

# Polymers with Pendant Coumarins:

## Synthesis and Characterization of Polystyrenes and Polymethacrylates with Pendant Coumarin Moieties

Masters of Science Thesis

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**Polymers with Pendant Coumarins: Synthesis and Characterization of Polystyrenes and  
Polymethacrylates with Pendant Coumarin Moieties**

**BY**

**Timothy Christopher Corkery**

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Manitoba in partial fulfillment of the requirement of the degree  
Of**

**Master of Science**

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## Abstract

A variety of new coumarins, chromenes and their derivatives were synthesized under facile conditions using a Michael rearrangement reaction in order to examine their antimicrobial activity. By incorporating specific terminal groups on the new molecules, it was possible to chemically link them to polymer precursors (4-vinylbenzylchloride or methacrylic acid) to create monomeric units. Polymerization of these monomeric units allowed for the synthesis of polymeric materials bearing pendant antimicrobial compounds in a potential drug delivery system. Only two of the new compounds exhibited antimicrobial properties, with zones of inhibition of 12mm and 15mm at concentrations of 25  $\mu\text{g/ml}$ .

Despite the low antimicrobial activity of the coumarins, they also possess potential as light harvesters for use in optoelectronic devices. With this new premise, several coumarin species were ether or ester bound to 4-vinylbenzylchloride. Polymerization led to a series of polystyrenes with pendant coumarins. The polymers had good thermal stability up to 300  $^{\circ}\text{C}$  and glass transition temperatures of approximately 120  $^{\circ}\text{C}$ . Solubility considerations limited the complete characterization and further handling of the materials.

To circumvent solubility as an issue, polymethylmethacrylate (PMMA) backbones were used. The higher freedom of movement within PMMA allowed for better solubility of the polymers. PMMA backbones with pendant coumarin moieties had comparable thermal stability to polystyrene polymers, higher solubility allowing better characterization and glass transition temperatures of 80  $^{\circ}\text{C}$ .

## Acknowledgement

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Of course, I also wish to thank everyone who helped me with this research or worked with me in the lab of Dr. Alaa Abd-El-Aziz. This work began with Shaune McFarlane and Dr. Erin Todd, who guided me into the lab through my first tentative steps as a researcher. Following this, Dr. Ahmed El-Agrody and Dr. Ahmed Hmam Bedair worked long and tirelessly with me to synthesize and help synthesize the coumarins and chromenes in this work. From them I learned what it is to be a synthetic chemist.

Thank-you as well to all of the people who are currently working with me or helping me with my research, especially: Hany Mohamed, for sharing my bench space, Dr. Scott Kroeker for solid-state NMR, advice, and good classes and Sarrah, Pat, Nelson and Jennilee for making the lab an enjoyable place to spend time, as well as work.

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## 1 Introduction

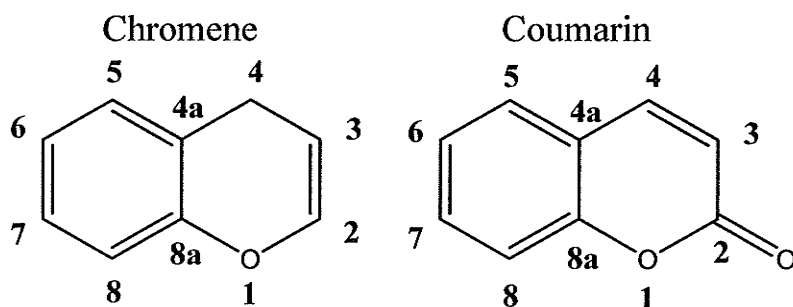
One of the largest branches of industrial chemistry is polymer science<sup>1,2</sup>. Polymers are long chemical chains with repeating units, called 'mers'. Combined, these units create solid materials with different properties from crystalline solids. This often includes easier handling and processing than with other materials. It is for their unique properties, low cost and ease of handling that polymers have grown to become so prevalent and important to our society in the last hundred years.

Plastics are materials made up of either manmade or refined polymers<sup>1</sup>. Thus, all of the plastics used by society are polymers. The first commercial plastic was developed just over a century ago, by John Wyatt. In the following century, more than 60,000 plastics were discovered or synthesized<sup>1</sup>. There are also many materials which are not plastics but are still polymers. Most organic (plant and animal based) materials are composed of polymers. The group of materials classified as 'polymers' is one of the largest used in our society. In addition to conventional 'plastics' there are a host of other uses for polymers. They are used in molecular switches, 'smart' materials, drug delivery systems, computer electronics and myriad other applications<sup>1</sup>.

The physical properties of a polymer may be altered in several ways: changing the number of mers in a polymer or altering the type of mer used, changing the branching or chemical bonding between the polymer chains, or simply adjusting the three-dimensional alignment of chains. This gives rise to the huge variety of tunable properties and applications. The potential of polymers as materials for use in the world is both vast and exciting.

## 1.1 Coumarins & Chromenes

Chromenes and coumarins, or chromene-2-ones, are molecules which are found in a large number of organisms (**Figure 1.1**). Chromenes are named for the latin word for colour, *chroma*, and are one of the earliest types of dyes. Both compounds are of interest medicinally; they often possess biological activity. Discovery and testing have led to a variety of physiological applications, particularly among the coumarins<sup>3</sup>.



**Figure 1.1** Basic chemical structures of chromenes and coumarins. The numbering provides for easy reference to specific carbon atoms.

Many researchers devote their energy to the discovery of new coumarins by extracting them from organisms. Following the discovery of a new coumarin, it is tested for a variety of potential properties. Coumarins have been found which demonstrate many biological functions, including: platelet aggregation, cytotoxic activity, enzyme inhibition, antiviral, antibacterial and antifungal activities<sup>3-12</sup>.

The development of laboratory syntheses of these molecules is important for two reasons. Firstly, it is often practically impossible to extract enough of the chemical from living organisms to meet the needs of our society. By developing methods to synthetically produce these compounds, it is possible to meet the medical demand for some of these chemicals.

Another value of synthetic development of naturally occurring chemicals is to discover new chemicals. By making slight alterations in the synthetic route, similar, but not identical, novel compounds may be discovered. These compounds, by virtue of their similarity to existing medical compounds, also have potential properties for application. For these reasons, the development of complete syntheses of naturally occurring chemicals from basic materials is often undertaken.

Coumarins are not only valuable for their bioapplications. The fused rings which make up their structure often possess optical properties. It is from this that these chemicals are often coloured and find roles as dyes<sup>3</sup>. More interestingly, these chemicals exhibit good non-linear optical properties<sup>13</sup>.

Molecules absorb electromagnetic radiation (light). This causes an excitation of one or more electrons to a higher energy, more excited state. When a molecule absorbs light in the visible region of the spectrum, it appears coloured to our eyes. Almost all absorbed energy is released as either heat or light. When this release of absorbed energy is light, the compound is said to be luminescent. This light energy released does is not necessarily at the same wavelength at which it was absorbed. This is an example of what is called a non-linear optical (NLO) effect<sup>13-15</sup>. Luminescence (both fluorescence and longer lasting phosphorescence) are optical properties which are common in coumarins<sup>16,17</sup>.

Some chemicals change the way they behave when they are influenced by electromagnetic radiation. They do not only alter the wavelength of light which they absorb (NLO effects), but they also change their chemical properties once they have absorbed light. There are even cases where this change may be shifted back, by the

absorption of light of a different wavelength, or the emission of absorbed light<sup>15</sup>. More advanced, or higher order, non-linear optical properties have potential applications in optical switching or storage<sup>18-30</sup>.

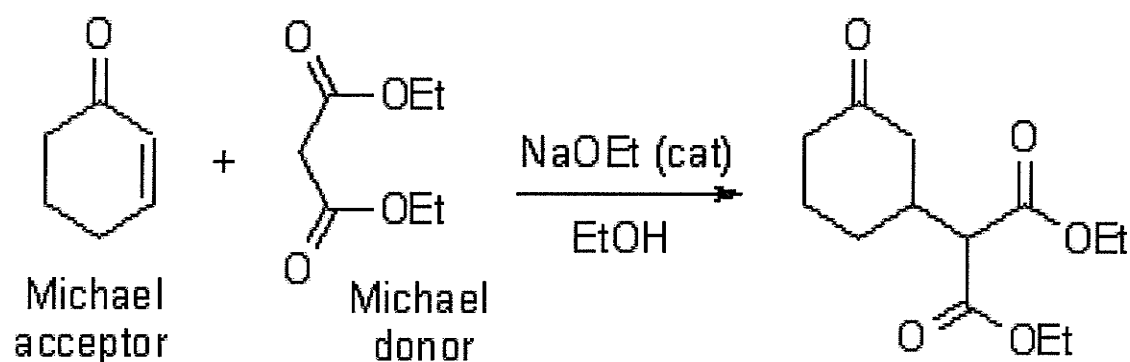
All of the previously mentioned properties are intramolecular properties; that is, properties which arise entirely inside a single molecule. Coumarins also have an intermolecular property which may occur between two coumarin molecules. When subject to ultraviolet light, two coumarin molecules will dimerize, forming one molecule. Visible light may then interact with the dimer to reverse the process. This has interesting possibilities, as the formation of a dimer in polymers with coumarins in them would change the physical properties of the polymer.

As either optical or biomedical chemicals, coumarins are of considerable interest to scientists. They may be potentially beneficial medications, valuable optical materials or used in combination as medications which behave as light responsive sensors. By incorporating these molecules into carefully designed polymeric materials, it is possible to combine the valuable properties of coumarins with the ease of handling and processing of polymeric materials.

## 1.2 Coumarin & Chromene Synthesis

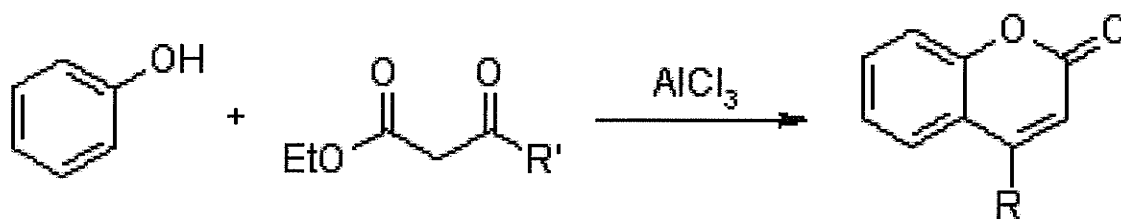
Two reactions were used in this work to synthesize coumarin and chromene molecules. The first method, used for the chromenes in **Chapter 2** and the coumarins in **Chapters 2 and 3**, is with a Michael condensation or Michael addition. This reaction was developed by A. Michael in the late 19<sup>th</sup> century<sup>31</sup>. It is a thermodynamically controlled

conjugate addition. The addition (**Scheme 1.1**) is of a Michael donor (a strong carbon acid) to a Michael acceptor (an electron rich olefin). In the reactions presented in this work, the Michael addition is followed by a ring closure and rearrangement to form the fused ring systems of chromenes or coumarins.



**Scheme 1.1** Basic Michael reaction<sup>32</sup>

The second named reaction which was used is the Pechmann condensation<sup>33</sup>. This reaction is specifically for the synthesis of coumarins using phenols and keto-esters (**Scheme 1.2**). With naphthols as starting materials, this method was utilized to create the benzocoumarins which are incorporated into polymers in **chapter 4**.



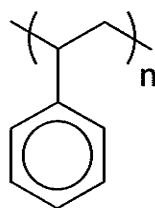
**Scheme 1.2** Basic Pechmann condensation<sup>34</sup>

### 1.3 Polymers

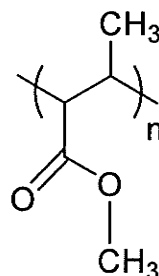
The two types of polymers which were synthesized and are described in this work are polystyrene (PS) and polymethacrylate (PMMA). In their basic form, both are very prevalent polymers in our world<sup>1</sup>. Polystyrene, commonly called Styrofoam<sup>™</sup>, is widely used in packaging, disposable tableware, building materials and electronic insulation.

Polymethacrylates are also widely used, with the common name of “acrylics”. One of the first types of PMMA developed was Plexiglas. In the Second World War, it was found that gunners treated for shards of Plexiglas shielding in their eyes did not have any biological reaction to the Plexiglas. This led to a host of bioapplications, from implants to hard contact lenses<sup>1</sup>. The differences in physical properties of these two materials are based upon the chemical structure of the repeating units in the polymer (Figure 1.2).

Polystyrene



Polymethacrylate



**Figure 1.2** Chemical structures of polystyrene & polymethacrylate.

Not all acrylics or Styrofoams have the same physical properties. This is partly due to the alignment of the chains in the bulk material. Materials with more ordered chains tend to be more rigid, resistant to chemicals and brittle. Styrofoam is often

'blown' when processed, which forces a large volume of air to be trapped inside the material, also changing the physical properties<sup>1</sup>.

Many of the physical properties of polymers also depend upon the length of the polymer, or how many repeating units are in it. In **Figure 1.2**, above, the  $n$  outside of the brackets represents the average number of repeating units in the polymer. As the length of the polymer chain increases, there are some basic changes in the material properties: they are less soluble, more rigid, have higher melting temperatures and are more thermally stable. As the number of units in a chain increases further, the polymer reaches a length where these material properties no longer change<sup>2</sup>.

The changing physical properties of polymers are a large part of what make them so useful to society. An example of this is polyethylene, the polymer composing plastic bags as well as milk jugs. The only difference in these materials is the length of the polymer chains and the amount of branching. The chains in the milk jug are longer and do not contain as many side chains. In a plastic bag, shorter polymer chains with many side chains result in a much more flexible material. Adjusting the average chain length is an excellent method of altering physical properties.

Another method of changing the physical properties is to change the units bound to the backbone of a polymer. For example, altering polyethylene slightly so that a chlorine atom replaces hydrogen on the backbone of the polymer gives polyvinyl chloride (PVC) used in industrial tubing and clothing.

One of the goals of this work is to produce optical polymeric materials, compounds which have useful optical properties coupled with the beneficial handling properties of polymers. Hopefully these materials maintain the optical properties of

coumarins and chromenes, yet provide the alterable bulk physical properties of polymers. This should produce materials in which it is possible to change the physical properties without a loss of chemical properties.

#### 1.4 Polymer Synthesis

Preparing the types of polymers in this work was a three-step process. Firstly, the specific coumarin or chromene to be incorporated into the polymer was synthesized. The second step was to attach this molecule to an individual unit (mer) which can be reacted with itself in order to form a polymer. Once the coumarin was attached to the styrene or methylmethacrylate unit, the monomer was formed. The final step was to polymerize the monomer, joining many identical monomers together in a long chain.

For this purpose, several coumarins were prepared. Many of these were new compounds and a few had been previously synthesized. The synthesis of these chemicals is examined in **Chapter 2**. After the coumarin was synthesized, it was chemically bound to either 4-vinylbenzylchloride (a polystyrene precursor) or methacrylic acid (a PMMA precursor). This binding was accomplished through the formation of either an ether or ester linkage.

Once prepared and purified, the monomer was reacted with itself in the presence of a radical initiator. This caused the monomer to link with itself, forming long polymer chains. These polymers were then tested to determine their physical and material properties. The synthesis of polystyrene based polymers is covered in **Chapter 3**. The



final chapter (**Chapter 4**) describes the synthesis and examination of polymers with polymethacrylate backbones.

## **1.5 Polymer Characterization**

With the incredibly wide variety of polymers and plastics being created, there is an ever growing variety of techniques used to characterize these materials. The examination techniques used for the projects here include: nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), mass spectrometry (MS), fluorimetry, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

NMR spectroscopy was the most frequently used technique. It was used to confirm that the structures hypothesized prior to a reaction were properly synthesized. The basic principle of NMR spectroscopy depends upon radiofrequency excitation of a nucleus with a non-zero spin. Each of these nuclear spins possesses a tiny magnetic moment. By placing a material in a strong magnetic field, all of these magnetic moments align. They may then be excited or perturbed by a radiofrequency pulse. It requires some time for a nucleus to reach an excited state and once excited it requires further time before the nucleus decays to a relaxed state. Small changes in the decays may be examined by a radiofrequency detector. These small changes in precession of the nuclear magnetic moments provide considerable information about the environment in which the atom resides<sup>35,36</sup>.

Infrared spectroscopy is also a diagnostic technique. Molecules are in a constant state of motion. When a quantum of light strikes a molecule, this light may be absorbed.

This absorption is not constant at all wavelengths; it is of an energy which corresponds to a change in vibrational or rotational states within the molecule. Therefore, bonds only absorb infrared radiation of energy which relates to the energy of transition between specific motions. The comparison of the different frequencies of absorbed light may be used to determine the presence or absence of a specific bond between specific elements. IR was used to determine if a desired bond had formed during a reaction and to confirm that expected functionalities were present<sup>36</sup>.

The third confirmation technique that was used, strictly for coumarin and chromene synthesis, was mass spectrometry. MS involves the atomization and subsequent ionization of a molecule. By examining the momentum of this electrically charged molecule in a strong magnetic field, it is possible to determine the mass of the molecule. Considerable information may also be gained through the fragmentation of the molecules. Charged, atomized molecules often break apart, with the charge remaining on one of the fragments. Once separated in terms of a charge to mass ratio ( $m/z$ ) by momentum, these charged ions are then counted. There are several methods of atomizing, ionizing and separating molecules. For this work, the molecules were directly injected (DI) into a low pressure chamber, ionized by electron impact (EI) and separated by a magnetic quadropole<sup>36</sup>.

Two samples were sent away for fluorimetry, to determine some of the optical properties of the coumarins. This is a process whereby the molecule is irradiated with a pulse of light and allowed to release the absorbed energy. By examining the duration and intensity of released light, it is possible to learn about the luminescent properties of a

molecule. Unfortunately this instrumentation was not readily available, so complete optical analyses were not possible.

Finally two techniques, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were used to determine some temperature-based stability and behavioral effects of the polymers. TGA involves the slow heating of a polymer in an inert, non-reactive atmosphere. As heat causes the material to degrade, a loss of atoms changes the weight of the sample. This allows for determination of thermal stability.

Polymers commonly possess two distinct solid phases, a more rigid 'glassy' phase and a more flexible 'rubbery' phase<sup>2</sup>. The temperature at which these phase transitions occur is called the glass transition temperature, or  $T_g$ . DSC determines the glass transition temperature by measuring the heat capacity over a temperature range. A phase change is always accompanied by a change in heat capacity. The temperature at which the heat capacity changes, yet the polymer is still in a solid state, is the  $T_g$ .

The initial goal of polymerization of coumarins for this work was to produce a solid material which could be used to transport biologically active compounds through living systems and release them photolytically<sup>16</sup>. When the antimicrobial properties of the synthesized compounds were found to be low, interest was redirected into the formation of optically active materials. Simple polymers with coumarin molecules bound to the polymer chains could find application in a wide variety of optical electronic devices such as: remote sensors, data storage devices, optical switches, electro-optic modulators and more<sup>13</sup>. The syntheses of these materials is relatively facile and further work with respect to synthesizing similar materials tailored for specific purposes is in order.

## **2 Synthesis of Coumarins & Chromenes**

### **2.1 Introduction**

Coumarins are most often found in plant oils and are often a source of fragrance. Naturally occurring coumarins have demonstrated several biomedical applications including: platelet aggregation, cytotoxic activity, enzyme inhibition, antiviral, antibacterial, and antifungal activities<sup>3-12</sup>. Coumarin and chromene derivatives are widely distributed in all of the plants belonging to Belliferae, Rutaceae, and Compositae families<sup>3</sup>. New derivatives of coumarins have been isolated from plants with an ever-increasing variety of potential applications, some of which are briefly introduced in the following paragraphs<sup>37-46</sup>.

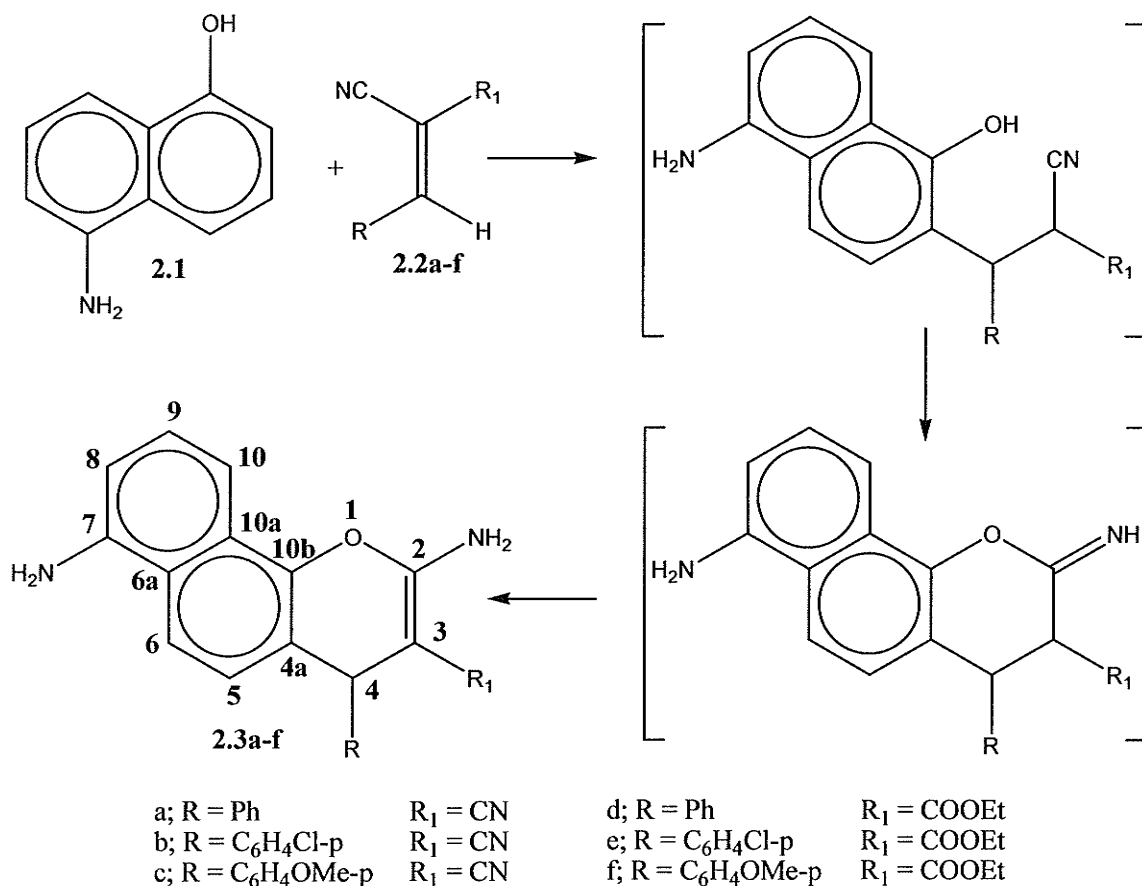
Studies have looked at the effects of coumarins as cytochrome p-450 inhibitors, a carcinogen-metabolizing enzyme<sup>47,48</sup>. The ability of some coumarins to inhibit acetyl cholinesterase and monoamine oxidase may decrease the depositions in the brain which lead to Alzheimer's disease<sup>49</sup>. Acting as selective dopamine antagonists, coumarins have been synthesized to reduce the negative effects of schizophrenia<sup>50</sup>. Coumarins have also been found to have beneficial effects on lymphedema and malaria<sup>51,52</sup>. In addition, there is evidence that coumarins prevent or slow tumor growth, by acting as antioxidants and inhibiting superoxide and nitric oxide production<sup>45,53-55</sup>. Based on these useful biological examples, novel coumarins, chromenes, and other benzo- derivatives have been synthesized<sup>56-59</sup>.

