SYNTHESIS OF AZO CONTAINING COMPOUNDS AND THEIR PHOTOISOMERIZATION WITH POLARIZED LIGHT

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ABSTRACT

SYNTHESIS OF AZO CONTAINING COMPOUNDS AND THEIR PHOTOISOMERIZATION WITH POLARIZED LIGHT

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Azo-containing compounds have recently been studied intensively due to their photoisomerization properties. Azo-containing compounds can be used in a wide variety of fields; *e.g.* pharmaceuticals, the paint industry, and molecular rotors. Use of such compounds for molecular rotors stems from its easy photoisomerization. These compounds are converted from *trans* to *cis* by irradiation. In addition, *cis* configurations of azo-containing compounds are inherently chiral properties due to their helical structure. In this thesis, new polymers and small compounds were synthesized and their photoisomerizations with/without polarized light were investigated. The photoisomerization studies of azobenzene in the presence of a chiral amine was expected to induce chirality on *cis* form, yet it did not. Moreover, chirality induction could be done with circulary and eliptically polarized light. Such investigations were also carried out. Although it was found that no chiral induction to *cis* form, it was postulated that this is due to the poor chiroptical properties of the *trans*/*cis* azobenzene unit.

Keywords: Azo compounds, photoisomerization, polarized light

ÖZ

AZO İÇEREN MADDELERİN SENTEZİ VE BUNLARIN POLARİZE IŞIK İLE FOTOİZOMERİZASYONU

Çakmak, Bulem
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Azo içeren bileşikler, fotoizomerizasyon özellikleri nedeniyle son zamanlarda yoğun bir şekilde çalışılmaktadır. Azo içeren bileşikler çok çeşitli alanlarda kullanılabilir; örneğin ilaç, boya endüstrisi ve moleküler rotorlar. Bu tür bileşiklerin moleküler rotorlar için kullanımı, kolay fotoizomerizasyonundan kaynaklanmaktadır. Bu bileşikler irradyasyon ile *trans* formundan *cis* formuna dönüştürülür. Buna ek olarak, azo içeren bileşiklerin *cis* konfigürasyonları, sarmal yapıları nedeniyle doğal olarak kiral özelliktedir. Bu tezde, yeni polimerler ve küçük bileşikler sentezlenmiş ve bunların polarize ışıklı/ışıksız fotoizomerizasyonları incelenmiştir. Kiral bir amin varlığında azobenzenin fotoizomerizasyon çalışmalarının *cis* formunda kiraliteyi indüklemesi bekleniyordu, ancak olmadı. Ayrıca, kiralite indüksiyonu dairesel ve eliptik polarize ışık ile yapılabilmiştir. Bu tür araştırmalar da gerçekleştirilmiştir. Her ne kadar *cis* formuna kiral indüksiyon olmadığı bulunsa da, bunun *trans/cis* azobenzen biriminin zayıf kiroptik özelliklerinden kaynaklandığı varsayılmıştır.

Anahtar Kelimeler: Azo bileşikler, fotoizomerizasyon, polarize ışık

In memory of my beloved grandmother,

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ABBREVIATIONS

CD	Circular Dichroism
CPL	Circularly Polarized Light
EPL	Elliptical Polarized Light
HRMS	High-resolution mass spectrometry
LCPL	Left-Handed Circularly Polarized Light
LEPL	Left -Handed Elliptically Polarized Light
NCS	*N*-Chlorosuccinimide
RCPL	Right-Handed Circularly Polarized Light
REPL	Right -Handed Elliptically Polarized Light

CHAPTER 1

INTRODUCTION

1.1 Azo Dyes

The nitrogen atoms of azo dyes are linked to sp^2-hybridized carbon atoms via a chromophoric azo group, N=N. There are two carbon atoms adjacent to the azo group; one of them is part of an aromatic carbocycle like benzene or naphthalene derivative or heterocycle like pyrazolone, thiazole; the other carbon atom may be part of an enolizable aliphatic derivative (Figure 1). The majority of azo dyes are of the aryl-N=N-R kind, where R is typically an aryl, heteroaryl, or aryl-CH=C(OH)-alkyl group.[1] Additionally, the -N=N- bond stretching frequency for azo compounds is approximately 1630-1575 cm^{-1}. In the situation of an asymmetric azo derivative, this frequency may not be present.[2,3] This is because the nitrogen atoms are more likely to be in the same plane in the symmetric azo molecule, resulting in a shorter and stronger connection.[4]

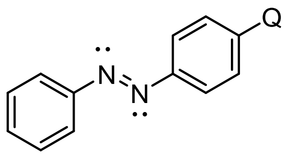


Figure 1. An azo compound

Due to conjugation between the two aromatic rings enabled by the azo group, these compounds typically display intensely colored. Azo dyes are absorb light in the visible region because this conjugation results in an extended system of delocalized p electrons. Azo dyes are applicable in many different area because they have intense colors and can be synthesized from relativly cheap starting materials.

Because of their versatility and ease of production, azo dyes can be derived from a wide range of sources. A further expansion of the spectrum of potential colors is possible by including multiple azo groups in a single molecule. Inexpensive azo dye production opens up the possibility for a variety of colors and properties that may be used across a wide spectrum of substrates. Although several dyes with azoxy groups are known, no naturally occurring azo dyes have been discovered. However, the azo dyes represent the most numerous and widely manufactured synthetic dyes. [1]

1.1.1 History of Azo Dyes

Approximately 70% of all dyes manufactured are azo dyes, making them the most widely used form of dye in the world.[5,6] They have many different uses, including in the production of dyes for both natural and manmade materials, as well as in pharmaceuticals, inks, cosmetics, foods, and paints. The success of azo dyes can be attributed to various factors, including the simple synthesis techniques involved, the wide structural diversity of these dyes, and their high molar extinction coefficient. Additionally, azo dyes often exhibit medium-to-high fastness qualities with respect to both light and moisture. In 1861, Mene synthesized aniline yellow (the first azo dye), and in 1863, Martius synthesized a similar compound (Bismarck Brown; Figure 2). In 1875, Caro and Witt at the German company BASF (Badische Anilin & Soda-Fabrik) produced the first colors using diazotization and azo coupling (Morris and Travis 1992) [7]

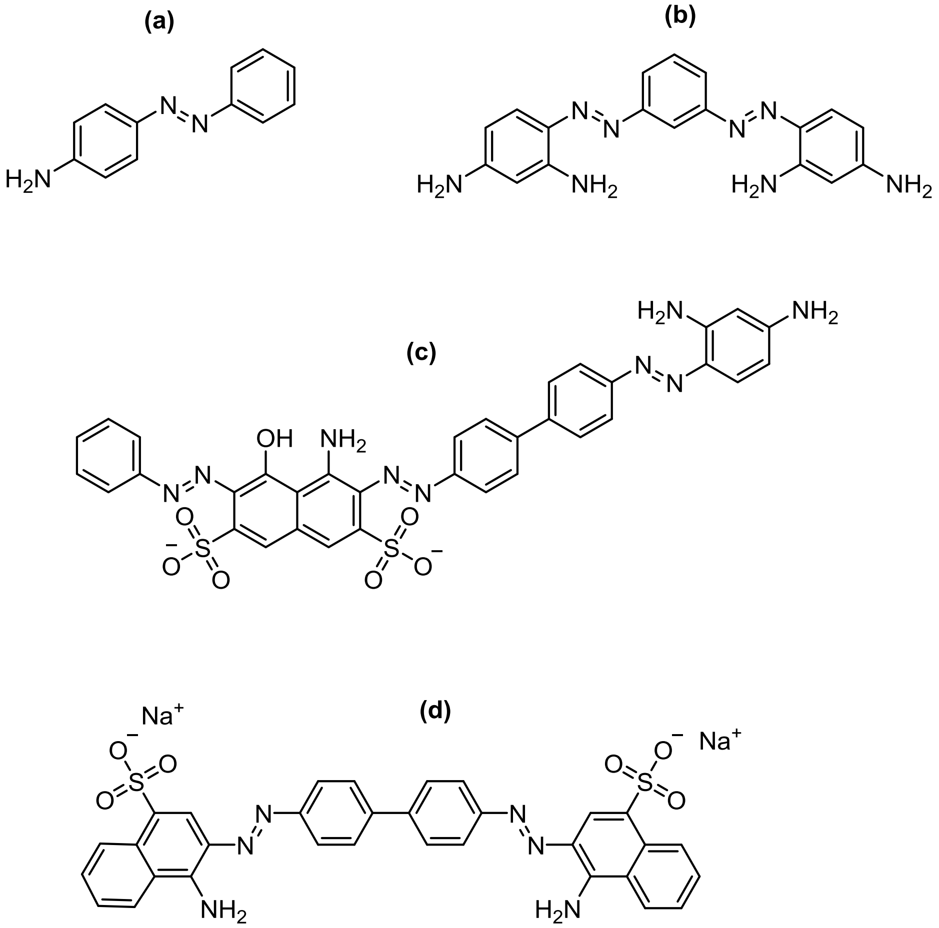


Figure 2. Structure of Aniline Yellow (a), Bismarc Brown (b), Direct Black 38 (c) and Direct Red 28 (Congo Red) (d)

Neither the IUPAC nor the CAS nomenclature is commonly used for azo dyes because of how complicated it is.[6] Main composition or color are the most common categories used to divide azo colorants in the technical literature. The chemical class of azo colorants is represented by the numbers 11000–39999 in the Color Index system (Color Index 2001). (Table 1).[7]

Table 1. Classification of azo dyes in Colour Index

Chemical Class	CI no.
Mono azo	11000-19999
Bis-azo	20000-29999
Tri-azo	30000-34999
Polyazo	35000-36999
Azoic	37000-39999

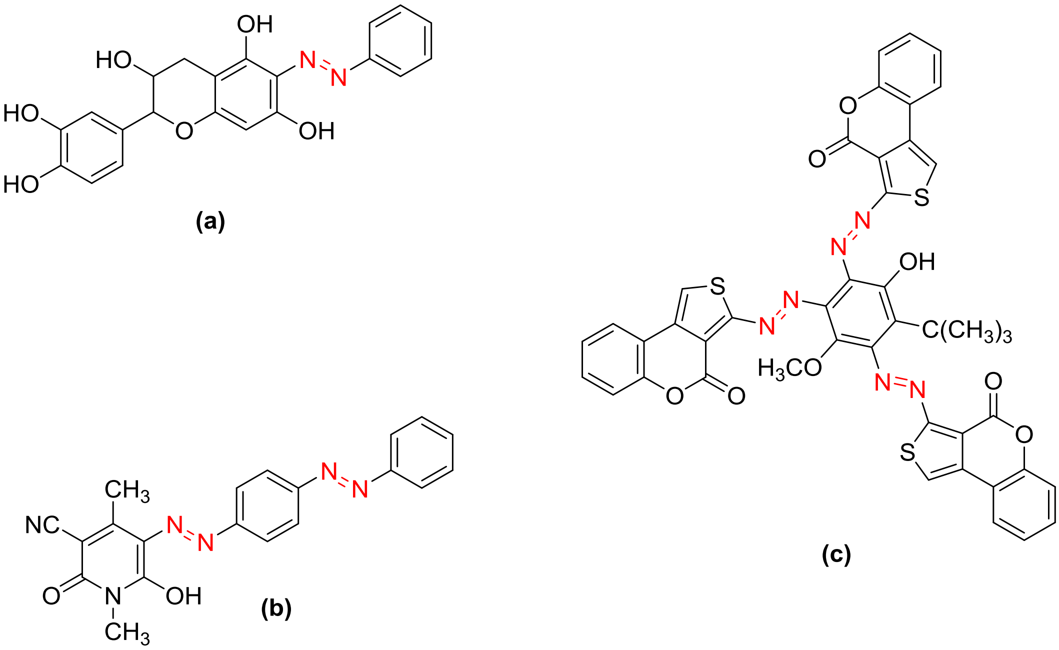
In the Colour Index, you can find details such as the brand names, colour characteristics, and chemical composition of many dyes. Color and chemical characteristics are used to organize the dyes.[1]

1.1.2 Application of Azo Dyes

Azo dyes are a wide-ranging and highly versatile group of synthetic dyes that find applications in many different fields, from pharmacy and plastics to hypnotic medicine and cancer treatment.[8] They are also used in high-tech applications such as lasers and nonlinear optical systems, as well as thermal transfer printers and fuel cells.[9] Additionally, azo dyes can be used to sensitized solar cells,[10] or as photodynamic therapy,[9] metallochromic indicators,[11] or for dyeing textiles,[10] leather, paper, food,[12–15] cosmetics,[16,17] and medicines.[18,19] The versatility of azo dyes results from the combination of the properties of the azo group with different types of substituted aromatic ligands. Azo dyes are known for their involvement in various biological reactions, such as DNA inhibition, RNA and protein synthesis, carcinogenesis, and nitrogen fixation.[20] They are also characterized by their physicochemical stability and optical properties,[21,22] which make them useful in applications such as liquid crystals[23] and nanotubes[24]. In recent years, azo-functionalized dyes bearing aromatic heterocyclic compounds have become increasingly popular due to their wide range of colors, luminosity, and simple manufacturing process.

1.1.3 Nomenclature

Depending on how many azo groups they have, azo dyes are put into one of several categories. Monoazo dyes are those with just one azo group, while disazo dyes have two. The azo groups of trisazo and tetrakisazo dyes number three and four, respectively. There are three or more azo groups in polyazo dyes(Figure 3).[7]



(a)

(b)

(c)

Figure 3. Mono-azo (a), Dis-azo (b) and Tris-azo (c) dyes

There are three ways to describe the structure of an azo dye: a structural formula, IUPAC nomenclature, or practical nomenclature. For example:[1]

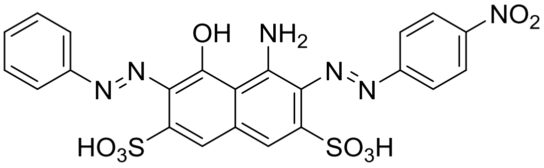


Figure 4. Azo Dye example

Figure 4 shows the structural formula of one of the examples of azo dyes. The IUPAC nomenclature of the example is ‘’1-hydroxy-2-phenylazo-7-(4-nitrophenylazo)- 8-aminonaphthalene-3,6-disulfonic acid’’. On the other hand, practical nomenclature of this example is shows like this general formula: D $-^{1}\rightarrow$ K $\leftarrow^{2}-$D. That is, while D represents the diazo component and K represents the coupling component. On the other hand, arrows represent the direction of the coupling. In this example, practical nomenclature of this compound is p-nitroaniline $-^{1}\rightarrow$H acid$\leftarrow^{2}-$ aniline. The reaction equation like in Figure 5:[1]

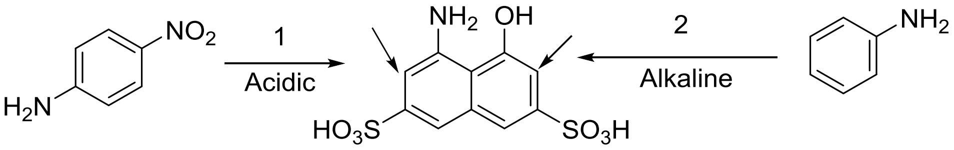


Figure 5. Reaction equation of Azo Dye example

The more practical nomenclature , which is based on the most commonly used synthesis, i.e., it characterizes the azo dye by the starting compounds and the direction of coupling, is shorter and is more commonly used in industry and technical literature. Moreover, the azo dye in the Figure 4 can be found under its trade name C. I. Acid Black 1 or C. I. 20470.[1]

Directional arrows and numbers above the arrows indicate the order of steps in the synthesis of disazo and polyazo dyes. The terms acid and alkaline are used to specify the coupling conditions (alkaline). In addition, arrows are utilized to illustrate the connection locations of both components across the azo groups.[1]

1.1.4 Classification

There are two main ways to categorize azo dyes: first, based on chemical rules, which involve different chemical classes, and second, based on color considerations, which depend on how the dye is used in practice. However, azo dyes can be categorized based on their azo grouping number. Although there may be times when something cannot be placed in any of the three categories, there is always possibility for overlap.[1]

1.1.5 Chemical Properties of Azo dyes

1.1.5.1 Reactivity

Dye reactivity is depend on the structure of the reactive part of the dye. Figure 6 represents dichlorotriazines (c) are the most reactive,[25] followed by di or tetrafluoropyrimidines[26] (d) and dichloroquinoxalines[27] (e) followed by monofluorotriazines[28] (f) . Vinylsulfones are of medium reactivity, while the bifunctional dye type monochlorotriazine/vinylsulfone is next. Oxymethylchlorotriazines derived from the structure of aminochlorotriazines having low reactivity are found finally. Trichloropyrimidines have the lowest reactivity.[4]

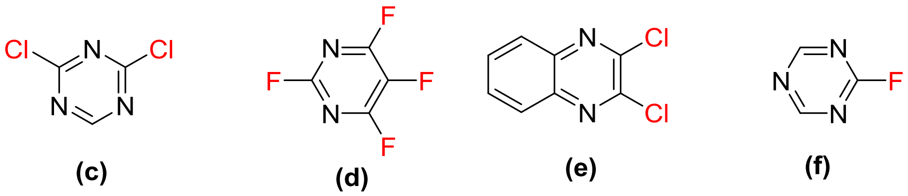


Figure 6. Reactivity of Azo Dyes

The absorption ability of a textile support surface of a dye is known as substantivity. The degree to which a surface can absorb a dye is dependent on the reactive part of the dye being studied.[29] The substantivity of various azo dyes in ascending order, according to the reactive part of the dye like this:[30]

Aminochlorotriazine<Dichlorotiriazine<Difluoropyridine<Dichloroquinoxaline<
Fluorotriazine <Trichloropyrimidine<Sulphatoethysulfone

1.1.5.2 Z/E Isomerism

Isomerization is the process by which a molecule is transformed into another molecule with the same atoms, but a different layout. In some molecules and under certain conditions, isomerization occurs spontaneously.[4]

There are two isomers of azobenzene, called Z and E, [31]respectively. The form E is unstable and is derived from the *trans* form via photo-isomerization(Figure 7).[31]

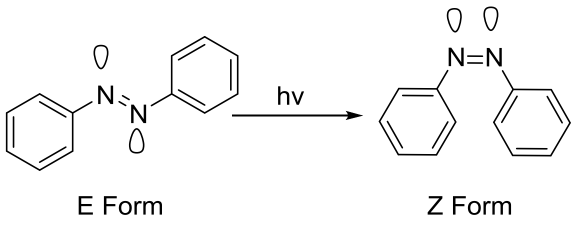


Figure 7. Z and E form of azobenzene molecule

The fact that the more thermodynamically stable E configuration can be isomerized to the metastable Z form via an azo bond makes azobenzene useful in a variety of contexts.[32,33] The two azobenzene forms, *trans* and *cis,* each result in the formation of a different conformation of conjugated acid in an acidic solution (Figure 8).[4]

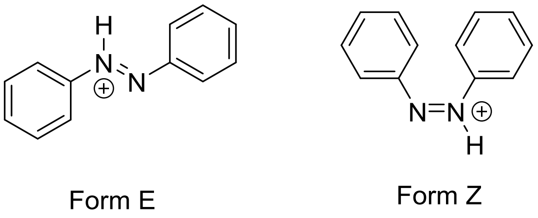


Figure 8. *Trans* and *Cis* configuration of conjugated acids

1.1.5.3 Tautomerism

Allomerisms like the azo/hydrazone tautomerism occur when a proton moves from one element inside the molecule to another (Figure9).[16,34] Light fastness and tinctorial power are two properties that may benefit from this form of tautomerism in azo dyes. The dye's commercial feasibility depends on these qualities. [4]

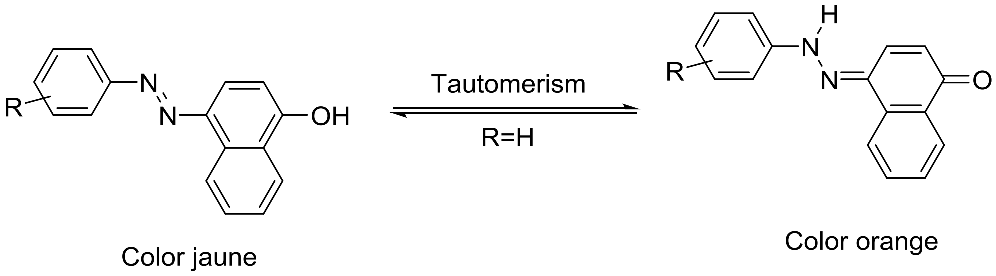


Figure 9. Tautomerism of azo dye

Benzene diazonium chloride and 1-naphthol were coupled, and then phenylhydrazine and 1,4-naphthoquinone were condensed to make an orange dye to study tautomerism. In the process of tautomerization, a double bond and a hydrogen atom swap places. The results confirmed the existence of tautomerism in this colorant.[16]

1.1.6 Synthesis

The creation of azo dyes relies on a number of procedures. These reactions can be subdivided into several catagories, including azo group synthesis, diazotization and coupling, nitro compound condensation with amines, nitro compound reduction, and amino compound oxidation.

