DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF SOME ACENAPHTHOIMIDAZOLE DERIVATIVES

by

Zaynab DAHI

July, 2018

İZMİR

SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF SOME ACENAPHTHOIMIDAZOLE DERIVATIVES

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by

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M.Sc THESIS EXAMINATION RESULTS FORM

We have read the thesis entitled **"SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF SOME ACENAPHTHOIMIDAZOLE DERIVATIVES"** completed by **ZAYNAB DAHI** under supervision of **PROF.DR. GÜLSİYE ÖZTÜRK ÜRÜT** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF SOME ACENAPHTHOIMIDAZOLE DERIVATIVES

ABSTRACT

Heterocyclic molecules are pervasive in many aspects of our life and have been used recently in many different domains. As the name may imply, such molecules contain at least one heteroatom (N, O, S...) in addition to the C and H atoms. Indeed, a derivative of the heterocyclic molecule that embodies N-element as the heteroatom is common in the pharmaceutical, biological and medical as well as technological uses. Specifically speaking, any five-ring heterocyclic molecule that includes two N-atoms is known as a diazole and happens in compounds like 1,2-diazol (Pirazole) and 1,3-Diazol (Imidazole).

In this study, three new imidazole derivatives with fluorophore characteristics and known as 7,8-diphenyl-7H-acenaphtho[1,2-d]imidazole, 8-(4-methoxyphenyl)- 7-phenyl-7H-acenaphtho[1,2-d]imidazole and 8-(4-cyanophenyl)-7-phenyl-7H-acenaphtho[1,2-d]imidazole were synthesized. These derivatives were purified by utilizing column chromatography and recrystallization processes. And then using FT-IR and ^{1}H-NMR techniques, the structural characteristics of these compounds were proved by some extensive studies. Thereafter, using the UV-vis and fluorescence spectrophotometers respectively, the absorption and emission spectra of these compounds and consequently their photophysical behaviours were resolved. That is, absorption and emission maxima, Stokes' shifts, molar extinction coefficients and photostabilities of the concerned compounds embedded in several different solvents were differently explored.

Keywords: Imidazole, acenaphthoimidazole, fluorophore

BAZI ASENAFTOİMİDAZOL TÜREVLERİNİN SENTEZLERİ VE SPEKTROSKOPİK KARAKTERİZASYONLARI

ÖZ

Heterohalkalı moleküller hayatımızın birçok alanında yaygın olarak yer almaktadır ve son zamanlarda birçok farklı alanda kullanılmıştır. Adından da anlaşılacağı gibi, bu tür moleküller C ve H atomlarına ek olarak en az bir heteroatom (N, O, S ...) içerir. N-hetero atomunu içeren heterohalkalı moleküllerin türevleri, farmasötik, biyolojik, tıbbi ve teknolojik kullanımlarda yaygındır. Spesifik olarak, iki N-atomu içeren herhangi bir beş halkalı heterohalkalı molekülü, diazol olarak bilinir; 1,2-diazol (pirazol) ve 1,3-diazol (imidazol) bileşikleri gibi.

Bu çalışmada, fluorofor özelliklerine sahip olan ve 7,8-difenil-7H-asenafto[1,2-d]imidazol, 8-(4-metoksifenil)-7-fenil-7H-asenafto[1,2-d]imidazol ve 8-(4-sianofenil)-7-fenil-7H-asenafto[1,2-d]imidazol olarak adlandırılan üç yeni imidazol türevi sentezlenmiştir. Bu türevler kolon kromatografisi ve kristallizasyon yöntemleri kullanılarak saflaştırılmıştır. Söz konusu türevlerin yapıları FT-IR ve ^{1}H-NMR teknikleri kullanılarak kanıtlanmıştır. UV-vis ve fluoresans spektrofotometreler kullanılarak, bu bileşiklerin absorpsiyon ve emisyon spektrumları ve sonuç olarak fotofiziksel davranışları incelenmiştir. Yani, farklı çözücüler içerisinde absorpsiyon ve emisyon maksimumları, Stokes' kaymaları, molar absorptivite katsayıları ve fotokararlılıkları araştırılmıştır.

Anahtar Kelimeler: İmidazol, asenaftoimidazol, fluorofor

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CHAPTER ONE
INTRODUCTION

1.1 Heterocyclic compounds

The Heterocyclic chemistry is one of the most important part in the organic chemistry (J. A. Joule and G. F. Smith, 1987). We can say that the heterocyclic compounds represent two thirds of organic compounds. The heterocyclic compound is formed by at least one heteroatom (such as nitrogen, oxygen and/or sulfur) in the cyclic system. Such compounds are either made up of 3 or 4 cyclic systems or as is popular 5 to 7 cyclic systems. The aromatic heterocyclic compounds do usually have some comparable aspects to benzene (T. L. Gilchrist, 1985). On the other hand, heterocyclic compounds respond to Huckel's rule. In addition to that, such heterocycles are also a main constituent in organic molecules like DNA and RNA.

There are wide variety uses of Heterocycles as is represented in many medicines, vitamins, chemical-free goods, biomolecules, and biologically active compounds (J. A. Joule and G. F. Smith, 1987). Besides that, the heterocycles can have many different uses such as dyestuff materials, sensors, brightening agents, plastics, data storage and analytical reagents.

1.2 Imidazole

The main subject of our study is imidazole and its derivatives (Bhatnagar, Sharma & Kumar, 2011). Imidazole is an organic compound because of the existence of π-electrons and belongs to the well-known alkaloid group. They are soluble in water and polar solvents. Imidazole is presented in drugs. The general chemical formula of imidazole is $C_3H_4N_2$ (1,3-diazole) (Figure1.1).

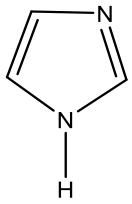

Figure 1.1 1,3-diazole

Imidazole ring system is an important biological building block among similar ring structures. Histidine and histamine can be given as an example for the important biological building blocks consisting imidazole ring (Figure 1.2 and Figure1.3).

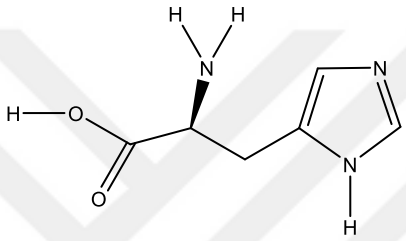

Figure 1.2 Histidine

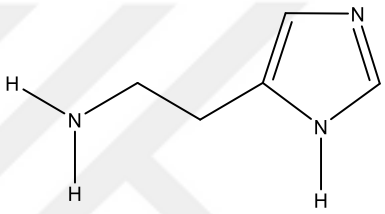

Figure 1.3 Histamine

1.2.1 Structure and properties

Imidazole can form crystalline salts with acids due to its monoacidic base (Anshul Chawla et al, 2012). Two equivalent tautomeric forms are presented for imidazole; the hydrogen atom can be located as 1H-imidazole and 3H-imidazole (Figure 1.4). Also imidazole has amphoteric abilities because it can act as both an acid and a base. Imidazole is colourless and its melting point is around 90°C and the boiling point is around 256°C. This compounds' boiling point is higher than that of heterocyclic compounds with five members because of the H-bonding existing between molecules (Figure 1.5) (Bhatnagar A.et.al 2011).

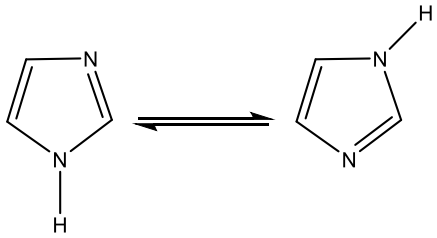

Figure 1.4 Tautomeric forms

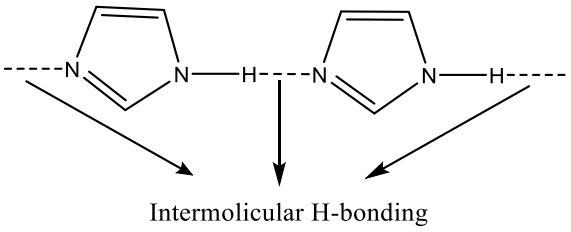

Figure 1.5 H-bonding

1.2.2 Applications of imidazole

1.2.2.1 Pharmacological properties

Imidazole is a member of almost all chemical-free molecules. (Bhatnagar A., Sharma P. K., Kumar. 2011). In past few years imidazole and its derivatives were synthesized with different methods. Because of its pharmacological properties, it has gained attention of many medicinal chemists and they explored their pharmacological potentials. The amino acid histidine which is present in enzymes and proteins is a member of imidazole compound. It exists in several parts of human body and performs many biological activities. There are anticancer, antifungal and anti-inflammatory effects of these compounds.

1.2.3 General methods of preparation

Various imidazole derivatives and substituted imidazoles are synthesized by changing the reactant's functional group. There are many different ways for imidazole synthesis (Arunkumar S, 2015). Some of them are:

- Debus
- Radiszewski
- Wallach,
- Marcwald synthesis
- dehydrogenation of imidazoline
- cyclization of α-acylamininoketons
- from aminonitrile, α-halo ketone, and aldehyde
- from formaldehyde and tartaric acid dinitrate
- microwave reactions

1.2.3.1 Debus synthesis

In 1858 Heinrich Debus synthesized imidazole, but in 1840`s derivatives of imidazole were synthesized as well (Anshul Ch. et al, 2012). Debus used gyloxal and formaldehyde to produce imidazole in ammonia **(**H. Debus, 1858). Debus method provides synthesis C-substituted imidazoles (Figure1.6).

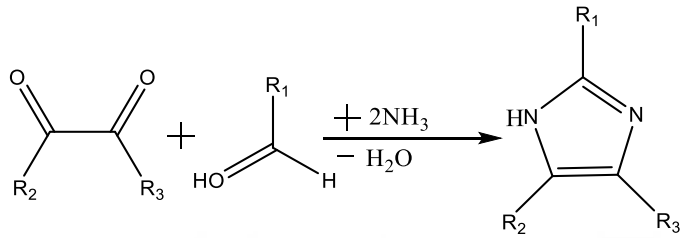

Figure 1.6 Debus synthesis

1.2.3.2 Radiszewski Synthesis

Radiszewski offered 2, 4, 5-triphenylimidazole synthesis applying dicarbonyl compound, benzil and α- keto aldehyde, benzaldehyde or α-diketones with ammonia (Hoffman K., 1953), (Lunt E., Newton C.G., Smith C., Stevens G.P., Stevens M.F., Straw C.G., Walsh R.J., Warren P.J., Fizames C., Lavelle F., J. Med. Chem., 1987; Bredereck H., Gompper R. and Hayer D., 1959) (Figure 1.7).

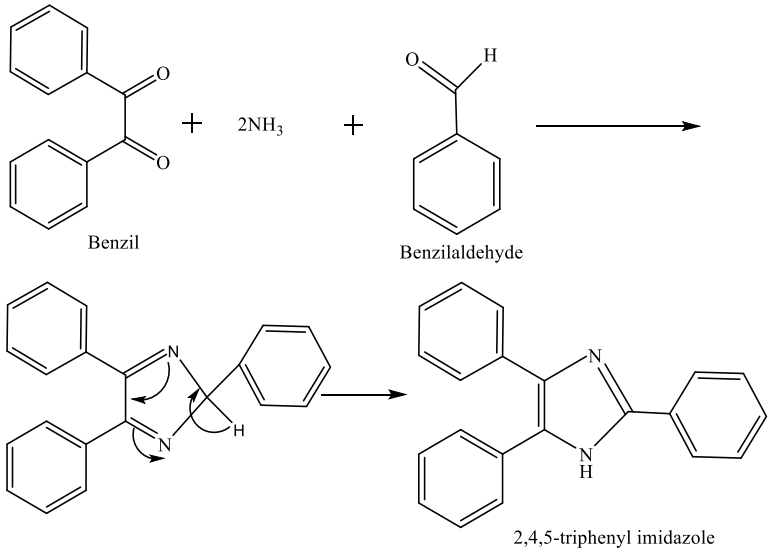

Figure 1.7 Radiszewski Synthesis

1.2.3.3 Dehydrogenation of Imidazoline

Imidazolines were converted to imidazoles with existence of sulphur by using barium managnate (C.Robert, Elderfield**,** 1957). Imidazolines were synthesized by the reaction of 1, 2 ethanediamine with alkyl nitriles. Then 2-substituted imidazoles were obtained by the reaction with $BaMnO_4$ (Bhatnagar A, et al. 2011) (Figure 1.8).

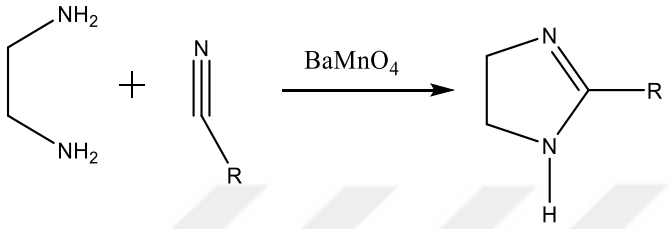

Figure 1.8 Dehydrogenation of Imidazoline

1.2.3.4 Wallach Synthesis

Wallec reacted N, N- dimethyloxamide with phosphorus and obtained a chlorine bearing N- methyl imidazole derivative (Wallach & Schuelze, *Ber*., 1881; Ber., 1880; Sarasin & Weymann, Helv, 1924). Moreover, N, N-diethyloxamide is converted to 1- ethyl –2- methyl imidazole under the same condition which is also chlorine derivative (Figure 1.9).

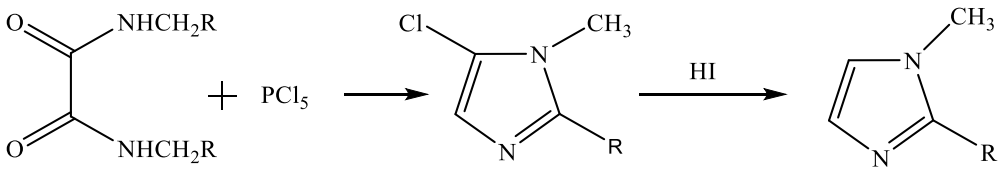

Figure 1.9 Wallach Synthesis

1.2.3.5 From α- Halo Ketone

Synthesis of imidzole derivate from α- Halo Ketone was performed with imidine (C.Robert, Elderfield, 1957). As a result 2, 4- or 2, 5- biphenyl imidazole was obtained. Also an interaction between acyloin with amidine or alpha halo ketones yielded imidazoles (Figure 1.10).

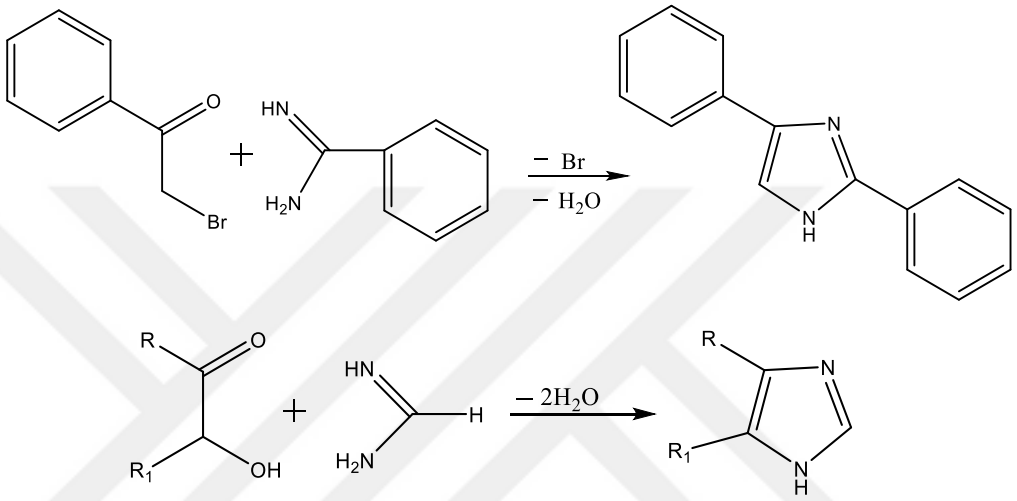

Figure 1.10 From α- Halo Ketone

1.2.3.6 Markwald Synthesis

By treatment of α-amino ketones or aldehydes with potassium thiocyanate, 2-mercaptoimidazoles were obtained (C.Robert, Elderfield, 1957). This synthesis method was utilized for obtaining of 2-thiol substituted imidazoles. By removing sulfur via oxidative method, the desired imidazoles can be synthesized (Figure 1.11).

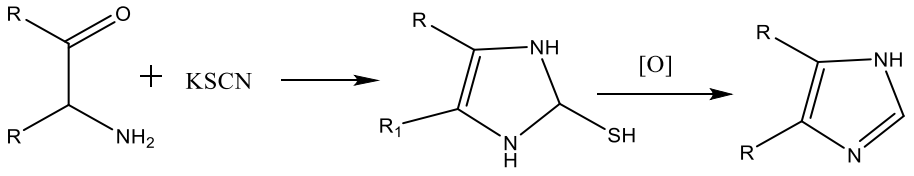

Figure 1.11 Markwald Synthesis

1.2.3.7 Cyclization of α-Acylaminoketones

Cyclization of α-acylaminoketones which behave as 1, 4-diketo compounds in presence of ammonium acetate yielded imidazole structures (I.L. Finar, 2006) (Figure 1.12).

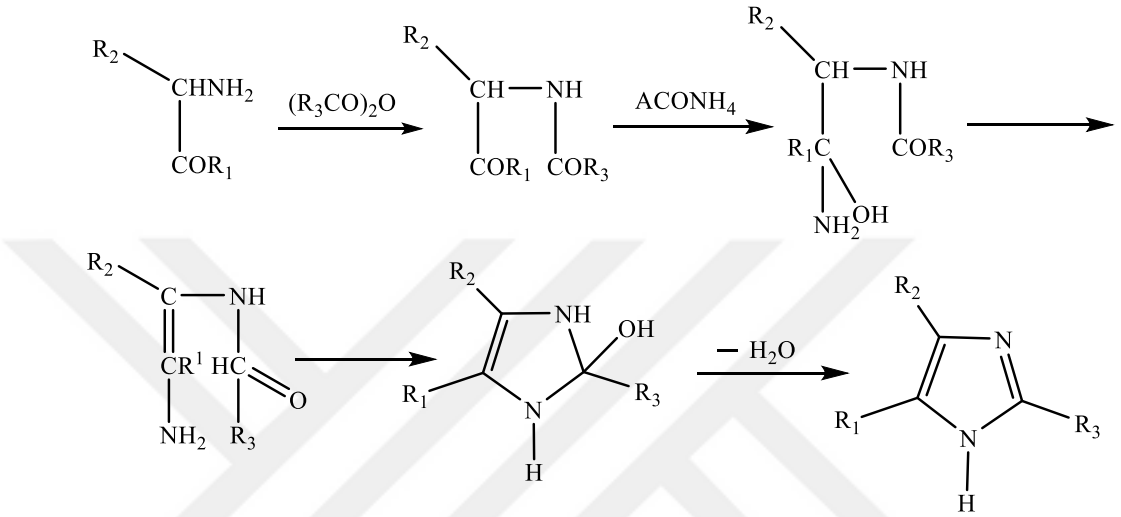

Figure 1.12 Cyclization of α-Acylaminoketones

1.2.3.8 From Aminonitrile and Aldehyde

By the introduction of aldehyde and aminonitrile under suitable conditions substituted imidazoles were obtained as shown below (A. Bhatnagar ,P.K. Sharma ,N. Kumar, 2011) (Figure 1.13).

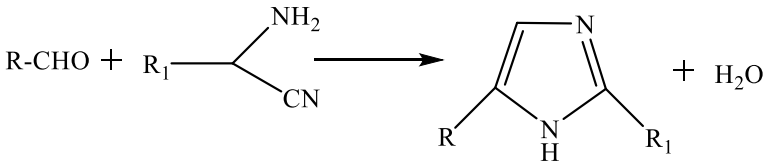

Figure 1.13 From Aminonitrile and Aldehyde

1.2.3.9 From formaldehyde and tartaric acid dinitrate

The mixture of tartaric acid dinitrate and formaldehyde were interacted in the presence of ammonia in order to obtain 2-alkyl substituted 4,5- dicarboxylic acid

imidazole derivative. After that in the presence of copper, the synthesized dicarboxylic acid was heated with quinoline **(**I.L.Finar**) (**Figure 1.14**)**

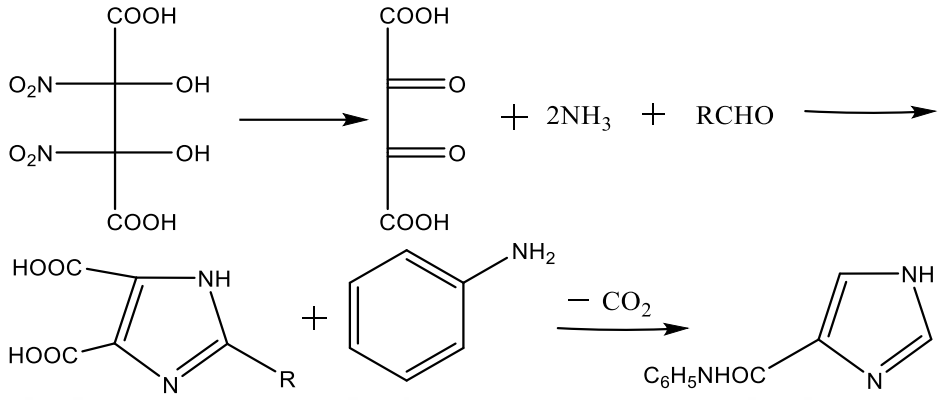

Figure 1.14 From formaldehyde and tartaric acid dinitrate

1.2.3.10 By the formation of one bond

Imidazole can be isolated via a one-bond creation process. To obtain this (1,5) or (3,4) bond imidate and an α-aminoaldehyde or α-aminoacetal were reacted. The imidine obtained was cyclized and imidazole was formed (Anshul Chawla, et al. 2012) (Figure 1.15).

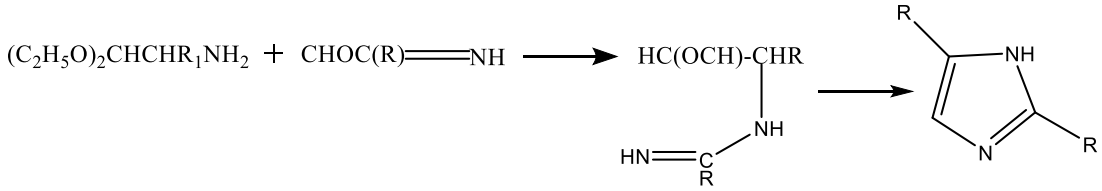

Figure 1.15 By the formation of one bond

1.2.4 Synthesis of imidazole derivatives by microwave reactions

Due to their rapid transformation of heat energy to molecules, microwave ovens are considered so productive and energy saving (A. G. Horeis et al, 2001). Microwaves are an example of electromagnetic radiations. Microwaves at first time were used for chemical purposes in 1986. By using Microwave method, the faster

temperature rising and cleaner chemicals were obtained from faster reactions. The main two fundamental mechanisms for microwave method were dipole rotation and ionic conduction to transferring energy to the reaction chemicals (Lidstrom Pelle et al, 2001). Many studies for synthesis of imidazole derivatives had been investigated by microwave technic. One of them is the study of Nalage. Nalage *et al* (2010) synthesized 2, 4, 6-triaryl-1H-imidazole by microwave in excellent yield as shown below (Figure 1.16).

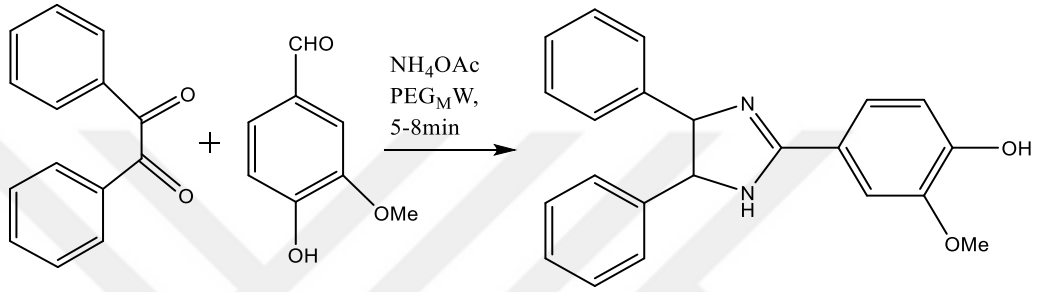

Figure 1.16 Synthesis of imidazole derivatives by microwave reactions

1.3 Fluorescence

1.3.1 Fluorescence phenomenon

Fluorescence technology -as compared to radioactive tracer technology- is a cheap and easy way to detect some hidden object or describe some unknown (Joseph R. Lakowicz,2006). It was not only restricted to chemical sciences, but has been also used in many different branches of science including biology, biochemistry, biophysics and even medicine.

With some exceptions, a substance (whether a solid, a liquid or a gas) which is subject to some radiation of light emits the light again with different wavelength (or frequency) within some interval of time through a process known as luminescence. Some substances, however, emits the light rapidly and turn off while some others take a longer period of time during emission. The former kind of substances are known as fluorophores in a process dubbed fluorescence while the latter are known

as phosphors in a process dubbed phosphorescence.

Fluorescence is a consequence of transitions from singlet excited states where the electron in the excited state has opposite spin direction compared to that in the ground state (Joseph R. Lakowicz,2006).

Phosphorescence, on the other hand, is a result of transitions from triplet excited states where the electron in the excited state has the same spin direction of that in the ground state.

