รายงานวิจัยฉบับสมบูรณ์

โครงการ

ปฏิกิริยาโอ-อัลลิเลชันภายใต้สภาวะปฏิกิริยาที่ไม่รุนแรงและทำได้ง่ายเพื่อสังเคราะห์มอนอเมอร์ต้านเชื้อรา

(Mild and Facile O-Allylation for the Synthesis of Antifungal Monomers)

โดย นายสรวง สมานหมู่ และคณะ

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สัญญาเลขที่ TRG5380029

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คณะผู้วิจัย

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นักวิจัยศูนย์พันธุวิศวกรรมและเทคโนโลยีชีวภาพแห่งชาติ

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

และศูนย์พันธุวิศวกรรมและเทคโนโลยีชีวภาพแห่งชาติ

บทคัดย่อ

ปฏิกิริยาโอ-อัลลิเลชันถูกใช้เพื่อเตรียมสารอัลลิลแอลกอฮอล์ ซึ่งเป็นปฏิกิริยาระหว่างสารตั้งต้นแอลกอฮอล์หรือเอไมด์กับอัลลิลโบรไมด์ สภาวะที่เหมาะสมที่สุดในการเตรียมอัลลิลแอลกอฮอล์และอัลลิลเอไมด์คือสภาวะที่ใช้เบส DBU ในการทำปฏิกิริยาเพราะเกิดสารผลิตภัณฑ์ได้ดีที่สุด สภาวะของปฏิกิริยาดังกล่าวสามารถใช้เตรียม อัลลิลแอลกอฮอล์จากแอลกอฮอล์ทั้งชนิดปฐมภูมิ ทุติยภูมิ และตติยภูมิ เนื่องจากปฏิกิริยาดังกล่าวมีสภาวะที่ไม่รุนแรงและไม่ใช้ความร้อนในปฏิกิริยา สภาวะดังกล่าวจึงถูกใช้เพื่อเตรียมสาร อัลลิลนิวคลีโอไซด์

คำสำคัญ: โอ-อัลลิเลชัน, อัลลิลแอลกอฮอล์, อัลลิลเอไมด์, เบส DBU

ABSTRACT

O-allylation was achieved from the reaction between corresponding amides/alcohols and allyl bromide. The reaction condition was optimized and found that DBU was the best reaction base catalyzing the highest allyl transfer. The utility of this method has been demonstrated in the allylation of primary, secondary and tertiary alcohols. Since the reaction condition was mild and required no heat, the condition was employed for the preparation of allylated nucleoside.

Keywords: *O*-allylation**,** allyl bromide**,** DBU

ACKNOWLEDGEMENT

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

s	=	singlet
d	=	doublet
t	=	triplet
m	=	multiplet
dd	=	doublet of doublets
δ	=	chemical shift
J	=	coupling constant
CC	=	column chromatography
TLC	=	thin layer chromatography
^{1}H-NMR	=	proton nuclear magnetic resonance Spectroscopy
^{13}C-NMR	=	carbon nuclear magnetic resonance spectroscopy
Hz	=	Hertz
g	=	gram
mg	=	milligram
R_f	=	retention factor, in TLC ratio of movement of the band to the front of the solvent

CHAPTER 1

INTRODUCTION

1.1 History and significance of problem

In biochemical process, H_2O_2 plays significant roles in various biochemical pathways ranging from metabolic processes to self-defense mechanism. H_2O_2 has shown the correlation to the healing process since the cell damage causes the production of H_2O_2 which provokes the production of white blood cell for the healing. It is found that for the H_2O_2 produced gene when it is mutated, no white blood cell performs the healing function at the cell damage site. H_2O_2 has also linked to patient asthma. This disease is the result from the accumulation of higher levels of H_2O_2 in their lungs. This clearly indicates that the patient with asthma has inappropriate levels of white blood cells in their lungs.

In the present time, only a few chemosensors for H_2O_2 based on allylic substrate (Figure 1.1) is reported. Therefore, this project is aim to employ an allylic substrate as a chemosensor for H_2O_2 via the epoxidation of allylic substrate induced the fluorescent response.

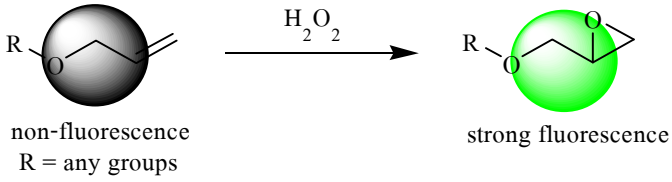
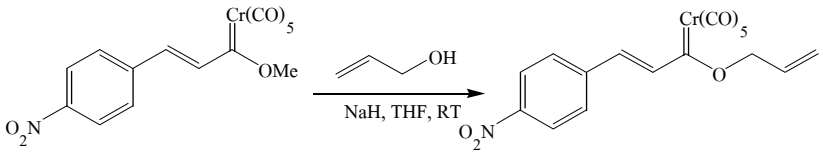
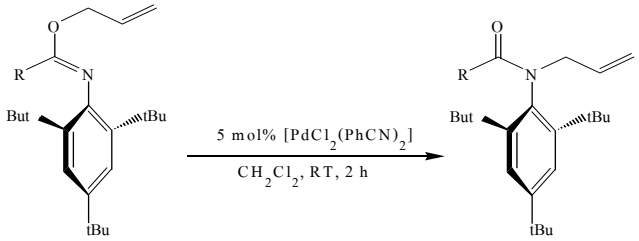


Figure 1.1 Chemosensor for H_2O_2 based on allylic substrate

Although in the past, there are several methods available for the preparation of allylic alcohols and/or amides, these methods generally required the use of harsh and severe conditions. Mild and facile allylation are highly required for the installation of the allylic functional groups to the sensitive substrates, e.g. nucleosides and nucleotides, for example, the synthesis method of *O*-allylation (Scheme 1.1), reaction of α, β-unsaturated Fischer carbine complexes with allyl alkoxide [1], and *N*-allylation, Highly selective stereodivergent synthesis of separable amide rotamer, by using palladium (Pd) chemistry, and their thermodynamic behavior (Scheme 1.2) [14].



Scheme 1.1 Reaction of electron deficient mononuclear carbine complex with allyl alkoxide



Scheme 1.2 Stereoselective synthesis of E rotamer though a Pd^{II}-catalyzed Claisen rearrangement

So this research project aim to investigate the mild and facile *N*- and/or *O*-allylation of alcohols and amides using 1,8-diazabicycloundec-7-ene (DBU) as a reaction base.

1.2 Objective

1.2.1 To investigate the optimized condition for *N*- and/or *O*-allylation

1.3 Advantage

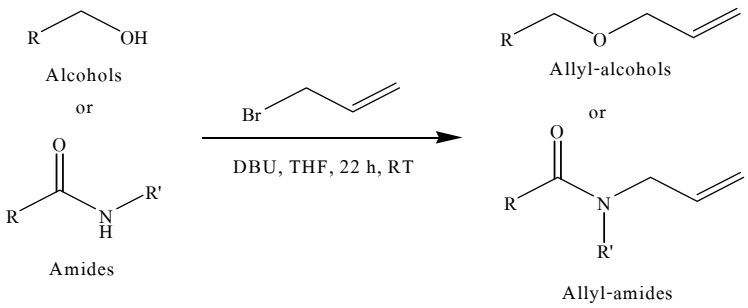
1.3.1 Allylation of alcohols and amides was achieved with facile and mild conditions employing DBU.

1.3.2 The allylation of biologically significant substrate was achieved.

1.3.3 To employ the optimized condition for the allylation of biologically significant compounds

1.4 Scope of research

1.4.1 Synthesis of *O*- and/or *N*-allylated compounds employing DBU



1.4.2 Characterization of *O*- and/or *N*-allylated products

1.5 Research methodology

1.5.1 Literature review

1.5.2 Synthesis of *N*- and/or *O*-allylated compounds and characterization

1.5.3 Conclusion and report writing

1.6 Period of the thesis

November 2010 – March 2011

1.7 Research plan

Table 1.1 Research plan

Operation	**Period of time**				
	2553		**2554**		
	Nov.	**Dec.**	**Jan.**	**Feb.**	**Mar.**
Literature review	←	—	—	→	
Synthesis of *O*/*N*-allylated compounds and purification	←	→			
Characterization of pure *O*/*N*-allylated compounds			←	→	
Conclusion and report writing				←	→

1.8 Place for research

National Center for Genetic Engineering and Biotechnology (BIOTEC)

CHAPTER 2

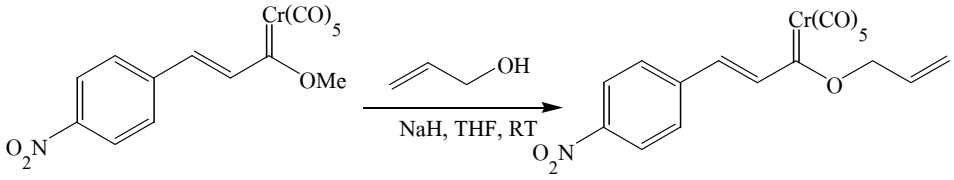
LITERATURE REVIEW

2.1 Definition of allylation

Allylation is the installation of allylic group into an alcoholic and/or amide substrates. Such as allyl ether is known as a synthetically useful synthon extensively which employed in organic synthesis. The allylic synthon is known as a precursor for total the syntheses of a beta blocker and an antineoplastic [1, 2].

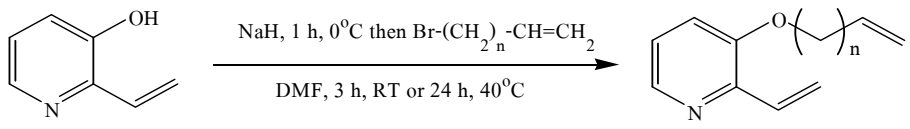
2.2 Synthesis of *O*-allylation

There are several approach for the synthesis of *O*-allyl ether via the *O*-allylation. For example, reaction of α , β -unsaturated Fischer carbine complexes with allyl alkoxide were studied by Kamikawa in 2006. In the study, it mentioned of the conventional way for the *O*-allylation of alcoholic substrate which generally required the use of strong base (e.g. NaH) and high reaction temperature (reflux temperature) (Scheme 2.1). This reaction condition, however, is not suitable for sensitive substrates [3].



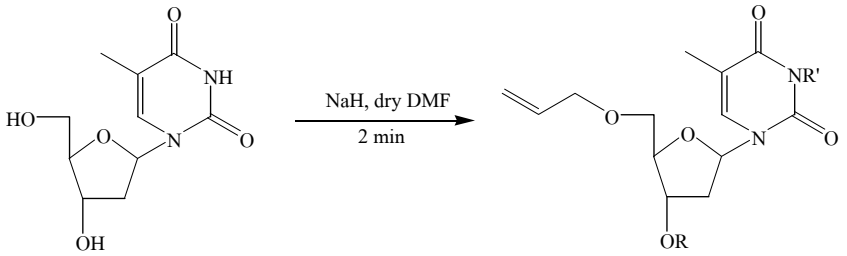
Scheme 2.1 Reaction of electron deficient mononuclear carbine complex with allyl alkoxide

In 2006, Banaszak et al. investigated the new and efficient ring closing metathesis (RCM) with pyridine derivatives synthesis. The reaction condition employed is similar to the condition that reported Kamikawa in which the synthesis of 3-alkenyloxy-2-vinylpyridines is achieved (Scheme 2.2). Both Ken and Estelle reaction condition gave good yields of allylated products [4].



Scheme 2.2 Synthesis of 3-alkenyloxy-2-vinylpyridine

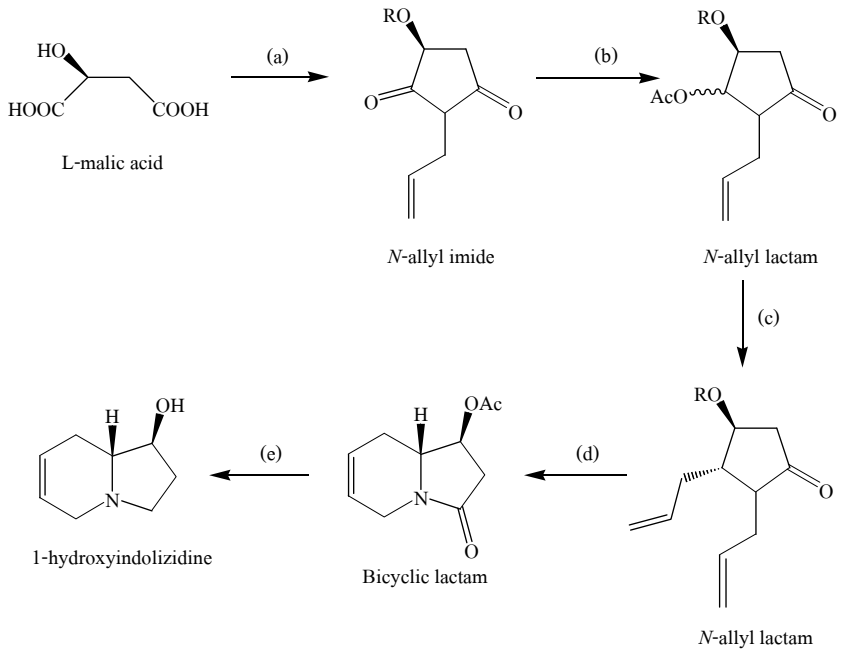
Roy et al. reported one-step selective 5′-*O*-allylation of thymidine using microwave or ultrasound activation. Recently, Zerrouki introduced an improved protocol for *O*-allylation of thimidine employing microwave or ultrasound activation (Scheme 2.3). This condition gave the allylated thymidine with good yield and short reaction time. Although, this method obtains allylated thymidine within very short reaction time, its applicability to other alcoholic substrates is limited [5].



Scheme 2.3 Synthesis of *O*-allylation by employing microwave of thymidine

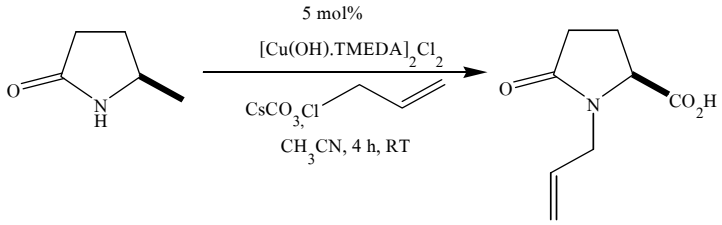
2.3 Synthesis and/or application of *N*-allylation

N-allylation of amide has been reported by many research groups. For example, the enhancement of *trans* diastereoselection for the allylation of cyclic chiral *N*-cyliminium ions. Synthesis of hydroxylated indolizadines was achieved by Klitzke et al. The reaction condition was further improved by Fernando and his co-worker for the short synthesis of hydroxylate indolizidines (Scheme 2.4)[6]. Haris et al. has also reported the synthesis of 1-hydroxyindolizidine enantiomer and used as the biosynthetic precursor of swainsonine [7].



Scheme 2.4 Synthesis of hydroxylate indolizidine

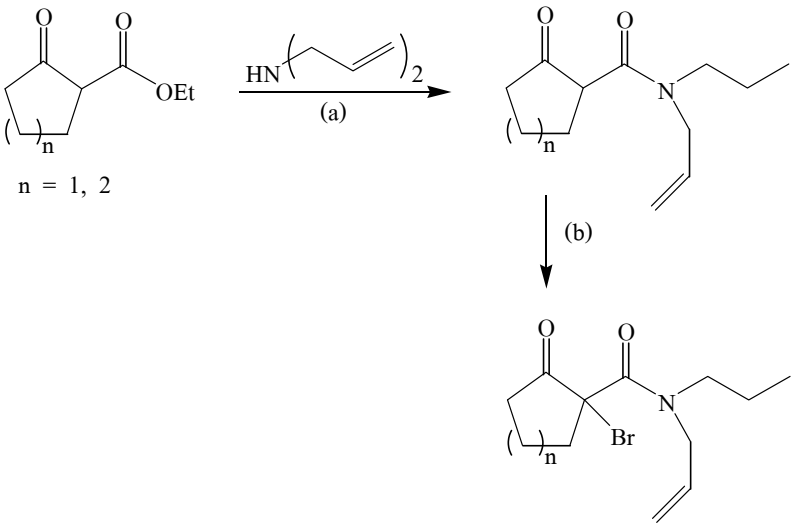
Kumaraswamy has reported on the synthesis of di-μ -hydroxyl–bis (*N*, *N*, *N'*, *N'* -tetramethylenediamine)-copper (II) chloride $[Cu(OH).TMEDA]_2Cl_2$, an efficient and practical catalyst for the benzylation and allylation of amides which discloses an efficient protocol for allylation of amide using the ally-chloride as electrophile under the basic condition (5 mol% of $[Cu(OH).TMEDA]_2Cl_2$) (Scheme 2.5) [8].



Scheme 2.5 The synthesis of allyl amide

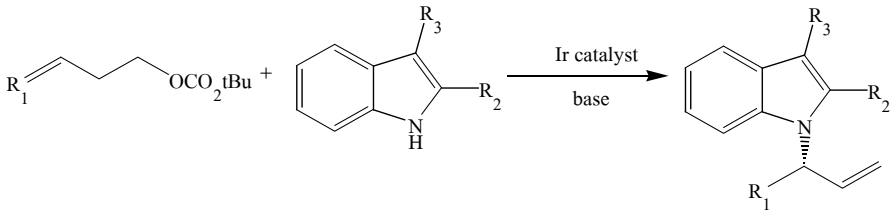
Kumaraswamy et al. subsequently reported that this work was the continuant work on the synthetic congeners of the antitumor, antibiotic Belactocin. In this protocol, various amide analogues have been prepared [9].

Yang et al. investigated lewis acid-catalyzed atom transfer radical cyclization of unsaturated β -keto amide. In this reaction condition, it was mentioned that *N*-alkenyl β -keto amide were achieved by a trans-amidation reaction of a β -keto ester with an unsaturated amine (Scheme 2.6) [10].



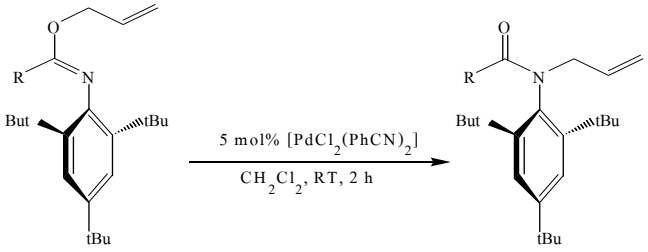
Scheme 2.6 Synthesis of *N*-alkenyl β -keto amide

Levi et al. has reported on iridium-catalyzed regio- and enantioselective *N*-allylation of indole. Cao et al. also reported that chiral indole architectures are present in a wide variety of natural products and have been identified as promising lead compounds in medicinal chemistry [11]. Bandini et al. reported on the synthesis of enantioenriched indole derivatives by catalytic and enantioselective reaction [12]. As this, Leiv and his co-workers synthesized of enantioenrich, branched *N*-allylindoles from the reactions of 2-subsituted, 3-subsituted and 2,3-subsituted indoles with achiral linear allylic carbonate in the presence of a single-component iridium catalyst (Scheme 2.7) [13].