Synthesis can be performed on compounds that already have the azo group present. Taking this approach involves revealing amino groups that are normally hidden. Acylation of aminoazo compounds, alkylation and acylation of phenolic hydroxyl groups, and metal-complex formation are also further options.[1]

1.1.6.1 Diazotization and Coupling

An aromatic amine undergoes azo coupling, where this joins a nucleophilic partner RH to produce an aromatic azo molecule in the presence of a nitrosyl-eliminating agent XNO. Specifically, the reaction equation looks like in Figure 10: [1]

$$Ar{-}NH_2 + X{-}NO + Ar'H \xrightarrow{-H_2O} Ar{-}N{=}N{-}Ar' + HX$$

$$X = Cl, Br, NO_2, HSO_4$$

Figure 10. Reaction equation of azo coupling

Creating the diazonium salt (diazotization) and the azo coupling are the two main components of the producing azo dye.

1.1.6.1.1 Diazotization

Primary aromatic amines are diazotized by reacting with nitrites, particularly sodium nitrite, in an aqueous mineral acid solution at temperatures near absolute zero (Figure 11). The amine is transformed into its matching diazonium salt during this reaction.[1]

$$Ar{-}NH_2 + 2HY + NaNO_2 \longrightarrow N{\equiv}\overset{+}{N}{-}Ar\ Y^{-} + NaY + 2H_2O$$

$$Y = Cl, HSO_4, \text{etc.}$$

Figure 11. Diazonium salt equation

There is a methodical process involved in diazotizing a primary amine. Dissociation of nitrous acid into ^{+}NO ions occurs in the presence of strong acid. An intermediate, N-nitrosoaminium ion, is formed when these ions react with the nitrogen in the amine. This intermediate then undergoes proton loss to generate an N-nitrosoamine, which tautomerizes to a diazohydroxide in a pattern similar to keto-enol tautomerization. The diazonium ion is then formed when the diazohydroxide loses its water moiety in an acidic environment.[4] Reaction mechanism of diazonium salt formation represents in the Figure 12.

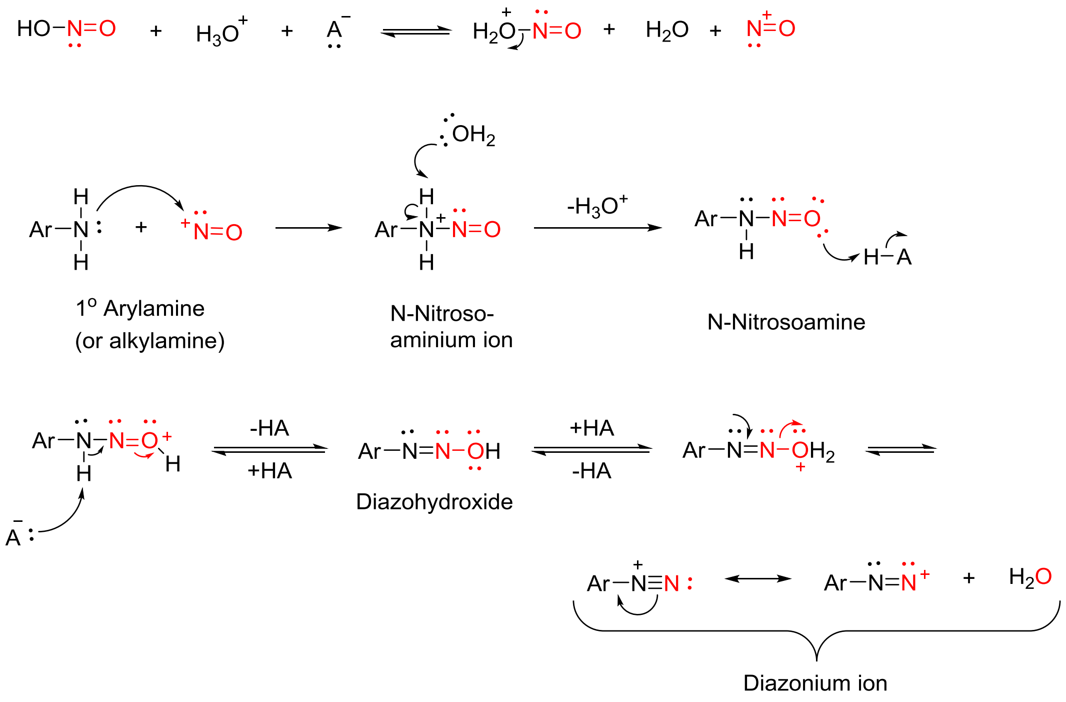


Figure 12. Reaction mechanism of diazonium salt

1.1.6.1.2 Diazonium Coupling

Electrophilic aromatic substitution reactions, also known as diazo coupling reactions, occur when arenediazonium ions react with highly reactive aromatic chemicals such phenols and tertiary arylamines to produce azo compounds (Figure 13).[4]

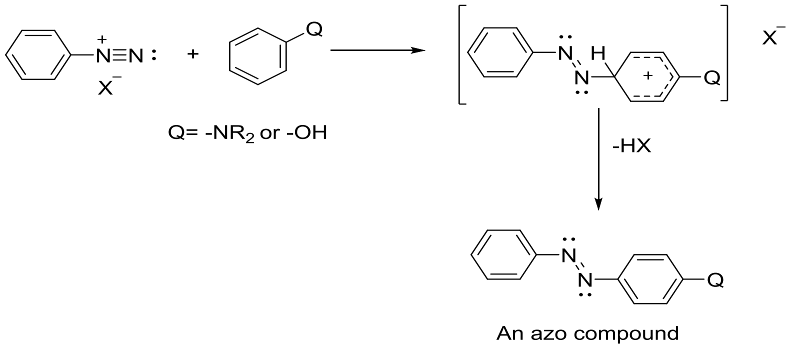


Figure 13. General reaction o azo coupling

Arenediazonium cation-amine coupling rate is maximum in mildly acidic solutions (pH 5-7). This is because the amount of amine that has been transformed to an unreactive aminium salt is not excessive, but the concentration of arenediazonium cations is at a maximum (Figure 14).[4]

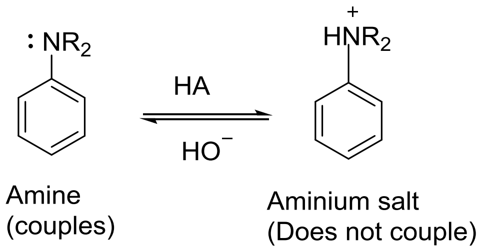


Figure 14. Amine and Aminium salt

1.1.6.2 Condensation of Nitro Compounds with Amines

Condensation of nitro compounds and amines produce of aromatic azo and polyazo compounds. The reaction is carried out by heating the reactants in an aqueous sodium hydroxide solution for several hours at a temperature of 40 to 120 °C. The equation for this reaction is as follows in Figure 15:[1]

$$R^1\text{-}NO_2 \quad + \quad H_2N{-}R^2 \longrightarrow R^1\text{-}N{=}N{-}R^2 \quad + \quad H_2O(+O)$$

Figure 15. General representation of Condensation of Nitro Compounds with Amines

The industrial manufacture of dye intermediates via condensation reactions of 4,4-dinitrostilbene-2,2-disulfonic acid with aromatic amines is of interest. If specific sodium hydroxide solution concentrations, temperatures, and reaction times are precisely observed, it is possible to produce homogeneous monoazo and disazo dyes using 1,4-diamines, 4-aminophenols, and their sulfonic and carboxylic acids (Figure 16).[1]

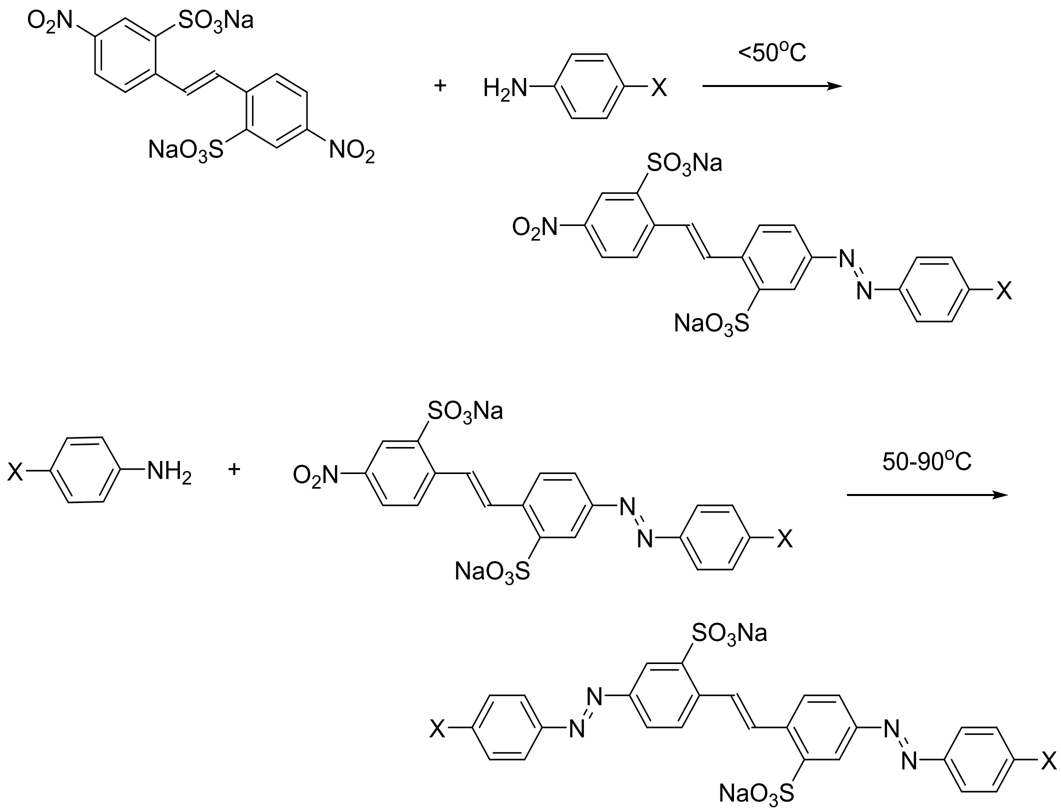


Figure 16. Condensation of Nitro Compounds with Amines example

Direct cotton dyes in orange, scarlet, and brown can be made using 4,4-dinitrostilbene-2,2-disulfonic acid in an industrial setting. This is achieved through a condensation reaction with aminoazo molecules.[1]

1.1.6.3 Reduction of Nitro Compounds

Azoxy compounds, which can be transformed into azo compounds, can be formed when aromatic nitro compounds are reduced. The intermediate nitro and hydroxylamino derivatives condense during this process (Figure 17).[1]

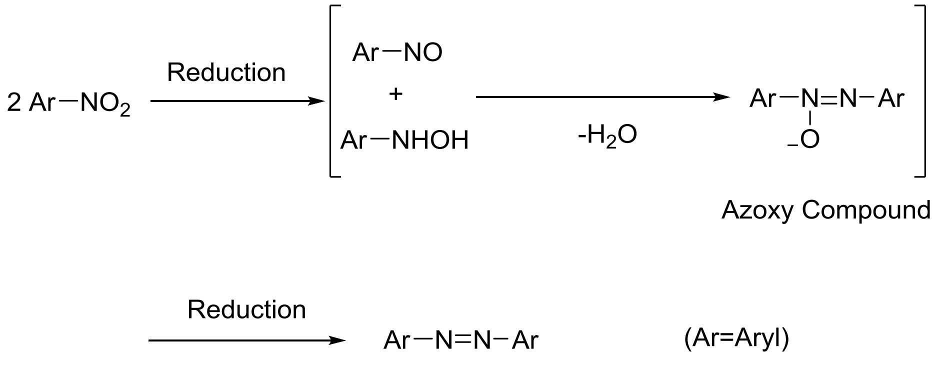


Figure 17. General representation of reduction of nitro compound

The synthesis of asymmetric azo compounds is outside the scope of this technique. Mixtures of all possible permutations are produced when two different nitro compounds are utilized (Figure 18).[1]

$$\mathrm{Ar{-}NO_2} \quad + \quad \mathrm{Ar^1{-}NO_2} \longrightarrow \mathrm{Ar{-}N{=}N{-}Ar} \quad + \quad \mathrm{Ar{-}N{=}N{-}Ar^1} + \quad + \quad \mathrm{Ar^1{-}N{=}N{-}Ar^1}$$

Figure 18. All possible combinations of different nitro compounds in the reaction medium

1.1.6.4 Oxidation of Amino Compounds

Symmetrical azo compounds are produced when primary aromatic amines are treated with an appropriate oxidizing agent (Figure 19). Hypochlorites can use as oxidizing agents for these sorts of reactions. Peroxy compounds (hydrogen peroxide, sodium perborate), oxygen or air with a pyridine-Cu(I) chloride catalyst, and chromic acid are also viable options for oxidizing agents.[1]

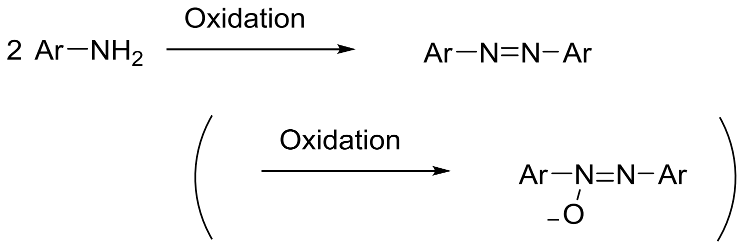


Figure 19. General representation of oxidation of amino compound

It is possible to make symmetrical azo compounds from primary aromatic amines by reacting them with appropriate oxidizing agents. It is possible, in some circumstances, for the azo step to be further oxidized, resulting in a variety of azoxy molecules.[1]

1.1.7 Helical Chirality

Helical chirality is one example of chiral systems. Even if there is no stereogenic center in a molecule, that molecule can be chiral due to its helical property. When looking at the mirror image of a molecule with a helical structure, it is seen that it does not overlap with the mirror image (Figure 20). In such molecules, we can talk about the presence of a stereogenic axis, not the presence of a stereogenic center. This is why helical chirality is also known as axial chirality.

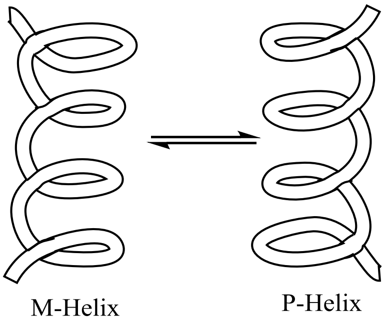
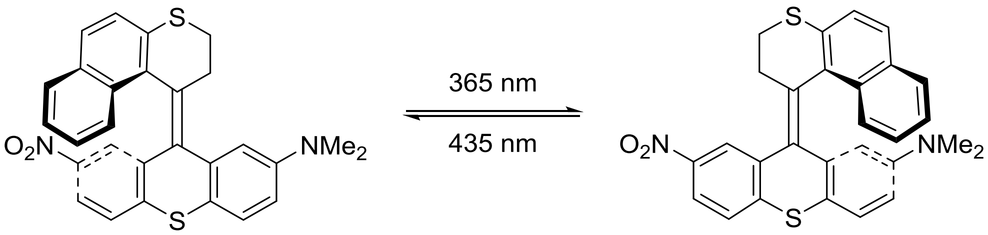


Figure 20. Representation of P and M Helixes

Naturally, helicity can be induced in non-helical chiral structures. For example, DNA which is a flexible molecule, has helical chirality because it has hydrogen bonding which is specific directional non-covalent interactions in their structure. Steric interactions or strains can lead the helical conformations of non-helical rigid molecules. In other words, steric interactions or strains can create helical conformations which are energetically favoured.[35]

1.1.7.1 Helical Chirality of Alkenes

Without the use of circularly polarized light (CPL), photochemical isomerization (including the interconversion between enantiomers) will always result in racemization. According to the study of Feringa (2007), helical shaped overcrowded alkenes were synthesized. These molecules have chiroptical switching properties (Figure 21). Their switching was caused from change in their helicity. These molecules were exposed linear polarized light and it was resulted racemic mixtures was observed. Thus, when they measured the CD spectrum of these molecules, they did not observe and meaningful CD spectrum. Then they exposed these molecules circular polarized light and measured the CD spectrum and they observed CD spectrum. This study is evidence of the helical structures have and chiral property.[36]



(P)-cis-2

(M)-trans-2

Figure 21. Helical Shaped Overcrowded Alkenes in the Feringa's Study

1.1.7.2 Helical Chirality of Azo Dyes

Inherent helicity makes the *cis*-azobenzene isomer chiral (Figure 22).[37] Without chiral perturbation, the helical conformations exist as a combination of M and P helices that can freely exchange places with one another.[38]

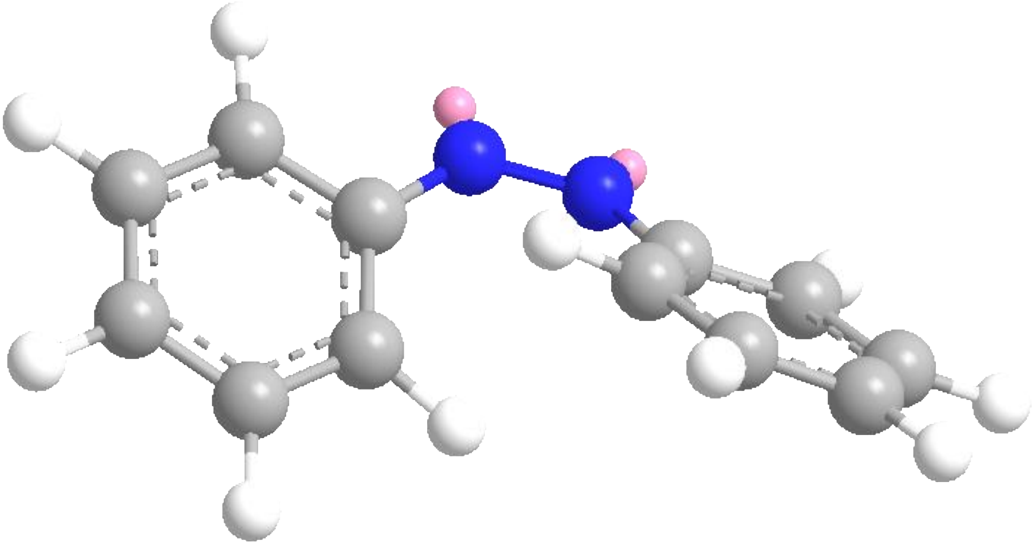


Figure 22. 3D-Representation of *Cis*-Azobenzene

In recent years, optically induced conformational chirality has been the focus of a great deal of research, notably in the context of photochromic molecules and polymers. To mention a few, photochromophores can be found in azobenzenes, overcrowded alkenes, diarylethens, binaphthalenes, and spiropyranes. Because of their capacity to undergo *trans-cis-trans* photoisomerization, which results in linear orientation, azobenzenes are a well-known class of chromophores. Researchers have looked into photoinduced chirality in polymethacrylates, polypeptides, and polyisocyanates. Chiral centers can be found in these azobenzene polymers.[39,40]

Epoxy-based azobenzene polymer PDO3, which lacks chiral centers, was used to create the amorphous polymeric characteristic (Figure 23). At first, the films were achiral, meaning they did not exhibit circular dichroism when illuminated with either right- or left-handed circularly polarized light (CPL). On the other hand, a significant CD signal was observed when the films were subjected to elliptically polarized light (EPL) that included a linear polarized component. Chiral orientation of azobenzene chromophores on amorphous polymer films could be seen to be optically induced by utilizing Ar+ laser light with elliptical polarization. It was discovered that the chiral structures were highly sensitive to the exposure energy. Chirality is induced when light propagation causes a gradual change in the linear orientation of the azobenzene groups.[40]

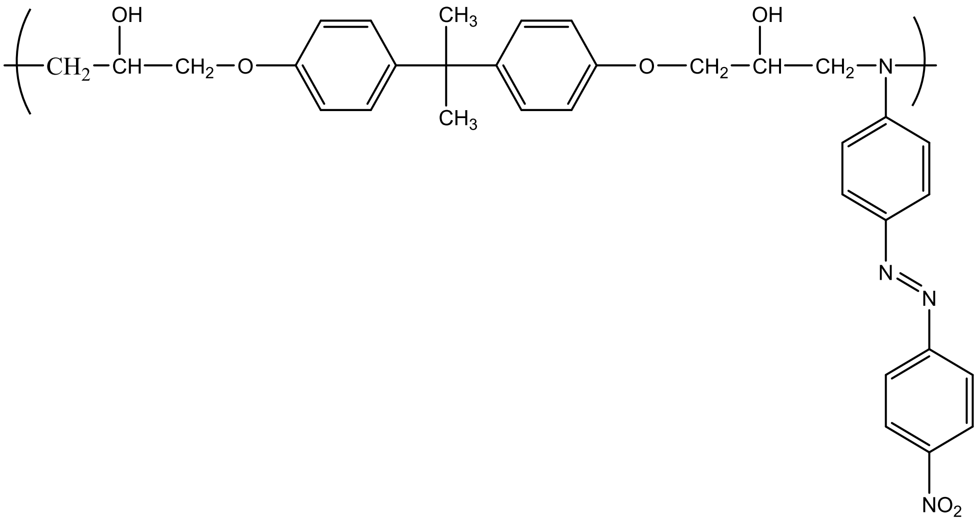
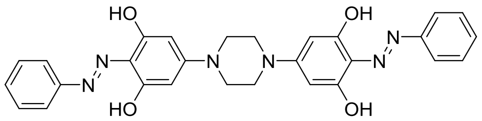


Figure 23. Epoxy-based azobenzene polymer PDO3, which contains no chiral centers

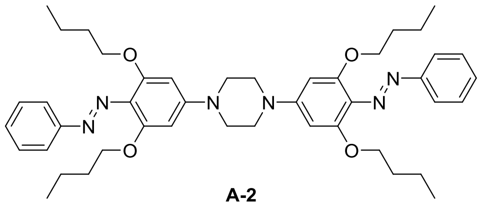
CHAPTER 2

AIM OF THE STUDY

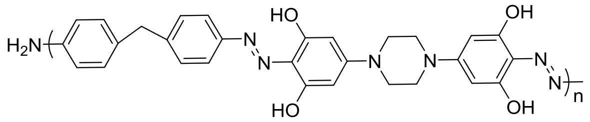
Azo containing compounds are substances that have a wide range of uses, and show photoisomerism under light. In addition, there are articles in the literature that *cis* azo polymers show chiral properties due to their helical properties, upon irradiation with circularly polarized light or eliptically polarized light. Our aim in this study is to synthesize novel azo dyes and polymers to investigate the photoisomerism properties of these synthesized azo dyes and polymers. Furthermore, we will investigate the *trans-cis* photoisomerization with polarized light. In addition, the the chirality control will be investigated in the presence of a chiral additive. The azo dyes **A-1**, **A-2** and polymers **AP-1**, **AP-2** and **AP-3** to be synthesized in this context are given below.



