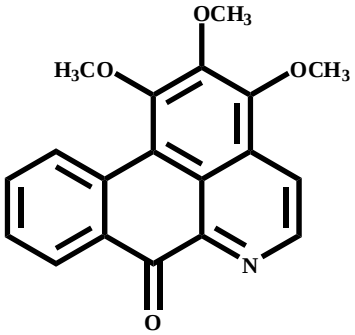
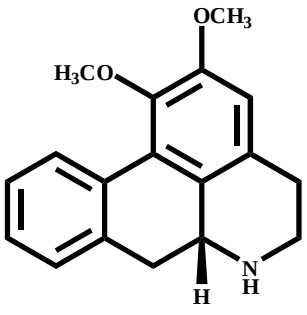


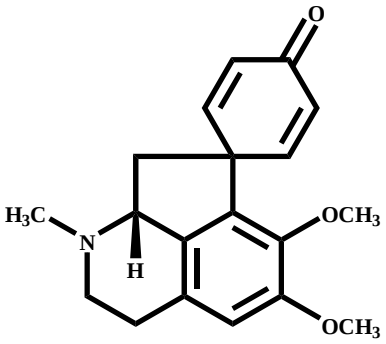
O-Methylisopiline, **b11**



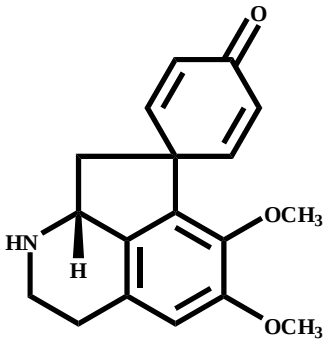
O-Methylmoschatoline, **b12**



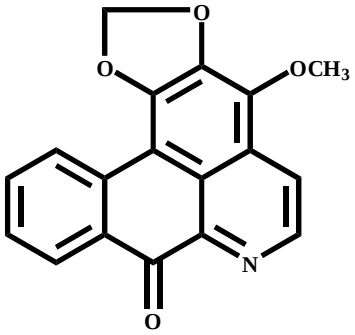
Nornuciferine, **b13**



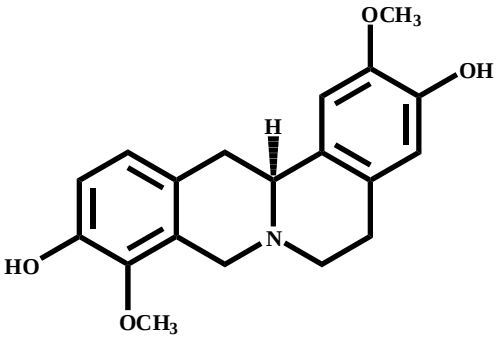
Pronuciferine, **b14**



Stepharine, **b15**



Antherospermidine, **b16**



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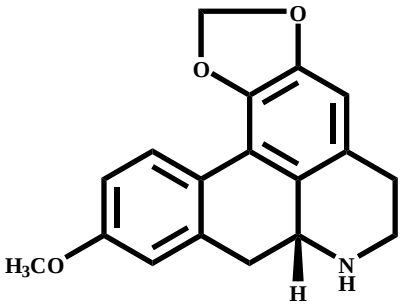

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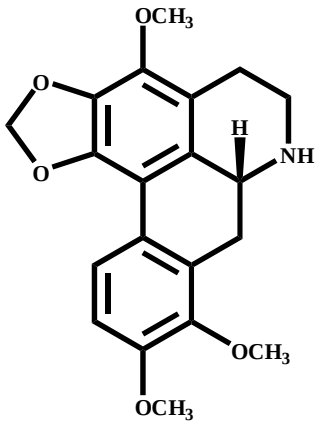
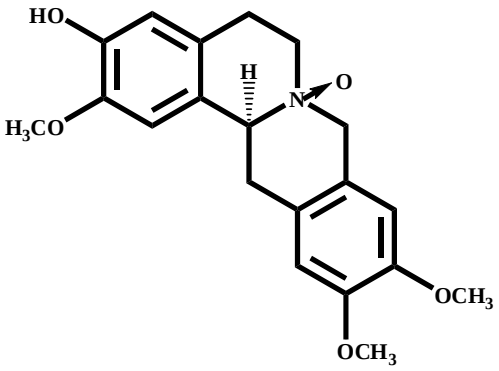
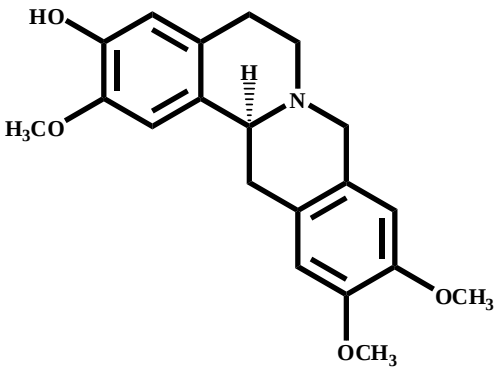


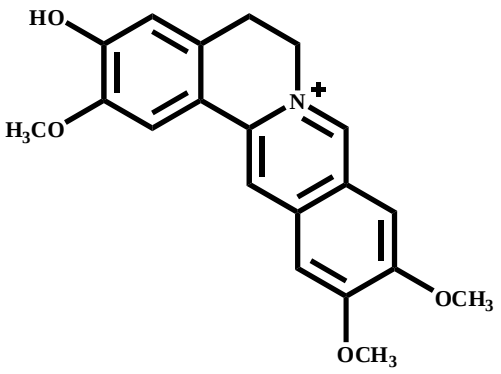
Desmorostratine, **b19**



Discretine-*N*-oxide, **b20**



Discretine, **b21**



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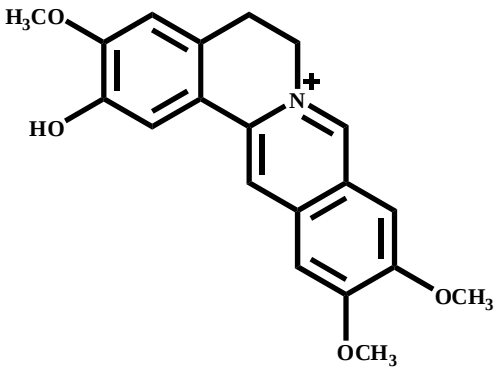

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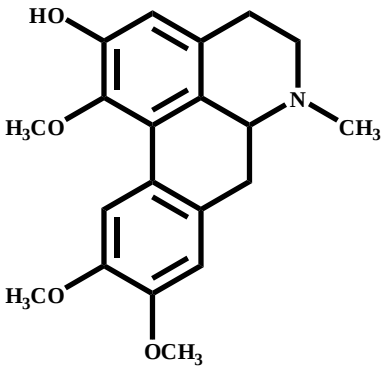
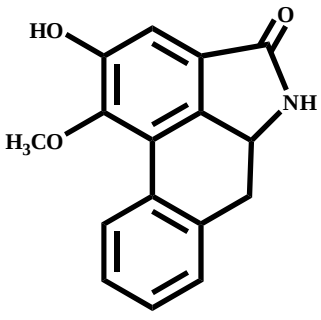
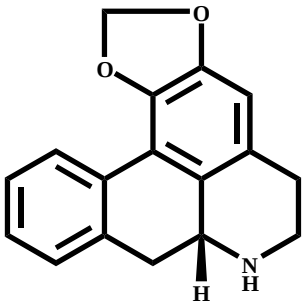


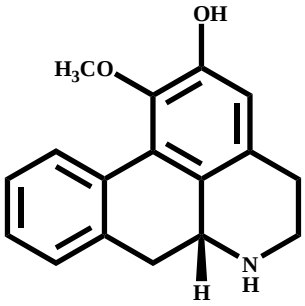
Predicentrine, **b24**



Aristolactam AII, **b25**



Anonaine, **b26**



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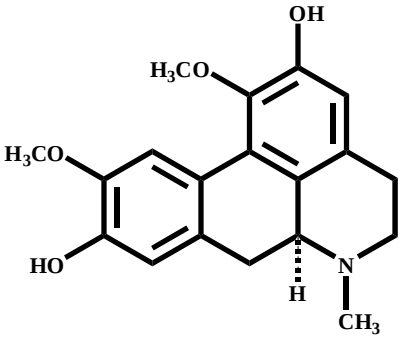

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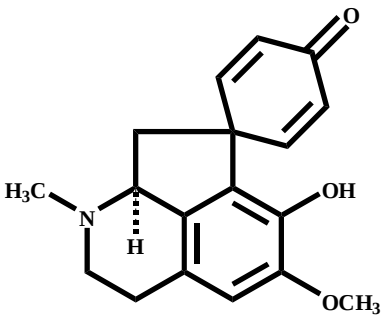

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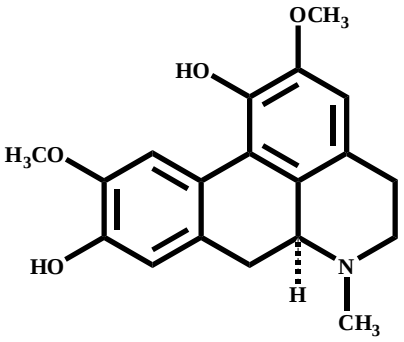

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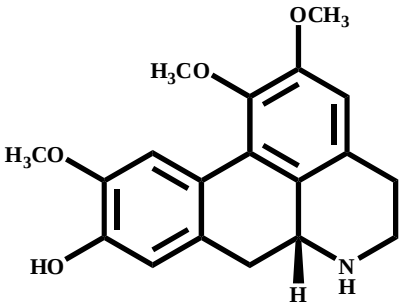

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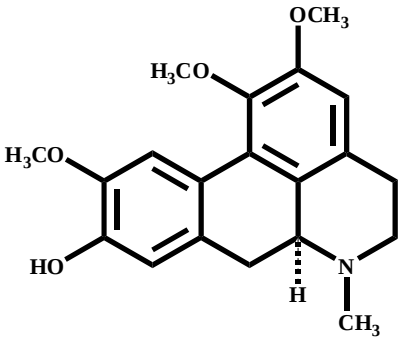
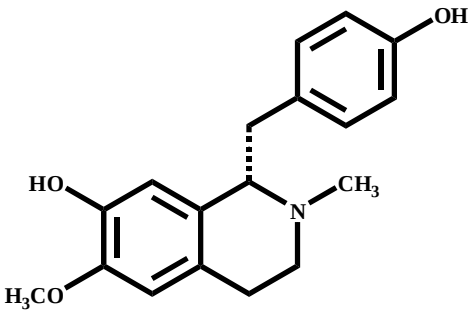


N-Methyllaurotetanine, **b32**



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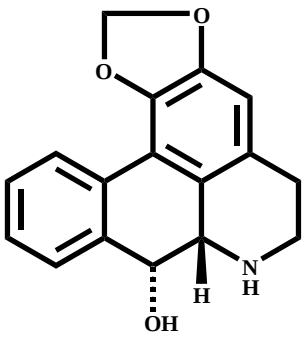
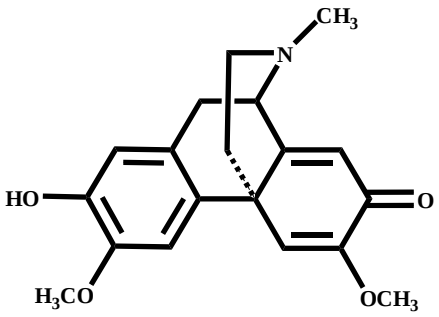
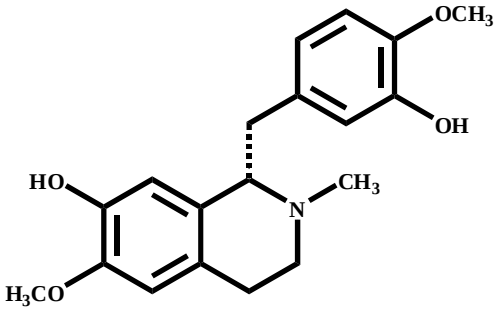


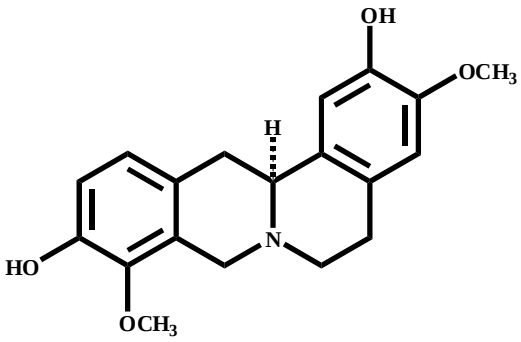
Norushinsunin, **b34**



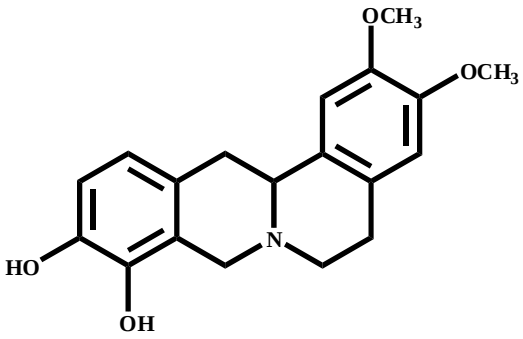
Pallidine, **b35**



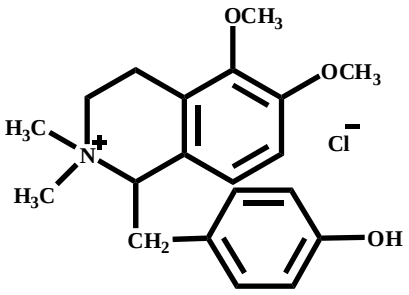
Reticuline, **b36**



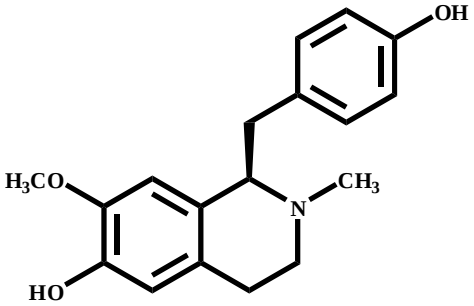
Stepholidine, **b37**



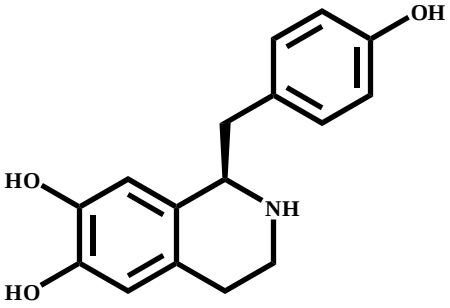
Demethylcorydalmine, **b38**



5,6-Dimethoxy-2,2-dimethyl-1-(4-hydroxybenzyl)-1,2,3,4-tetrahydroisoquinoline chloride, **b39**



N-methylisococlaurine, **b40**



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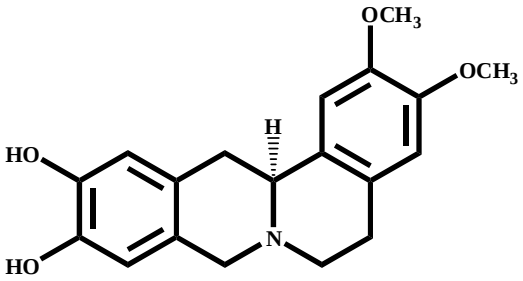
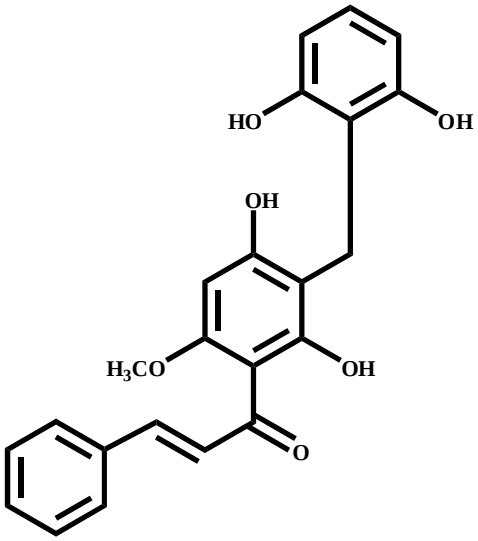
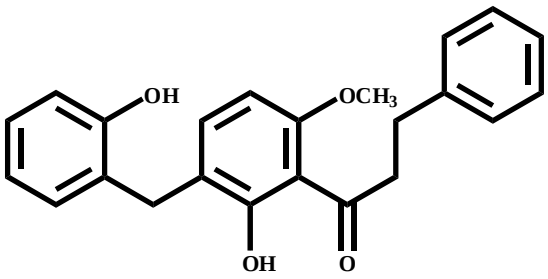


Spinosine, **b42**

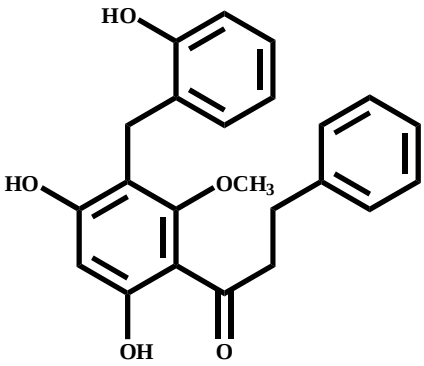
c. Chalcones



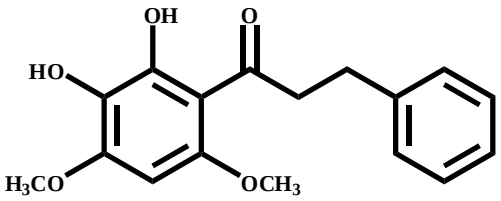
2',4'-Dihydroxy-3'-(2,6-dihydroxybenzyl)-6'-methoxychalcone, **c1**



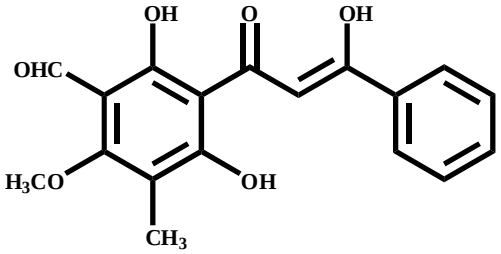
Uvaretin, **c2**



Isouvaretin, **c3**

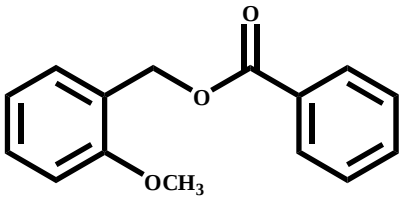


2',3'-Dihydroxy-4',6'-dimethoxydihydrochalcone, **c4**



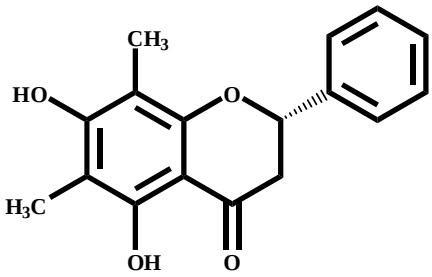
2-Methoxy-3-methyl-4,6-dihydroxy-5-(3′-hydroxy) cinnamoylbenzaldehyde, **c5**

d. Ester

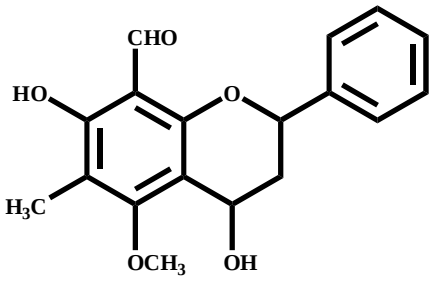


2-Methoxybenzyl benzoate, **d1**

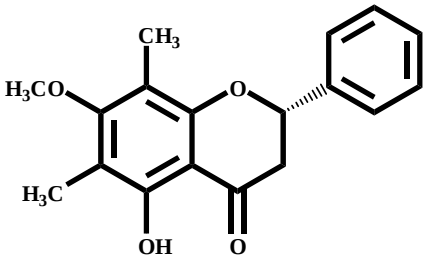
e. Flavonoids



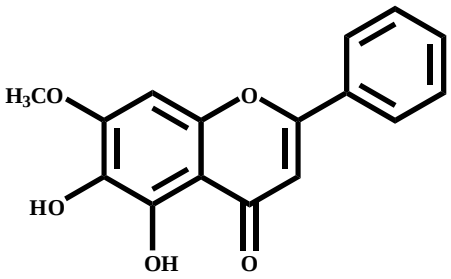
Desmethoxymatteucinol, **e1**



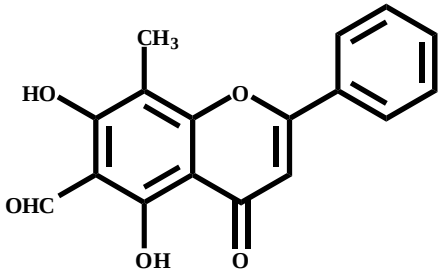
4,7-Dihydroxy-5-methoxy-
6-methyl-8-formylflavane, **e2**



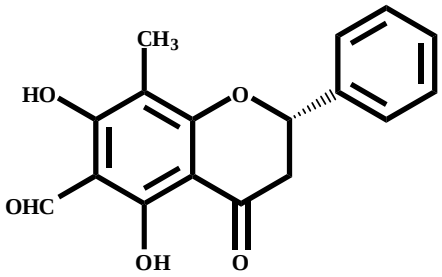
Desmethoxymatteucinol
7-methyl ether, **e3**



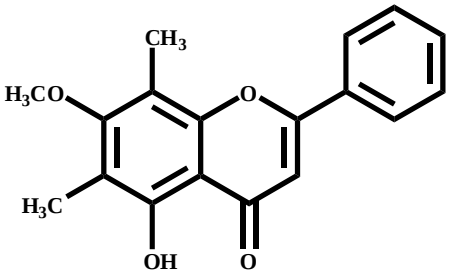
Negletein, **e4**



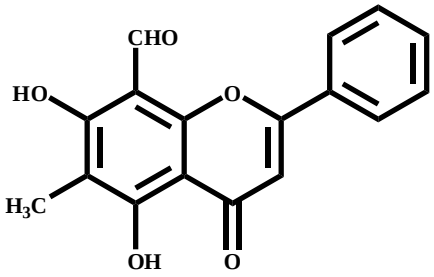
Unonal, **e5**



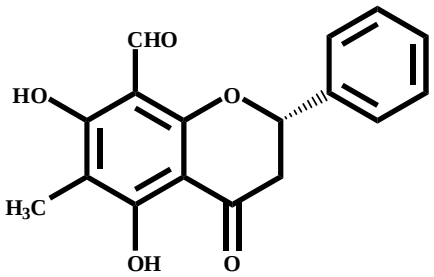
Desmosal, **e6**



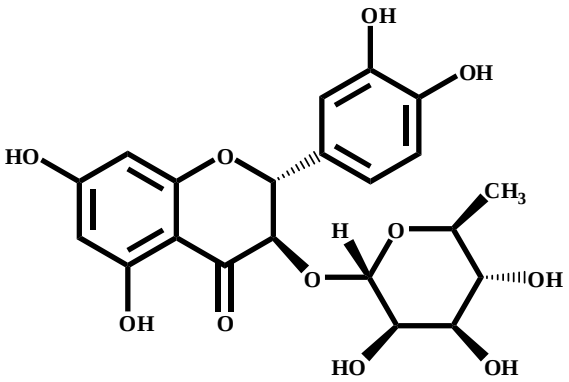
Desmosflavone, **e7**



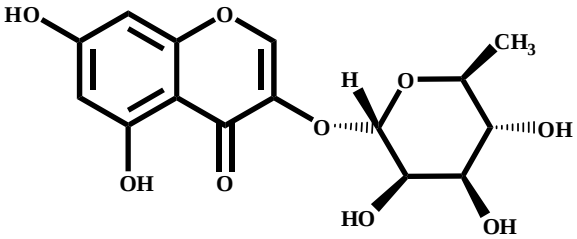
Isounonal, **e8**



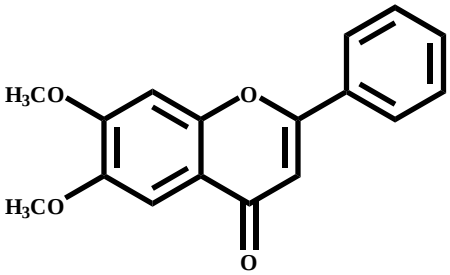
Lawinal, **e9**



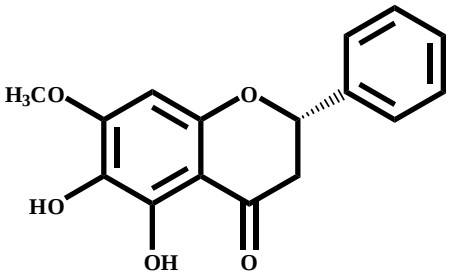
Astilbin, **e10**



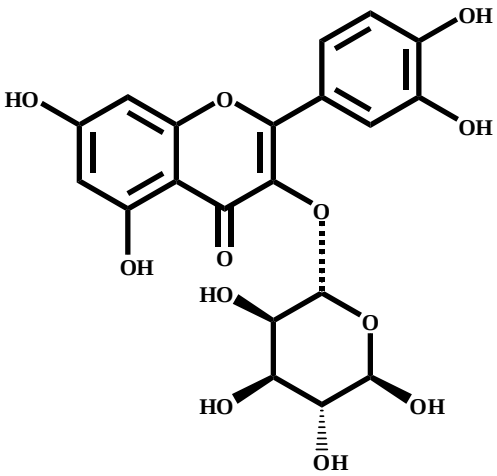
Eucryphin, **e11**



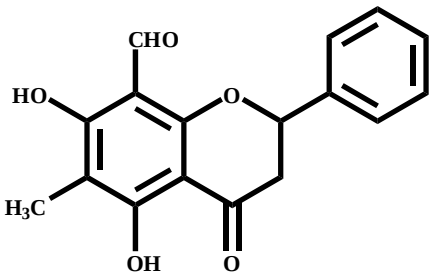
Mosloflavone, **e12**



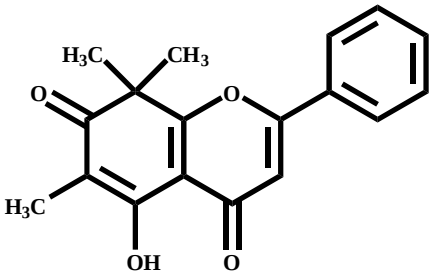
5,6-Dihydroxy-7-methoxy-dihydroflavone, **e13**



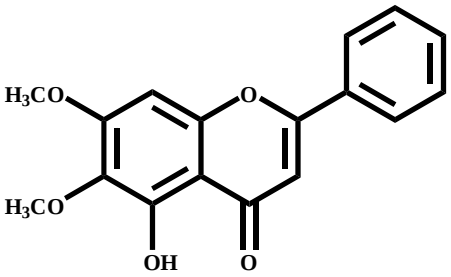
Quercitrin, **e14**



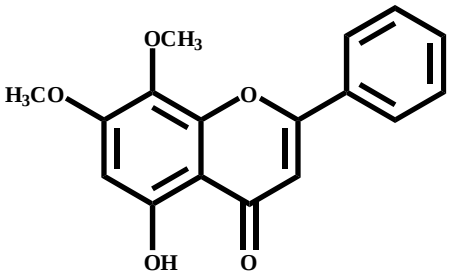
5,7-Dihydroxy-8-formyl-6-methylflavanone, **e15**



5-Hydroxy-7-one-6,8,8-trimethylflavone, **e16**

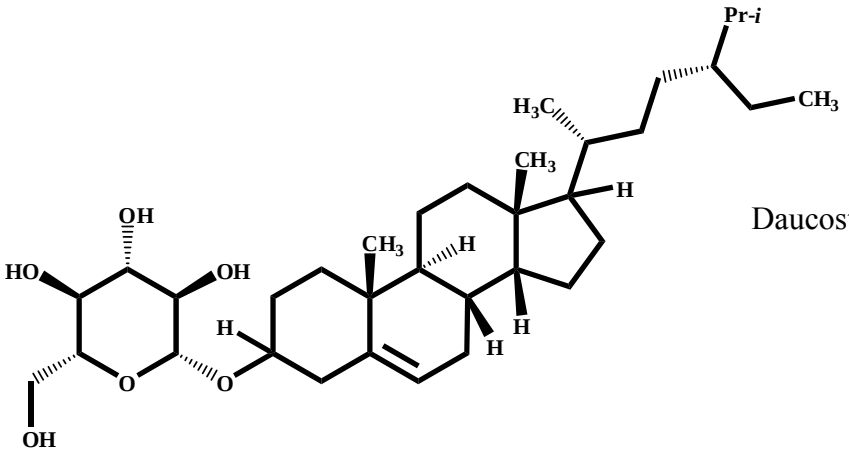


5-Hydroxy-6,7-dimethoxyflavone, **e17**

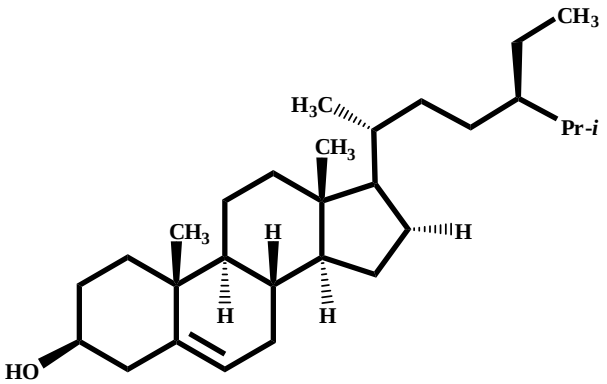


5-Hydroxy-7,8-dimethoxyflavone, **e18**

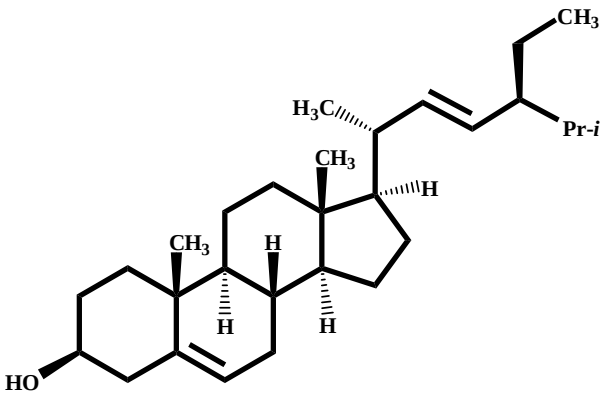
f. Steroids



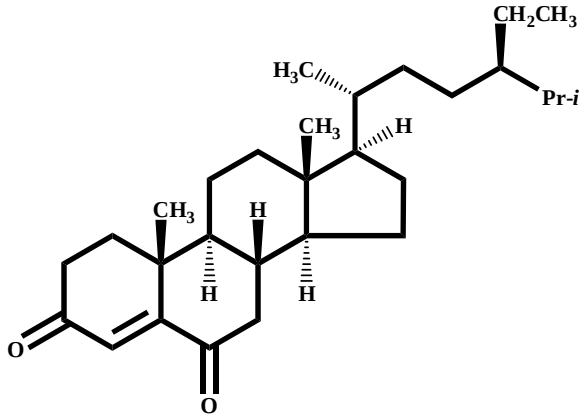
Daucosterol, **f1**



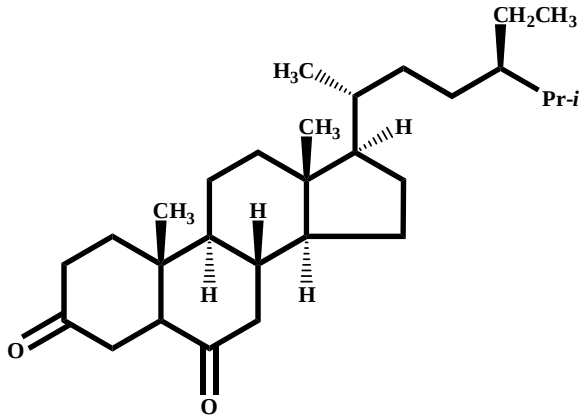
β-Sitosterol, **f2**



Stigmasterol, **f3**

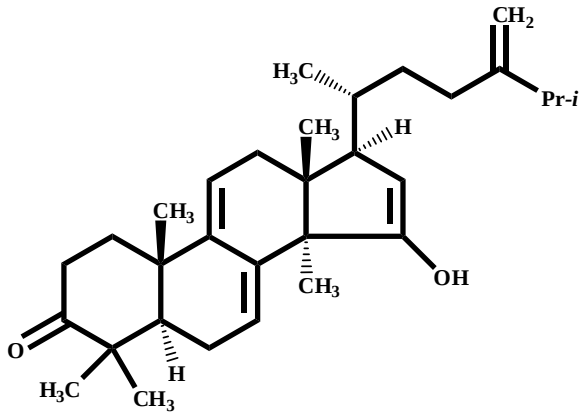


Stigmast-4-ene-3,6-dione, **f4**



Stigmastane-3,6-dione, **f5**

g. **Triterpenoids**



15a-Hydroxy-24-methylenelanosta-7,9(11)-dien-3-one, **g1**

1.3 Objective

This research work involved isolation, purification and structure elucidation of chemical constituents from the leaves of *Desmos chinensis* Lour.

CHAPTER 2
EXPERIMENTAL

2.1 Instruments and Chemicals

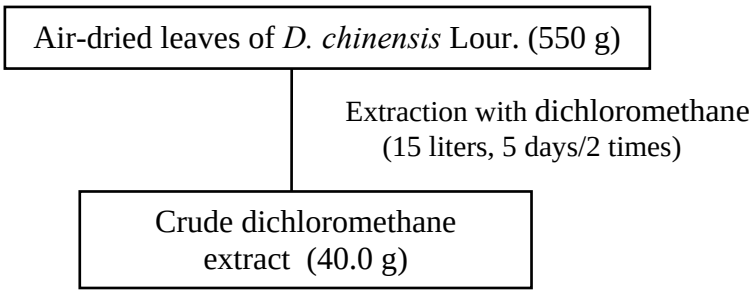
Melting point was recorded in ^{o}C on a digital Electrothermal 9100 Melting Point Apparatus. Ultraviolet spectra were measured with a UV-160A spectrophotometer (SHIMADZU) and principle bands (λ_{max}) were recorded as wavelengths (nm) and log ε in methanol solution. The optical rotation $[\alpha]_D$ was measured in chloroform solution with Sodium D line (590 nm) on a JASCO P-1020 digital polarimeter. The IR spectra were measured with a Perkin-Elmer 783 FTS165 FT-IR spectrophotometer. ^{1}H and ^{13}C – Nuclear magnetic resonance spectra were recorded on a FT-NMR Bruker Ultra Shield^{TM} 300, 500 and 600 MHz spectrometer. Spectra were recorded in deuterochloroform and dimethylsulfoxide-d_6 as δ value in ppm downfield from TMS (internal standard δ 0.00) and coupling constant (*J*) are expressed in hertz. EI and HREI mass spectra were measured on MAT 95 XL Mass spectrometer. Quick column chromatography (QCC) and column chromatography was performed by using silica gel 60 H (Merck) and silica gel 100 (70-230 Mesh ASTM, Merck), respectively. For thin-layer chromatography (TLC), aluminum sheets of silica gel 60 F_{254} (20×20 cm, layer thickness 0.2 mm, Merck) were used for analytical purposes and the compounds were visualized under ultraviolet light. Solvents for extraction and chromatography were distilled at their boiling ranges prior to use except chloroform was analytical grade reagent.

2.2 Plant Material

The leaves of *D.chinensis* Lour. was collected from Krabi province in the southern part of Thailand, in April 2009. Identification was made by Assoc. Prof. Dr. Kitichate Sridith and a specimen (No.T. Rittiwong.) deposited at PSU Herbarium, Department of Biology, Faculty of Science, Prince of Songkla University.

2.3 Extraction and Isolation

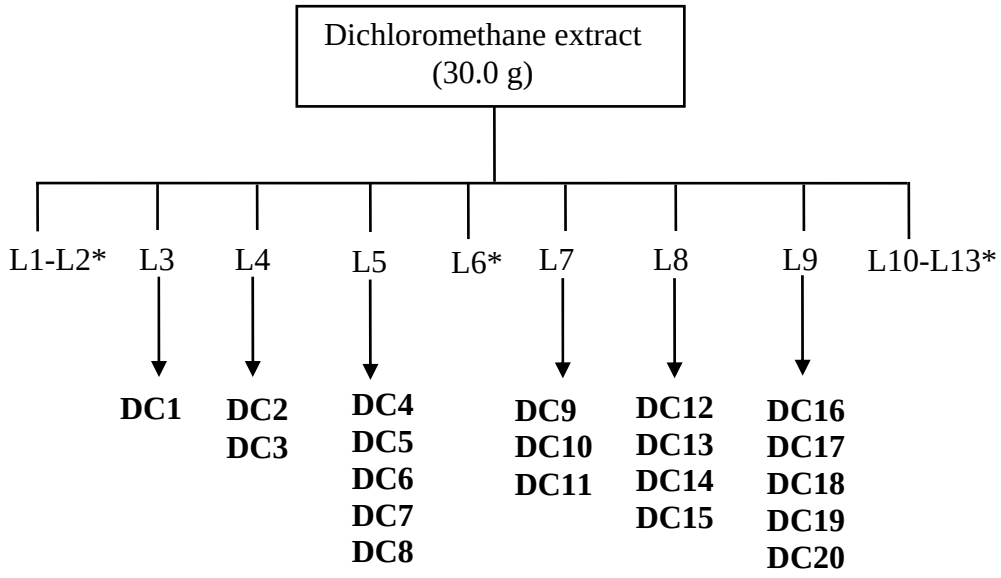
The air-dried leaves of *D. chinensis* Lour. (550 g) were extracted with dichloromethane for 5 days (2 times) at room temperature. The solvent was evaporated under reduced pressure to give concentrated solution of dichloromethane extract as brown residue (40.0 g). The process of extraction was shown in **Scheme 1**.



Scheme 1 Extraction of the leaves of *D. chinensis* Lour.

2.4 Isolation and Chemical Investigation

Dichloromethane extract (30.0 g) was subjected to quick column chromatography using silica gel as stationary phase and eluted with a gradient of hexane-dichloromethane, dichloromethane, dichloromethane-methanol and methanol as eluents. On the basis of their TLC characteristics, the fractions which contained the same major components were combined to give fractions L1-L13. Twenty pure compounds were obtained as shown in **Scheme 2**.



*No further investigation

Scheme 2 Isolation of compounds **DC1-DC20** from the dichloromethane extract

Table 2 Physical characteristics and weights of the fractions from the dichloromethane extract

Fraction	Weight (g)	Physical characteristic
L1	1.6772	orange viscous liquid
L2	3.0001	orange viscous liquid
L3	0.1408	white viscous liquid
L4	2.1483	white viscous liquid
L5	2.1101	red viscous liquid
L6	3.3764	red viscous liquid
L7	2.7282	yellow solid
L8	4.9946	green solid
L9	0.8138	green solid
L10	0.7175	green solid
L11	0.5054	green solid
L12	3.8592	green solid

Table 2 continued

Fraction	Weight (g)	Physical characteristic
L13	2.9282	green solid
Total	28.9998	-

Fraction L3 (0.1408 g) gave **DC1**: benzyl 2-hydroxybenzoate (0.1408 g) as white viscous liquid.

Fraction L4 (2.1483 g) was purified by column chromatography with ethyl acetate-hexane (0.5:9.5) to give **DC2**: benzyl benzoate (0.2421 g) and **DC3**: benzyl 2,6-dihydroxybenzoate (0.1325 g).

Fraction L5 (2.1101 g) was purified by column chromatography with dichloromethane-hexane (3.5:6.5) to afford 8 fractions (5A-5H).

Subfraction 5D (0.3200 g) was purified by column chromatography over silica gel and eluted with ethyl acetate-hexane (0.3:9.7) to afford 5 fractions (5D1-5D5).

Subfraction 5D2 (0.0708 g) was purified by column chromatography over silica gel and eluted with acetone-hexane (1.0:9.0) to afford 6 fractions (5D2A-5D2F).

Subfraction 5D2D (0.0118 g) was further purified on preparative TLC and eluted with dichloromethane-hexane (3.5:6.5) to afford 2 fractions (5D2D1-5D2D2).

Subfraction 5D2D2 (0.0070 g) was further purified on preparative TLC and eluted with ethyl acetate-hexane (0.3:9.7) to give **DC4**: cinnamyl benzoate (0.0018 g).

Subfraction 5D2E (0.0128 g) was further purified on preparative TLC and eluted with ethyl acetate-hexane (0.3:9.7) to afford 4 fractions (5D2E1-5D2E4).

Subfraction 5D2E3 was as colourless viscous liquid of **DC5**: benzyl 2-hydroxy-5-methoxybenzoate (0.0040 g).

Subfraction 5D2E4 was further purified on preparative TLC and eluted with dichloromethane-hexane (3.5:6.5) to give **DC6**: 2-methoxybenzyl benzoate (0.0015 g).

Subfraction 5E (1.1612 g) was purified by column chromatography over silica gel and eluted with ethyl acetate-hexane (0.3:9.7) to afford 7 fractions (5E1-5E7).

Subfraction 5E4 (0.1824 g) was purified by column chromatography over silica gel and eluted with acetone-hexane (1.0:9.0) to give **DC7**: benzyl 2-hydroxy-6-methoxybenzoate (0.0776 g).

Subfraction 5F (0.1626 g) was purified by column chromatography over silica gel and eluted with ethyl acetate-hexane (1.0:9.0) to afford 5 fractions (5F1-5F5).

Subfraction 5F3 (0.1013 g) was purified by column chromatography over silica gel and eluted with ethyl acetate-hexane (0.5:9.5) to afford 7 fractions (5F3A-5F3G).

Subfraction 5F3D (0.0711 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (4.0:6.0) to give **DC8**: phytol (0.0096 g).

Fraction L7 (2.7282 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (1.0:1.0) to afford 8 fractions (7A-7H).

Subfraction 7B (0.1805 g) was purified by column chromatography over silica gel and eluted with ethyl acetate-hexane (1.0:9.0) to give **DC9**: benzyl 2-methoxybenzoate (0.0376 g).

Subfraction 7D (0.5701 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (1.0:1.0) to give **DC10**: isounonal (0.2783 g) and **DC11**: unonal (0.0420 g).

Fraction L8 (4.9946 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (7.0:3.0) to afford 9 fractions (8A-8I).

Subfraction 8F (3.000 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (7.0:3.0) to afford 10 fractions (8F1-8F10).

Subfraction 8F9 (0.1310 g) was purified by column chromatography over silica gel and eluted with dichloromethane to afford 8 fractions (8F9A-8F9H).

Subfraction 8F9D (0.0153 g) was further purified on preparative TLC and eluted with dichloromethane-hexane (9.0:1.0) to give a mixture of **DC12**: 6-formyl-2,5,7-trihydroxy-8-methylflavanone and **DC13**: 8-formyl-2,5,7-trihydroxy-6-methylflavanone (0.0059 g), and **DC14**: benzyl 3-hydroxybenzoate (0.0020 g).

Subfraction 8G (0.8800 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (7.0:3.0) to afford 9 fractions (8G1-8G9).

Subfraction 8G7 (0.0382 g) was purified by column chromatography over silica gel and eluted with acetone-hexane (2.0:8.0) to give **DC15**: 2-methoxybenzoic acid (0.0092 g).

Fraction L9 (0.8138 g) was purified by column chromatography over silica gel and eluted with dichloromethane to afford 8 fractions (9A-9H).

Subfraction 9C (0.0314 g) was purified by column chromatography over silica gel and eluted with dichloromethane-hexane (6.0:4.0) to afford 5 fractions (9C1-9C5).

Subfraction 9C4 (0.0059 g) was further purified on preparative TLC and eluted with dichloromethane-hexane (7.0:3.0) to give **DC16**: (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(5′′,7′′-dihydroxy-8′′-methylflavone) (saiyunensis A) (0.0023 g).

Subfraction 9F (0.0799 g) was purified by column chromatography over silica gel and eluted with dichloromethane to afford 7 fractions (9F1-9F5).

Subfraction 9F2 (0.0374 g) was purified by column chromatography over silica gel and eluted with acetone-hexane (2.5:7.5) to afford 7 fractions (9F2A-9F2G).

Subfraction 9F2E (0.0050 g) was further purified on preparative TLC and eluted with dichloromethane to give **DC17**: saiyunensis B (0.0017 g) and **DC18**: (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(2′′,5′′,7′′-trihydroxy-8′′-methylflavanone) (saiyunensis C) (0.0025 g).

Subfraction 9F5 (0.0135 g) was recrystallized from dichloromethane-hexane (1.0:1.0) to give a yellow solid of **DC19**: matteuorien (0.0077 g).

Subfraction 9G (0.1073 g) was purified by column chromatography over silica gel and eluted with acetone-hexane (2.0:8.0) to afford 8 fractions (9G1-9G8).

Subfraction 9G5 (0.0148 g) was further purified on preparative TLC and eluted with ethyl acetate-hexane (2.0:8.0) to afford 5 fractions (9G5A-9G5E).

Subfraction 9G5A (0.0047 g) was further purified on preparative TLC and eluted with methanol-dichloromethane to give **DC20**: saiyunensis D (0.0016 g).

Compound DC1: Benzyl 2-hydroxybenzoate, white viscous liquid; UV λ_{max} (MeOH) (log ε): 203 (4.57), 239 (3.76) and 309 (3.38) nm; IR (Neat) ν (cm^{-1}): 3200 (O-H stretching), 1685 (C=O stretching), 1557 and 1485 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 3.

Compound DC2: Benzyl benzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 229 (4.24), 268 (3.50) and 273 (3.46) nm; IR (Neat) ν (cm^{-1}): 1716 (C=O stretching), 1602 and 1496 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 4.

Compound DC3: Benzyl 2,6-dihydroxybenzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 202 (4.02), 254 (3.38) and 325 (3.88) nm; IR (Neat) ν (cm^{-1}): 3443 (O-H stretching), 1670 (C=O stretching), 1578 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 5.

Compound DC4: Cinnamyl benzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 245 (4.31), 281 (3.36) and 292 (3.05) nm; IR (Neat) ν (cm^{-1}): 1716 (C=O stretching), 1550 and 1455 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 6.

Compound DC5: Benzyl 2-hydroxy-5-methoxybenzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 212 (4.21), 253 (3.75) and 316 (3.31) nm; IR (Neat) ν (cm^{-1}): 3034 (O-H stretching), 1680 (C=O stretching), 1614 and 1445 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 7.

Compound DC6: 2-Methoxybenzyl benzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 201 (4.19), 222 (4.02) and 272 (3.34) nm; IR (Neat) ν (cm^{-1}): 1720 (C=O stretching), 1603 and 1496 (aromatics). For ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectral data, see Table 8.

Compound DC7: Benzyl 2-hydroxy-6-methoxybenzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 212 (4.17), 255 (3.79) and 316 (3.31) nm; IR (Neat) ν (cm^{-1}): 3034 (O-H stretching), 1660 (C=O stretching), 1614 and 1455 (aromatics).

For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 9.

Compound DC8: Phytol, colourless viscous liquid, $[\alpha]_D^{25} = -1.3°$ (c = 1.00, $CHCl_3$); UV λ_{max} (MeOH) (log ε): 203 (3.90) and 236 (2.85) nm; IR (Neat) ν (cm^{-1}): 3389 (OH stretching), 1669 (double bond). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 10.

Compound DC9: Benzyl 2-methoxybenzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 234 (4.53), 220 (4.45) and 294 (4.15) nm; IR (Neat) ν (cm^{-1}): 1725 (C=O stretching), 1600 and 1491 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 11.

Compound DC10: 6-Methyl-5,7-dihydroxy-8-formylflavone (isounonal), a pale yellow solid, m.p. 144-145°C; UV λ_{max} (MeOH) (log ε): 253 (4.12), 302 (3.99) and 227 (3.99) nm; IR (KBr) ν (cm^{-1}): 3494 (O-H stretching), 1655, 1625 (C=O stretching), 1559 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 12.

Compound DC11: 6-Formyl-5,7-dihydroxy-8-methylflavone (unonal), yellow solid, m.p. 125-126°C; UV λ_{max} (MeOH) (log ε): 289 (4.26), 204 (3.96) and 221 (3.96) nm; IR (KBr) ν (cm^{-1}): 3472 (O-H stretching), 1650 (C=O stretching), 1589 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 13.

Compound DC12: 6-Formyl-2,5,7-trihydroxy-8-methylflavanone, a pale yellow solid, m.p. 164-165°C, $[\alpha]_D^{25} = +3.1°$ (c = 1.00, $CHCl_3$); UV λ_{max} (MeOH) (log ε): 272 (4.37), 236 (3.91) and 343 (3.75) nm; IR (Neat) ν (cm^{-1}): 3341 (O-H stretching), 1630 (C=O stretching), 1546 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 14.

Compound DC13: 8-Formyl-2,5,7-trihydroxy-6-methylflavanone (desmal), a pale yellow solid, m.p. 164-165°C, $[\alpha]_D^{25}$ = +3.1° (*c* = 1.00, $CHCl_3$); UV λ_{max} (MeOH) (log ε): 272 (4.37), 236 (3.91) and 343 (3.75) nm; IR (Neat) ν (cm^{-1}): 3341 (O-H stretching), 1630 (C=O stretching), 1546 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 15.

Compound DC14: Benzyl 3-hydroxybenzoate, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 203 (4.57), 239 (3.76) and 309 (3.38) nm; IR (Neat) ν (cm^{-1}): 3368 (O-H stretching), 1716 (C=O stretching), 1698 and 1455 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 16.

Compound DC15: 2-Methoxybenzoic acid, colourless viscous liquid; UV λ_{max} (MeOH) (log ε): 204 (4.45) and 281 (3.36) nm; IR (Neat) ν (cm^{-1}): 3450 (O-H stretching), 1722 (C=O stretching), 1603 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 17.

Compound DC16: (8-Formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(5′′,7′′-dihydroxy-8′′-methylflavone), (Saiyunensis A), a pale yellow solid, m.p. 229-230 °C; UV λ_{max} (MeOH) (log ε): 203 (4.19), 248 (3.94) and 281 (4.06) nm; IR (KBr) ν (cm^{-1}): 3494 (O-H stretching), 1655 (C=O stretching). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 18.

Compound DC17: Saiyunensis B, a pale yellow solid, m.p. 190-191 °C; UV λ_{max} (MeOH) (log ε): 203 (3.86), 274 (3.73) and 485 (2.63) nm; IR (KBr) ν (cm^{-1}): 3447 (O-H stretching), 1739, 1633 (C=O stretching), 1542 (aromatics). For ^1H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHz) spectral data, see Table 19.

Compound DC18: (8-Formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6′′-(2′′,5′′,7′′-trihydroxy-8′′-methylflavanone), (Saiyunensis C), a pale yellow solid, m.p. 199-200 °C, $[\alpha]_D^{25}$ = +1.4° (*c* = 1.00, $CHCl_3$); UV λ_{max} (MeOH) (log ε): 203 (4.40), 294 (4.18) and 430 (2.37) nm; IR (KBr) ν (cm^{-1}): 3341 (O-H stretching), 1630

(C=O stretching). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 20.

Compound DC19: 5,7-Dihydroxy-6,8-dimethylflavone (matteuorien), a pale yellow solid, m.p. 180-181 °C; UV λ_{max} (MeOH) (log ε): 204 (4.90), 278 (4.20) and 321 (4.77) nm; IR (KBr) ν (cm^{-1}): 3494 (O-H stretching), 1655 (C=O stretching), 1487 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 21.

Compound DC20: Saiyunensis D, a pale yellow solid, m.p. 180-182 °C; UV λ_{max} (MeOH) (log ε): 203 (3.62), 278 (3.11) and 413 (1.67) nm; IR (KBr) ν (cm^{-1}): 3439 (O-H stretching), 1720, 1643 (C=O stretching), 1542 (aromatics). For ^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150 MHz) spectral data, see Table 22.

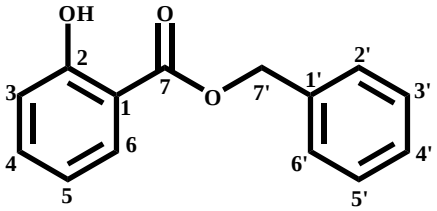
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Structure elucidation of compounds from the leaves of *D. chinensis*

The crude dichloromethane extract from the leaves of *D. chinensis* was subjected to quick column chromatography and repeated column chromatography over silica gel to furnish twenty compounds: benzyl 2-hydroxybenzoate **(DC1)**, benzyl benzoate **(DC2)**, benzyl 2,6-dihydroxybenzoate **(DC3)**, cinnamyl benzoate **(DC4)**, benzyl 2-hydroxy-5-methoxybenzoate **(DC5)**, 2-methoxybenzyl benzoate **(DC6)**, benzyl 2-hydroxy-6-methoxybenzoate **(DC7)**, phytol **(DC8)**, benzyl 2-methoxybenzoate **(DC9)**, isounonal **(DC10)**, unonal **(DC11)**, 6-formyl-2,5,7-trihydroxy-8-methylflavanone **(DC12)**, desmal **(DC13)**, benzyl 3-hydroxybenzoate **(DC14)**, 2-methoxybenzoic acid **(DC15)**, saiyunensis A **(DC16)**, saiyunensis B **(DC17)**, saiyunensis C **(DC18)**, matteuorien **(DC19)** and saiyunensis D **(DC20)**.

Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data: ^{1}H, ^{13}C NMR, DEPT 135°, DEPT 90°, HMQC, HMBC and COSY. Mass spectra were determined for the new compounds: **DC16-DC18** and **DC20**. The physical data of the known compounds were also compared with the reported values.

Compound DC1



DC1 was obtained as white viscous liquid. Its IR spectrum revealed hydroxyl (3200 cm^{-1}), ester carbonyl (1685 cm^{-1}) and aromatic ring (1557 and 1485 cm^{-1}).

The ^{1}H NMR spectrum of **DC1** showed the signals of one oxymethylene protons at δ 5.42, (2H, *s*, H-7') and nine aromatic protons at δ 6.87 (1H, *t*, *J* = 7.5 Hz, H-5), δ 6.98 (1H, *d*, *J* = 8.3 Hz, H-3), δ 7.45-7.37 (6H, *m*, H-4, H-2', H-3', H-4', H-5', H-6') and δ 7.89 (1H, *dd*, *J* = 7.5, 3.0 Hz, H-6) of which five (δ 7.45-7.37) showed the coupling pattern of a monosubstituted phenyl ring. Additionally, the ^{1}H NMR spectrum disclosed a singlet signal of a chelated hydroxyl group at δ 10.84 (2-OH). The ^{13}C NMR indicated the presence of 14 carbons including one ester carbonyl (δ 169.8), one methylene (δ 66.8) and two aromatic rings. The HMBC spectrum showed correlations between oxymethylene protons H_2-7' (δ 5.42) and C-7 (δ 169.8), C-1' (δ 135.2) and C-2'/6' (δ 128.1); aromatic proton H-6 (δ 7.89) and C-2 (δ 161.7), C-4 (δ 135.7) and C-7 (δ 169.8), confirming that the methylene group was connected to C-1' of the aromatic ring while the carbonyl group was connected to the other aromatic ring. The location of the hydroxyl group at C-2 was assigned by HMBC correlations between the hydroxyl proton 2-OH (δ 10.84) and C-1 (δ 112.3), C-2 (δ 161.7) and C-3 (δ 117.5). The structure of compound **DC1** was identified as benzyl 2-hydroxybenzoate, (Kodpinid *et al*., 1983).

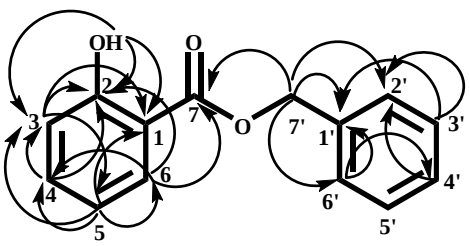


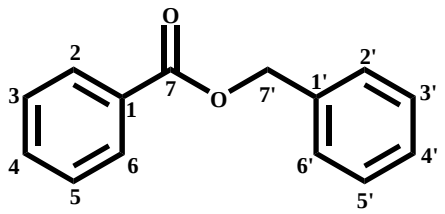
Figure 2 Selected HMBC correlations of **DC1**

Table 3 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC1** and benzyl 2-hydroxybenzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC1[a]	**R**[b]	**DC1**[c]	
1	-	-	112.3 (C)	-
2	-	-	161.7 (C)	-
3	6.98 (d, J = 8.3 Hz)	7.51-6.81 (m)	117.5 (CH)	C-1, C-2, C-5
4	7.45-7.37 (m)	7.51-6.81 (m)	135.7 (CH)	C-2, C-3
5	6.87 (t, J = 7.5 Hz)	7.51-6.81 (m)	119.1 (CH)	C-1, C-3, C-4, C-6
6	7.89 (dd, J = 7.5, 3.0 Hz)	7.86 (dd, J = 8.0, 2.0 Hz)	129.9 (CH)	C-2, C-4, C-7
7	-	-	169.8 (C)	-
1′	-	-	135.2 (C)	-
2′, 6′	7.45-7.37 (m)	7.38 (s)	128.1 (CH)	C-4′, C-7′
3′, 5′	7.45-7.37 (m)	7.38 (s)	128.6 (CH)	C-1′, C-2′, C-6′
4′	7.45-7.37 (m)	7.38 (s)	128.4 (CH)	C-2′
7′	5.42 (s)	5.35 (s)	66.8 (CH_2)	C-7, C-1′, C-2′, C-6′
2-OH	10.84 (s)	10.73 (s)	-	C-1, C-2, C-3

[a]300 MHz, [b]60 MHz, [c]75 MHz

Compound DC2



DC2 was obtained as colourless viscous liquid. Its IR spectrum revealed ester carbonyl (1716 cm^{-1}), and aromatic ring (1602 and 1496 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC2** were similar to those of **DC1**, except for the appearance of an additional aromatic proton signal at δ 8.00 (*d*, *J* = 7.3 Hz, H-2) instead of the singlet signal of the hydroxyl group due to 2-OH in **DC1**. These suggested the presence of two monosubstituted phenyl rings. Therefore the structure of compound **DC2** was identified as benzyl benzoate, (Kodpinid *et al*., 1983).

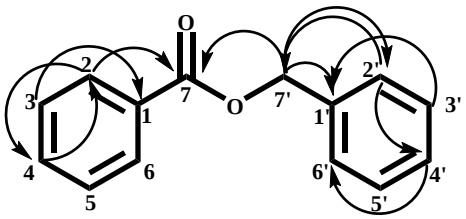
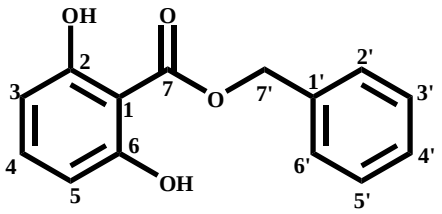


Figure 3 Selected HMBC correlations of **DC2**

Table 4 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC2** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	129.8 (C)	-
2, 6	8.00 (d, J = 7.3 Hz)	129.3 (CH)	C-4, C-7
3, 5	7.39-7.26 (m)	128.2 (CH)	C-1
4	7.50 (t, J = 7.3 Hz)	132.5 (CH)	C-2, C-6
7	-	165.7 (C)	-
1′	-	135.8 (C)	-
2′, 6′	7.39-7.26 (m)	127.7 (CH)	C-4′, C-7′
3′, 5′	7.39-7.26 (m)	127.9 (CH)	C-1′
4′	7.39-7.26 (m)	127.8 (CH)	C-2′, C-6′
7′	5.29 (s)	66.2 (CH_2)	C-7, C-1′, C-2′, C-6′

Compound DC3



DC3 was obtained as colourless viscous liquid. Its IR spectrum revealed hydroxyl (3443 cm^{-1}), ester carbonyl (1670 cm^{-1}) and aromatic ring (1578 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC3** were similar to those of **DC1**, except for the disappearance of the signal of an aromatic proton at δ 7.89 (H-6) and the appearance of the hydroxyl broad singlet signal at δ 9.60 (2H, 2,6-OH), indicating a 1,2,6-trisubstituted symmetrical aromatic ring as evidenced from the signals at δ 7.17 (1H, *t*, *J* = 8.3 Hz, H-4) and 6.35 (2H, *d*, *J* = 8.3 Hz, H-3, H-5). The positions of the substituents were confirmed from HMBC spectrum which showed the correlations between aromatic protons H-3/H-5 (δ 6.35) and C-1 (δ 99.9), C-2/C-6 (δ 160.9) and from the correlations of an aromatic proton H-4 (δ 7.17) with C-2/C-6 (δ 160.9) and C-3/C-5 (δ 108.2). The structure of compound **DC3** was identified as benzyl 2,6-dihydroxybenzoate, (Kodpinid *et al*., 1983).

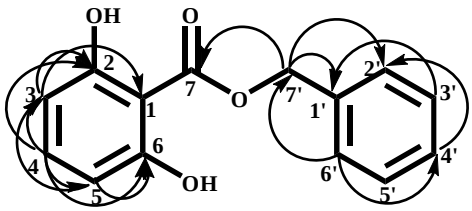


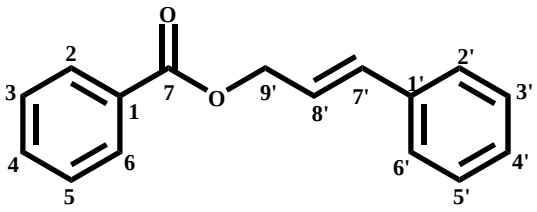
Figure 4 Selected HMBC correlations of **DC3**

Table 5 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC3** and benzyl 2,6-dihydroxybenzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC3[a]	**R**[b]	**DC3**[c]	
1	-	-	99.9 (C)	-
2, 6	-	-	160.9 (C)	-
3, 5	6.35 (d, J = 8.3 Hz)	6.28 (d, J = 8.0 Hz)	108.2 (CH)	C-1, C-2, C-6
4	7.17 (t, J = 8.3 Hz)	7.07 (t, J = 8.0 Hz)	136.6 (CH)	C-2, C-3, C-5, C-6
7	-	-	169.4 (C)	-
1′	-	-	133.8 (C)	-
2′, 6′	7.30-7.29 (m)	7.32 (s)	128.6 (CH)	C-4′, C-7′
3′, 5′	7.30-7.29 (m)	7.32 (s)	129.0 (CH)	C-1′
4′	7.30-7.29 (m)	7.32 (s)	129.2 (CH)	C-2′, C-6′
7′	5.34 (s)	5.38 (s)	68.1 (CH_2)	C-7, C-1′, C-2′, C-6′
2,6-OH	9.60 (br s)	9.40 (s)	-	-

[a]300 MHz, [b]60 MHz, [c]75 MHz

Compound DC4



DC4 was obtained as colourless viscous liquid. Its IR spectrum revealed ester carbonyl (1716 cm^{-1}) and aromatic ring (1550 and 1455 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC4** showed the signals similar to those of **DC2**, except for the additional signals of an AB system of two olefinic protons at δ 6.77 (1H, *d*, *J* = 15.9 Hz, H-7′) and 6.43 (1H, *dt*, *J* = 15.9, 6.3 Hz, H-8′). The large coupling constant (*J* = 15.9 Hz) between H-7′ and H-8′ indicated a *trans* configuration of the double bond. The spectral data suggested a cinnamyl group connecting to an oxygen of a benzoate group as showed from the HMBC correlations of oxymethylene protons H_2-9′ (δ 5.01) to C-7 (δ 166.3), C-7' (δ 134.3) and C-8' (δ 123.3). The structure of compound **DC4** was identified as cinnamyl benzoate, (Correria *et al*., 2001).

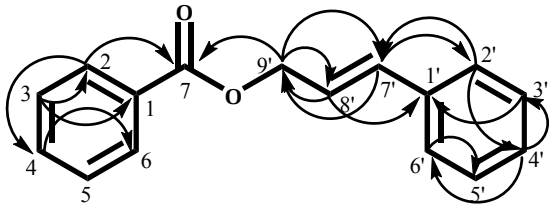


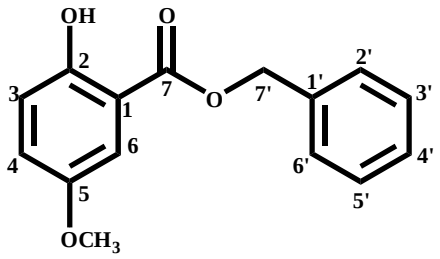
Figure 5 Selected HMBC correlations of **DC4**

Table 6 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC4** ($CDCl_3$) and cinnamyl benzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC4[a]	**R**[b]	**DC4**[c]	
1	-	-	130.3 (C)	-
2, 6	8.11 (dd, *J* = 7.1, 1.5 Hz)	8.09 (d, *J* = 7.9 Hz)	129.6 (CH)	C-4, C-7
3, 5	7.50-7.43 (m)	7.59-7.22 (m)	128.4 (CH)	C-1, C-2, C-6
4	7.59 (dt, *J* = 7.4, 1.5 Hz)	7.59-7.22 (m)	133.0 (CH)	C-2, C-6
7	-	-	166.3 (C)	-
1′	-	-	136.3 (C)	-
2′, 6′	7.50-7.43 (m)	7.59-7.22 (m)	126.6 (CH)	C-3′, C-4′, C-5′, C-7′
3′, 5′	7.38-7.30 (m)	7.59-7.22 (m)	128.6 (CH)	C-1′
4′	7.38-7.30 (m)	7.59-7.22 (m)	128.1 (CH)	C-2′, C-6′
7′	6.77 (d, *J* = 15.9 Hz)	6.74 (d, *J* = 15.9 Hz)	134.3 (CH)	C-2′, C-6′, C-9′
8′	6.43 (dt, *J* = 15.9, 6.3 Hz)	6.41 (dt, *J* = 15.9, 6.4 Hz)	123.3 (CH)	C-1′, C-9′
9′	5.01 (dd, *J* = 6.3, 1.2 Hz)	4.98 (d, *J* = 6.4 Hz)	65.5 (CH_2)	C-7, C-7′, C-8′

[a]300 MHz, [b]400 MHz, [c]75 MHz

Compound DC5



DC5 was obtained as colourless viscous liquid. Its IR spectrum revealed hydroxyl (3034 cm^{-1}), ester carbonyl (1680 cm^{-1}) and aromatic ring (1614 and 1445 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC5** were similar to those of **DC3**, except for the appearance of an additional methoxyl singlet signal at δ 3.77 (5-OCH_3) and the disappearance of the signal of an aromatic proton at δ 6.35 (H-5), indicating a 1,2,4-trisubstituted aromatic ring. In the HMBC spectrum, the hydroxyl proton at δ 10.36 (2-OH) correlated with C-2 (δ 156.3), C-1 (δ 111.9) and C-3 (δ 118.6) and the methoxyl protons at δ 3.77 (5-OCH_3) correlated with C-5 (δ 152.1) as well as the correlations of H-4 (δ 7.09) with C-2 (δ 156.3), C-5 (δ 152.1) and C-6 (δ 112.4) and of H-3 (δ 6.92) with C-5 (δ 152.1) and C-1 (δ 111.9), resulting in the assignment of a hydroxyl group at C-2 and a methoxyl group at C-5, respectively. The structure of compound **DC5** was identified as benzyl 2-hydroxy-5-methoxybenzoate, (Kodpinid *et al*., 1983).

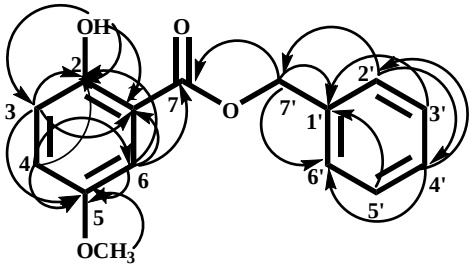


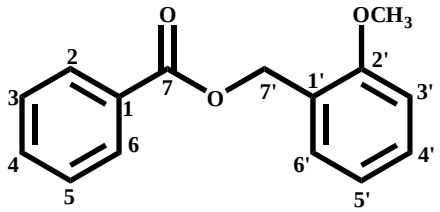
Figure 6 Selected HMBC correlations of **DC5**

Table 7 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC5** and benzyl 2-hydroxy-5-methoxybenzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC5[a]	**R**[b]	**DC5**[c]	
1	-	-	111.9 (C)	-
2	-	-	156.3 (C)	-
3	6.92 (d, J = 9.1 Hz)	7.40-6.66 (m)	118.6 (CH)	C-1, C-2, C-5
4	7.09 (dd, J = 9.1, 3.2 Hz)	7.40-6.66 (m)	123.9 (CH)	C-2, C-5, C-6
5	-	-	152.1 (C)	-
6	7.33 (d, J = 3.2 Hz)		112.4 (CH)	C-1, C-2, C-4, C-5, C-7
7	-	-	169.7 (C)	-
1′	-	-	135.4 (C)	-
2′, 6′	7.47-7.36 (m)	7.30 (s)	128.3 (CH)	C-4′, C-7′
3′, 5′	7.47-7.36 (m)	7.30 (s)	128.7 (CH)	C-1′
4′	7.47-7.36 (m)	7.30 (s)	128.6 (CH)	C-2′, C-6′
7′	5.39 (s)	5.26 (s)	67.0 (CH_2)	C-7, C-1′, C-2′, C-6′
2-OH	10.36 (s)	10.18 (s)	-	C-1, C-2, C-3
5-OCH_3	3.77 (s)	3.67 (s)	55.9 (OCH_3)	C-5

[a]300 MHz, [b]60 MHz, [c]75 MHz

Compound DC6



DC6 was obtained as colourless viscous liquid. Its IR spectrum revealed ester carbonyl (1720 cm^{-1}), and aromatic ring (1603 and 1496 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC6** were similar to those of **DC2**, except for the appearance of the methoxyl singlet signal at δ 3.87 (2′-OCH_3). The location of the methoxyl group at C-2′ was assigned by HMBC correlations of the methoxyl protons at δ 3.87 (2′-OCH_3) to the carbon at δ 157.4 (C-2′), as well as the correlations of H-6′ (δ 7.54-7.52), H-4′ (δ 7.32) and H-7′ (δ 5.42) to the carbon at δ 157.4 (C-2′). The structure of compound **DC6** was identified as 2-methoxybenzyl benzoate, (Kodpinid *et al*., 1983).

