BOLU ABANT IZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF CHEMISTRY

# SYNTHESIS OF SOME NANO DISPERSE DYES AND THEIR DYEING CHARACTERISTICS ON POLYESTER FABRICS

MASTER OF SCIENCE

ABDULHADİ ÖZTEKİN

BOLU, JUNE 2019

# APPROVAL OF THE THESIS

**SYNTHESIS OF SOME NANO DISPERSE DYES AND THEIR DYEING CHARACTERISTICS ON POLYESTER FABRICS** submitted by **Abdulhadi ÖZTEKİN** in partial fulfillment of the requirements for the degree of **Master of Science** in **Department of Chemistry, The Graduate School of Natural and Applied Sciences of BOLU ABANT IZZET BAYSAL UNIVERSITY** in **12/06/2019** by

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To my family

# DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Abdulhadi ÖZTEKİN

# ABSTRACT

## SYNTHESIS OF SOME NANO DISPERSE DYES AND THEIR DYEING CHARACTERISTICS ON POLYESTER FABRICS

**MSC THESIS**
**ABDULHADİ ÖZTEKİN**
**BOLU ABANT IZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**
**DEPARTMENT OF CHEMISTRY**
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**BOLU, JUNE 2019**

Disperse dye molecules are small, planar, non-ionic with attached polar functional groups, so they have poor water solubility while interaction with polymer structures over weak-moderate intermolecular forces. Due to their compatibility with hydrophobic fibers (e.g. polyester, nylon), disperse dyestuffs have been used in dyeing of many synthetic fabrics in dye related researches since 1950s and they were traditionally applied to synthetic fibers at different temperatures in the dyebath. However, for last twenty years, intense efforts on dyeing the variety of textile fabrics were given by the nanotechnology, ultrasonication or microwave applications. Since dyeing with nanoscale dyestuffs decreased the amounts of dye needed to dye the same size of textile fabric and exhibited much better color shades or properties on the synthetic fabrics.

Due to such advantages of nanocolorants, the preparation of new nano disperse dyes and the investigation of their dyeing performance in traditional way and nanoscale forms on polyester fabrics comparatively were aimed to perform in the present study. To achieve these goals, in the first part of the study, *β*-dimethylamino *p*-arylpropenone and aryldiazonium tetrafluoroborate precursors were prepared and isolated in good yields. Then, their structures were determined by IR and NMR analyses.

In the second part of the work, arylpropenone-based disperse dyes were efficiently prepared through diazo coupling reactions of new *β*-(dimethylamino)arylpropenones with diazonium tetrafluoroborate salts under slightly basic conditions. The structures of dyestuffs were fully characterized by IR, NMR and HRMS analyses.

In the last part of the study, dyeing and fastness properties of new arylpropenone dyes were studied using standard and nanoemulsion forms of the dyes on polyester fabric samples. A color range from beige to orange were obtained on polyester fabrics with standard and nanodyestuffs. In general, dyeing with nanodyestuffs imparted much deeper color shades. Washing, water, acidic-basic perspiration and rubbing fastnesses of dyed polyester fabric samples were mostly obtained good to excellent, however, light and sublimation/staining fastnesses of same polyester fabric samples dyed with disperse dyestuffs were obtained in satisfactory levels.

**KEYWORDS:** Enaminone, nanodisperse dye, nanoemulsion, dyeing, fastness.

# ÖZET

## BAZI NANODİSPERS BOYARMADDELERİN SENTEZİ VE POLYESTER KUMAŞLAR ÜZERİNDEKİ BOYAMA ÖZELLİKLERİ
YÜKSEK LISANS TEZI
ABDULHADİ ÖZTEKİN
BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
KIMYA ANABILIM DALI
(TEZ DANIŞMANI:DOÇ.DR.MUHAMMET YILDIRIM)

BOLU, HAZİRAN - 2019

Dispers boya molekülleri üzerlerindeki polar gruplarla birlikte, küçük, düzlemsel ve noniyoniklerdir, bu nedenle zayıf-orta kuvvette moleküllerarası çekimlerle polimerlerle etkileşirken suda düşük çözünürlükleri vardır. Hidrofob fiberlerle (polyester, naylon) uyumluluklarından dolayı, dispers boyarmaddeler, 1950lerden beri, boya ile ilgili araştırmalarda çeşitli sentetik kumaşların boyanmasında kullanılmışlar ve geleneksel olarak, boya banyoları içerisinde farklı sıcaklıklarda sentetik fiberlere uygulanmışlardır. Bununla birlikte, son 20 yılda, nanoteknoloji, ultrases veya mikrodalga uygulamarıyla çeşitli tekstil ürünlerinin boyanması için yoğun çabalar harcanmıştır. Çünkü nanoölçekli boyarmaddeler, aynı ölçüdeki tekstil ürününü boyamak için gerekli olan boya miktarını düşürmekte ve sentetik ürünler üzerinde daha iyi renk derinlikleri ve özellikleri göstermektedir.

Nanorenklendiricilerin bu tür avantajlarından dolayı, bu çalışmada yeni nanodispers boyaların hazırlanması ve polyester kumaşlar üzerinde karşılaştırmalı olarak geleneksel şekilde ve nanoboyutta boyama performanslarının araştırılması amaçlanmıştır. Bu hedeflere ulaşmak için, çalışmanın ilk kısmında, *β*-dimetilamino *p*-arilpropenon ve arildiazonyum tetrafloroborat başlangıç maddeleri hazırlanıp iyi verimlerde izole edilmiştir. Daha sonra, yapıları IR ve NMR analizleriyle belirlenmiştir.

Çalışmanın ikinci kısmında, arilpropenon-bazlı dispers boyalar, *β*-(dimetilamino)arilpropenonların diazonyum tetrafloroborat tuzlarıyla diazo kenetlenme reaksiyonlarıyla hafif bazik koşullarda etkili şekilde hazırlanmıştır. Boyarmaddelerin yapıları, IR, NMR ve HRMS analizleriyle tam olarak karakterize edilmiştir.

Çalışmanın son kısmında, yeni arilpropenon boyaların standart ve nanoemulsiyon çözeltileriyle, polyester kumaşlar üzerinde boyama ve haslık özellikleri çalışılmıştır. Standart ve nanoboyarmaddelerle, polyester kumaşlar üzerinde bej-turuncu renk tonları elde edilmiştir. Genellikle, nanoboyarmaddelerle yapılan boyamalar daha koyu renk tonları vermiştir. Boyanan polyester kumaş örneklerinin, yıkama, su, terleme (asidik-bazik) ve sürtünme haslıkları iyi-mükemmel seviyede elde edilmiş, fakat, aynı örneklerin ışık ve süblimleşme/lekelenme haslıkları orta seviyede elde edilmiştir.

**ANAHTAR KELİMELER:** Enaminon, nanodispers boya, nanoemülsiyon, boyama, haslık.

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# LIST OF ABBREVIATIONS AND SYMBOLS

**Ac** : Acetate
**AcOH** : Acetic acid
**Ar** : Aryl
**ATR** : Attenuated total reflectance
**BDC** : British Dyestuff Corporation
**$BOD_5$** : Biological oxygen demand (5-day)
**CC** : Column chromatography
**$CDCl_3$** : Deuterated chloroform
**$CF_3$** : Trifluoromethyl
**Cl** : Chloro
**CMC** : Critic micelle concentration
**COD** : Chemical oxygen demand
**COOH** : Carboxy
**DCM** : Dichloromethane
**DMF** : N,N-dimethyformamide
**DMF-DMA** : Dimethylformamide dimethyl acetal
**DMSO-$d_6$** : Deuterated dimethylsulfoxide
**ED** : Electron-donating
**equiv.** : Equivalent
**EtOAc** : Ethyl acetate
**EtOH** : Ethanol
**EW** : Electron-withdrawing
**FTIR** : Fourier transform infrared
**g** : Gram
**h** : hour
**$HBF_4$** : Tetrafluoroboric acid
**HRMS** : High resolution mass spectrometry
**hυ** : Light energy
**ICI** : International color index
**IR** : Infrared
**J** : Coupling constant
**KBr** : Potassium bromide
**$LC_{50}$** : Lethal concentration (%50)
**$LD_{50}$** : Lethal dose (%50)
**m.p.** : Melting point
**Me** : Methyl
**MHz** : Megahertz
**min** : Minutes
**mmol** : Milimole
**mL** : Mililiter
**MPC** : Polymer concentration method
**NaOAc** : Sodium acetate
**nm** : Nanometer
**NMR** : Nuclear Magnetic Resonance
**$NO_2$** : Nitro
**O/W** : Oil-in-water
**$^{o}C$** : Degree Celsius

**OEt** : Ethoxy
**OH** : Hydroxy
**OMe** : Methoxy
**OPh** : Phenoxy
**PET** : poly(ethylene terephthalate)
**Ph** : Phenyl
**ppm** : Parts per million
**R** : Radical group
**rpm** : Rotation per minute
**RT** : Room temperature
**SLS** : Sodium laurylsulfate
**$SO_3H$** : Sulfonic acid
**SRA** : Sulpho ricinoleic acid
**TLC** : Thin-layer Chromatography
**TMS** : Tetramethyl silane
**TOF** : Time of flight
**UV** : Ultraviolet
**w/w** : weight/weight
**δ** : Chemical shift

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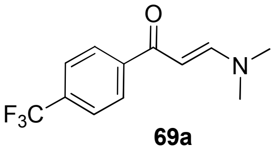
# FORMULAE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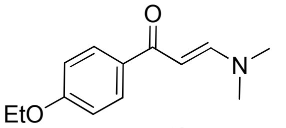
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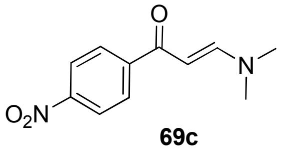
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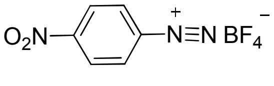
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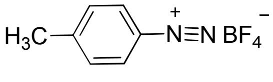
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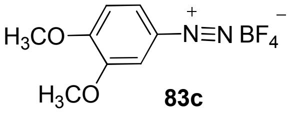
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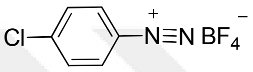
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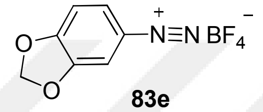
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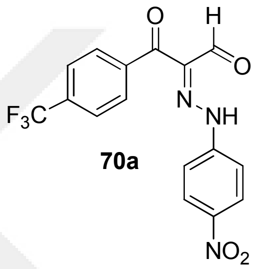
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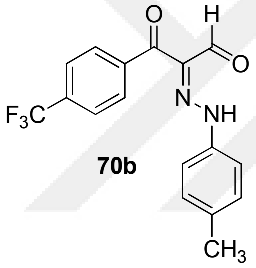
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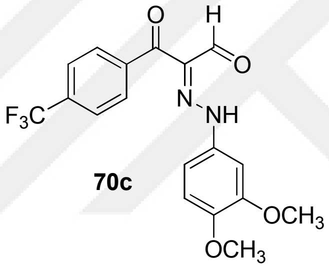
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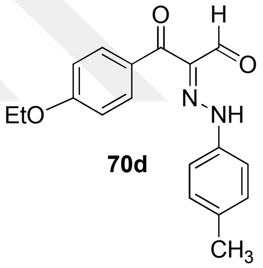
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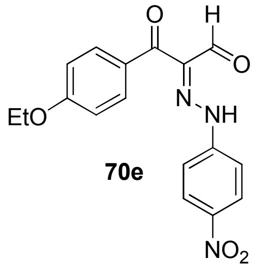
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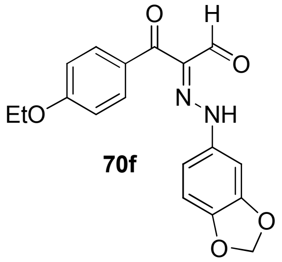
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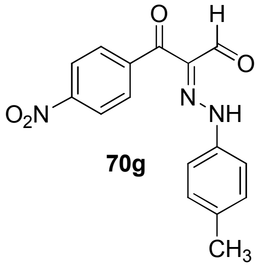
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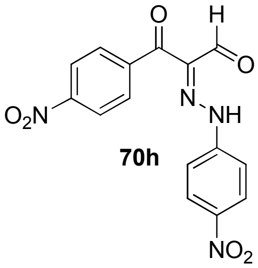
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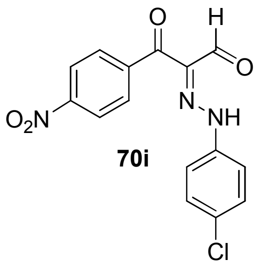
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# 1. INTRODUCTION

Textile initially appeared as a need but then it turned into art and science with the development of human intelligence. Dyestuffs and dyeing technologies have been developed regarding the structure of fibers which are mostly hydrophobic.

Until the mid-1950s, all classical fabrics were dyed in aqueous solutions containing dyestuffs in classical dye baths. Newer synthetic fabrics, such as cellulose acetate, are often not dyed in aqueous solutions due to their hydrophobic nature. However, after 1920s, these type synthetic fabrics was able to be dyed by the invention and use of disperse dyestuffs (Broadbent,2001). In 1922, BDC produced the neutral or basic ionic dyestuffs containing the hydroxyl and amino groups, and this provided dyeing of synthetic fibers (Green & Saunders, 1923). The dyestuffs bearing soluble ionic groups (SRA, Duranol) were produced by different companies and then they were inspired by the properties of dyes such as ionamine. Synthetic fabrics (nylon, acrylic and polyester) have been widely used in dyeing in the beginning of 1950 (Burkinshaw, 1995). Thus, effective use of disperse dyestuffs in dyeing synthetic fabrics and dye-related researches have begun.

## 1.1 DISPERSE DYES

### 1.1.1 Chemical and Physical Properties of Disperse Dyes

The general structure of disperse dye molecules is small, planar and non-ionic, with attached polar functional groups (hydroxyalkyl, nitro and cyano). This shape of the dye cause an easy interaction of it with tightly packed synthetic polymer chains, and also the polar groups provide water solubility and dipolar interaction between dye and polymer, as well as influencing the shade of dye. These interactions between dye and polymer structures are mostly the weak intermolecular forces such as van der Waals and dipole-dipole. Owing to such characteristics of disperse dyestuffs, they are especially used for dyeing of hydrophobic fibers (polyester, nylon, acetate).

Since the disperse dye particles have a very small particle size (≤1 μm) and also have a low molecular weight (400-600 g / mol), this will provide a larger surface area which helps dissolution to allow uptake by the synthetic fiber. Because the dye particles show dispersion on the surface of the surfactants, their names are called **disperse dyes** (Ingamells, 1993). In general, disperse dyes do not have water-soluble groups and genarally they can be substituted with azo, anthraquinone and diphenylamino groups.

Disperse dyestuffs are usually prepared by milling the press cake with an equal amount of an auxiliary agent and small amount of water. Then this mixture is dried and mixed with suitable diluents to obtain a commercial product having 15-40% dye. The choice of dispersing agent used while the grinding will affect the dyeing rate significantly.

Disperse dyes usually have a density of 0.4-0.6, pH value of 7-9, COD about 1-2g $O_2$/g, $BOD_5$ about <0.01– 0.05g $O_2$/g, $LC_{50}$ (rainbow trout) of >100 mg/L for 96 h and $LD_{50}$ of >2-5g/kg.

The solubility of these dyes are mostly linked with the polar groups such as amino, hydroxyethylamino, azo, carbonyl in the dye molecule, since the groups have electronegative atoms (N,O,S) interacting with water molecules strongly. Sometimes, aromatic rings in the absence of such atoms can also have strong interactions water molecules and this alters the solubility of dyes (Jones, 1984).

Birch (1954) stated that aqueous solubility of dyes are related with the dyeing rate of disperse dyes and it affects their levelling power mostly. Also, the inclusion of dispersing agents support dye solubilization, especially above the CMC of the agent. In some studies, the solubility of the dyes was found in a range of 5-30 mg/L between 25-90°C, however, in some other studies, the solubility of dyes have been tested by pressure filtration, MPC and titration between 60-140°C and they were found between 3.3-419 mg/L (Datyner, 1978; Přikrylet al., 1979; Braun, 1991).

In addition, the solubilization rate of the dye can also affect the dyeing rate of disperse dyes (Odvárka & Huková, 1983) and also, disperse dye particles under 1 µm size create unstable colloids entering the solution (Braun,1983). Moreover, degree of crystallinity are effective on the solubility of the dyes (Cyung et al., 2001). The particle size of disperse dyes also affect the dyeing properties of the dye molecules which were investigated in many studies. Besides, different crystalline properties of disperse dyes cause many different dispersion behaviours and this effect on dyeing performance of dyes were demonstrated by many reports in literature (Leube, 1978; Apperley, 1969; Biedermann, 1971; Shenai & Sadhu, 1976). Ultrasonication can reduce the particle size and crystallinity of dyestuffs and this technique is much more effective on the breaking of fine dye crystals rather than on poor ones (Lee et al., 2001).

### 1.1.2 Constitution and Fastness Properties of Disperse Dyes

In textile industry, strength of disperse dyes after application and the compatibility of the materials they included in terms of health are called **fastness properties**. Many approaches have been made to follow connection between the chemical structure of the dye and its fastness characteristics. But, finding these relationships would be somewhat complicated. Some general things can be identified, however more delicate interactions such as electronic and steric effects make more difficult to understand the essence of fast rules. Recently, some studies to obtain clearer information on this subject showed that the groups of very closely related dyes having minor structural changes had changed their fastness properties. Sufficient fastnesses to light, washing, sublimation, friction, rubbing, and burnt gas fumes, are especially important for disperse dyes (Dawson, 1983; Dawson, 1984).

Disperse dyes are often applied to hydrophobic fibres as a dispersion in aqueous solution (Mock, 2004) and are mostly used on polyester fibers. These dyestuffs should be resistant to different conditions such as pH and temperature, making little change in color shade and light fastness (Aspland, 1992).

Disperse dyes are generally applied to polyester at the boil with a carrier substance in the dyebath to get better diffusion of dye into the polyester fabric.

Moreover, surface active agents can be applied into the dyebaths in order to improve the solubility and stability of the dispersion. As follows, these agents are adsorbed by the surface of dye particle by producing negatively charged surface resulting in the repulsion of the particles. Thus, disperse dyes are solubilized in the micelles of the surface active agents, so a dye dispersion containing the dye solubilised in water is obtained. Ultimately, the dye distributes well between the aqueous phase, the micelle core and surface during the dyeing process (Jones,1984).

In polyester fabrics, high fastness values are desired for washing. Normally, washing and perspiration fastnesses of polyester fabrics dyed with a disperse dye are better than nylon and acetate fabrics. Also, in most applications of disperse dyes to nylon, cellulose acetate and acrylic fibres, the wet-fastness properties of the dyes are poor on these substrates. However, a reduction clear on dyed substrate is usually performed after dyeing in order to clean the substrate surface from dye stains.

Moreover, sublimation fastness of polyester fibers dyed with disperse dyes is an essential parameter due to the thermal applications at the last stage of fabric production, and disperse dye molecules should be as small as possible and non-ionic. For instance, in the ironing, dye molecule may sublimate and cause stains on the fabric (Gordon & Gregory, 1983). When the size and polarity of dye molecule is high, its vapor pressure will be low. Eventually, dye molecule cannot leave the dyed fiber easily and this increase its sublimation (or temperature) fatsness.

ICI system classify the disperse dyestuffs into four main classes using letters A-D regarding their fastness to sublimation and dyeing properties. According to this classification of disperse dyes, Class A dyes have good dyeing characteristics and poor temperature fastness but Class D dyes have weak dyeing characteristics and good temperature fastness (table 1).

**Table 1.1.** Classification of dyes by ICI

| | |
|---|---|
| Class A | low molecular weight, poor sublimation fastness, good dyeing properties |
| Class B-C | Class A and Class D must be among the extreme values |
| Class D | high molecular weight, good sublimation fastness, poor staining properties |

To ensure the Class A characteristics, changes in the amino group, the addition of hydroxyl or acetylamino substitutents to ED ring can be done to increase the temperature fastness of dyestuffs (Hallas, 1979). So that, increasing the number of polar groups that can make more hydrogen bonding will decrease the possibility of sublimation.

When the dyed fabrics are exposed to sunlight for a while, the color shades on the fabrics will fade, this is another important issue of dyestuffs (Zollinger, 1991). The dyestuffs on the dyeing of fabrics should be between the acceptable values in the light fastness scale (1-5). Even though there is a close connection between the light fastness and chemical structure of the dye, some other factors govern this relation. Different groups attached to the main chromophore, concentration of used dyestuff, chemical nature of the fabric fiber and atmospheric conditions (wavelength range of the light, humidity) can be given as examples to these factors (Giles, 1991).

Two other most significant factors affecting the dispersion of dyestuffs are oxidation and reduction reactions. Nonetheless, photooxidation reactions also cause high fading results on dyed polyester and acetate fabrics (Kassim & Peters, 1973). Besides, color fading effect is known to be accelerated by the oxygen density of the environment.

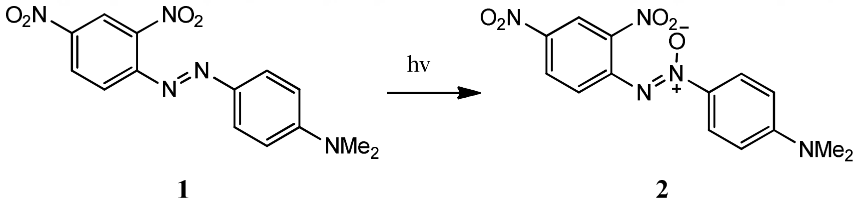


**Figure 1.1.** Conversion of azo group to azoxy group by photooxidation and fading of color

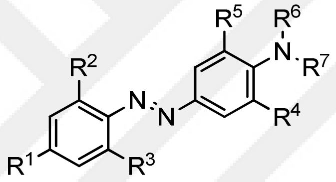
Also, the carriers used in dyeing may cause a reduction in light fastness of dyed fabrics due to residual of carrier substance. Now, no need to carriers, these dyes can be applied to polyester at around 130°C in pressurized machines and the dyeing is followed by a reduction clear.

In many studies, it was stated that the light fastnesses of disperse dyes in polyester fabrics are much better than in acetate or nylon fabrics, therefore both commercial interest and research studies in disperse dyes are much more concentrated on dyeing polyester fibers rather than others.

A chemical classification done according to the chromogen core of the dye molecules are known as ICI system. These general chemical classes are given as azo, anthraquinone, nitrodiphenylamine, xanthene, aminoketone, quinoline. Thus, approximately 1150 disperse dyestuffs are present in the ICI system today.

### 1.1.3 Azo Disperse Dyes

Azo disperse dyes (**1**) may constitute the entire color scale (yellow-blue-green), especially by azo linkage of aminobenzene groups bearing variety of heterocycles and ED groups. Even so, azo dyestuffs have some disadvantages such as more pale color shades and light resistance, formation of some carcinogenic amino groups by cleaving the azo groups (Fig.2) (Nunn, 1979).



$R^1$ = EW group; $R^2$ and $R^3$ = H or EW group
$R^4$ and $R^5$ = H or ED group;
$R^6$ and $R^7$ = H or alkyl group

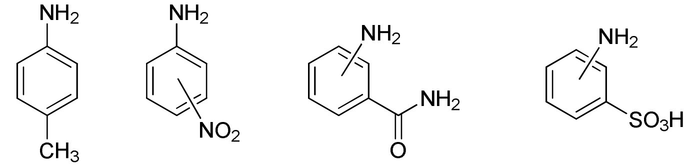
**1**

**Figure 1.2.** General structure of the azo dyes

#### 1.1.3.1 Diazo Components of Azo Dyes

Diazo groups used in azo dye production are generally divided into the two main aromatic amine derivatives as follows:

***Aniline and Substituted Anilines:*** -Me, -Cl, -$NO_2$, -OMe, -OEt, -OPh, -OH, COOH, -C(O)OAlk-, -CONH-, and $SO_3H$ groups are used as primary substituents.



Toluidines Nitroanilines Aminobenzoylamide Anilinosulfonic acids

**3** **4** **5** **6**

**Figure 1.3.** Aniline substituted azo components

***Naphthylamines and Naphthylaminesulfonic Acids:*** Naphthylaminosulfonic acid azo components are given below with their common names.

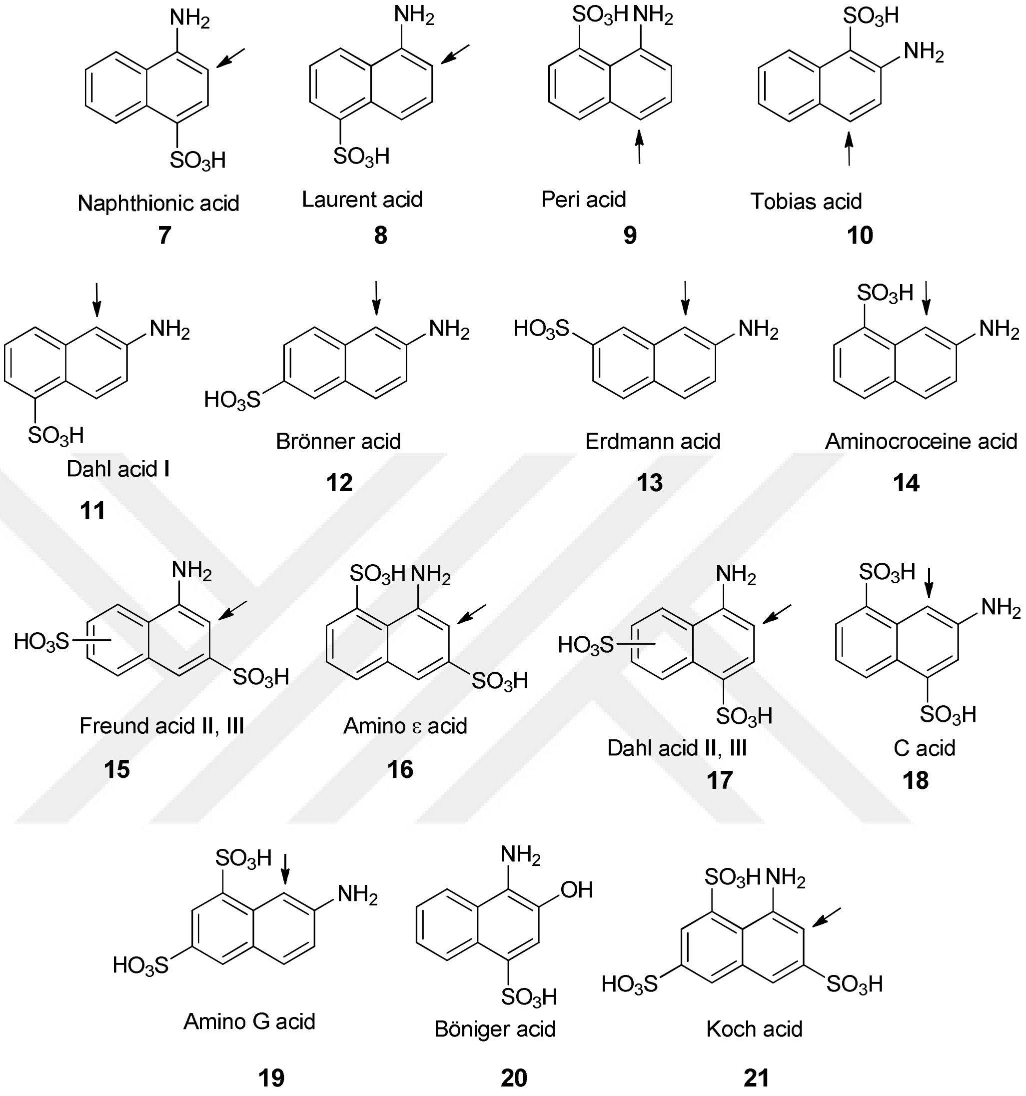
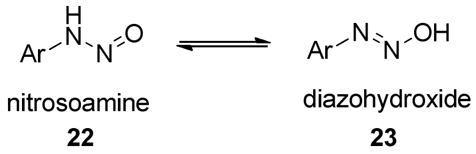


**Figure 1.4.** Naphthylamino substituted azo components

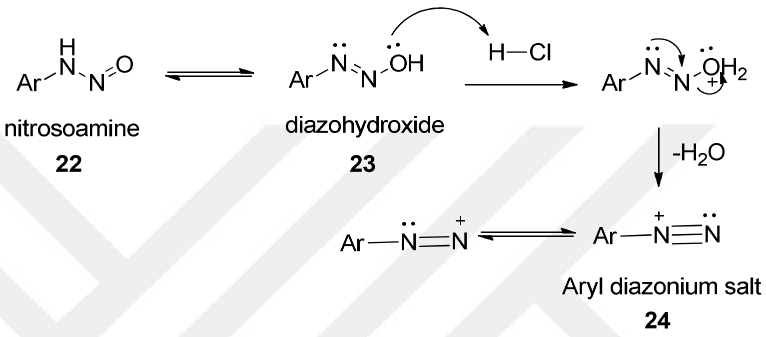
### 1.1.3.2 Synthesis of Azo Disperse Dyes

All azo dyes can be obtained by the azo coupling reaction of primary aromatic amines, diazonium salts bearing an electron-rich nucleophile. A diazotization reaction is done by the reaction of primary aromatic amine with nitrous acid which is produced in situ using HCl and $NaNO_2$. Firstly, the nitrous acid reacts with amine to generate the *N*-nitrosoamine **22** which tautomerizes into the hydroxydiazoarene **23**.



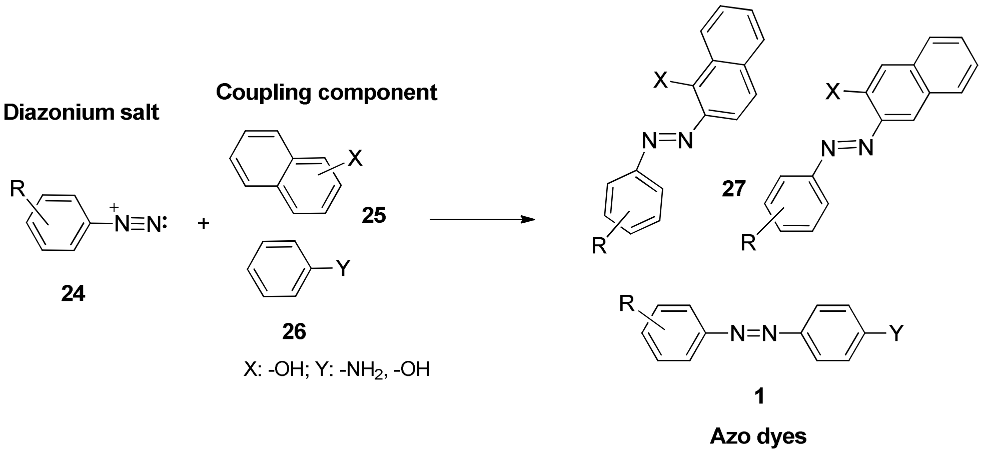
**Scheme 1.1.** Tautomerization of nitrosoamine **22**

Then, the protonation of the hydroxy group and elimination of one mole of water give the resonance-stabilized diazonium salts **24** (Scheme 2).



**Scheme 1.2.** Mechanism for the formation of aryl diazonium salts

When weakly basic amines have several EW groups, nitrosylsulfuric acid ($ONOSO_3H$) can used as a nitrosating agent and it is also mixed with phosphoric, acetic, or propionic acid. Since diazonium salts **24** are weak electrophiles they reacts only with highly electron-rich compounds (**26**) bearing amino and hydroxy groups. Especially, phenols and naphthols as hydroxy compounds (**25**, **26**) can couple with diazonium salts in alkaline medium (pH 7-11), but aromatic amines such as *N*,*N*-dialkylamines can couple in slightly acid medium (pH 1.5). Therefore, optimum stability of diazonium salt is provided without deactivating the nucleophile (protonation of the amine).



**Scheme 1.3.** General synthesis of azo dyes

Aminobenzene dyes (**28-32**) are frequently used in dyeing of polyester fibers in textile industry. Azo dyes bearing EW groups (A, B, C) and ED groups ($R^1$, $R^2$) on their aromatic rings give different colors from yellow-red to blue, this is a typical example of electron-donating-attracting chromogen system.

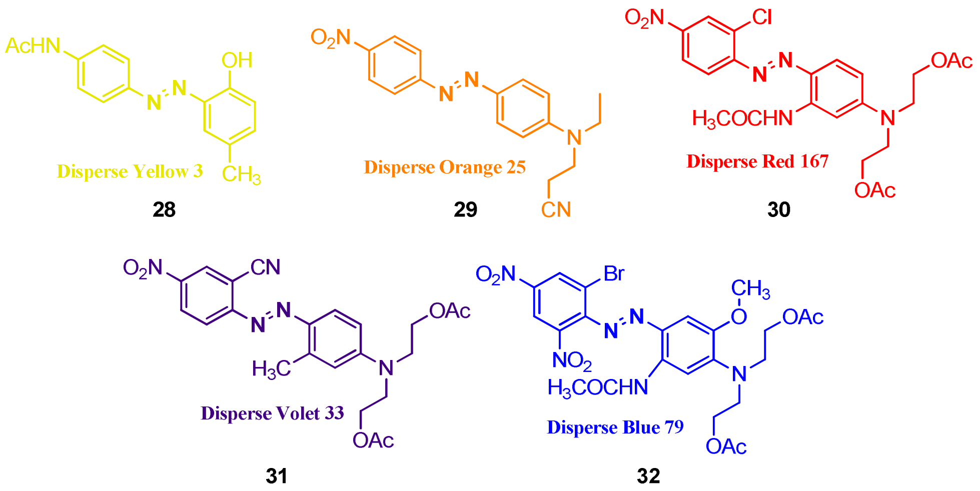
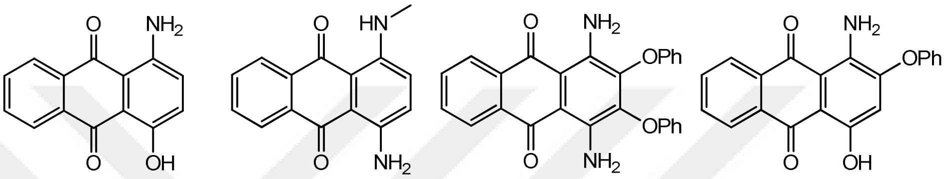


**Figure 1.5.** Examples of some of the azo disperse dyes

Moderate-to-good washing fastnesses of azo disperse dyes are obtained on synthetic materials. In general, washing fastness for azo diperse dyes is obtained between three and five. A better washing fastness depends upon the insolubility of disperse dye molecules and hydrophobicity of applied synthetic fibres. Their light fastness values differ between four and five. Fair or better light fastness results are based on the nonionic part of dye molecule which will not easily interact with water or other polar molecules that may cause an acceleration on light fading. Prolonged exposure of dyed fabrics to UV component of sunlight will cause some colour fadings on these materials.

### 1.1.4 Other disperse dyes

One of the common disperse dyestuffs are the anthraquinone disperse dyes which are also known as acetate dyes. Monoazo and bisazo anthraquinone disperse dyes (**33-36**) are significant classes of disperse dyes in textile industry.

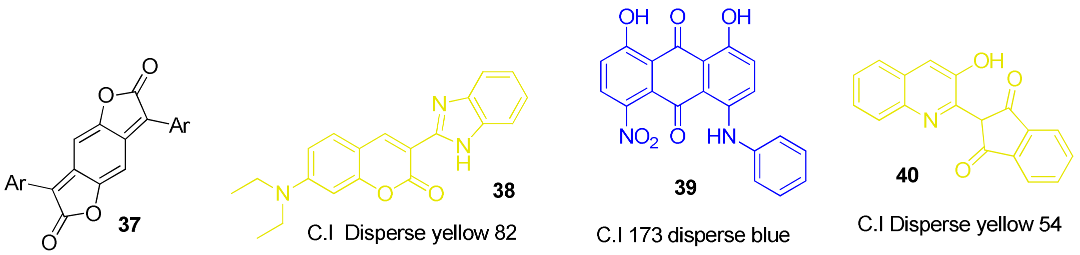


Disperse Red 15 **33** Disperse Violet 4 **34** Disperse Violet 26 **35** Disperse Red 60 **36**

**Figure 1.6.** Structures of some commercial anthraquinone disperse dyes

Anthraquinone disperse dyes are used to get some purple-blue bright colors and their light fastnesses are usually obtained in good levels, but, they usually fade in the presence of nitrous oxide originating from polluted air. Fading caused by nitrous oxide can be eliminated by treating the dyed material with an azoic thiophene-benzene complex (Gordon & Gregory, 1983). When the nitrous oxide reacts with this complex instead of disperse dye molecule, the resistance of dyed fabric to gas fading will be improved more.

Besides, there are many other important classes of disperse dyestuffs such as benzodifuranone (**37**), coumarin (**38**), methane (**41**), nitroarylaamino (**39**) and quinophthalone (**40**) disperse dyes.


37 38 39 40

C.I Disperse yellow 82

C.I 173 disperse blue

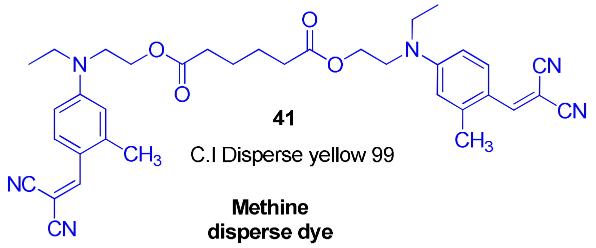
C.I Disperse yellow 54

Benzodifuranone disperse dye

Coumarin disperse dye

Nitroarylamino disperse dye

Quinophthalone disperse dye


41

C.I Disperse yellow 99

Methine disperse dye

**Figure 1.7.** Examples of other important disperse dye classes

## 1.2 HYDROPHOBIC FIBERS

Disperse dyes are primarily applied to synthetic fibers (hydrophobic, acetate, acrylic, nylon, polyester and polyurethane). Among them, polyester and cellulose acetate fibers are the most significant ones for disperse dyeing (Aspland, 1992).

### 1.2.1 Polyester fibers

Polyester synthetic fibers (**44**) are obtained by esterification of terephthalic acid **42** and a diol (ethylene glycol **43**) (Heimanns, 1981). Polyester fabrics commonly used in textile industry are the derivatives of PET obtained by this polymerization reaction.

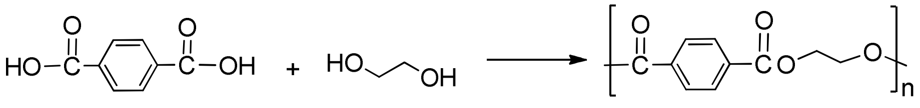

**42** **43** **44**

**Figure 1.8.** A basic PET polymerization reaction

The first commercial PET fiber was first discovered in 1941 in UK and it was commercially sold under the trade names such as Terylene and Dacron. Polyester fibers are the synthetic fibers but they are quite resistant to chemicals and moths. Also, they have great washing and wearing characteristics and when mixed with wool and cotton their fabric quality is substantially improved. Nowadays, new polyester fibers can be produced in physical and aesthetic quality using advanced dyeing with thanks to polymer compositions. Thus, the addition of ionic moieties to the modified polyester fibers increased the dyeing ability using ionic dyes.

### 1.2.1.1 Physical properties of polyester fibers

**Transverse section and longitudinal appearance:** Polyester fibers are observed as a smooth rod under a microscope, also their cross-sections are round.

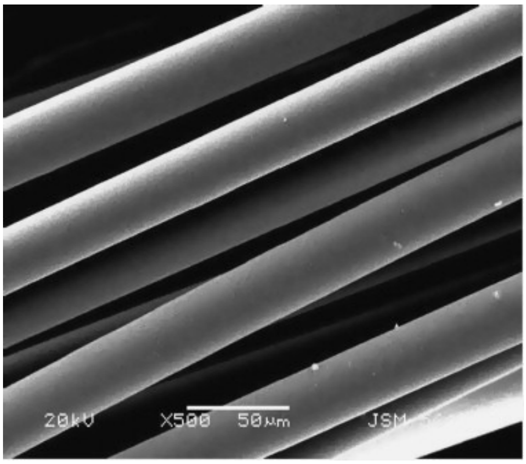


**Figure 1.9.** SEM images of polyester fibers in microscale (Wu et al., 2008)

**Color and gloss:** Polyester fibers are often white in colour, bright, semi-matte or matte.

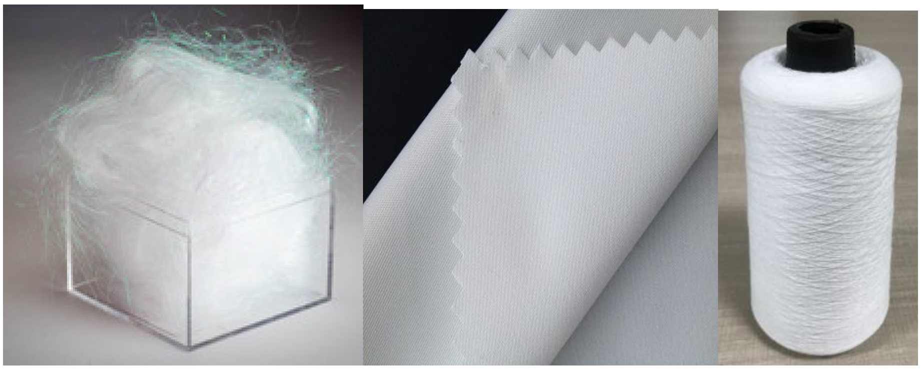


**Figure 1.10.** Appearance of polyester fibers and products (Nunn, 1979)

**Thinness, length and strength**: Polyester fibers are produced in various lengths, size and strengths depending upon the area of their use and way of production. Their fibers in the filament state are between 4-7 g / denier.

**Moisture absorption**: Polyester fibers do not absorb moisture and hydrophobic in nature. Their moisture absorption rate is about 0.2-0.8%. The moisture regain of a polyester fiber is about 0.4-65% relative humidity at 20°C (Moncriff, 1970). Since polyester fibers can keep moisture on the surface, the products of polyester fabric should be worn in hot weather.

**Figure 1.11.** Hydrophobic nature of polyester fibers (Moncriff, 1970)

Moreover, polyester fibers have very good abrasion resistance and polyester fabrics with hot fixing can attract high temperatures. Also, the elasticity of polyester fibers is generally good and elongation rate of them in filament ranges from 15-30% and from 30-50% in batch. Polyester fibers are lightweight fibers (a specific gravity: 1.38 g / cm³) (Nunn, 1979).

Medium strength yarns shrink by about 6% in boiling water, however, when polyester fibres will have a permanent structure when treated with high temperature applications. When polyester fibre is exposed to sunlight for about 600 hours and its strength will still stay same as 60-70% of its original strength (Moncriff, 1970).

#### 1.2.1.2 Chemical properties of polyester fibers

Polyester fibers exhibit superior resistance to the damage of most common chemicals under several conditions of exposure and many kinds of substances have slight or no effect on their structures. The strength to oxidizing or reducing agents is quite high and therefore, bleaching treatments with $NaClO_2$, NaOCl or $H_2O_2$ can be easily performed. Concentrated formic acid, acetic and oxalic acids may result in loss in their strength. Polyester fibers are chemically resistant to acids, dry cleaning solvents and bleaching agents, but strong alkali medium (pH>8) will damage polyester fibers at high-temperature dyebaths in prolonged treatments. The caustic alkali solutions affect and hydrolyze the polymer, but this effect is limited to the surface of the fibre at temperatures up to the boil, however, this essential property can be used for the production of silk-like polyester materials.

Polyester polymers are hydrolyzed using dilute alkali or acid or water alone as in typical reactions of ester groups. No serious reaction may take place in the textile-processing properties of these fibers and yarns dyed for 1-2 h as long as the pH of the bath was adjusted about 7. But, in an acidic bath at $130^oC$ where pH was seriously below 4 or alkaline, more rapid hydrolysis will happen (Nunn, 1979).

The resistance of polyester fibers to sunlight is quite good when compared to many other synthetic fibers, but long exposure to sunlight will harm the fibers. Bacteria, fungi, mold and other pests are harmless to polyester fibers.

Besides, polyester fibers exhibit very low electrical conductivity and they can be charged with static electricity. Since the polyester fibers have high m.p. (250°C), they do not wrinkle too much. However, they can be ironed at low temperatures (about 140°C) for short periods. When polyester fibres are exposed to flame, they will melt down with a chemical odour and a black surface.

## 1.3 DISPERSE DYEING

Dyeing of polyester fabrics is actually performed using disperse dyes. Due to hydrophobic properties of polyester fibers, disperse dyes easily penetrate between hydrophobic fibers. Because disperse dyes have low solubility in water, they are put into the dyebath with dispersion agents to supply dispersion stability (Burkinshaw, 1995). In this technique, application of dispersing agent is critical due to its bidirectional function. Dispersing agent maintains the disperse dyestuff in critically low concentration by directing the hydrophobic ends of the disperse dye molecules inward. Hence, the hydrophilic ends of the agent are also directed to the aqueous part. In brief, the micelle holds and carries the disperse dye and transports it to the fiber and the dye is absorbed molecularly by the fiber. So, the empty micelle provides an efficient dissolution and dyeing function by holding and carrying the disperse dye over and over (Ingamells, 1993). As a result, in dyeing process, a dynamic balance is provided between the absorbed disperse dye by the fiber and the dye remaining in the bath. In this way, this resulting balance can be illustrated as given below.

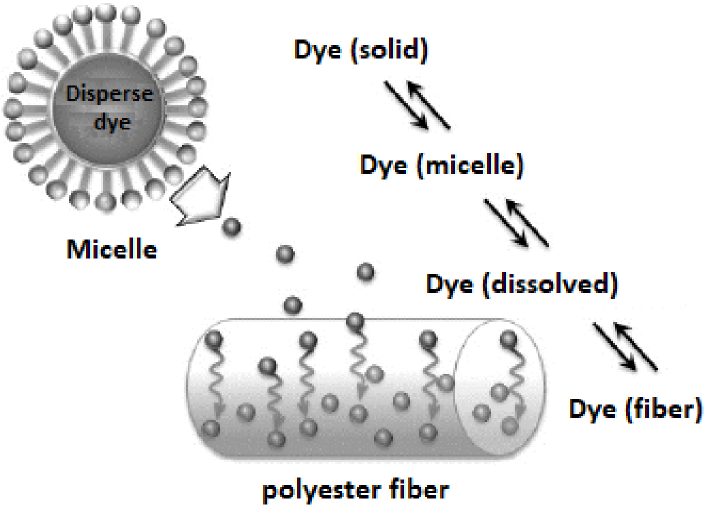


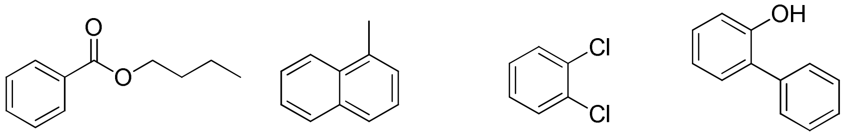
**Figure 1.12.** Disperse dyeing mechanism (Johnson, 1989)

Mechanism of dyeing in the aqueous environment is therefore similar to the addition of solid compound with a non-immiscible solvent to get a dispersion. Thus, disperse dyes absorbed by water and fiber $[D]_{em}$, the amount remaining in the bath $[D]_s$ ratio is found by the distribution coefficient (K);

$$K = [D]_{em}/ [D]_s$$

The crystalline structure and particle size of disperse dye, dispersing agent, pH of the dye bath, dyeing temperature and the thinness of fiber are the factors affecting the disperse dyeing. For instance, the solubility of disperse dye in an aqueous dispersion promotes with decreasing particle size. Moreover, in order to get the desired particle size and distribution, disperse dyes are often mixed with the dispersing agents in certain time periods. In general, the dispersion of polyester fibers using disperse dyes is prepared between pH-5.5-6.5, otherwise higher or lower pH values result in degradation of dyes or hydrolysis of fibers (Hallas, 1979). Since the affinity of dyes decrease with increasing dyeing temperature, polyester fibers are usually dyed at temperatures below 100°C. However, higher dyeing temperatures will lead the saturation of dye in the fiber (Bird et al., 1959; White, 1960).

In disperse dyeing of polyester fibers, in general, three main dyeing methods are often used, they are carrier dyeing, high temperature dyeing and thermosol dyeing. In carrier dyeing technique, a carrier compound is carried to the fiber in the form of a complex with the dye, this will provide faster dyeing (Johnson, 1989). The carriers in polyester dyeing are the organic compounds which are dissolved or emulsified in dyebath. Common carrier compounds are butylbenzoate **45**, methylnaphthalene **46**, dichlorobenzene **47** and *o*-phenylphenol **48**.



butyl benzoate **45** methylnaphthalene **46** dichlorobenzene **47** o-phenylphenol **48**

**Figure 1.13.** Commonly used carriers in polyester dyeing

High temperature dyeing is one of the most widely applied dyeing technique. This dyeing method needs 130°C and the use of pressurized equipment to increase the diffusion rate and kinetic energy of dyestuff, in this way, faster and more effective dyeing results are obtained.

High temperature dyeing consists of three main phases, they are adsorption, diffusion and clearing, respectively.

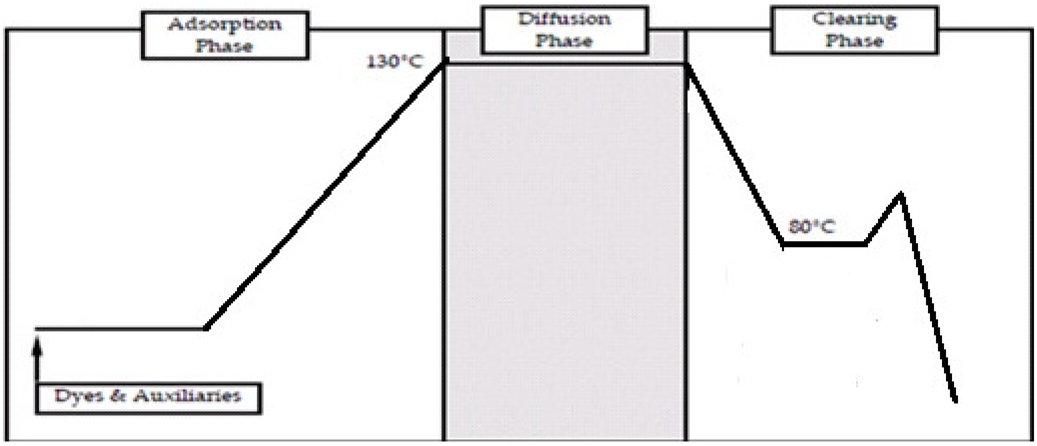


**Figure 1.14.** Main phases in high temperature dyeing (General diagram)

Lastly, thermosol dyeing method using disperse dyes is applied for continuous dyeing of polyester and polyester-cellulose composite fibers. In this technique, the polyester fabric is covered with dispersion of the disperse dye and then the dye dispersed on the fabric is dried using hot air dryer and infrared heater. The fiber coated with dye is heated with dry air at about 190-220°C. When the maximum temperature reaches to the maximum, the vapour of the dye is absorbed by the polyester and the dyeing occurs (Broadbent, 2001).

## 1.4 NANOTECHNOLOGY IN DYEING WITH DISPERSE DYES

Nanotechnology stands out with its examples in different scientific branches, one of which is textiles. Because textile is categorized itself as other scientific fields, nanotechnology have potential applications in textile, fiber, material coating and colorant agents.

Polyester fiber has a hydrophobic nature, therefore it is necessary to use higher temperatures about 130$^{o}$C if it will be dyed by using exhaust dyeing and a temperature of 180-210$^{o}$C if it will be dyed by using thermosol method.

Accordingly, in the last twenty years, the research studies mostly focused on the application of new dyeing techniques such as nanotechnology, electrochemistry, supercritical carbon dioxide dyeing and the use of plasma, ultrasonic and microwave to modify and develop new dyeable polyester fibers (Nahed & El-Shishtawy, 2010).

Since the polyester is the most hydrophobic, compact and crystalline synthetic fiber, its dyeing using disperse dyes can be performed in aqueous solutions at high temperature and pressure (Choi et al., 2001).

The dyes in nanoscale show superior chromatic properties assigned to the nano scale effects of more homogeneous nano colouring agents (Hu et al., 2008).

The disperse means that the better and homogenous distribution of dye molecules to provide the dyeing more smooth and healthy. The most important rules in the polyester dyeing method are based on the rules affecting the mechanism of chemistry, concentration, temperature and pH.

Normally, the industry aims easier and cheaper production of any material. The main reason for searching alternatives like nanotechnology arise from the question of how to provide more economical, more effective and cheaper production of a material.

Since the nature of disperse dyes are non-ionic, sparing soluble in water and often crystalline, these properties are not enough for dispersing the dyes in water and this causes unsmooth dyeing of hydrophobic materials. In order to provide the suitable particle size and distribution, the disperse dyes are mixed with a dispersing agent and grounded by mills (Heimanns, 1981; Derbyshire et al., 1972). In conventional dyeing method, the disperse dyes are applied as fine aqueous dispersions on polyester fabrics at 130°C and on nylon fabrics at 100°C (Choi & Kang, 2006).

Nanoemulsions are very fine droplets of oil dispersed in water and their droplet size are between 20-600 nm (El-Aasser et al., 1988; Liu et al., 2006). These homogeneous nanocolorants have excellent chromatic properties due to their nano scale effects (Hu, 2008). Nanoemulsions or nanodisperse dyestuffs can be produced as aqueous nanoemulsions of surfactants such as SLS **49**, capric triglyceride **50**, Tween 80 **51** by mixing of dye particles in oil spheres using ultrasonication (Nakajima, 1997; Tomomasa et al., 1988).

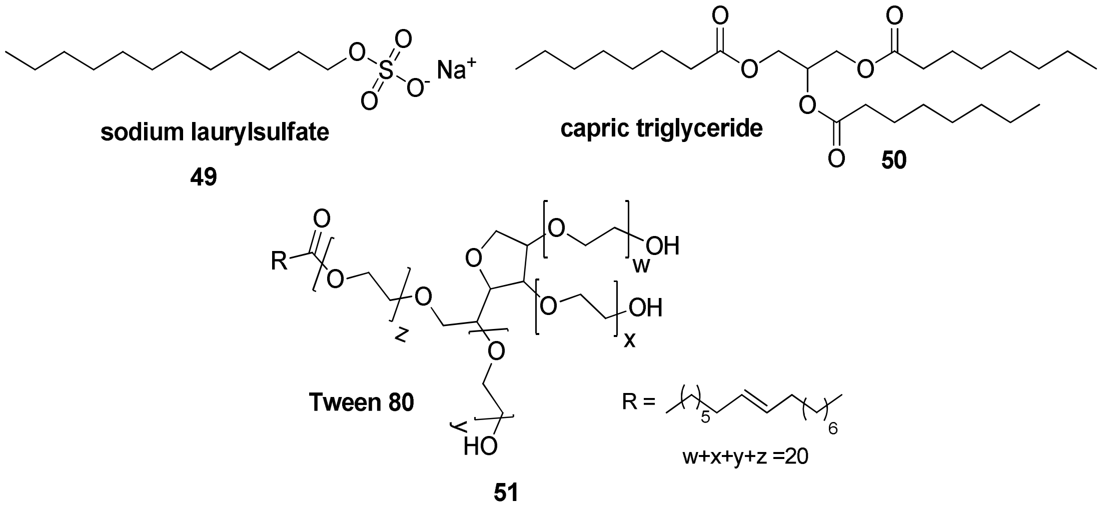


**Figure 1.15.** Common surfactant used in nanoemulsions

Nanoemulsions are thermodynamically stable structures and need very low concentration of surfactant to be used. Dye nanoparticles can be obtained by direct addition of dye molecules in the form of liquid solution to the primary reactant which is found in nanoemulsion.

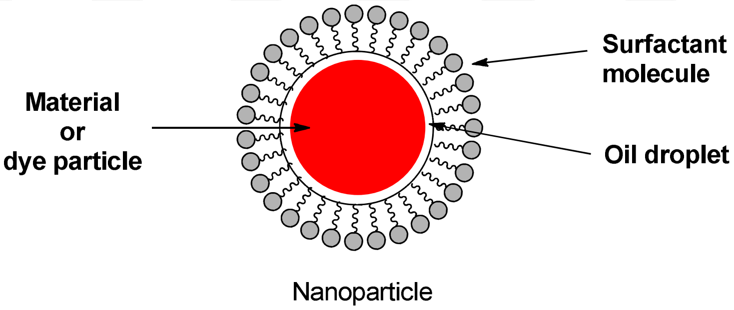


**Figure 1.16.** O/W nanoemulsion system

At first, dye particle is collected in the oil core of nanoemulsion system. Afterwards, the nuclei forms inner part of the oil core and this core grows in time until the nanoemulsion droplet precipitates out. Ultimately, the degree of particle growth will be limited by the size of the oil droplets in nanoemulsion system.

