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Research Article

Synthesis and Characterization of Some New Esters Containing Heterocyclic and Derived From Azo Dyes

Zena. G. Alrecabi, Zainab Amer, Naeemah Al-Lami

Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.

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ABSTRACT
This study including prepared new colored esters containing heterocyclic with high molecular weights. In the first part of work we synthesized azo dyes [1,2] from the reaction p-toluidine with β-naphthol and o-nitro phenol, thin we synthesized Schiff bases [3,4] by the reaction anthranilic acid with benzaldehyde and dimethyl benzaldehyde. The reaction azo dyes (contain OH group) with Schiff base (contain COOH group) these led to produce the new colored esters [A_1-A_4]. The second part of work was modification the (C=N-) group in esters to heterocyclic compounds by reacting with phenyl iso cyanide to produce new β-lactam [B_1-B_4] and with anthranilic acid to get new hydroquinazoline [C_1-C_4]. All these compounds were characterized by physical properties and spectral methods FTIR, ^{1}H-NMR and ^{13}C-NMR.

Keywords: azo dyes, Schiff bases, esters, β-lactam, hydroquinazoline.

INTRODUCTION

Azo compounds are the most common prepared colorings used in pharmaceuticals, cosmetics and food. Although they have been used in this way for along time[1]. Aromatic azo compounds are formed by coupling reaction between diazonium salt and activated aromatic rings containing OH or NH_2 groups[2]. If the azo dye produce from the reaction with phenol there is a chance to enter in other reactions led to esters formation. The OH group of azo reacted with carboxylic acid, if the carboxylic acid was substituted by amino group (anthranilic acid), the amino group can be converted to imine (C=N) group when reacted with the carbonyl of aldehyde[3]. From this active group we can get many types of heterocyclic compounds which reported as a common medicinal and biochemical activities[4]. Among these types of heterocyclic the four membered rings and six membered rings containing nitrogen atom have been studied more than contain other elements[5]. The four membered rings are derived from azacyclobutadiene. There are a large number of synthetic derivatives with additional important applications and many are valuable intermediates in synthesis[6]. On the other hand six membered rings containing two nitrogen atom are derived from quinazoline which received its name from being an aza derivative of quinoline substituted derivatives have been synthesized for medicinal purposes such as antimalarial and anticancer agent[7,8].

MATERIALS AND METHODS

Experimental part

Preparation of azo compounds[9] [1,2]

Dissolve (0.02 mole) from p- toluidine in (8 ml) of 10% hydrochloric acid and cooling the solution to $0C^0$. Added this solution to (0.02 mole) of sodium nitrate in (8 ml) of water drop by drop in ice bath. Pour the resulting mixture (diazonuim salt) in ice bath to third solution containing (0.02 mole) of phenol in basic solution of 10% NaOH. The addition should be graudly with keeping low temperature. The resulting product is red to orange precipitate of azo compounds [1,2] and recrystallised from water.

Preparation of Schiff bases[10] [3,4]

To a stirred solution of benzaldehyde or dimethyl benzaldehyde (0.03 mole) in methanol (12 ml) added (2-4) drops of glacial acetic acid. Anthanilic acid (0.03 mole) in (7 ml) of methanol was slowly added and mixture was refluxed in water bath for (4 hrs.) after complete of reaction removing the excess of solvent and cooling the residue until precipitate the product and recrystallised from ethanol.

Preparation of esters[11] [A_1-A_4]