Scheme 2.7 The synthesis of enantioenriched *N*-allylindoles

Ototake et al. investigated on the highly selective stereodivergent synthesis of separable amide rotamer using palladium chemistry. In the study, it was mentioned of the allylation of 2,4,6-tri-tert-bu-tylanilides using a π -allyl-Pd catalyst to give *N*-allylate anilide with moderate to excellent Z-rotamer selectivity (Scheme 2.8) [14].

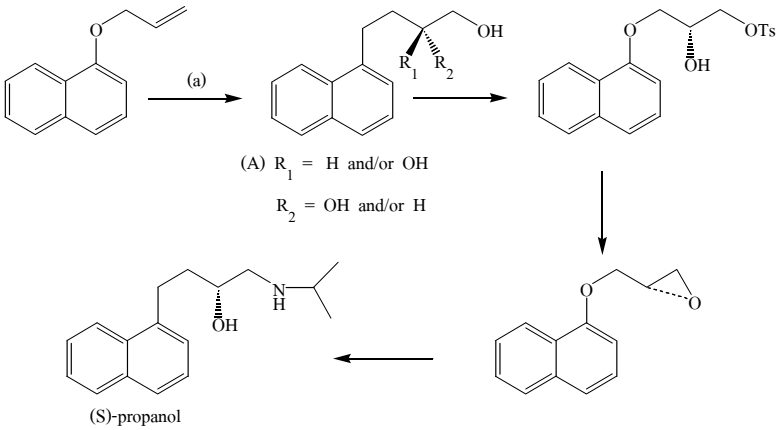


Scheme 2.8 Stereoselective synthesis of E rotamer though a Pd^{II}-catalyzed Claisen rearrangement

Tanatami et al. reported that rotational isomer based on an amide C(O)-N bond playing an important role in the regulation of action of biologically active peptides and functional molecules that have amide skeletons [15].

2.4 Application of *O*-allylation

There are different applications of *O*-allylation. For example, the Sharpless asymmetric dihydroxylation of aryloxy allyl ether: a simple rout to chiral β-blockers were studied by Rao et al. The reaction condition is of interest since the Sharpless asymmetric dihydroxylation of allyloxyethers indicating the influence of oxygen on the steriochemical outcome of this reaction (Scheme 2.9). Moreover, this protocol also provided a new synthetic route to chiral substituted glycerol derivative, valuable intermediates for the synthesis of chiral β-blocker drug (Figure 2.2) [1].



Scheme 2.9 The combination of OsO_4-K_3-Fe-$(CN)_6$

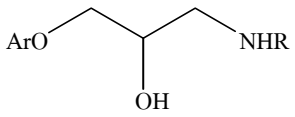
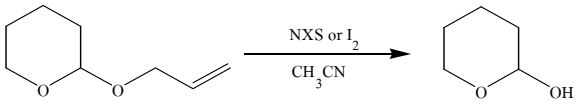


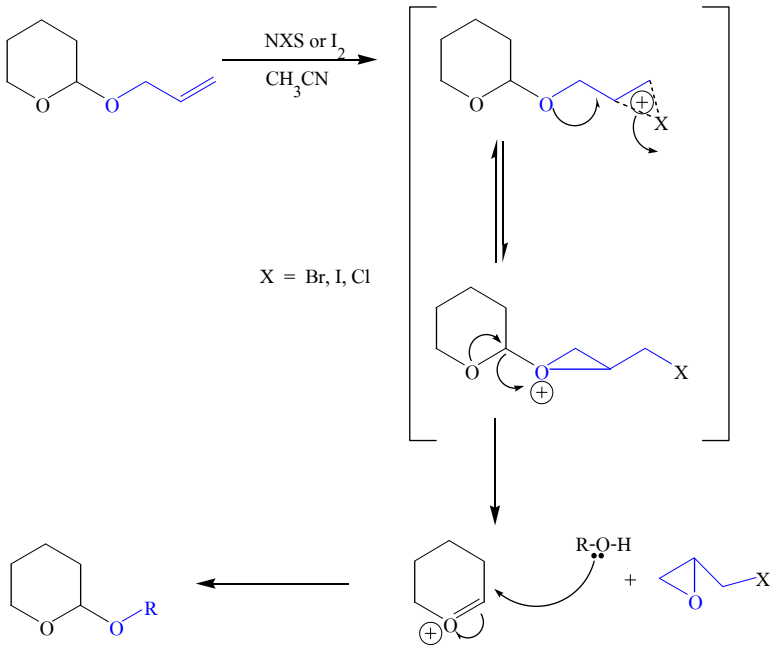
Figure 2.2 Chiral β-blocker drug

Sharplessa symmetric dihydroxylation of guaifensin precursor yielded enantiomerically pure (S)-guaifensin, a muscle relaxant and expectorant.

Kumar et al. has reported on the synthesis of allyl tetrahydropyranyl ether: a versatile alcohol/thiol protecting reagent. In the study, it was mentioned that allyl tetrahydropyranyl ether (ATHPE) was employed as a versatile protecting reagent (Scheme 2.10). With the combination of NBS/I_2, *O*-allyl group can easily be replaced by hydroxyls (including tertiary-OH) or thiols (Scheme 2.11) [16].



Scheme 2.10 Formation of 2-hydroxyltetrahydropyran from ATHPE



Scheme 2.11 Plausible mechanism of *O*-allyl group by alcohol and thiol nucleophiles

The reagent system may also prove to be useful for the protection protocols of polyfunctional molecules. Applications of the present protection protocol for carbohydrate substrates are in progress.

The Allyl ether as apparent initiators of radical polymerizations was studied by Bevington. In polymer chemistry, an allyl moiety is one of the reactive functional group of monomer serving as a polymerizable unit. The monomer with different functional groups offers the polymer with various functionalities. Generally, the allylic monomer participates in the polymerization process via a free radical mechanism and often copolymerizes with non-allyl monomers. Recently, Bevington has report that allyl ether can act as an initiator in the radical polymerizations of methyl methacrylate (MMA), styrene (STY) and acrylonitrile (ACN) [17].

CHAPTER 3

EXPERIMENTAL

3.1 Equipments and chemicals

3.1.1 Equipments

1. Analytical Balance ± 0.0001 g, AND, GR-200
2. Fumehood, Lab Tech, LFH-150SCI
3. Magnetic Stirrer, IKA, C-MAG HS7
4. Rotary Evaporator, BUCHI, R-220
5. Thin Layer Chromatography (TLC), Merk, silica gel 60 F_{254}
6. Mass spectrometer, Thermo Phinnigan, MAT 95XL
7. Nuclear Magnetic Resonance (NMR) Spectroscopy
   - 7.1 Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy, Bruker DRX-400 spectrometer
   - 7.2 Carbon Nuclear Magnetic Resonance (^{13}C-NMR) spectroscopy, Bruker AV500D spectrometer

3.1.2 Chemicals

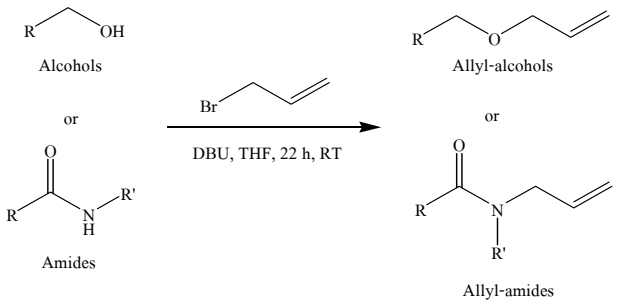
1. Eugenol, Aross, LAB grade
2. Methylparaben, LAB grade
3. Nitrophenol, Across, LAB grade
4. Thymine, Across, LAB grade
5. Uracil, Across, LAB grade
6. 1,8-Diazabicycloundec-7-ene (DBU), Sigma-Aldrich
7. Tetrahydrofuran (THF), Sigma-Aldrich
8. Hydrochloric (HCl), Fluka
9. Ethyl acetate (EtOAc), Fluka, Analytical grade
10. Hexane, Fluka, Analytical grade
11. Ethanol (Ethanol), Fluka, Analytical grade
12. Dichloromethane (CH_2Cl_2), Fluka, Analytical grade

3.2 Experimental

In this section, full characterizations of *N*- and *O*-allylated products were demonstrated.

3.2.1 Synthesis

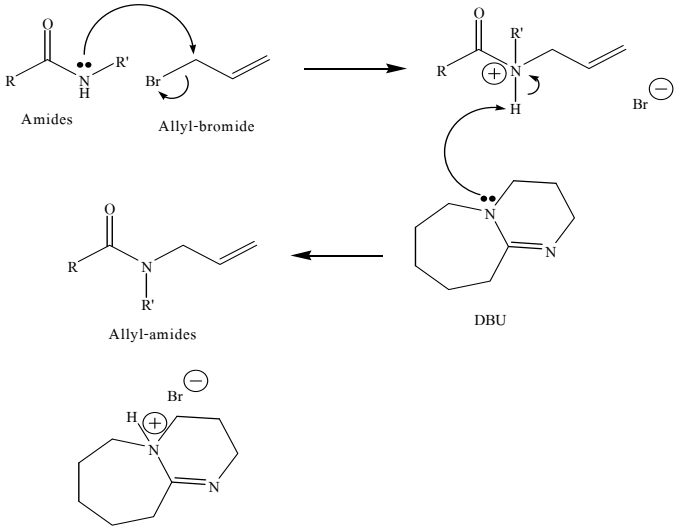
The synthesis of *N*- and/or *O*-allylated compounds was carried out using corresponding alcohols or amides and allyl-bromide. The allylation was promoted employing DBU as a reaction base (Scheme 3.1).



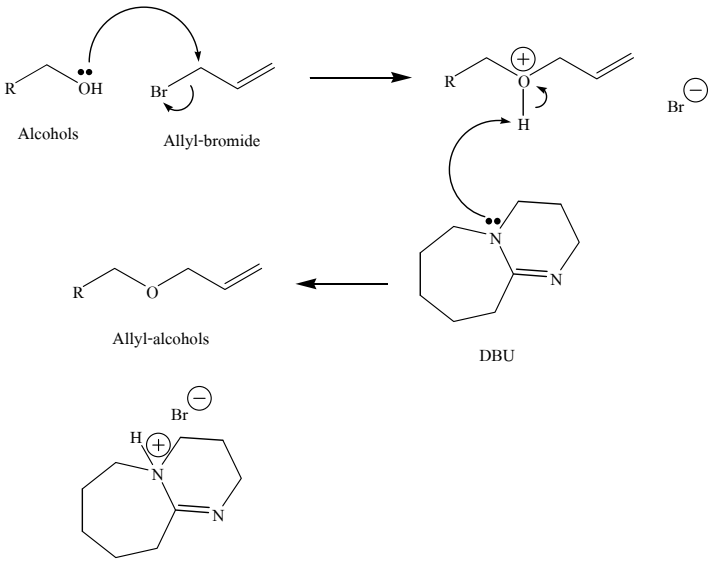
Scheme 3.1 The synthesis of *N*- and/or *O*-allylated compounds

All reaction was carried out in the presence of 1 mol of allyl-bromide, 1.1 mol of DBU, 1 mol of alcohols/amides and 5 mL of tetrahydrofuran (THF). The synthesis was a one-pot reaction. The reaction was kept stirring at room temperature for at least 22 hours for completion under nitrogen atmosphere.

The mechanism of *N*- and/or *O*-allylation promoted by DBU was based on the nucleophilic addition from alcohols or amides before abstracting the proton by DBU (Scheme 3.2, Scheme 3.3).



Scheme 3.2 The mechanism of *N*-allylation



Scheme 3.3 The mechanism of *O*-allylation

Following substrates, eugenol, methylparaben, nitrophenol, thymine and uracil were achieved employing the optimized allylation reaction. Allyl-thymine (A), (B) and allyl-uracil (A), *O*-allyl compounds, allyl-eugenol, allyl-methylparaben and allyl-nitrophenol were obtained in good yields (Table 3.1).

Table 3.1 Structure of substrates and products

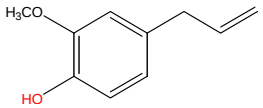
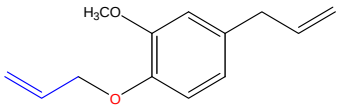
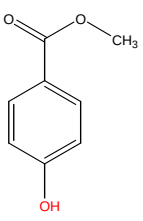
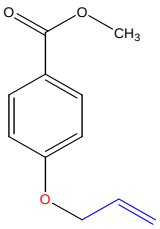
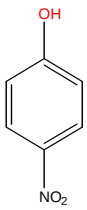
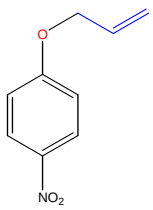
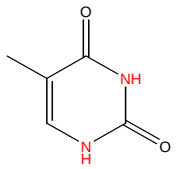
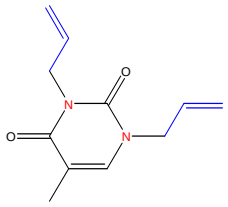
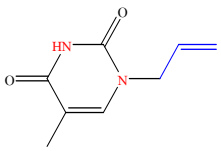
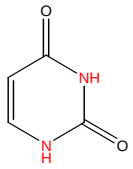
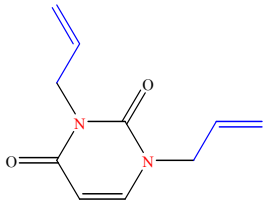
Alcohols	
Substrates	**Products**
Eugenol 	**Allyl-eugenol** 
Methylparaben 	**Allyl-methylparaben** 
Nitrophenol 	**Allyl-nitrophenol** 

Table 3.1 (Con.) Structure of substrates and products

Amides		
Reactants	**Products**	
Thymine 	**Allyl-thymine (A)** 	**Allyl-thymine (B)** 
Uracil 	**Allyl-uracil (A)** 	

3.2.2 Purification

The purification of *O*- and *N*-allylated compounds was achieved using column chromatography.

For a suitable mobile phase for column chromatography, this could be achieved by pre-checked with thin layer chromatography (TLC) prior to the isolation (Table 3.2).

Table 3.2 Mobile phase in the purification

Product	Mobile phase	R_f (Experimental)
Allyl-eugenol	10% EtOH in hexane	0.8
Allyl-methylparaben	10% EtOAc in hexane	0.6
Allyl-nitrophenol	10% EtOAc in hexane	0.7
Allyl-thymine (A)	70% EtOAc in hexane	0.8
Allyl-thymine (B)	70% EtOAc in hexane	0.6
Allyl-uracil	50% EtOAc in hexane	0.5

Retardation factor (R_f) is defined as the ratio of the distance traveled by the center of a spot to the distance traveled by the solvent front. R_f can be mathematically described by the following ratio.

$$R_f = \frac{\text{migration distance of substance}}{\text{migration distance of solvent front}}$$

3.2.3 Characterization

^{1}H and ^{13}C spectra were obtained and operated by Bruker AVANCE 400 MHz and AV500D spectrometer with solvent signal as an internal reference. The chemical shifts (δ_H and δ_C) were recorded in ppm with reference to residual solvent signal, $CDCl_3$ (δ_H 7.24, δ_C 77.00).

3.2.4 Calculation of percent yield

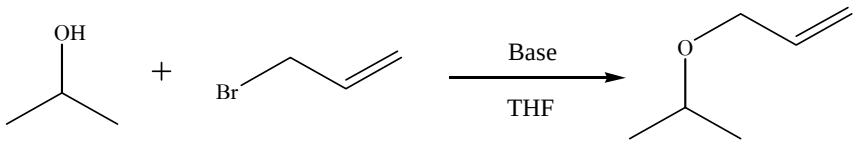
Percent yield (% yield) was defined as the percentage by mole fraction of obtained and theoretical products and theoretical. The percent yield was calculated as followed.

$$\%\ \text{yield} = \frac{\text{mol of obtained product}}{\text{mol of theoretical product}} \times 100$$

Mole was a unit of measurement for the amount of substance or chemical amount. It was one of the base units in the International System of Units, and has the unit symbol mol. Mole of reactants and products can be calculated from weight of them which the mole was calculated as followed.

$$\text{mol} = \frac{\text{weight of substance (g)}}{\text{molecular weight of substance (g/mol)}}$$

These are results for the optimization of allylation condition. The reactions investigated the effect of base, reaction temperature and reaction time. After the optimization, the best reaction condition that provided mild and facile condition was chosen for subsequent experiment (Scheme 3.4).



Scheme 3.4 The reaction between isopropanol with allyl-bromide in the optimization

DBU was chosen as the proton scavenger in the reaction since it gave good yield (84%) of allylated isopropanol (representing alcohol) (Table 3.3).

Table 3.3 The effect of base

Entry	Base	Solvent	Time(24)	Yield[A] (%)
1	Et_3N	THF	24	5
2	Pyridine	THF	24	10
3	Piperidine	THF	24	5
4	DABCO	THF	24	15
5	DBU	THF	24	84

[A] Based on isolated product

Room temperature was chosen as the optimal condition since under this condition it gave the highest yield (84%) of allylated isopropanol (Table 3.4).

Table 3.4 The effect of reaction temperature

Entry	Base	Temp. (°C)	Time (h)	Yield[A] (%)
1	DBU	60	24	62
2	DBU	RT	24	84
3	DBU	0	24	12
4	DBU	-10	24	5

[A] Based on isolated product

Finally, the reaction time was investigated and 22 hours was the optimal reaction time since at this time the yield of allylated product was the highest (Figure 3.1).

