Chemical Constituents from the Green Fruits of *Aegle marmelos*

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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 Green Fruits of *Aegle marmelos*
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PW9

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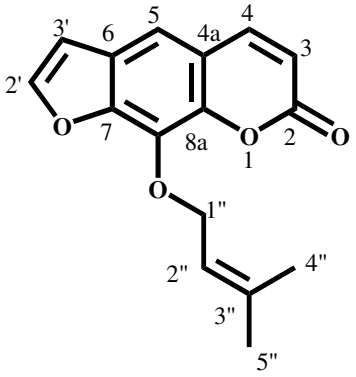
(Assoc. Prof. Dr. Krerkchai Thongnoo)

Dean of Graduate School

ชื่อวิทยานิพนธ์	องค์ประกอบทางเคมีจากผลดิบมะตูม (*Aegle marmelos*)
ผู้เขียน	นางสาวเปาซีหยะ แวอายี
สาขาวิชา	เคมีศึกษา
ปีการศึกษา	2552

บทคัดย่อ

การศึกษาองค์ประกอบทางเคมีของส่วนสกัดหยาบอะซีโตนจากผลดิบมะตูม สามารถแยกสารใหม่ได้ 5 สาร เป็นสารประกอบประเภท alkaloid 1 สาร คือ marmesiline (**PW11**), สารประเภท coumarin 1 สาร คือ 6-(4'-acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin (**PW15**), และสารประเภท dihydrofuranocoumarins 3 สาร คือ marmelonine A (**PW17**), 8-hydroxysmyrindiol (**PW18**) และ mamelonine B (**PW19**) นอกจากนี้ยังได้พบสารที่มีการรายงานมาแล้ว 16 สาร ประกอบด้วยสารประเภท furanocoumarins 5 สาร คือ imperatorin (**PW1**), 8-[(3"-methyl-2"-oxo-3"-buten-1-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one (**PW3**), xanthotoxol (**PW4**), isogosferol (**PW5**) และ xanthotoxin (**PW6**), สารประเภท อนุพันธ์ของกรดเบนโซอิก 1 สาร คือ valencic acid (**PW2**), สารประเภท dihydropyranocoumarin 1 สาร คือ decursinol (**PW8**), สารประเภท alkaloid 1 สาร คือ marmeline (**PW13**), สารประเภท coumarins 5 สาร คือ scoparone (**PW7**), demethylsuberosin (**PW9**), 6-formylumbilliferone (**PW10**), isofraxidin (**PW16**) และ isophellodenol C (**PW20**) และสารประเภท dihydrofuranocoumarins 3 สาร คือ marmesin (**PW12**), isoangenomalin (**PW14**) และ xanthoarnol (**PW21**) โครงสร้างของสารประกอบเหล่านี้วิเคราะห์โดยใช้ข้อมูลทางสเปกโทรสโกปี UV IR NMR MS และเปรียบเทียบกับสารที่มีรายงานการวิจัยแล้ว



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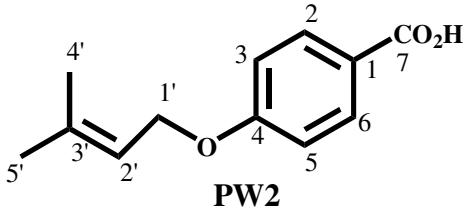

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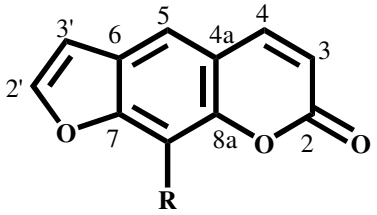

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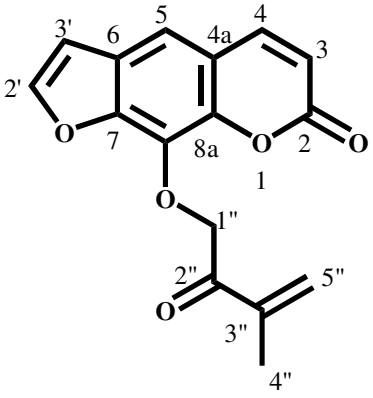

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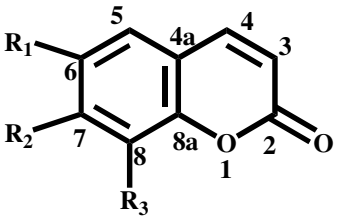

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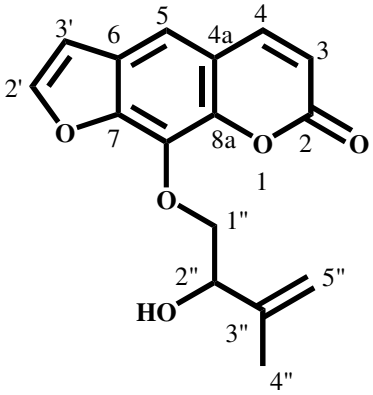
PW10: R_1 = CHO R_2 = OH R_3 = H

PW16: R_1 = OMe R_2 = OH R_3 = OMe



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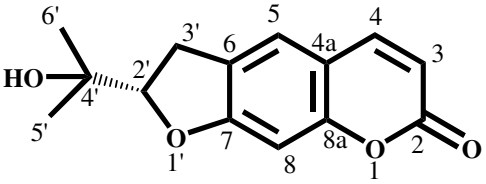

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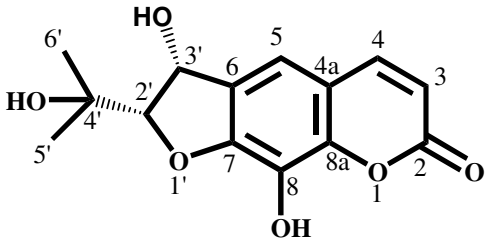

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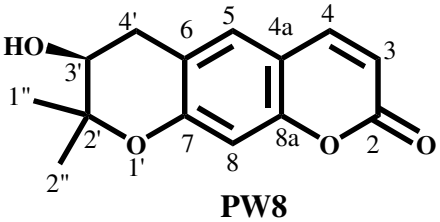

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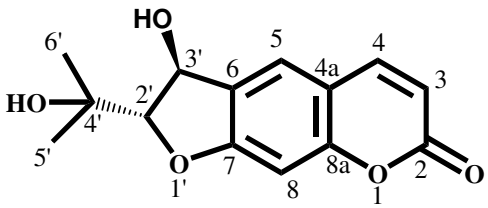

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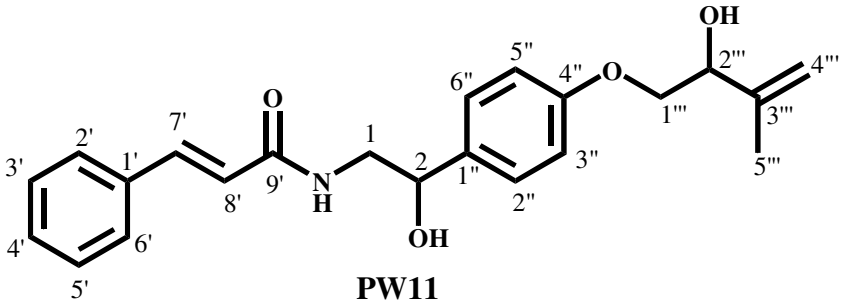

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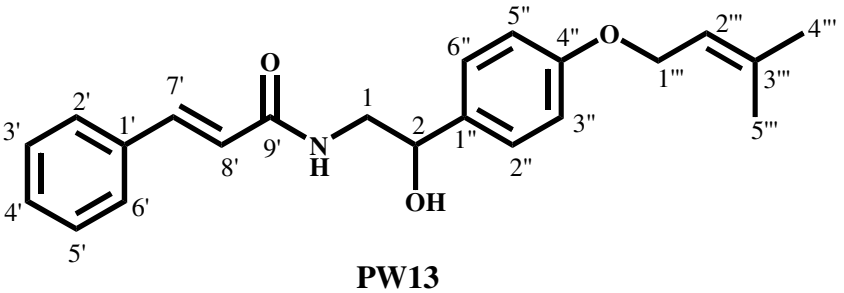

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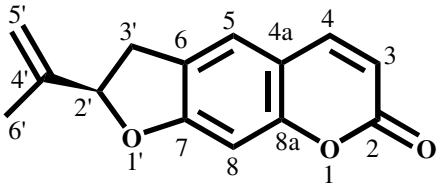

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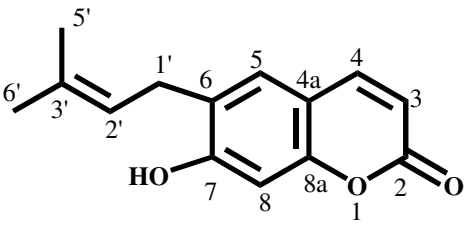

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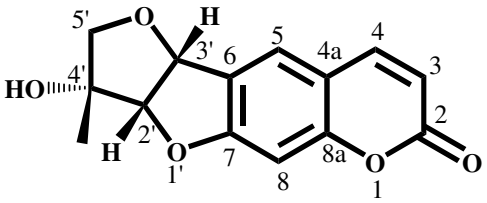

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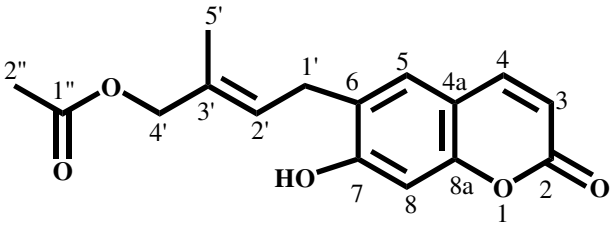

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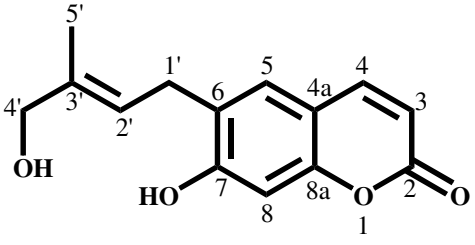

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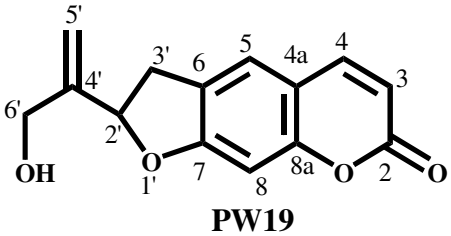


PW19

Thesis Title Chemical Constituents from the Green Fruits of *Aegle marmelos*

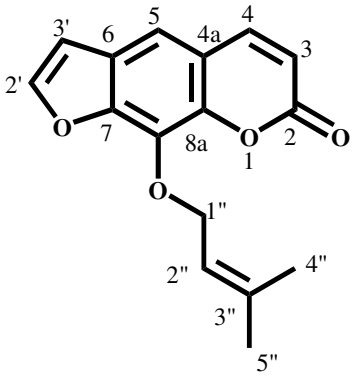
Author Miss Paosiyah Weaaryee

Major Program Chemical Studies

Academic Year 2009

ABSTRACT

Investigation of the crude acetone extracts of the green fruits of *Aegle marmelos* yielded five new compounds; an alkaloid: marmesiline (**PW11**), a new coumarin: 6-(4'-acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin (**PW15**), three dihydrofuranocoumarins: marmelonine A (**PW17**), 8-hydroxysmyrindiol (**PW18**) and marmelonine B (**PW19**), together with sixteen known compounds: five furanocoumarins: imperatorin (**PW1**), 8-[(3"-methyl-2"-oxo-3"-buten-1-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one (**PW3**), xanthotoxol (**PW4**), isogosferol (**PW5**) and xanthotoxin **(PW6)**, a benzoic acid derivative: valencic acid (**PW2**), one dihydropyranocoumarin: decursinol (**PW8**), one alkaloid: marmeline (**PW13**), five coumarins: scoparone (**PW7**)**,** demethylsuberosin (**PW9**), 6-formylumbilliferone (**PW10**), isofraxidin **(PW16)** and isophellodenol C **(PW20)** and three dihydrofuranocoumarins: marmesin **(PW12)**, isoangenomalin **(PW14)** and xanthoarnol **(PW21)**. 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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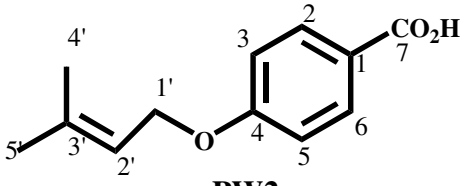

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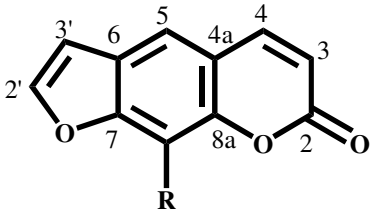

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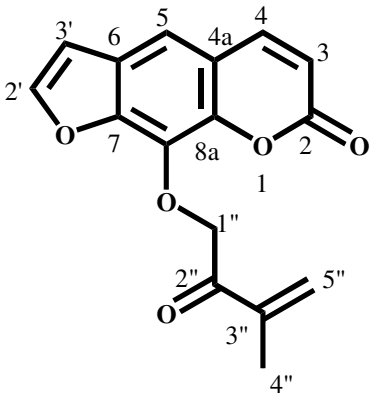

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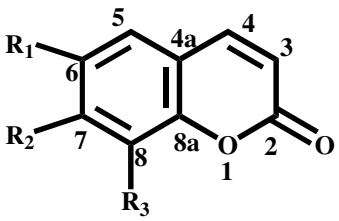

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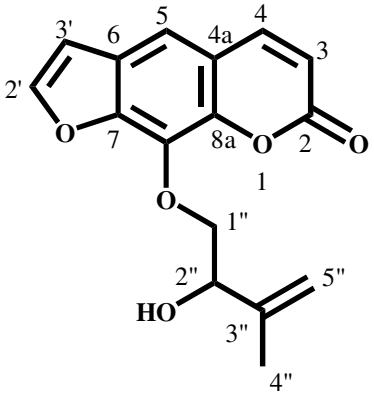

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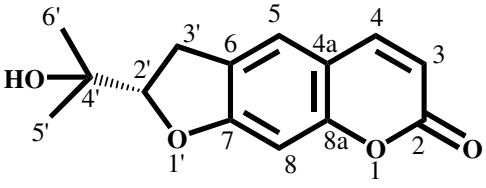

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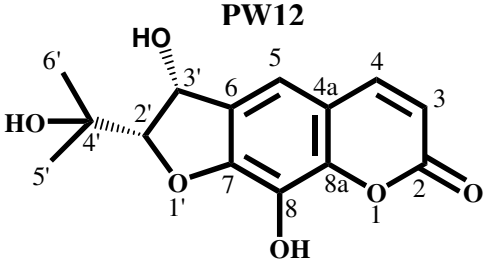

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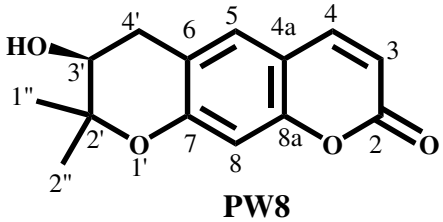

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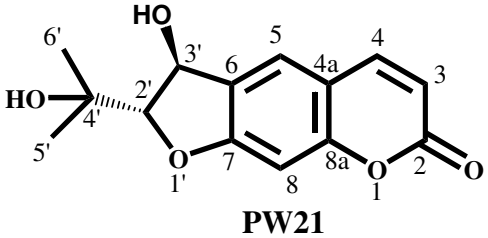

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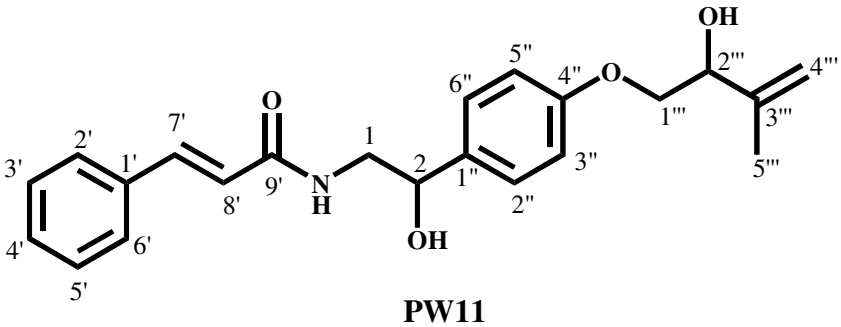

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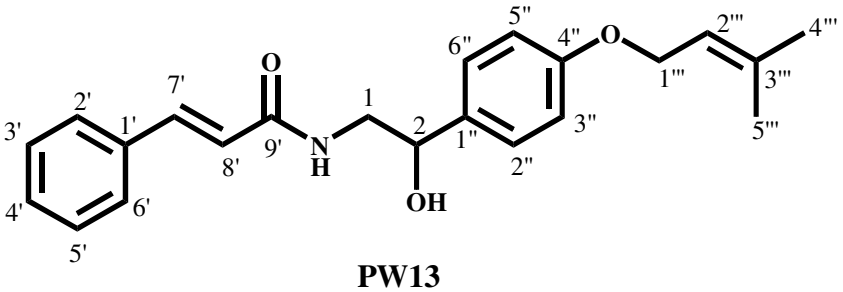

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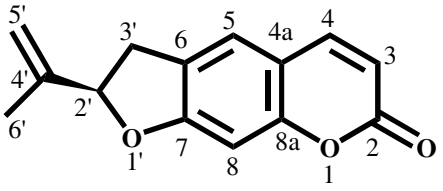

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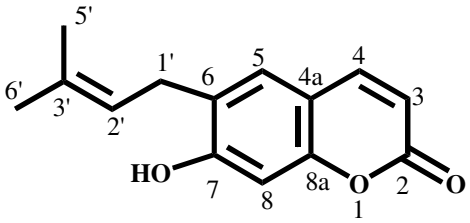

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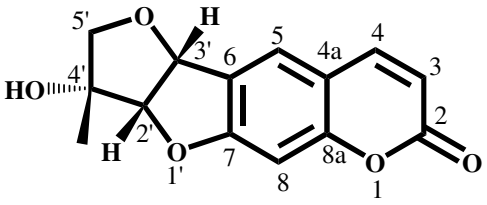

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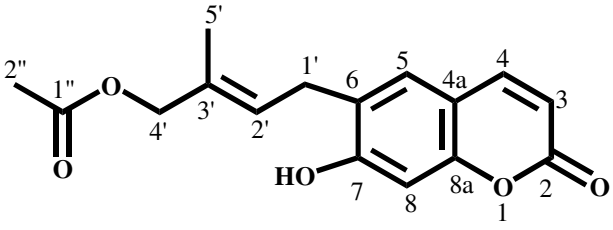

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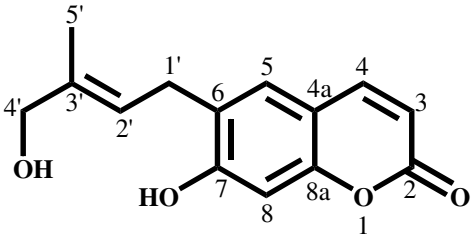

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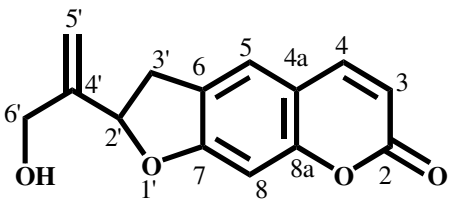

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Paosiyah Weaaryee

THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The purpose of this research is to investigate the chemical constituents from the green fruits of *Aegle marmelos.* They are a part of the basic research on the Thai medicinal plants. A derivative of benzoic acid, two alkaloids, five furanocoumarins, six coumarins, one dihydropyranocoumarin and six dihydrofuranocoumarins were isolated from the green fruits of *Aegle marmelos*.

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LIST OF ILLUSTATIONS (Continued)

LIST OF ILLUSTATIONS (Continued)

LIST OF ABBREVIATIONS AND SYMBOLS

s	=	singlet
d	=	doublet
t	=	triplet
q	=	quartet
m	=	multiplet
dd	=	doublet of doublet
dt	=	doublet of triplet
br s	=	broad singlet
br d	=	broad doublet
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

LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

ν	=	absorption frequencies
ε	=	molar extinction coefficient
m/z	=	a value of mass divided by charge
°C	=	degree celcius
MHz	=	Megahertz
ppm	=	part per million
c	=	concentration
IR	=	Infrared
UV	=	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

LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

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
CD_3OD	=	deuteromethanol

CHAPTER 1
INTRODUCTION

1.1 Introduction

Aegle marmelos (L.) Correa ex Roxb. is a large fruit-bearing tree indigenous to dry forests on hills, commonly known as Bael, known in thai as "มะตูม", belonging to the family Rutaceae. This tree, which is the only species in the genus *Aegle*, grows up to 18 meters tall and bears thorns and fragrant flowers. It has a woody-skinned, smooth fruit 5-15 cm in diameter. The plant *Aegle marmelos* is distributed throughout Burma, Pakistan, Bangladesh, Sri Lanka, Thailand and various parts of South-eastern Asia (Mishra *et al*., 2010). In India, the tree is often found in temple gardens and its leaves are used in religious celebrations. In the traditional culture of Nepal and Bangladesh (Govindachari *et al*., 1983), *Aegle marmelos* is part of an important fertility ritual for girls known as the *Bel baha*.

According to Smitinan (2001), there are twenty four genus of family Rutaceae found in Thailand as follows.

1. Acronychia
2. Aegle
3. Atalantin
4. Citrus
5. Clausena
6. Euodia
7. Feroniella
8. Fortunella
9. Glycosmis
10. Limonia
11. Luvunga
12. Maclurodendron
13. Melicope
14. Merope
15. Merrillia
16. Micromelum
17. Murraya
18. Naringi
19. Paramignya
20. Ravenia
21. Ruta
22. Toddalia
23. Triphasia
24. Zanthoxylum

All parts of this tree, viz. root, leaf, bark, fruit and seed are useful in several aliments (Alam *et al*., 1990). The leaf extract has been found effective in the regeneration of damaged pancreas (*β*-cell) in diabetic rat (Das *et al*., 1996). A decoction of the root and the bark are used in the treatment of fever significantly against malaria (Arumugam *et al*., 2008). The ripe fruits is a good cure for diabetes, dyspepsia, constipation and body heating problem (Kalaivani *et al*., 2009). The seed extract is known to exhibit significant activity against *Vibrio cholerae*, *Staphylococus aureus* and *Escherichia coli* (Acharyya *et al*., 2009). Essential oils isolated from *A. marmelos* have shown promising antifungal activities against *Physalospora tucumanensis*, *Ceratocystis paradoxa*, *Sclrrotium rolfsii*, *Curvularia lunata*, *Helminthosporium sacchari*, *Fusarium moniliforme* and *Cephalosporium sacchari* (Runa *et al*., 1997).

Trees

Stem

Flowers

Leaves

Fruits

Figure 1 Different parts of *Aegle marmelos*

1.2 Review of Literatures

The chemical constituents isolated from the five genus and six species of family Rutaceae were summarized in **Table 1**. Information obtained from SciFinder Scholar copyright in 2009 will be presented and classified into groups: Acridone alkaloids, Alkaloids, Anthraquinones, Aromatics, Coumarins, Flavonoids, Glucoside Limonoids, Sesquiterpenoids and Triterpenoids.

1.2.1 The Biological Activity of *A. marmelos*

The coumarin compounds isolated from *A. marmelos* have been investigated for biological activity. For example, (+)-4-(2′-hydroxy-3′-metylbut-3′-enyloxy)-8*H*[1,3]-dioxol[4,5-*h*]chromen-8-one isolated from seeds of *A. marmelos* exhibited efficient antifungal activity against *A.fumigatus*, *Candida albicaneoformansns ,T.* mentagrophytes and *Cryptococus neoformans* with the minimum inhibitory concentration (MICs) of 6.25 μg/disc, 31.25 μg/ml and 31.25 μg/ml in DDA, BMA and PSGIA, respectively (Mishra *et al*., 2010), 7-(6′R-hydroxy-3′, 7′-dimetyl-2′E, 7′-octadienylloxy) coumarin and auraptene inhibited MAO activity in a concentration-dependent manner with IC_{50} values of 0.7 and 1.7 μM respectively and showed a slight and potentl selective inhibitory effect against MAO-B (IC_{50} 0.5 and 0.6 μM, respectively) compared to MAO-A (IC_{50} 1.3 and 34.6 μM, respectively) (Jeong *et al*., 2006).

Some of alkaloids from *A. marmelos* have been investigated for biological activity. Anhydroaegeline isolated from leaves of *A. marmelos* revealed the most potent inhibitory effect against α-glucosidase with IC_{50} value of 35.8 μM (Phuwapraisirisan *et al*., 2008) and shahidine showed activity against a few Gram-positive bacteria (Faizi *et al*., 2009).

Table 1 Compounds from plants of Family Rutaceae.

a. Acridone alkaloids
b. Alkaloids
c. Anthraquinones
d. Aromatics
e. Coumarins
f. Flavonoids
g. Glucoside
h. Limonoids
i. Sesquiterpenoids
j. Triterpenoids

Scientific name	Part	Compounds	Bibliography
Aegle marmelos	Bark	(+) Lyoniresinol 3α-*O*-β-D-glucopyranoside, **g1**	Ohashi *et al*., 1994
		(-) Lyoniresinol 3α-*O*-β-D-glucopyranoside, **g2**	
		(-)-2α-*O*-(β-D-glucopyranosyl)lyoniresinol, **g3**	
		(-)-4-epi-lyoniresinol-3α-*O*-β-D-glucopyranoside, **g4**	
		Chloromarmin, **e1**	Ohashi *et al*., 1995
		Aeglin, **e2**	
	Heart wood	Xanthoxol, **e3**	Srivastava *et al*., 1996
		Marmin, **e4**	
		1-Hydroxy-7,8-dimethoxy-2-methylanthraquinone, **c1**	
		6-Hydroxy-1-dimethoxy-3-methylanthraquinone, **c2**	
		β-Sitosterol, **j1**	Jain *et al*., 1991

tific name	Part	Compounds	Bibliography
marmelos	Bark	Xanthotoxol-8-*O*-β-D-glucopyranoside, **e5**	Srivastava *et al.*, 1996
		2-(2-hydroxy-4-methoxyphenyl)vinyl acetate, **d1**	
		Lupeol, **j2**	
	Leaves	Aegelinoside A, **g5**	Phuwapraisirisan *et al.*, 2008
		Aegelinoside B, **g6**	
		Aegeline, **b1**	
		Anhydromarmeline, **b2**	
		Tembamide, **b3**	
		Dehydromarmeline, **b4**	
		Anhydroaegeline, **b5**	
		Marmenol, **e6**	Ali *et al.*, 2004
		Praealtin D, **e7**	
		Valencic acid, **d2**	
		4-Methoxybenzoic acid, **d3**	
		Betulinic acid, **j3**	
		N-(*p*-trans- coumaroyl)tyramine, **b6**	
		Montanine, **b7**	
		Rutaretin, **e8**	
		Rutin, **f4**	Sharma *et al.*, 1980
		β-Sitosterol, **j1**	
		Xanthoxol, **e3**	
		β-sitosterol-3-*O*-β-D-glucoside, **j5**	
		Scoparone, **e10**	
		Scopoletol, **e11**	
		Umbelliferone, **e14**	
		Marmesin, **e13**	

ific name	Part	Compounds	Bibliography
armelos		Skimmianin, **b10**	
	Dry leaves	Marmelin, **b8**	Govindachari et al.,
		Dehydromarmeline, **b4**	1983
		O-Demethylaegeline, **b9**	
	Root	Anhydroaegeline, **b5**	Shoeb *et al.*, 1973
		Xanthotoxin, **e9**	
		Scoparone, **e10**	
		Scopoletol, **e11**	
		Tembamide, **b3**	
		Umbelliferone glucoside, **e12**	
		Marmesin, **e13**	
		Marmin, **e4**	
		Skimmianin, **b10**	
	Root bark	Skimmianin, **b10**	Basu *et al.*, 1974
		Umbelliferone, **e14**	
		Xanthotoxin, **e9**	
		Fagarine, **b11**	
		Marmesin, **e13**	
		Marmin, **e4**	
		Decursinol, **e15**	
	Ripe fruits	Alloimperatorin methyl ether, **e16**	Sharma *et al.*, 1981
		O-Isopentenylhalfordinol, **b12**	
		O-Methylhalfordinol, **b13**	
	Unripe fruits	Aegeline, **b1**	Sharma *et al.*, 1981
		Imperatorin, **e17**	
		Alloimperatorin, **e18**	
	Matured bark	Xanthoxol, **e3**	Chatterjee *et al.*,
		Marmelin, **b8**	1949
		Marmesin, **e13**	
		Umbelliferone, **e14**	

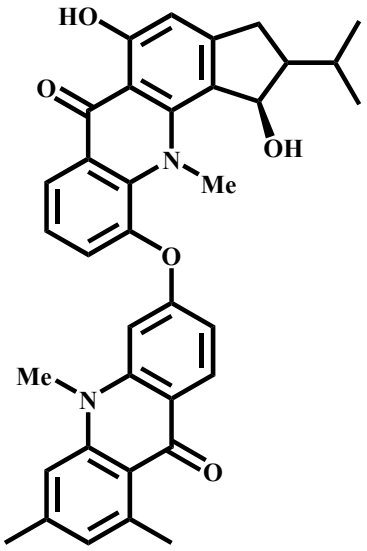
Aegle marmelos	Matured bark	Fagarine, **b11** Anhydromarmesin, **e19** Nodakenetin, **e20** Umbelliferone-6-carboxylic acid, **e21** Anhydromarmesin, **e19** Marmesic acid, **d4** 7-Hydroxydimethyl-3,4-dimethy-2-oxo-2*H*-1-benzopyran-6-carboxylic acid, **e22**	Chatterjee *et al*., 1949
Atalantia ceylantica	Bark Root bark Seed	Atalatine, **a1** Xanthotoxin, **e9** Racemosin, **e23** Ceylantin, **e24** Cycloatalantin, **h1** Cycloatalantinone, **h2** Cycloatalantin-16-oic acid, **h3** Isocycloatalantin, **h4** Cycloepiatalantin, **h5** Dehydrocycloatalantin, **h6** Ataloxime, **b14** Xanthotoxine, **e9** Imperatorin, **e17** Bergapten, **e25** Heraclenin, **e26** Oxypeucedanin, **e27**	Fraser *et al*., 1973 Murray *et al*., 1985 Bacher *et al*., 1999

Scientific name	Part	Compounds	Bibliography
Atalantia racemosa	Heart wood	Xanthotoxin, **e9** Isoevodionol, **e28** Umbelliferone, **e14** Luvangetin, **e29** Xanthyletin, **e30** Rutaretin, **e8** Rutarin, **e31** Racemosin, **e23** Racemoflavone, **f1** Atalantaflavone, **f2**	Banerj *et al*., 1988b
Atalantia wightii	Root	Kokusaginin, **b15** Xanthyletin, **e30** Cinnamic acid lactone, **e32** Isoimpinellin, **e33** Ostol, **e34** Marmesin, **e13** Xanthotoxin, **e9** Obacylactone, **h7** Atalantin, **h8** Phebalosin, **e35** *N*-methylatalaphyllin, **a2** *N*-methylatalaphyllinine, **a3** Auraptene, **e36** Umbelliferone, **e14** Micromelumin, **e37** Murrangatin, **e38**	Banerj *et al*., 1982

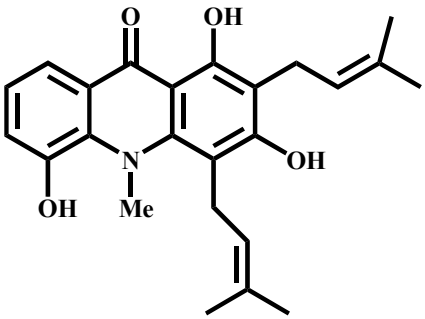
Scientific name	Part	Compounds	Bibliography
Atalantia wightii	Stem bark	Skimmianin, **b10** Heplopine, **b16** *p*-Coumaric acid ethyl ester, **d5** Imperatorin, **e17** Scopoletol, **e11** Marmin, **e4** Limettin, **e39** Crenyllatin, **e40** Phebalosin, **e35**	Banerj *et al*., 1988a
Citrus limonia	Stem	Imperatorin, **e17** Xanthotoxin, **e9** Bergapten, **e25** Isoimpinellin, **e33** Limettin, **e39** Scopoletol, **e11** Umbelliferone, **e14** Xanthoxol, **e3** Aesculetin, **e41** Stigmasterol, **j4** β-sitosterol-3-*O*-β-glucoside, **j5**	Abdel-Fattah *et al*., 2003

Scientific name	Part	Compounds	Bibliography
Citrus nobilis	Seeds	Citrobilin, **h9**	Bui *et al*., 2004
		Limonin, **h10**	
		Nomilin, **h11**	
		Deacetyl nomilin, **h12**	
		Obacunon, **h13**	
		Limonexic acid, **h14**	
		β-sitosterol-3-*O*-β-D-glucoside, **j5**	
	Root bark	2,2-dimethylpyranoflavanol, **f3**	Wu *et al*., 1987
		Elemol, **i1**	
		Suberosin, **e42**	
		Suberenol, **e43**	
		Crenyllatin, **e40**	
		Xanthyletin, **e30**	
		Xanthoxyletin, **e44**	
		Nordentatin, **e45**	
		Citropone A, **a4**	
		5-Hydroxynoracronycine, **a5**	
		Citrusinine I, **a6**	
		Citracridone I, **a7**	

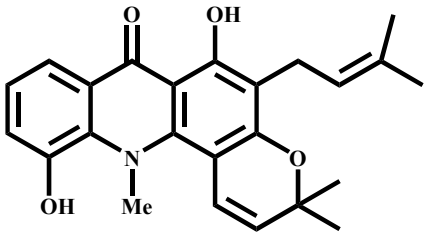
a. Acridone alkaloids



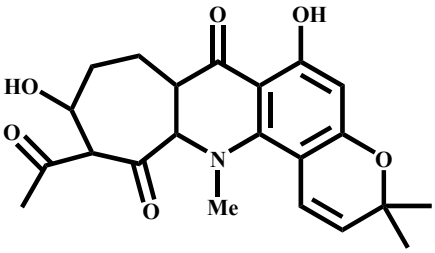
Atalantine, **a1**



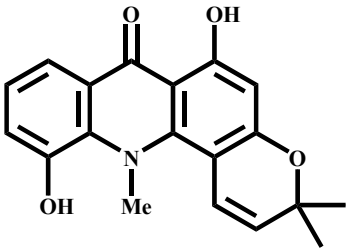
N-Methylatalaphyllin, **a2**



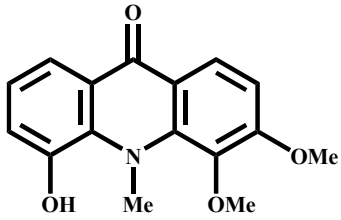
N-methylatalaphyllinine, **a3**



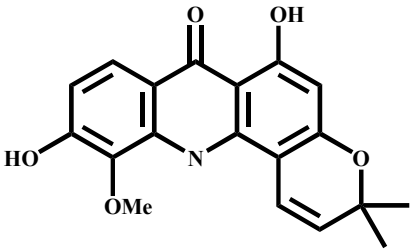
Citropone A, **a4**



5-Hydroxynoracronycine, **a5**

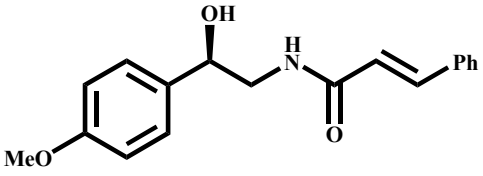


Citrusinnine I, **a6**

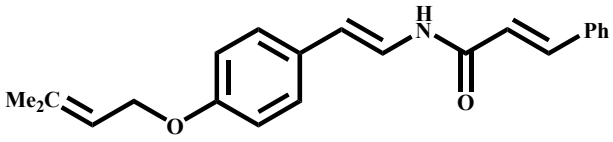


Citracridone I, **a7**

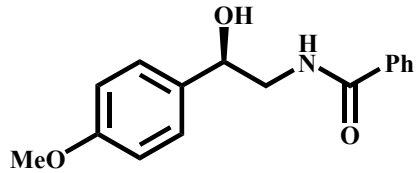
b. Alkaloids



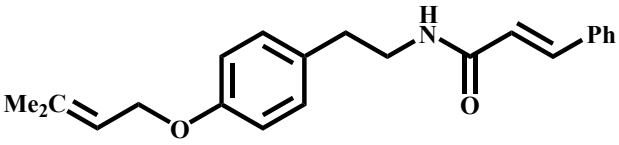
Aegeline, **b1**



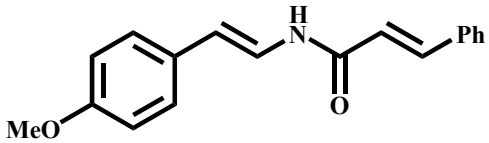
Anhydromarmeline, **b2**



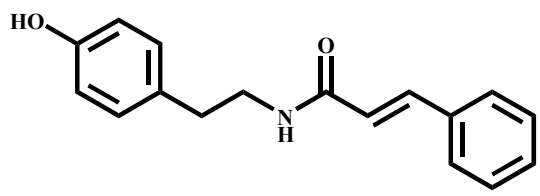
Tembamide, **b3**



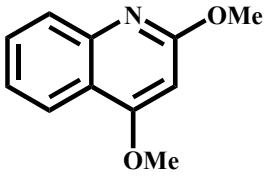
Dehydromarmeline, **b4**



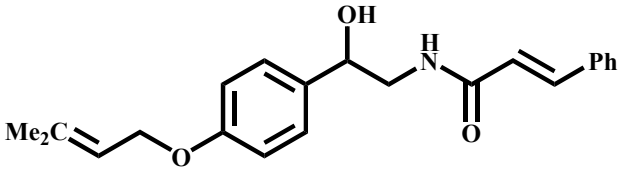
Anhydroaegeline, **b5**



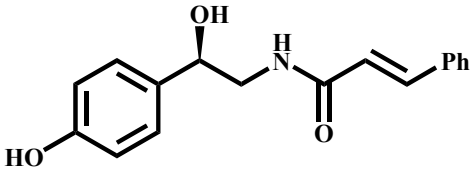
N-(*p*-trans-coumaroyl)tyramine, **b6**



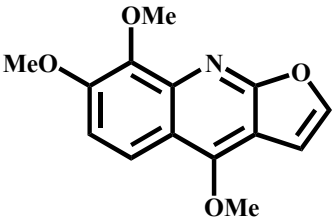
Montanin, **b7**



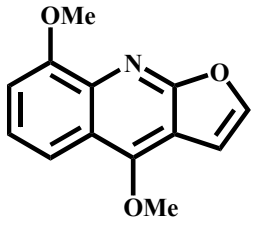
Marmelin**, b8**



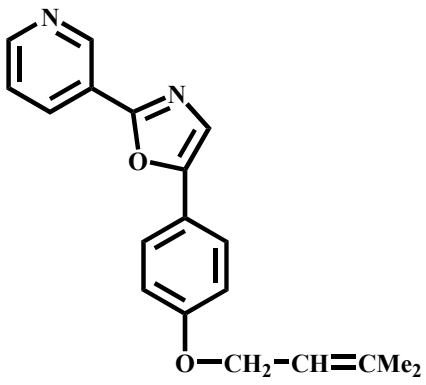
O-Demethylaegeline, **b9**



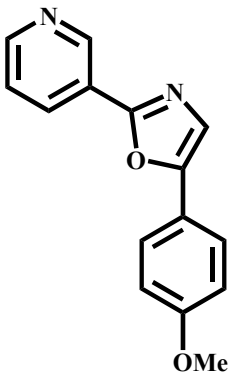
Skimmianin, **b10**



Fagarine, **b11**



O-Isopentenylhalfordinol, **b12**



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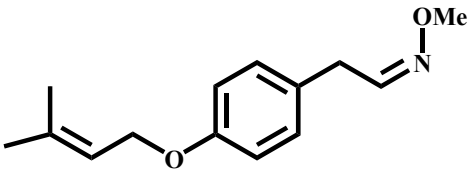
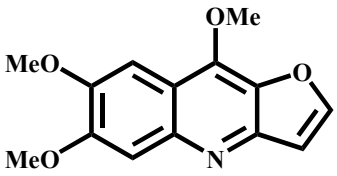
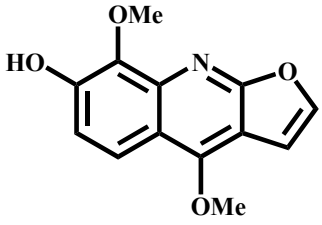


Ataloxime, **b14**

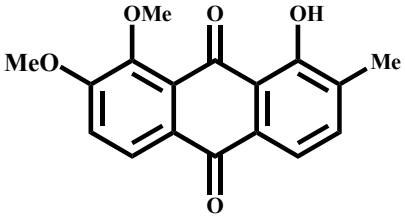


Kokusaginin, **b15**

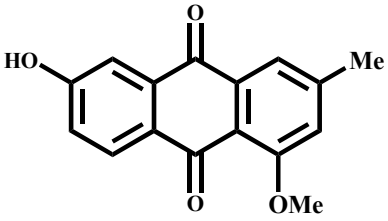


Heplopine, **b16**

c. Anthraquinone

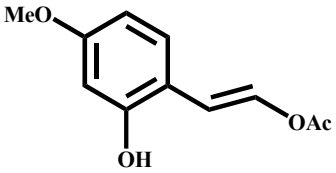


1-Hydroxy-7,8-dimethoxy-2-methylanthraquinone, **c1**

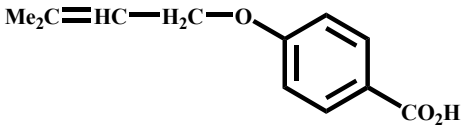


6-Hydroxy-1-methoxy-3-methylanthraquinone, **c2**

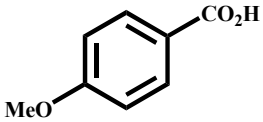
d. Aromatics



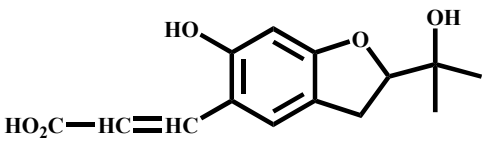
2-(2-hydroxy-4-methoxyphenyl)vinyl acetate, **d1**



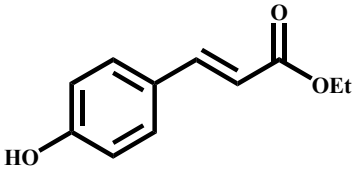
Valencic acid, **d2**



4-Methoxybenzoic acid, **d3**

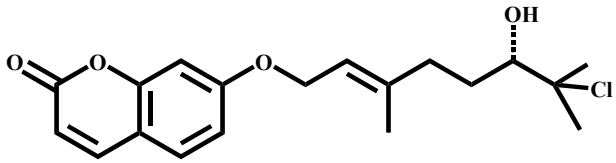


Marmesic acid, **d4**

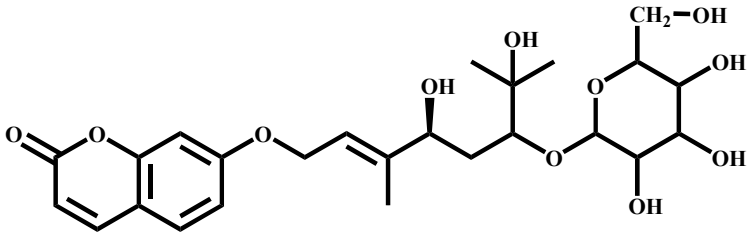


p-Coumaric acid ethyl ester, **d5**

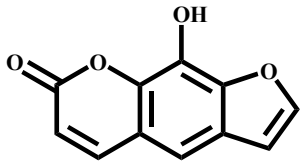
e. Coumarins



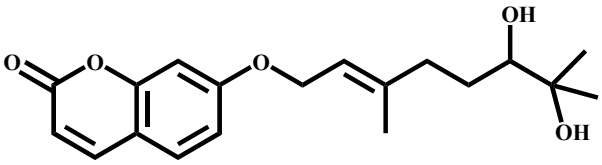
Chloromarmin, **e1**



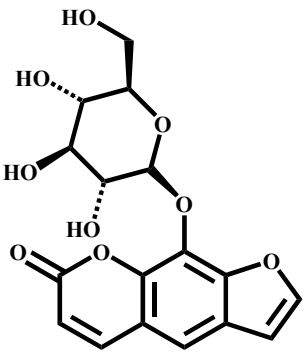
Aeglin, **e2**



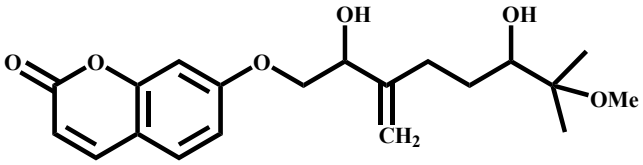
Xanthoxol, **e3**



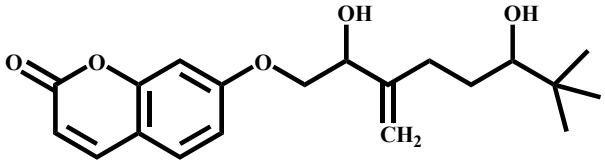
Marmin, **e4**



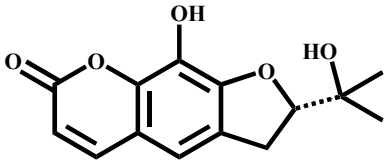
Xanthoxol-8-*O*-β-D-glucopyranoside, **e5**



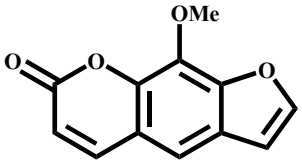
Marmenol, **e6**



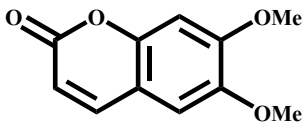
Praealtin D, **e7**



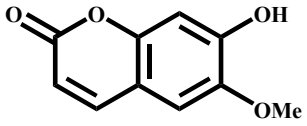
Rutaretin, **e8**



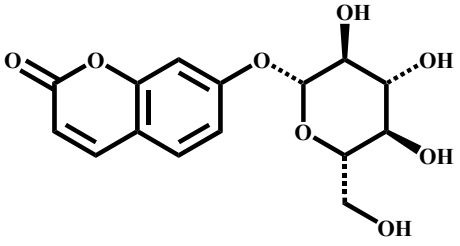
Xanthotoxin, **e9**

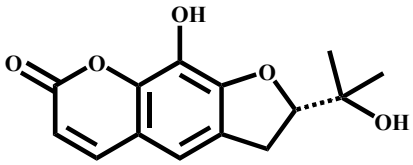


Scoparone, **e10**



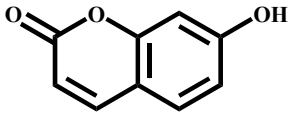
Scopoletol, **e11**



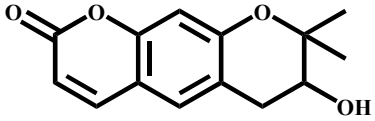


Umbelliferone glucoside, **e12**

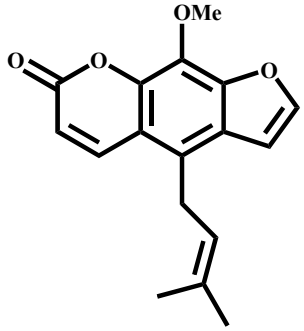
Marmesin, **e13**



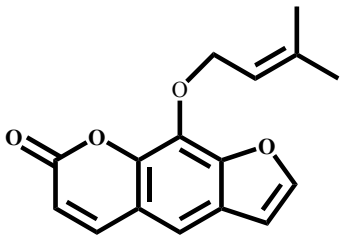
Umbelliferone, **e14**



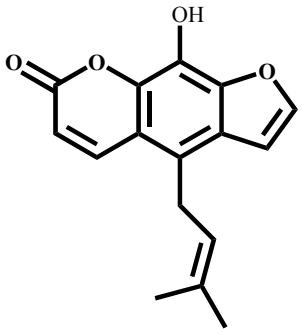
Decursinol, **e15**



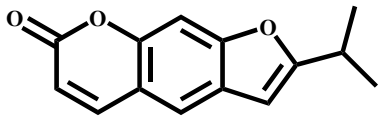
Alloimperatorin methyl ether, **e16**



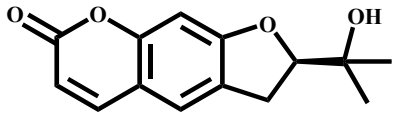
Imperatorin, **e17**



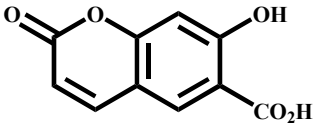
Alloimperatorin, **e18**



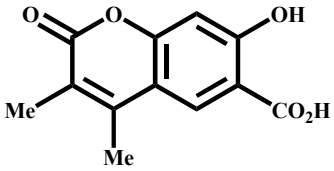
Anhydromarmesin, **e19**



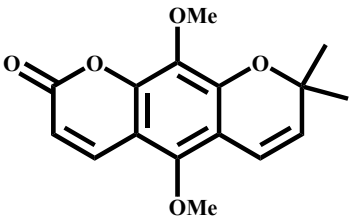
Nodakenetin, **e20**



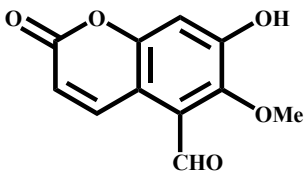
Umbelliferone-6-carboxylic acid, **e21**



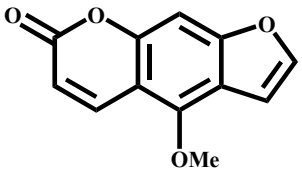
7-Hydroxy-3,4-dimethyl-2-oxo-2*H*-1-benzopyran-6-carboxylic acid, **e22**



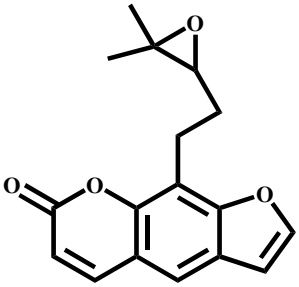
Racemosin, **e23**



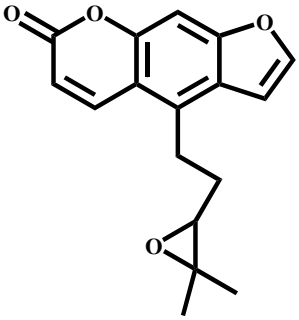
Ceylantin, **e24**



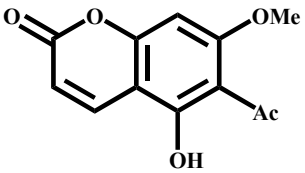
Bergapten, **e25**



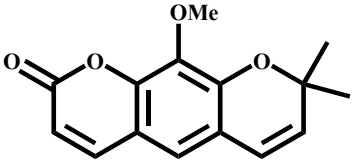
Heraclenin, **e26**



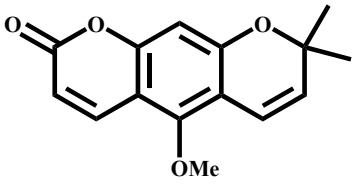
Oxypeucedanin, **e27**



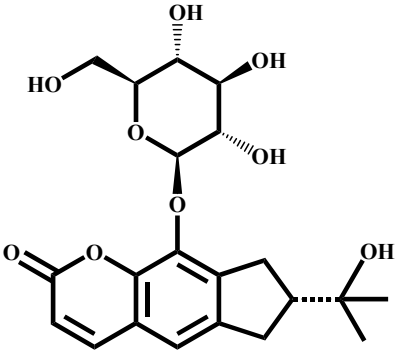
Isoevodionol, **e28**



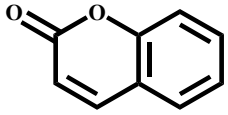
Luvangetin, **e29**



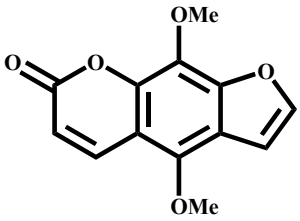
Xanthyletin, **e30**



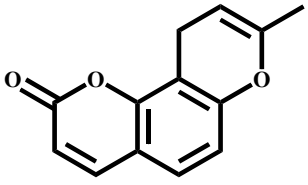
Rutarin, **e31**



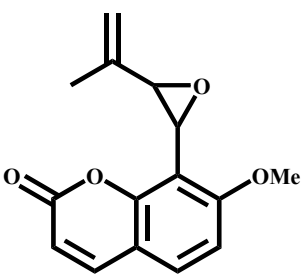
Cinnamic acid lactone, **e32**



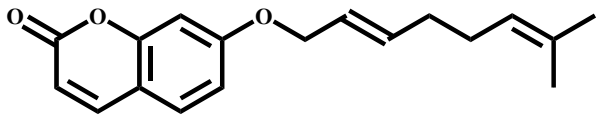
Isoimpinellin, **e33**



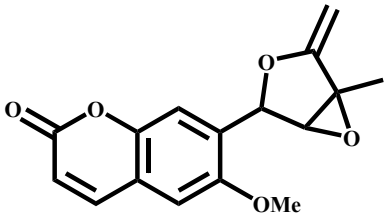
Ostol, **e34**



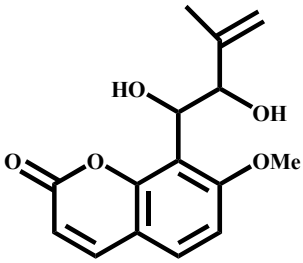
Phebalosin, **e35**



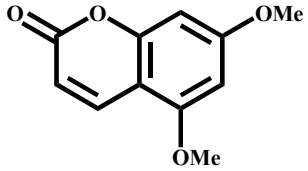
Auraptene, **e36**



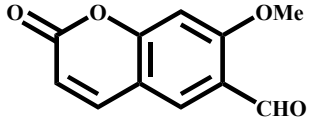
Micromelumin, **e37**



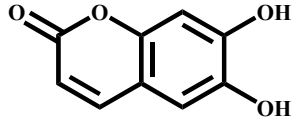
Murrangatin, **e38**



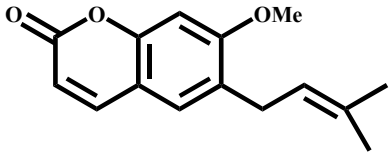
Limettin, **e39**



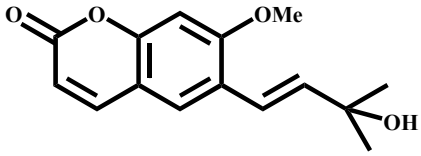
Crenyllatin, **e40**



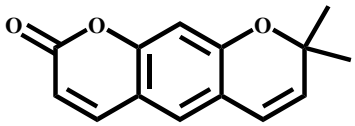
Aesculetin, **e41**



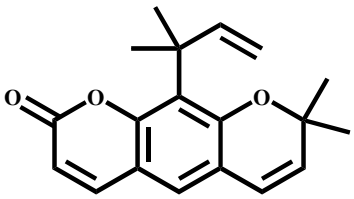
Suberosin, **e42**



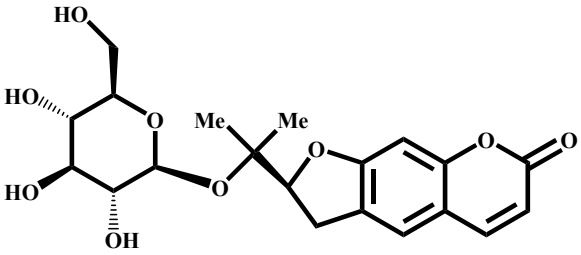
Suberenol, **e43**



Xanthoxyletin, **e44**

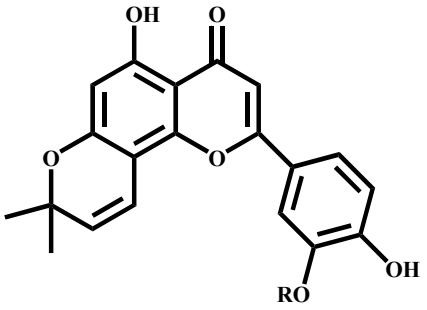


Nordentatin, **e45**



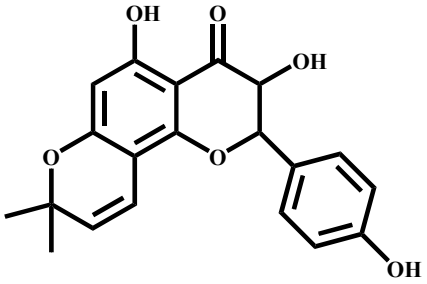
Marmesinin, **e46**

f. Flavonoids

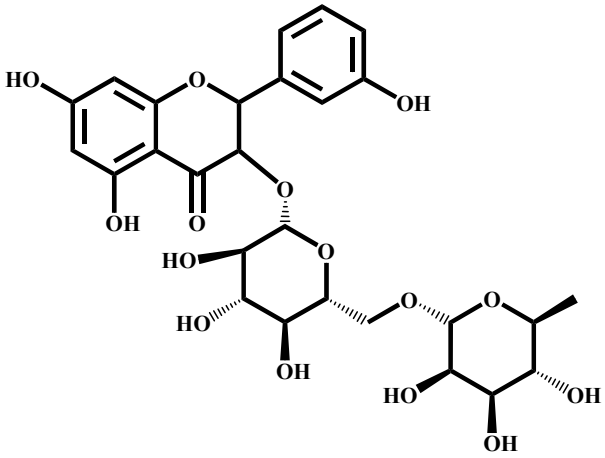


R = OMe : Racemoflavone, **f1**

R = H : Atalantaflavone, **f2**

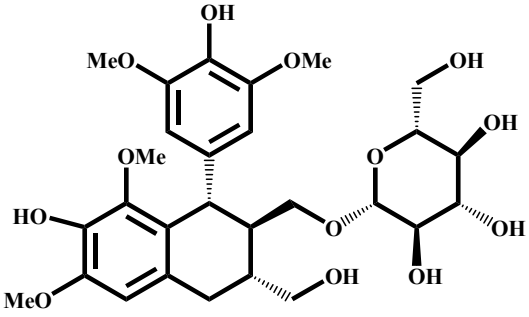


2,2-dimethylpyranoflavanol, **f3**

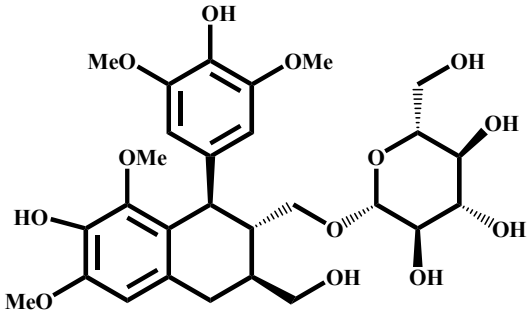


Rutin, **f4**

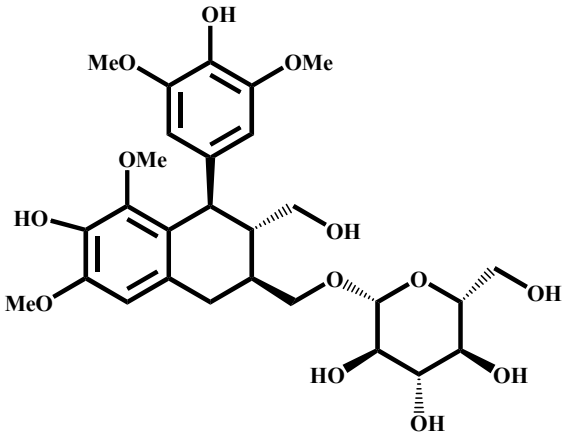
g. Glucosides



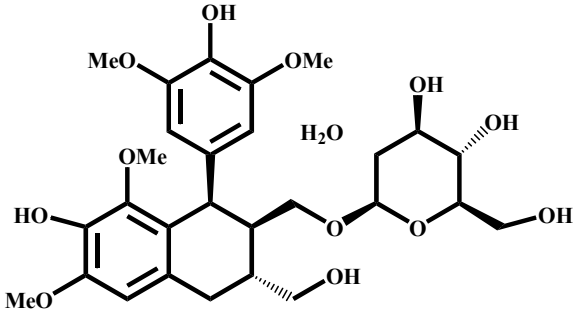
(+) Lyoniresinol 3α-*O* -β-D-glucopyranoside, **g1**



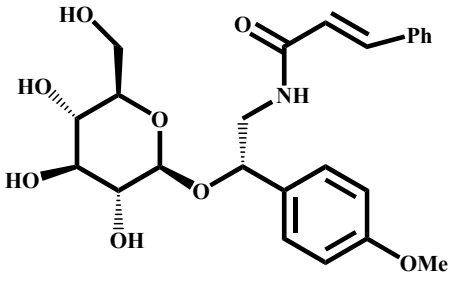
(-) Lyoniresinol 3α-*O*-β-D-glucopyranoside, **g2**



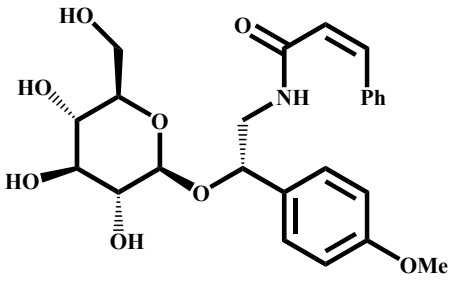
(-)-2α-*O*-(β-D-glucopyranosyl)lyoniresinol, **g3**



(-)-4-*epi*-lyoniresinol-3α-*O*-β-D-glucopyranoside, **g4**

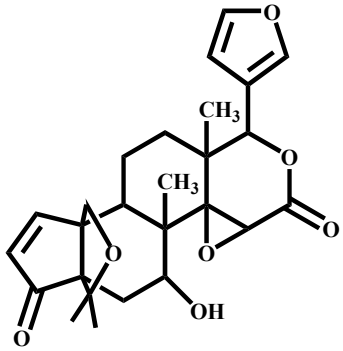


Aegelinoside A, **g5**

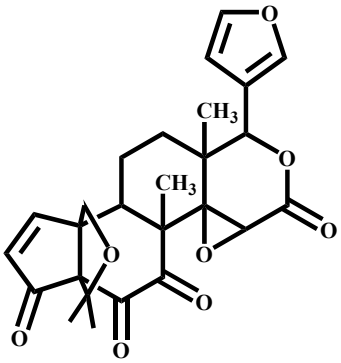


Aegelinoside B, **g6**

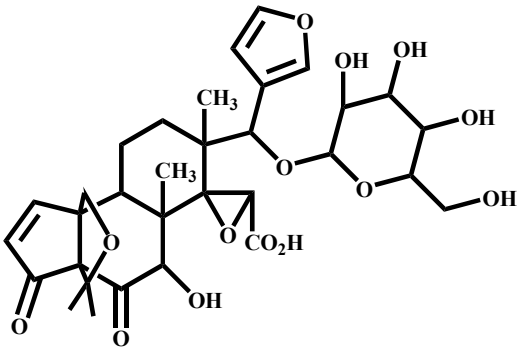
h. Limonoids



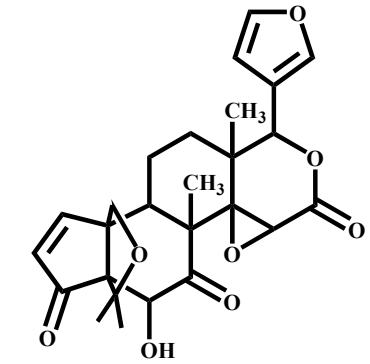
Cycloatalantin, **h1**



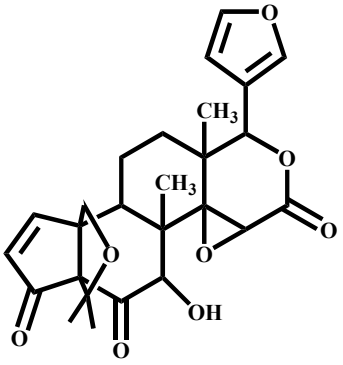
Cycloatalantinone, **h2**



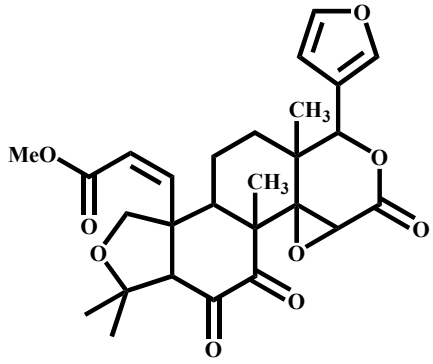
Cycloatalantin-16-oic acid, **h3**



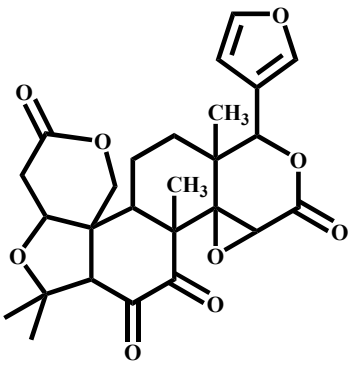
Isocycloatalantin, **h4**



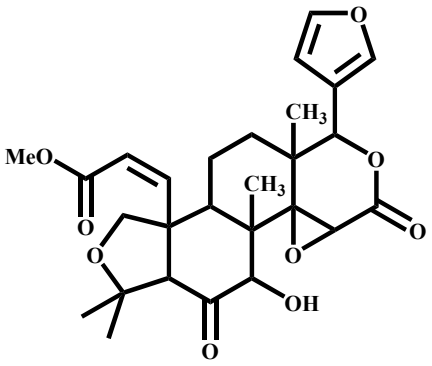
Cycloepiatalantin, **h5**



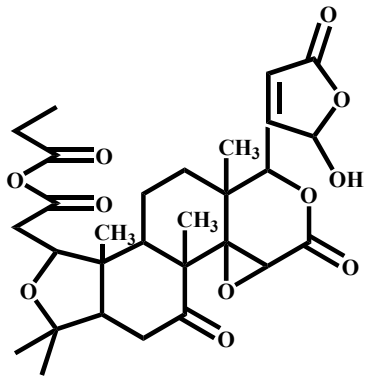
Dehydrocycloatalantin, **h6**



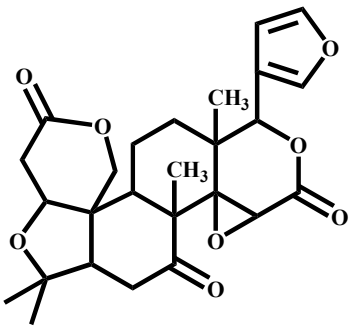
Obacylactone, **h7**



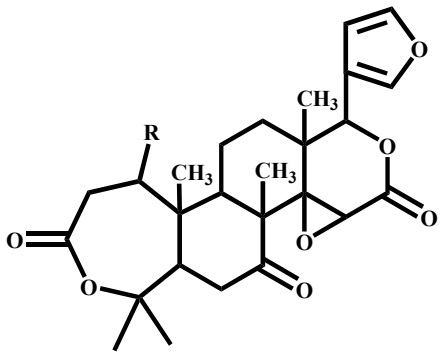
Atalantin, **h8**



Citrobilin, **h9**



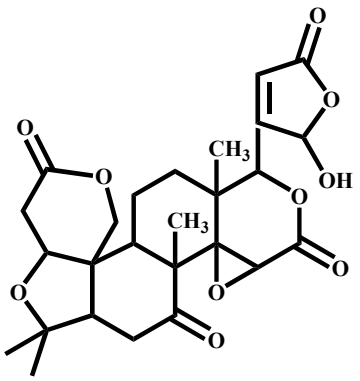
Limonin, **10**



R = OAc : Nomilin, **h11**

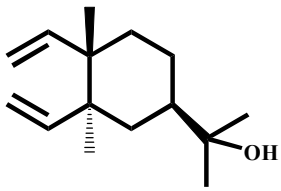
R = OH : Deacetyl nomilin, **h12**

R = H : Obacunon, **h13**



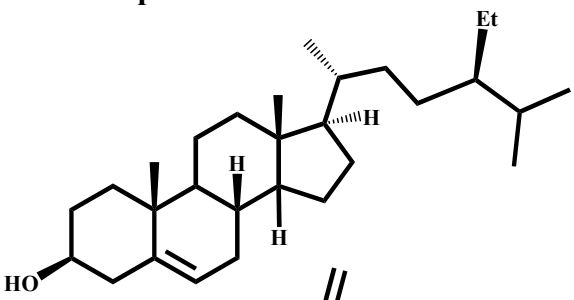
Limonexic acid, **h14**

I. Sesquiterpenoids

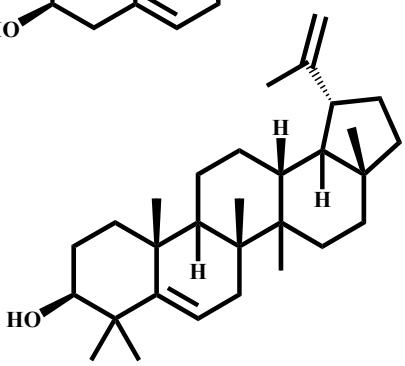


Elemol, **i1**

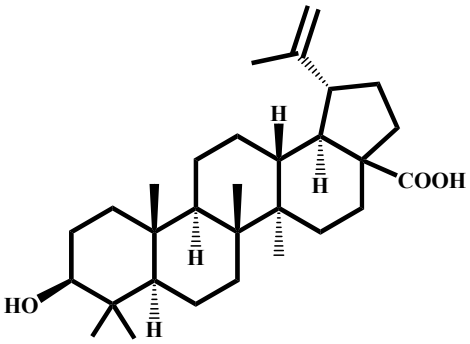
J. Triterpenoids



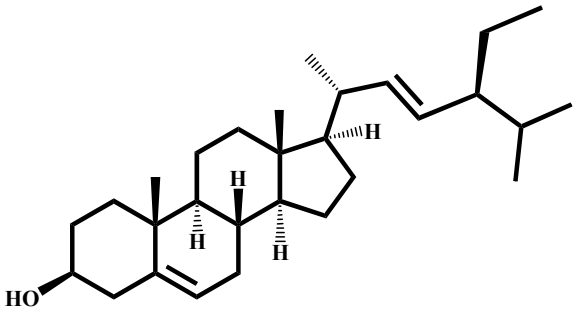
β-Sitosterol, **j1**



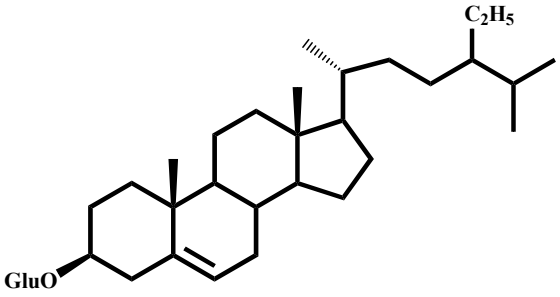
Lupeol, **j2**



Betulinic acid, **j3**



Stigmasterol, **j4**



β-Sitosterol-3-*O*-β-D-glucoside, **j5**

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, acetone and methanol 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 and 500 MHz spectrometer at Department of Chemistry, Faculty of Science, Prince of Songkla University and a Unity Inova Varian 500 MHz at Scientific Equipment Center, Prince of Songkla University. Spectra were recorded in deuterochloroform as δ value in ppm down field 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 60H (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.

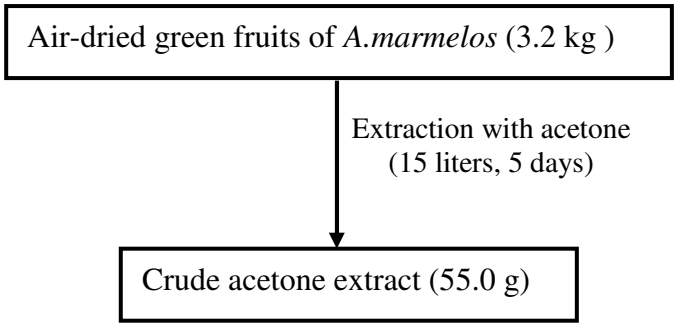
2.2 Plant material

The green fruits of *A. marmelos* (L.) Corrêa ex Roxb. were collected from Songkhla province in the Southern part of Thailand, in October, 2008. Identification

was made by Mr. Ponlawat Pattarakulpisutti, Department of Biology, Facutly of Science, Prince of Songkla University. The specimen (Paosiyah 01) has been deposited in the Herbarium of Department of Biology, Facutly of Science, Prince of Songkla University, Thailand.

2.3 Extraction and Isolation

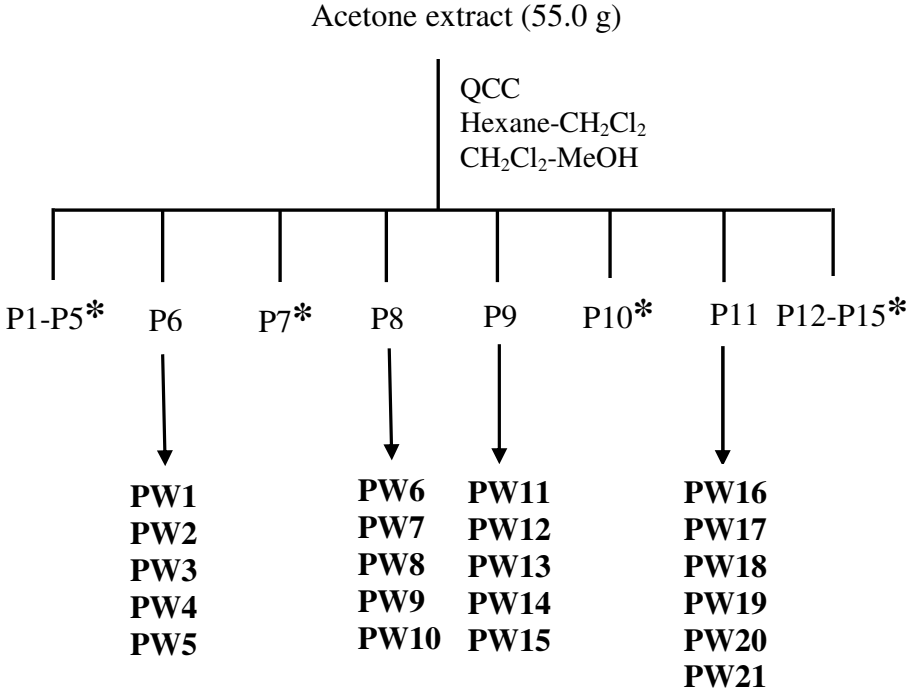
Chopped-dried green fruits of *A. marmelos* (3.2 kg) were immersed in acetone at room temperature for 5 days. After evaporation, a dark green gum of acetone extract (55.0 g) was obtained. The process of extraction was shown in **Scheme 1**.