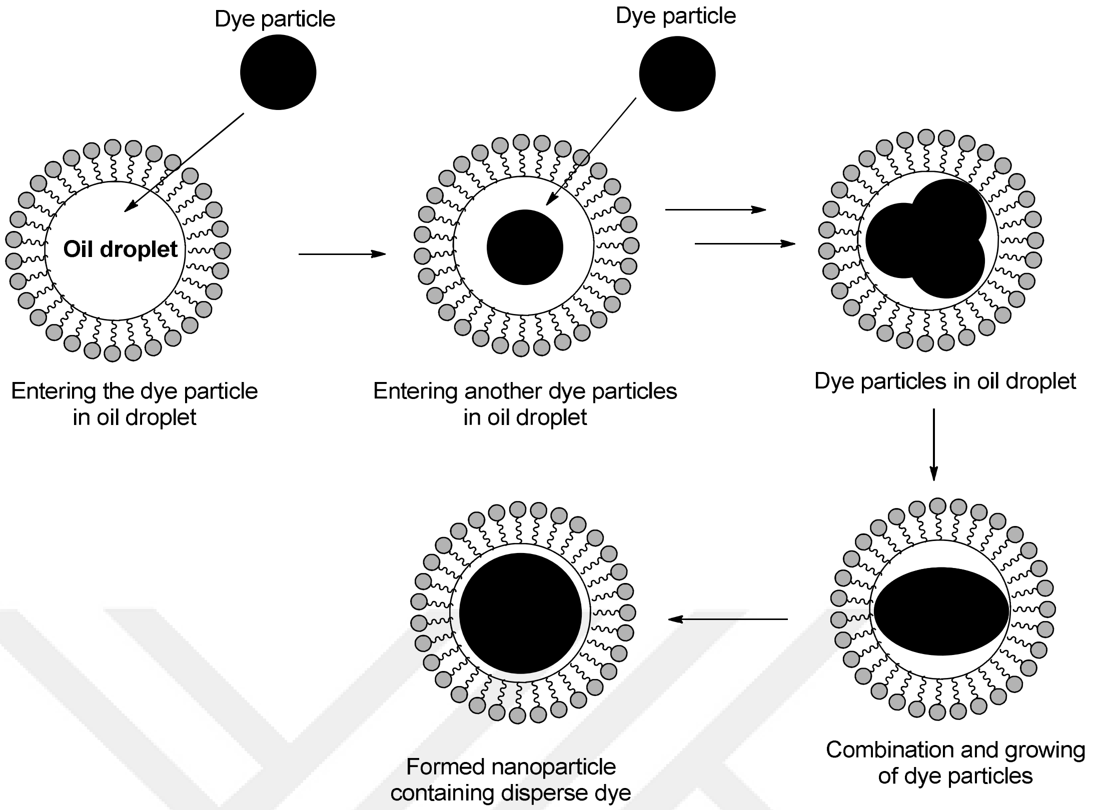
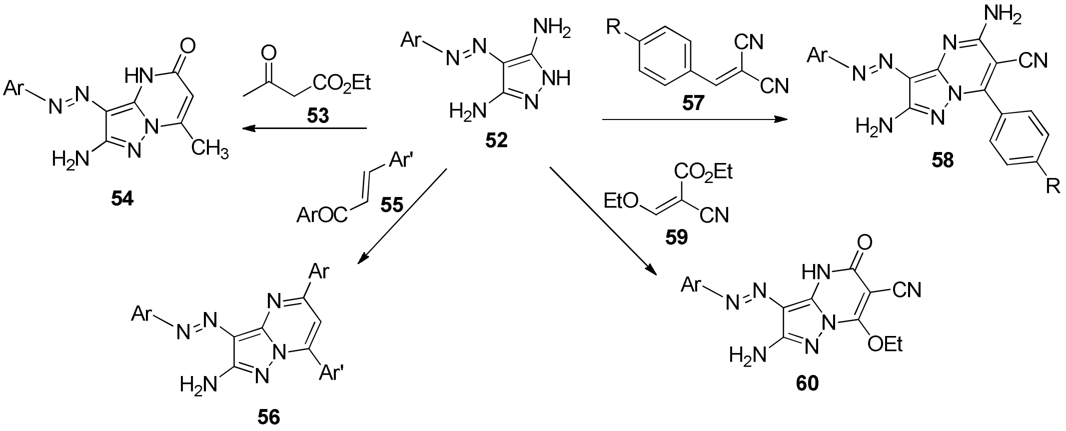


**Figure 1.17** Formation of nanoparticles containing disperse dye (Choi & Kang, 2006)

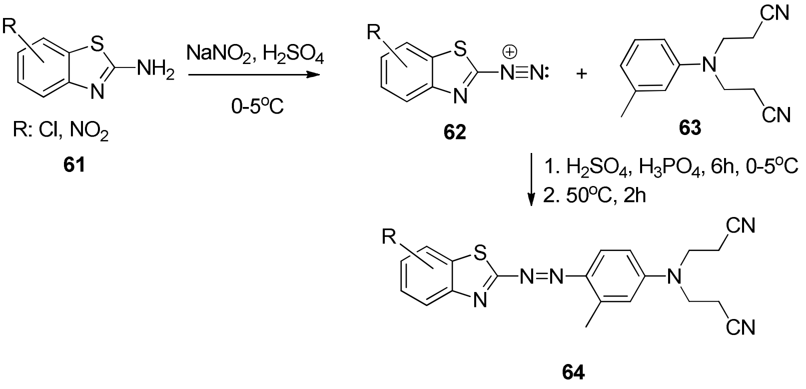
## 1.5 RECENT STUDIES ON DYEING AND BIOLOGICAL PROPERTIES OF DISPERSE AND NANODISPERSE DYESTUFFS

Recently, many studies on the preparation of various disperse dyes have been performed to dye the synthetic fibers, particularly polyesters and to develop their dyeing properties. Sayed et al (2012) prepared some pyrazolo[1,5-*a*]pyrimidine bisazo dyestuffs (**54, 56, 58, 60**) to provide satisfactory dyeing and fastness properties on polyester-based fabrics, meanwhile bisazo dyestuffs have been found to exhibit strong antimicrobial activities against some bacteria and fungi.



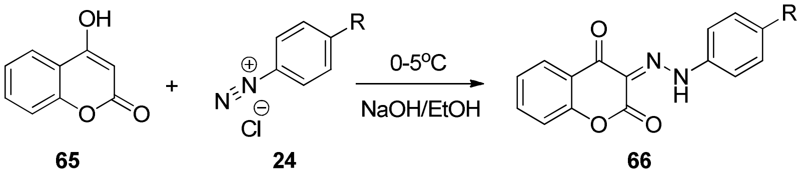
**Scheme 1.4.** Preparation of pyrazolo[1,5-*a*]pyrimidine bisazo dyestuffs

Besides, in the study of Liu et al (2012), yellow, red, purple and blue color shades were obtained on polyester fabrics dyed with newly synthesized dicyanoethyl-based disperse dyes (**64**), and light and washing fastnesses of dyed fibers were quite good.



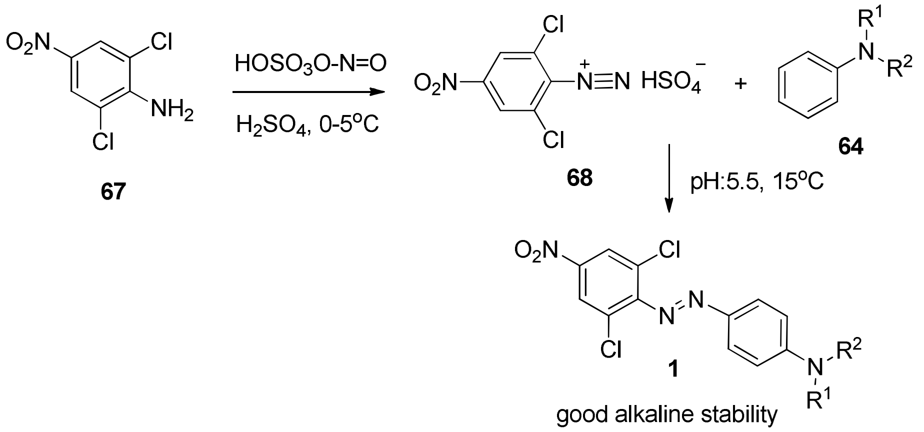
**Scheme 1.5.** Preparation of dicyanoethyl-based disperse dyes

In another study conducted by Metwally et al. (2012) in the same year, new chroman-based azo disperse dyestuffs **66** were prepared and the dyed polyester fabrics were found to have good washing, perspiration, sublimation and light fastness values.



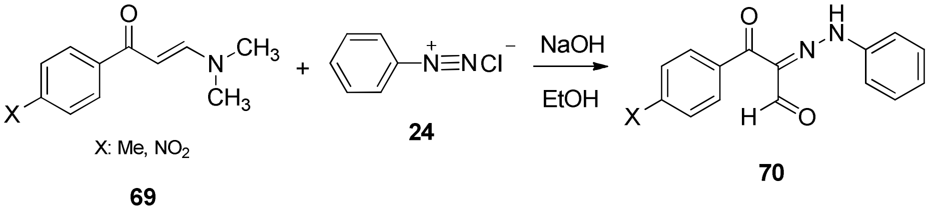
**Scheme 1.6.** Synthesis of chroman-based azo disperse dyes

In addition, after the synthesis and characterization of new 2,6-dichloro-4-nitroaniline-based azodisperse dyestuffs (**1**), PET fabrics were dyed using these dyestuffs and the alkaline stability of the dyestuffs was reported to be very good as the result of the dyeing studies (Li et al., 2016).



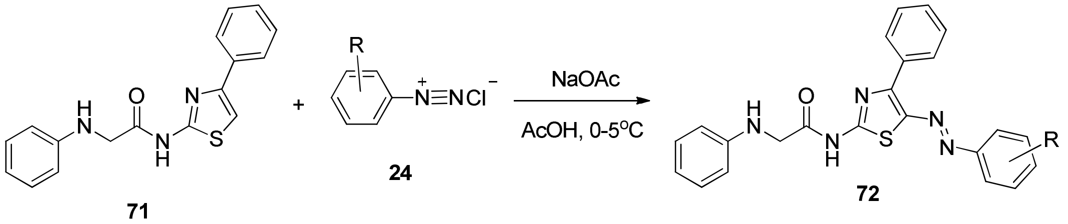
**Scheme 1.7.** Synthesis of nitroaniline-based azodisperse dyes exhibiting good alkaline stability

In another study conducted in 2016, two azo disperse dyestuffs with dimethylamino-*p*-arylpropenone **70** were prepared, polyester fabrics are dyed using carrier dyeing technique and washing, squeezing, persipiration and light fastness of the dyestuff were found excellent (Al-Etaibi et al., 2016).



**Scheme 1.8.** Synthesis of 3-oxo-3-propanal-based azodisperse dyes

Biological effects of some azo disperse dyestuffs have also been studied. For instance, after preparation of new azodisperse dyes based on acetamide (**72**), their dyeing properties were tested on polyester fabrics and good fastness properties were obtained. Also, their strong antibacterial properties against *E.coli*, *P.aeruginosa S.aureus* and antifungal properties against *C.albicans* were determined (Zadafiya & Malik, 2013).



**Scheme 1.9.** Synthesis of azodisperse dyes exhibiting antibacterial and antifungal properties

In another study (2015), the important antioxidant properties of piperazine-based azo disperse dyes (**74**) prepared with good light, washing and squeezing fastness were determined (Mohammadi et al., 2015).

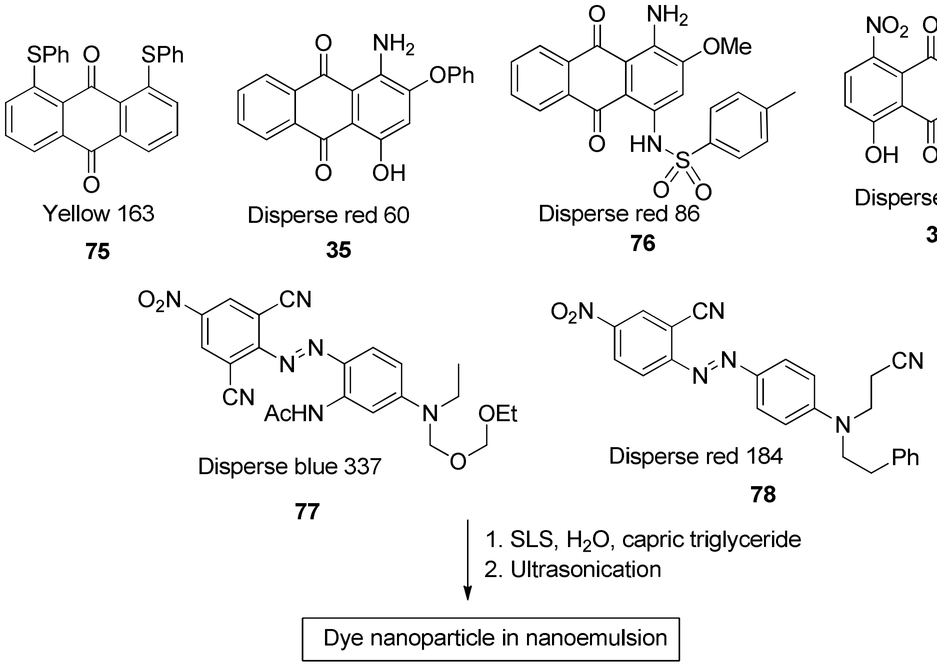
Ar: *p*-$NO_2$-Ph ; triazole; 1,3-thiazole;
benzothiazole derivatives

**Scheme 1.10.** Synthesis of piperazine-based azodisperse dyes exhibiting antioxidant properties

Recently, some nanoformulation and nanodyestuff studies were also performed on polyesters and nylon synthetic fabrics to improve the dyeing properties using various techniques.

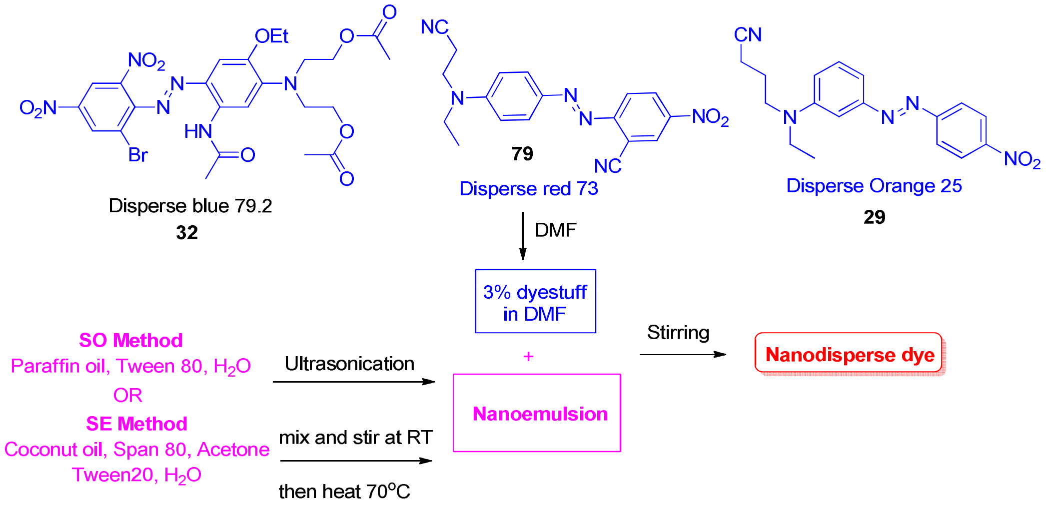
In the study of Maamoun (2014), polyester fabrics were treated with burn-out technique utilizing strong acids and dyed with azo nanodisperse dyes produced by ultrasonication after milling. The dyeing results showed that the color depth has increased with dyeing using dyestuff in nanoscale.

Disperse dyestuffs can be applied in nanoscale to polyester fabrics using certain surfactants. For instance, six different nanodisperse commercial dyestuff mixed with SLS and capric triglyceride was converted into nanoemulsion in 110-130 nm sizes separately and applied to polyester fabrics. Thus, more effective dyeing properties were obtained with these nano dyestuffs than ordinary dyeing applications with disperse dyes (Choi & Kang, 2006).



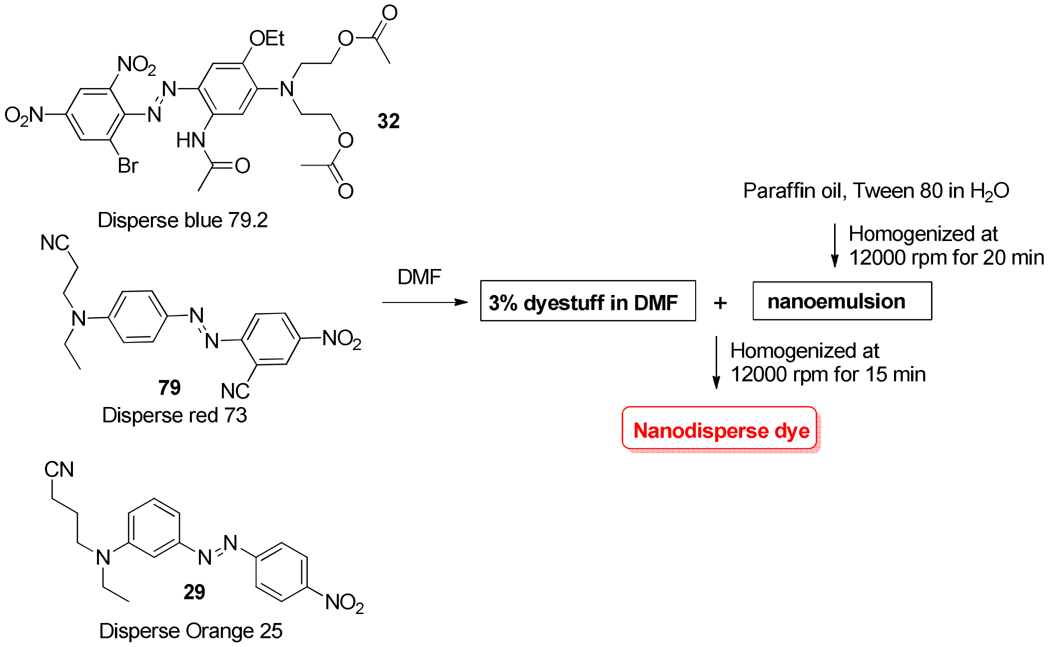
**Scheme 1.11.** Method for the production of nanodisperse dyes

In a more recent study (2014), nanodisperse dye solutions were prepared with commercially available disperse dyes by ultrasonication (SO) and spontaneous emulsion (SE) formation, and higher depth in colors were obtained in dyeing studies on microdenier polyester fabrics (Kale et al., 2014).



**Scheme 1.12.** Preparation of nanodisperse dyes using different methods

In a very recent study (2017), nanoemulsions obtained with commercial azodisperse dyes as oil emulsion in water were applied on nylon fibers and similar dyeing and fastness values were obtained using Flexi dyeing at 100°C (Kale et al., 2017).



**Scheme 1.13.** Preparation of nanodisperse dyes

# 2. AIM AND SCOPE OF THE STUDY

Disperse dyes, in particular azo disperse dyes are commercially important group of organic molecules used in coloring the variety of materials in textile, paper, leather or cosmetic industry. Meanwhile, the synthetic fibers such as polyester, nylon, PET etc. are versatile polymeric materials used especially in textile industry to produce many types of textile fabrics for different purposes. Therefore, the development of new generation synthetic or semi-synthetic fibers are quite important but it is also important to dye these fibers in the desired shades of color. As the dyeing of textile products is complex and it requires the use of different technologies and various dyestuffs. For this reason, many studies have been carried out to produce new dyestuffs and to try their dyeing properties on various fabrics for many years. Recently, nanodisperse dyestuffs have also been prepared by the use of nanotechnology and more sophisticated and higher quality dyeing of various fabrics have been provided.

For this purpose, firstly, it was aimed the preparation of a new series of arylpropenone-based disperse dyestuffs (**70**) following simple and effective two-step synthetic protocol. After purification and characterization of the disperse dyestuff, they were applied on commercial polyester fabric samples to determine their dyeing characteristics. The dyestuff were applied on polyester fabrics in two ways. First dyeing technique included the direct addition of dye solution as a dispersion in water at high temperature but in the second technique, dyestuff was mixed with a surfactant and mineral oil in water and resulting mixture was homogenized and ultrasonicated to form nanodisperse dyestuff in the form of nanoemulsion. Then, this nanoemulsion form was added in aqueous dyebath for dyeing of polyester fabrics at high temperature.

Finally, the dyeing characteristics and fastness (light, washing, water, acidic-basic perspiration, rubbing, sublimation) properties of dyestuffs on polyester fabrics were determined by following standard ISO protocols. Hence, the current study was completed successfully in three main parts; synthesis, dyeing and color-fastness tests (Figure 2.1).

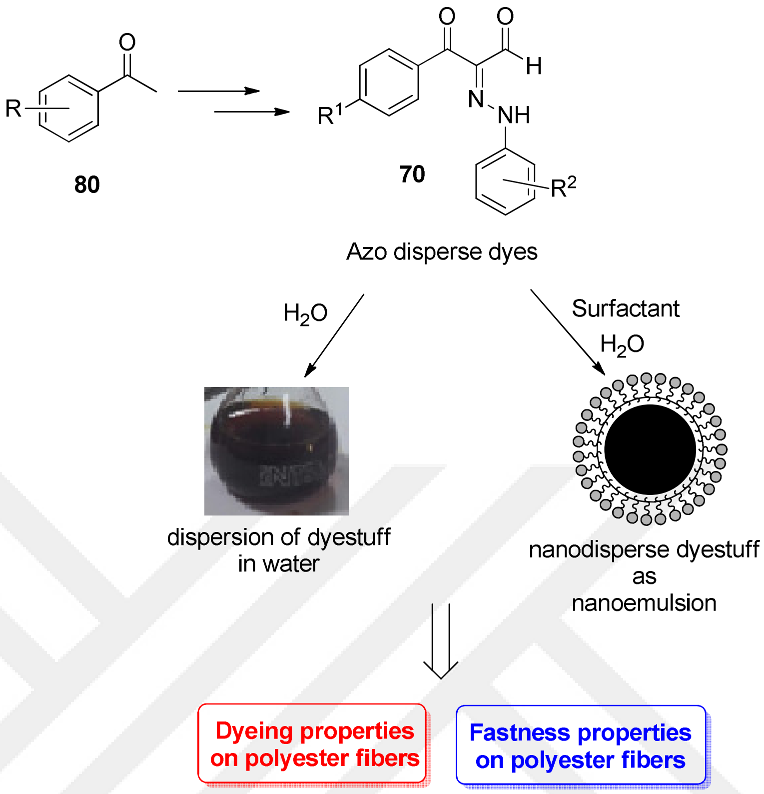


**Figure 2.1.** Main strategy for the preparation and dyeing fastness properties of dyestuffs throughout the thesis study

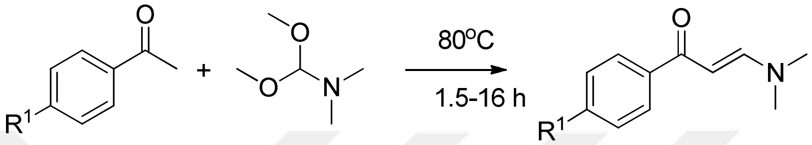
# 3. MATERIALS AND METHODS

The reagents and solvents were purchased from commercial suppliers in analytical and reagent grades (Merck, Acros, Sigma-Aldrich). All reactions were stirred either at room temperature or reflux using Heidolph MEI magnetic stirrer-heaters. High-temperature jet dyeing of polyester samples with disperse dye solutions and nanoemulsions were performed using a TERMAL mini high-temperature jet dyeing machine. Colors of dyed polyester samples were measured in a datacolor SF600 color spectrophotometer. Ultrasonication and homogenation of nanoemulsions were performed using an IKA T25 Ultra-Turrax Homogenizator. All NMR spectra of the dyes and precursors were recorded on a 400-MHz JEOL ECS400 Delta2 spectrometer at room temperature. The chemical shifts were reported in ppm downfield from TMS; *J* values are given in Hz. The abbreviations used for NMR signals are: br s= broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd=doublet of doublets. IR spectra were recorded on a SHIMADZU FTIR-8400S instrument using KBr pellets or on a PERKIN-ELMER Spectrum Two ATR equipped FTIR system. HRMS measurements were run on a Waters Lct Premier XE oa-TOF Mass Spectrometer. Melting points of solid compounds were determined on a MELTEMP apparatus and they are uncorrected. TLC analyses were carried out for monitoring the reaction progress on pre-coated plates with fluorescent indicator (Merck 5735). Column chromatographic separations were performed on silica gel (Merck, 230–400 mesh ASTM) and the eluents were mixtures of ethyl acetate (EA) and hexanes (H). Staining solutions of potassium permanganate and UV-254-366 were used for visualization of the TLC spots.

## 3.1 EXPERIMENTAL

### 3.1.1 Synthesis of Precursor Compounds

#### 3.1.1.1 General Procedure for Synthesis of Precursor 1 (Dimethylamino-*p*-arylpropenones) (69) (Zhu et al., 2016)

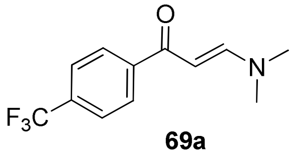


**80** **81** **69**

$R^1$: -$CF_3$, -OEt, -$NO_2$

A mixture of 1-phenylethanone **80** (1 equiv.) and DMF-DMA **81** (3 equiv.) was boiled at 80°C, the consumption of starting material was controlled by TLC. When the reaction is complete, the reaction mixture was cooled to room temperature and poured into a mixture of petroleum ether / diethylether (4:1) and stirred for a further half an hour. The precipitated solid was filtered off through sintered funnel by vacuum filtration. Collected solid was first dried at RT, then under high-vacuum. The precursor compound 1 (**69**) was isolated as solid in very pure state and good yields.

**(*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (69a)** (Mohebbi et al., 2011)

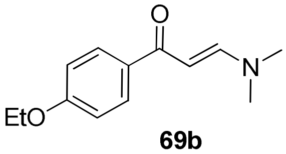


**69a**

Heated at 80°C for 4 h and precipitated from petroleum ether/diethylether mixture to afford bright yellow crystalline solid. (1.567 g, 67%), m.p. 101-103°C; $R_f$ (50% EtOAc/hexane) 0.15; IR (KBr) υ: 3456, 2924, 2816, 1643, 1589, 1550, 1435, 1327, 1118, 1064, 902, 856, 779 cm$^{-1}$; $^1$H-NMR (500 MHz, DMSO-d$_6$) δ: δ 8.02 ( 2H, d, *J* 8.09 Hz), 7.72-7.75 (3H,m), 5.80 (1H, d, *J* 12.20 Hz), 3.13 (3H, br s), 2.90 (3H, br s);

(TOF-MS ESI$^+$) *m/z*: 244 (100, $[M+H]^+$) $C_{12}H_{12}F_3NO$ requires 243.22. Anal. Found: C, 59.18; H, 4.98; N, 5.78. Calcd for $C_{12}H_{12}F_3NO$: C, 59.26; H, 4.97; N, 5.76 %.

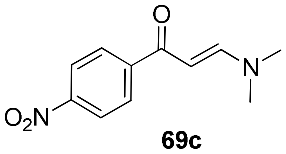
**(*E*)-3-(dimethylamino)-1-(4-ethoxyphenyl)prop-2-en-1-one (69b)**



**69b**

Heated at 80-100°C for 16 h and precipitated from petroleum ether/diethylether mixture to afford an orange solid. (1.250 g, 63%); $R_f$ (50% EtOAc/hexane) 0.20; IR (KBr) υ: 3456, 2980, 2875, 1647, 1602, 1585, 1550, 1438, 1363, 1238, 1178, 1043, 904, 854, 777 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 7.86 (2H, d, *J* 8.4 Hz), 7.76 (1H, d, *J* 12.4 Hz), 6.87 (2H, d, *J* 8.4 Hz), 5.68 (1H, d, *J* 12.3 Hz), 4.04 (2H, q, *J* 6.8 Hz), 3.08 (3H, br s), 2.90 (3H, br s), 1.40 (3H, t, *J* 7.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 187.5, 161.5, 153.8, 133.0, 129.5, 113.7, 91.8, 63.4, 14.8.

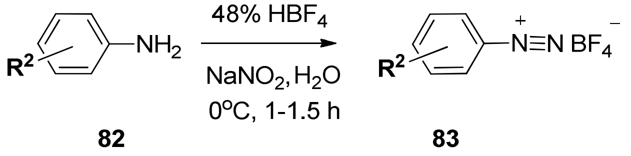
**(*E*)-3-(dimethylamino)-1-(4-nitrophenyl)prop-2-en-1-one (69c)** (Kantevari et al., 2007)



**69c**

Heated at 80°C for 1 h 30 min and precipitated from petroleum ether/diethylether mixture to afford a brown solid. (1.63 g, 82%), m.p. 151-153°C; $R_f$ (50% EtOAc/hexane) 0.15; IR (KBr) υ: 2918, 2806, 1641, 1604, 1554, 1410, 1340, 1273, 1058, 977, 898, 788 cm$^{-1}$; $^1$H-NMR (300 MHz, $CDCl_3$) δ: 8.22 (2H, d, *J* 8.5 Hz), 7.95 (2H, d, *J* 8.5 Hz), 7.78 (1H, d, *J* 12.1 Hz), 5.61 (1H, d, *J* 12.8 Hz), 3.25 (3H, br s), 2.90 (3H, br s); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ: 185.8, 155.0, 148.8, 145.9, 128.1, 123.2, 91.7, 45.1, 37.2; MS (EI) *m/z*: 220 ($M^+$, 32%), 204 (82), 157 (10), 70 (25), 55 (22), 44 (7); Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.86; H, 5.56; N, 12.80.

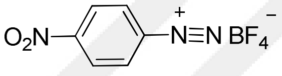
### 3.1.1.2 General Procedure for Synthesis of Precursor 2 (Aryl diazonium tetrafluoroborates) (83) (Collevile et al., 2014)



$R^2$: $-CH_3$, $-OCH_2CH_2O-$, -OMe, $-NO_2$, Cl

48% of $HBF_4$ solution (2.6 equiv.) were mixed with the corresponding aniline derivative **82** (1.0 equiv.) at 0°C. Then, 1.5 volume aqueous solution of sodium nitrite (1.1 equiv.) was added dropwise with stirring to this solution. The resulting mixture was stirred at 0°C for 30 min and allowed to warm at RT for 30 minutes. The precipitate was filtered, washed with a small amount of water and dried at room temperature to afford the corresponding diazonium tetrafluoroborate salt **83** as solid in very pure state.

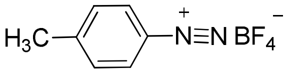
**4-nitrobenzenediazonium tetrafluoroborate (83a)** (Reay et al., 2017)



**83a**

Stirred at 0-25°C for 1 h 30 min and the filtration afforded white solid. (2.08 g, 82%), m.p. 148-151°C; IR (KBr) υ: 3117, 2306 (N≡N), 1612 (C-N), 1543, 1357, 1049, 864, 740, 524 $cm^{-1}$; $^1$H-NMR (400 MHz, DMSO-$d_6$) δ: 8.77 (2H, d, *J* 9.0 Hz), 8.63 (2H, d, *J* 9.0 Hz); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 153.3, 134.6, 126.1, 121.9; $^{11}$B-NMR (128 MHz, DMSO-$d_6$) δ: -2.3; $^{19}$F-NMR (376 MHz, DMSO-$d_6$) δ: -148.1 (m, 1JF–10B, 4F), -148.1 (m, 1JF– 11B, 4F); (TOF-MS $ESI^-$) m/z: 150 (100%, $([M–BF_4]^+)$; HRMS (TOF-MS $ESI^-$): $[M–BF_4]^+$ found 150.0304. $C_6H_4N_3O_2$ requires 150.0298.

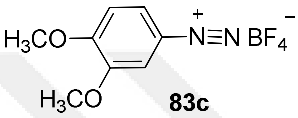
**4-methylbenzenediazonium tetrafluoroborate (83b)** (Reay et al., 2017; Shiraki et al., 2017)



**83b**

Stirred at 0-25$^{o}$C for 1 h 20 min and the filtration afforded silver gray solid. (1.19 g, 57%), m.p. 106-107°C; IR (KBr) υ: 3417, 3109, 2291(N≡N), 1581(C-N), 1311, 1072, 817, 505 cm$^{-1}$; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ: 8.58–8.51 (2H,m), 7.83–7.75 (2H, m), 2.57 (3H, m); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 153.94, 132.7, 131.8, 112.0, 22.4; $^{11}$B-NMR (128 MHz, DMSO-$d_6$) δ: -2.3; $^{19}$F-NMR (376 MHz, DMSO-$d_6$) δ: -148.1 (m, 1JF– 10B, 4F), -148.1 (m, 1JF–11B, 4F); (TOF-MS ESI$^-$) *m/z*: 119 (100%, $[M-BF_4]^+$); HRMS (TOF-MS ESI$^-$): $[M-BF_4]^+$, found 119.0603. $C_7H_7N_2$ requires 119.0604.

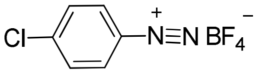
**3,4-dimethoxybenzenediazonium tetrafluoroborate (83c)** (Nyugen et al., 2009)



**83c**

Stirred at 0-25$^{o}$C for 1 h and the filtration afforded brown solid. (1.51 g, 56%), m.p. 123°C; IR (KBr) υ: 3124, 2970, 2252(N≡N), 1581(C-N), 1512, 1296, 1057, 856, 810, 516 cm$^{-1}$; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ: 8.55 (1H, dd, *J* 9.1, 2.5 Hz), 8.22 (1H, d, *J* 2.5 Hz), 7.57 (1H, d, *J* 9.1), 4.17 (3 H, s), 3.99 (3 H,s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 161.7, 151.2, 131.9, 114.4, 113.4, 103.2, 57.8, 57.3. $^{19}$F-NMR (DMSO-$d_6$) δ: -148.2; (TOF-MS ESI$^+$) *m/z*: 165 (100%, $[M+H]^+$); HRMS (TOF-MS ESI$^+$): $[M+H]^+$, found 165.0664. $C_8H_9N_2O_2$ requires 165.0653.

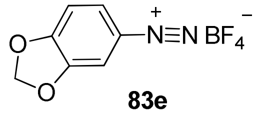
**4-chlorobenzenediazonium tetrafluoroborate (83d)** (Reay et al., 2017)



**83d**

Stirred at 0-25$^{o}$C for 1 h 30 min and the filtration afforded a white solid. (1.10 g, 48%), m.p. 138-139°C; IR (KBr) υ: 3396, 3080, 2274(N≡N), 1622(C-N), 1560, 1464, 1311, 1093, 1031, 833, 520 cm$^{-1}$; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ: 8.73–8.64 (2H, m), 8.15–8.07 (2H, m); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 146.5, 134.4, 131.6, 114.8; $^{11}$B-NMR (128 MHz, DMSO-$d_6$) δ: −2.3; $^{19}$F-NMR (376 MHz, DMSO-$d_6$) δ: -148.1 (m, 1JF–10B, 4F), -148.1 (m, 1JF–11B, 4F); (TOF-MS ESI$^-$) *m/z*: 139 (100%, $[M-BF_4]^+$); HRMS (TOF-MS ESI$^-$): $[M-BF_4]^+$, found 139.0054. $C_6H_4ClN_2$ requires 139.0058.

**Benzo[*d*][1,3]dioxole-5-diazonium tetrafluoroborate (83e)** (Nyugen et al., 2009)

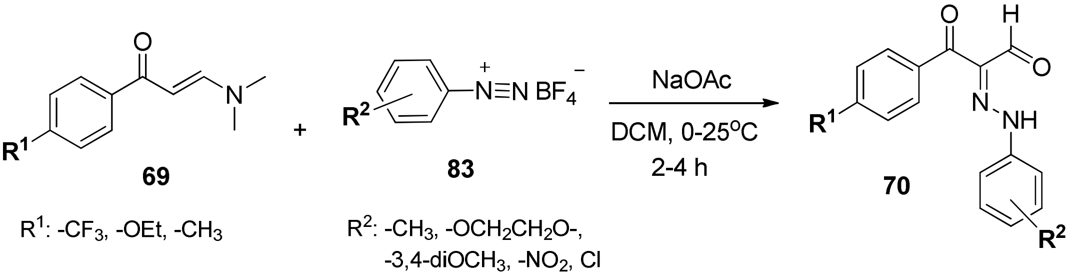


**83e**

Stirred at 0-25°C for 1 h 30 min and the filtration afforded brown solid. (3.40 g, 72%), m.p. 121°C; IR (KBr) υ: 3414, 3119, 3018, 2252(N≡N), 1595(C-N), 1496, 1475, 1373, 1282, 1261, 1070, 914, 871, 520 $cm^{-1}$; $^1$H-NMR (400 MHz, DMSO-$d_6$) δ: 8.36 (1H, dd, *J* 8.8, 2.3 Hz), 7.89 (1H, d, *J* 2.3 Hz), 7.34 (1H, d, *J* 8.8 Hz), 6.41 (2H, s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 161.5, 151.0, 135.4, 112.0 (2x C), 110.3, 107.3; $^{19}$F-NMR (DMSO-$d_6$) δ: -148.2; (TOF-MS ESI$^+$) *m/z*: 149 (100%, $[M+H]^+$); HRMS (TOF-MS ESI$^+$): $[M+H]^+$, found 149.0341. $C_7H_5N_2O_2$ requires 149.0351.

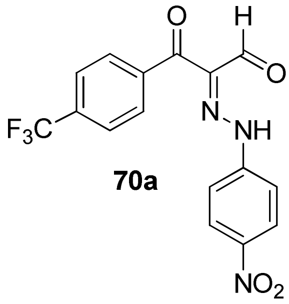
### 3.1.2 Synthesis of Disperse Dyes

#### 3.1.2.1 General Procedure for Preparation of Arylpropenone Azo Disperse Dyes (70) (Al-Etaibi et al., 2016)



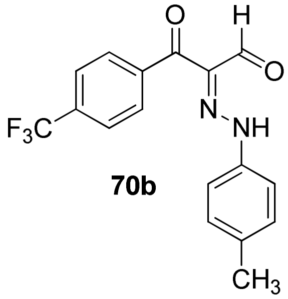
A cooled aqueous solution of diazonium tetrafluoroborate salt **83** (1.5 equiv.) at 0°C was added into a solution of NaOAc (3.0 equiv.) and dimethylamino-*p*-arylpropenone derivative **69** (1.0 equiv.) in DCM (15 mL). The resulting mixture was stirred at RT for 1-2 h, the resulting precipitate was filtered off using sintered funnel via suction filtration and dried under high-vacuum to afford corresponding azo disperse dye (**70**) as a solid. Solid residue of disperse dyes (**70**) were further purified by flash CC using mixtures of hexanes-EtOAc and obtained in pure state.

### (*E*)-2-(2-(4-nitrophenyl)hydrazono)-3-oxo-3-(4-(trifluoromethyl)phenyl) propanal (70a)


**70a**

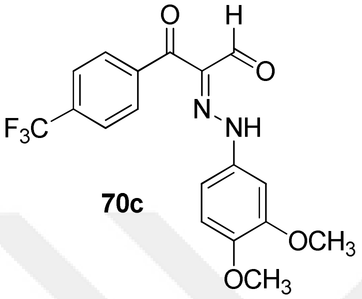
With stirring at RT for 3 h 15 min and flash chromatography (25% EtOAc/hexane) afforded light brown solid. (1.131 g, 74%), m.p. 88-90°C; $R_f$ (50% EtOAc/hexane) 0.80; IR (KBr) υ: 3109 (NH), 3086, 1697 (C=O), 1651 (C=O), 1597 (NH bending), 1519, 1327, 1257, 1165, 1111, 1064, 949, 848 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.22 (1H, s, CHO), 8.28-8.26 (2H,d, *J* 9.0 Hz), 8.04-8.02 (2H,d, *J* 8.2 Hz), 7.78-7.76 (2H, d, *J* 8.2 Hz), 7.40-7.38 (2H,d, *J* 9.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 190.1 (C=O), 190.0 (C=O), 145.9, 145.2, 139.4, 134.2-133.9 ($^2J_{CF(ortho)}$ = 32.8 Hz), 133.3, 130.6, 125.9, 125.3-125.2 ($^3J_{CF(meta)}$ = 3.2 Hz), 124.9, 124.7-122.0 ($^1J_{CF}$ = 277.1 Hz), 120.6, 116.4; (TOF-MS ESI$^-$) *m/z*: 364 (100, $[M-H]^+$), 365 (15%); HRMS (TOF-MS ESI$^-$): $[M-H]^+$, found 364.0544. $C_{16}H_9F_3N_3O_4$ requires 364.0550.

### (*E*)-3-oxo-2-(2-(p-tolyl)hydrazono)-3-(4-(trifluoromethyl)phenyl)propanal (70b)


**70b**

With stirring at RT for 1 h 45 min and flash chromatography (25% EtOAc/hexane) afforded pale orange solid. (0.856 g, 60%), m.p. 114-116°C; $R_f$ (50% EtOAc/hexane) 0.70; IR (KBr) υ: 3117 (NH), 3016, 2924, 1643 (C=O), 1527, 1419, 1327, 1288, 1165, 1118, 1072, 956, 810 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.17 (1H, s, CHO), 8.02-8.00 (2H,d, *J* 8.2 Hz), 7.74-7.72 (2H,d, *J* 8.5 Hz), 7.19 (4H, s), 2.34 (3H,s); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 190.3 (C=O), 189.1 (C=O), 138.6, 137.3, 133.8-132.9 ($^2J_{CF(ortho)}$ = 32.6 Hz), 130.6, 130.3, 130.1, 129.1, 124.9-124.8 ($^3J_{CF(meta)}$ = 3.8 Hz), 125.2-122.5 ($^1J_{CF}$ = 272.5 Hz), 119.5, 116.7, 21.0; (TOF-MS ESI$^-$) *m/z*: 333 (100, [M-H]$^+$), 334 (20%); HRMS (TOF-MS ESI$^-$): [M-H]$^+$, found 333.0821. $C_{17}H_{12}F_3N_2O_2$ requires 333.0856.

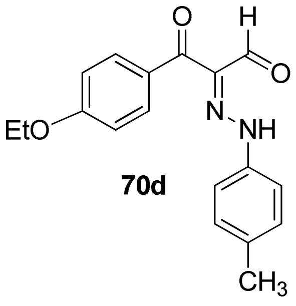
**(*E*)-2-(2-(3,4-dimethoxyphenyl)hydrazono)-3-oxo-3-(4-(trifluoromethyl)phenyl) propanal (70c)**



**70c**

With stirring at RT for 2 h 50 min and flash chromatography (25% EtOAc/hexane) afforded brick-red solid. (0.460 g, 65%), m.p. 138-139°C; $R_f$ (50% EtOAc/hexane) 0.80; IR (KBr) υ: 3093 (NH), 2939, 1651, 1627, 1597 (C-N), 1519 (C=C), 1404, 1311, 1265, 1126, 826 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.16 (1H, s, CHO), 7.98-7.96 (2H,d, *J* 8.2 Hz), 7.71-7.69 (2H,d, *J* 8.2 Hz), 6.87-6.80 (3H,m), 3.86 (3H,s,$OCH_3$), 3.77 (3H,s,$OCH_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 190.5 (C=O), 188.7 (C=O), 150.4, 148.5, 140.9, 134.6, 133.6-132.6 ($^2J_{CF(ortho)}$ = 32.8 Hz), 131.4, 130.4, 124.7-124.6 ($^3J_{CF(meta)}$ = 3.6 Hz), 125.2-122.4 ($^1J_{CF}$ = 272.2 Hz), 111.5, 109.5, 99.8, 56.2, 55.8; (TOF-MS ESI$^-$) *m/z*: 379 (100, [M-H]$^+$), 380 (15%); HRMS (TOF-MS ESI$^-$): [M-H]$^+$, found 379.0920. $C_{18}H_{14}F_3N_2O_4$ requires 379.0920.

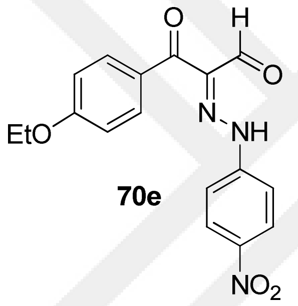
**(*E*)-3-(4-ethoxyphenyl)-3-oxo-2-(2-(p-tolyl)hydrazono)propanal (70d)**



**70d**

With stirring at RT for 1 h 30 min and flash chromatography (25% EtOAc/hexane) afforded red solid. (0.400 g, 55%), m.p. 110-112°C; $R_f$ (50% EtOAc/hexane) 0.75; IR (ATR) υ: 2983, 2921, 1638, 1598 (C-N), 1505 (C=C), 1451, 1390, 1247, 1157, 1080, 819 $cm^{-1}$; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 10.10 (1H, s, CHO), 7.99-7.97 (2H,d, *J* 8.9 Hz), 7.25-7.22 (2H,d, *J* 8.8 Hz), 7.18-7.16 (2H, d, *J* 8.4 Hz), 6.95-6.93 (2H,d, *J* 7.1 Hz), 4.14-4.09 (2H, q, *J* 7.0 Hz), 2.33 (3H,s), 1.45 (3H, t, *J* 7.0 Hz); $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 189.6, 189.0, 162.4, 139.0, 136.5, 132.9, 132.4, 130.4, 129.4, 116.5, 113.7, 63.8, 21.1, 14.8; (TOF-MS $ESI^-$) *m/z*: 309 (100, $[M-H]^+$), 310 (25%); HRMS (TOF-MS $ESI^-$): $[M-H]^+$, found 309.1245. $C_{18}H_{17}N_2O_3$ requires 309.1244

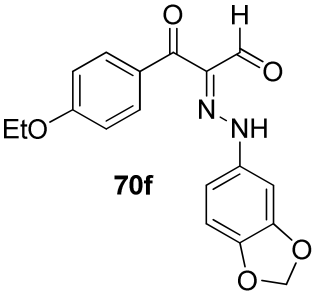
**(*E*)-3-(4-ethoxyphenyl)-2-(2-(4-nitrophenyl)hydrazono)-3-oxopropanal (70e)**



**70e**

With stirring at RT for 2 h and flash chromatography (25% EtOAc/hexane) afforded yellow-orange solid. (0.845 g, 65%), m.p. 124-126°C; $R_f$ (50% EtOAc/hexane) 0.80; IR (ATR) υ: 3115 (NH), 2987, 1627, 1597 (C-N), 1503 (C=C), 1336, 1240, 1108, 848 $cm^{-1}$; $^1H$-NMR (400 MHz, $CDCl_3$) δ: 10.12 (1H, s, CHO), 8.25-8.23 (2H,d, *J* 8.9 Hz), 7.99-7.97 (2H,d, *J* 8.9 Hz), 7.41-7.39 (2H, d, *J* 9.1 Hz), 6.97-6.95 (2H,d, *J* 8.9 Hz), 4.16-4.11 (2H, q, *J* 7.0 Hz), 1.46 (3H, t, *J* 7.0 Hz); $^{13}C$-NMR (100 MHz, $CDCl_3$) δ: 190.6, 189.0, 163.1, 146.5, 144.7, 134.1, 132.9, 128.4, 125.9, 116.2, 114.1, 63.9, 14.7; (TOF-MS $ESI^-$) *m/z*: 340 (100, $[M-H]^+$), 341 (30%); HRMS (TOF-MS $ESI^-$): $[M-H]^+$, found 340.0927. $C_{17}H_{14}N_3O_5$ requires 340.0938.

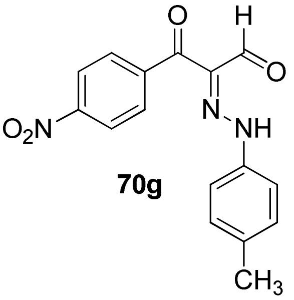
**(*E*)-2-(2-(benzo[d][1,3]dioxol-5-yl)hydrazono)-3-(4-ethoxyphenyl)-3-oxo propanal (70f)**



**70f**

With stirring at RT for 1 h 30 min and flash chromatography (25% EtOAc/hexane) afforded brown solid. (0.800 g, 90%), m.p. 108-110°C; $R_f$ (50% EtOAc/hexane) 0.75; IR (ATR) υ: 3062 (NH), 2983, 2919, 1736, 1627 (C=O), 1600 (C-N), 1502 (C=C), 1448, 1304, 1250, 1176, 1033, 834 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.07 (1H, s, CHO), 7.95-7.93 (2H,d, *J* 7.0 Hz), 6.95-6.93 (3H,d, *J* 8.8 Hz), 6.79-6.77 (1H, d, *J* 8.3 Hz), 6.73-6.70 (1H,dd, *J* 8.4, 2.1 Hz), 5.98 (2H,s), 4.14-4.09 (2H, q, *J* 7.0 Hz), 1.44 (3H,t, *J* 7.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 189.6, 189.4, 162.4, 149.2, 146.4, 136.4, 132.7, 132.2, 129.4, 113.6, 110.6, 108.6, 101.8, 97.8, 63.7, 14.7; (TOF-MS ESI$^-$) *m/z*: 339 (100, $[M-H]^+$), 340 (20%); HRMS (TOF-MS ESI$^-$): $[M-H]^+$, found 339.0967. $C_{18}H_{15}N_2O_5$ requires 339.0986.

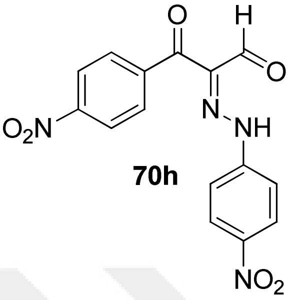
**(*E*)-3-(4-nitrophenyl)-3-oxo-2-(2-(p-tolyl)hydrazono)propanal (70g)**



**70g**

With stirring at RT for 2 h and flash chromatography (25-33% EtOAc/hexane) afforded brick-red solid. (0.652 g, 83%), m.p. 143-145°C; $R_f$ (50% EtOAc/hexane) 0.80; IR (ATR) υ: 3103 (NH), 3073, 2930, 1732, 1648 (C=O), 1632 (C=O), 1590 (C-N), 1548, 1512 (C=C), 1315, 1300, 957, 806, 706 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.17 (1H, s, CHO), 8.31-8.29 (2H,d, *J* 8.3 Hz), 8.04-8.02 (2H,d, *J* 8.7 Hz), 7.20-7.16 (4H, m), 2.34 (3H,s); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 189.7, 188.9, 149.5, 142.9, 138.4, 137.6, 131.1, 130.7, 130.5, 123.1, 116.9, 21.2; (TOF-MS ESI$^-$) *m/z*: 310 (100, [M-H]$^+$), 311 (20%); HRMS (TOF-MS ESI$^-$): [M-H]$^+$, found 310.0837. $C_{16}H_{12}N_3O_4$ requires 310.0833.

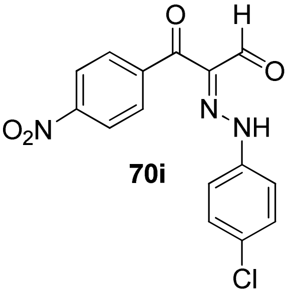
**(*E*)-3-(4-nitrophenyl)-2-(2-(4-nitrophenyl)hydrazono)-3-oxopropanal (Mixture of two isomers)** (1:0.90) **(70h)**



**70h**

With stirring at RT for 2 h and flash chromatography (25% EtOAc/hexane) afforded red-brown solid. (0.444 g, 45%), m.p. 113-115°C; $R_f$ (50% EtOAc/hexane) 0.85; IR (ATR) υ: 3116 (NH), 2923, 2854, 1736, 1649, 1581 (C-N), 1505 (C=C), 1336, 1297 1247, 1106, 846, 698 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.24 (1H, s, CHO), *9.81 (1H, s, CHO)*, 8.37-8.35 (2H,d, *J* 8.7 Hz), 8.30-8.27 (2H,d, *J* 9.0 Hz), *8.23-8.21 (2H,d, J 8.6 Hz)*, *8.18-8.16 (2H,d, J 8.9 Hz)*, 8.13-8.11 (2H, d, *J* 8.9 Hz), *8.08-8.05 (2H,d, J 8.7 Hz)*, 7.50-7.47 (2H, d, *J* 9.0 Hz), *7.39-7.37 (2H,d, J 9.1 Hz)*; $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 189.9, 189.4, 131.1, 129.5, 126.0, 125.6, 124.9, 124.2, 123.4, 120.6, 115.6; (TOF-MS ESI$^-$) *m/z*: 341 (100, [M-H]$^+$), 342 (20%); HRMS (TOF-MS ESI$^-$): [M-H]$^+$, found 341.0575. $C_{15}H_9N_4O_6$ requires 341.0527.

**(*E*)-2-(2-(4-chlorophenyl)hydrazono)-3-(4-nitrophenyl)-3-oxopropanal (Mixture of two isomers)** (1:0.50) **(70i)**



**70i**

With stirring at RT for 1 h 45 min and flash chromatography (25% EtOAc/hexane) afforded orange-red solid. (0.810 g, 81%), m.p. 116-118°C; $R_f$ (50% EtOAc/hexane)

0.75; IR (ATR) υ: 3111 (NH), 2931, 2859, 1726, 1649, 1603 (C-N), 1511(C=C), 1311, 1088, 827, 708 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ: 10.20 (1H, s, CHO), 8.34-8.31 (2H,d, *J* 9.1 Hz), *8.29-8.27 (2H,d, J 8.9 Hz)*, *8.21-8.19 (2H,d, J 9.0 Hz)*, 8.04-8.02 (2H, d, *J* 8.9 Hz), *7.55-7.53 (2H,d, J 8.9 Hz)*, *7.44-7.42 (2H,d, J 8.8 Hz)*, 7.38-7.32 (2H, d, *J* 8.9 Hz), 7.23-7.20 (2H,d, J 8.8 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 189.6, 189.3, 149.7, 142.5, 139.3, 135.2, 131.0, 130.2, 123.3, 120.8, 117.9; (TOF-MS ESI$^-$) *m/z*: 330 (100, $[M-H]^+$), 331 (20%), 332 (30%); HRMS (TOF-MS ESI$^-$): $[M-H]^+$, found 330.0286. $C_{15}H_9ClN_3O_4$ requires 330.0287.

### 3.1.3 Preparatıon of Disperse Dye Solutions

#### 3.1.3.1 Preparation of standard dye solutions with disperse dyes

Prior to the preparation of standard dye solutions, purified solid dyestuffs (**70a-i**) were first milled 2-3 times in porcelain mortar to obtain more disperse and fine powder form. And then, 0.3 g of each solid dyestuff (**70a-i**) and also the equal amount (0.3 g) of commercial dispersing agent (Setalan SW powder™) were weighed precisely. Each solid dye (**70a-i**) in fine powder form were then mixed with commercial dispersing agent in 1:1 ratio (w/w) and homogenous solid mixtures were prepared.

After milling and mixing of solid dyestuffs (**70a-i**) with dispersing agent, 1% (w/v) disperse dye solutions were prepared in water using 50-mL volumetric flasks. Each mixture of solid dyestuff with commercial dispersing agent was first mixed with small amount of water (5 mL) and shaken well to get a dispersion of solid dyestuff mixture. Then, each mixture was diluted with water to a final volume of 30 mL in volumetric flasks. Finally, the dispersion characteristics of the each dye solution were observed and noted.

#### 3.1.3.2 Preparation of nanodisperse dye solutions with disperse dyes

Prior to preparation of nanodisperse dye solutions, a suitable nanoemulsion was first prepared and then mixed with % 1 dye solution in DMF (4:1 v/v).

##### 3.1.3.2.1 Preparation of Nanoemulsion by Ultrasonication

In general, nanoemulsions can be prepared by using three kinds of methods. They are the ultrasonication, spontaneous emulsification and phase inversion composition techniques. Regarding the simplicity and applicability of ultrasonication in previous studies (Kale et al., 2017), this method was chosen and applied for the preparation of nanoemulsion with disperse dyestuffs.

**General Method**

15mL of paraffin oil, 5 mL of Tween 80 and 80 mL of distilled water were mixed and stirred under magnetic stirring at 4000 rpm for 30 minutes and then subjected to ultrasonication for 20 min. using an IKA T25 Ultra-Turrax Homogenizator of power 250 W and diameter probe 20 mm.

##### 3.1.3.2.2 Preparation of nanodisperse dye solutions

Solid dyestuff (0.5g) were weighed to get 1% shade in dye solution and then dissolved in 10 mL of DMF. Resulting solution was added dropwise into 40 mL of nanoemulsion and homogenized by stirring at 4000-5000 rpm for 30 min and then subjected to ultrasonication for 20 min. using an IKA T25 Ultra-Turrax Homogenizator of power 250 W and diameter probe 20 mm. Totally, 50 mL of nanodisperse dye solution has been prepared for dyeing.

### 3.1.4 Dyeing Studies Using High Temperature Jet Dyeing

#### 3.1.4.1 Preparation of 100% polyester fabric and HT dyeing

The 1/10 flotte ratio was applied and therefore, 100% polyester fabrics were cut into 5 g/m$^2$ pieces in the laboratory weighed on the balance precisely to provide 1% ratio in dye solution.

High tempetature (HT) jet dyeing was selected as suitable dyeing method using disperse dyestuffs on polyester fabrics.

##### 3.1.4.1.1 General dyeing recipe

A suitable dyeing recipe was established for dyeing of polyester fabrics with disperse dye solutions under HT dyeing conditions.