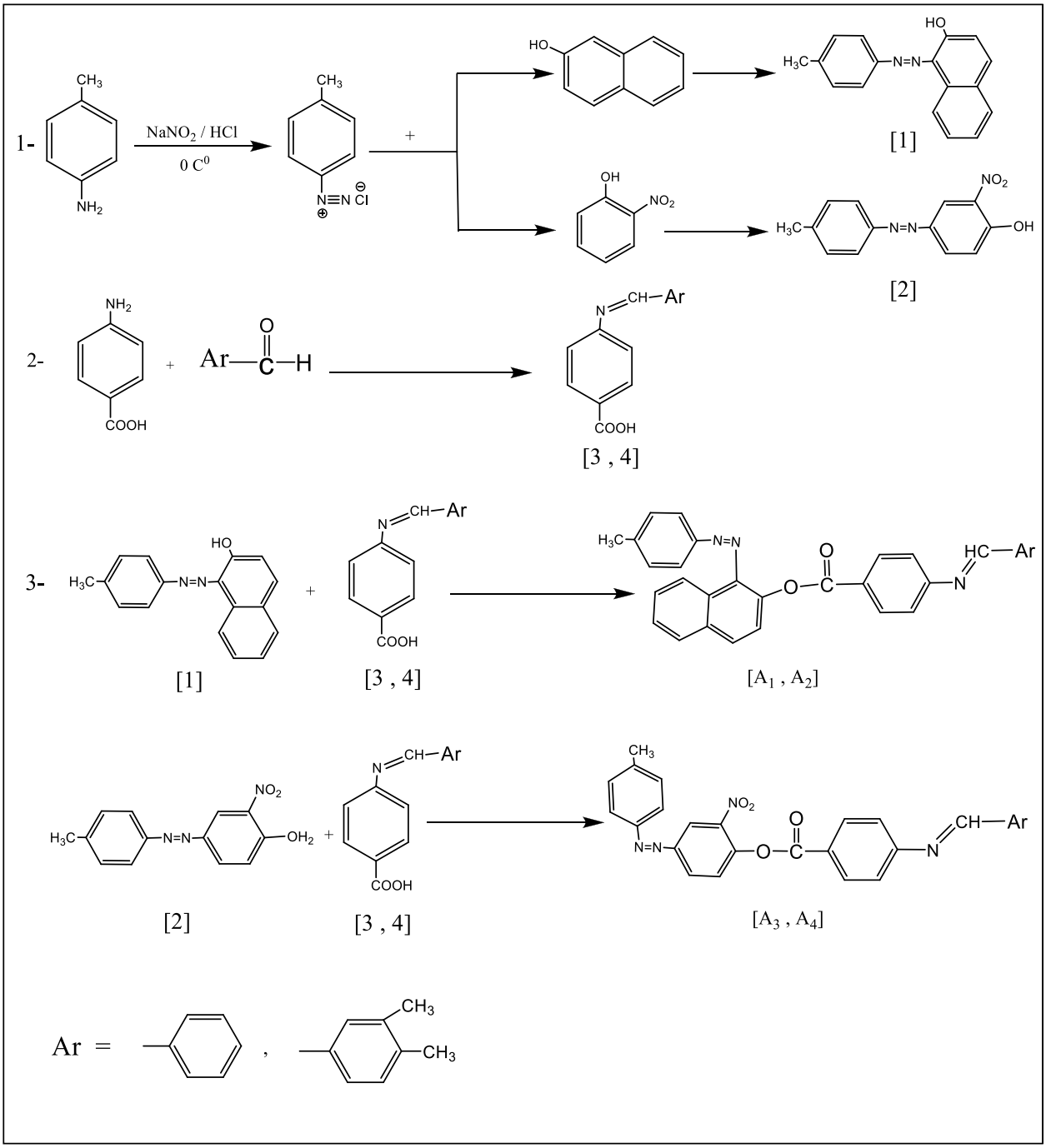
A solution of equimolar of azo compounds [1,2] and Schiff bases substituted anthanilic acid [3,4] in absolute ethanol were heated under reflux with adding a few drops of concentrated sulfuric acid. The period of reflux (5-6) hrs. after that evaporating the excess of solvent and cooling the residue to get colored esters.

Preparation of beta-lactam derivatives of esters[12] [B_1-B_4]

(0.02 mole) of esters containing Schiff bases group [A_1-A_4] was dissolved in (10 ml) of DMF. Equimolar of phenyl iso cyanide was addae drop by drop to solution which heated under reflux for (6 hrs.). The excess of solvent was removed under reduced pressure and the residue cooled in ice bath until the precipitate formed.