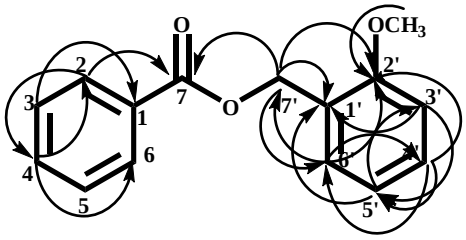


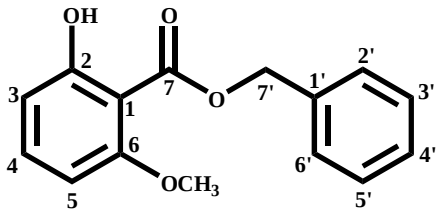
Figure 7 Selected HMBC correlations of **DC6**

Table 8 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC6** and 2-methoxybenzyl benzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC6[a]	**R**[b]	**DC6**[c]	
1	-	-	130.5 (C)	-
2, 6	8.09 (d, J = 7.3 Hz)	8.17-7.97 (m)	129.7 (CH)	C-4, C-7
3, 5	7.54-7.42 (m)	7.50-6.72 (m)	128.3 (CH)	C-1
4	7.55 (t, J = 7.3 Hz)	7.50-6.72 (m)	132.8 (CH)	C-2, C-6
7	-	-	166.5 (C)	-
1′	-	-	124.5 (C)	-
2′	-	-	157.4 (C)	-
3′	6.92 (d, J = 8.0 Hz)	7.50-6.72 (m)	110.5 (CH)	C-1′, C-5′
4′	7.32 (t, J = 8.0 Hz)	7.50-6.72 (m)	129.5 (CH)	C-2′, C-5′, C-6′
5′	6.98 (t, J = 8.0 Hz)	7.50-6.72 (m)	120.5 (CH)	C-1′, C-3′
6′	7.54-7.42 (m)	7.50-6.72 (m)	129.4 (CH)	C-2′, C-4′, C-7′
7′	5.42 (s)	5.33 (s)	62.2 (CH_2)	C-7, C-1′, C-2′, C-6′
2′-OCH_3	3.87 (s)	3.87 (s)	55.5 (CH_3)	C-2′

[a]500 MHz, [b]60 MHz, [c]125 MHz

Compound DC7



DC7 was obtained as colourless viscous liquid. Its IR spectrum revealed hydroxyl (3034 cm^{-1}), ester carbonyl (1660 cm^{-1}) and aromatic ring (1614 and 1455 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC7** were similar to those of **DC3**, except for the appearance of an additional methoxyl singlet signal at δ 3.82, indicating that a hydroxyl group in **DC3** was replaced by a methoxyl group. In the HMBC spectrum, the methoxyl protons at δ 3.82 (6-OCH_3) correlated with C-6 (δ 161.0) and from the correlations of H-4 (δ 7.39-7.27) aromatic proton with C-6 (δ 161.0) and C-2 (δ 163.5), resulting in the assignment of a methoxyl group at C-6. The structure of compound **DC7** was identified as benzyl 2-hydroxy-6-methoxybenzoate, (Kodpinid *et al*., 1983).

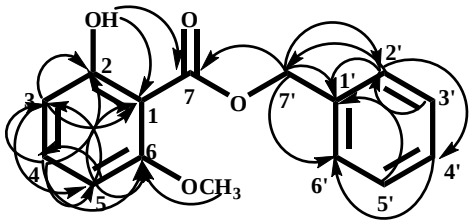


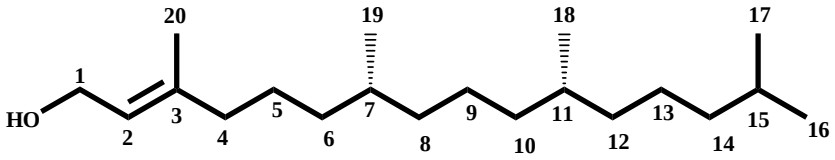
Figure 8 Selected HMBC correlations of **DC7**

Table 9 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC7** and benzyl 2-hydroxy-6-methoxybenzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC7[a]	**R**[b]	**DC8**[c]	
1	-	-	103.1 (C)	-
2	-	-	163.5 (C)	-
3	6.58 (d, *J* = 8.4 Hz)	6.47 (dd, *J* = 8.0, 2.0 Hz)	109.9 (CH)	C-1, C-2, C-5, C-6, C-7
4	7.39-7.27 (m)	7.42-7.06 (m)	135.1 (CH)	C-2, C-3, C-5, C-6
5	6.38 (d, *J* = 8.4 Hz)	6.27 (dd, *J* = 8.0, 2.0 Hz)	102.2 (CH)	C-1, C-4, C-3, C-6, C-7
6	-	-	161.0 (C)	-
7	-	-	170.8 (C)	-
1′	-	-	135.6 (C)	-
2′, 6′	7.45 (d, *J* = 7.0 Hz)	7.42-7.06 (m)	127.3 (CH)	C-1′, C-4′, C-7′
3′, 5′	7.39-7.27 (m)	7.42-7.06 (m)	128.4 (CH)	C-1′, C-2′, C-6′
4′	7.39-7.27 (m)	7.42-7.06 (m)	127.9 (CH)	C-2′, C-6′
7′	5.38 (s)	5.32 (s)	66.7 (CH_2)	C-1, C-7, C-1′, C-2′, C-6′
2-OH	11.44 (s)	11.28 (s)	-	C-1, C-2, C-3, C-4, C-7
6-OCH_3	3.81 (s)	3.88 (s)	55.9(OCH_3)	C-5, C-6

[a]300 MHz, [b]60 MHz, [c]75 MHz

Compound DC8



DC8 was obtained as colourless viscous liquid. Its IR spectrum revealed hydroxyl (3389 cm^{-1}) and double bond (1669 cm^{-1}).

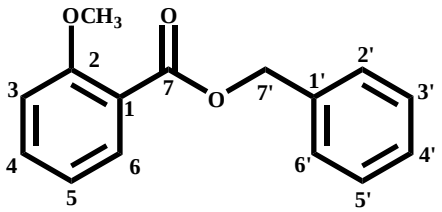
The ^{1}H NMR spectral data showed the signals of oxymethylene protons at δ 4.09 (*d*, *J* = 6.9 Hz, H_2-1) and an olefinic proton at δ 5.34 (*t*, *J* = 6.9 Hz, H-2). Additionally, the ^{1}H NMR spectrum showed the singlet signal at δ 1.62 (Me-19), representing a methyl group attached to a quaternary carbon whereas four methyl groups appeared as three doublet signals at δ 0.79 (*d*, *J* = 6.6 Hz, Me-16 and Me-17), 0.78 (*d*, *J* = 6.5 Hz, Me-18) and 0.77 (*d*, *J* = 6.5 Hz, Me-19). In addition, the ^{1}H NMR spectrum displayed several methine or methylene signals indicating **DC8** to be an aliphatic alcohol with one double bond. In the ^{13}C NMR spectrum nineteen signals of twenty carbons consisting of an olefinic quaternary (δ 140.3) and an olefinic methine (δ 123.1), one oxygenated methylene C-1 (δ 59.4), five methyls (δ 22.7, 22.6, 19.7, 19.7 and 16.2), nine methylene and three methine signals were observed. These results led to the conclusion for **DC8** to be a non-cyclic aliphatic diterpenoid. The structure of compound **DC8** was identified as phytol, an aliphatic acyclic diterpenoid, usually found as a component part of chlorophyll (Bang *et al*., 2002 and Menkham *et al*., 2003).

Table 10 ^{1}H and ^{13}C NMR spectral data of **DC8** and phytol (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	
	DC8[a]	R[b]	**DC8**[c]	R
1	4.09 (d, J = 6.9 Hz)	4.15 (d, J = 6.9 Hz)	59.4 (CH_2)	59.4
2	5.34 (t, J = 6.9 Hz)	5.40 (t, J = 6.9 Hz)	123.1 (CH)	123.1
3	-	-	140.3 (C)	140.3
4	1.92 (t, J = 7.2 Hz)	1.96 (m)	39.9 (CH_2)	39.9
5	-	-	39.4 (CH_2)	39.4
6	-	-	37.4 (CH_2)	37.5
7	-	-	32.8 (CH)	32.8
8	-	-	37.4 (CH_2)	37.4
9	-	-	37.3 (CH_2)	37.3
10	-	-	36.7 (CH_2)	36.9
11	-	-	32.7 (CH)	32.7
12	-	-	25.1 (CH_2)	25.2
13	-	-	24.8 (CH_2)	24.8
14	-	-	24.5 (CH_2)	24.5
15	-	-	27.9 (CH)	27.9
16	0.79 (d, J = 6.6 Hz)	0.84 (d, J = 6.7 Hz)	22.7 (CH_3)	22.7
17	0.79 (d, J = 6.6 Hz)	0.84 (d, J = 6.7 Hz)	22.6 (CH_3)	22.6
18	0.78 (d, J = 6.5 Hz)	0.82 (d, J = 6.7 Hz)	19.7 (CH_3)	19.7
19	0.77 (d, J = 6.5 Hz)	0.82 (d, J = 6.7 Hz)	19.7 (CH_3)	19.7
20	1.62 (s)	1.64 (s)	16.2 (CH_3)	16.2

[a]300 MHz, [b]270 MHz, [c]75 MHz

Compound DC9



DC9 was obtained as colourless viscous liquid. Its IR spectrum revealed ester carbonyl (1725 cm^{-1}) and aromatic (1600, 1491 cm^{-1}).

The ^{1}H and ^{13}C NMR spectral data of **DC9** were similar to those of **DC1**, except for the appearance of the methoxyl singlet signal at δ 3.82 (2-OCH_3) and the disappearance of chelated hydroxyl at δ 10.84 (2-OH) of **DC1**, indicating that a hydroxyl group in **DC1** was replaced by a methoxyl group. The location of the methoxyl group at C-2 was assigned by HMBC correlations of the methoxyl protons at δ 3.82 (2-OCH_3) to the carbon at δ 159.3 (C-2), as well as the correlations of H-6 (δ 7.55) and H-4 (δ 7.18-7.41) to the carbon at δ 159.3 (C-2). The structure of compound **DC9** was identified as benzyl 2-methoxybenzoate, (Kodpinid *et al*., 1983).

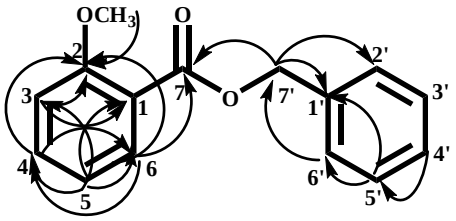


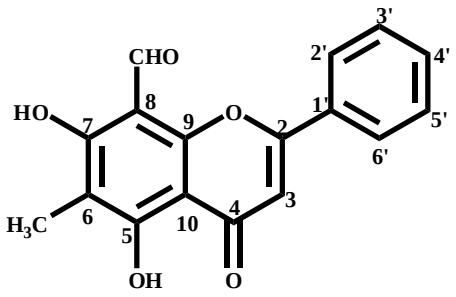
Figure 9 Selected HMBC correlations of **DC9**

Table 11 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC9** and benzyl 2-methoxybenzoate (**R**, $CDCl_3$)

position	δ_H (multiplicity)		δ_C (C- type)	HMBC
	DC9[a]	**R**[b]	**DC9**[c]	
1	-	-	120.0 (C)	-
2	-	-	159.3 (C)	-
3	6.88 (m)	7.50-6.78 (m)	112.0 (CH)	C-1, C-2, C-5
4	7.41-7.18 (m)	7.50-6.78 (m)	133.7 (CH)	C-2, C-6
5	6.88 (m)	7.50-6.78 (m)	120.1 (CH)	C-1, C-3, C-4, C-6
6	7.75 (dd, J = 7.9, 1.6 Hz)	7.72 (dd, J = 8.0, 2.0 Hz)	131.7 (CH)	C-2, C-4, C-7
7	-	-	165.8 (C)	-
1′	-	-	136.2 (C)	-
2′, 6′	7.41-7.18 (m)	7.35 (s)	128.1 (CH)	C-3′, C-5′, C-7′
4′	7.41-7.18 (m)	7.35 (s)	128.1 (CH)	C-3′, C-5′
3′, 5′	7.41-7.18 (m)	7.35 (s)	128.5 (CH)	C-1′, C-2′, C-6′
7′	5.27 (s)	5.28 (s)	66.4 (CH_2)	C-7, C-1′, C-2′, C-6′
2-OCH_3	3.82 (s)	3.86 (s)	55.9 (OCH_3)	C-2

[a]300 MHz, [b]60 MHz, [c]75 MHz

Compound DC10



DC10 was obtained as a pale yellow solid, m.p. 144-145°C. Its IR spectrum revealed hydroxyl (3494 cm^{-1}), carbonyl (1655, 1625 cm^{-1}) and aromatic (1559 cm^{-1}).

The ^{1}H NMR spectrum of **DC10** showed two singlets of chelated hydroxyl groups at δ 12.84 (7-OH) and δ 13.69 (5-OH), a singlet proton at δ 6.71 (1H) and aromatic multiplets at δ 7.49-7.46 (3H) and δ 7.77 (2H, *d*, *J* = 6.7 Hz), suggesting a 5,7-dihydroxyflavone with an unsubstituted phenyl moiety (B-ring). The ^{1}H NMR spectrum further showed an aromatic methyl singlet at δ 2.02 (3H, 6-CH_3) and a formyl singlet at δ 10.39 (1H, 8-CHO), confirming the chelation of downfield shift 7-OH proton (δ 12.84) with a formyl oxygen, while the downfield shift 5-OH proton (δ 13.69) with the oxygen of the α,β-unsaturated keto carbon at C-4.

In the HMBC spectrum, the 5-OH proton signal at δ 13.69 showed correlations with the carbons at δ 165.5 (C-5), 108.5 (C-6) and 104.1 (C-10). In addition, the 7-OH proton signal at δ 12.84 showed correlations with C-8 (δ 102.7), C-6 (δ 108.5) and C-7 (δ 166.9). Correlations between the methyl proton at δ 2.02 and C-5 (δ 165.5), C-6 (108.5) and C-7 (166.9), confirmed the position of the methyl group at C-6. These assignments left the formyl substituent to be located at C-8, in agreement with correlations between C-7 and the formyl proton. These data led to the assignment of the structure of **DC10** as isounonal, (Jianhua *et al*.,1999).

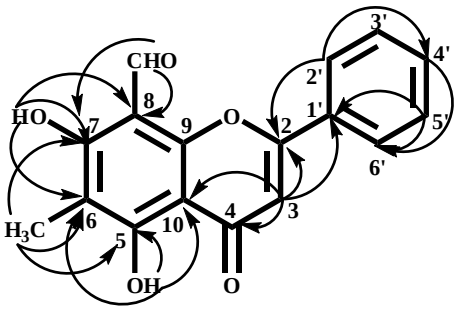
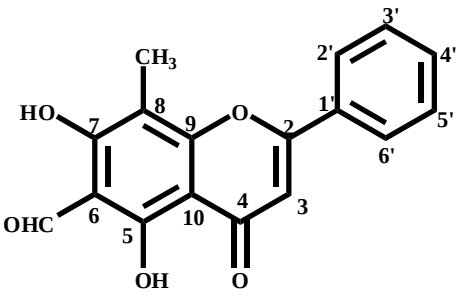


Figure 10 Selected HMBC correlations of **DC10**

Table 12 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC10** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	163.7 (C)	-
3	6.71 (s)	106.9 (CH)	C-2, C-4, C-10, C-1′
4	-	181.6 (C)	-
5	-	165.5 (C)	-
6	-	108.5 (C)	-
7	-	166.9 (C)	-
8	-	102.7 (C)	-
9	-	157.9 (C)	-
10	-	104.1 (C)	-
1′	-	130.5 (C)	-
2′, 6′	7.77 (d, J = 6.7 Hz)	126.2 (CH)	C-2, C-4′
3′, 5′	7.49-7.46 (m)	129.3 (CH)	C-1′, C-2′, C-6′
4′	7.49-7.46 (m)	132.4 (CH)	C-2′, C-6′
5-OH	13.69 (s)	-	C-5, C-6, C-10
6-CH_3	2.02 (s)	6.2 (CH_3)	C-5, C-6, C-7
7-OH	12.84 (s)	-	C-6, C-7, C-8
8-CHO	10.39 (s)	189.5 (CH)	C-7, C-8

Compound DC11



DC11 was obtained as a yellow solid, m.p. 125-126°C. IR spectrum revealed hydroxyl (3472 cm^{-1}), carbonyl (1650 cm^{-1}) and aromatic (1589 cm^{-1}).

The ^{1}H NMR spectrum was also very similar to that of compound **DC10**, with only a phenolic hydroxyl located on C-5 shifted to lowerfield, while another phenolic hydroxyl located on C-7 shifted to higherfield. This was used to assign the position of the formyl group at C-6, leaving the C-methyl to be located at C-8. The positions of 6-CHO (δ 10.28) and 8-CH_3 (δ 2.21) were assigned from HMBC spectrum which showed the correlations of the former with C-7 (δ 165.6) and C-5 (δ 165.5) and the latter with C-7 (δ 165.6), C-8 (δ 103.2) and C-9 (δ 159.3), confirming that the formyl group was connected to C-6 and the methyl group was connected to C-8. Therefore, flavone **DC11** was determined to be unonal, a structural isomer of **DC10**, (Jianhua *et al*., 1999).

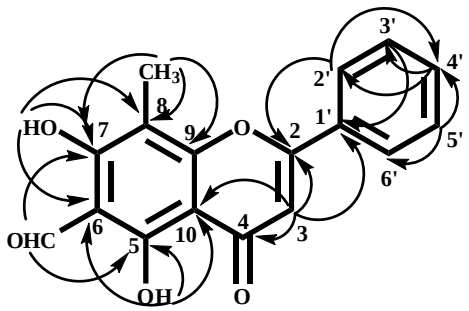
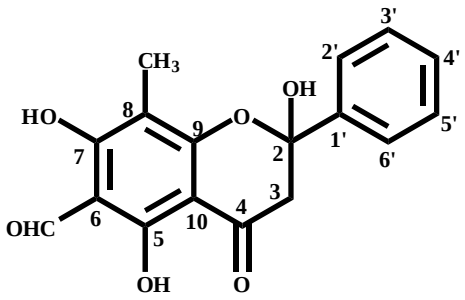


Figure 11 Selected HMBC correlations of **DC11**

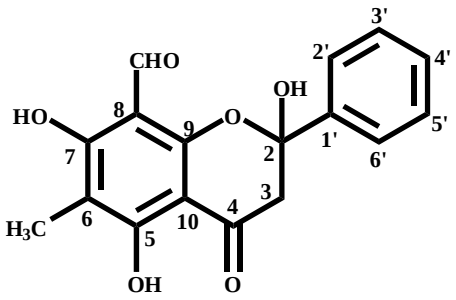
Table 13 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC11** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	164.4 (C)	-
3	6.61 (s)	105.4 (CH)	C-2, C-4, C-10, C-1′
4	-	182.9 (C)	-
5	-	165.5 (C)	-
6	-	106.3 (C)	-
7	-	165.6 (C)	-
8	-	103.2 (C)	-
9	-	159.3 (C)	-
10	-	103.7 (C)	-
1′	-	130.9 (C)	-
2′, 6′	7.83 (dd, J = 9.9, 2.2 Hz)	126.3 (CH)	C-2, C-4′
3′, 5′	7.53-7.45 (m)	129.3 (CH)	C-1′, C-2′, C-4′, C-6′
4′	7.53-7.45 (m)	132.4 (CH)	C-2′, C-3′, C-6′
5-OH	14.01 (s)	-	C-5, C-6, C-10
6-CHO	10.28 (s)	192.6 (CH)	C-5, C-7
7-OH	12.62 (s)	-	C-6, C-7, C-8
8-CH_3	2.21 (s)	6.8 (CH_3)	C-7, C-8, C-9

Compound DC12 and DC13



DC12



DC13

DC12 and **DC13** were isolated as a mixture (**DC12** : **DC13** = 1 : 0.69) of a pale yellow solid, m.p. 164-165°C, $[\alpha]_D^{25}$ = +3.1° (*c* = 1.00, $CHCl_3$). Its IR spectrum revealed hydroxyl (3341 cm^{-1}), carbonyl (1630 cm^{-1}) and aromatic ring (1546 cm^{-1}).

The ^{1}H NMR spectrum of **DC12**, the major compound of a mixture, showed two singlets of chelated hydroxyl groups at δ 13.03 and δ 13.09, a singlet proton at δ 3.11 (2H) and aromatic multiplets at δ 7.52-7.47 (3H) and δ 7.69-7.65 (2H), suggesting a 5,7-dihydroxyflavanone with an unsubstituted phenyl moiety (B-ring). The ^{1}H NMR spectrum further showed an aromatic methyl singlet at δ 2.08 (3H, 8-CH_3) and a formyl singlet at δ 10.22 (1H, 6-CHO). In the HMBC spectrum, the 5-OH proton signal at δ 13.03 showed correlations with the carbons at δ 166.1 (C-5), 105.1 (C-6) and 100.8 (C-10). In addition, the 7-OH proton signal at δ 13.09 showed correlations with C-6 (δ 105.1), C-8 (δ 105.1) and C-7 (δ 169.1). Correlations between the methyl protons at δ 2.08 and C-7 (δ 169.1), C-8 (105.1) and C-9 (161.6) and correlations between the formyl proton at δ 10.22 and C-6 (δ 105.1) and C-7 (δ 169.1), confirmed the position of the methyl group at C-8 and the formyl group at C-6, respectively. The absence of a doublet of doublet in the region of δ 5.20 suggested the absence of an H-2 proton which normally coupled with the H-3 protons in flavanones. That this proton was substituted by a hydroxyl group was supported by the presence of a doubly oxygenated sp^3 carbon signal at δ 102.1 (C-2) in the ^{13}C NMR spectrum. The position of this carbon was assigned by HMBC correlations with the H-3 (δ 3.11) and H-2′/H-6′ (δ 7.69-7.65). These data led to the assignment of the structure of **DC12** as 6-formyl-2,5,7-trihydroxy-8-methylflavanone. **DC13** gave

signals similar to and sometimes overlapping with those of **DC12** in both the ^{1}H and ^{13}C NMR spectra (Table 15). These data led to the assignment of the structure of **DC13** as 8-formyl-2,5,7-trihydroxy-6-methylflavanone, (Kakeya *et al*.,1993).

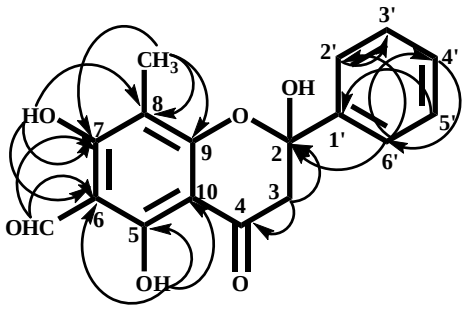


Figure 12 Selected HMBC correlations of **DC12**

Table 14 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC12** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	102.1 (C)	-
3	3.11 (s)	48.0 (CH_2)	C-2, C-4
4	-	194.6 (C)	-
5	-	166.1 (C)	-
6	-	105.1 (C)	-
7	-	169.1 (C)	-
8	-	105.1 (C)	-
9	-	161.6 (C)	-
10	-	100.8 (C)	-
1′	-	141.1 (C)	-
2′, 6′	7.69-7.65 (m)	124.9 (CH)	C-2, C-3′, C-4′, C-5′
3′, 5′	7.52-7.47 (m)	129.0 (CH)	C-1′
4′	7.52-7.47 (m)	129.7 (CH)	C-2′, C-6′
5-OH	13.03 (s)	-	C-5, C-6, C-10
6-CHO	10.22 (s)	192.0 (CH)	C-6, C-7
7-OH	13.09 (s)	-	C-6, C-7, C-8
8-CH_3	2.08 (s)	6.9 (CH_3)	C-7, C-8, C-9

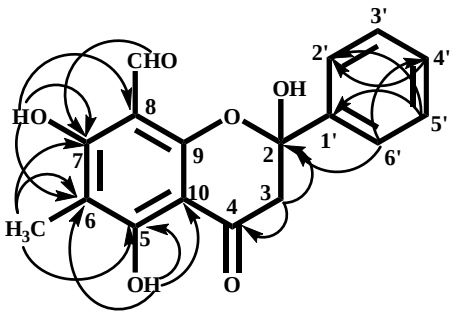
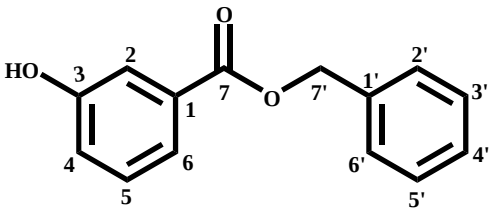


Figure 13 Selected HMBC correlations of **DC13**

Table 15 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC13** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	103.2 (C)	-
3	3.13 (s)	48.2 (CH_2)	C-2, C-4
4	-	193.8 (C)	-
5	-	166.6 (C)	-
6	-	106.0 (C)	-
7	-	168.2 (C)	-
8	-	105.1 (C)	-
9	-	162.3 (C)	-
10	-	100.9 (C)	-
1′	-	141.0 (C)	-
2′, 6′	7.69-7.65 (m)	124.8 (CH)	C-2, C-4′
3′, 5′	7.52-7.47 (m)	129.1 (CH)	C-1′, C-2′, C-6′
4′	7.52-7.47 (m)	129.9 (CH)	C-2′, C-6′
5-OH	12.71 (s)	-	C-5, C-6, C-10
6-CH_3	2.03 (s)	6.0 (CH_3)	C-5, C-6, C-7
7-OH	12.84 (s)	-	C-6, C-7, C-8
8-CHO	10.17 (s)	191.2 (CH)	C-7

Compound DC14



DC14 was obtained as colourless viscous liquid. Its IR spectrum revealed hydroxyl (3368 cm^{-1}), ester carbonyl (1716 cm^{-1}) and aromatic ring (1698 and 1455 cm^{-1}).

The ^{1}H and ^{13}C NMR spectra of **DC14** were similar to those of **DC1**, except for the disappearance of a singlet signal of a chelated hydroxyl group at δ 10.84 but the appearance of aromatic protons at δ 7.53 (*dd*, *J* = 2.6, 1.2 Hz, H-2), 7.04 (*ddd*, *J* = 8.1, 2.6, 1.2 Hz, H-4), 7.31 (*t*, *J* = 8.1 Hz, H-5) and 7.66 (*ddd*, *J* = 8.1, 1.2, 1.2 Hz, H-6), implied the presence of 1,3-disubstituted aromatic ring. In the HMBC spectrum, an aromatic proton at δ 7.31 (H-5) correlated with C-1 (δ 131.7), C-3 (δ 155.6) and C-4 (δ 120.2), confirming that the hydroxyl group was connected to C-3. The structure of compound **DC14** was identified as benzyl 3-hydroxybenzoate (Rivero-Cruz *et al*., 2007).

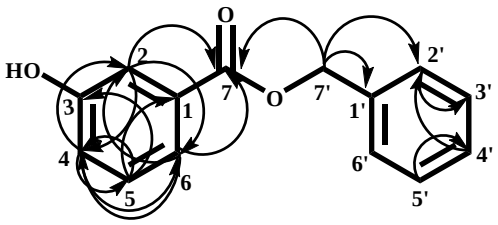
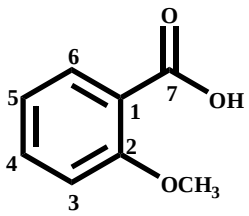


Figure 14 Selected HMBC correlations of **DC14**

Table 16 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC14** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	131.7 (C)	-
2	7.53 (dd, J = 2.6, 1.2 Hz)	116.3 (CH)	C-4, C-6, C-7
3	-	155.6 (C)	-
4	7.04 (ddd, J = 8.1, 2.6, 1.2 Hz)	120.2 (CH)	C-2, C-5, C-6
5	7.31 (t, J = 8.1 Hz)	129.7 (CH)	C-1, C-3, C-4
6	7.66 (ddd, J = 8.1, 1.2, 1.2 Hz)	122.2 (CH)	C-2, C-4, C-7
7	-	166.1 (C)	
1′	-	135.9 (C)	-
2′, 6′	7.46-7.35 (m)	128.2 (CH)	C-3′, C-5′
3′, 5′	7.46-7.35 (m)	128.6 (CH)	C-4′
4′	7.46-7.35 (m)	128.3 (CH)	C-2′, C-6′
7′	5.35 (s)	66.8 (CH_2)	C-7, C-1′, C-2′, C-6′

Compound DC15



DC15 was obtained as colourless viscous liquid. Its IR spectrum revealed hydroxyl (3450 cm^{-1}), carbonyl (1722 cm^{-1}) functions and aromatic (1603 cm^{-1}).

The ^{1}H NMR spectrum of **DC15** indicated a 1,2-disubstituted aromatic ring due to the signals at δ 7.07 (1H, *d*, *J* = 7.5 Hz, H-3), 7.14 (1H, *t*, *J* = 7.5 Hz, H-5), 7.58 (1H, *td*, *J* = 7.5, 1.5 Hz, H-4) and 8.17 (1H, *dd*, *J* = 7.5, 1.5 Hz, H-6). Additionally, the ^{1}H NMR spectrum showed the appearance of the methoxyl singlet signal at δ 4.08 (2-OCH_3). Furthermore, the ^{13}C NMR spectral data exhibited a carboxyl carbon at δ 165.5. In the HMBC spectrum, the methoxy protons at δ 4.08 (2-OCH_3) correlated with C-2 (δ 158.1), as well as the correlations of H-4 (δ 7.58) to the carbon C-2 (δ 158.1) and the correlations of H-6 (δ 8.17) aromatic proton with C-2 (δ 158.1), C-4 (δ 135.0) and C-7 (δ 165.5), confirming that the methoxyl group was connected to C-2 while the carboxylic group was connected to C-1 of the aromatic ring. All these data suggested that **DC15** was identified as 2-methoxybenzoic acid.

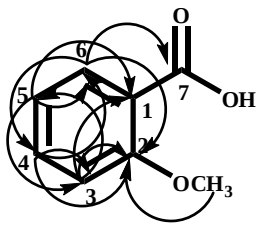
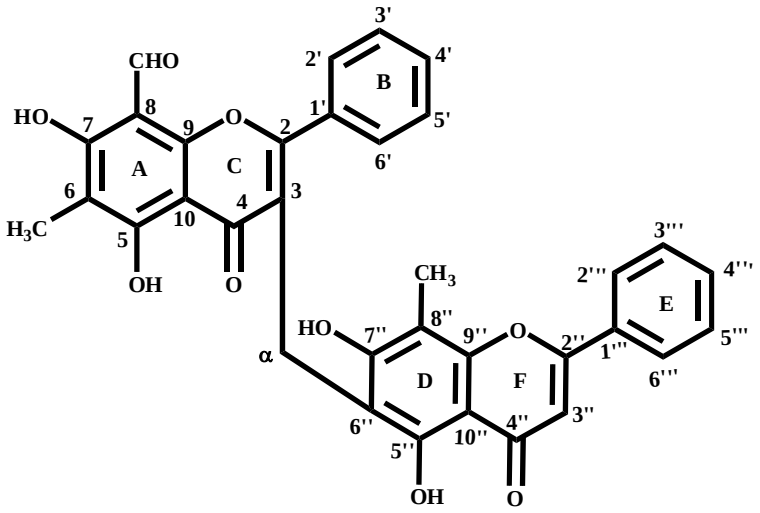


Figure 15 Selected HMBC correlations of **DC15**

Table 17 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC15** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	117.6 (C)	-
2	-	158.1 (C)	-
3	7.07 (d, J = 7.5 Hz)	111.7 (CH)	C-1, C-2, C-5
4	7.58 (td, J = 7.5, 1.5 Hz)	135.0 (CH)	C-2, C-3, C-6
5	7.14 (t, J = 7.5 Hz)	122.1 (CH)	C-1, C-3, C-4, C-6
6	8.17 (dd, J = 7.5, 1.5 Hz)	133.7 (CH)	C-2, C-4, C-7
7	-	165.5 (C)	-
2-OCH_3	4.08 (s)	55.6 (OCH_3)	C-2

Compound DC16



DC16 was obtained as a pale yellow solid, m.p. 229-230°C. Its IR spectrum revealed hydroxyl (3494 cm^{-1}) and carbonyl (1655 cm^{-1}).

The ^{13}C NMR spectrum of **DC16** showed a total of 34 signals, which was clearly twice the signals of the isounonal (**DC10**). The EIMS displayed a molecular ion $[M]^+$ at *m/z* 576, consistent with the molecular formula $C_{34}H_{24}O_9$.

The ^1H NMR spectrum of **DC16** showed the presence of four hydroxyl protons, a formyl proton, a vinylic methine proton, methylene protons, ten aromatic protons and six protons for two methyl groups, suggesting that **DC16** could be a biflavone with an interflavonoid methylene linkage. The two chelated hydroxyl protons resonating at δ 12.34 (5″-OH) and δ 13.16 (5-OH), suggested the chelation with oxygen of the α,β-unsaturated keto carbon at C-4″ (δ 182.7) and C-4 (δ 182.9), respectively. Furthermore, the downfield singlet signal at δ 13.06 corresponded to 7-OH proton which chelated with oxygen of the formyl substituent at C-8. Another hydroxyl proton singlet appearing at δ 10.04 represented 7″-OH proton of ring D. The presence of two sets of monosubstituted aromatic protons at δ 7.65-7.61 (3H, *m*) and δ 7.71 (2H, *dd*, *J* = 7.2, 1.8 Hz); δ 7.54-7.51 (3H, *m*) and δ 7.89 (2H, *dd*, *J* = 7.2, 1.7 Hz) were assigned to ten aromatic protons of ring B and ring E, respectively. The upfield signal of the ^1H NMR spectrum showed two methyl singlets at δ 2.12 and 2.39. The signal at δ 2.12 was assigned to the methyl group at C-6 since it showed

HMBC correlations to the signals of the C-5 (δ 164.7), C-6 (δ 108.9) and C-7 (δ 168.0), whereas the signal at δ 2.39 showed correlations to the signals of the C-7″ (δ 160.0), C-8″ (δ 104.6) and C-9″ (154.0), establishing the location of the second methyl group at C-8″. The remaining two singlets at δ 6.58 and 4.01 were assigned to a vinylic methine proton (H-3″) of ring F and the methylene protons, respectively, which implied that the methylene carbon at C-6″ of ring D was involved in the interflavonoid linkage with C-3 of ring C. In the HMBC spectrum, the hydroxyl proton signal at δ 13.06 showed correlations with C-6 (δ 108.9), C-7 (δ 168.0) and C-8 (δ 102.3) and the formyl proton signal at δ 10.28 showed correlations with C-7 (δ 168.0) and C-8 (δ 102.3), suggesting that the hydroxyl group at δ 13.06 was located at C-7, leaving the formyl group at C-8. The correlations of the hydroxyl proton signal at δ 10.04 (7″-OH) to C-6″ (δ 108.6), C-7″ (δ 160.1) and C-8″ (δ 104.6) confirmed the position of this hydroxyl group at C-7″. Additionally, the methylene protons signal at δ 4.01 showed correlations with C-2 (δ 165.1), C-3 (δ 119.3), C-4 (δ 182.9), C-5″ (δ 158.0), C-6″ (δ 108.6) and C-7″ (δ 160.1), implying that a methylene bond linked the two flavonoid units at C-6″ and C-3. The structure of **DC16** was therefore composed of 8-formyl-5,7-dihydroxy-6-methylflavone and 5″,7″-dihydroxy-8″-methylflavone with a methylene linkage between C-3 and C-6″. Thus the structure of compound **DC16** was identified as (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6″-(5″,7″-dihydroxy-8″-methylflavone) and named as saiyunensis A, a new compound.

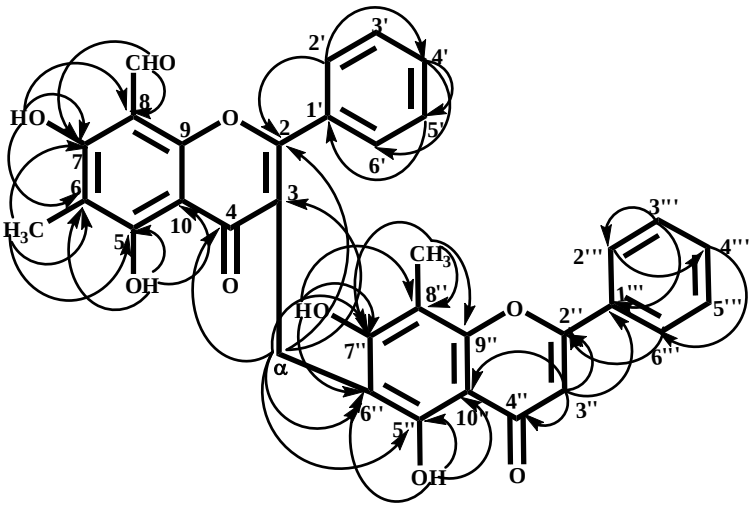


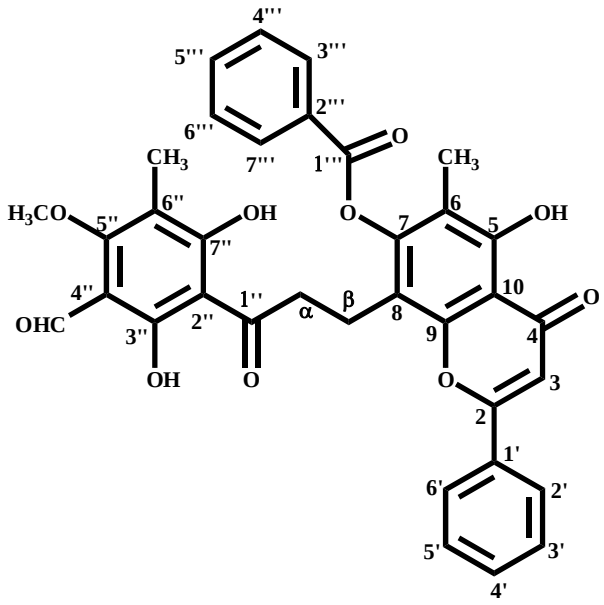
Figure 16 Selected HMBC correlations of **DC16**

Table 18 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC16** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	165.1 (C)	-
3	-	119.3 (C)	-
4	-	182.9 (C)	-
5	-	164.7 (C)	-
6	-	108.9 (C)	-
7	-	168.0 (C)	-
8	-	102.3 (C)	-
9	-	156.9 (C)	-
10	-	103.0 (C)	-
1′	-	132.5 (C)	-
2′, 6′	7.71 (dd, J = 7.2, 1.8 Hz)	129.2 (CH)	C-2, C-4′
3′, 5′	7.65-7.61 (m)	128.7 (CH)	C-1′
4′	7.65-7.61 (m)	131.1 (CH)	C-2′, C-3′, C-5′, C-6′
1″	-	-	-
2″	-	163.4 (C)	-
3″	6.58 (s)	105.1 (CH)	C-2″, C-4″, C-10″, C-1‴

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
4″	-	182.7 (C)	-
5″	-	158.0 (C)	-
6″	-	108.6 (C)	-
7″	-	160.1 (C)	-
8″	-	104.6 (C)	-
9″	-	154.0 (C)	-
10″	-	104.7 (C)	-
1‴	-	131.7 (C)	-
2‴, 6‴	7.89 (dd, J = 7.2, 1.7 Hz)	126.2 (CH)	C-2″, C-4‴
3‴, 5‴	7.54-7.51 (m)	129.1 (CH)	C-1‴, C-2‴, C-6‴
4‴	7.54-7.51 (m)	131.7 (CH)	C-2‴, C-6‴
5-OH	13.16 (s)	-	C-5, C-6, C-10
6-CH_3	2.12 (s)	6.4 (CH_3)	C-5, C-6, C-7
7-OH	13.06 (s)	-	C-6, C-7, C-8
8-CHO	10.28 (s)	189.8 (CH)	C-7, C-8
5″-OH	12.34 (s)	-	C-5″, C-6″, C-10″
α	4.01 (s)	19.6 (CH_2)	C-2, C-3, C-4, C-5″, C-6″, C-7″
7″-OH	10.04 (s)	-	C-6″, C-7″, C-8″
8″-CH_3	2.39 (s)	8.3 (CH_3)	C-7″, C-8″, C-9″

Compound DC17



DC17 was obtained as a pale yellow solid, m.p. 190-191°C. IR spectrum revealed hydroxyl (3447 cm^{-1}), carbonyl (1739, 1633 cm^{-1}) and aromatic (1542 cm^{-1}).

The ^{13}C NMR spectrum of **DC17** showed a total of 35 signals. The EIMS displayed a molecular ion $[M]^+$ at *m/z* 608, consistent with the molecular formula $C_{35}H_{28}O_{10}$.

The ^{1}H NMR spectrum of **DC17** displayed signals of methoxyl protons at δ 3.84 (*s*, 5″-OCH_3), methyl protons at δ 2.02 (*s*, 4″-CH_3), a formyl proton at δ 9.87 (*s*, 6″-CHO) and two chelated hydroxyl protons at δ 14.87 (3″-OH) and 14.04 (7″-OH), suggesting the chelation with oxygens of the keto carbon at C-1″ (δ 205.6) and the formyl substituent at C-6″, respectively. Furthermore, the ^{1}H NMR spectrum showed the signal of a methylene triplet at δ 3.51 (4H, J = 7.3 Hz, H_2-β and H_2-α). In the HMQC spectrum of **DC17**, the methylene signal at δ_C 43.5 was correlated with a methylene triplet at δ_H 3.51 indicating that two methylenes (H_2-β and H_2-α) had the same chemical shifts and their carbon signals were overlapped at δ_C 43.5 in the ^{13}C NMR spectrum. Accordingly, this suggested that **DC17** has a 1-(5-formyl-2,6-dihydroxy-4-methoxy-3-methylphenyl)propane-1-one moiety in the molecule, which was supported by fragment ions at *m/z* 223 and 385 in the EIMS (Scheme 3). In the HMBC spectrum, the hydroxyl proton signal at δ 14.04 showed correlations with C-6″ (δ 107.1) and C-7″ (δ 167.0) and the formyl proton signal at δ 9.87 showed

correlations with C-6″ (δ 107.1) and C-7″ (δ 167.0), suggesting that the hydroxyl group at δ 14.04 was located at C-7″, leaving the formyl group at C-6″. The correlations of the hydroxyl proton signal at δ 14.87 (3″-OH) to C-3″ (δ 172.3), C-4″ (δ 110.9) and C-2″ (δ 106.2) confirmed the position of this hydroxyl group at C-3″. The signal at δ 2.02 was assigned to the methyl group at C-4″ since it showed HMBC correlations to C-3″ (δ 172.3), C-4″ (δ 110.9) and C-5″ (δ 166.5), whereas the methoxyl signal at δ 3.84 showed correlations to C-5″ (δ 166.5), establishing the location of the methoxyl group at C-5″. In the NOESY spectrum of **DC17**, the correlations from the methyl group at δ 2.02 to the methoxyl group at δ 3.84 and the methoxyl group at δ 3.84 to the formyl group at δ 9.87 were clearly observed. The presence of methyl protons at δ 2.11 (*s*, 6-CH_3), a vinylic methine proton at δ 6.77 (*s*, H-3), a monosubstituted aromatic ring at δ 7.92 (2H, *d*, *J* = 7.2 Hz, H-2′ and H-6′) and 7.55-7.50 (3H, *m*, H-3′, H-4′ and H-5′) and another chelated hydroxyl proton at δ 12.98 (5-OH) suggested the chelation with oxygen of the α,β-unsaturated keto carbon at C-4 (δ 183.3) of a flavones moiety. The correlations of the hydroxyl proton signal at δ 12.98 (5-OH) to C-5 (δ 157.9), C-6 (δ 114.7) and C-10 (δ 108.9) and of the methyl proton signal at δ 2.11 to C-5 (δ 157.9), C-6 (δ 114.7) and C-7 (δ 153.7) confirmed the position of this hydroxyl group at C-5 and the methyl group at C-6, respectively. Additionally the methylene proton signal at δ 3.51 showed the correlations with C-8 (δ 112.0) and C-1″ (δ 205.6) suggesting that a phenylpropanone unit was linked at C-8 of a flavones moiety. Furthermore, the ^{1}H NMR spectra and the EIMS fragment of **DC17** (*m/z* 105 and 503) showed that the flavones moiety had a benzoyl group at δ 8.25 (2H, *d*, *J* = 7.2 Hz, H-3‴ and H-7‴), 7.57-7.50 (2H, *m*, H-4‴ and H-6‴), 7.70 (1H, *t*, *J* = 7.2 Hz, H-5‴) and δ_C 163.9 (C-1‴). The downfield shift of H_2-β proton was caused by the anisotropic effect of the benzoyl group adjacent to an oxygen of a flavones unit at C-7 (Scheme 3). The structure of **DC17** was proposed to be an unusual biflavone, named as saiyunensis B, a new compound.

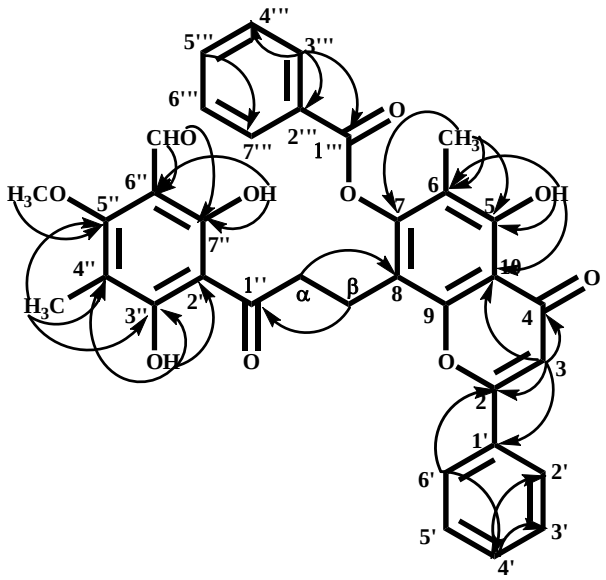
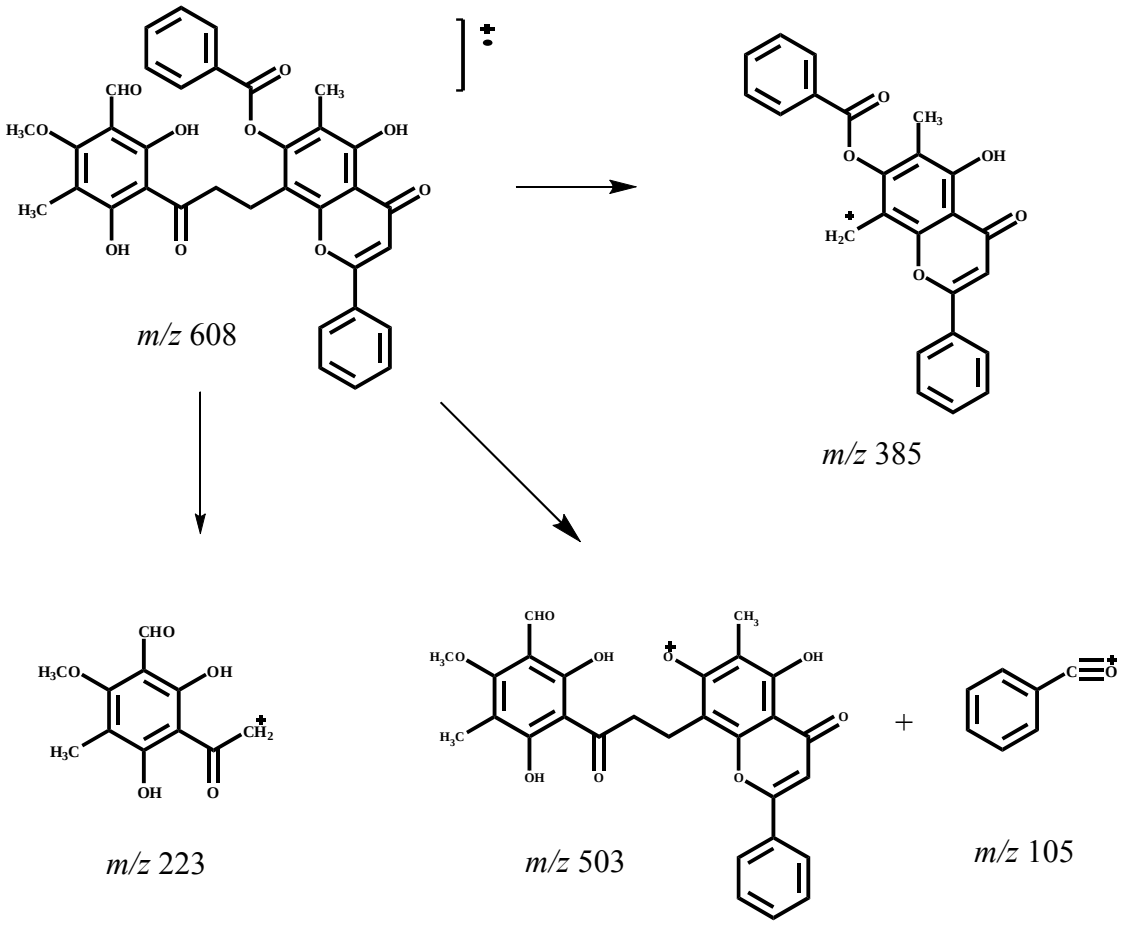


Figure 17 Selected HMBC correlations of **DC17**

Table 19 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC17** ($CDCl_3$)

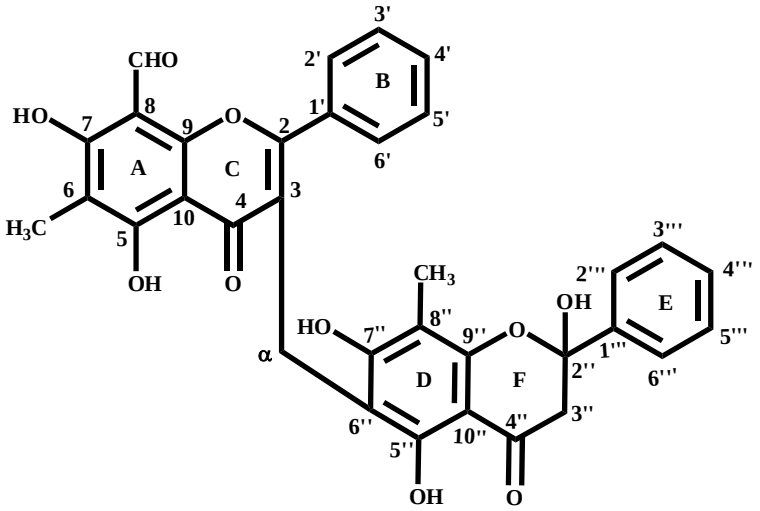
position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	163.4 (C)	-
3	6.77 (s)	105.9 (CH)	C-2, C-4, C-10, C-1′
4	-	183.3 (C)	-
5	-	157.9 (C)	-
6	-	114.7 (C)	-
7	-	153.7 (C)	-
8	-	112.0 (C)	-
9	-	159.0 (C)	-
10	-	108.9 (C)	-
1′	-	131.4 (C)	-
2′, 6′	7.92 (d, J = 7.2 Hz)	126.3 (CH)	C-2, C-4′
3′, 5′	7.57-7.50 (m)	129.2 (CH)	C-2′, C-6′
4′	7.57-7.50 (m)	131.9 (CH)	C-3′, C-5′

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
α	3.51 (t, J = 7.3 Hz)	43.5 (CH_2)	C-8, C- 1″
β	3.51 (t, J = 7.3 Hz)	43.5 (CH_2)	C-8, C- 1″
1″	-	205.6 (C)	-
2″	-	106.2 (C)	-
3″	-	172.3 (C)	-
4″	-	110.9 (C)	-
5″	-	166.5 (C)	-
6″	-	107.1 (C)	-
7″	-	167.0 (C)	-
1‴	-	163.9 (C)	
2‴	-	131.4 (C)	-
3‴, 7‴	8.25 (d, J = 7.2 Hz)	130.3 (CH)	C-β, C-2‴, C-5‴
4‴, 6‴	7.57-7.50 (m)	128.8 (CH)	C-3‴, C-5‴, C-7‴
5‴	7.70 (t, J = 7.2 Hz)	134.0 (CH)	C-3‴, C-7‴
5-OH	12.98 (s)	-	C-5, C-6, C-10
6-CH_3	2.11 (s)	8.7 (CH_3)	C-5, C-6, C-7
3″-OH	14.87 (s)	-	C-2″, C-3″, C-4″
4″-CH_3	2.02 (s)	7.9 (CH_3)	C-3″, C-4″, C-5″
5″-OCH_3	3.84 (s)	62.8 (CH_3)	C-5″
6″-CHO	9.87 (s)	192.4 (CH)	C-6″, C-7″
7″-OH	14.04 (s)	-	C-6″, C-7″



Scheme 3 Fragmentation pathway of compound **DC17**

Compound DC18



DC18 was obtained as a pale yellow solid, m.p. 199-200°C, $[\alpha]_D^{25}$ = +1.4° (*c* = 1.00, $CHCl_3$). Its IR spectrum revealed hydroxyl (3341 cm^{-1}) and carbonyl (1630 cm^{-1}).

The ^{13}C NMR spectrum of **DC18** showed a total of 34 signals, suggesting a biflavone structure. The EIMS displayed a molecular ion $[M]^+$ at *m/z* 594, consistent with the molecular formula $C_{34}H_{26}O_{10}$.

The ^1H NMR spectrum was also very similar to that of compound **DC16**, except for the appearance of a singlet signal of a methylene group at C-3″ (δ 2.96) instead of a vinylic methine proton, suggesting a flavone-flavanone biflavonoid structure. The absence of a H-2″ proton which normally coupled with the H-3″ proton in flavanones suggested that the H-2″ proton was substituted by a hydroxyl group which was supported by the presence of a doubly oxygenated carbon signal at δ 100.9 (C-2″) in the ^{13}C NMR spectrum. The location of the methylene proton at C-3″ was assigned by the HMBC correlations of the signal at δ 2.96 (H_2-3″) to the carbons at δ 100.9 (C-2″), δ 194.3 (C-4″) and δ 142.2 (C-1‴) and the hydroxyl group at C-2″ from the correlations of H-2‴/H-6‴ with C-2″ (δ 100.9). Thus the structure of compound **DC18** was identified as (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6″-(2″,5″,7″-trihydroxy-8″-methylflavanone) and named as saiyunensis C, a new compound.

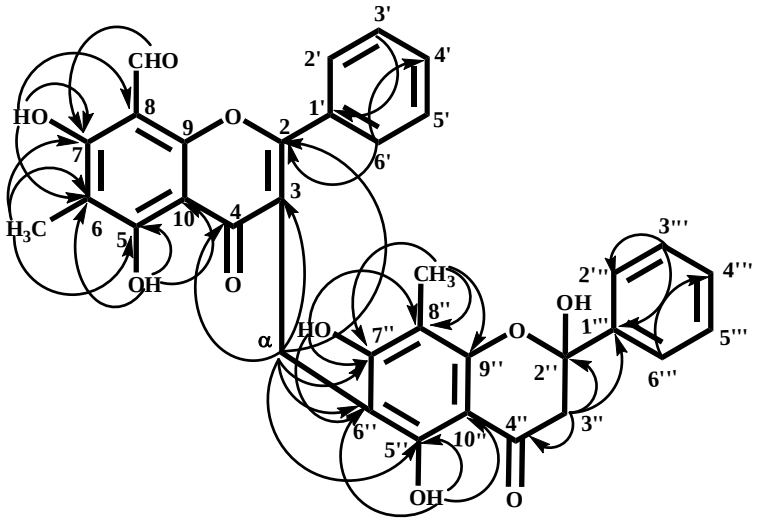


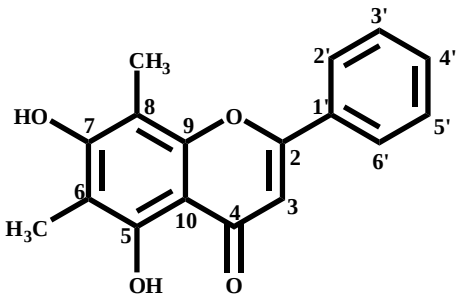
Figure 18 Selected HMBC correlations of **DC18**

Table 20 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC18** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	164.8 (C)	-
3	-	119.5 (C)	-
4	-	182.9 (C)	-
5	-	164.7 (C)	-
6	-	108.6 (C)	-
7	-	168.1 (C)	-
8	-	102.3 (C)	-
9	-	160.4 (C)	-
10	-	103.1 (C)	-
1′	-	132.6 (C)	-
2′, 6′	7.68-7.65 (m)	129.2 (CH)	C-2, C-4′
3′, 5′	7.63-7.59 (m)	128.7 (CH)	C-1′
4′	7.63-7.59 (m)	131.1 (CH)	-
1″	-	-	-
2″	-	100.9 (C)	-
3″	2.96 (s)	48.1 (CH_2)	C-2″, C-4″, C-1‴

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
4″	-	194.3 (C)	-
5″	-	159.9 (C)	-
6″	-	105.8 (C)	-
7″	-	163.0 (C)	-
8″	-	106.3 (C)	-
9″	-	155.1 (C)	-
10″	-	101.8 (C)	-
1‴	-	142.2 (C)	-
2‴, 6‴	7.68-7.65 (m)	124.9 (CH)	C-2″, C-4‴
3‴, 5‴	7.45-7.42 (m)	128.6 (CH)	C-1‴, C-2‴, C-6‴
4‴	7.45-7.42 (m)	129.2 (CH)	-
5-OH	13.17 (s)	-	C-5, C-6, C-10
6- CH_3	2.13 (s)	6.4 (CH_3)	C-5, C-6, C-7
7-OH	13.06 (s)	-	C-6, C-7, C-8
8-CHO	10.27 (s)	189.8 (CH)	C-7
5″-OH	11.56 (s)	-	C-5″, C-6″, C-10″
α	3.93 (d, J = 3.3 Hz)	19.2 (CH_2)	C-2, C-3, C-4, C-5″, C-6″, C-7″
7″-OH	10.13 (s)	-	C-6″, C-7″, C-8″
8″-CH_3	2.15 (s)	8.3 (CH_3)	C-7″, C-8″, C-9″

Compound DC19



DC19 was obtained as a yellow solid, m.p. 180-181°C. Its IR spectrum revealed hydroxyl (3494 cm^{-1}), carbonyl (1655 cm^{-1}) and aromatic (1487 cm^{-1}) functions.

The ^{1}H NMR spectrum of **DC19** showed a signal pattern similar to those of **DC10**, except for the appearance of an additional singlet signal at δ 2.37 assignable to the methyl group, instead of the singlet of the formyl group due to 8-CHO in the ^{1}H NMR spectrum of **DC10**. The position of 8-CH_3 (δ 2.37) was assigned from HMBC spectrum which showed correlations with C-7 (δ 159.4), C-8 (δ 102.0) and C-9 (δ 153.1). The structure of compound **DC19** was identified as matteuorien, (Zhang *et al*., 2008).

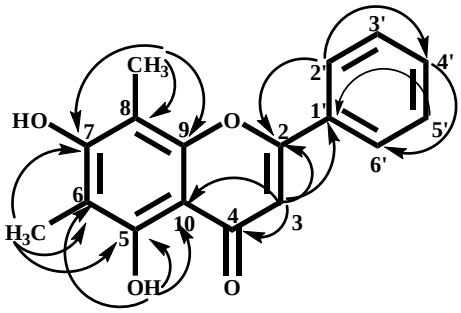
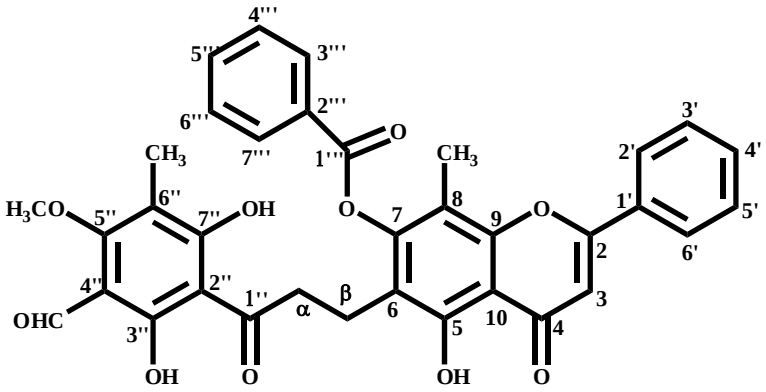


Figure 19 Selected HMBC correlations of **DC19**

Table 21 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC19** ($CDCl_3$ and DMSO-d_6)

Position	δ_H (multiplicity)		δ_C (C- type)		HMBC
	DMSO-d_6	$CDCl_3$	DMSO-d_6	$CDCl_3$	
1	-	-	-	-	-
2	-	-	163.3 (C)	163.3 (C)	-
3	6.90 (s)	6.69 (s)	105.2 (CH)	105.2 (CH)	C-2, C-4, C-10, C-1′
4	-	-	182.7 (C)	182.9 (C)	-
5	-	-	156.5 (C)	156.4 (C)	-
6	-	-	107.7 (C)	107.0 (C)	-
7	-	-	160.5 (C)	159.4 (C)	-
8	-	-	102.5 (C)	102.0 (C)	-
9	-	-	153.0 (C)	153.1 (C)	-
10	-	-	104.3 (C)	104.7 (C)	-
1′	-	-	131.5 (C)	131.5 (C)	-
2′, 6′	8.03-8.00 (m)	7.95-7.92 (m)	126.7 (CH)	126.1 (CH)	C-2, C-4′
3′, 5′	7.55-7.51 (m)	7.56-7.53 (m)	129.7 (CH)	129.0 (CH)	C-1′
4′	7.55-7.51 (m)	7.56-7.53 (m)	132.4 (CH)	131.6 (CH)	C-2′, C-6′
5-OH	12.94 (s)	12.87 (s)	-	-	C-5, C-6, C-10
6-CH_3	2.01 (s)	2.18 (s)	8.5 (CH_3)	7.3 (CH_3)	C-5, C-7, C-6
7-OH	-	-	-	-	-
8-CH_3	2.24 (s)	2.37 (s)	8.8 (CH_3)	7.9 (CH_3)	C-7, C-8, C-9

Compound DC20



DC20 was obtained as a pale yellow solid, m.p. 180-182°C. IR spectrum revealed hydroxyl (3439 cm^{-1}), carbonyl (1720, 1648 cm^{-1}) and aromatic (1542 cm^{-1}).

The ^{13}C NMR spectrum of **DC17** showed a total of 35 signals. The EIMS displayed a molecular ion $[M]^+$ at *m/z* 608, consistent with the molecular formula $C_{35}H_{28}O_{10}$.

The ^1H NMR spectrum of **DC20** was superimposable to those of **DC17**. The EIMS and ^1H NMR spectrum including NOESY experiment of **DC20** showed that **DC20** had the same phenylpropanone moiety as **DC17**. In the ^1H NMR spectrum the methyl singlet signal based on a flavones moiety were observed at a lower field (δ 2.31 (8-CH_3). In the HMBC spectrum, the methyl protons at δ 2.31 correlated with C-7 (δ 153.4), C-8 (δ 109.1) and C-9 (δ 152.7) resulting in the assignment of this methyl group at C-8. The phenylpropanone unit was linked at C-6 of a flavones moiety. Thus the structure of compound **DC20** was a structural isomer of **DC17**, a new compound and named as saiyunensis D.

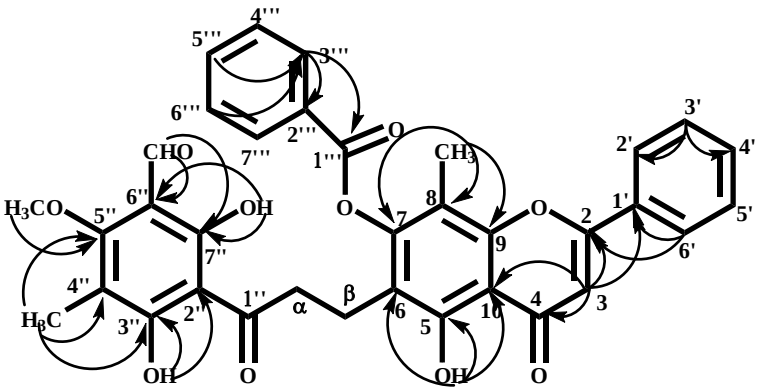


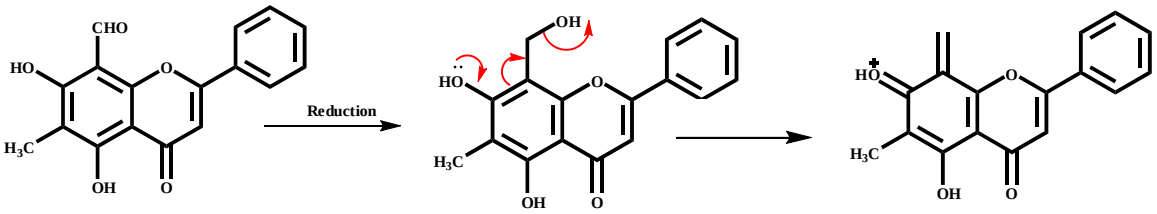
Figure 20 Selected HMBC correlations of **DC20**

Table 22 ^{1}H, ^{13}C NMR and HMBC spectral data of **DC20** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	164.3 (C)	-
3	6.77 (s)	105.9 (CH)	C-2, C-4, C-10, C-1′
4	-	183.4 (C)	-
5	-	157.5 (C)	-
6	-	117.1 (C)	-
7	-	153.4 (C)	-
8	-	109.1 (C)	-
9	-	152.7 (C)	-
10	-	108.8 (C)	-
1′	-	131.9 (C)	-
2′, 6′	7.93 (d, J = 6.8 Hz)	126.3 (CH)	C-2, C-1′
3′, 5′	7.60-7.52 (m)	129.1 (CH)	C-2′, C-4′, C-6′
4′	7.60-7.52 (m)	133.9 (CH)	-
α	3.51 (t, J = 7.8 Hz)	42.9 (CH_2)	-
β	3.51 (t, J = 7.8 Hz)	42.9 (CH_2)	-
1′′	-	206.0 (C)	-
2′′	-	106.2 (C)	-

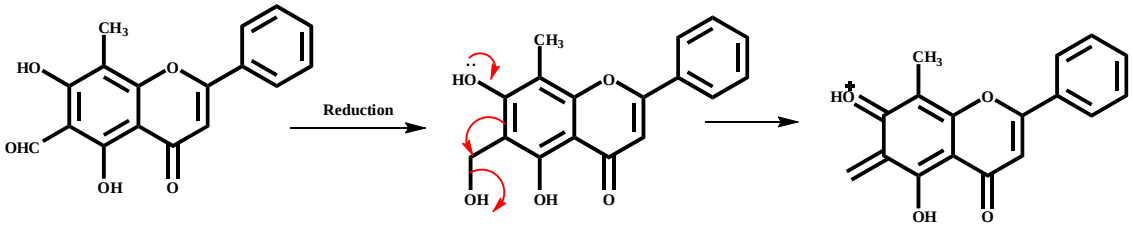
position	δ_H (multiplicity)	δ_C (C- type)	HMBC
3″	-	172.4 (C)	-
4″	-	110.8 (C)	-
5″	-	166.3 (C)	-
6″	-	107.1 (C)	-
7″	-	167.1 (C)	-
1‴	-	164.0 (C)	-
2‴	-	131.9 (C)	-
3‴, 7‴	8.23 (d, J = 7.5 Hz)	130.3 (CH)	C-1‴, C-2‴
4‴, 6‴	7.60-7.52 (m)	128.7 (CH)	C-3‴, C-7‴
5‴	7.60-7.52 (m)	133.9 (CH)	C-3‴, C-7‴
5-OH	12.96 (s)	-	C-5, C-6, C-10
8-CH_3	2.31 (s)	9.1 (CH_3)	C-7, C-8, C-9
3″-OH	14.97 (s)	-	C-2″, C-3″
4″-CH_3	2.05 (s)	7.9 (CH_3)	C-3″, C-4″, C-5″
5″-OCH_3	3.86 (s)	62.8 (CH_3)	C-5″
6″-CHO	9.91 (s)	192.3 (CH)	C-6″, C-7″
7″-OH	14.02 (s)	-	C-6″, C-7″

The biosynthesis of saiyunensis A and B could involve an oxidative coupling between 3-formyl-2,6-dihydroxy-4-methoxy-5-methyl dibenzoylmethane and flavones derivatives, followed by nucleophilic addition to give a cyclic ketal product. Then a ring opening led to linkage of these units through C-β and C-8 and C-β and C-6 bonds, respectively.



