

The Final Year Project Report entitled "**Synthesis and Decarboxylation of 2,3-Dioxopyrrolidine-3-Carboxylic Acid Ethyl Ester**" was submitted by Syed Mohd Anuar Bin Syed Kamaruddin, in partial fulfillment of the requirements for the Degree of Bachelor of Science (Hons) Chemistry, in the Faculty of Applied Science, and was approved by

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TABLE OF CONTENT

	PAGES
ACKNOWLEDGEMENT	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	viii
ABSTRACT	ix
ABSTRAK	x
CHAPTER 1 INTRODUCTION	
1.1 Definition of organic synthesis	1
1.2 What is polyphenylene vinylene (PPV)	2
1.2.1 What is poly 2-methoxy-5-(2-ethyl-hexyloxy) polyphenylene vinylene (MEH-PPV)	3
1.2.2 Other polyphenylene vinylenes (PPV)	5
1.3 Alkylation	7
1.3.1 <i>O</i> -Alkylation	7
1.3.2 <i>C</i> -alkylation	7
1.3.3 Naming Alkyls	8
1.4 Significance of study	8
1.5 Objective	9
CHAPTER 2 LITERATURE REVIEW	
2.1 Synthesis of MEH-PPV	10
2.1.1 Synthesis of MEH-PPV using different base	11
2.2 Alkylation of MEH-PPV	11
2.3 Characterization method	12
2.3.1 Infrared Spectroscopy	12
2.3.2 NMR Spectroscopy	13
2.3.3 Elemental analysis	14
CHAPTER 3 METHODOLOGY	
3.1 Materials	15
3.2 Methods	16
3.2.1 Synthesis of methoxy-4-(2-ethylhexyloxy) benzene	16
3.3 Characterization instruments	17

CHAPTER 4 RESULT AND DISSCUSSION	
4.1 Analysis and Physical Characteristic	18
4.2 FTIR Spectroscopy	19
4.3 ¹ H NMR Spectroscopy	21
4.4 ¹³ C NMR Spectroscopy	24
CHAPTER 5 CONCLUSION AND RECOMMENDATION	
5.1 Conclusion	27
5.2 Recommendations	29
REFERENCES	30
APPENDICES	31
CURRICULUM VITAE	41

LIST OF TABLES

Table	Caption	Page
1.1	The naming of alkyls with different carbon	8
4.1	Analytical and physical characteristics data of compound	18
4.2	Important infrared spectral bands of 4-methoxyphenol and products	19
4.3	^1H NMR spectra data for 1-(heptyloxy)-4-methoxyphenol	21
4.4	^1H NMR spectra data for 1-(benzyloxy)-4-methoxybenzene	22
4.5	^1H NMR spectra data for 1-(allyloxy)-4-methoxybenzene	23
4.6	^{13}C NMR spectra data for 1-(heptyloxy)-4-methoxybenzene	24
4.7	^{13}C NMR spectra data for 1-(benzyloxy)-4-methoxybenzene	25
4.8	^{13}C NMR spectra data for 1-(allyloxy)-4-methoxybenzene	26

LIST OF FIGURES

Figures	Caption	Page
1.1	Polyphenylene vinylene (PPV) (S.J. Martin <i>et al.</i> , 1998)	2
1.2	Methoxy-4-(2-ethylhexyloxy)benzene (MEH-PPV) (C. J. Neef <i>et al.</i> , 1999)	3
1.3	(Z)-(1- <i>p</i> -tolylprop-1-ene-1,2-diyl)dibenzene(PPV-DP) (R. H. Greenham <i>et al.</i> , 1998)	5
1.4	(E)-3-(4-((E)-2-cyano-2(2-(2-ethylhexyloxy)-5-methoxy-4-methylphenyl)vinyl)phenyl)-2-methylacrylonitrile (MEH-PPV-CN) (R. H. Greenham <i>et al.</i> , 1998)	5
1.5	(Z)-1-(2-ethylhexyloxy)-4-methoxy-5-nitro-2-(2-nitrovinyl) benzene (MEH-PPV-NO ₂) (R. H. Greenham <i>et al.</i> , 1998)	6
1.6	1-dodecyl-5-(2-dodecyl-4,5-dimethylstyryl)-2(2-methoxypropyl)- 4-methylbenzene(A-PPV) (R. H. Greenham <i>et al.</i> , 1998)	6
2.1	synthesis of MEH-PPV (J. P. Ferraris <i>et al.</i> , 1999).	10
2.2	Alkylation of MEH-PPV (R. H. Friend Nature <i>et al.</i> , 1990)	11
2.3	MEH-PPV IR (Griffith, <i>et al.</i> (2007)	11
3.1	Characterization Instruments	15
5.1	1-(heptyloxy)-4-methoxybenzene	27
5.2	1-(benzyloxy)-4-methoxybenzene	28
5.3	1-(allyloxy)-4-methoxybenzene	28

LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infrared Spectroscopy
^1H NMR	Proton Nuclear Magnetic Resonance
^{13}C NMR	Carbon Nuclear Magnetic Resonance
δ	Chemical shift
C=O	Carbonyl
KOH	Potassium hydroxide
H ₂ O	Water
TBABr	Tetrabutylammonium Bromide
TLC	Thin Liquid Chromatography
Theo.	Theoretical
Exp.	Experimental
PMMA	Poly(methylmethacrylate)

ABSTRACT

O-ALKYLATION OF 4-METHOXYPHENOL TOWARD SYNTHESIS OF POLYPHENYLENE VINYLENE

Polyphenylene vinylene is prepared by using O-alkylation reaction of 4-methoxyphenol react with different electrophiles. The compound was successfully synthesized with moderate yield 1-(heptyloxy)-4-methoxyphenol(21%), 1-(benzyloxy)-4-methoxybenzene(37%), 1-(allyloxy)-4-methoxybenzene(29%). The electrophiles that use in this experiment can be characterized using elemental and spectral studies. The spectra data suggested that electrophile in the products will give different peaks in IR spectroscopy and different values of resonance in NMR.

ABSTRAK

***O*-ALKILASI 4-METOKSIFENOL TERHADAP SINTESIS DARI POLIFENILENE VINILENE**

Polifenilene vinilene dihasilkan dengan menggunakan tindakbalas *O*-alkilasi daripada 4-metoksifenol bereaksi dengan elektrofil berbeza. Produk yang dihasilkan telah berjaya disintesis memberikan keputusan sederhana. Para elektrofil yang digunakan dalam percubaan ini boleh menjadi ciri menggunakan spektrum mendasar dan pengajian. Data Spektra menunjukkan bahawa elektrofil dalam produk akan memberikan pelbagai puncak dan nilai yang berbeza dalam resonansi.

CHAPTER 1

INTRODUCTION

1.1 Definition of organic synthesis

Organic synthesis is the construction of organic molecules *via* chemical processes. Organic molecules can often contain a higher level of complexity compared to purely inorganic compounds; therefore the synthesis of organic compounds has developed into one of the most important aspects of organic chemistry.

Organic synthesis plays an important role by allowing creation of specific molecules for scientific and technology investigation from simple starting material. The heart of organic synthesis is a design synthetic route to a molecule. The simplest synthesis of a molecule is one in which target molecule can be obtained by submitting a readily available starting material to a single reaction that convert it to the desired the target molecule. However, on most case the synthesis is not straightforward as in order to convert a chosen starting material to the target molecule; numerous steps that add, change or remove functional groups and also steps that build the carbon atom framework of the target molecule may need to be done.

There are four reasons to why organic compounds need to synthesized:

- a) To proof the structure of a natural compound by ‘putting it together’ from simpler molecules.
- b) To prepare compounds that are useful to mankind e.g. pharmaceuticals, polymer, dyes etc.
- c) To prepare specific compounds in order to study reaction mechanism or biological metabolism.

- d) For intellectual challenges; to solve problems which demand new solutions and thus, can lead to the development of new chemistry knowledge.

1.2 What is polyphenylene vinylene (PPV)

Polyphenylene vinylene (PPV) is a conducting polymer of the rigid-rod polymer host family. PPV is the only polymer of this type that has so far been successfully processed into a highly ordered crystalline thin film. PPV is prepared by thermal processing of a precursor polymer. PPV is insoluble which is usually obtained in thin film form by thermal conversion of a soluble non-conjugated precursor polymer. PPV is capable of electroluminescence(EL), leading to applications in polymer-based organic light emitting diodes. Electroluminescence (EL) is an optical and electrical phenomenon in which material emits light in response to an electric current passed through it, or to a strong electrical field. This is different from light emission resulting from heat (incandescence), chemical reaction, sound, or other mechanical reactions (S.J. Martin *et al.*, 1998).

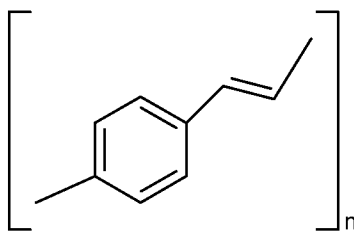


Figure 1.1: Polyphenylene vinylene (PPV)

(S.J. Martin *et al.*, 1998)

PPV was used as the emissive layer in the first polymer light-emitting diodes. Devices based on PPV emit yellow-green light, and derivatives of PPV obtained by substitution are often used when light of a different color is required. In the presence of even a small amount of oxygen, singlet oxygen is formed during operation, by energy transfer from the excited polymer molecules to oxygen molecules. These oxygen radicals then attack the structure of the polymer, leading to its degradation. Special precautions therefore have to be taken during manufacturing of PPV in order to prevent oxygen contamination (R.Koike *et al.*, 2005)

1.2.1: What is poly 2-methoxy-5-(2-ethyl-hexyloxy)polyphenylene vinylene (MEH-PPV)

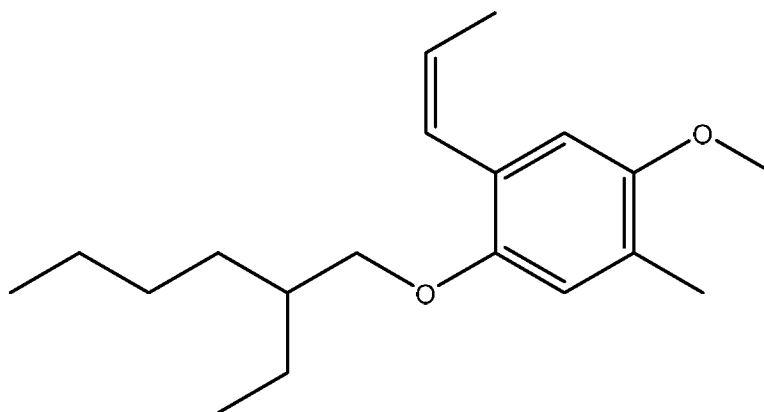


Figure1.2: MEH-PPV

(C. J. Neef *et al.*, 1999)

The electronic and optical properties of conjugated polymers have been widely investigated due to the utility of materials of this type in various molecular

optoelectronic devices, such as organic light-emitting diodes (OLED), plastic electronics, sensors, and solar cells. Furthermore, many important fundamental issues regarding the electronic properties and processes of this unique class of semi conducting materials remain to be resolved (Z-K. Chen *et al* 2000). This contribution is focused on the prototypical conjugated polymer, poly [2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), which has been extensively investigated. For the MEH-PPV molecules in this study, there are 200 effective chromophores, each with 10-17 repeating units in conjugation length, in a single molecule. Recently, nanostructures comprising single MEH-PPV molecules have been orientated perpendicularly to the support substrate, and highly polarized and narrow bandwidth emission was observed from these individual molecules. In present study, we investigate MEH-PPV molecules dispersed in PMMA and polystyrene using low temperature single-molecule imaging and spectroscopy.