Preparation of hydroquinazoline derivatives of esters[13] [C_1-C_4]

**Author for Correspondence: zainabamer34@yahoo.com*



Scheme (1) structure of synthesized compounds [A_1 – A_4]

Dissolved of 2-amino benzoic acid (0.02 mole) in dioxane (10 ml) was added to the ester which contain Schiff bases (0.02 mole) with a few drops of DMF. This solution was heated under reflux for (16 hrs.) The solvent was removed under reduced pressure and neutralized the remains with 10% of sodium bicarbonate, filter the precipitate and recrystallised from mthanol.

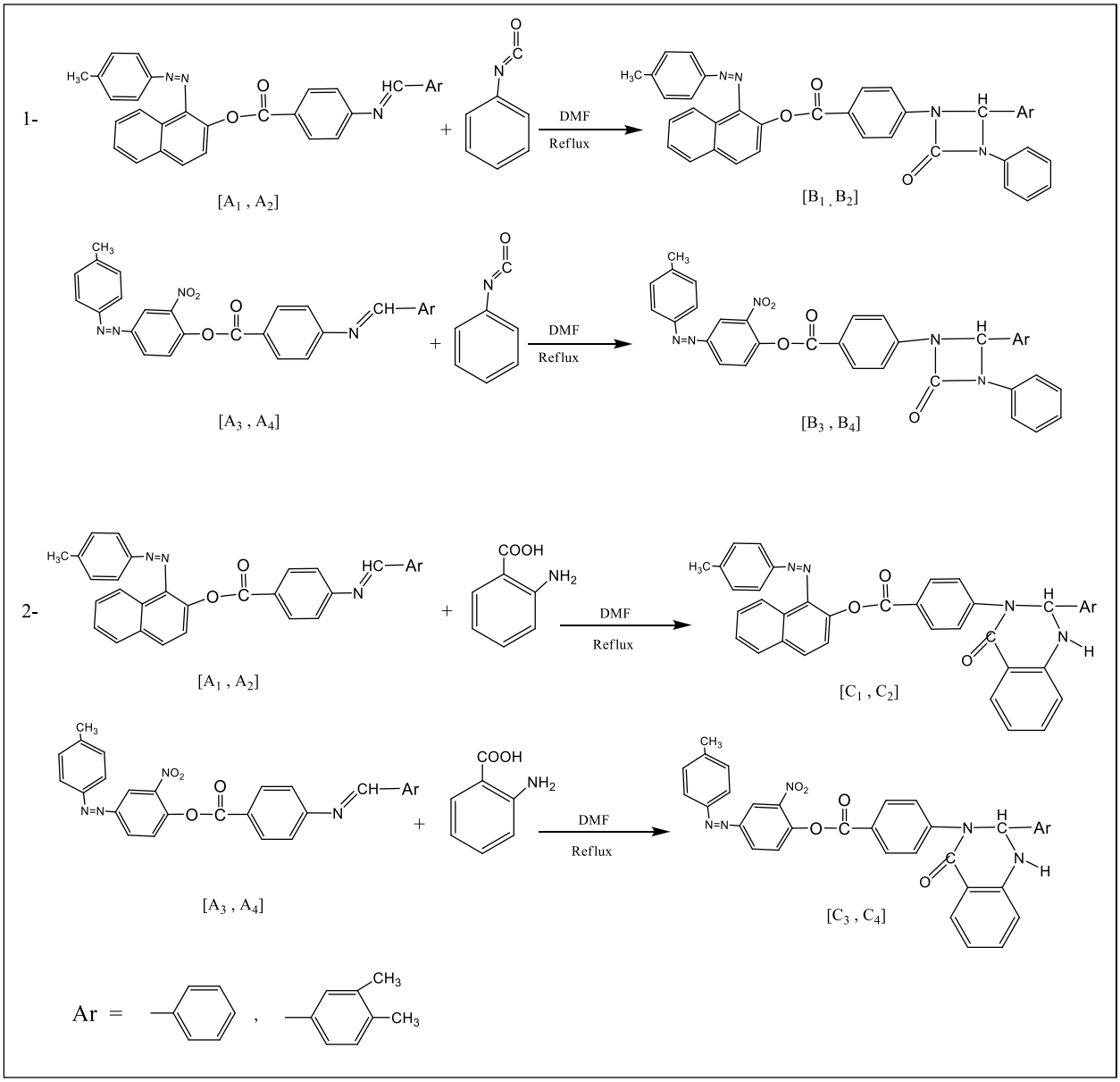
All the physical properties were listed in table (1).