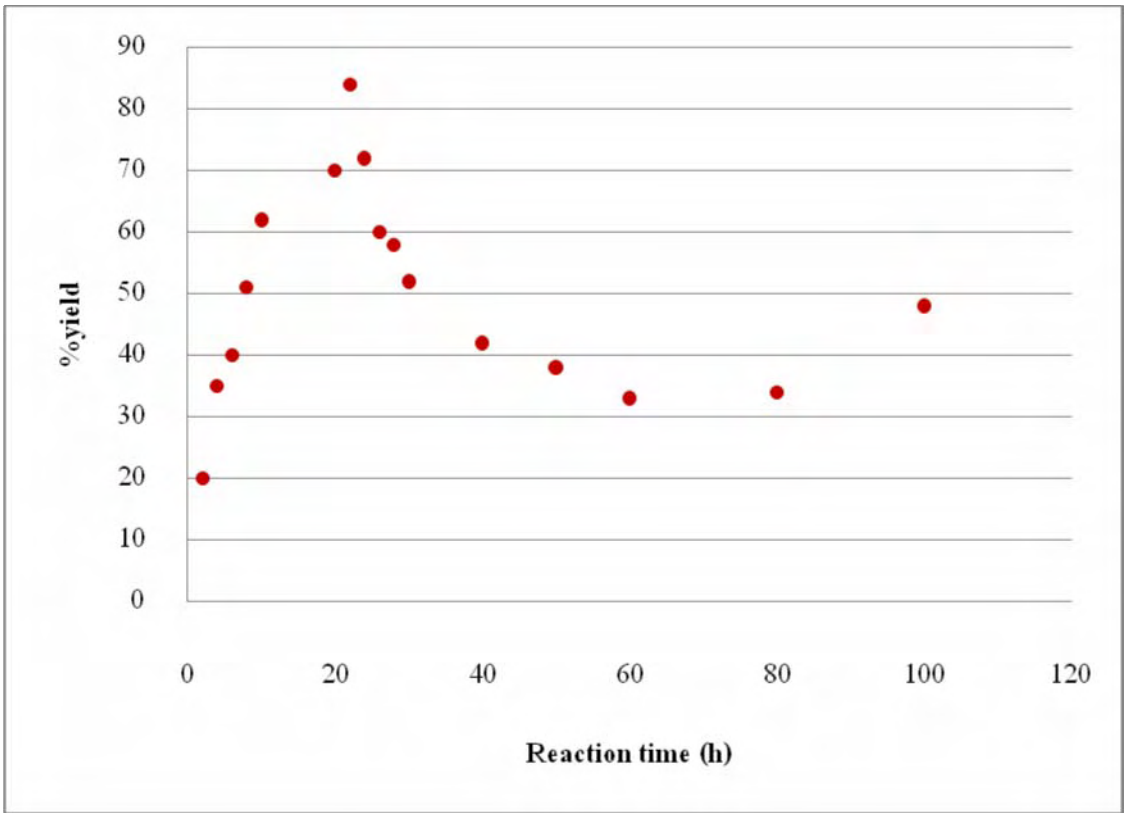


Figure 3.1 The effect of reaction time

CHAPTER 4

RESULTS AND DISCUSSION

This project aims to prepare *N*- and/or *O*-allyl compounds. *N*-allyl compounds are allyl-thymine (A), allyl-thymine (B), allyl-uracil while *O*-allyl compounds are allyl-eugenol, allyl-methylparaben and allyl-nitrophenol. This section reported ^{1}H-NMR and ^{13}C-NMR spectra of allylated compounds which were compared to the starting materials, e.g. thymine, uracil, eugenol, methylparaben and nitrophenol. Mass spectra of corresponding compounds are also reported.

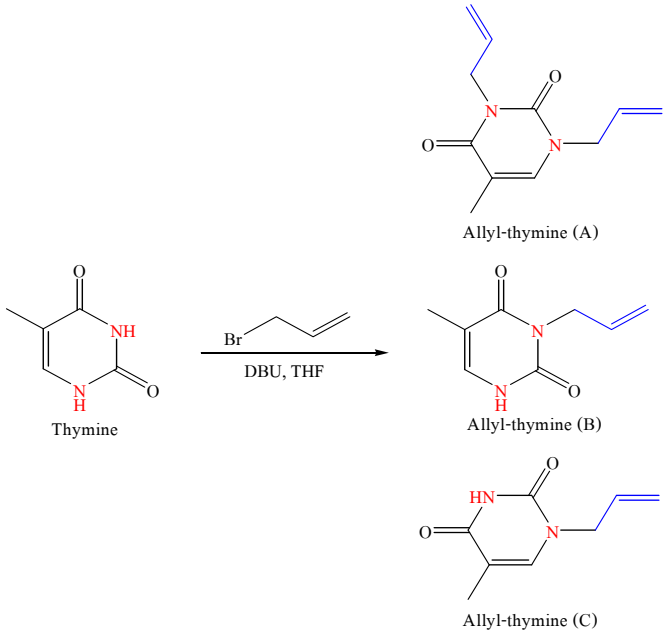
4.1 *N*-allyl compounds

N-allyl compounds: allyl-thymine (A), allyl-thymine (B) and allyl-uracil (A)

^{1}H-NMR spectrum of *N*-allyl compound indicated the amount of proton (H) present in synthesized compounds. ^{13}C-NMR of *N*-allyl compound was obtained and indicated the amount of carbon (C) and its environment in synthesized compounds.

4.1.1 Allyl-thymine (A)

From the experimental data, the synthesis reaction of allyl-thymine (Scheme 4.1) indicated the structure of synthetic compound which is corresponding to ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic data.



Scheme 4.1 The synthesis reaction of allyl-thymine

This represents ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of allyl-thymine (A) which detected by ^{1}H-NMR spectroscopy (Figure 4.1).

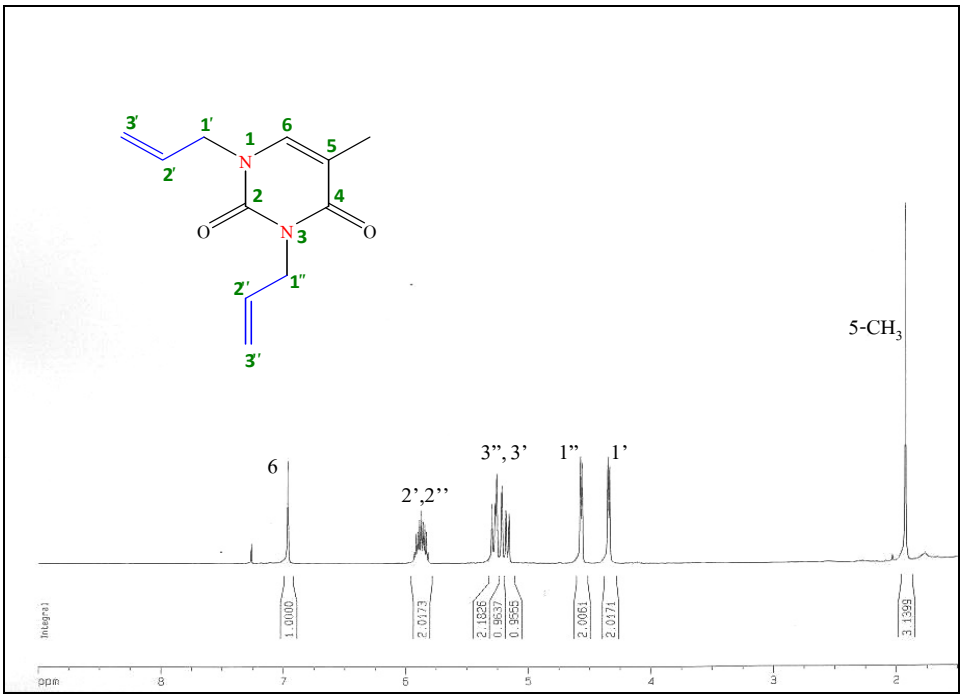


Figure 4.1 ^{1}H-NMR spectrum of allyl-thymine (A)

^{1}H-NMR data indicated the proton signal of allyl-thymine (A) which clearly showed the chemical shift (δ) and coupling constant (Table 4.1).

Table 4.1 ^{1}H-NMR spectroscopic data of allyl-thymine (A)

Position	δ_H (ppm)
H-6	6.97 (1H, s)
H-1'	4.35 (2H, d, *J* = 5.7 Hz)
H-2', 2''	5.88 (2H, m)
H-3'	5.17 (1H, dd, *J* = 10.17)
	5.22 (1H, s)
H-1''	4.57 (2H, d, *J* = 5.9 Hz)
H-3''	5.29 (2H, dd, *J* = 10.39)
5-C*H*$_3$	1.93 (3H, s)

The ^{1}H-NMR spectrum and spectroscopic data indicated allyl signal at δ_H 4.35 (2H, d, J = 5.7 Hz, H-1'), δ_H 5.88 (2H, m, H-2', 2''), δ_H 5.17 (1H, dd, J = 10.17, H-3'), δ_H 5.22 (1H, s, H-3'), δ_H 4.57 (2H, d, J = 5.9 Hz, H-1''), δ_H 5.29 (2H, dd, J = 10.39, H-3''), methyl signal at δ_H 1.93(3H, s, 5-CH_3) and aromatic proton at δ_H 6.97 (1H, s, H-6). ^{1}H-NMR spectroscopic data confirmed the structure of allyl-thymine (A) (Figure 4.2).

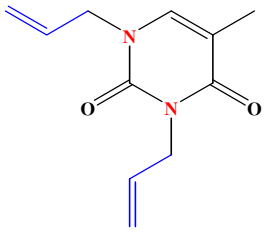


Figure 4.2 Structure of allyl-thymine (A), 1,3-diallyl-5-methyl-1*H*-pyrimidine-2,4-dione

This reported ^{13}C-NMR (500 MHz, $CDCl_3$) spectrum of allyl-thymine (A) which detected by ^{13}C-NMR spectroscopy (Figure 4.3).

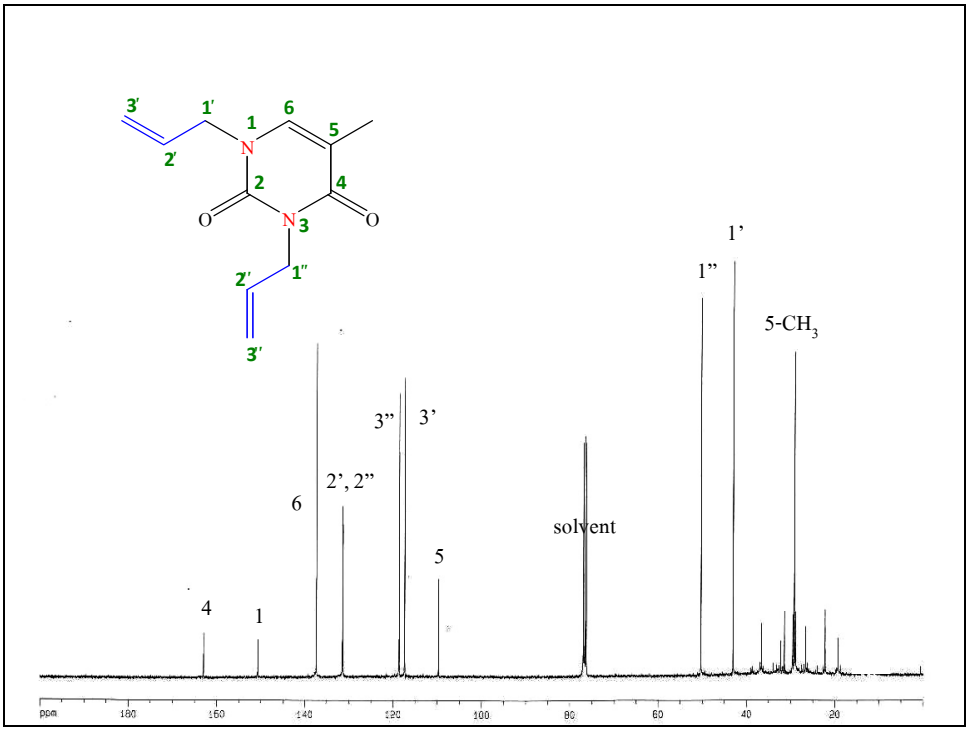


Figure 4.3 ^{13}C-NMR spectrum of allyl-thymine (A)

This represents ^{13}C-NMR data indicating the carbon signal of allyl-thymine (A) which showed the result as chemical shift (δ) (Table 4.2).

Table 4.2 ^{13}C-NMR spectroscopic data of allyl-thymine (A)

Position	δ_C (ppm)
C-2	150.69
C-4	162.98
C-5	109.69
C-6	137.40
C-1'	43.06
C-2', 2''	131.41
C-3'	117.38
C-1''	50.34
C-3''	118.62
5-*C*H$_3$	29.26

The spectrum of allyl-thymine (A) in $CDCl_3$ showed eleven carbon signals which consisted of one methyl, four methylenes, three methines and three quaternary carbons including two ketones and one aromatic quaternary carbon.

Finally, the structure of allyl-thymine (A) was confirmed by mass spectrometry (Figure 4.4). Mass spectra indicated base peak $[M + Na]^+$ at 228.94 which confirmed the molecular weight of synthetic product as allyl-thymine (A), (206.24 g/mol, calculation).

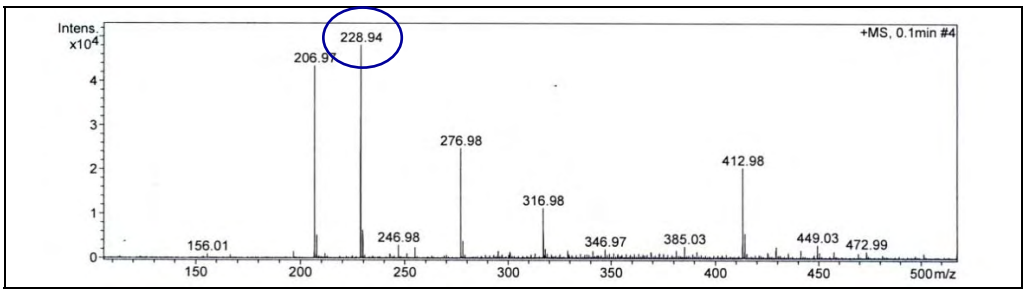


Figure 4.4 Mass spectroscopic data of allyl thymine (A), high resolution report

4.1.2 Allyl-thymine (B)

From the experimental data, the synthesis reaction of allyl-thymine (Scheme 4.1) indicated the structure of synthetic compound which is corresponding to ^{1}H-NMR and ^{13}C-NMR spectroscopy.

This represents ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of allyl-thymine (B) which detected by ^{1}H-NMR spectroscopy (Figure 4.5).

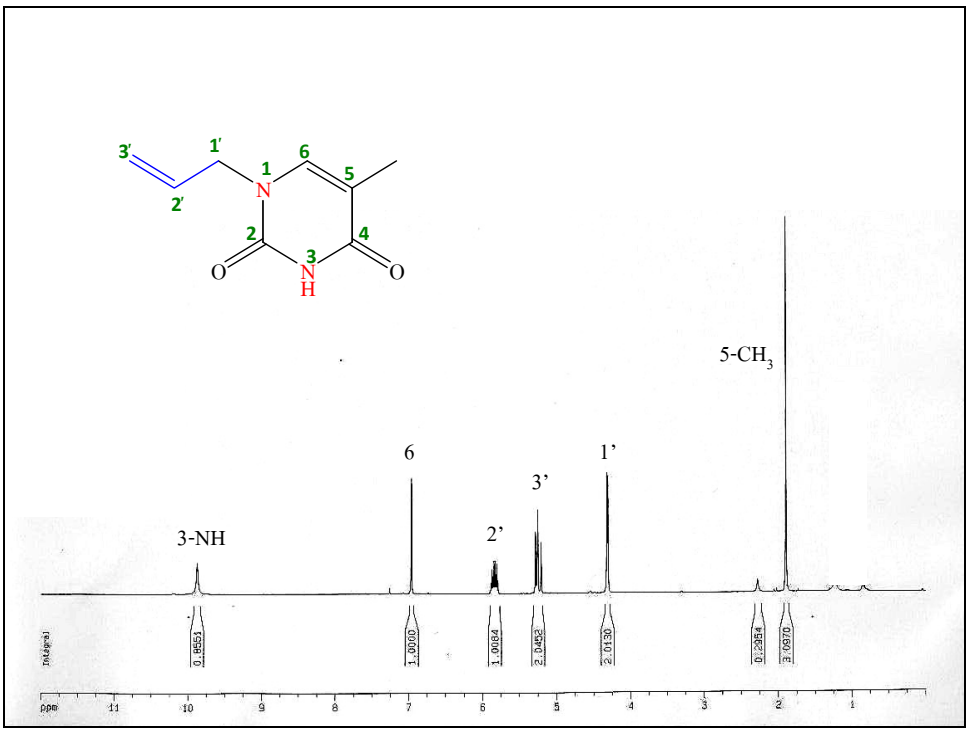


Figure 4.5 ^{1}H-NMR spectrum of allyl-thymine (B)

^{1}H-NMR data indicated the proton signal of allyl-thymine (B) which clearly showed the chemical shift (δ) and coupling constant (Table 4.3).

Table 4.3 ^{1}H-NMR spectroscopic data of allyl-thymine (B)

Position	δ_H (ppm)
H-6	6.97 (1H, s)
H-1’	4.32 (2H, d, *J* = 5.8 Hz)
H-2’	5.84 (1H, m)
H-3’	5.25 (2H, t, *J* = 7.6 Hz)
1-N*H*	9.85 (1H, s)
5-CH_3	1.96 (3H, s)

The ^{1}H-NMR spectrum and spectroscopic data indicated allyl signal at δ_H 4.32 (2H, d, *J* = 5.8 Hz, *H*-1'), δ_H 5.84 (1H, m, *H*-2'), δ_H 5.25 (2H, t, *J* = 7.6, *H*-3'), methyl signal at δ_H 1.96 (3H, s, 5-CH_3), aromatic proton at δ_H 6.97 (1H, s, *H*-6) and amine signal at δ_H 9.85 (1H, s, 1-N*H*). ^{1}H-NMR spectroscopic data conformed to structure of allyl-thymine (B) (Figure 4.6).

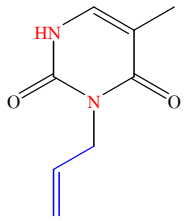


Figure 4.6 The structure of allyl-thymine (B), 3-allyl-5-methyl-1*H*-pyrimidine-2,4-dione

This reported ^{13}C-NMR (500 MHz, $CDCl_3$) spectrum of allyl-thymine (B) which detected by ^{13}C-NMR spectroscopy (Figure 4.7).