1.3.2 Jablonski Diagram

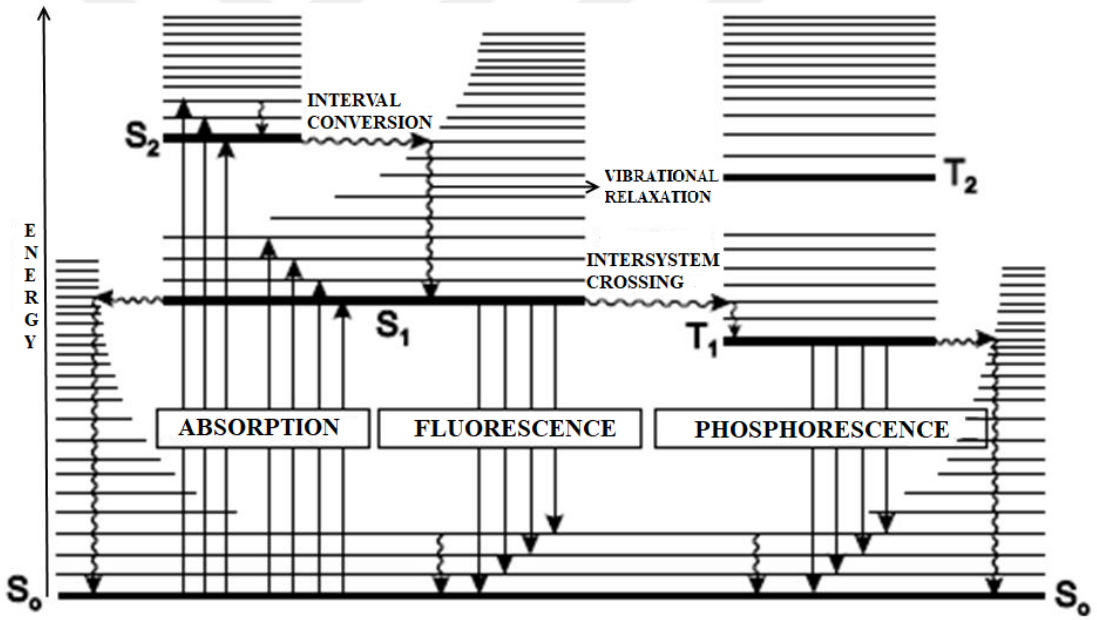

Figure 1.17 Jablonski Diagram

Known as a great tool to describe the processes between absorption and emission, Jablonski diagram is a super-simplified image of the complicated operations that happen during exposing a compound to some external excitation (like light) (Joseph R. Lakowicz, 2006). One simple example of a Jablonski diagram, excluding all other sophisticated internal processes, is shown in (Figure1.17) The time a compound absorbs some external light, the electrons in the ground electronic state jump to the

higher excited electronic state of S_1 or S_2, depending on the energy of the incident photons, in a process dubbed "absorption". In about 10^{-12} sec after absorption, another process known as "internal conversion" do take place through which the electrons drop all the way down to the lowest vibrational level of the excited electronic state S_1. At this stage, and depending on the nature of the compound under study, the system can decide to go in two ways. In case the compound in hand is a fluorphore, a direct spin-conversion to the singlet ground state is allowed in a process known as "emission" which typically happens in 10^{-8} sec after absorption. If, however, the compound is a phosphorescent, a direct spin-conversion to the ground state is not allowed and instead a process named "intersystem crossing" happens which as the name may imply transfers the system from the lowest vibrational energy level (marked by 0) of the first singlet excited state S_1 to the first triplet excited state T1 from which it goes back again to the thermally equilibrium state S_0 after some spin flipping. This, indeed, is the reason behind the low emission energy of a phosphorescent as compared to that of a fluorophore.

1.3.3 Fluorescence Emission Properties

Fluorescence has several characteristics with some exceptions (Joseph R. Lakowicz,2006). Generally speaking, most fluorophores share the following two properties with some very rare exceptions that can be classified under a category for special fluorophores.

1.3.3.1 The Stokes' Shift

One of the properties that the fluorophers are best known of is what is called the Stokes' shift discovered by the physicist Stoke using a very basic mechanism of light absorption and emission (Valeur, 2002). The emission energy is less than the absorption energy due to some energy losses. One of the main reasons of energy loss in a fluorophore is the very quick internal conversion process from the higher vibrational levels of the excited states to the thermally equilibrated level of the S_1 excited state as such a process happens before the main emission process starts.

Another significant reason for such an energy loss is that during emission a fluorophore usually descend to the highest vibrational level of the singlet ground state S_0 before landing on the lowest thermally equilibrated level S_0. So actually, the Stokes' shift is the reason why fluorescence occurs at lower energies or larger wavelengths.

1.3.3.2 Independence of emission epectra on the excitation wavelength

Fluorescence's second property identifies the independency of the fluorescence emission from the excitation wavelength) (Joseph R. Lakowicz,2006). Experiments showed that no matter the energy (or equivalently the wave length) of an incident excitation was, the emission spectra of almost all the fluorophores are nearly roughly identical. This is because of the high tendency of a fluorophore to transit rapidly from high vibrational energy levels to the lowest vibrational energy level of the first excited electronic state S_1 losing in the way the excess energy before the predominant main emission S_0 takes place. Thus, it is mainly because of this so-called rapid relaxation, the emission spectra of fluorophores are independent of the excitation wavelength.

1.3.4 Fluorescence Lifetimes and Quantum Yields

The fluorophore is also characterized by its quantum yields and life time (Joseph R. Lakowicz, 2006). To illustrate more, the quantum yield of a fluorophore is the number of emitted photons relative to the number of absorbed ones and is calculated via (Q=Kr/(Kr+Knr)). When this quantity is very near to unity or in other words when the non-radiative emission rate constant (Knr) is very small compared to the radiative emission rate constant (Kr), the fluorophore has the brightest emission spectrum. As has been seen in Stokes' shift, however, the quantum yield is never unity because of the energy losses from the non-radiative emissions that occur during the internal conversion process among the vibrational energy levels of an electron state. The life time of a fluorophore, on the other hand, is considered to be the value of the time a fluorophore can spend in the excited state before returning back to the

ground state and is roughly given by (T=1/(Kr+Knr)), though the average time is what matters at the end because of the randomness of the emission processes of a fluorophore. As pointed before, the dominant emission process of a fluorophore through which a radiation takes place occurs at about 10^{-18} s or 10 ns after absorption.

1.3.4.1 Fluorescence Quenching

The process of fluorescence quenching i.e decreasing its intensity can occur by several ways (B. Mark, 1999 – 2010). There are many different factors that can lead to fluorescence quenching and the following are the main two of them. Either through the collisional quenching process which occurs when the excited fluorophore merge, collides or gets in contact with other molecules (like oxygen, halogen..) resulting in its deactivation and returning it back to the ground state with the quencher molecule via different mechanisms depending on the type of the quencher of interest, or through the so-called static quenching process in which the fluorophores form non-fluorescent complexes with the quencher at the ground state, the reason it is dubbed a static quenching process (Lakowicz, 1999).

1.3.4.2 Timescale of Molecular Processes in Solution

This phenomenon in return has provided us with the different criteria of the absorption and emission process (Joseph R. Lakowicz, 2006). During the absorption process which is nearly about 10^{-15} s, a fluorophore can absorb the photon rapidly so that molecules stay fixed on the average ground state. However, fluorescence emission takes a longer period of time consequently expanding the life-time of a fluorophore in the excited state and giving it a chance to interact with another molecule.

1.4 Literature review

Ozturk G. et al. (2012) synthesized four new y-shaped fluorophores 1a, 1b, 1c and 1d which bear an imidazole core for the first time via intermediate 1,6-Bis(2,4,6-trimethoxyphenyl)hexa-1,5-diene-3,4-dion with different aldehydes.

The synthesized derivatives' compositions were proved by ^{1}H NMR, ^{13}C NMR and FT-IR. The optical properties such as absorption and emission maxima, Stokes' shift and quantum yield values were investigated in solvents of toluene, tetrahydrofuran and acetonitrile. They reflected a condense emission maxima in the range of 440–630 nm. The imidazole derivatives exhibited excellent photostabilities.

In a study, Ümit D. et al. (2015) synthesized Y-shaped fluorophore of 2-(1,4,7,10,13-benzopentaoxacyclopentadecyl)-4,5-[2,2'bis(phenyl)vinyl]-1H-imidazole. "1,6-diphenylhexa-1,5-diene-3,4-dione" and "4-formylbenzo-15-crown-5" had been put to react by the known "Vilsmeier-Haake reaction". After that obtained compound was purified by precipitation processes and column chromatography. FT-IR and ^{1}H-NMR spectroscopic techniques were used to define the structure of the new derivative. Also photophysical response were determined via UV-vis spectrophotometer and emission measurements with fluorescence spectrophotometer.

Qasim et al. (2011) studied the synthesis of 2- phenylimidazophenanthroline derivatives via acid catalysed reaction and perfect yield was obtained. This reaction was carried out with a dicarbonyl compound and *p*-substituted benzaldehyde. Microwave method used to synthesis in a neutral ionic liquid. The advantages of this way are being ecology friendly, obtaining higher yields and being easily worked (Figure 1.18).

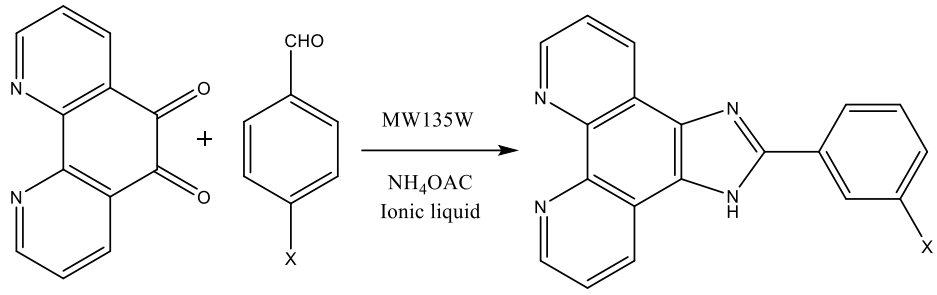

Figure 1.18 Synthesis of 2- phenylimidazo Phenanthroline derivatives

Safari et al. (2010) researched rapid synthesis of 2,4,5-trisubstituted imidazoles. They used microwave method with $(NH_4)_6.Mo.7O_2.4H_2O$ catalyst and three-components without solvent (Figure 1.19). These components are benzil, aryl aldehydes and ammonium acetate and the synthesis resulted in good yield.

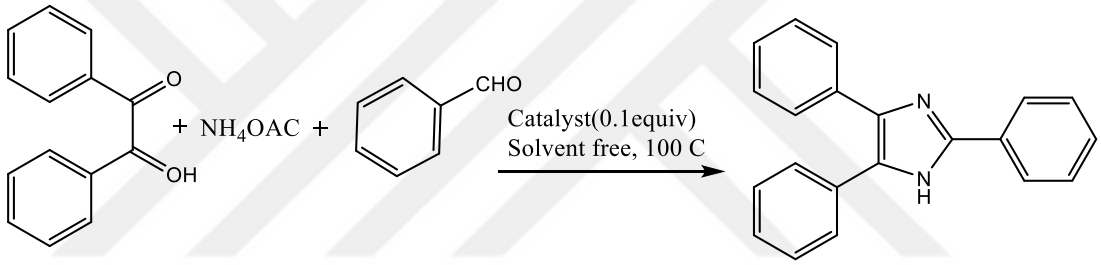

Figure 1.19 2,4,5-trisubstituted imidazoles

Jun Ren and others (2008) studied synthesis of Y-shaped NLO molecules containing thiazole and imidazole chromophores. As the result they synthized Two new second-order NLO molecules which contain multiple donor or acceptor substituents and thermally stable imidazole or thiazole ring, as ‘‘Y shaped’’ molecules. They used a five-membered heterocyclic ring (thiazole and imidazole). As a result, good nonlinearity transparency-thermal stability trade-off was achieved. The obtained compounds showed good properties in nonlinearity-transparency.

Danko M. and others (2012) investigated the spectral features imidazole fluorophores with two electron-donating N,N-dimethylaminophenyl groups at C4 and C5 and one electron-withdrawing cyano group at C2. These two groups are segregated by a so-called π-connector consisting of 6 coupled tracks dubbed

respectively 1,4-phenylene, (E)-phenylethenyl, (E)-phenylbuta-1,3-dienyl, biphenyl, (E)-phenylethenylphenyl and phenylethynylphenyl. Many different mediums, such as liquid solvents like toluene, dichloromethane, acetonitrile, methanol and solid polymer matrices like polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinylchloride) (PVC), were used in getting separately the absorption and emission spectra of the above mentioned coupled-track π-connector fluorophores in the imidazole of interest. The absorption spectra, on one side, showed that the absorption bands of all the fluorophores occurred in the region between 283 nm and 330 nm with some other less intense bands corresponding to the convey of charge in the range of 380 nm – 430 nm depending on the nature of the medium used. The emission spectra, on the other side, revealed an intense emission for nonpolar toluene and polystyrene in the visible region with a Stokes' shift of about 4300 cm^{-1} – 5800 cm^{-1} and for polar methanol and acetonitrile with a large Stokes' shift of about 6500 cm^{-1} – 7800 cm^{-1} that could be due to the large asymmetry in the spatial layout of the chromophore between the absorbing and emitting states. The rather most intense emission, with a quantum yield of about 0.12-0.69, was seen only for derivative 1 (1,4-phenylene) regardless of the used medium excluding methanol. It can be observed that the fluorophores immersed in solid polymer matrices have a brighter emission spectra compared to that of those immersed in liquid solvents which means that solid matrices have the ability to decrease the chance of developing non-emissive excited states. The emission lifetimes, however, were the same for all the six fluorophore derivatives (about 1 ns – 4 ns) whether in solvents or in solid matrices.

Zhang M. et al (2007) manufactured a two-photon excited fluorescent (TPEF) FD3 material embracing an imidazole loop. It showed a huge two-photon absorption cross-section that exceeded 9000 GM. It also showed that it has the capacity to work as a fluorescent sensor for both Cysteine (Cys) and Homocysteine (Hcy) from the intense blue-shift of TPEF upon the addition of Cys/Hcy.

CHAPTER TWO
EXPERIMENTAL SECTION

2.1 Materials

Almost of the materials of interest were purchased from different cities of Germany; for instance, aniline as well as 4-methoxybenzaldehyde and 4-cyanobenzaldehyde were purchased from Merck (Hohenbrunn), ethanol absolute and benzaldehyde from Sigma-Aldrich (Steinheim). The solvents for spectroscopic measurements, were supplied by Merck (Darmstadt), Panreac and Carlo Erba Reagents Group. Besides that, Silica Gel (0.063-0.200mm) and Aluminium Oxide (particle size 0.1-0.2 mm) were purchased from Merck (Darmstadt) and a thin layer chromatography (TLC) was executed using the former gel 60F254. The solvents used for purification of the synthesized derivatives (n-hexane, ethyl acetate and dichloromethane) were of technical purity and were distilled before usage.

2.2 Synthesis

2.2.1 Synthesis of Derivative A

0.25 g of Acenaphthenequinone and 10 ml of ethanol were mixed together in a two-necked round bottom flask and were stirred enough to allow acenaphthenequinone to dissolve. The mixture was kept stirring at an adequate medium temperature (about 20ºC) with a nitrogen-suffused medium inasmuch as 30 minutes. Then 0.7 ml of benzaldehyde was added to the mixture bit by bit in drops under one hour. After that ammonium acetate (0.15 g) was added to the mixture followed by a continuous stirring until ammonium acetate was dissolved. In addition, as a last reagent, aniline was added to the reaction combination followed again by a stable stirring at an adequate medium temperature under nitrogen-suffused medium for 30 minutes. With this nitrogen-suffused medium, the temperature of the mixture was increased slowly along with refluxing for one week. When the dissipation of

acenaphthenequinone, tracked by the TLC, was detected, the mixture's temperature was decreased again to near the normal medium temperature. It was then extracted in dichloromethane and washed with pure water for several times. Thereafter, the unrefined extra produced outcome was separated via column chromatography adopting ethyl acetate/ n-hexane (1/4) as eluent (Figure 2.1).

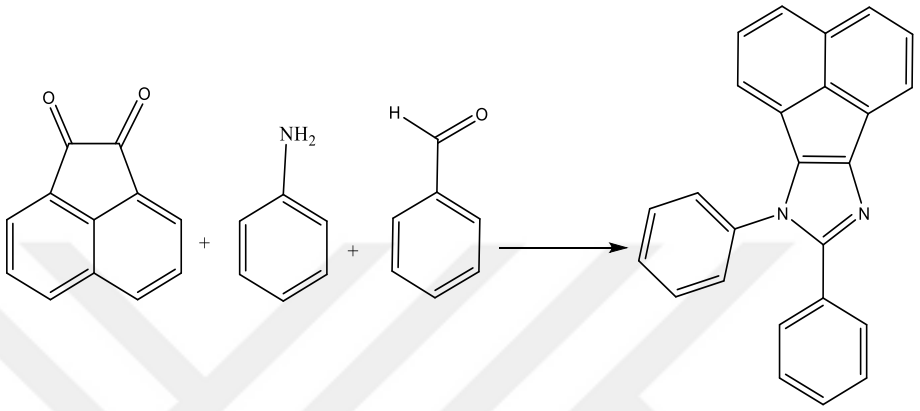

Figure 2.1 Synthesis of Derivative A

2.2.2 Synthesis of Derivatives B

0.25 g of acenaphthenequinone and 10 ml of ethanol were mixed together in a two-necked round bottom flask and were stirred enough to allow acenaphthenequinone to dissolve The mixture was kept stirring at an adequate medium temperature (about 20ºC) with a nitrogen-suffused medium inasmuch as 30 minutes. Then 0.27 ml of 4-methoxybenzaldehyde was added to the mixture bit by bit in drops under one hour. After that ammonium acetate (0.15 g) was added to the mixture followed by a continuous shaking until ammonium acetate was dissolved. In addition, as a last reagent, aniline was added to the reaction combination followed again by a stable shaking at an adequate medium temperature under nitrogen-suffused medium for 30 minutes. With this nitrogen-suffused medium, the temperature of the mixture was increased slowly along with refluxing for one week. When the dissipation of acenaphthenequinone, tracked by the TLC, was detected the mixture's temperature was decreased again to near the normal medium temperature. It was then extracted in dichloromethane and washed with pure water for several times. Thereafter, the unrefined extra produced outcome was separated via column

chromatography adopting ethyl acetate/n-hexane as eluent (1/4) (Figure 2.2).

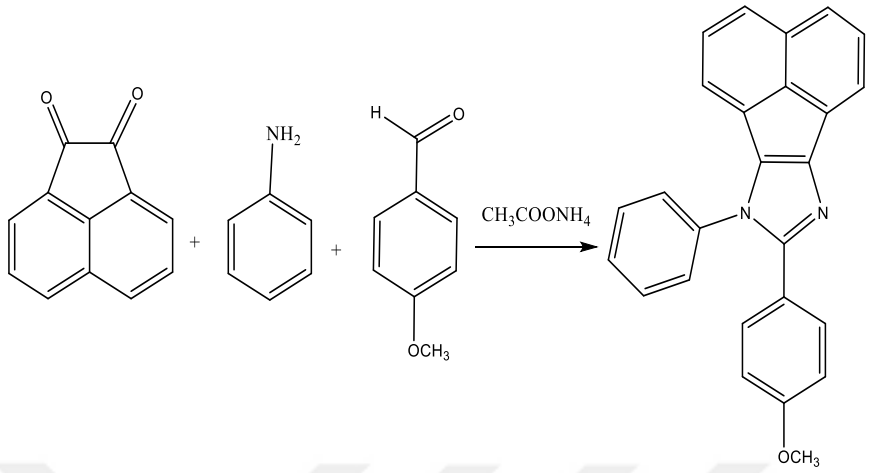

Figure 2.2 Synthesis of Derivative B

2.2.3 Synthesis of Derivatives C

0.25 g of acenaphthenequinone and 10 ml of ethanol were mixed together in a two-necked round bottom flask and were agitated much enough to allow acenaphthenequinone to dissolve. The mixture was kept stirring at an adequate medium temperature (about 20ºC) with a nitrogen-suffused medium inasmuch as 30 minutes. Then 0.22 g of 4-cyanobenzaldehyde was added to the mixture bit by bit in drops under one hour. After that ammonium acetate (0.15) was put to the mixture followed by a continuous shaking until ammonium acetate was dissolved. In addition, as a last reagent, aniline was put to the reaction combination followed again by a stable shaking at an adequate medium temperature under nitrogen-suffused medium for 30 minutes. With this nitrogen-suffused medium, the temperature of the mixture was increased slowly along with refluxing for one week. When the dissipation of acenaphthenequinone, tracked by the TLC, was detected, the mixture's temperature was decreased again to near the normal medium temperature. It was then extracted with pure water for several times. Thereafter, the unrefined extra produced outcome was separated via column chromatography adopting ethyl acetate/n-hexane (1/4) as eluent (Figure 2.3).

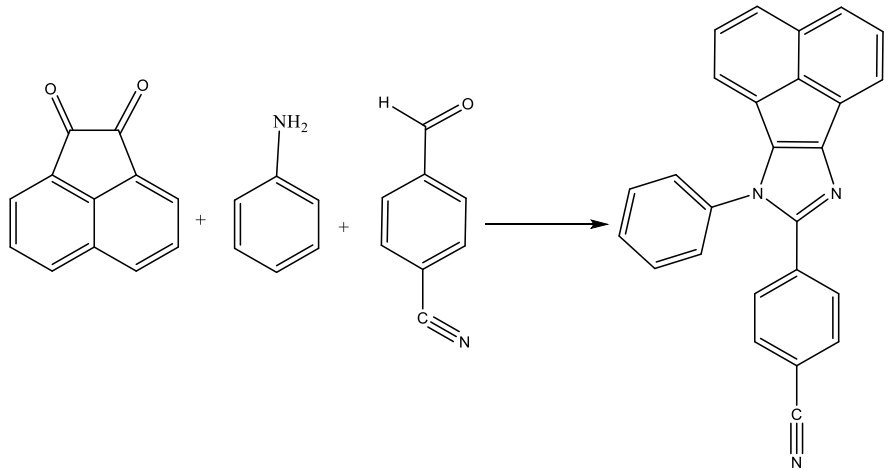

Figure 2.3 Synthesis of Derivative C

2.3 Structural and Spectral Analysis

The structures of synthesized compounds were confirmed by FT-IR and ^{1}H-NMR. ^{1}H-NMR spectra were recorded on a Varian Mercury AS-400 (400 MHz) spectrometer. Fourier transform infrared spectra were measured on a Perkin Elmer FTIR spectrometer by Universal ATR sampling Accessory. The UV-visible absorption spectra were obtained with Shimadzu UV-1800 spectrophotometer. The emission spectra were obtained on Varian-Cary Eclipse fluorescence spectrophotometer. By using Electro thermal digital melting points apparatus (Southend, UK), the melting points were determined.

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Structural Analysis of the Synthesized Derivatives

3.1.1 Structural Analysis of Derivatives A, B, C

3.1.1.1 Structural Analysis of A

Compound A, 7,8-diphenyl-7H-acenaphtho[1,2-d]imidazole (Figure 3.1). Yield: 5 % M.P. 377-380 ºC. M.W. 344.42g/mol. FT-IR(ATR): υ_{max} (cm^{-1}) 3054 (=C−H), 1694 (−C=N −), 1279 (−C−N −). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.68 (m, 4H), 7.77-7.8 (m, 3H), 7.83-7.87 (t, 1H), 8.07-8.09 (d, 2H), 8.31-8.33 (d, 2H), 8.41-8.43 (d, 2H), 8.75-8.77 (d, 2H).

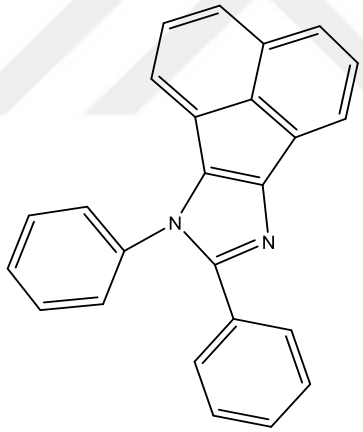

Figure 3.1 The structure of A

3.1.1.1 Structural Analysis of B

Derivative B, 8-(4-methoxyphenyl)-7-phenyl-7H-acenaphtho[1,2-d]imidazole (Figure 3.2). Yield 8 % M.P. 379-382 ºC. M.W. 359.408 g/mol. FT-IR(ATR): υ_{max} (cm^{-1}) 3048 (=C−H), 1690 (−C=N −), 1280 (−C−N −), 1229 (−C−O), 2929 (−C−H). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.7(s, 3H) 7.61-7.67(m, 3H), 7.77-7.86(m, 5H), 8.05-8.08 (m, 3H), 8.30-8.32 (d,1H), 8.41-42 (d, 1H), 8.75-8.77 (d, 1H), 8.85-88 (dd, 1H).

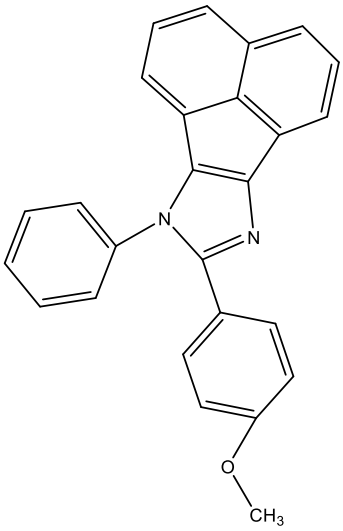

Figure 3.2 The structure of B

3.1.1.1 Structural Analysis of C

The compound C, 8-(4-cyanophenyl)-7-phenyl-7H-acenaphtho[1,2-d]imidazole (Figure 3.3). Yield about 2 %, M.P. 332-335 ºC. M.W. 379 g/mol. FT-IR(ATR): υ_{max} (cm^{-1}) 3049 (=C−H), 2227 (−C ≡N), 1675 (−C=N −), 1275 (−C−N −). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.67 (m, 4H), 7.76-7.85 (m,5H), 8.04-8.07 (dd, 2H), 8.28-8.31 (d, 1H), 8.39-8.41 (d, 1H), 8.73-8.75 (d, 1H), 8.84-8.86 (d, 1H).