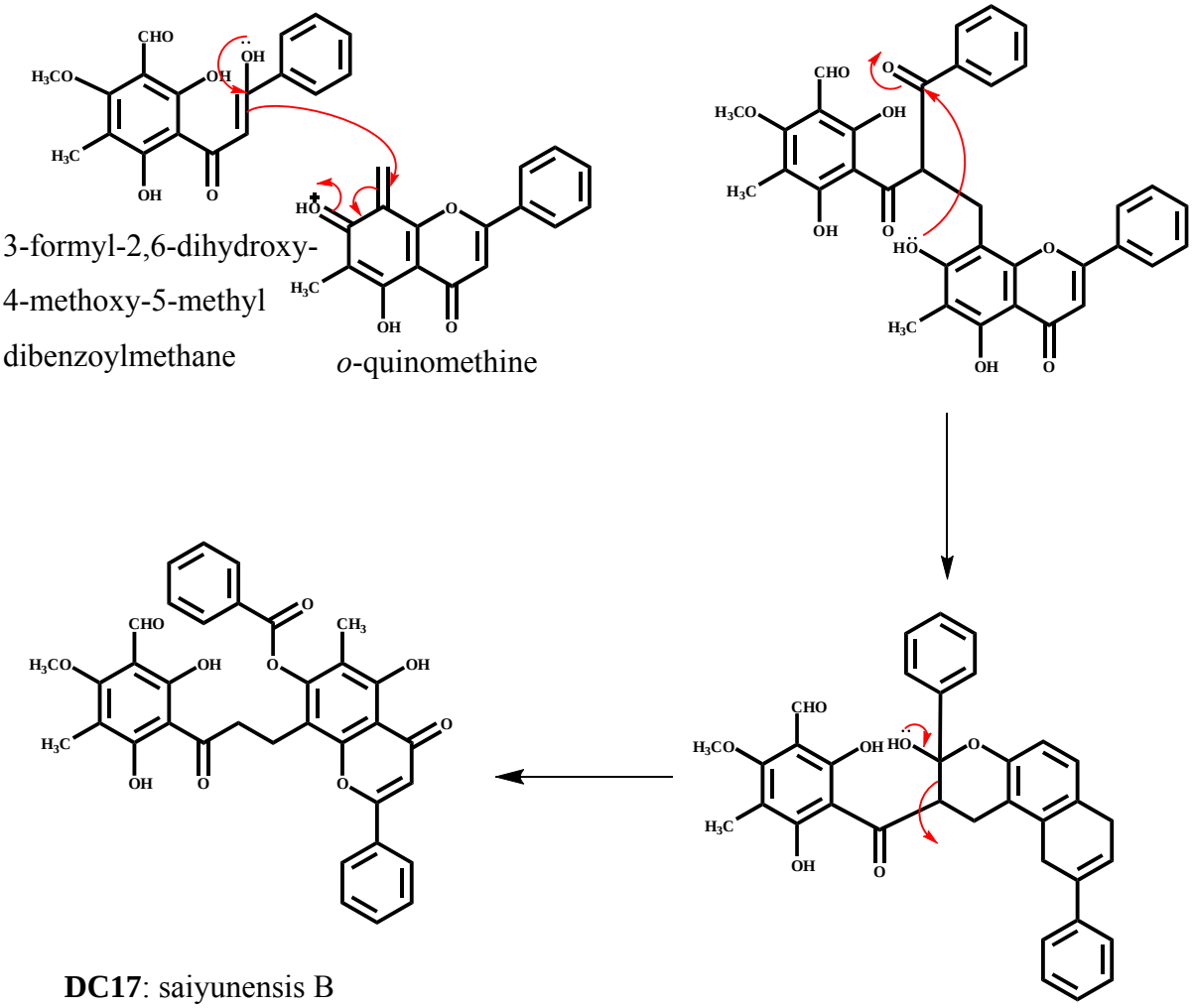
Isounonal *o*-quinomethine

Scheme 4 Plausible biosynthetic route for *o*-quinomethine from isounonal

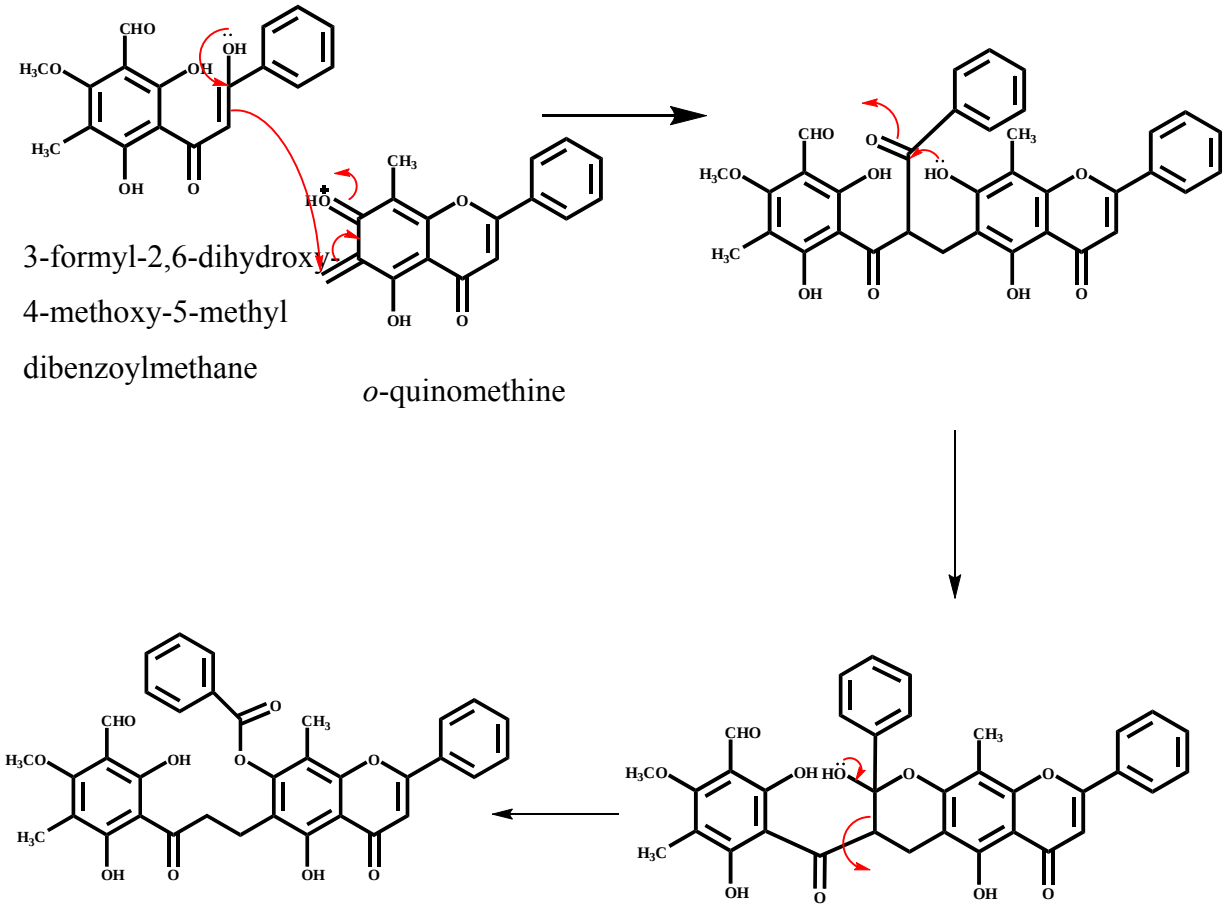


Unonal *o*-quinomethine

Scheme 5 Plausible biosynthetic route for *o*-quinomethine from unonal



Scheme 6 Plausible biosynthetic route for saiyunensis B **(DC17)** from 3-formyl-2,6-dihydroxy-4-methoxy-5-methyl dibenzoylmethane and isounonal



Scheme 7 Plausible biosynthetic route for saiyunensis D **(DC20)** from 3-formyl-2,6-dihydroxy-4-methoxy-5-methyl dibenzoylmethane and unonal

Conclusion

Investigation of the crude dichloromethane extract from the leaves of *D. chinensis* led to the isolation of twenty compounds of nine benzoate esters: benzyl 2-hydroxybenzoate **(DC1)**, benzyl benzoate **(DC2)**, benzyl 2,6-dihydroxybenzoate **(DC3)**, cinnamyl benzoate **(DC4)**, benzyl 2-hydroxy-5-methoxybenzoate **(DC5)**, 2-methoxybenzyl benzoate **(DC6)**, benzyl 2-hydroxy-6-methoxybenzoate **(DC7)**, benzyl 2-methoxybenzoate **(DC9)** and benzyl 3-hydroxybenzoate **(DC14)**, one diterpene: phytol **(DC8)**, five flavones: isounonal **(DC10)**, unonal **(DC11)**, 6-formyl-2,5,7-trihydroxy-8-methylflavanone **(DC12)**, desmal **(DC13)** and matteuorien **(DC19)**, one acid: 2-methoxybenzoic acid **(DC15)**, four biflavones: saiyunensis A **(DC16)**, saiyunensis B **(DC17)**, saiyunensis C **(DC18)** and saiyunensis D **(DC20)**.