RESULTS AND DISCUSSION

In this study including prepared new colored esters containing heterocyclic with azo group. In the first part of work we synthesized azo dyes [1,2] from the reaction p-toluidine with β-naphthol and o-nitro phenol, thin we synthesized Schiff bases [3,4] by the reaction anthranilic acid with benzaldehyde and dimethyl benzaldehyde. The reaction azo dyes (contain OH group) with Schiff base (contain COOH group) these led to produce the new colored esters [A_1-A_4] as shown in scheme (1).

The second part of work was modification the (C=N-) group in esters to heterocyclic compounds by reacting with phenyl iso cyanide to produce new β-lactam [B_1-B_4] and with anthranilic acid to get new hydroquinazoline [C_1-C_4] as shown in scheme (2).

The FTIR of azo dyes [1,2] show disappearance of two absorption bands at (3420 cm^{-1}) and (3330 cm^{-1}) were due



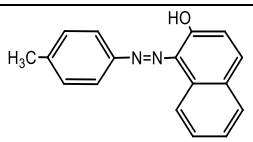
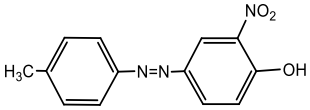
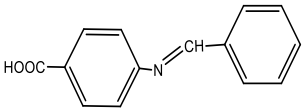
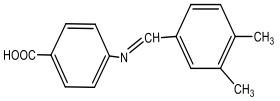
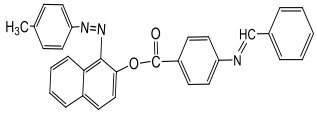
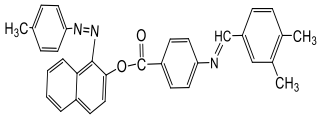
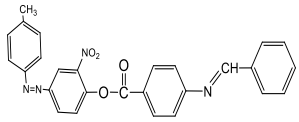
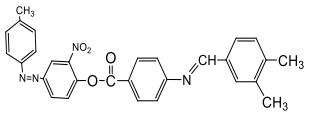
Scheme (2) structure of synthesized compounds [$B_1 – B_4$] and [$C_1 – C_4$]

to the ν(NH_2) of 4-methyl aniline and appearance the strong band at (3400 cm^{-1}) was due to the ν(OH) group. FTIR of Schiff base [3,4] show disappearance of two absorption bands at (3410 cm^{-1}) and (3318 cm^{-1}) were belong to the ν(NH_2) of 4-amino benzoic acid and appear band at (1627,1620) cm^{-1} belong to ν(C=N) imine group[14]. FTIR of ester [A_1-A_4] show disappearance of absorption band at (3448 cm^{-1}) due to of ν(COOH) group and appear absorption band at (1677-1689) cm^{-1} due to the ν(C=O) of ester, other data were shown in table [1].

FTIR of β-lactam [B_1-B_4] show disappearance of (1610-1620) cm^{-1} belong to ν(C=N) imine group and appear absorption at (1640-1649) cm^{-1} due to the ν(C=O) of lactam and band at (1700-1739) cm^{-1} due to the ν(C=O) of ester, Table [2] shown other data. ^{1}H-NMR of lactam derivatives [B_1, B_2] showed multiple signals at δ(7.9-9.3) ppm, δ(6.99-8.45) ppm due to aromatic proton, δ(6.9) ppm, δ(6.5) ppm attributed to (CH) and δ(2.3) ppm, δ(2.8) ppm due to (CH_3) group[15]. ^{13}C-NMR of lactam derivatives [B_1, B_2] shown signals at δ(122-146) ppm, δ(118-144) ppm due to aromatic carbon, δ(91) ppm, δ(89) ppm due to (CH) and δ(155) ppm, δ(165) ppm attributed to (C=O) ester, Table [3] shown other data.