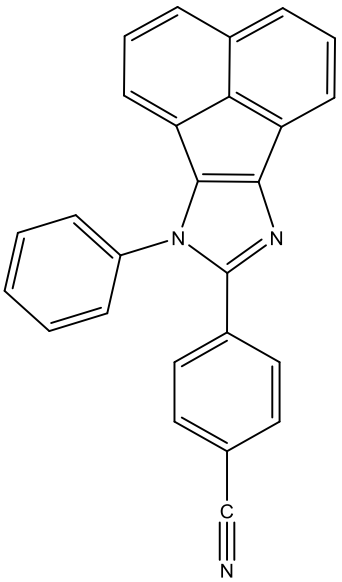

Figure 3.3 The structure of C

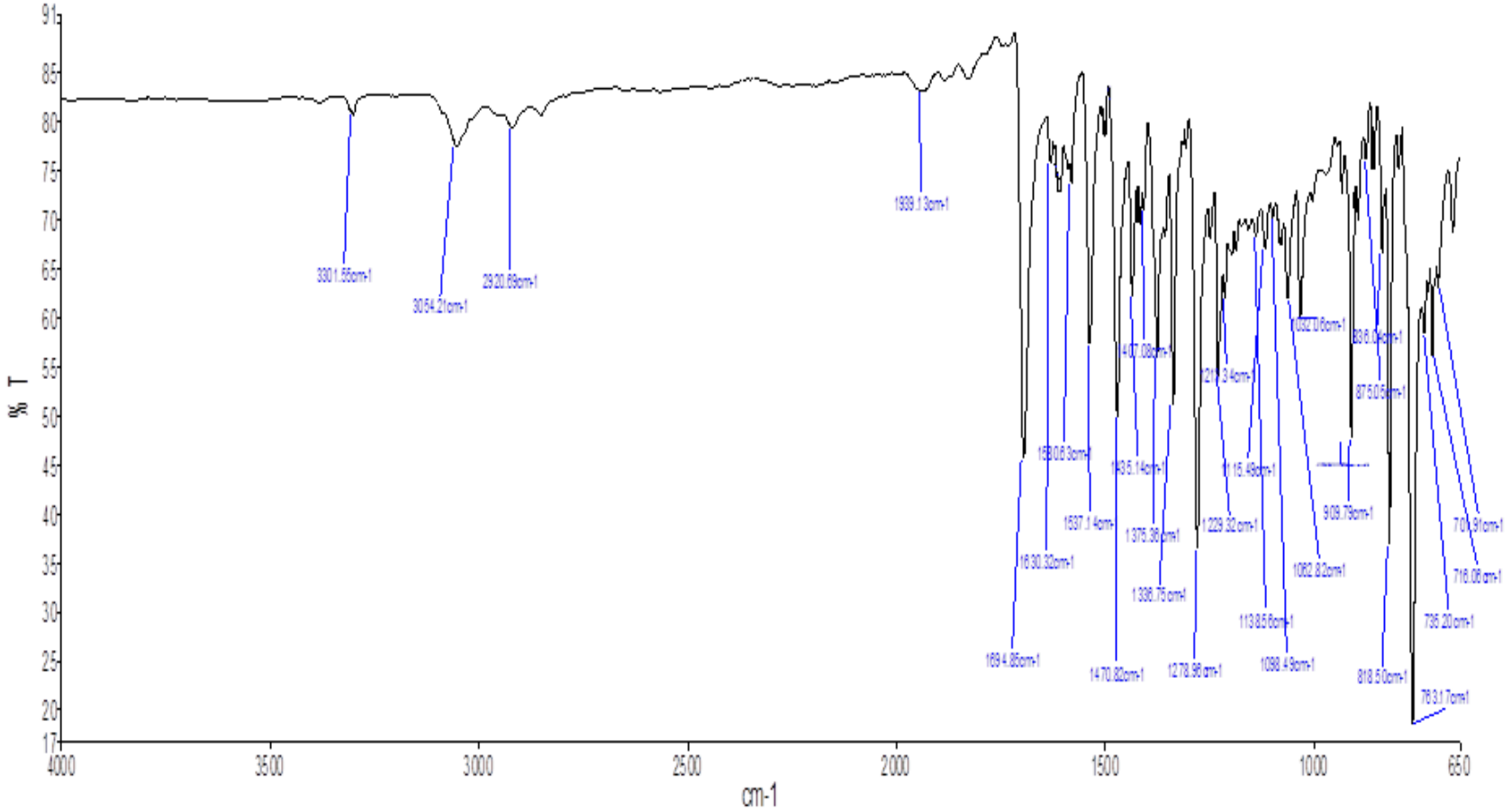

Figure 3.4 FT-IR spectrum of derivative A

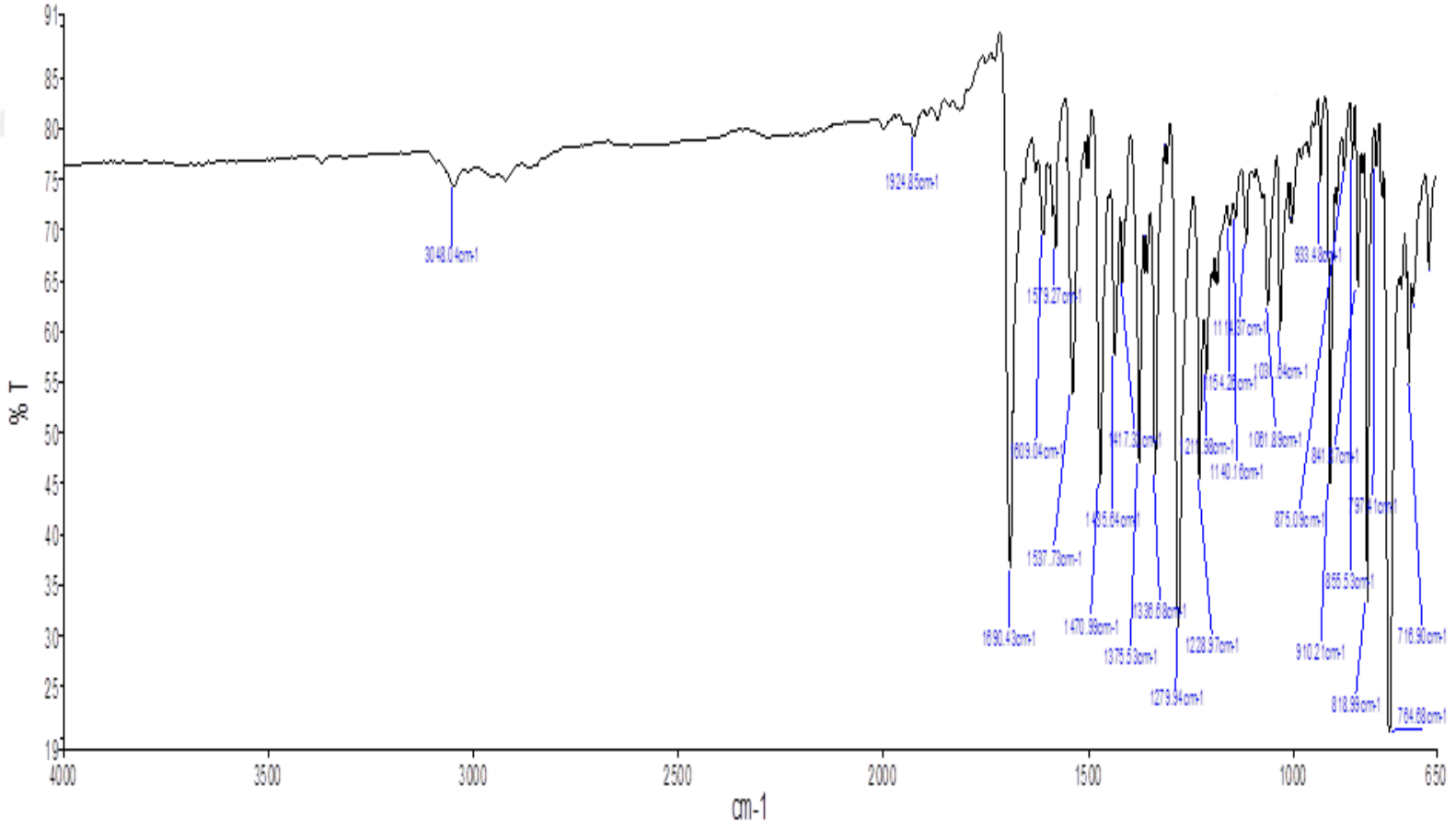

Figure 3.5 FT-IR spectrum of derivative B

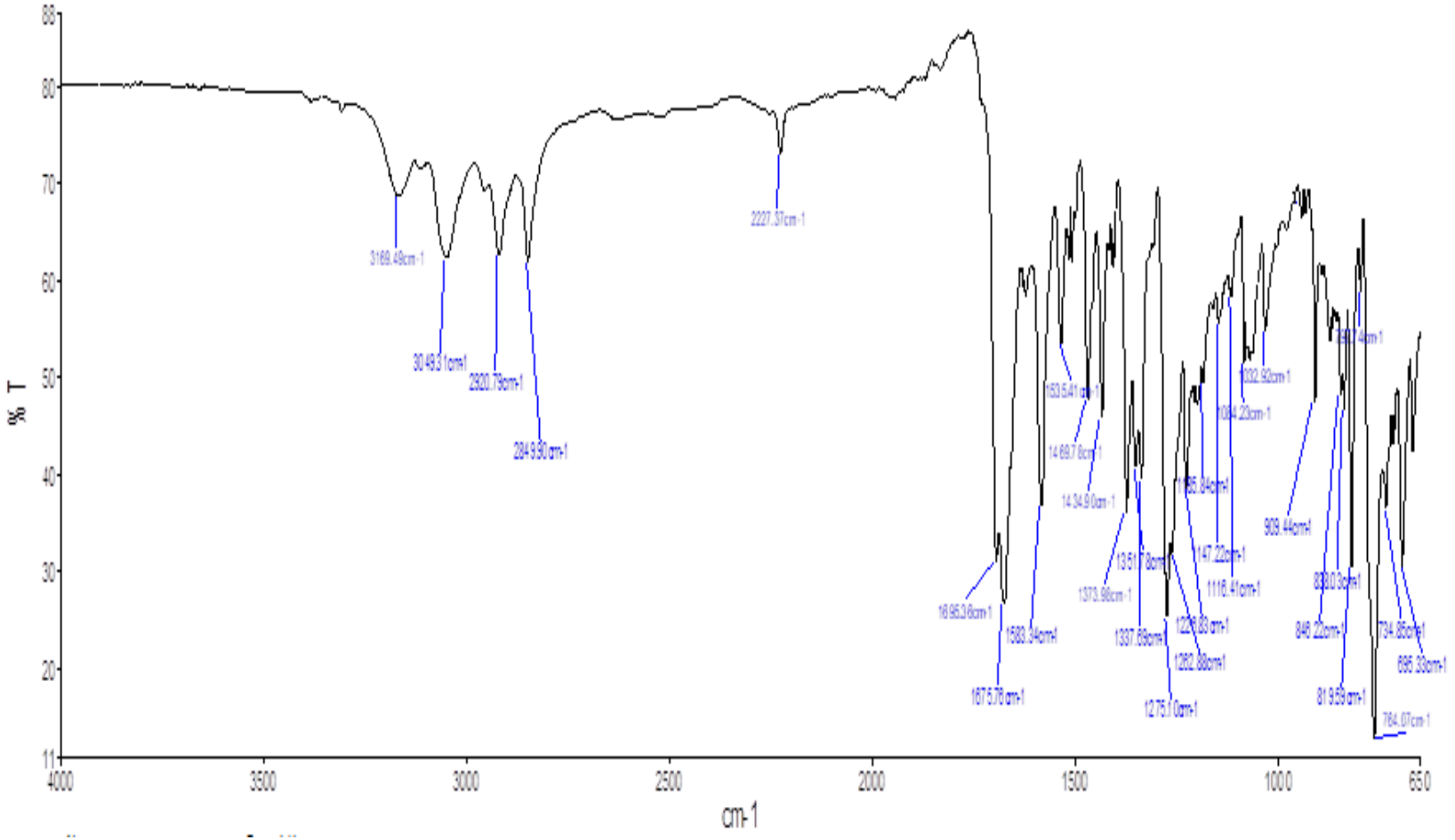

Figure 3.6 FT-IR spectrum of derivative C

3.2 Fluorescence Features of A, B and C Derivatives

Displayed in Table 3.1 the emission and absorption spectra of A, B and C compounds have been established using the following series of different solvents with different polarities: toluene (TOL), dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (EA), acetonitrile (ACN), chloroform and N,N-dimethylformamide (DMF) with 10^{-5} M concentration. While the absorption spectra were obtained by utilizing an "UV-vis spectrophotometer", the emission spectra on the other hand were obtained by utilizing a "fluorescence spectrophotometer" all in the 400-800 nm wavelength range.

By analysing the resulted absorption and emission spectra, we had been able to figure out many valuable photophysical features (like, maximum emission and absorption wavelengths, Stokes' shift values, molar extinction coefficients, singlet energies and photostabilities) of the concerned derivative compounds at hand.

Table 3.1 Absorption and fluorescence emission data of A, B and C (UV-vis absorption maxima, λ_{max}^{abs} (nm), fluorescence emission maxima, λ_{max}^{f} (nm), Stokes' shift $\Delta\lambda$ (nm), molar extinction coefficient, ε ($L \cdot mol^{-1} \cdot cm^{-1}$), and singlet energy and E_s (kcal/mol))

Compound	Solvent	λ_{max}^{abs}	λ_{max}^{f}	$\Delta\lambda$	ε	E_s
A	Toluene	487	587	100	6000	48.6
	Chloroform	486	593	107	6400	48.1
	Ethyl acetate	483	591	108	6100	48.3
	Tetrahydrofuran	477	594	117	7300	48.0
	Ethanol	477	563	86	28000	50.5
	Dimethylformamide	479	606	127	6400	47.1
	Acetonitrile	477	606	129	5300	47.1
B	Toluene	490	586	96	12400	48.7
	Chloroform	486	590	104	12000	48.4
	Ethyl acetate	482	596	114	10700	47.9
	Tetrahydrofuran	483	590	107	10900	48.4
	Ethanol	473	572	99	7200	49.9
	Dimethylformamide	480	603	123	10400	47.3
	Acetonitrile	476	602	126	10400	47.4
C	Toluene	489	584	95	5500	48.9
	Chloroform	486	590	104	5400	48.4
	Ethyl acetate	489	593	104	4900	48.1
	Tetrahydrofuran	484	594	110	6000	48.0
	Ethanol	477	572	95	5600	50.8
	Dimethylformamide	479	604	125	5600	47.2
	Acetonitrile	476	600	124	5800	47.6

Absorption spectra of the derivatives were recorded in seven solvents at the concentration of 10^{-5} M.