- 1/10 Flotte ratio (50 mL of solution for 5 g/m$^2$ fabric sample)
- % 2 Disperse dye / 0.1 g of fabric sample
- 0.5 g/L Setalup ace conz (commercial anti-crease lubricant and dispersant)
- 0.5 g/L Setalan ps 75 (commercial levelling agent)
- pH-4.5 Setacid pbs (pH buffering agent)

##### 3.1.4.1.2 HT Dyeing Process

High-temperature dyeing method was applied in a laboratory-scale HT jet dyeing machine (Termal TM) for dyeing the polyester samples with disperse dye solutions by following the steps given below;

- **Step 1.** Prepare the chemical dye-bath using above prescribed recipe in the dyeing container, soak the 5 g /m$^2$ cut fabric in a sample dyeing tube and put sample dyeing tube in the dyeing container and close the lid.
- **Step 2.** Run the dyeing machine at 60°C for 10 minutes.
- **Step 3.** Increase the temperature up to 130°C by 1°C per minute and run the dyeing machine at 130°C for another 45 minutes.

- **Step 4.** Decrease the temperature to 80$^{o}$C by 1$^{o}$C per minute and run the dyeing machine at 80$^{o}$C for 30 minutes more.

- **Step 5.** Taken the dyeing tube out of the jet dyeing machine and leave for cooling.
- **Step 6.** Then, open the lid of dyeing container and take the sample dyeing tube out of the machine.
- **Step 7.** Then, take dyed polyester fabric sample out of sample dyeing tube and wash and dry the dyed polyester fabric in a laboratory type mini dryer prior to the color control.

**Figure 3.1.** Mini high-temperature jet dyeing machine (TERMAL TM) used in dyeing process

### 3.1.5 Color Control Measurements and Fastness Properties

Each dyed polyester sample is placed and fixed with a special holder against the measuring aperture of the datacolor instrument. The sample is highlighted from the light source inside the instrument. Instrument measures the wavelengths of reflected and absorbed parts of the incident light. Measured data are stored in the computer database and they are evaluated by the software to sort out and calculate the colour parameter values necessary for defining the colour, whiteness or colour matching of the dyed samples.

**Figure 3.2.** Datacolor SF 600 colour spectrophotometer for color control

### 3.1.6 Fastness Properties of Disperse Dyes on Polyester Fabrics

Washing, water, acidic-basic perspiration and rubbing fastness tests were performed in Linter Textile Company Laboratories. However, sublimation and light fastness tests were performed in SETAŞ Chemistry Company Laboratories.

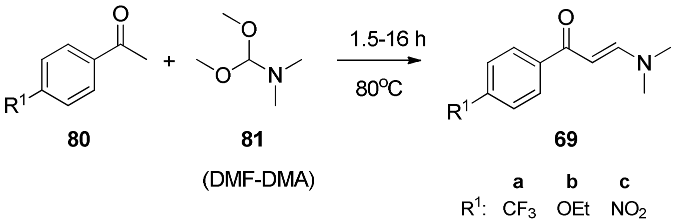
Washing fastness (commercial and domestic washing staining), water fastness staining, perspiration acid and alkaline and rubbing fastness test results were evaluated according to BS EN ISO CO6, BS EN ISO 105 E01, BS EN ISO E04 (pH:5.5), BS EN ISO E04 (pH:8-9) and BS EN ISO 105X12 standards, respectively.

# 4. RESULTS AND DISCUSSIONS

## 4.1 SYNTHESIS AND CHARACTERIZATION OF PRECURSOR COMPOUNDS

Enaminones are versatile and suitable starting materials for the preparation of different pyridine or pyrimidine-based heterocycles and drug molecules used in the area of medicinal and pharmaceutical chemistry. (Zhu et al., 2016; Mohebbi et al., 2011; Kantevari et al., 2007). Also, their use for the preparation of some azo dye compounds were reported to test their dyeing properties in a few recent studies. (Al-Etaibi et al., 2016; Al-Etaibi & El-Apasery, 2016). In the present study, *p*-substituted arylpropenones (**69a-c**) and aryl diazonium tetrafluoroborates (**83a-e**) were prepared as the precursors of new azo disperse dyestuff molecules (**70**).

Firstly, three *p*-substituted arylpropenone precursors (**69a-c**) were prepared in good yields (63-82%) by the condensation reaction of *p*-substituted acetophenones (**80a-c**) with DMF-DMA (**81**) by heating at 80°C (Scheme 4.1 and Table 4.1) (Zhu et al., 2016).



**Scheme 4. 1.** Preparation of dimethylamino-*p*-arylpropenones (**69a-c**)

**Table 4.1.** Reaction conditions and yields of *p*-substituted arylpropenones (**69**)

| Entry | **69** | R$^1$ | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | **a** | $CF_3$ | 4 | 67 |
| 2 | **b** | EtO | 16 | 63 |
| 3 | **c** | $NO_2$ | 1.5 | 82 |

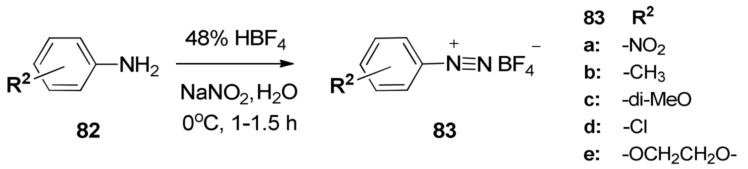
The structures of *p*-substituted arylpropenones (**69a-c**) were determined by means of IR, NMR and HRMS data or by comparing data with the reported ones in recent literature (Mohebbi et al., 2011; Kantevari et al., 2007). In the IR spectra of arylpropenones (**69**), C=O, C-N and C=C stretching vibrations were observed at around 1641-1647, 1585-1604 and 1550-1554 $cm^{-1}$, respectively. Also, the proton NMR spectra of arylpropenones (**69**) showed the olefinic CH proton signals at around 7.75-7.78 and 5.61-5.80 ppm as two distinct doublets. These data were supported by the olefinic CH carbon signals (155 and 92 ppm) in $^{13}$C-NMR spectra of arylpropenones (**69**) (Table 4.2).

**Table 4.2.** Indicative IR and NMR data for arylpropenone precursors **69a-c**

| **Comp.** | **IR** ($\nu_{max}/cm^{-1}$) | | | **$^1$H-NMR** (δ,ppm) | **$^{13}$C-NMR** (δ,ppm) |
|---|---|---|---|---|---|
| **69** | C=O | C-N | C=C | C=C**H** | **H**C=C |
| **a** | 1643 | 1589 | 1550 | 7.75, 5.80 | -[a] |
| **b** | 1647 | 1585 | 1550 | 7.76, 5.68 | -[a] |
| **c** | 1641 | 1604 | 1554 | 7.78, 5.61 | 155.0, 91.7 |

[a] No available data

Secondly, the aryldiazonium tetrafluoroborate precursors (**83a-e**) were prepared efficiently by the reaction of aniline derivatives (**82**) with tetrafluoroboric acid in the presence of sodium nitrite at 0°C and isolated as solid products in moderate to good yields (48-82%) (Scheme 4.2 and Table 4.3) (Colleville et al., 2014). Aryldiazonium tetrafluoroborates (**83a-e**) were isolated directly by precipitation from water and completely dried under vacuum.



**Scheme 4.2.** Preparation of aryldiazonium tetrafluoroborates (**83a-e**)

**Table 4.3.** Reaction conditions and yields for aryldiazonium tetrafluoroborates (**83**)

| Entry | **83** | $R^2$ | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | **a** | $NO_2$ | 1.5 | 82 |
| 2 | **b** | $CH_3$ | 1.5 | 57 |
| 3 | **c** | di-MeO | 1.0 | 56 |
| 4 | **d** | Cl | 1.5 | 48 |
| 5 | **e** | $OCH_2CH_2O$ | 1.5 | 72 |

Aryldiazonium tetrafluoroborate salts (**83a-e**) were primarily characterized by N≡N (2306-2252 $cm^{-1}$), C-N (1622-1581 $cm^{-1}$) and B-F (1030-1072, 516-524 $cm^{-1}$) stretching vibrations in their IR spectra (Table 4.4). In $^1$H-NMR spectra of diazonium salts, aromatic protons resonated at around 8.77-7.34 ppm as doublets or multiplets. However, the signals of C-N carbons in $^{13}$C-NMR spectra of the salts were more evident (121.9-103.2 ppm) to support the expected structure (Table 4.4). Besides, $^{11}$B-NMR (-2.3 ppm) and $^{19}$F-NMR (-148.1-148.2 ppm) data showing the B-F couplings were the extra proof for the expected tetrafluoroborate structures (Table 4.4) (Reay et al., 2017; Nyugen et al., 2009). Lastly, the accurate mass data of diazonium tetrafluoroborates (**83**) were obtained in good agreement with their expected accurate mass values (see experimental part).

**Table 4.4.** Indicative IR and NMR data for aryldiazonium tetrafluoroborates **83a-e**

| **Comp.** | **IR** ($\nu_{max}$/cm$^{-1}$) | | | **$^{1}$H-NMR** (δ,ppm) | **$^{13}$C-NMR** (δ,ppm) | **$^{11}$B-NMR** (δ,ppm) | **$^{19}$F-NMR** (δ,ppm) |
|---|---|---|---|---|---|---|---|
| **83** | **N≡N** | **C-N** | **B-F** | **Arom.CH** | C-N | **B-F** | **B-F** |
| **a** | 2306 | 1612 | 1049, 524 | 8.77-8.63 | 121.9 | -2.3 | -148.1 |
| **b** | 2291 | 1581 | 1072, 505 | 8.58-7.75 | 112.0 | -2.3 | -148.1 |
| **c** | 2252 | 1581 | 1057, 516 | 8.55-7.57 | 103.2 | -[a] | -148.2 |
| **d** | 2274 | 1622 | 1031, 520 | 8.73-8.07 | 114.8 | -2.3 | -148.1 |
| **e** | 2252 | 1595 | 1070, 520 | 8.36-7.34 | 110.3 | -[a] | -148.2 |

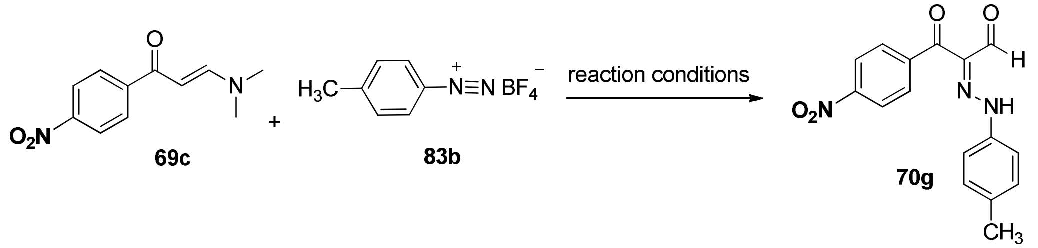
[a] No available data

## 4.2 SYNTHESIS AND CHARACTERIZATION OF DISPERSE DYES

Diverse number of research studies have been performed using several disperse dyestuffs for dyeing the synthetic fibers such polyester or nylon…etc. in last two decades. In particular, two examples of arlypropenone-based azo dye molecules have been recently prepared and tested for their dyeing, fastness or biological properties and the results were promising on the dyeing and biological properties of these derivatives of arylpropenone-based azo dyes (Al-Etaibi et al., 2016; Al-Etaibi & Al-Apasery, 2016; Al-Etaibi et al., 2015). Therefore, we prompted for the preparation of new arylpropenone-based azo disperse dye derivatives (**70**) after preparation and characterization of the enaminone (**69**) and diazonium tetrafluoroborate (**83**) precursors. The synthesis of new arylpropenone-based azo disperse dye derivatives (**70**) were planned to perform via diazo coupling reactions of new *β*-(dimethylamino)arylpropenones (**69**) with diazonium tetrafluoroborate salts

**83** in the presence of sodium acetate or sodium hydroxide at RT or reflux in suitable solvents.

**Table 4.5.** Optimization of reaction conditions for the synthesis of compound **70g**



| Entry | Reaction conditions | Time | Yield (%)[a] |
|---|---|---|---|
| 1 | EtOH, **69c** (1eq)**, 83b** (1.5eq), **NaOH** (2.0 eq), 25°C | 3h | 33 |
| 2 | MeOH, **69c** (1eq)**, 83b** (2.0eq), **NaOH** (3.0 eq), 25°C | 2h | 38 |
| 3 | DCM, **69c** (1eq)**, 83b** (1.5eq), **NaOH** (3.0 eq), 25°C | 3h | 52 |
| 4 | EtOH, **69c** (1eq)**, 83b** (1.5eq), **NaOAc** (2.0 eq), 25°C | 4h | 44 |
| 5 | $CH_3CN$, **69c** (1eq)**, 83b** (2.0eq), **NaOAc** (2.0 eq), 25°C | 3h | 48 |
| 6 | $CH_3CN$, **69c** (1eq)**, 83b** (1.5eq), **NaOAc** (3.0 eq), 80°C | 2h | 62 |
| 7 | DCM, **69c** (1eq)**, 83b** (1.5eq), **NaOAc** (3.0 eq), 25°C | **2h** | **83** |
| 8 | DCM, **69c** (1eq)**, 83b** (2.0eq), **NaOAc** (3.0 eq), 40°C | 1.5h | 63 |

[a] Yields after purification by precipitation.

Firstly, a few trials have been performed to find out the best reaction conditions for the preparation of new azo disperse dyes (**70**). Therefore, condensation reaction of (*E*)-3-(dimethylamino)-1-(4-nitrophenyl)prop-2-en-1-one (**69c**) with 4-methylbenzenediazonium tetrafluoroborate (**83b**) was used as a model under different conditions (Table 4.5). In all trial experiments, at least 1.5 equivalents of compound **83b** were used with respect to the enaminone **69c** and the completion of each reaction was decided by the consumption of enaminone **69c** on TLC analysis. All the trial reactions by the use of NaOH (2-3 equiv.) in different solvents (MeOH, EtOH, DCM) afforded the expected disperse dye **70g** in low to moderate yields (Table 4.5, entries 1-3). The reaction trials with a milder base, NaOAc in EtOH and $CH_3CN$ at RT or under reflux caused some increases in the product yields (Table 4.5, entries 4-6). However, the best yield (83%) for the model reaction was obtained in DCM by the use of NaOAc (3 equiv.) in two hour (Table 4.5, entry 7). When the same reaction was carried out in DCM under reflux, the yield of expected product **70g** has decreased (Table 4.5, entry 8).

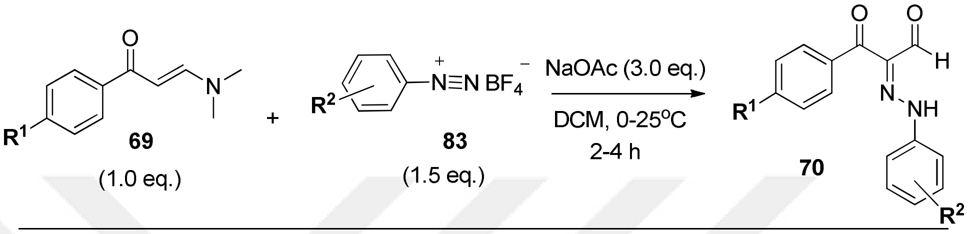
After optimizing the reaction conditions, all the *β*-(dimethylamino) arylpropenones (**69a-c**) were reacted with different diazonium tetrafluoroborate salts

**83a-e** in the presence of sodium acetate under specified reaction conditions to afford new derivatives of arylpropenone-based azo disperse dyes (**70**). Thus, nine derivatives of arylpropenone disperse azo dyestuffs (**70a-i**) were isolated in good yields with one or two exceptions under optimized reaction conditions (Table 4.6) after purification by flash column chromatography using 25-33% EtOAc/hexane mixtures as eluent.

Diazo coupling reactions of 3-(dimethylamino)-1-(4-(trifluoromethyl) phenyl)propenone **69a** with *p*-nitrophenyl diazonium tetrafluoroborate **83a**, *p*-tolyl diazonium tetrafluoroborate **83b**, 3,4-dimethoxyphenyl diazonium tetrafluoroborate **83c** afforded the products **70a-c** in moderate to good yields (60-74%) in 2-3 h (Table 4.6, entries 1-3). Among this series of products (**70a-c**), the best yield (74%) was obtained in diazo coupling reaction with *p*-nitrodiazonium tetrafluoroborate **83a** for about 3 h (Table 4.6, entry 1). Besides, diazo coupling reactions of 3-(dimethylamino)-1-(4-ethoxyphenyl)propenone **69b** with diazonium tetrafluoroborates (**83a-b**,**83e**) afforded the expected azo dyes (**70d-f**) in moderate to good yields. The best yield (90%) in diazo coupling of compound **69b** were obtained with benzo[*d*][1,3]dioxole-5-diazonium tetrafluoroborate **83e** in short reaction time (1.5 h) (Table 4.6, entry 6). However, the diazo coupling reactions of enaminone precursor **69b** with diazonium tetrafluoroborates **83a** (*p*-nitrophenyl), **83b** (*p*-tolyl) furnished the azo dye products (**70d-e**) in lower yields (55-65%) within 1.5-2h (Table 4.6, entries 4-5). Furthermore, the diazo coupling reactions of 3-(dimethylamino)-1-(4-nitrophenyl)propenone **69c** with diazonium tetrafluoroborates **83b** (*p*-tolyl), **83d** (*p*-chlorophenyl) gave the azo dye products (**70g, 70i**) in very good yields (81-83%) within 2 hour (Table 4.6, entries 7 and 9). In term of reaction yields, only the exception in this series was the reaction of enaminone precursor **69c** with *p*-nitrophenyl diazonium tetrafluoroborate **83a**, the azo dye product **70h** was isolated in quite low yield (45%) (Table 4.6, entry 8). According to these findings, the reaction of arylpropenone bearing ED group (4-EtO) with a diazonium salt bearing EW group (benzo[1,3]dioxol) was the most efficient one (90%) in the formation of azo disperse dyes under optimized reaction conditions. On the contrary, the least efficient coupling reaction with 45% yield was observed between arylpropenone and diazonium salt both bearing strong EW group (4-$NO_2$). It is also clear that arylpropenones bearing strong EW group ($NO_2$) gave excellent yields (81-

83%) with diazonium salts having weak ED groups such as $CH_3$, Cl. However, reaction of arylpropenone bearing strong EW group ($CF_3$) with diazonium salt having strong ED group (OMe) afforded the products in slightly lower yields (60-65%). In diazo coupling reactions affording the products **70h** and **70i**, formation of some isomers along with the products were determined through their NMR spectra (see experimental section 3.1.2.1).

**Table 4.6.** Arylpropenone azo disperse dyes **70a-i** and reaction yields



| Entry | Product | $R^1$ | $R^2$ | Time | Yield (%)[a] |
|---|---|---|---|---|---|
| **1** | **70a** | 4-$CF_3$ | 4-$NO_2$ | 3h 15min | 74 |
| **2** | **70b** | 4-$CF_3$ | 4-$CH_3$ | 1h 45min | 60 |
| **3** | **70c** | 4-$CF_3$ | 3,4-diMeO | 2h 50min | 65 |
| **4** | **70d** | 4-EtO | 4-$CH_3$ | 1h 30min | 55 |
| **5** | **70e** | 4-EtO | 4-$NO_2$ | 2h | 65 |
| **6** | **70f** | 4-EtO | 3,4-$OCH_2CH_2O$ | **1h 30min** | **90** |
| **7** | **70g** | 4-$NO_2$ | 4-$CH_3$ | 2h | 83 |
| **8** | **70h** | 4-$NO_2$ | 4-$NO_2$ | 2h | 45[b] |
| **9** | **70i** | 4-$NO_2$ | 4-Cl | 1h 45min | 81[c] |

[a] Total yields after CC using EA:H mixtures. [b] isomeric mixture (1:0.9). [c] isomeric mixture (1:0.5)

The structures of azo dye products (**70a-i**) were fully characterized by means of IR, $^1$H-NMR, $^{13}$C-NMR and HRMS analyses. As an example characterization data, the structure of product **70c** was primarily determined by the disappearance of N≡N (2252 $cm^{-1}$), B-F stretchings (1057,516 $cm^{-1}$) in IR spectra of precursor **83c** and by slight shift of ketone C=O stretching (1643 $cm^{-1}$) in the IR spectra of precursor **69a**. Also the formation of N-H (3093 $cm^{-1}$), C=O peaks (1651,1627 $cm^{-1}$) in the IR spectrum of the product **70c** confirmed the expected structure (Fig. 4.1).

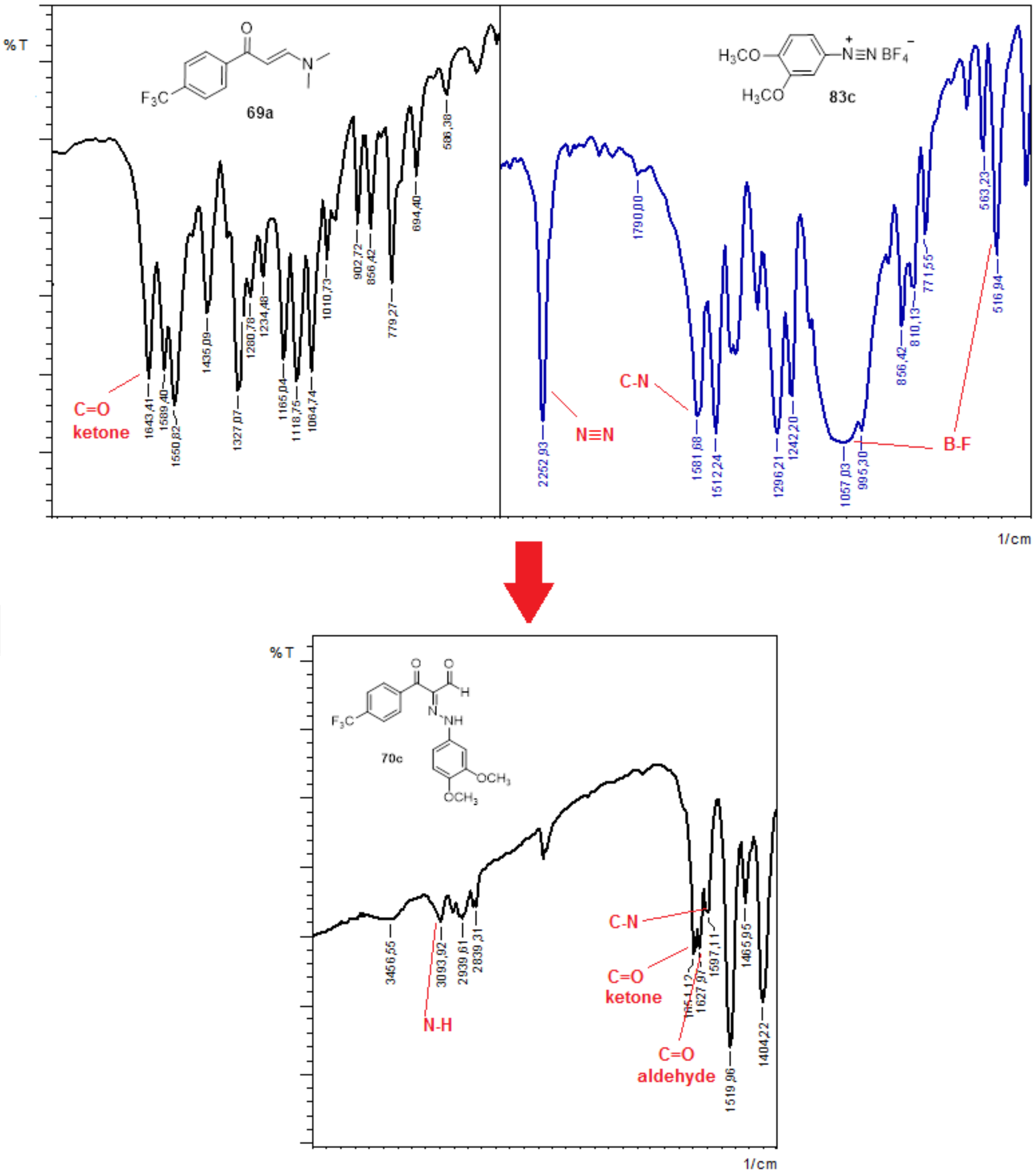


**Figure 4.1.** IR spectra of the precursors **69a, 83c** and product **70c**

Moreover, aromatic protons of *p*-$CF_3$-phenyl ring (7.97,7.70 ppm) and of 3,4-dimethoxyphenyl ring (6.87-6.80 ppm) in proton NMR of compound **70c** showed the presence of aromatic rings on the expected structure. The aldehyde proton signal at 10.16 ppm confirmed the expected structure of **70c** more clearly. The singlet peaks of methoxy protons (3.86-3.77 ppm) were the additional data supporting the expected structure of **70c** (Figure 4.2). In $^{13}$C-NMR of product **70c**, the aldehyde (**C**HO), quarternary N=**C** and =C-NH carbon signals at 190.5, 131.3 and 134.6 ppm provided extra supporting data for the expected structure (Figure 4.3). Besides, $^{17}$F-$^{13}$C coupling constants (*p*-$CF_3$-Ph) in $^{13}$C-NMR of the product **70c** were found as follows; $^1J$(C-F) = 272.2 Hz (125.1-122.4 ppm), $^2J$(C-F$_{ortho}$) = 32.8 Hz (133.6-132.6

ppm), $^3J(C\text{-}F_{meta})$ = 3.6 Hz (124.6-123.8 ppm). It is obvious that they are in accordance with early reported values in the literature (Reichenbacher and Popp, 2012; Schaefer et al., 1983; Ingeborg and Schuster, 1969) (Fig. 4.3). Finally, the expected structure of **70c** was confirmed by HRMS data (379.0920, $[M\text{-}H]^+$) accurately by applying TOF-MS ($ESI^-$) technique (figures 4.4).

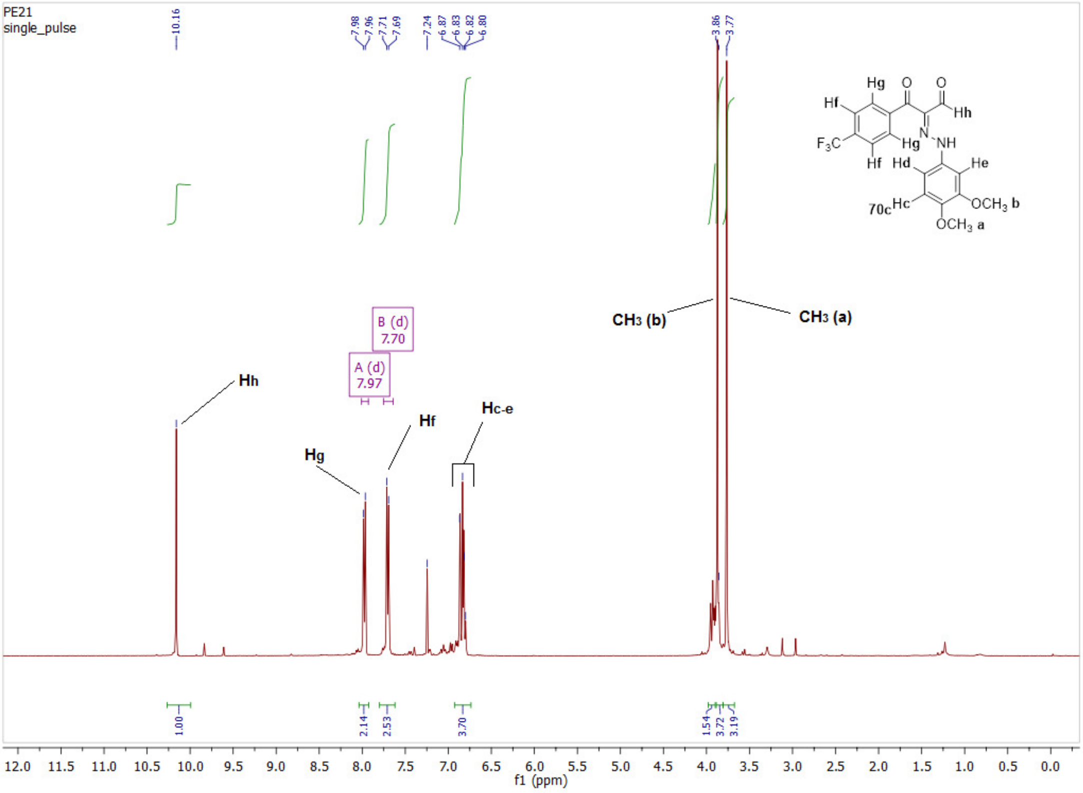


**Figure 4.2.** $^1$H-NMR spectrum of the product **70c**

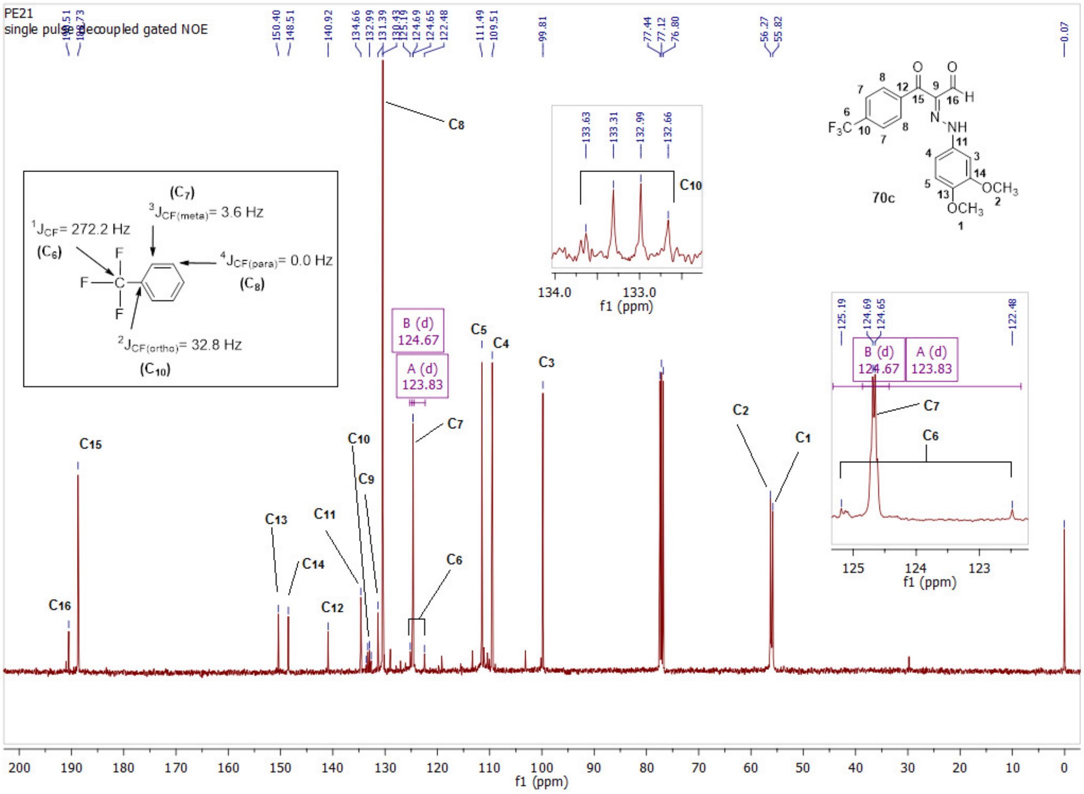


Figure 4.3. $^{13}$C-NMR spectrum of the product **70c**

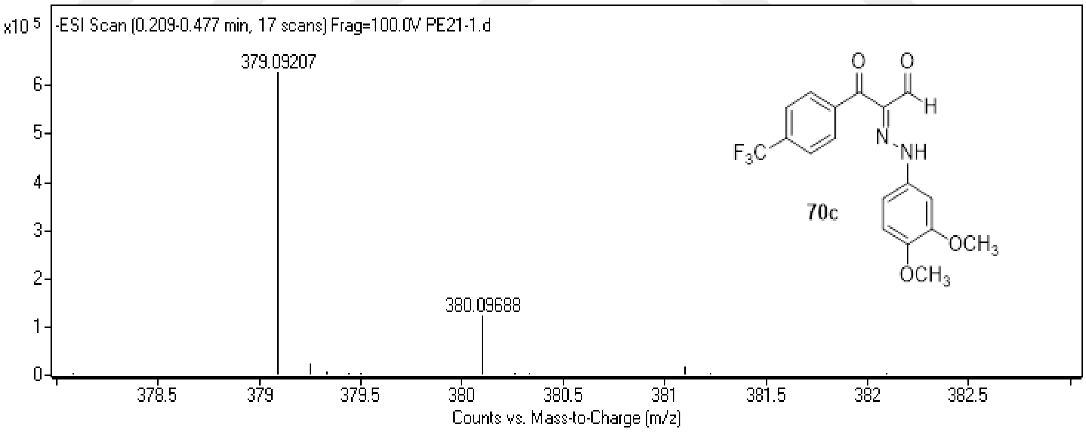


**Figure 4.4.** HRMS spectrum of the product **70c**

**Table 4.7.** Indicative IR and NMR data for the azo dye products (**70a-i**)

| **Comp.** | **IR** ($\nu_{max}$/cm$^{-1}$) | | | **$^1$H-NMR** (δ,ppm) | | **$^{13}$C-NMR** (δ,ppm) | | |
|---|---|---|---|---|---|---|---|---|
| **70** | NH | C=O (ald.) | C=O ketone | C**H**O | Arom. C**H** | **C**HO | **C**-NH | N=**C** |
| **a** | 3109 | 1697 | 1651 | 10.22 | 8.28-8.02<br>7.76-7.38 | 190.1 | 145.9 | 130.6 |
| **b** | 3117 | 1643 | - | 10.17 | 8.02-7.72,<br>7.19 | 190.3 | 138.6 | 130.6 |
| **c** | 3093 | 1651 | 1627 | 10.16 | 7.97,7.70;<br>6.87-6.80 | 190.5 | 134.6 | 131.3 |
| **d** | - | 1638 | - | 10.10 | 7.99-7.22<br>7.18-6.93 | 189.6 | 139.0 | 132.9 |
| **e** | 3115 | 1627 | - | 10.12 | 8.25-7.97<br>7.41-6.95 | 190.6 | 146.5 | 134.1 |
| **f** | 3062 | 1627 | - | 10.07 | 7.95-6.93<br>6.79-6.70 | 189.6 | 136.4 | 132.7 |
| **g** | 3103 | 1648 | 1632 | 10.17 | 8.31-8.02<br>7.20-7.16 | 189.7 | 138.4 | 131.1 |
| **h** | 3116 | 1649 | - | 10.24 | 8.37-8.27<br>8.13-7.47 | 189.9 | 131.1 | 129.5 |
| **i** | 3111 | 1649 | - | 10.20 | 8.34-8.02<br>7.38-7.20 | 189.6 | 142.5 | 135.2 |

Applying the same characterization techniques, all other azo disperse dyes **70a-b, 70d-i** were characterized by regarding their indicative IR, $^1$H-NMR, $^{13}$C-NMR and accurate HRMS data as presented in the examples (Table 4.7). HRMS data of all other disperse azo dyes (**70a-b, 70d-i**) were in accordance with their calculated mass values (Table 4.8).

**Table 4.8.** HRMS (TOF-MS) data for the products **70a-i**

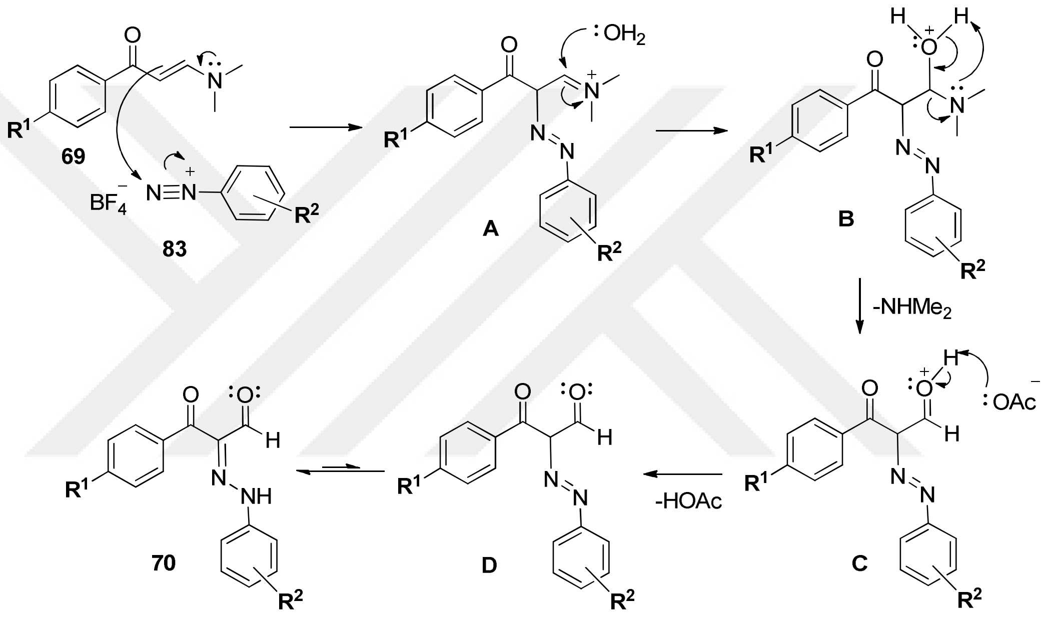
| **Comp.** | **HRMS** | | |
|---|---|---|---|
| **70** | **Found (*m/z*)** | **Calculated (*m/z*)** | **Ionization method** |
| **a** | 364.0544 | 364.0550 | ESI$^-$ |
| **b** | 333.0821 | 333.0856 | ESI$^-$ |
| **c** | 379.0920 | 379.0920 | ESI$^{--}$ |
| **d** | 309.1245 | 309.1244 | ESI$^-$ |
| **e** | 340.0927 | 340.0938 | ESI$^-$ |
| **f** | 339.0967 | 339.0986 | ESI$^-$ |
| **g** | 310.0837 | 310.0833 | ESI$^-$ |
| **h** | 341.0575 | 341.0527 | ESI$^-$ |
| **i** | 330.0286 | 330.0287 | ESI$^-$ |

ESI$^-$: Accurate mass found as [M-H]$^+$

In general, arylpropenone-based azo disperse dyes (**70a-i**) were prepared very efficiently in gram scale in order to be tested for their dyeing properties on synthetic fiber (Table 4.6). Similarly, the preparation of two arylpropenone-based azo dyes in excellent yields have been reported in a few recent studies (Al-Etaibi et al., 2016; Al-

Etaibi et al., 2015). To the best of our knowledge, no other study on the preparation of arylpropenone-based azo dyes is present until today.

A suitable mechanism was proposed as follow; firstly, the formation of coupling product (**A**) by the nucleophilic attack of *N*,*N*-dimethylarylpropenone **69** to diazonium salt **83**, then the elimination of dimethylamine after the attack of water to iminium carbon on structure **A** giving protonated aldehyde (**C**), lastly this is followed by deprotonation of structure **C** by acetate ion and imine-enamine tautomerization of structure **D** to afford the disperse dye molecule **70** (Scheme 4.3).



**Scheme 4.3.** Mechanism for the formation of arylpropenone azo dyes **(70)**

## 4.3 PHYSICAL AND DYEING PROPERTIES OF DISPERSE DYES

### 4.3.1 Preparation of Disperse Dye Solutions and Their Physical Properties

30 mL of each standard disperse or nanodisperse dye solution was prepared from dyestuffs (**70a-i**) as %1 in solution using volumetric flasks. Then, the dispersion characteristics of each dye solution were observed and given in table.

**Table 4.9.** Dispersion characteristics of dye solutions **70a-i**

| Dye | Dye Solution | Dispersion | Appearance |
|---|---|---|---|
| **70a** | Disperse PE18 | well dispersed | homogeneous |
| **70a** | Disperse PE18Nano | well dispersed | homogeneous but blurred |
| **70b** | Disperse PE20 | well dispersed | homogeneous but ppt at the bottom |
| **70c** | Disperse PE21 | well dispersed | homogeneous |
| **70d** | Disperse PE22 | poor dispersed | homogeneous but ppt at the bottom |
| **70e** | Disperse PE23 | well dispersed | homogeneous |
| **70f** | Disperse PE24 | poor dispersed | homogeneous |
| **70g** | Disperse PE25 | well dispersed | homogeneous |
| **70h** | Disperse PE26 | poor dispersed | homogeneous |
| **70i** | Disperse PE27 | poor dispersed | homogeneous |
| **70i** | Disperse PE27Nano | well dispersed | homogeneous |

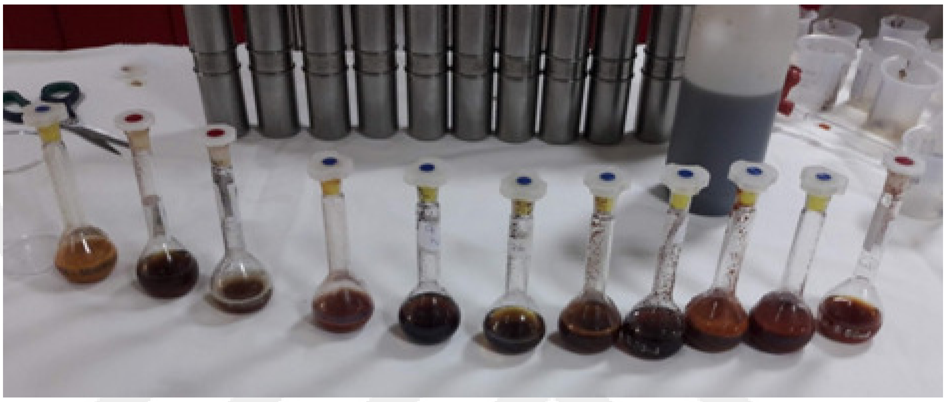


**Figure 4.5.** General appearance of disperse dye solutions (standard and nano dyes) and sample dyeing tubes

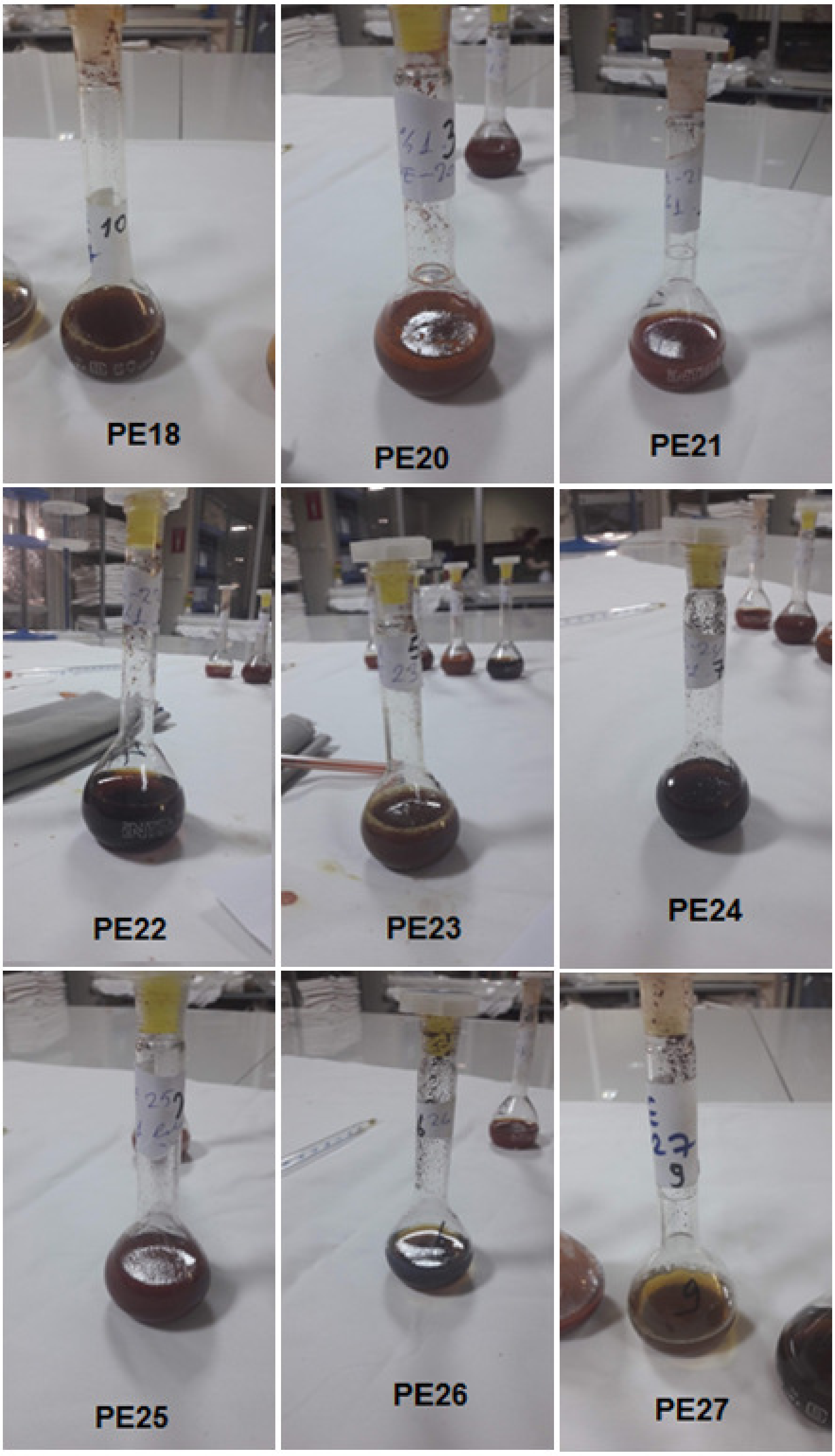


**Figure 4.6.** Standard disperse dyes solutions with compounds **70a-i**

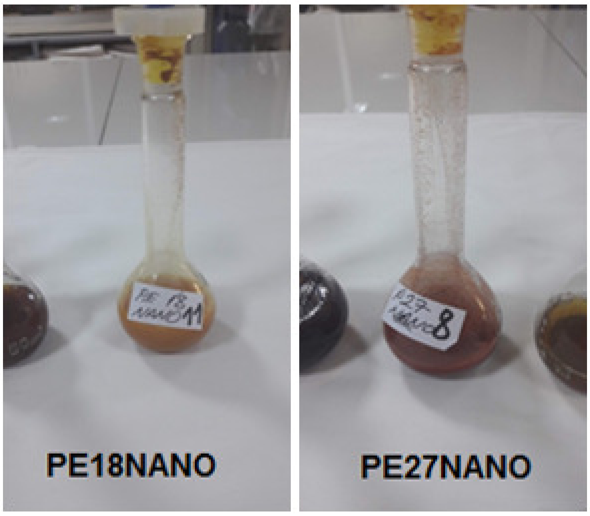


**Figure 4.7.** Nano disperse dye solutions with compounds **70a** and **70i**

### 4.3.2 Coloring Properties of Disperse Dyes on Polyester Fabrics

Polyester fabric samples in 5g/m$^2$ were colored using 11 dye solutions by applying high-temperature (HT) dyeing process at 130$^o$C for 45 minutes and a range of colors from beige to orange were observed as in figure 4.8 and table 4.10.

**Table 4.10.** Colors observed on polyester fabrics with dyestuffs (PE18-27)

| Disperse Dye | Substituents | Color on polyester fabric |
|---|---|---|
| PE18 (**70a**) | **R**$^1$: 4-$CF_3$ **R**$^2$: 4-$NO_2$ | Light yellow |
| PE18 Nano (**70a**) | **R**$^1$: 4-$CF_3$ **R**$^2$: 4 -$NO_2$ | Dark yellow |
| PE20 (**70b**) | **R**$^1$: 4-$CF_3$ **R**$^2$: 4-$CH_3$ | Beige |
| PE21 (**70c**) | **R**$^1$: 4-$CF_3$ **R**$^2$: 3,4-di$OCH_3$ | Orange-yellow |
| PE22 (**70d**) | **R**$^1$: 4-EtO **R**$^2$: 4-$CH_3$ | Pale yellow |
| PE23 (**70e**) | **R**$^1$: 4-EtO **R**$^2$: 4-$NO_2$ | Dark yellow |
| PE24 (**70f**) | **R**$^1$: 4-EtO **R**$^2$: 3,4-$OCH_2CH_2O$ | Bright orange-yellow |
| PE25 (**70g**) | **R**$^1$: 4- $NO_2$ **R**$^2$: 4-$CH_3$ | Orange |
| PE26 (**70h**) | **R**$^1$: 4- $NO_2$ **R**$^2$: 4-$NO_2$ | Pale orange-yellow |
| PE27 (**70i**) | **R**$^1$: 4- $NO_2$ **R**$^2$: 4-Cl | Pale orange |
| PE27 Nano (**70i**) | **R**$^1$: 4- $NO_2$ **R**$^2$: 4-Cl | Dark orange |

When the polyester samples were dyed with **70a-c** derivatives, mostly yellow and beige color shades were observed on the polyester fabrics. Besides, a darker yellow color were obtained by applying the nanoemulsion form of **70a** on polyester fabric sample. In this series, much deeper color shades were observed by the change of substituents ($R^2$) from nitro to methoxy on diazophenyl group, but when the substituent ($R^2$) was methyl group on diazophenyl group, lighter colour shade (beige) were obtained on fabric samples.

**Figure 4.8.** Colors produced on polyester fabrics using dyestuffs (**70a-i**)

With the **70d-f** derivatives bearing ethoxy group ($R^1$), pale yellow to orange yellow color shades were obtained on polyester fabric samples. Not surprisingly, pale yellow color shade were observed when the substituent ($R^2$) on diazophenyl ring was methyl group. By the substitutions with nitro or 3,4-dioxophenyl groups ($R^2$) on diazophenyl ring, the color shades became darker (dark-orange yellow) on polyester fabrics. In the last series of dyes (**70g-i**) bearing nitro group ($R^1$), orange-yellow to orange color shades were obtained on polyester fabrics. Much deeper orange color were observed with methyl substituent ($R^2$) on diazophenyl ring while nitro and chloro substituents ($R^2$) have produced much lighter color shades (pale orange-yellow to pale orange). However, when polyester samples were colored with nanoemulsion of **70i**, much deeper colors were observed in comparison to the polyester fabric colored with standard dye solution of **70i**. The results with nanoemulsions of **70a** and **70i** supported that the dyeing in nanoemulsion form was much more effective than the dyeing with standard dye solutions on polyester fabrics.

Datacolor color spectroscopy was used for the measurements of colors obtained on polyester fabrics. This spectroscopic technique which is based on reflection or scattering of light by a material aims the measuring of colour parameters of textile, plastic, metal or paper substrates. It also allows the measurement of remission spectrum of incident light within the visible part of the spectrum (360-700 nm) and the measurement of whiteness, optical brightness and fluorescent colours. Obtained CIE LAB color coordinate data and K/S (color strength) graphs are presented below (Fig.4.9 and Table 4.11-12, also see appendices for all graphs). The K/S values are basicly determined by applying the Kubelka-Munk equation:

$$K/S = [(1-R)^2/2R] - [(1-R_o)^2/2R_o]$$

where R is the reflectance of colored samples and K and S are the absorption and scattering coefficients, respectively. Ro = decimal fraction of the reflectance of the undyed fabric.

$$\text{CIE Lab Difference} \quad \Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

ΔE: Total color difference between the sample and the standard: L represents the white-black axis, a represents the red-green axis and finally b represents the yellow-blue axis.