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APPENDIX

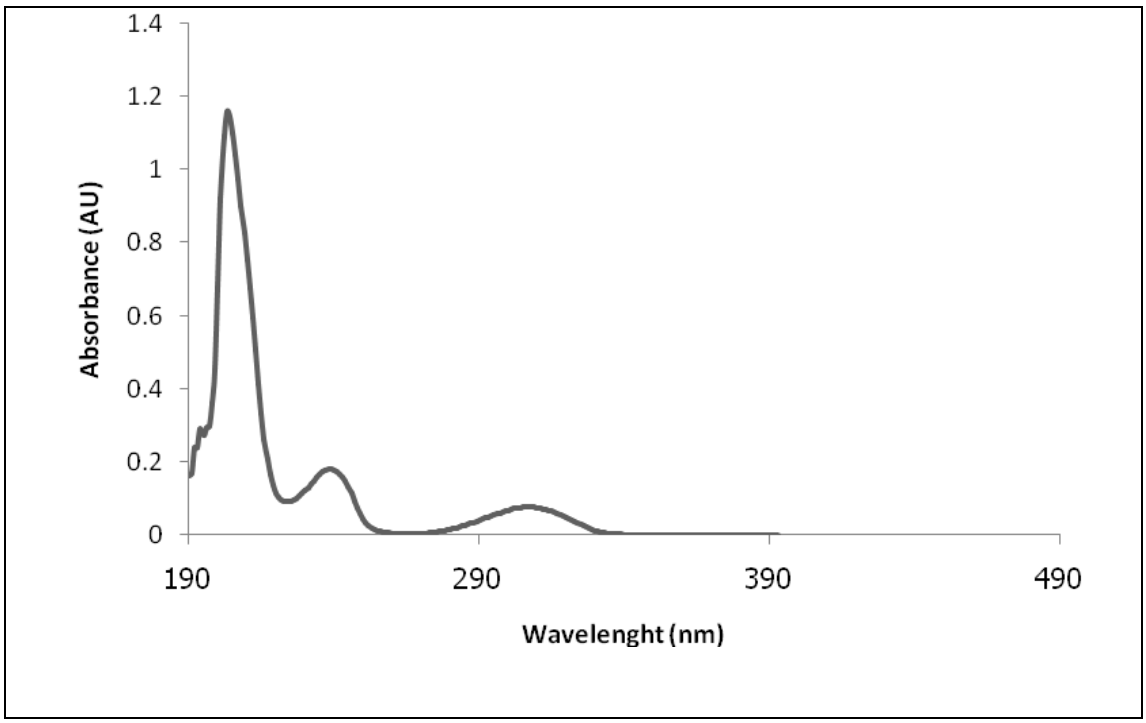

Figure 21 UV (MeOH) spectrum of compound **DC1**

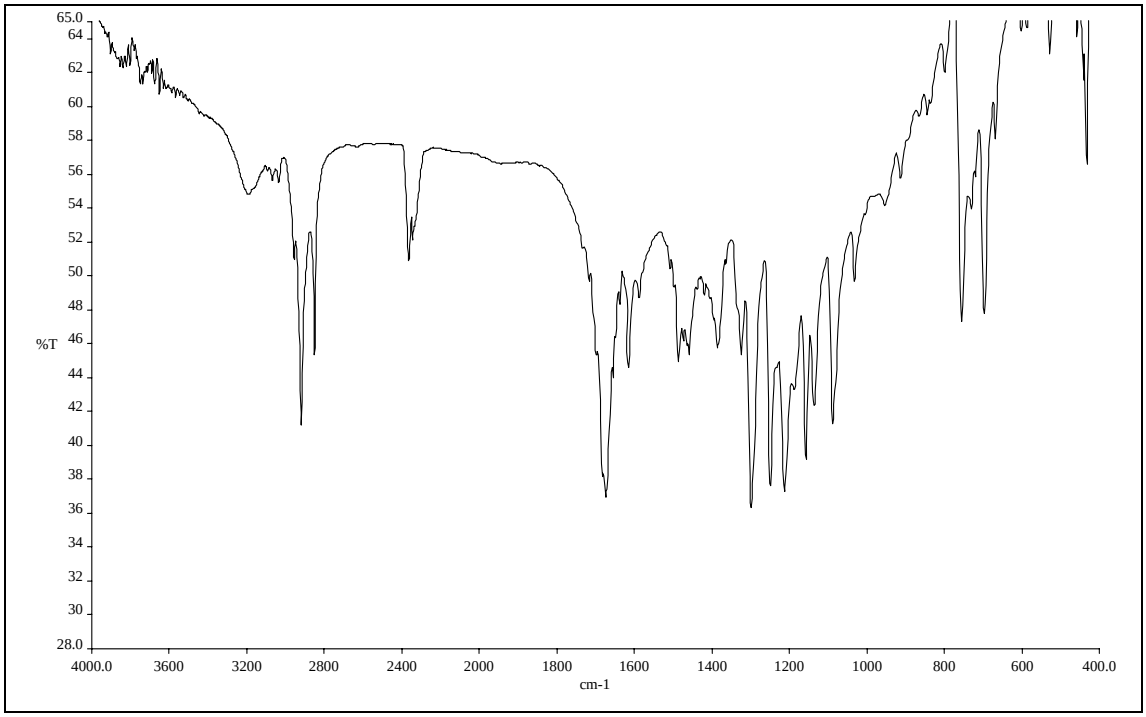

Figure 22 IR (neat) spectrum of compound **DC1**

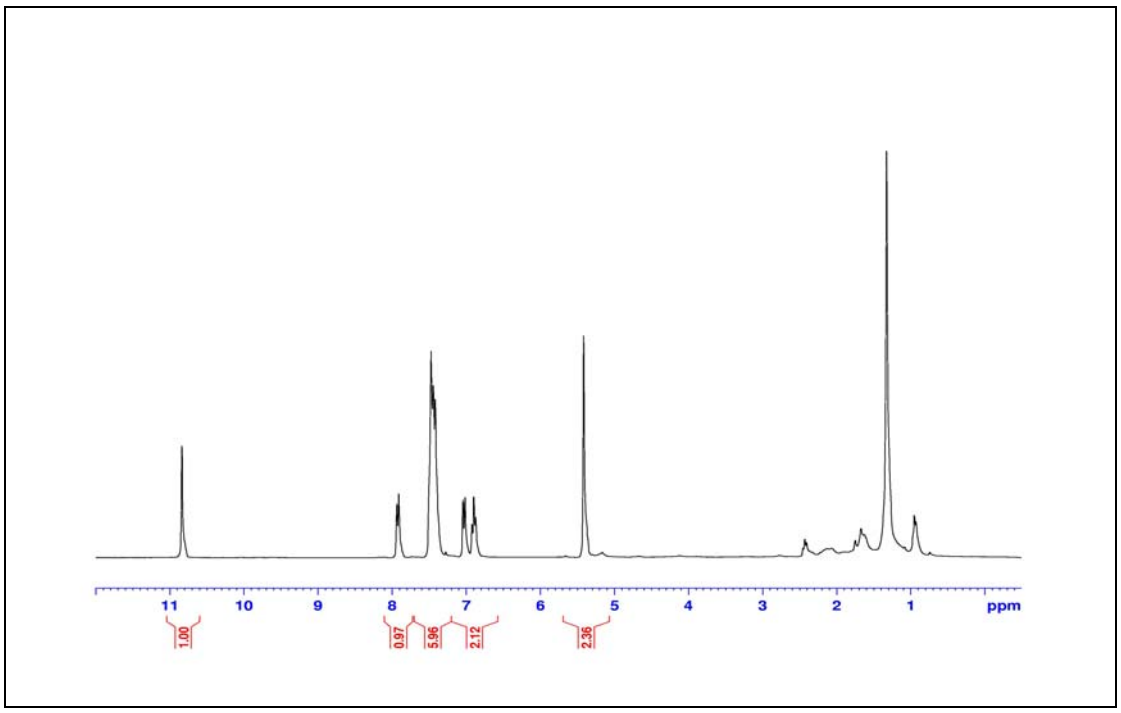

Figure 23 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC1**

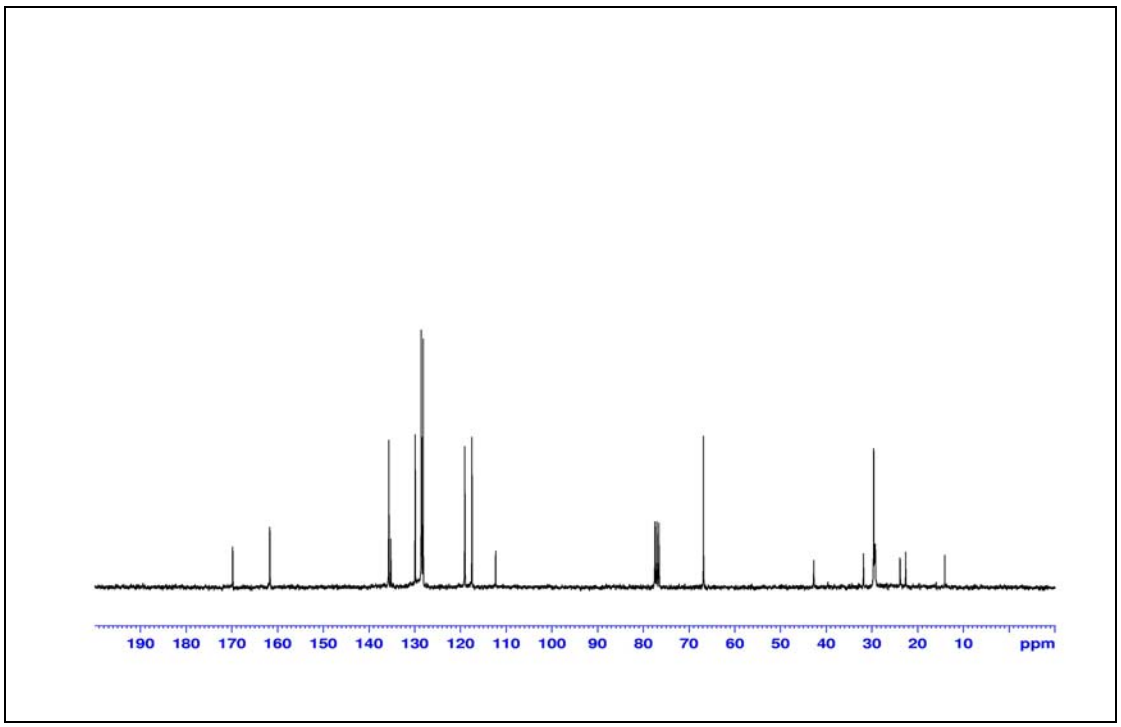

Figure 24 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC1**

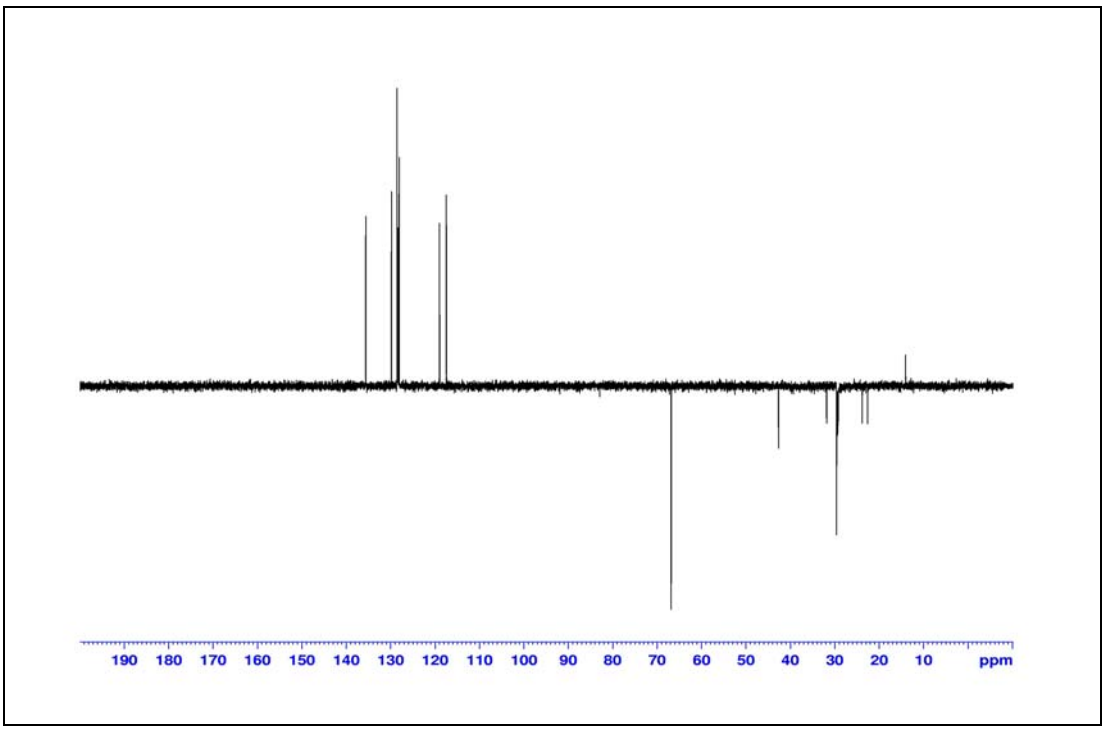

Figure 25 DEPT 135° ($CDCl_3$) of compound **DC1**

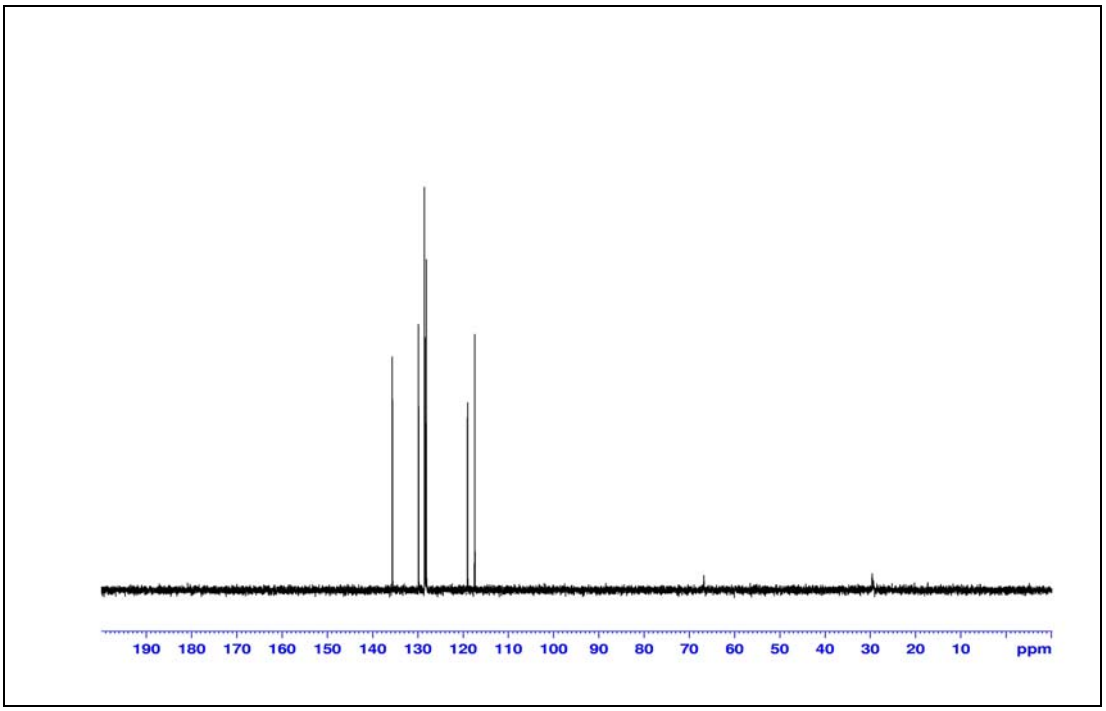

Figure 26 DEPT 90° ($CDCl_3$) of compound **DC1**

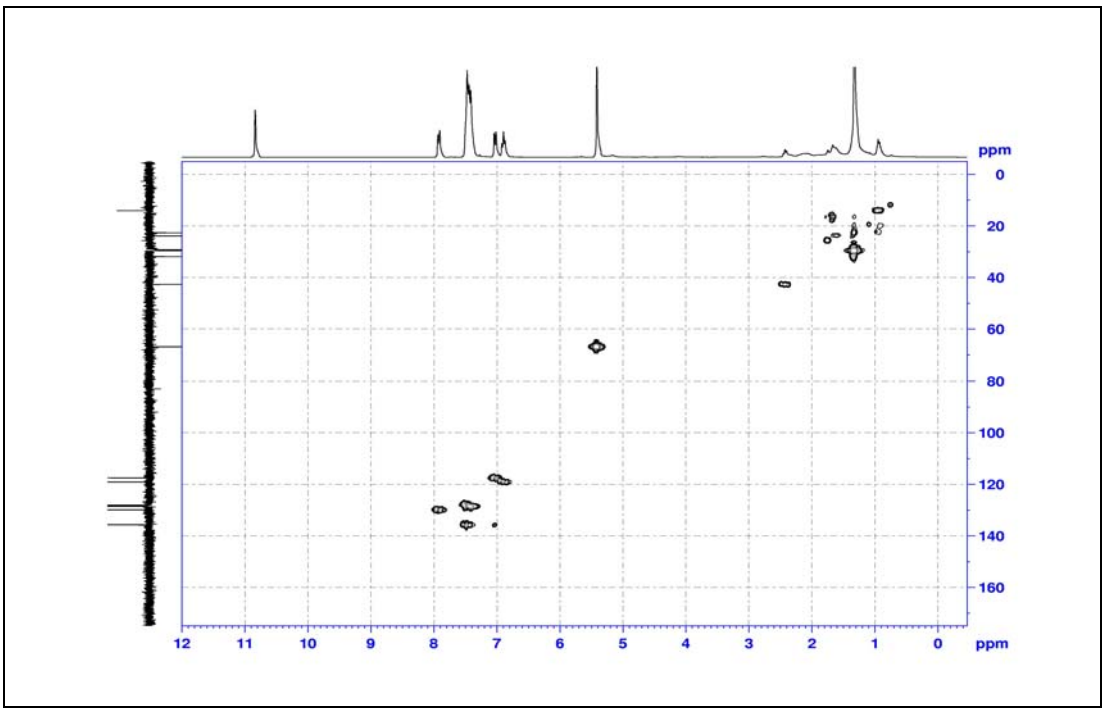

Figure 27 2D HMQC ($CDCl_3$) of compound **DC1**

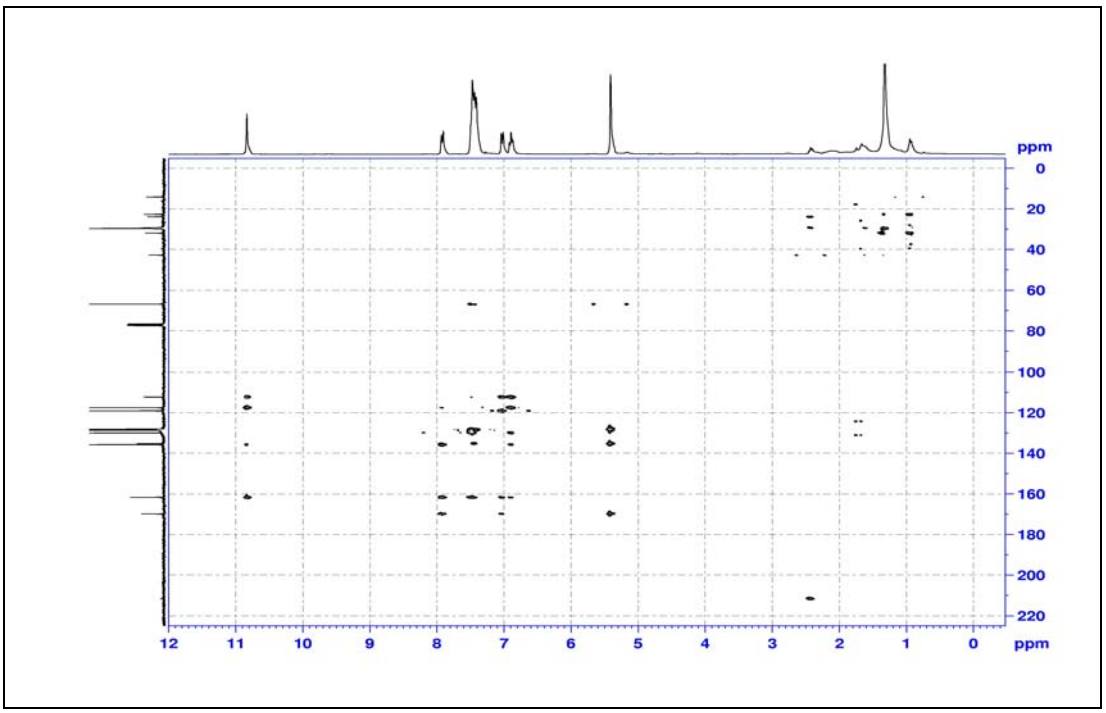

Figure 28 2D HMBC ($CDCl_3$) of compound **DC1**

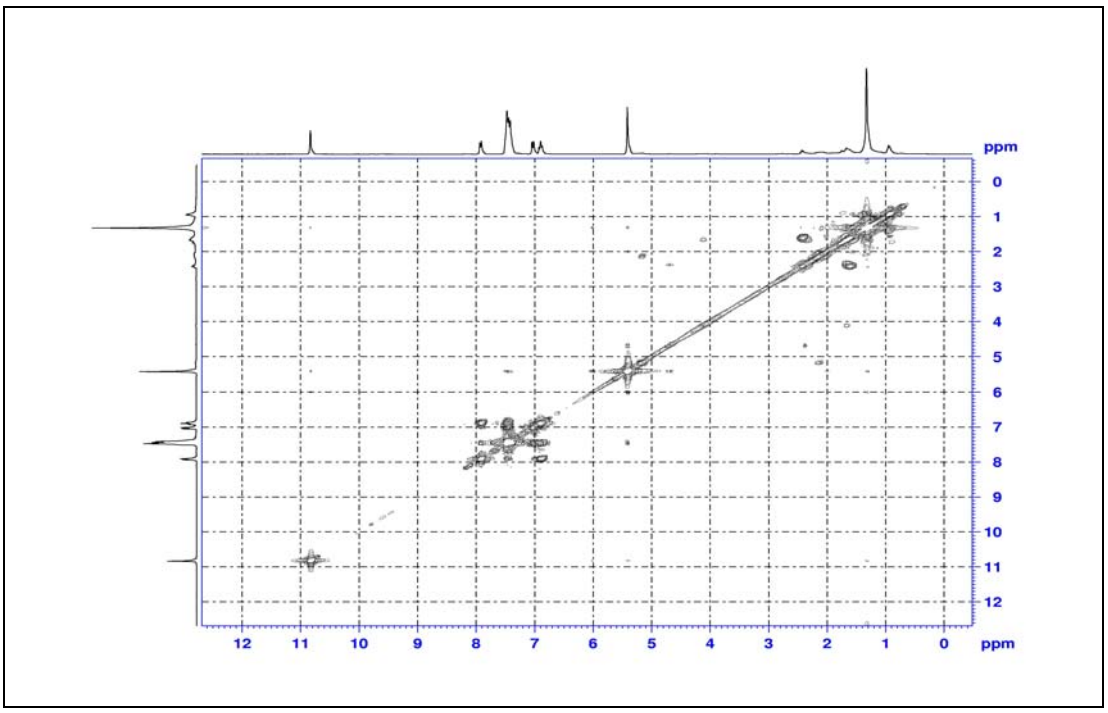

Figure 29 2D COSY ($CDCl_3$) of compound **DC1**

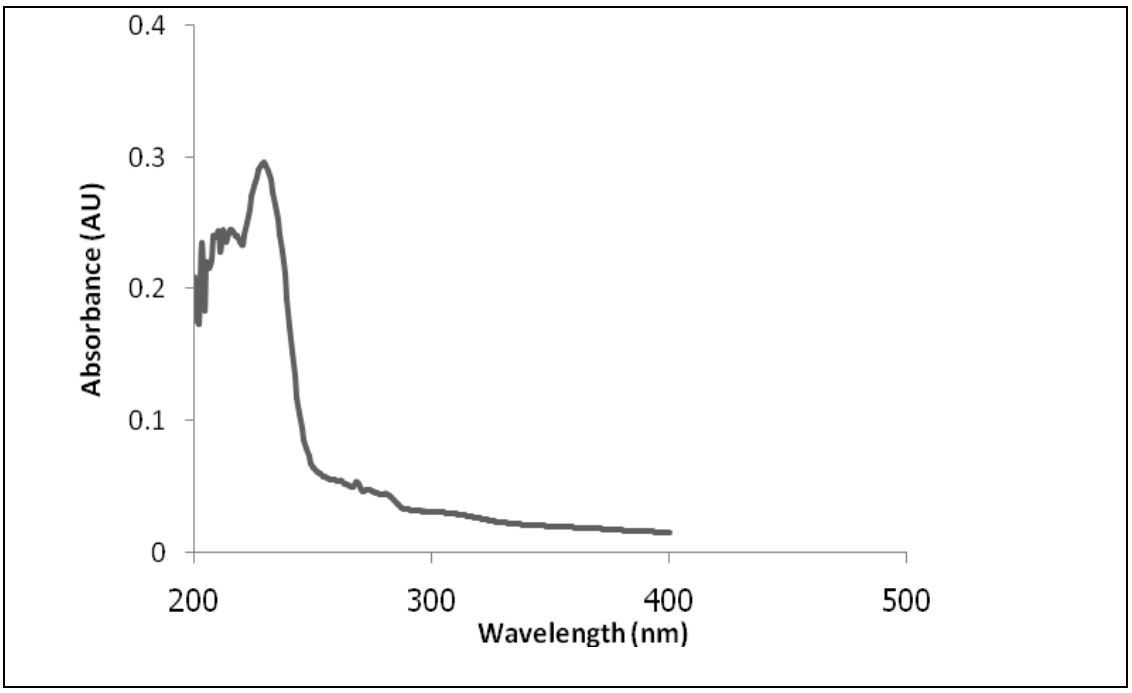

Figure 30 UV (MeOH) spectrum of compound **DC2**

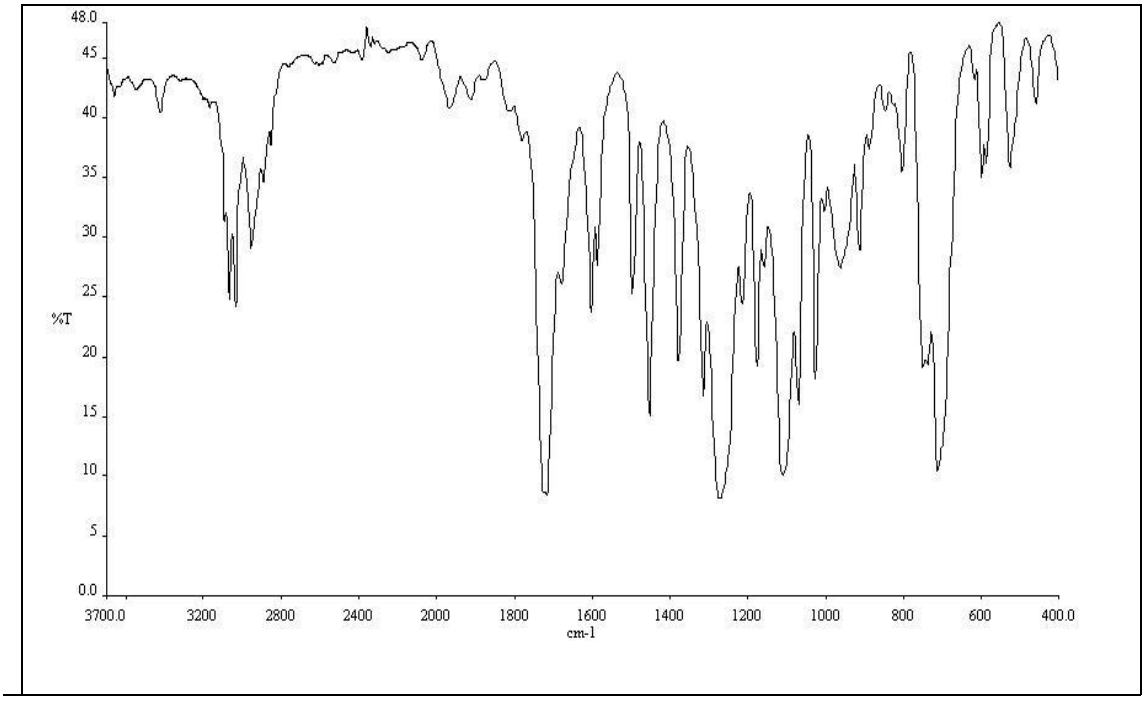

Figure 31 IR (neat) spectrum of compound **DC2**

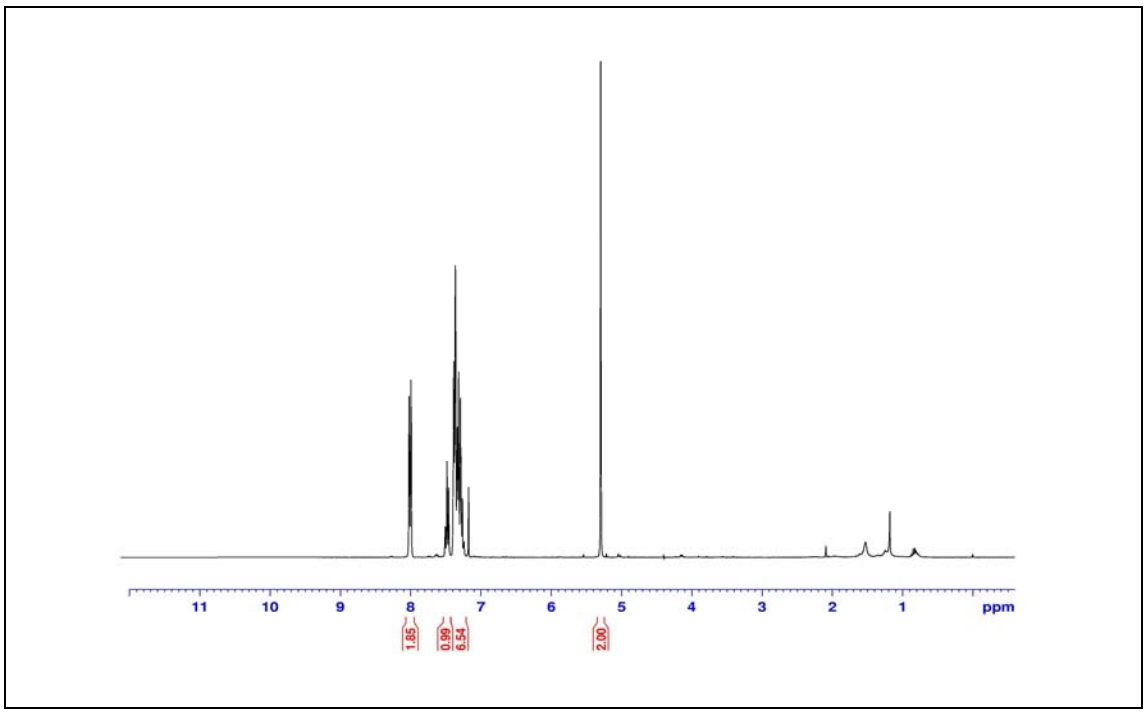

Figure 32 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC2**

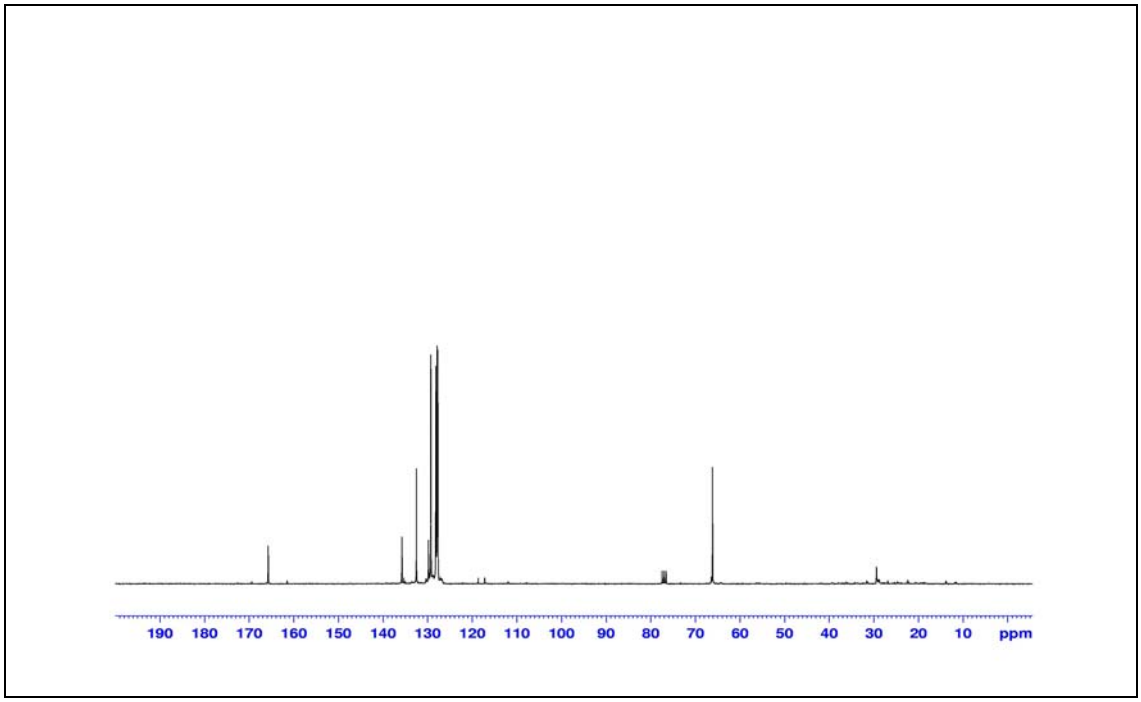

Figure 33 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC2**

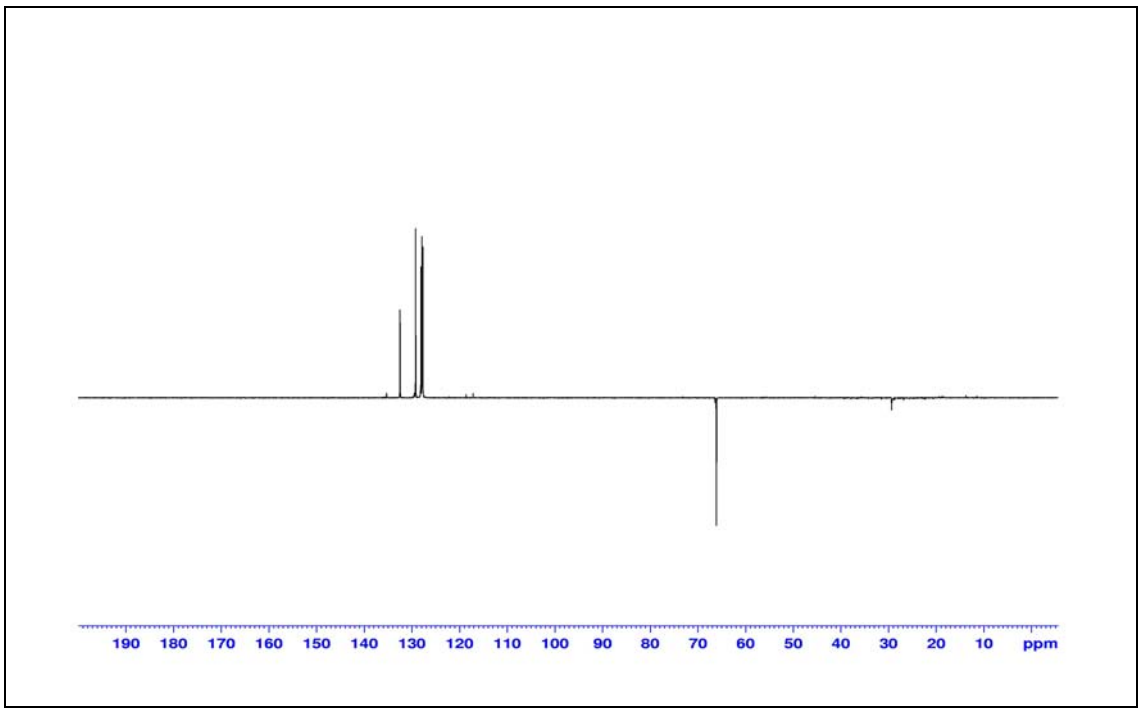

Figure 34 DEPT 135° ($CDCl_3$) of compound **DC2**

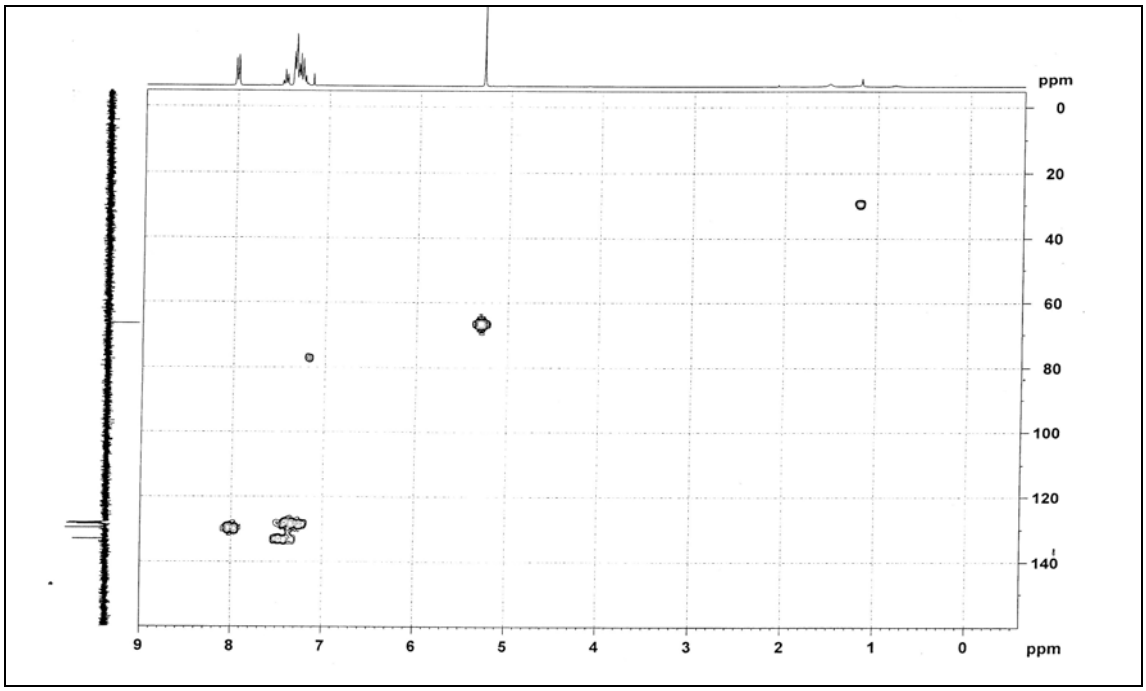

Figure 35 2D HMQC ($CDCl_3$) of compound **DC2**

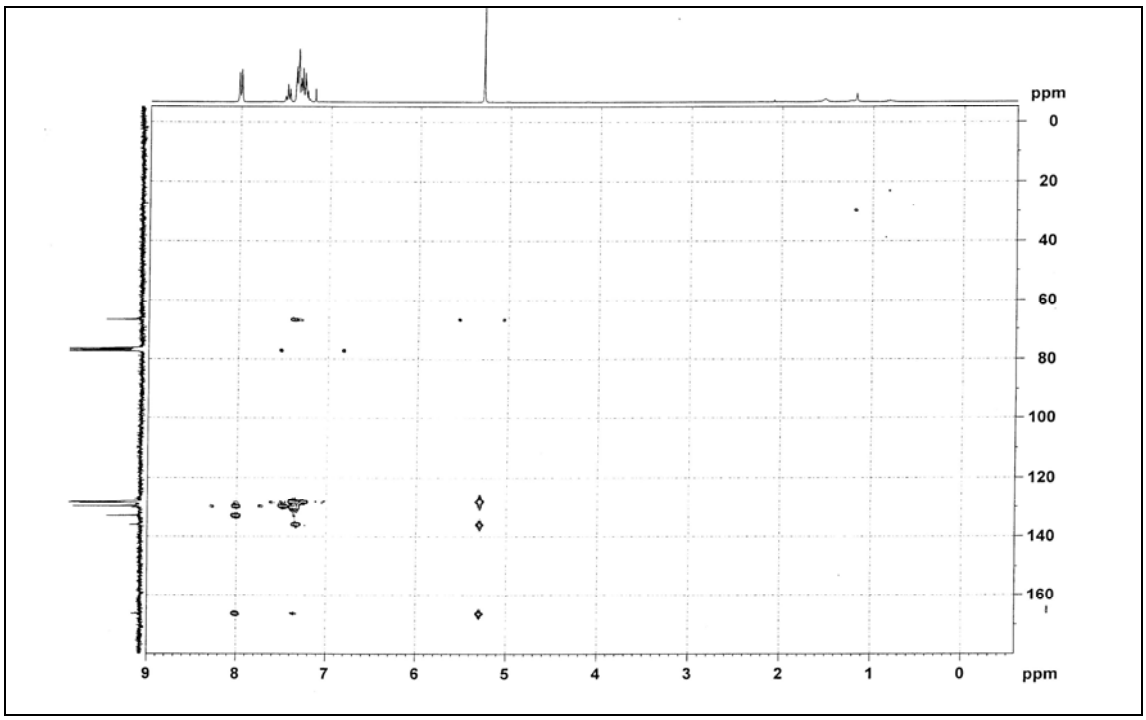

Figure 36 2D HMBC ($CDCl_3$) of compound **DC2**

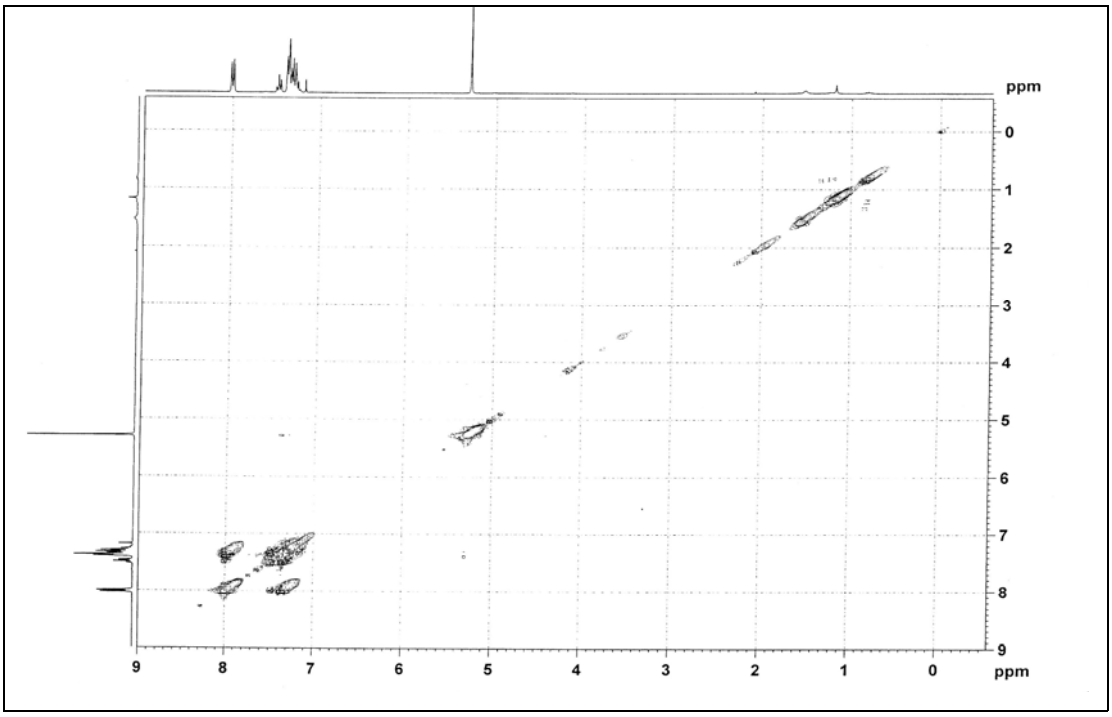

Figure 37 2D COSY ($CDCl_3$) of compound **DC2**

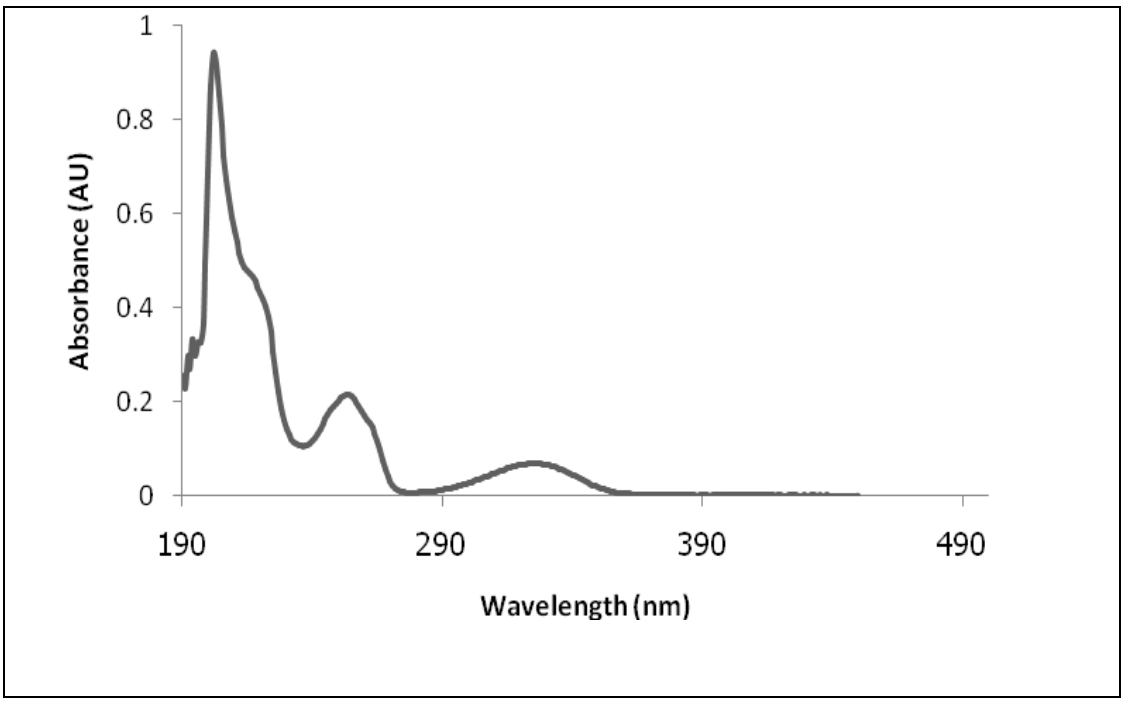

Figure 38 UV (MeOH) spectrum of compound **DC3**

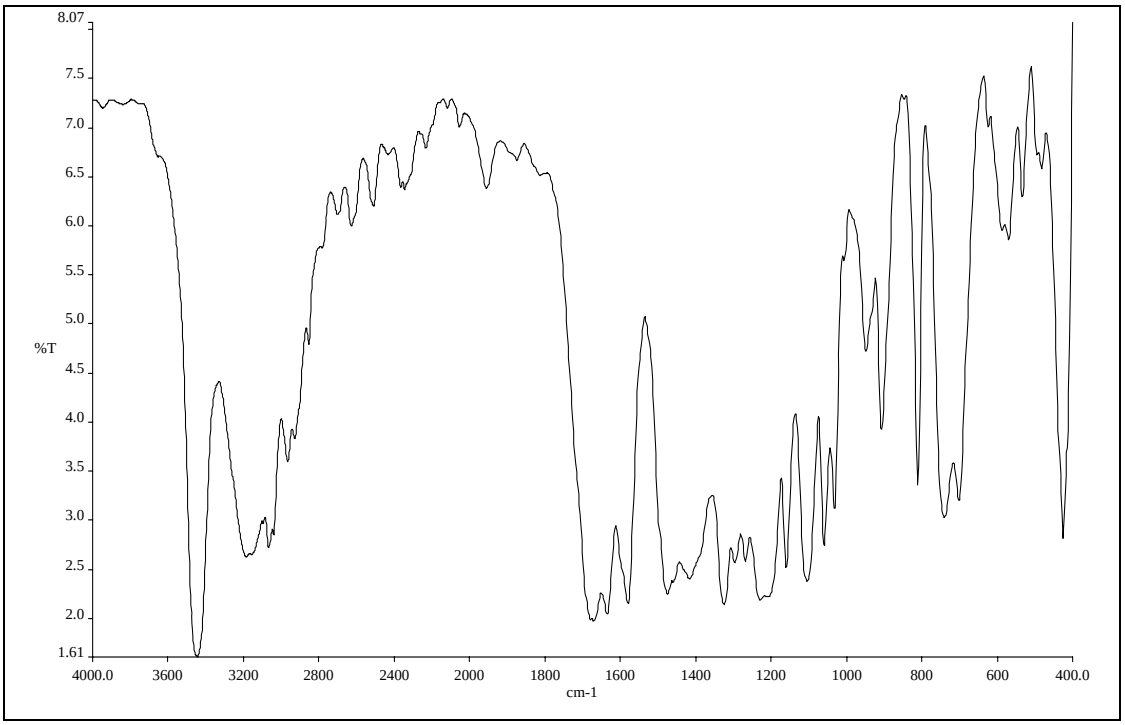

Figure 39 IR (neat) spectrum of compound **DC3**

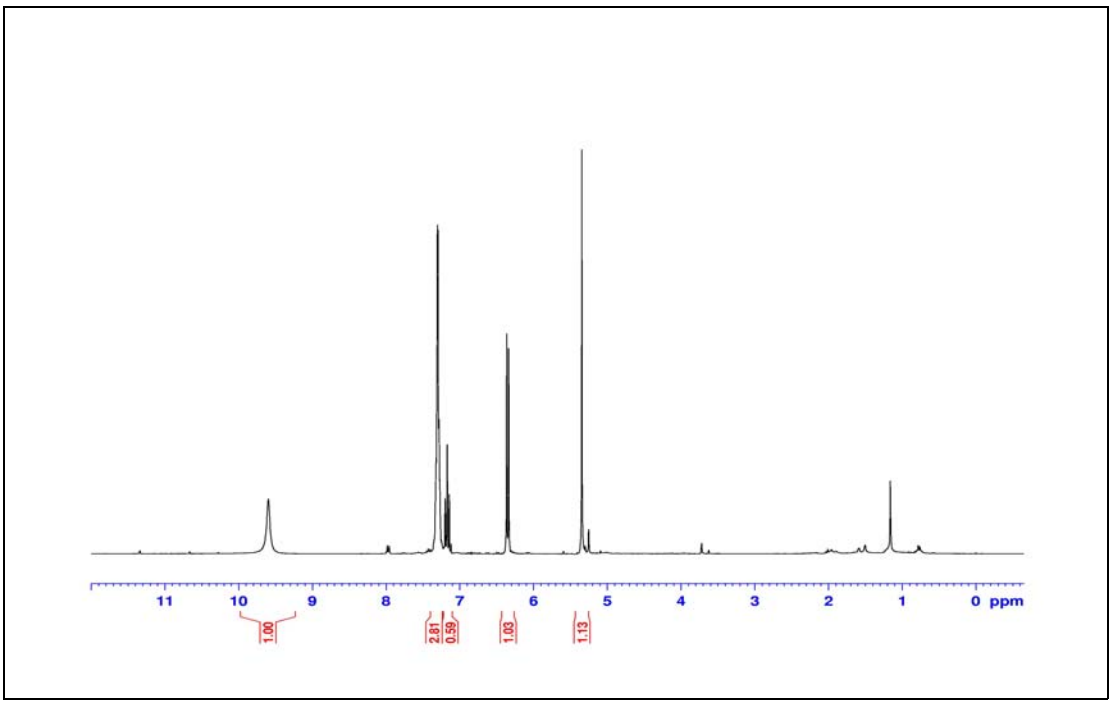

Figure 40 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC3**

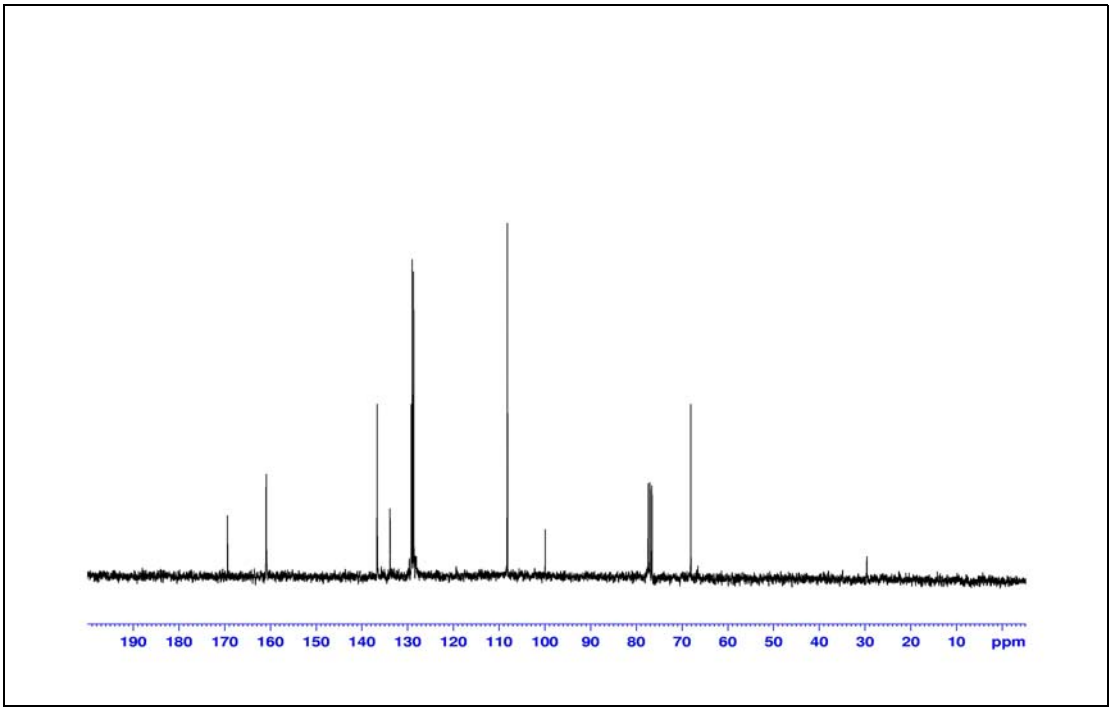

Figure 41 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC3**

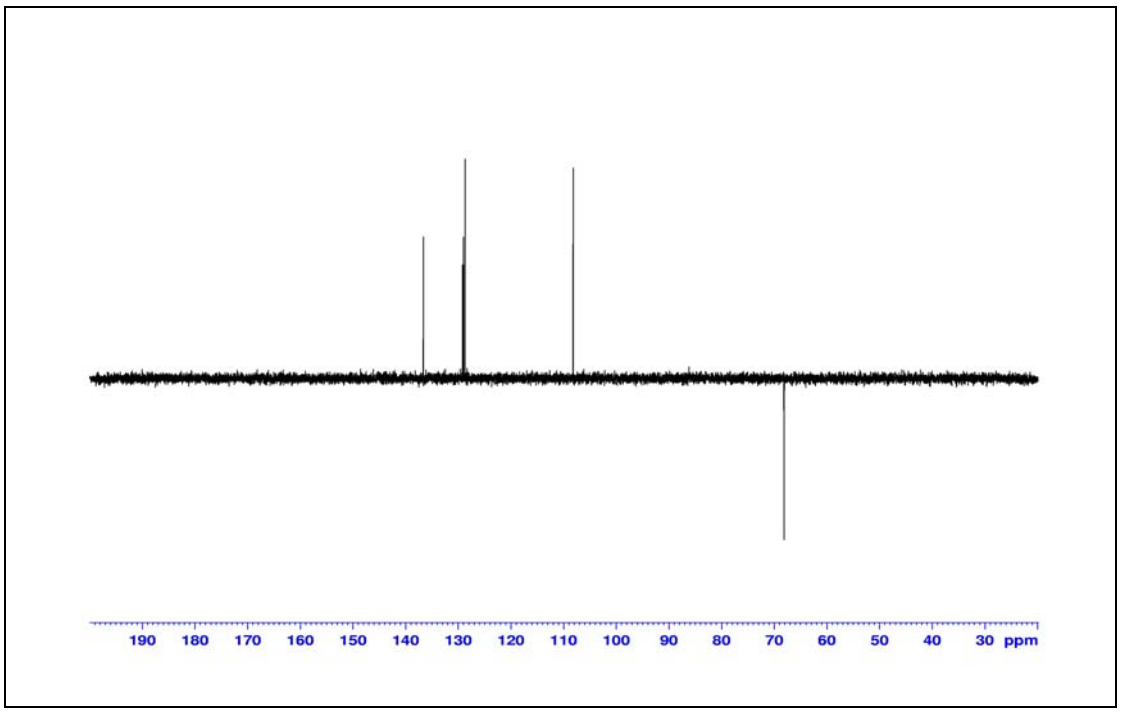

Figure 42 DEPT 135° ($CDCl_3$) of compound **DC3**

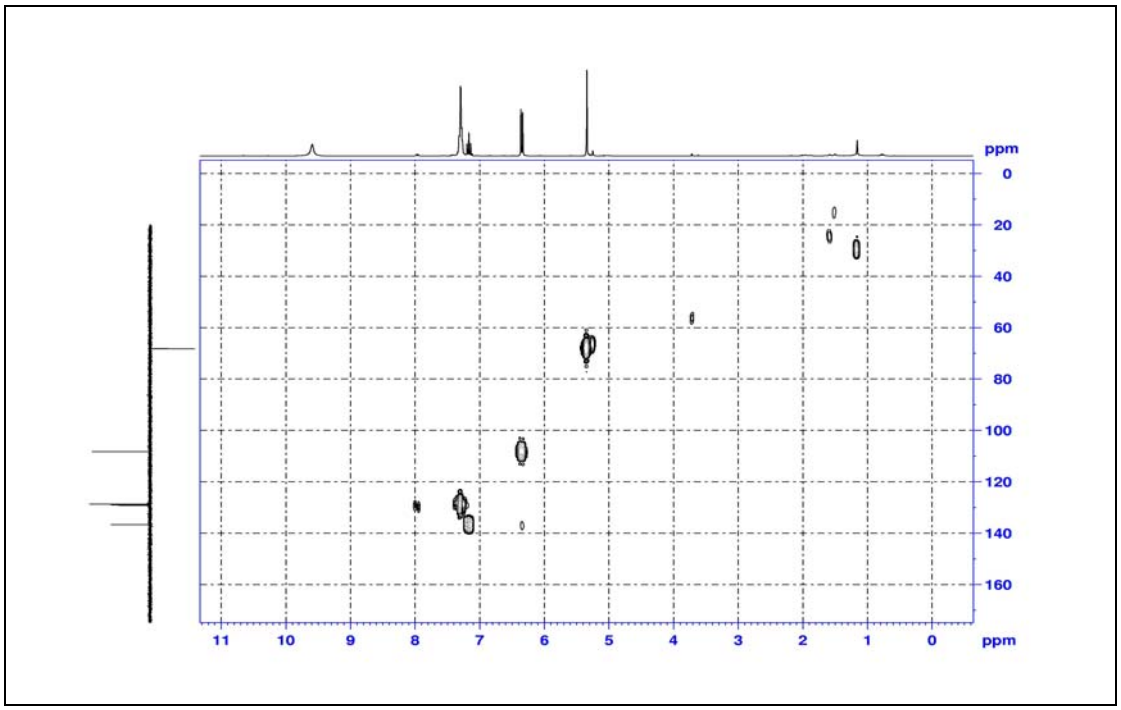

Figure 43 2D HMQC ($CDCl_3$) of compound **DC3**

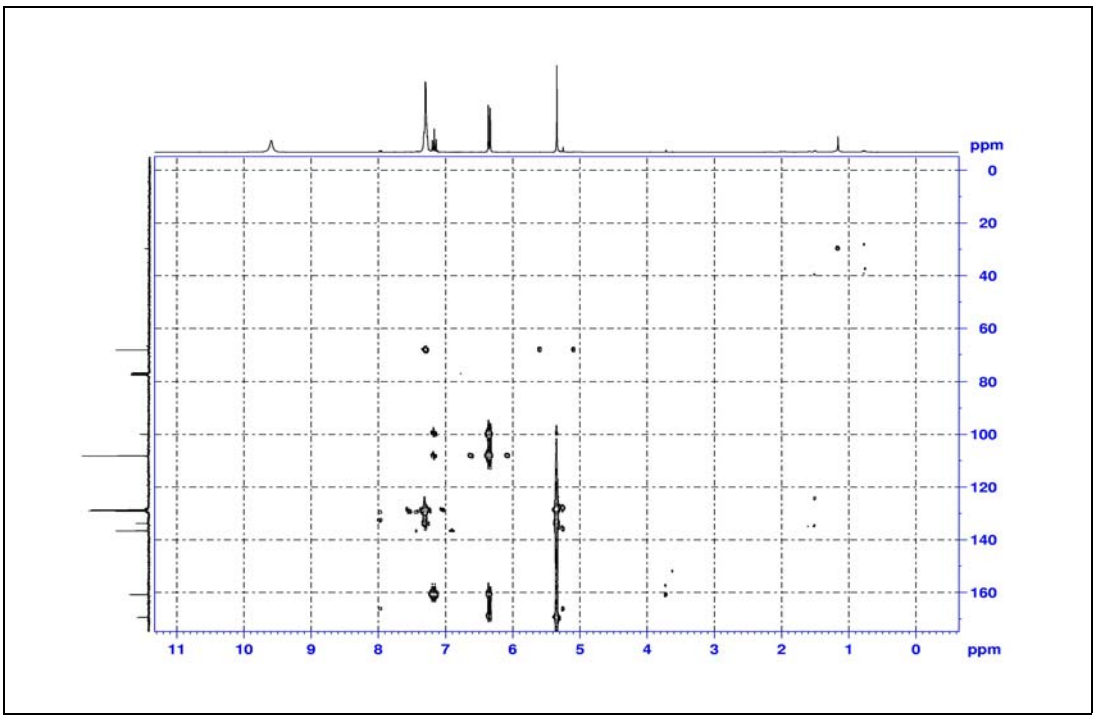

Figure 44 2D HMBC ($CDCl_3$) of compound **DC3**

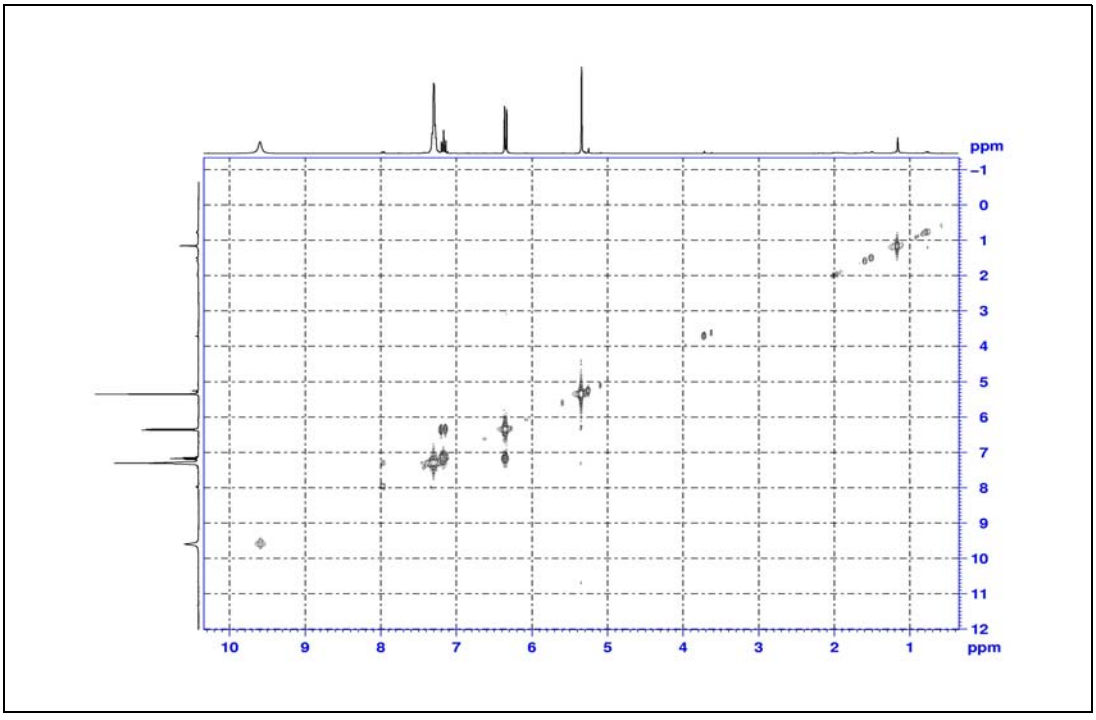

Figure 45 2D COSY ($CDCl_3$) of compound **DC3**

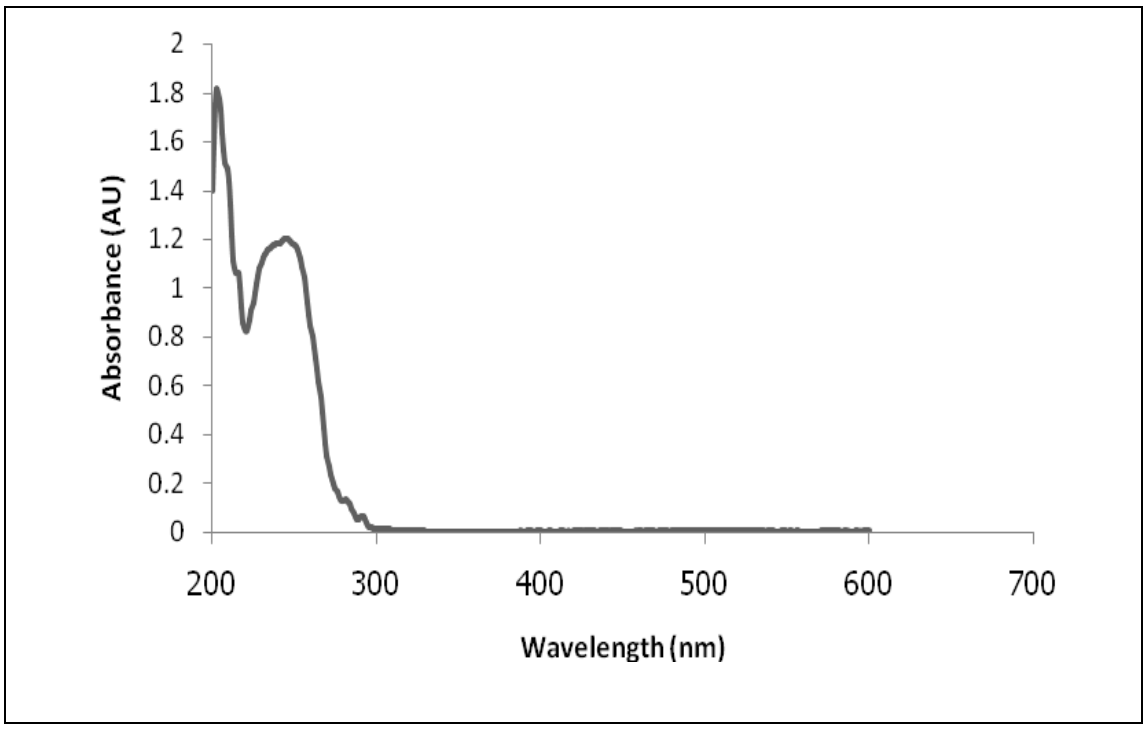

Figure 46 UV (MeOH) spectrum of compound **DC4**

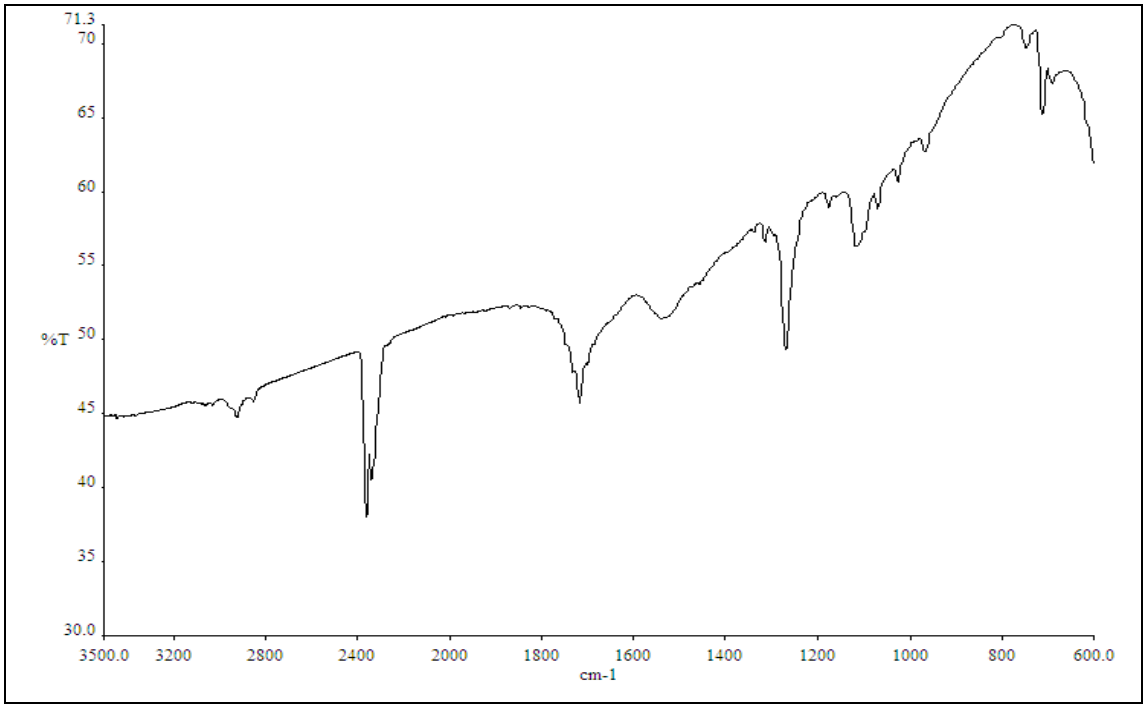

Figure 47 IR (neat) spectrum of compound **DC4**

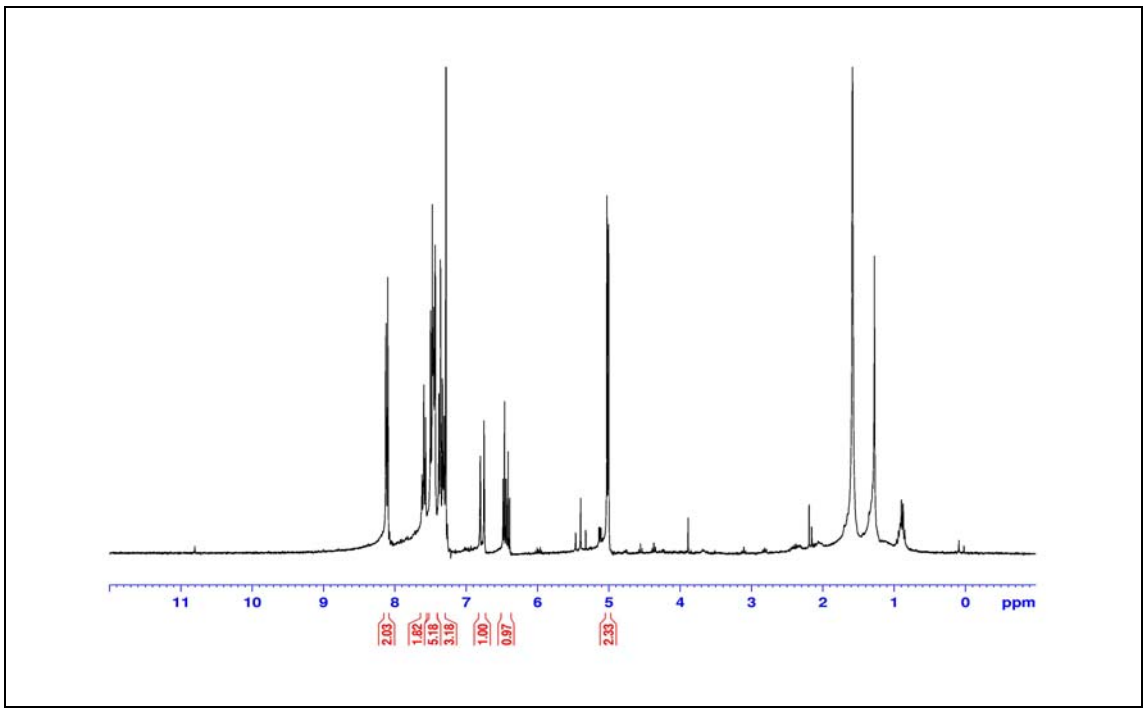

Figure 48 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC4**

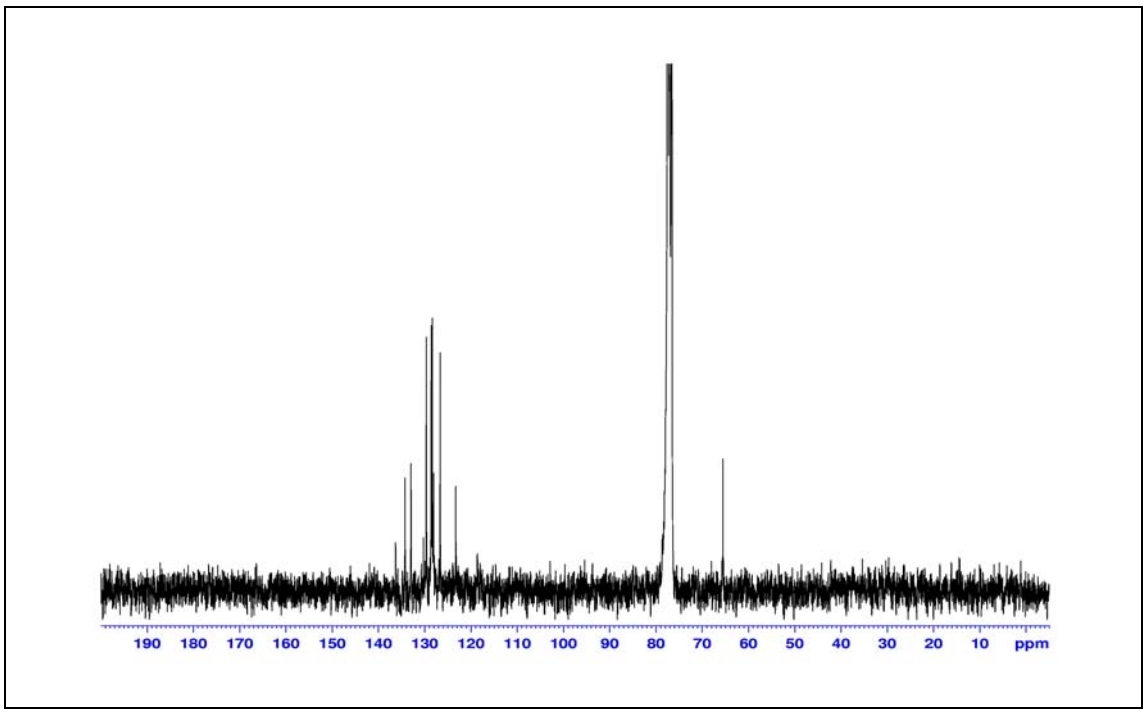

Figure 49 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC4**

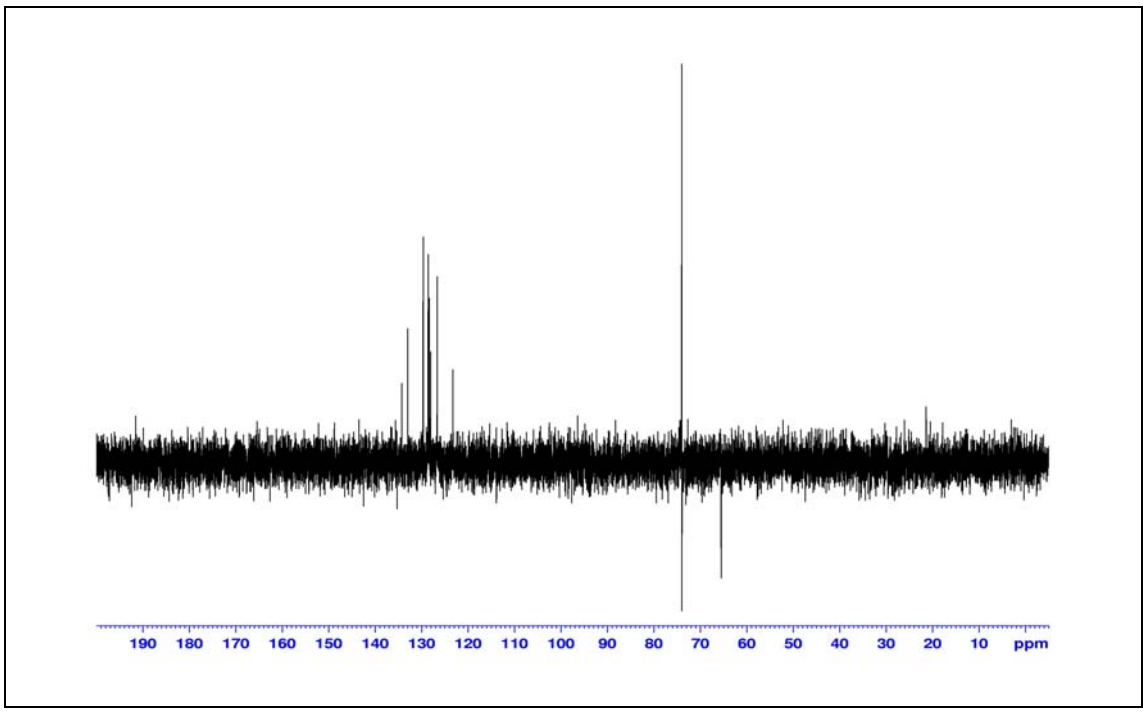

Figure 50 DEPT 135° ($CDCl_3$) of compound **DC4**

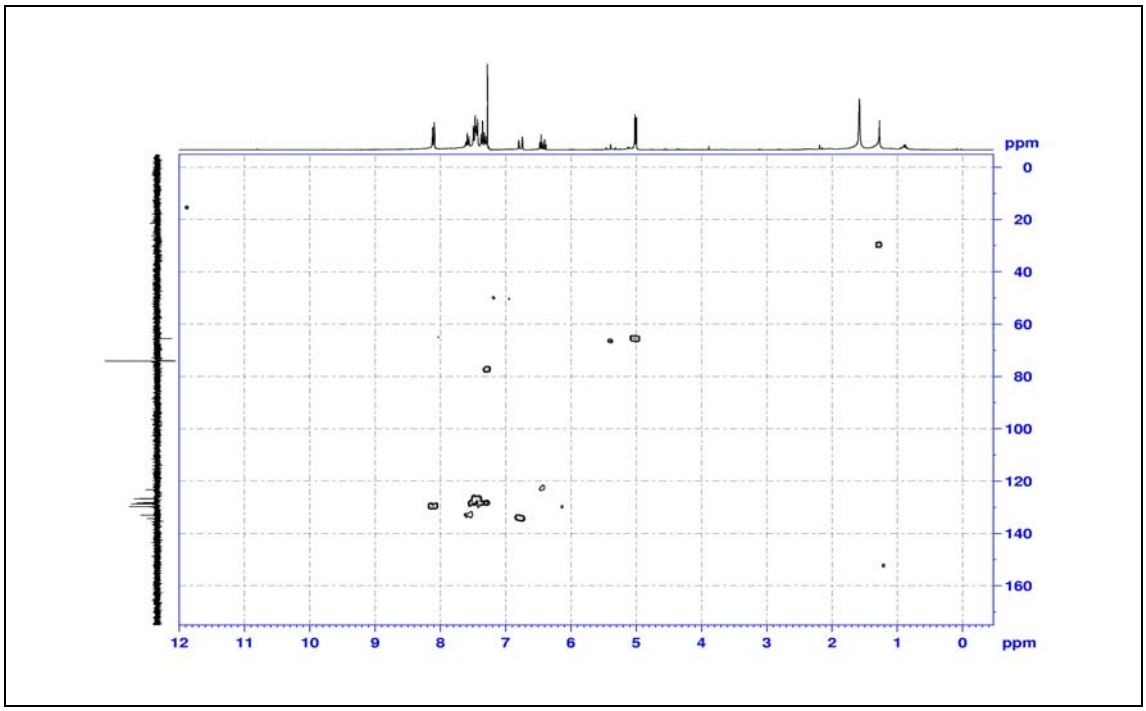

Figure 51 2D HMQC ($CDCl_3$) of compound **DC4**