1.2.2 Other polyphenylene vinylenes (PPV)

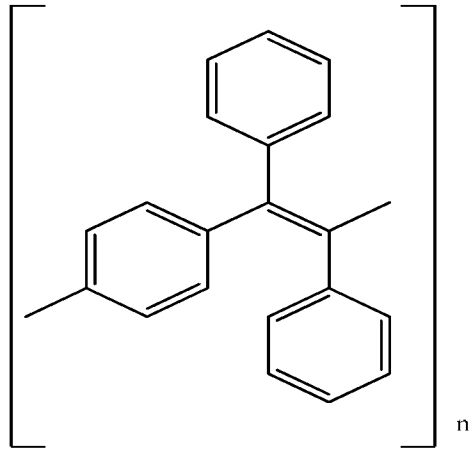


Figure 1.3: PPV-DP

(R. H. Greenham *et al.*, 1998)

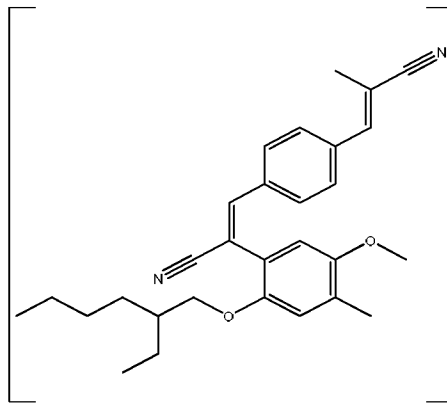


Figure 1.4: MEH-PPV-CN

(R. H. Greenham *et al.*, 1998)

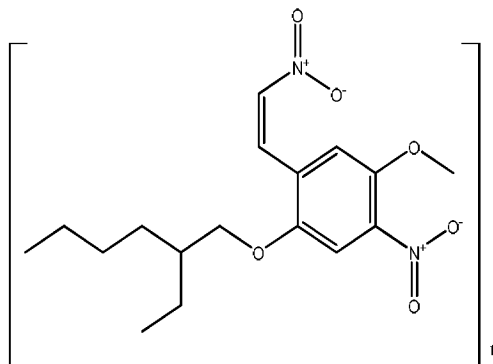


Figure1.5: MEH-PPV-NO₂
 (R. H. Greenham *et al.*, 1998)

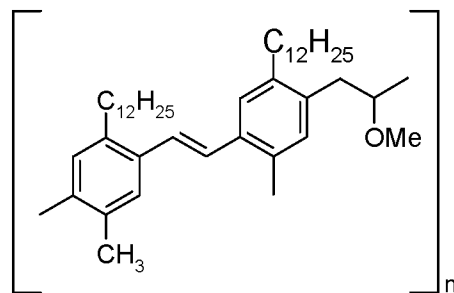


Figure1.6: A-PPV
 (R. H. Greenham *et al.*, 1998)

1.3 ALKYLATION

Alkylation is the transfer of an alkyl group from one molecule to another. The alkyl group may be transferred as an alkyl carbocation, a free radical, a carbanion or a carbene (or their equivalents). Alkylating agents are widely used in chemistry because the alkyl group is probably the most common group encountered in organic molecules. Many biological target molecules or their synthetic precursors comprise of an alkyl chain, with specific functional groups in a specific order. Selective alkylation, or adding parts to the chain with the desired functional groups, is used, especially if there is no commonly available biological precursor (Marotti *et al.*, 1998)

1.3.1 *O*-Alkylation

O-Alkylation of substituted phenols with alkyl halides (the Williamson Reaction) could be carried out in aprotic solvents in the presence of a base. When NaOH or KOH added the main by products are alcohols and alkenes.

1.3.2 *C*-alkylation

C-Alkylation occurs when an alkyl group is attached by the aromatic carbon in phenol. The hydroxyl group in phenol is an ortho and para director, the alkyl group will be attached at carbon two or four. This reaction is called *C*-alkylation

1.3.3 Naming Alkyls

The naming convention for alkyls is much the same as alkanes. The suffix is always -yl. The prefix depends on how many carbon atoms are in the molecule. This uses the same system as for alkanes as shown in table 1.1 (taken from IUPAC nomenclature):

Table 1.1: The naming of alkyls with different carbon

Number of carbons	1	2	3	4	5	6	7	8	9	10
Prefix	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-	Non-	dec-
Molecule name	Methyl	Ethyl	Propyl	Butyl	Pentyl	Hexyl	Heptyl	Octyl	Nonyl	Decyl

1.4 Significance of study

- I. To enhance knowledge in the area of organic chemistry generally and in organic synthesis specifically
- II. The monomers obtained can be used towards the synthesis of novel PPV polymers
- III. The results or findings obtained in this study can lead to the discovery of new knowledge.

1.5 Objectives

- I. To *O*-alkylate 4-methoxyphenol using different electrophiles *via* NaOH as the base
- II. To characterize all synthesized or alkylated compounds or monomers using spectroscopic technique such as NMR, FTIR and CHNS/O analyzer (elemental analyzer)

CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of MEH-PPV

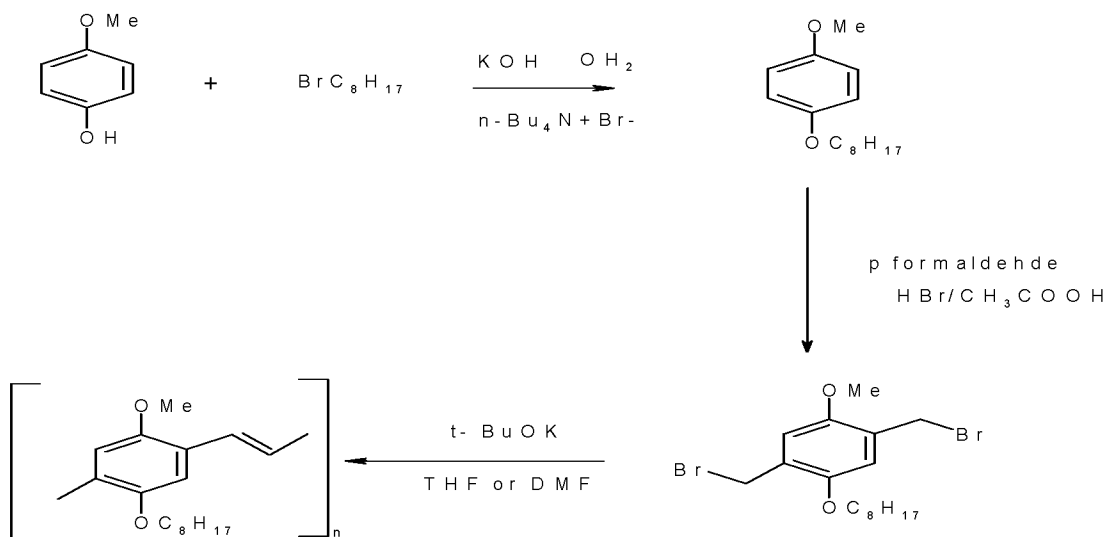


Figure 2.1: synthesis of MEH-PPV

(J. P. Ferraris *et al.*, 1999).

The synthesis of dibromo-2-methoxy-5-(2-ethylenexyloxy)xylene was accomplished in two steps from 4-methoxyphenol (C.J. Neef *et al.*, 1999). 4-methoxyphenol was reacted with 2-ethylhexyl bromide under phase transfer condition to give 2-methoxy-5-(2-ethylenexyloxy)xylene in 83% yield. 2-methoxy-5-(2-ethylenexyloxy)xylene was then treated with paraformaldehyde and HBr in acetic acid to give dibromo-2-methoxy-5-(2-ethylenexyloxy)xylene in 80% yield, resulting in an overall yield of 60%. The synthesis of dibromo-2-methoxy-5-(2-ethylenexyloxy)xylene was more convenient than the chloromethyl

derivative since gaseous HCl was not used in the synthesis. The yield of dibromo-2-methoxy-5-(2-ethylenoxyloxy)xylene was obtained to be higher than the reported yield of the chloromethyl derivative. Spectral analyses and elemental analysis of dibromo-2-methoxy-5-(2-ethylenoxyloxy)xylene were consistent with the proposed structure (J. P. Ferraris *et al.*, 1999).

2.1.1 Synthesis of MEH-PPV using different base

4-methoxy-1-(2-ethylhexyloxy)benzene was synthesized from the reaction of 4-methoxyphenol with 2-ethylhexylbromide in presence of K_2CO_3 (A. Kraft *et al.*, 1998). The monomer, 2-methoxy-5-(2-ethylhexyloxy)-p-bis(bromomethyl)benzene was then prepared by bromomethylation of its precursor in the system of the paraformaldehyde and HBr in acetic acid solution.