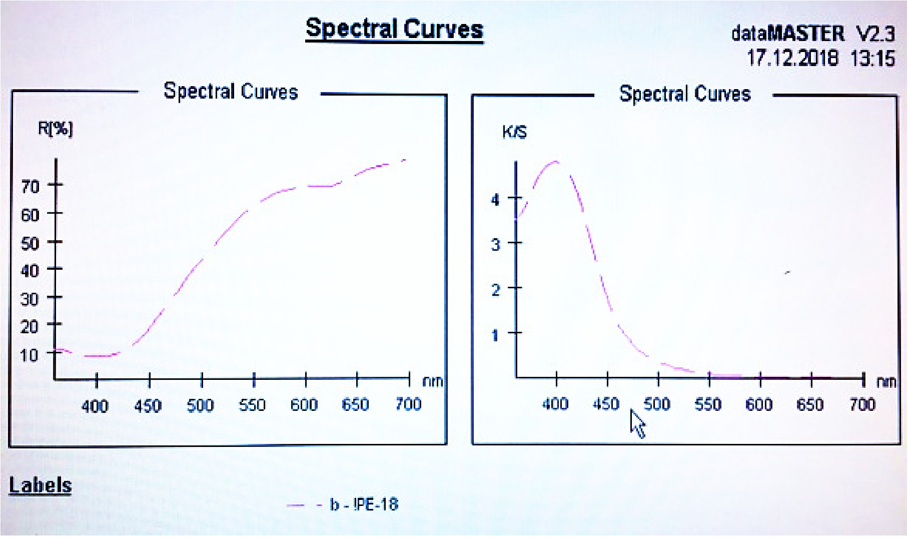


**Figure 4.9.** Example K/S and %R graphs obtained by reflectance spectrophotometry for sample dyed with PE18 dye solution

**Table 4.11.** Optical measurements of dyed polyester fabrics with **70a-i** derivatives.

| | | **Color coordinates** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **Light sources** | *L** | *a** | *b** | *C** | *h** | *X* | *Y* | *Z* | *x* | *y* |
| **PE18** | D65/10 | 80.86 | -0.13 | 49.38 | 49.38 | 90.15 | 55.14 | 58.22 | 21.83 | 0.4079 | 0.4306 |
| | A/10 | 83.38 | 7.66 | 49.19 | 49.79 | 81.15 | 73.70 | 62.88 | 8.02 | 0.5097 | 0.4349 |
| | F11/10 | 82.76 | 0.48 | 55.93 | 55.93 | 89.51 | 64.32 | 61.72 | 12.26 | 0.4651 | 0.4463 |
| | TL83/10 | 83.63 | 2.90 | 59.24 | 59.31 | 87.20 | 73.22 | 63.38 | 7.21 | 0.5058 | 0.4437 |
| **PE18 Nano** | D65/10 | 82.51 | 3.53 | 42.56 | 42.71 | 85.26 | 59.52 | 61.24 | 27.66 | 0.4010 | 0.4126 |
| | A/10 | 85.19 | 10.84 | 43.55 | 44.88 | 76.02 | 79.41 | 66.38 | 9.87 | 0.5102 | 0.4264 |
| | F11/10 | 84.30 | 5.01 | 48.07 | 48.33 | 84.05 | 69.50 | 64.64 | 15.96 | 0.4630 | 0.4306 |
| | TL83/10 | 85.32 | 7.09 | 51.53 | 52.02 | 82.16 | 78.12 | 66.63 | 9.45 | 0.5066 | 0.4321 |
| **PE20** | D65/10 | 84.09 | 3.01 | 54.47 | 54.55 | 86.84 | 62.18 | 64.24 | 22.09 | 0.4187 | 0.4325 |
| | A/10 | 87.14 | 10.72 | 55.22 | 56.25 | 79.02 | 83.90 | 70.29 | 8.11 | 0.5170 | 0.4331 |
| | F11/10 | 86.37 | 3.47 | 61.35 | 61.45 | 86.76 | 73.08 | 68.72 | 12.52 | 0.4735 | 0.4453 |
| | TL83/10 | 87.46 | 5.91 | 64.26 | 64.53 | 84.74 | 82.45 | 70.94 | 7.52 | 05124 | 0.4409 |
| **PE21** | D65/10 | 71.76 | 12.07 | 73.83 | 74.81 | 80.72 | 45.12 | 43.31 | 6.24 | 0.4766 | 0.4575 |
| | A/10 | 76.14 | 16.42 | 78.48 | 80.18 | 78.18 | 62.90 | 50.12 | 2.29 | 0.5455 | 0.4347 |
| | F11/10 | 75.86 | 5.70 | 81.52 | 81.72 | 86.00 | 53.84 | 49.66 | 3.72 | 0.5021 | 0.4632 |
| | TL83/10 | 77.21 | 7.45 | 82.79 | 83.13 | 84.86 | 61.24 | 51.88 | 2.39 | 0.5302 | 0.4491 |
| **PE22** | D65/10 | 85.12 | -5.70 | 47.10 | 47.44 | 96.90 | 60.38 | 66.25 | 27.64 | 0.3914 | 0.4294 |
| | A/10 | 87.00 | 3.04 | 45.64 | 45.74 | 86.19 | 79.41 | 70.00 | 10.11 | 0.4978 | 0.4388 |
| | F11/10 | 86.63 | -4.20 | 52.93 | 53.09 | 94.54 | 69.90 | 69.25 | 15.64 | 0.4515 | 0.4474 |
| | TL83/10 | 87.23 | -1.52 | 55.98 | 55.40 | 91.57 | 77.93 | 70.48 | 9.32 | 0.4941 | 0.4468 |
| **PE23** | D65/10 | 79.42 | 1.83 | 58.68 | 58.71 | 88.21 | 53.48 | 55.66 | 15.91 | 0.4277 | 0.4451 |
| | A/10 | 82.43 | 10.56 | 58.32 | 59.27 | 79.73 | 73.09 | 61.09 | 6.08 | 0.5211 | 0.4355 |
| | F11/10 | 81.56 | 2.76 | 66.17 | 66.23 | 87.61 | 63.02 | 59.49 | 8.71 | 0.4802 | 0.4534 |
| | TL83/10 | 82.62 | 5.40 | 69.28 | 69.49 | 85.55 | 71.31 | 61.46 | 5.17 | 0.5169 | 0.4455 |
| **PE24** | D65/10 | 77.51 | 11.69 | 70.45 | 71.41 | 80.58 | 54.11 | 52.38 | 10.03 | 0.4644 | 0.4495 |
| | A/10 | 81.85 | 17.67 | 74.24 | 76.31 | 76.61 | 75.46 | 60.03 | 3.71 | 0.5421 | 0.4312 |
| | F11/10 | 80.94 | 9.17 | 77.79 | 78.33 | 83.28 | 64.70 | 58.37 | 5.85 | 0.5019 | 0.4528 |
| | TL83/10 | 82.46 | 11.11 | 79.80 | 80.57 | 82.07 | 73.82 | 61.15 | 3.68 | 0.5324 | 0.4410 |
| **PE25** | D65/10 | 71.14 | 23.19 | 64.25 | 68.31 | 70.15 | 48.10 | 42.39 | 8.53 | 0.4858 | 0.4281 |
| | A/10 | 76.53 | 28.08 | 69.86 | 75.30 | 68.10 | 69.19 | 50.76 | 3.17 | 0.5620 | 0.4123 |
| | F11/10 | 74.21 | 22.60 | 71.40 | 74.89 | 72.44 | 57.86 | 47.02 | 4.88 | 0.5271 | 0.4284 |
| | TL83/10 | 76.35 | 23.71 | 75.12 | 78.77 | 72.48 | 67.06 | 50.46 | 3.01 | 0.5564 | 0.4187 |

**Table 4.11 (continued).** Optical measurements of dyed polyester fabrics with **70a-i** derivatives.

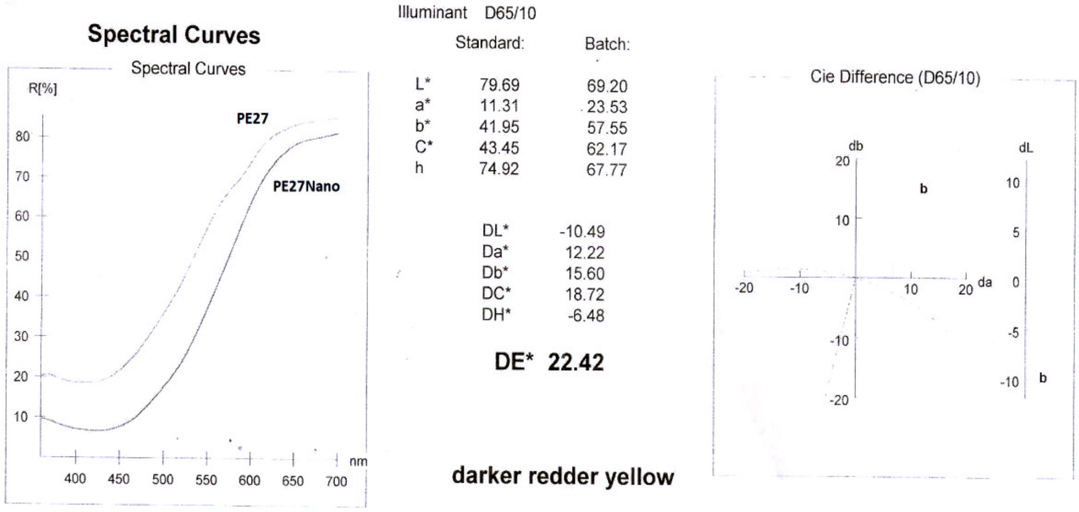
| | | **Color coordinates** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **Light sources** | *L** | *a** | *b** | *C** | *h** | *X* | *Y* | *Z* | *x* | *y* |
| **PE26** | D65/10 | 86.90 | -1.14 | 42.40 | 42.41 | 91.55 | 65.67 | 69.80 | 33.02 | 0.3898 | 0.4143 |
| | A/10 | 89.08 | 7.14 | 41.86 | 42.47 | 80.32 | 86.59 | 74.34 | 11.90 | 0.5010 | 0.4301 |
| | F11/10 | 88.38 | 1.24 | 48.21 | 48.22 | 88.53 | 76.31 | 72.87 | 18.76 | 0.4544 | 0.4339 |
| | TL83/10 | 89.20 | 3.67 | 51.80 | 51.93 | 85.95 | 85.38 | 74.60 | 11.01 | 0.4993 | 0.4363 |
| **PE27** | D65/10 | 79.69 | 11.31 | 41.95 | 43.45 | 74.92 | 57.71 | 56.13 | 24.98 | 0.4157 | 0.4043 |
| | A/10 | 83.21 | 16.57 | 45.78 | 48.69 | 70.10 | 77.90 | 62.54 | 8.65 | 0.5225 | 0.4195 |
| | F11/10 | 82.11 | 10.50 | 47.47 | 48.61 | 77.53 | 67.64 | 60.51 | 14.78 | 0.4733 | 0.4233 |
| | TL83/10 | 83.42 | 12.05 | 50.22 | 51.65 | 76.50 | 76.43 | 62.96 | 9.00 | 0.5151 | 0.4243 |
| **PE27 Nano** | D65/10 | 69.20 | 23.53 | 57.55 | 62.17 | 67.77 | 45.25 | 39.62 | 9.57 | 0.4792 | 0.4195 |
| | A/10 | 74.46 | 27.92 | 63.97 | 69.79 | 66.42 | 64.86 | 47.42 | 3.43 | 0.5605 | 0.4099 |
| | F11/10 | 72.42 | 21.93 | 64.48 | 68.11 | 71.21 | 54.41 | 44.29 | 5.58 | 0.5217 | 0.4247 |
| | TL83/10 | 74.47 | 22.92 | 68.19 | 71.94 | 71.42 | 62.89 | 47.43 | 3.42 | 0.5529 | 0.4170 |

CIELAB color coordinates (L,a$^*$,b$^*$): L: lightness; a$^*$: red-green coordinate, with +a$^*$ indicating red and –a$^*$ indicating green; b$^*$: yellow-blue coordinate, with +b$^*$ indicating yellow and –b$^*$ indicating blue ; X,Y,Z: Tristumulus values computed from the light-object-observer data.; h: hue angle, expressed in degree ; C$^*$: chroma coordinate, the distance from lightness axis.

**Table 4.12.** K/S and %R values obtained for dyed polyester samples.

| | **PE18** | **PE18 nano** | **PE20** | **PE21** | **PE22** | **PE23** | **PE24** | **PE25** | **PE26** | **PE27** | **PE27 nano** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **K/S** | 4.5 | 3.5 | 3.25 | 9.8 | 2.7 | 7.0 | 6.0 | 8.3 | 2.7 | 1.8 | 7.0 |
| **%R** | 10 | 12 | 12 | 5 | 15 | 7 | 7 | 5 | 15 | 20 | 5 |

Color strength or surface color yield (K/S) is an important paramater to give the information on absorption of dye in what amounts by the surface of the material. K/S values with standard dye solutions were mainly obtained high in HT dyeing treatment at 130°C (Table 4.12). In general, most of the dyes exhibited good affinities to polyester samples with higher K/S values (3.25-9.8). A few dyestuffs (**70d**, **70h-i**) exhibited moderate affinities to the surface of polyester samples with lower K/S values (1.8-2.7). Observed %R values are in accordance with obtained K/S values for dyeing with standard dye solutions (Table 4.12). However, K/S value with nanodisperse dye solutions were mainly much higher in HT dyeing process at same temperature. For instance, nanodisperse dye solution of **70i** exhibited stronger dyeing performance on polyester samples with much higher K/S value (7.0) than the one dyed with standard dye solution of **70i** (K/S:1.8). Regarding the ΔE and %R values on the graphs, it is clear that the dyeing with nanodisperse dye solution of **70i** is at least 2 times more effective than the dyeing with its standard dye solution (Figure 4.10).



Illuminant D65/10

|  | Standard: | Batch: |
|---|---|---|
| L* | 79.69 | 69.20 |
| a* | 11.31 | 23.53 |
| b* | 41.95 | 57.55 |
| C* | 43.45 | 62.17 |
| h | 74.92 | 67.77 |

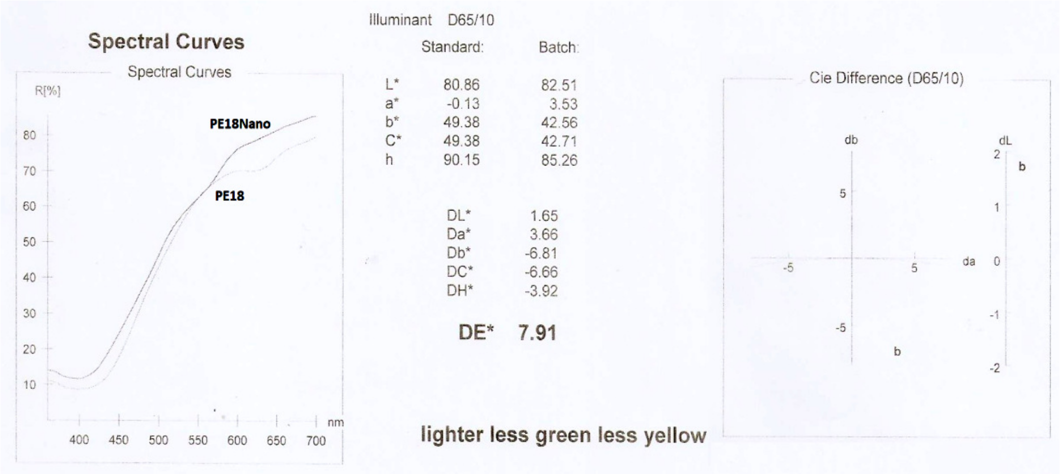
| | |
|---|---|
| DL* | -10.49 |
| Da* | 12.22 |
| Db* | 15.60 |
| DC* | 18.72 |
| DH* | -6.48 |

**DE* 22.42**

**darker redder yellow**

**Figure 4.10.** Comparison the coloring properties of PE27 and PE27nano dyes on polyester samples

However, nanodisperse dye solution of **70a** exhibited slightly weaker dyeing performance on polyester samples with a bit lower K/S value (3.5) than the one dyed with standard dye solution of **70a** (K/S:4.5). Besides, the ΔE and %R values supported that the dyeing with nanodisperse dye solution of **70a** is about 7.9 percent less effective than the dyeing with its standard dye solution (Figure 4.11). This result was the surprising one and it was possibly originated from poor dispersion of dyestuff by inefficient ultrasonication during the preparation of its nanodisperse dye solution.



Illuminant D65/10

|  | Standard: | Batch: |
|---|---|---|
| L* | 80.86 | 82.51 |
| a* | -0.13 | 3.53 |
| b* | 49.38 | 42.56 |
| C* | 49.38 | 42.71 |
| h | 90.15 | 85.26 |

| | |
|---|---|
| DL* | 1.65 |
| Da* | 3.66 |
| Db* | -6.81 |
| DC* | -6.66 |
| DH* | -3.92 |

**DE* 7.91**

**lighter less green less yellow**

**Figure 4.11.** Comparison the coloring properties of PE18 and PE18 nano dyes on polyester samples

### 4.3.3 Fastness Properties of Disperse Dyes on Fabrics

Washing, water, acidic-basic perspiration fastness test results were mostly obtained good. Besides, the rubbing fastness results of all samples were obtained excellent (Table 4.13). These fastness results of tested dyes (**70a-i**) on polyester samples are as expected and similar to test results of dyeing applications with different disperse dyes on polyester fabrics in different literature studies (Liu et al., 2012; Metwally et al., 2012; Maamoun, 2014; Al-Etaibi et al., 2016; Zadafiya & Malik, 2013).

**Table 4.13.** Washing, water, acidic-basic perspiration, rubbing fastness results of dyed polyester samples

| Dye code | Washing fastness | Water fastness | Perspiration Fastness (acidic) | Perspiration Fastness (basic) | Rubbing fastness |
|---|---|---|---|---|---|
| PE 18 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 18 NANO | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 20 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 21 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 22 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 23 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 24 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 25 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 26 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE27 | 4-5 | 4-5 | 4-5 | 4-5 | 5 |
| PE 27 NANO | 4-5 | 4-5 | 4-5 | 4-5 | 5 |

5: Excellent; 4-5: Good; 3-4: satisfactory; 1-2: Bad.

Besides, light and sublimation/staining fastness results were obtained according to ISO 105 BO2 light fastness and ISO 105 P01 color fastness (sublimation) standards, respectively. Light fastness results of all standard dye solutions (**70a-i**) were obtained low (1-2) on polyester samples, however, light fastness results of two nanodye emulsions with **70a** and **70i** (PE18nano, PE27nano) were found more satisfactory (3) when compared with standard dye solution results. This finding indicates that nanoemulsion form of dyestuffs (**70a,70i**) were much more stable on the surface of polyester fabric samples due to smaller particle size of dyes. Moreover, all type of dye solutions exhibited satisfactory sublimation fastnesses (3-4) on polyester samples. Even the sublimation fastness results may seem disadvantageous, these results imply that those dyestuffs (**70a-i**) would be more convenient to use in digital printing technology. Besides, staining fastness test results were found in satisfactory levels (1-4) for all type of dye solutions (standard or nano). Therefore, it is thought that the transfer of dyes from the surface will be easier by the effect of heat.

**Table 4.14.** Light, sublimation/staining fastness results of dyed polyester samples

| Dye code | Light Fastness | Sublimation/ Staining Fastness |
|---|---|---|
| PE 18 | 2 | 3-4/3 |
| PE18 NANO | 3 | 3/3 |
| PE 20 | 1 | 3/2 |
| PE 21 | 1-2 | 4/1 |
| PE 22 | 1 | 3/2-3 |
| PE 23 | 2 | 4/3 |
| PE 24 | 1-2 | 4/2 |
| PE 25 | 1-2 | 3-4/1-2 |
| PE 26 | 2 | 3-4/4 |
| PE27 | 1 | 3-4/3-4 |
| PE 27 NANO | 2-3 | 3-4/2 |

5: Excellent; 4-5: Good; 3-4: satisfactory; 1-2: Bad

# 5. CONCLUSIONS

The general outcomes obtained in the current dissertation study are summarized and given in order below.

- ✓ In the first part, three *p*-substituted arylpropenones (**69a-c**) and five aryl diazonium tetrafluoroborates (**83a-e**) were prepared as the precursors by following the literature methods and characterized by IR and NMR analyses.

- ✓ In the second part of the study, after optimization of the reaction conditions, the synthesis of new arylpropenone-based azo disperse dyes (**70a-i**) were performed via diazo coupling reactions of *β*-(dimethylamino)arylpropenones (**69**) and diazonium tetrafluoroborates **83** in the presence of sodium acetate very efficiently. The structures of new azo disperse dyes (**70a-i**) were elucidated by means of IR, NMR ($^1$H,$^{13}$C) and HRMS measurements. An easy, gram-scale and efficient access to new arylpropenone-based azo disperse dyes (**70**) were provided under very mild conditions.

- ✓ In the third part of the study, nine new arylaminopropenone azo dyes (**7a-i**) were studied for their dyeing and fastness properties using standard and nanoemulsion forms of the dyes on polyester fabric samples. To the best of our knowledge, only two examples of arylaminopropenone azo dyestuffs are present in recent literature.

- ✓ In general, homogenous and well-dispersed aqueous dye solutions were obtained either in standard or nanoemulsion forms. Besides, a range of colors from beige to orange were observed after application of standard and nanoemulsion solutions of dyes on polyester fabrics.

- ✓ The properties of color shades on polyester fabrics were analysed by remission spectroscopy and K/S and %R values were determined to understand the stability of dyestuffs on polyester fibres. Other color index parameters were also determined to support these values.

- ✓ Dyeing with nanoemulsion forms of dyestuffs produced much deeper color shades and were much more effective than dyeing with standard dye solutions of same disperse dyestuff. These observations were supported by determining % ΔE, %R and CIE difference values from graphs.

- ✓ Lastly, washing, water, acidic-basic perspiration and rubbing fastnesses of polyester fabric samples dyed with disperse dyestuffs (**70a-i**) were mostly obtained good and excellent. Light and sublimation/staining fastnesses of same polyester fabric samples dyed with disperse dyestuffs (**70a-i**) were obtained in satisfactory levels. Light fastnesses of polyester samples dyed with nanoemulsions were slightly higher than the standard dye solutions. In particular, regarding the sublimation fastness results, those dyestuffs (**70a-i**) would be more suitable to use in digital printing technology on different synthetic materials.

- ✓ As future perspectives, the nanoemulsions of prepared disperse dyes (**70a-i**) will be prepared using different methods and their dyeing effieciency and properties will be studied in near advance. Besides, some commercial dyes will also be converted into nanoemulsions and their dyeing abilities on different fiber types will be investigated by applying different dyeing methods.