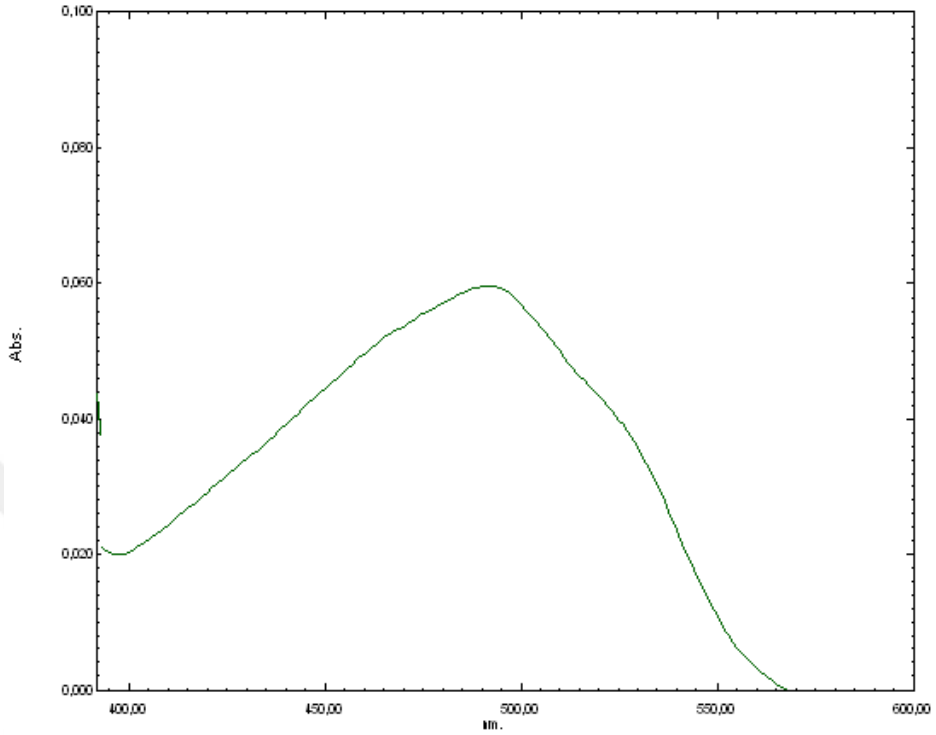

Figure 3.7 Absorption spectra of A in toluene

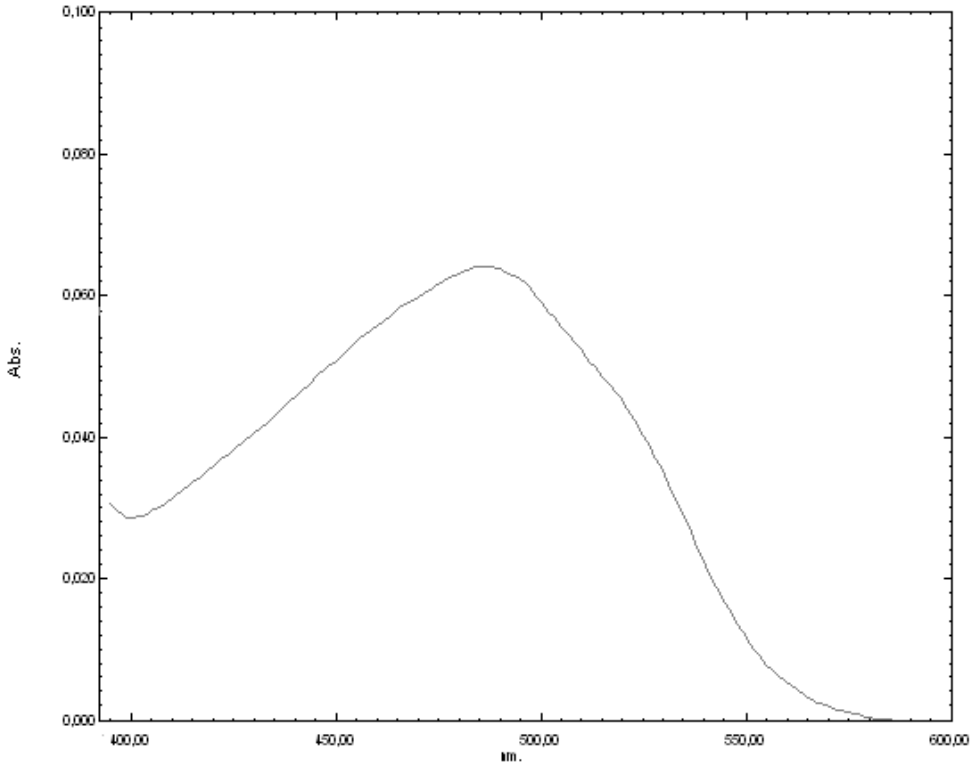

Figure 3.8 Absorption spectra of A in chloroform

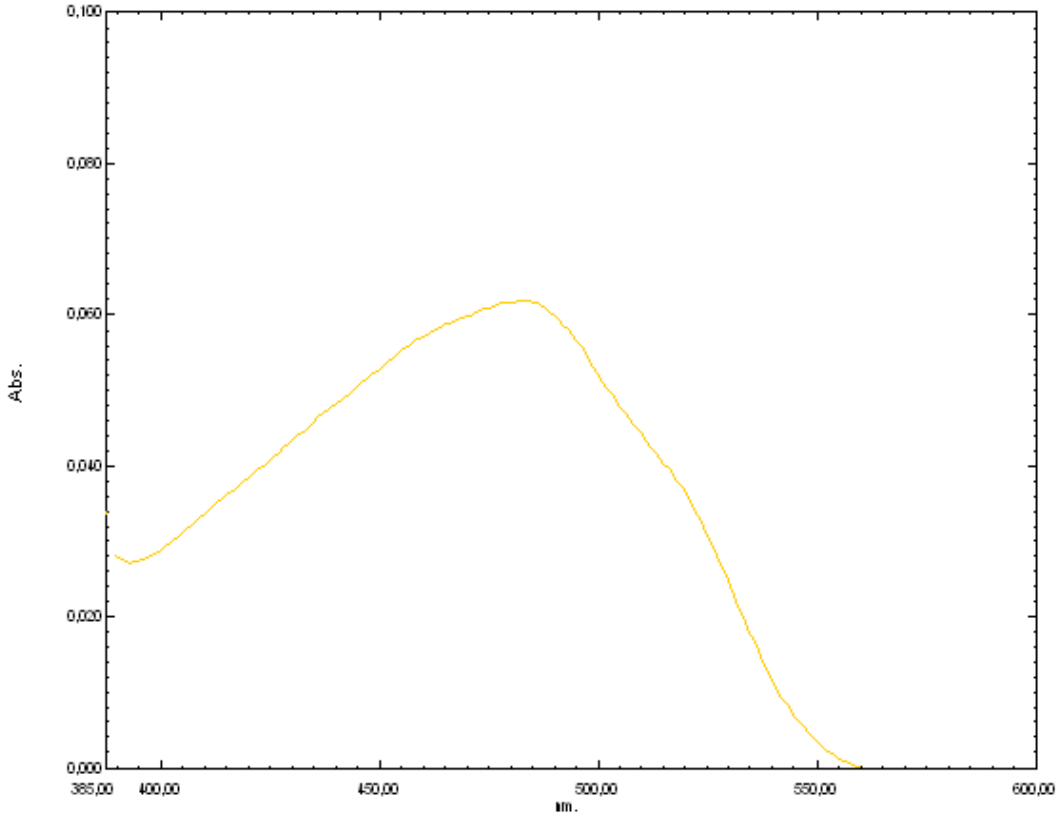

Figure 3.9 Absorption spectra of A in ethyl acetate

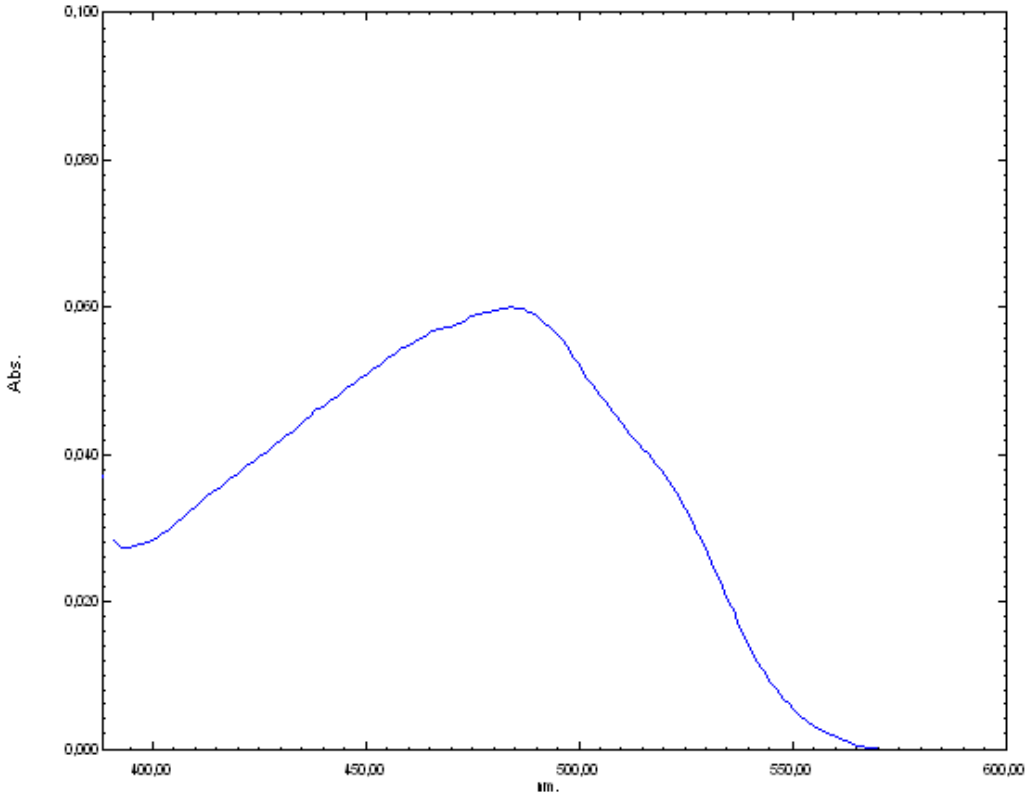

Figure 3.10 Absorption spectra of A in tetrahydrofuran

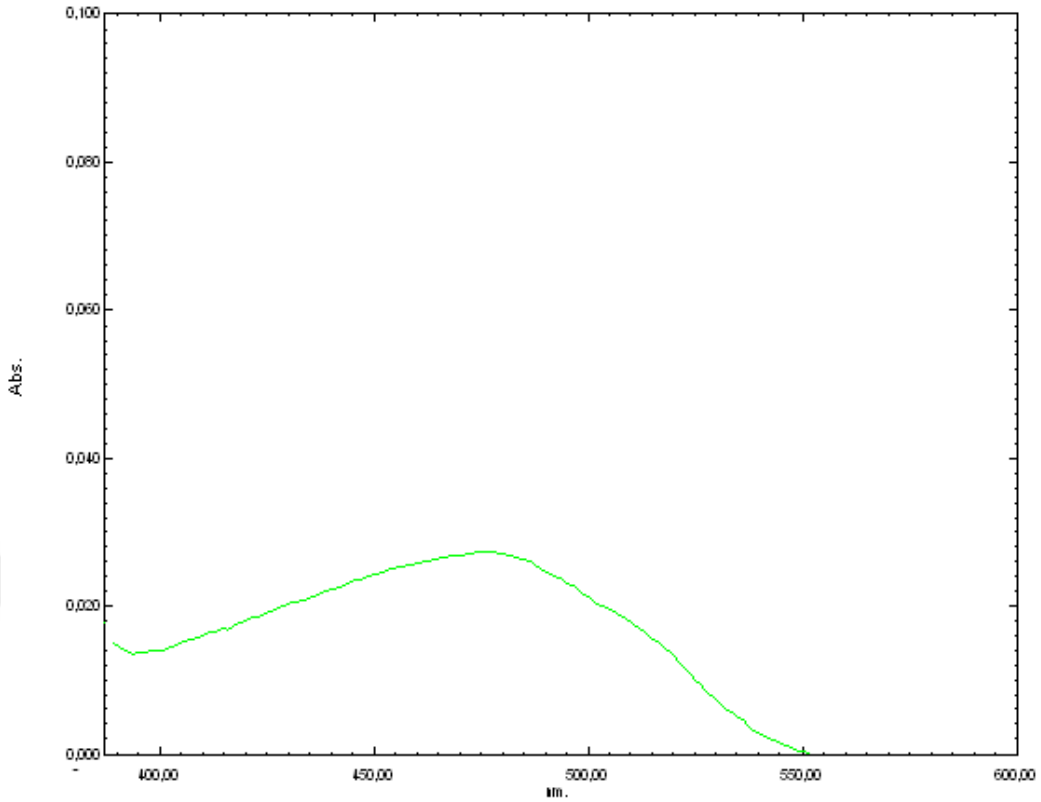

Figure 3.11 Absorption spectra of A in ethanol

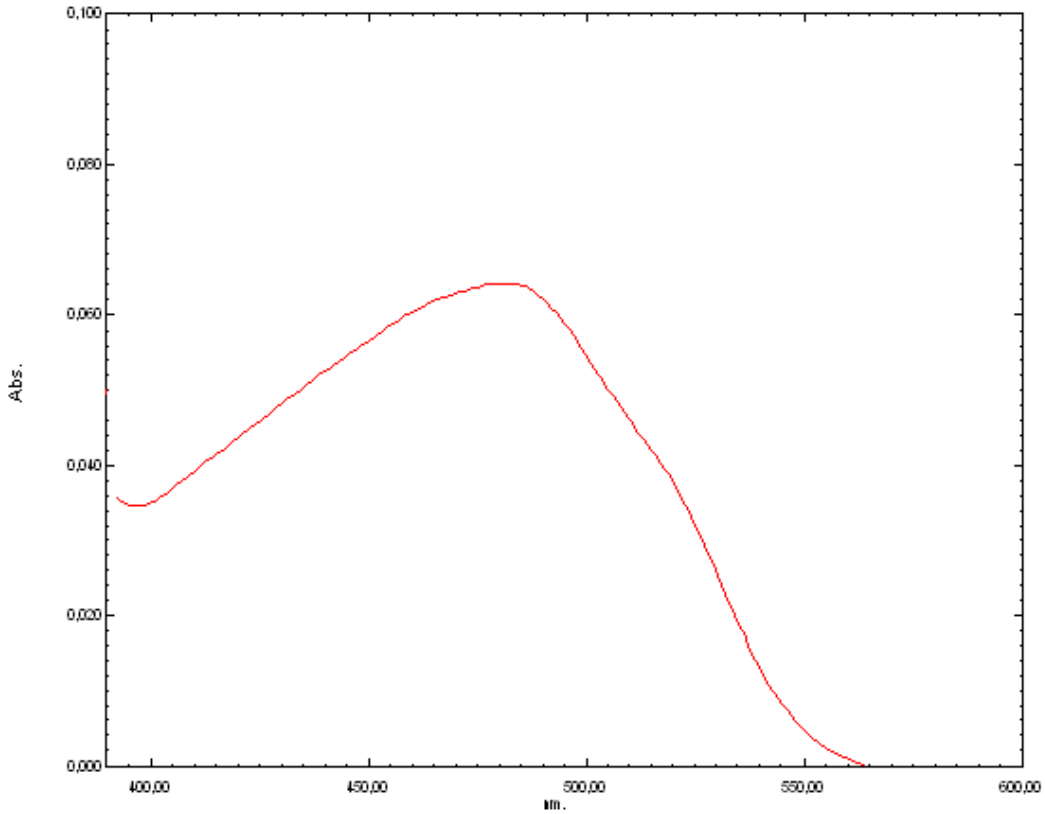

Figure 3.12 Absorption spectra of A in dimethylformamide

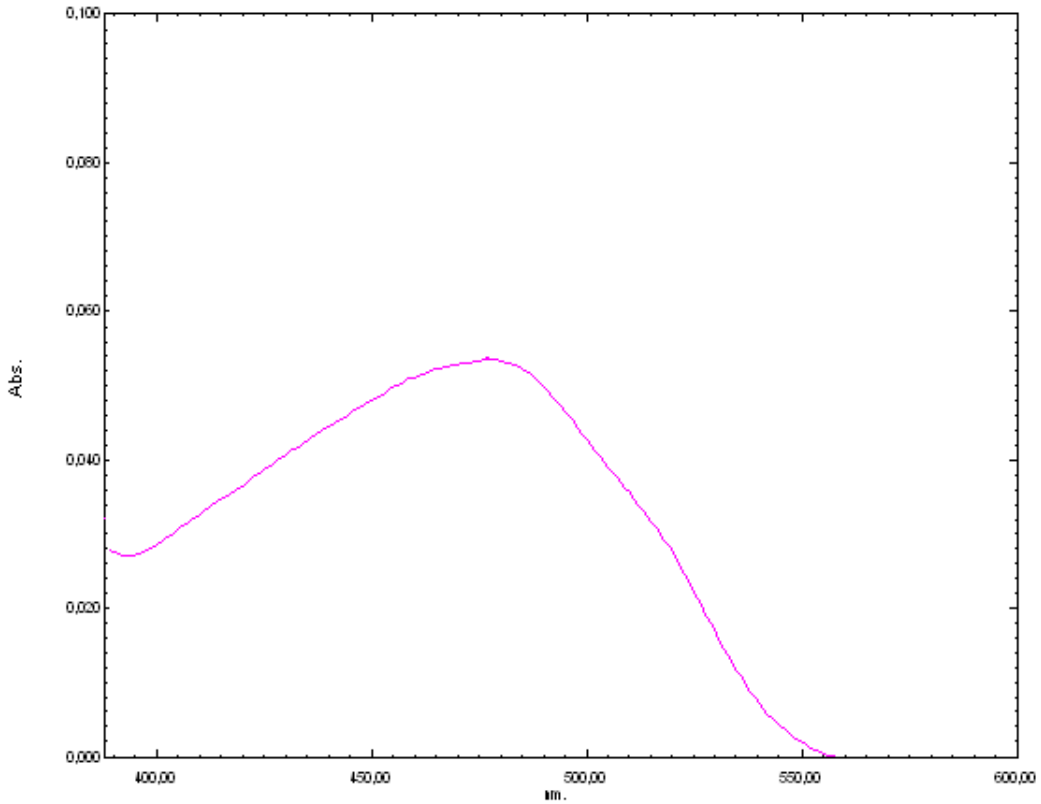

Figure 3.13 Absorption spectra of A in acetonitrile

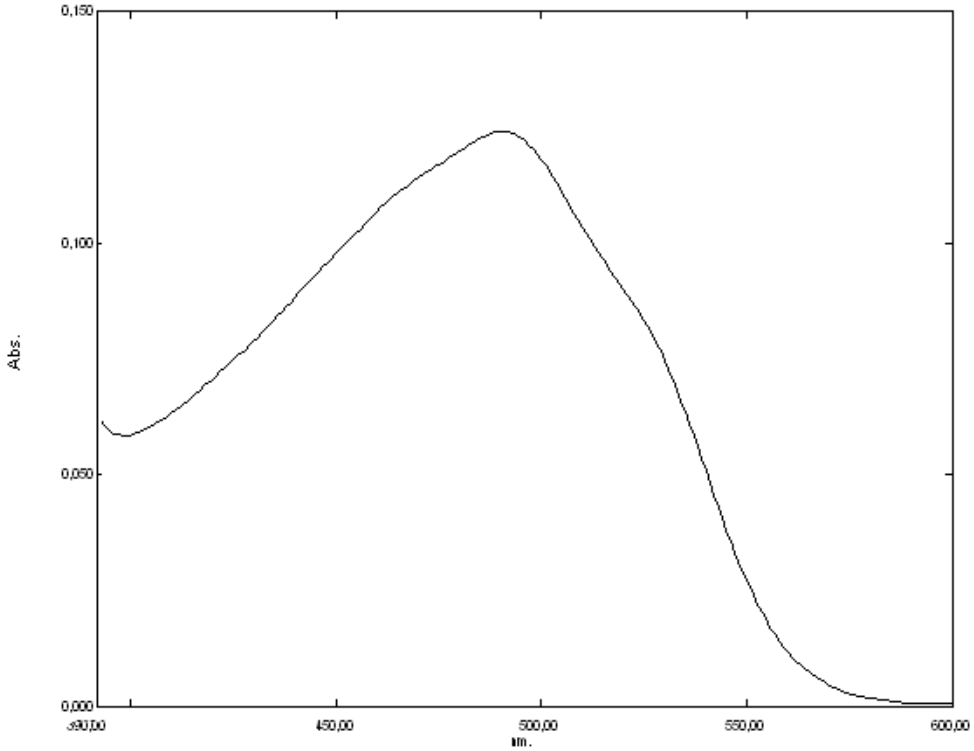

Figure 3.14 Absorption spectra of B in toluene

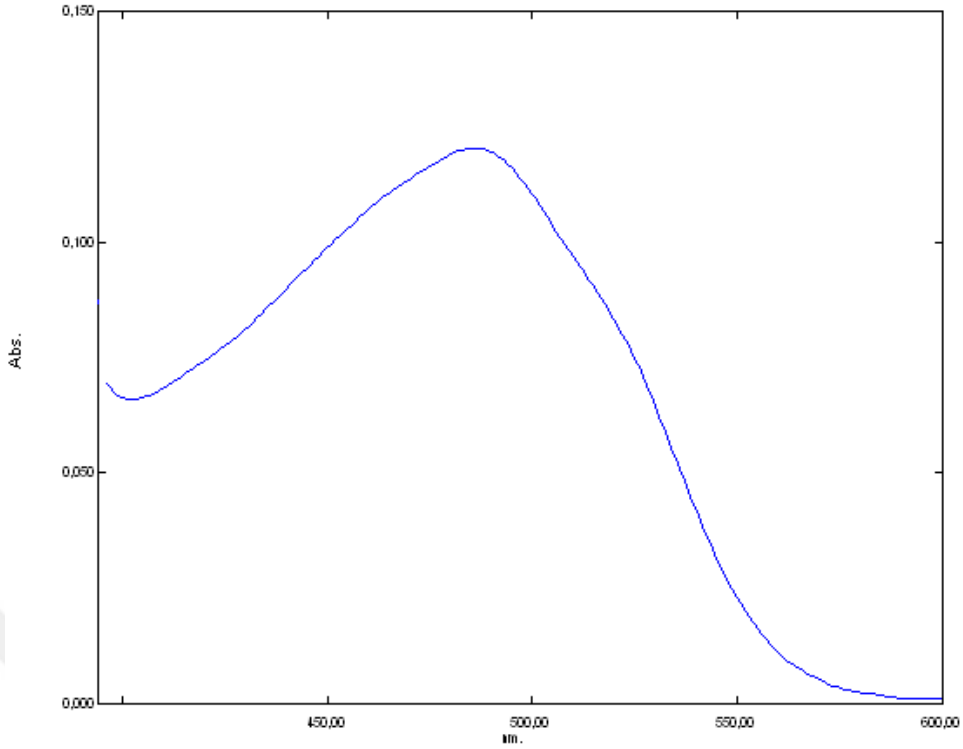

Figure 3.15 Absorption spectra of B in chloroform

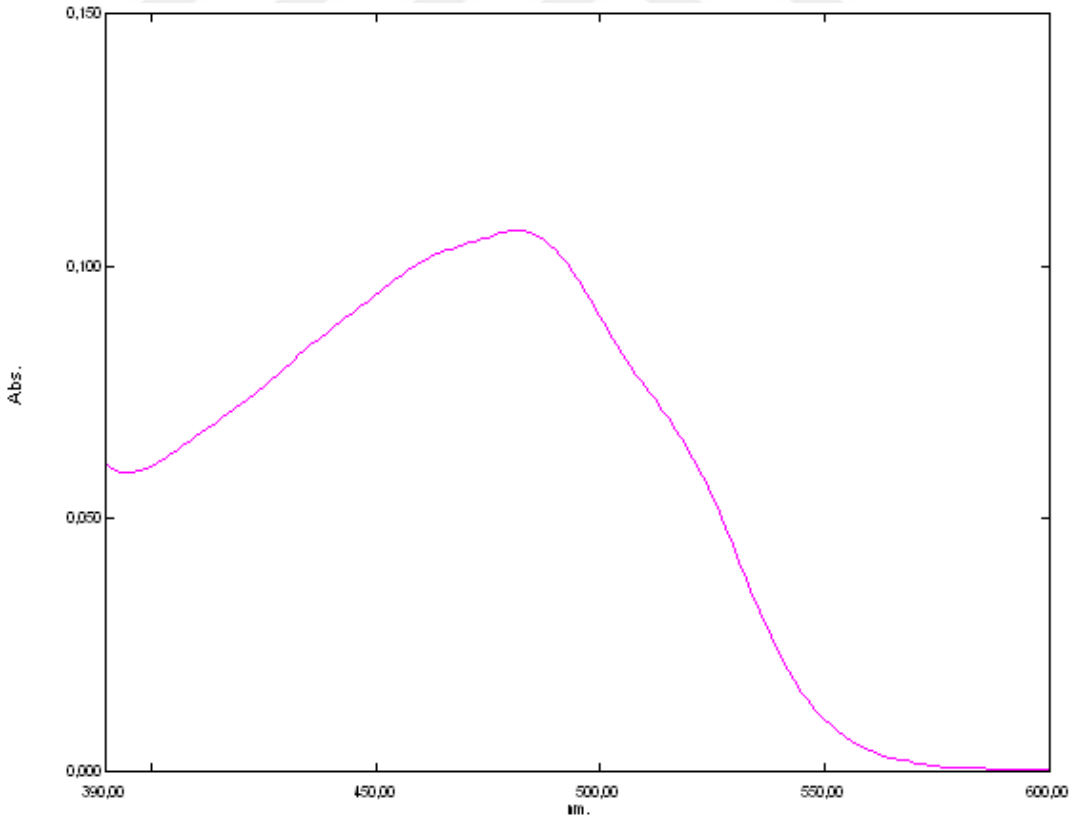

Figure 3.16 Absorption spectra of B in ethyl acetate

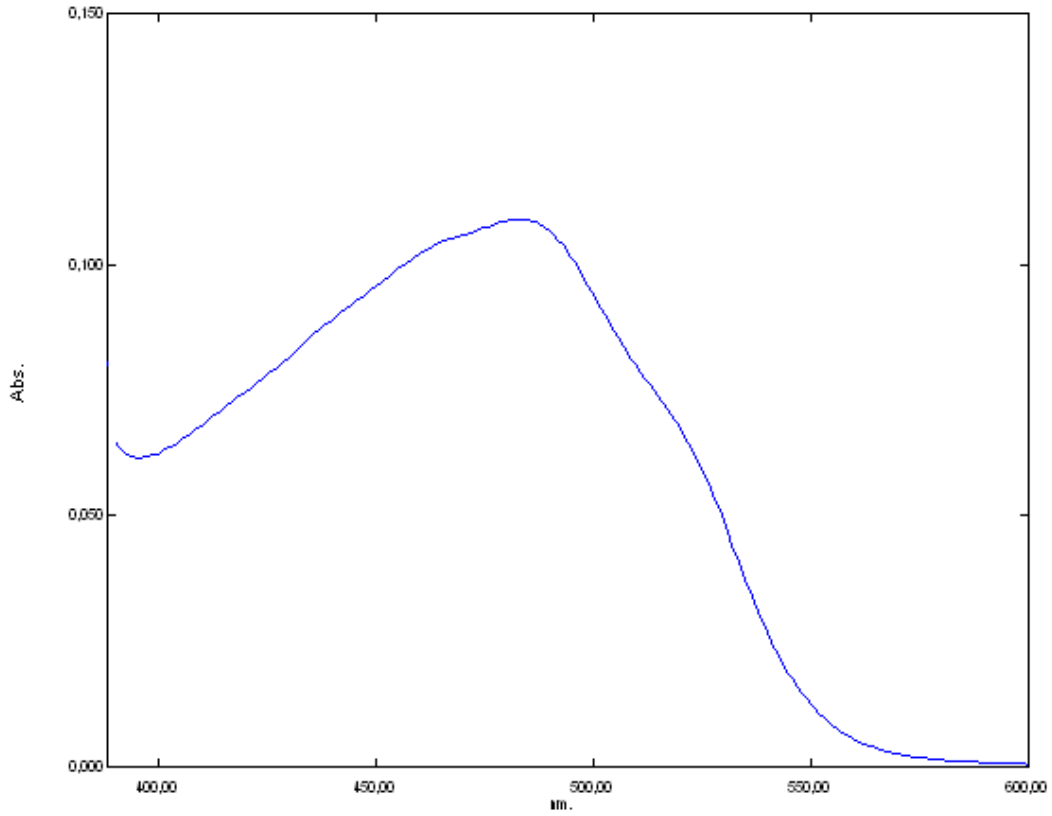

Figure 3.17 Absorption spectra of in tetrahydrofuran