In other applications, binding coumarins to biological effector molecules has been used to trace the path of the molecule through a biological system<sup>60</sup>. The removal of a coumarin unit through photolysis has been used to selectively release compounds in living systems by breaking the bond linking the coumarin to a carrier molecule<sup>21,61</sup>. Industrially, coumarins also find use as flavouring in foods and scents in personal products.

In this chapter, we examine the results of a project to synthesize fused chromene and coumarin derivatives, initially aiming at evaluating their potential antimicrobial activity<sup>5,6,62-65</sup>.

## 2.2 Syntheses with 5-amino-1-naphthol

In the first of these syntheses, compounds **2.3a-f** were synthesized through the condensation of 5-amino-1-naphthol (**2.1**) with substituted  $\alpha$ -cyanocinnamitriles (**2.2a-c**) and ethyl  $\alpha$ -cyanocinnamates (**2.2d-f**) in ethanolic piperidine (**Scheme 2.1**). The formation of **2.3a-f** indicated that the naphtholate anion attacked at the carbon adjacent to the aryl ring of **2.2a-f** to produce an acyclic Michael adduct which then undergoes cyclization.



**Scheme 2.1**

Compounds **2.3a-f** were isolated as stable gray or red solids and their structures were confirmed with the aid of spectroscopic data. In the IR spectra of **2.3a-f**, bands at 3463-3167 cm<sup>-1</sup> were attributed to the two NH<sub>2</sub> functionalities. The bands at 2201-2186 cm<sup>-1</sup> were assigned to the CN moieties for compounds **3a-c** while those with absorbances of 1667-1677 cm<sup>-1</sup> were due to CO stretching of the chelated carbonyl group for compounds **3d-f**. In the <sup>1</sup>H NMR spectra of **3a-f**, characteristic signals for H-4 appeared as singlets at δ 4.77-5.00 ppm (**Table 2.1**).

**Table 2.1: Selected <sup>1</sup>H NMR Data of 4 H-Chromene derivatives (CDCl<sub>3</sub>)**

	H-4	H-5	H-6	H-8	H-10	NH <sub>2</sub> -2	NH <sub>2</sub> -7
<b>2.3a</b>	4.83	6.93	7.74	6.71	7.44	7.08	5.77
<b>2.3b</b>	4.88	6.70	7.74	6.70	7.42	7.11	5.77
<b>2.3c</b>	4.77	6.87	7.71	6.70	7.42	7.00	5.77
<b>2.3d</b>	4.98	7.11	7.21- 7.72	6.70	7.21- 7.72	7.75	5.75
<b>2.3e</b>	5.00	7.10	7.14- 7.73	6.72	7.14- 7.73	7.78	5.76
<b>2.3f</b>	4.91	6.76	7.06- 7.74	6.68	7.06- 7.74	7.69	5.74

The <sup>13</sup>C NMR spectra of compounds **2.3a-f** are presented in **Table 2.2**. The multiplicity of each signal was determined using an attached proton test (APT). The <sup>13</sup>C-NMR chemical shifts for all carbon atoms were assigned by comparing with electronically predicted values.

**Table 2.2: Selected <sup>13</sup>C NMR Data of 4 H-Chromene derivatives (CDCl<sub>3</sub>)**

	C-2	C-3	C-4	C-4a	C-6a	C-7	C-10a	C-10b
<b>2.3a</b>	159.7	55.6	40.3	120.0	121.4	144.2	123.4	145.2
<b>2.3b</b>	160.4	55.9	40.2	120.6	122.2	144.8	124.1	144.9
<b>2.3c</b>	160.2	56.5	40.1	120.7	122.0	142.8	124.1	144.9
<b>2.3d</b>	161.1	76.5	40.1	120.1	122.0	143.1	124.2	148.0
<b>2.3e</b>	161.4	76.5	40.3	120.3	122.5	143.5	124.6	147.5
<b>2.3f</b>	160.9	76.7	39.2	120.8	121.9	142.9	124.1	144.8

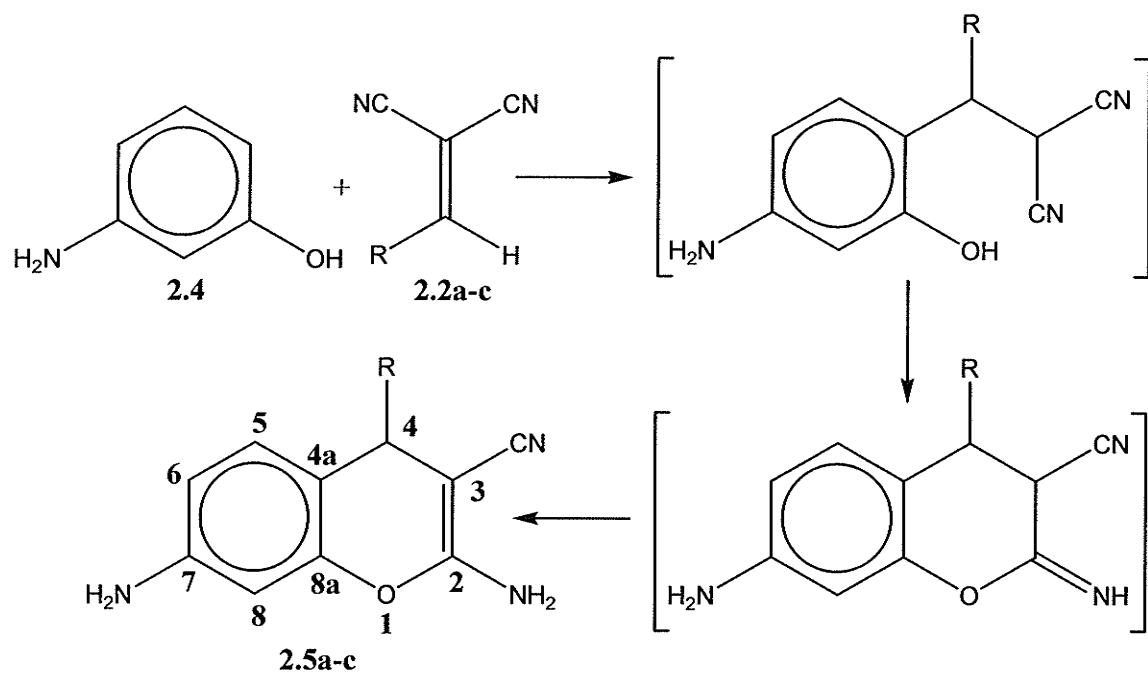
Attempts to react **2.3c** with triethyl orthoformate to produce a fourth fused ring were unsuccessful. The triethyl orthoformate attacked the C-7 amino group instead of the amino group in the C-2 position, thus there was no ring closure. The reaction was supported by NMR. In the  $^1\text{H}$  NMR spectrum the C-7  $\text{NH}_2$  did not resonate and the  $^{13}\text{C}$  NMR spectrum showed the resonance of C-3 at  $\delta$  56.6 ppm. This was further confirmed via reaction with hydrazine hydrate in ethanol or benzene at room temperature. The elimination of ethyl formate hydrazone gave the original enaminonitrile (**2.3c**)<sup>6,66-68</sup>.

### 2.3 Syntheses with 3-aminophenol

Condensation of 3-aminophenol (**2.4**) with  $\alpha$ -cyanocinnamonnitriles (**2.2a-c**) in ethanolic piperidine resulted in chromenes (**2.5a-c**) with the reactions going to completion (**Scheme 2.2**).

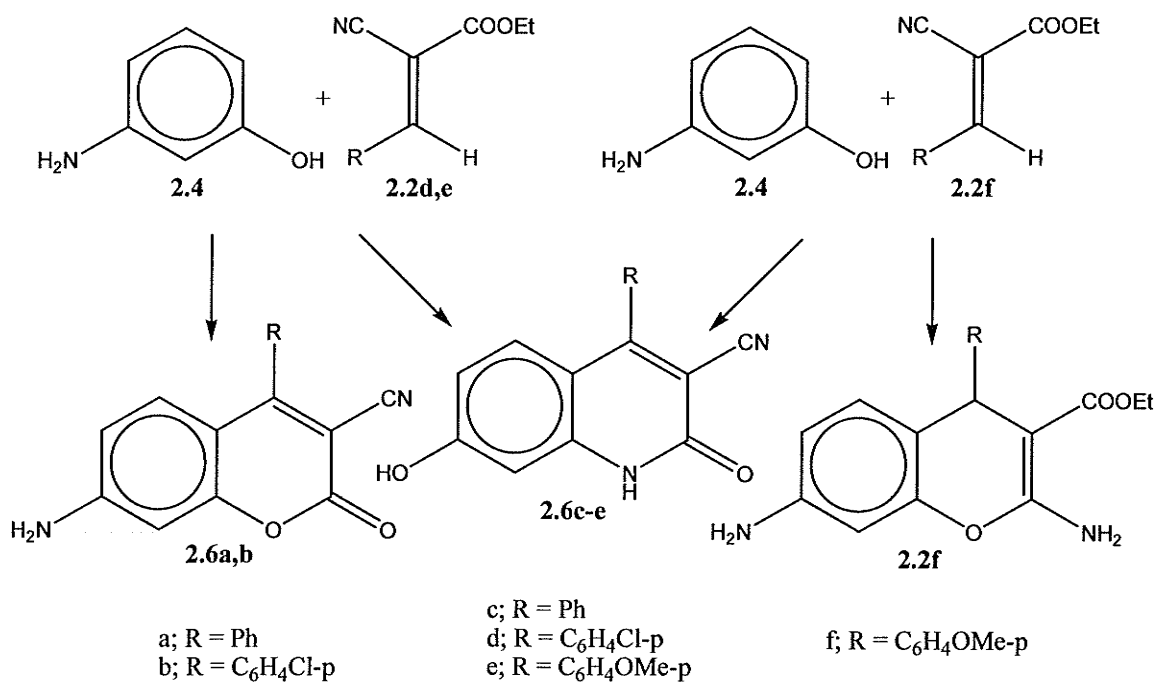
Interaction of **2.4** with ethyl  $\alpha$ -cyanocinnamates (**2.2d,e**) gave the coumarin derivatives (**2.6a,b**) along with the quinoline derivatives (**2.6c,d**). Reaction of 3-aminophenol (**2.4**) with **2.2f** produced both the quinoline derivative (**2.6e**) and the chromene derivative (**2.6f**) (**Scheme 2.3**). The formation of **2.5a-c** and **2.6f** indicates that the phenolate anion (C-6) attacked at the  $\beta$ -carbon of **2.2a-c,f**, giving another acyclic Michael adduct, which again underwent intramolecular cyclization.





a; R = Ph  
 b; R = C<sub>6</sub>H<sub>4</sub>Cl-p  
 c; R = C<sub>6</sub>H<sub>4</sub>OMe-p

**Scheme 2.2**



**Scheme 2.3**

In contrast, the formation of **2.6a,b** indicates that the phenolate anion (C-6) attacked at  $\beta$ -carbon of **2.2d,e**. The elimination of ethanol and aromatization yielded **2.6a,b**. The synthesis of **2.6c-e** occurs when the phenolate anion (C-4) attacks at the  $\beta$ -carbon of **2.2d-f**. Again, elimination of ethanol followed by aromatization gave the products.

Compounds **2.5a-c** and **2.6a-f** also had their structures confirmed with spectroscopic analysis. IR peaks at 3200 to 3450  $\text{cm}^{-1}$  were assigned to the two  $\text{NH}_2$  groups for compounds **2.5a-c** and **2.6f** as well as the single  $\text{NH}_2$  group in compounds **2.6a-b**. In **2.5a-c** and **2.6a-e** the CN group always absorbed within 20 reciprocal centimeters of 2205  $\text{cm}^{-1}$ . In the molecules with carbonyls, the absorbance peaks for them fell between 1650 and 1700  $\text{cm}^{-1}$ .

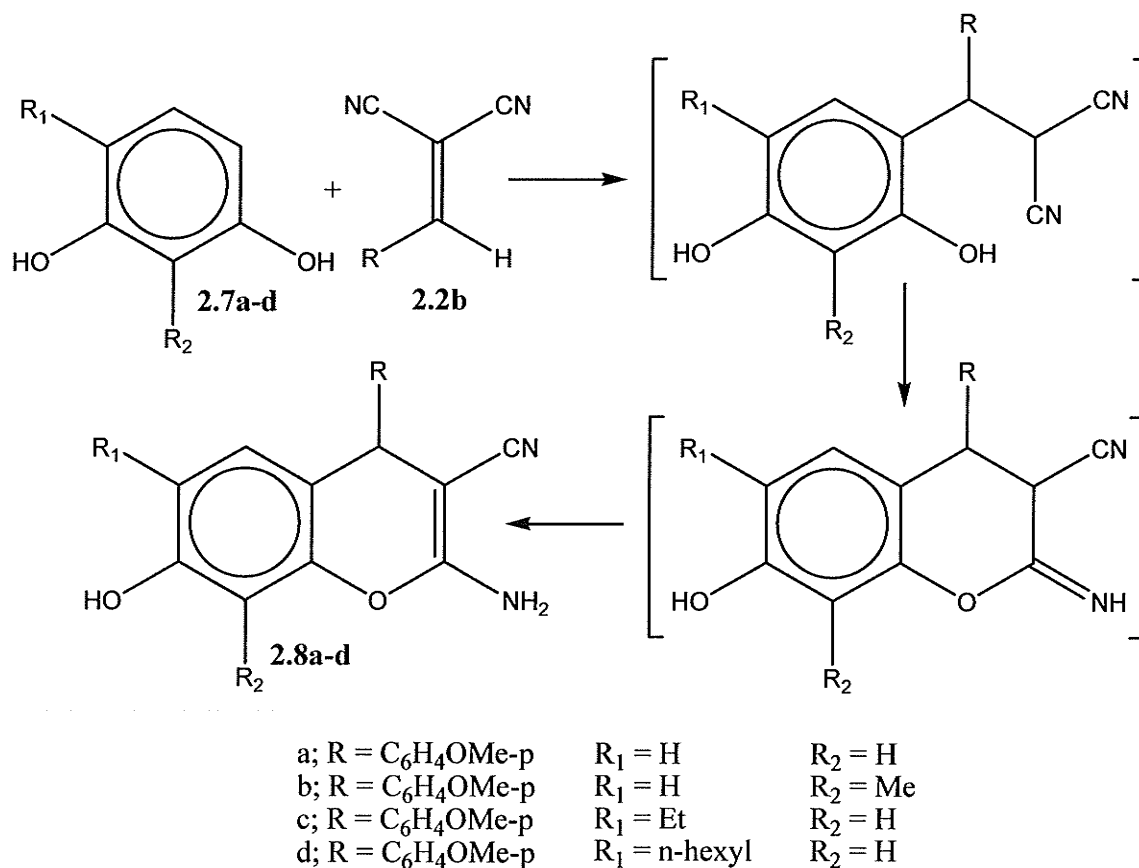
**Table 2.3: Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data of aminophenol derivative coumarins and chromenes ( $\text{CDCl}_3$ )**

	C-2	C-3	C-4	C-7	H-4	$\text{NH}_2$ -2	$\text{NH}_2$ -7
<b>2.5a</b>	160.4	56.5	40.1	148.8	4.53	6.80	5.24
<b>2.5b</b>	160.4	56.0	39.4	148.9	4.56	6.83	5.25
<b>2.5c</b>	160.3	56.8	39.3	148.7	4.46	6.73	5.21
<b>2.6a</b>	163.1	97.7	156.8	152.0	-	-	7.03
<b>2.6b</b>	161.8	91.0	158.3	156.7	-	-	7.07
<b>2.6c</b>	162.8	97.7	160.0	159.2	-	10.84 (NH-1)	12.31 (OH-7)
<b>2.6d</b>	162.8	98.3	160.3	159.8	-	10.90 (NH-1)	12.30 (OH-7)
<b>2.6e</b>	163.1	97.8	162.9	159.8	-	10.83 (NH-1)	12.30 (OH-7)
<b>2.6f</b>	161.2	77.2	38.2	148.2	4.65	7.52	5.14

**Table 2.3** shows NMR resonances of several selected atoms on the molecules. The proton bound to the C-4 carbon of the molecules typically resonated at a shift of 4.46 to 4.65 ppm in  $^1\text{H}$  NMR. The associated carbon (C-4) resonated at a shift of 38.2 to 40.1 ppm in the  $^{13}\text{C}$  NMR. When the C-4 carbon was aromatic, and there was no C-4 proton, (**2.6a-e**) the  $^{13}\text{C}$  resonance was 156.8-162.9 ppm.

## 2.4 Syntheses with Resorcinol and Resorcinol Derivatives

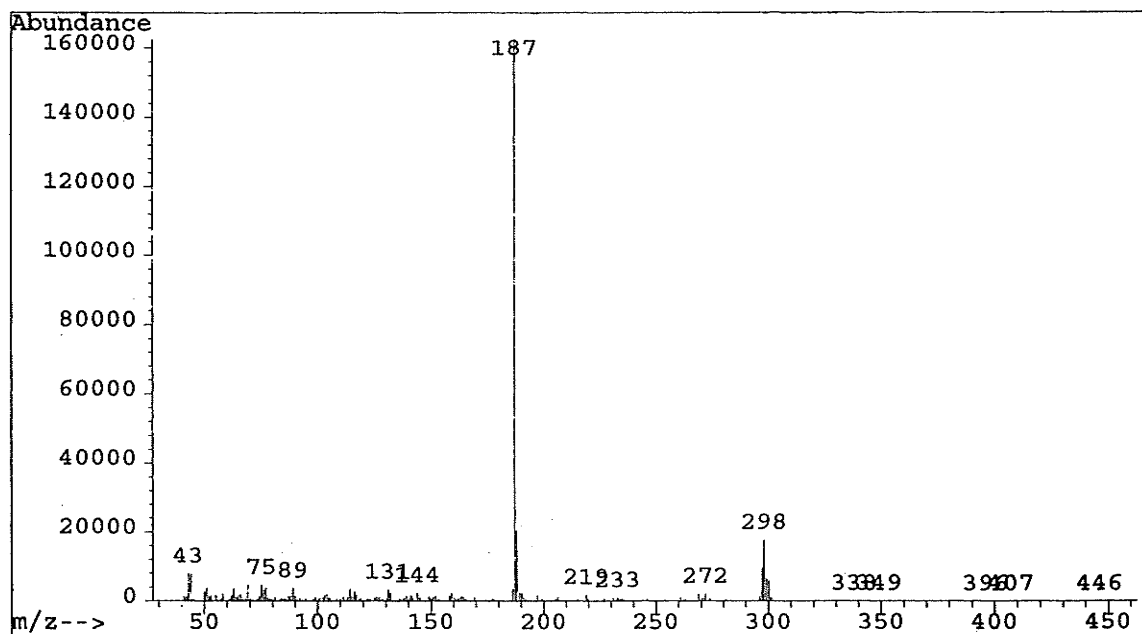
Compounds **2.8a-d** were synthesized through condensation of resorcinol (**2.7a**) or resorcinol derivatives (**2.7b-d**) with  $\alpha$ -cyanocinnamionitrile (**2.2b**) (**Scheme 2.4**).



**Scheme 2.4**

Spectroscopic characterization yielded results comparable to the similar compounds presented above (**2.5a-c**, **2.6f**). IR shifts of 3200 and 3500  $\text{cm}^{-1}$  were attributed to the  $\text{NH}_2$  and OH groups, respectively. The CN moiety absorbed at 2180 to 2198  $\text{cm}^{-1}$ .

As with all of the coumarins and chromenes synthesized in this chapter, mass spectrometry was used to verify the formation of the expected chromene or coumarin. **Figure 2.1** shows the fragmentation pattern for **2.8a**, typical to the compounds synthesized in this work. The peak at a charge to mass ratio of 298 is the molecular peak for compound **2.8a**. The aromatic ring (represented by R in all **Chapter 2** schemes) is a commonly lost portion of the molecule. This fragmentation pattern is very evident in the spectrum below, with a fragment peak of the chromene appearing with a mass of 187.

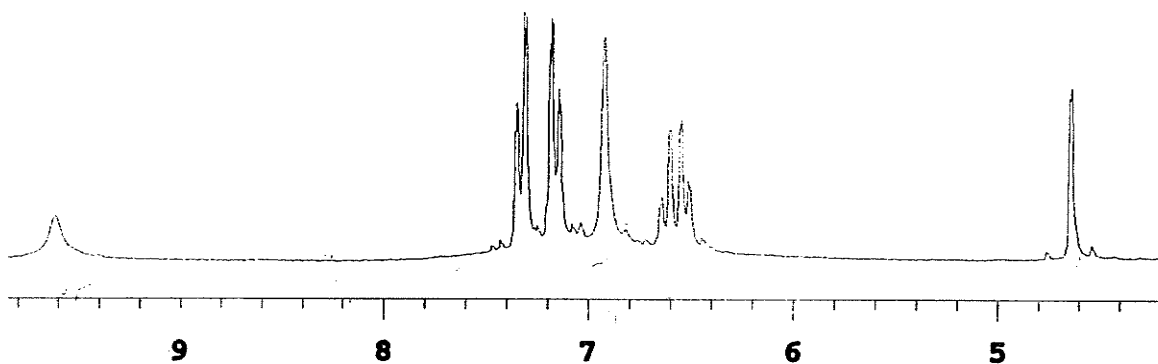


**Figure 2.1** DI-EIMS spectrum showing the fragmentation of **2.8a**. The molecular ion peak appears at a mass of 298. The major fragment at 187 is the loss of the aromatic ring,  $-\text{C}_6\text{H}_4\text{Cl}$ .

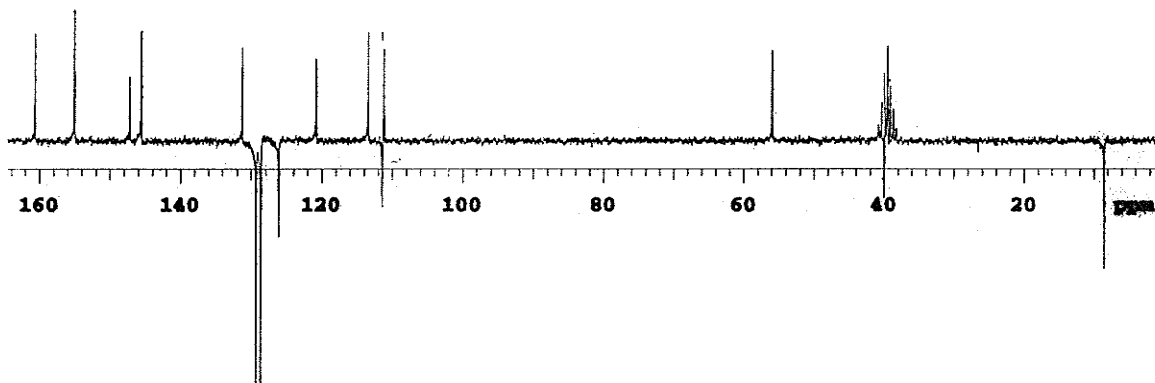
$^1\text{H}$  and  $^{13}\text{C}$  NMR were as predicted, further supporting the syntheses, with the C-4 carbons and protons resonating where expected in all cases. **Table 2.4** shows some of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts. **Figures 2.2** and **2.3** show the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR traces of **2.8b**, respectively.