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# APPENDICES

# 7. APPENDICES

## 7.1 SPECTRA FOR STARTING MATERIALS

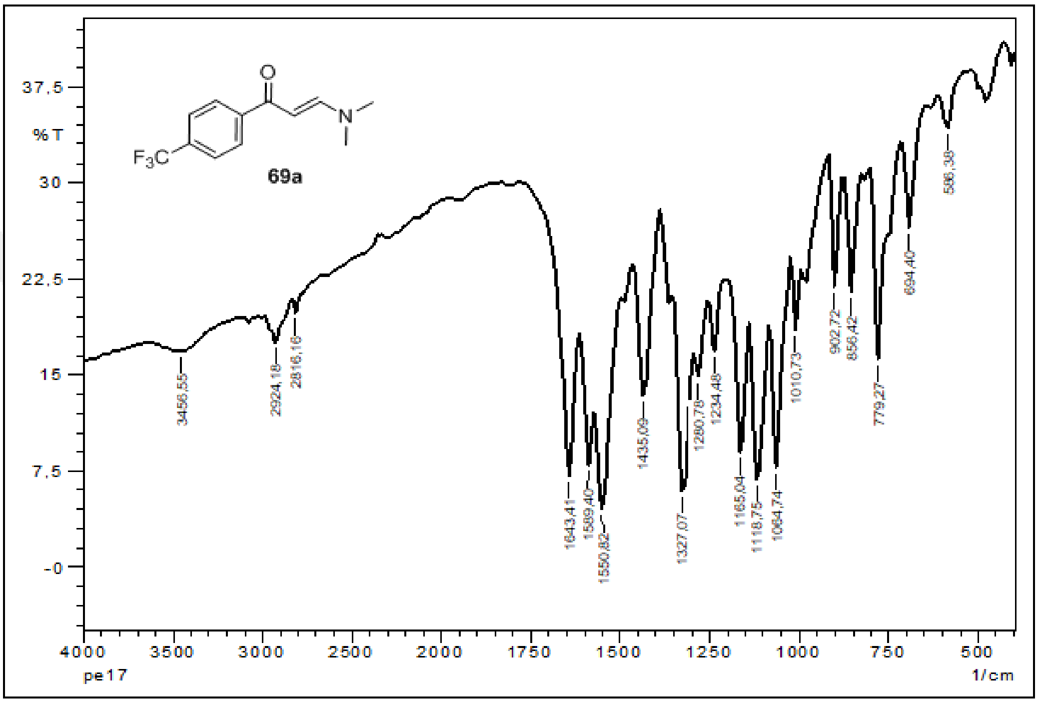


**Figure 7.1.** IR spectrum of compound **69a**

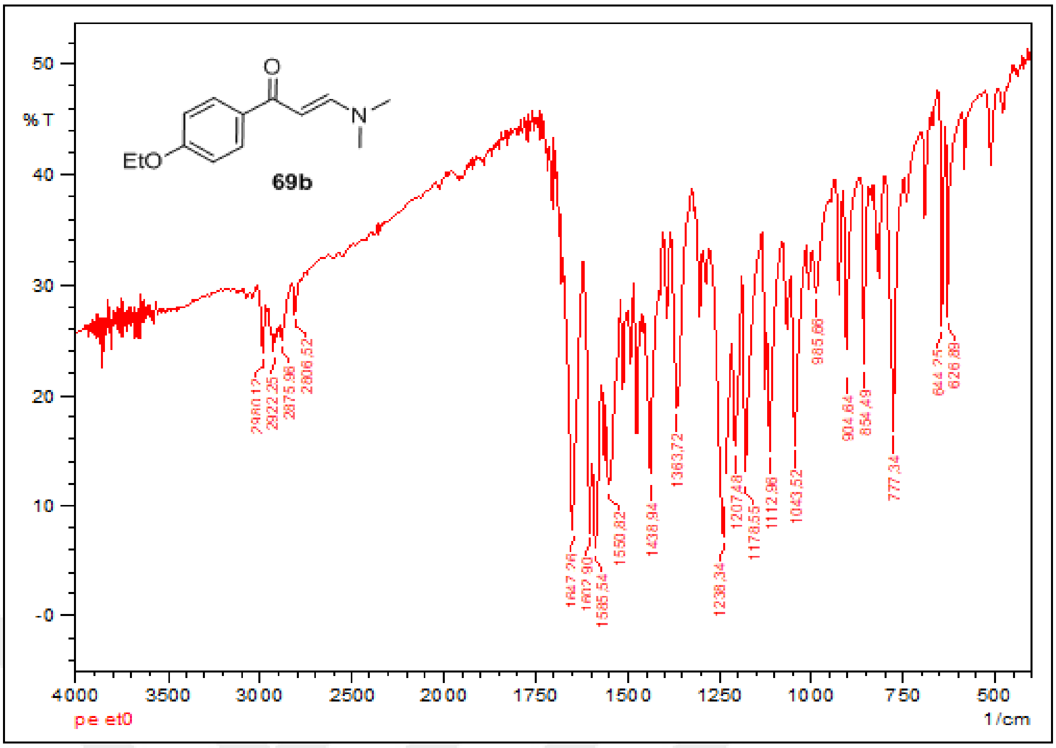


**Figure 7.2.** IR spectrum of compound **69b**

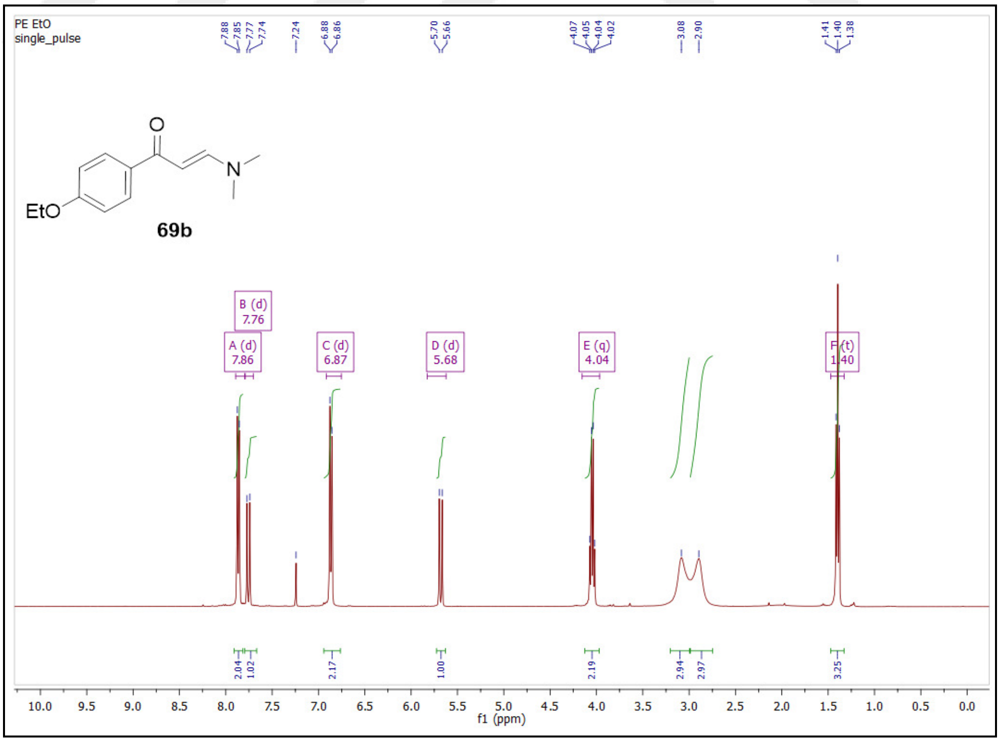


**Figure 7.3.** $^{1}$H-NMR spectrum of compound **69b**

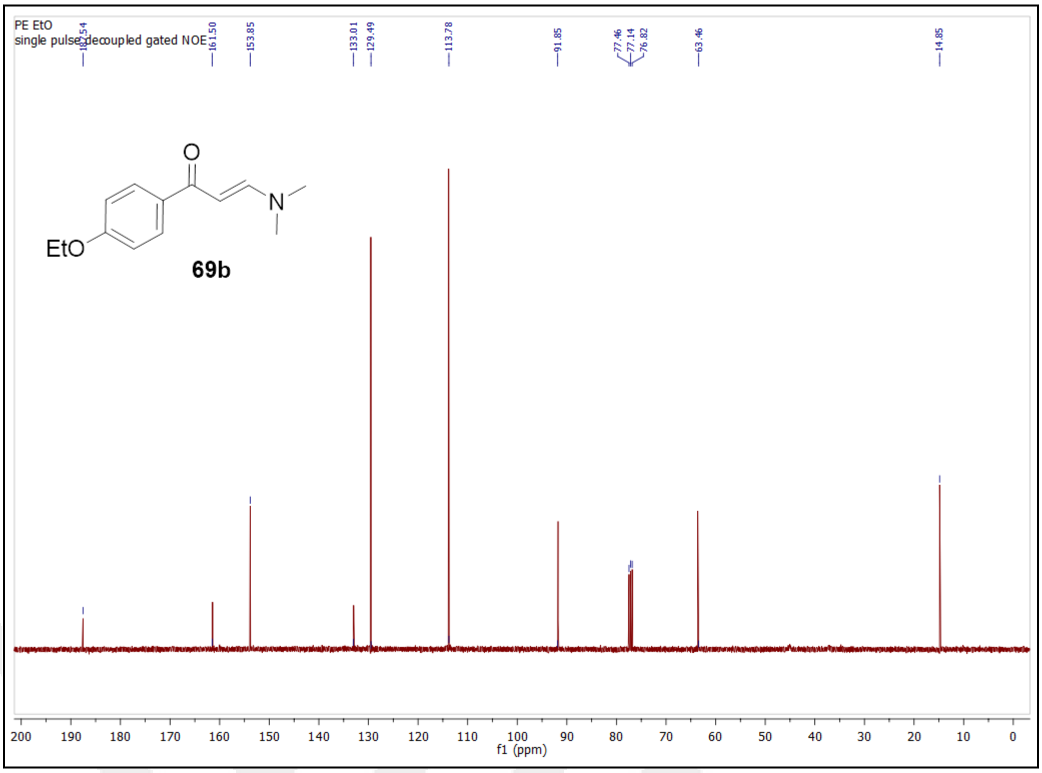


**Figure 7.4.** $^{13}$C-NMR spectrum of compound **69b**

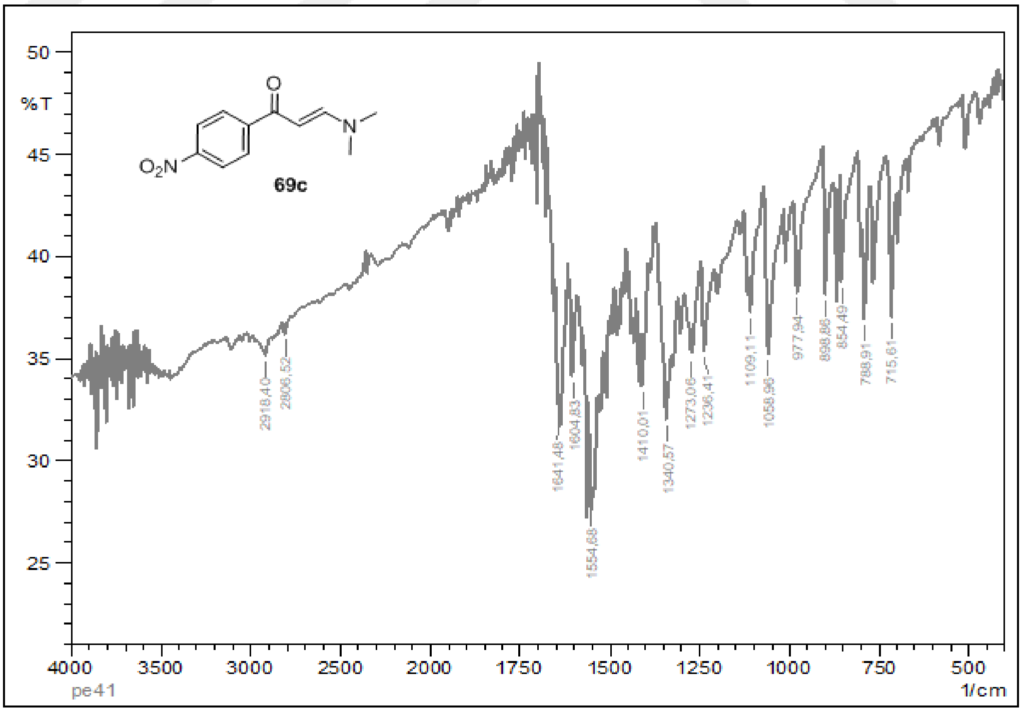


**Figure 7.5.** IR spectrum of compound **69c**

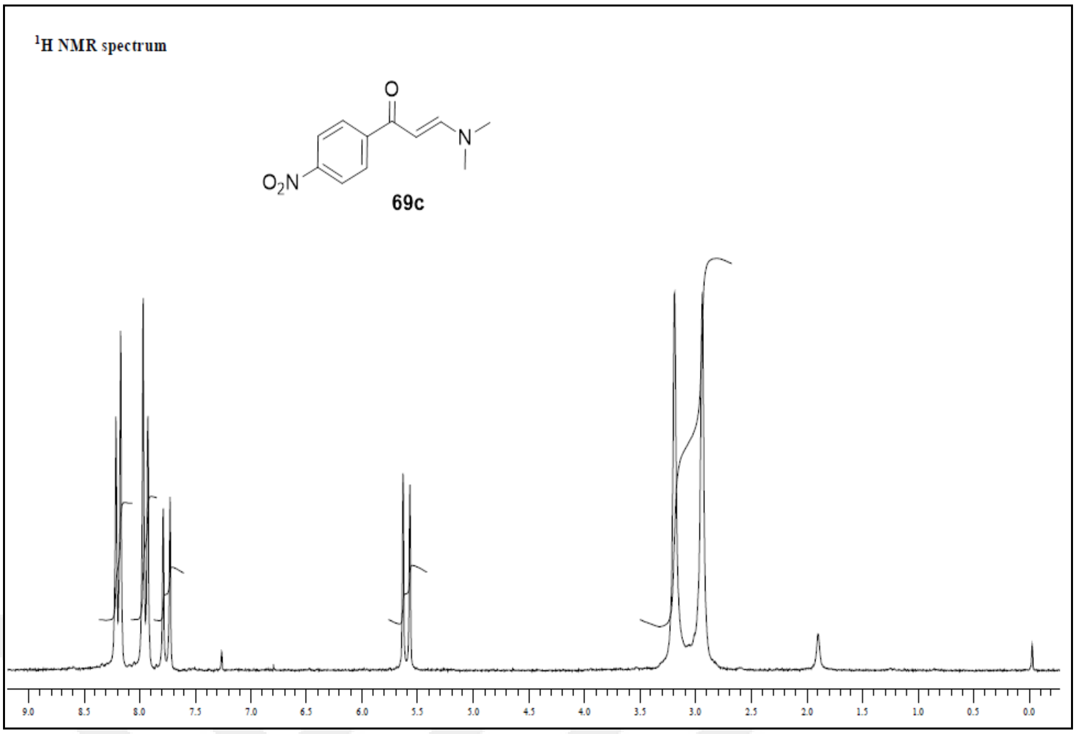


**Figure 7.6.** $^{1}$H-NMR spectrum of compound **69c**

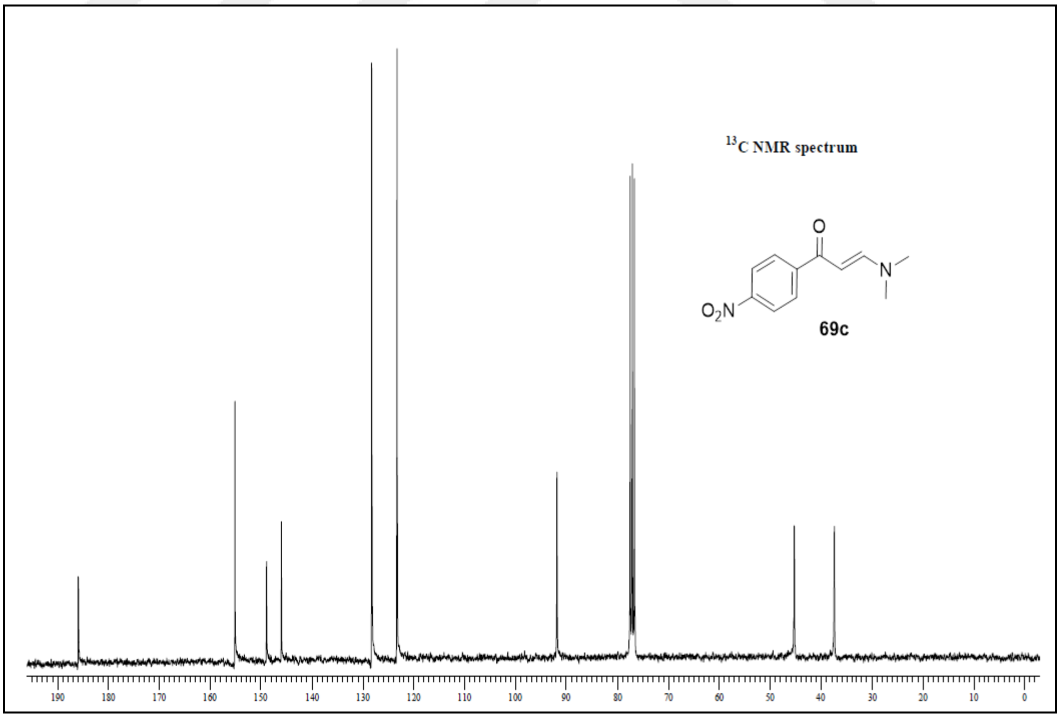


**Figure 7.7.** $^{13}$C-NMR spectrum of compound **69c**

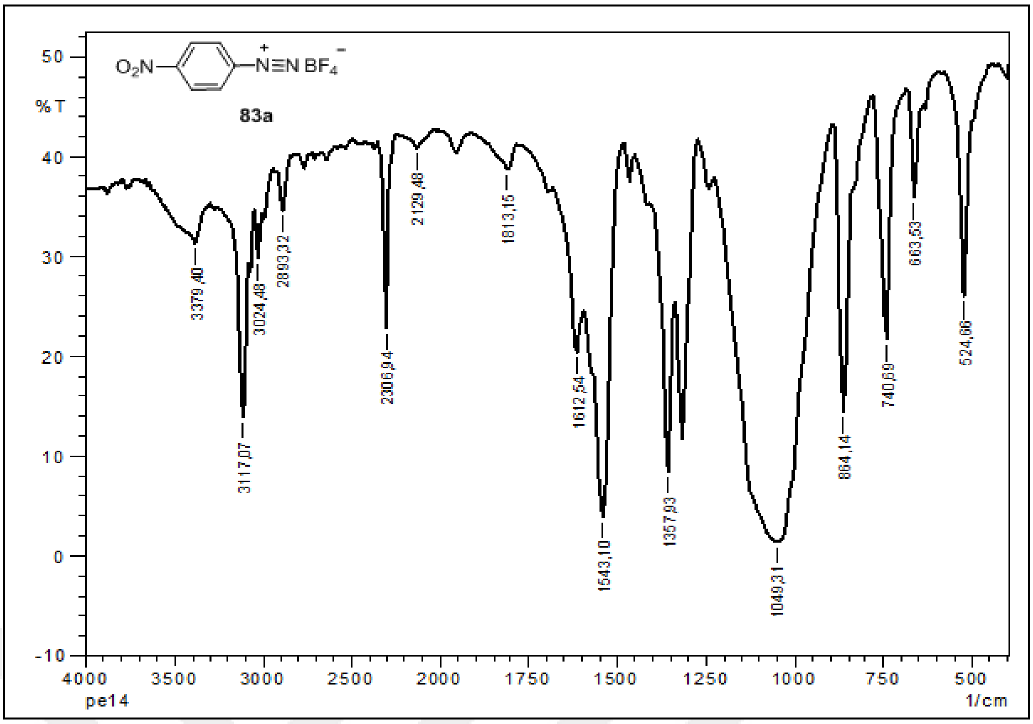


Figure 7.8. IR spectrum of compound **83a**

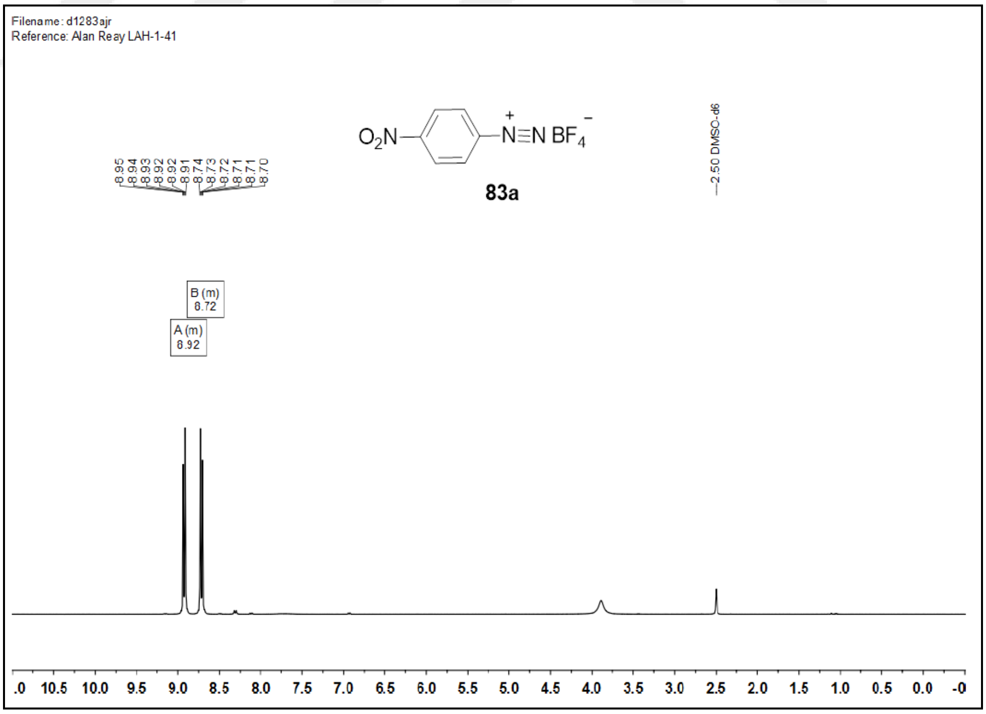


**Figure 7.9.** $^1$H-NMR spectrum of compound **83a**

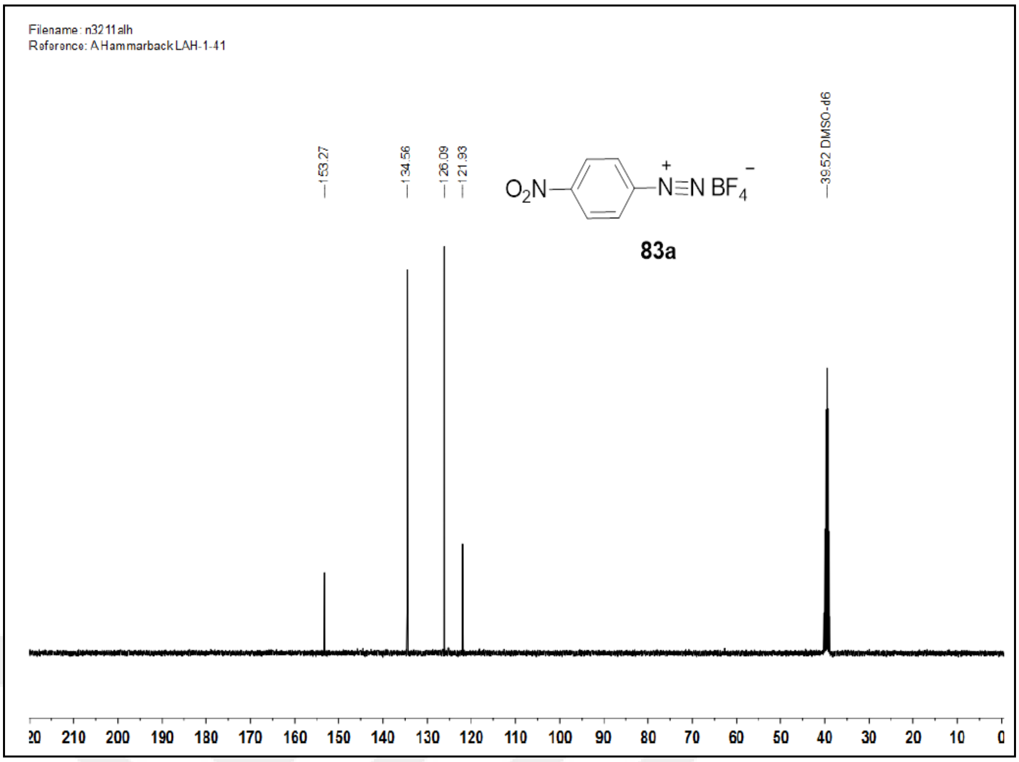


**Figure 7.10.** $^{13}$C-NMR spectrum of compound **83a**

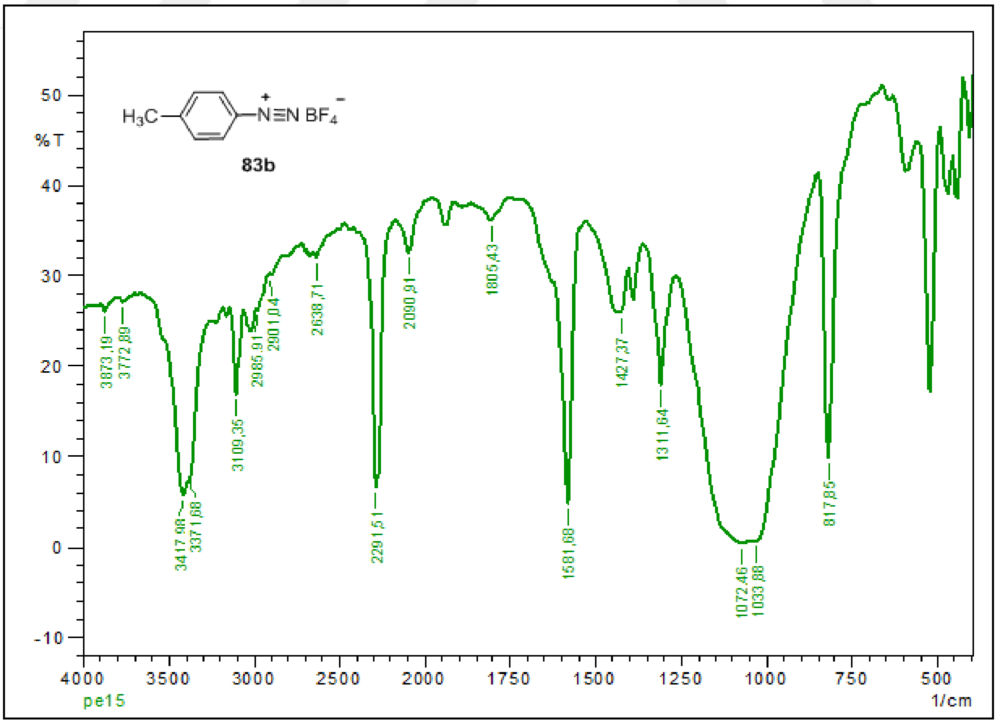


**Figure 7.11.** IR spectrum of compound **83b**

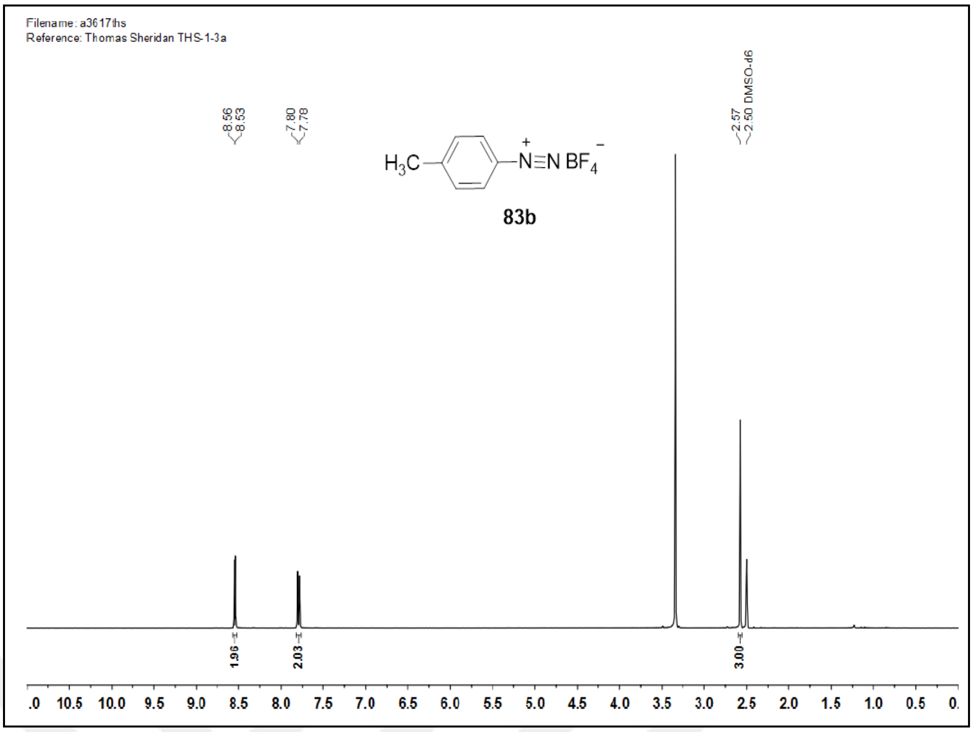


**Figure 7.12.** $^1$H-NMR spectrum of compound **83b**

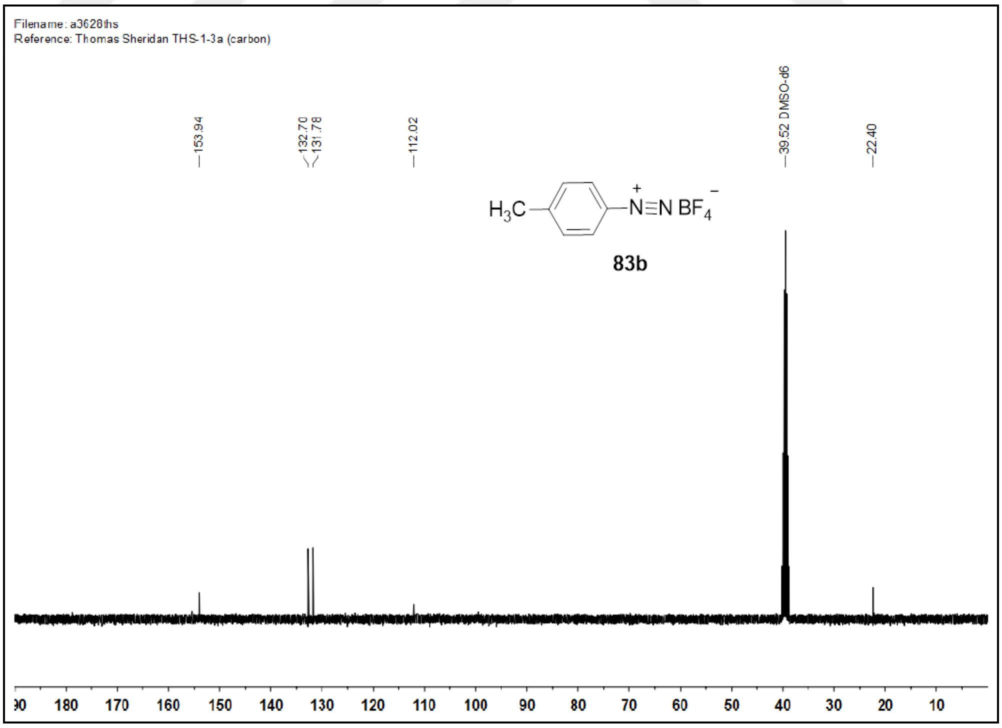


**Figure 7.13.** $^{13}$C-NMR spectrum of compound **83b**

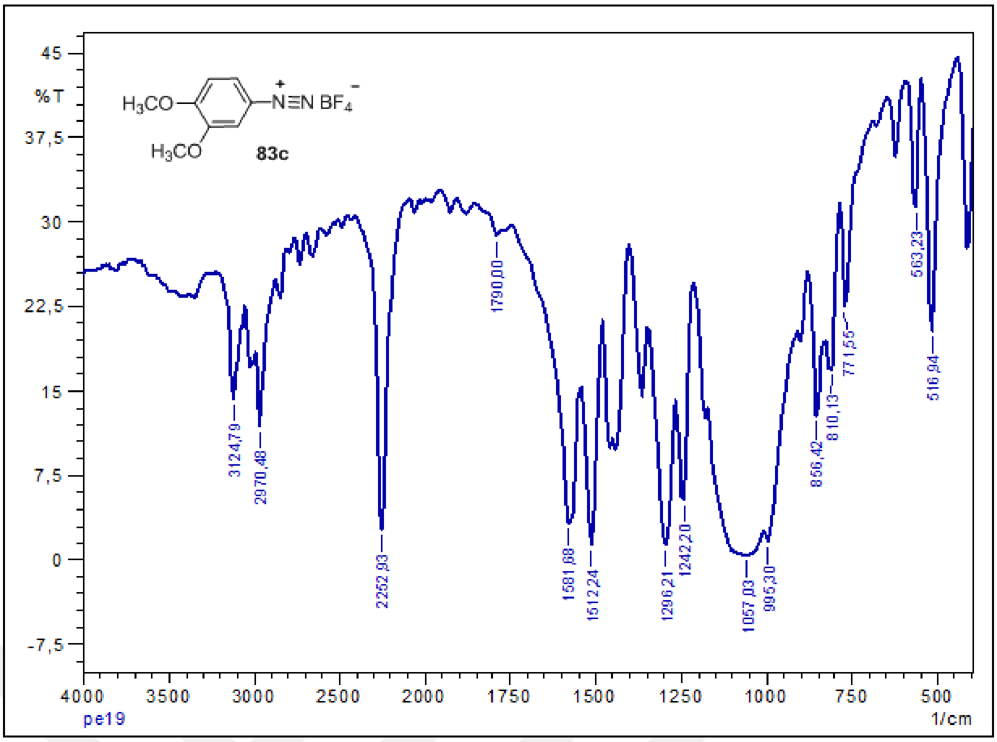


**Figure 7.14.** IR spectrum of compound **83c**

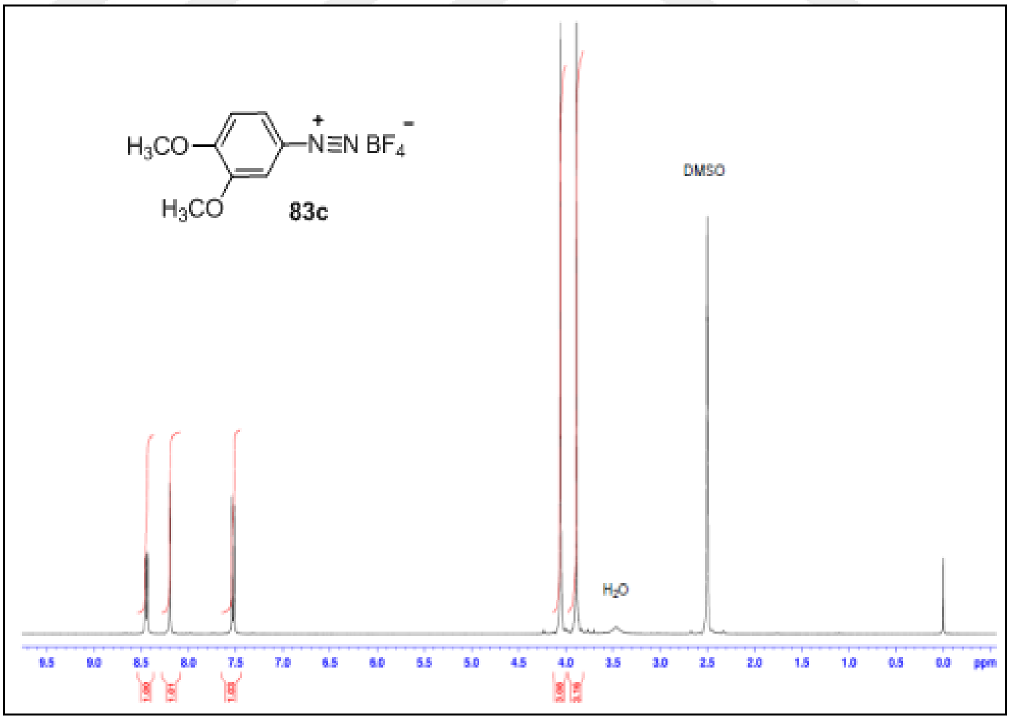


**Figure 7.15.** $^1$H-NMR spectrum of compound **83c**

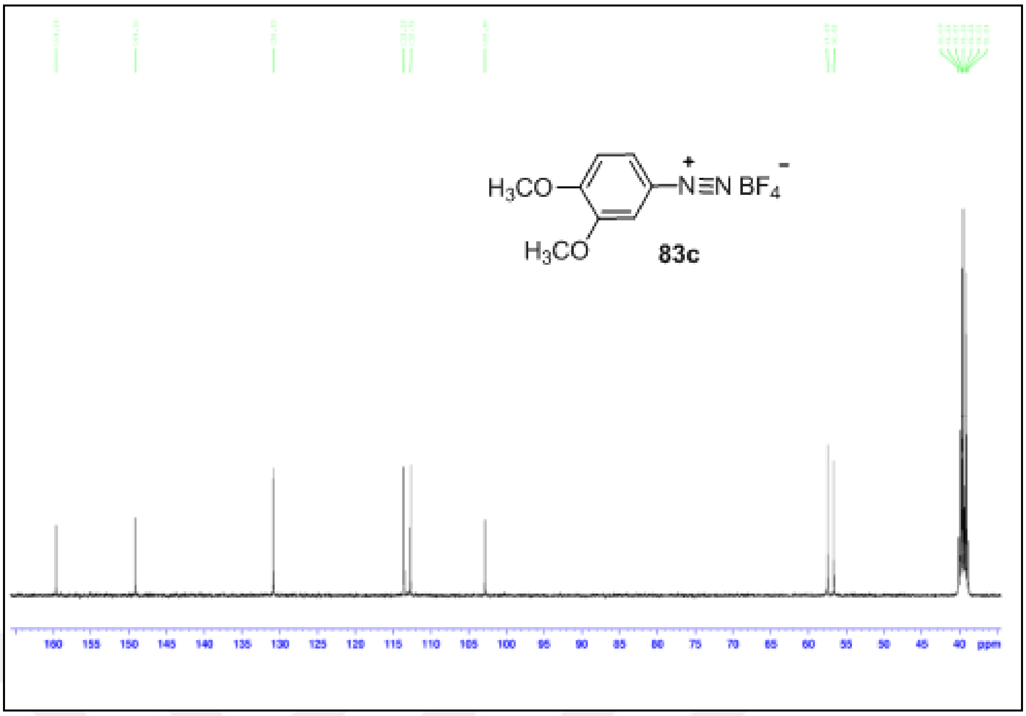


**Figure 7.16.** $^{13}$C-NMR spectrum of compound **83c**

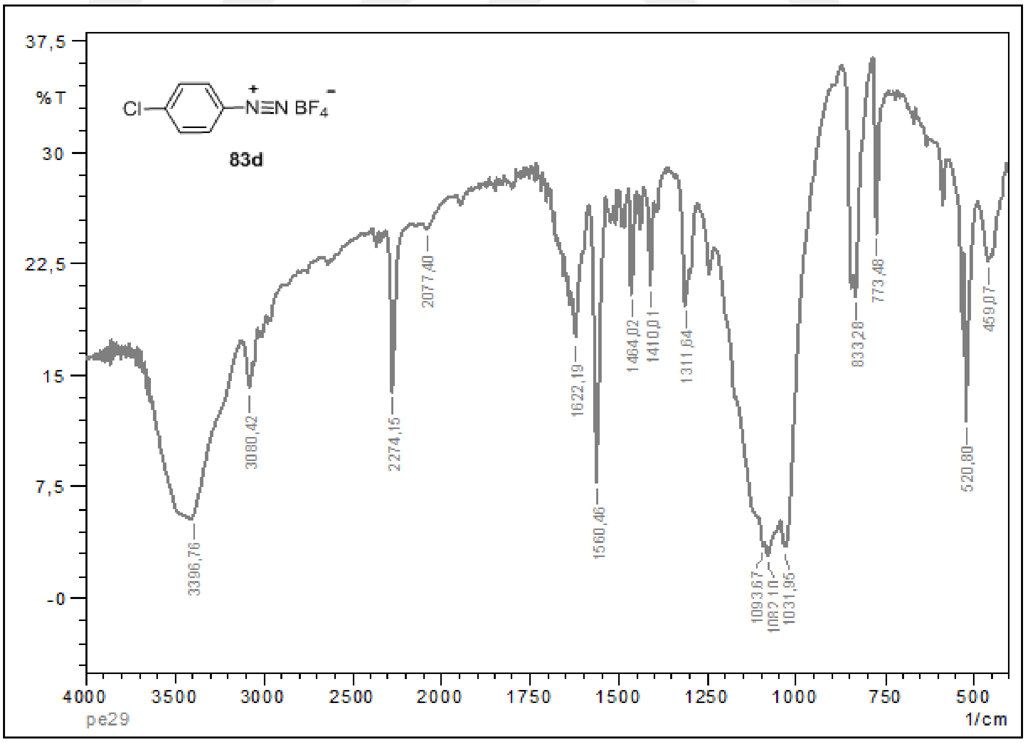


**Figure 7.17.** IR spectrum of compound **83d**

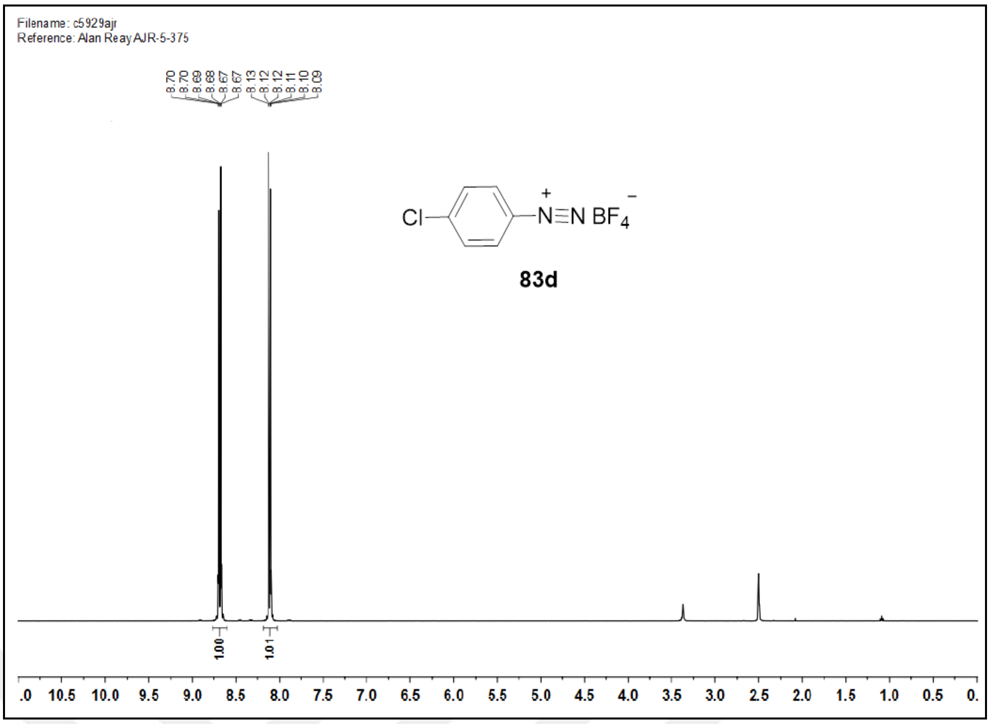


**Figure 7.18.** $^1$H-NMR spectrum of compound **83d**

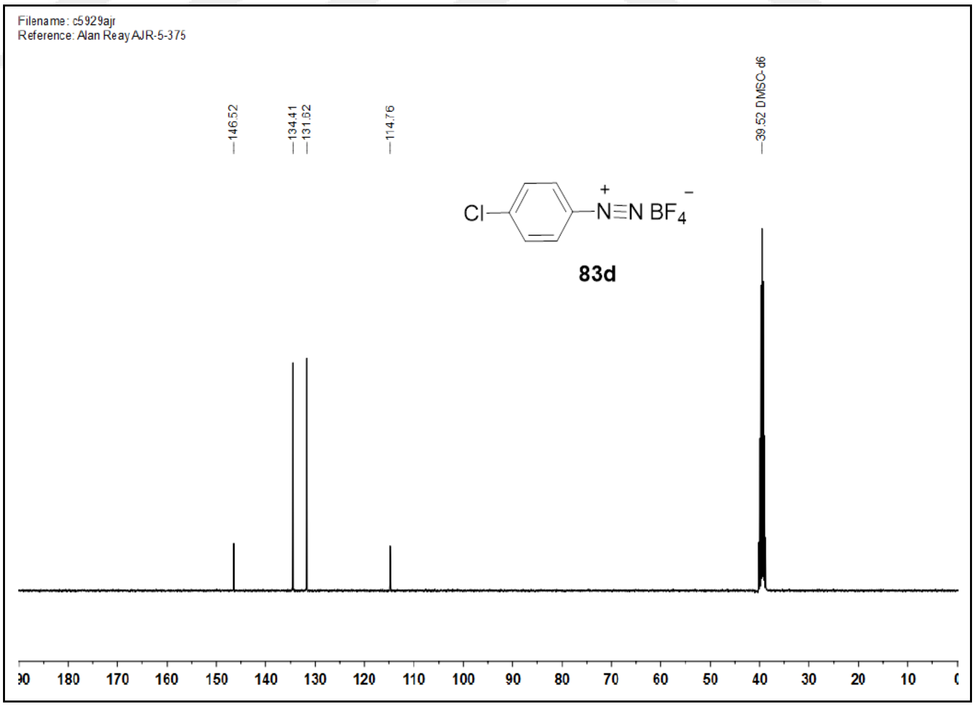


**Figure 7.19.** $^{13}$C-NMR spectrum of compound **83d**

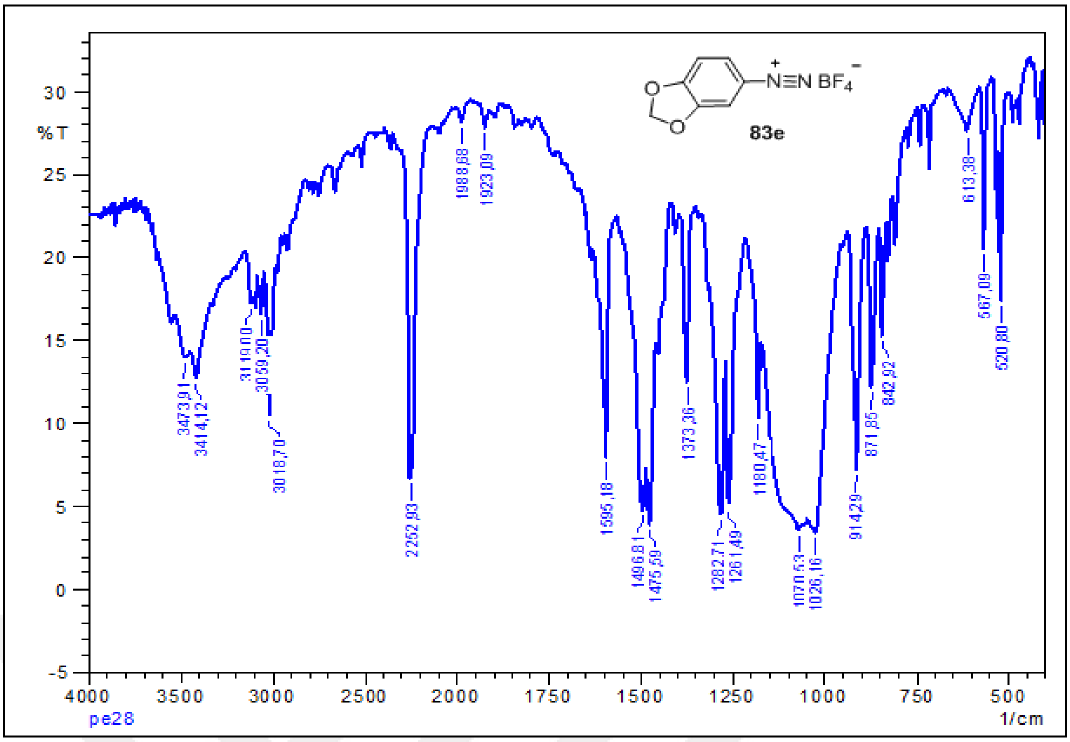


**Figure 7.20.** IR spectrum of compound **83e**

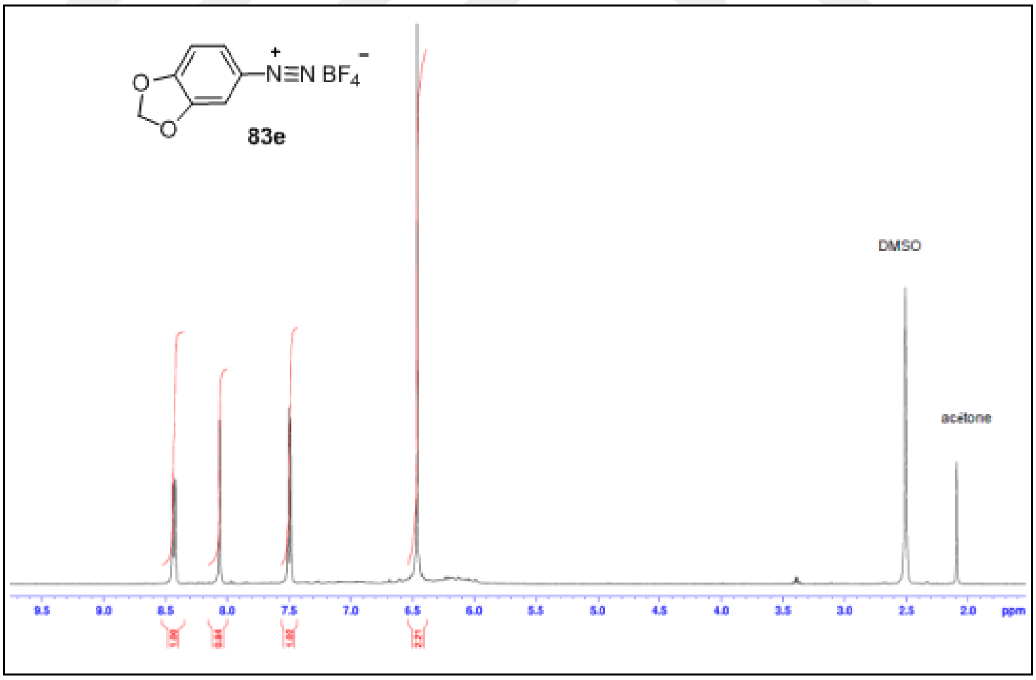


**Figure 7.21.** $^1$H-NMR spectrum of compound **83e**

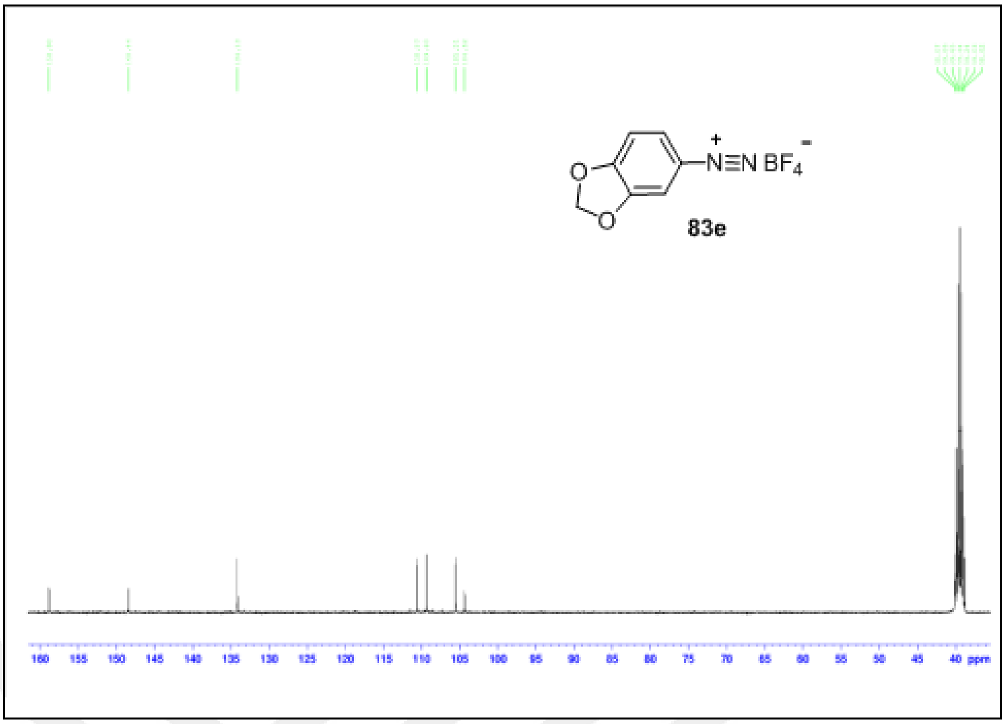


Figure 7.22. $^{13}$C-NMR spectrum of compound **83e**

## 7.2 SPECTRA FOR DISPERSE DYESTUFFS (70a-i)

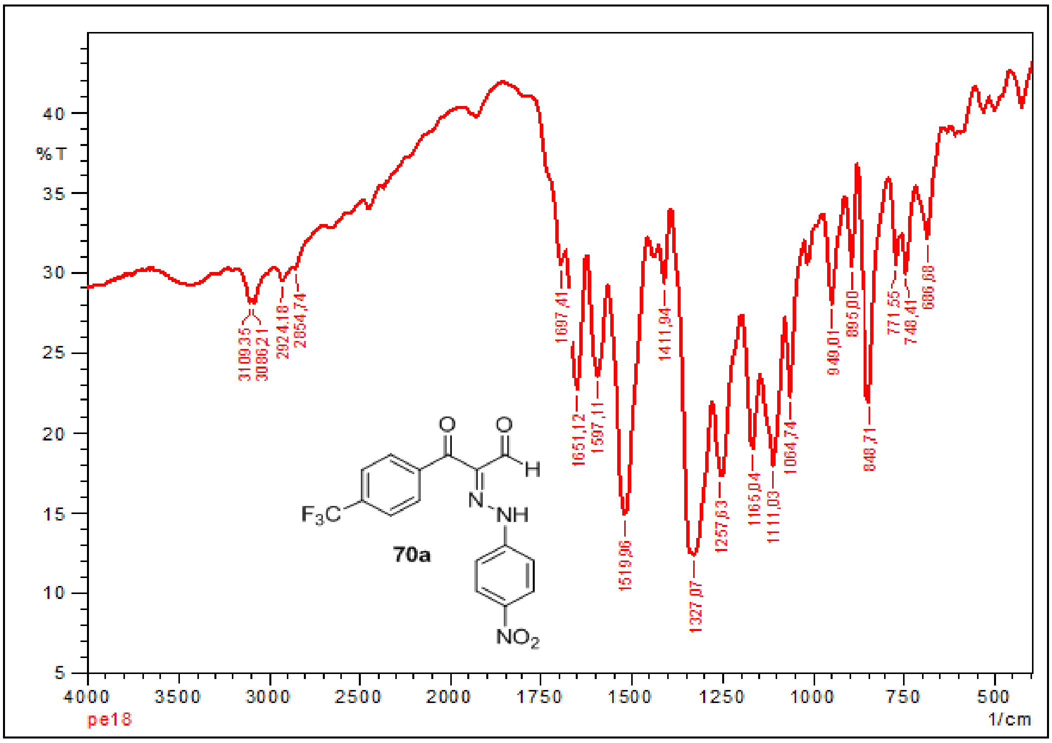


**Figure 7.23.** IR spectrum of compound **70a**

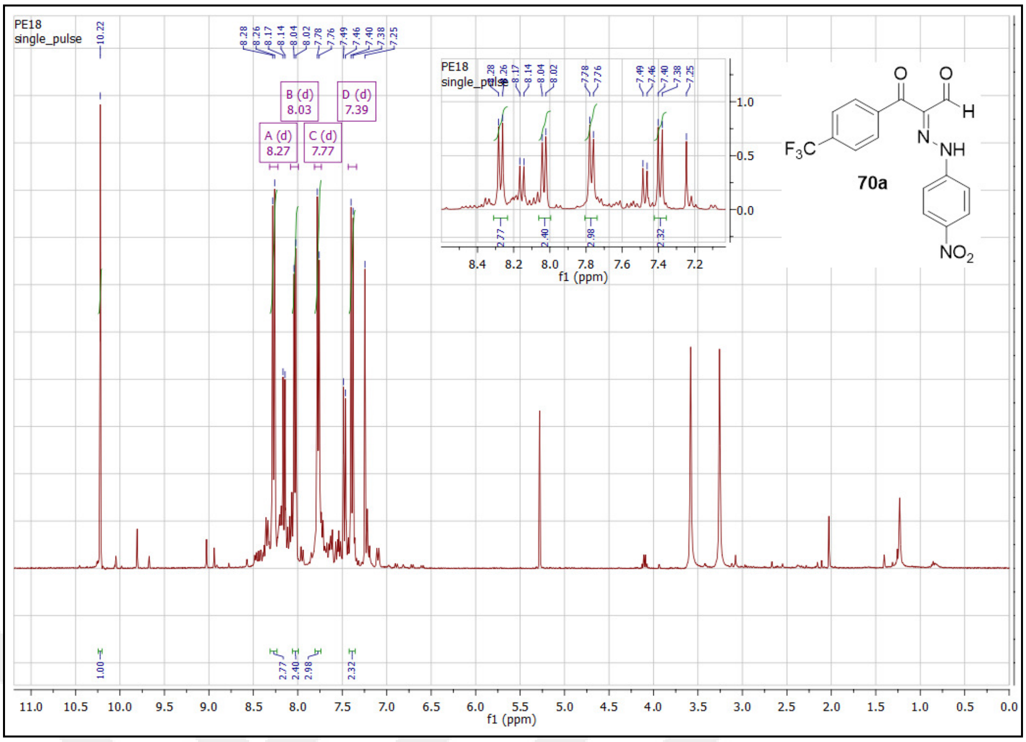


**Figure 7.24.** $^1$H-NMR spectrum of compound **70a**

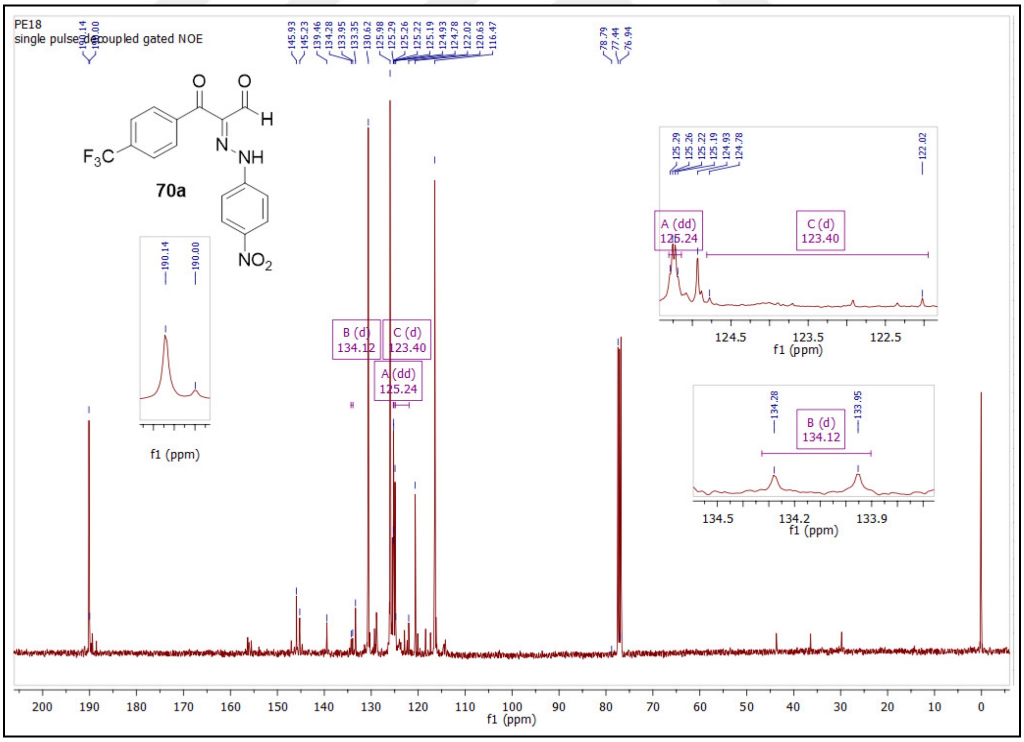


**Figure 7.25.** $^{13}$C-NMR spectrum of compound **70a**

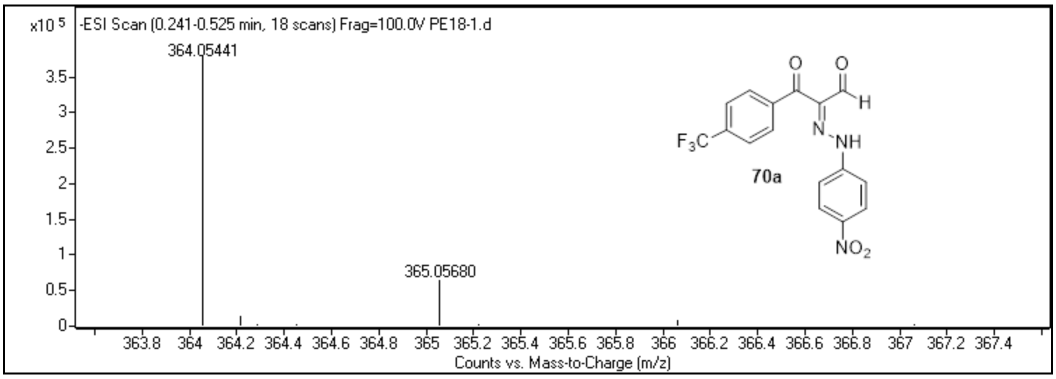


**Figure 7.26.** HRMS spectrum of compound **70a**

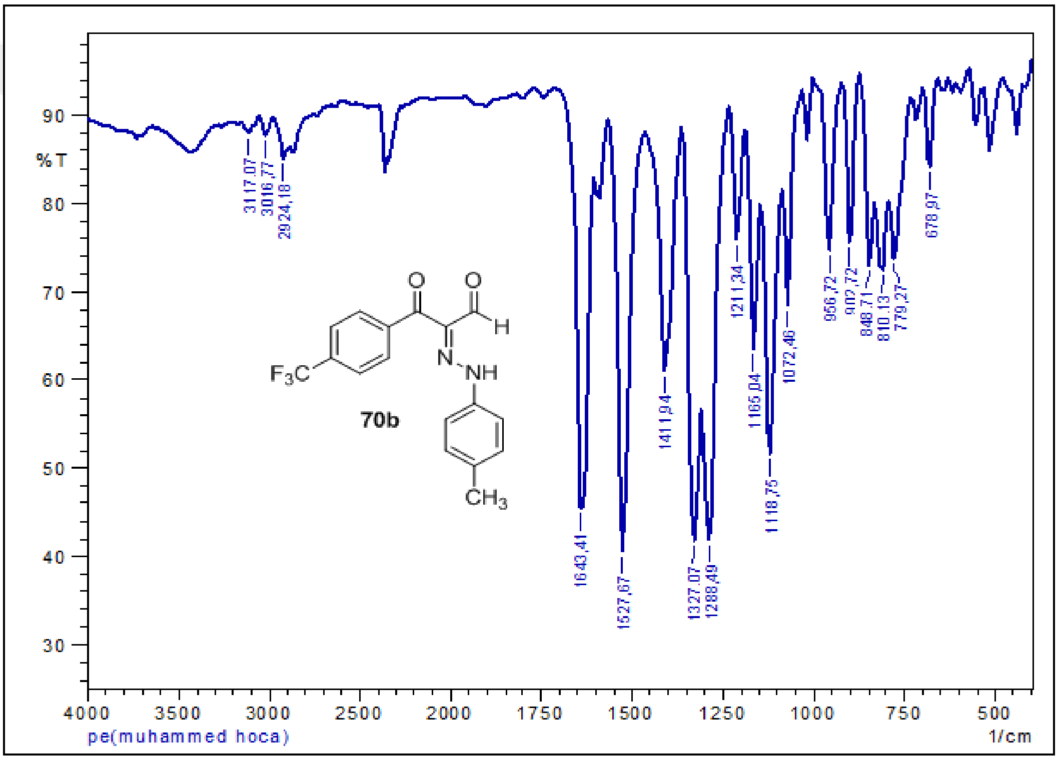


**Figure 7.27.** IR spectrum of compound **70b**

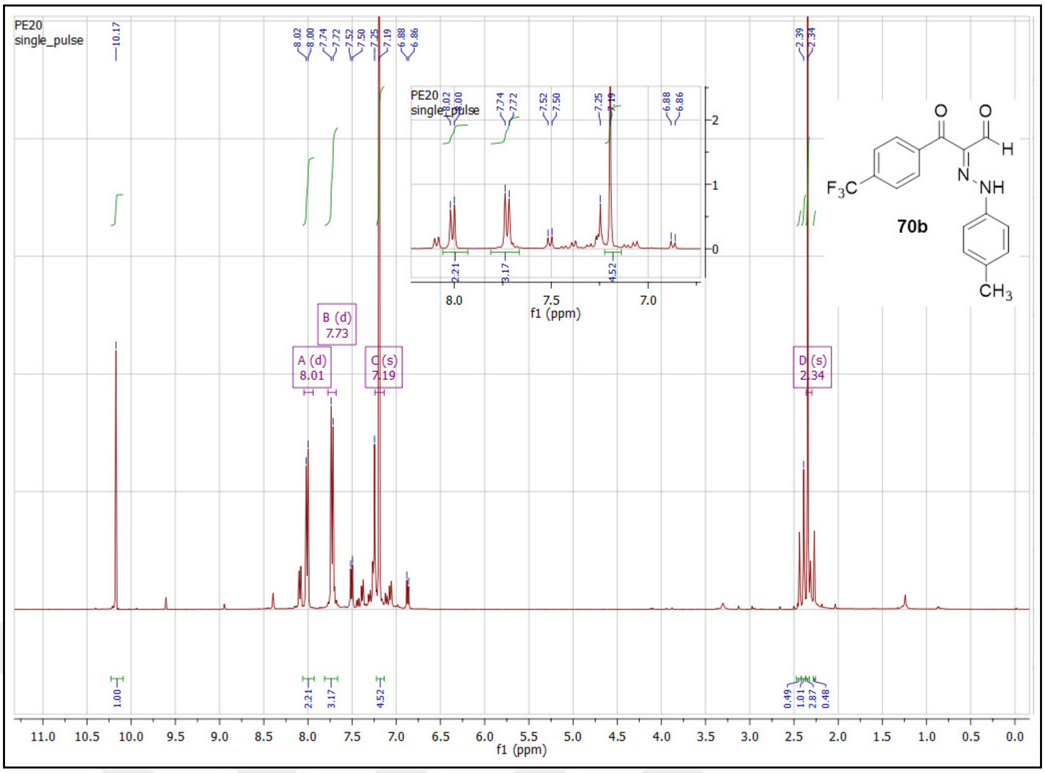


Figure 7.28. $^1$H-NMR spectrum of compound **70b**

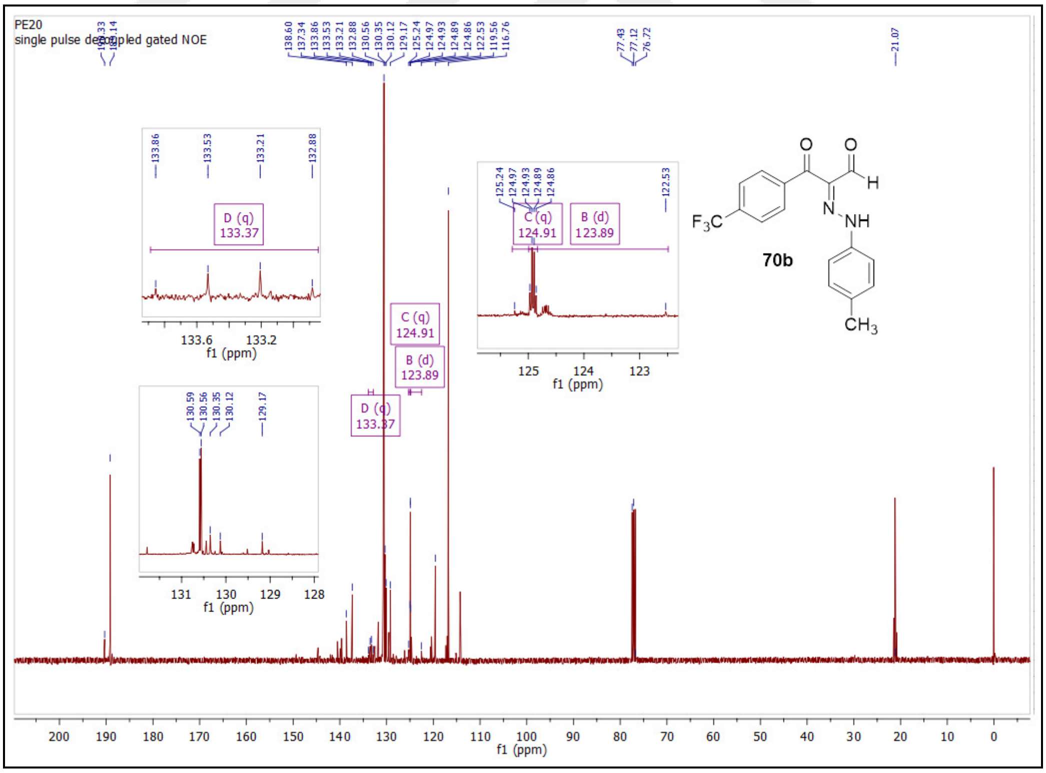


Figure 7.29. $^{13}$C-NMR spectrum of compound **70b**

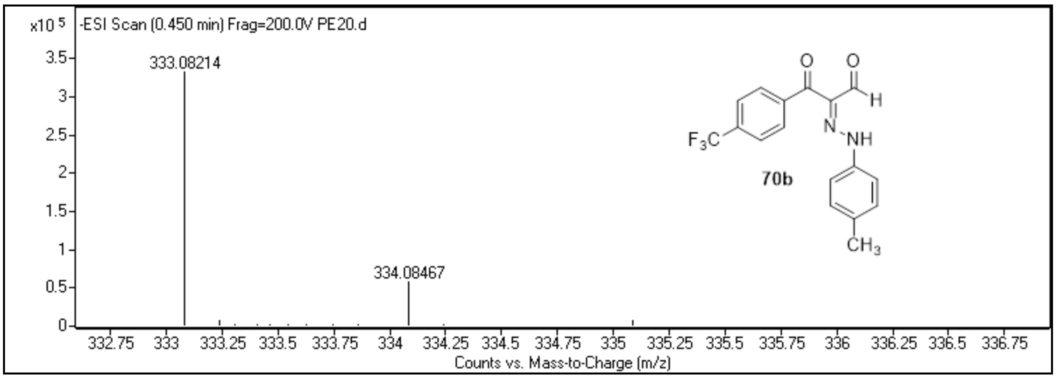


**Figure 7.30.** HRMS spectrum of compound **70b**

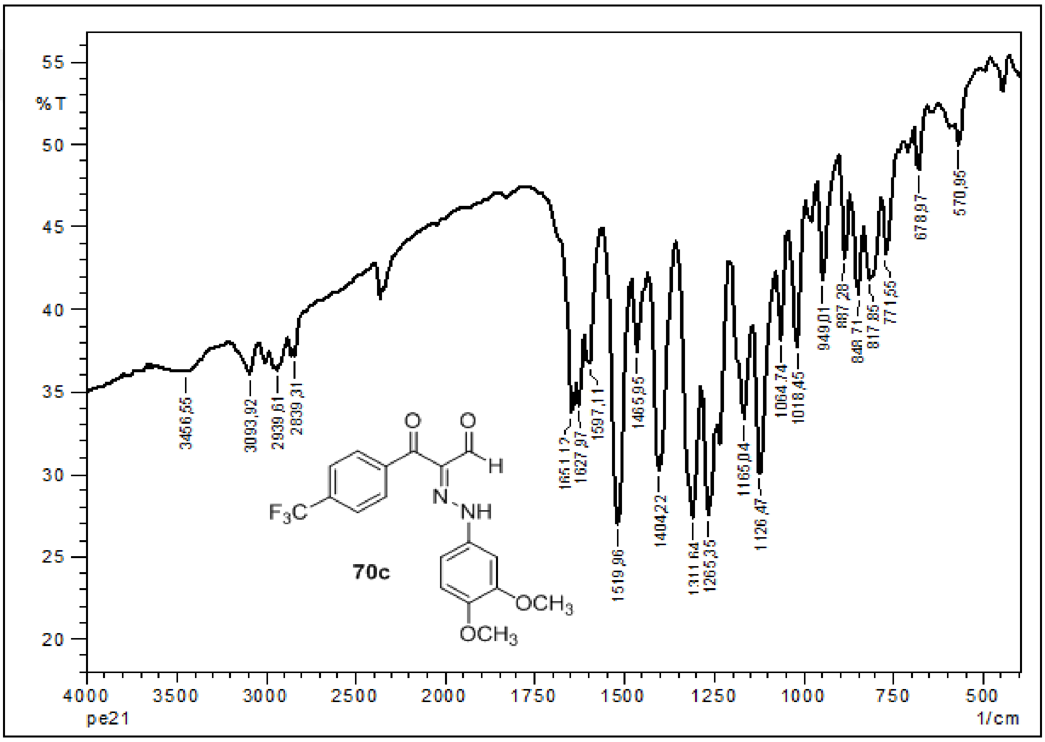


**Figure 7.31.** IR spectrum of compound **70c**

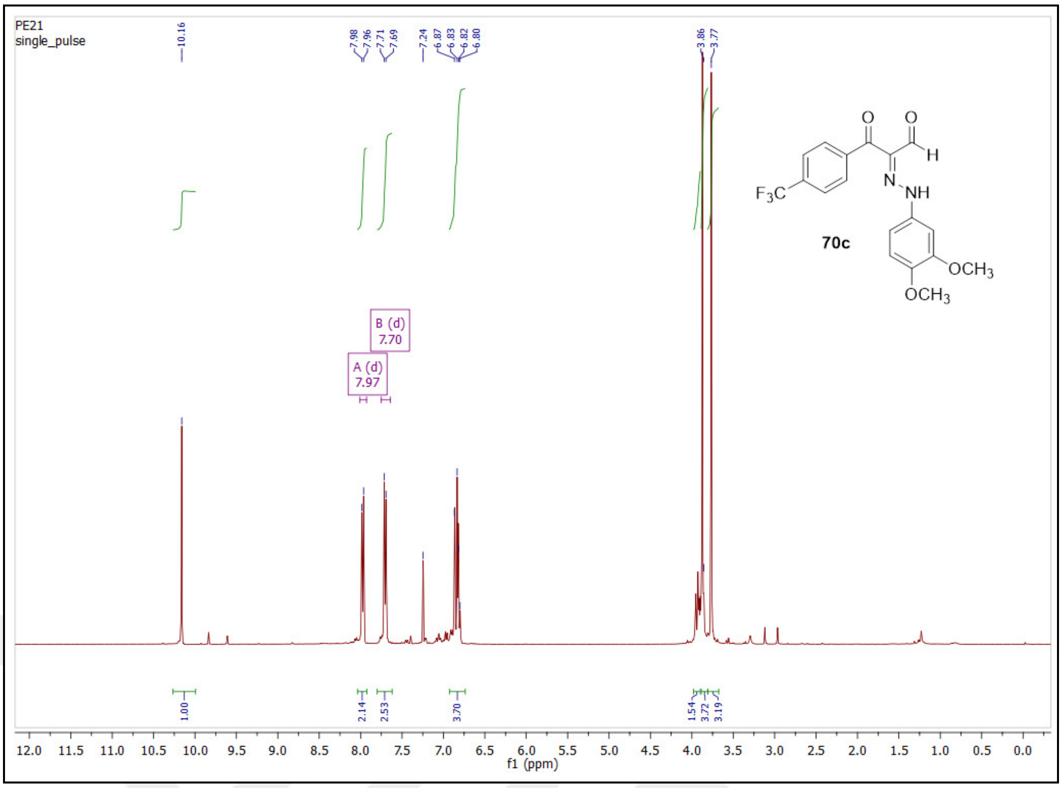


Figure 7.32. $^1$H-NMR spectrum of compound **70c**

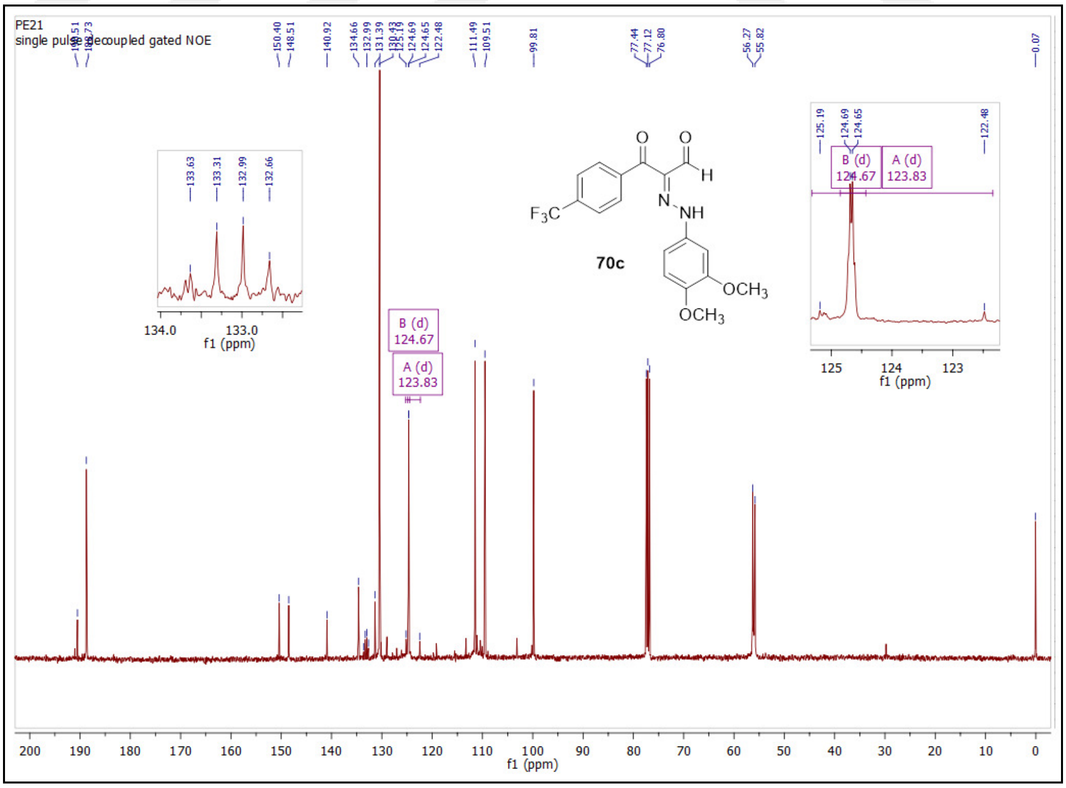


Figure 7.33. $^{13}$C-NMR spectrum of compound **70c**

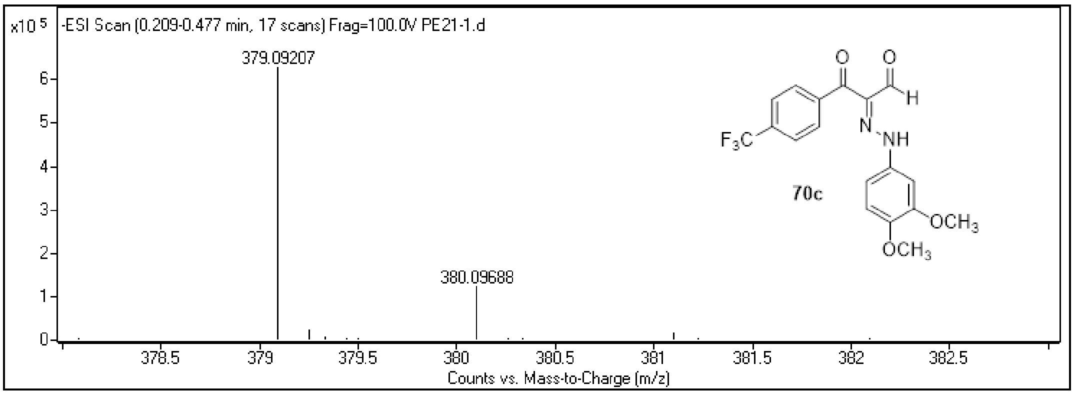


**Figure 7.34.** HRMS spectrum of compound **70c**

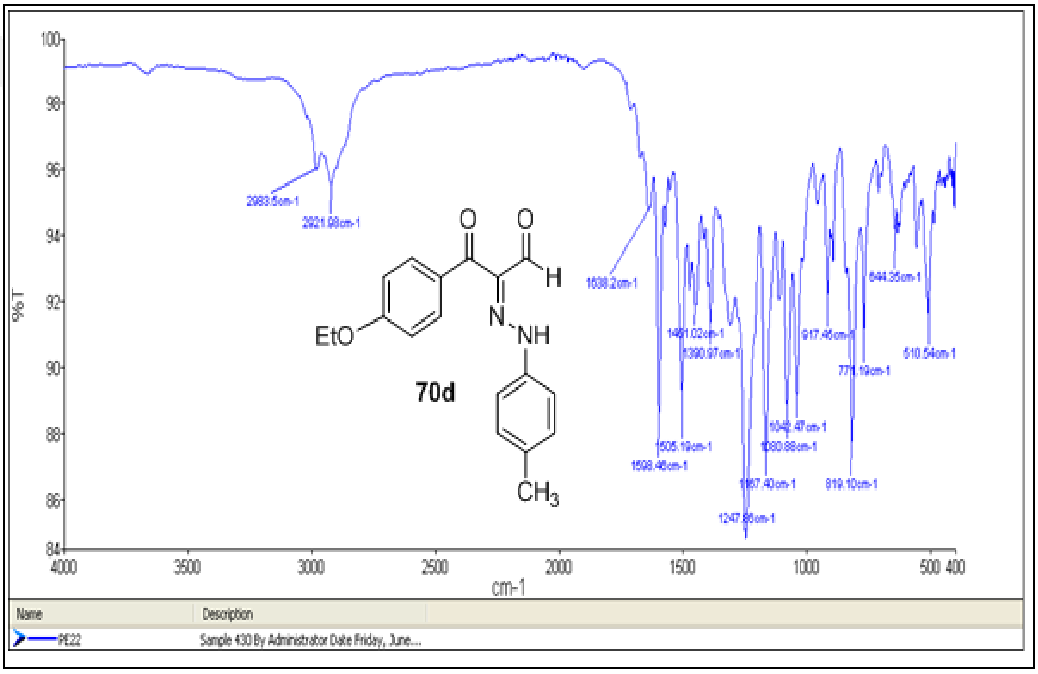


**Figure 7.35.** IR spectrum of compound **70d**

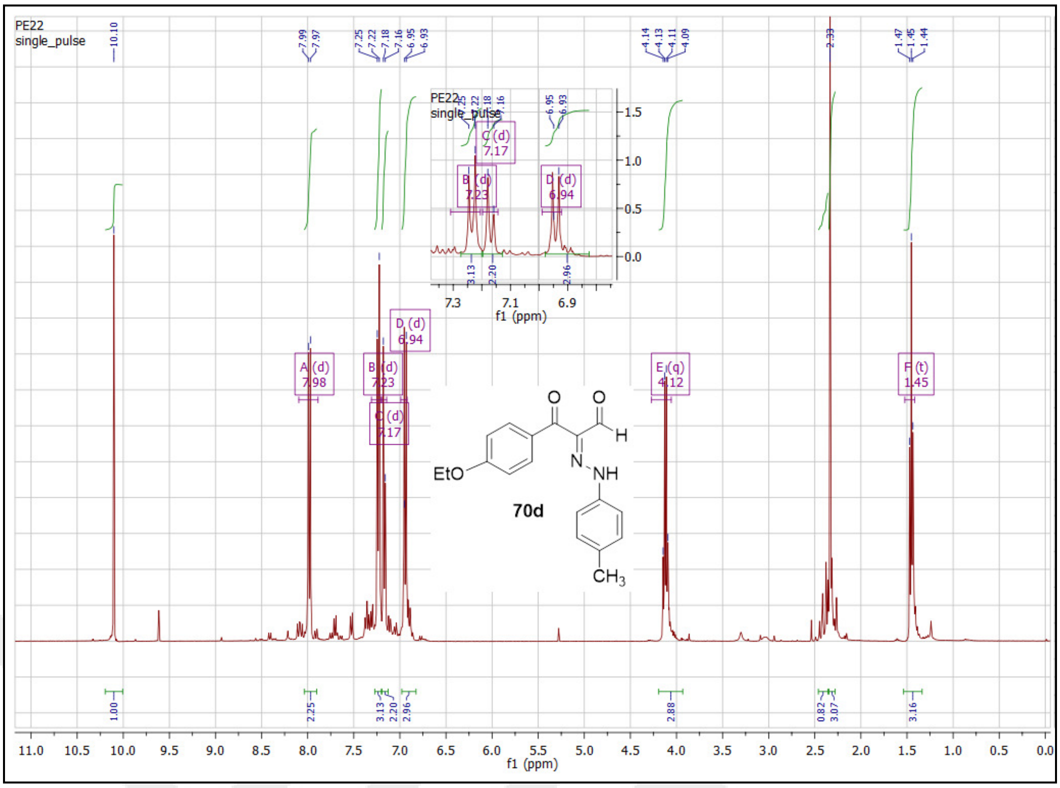


**Figure 7.36.** $^{1}$H-NMR spectrum of compound **70d**

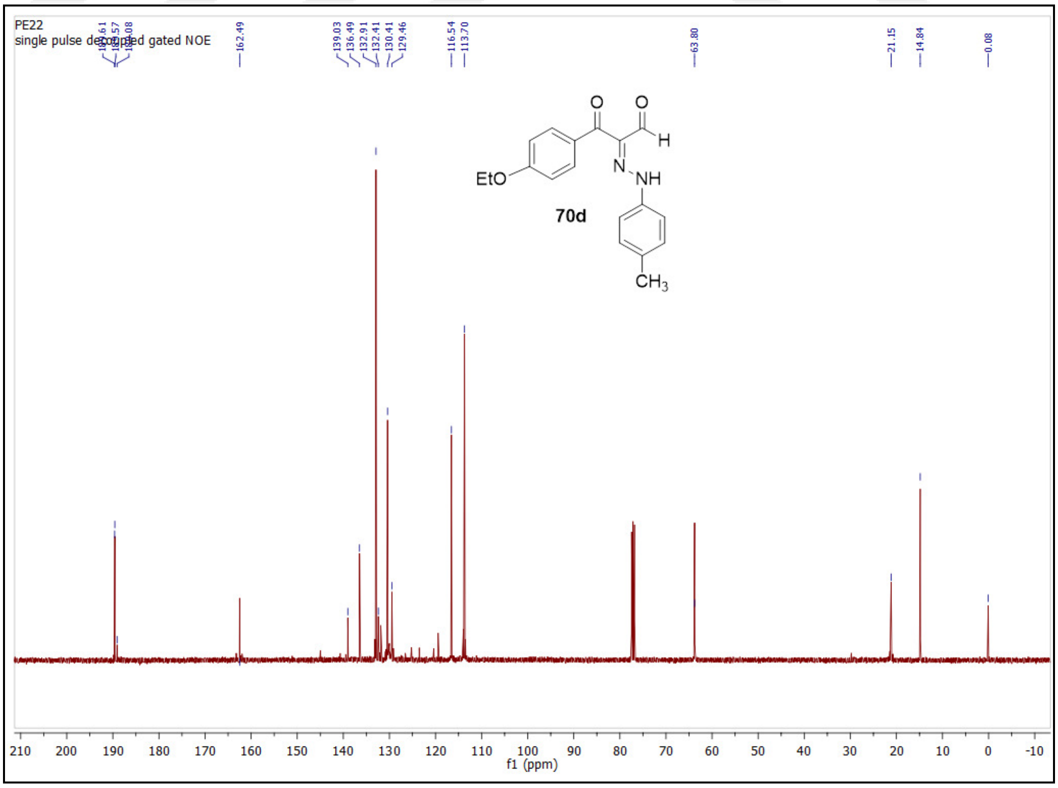


**Figure 7.37.** $^{13}$C-NMR spectrum of compound **70d**

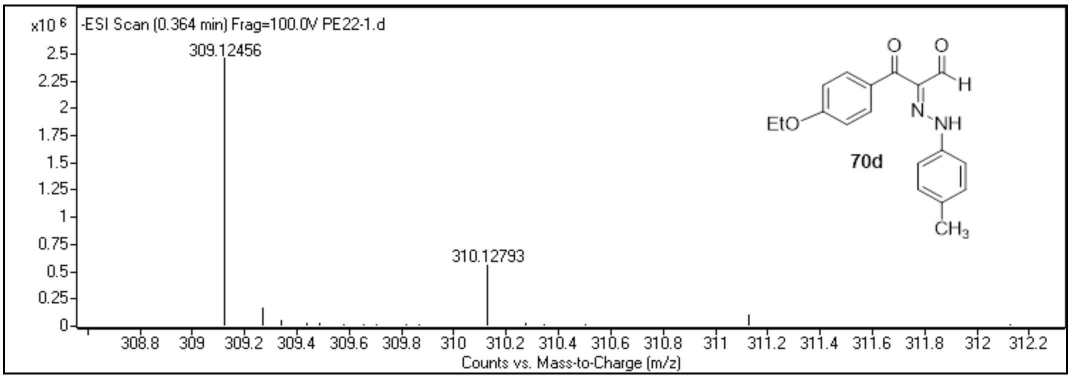


**Figure 7.38.** HRMS spectrum of compound **70d**

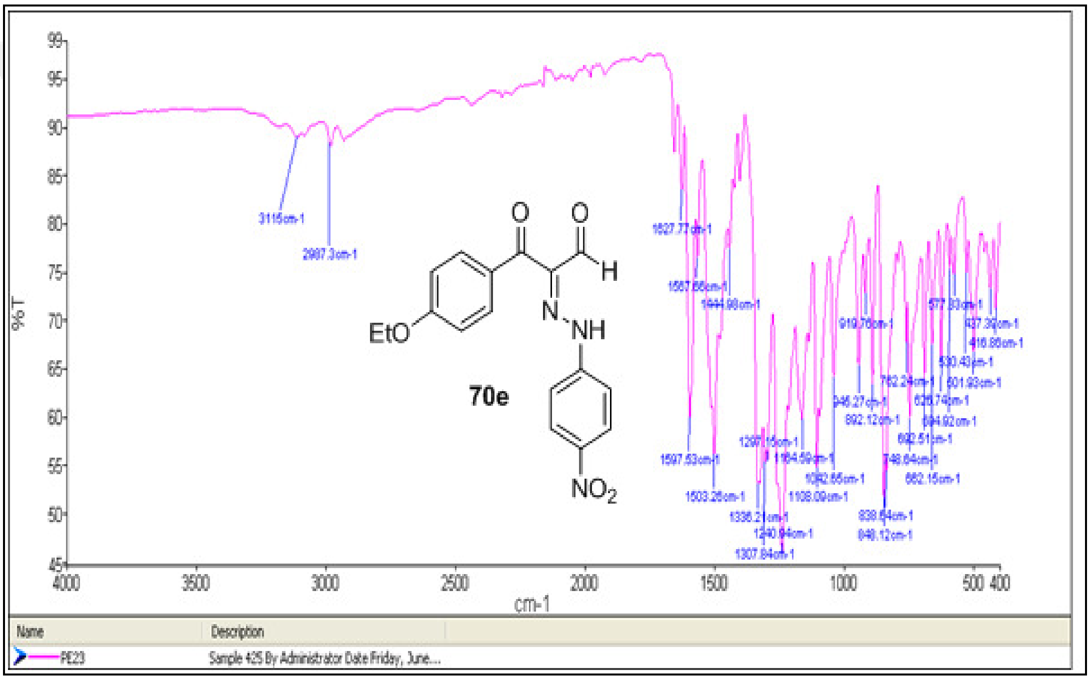


**Figure 7.39.** IR spectrum of compound **70e**

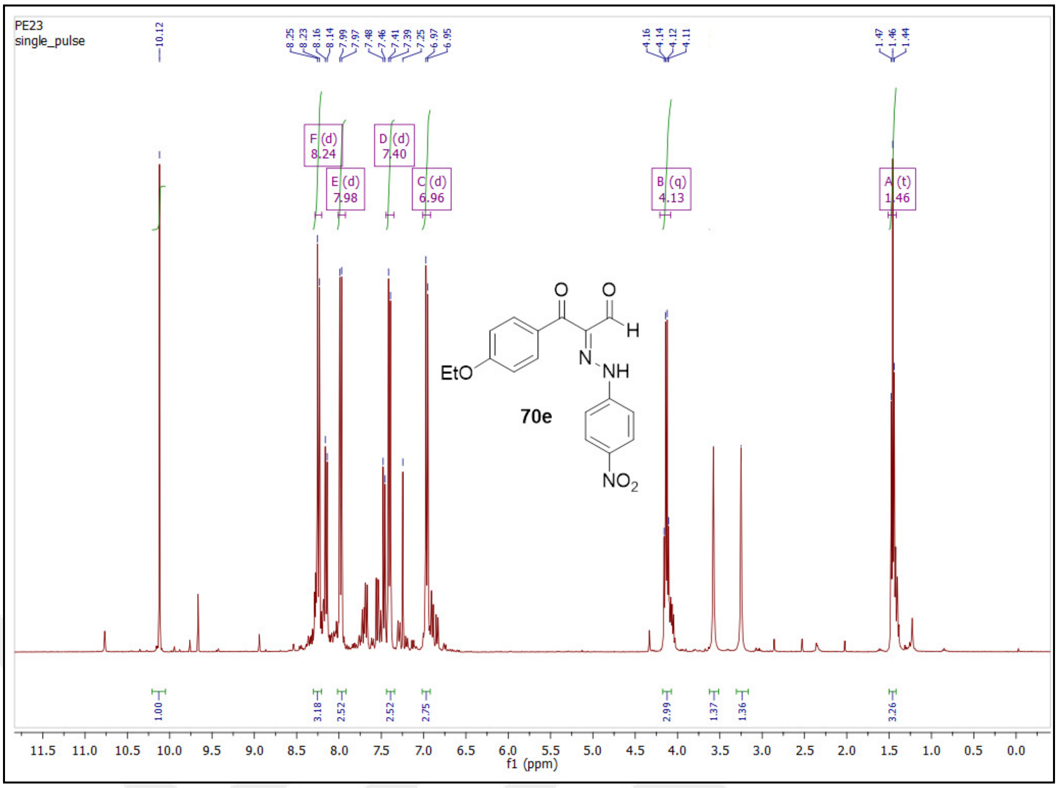


**Figure 7.40.** $^{1}$H-NMR spectrum of compound **70e**

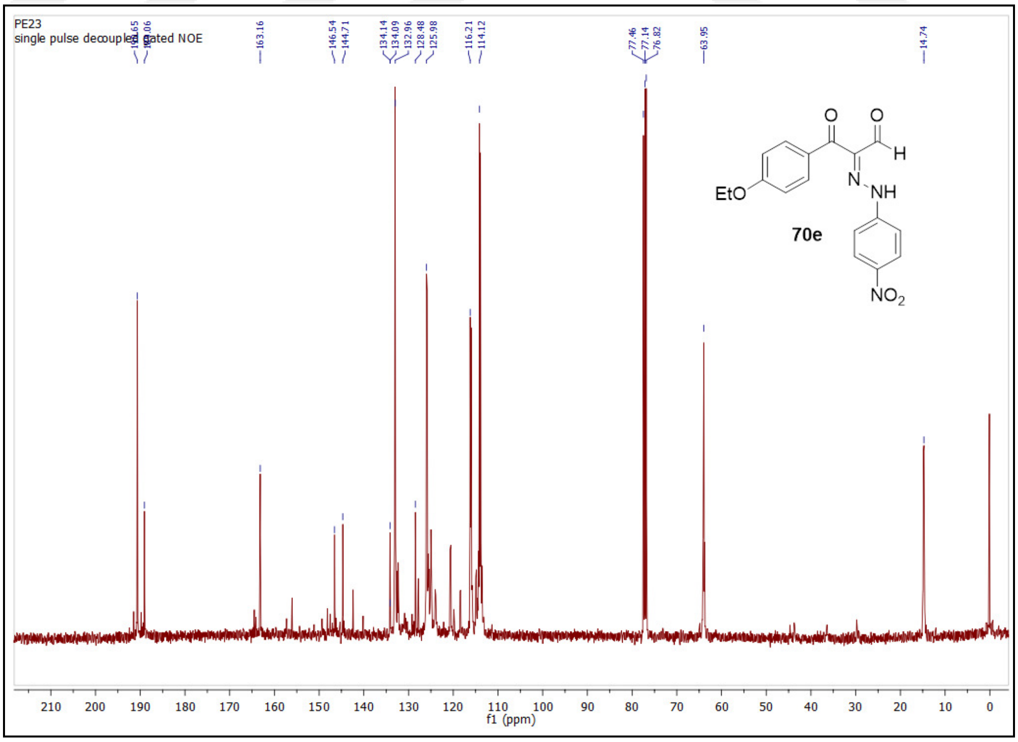


**Figure 7.41.** $^{13}$C-NMR spectrum of compound **70e**

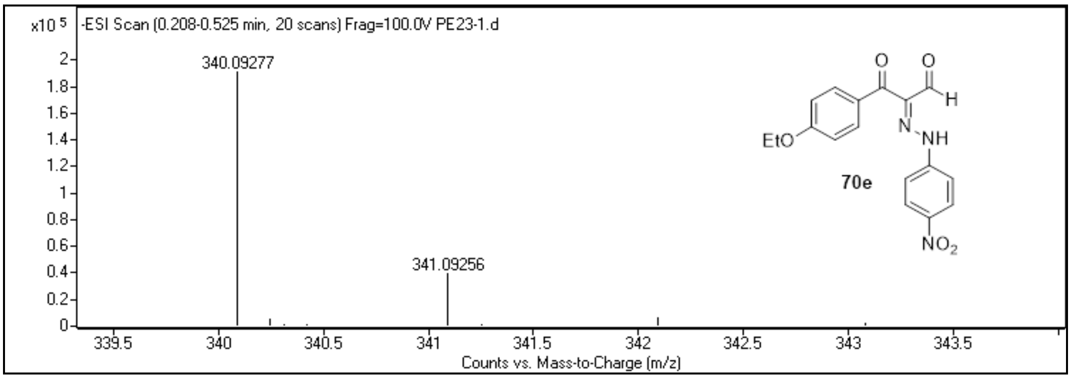


**Figure 7.42.** HRMS spectrum of compound **70e**

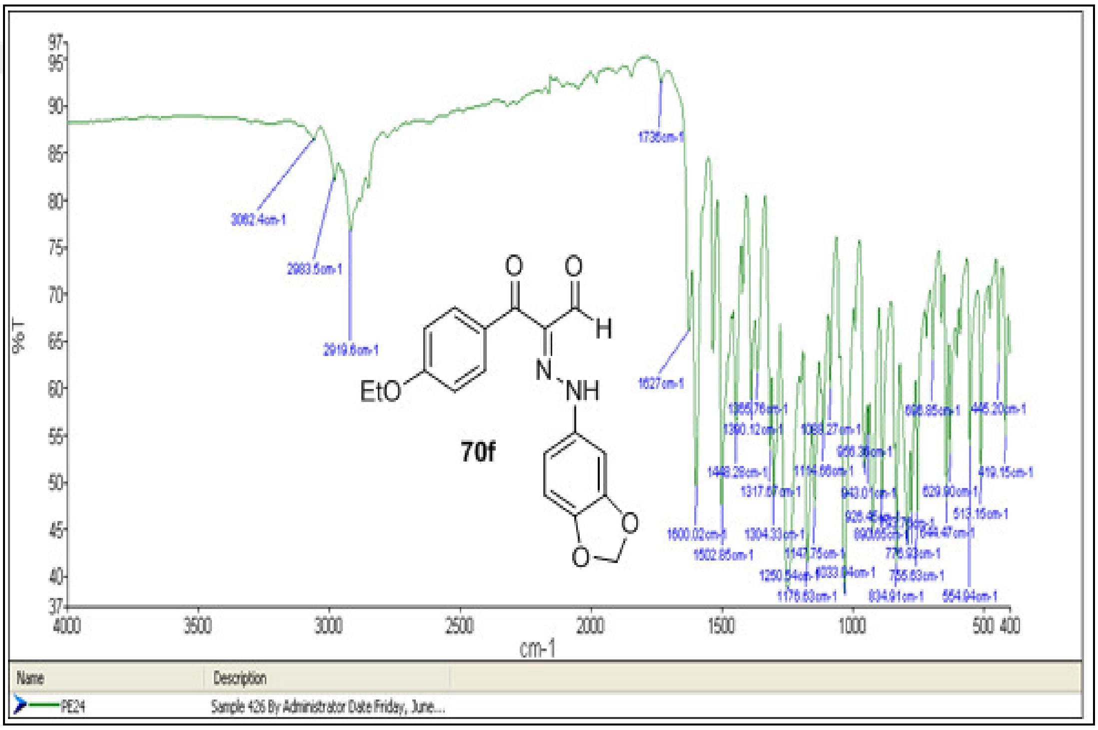


**Figure 7.43.** IR spectrum of compound **70f**

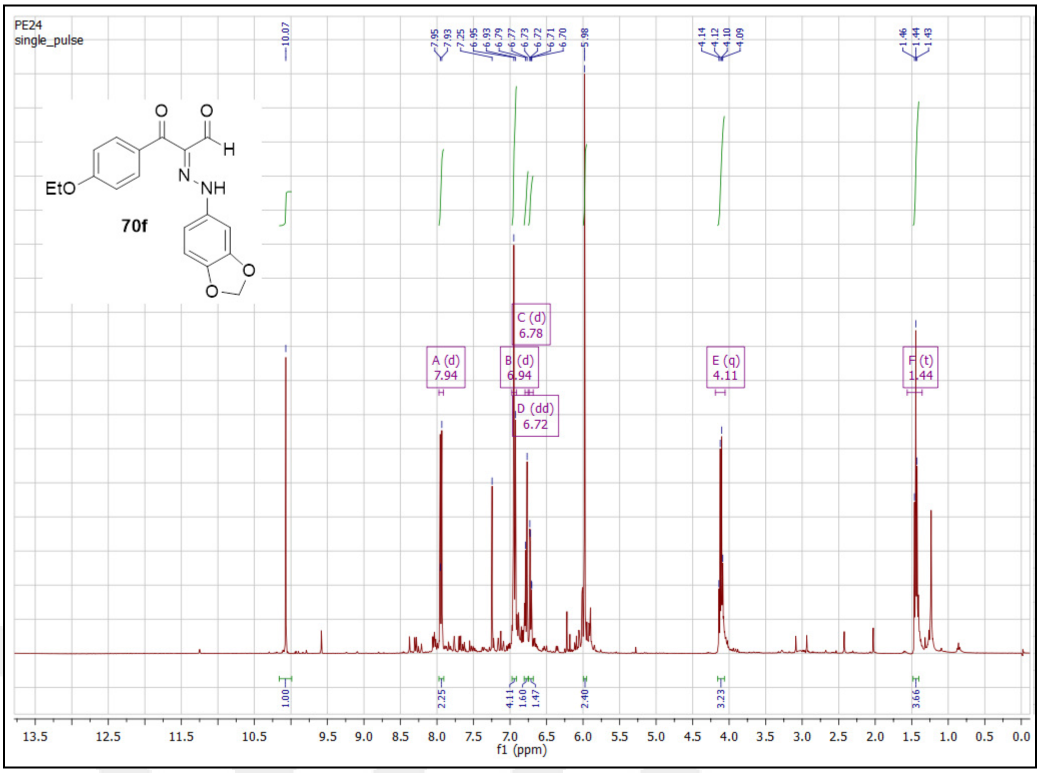


**Figure 7.44.** $^1$H-NMR spectrum of compound **70f**

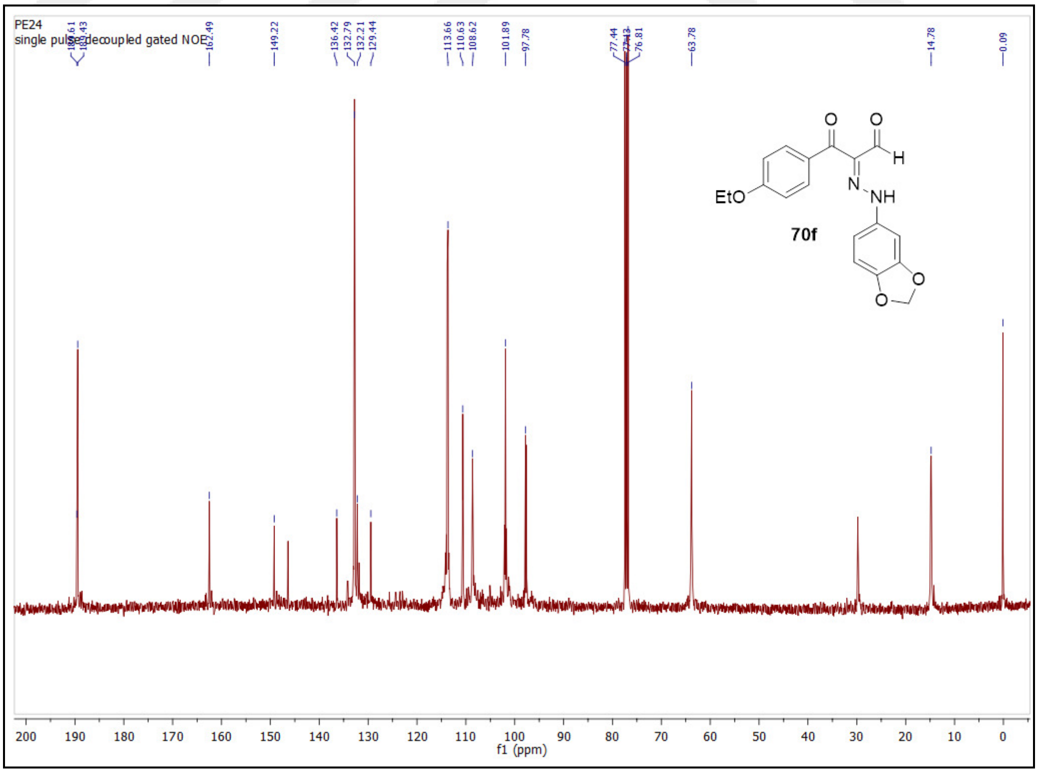


**Figure 7.45.** $^{13}$C-NMR spectrum of compound **70f**

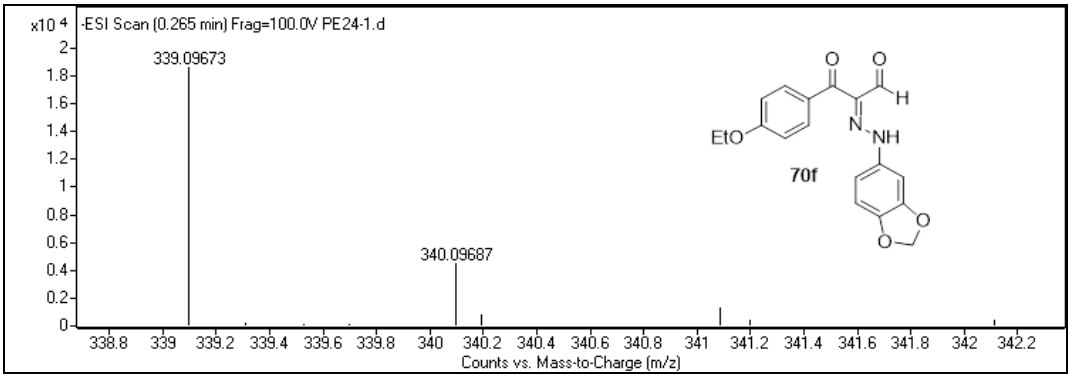


**Figure 7.46.** HRMS spectrum of compound **70f**

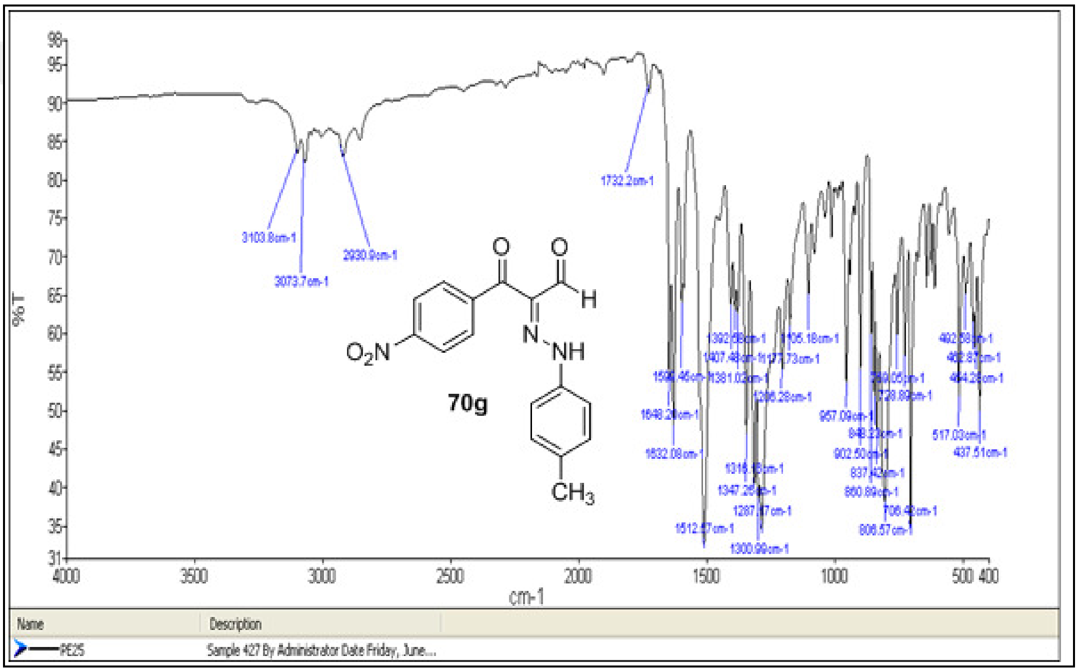


**Figure 7.47.** IR spectrum of compound **70g**

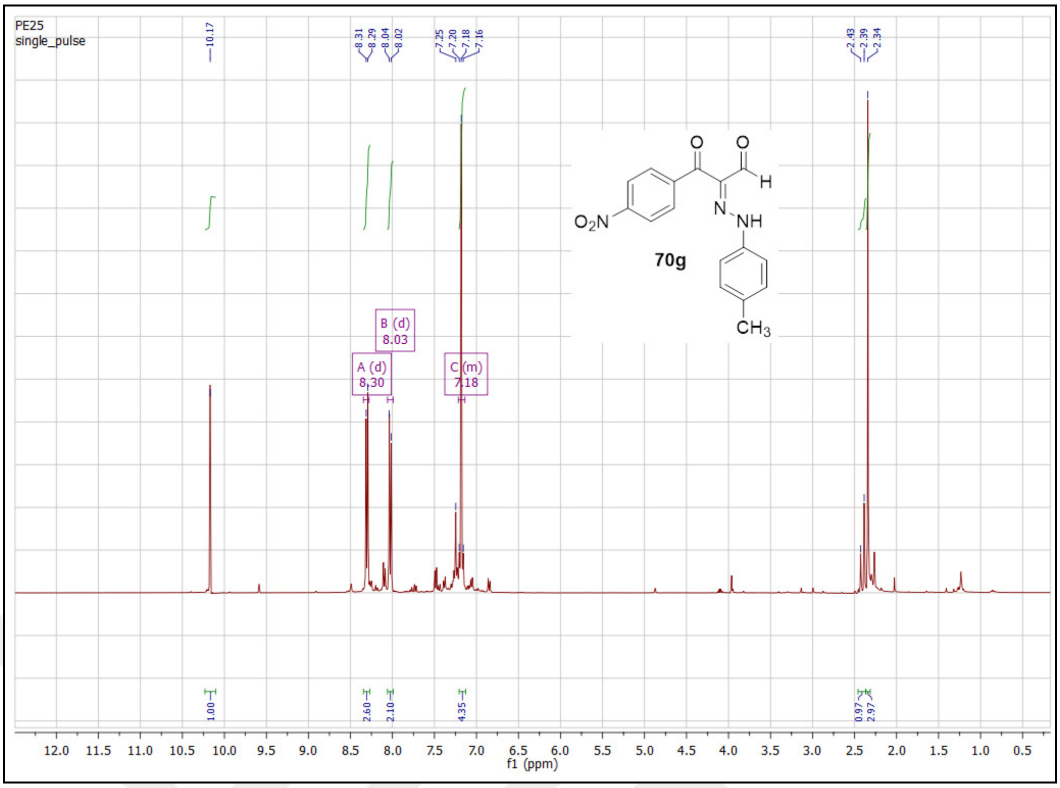


**Figure 7.48.** $^1$H-NMR spectrum of compound **70g**

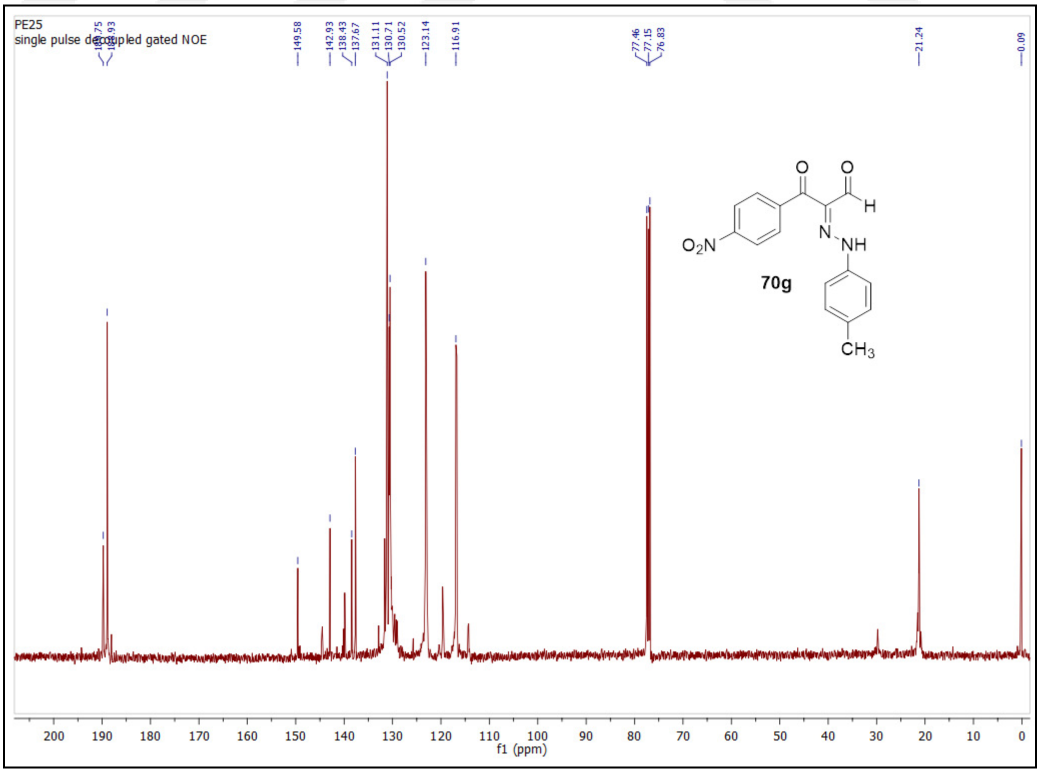


**Figure 7.49.** $^{13}$C-NMR spectrum of compound **70g**

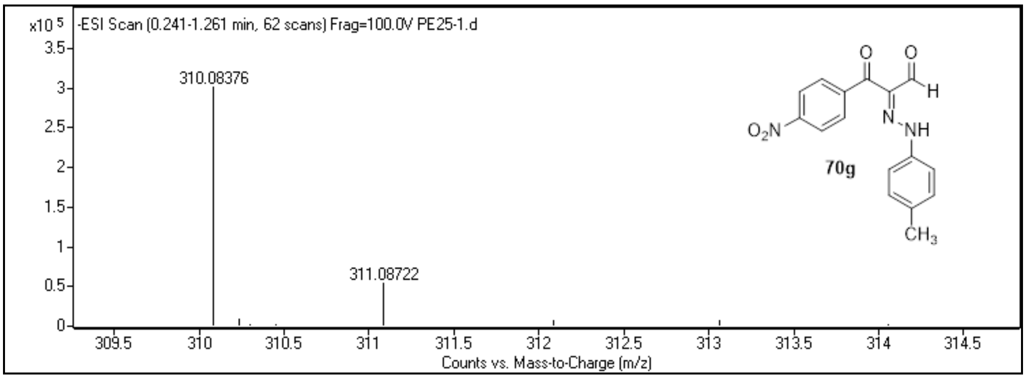


**Figure 7.50.** HRMS spectrum of compound **70g**

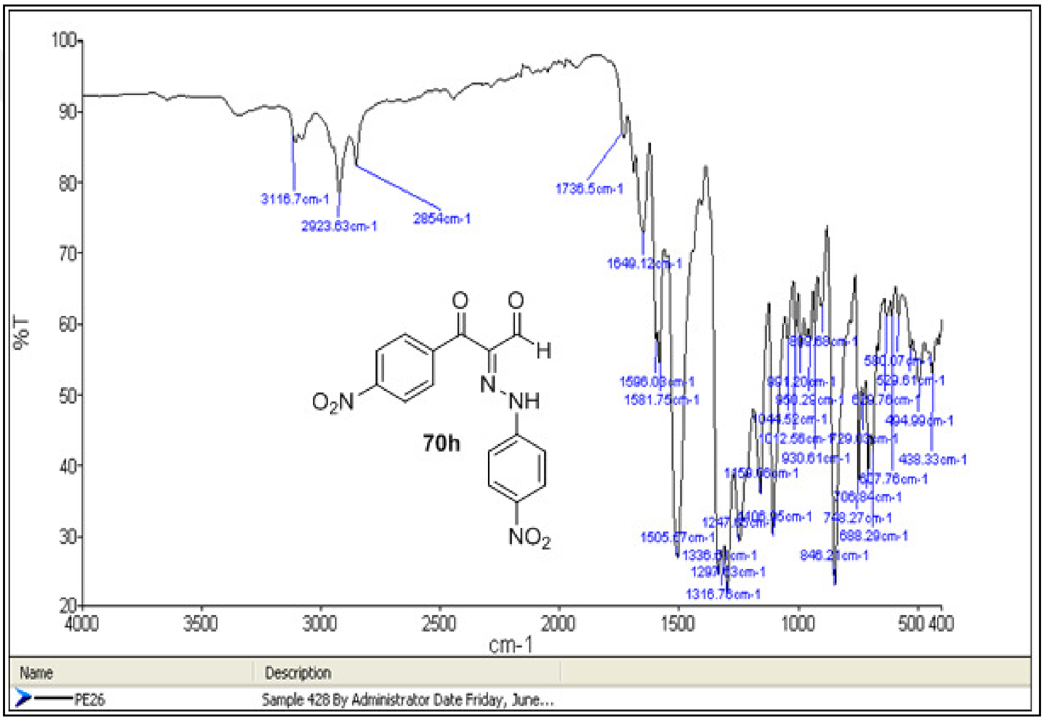


**Figure 7.51.** IR spectrum of compound **70h**

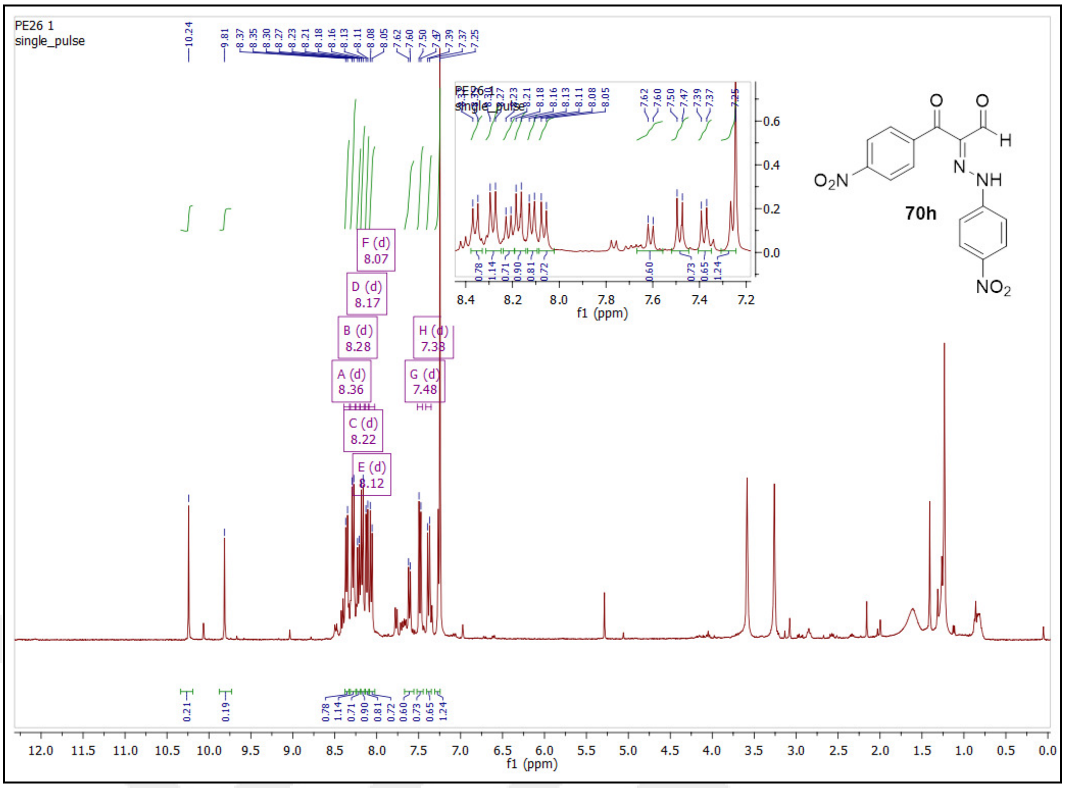


**Figure 7.52.** $^1$H-NMR spectrum of compound **70h**

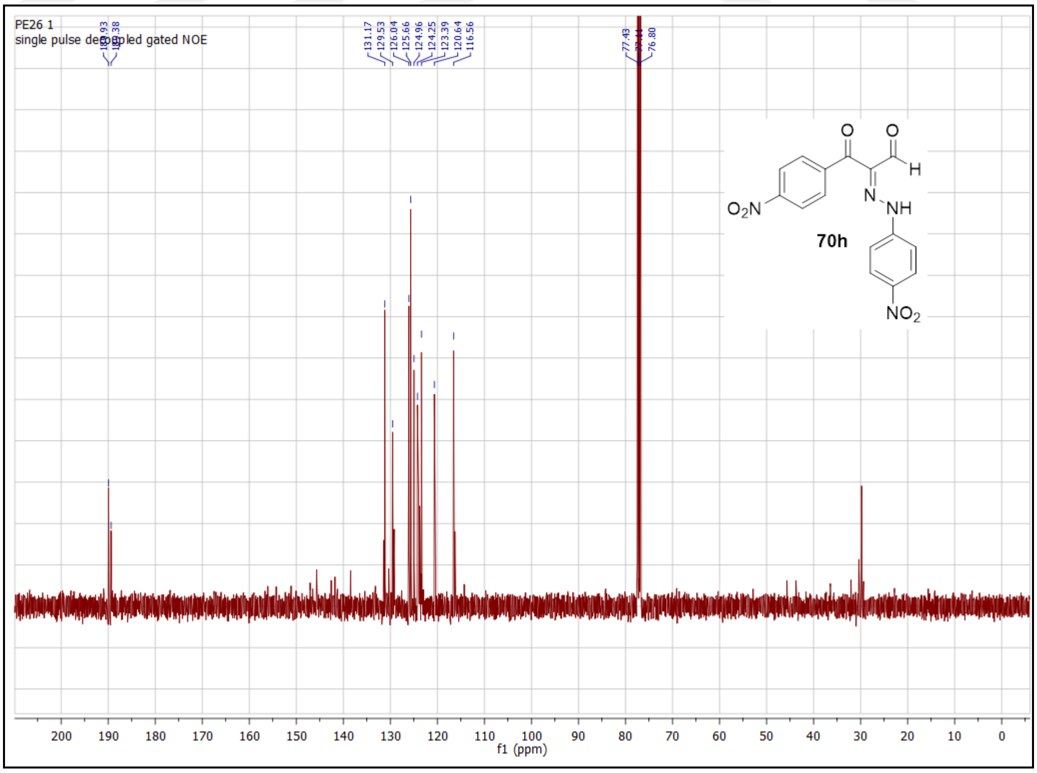


**Figure 7.53.** $^{13}$C-NMR spectrum of compound **70h**

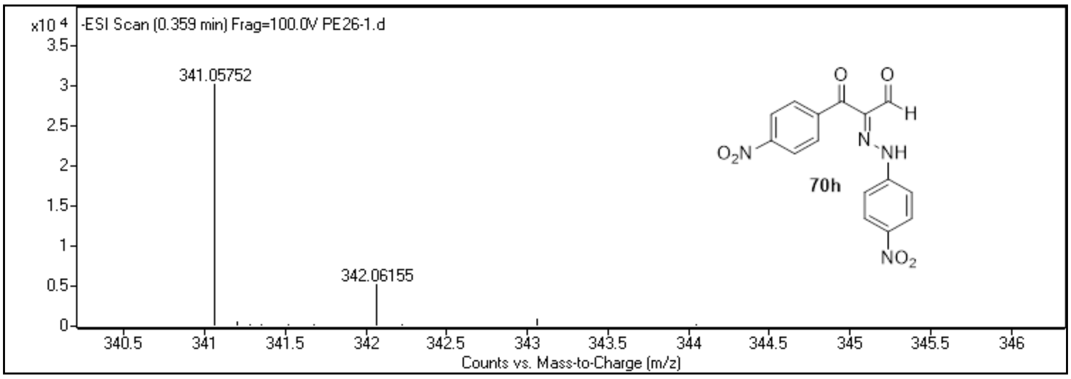
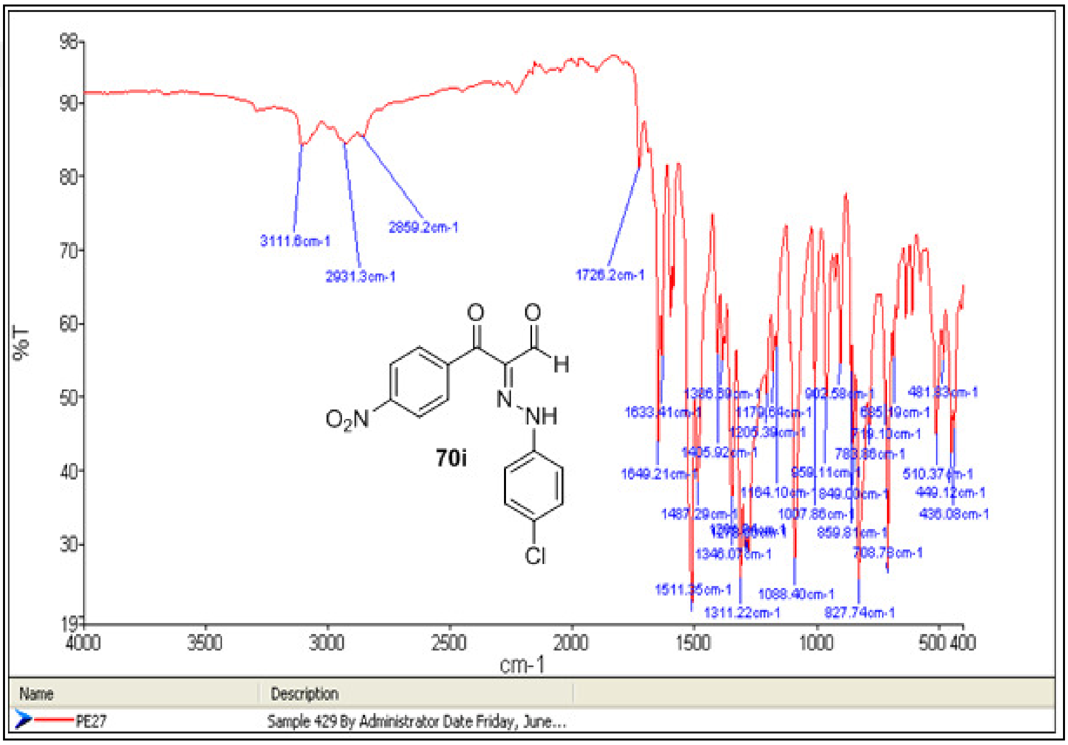


**Figure 7.54.** HRMS spectrum of compound **70h**



Name Description
PE27 Sample 429 By Administrator Date Friday, June...

**Figure 7.55.** IR spectrum of compound **70i**

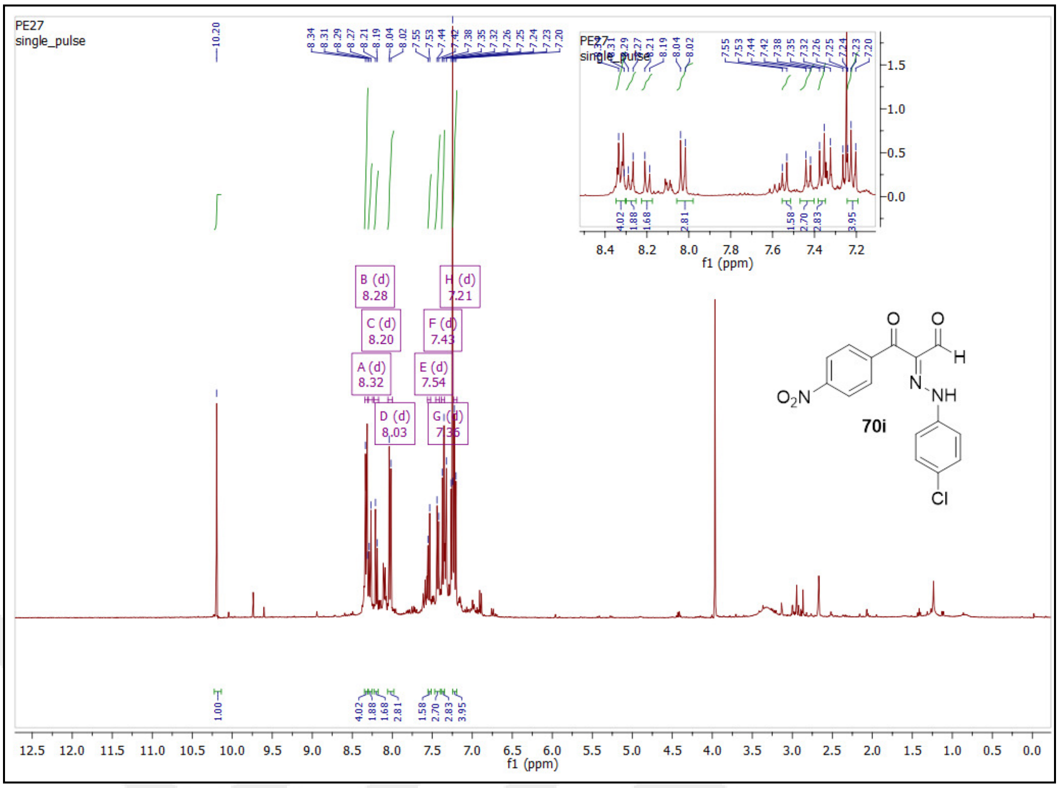


**Figure 7.56.** $^{1}$H-NMR spectrum of compound **70i**

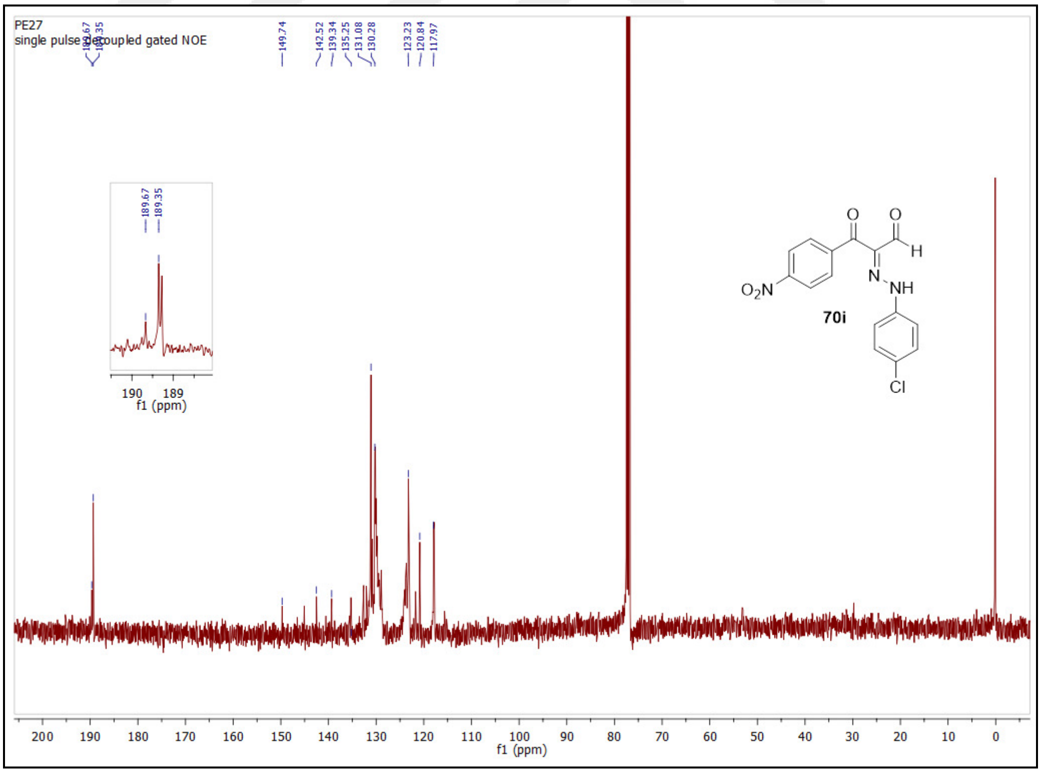


**Figure 7.57.** $^{13}$C-NMR spectrum of compound **70i**

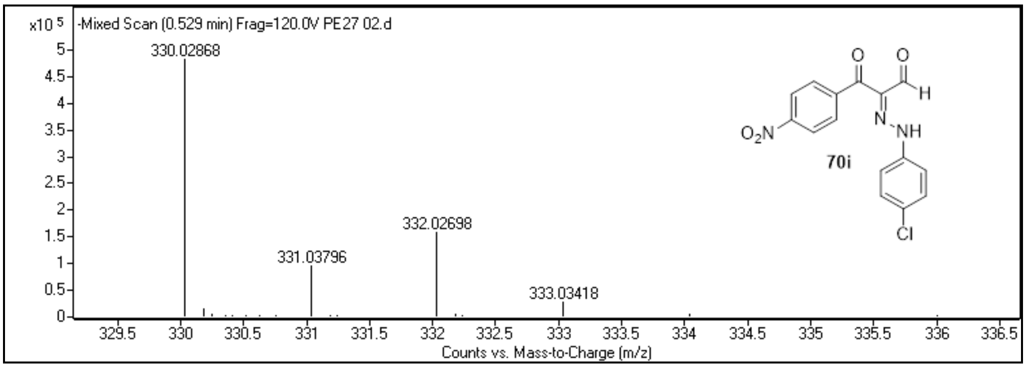
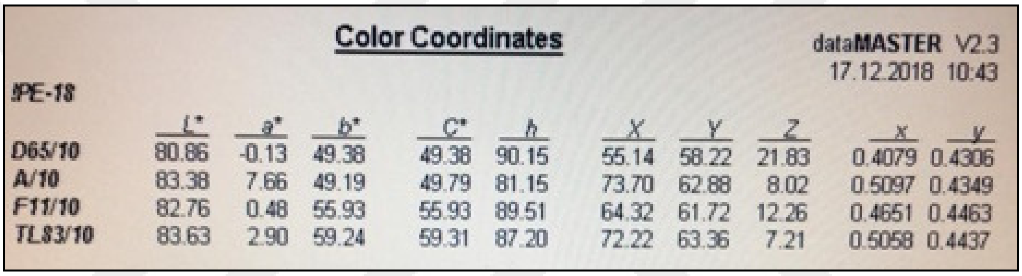