Scheme 1 Isolation of crude extract from the green fruits of *A. marmelos*

2.4 Isolation and Chemical Investigation

Acetone extract (55.0 g) was subjected to quick column chromatography using silica gel as stationary phase and eluted with 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 P1-P15. Twenty-one pure compounds were obtained as shown in **Scheme 2**.



* No further investigation

Scheme 2 Isolation of compounds **PW1-PW21** from acetone extract

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

Fraction	Weight (g)	Physical characteristic
P1	1.0283	white solid
P2	0.5929	white solid
P3	4.9487	yellow solid
P4	2.3342	brown viscous liquid
P5	1.5392	brown viscous liquid
P6	4.9652	brown viscous liquid
P7	6.1923	brown viscous liquid
P8	17.3981	brown viscous liquid
P9	1.0000	brown viscous liquid
P10	2.7849	black viscous liquid
P11	2.1317	black viscous liquid
P12	2.6605	black viscous liquid
P13	2.3373	black viscous liquid

Table 2 continued

Fraction	Weight (g)	Physical characteristic
P14	0.1626	black viscous liquid
P15	1.8644	black viscous liquid
Total	51.9403	-

Fraction P6 (4.9652 g) was further purified by column chromatography over silica gel and eluted with dichloromethane to give 7 fractions (6A-6G).

Subfraction 6B (1.0717 g), containing one major component, was recrystallized from dichloromethane-hexane (1.0:1.0) to give a white solid of **PW1**: imperatorin (0.8289 g).

Subfraction 6F (0.2795 g) was purified by column chromatography over silica gel and eluted with methanol-dichloromethane (0.2:9.8) to afford 10 fractions (6F1-6F10). Subfraction 6F9 was a white solid of **PW2**: valencic acid (0.0477 g).

Subfraction 6F3 (0.0300 g) was purified by column chromatography over silica gel and eluted with methanol-dichloromethane (0.1:9.9) to afford 5 fractions (6F3A-6F3E).

Subfraction 6F3B (0.0111 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.2:9.8) to give a white powder of **PW3**: 8-[(3"-methyl-2"-oxo-3"-buten-1-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one (0.0093 g).

Subfraction 6F5 (0.0166 g) was separated by column chromatography with Sephadex LH-20, and eluted with methanol to afford 3 fractions (6F5A-6F5C). Subfraction 6F5C gave a white solid of **PW4**: xanthotoxol (0.0115 g).

Subfraction 6F6 (0.0199 g) was separated by column chromatography with Sephadex LH-20, eluted with methanol to afford 6 fractions (6F6A-6F6F).

Subfraction 6F6D (0.0087 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.2:9.8) to give a white solid of **PW5**: isogosferol (0.0036 g).

Fraction P8 (17.3981 g) was further purified by column chromatography over silica gel and eluted with a gradient of dichloromethane-methanol of increasing polarity to give 9 fractions (8A-8I). Subfraction 8B was a white solid of **PW6**: xanthotoxin (0.0073 g).

Subfraction 8F (0.3778 mg) was purified by column chromatography over silica gel and eluted with a gradient of dichloromethane-methanol of increasing polarity to give 13 fractions (8F1-8F13). Subfraction 8F7 was a yellow solid of **PW7**: scoparone (0.048 g).

Subfraction 8H (0.2551 g) was purified by column chromatography over silica gel and eluted with a methanol-dichloromethane (0.2:9.8) to give 9 fractions (8H1-8H9).

Subfraction 8H5 (0.0505 g) was further purified by column chromatography over silica gel and eluted with methanol-dichloromethane (0.1:9.9) to give 9 fractions (8H5A-8H5I). Subfraction 8H5C was a yellow solid of **PW10**: 6-formylumbilliferone (0.0051 g).

Subfraction 8H5F (0.0197 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.2:9.8) to give a white solid of **PW8**: decursinol (0.0018 g) and white powder of **PW9**: demethylsuberosin (0.0027 g).

Fraction P9 (1.0000 g) was further purified by column chromatography over silica gel and eluted with a gradient of dichloromethane-methanol of increasing polarity to give 7 fractions (9A-9G).

Subfraction 9E (0.2688 g) was purified by column chromatography over silica gel and eluted with a methanol-dichloromethane (0.3:9.7) to give 10 fractions (9E1-9E10).

Subfraction 9E7 (0.0057 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.4:9.6) to give white powder of **PW11**: marmesiline (0.0020 g).

Subfraction 9F (0.3980 g) was purified by column chromatography over silica gel and eluted with a gradient of dichloromethane-methanol of increasing polarity to give 8 fractions (9F1-9F8). Subfraction 9F4 was white powder of **PW12**: marmesin (0.0071 g).

Subfraction 9F5 (0.0444 g) was purified by column chromatography over silica gel and eluted with methanol-dichloromethane (0.5:9.5) to give 5 fractions (9F5A-9F5E).

Subfraction 9F5C (0.0183 g) was separated by column chromatography with Sephadex LH-20 and eluted with methanol-dichloromethane (1.0:1.0) to afford 3 fractions (9F5C1-9F5C3).

Subfraction 9F5C3 (0.0140 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.3:9.7) to give white powder of **PW13**: marmeline (0.0028 g), a white powder of **PW14**: isoangenomalin (0.0022 g) and white powder of **PW15**: 6-(4'-acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin (0.0019 g).

Fraction P11 (2.1317 g) was further purified by column chromatography over silica gel and eluted with methanol-dichloromethane (1.0:9.0) to give 10 fractions (11A-11J).

Subfraction 11C (0.0597 g) was purified by column chromatography over silica gel and eluted with ethyl acetate-hexane (4.0:6.0) to give 11 fractions (11C1-11C11).

Subfraction 11C10 (0.0130 g) was further purified on preparative TLC and eluted with acetone-dichloromethane (1.0:9.0) to give white powder of **PW16**: isofraxidin (0.0032 g) and a yellow solid of **PW17**: marmelonine A (0.0039 g).

Subfraction 11E (0.1213 g) was purified by column chromatography over silica gel and eluted with methanol-dichloromethane (0.3:9.7) to give 8 fractions (11E1-11E8).

Subfraction 11E4 (0.0073 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.3:9.7) to give white powder of **PW18**: 8-hydroxysmyrindiol (0.0035 g).

Subfraction 11E7 (0.0051 g) was further purified on preparative TLC and eluted with methanol-dichloromethane (0.5:9.5) to give white powder of **PW19**: marmelonine B (0.0025 g).

Subfraction 11F (0.0851 g) was purified by column chromatography over silica gel and eluted with acetone-dichloromethane (1.5:8.5) to give 8 fractions (11F1-11F8). Subfraction 11F5 was white powder of **PW21**: xanthoarnol (0.0028 g).

Subfraction 11F4 (0.0046 g) was further purified on preparative TLC and eluted with ethyl acetate-hexane (6.0:4.0) to give white powder of **PW20**: isophellodenol C (0.0023 g).

Compound PW1: Imperatorin, white solid, m.p. 101-102℃**;** UV λ_{max} (MeOH) (log ε): 215 (4.69), 245 (4.55) and 298 (4.25) nm; IR (Neat) ν (cm^{-1}): 1713 (C=O stretching), 1623, 1587 and 1446 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 3.

Compound PW2: Valencic acid, white solid, m.p. 189-190℃**;** UV λ_{max} (MeOH) (log ε): 202 (4.51) and 249 (4.43) nm; IR (Neat) ν (cm^{-1}): 3390 (O-H stretching), 1672 (C=O stretching) and 1250 (C-O stretching). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 4.

Compound PW3: 8-[(3"-methyl-2"-oxo-3"-buten-1-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one, white powder, m.p. 145-146℃**;** UV λ_{max} (MeOH) (log ε): 220 (4.66), 249 (4.56) and 300 (4.32) nm; IR (Neat) ν (cm^{-1}): 1728, 1680 (C=O stretching), 1623, 1587 and 1446 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 5.

Compound PW4: Xanthotoxol, white solid, m.p. 246-247 ℃**;** UV λ_{max} (MeOH) (log ε): 219 (4.25), 250 (4.41), 261 (4.53), 268 (4.59) and 307 (4.74) nm; IR (Neat) ν (cm^{-1}): 3307 (O-H stretching), 1705 (C=O stretching), 1594, 1447 and 1414 (aromatics). For ^{1}H NMR ($CDCl_3$+CD_3OD (1 drop), 300 MHz) and ^{13}C NMR ($CDCl_3$+CD_3OD (1 drop), 75 MHz) spectral data, see Table 6.

Compound PW5: Isogosferol, white solid, m.p. 166-167 ℃**;** UV λ_{max} (MeOH) (log ε): 218 (4.31), 249 (4.53) and 299 (4.69) nm; IR (Neat) ν (cm^{-1}): 3413 (O-H stretching), 1721 (C=O stretching), 1620, 1588 and 1442 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 7.

Compound PW6: Xanthotoxin, white solid, m.p. 147-148 ℃**;** UV λ_{max} (MeOH) (log ε): 217 (4.33), 253 (4.41) and 299 (4.50) nm; IR (Neat) ν (cm^{-1}): 1716 (C=O stretching), 1617, 1580 and 1456 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 8.

Compound PW7: Scoparone, yellow solid, m.p. 148-149 ℃**;** UV λ_{max} (MeOH) (log ε): 203 (4.23), 285 (4.57) and 338 (4.54) nm; IR (Neat) ν (cm^{-1}): 1719 (C=O stretching), 1618, 1514 and 1456 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 9.

Compound PW8: (+) Decursinol, white solid, m.p. 170-171℃, $[\alpha]_D^{25}$ = +8.7° (*c* = 0.53, $CHCl_3$)**;** UV λ_{max} (MeOH) (log ε): 205 (4.66) and 331 (4.29) nm; IR (Neat) ν (cm^{-1}): 3410 (O-H stretching), 1717 (C=O stretching), 1625, 1563 and 1488 (aromatics). For ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectral data, see Table 10.

Compound PW9: Demethylsuberosin, white powder, m.p. 132-133℃**;** UV λ_{max} (MeOH) (log ε): 205 (4.40), 224 (4.35), 238 (4.39) and 330 (4.25) nm; IR (Neat) ν (cm^{-1}): 3420 (O-H stretching), 1717 (C=O stretching), 1625, 1571 and 1489 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 11.

Compound PW10: 6-Formylumbilliferone, yellow solid, m.p. 148-150 ℃**;** UV λ_{max} (MeOH) (log ε): 202 (4.69), 257 (4.58), 336 (4.33) and 392 (3.97) nm; IR (Neat) ν (cm^{-1}): 3484 (O-H stretching), 1741 and 1665 (C=O stretching), 1627, 1559, 1459 (aromatics). For ^{1}H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 12.

Compound PW11: Marmesiline, white powder, m.p. 163-164℃, $[\alpha]_D^{25}$ = +2.3℃(*c* = 0.5, $CHCl_3$)**;** UV λ_{max} (MeOH) (log ε): 217 (3.59), 223 (3.58) and 272 (3.43) nm; IR (Neat) ν (cm^{-1}): 3417 (O-H stretching), 1661 (C=O stretching), 1621, 1539, 1456 (aromatics). For ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectral data, see Table 13.

Compound PW12: (+) Marmesin, white powder, m.p. 170-171℃, $[\alpha]_D^{26}$ = +20.6° (*c* = 0.9, $CHCl_3$)**;** UV λ_{max} (MeOH) (log ε): 203 (4.44) and 330 (4.25) nm; IR (Neat) ν (cm^{-1}): 3441 (O-H stretching), 1704 (C=O stretching), 1627, 1563, 1503 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 14.

Compound PW13: Marmeline, white powder, m.p. 128-129 ℃**;** UV λ_{max} (MeOH) (log ε): 202 (4.34), 224 (4.42) and 274 (4.44) nm; IR (Neat) ν (cm^{-1}): 3259 (O-H stretching), 1660 (C=O stretching), 1619, 1569, 1443 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 15.

Compound PW14: Isoangenomalin, white powder, m.p. 120-121 ℃, $[\alpha]_D^{26}$ = +9.7° (*c* = 1.0, $CHCl_3$)**;** UV λ_{max} (MeOH) (log ε): 203 (4.51), 287 (4.48) and 329 (3.43) nm; IR (Neat) ν (cm^{-1}): 1711 (C=O stretching), 1620, 1567, 1401 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 16.

Compound PW15: 6-(4'-Acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin, white powder, m.p. 133-134℃**;** UV λ_{max} (MeOH) (log ε): 205 (4.18), 297 (3.58) and 330 (3.70) nm; IR (Neat) ν (cm^{-1}): 3392 (O-H stretching), 1720 (C=O stretching), 1618, 1570, 1421 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 17.

Compound PW16: Isofraxidin, white powder, m.p. 151-152℃**;** UV λ_{max} (MeOH) (log ε): 207 (4.55), 343 (4.27) and 383 (4.19) nm; IR (Neat) ν (cm^{-1}): 3356 (O-H stretching), 1712 (C=O stretching), 1606, 1576, 1498 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 18.

Compound PW17: Marmelonine A, yellow solid, m.p. 195-196℃, $[\alpha]_D^{26}$ = -3.8° (*c* = 1.0, MeOH)**;** UV λ_{max} (MeOH) (log ε): 205 (4.41), 257 (3.57) and 325 (3.95) nm; IR (Neat) ν (cm^{-1}): 3415 (O-H stretching), 1721 (C=O stretching), 1625, 1575, 1491 (aromatics). For ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz) spectral data, see Table 19.

Compound PW18: 8-Hydroxysmyrindiol, white powder, m.p. 179-180℃, $[\alpha]_D^{26}$ = +20.1° (*c* = 1.0, MeOH)**;** UV λ_{max} (MeOH) (log ε): 210 (4.39), 268 (3.72) and 326 (3.99) nm; IR (Neat) ν (cm^{-1}): 3393 (O-H stretching), 1707 (C=O stretching), 1623, 1588, 1418 (aromatics). For ^{1}H NMR ($CDCl_3$+CD_3OD (1 drop), 300 MHz) and ^{13}C NMR ($CDCl_3$+CD_3OD (1 drop), 75 MHz) spectral data, see Table 20.

Compound PW19: Marmelonine B, white powder, m.p. 279-280℃**;** UV λ_{max} (MeOH) (log ε): 205 (4.42), 256 (3.49) and 331 (3.93) nm; IR (Neat) ν (cm^{-1}): 3432 (O-H stretching), 1726 (C=O stretching), 1621, 1557, 1488 (aromatics). For ^{1}H NMR ($CDCl_3$+CD_3OD (1 drop), 300 MHz) and ^{13}C NMR ($CDCl_3$+CD_3OD (1 drop), 75 MHz) spectral data, see Table 21.

Compound PW20: Isophellodenol C, white powder, m.p. 140-141℃, $[\alpha]_D^{26}$ = +39.7° (*c* = 1.0, MeOH)**;** UV λ_{max} (MeOH) (log ε): 204 (4.44) and 331 (4.32) nm; IR (Neat) ν (cm^{-1}): 3335 (O-H stretching), 1717 (C=O stretching), 1617, 1570, 1457 (aromatics). For ^{1}H NMR ($CDCl_3$+CD_3OD (1 drop), 300 MHz) and ^{13}C NMR ($CDCl_3$+CD_3OD (1 drop), 75 MHz) spectral data, see Table 22.

Compound PW21: Xanthoarnol, white powder, m.p. 178-179℃, $[\alpha]_D^{26}$ = +33.1° (*c* = 0.4, acetone)**;** UV λ_{max} (MeOH) (log ε): 204 (4.67), 224 (4.62), 248, (4.56) and 331 (4.47) nm; IR (Neat) ν (cm^{-1}): 3392 (O-H stretching), 1715 (C=O stretching), 1627, 1572, 1488 (aromatics). For ^{1}H NMR ($CDCl_3$+CD_3OD (1 drop), 300 MHz) and ^{13}C NMR ($CDCl_3$+CD_3OD (1 drop), 75 MHz) spectral data, see Table 23.

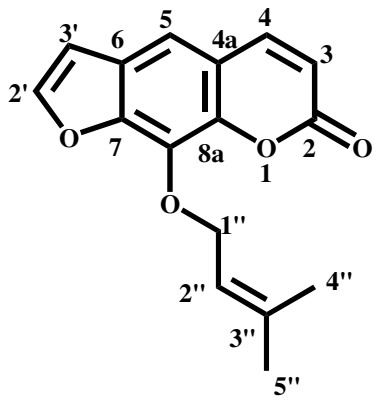
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Structure elucidation of compounds from the green fruits of *A. marmelos*

The crude acetone extract from the green fruits of *A. marmelos* was subjected to quick column chromatography and repeated column chromatography over silica gel to furnish twenty-one compounds: imperatorin **(PW1**), valencic acid **(PW2)**, 8-[(3"-methyl-2"-oxo-3"-buten-1-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one **(PW3)**, xanthotoxol **(PW4)**, isogosferol **(PW5)**, xanthotoxin **(PW6)**, scoparone **(PW7)**, decursinol **(PW8)**, demethylsuberosin **(PW9)**, 6-formylumbilliferone **(PW10)**, marmesiline **(PW11)**, marmesin **(PW12)**, marmeline **(PW13)**, isoangenomalin **(PW14)**, 6-(4'-acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin (**PW15**), isofraxidin **(PW16)**, marmelonin A **(PW17),** 8-hydroxysmyrindiol (**PW18**), marmelonin B **(PW19)**, isophellodenol C **(PW20)** and xanthoarnol **(PW21)**.

Their structures were elucidated mainly by 1D and 2D NMR spectroscopic data: ^{1}H, ^{13}C NMR, DEPT 135°, DEPT 90°, HMQC, HMBC, COSY and NOESY. Mass spectra were determined for the new compounds: **PW11**, **PW15**, and **PW17-PW19**. The physical data of the known compounds were also compared with the reported values.

Compound PW1



PW1 was isolated as a white solid, m.p. 101-102℃ (lit.102 ℃). The UV spectrum exhibited the presence of a linear-type furanocoumarin at 215, 245, 263 and 298 nm. The IR spectrum indicated the presence of a lactone carbonyl at 1718 cm^{-1}, aromatic ring at 1691, 1587 and 1446 cm^{-1} and furan ring at 887 cm^{-1}.

The ^{1}H NMR spectral data **(Table 3)** of **PW1** exhibited the signal of two pairs of downfield doublets, one at δ_H 7.74 and 6.31 (1H each, d, J = 9.6 Hz) attributable to H-4 and H-3 of the coumarin nucleus while the second pair of signals at δ_H 7.65 and 6.78 (1H each, d, J = 2.2 Hz, H-2' and H-3') confirmed the presence of the benzofuran moiety. The singlet aromatic proton signal at δ_H 7.32 was assigned to H-5. The upfield region exhibited an oxyprenyl side chain which contained two methyl groups at δ_H 1.67 (3H, s) and 1.68 (3H, s) of H-4" and H-5", one methine proton at δ_H 5.56 (1H, t, J = 7.2 Hz, H-2") and methylene protons at δ_H 4.95 (2H, d, J = 7.2 Hz, H-1").

The ^{13}C NMR **(Table 3)** and DEPT spectral data displayed signal corresponded sixteen carbon atoms, among which were 11 sp^2 carbon atoms of furanocoumarin nucleus and the five-carbon side chain which included two methyl carbons at δ_C 17.9, 25.6, one quaternary carbon at δ_C 139.4, one methine carbon at δ_C 119.6 and one oxymethylene carbon at δ_C 69.9. The assignment of the coumarin was confirmed by HMBC correlation of H-4 (δ_H 7.74) with δ_C 160.4 (C-2), 113.1 (C-5) and 143.5 (C-8a), of H-3 (δ_H 6.31) with δ_C 160.4 (C-2) and 116.2 (C-4a), whereas that of a benzofuran ring was confirmed by HMBC correlations of H-2' (δ_H 7.65) with δ_C 125.7 (C-6) and 148.3 (C-7), of H-3' (δ_H 6.78) with δ_C 146.4 (C-2') and 148.3 (C-

7), of H-5 (δ_H 7.32) with δ_C 106.6 (C-3'), 148.3 (C-7) 144.3 (C-4) and 143.5 (C-8a). The oxyprenyl group was attached at C-8 due to the correlation between a proton signal at δ_H 4.95 (H-1") with δ_C 131.3 (C-8) as well as with δ_C 119.6 (C-2") and 139.4 (C-3"). Based on these data, the structure of **PW1** was assigned as imperatorin (Razdan *et al*., 1987).

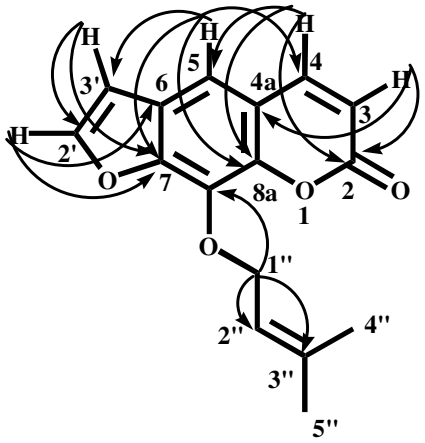


Figure 2 Selected HMBC correlations of **PW1**

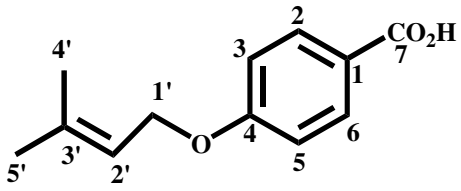
Table 3 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW1** ($CDCl_3$)

Position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	160.4 (C)	-
3	6.31 (d, *J* = 9.6 Hz)	114.3 (CH)	C-2, C-4a
4	7.74 (d, *J* = 9.6 Hz)	144.3 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	116.2 (C)	-
5	7.32 (s)	113.1 (CH)	C-4, C-6, C-7, C-8, C-4a, C-8a, C-3’
6	-	125.7 (C)	-
7	-	148.3 (C)	-
8	-	131.3 (C)	-
8a	-	143.5 (C)	-
1′	-	-	-
2′	7.65 (d, *J* = 2.2 Hz)	146.4 (CH)	C-6, C-7, C-3′
3′	6.78 (d, *J* = 2.2 Hz)	106.6 (CH)	C-6, C-7, C-2′
1″	4.95 (d, *J* = 7.2 Hz)	69.9(CH_2)	C-8, C-2″, C-3″

Table 3 continued

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
2″	5.56 (d, J = 7.2 Hz)	119.6 (CH)	C-4″, C-5″
3″	-	139.4 (C)	-
4″	1.67 (s)	17.9 (CH_3)	C-2″, C-3″, C-4″, C-5″
5″	1.68 (s)	25.6 (CH_3)	C-2″, C-3″, C-4″, C-5″

Compound PW2



PW2 was isolated as a white solid, m.p. 189-190℃. The UV spectrum exhibited the absorption bands at 202 and 249 nm. The IR spectrum showed absorption bands for hydroxyl at 3390 cm^{-1}, carbonyl group at 1672 cm^{-1}, and ether at 1250 cm^{-1}.

The ^{1}H NMR spectral data **(Table 4)** of **PW2** showed the signals of AA′BB′ aromatic system at δ_H 6.94 (2H, d, J = 8.9 Hz) and δ_H 8.04 (2H, d, J = 8.9 Hz) of H-4, H-6 and H-3, H-7 respectively, which was a characteristic of a *para*-disubstituted benzene. The substituent at C-5 was identified as an oxyprenyl group according to these signals: two singlets at δ_H 1.75 and 1.80 (3H each, s, H-4' and H-5', respectively) for two methyl protons, one doublet at δ_H 4.57 (2H, d, J = 6.7 Hz, H_2-1') for methylene protons and one triplet at δ_H 5.48 (1H, t, J = 6.7 Hz, H-2') for a methine proton.

The ^{13}C NMR spectral data **(Table 4)** exhibited 10 carbon signals, of which four [δ_C 114.3 (C-4), 121.6 (C-2), 132.2 (C-3) and 163.3 (C-5)] were attributed to aromatic ring, whereas five [δ_C 18.2 (C-5'), 25.8 (C-4'), 65.0 (C-1'), 118.9 (C-2') and 138.8 (C-3')] were characteristic of the carbons an oxyprenyl side chain. A signal of carboxyl carbon was shown at δ_C 171.6 (C-1). The locations of an oxyprenyl side chain at C-5 was confirmed by HMBC correlations of H_2-1' (δ_H 4.57) with δ_C 163.3 (C-5), 118.9 (C-7) and 138.8 (C-8), whereas that of a carboxyl group at C-2 was confirmed by HMBC correlations of H-3 (δ_H 8.04) with δ_C 171.6 (C-1), 121.6 (C-2), 114.3 (C-4) and 163.3 (C-5). Accordingly, the structure of **PW2** was assigned as valencic acid (Ito *et al*., 1988).

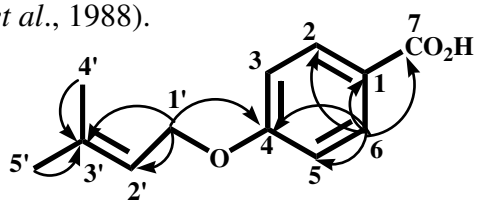


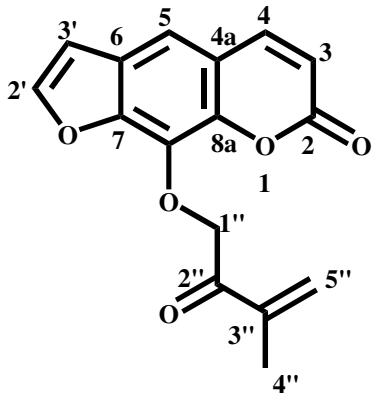
Figure 3 Selected HMBC correlations of **PW2**

Table 4 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW2** ($CDCl_3$)

Position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	121.6 (C)	-
2,6	8.04 (d, J = 8.9 Hz)	132.2 (CH)	C-1, C-2, C-4, C-5
3,5	6.94 (d, J = 8.9 Hz)	114.3 (CH)	C-1, C-2, C-3, C-5
4	-	163.3 (C)	-
7	-	171.6 (C)	-
1'	4.57 (d, J = 6.7 Hz)	65.0 (CH_2)	C-5, C-7, C-8
2'	5.48 (t, J = 6.7 Hz)	118.9 (CH)	C-6, C-9, C-10
3'	-	138.8 (C)	-
4'	1.80 (s)*	25.8 (CH_3)	C-7, C-8, C-10
5'	1.75 (s)*	18.2 (CH_3)	C-6, C-7, C-8, C-9

* May be interchangeable

Compound PW3



PW3 was isolated as white powder, m.p. 145-146℃. The UV spectrum exhibited the presence of a linear-type furanocoumarin at 220, 249 and 300 nm. The IR spectrum indicated the presence of a lactone carbonyl at 1728 cm^{-1}, a keto carbonyl at 1680 cm^{-1}, aromatic ring at 1623, 1587 and 1446 cm^{-1} and furan ring at 871 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 5)** of **PW3** showed the signals of a furanocoumarin which were similar to those of compound **PW1 (Table 3)**. The difference was shown as the absence of signals for a dimethylallyl side chain as in **PW1** but the presence of a 3-methyl-2-oxo-3-butenyl side chain in **PW3**. The ^{1}H NMR signals of the latter side chain were shown as a singlet methylene protons at δ_H 5.52: δ_C 73.5, olefinic methylene protons at δ_H 5.83 and 5.98: δ_C 125.3 and a methyl singlet at δ_H 1.85: δ_C 17.5 including a carbonyl carbon at δ_C 195.3. The oxybutenyl side chain was placed at C-8 from HMBC correlations **(Table 5)** of the methylene protons at δ_H 5.52 (H_2-1") with the signals at δ_C 131.1 (C-8), δ_C 195.3 (C-2") and δ_C 142.1 (C-3"). Therefore, compound **PW3** was assigned as 8-[(3"-methyl-2"-oxo-3"-buten-1"-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one (De Mol *et al*., 1984).

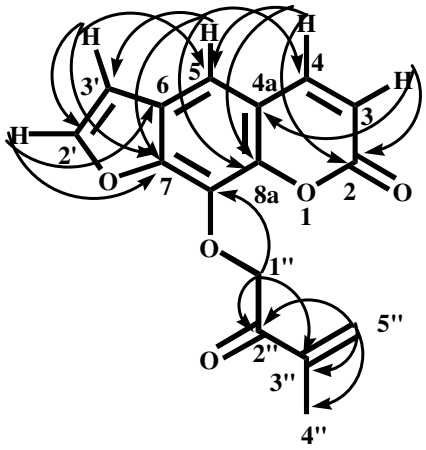
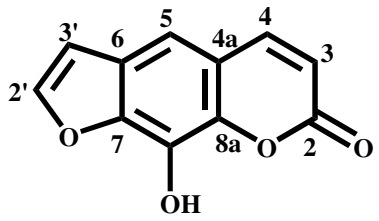


Figure 4 Selected HMBC correlations of **PW3**

Table 5 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW3** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	160.1 (C)	-
3	6.29 (d, J = 9.6 Hz)	114.7 (CH)	C-2, C-4a
4	7.69 (d, J = 9.6 Hz)	144.3 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	116.5 (C)	-
5	7.28 (s)	113.2 (CH)	C-4, C-6, C-7, C-8, C-4a, C-8a, C-3′
6	-	126.0 (C)	-
7	-	147.1 (C)	-
8	-	131.1 (C)	-
8a	-	142.5 (C)	
1′	-	-	-
2′	7.58 (d, J = 2.2 Hz)	146.7 (CH)	C-6, C-7, C-3′
3′	6.73 (d, J = 2.2 Hz)	106.7 (CH)	C-5, C-6, C-2′
1″	5.52 (s)	73.5 (CH_2)	C-8, C-2″, C-3″
2″	-	195.3 (C)	-
3″	-	142.1 (C)	-
4″	1.85 (s)	17.5 (CH_3)	C-2″, C-3″, C-5″
5″	5.83 (d, J = 1.4 Hz)	125.3 (CH_2)	C-2″, C-3″, C-4″
	5.98 (s)		

Compound PW4



PW4 was isolated as a white solid, m.p. 246-247 ℃ (lit. 248 ℃). The UV spectrum indicated the presence of a linear-type furanocoumarin at maximum absorptions 219, 250, 261, 268 and 307 nm. The IR spectrum showed absorptions of hydroxyl at 3307 cm^{-1}, lactone carbonyl at 1705 cm^{-1}, aromatic ring at 1594, 1447 and 1414 cm^{-1} and furan ring at 864 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 6)** of **PW4** were comparable to those of **PW3**, except for the absence of signals for an oxyoxobutenyl side chain ($OCH_2COC(CH_3)=CH_2$). Since the ^{1}H NMR spectrum of **PW4** displayed only five proton resonance signals, it was possible to conclude that there was a hydroxyl group positioned at C-8 (δ_C 130.5). The complete HMBC correlations were summarized in **Table 6**. Therefore, compound **PW4** was assigned as xanthotoxol (Razdan *et al*., 1987).

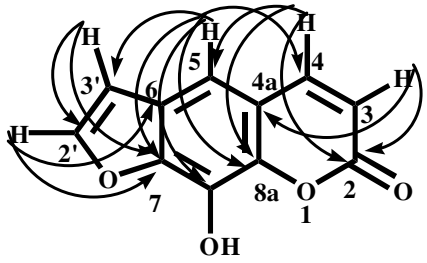
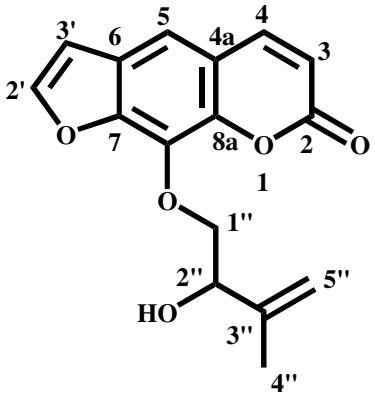


Figure 5 Selected HMBC correlations of **PW4**

Table 6 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW4** ($CDCl_3$+CD_3OD (1 drop))

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	161.9 (C)	-
3	6.28 (d, J = 9.5 Hz)	113.4 (CH)	C-2, C-4a
4	7.78 (d, J = 9.5 Hz)	145.7 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	116.0 (C)	-
5	7.16 (s)	109.8 (CH)	C-4, C-6, C-7, C-8, C-4a, C-8a, C-3′
6	-	125.9 (C)	-
7	-	145.6 (C)	-
8	-	130.5 (C)	-
8a	-	139.3 (C)	-
1′	-	-	-
2′	7.64 (d, J = 2.1 Hz)	146.8 (CH)	C-6, C-7, C-3′
3′	6.73 (d, J = 2.1 Hz)	106.6 (CH)	C-5, C-6, C-7, C-2′

Compound PW5



PW5 was isolated as a white solid, m.p 166-167 ℃. The UV spectrum exhibited the presence of a linear-type furanocoumarin at 218, 249 and 299 nm. The IR spectrum indicated the presence of a hydroxyl group at 3413 cm^{-1}, lactone carbonyl at 1721 cm^{-1}, aromatic ring at 1620, 1588 and 1442 cm^{-1} and furan ring at 871 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 7)** of **PW5** were similar to those of **PW3** except in the side chain. A 3-methyl-2-oxo-3-butenyl side chain of **PW3** was replaced by a 3-methyl-2-hydroxy-3-butenyl side chain in **PW5**. The signals of the latter side chain were shown as an oxymethine proton at δ_H 4.47 (dd, J = 8.3, 2.8 Hz, H-2"), oxymethylene protons at δ_H 4.53 (dd, J = 9.9, 2.8 Hz, H-1") and δ_H 4.25 (dd, J = 9.9, 8.3 Hz, H-1"), a methyl singlet at δ_H 1.76 (Me-4") and terminal olefinic methylene protons H_2-5" at δ_H 4.93 (d, J = 0.6 Hz) and 5.10 (s). The side chain was placed at C-8 of furanocoumarin moiety due to HMBC correlation of H_2-1" (δ_H 4.53) with C-8 (δ_C 131.6). Based on these data, the structure of **PW5** was assigned as isogosferol (Adebajo *et al*., 2000).

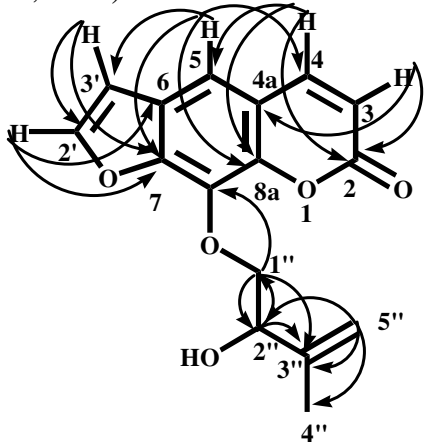
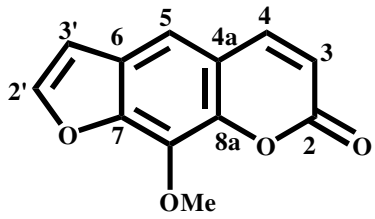


Figure 6 Selected HMBC correlations of **PW5**

Table 7 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW5** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	160.3 (C)	-
3	6.31 (d, J = 9.6 Hz)	114.7 (CH)	C-2, C-4a
4	7.72 (d, J = 9.6 Hz)	144.4 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	116.5 (C)	-
5	7.33 (s)	113.7 (CH)	C-4, C-6, C-7, C-8, C-4a, C-8a, C-3′
6	-	126.0 (C)	-
7	-	148.0 (C)	-
8	-	131.6 (C)	-
8a	-	143.4 (C)	-
1′	-	-	-
2′	7.63 (d, J = 2.2 Hz)	146.8 (CH)	C-6, C-7, C-3′
3′	6.77 (d, J = 2.2 Hz)	106.8 (CH)	C-5, C-6, C-7, C-2′
1″	4.53 (dd, J = 9.9, 2.8 Hz)	77.3 (CH_2)	C-8, C-2″, C-3″
	4.25 (dd, J = 9.9, 8.3 Hz)	-	C-8, C-2″, C-3″
2″	4.47 (dd, J = 8.3, 2.8 Hz)	73.8 (CH)	C-1″, C-3″
3″	-	142.8 (C)	-
4″	1.76 (s)	19.0 (CH_3)	C-2″, C-3″, C-5″
5″	4.93 (d, J = 0.6 Hz)	112.8 (CH_2)	C-2″, C-4″
	5.10 (s)		C-2″, C-3″, C-4″

Compound PW6



PW6 was isolated as a white solid, m.p. 147-148 ℃ (lit. 147 ℃). The UV spectrum exhibited the absorption bands at 217, 253 and 299 nm. The IR spectrum showed absorption bands for lactone carbonyl at 1716 cm^{-1}, aromatic ring at 1617, 1580 and 1456 cm^{-1} and furan ring at 750 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 8)** of **PW6** were closely related to compound **PW4**, except that **PW6** had an additional singlet signal of methoxyl protons at δ_H 4.15 (3H, s) (δ_C 60.9). The position of the methoxyl group at C-8 was determined through HMBC correlations of δ_H 4.15 (8-OMe) with the signal at δ_C 132.3 (C-8). Based on these data, the structure of **PW6** was assigned as xanthotoxin (Razdan *et al*., 1987).

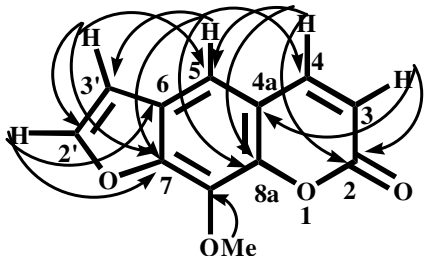
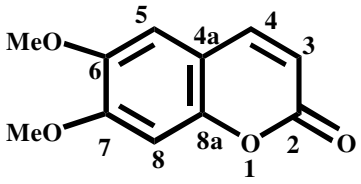


Figure 7 Selected HMBC correlations of **PW6**

Table 8 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW6** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	160.2 (C)	-
3	6.22 (d, J = 9.6 Hz)	114.2 (CH)	C-2, C-8a
4	7.66 (d, J = 9.6 Hz)	144.3 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	116.1 (C)	-
5	7.21 (s)	112.8 (CH)	C-4, C-6, C-7, C-8, C-4a, C-8a, C-3′
6	-	125.9 (C)	-
7	-	147.2 (C)	-
8	-	132.3 (C)	-
8a	-	142.5 (C)	-
1′	-	-	-
2′	7.57 (d, J = 2.2 Hz)	146.4 (CH)	C-6, C-7, C-3′
3′	6.70 (d, J = 2.2 Hz)	106.5 (CH)	C-6, C-7, C-2′
8-OMe	4.15 (s)	60.9 (CH_3)	C-8

Compound PW7



PW7 was isolated as a yellow solid, m.p. 148-149 ℃ (lit. 147 ℃). The UV spectrum exhibited the absorption bands characteristic of coumarin at 203, 285 and 338 nm. The IR spectrum showed absorption bands for lactone carbonyl at 1719 cm^{-1} and aromatic ring at 1618, 1514 and 1456 cm^{-1}.

The ^{1}H NMR spectral data **(Table 9)** of **PW7** showed the signals of a typical pair of doublets at δ_H 6.25 and 7.61 (1H each, d, J = 9.6 Hz,) for H-3 and H-4, respectively, and two uncoupled aromatic protons at δ_H 6.84 and 6.79 (1H each, s) of H-5 and H-8, characteristic of 1, 2, 4, 5-tetrasubstituted benzene. In addition, the ^{1}H NMR spectrum exhibited two methoxyl singlet signals at δ_H 3.89 and 3.92 (3H each), indicating that these two methoxyl groups were attached to C-6 and C-7 in coumarin moiety.

The ^{13}C NMR **(Table 9)** and DEPT spectral data exhibited 11 carbon resonances including two methoxyl groups at δ_C 56.2 (2 × OCH_3), two olefinic methine carbons at δ_C 113.4 (C-3) and 143.3 (C-4), two aromatic methine carbons at δ_C 107.9 (C-5) and 99.8 (C-8), four quaternary aromatic carbons at δ_C 111.3 (C-4a), 152.7 (C-6), 146.2 (C-7) and 149.8 (C-8a), and one carbonyl carbon at δ 161.3 (C-2). In HMBC correlations two methoxyl proton signals at δ_H 3.92 and 3.89 showed correlations with the signals at δ_C152.7 (C-7) and 146.2 (C-6), respectively, as well as correlations from δ_H 6.84 (H-5) and 6.79 (H-8) to δ_C 152.7 (C-7) and 146.2 (C-6) which confirmed that these methoxyl groups were located at the C-7 and C-6, respectively. Based on these data, the structure of **PW7** was assigned as scoparone (Razdan *et al*., 1987).

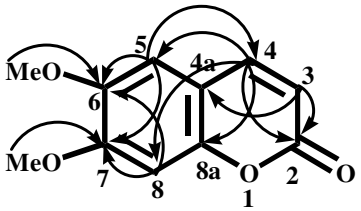


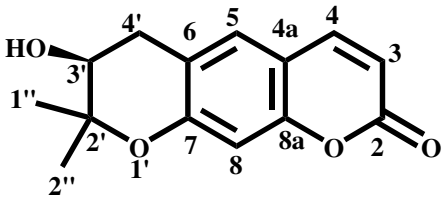
Figure 8 Selected HMBC correlations of **PW7**

Table 9 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW7** ($CDCl_3$)

Position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	161.3 (C)	-
3	6.25 (d, J = 9.5 Hz)	113.4 (CH)	C-2, C-4a
4	7.61(d, J = 9.5 Hz)	143.3 (CH)	C-2, C-5, C-8, C-8a
4a	-	111.3 (C)	-
5	6.84 (s)	107.9 (CH)	C-4, C-6, C-7, C-8a
6	-	146.2 (C)	-
7	-	152.7 (C)	-
8	6.79 (s)	99.8 (CH)	C-6, C-7, C-4a, C-8a
8a	-	149.8 (C)	-
6-OMe	3.89 (s)*	56.2 (CH_3)	C-6
7-OMe	3.92 (s)*	56.2 (CH_3)	C-7

* May be interchangeable

Compound PW8



PW8 was isolated as a white solid, m.p. 170-171℃, $[\alpha]_D^{25}$ = +8.7° (*c* = 0.53, $CHCl_3$) (lit. $[\alpha]_D^{22}$ = +6.8° (*c* = 0.65, $CHCl_3$)). The UV spectrum exhibited the absorption bands characteristic of coumarin at 205 and 331 nm. The IR spectrum showed absorption bands for hydroxyl group at 3410 cm^{-1}, lactone carbonyl at 1717 cm^{-1} and aromatic ring at 1625, 1563 and 1488 cm^{-1}.

In the ^{1}H NMR spectra of **PW8**, characteristic signals were observed for a geminal dimethyl group at δ_H 1.30 and 1.33 (3H each, s), a C*H*$_2$-C*H*-*O* system (δ_H 2.77 and 3.04, each 1H, H-4' and δ_H 3.81, 1H, H-3'), two aromatic *para* protons at δ_H 6.72 and 7.11 (1H each, s), and H-3 and H-4 of the coumarin nucleus (δ_H 6.16 and 7.51, each 1H, d, *J* = 9.5 Hz), showing that **PW8** contained the decursinol moiety, a dihydropyranocoumarin.

The ^{13}C NMR **(Table 10)** and DEPT spectral data exhibited 14 carbons signal, attributable to five methine, one methylene, two methyl and six quaternary carbons. The key HMBC correlations between H-3' (δ_H 3.81) and C-6 (δ_C 116.4), H-4' (δ_H 2.77 and 3.04) and C-5 (δ_C 129.0), C-7 (δ_C 156.5) and C-2' (δ_C 78.2) suggested that the 2,2-dimethylpyran ring was fused to the coumarin nucleus with linear orientation at C-6 and C-7. Based on these data, the structure of **PW8** was assigned as (+) decursinol (Nemoto *et al*., 2003).

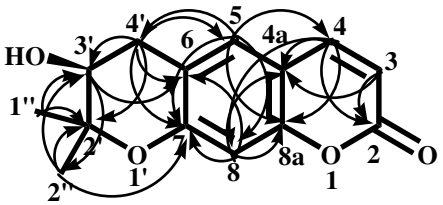
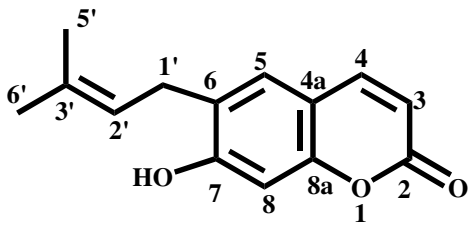


Figure 9 Selected HMBC correlations of **PW8**

Table 10 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW8** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	161.3 (C)	-
3	6.16 (d, J = 9.5 Hz)	113.4 (CH)	C-2, C-4a
4	7.51 (d, J = 9.5 Hz)	143.1 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	113.0 (C)	-
5	7.11 (s)	129.0 (CH)	C-4, C-7, C-8, C-4a, C-8a, C-1′
6	-	116.4 (C)	-
7	-	156.5 (C)	-
8	6.72 (s)	104.8 (CH)	C-6, C-7, C-4a, C-8a, C-1′
8a	-	154.2 (C)	-
4′	2.77 (dd, J = 16.7, 5.8 Hz)	30.7 (CH_2)	C-5, C-6, C-7, C-2′, C-3′
	3.04 (dd, J = 16.7, 4.7 Hz)		
3′	3.81 (dd, J = 5.8, 4.7 Hz)	69.2 (CH)	C-6, C-1", C-2″
2′	-	78.2 (C)	-
1	-	-	-
1″	1.30 (s)	25.0 (CH_3)	C-2′, C-3′, C-2″
2″	1.33 (s)	22.1 (CH_3)	C-7, C-2′, C-3′, C-1″

Compound PW9



PW9 was isolated as a white powder, m.p.132-133℃ (lit. 134-136 ℃). The UV spectrum exhibited the absorption bands characteristic of coumarin at 205, 224, 238 and 330 nm. The IR spectrum showed absorption bands for hydroxyl group at 3420 cm^{-1}, lactone carbonyl at 1717 cm^{-1} and aromatic ring at 1625, 1571 and 1489 cm^{-1}.

The ^{1}H NMR spectral data (**Table 11**) of **PW9** showed the signals of 6,7-disubstituted coumarin unit at δ_H 6.16 (1H, d, J = 9.4 Hz, H-3), 7.55 (1H, d, J = 9.4 Hz, H-4), 7.12 (1H, s, H-5), 6.77 (1H, s, H-8). An isoprenyl group was shown as signals at δ_H 3.31 (2H, d, J = 7.2 Hz, H-1'), 5.24 (1H, t, J = 7.2 Hz, H-2'), 1.73, 1.71 (3H each, s, H-5', H-6'), whose HMBC correlations of H_2-1' at δ_H 3.31 with the carbons at δ_C 135.7 (C-3'), 120.8 (C-2'), 158.3 (C-7), 124.8 (C-6) and 128.4 (C-5), indicated a connection of an isoprenyl group at C-6 and a hydroxyl group at C-7 Therefore, compound **PW9** was assigned as demethylsuberosin (Patre *et al*., 2009).

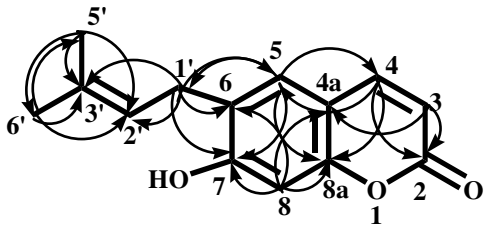
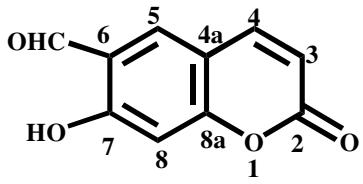


Figure 10 Selected HMBC correlations of **PW9**

Table 11 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW9** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	162.8 (C)	-
3	6.16 (d, J = 9.4 Hz)	112.4 (CH)	C-2, C-4a
4	7.55 (d, J = 9.4 Hz)	143.7 (CH)	C-2, C-5, C-8a
4a	-	112.5 (C)	-
5	7.12 (s)	128.4 (CH)	C-4, C-7, C-8a, C-1'
6	-	124.8 (C)	-
7	-	158.3 (C)	-
8	6.77 (s)	103.4 (CH)	C-6, C-7, C-4a, C-8a
8a	-	154.3 (C)	-
1´	3.31 (d, J = 7.2 Hz)	28.9 (CH_2)	C-5, C-6, C-7, C-2´, C-3´
2´	5.24 (t, J = 7.2 Hz)	120.8 (CH)	-
3´	-	135.7 (C)	-
5'	1.73 (s)	25.8 (CH_3)	C-2´, C-3´, C-6'
6'	1.71 (s)	17.9 (CH_3)	C-2´, C-3´, C-5'

Compound PW10



PW10 was isolated as a yellow solid, m.p. 148-150 ℃. The UV spectrum exhibited the absorption bands characteristic of coumarin at 202, 257, 336 and 392 nm. The IR spectrum showed absorption bands for hydroxyl group at 3484 cm^{-1}, lactone carbonyl at 1741 cm^{-1}, aldehyde group at 1665 cm^{-1} and aromatic ring at 1627, 1559 and 1459 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 12)** of **PW10** were similar to those of **PW9** except for the disappearance of the signals of an isoprenyl group at C-6 and appearance of a singlet of an aldehydic group at δ_H 9.86 (1H, s, CHO-6). A chelated proton singlet signal of a phenolic hydroxyl at C-7 was displayed at δ_H 11.34. The location of the aldehyde group at C-6 was assigned by HMBC correlations **(Figure 12)** of the aldehyde proton at δ_H 9.86 to the carbons at δ_C 134.5 (C-5), 118.3 (C-6), 164.5 (C-7) and 105.2 (C-8), and phenolic hydroxyl proton showed correlations with the carbons at δ_C 118.3 (C-6), 164.5 (C-7), 105.2 (C-8) and 159.8 (C-8a). The complete HMBC data were summarized in **Table 12**. Therefore, compound **PW10** was identified as 6-formylumbilliferone (Ito *et al*, 1988).

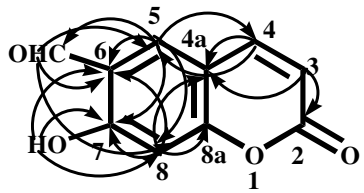
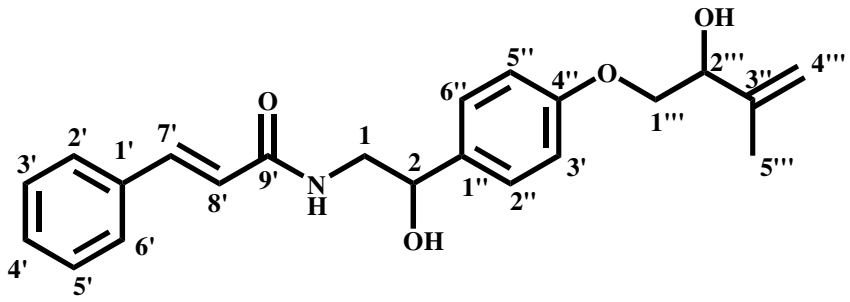


Figure 11 Selected HMBC correlations of **PW10**

Table 12 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW10** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	159.5 (C)	-
3	6.27 (d, *J* = 9.6 Hz)	114.6 (CH)	C-2, C-4a
4	7.61 (d, *J* = 9.6 Hz)	142.4 (CH)	C-5, C-4a, C-8a
4a	-	112.6 (C)	-
5	7.66 (s)	134.5 (CH)	C-4, C-7, C-8a, C-1´
6	-	118.3 (C)	-
7	-	164.5 (C)	-
8	6.82 (s)	105.2 (CH)	C-6, C-7, C-4a, C-8a
8a	-	159.8 (C)	-
6-CHO	9.86 (s)	194.5 (CH)	C-5, C-7, C-8
7-OH	11.34 (s)	-	C-6, C-7, C-8, C-8a, C-4a

Compound PW11



PW11 was isolated as a white powder, m.p. 163-164 ℃. The UV spectrum exhibited the absorption bands characteristic of cinnamide moiety at 217, 223 and 272 nm. The IR spectrum showed absorption bands for hydroxyl group at 3417 cm^{-1}, conjugated carbonyl at 1661 cm^{-1}, aromatic ring at 1621, 1539 and 1456 cm^{-1}.

The ^{1}H NMR spectral data **(Table 13)** of **PW11** displayed characteristic sets of signals of the cinnamide group at δ_H 6.37 (1H, d, *J* = 15.6 Hz, H-8'), 7.64 (1H, d, *J* = 15.6 Hz, H-7'), 7.49 (2H, dd, *J* = 7.6, 1.9 Hz, H-2', H-6') and 7.34-7.36 (3H, m, H-3', H-4', H-5'). Furthermore, the ^{1}H NMR spectrum exhibited the doublet of doublet signals of the benzylic oxymethine proton at δ_H 4.86 (*J* = 7.8, 2.9 Hz, H-2) which was coupled with non-equivalent methylene protons adjacent to the nitrogen of amide at δ_H 3.43 (ddd, *J* = 13.8, 8.0, 4.8 Hz, H-1a) and 3.80 (ddd, *J* = 13.8, 7.0, 2.7 Hz, H-1b). The aromatic proton signals at δ_H 7.30 (2H, d, *J* = 8.5 Hz, H-2'', H-6'') and 6.90 (2H, d, *J* = 8.5 Hz, H-3'', H-5'') could be assigned as 1,4-disubstituted aromatic protons. Additionally, the ^{1}H NMR signals at δ_H 4.04 (1H, ddd, *J* = 9.5, 3.2, 1.0 Hz, H-1'''a), 4.46 (1H, d, *J* = 5.1 Hz, H-1'''b): δ_C 71.2, 3.90 (1H, dt, *J* = 8.8, 1.0 Hz, H-2'''): δ_C 73.6, 5.00 (1H, s, H-4'''a), 5.13 (1H, s, H-4'''b): δ_C 112.8 and a singlet at δ 1.80 (3H): δ_C 18.9 were assigned to an oxyisoprenyl unit. In the HMBC spectrum, the H-2''/H-6'' aromatic protons showed long-range correlations with C-2 (δ_C 73.4), C-1'' (δ_C 134.5) and C-4'' (δ_C 158.2) and the remaining H-3''/H-5'' aromatic protons correlated with C-1'' (δ_C 134.5) and C-4'' (δ_C 158.2). The side chain methylene protons H_2-1''' correlated with C-2''' (δ_C 73.6) and C-4'' (δ_C 158.2), indicating the attachment of a hydroxyethylcinnamamide chain at C-1'' and a hydroxyloxyprenyl group at C-4'' of the benzene ring. The structure of **PW11** was a new compound and named as marmesiline.

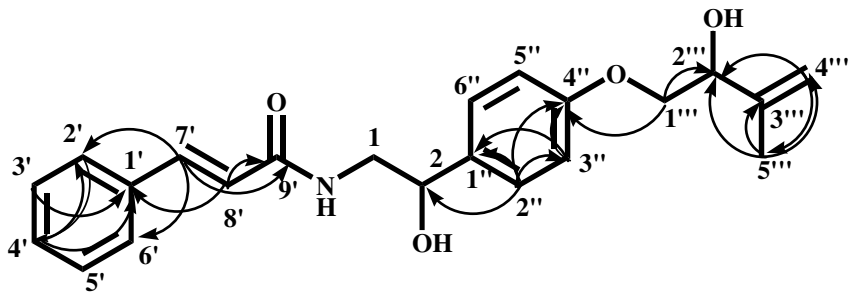
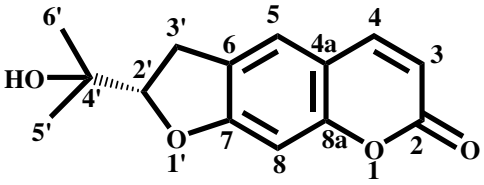


Figure 12 Selected HMBC correlations of **PW11**

Table 13 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW11**

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	3.43 (ddd, *J* = 13.8, 8.0, 4.8 Hz) 3.80 (ddd, *J* = 13.8, 7.0, 2.7 Hz)	47.7 (CH_2)	-
2	4.86 (dd, *J* = 7.8, 2.9 Hz)	73.4 (CH)	-
1′	-	134.5 (C)	
2′,6′	7.49 (dd, *J* = 7.6, 1.9 Hz)	127.9 (CH)	C-4′
3′,5′	7.34-7.36 (m)	128.9 (CH)	C-1′
4′	7.34-7.36 (m)	129.9 (CH)	C-2′, C-6′
7′	7.64 (d, *J* = 15.6 Hz)	141.8 (CH)	C-2′, C-6′, C-9′
8′	6.37 (d, *J* = 15.6 Hz)	119.9 (CH)	C-1′, C-9′
9′	-	167.1 (C)	-
1″	-	134.5 (C)	-
2″,6″	7.30 (d, *J* = 8.5 Hz)	127.1 (CH)	C-2, C-1", C-4", C-5"
3″,5″	6.90 (d, *J* = 8.5 Hz)	114.7 (CH)	C-1″, C-4″
4″	-	158.2 (C)	-
1‴	4.04 (ddd, *J* = 9.4, 3.2, 1.0 Hz) 4.46 (dd, *J* = 9.4, 8.3 Hz)	71.2 (CH_2)	C-4″, C-2‴
2‴	3.90 (dd, *J* = 8.3, 3.2 Hz)	73.6 (CH)	-
3‴	-	143.3 (C)	-
4‴	5.00 (s) 5.13 (s)	112.8 (CH_2)	C-2‴, C-5‴
5‴	1.80 (s)	18.9 (CH_3)	C-2‴, C-3‴, C-4‴
N-H	6.00 (br t, *J* = 7.8 Hz)		-

Compound PW12



PW12 was isolated as white powder, m.p. 170-171 ℃, $[\alpha]_D^{26}$ = +20.6 ° (*c* = 0.9, $CHCl_3$) [lit. $[\alpha]_D^{22}$ = +21.7°, (*c* = 0.9, $CHCl_3$) (Nemoto *et al*., 2003)]. The UV spectrum exhibited the absorption bands characteristic of coumarin at 203 and 330 nm. The IR spectrum showed absorption bands for hydroxyl group at 3441 cm^{-1}, lactone carbonyl at 1704 cm^{-1} and aromatic ring at 1627, 1563 and 1503 cm^{-1}.

The ^{1}H NMR spectral data **(Table 14)** of **PW12** showed the signals of 6,7-disubstituted coumarin unit as signals at δ_H 6.22 (1H, d, *J* = 9.5 Hz, H-3), 7.60 (1H, d, *J* = 9.5 Hz, H-4), 7.23 (1H, s, H-5) and 6.75 (1H, s, H-8). In addition three mutually coupled protons at δ_H 4.75 (1H, dd, *J* = 9.1, 8.5 Hz, H-2'), 3.18 (1H, ddd, *J* = 15.9, 8.8, 1.2 Hz, H-3') and 3.26 (1H, ddd, *J* = 15.9, 8.3, 1.2 Hz, H-3') and two methyls at δ_H 1.25 (3H, s), 1.38 (3H, s) suggested that **PW12** contained a hydroxyisopropyldihydrofurano moiety whose location was placed between C-6 and C-7 of the coumarin unit. The location of the hydroxyisopropyldihydrofurano group was confirmed by HMBC correlations of H-3' (δ_H 3.18 and 3.26) with the carbons at δ_C 123.4 (C-5), 125.5 (C-6), 163.2 (C-7), 91.1 (C-2') and 71.1 (C-4'). A methine proton at δ_H 4.75 (H-2') showed correlations with the carbon at δ_C 163.2 (C-7), 26.1 (C-6') and 24.3 (C-5'), methyl protons at δ_H 1.25 (H_3-5') with the carbons at δ 26.1 (C-6'), 71.7 (C-4') and 91.1 (C-2') and δ_H 1.38 (H-6') with the carbons at δ 24.3 (C-5'), 71.7 (C-4') and 91.1 (C-2'). The complete HMBC data were summarized in **Table 14**. Therefore, compound **PW12** was marmesin (Kim *et al*., 2006).

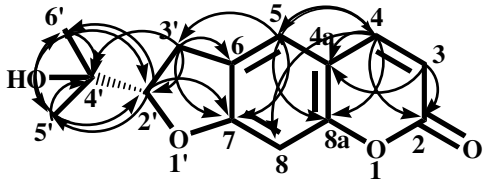
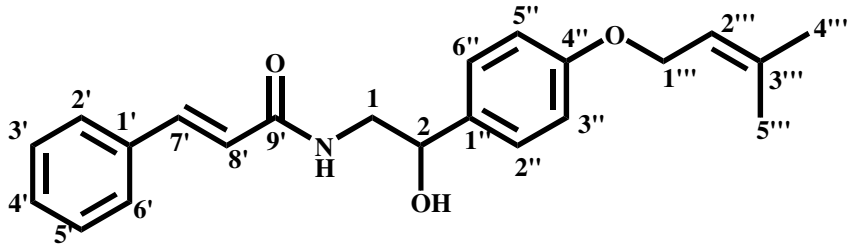


Figure 13 Selected HMBC correlations of **PW12**

Table 14 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW12** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	161.4 (C)	-
3	6.22 (d, J = 9.5 Hz)	112.4 (CH)	C-2, C-4a
4	7.60 (d, J = 9.5 Hz)	143.8 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	112.8 (C)	-
5	7.23 (s)	123.4 (CH)	C-4, C-7, C-8a, C-3′
6	-	125.0 (C)	-
7	-	163.2 (C)	-
8	6.74 (s)	98.0 (CH)	C-4, C-6, C-7, C-4a, C-8a, C-3′
8a	-	155.7 (C)	-
1′	-	-	-
2′	4.75 (dd, J = 9.1, 8.5 Hz)	91.1 (CH)	C-7, C-5′, C-6′
3′	3.18 (ddd, J = 15.9, 8.8, 1.2 Hz)	29.5 (CH_2)	C-5, C-6, C-7, C-2′, C-4′
	3.26 (ddd, J = 15.9, 8.3, 1.2 Hz)		
4′	-	71.1 (C)	-
5′	1.25 (s)	24.3 (CH_3)	C-2′, C-4′, C-6′
6′	1.38 (s)	26.1 (CH_3)	C-2′, C-4′, C-5′

Compound PW13



PW13 was isolated as a white powder, m.p. 128-129 ℃. The UV spectrum exhibited the absorption bands characteristic of cinnamide structure at 202, 224 and 274 nm. The IR spectrum showed absorption bands for hydroxyl group at 3259 cm^{-1}, carbonyl at 1660 cm^{-1} and aromatic ring at 1619, 1569 and 1443 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 15)** of **PW13** were closely comparable with those of **PW11** except for the disappearance of the terminal olefinic methylene protons at δ_H 5.00 and 5.13: δ_C 112.8 and a hydroxymethine proton at δ_H 3.90: δ_C 73.6 in **PW11** but the appearance of an additional olefinic methyl singlet at δ_H 1.72: δ_C 25.8 and an olefinic methine proton at δ_H 5.42: δ_C 119.6 in **PW13**. The HMBC spectrum showed correlations of H-4''' at δ_H 1.72 with the carbons at δ_C 18.2 (C-5'''), 138.2 (C-3''') and 119.6 (C-2'''). Based on these data, the structure of **PW13** was assigned as marmeline (Sharma *et al*., 1981).

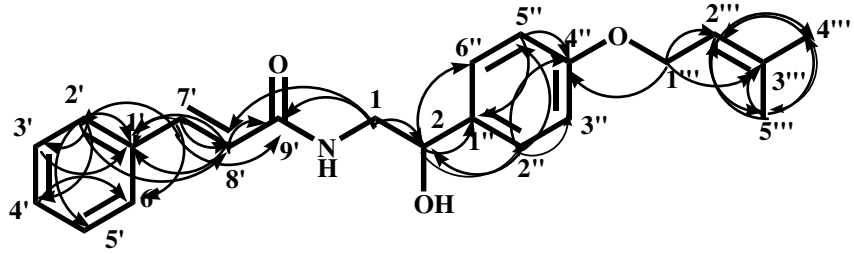
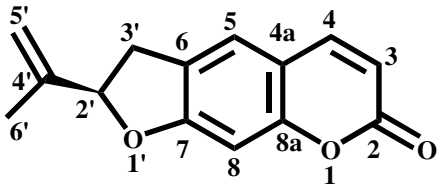


Figure 16 Selected HMBC correlations of **PW13**

Table 17 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW13** ($CDCl_3$)

Position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	3.80 (m)	47.6 (CH_2)	C-8′, C-9′
	3.40 (m)		
2	4.80 (dd, *J* = 7.7, 3.3 Hz)	73.5 (CH)	C-1″, C-2″, C-6″
1′	-	134.7 (C)	-
2′,6′	7.43 (m)	127.9 (CH)	C-1′, C-3′, C-4′, C-5′, C-8′
3′,5′	7.30 (m)	128.8 (CH)	C-1′
4′	7.30 (m)	129.9 (CH)	C-2′, C-6′
7′	7.59 (d, *J* = 15.6 Hz)	141.7 (CH)	C-1′, C-2′, C-6′, C-8′, C-9′,
8′	6.33 (d, *J* = 15.6 Hz)	120.1 (CH)	C-1′, C-9′
9′	-	167.0 (C)	-
1″	-	133.8 (C)	-
2″,6″	7.24 (d, *J* = 8.7 Hz)	127.1 (CH)	C-2, C-3″, C-4″, C-5″
3″,5″	6.84 (d, *J* = 8.7 Hz)	114.8 (CH)	C-1″, C-4″
4″	-	158.7 (C)	-
1‴	4.45 (d, *J* = 6.7 Hz)	64.9 (CH_2)	C-4″, C-2‴, C-3‴
2‴	5.42 (t, *J* = 6.7 Hz)	119.6 (C)	C-4‴, C-5‴
3‴	-	138.2 (C)	-
4‴	1.72 (s)	25.8 (CH_3)	C-2‴, C-5‴
5‴	1.67 (s)	18.2 (CH_3)	C-2‴, C-4‴
N-H	5.98 (t, *J* = 5.4 Hz)	-	-

Compound PW14



PW14 was isolated as a white powder, m.p. 120-121 ℃ (lit. 116-117 ℃). The UV spectrum exhibited the absorption bands characteristic of coumarin at 203, 287 and 329 nm. The IR spectrum showed absorption bands for lactone carbonyl at 1711 cm^{-1} and aromatic ring at 1620, 1567 and 1401 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 16)** of **PW14** were similar to those of **PW12**, except for the presence of the two singlet signals of terminal olefinic methylene protons at δ_H 4.84 and 4.93 (H_2-5') and only one methyl singlet at δ_H 1.73 (H_3-6') corresponding to an isopropenyl group in **PW14**. The location of an isopropenyl group at C-2' was confirmed by HMBC correlations of H_2-5' (δ_H 4.84 and 4.93) and H-6' (δ_H 1.73) with the carbons at δ_C 78.0 (C-2'). The complete HMBC data were summarized in **Table 16**. Therefore, compound **PW14** was isoangenomalin (Yamaguchi *et al*., 2003).

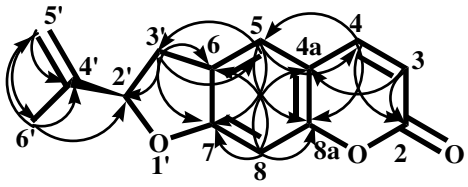
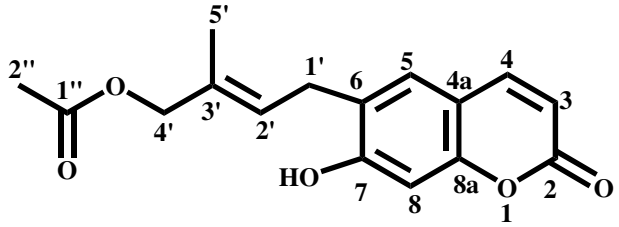


Figure 15 Selected HMBC correlations of **PW14**

Table 16 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW14** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	161.5 (C)	-
3	6.14 (d, J = 9.5 Hz)	112.9 (CH)	C-2, C-4a
4	7.50 (d, J = 9.5 Hz)	143.2 (CH)	C-2, C-5, C-8a
4a	-	112.2 (C)	-
5	7.04 (s)	130.2 (CH)	C-4, C-7, C-8a, C-3′
6	-	123.0 (C)	-
7	-	159.8 (C)	-
8	6.80 (s)	105.1 (CH)	C-6, C-7, C-4a, C-8a
8a	-	155.0 (C)	-
1′	-	-	-
2′	4.36 (dd, J = 7.9, 2.4 Hz)	78.0 (CH)	-
3′	2.82 (dd, J = 15.0, 2.4 Hz)	37.6 (CH_2)	C-5, C-6, C-7, C-2′
	2.92 (dd, J = 15.0, 7.9 Hz)		
4′	-	145.8 (C)	-
5′	4.84 (s)	111.7 (CH_2)	C-2′, C-3″
	4.93 (s)		
6′	1.73 (s)	18.2 (CH_3)	C-2′, C-1″, C-2″

Compound PW15



PW15 was isolated as white powder, m.p. 133-134℃. The UV spectrum exhibited the absorption bands characteristic of coumarin at 205, 297 and 330 nm. The IR spectrum showed absorption bands for hydroxyl group at 3392 cm^{-1}, lactone carbonyl at 1720 cm^{-1} and aromatic ring at 1618, 1570 and 1421 cm^{-1}.

The ^{1}H NMR spectral data **(Table 17)** of **PW15** showed the signals of 6,7-disubstituted coumarins which were similar to those of compound **PW9**, except for the presence of characteristic signals of a 4-acetoxy-3-methyl-2-butenyl side chain at δ_H 3.36 (2H, d, J = 7.1 Hz, H-1'), 5.58 (1H, t, J = 7.1 Hz, H-2'), 4.46 (2H, s, H-4'), 1.73 (3H, s, H-5') and 2.02 (3H, s, H-2'') in **PW15** instead of the signal of an isoprenyl group as in **PW9**.

The ^{13}C-NMR spectrum showed sixteen carbons; two methyl at δ_C 14.1 (H-5') and 20.9 (H-2''), two methylene at δ_C 27.9 (C-1') and 69.7 (C-4'), five methine at δ_C 112.9 (C-3), 143.7 (C-4), 128.5 (C-5), 103.2 (C-8) and 125.6 (C-2'), five quaternary at δ_C 112.0 (4a), 154.1 (C-8a), 124.5 (C-6), 157.6 (C-7) and 132.7 (C-3') and two carbonyl carbons at δ_C 161.6 (C-2) and 171.0 (C-1''). In the HMBC spectrum, the methylene protons at δ_H 3.36 (H-1') correlated with the carbons at δ_C 128.5 (C-5), 124.5 (C-6), 157.6 (C-7), 125.6 (C-2') and 132.7 (C-3'), indicating the location of a side chain positioned at C-6 and a hydroxyl group at C-7. Furthermore, the methylene protons at δ_H 4.46 (C-4') correlated with signals at δ_C 171.0 (C-1''), 132.7 (C-3') and 125.6 (C-2') and a methyl signal at δ_H 2.02 (H-2'') correlated with the resonance at δ_C 171.0 (C-1''), resulting in the assignment of an acetoxyl group at C-4'. The methyl acetyl group was *trans* with respect to the methylene group of the prenyl substituent on the basis of a NOESY correlation between H_2-1' and H_3-5', and H-2' and H_2-4'. Based on these data, **PW 15** was a new compound and named as 6-(4'-acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin.

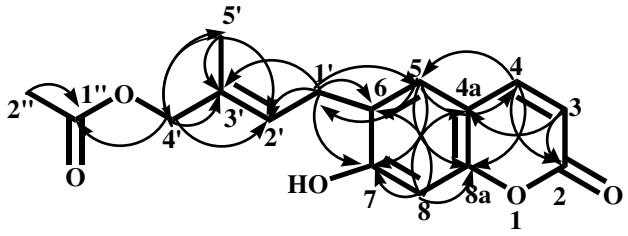
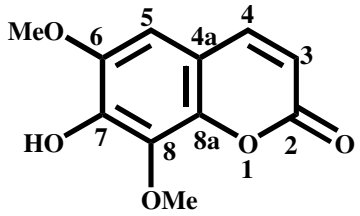


Figure 16 Selected HMBC correlations of **PW15**

Table 17 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW15** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC	NOESY
1	-	-	-	
2	-	161.6 (C)	-	
3	6.17 (d, *J* = 9.5 Hz)	112.9 (CH)	C-2, C-4a	H-4
4	7.56 (d, *J* = 9.5 Hz)	143.7 (CH)	C-2, C-5, C-4a, C-8a	H-3
4a	-	112.0 (C)	-	
5	7.12 (s)	128.5 (CH)	C-4, C-7, C-8a, C-1′	
6	-	124.5 (C)	-	
7	-	157.6 (C)	-	
8	6.80 (s)	103.2 (CH)	C-6, C-7, C-4a, C-8a	
8a	-	154.1 (C)	-	
1′	3.36 (d, *J* = 7.1 Hz)	27.9 (CH_2)	C-5, C-6, C-7, C-2′, C-3′	H-5′
2′	5.58 (t, *J* = 7.1 Hz)	125.6 (CH)	3′-Me	H-4′
3′	-	132.7 (C)	-	
4′	4.46 (s)	69.7 (CH_2)	C-2′, C-3′, C-5′, 3′-Me	H-2′
5′	1.72 (s)	14.1 (CH_3)	C-2′, C-3′, C-4′	H-1′
1″	-	171.0 (C)	-	
2″	2.02 (s)	20.9 (CH_3)	C-5′	
7-OH	6.44 (br s)	-	-	

Compound PW16



PW16 was isolated as white powder, m.p. 151-152℃ (lit. 149-150 ℃). The UV spectrum exhibited the absorption bands characteristic of coumarin at 207, 343 and 383 nm. The IR spectrum showed absorption bands for hydroxyl group at 3356 cm^{-1}, lactone carbonyl at 1712 cm^{-1} and aromatic ring at 1606, 1576 and 1498 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 18)** of **PW16** were closely related to those of **PW10**. The differences were shown as a replacement of a singlet signal of an aromatic proton (δ_H 6.81) at C-8 and aldehyde group (δ_H 9.86) at C-6 in **PW10** by signals of two methoxyl groups (δ_H 4.10 and 3.94) in **PW10**. The positions of the methoxyl group (δ_H 4.10) at C-8 was confirmed by its HMBC correlation with the carbon at δ_C 134.5 (C-8) and 6-OMe (δ_H 3.94) with the carbon at δ_C 144.6 (C-6). In addition an aromatic proton H-5 (δ_H 6.66) showed correlation with the carbons at δ_C 143.8 (C-4), 144.6 (C-6), 142.4 (C-7) and 143.1 (C-8a), confirming the presence of 6,7,8-trioxygenatedcoumarin. Based on these data, the structure of **PW16** was assigned as isofraxidin (Banthorpe *et al*., 1989).