2.2 Alkylation of MEH-PPV

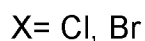
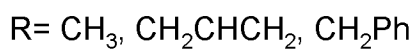
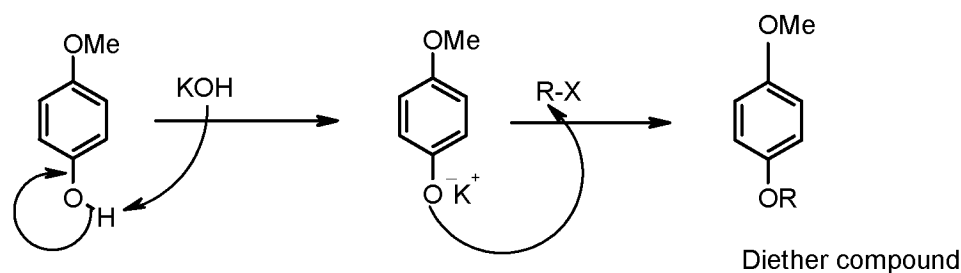


Figure 2.2: Alkylation of MEH-PPV

(R. H. Friend Nature *et al.*, 1990)

For alkylation reaction of 4-methoxyphenol that propose by R.H Friend Nature 347 (1990) to produce diether compound was accomplished in several steps. Firstly, NaOH would abstract the hydrogen from hydroxyl group. The oxygen would become negative nucleophile that will react with an electrophile. The negative electrophile will attack the carbon of the alkylhalides removing chlorine or bromine to produce diether compounds.

2.3 Characterization method

The structure of the compound can be characterized using various instruments such as FTIR spectroscopy, ^1H NMR spectroscopy and ^{13}C NMR spectroscopy and elemental analysis.

2.3.1 Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy.

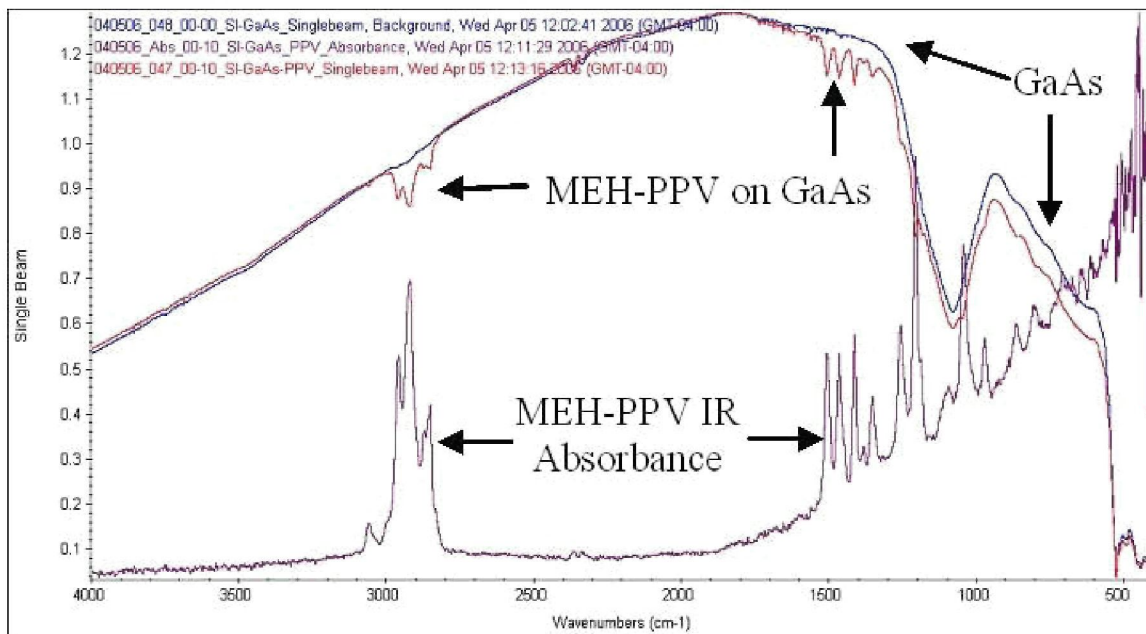


Figure 2.3: MEH-PPV IR
(Griffith, *et al.* (2007))

FTIR spectrometers are cheaper than conventional spectrometers because building of interferometers is easier than the fabrication of a monochromator. In addition, measurement of a single spectrum is faster for the FTIR technique because the information at all frequencies is collected simultaneously. This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity. Because of its various advantages, virtually all modern infrared spectrometers are FTIR instruments (Griffith, *et al.*, 2007).

NMR spectroscopy

Another characterization method is the usage of NMR spectroscopy. Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is the name given to a technique which exploits the magnetic properties of certain

nuclei. This phenomenon and its origins are detailed in a separate section on nuclear magnetic resonance. The most important applications for the organic chemist are proton NMR and carbon-13 NMR spectroscopy. In principle, NMR is applicable to any nucleus possessing spin. Many types of information can be obtained from an NMR spectrum. Much like using infrared spectroscopy to identify functional groups, analysis of a 1D NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR. The impact of NMR spectroscopy on the natural sciences has been substantial. It can, among other things, be used to study mixtures of analytes, to understand dynamic effects such as the change in temperature and reaction mechanisms, and is an invaluable tool in understanding protein and nucleic acid structure and function. It can be applied to a wide variety of samples, both in the solution and the solid state (James Keeler *et al.*, 2007).

Elemental analysis

The elemental analysis is used to indicate the success of synthesis by comparing the theoretical of the elements and experimental of the elements. The potential elements being characterized are carbon C, hydrogen H, nitrogen N and oxygen (O) (Griffith *et al.*, 2005).

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Chemicals

- I. 4-methoxyphenol
- II. benzylbromide
- III. alkylbromide
- IV. iodoheptane
- V. potassium hydroxide
- VI. tetrabutylammonium bromide

3.1.2 Instruments for analysis

- I. NMR spectroscopy
- II. FTIR spectroscopy
- III. Elemental analyzer

Methods

Synthesis of methoxy-4-(2-ethylhexyloxy) benzene

0.040 mole 4-methoxyphenol was added in round bottom flask. 0.049 mole potassium hydroxide was added in the same flask. 0.084 mole tetrabutylammoniumbromide and water was followed after the second step. The flask will be stirred until all compound dissolve to become a solution. 0.044 mole electrophile was added and N₂ atmosphere was will be established. The reaction was heated to reflux for 3 days. After allowing the reaction to cool down to room temperature, the compound was separated the layer followed by extraction of the organic layer with water. This step was repeated with using another electrophile.

3.3 Physical Measurement



(a) NMR spectroscopy



(b) FTIR spectroscopy



(c) Elemental analyzer

Figure 3.1: Characterization Instruments

CHAPTER 4

RESULT AND DISCUSSION

4.1 Analysis and Physical Characteristic

Table 4.1 Percentage yield and physical appearance of compound obtained

Compound	Color	%yield
1-(heptyloxy)- 4-methoxyphenol	white milky (liquid)	31
1-(benzyloxy)- 4-methoxybenzene	white solid (solid)	27
1-(allyloxy)- 4-methoxybenzene	colorless yellow (liquid)	29

Table 4.1 shows the percentage yield and physical characteristic 1-(heptyloxy)-4-methoxybenzene, 1-(benzyloxy)-4-methoxybenzene and 1-(allyloxy)-4-methoxybenzene. 1-(heptyloxy)-4-methoxyphenol is in the form of white milky color liquid and the percentage yield is 31%. For the second product is 1-(benzyloxy)-4-methoxybenzene is in the form of with white solid percentage yield of 27%. While 1-(allyloxy)-4-methoxybenzene, formed colorless yellow liquid and percentage yield is 29%. The results obtained were in good agreement with those predict structure. The result also showed the following compounds were successfully synthesized. The compounds were obtained in moderate yield from 27-31%.

4.2 FTIR Spectroscopy

All compounds were characterized and recorded by using FTIR PerkinElmer Precisely Spectrum One FT-IR Spectrometer. The frequency of important peaks was determined by comparing the obtained values with the 4-methoxyphenol values as starting material to identify the functional groups in these compounds. Table 4.2 shows some important peaks of 4-methoxyphenol and all products.

Table 4.2: Important infrared spectral bands of 4-methoxyphenol and products

IR bands (cm ⁻¹)	Compounds			
	CH ₃ O(C ₆ H ₄)-OH	CH ₃ O(C ₆ H ₄)-OC ₇ H ₁₅	CH ₃ O(C ₆ H ₄)-OCH ₂ (C ₆ H ₅)	CH ₃ O(C ₆ H ₄)-OC ₃ H ₅
$\nu(\text{OH})$	3392.1			
$\nu(\text{C-O})$	1102.1	1033.58	1111.9	1106.6
$\nu(\text{C=C})$			1603.3	1591.0
$\nu(\text{C-H})$	2951.5	2950.2	2950.6	2934.1
$\nu(\text{C-H}_2)$		1462.4	1460.5	1462.2
$\nu(\text{C-H}_3)$		1365.2		

The table 4.2 shows a broad OH appeared at 3392 cm⁻¹ in 4-methoxyphenol. If we compared to the product, broad OH was removed when starting material react with electrophile. The electrophile that used in this experiment is iodoheptane that can produce CH₃O(C₆H₄)-OC₇H₁₅ as first product. In this product, $\nu(\text{C-H}_2)$ was appeared at 1462.4 cm⁻¹. $\nu(\text{C-H}_2)$ are not appeared in starting material. The position $\nu(\text{C-H}_3)$ in this product

at 1365 cm^{-1} . $\nu(\text{C-H}_3)$ are not appeared in others two product and in the starting material. The $\nu(\text{C-H}_3)$ in this product can refer to heptane as an electrophile that was used in experiment. For the $\text{CH}_3\text{O}(\text{C}_6\text{H}_4)\text{-OCH}_2(\text{C}_6\text{H}_5)$ as second product, significant differences is the benzyl group was appeared in this product. $\nu(\text{C=C})$ for the benzyl group is 1603 cm^{-1} . All products have benzene group because the starting material that are used has benzene group. In second product benzyl bromide are used as electrophile. For the last product, significant differences at C=C in ally group. $\nu(\text{C=C})$ for C=C in ally group is 1591 cm^{-1} . For others values that was appeared in all product is $\nu(\text{C-O})$ and $\nu(\text{C-H})$ that C-O between 1033 cm^{-1} and 1111 cm^{-1} , C-H between 2934 cm^{-1} and 2951 cm^{-1} .