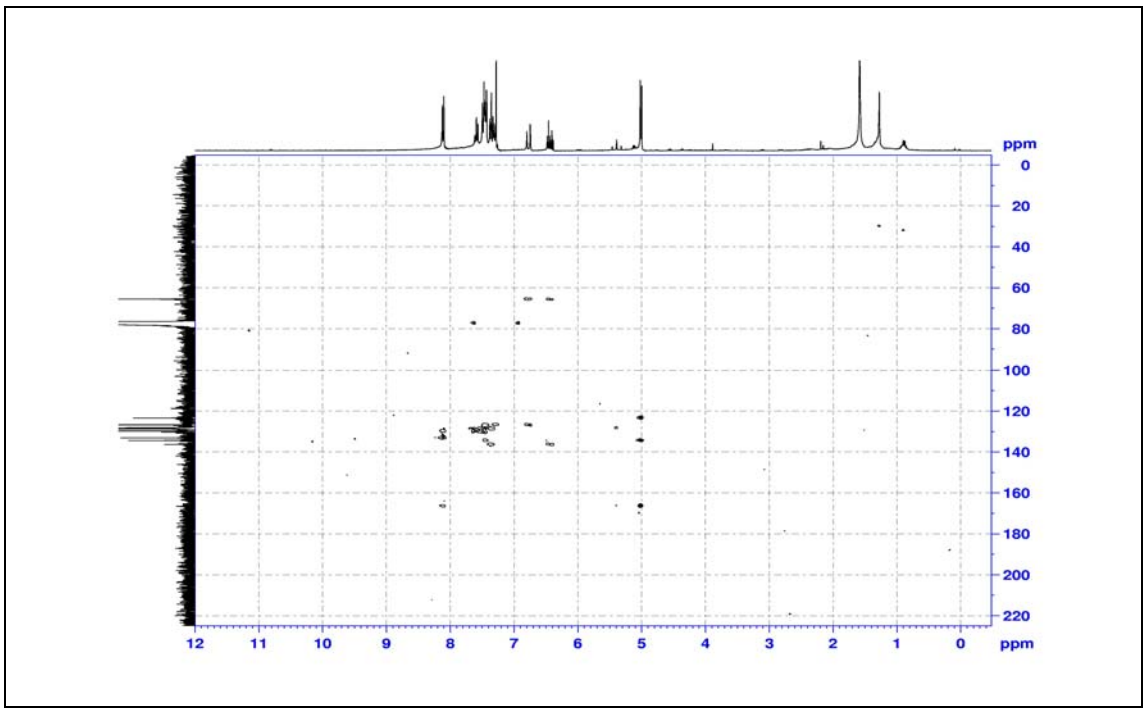

Figure 52 2D HMBC ($CDCl_3$) of compound **DC4**

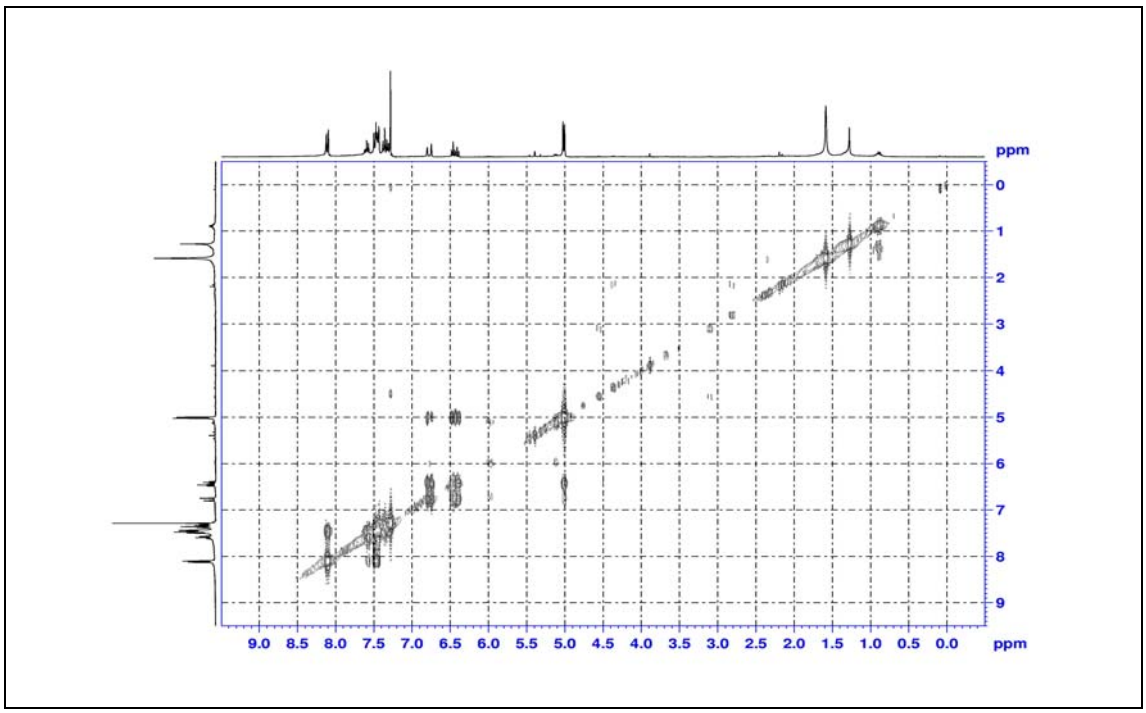

Figure 53 2D COSY ($CDCl_3$) of compound **DC4**

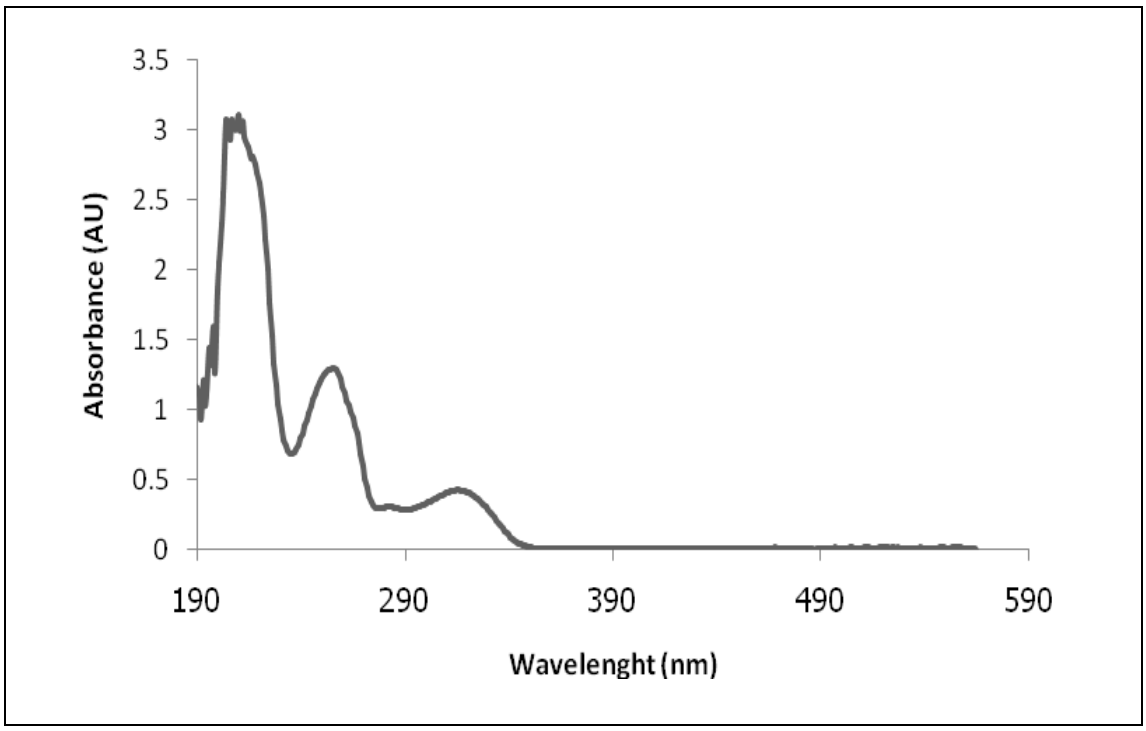

Figure 54 UV (MeOH) spectrum of compound **DC5**

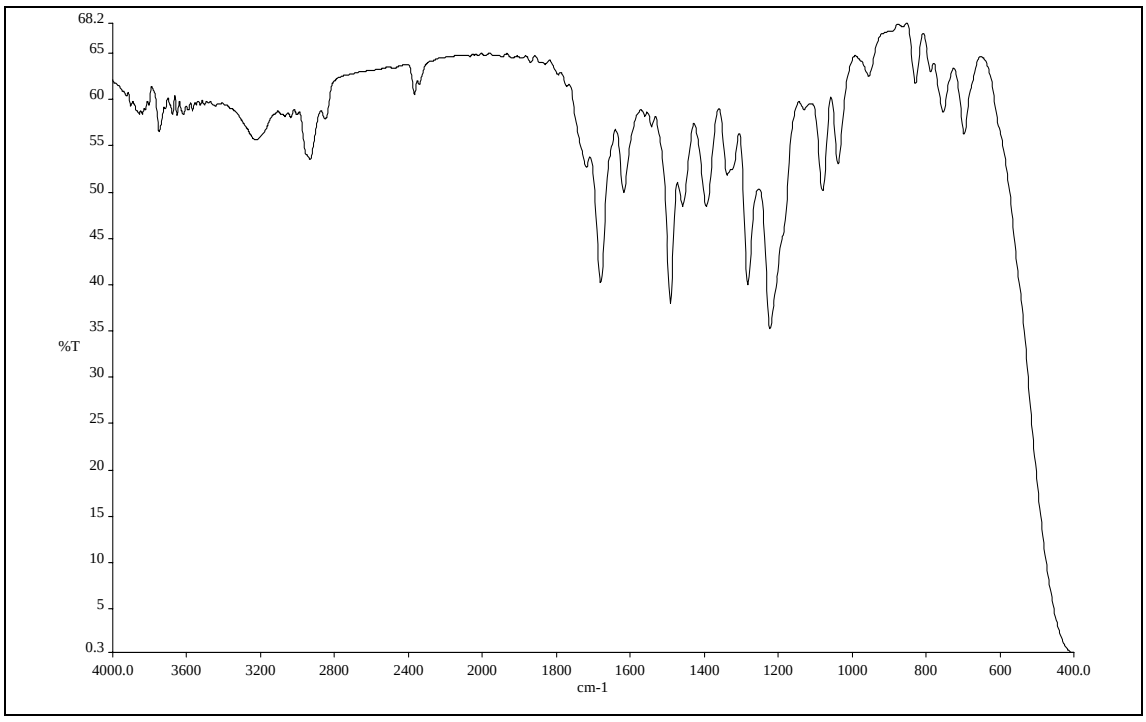

Figure 55 IR (neat) spectrum of compound **DC5**

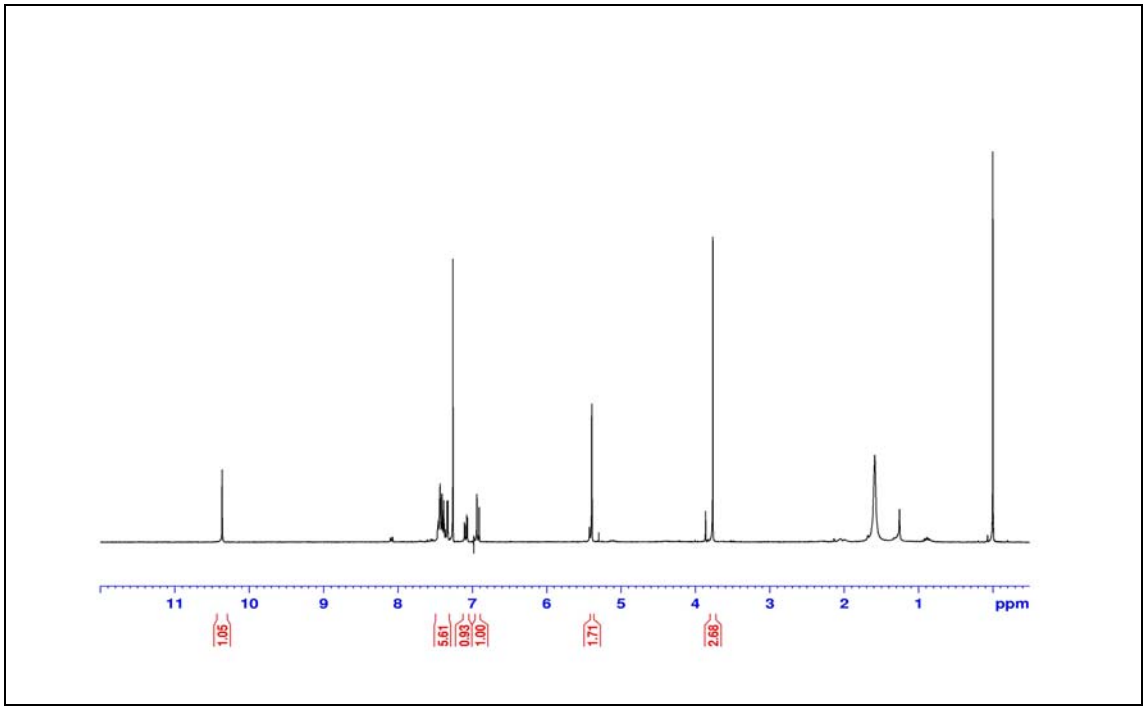

Figure 56 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC5**

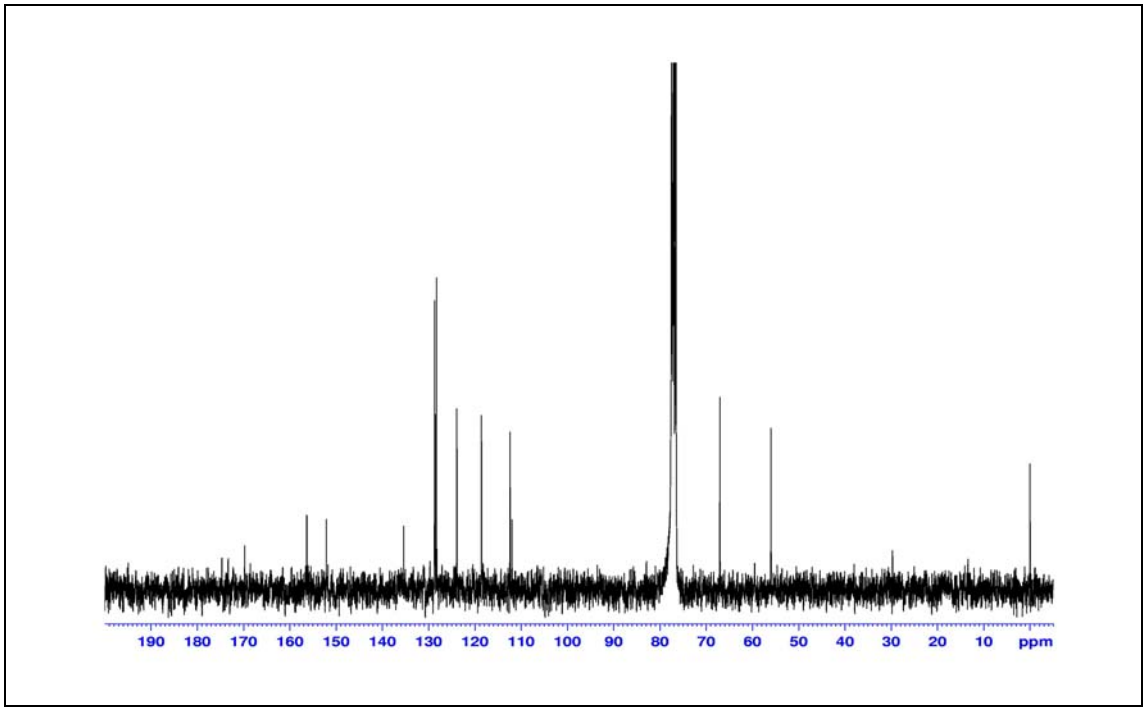

Figure 57 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC5**

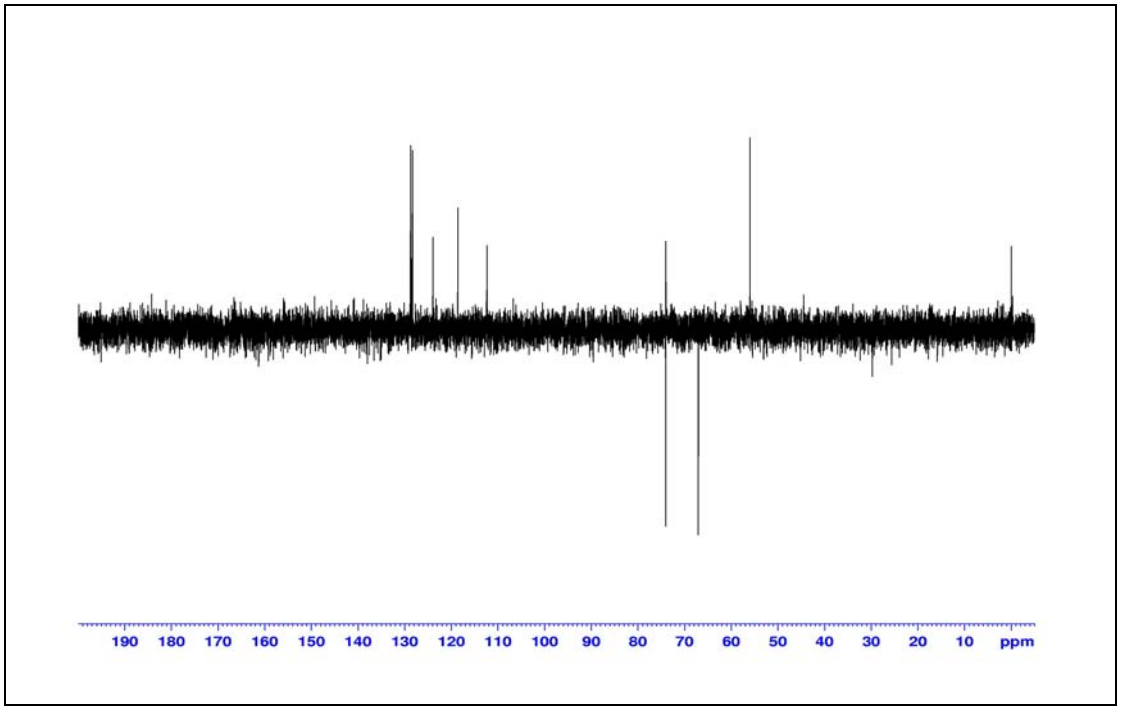

Figure 58 DEPT 135° ($CDCl_3$) of compound **DC5**

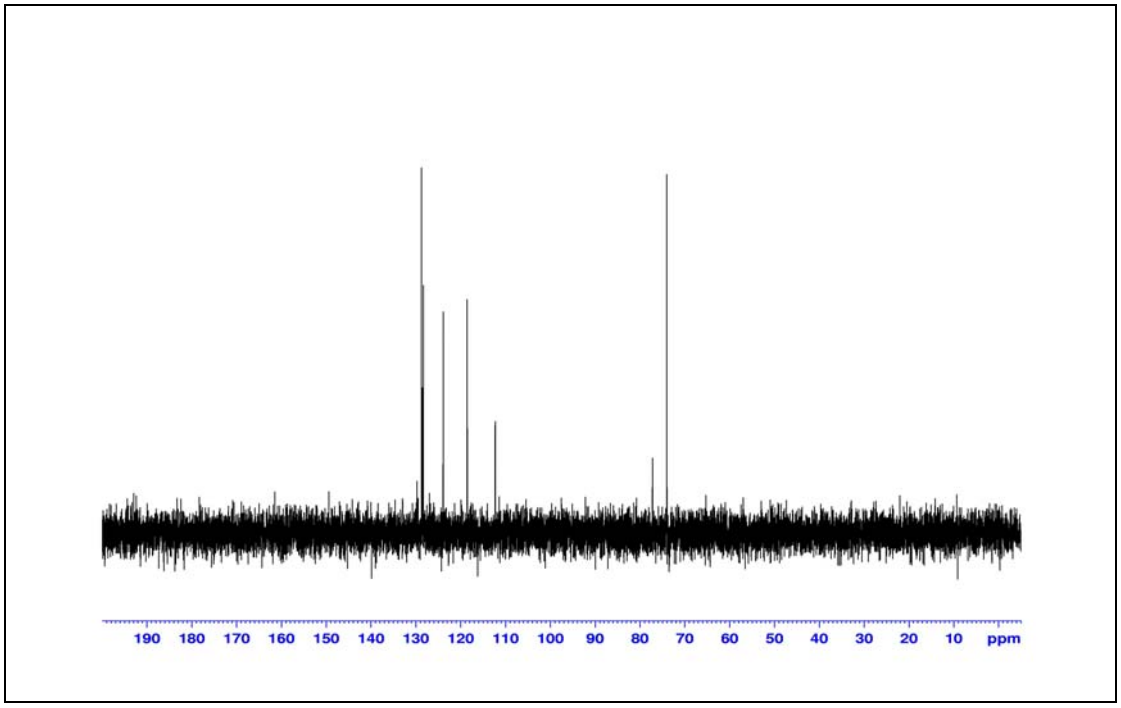

Figure 59 DEPT 90° ($CDCl_3$) of compound **DC5**

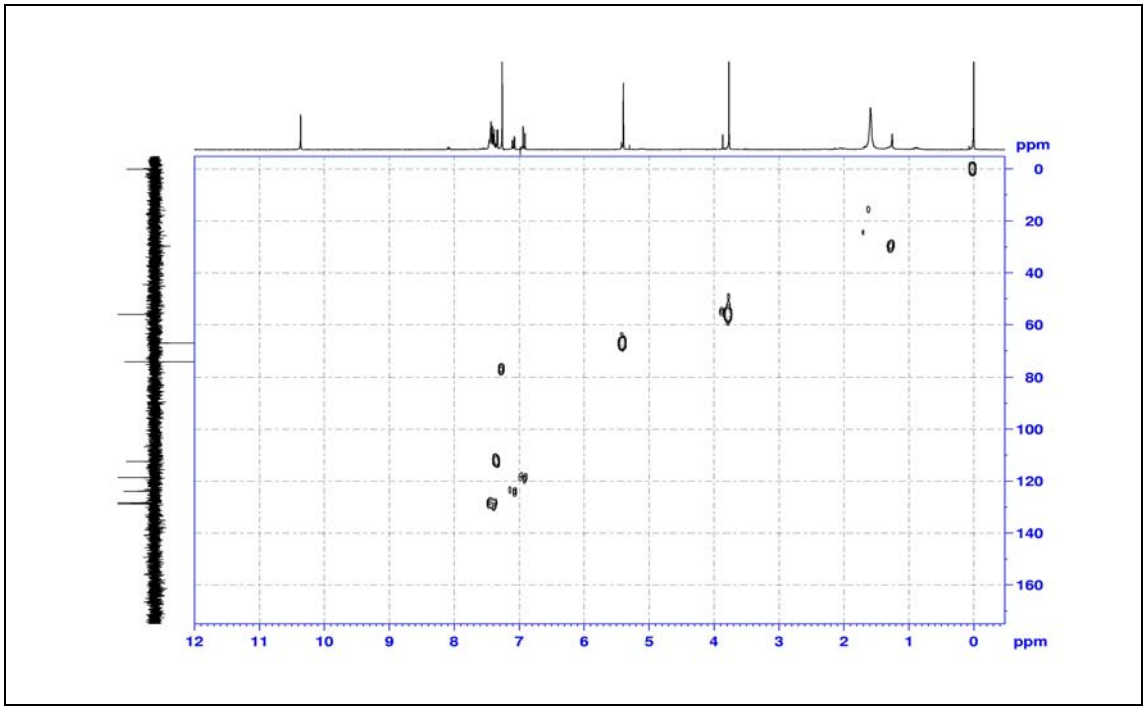

Figure 60 2D HMQC ($CDCl_3$) of compound **DC5**

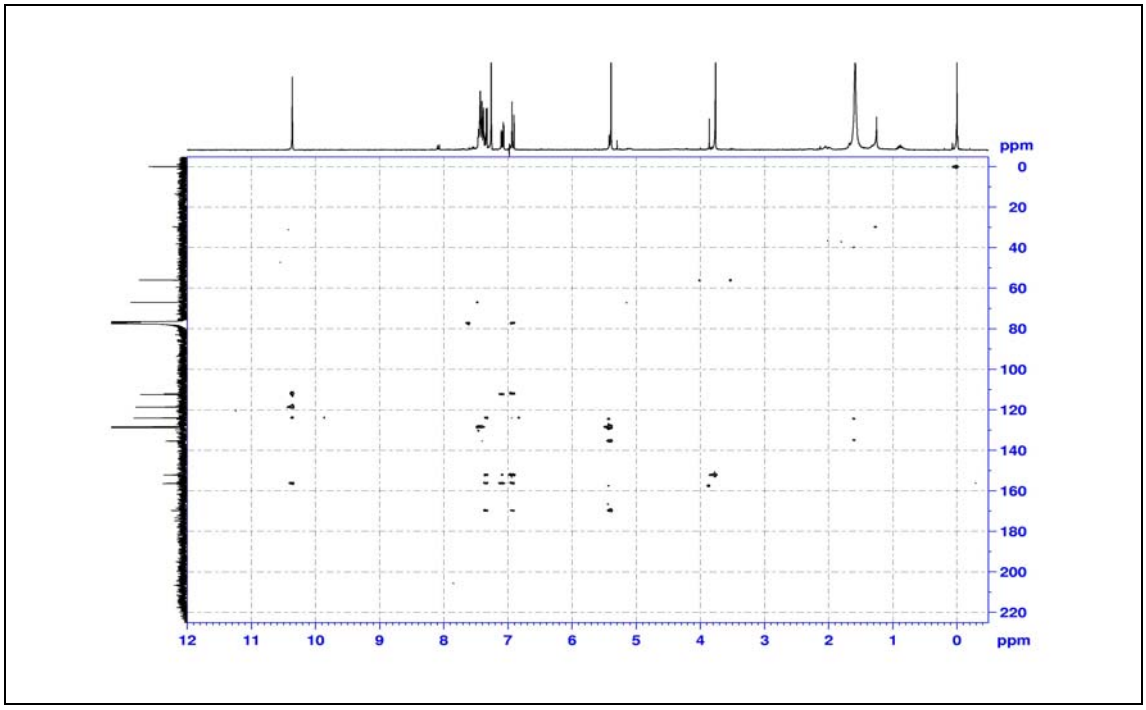

Figure 61 2D HMBC ($CDCl_3$) of compound **DC5**

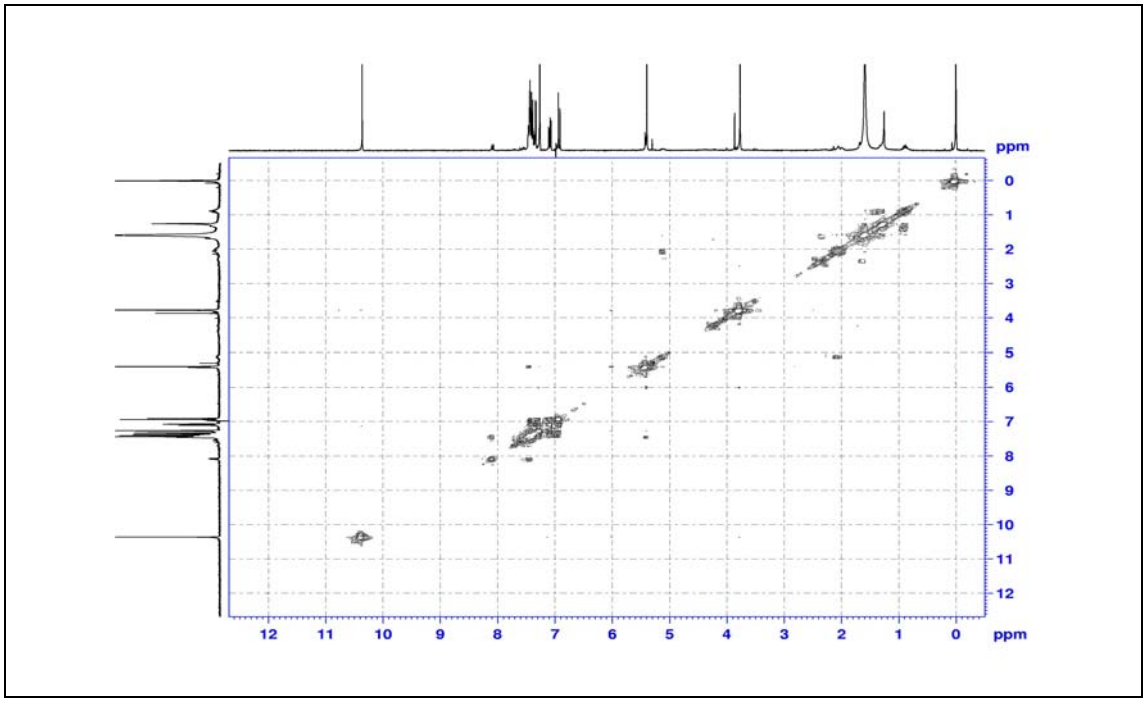

Figure 62 2D COSY ($CDCl_3$) of compound **DC5**

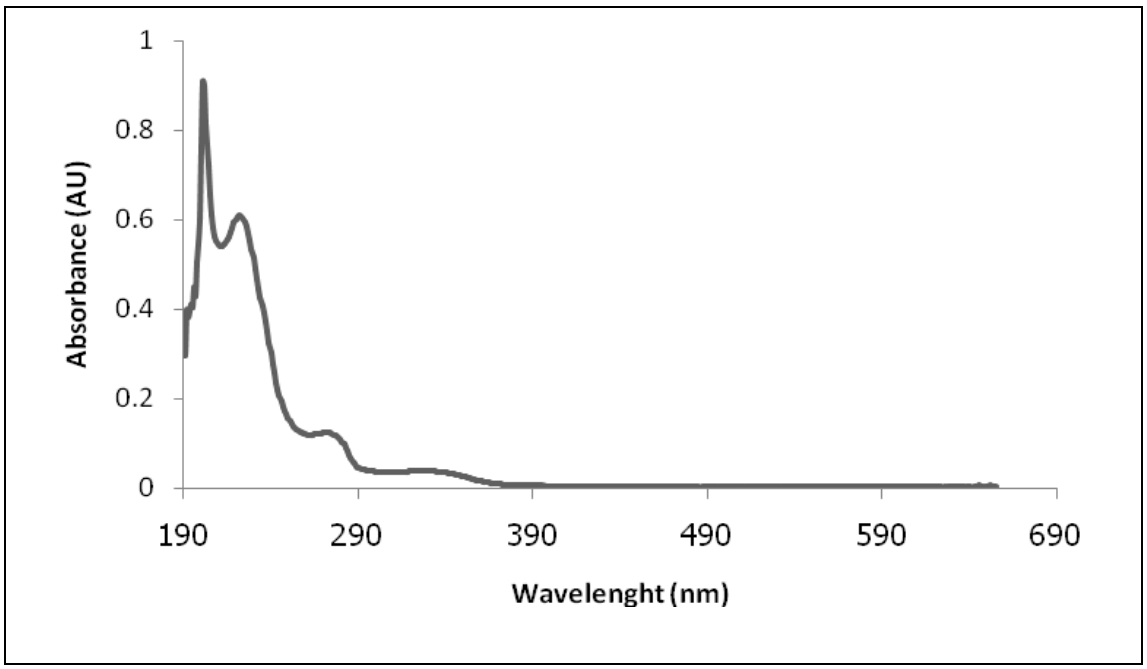

Figure 63 UV (MeOH) spectrum of compound **DC6**

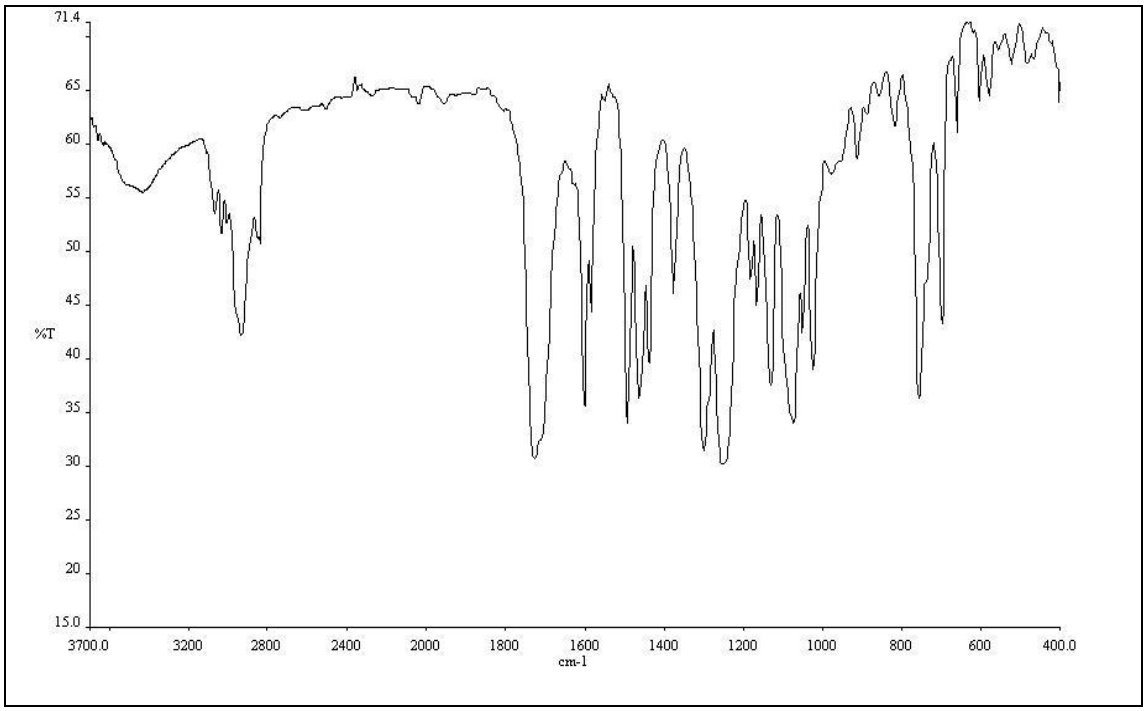

Figure 64 IR (neat) spectrum of compound **DC6**

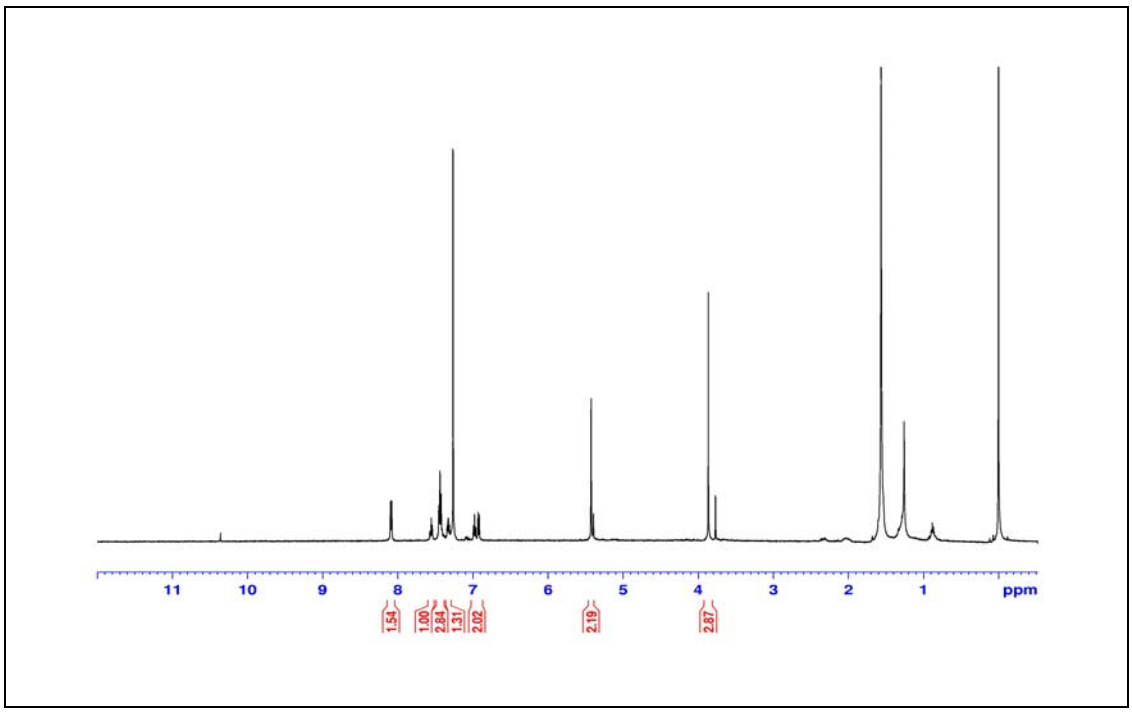

Figure 65 ^{1}H NMR (500 MHz) ($CDCl_3$) of compound **DC6**

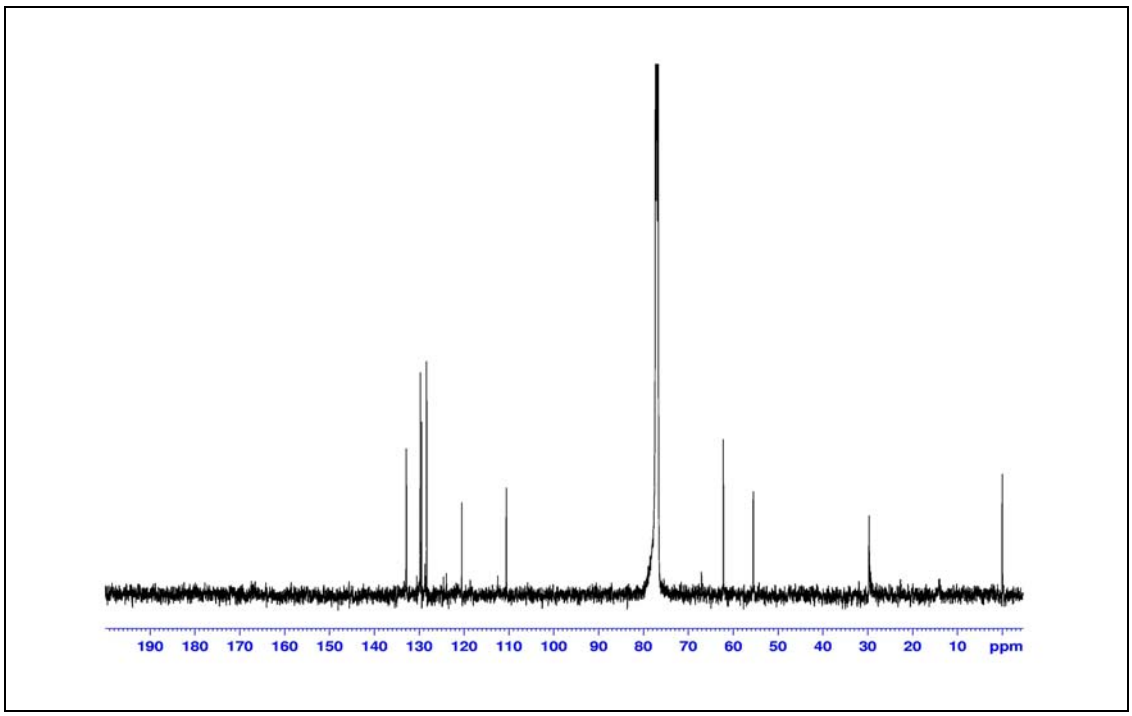

Figure 66 ^{13}C NMR (125 MHz) ($CDCl_3$) of compound **DC6**

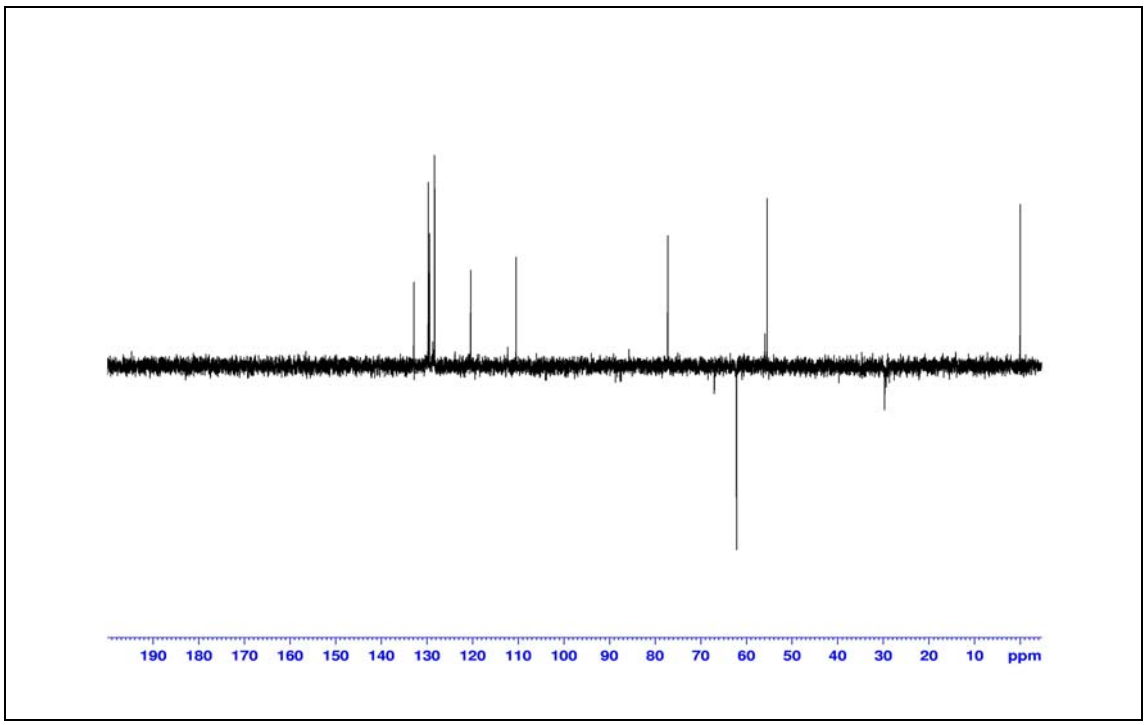

Figure 67 DEPT 135° ($CDCl_3$) of compound **DC6**

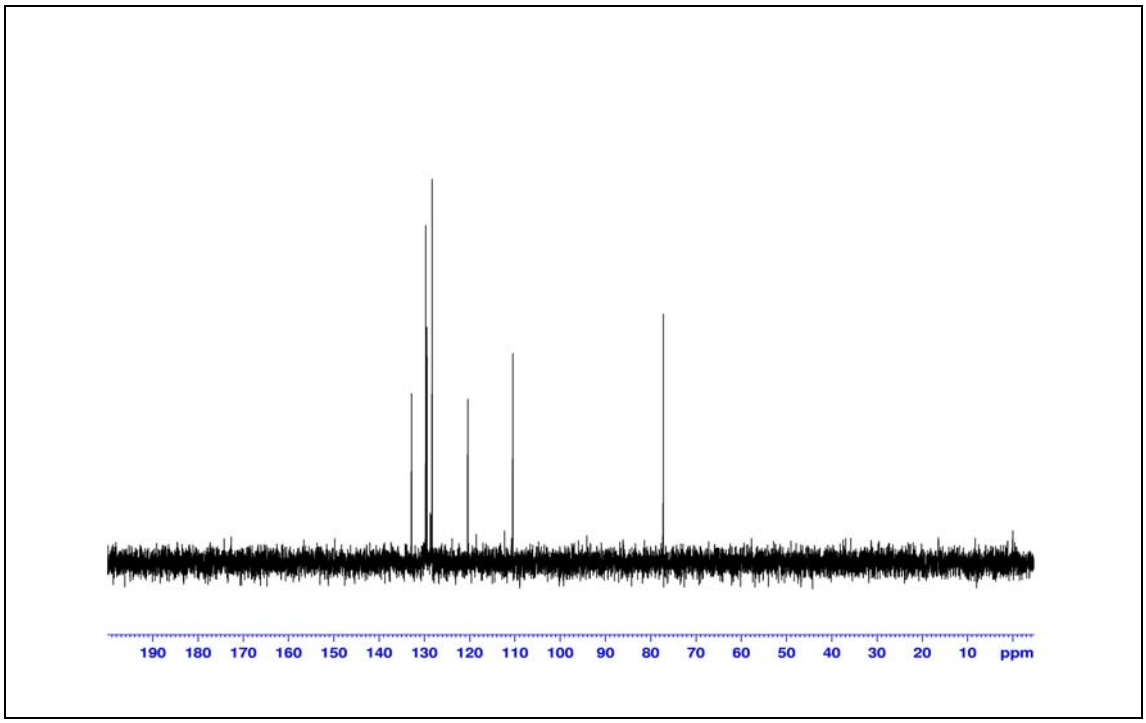

Figure 68 DEPT 90° ($CDCl_3$) of compound **DC6**

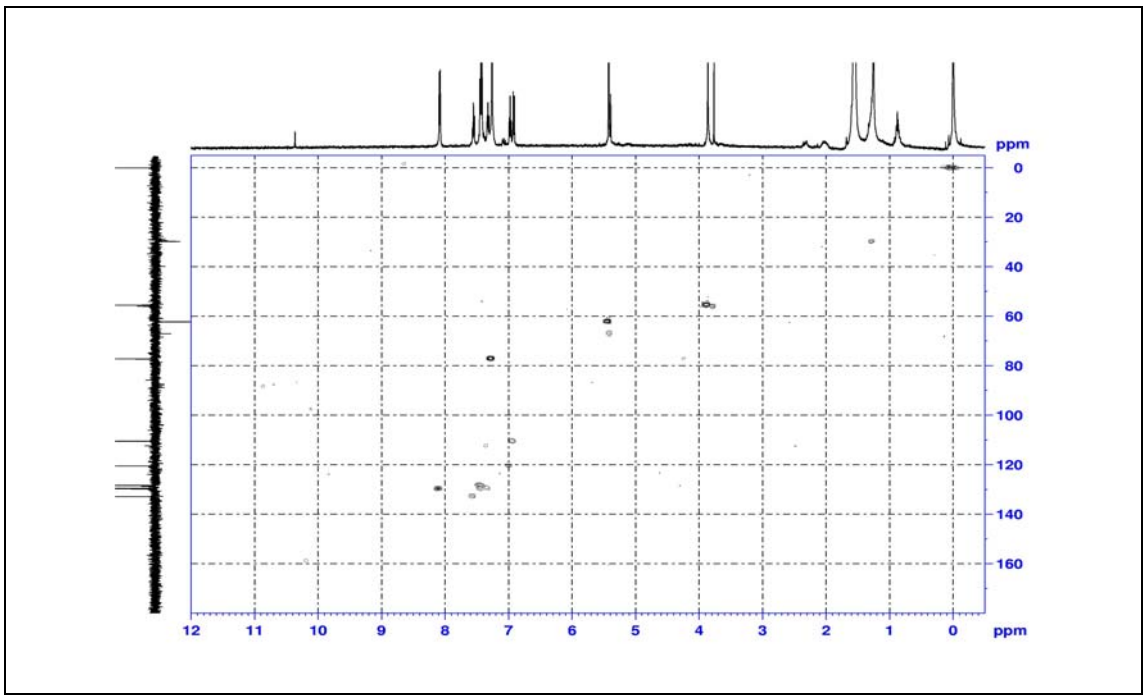

Figure 69 2D HMQC ($CDCl_3$) of compound **DC6**

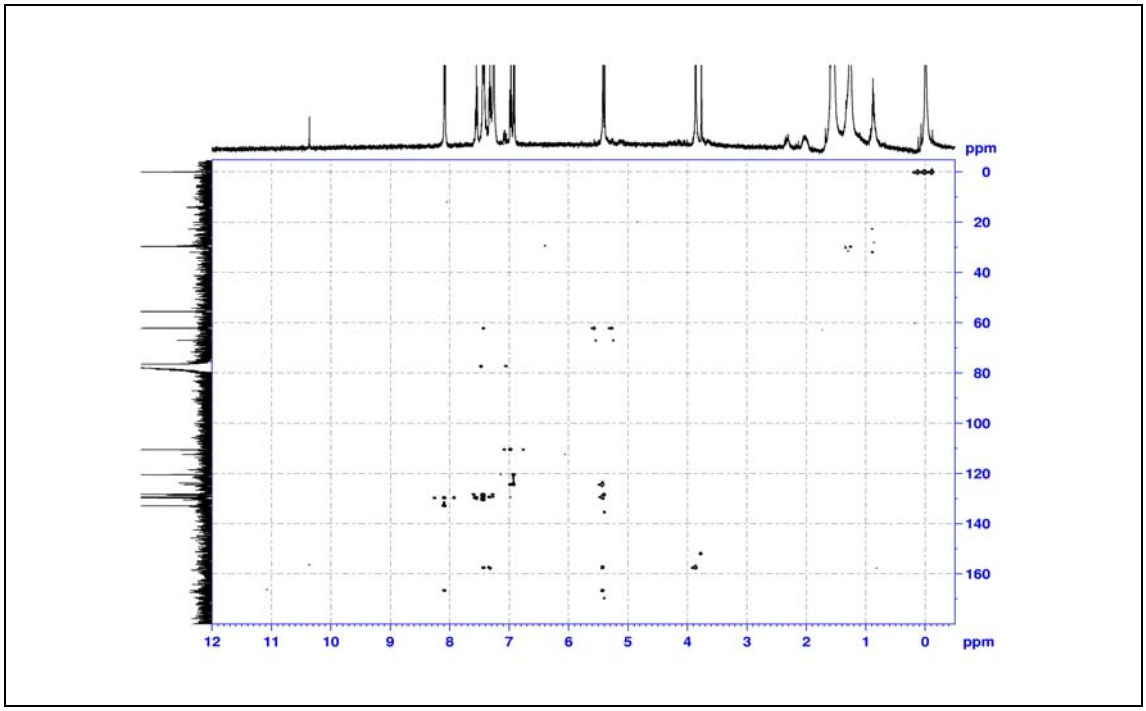

Figure 70 2D HMBC ($CDCl_3$) of compound **DC6**

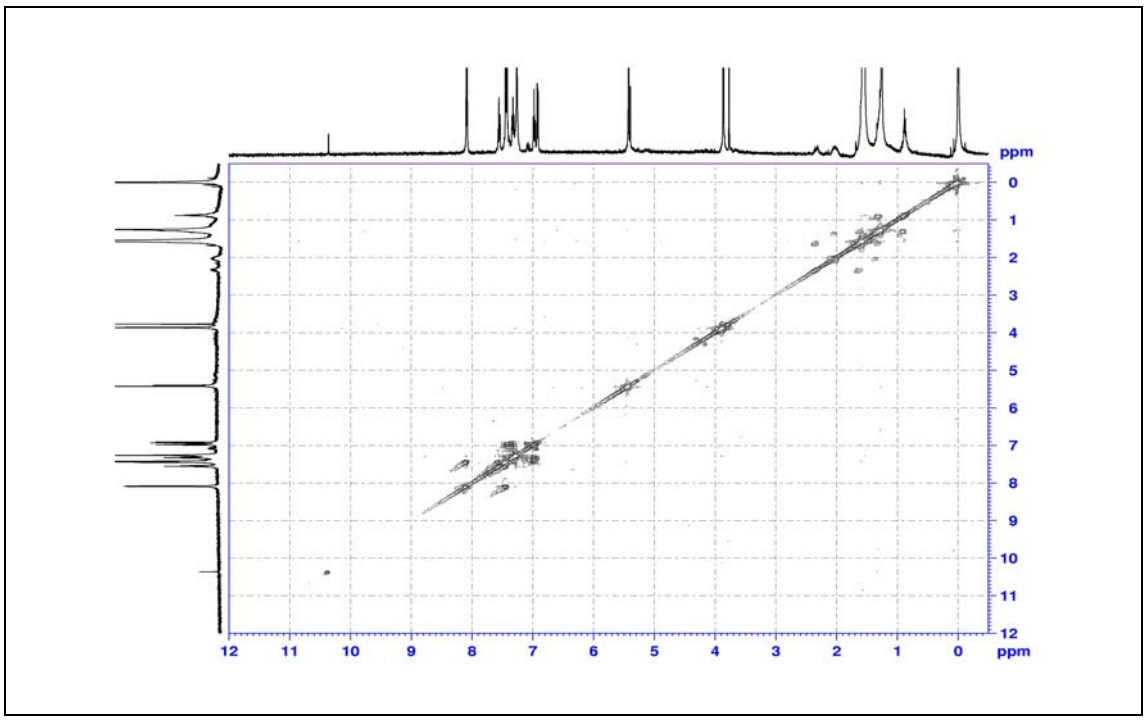

Figure 71 2D COSY ($CDCl_3$) of compound **DC6**

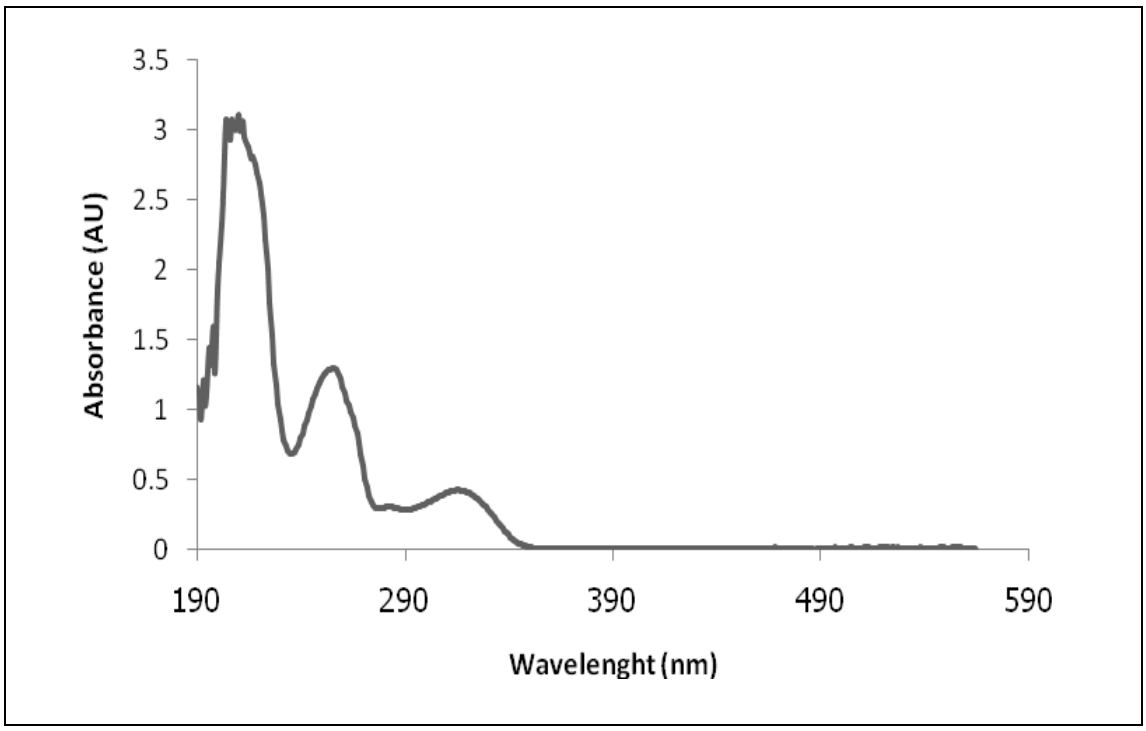

Figure 72 UV (MeOH) spectrum of compound **DC7**

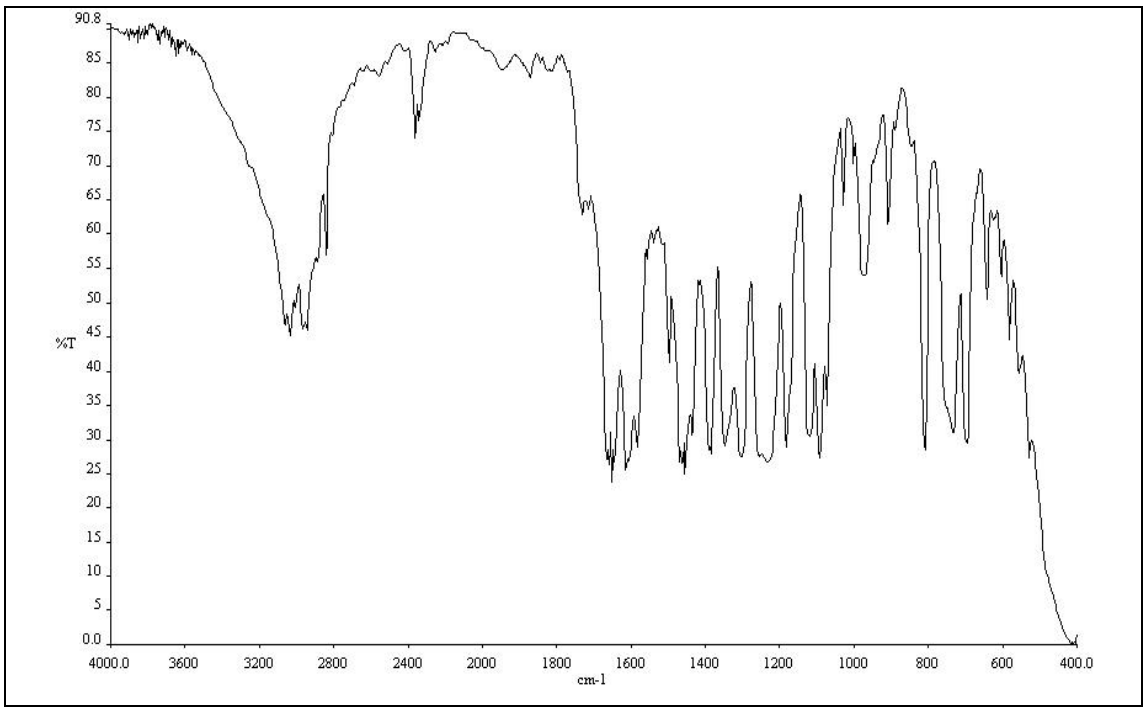

Figure 73 IR (neat) spectrum of compound **DC7**

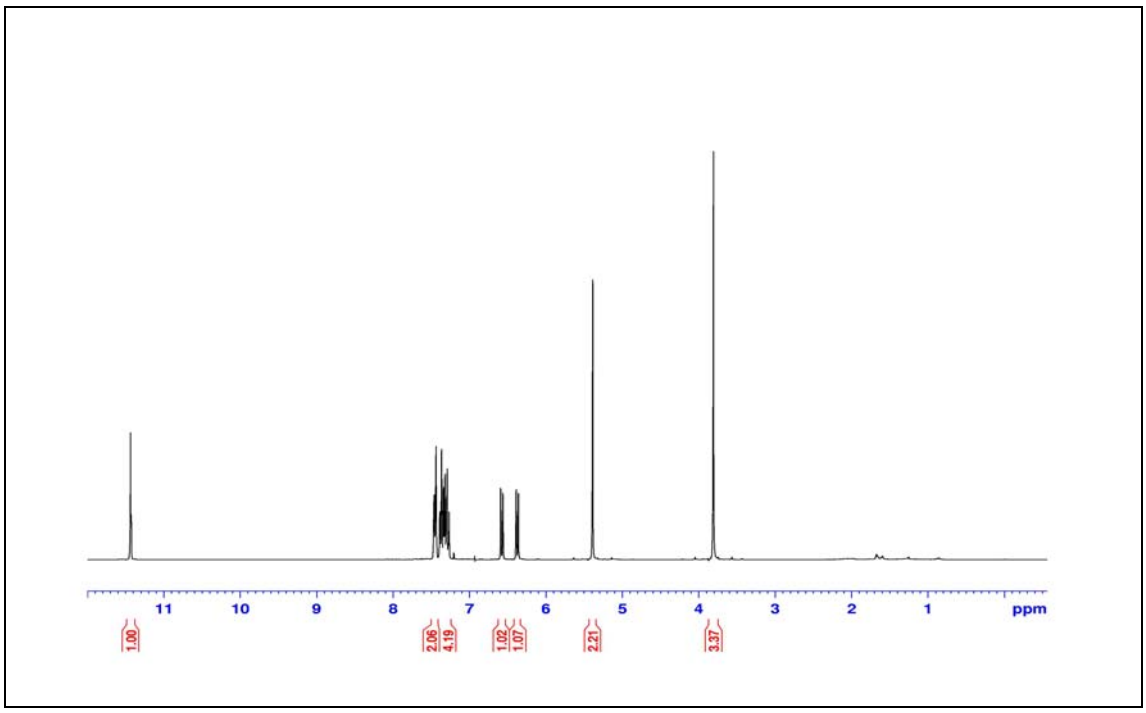

Figure 74 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC7**

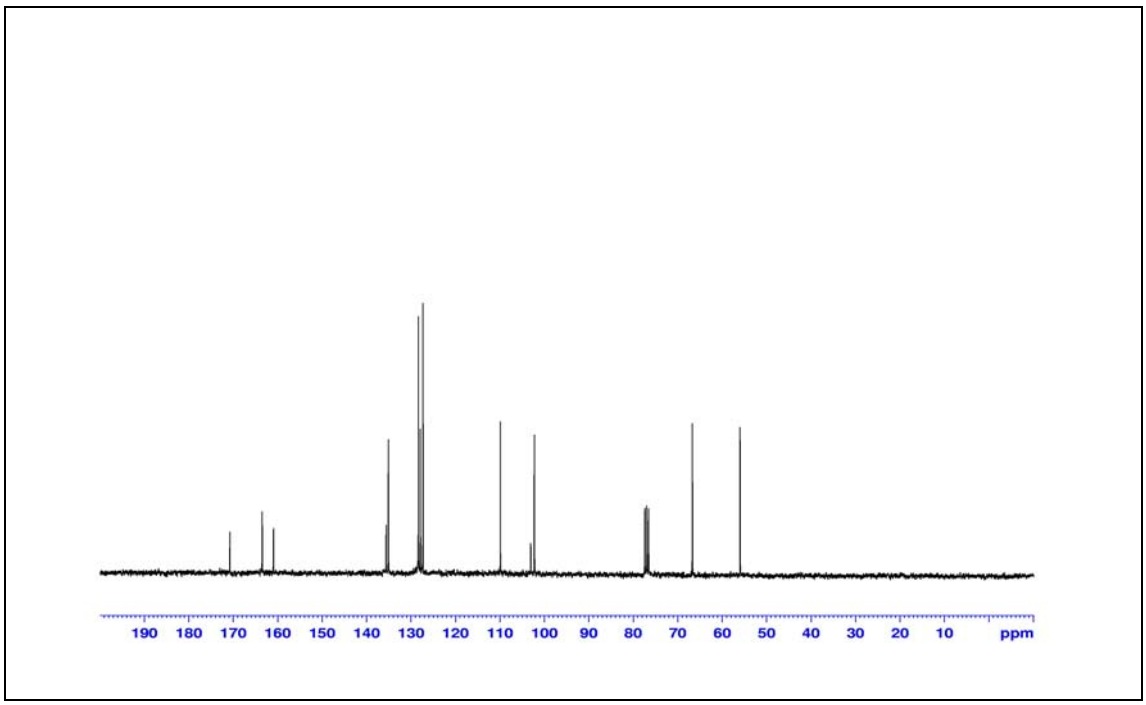

Figure 75 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC7**

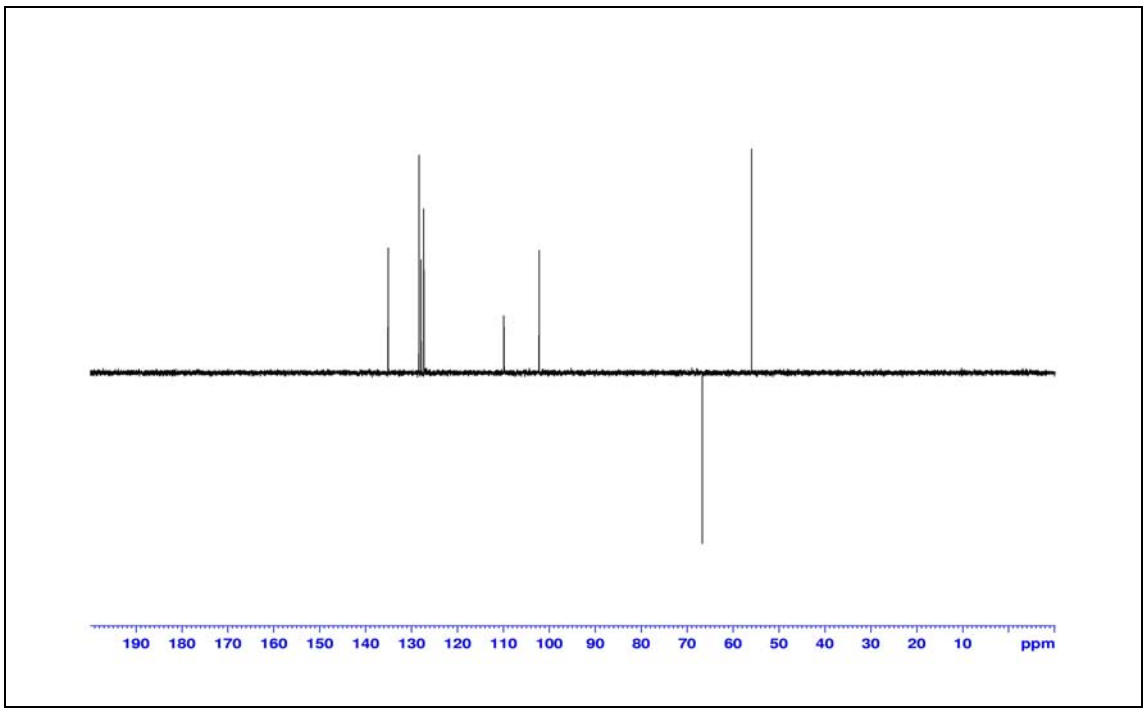

Figure 76 DEPT 135° ($CDCl_3$) of compound **DC7**

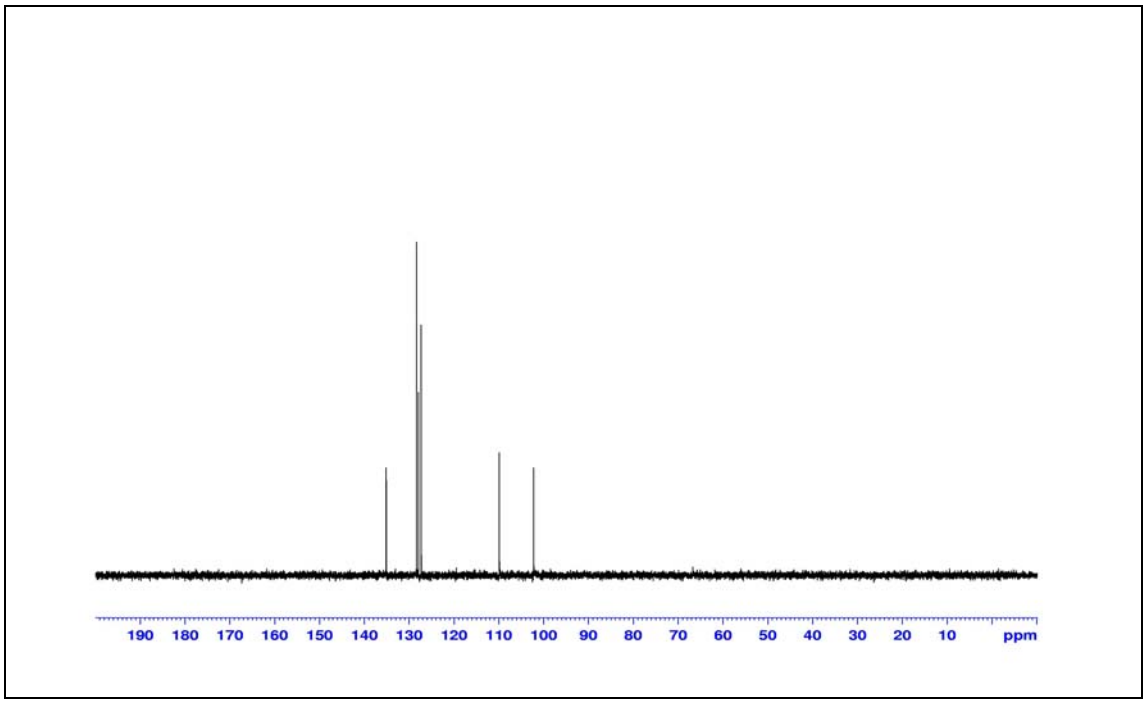

Figure 77 DEPT 90° ($CDCl_3$) of compound **DC7**

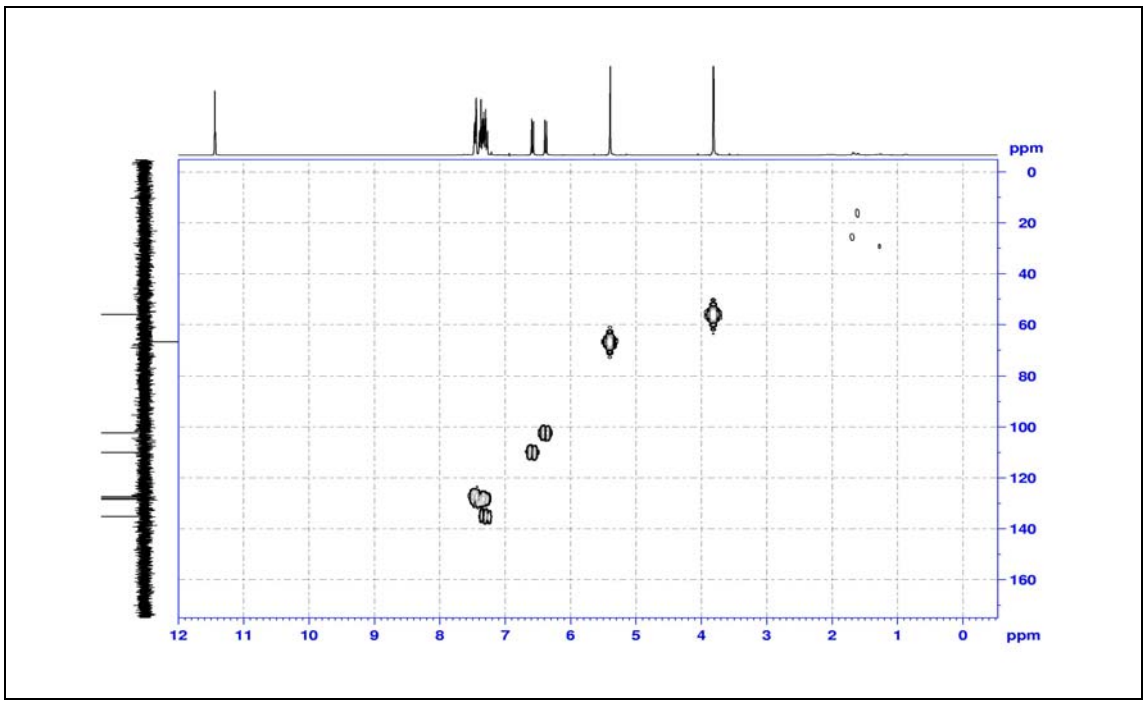

Figure 78 2D HMQC ($CDCl_3$) of compound **DC7**

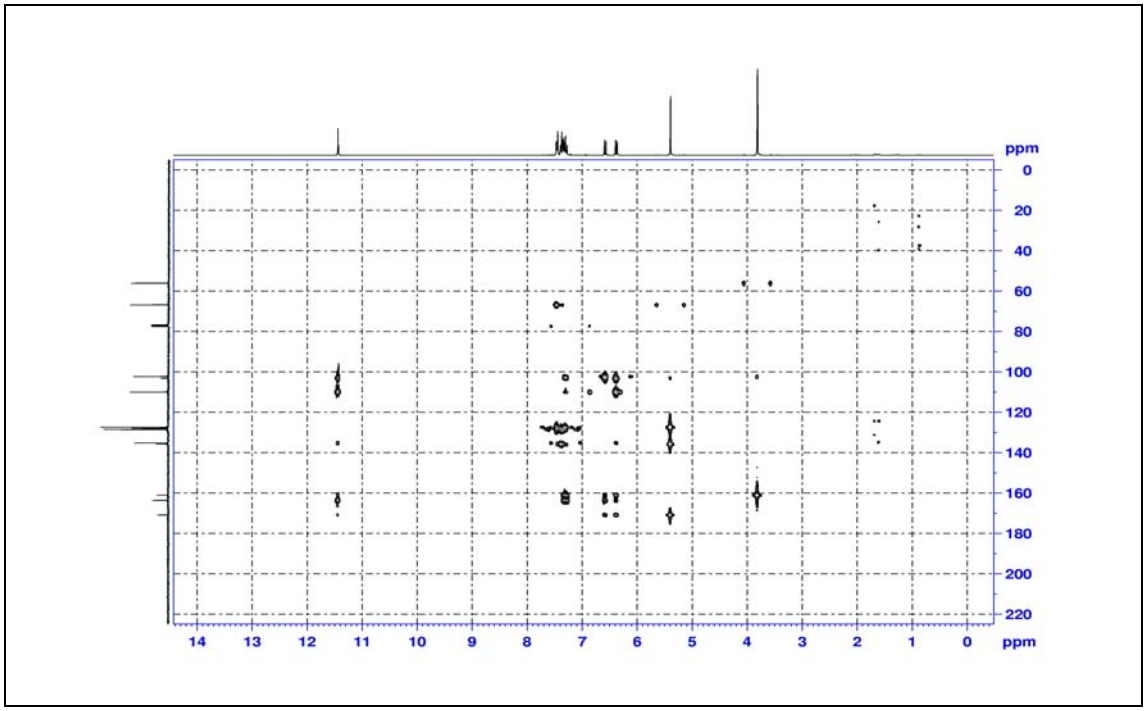

Figure 79 2D HMBC ($CDCl_3$) of compound **DC7**

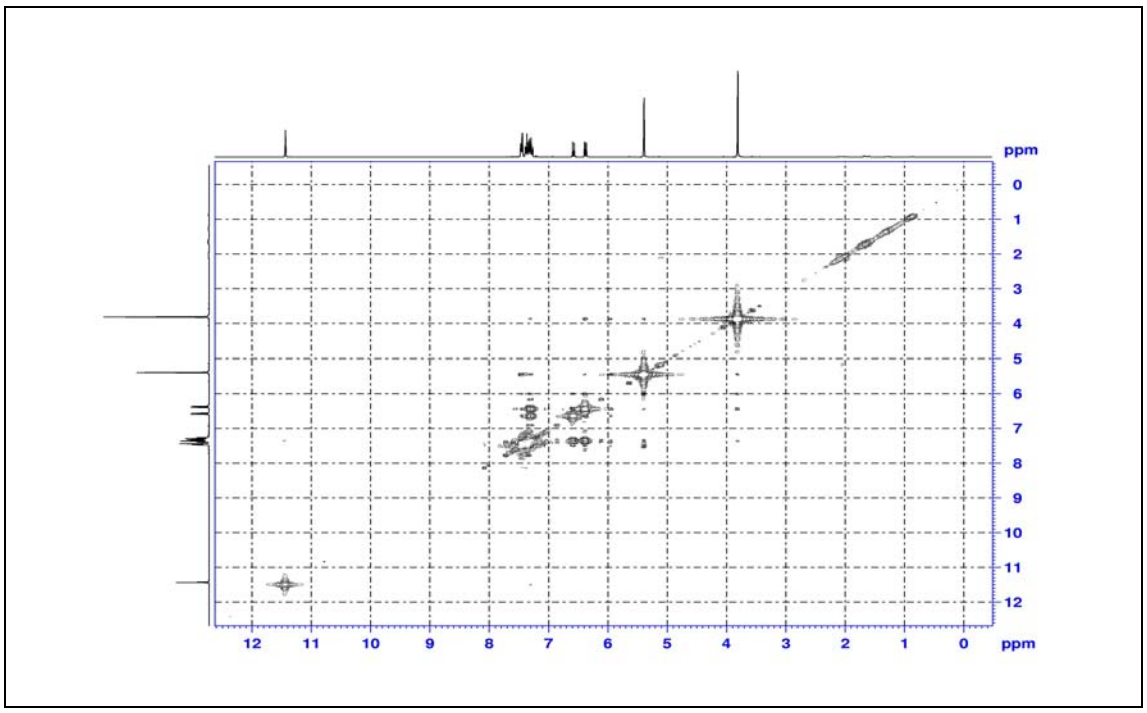

Figure 80 2D COSY ($CDCl_3$) of compound **DC7**

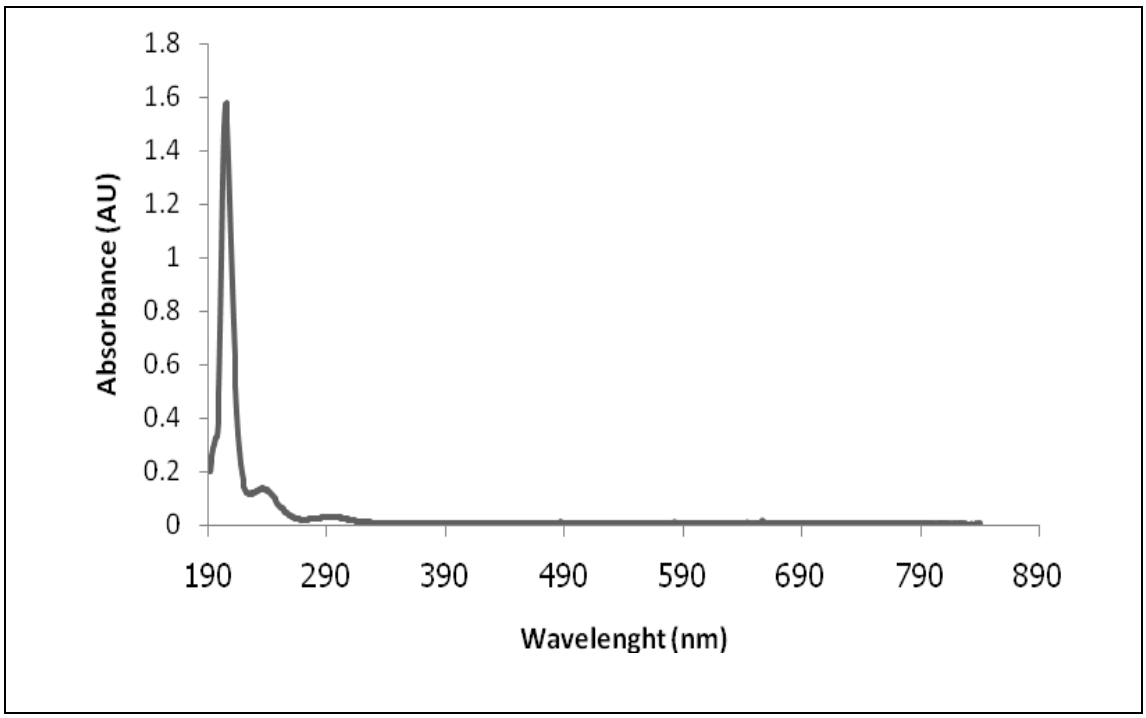

Figure 81 UV (MeOH) spectrum of compound **DC8**

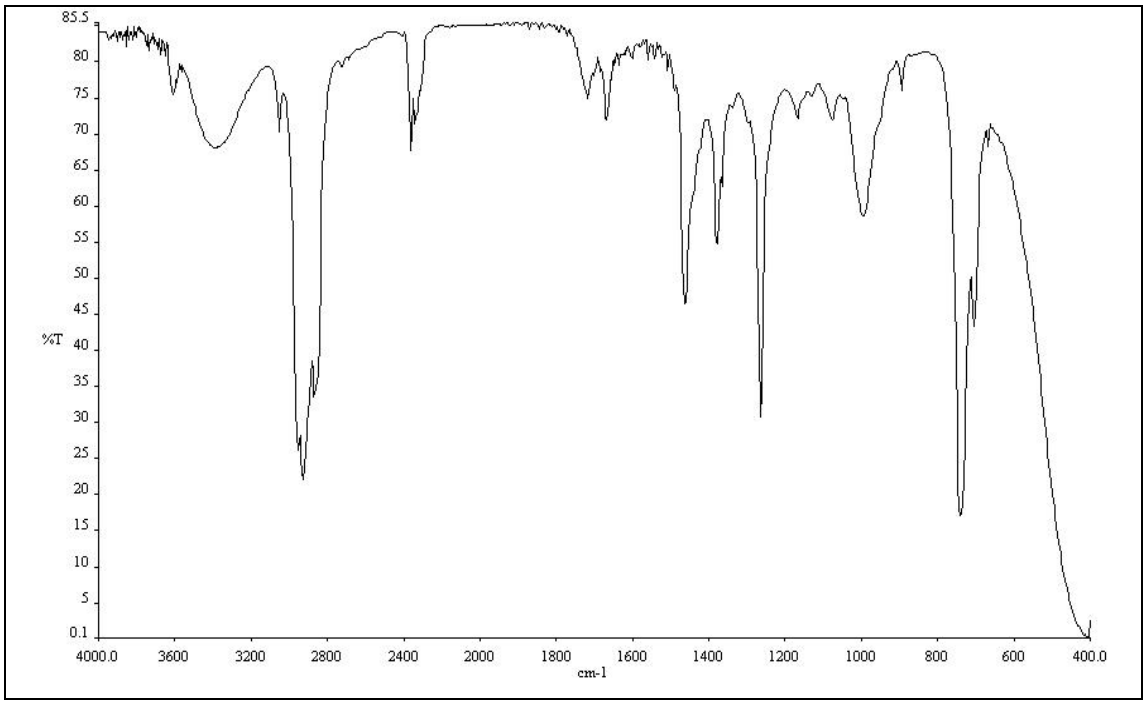

Figure 82 IR (neat) spectrum of compound **DC8**

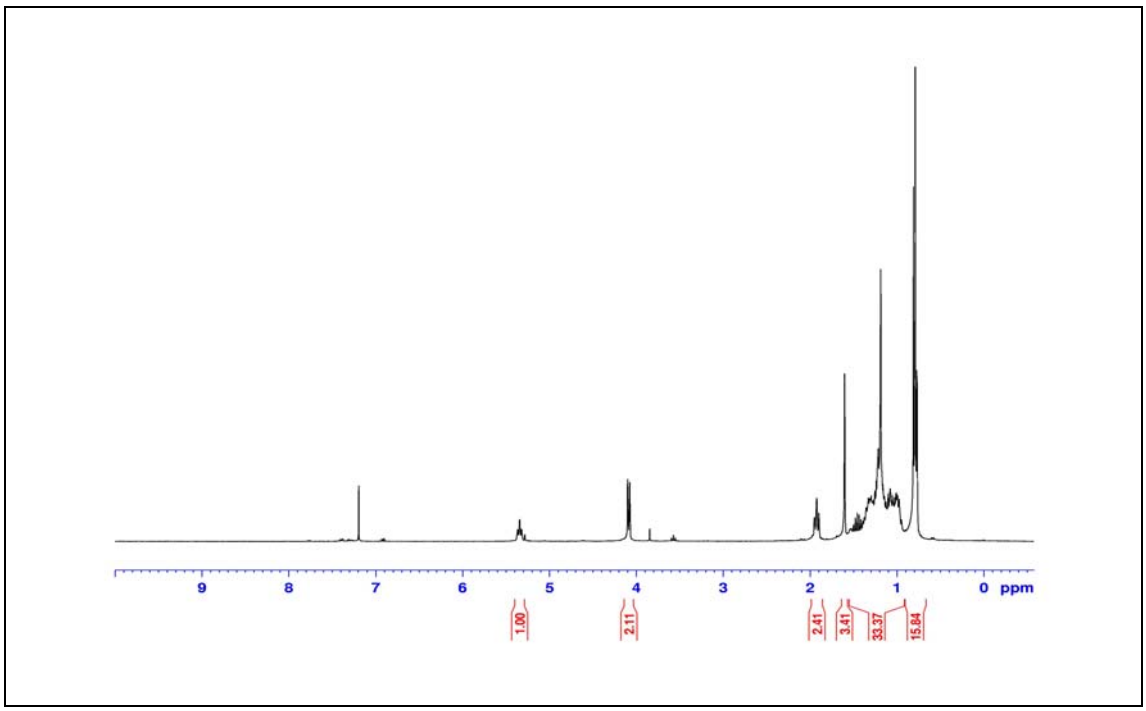

Figure 83 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC8**

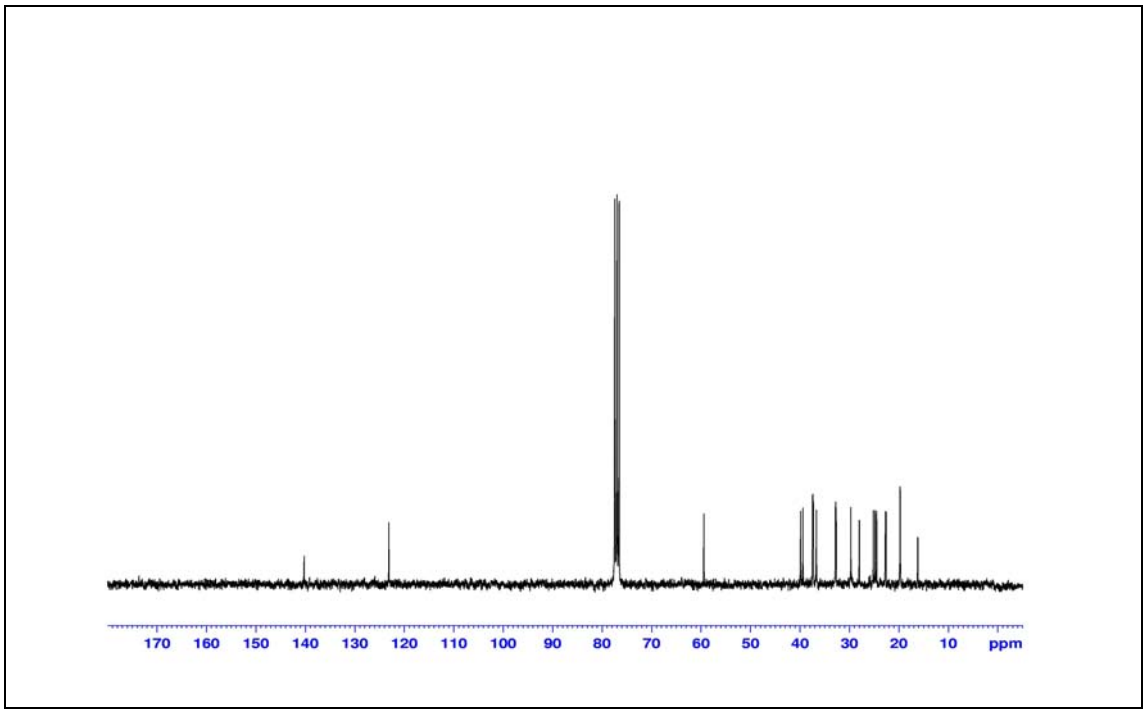