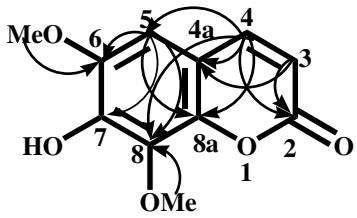
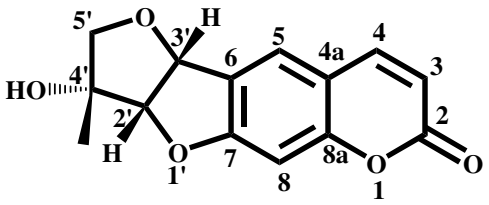


Figure 17 Selected HMBC correlations of **PW16**

Table 18 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW16** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC
1	-	-	-
2	-	160.5 (C)	-
3	6.28 (d, *J* = 9.5 Hz)	113.6 (CH)	C-2, C-4a
4	7.59 (d, *J* = 9.5 Hz)	143.8 (CH)	C-2, C-5, C-8, C-4a, C-8a
4a	-	111.2 (C)	-
5	6.66 (s)	103.3 (CH)	C-4, C-6, C-7, C-8, C-8a
6	-	144.6 (C)	-
7	-	142.4 (C)	-
8	-	134.5 (C)	-
8a	-	143.1 (C)	-
6-OMe	3.94 (s)	56.5 (CH_3)	C-6
8-OMe	4.10 (s)	61.6 (CH_3)	C-8

Compound PW17



PW17 was isolated as a yellow solid, m.p. 195-196℃. The UV spectrum exhibited the presence of the absorption bands characteristic of coumarin at 205, 257, 325 nm. The IR spectrum showed absorption bands for hydroxyl group at 3415 cm^{-1}, lactone carbonyl at 1721 cm^{-1} and aromatic ring at 1625, 1575 and 1491 cm^{-1}.

The ^{1}H and ^{13}C NMR were closely related with those of marmesin (**PW 12**). However, instead of two gem-dimethyl groups as in **PW12**, the appearance of only one methyl singlet (δ_H 1.52) on C-4' was proposed for **PW17**. Furthermore, the ^{1}H NMR spectrum also showed the signal of oxymethine proton at δ_H 5.70 (d, J = 5.8 Hz, H-3') and the signal of non-equivalent oxymethylene protons at δ_H 3.67 and 3.27 (1H each, *d*, J = 9.0 Hz, H-5') which linked to the carbon signal at δ_C 73.8 in HMQC spectrum. The methyl protons at δ_H 1.52 (Me-4') showed long-range correlations with C-2' (δ_C 90.7), C-4' (δ_C 77.7) and an oxymethylene carbon C-5' (δ_C 73.8). In turn, the methylene protons at δ_H 3.67 and 3.27 (H_2-5') correlated with C-3' (δ 80.8), C-2' (δ_C 90.7) and a tertiary methyl carbon (δ_C 23.6), as well as the small coupling between H-5' and the methyl protons in the COSY spectrum, suggesting the location of a methyl group at C-4'. The large vicinal coupling constant (5.8 Hz) of two doublets at δ 5.70 (H-3') and 4.78 (H-2') indicated their *cis* orientation. Moreover, the NOESY spectrum showed correlation between H-2' and H-3' and H-2' and Me-4'. These results confirmed the *cis*-relationship between H-2', H-3' and Me-4'. Thus, compound **PW17** was assigned as 1-hydroxy-1-methyl-1,2,3a,10a-tetrahydro-3,8,10-trioxa-pentaleno[1,2-*b*]naphthalen-7-one and named as marmelonine A.

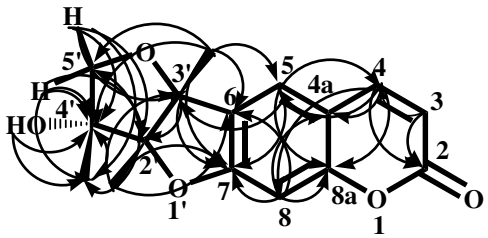
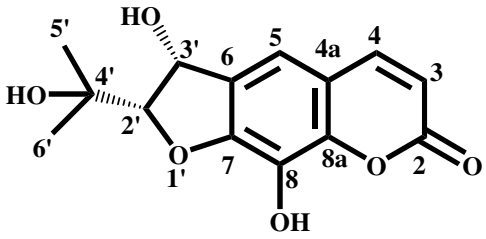


Figure 18 Selected HMBC correlations of **PW17**

Table 19 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW17** ($CDCl_3$)

position	δ_H (multiplicity)	δ_C (C- type)	HMBC	NOESY
1	-	-	-	
2	-	160.6 (C)	-	
3	6.30 (d, J = 9.6 Hz)	113.4 (CH)	C-2, C-4a	H-4
4	7.67 (d, J = 9.6 Hz)	143.4 (CH)	C-2, C-5, C-8, C-4a, C-8a	H-3
4a	-	114.1 (C)	-	
5	7.53 (s)	125.6 (CH)	C-4, C-7, C-8, C-8a, C-3′	
6	-	123.6 (C)	-	
7	-	163.1 (C)	-	
8	6.87 (s)	98.7 (CH)	C-6, C-7, C-4a, C-8a	
8a	-	157.1 (C)	-	
1′	-	-	-	
2′	4.78 (d, J = 5.8 Hz)	90.7 (CH)	C-6, C-7, C-3′, C-5′, Me-4′	H-3′, Me-4'
3′	5.70 (d, J = 5.8 Hz)	80.8 (CH)	C-5, C-6, C-7, C-4′, C-5′	H-2′
4′	-	77.7 (C)	-	
5′	3.27 (d, J = 9.0 Hz)	73.8 (CH_2)	C-2′, C-4′, Me-4′	
	3.67 (d, J = 9.0 Hz)		C-2′, C-3′, C-4′, Me-4′	
Me-4′	1.52 (s)	23.6 (CH_3)	C-2′, C-4′, C-5′	H-2′
OH-4′	2.55 (s)	-	C-4′, Me-4′	

Compound PW18



PW18 was isolated as a white powder, m.p. 179-180℃, $[\alpha]_D^{26}$ = +20.1° (*c* = 1.0, MeOH). The UV spectrum exhibited the absorption bands characteristic of coumarin at 210, 268 and 326 nm. The IR spectrum showed absorption bands for hydroxyl group at 3393 cm^{-1}, lactone carbonyl at 1707 cm^{-1} and aromatic ring at 1623, 1588 and 1418 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 19)** of **PW18** were similar to those of **PW12**, except for the appearance of a doublet signal at δ_H 5.36 (1H, d, *J* = 5.9 Hz) assignable to an oxymethine proton, instead of two doublet of doublet signals of methylene protons at C-3' in **PW12**, indicating a hydroxyl substituent at C-3' in **PW18**. The oxymethine proton (δ_H 5.36, δ_C 72.3) was located at C-3' on the basis of HMBC correlations between δ_H 5.36 (H-3') and δ_C 114.8 (C-5), 128.4 (C-6), 150.5 (C-7) and 91.1 (C-2'). Furthermore, the disappearance of an aromatic proton at δ_H 6.74 (H-8) of **PW12** implied a hydroxyl group at C-8 of **PW18** which was confirmed by additional quaternary carbon signal at δ_C 129.3. NOESY spectrum showed cross peak between H-2' and H-3' supporting **PW18** to possess *cis* configuration. On the basis of the above analysis, the structure of **PW18** was a new compound and named as 8-hydroxysmyrindiol.

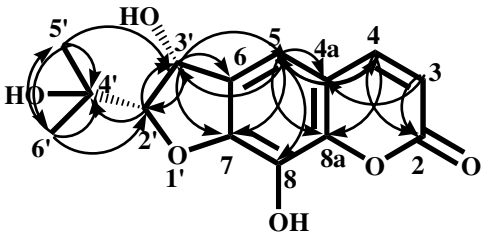
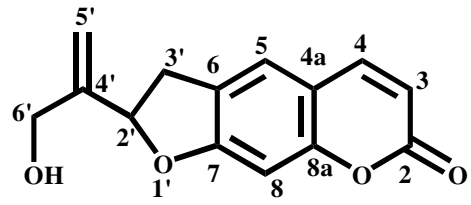


Figure 19 Selected HMBC correlations of **PW18**

Table 20 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW18** ($CDCl_3$+CD_3OD(1 drop))

position	δ_H (multiplicity)	δ_C (C- type)	HMBC	NOESY
1	-		-	
2	-	161.7 (C)	-	
3	6.20 (d, *J* = 9.5 Hz)	111.9 (CH)	C-2, C-4a	H-4
4	7.68 (d, *J* = 9.5 Hz)	145.1 (CH)	C-2, C-5, C-8a	H-3, H-5
4a	-	114.1 (C)		
5	7.08 (s)	114.8 (CH)	C-4, C-7, C-8, C-4a, C-8a, C-3′	H-4
6	-	128.4 (C)	-	
7	-	150.5 (C)	-	
8	-	129.3 (C)	-	
8a	-	144.3 (C)	-	
1′	-	-	-	
2′	4.33 (d, *J* = 5.9 Hz)	91.0 (CH)	C-3′, C-4′	H-3′
3′	5.36 (d, *J* = 5.9 Hz)	72.3 (CH)	C-5, C-6, C-7, C-2′	H-2′
4′	-	72.4 (C)	-	
5′	1.54 (s)	27.5 (CH_3)	C-2′, C-4′, C-6′	
6′	1.56 (s)	25.7 (CH_3)	C-2′, C-4′, C-5′	

Compound PW19



PW19 was isolated as a white powder, m.p. 279-280℃. The UV spectrum exhibited the absorption bands characteristic of coumarin at 205, 256, 331 nm. The IR spectrum showed absorption bands for hydroxyl group at 3432 cm^{-1}, lactone carbonyl at 1726 cm^{-1} and aromatic ring at 1621, 1557 and 1488 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 20)** of **PW19** and **PW14** showed structural similarity, except for **PW19** a methyl singlet at δ_H 1.75 as in **PW14** disappeared but two doublets of methylene protons at δ_H 4.10 and 4.07 (1H each, J = 13.6 Hz) were evidenced, indicating that the methyl group in **PW14** was oxidized to a hydroxymethyl group in **PW19**. The hydroxymethyl was connected to C-4' due to the HMBC correlations with the carbons at δ_C 73.1 (C-2'), 149.5 (C-4') and 111.3 (C-5'). The complete HMBC data were summarized in **Table 21**. Based on these data, **PW19** was assigned as 2-(3-hydroxyprop-1-en-2-yl)-2,3-dihydrofuro[3,2-g]chromen-7-one and named as marmelonine B.

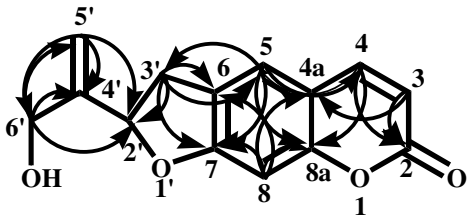
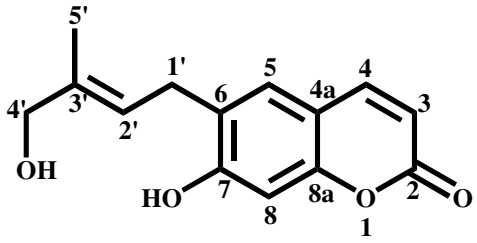


Figure 20 Selected HMBC correlations of **PW19**

Table 21 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW19** ($CDCl_3$+CD_3OD (1 drop))

position	δ_H (multiplicity)	δ_C (C- type)	HMBC	NOESY
1	-	-	-	
2	-	162.5 (C)	-	
3	6.08 (d, *J* = 9.4 Hz)	111.5 (CH)	C-2, C-4a	H-4
4	7.57 (d, *J* = 9.4 Hz)	144.3 (CH)	C-2, C-5, C-8a	H-3
4a	-	111.6 (C)	-	
5	7.13 (s)	130.2 (CH)	C-4, C-7, C-8a, C-3′	H-3′
6	-	123.6 (C)	-	
7	-	159.8 (C)	-	
8	6.67 (s)	103.1 (CH)	C-6, C-7, C-4a, C-8a	
8a	-	154.4 (C)	-	
1′	-	-	-	
2′	4.43 (dd, *J* = 7.9, 4.3 Hz)	73.1 (CH)	C-5′	
3′	2.81 (dd, *J* = 14.3, 8.0 Hz)	37.4 (CH)	C-5, C-6, C-7, C-2′, C-4′	H-5
	2.89 (dd, *J* = 14.3, 4.3 Hz)			
4′	-	149.5 (C)	-	
5′	4.98 (s)	111.3 (CH_2)	C-2′, C-4′, C-6′, C-4′	H-6′
	4.99 (s)			
6′	4.10 (d, *J* = 13.6 Hz)	62.8 (CH_2)	C-2′, C-4′, C-5′	H-5′
	4.07 (d, *J* = 13.6 Hz)			

Compound PW20



PW20 was isolated as white powder, m.p. 140-141°C. The UV spectrum exhibited the absorption bands characteristic of coumarin at 204 and 331 nm. The IR spectrum showed absorption bands for hydroxyl group at 3335 cm^{-1}, lactone carbonyl at 1717 cm^{-1} and aromatic ring at 1617, 1570 and 1457 cm^{-1}.

The ^{1}H and ^{13}C NMR spectral data **(Table 22)** of **PW20** were similar to those of **PW15**, except for the disappearance of an acetoxyl signal in **PW15**. In addition the signal of the methylene protons at C-4' had shifted more highfield than those in **PW15**. The ^{1}H and ^{13}C NMR spectrum of **PW20** showed only twelve protons and fourteen carbons, so it was possible to conclud that there was a hydroxyl group at C-4' (δ_C 68.2). The NOESY spectrum of **PW20** showed correlations between H-1' and H-5', and H-2' and H-4', supporting that **PW20** possessed the same configuration as **PW15**, implying *trans* configuration of the double bond. The complete HMBC data were summarized in **Table 22**. Therefore, compound **PW20** was isophellodenol C (Nakamori *et al*., 2008).

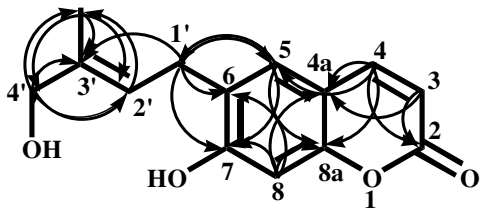
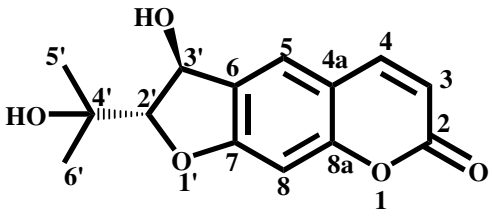


Figure 21 Selected HMBC correlations of **PW20**

Table 22 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW20** ($CDCl_3$+CD_3OD (1 drop))

position	δ_H (multiplicity)	δ_C (C- type)	HMBC	NOESY
1	-	-	-	
2	-	162.4 (C)	-	
3	6.11 (d, *J* = 9.4 Hz)	111.6 (CH)	C-2, C-4a	H-4
4	7.58 (d, *J* = 9.4 Hz)	144.2 (CH)	C-2, C-3, C-5, C-4a, C-8a	H-3
4a	-	111.6 (C)	-	
5	7.12 (s)	128.1 (CH)	C-4, C-7, C-8a, C-1′	
6	-	125.8 (C)	-	
7	-	159.1 (C)	-	
8	6.68 (s)	102.2 (CH)	C-6, C-7, C-4a, C-8a	
8a	-	154.1 (C)	-	
1′	3.32 (d, *J* = 7.3 Hz)	27.5 (CH_2)	C-5, C-6, C-7, C-2′, C-3′	H-5′
2′	5.53 (t, *J* = 7.3 Hz)	122.8 (CH)	C-4', C-5′	H-4′
3′	-	136.4 (C)	-	
4′	3.96 (s)	68.2 (CH_2)	C-2′, C-3′, C-5′-Me	H-2′
5'	1.69 (s)	13.5 (CH_3)	C-2′, C-3′, C-4′	H-1′

Compound PW21



PW21 was isolated as white powder, m.p. 178-179°C, $[\alpha]_D^{26}$ = +33.1° (*c* = 0.4, acetone) (lit. $[\alpha]_D^{26}$ = +37.0° (*c* = 0.4, acetone). The UV spectrum exhibited the absorption bands characteristic of coumarin at 204, 224, 248 and 331 nm. The IR spectrum showed absorption bands for hydroxyl group at 3392 cm^{-1}, lactone carbonyl at 1715 cm^{-1} and aromatic ring 1627, 1572 and 1488 cm^{-1}.

The ^1H and ^{13}C NMR spectral data **of PW21 (Table 23)** and **PW18** showed structural similarity, except that in **PW21** an additional aromatic proton at δ_H 6.80 (s, H-8) replaced the hydroxyl group of **PW18** at C-8, whose HMBC correlations with the carbons at δ_C 126.7 (C-6), 163.0 (C-7), 113.4 (C-4) and 156.9 (C-8a) supported the assignment. A small vicinal coupling constant (3.9 Hz) of two doublets at δ_H 4.42 (H-2′) and 5.44 (H-3′) as well as a lack of NOESY cross peak between H-2′ and H-3′, supported 2′,3′-*trans*-configuration of **PW21**. The complete HMBC data were summarized in **Table 23**. Therefore, compound **PW21** was xanthoarnol (Zou *et al*., 2005).

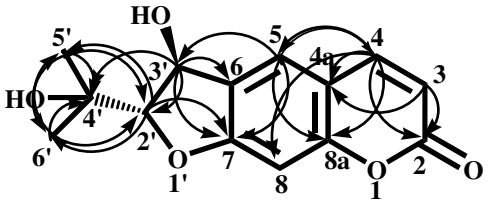


Figure 22 Selected HMBC correlations of **PW21**

Table 23 ^{1}H, ^{13}C NMR and HMBC spectral data of **PW21** ($CDCl_3$+CD_3OD (1 drop))

position	δ_H (multiplicity)	δ_C (C- type)	HMBC	NOESY
1	-	-	-	
2	-	160.9 (C)	-	
3	6.25 (d, J = 9.5 Hz)	112.9 (CH)	C-2, C-4a	H-4
4	7.64 (d, J = 9.5 Hz)	143.6 (CH)	C-2, C-5, C-8a	H-3, H-5
4a	-	113.4 (C)	-	
5	7.48 (s)	124.7 (CH)	C-4, C-7, C-8a, C-3′	H-4
6	-	126.7 (C)	-	
7	-	163.0 (C)	-	
8	6.80 (s)	98.7 (CH)	C-6, C-7, C-4a, C-8a	
8a	-	156.9 (C)	-	
1′	-	-	-	
2′	4.42 (d, J = 3.9 Hz)	98.4 (CH)	C-7, C-3′, C-5′, C-6′	
3′	5.44 (br d, J = 3.9 Hz)	72.3 (CH)	-	
4′	-	71.2 (C)	-	
5′	1.33 (s)	24.9 (CH_3)	C-2′, C-4′, C-6′	
6′	1.37 (s)	25.7 (CH_3)	C-2′, C-4′, C-5′	

Conclusion

Investigation of the crude acetone extract of the green fruits of *Aegle marmelos* led to the isolation of twenty-one compounds of five furanocoumarins: imperatorin **(PW1**), 8-[(3"-methyl-2"-oxo-3"-buten-1-yl)oxy]-7*H*-furo[3,2-g]benzopyran-2-one **(PW3)**, xanthotoxol **(PW4)**, isogosferol **(PW5)** and xanthotoxin **(PW6)**, one acid: valencic acid **(PW2)**, six coumarins: scoparone **(PW7)**, demethylsuberosin **(PW9)**, 6-formylumbilliferone **(PW10)**, 6-(4'-acetoxy-3'-methyl-2'-butenyl)-7-hydroxycoumarin (**PW15**), isofraxidin **(PW16)** and isophellodenol C **(PW20)**, one dihydropyranocoumarin**:** decursinol **(PW8)**, two alkaloids: marmesiline **(PW11)**, marmeline **(PW13)**, six dihydrofuranocoumarins: marmesin **(PW12)**, isoangenomalin **(PW14)**, marmelonine A **(PW17)**, 8-hydroxysmyrindiol (**PW18**), marmelonine B **(PW19)** and xanthoarnol **(PW21)**.

REFERENCES

Abdel-Fattah, M. E.; Taha, K. E.; Abdel Aziz, M. H.; Missalem, A. A.; El-Khrisy, E. A. M. **2003**. "Chemical constituents of *Citrus limonia* and *Foeniculum vulgare*", *Indian J. Heterocycl. Chem.*, 13(1), 45-48.

Acharyya, S.; Patra, A.; Bag, P. K. **2009**. "Evaluation of the antimicrobial activity of some medicinal plants against enteric bacteria with particular reference to multi-drug resistant *Vibrio cholerae*", *Trop. J. Pharm. Res*., 8, 231-237.

Adebajo, A. C.; Reisch, J. **2000.** "Minor furanocoumarins of *Murraya koenigii*", *Fitoterapia*, 71, 334-337.

Alam, M. M.; Siddiqui, M. B.; Husain, W. **1990**. "Treatment of diabetes through herbal drug in rural India", *Fitoterapia*, 61, 240-242.

Ali, M. S.; Pervez, M. K. **2004**. "Marmenol: A 7-geranyloxycoumarin from the leaves of *Aegle marmelos* Corr.", *Nat. Prod. Res*., 18(2), 141-146.

Arumugam, S.; Kavimani, S.; Kadalmani, B.; Ahmed, A. B. A.; Akbarshac, M. A.; Rao, M. V. **2008**. "Antidiabetic activity of leaf and callus extracts of *Aegle marmelos* in rabbit", *Sci. Asia*, 34, 317-321.

Bacher, M.; Brader, G.; Hofer, O.; Greger, H. **1999**. "Oximes from seeds of *Atalantia ceylanica*"**,** *Phytochemistry*, 50(6), 991-994.

Banerji, J.; Das, A. K.; Ghoshal, N.; Das B. **1988**a. "Studies on Rutaceae. Part VIII. Chemical investigation on the constituents of *Atalantia wightii* Tanaka, *Aegle marmelos* Correa ex Koen, *Ruta gravelens* Linn. And *Micromelum pubescens* Blume", Indian Journal of Chemistry, Section B: Organic Chemistry Including Medicinal Chemistry, 27B(6), 594-596.

Banerji, J.; Ghoshal, N.; Sarkar, S.; Kumar, M. **1982**. "Studies on Rutaceae. Part II. Chemical investigations of the constituents of *Atalantia wightii*, *Limonia crenulata*, *Feronia limonia*, *Citrus limon* and synthesis of luvangetin, xanthyletin, and marmin", *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem*., 21B(5), 496-498.

Banerji, A.; Luthria, D. L; Prabhu, B. R. **1988b**. "Prenylated compounds from *Atalantia racemosa*: isolation and synthesis of two pyranoflavones", *Phytochemistry*, 27(11), 3637-3640.

Banthorpe, D. V.; Brown, G. D. **1989**. "Two unexpected coumarin derivatives from tissue cultures of compositae species", *Phytochemistry*, 28(11), 3003-3007.

Basu, D.; Sen, R. **1974**. "Alkaloids and coumarins from root bark of *Aegle marmelos*", *Phytochemistry*, 13(10), 2329-2330.

Bui, K. A.; Duong, A. T. ; Tran, V. S.; Seip, S. **2004**. "Isolation and structure elucidation of a new limonoid from Vietnamese *Citrus nobilis* seeds", *Tap Chi Hoa Hoc*, 42(4), 520-523.

Chatterjee, A.; Mitra, S. S. **1949**. "Constitution of the active principles isolated from the matured bark of *Aegle marmelos* Correa", *J. Am. Chem. Soc.*, 71, 606-609.

Das, A. V.; Padayatti, P. S.; Paulose, C. S. **1996**. "Effect of leaf extract of *Aegle marmelos* (L) Correa ex Roxb. On histological and ultra-structural changes in tissue of streptozotocin induced diabetic rats", *Indian J. Exp. Biol*., 34, 341-345.

De Mol, N. J.; Reisch, J.; Van Henegouwen, G. M. J. B.; Gerardus, M. J. B. **1984**. "On the involvement of singlet oxygen in the biosynthesis of oxygenation products of the furocoumarin imperatorin", *Zeitschrift fuer Naturforschung, Teil B: Anorganische Chemie, Organische Chemie*, 39B(10), 1433-1441.

Faizi, S.; Farooqi, F.; Zikr-Ur-Rehman, S.; Naz, A.; Norr, F.; Ansari, F.; Ahmad, A.; Khan, S. A. **2009**. "Shahidine, a novel and highly labile oxazoline from *Aegle marmelos*: the parent compound of aegeline and related amides", *Tetrahedron*, 65, 998-1004.

Fraser, A. W.; Lewis, J. R. **1973**. "Two novel acridone alkaloids from *Atalantia ceylanica*", *J. Chem. Soc*., *Chem. Commun*., 17, 615-616.

Govindachari, T. R.; Premila, M. S. **1983.** "Some alkaloids from *Aegle marmelos*", *Phytochemistry*, 22, 755-757.

Ito, C.; Matsuoka, M.; Mizuno, T.; Sato, K.; Kimura, Y.; Jiichi, M.; Inoue, M.; Kajiura, I.; Omura, M.; Furukawa, H. **1988**. "Constituents of domestic Citrus plants. Part VIII. New coumarins from some Citrus plans", *Chem. Pharm. Bull*., 36(10), 3805-3810.

Ito, C.; Mizono, C.; Matsuoka, M.; Kimura, Y.; Sato, K.; Kajiura, I.; Omura, M.; Ju-Ichi, M.; Furukawa, H. **1988.** "A new flavonoid and other components from Citrus Plants", *Chem. Pharm. Bull.,* 36(9), 3292-3295.

Jain, A. K.; Srivastava, S. K.; Srivastava, S. D. **1991**. "Some new constituents from heartwood of *Aegle marmelos* Corr.", *J. Indian Chem. Soc.*, 68(8), 452-454.

Jeong, S. H.; Han, X. H.; Hong, S. S.; Hwang, J. S.; Hwang, J. H.; Lee, D.; Lee, M. K.; Ro, J. S.; Hwang, B. Y. **2006.** "Monoamine oxidase inhibitory coumarins from the aerial parts of *Dictamnus albus*", *Arch. Pham. Res.*, 29(12), 1119-1124.

Kalaivani, T.; Premkumar, N.; Ramya, S.; Siva, R.; Vijayakumar, V.; Meignanam, E.; Rajasekaran, C.; Jayakumararaj, R. **2009**. "Investigations on hepatoprotective activity of leaf extracts of *Aegle marmelos* (L.) Corr. (Rutaceae)", *Ethnobot. Leafl*, 13, 47-50.

Kim, J. S.; Kim, J. C.; Shim, S. H.; Lee, E. J.; Jin, W. Y.; Bae, K.; Son, K. H.; Kim, H. P.; Kang, S. S.; Chang, H. W. **2006**. "Chemical constituents of the root of *Dystaenia takeshimana* and their anti-inflammatory activity", *Arch. Pharm. Res.*, 29(8), 617-623.

Mishra, B. B.; Singh, D. D.; Kishore, N.; Tiwari, V. K.; Tripathi, V. **2010**. "Antifungal constituents isolated from the seeds of *Aegle marmelos*", *Phytochemistry*, 71, 230-234.

Murray, R. D. H; Hall, D. A. **1985**. "Structure revision of the coumarin, ceylantin", *Phytochemistry*, 24(10), 2465-2466.

Nakamori, T.; Taniguchi, M.; Shibano, M.; Wang, N.-H.; Baba, K. **2008**. "Chemical studies on the root of *Heracleum candicans* WALL.", *J. Nat. Med.*, 62, 403-412.

Nemoto, T.; Ohshima, T.; Shibasaki, M. **2003**. "Enantioselective total syntheses of (+)-decursin and related natural compounds using catalytic asymmetric epoxidation of an enone", *Tetrahedron*, 59, 6889-6897.

Ohashi, K.; Watanabe, H.; Ohi, K.; Arimoto, H.; Okumura, Y. **1995**. "Two new 7-geranyloxycoumarins from the bark of *Aegle marmelos*, and Indonesian medicinal plant", *Chemistry Lett.*, (10), 881-882.

Ohashi, K.; Watanabe, H.; Okumura, , H.; Okumura, Y.; Uji, T.; Kitagawa, I. **1994**. "Indonesian medicinal plants. XII. Four isomeric lignan-glucosides from the bark of *Aegle marmelos* (Rutaceae)", *Chem. Pharm. Bull*., 42(9), 1924-1926.

Patre, R. E.; Shet, J. B.; Parameswaran, P. S.; Tilve, S. G. **2009**. "Cascade Wittig reaction-double Claisen and Cope rearrangements: one-pot synthesis of diprenylated coumarins gravelliferone, balsamiferone, and 6,8-diprenylumbelliferone", *Tetrahedron*, 50, 6488-6490.

Phuwapraisirisan, P.; Puksasook, T.; Jong-aramruang, J.; Kokpol, U. **2008**. "Phenylethyl cinnamides: A new series of α-glucosidase inhibitors from the leaves of *Aegle marmelos*", *Bioorg. Med. Chem. Lett.*, 18, 4956-4958.

Razdan,T. K.; Qadri, B.; Harkar, S.; Waight, E. S. **1987**. "Chromones and coumarins from *Skimmia laureola*", *Phytochemistry*, 26(7), 2063-2069.

Runa, B. K.; Singh, U. P.; Taneja, V. **1997**. "Antifungal activity and kinetics of inhibition by essential oil isolated from leaves of *Aegle marmelos* (L.) Corr.", *J. Ethnopharmacol*., 57, 29-34.

Saha, S. K.; Chatterjee, A. **1957**. "Isolation of alloimperatorin and β-sitosterol from the fruits of *Aegle marmelos*", *J. Indian Chem. Soc.*, 34, 228-230.

Sharma, B. R.; Rattan, R. K.; Sharma, P. **1981**. "Marmeline, an alkaloid, and other components of unripe fruits of *Aegle marmelos*", *Phytochemistry*, 20(11), 2606-2607.

Sharma, B. R.; Rattan, R. K.; Sharma, P. **1980**. "Constituents of leaves and fruits of *Aegle marmelos*", *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 19B(2), 162.

Sharma, B. R.; Sharma, P. **1981**. "Constituents of *Aegle marmelos*. II. Alkaloids and coumarin from fruits", *Planta Med*., 43(1), 102-103.

Shoeb, A.; Kapil, R. S.; Popli, S. P. **1973**. "Coumarins and alkaloids of *Aegle marmelos*", *Phytochemistry*, 12(8), 2071-2072.

Smittinan, T. **2001**. "Thai Plant Names". Prachachon publisher: Bangkok.

Srivastava, S. D.; Srivastava, S.; Srivastava, S. K. **1996**. "New anthraquinones from the heartwood of *Aegle marmelos*", *Fitoterapia*, 67(1), 83-84.

Wu, T. S. **1987**. "A 2,2-dimethylpyranoflavonol from *Citrus nobilis*", *Phytochemistry*, 26(11), 3094-3095.

Yamaguchi, S.; Muro, S.; Kobayashi, M.; Miyazawa, M.; Hirai, Y. **2003**. "Absolute structures of some naturally occurring isopropenyldihydrobenzofurans, remirol, remiridiol, angenomalin and isoangenomalin", *J. Org. Chem.*, 68, 6274-6278.

Zou, Y.; Lobera, M.; Snider, B. B. **2005**. "Synthesis of 2,3-dihydro-3-hydroxy-2-hydroxyalkylbenzofurans from epoxy aldehydes. One–step syntheses of brosimacutin G, vaginidiol, vaginol, smyrindiol, xanthoarnol, and avicenol A. Biomimetic Syntheses of angelicin and psoralen", *J. Org. Chem.*, 70, 1761-1770.