4.3 ¹H NMR Spectroscopy

¹H NMR spectrum gives information on the numbers and types of hydrogen atoms on the carbon skeleton. NMR data can also be used to help determine the structure of the compounds. The experimental spectra were compared to reported literature. Table below shows the chemical shift, (δ /ppm) for the products.

Table 4.3: ¹H NMR spectra data for 1-(heptyloxy)-4-methoxyphenol

Compound	δ_H (ppm)	Literature δ_H (ppm)	Number of Hydrogen	Indicative of
1-(heptyloxy)- 4-methoxybenzene	6.87	6.88	4	CH (benzene)
	3.95	4.06	2	O-CH ₂
	3.77	3.83	3	O-CH ₃
	1.80	1.76	2	CH ₂
	1.46	1.43	10	CH ₂ (methylene)
	0.98	0.88	3	CH ₃ (methyl)

Table 4.3 shows the ¹H NMR spectrum of the 1-(heptyloxy)-4-methoxyphenol. The C-H for benzene resonance at 6.87ppm and known as a singlet since it has proton at the neighbour carbon. At resonance 3.95ppm the peak referred to O-CH₂ and act as triplet because the neighbors have two protons. For other peaks have resonance at 3.77ppm as singlet that refer to O-CH₃, 1.80ppm as triplet and refer to CH₂, 1.46ppm as a multiplet and refer to CH₂ and the last peak at 0.98 as triplet and refer to CH₃ (methyl).

Table 4.4: ¹H NMR spectra data for 1-(benzyloxy)-4-methoxybenzene

Compound	δ_{H} (ppm)	Literature δ_{H} (ppm)	Number of Hydrogen	Indicative of
1-(benzyloxy)- 4-methoxybenzene	6.85	6.88	4	CH (benzene)
	7.34	7.47	5	CH(benzyl)
	3.69	3.83	3	O-CH ₃
	4.95	5.16	2	O-CH ₂

Table 4.4 shows the ¹H NMR spectra of the 1-(benzyloxy)-4-methoxybenzene. The C-H for benzene resonance at 6.85ppm and known as a singlet because don't have any proton at carbon neighbors. At resonance 7.34ppm that can refer to CH₂ at benzyl. For other two peaks have resonance at 3.69ppm as singlet that refer to O-CH₃, 4.95ppm as singlet and refer to O-CH₂.

Table 4.5: ^1H NMR spectra data for 1-(allyloxy)-4-methoxybenzene

Compound	δ_{H} (ppm)	Literature δ_{H} (ppm)	Number of Hydrogen	Indicative of
1-(allyloxy)-	6.89	6.92	4	CH (benzene)
4-methoxybenzene	3.76	3.83	3	O-CH ₃
	4.92	4.68	2	O-CH ₂
	6.08	6.06	1	CH (ethylene)
	5.41	5.42	1	CH (ethylene)
	5.29	5.28	1	CH (ethylene)

Table 4.5 shows the ^1H NMR spectra data for 1-(allyloxy)-4-methoxybenzene. The C-H for benzene resonance at 6.85ppm and known as a singlet because don't have any proton at carbon neighbors. The O-CH₃ and O-CH₂ has resonances at 3.76ppm and 4.92ppm respectively. For other peaks have resonance at 6.08ppm for CH, 5.41ppm also for CH that have -C-O *cis* and the last one at 5.29ppm that refer to -C-O *trans* (Griffith *et al.* 2005).

4.4 ^{13}C NMR Spectroscopy

^{13}C NMR spectra can be used to determine the number of nonequivalent carbons and to identify the type of carbon (methyl, methylene, aromatic, carbonyl and so on) that may be present in a compounds. NMR data can also be used to help determine the structure of the compounds. The experimental spectra were compared to reported literature. Table below shows the chemical shift, (δ /ppm) for the products.

Table 4.6: ^{13}C NMR spectra data for 1-(heptyloxy)-4-methoxybenzene

Compound	δ_{H} (ppm)	Literature δ_{H} (ppm)	Indicative of
1-(heptyloxy)- 4-methoxybenzene	154.0	152.2	Ar-OCH ₃
	153.7	151.7	Ar-OCH ₂
	114.8	114.9	CH (benzene)
	115.6	115.4	CH (benzene)
	55.7	55.8	O-CH ₃
	68.7	68.7	O-CH ₂
	27.5	27.8	CH ₂ (heptyl)
	14.3	14.1	-CH ₃

The table shows ^{13}C NMR spectra data 1-(heptyloxy)-4-methoxybenzene. From the table the resonance of Ar-OCH₃ and Ar-OCH₂ has different values that are 154.0ppm and 153.2ppm. This happen because electronegativity affect to the resonance of Ar-OCH₃ and

Ar-OCH₂. For CH in aromatic benzene have resonance at 114.8ppm and 115.6ppm. Electronegativity also gives affect to O-CH₃ and O-CH₂ that have values 55.7ppm and 68.7ppm. The others resonance is CH₂ (heptyl) that have value 27.5ppm and -CH₃ that have value 14.3ppm.

Table 4.7: ¹³C NMR spectra data for 1-(benzyloxy)-4-methoxybenzene

Compound	δ_H (ppm)	Literature δ_H (ppm)	Indicative of
1-(benzyloxy)- 4-methoxybenzene	153.7	152.9	Ar-OCH ₃
	154.0	154.0	Ar-OCH ₂
	55.9	55.8	O-CH ₃
	70.9	70.8	O-CH ₂
	114.9	115.3	CH (benzene)
	128.1	128.9	CH (benzyl)

The table shows ¹³C NMR spectra data 1-(benzyloxy)-4-methoxybenzene. From the table the resonance of Ar-OCH₃ and Ar-OCH₂ has different values that are 153.7ppm and 154.0ppm. This happen because electronegativity affect to the resonance of Ar-OCH₃ and Ar-OCH₂. For CH in aromatic benzene and benzyl have resonance at 114.9ppm and 128.1ppm. Electronegativity also gives affect to O-CH₃ and O-CH₂ that have values 55.9ppm and 70.9ppm.

Table 4.8: ^{13}C NMR spectra data for 1-(allyloxy)-4-methoxybenzene

Compound	δ_{H} (ppm)	Literature δ_{H} (ppm)	Indicative of
1-(allyloxy)- 4-methoxybenzene	153.1	152.9	Ar-OCH ₃
	154.1	150.4	Ar-OCH ₂
	55.7	55.8	O-CH ₃
	69.6	70.2	O-CH ₂
	115.3	115.3	CH (benzene)
	134.1	133.5	CH (ethylene)
	117.3	118.2	CH ₂ (ethylene)

The table shows ^{13}C NMR spectra data 1-(allyloxy)-4-methoxybenzene. From the table the resonance of Ar-OCH₃ and Ar-OCH₂ has different values that are 153.1ppm and 154.1ppm. This happen because electronegativity affect to the resonance of Ar-OCH₃ and Ar-OCH₂. For CH in aromatic benzene have resonance at 114.9ppm. Electronegativity also gives affect to O-CH₃ and O-CH₂ that have values 55.7ppm and 69.6ppm. For other resonance is 134.1 that refer to CH in ethylene and 117.1 that refer to CH₂ also in ethylene.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

Conclusion

All products that are produced in this experiment have been successfully synthesized and characterized using Fourier Transformed Infrared (FTIR) and ^1NMR spectroscopy studies. For the 1-heptyloxy-4-methoxybenzene compound, the present of impurities making that compound not clean. From the results obtained, an improved synthesized method has been illustrated for synthesis of MEH-PPV. The products that are produced can be used to proceed the next step in synthesizing the PPV polymer. Figure 5.1, 5.2 and 5.3 depict the proposed structures of products.