**Table 2.4: Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data of resorcinol and resorcinol derivative chromenes ( $\text{CDCl}_3$ )**

	C-2	C-3	C-4	C-7	H-4	NH <sub>2</sub> -2	OH-7
<b>2.8a</b>	160.3	55.8	39.3	148.8	4.65	6.91	9.80
<b>2.8b</b>	160.6	55.9	39.5	147.3	4.64	6.93	9.62
<b>2.8c</b>	160.3	55.9	39.4	146.7	4.63	6.78	9.37
<b>2.8d</b>	160.3	55.9	39.4	146.7	4.63	6.86	9.60



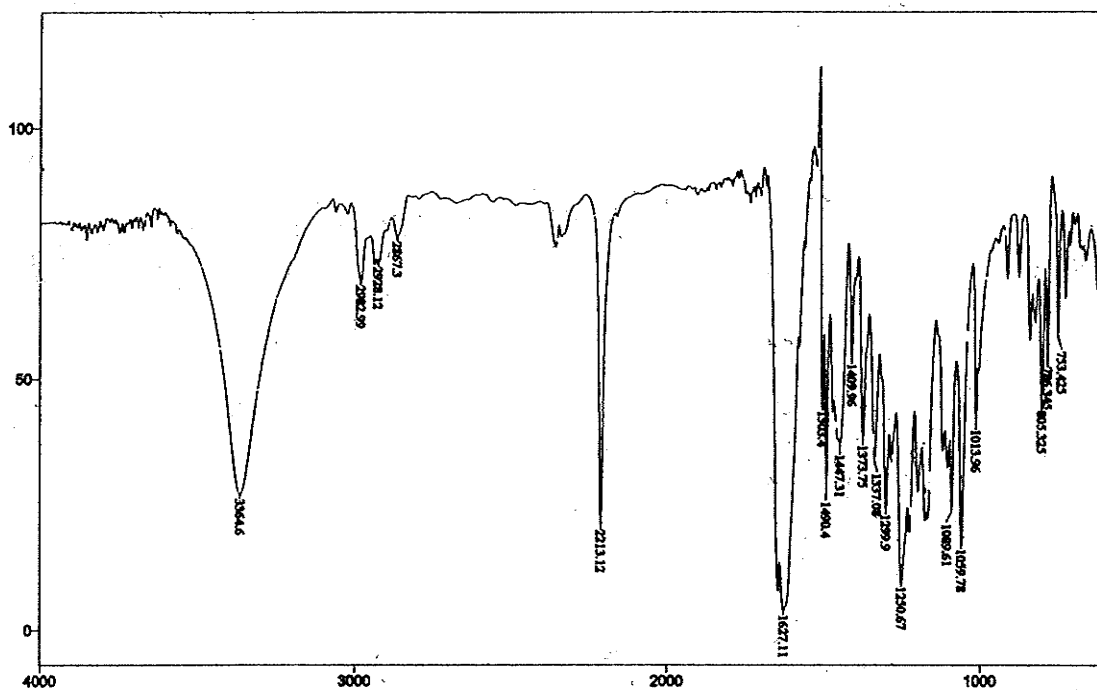
**Figure 2.2**  $^1\text{H}$  NMR spectrum of chromene **2.8b** in acetone- $d_6$ . The C-4 proton resonates at 4.64 ppm and the OH-7 proton resonates at 9.62 ppm.



**Figure 2.3**  $^{13}\text{C}$  NMR spectrum of chromene **2.8b** in DMSO- $d_6$ . This is an attached proton test spectrum (APT). Carbons with one or three attached protons appear as negative peaks; carbons with none, two or four protons as positive peaks. The peak due to the C-4 carbon (one proton) is therefore found as a negative peak, below the DMSO peaks at 39.5 ppm. The methyl carbon resonates at 8.5 ppm.

Reaction of these compounds with triethyl orthoformate was examined. The triethyl orthoformate attacked the  $\text{NH}_2$  at the C-2 position, without the problem of an attack at the C-7 amino group as with compound **2.3c**. Despite the addition in a location which could undergo ring closure, this did not readily occur; the product contained an aliphatic, ether linked ethyl group.

These reactions were confirmed by IR and  $^1\text{H}$  NMR. The IR spectrum (**Figure 2.4**) has a large peak at  $3500\text{ cm}^{-1}$ , representative of the C-7 OH stretch. However, the  $\text{NH}_2$  stretch located at  $3200\text{ cm}^{-1}$  from the C-2  $\text{NH}_2$  was not present. Further, in the  $^1\text{H}$  NMR spectrum, the C-2  $\text{NH}_2$  did not resonate. A quadruplet at 4.37 ppm and a triplet at 1.33 ppm also support this addition, with these peaks being characteristic of  $-\text{OCH}_2\text{CH}_3$  groups.

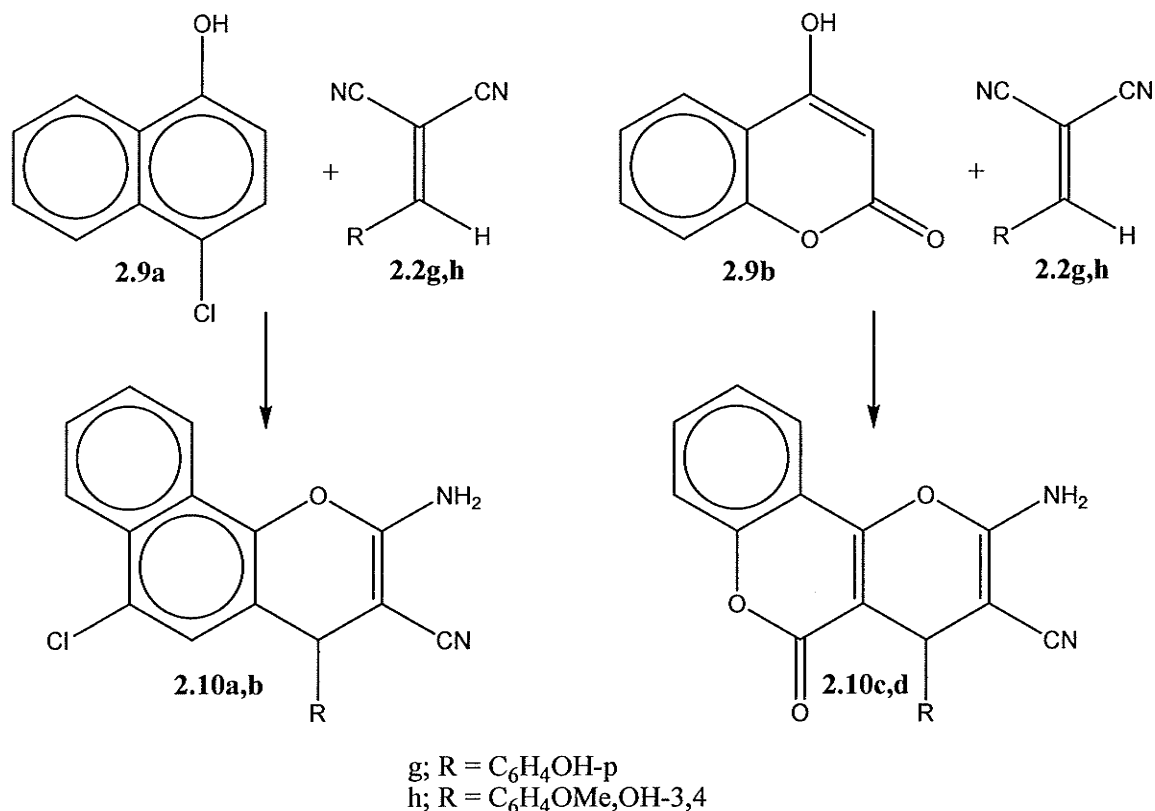


**Figure 2.4** IR spectrum of chromene **2.8b** following reaction with triethyl orthoformate. The lack of any peak at  $3200\text{ cm}^{-1}$  is indicative of the completed reaction. The OH stretch at  $3500\text{ cm}^{-1}$  is still very evident, as is the CN stretch at  $2213\text{ cm}^{-1}$ .

## 2.5 Syntheses with 4-chloro-1-naphthol and 4-hydroxycoumarin

Condensation of 4-chloro-1-naphthol (**2.9a**) and 4-hydroxycoumarin (**2.9b**) with substituted  $\alpha$ -cyanocinnamonnitriles (**2.2g,h**) in ethanolic piperidine resulted in products **2.10a-d** (Scheme 2.5). In these reactions the phenolate or naphtholate anion attacked at the  $\beta$ -carbon of **2.2** to again yield an acyclic Michael adduct which then cyclized.

The four  $\alpha$ -naphthol and 4-hydroxycoumarin compounds (**2.10a-d**) also had their structures confirmed using IR, NMR and mass spectrometry. IR absorbences for the  $\text{NH}_2$  group as well as the OH groups on the aromatic ring were found from roughly  $3200$  to  $3500\text{ cm}^{-1}$ . CN peaks were sharp and uniform, appearing between  $2191$  and  $2199\text{ cm}^{-1}$ . The carbonyls (**2.10c,d**) absorbed at  $1708$  and  $1711\text{ cm}^{-1}$ , respectively.



**Scheme 2.5**

NMR characterization was supportive of the expected products, as in all previous cases (Table 2.5). The 4-hydroxycoumarin derivative compounds (**2.10c,d**) differed in the <sup>13</sup>C spectra from the α-naphthol derived compounds (**2.10a,b**) at the C-5 carbon, as it was a carbonyl as opposed to aromatic carbon.

**Table 2.5: Selected <sup>1</sup>H and <sup>13</sup>C NMR Data of α-naphthol and 4-hydroxycoumarin derivative compounds (CDCl<sub>3</sub>)**

	C-2	C-3	C-4	C-5	H-4	NH <sub>2</sub> -2	OH-Ar
<b>2.10a</b>	159.8	56.6	39.9	127.8	4.78	7.15	9.37
<b>2.10b</b>	159.8	56.4	40.2	127.6	4.78	7.16	8.94
<b>2.10c</b>	158.0	58.6	36.3	159.6	4.32	7.32	9.34
<b>2.10d</b>	158.0	58.4	36.5	159.6	4.35	7.32	8.92



## 2.6 Antibacterial Activity

All of the newly synthesized compounds were tested for antibacterial activity against *Streptococcus pyogenes* (ATCC 19615), *Staphylococcus aureus* (ATCC 25923), *Enterococcus faecalis* (ATCC 19433), *Escherichia coli* (ATCC 25933), and *Pseudomonas aeruginosa* (ATCC 27853) at the concentration of 25 µg/ml, 50 µg/ml and 100 µg/ml by using disc agar diffusion method. This testing was done with the assistance of Dr. Athar Ata and his research group.

It was found that only compounds **2.8b** and **2.8c** exhibited antibacterial activity against *Staph. aureus* at all of the above-mentioned concentrations. The diameters of zones of inhibition of compounds **2.8b** and **2.8c** at the concentration of 25 µg/ml were measured 15 mm and 12 mm, respectively.

The four strains tested were used with the intention of examining different basic types of bacterium with currently available strains. In order for a previously untested compound to receive further testing it would normally demonstrate stronger inhibition<sup>65</sup>. The values obtained here are not within the range of commercial viability. Minimum inhibition concentrations (MIC) orders of magnitude lower than this would have been favourable<sup>65,69-71</sup>.

## 2.7 Experimental

Full experimental and characterization results, including full MS and NMR peak assignments, may be found in **Appendix 1**.

## *Materials*

Coumarin precursors, other reagents and solvents are commercially available, and were purchased in highest available purity from the Aldrich Chemical Co.

## *Characterization*

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Gemini 200 MHz NMR spectrometer, at 200 and 50 MHz, respectively, with chemical shifts calculated from deuterated solvent residues. NH,  $\text{NH}_2$  and OH groups were verified by adding  $\text{D}_2\text{O}$  to the solvated sample and observing which peaks were no longer present.

IR spectra were obtained using a Bomem, Hartmann & Braun Fourier transform infrared spectrophotometer with KBr pellets. Melting points were determined in open capillary tubes and are uncorrected.

Direct Injection – Electron Impact Mass Spectrometry (DI-EIMS) was used to verify the formation of the desired product, particularly in cases where low solubility of the product made for sensitivity issues with solution NMR. The spectrometer used was a Hewlett Packard 5989 B Mass Spectrometer.

Antibacterial activity testing was performed by Leigha Conci of Dr. Athar Ata's research group. The disc agar diffusion method was used, with disc concentrations of 25  $\mu\text{g/ml}$ , 50  $\mu\text{g/ml}$  and 100  $\mu\text{g/ml}$ .

## *General Procedure for the synthesis of (2.3a-f; 2.5a-c; 2.6a-f; 2.8a-d; 2.10a-d):*

A solution of phenolic compounds (2.1, 2.4, 2.7a-d, 2.9) or 4-hydroxycoumarin (2.9b) (10 mmol) in ethanol was treated with substituted  $\alpha$ -cyanocinnamionitriles (2.2a-

**c,g,h**) (10 mmol) or ethyl  $\alpha$ -cyanocinnamates (**2.2d-f**) (10 mmol) and piperidine (0.2 g, 2 mmol). The reaction mixture was heated with stirring until complete precipitation (reaction time: approx. 15 min. for **2.2a-c,g,h**; 120 min. for **2.2d-f**). The solid product, which formed, was collected by filtration and recrystallized from ethanol to give **2.3a-f**, **2.5a-c**, **2.6a-f**, **2.8a-d** and **2.10a-d**.

## 2.8 Conclusions & Future Work

Using a non-rigorous method, chromene, coumarin and quinoline derivatives containing an amino or hydroxy group have been synthesized. Two of the compounds demonstrated weak antibacterial activity. They may be used as intermediates for the preparation of new materials containing fused chromenes, coumarins and quinolines.

As discussed in **Chapter 1** coumarins and their derivatives may also have potentially useful optical properties, especially the 3-heteraryl coumarins<sup>59,72-74</sup>. Although this research was initially stimulated with the intention of examining new materials for biomedical applications, interest in their optical properties developed as the work progressed. When the antimicrobial inhibitions were found to be very low, the potential of synthesizing coumarin polymers for their optical possibilities developed.

With respect to the further research presented in this thesis, compounds will be incorporated into polystyrenes and polymethacrylates. It is the hope that the incorporation into polymeric materials expands the potential uses for these chemicals. The remaining chapters of this work consist of the synthesis and characterization of polymers with coumarin moieties pendant to the polymeric backbone.

### 3 Coumarins Pendant to Polystyrene Backbones

#### 3.1 Introduction

Here we combine the varied and promising properties of coumarin molecules with the tunable bulk physical properties of polymers. It has been found that polymer-bound coumarins usually maintain their optical properties with little change to the optical properties<sup>75</sup>. Thus a coumarin with a known and targeted optical property could be incorporated into a polymer with little or no change in that optical property. This would greatly increase the options for physically manipulating coumarins.

In addition, the photodimerizability of coumarin molecules mentioned earlier (**Chapter 1**) gives rise to several interesting possibilities when incorporated into polymers. When the C-3 and C-4 carbons of a coumarin form a link with the C-3 and C-4 carbons of a second coumarin, the resulting 4-membered ring could form a bridge to another polymer. This would cross-link the polymer, altering the physical properties<sup>76-78</sup>. As this photodimerization is reversible, the potential exists to optically and reversibly alter the properties of a material.

One of the most common polymers used today is polystyrene<sup>1</sup>. Along with other common plastics, it is synthesized by opening the vinyllic double bond to form an aliphatic chain<sup>78-80</sup>. This may be accomplished from styrene monomers in a variety of ways, including radical and ionic processes<sup>81</sup>.

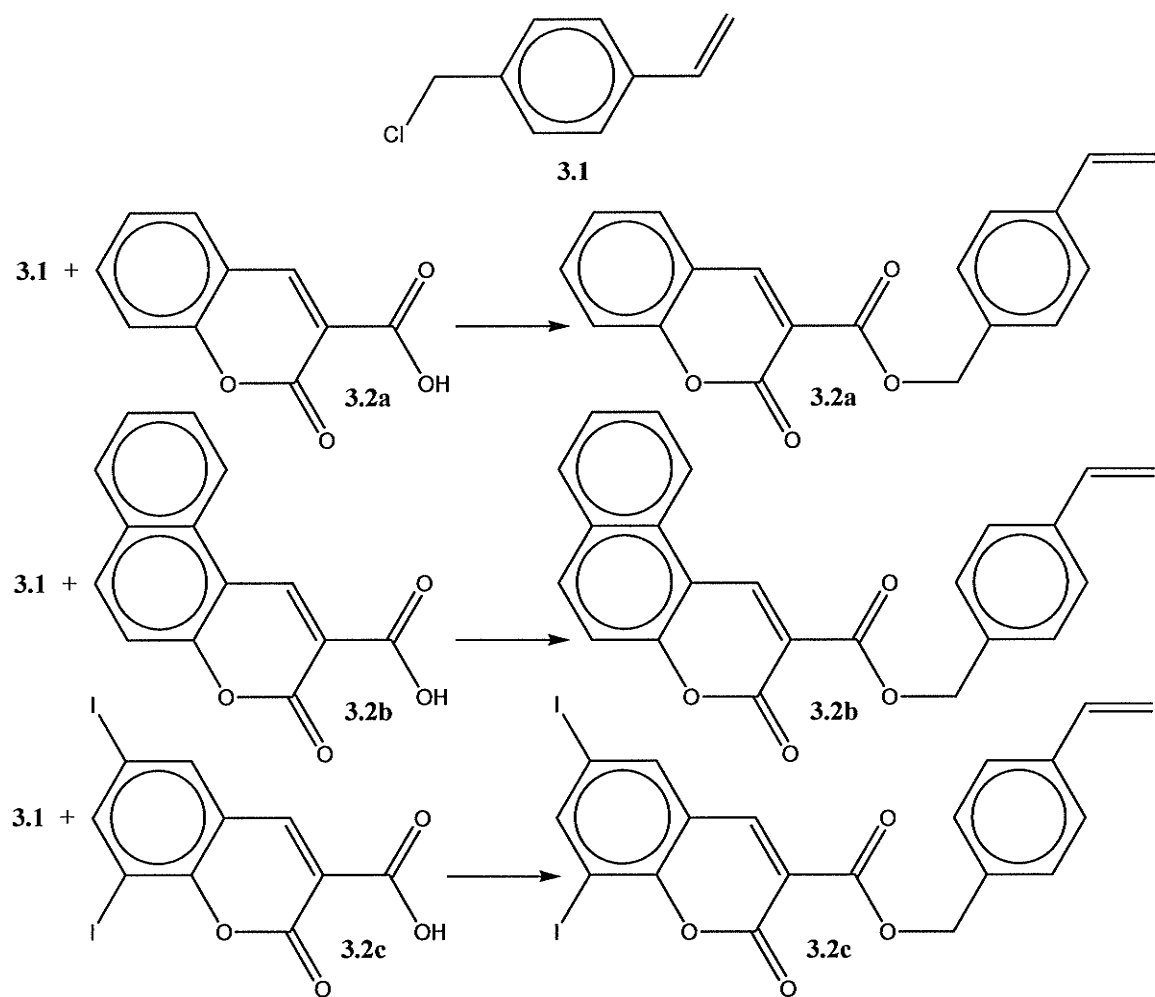
There were two possible synthetic routes for this work: the incorporation of molecules into already existing polymers, and the polymerization of monomeric units to

which the coumarins are already bound. The latter was used, giving complete control over the ratio of coumarins pendant to polystyrene moieties in the backbone, as opposed to incomplete addition to a preexisting polymer. In this way, each monomer contained a potentially optically active molecule, the maximum possible.

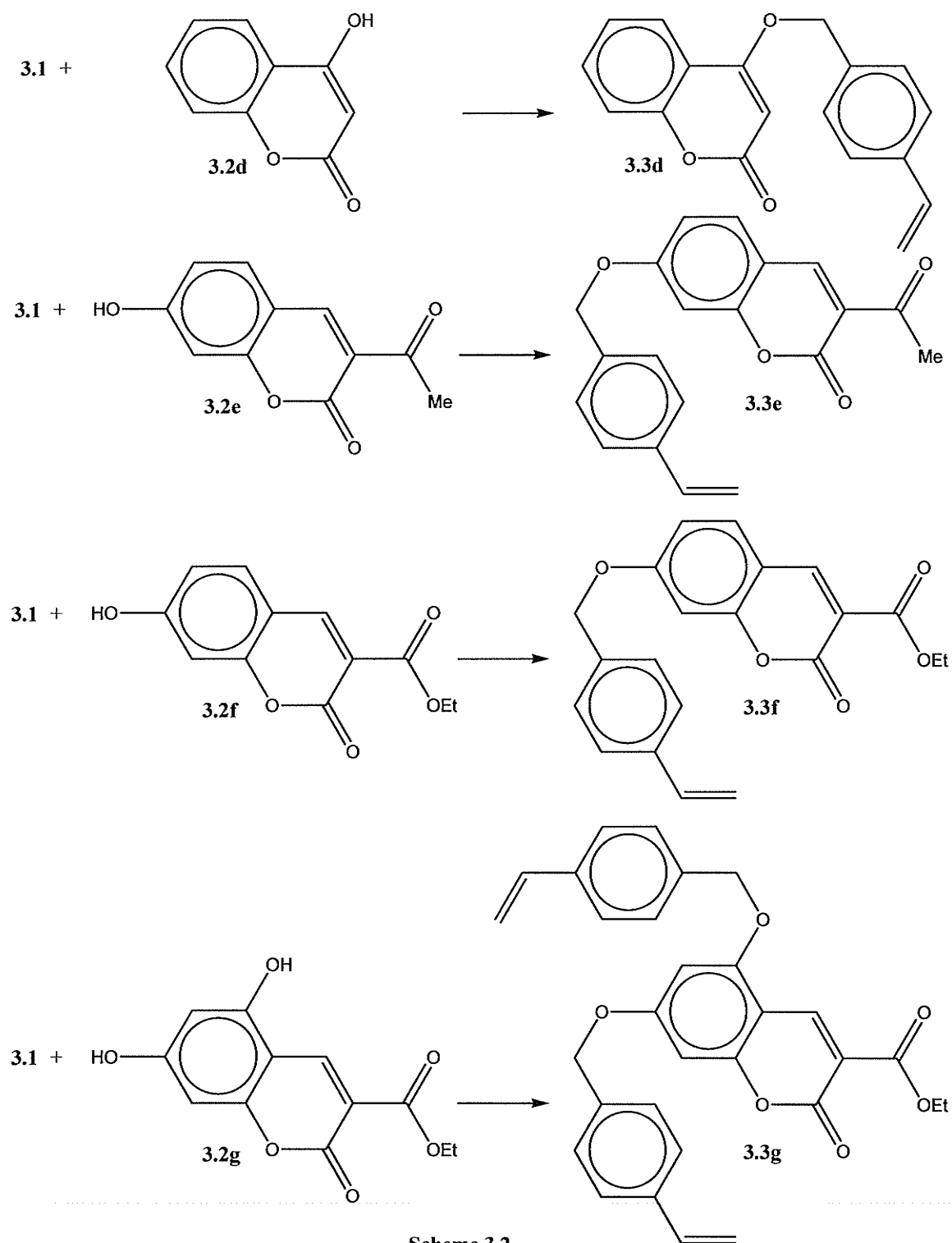
### 3.2 Synthesis of Monomeric Styrene Units

Seven different monomers (**3.3a-3.3g**) were initially prepared, all from previously synthesized coumarins, using the method in **Chapter 2**<sup>82</sup>. In order to incorporate a functionalized styrene group in all of the monomers, 4-vinylbenzylchloride (**3.1**) was combined with coumarin molecules in two different ways.