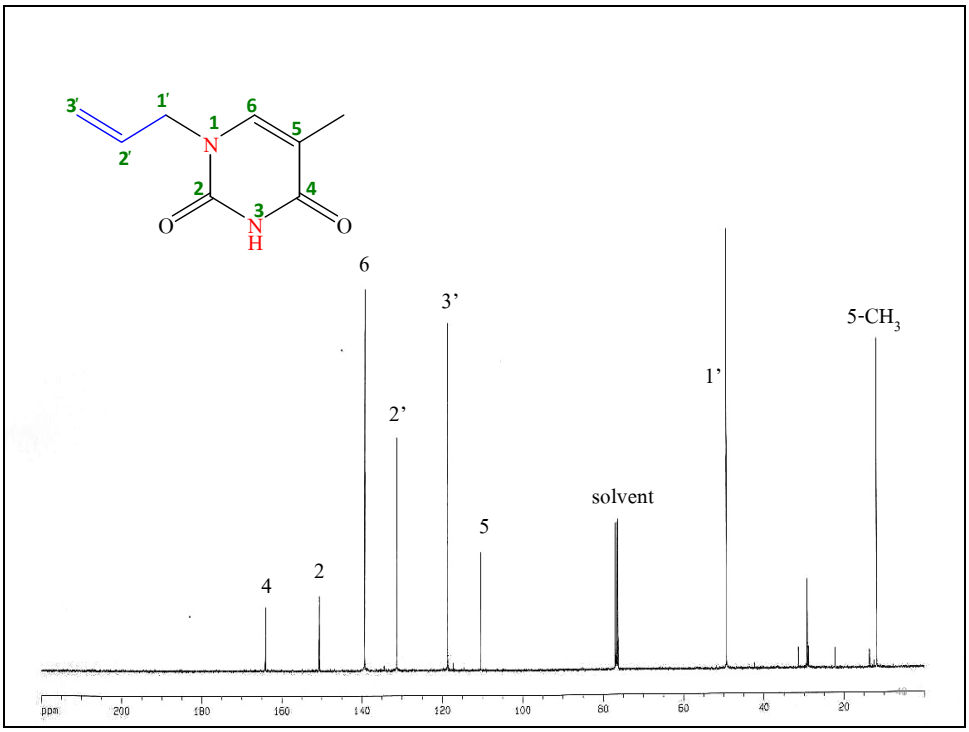


Figure 4.7 ^{13}C-NMR spectrum of allyl-thymine (B)

This represents ^{13}C-NMR data indicating the carbon signal of allyl-thymine (B) which showed the result as chemical shift (δ) (Table 4.4).

Table 4.4 ^{13}C-NMR spectroscopic data of allyl-thymine (B)

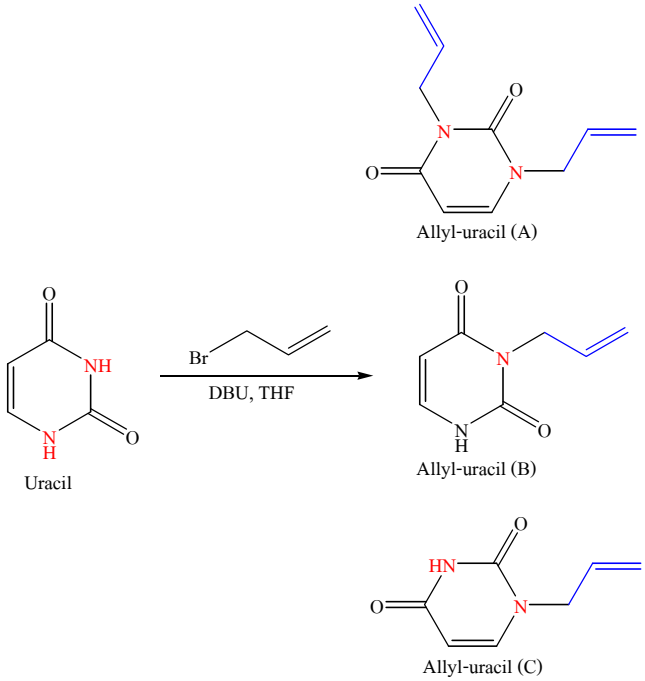
Position	δ_C (ppm)
C-2	150.66
C-4	154.16
C-5	110.55
C-6	139.02
C-1'	49.40
C-2'	131.36
C-3'	118.45
5-*C*H$_3$	12.64

The spectrum of allyl-thymine (B) in $CDCl_3$ showed eight carbon signals which consisted of one methyl, two methylenes, three quaternary carbons including two ketones and one aromatic quaternary carbon.

Allyl-thymine (C) in scheme 4.1, when through the synthesis, extract, check by TLC (thin layer chromatography) and purification found that synthesis reaction of allyl-thymine (C) not occur.

4.1.3 Allyl-uracil (A)

From the experimental data, the synthesis reaction of allyl-uracil (Scheme 4.2) indicated the structure of synthetic compound which is corresponding to ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic data.



Scheme 4.2 The synthesis reaction of allyl-uracil

This represents ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of allyl-uracil (A) which detected by ^{1}H-NMR spectroscopy (Figure 4.8).

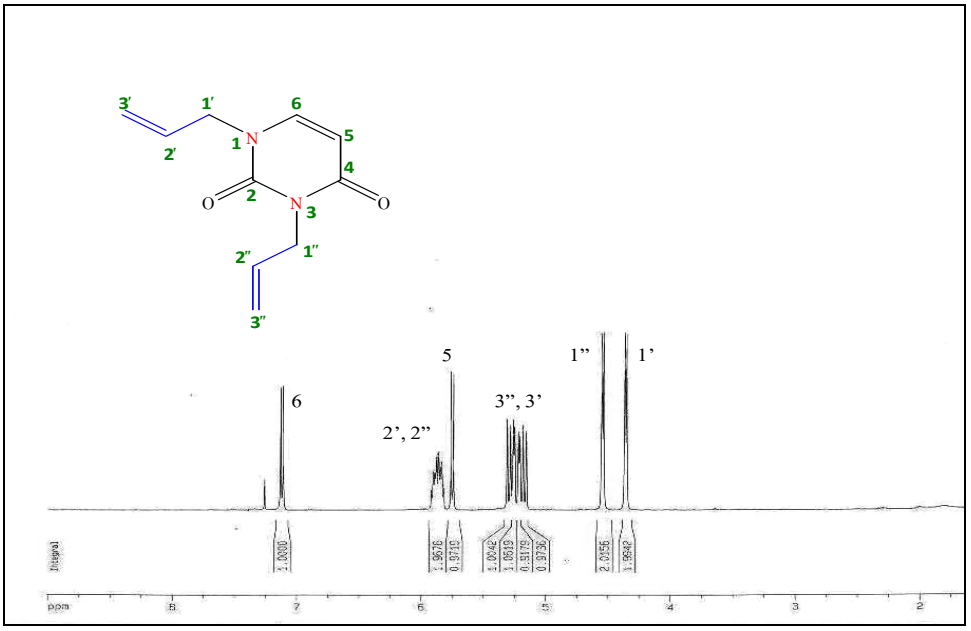


Figure 4.8 ^{1}H-NMR spectrum of allyl-uracil (A)

^{1}H-NMR data indicated the proton signal of allyl-uracil (A) which clearly showed the chemical shift (δ) and coupling constant (Table 4.5).

Table 4.5 ^{1}H-NMR spectroscopic data of allyl-uracil (A)

Position	δ_H (ppm)
H-5	5.76 (1H, d, *J* = 7.9 Hz)
H-6	7.12 (1H, d, *J* = 7.9 Hz)
H-1'	4.36 (2H, d, *J* = 5.8 Hz)
H-2', 2''	5.87 (2H, m)
H-3'	5.17 (1H, dd, *J* = 9.9 Hz)
	5.22 (1H, d, *J* = 5.1 Hz)
H-1''	4.55 (2H, d, *J* = 5.7 Hz)
H-3''	5.26 (1H, d, *J* = 5.2 Hz)
	5.30 (1H, dd, J = 10.2 Hz)

The ^{1}H-NMR spectrum and spectroscopic data indicated allyl signal at δ_H 4.36 (2H, d, *J* = 5.8 Hz, *H*-1'), δ_H 5.87 (2H, m, *H*-2', 2''), δ_H 5.17 (1H, dd, *J* = 9.9, *H*-3'), δ_H 5.22 (1H, d, *J* = 5.1 Hz, *H*-3'), δ_H 4.55 (2H, d, *J* = 5.7 Hz, *H*-1''), δ_H 5.26 (1H, d, *J* = 5.2, *H*-3''), δ_H 5.30 (1H, dd, *J* = 10.2 Hz, *H*-3''), δ_H and aromatic protons at δ_H 5.76 (1H, d, *J* = 7.9 Hz, *H*-5) and δ_H 7.12 (1H, d, *J* = 7.9 Hz, *H*-6). ^{1}H-NMR spectroscopic data confirmed the structure of allyl-uracil (A) (Figure 4.9).

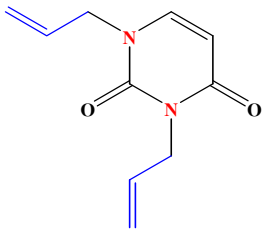


Figure 4.9 Structure of allyl-uracil (A), 1,3-diallyl-1*H*-pyrimidine-2,4-dione

This reported ^{13}C-NMR (500 MHz, $CDCl_3$) spectrum of allyl-uracil (A) which detected by ^{13}C-NMR spectroscopy (Figure 4.10).

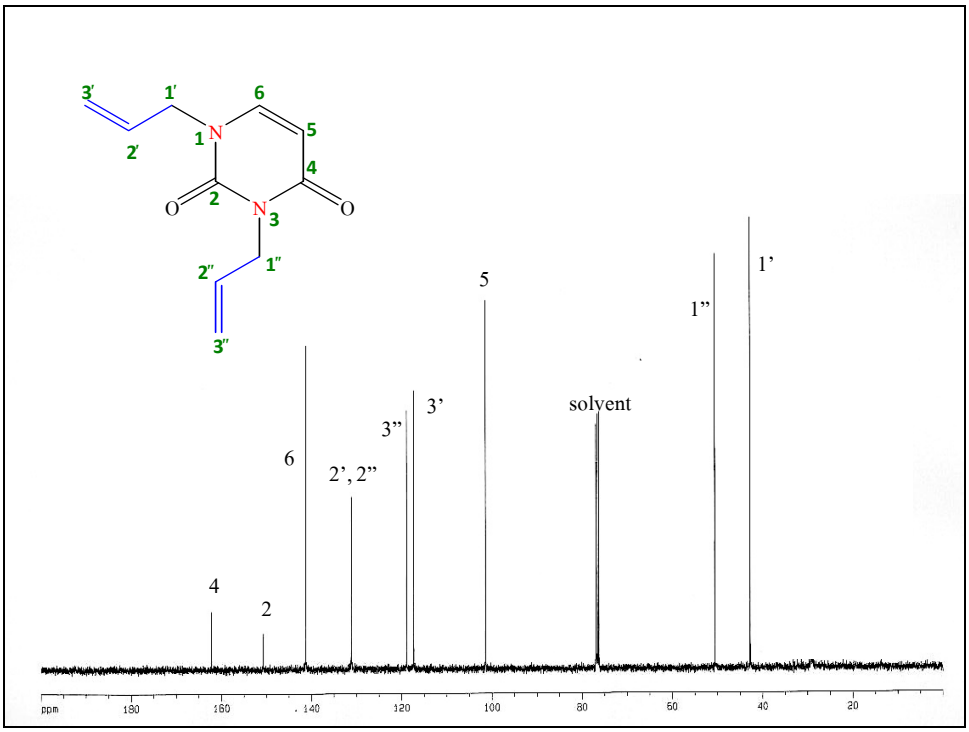


Figure 4.10 ^{13}C-NMR spectrum of allyl-uracil (A)

This represents ^{13}C-NMR data indicating the carbon signal of allyl-uracil (A) which showed the result as chemical shift ( ) (Table 4.6).

Table 4.6 ^{13}C-NMR spectroscopic data of allyl-uracil (A)

Position	δ_C (ppm)
C-2	150.70
C-4	152.21
C-5	101.48
C-6	141.28
C-1'	42.795
C-2', 2''	131.15
C-3'	117.36
C-1''	50.58
C-3''	118.94

The spectrum of allyl-uracil (A) in $CDCl_3$ showed ten carbon signals which consisted four methylenes, four methines and two quaternary carbons including two ketones.

Finally, the structure of allyl-uracil (A) was confirmed by mass spectrometry (Figure 4.11). Mass spectra indicated base peak $[M + H]^+$ at 193.10 which confirmed the molecular weight of synthetic product as allyl-uracil (A), (192.21 g/mol, calculation).

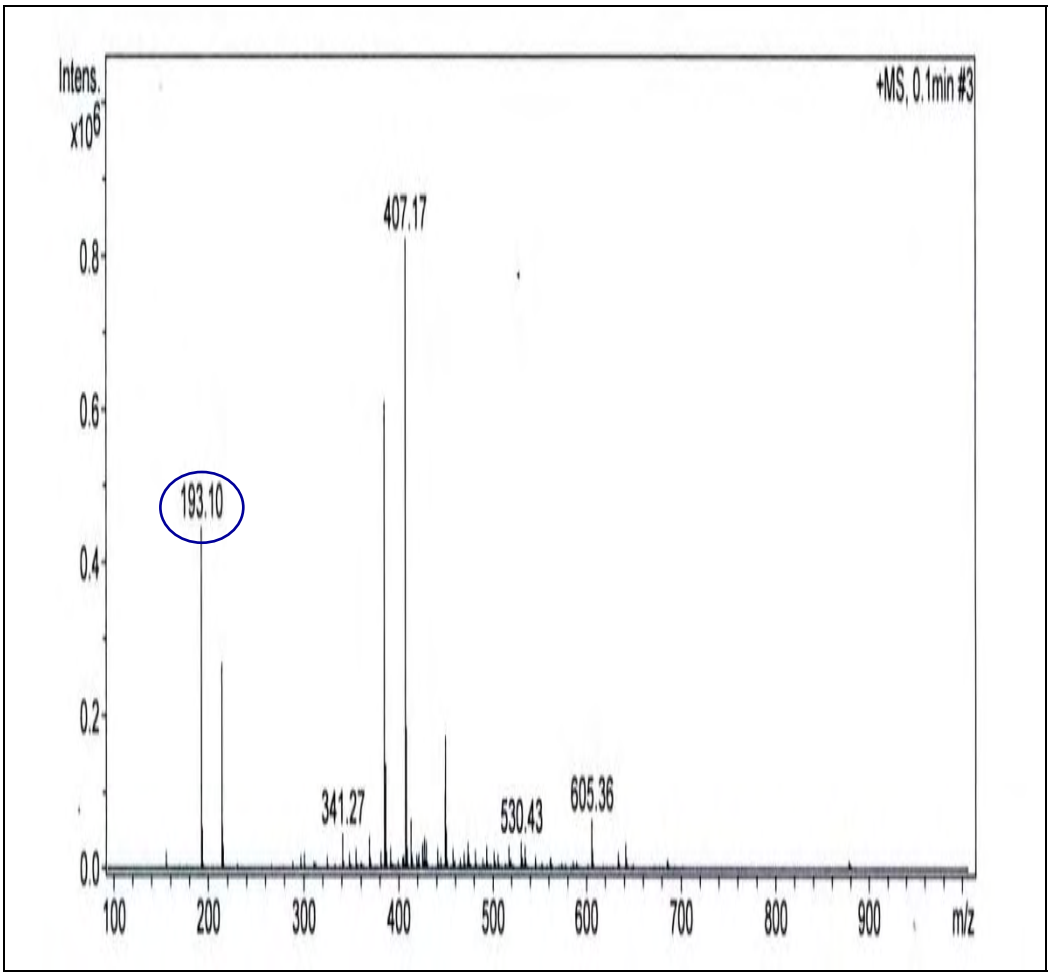


Figure 4.11 Mass spectroscopic data of allyl-uracil (A), high resolution report

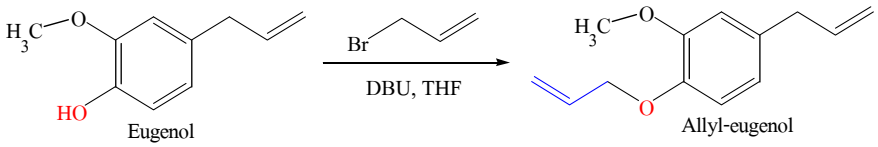
4.2 *O*-allyl compounds

O-allyl compounds: allyl-eugenol, allyl-methylparaben and allyl-nitrophenol

^{1}H-NMR spectrum of *O*-allyl compound indicated the amount of proton (H) present in synthesized compounds. ^{13}C-NMR of *O*-allyl compound was obtained and indicated the amount of carbon (C) and its environment in synthesized compounds.

4.2.1 Allyl-eugenol

From the experimental data, the synthesis reaction of allyl-eugenol (Scheme 4.3) indicated the structure of synthetic compound which is corresponding to ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic data.



Scheme 4.3 The synthesis reaction of allyl-eugenol

This represents ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of allyl-eugenol which detected by ^{1}H-NMR spectroscopy (Figure 4.12) and compared to ^{1}H-NMR spectrum of eugenol (Figure 4.13).

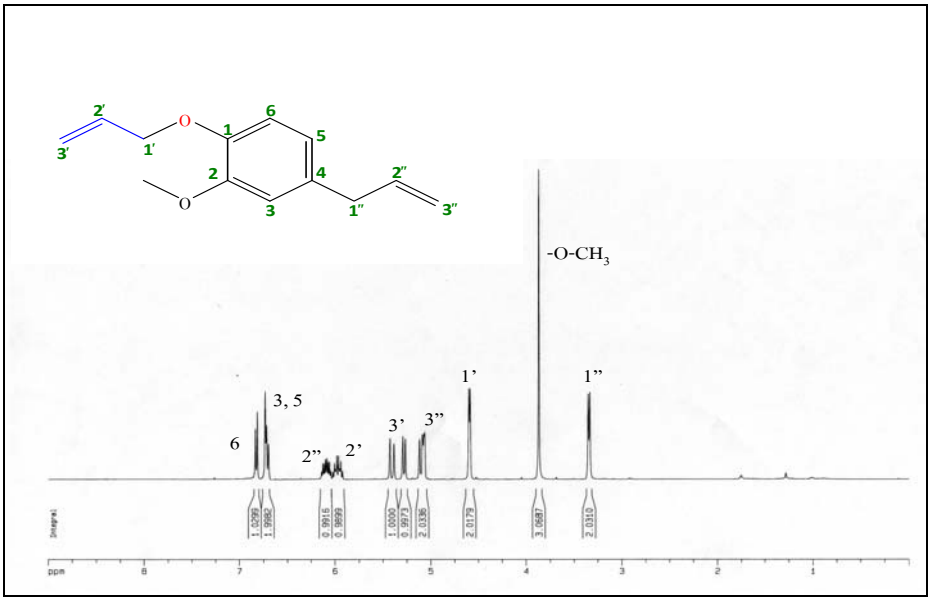


Figure 4.12 ^{1}H-NMR spectrum of allyl-eugenol

Figure 4.13 [1]H-NMR spectrum of eugenol

[1]H-NMR data indicated the proton signal of allyl-eugenol which clearly showed the chemical shift (δ) and coupling constant (Table 4.7).