**Figure 7.58.** HRMS spectrum of compound **70i**

## 7.3 COLOR COORDINATE DATA FILES AND GRAPHS



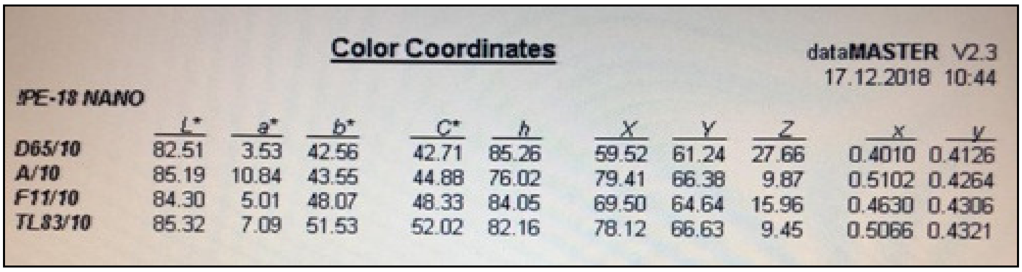
Color Coordinates

dataMASTER V2.3
17.12.2018 10:43

!PE-18

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 80.86 | -0.13 | 49.38 | 49.38 | 90.15 | 55.14 | 58.22 | 21.83 | 0.4079 | 0.4306 |
| A/10 | 83.38 | 7.66 | 49.19 | 49.79 | 81.15 | 73.70 | 62.88 | 8.02 | 0.5097 | 0.4349 |
| F11/10 | 82.76 | 0.48 | 55.93 | 55.93 | 89.51 | 64.32 | 61.72 | 12.26 | 0.4651 | 0.4463 |
| TL83/10 | 83.63 | 2.90 | 59.24 | 59.31 | 87.20 | 72.22 | 63.36 | 7.21 | 0.5058 | 0.4437 |

**Figure 7.59.** Color coordinates for polyester fabrics with PE18 dye



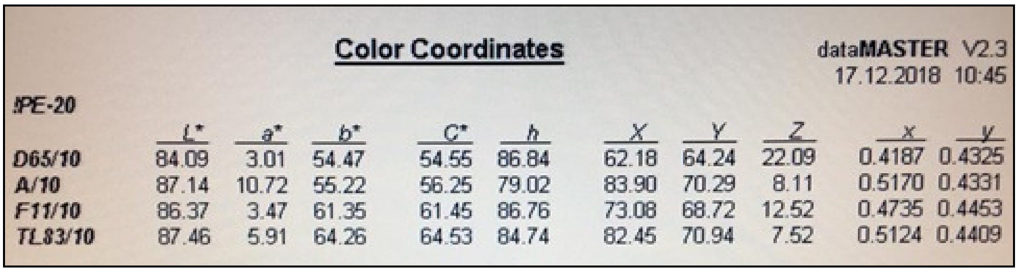
Color Coordinates

dataMASTER V2.3
17.12.2018 10:44

!PE-18 NANO

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 82.51 | 3.53 | 42.56 | 42.71 | 85.26 | 59.52 | 61.24 | 27.66 | 0.4010 | 0.4126 |
| A/10 | 85.19 | 10.84 | 43.55 | 44.88 | 76.02 | 79.41 | 66.38 | 9.87 | 0.5102 | 0.4264 |
| F11/10 | 84.30 | 5.01 | 48.07 | 48.33 | 84.05 | 69.50 | 64.64 | 15.96 | 0.4630 | 0.4306 |
| TL83/10 | 85.32 | 7.09 | 51.53 | 52.02 | 82.16 | 78.12 | 66.63 | 9.45 | 0.5066 | 0.4321 |

**Figure 7.60.** Color coordinates for polyester fabrics with PE18nano dye



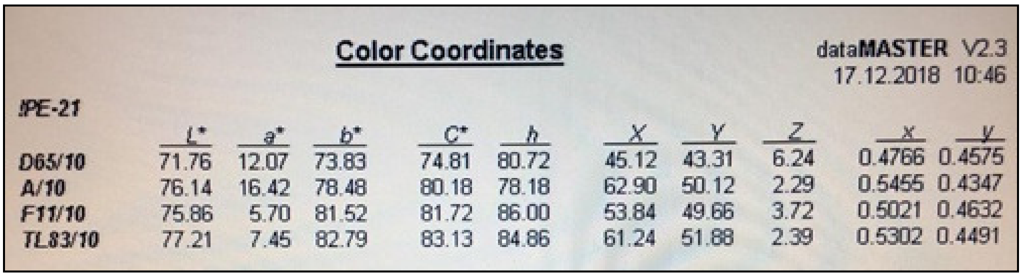
Color Coordinates

dataMASTER V2.3
17.12.2018 10:45

!PE-20

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 84.09 | 3.01 | 54.47 | 54.55 | 86.84 | 62.18 | 64.24 | 22.09 | 0.4187 | 0.4325 |
| A/10 | 87.14 | 10.72 | 55.22 | 56.25 | 79.02 | 83.90 | 70.29 | 8.11 | 0.5170 | 0.4331 |
| F11/10 | 86.37 | 3.47 | 61.35 | 61.45 | 86.76 | 73.08 | 68.72 | 12.52 | 0.4735 | 0.4453 |
| TL83/10 | 87.46 | 5.91 | 64.26 | 64.53 | 84.74 | 82.45 | 70.94 | 7.52 | 0.5124 | 0.4409 |

**Figure 7.61.** Color coordinates for polyester fabrics with PE20 dye



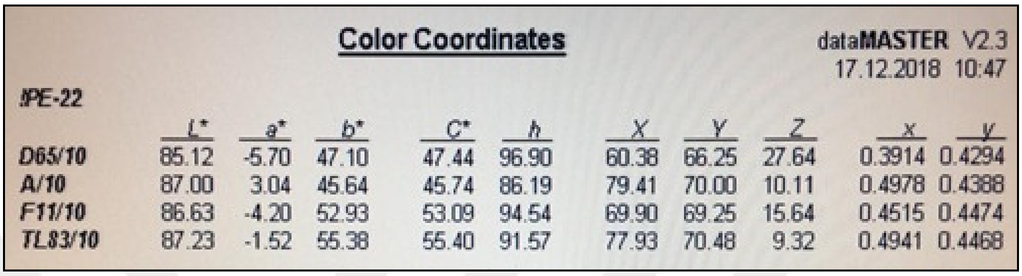
Color Coordinates

dataMASTER V2.3
17.12.2018 10:46

!PE-21

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 71.76 | 12.07 | 73.83 | 74.81 | 80.72 | 45.12 | 43.31 | 6.24 | 0.4766 | 0.4575 |
| A/10 | 76.14 | 16.42 | 78.48 | 80.18 | 78.18 | 62.90 | 50.12 | 2.29 | 0.5455 | 0.4347 |
| F11/10 | 75.86 | 5.70 | 81.52 | 81.72 | 86.00 | 53.84 | 49.66 | 3.72 | 0.5021 | 0.4632 |
| TL83/10 | 77.21 | 7.45 | 82.79 | 83.13 | 84.86 | 61.24 | 51.88 | 2.39 | 0.5302 | 0.4491 |

**Figure 7.62.** Color coordinates for polyester fabrics with PE21 dye



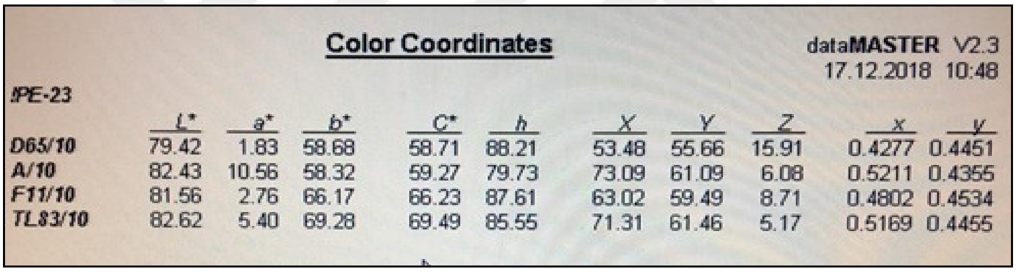
Color Coordinates

dataMASTER V2.3
17.12.2018 10:47

!PE-22

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 85.12 | -5.70 | 47.10 | 47.44 | 96.90 | 60.38 | 66.25 | 27.64 | 0.3914 | 0.4294 |
| A/10 | 87.00 | 3.04 | 45.64 | 45.74 | 86.19 | 79.41 | 70.00 | 10.11 | 0.4978 | 0.4388 |
| F11/10 | 86.63 | -4.20 | 52.93 | 53.09 | 94.54 | 69.90 | 69.25 | 15.64 | 0.4515 | 0.4474 |
| TL83/10 | 87.23 | -1.52 | 55.38 | 55.40 | 91.57 | 77.93 | 70.48 | 9.32 | 0.4941 | 0.4468 |

**Figure 7.63.** Color coordinates for polyester fabrics with PE22 dye



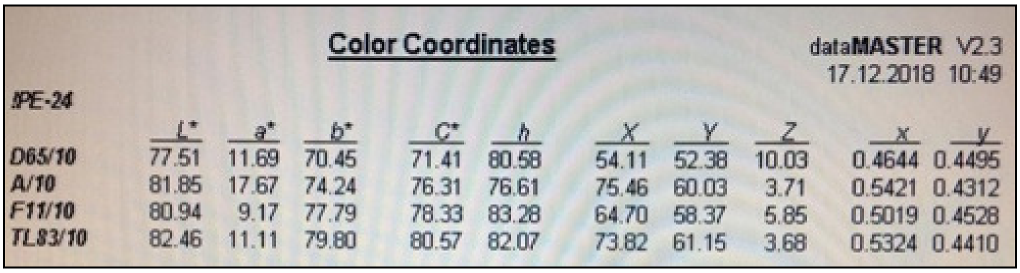
Color Coordinates

dataMASTER V2.3
17.12.2018 10:48

!PE-23

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 79.42 | 1.83 | 58.68 | 58.71 | 88.21 | 53.48 | 55.66 | 15.91 | 0.4277 | 0.4451 |
| A/10 | 82.43 | 10.56 | 58.32 | 59.27 | 79.73 | 73.09 | 61.09 | 6.08 | 0.5211 | 0.4355 |
| F11/10 | 81.56 | 2.76 | 66.17 | 66.23 | 87.61 | 63.02 | 59.49 | 8.71 | 0.4802 | 0.4534 |
| TL83/10 | 82.62 | 5.40 | 69.28 | 69.49 | 85.55 | 71.31 | 61.46 | 5.17 | 0.5169 | 0.4455 |

**Figure 7.64.** Color coordinates for polyester fabrics with PE23 dye



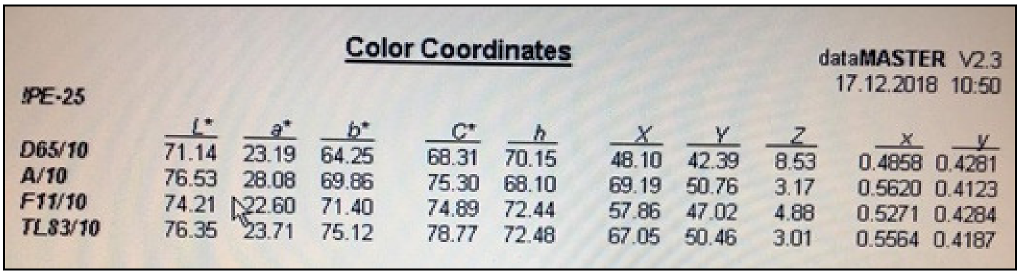
Color Coordinates

dataMASTER V2.3
17.12.2018 10:49

!PE-24

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 77.51 | 11.69 | 70.45 | 71.41 | 80.58 | 54.11 | 52.38 | 10.03 | 0.4644 | 0.4495 |
| A/10 | 81.85 | 17.67 | 74.24 | 76.31 | 76.61 | 75.46 | 60.03 | 3.71 | 0.5421 | 0.4312 |
| F11/10 | 80.94 | 9.17 | 77.79 | 78.33 | 83.28 | 64.70 | 58.37 | 5.85 | 0.5019 | 0.4528 |
| TL83/10 | 82.46 | 11.11 | 79.80 | 80.57 | 82.07 | 73.82 | 61.15 | 3.68 | 0.5324 | 0.4410 |

**Figure 7.65.** Color coordinates for polyester fabrics with PE24 dye



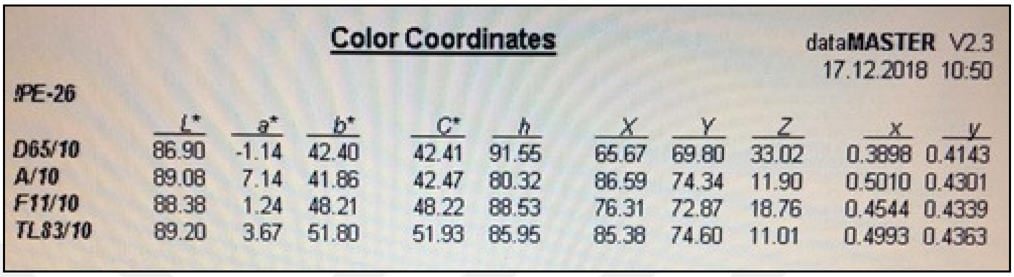
Color Coordinates

dataMASTER V2.3
17.12.2018 10:50

!PE-25

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 71.14 | 23.19 | 64.25 | 68.31 | 70.15 | 48.10 | 42.39 | 8.53 | 0.4858 | 0.4281 |
| A/10 | 76.53 | 28.08 | 69.86 | 75.30 | 68.10 | 69.19 | 50.76 | 3.17 | 0.5620 | 0.4123 |
| F11/10 | 74.21 | 22.60 | 71.40 | 74.89 | 72.44 | 57.86 | 47.02 | 4.88 | 0.5271 | 0.4284 |
| TL83/10 | 76.35 | 23.71 | 75.12 | 78.77 | 72.48 | 67.05 | 50.46 | 3.01 | 0.5564 | 0.4187 |

**Figure 7.66.** Color coordinates for polyester fabrics with PE25 dye



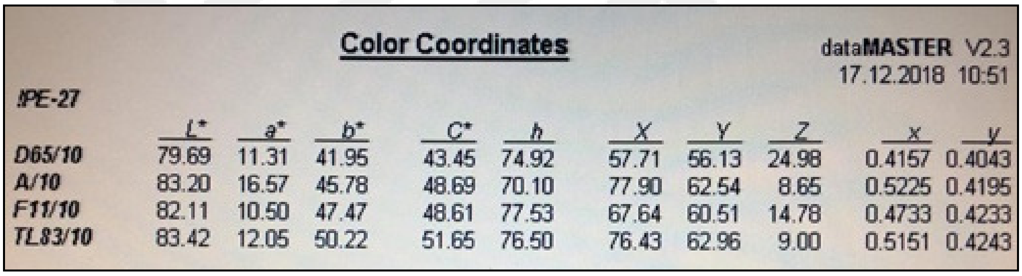
Color Coordinates

dataMASTER V2.3
17.12.2018 10:50

!PE-26

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 86.90 | -1.14 | 42.40 | 42.41 | 91.55 | 65.67 | 69.80 | 33.02 | 0.3898 | 0.4143 |
| A/10 | 89.08 | 7.14 | 41.86 | 42.47 | 80.32 | 86.59 | 74.34 | 11.90 | 0.5010 | 0.4301 |
| F11/10 | 88.38 | 1.24 | 48.21 | 48.22 | 88.53 | 76.31 | 72.87 | 18.76 | 0.4544 | 0.4339 |
| TL83/10 | 89.20 | 3.67 | 51.80 | 51.93 | 85.95 | 85.38 | 74.60 | 11.01 | 0.4993 | 0.4363 |

**Figure 7.67.** Color coordinates for polyester fabrics with PE26 dye



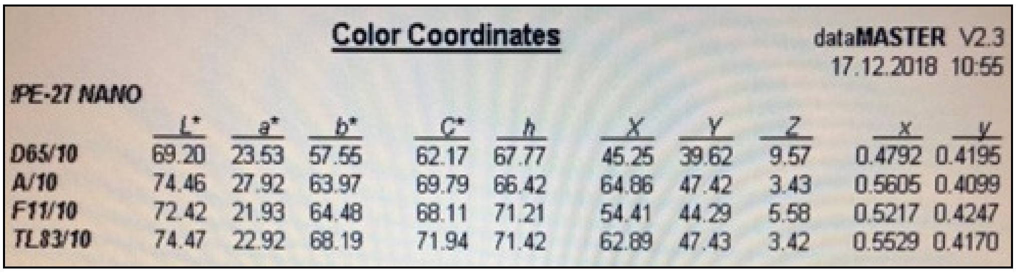
Color Coordinates

dataMASTER V2.3
17.12.2018 10:51

!PE-27

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 79.69 | 11.31 | 41.95 | 43.45 | 74.92 | 57.71 | 56.13 | 24.98 | 0.4157 | 0.4043 |
| A/10 | 83.20 | 16.57 | 45.78 | 48.69 | 70.10 | 77.90 | 62.54 | 8.65 | 0.5225 | 0.4195 |
| F11/10 | 82.11 | 10.50 | 47.47 | 48.61 | 77.53 | 67.64 | 60.51 | 14.78 | 0.4733 | 0.4233 |
| TL83/10 | 83.42 | 12.05 | 50.22 | 51.65 | 76.50 | 76.43 | 62.96 | 9.00 | 0.5151 | 0.4243 |