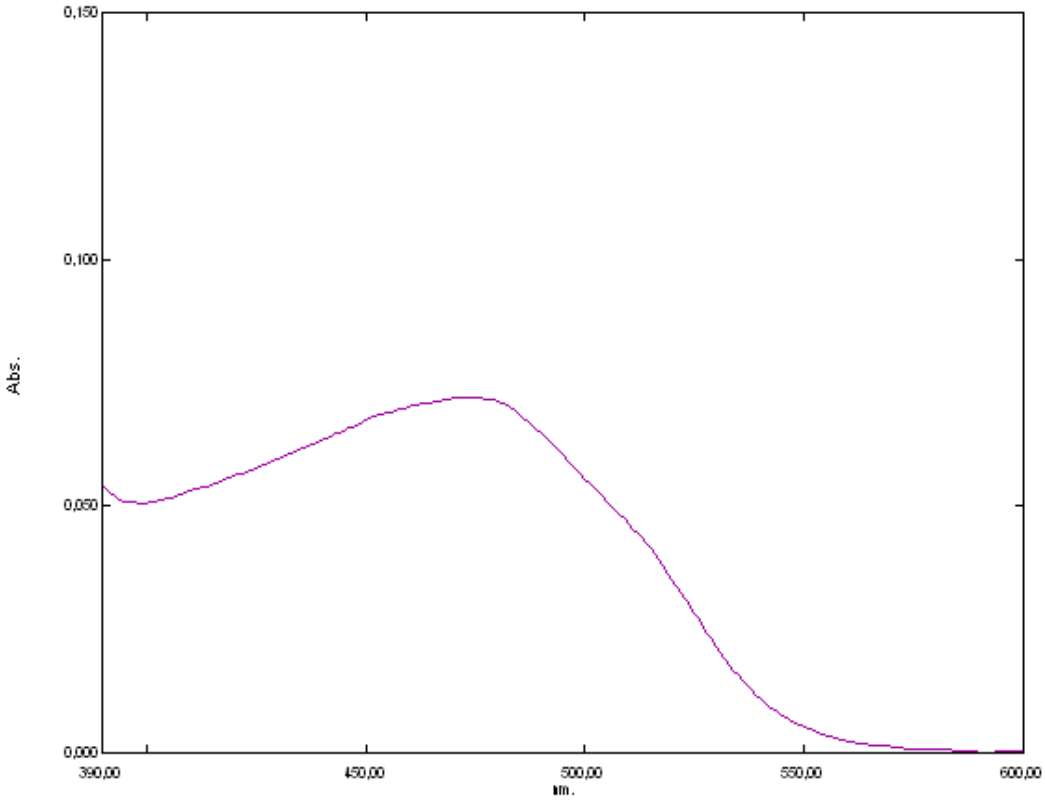

Figure 3.18 Absorption spectra of B in ethanol

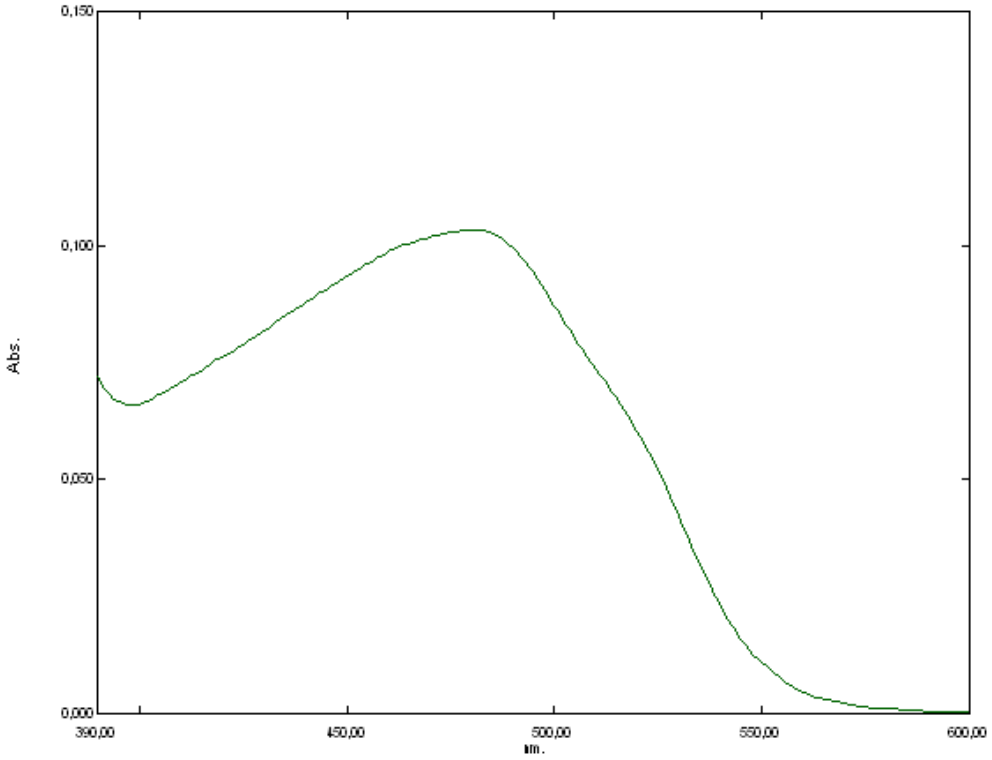

Figure 3.19 Absorption spectra of B in dimethylformamide

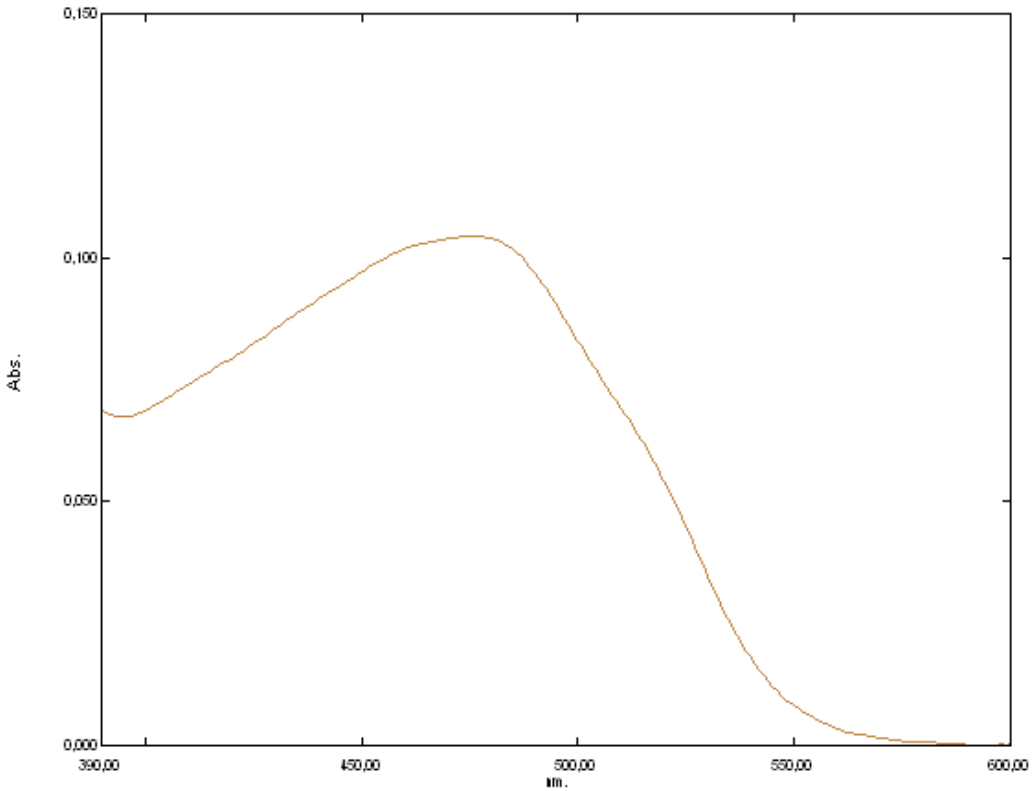

Figure 3.20 Absorption spectra of B in acetonitril

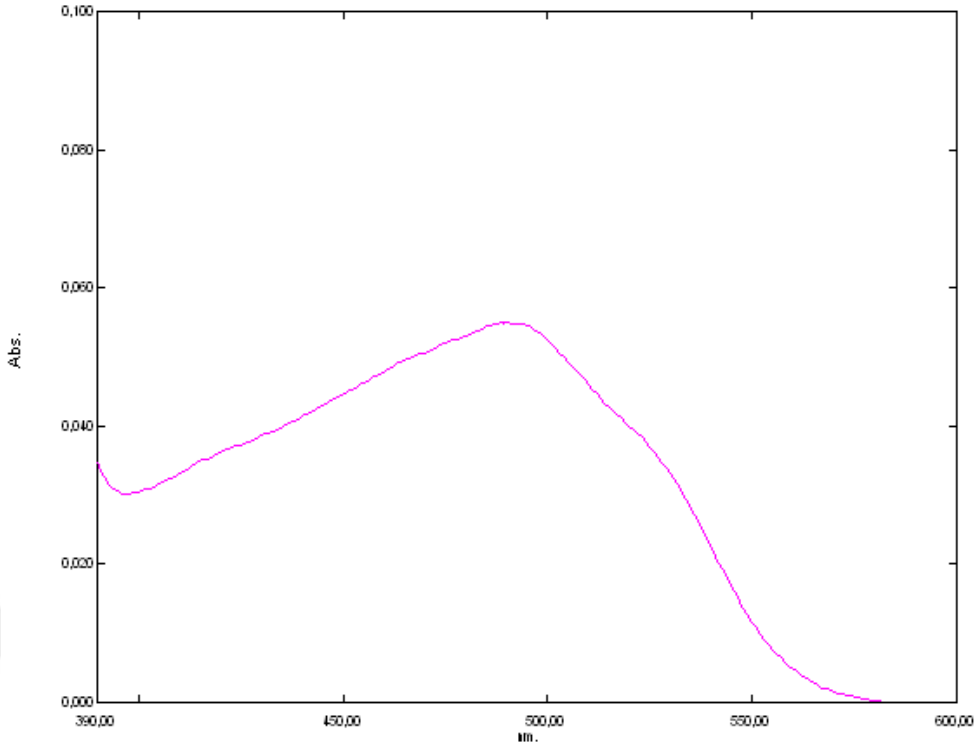

Figure 3.21 Absorption spectra of C in toluene

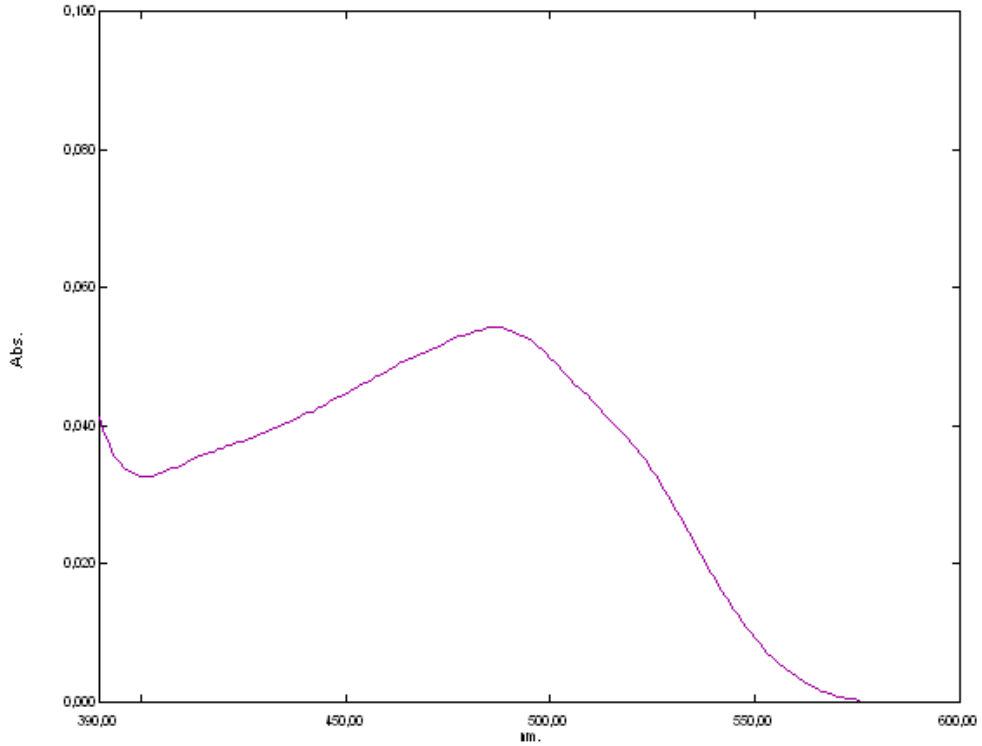

Figure 3.22 Absorption spectra of C in chloroform

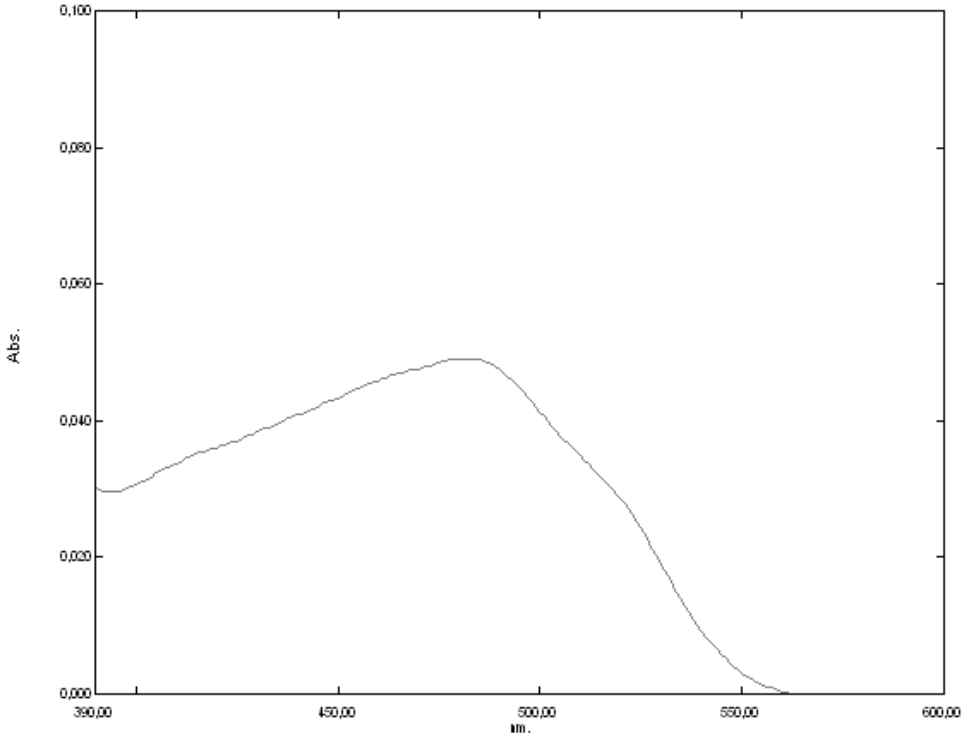

Figure 3.23 Absorption spectra of C in ethyl acetate

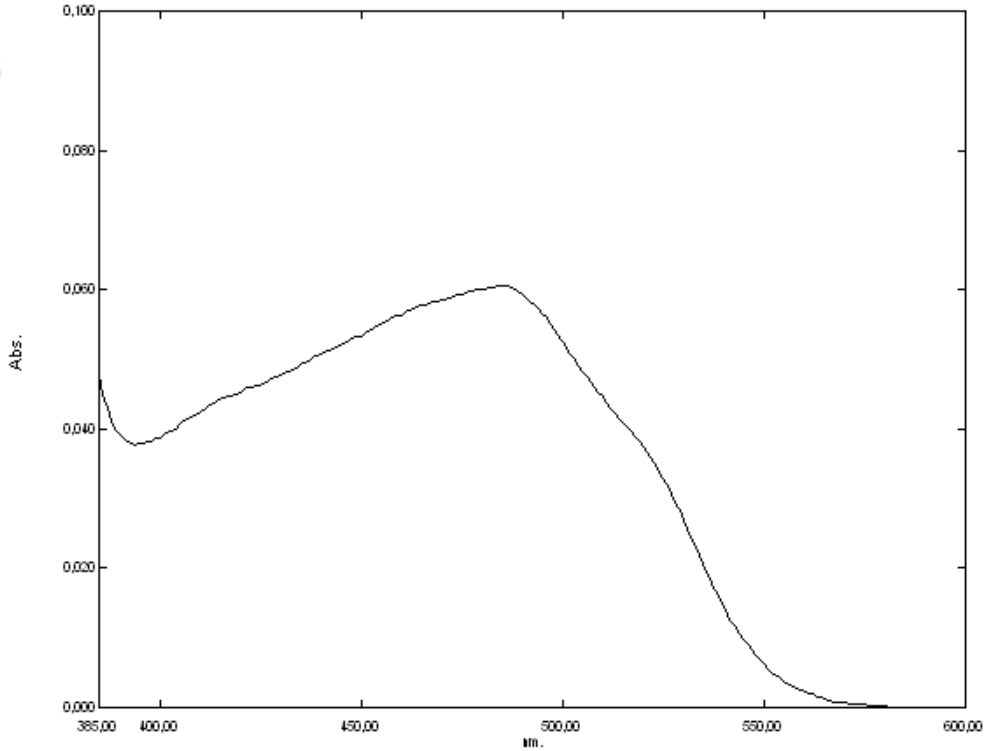

Figure 3.24 Absorption spectra of C in tetrahydrofuran

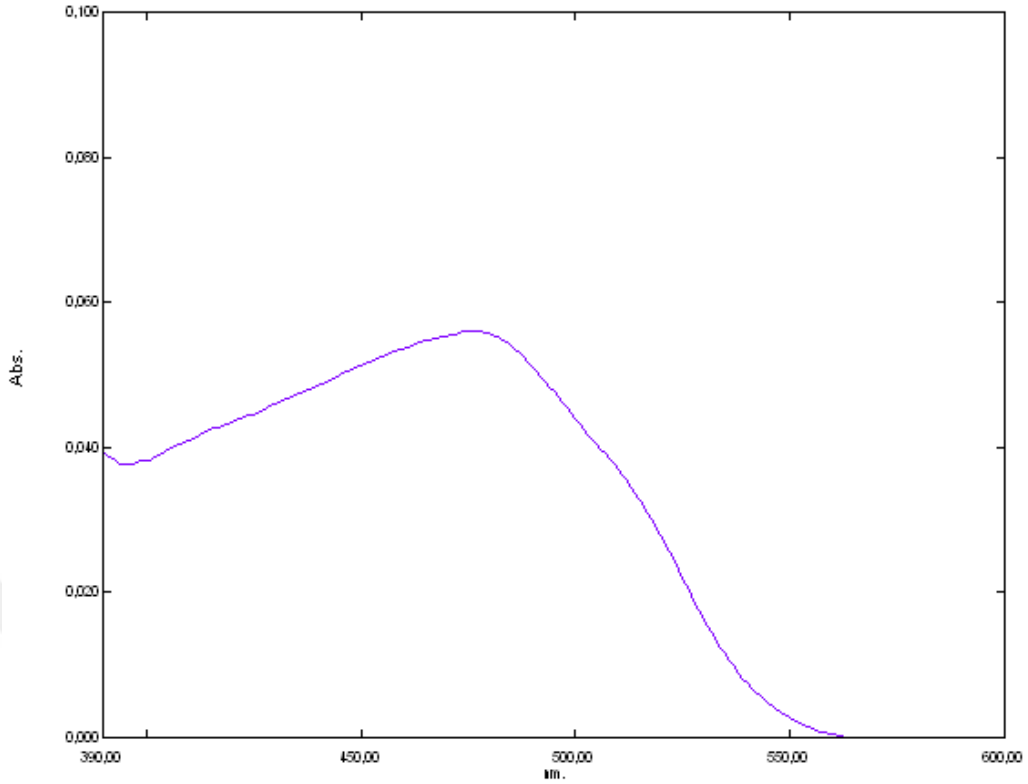

Figure 3.25 Absorption spectra of C in ethanol

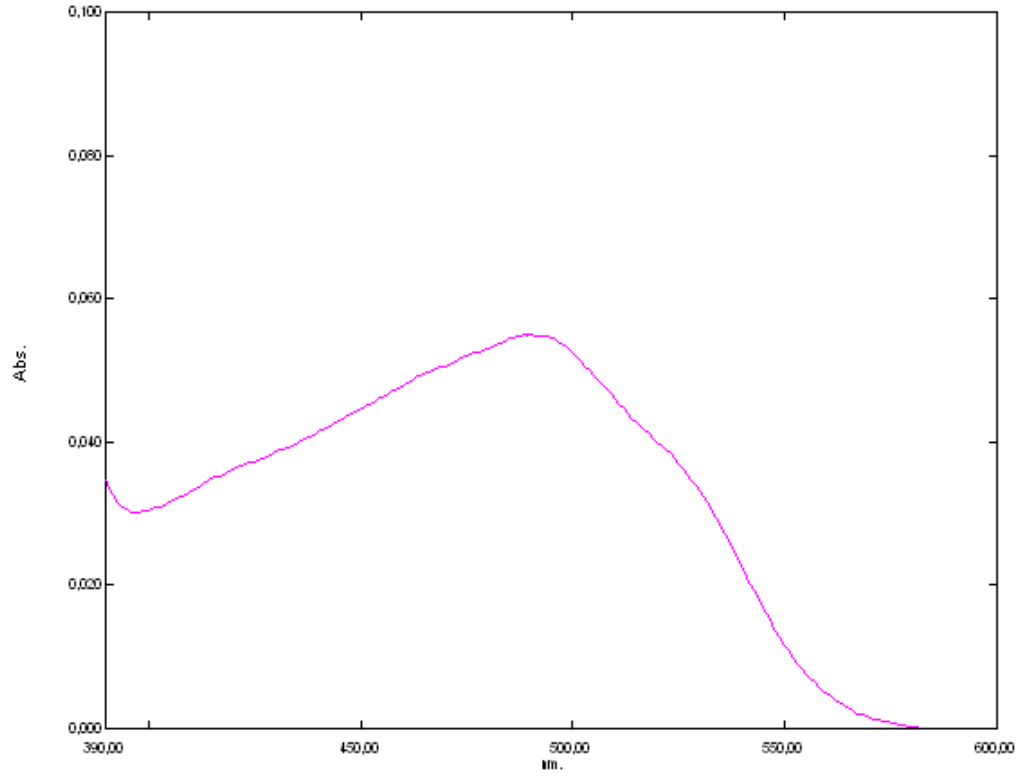

Figure 3.26 Absorption spectra of C in dimethylformamide

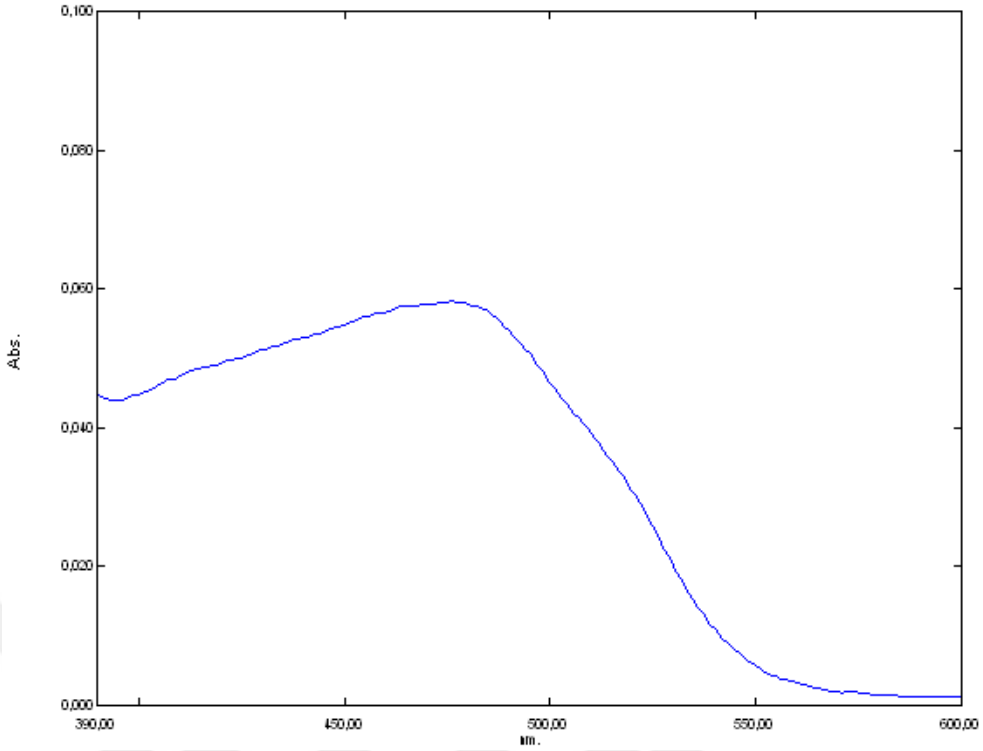

Figure 3.27 Absorption spectra of C in acetonitrile

Emission spectra of the derivatives were recorded in seven solvents at the concentration of 10^{-5} M.