APPENDIX

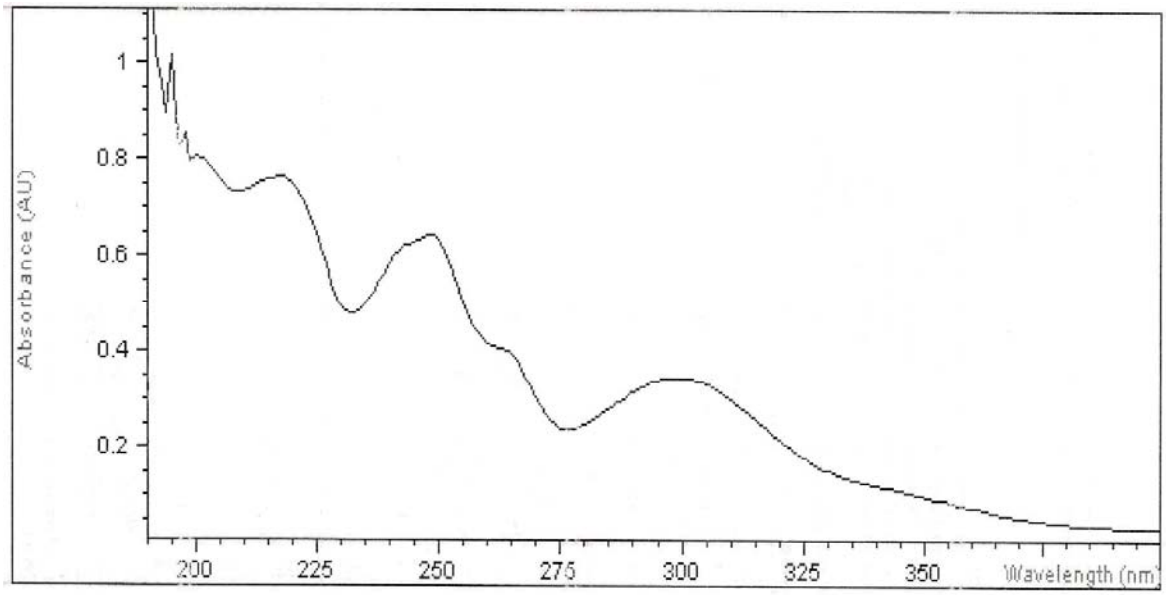


Figure 23 UV (MeOH) spectrum of compound **PW1**

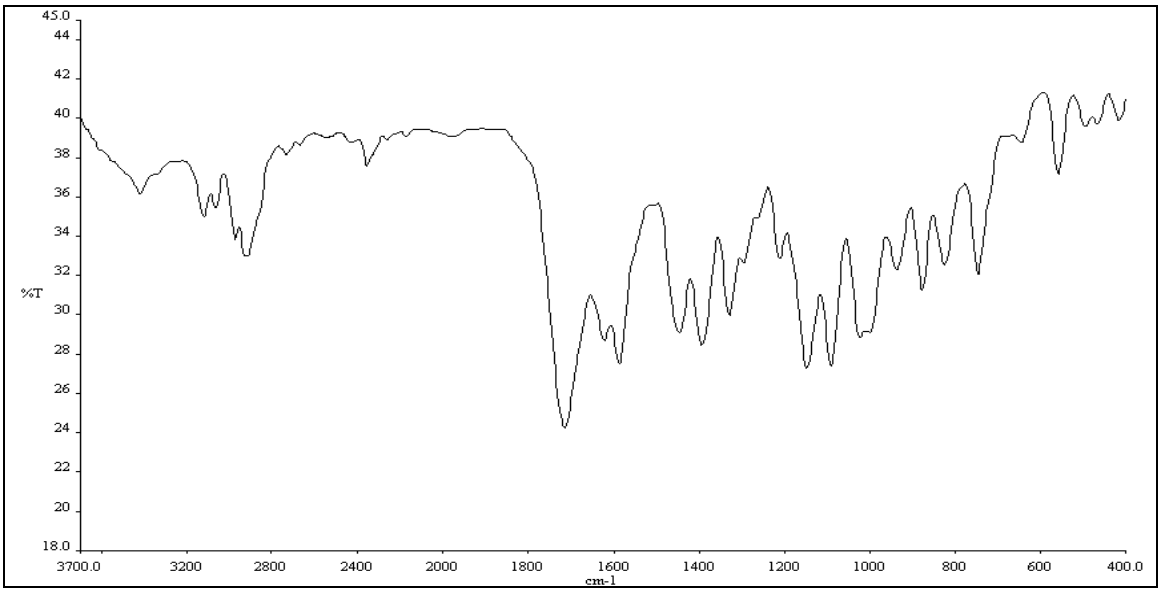


Figure 24 IR (neat) spectrum of compound **PW1**

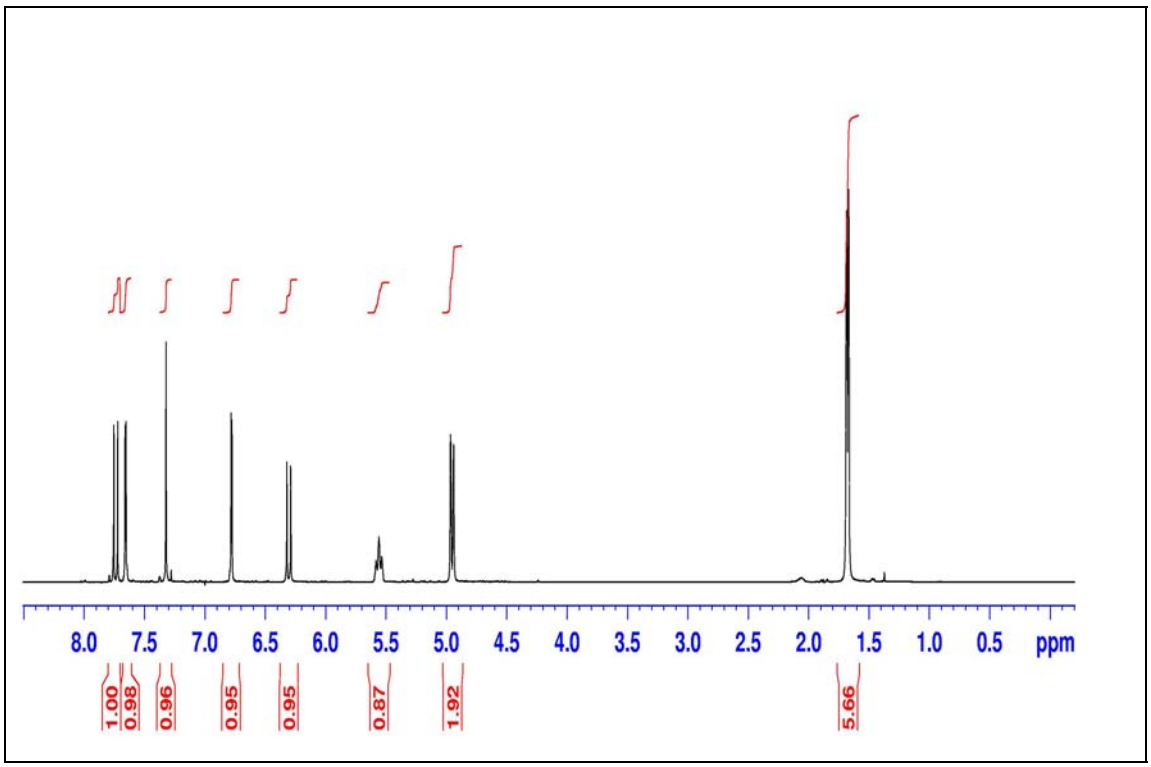


Figure 25 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW1**

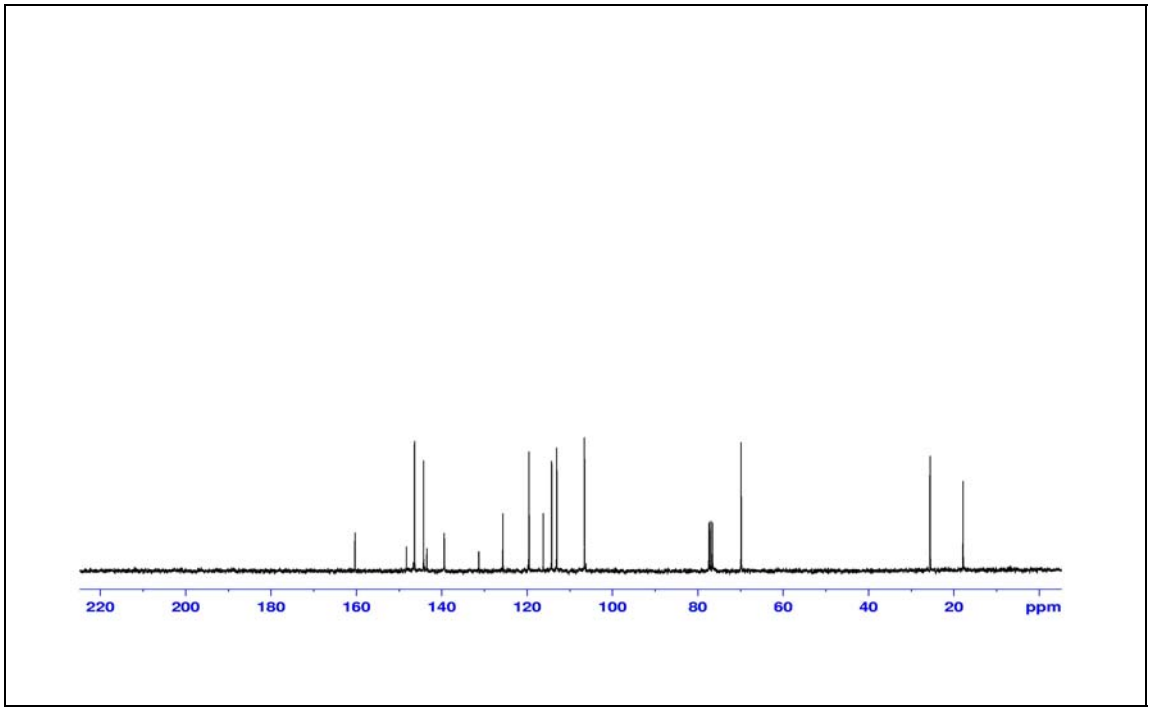


Figure 26 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW1**

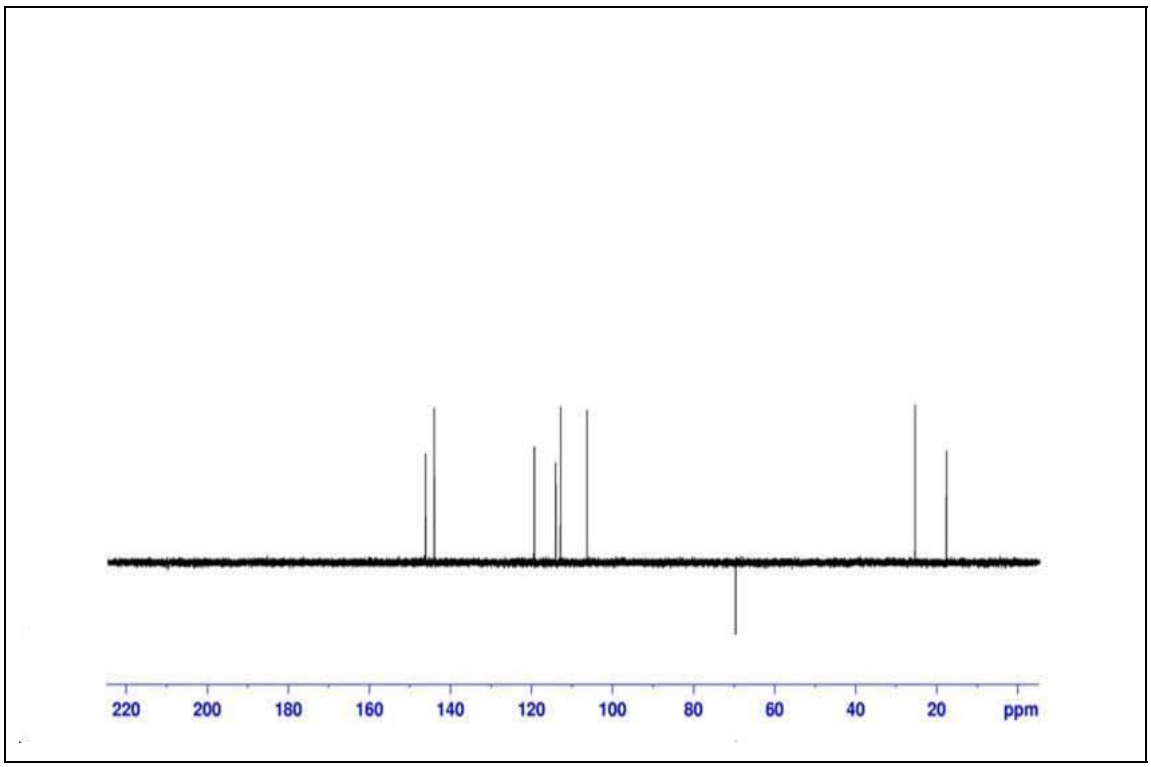


Figure 27 Dept 135° ($CDCl_3$) of compound **PW1**

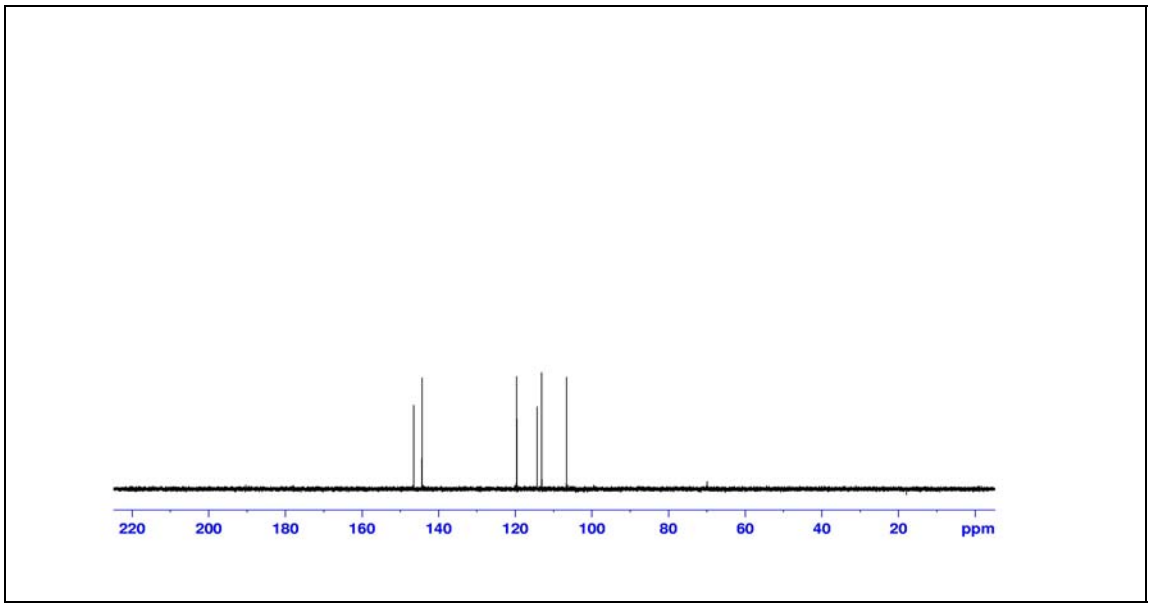


Figure 28 Dept 90° ($CDCl_3$) of compound **PW1**

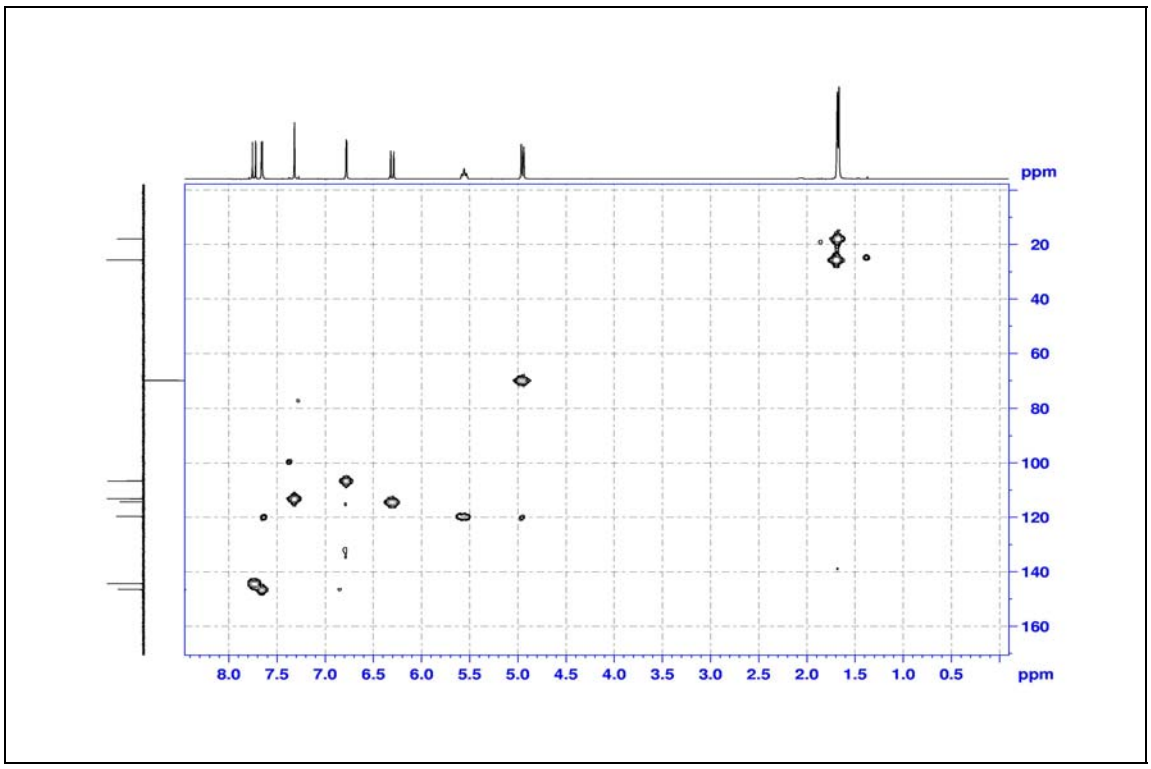


Figure 29 2D HMQC ($CDCl_3$) of compound **PW1**

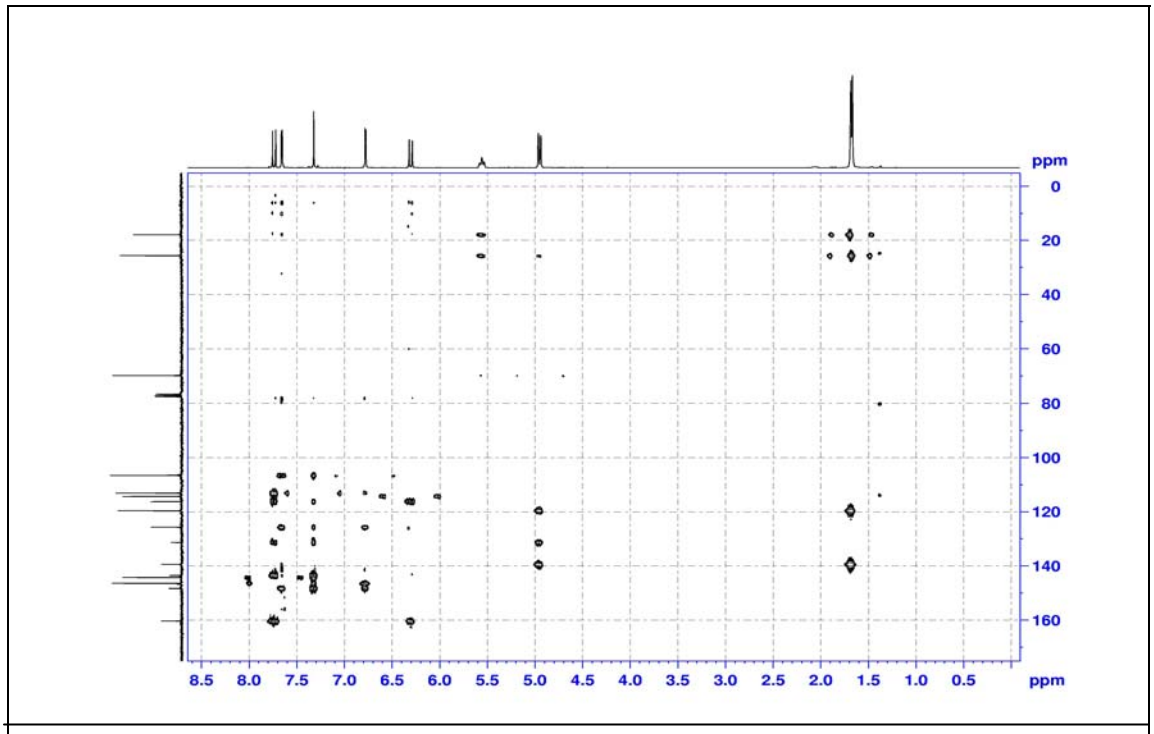


Figure 30 2D HMBC ($CDCl_3$) of compound **PW1**

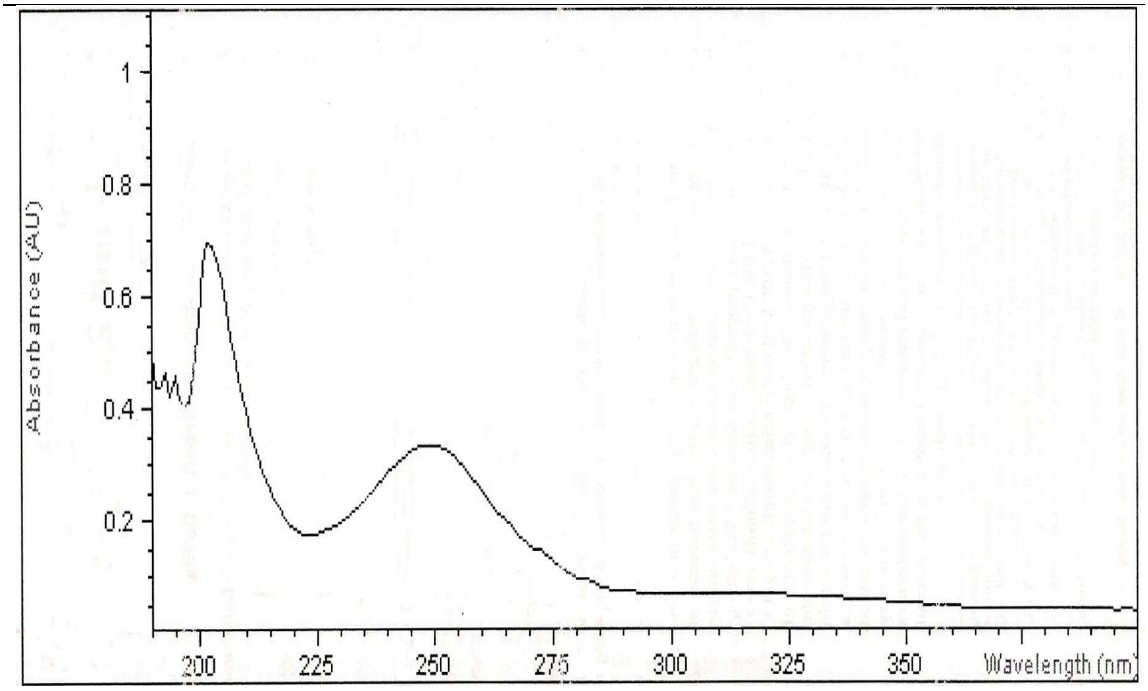


Figure 31 UV (MeOH) spectrum of compound **PW2**

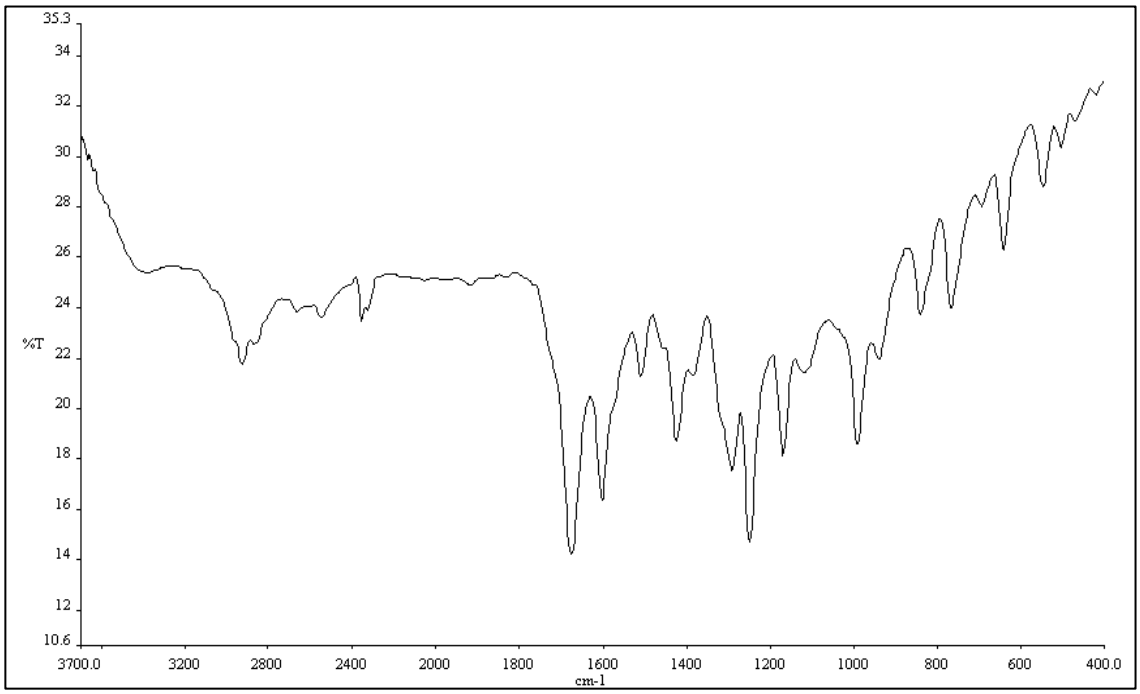


Figure 32 IR (neat) spectrum of compound **PW2**

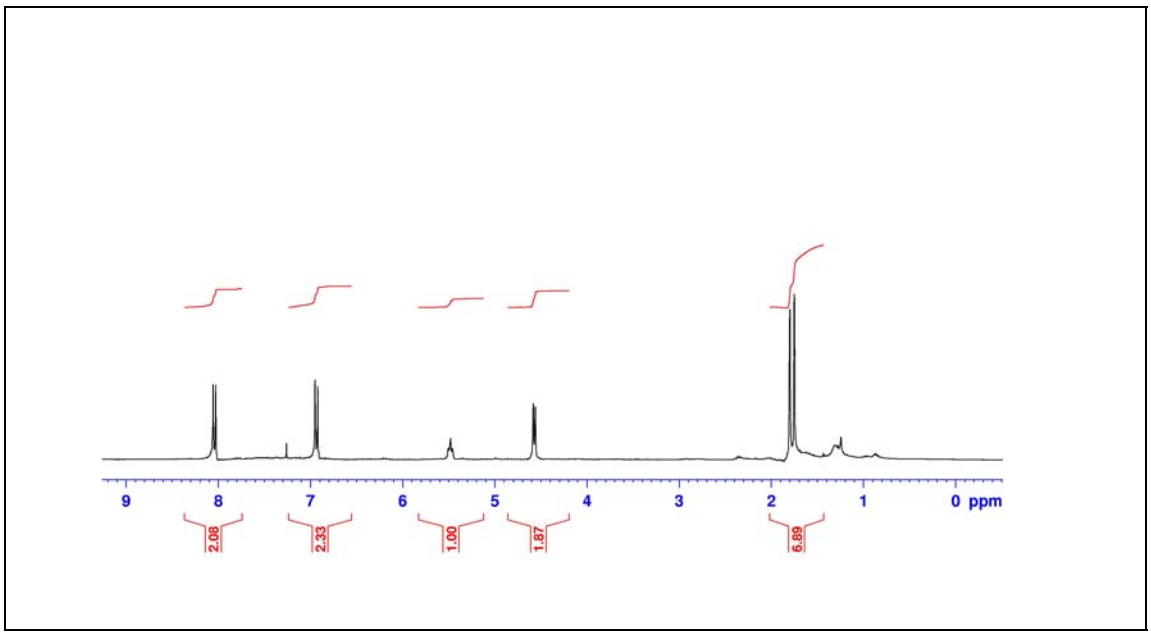


Figure 33 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW2**

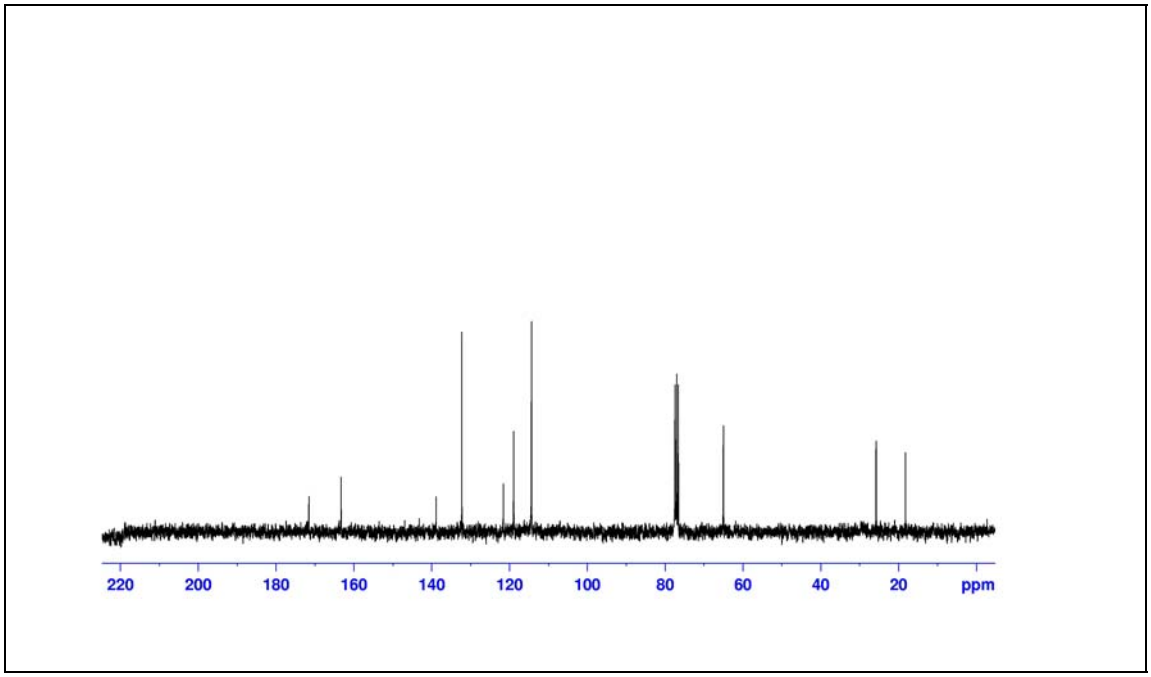


Figure 34 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW2**

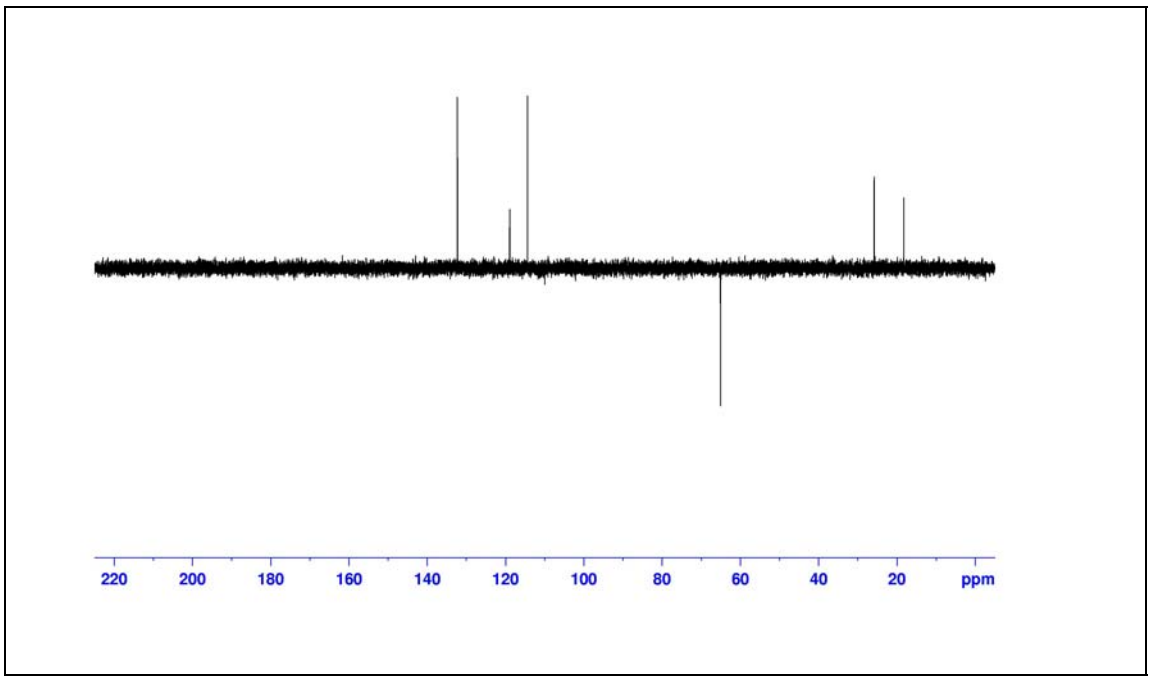


Figure 35 Dept 135° ($CDCl_3$) of compound **PW2**

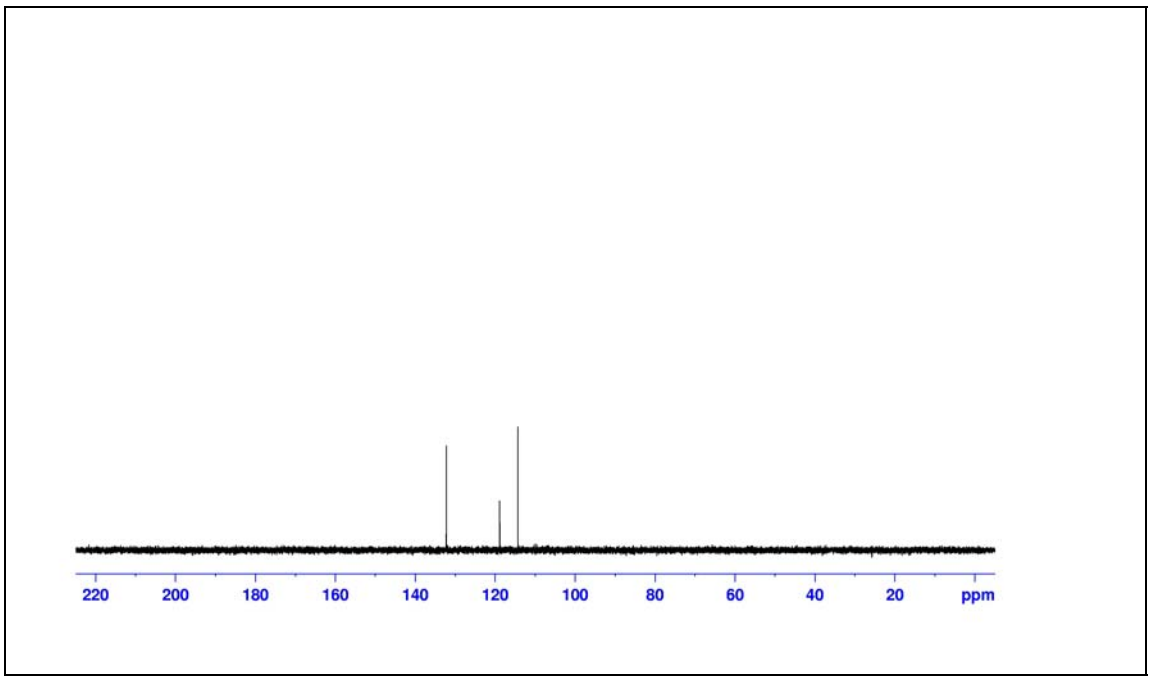


Figure 36 Dept 90° ($CDCl_3$) of compound **PW2**

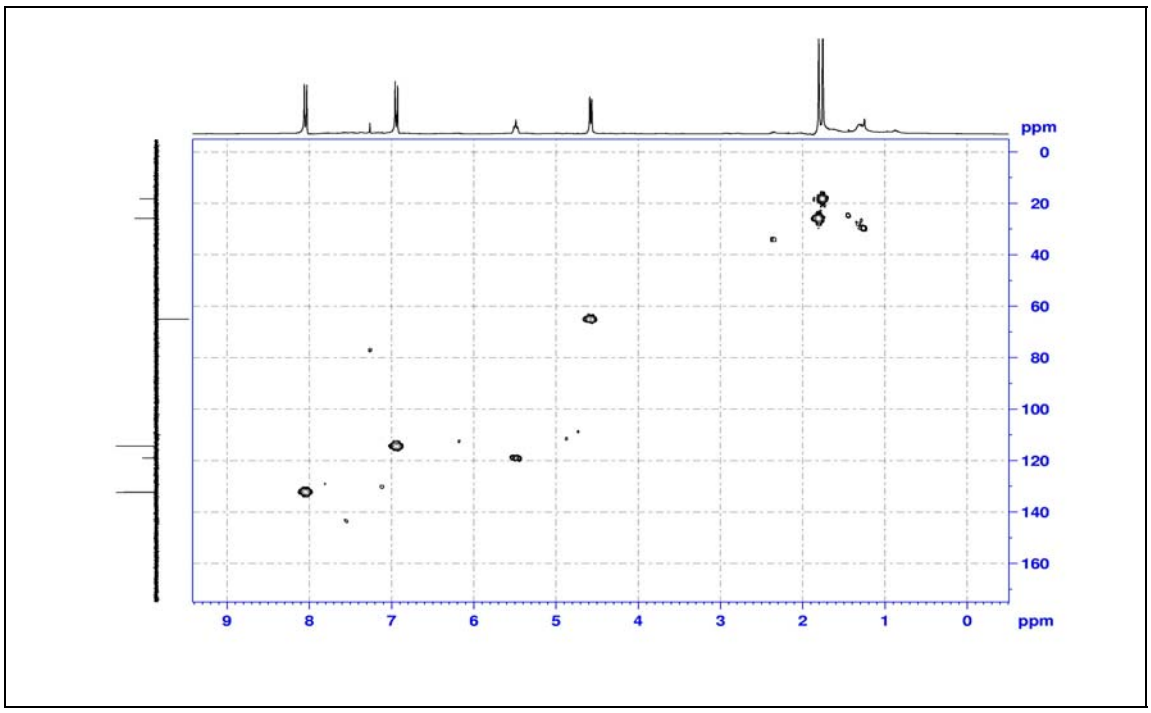


Figure 37 2D HMQC ($CDCl_3$) of compound **PW2**

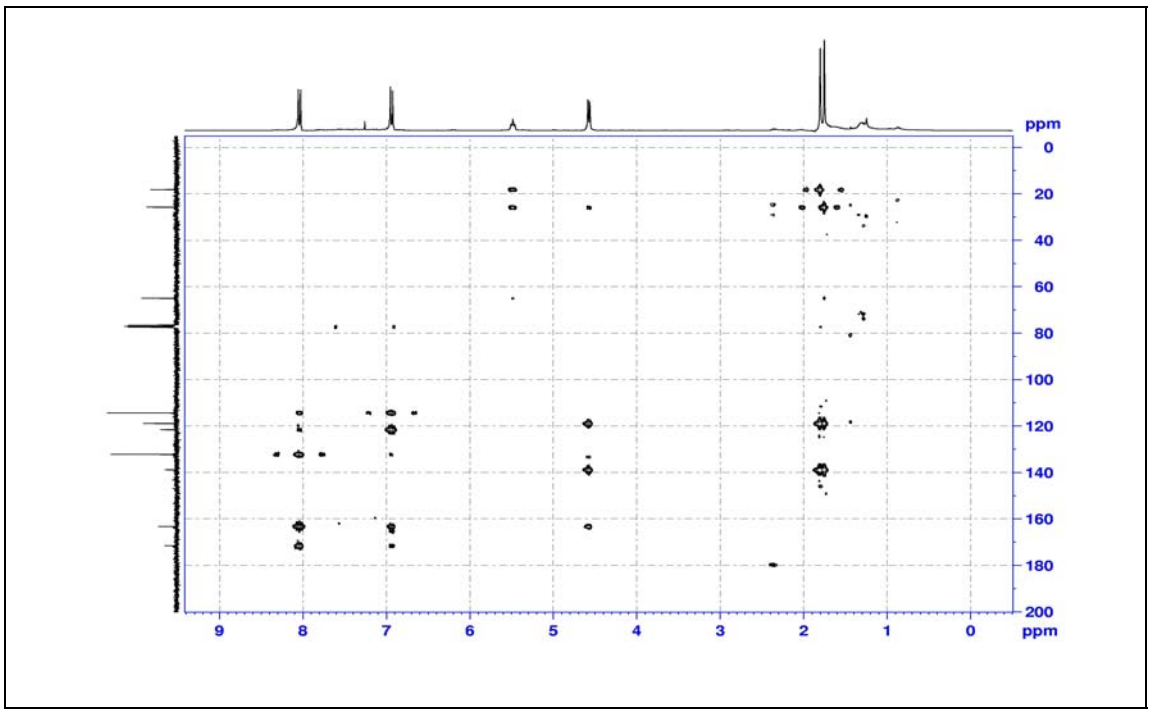


Figure 38 2D HMBC ($CDCl_3$) of compound **PW2**

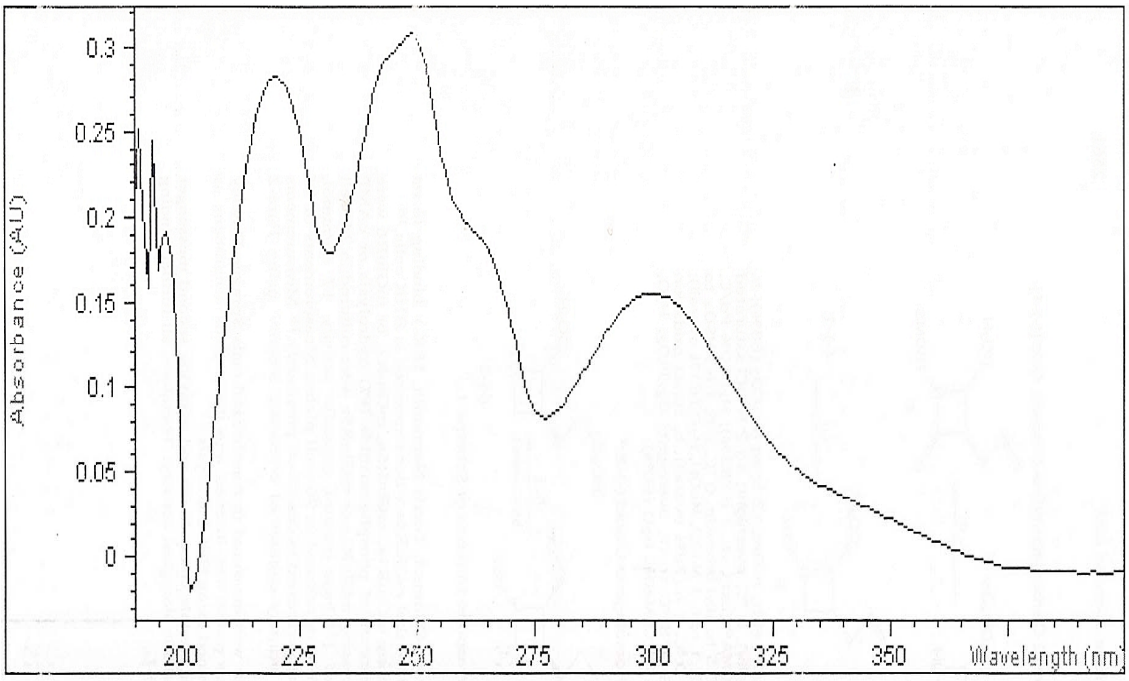


Figure 39 UV (MeOH) spectrum of compound **PW3**

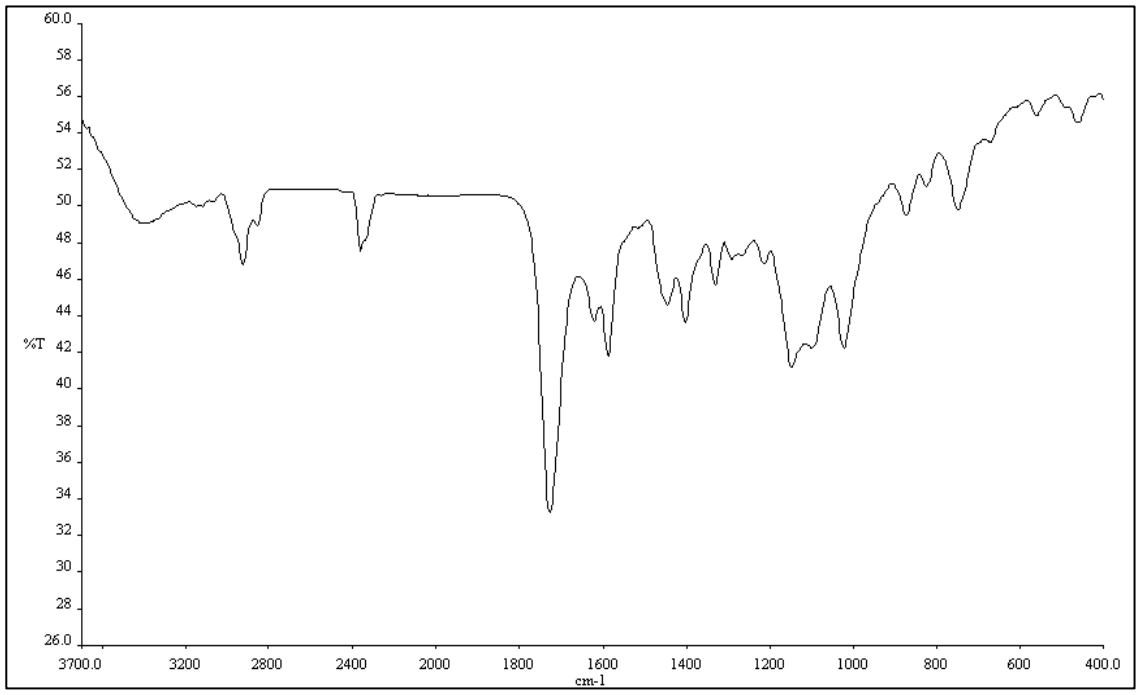


Figure 40 IR (neat) spectrum of compound **PW3**

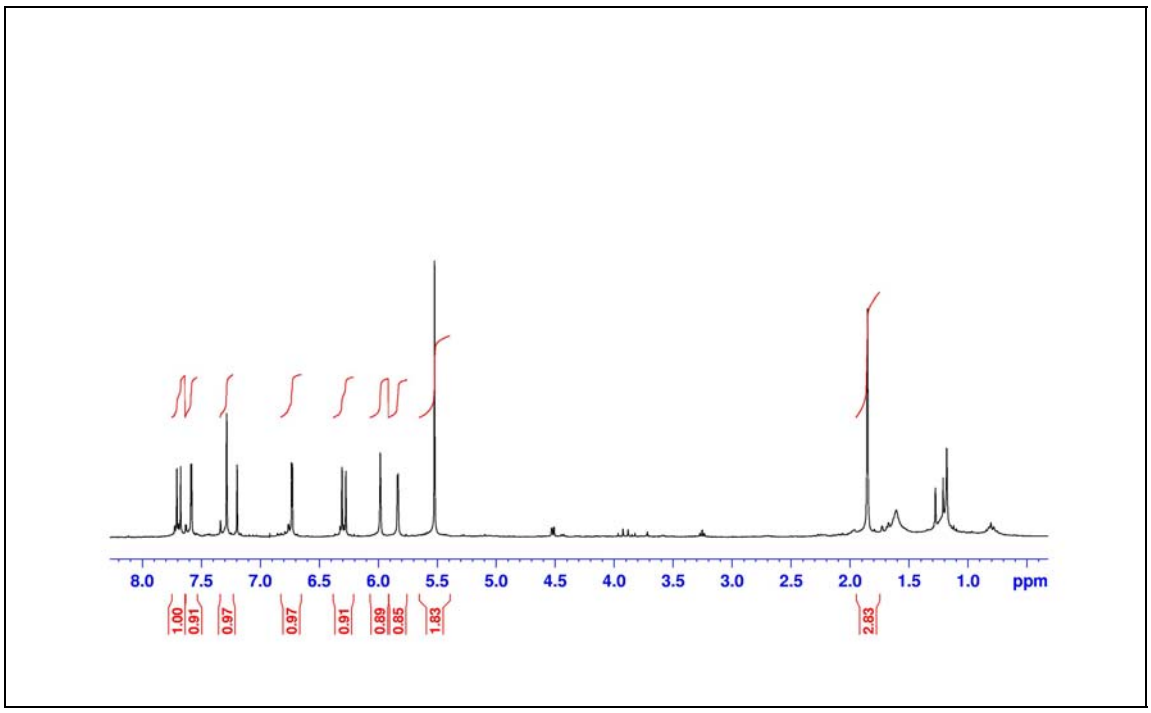


Figure 41 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW3**

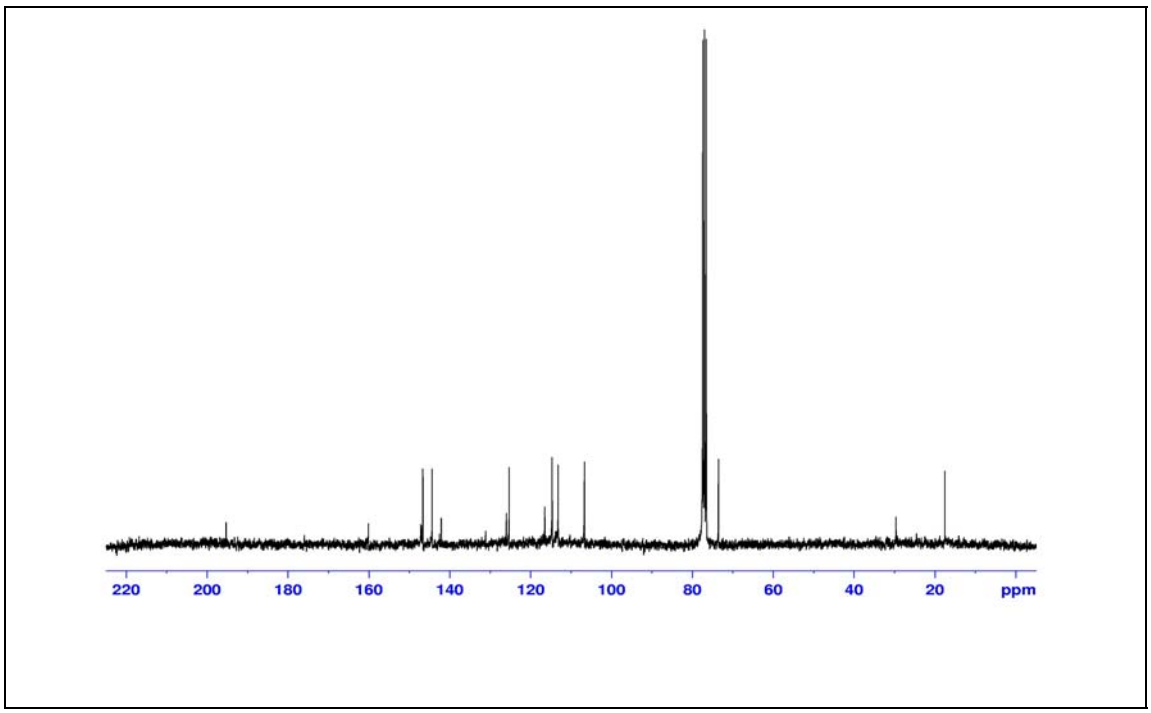


Figure 42 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW3**

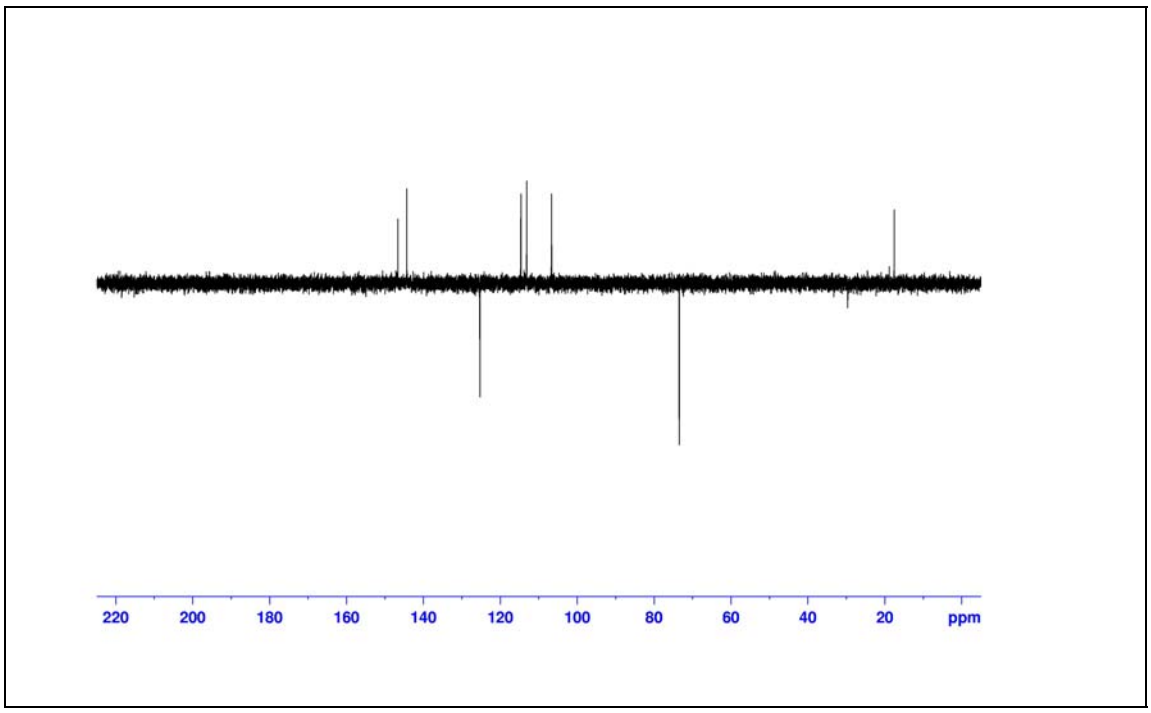


Figure 43 Dept 135° ($CDCl_3$) of compound **PW3**

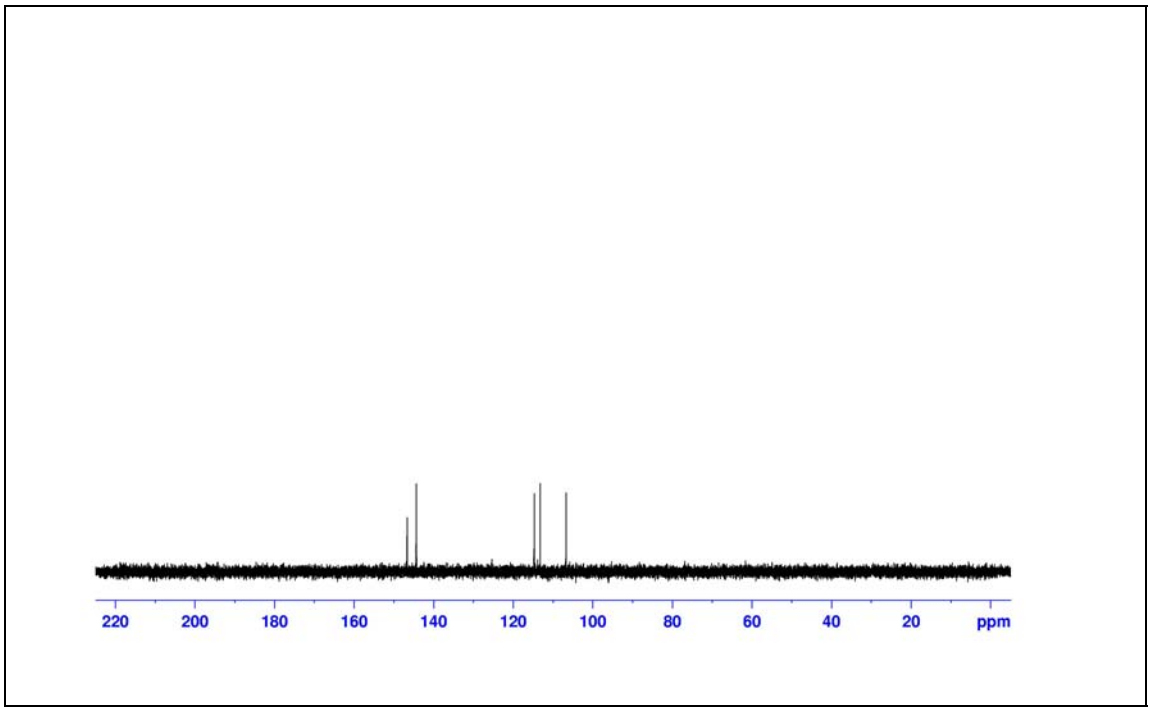


Figure 44 Dept 90° ($CDCl_3$) of compound **PW3**

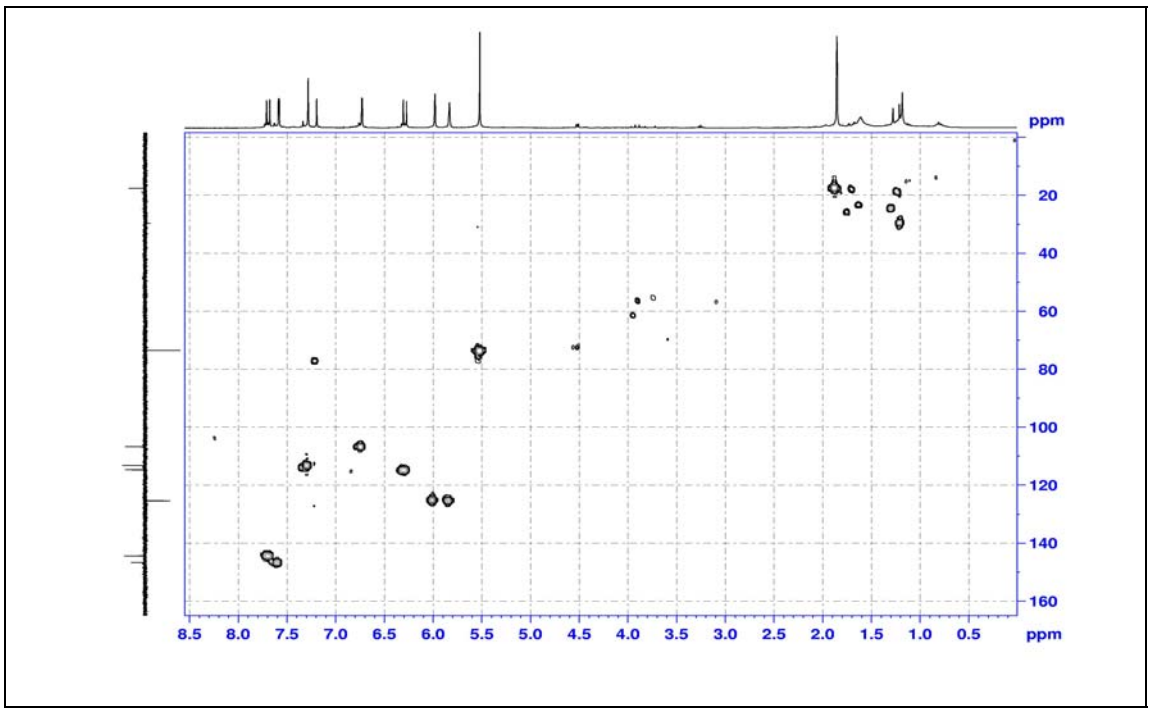


Figure 45 2D HMQC ($CDCl_3$) of compound **PW3**

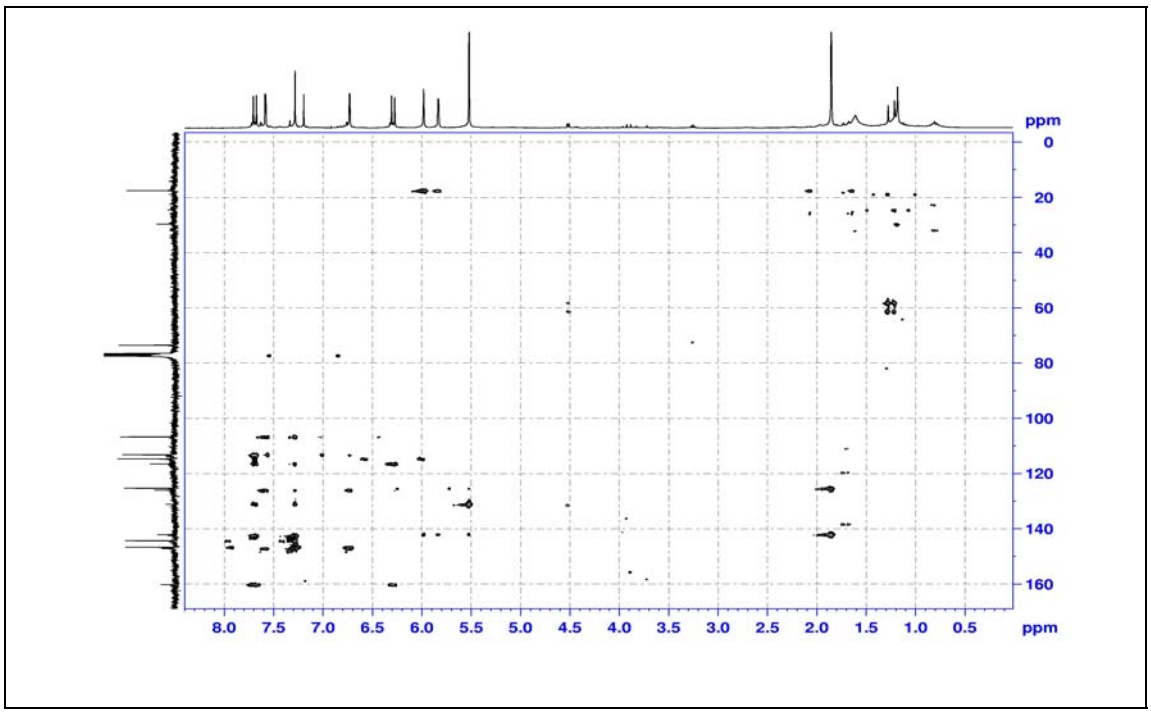


Figure 46 2D HMBC ($CDCl_3$) of compound **PW3**

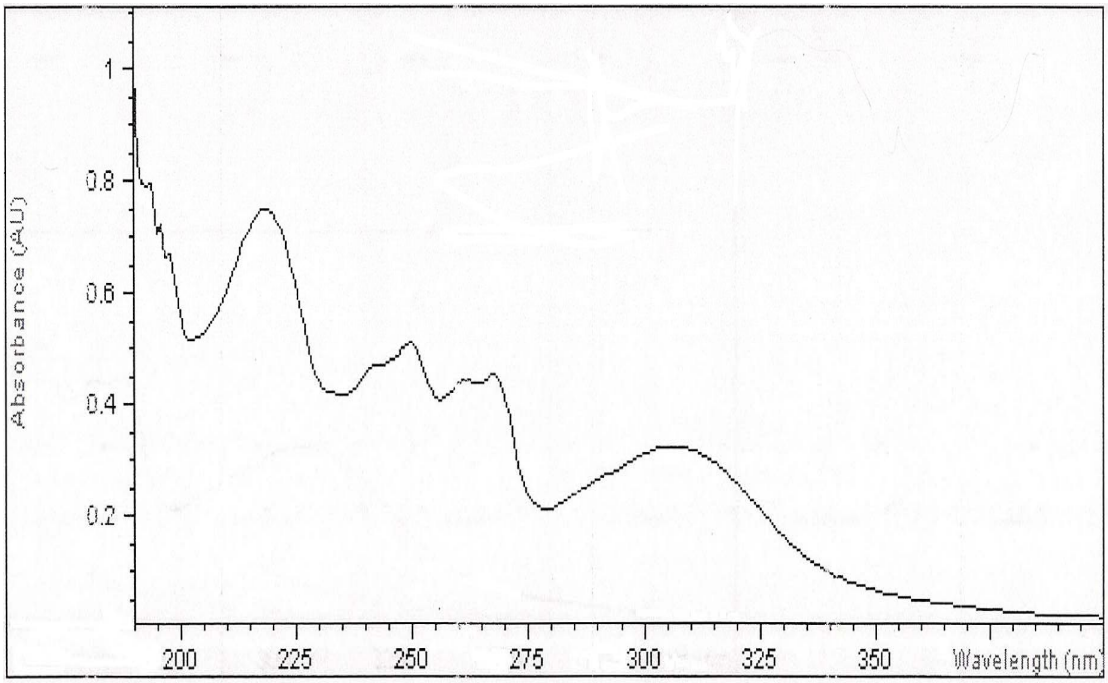


Figure 47 UV (MeOH) spectrum of compound **PW4**

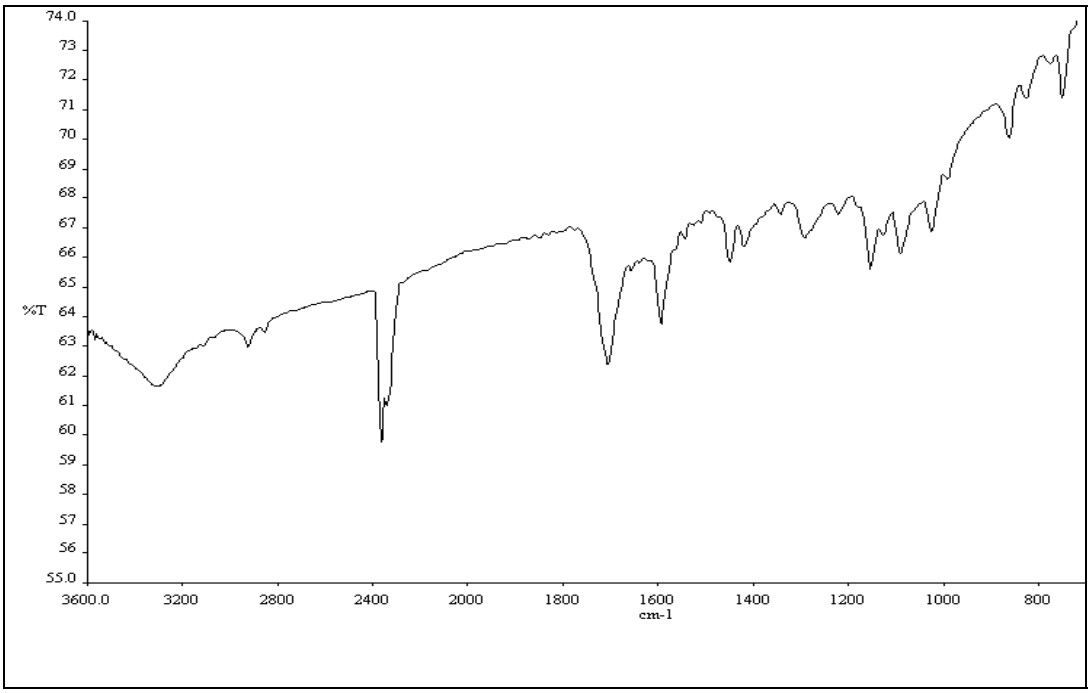


Figure 48 IR (neat) spectrum of compound **PW4**

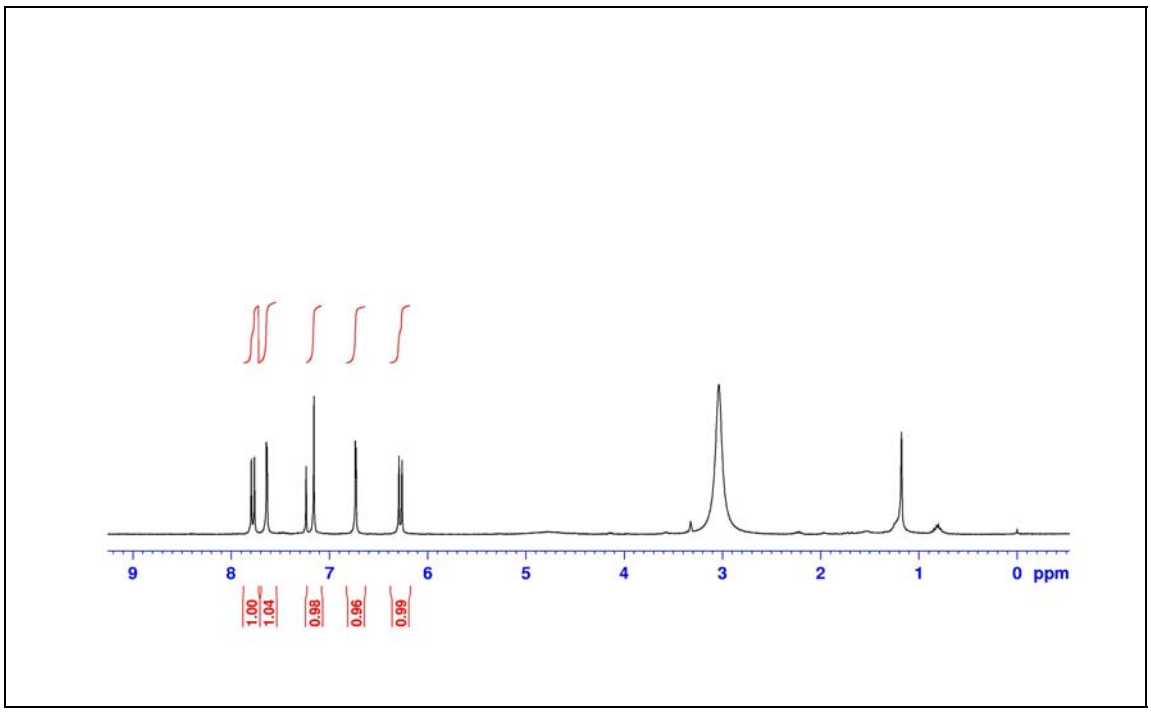


Figure 49 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD (1 drop)) of compound **PW4**