**Figure 7.68.** Color coordinates for polyester fabrics with PE27 dye



Color Coordinates

dataMASTER V2.3
17.12.2018 10:55

!PE-27 NANO

| | L* | a* | b* | C* | h | X | Y | Z | x | y |
|---|---|---|---|---|---|---|---|---|---|---|
| D65/10 | 69.20 | 23.53 | 57.55 | 62.17 | 67.77 | 45.25 | 39.62 | 9.57 | 0.4792 | 0.4195 |
| A/10 | 74.46 | 27.92 | 63.97 | 69.79 | 66.42 | 64.86 | 47.42 | 3.43 | 0.5605 | 0.4099 |
| F11/10 | 72.42 | 21.93 | 64.48 | 68.11 | 71.21 | 54.41 | 44.29 | 5.58 | 0.5217 | 0.4247 |
| TL83/10 | 74.47 | 22.92 | 68.19 | 71.94 | 71.42 | 62.89 | 47.43 | 3.42 | 0.5529 | 0.4170 |

**Figure 7.69.** Color coordinates for polyester fabrics with PE27nano dye

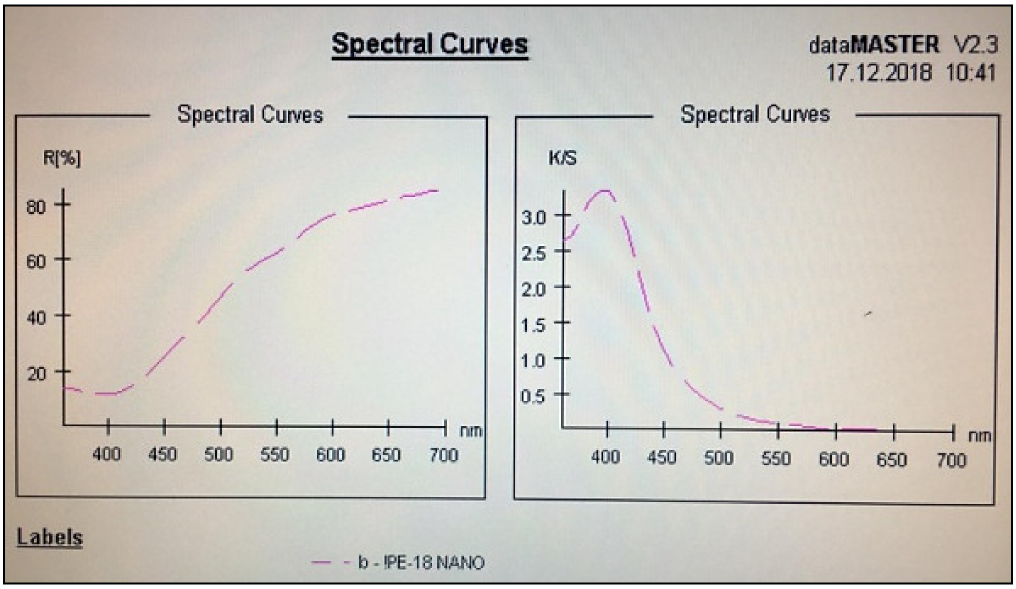


**Figure 7.70.** K/S and %R graphs for polyester samples with PE18nano dye

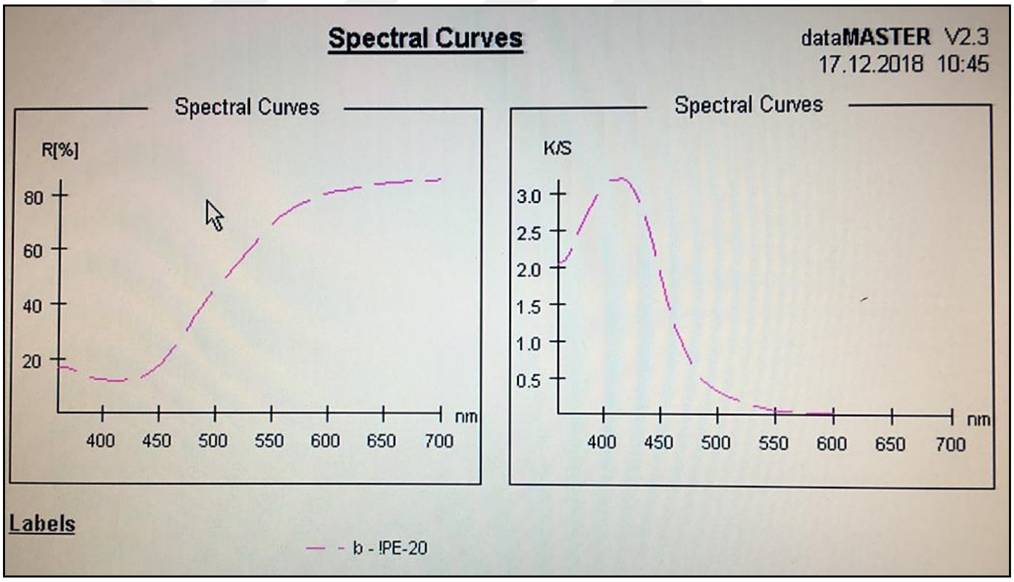


**Figure 7.71.** K/S and %R graphs for polyester samples with PE20 dye

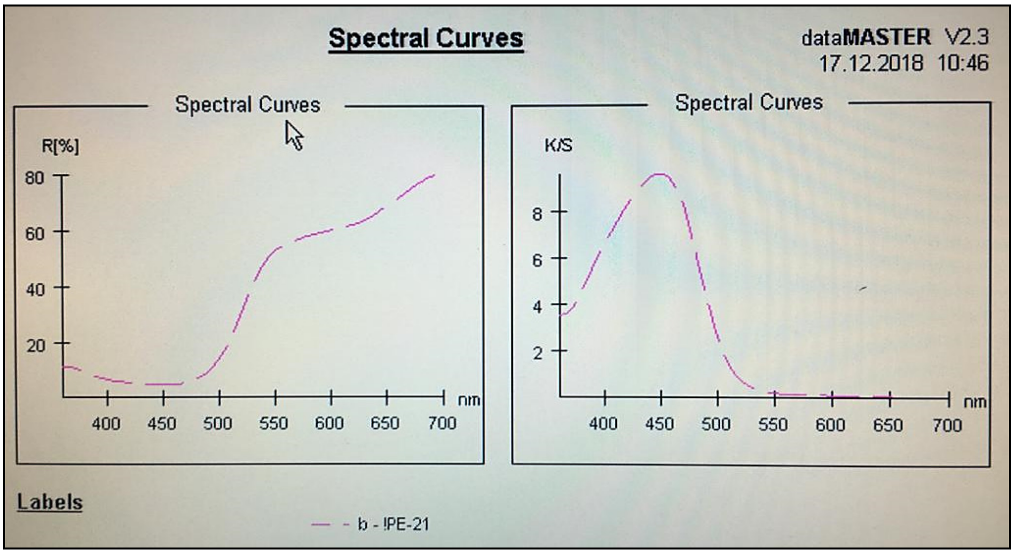


**Figure 7.72.** K/S and %R graphs for polyester samples with PE21 dye

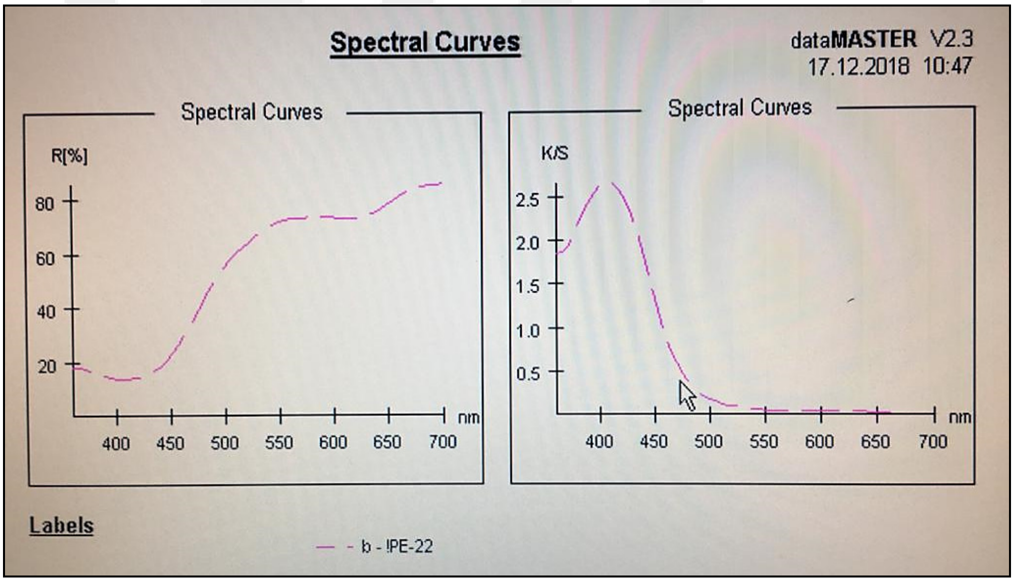


**Figure 7.73.** K/S and %R graphs for polyester samples with PE22 dye

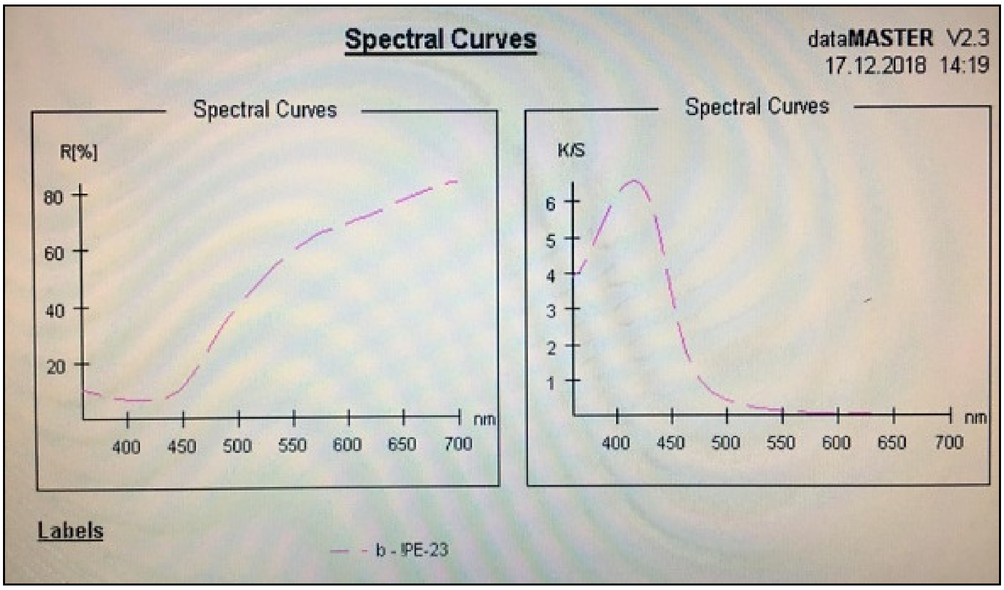


**Figure 7.74.** K/S and %R graphs for polyester samples with PE23 dye

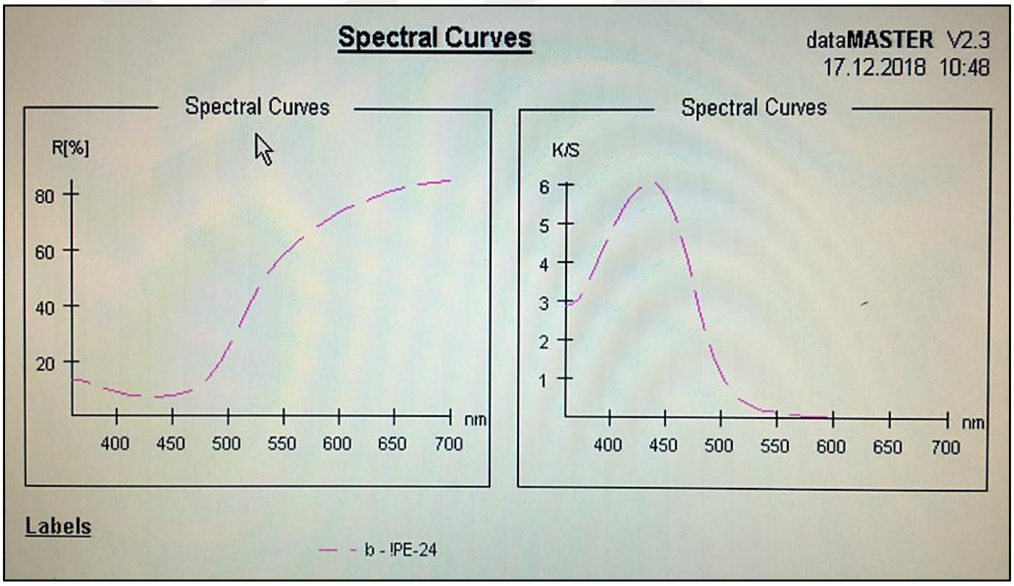


**Figure 7.75.** K/S and %R graphs for polyester samples with PE24 dye

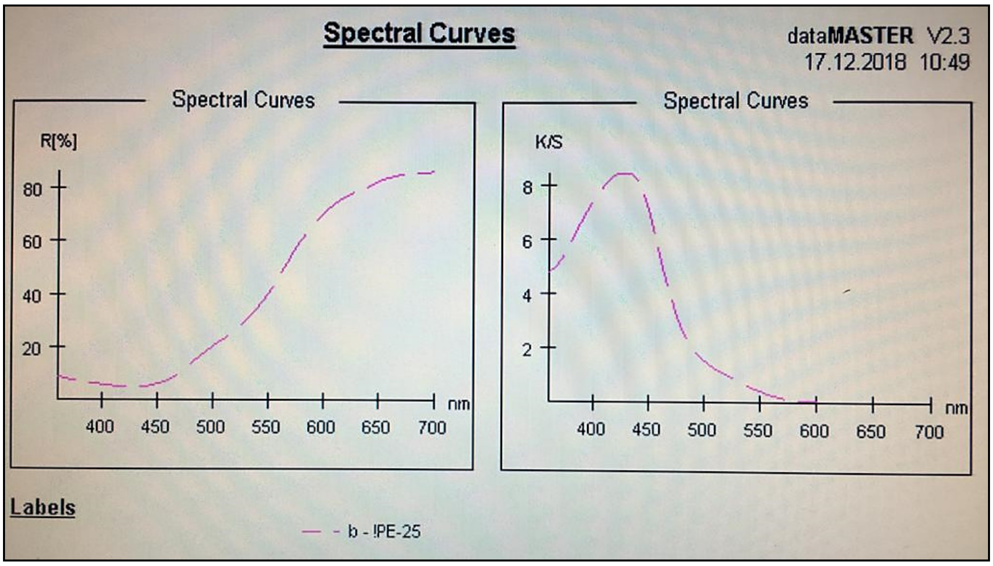


**Figure 7.76.** K/S and %R graphs for polyester samples with PE25 dye

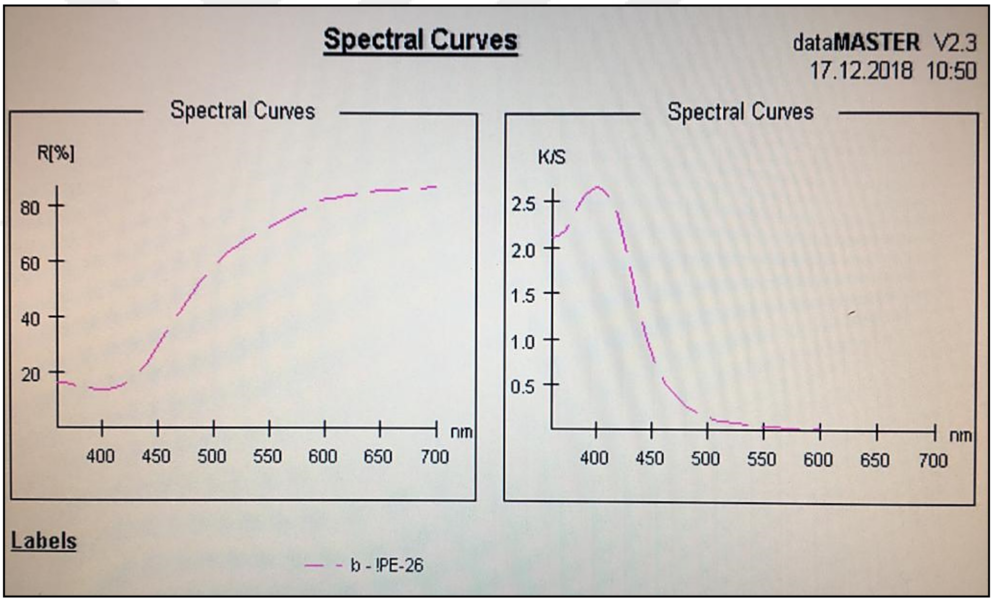


**Figure 7.77.** K/S and %R graphs for polyester samples with PE26 dye

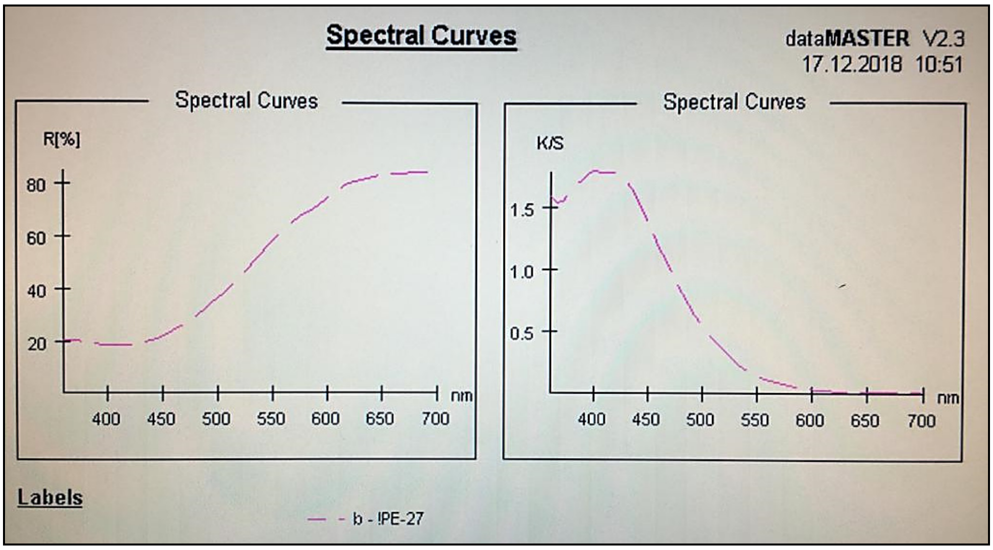


**Figure 7.78.** K/S and %R graphs for polyester samples with PE27 dye

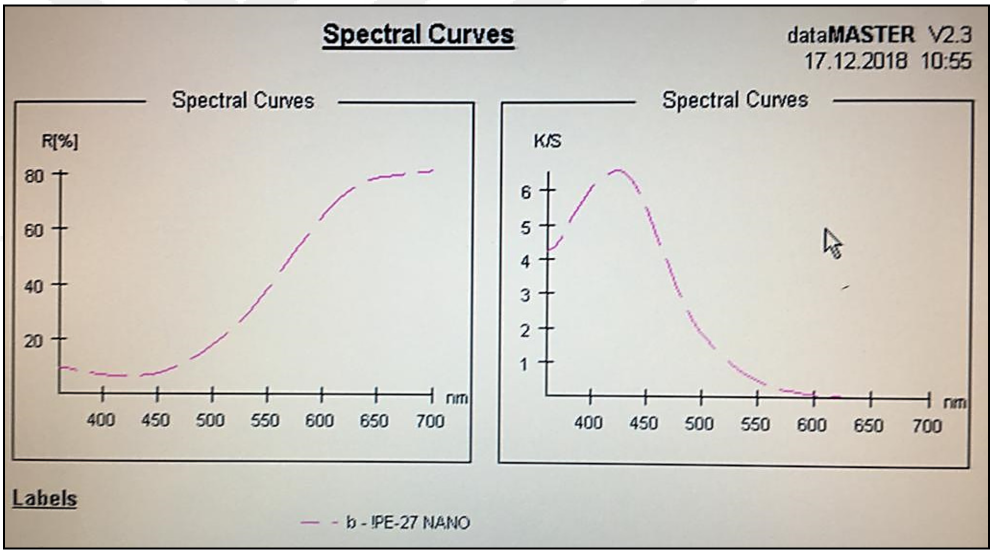
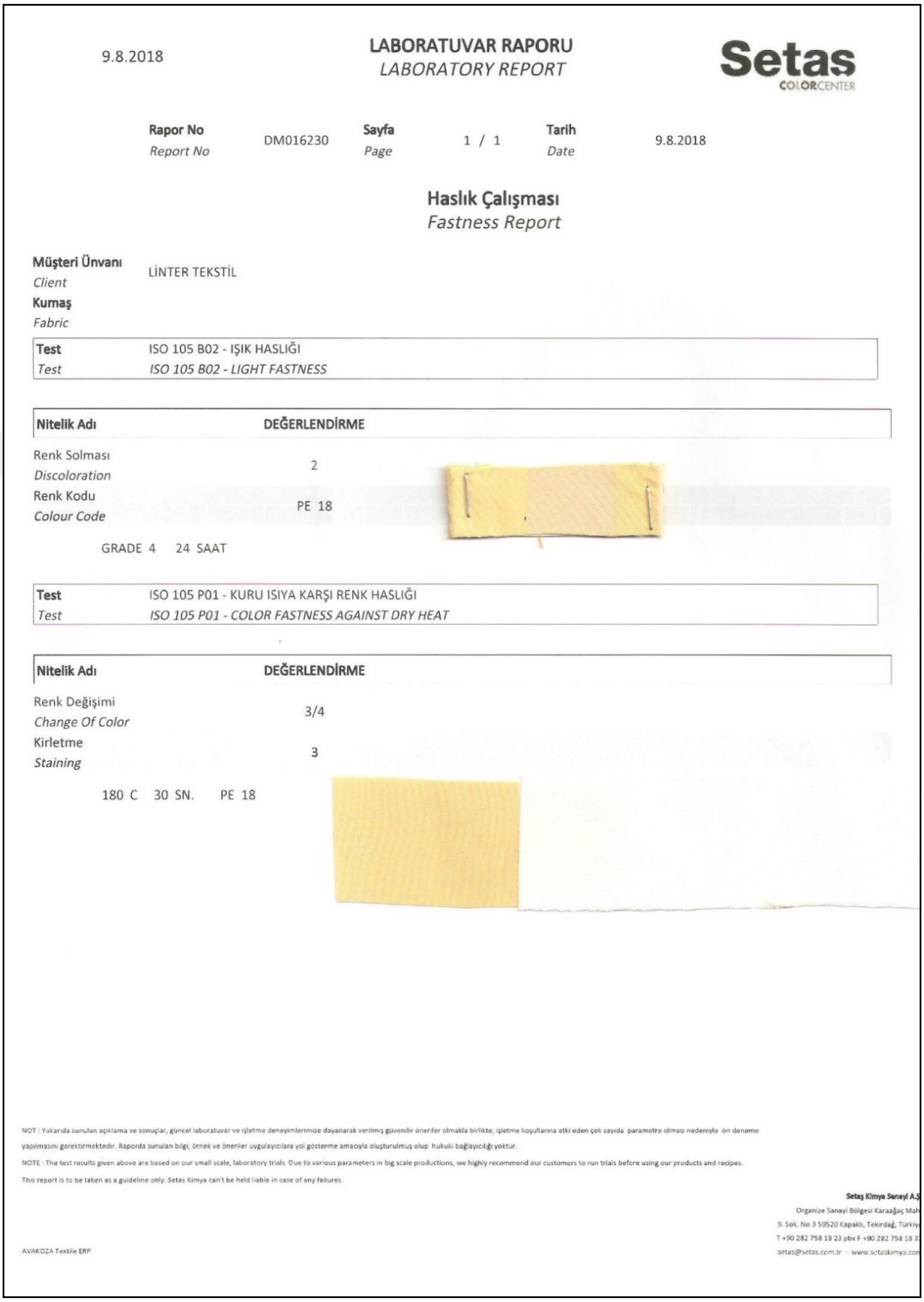


**Figure 7.79.** K/S and %R graphs for polyester samples with PE27nano dye

## 7.4 FASTNESS TEST RESULTS



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016230 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

| | |
|---|---|
| **Müşteri Ünvanı**<br>*Client* | LİNTER TEKSTİL |
| **Kumaş**<br>*Fabric* | |

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 2 |
| Renk Kodu<br>*Colour Code* | PE 18 |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3/4 |
| Kirletme<br>*Staining* | 3 |

180 C 30 SN. PE 18

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

NOTE : The test results given above are based on our small scale, laboratory trials. Due to various parameters in big scale productions, we highly recommend our customers to run trials before using our products and recipes.

This report is to be taken as a guideline only. Setas Kimya can't be held liable in case of any failures.

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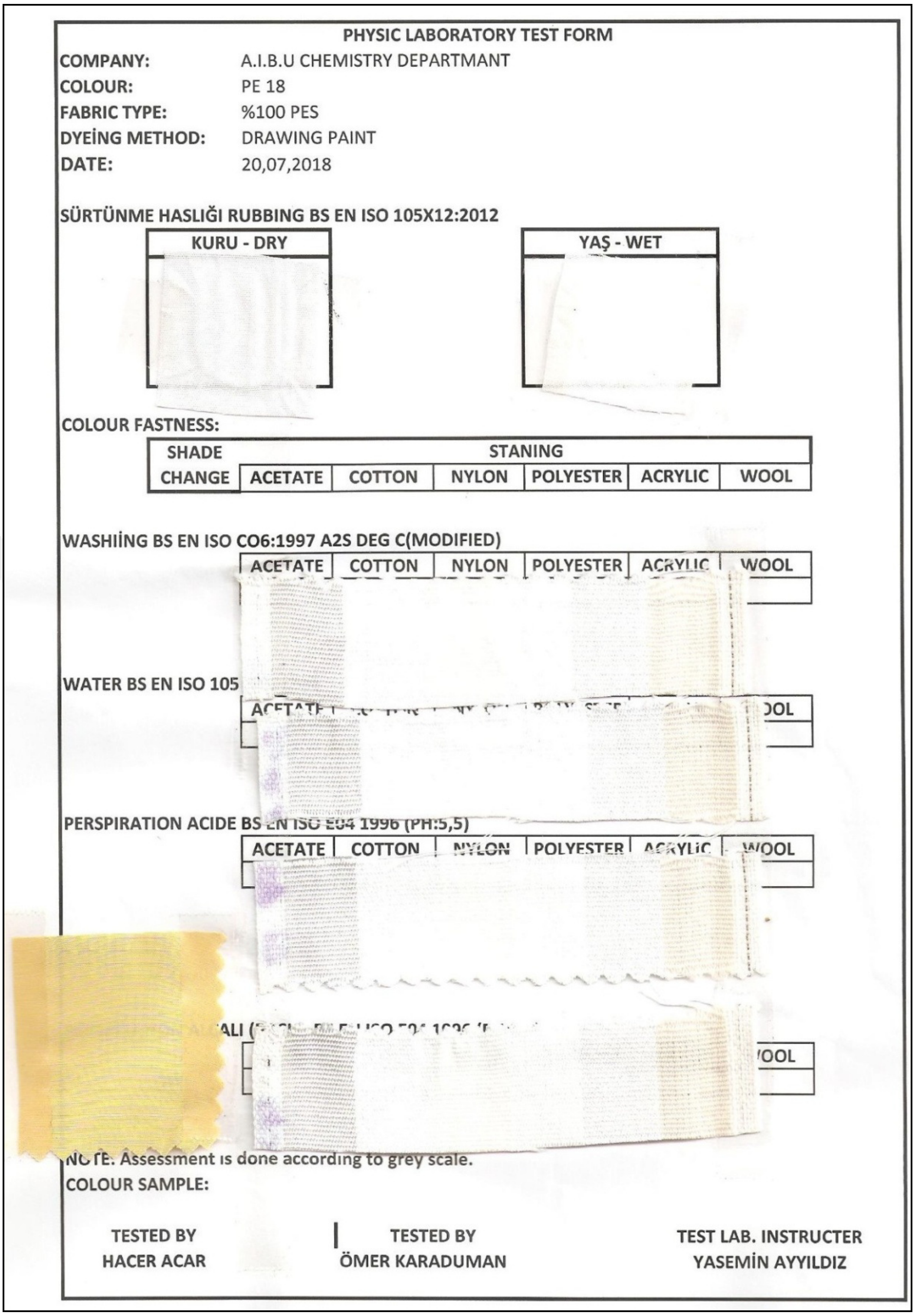
setas@setas.com.tr - www.setaskimya.co

AVAKOZA Textile ERP

**Figure 7.80.** Light and sublimation fastnesses of PE fabric with PE18 dye



PHYSIC LABORATORY TEST FORM

**COMPANY:** A.I.B.U CHEMISTRY DEPARTMANT
**COLOUR:** PE 18
**FABRIC TYPE:** %100 PES
**DYEİNG METHOD:** DRAWING PAINT
**DATE:** 20,07,2018

**SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012**

KURU - DRY
YAŞ - WET

**COLOUR FASTNESS:**

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

**WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**WATER BS EN ISO 105**

| ACETATE | | | | | OOL |
|---|---|---|---|---|---|
| | | | | | |

**PERSPIRATION ACIDE BS EN ISO E04 1996 (PH:5,5)**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**ALI**

| | | | | | OOL |
|---|---|---|---|---|---|
| | | | | | |

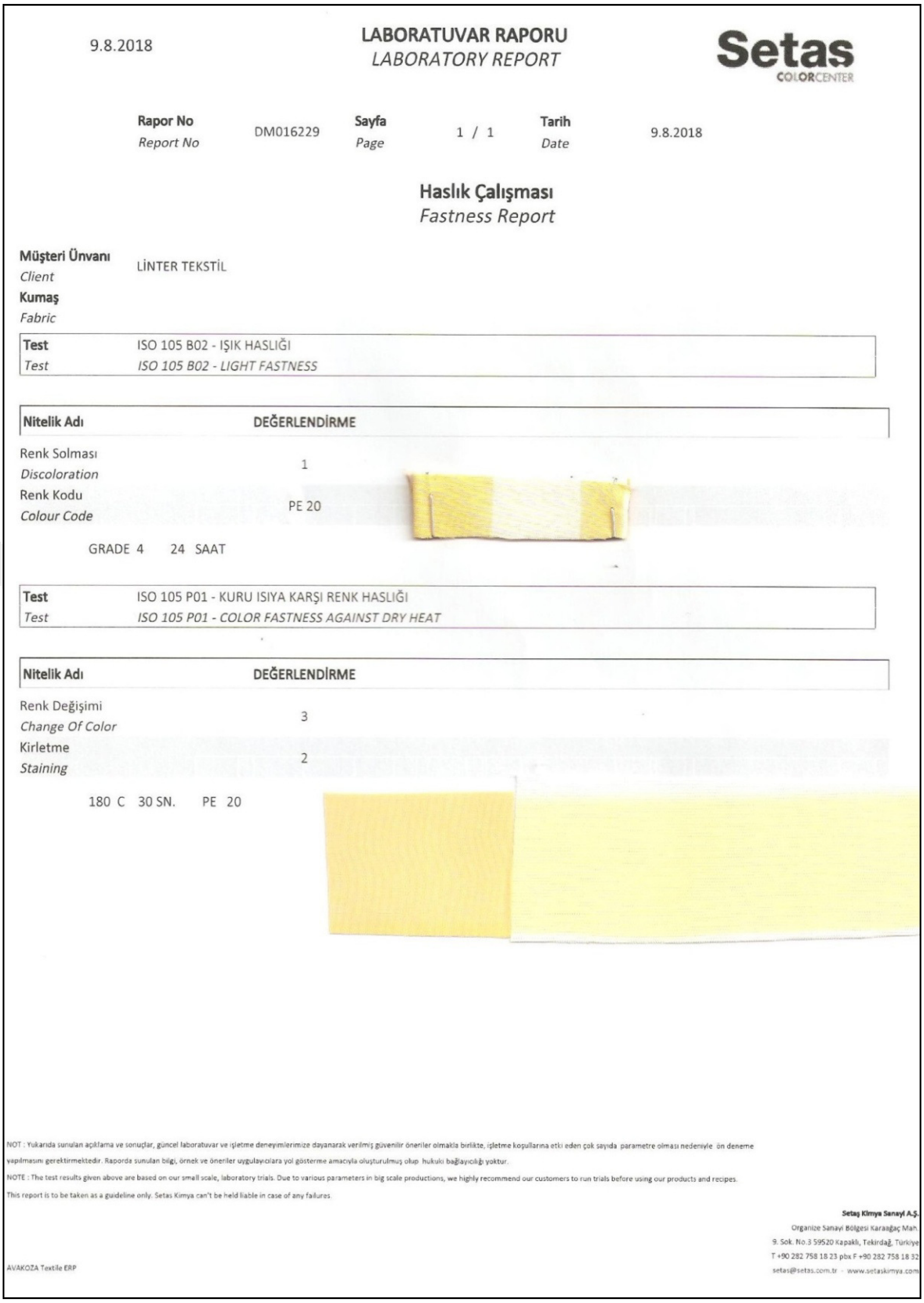
**NOTE.** Assessment is done according to grey scale.
**COLOUR SAMPLE:**

**TESTED BY**
**HACER ACAR**

**TESTED BY**
**ÖMER KARADUMAN**

**TEST LAB. INSTRUCTER**
**YASEMİN AYYILDIZ**

**Figure 7.81.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE18 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016229 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** *Client*: LİNTER TEKSTİL
**Kumaş** *Fabric*:

**Test** ISO 105 B02 - IŞIK HASLIĞI
*Test* *ISO 105 B02 - LIGHT FASTNESS*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 1 |
| Renk Kodu<br>*Colour Code* | PE 20 |

GRADE 4 24 SAAT

**Test** ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI
*Test* *ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3 |
| Kirletme<br>*Staining* | 2 |

180 C 30 SN. PE 20

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

NOTE : The test results given above are based on our small scale, laboratory trials. Due to various parameters in big scale productions, we highly recommend our customers to run trials before using our products and recipes.

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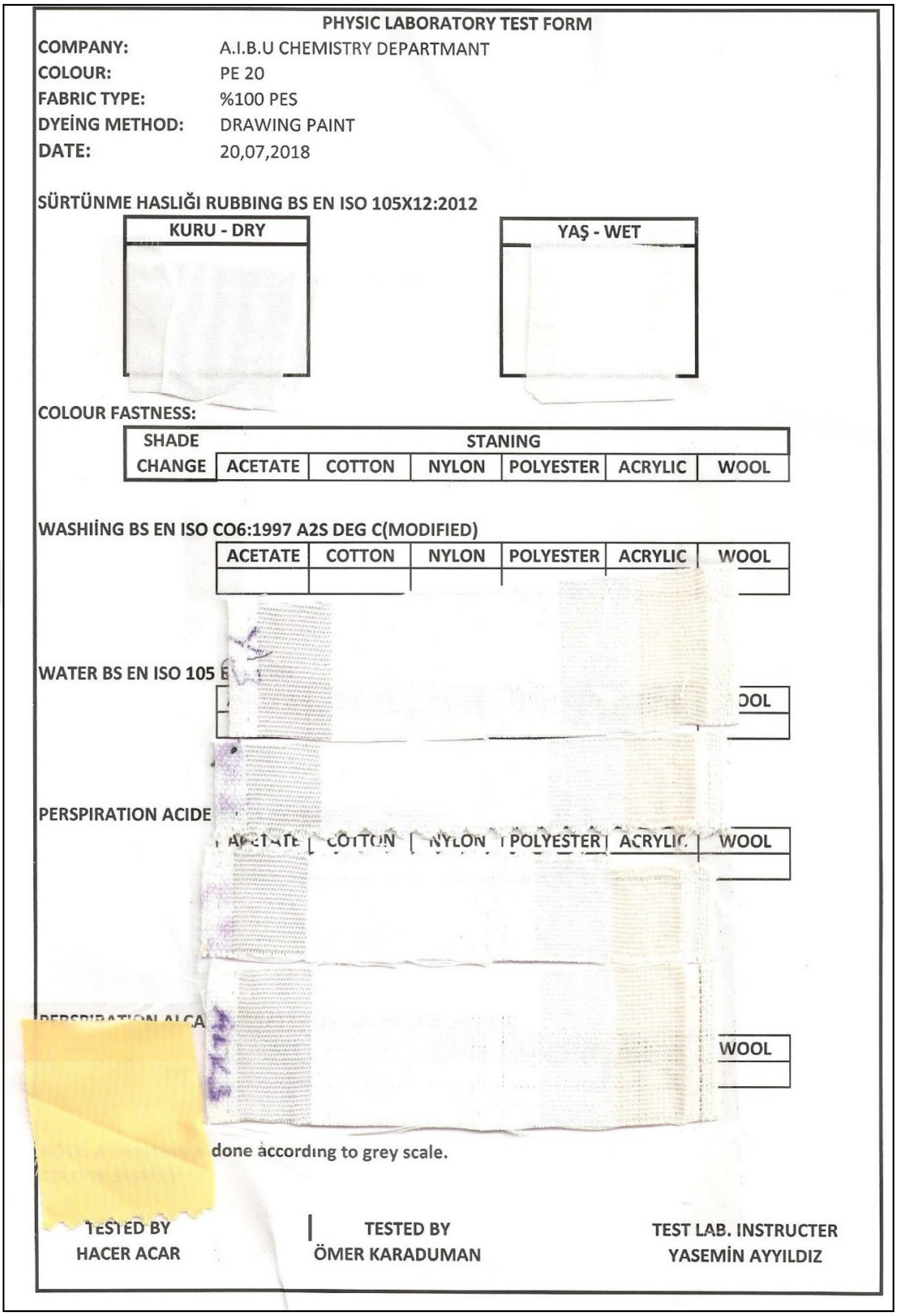
setas@setas.com.tr - www.setaskimya.com

AVAKOZA Textile ERP

**Figure 7.82.** Light and sublimation fastnesses of PE fabric with PE20 dye



PHYSIC LABORATORY TEST FORM

| | |
|---|---|
| **COMPANY:** | A.I.B.U CHEMISTRY DEPARTMANT |
| **COLOUR:** | PE 20 |
| **FABRIC TYPE:** | %100 PES |
| **DYEİNG METHOD:** | DRAWING PAINT |
| **DATE:** | 20,07,2018 |

**SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012**

| KURU - DRY | YAŞ - WET |
|---|---|
| | |

**COLOUR FASTNESS:**

| SHADE | STANING | | | | | |
|---|---|---|---|---|---|---|
| CHANGE | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

**WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**WATER BS EN ISO 105 E**

OOL

**PERSPIRATION ACIDE**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**PERSPIRATION ALCA**

WOOL

done according to grey scale.

**TESTED BY**
**HACER ACAR**

**TESTED BY**
**ÖMER KARADUMAN**

**TEST LAB. INSTRUCTER**
**YASEMİN AYYILDIZ**

**Figure 7.83.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE20 dye

9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016228 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

| | |
|---|---|
| **Müşteri Ünvanı**<br>*Client* | LİNTER TEKSTİL |
| **Kumaş**<br>*Fabric* | |

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 1/2 |
| Renk Kodu<br>*Colour Code* | PE 21 |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 4 |
| Kirletme<br>*Staining* | 1 |

180 C 30 SN. PE 21

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

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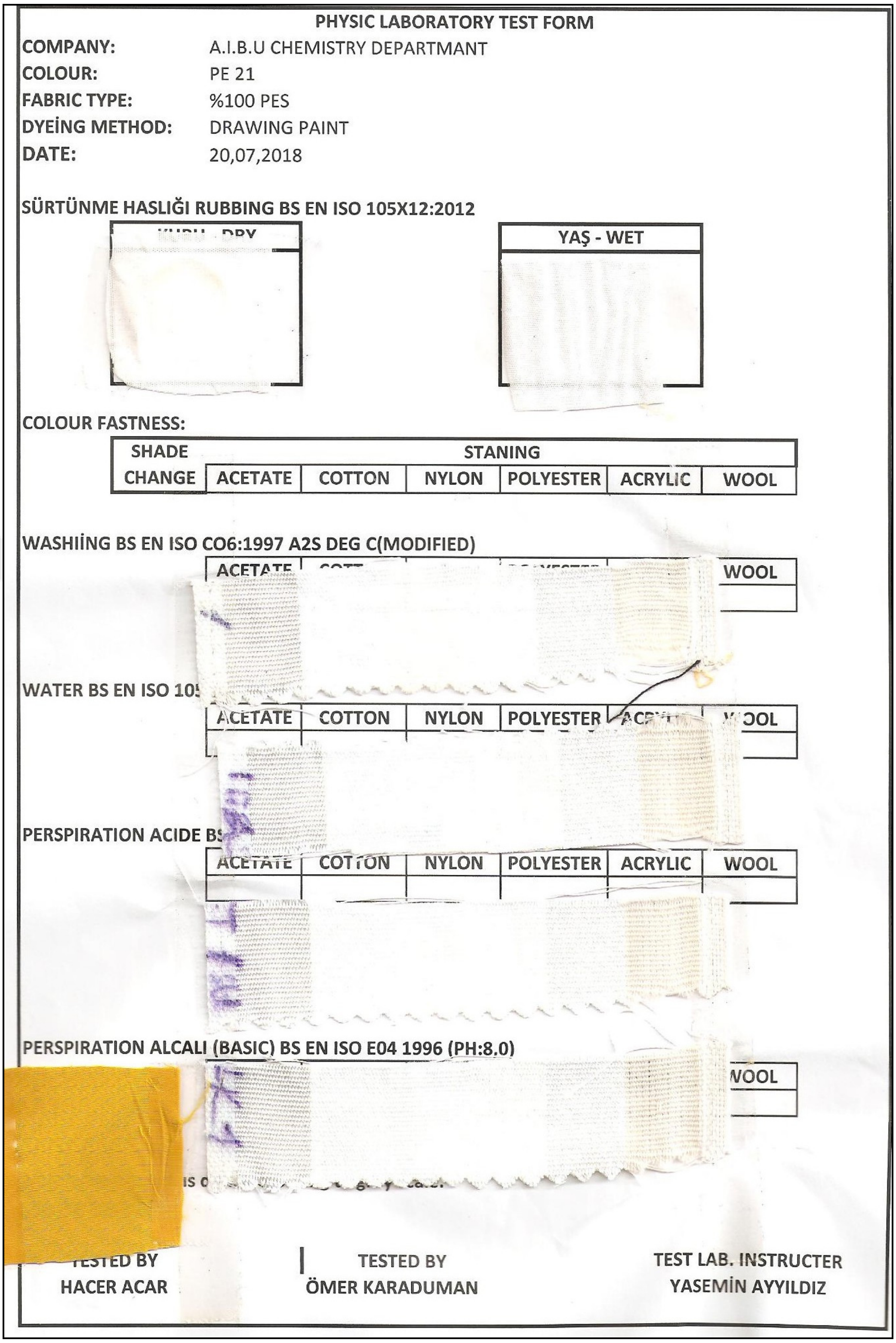
AVAKOZA Textile ERP

**Figure 7.84.** Light and sublimation fastnesses of PE fabric with PE21 dye



PHYSIC LABORATORY TEST FORM

COMPANY: A.I.B.U CHEMISTRY DEPARTMANT
COLOUR: PE 21
FABRIC TYPE: %100 PES
DYEİNG METHOD: DRAWING PAINT
DATE: 20,07,2018

SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012

DRY

YAŞ - WET

COLOUR FASTNESS:

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)

| ACETATE | | | | | WOOL |
|---|---|---|---|---|---|
| | | | | | |

WATER BS EN ISO 10

| ACETATE | COTTON | NYLON | POLYESTER | | |
|---|---|---|---|---|---|
| | | | | | |

PERSPIRATION ACIDE B

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

PERSPIRATION ALCALI (BASIC) BS EN ISO E04 1996 (PH:8.0)

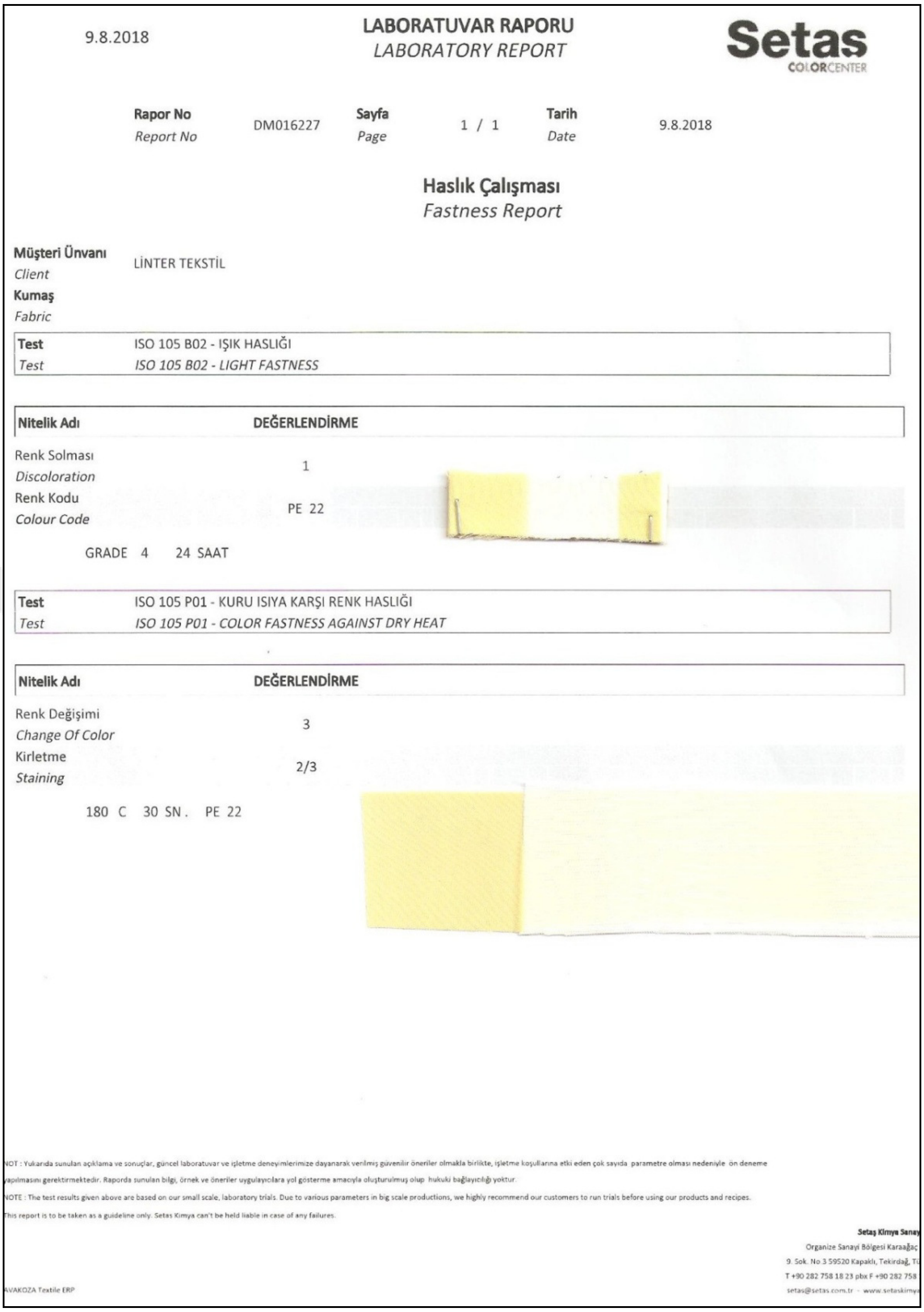
| | | | | | WOOL |
|---|---|---|---|---|---|
| | | | | | |

TESTED BY
HACER ACAR

TESTED BY
ÖMER KARADUMAN

TEST LAB. INSTRUCTER
YASEMİN AYYILDIZ

**Figure 7.85.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE21 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016227 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** / *Client*: LİNTER TEKSTİL
**Kumaş** / *Fabric*:

**Test** ISO 105 B02 - IŞIK HASLIĞI
*Test* *ISO 105 B02 - LIGHT FASTNESS*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 1 |
| Renk Kodu<br>*Colour Code* | PE 22 |

GRADE 4 24 SAAT

**Test** ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI
*Test* *ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3 |
| Kirletme<br>*Staining* | 2/3 |

180 C 30 SN . PE 22

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

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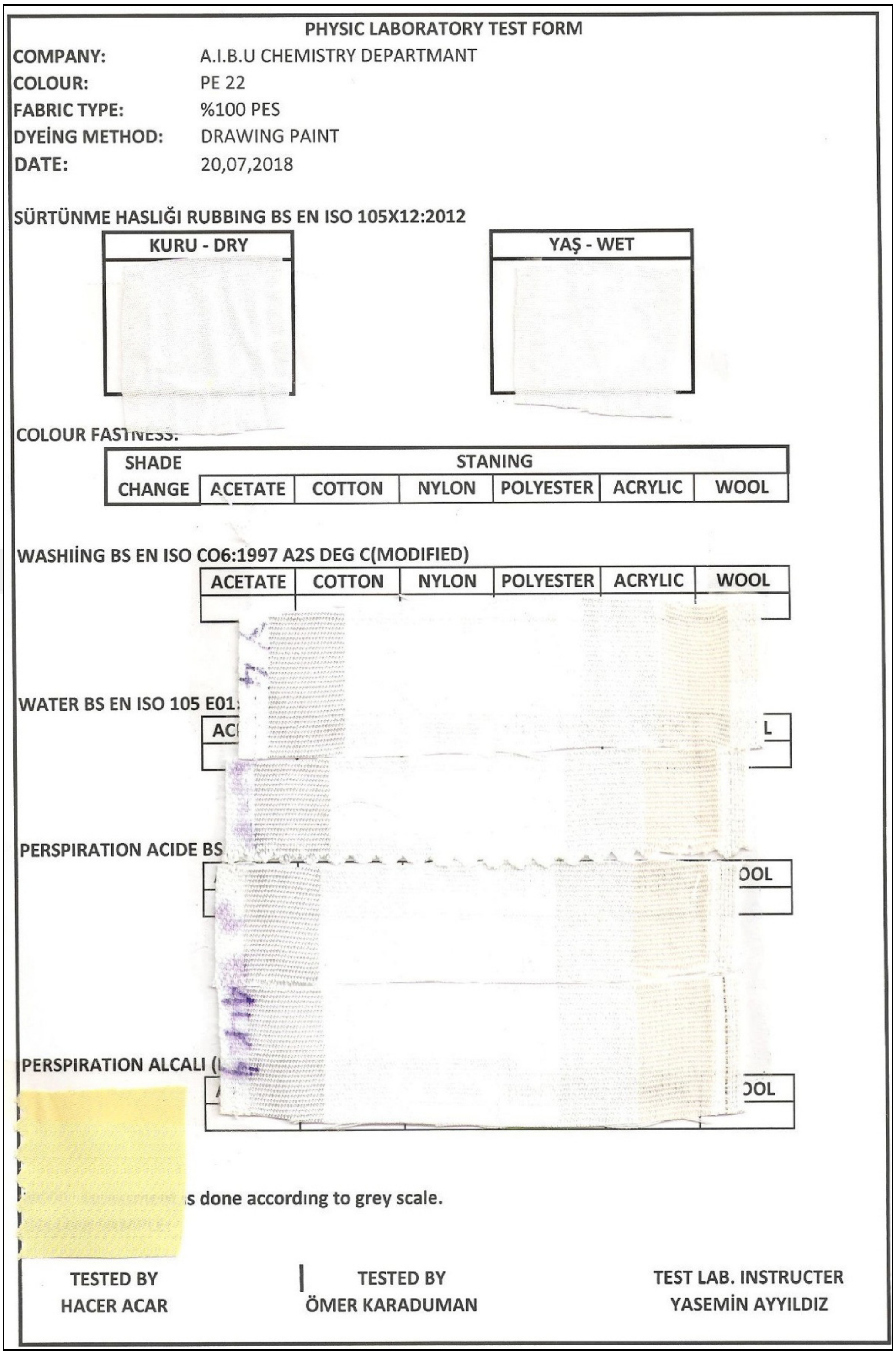
setas@setas.com.tr - www.setaskimya

AVAKOZA Textile ERP

**Figure 7.86.** Light and sublimation fastnesses of PE fabric with PE22 dye



PHYSIC LABORATORY TEST FORM

**COMPANY:** A.I.B.U CHEMISTRY DEPARTMANT
**COLOUR:** PE 22
**FABRIC TYPE:** %100 PES
**DYEİNG METHOD:** DRAWING PAINT
**DATE:** 20,07,2018

**SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012**

| KURU - DRY | YAŞ - WET |
|---|---|

**COLOUR FASTNESS:**

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

**WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**WATER BS EN ISO 105 E01:**

AC L

**PERSPIRATION ACIDE BS**

OOL

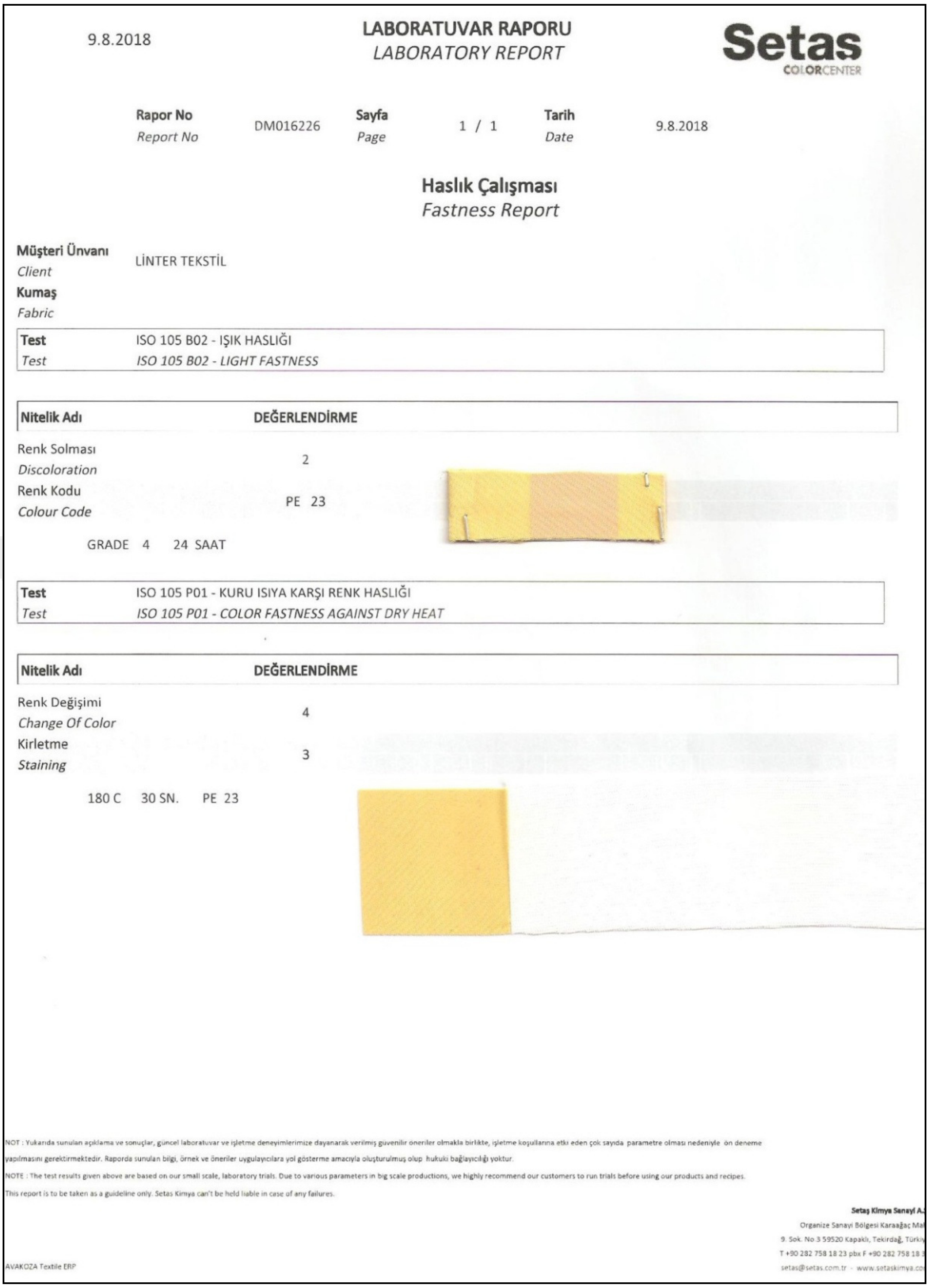
**PERSPIRATION ALCALI (**

OOL

s done according to grey scale.

| TESTED BY<br>HACER ACAR | TESTED BY<br>ÖMER KARADUMAN | TEST LAB. INSTRUCTER<br>YASEMİN AYYILDIZ |
|---|---|---|

**Figure 7.87.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE22 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016226 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

| | |
|---|---|
| **Müşteri Ünvanı**<br>*Client* | LİNTER TEKSTİL |
| **Kumaş**<br>*Fabric* | |

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 2 |
| Renk Kodu<br>*Colour Code* | PE 23 |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 4 |
| Kirletme<br>*Staining* | 3 |

180 C 30 SN. PE 23

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

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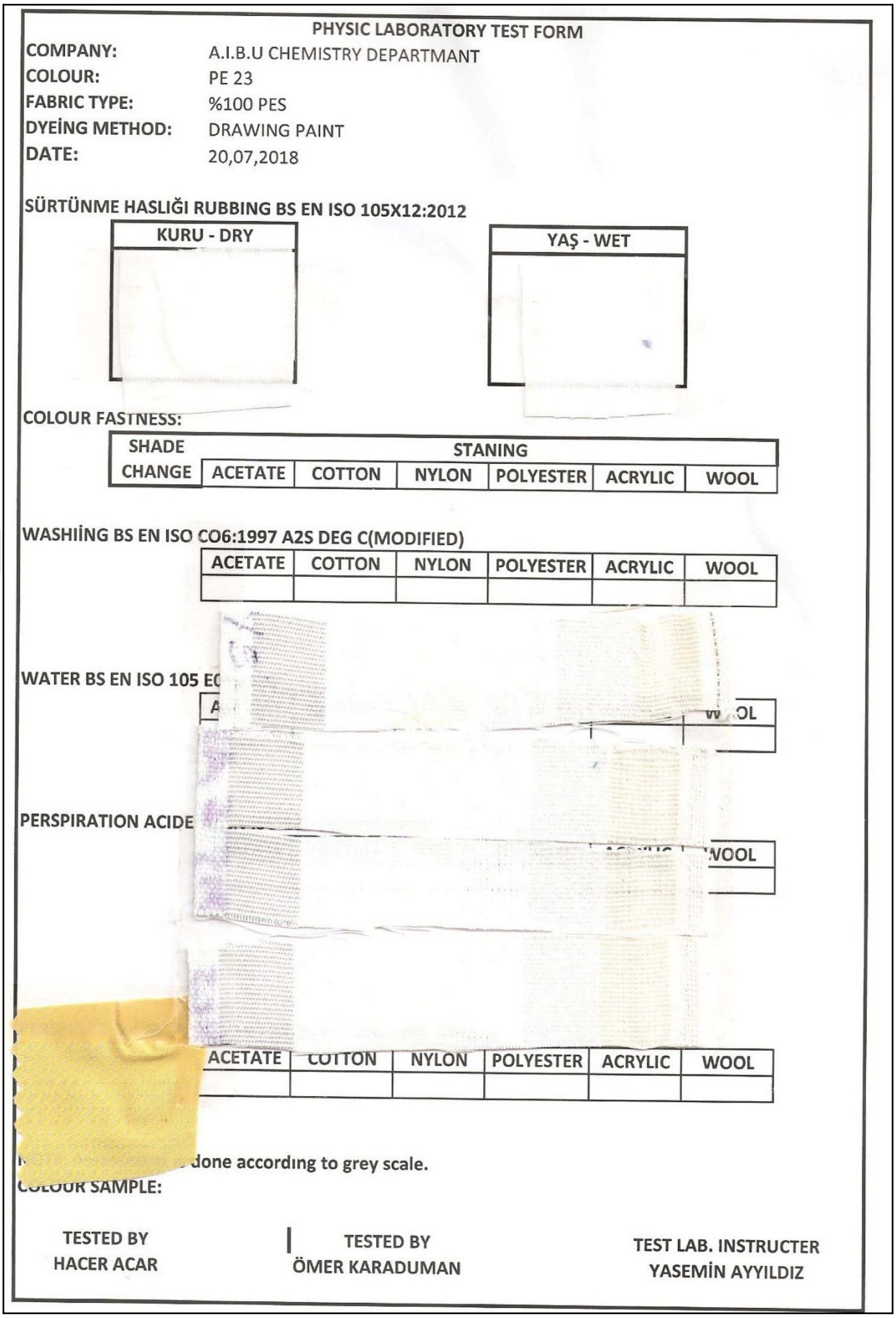
AVAKOZA Textile ERP

Figure 7.88. Light and sublimation fastnesses of PE fabric with PE23 dye



PHYSIC LABORATORY TEST FORM

COMPANY: A.I.B.U CHEMISTRY DEPARTMANT
COLOUR: PE 23
FABRIC TYPE: %100 PES
DYEİNG METHOD: DRAWING PAINT
DATE: 20,07,2018

SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012

KURU - DRY

YAŞ - WET

COLOUR FASTNESS:

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

WATER BS EN ISO 105 E

PERSPIRATION ACIDE

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

done according to grey scale.