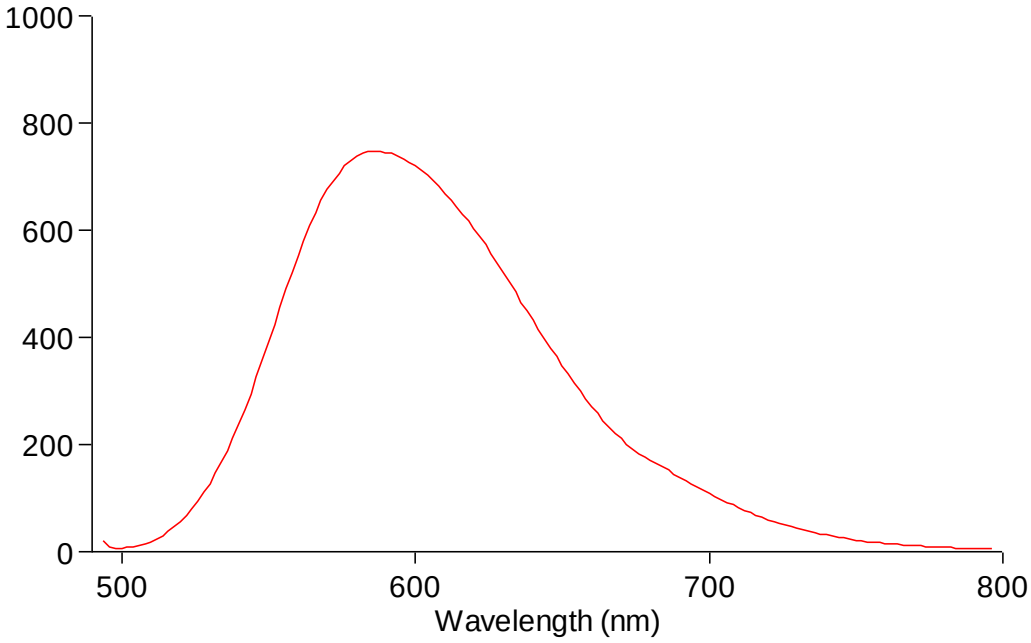

Figure 3.28 Emission spectra of A in toluene

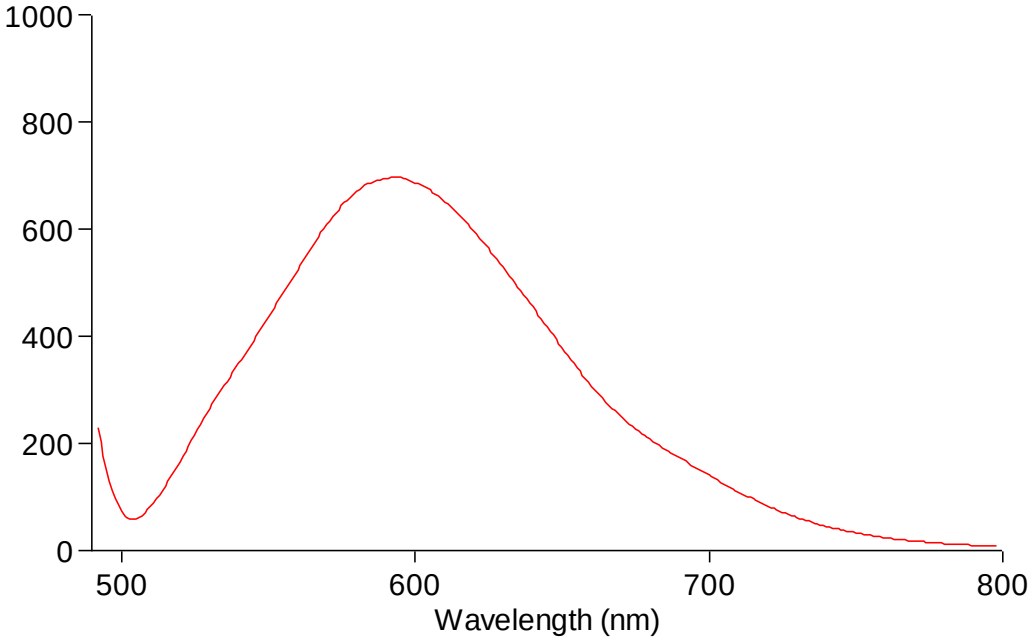

Figure 3.29 Emission spectra of A in chloroform

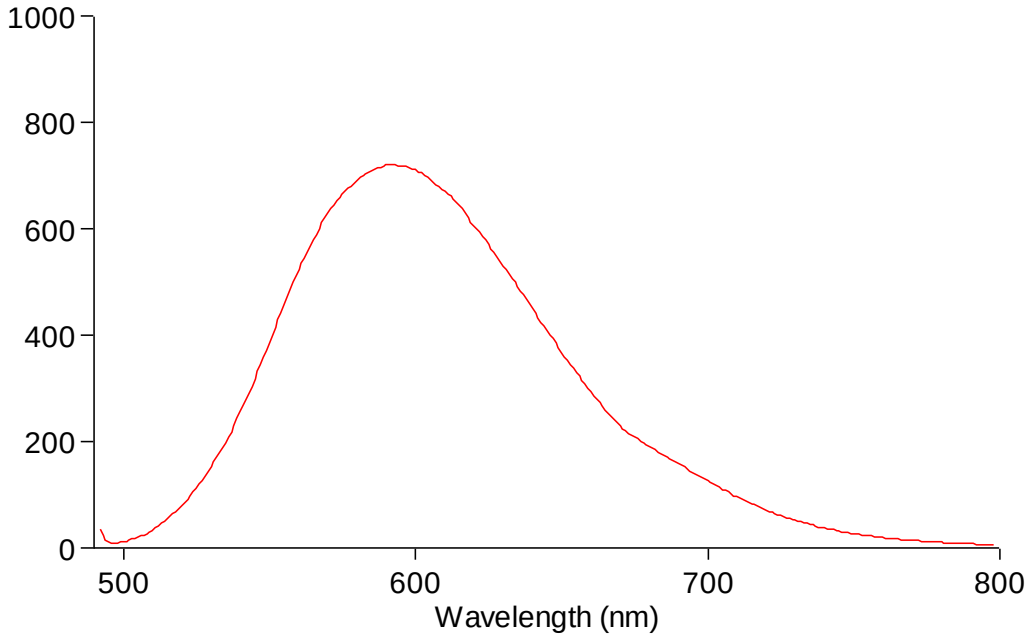

Figure 3.30 Emission spectra of A in ethyl acetate

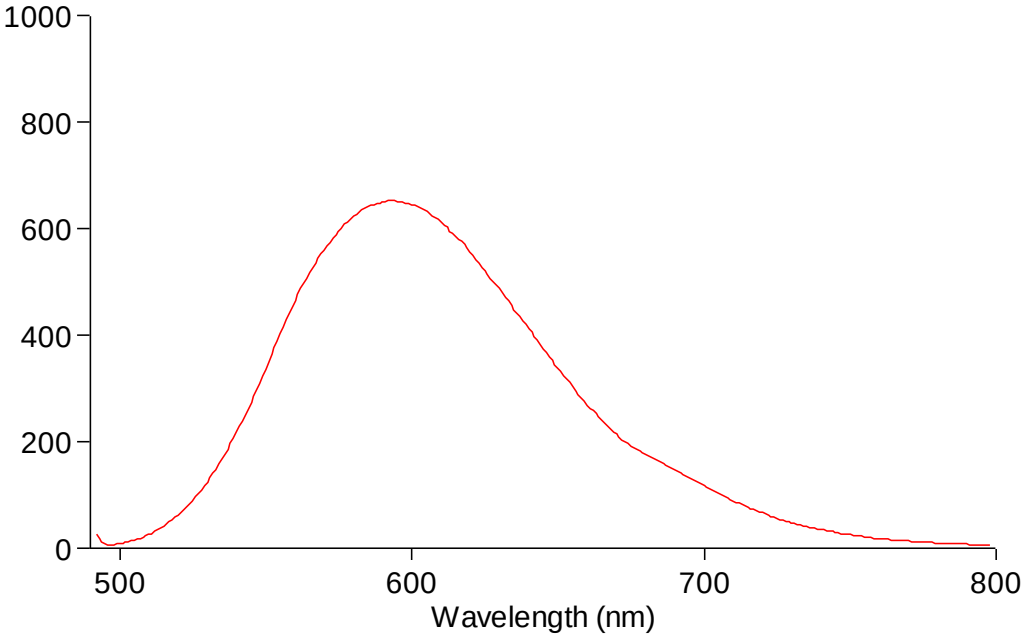

Figure 3.31 Emission spectra of A in tetrahydrofuran

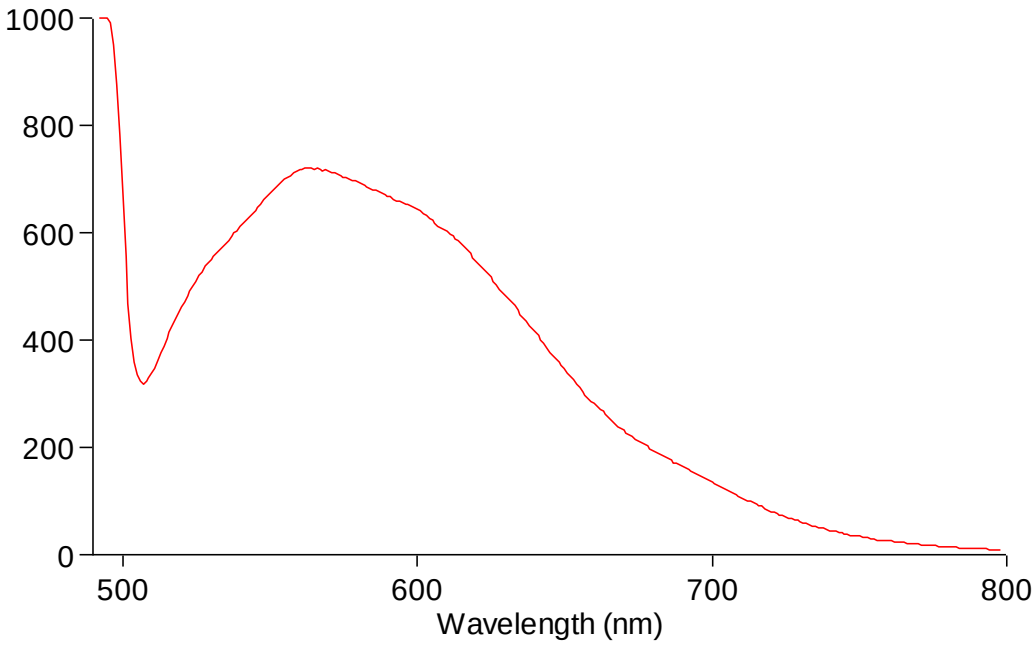

Figure 3.32 Emission spectra of A in ethanol

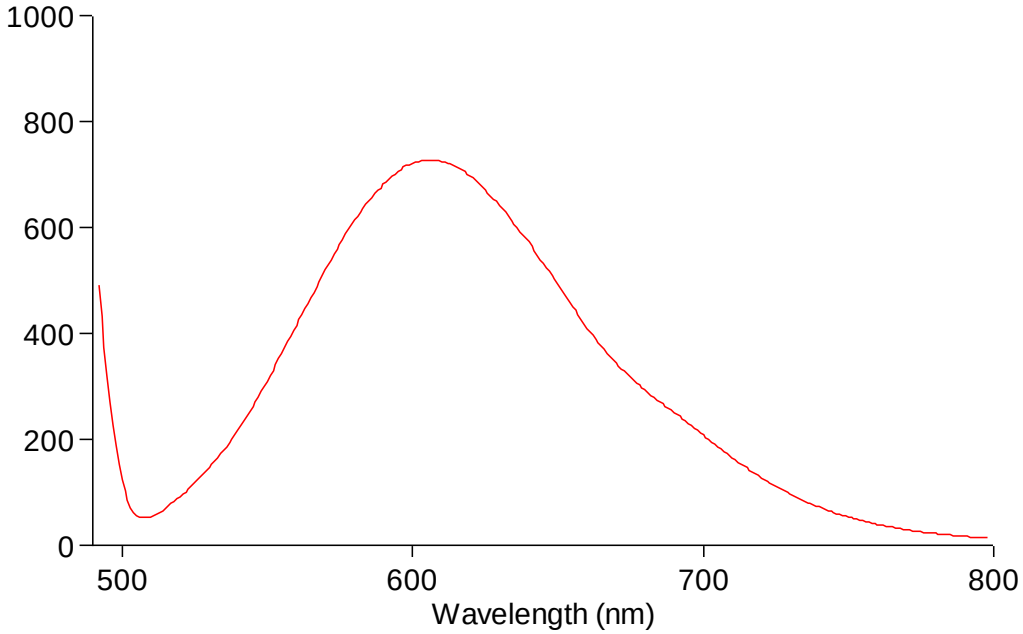

Figure 3.33 Emission spectra of A in dimethylformamide

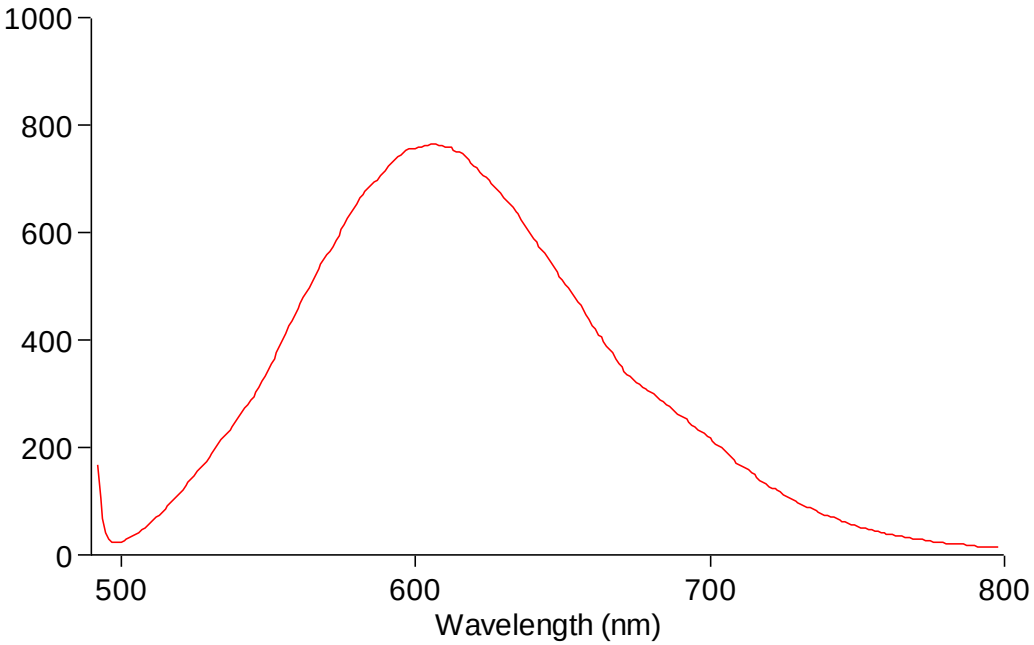

Figure 3.34 Emission spectra of A in acetonitrile

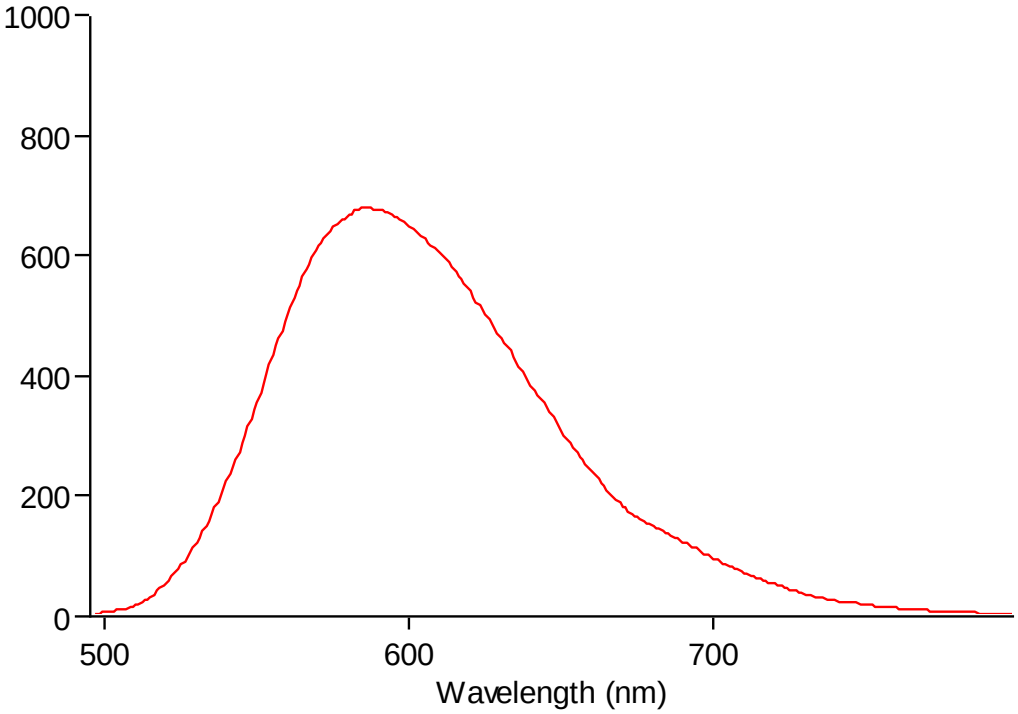

Figure 3.35 Emission spectra of B in toluene

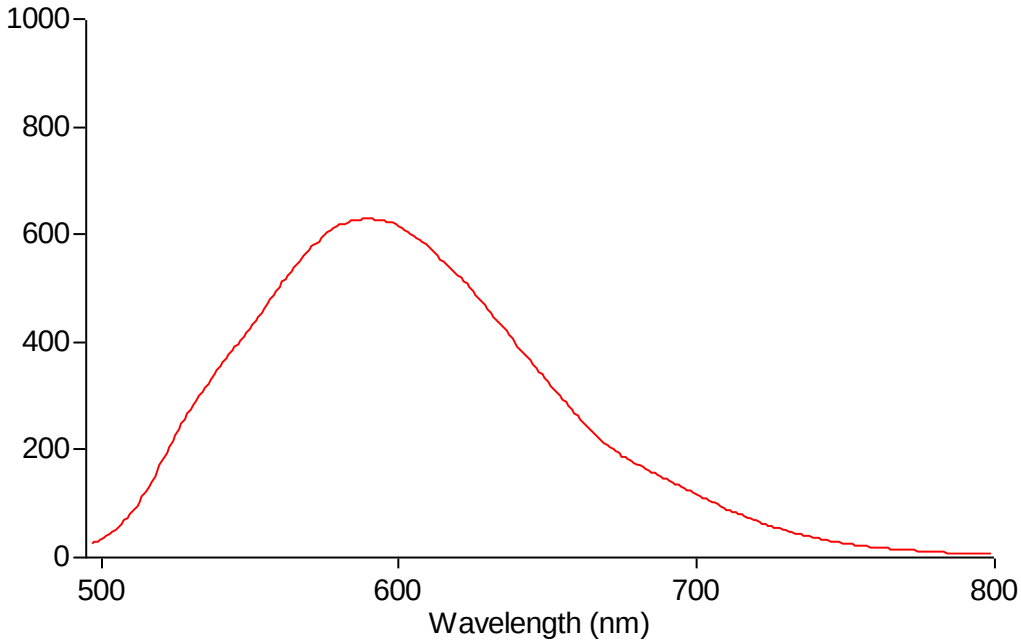

Figure 3.36 Emission spectra of B in chloroform

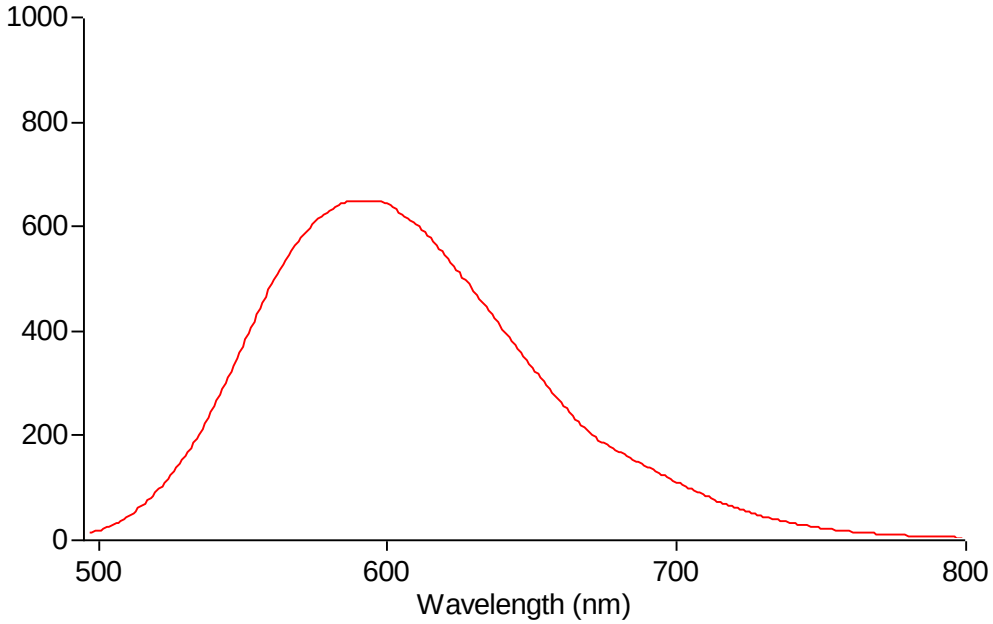

Figure 3.37 Emission spectra of B in ethyl acetate

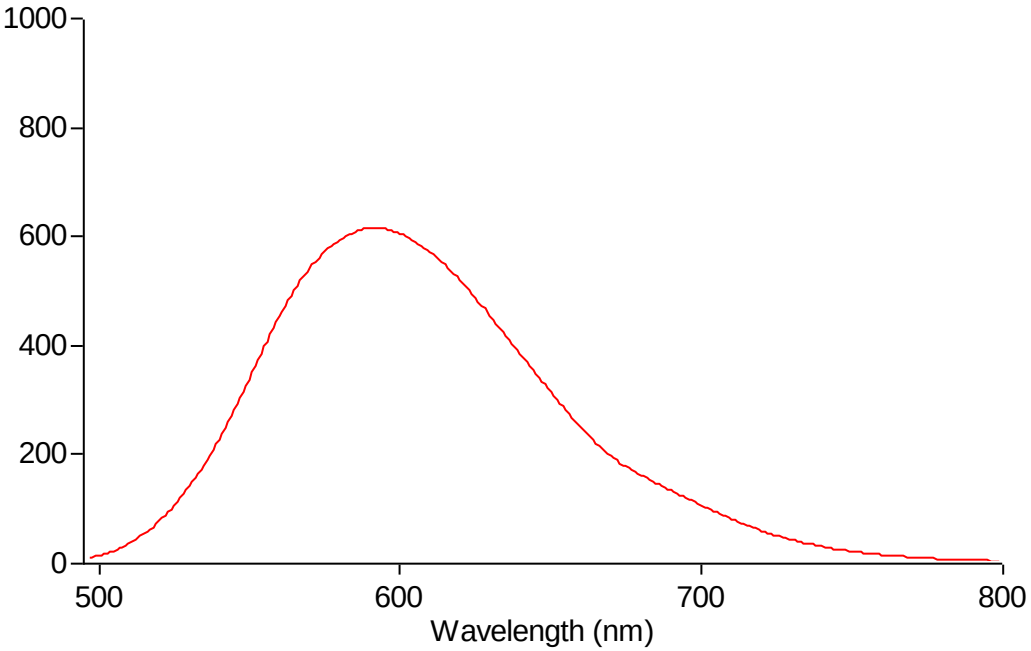

Figure 3.38 Emission spectra of B in tetrahydrofuran

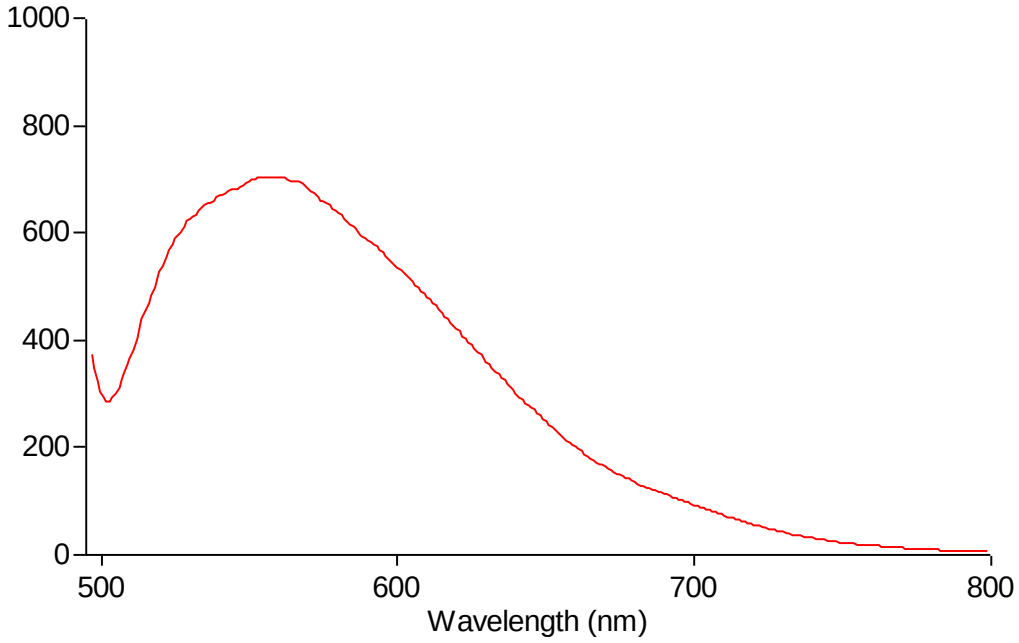

Figure 3.39 Emission spectra of B in ethanol

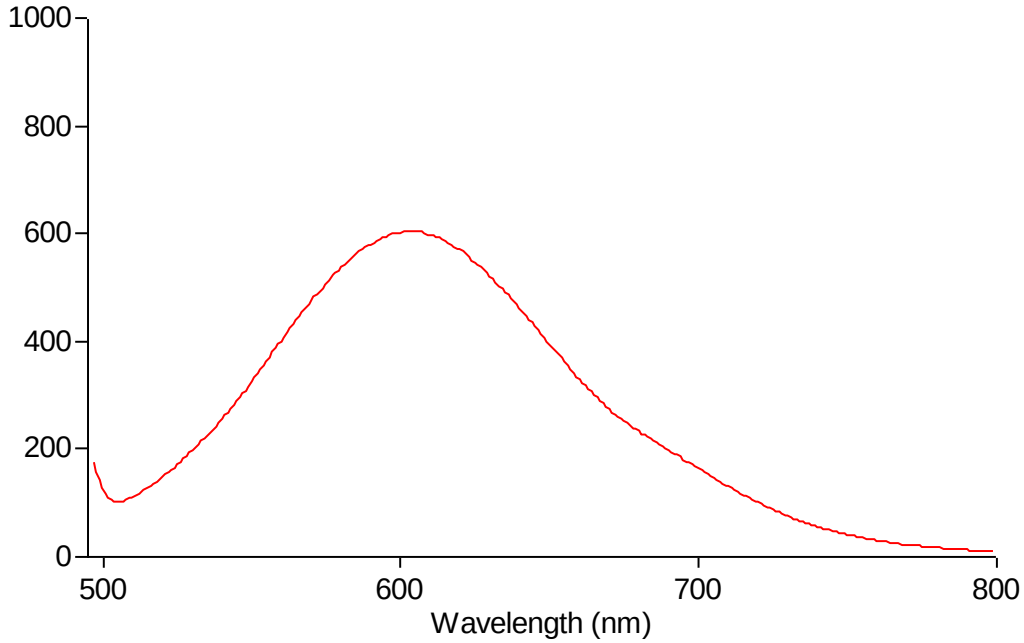

Figure 3.40 Emission spectra of B in dimethylformamide

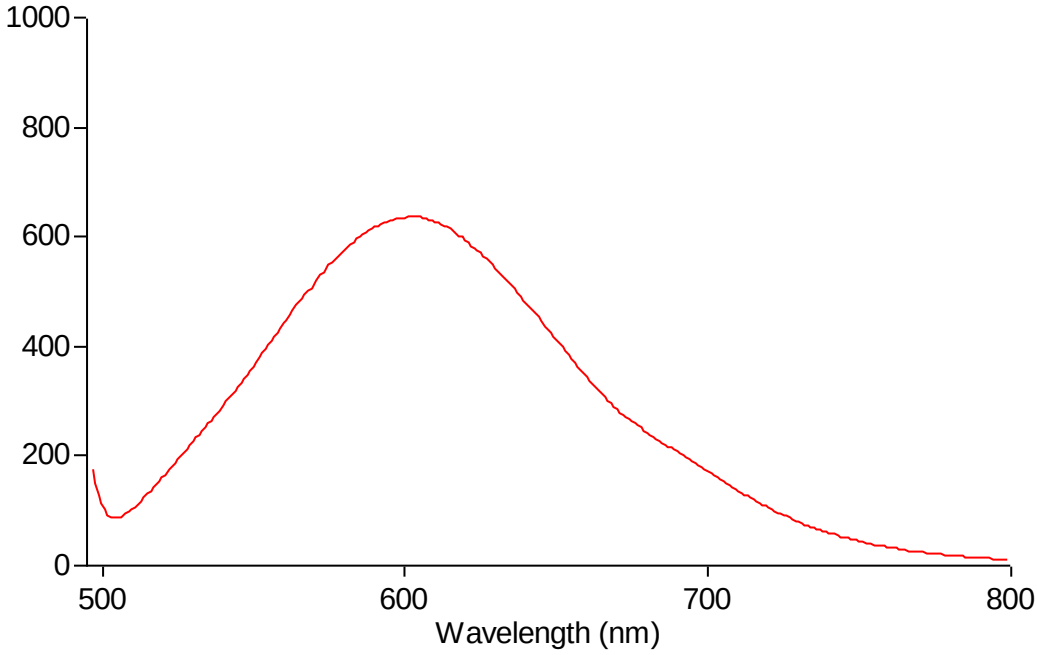

Figure 3.41 Emission spectra of B in acetonitrile

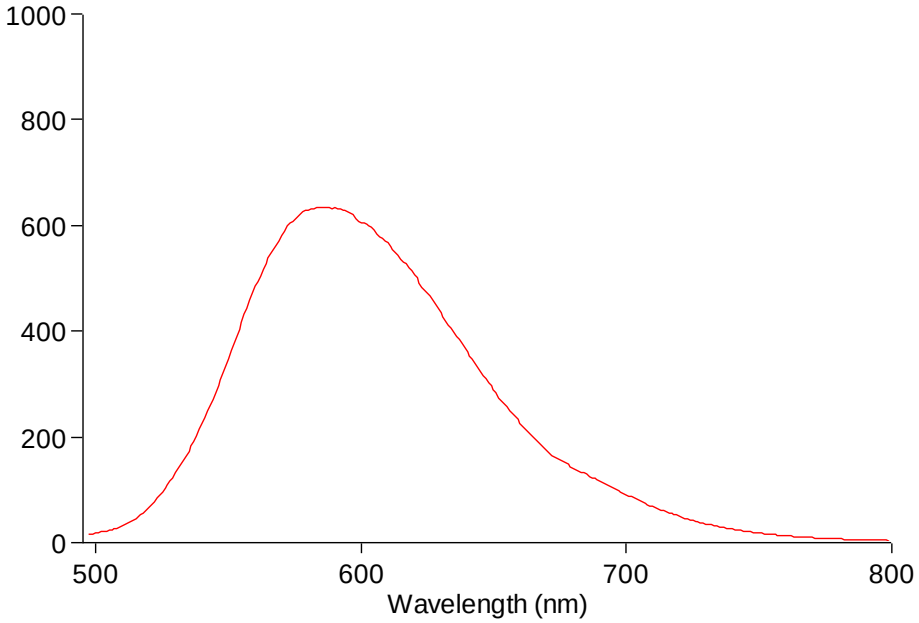

Figure 3.42 Emission spectra of C in toluene

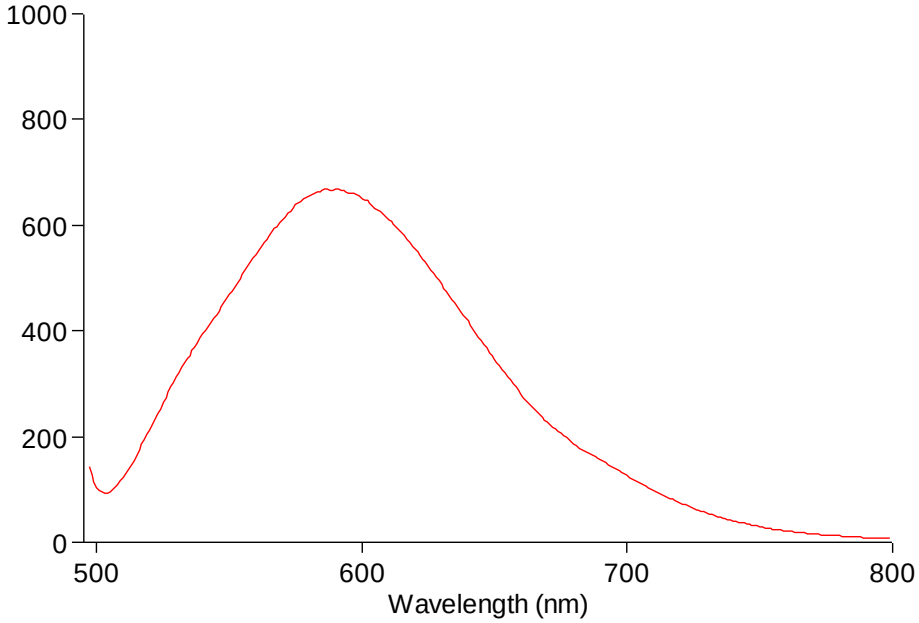

Figure 3.43 Emission spectra of C in chloroform

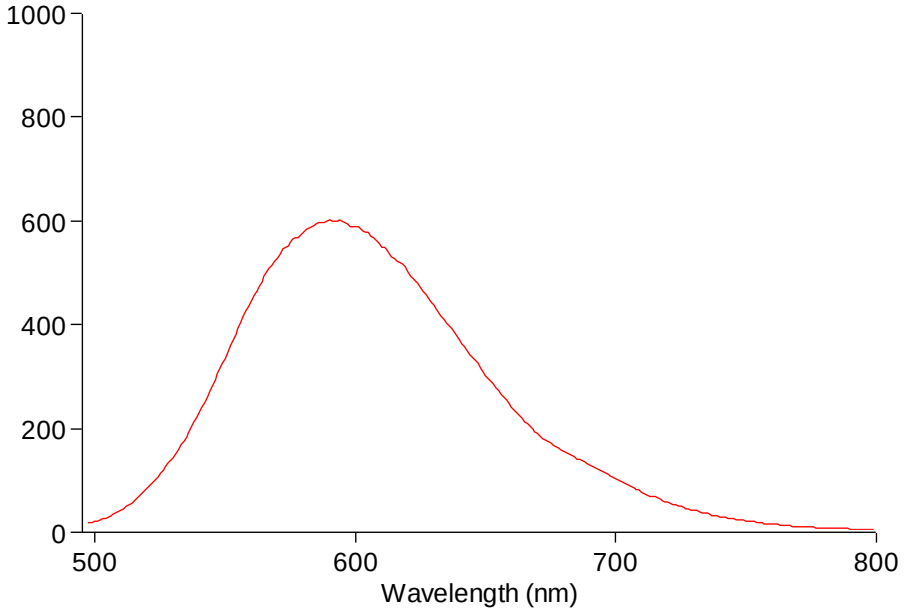

Figure 3.44 Emission spectra of C in ethyl acetate

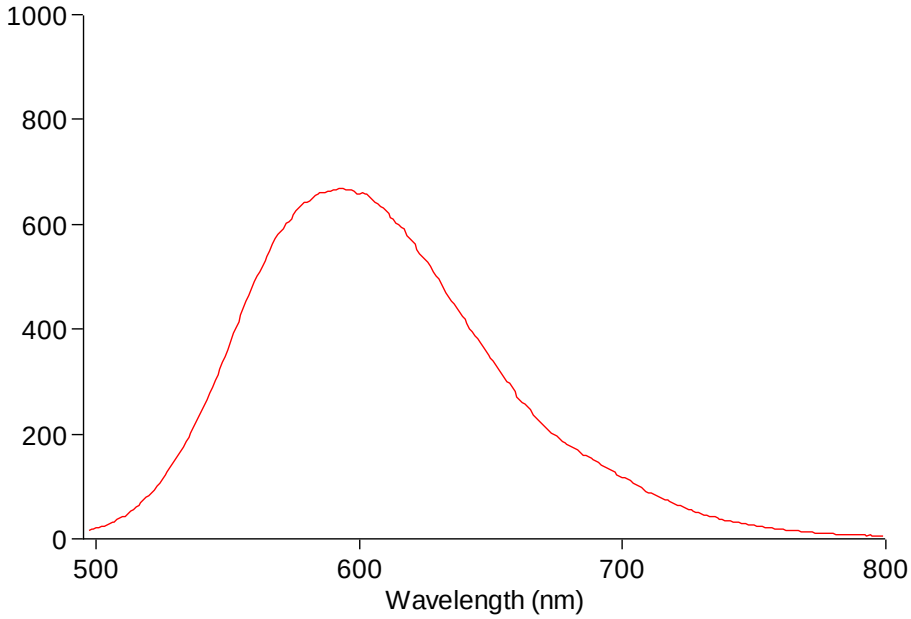

Figure 3.45 Emission spectra of C in tetrahydrofuran

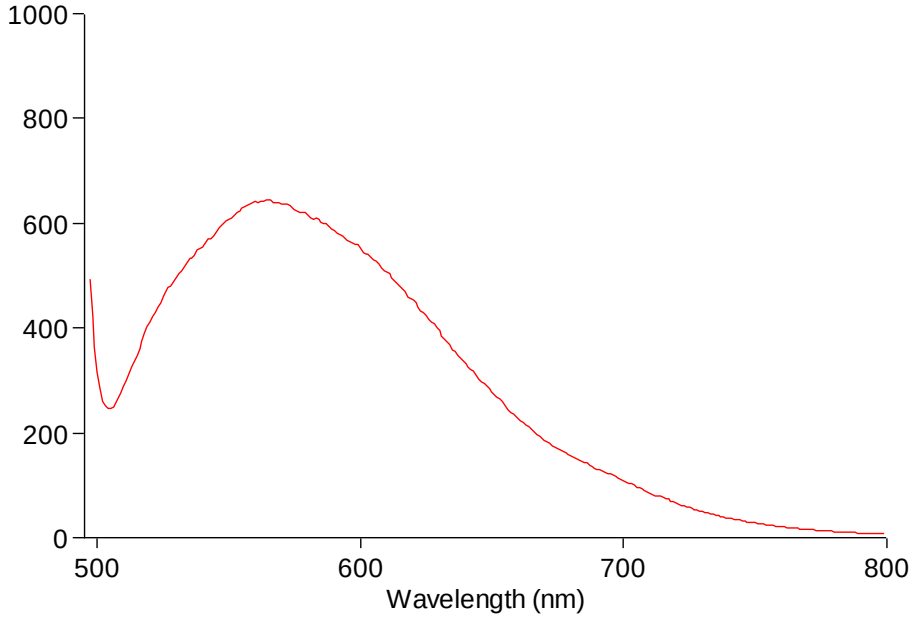

Figure 3.46 Emission spectra of C in ethanol

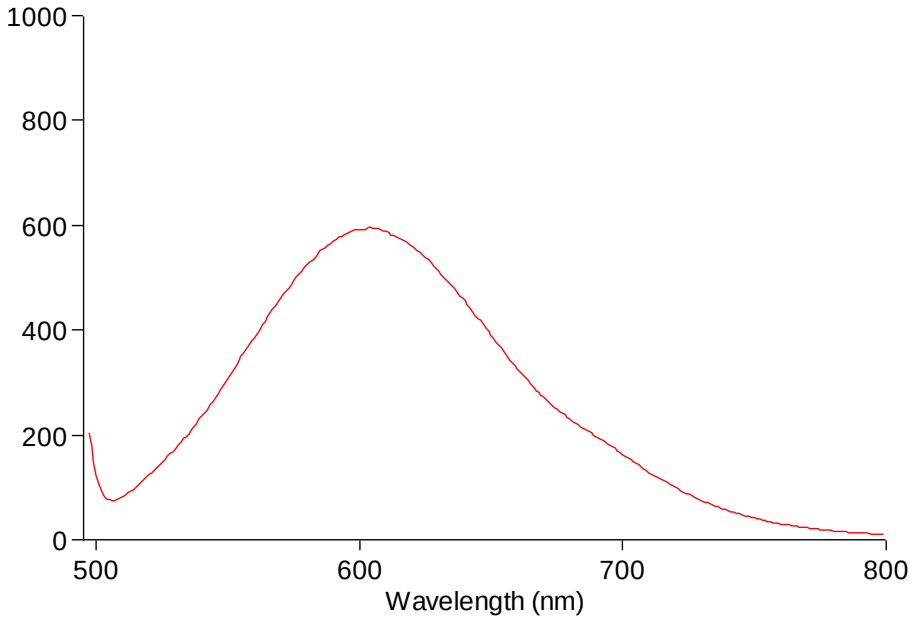

Figure 3.47 Emission spectra of C in dimethylformamide

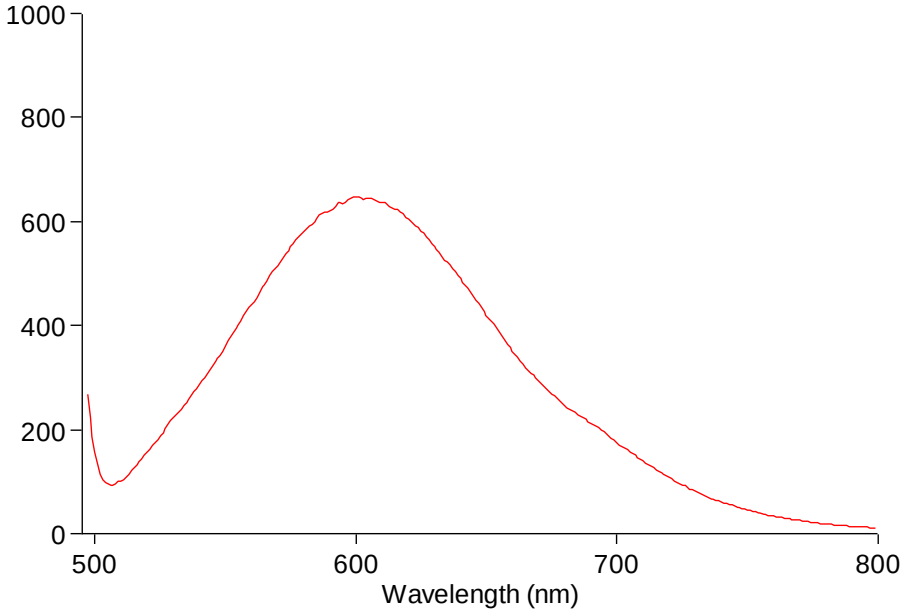

Figure 3.48 Emission spectra of C in acetonitrile

The photostabilities of the derivatives were recorded in seven solvents after 1 h of monitoring and they are shown in Figures given below.