Table 4.7 [1]H-NMR spectroscopic data of allyl-eugenol and eugenol

Position	δ_H (ppm)	δ_H (ppm) (Eugenol)
H-3, 5	6.72 (2H, t, *J* = 3.4 Hz)	6.67
H-6	6.83 (1H, d, *J* = 7.5 Hz)	6.82
H-1’	4.65 (2H, d, J = 6.23 Hz)	-
H-2’	6.00 (1H, m)	-
H-3’	5.28 (1H, dd, *J* = 10.5 Hz)	-
	5.40 (1H, dd, *J* = 17.1 Hz)	
H-1’’	3.35 (2H, d, *J* = 6.7 Hz)	3.29
H-2’’	6.10 (1H, m)	5.91
H-3’’	5.09 (2H, dd, *J* = 8.12 Hz)	5.04
-O-CH_3	3.87 (3H, s)	3.81
1-O*H*	-	5.53

The ^{1}H-NMR spectrum and spectroscopic data indicated allyl signal at δ_H 4.65 (2H, d, *J* = 6.23 Hz, *H*-1'), δ_H 6.00 (1H, m, *H*-2'), δ_H 5.28 (1H, dd, *J* = 10.5, *H*-3'), δ_H 5.40 (1H, dd, *J* = 17.1 Hz, *H*-3'), δ_H 3.35 (2H, d, *J* = 6.7 Hz, *H*-1''), δ_H 6.10 (1H, m, *H*-3''), aromatic proton at δ_H 6.72 (2H, t, *J* = 3.4 Hz, *H*-3, 5) δ_H 6.83 (1H, d, *J* = 7.5 Hz, *H*-6) and -*O*-methyl proton at δ_H 3.87 (3H, s). ^{1}H-NMR spectroscopic data confirmed the structure of allyl-eugenol (Figure 4.14).

Confirmation the result by comparison ^{1}H-NMR specetroscopic data of allyl-eugenol with eugenol found that conform.

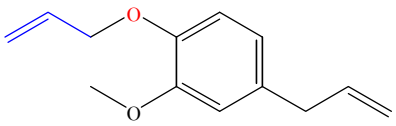


Figure 4.14 Structure of allyl-eugenol, 4-allyl-1-allyloxy-2-methoxy-benzene

This reported ^{13}C-NMR (500 MHz, $CDCl_3$) spectrum of allyl-thymine (A) which detected by ^{13}C-NMR spectroscopy (Figure 4.15), and compared to ^{13}C-NMR spectrum of eugenol (Figure 4.16) [18].

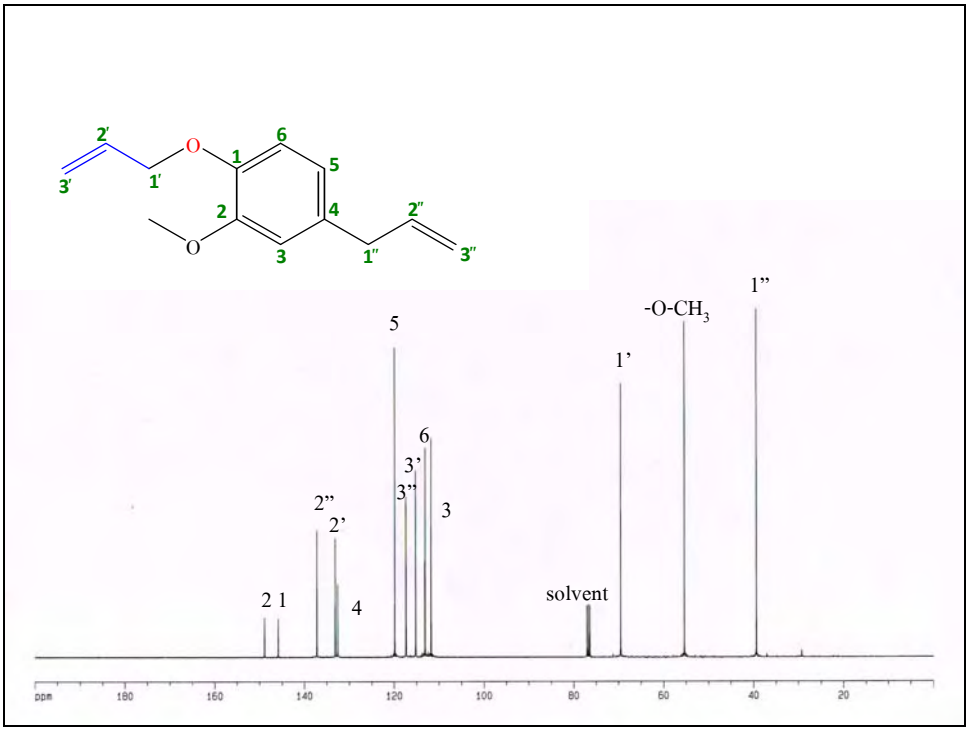


Figure 4.15 ^{13}C-NMR spectrum of allyl-eugenol

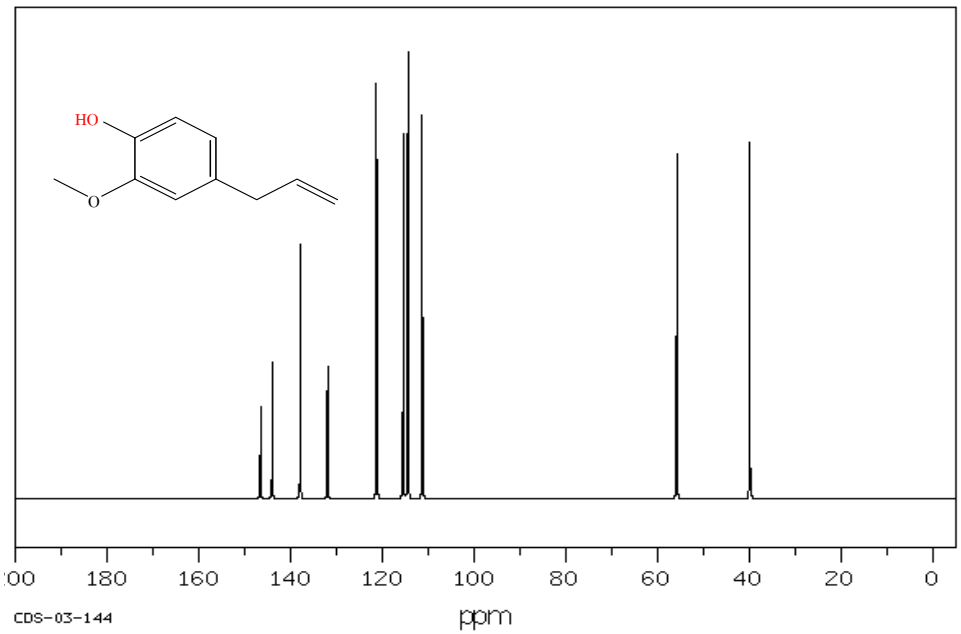


Figure 4.16 ^{13}C-NMR spectrum of eugenol [18]

This represents ^{13}C-NMR data indicating the carbon signal of allyl-eugenol which showed the result as chemical shift ( ), and compared to ^{13}C-NMR spectroscopic data of eugenol (Table 4.8).

Table 4.2 ^{13}C-NMR spectroscopic data of allyl-eugenol and eugenol [18]

Position	δ_C (ppm)	δ_C (ppm) (Eugenol)
C-1	145.86	144.03
C-2	148.94	146.60
C-3	111.77	114.46
C-4	132.61	131.94
C-5	119.91	121.26
C-6	113.12	115.49
C-1’	69.55	-
C-2’	133.12	-
C-3’	115.22	-
C-1’’	39.40	39.92
C-2’’	137.24	137.91
C-3’’	117.38	111.28
O-*C*H$_3$	55.41	55.84

The spectrum of allyl-eugenol in $CDCl_3$ showed thirteen carbon signals which consisted of one methyl, four methylenes, five methines and three quaternary carbons including two olefinic quaternary carbon.

Confirmation the result by comparison ^{13}C-NMR spectroscopic data of allyl-eugenol with eugenol found that conform.

Finally, the structure of allyl-eugenol was confirmed by mass spectrometry (Figure 4.17). Mass spectra indicated base peak $[M + Na]^+$ at 227.1052 which confirmed the molecular weight of synthetic product as ally-eugenol, (204.26 g/mol, calculation).

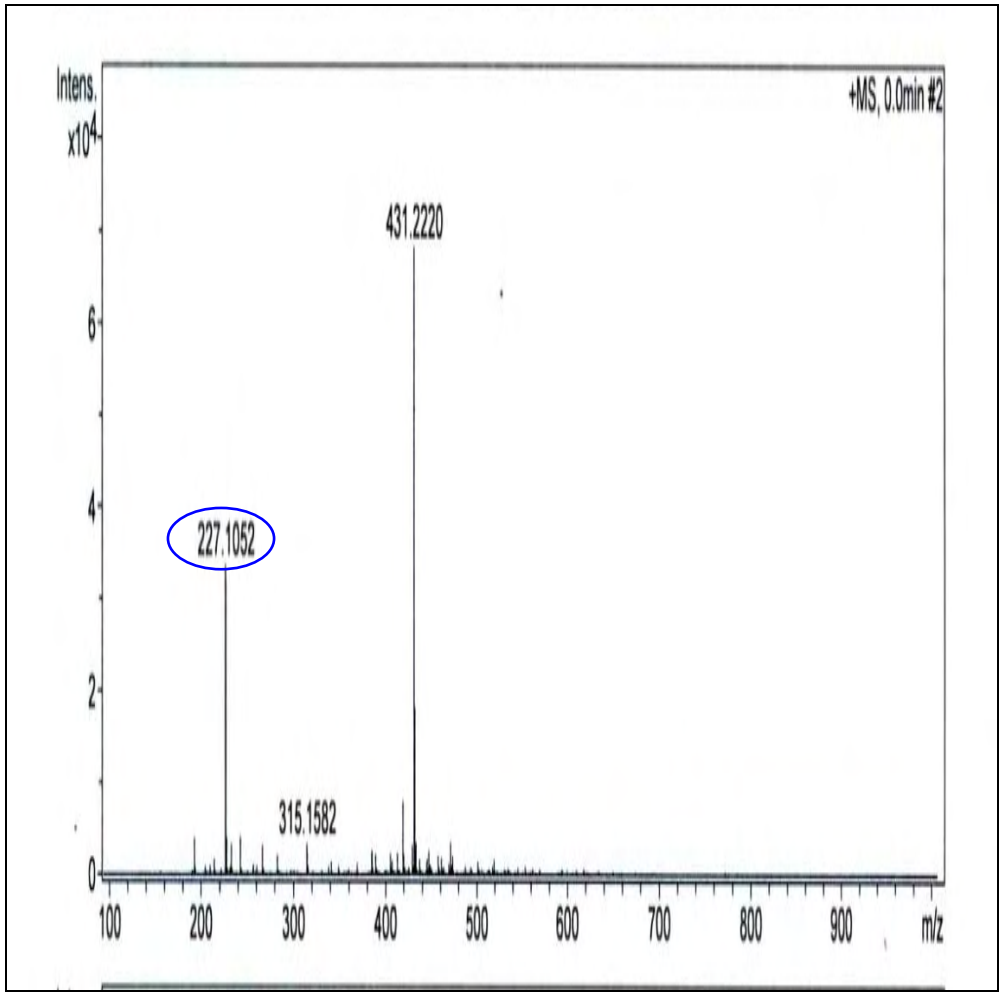
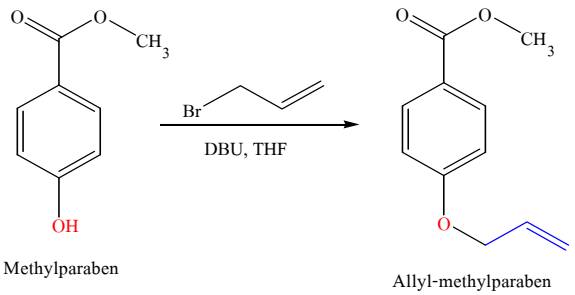


Figure 4.17 Mass spectroscopic data of allyl-eugenol, high resolution report

4.2.2 Allyl-methylparaben

From the experimental data, the synthesis reaction of allyl-methylparaben (Scheme 4.4) indicated the structure of synthetic compound which is corresponding to ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic data.



Scheme 4.4 The synthesis reaction of allyl-methylparaben

This represents ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of allyl-methylparaben which detected by ^{1}H-NMR spectroscopy (Figure 4.18), and compared to ^{1}H-NMR spectrum of methylparaben (Figure 4.19).

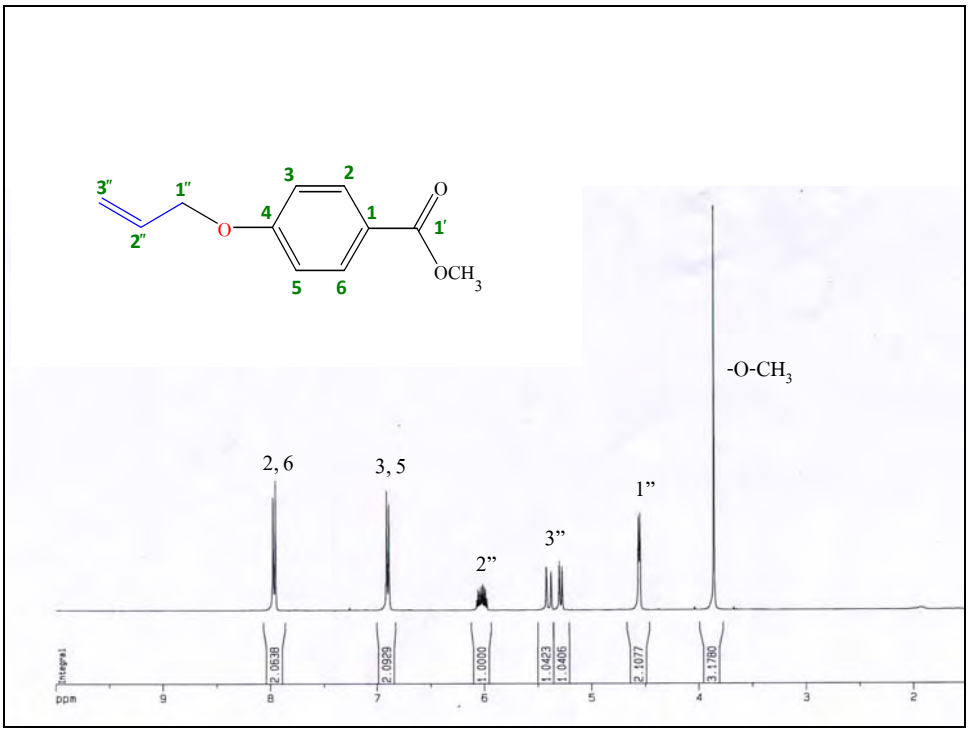


Figure 4.18 ^{1}H-NMR spectrum of allyl-methylparaben

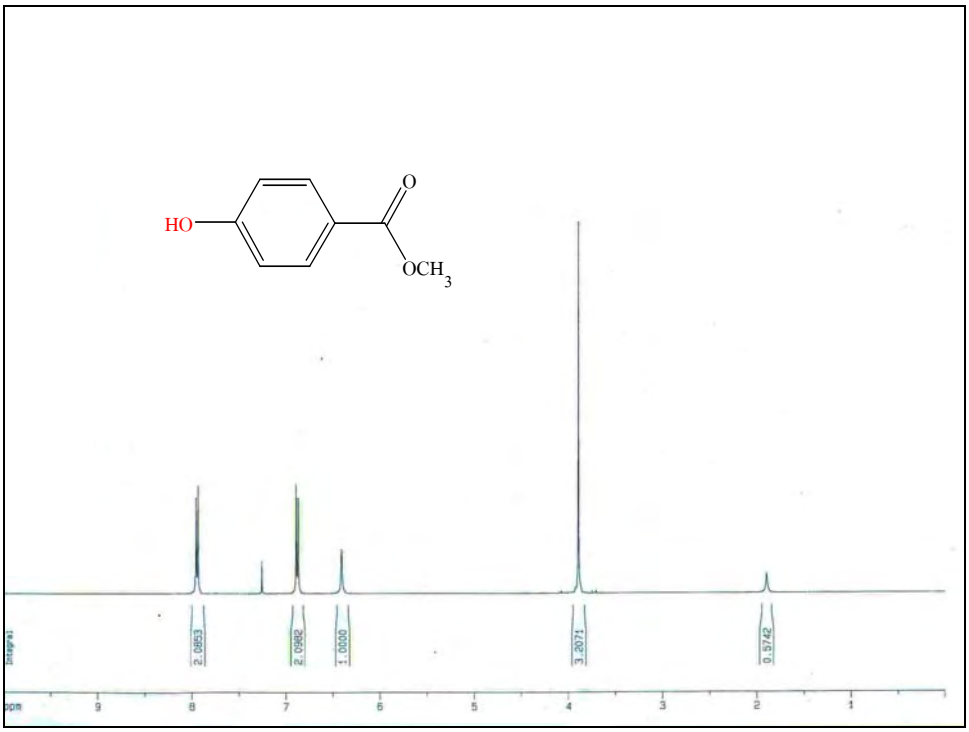


Figure 4.19 ^{1}H-NMR spectrum of methylparaben

^{1}H-NMR data indicated the proton signal of allyl-methylparaben which clearly showed the chemical shift (δ) and coupling constant (Table 4.9).

Table 4.9 ^{1}H-NMR spectroscopic data of allyl-methylparaben and methylparaben

Position	δ_H (ppm)	δ_H (ppm) (Methylparaben)
H-2, 6	7.97 (2H, d, *J* = 7.5 Hz)	7.84
H-3, 5	6.90 (2H, d, *J* = 8.9 Hz)	6.88
H-1''	4.55 (2H, d, *J* = 3.9 Hz)	-
H-2''	6.02 (1H, m)	-
H-3''	5.28 (1H, dd, *J* = 10.4 Hz)	-
	5.40 (1H, d, *J* = 17.4 Hz)	
-O-C*H*$_3$	3.85 (3H, s)	3.80
4-O*H*	-	10.3

The ^{1}H-NMR spectrum and spectroscopic data indicated allyl signal at δ_H 4.55 (2H, d, J = 3.9 Hz, H-1''), δ_H 6.02 (1H, m, H-2''), δ_H 5.28 (1H, dd, J = 10.4, H-3''), 5.40 (1H, d, J = 17.4 Hz, H-3'') aromatic proton at δ_H 7.97 (2H, d, J = 7.5 Hz, H-2, 6), δ_H 6.90 (2H, d, J = 8.9 Hz, H-3, 5) and -O-methyl proton at δ_H 3.85 (3H, s). ^{1}H-NMR spectroscopic data confirmed the structure of allyl-eugenol (Figure 4.20).