In the first method, the chloride (**3.1**) was reacted with a carboxylic acid (**Scheme 3.1**) to form an ester linkage between the styrene and the coumarin. In the second set of monomers, an ether link was formed by reaction with an hydroxyl group (**Scheme 3.2**).

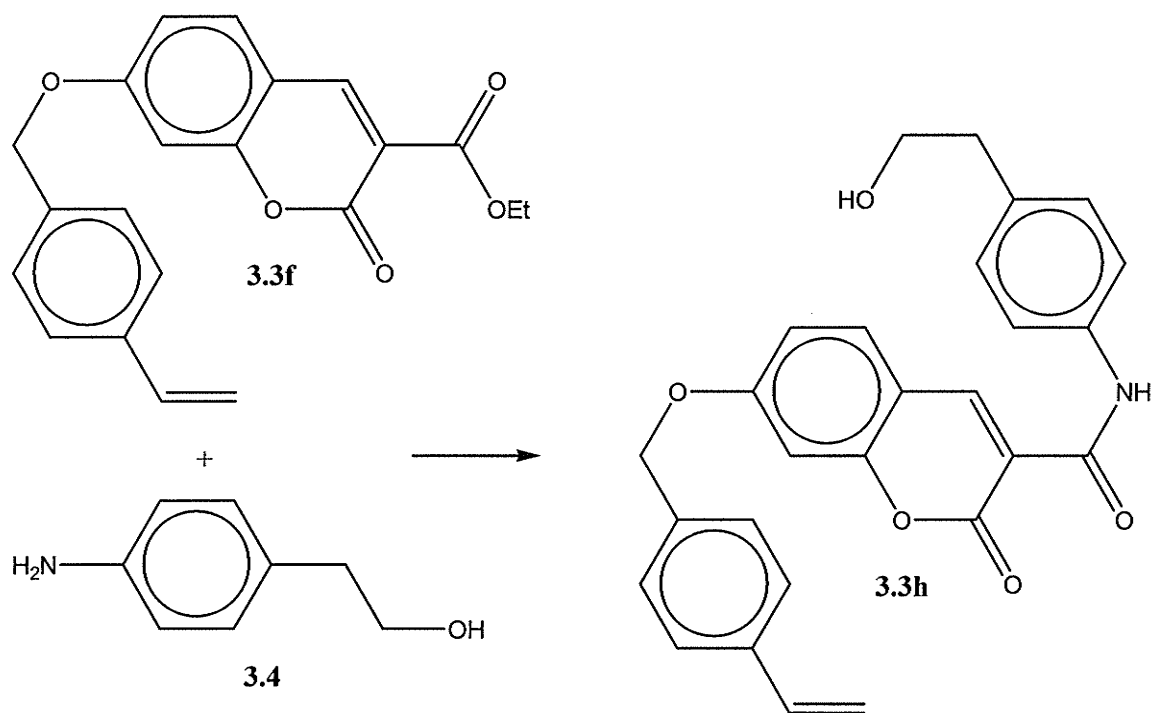


**Scheme 3.1**



Scheme 3.2

Monomer **3.3g** differs from the others in that it contains two styrene units per coumarin molecule. When polymerized, this will form a cross-linked network polymer, which is expected to be insoluble<sup>2</sup>. An eighth monomer (**3.3h**) was prepared by combining monomer **3.3f** with compound **3.4** in a fusion reaction (Scheme 3.3). This yielded eight different monomers.

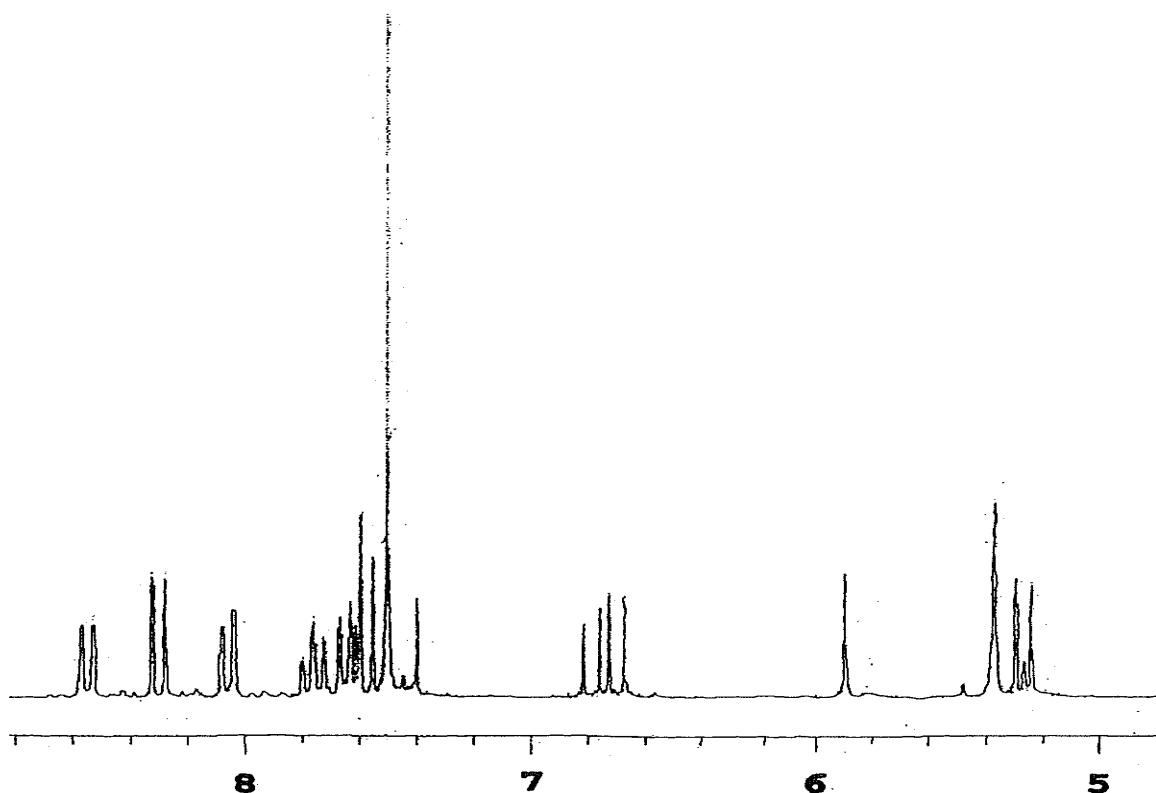


Scheme 3.3

Monomers were all characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and TGA. In addition, monomers **3.3b** and **3.3e** were examined for fluorescence, and both demonstrated fluorescent effects. Finally, due to the low solubility of the polymers, monomer **3.3e** was sent for solid-state <sup>13</sup>C cross-polarization magic angle spinning (CPMAS) NMR.

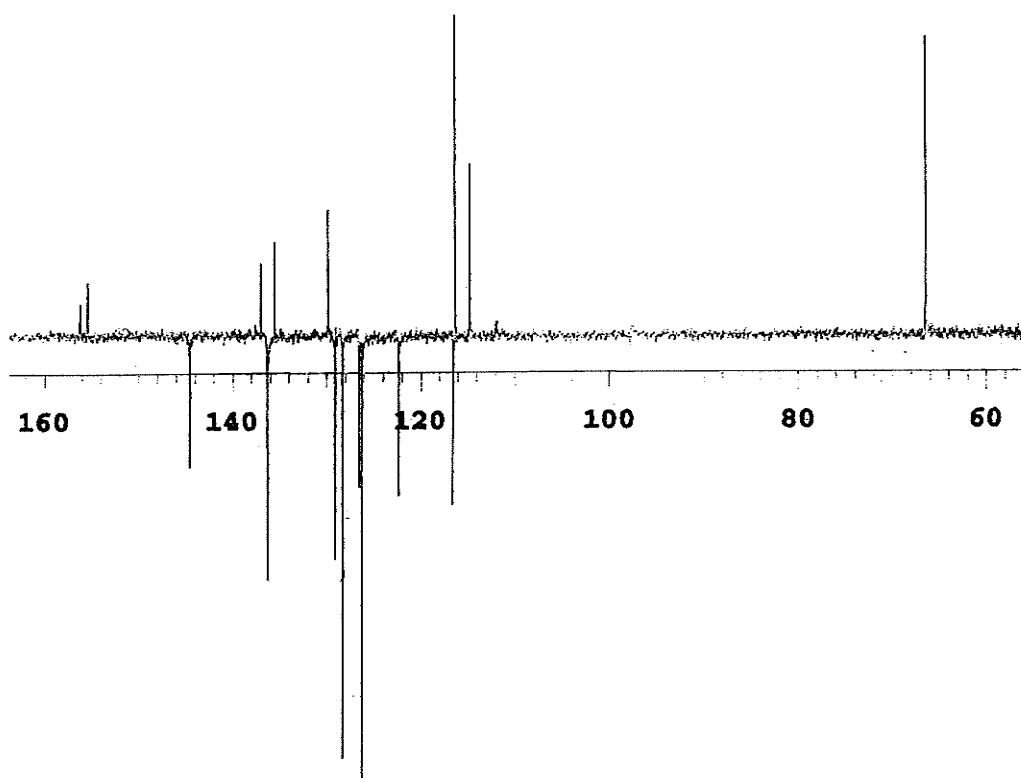


For all of the monomers, the  $^1\text{H}$ -NMR olefin protons resonate as two doublets at shifts of approximately 5.25 and 5.75 ppm for the olefinic  $\text{CH}_2$  protons and a doublet of doublets at 6.75 ppm for the olefinic  $\text{CH}$  proton. The linking  $\text{CH}_2$  protons which connect the coumarin to the styrene resonate as a singlet between 5.5 and 5.75 ppm, sometimes overlapping one of the olefinic  $\text{CH}_2$  protons. It is also important to note in cases where a proton is attached to the C-4 carbon (**Scheme 2.1, 2,2**) it is even more deshielded than aromatic protons, appearing at shifts between 8.5 and 9 ppm. The  $^1\text{H}$  NMR spectrum for monomer **3.3b** is shown in **Figure 3.1**.



**Figure 3.1**  $^1\text{H}$  NMR spectrum of monomer **3.3b** in  $\text{DMSO-d}_6$ . The pair of doublets at 5.27 and 5.56 are due to the olefinic  $\text{CH}_2$ . The small doublet of doublets at 6.75 arises from the olefinic  $\text{CH}$ .

The corresponding  $^{13}\text{C}$  spectrum of monomer **3.3b** is shown in **Figure 3.2**. Common to all of the monomers, the linking  $\text{CH}_2$  peak resonates at a shift of approximately 66 ppm. The olefinic peaks resonate at shifts of 110-115 ppm ( $=\text{CH}_2$ ) and shifts of 132-136 ppm ( $=\text{CH}$ ). The coumarin carbonyl resonates at shifts between 155 and 165 ppm. Pertinent  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are shown in **Table 3.1** and **Table 3.2**, respectively. In the case of monomers **3.3d** and **3.3g**, very low solubility prevented the acquisition of useful  $^{13}\text{C}$  spectra.



**Figure 3.2**  $^{13}\text{C}$  NMR spectrum of monomer **3.3b** in  $\text{DMSO-d}_6$ . Peaks at shifts of 114 ppm and 135 ppm are due to olefinic carbons. The peak at a shift of 66 ppm arises from the resonance of the linking  $\text{CH}_2$ .

**Table 3.1:  $^1\text{H}$  NMR Data for Monomers ( $\text{CDCl}_3$  for 3.3a, Acetone- $d_6$  for 3.3g, DMSO- $d_6$  for all others)**

Monomer	Linking $\text{CH}_2$	Olefinic $\text{CH}_2$	Olefinic CH	H-4
<b>3.3a</b>	5.38 (s, 2H)	5.27 (d, $J = 10.9$ Hz, 1H), 5.77 (d, $J = 17.6$ Hz, 1H)	6.73 (dd, $J = 10.5$ & 6.6 Hz, 1H)	8.53 (s, 1H)
<b>3.3b</b>	5.37 (s, 2H)	5.27 (d, $J = 10.9$ Hz, 1H), 5.56 (d, $J = 17.6$ Hz, 1H)	6.75 (dd, $J = 10.8$ & 7.0 Hz, 1H)	9.39 (s, 1H)
<b>3.3c</b>	5.32 (s, 2H)	5.27 (d, $J = 10.7$ Hz, 1H), 5.84 (d, $J = 17.6$ Hz, 1H)	6.74 (dd, $J = 10.9$ & 7.0 Hz, 1H)	8.65 (s, 1H)
<b>3.3d</b>	5.36 (s, 2H)	5.16 (d, $J = 8.4$ Hz, 1H), 5.73 (d, $J = 17.6$ Hz, 1H)	6.63 (dd, $J = 10.6$ & 7.0 Hz, 1H)	-
<b>3.3e</b>	5.23 (s, 2H)	5.26 (d, $J = 8.9$ Hz, 1H), 5.84 (d, $J = 17.6$ Hz, 1H)	6.73 (dd, $J = 10.9$ & 6.7 Hz, 1H)	8.61 (s, 1H)
<b>3.3f</b>	5.24 (s, 2H)	5.26 (d, $J = 8.9$ Hz, 1H), 5.84 (d, $J = 18.0$ Hz, 1H)	6.74 (dd, $J = 11.0$ & 6.6 Hz, 1H)	8.71 (s, 1H)
<b>3.3g</b>	5.15 (s, 2H)	5.24 (d, $J = 12.9$ Hz, 1H), 5.77 (d, $J = 17.4$ Hz, 1H)	6.75 (dd, $J = 11.2$ & 6.1, 1H)	-
<b>3.3h</b>	5.26 (s, 2H)	5.28 (d, $J = 7.4$ Hz, 1H), 5.85 (d, $J = 17.6$ Hz, 1H)	6.74 (dd, $J = 10.9$ & 6.6 Hz, 1H)	8.89 (s, 1H)

**Table 3.2:  $^{13}\text{C}$  NMR Data for Monomers ( $\text{CDCl}_3$  for 3.3a,  $\text{DMSO-d}_6$  for all others)**

Monomer	Linking $\text{CH}_2$	Olefinic $\text{CH}_2$	Olefinic $\text{CH}$	$\text{C}=\text{O}$
<b>3.3a</b>	66.54	113.94	135.76	156.01, 162.16
<b>3.3b</b>	66.42	114.69	136.25	156.12, 163.00
<b>3.3c</b>	66.44	114.64	136.14	155.20, 161.82
<b>3.3e</b>	69.93	114.71	136.19	163.75, 194.71
<b>3.3f</b>	69.90	114.67	136.17	162.77, 163.68
<b>3.3h</b>	69.94	114.72	136.18	161.13, 163.52

**Table 3.3** shows the carbonyl peaks observed in the IR spectra, as well as experimental yield information. The carbonyl absorbances were compared with the absorbances of polymers as a preliminary method of determining the effects of polymerization on optical properties. Monomer **3.3d** was only obtained in low yields due to troubles with solubility and separation.

**Table 3.3: FT-IR of Carbonyls & Yields of Monomers**

Monomer	Yield	IR ( $\text{cm}^{-1}$ ) of $\text{C}=\text{O}$
<b>3.3a</b>	45 %	1697, 1764
<b>3.3b</b>	82 %	1691, 1762
<b>3.3c</b>	72 %	1706, 1758
<b>3.3d</b>	3.3 %	1704
<b>3.3e</b>	98 %	1614, 1741
<b>3.3f</b>	69 %	1622, 1761
<b>3.3g</b>	97 %	1596, 1748
<b>3.3h</b>	38 %	1602, 1696

Through the assistance of Dr. Pierre Harvey and his research group, two of the monomers were sent away for luminescence studies, which were unavailable to us within our facility. Monomer **3.3b** exhibited strong fluorescence with a  $\lambda_{\text{max}}$  of 432 nm (intensity 11500 V) at 77 K.  $\lambda_{\text{max}}$  was 431 nm (intensity 6000 V) at room temperature. Monomer **3.3e** fluoresced with a  $\lambda_{\text{max}}$  of 415 nm (intensity 8.6 V) at 77 K and  $\lambda_{\text{max}}$  of 436 nm (intensity 750 V) at room temperature. Monomer **3.3e** also exhibited a higher wavelength, phosphorescent effect at lower temperatures, phosphorescing at a  $\lambda_{\text{max}}$  of 500 nm (intensity 7.9 V) at 77 K. It should be noted that this phosphorescence is of a lower intensity, which is expected<sup>36</sup>.

Due to the low solubility of some of the monomers, difficulty in obtaining NMR data for the polymers was anticipated. For this reason, the monomers were characterized using thermogravimetric analysis (TGA). Slow heating of the sample determines at what temperatures degradative breakdowns of the molecules occur. It was expected that the monomers would have a larger percent weight loss at the first loss temperature, and less of a loss at higher temperatures (**Table 3.4**) due to the increased stability effects of polymeric materials.

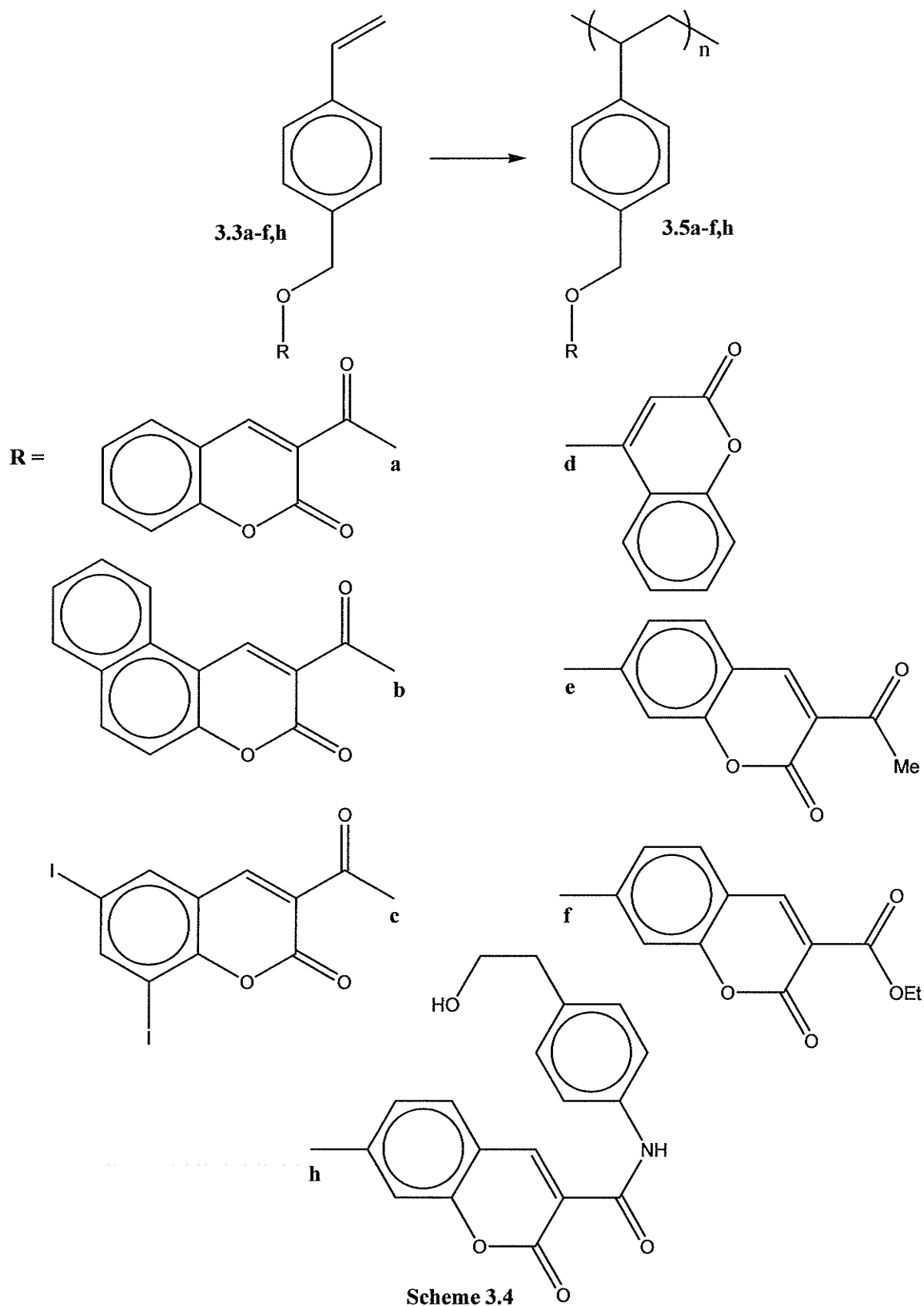
**Table 3.4: TGA Data for Monomers**

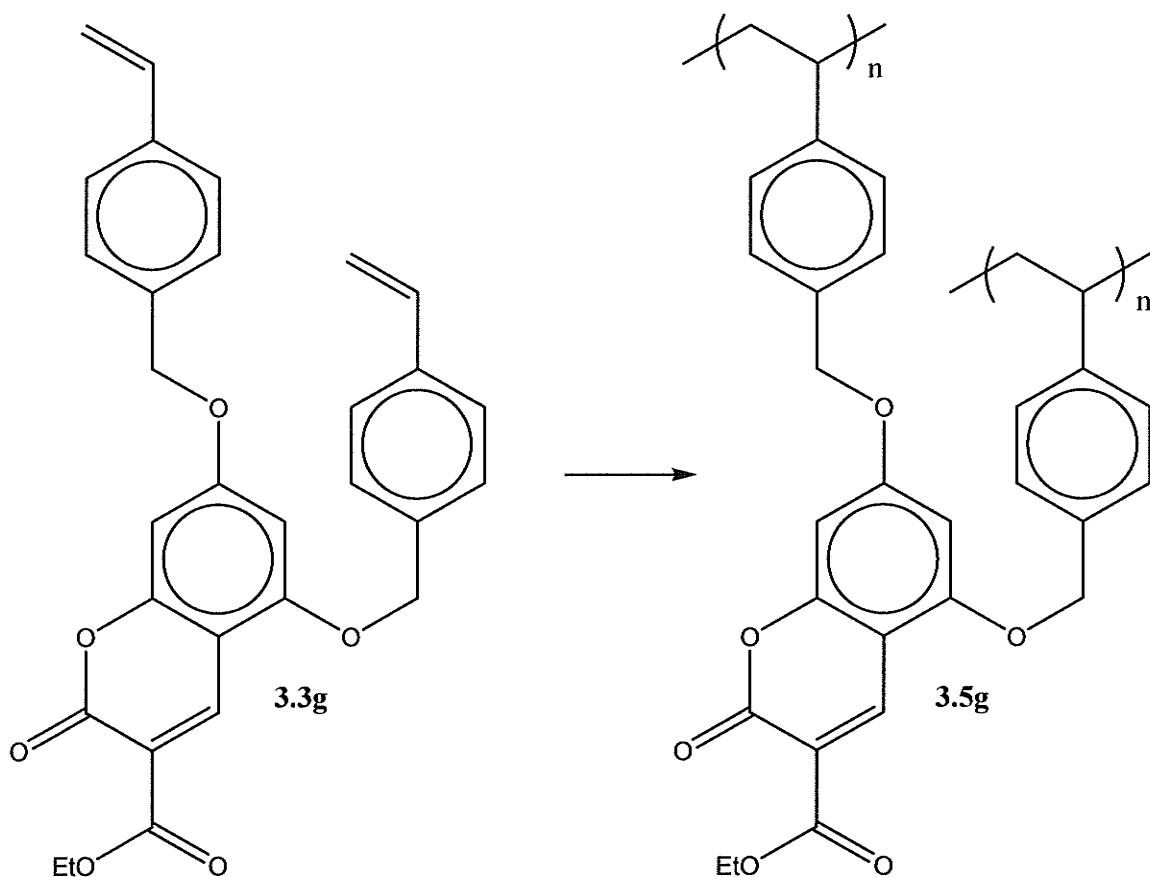
Compound	Onset °C	Endset °C	Loss	Onset °C	Endset °C	Loss
<b>3.3a</b>	311	402	72.6%	-	-	-
<b>3.3b</b>	349	422	72.5%	-	-	-
<b>3.3c</b>	317	341	61.1%	-	-	-
<b>3.3d</b>	394	463	55.1%	-	-	-
<b>3.3e</b>	313	366	19.9%	436	476	32.3%
<b>3.3f</b>	339	364	23.4%	453	490	31.5%
<b>3.3g</b>	157	205	8.9%	412	475	37.7%
<b>3.3h</b>	334	373	29.3%	442	478	30.8%

### 3.3 Polymerization of Styrene Monomers

Each of the monomers was then polymerized in one- to two-day reactions using the radical initiation method. The polymerization reactions are shown in **Scheme 3.4** with the exception of the polymerization of monomer **3.3f** which is represented in **Scheme 3.5** to better elaborate on the formation of a cross-linked polymer.

