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Synthesis and characterization of new yrazoles rings from Schiff base

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Abstract

In this work a new pyrazole heterocyclic compounds has been prepared from Schiff base as a starting materials then reduction of the Schiff base with $NaBH_4$ which gave the secondary amine (the starting material). The heterocyclic compounds prepared form the hydrazid derivatives. The compounds were identified by melting point , FTIR (KBr disc) , TLC the prepared compounds may have biological activity. All compounds names according to the chem. Draw version12 2010.

الخلاصة

في هذا البحث حضرت مشتقات جديدة للبايروزول من قواعد شف كمادة اولية حيث اختزلت بواسطة صوديوم بوروهيدرايد الذي اعطى امين ثانوي . ثم حضرت المركبات الحلقية غير المتجانسة من مشتقات الهيدرازايد .شخصت المركبات المحضرة بواسطة جهاز الاشعة تحت الحمراء ، وقياس درجة الانصهار و كروماتوغرافيا الطبقة الرقيقة ، ان المركبات المحضرة ممكن ان تكون ذات فعالية بايولوجية ، جميع المركبات سميت على نضام كيك اوفس عدد ١٢ و ٢٠١٠

Introduction

In 1864 the German chemist H. Schiff first described the formation of N – substituted imines so they are often called Schiff Bases
(JIGNA PAREKH. et.al. 70 (10) 1155–1161 (2005))(Schmide George . 14 (589 – 649), **1995)** .Schiff bases contain an azomethine group (N=C) (Ali Hammedi 2004) and the general formula of these bases are ((R N= CR_2)(More, P. G. et.al 78, 474-475, **2001**)
Schiff bases are used in ring closure, cycloaddition,to prepare heterocyclic compounds (Ahmad Thamer 2008) Schiff bases are substrates used in antimicrobial, biologically active (*ARKIVOC 2006*) , (Baseer, M. A et.al. 16, 553-556 2000),(El-Masry et.al. 5, 1429-1438, **2000**). (Pandeya, S. et.al. 54, 624-628, **1999**) ,and antituberculosis compounds (**Nilufer Solak** *2006 (xii) 173-181)*
The pyrazole molecule is planar. Bond lengths and bond angles have been calculated from microwave spectra (see Fig. 1.1). Consistent with the structural formula, the bond between atoms 3 and 4 is the longest.

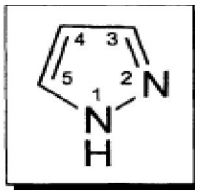
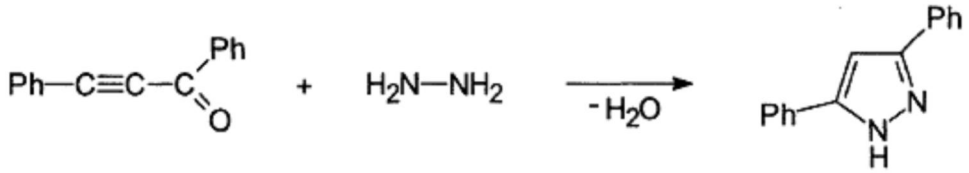


Fig. 1.1

Pyrazoles prepared by the reaction of Hydrazine, and alkyl- or arylhydrazines undergo cyclocondensation with 1,3-dicarbonyl compounds to give pyrazoles acetylenic ketones are used as bifunctional components (Theophil Eicher 2003)



They have very important medical application they used as, analgesic (Mohd Amir et.al, 2005, pp. 2532-2537) inflammatory (Shambabu et.al. 2004, pp. 2410-2415) and antimicrobial (M. A.; Jadhav et.al. 16, 553-556, **2000**.)

Experimental part

1- **Preparation of compounds 1 (a,b) (**Singh, W. M et.al. 22, 33-37, **1988**.)
A mixture of aniline (0.003mole, 0.31g) and N,N-dimethylaminobenzaldehyde (0.003 mole 0.05g) in 15ml of absolute ethanol was reflux for 6hours the end of reaction determinate by TLC. the reaction mixture was cooled and the solid product was filtrated and dried

Preparation of compounds 2(a,b)
Dissolve (0.08mole) of compound 1 in 20ml of methanol and cooled to (0^oC) then add excess of sodiumborohydride ($NaBH_4$) then stirring for 24hour , wash the product with water then extract the product with methylene chloride and dring the organic layer

Preparation of compounds 3(a,b)
Dissolve (0.005mole, 1.1g) of compound (2) in 20ml of dry benzene in ice bath then add a few drops of triethylamine.
Dissolve (0.005mole, 0.5ml) of chloroacetyl chloride in dry benzene , add the second solution to the first one dropwise with stirring for 10minuts a precipitate will formed directly which filtrated washed with sodium bicarbonate to remove the acid impurities

Preparation of compounds 4(a,b)
Dissolve (0.001 mole, 3.06 g) of compound (3) in 20ml absolute ethanol then excess of hydrazine hydrate was added the mixture was refluxed for 4 hours the a precipitate was formed then filtrated and dried.