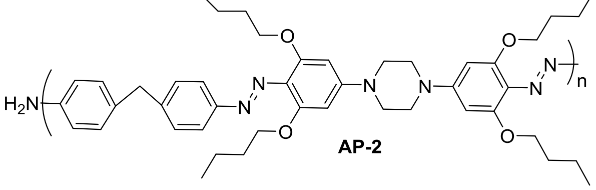
A-1



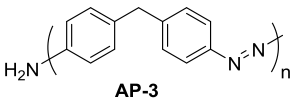
A-2



AP-1



AP-2



AP-3

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis

Azo dyes could be synthesized via numerous methods as some were summarized in the introduction part. We employed two methods: diazotization and oxidative coupling. These methods were chosen based on the structure of resulting azo dye as depicted in Figure 24.

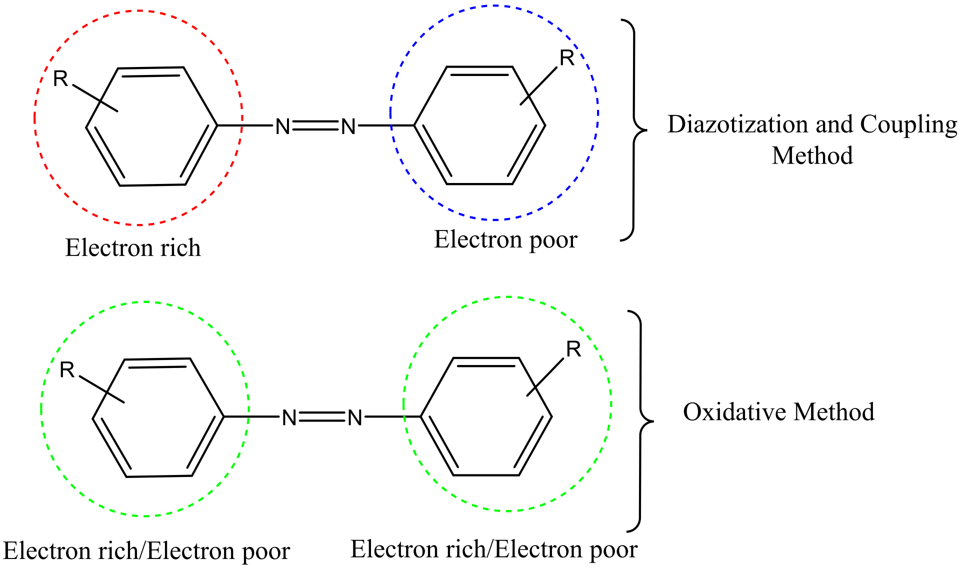
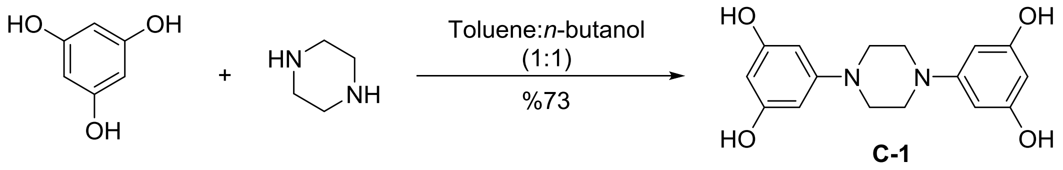


Figure 24. Structure of Azo Dyes and their synthesis route

If the desired azo dye is not symmetric with respect to electron density, diazotization on electron poor unit is made, then the electron rich unit is coupled with it. On the other hand, the diazotization method will not be employed due to poor power of aryl unit to attack the diazonium unit. Therefore, an oxidation method is proposed.

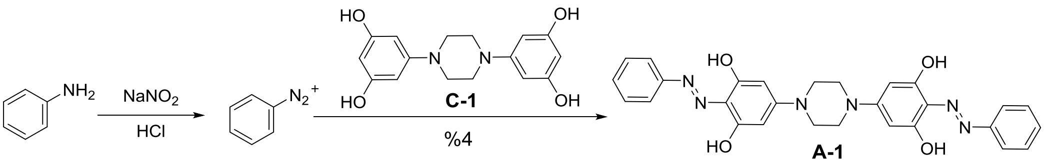
3.1.1.1 Synthesis of A-1

Since the designed azo dye, **A-1** is not symmetric with respect to electron density, the diazotization method was preferred. The electron-rich coupling agent to be used in the diazotization method was synthesized. 1,3,5-benzenetriol and piperazine were refluxed overnight in a mixture of toluene and *n*-butanol using dean stark apparatus. The dean stark apparatus was used to remove water from the experimental medium. After the experiment was completed, the solids were filtered and washed with *n*-butanol and purified by recrystallization method. According to the NMR results, it was seen that the substance was present (Appendix A). As a result of the experiment, pink solids **C-1** was synthesized with 73 % yield (Scheme 1).



Scheme 1. Synthesis of **C-1**

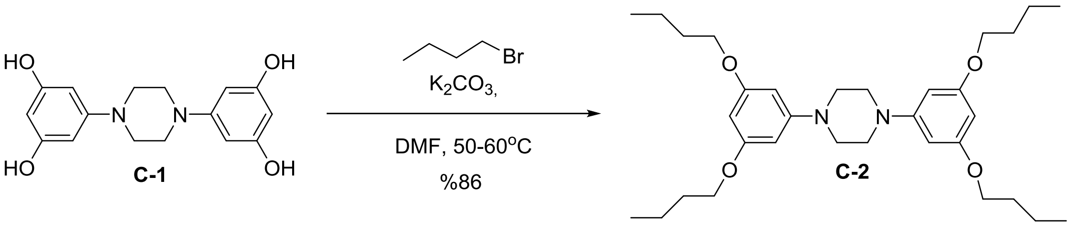
Diazotization method was used for synthesis of **A-1**. Since aniline is the electron-poor part of the dye. Aniline was reacted with $NaNO_2$ in acidic medium and stirred for 1 hour. The diazotization experiment was carried out in an ice bath to prevent the experimental temperature from rising above 5°C. As a result of this experiment, diazonium salt of aniline was obtained. The electron-rich substance **C-1** was dissolved in DMF and kept in the refrigerator to cool it to 0-5 °C. The reason for this was not to increase the ambient temperature when added to the experimental medium. Substance **C-1** dissolved in DMF and kept in the refrigerator was then added to the diazonium salt experimental medium. The mixture was stirred in the ice bath for another 2 hours. After 2 hours, the red colored solids were filtered and washed with water and dried. IR spectroscopy was used to determine whether azo dye was formed (Scheme 2). According to the IR measurements, 1619 cm^{-1} peak belonged to the stretching frequency of N=N bond, which is characteristic of azo dyes (Appendix B). The yield of the experiment was calculated as 4%.



Scheme 2. Synthesis of **A-1**

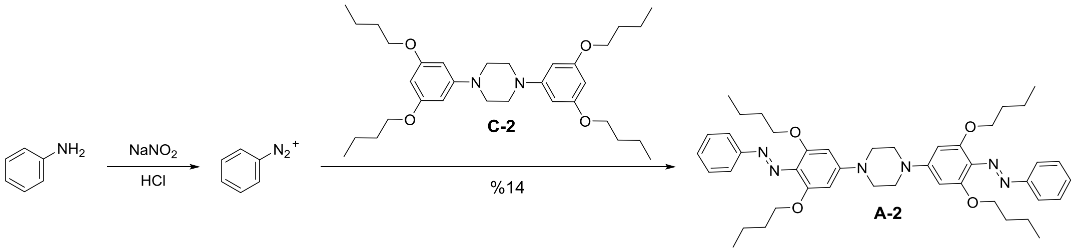
3.1.1.2 Synthesis of A-2

Since the designed azo substance, **A-2** is not symmetrical in terms of electron density, diazotization method was preferred. The electron-rich coupling agent to be used in the diazotization method was synthesized. Substance **C-1** was reacted with 1-bromobutane in DMF in the presence of potassium carbonate. The desired substance was obtained by mixing the substances overnight at 50-60 ℃. When the reaction was completed, the solids were filtered, and the remaining solvent was concentrated to obtain the desired compound **C-2** (Scheme 3). Compound C-3 was measured with NMR (Appendix A). The yield of this experiment was calculated to be 86%.



Scheme 3. Synthesis of **C-2**

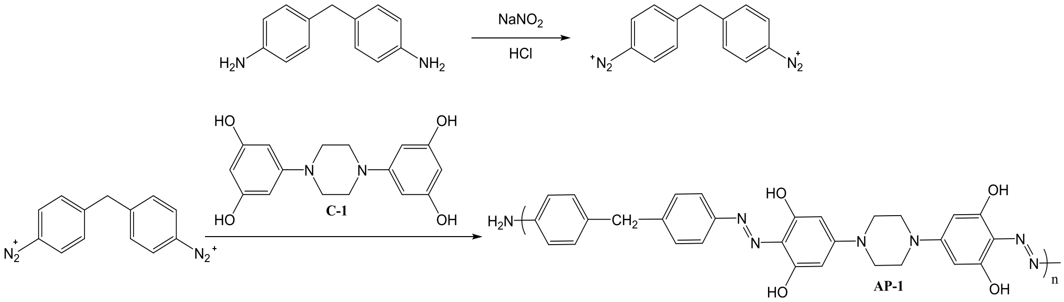
For aniline, the electron-weak moiety, the diazotization method was used. Aniline was treated with $NaNO_2$ in acidic medium and stirred for 1 hour. The diazotization experiment was carried out in an ice bath to prevent the experimental temperature from rising above 5°C. This experiment yielded the diazonium salt of aniline. The electron-rich substance was dissolved in **C-2** DMF and kept in the refrigerator for a while. This was so that the ambient temperature would not increase when added to the experimental medium. The **C-2** dissolved in DMF and kept in the refrigerator was then added to the diazonium salt experimental medium. The mixture was stirred in an ice bath for another 2 hours. After 2 hours, the dark brown colored solids were filtered and washed with water and dried (Scheme 4). IR spectroscopy was used to determine whether azo dye was formed. According to the IR measurements, 1591 cm^{-1} peak belonged to the stretching frequency of N=N bond, which is characteristic of azo dyes (Appendix B). The yield of the experiment was calculated as 14%.



Scheme 4. Synthesis of **A-2**

3.1.1.3 Synthesis of AP-1

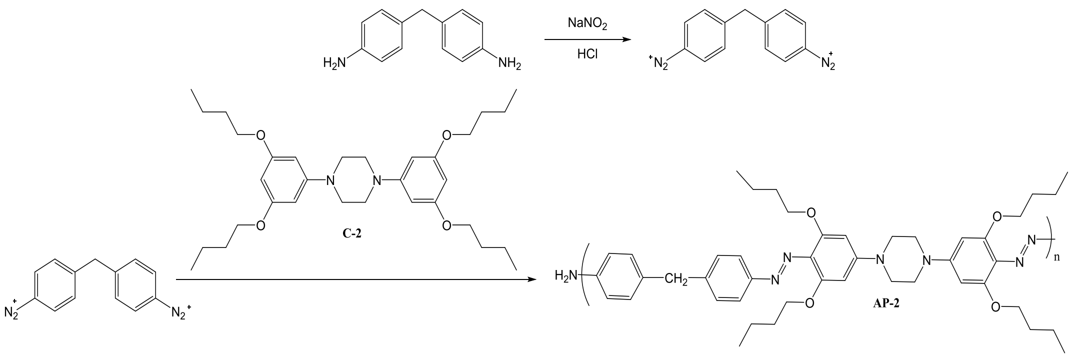
For the electron weak moiety 4,4-diaminodiphenyl methane, the diazotization method was used. 4,4-diaminodiphenyl methane was reacted with 2 equivalents of $NaNO_2$ in acidic medium and stirred for 1 hour. The purpose of using 2 equivalents of $NaNO_2$ is to convert the molecule into diazonium salt from both sides. The diazotization experiment was carried out in an ice bath to prevent the experimental temperature from rising above 5°C. This experiment yielded the diazonium salt of aniline. The electron-rich substance was dissolved in **C-1** DMF and kept in the refrigerator for a while. This was so that the ambient temperature would not increase when added to the experimental medium. Substance **C-1** dissolved in DMF and kept in the refrigerator was then added to the diazonium salt experimental medium. The mixture was stirred in an ice bath for another 2 hours. After 2 hours the solids were filtered, washed with water, and dried (Scheme 5). IR spectroscopy was used to determine whether azo dye was formed. According to the IR measurements, 1625 cm^{-1} peak belonged to the stretching frequency of N=N bond, which is characteristic of azo dyes (Appendix B).



Scheme 5. Synthesis of **AP-1**

3.1.1.4 Synthesis of AP-2

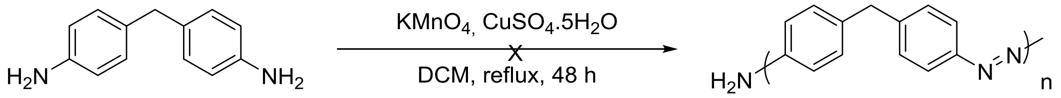
For the electron weak moiety 4,4-diaminodiphenyl methane, the diazotization method was used. 4,4-diaminodiphenyl methane was reacted with 2 equivalents of $NaNO_2$ in acidic medium and stirred for 1 hour. The purpose of using 2 equivalents of $NaNO_2$ is to convert the molecule into diazonium salt from both sides. The diazotization experiment was carried out in an ice bath to prevent the experimental temperature from rising above 5°C. This experiment yielded the diazonium salt of aniline. The electron-rich substance was dissolved in **C-2** DMF and kept in the refrigerator for a while. This was so that the ambient temperature would not increase when added to the experimental medium. Substance **C-2** dissolved in DMF and kept in the refrigerator was then added to the diazonium salt experimental medium. The mixture was stirred in an ice bath for another 2 hours. After 2 hours the solids were filtered, washed with water and dried (Scheme 6). IR spectroscopy was used to determine whether azo dye was formed. According to the IR measurements, 1592 cm^{-1} peak belonged to the stretching frequency of N=N bond, which is characteristic of azo dyes (Appendix B).



Scheme 6. Synthesis of **AP-2**

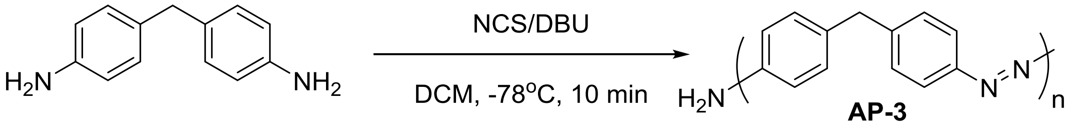
3.1.1.5 Synthesis of AP-3

Since the designed **AP-3** polymer is symmetric with respect to electron density, the oxidation method was used to synthesize this material. In the first synthesis attempt, $KMnO_4$ and $CuSO_4.5H_2O$ were chosen as oxidizing agents. 4,4-diphenylmethane and oxidation agents were mixed in DCM and refluxed at 55-60℃ for 48 hours (Scheme 7). After refluxing, we collected and dried the solids formed in the upper part of the experimental medium, thinking that they were the desired polymer, but we observed that the solids we collected were not the desired solids as a result of the measurement of IR Spectra.



Scheme 7. First Reaction Pathway of **AP-3**

After the failure of the first oxidation method, we found a new oxidation method due to the long experimental time of the first method. In this method, 4,4-diaminodiphenyl methane was reacted with the appropriate oxidizing agents NCS and DBU in DCM. The reaction was stirred at -78 ℃ for 20 minutes. A mixture of dry ice and acetone was used to reach -78℃. After 20 minutes, saturated sodium bicarbonate solution was added to the experimental medium and the experiment was stirred for another 40 minutes. After completion of the experiment, the organic fraction was washed with water and 1N HCl solution and concentrated under vacuum (Scheme 8). IR spectroscopy was used to determine whether azo dye was formed. According to the IR measurements, 1596 cm^{-1} peak belonged to the stretching frequency of N=N bond, which is characteristic of azo dyes (Appendix B).



Scheme 8. Synthesis of **AP-3**

3.1.2 Spectroscopic Studies

3.1.2.1 Spectroscopic Studies of Azobenzene

Since *cis* azobenzene is inherently chiral, it was thought that the chirality could be controlled by a chiral additive. For this purpose, *S*-methylbenzylamine was added to *trans* azobenzene solution in acetonitrile. This solution was irradiated with 365 nm lamp. The conversion from *trans* to *cis* was observed with UV-Vis spectrum as seen in Figure 25.

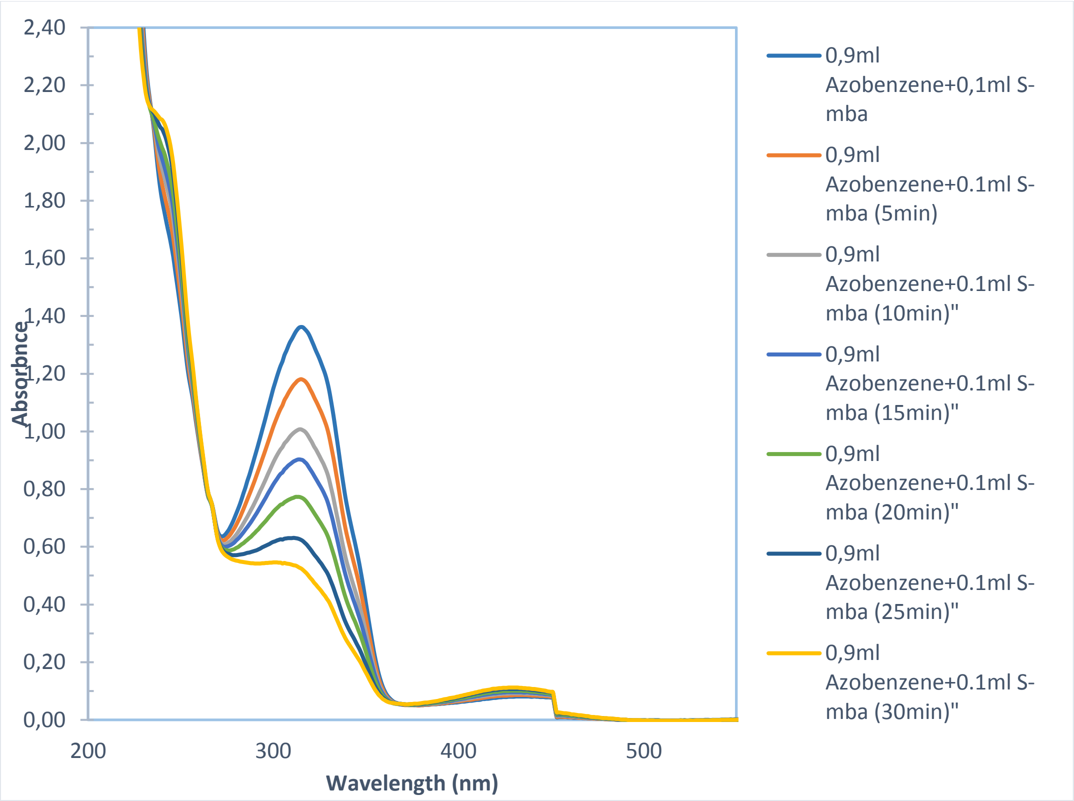


Figure 25. UV-Vis Spectrum of photoisomerism of *trans* azobenzene and *S*-methylbenzylamine under 365 nm UV irradiation during 30 min

After *trans-cis* conversion, CD was also measured. As it is seen in Figure 26, there was no chiral induction to the *cis* azobenzene. Similar results were observed for *R*-methylbenzylamine additive (Appendix D). Therefore, it was concluded that the CD signals obtained at 300-320 nm were not expected CD signals rather noise (Appendix E).