FTIR of hydroquinazoline [C_1-C_4] show disappearance of (1610-1620) cm^{-1} belong to ν(C=N) imine group and appear absorption at (1630-1652) cm^{-1} due to the ν(C=O) of lactam, (1736-1752) cm^{-1} due to the ν(C=O) of ester and (3375-3381) cm^{-1} belong to ν(NH) group Table [2] shown other data. ^{1}H-NMR of derivatives [C_2, C_3] showed multiple signals at δ(6.81-8.48) ppm, δ(6.91-8.73) ppm due to aromatic proton, δ(6.4) ppm, δ(6.05) ppm due to (CH) and δ(2.5) ppm, δ(2.4) ppm due to (CH_3) group. ^{13}C-NMR of derivatives [C_2, C_3] shown signals at δ(113-149) ppm, δ(117-151) ppm attributed to aromatic carbon, δ(82)

Table 1: Physical properties and FTIR spectra data of compounds [1-4] and [A_1- A_4]

Comp No	Compound Structure	M.P. ^{0}C	% Yield	Color	Major FTIR Absorptions cm^{-1}				
					υ(C-H) aromatic	υ(N=N) azo	C=C) υ(aromatic	υ(C=N) Schiff base	Others
1		122-124	80	Red	3053	1498	1568	-	υ(O-H) =3400
2		110-112	85	Orange	3050	1515	1600	-	υ(O-H) =3430 υ(NO_2)=1312
3		78-80	78	yellow	3068	-	1595	1627	υ(O-H) =3448
4		146-148	90	Off white	3032	-	1593	1620	υ(O-H) =3439
A_1		105-107	70	Brown	3058	1502	1598	1618	C=O) ester =1687 υ(
A_2		Oily	65	Orange	3014	1490	1599	1610	C=O) ester =1677 υ(
A_3		Oily	78	Brown	3006	1512	1589	1620	υ(C=O) ester =1689 υ(NO_2)=1319
A_4		Oily	60	Brown	3011	1500	1590	1615	C=O) ester =1681 υ(υ(NO_2)=1323

ppm, δ(85) ppm belong to (CH) and δ(163) ppm, δ(161) ppm due to (C=O) ester, other data were shown in table [3].

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11.

Table 2: Physical properties and FTIR spectra data of compounds [B_1-B_4] and [C_1-C_4]