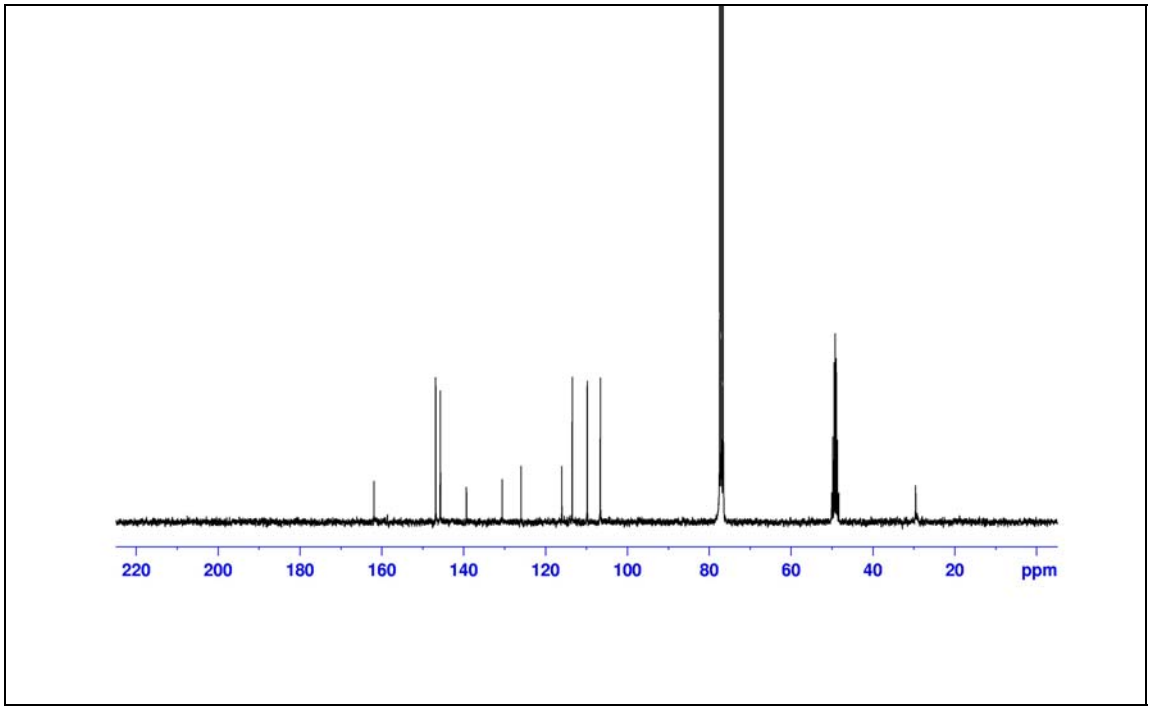


Figure 50 ^{13}C NMR (75 MHz) ($CDCl_3$+CD_3OD (1 drop)) of compound **PW4**

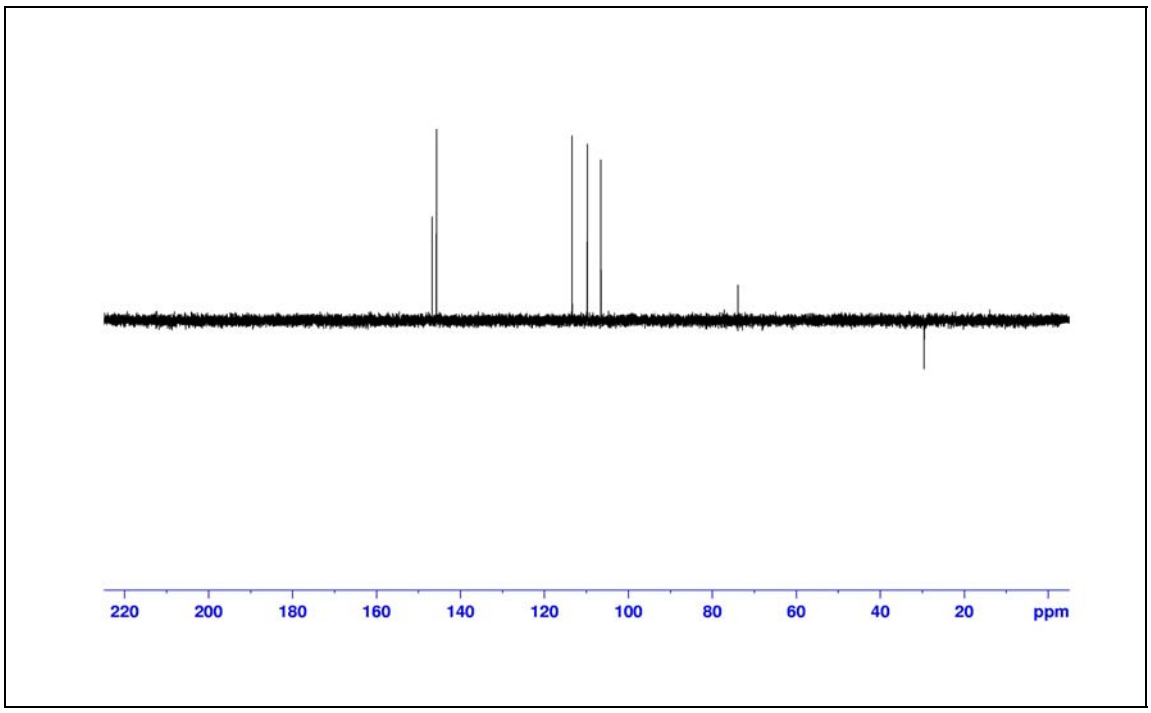


Figure 51 Dept 135° ($CDCl_3$+CD_3OD (1 drop)) of compound **PW4**

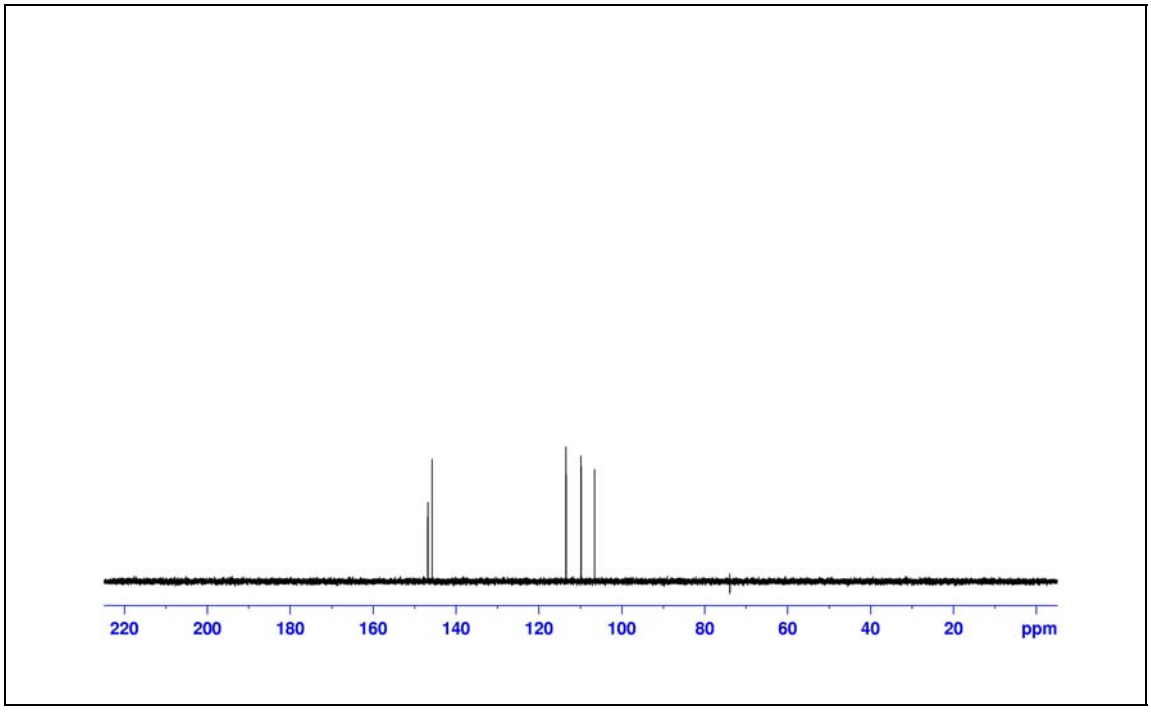


Figure 52 Dept 90° ($CDCl_3$+CD_3OD (1 drop)) of compound **PW4**

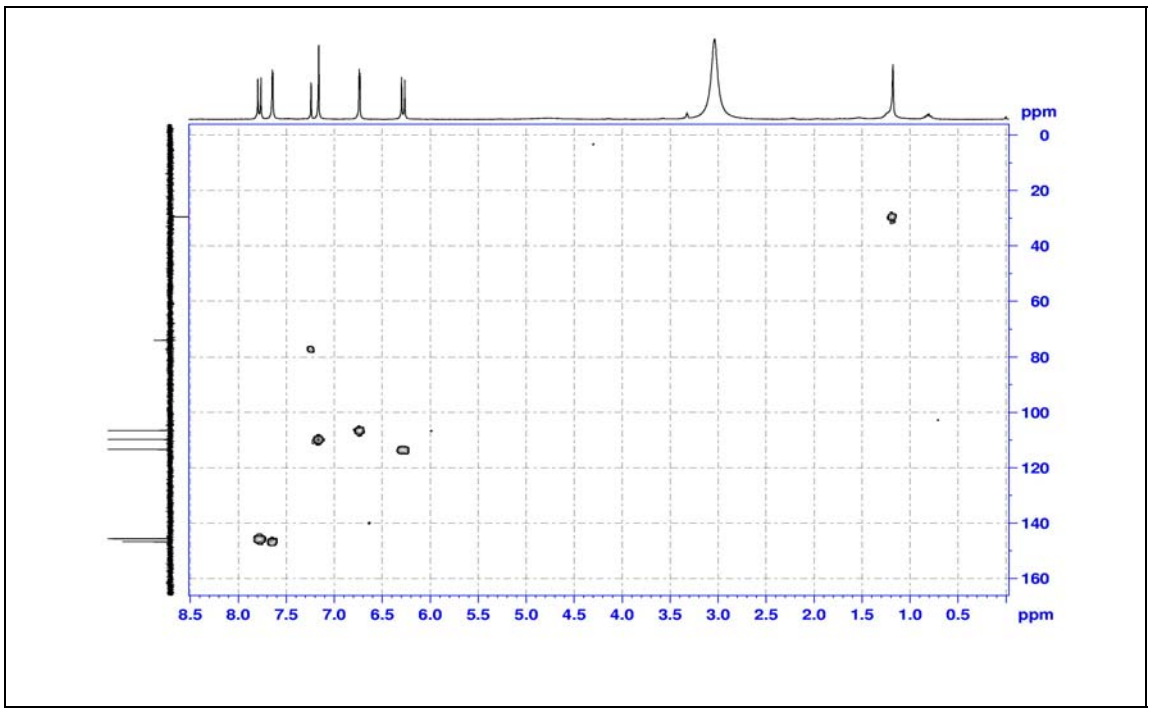


Figure 53 2D HMQC ($CDCl_3$+CD_3OD (1 drop)) of compound **PW4**

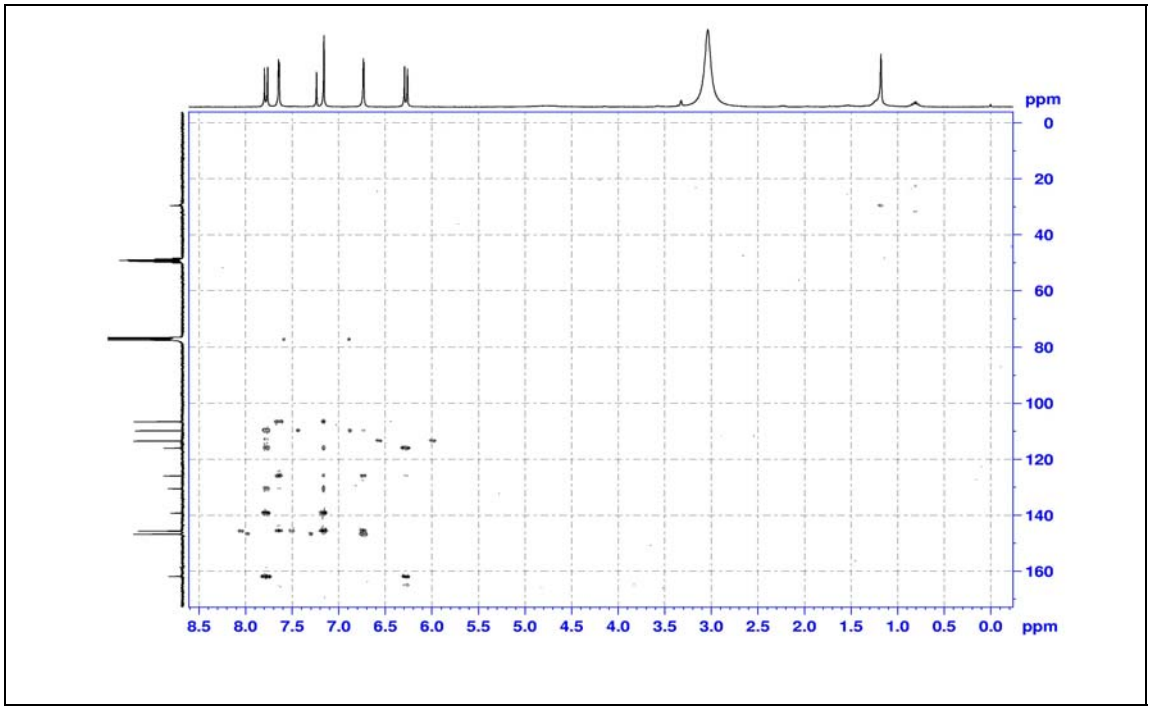


Figure 54 2D HMBC ($CDCl_3$+CD_3OD (1 drop)) of compound **PW4**

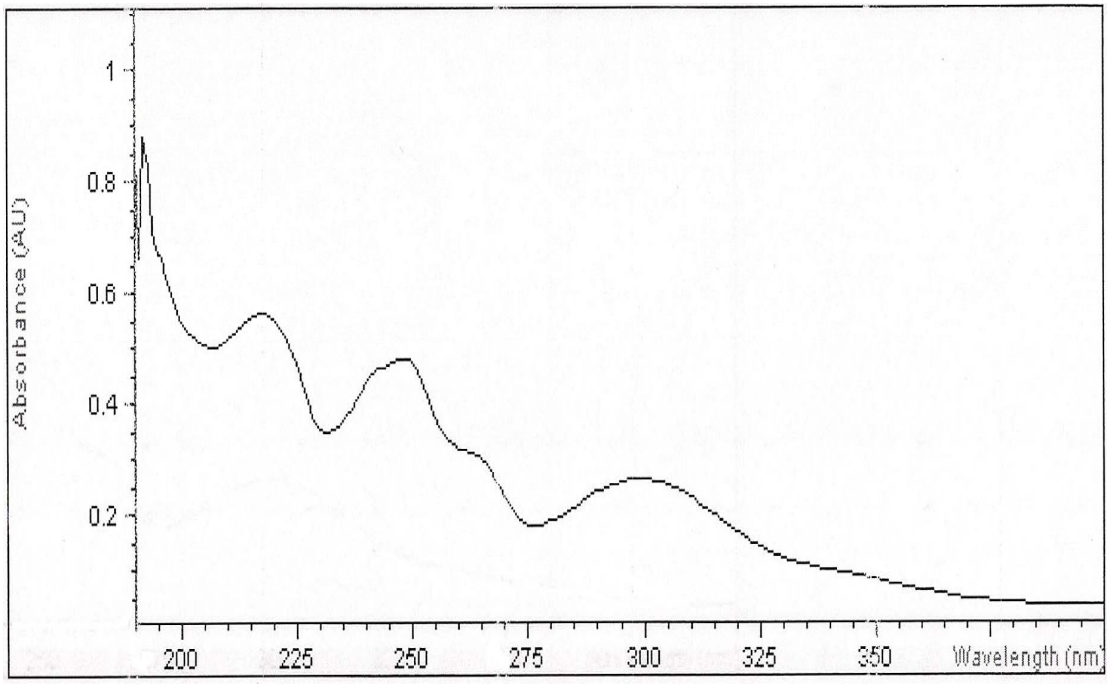


Figure 55 UV (MeOH) spectrum of compound **PW5**

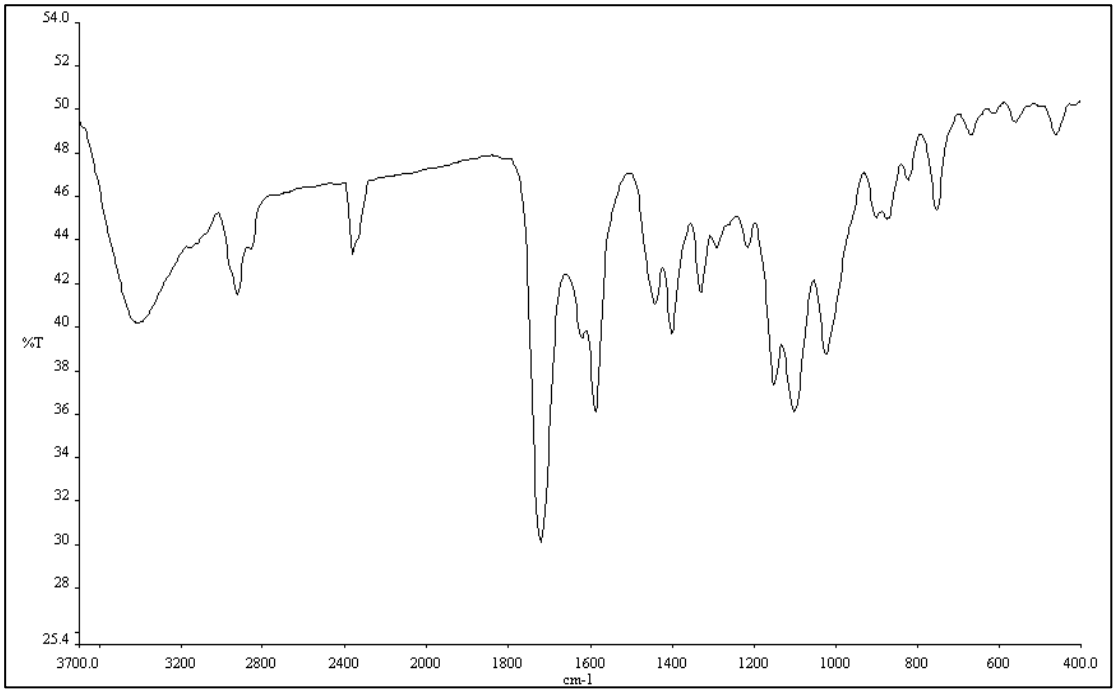


Figure 56 IR (neat) spectrum of compound **PW5**

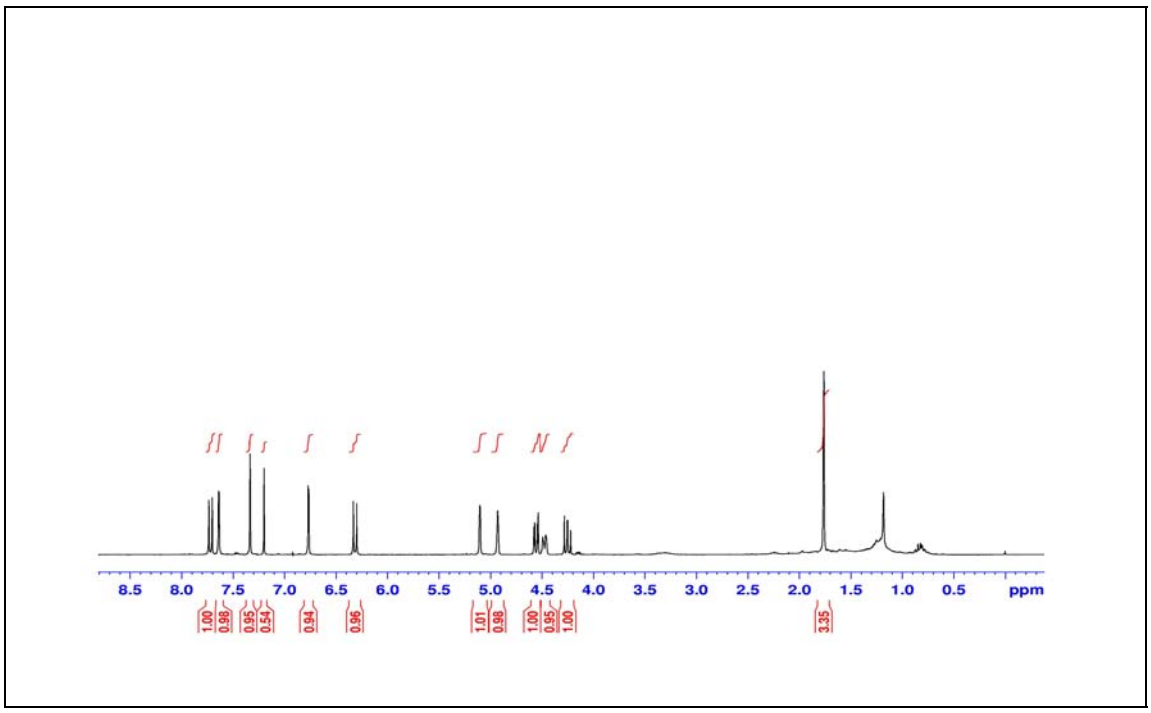


Figure 57 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW5**

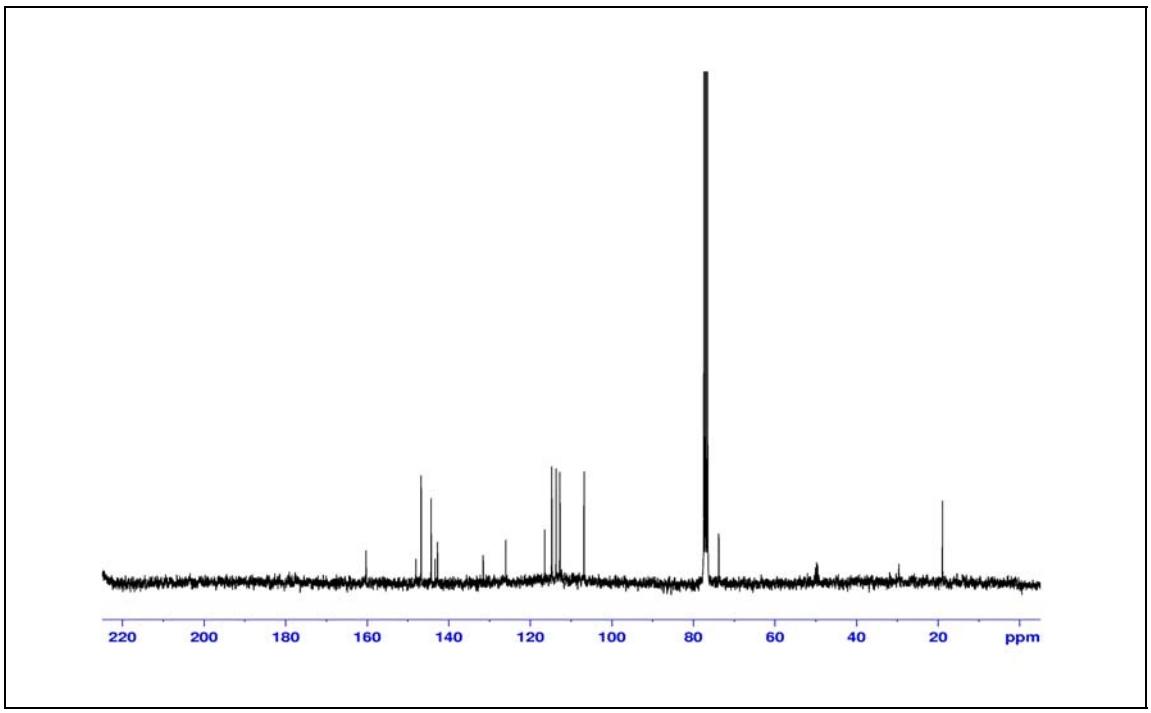


Figure 58 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW5**

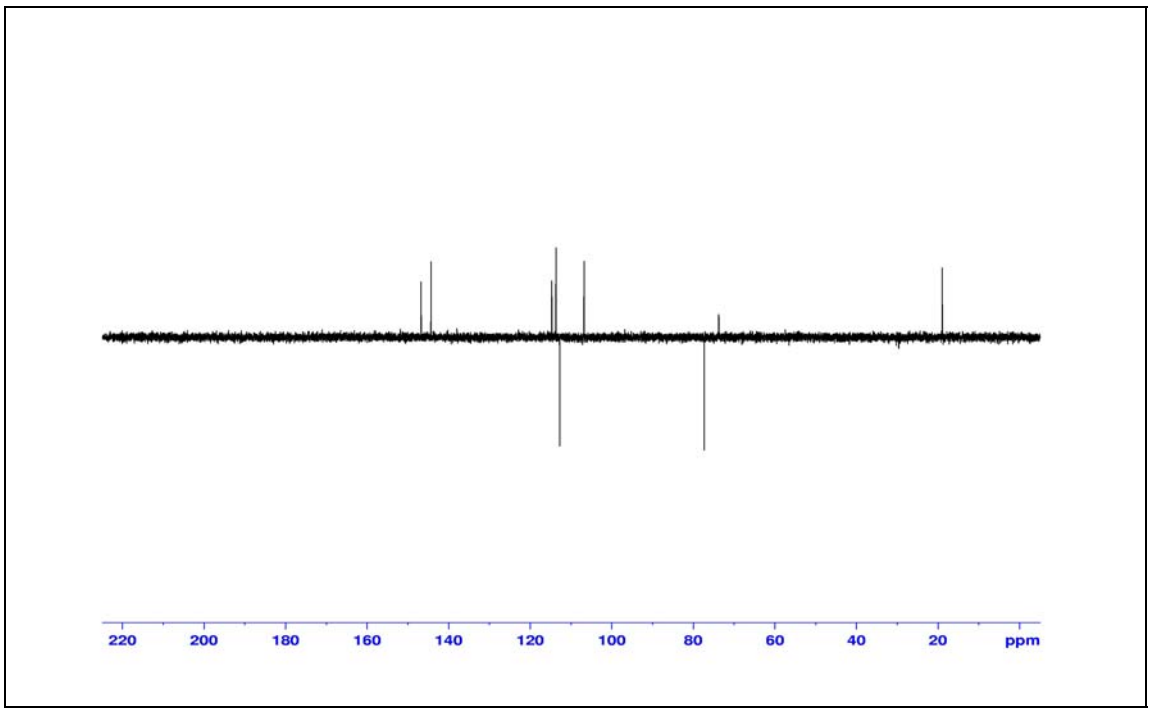


Figure 59 Dept 135° ($CDCl_3$) of compound **PW5**

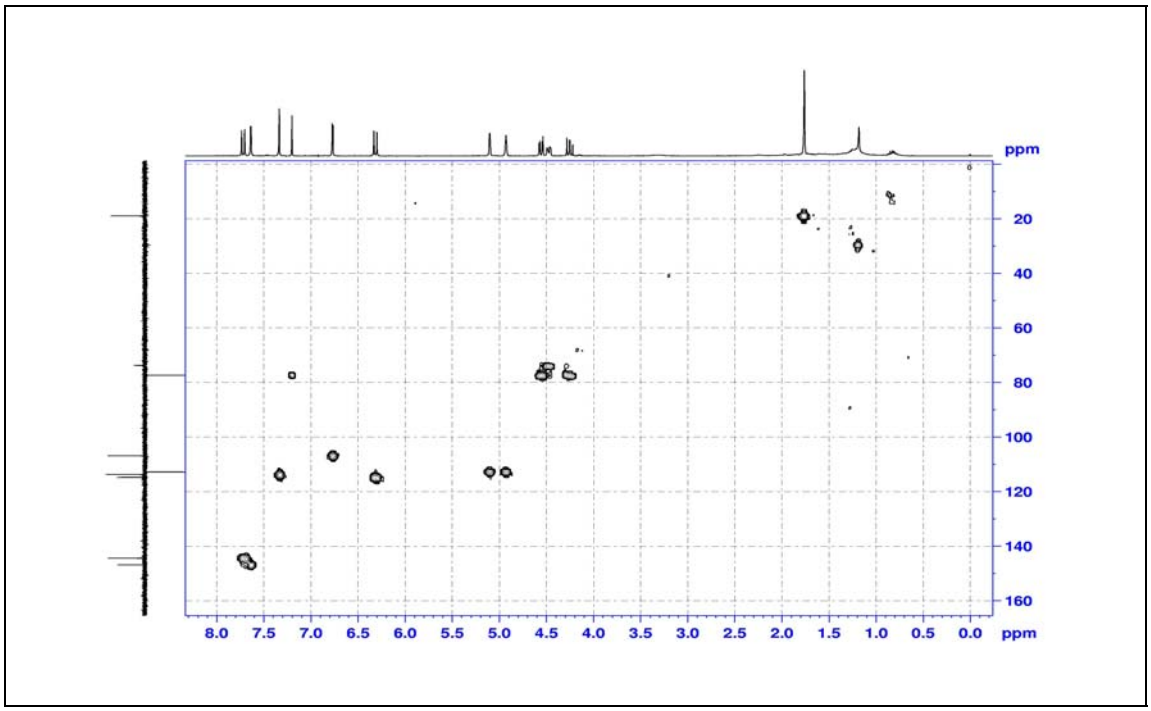


Figure 60 2D HMQC ($CDCl_3$) of compound **PW5**

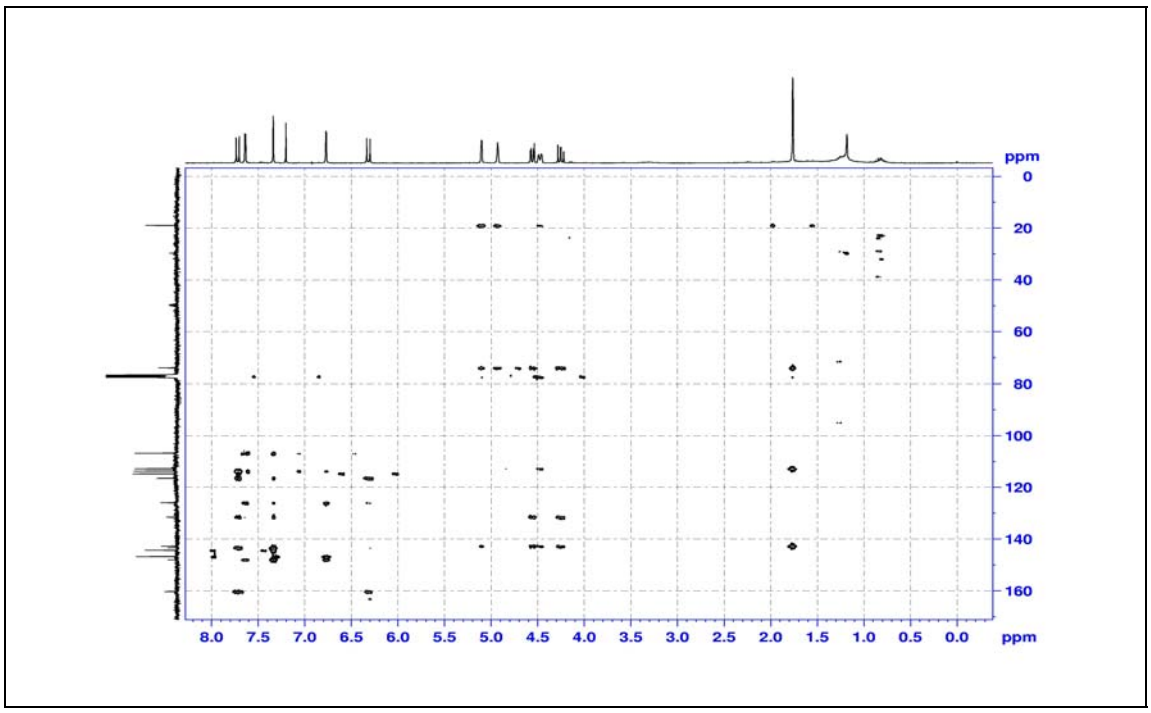


Figure 61 2D HMBC ($CDCl_3$) of compound **PW5**

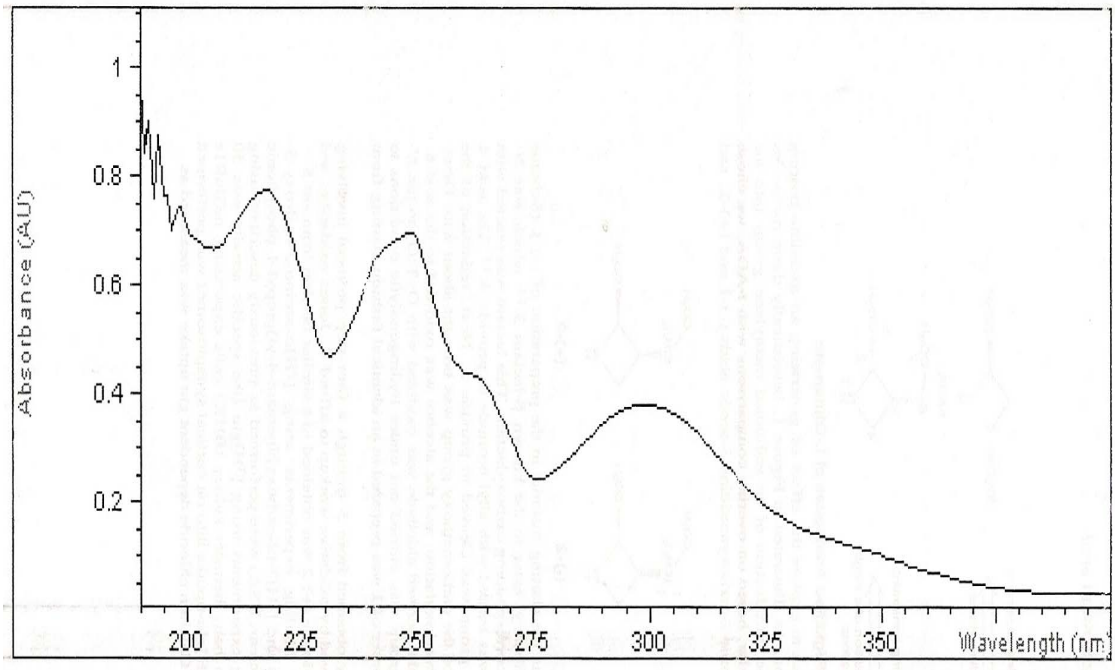


Figure 62 UV (MeOH) spectrum of compound **PW6**

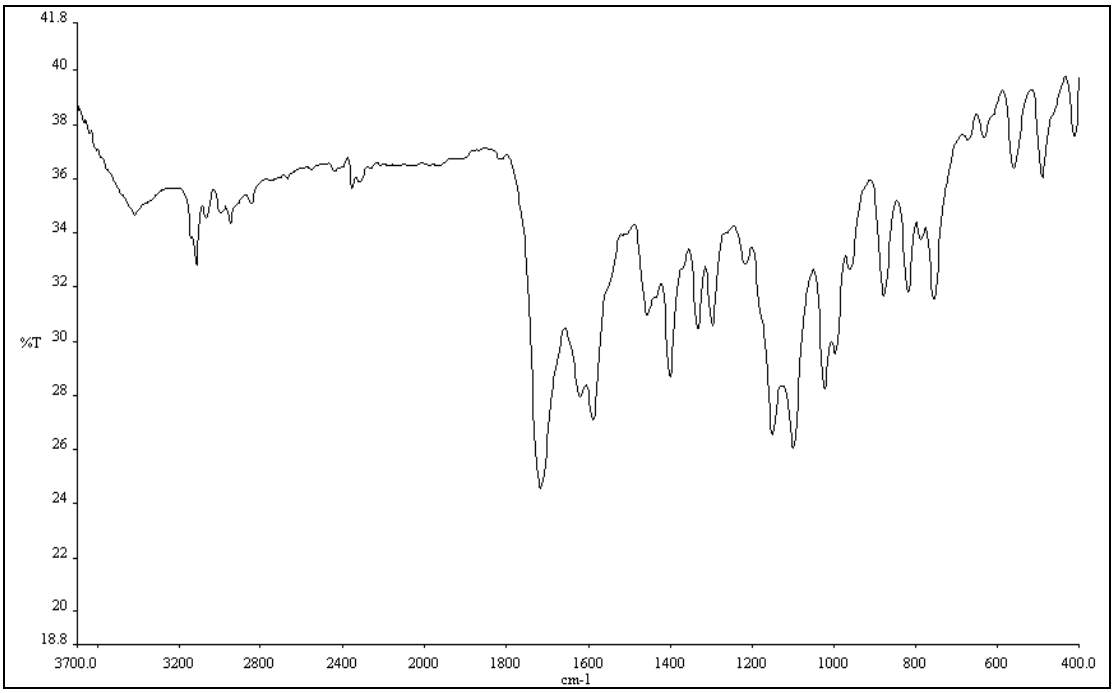


Figure 63 IR (neat) spectrum of compound **PW6**

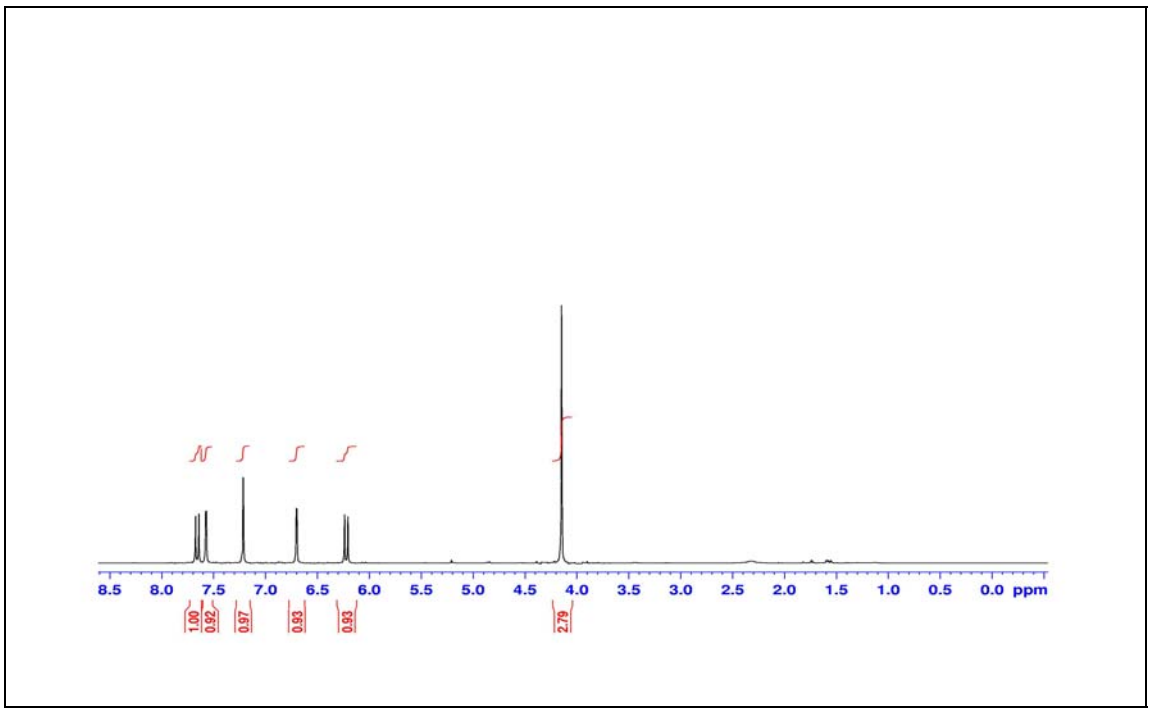


Figure 64 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW6**

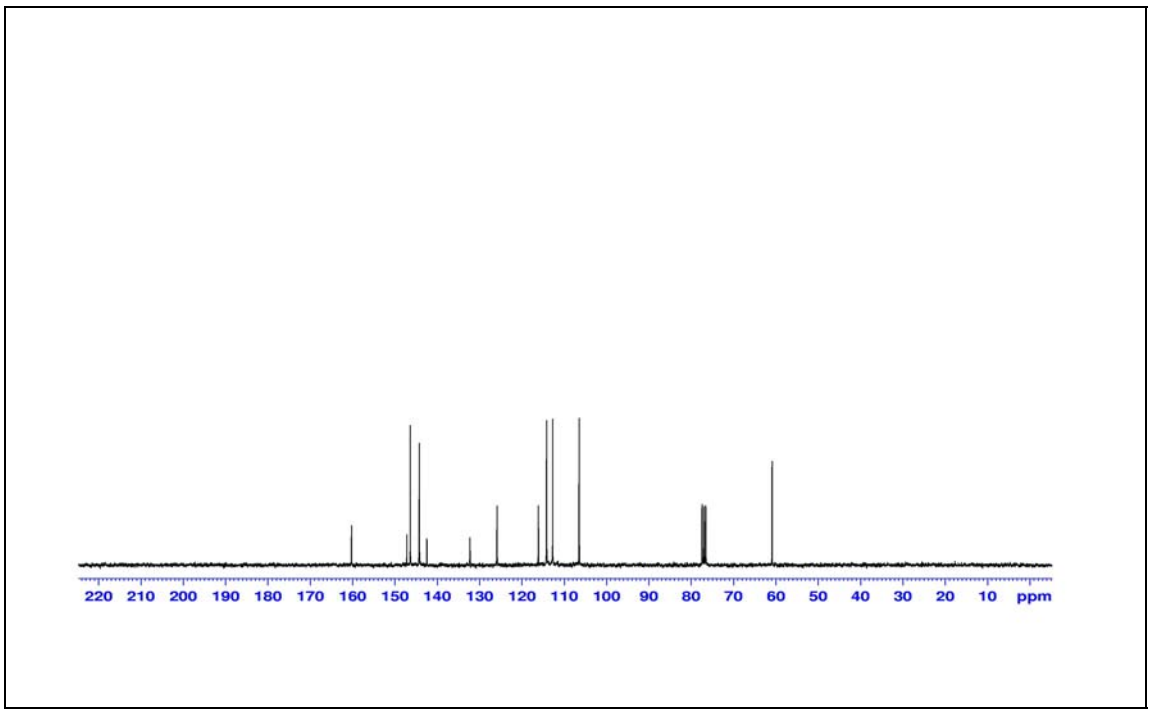


Figure 65 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW6**

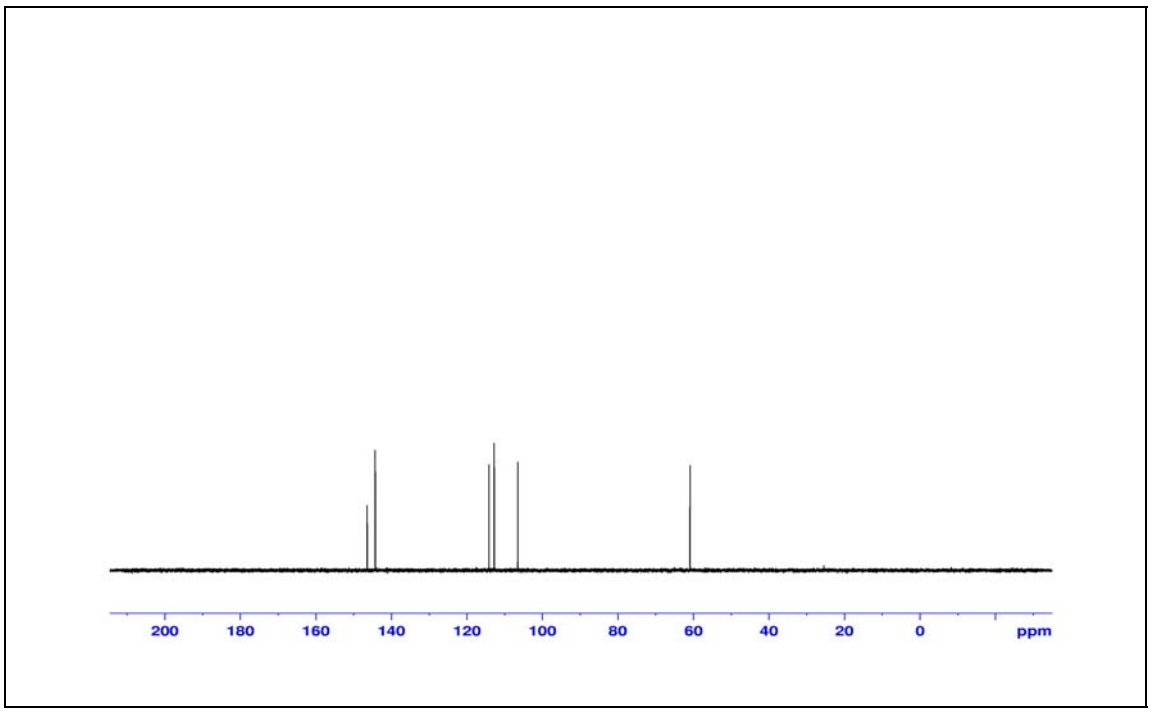


Figure 66 Dept 135° ($CDCl_3$) of compound **PW6**

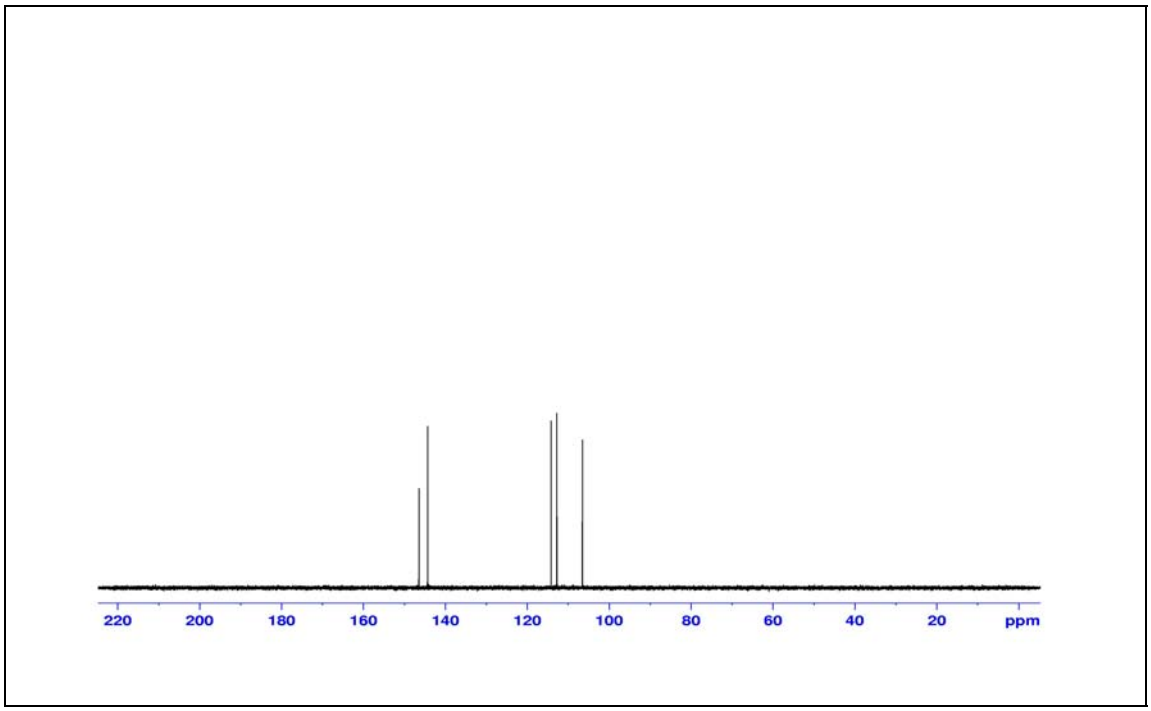


Figure 67 Dept 90° ($CDCl_3$) of compound **PW6**

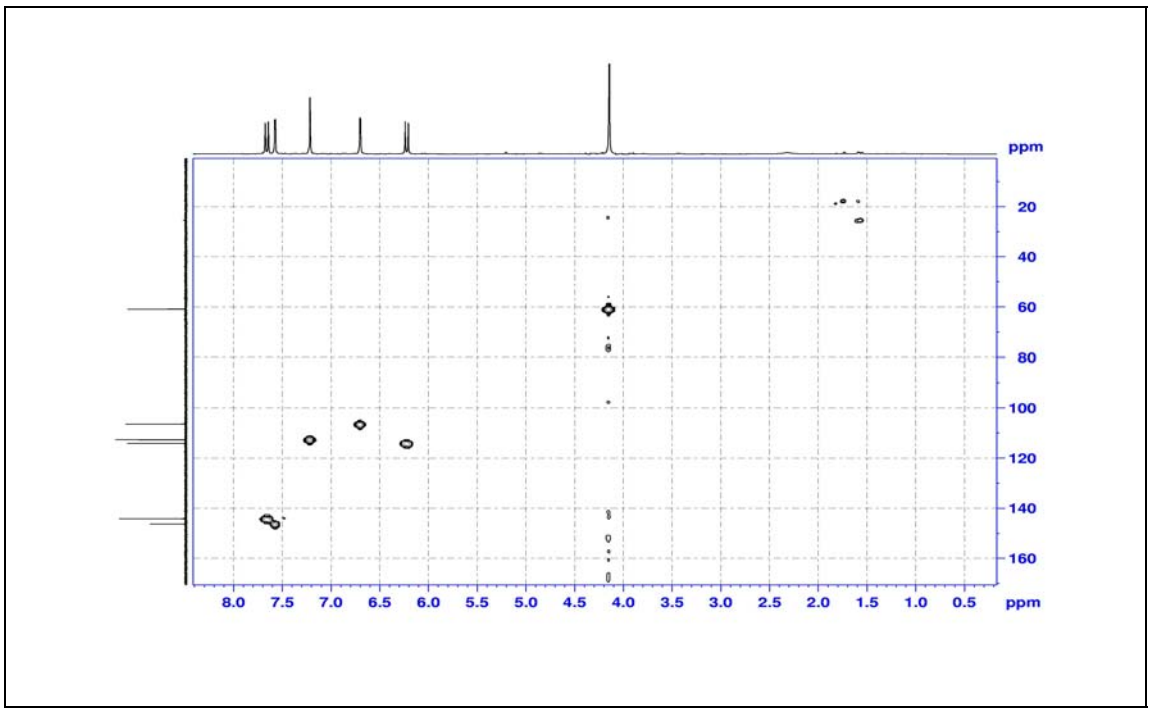


Figure 68 2D HMQC ($CDCl_3$) of compound **PW6**

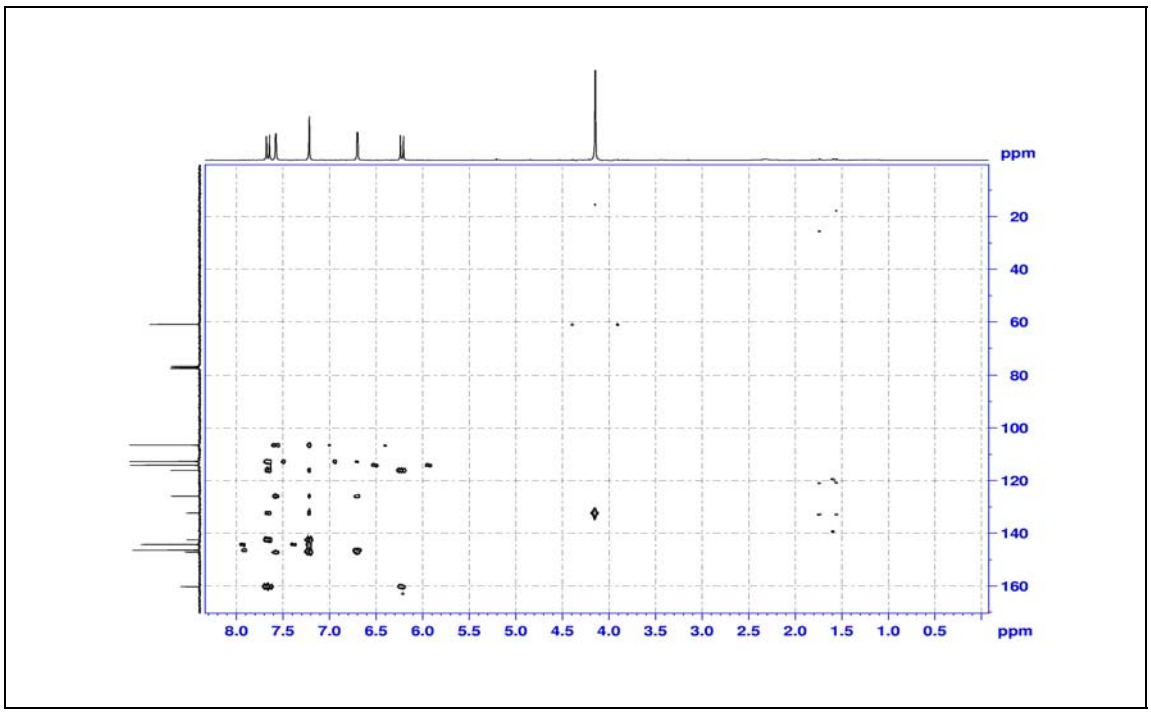


Figure 69 2D HMBC ($CDCl_3$) of compound **PW6**

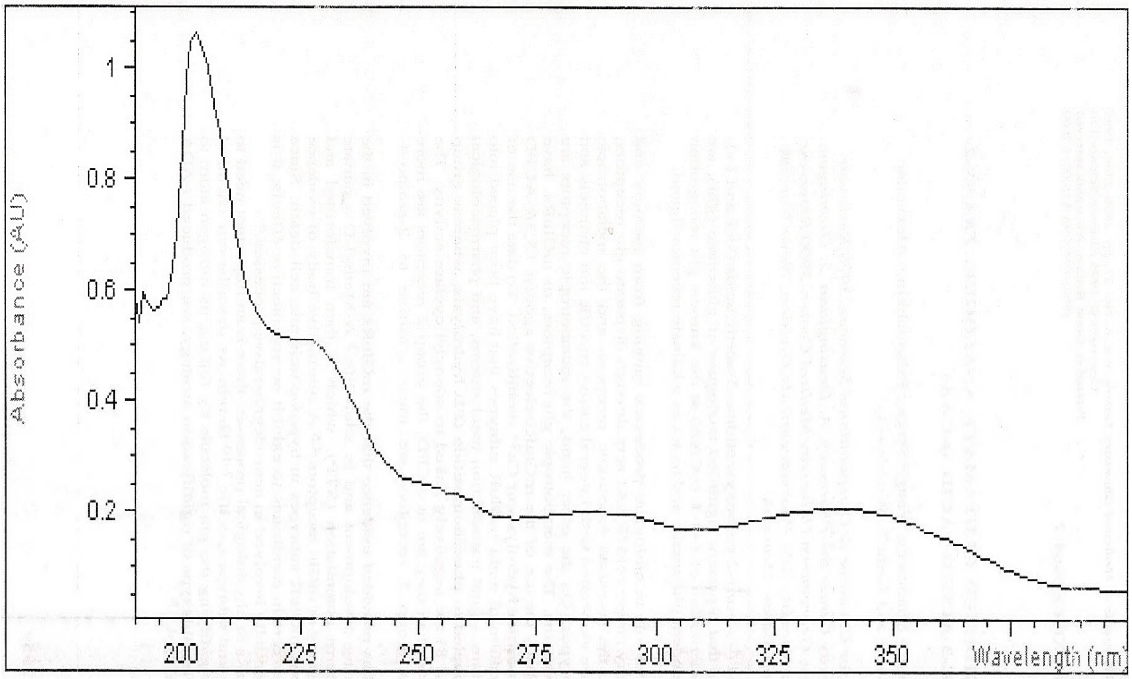


Figure 70 UV (MeOH) spectrum of compound **PW7**

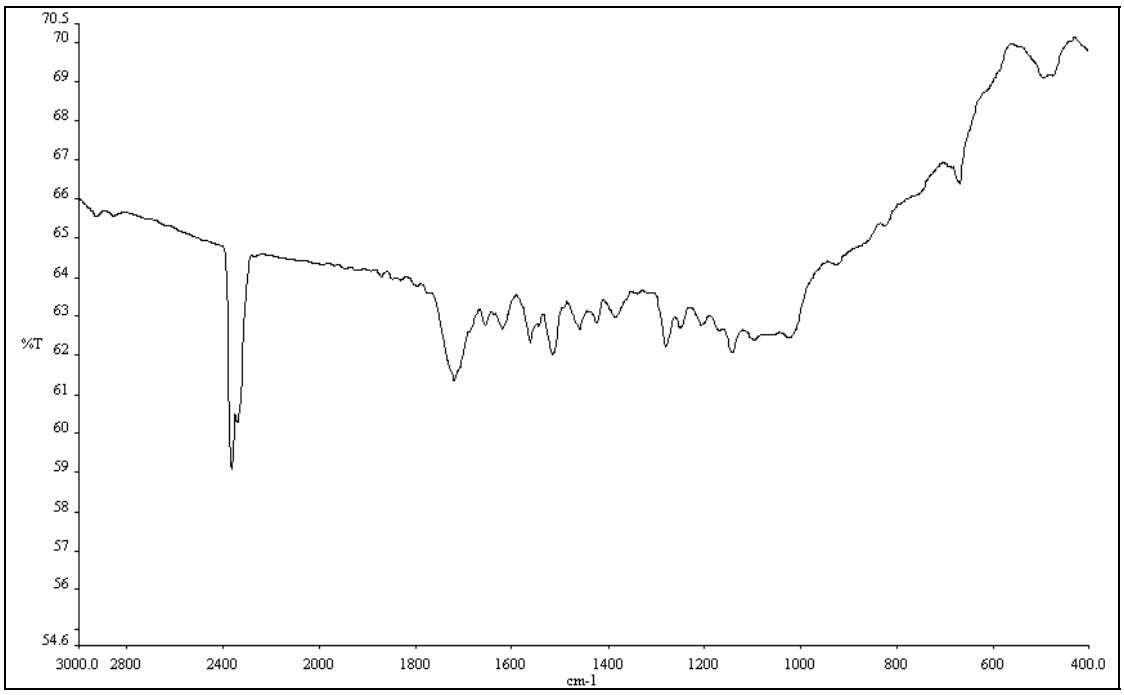


Figure 71 IR (neat) spectrum of compound **PW7**

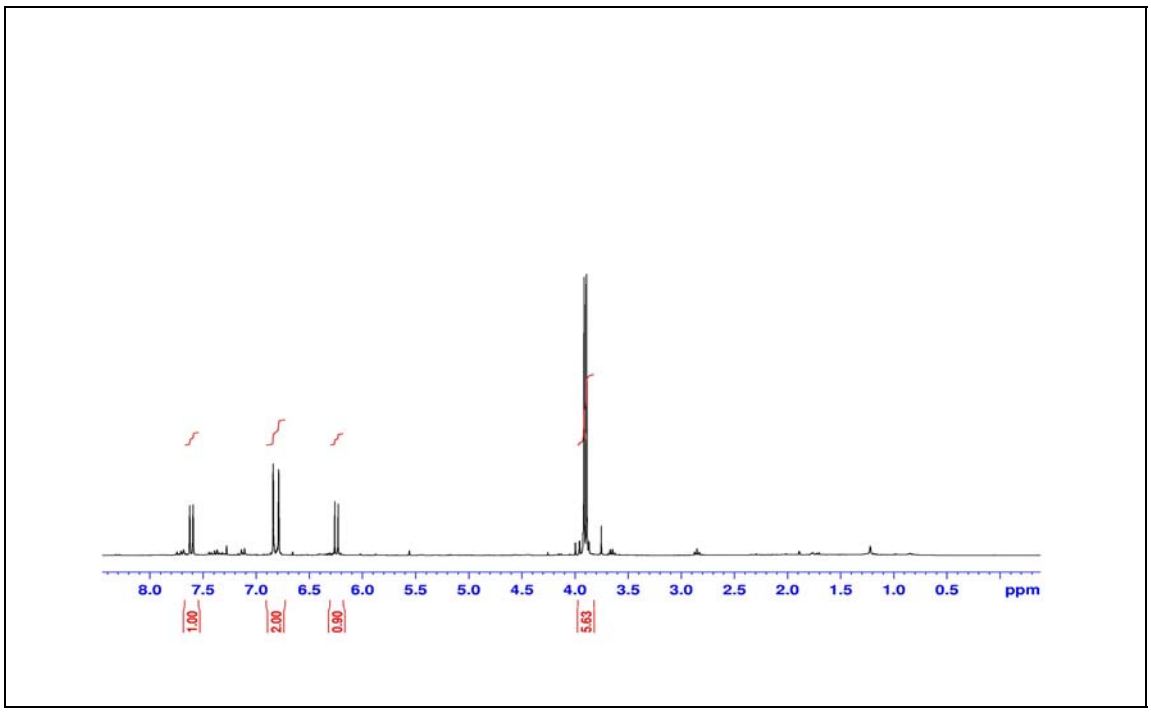


Figure 72 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW7**

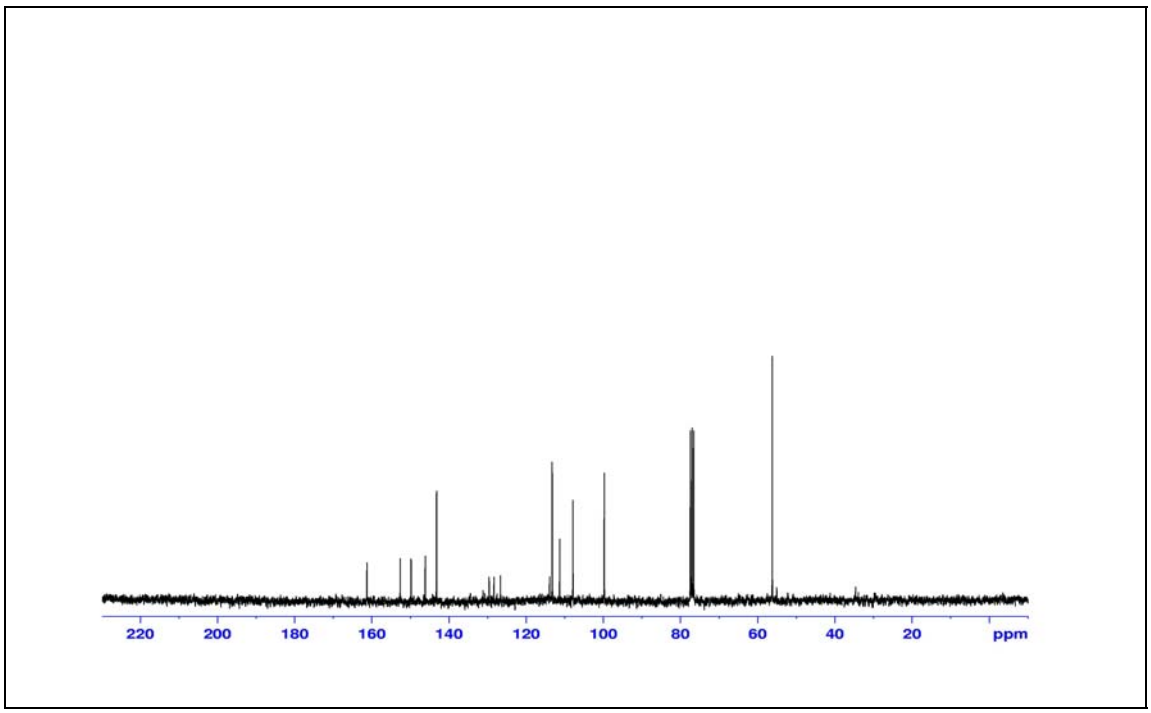


Figure 73 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW7**

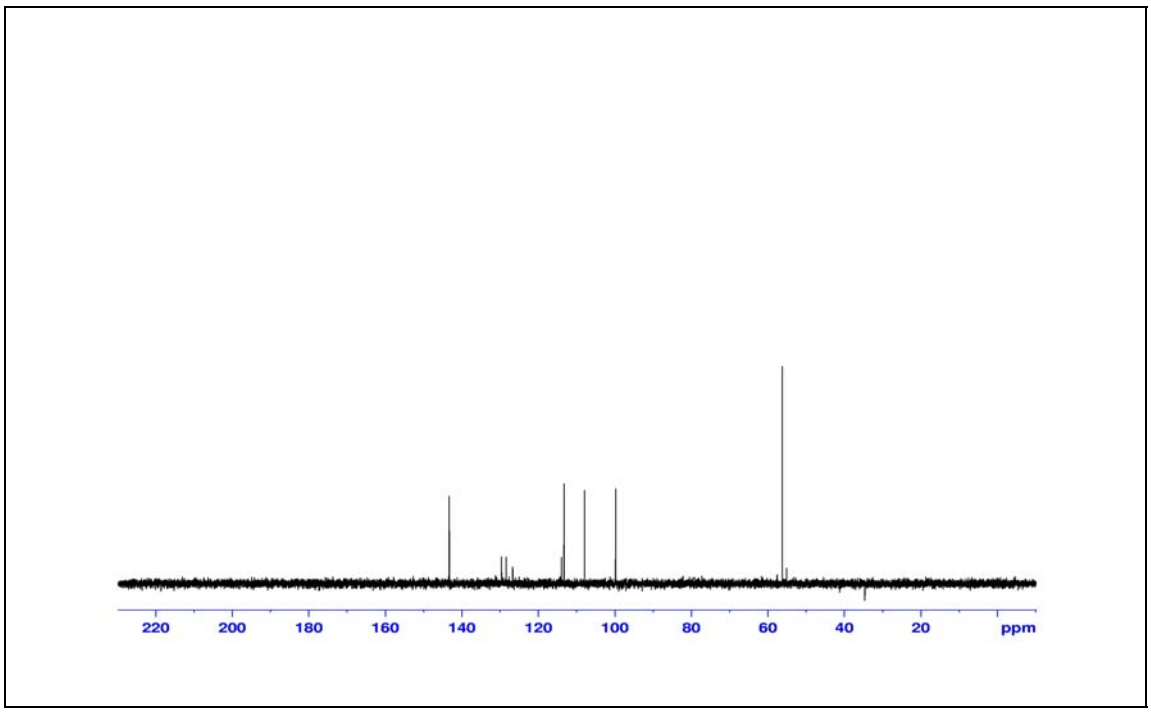


Figure 74 Dept 135° ($CDCl_3$) of compound **PW7**

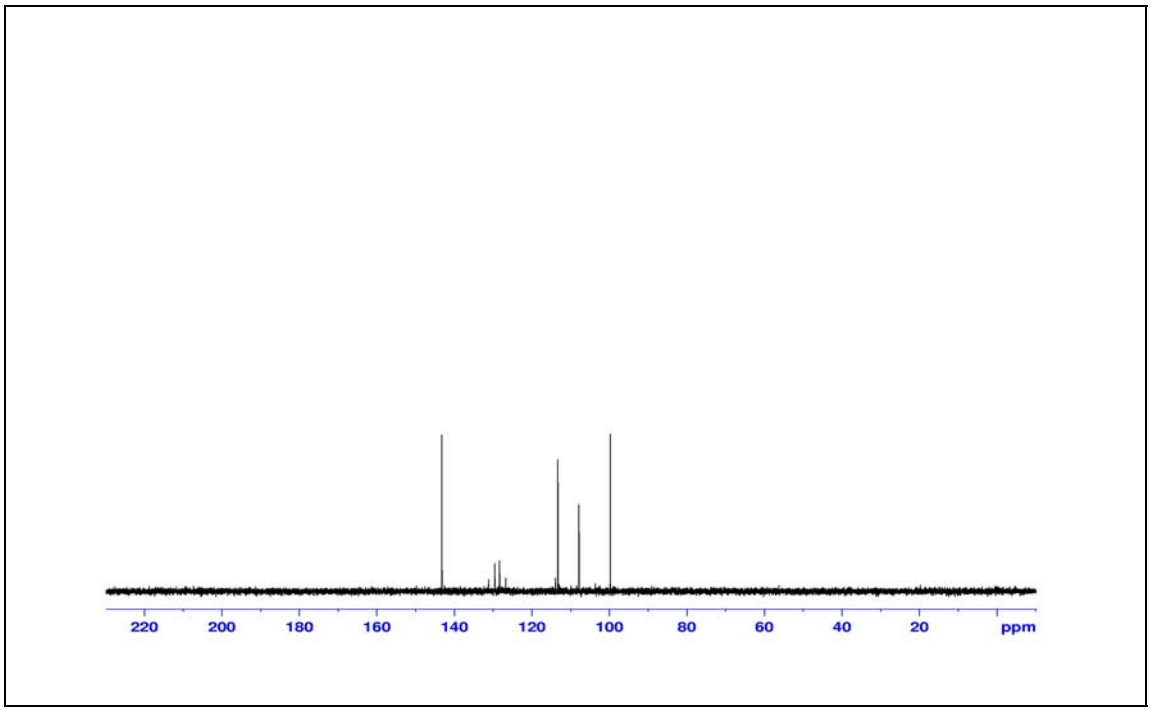


Figure 75 Dept 90° ($CDCl_3$) of compound **PW7**

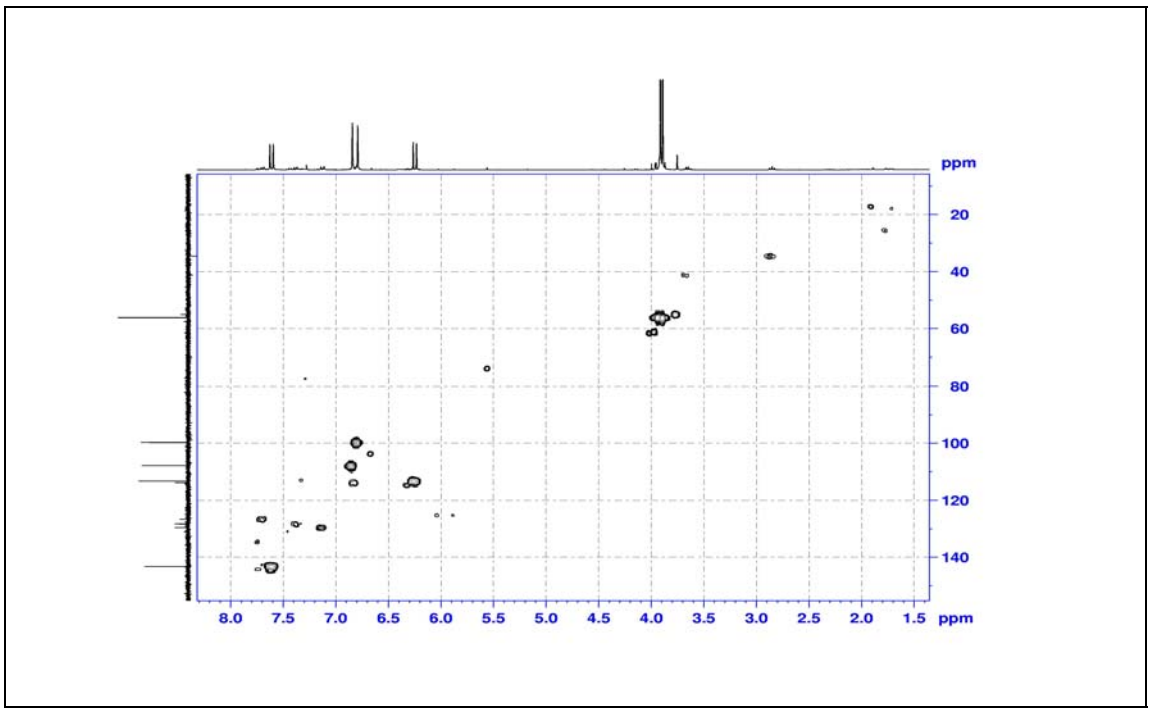


Figure 76 2D HMQC ($CDCl_3$) of compound **PW7**

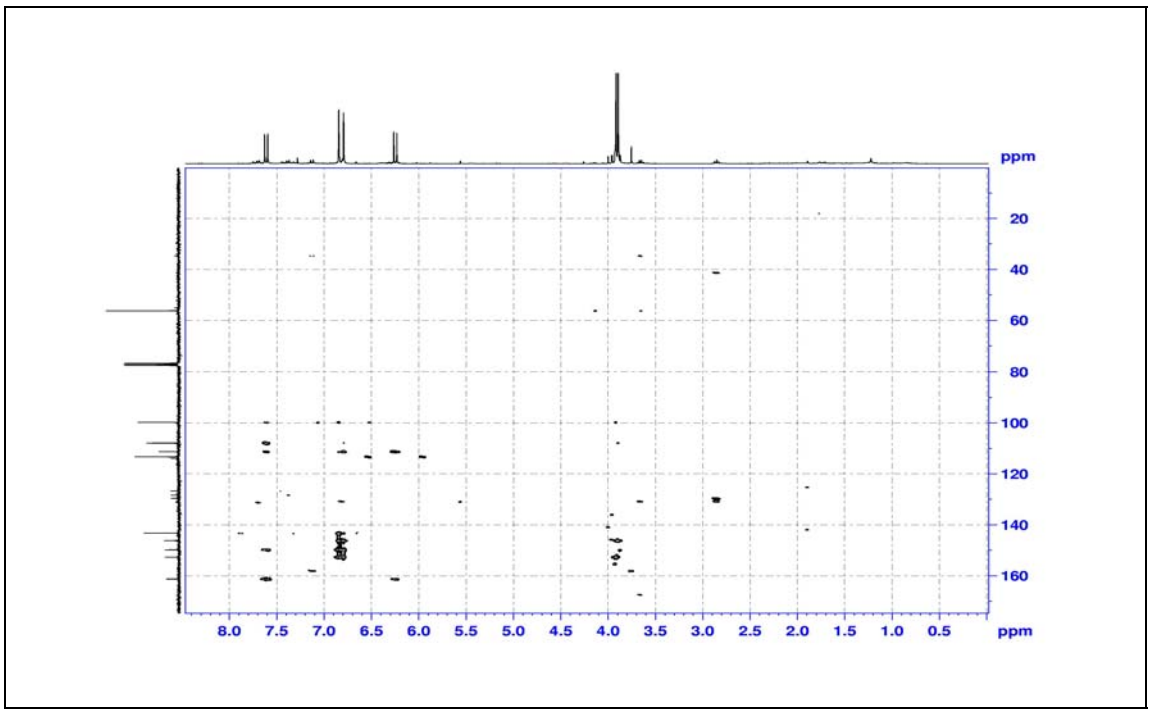


Figure 77 2D HMBC ($CDCl_3$) of compound **PW7**

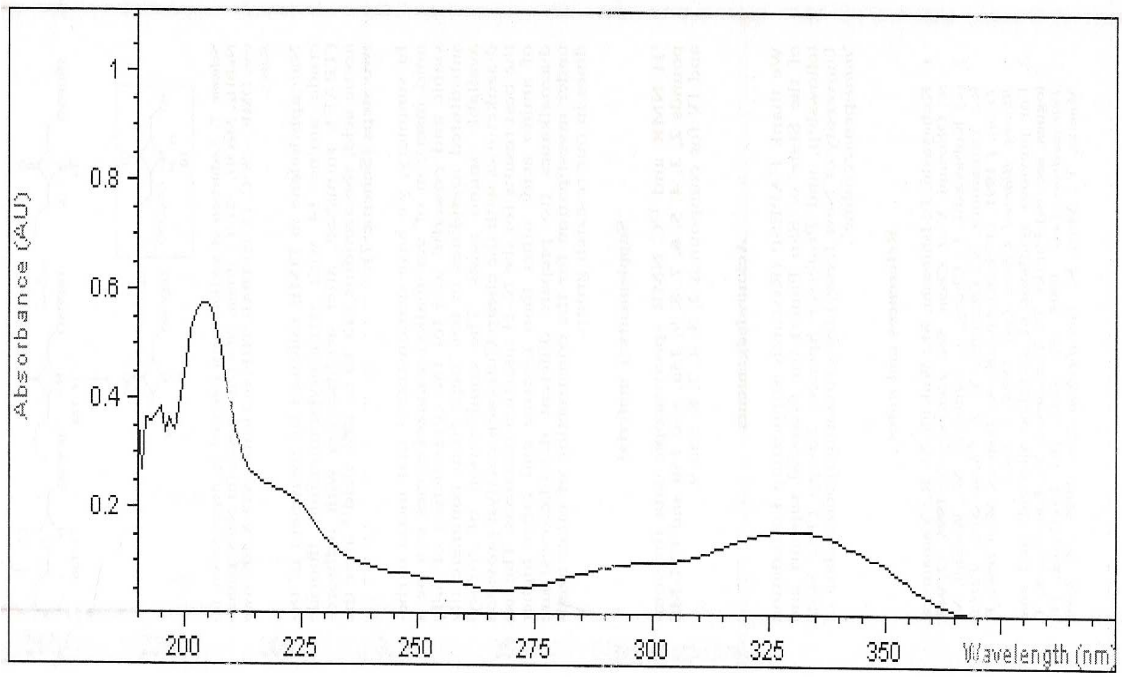


Figure 78 UV (MeOH) spectrum of compound **PW8**

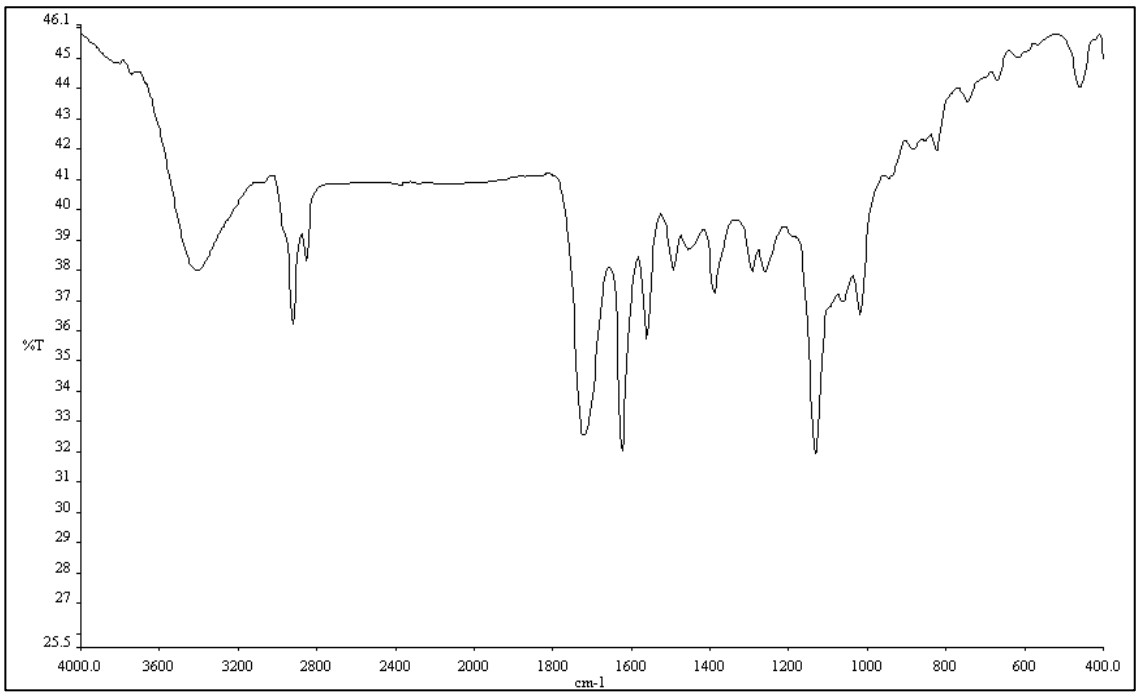


Figure 79 IR (neat) spectrum of compound **PW8**

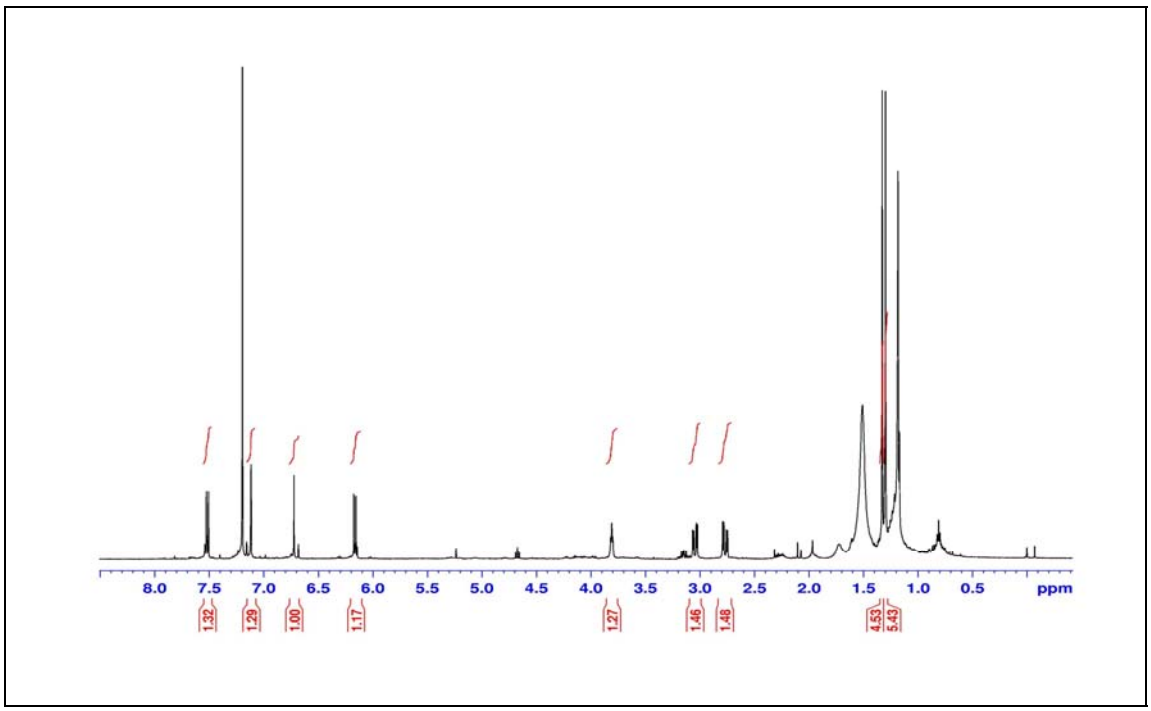


Figure 80 ^{1}H NMR (500 MHz) ($CDCl_3$) of compound **PW8**

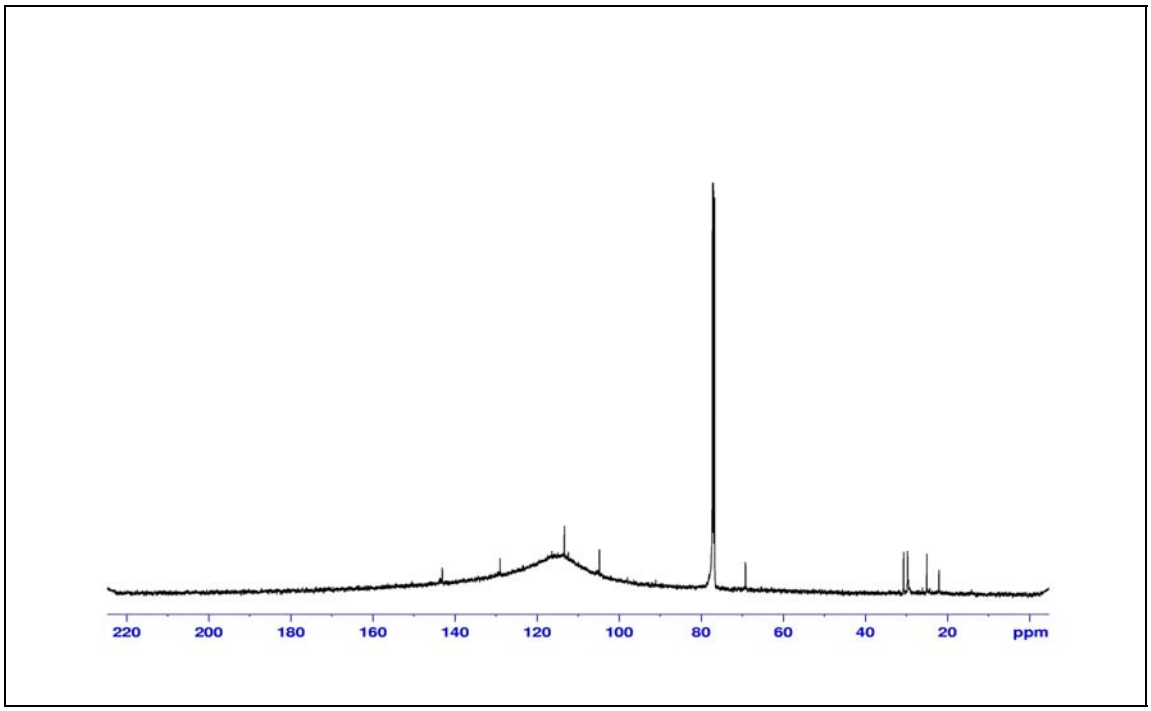


Figure 81 ^{13}C NMR (125 MHz) ($CDCl_3$) of compound **PW8**

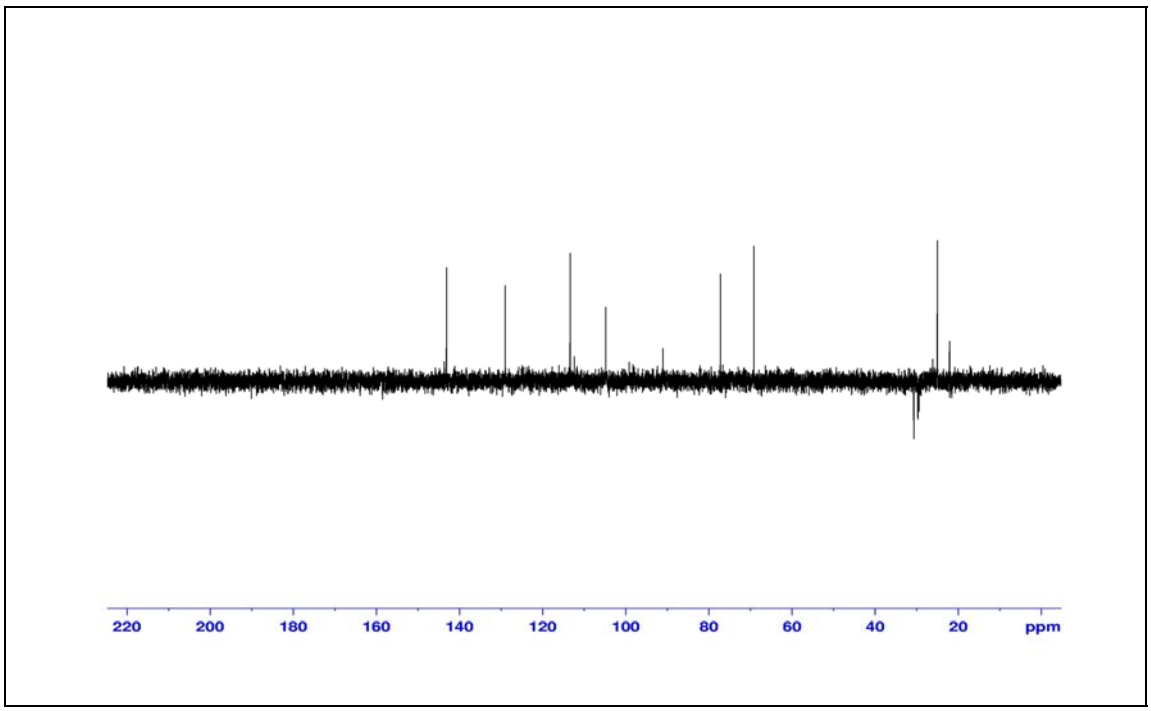


Figure 82 Dept 135° ($CDCl_3$) of compound **PW8**

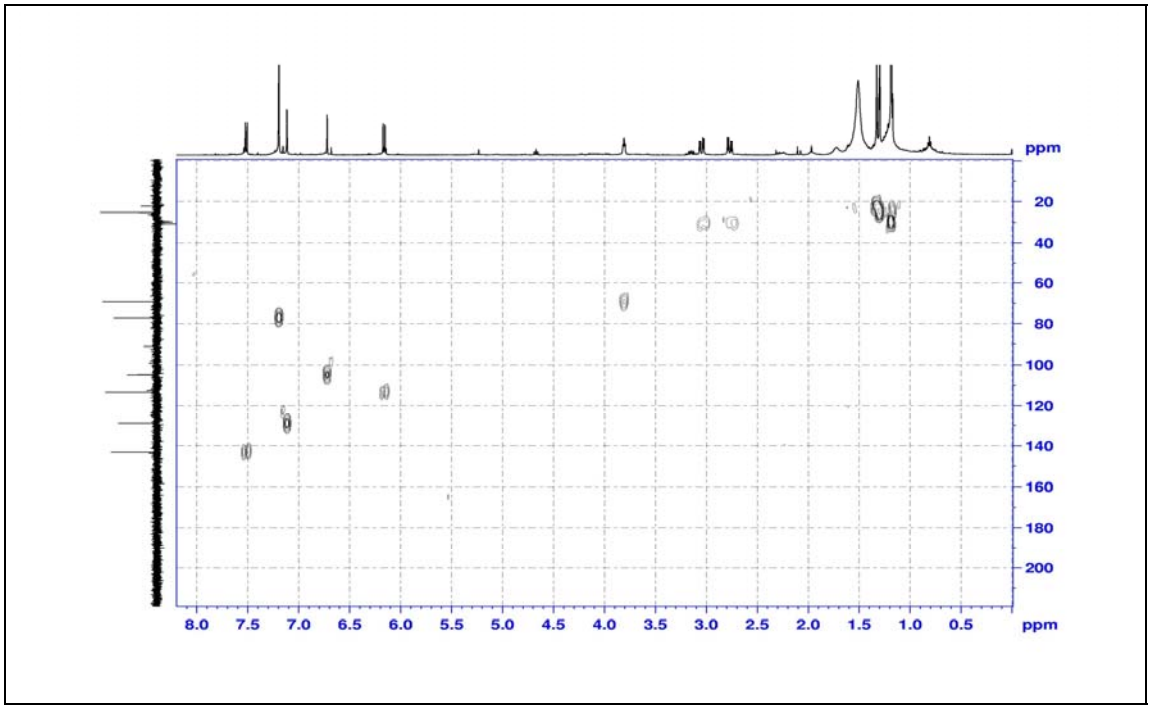


Figure 83 2D HMQC ($CDCl_3$) of compound **PW8**

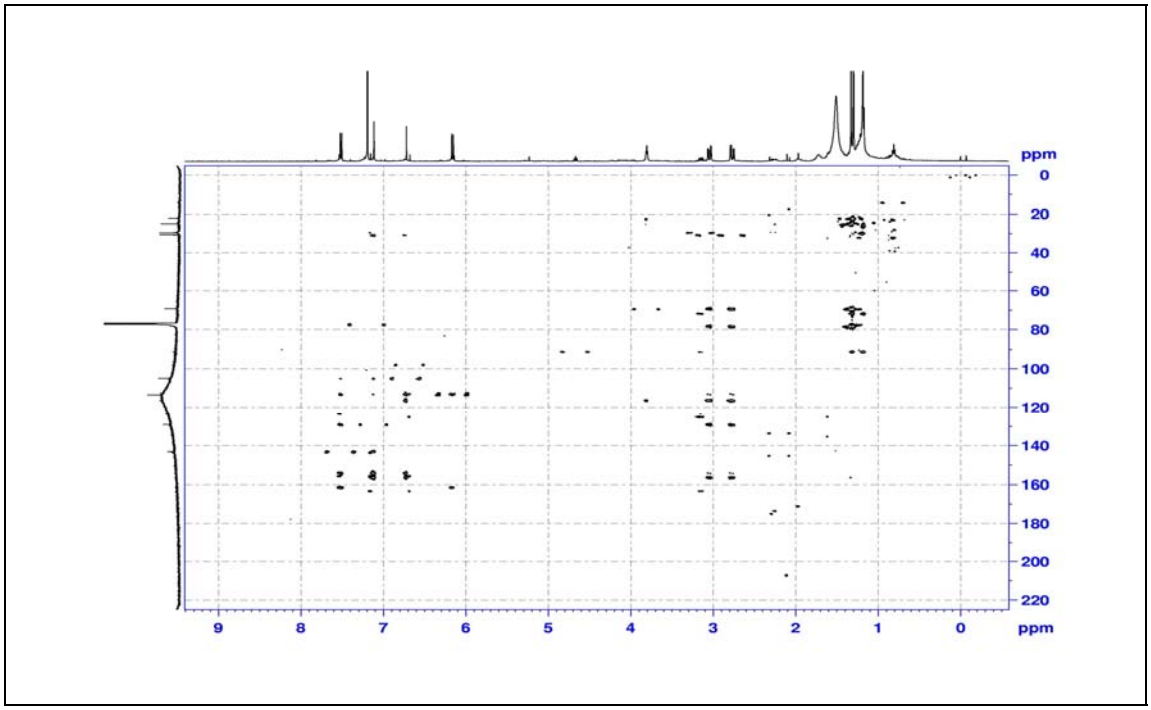


Figure 84 2D HMBC ($CDCl_3$) of compound **PW8**

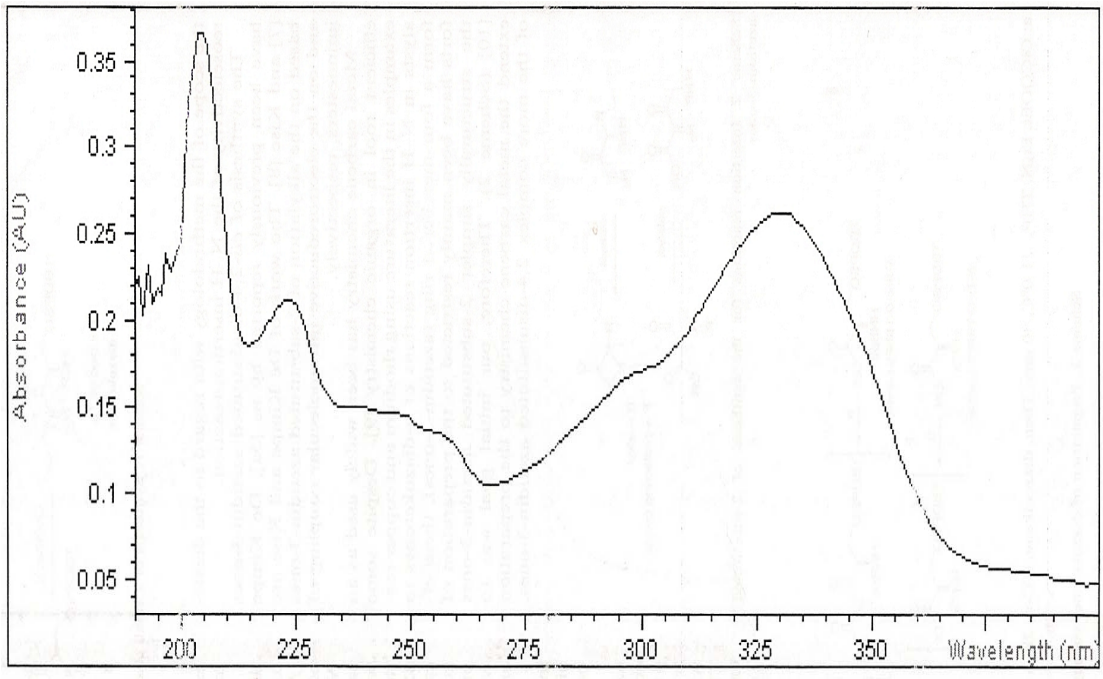