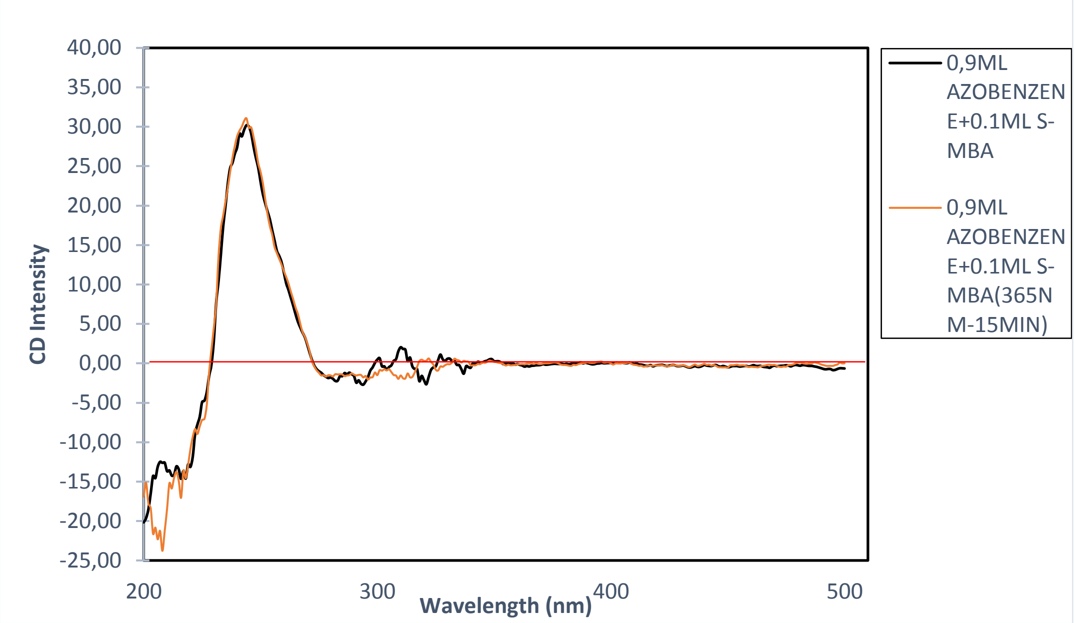


Figure 26. CD spectrum of *trans* azobenzene *S*-methylbenzylamine mixture before and after UV irradiation with 365 nm light.

With these results in hand, we repeated *trans-cis* conversion with only azobenzene. This was done with changes the 365 nm light expose time. It was interesting to see that the amine included azobenzene *trans-cis* conversion was faster than sole azobenzene in acetonitrile (Figure 27). The rate constant for azobenzene photoisomerization is 0.0184 1/s, and the constant for *S*-methylbenzylamine added solution is 0.0315 1/s.

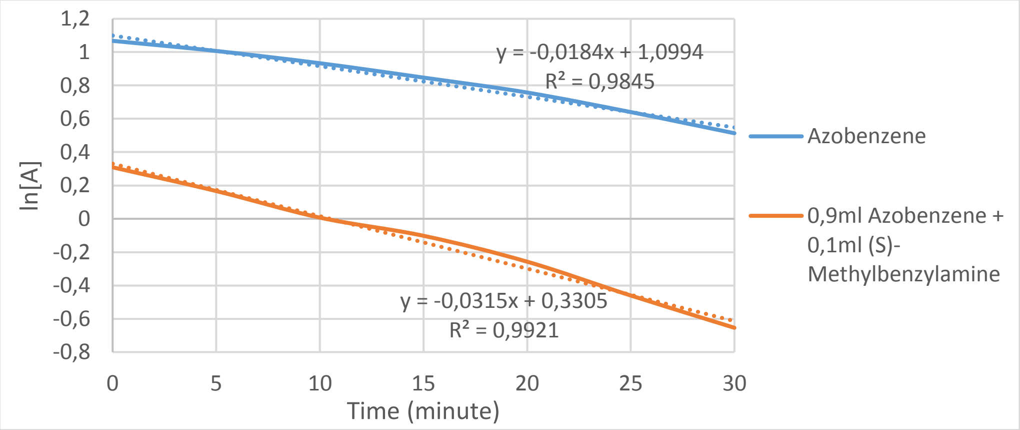


Figure 27. Reaction rate comparision between azobenzene and amine included azobenzene mixture

3.1.2.2 Spectroscopic Studies of A-1

Compound **A-1** was dissolved in acetonitrile and exposed to 365 nm light for 30 minutes and UV-Vis measurements were taken every five minutes. According to the UV-Vis spectrum of substance **A-1**, we could not observe *trans-cis* transformation of substance **A-1** as a result of exposure to light as it could be seen on UV-Vis spectrum of substance **A-1** in Figure 28. This could be due to the hydrogen bonding between H in the -OH group and N in the chromophoric group as represented in the Figure 29.

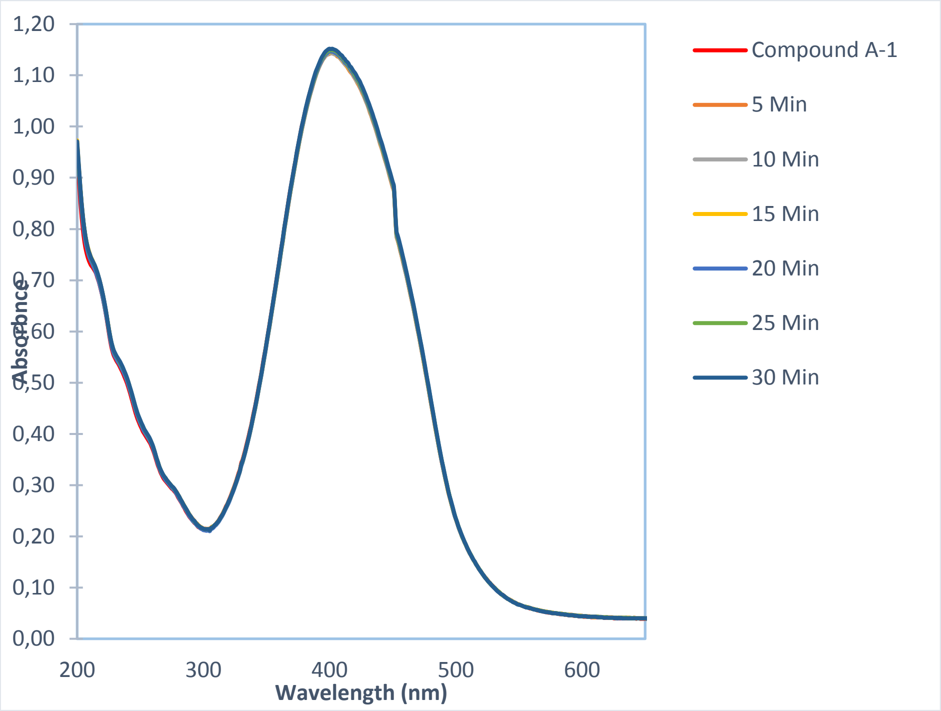


Figure 28. UV-Vis Spectrum of **A-1** under 365 nm light during 30 min

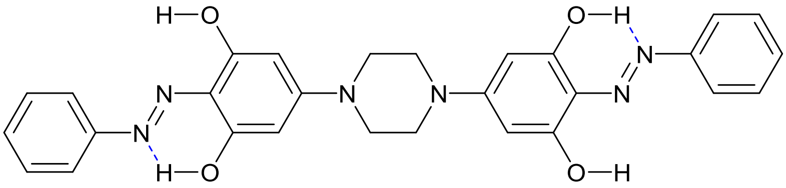


Figure 29. H bonding between H and N in **Azo-1**

To observe the effect of amine on the photoisomerization of substance **A-1**, we prepared a mixture of substance **A-1** and *S*-methylbenzyl amine. We exposed this mixture to 365 nm light for 30 minutes and measured the UV-Vis spectrum every five minutes. As a result of the UV-Vis measurements of the mixture of substance **A-1** and *S*-methylbenzylamine, we observed that substance **A-1** changed from *trans* to *cis*. One of the reasons for this could be that the amine affected the acid-base relationship between H and N. Another reason could be that the amine increased the rate of photoisomerization, as we observed in *trans* azobenzene.

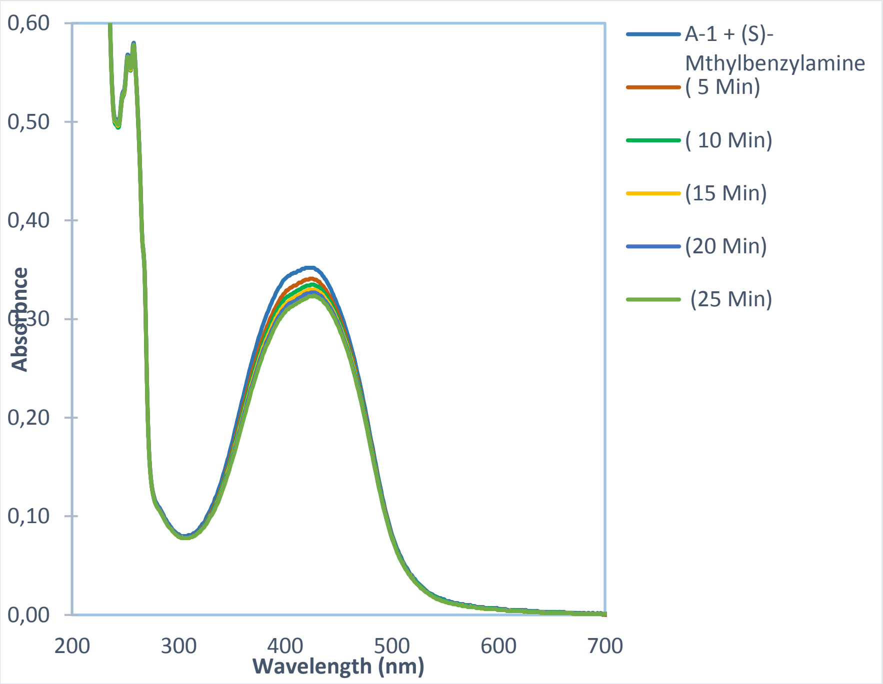


Figure 30. UV-Vis Spectrum of **A-1** and *S*-Methylbenzylamine under 365 nm light

After UV-Vis spectrum measurement of **A-1** and *S*-Methylbenzylamine, CD was also measured. As azobenzene results, there was no chiral induction to the **A-1**.

3.1.2.3 Spectroscopic Studies of A-2

Since we could not observe photoisomerization under light due to the hydrogen bonding in substance **A-1**, we designed and synthesized substance **A-2**, which is formed by replacing the H in the OH group with a butyl group.

Compound **A-2** was dissolved in acetonitrile and exposed to 365 nm light for 30 minutes and UV-Vis measurements were taken every five minutes. According to the UV-Vis spectrum of substance **A-2**, we could not observe the *trans-cis* transformation of substance **A-2** as a result of exposure to light. UV-Vis spectrum of substance **A-2** is given in Figure 31. The reason why **A-2** does not transform from *trans* to *cis* under light is that the substance is sterically hindered.

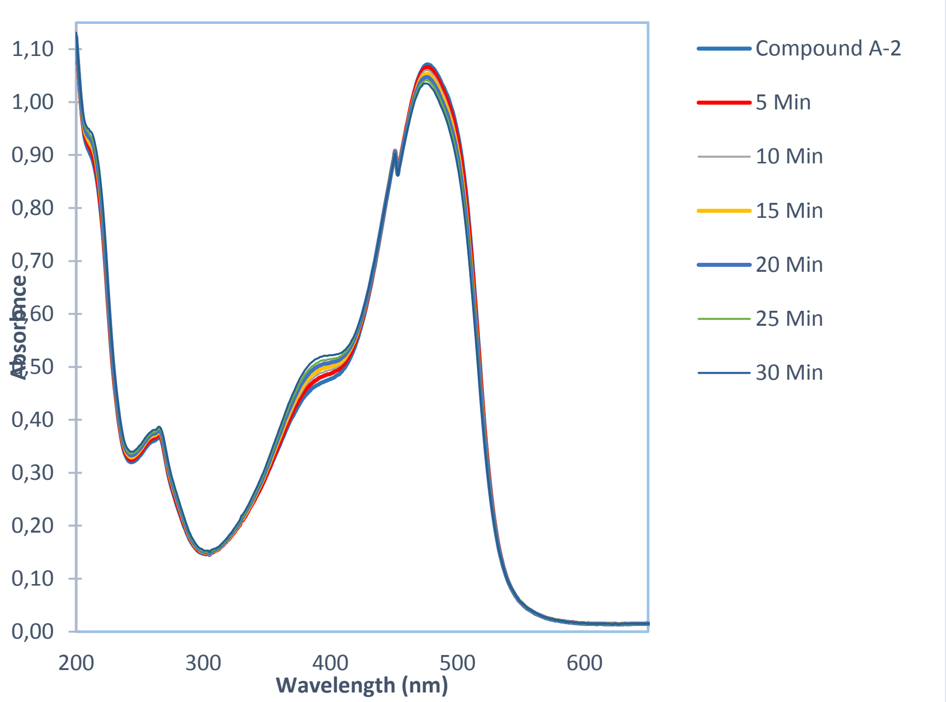


Figure 31. UV-Vis Spectrum of **A-2** under 365 nm light during 30 min

To observe the effect of amine on the photoisomerization of substance **A-2**, we prepared a mixture of substance **A-2** and *S*-methylbenzyl amine. We exposed this mixture to 365 nm light for 30 minutes and measured the UV-Vis spectrum every five minutes. As a result of the UV-Vis measurements of the mixture of substance

A-2 and *S*-methylbenzylamine, we did not observe significant conversion from *trans* to *cis*. Nevertheless, it could be concluded that small **A-1** amine mixture photoisomerization is the acid-base reaction that breaks the hydrogen bonding.

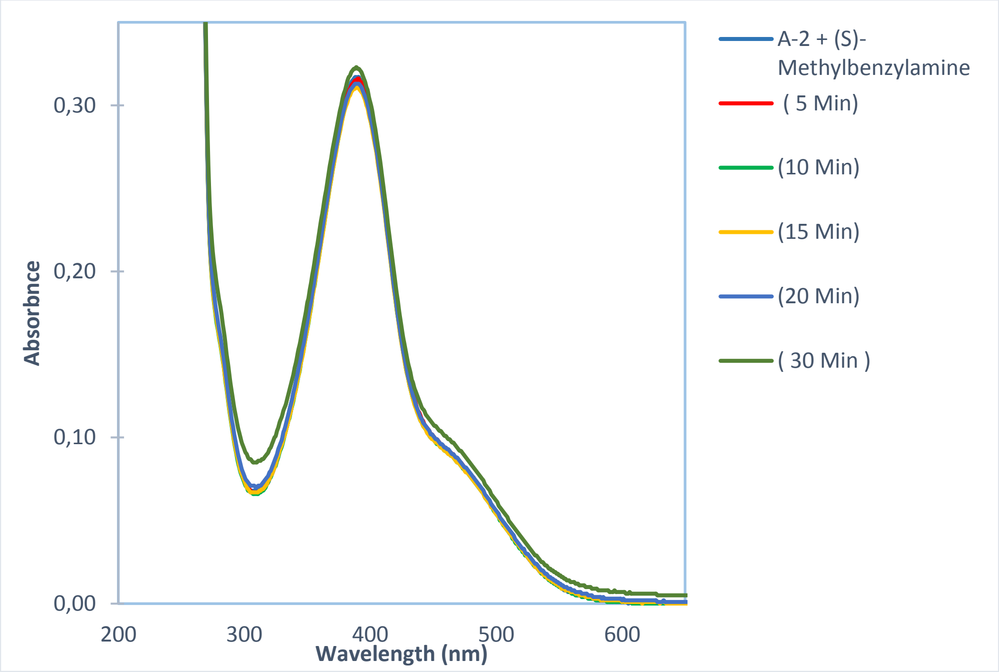


Figure 32. UV-Vis Spectrum of **A-2** and *S*-Methylbenzylamine under 365 nm light

After UV-Vis spectrum measurement of **A-2** and *S*-Methylbenzylamine, CD was also measured. As previous results, there was no chiral induction to the **A-2** .

Since **A-1** and **A-2** are the monomers of **AP-1** and **AP-2** polymers, respectively; and we did not see any photoisomerism in the UV-Vis spectrometer measurements of these monomers. The polymers we synthesized have the problem of dissolution in common organic solvents, UV-Vis measurements could not be performed on **A-1** and **A-2** polymers.

3.1.2.4 Spectroscopic Studies of AP-3

Polymer **AP-3** was sparingly soluble in chloroform, therefore we continued with *trans-cis* isomerization studies in chloroform with irradiating 365 nm light. As seen in Figure 33 *trans* to *cis* conversion was observed.

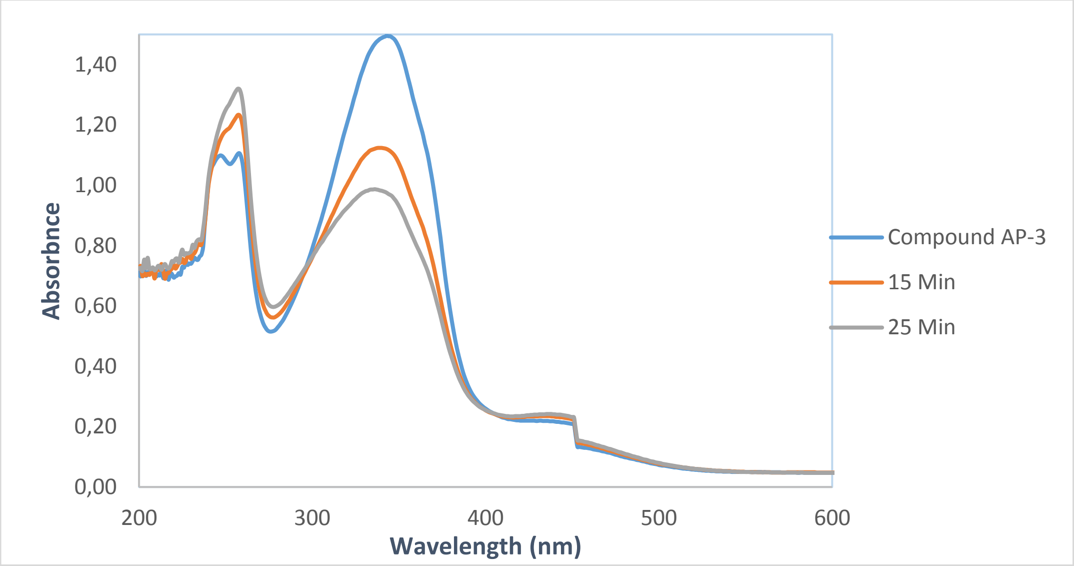


Figure 33. UV-Vis Spectrum of **AP-3** under 365 nm light

However, it was realized soon that chloroform decomposes under light illumination. To overcome this problem, the polymer was attempted to be dissolved in DCM. It was sparingly soluble in DCM. In this case due to the lover boiling point of DCM during, the irradiation DCM was evaporated (Appendix D). This results in hand; the polymer was dissolved in THF. *Trans* to *cis* conversion was observed in this solution as well. (Figure 34)

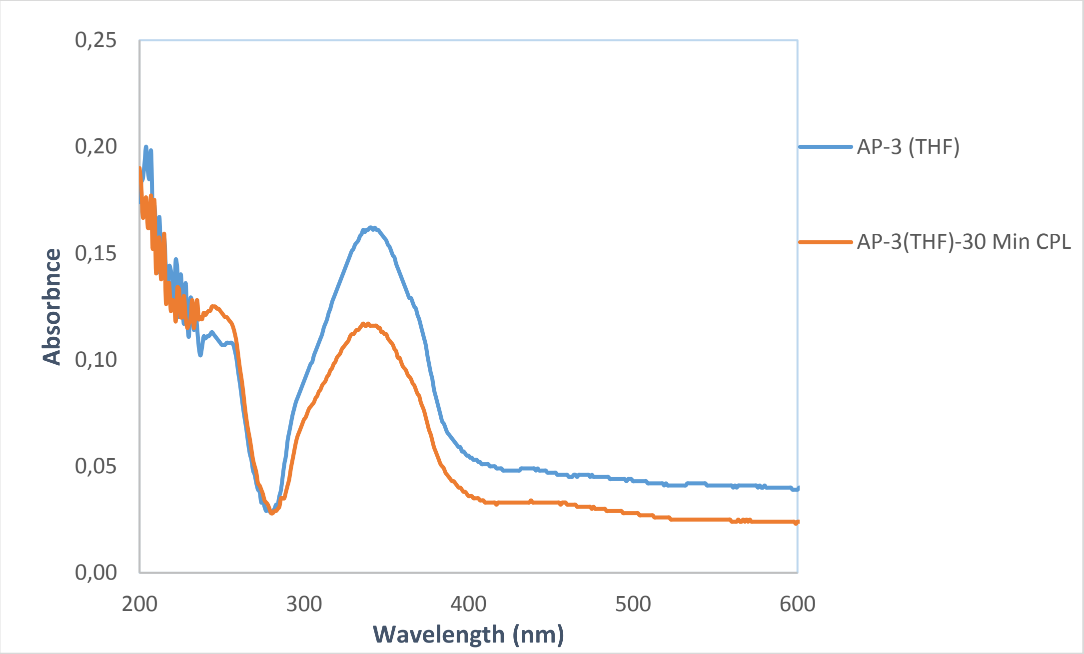


Figure 34. UV-Vis Spectroscopy of **AP-3** in THF before and after exposed CPL

The *cis* form of the **AP-3** polymer was converted to back trans by keeping *cis* form overnight in the dark.