Using azobispropionitrile (AIBN) as an initiator, the polymerization reactions were performed in refluxing toluene. There are several reasons for the choice of toluene: heat produces energy increasing the rate of reaction, the higher temperature solvent kept the polymers dissolved longer leading to higher molecular weights and the materials were partially soluble in toluene to begin with. These polymerizations give rise to the series of eight coumarin–styrene polymers (**3.5a-3.5g**) which are the subject of this chapter.





**Scheme 3.5**

Unfortunately, this also led to the formation of polymers which were either totally insoluble or sparingly soluble in the deuterated solvents available for NMR studies. A series of reactions were carried out on monomer **3.3f** (chosen for good solubility of the monomer) for shorter times. It was found that after three hours, very little polymer had formed, with increasing polymer formation as time progressed, to a point at which a solubility maxima was reached (18 hours).

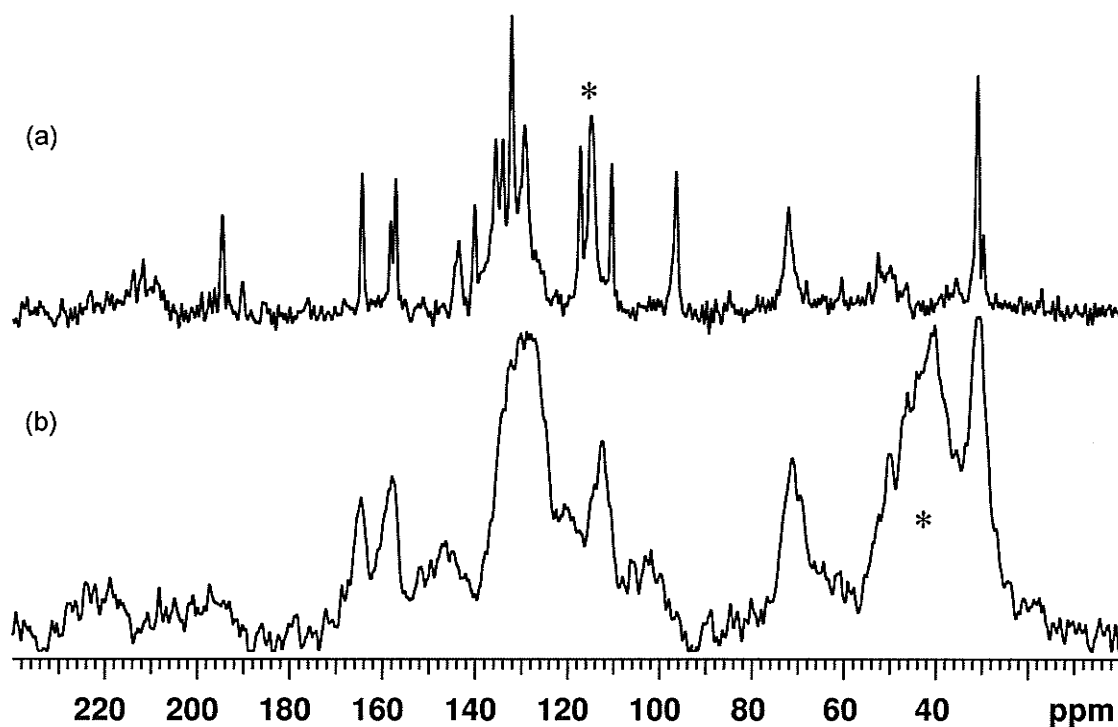
From this, it was determined that the maximum length of polymer produced was based upon solubility in the reaction solution. All of the characterizations for polymers



were performed upon polymers which had been allowed to polymerize until they dropped out of solution.

Due to the low solubility, solution NMR was not an effective method to characterize the materials. Polymers (**3.5a-3.5g**) were characterized with FT-IR, TGA and DSC. In order to compare with monomer (**3.3e**), the corresponding polymer (**3.5e**) was also sent for solid-state  $^{13}\text{C}$  CPMAS NMR. This work was done with the assistance of Dr. Scott Kroeker and his research group.

$^{13}\text{C}$  cross-polarization magic-angle spinning (CPMAS) NMR of the monomer and insoluble polymer assessed the extent of polymer formation (**Figure 3.3**).



**Figure 3.3**  $^{13}\text{C}$  CPMAS NMR spectra of (a) monomer **3.3e** and (b) polymer **3.5e**. Asterisks indicate positions of diagnostic olefinic (monomer) and aliphatic (polymer backbone) peaks.

The olefinic peak between 110 and 120 ppm in the monomer does not resonate in the polymer spectrum and aliphatic backbone peaks appear at 35-50 ppm in the polymeric material, further confirming the success of the polymerization reaction.

**Table 3.5** shows the FT-IR and yield information for the polymers (**3.5a-3.5g**) to further compare the carbonyl absorbances. The peaks associated with the carbonyls in the monomers compare well with the polymer carbonyl peaks. This indicates that there was probably no change in basic coumarin optical behaviour following polymerization. After the polymerization reaction, products were washed with solvent in which the monomers were soluble to remove any unreacted monomers. This process also removed oligomeric material in some cases. All polymeric yield calculations were made following the washing procedure.

**Table 3.5: FT-IR and Reaction Data for Polymers**

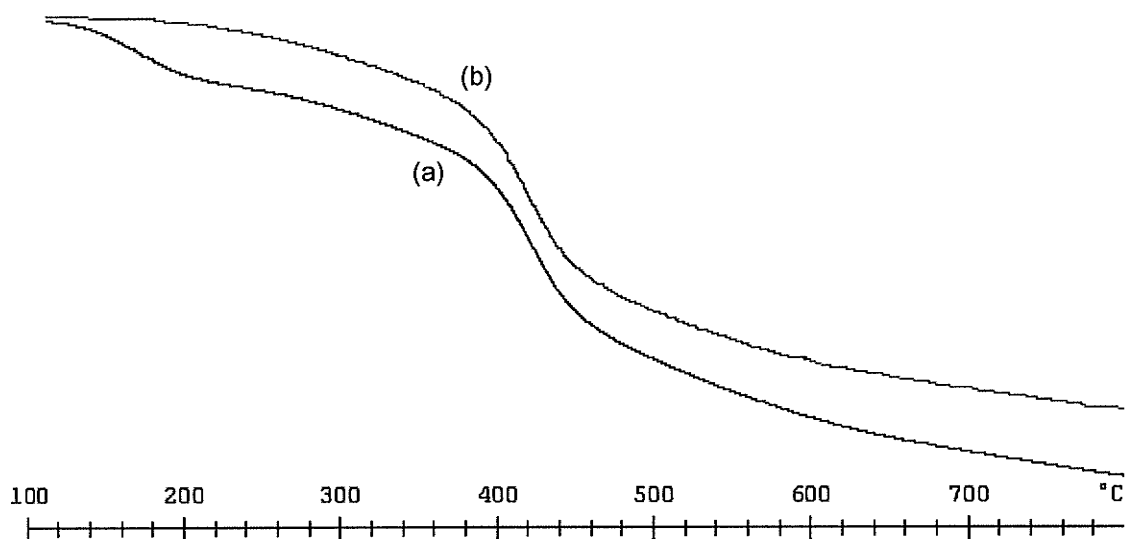
Polymer	Yield	IR (cm <sup>-1</sup> ) of C=O
<b>3.5a</b>	30 %	1717, 1762
<b>3.5b</b>	80 %	1701, 1750
<b>3.5c</b>	64 %	1698, 1764
<b>3.5d</b>	98 %	1700
<b>3.5e</b>	63 %	1615, 1733
<b>3.5f</b>	69 %	1608, 1766
<b>3.5g</b>	95 %	1602, 1748
<b>3.5h</b>	85 %	1602, 1696

One common property of polymeric materials is increased thermal stability<sup>2</sup>. Based on this, increased stability was expected for polymers **3.5a-3.5g** as compared to the monomers (**Table 3.6**).

**Table 3.6: TGA Data for Polymers**

Compound	Onset °C	Endset °C	Loss	Onset °C	Endset °C	Loss
<b>3.5a</b>	312	363	53.0%	427	462	27.9%
<b>3.5b</b>	323	370	49.0%	430	466	19.2%
<b>3.5c</b>	296	339	59.8%	606	653	29.1%
<b>3.5d</b>	-	-	-	405	459	50.8%
<b>3.5e</b>	321	362	19.2%	439	475	27.3%
<b>3.5f</b>	342	381	28.0%	435	472	24.7%
<b>3.5g</b>	-	-	-	411	469	34.7%
<b>3.5h</b>	337	375	28.7%	445	481	23.4%

In all cases except polymer **3.5c**, the polymerization yielded either increased stability at lower temperatures and/or a reduction in the % weight loss at this first step. In each case, polymerization produced greater stability for the material at higher temperatures. **Figure 3.4** is the combined traces of two thermograms.



**Figure 3.4** TGA thermograms for the monomer-polymer pair **3.3d** (a) & **3.5d** (b). The upper curve represents the polymer. The vertical axis represents weight loss, with the horizontal axis representing temperature. This shows less weight lost both at lower temperatures and all temperatures for the polymeric material.

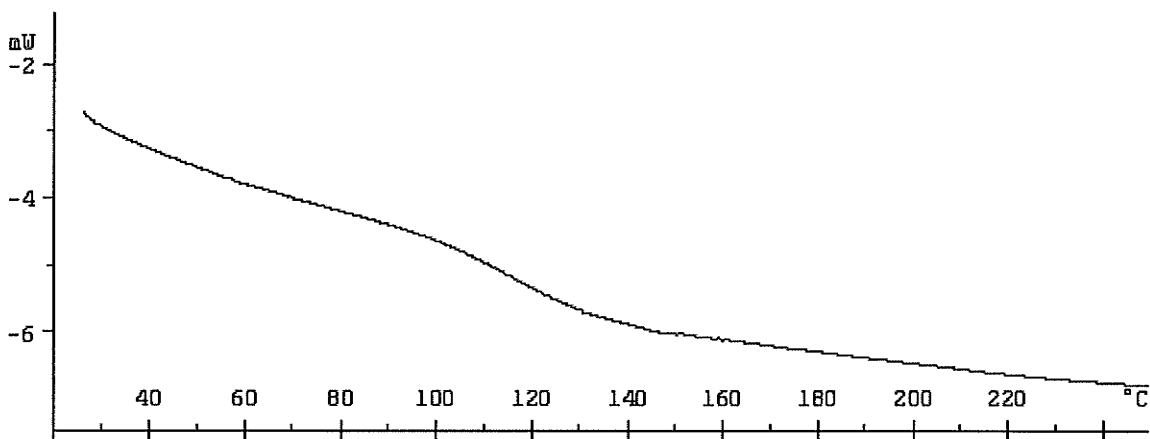
It follows that the polymerization does not reduce the thermal stability of the coumarins, but does not necessarily produce higher thermal stability for the pendant moieties. Only polymers **3.5d** and **3.5g** showed any increased thermal stability. However, coumarins are fairly stable molecules to begin with, the most fragile of the molecules examined here (**3.3g**) not degrading until 150 °C and all of the others exhibiting stability to over 300 °C.

Each of the eight polymers (**3.5a-3.5g**) was examined with differential scanning calorimetry (DSC) to determine their glass transition temperatures (**Table 3.7**). The glass transition temperature of a polymer is the temperature at which a solid-state to solid-state phase change occurs. It is obtained by examining the change in heat capacity of a polymer over a slow change in temperature. A sample DSC trace (**polymer 3.5b**) is shown in **Figure 3.5**. Combining this information with thermal data, we can conclude

that the polymers degrade before they melt, but have  $T_g$ 's well below their degradation temperature.

**Table 3.7: DSC Data for Polymers**

Compound	Onset °C	$T_g$ °C
<b>5a</b>	110.0	112.6
<b>5b</b>	109.0	115.8
<b>5c</b>	100.0	116.9
<b>5d</b>	118.6	123.8
<b>5e</b>	125.8	122.7
<b>5f</b>	102.8	114.7
<b>5g</b>	83.5	119.7
<b>5h</b>	88.7	114.3



**Figure 3.5** DSC trace of polymer **3.5b**. The line represents the energy required to change the temperature of the polymer. The slope of the line can be viewed as the heat capacity of the material. The  $T_g$  is found where the heat capacities change (the slopes of the intersecting lines change).

### 3.4 Experimental

Full experimental and characterization results may be found in **Appendix 1**.

#### *Materials*

The coumarins (**3.2a-3.2g**) were all synthesized in the lab using previously developed methodology<sup>5,6,58-61,70</sup>. Coumarin precursors, other reagents and solvents are commercially available, and were purchased in highest available purity from the Aldrich Chemical Co. AIBN was purchased from Alfa Aesar.

#### *Characterization*

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 200 MHz NMR spectrometer, at 200 and 50 MHz, respectively, with chemical shifts calculated from deuterated solvent residues (DMSO-d<sub>6</sub>, acetone-d<sub>6</sub>).

IR spectra were obtained using a Bomem, Hartmann & Braun Fourier-transform infrared spectrophotometer with KBr pellets.

Thermogravimetric analysis was accomplished using a Mettler TGA/SDTA851<sup>°</sup> with a heating rate of 20 °C/min under nitrogen. Sample sizes ranged from 3.0 to 6.5 mg, in a ceramic crucible.

Differential scanning calorimetry was performed on a Mettler DSC821<sup>°</sup> with a heating rate of 20<sup>°</sup>C/min under nitrogen. Sample sizes were 2.5 to 3.5 mg, in aluminum crucibles.

Solid state  $^{13}\text{C}$  NMR was performed at 150.79 MHz on a Varian Inova 600 MHz spectrometer by Pedro Aguiar of Dr. Scott Kroeker's research group. The spinning speed was varied to confirm isotropic peak assignments over the range 8 to 14 kHz. 11 mg of sample was packed into a 3.2 mm rotor. Cross-polarization from  $^1\text{H}$  was effected by variable-amplitude CP, increased linearly from 25 to 45 kHz rf field strength on the observe channel, using a 5  $\mu\text{s}$  excitation pulse on the proton channel, and a contact time of 4 ms followed by  $^1\text{H}$  decoupling of 68 kHz during acquisition. Relaxation delays were 15 s, and the spectra are the result of 512 (monomer) and 1024 (polymer) co-added transients. Chemical shifts are referenced to TMS using the secondary standard of adamantane.

Emission spectra were measured by Patrick Shipman with the assistance of Dr. Pierre Harvey's research group. They were measured using a nanosecond  $\text{N}_2$  laser system from PTI (model GL-3300 pumping a dye laser model GL-302) with an excitation wavelength of 311 nm. Emission spectra were measured using a SPEX Fluorolog II.

#### *Synthesis of Styrene Monomers (3.3a-3.3g)*

For the preparation of compounds (3.3a-3.3c), the respective coumarins (3.2a-3.2c) were reacted with 1.1 equivalents of 4-vinylbenzylchloride (3.1) to form the ester linkages. The reactions were carried out in DMF with 1.5 molar equivalents of potassium carbonate overnight at approximately 50  $^\circ\text{C}$ , with the exception of 3.3c, which yielded higher at 100  $^\circ\text{C}$  due to increased solubility. All compounds were precipitated in water, dried under reduced pressure, and washed with ether.

Compound (**3.3d**) was prepared with the same method, at reflux for 24 hours. Due to the low solubility of the starting material, the reaction did not go to completion, and the starting material was dissolved in hot ethanol and rereacted.

The three monomers (**3.3e-3.3g**) were synthesized as **3.3a-3.3c** with 2 equivalents of potassium carbonate. They were also reacted as **3.3d** at a temperature of approximately 100 °C.

#### *Fusion to form Monomer (3.3h)*

Monomer (**3.3h**) was synthesized using a fusion reaction. 0.9 mol of **3.3f** were combined in a 50 ml RBF with 1.0 mol 4-aminophenylethanol (**3.4**). The reaction was heated to 10 °C over complete melting (approx 120 °C) and stirred for 90 minutes. The product was separated by removal of the excess 4-aminophenylether in alcohol, washed with ether, and dried under reduced pressure.

#### *Synthesis of Polymers (3.5a-3.5h)*

All of the monomers were polymerized by a radical initialization method. AIBN was combined with monomers (**3.3a-3.3h**) in ratios from 1:5 to 1:20 in toluene. The toluene was refluxed under nitrogen for varying lengths of time (3 hours – 2 days). All polymers which were tested by TGA and DSC were reacted for at least 24 hours. Following reaction time, the polymers were washed with chloroform to remove the AIBN and solvent, precipitated in hexane and dried under reduced pressure.



### 3.5 Conclusions & Future Work

Polystyrenes with pendant coumarin moieties may be easily synthesized. The polymers had increased stability with respect to the monomers. Glass transition temperatures were significantly lower than the temperature at which the first degradations occurred. This has value in terms of processibility; a material which may be softened and manipulated without degrading allows for easier molding. These materials may be heated up, reshaped or manipulated and then cooled, as with liquid molding.

Unfortunately, the styrene backbone of a polymer only further reduces the already low solubility of coumarin molecules. This has a negative impact in terms of bulk synthesis. In the next chapter, the effect on the use of a polymethacrylate (PMMA) backbone instead of a polystyrene backbone is examined. PMMA is considerably more soluble than PS.

It would also be interesting to conduct tests on the photodimerization property of these coumarins. This was not done due to the lack of available suitable equipment to induce the dimerization. The changes in physical and optical properties of the polymers could be applicable in terms of physical curing and optical switching and storage, respectively.

## 4 Coumarins Pendant to Polymethacrylate Backbones

### 4.1 Introduction

This chapter examines the combination of coumarin molecules with polymer backbones. Polymethacrylate (PMMA) is a more soluble polymer than polystyrene<sup>1,2</sup>. The intent of using PMMA is to produce a polymeric material with greater ease of handling than the polystyrenes discussed in the previous chapter. Currently, methacrylate polymers are being synthesized with coumarins and tested for their potential in such applications as: optical storage films, photo curable materials, light harvesters and controlled drug-release materials<sup>17,83-85</sup>.

In **Chapter 3**, coumarins were linked to the polymer backbone with either an ester or ether linkage. The polymers in this chapter are attached to coumarins with an ester linkage. The 4-vinylbenzylchloride (**3.1**) has a terminal chloride, which can be used to form both ester and ether bonds. Methylmethacrylic acid (**4.4**), a monomer which polymerizes into PMMA, has a terminal acid moiety. In a single reaction step, increasing ease of production, it is only possible to form an ester.

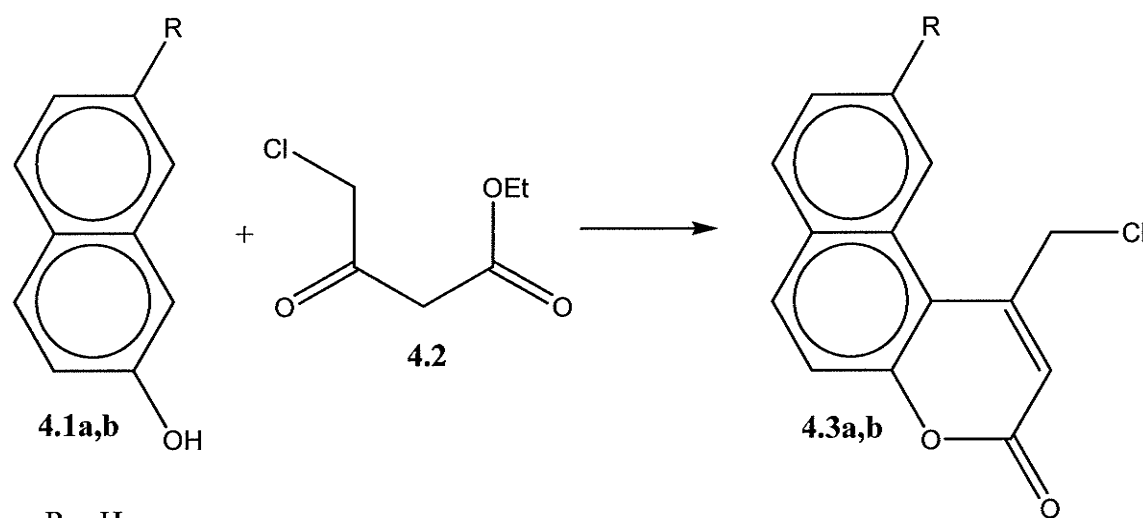
PMMA is a slightly less commonly used polymer than polystyrene in society<sup>1</sup>. In addition to having higher solubility, these polymers tend to have lower glass transition temperatures. These properties arise from the backbone flexibility of the polymer.

Polymerization of the methacrylic acid monomers may be accomplished in analogous ways to the polymerization of other vinyllic monomers. For the polymerization of the methacrylic coumarin monomers in this chapter, AIBN was used as

a radical initiator, as with polymerizations in **Chapter 3**. The coumarin was bonded to the methacrylic acid prior to any polymerization. This was done to ensure that every possible site on the PMMA backbone was occupied by a coumarin molecule.