Figure 85 UV (MeOH) spectrum of compound **PW9**

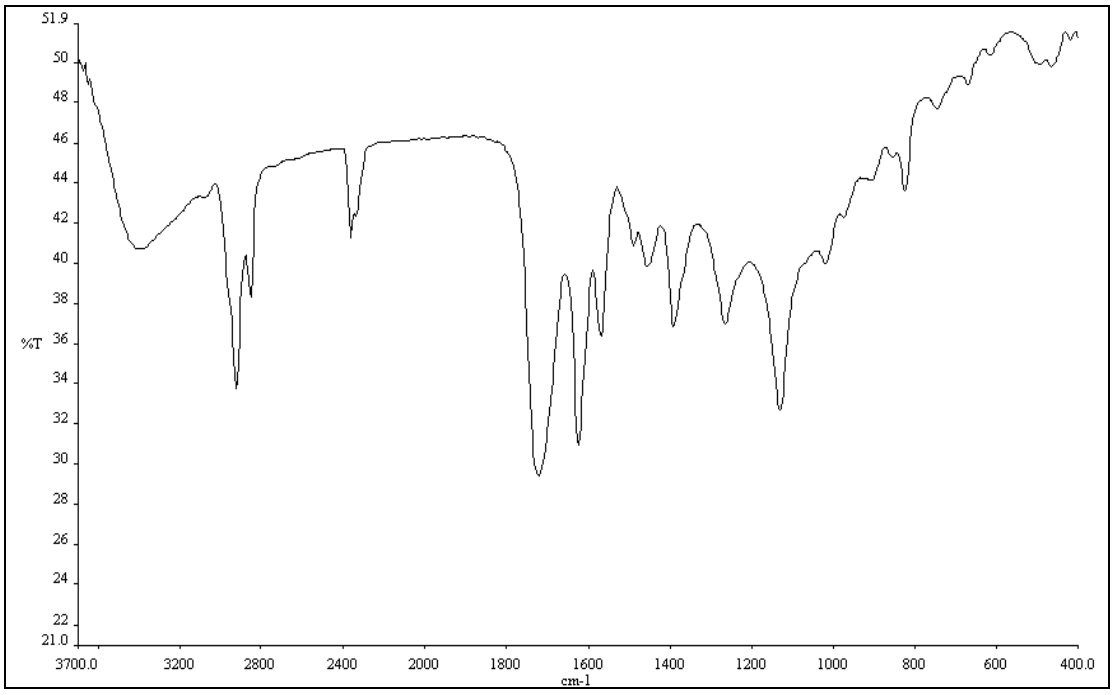


Figure 86 IR (neat) spectrum of compound **PW9**

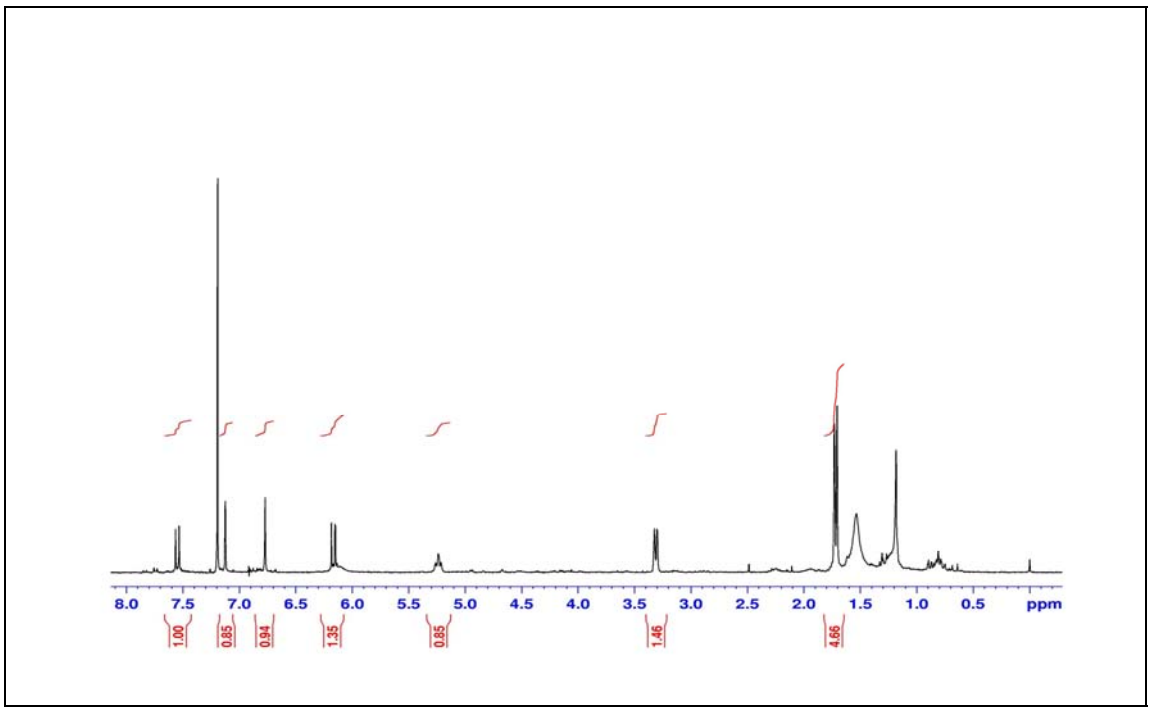


Figure 87 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW9**

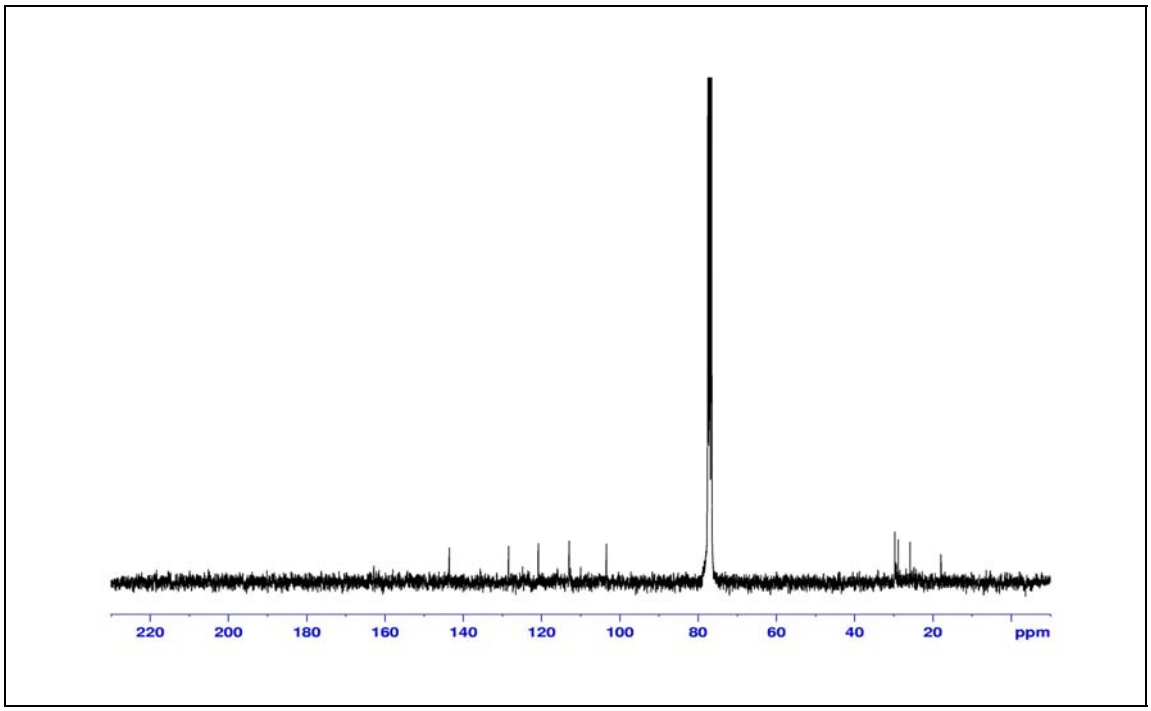


Figure 88 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW9**

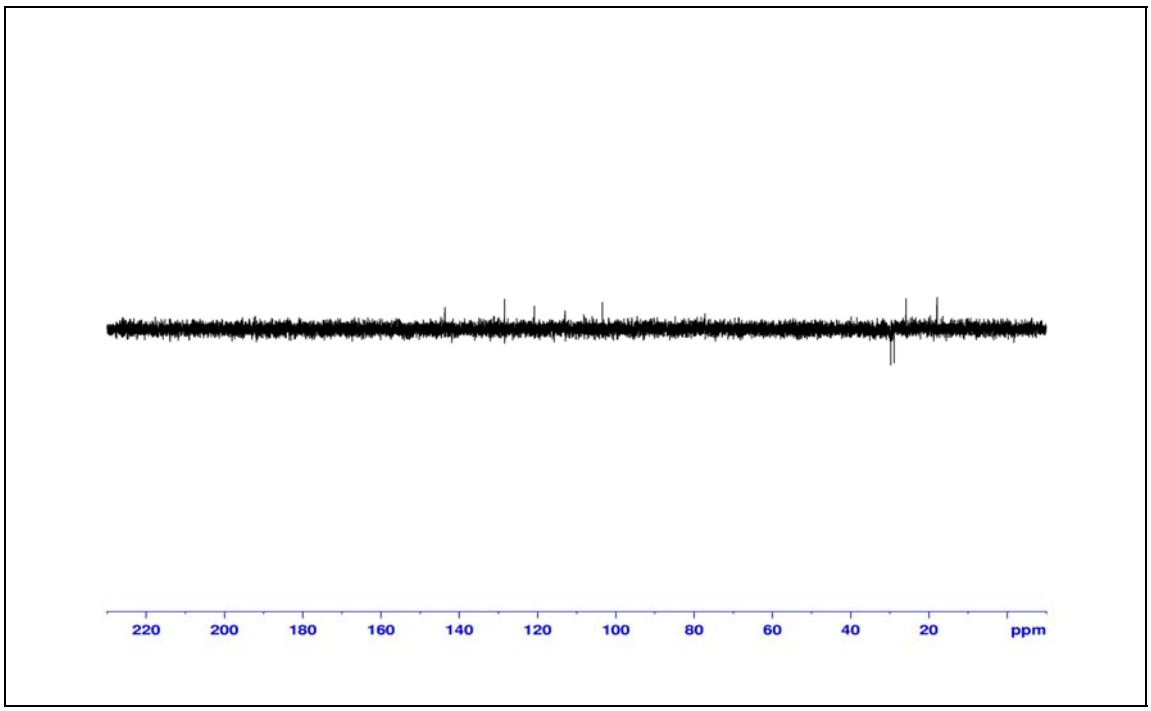


Figure 89 Dept 135° ($CDCl_3$) of compound **PW9**

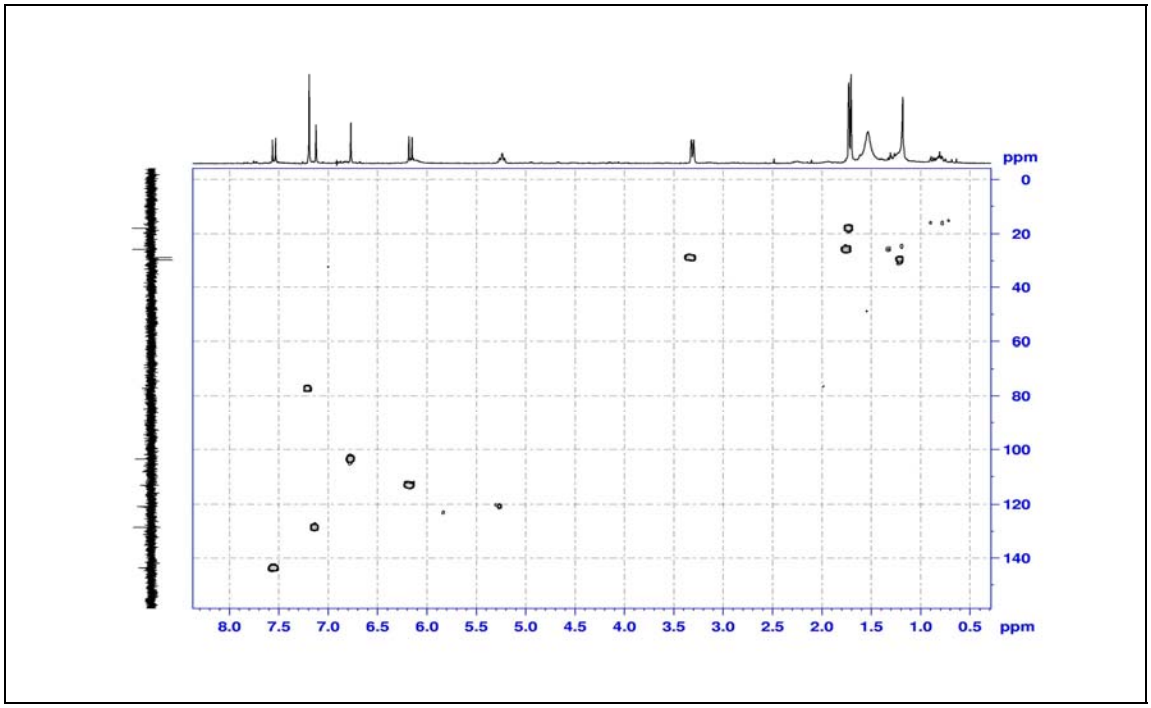


Figure 90 2D HMQC ($CDCl_3$) of compound **PW9**

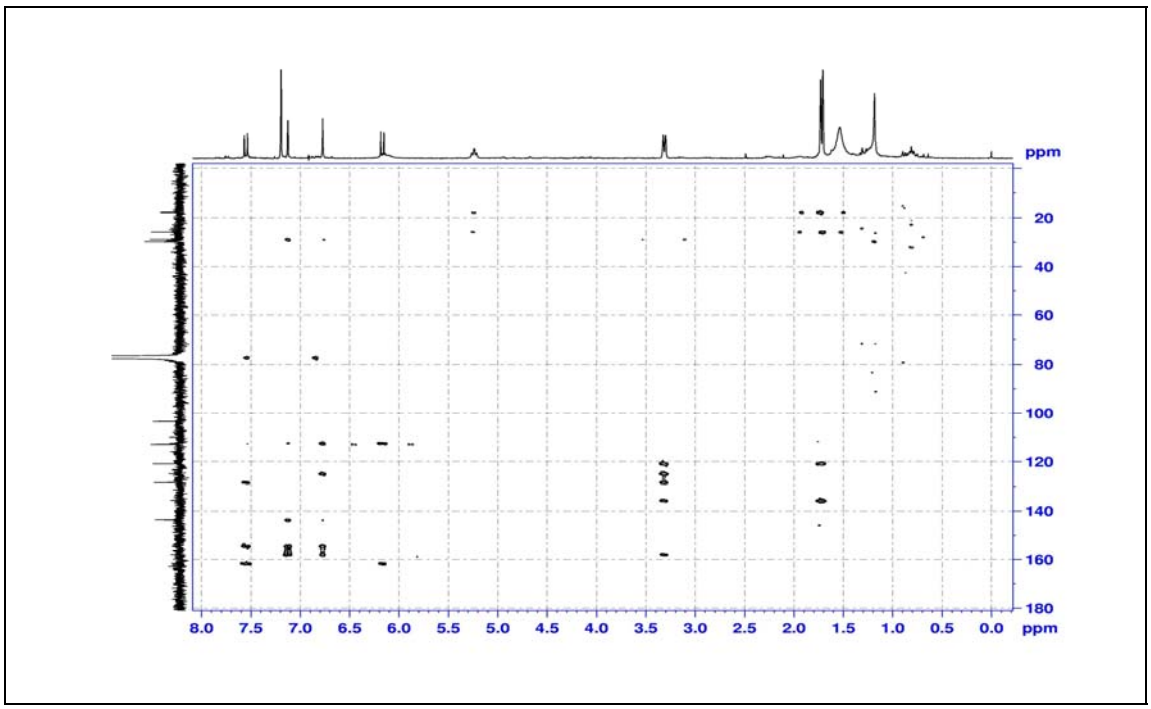


Figure 91 2D HMBC ($CDCl_3$) of compound **PW9**

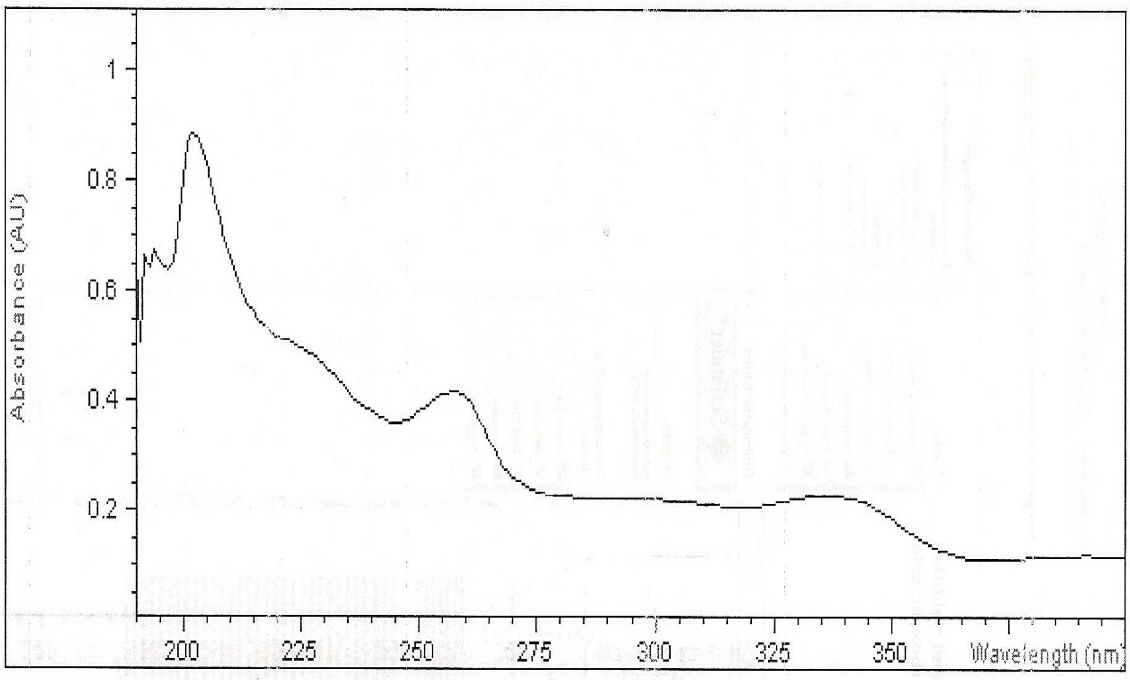


Figure 92 UV (MeOH) spectrum of compound **PW10**

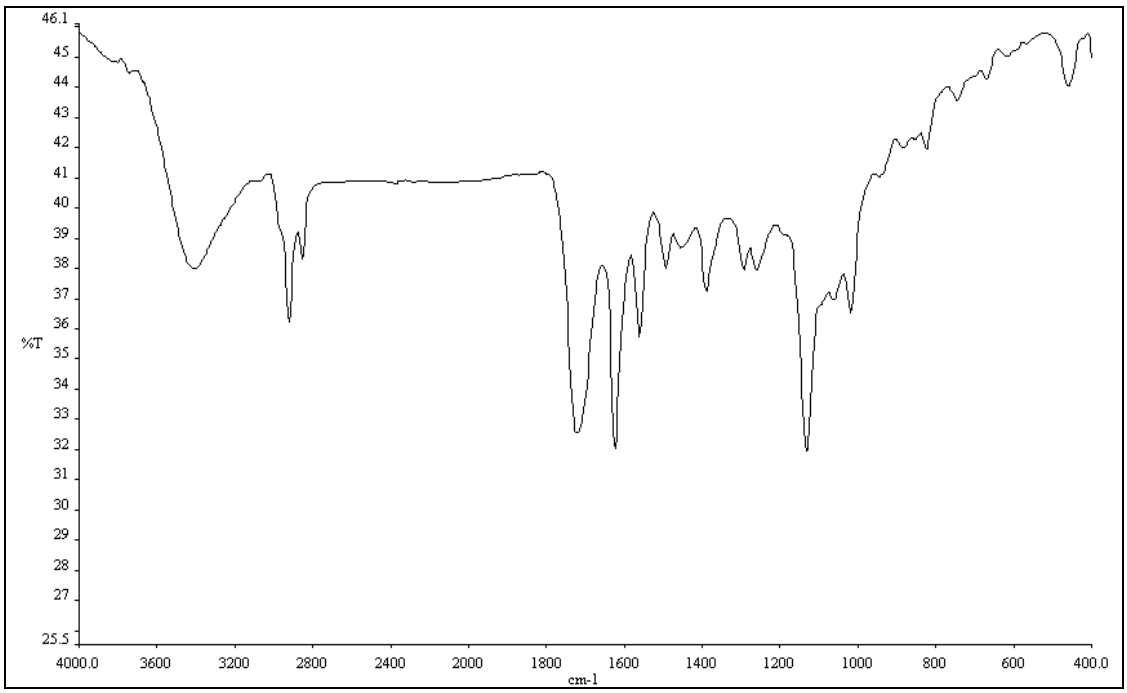


Figure 93 IR (neat) spectrum of compound **PW10**

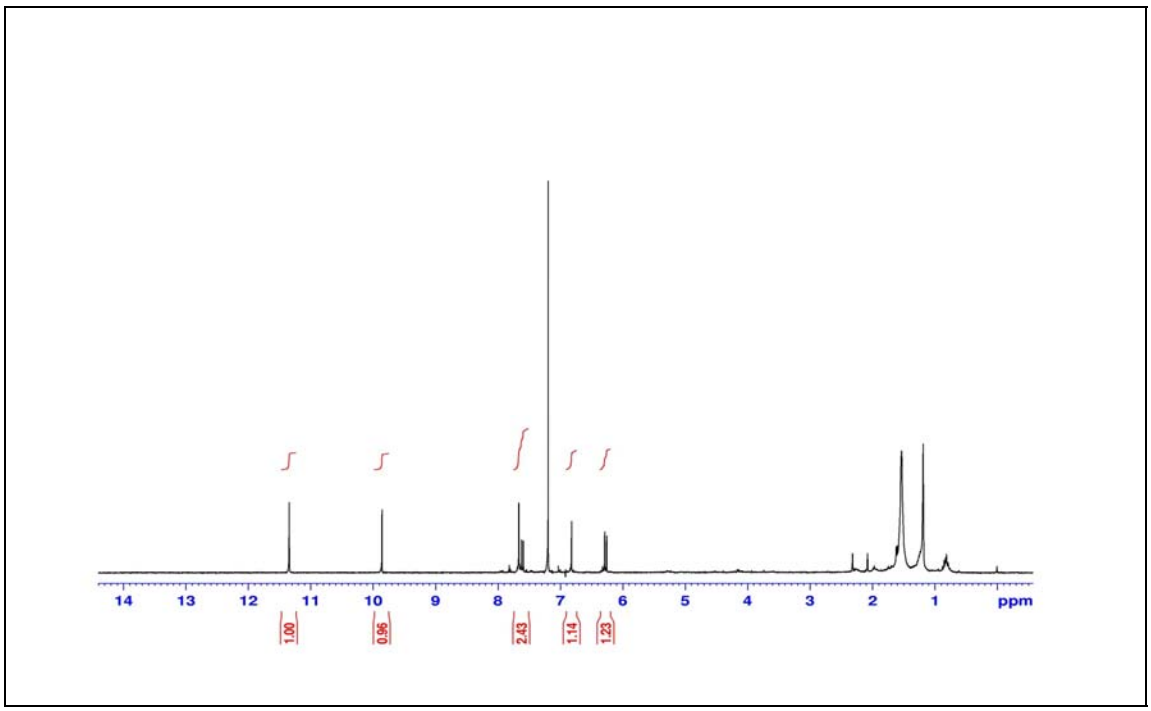


Figure 94 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW10**

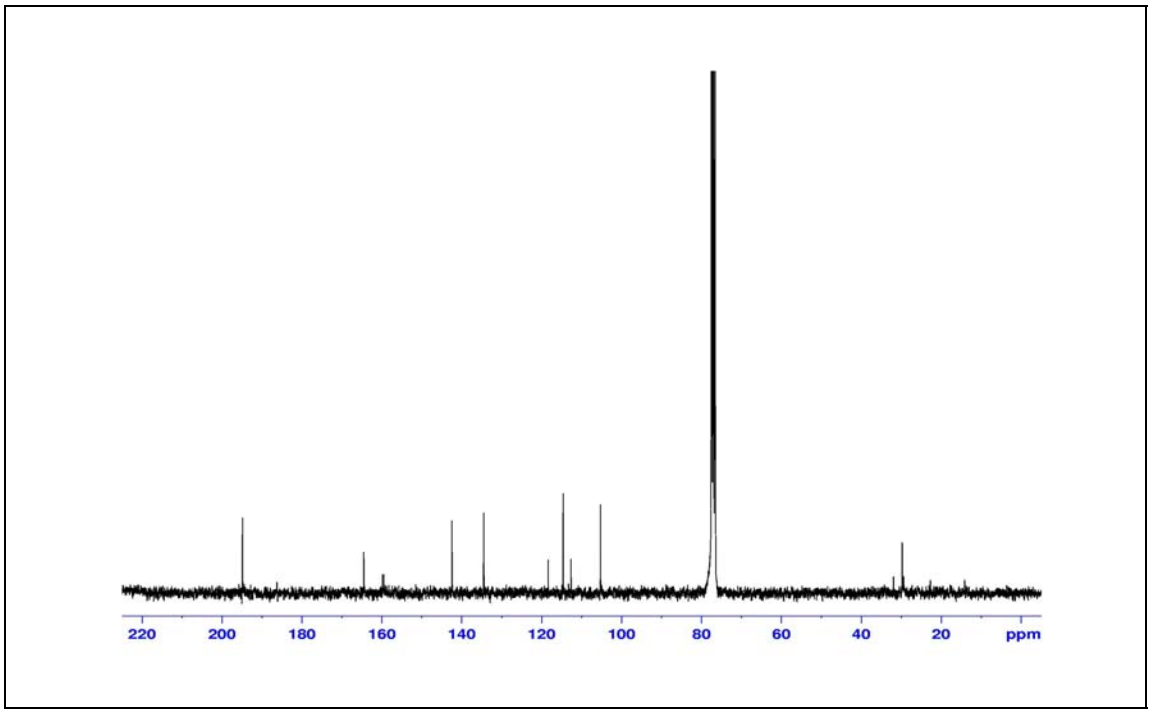


Figure 95 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW10**

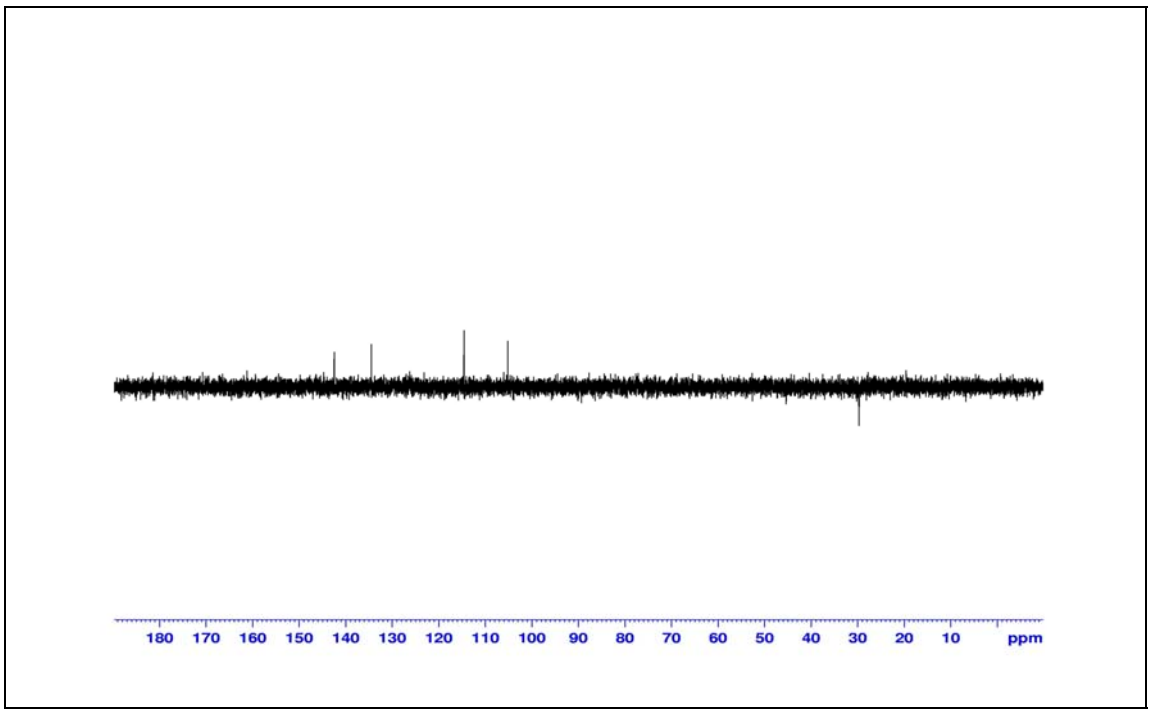


Figure 96 Dept 135° ($CDCl_3$) of compound **PW10**

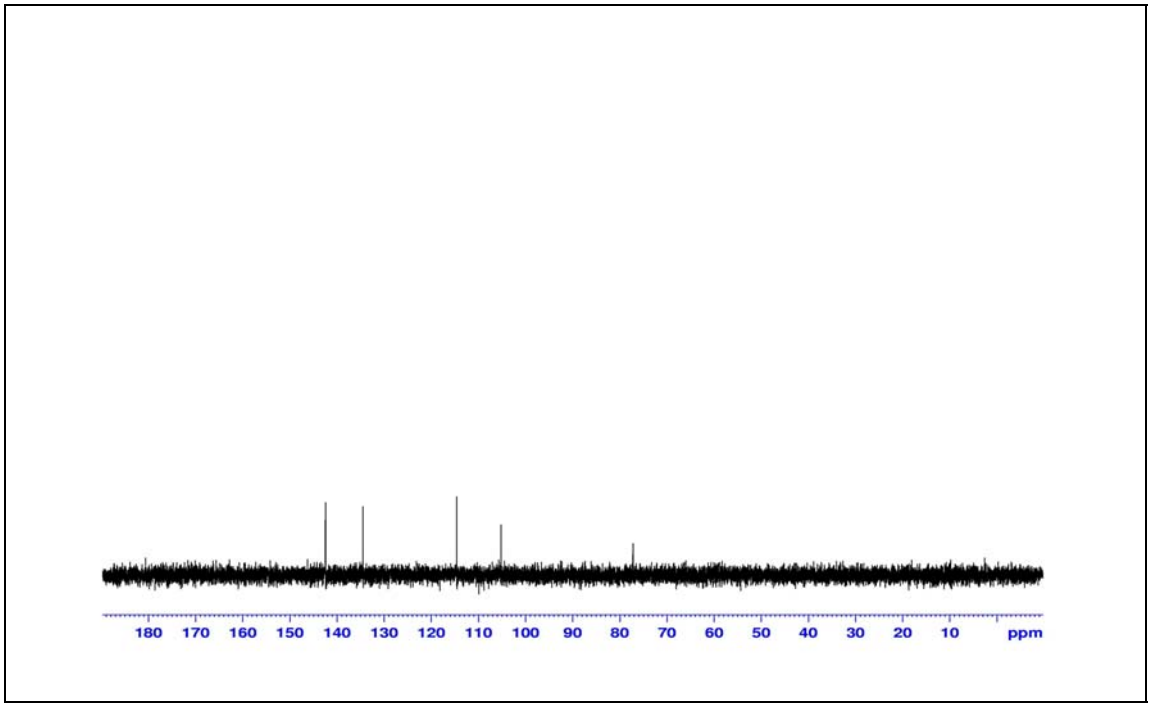


Figure 97 Dept 90° ($CDCl_3$) of compound **PW10**

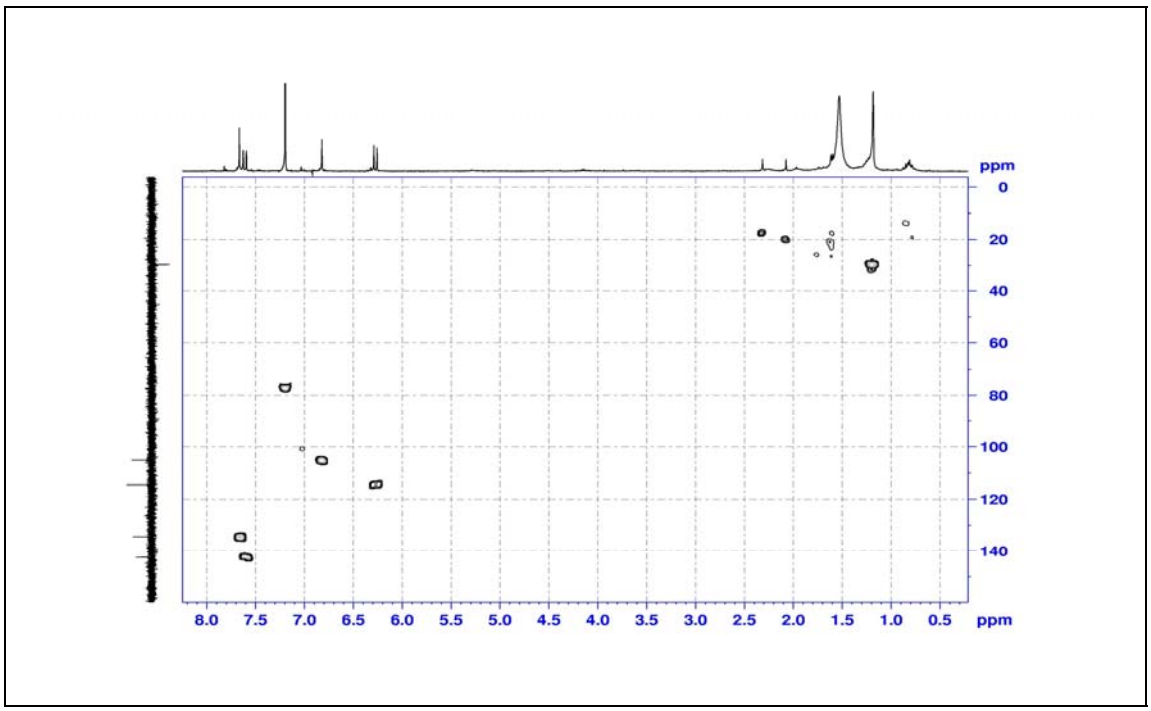


Figure 98 2D HMQC ($CDCl_3$) of compound **PW10**

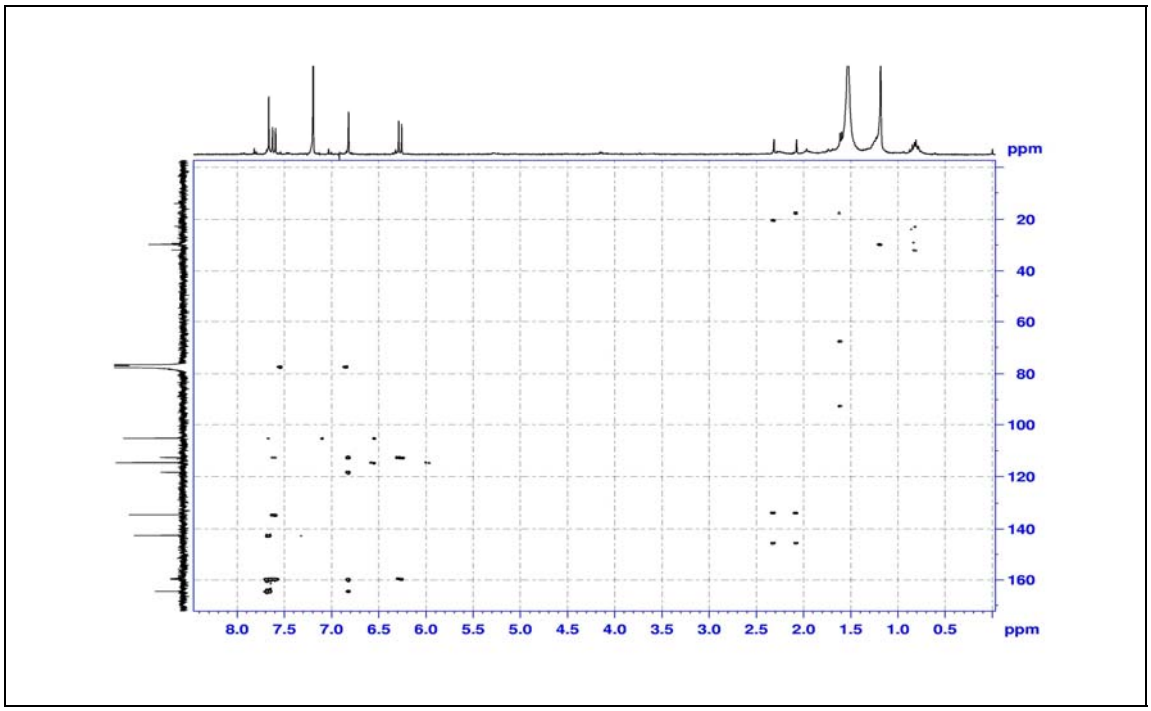


Figure 99 2D HMBC ($CDCl_3$) of compound **PW10**

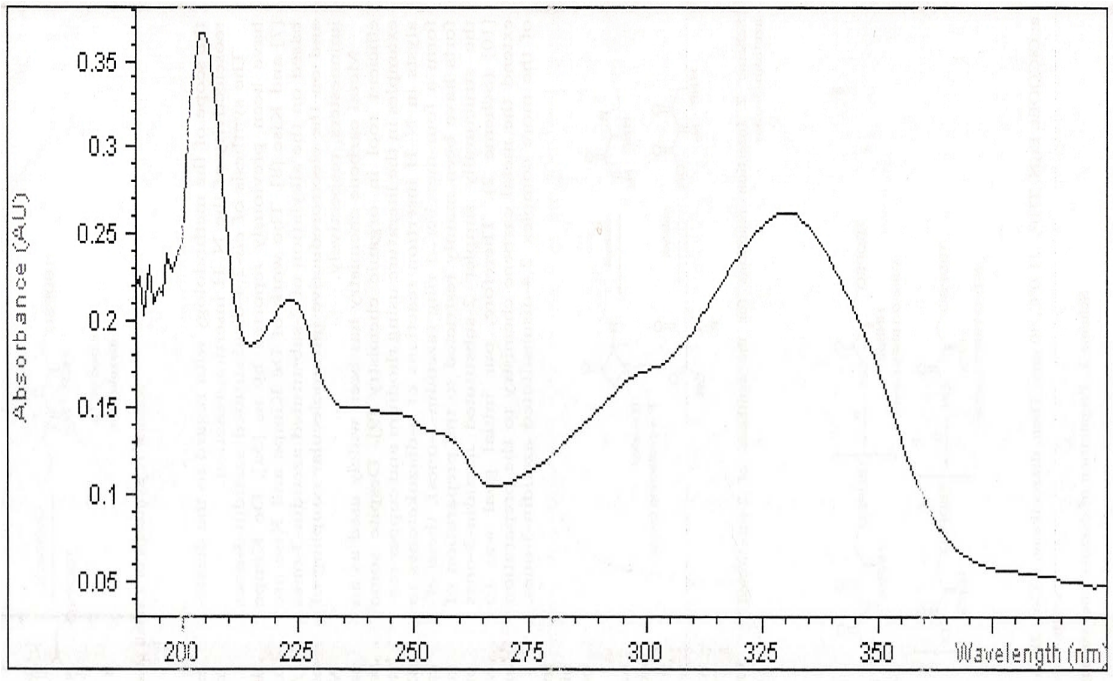


Figure 100 UV (MeOH) spectrum of compound **PW11**

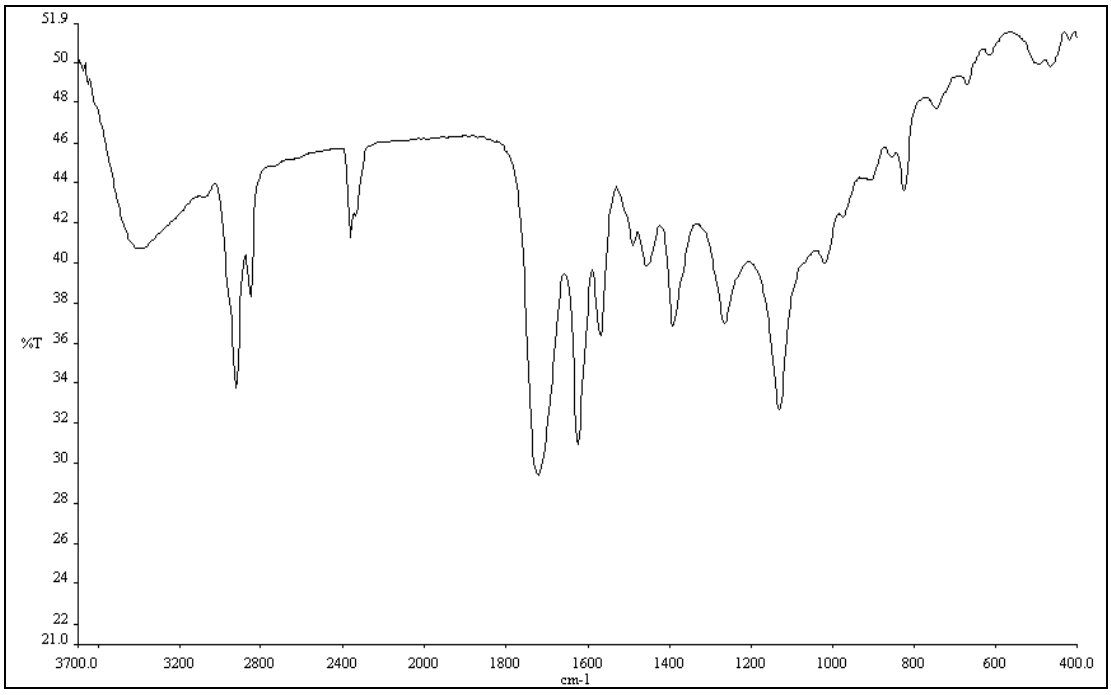


Figure 101 IR (neat) spectrum of compound **PW11**

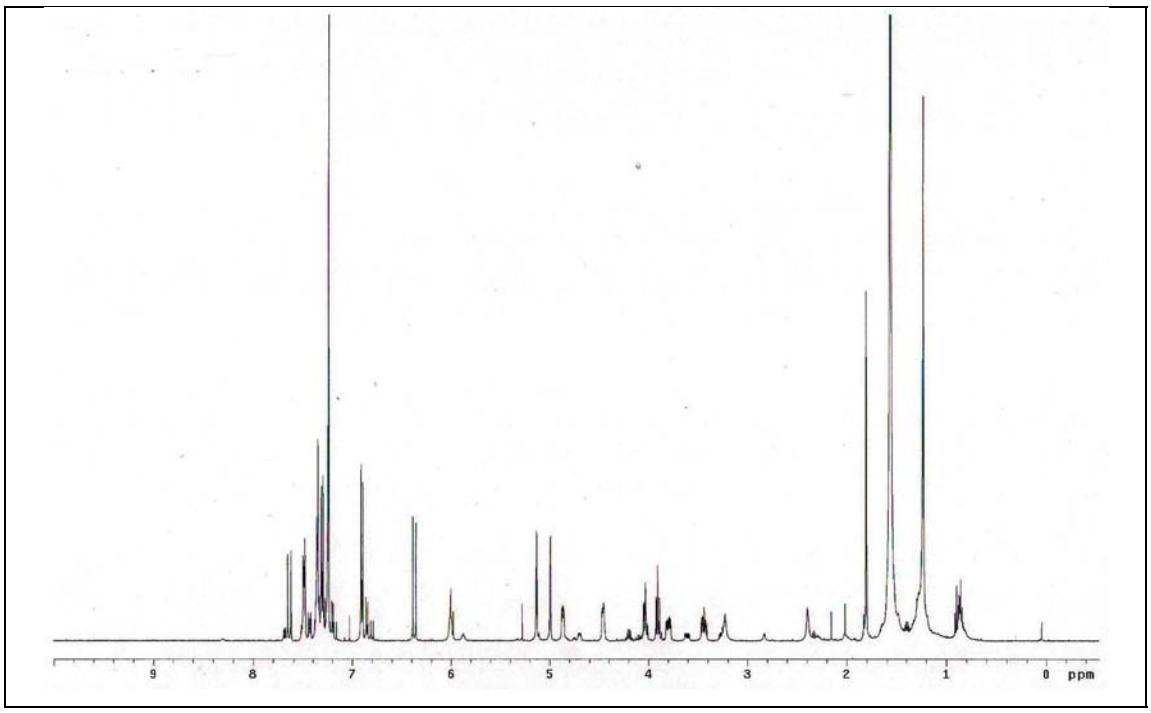


Figure 102 ^{1}H NMR (500 MHz) ($CDCl_3$) of compound **PW11**

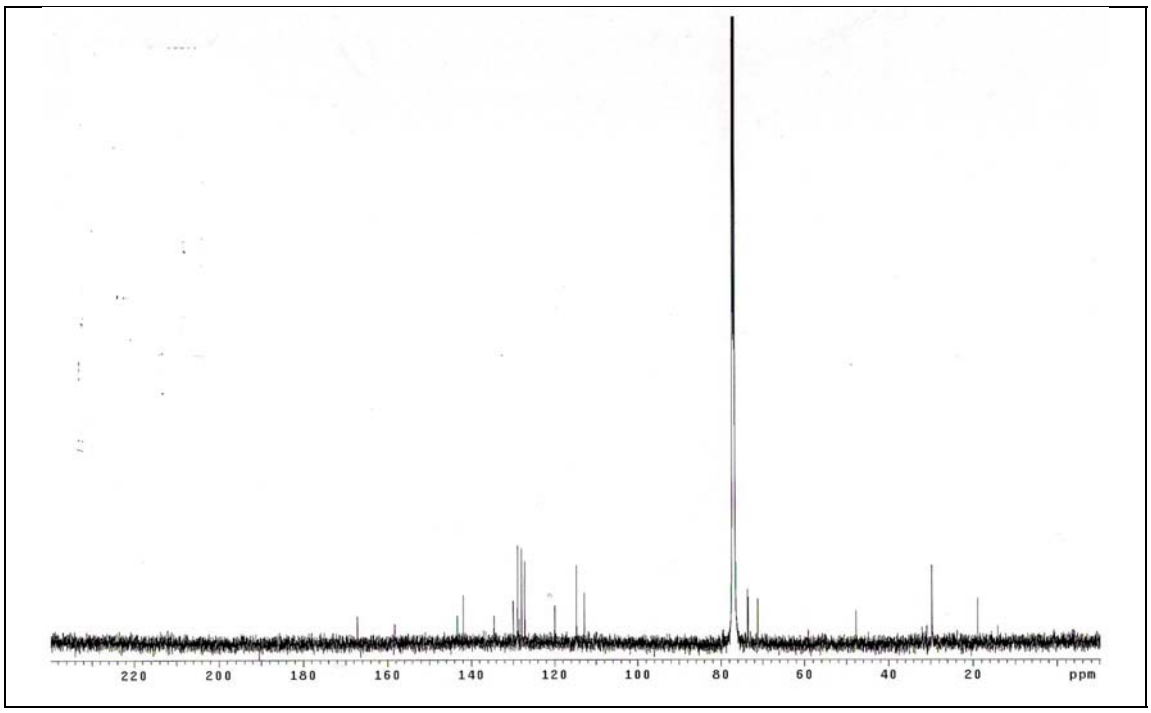


Figure 103 ^{13}C NMR (1255 MHz) ($CDCl_3$) of compound **PW11**

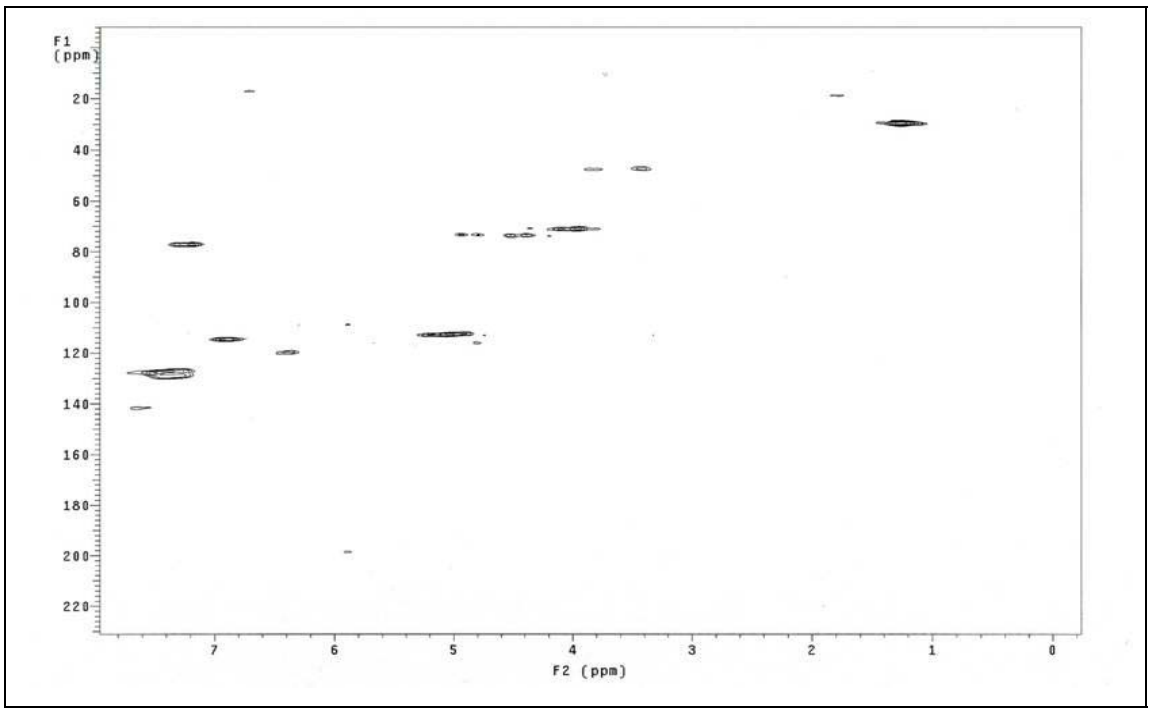


Figure 104 2D HMQC ($CDCl_3$) of compound **PW11**

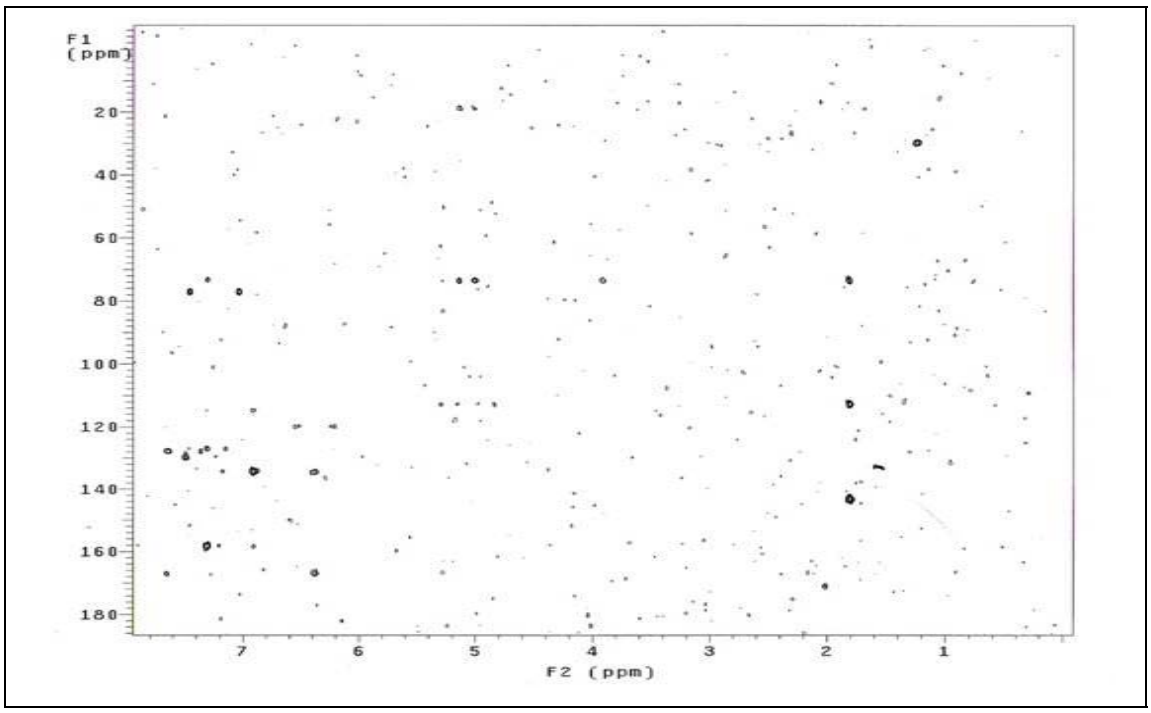


Figure 105 2D HMBC ($CDCl_3$) of compound **PW11**

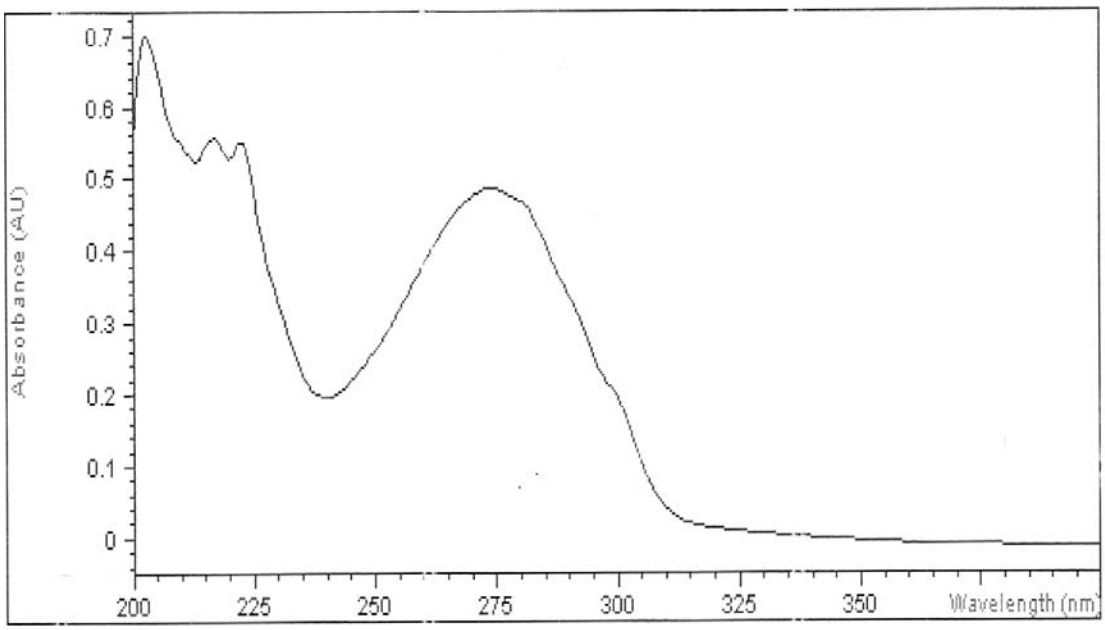


Figure 106 UV (MeOH) spectrum of compound **PW12**

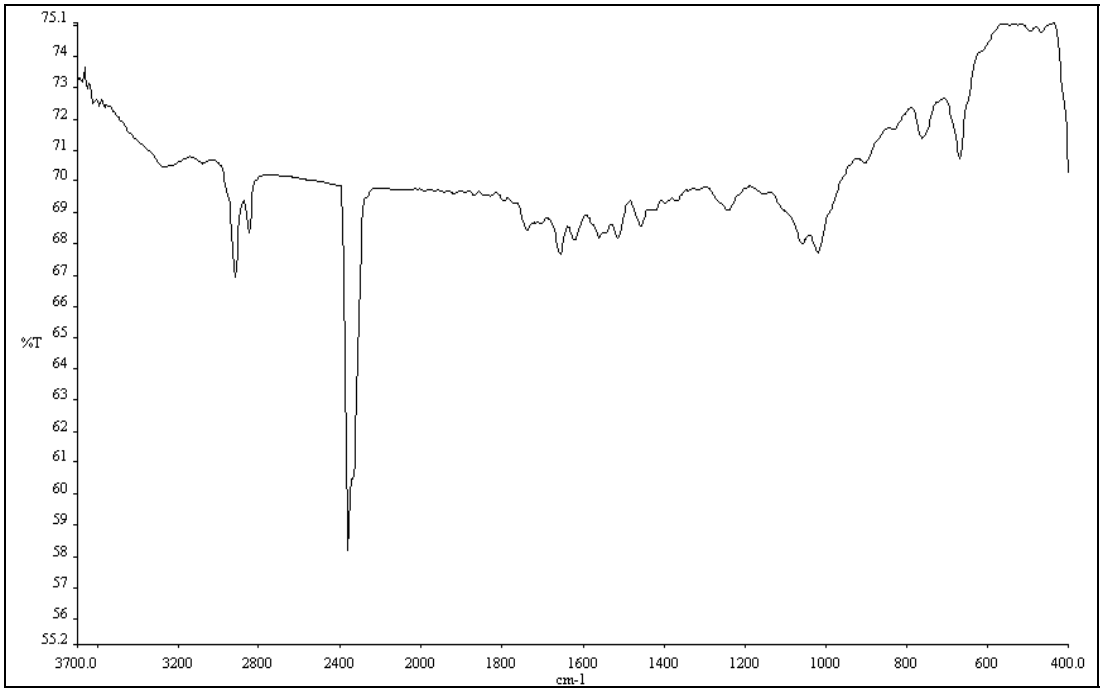


Figure 107 IR (neat) spectrum of compound **PW12**

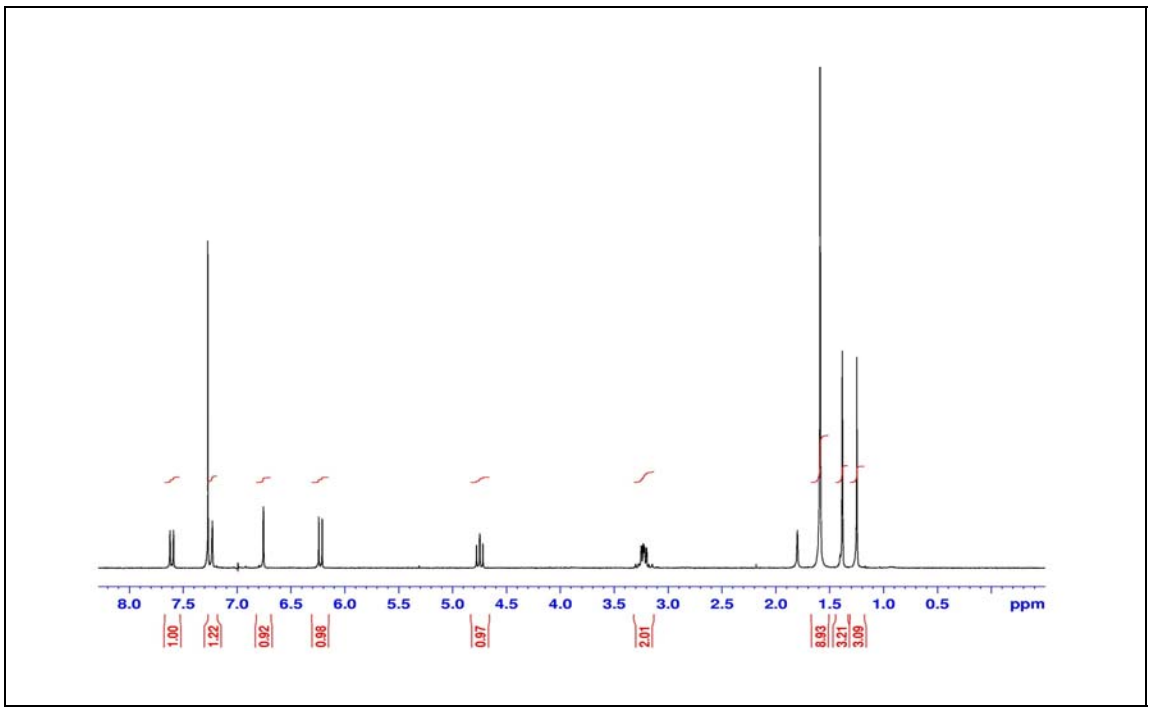


Figure 108 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW12**

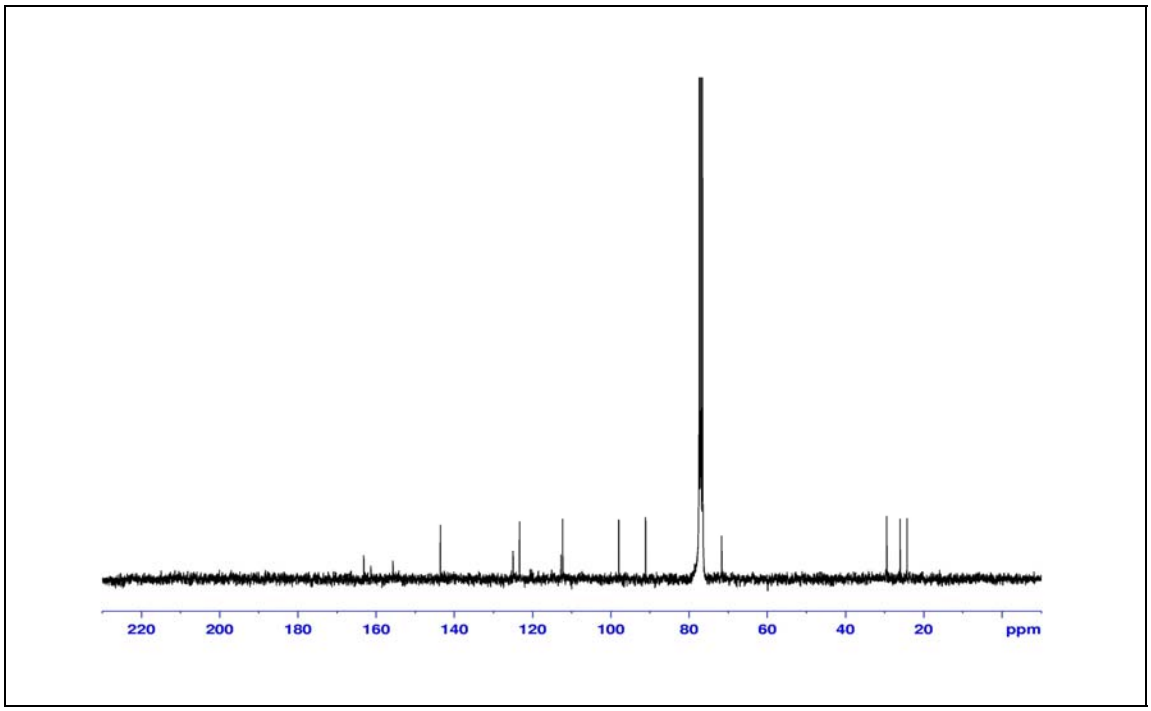


Figure 109 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW12**

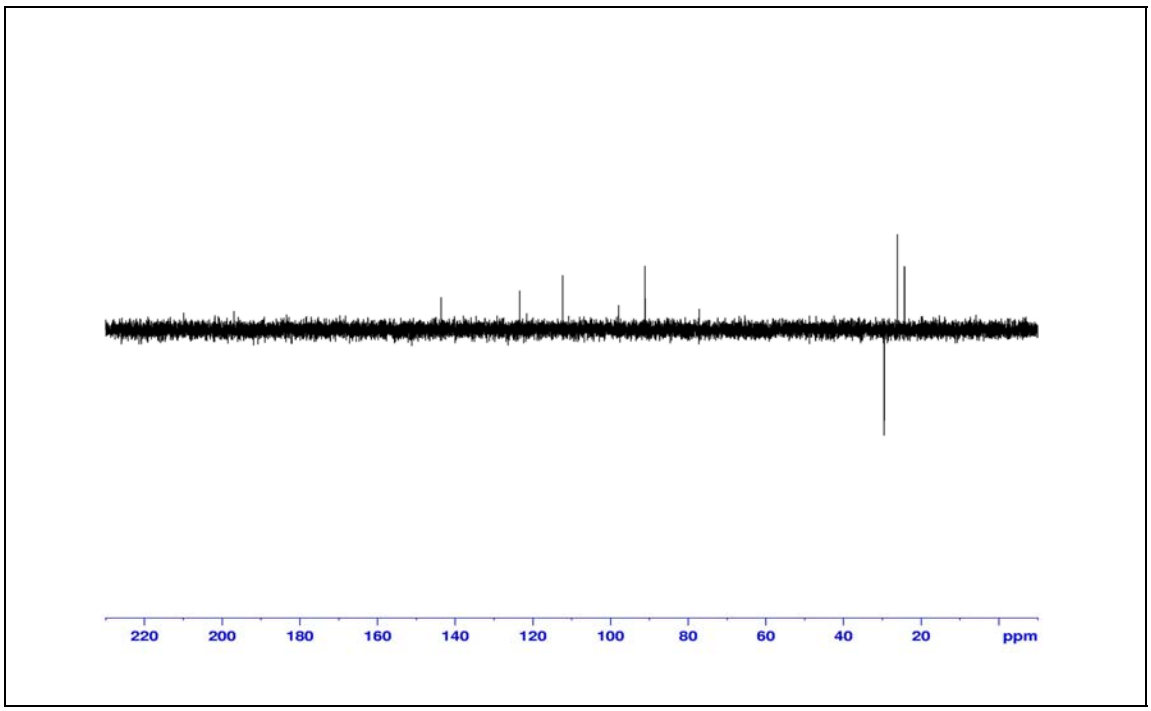


Figure 110 Dept 135° ($CDCl_3$) of compound **PW12**

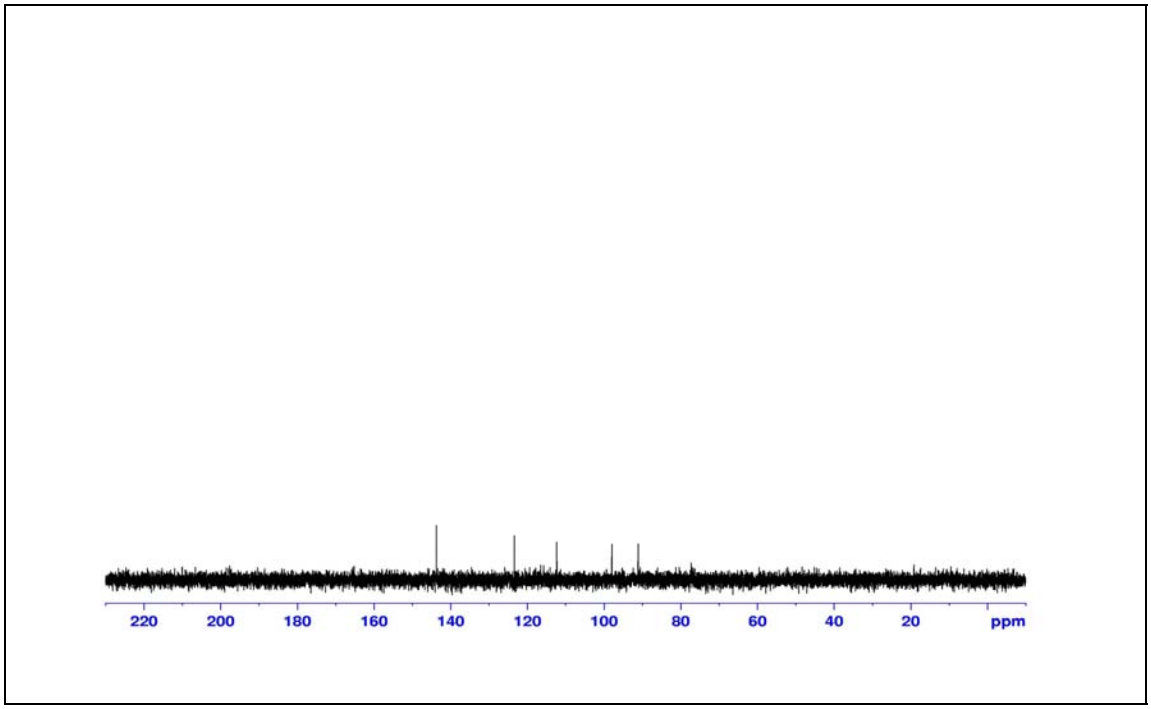


Figure 111 Dept 90° ($CDCl_3$) of compound **PW12**

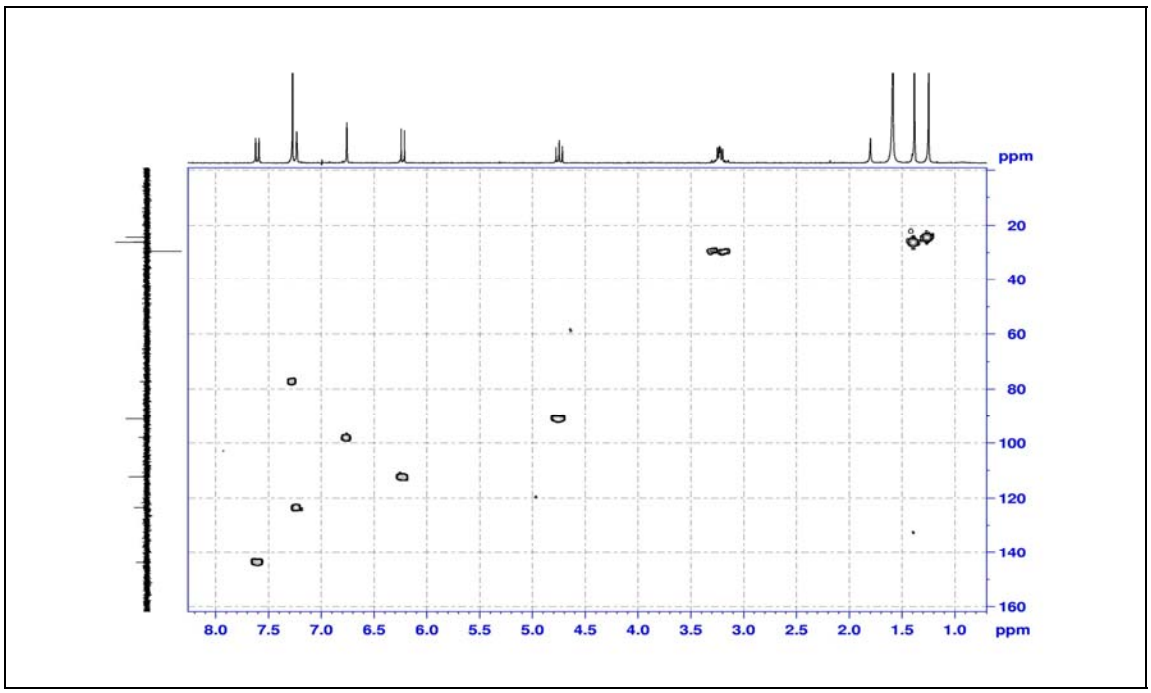


Figure 112 2D HMQC ($CDCl_3$) of compound **PW12**

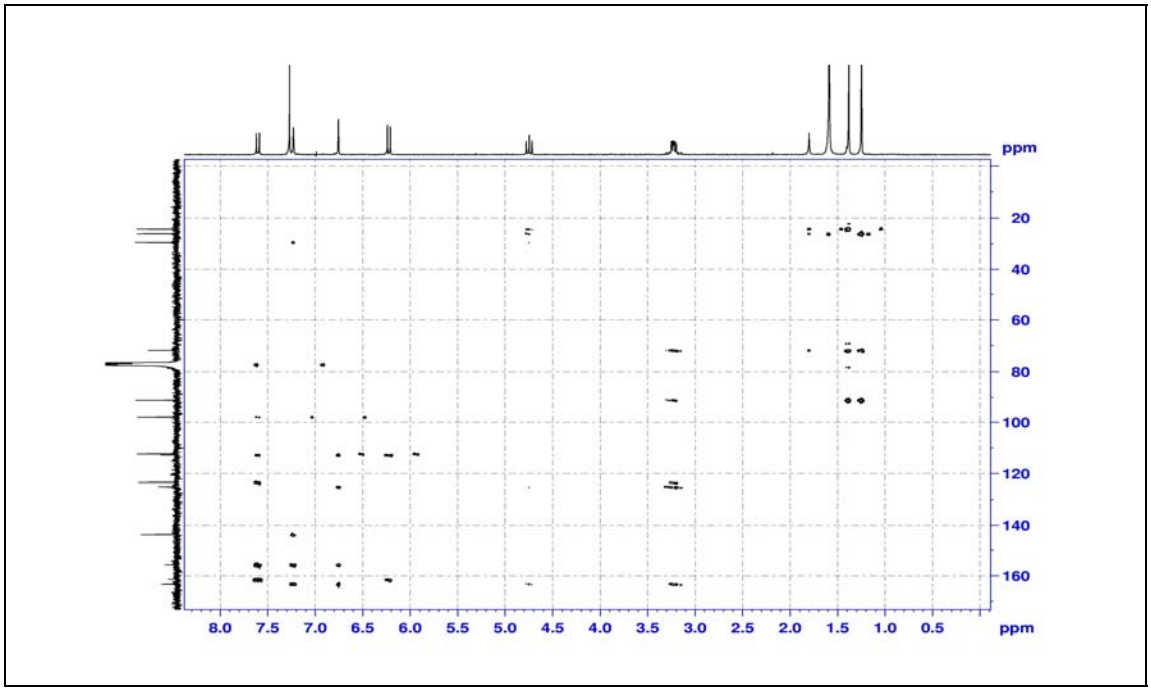


Figure 113 2D HMBC ($CDCl_3$) of compound **PW12**

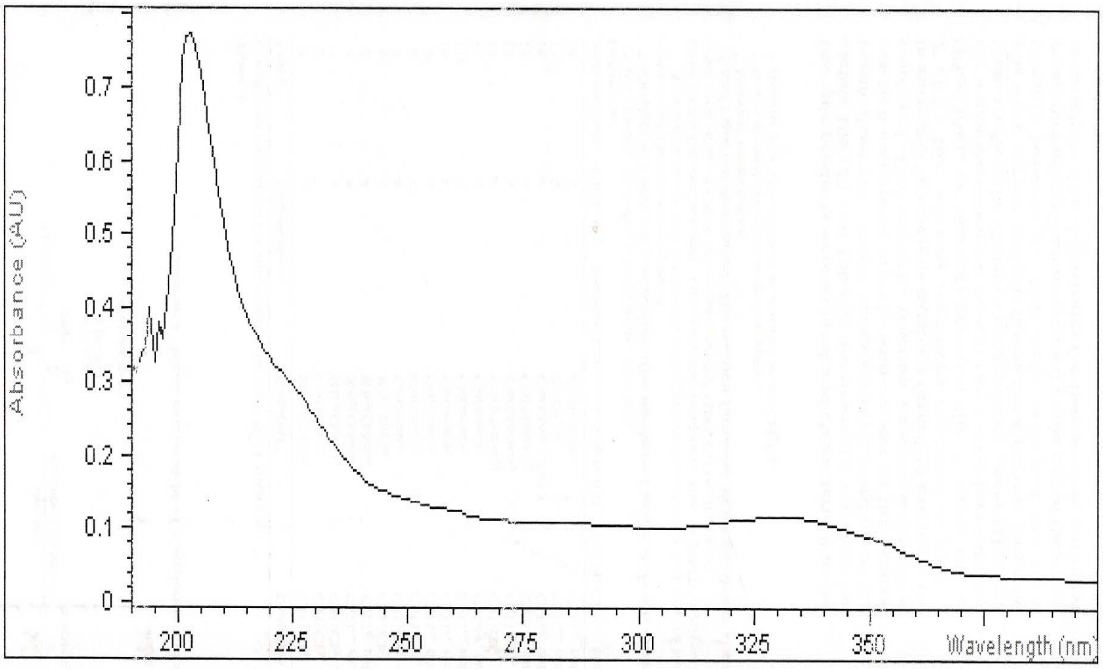


Figure 114 UV (MeOH) spectrum of compound **PW13**

Figure 115 IR (neat) spectrum of compound **PW13**

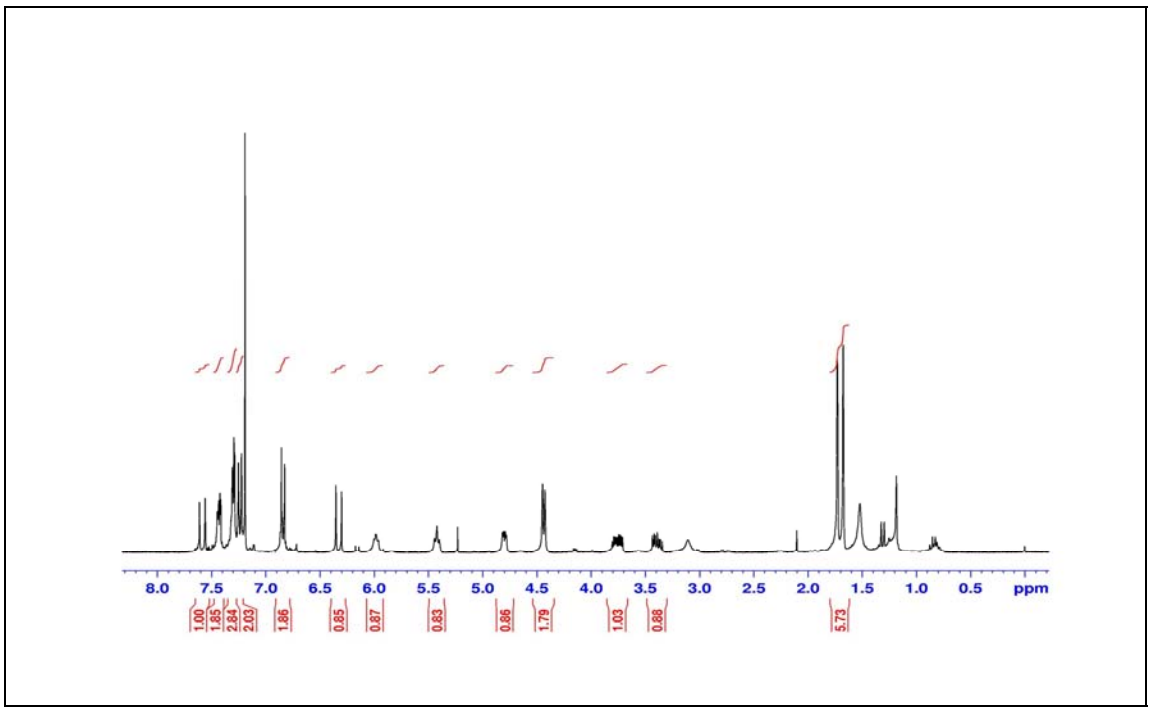


Figure 116 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW13**

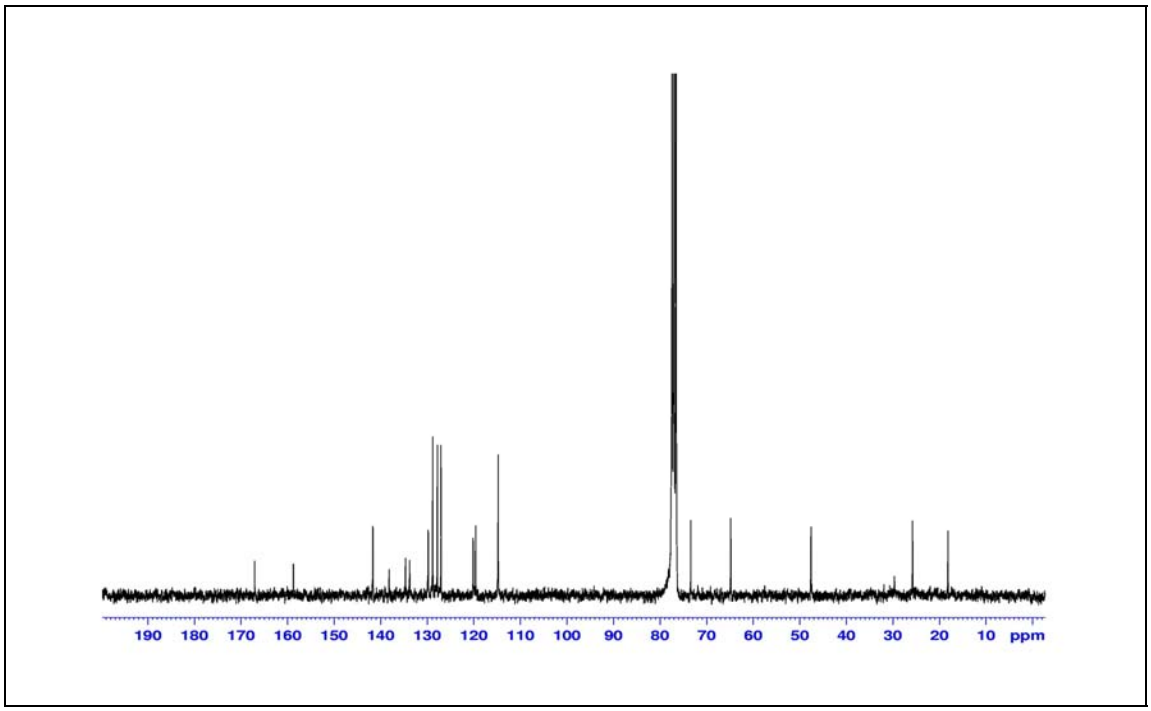


Figure 117 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW13**

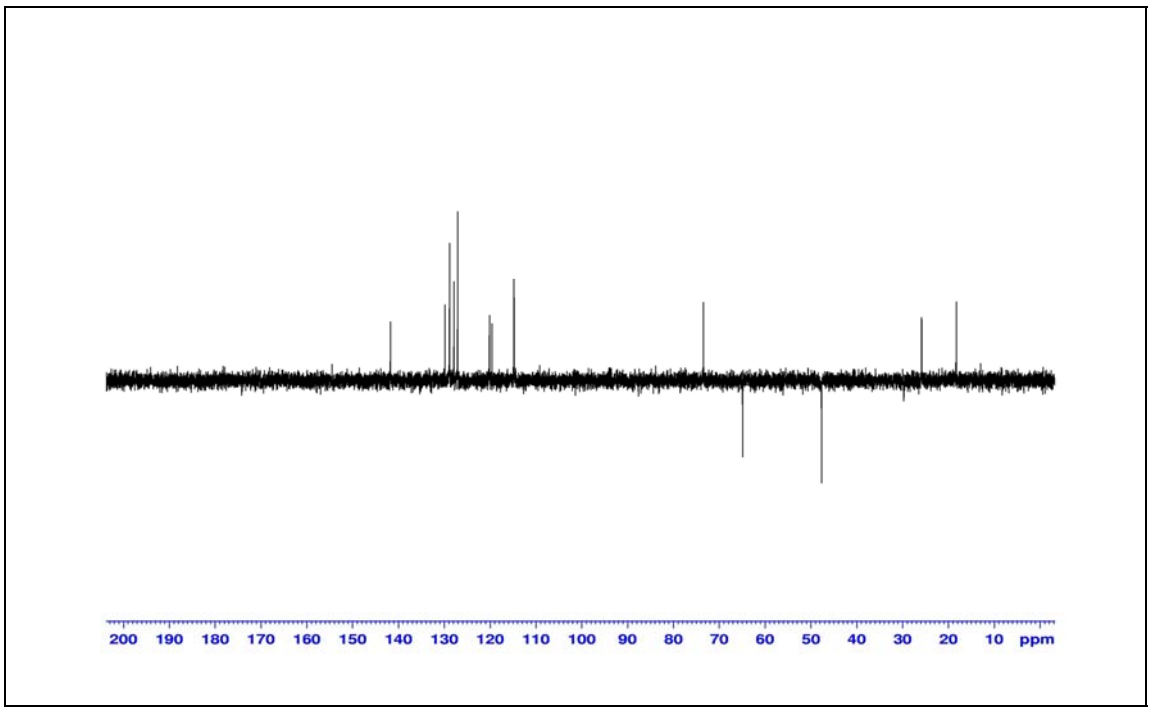


Figure 118 Dept 135° ($CDCl_3$) of compound **PW13**

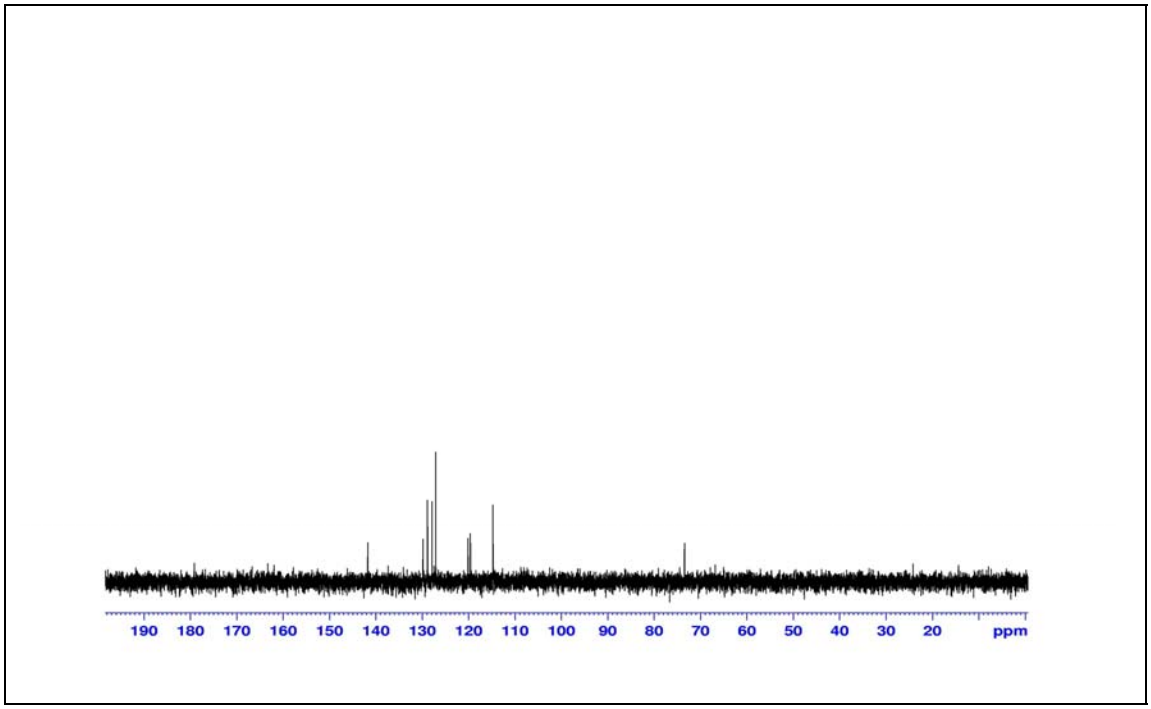


Figure 119 Dept 90° ($CDCl_3$) of compound **PW13**

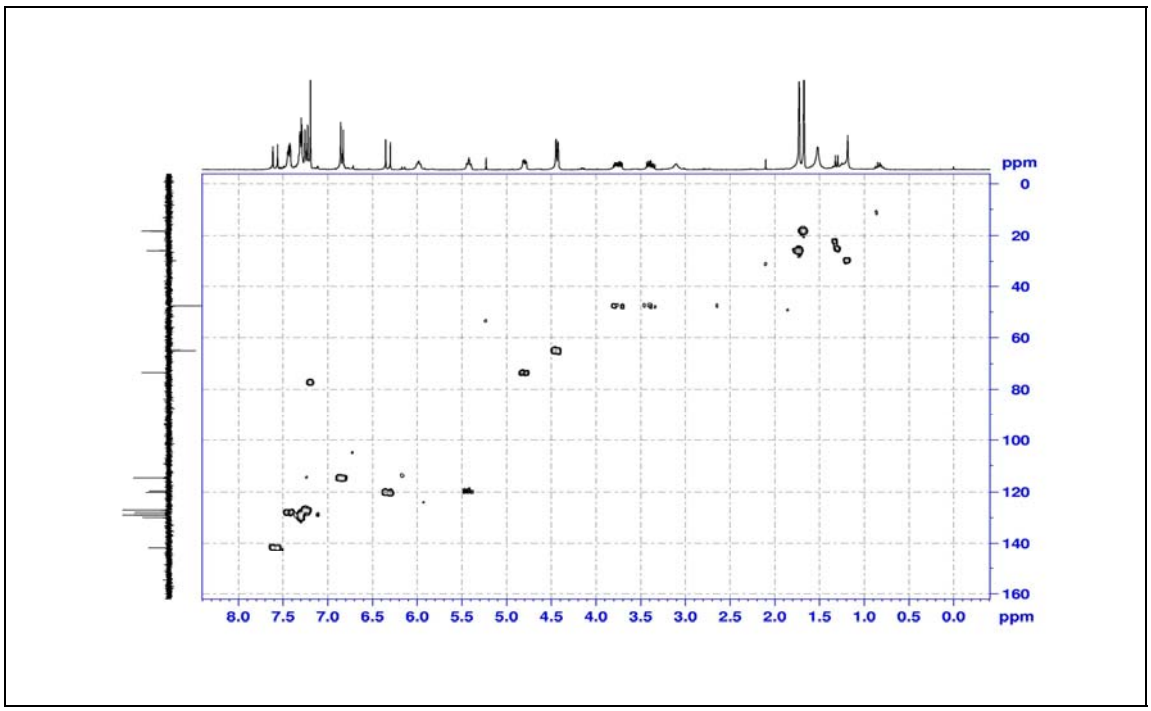


Figure 120 2D HMQC ($CDCl_3$) of compound **PW13**

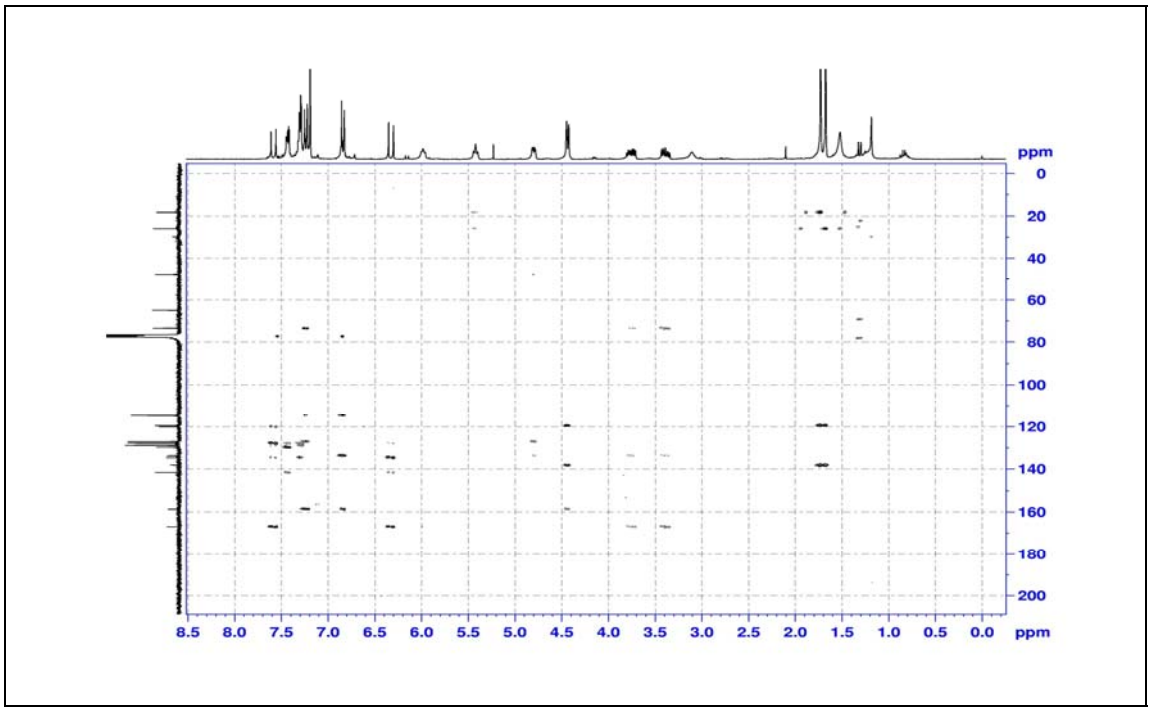