Confirmation the result by comparison ^{1}H-NMR specetroscopic data of allyl-methylparaben with methylparaben found that conform.

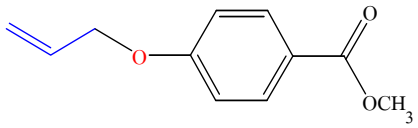


Figure 4.20 Structure of allyl-methylparaben, 4-allyloxy-benzoic acid methyl ester

This reported ^{13}C-NMR (500 MHz, $CDCl_3$) spectrum of allyl-methylparaben which detected by ^{13}C-NMR spectroscopy (Figure 4.21), and compared to ^{13}C-NMR spectrum of methylparaben (Figure 4.22) [19].

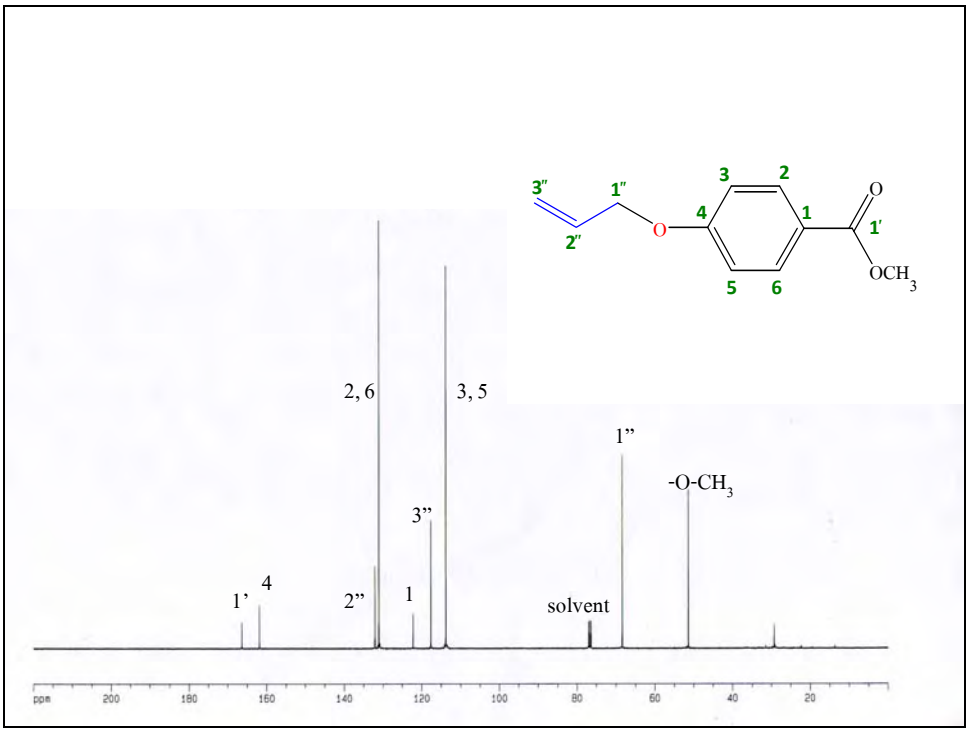


Figure 4.21 ^{13}C-NMR spectrum of allyl-methylparaben

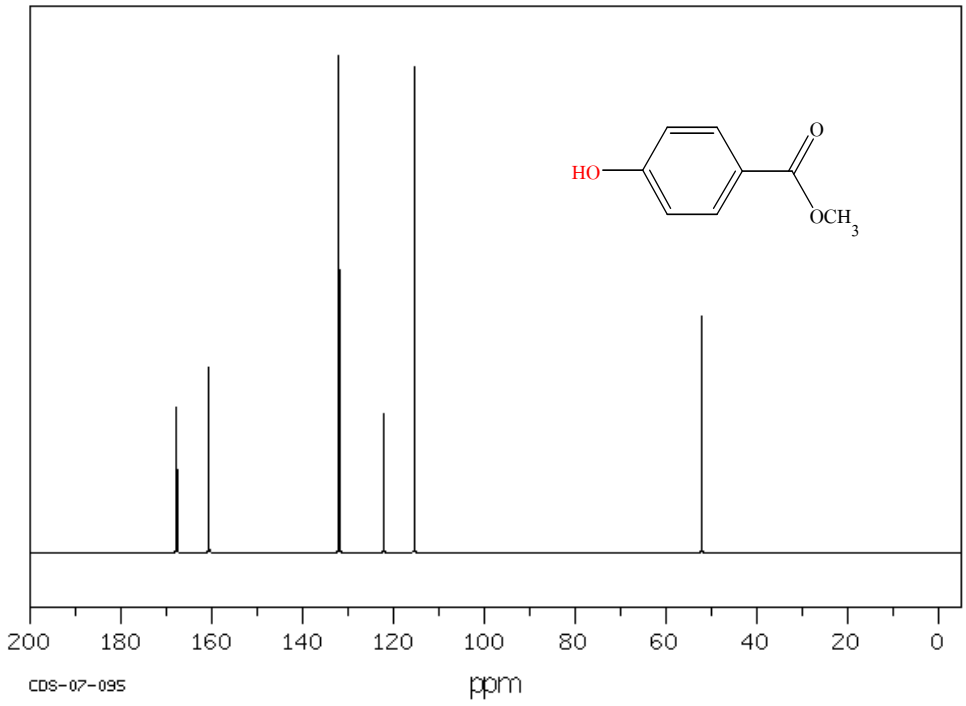


Figure 4.22 ^{13}C-NMR spectrum of methylparaben [19]

This represents ^{13}C-NMR data indicating the carbon signal of allyl-methyl-paraben which showed the result as chemical shift (δ), and compared to ^{13}C-NMR spectroscopic data of methylparaben (Table 4.10).

Table 4.10 ^{13}C-NMR spectroscopic data of allyl-methylparaben and methylparaben [19]

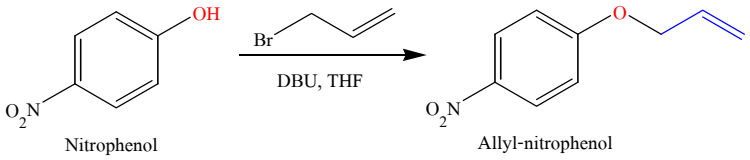
Position	δ_C (ppm)	δ_C (ppm) (Methylparaben)
C-1	122.23	122.11
C-2, 6	131.11	131.98
C-3, 5	117.63	115.39
C-4	161.87	160.62
C-1’	166.35	167.72
C-2’’	132.11	-
C-1’’	68.36	-
C-3’’	117.79	-
-O-*C*H$_3$	51.73	52.12

The spectrum of allyl-methylparaben in $CDCl_3$ showed eleven carbon signals which consisted of one methyl, two methylenes, five methines which consisted of four aromatic and one olefinic methines. and three quaternary carbons including two aromatic quaternary carbon.

Confirmation the result by comparison ^{13}C-NMR spectroscopic data of allyl-methylparaben with methylparaben found that conform.

4.2.1 Allyl-nitrophenol

From the experimental data, the synthesis reaction of allyl-nitrophenol (Scheme 4.5) indicated the structure of synthetic compound which is corresponding to ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic data.



Scheme 4.5 The synthesis reaction of allyl-nitrophenol

This represents ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of allyl-nitrophenol which detected by ^{1}H-NMR spectroscopy (Figure 4.23), and compared to ^{1}H-NMR spectrum of nitrophenol (Figure 4.24).

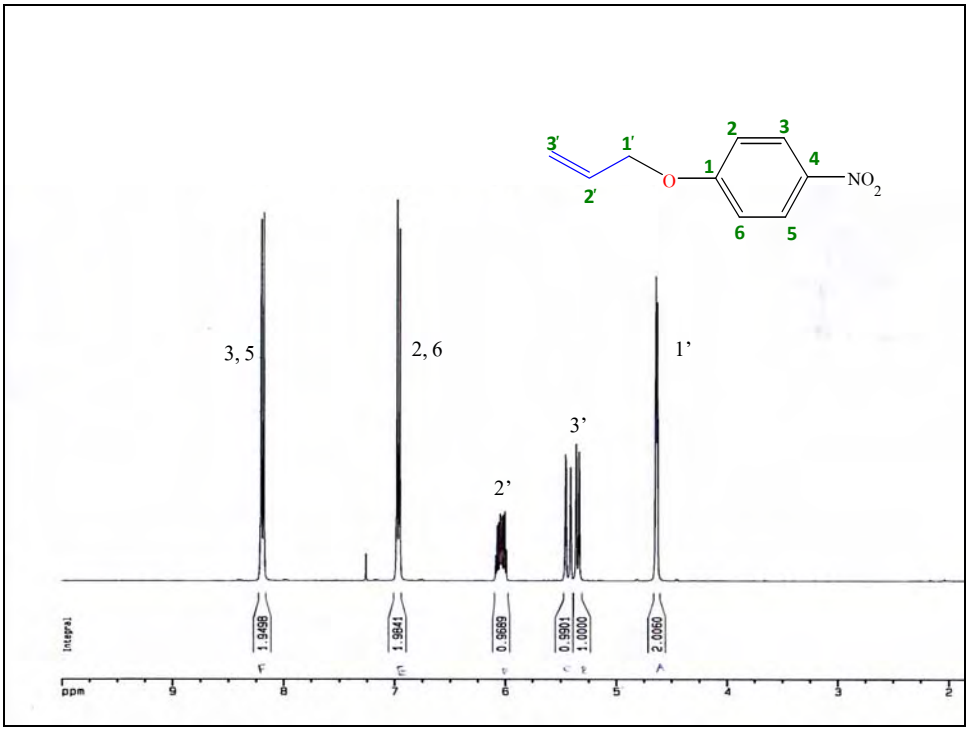


Figure 4.23 ^{1}H-NMR spectrum of allyl-nitrophenol

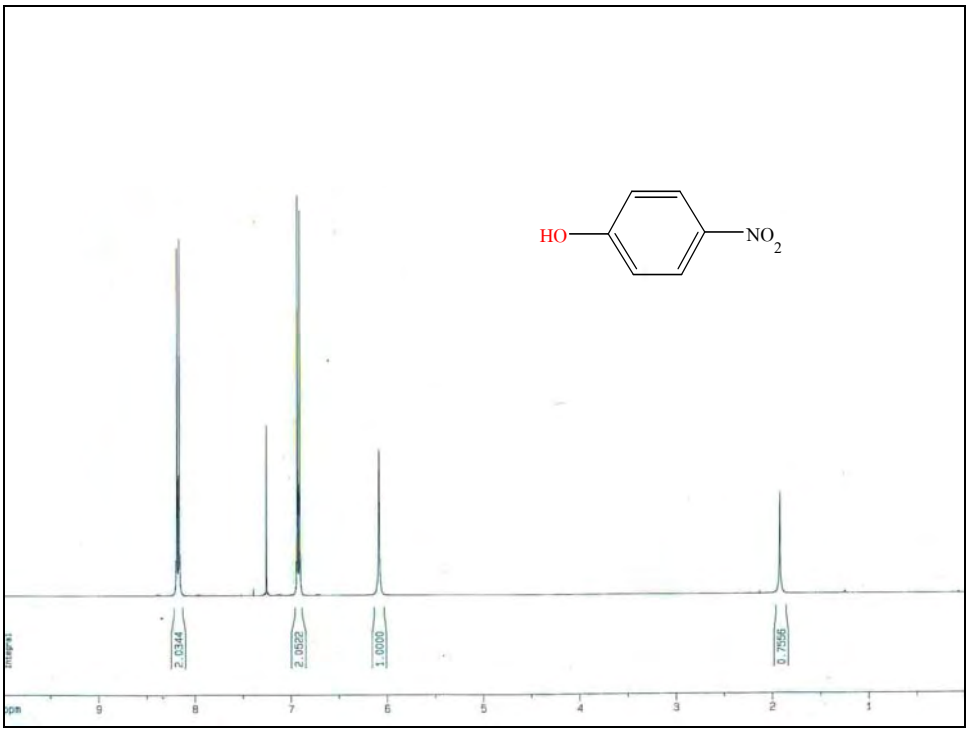


Figure 4.24 ^{1}H-NMR spectrum of nitrophenol

^{1}H-NMR data indicated the proton signal of allyl-nitrophenol which clearly showed the chemical shift (δ) and coupling constant (Table 4.11).

Table 4.11 ^{1}H-NMR spectroscopic data of allyl-nitrophenol and nitrophenol

Position	δ_H (ppm)	δ_H (ppm) (Nitrophenol)
H-2, 6	6.97 (2H, d, J = 9.1 Hz)	6.96
H-3, 5	8.19 (2H, d, J = 9.1 Hz)	8.14
H-1’	4.64 (2H, d, J = 5.2 Hz)	-
H-2’	6.04 (1H, m)	-
H-3’	5.35 (1H, d, J = 16.5 Hz)	-
	5.44 (1H, d, J = 17.3 Hz)	
1-O*H*	-	11.11

The ^{1}H-NMR spectrum and spectroscopic data indicated allyl signal at δ_H 4.64 (2H, d, J = 5.2 Hz, H-1'), δ_H 6.04 (1H, m, H-2'), δ_H 5.35 (1H, d, J = 16.5, H-3') and δ_H 5.44 (1H, d, J = 17.3 Hz), aromatic proton at δ_H 6.97 (2H, d, J = 9.1 Hz, H-2, 6) and δ_H 8.19 (2H, d, J = 9.1 Hz, H-3, 5). ^{1}H-NMR spectroscopic data confirmed the structure of allyl-nitrophenol (Figure 4.25).

Confirmation the result by comparison ^{1}H-NMR specetroscopic data of allyl-nitrophenol with nitrophenol found that conform.

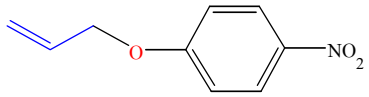


Figure 4.25 Structure of allyl-nitrophenol, 1-allyloxy-4-nitro-benzene

This reported ^{13}C-NMR (500 MHz, $CDCl_3$) spectrum of allyl-nitrophenol which detected by ^{13}C-NMR spectroscopy (Figure 4.26), and compared to ^{13}C-NMR spectrum of nitrophenol (Figure 4.27) [20].

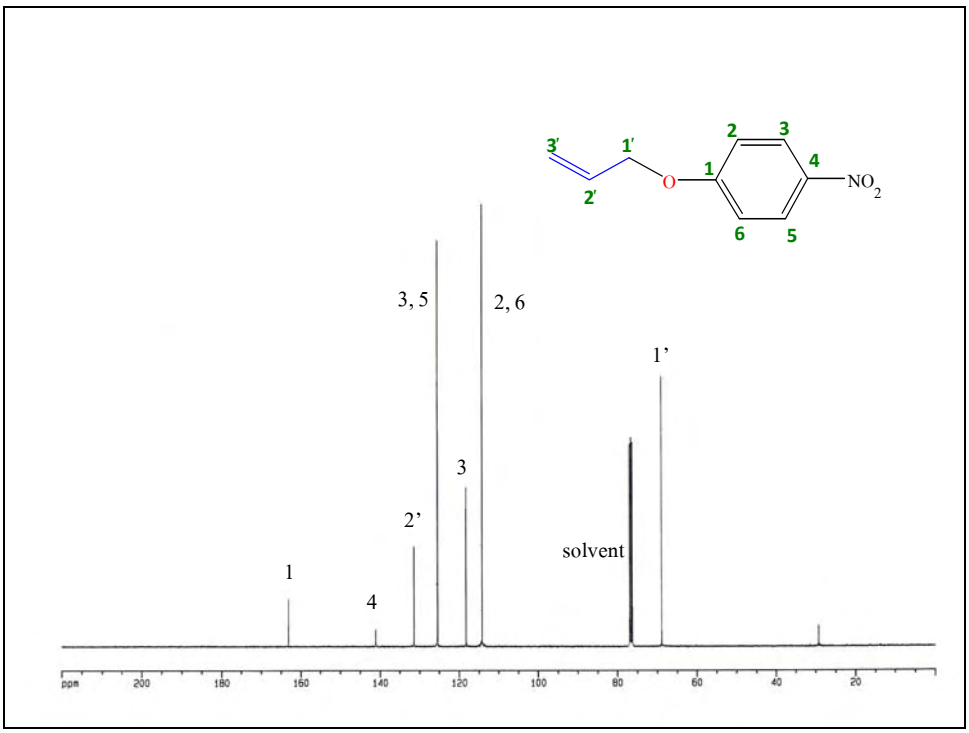


Figure 4.26 ^{13}C-NMR spectrum of allyl-nitrophenol

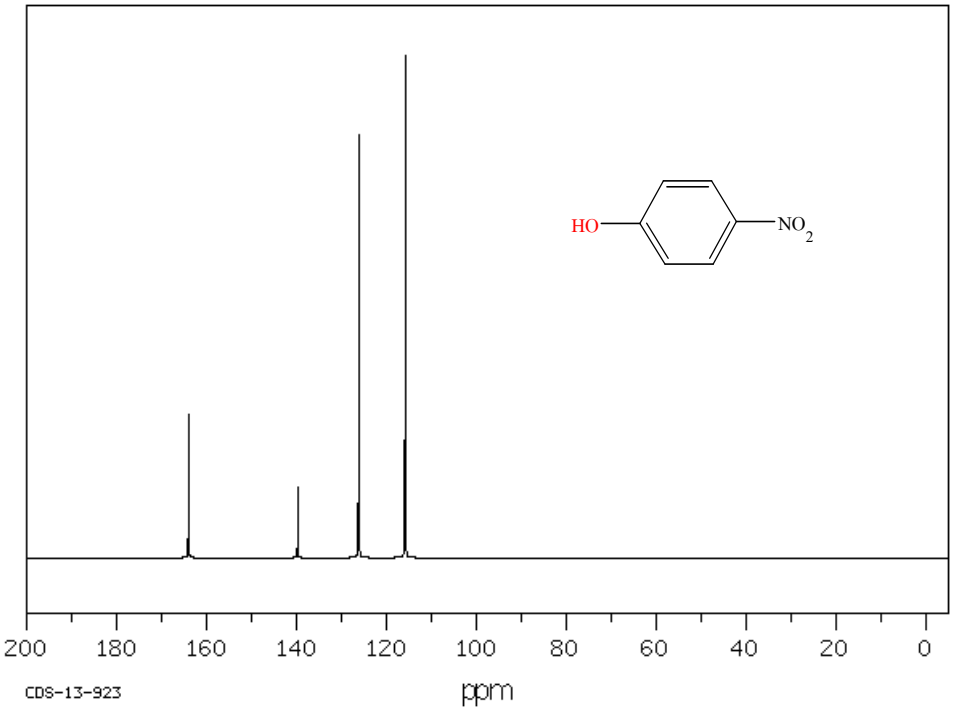


Figure 4.27 ^{13}C-NMR spectrum of nitrophenol [20]

This represents ^{13}C-NMR data indicating the carbon signal of allyl-nitrophenol which showed the result as chemical shift (δ), and compared to ^{13}C-NMR spectroscopic data of nitrophenol (Table 4.11).