Figure 84 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC8**

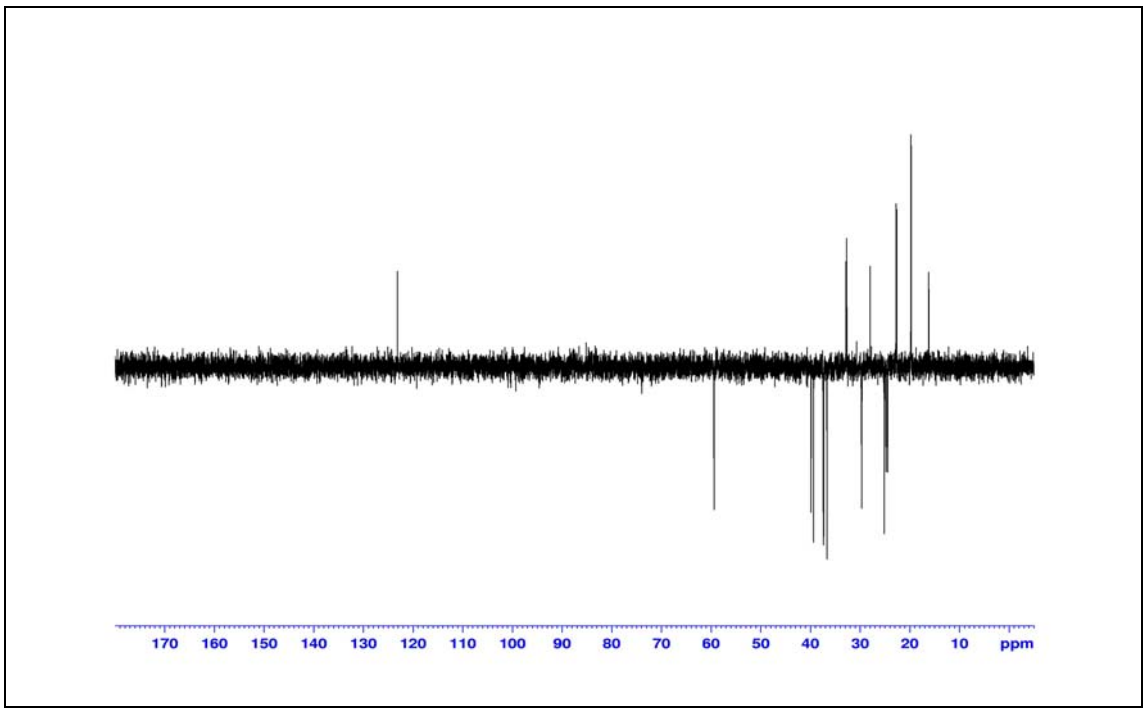

Figure 85 DEPT 135° ($CDCl_3$) of compound **DC8**

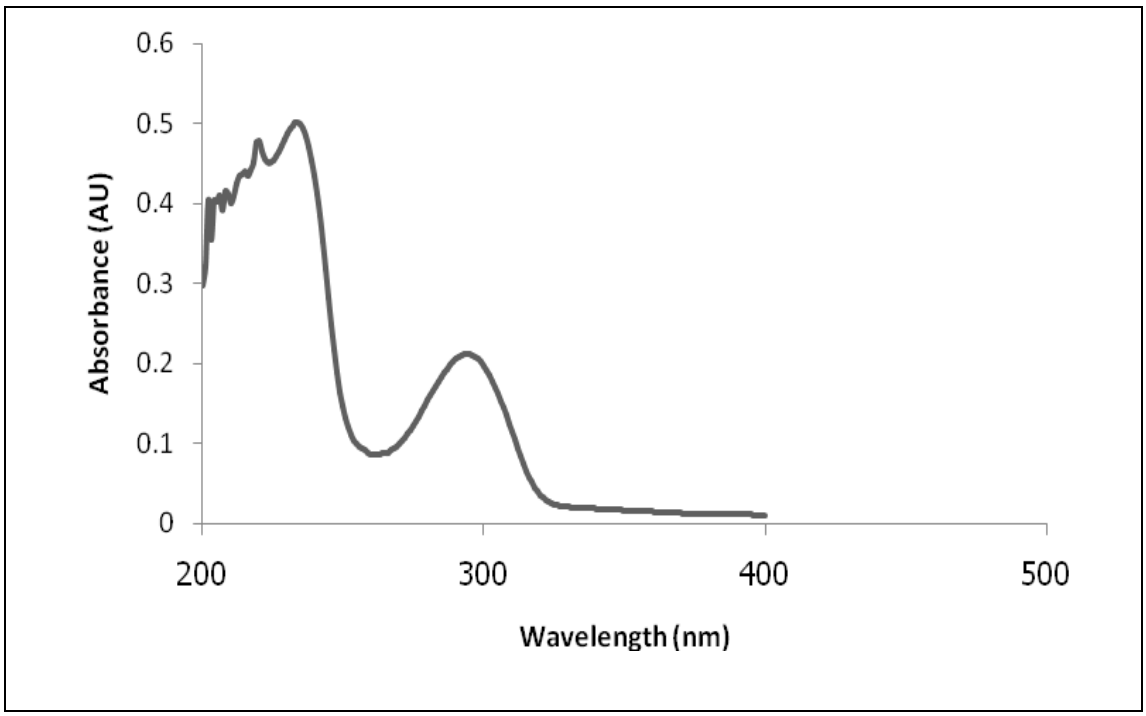

Figure 86 UV (MeOH) spectrum of compound **DC9**

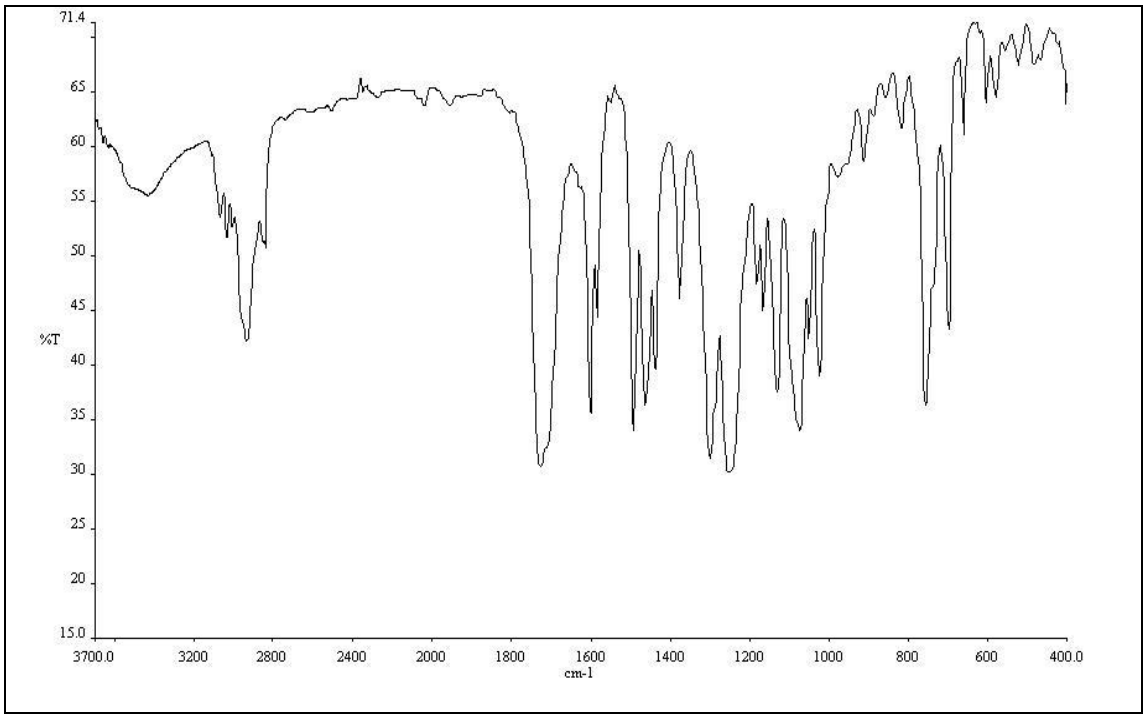

Figure 87 IR (neat) spectrum of compound **DC9**

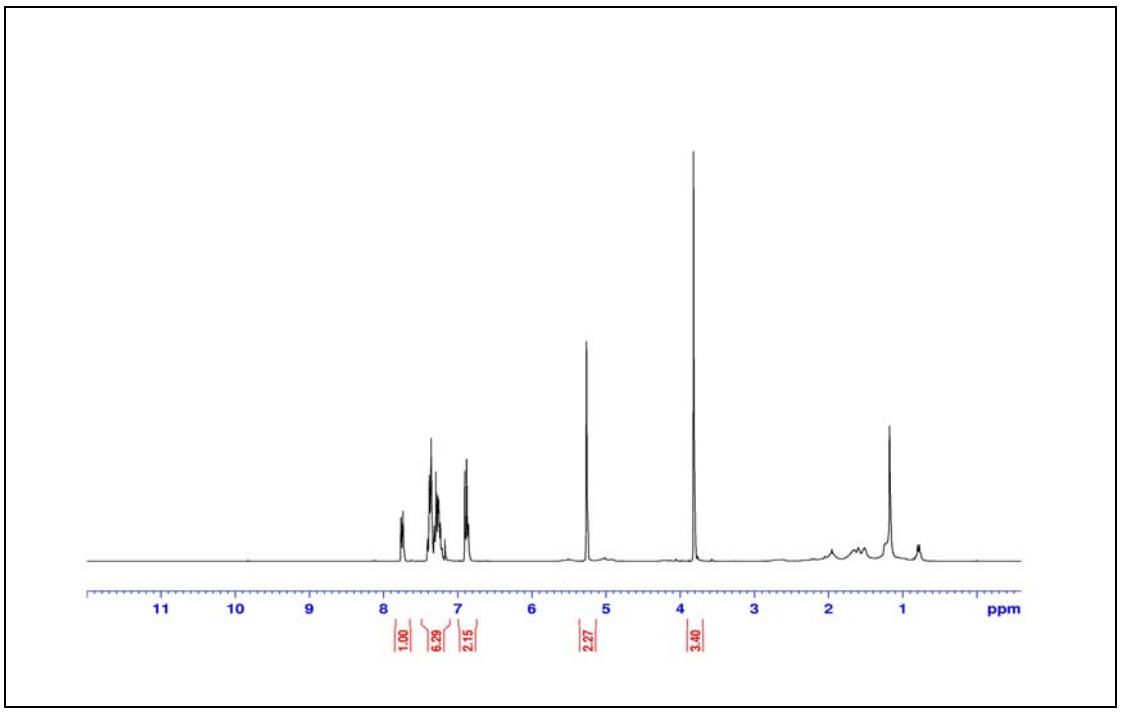

Figure 88 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC9**

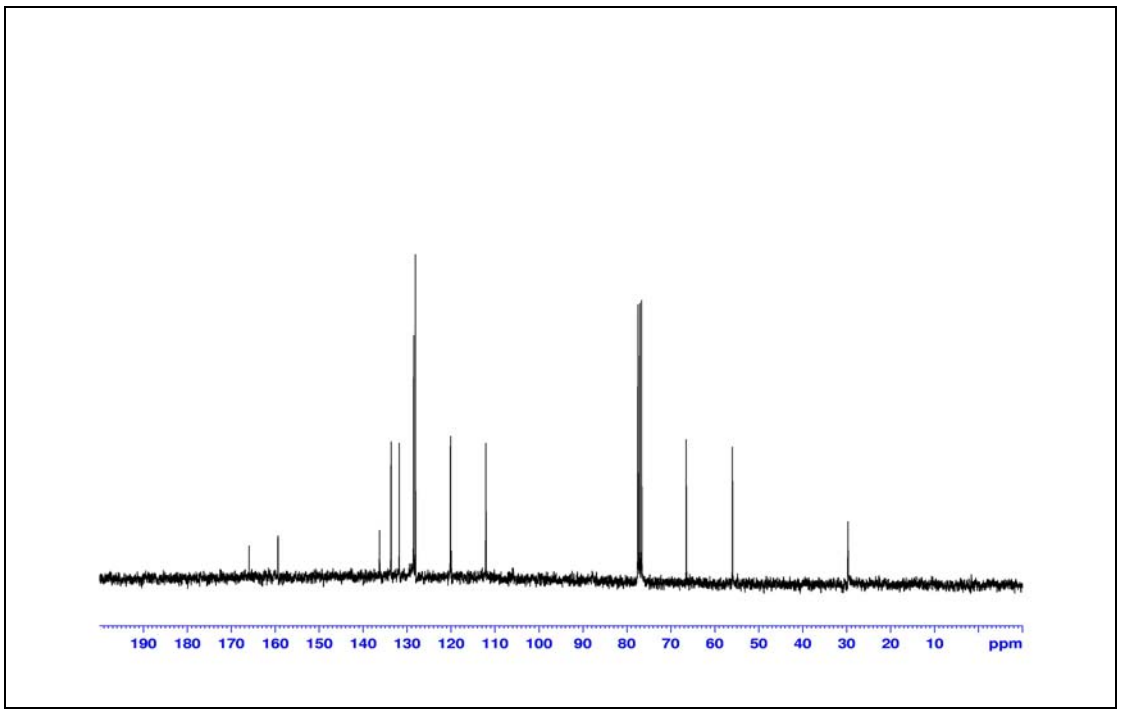

Figure 89 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC9**

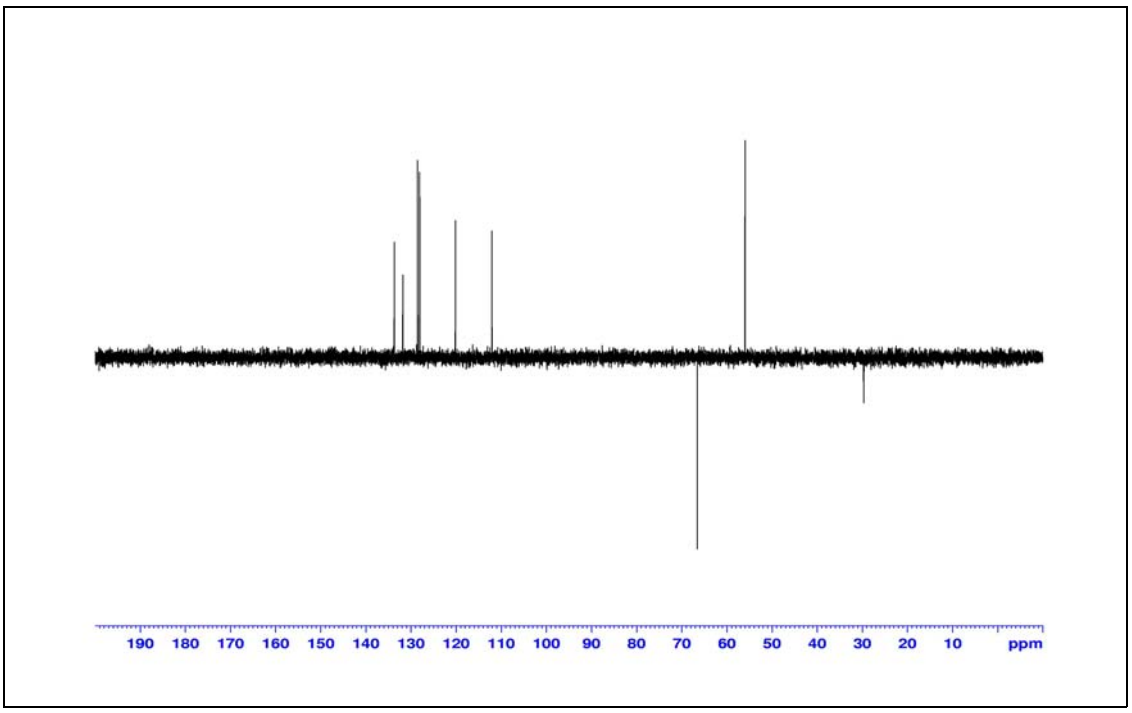

Figure 90 DEPT 135° ($CDCl_3$) of compound **DC9**

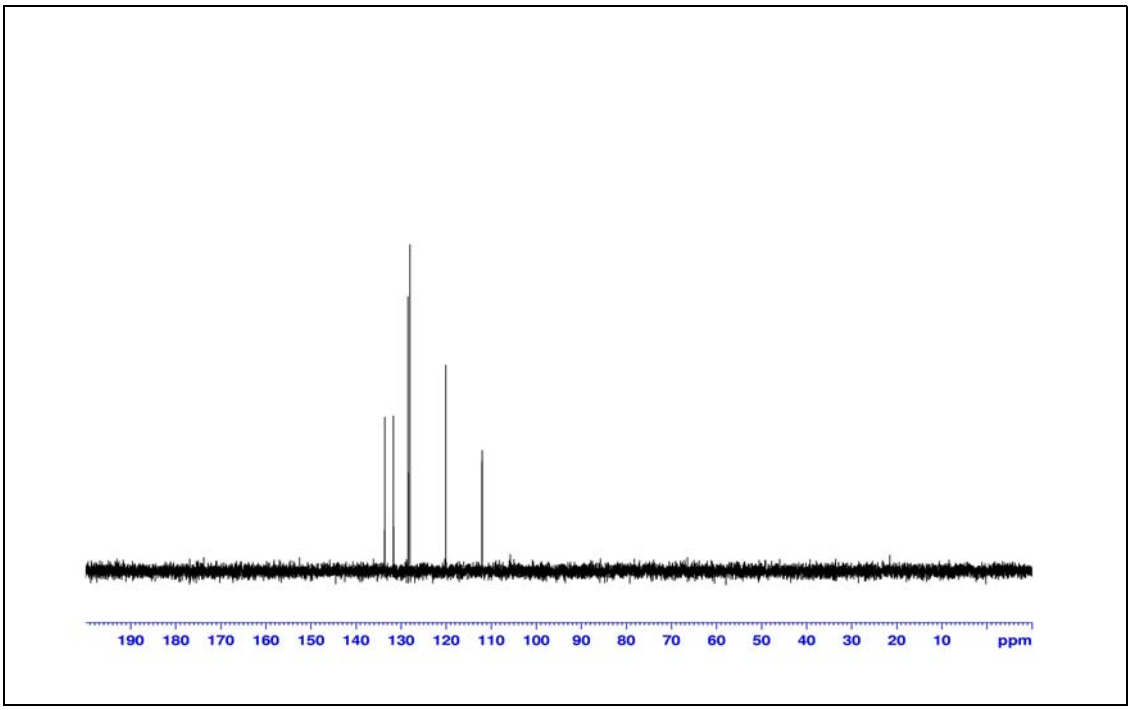

Figure 91 DEPT 90° ($CDCl_3$) of compound **DC9**

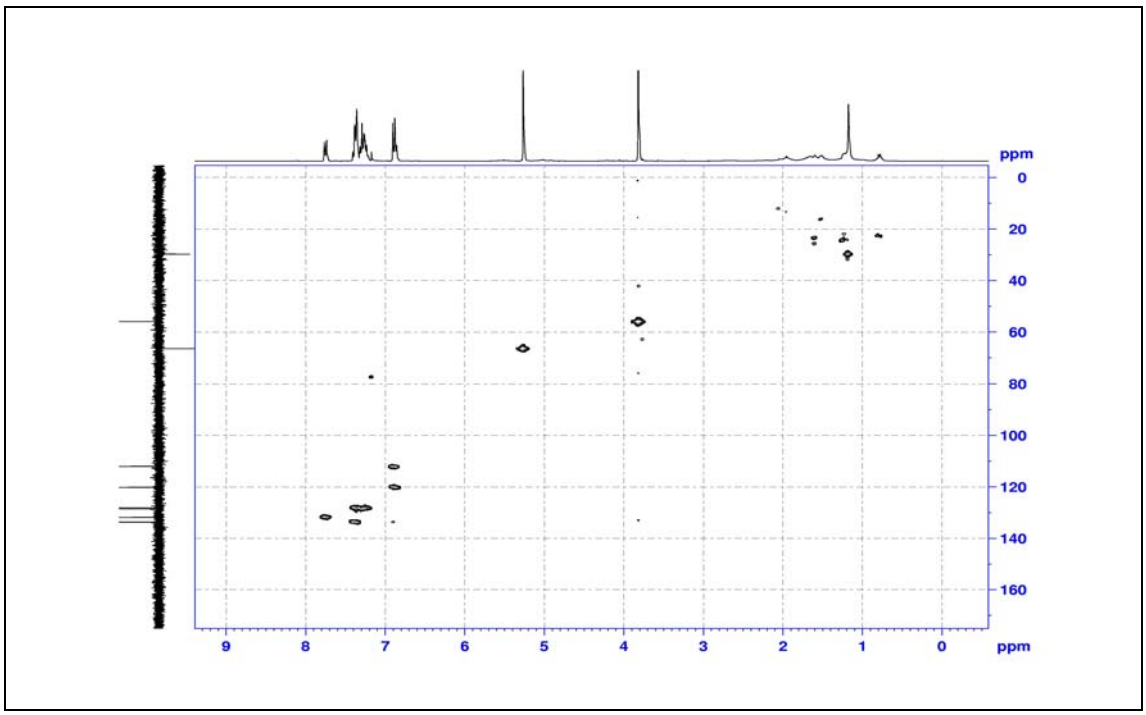

Figure 92 2D HMQC ($CDCl_3$) of compound **DC9**

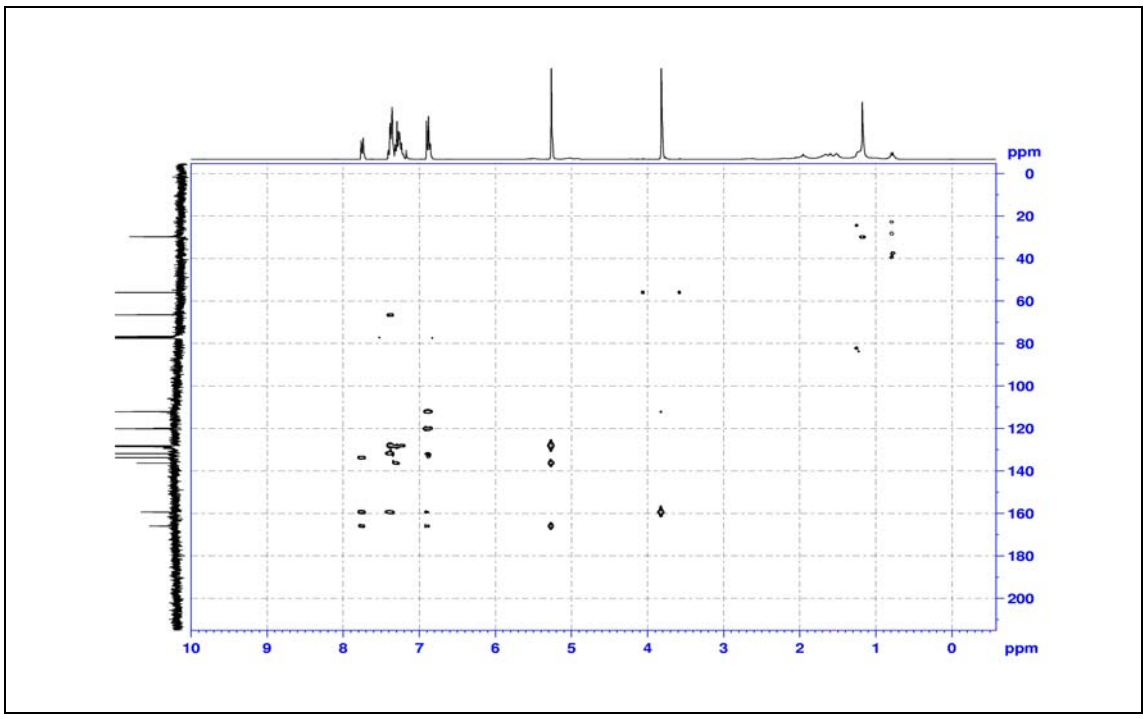

Figure 93 2D HMBC ($CDCl_3$) of compound **DC9**

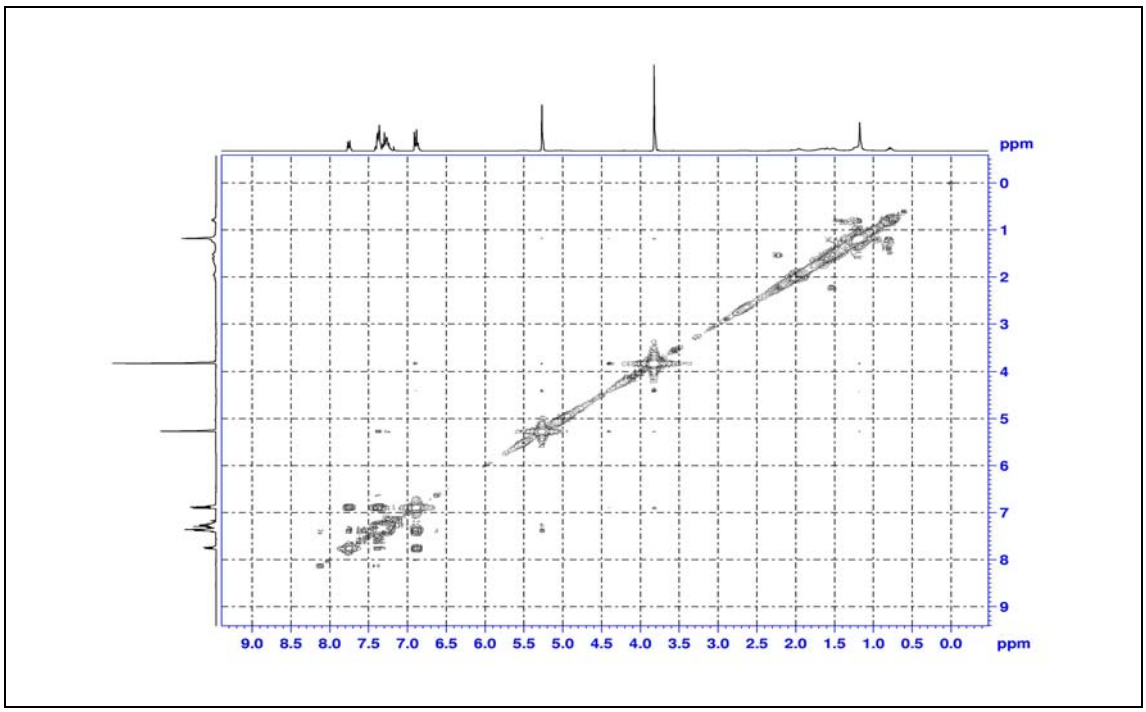

Figure 94 2D COSY ($CDCl_3$) of compound **DC9**

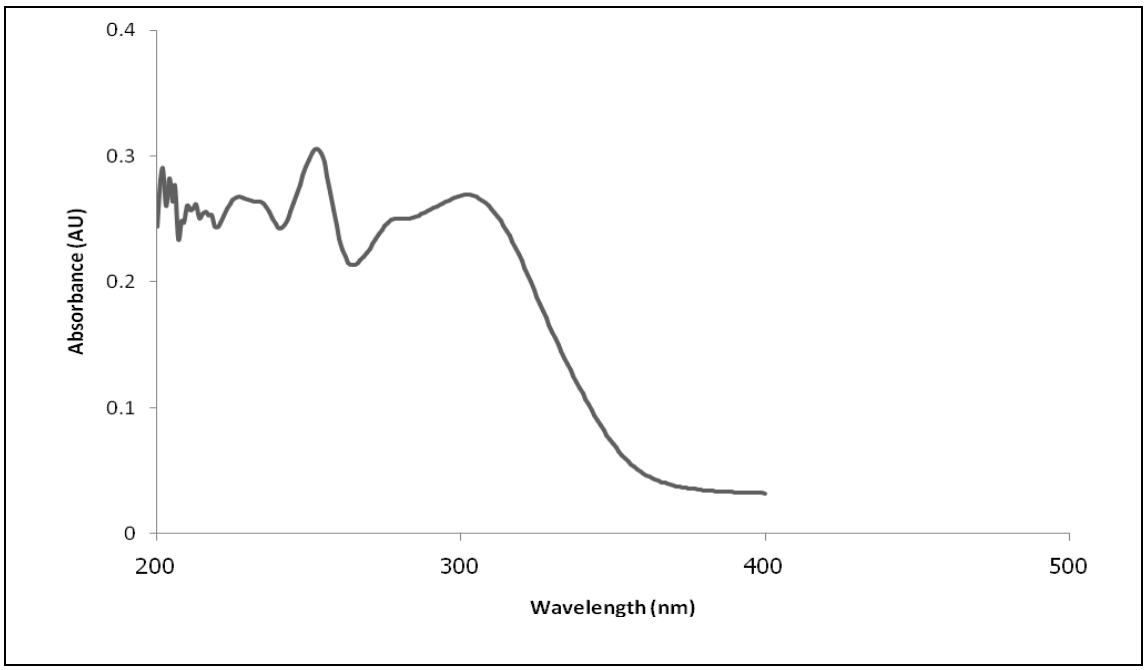

Figure 95 UV (MeOH) spectrum of compound **D10**

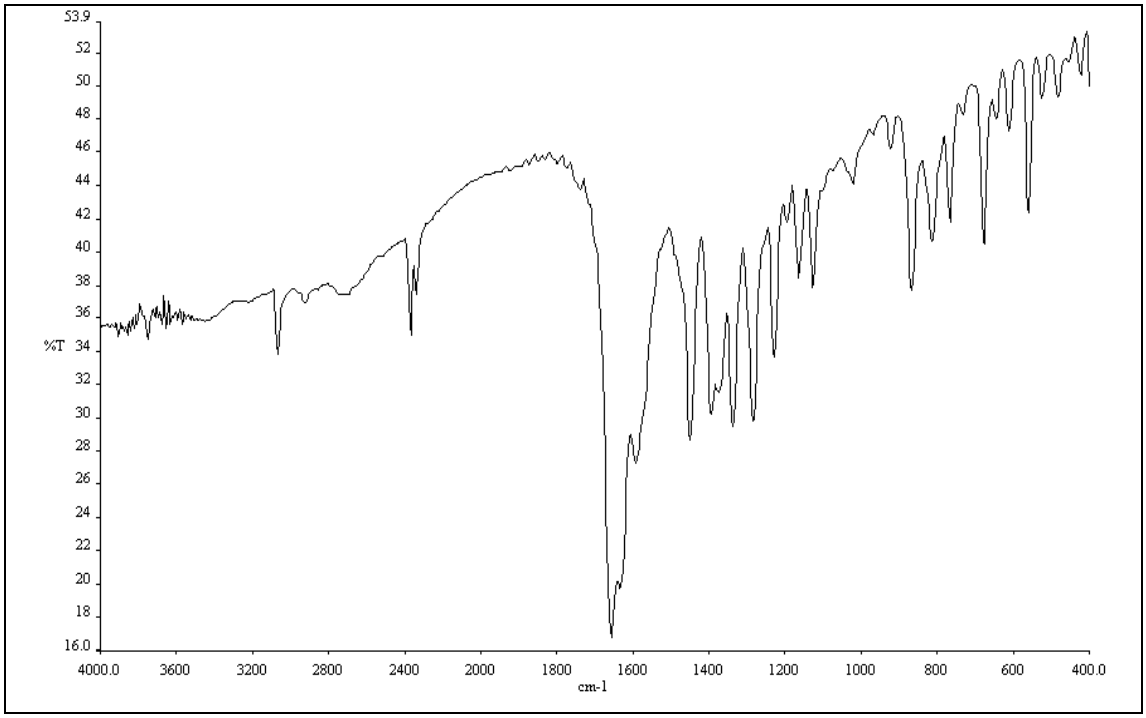

Figure 96 IR (KBr) spectrum of compound **DC10**

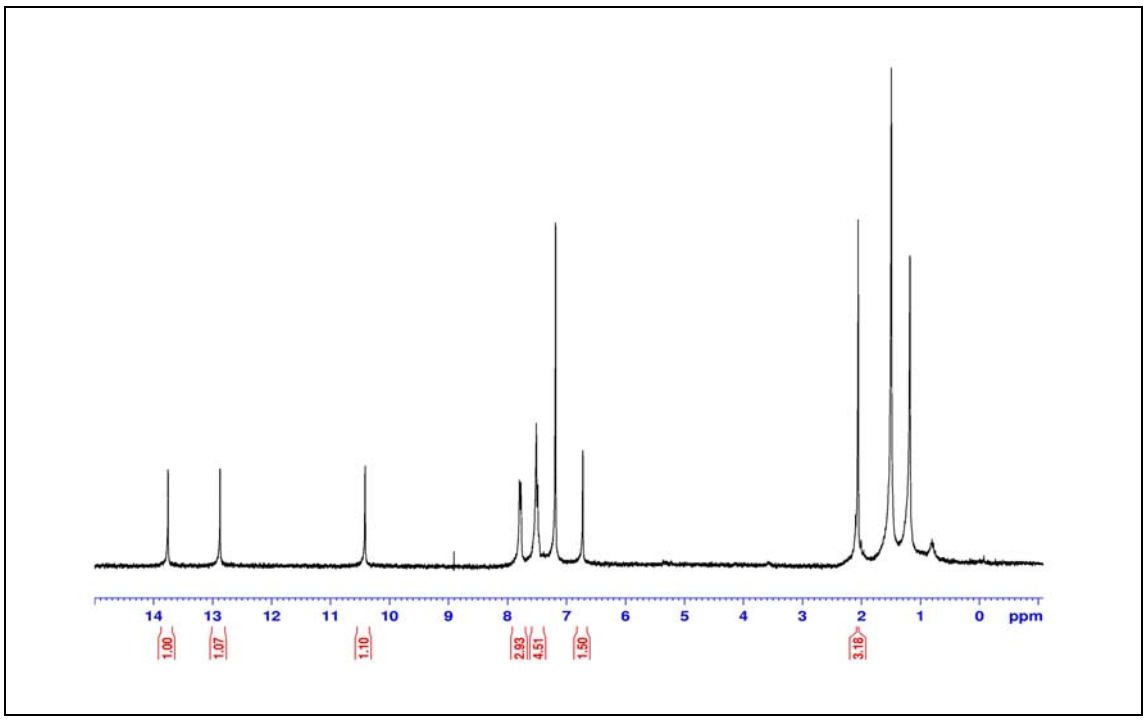

Figure 97 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC10**

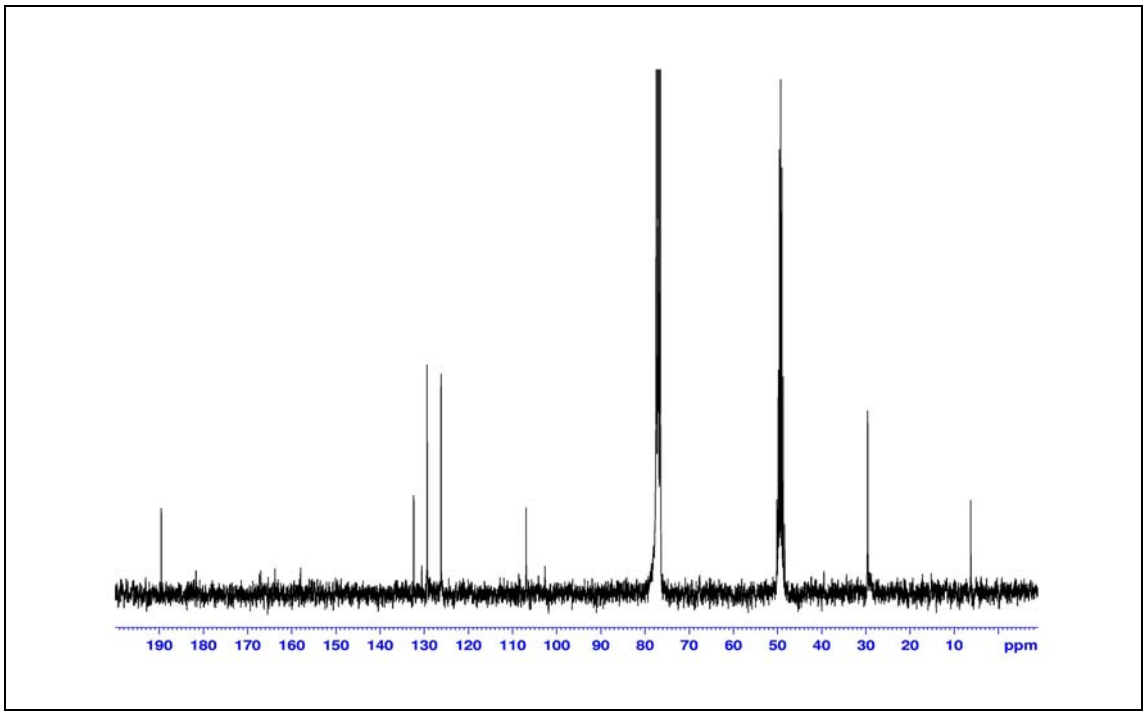

Figure 98 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC10**

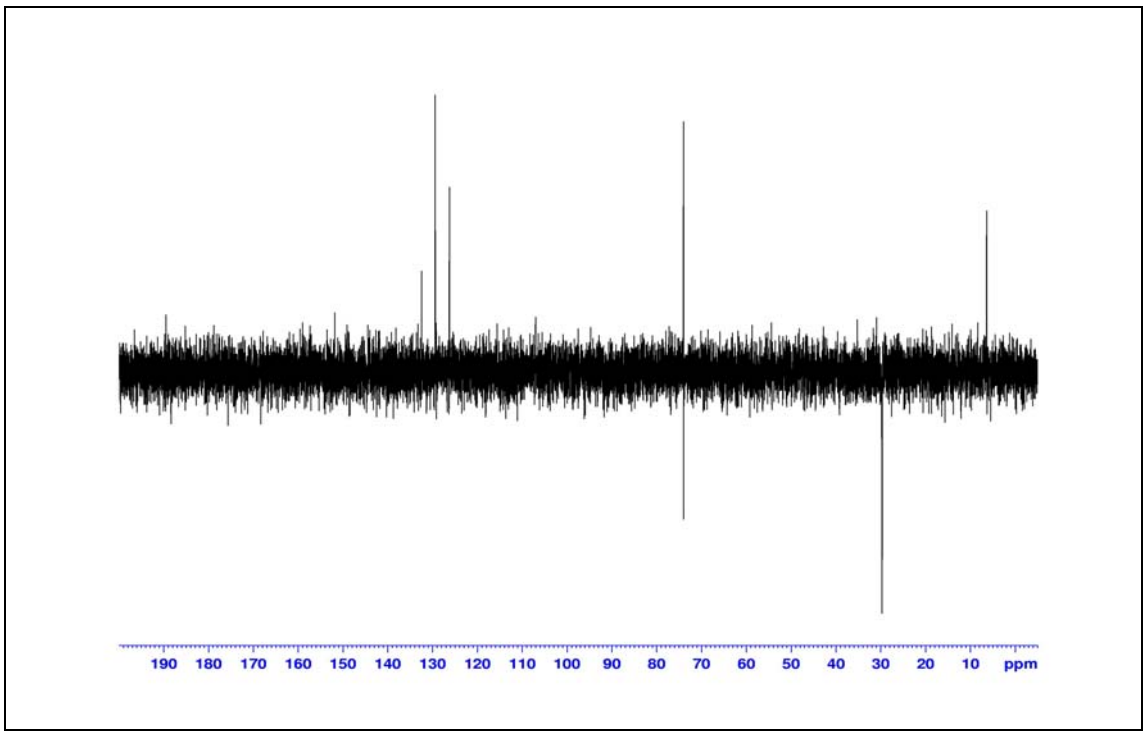

Figure 99 DEPT 135° ($CDCl_3$) of compound **DC10**

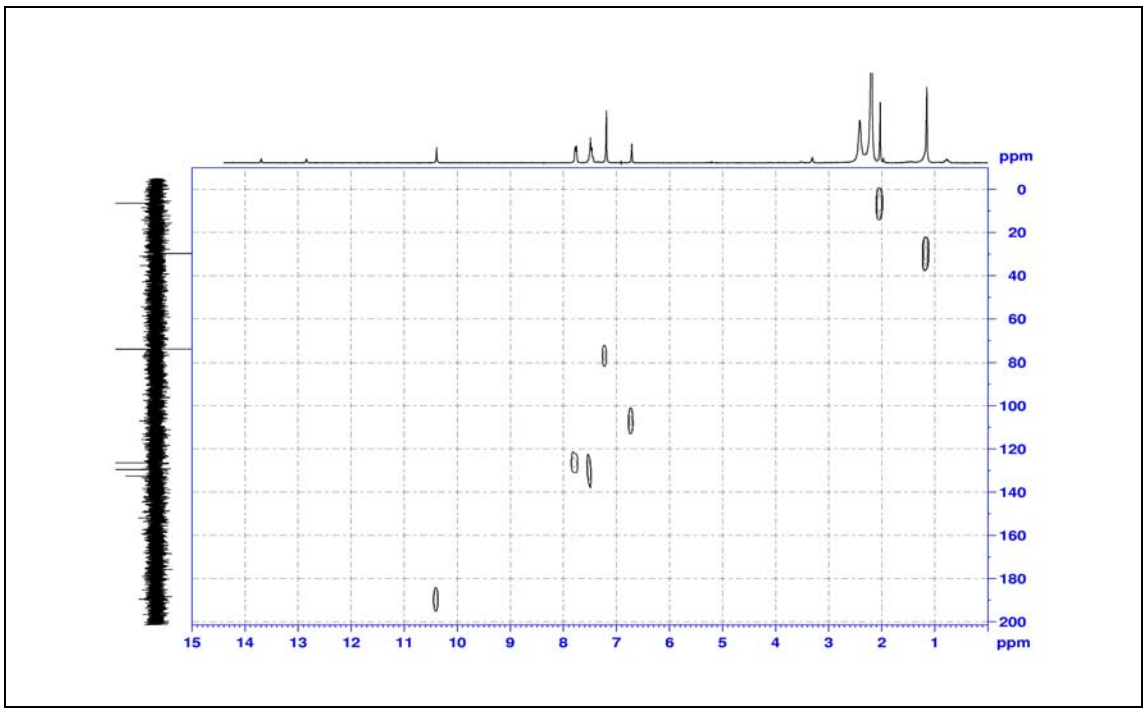

Figure 100 2D HMQC ($CDCl_3$) of compound **DC10**

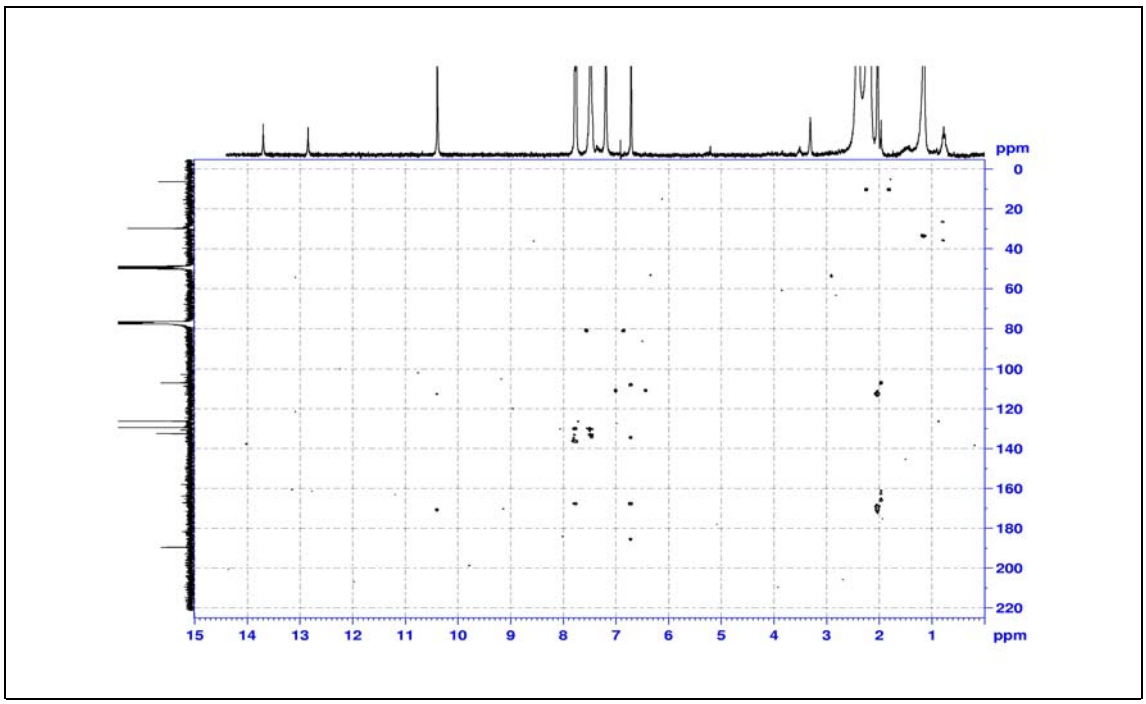

Figure 101 2D HMBC ($CDCl_3$) of compound **DC10**

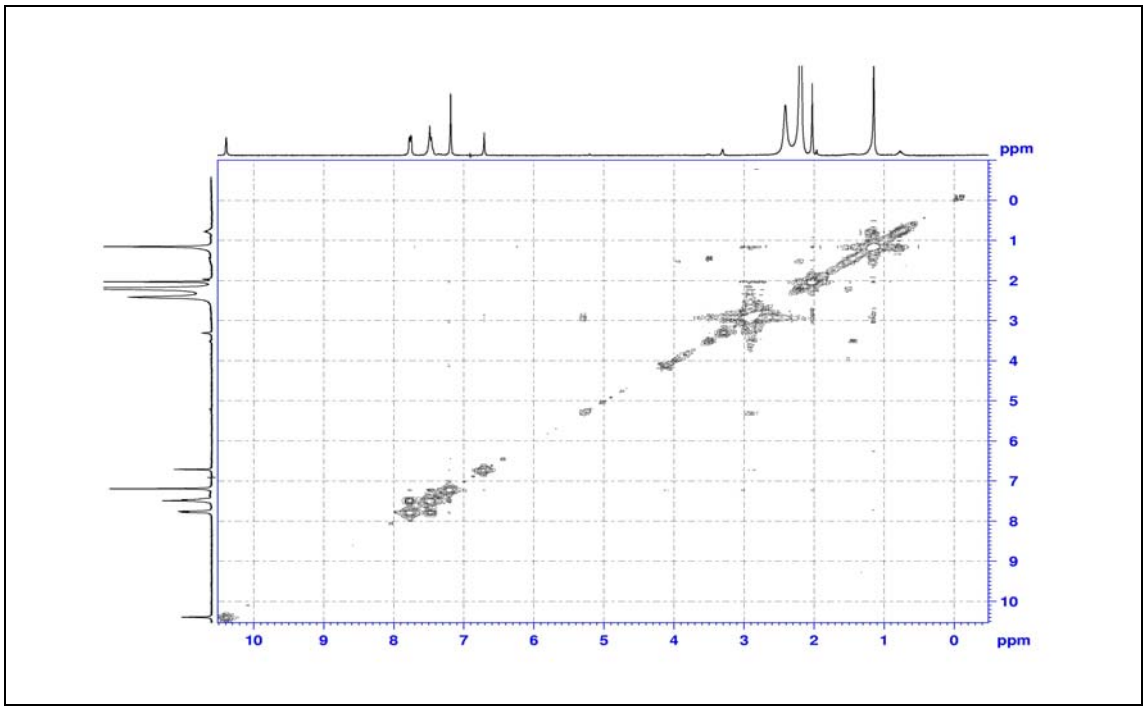

Figure 102 2D COSY ($CDCl_3$) of compound **DC10**

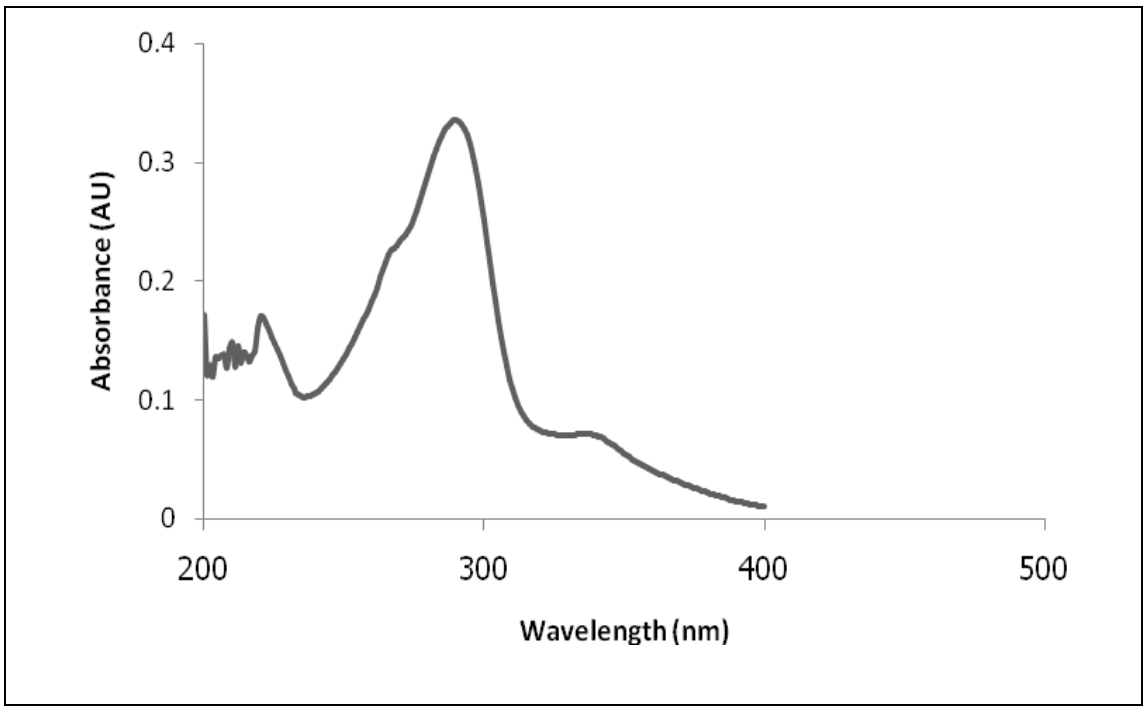

Figure 103 UV (MeOH) spectrum of compound **D11**

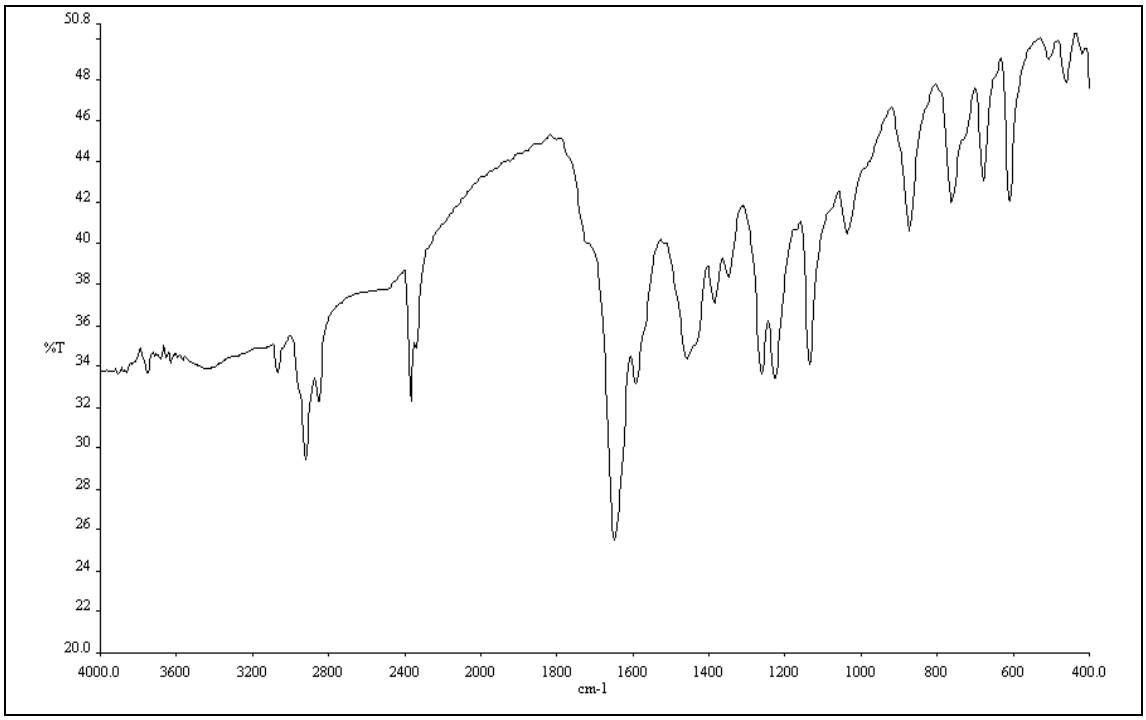

Figure 104 IR (KBr) spectrum of compound **DC11**

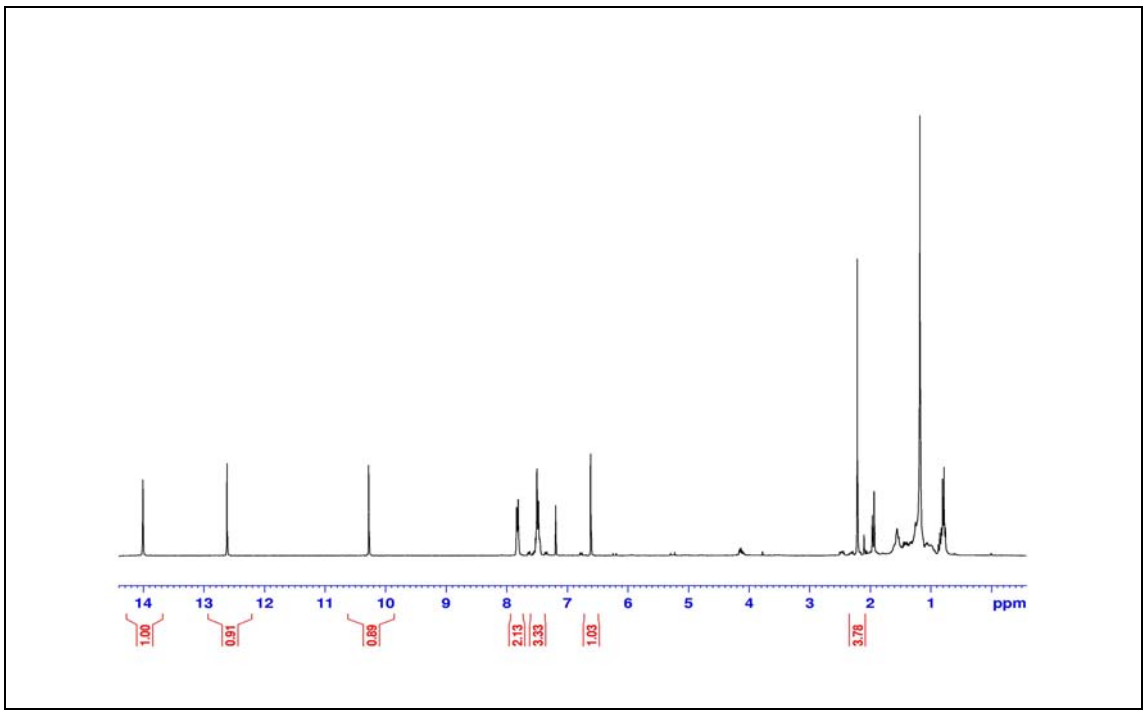

Figure 105 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC11**

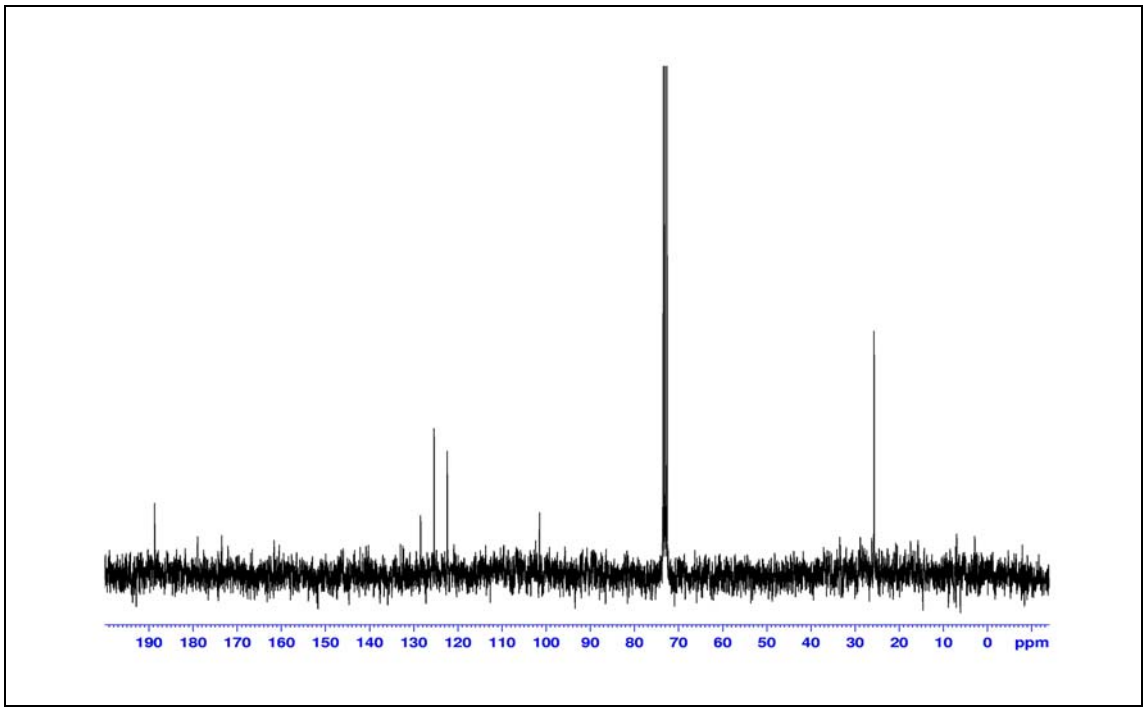

Figure 106 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC11**

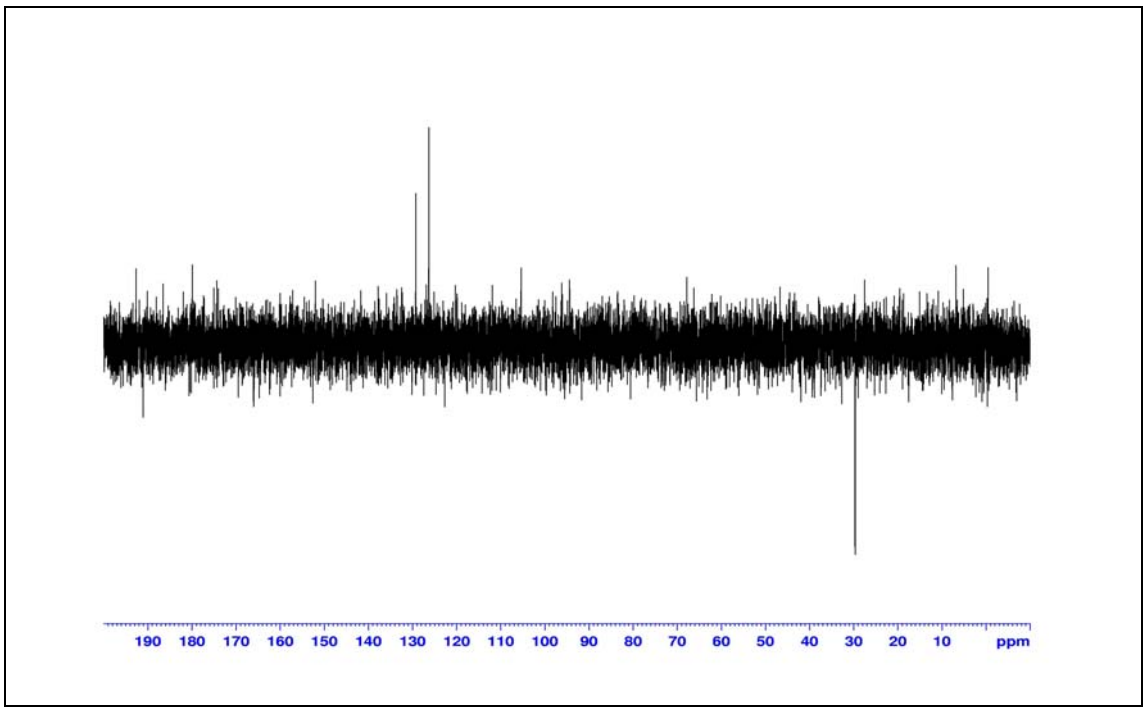

Figure 107 DEPT 135° ($CDCl_3$) of compound **DC11**

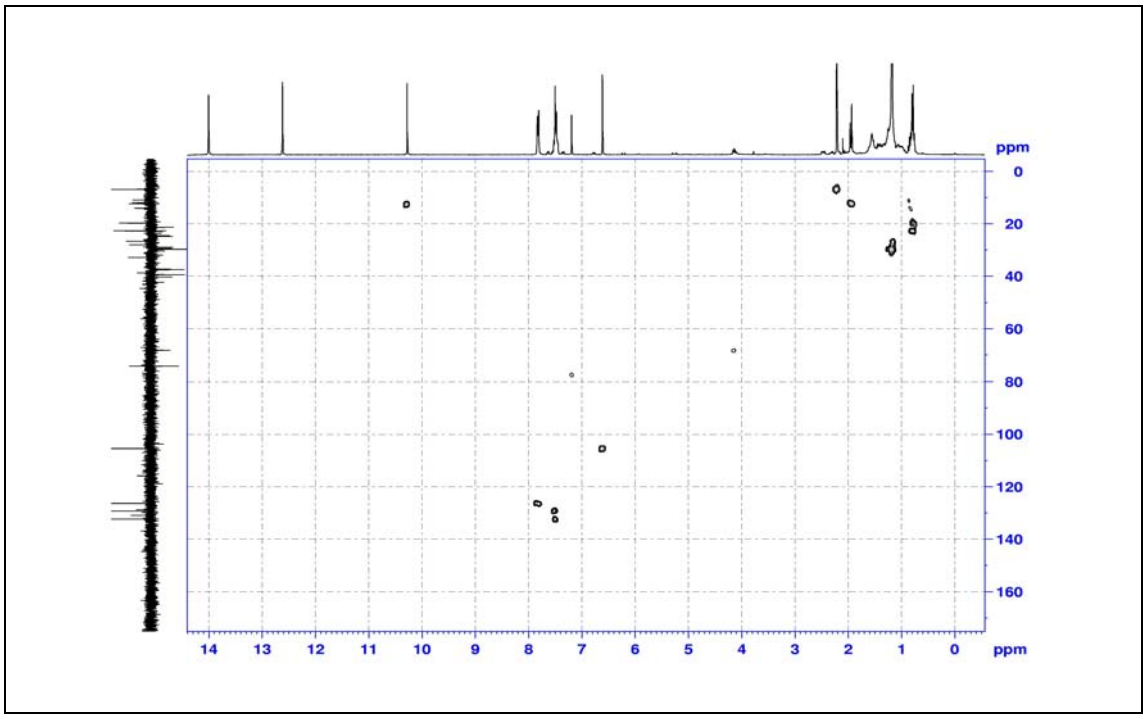

Figure 108 2D HMQC ($CDCl_3$) of compound **DC11**

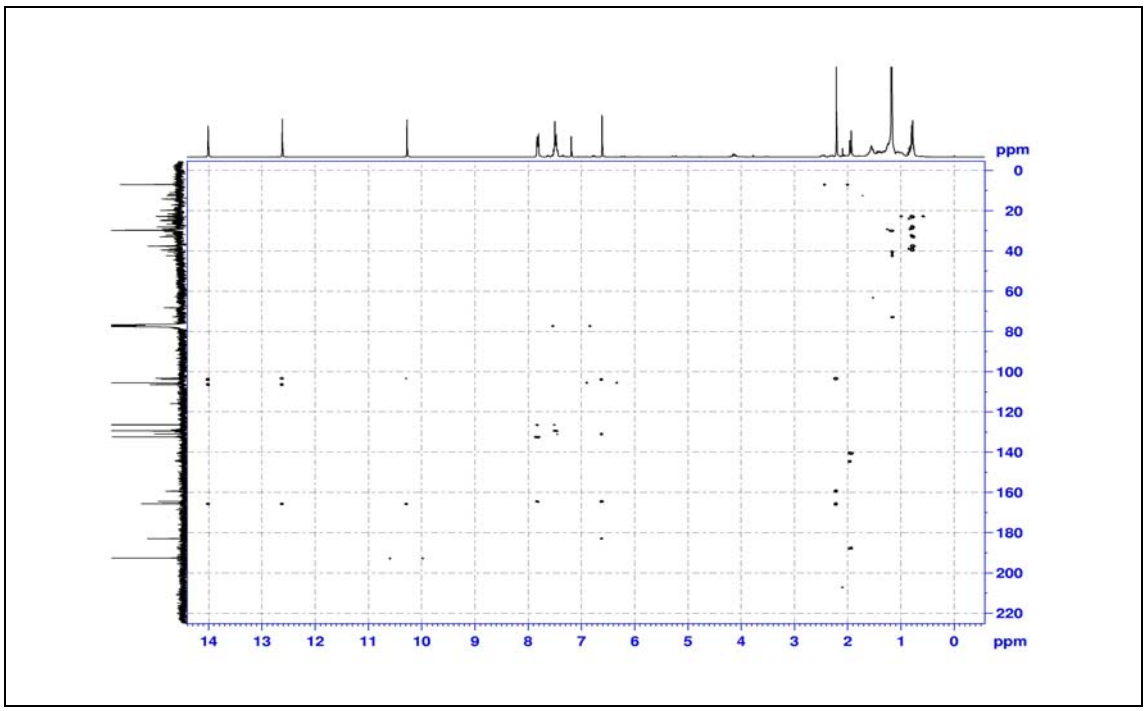

Figure 109 2D HMBC ($CDCl_3$) of compound **DC11**

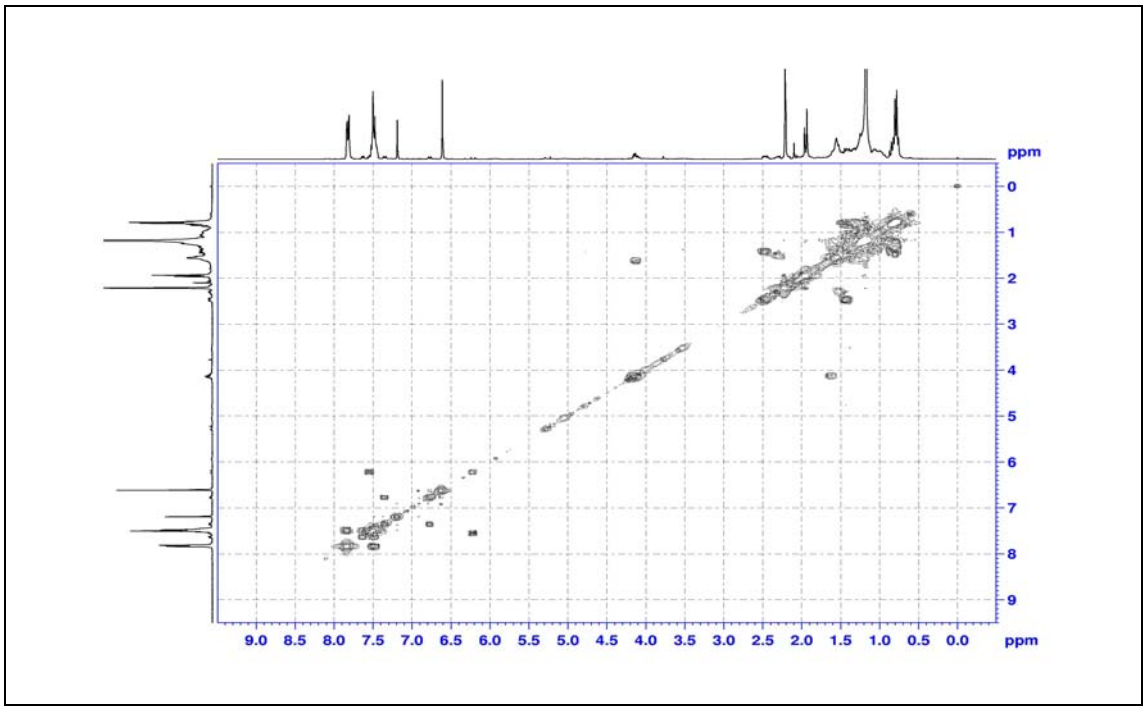

Figure 110 2D COSY ($CDCl_3$) of compound **DC11**

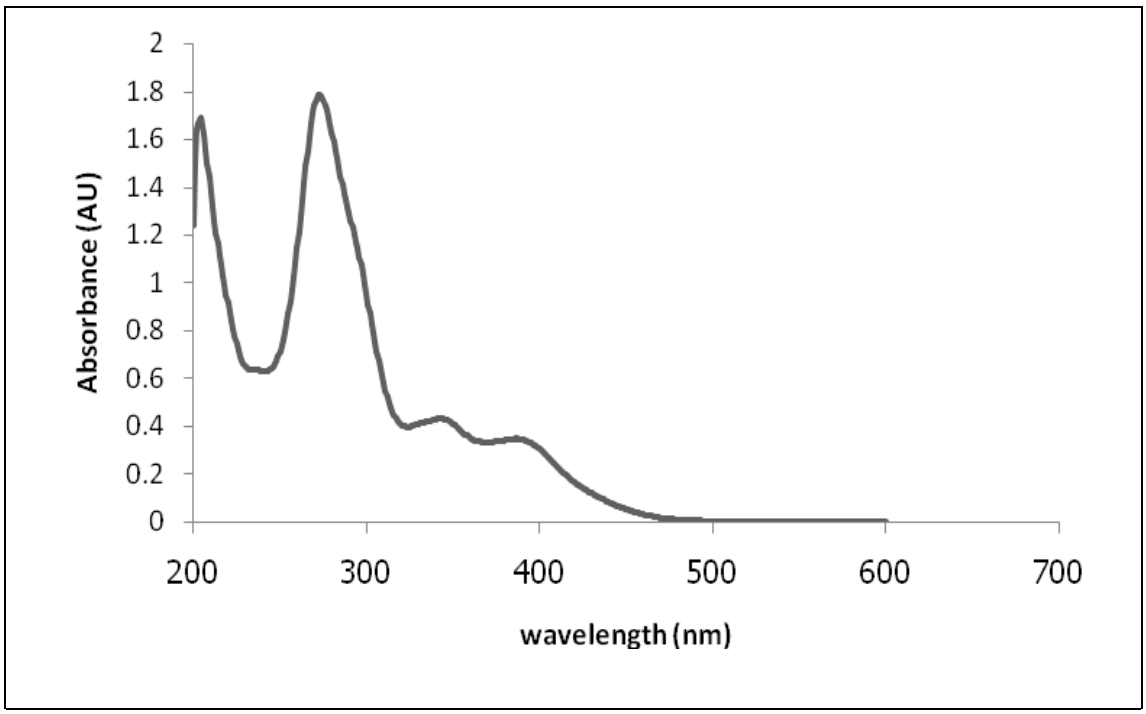

Figure 111 UV (MeOH) spectrum of compound **D12** and **DC13**

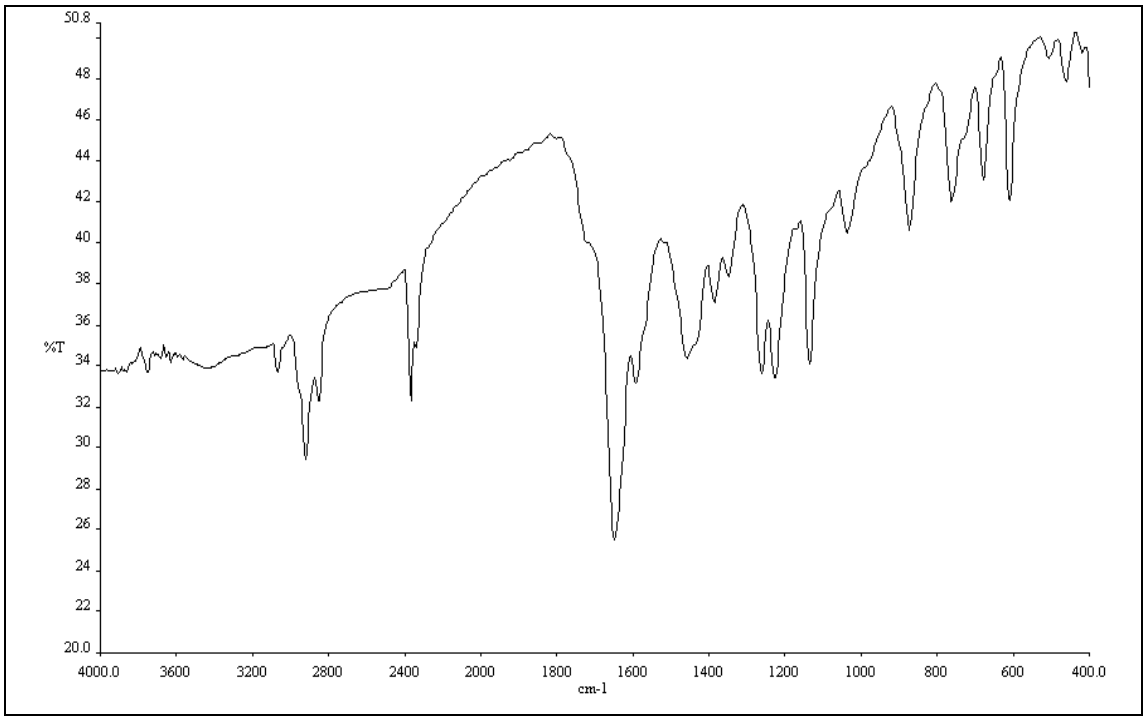

Figure 112 IR (KBr) spectrum of compound **DC12** and **DC13**

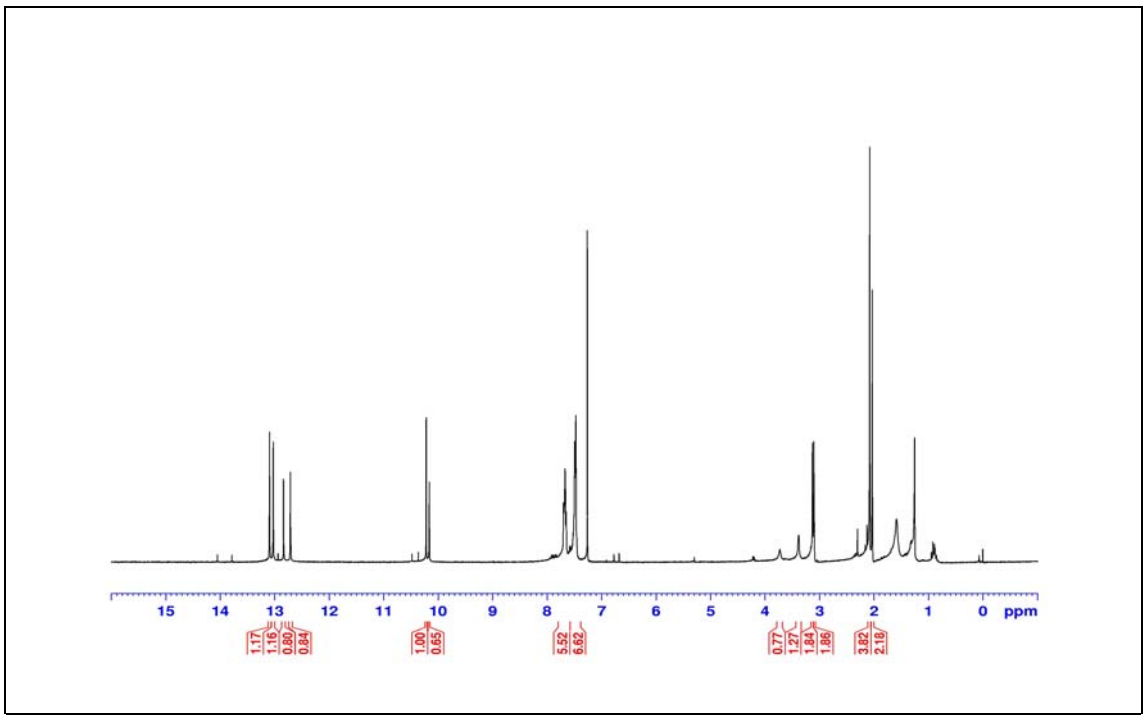

Figure 113 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC12** and **DC13**

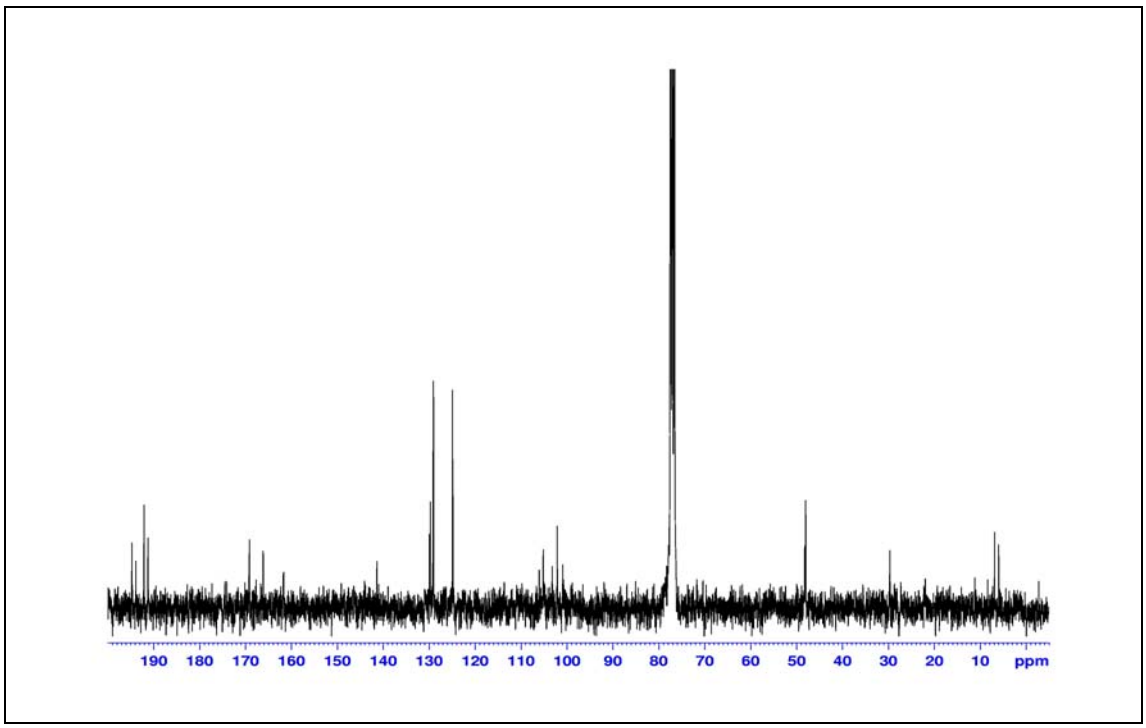

Figure 114 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC12** and **DC13**