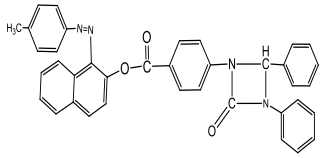
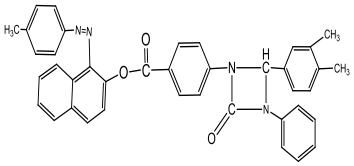
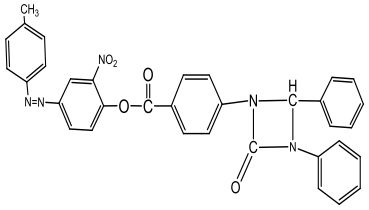
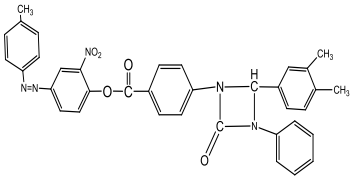
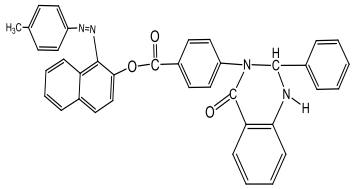
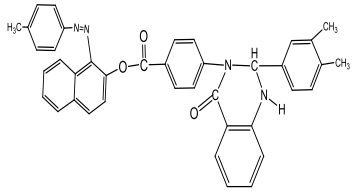
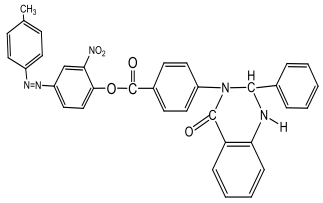
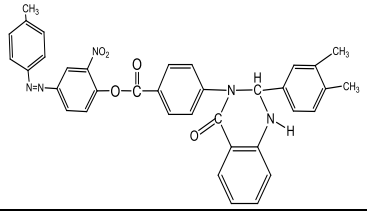
Comp No.	Compound Structure	M.P. ^{0}C	% Yield	Color	Major FTIR Absorptions cm^{-1}					
					υ(C-H) aromatic	υ(C=N) azo	C=C) υ(aromatic	υ(C=O) Lactam	υ(C=O) ester	Others
B_1		170-172	55	Brown	3045	1496	1596	1649	1700	-
B_2		122-124	63	Brown	3058	1490	1598	1647	1716	-
B_3		160-162	72	Deep Brown	3062	1498	1597	1640	1729	υ(NO_2)= 1311
B_4		216-218	50	Deep Brown	3035	1494	1596	1649	1737	υ(NO_2)= =1313
C_1		oily	63	Deep Brown	3062	1502	1598	1630	1736	υ(N-H) =3373
C_2		155-157	58	Orange	3037	1500	1600	1635	1756	υ(N-H) =3379
C_3		oily	60	Brown	3070	1587	1587	1641	1759	υ(N-H)=3375 υ(NO_2)= 1300
C_4		oily	68	Brown	3064	1585	1590	1652	1765	υ(N-H)=3381 υ(NO_2)= 1380

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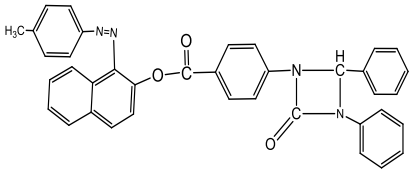
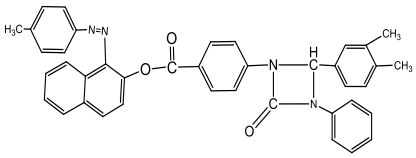
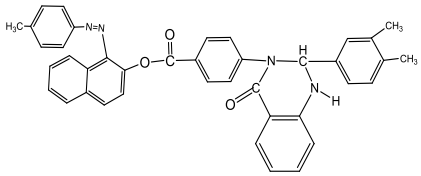
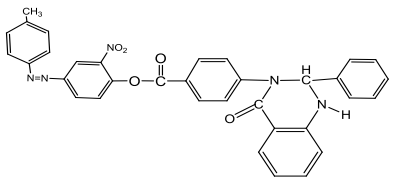
Table [3] ^{1}HNMR data and ^{13}C-NMR data for compounds [B_1, B_2, C_2 and C_3]

Comp. No.	Compound structure	^{1}H-NMR spectral data δ ppm	^{13}C-NMR spectral data δ ppm
B_1		(7.9-9.3) aromatic proton, (6.9) H of lactam ring and (2.3) CH_3 group	(122-146) aromatic carbon, (91) C-H, (155) C=O ester, (150) C=O lactam and (23) CH_3
B_2		(6.99-8.45) aromatic proton, (6.5) H of lactam ring and (2.8) CH_3 group	(118-144) aromatic carbon, (89) C-H, (165) C=O ester, (154) C=O lactam and (25) CH_3
C_2		(6.81-8.48) aromatic proton, (6.4) H of six ring, (5.3) NH and (2.5) CH_3 group	(113-149) aromatic carbon, (82) C-H, (163) C=O ester, (160) C=O lactam and (21) CH_3
C_3		(6.91-8.73) aromatic proton, (6.05) H of six ring, (5.5) NH and (2.3) CH_3 group	(117-151) aromatic carbon, (85) C-H, (161) C=O ester, (155) C=O lactam and (26) CH_3

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