Table 4.11 ^{13}C-NMR spectroscopic data of allyl-nitrophenol and nitrophenol [20]

Position	δ_C (ppm)	δ_C (ppm) (Nitrophenol)
C-1	163.14	164.03
C-2, 6	114.23	115.83
C-3, 5	125.47	126.18
C-4	141.10	129.73
C-1’	68.96	-
C-2’	131.42	-
C-3’	118.27	-

The spectrum of allyl-nitrophenol in $CDCl_3$ showed nine carbon signals which consisted of two methylenes, five methines and two quaternary carbons including two aromatic quaternary carbons.

Confirmation the result by comparison ^{13}C-NMR spectroscopic data of allyl-nitrophenol with nitrophenol found that conform.

Finally, the structure of allyl-nitrophenol was confirmed by mass spectrometry (Figure 4.28). Mass spectra indicated base peak $[M + Na]^+$ at 202.0470 which confirmed the molecular weight of synthetic product as ally-nitrophenol, (179.17 g/mol, calculation).

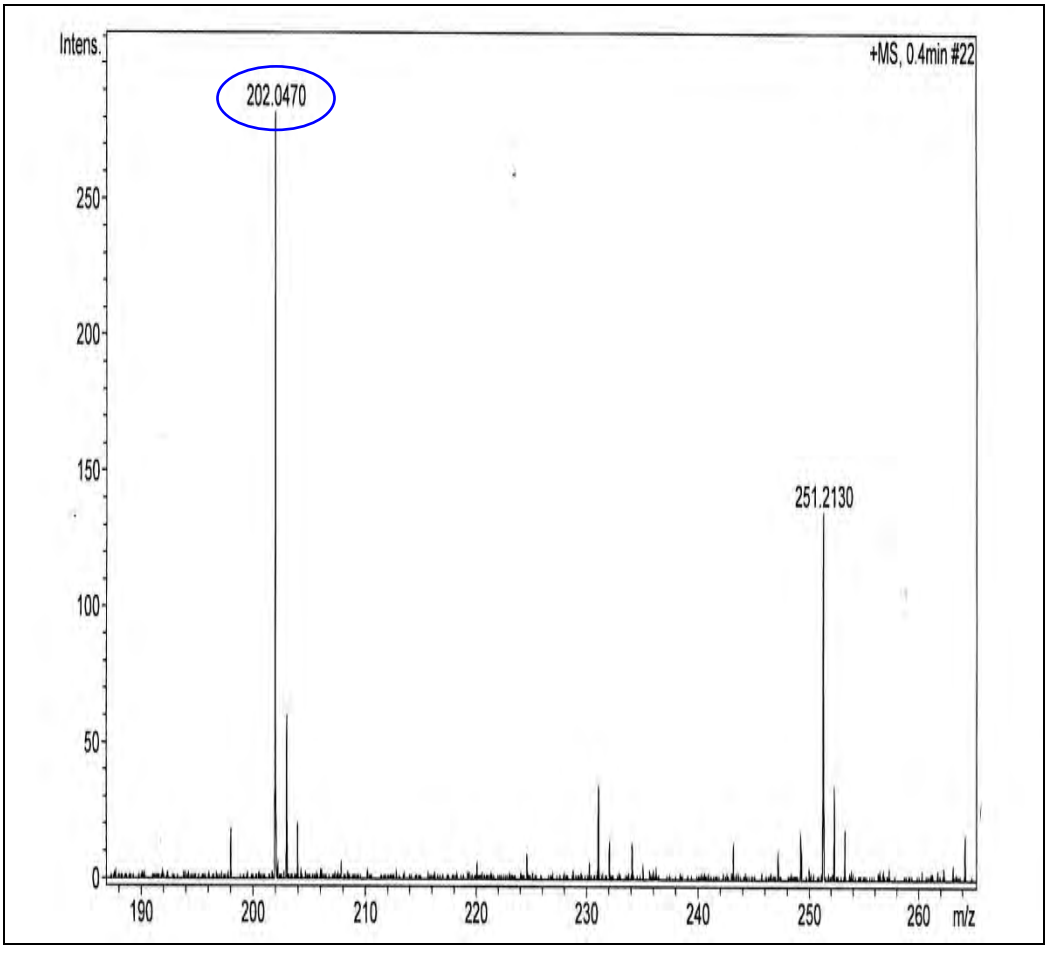
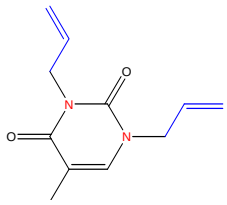
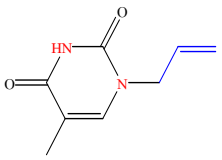
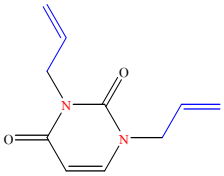
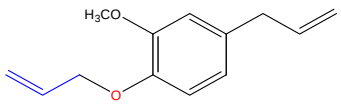
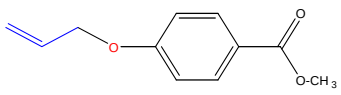
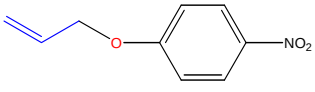


Figure 4.28 Mass spectroscopic data of allyl-nitrophenol, high resolution report

4.3 Percent yield

Synthetic compounds, allyl-thymine (A), allyl-thymine (B), allyl-uracil, allyl-eugenol, allyl-methylparaben and allyl-nitophenol there are different yield depend on starters as reacted.

Table 16: The percent yield of synthetic compounds

Synthetic compounds		%yield (Isolate)
***N*-allyl compounds**	Allyl-thymine (A) 	72.64
	Allyl-thymine (B) 	20.45
	Allyl-uracil (A) 	54.32
***O*-allyl compounds**	Allyl-eugenol 	6.06
	Allyl-methylparaben 	43.91
	Allyl-nitrophenol 	21.53

Ratio of allyl-thymine (A) with allyl-thymine (B) was 3.5: 1, allyl-uracil (A) there is one compounds but when through the synthesis and was checked by TLC found that there are two spot, we assume that there are two compounds but through the purification found only allyl-uracil (B). %yield of allyl-eugenol was low because in the structure there is allyl group which sensitive reaction than hydroxy group (Figure 4.29). %yield of Allyl-nitrophenol was very low because in the structure there is nitro group which reactivity than hydroxy group (Figure 4.30).

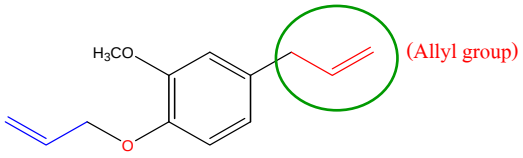


Figure 4.29 The structure of allyl-eugenol

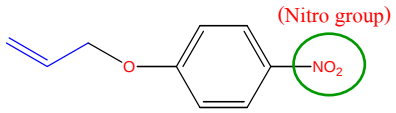


Figure 3.30 The structure of allyl-nitrophenol

CHAPTER 5

CONCLUSION

This research successfully discovered mild and facile approach for *N*- and/or *O*-allylation of alcoholic and amide substrates, e.g. eugenol, methylparaben, nitrophenol, uracil, thymine. The allylic reaction utilized the reaction between corresponding alcoholic and/or amide substrates catalyzed by DBU. After the optimizations, the reaction was found to give good yields of corresponding allylic products. It is interesting that the allylation of several nucleosides was achieved under the optimized condition.

Suggestion

During the addition of DBU into the reaction, heat was subsequently generated indicating the reaction is exothermic. The heat generated from the reaction might limit the use of heat-labile substrates. Therefore, the reaction is needed to crash in the ice-bath during the DBU addition.

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Appendix

APPENDIX A.

***N*-allylation compounds**

This part showed ^{1}H-NMR spectrum of allyl-thymine (A) (figure 1A), allyl-thymine (B) (figure 2A) and allyl-uracil (A) (figure 3A) which was zoomed. The zoom was showed clearly the singlet (s), doublet (d), triplet (t), doublet of doublet (dd) and multiplex (m). This value indicated the specific characteristic of protons by base on the number of protons on the side for display.

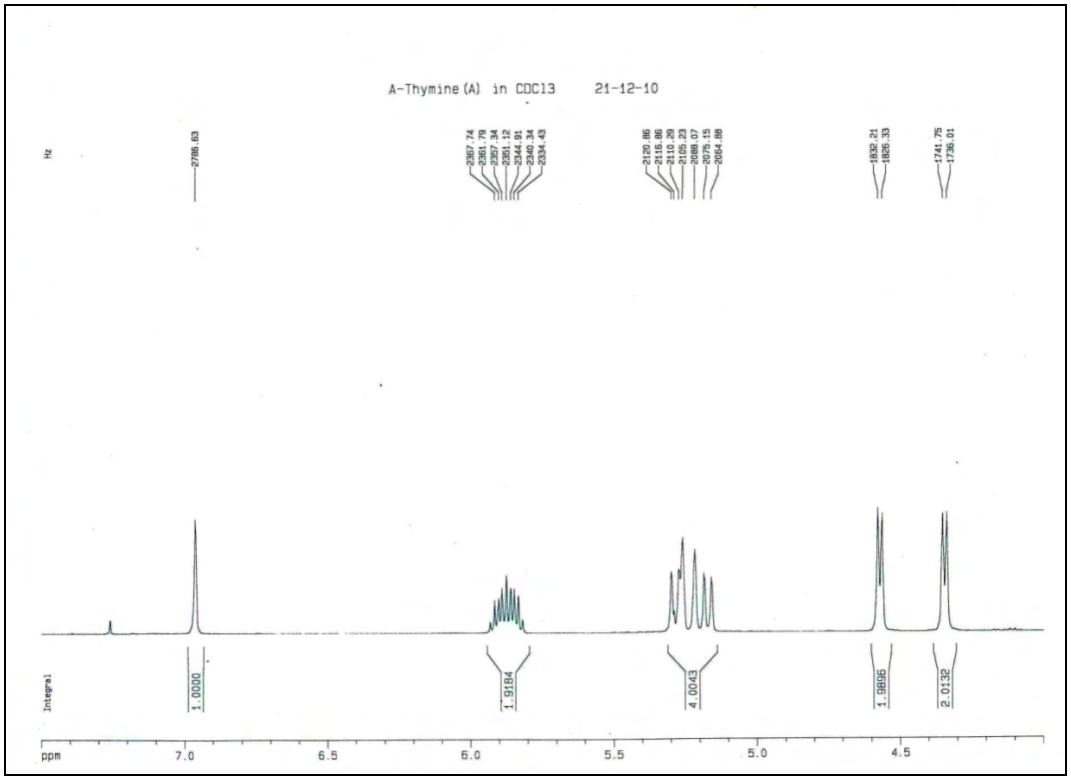


Figure 1A ^{1}H-NMR spectrum of allyl-thymine (A), 0.2 g: 5 ml deuterium oxide ($CDCl_3$)

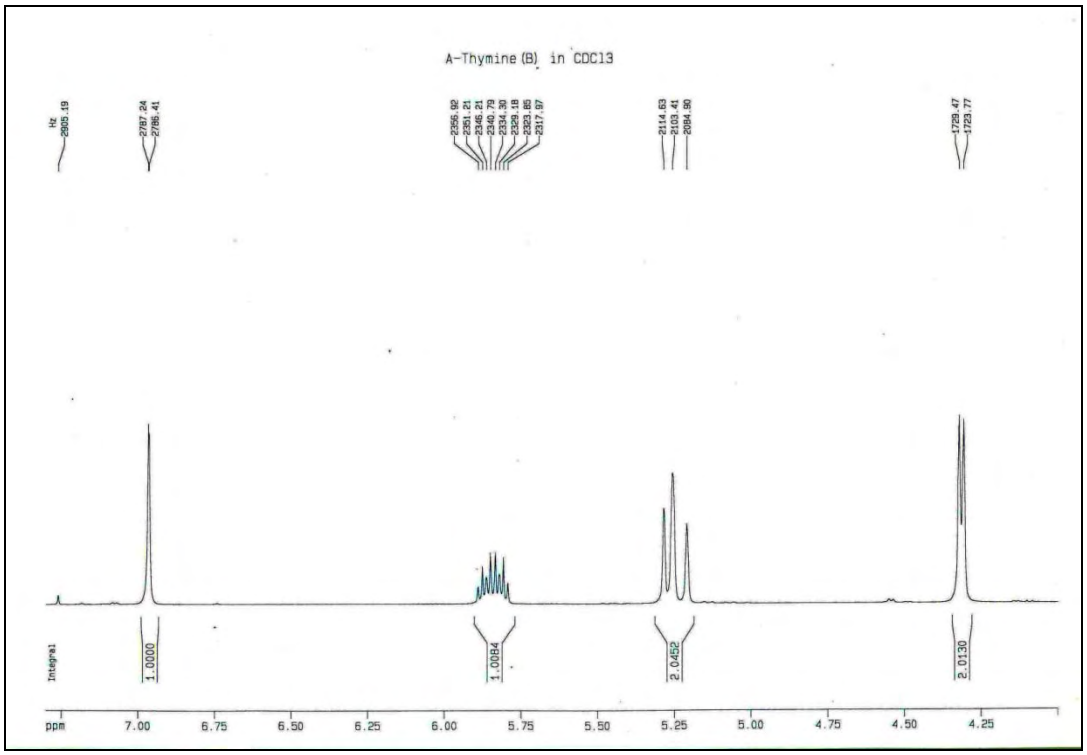


Figure 2A ^{1}H-NMR spectrum of allyl-thymine (B), 0.2 g: 5 ml deuterium oxide ($CDCl_3$)

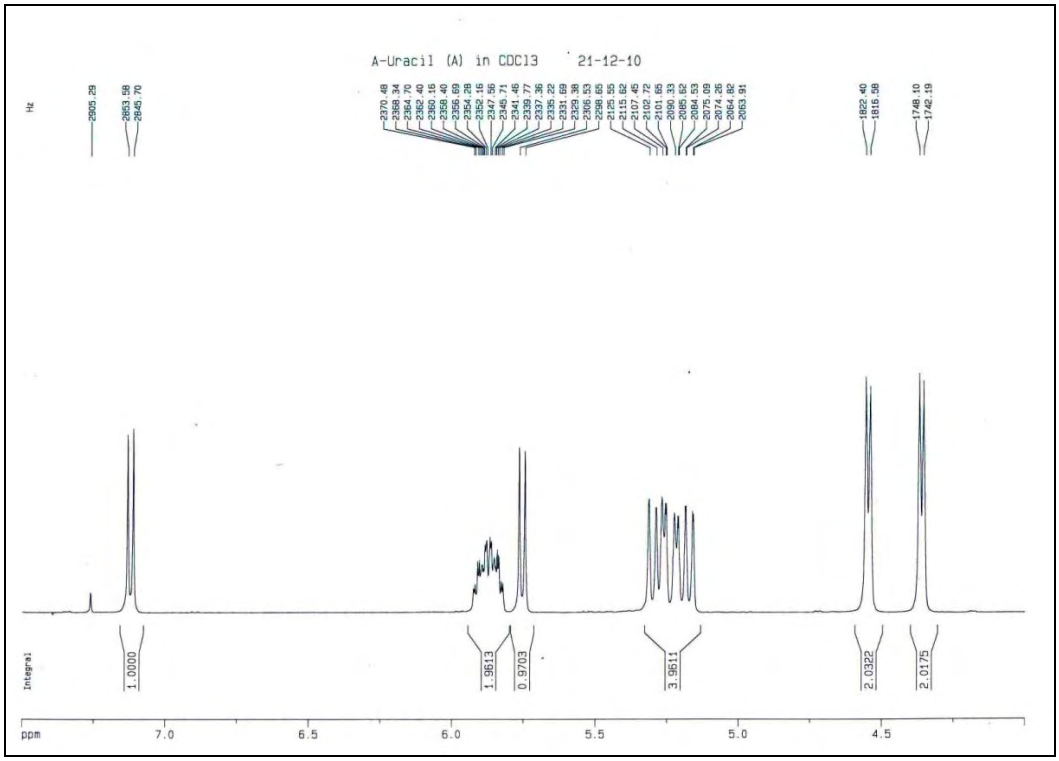


Figure 3A ^{1}H-NMR spectrum of allyl-uracil (A), 0.2 g: 5 ml deuterium oxide ($CDCl_3$)

APPENDIX B.

O-allyl compounds

This part showed ^{1}H-NMR spectrum of allyl-ugenol (figure 1B), allyl-methylparaben (figure 2B) and allyl-nitrophenol (figure 3B) which showed detail like the appendix A.