## 4.2 Synthesis of Methacrylate Monomers

Two coumarins (**4.3a**, **4.3b**) were prepared via a Pechmann condensation reaction.  $\beta$ -Naphthol (**4.1a**) or 2,7-dihydroxynaphthalene (**4.1b**) was reacted with ethyl 4-chloroacetoacetate (**4.2**) in concentrated  $\text{H}_2\text{SO}_4$  at room temperature to give the 1-chloromethyl-9-substituted benzocoumarins (**Scheme 4.1**)<sup>33,86</sup>.

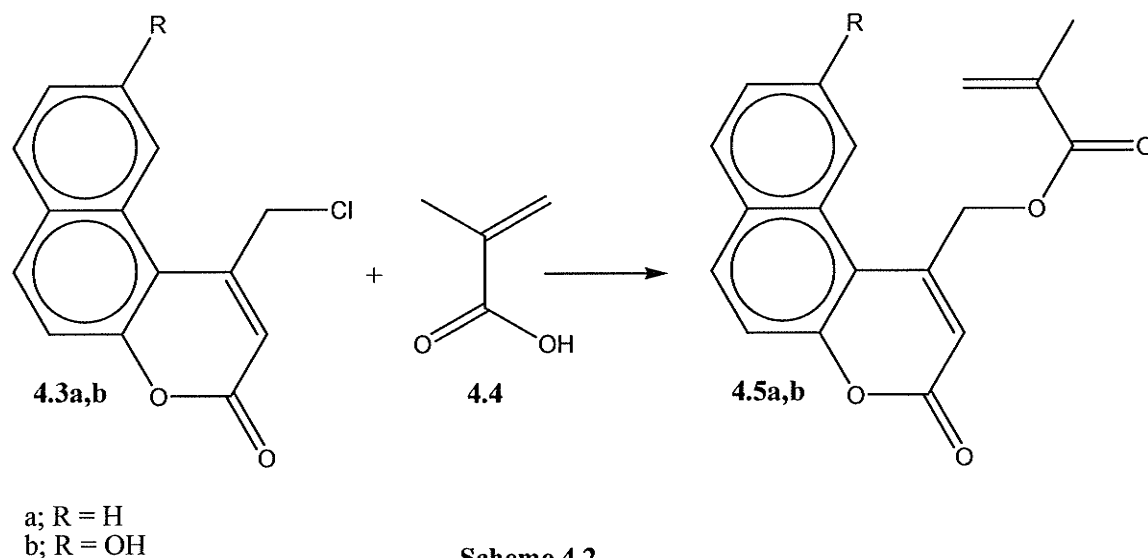


a; R = H  
b; R = OH

**Scheme 4.1**

Following verification by NMR and IR of the synthesis, the coumarins (**4.3a**, **4.3b**) were reacted with methacrylic acid (**4.4**). The reaction was carried out in dimethyl sulfoxide (DMSO), with dicyclocarbodiimide (DCC) and triethylamine (TEA) present (**Scheme 4.2**).

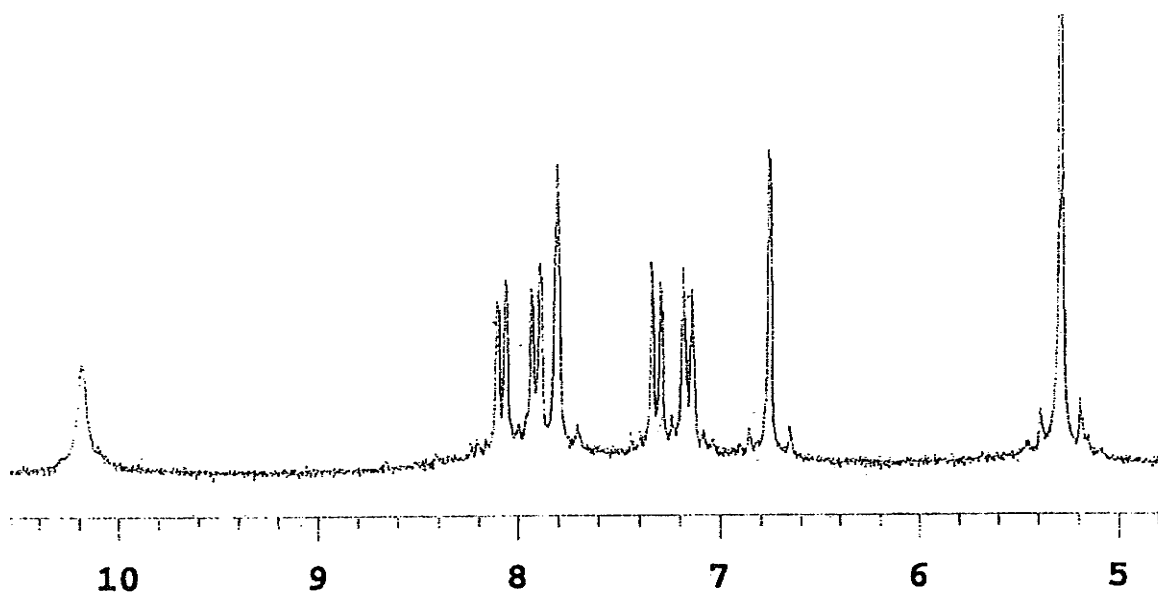
The byproduct of DCC protonation (dihydrourrea) was difficult to separate from the monomers. By precipitating the reaction in a minimum of ethanol, the more soluble DHU was retained in solution and the monomers precipitated out. The resulting products (**4.5a**, **4.5b**) were the monomeric units.



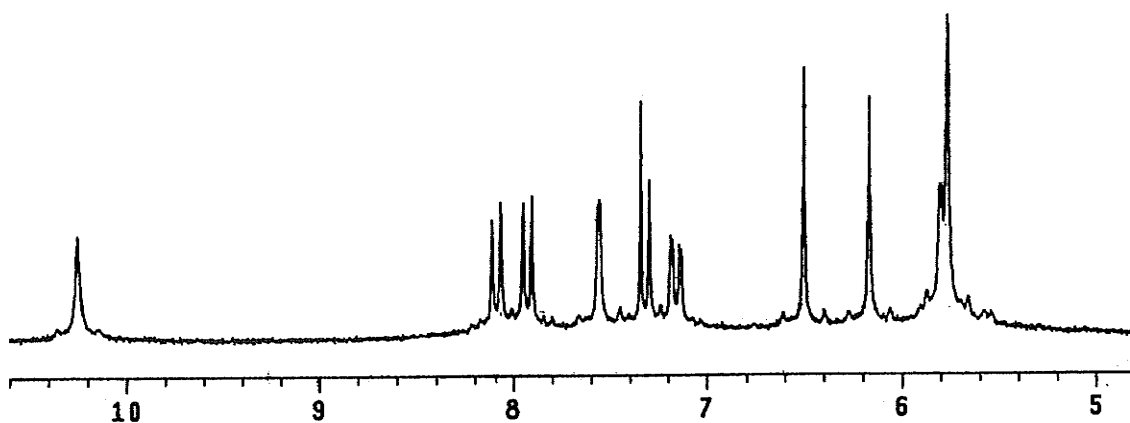
Structures of the coumarins and monomers were characterized with  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and FT-IR. The  $^1\text{H}$  NMR spectra of the initial coumarins (**4.3a**, **4.3b**) displayed peaks at 5.36 and 5.29 ppm for the  $\text{CH}_2\text{-Cl}$  protons, respectively. These peaks shifted slightly in the monomers, to 5.84 and 5.77 ppm, concordant with the formation of an ester.

The monomers also gave two characteristic singlets for the olefinic  $\text{CH}_2$  protons. These singlets resonate at 5.78 and 6.14 ppm for **4.5a** and 5.81 and 6.17 ppm for **4.5b**. The proton in the C-4 position of the coumarin was also of interest, resonating at approximately 6.8 ppm in the coumarins, and shifting to approximately 6.5 ppm in the monomers. The proton NMR spectrum of compound **4.3b** is shown as **Figure 4.1** and

the spectrum of **4.5b** is shown just below it (Figure 4.2). Table 4.1 lists the  $^1\text{H}$  NMR resonances of interest for the coumarins and monomers.



**Figure 4.1**  $^1\text{H}$  NMR spectrum of monomer **4.3b** in DMSO- $\text{d}_6$ . The peak at a shift of 5.29 ppm is due to the  $\text{CH}_2$  attached to the C-4 carbon of the coumarin. This will be the linking location for the monomer.



**Figure 4.2**  $^1\text{H}$  NMR spectrum of monomer **4.5b** in DMSO- $\text{d}_6$ . The linking  $\text{CH}_2$  peak now resonates at 5.77 ppm. The olefinic protons resonate at shifts of 5.81 and 6.17 ppm.

**Table 4.1: <sup>1</sup>H NMR Data for Coumarins & Monomers (DMSO-d<sub>6</sub>)**

Compound	CH <sub>3</sub>	Linking CH <sub>2</sub>	Olefinic CH <sub>2</sub>	H-3	OH
<b>4.3a</b>	-	5.36 (s, 2H)	-	6.87 (s, 1H)	-
<b>4.3b</b>	-	5.29 (s, 2H)	-	6.76 (s, 1H)	10.19 (bs, 1H)
<b>4.5a</b>	1.92 (s, 3H)	5.84 (s, 2H)	5.78 (s, 1H), 6.14 (s, 1H)	6.60 (s, 1H)	-
<b>4.5b</b>	1.95 (s, 3H)	5.77 (s, 2H)	5.81 (s, 1H), 6.17 (s, 1H)	6.51 (s, 1H)	10.20 (bs, 1H)

In the <sup>13</sup>C spectra, the CH<sub>2</sub>-Cl peaks resonated at 46 ppm in the coumarins (**4.3a**, **4.3b**) and shifted after ester formation to 64 ppm in the monomers (**4.5a**, **4.5b**). The coumarin carbonyl resonances did not change appreciably with the formation of the monomer, resonating at roughly 159 ppm in all cases. As in **Chapter 3**, this is important, as the optical properties of coumarin molecules arise from the interaction of electrons between the carbonyl and C-3 – C-4 double bonds. Preserving the original properties of the coumarin is important to this work. <sup>13</sup>C NMR peaks of interest are tabulated below (**Table 4.2**).

**Table 4.2: <sup>13</sup>C NMR Data for Coumarins & Monomers (DMSO-d<sub>6</sub>)**

Compound	CH <sub>3</sub>	Linking CH <sub>2</sub>	Olefinic CH <sub>2</sub>	Olefinic Carbon	Coumarin Carbonyl	Ester Carbonyl
<b>4.3a</b>	-	45.5	-	-	158.5	-
<b>4.3b</b>	-	46.1	-	-	159.3	-
<b>4.5a</b>	17.9	64.5	127.1	135.2	159.4	165.9
<b>4.5b</b>	17.9	64.4	127.1	135.3	159.3	165.8

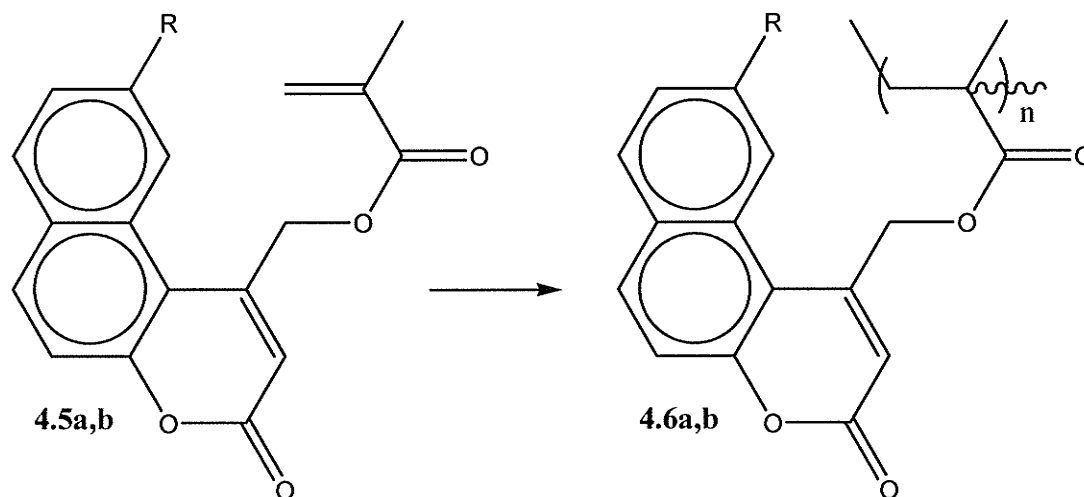
The final method used to characterize the coumarins (**4.3a**, **4.3b**) and monomers (**4.5a**, **4.5b**) was FT-IR. The coumarins were also tested to determine their melting point. **Table 4.3** shows the yield data, IR data for the carbonyl and hydroxyl peaks and melting point information for the coumarins. A broadening of the carbonyl peak in the IR spectrum of each monomer was indicative of the ester formation in the linkage.

**Table 4.3: FT-IR for Coumarins & Monomers**

Compound	IR (cm <sup>-1</sup> ) of C=O	IR (cm <sup>-1</sup> ) of -OH	Melting Point °C
<b>4.3a</b>	1734	-	125
<b>4.3b</b>	1688	3287	255
<b>4.5a</b>	1718	-	-
<b>4.5b</b>	1710	3360	-

### 4.3 Polymerization of Methacrylate Monomers

The monomers (**4.5a**, **4.5b**) were polymerized in xylenes (to allow for higher temperatures than with toluene) using AIBN as a radical initiator. The polymerization reaction is shown in **Scheme 4.3**. As the boiling temperature of xylene is considerably higher than toluene, which was used for the styrene polymers in **Chapter 3**, the solutions were not refluxed, but kept steady at a temperature of 150 – 160 °C. Following the polymerization reaction, the products were precipitated in and washed with ether. These polymerizations produced polymethacrylates with benzocoumarin moieties pendant to the backbone (**4.6a**, **4.6b**).



a; R = H  
b; R = OH

**Scheme 4.3**

Unfortunately, while more soluble than the polymers from **Chapter 3**, both of these polymers (**4.6a**, **4.6b**) were not soluble enough to characterize using solution NMR spectroscopy or gel permeation chromatography (GPC). Successful synthesis was determined based upon FT-IR, the large reduction in solubility and solution  $^1\text{H}$  NMR. The polymers were further characterized with TGA and DSC.

The  $^1\text{H}$  NMR spectra obtained were indicative of polymerization of the olefin. There was only one peak in the 5-6 ppm region, representing the shift of the linking  $\text{CH}_2$ . The absence of the olefinic protons as well as peaks resonating at 1.24 for **4.6a**, and 1.42 for **4.6b** confirmed the formation of polyolefins (**Table 4.4**).



**Table 4.4: <sup>1</sup>H NMR Data for Polymers (DMSO-d<sub>6</sub>)**

Polymer	CH <sub>3</sub>	Linking CH <sub>2</sub>	Backbone CH <sub>2</sub>	H-3
<b>4.6a</b>	1.67 (bs, 3H)	5.56 (bs, 2H)	1.24 (bs, 2H)	6.66 (bs, 1H)
<b>4.6b</b>	1.60 (bs, 3H)	5.53 (bs, 2H)	1.42 (bs, 2H)	6.65 (bs, 1H)

IR absorbances of 1732 and 1736 cm<sup>-1</sup>, respectively, represented the C=O bond. **4.6b** also had a peak at 3438 cm<sup>-1</sup> for the OH stretch. The presence of this absorbance was important, as the <sup>1</sup>H NMR was not of high enough sensitivity to observe the presence of the OH, which was expected between 10 and 11 ppm.

Thermal properties of the polymers were also examined. The results of TGA tests to determine thermal stability may be found on **Table 4.5**. Both polymers were stable to over 330 °C. This compares with the stability of the polystyrenes (**Chapter 3**).

**Table 4.5: TGA Data for Polymers**

Compound	Onset °C	Endset °C	Loss	Onset °C	Endset °C	Loss
<b>4.6a</b>	339	381	49.0%	518	628	30.7%
<b>4.6b</b>	332	400	34.5%	704	787	50.6 %

From the degradation it would appear that the different polymer backbone had little effect on the thermal stability of the coumarins. The second loss was found to be at higher temperatures than with the polystyrenes (**Chapter 3**). This is likely due to more complete polymerization of the monomers, resulting in longer, more stable chains. Lower solubility of the styrene monomers may have led to shorter chain polymers, which are less thermally resistant.

Differential scanning calorimetry (DSC) was also used to determine the temperature at which the glassy phase changes to the rubbery phase. The  $T_g$ 's of the two polymers were both approximately 65 °C. This is roughly fifty degrees lower than the polystyrene polymers. Hence, the polymers degrade before they melt, but have  $T_g$ 's well below their degradation temperature. The lower glass transition temperature is more conducive to industrial manufacturing, but less useful in optical instruments which could have a build-up of excess heat over time during use.

#### **4.4 Experimental**

Full experimental and characterization results may be found in **Appendix 1**.

##### *Materials*

Starting materials and solvents are commercially available, and were purchased in highest available purity from the Aldrich Chemical Co. AIBN was purchased from Alfa Aesar.

##### *Characterization*

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Gemini 200 MHz NMR spectrometer, at 200 and 50 MHz, respectively, with chemical shifts calculated from deuterated solvent residues.

IR spectra were obtained using a Bomem, Hartmann & Braun Fourier transform infrared spectrophotometer with KBr pellets.

Thermogravimetric analysis was accomplished using a Mettler TGA/SDTA851<sup>e</sup> with a heating rate of 20 °C/min under nitrogen. Sample sizes ranged from 3.0 to 6.5 mg, in a ceramic crucible.

Differential scanning calorimetry was performed on a Mettler DSC821<sup>e</sup> with a heating rate of 20 °C/min under nitrogen. Sample sizes were 2.5 to 3.5 mg, in aluminum crucibles.

#### *Coumarin Preparation and Synthesis (4.3a, 4.3b)*

Compounds **4.3a** and **4.3b** was synthesized by combining  $\alpha$ -naphthol or 2,7-dihydroxynaphthalene, respectively, with ethyl 4-chloroacetoacetate in concentrated H<sub>2</sub>SO<sub>4</sub> at room temperature. The very dark solution was poured into water to precipitate the product. Green powder was filtered out of the mixture by suction filtration, washed with water and dried under reduced pressure.

#### *Synthesis of Methacrylate Monomers (4.4a, 4.4b)*

To synthesize the monomers, compounds **4.3a** and **4.3b** were reacted with methacrylic acid in DMSO with DCC and TEA in an inert atmosphere for 16 hours. A ratio of approximately 1:1.5 coumarin to methacrylic acid was used. The resulting dark brown solutions were poured into a minimum of ethanol to precipitate the desired product as a light brown solid, removing the DHU. The monomers were washed with water, followed by ether, then dried under reduced pressure.

### *Synthesis of Polymers (4.5a, 4.5b)*

Again, the monomers were polymerized by a radical initialization method. AIBN was combined with monomers **4.4a** and **4.4b** in a ratio of 1:10 in xylene. The solutions were stirred under nitrogen at approximately 160 °C for two (**4.4b**) or three (**4.4a**) days. The hot solutions were precipitated into ether, filtered in sintered glass crucibles, washed with ether and dried under reduced pressure.

## **4.5 Conclusions & Future Work**

The synthesis of polymethacrylates with pendant coumarin moieties was no more complicated than the synthesis of the similar polystyrene polymers (**Chapter 3**). Glass transition temperatures were significantly lower than the polystyrenes and solubility was enhanced, but not enough for easy handling.

The solubility of coumarins is such that they limit handling and processability. This might be solved by incorporating longer aliphatic chains onto the coumarin, perhaps at the hydroxy site of **4.5b**, to increase the solubility. Another possible solution would be to reduce the number of coumarin moieties per unit of PMMA in the backbone. This could be accomplished by either copolymerization with methylmethacrylic acid, or the addition of the coumarins in stoichiometrically lower amounts post polymerization.

It would also be interesting to determine what physical and optical properties of these materials can be reversibly altered through photodimerization.

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## Appendices: Full Experimental Results

### A Experimental Data for Chapter 2

#### (2.3a)

Off white crystals from ethanol/benzene; mp 267-268 °C; yield 83 %; <sup>1</sup>H NMR (200 MHz) δ 7.74 (d, aromatic, J = 8.6 Hz, 1H), 7.44 (d, aromatic, J = 7.8 Hz, 1H), 7.34-7.16 (m, aromatic, 6H), 7.08 (br s, NH<sub>2</sub>-3, 2H), 6.93 (d, aromatic, J = 8.6 Hz, 1H), 6.71 (d, aromatic, J = 7.4, 1.2 Hz, 1H), 5.77 (br s, NH<sub>2</sub>-8, 2H), 4.83 (s, 1H, H-1); <sup>13</sup>C NMR (50 MHz) δ 159.7 (C-3), 145.2 (C-4a), 144.2 (C-8), 123.4 (C-4b), 121.4 (C-8a), 120.0 (C-10a), 55.6 (C-2), 40.3 (C-1), 116.8 (CN), 142.3, 128.0, 126.9, 126.8, 126.2, 122.7, 118.0, 107.8, 107.4 (aromatic); IR cm<sup>-1</sup> (KBr) 3428, 3401, 3338, 3299, 3179 (2 NH<sub>2</sub>), 2201 (CN); MS m/z (%): 313 (M<sup>+</sup>, 36), 276 (14), 236 (100), 208 (3), 181 (4), 149 (3), 118 (7), 97 (10), 57 (24) .

#### (2.3b)

Off white crystals from ethanol/benzene; mp 235-236 °C; yield 75 %; <sup>1</sup>H NMR (200 MHz) δ 7.74 (d, aromatic, J = 7.4 Hz, 1H), 7.42 (d, aromatic, J = 7.8 Hz, 1H), 7.36-7.23 (m, aromatic, 5H), 7.11 (br s, NH<sub>2</sub>-3, 2H), 6.90 (d, aromatic, J = 9.0 Hz, 1H), 6.70 (d, aromatic, J = 5.6 Hz, 1H), 5.77 (br s, NH<sub>2</sub>-8, 2H), 4.88 (s, 1H, H-1); <sup>13</sup>C NMR (50 MHz) δ 160.4 (C-3), 144.9 (C-4a), 144.8 (C-8), 124.1 (C-4b), 122.2 (C-8a), 120.6 (C-10a), 55.9 (C-2), 40.2 (C-1), 117.0 (CN), 143.0, 131.5, 129.6, 128.7, 127.6, 123.3, 118.8, 108.6, 108.2 (aromatic); IR cm<sup>-1</sup> (KBr) 3463, 3445, 3415, 3342, 3287 (2 NH<sub>2</sub>), 2187 (CN); MS m/z (%): 347 (M<sup>+</sup>, 25), 349 (M<sup>+</sup> + 2, 9), 276 (36), 236 (100), 208 (3), 181 (4), 101 (3), 77 (4) .