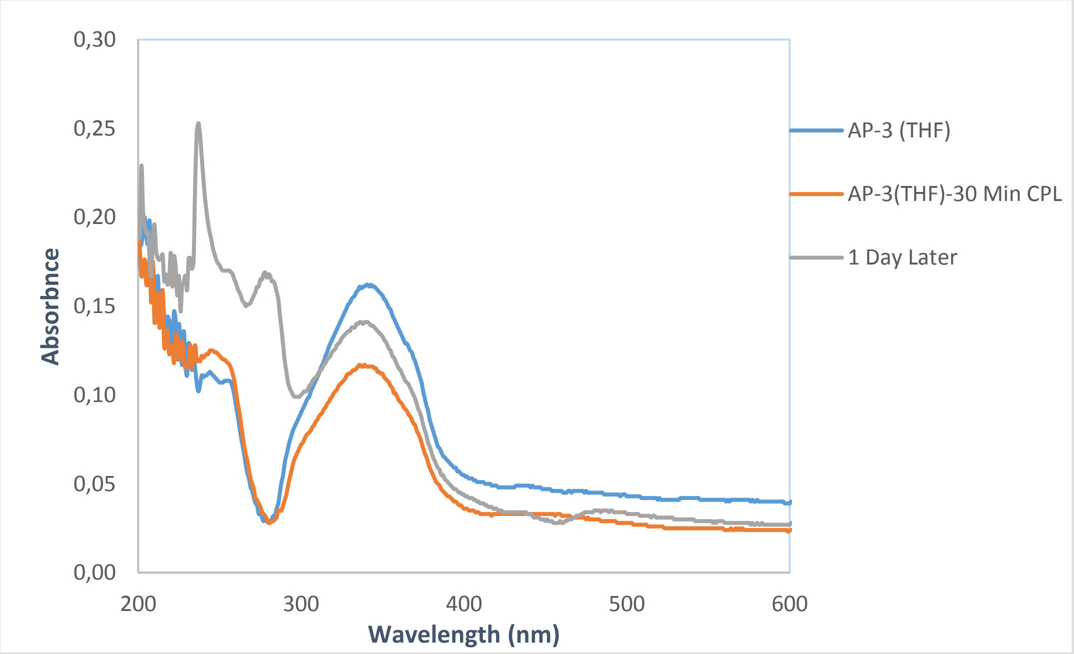


Figure 35. UV-Vis Spectroscopy of **AP-3** in THF before and after exposed CPL and 1 day later

3.1.3 Generation of Circularly and Elliptically Polarized Light

The circular polarized light was generated by placing a linear polarizer (Thompson) in front of the light. The light pass-through polarizer is linearly polarized. The linearly polarized light was let go thought Fresnel $\lambda/4$ quarter waveplate which is placed 45 degrees to the polarization axis. The result in light is circularly polarized.

The circular polarization of light was checked with another polarizer which is placed after the quarter waveplate. Rotating the second polarizer light intensity did not change for all angles. This proves that the light is circularly polarized. The picture shown in Figure 36 shows experimental set-up.

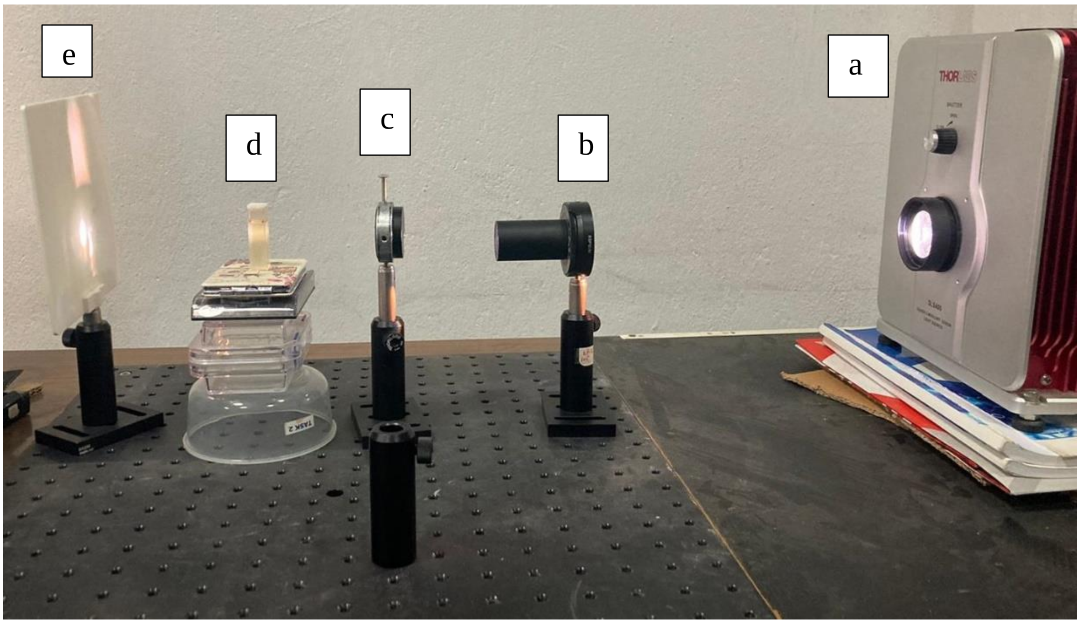


Figure 36. Polarized Light Experimental Set-up (**a:** Xe Lamp, **b:** Linear Polarizer, **c:** Quarter Waveplate, **d:** sample, **e:** Screen)

Elliptically polarized light was generated by changing the first linearly polarizer less than 45 degrees to the quarter waveplate. This produces elliptically polarized light. This was checked with second linear polarizer again by rotation the second linear polarizer. In some angles, the intensity of light diminishes well as never vanished.

The polymer **AP-3** was placed in front of circularly polarized light and then *trans* to *cis* conversion was checked with UV-Vis spectroscopy than the same converted solution was taken to CD spectroscopy and CD was measured. It was seen that no chirality information was induced to the polymer.

The linear polarizer was set to 0, 25, 90 and 110 degrees respectively while the **AP-3** polymer was irradiated. When the linear polarizer is at 0 and 90 degrees, circular polarized light is formed in opposite directions, while at 25 and 110 degrees, elliptical polarized light is formed in opposite directions.

When **AP-3** was exposed to right-handed circularly polarized light (vertical polarization to quarter waveplate) for 30 minutes, it was observed that the *trans-cis* conversion occurred (Figure 37). The CD spectrum of *cis* containing solution was then measured. It was seen that no chiral induction to **AP-3** with the RCPL (Figure 38).

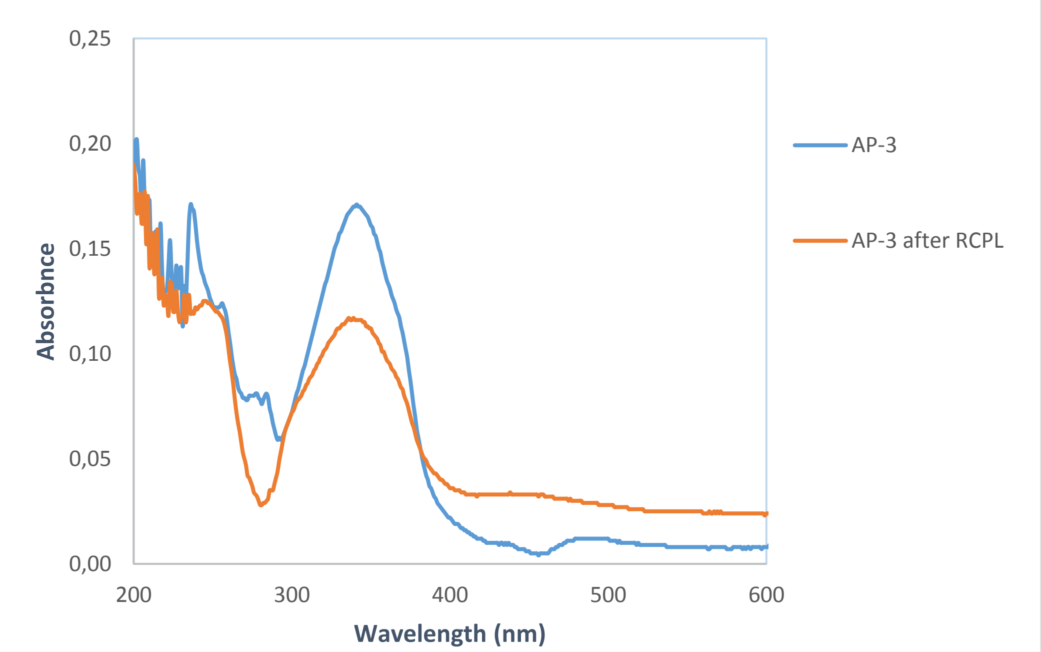


Figure 37. UV-Vis Spectra of Compound **AP-3** before and after 30 min RCPL

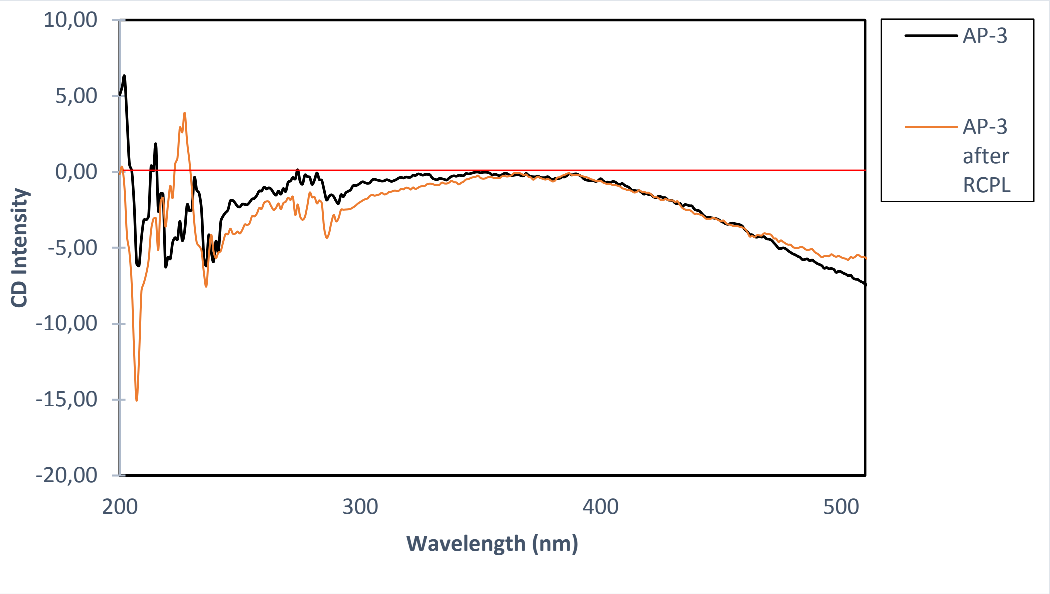


Figure 38. CD Spectra of Compound **AP-3** before and after 30 min RCPL

Polarizer was set to 90 degrees, so it produced left-handed circularly polarized light. When **AP-3** was exposed to left-handed circularly polarized light for 30 minutes, it was observed that the *trans*-*cis* conversion occurred (Figure 39). The CD spectrum of *cis* containing solution was then measured. It was seen that no chiral induction to **AP-3** with the LCPL (Figure 40).

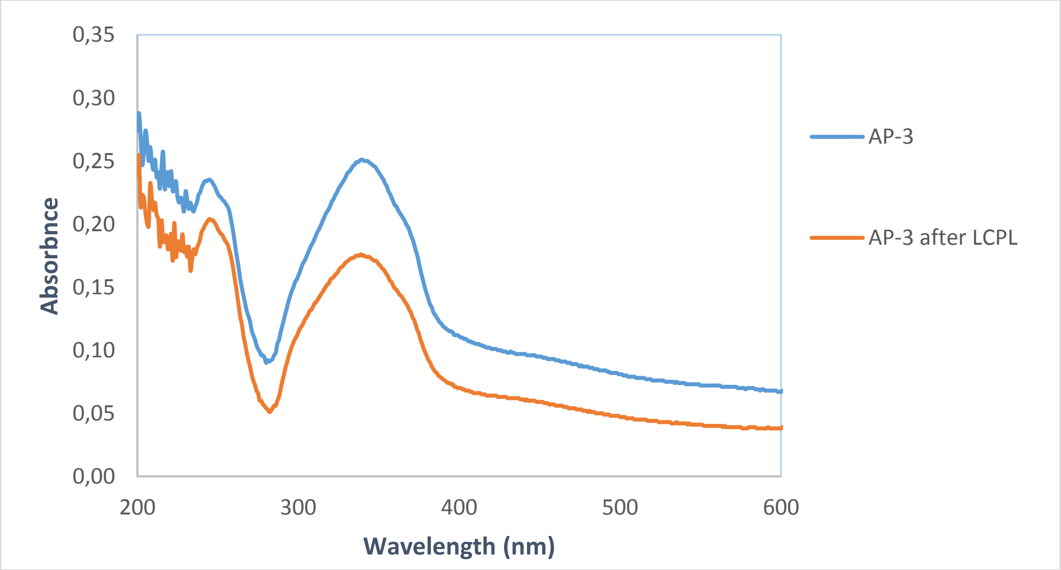


Figure 39. UV-Vis Spectra of Compound **AP-3** before and after 30 min LCPL

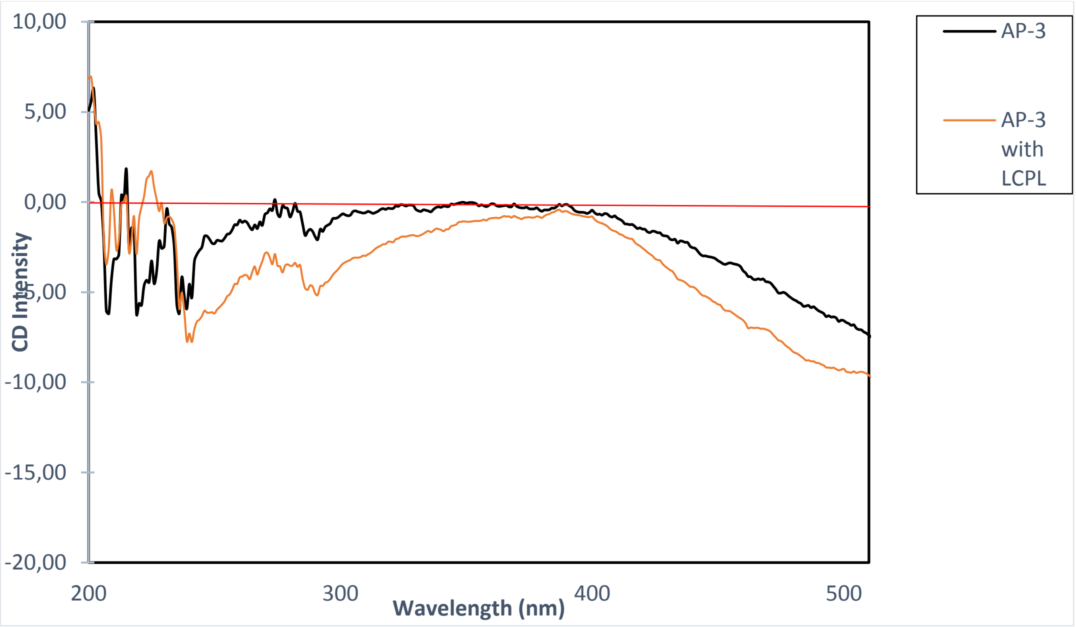


Figure 40. CD Spectra of Compound **AP-3** before and after 30 min LCPL

Polarizer was set to 25 degrees, so it produced right-handed elliptically polarized light. When **AP-3** was exposed to right-handed elliptically polarized light for 30 minutes, trans-*cis* conversion was observed (Figure 41). The CD spectrum of *cis* containing solution was then measured. It was seen that no chiral induction to **AP-3** with the LEPL (Figure 42).

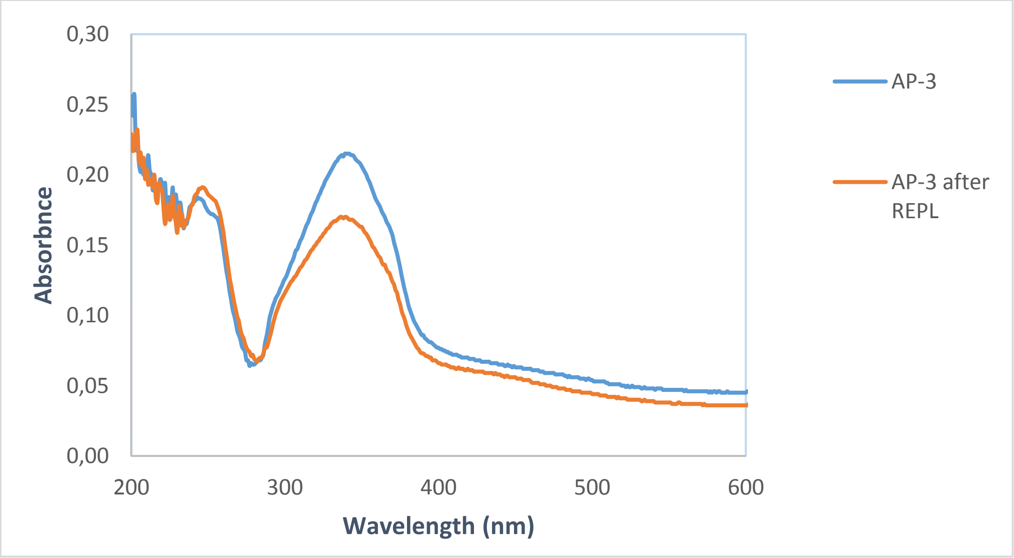


Figure 41. UV-Vis Spectra of Compound **AP-3** before and after 30 min REPL

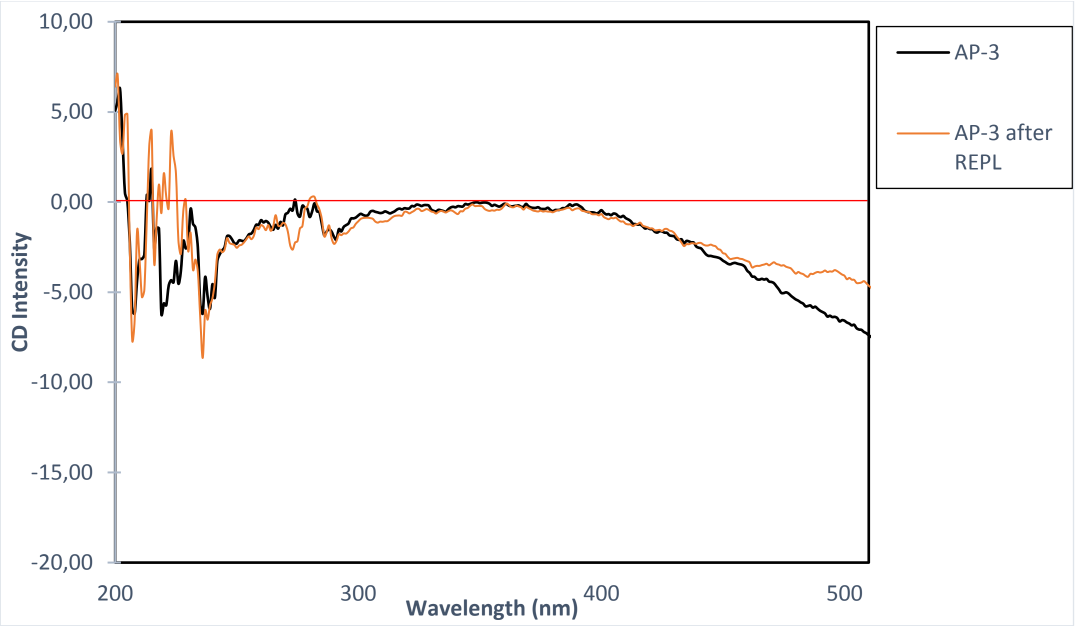


Figure 42. CD Spectra of Compound **AP-3** before and after 30 min REPL

Polarizer was set to 110 degrees, so it produced left-handed elliptically polarized light. When **AP-3** was exposed to left-handed elliptically polarized light for 30 minutes, it was observed that the *trans-cis* conversion occurred (Figure 43). The CD spectrum of *cis* containing solution was then measured. It was seen that no chiral induction to **AP-3** with the LEPL (Figure 44).