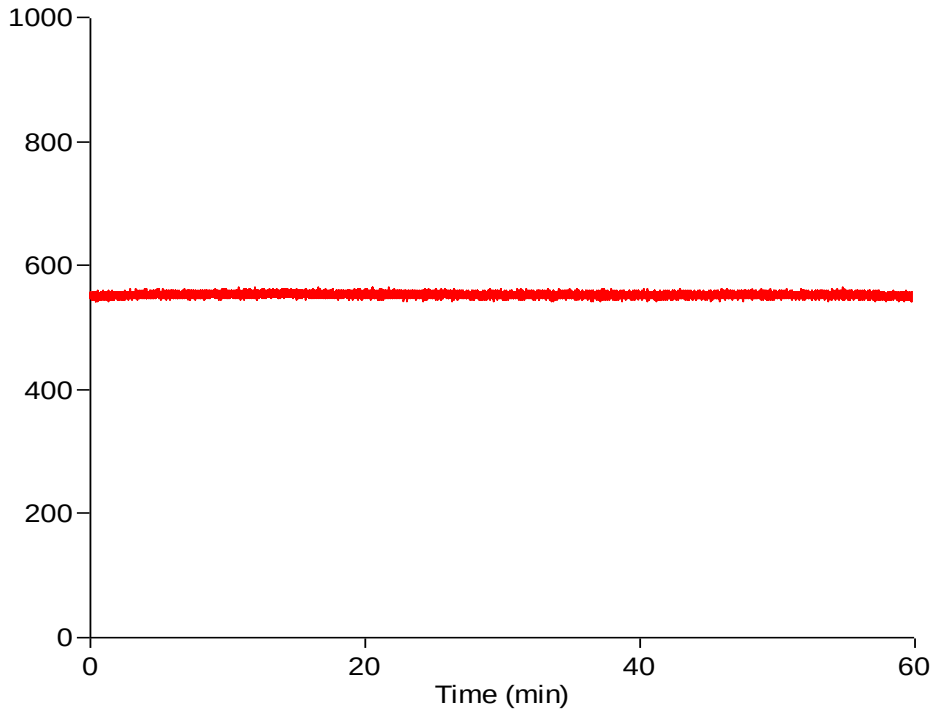

Figure 3.49 The photostability test result of A in toluene

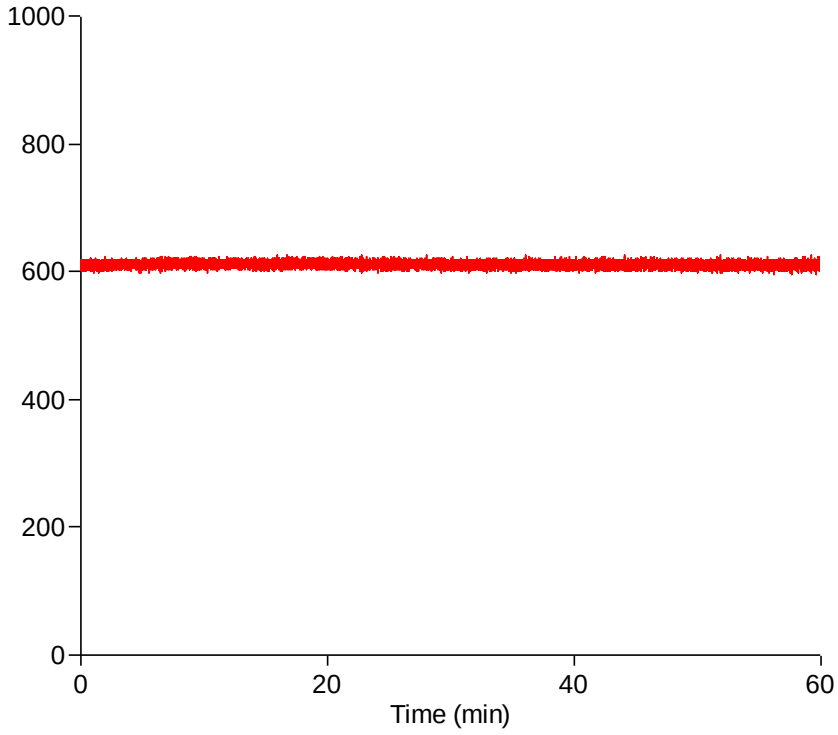

Figure 3.50 The photostability test result of A in chloroform

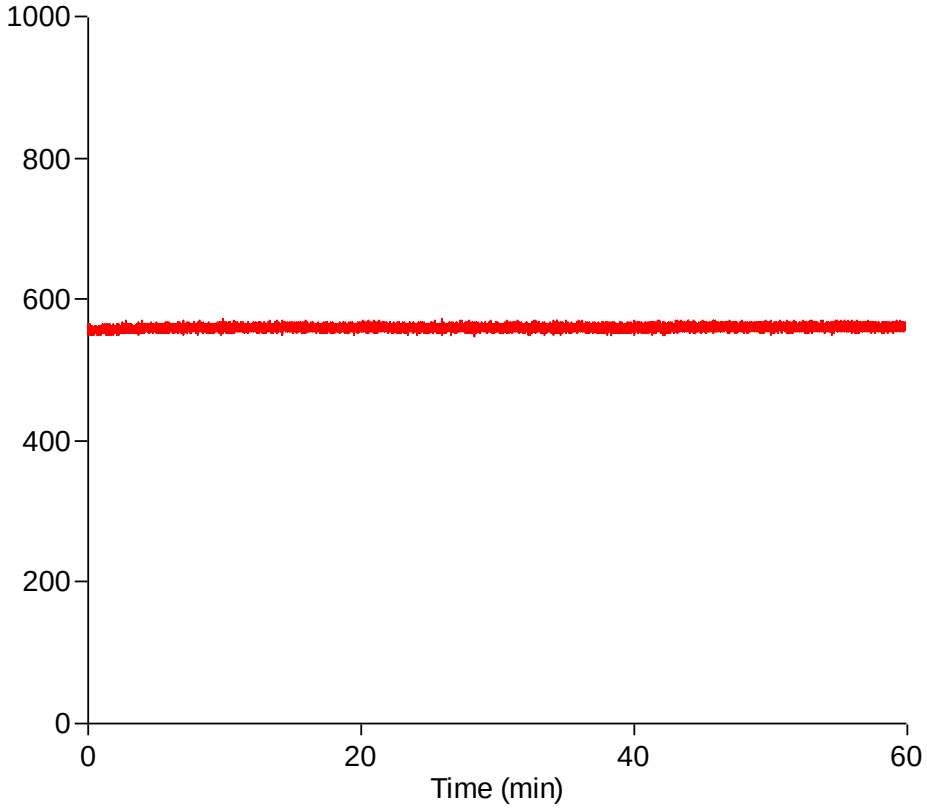

Figure 3.51 The photostability test result of A in ethyl acetate

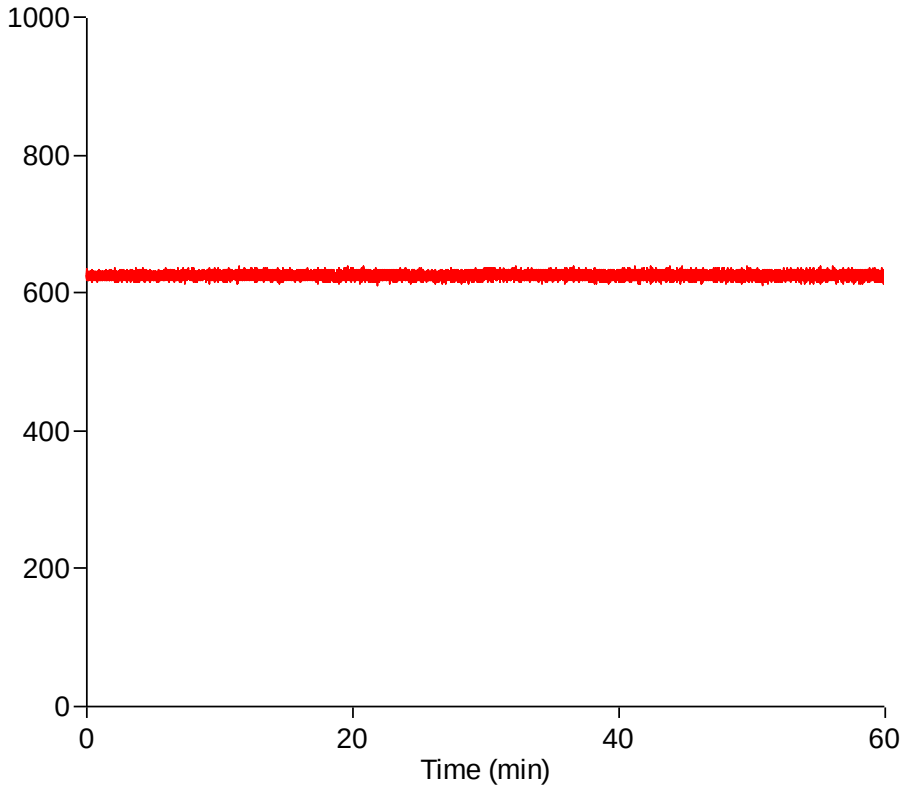

Figure 3.52 The photostability test result of A in tetrahydrofuran

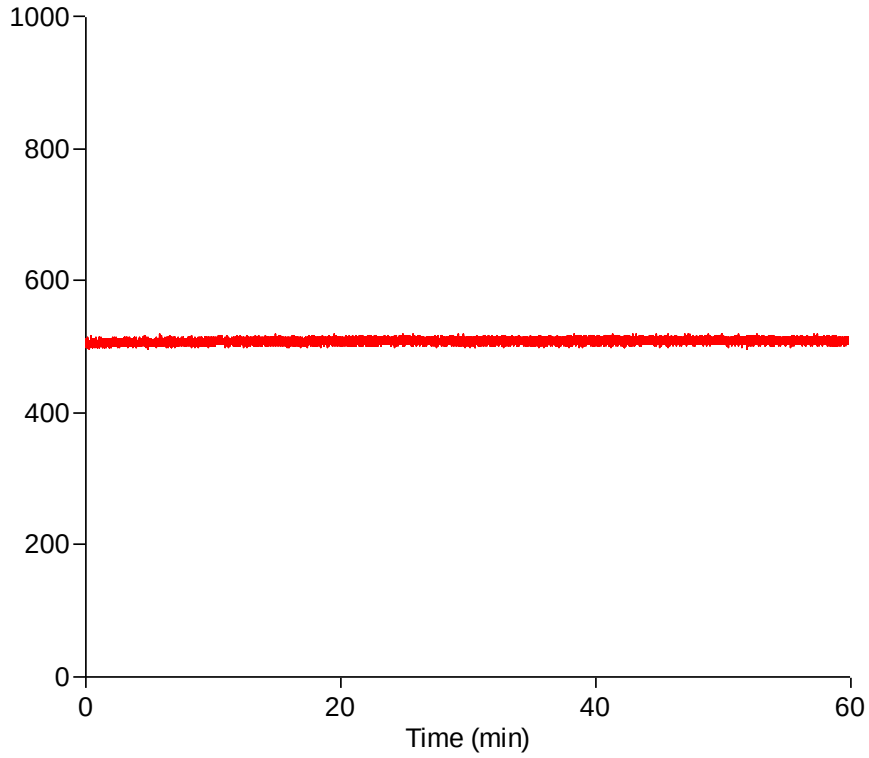

Figure 3.53 The photostability test result of A in ethanol

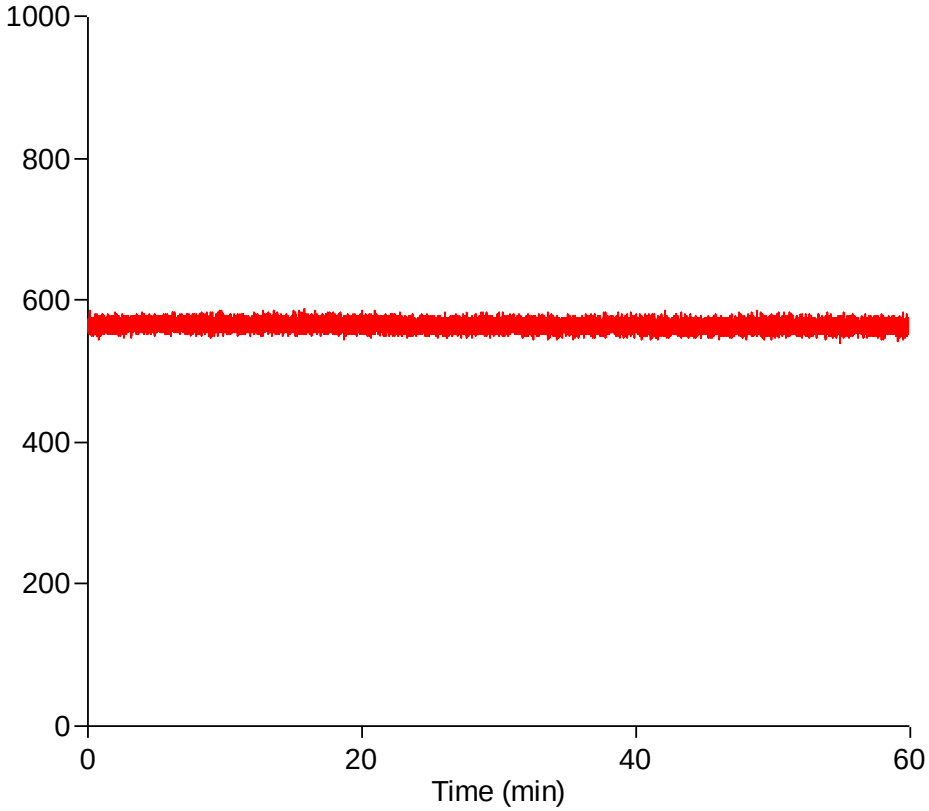

Figure 3.54 The photostability test result of A in dimethylformamide

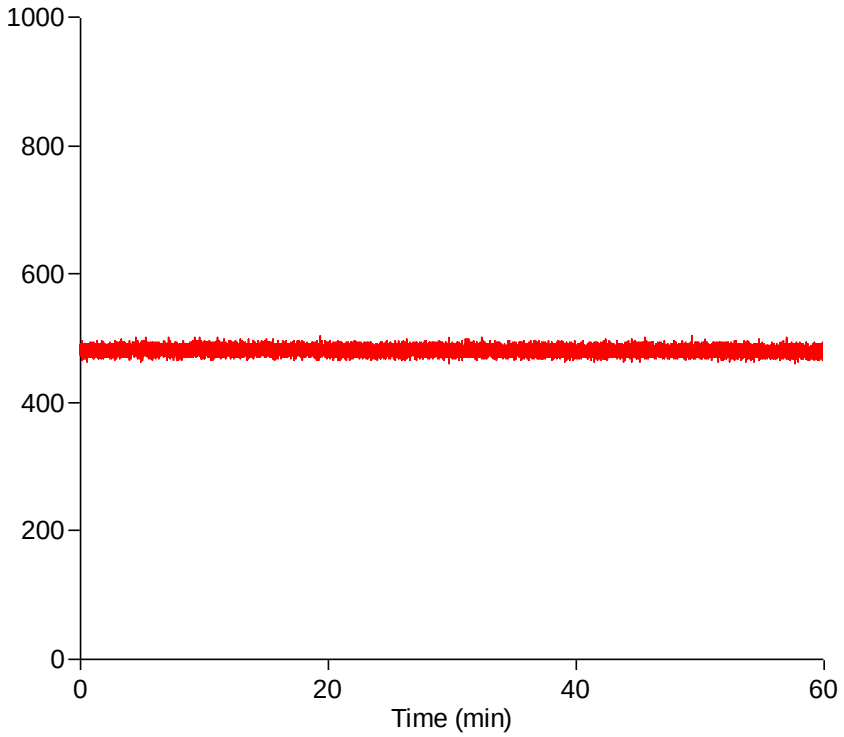

Figure 3.55 The photostability test result of A in acetonitrile

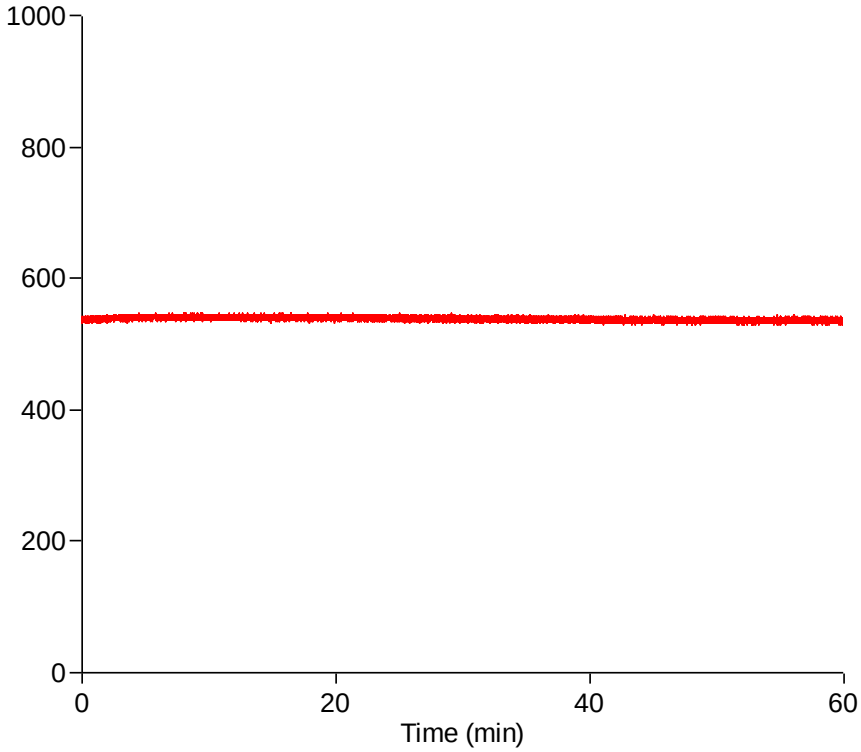

Figure 3.56 The photostability test result of B in toluene

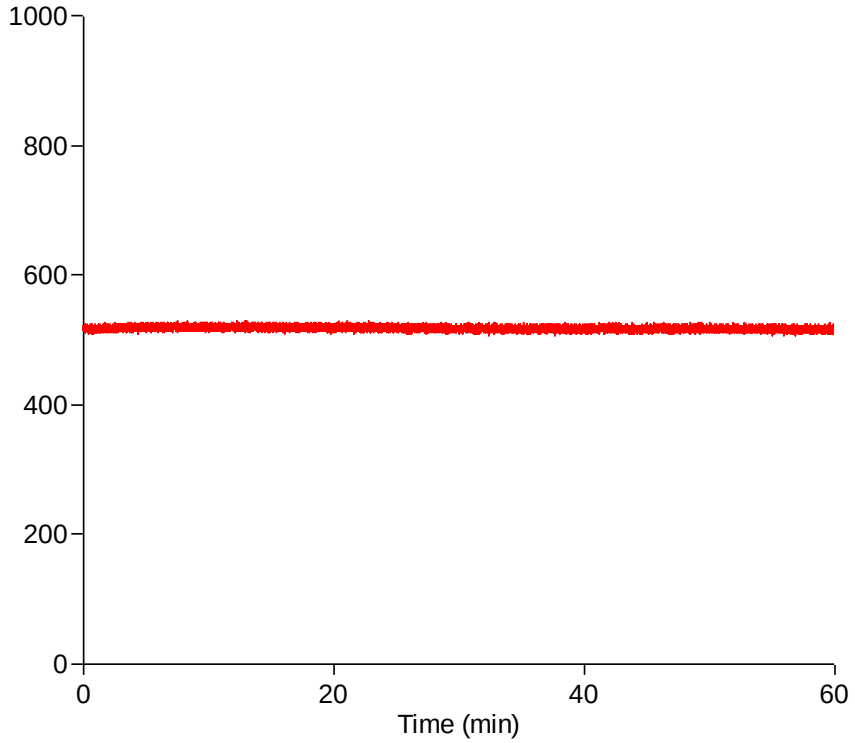

Figure 3.57 The photostability test result of B chloroform

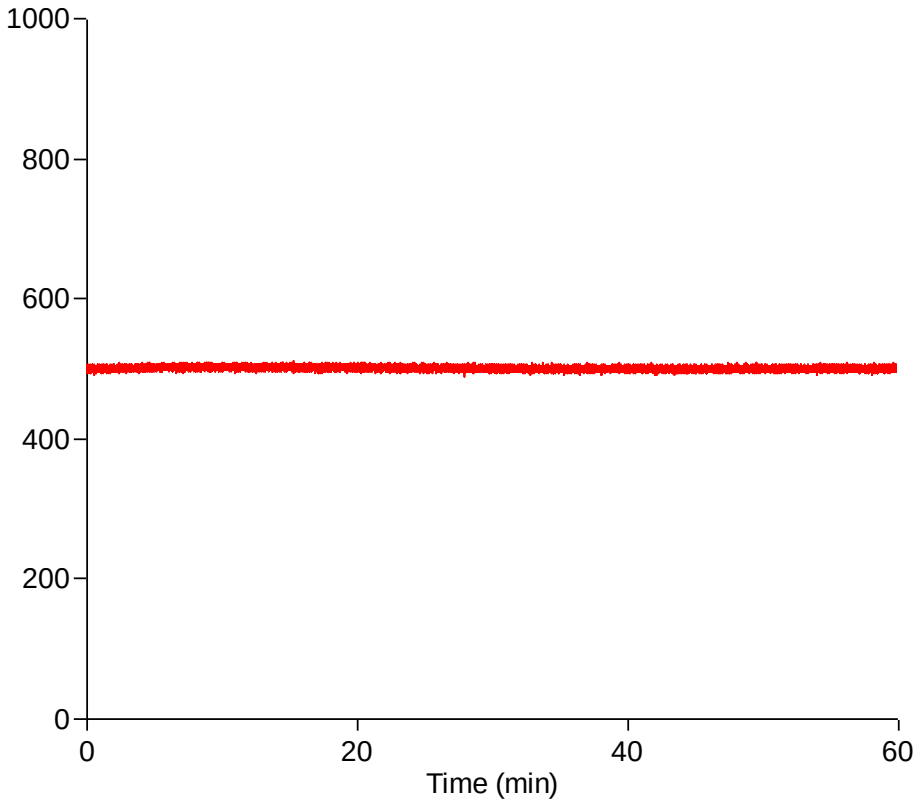

Figure 3.58 The photostability test result of B ethyl acetate

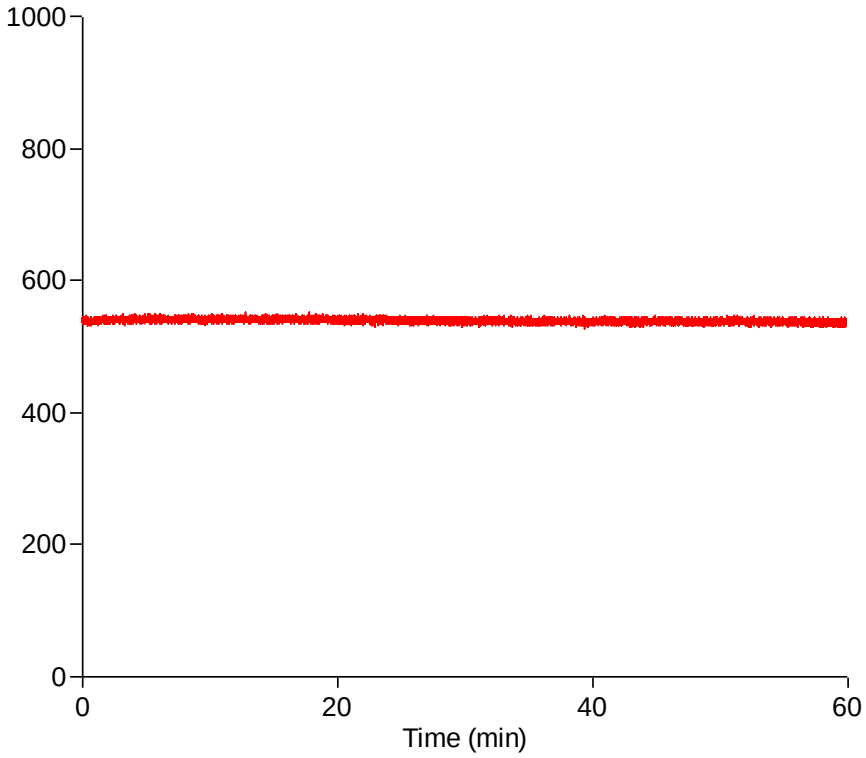

Figure 3.59 The photostability test result of B tetrahydrofuran

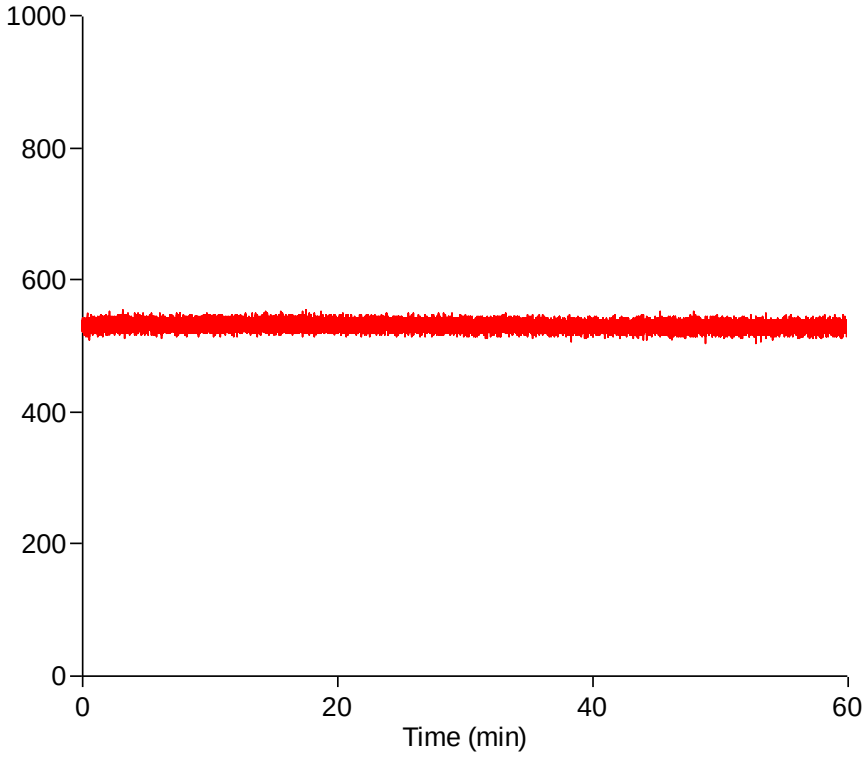

Figure 3.60 The photostability test result of B ethanol

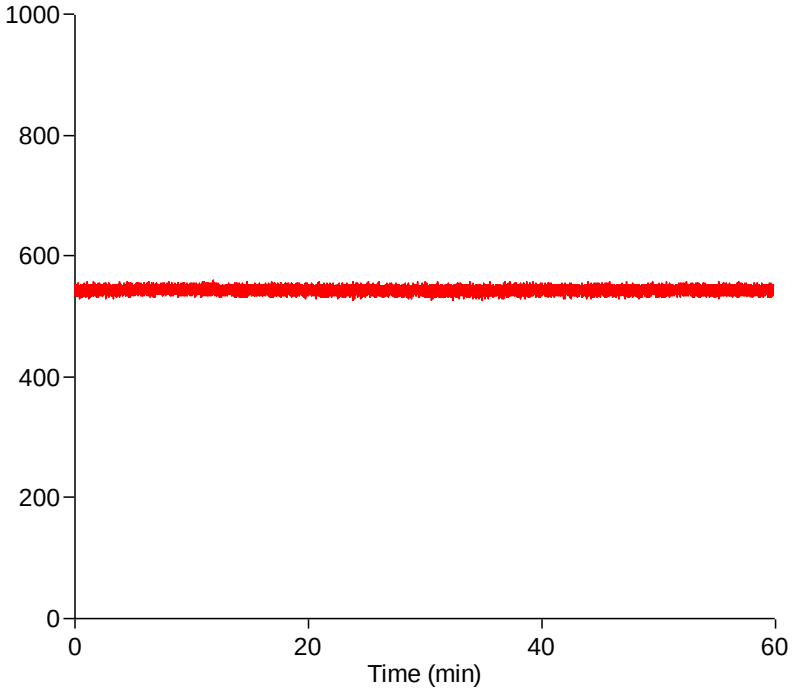

Figure 3.61 The photostability test result of B dimethylformamide

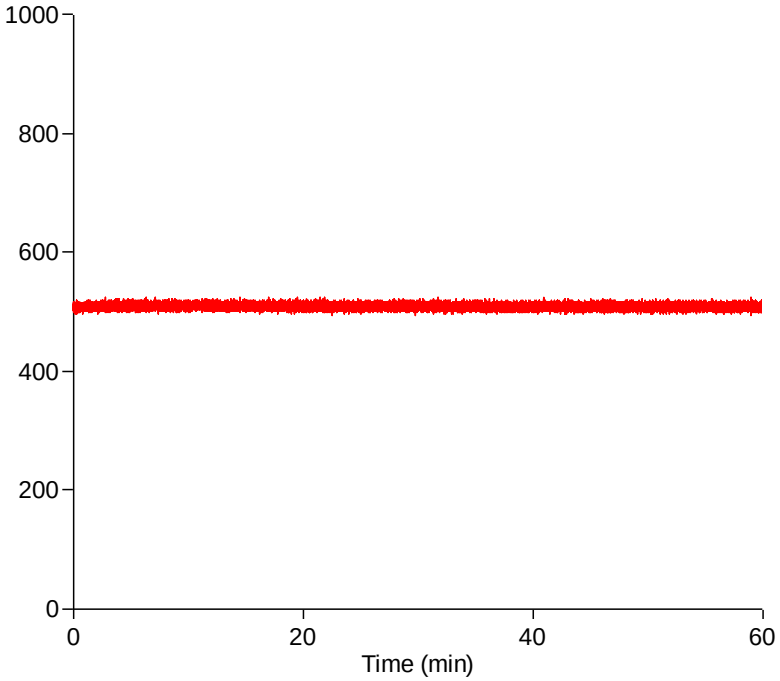

Figure 3.62 The photostability test result of B acetonitrile

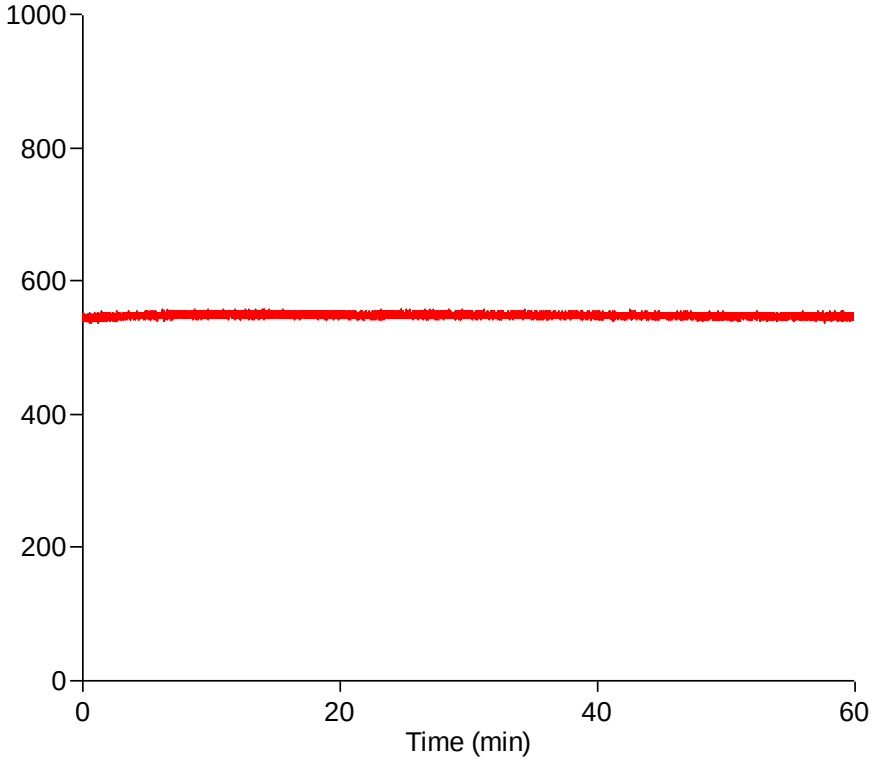

Figure 3.63 The photostability test result of C in toluene

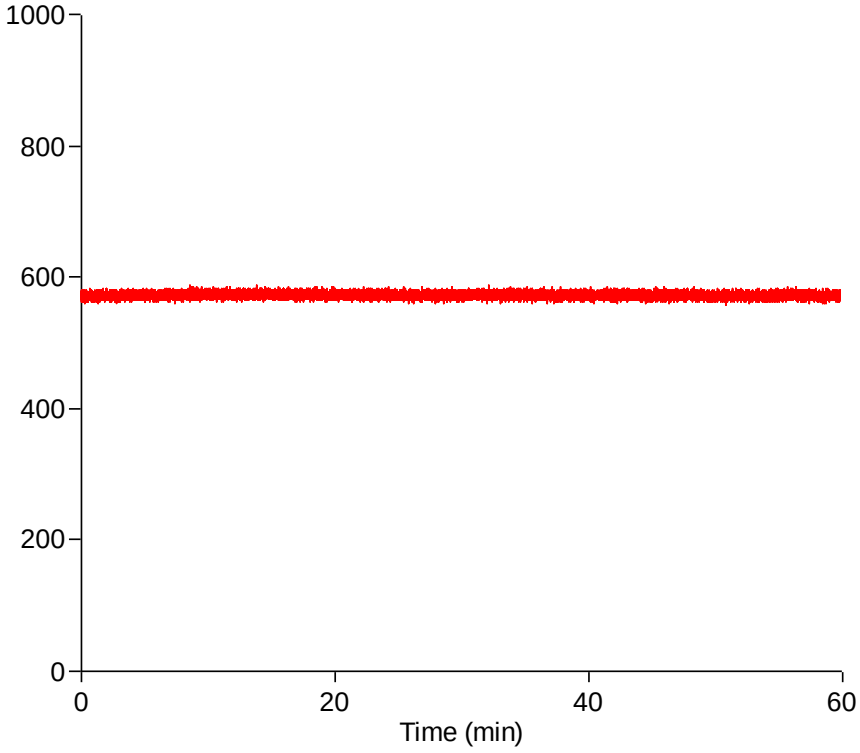

Figure 3.64 The photostability test result of C in chloroform

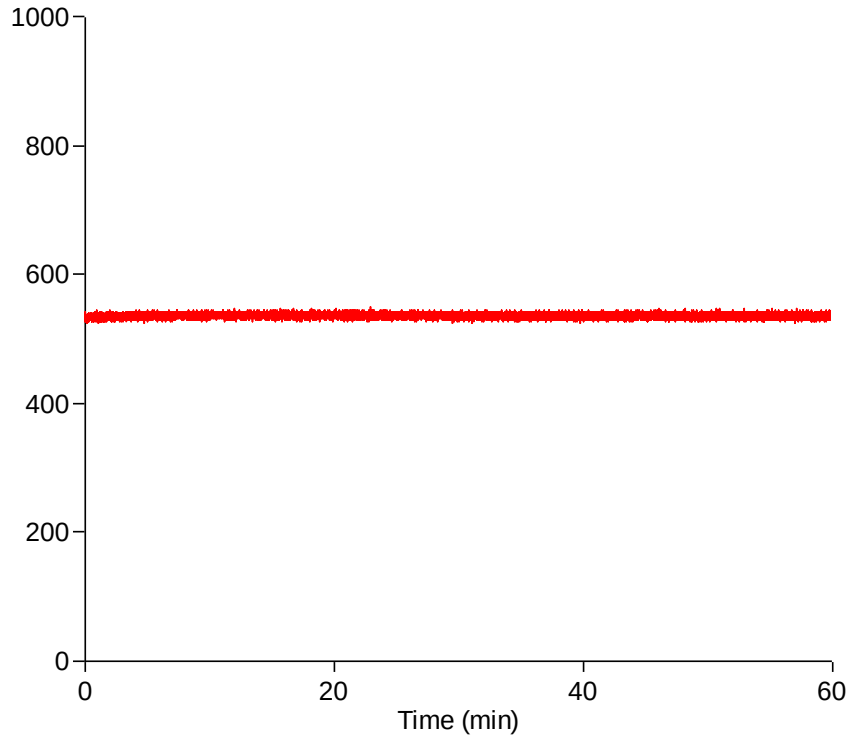

Figure 3.65 The photostability test result of C in ethyl acetate

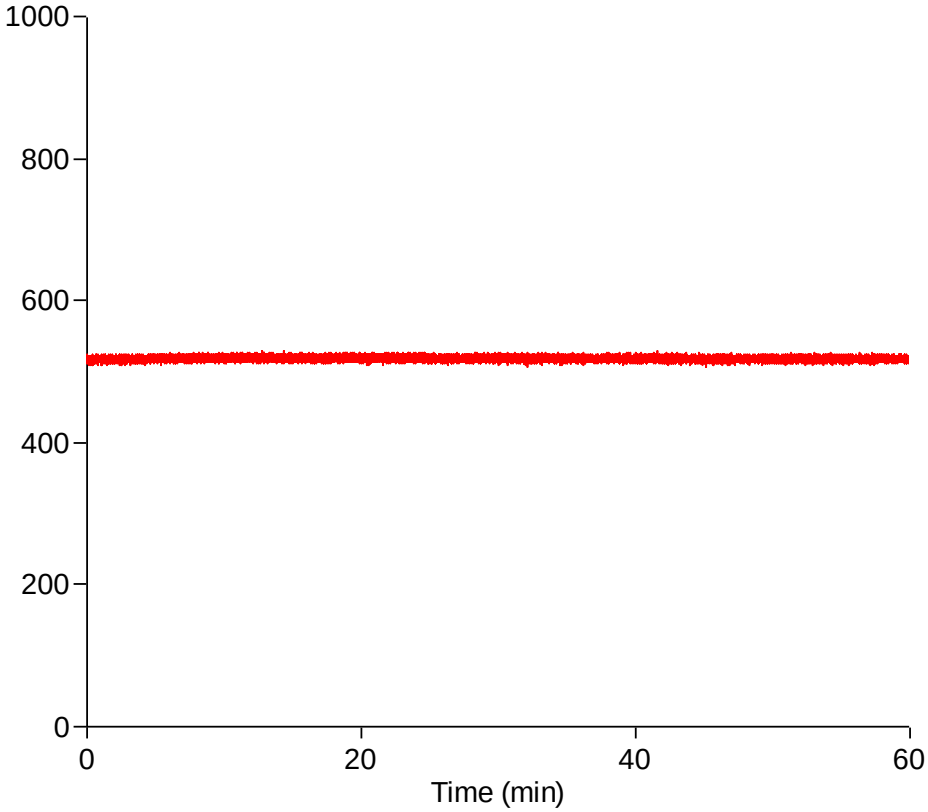

Figure 3.66 The photostability test result of C in tetrahydrofuran

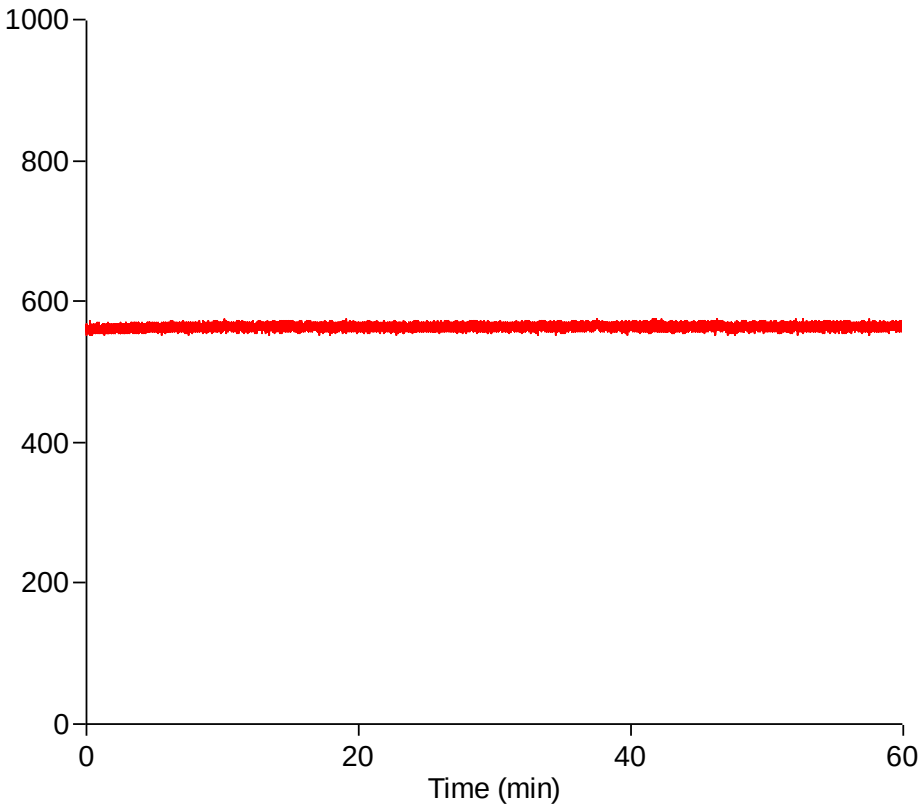

Figure 3.67 The photostability test result of C in ethanol

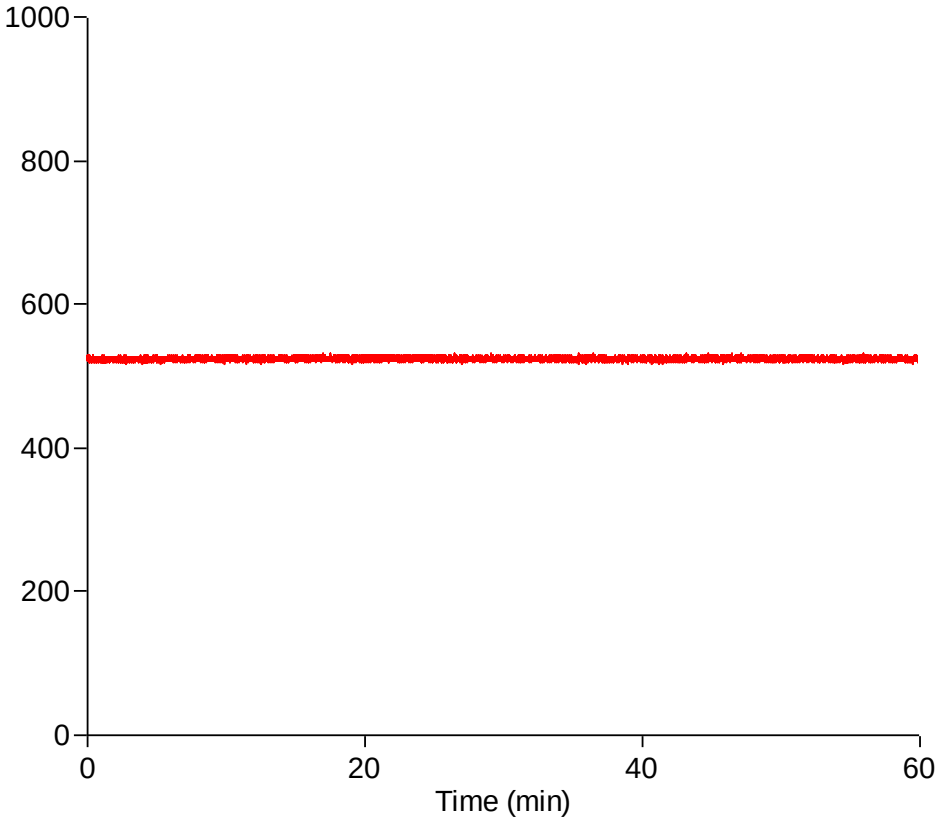

Figure 3.68 The photostability test result of C in dimethylformamide

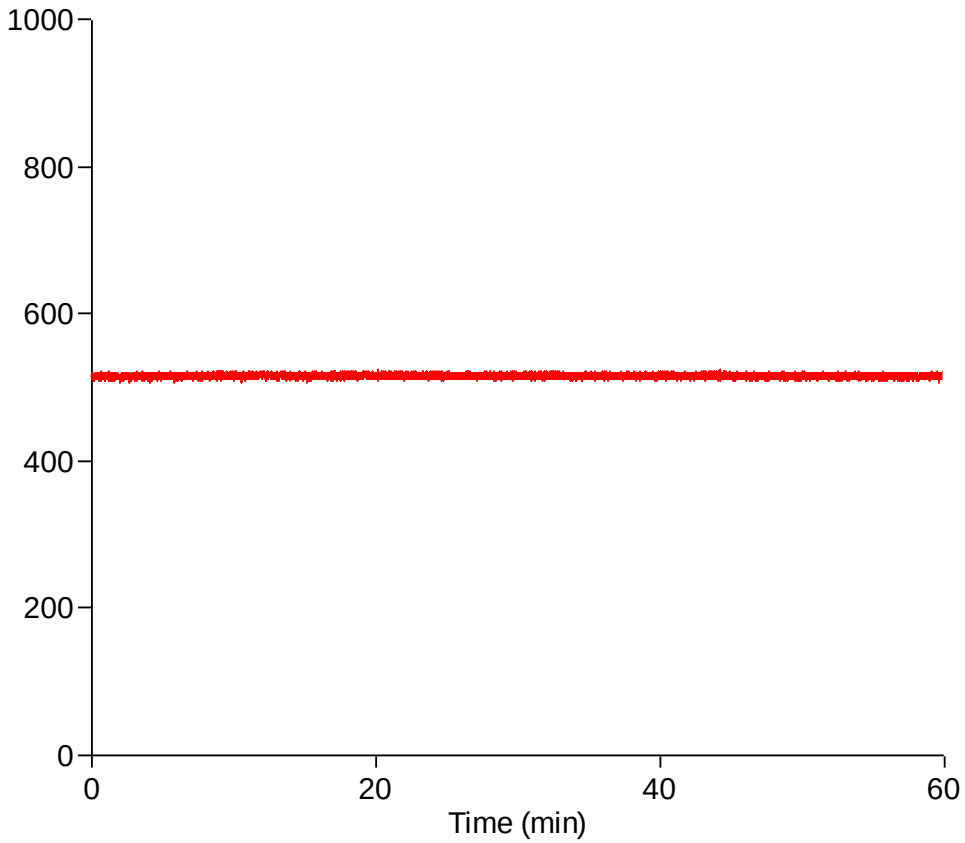

Figure 3.69 The photostability test result of C in acetonitrile

CHAPTER FOUR
CONCLUSION

In this work three new acenaphthoimidazole derivatives A, B and C which are containing imidazole core have been synthesized. The synthesized products were purified using recrystallization and chromatographic methods. The synthesized A, B and C derivatives after purification were determined to have melting points of A: 377-380 ºC, B: 379-382 ºC and C: 332-335 ºC.