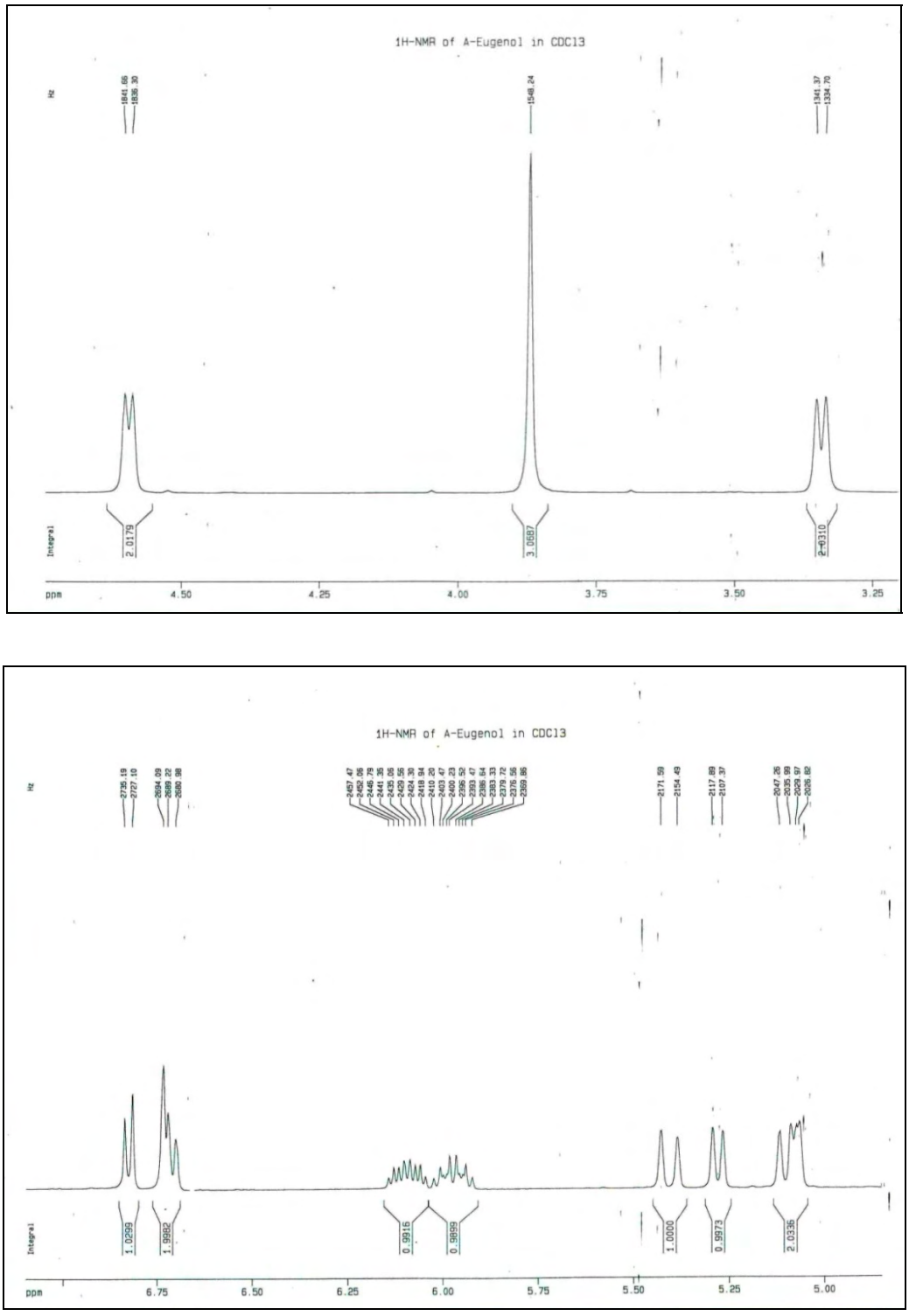


Figure 1B ^{1}H-NMR spectrum of allyl-eugenol, 0.2 g: 5 ml deuterated chloroform ($CDCl_3$)

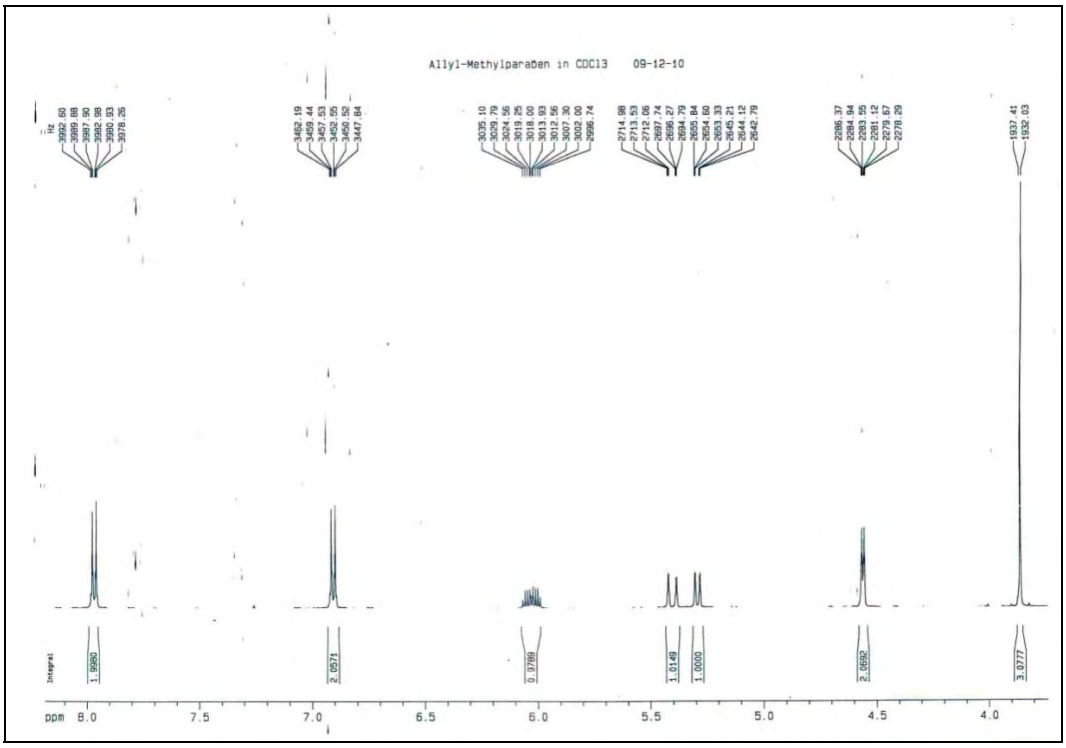


Figure 2B ^{1}H-NMR spectrum of allyl-Methylparaben, 0.2 g: 5 ml deuterated chloroform ($CDCl_3$)

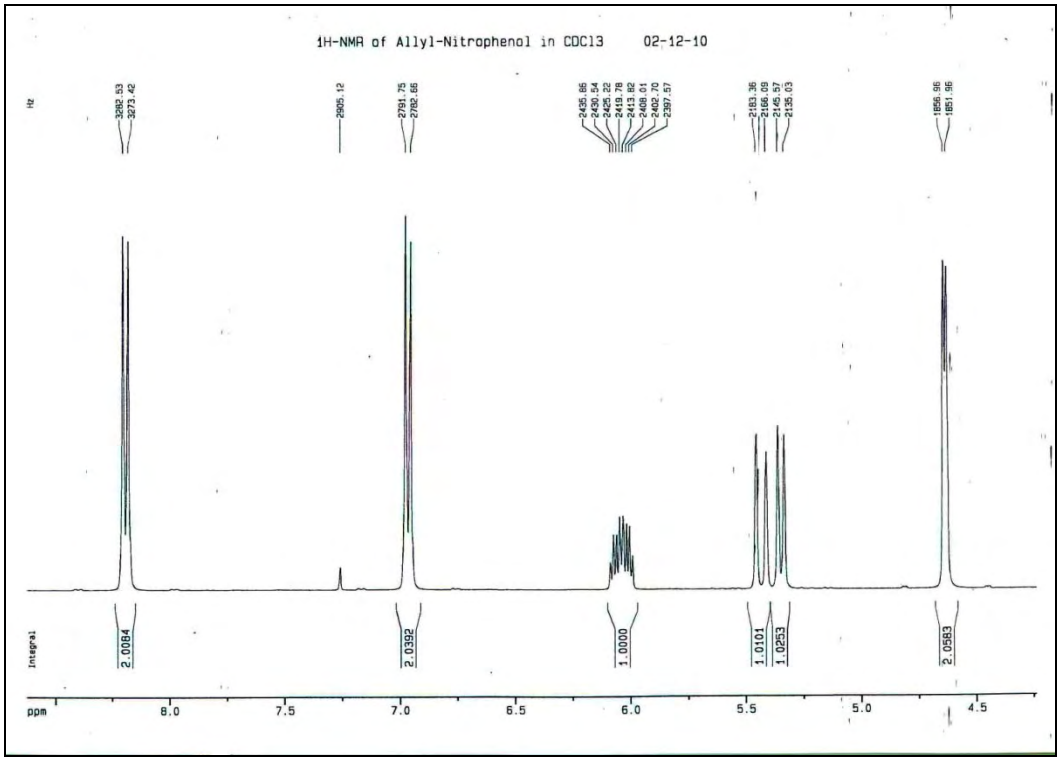
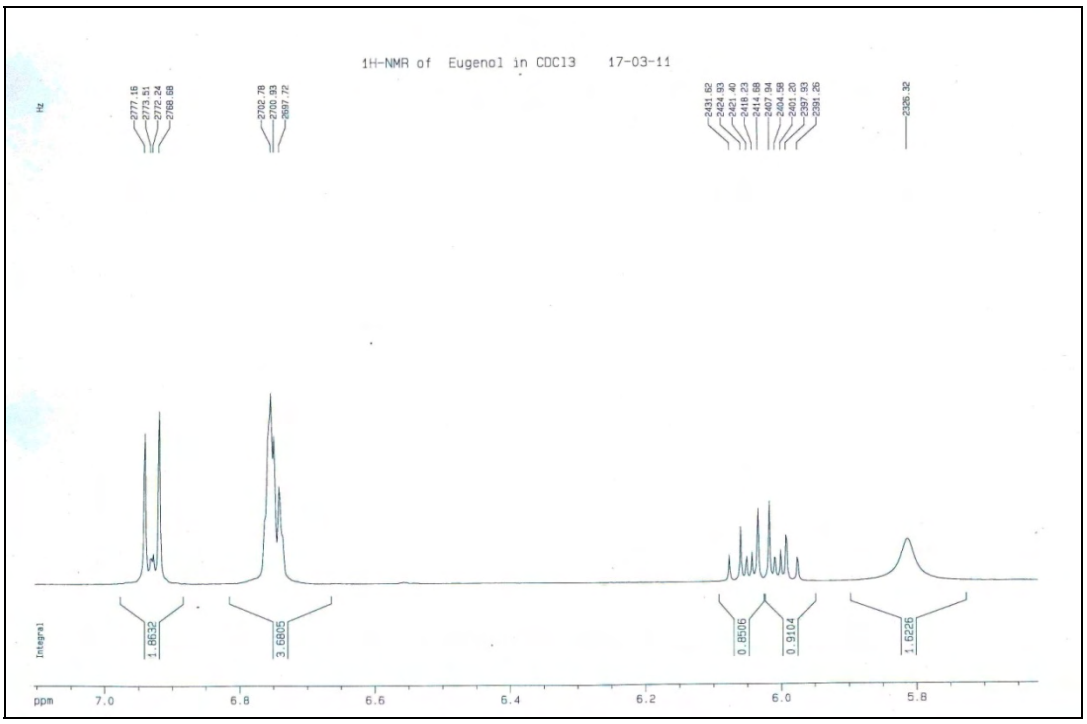


Figure 3B ^{1}H-NMR spectrum of allyl-nitrophenol, 0.2 g: 5 ml deuterated chloroform ($CDCl_3$)

APPENDIX C.

Starters

This part showed ^{1}H-NMR spectrum of ugenol (figure 1C), methylparaben (figure 2C) and nitrophenol (figure 3C) which showed detail like the appendix A.



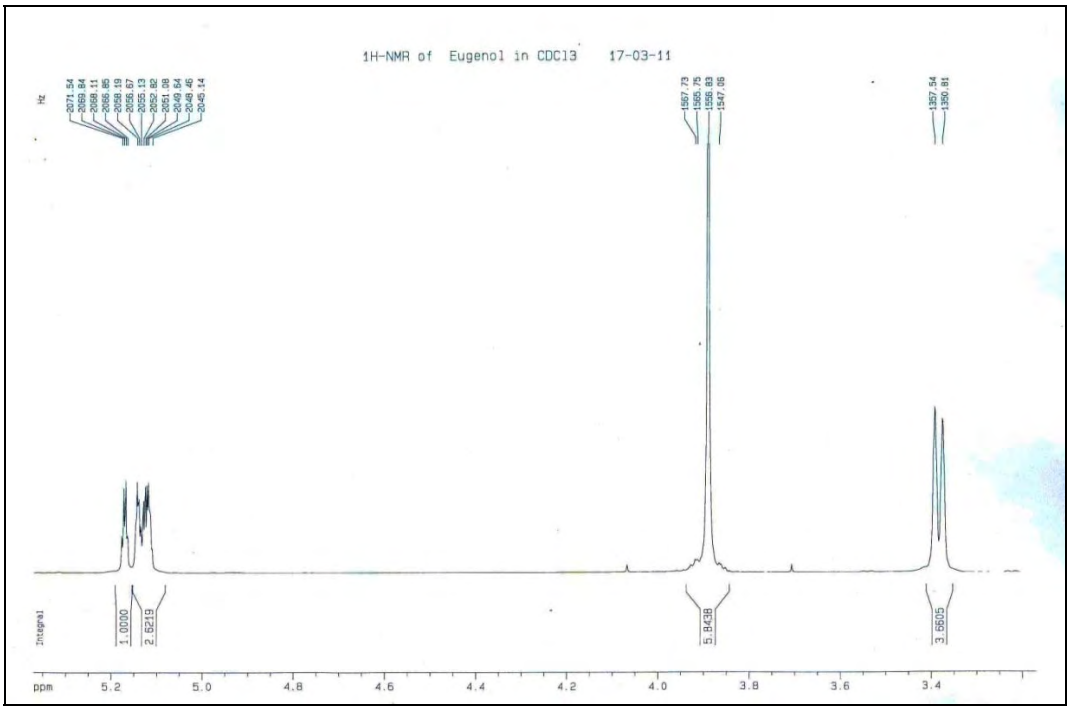


Figure 1C ^{1}H-NMR spectrum of eugenol, 0.2 g: 5 ml deuterated chloroform ($CDCl_3$)

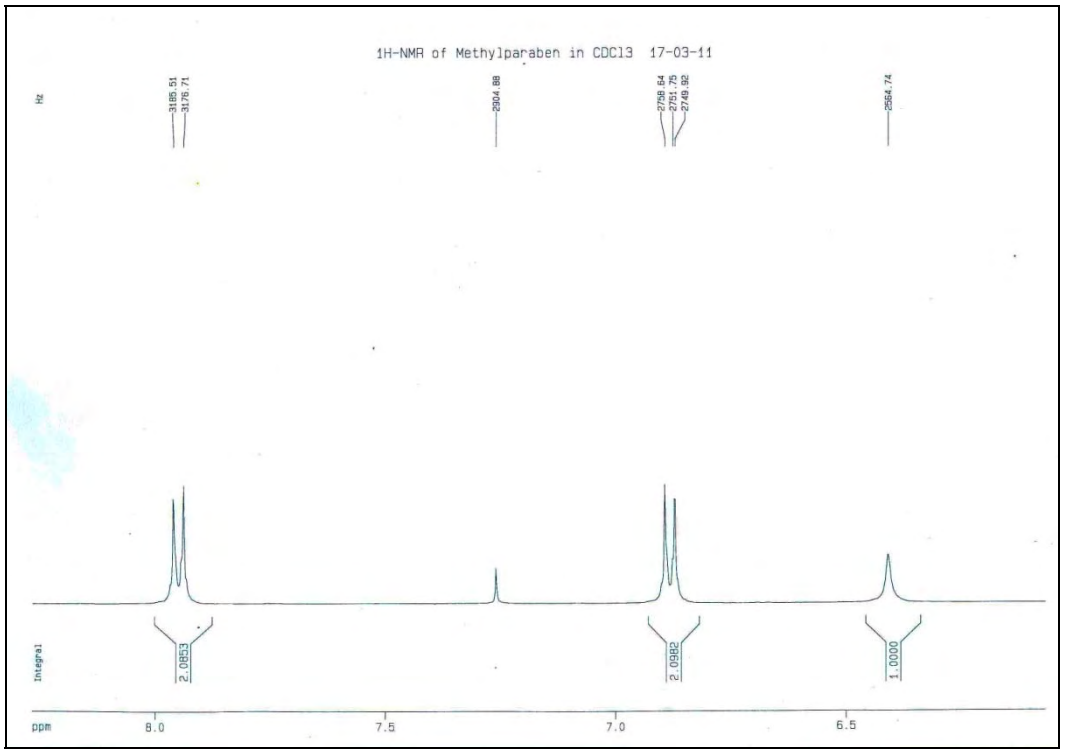


Figure 2C ^{1}H-NMR spectrum of methylparaben, 0.2 g: 5 ml deuterated chloroform ($CDCl_3$)

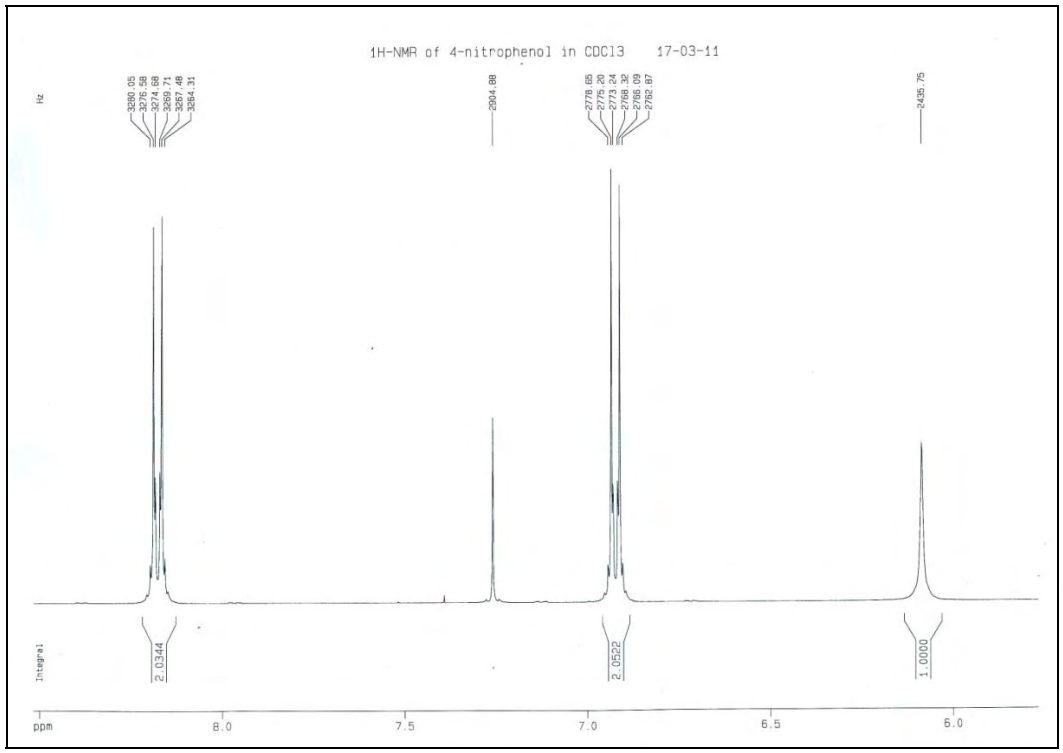


Figure 3C ^{1}H-NMR spectrum of methylparaben, 0.2 g: 5 ml deuterated chloroform ($CDCl_3$)