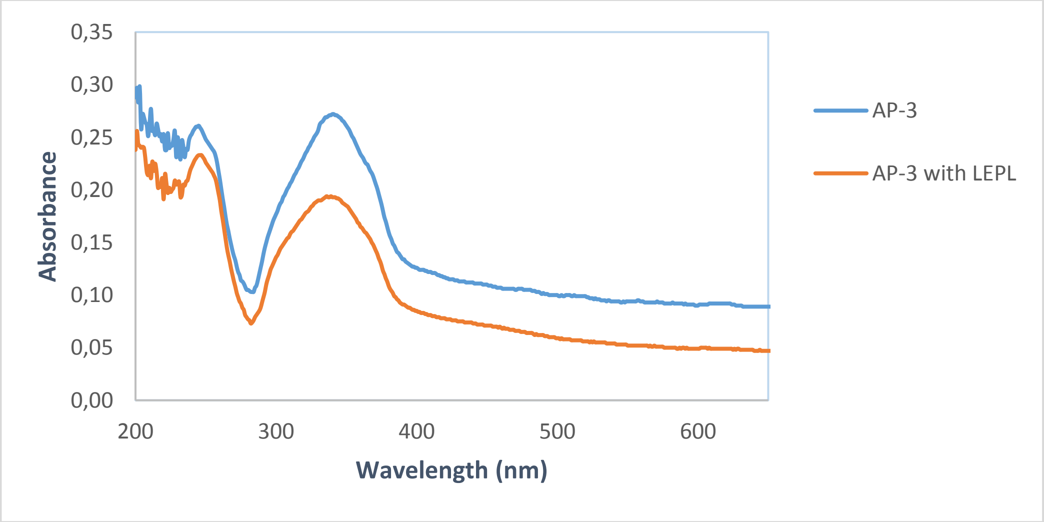


Figure 43. UV-Vis Spectra of Compound **AP-3** before and after 30 min LEPL

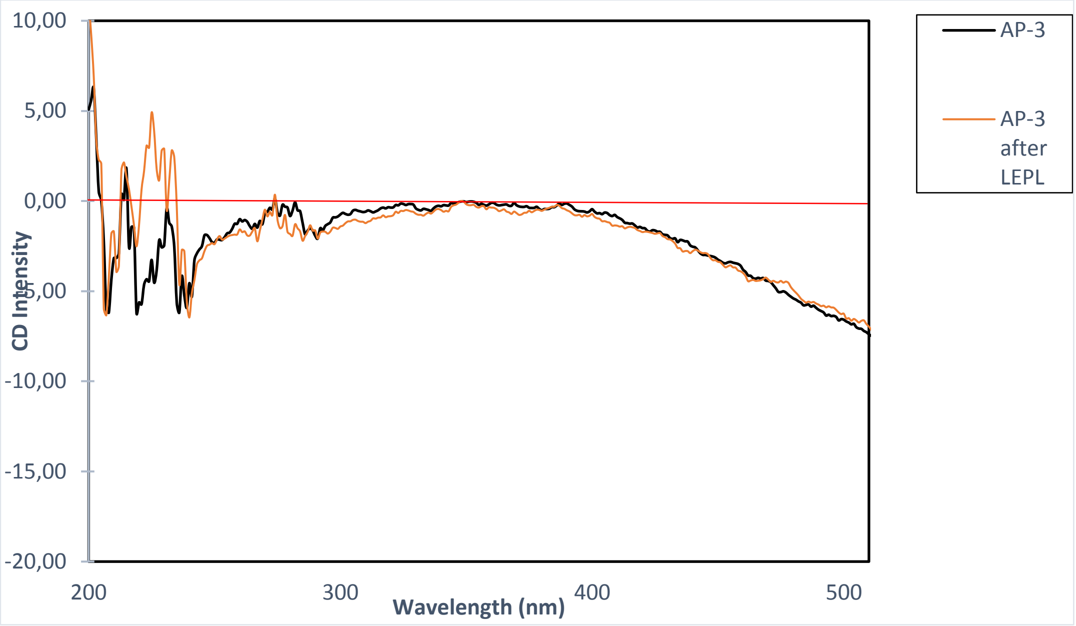


Figure 44. CD Spectra of Compound **AP-3** before and after 30 min LEPL

CHAPTER 4

CONCLUSION

In this study, 2 new azo substances and 3 new azo polymers were synthesized. These synthesized materials were charaterized by IR and NMR. UV-Vis spectroscopy was used not only for monitoring *trans-cis* conversion, but it was used also for characterization. Except for one polymer **AP-3**, the polymers did not dissolve in common solvents. We could not investigate photoisomerization of these polymers. However, the monomeric units **A-1** and **A-2** of these polymers were studied. It could that intramolecular hydrogen bonding and steric hindrance around the azo unit hinders the *trans-cis* conversion.

Trans-azobenzene was converted into *cis*-azobenzene easily by exposing to the 365 nm light.Since *cis*-azobenzene is inherentlt chiral due to it's helicity, it was thoght that one form (P or M) could be obtained in the presence of chiral amine(*S*-methylbenzylamine) additive. When the mixture was exposed to irradiation *trans* to *cis* conversion was observed with faster kinetic than bare azobenzene conversion. Yet, CD measurements did not show any chiral induction.

AP-3 polymer consist of azobenzene units attacht to each other with CH_2 units from four positions of benzene. Irradiation of this presumably convers **AP-3** into a helical polymer. Encourage by previous studies in the literature, this polymer was irradiated with polrized light (circularly and eliptically) to induce chirality to the *cis* form of the polymer. It was founded no chiral induction to the azo polymers. However, this could be just because of poor chiroptical properties of azobenzene unit. With this in mind, we proposed that in order to observe P or M form of *cis*-azobenzene, one should attach a good chiroptical chromophore to azobenzene. Such a task could be accomplished with cumarine, as it was shown in our group previously.[41]

CHAPTER 5

EXPERIMENTAL

5.1 Methods and Materials

All materials and liquids required for the experiment were purchased from Sigma Aldrich and did not need to be cleaned separately. Thin layer chromatography (TLC) (Merck Silica Gel 60 F254) was used to ensure that the experiment worked and then UV light at 254 nm were used for visualization of experimental results. Moreover iodine was used for visualization of this TLC.

Structural investigation of the synthesized compounds was performed by the following methods and the tools are given below.

Stuart SMP11 tool was used fort he observation of the melting point of the new molecules.

Using a Bruker Avance III Ultrashield 400 Hz NMR spectrometer, the compounds' ^{1}H and ^{13}C nuclear magnetic resonance spectra were obtained. Tetramethylsilane (TMS), which served as an internal reference, was used to measure the chemical changes in parts per million (ppm). Spin multiplicities were denoted by the letters s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), tt (triplet of triplet), and m (multiplet), whereas coupling constants (J) were given in hertz (Hz) (Hertz). Compounds ^{1}H NMR, ^{13}C NMR, and other NMR spectra are provided in Appendix A. The MestReNova program was used to process NMR spectra.

The Nicolet iS10 ATR-IR spectrometer from Thermo Scientific was used to record infrared (IR) spectra. The reciprocal centimeter (cm^{-1}) was used to report signal locations. In Appendix B, the IR spectra of the produced compounds are provided. OriginPro 2015 was used to process IR spectra.

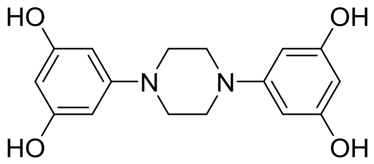
Time of Flight mass spectrometer was used to process High Resolution Mass Spectra (HRMS) in positive mode on (ES+). Appendix C contains the high-resolution mass spectra of the produced molecules.

With the use of a Shimadzu UV-2450 spectrophotometer, UV-Vis measurements were taken. Measurements of the spectrum were made in acetonitrile, chloroform, DCM and THF of varying grades. The UV-Vis spectra were then drawn using Microsoft Excel. Appendix D contains the UV-Vis spectra of the compounds.

It was a Jasco J-1500 CD Spectrometer that was used to take the CD measurements. All of our spectroscopic measurements were taken in spectroscopic grade solvents such acetonitrile, tetrahydrofuran, and chloroform. The CD spectra were made in Microsoft Exel. Appendix E contains the CD spectra of the compounds.

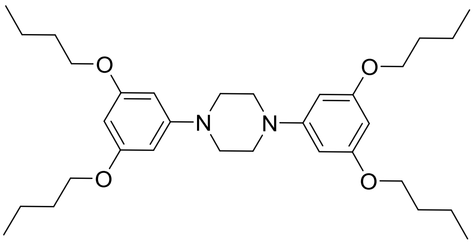
5.2 Synthesis of Coupling Compounds

5.2.1 Synthesis of C-1



Piperazine (1.97 g, 54.72 mmole, 2.40 eq.) and 1,3,5 benzenetriol (1.97 g, 22.80 mmol, 1.00 eq) were dissolved in 100 ml solvent system which occurs 50 ml of toluene and 50 ml of the *n*-butanol. Dean Stark apparatus was used to get rid of the water. The solvent is heated all night at 130°C. The mixture was cooled to room temperature. Pink precipitates were filtered and wash with *n*-butanol. For purification, recrystallization was applied for pink precipitates in the water. Finally, pink precipitates were washed with DCM. The yield was calculated as %73. Final product appeared pinkish solid and soluble in DMF and DMSO. ^{1}H NMR (DMSO, d_6, 400 MHz): δ 8.99 (brs, 4H, OH), 5.75 (m, 6H, Ar-H), 3.10 (s, 8H, CH_2). Mp> 248°C.

5.2.2 Synthesis of C-2

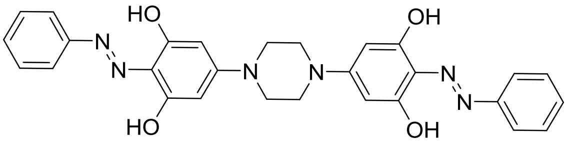


Compound **C-1** (1.00 g, 3.31 mmol, 1.00 eq.), 1-bromobutane (2.49g, 18.19 mmol, 5.50 eq.) and anhydrous potassium carbonate (2.51 g, 18.19 mmol, 5.50 eq.) were mixed in DMF. After overnight stirring at 60°C, mixture was filtered. The filtrate part was concentrated under vacuo. The reaction yield was calculated as 86%.^{1}H

NMR (CDCl3, 400 MHz): δ 6.00-6.25 (m, 6H, Ar-H), 3.93 (m, 8H, CH_2-O), 3.30 (m, 8H, CH_2), 1.75 (m, 8H, CH_2), 1.50 (m, 8H, CH_2), 1.0 (t, J=0.98, 0.96 Hz, 12H, CH_3). ^{13}C NMR (75 MHz, CDCl3) δ 13.9, 19.3, 31.4, 49.3, 67.6, 92.8, 95.7, 153.1, 161.0. HRMS: (TOF-MS) m/z: $[M+H]^+$ Calcd for $C_{32}H_{51}N_2O_4^+$ 527.3849, found 527.3791. Mp 63 ℃.

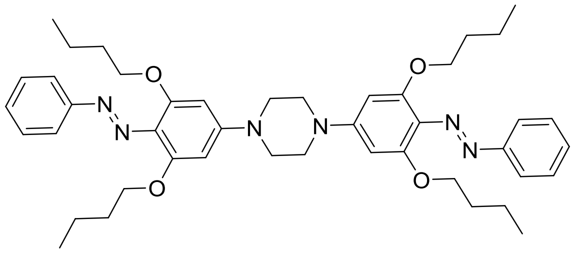
5.3 Synthesis of Azo Compounds

5.3.1 Synthesis of A-1



Aniline (0.15 g, 1.65 mmol, 2.50 eq.) was converted to corresponding diazonium salt with $NaNO_2$ (0.13 g, 1.82 mmol, 2.75 eq.) in HCl solution. The HCl solution was prepared with 1.6 ml 37% HCl diluted in 4.8 ml H_2O). This mixture was stirred for one hour. Then compound **C-1** was dissolved in 5 ml DMF and waited in the refrigerator. After 1 hour waiting for diazonium salt formation, compound **C-1** in DMF add into the mixture. Then mixture was waited 2 more hours on the 0°C. The mixture was filtered, and all solid precipitates washed with distilled water.0.03 gram reddish solid product was calculated and the yield of the reaction was calculated as %4. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 16.00-15.00 (m, 4H, OH) 8.00-7.00 (m, 10H, Ar-H), 6.70-5.50 (m, 2H, Ar-H), 3.9 (s, 8H, CH_2) . IR: 1619 cm^{-1} (N=N), 3100-3500 cm^{-1} (OH). HRMS: (TOF-MS) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}N_6O_4^+$ 511.2094, found 511.2097. Mp>248 ℃.

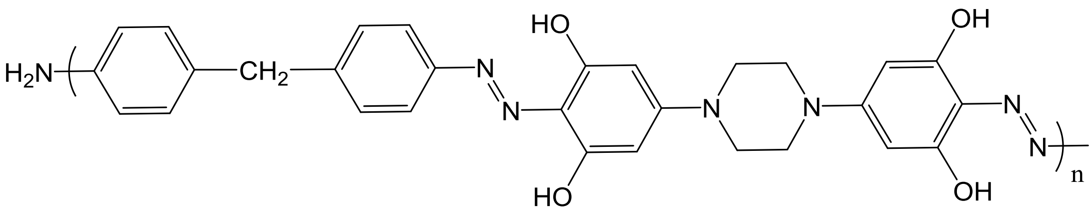
5.3.2 Synthesis of A-2



Aniline (0.09 g, 0.95 mmol, 2.50 eq.) was converted to corresponding diazonium salt with $NaNO_2$ (0.07 g, 1.05 mmol, 2.75 eq.) in HCl solution. The HCl solution was prepared with 1.6 ml 37% HCl diluted in 4.8 ml H_2O). This mixture was stirred for one hour. Then compound **C-2** (0.20g, 0.38 mmol, 1.00 eq.) was dissolved in 5 ml DMF and waited in the refrigerator. After 1 hour waiting for diazonium salt formation, compound **C-2** in DMF add into the mixture. Then mixture was waited 2 more hours on the 0°C. The mixture was filtered, and all solid precipitates washed with distilled water. The yield was calculated as 14%. ^1H NMR (DMSO-d_6, 400 MHz): δ 7.50 (m, 10H, Ar-H), 6.36 (m, 4H, Ar-H), 4.20 (m, 16H, CH_2), 1.80 (brs, 8H, CH_2), 1.50 (brs, 8H, CH_2), 0.96 (brs, 12H, CH_3). IR: 1591 cm^{-1} (N=N), 2990 cm^{-1} (C-H), 1190 cm^{-1} (C-O-C). HRMS: (TOF-MS) m/z: $[M+H]^+$ Calcd for $C_{44}H_{59}N_6O_4^+$ 735.4598, found 735.4554. Mp 113 ℃.

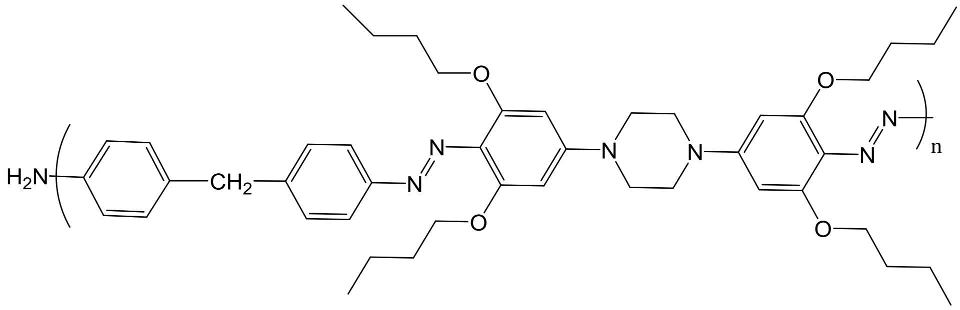
5.4 Synthesis of Azo Polymers

5.4.1 Synthesis of AP-1



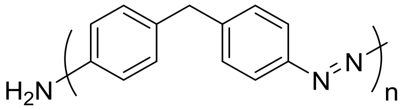
4,4-diaminodiphenylmethane (0.13 g, 0.66 mmol, 1.00 eq.) was converted to corresponding di-diazonium salt with $NaNO_2$ (0.10 g, 1.46 mmol, 2.20 eq.) in HCl solution. The HCl solution was prepared with 1.6 ml 37% HCl diluted in 4.8 ml H_2O). This mixture was stirred for one hour. Then compound **C-1** (0.20 g, 0.66 mmol, 1.00 eq.) was dissolved in 5 ml DMF and waited in the refrigerator. After 1 hour waiting for diazonium salt formation, compound **C-1** in DMF add into the mixture. Then mixture was waited 2 more hours on the 0°C. The mixture was filtered, and all solid precipitates washed with distilled water. IR: 1625 cm^{-1} (N=N), 3100-3500 cm^{-1} (OH).

5.4.2 Synthesis of AP-2



4,4-diaminodiphenylmethane (0.08 g, 0.38 mmol, 1.00 eq.) was converted to corresponding di-diazonium salt with $NaNO_2$ (0.10 g, 1.45 mmol, 2.50 eq.) in HCl solution. The HCl solution was prepared with 1.6 ml 37% HCl diluted in 4.8 ml H_2O). This mixture was stirred for one hour. Then compound **C-2** (0.20 g, 0.38 mmol, 3.80 eq.) was dissolved in 25 ml DMF and waited in the refrigerator. After 1 hour waiting for diazonium salt formation, compound **C-2** in DMF add into the mixture. Then mixture was waited 2 more hours on the 0°C. The mixture was filtered, and all solid precipitates washed with distilled water. IR: 1592 cm^{-1} (N=N), 2990 cm^{-1} (C-H), 1190 cm^{-1} (C-O-C).

5.4.3 Synthesis of AP-3



4,4-diamindiphenylmethane (2.00 gr, 10.09 mmol, 1.00 eq.) was dissolved in 15 ml DCM. Then, DBU (3.07 g, 20.18 mmol, 2.00 eq.) was added to the mixture and stirred 5 minutes in room temperature. Then, mixture was cooled to -78 °C and NCS (2.70 gr, 20.18 mmol, 2.00 eq.) was added to the mixture as an oxidizing agent. The reaction was stirred 20 minutes at -78 °C. After 20 minutes, 50 ml of saturated sodium bicarbonate solution was added into the mixture. The mixture was stirred additionally 40 minutes in room temperature. 50 ml of water and 50 ml of 1N HCl was used for washing the organic layer. Anhydrous sodium sulfate was used for drying agent and organic part was concentrated under vacuo. IR: 1596 cm^{-1} (N=N), 2990 cm^{-1} (C-H).

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APPENDICES

A. NMR Spectra

Bruket Avance III Ultrashield 400 Hz was used to record NMR spectra, and CDCl3 and DMSO were the solvents of choice throughout all of the recordings.