Structural determinations and characterizations of the synthesized compounds are given in the tables obtained by FTIR and ^{1}H-NMR spectroscopic techniques.

From FT-IR results we can see the characteristic bands in these ranges. For compound A, the =C−H bands at 3054 cm^{-1}, −C=N – bands at 1694 cm^{-1}, and the −C−N − at 1279 cm^{-1}. For compound B, the =C−H bands at 3048 cm^{-1}, −C=N – bands at 1690 cm^{-1}, −C−N –bands at1280 cm^{-1}, −C−O bands at 1229 cm^{-1} and the −C−H bands at 2929 cm^{-1}. For compound C, =C−H bands at 3049 cm^{-1}, −C ≡N bands at 2227 cm^{-1}, −C=N – bands at 1675 cm^{-1}, −C−N − bands at 1275 cm^{-1}.

The ^{1}H-NMR spectral data of compounds recorded in $CDCl_3$ is in agreement with the structures which reveals the molecules.

The photophysical parameters of the synthesized compounds were determined by UV-vis absorption and emission spectroscopic methods in various solvents.

The absorption and emission spectra of derivatives A, B and C were recorded in seven solvents of: toluene (TOL), dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (EA), acetonitrile (ACN), chloroform and N, N-dimethylformamide (DMF) with different polarity and the spectral properties such as maximum absorption wave length, maximum emission wavelength, Stokes' shift values, molar extinction coefficients and singlet energies are summarized in Table 3.18.

The molecules absorption bands were observed in the visible region between 473-490 nm. The emission maxima of the derivatives were determined between 584-606 nm. The longest emission maximum was observed for compound A in dimethylformamide and acetonitrile. As the polarities of solvents increased from toluene to acetonitrile the absorption maxima of compounds are blue shifted while the fluorescence emission maxima of the compounds are red shifted except for ethanol. The deviation of emission and absorption maxima trend in ethanol in comparison to the other polar solvents could be attributed to being different in nature than other polar solvents, i.e. being polar protic solvent while the other polar solvents are polar aprotic. Stokes' shift values increases as the solvent polarity increases except for ethanol presumably due to the same factor. The highest Stokes' shift value was observed as 129 nm for compound A in acetonitrile.

The photostability of A, B and C compounds were recorded after 1 h of monitoring in seven different solvents of toluene, dichloromethane, tetrahydrofuran, ethyl acetate, acetonitrile, chloroform and dimethylformamide. The data were acquired at their maximum emission wavelengths and all of derivatives exhibited excellent photostabilities.

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