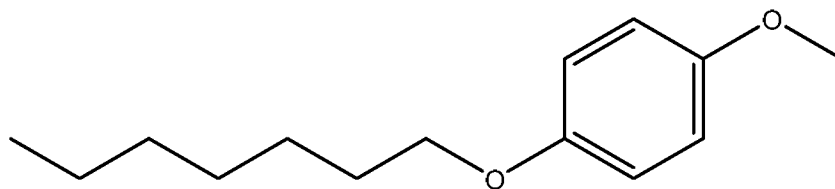


Figure 5.1: 1-(heptyloxy)-4-methoxybenzene

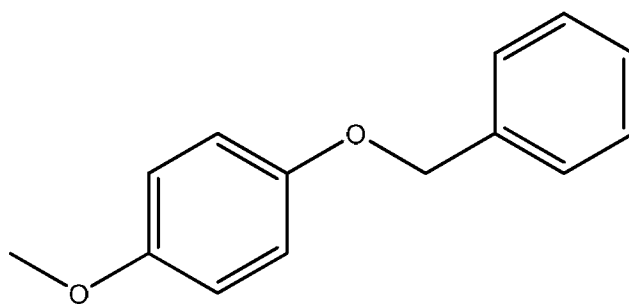


Figure 5.2: 1-(benzyloxy)-4-methoxybenzene

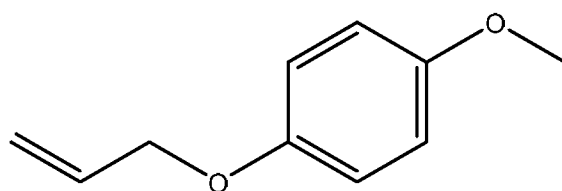


Figure 5.3: 1-(allyloxy)-4-methoxybenzene

Recommendations

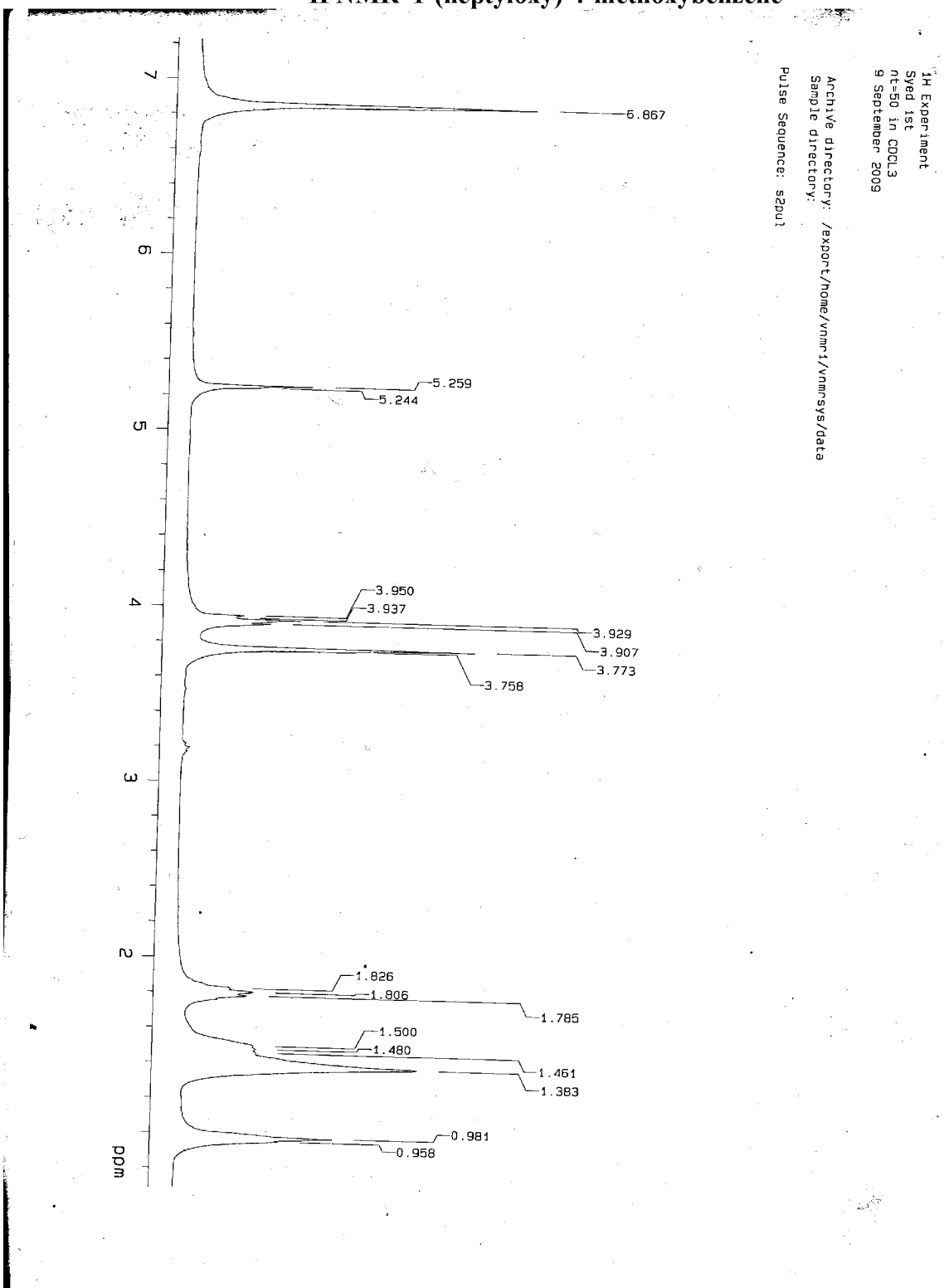
Different electrophile can be employed to improve the experiment. The different electrophile can be such as iodomethane, benzylbromide and allybromide. In order to ensure the purity of the compounds, several techniques such as Thin Liquid Chromatography (TLC) or column chromatography could be carried out. By using different method such as used different base.

CITED REFERENCE:

- A. Haevath, G. Weiser, *Mol. Cryst. Liq. Cryst.* 256 (1994). Use of DMF as Solvent Allows for the Facile Synthesis of Soluble MEH-PPV .79.
- A. Kraft, A.C, Grimsdale, A.B. Holmes, *Angew. Chem. Int. Ed.* 37 (1998). Electroabsorbtion studies of PPV and MEH-PPV 402.
- Denton, F, R; Sarker, A.; Lathi, P. M.; Garay, R. O.; Karsz, J.*polym. Sci.; Part A: Polym. Chem.* 1992. 30. 2233.
- E.D. Oven. *Degradation and stability of PVC*, Elsevier, New York, 1984. Short lifetimes of light emitting polymer
- J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N> Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, *Nature* 347 (1990). Improved synthetic procedure and molecular weight control 539.
- J.-L. Bredas, J.Cornil, A.J. Heeger, *Adv. Mater.* 8 (1996). Two photon absorbing phenylenevinylene derivative having silyloxy moieties in donor units. 447.
- J.L. Segura, *Acta Polym.* 49 (1998). Poly(benzylether) dendrimers with strongly fluorescent distyrylbenzene cores as the fluorophores for peroxyoalate chemiluminescence: insulating effect of dendritic structures on fluorescent sites. 319.
- L. Sebastin, G.Weiser. *Chem. Phys.* 61 (1981). Photooxidative Stability of Substituted Poly (PhenyleneVinylene) (PPV) and Poly(Phenylene Acetylene) (PPA) 125.
- Parker, I.D.; Gymer, r.W.; Harrison, M.g.; Friend, R.H.; Ahmend, H. *Appl. Phys. Let.* 1993. Fully soluble poly(p-phenylenevinylene)s via propagation control chain conjugated lengths. 62, 1529.
- R. Garay, R.W. Lenz, *Makromol. Chem. Suppl.* 15 (1989). Friedel-Crafts Alkylolation Reaction Preparation of 1, 4-Di-t-butyl-2, 5-dimethoxybenzene 1.
- Griffith, D., Bergamo, A., Pin, S., Vadori, M., Bunz, H.M., Sava, G. and Marmion, C.J., (2007). Novel Platinum pyridinehydroxamic acid complexes: Synthesis, Characterization, X-ray crystallographic study and nitric oxide related properties. *Polyhedron.* 26, 4697-4706.