Figure 121 2D HMBC ($CDCl_3$) of compound **PW13**

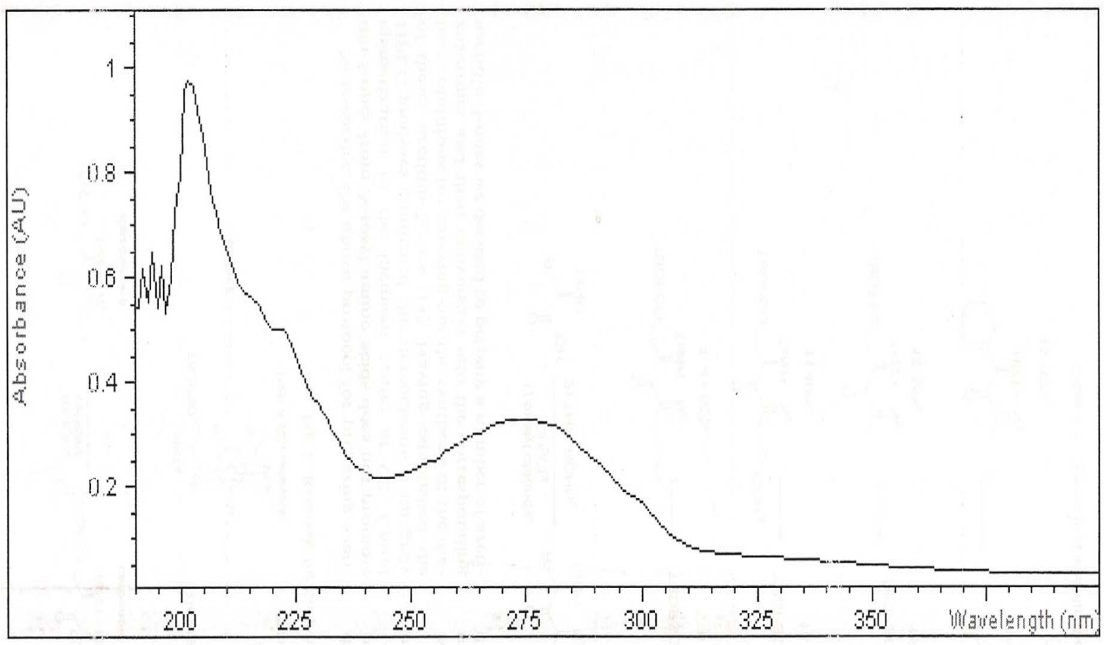


Figure 122 UV (MeOH) spectrum of compound **PW14**

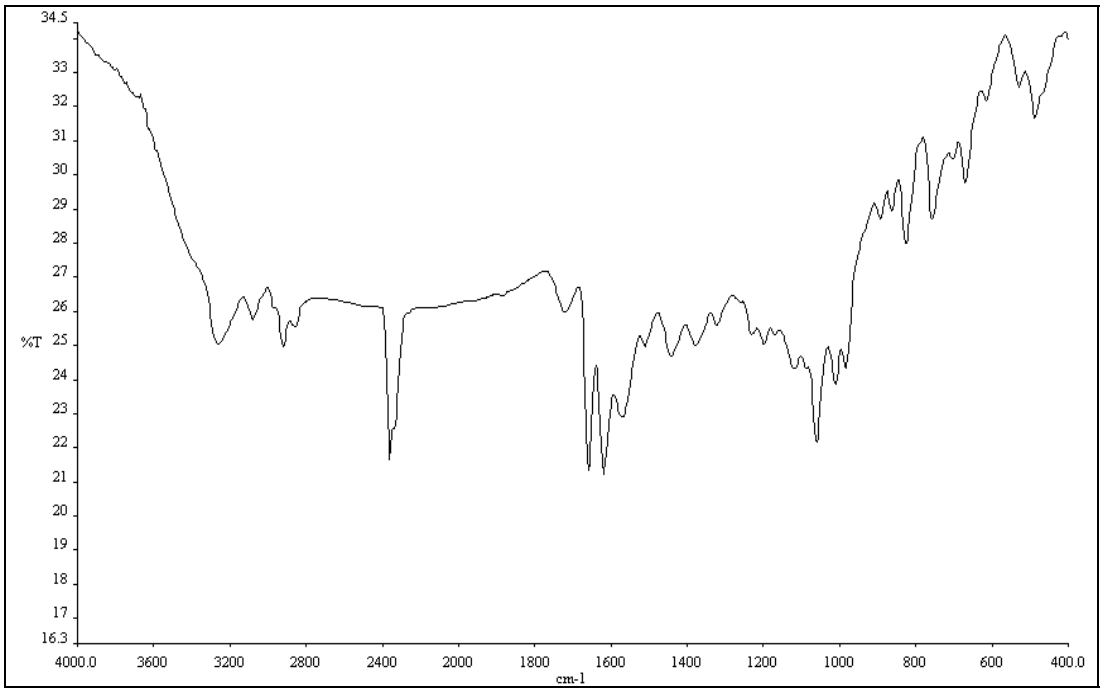


Figure 123 IR (neat) spectrum of compound **PW14**

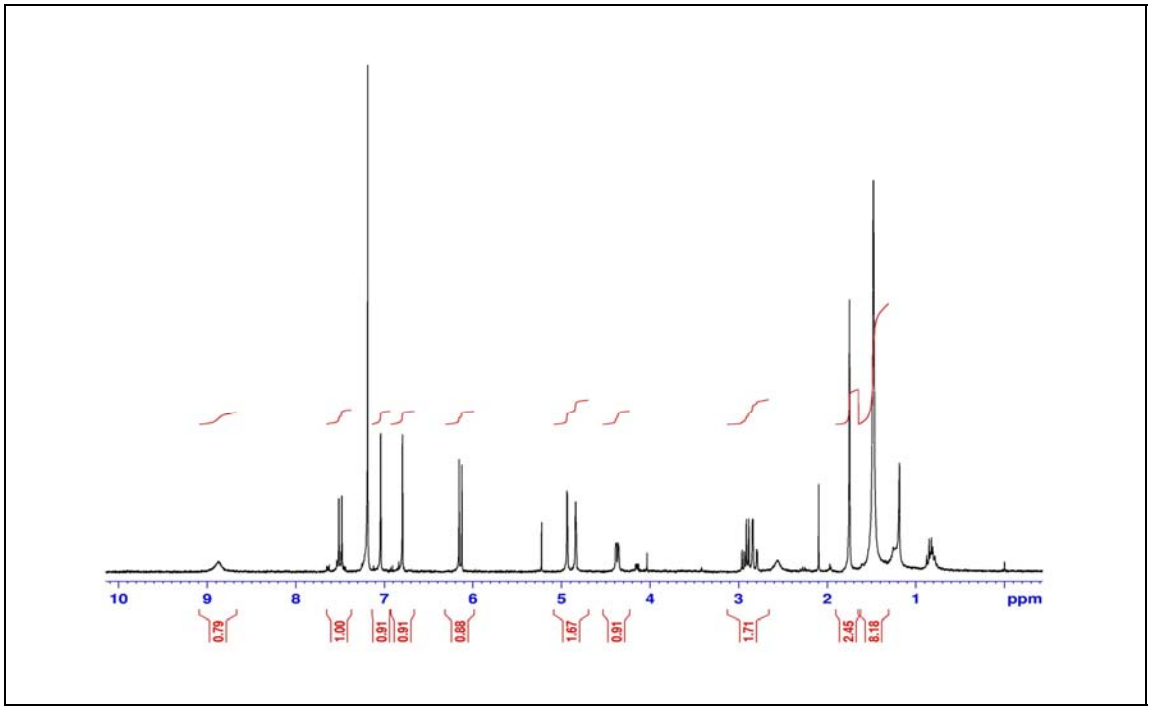


Figure 124 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW14**

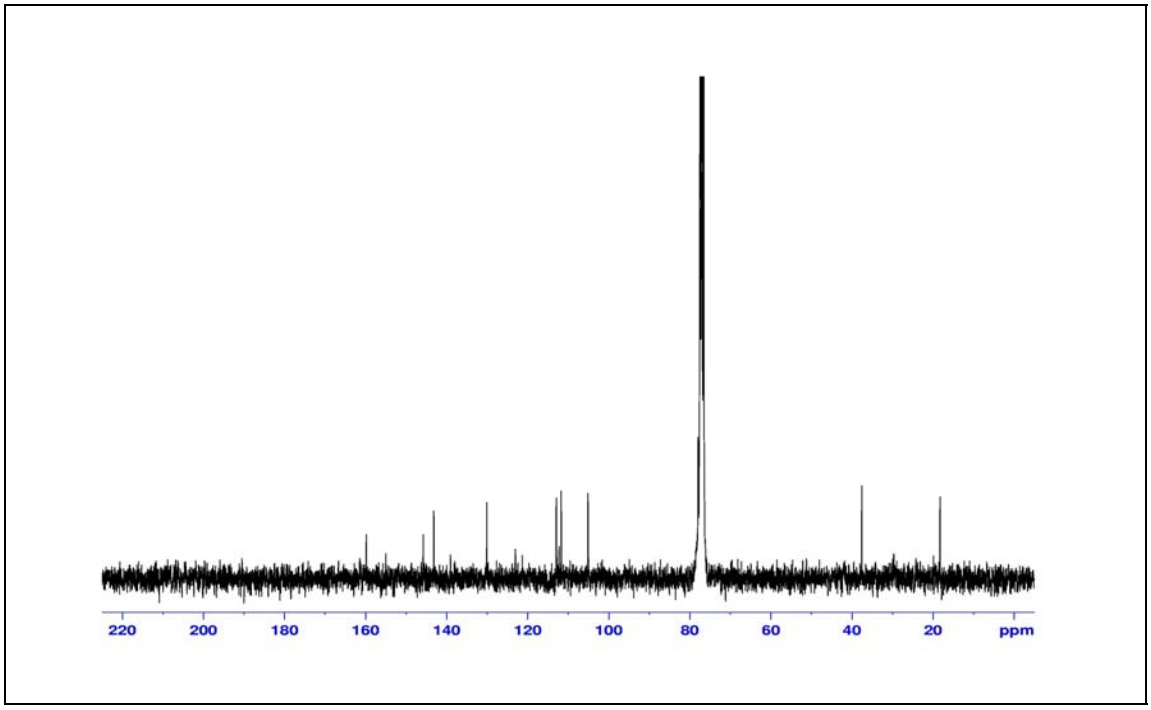


Figure 125 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW14**

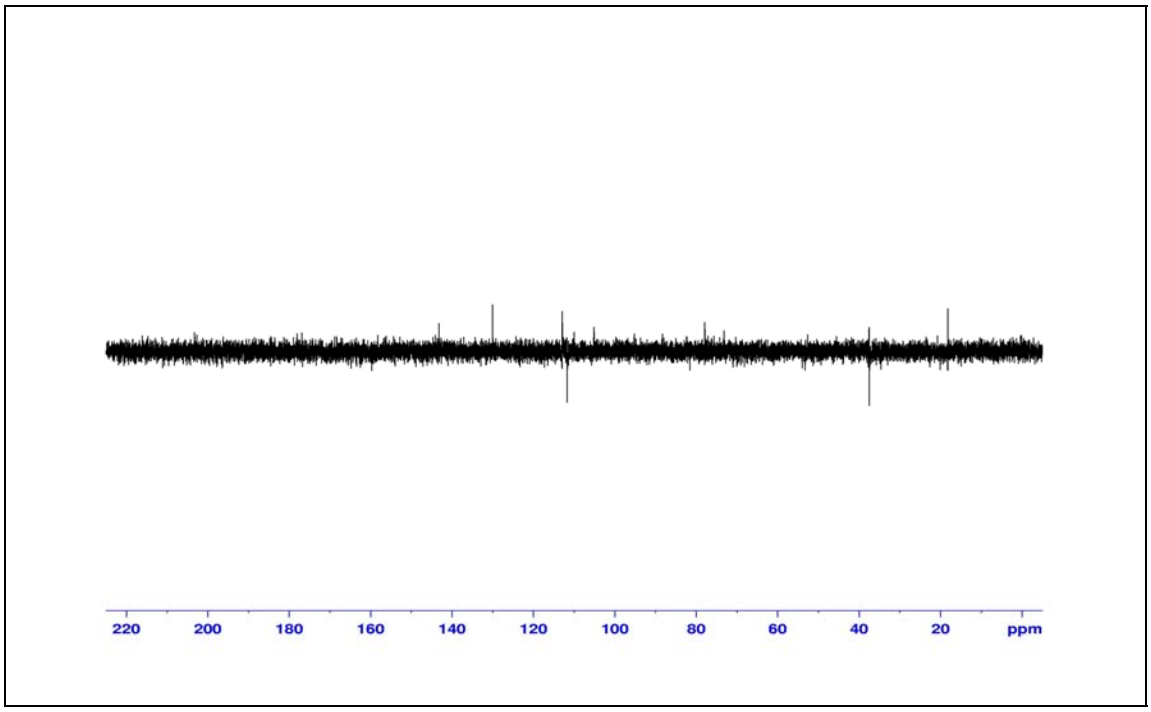


Figure 126 Dept 135° ($CDCl_3$) of compound **PW14**

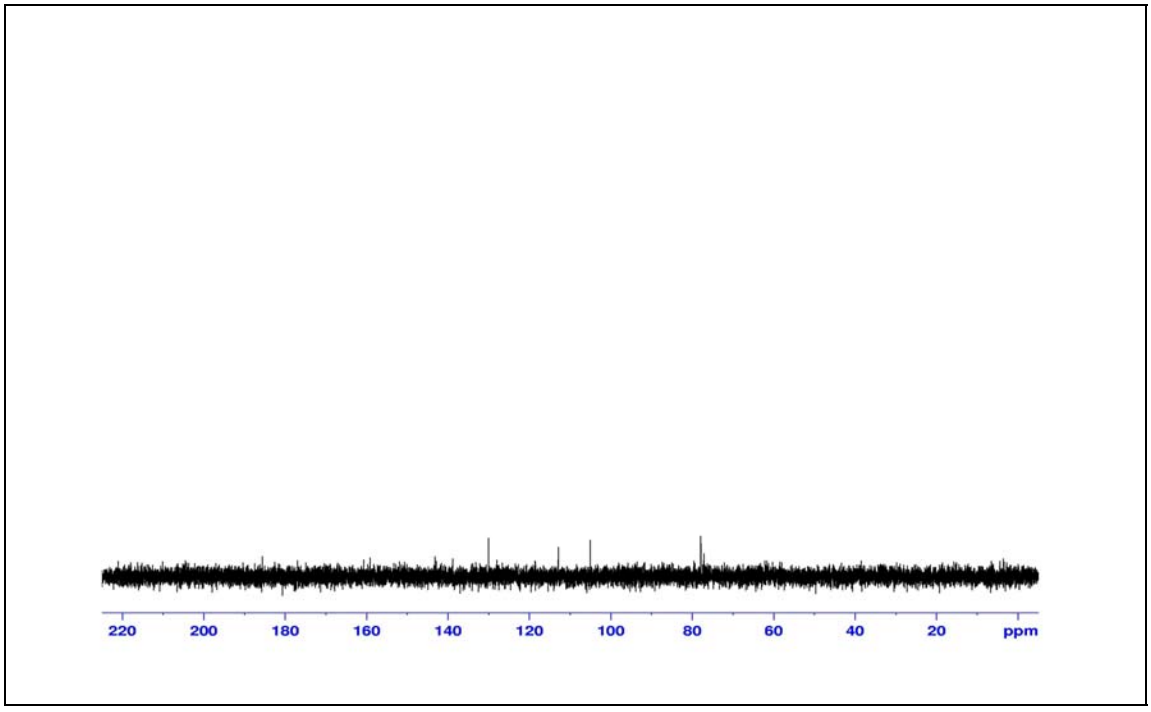


Figure 127 Dept 90° ($CDCl_3$) of compound **PW14**

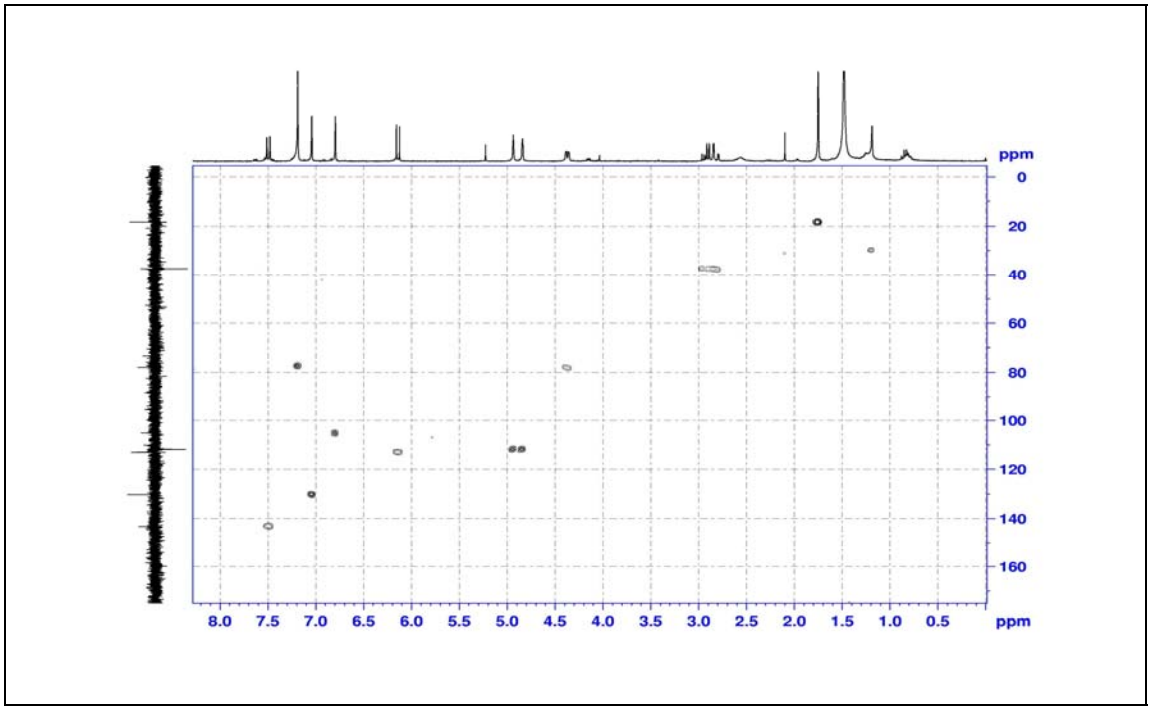


Figure 128 2D HMQC ($CDCl_3$) of compound **PW14**

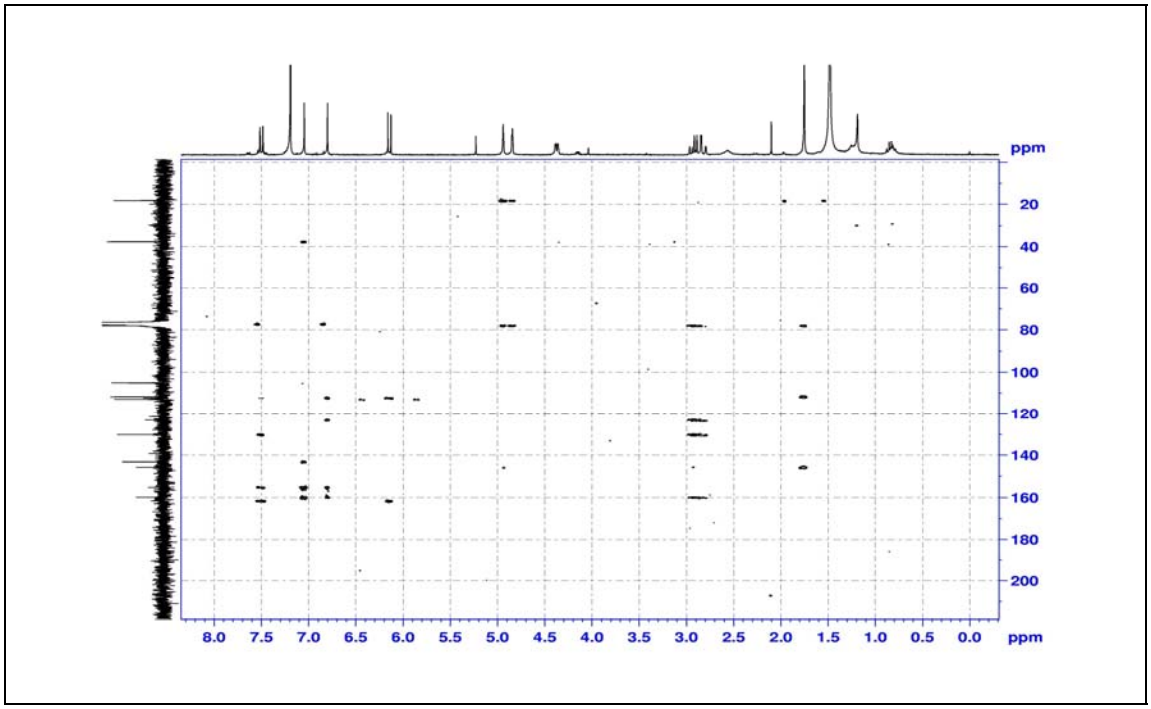


Figure 129 2D HMBC ($CDCl_3$) of compound **PW14**

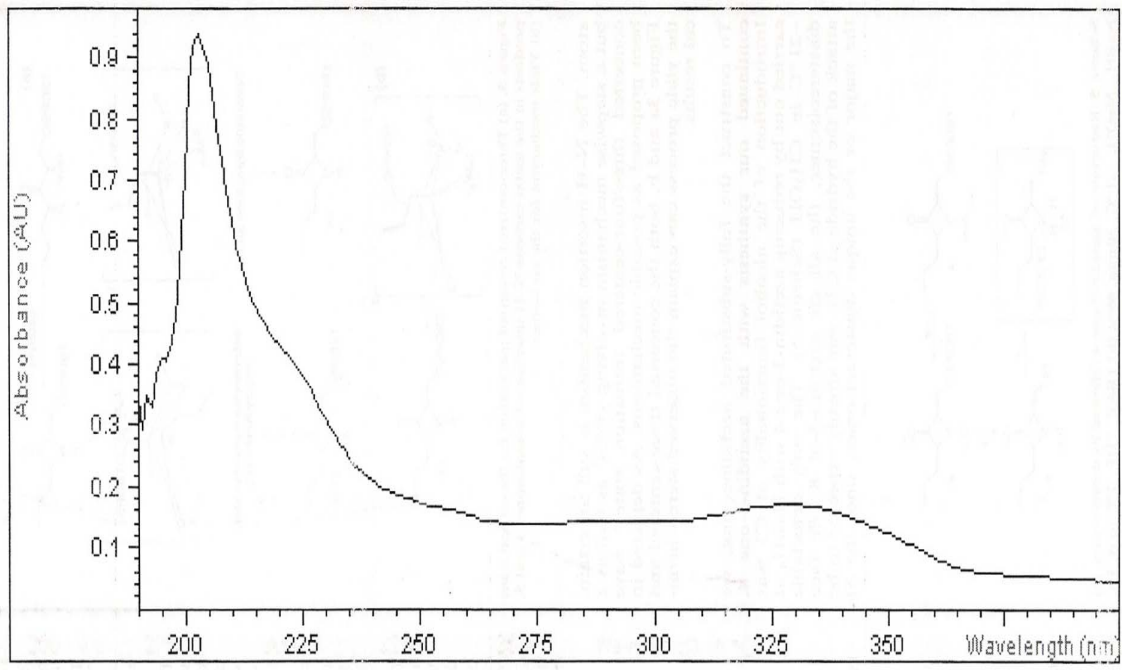


Figure 130 UV (MeOH) spectrum of compound **PW15**

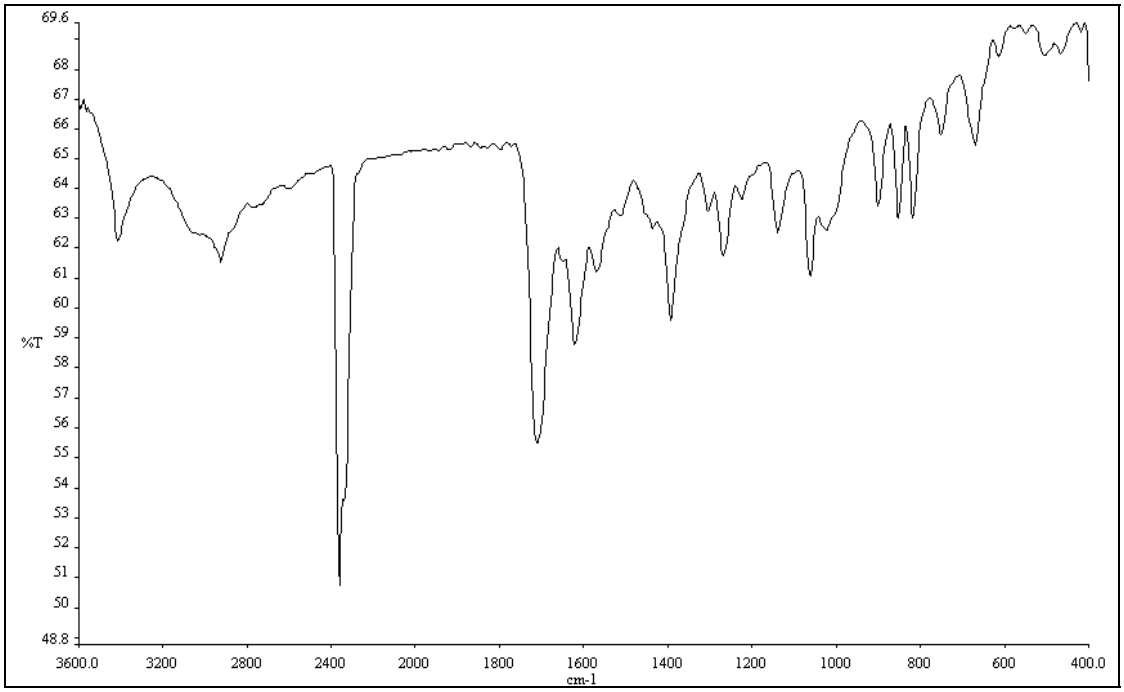


Figure 131 IR (neat) spectrum of compound **PW15**

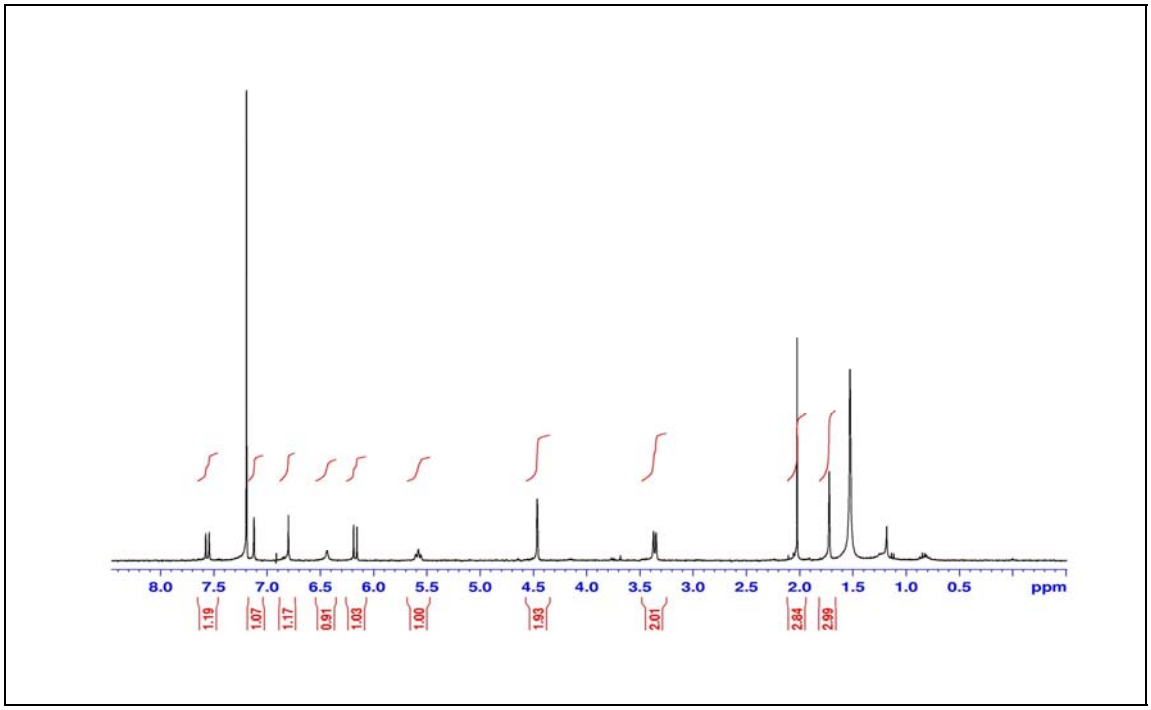


Figure 132 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW15**

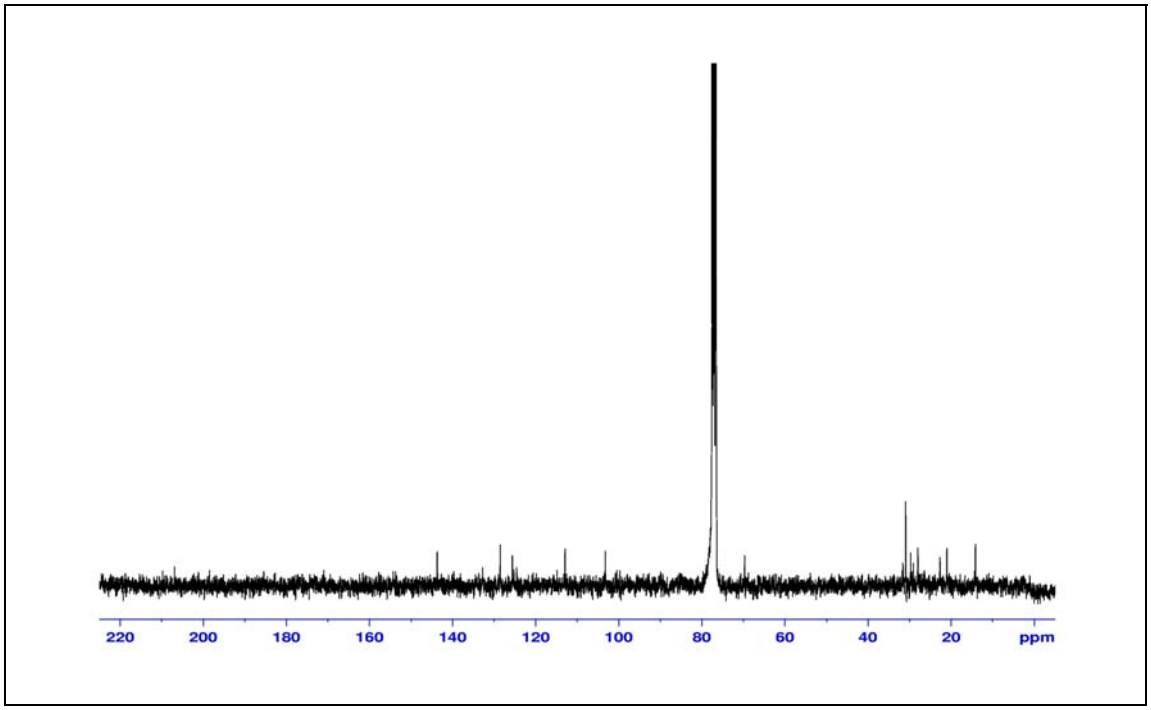


Figure 133 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW15**

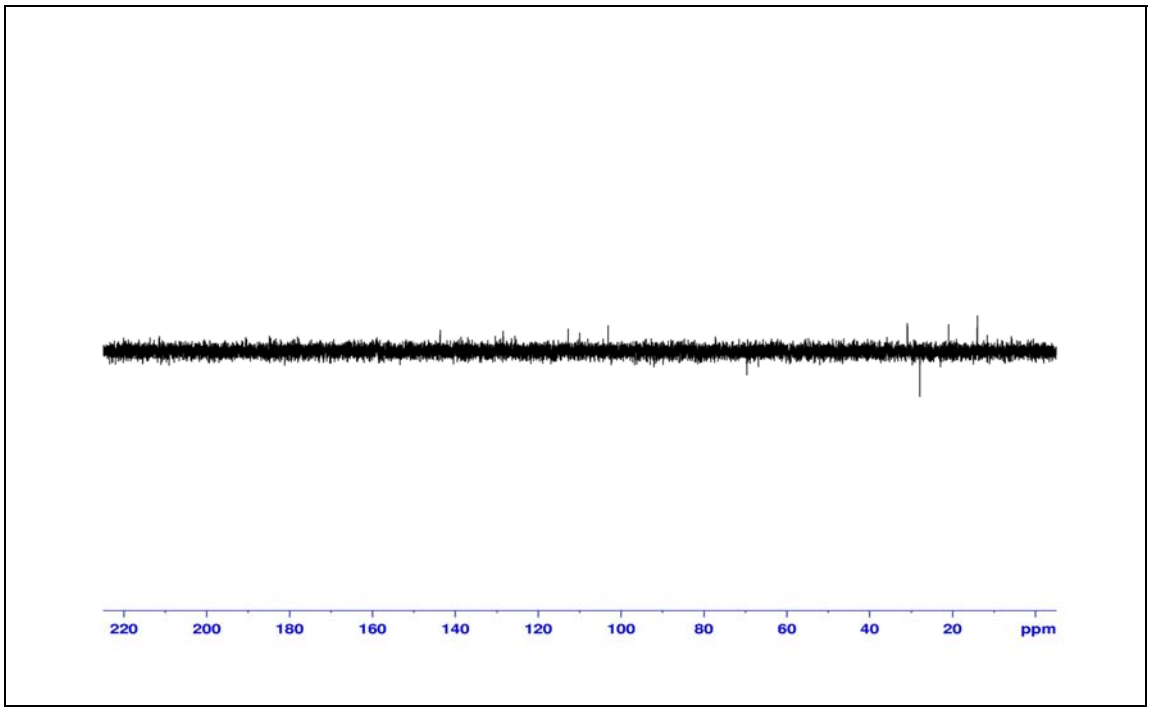


Figure 134 Dept 135° ($CDCl_3$) of compound **PW15**

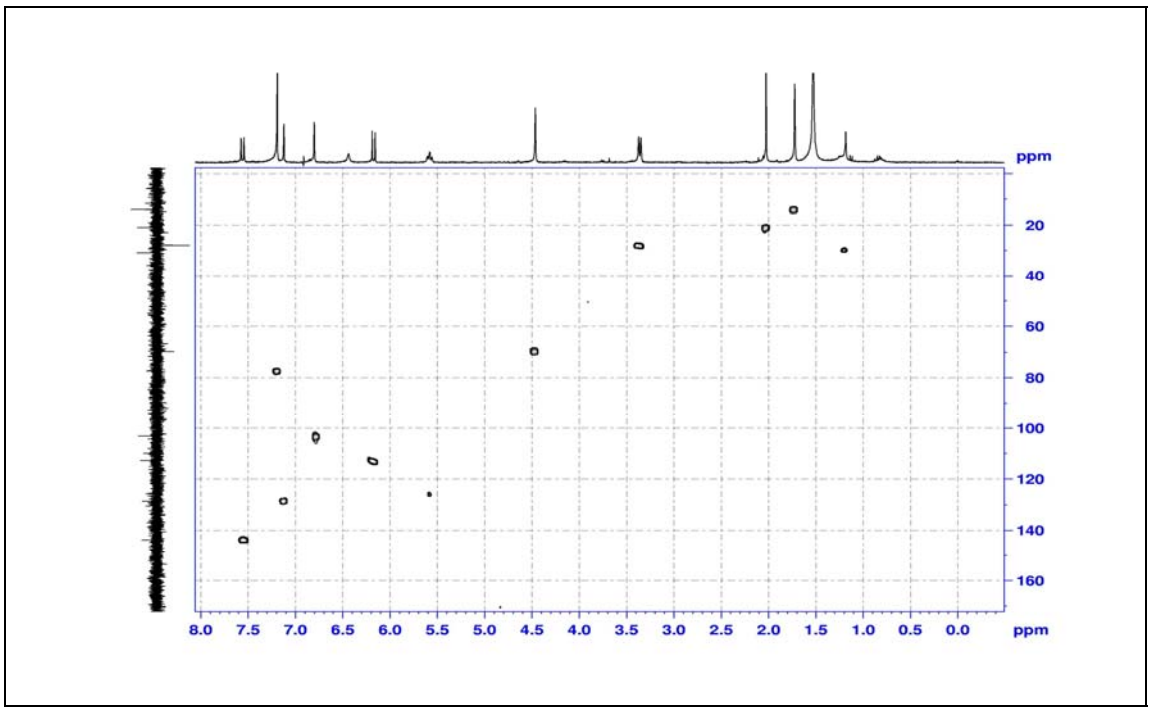


Figure 135 2D HMQC ($CDCl_3$) of compound **PW15**

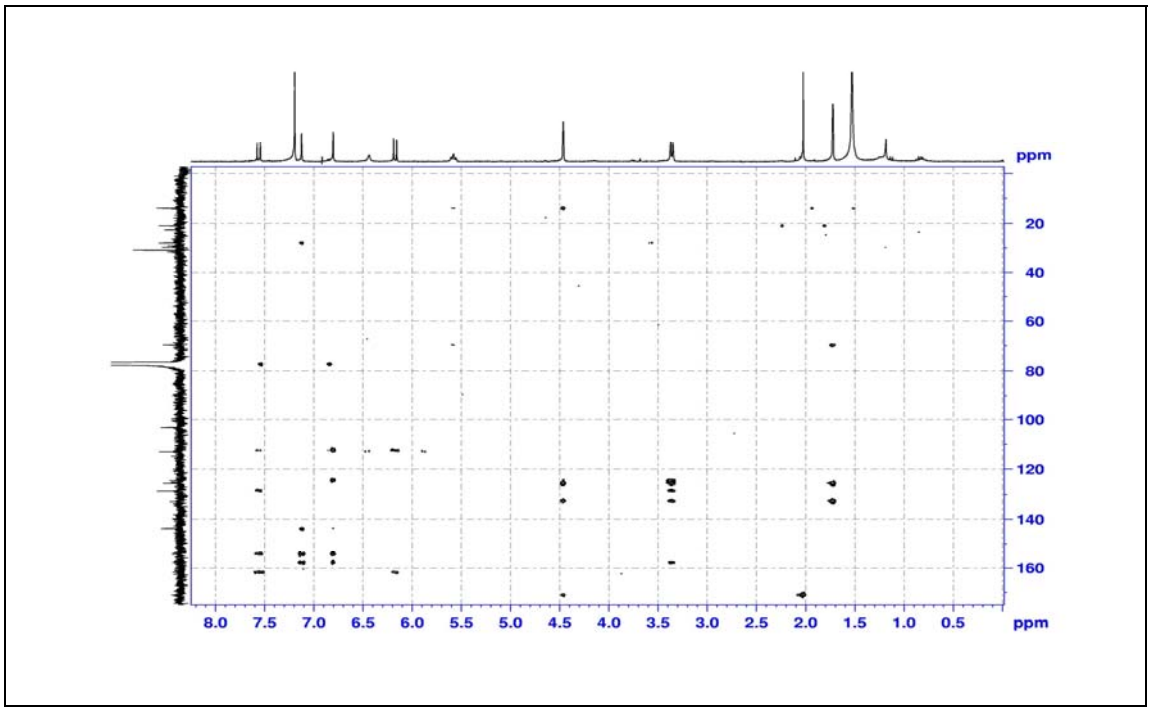


Figure 136 2D HMBC ($CDCl_3$) of compound **PW15**

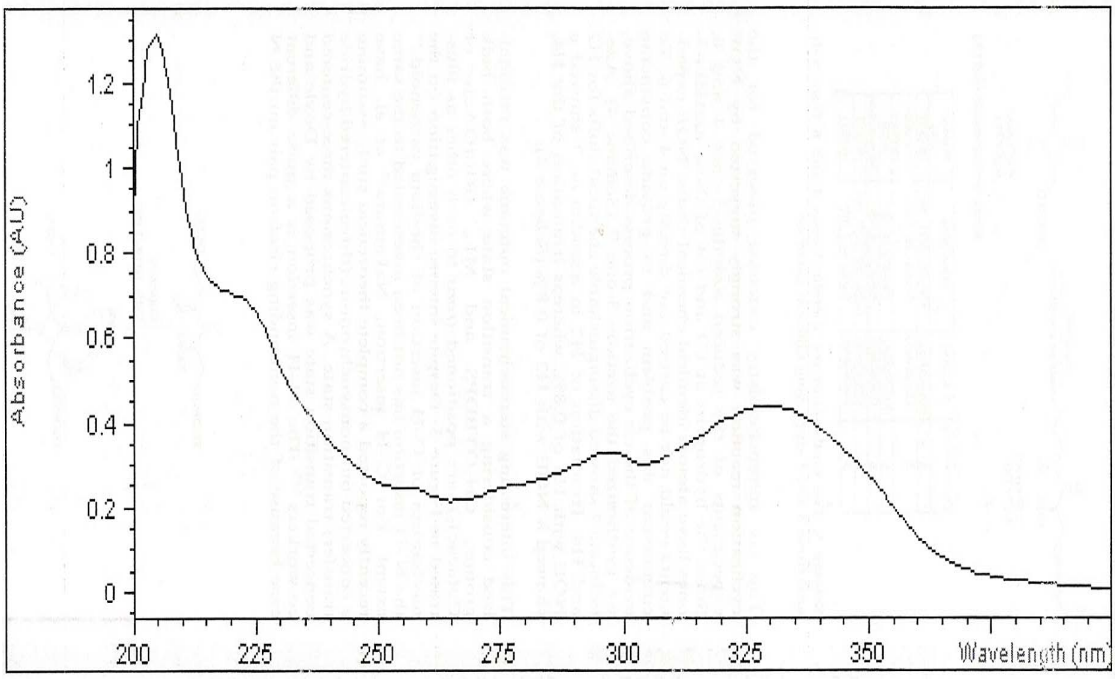


Figure 137 UV (MeOH) spectrum of compound **PW16**

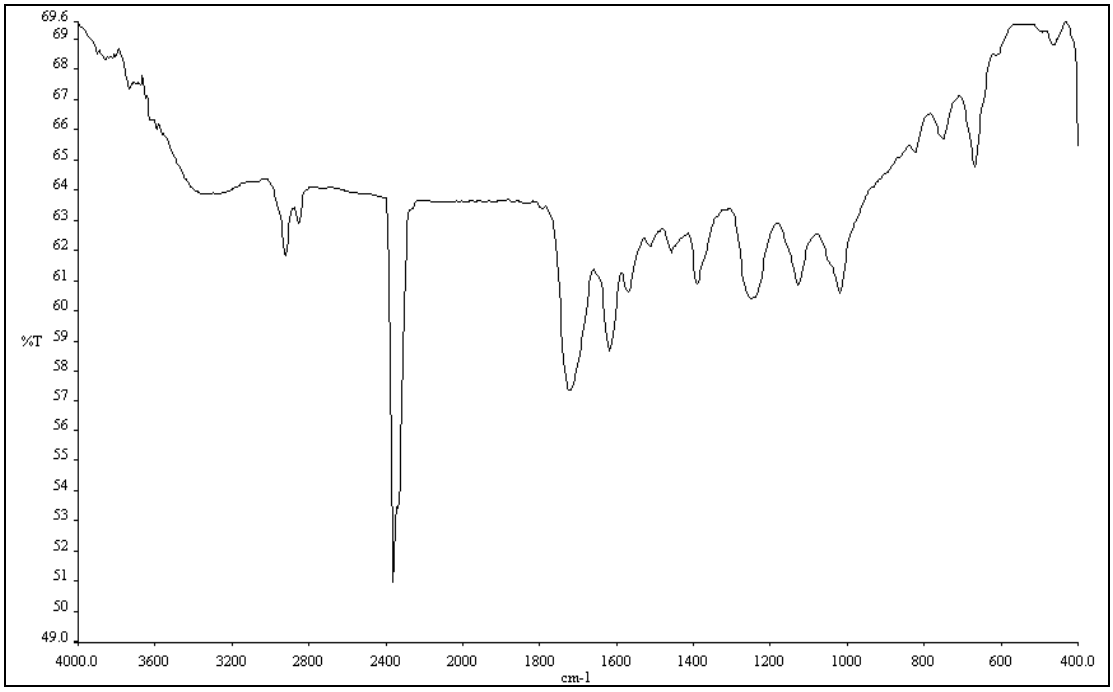


Figure 138 IR (neat) spectrum of compound **PW16**

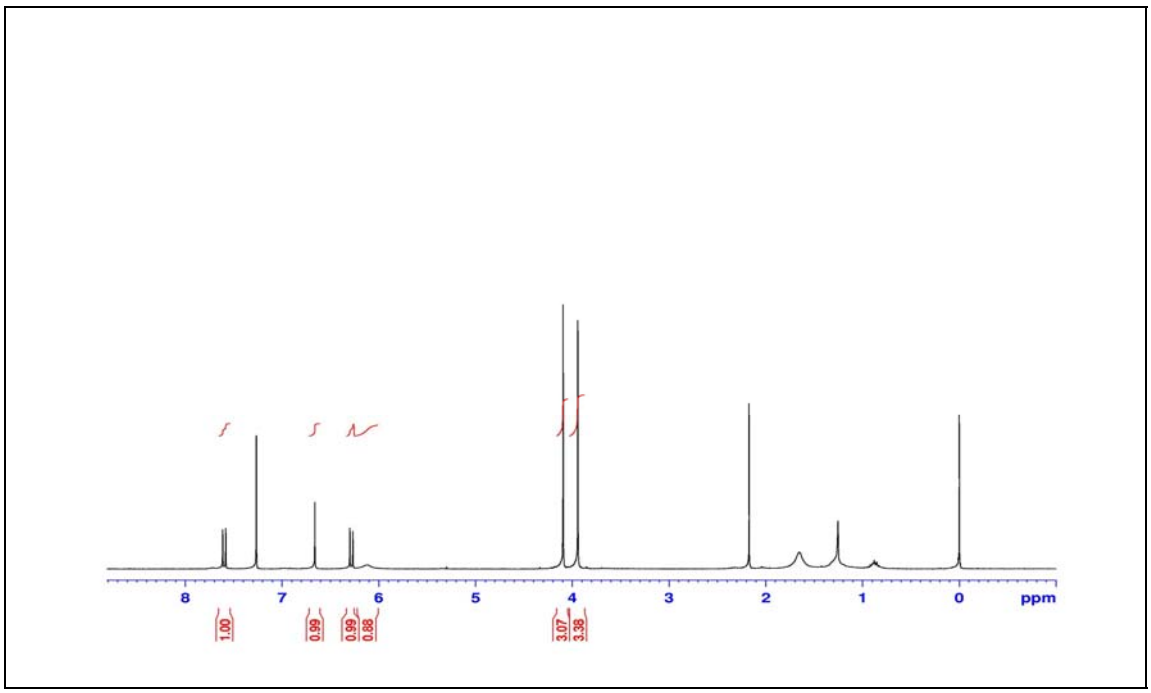


Figure 139 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW16**

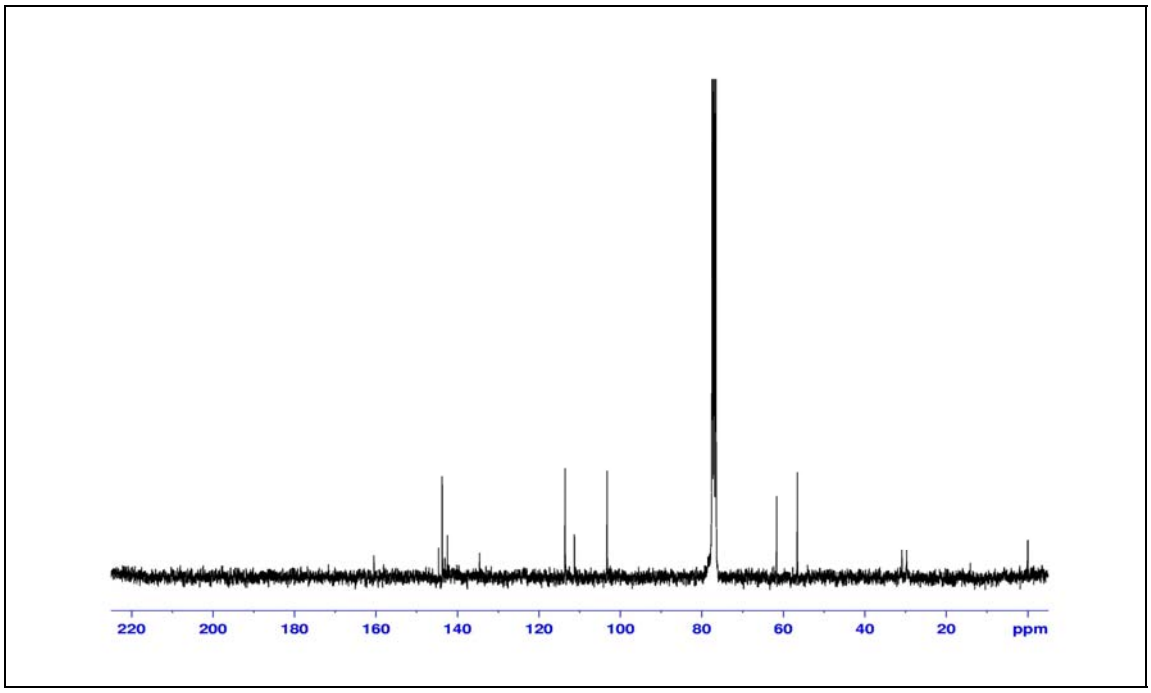


Figure 140 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW16**

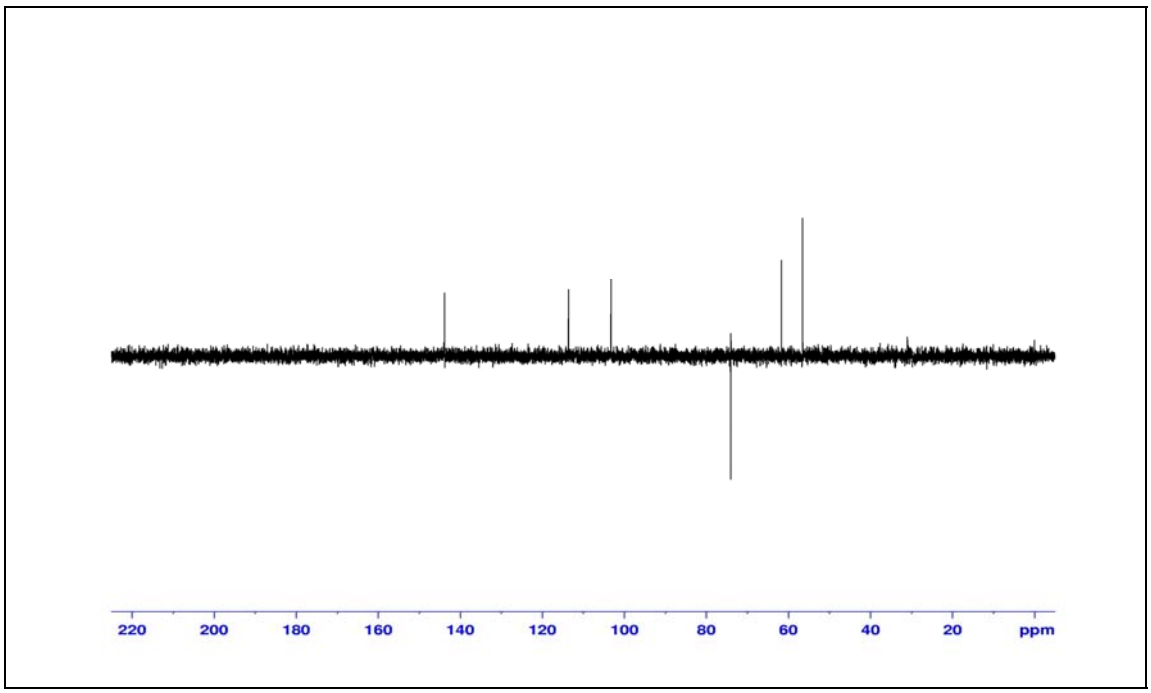


Figure 141 Dept 135° ($CDCl_3$) of compound **PW16**

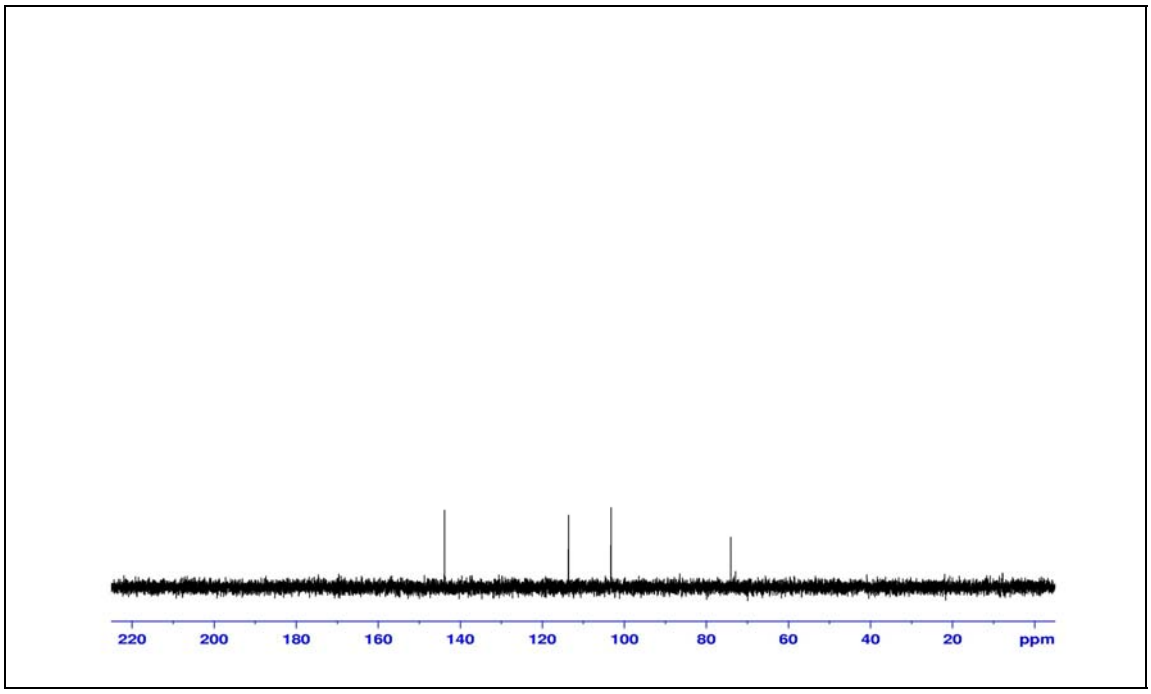


Figure 142 Dept 90° ($CDCl_3$) of compound **PW16**

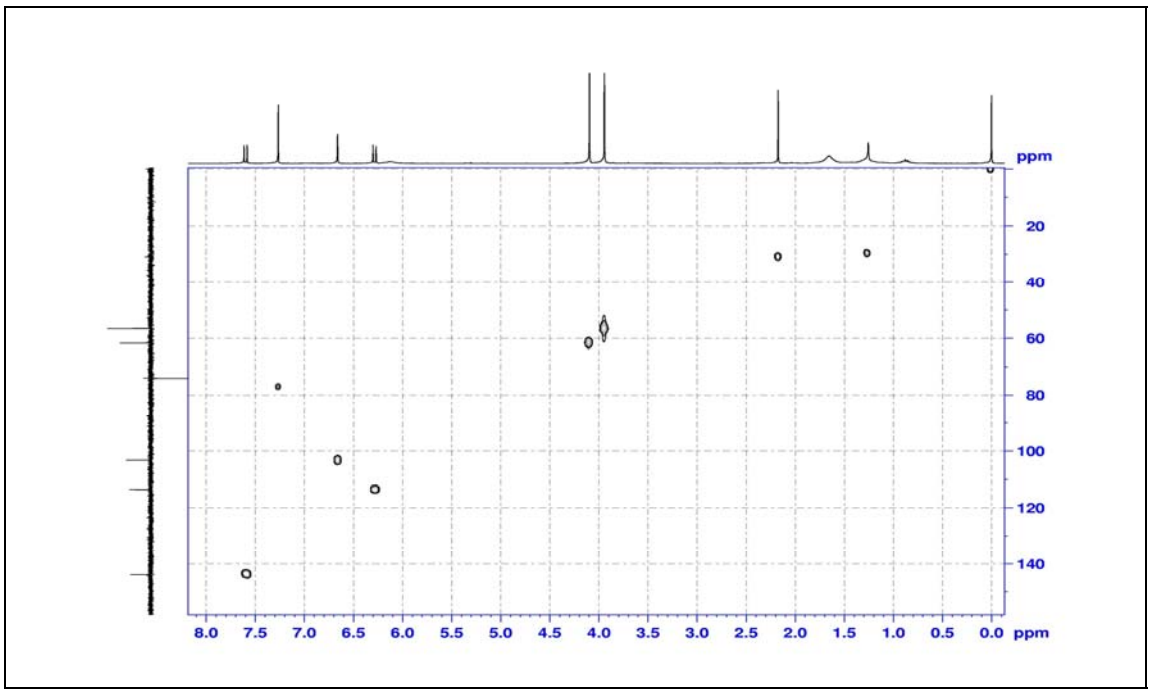


Figure 143 2D HMQC ($CDCl_3$) of compound **PW16**

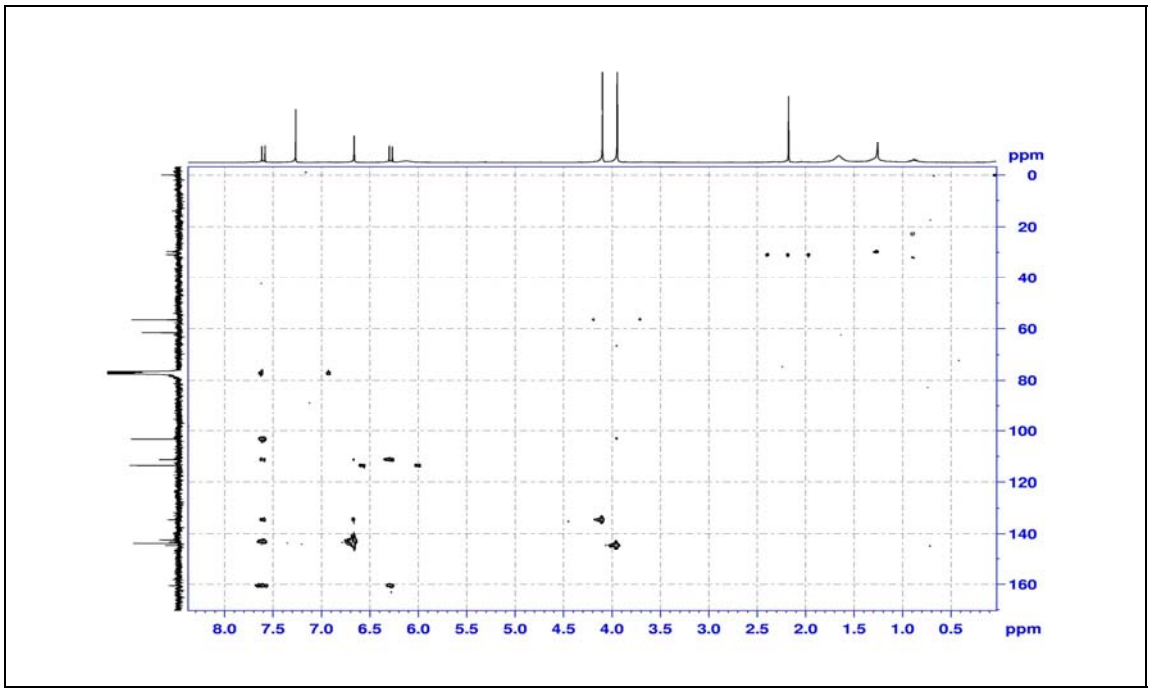


Figure 144 2D HMBC ($CDCl_3$) of compound **PW16**

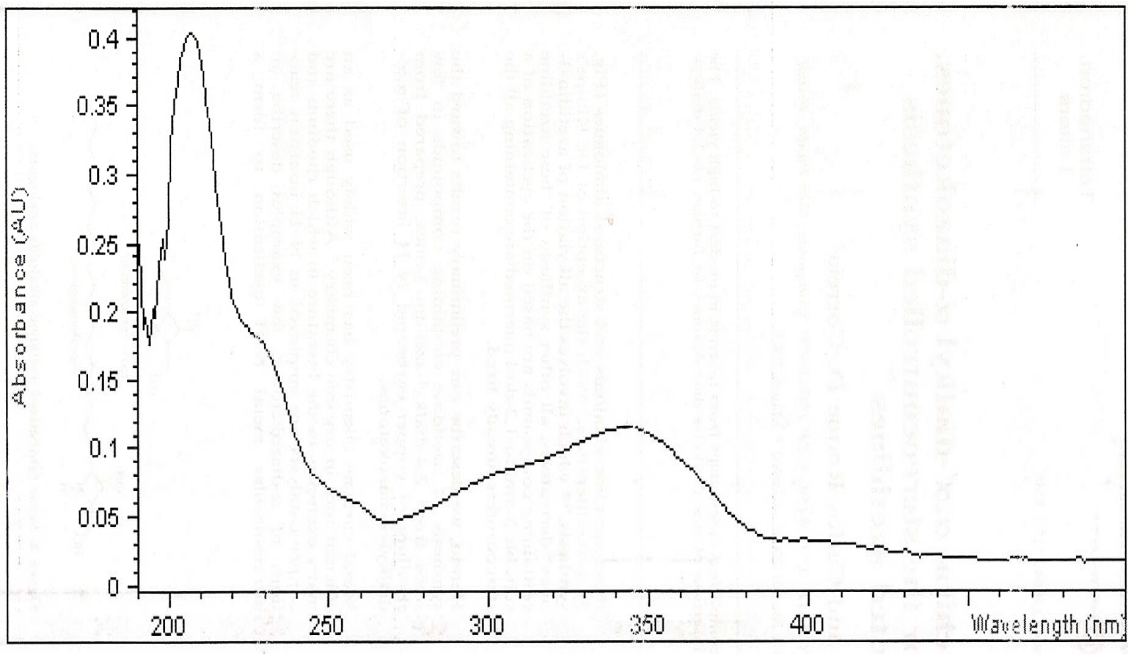


Figure 145 UV (MeOH) spectrum of compound **PW17**

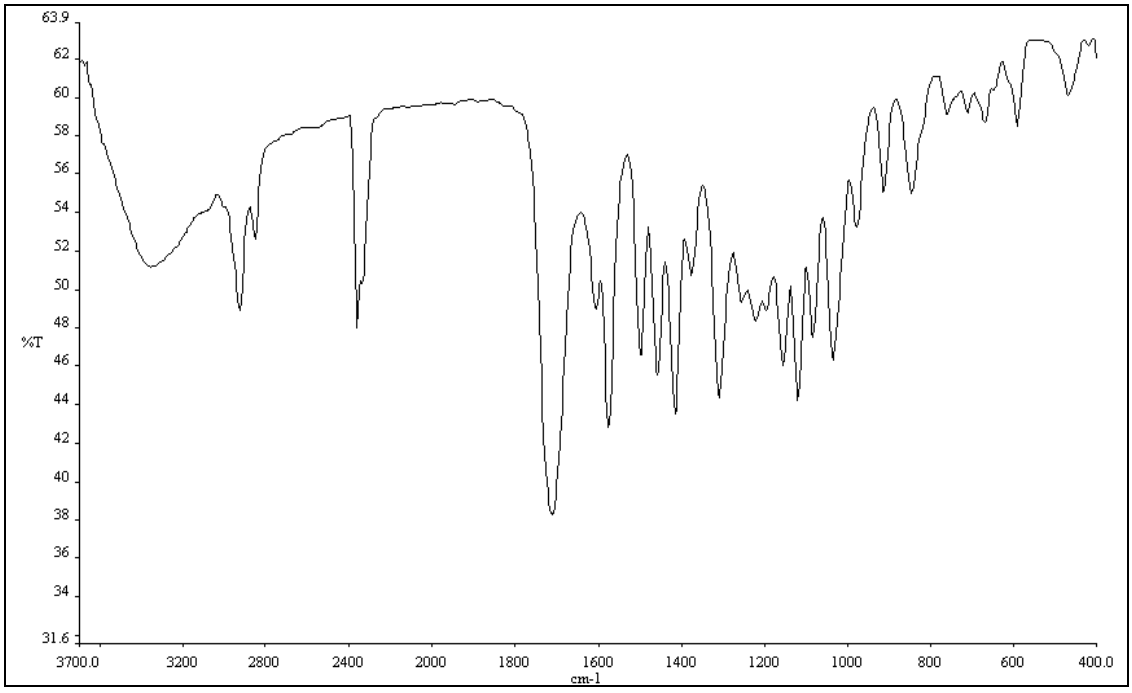


Figure 146 IR (neat) spectrum of compound **PW17**

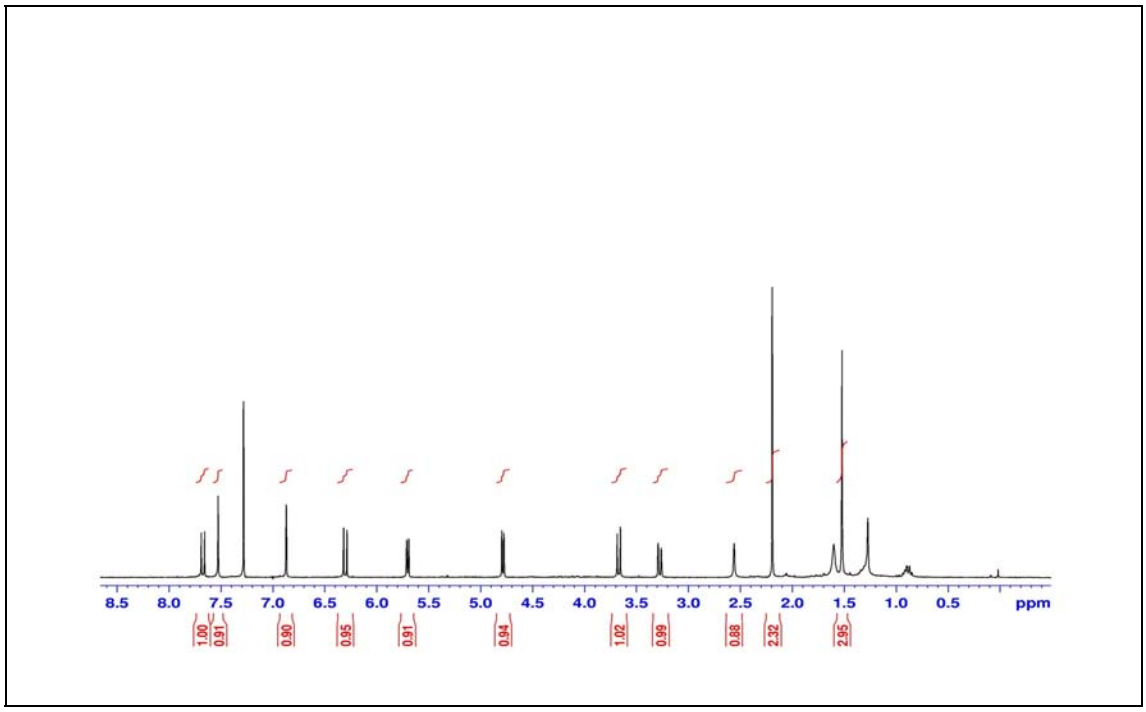


Figure 147 ^{1}H NMR (300 MHz) ($CDCl_3$) of compound **PW17**

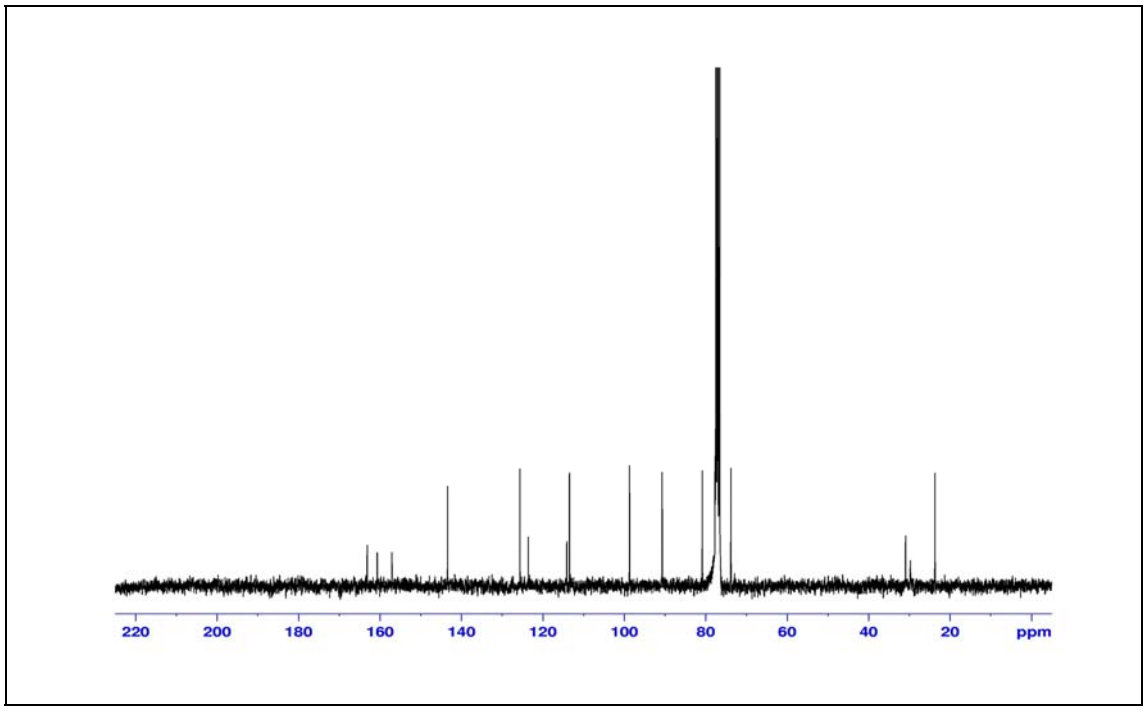


Figure 148 ^{13}C NMR (75 MHz) ($CDCl_3$) of compound **PW17**

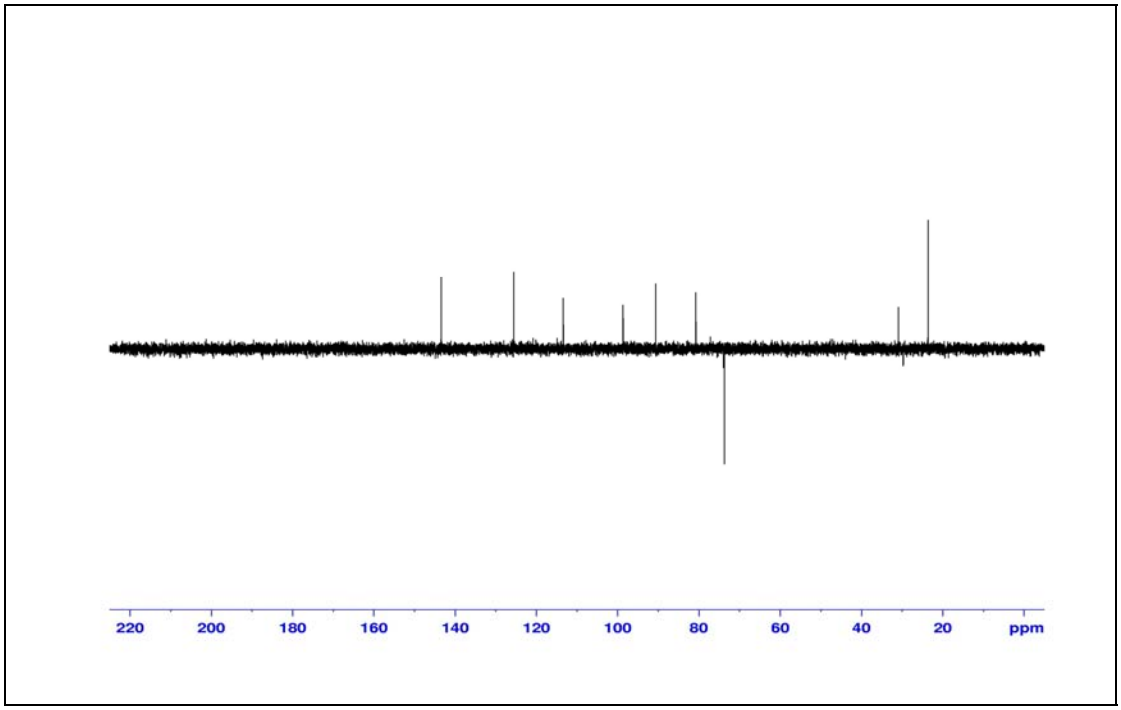


Figure 149 Dept 135° ($CDCl_3$) of compound **PW17**

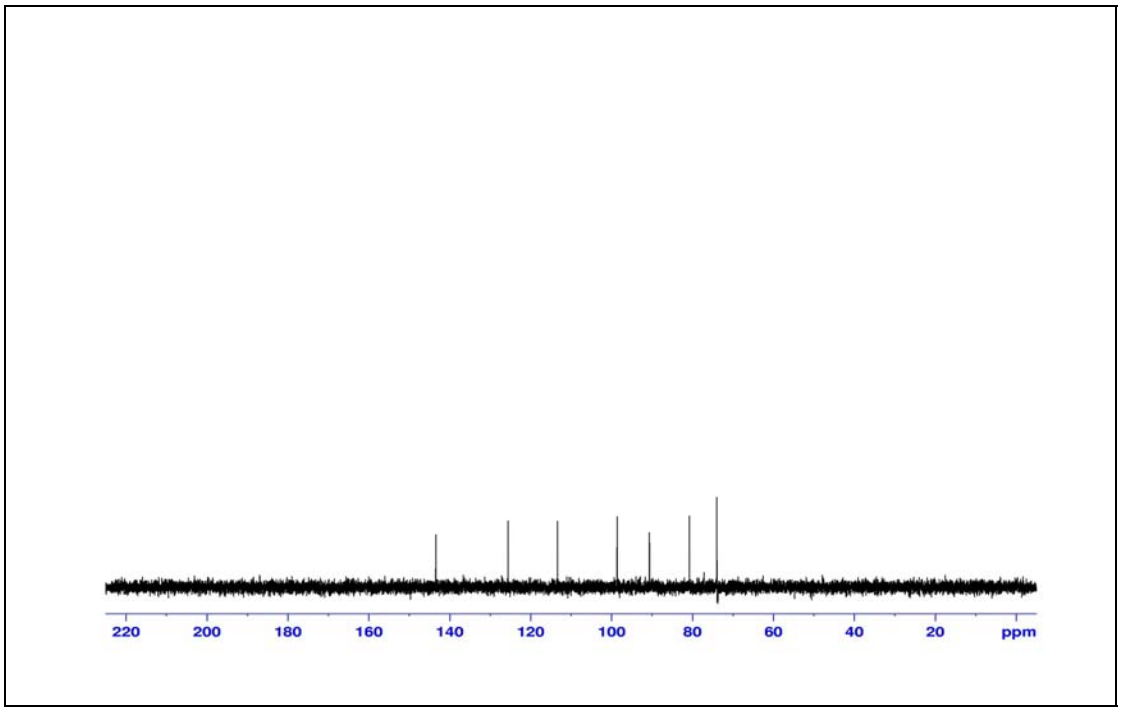


Figure 150 Dept 90° ($CDCl_3$) of compound **PW17**

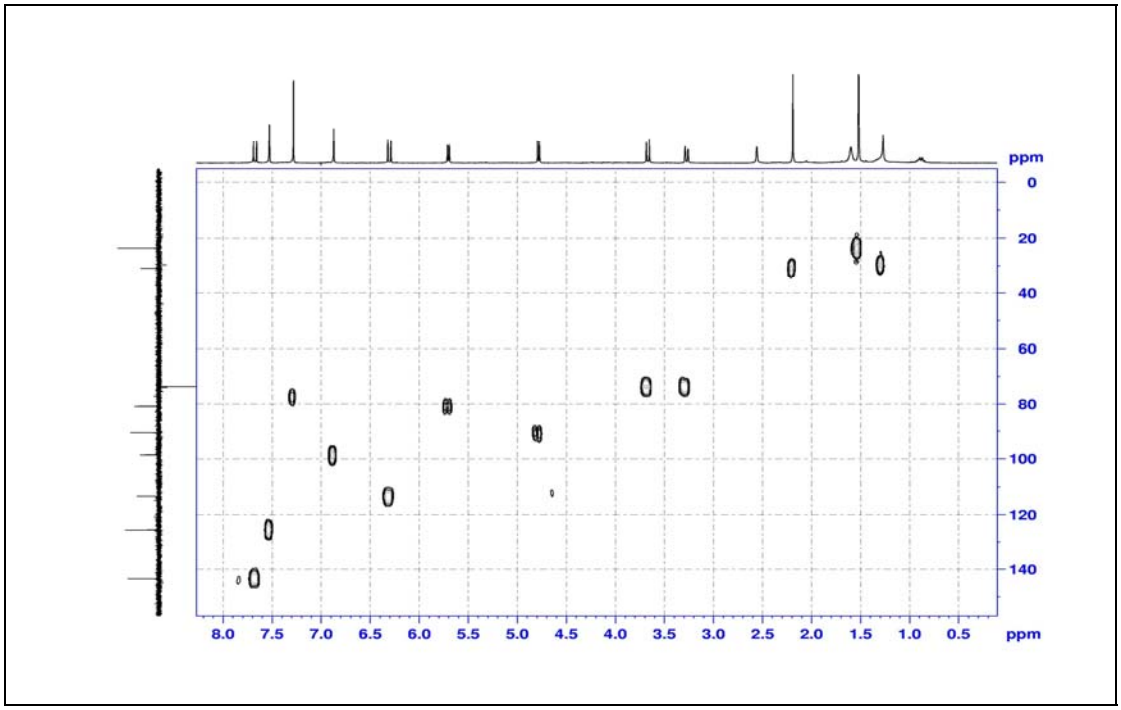


Figure 151 2D HMQC ($CDCl_3$) of compound **PW17**

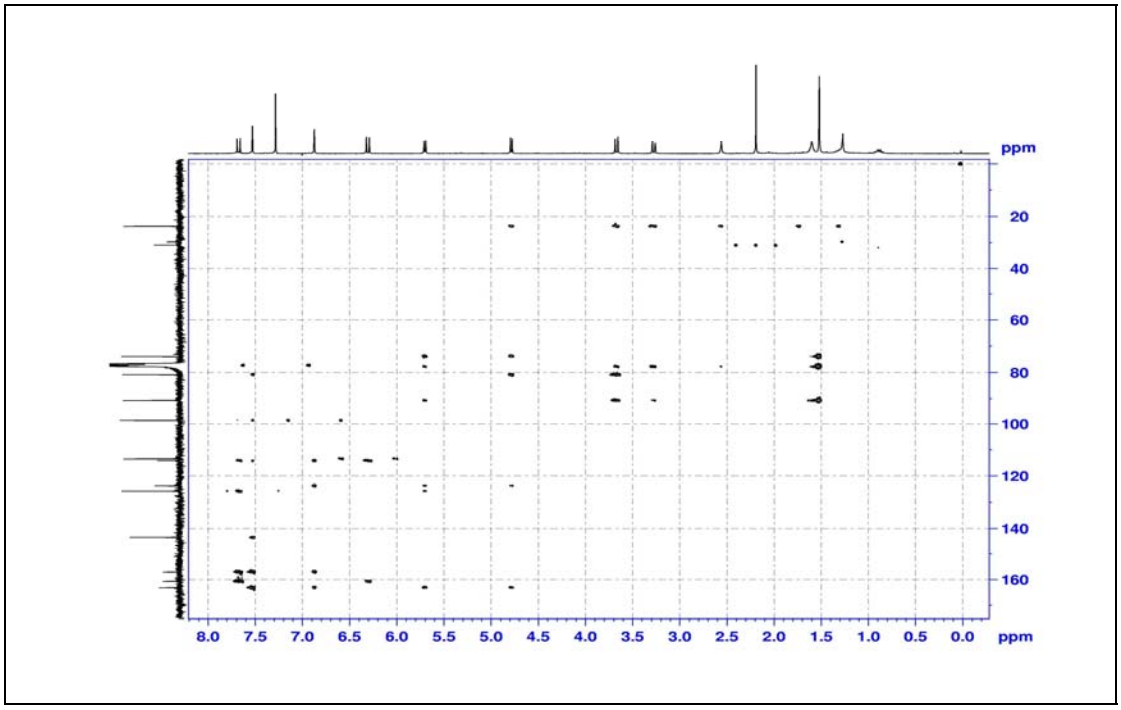


Figure 152 2D HMBC ($CDCl_3$) of compound **PW17**

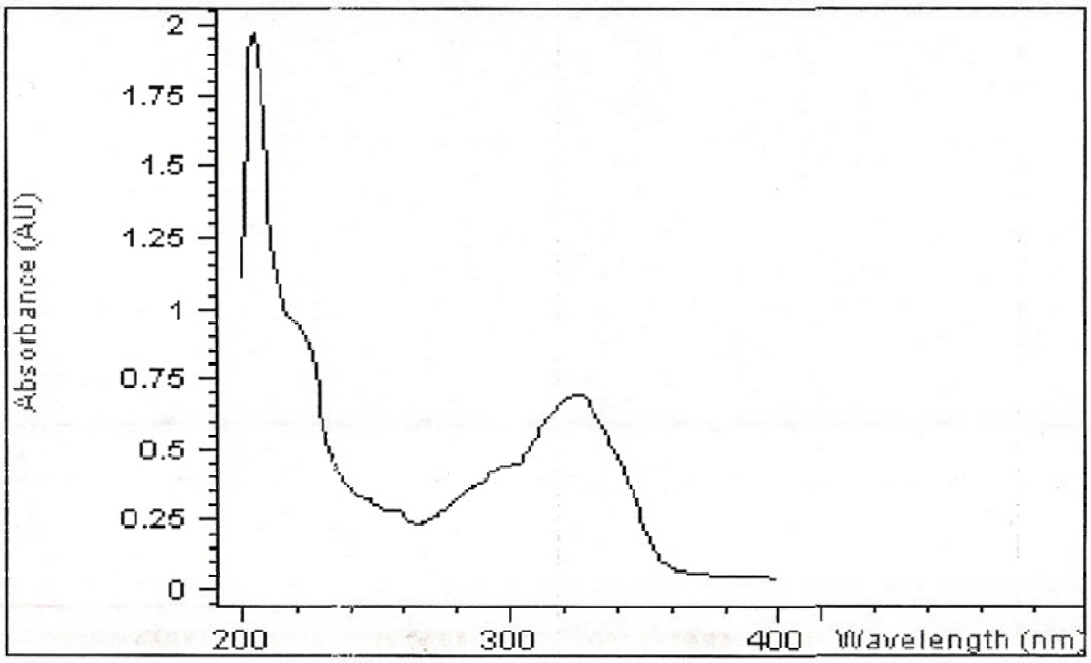


Figure 153 UV (MeOH) spectrum of compound **PW18**

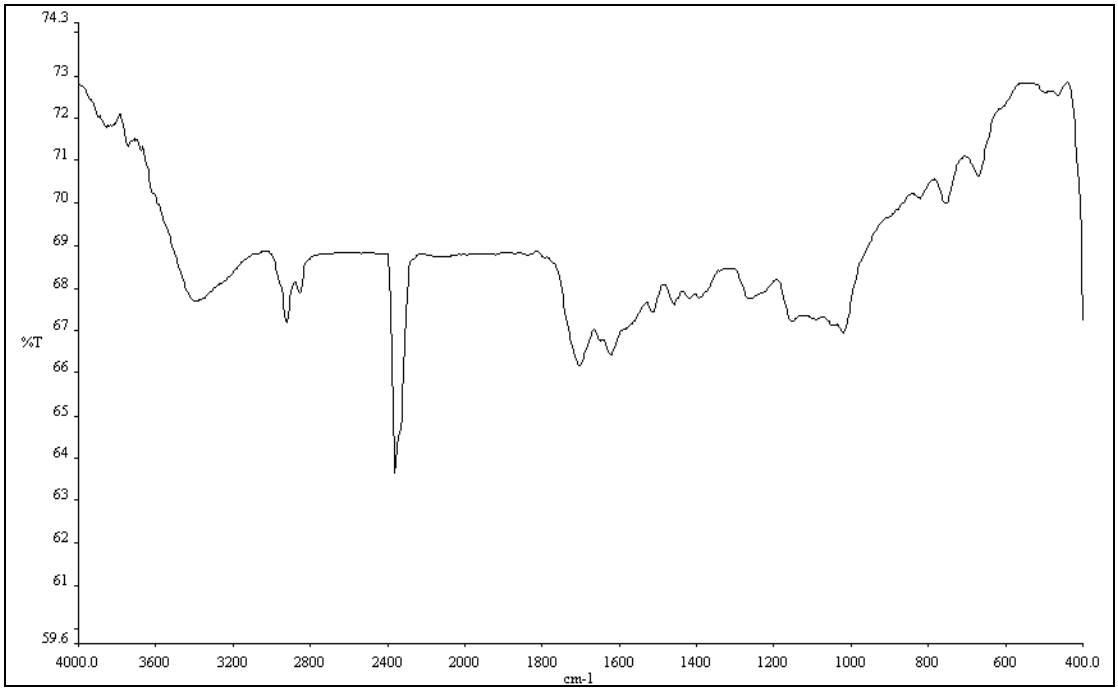


Figure 154 IR (neat) spectrum of compound **PW18**

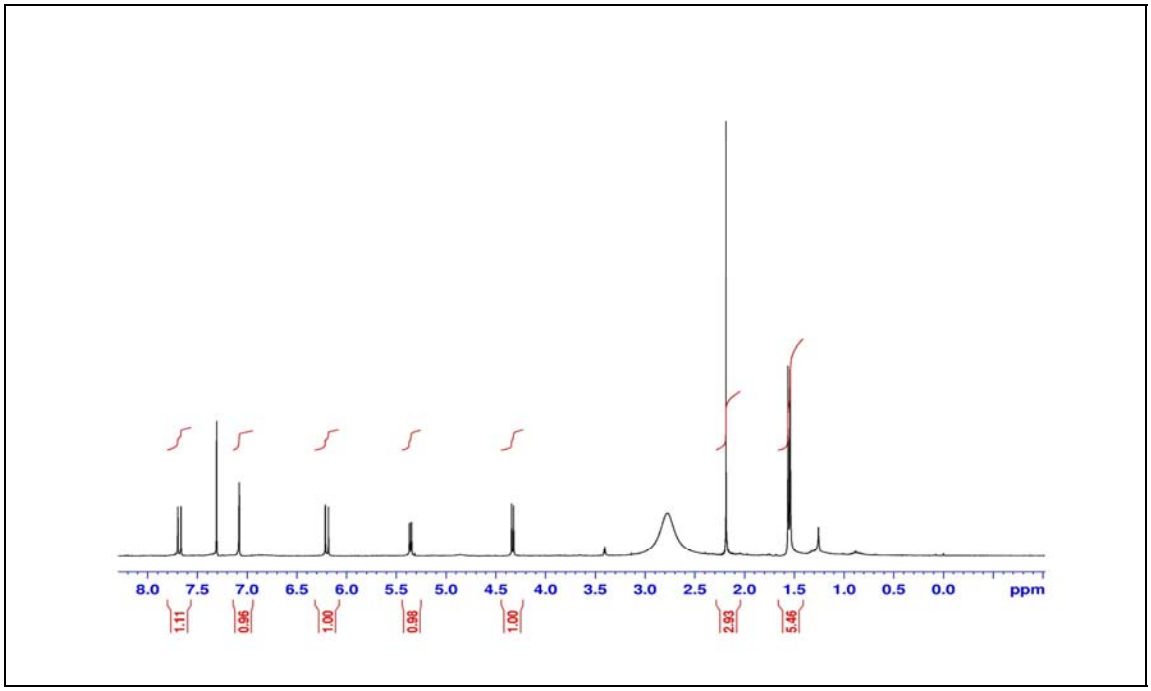


Figure 155 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW18**

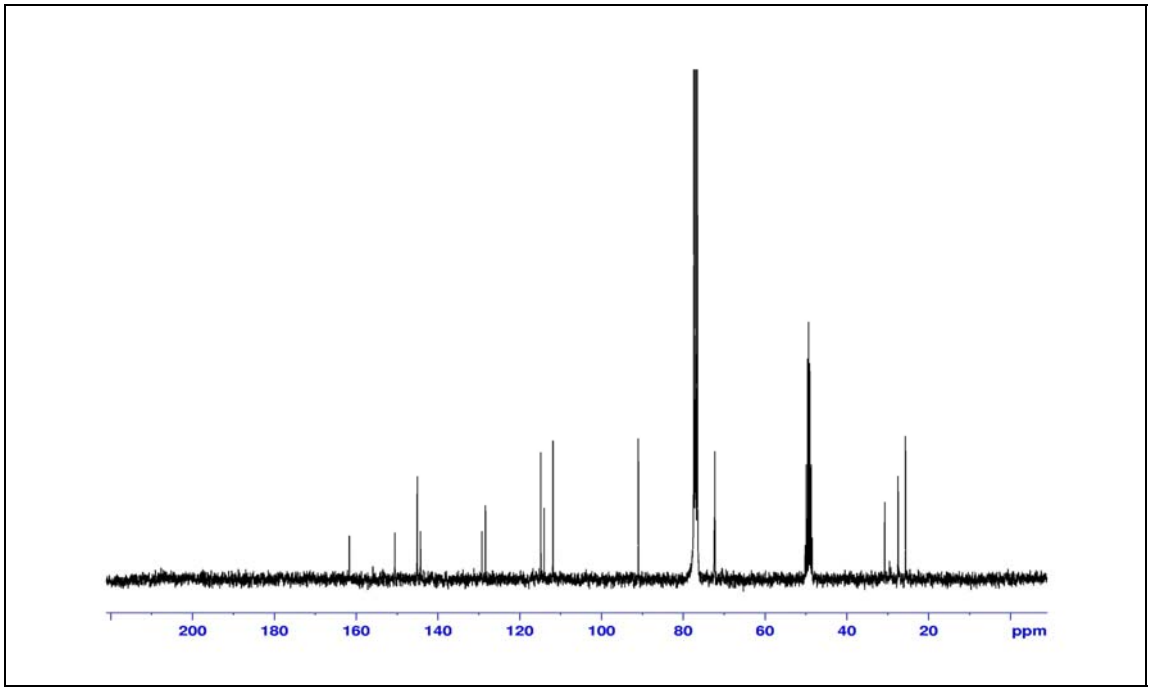


Figure 156 ^{13}C NMR (75 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW18**