#### (2.3c)

Off white crystals from ethanol/benzene; mp 209-210 °C; yield 84 %; <sup>1</sup>H NMR (200 MHz) δ 7.71 (d, aromatic, J = 8.6 Hz, 1H), 7.42 (d, aromatic, J = 7.4 Hz, 1H), 7.30-7.11 (m, aromatic, 5H), 7.00 (br s, NH<sub>2</sub>-3, 2H), 6.87 (d, aromatic, J = 8.2 Hz, 1H), 6.70 (d, aromatic, J = 7.0 Hz, 1H), 5.77 (br s, NH<sub>2</sub>-8, 2H), 4.77 (s, 1H, H-1), 3.70 (s, 3H,

MeO);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  160.2 (C-3), 144.9 (C-4a), 142.8 (C-8), 124.1 (C-4b), 122.0 (C-8a), 120.7 (C-10a), 56.5 (C-2), 40.1 (C-1), 117.8 (CN), 158.1, 138.0, 128.7, 127.5, 123.5, 118.6, 114.0, 108.4, 108.1 (aromatic); IR  $\text{cm}^{-1}$  (KBr) 3421, 3378, 3330, 3202 (2  $\text{NH}_2$ ), 2186 (CN); MS  $m/z$  (%): 343 ( $\text{M}^+$ , 23), 276 (100), 236 (46), 220 (4), 184 (4), 164 (4), 130 (4), 101 (2), 77 (3) .

### (2.3d)

Off white crystals from ethanol/benzene; mp 203-204  $^{\circ}\text{C}$ ; yield 75 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.75 (br s,  $\text{NH}_2$ -3, 2H), 7.72-7.21 (m, aromatic, 8H), 7.11 (d, aromatic,  $J = 8.6$  Hz, 1H), 6.70 (d, aromatic,  $J = 7.0$  Hz, 1H), 5.75 (br s,  $\text{NH}_2$ -8, 2H), 4.98 (s, 1H, H-1), 3.98 (q,  $\text{CH}_2$ , 2H,  $J = 7.0$  Hz), 1.07 (t, Me,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  168.7 (CO), 161.1 (C-3), 148.0 (C-4a), 143.1 (C-8), 124.2 (C-4b), 122.0 (C-8a), 120.1 (C-10a), 76.5(C-2), 40.1(C-1), 144.9, 128.2, 127.3, 126.0, 123.8, 118.5, 108.2, 108.1 (aromatic), 58.6 ( $\text{CH}_2$ ), 14.3 (Me); IR  $\text{cm}^{-1}$  (KBr) 3433, 3397, 3354, 3281 (2  $\text{NH}_2$ ), 1677 (CO); MS  $m/z$  (%): 360 ( $\text{M}^+$ , 28), 283 (100), 237 (40), 209 (6), 181 (5), 143 (5), 118 (6), 105 (3), 77 (5) .

### (2.3e)

Red crystals from ethanol; mp 185-186  $^{\circ}\text{C}$ ; yield 72 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.78 (br s,  $\text{NH}_2$ -3, 2H), 7.73-7.14 (m, aromatic, 7H), 7.10 (d, aromatic,  $J = 8.6$  Hz, 1H), 6.72 (d, aromatic,  $J = 8.0$  Hz, 1H), 5.76 (br s,  $\text{NH}_2$ -8, 2H), 5.00 (s, 1H, H-1), 4.00 (q,  $\text{CH}_2$ , 2H,  $J = 7.0$  Hz), 1.11 (t, Me, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  168.7 (CO), 161.4 (C-3), 147.5 (C-4a), 143.5 (C-8), 124.6 (C-4b), 122.5 (C-8a), 120.3 (C-10a), 76.5(C-2), 40.3(C-1), 145.3, 130.9, 129.6, 128.5, 127.8, 124.1, 119.1, 108.8, 108.6 (aromatic), 56.1 ( $\text{CH}_2$ ), 14.7 (Me); IR  $\text{cm}^{-1}$  (KBr) 3463, 3420, 3397, 3323, 3251 (2  $\text{NH}_2$ ), 1668 (CO); MS  $m/z$  (%): 394 ( $\text{M}^+$ , 27), 396 ( $\text{M}^+ + 2$ , 9), 283 (100), 237 (36), 209 (6), 181 (5), 154 (4), 118 (5), 101 (3), 77 (3) .

**(2.3f)**

Red crystals from ethanol; mp 192-193 °C; yield 75 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.69 (br s,  $\text{NH}_2$ -3, 2H), 7.74-7.06 (m, aromatic, 7H), 6.76 (d, aromatic,  $J$  = 8.6 Hz, 1H), 6.68 (d, aromatic,  $J$  = 6.7 Hz, 1H), 5.74 (br s,  $\text{NH}_2$ -8, 2H), 4.91 (s, 1H, H-1), 3.98 (q,  $\text{CH}_2$ , 2H,  $J$  = 7.0 Hz), 3.64 (s, 3H, MeO), 1.09 (t, Me, 3H,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  168.4 (CO), 160.9 (C-3), 144.8 (C-4a), 142.9 (C-8), 124.1 (C-4b), 121.9 (C-8a), 120.8 (C-10a), 76.7 (C-2), 39.2 (C-1), 157.5, 140.2, 128.2, 127.3, 123.9, 118.4, 113.5, 108.8, 108.1 (aromatic), 58.6 ( $\text{CH}_2$ ), 54.9 (MeO), 14.32 (Me); IR  $\text{cm}^{-1}$  (KBr) 3463, 3366, 3342, 3257 (2  $\text{NH}_2$ ), 1667 (CO); MS  $m/z$  (%): 390 ( $\text{M}^+$ , 32), 361 (10), 317 (18), 283 (100), 237 (37), 209 (6), 181 (5), 172 (7), 123 (3), 109 (2), 77 (3).

**(2.5a)**

Pale yellow crystals from ethanol; mp 236-237 °C; yield 81%;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.33-7.14 (m, aromatic, 5H), 6.80 (br s,  $\text{NH}_2$ -2, 2H), 6.64 (d, aromatic,  $J$  = 8.2 Hz, 1H), 6.31, 6.27 (dd, aromatic,  $J$  = 8.2, 2.4 Hz, 1H), 6.24 (d, aromatic,  $J$  = 1.8 Hz, 1H), 5.24 (br s,  $\text{NH}_2$ -7, 2H), 4.53 (s, 1H, H-4);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  160.4 (C-2), 148.9 (C-8a), 148.8 (C-7), 129.4 (C-5), 120.2 (C-4a), 111.2 (C-6), 100.0 (C-8), 56.5 (C-3), 40.1 (C-4), 110.2 (CN), 146.8, 128.5, 127.4, 126.5 (aromatic); IR  $\text{cm}^{-1}$  (KBr) 3429, 3353, 3305, 3163 (2  $\text{NH}_2$ ), 2198 (CN); MS  $m/z$  (%): 263 ( $\text{M}^+$ , 13), 226 (42), 186 (100), 170 (3), 104 (3), 106 (3), 58 (7).

**(2.5b)**

Pale yellow crystals from ethanol; mp 226-227 °C; yield 77 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.34 and 7.17 (2 d, aromatic,  $J$  = 8.2 Hz, 4H), 6.83 (br s,  $\text{NH}_2$ -2, 2H), 6.60 (d, aromatic,  $J$  = 8.2 Hz, 1H), 6.29, 6.25 (dd, aromatic,  $J$  = 8.2, 2.4 Hz, 1H), 6.21 (d, aromatic,  $J$  = 2.0 Hz, 1H), 5.25 (br s,  $\text{NH}_2$ -7, 2H), 4.56 (s, 1H, H-4);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  160.4 (C-2), 155.6 (C-8a), 148.9 (C-7), 129.4 (C-5), 120.7 (C-4a), 111.2 (C-6), 99.9 (C-8), 56.0 (C-3), 39.4 (C-4), 109.5 (CN), 145.7, 131.1, 129.2, 128.5 (aromatic); IR  $\text{cm}^{-1}$  (KBr) 3443, 3367, 3317, 3240, 3221 (2  $\text{NH}_2$ ), 2190 (CN); MS  $m/z$  (%): 297 ( $\text{M}^+$ , 10), 299 ( $\text{M}^+ + 2$ , 3), 226 (37), 186 (100), 170 (3), 131 (3), 114 (1), 58 (6).

**(2.5c)**

Pale yellow crystals from ethanol; mp 218-219 °C; yield 90 %; <sup>1</sup>H NMR (200 MHz) δ 7.05, 6.84 (d, aromatic, J = 8.6 Hz, 4H), 6.73 (br s, NH<sub>2</sub>-2, 2H), 6.59 (d, aromatic, J = 8.2 Hz, 1H), 6.27, 6.23 (dd, aromatic, J = 8.2, 2.4, Hz, 1H), 6.19 (d, aromatic, J = 2.0 Hz, 1H), 5.21 (br s, NH<sub>2</sub>-7, 2H), 4.46 (s, 1H, H-4), 3.70 (s, 3H, MeO); <sup>13</sup>C NMR (50 MHz) δ 160.3 (C-2), 148.9 (C-8a), 148.7 (C-7), 129.5 (C-5), 121.0 (C-4a), 111.2 (C-6), 100.0 (C-8), 56.8 (C-3), 39.3 (C-4), 110.5 (CN), 158.0, 138.9, 128.4, 113.9 (aromatic), 55.0 (MeO); IR cm<sup>-1</sup> (KBr) 3444, 3372, 3311, 3226, 3226 (2 NH<sub>2</sub>), 2958, 2897, 2837, (CH aliphatic), 2188 (CN); MS m/z (%): 293 (M<sup>+</sup>, 23), 226 (56), 186 (100), 170 (5), 141 (3), 114 (4), 77 (4).

**(2.6a)**

Yellow crystals from ethanol/benzene; mp 285-286 °C; yield 42 %; <sup>1</sup>H NMR (200 MHz) δ 7.60-7.49 (m, aromatic, 5H), 7.03 (br s, NH<sub>2</sub>-7, 2H), 6.90 (d, aromatic, J = 8.6 Hz, 1H), 6.60, 6.55 (dd, aromatic, J = 8.2, 2.4 Hz, 1H), 6.50 (d, aromatic, J = 1.6 Hz, 1H); <sup>13</sup>C NMR (50 MHz) δ 163.1 (CO), 156.8 (C-4), 156.6 (C-8a), 152.0 (C-7), 128.3 (C-5), 115.7 (C-4a), 112.9 (C-6), 98.3 (C-8), 97.7 (C-3), 107.3 (CN), 132.9, 130.3, 130.2, 128.7 (aromatic); IR cm<sup>-1</sup> (KBr) 3457, 3366, 3250 (NH<sub>2</sub>), 2217 (CN), 1693 (CO); MS m/z (%): 262 (M<sup>+</sup>, 100), 234 (57), 205 (41), 178 (7), 151 (10), 117 (6), 103 (10), 76 (16), 44 (9).

**(2.6b)**

Yellow crystals from ethanol/benzene; mp 335-336 °C; yield 37 %; <sup>1</sup>H NMR (200 MHz) δ 7.67, 7.52 (2d, aromatic, J = 8.6 Hz, 4H), 7.07 (br s, NH<sub>2</sub>-7, 2H), 6.90 (d, aromatic, J = 9.0 Hz, 1H), 6.60, 6.56 (dd, aromatic, J = 8.6, 2.4 Hz, 1H), 6.49 (d, aromatic, J = 1.8 Hz, 1H); <sup>13</sup>C NMR (50 MHz) δ 161.8 (CO), 158.3 (C-4), 156.8 (C-8a), 156.7 (C-7), 128.9 (C-5), 115.6 (C-4a), 113.0 (C-6), 98.3 (C-8), 91.0 (C-3), 107.2 (CN), 135.1, 131.8, 130.3, 130.2 (aromatic); IR cm<sup>-1</sup> (KBr) 3457, 3359, 3251 (NH<sub>2</sub>), 2220 (CN), 1699 (CO); MS m/z (%): 296 (M<sup>+</sup>, 100), 298 (M<sup>+</sup> + 2, 34), 268 (57), 205 (58), 177 (13), 151 (11), 117 (9), 89 (13), 44 (20).

**(2.6c)**

Yellow crystals from ethanol/benzene; mp > 360 °C; yield 38 %; <sup>1</sup>H NMR (200 MHz) δ 12.31 (s, OH, 1H), 10.84 (br s, NH, 1H), 7.60-7.47 (m, aromatic, 5H), 7.00 (d, aromatic, J = 9.0 Hz, 1H), 6.80, 6.70 (dd, aromatic, J = 8.2, 2.4 Hz, 1H), 6.65 (d, aromatic, J = 2.4 Hz, 1H); <sup>13</sup>C NMR (50 MHz) δ 162.8 (CO), 160.0 (C-4), 159.2 (C-7), 142.3 (C-8a), 128.5 (C-5), 116.0 (C-4a), 113.6 (C-6), 100.2 (C-8), 97.7 (C-3), 111.4 (CN), 134.2, 130.0, 129.6, 128.7 (aromatic); IR cm<sup>-1</sup> (KBr) 3461, 3372 (NH), 3245 (OH), 2221 (CN), 1693 (CO); MS m/z (%): 262 (M<sup>+</sup>, 100), 234 (35), 205 (12), 178 (5), 151 (8), 131 (4), 89 (9), 76 (15), 51 (4).

**(2.6d)**

Pale yellow crystals from acetic acid; mp > 360 °C; yield 41 %; <sup>1</sup>H NMR (200 MHz) δ 12.30 (s, OH, 1H), 10.90 (br s, NH, 1H), 7.66, 7.50 (2d, aromatic, J = 7.8 Hz, 4H), 7.00 (d, aromatic, J = 7.8 Hz, 1H), 6.79- 6.70 (m, aromatic, 2H); <sup>13</sup>C NMR (50 MHz) δ 162.8 (CO), 160.3 (C-4), 159.8 (C-7), 142.3 (C-8a), 128.5 (C-5), 115.8 (C-4a), 113.7 (C-6), 100.2 (C-8), 98.3 (C-3), 111.2 (CN), 135.1, 130.5, 130.3, 129.9 (aromatic); IR cm<sup>-1</sup> (KBr) 3463, 3368, (NH), 3241 (OH), 2225 (CN), 1693 (CO); MS m/z (%): 296 (M<sup>+</sup>, 100), 298 (M<sup>+</sup>+ 2, 34), 268 (10), 233 (51), 205 (6), 177 (10), 151 (7), 116 (7), 89 (10), 75 (16), 44 (41).

**(2.6e)**

Yellow crystals from dioxane; mp 355-356 °C; yield 37 %; <sup>1</sup>H NMR (200 MHz) δ 12.30 (s, OH, 1H), 10.83 (br s, NH, 1H), 7.42, 7.36 (2d, aromatic, J = 8.6 Hz, 4H), 7.10 (d, aromatic, J = 8.6 Hz, 1H), 6.75, 6.70 (dd aromatic, J = 10.2, 2.2 Hz, 1H), 6.65 (d, aromatic, J = 2.2 Hz, 1H); <sup>13</sup>C NMR (50 MHz) δ 163.1 (CO), 162.9 (C-4), 159.8 (C-7), 142.4 (C-8a), 126.2 (C-5), 116.4 (C-4a), 113.7 (C-6), 100.4 (C-8), 97.8 (C-3), 111.5 (CN), 156.8, 130.1, 129.5, 124.9 (aromatic), 56.3 (MeO); IR cm<sup>-1</sup> (KBr) 3480, 3370 (NH), 3246 (OH), 2971, 2946, 2849 (CH aliphatic), 2225 (CN), 1699 (CO); MS m/z (%): 292 (M<sup>+</sup>, 100), 264 (25), 249 (15), 221 (12), 192 (6), 146 (5), 121 (6), 97 (6), 57 (14).

**(2.6f)**

Colourless crystals from ethanol; mp 175-176 °C; yield 46 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.52 (br s,  $\text{NH}_2$ -2, 2H), 7.03, 6.75 (2d, aromatic,  $J = 8.6$ , Hz, 4H), 6.76 (d, aromatic,  $J = 8.2$  Hz, 1H), 6.29, 6.26 (dd, aromatic,  $J = 7.2, 2.0$  Hz, 1H), 6.14 (d, aromatic,  $J = 2.4$  Hz, 1H) 5.14 (br s,  $\text{NH}_2$ -7, 2H), 4.65 (s, 1H, H-4), 3.94 (q,  $\text{CH}_2$ , 2H,  $J = 7.0$  Hz), 3.65 (s, 3H, MeO), 1.06 (t, Me, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  168.6 (CO), 161.2 (C-2), 149.2 (C-8a), 148.2 (C-7), 129.4 (C-5), 113.8 (C-4a), 111.0 (C-6), 100.1 (C-8), 77.2 (C-3), 38.2 (C-4), 157.2, 141.4, 127.9, 113.4 (aromatic), 58.5 ( $\text{CH}_2$ ), 54.9 (MeO), 14.3 (Me); IR  $\text{cm}^{-1}$  (KBr) 3417, 3372, 3325, 3224 (2  $\text{NH}_2$ ), 2983, 2959, 2899, 2831 (CH aliphatic), 1665 (CO); MS  $m/z$  (%): 340 ( $\text{M}^+$ , 11), 293 (9), 273 (55), 233 (100), 187 (65), 159 (6), 131 (6), 104 (5), 58 (9), 43 (12).

**(2.8a)**

Colourless crystals from ethanol; mp 230-231 °C ( Literature<sup>44</sup> mp 178 °C ); yield 85 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  9.80 (br, OH, 1H), 7.36, 7.18 (2d, aromatic,  $J = 8.6$  Hz, 4H), 6.91 (br s,  $\text{NH}_2$ -2, 2H), 6.77 (d, aromatic,  $J = 8.6$  Hz, 1H), 6.49, 6.45 (dd, aromatic,  $J = 8.2, 2.2$  Hz, 1H), 6.39 (d, aromatic,  $J = 2.4$  Hz, 1H), 4.65 (s, 1H, H-4);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  160.3 (C-2), 157.4 (C-8a), 148.8 (C-7), 129.8 (C-5), 120.5 (C-4a), 112.5 (C-6), 102.2 (C-8), 55.8 (C-3), 39.3 (C-4), 113.0 (CN), 145.3, 131.2, 129.8, 129.3 (aromatic); IR  $\text{cm}^{-1}$  (KBr) 3400, 3336, 3214 (OH,  $\text{NH}_2$ ), 2186 (CN); MS  $m/z$  (%): 298 ( $\text{M}^+$ , 11), 300 ( $\text{M}^+ + 2$ , 4), 187 (100), 144 (1), 131 (2), 89 (2), 75 (3), 43 (5).

**(2.8b)**

Beige needles from ethanol; mp 220-221 °C ; yield 89 %;  $^1\text{H}$  NMR (200 MHz)  $\delta$  9.62 (br, OH, 1H), 7.33, 7.16 (2d, aromatic,  $J = 7.8$  Hz, 4H), 6.93 (br s,  $\text{NH}_2$ -2, 2H), 6.63 (d, aromatic,  $J = 8.2$  Hz, 1H), 6.54 (d, aromatic,  $J = 8.2$  Hz, 1H), 4.64 (s, 1H, H-4), 2.09 (s, Me, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  160.6 (C-2), 155.1 (C-8a), 147.3 (C-7), 129.3 (C-5), 120.8 (C-4a), 111.4 (C-6), 111.2 (C-8), 55.9 (C-3), 39.5 (C-4), 113.5 (CN), 145.6, 131.3, 128.6, 126.1 (aromatic), 8.5 (Me); IR  $\text{cm}^{-1}$  (KBr) 3458, 3380, 3322, 3213 (OH,  $\text{NH}_2$ ), 2196 (CN); MS  $m/z$  (%): 312 ( $\text{M}^+$ , 10), 314 ( $\text{M}^+ + 2$ , 3), 201 (100), 156 (1), 128 (3), 103 (2), 75 (4), 51 (1).



**(2.8c)**

Colourless crystals from ethanol; mp 215-216 °C ; yield 92 %; <sup>1</sup>H NMR (200 MHz) δ 9.37 (br, OH, 1H), 7.35, 7.19 (2d, aromatic, J = 7.0 Hz, 4H), 6.78 (br s, NH<sub>2</sub>-2, 2H), 6.65 (s, aromatic, 1H), 6.47 (s, aromatic, 1H), 4.63 (s, 1H, H-4), 2.41 (q, CH<sub>2</sub>, 2H, J = 7.4 Hz), 1.02 (t, Me, 3H, J = 7.4 Hz); <sup>13</sup>C NMR (50 MHz) δ 160.3 (C-2), 154.7 (C-8a), 146.7 (C-7), 129.2 (C-5), 127.2 (C-4a), 120.6 (C-6), 101.8 (C-8), 55.9 (C-3), 39.4 (C-4), 112.7 (CN), 145.4, 131.1, 128.7, 128.5, (aromatic), 22.2 (CH<sub>2</sub>) 14.1 (Me); IR cm<sup>-1</sup> (KBr) 3419, 3333, 3221 (OH, NH<sub>2</sub>), 2966, 2935, 2874 (CH aliphatic), 2180 (CN); MS m/z (%): 326 (M<sup>+</sup>, 9), 328 (M<sup>+</sup>+ 2, 3), 215 (100) 171 (3), 115 (3), 89 (2), 69 (4), 51 (1).

**(2.8d)**

Colourless crystals from ethanol; mp 195-196 °C; yield 89 %; <sup>1</sup>H NMR (200 MHz) δ 9.60 (br, OH, 1H), 7.34, 7.17 (2d, aromatic, J = 7.0 Hz, 4H), 6.86 (br s, NH<sub>2</sub>-2, 2H), 6.61 (s, aromatic, 1H), 6.47 (s, aromatic, 1H), 4.63 (s, 1H, H-4), 2.30 (t, CH<sub>2</sub>, 2H, J = 7.2 Hz), 1.36-1.14 (m, 4 CH<sub>2</sub>, 8H), 0.78 (t, Me, J = 4.6 Hz); <sup>13</sup>C NMR (50 MHz) δ 160.3 (C-2), 154.7 (C-8a), 146.7 (C-7), 129.6 (C-5), 125.6 (C-4a), 120.6 (C-6), 101.8 (C-8), 55.9 (C-3), 39.4 (C-4), 112.5 (CN), 145.4, 131.2, 129.2, 128.5 (aromatic), 31.0 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 22.1 (CH<sub>2</sub>) 13.8 (Me); IR cm<sup>-1</sup> (KBr) 3468, 3334, 3215 (OH, NH<sub>2</sub>), 2966, 2923, 2875, 2850 (CH aliphatic), 2198 (CN); MS m/z (%): 382 (M<sup>+</sup>, 7), 384 (M<sup>+</sup>+ 2, 3), 271 (100), 200 (12), 171 (3), 128 (1), 89 (1), 69 (6), 43(9).

**(2.10a)**

Pale yellow crystals from ethanol; mp 241-242 °C; yield 81 %; <sup>1</sup>H NMR (200 MHz) δ 9.37 (br, OH, 1H), 8.29, 8.09 (2d, aromatic, J = 7.4 Hz, 4H), 7.74 (d, aromatic, J = 7.8 Hz, 1H), 7.25 (s, aromatic, 1H), 7.15 (br s, NH<sub>2</sub>-2, 2H), 7.07-6.68 (m, aromatic, 3H), 4.78 (s, 1H, H-4); <sup>13</sup>C NMR (50 MHz) δ 159.8 (C-2), 141.9 (C-10b), 129.2 (C-6a), 128.3 (C-9), 127.8 (C-5), 126.1 (C-8), 125.5 (C-10a), 124.0 (C-6), 123.9 (C-7), 121.5 (C-10), 120.4 (C-4a), 56.6 (C-3), 39.9 (C-4), 119.2 (CN), 156.5, 135.7, 128.8, 115.6 (aromatic); IR cm<sup>-1</sup> (KBr) 3427, 3384, 3348 (OH, NH<sub>2</sub>), 2196 (CN); MS m/z (%): 348 (M<sup>+</sup>, 24), 350 (M<sup>+</sup>+ 2, 8), 255 (100), 200 (2), 128 (2), 100 (3), 65 (2), 43 (2).