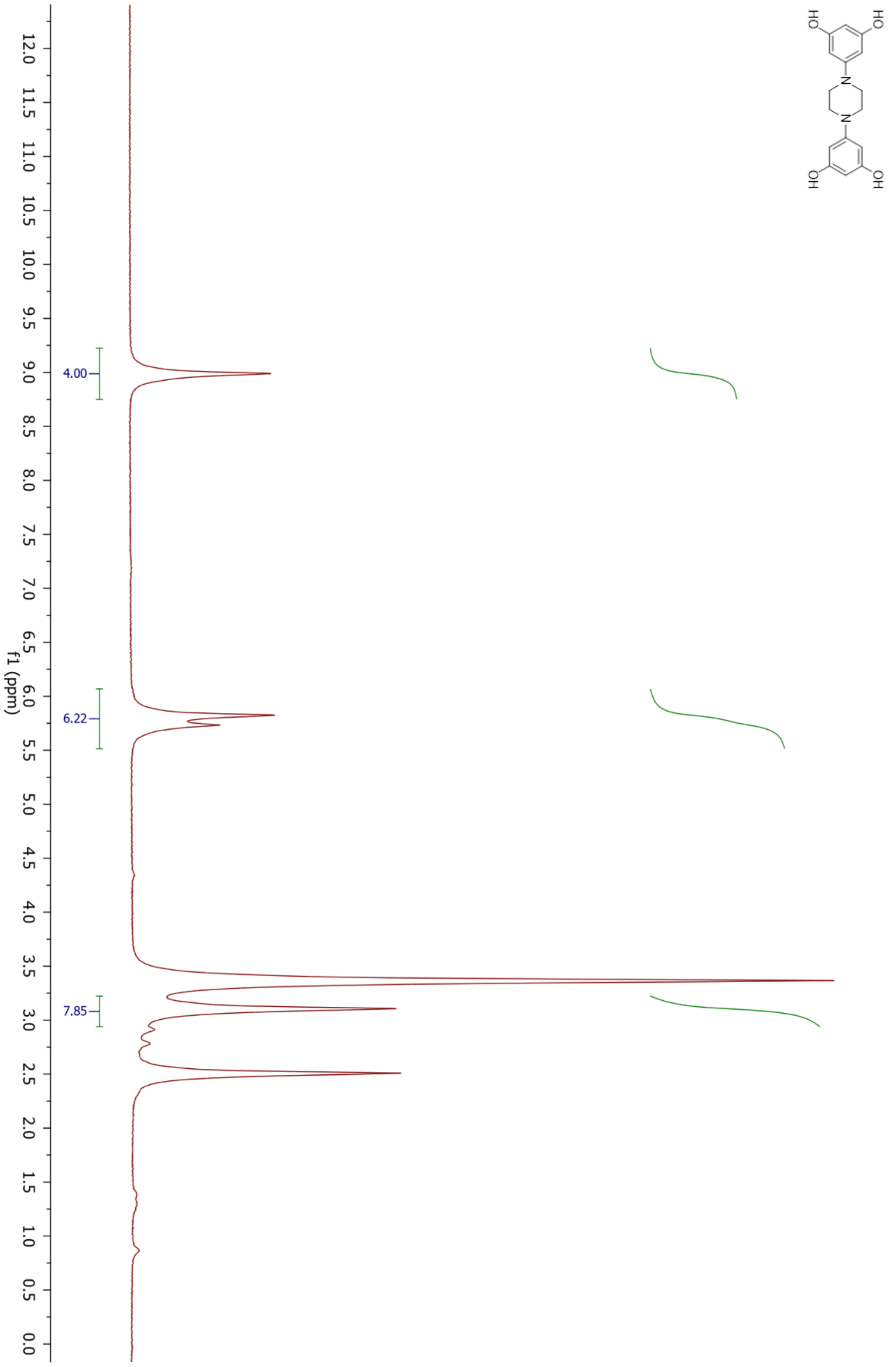


Figure 45. ^{1}H NMR spectrum of Compound **C-1**.

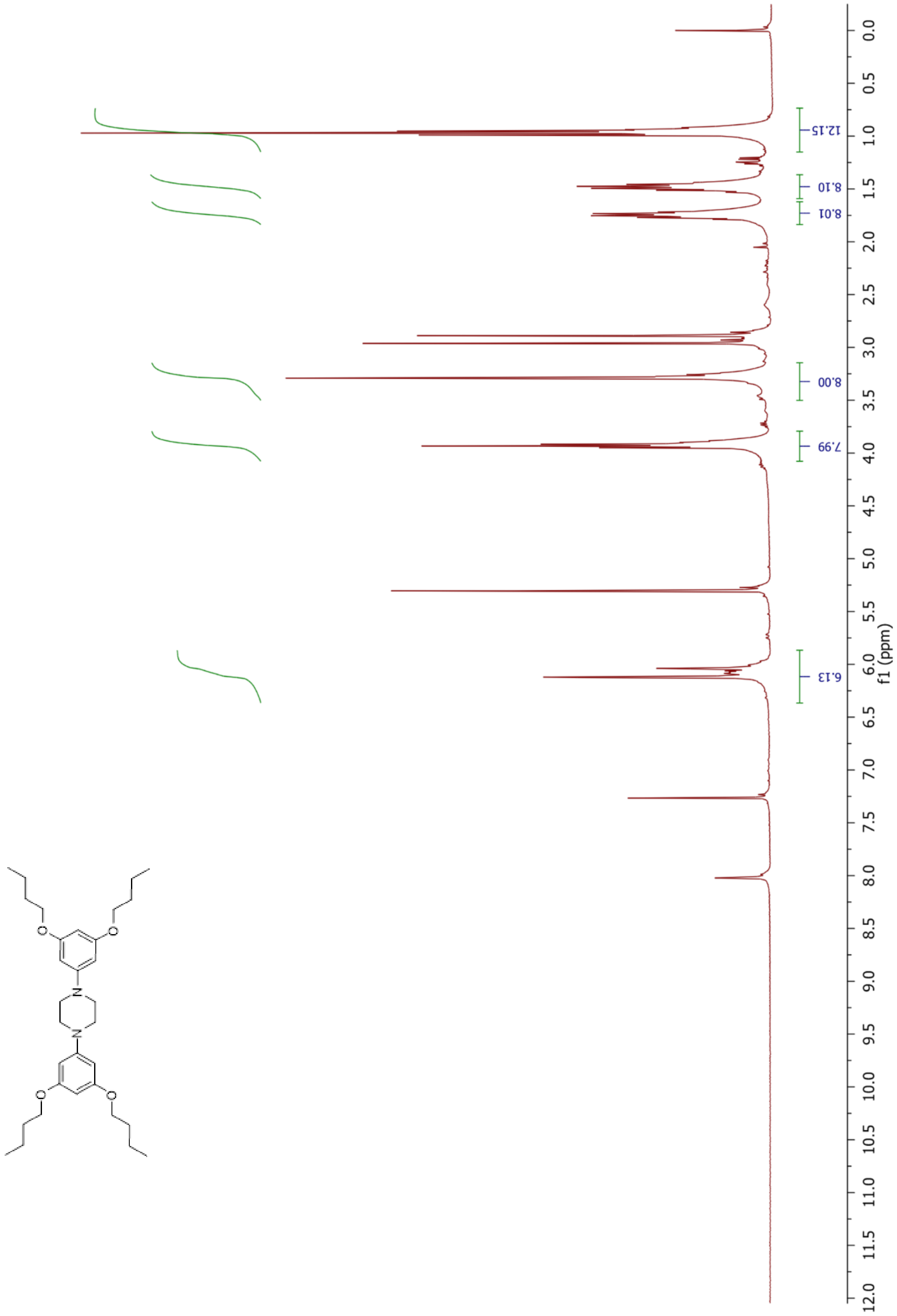


Figure 46. ^{1}H NMR spectrum of Compound **C-2**.

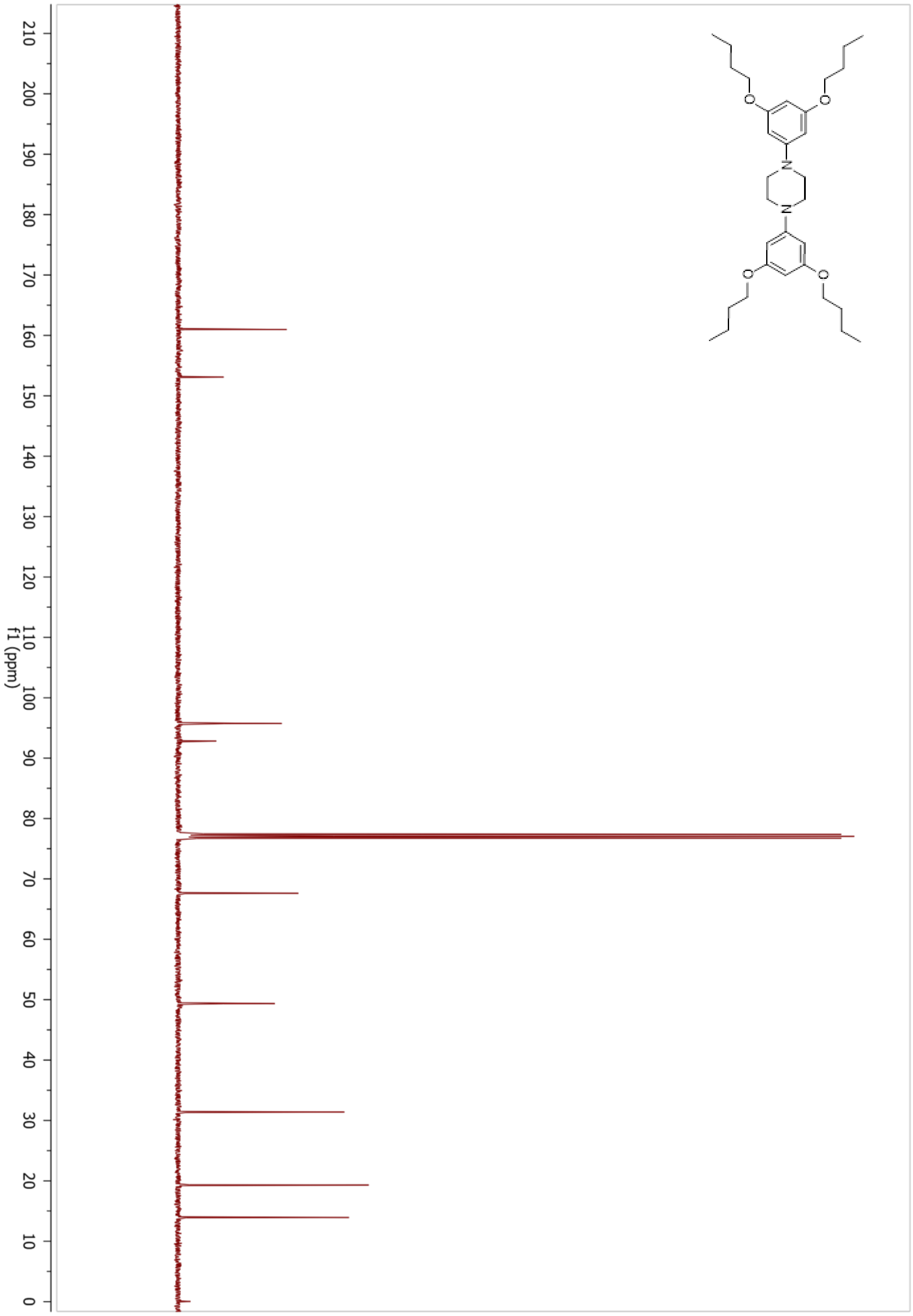


Figure 47. ^{13}C NMR Spectrum of **C-2**

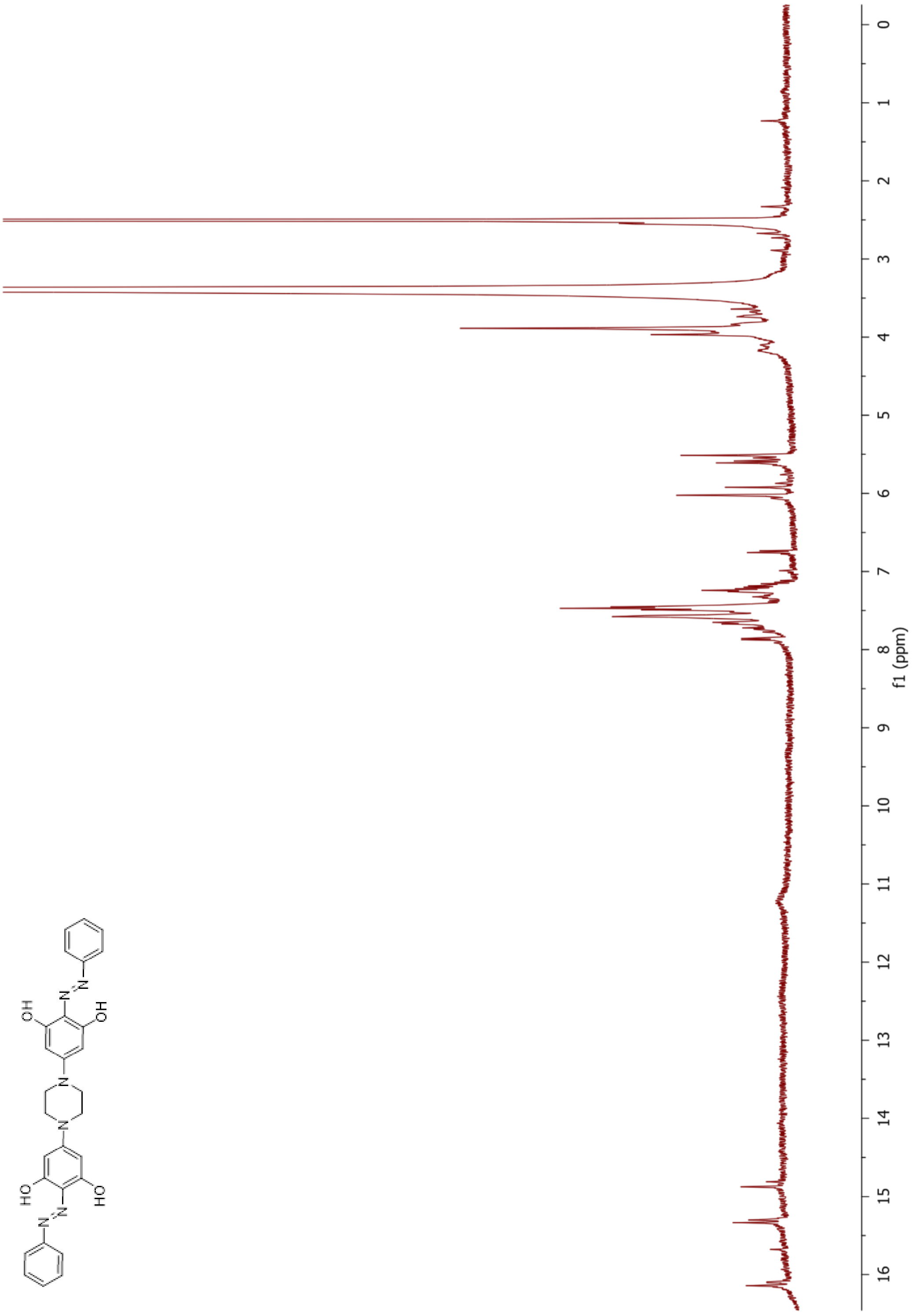


Figure 48. ^{1}H NMR spectrum of Compound **A-1**.

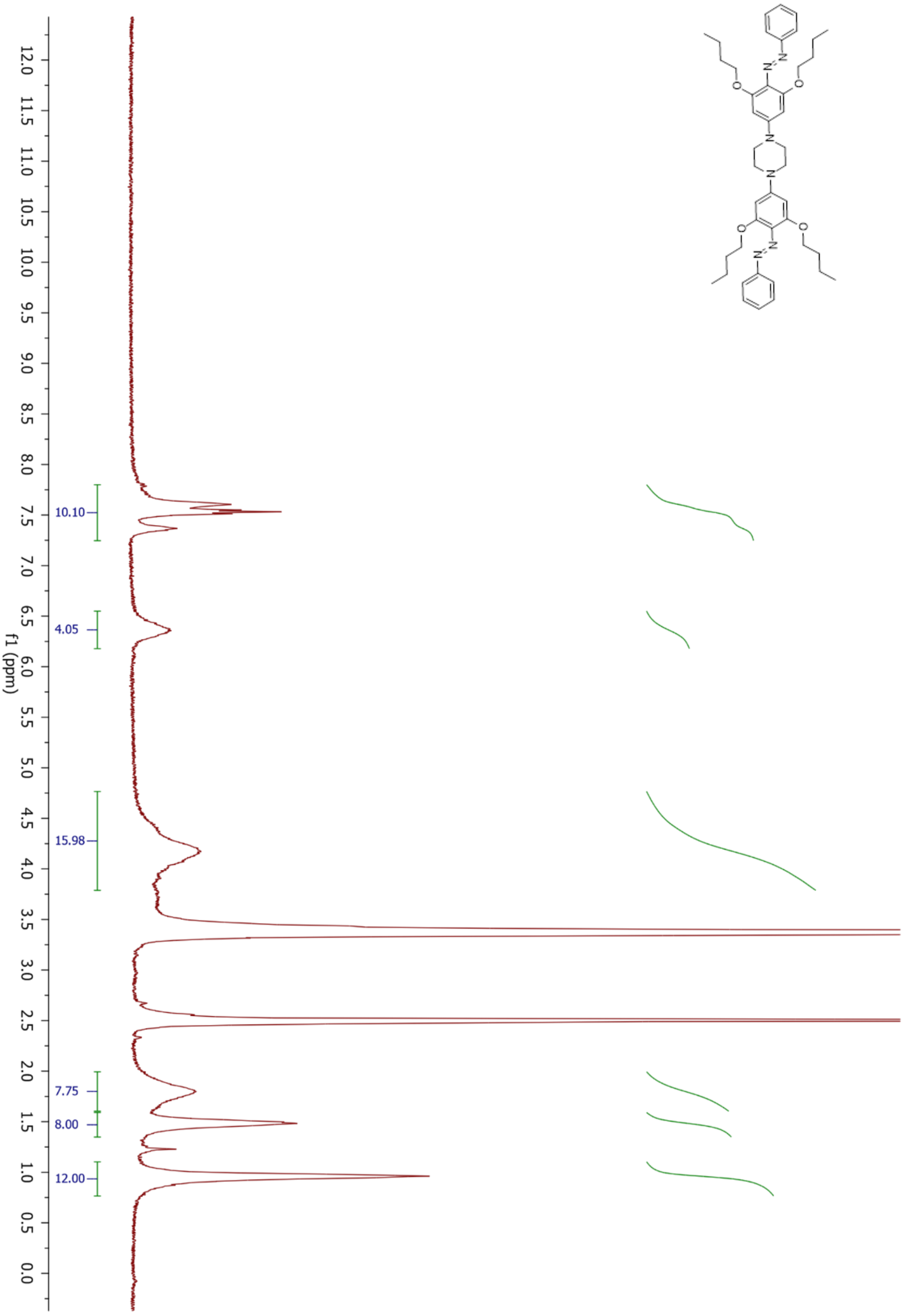


Figure 49. ^{1}H NMR spectrum of Compound **A-2**.

B. IR Spectra

The IR spectra were taken using a Thermo Scientific Nicolet iS10 ATR-IR spectrometer.

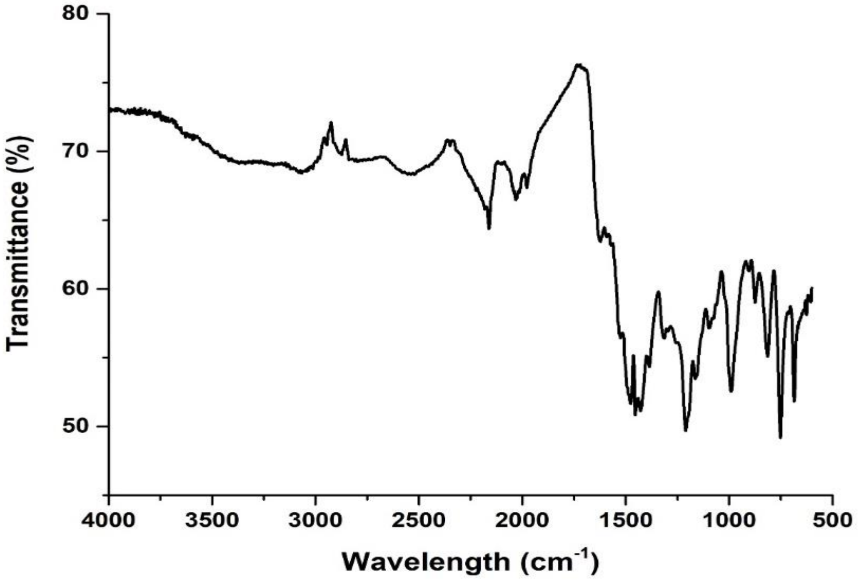


Figure 50. IR spectrum of **A-1**.

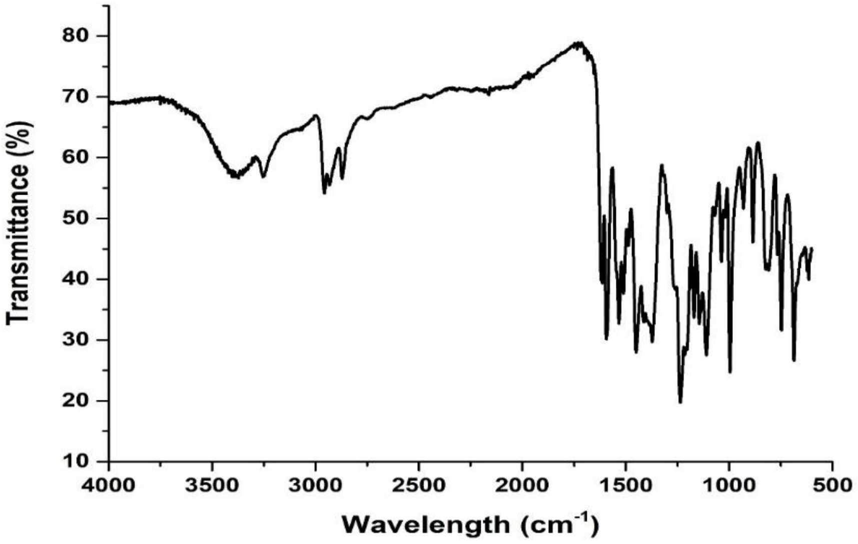


Figure 51. IR spectrum of **A-2**.