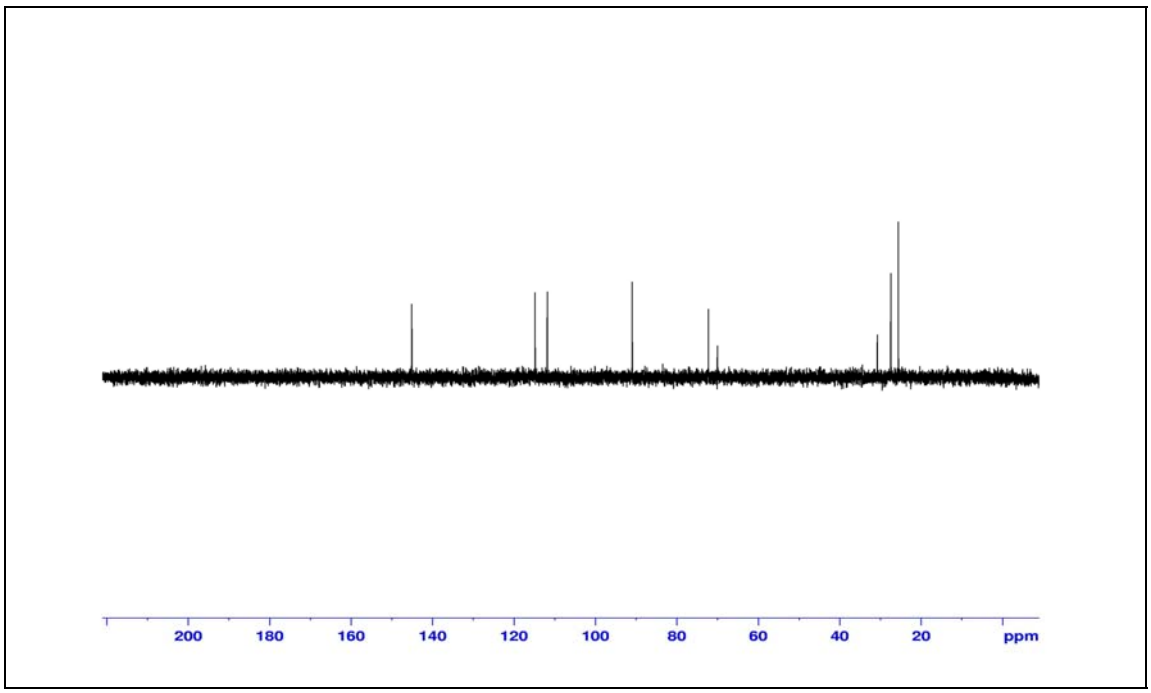


Figure 157 Dept 135° ($CDCl_3$+CD_3OD (1drop)) of compound **PW18**

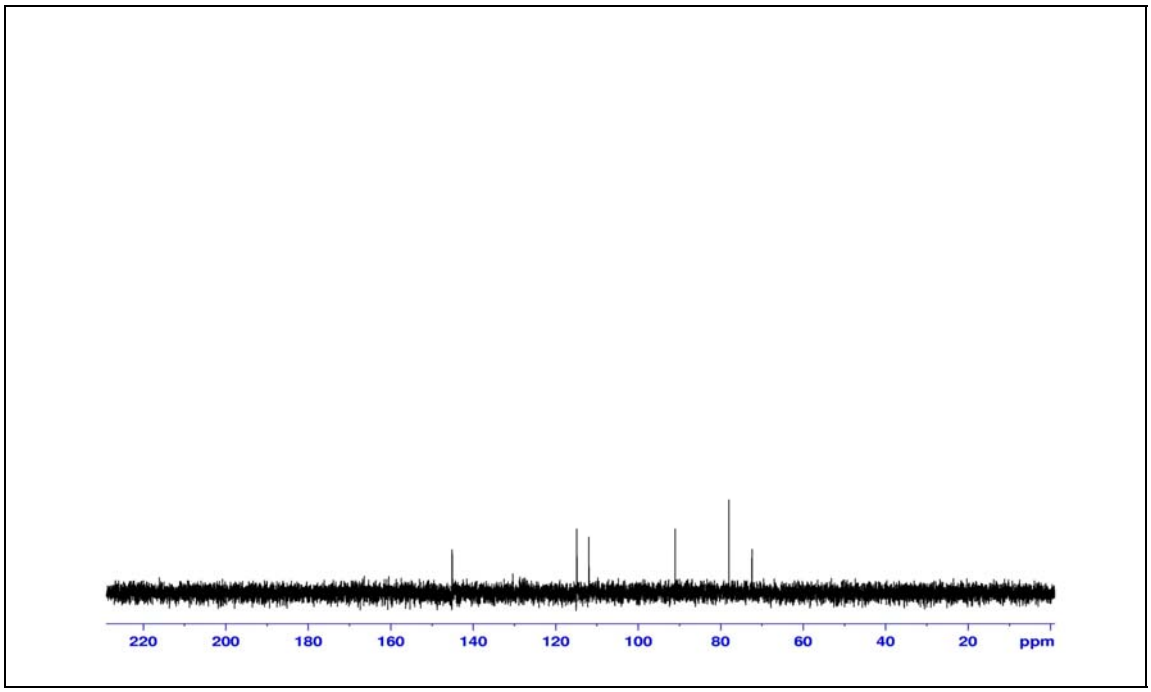


Figure 158 Dept 90° ($CDCl_3$+CD_3OD (1drop)) of compound **PW18**

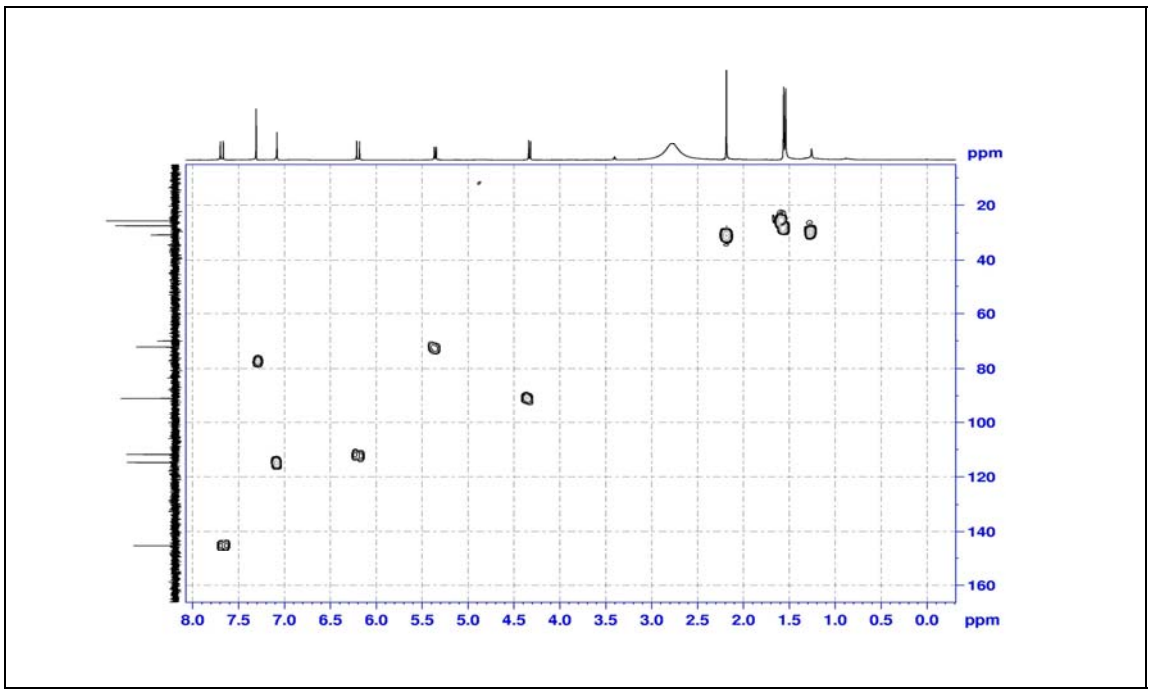


Figure 159 2D HMQC ($CDCl_3$+CD_3OD (1drop)) of compound **PW18**

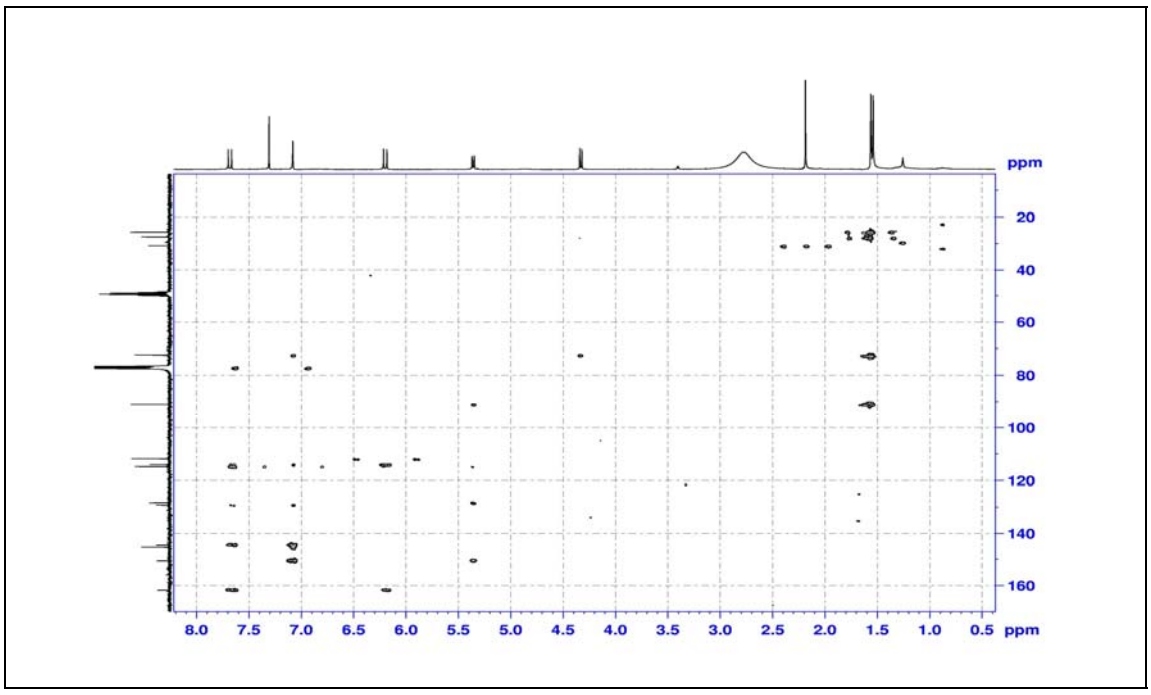


Figure 160 2D HMBC ($CDCl_3$+CD_3OD (1drop)) of compound **PW18**

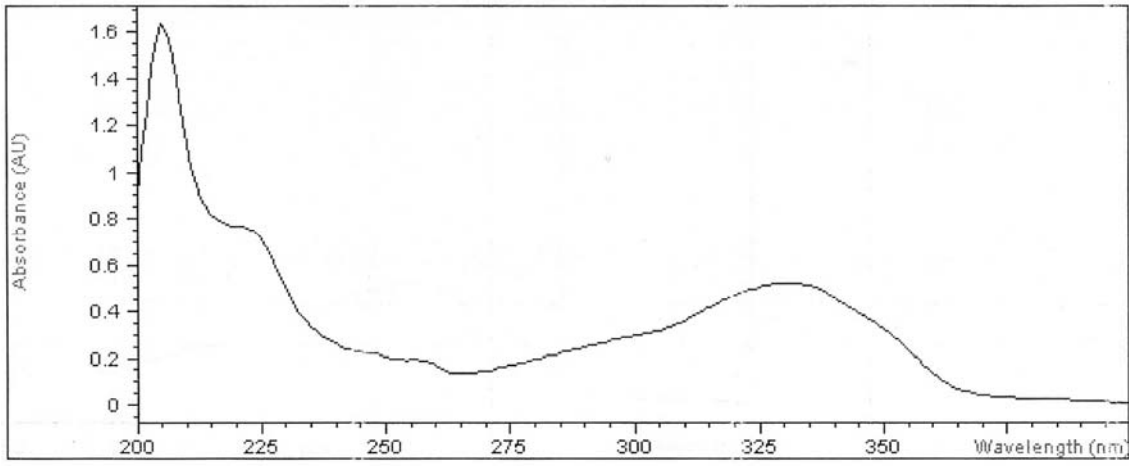


Figure 161 UV (MeOH) spectrum of compound **PW19**

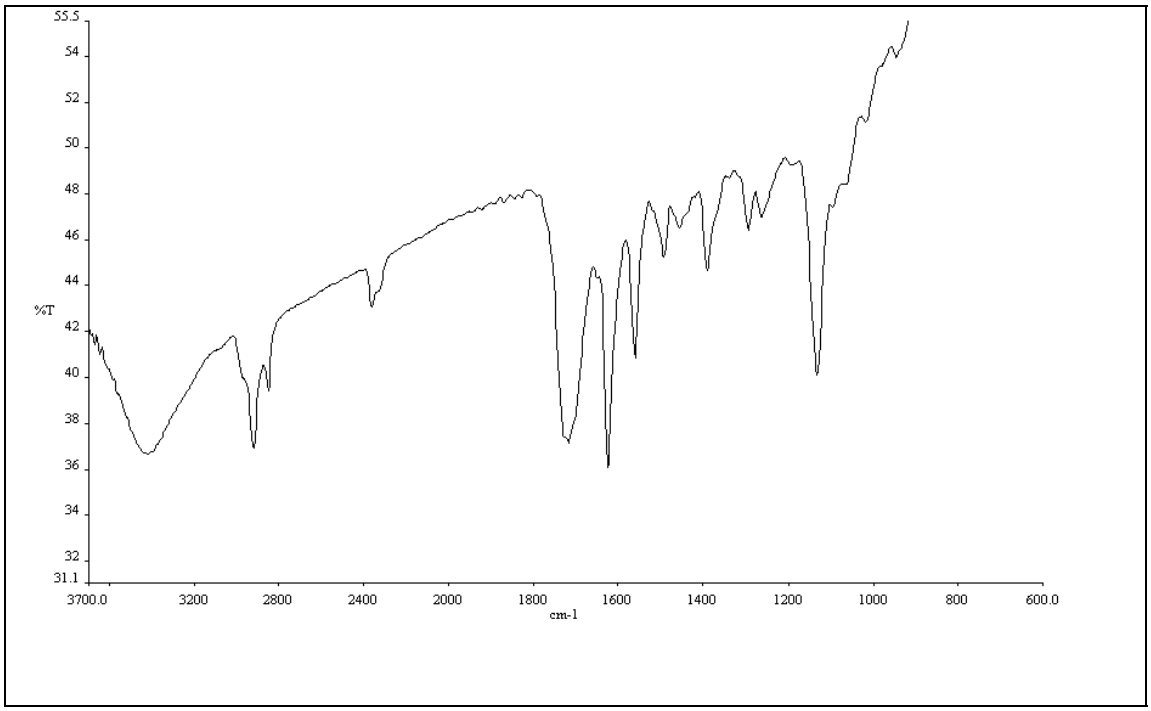


Figure 162 IR (neat) spectrum of compound **PW19**

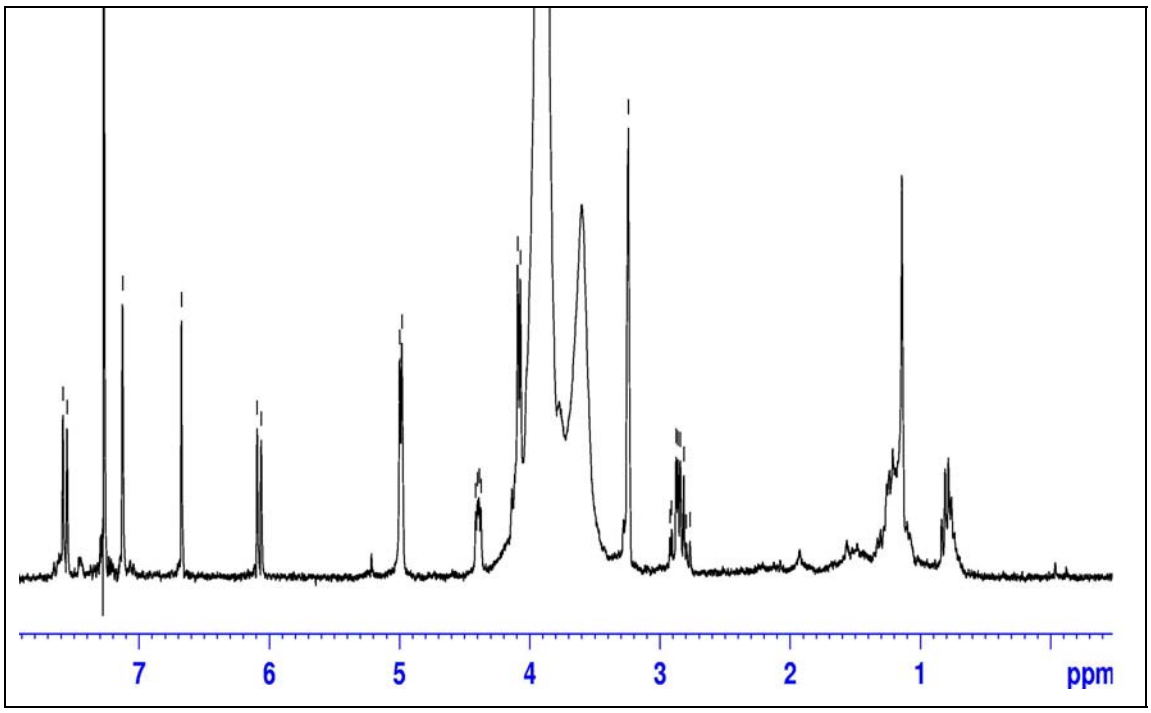


Figure 163 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD (1drop))of compound **PW19**

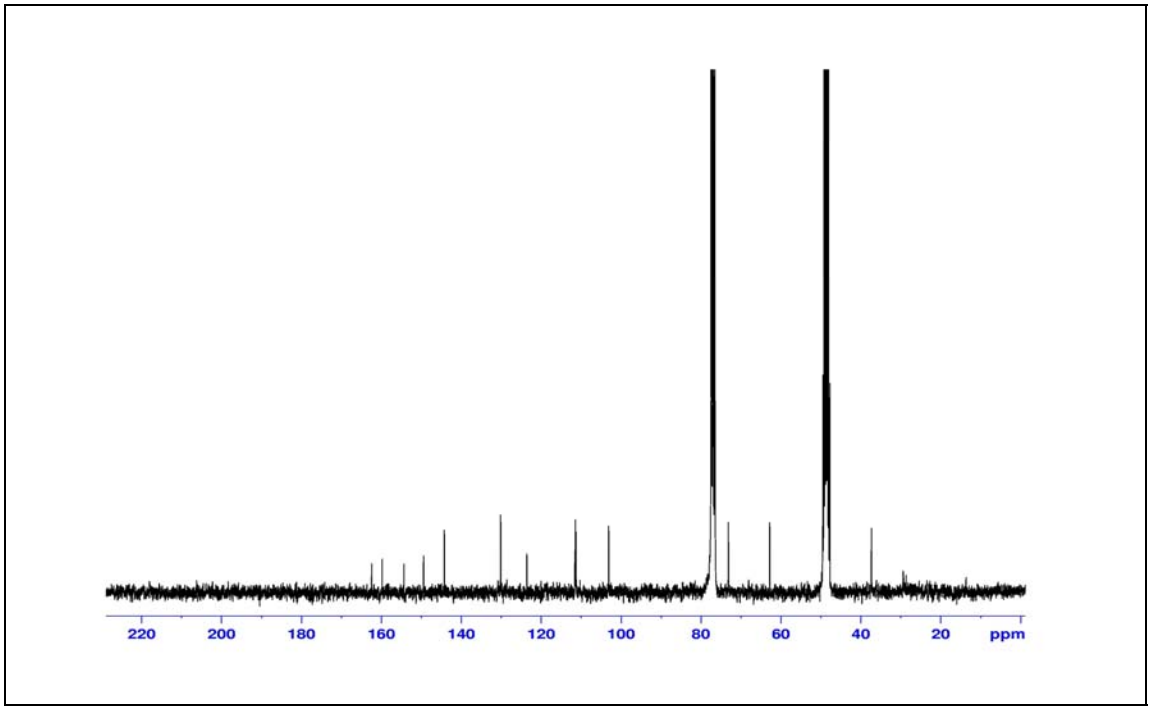


Figure 164 ^{13}C NMR (75 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW19**

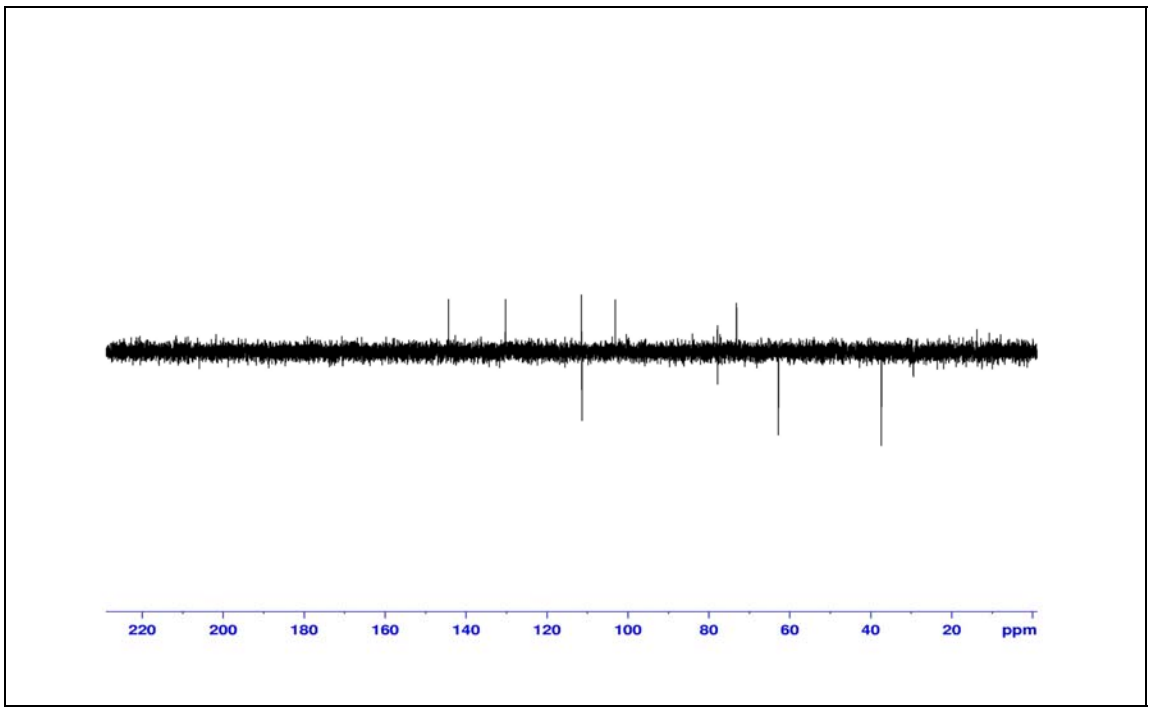


Figure 165 Dept 135° ($CDCl_3$+CD_3OD (1drop)) of compound **PW19**

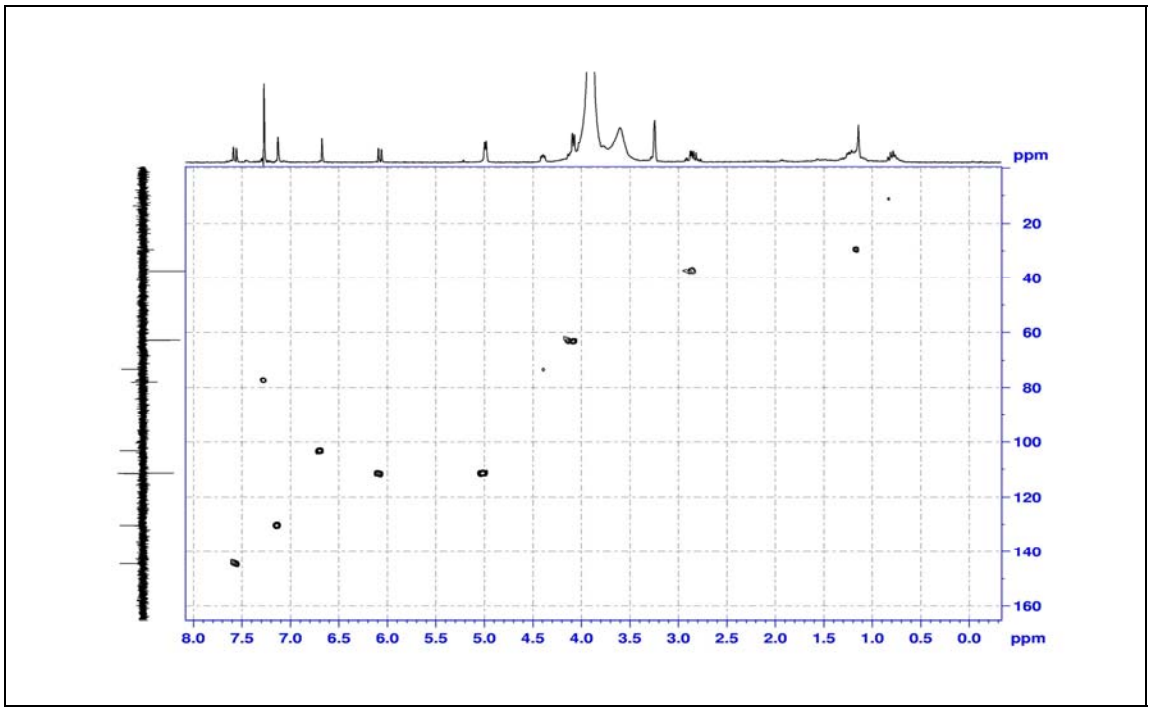


Figure 166 2D HMQC ($CDCl_3$+CD_3OD (1drop)) of compound **PW19**

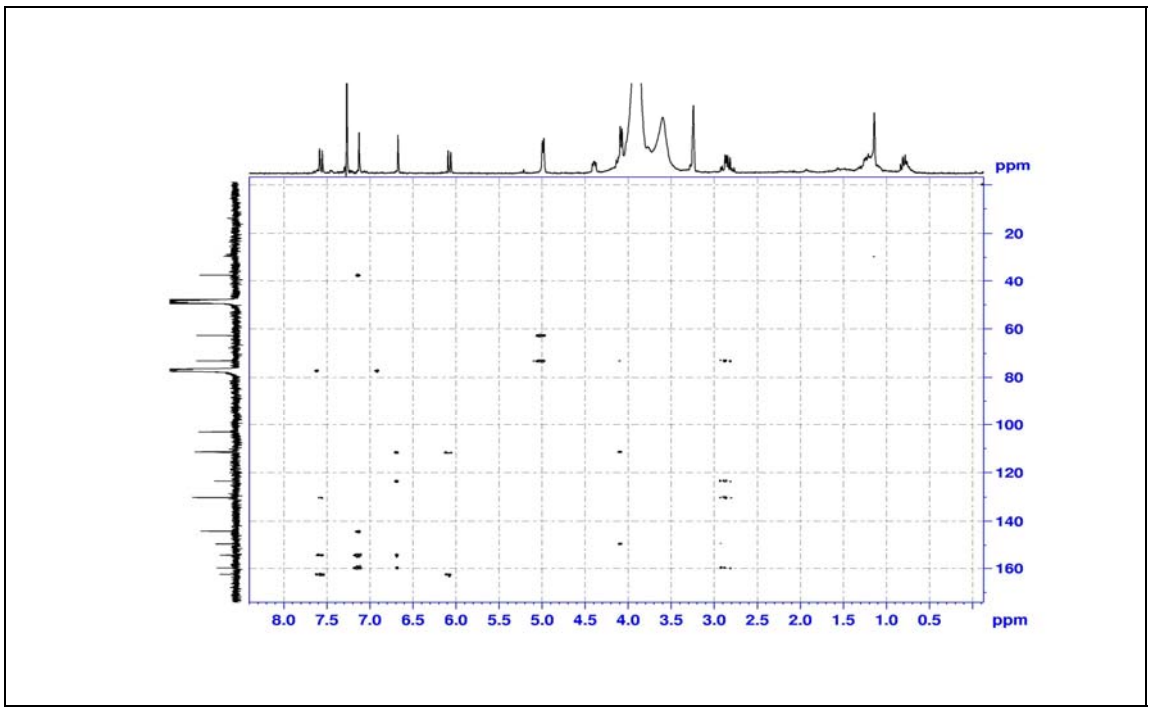


Figure 167 2D HMBC ($CDCl_3$+CD_3OD (1drop)) of compound **PW19**

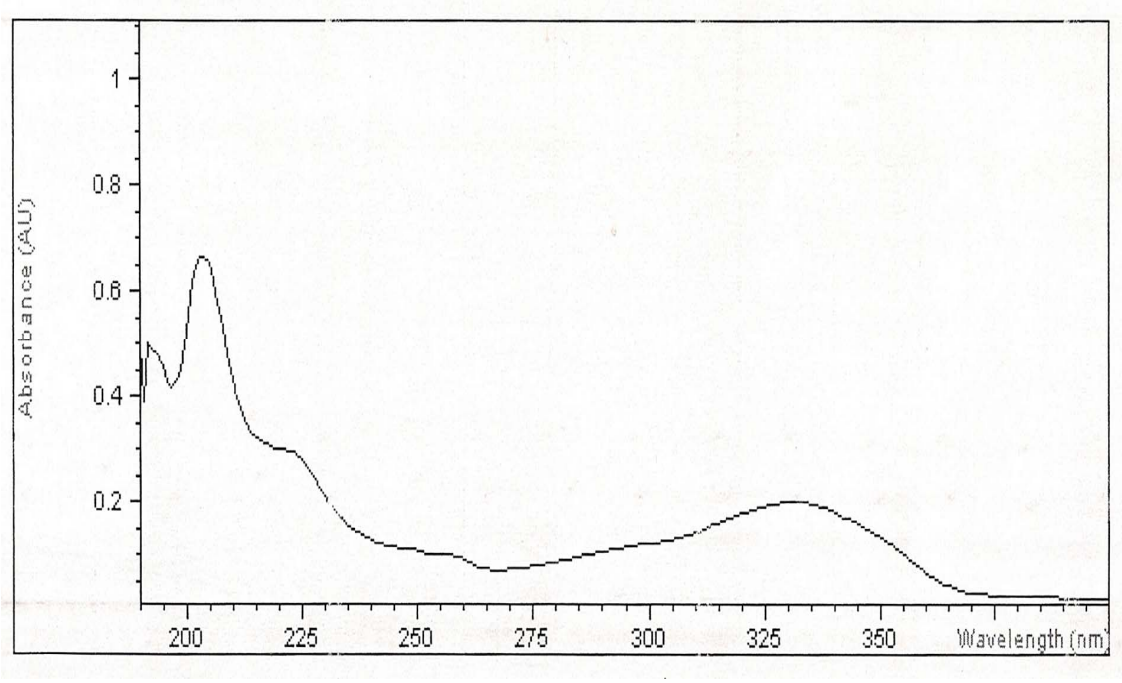


Figure 168 UV (MeOH) spectrum of compound **PW20**

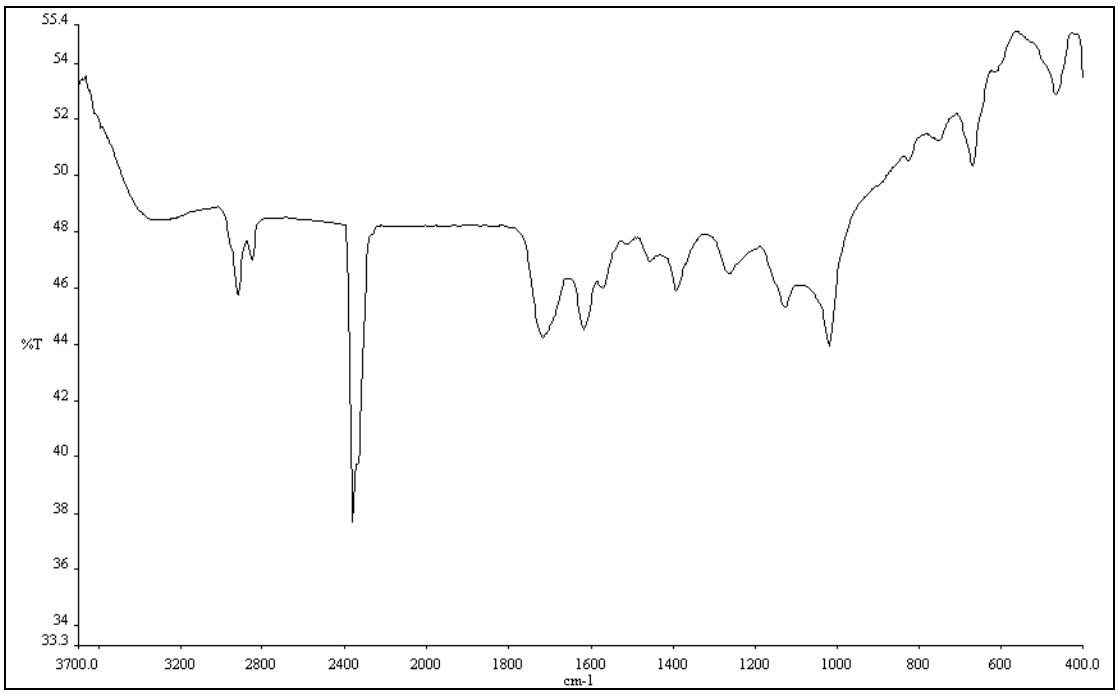


Figure 169 IR (neat) spectrum of compound **PW20**

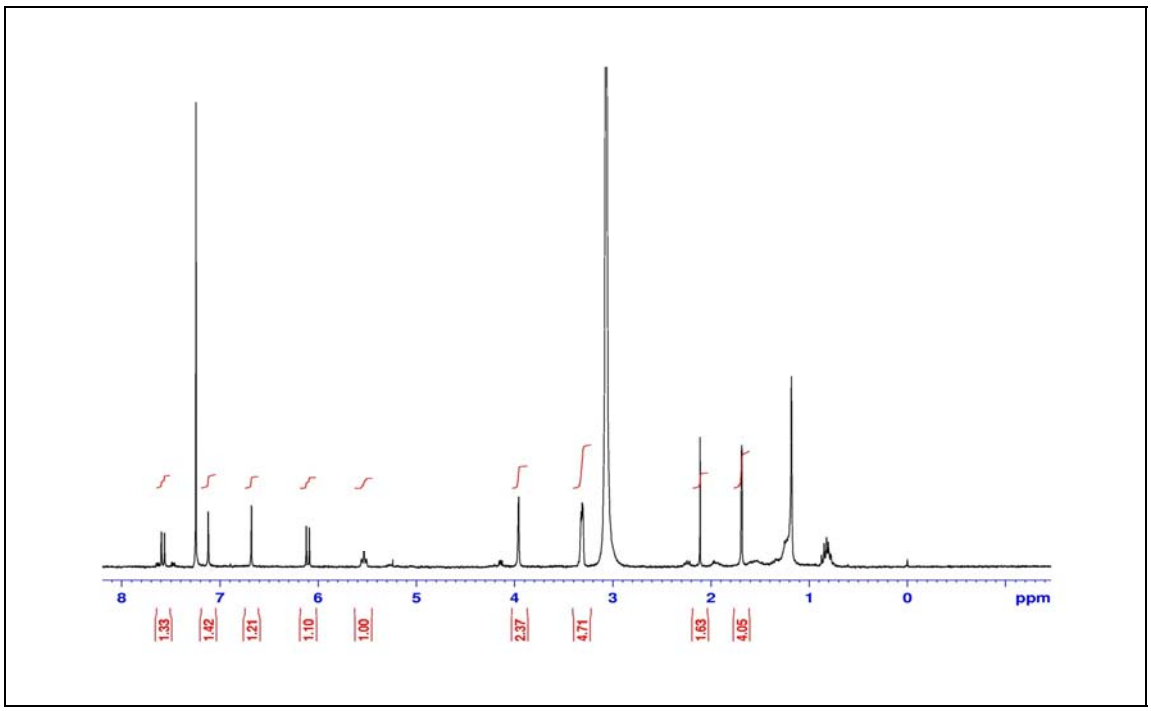


Figure 170 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW20**

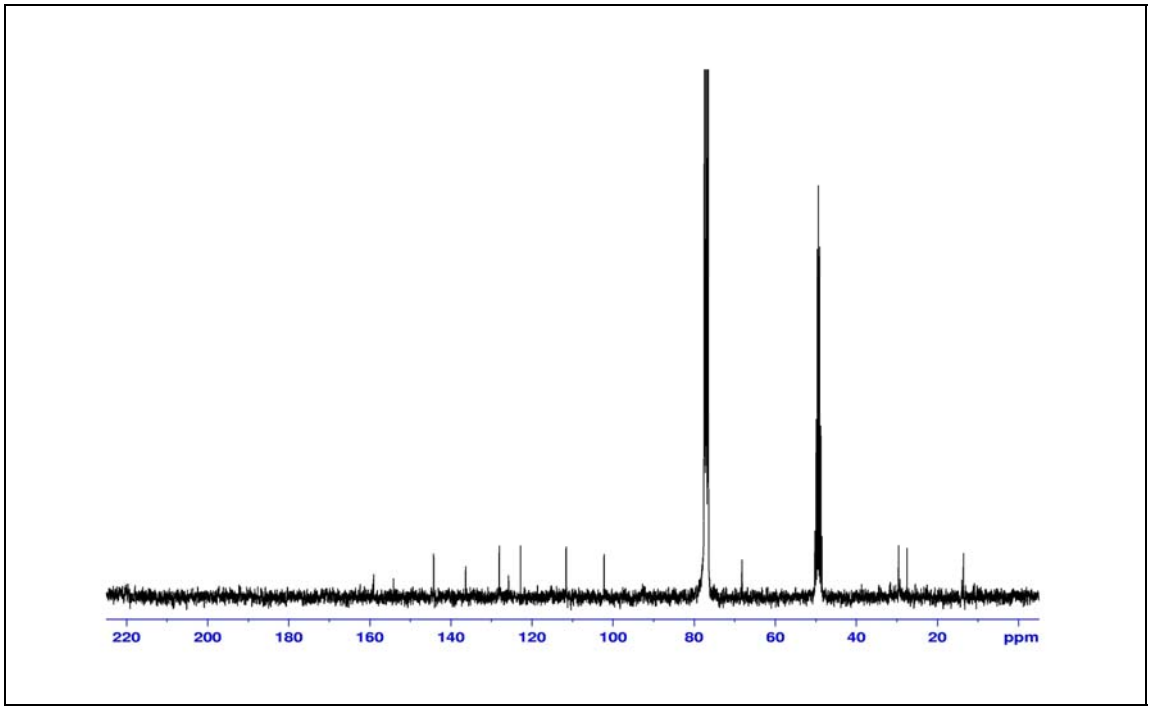


Figure 171 ^{13}C NMR (75 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW20**

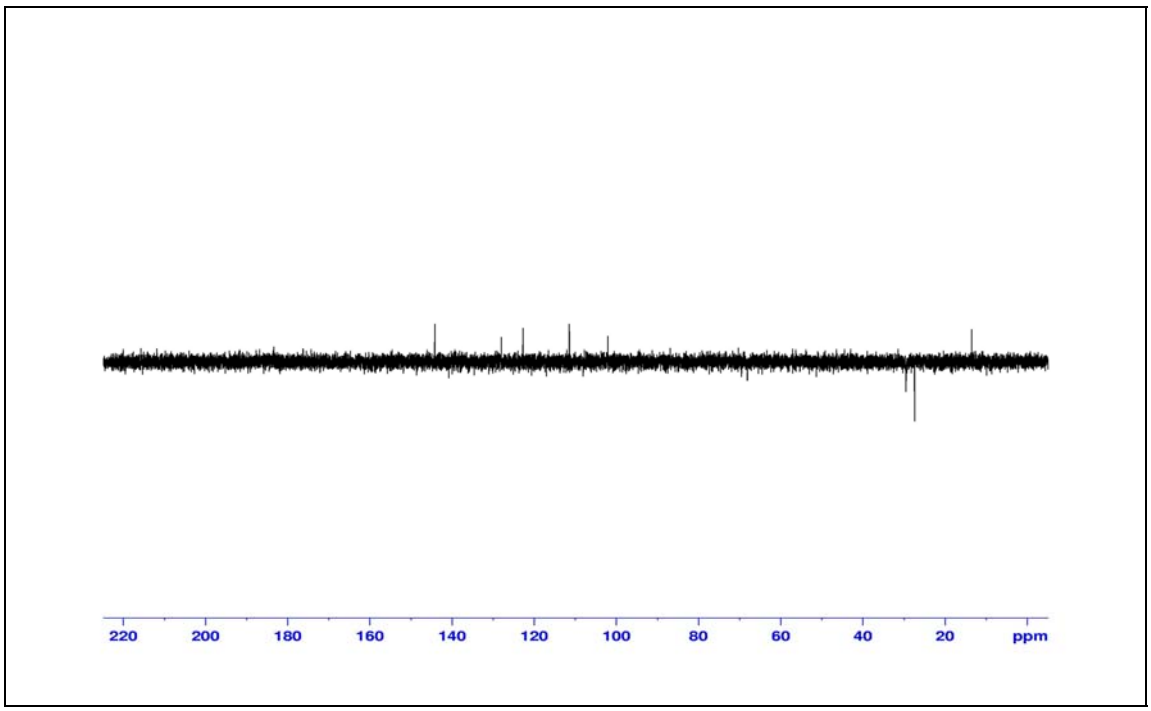


Figure 172 Dept 135° ($CDCl_3$+CD_3OD (1drop)) of compound **PW20**

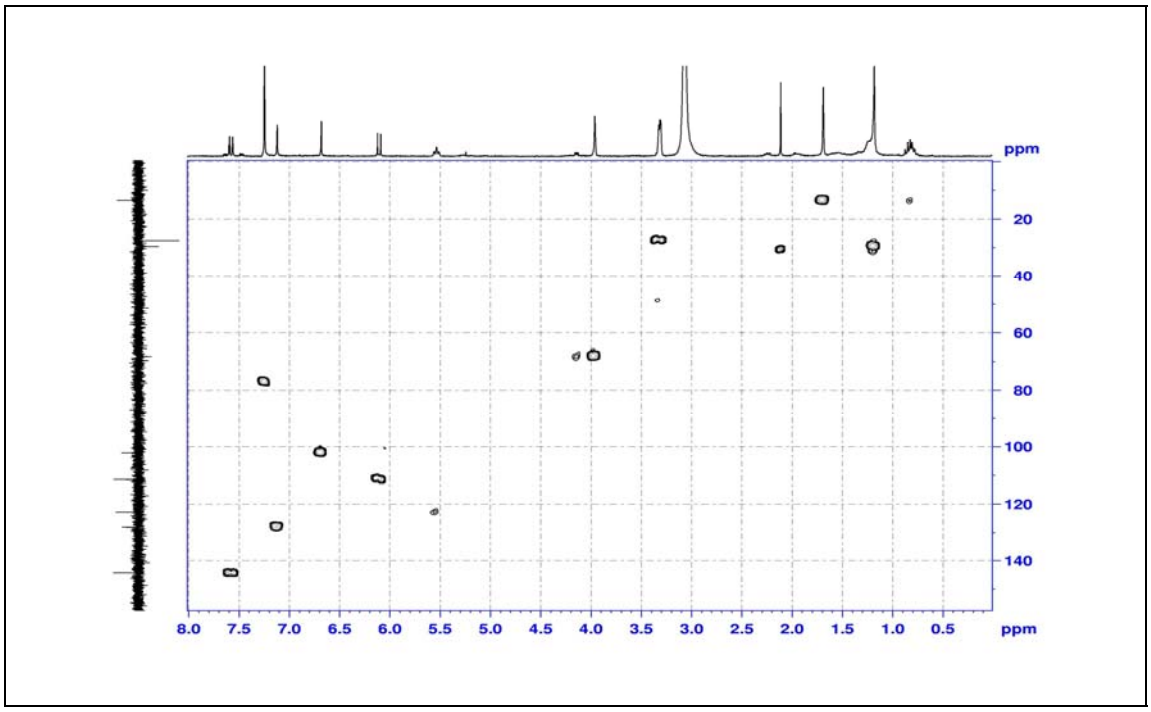


Figure 173 2D HMQC ($CDCl_3$+CD_3OD (1drop)) of compound **PW20**

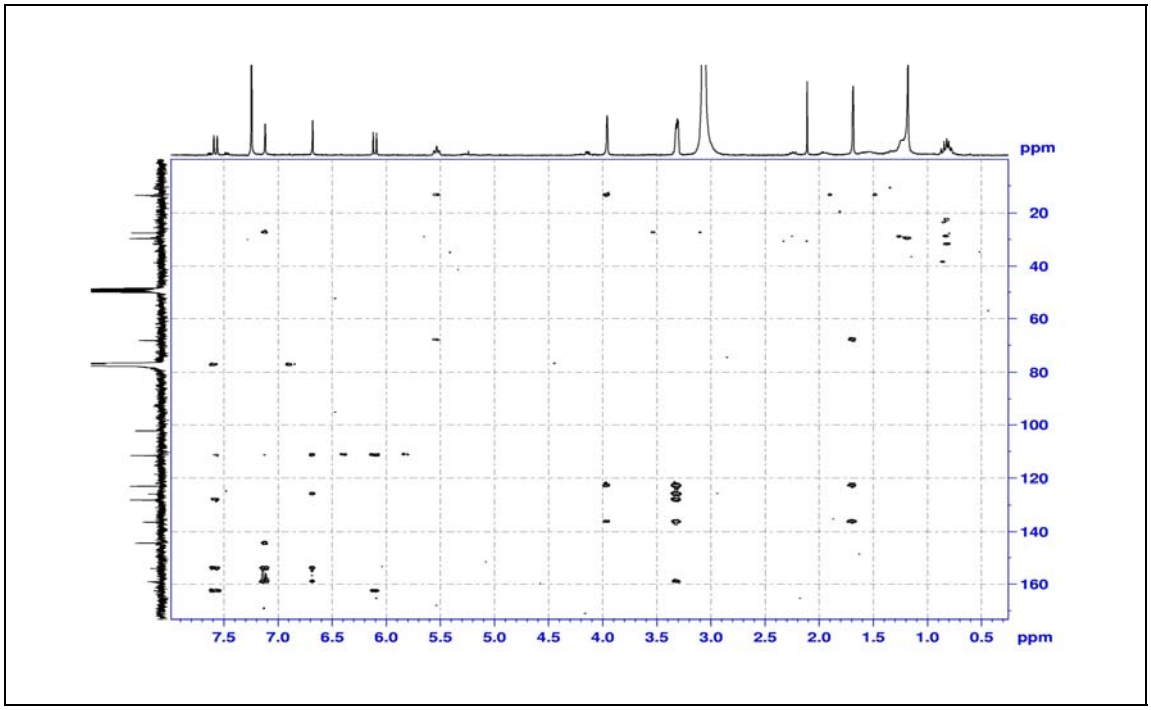


Figure 174 2D HMBC ($CDCl_3$+CD_3OD (1drop))of compound **PW20**

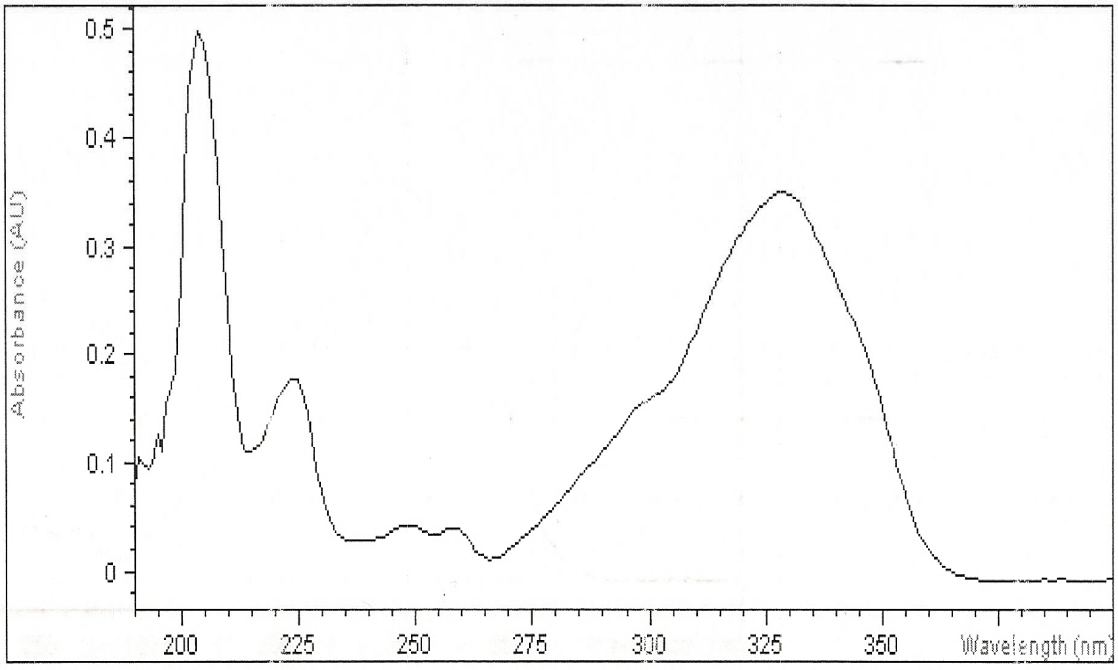


Figure 175 UV (MeOH) spectrum of compound **PW21**

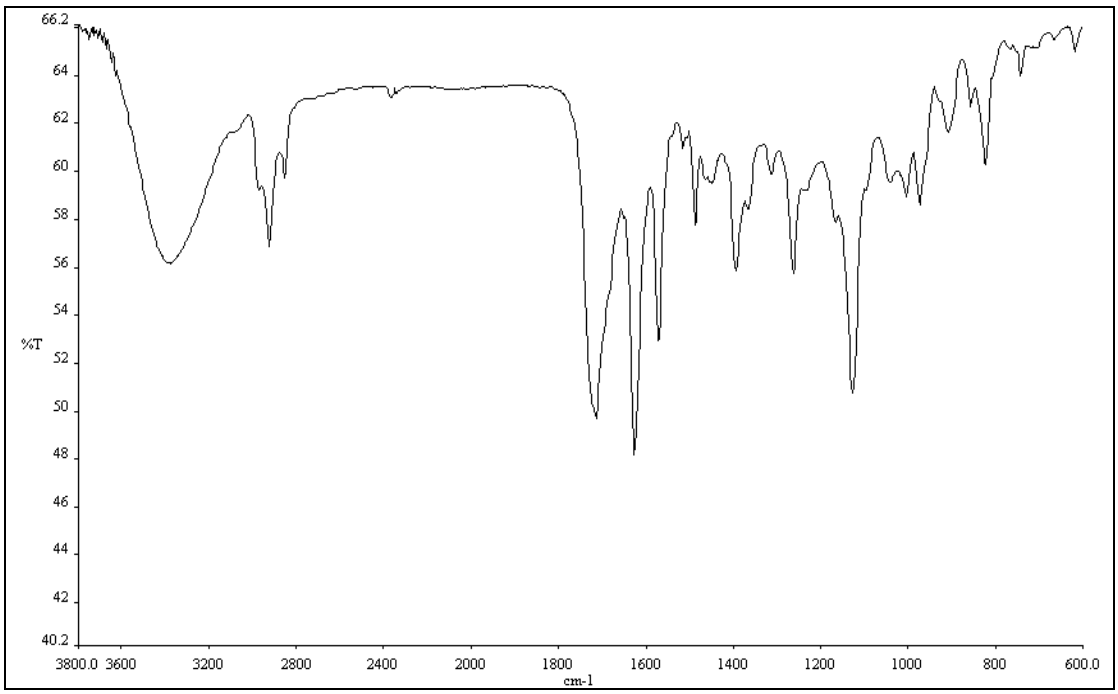


Figure 176 IR (neat) spectrum of compound **PW21**

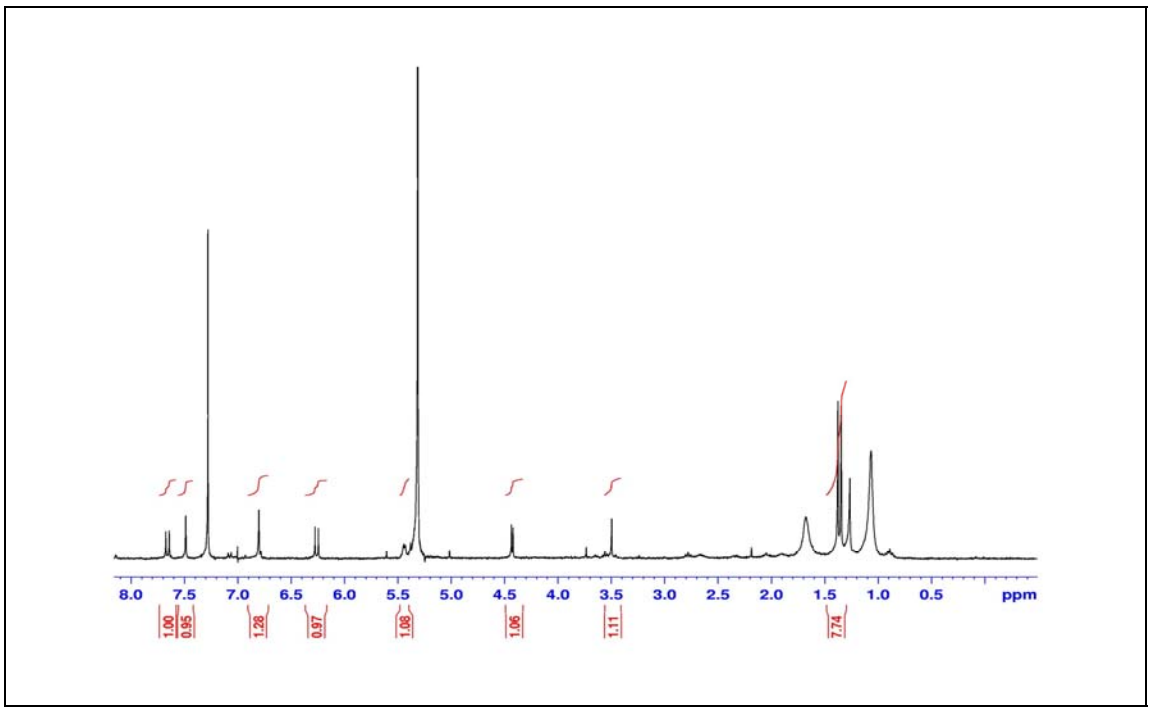


Figure 177 ^{1}H NMR (300 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW21**

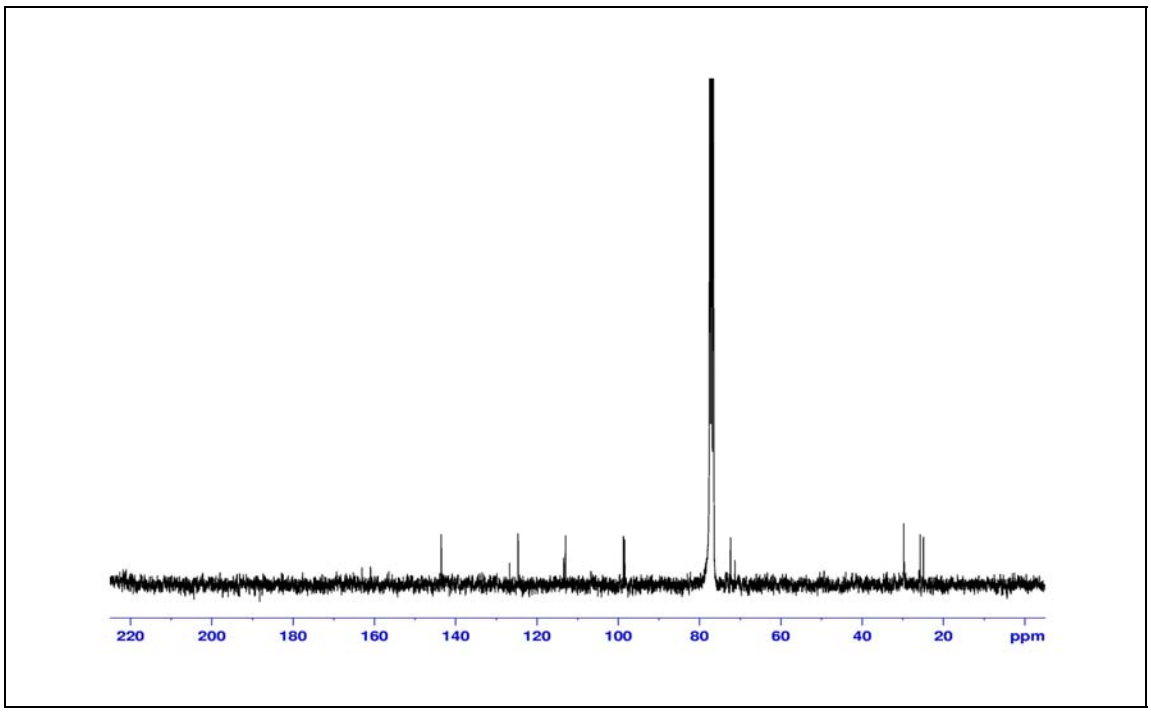


Figure 178 ^{13}C NMR (75 MHz) ($CDCl_3$+CD_3OD (1drop)) of compound **PW21**

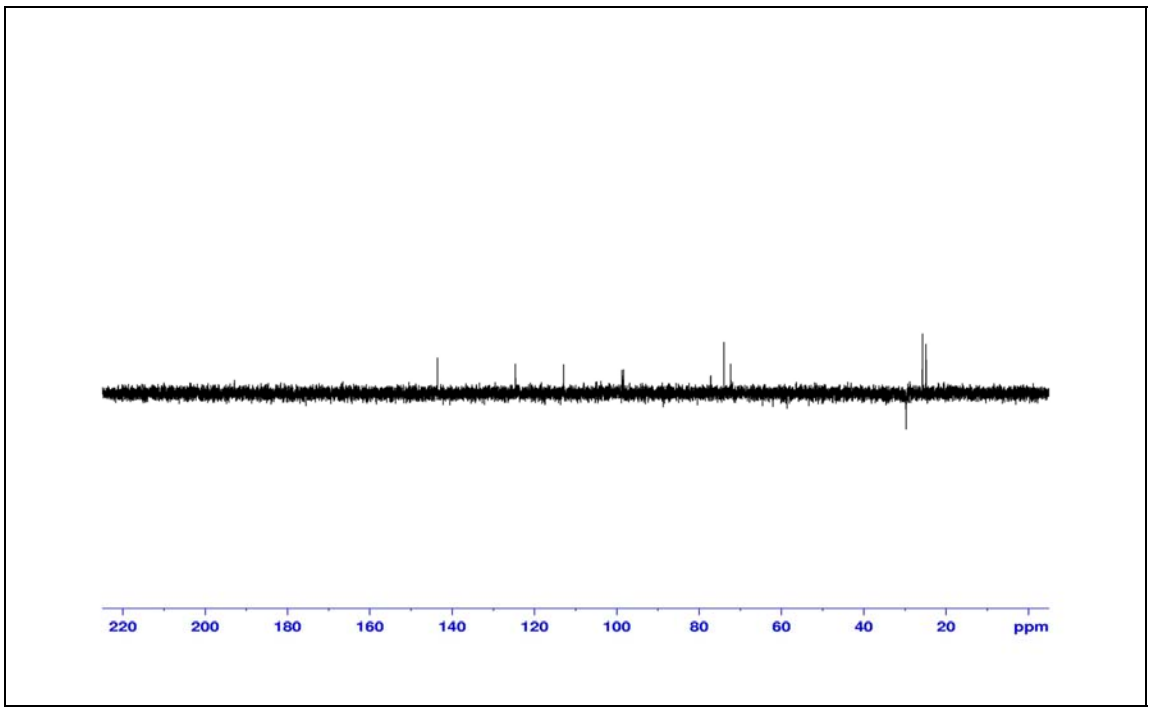


Figure 179 Dept 135° ($CDCl_3$+CD_3OD (1drop)) of compound **PW21**

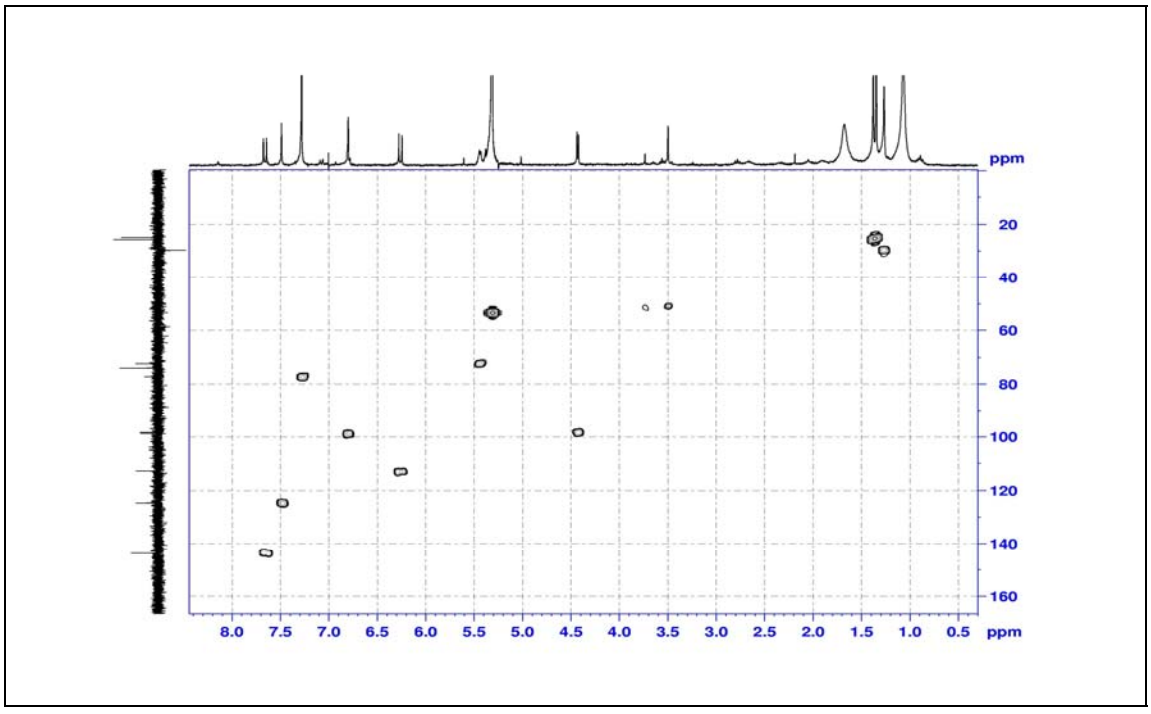


Figure180 2D HMQC ($CDCl_3$+CD_3OD (1drop)) of compound **PW21**

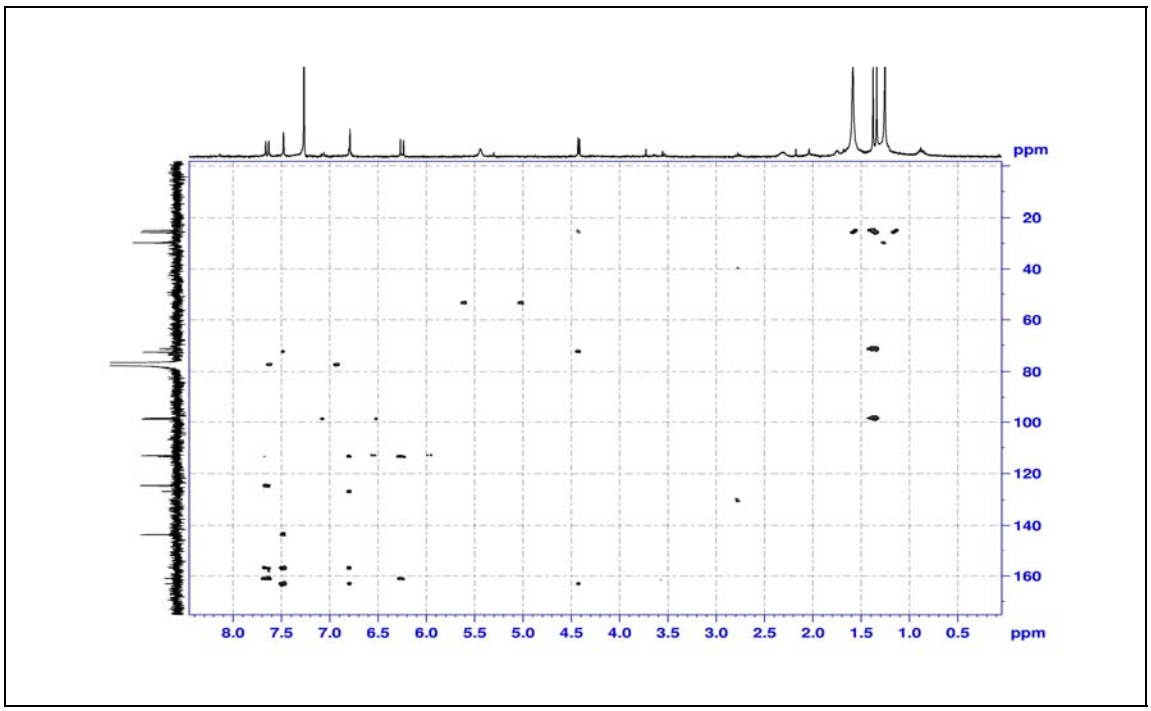


Figure 181 2D HMBC ($CDCl_3$+CD_3OD (1drop)) of compound **PW21**

VITAE

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Educational Attainment

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Scholarship Awards during Enrolment

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

List of Publication and Proceeding

1. Paosiyah Weaaryee, Pongsak Puangphet and Suda Chakthong. "Furanocoumarins and Valencic acid from Unripe Fruits of *Aegle marmelos*". 4th BUU Grad Research Conference, Burapha University, Chon Buri, Thailand, 13 March 2009. (Poster presentation)