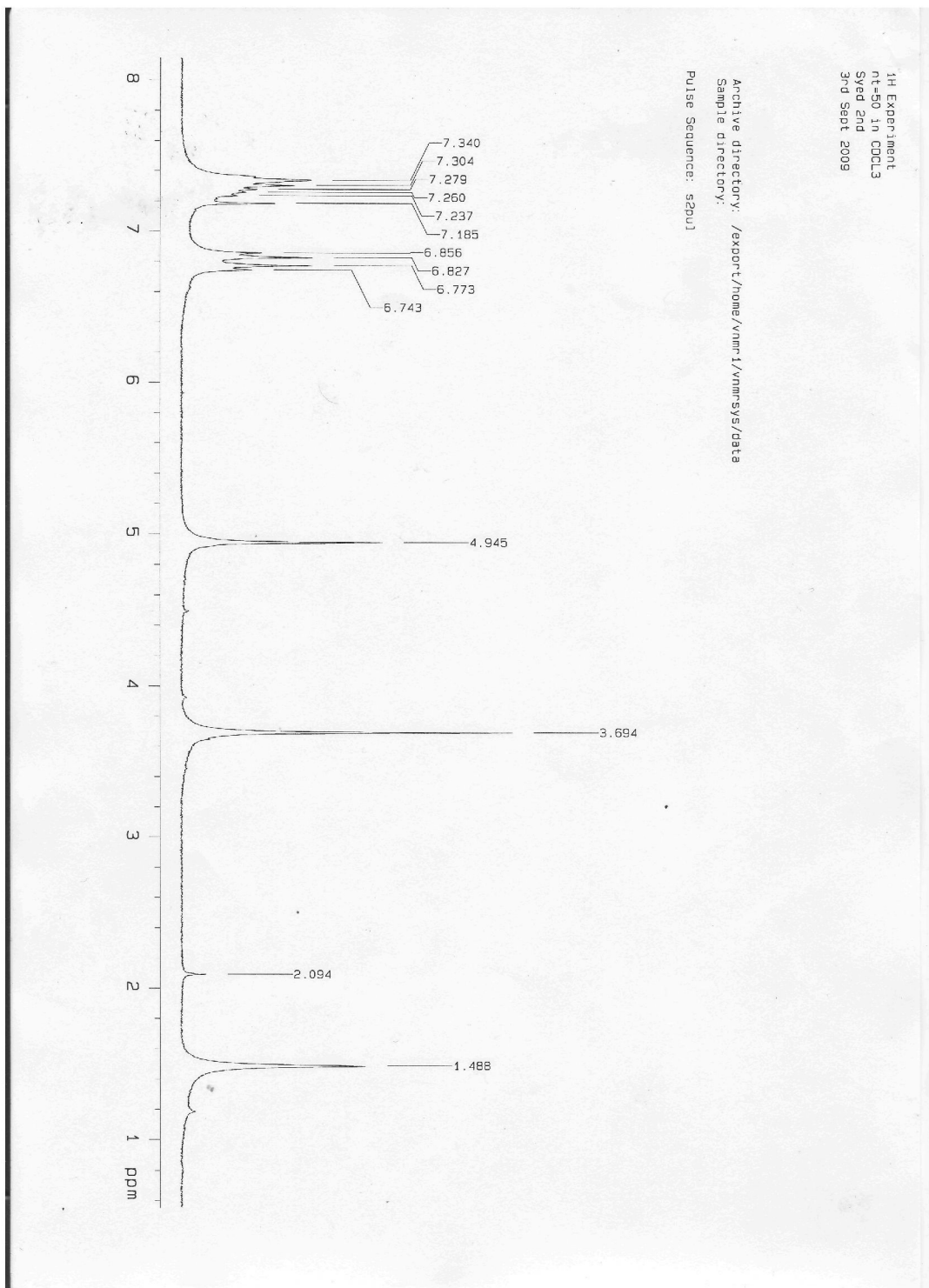
APPENDIX A

¹H NMR 1-(heptyloxy)-4-methoxybenzene



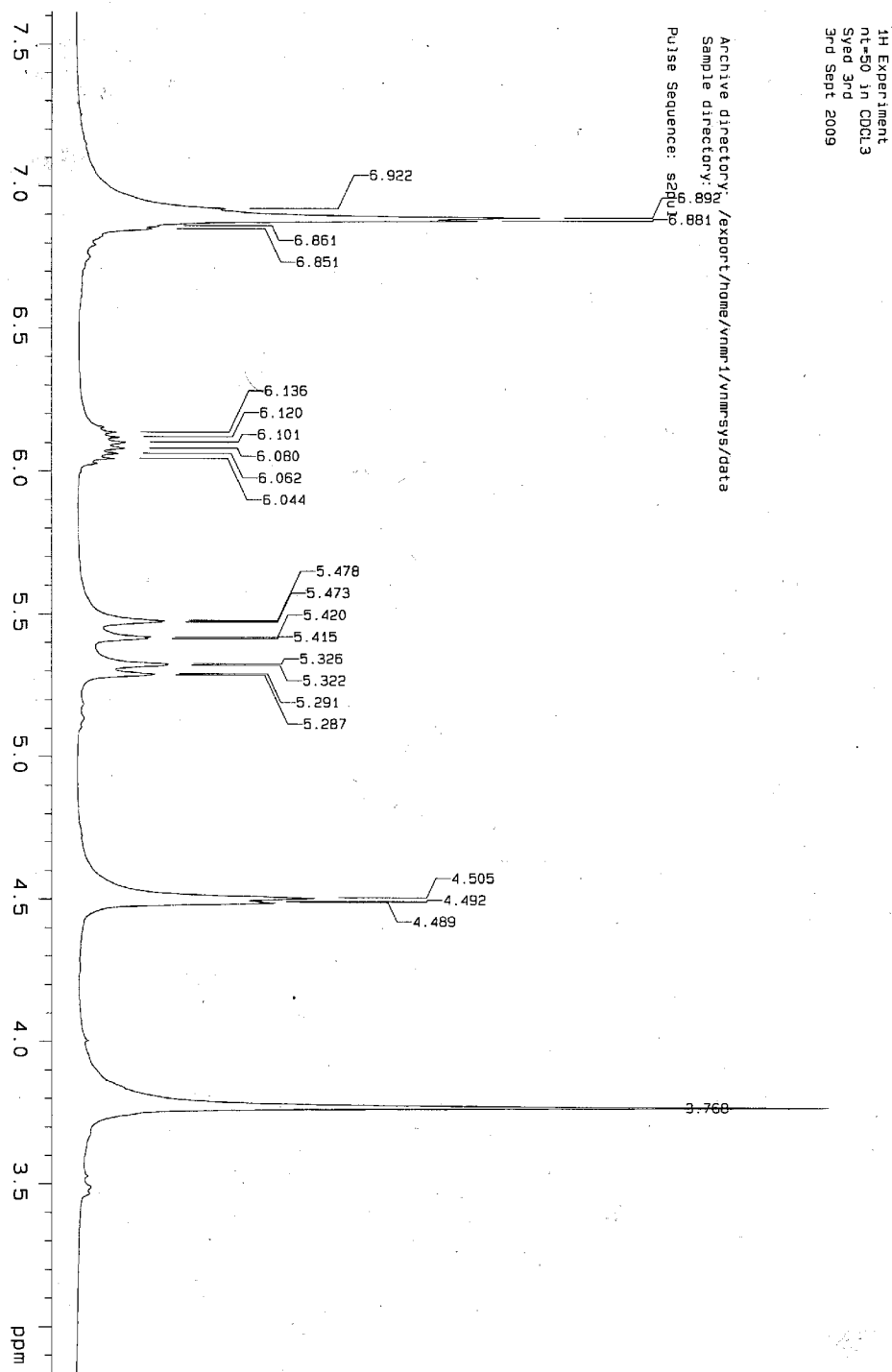
APPENDIX B

¹H NMR 1-(benzyloxy)-4-methoxybenzene



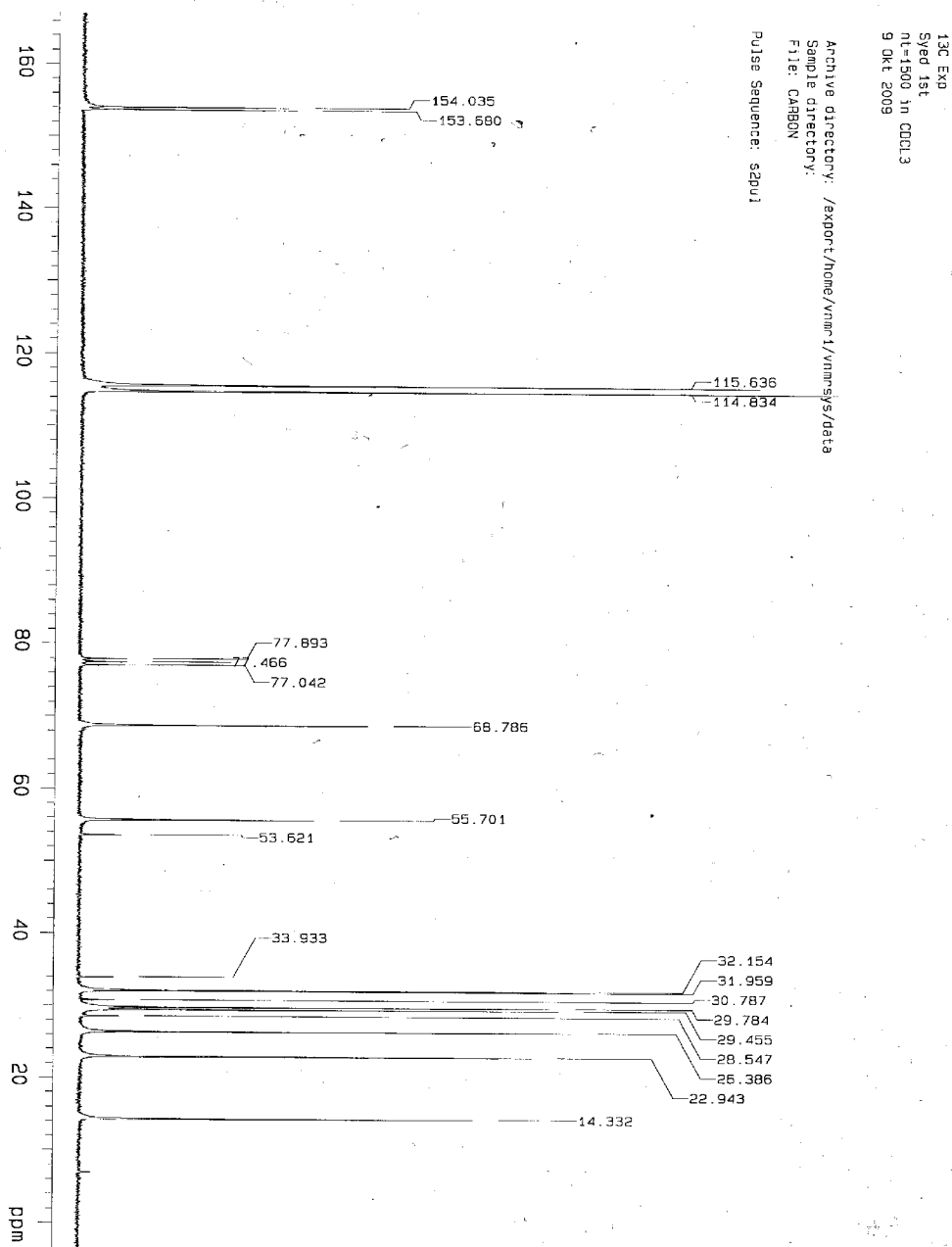
APPENDIX C

¹H NMR 1-(allyloxy)-4-methoxybenzene



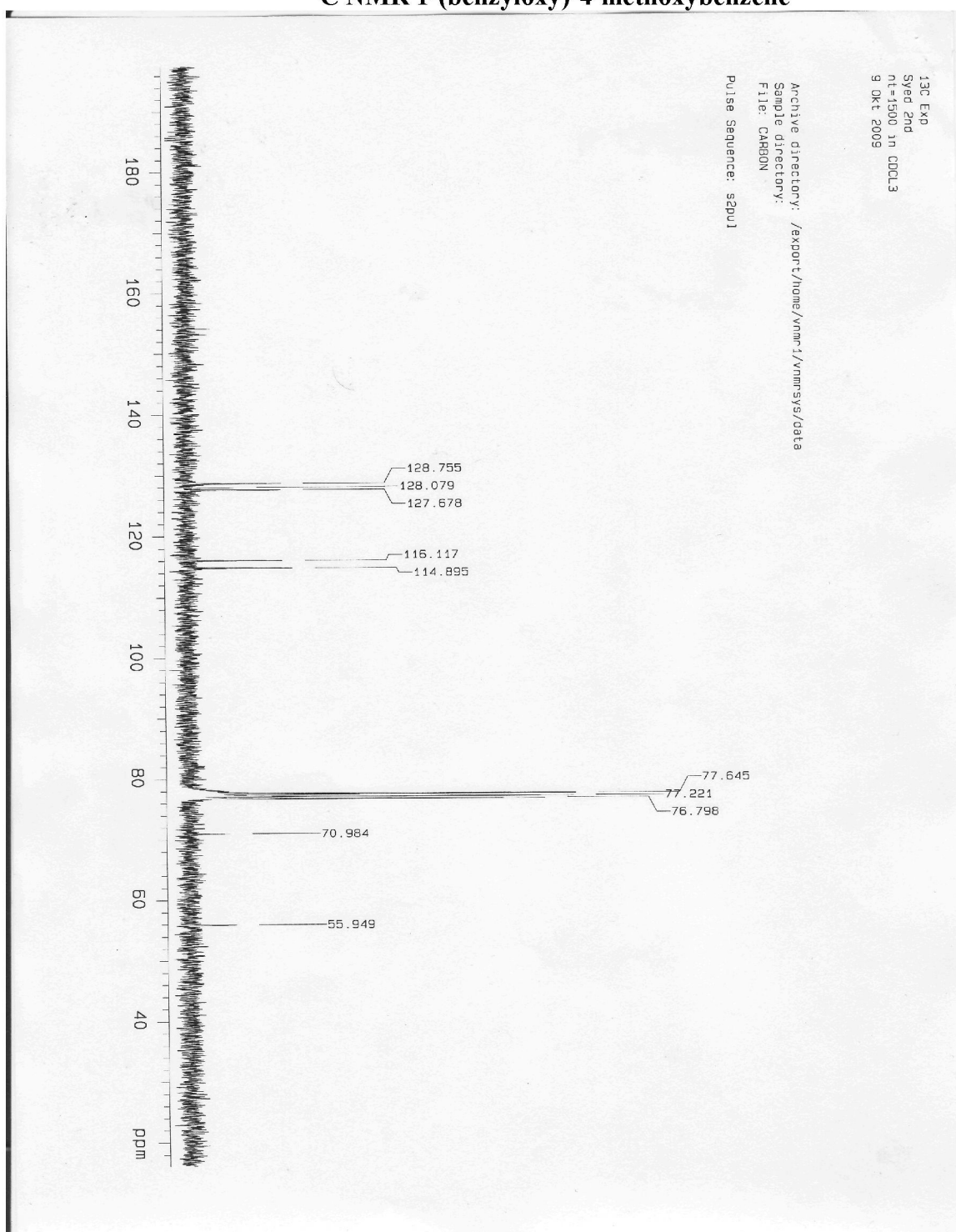
APPENDIX D

¹³C NMR 1-(benzyloxy)-4-methoxybenzene



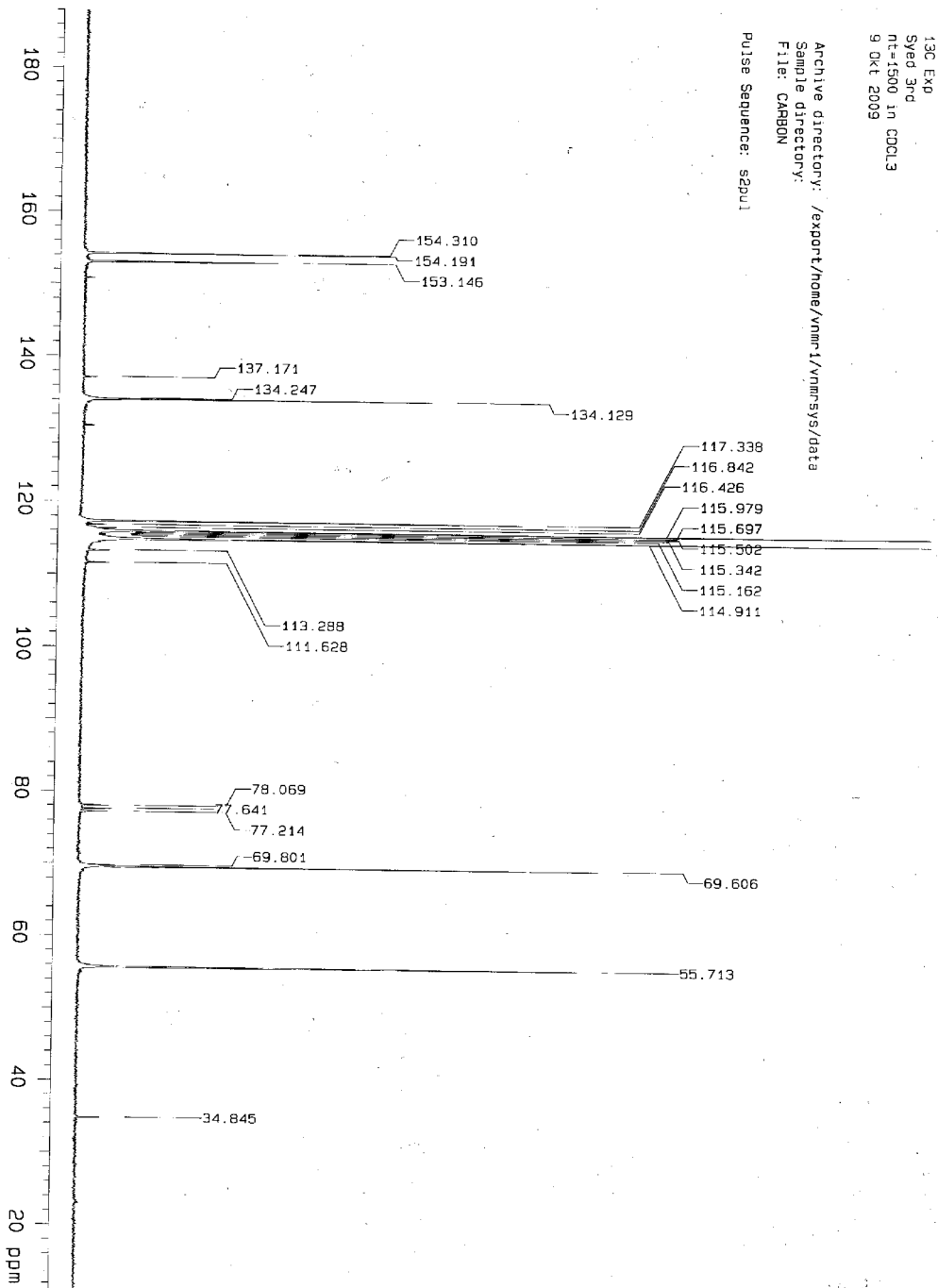
APPENDIX E

¹³C NMR 1-(benzyloxy)-4-methoxybenzene

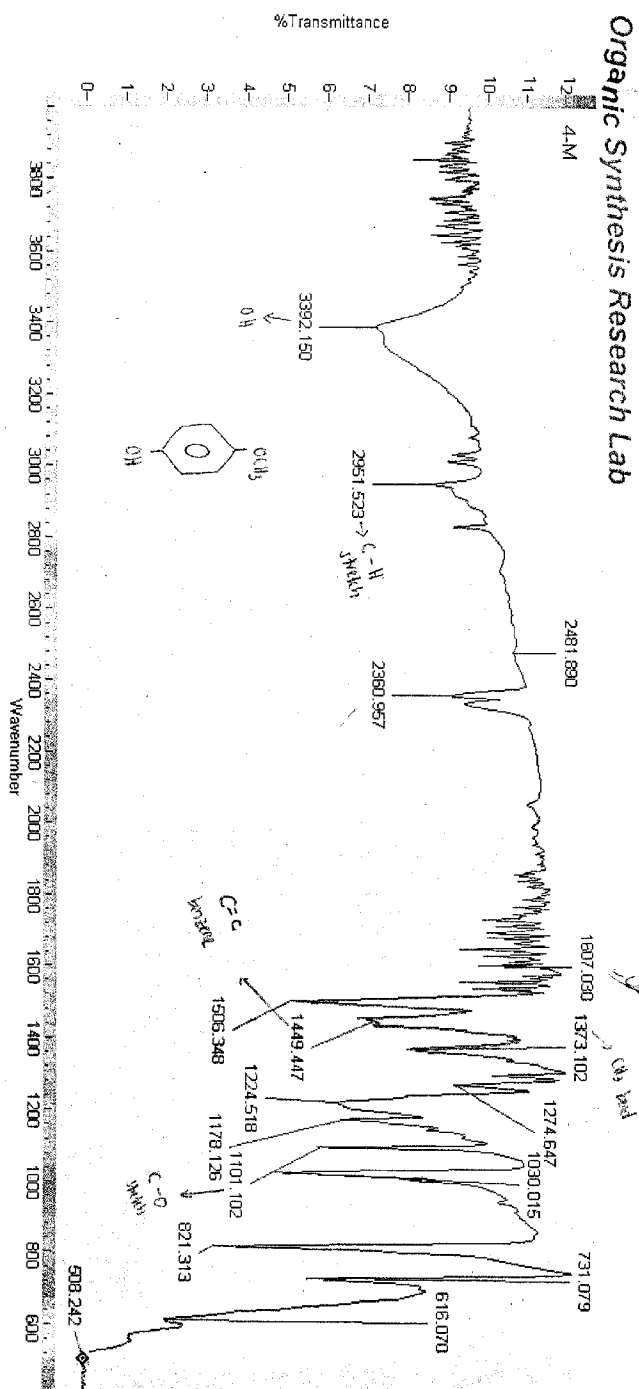


APPENDIX F

¹H NMR 1-(allyloxy)-4-methoxybenzene



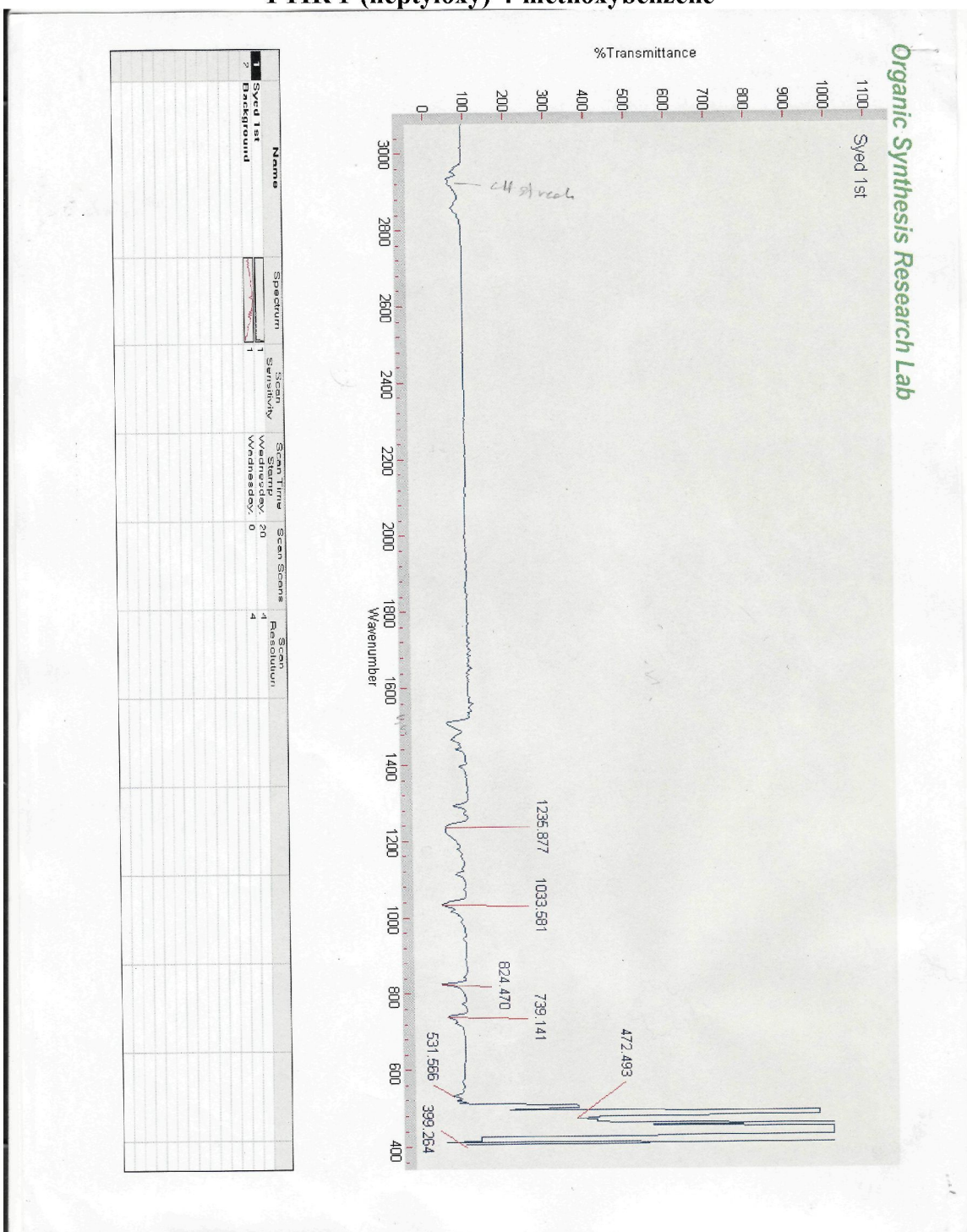
APPENDIX G
FTIR 4-
METHOXYPHENOL



Name	Spectrum
1 4M	
2 K2CO3	
3 KOH	
4 Background	