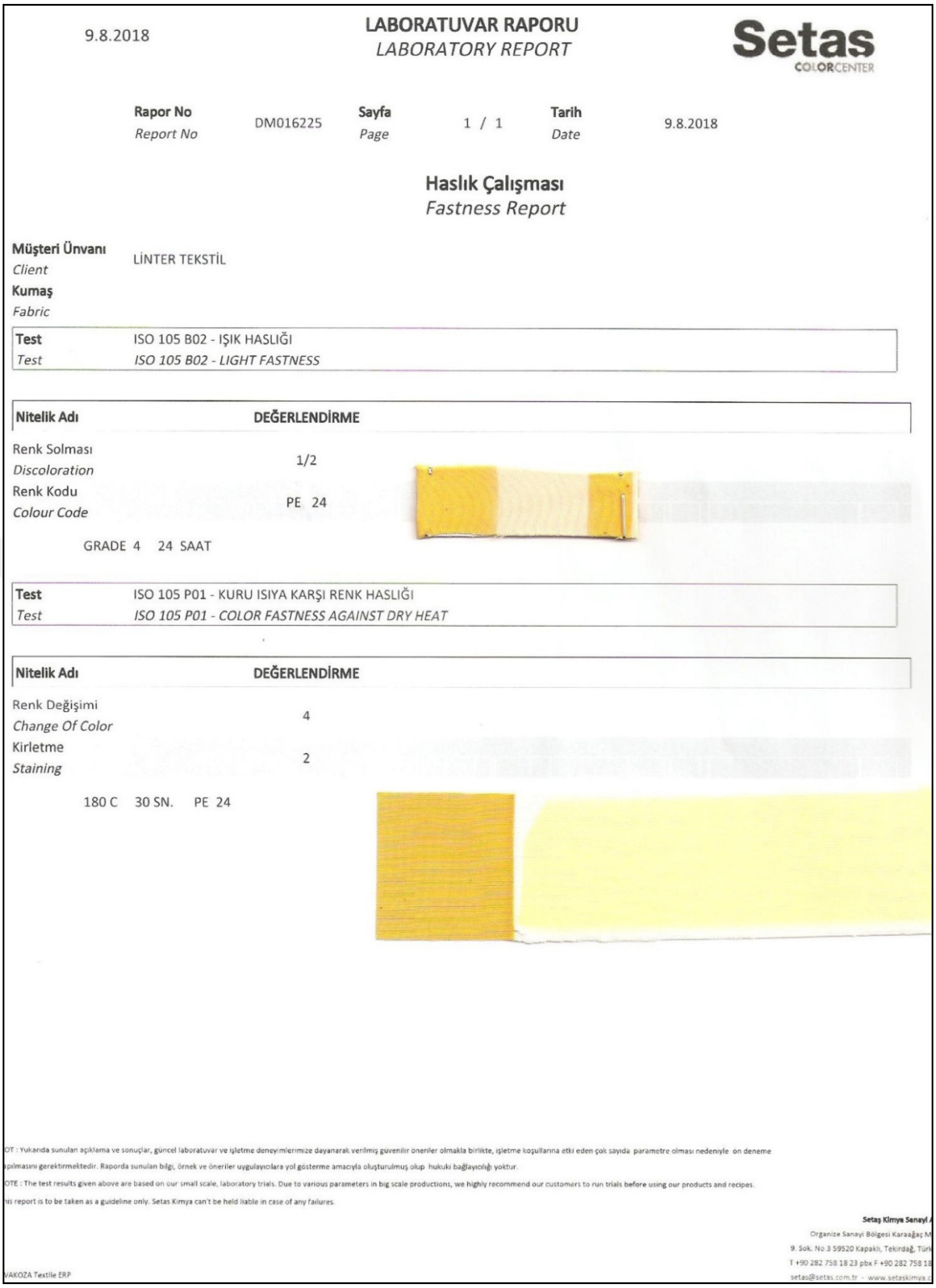
COLOUR SAMPLE:

TESTED BY
HACER ACAR

TESTED BY
ÖMER KARADUMAN

TEST LAB. INSTRUCTER
YASEMİN AYYILDIZ

**Figure 7.89.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE23 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

**Setas**
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016225 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

| | |
|---|---|
| **Müşteri Ünvanı**<br>*Client* | LİNTER TEKSTİL |
| **Kumaş**<br>*Fabric* | |

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 1/2 |
| Renk Kodu<br>*Colour Code* | PE 24 |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 4 |
| Kirletme<br>*Staining* | 2 |

180 C 30 SN. PE 24

OT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle on deneme apılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

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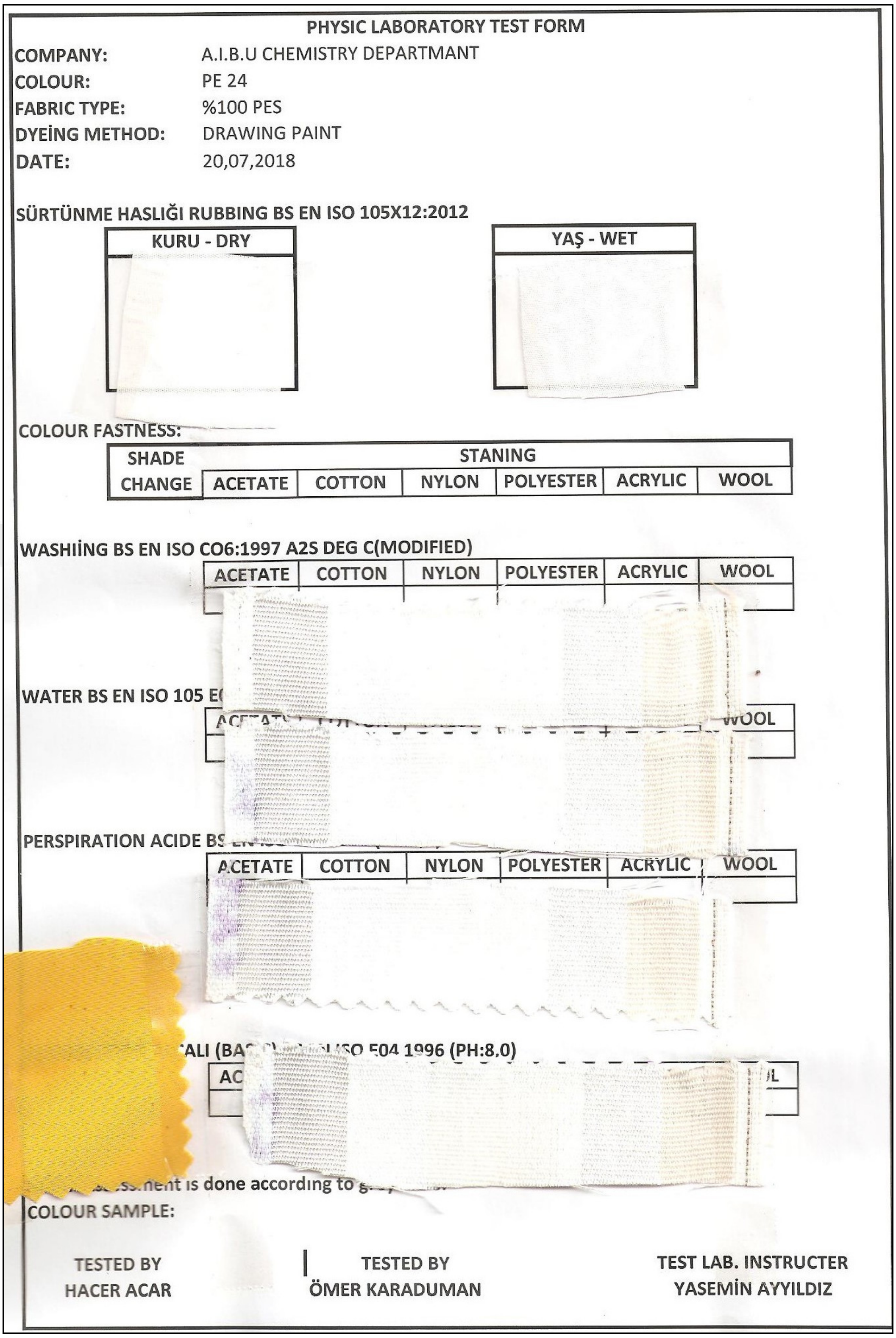
VAKOZA Textile ERP

Figure 7.90. Light and sublimation fastnesses of PE fabric with PE24 dye



PHYSIC LABORATORY TEST FORM

| | |
|---|---|
| COMPANY: | A.I.B.U CHEMISTRY DEPARTMANT |
| COLOUR: | PE 24 |
| FABRIC TYPE: | %100 PES |
| DYEİNG METHOD: | DRAWING PAINT |
| DATE: | 20,07,2018 |

SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012

| KURU - DRY | YAŞ - WET |
|---|---|
| | |

COLOUR FASTNESS:

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

WATER BS EN ISO 105 E

| AC | | | | | WOOL |
|---|---|---|---|---|---|
| | | | | | |

PERSPIRATION ACIDE BS

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

ALI (BA ISO E04 1996 (PH:8,0)

| AC | | | | | L |
|---|---|---|---|---|---|
| | | | | | |

ssment is done according to g

COLOUR SAMPLE:

| TESTED BY | TESTED BY | TEST LAB. INSTRUCTER |
|---|---|---|
| HACER ACAR | ÖMER KARADUMAN | YASEMİN AYYILDIZ |

**Figure 7.91.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE24 dye

9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016224 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** *Client*: LİNTER TEKSTİL
**Kumaş** *Fabric*:

**Test** *Test*: ISO 105 B02 - IŞIK HASLIĞI / *ISO 105 B02 - LIGHT FASTNESS*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 1/2 |
| Renk Kodu<br>*Colour Code* | PE 25 |

GRADE 4 24 SAAT

**Test** *Test*: ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI / *ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3/4 |
| Kirletme<br>*Staining* | 1/2 |

180 C 30 SN. PE 25

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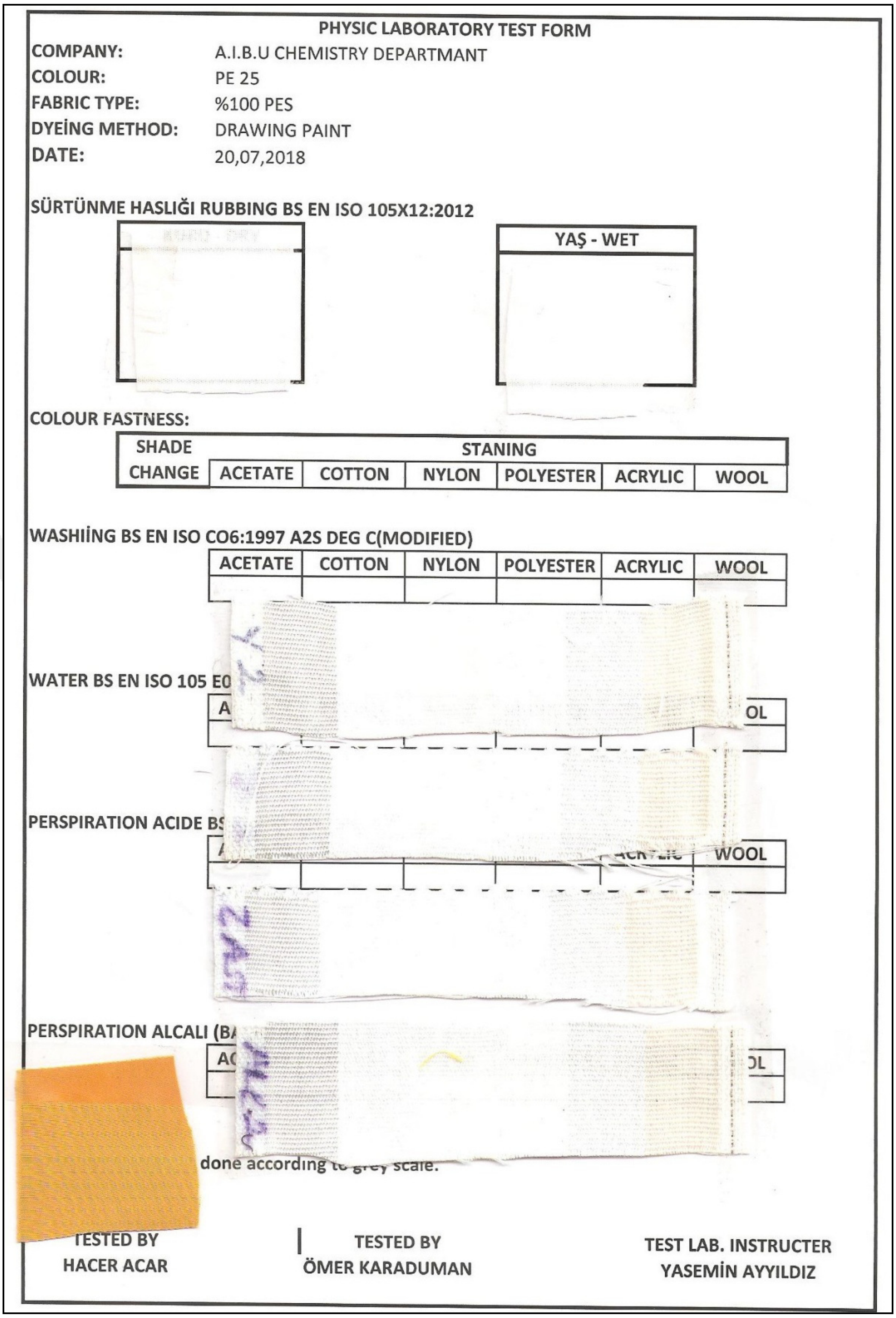
AVAKOZA Textile ERP

**Figure 7.92.** Light and sublimation fastnesses of PE fabric with PE25 dye



PHYSIC LABORATORY TEST FORM

COMPANY: A.I.B.U CHEMISTRY DEPARTMANT
COLOUR: PE 25
FABRIC TYPE: %100 PES
DYEİNG METHOD: DRAWING PAINT
DATE: 20,07,2018

SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012

KURU - DRY

YAŞ - WET

COLOUR FASTNESS:

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

WATER BS EN ISO 105 E0

PERSPIRATION ACIDE BS

PERSPIRATION ALCALI (BA

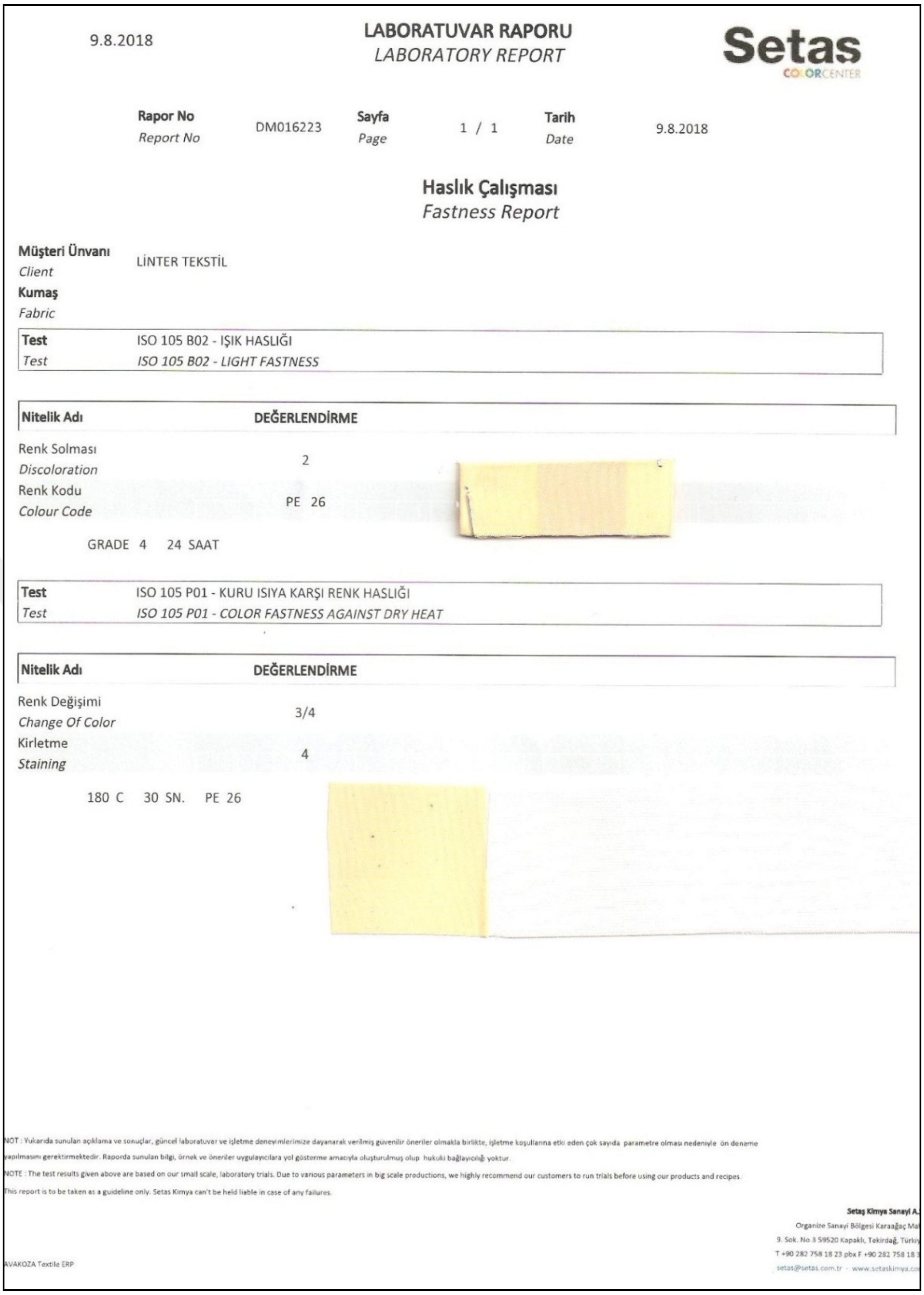
done according to grey scale.

TESTED BY
HACER ACAR

TESTED BY
ÖMER KARADUMAN

TEST LAB. INSTRUCTER
YASEMİN AYYILDIZ

**Figure 7.93.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE25 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

**Rapor No** *Report No* DM016223 **Sayfa** *Page* 1 / 1 **Tarih** *Date* 9.8.2018

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** *Client* LİNTER TEKSTİL
**Kumaş** *Fabric*

**Test** ISO 105 B02 - IŞIK HASLIĞI
*Test* *ISO 105 B02 - LIGHT FASTNESS*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 2 |
| Renk Kodu<br>*Colour Code* | PE 26 |

GRADE 4 24 SAAT

**Test** ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI
*Test* *ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT*

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3/4 |
| Kirletme<br>*Staining* | 4 |

180 C 30 SN. PE 26

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

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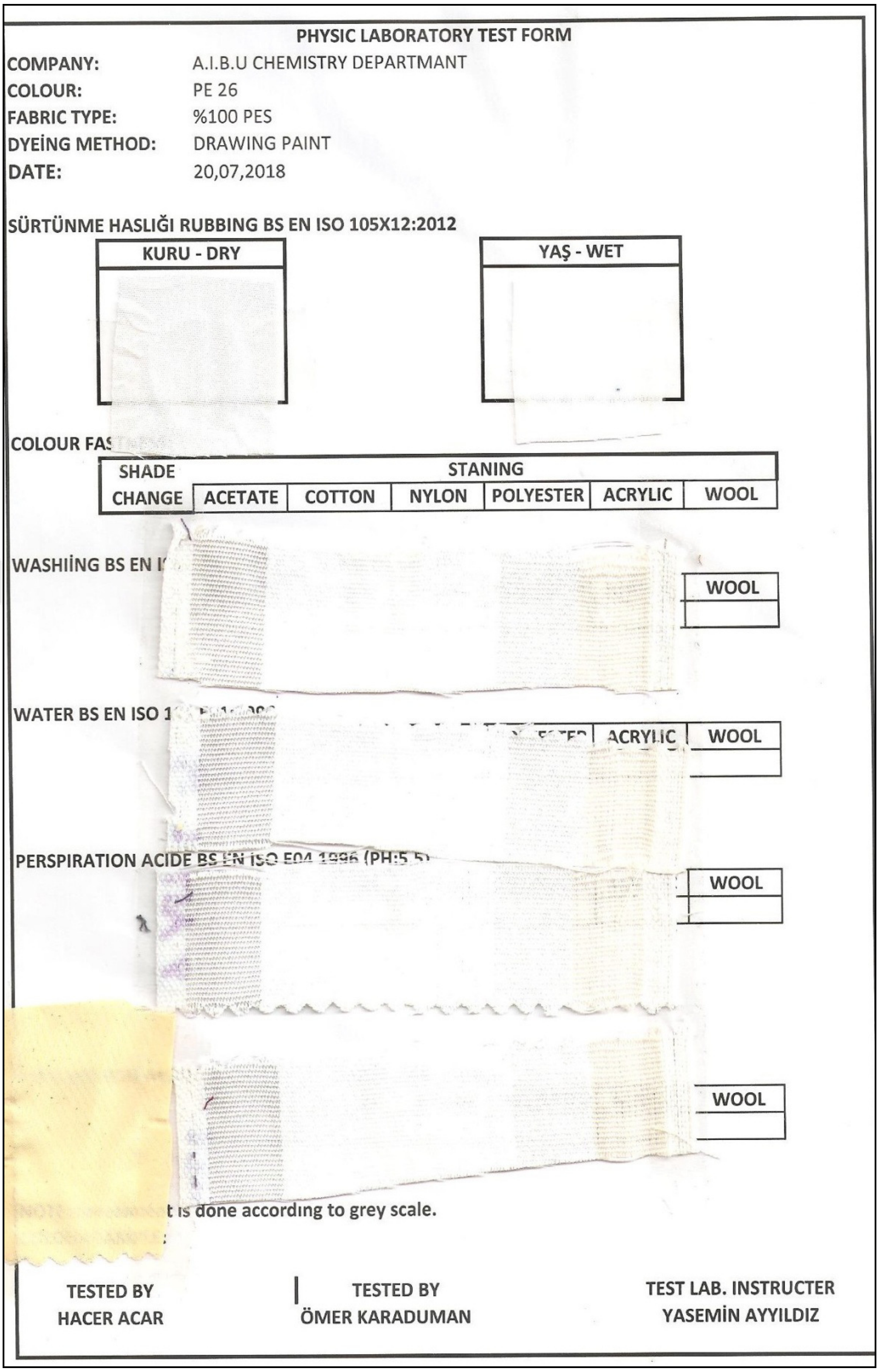
AVAKOZA Textile ERP

**Figure 7.94.** Light and sublimation fastnesses of PE fabric with PE26 dye



PHYSIC LABORATORY TEST FORM

| | |
|---|---|
| COMPANY: | A.I.B.U CHEMISTRY DEPARTMANT |
| COLOUR: | PE 26 |
| FABRIC TYPE: | %100 PES |
| DYEİNG METHOD: | DRAWING PAINT |
| DATE: | 20,07,2018 |

SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012

| KURU - DRY | YAŞ - WET |
|---|---|
| | |

COLOUR FAS

| SHADE | STANING | | | | | |
|---|---|---|---|---|---|---|
| CHANGE | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

WASHIİNG BS EN I

WOOL

WATER BS EN ISO 1

ACRYLIC
WOOL

PERSPIRATION ACIDE BS EN ISO E04 1996 (PH:5 5)

WOOL

WOOL

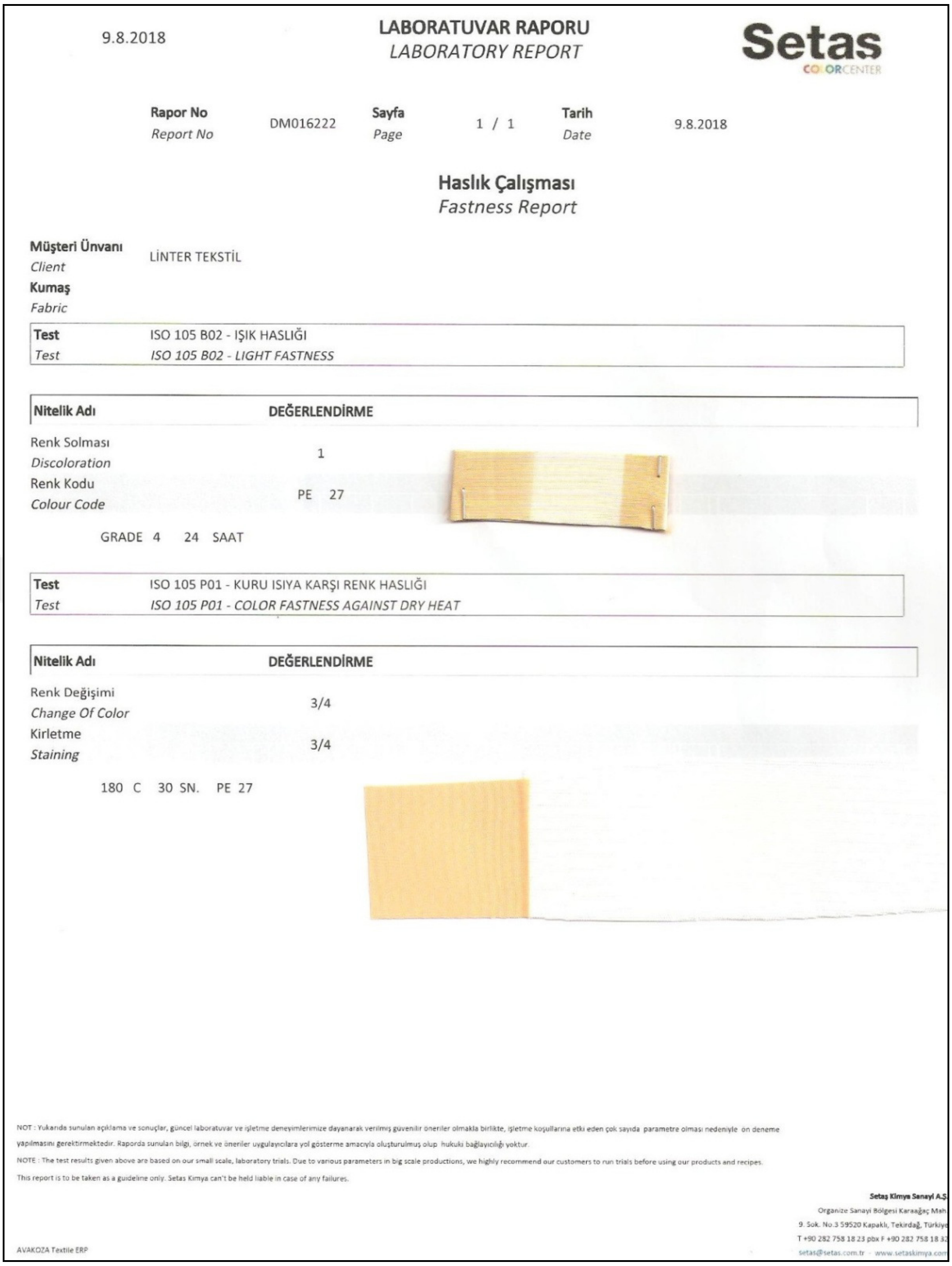
t is done according to grey scale.

TESTED BY
HACER ACAR

TESTED BY
ÖMER KARADUMAN

TEST LAB. INSTRUCTER
YASEMİN AYYILDIZ

**Figure 7.95.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE26 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016222 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** *Client*: LİNTER TEKSTİL
**Kumaş** *Fabric*:

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 1 |
| Renk Kodu<br>*Colour Code* | PE 27 |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3/4 |
| Kirletme<br>*Staining* | 3/4 |

180 C 30 SN. PE 27

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

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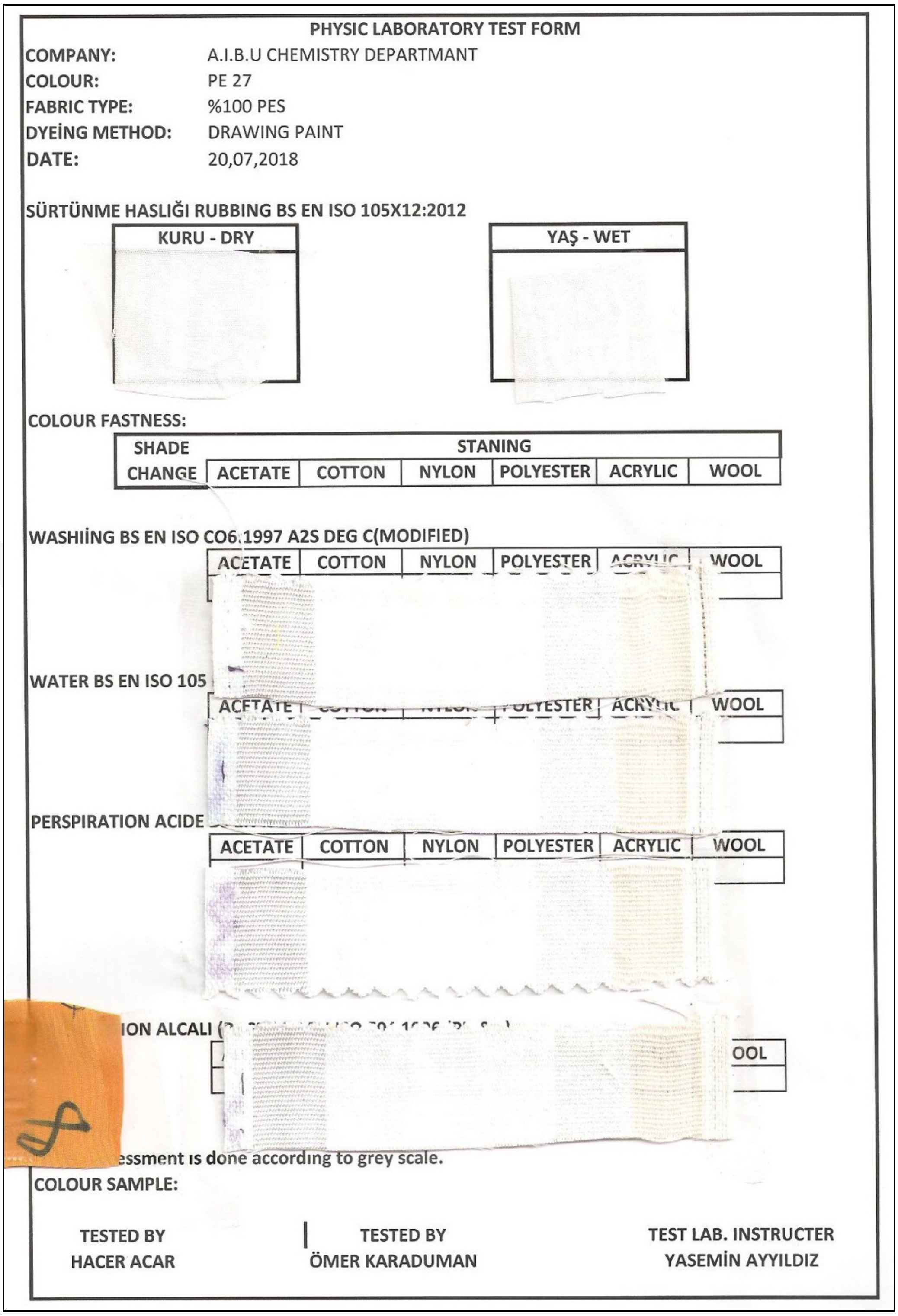
AVAKOZA Textile ERP

Figure 7.96. Light and sublimation fastnesses of PE fabric with PE27 dye



PHYSIC LABORATORY TEST FORM

**COMPANY:** A.I.B.U CHEMISTRY DEPARTMANT
**COLOUR:** PE 27
**FABRIC TYPE:** %100 PES
**DYEİNG METHOD:** DRAWING PAINT
**DATE:** 20,07,2018

**SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012**

| KURU - DRY | YAŞ - WET |
|---|---|
| | |

**COLOUR FASTNESS:**

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

**WASHIİNG BS EN ISO CO6.1997 A2S DEG C(MODIFIED)**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**WATER BS EN ISO 105**

| ACETATE | | | OLYESTER | ACRY | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**PERSPIRATION ACIDE**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

**ION ALCALI (**

| | | | | | OOL |
|---|---|---|---|---|---|
| | | | | | |

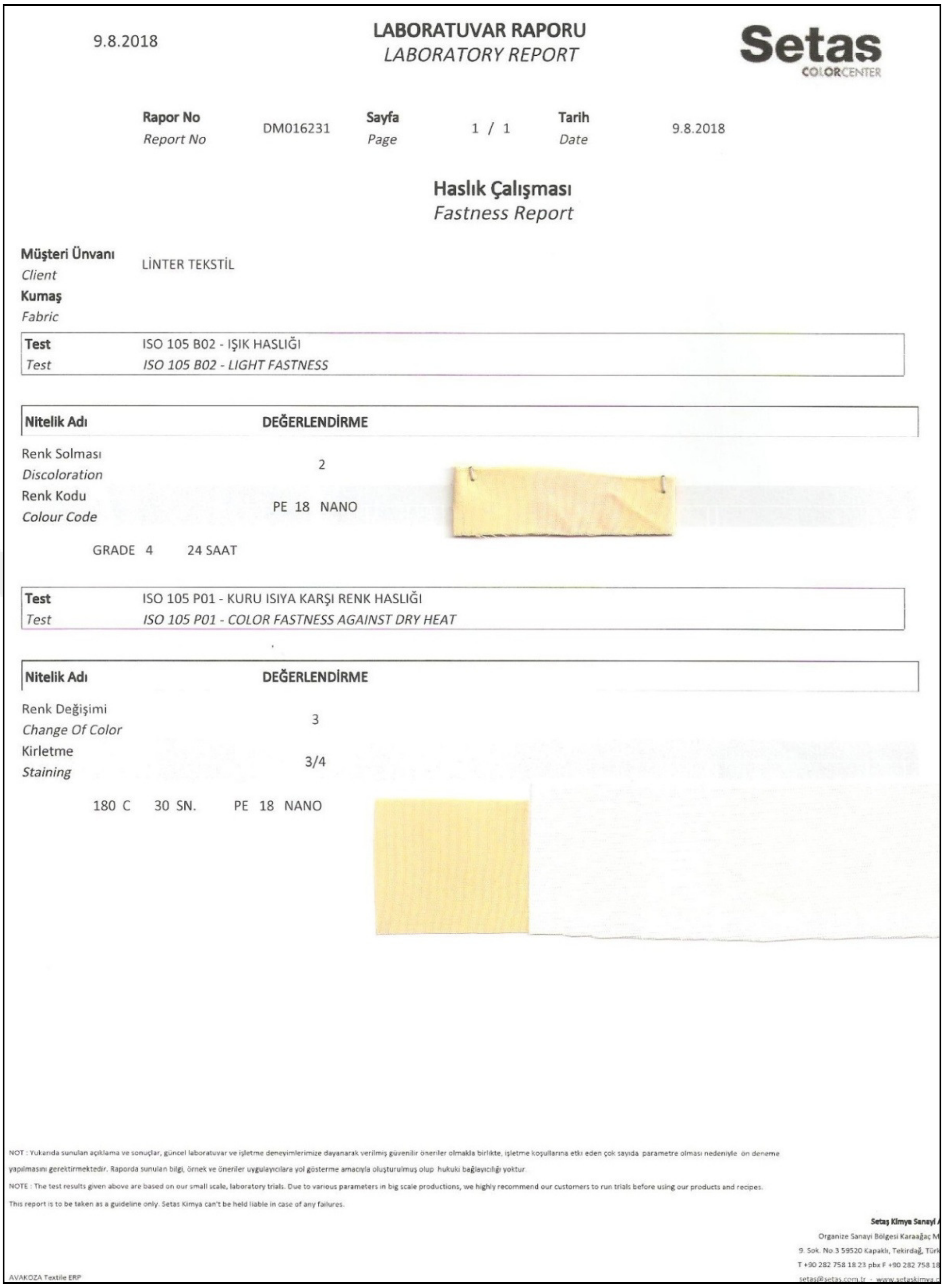
8

essment is done according to grey scale.

**COLOUR SAMPLE:**

| TESTED BY | TESTED BY | TEST LAB. INSTRUCTER |
|---|---|---|
| HACER ACAR | ÖMER KARADUMAN | YASEMİN AYYILDIZ |

**Figure 7.97.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE27 dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016231 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** *Client*: LİNTER TEKSTİL
**Kumaş** *Fabric*:

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 2 |
| Renk Kodu<br>*Colour Code* | PE 18 NANO |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3 |
| Kirletme<br>*Staining* | 3/4 |

180 C 30 SN. PE 18 NANO

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

NOTE : The test results given above are based on our small scale, laboratory trials. Due to various parameters in big scale productions, we highly recommend our customers to run trials before using our products and recipes.

This report is to be taken as a guideline only. Setas Kimya can't be held liable in case of any failures.

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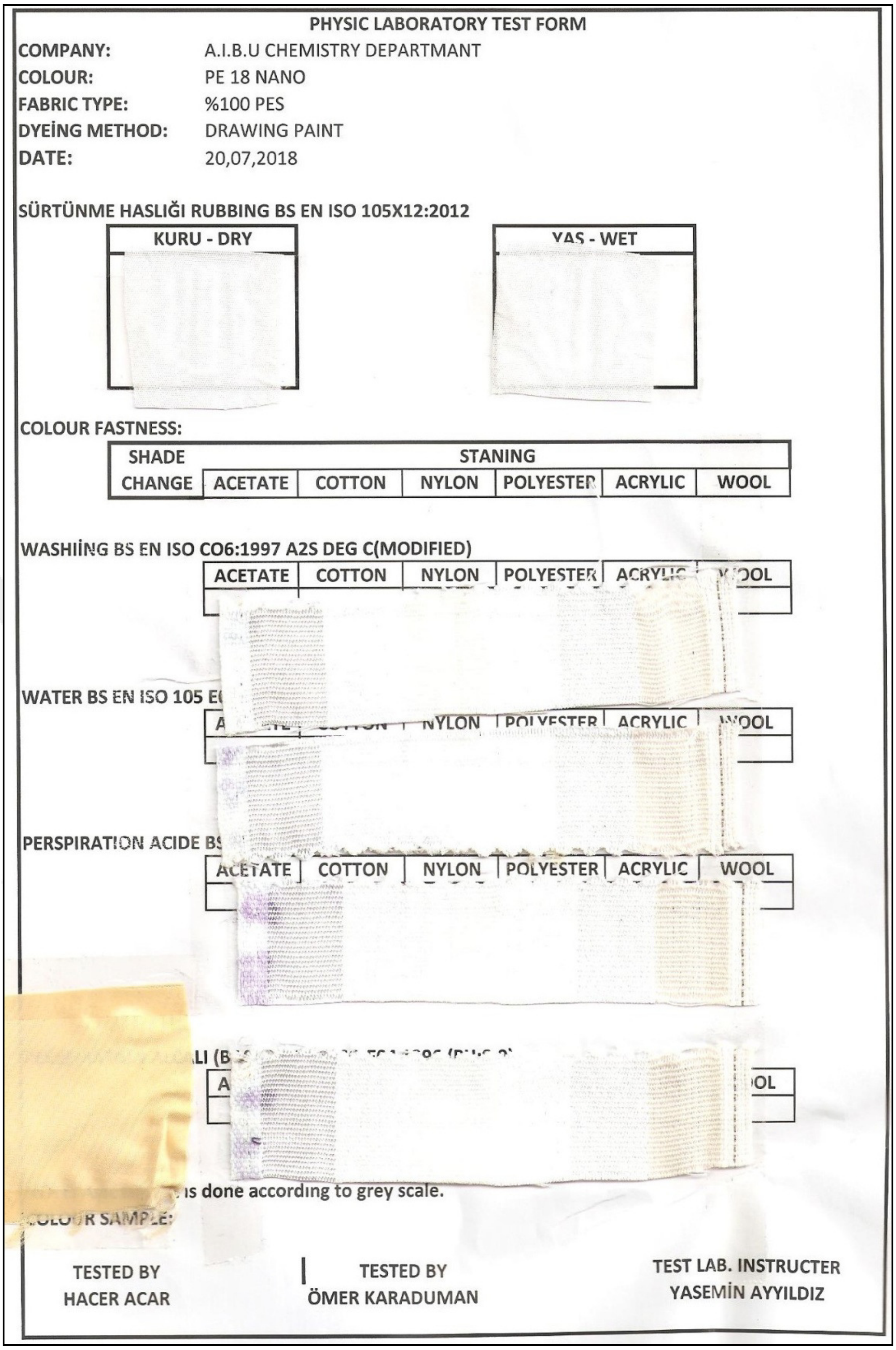
setas@setas.com.tr - www.setaskimya.

AVAKOZA Textile ERP

Figure 7.98. Light and sublimation fastnesses of PE fabric with PE18nano dye



**PHYSIC LABORATORY TEST FORM**

**COMPANY:** A.I.B.U CHEMISTRY DEPARTMANT
**COLOUR:** PE 18 NANO
**FABRIC TYPE:** %100 PES
**DYEİNG METHOD:** DRAWING PAINT
**DATE:** 20,07,2018

**SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012**

| KURU - DRY | YAS - WET |
|---|---|

**COLOUR FASTNESS:**

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

**WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|

**WATER BS EN ISO 105 E**

| A | | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|

**PERSPIRATION ACIDE BS**

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|

**LI (B**

| A | | | | | OL |
|---|---|---|---|---|---|

is done according to grey scale.

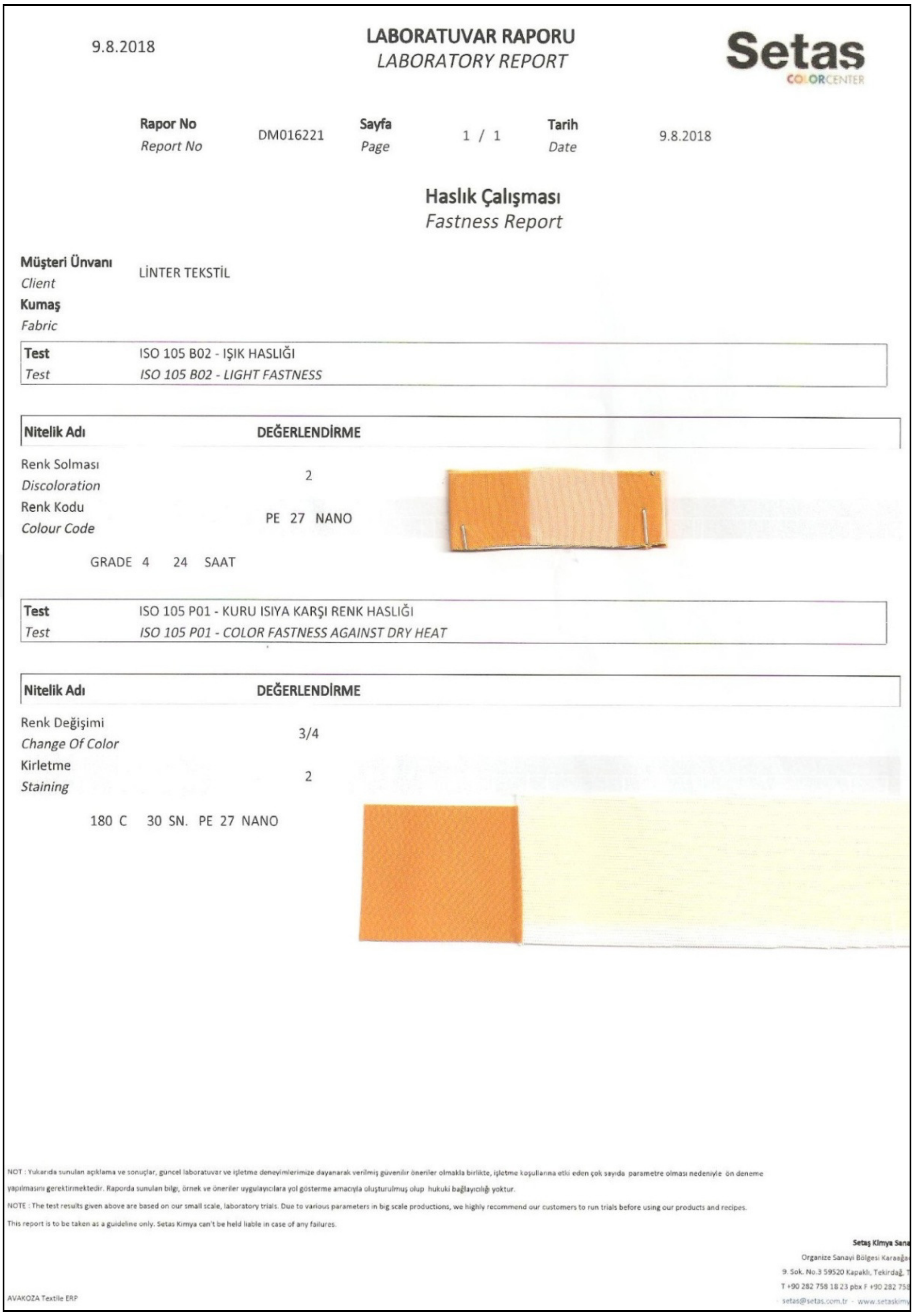
**OLOUR SAMPLE:**

**TESTED BY**
**HACER ACAR**

**TESTED BY**
**ÖMER KARADUMAN**

**TEST LAB. INSTRUCTER**
**YASEMİN AYYILDIZ**

**Figure 7.99.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE18nano dye



9.8.2018

**LABORATUVAR RAPORU**
*LABORATORY REPORT*

Setas
COLORCENTER

| | | | | | |
|---|---|---|---|---|---|
| **Rapor No**<br>*Report No* | DM016221 | **Sayfa**<br>*Page* | 1 / 1 | **Tarih**<br>*Date* | 9.8.2018 |

**Haslık Çalışması**
*Fastness Report*

**Müşteri Ünvanı** *Client*: LİNTER TEKSTİL

**Kumaş** *Fabric*

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 B02 - IŞIK HASLIĞI<br>*ISO 105 B02 - LIGHT FASTNESS* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Solması<br>*Discoloration* | 2 |
| Renk Kodu<br>*Colour Code* | PE 27 NANO |

GRADE 4 24 SAAT

| | |
|---|---|
| **Test**<br>*Test* | ISO 105 P01 - KURU ISIYA KARŞI RENK HASLIĞI<br>*ISO 105 P01 - COLOR FASTNESS AGAINST DRY HEAT* |

| **Nitelik Adı** | **DEĞERLENDİRME** |
|---|---|
| Renk Değişimi<br>*Change Of Color* | 3/4 |
| Kirletme<br>*Staining* | 2 |

180 C 30 SN. PE 27 NANO

NOT : Yukarıda sunulan açıklama ve sonuçlar, güncel laboratuvar ve işletme deneyimlerimize dayanarak verilmiş güvenilir öneriler olmakla birlikte, işletme koşullarına etki eden çok sayıda parametre olması nedeniyle ön deneme yapılmasını gerektirmektedir. Raporda sunulan bilgi, örnek ve öneriler uygulayıcılara yol gösterme amacıyla oluşturulmuş olup hukuki bağlayıcılığı yoktur.

NOTE : The test results given above are based on our small scale, laboratory trials. Due to various parameters in big scale productions, we highly recommend our customers to run trials before using our products and recipes.

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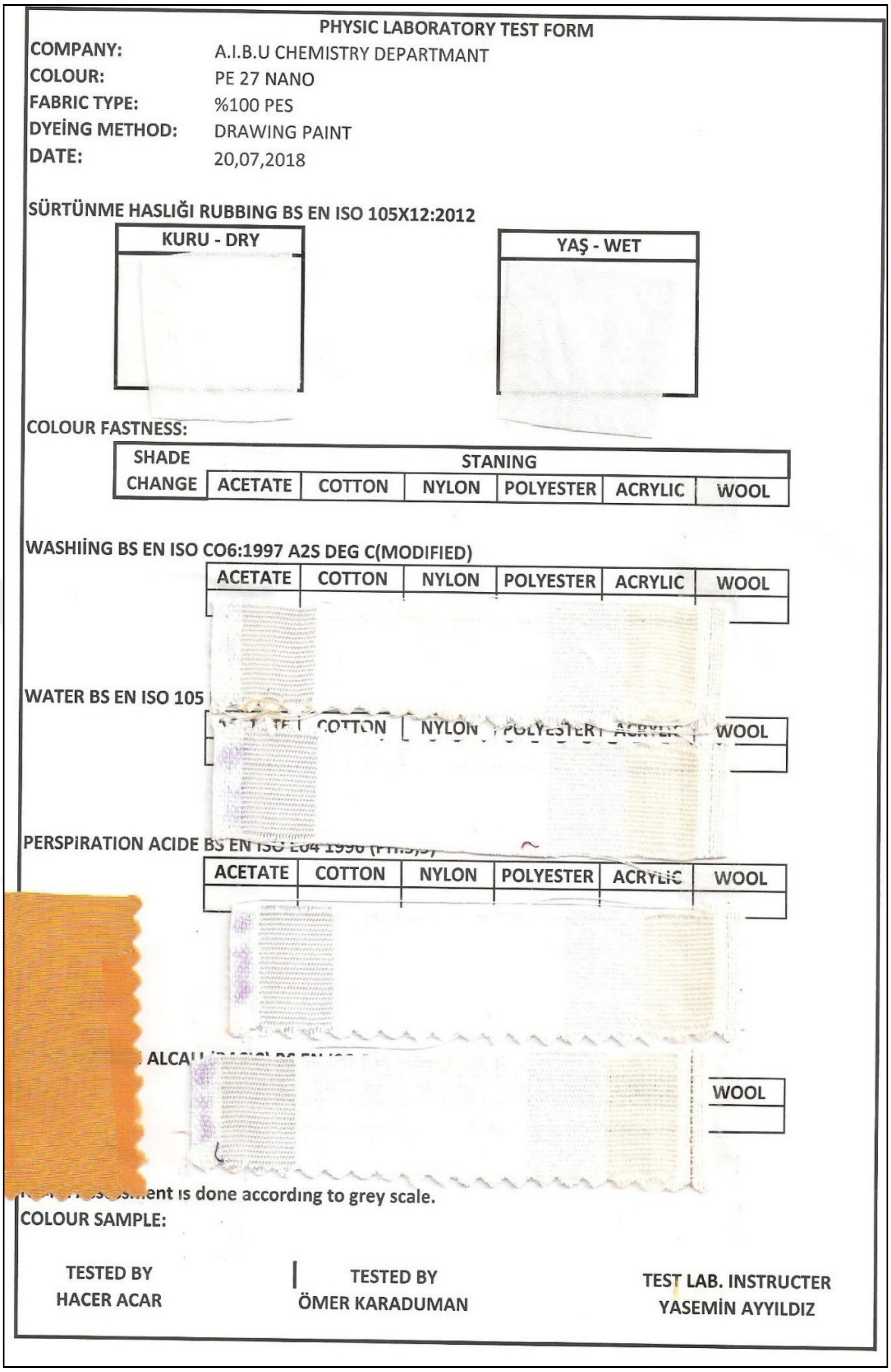
AVAKOZA Textile ERP

**Figure 7.100.** Light and sublimation fastnesses of PE fabric with PE27nano dye



PHYSIC LABORATORY TEST FORM

COMPANY: A.I.B.U CHEMISTRY DEPARTMANT
COLOUR: PE 27 NANO
FABRIC TYPE: %100 PES
DYEİNG METHOD: DRAWING PAINT
DATE: 20,07,2018

SÜRTÜNME HASLIĞI RUBBING BS EN ISO 105X12:2012

| KURU - DRY | YAŞ - WET |
|---|---|
| | |

COLOUR FASTNESS:

| SHADE CHANGE | STANING | | | | | |
|---|---|---|---|---|---|---|
| | ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |

WASHIİNG BS EN ISO CO6:1997 A2S DEG C(MODIFIED)

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

WATER BS EN ISO 105

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

PERSPIRATION ACIDE BS EN ISO E04 1996 (PH:5,5)

| ACETATE | COTTON | NYLON | POLYESTER | ACRYLIC | WOOL |
|---|---|---|---|---|---|
| | | | | | |

ALCALI (BASIC) BS EN ISO

| WOOL |
|---|
| |

ment is done according to grey scale.

COLOUR SAMPLE:

TESTED BY
HACER ACAR

TESTED BY
ÖMER KARADUMAN

TEST LAB. INSTRUCTER
YASEMİN AYYILDIZ

**Figure 7.101.** Washing, water, acidic-basic perspiration, rubbing fastnesses of PE fabric with PE27nano dye

# 8. CURRICULUM VITAE

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**Place and Date of Birth** **:** Çorum / 19.09.1977

**Bachelor's Degree** **:** 2000 **-** Karadeniz Teknik Üniversitesi

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