**(2.10b)**

Colourless needles from ethanol; mp 248-249 °C; yield 84 %; <sup>1</sup>H NMR (200 MHz) δ 8.94 (s, OH, 1H), 8.32-8.27 (m, aromatic, 6H), 7.31 (s, aromatic, 1H), 7.16 (br s, NH<sub>2</sub>-3, 2H), 6.88 (d, aromatic, J = 2.0, 1H), 4.78 (s, 1H, H-4), 3.72 (s, MeO, 3H); <sup>13</sup>C NMR (50 MHz) δ 159.8 (C-2), 141.8 (C-10b), 129.2 (C-6a), 128.2 (C-9), 127.6 (C-5), 126.0 (C-8), 125.4 (C-10a), 124.0 (C-6), 123.8 (C-7), 121.5 (C-10), 120.4 (C-4b), 56.4 (C-3), 40.2 (C-4), 119.1 (CN), 147.6, 141.8, 136.2, 120.2, 115.0, 111.9 (aromatic); IR cm<sup>-1</sup> (KBr) 3474, 3323, 3251, 3202 (OH, NH<sub>2</sub>), 2983, 2928, 2837 (CH aliphatic), 2199 (CN); MS m/z (%): 378 (M<sup>+</sup>, 23), 380 (M<sup>+</sup> + 2, 8), 255 (100), 220 (4), 193, (10), 164 (5), 124 (6), 94 (2), 75 (1), 43 (2).

**(2.10c)**

Colourless crystals from dioxane; mp 265-266 °C; yield 85 %; <sup>1</sup>H NMR (200 MHz) δ 9.34 (s, OH, 1H), 7.87, 7.65 (2d, aromatic, J = 8.2 Hz, 4H), 7.56 to 7.41 (m, aromatic, 2H), 7.32 (br s, NH<sub>2</sub>-2, 2H), 7.05, 7.02 (dd aromatic, J = 8.2, 1.6 Hz, 1H), 6.70, 6.66 (dd aromatic, J = 8.2, 1.6 Hz, 1H), 4.32 (s, 1H, H-4); <sup>13</sup>C NMR (50 MHz) δ 159.6 (CO), 158.0 (C-2), 156.6 (C-10b), 152.1 (C-6a), 128.8 (C-8), 124.6 (C-10), 122.4 (C-9), 119.5 (C-10a), 116.5 (C-7), 104.5 (C-4a), 58.6 (C-3), 36.3 (C-4), 113.0 (CN), 153.0, 133.8, 132.7, 115.3 (aromatic); IR cm<sup>-1</sup> (KBr) 3514, 3417, 3295, 3186 (OH, NH<sub>2</sub>), 2197 (CN), 1708 (CO); MS m/z (%): 332 (M<sup>+</sup>, 39), 265 (44), 239 (100), 211 (5), 184 (4), 145 (5), 121 (43), 92 (12), 66 (19), 55 (1).

**(2.10d)**

Colourless crystals from dioxane; mp 252-253 °C; yield 74 %; <sup>1</sup>H NMR (200 MHz) δ 8.92 (s, OH, 1H), 7.89-7.41 (m, aromatic, 4H), 7.32 (br s, NH<sub>2</sub>-2, 2H), 6.81-6.75 (m, aromatic, 3H), 4.35 (s, 1H, H-4) 3.72 (s, MeCO, 3H); <sup>13</sup>C NMR (50 MHz) δ 159.6 (CO), 158.0 (C-2), 153.0 (C-10b), 152.1 (C-6a), 132.8 (C-8), 124.6 (C-10), 122.4 (C-9), 119.4 (C-10a), 116.5 (C-7), 104.3 (C-4a), 58.4 (C-3), 36.5 (C-4), 113.0 (CN), 147.3, 145.8, 134.3, 119.9, 115.5, 112.1 (aromatic), 55.7 (Me); IR cm<sup>-1</sup> (KBr) 3417, 3299, 3251, 3190 (OH, NH<sub>2</sub>), 2191 (CN), 1711 (CO); MS m/z (%): 362 (M<sup>+</sup>, 40), 331 (23), 295 (23), 279 (19), 239 (100), 161 (5), 121 (43), 92 (12), 66 (18), 51 (6).

## B Experimental Data for Chapter 3

### (3.3a)

Yield 45%.  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ]: 5.27 (d,  $J = 10.9$  Hz, 1H,  $=\text{CH}_2$ ), 5.38 (s, 2H,  $\text{CH}_2$ ), 5.77 (d, 1H,  $J = 17.6$  Hz, 1H,  $=\text{CH}_2$ ), 6.73 (q, 1H,  $J = 10.5 + 6.6$  Hz,  $=\text{CH}$ ), 7.28-7.45 (m, 6H, Ar), 7.55-7.68 (m, 2H, Ar), 8.53 (s, 1H, C4-H).  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ]: 66.54 ( $\text{CH}_2$ ), 113.94 ( $=\text{CH}_2$ ), 135.76 ( $=\text{CH}$ ), 116.06, 124.40, 125.90, 128.04, 129.27, 134.02, 148.48 (Ar), 117.13, 117.26, 134.45, 137.12, 154.56 (quat. Ar), 156.01, 162.16 (CO). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1697, 1764 (C=O). TGA (100–800)  $^\circ\text{C}$ : Onset 311, Endset 402, Weight Loss 72.6%.

### (3.3b)

Yield 82%.  $^1\text{H}$  NMR [ $\text{DMSO}-d_6$ ]: 5.27 (d,  $J = 10.9$  Hz, 1H,  $=\text{CH}_2$ ), 5.37 (s, 2H,  $\text{CH}_2$ ), 5.56 (d, 1H,  $J = 17.6$  Hz, 1H,  $=\text{CH}_2$ ), 6.75 (q, 1H,  $J = 10.8$  &  $7.0$  Hz,  $=\text{CH}$ ), 7.40-7.67 (m, 6H, Ar), 7.76 (t,  $J = 6.33$  Hz, 1H, Ar), 8.06 (d,  $J = 7.62$  Hz, 1H, Ar), 8.30 (d,  $J = 8.98$  Hz, 1H, Ar), 8.55 (d,  $J = 8.20$  Hz, 1H, Ar), 9.39 (s, 1H, C4-H).  $^{13}\text{C}$  NMR [ $\text{DMSO}-d_6$ ]: 66.42 ( $\text{CH}_2$ ), 114.69 ( $=\text{CH}_2$ ), 136.25 ( $=\text{CH}$ ), 116.53, 122.31, 126.24, 126.52, 128.92, 129.11, 136.25, 136.30, 144.52 (Ar), 112.00, 116.27, 129.04, 129.83, 136.98, 155.36 (quat. Ar), 156.12, 163.00 (CO). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1691, 1762 (C=O). TGA (100–800)  $^\circ\text{C}$ : Onset 349, Endset 422, Weight Loss 72.5%. Fluorescence: (77  $^\circ\text{K}$ )  $\lambda_{\text{max}}$  432 nm, intensity 11500 V; (RT)  $\lambda_{\text{max}}$  431 nm, intensity 6000 V.

### (3.3c)

Yield 72%.  $^1\text{H}$  NMR [ $\text{DMSO}-d_6$ ]: 5.27 (d,  $J = 10.7$  Hz, 1H,  $=\text{CH}_2$ ), 5.32 (s, 2H,  $\text{CH}_2$ ), 5.84 (d, 1H,  $J = 17.6$  Hz, 1H,  $=\text{CH}_2$ ), 6.74 (q, 1H,  $J = 10.9 + 7.0$  Hz,  $=\text{CH}$ ), 7.35-7.58 (m, 4H, Ar), 8.31 (s, 1H, Ar), 8.42 (s, 1H, Ar), 8.65 (s, 1H, C4-H).  $^{13}\text{C}$  NMR [ $\text{DMSO}-d_6$ ]: 66.44 ( $\text{CH}_2$ ), 114.64 ( $=\text{CH}_2$ ), 136.14 ( $=\text{CH}$ ), 126.14, 128.21, 138.37, 147.71, 149.52 (Ar), 89.30, 89.28 (quat. Ar C-I), 118.54, 120.30, 135.17, 136.95, 153.68 (quat. Ar), 155.20, 161.82 (CO). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1706, 1758 (C=O). TGA (100–800)  $^\circ\text{C}$ : Onset 317, Endset 341, Weight Loss 61.1%.

**(3.3d)**

Yield 3.3%. Very low solubility reduced yields and prohibited  $^{13}\text{C}$  NMR.  $^1\text{H}$  NMR [DMSO- $d_6$ ]: 5.16 (d,  $J = 8.42$  Hz, 1H,  $=\text{CH}_2$ ), 5.36 (s, 2H,  $\text{CH}_2$ ), 5.73 (d, 1H,  $J = 17.6$  Hz, 1H,  $=\text{CH}_2$ ), 6.63 (q, 1H,  $J = 10.6 + 7.0$  Hz,  $=\text{CH}$ ), 6.79-6.89 (m, 2H, Ar), 7.13-7.54 (m, 6H, Ar), 7.81 (d,  $J = 8.1$ , 1H, Ar). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1632, 1704 (C=O). TGA (100–800)  $^\circ\text{C}$ : Onset 394, Endset 463, Weight Loss 55.1%.

**(3.3e)**

Yield 98%.  $^1\text{H}$  NMR [DMSO- $d_6$ ]: 2.54 (s, 3H,  $\text{CH}_3$ ), 5.23-5.29 (m, 3H,  $=\text{CH}_2$ ,  $\text{CH}_2$ ), 5.84 (d, 1H,  $J = 17.6$  Hz, 1H,  $=\text{CH}_2$ ), 6.73 (q, 1H,  $J = 10.9 + 6.7$  Hz,  $=\text{CH}$ ), 7.03-7.12 (m, 2H, Ar), 7.36-7.59 (m, 4H, Ar), 7.84 (d,  $J = 8.6$  Hz, 1H, Ar), 8.61 (s, 1H, C4-H).  $^{13}\text{C}$  NMR [DMSO- $d_6$ ]: 30.04 ( $\text{CH}_3$ ), 69.93 ( $\text{CH}_2$ ), 114.71 ( $=\text{CH}_2$ ), 136.19 ( $=\text{CH}$ ), 101.12, 114.03, 126.28, 128.28, 132.21, 147.54 (Ar), 111.95, 120.47, 135.52, 137.05, 156.98, 158.84 (quat. Ar), 163.75, 194.71 (CO). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1614, 1741 (C=O). Solid State  $^{13}\text{C}$  NMR: 31 ( $\text{CH}_3$ ), 72 ( $\text{CH}_2$ ), 111 ( $=\text{CH}_2$ ), 165, 195 (CO). TGA (100–800)  $^\circ\text{C}$ : Onset 313, Endset 366, Weight Loss 19.9%; Onset 436, Endset 476, Weight Loss 32.3%. Fluorescence: (77  $^\circ\text{K}$ )  $\lambda_{\text{max}}$  415 nm, intensity 8.6 V; (RT)  $\lambda_{\text{max}}$  436 nm, intensity 750 V. Phosphorescence: (77  $^\circ\text{K}$ )  $\lambda_{\text{max}}$  500 nm, intensity 7.9 V.

**(3.3f)**

Yield 69%.  $^1\text{H}$  NMR [DMSO- $d_6$ ]: 1.28 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 4.26 (q,  $J = 7.2$  Hz, 2H,  $\text{CH}_2$ ), 5.24-5.29 (m, 3H,  $=\text{CH}_2$ ,  $\text{CH}_2$ ), 5.84 (d, 1H,  $J = 18.0$  Hz, 1H,  $=\text{CH}_2$ ), 6.74 (q, 1H,  $J = 11.0 + 6.6$  Hz,  $=\text{CH}$ ), 7.04-7.12 (m, 2H, Ar), 7.41-7.54 (m, 4H, Ar), 7.84 (d,  $J = 8.6$  Hz, 1H, Ar), 8.71 (s, 1H, C4-H).  $^{13}\text{C}$  NMR [DMSO- $d_6$ ]: 14.08 ( $\text{CH}_3$ ), 60.92, 69.90 ( $\text{CH}_2$ ), 114.67 ( $=\text{CH}_2$ ), 136.17 ( $=\text{CH}$ ), 101.11, 113.79, 126.23, 128.23, 131.68, 149.06 (Ar), 113.07, 113.39, 135.52, 137.02, 156.19, 156.82 (quat. Ar), 162.77, 163.68 (CO). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1622, 1761 (C=O). TGA (100–800)  $^\circ\text{C}$ : Onset 339, Endset 364, Weight Loss 23.4%; Onset 453, Endset 490, Weight Loss 31.5%.

**(3.3g)**

Yield 97%. Very low solubility prohibited  $^{13}\text{C}$  NMR.  $^1\text{H}$  NMR [Acetone- $d_6$ ]: 1.26-1.30 (bs, 3H,  $\text{CH}_3$ ), 4.58-4.62 (bs, 2H,  $\text{CH}_2$ ), 5.12-5.29 (m, 6H,  $=\text{CH}_2$ ,  $\text{CH}_2$ ), 5.69-5.90 (m, 2H,  $\text{CH}_2$ ), 6.40-6.89 (m, 2H,  $=\text{CH}$ ), 7.20-7.52 (m, 10H, Ar), 8.53 (s, 2H, C4-H). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1596, 1748 ( $\text{C}=\text{O}$ ). TGA (100–800)  $^\circ\text{C}$ : Onset 157, Endset 205, Weight Loss 29.3%; Onset 412, Endset 475, Weight Loss 37.7%.

**(3.3h)**

Yield 38%.  $^1\text{H}$  NMR [DMSO- $d_6$ ]: 2.69 (t,  $J = 6.6$  Hz, 2H,  $\text{CH}_2$ ), 4.63 (t,  $J = 5.1$  Hz, 2H,  $\text{CH}_2$ ), 5.22-5.31 (m, 3H,  $=\text{CH}_2$ ,  $\text{CH}_2$ ), 5.85 (d, 1H,  $J = 17.6$  Hz, 1H,  $=\text{CH}_2$ ), 6.74 (q, 1H,  $J = 10.9 + 6.6$  Hz,  $=\text{CH}$ ), 7.10-7.26 (m, 4H, Ar), 7.41-7.64 (m, 6H, Ar), 7.94 (d,  $J = 8.6$  Hz, 1H, Ar), 8.89 (s, 1H, C4-H), 10.58 (s, 1H, NH).  $^{13}\text{C}$  NMR [DMSO- $d_6$ ]: 58.28, 62.14, 69.94 ( $\text{CH}_2$ ), 114.72 ( $=\text{CH}_2$ ), 136.18 ( $=\text{CH}$ ), 101.25, 114.36, 119.76, 126.28, 128.28, 129.33, 131.68, 147.93 (Ar), 112.38, 115.50, 119.76, 135.48, 135.89, 137.04, 156.09, 159.79 (quat. Ar), 161.13, 163.52 ( $\text{CO}$ ). IR (KBr)  $\nu/\text{cm}^{-1}$ : 1602, 1696 ( $\text{C}=\text{O}$ ). TGA (100–800)  $^\circ\text{C}$ : Onset 334, Endset 373, Weight Loss 29.3%; Onset 442, Endset 478, Weight Loss 30.8%.

**(3.5a)**

Yield 30%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1717, 1762 ( $\text{C}=\text{O}$ ). TGA (100–800)  $^\circ\text{C}$ : Onset 312, Endset 363, Weight Loss 53.0%; Onset 427, Endset 462, Weight Loss 27.9%. DSC ( $T_g$ )  $^\circ\text{C}$ : 112.6.

**(3.5b)**

Yield 80%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1701, 1750 ( $\text{C}=\text{O}$ ). TGA (100–800)  $^\circ\text{C}$ : Onset 323, Endset 370, Weight Loss 49.0%; Onset 430, Endset 466, Weight Loss 19.2%. DSC ( $T_g$ )  $^\circ\text{C}$ : 115.8.

**(3.5c)**

Yield 64%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1698, 1764 (C=O). TGA (100–800) °C: Onset 296, Endset 339, Weight Loss 59.8%; Onset 606, Endset 653, Weight Loss 29.1%. DSC ( $T_g$ ) °C: 116.9.

**(3.5d)**

Yield 98%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1633, 1700 (C=O). TGA (100–800) °C: Onset 405, Endset 459, Weight Loss 50.8%. DSC ( $T_g$ ) °C: 123.8.

**(3.5e)**

Yield 63%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1615, 1733 (C=O). TGA (100–800) °C: Onset 321, Endset 362, Weight Loss 19.2%; Onset 439, Endset 475, Weight Loss 27.3%. DSC ( $T_g$ ) °C: 122.7. Solid State  $^{13}\text{C}$  NMR: 30 ( $\text{CH}_3$ ), 35–50 ( $\text{CH}_2$ ), 73 ( $\text{CH}_2$ ), 167, 197 (CO).

**(3.5f)**

Yield 69%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1608, 1766 (C=O). TGA (100–800) °C: Onset 342, Endset 381, Weight Loss 28.0%; Onset 435, Endset 472, Weight Loss 24.7%. DSC ( $T_g$ ) °C: 114.7.

**(3.5g)**

Yield 95%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1602 (C=O). TGA (100–800) °C: Onset 411, Endset 469, Weight Loss 34.7%. DSC ( $T_g$ ) °C: 119.7.

**(3.5h)**

Yield 85%. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1602, 1696 (C=O). TGA (100–800) °C: Onset 337, Endset 375, Weight Loss 28.7%; Onset 445, Endset 481, Weight Loss 23.4%. DSC ( $T_g$ ) °C: 114.3.

## C Experimental Data for Chapter 4

### (4.3a)

IR: 1734.42 (C=O), 1551.2 (C=C);  $^1\text{H}$  NMR: 5.410 (s, 2H,  $-\text{CH}_2$ ), 6.869 (s, 1H, H-2), 7.577-7.752 (m, 3H, Ar-H), 8.069, 8.110 (d, 1H, Ar-H), 8.225, 8.270 (d, 1H, Ar-H), 8.524, 8.567 (d, 1H, Ar-H).

### (4.3b)

IR: 3286.55 (OH), 1688.2 (C=O), 1541.2 (C=C);  $^1\text{H}$  NMR: 5.291 (s, 2H,  $-\text{CH}_2$ ), 6.760 (s, 1H, H-2), 7.135, 7.180 (d, 1H, H-5), 7.893, 7.936 (d, 1H, H-6), 8.063, 8.106 (d, 1H, H-7), 10.190 (s, 1H, OH; cancelled by  $\text{D}_2\text{O}$ );  $^{13}\text{C}$  NMR (APT): 46.093 ( $\text{CH}_2$ ), 108.575 (C-10), 110.593 (C-10b), 113.809 (C-2), 115.660 (C-5), 117.170 (C-8), 125.151 (C-6a), 130.234 (C-10a), 131.250 (C-6), 134.217 (C-7), 152.106 (C-4a), 155.254 (C-9), 157.735 (C-1), 159.298 (C=O).

### (4.5a)

IR: 1718.08 (C=O), 1552.21 (C=C);  $^1\text{H}$  NMR: 1.920 (s, 3H,  $\text{CH}_3$ ), 5.779 (s, 1H, Ha of  $\text{CH}_2$ -acrylic), 5.842 (s, 2H,  $\text{CH}_2$ -Coumarin), 6.137 (s, 1H, Hb of  $\text{CH}_2$ -acrylic), 6.596 (s, 1H, H-2), 7.561-7.727 (m, 3H, Ar-H), 8.067, 8.106 (s, 1H, Ar-H), 8.209, 8.254 (s, 1H, Ar-H);  $^{13}\text{C}$  NMR: 17.871 ( $\text{CH}_3$ ), 64.543 ( $\text{CH}_2$ -coumarin), 112.537 (C-10b), 112.709 (C-2), 117.466 (C-5), 125.159 (C-10), 125.750 (C-8), 127.101 ( $\text{CH}_2$ -acrylic), 128.459 (C-9), 129.680 (C-7), 130.894 (C-10a), 134.315 (C-6), 135.180 (C-2-acrylic), 151.870 (C-1), 154.726 (C-4a), 159.357 (CO-coumarin), 165.862 (CO-acrylic).

### (4.5b)

IR: 3360.43 (OH), 1709.63 (C=O), 1556.49 (C=C);  $^1\text{H}$  NMR: 1.947 (s, 3H,  $\text{CH}_3$ ), 5.770 (s, 2H,  $\text{CH}_2$ -coumarin), 5.805 (s, 1H, Ha of  $\text{CH}_2$ -acrylic), 6.170 (s, 1H, Hb of  $\text{CH}_2$ -acrylic), 6.506 (s, 1H, H-2), 7.147-7.350 (dd, 2H, Ar-H), 7.815 (s, 1H, Ar-H), 7.891-8.106 (dd, 2H, Ar-H), 10.204 (brs, 1H, OH, cancelled by  $\text{D}_2\text{O}$ ).  $^{13}\text{C}$  NMR: 17.924 ( $\text{CH}_3$ ), 64.376 ( $\text{CH}_2$ -coumarin), 108.301 (C-10), 110.995 (C-10b), 111.541 (C-2), 113.855 (C-5), 117.261 (C-8), 125.189 (C-6a), 127.055 (C- $\text{CH}_2$ -acrylic), 130.553 (C-10a), 131.448 (C-

6), 134.240 (C-7), 135.286 (C-2-acrylic), 152.204 (C-1), 154.996 (C-4a), 157.849 (C-9), 159.305 (CO-coumarin), 165.761 (CO-acrylic).

**(4.6a)**

IR: 1732.14 (C=O); <sup>1</sup>H NMR: 1.242 (brs, 2H, CH<sub>2</sub>), 1.671 (brs, 3H, CH<sub>3</sub>), 5.574 (brs, 2H, CH<sub>2</sub>-Coumarin), 6.656 (brs, 1H, 2-H-Coumarin), 6.996-7.864 (brm, 6H, Ar-H); TGA: 49% Loss, Onset 338.7 Endset 380.9, 30.7% Loss, Onset 517.8, Endset 627.8; DSC: T<sub>g</sub> 68.0.

**(4.6b)**

IR: 3438.20 (OH), 1735.69 (C=O); <sup>1</sup>H NMR: 1.423 (brs, 2H, CH<sub>2</sub>), 1.599 (brs, 3H, CH<sub>3</sub>), 5.527 (brs, 2H, CH<sub>2</sub>-Coumarin), 6.645 (brs, 1H, 2-H-Coumarin), 6.996-8.133 (brm, 6H, Ar-H); TGA: 34.5% Loss, Onset 331.6 Endset 399.8, 50.6% Loss, Onset 703.9, Endset 786.8; DSC: T<sub>g</sub> 64.0.