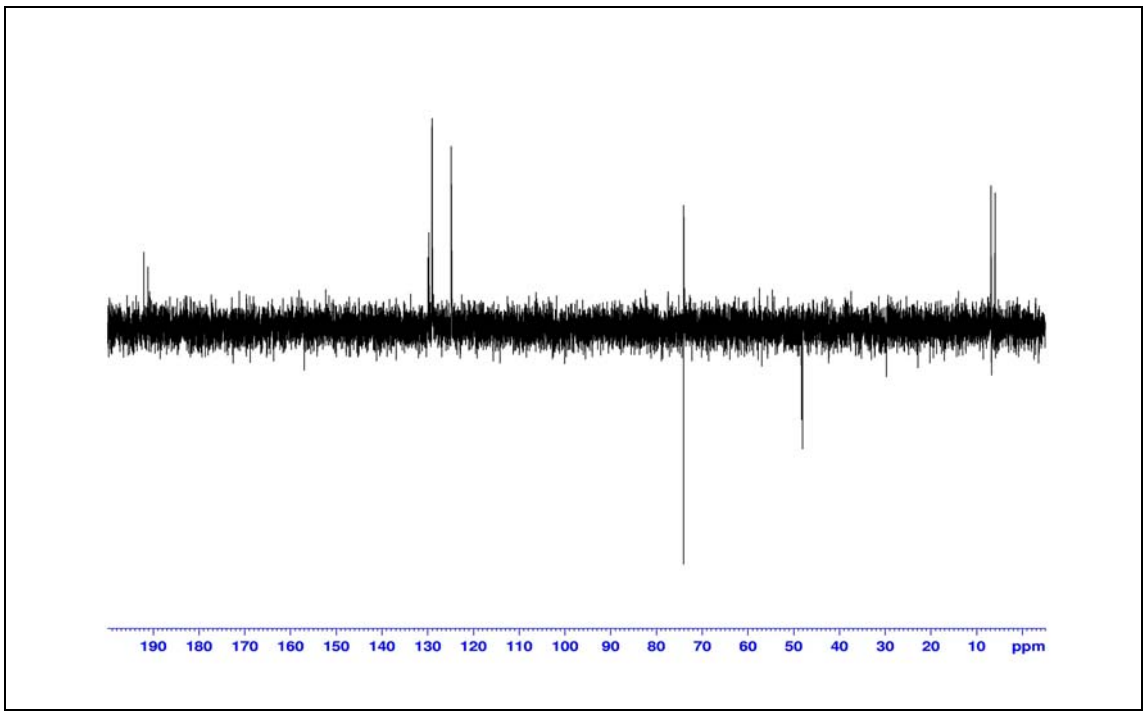

Figure 115 DEPT 135° ($CDCl_3$) of compound **DC12** and **DC13**

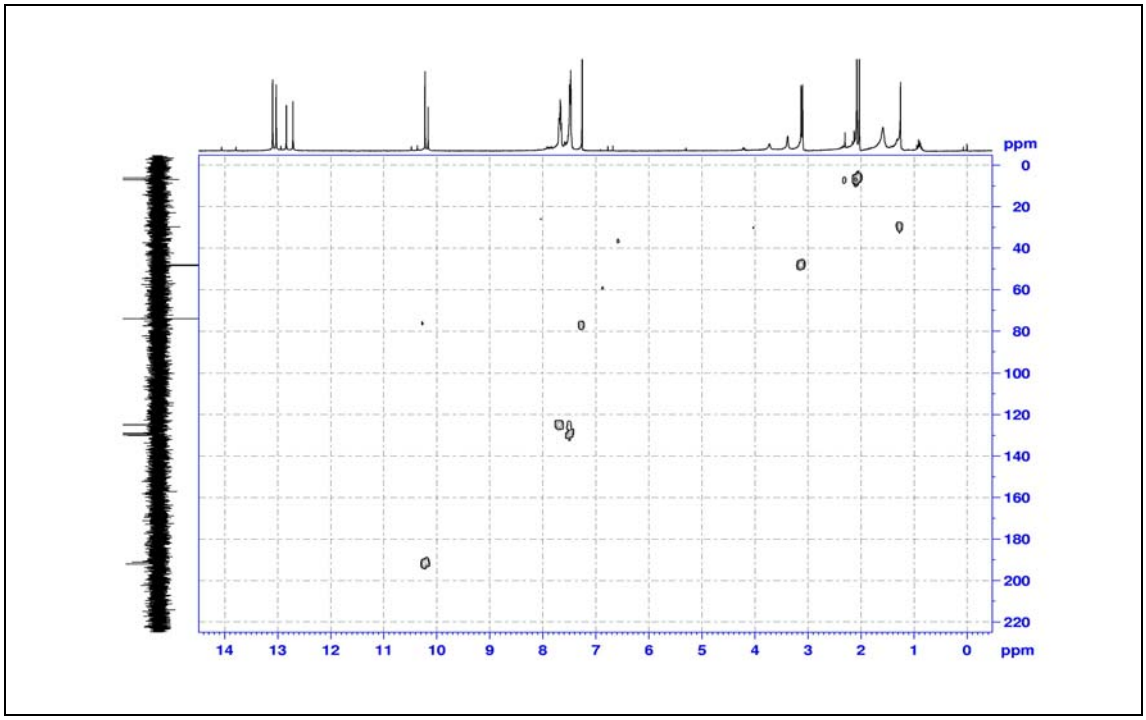

Figure 116 2D HMQC ($CDCl_3$) of compound **DC12** and **DC13**

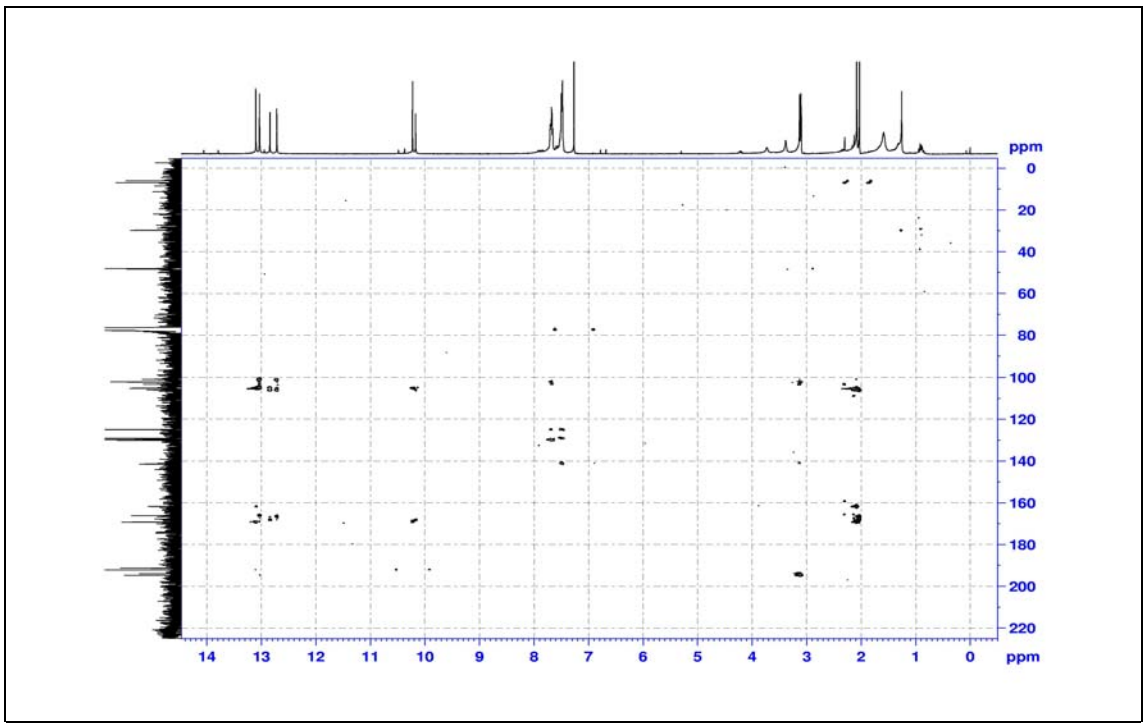

Figure 117 2D HMBC ($CDCl_3$) of compound **DC12** and **DC13**

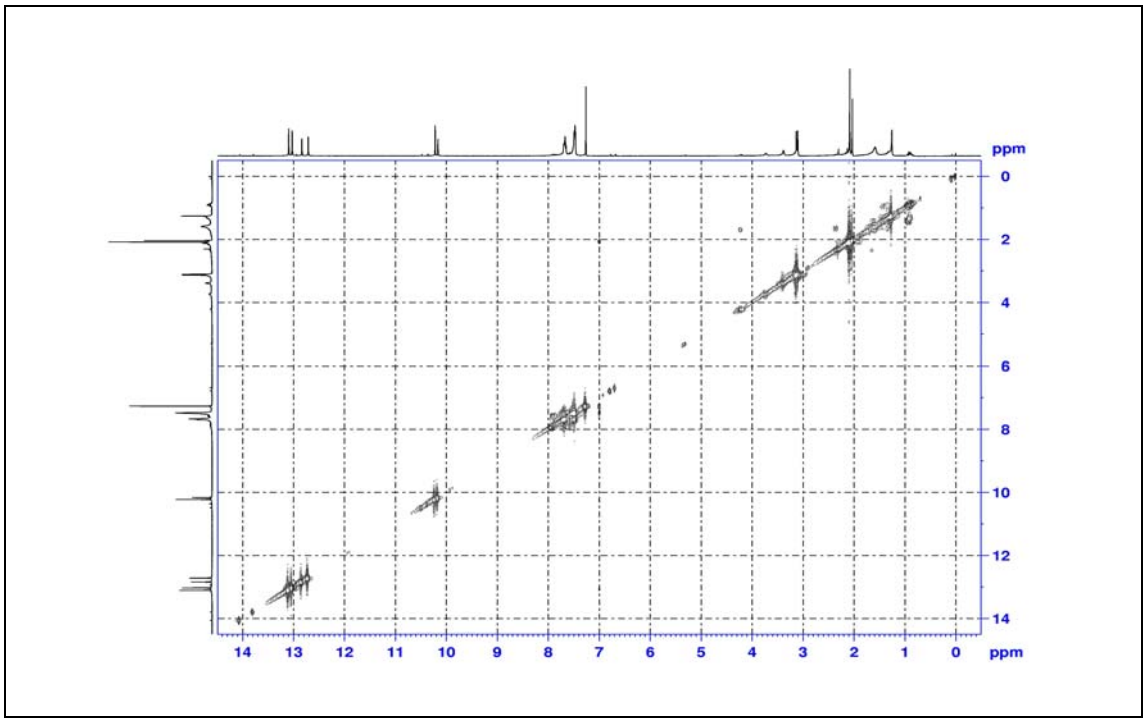

Figure 118 2D COSY ($CDCl_3$) of compound **DC12** and **DC13**

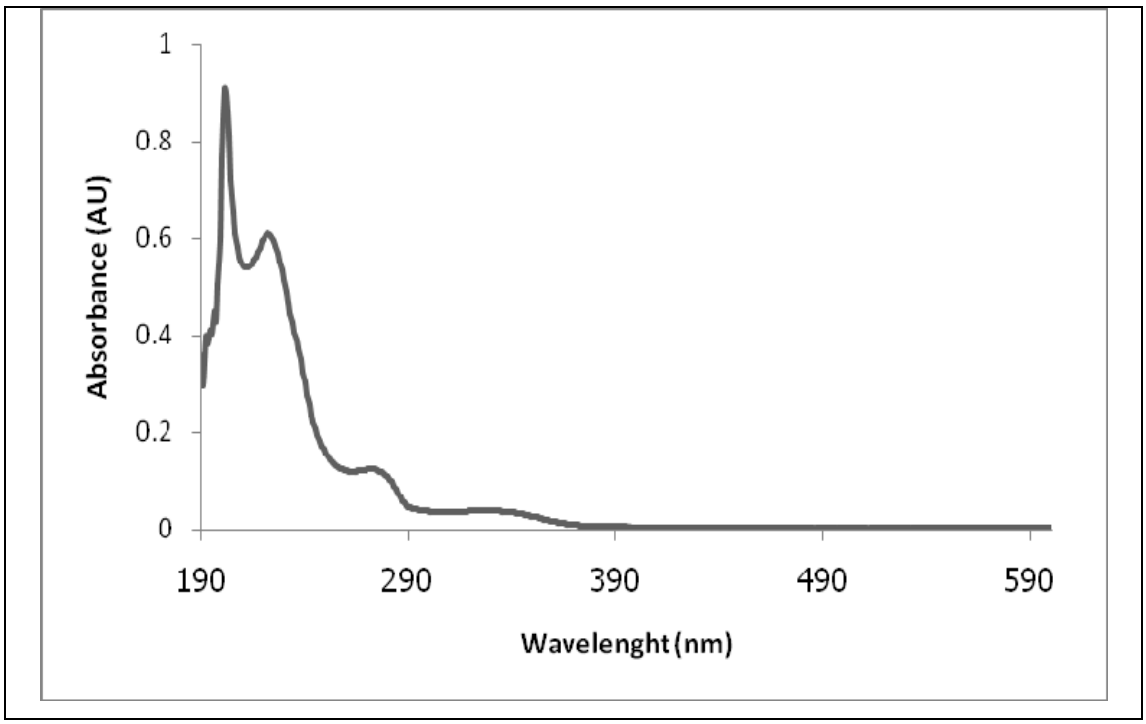

Figure 119 UV (MeOH) spectrum of compound **DC14**

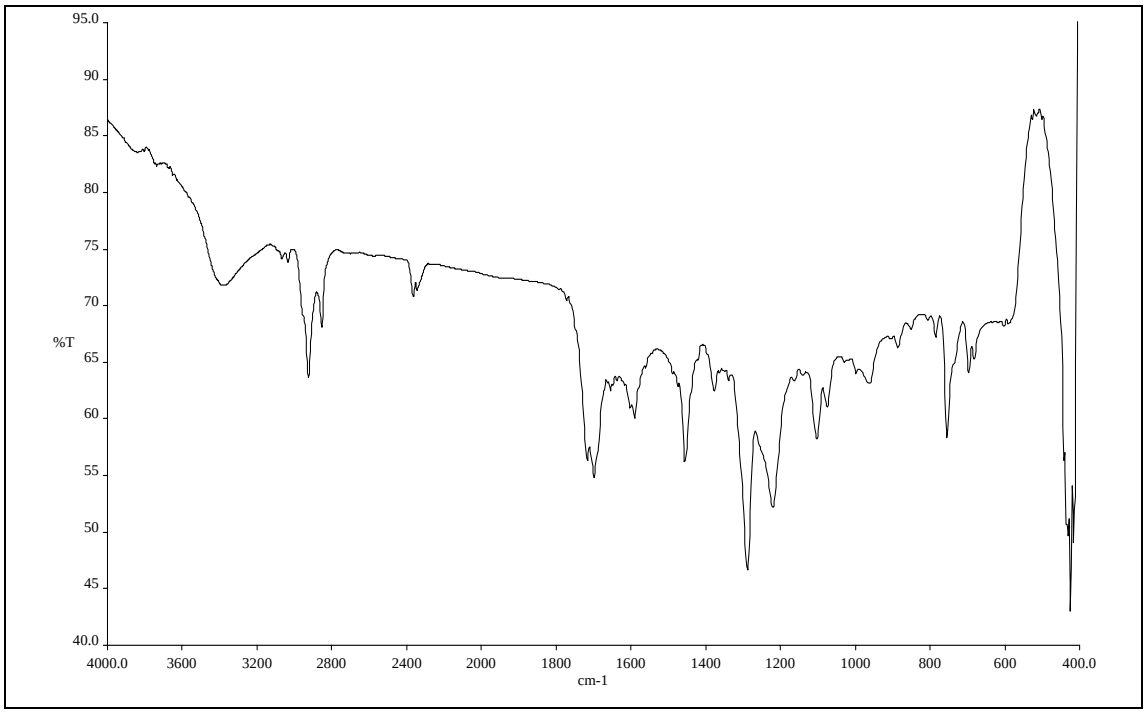

Figure 120 IR (neat) spectrum of compound **DC14**

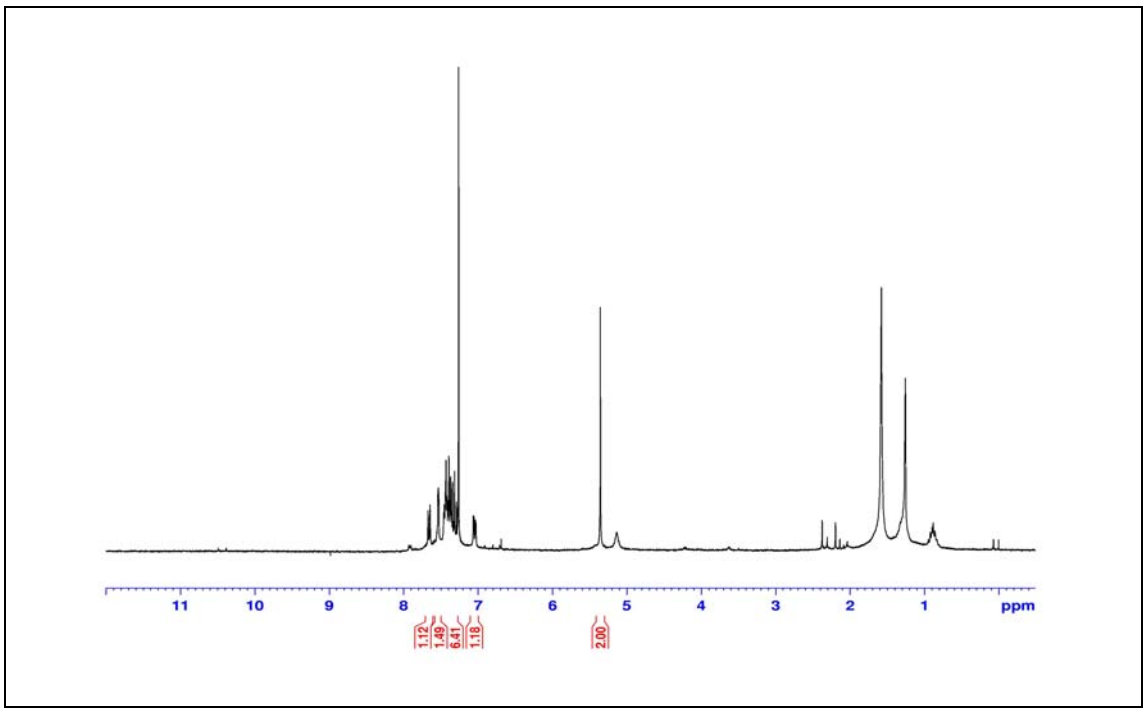

Figure 121 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC14**

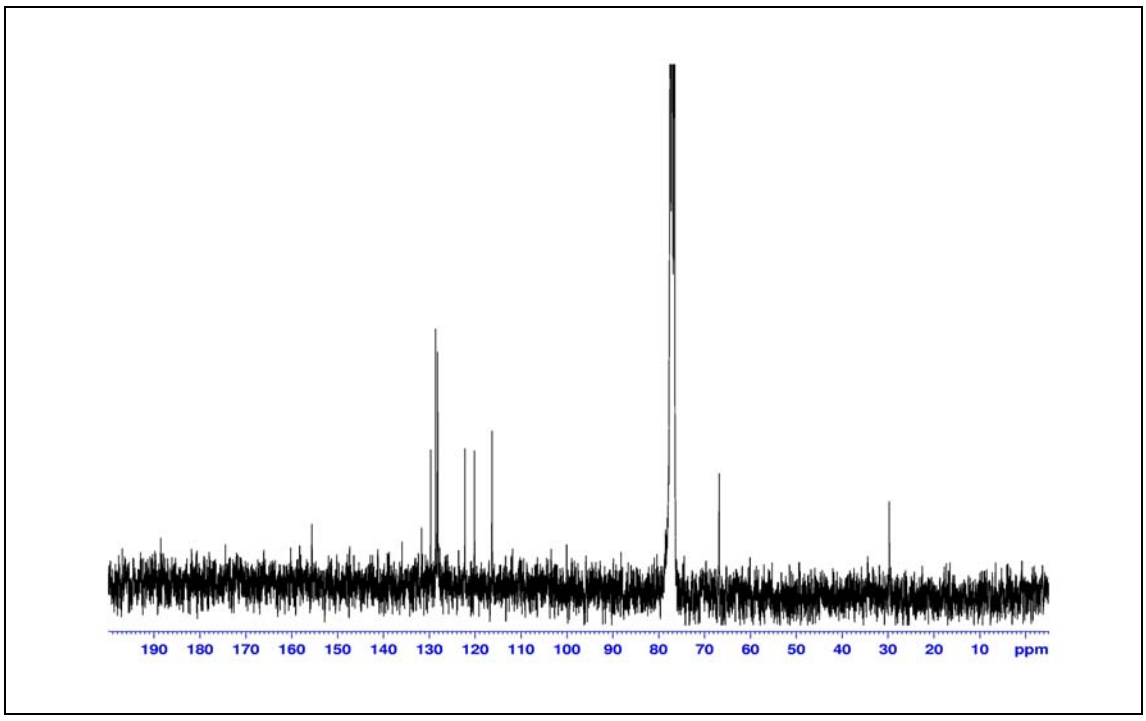

Figure 122 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC14**

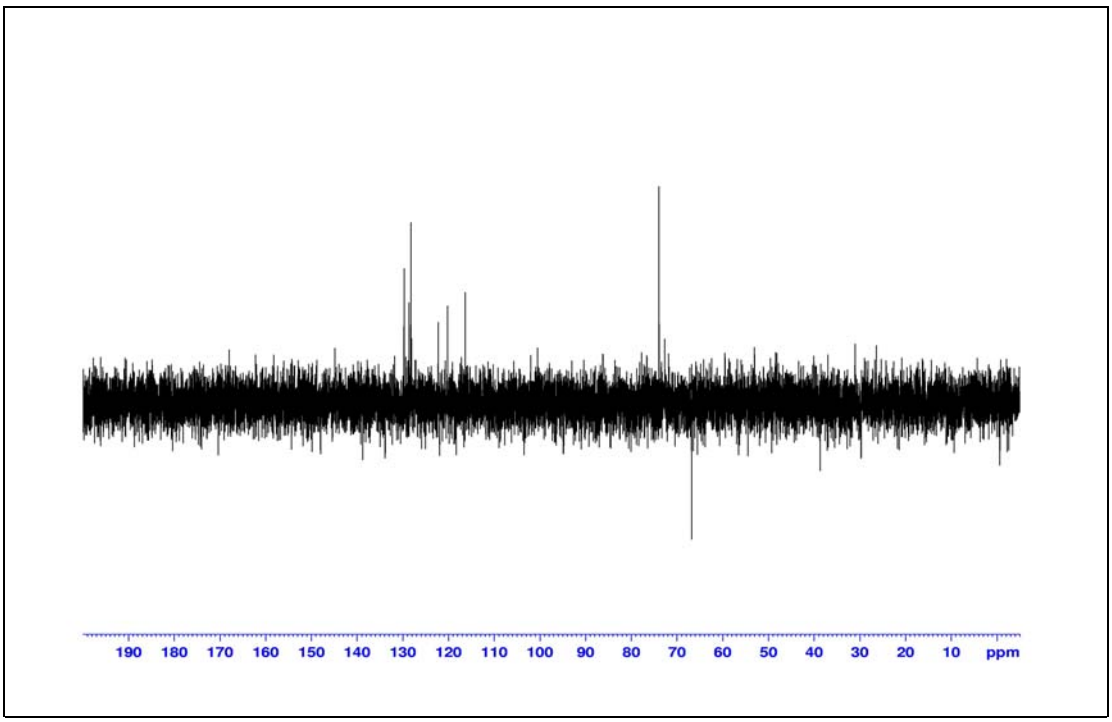

Figure 123 DEPT 135° ($CDCl_3$) of compound **DC14**

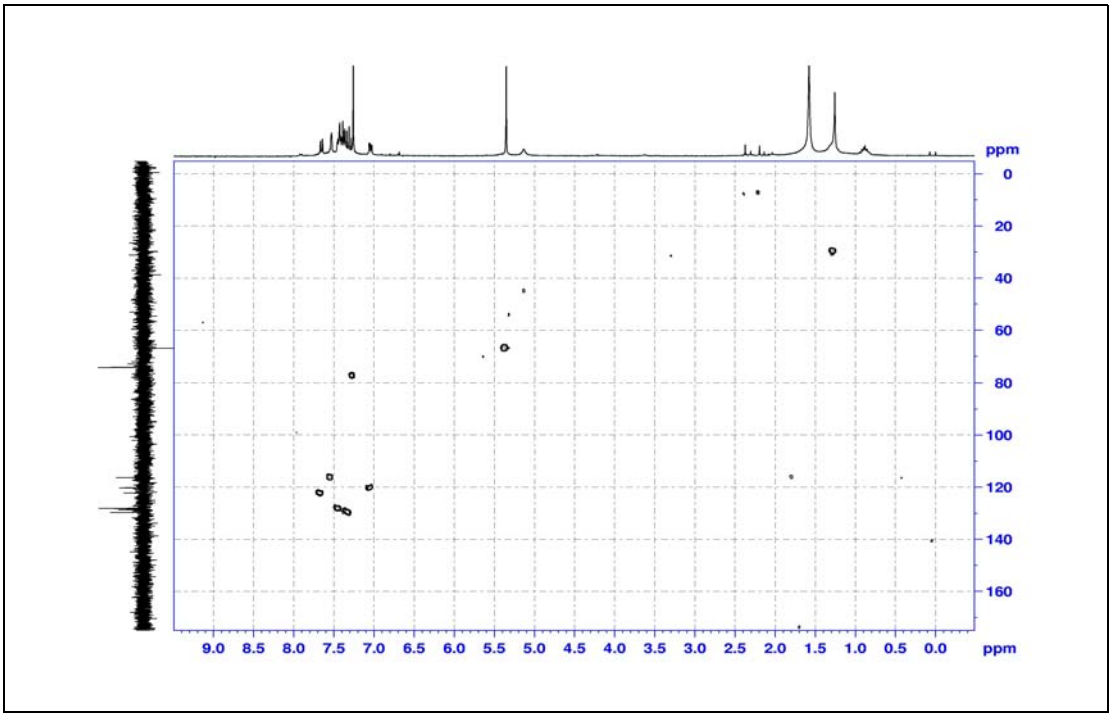

Figure 124 2D HMQC ($CDCl_3$) of compound **DC14**

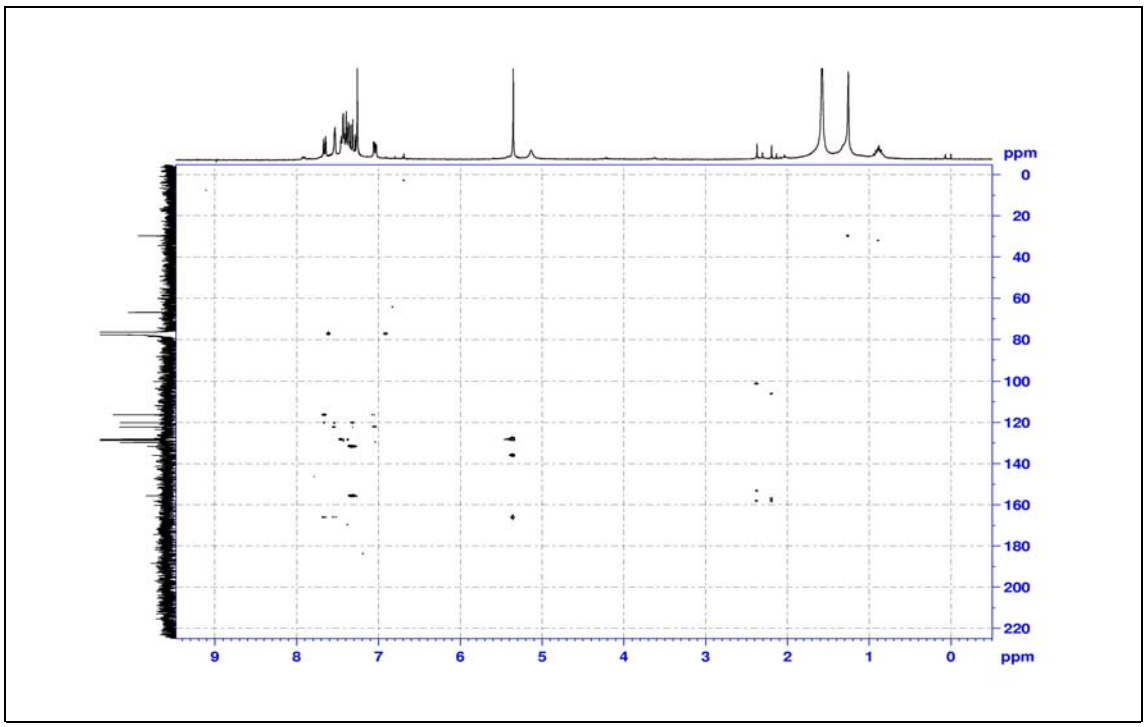

Figure 125 2D HMBC ($CDCl_3$) of compound **DC14**

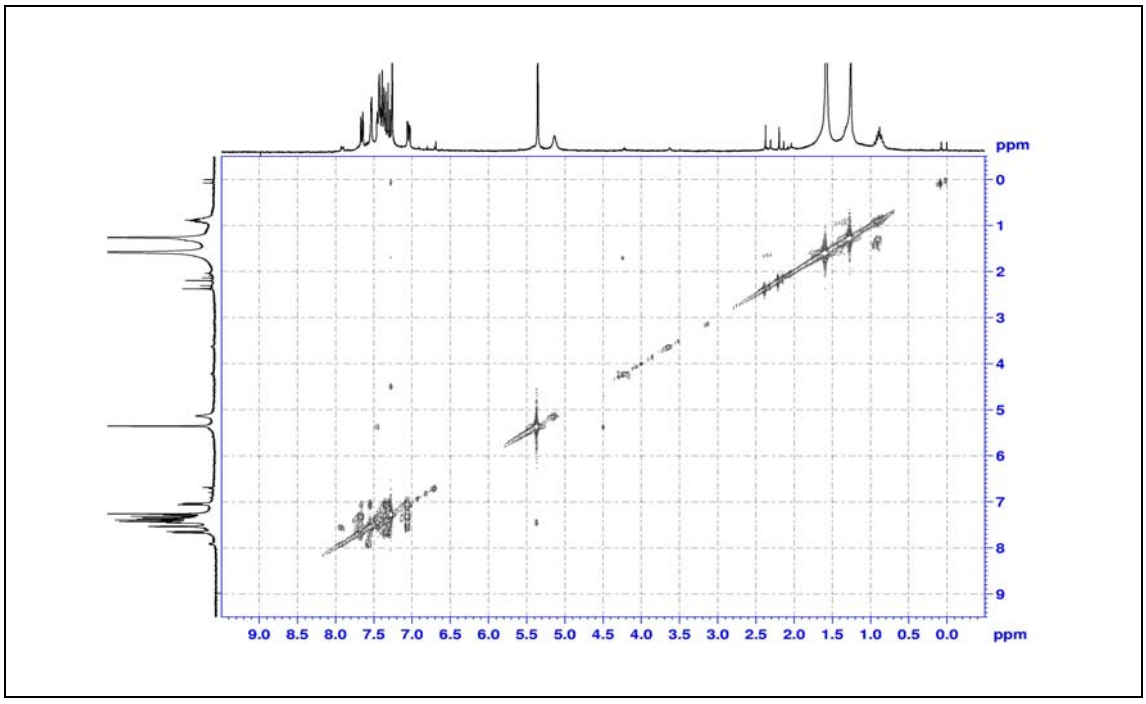

Figure 126 2D COSY ($CDCl_3$) of compound **DC14**

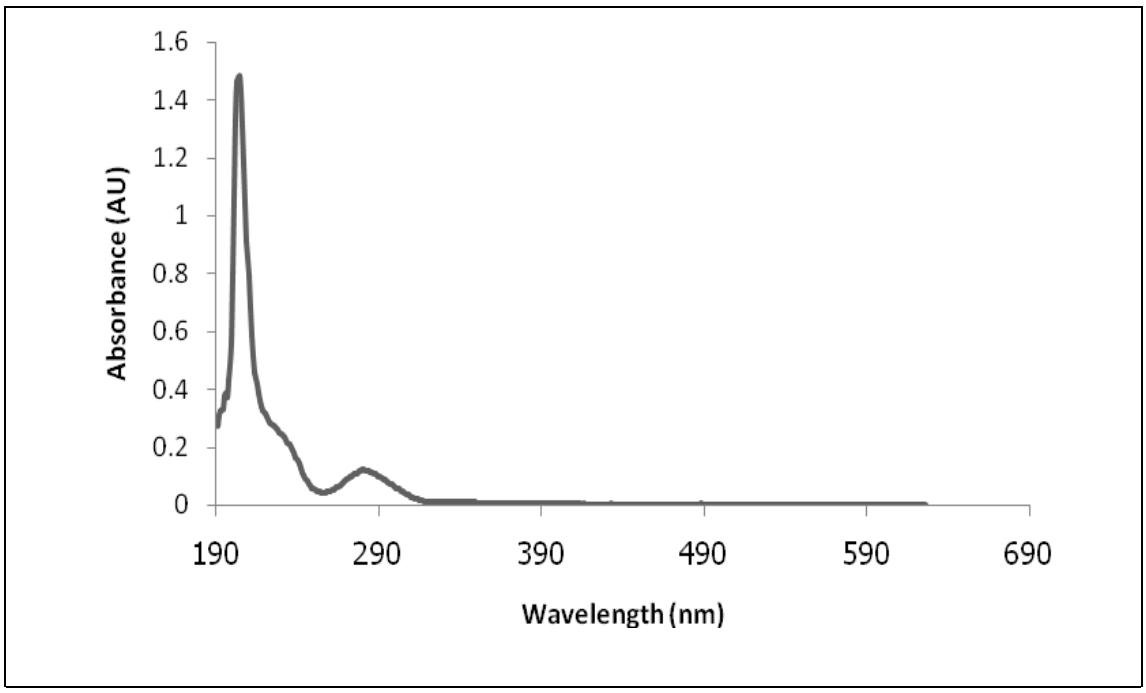

Figure 127 UV (MeOH) spectrum of compound **DC15**

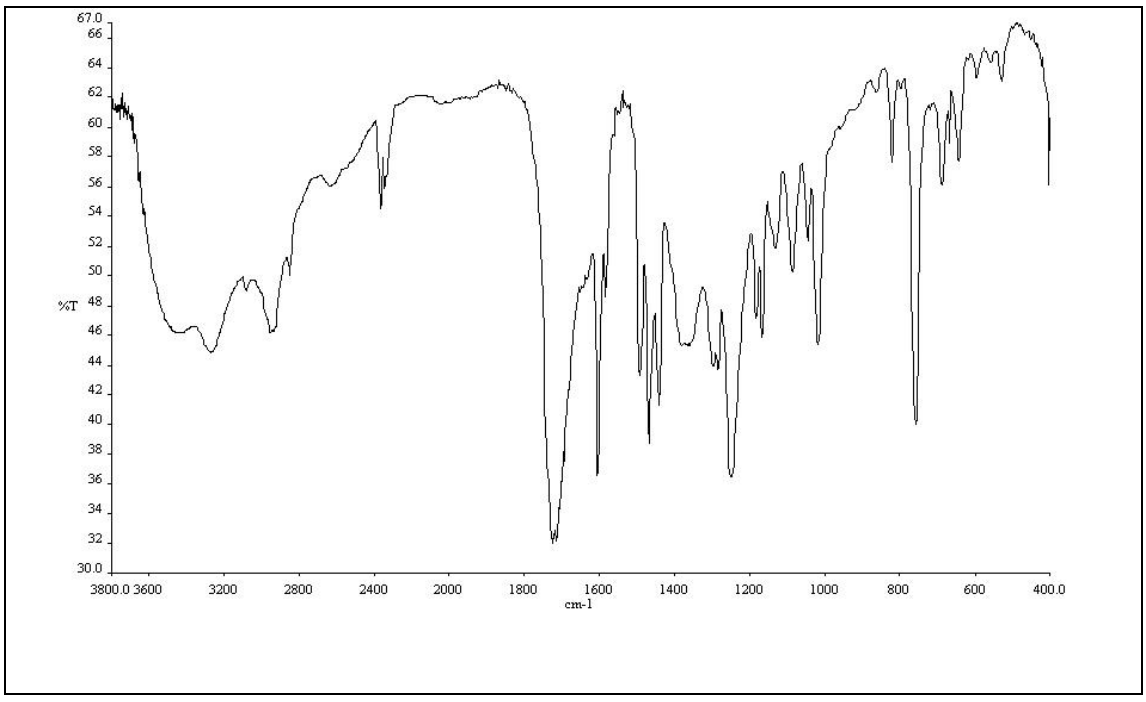

Figure 128 IR (neat) spectrum of compound **DC15**

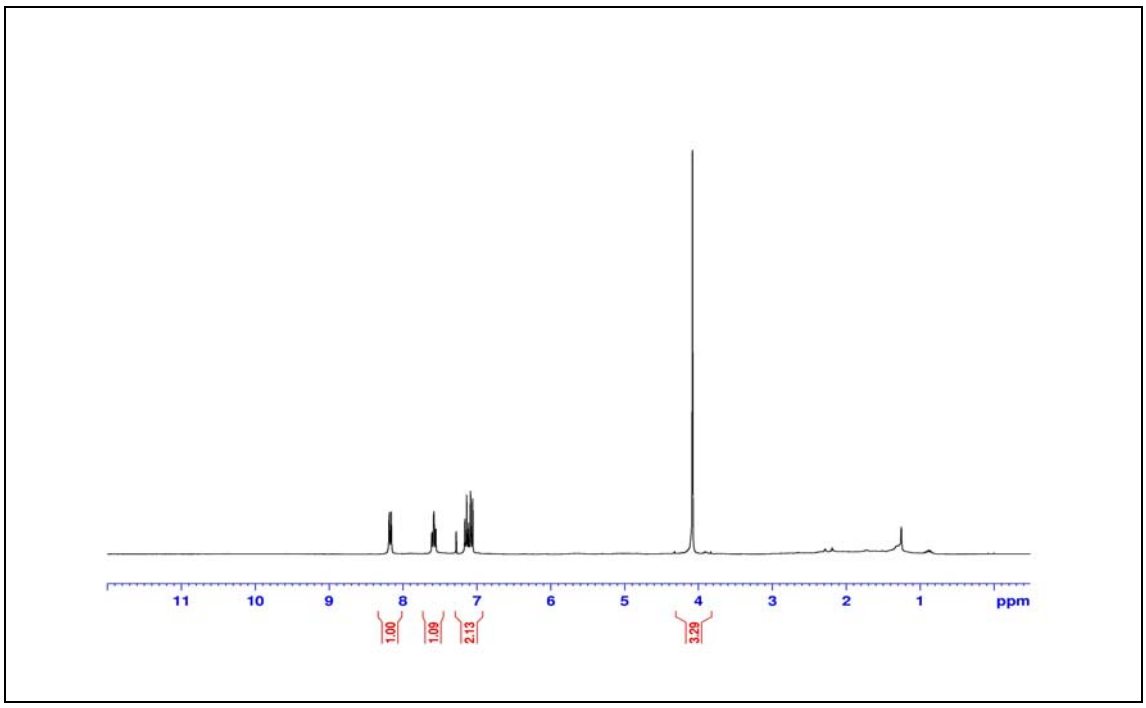

Figure 129 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC15**

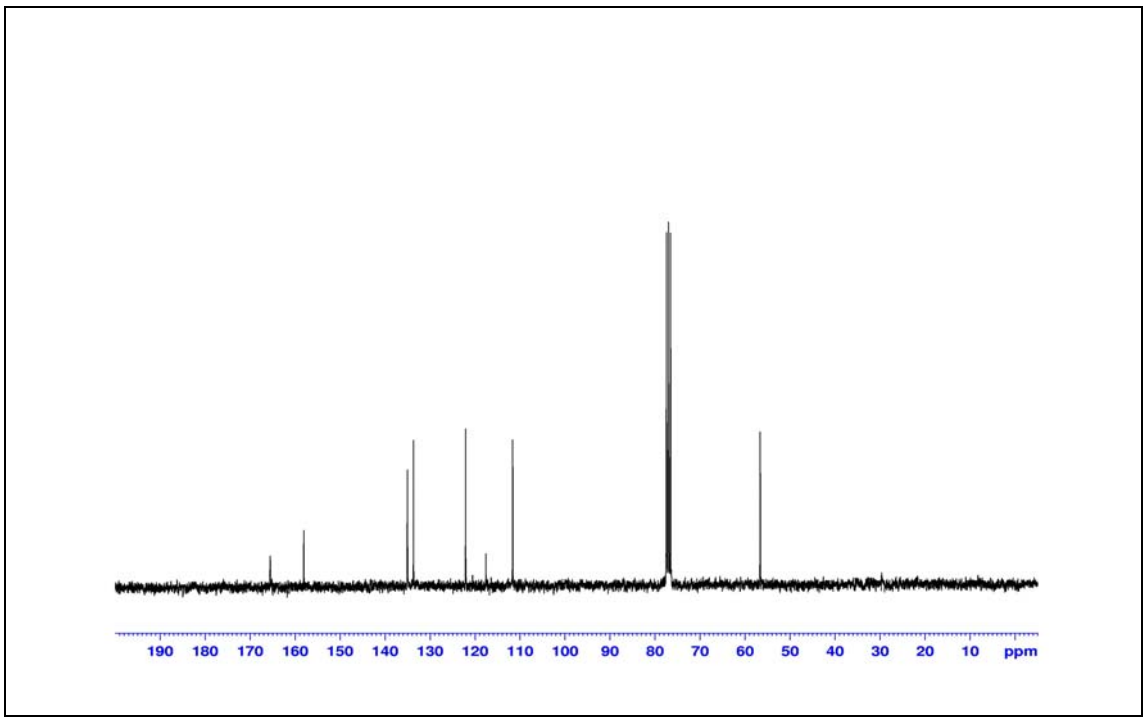

Figure 130 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC15**

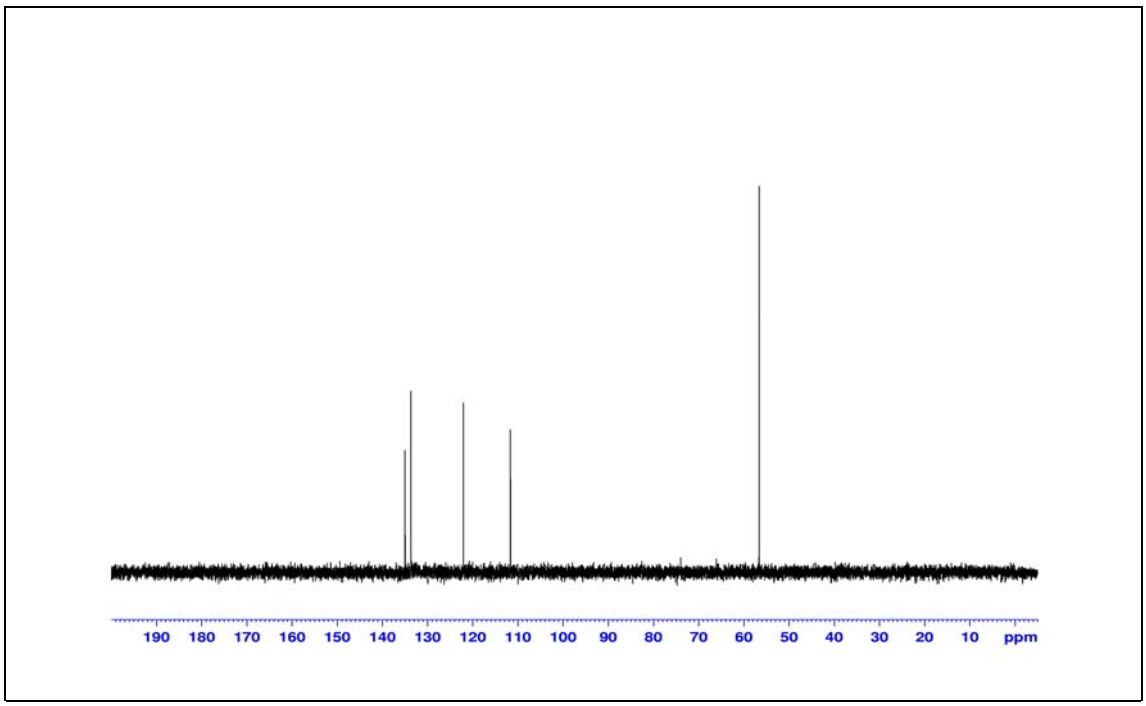

Figure 131 DEPT 135° ($CDCl_3$) of compound **DC15**

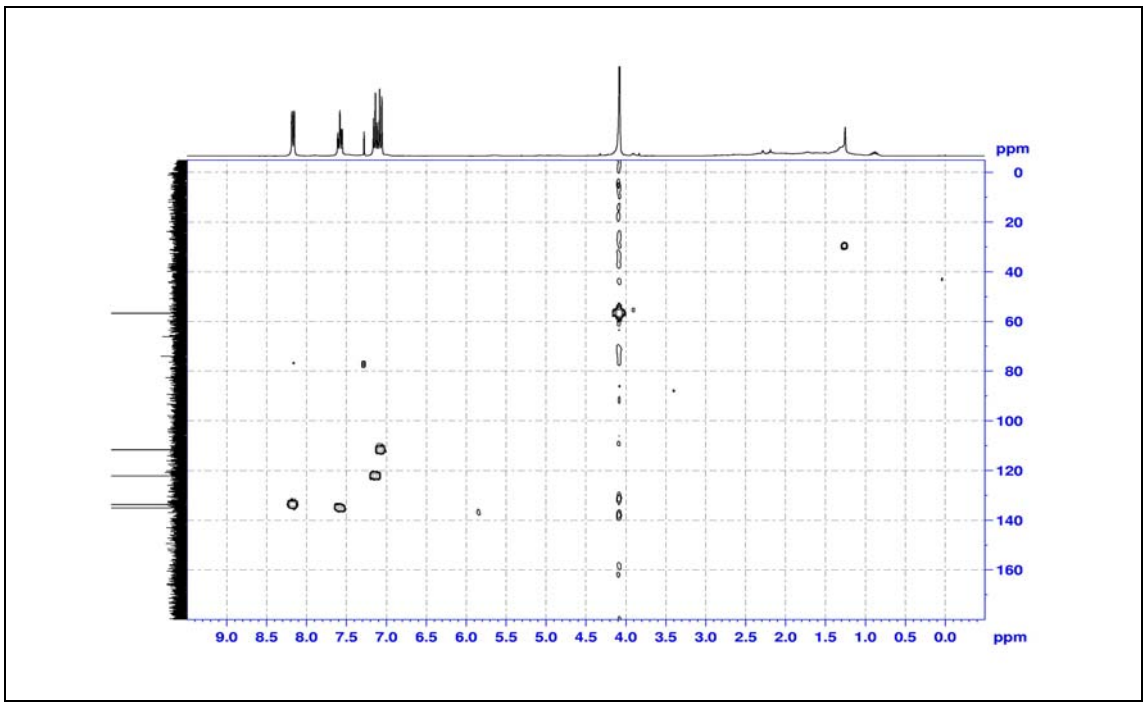

Figure 132 2D HMQC ($CDCl_3$) of compound **DC15**

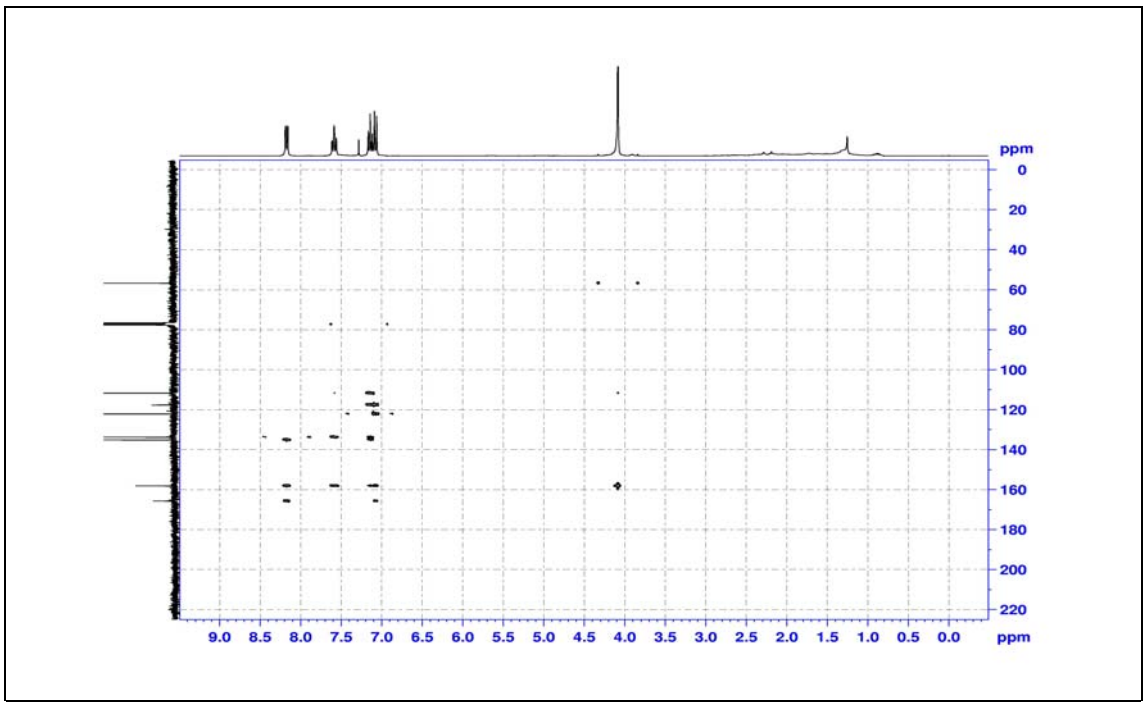

Figure 133 2D HMBC ($CDCl_3$) of compound **DC15**

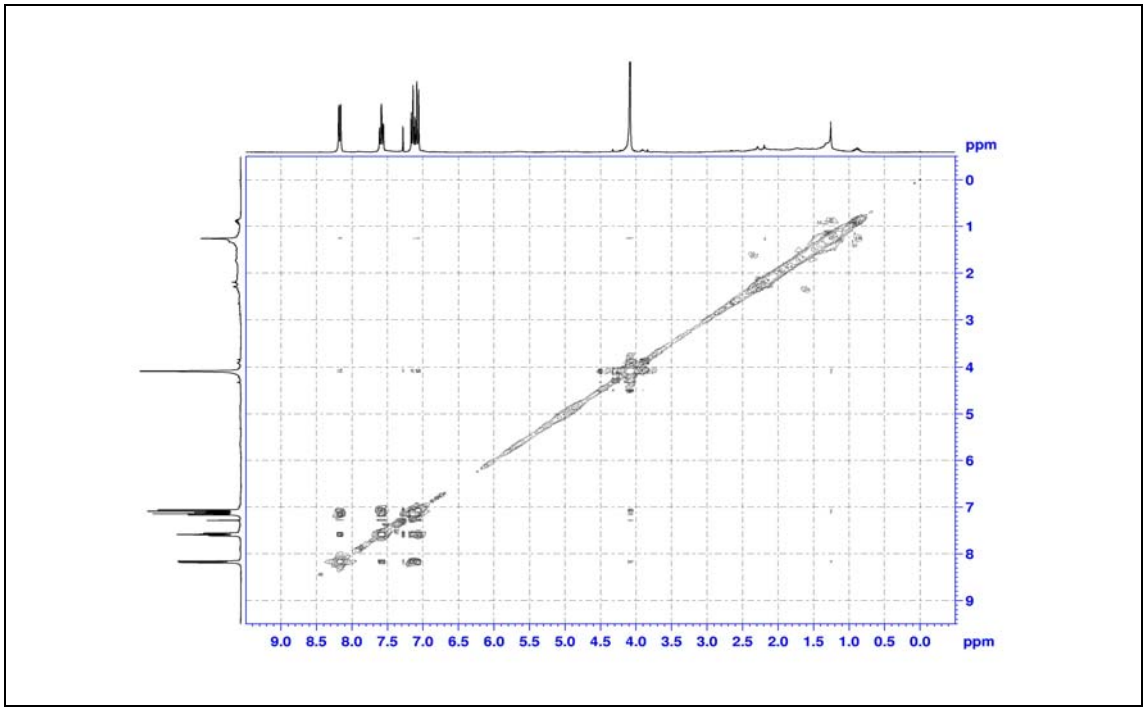

Figure 134 2D COSY ($CDCl_3$) of compound **DC15**

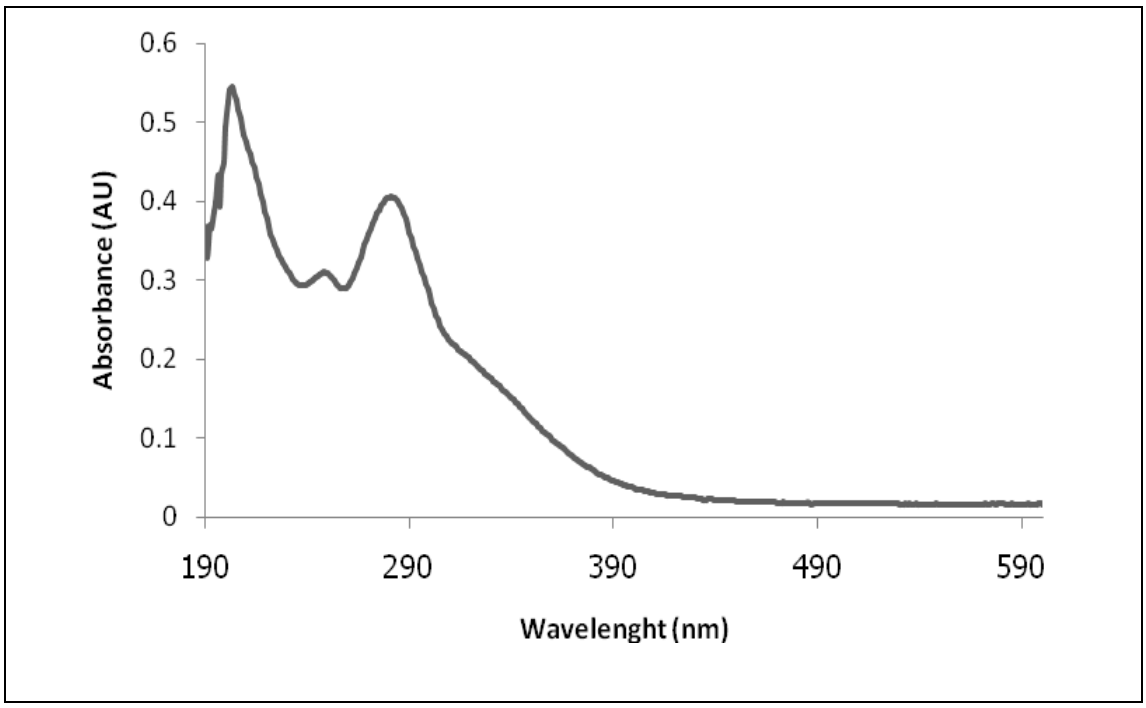

Figure 135 UV (MeOH) spectrum of compound **DC16**

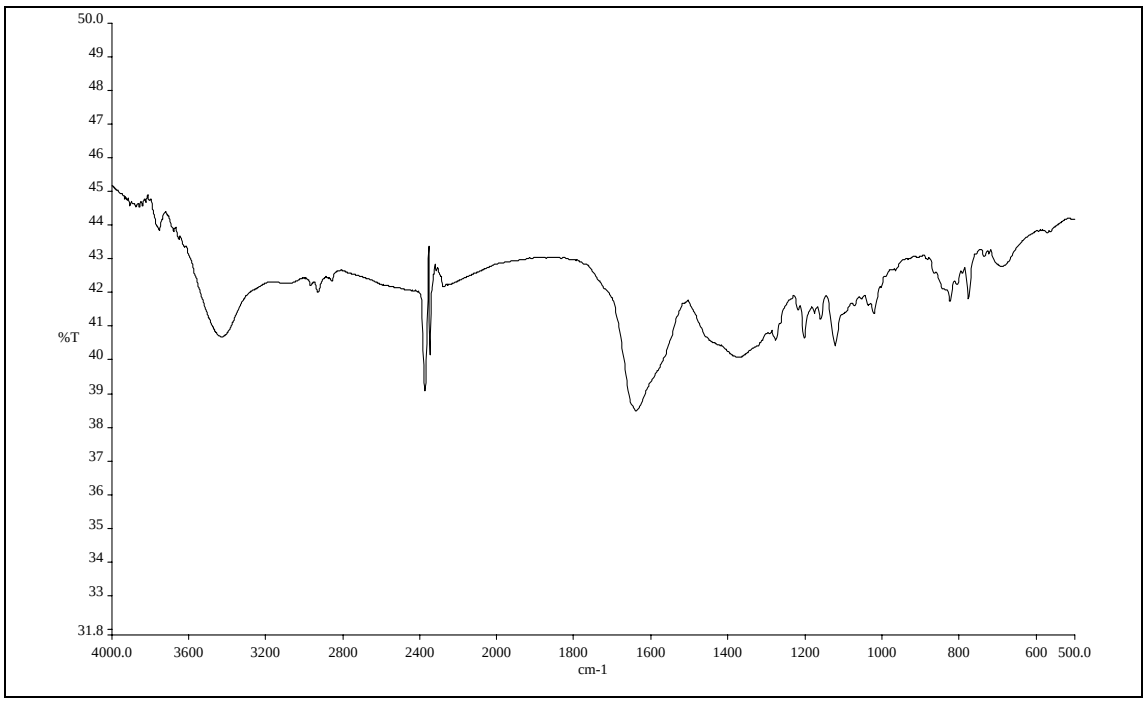

Figure 136 IR (KBr) spectrum of compound **DC16**

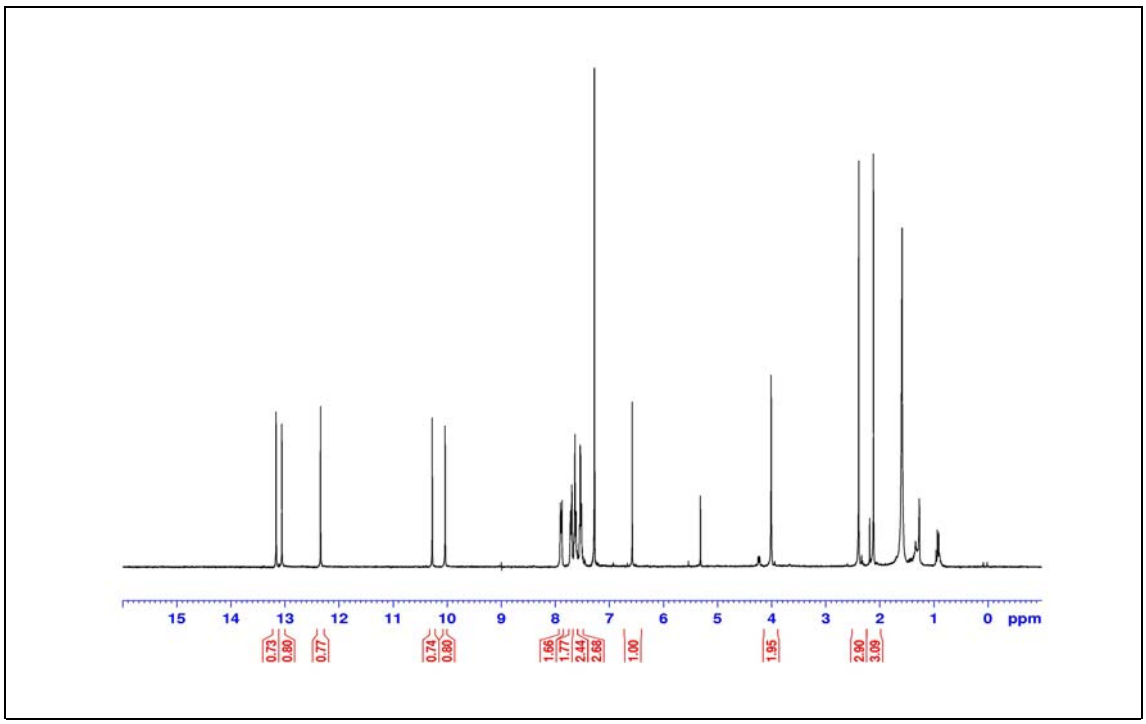

Figure 137 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC16**

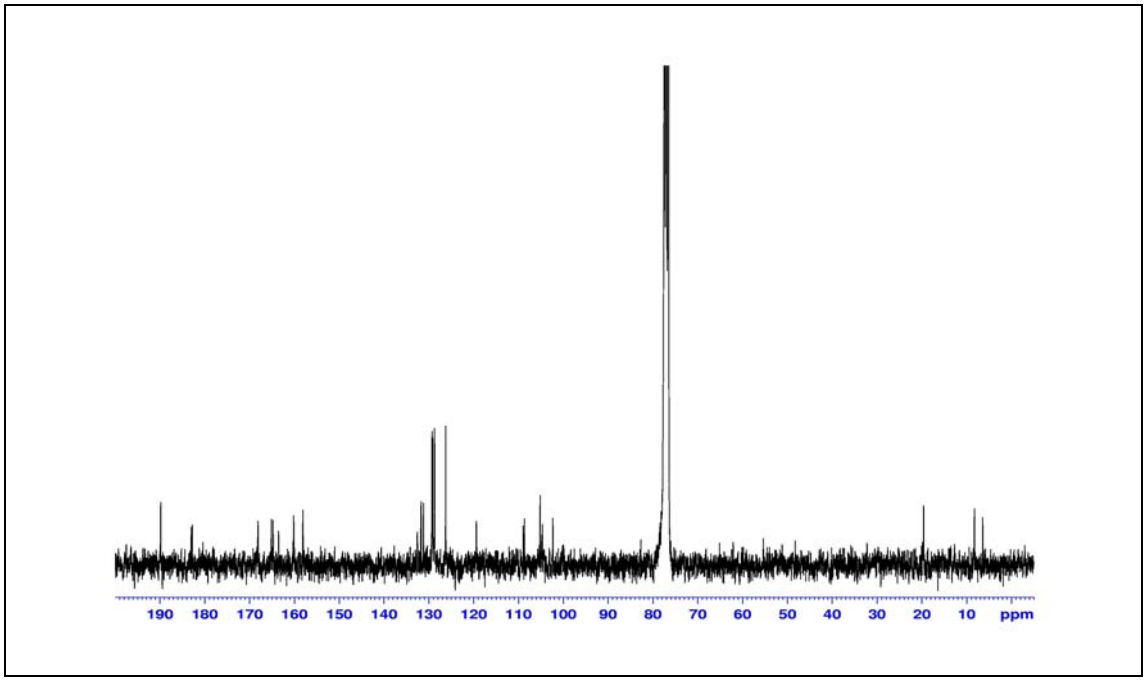

Figure 138 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC16**

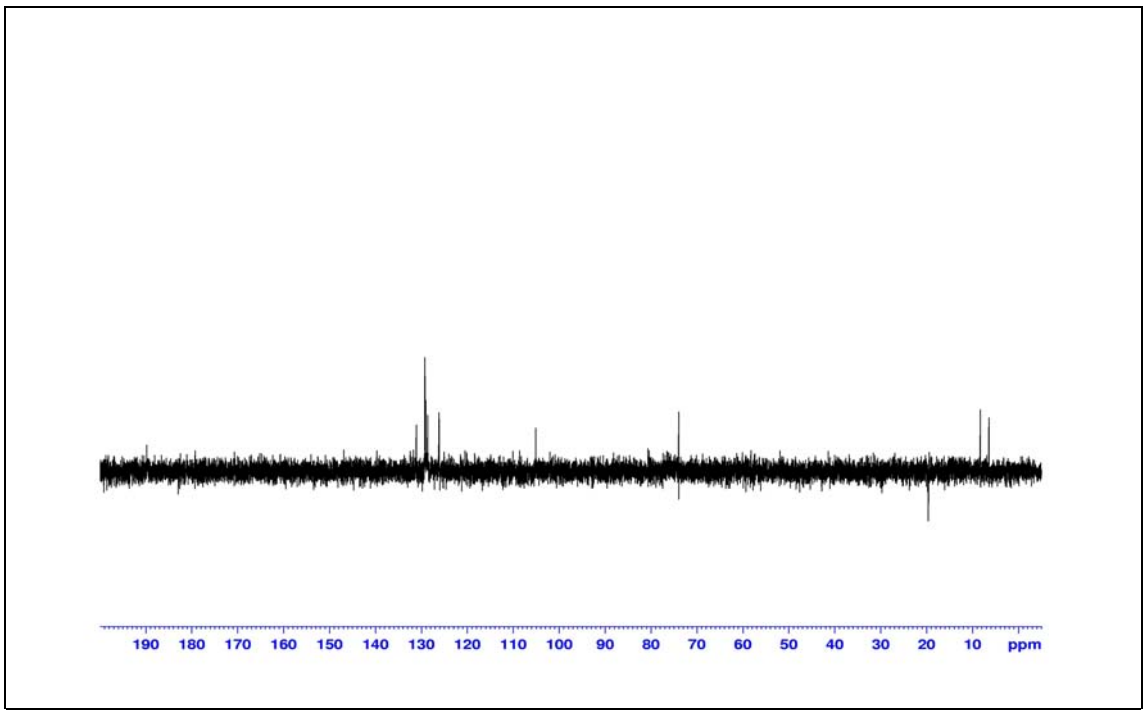

Figure 139 DEPT 135° ($CDCl_3$) of compound **DC16**

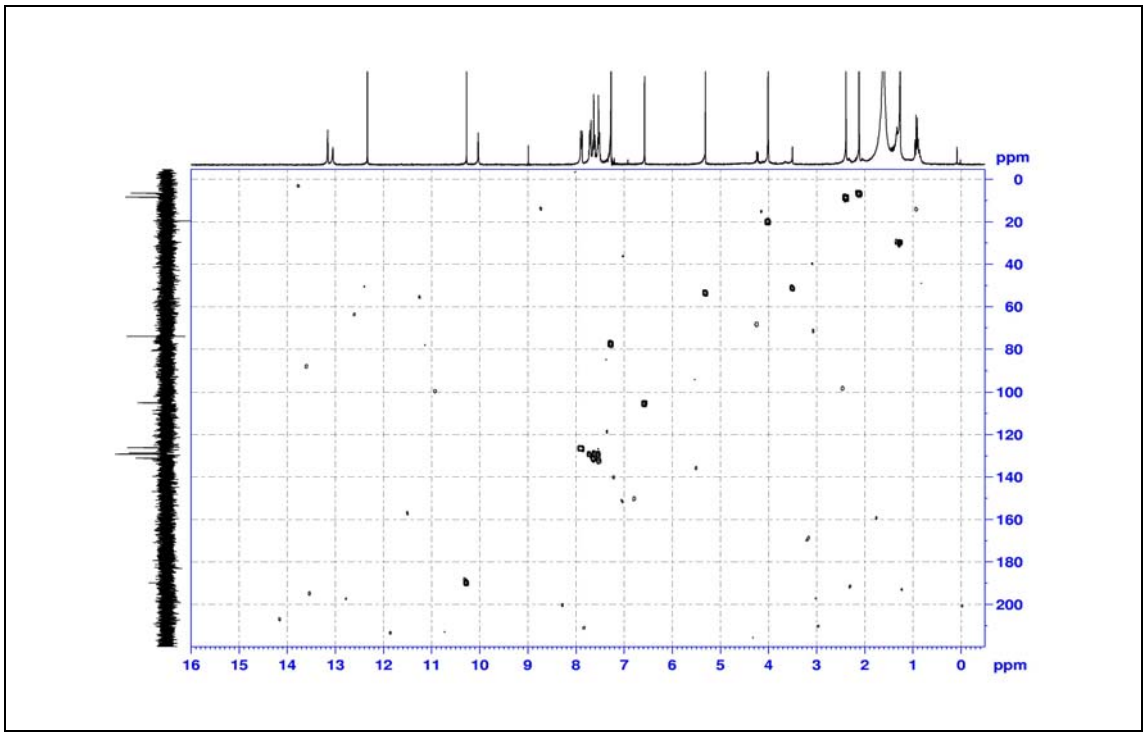

Figure 140 2D HMQC ($CDCl_3$) of compound **DC16**

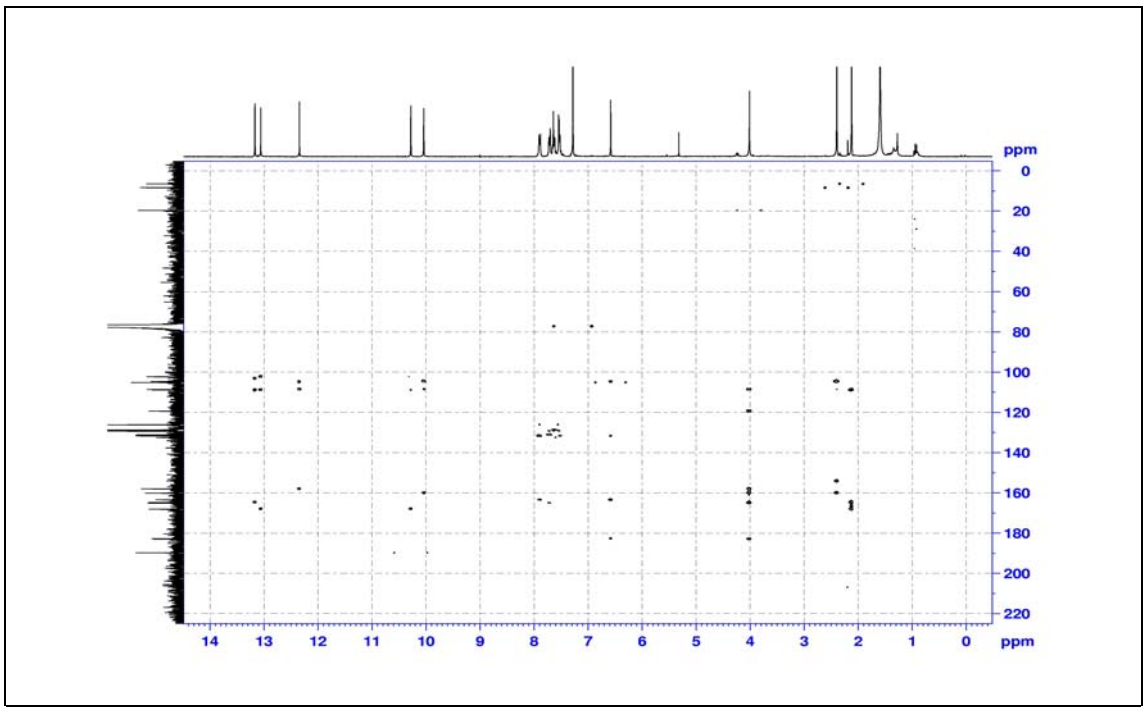

Figure 141 2D HMBC ($CDCl_3$) of compound **DC16**

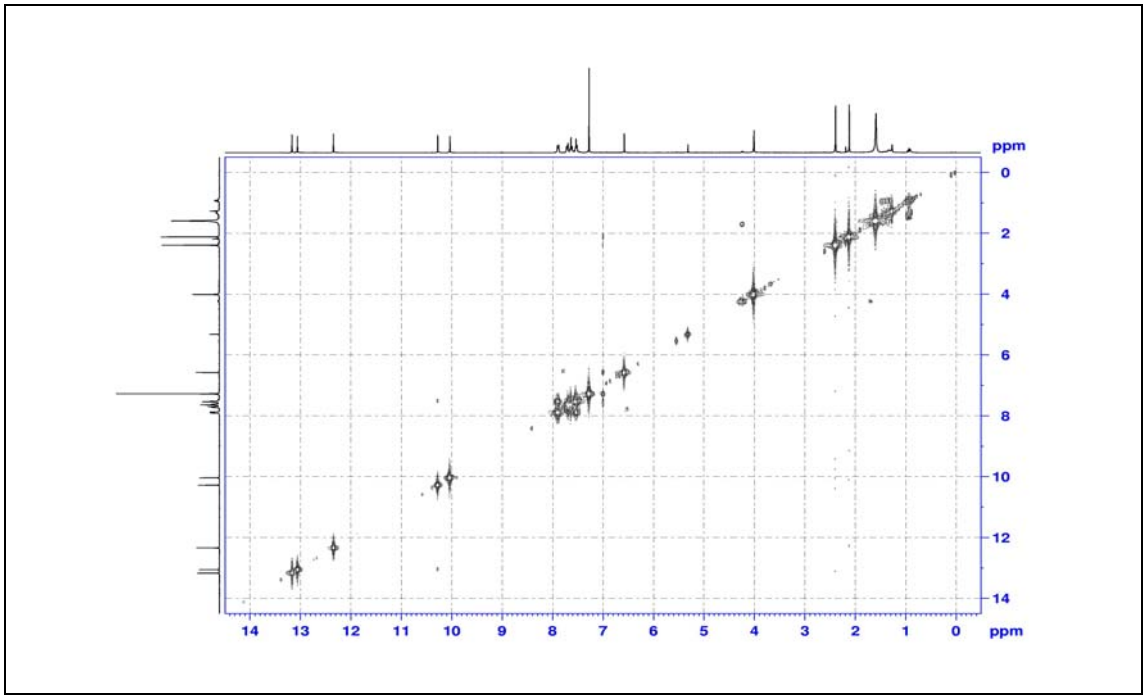

Figure 142 2D COSY ($CDCl_3$) of compound **DC16**

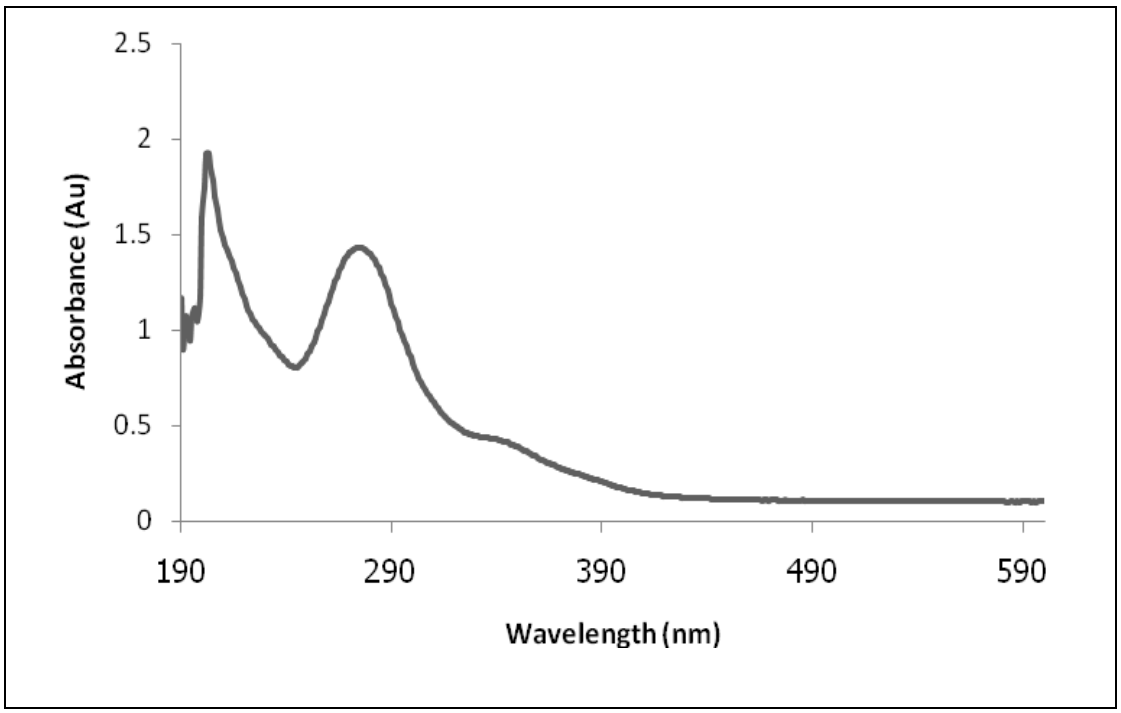

Figure 143 UV (MeOH) spectrum of compound **DC17**

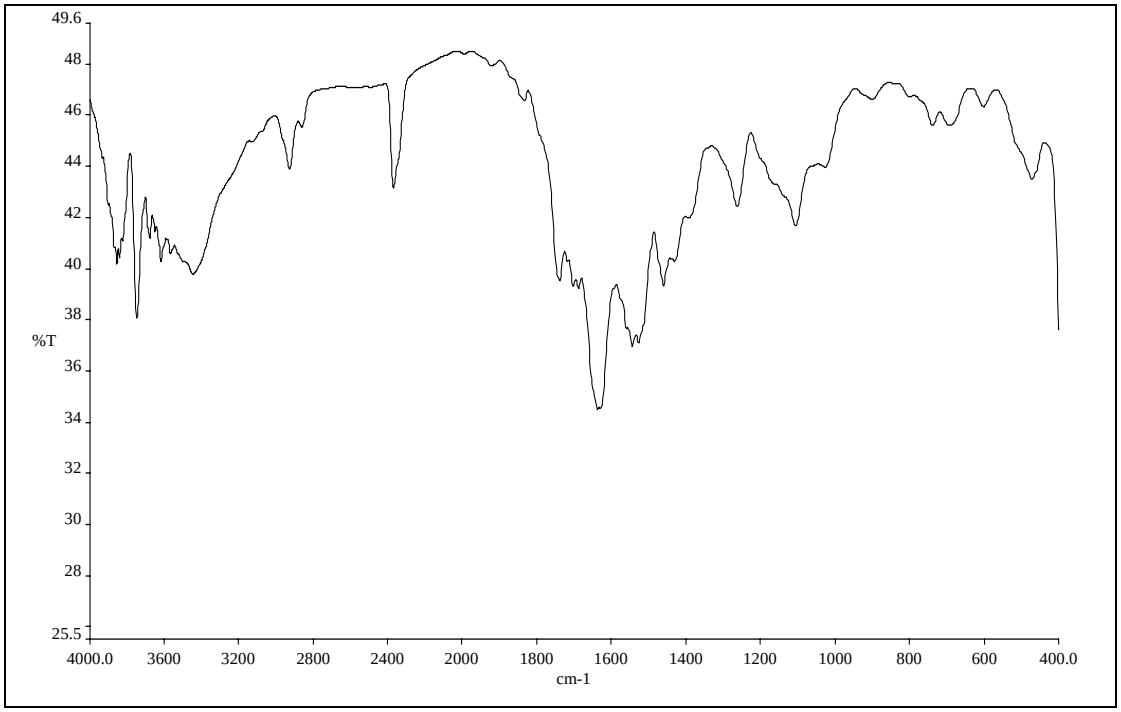

Figure 144 IR (KBr) spectrum of compound **DC17**

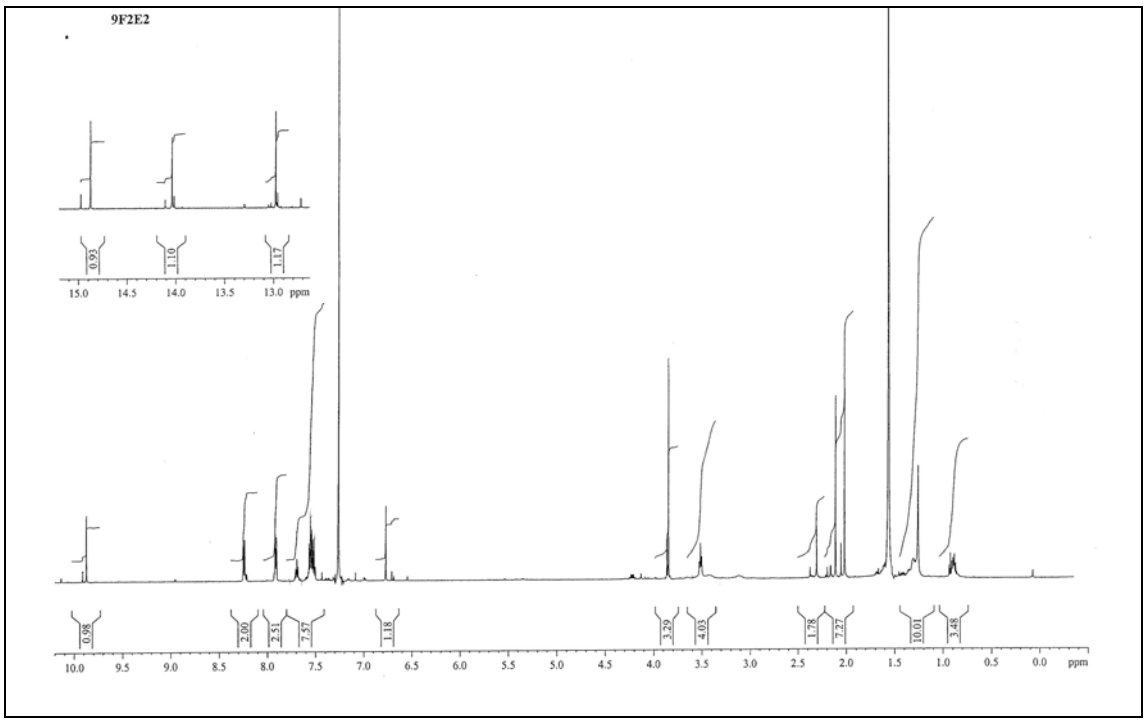

Figure 145 ^{1}H NMR (600 MHz) ($CDCl_3$) of compound **DC17**

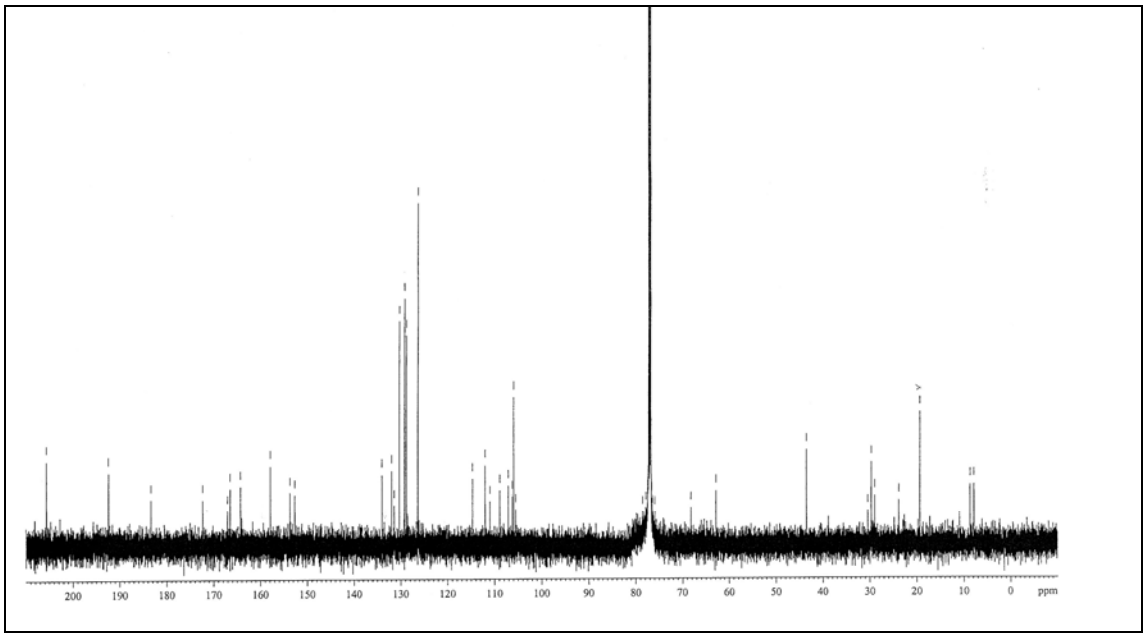

Figure 146 ^{13}C NMR (150 MHz) ($CDCl_3$) of compound **DC17**

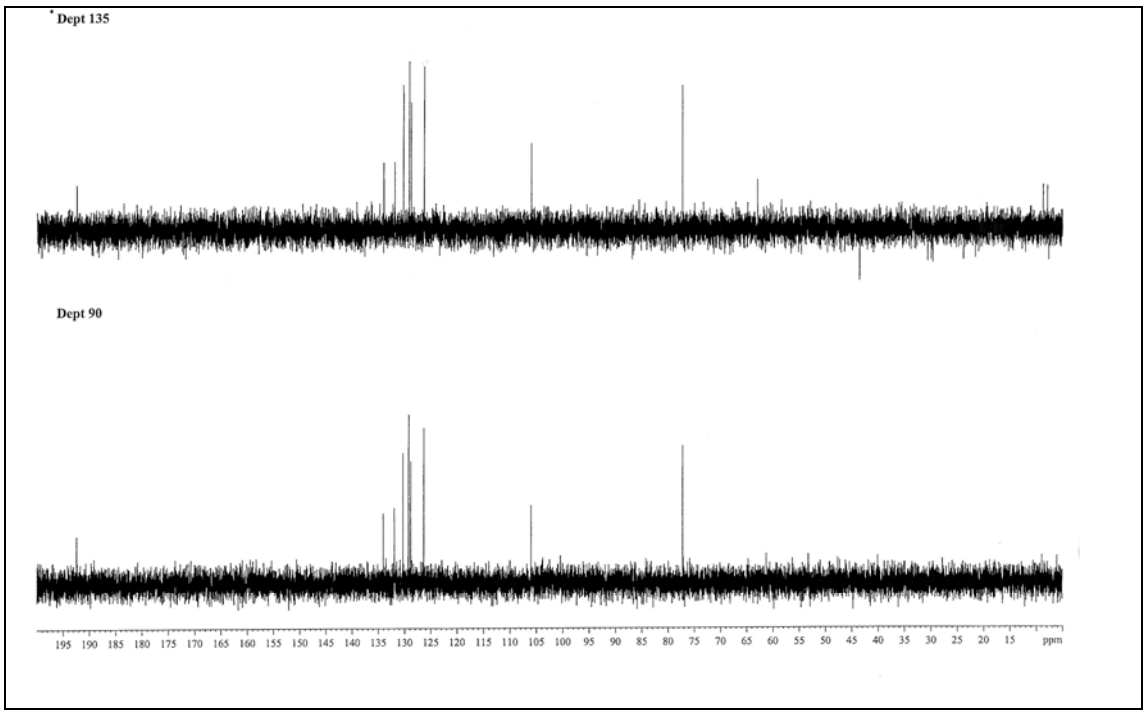

Figure 147 DEPT 135° and DEPT 90° ($CDCl_3$) of compound **DC17**

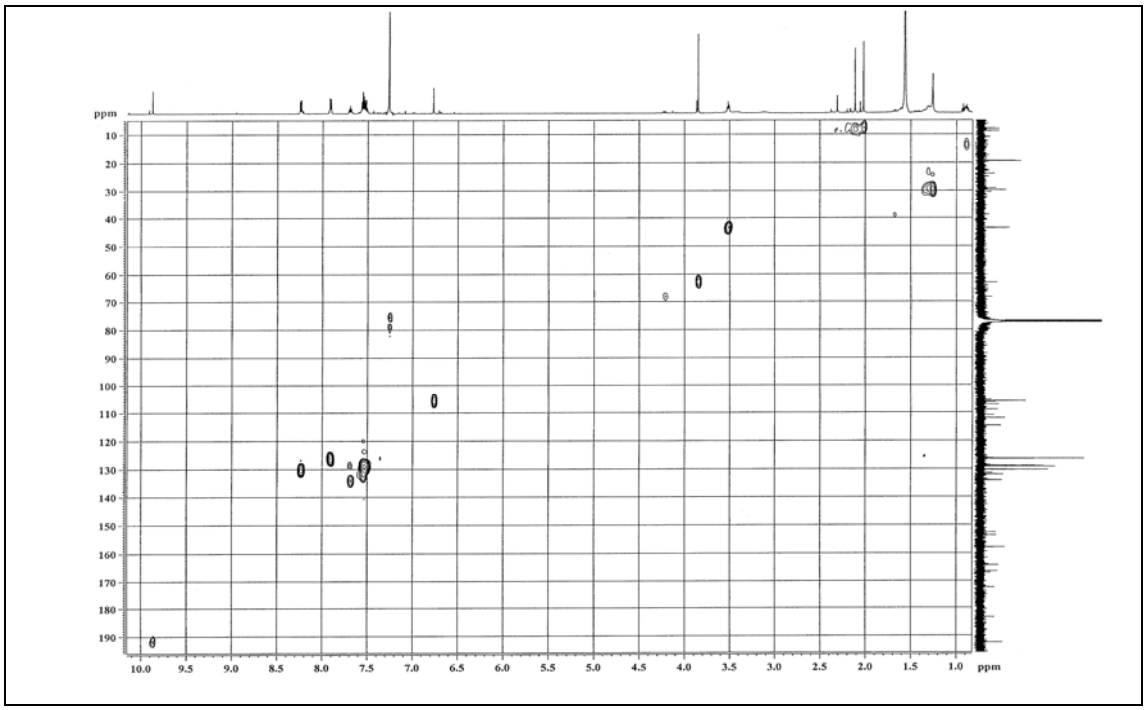

Figure 148 2D HMQC ($CDCl_3$) of compound **DC17**

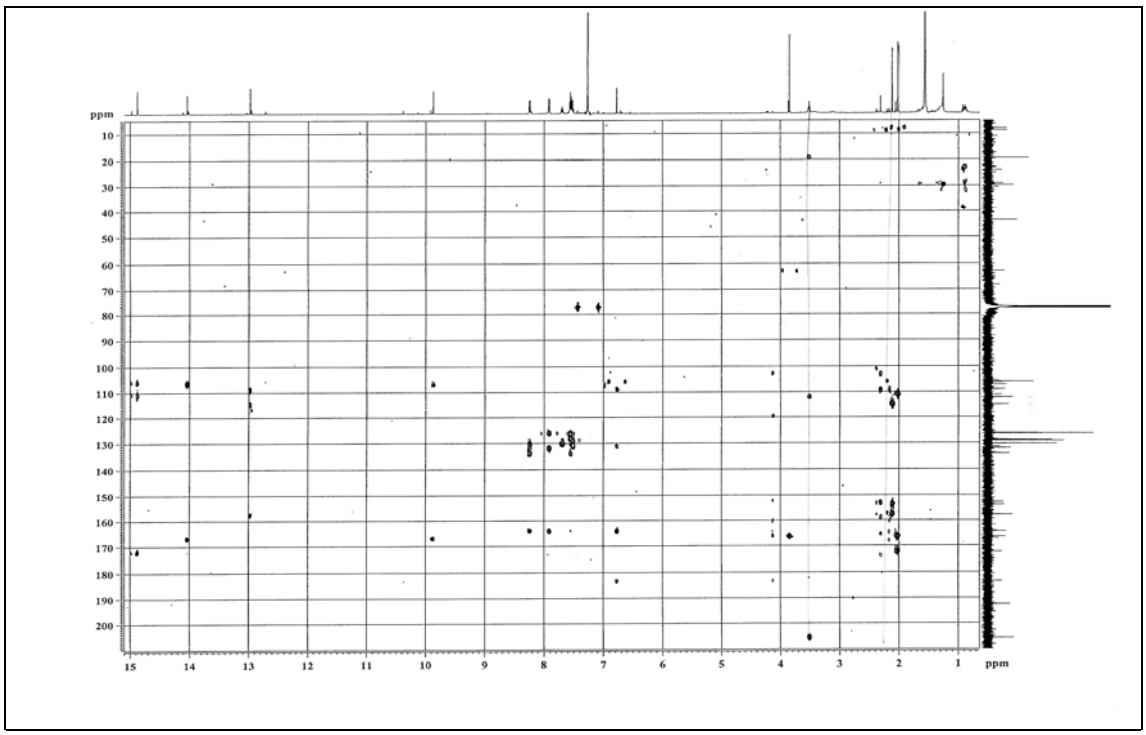

Figure 149 2D HMBC ($CDCl_3$) of compound **DC17**

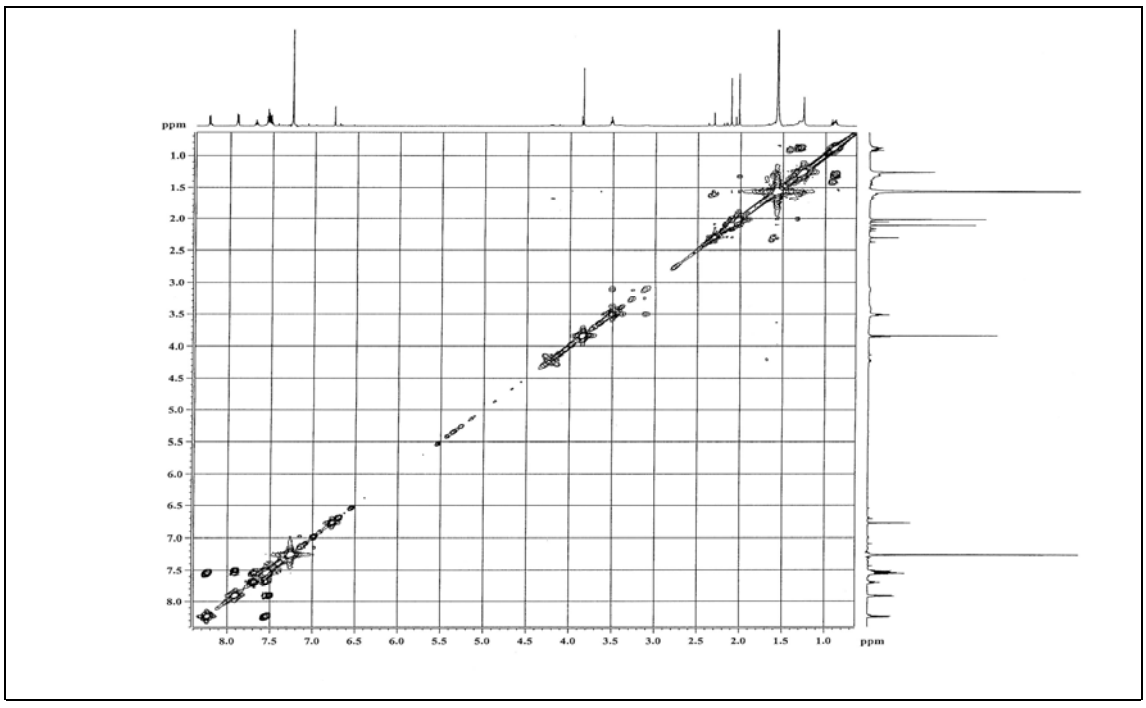