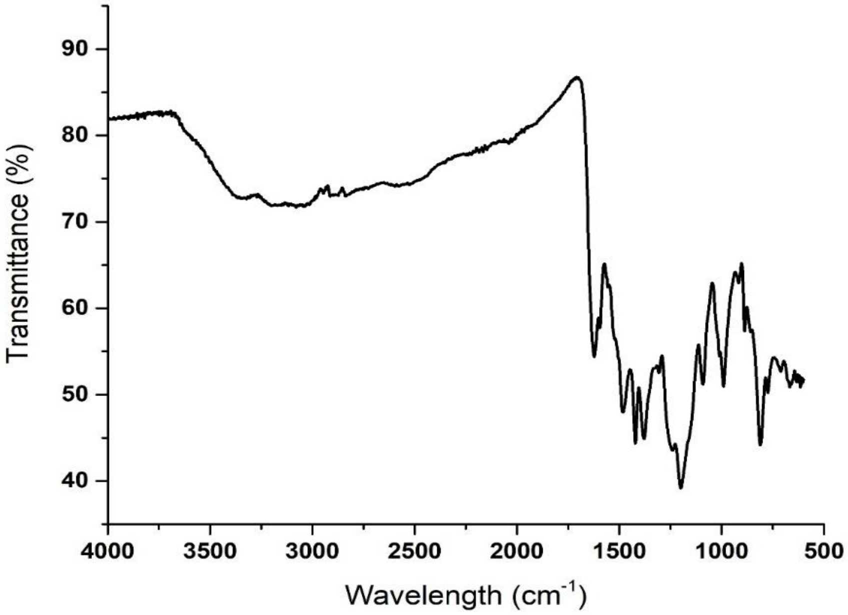


Figure 52. IR spectrum of **AP-1**.

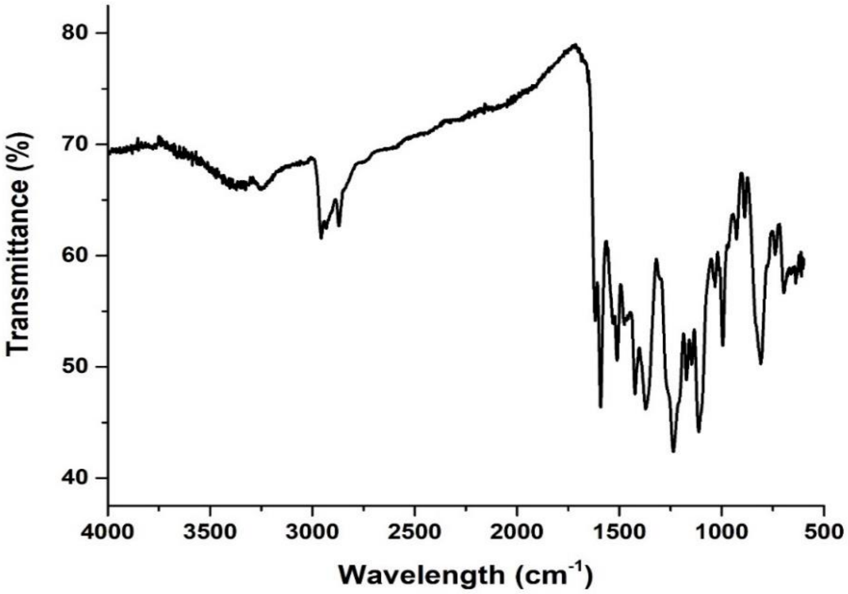


Figure 53. IR spectrum of **AP-2**.

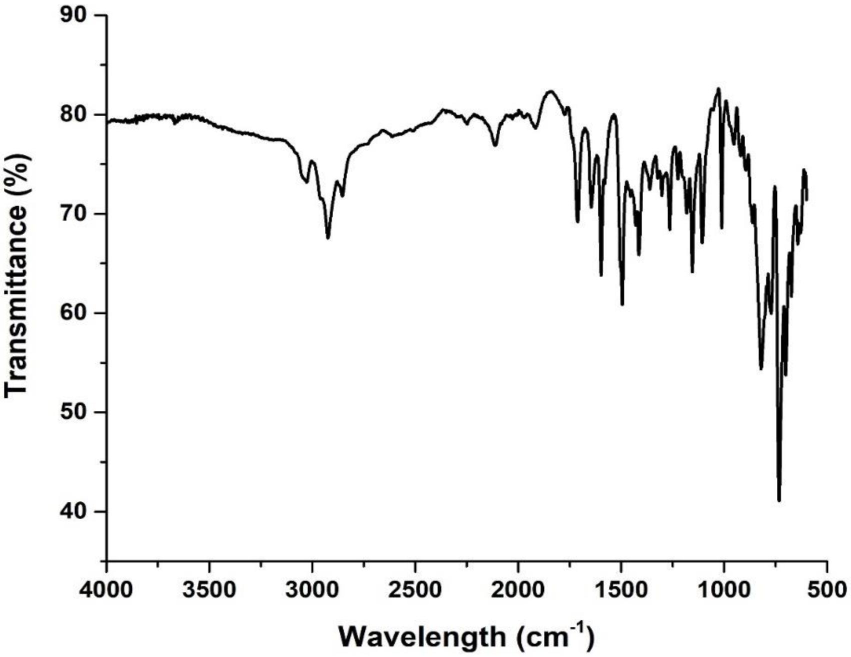
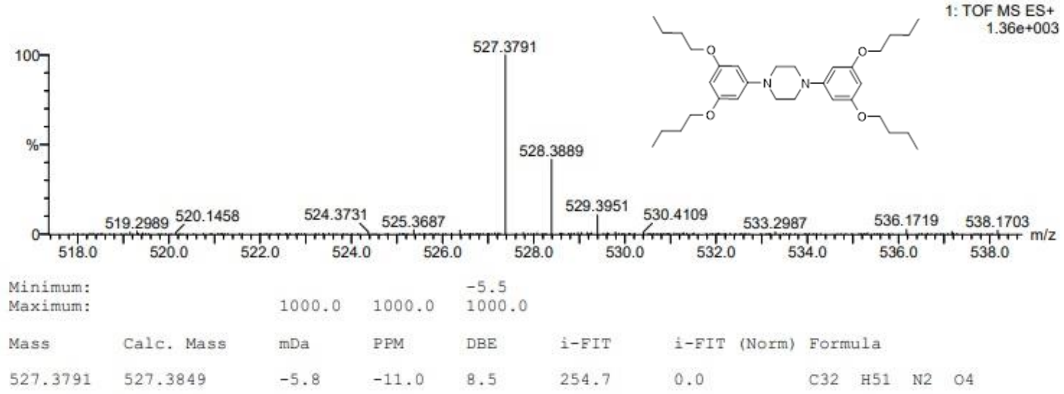


Figure 54. IR spectrum of **AP-3**.

C. High Resolution Mass Spectra (HRMS)

The Time of Flight mass analyzer was used to process High Resolution Mass Spectra (HRMS) spectra in positive mode on (ES+).

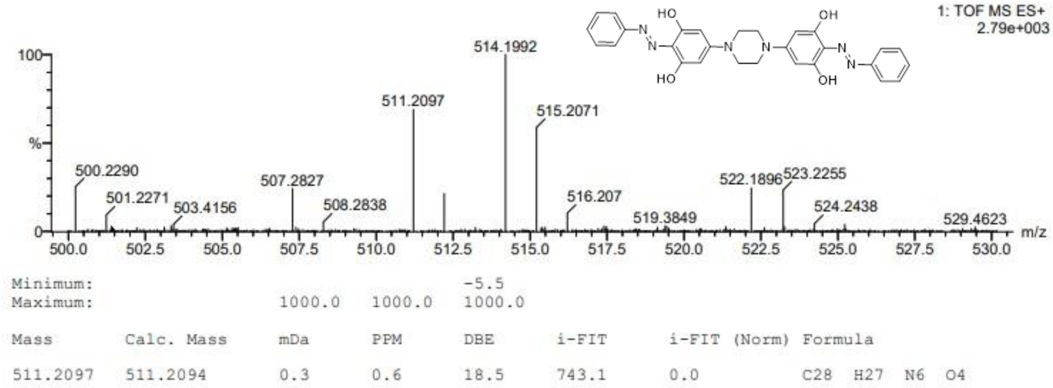


```
Minimum:                                     -5.5
Maximum:                  1000.0   1000.0   1000.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT      i-FIT (Norm) Formula

527.3791   527.3849       -5.8     -11.0    8.5      254.7      0.0          C32  H51  N2  O4
```

Figure 55. HRMS spectra of **C-2**

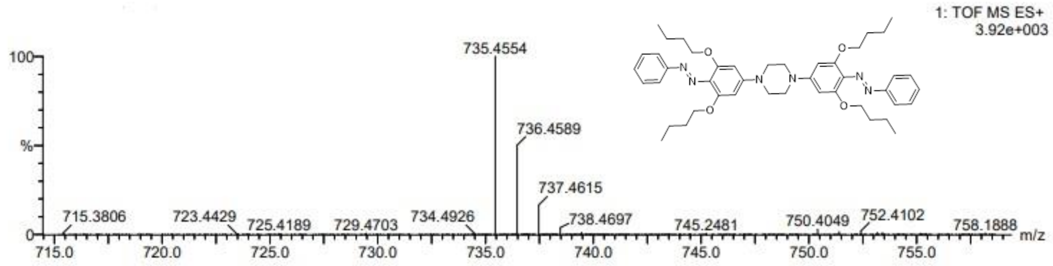


```
Minimum:                                     -5.5
Maximum:                  1000.0   1000.0   1000.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT      i-FIT (Norm) Formula

511.2097   511.2094       0.3      0.6      18.5     743.1      0.0          C28  H27  N6  O4
```

Figure 56. HRMS spectra of **A-1**



```
Minimum:                                      -5.5
Maximum:                  1000.0    1000.0    1000.0

Mass      Calc. Mass      mDa       PPM       DBE      i-FIT      i-FIT (Norm)  Formula

735.4554  735.4598        -4.4      -6.0      18.5     426.9      0.0           C44  H59  N6  O4
```

Figure 57. HRMS spectra of **A-2**

D. UV-Vis Spectra

The Shimadzu UV-2450 spectrophotometer was used to take the UV-Vis measurements.

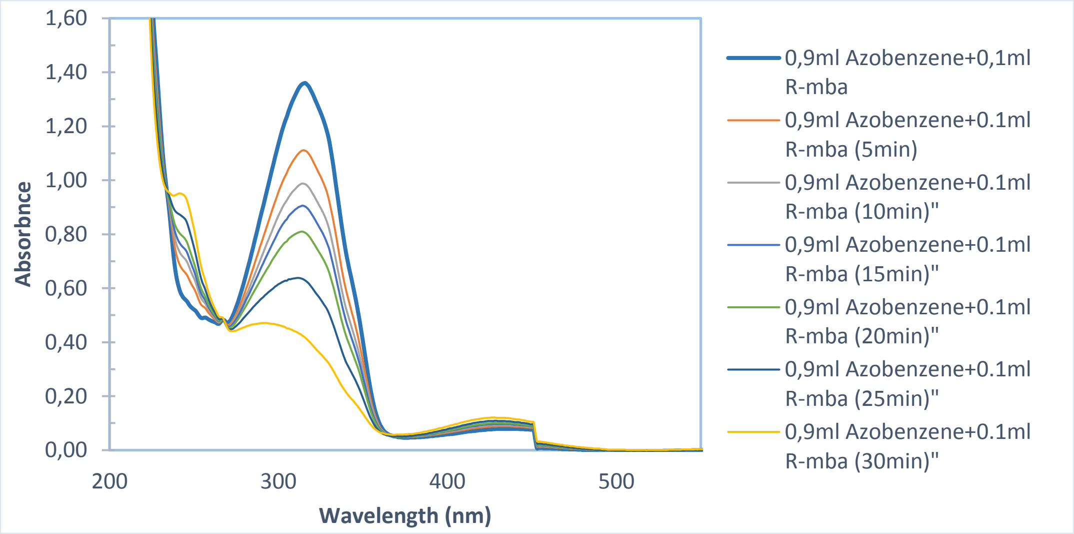


Figure 58. UV-Vis Spectra of Photoisomerization of Azobenzene and *R*-methylbenzylamine mixture under 356nm light

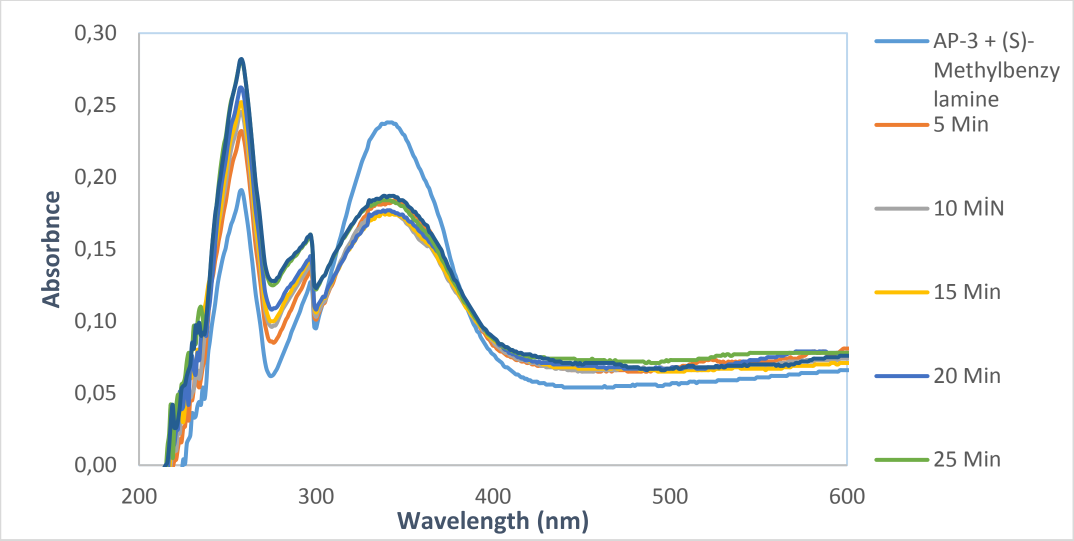


Figure 59. UV-Vis Spectra of Photoisomerization of **AP-3** and *S*-methylbenzylamine **mixture** in chloroform under 356nm light

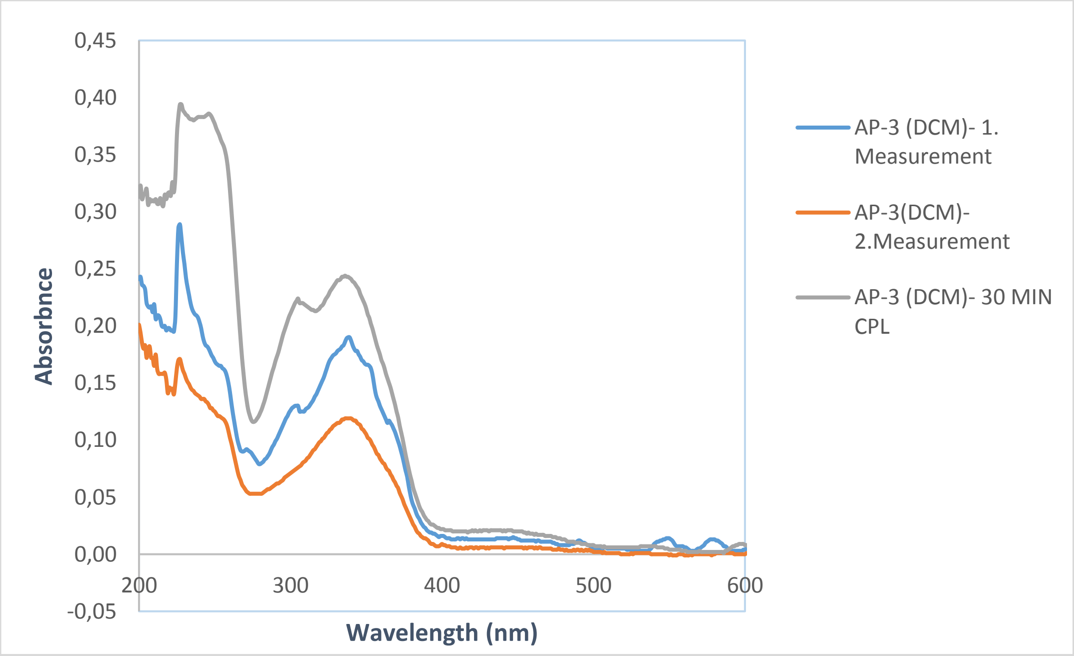


Figure 60. UV-Vis Spectra of Photoisomerization of **AP-3** in DCM under 356nm light

E. CD Spectra

It was a Jasco J-1500 CD Spectrometer that was used to take the CD measurements.

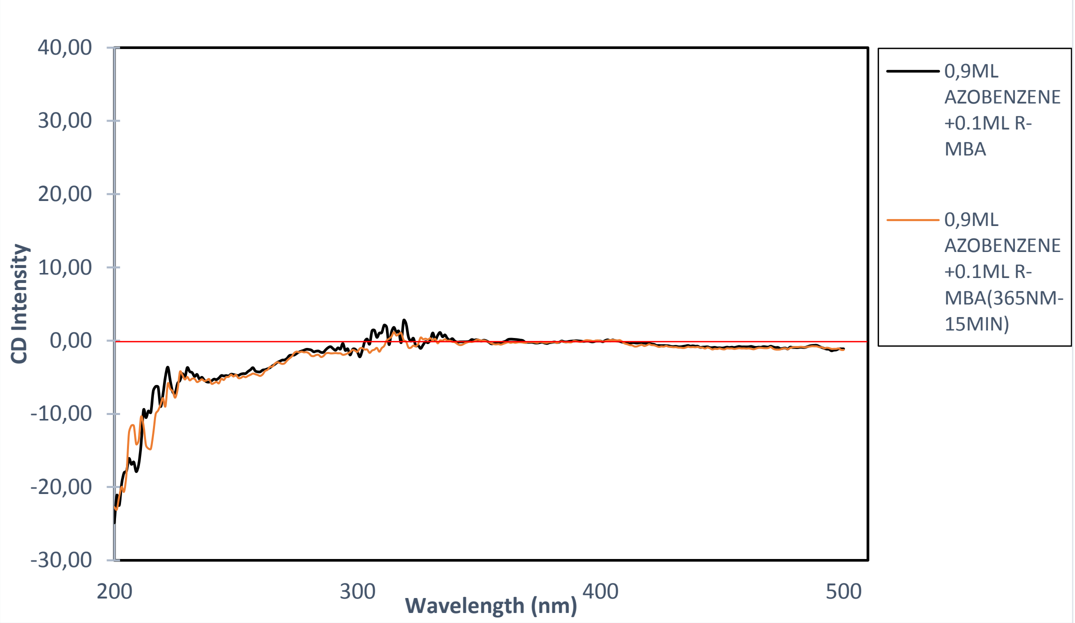


Figure 61. CD Spectra of the Azobenzene and *R*-methylbenzylamine before and after exposed light

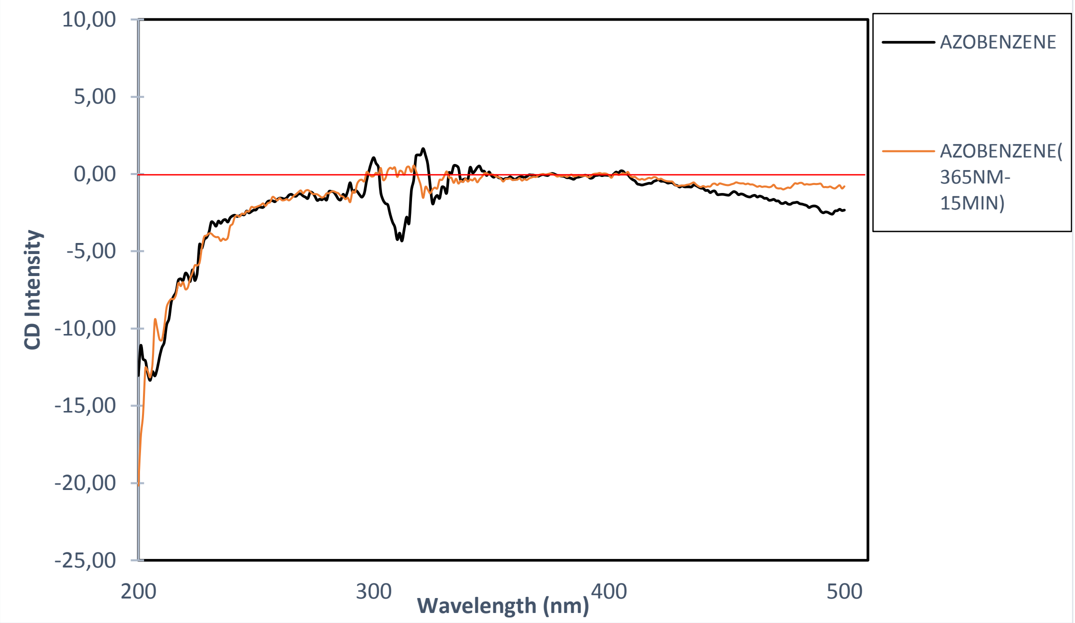


Figure 62. CD Spectra of the Azobenzene before and after exposed light