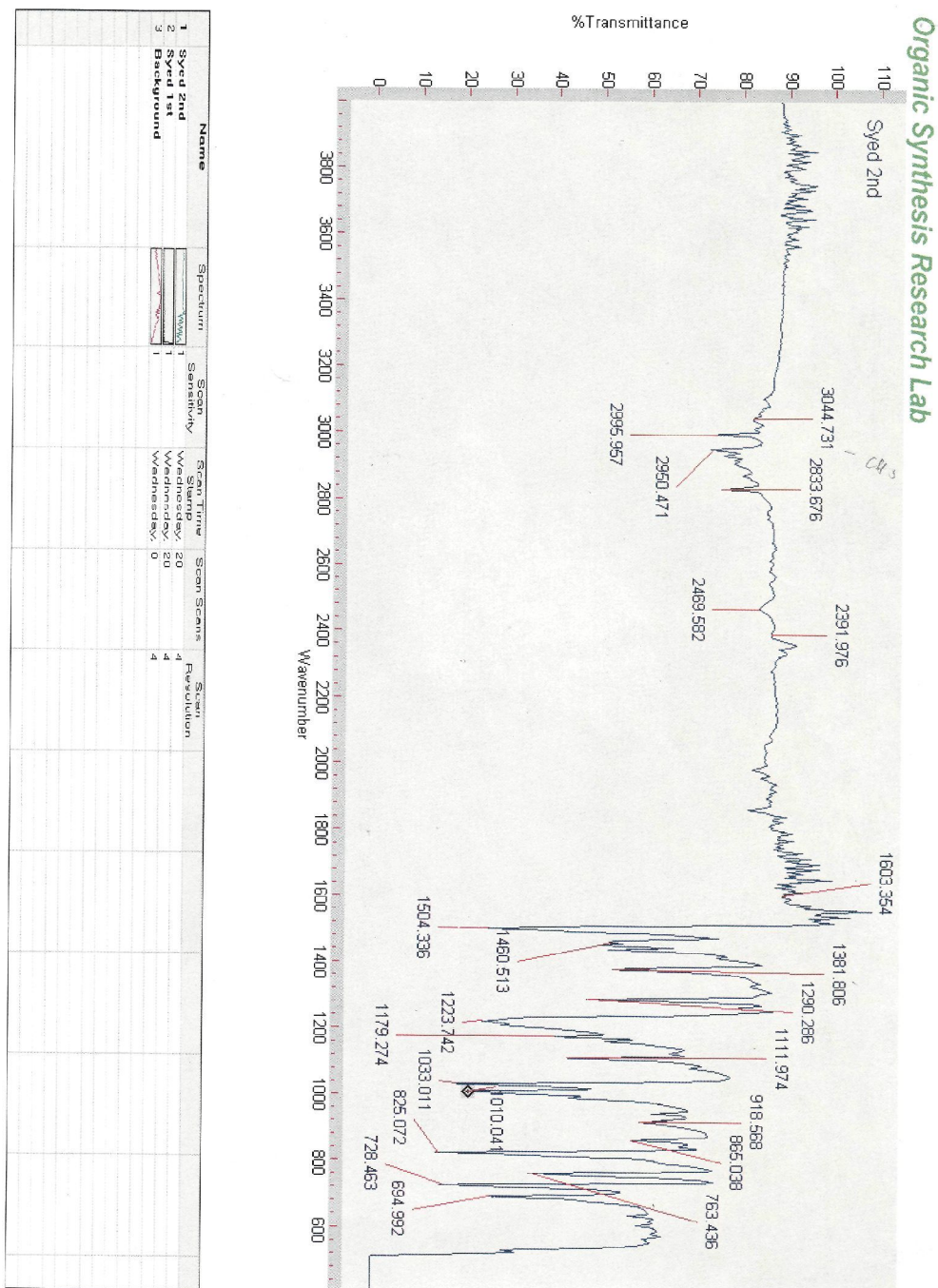
APPENDIX H

FTIR 1-(heptyloxy)-4-methoxybenzene



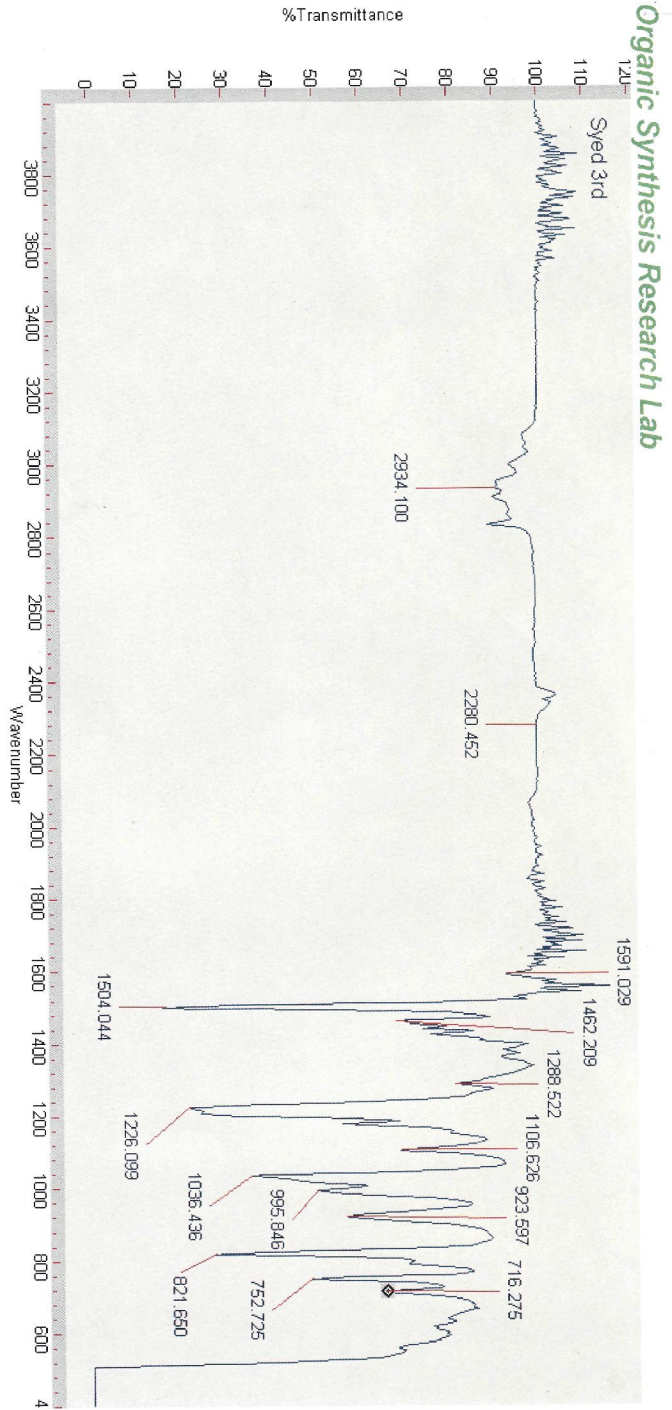
APPENDIX I

FTIR 1-(benzyloxy)-4-methoxybenzene



APPENDIX J

FTIR 1-(allyloxy)-4-methoxybenzene



Name	Spectrum	Scan Sensitivity	Scan Time	Scan Scans	Scan Resolution
1 Syed 3rd	WVA	1	Wednesday, 20	4	
2 Syed 2nd	WVA	1	Wednesday, 20	4	
3 Syed 1st	WVA	1	Wednesday, 20	4	
4 Background	WVA	1	Wednesday, 20	4	

CURRICULUM VITAE

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A. Hobbies and Interests

I enjoy reading, traveling and watching movies. I love sports. I am very fluent in written and spoken Malay, English and have basic knowledge of Arabic language.

B. Academic Qualifications

Degree awarded	Area	Institution/ School	Year
B.Sc. (Hons.)	Chemistry	Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia	Expected 2009
Diploma	Science	Universiti Teknologi MARA, Kuala Terengganu, Terengganu, Malaysia	2006
S.P.M	Science	Sek. Men. Keb. Bukit Tunggal, Kuala Trengganu, TerengganuMalaysia	2001

C. Working Experience

Post	Place	Year
Operator	Permintex (M) Sdn. Bhd	2002

D. Related Experience

Post	Place	Year
Exco	Asas Intekma Society, Universiti Teknologi MARA, Kuala Terengganu	2004-2005
Badminton Athlete	Representative of UiTM Kuala Terengganu in Sport Carnival of UiTM	2005 and 2006
Member	Chemistry Fusion Club, Universiti Teknologi MARA, Shah Alam	2006-2009