Figure 150 2D COSY ($CDCl_3$) of compound **DC17**

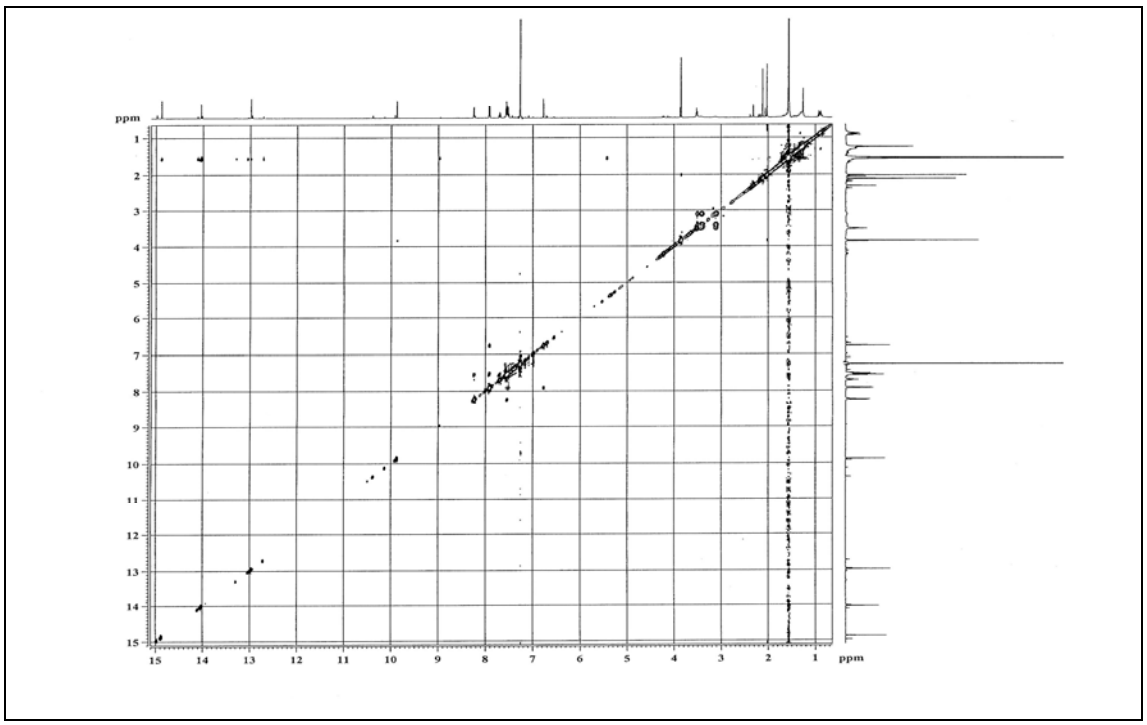

Figure 151 2D NOESY ($CDCl_3$) of compound **DC17**

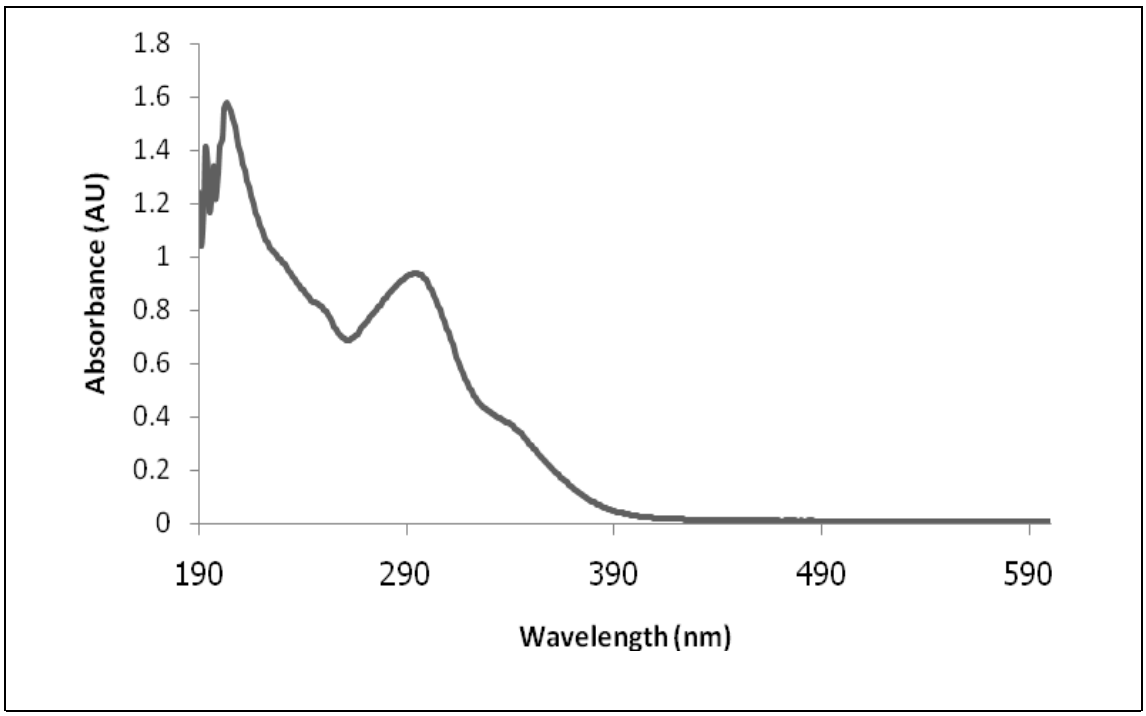

Figure 152 UV (MeOH) spectrum of compound **DC18**

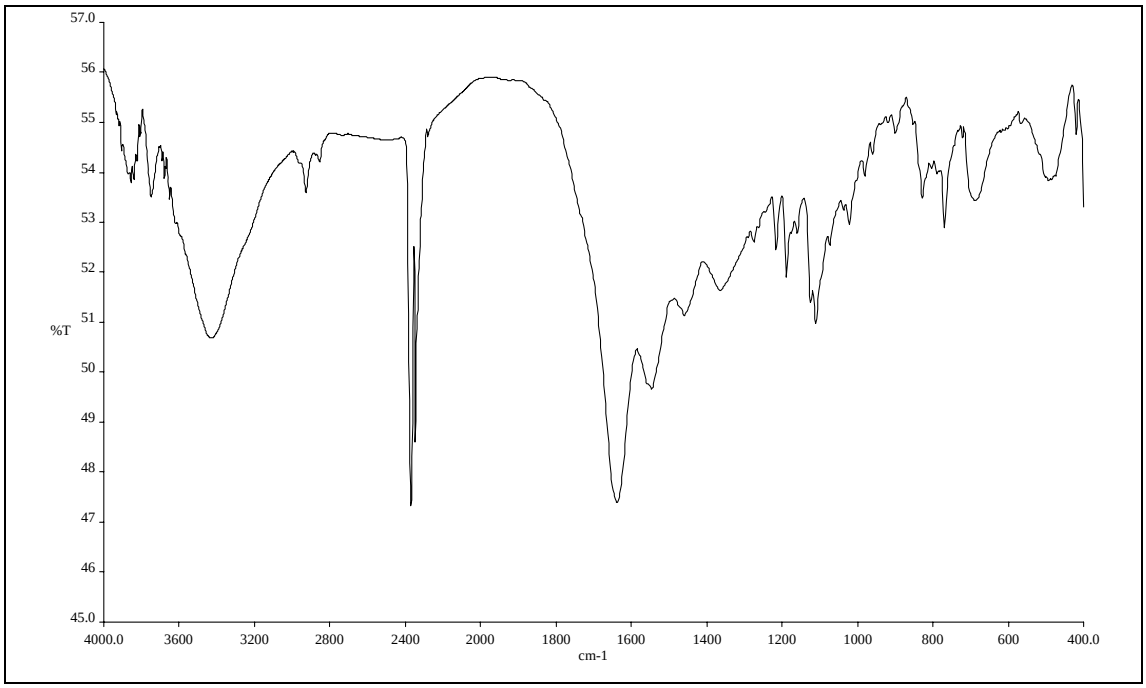

Figure 153 IR (KBr) spectrum of compound **DC18**

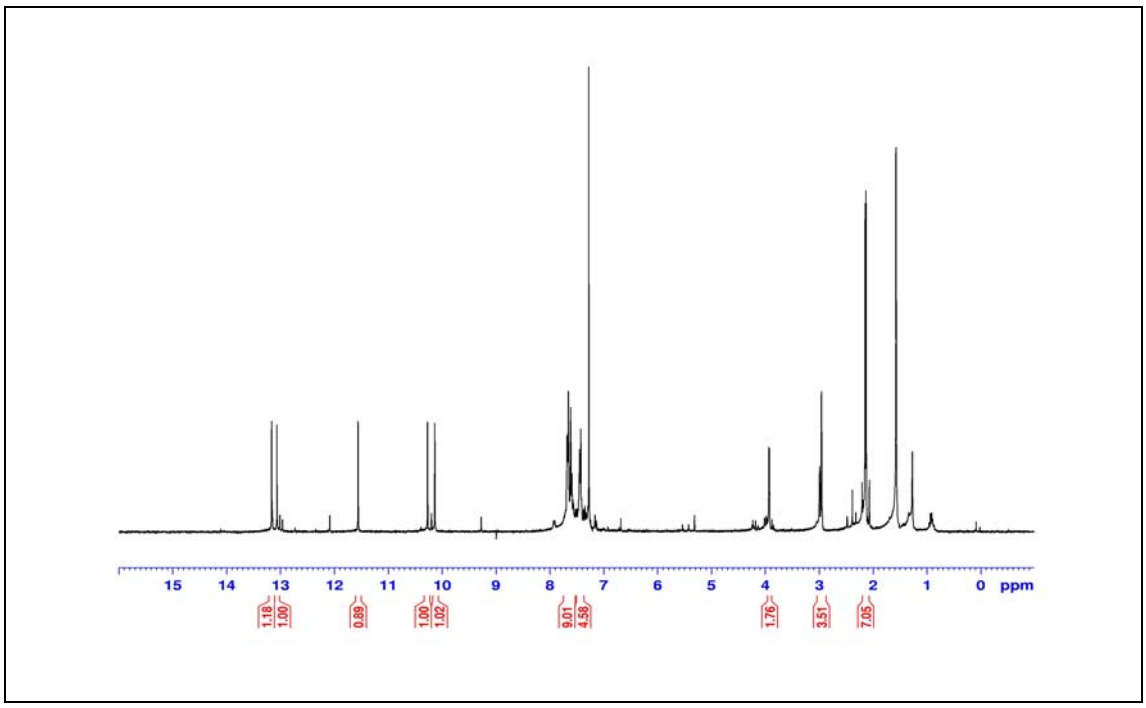

Figure 154 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **DC18**

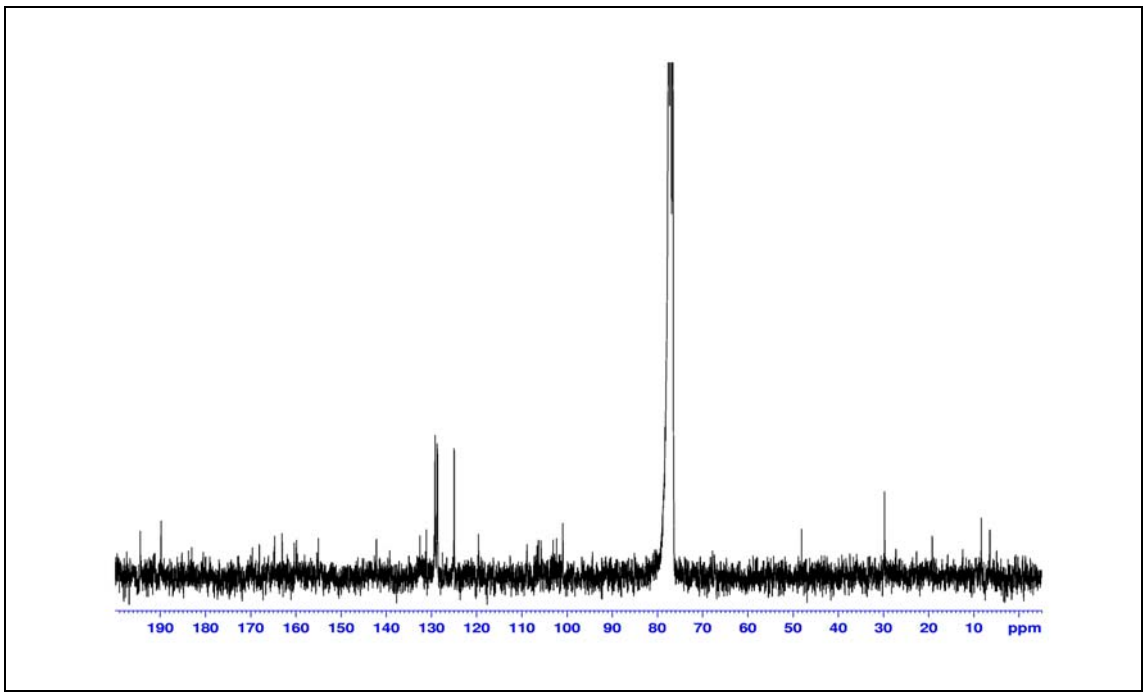

Figure 155 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **DC18**

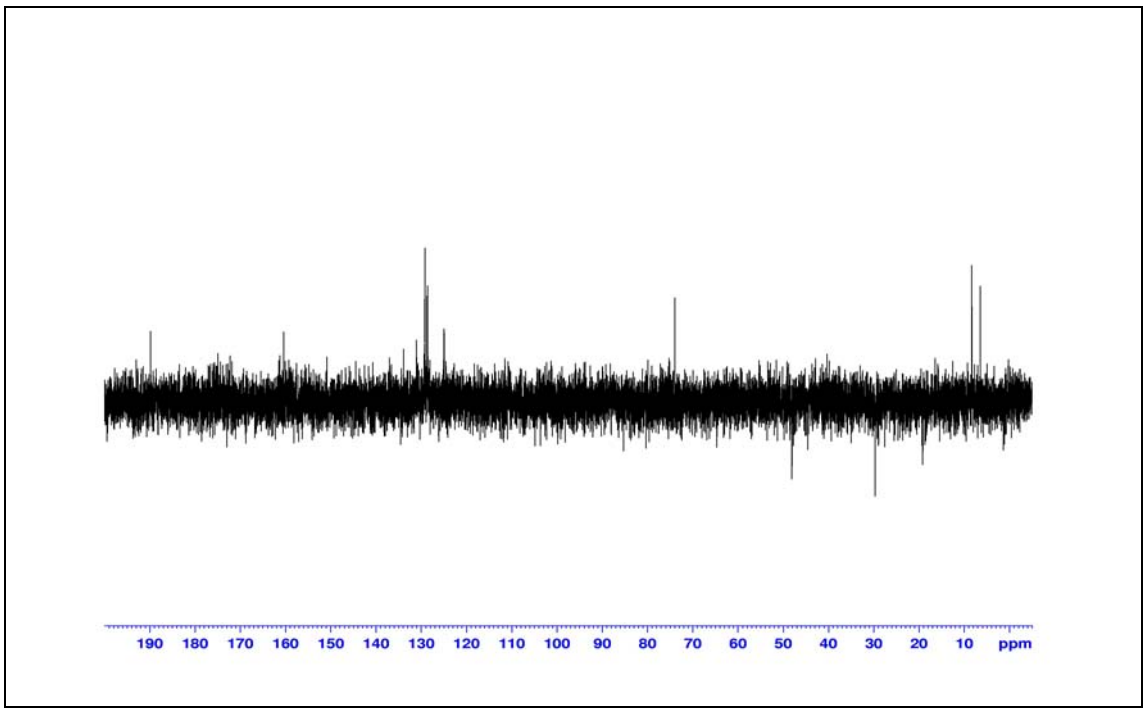

Figure 156 DEPT 135° ($CDCl_3$) of compound **DC18**

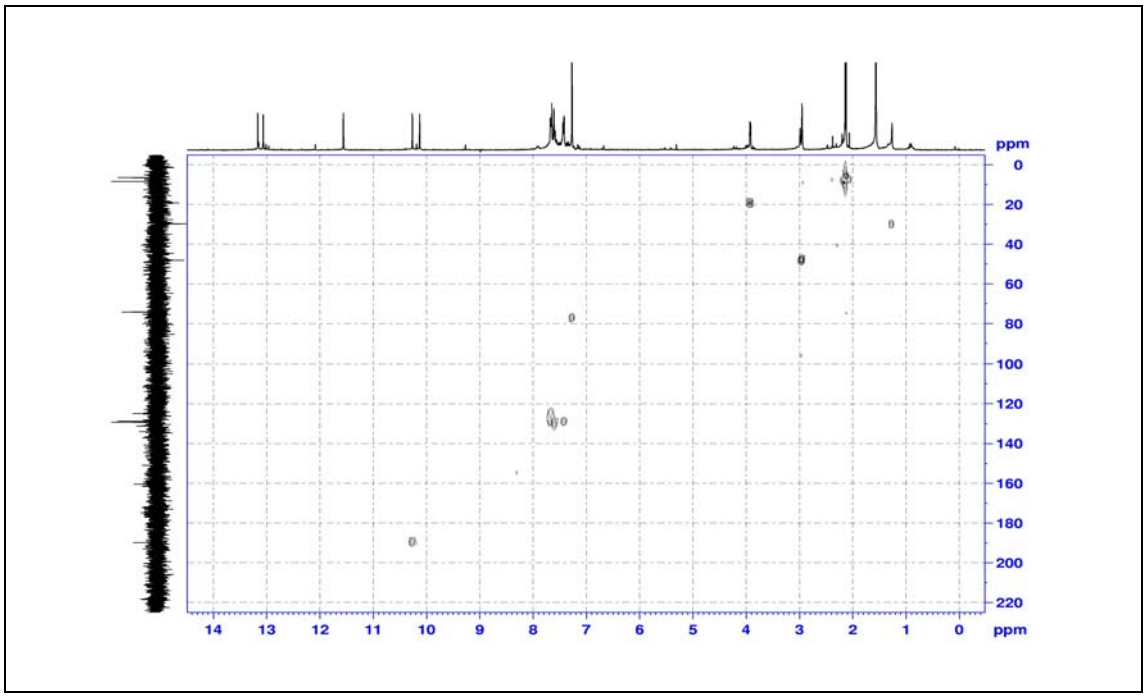

Figure 157 2D HMQC ($CDCl_3$) of compound **DC18**

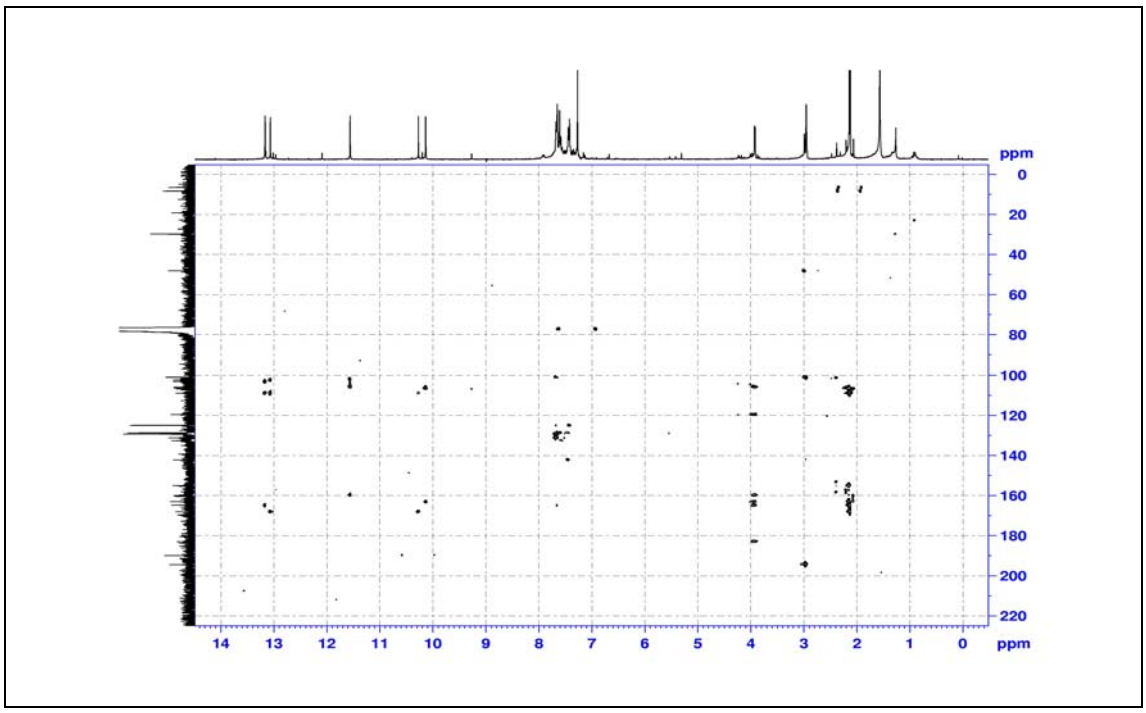

Figure 158 2D HMBC ($CDCl_3$) of compound **DC18**

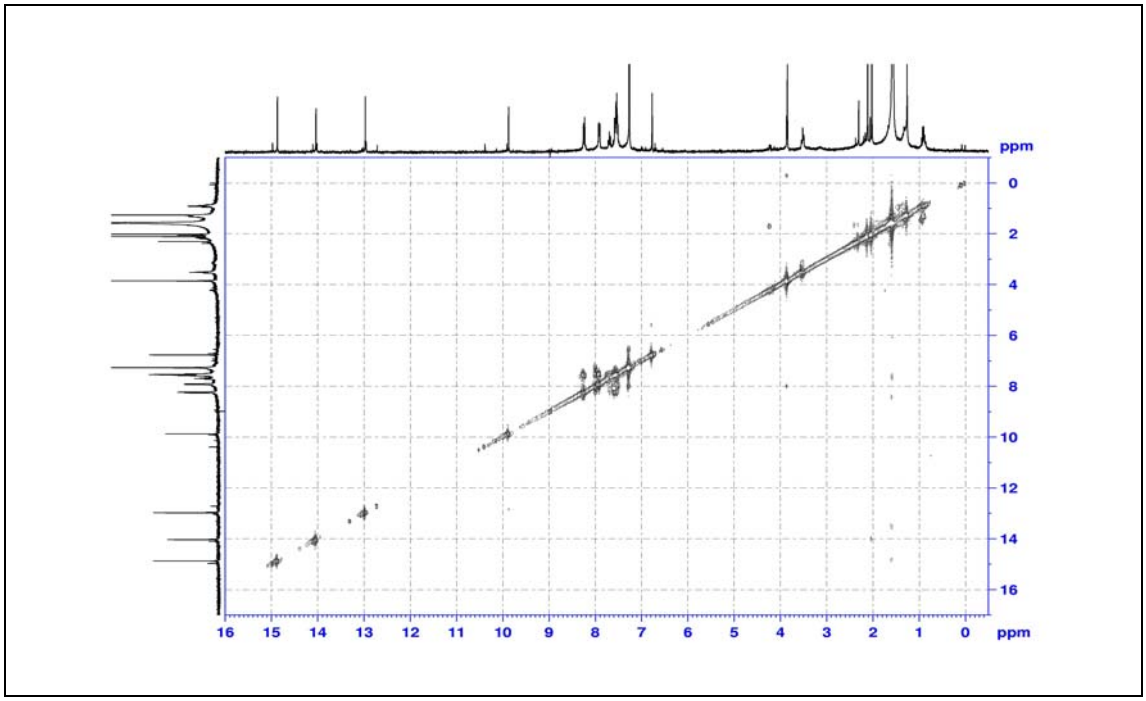

Figure 159 2D COSY ($CDCl_3$) of compound **DC18**

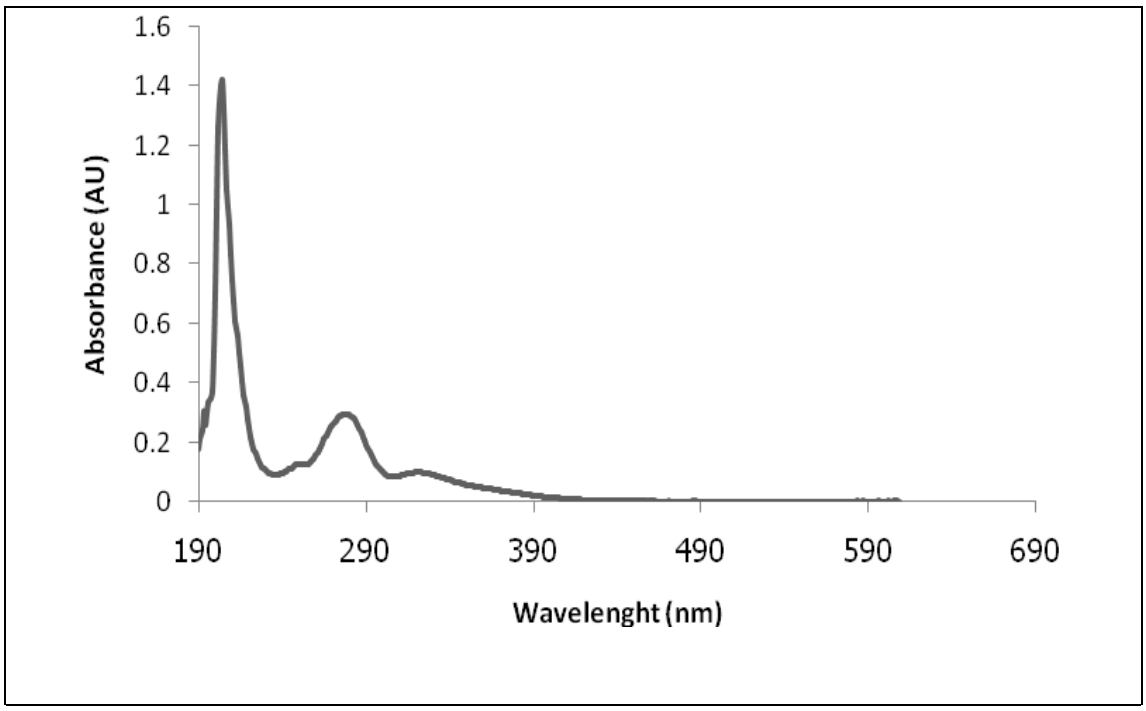

Figure 160 UV (MeOH) spectrum of compound **DC19**

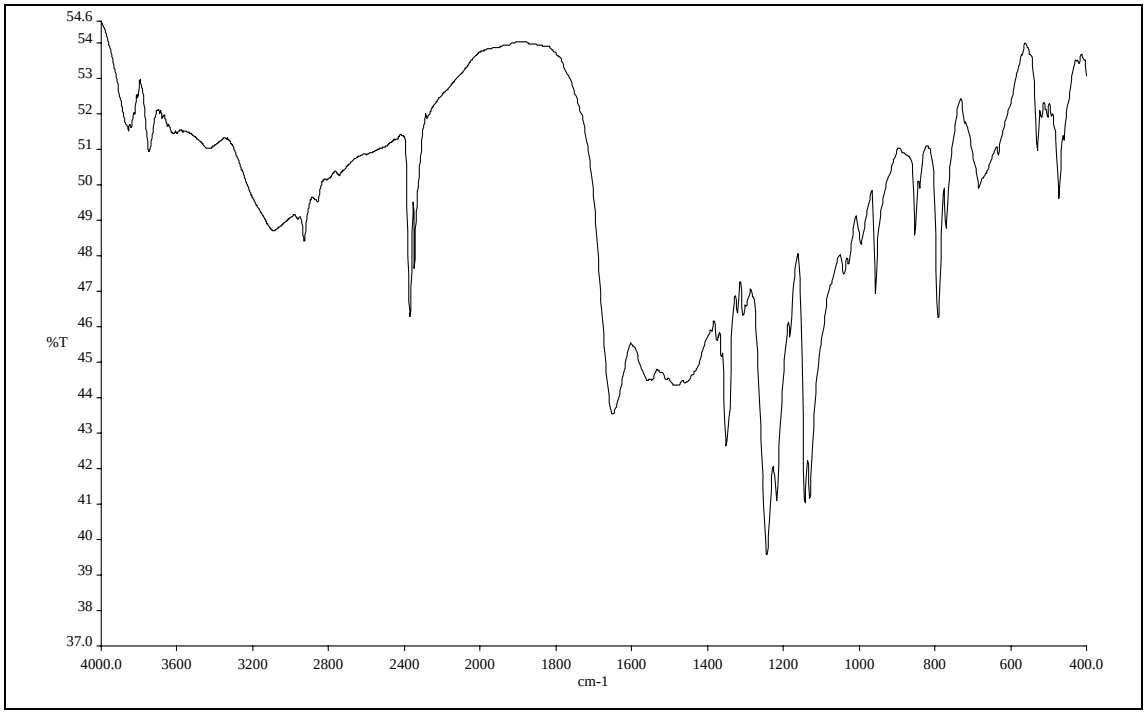

Figure 161 IR (KBr) spectrum of compound **DC19**

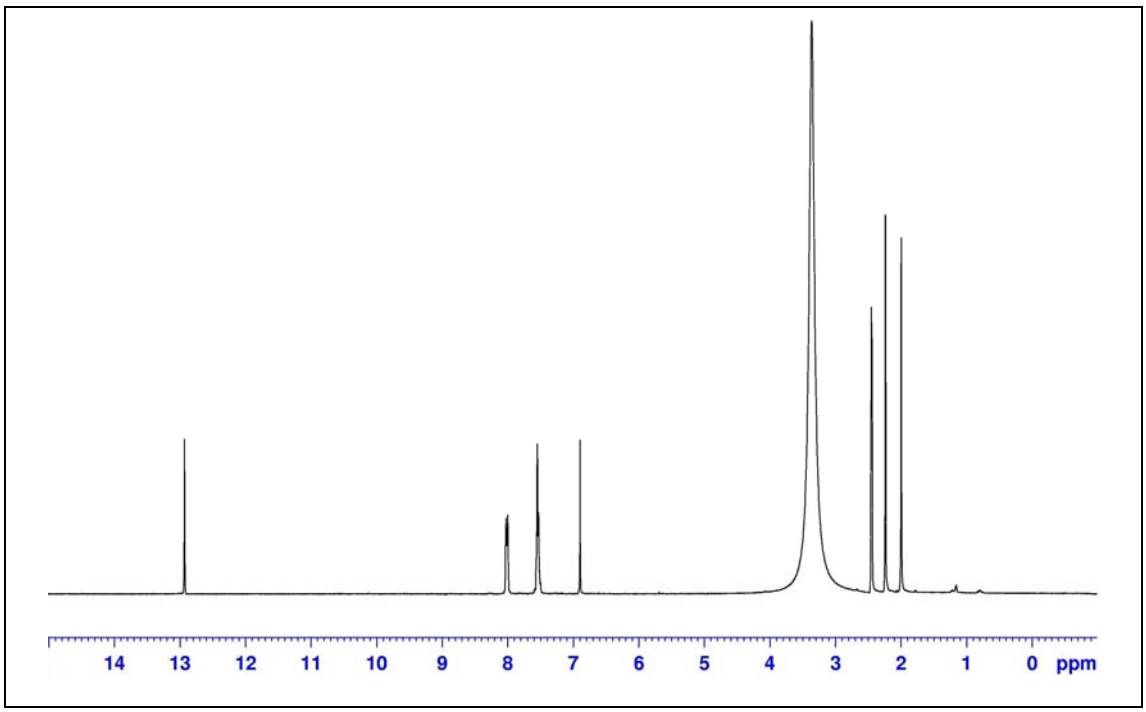

Figure 162 ^{1}H NMR (300 MHz) (DMSO-d_6) of compound **DC19**

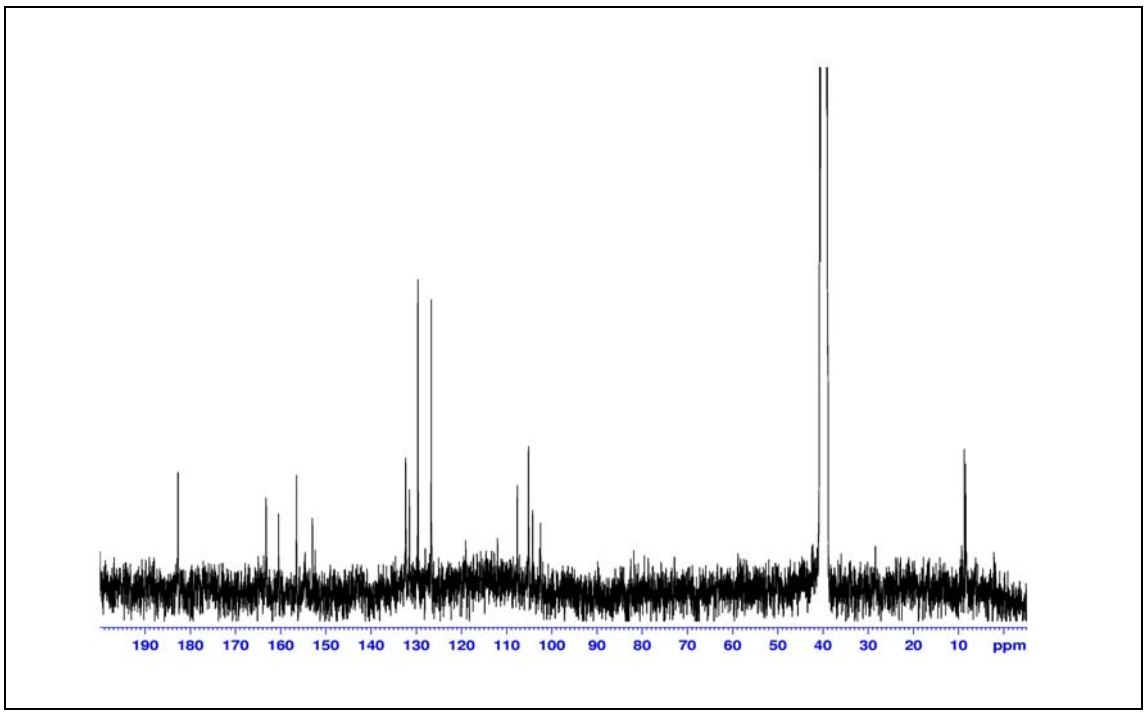

Figure 163 ^{13}C NMR (75 MHz) (DMSO-d_6) of compound **DC19**

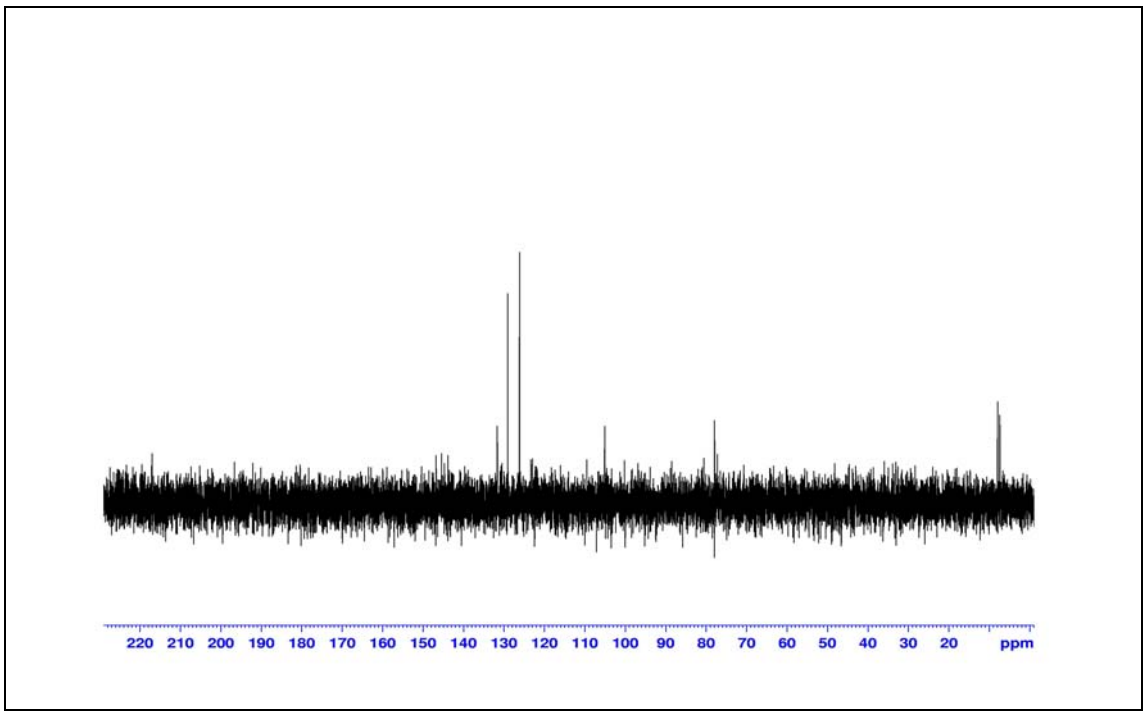

Figure 164 DEPT 135° (DMSO-d_6) of compound **DC19**

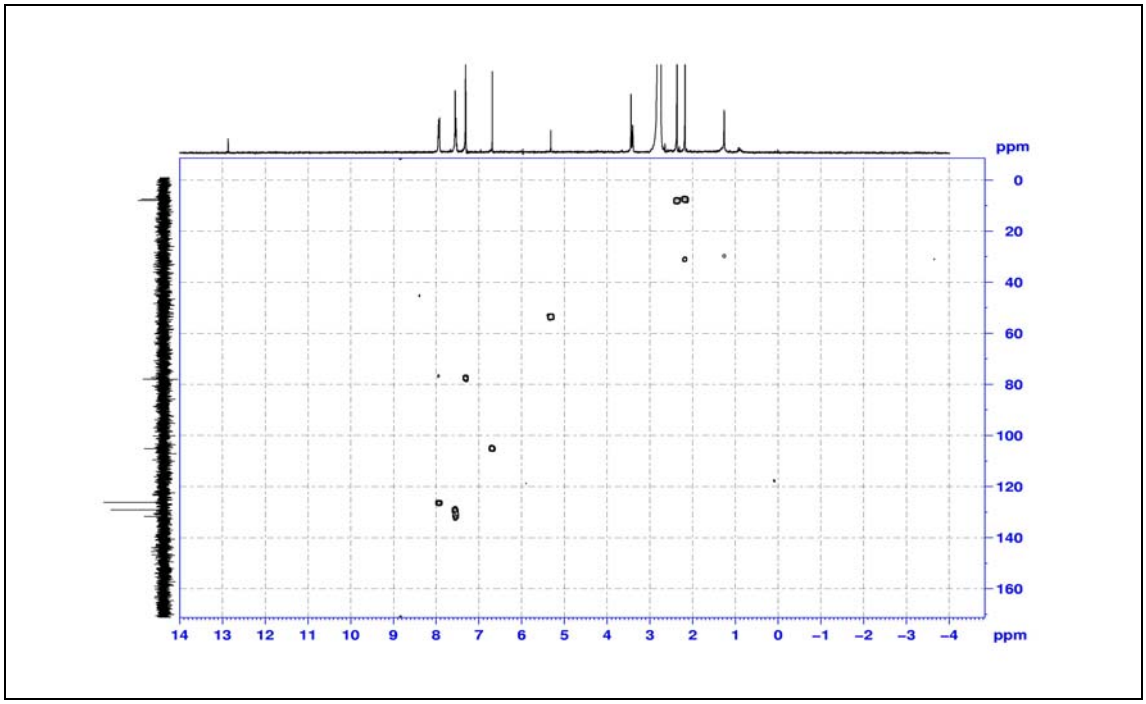

Figure 165 2D HMQC (DMSO-d_6) of compound **DC19**

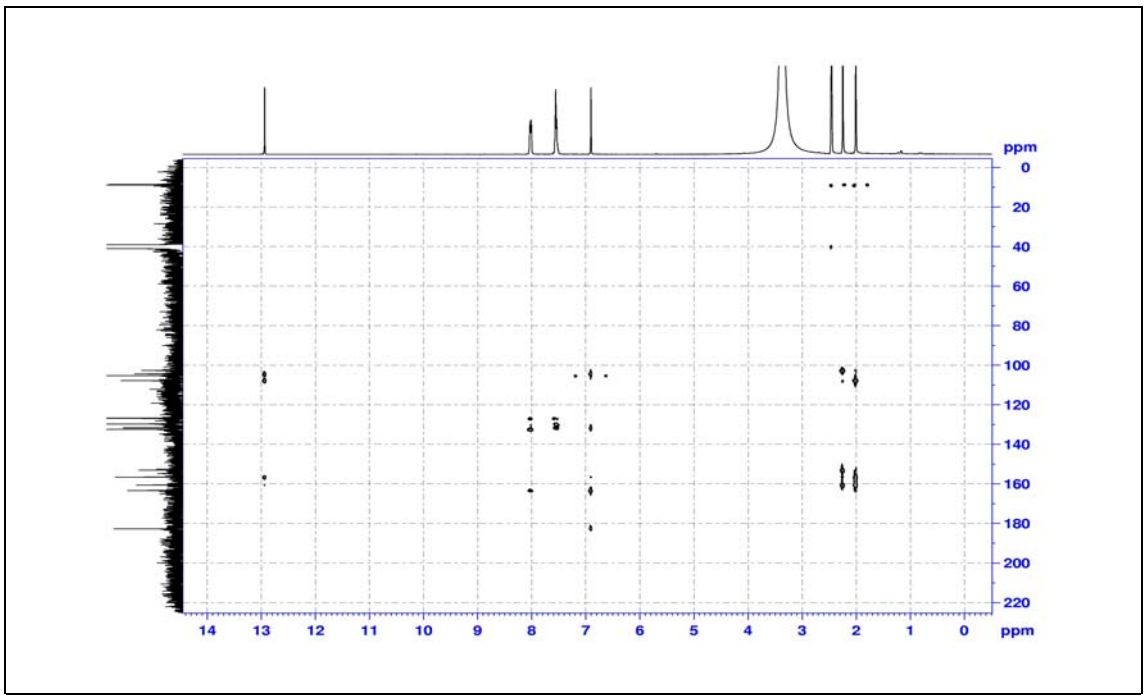

Figure 166 2D HMBC (DMSO-d_6) of compound **DC19**

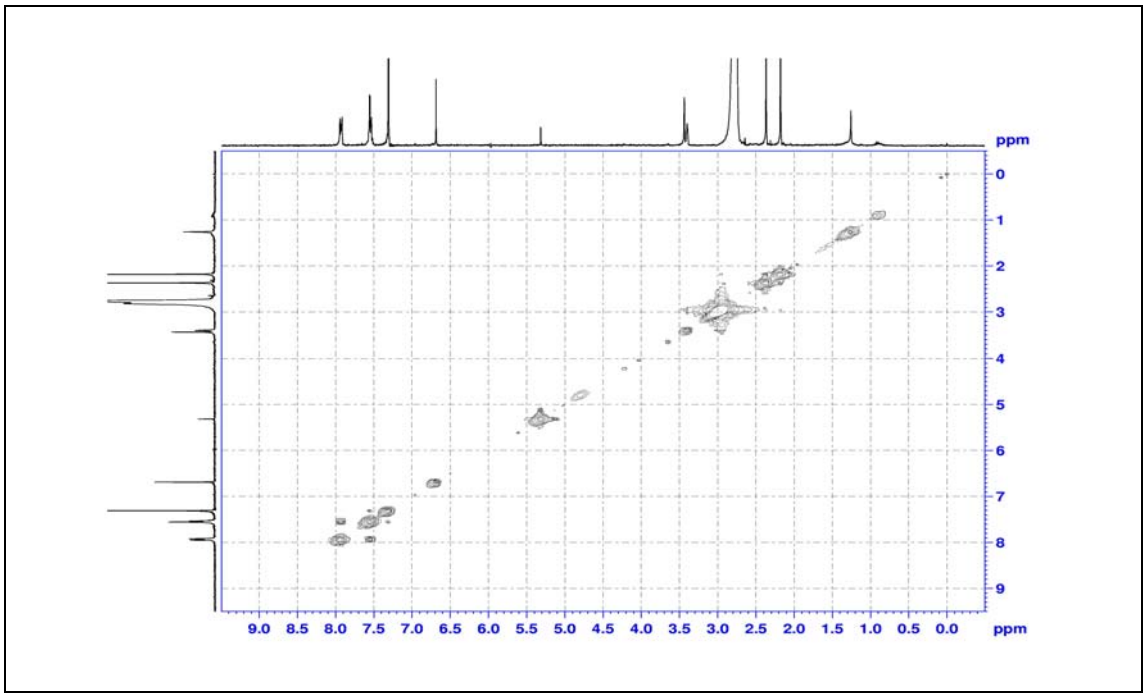

Figure 167 2D COSY (DMSO-d_6) of compound **DC19**

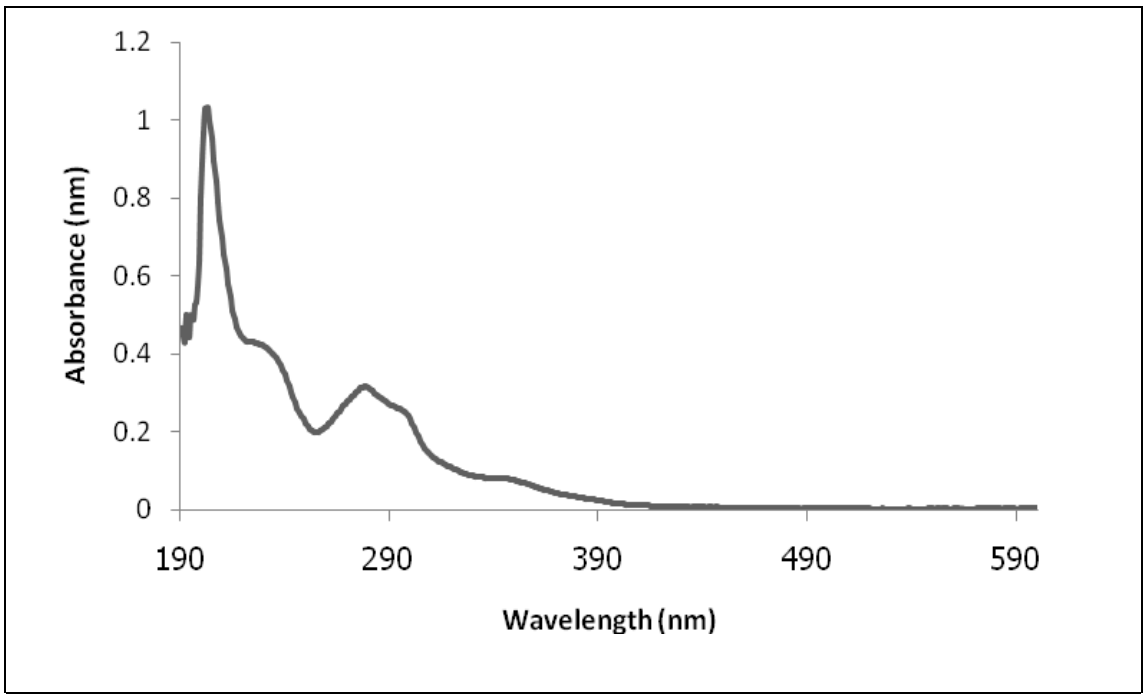

Figure 168 UV (MeOH) spectrum of compound **DC20**

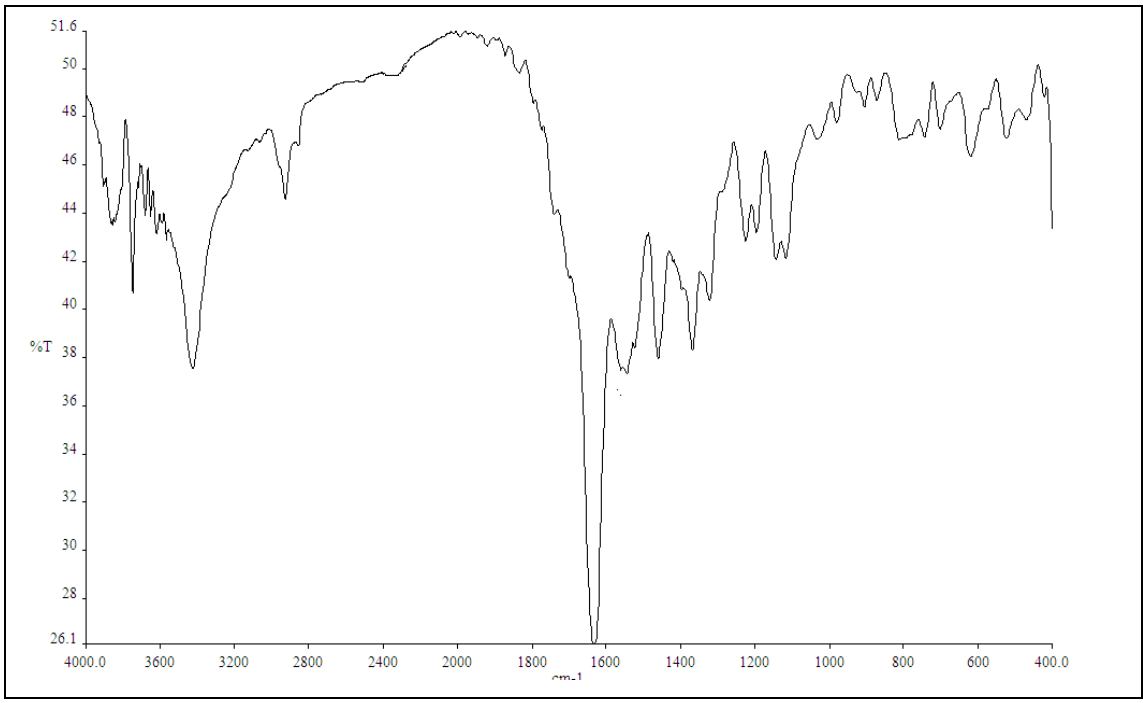

Figure 169 IR (KBr) spectrum of compound **DC20**

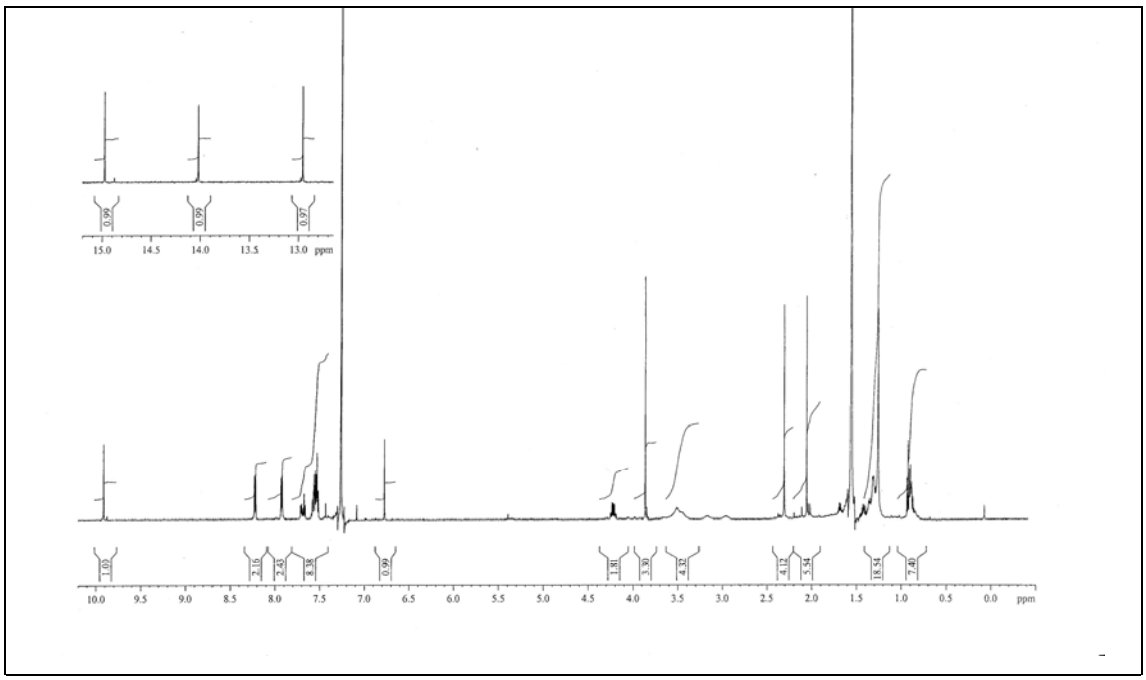

Figure 170 ^{1}H NMR (600 MHz) ($CDCl_3$) of compound **DC20**

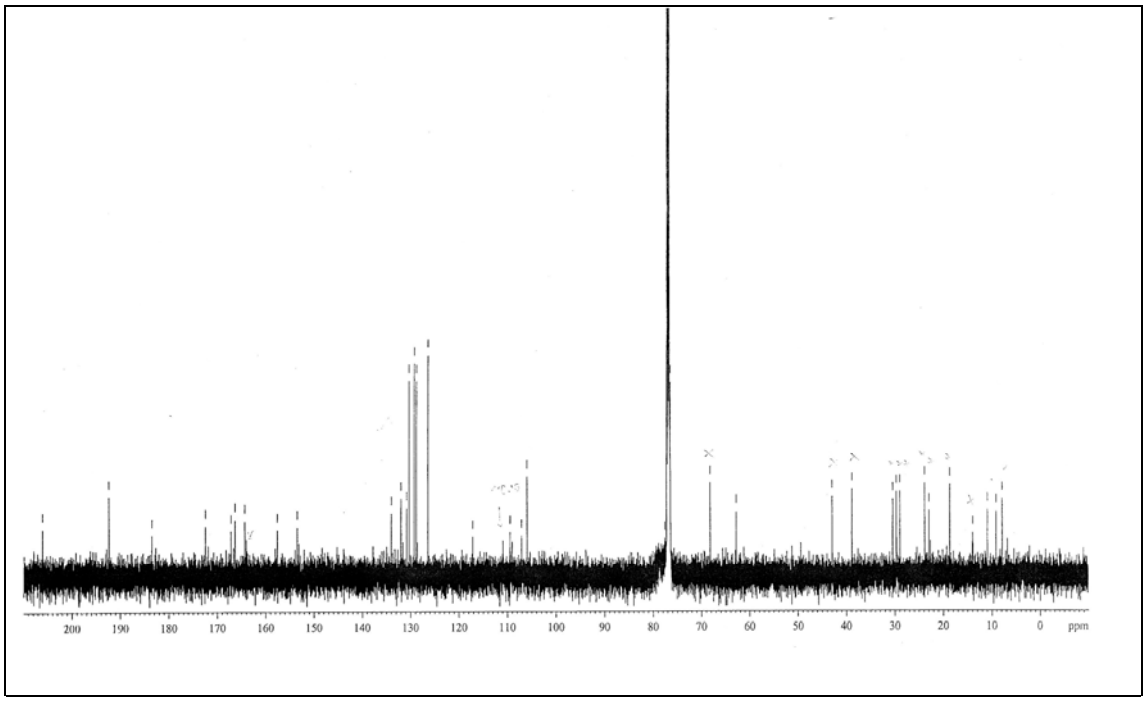

Figure 171 ^{13}C NMR (150 MHz) ($CDCl_3$) of compound **DC20**

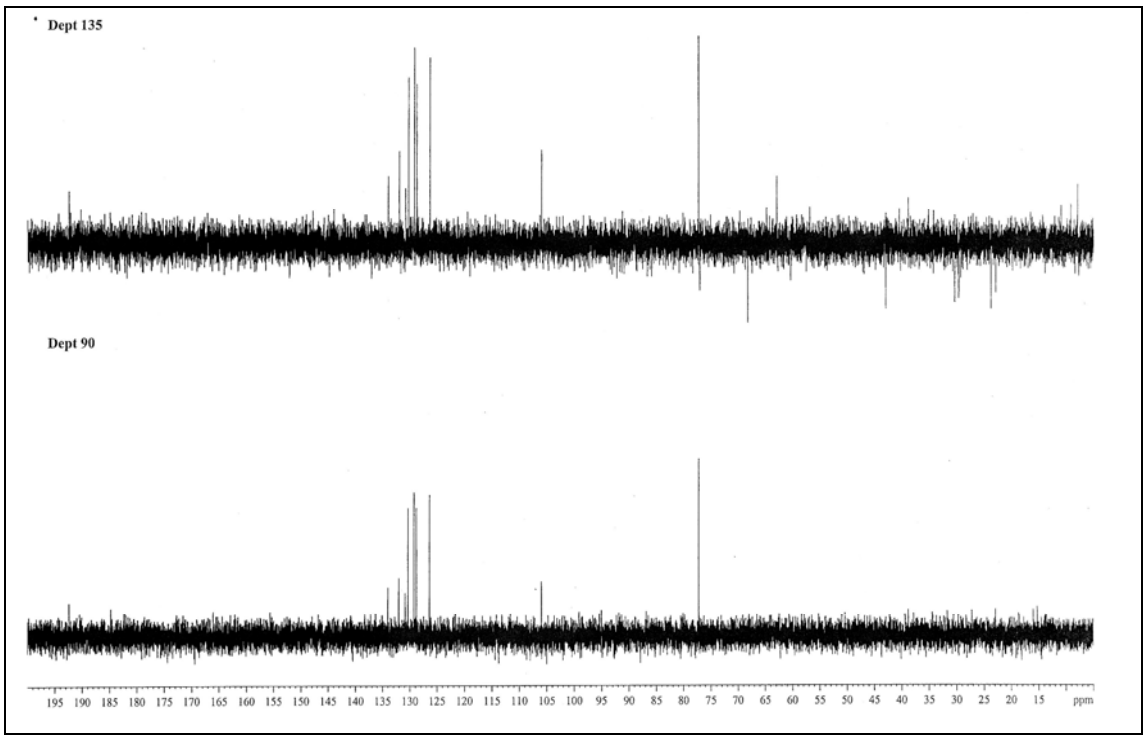

Figure 172 DEPT 135° and DEPT 90° ($CDCl_3$) of compound **DC20**

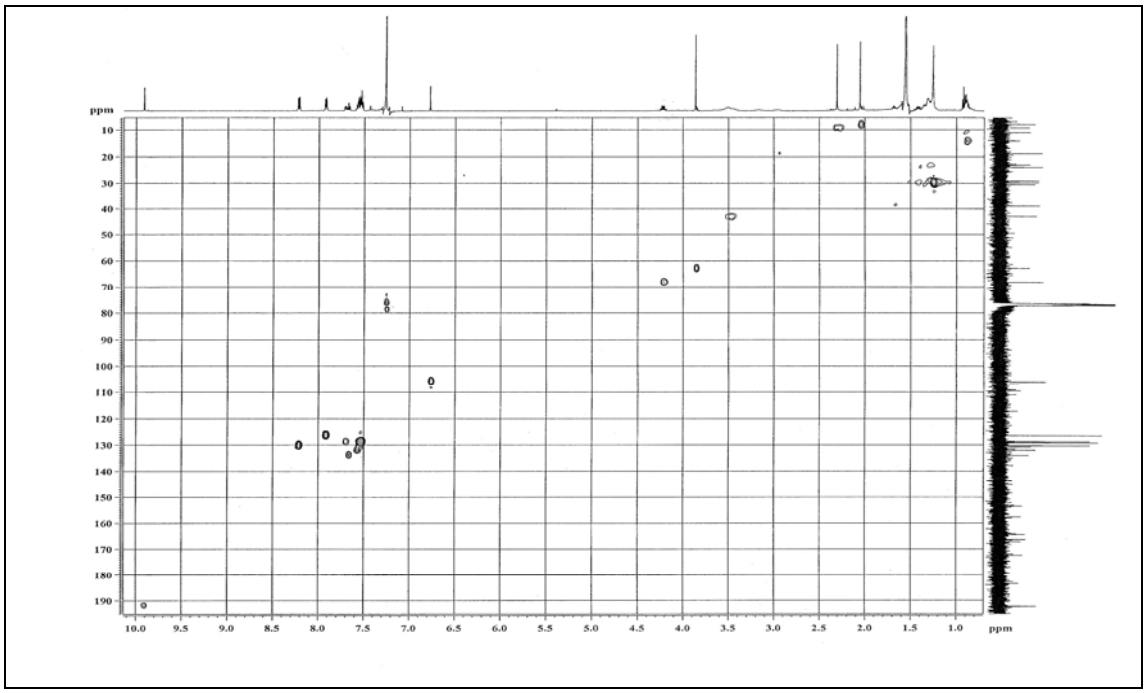

Figure 173 2D HMQC ($CDCl_3$) of compound **DC20**

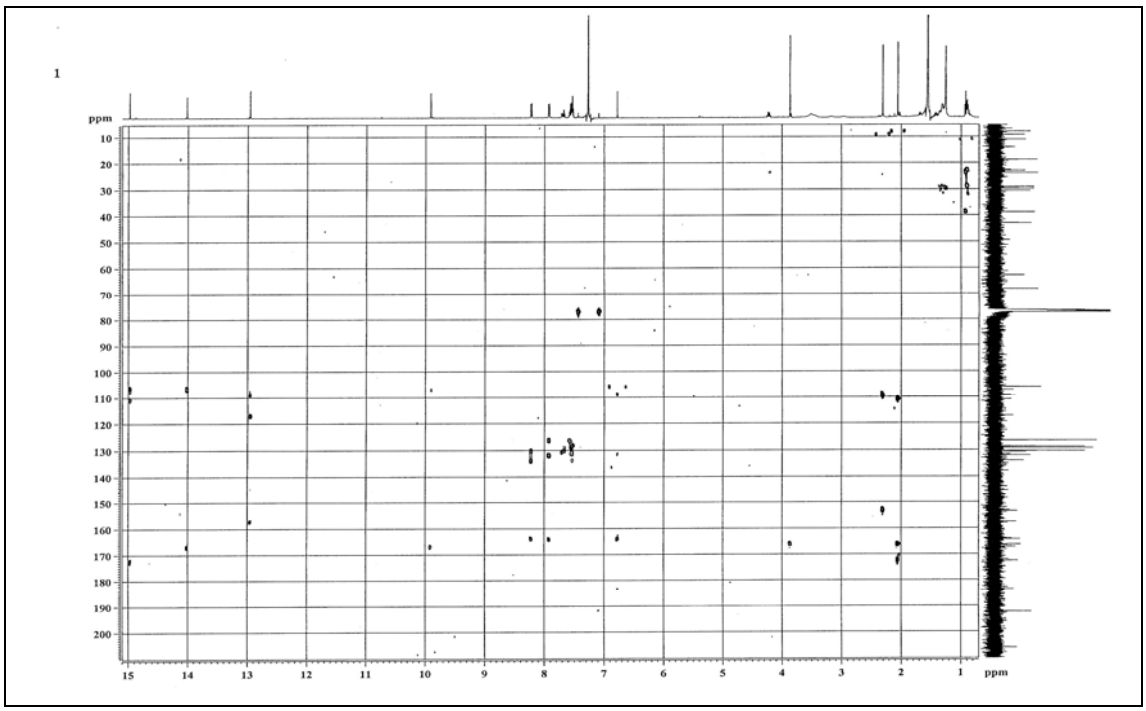

Figure 174 2D HMBC ($CDCl_3$) of compound **DC20**

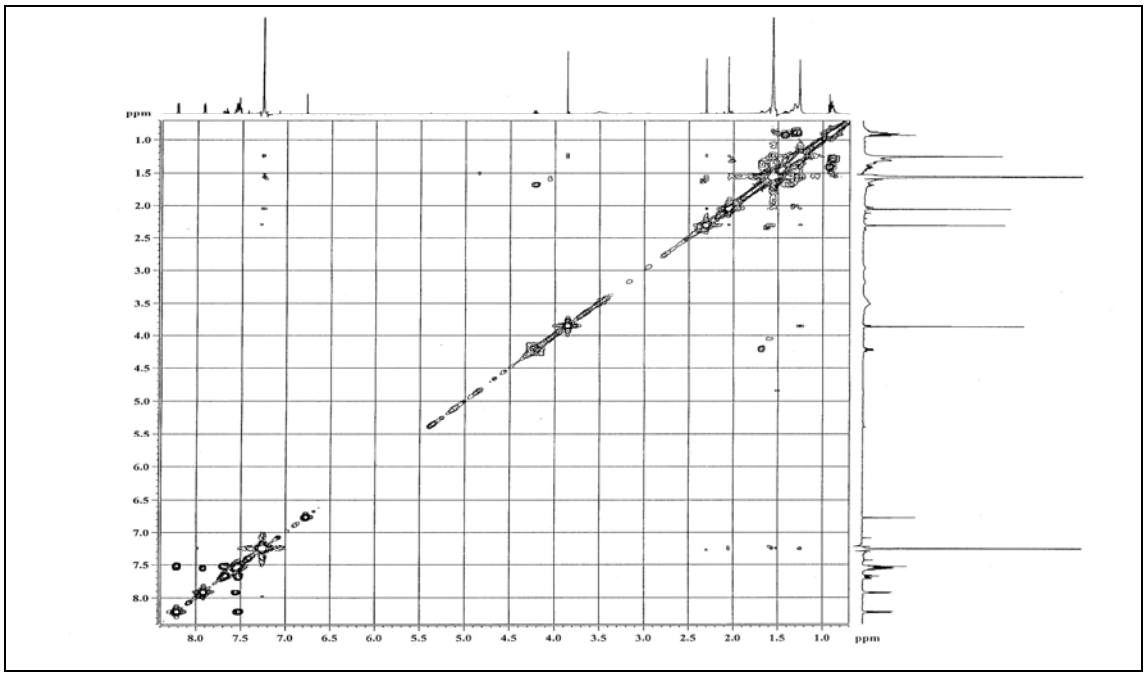

Figure 175 2D COSY ($CDCl_3$) of compound **DC20**

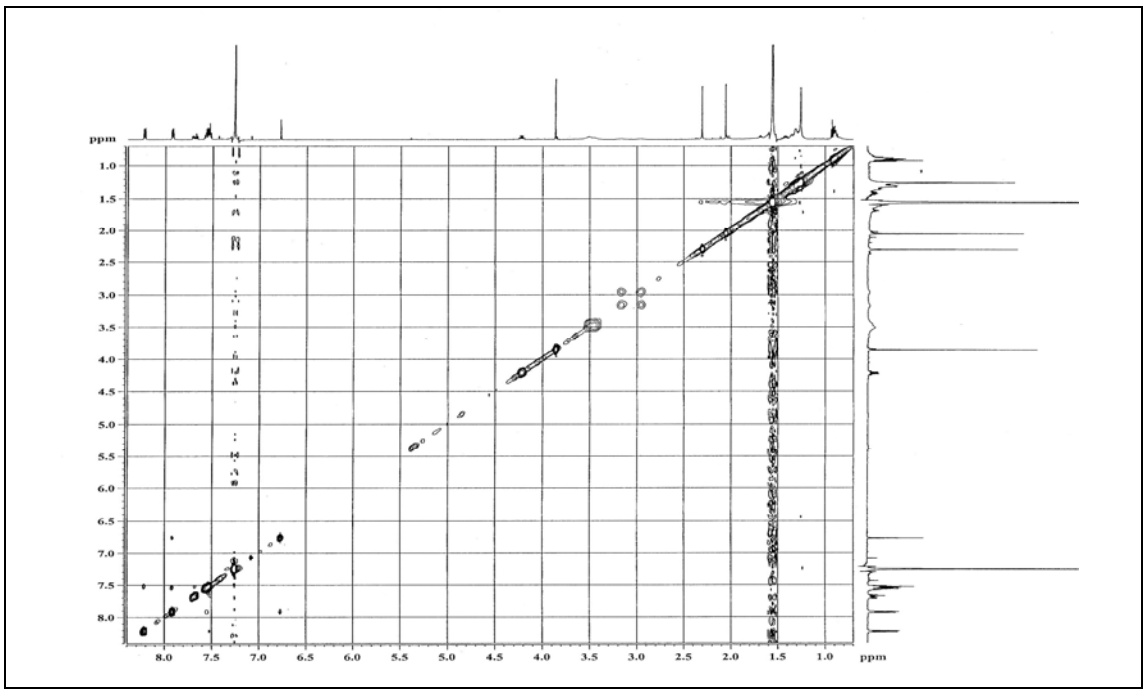

Figure 176 2D NOESY ($CDCl_3$) of compound **DC20**

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Student ID 5110220022

Educational Attainment

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Bachelor of Science (Industrial Chemistry)	Prince of Songkla University	2006

Scholarship Awards during Enrolment

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

List of Publication and Proceedings

1. Tharikarn Rittiwong and Suda Chakthong. "Chemical Constituents from the Leaves of *Desmos chinensis* Lour." The 16th National Graduate Research Conference, Maejo University, Chiang Mai, Thailand, 11-12 March 2010. (Poster presentation)

2. Tharikarn Rittiwong and Suda Chakthong. **"**Esters and Flavones from the Leaves of *Desmos chinensis* Lour." The 1st Current Drug Development International Conference, Woraburi Phuket Resort & Spa, Phuket, Thailand, 6-8 May 2010. (Poster presentation, Partial support from Natural Product Research Center)