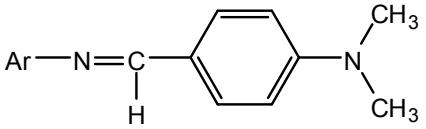
Preparation of compounds 5(a,b)
A mixture of compound(4)(0.01mole 1g) and acetylacetone (0.01mole, 3g) was refluxed in ethanol absolute for 5hours the formed precipitate was filtrated and dried

Table (2-1) show the physical properties of the prepared compounds

Comp. no.	Molecular formula	Color	Melting point	Molecular weight	Yield ercent
1a	$C_{15}H_{16}N_2$	Pale yellow	126 ^{o}C	224	95%
1b	$C_{17}H_{20}N_2$	Yellow	132^{0}C	252	97%
2a	$C_{15}H_{18}N_2$	White	218-219 ^{o}C	226	88%
2b	$C_{17}H_{22}N_2$	Pale brown	199-201^{0}C	254	81%
3a	$C_{17}H_{19}N_2OCl$	Brown	261-262	302.5	67%
3b	$C_{19}H_{23}OCl$	Yellowish white	257-259	340	72%
4a	$C_{17}H_{22}N_4O$	Orange	163-165	298	78%
4b	$C_{19}H_{26}N_4O$	Red	155-157	326	66%
5a	$C_{22}H_{26}N_4O$	Dark brown	210	285.5	54%
5b	$C_{26}H_{30}N_4O$	Purple	188-190	313.5	62%

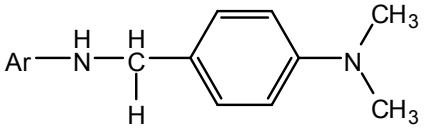
Result and discussion

Preparation of N,N-dimethyl-4-((phenylimino)methyl)aniline(1)



This compound was prepared by the reaction aniline or its derivative with N,N-4-dimethylaminobenzaldehyde the compound was identified by TLC by using absolute ethanol and FTIR by the disappearance of NH_2 group at 2400-3200cm^{-1} of aniline and C=O group at 1740cm^{-1} of aldehyde and the appearance of C=N group of Schiff base at 1640cm^{-1} , the results of this step were shown in table (I).

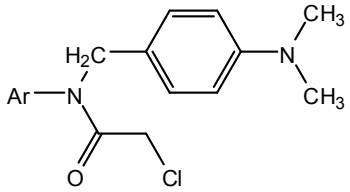
Preparation of N-(4-(dimethylamino)benzyl)arylamine(2)



This compound was prepared by the reduction of compound 1 using sodium borohydride ($NaBH_4$) the compound was identified by TLC (ethanol/ benzene (8:2)) and FTIR by the appearance of NH group at 3398cm^{-1} and the disappearing of C=N group at 1640cm^{-1} , and the results of this step were shown in table (1).

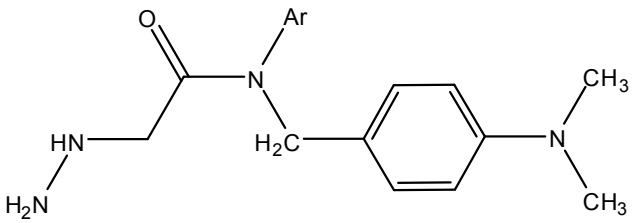
Sodium borohydride was used as selective reducing agent for the polar double bonds

Preparation of N-aryl-2-chloro-N-(4-(dimethylamino)benzyl)acetamide (3)



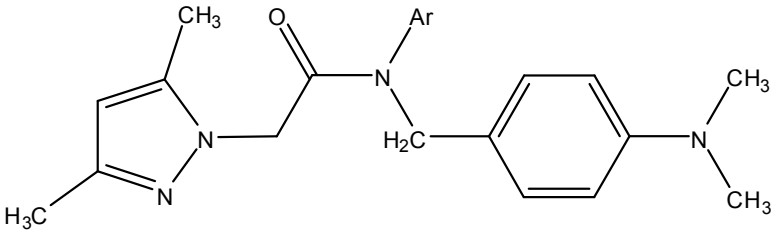
This compound was prepared by the reaction of compound 2 with chloroacetyl chloride the compound was identified by TLC and FTIR by the appearance of carbonyl group of amide at 1650 cm^{-1}, and C-Cl bond at 750 cm^{-1} and disappearance of N-H band at 3400 cm^{-1} the band at 3200 due to the enol form of carbony and $CH_2$the results of this step were shown in table (1).

Preparation of N-aryl-N-(4-(dimethylamino)benzyl)hydrazinecarboxamide (4)



This compound was prepared by the reaction of compound 3 with hydrazine hydrate the compound was identified by TLC and FTIR by the appearance HN_2 double bond 3400-3200 cm^{-1} and NH band at 3300 cm^{-1} , and the results of this step were shown in table (1).

Preparation of N-aryl-N-(4-(dimethylamino)benzyl)-3,5-dimethyl-1H-pyrazole-1-carboxamide (5)

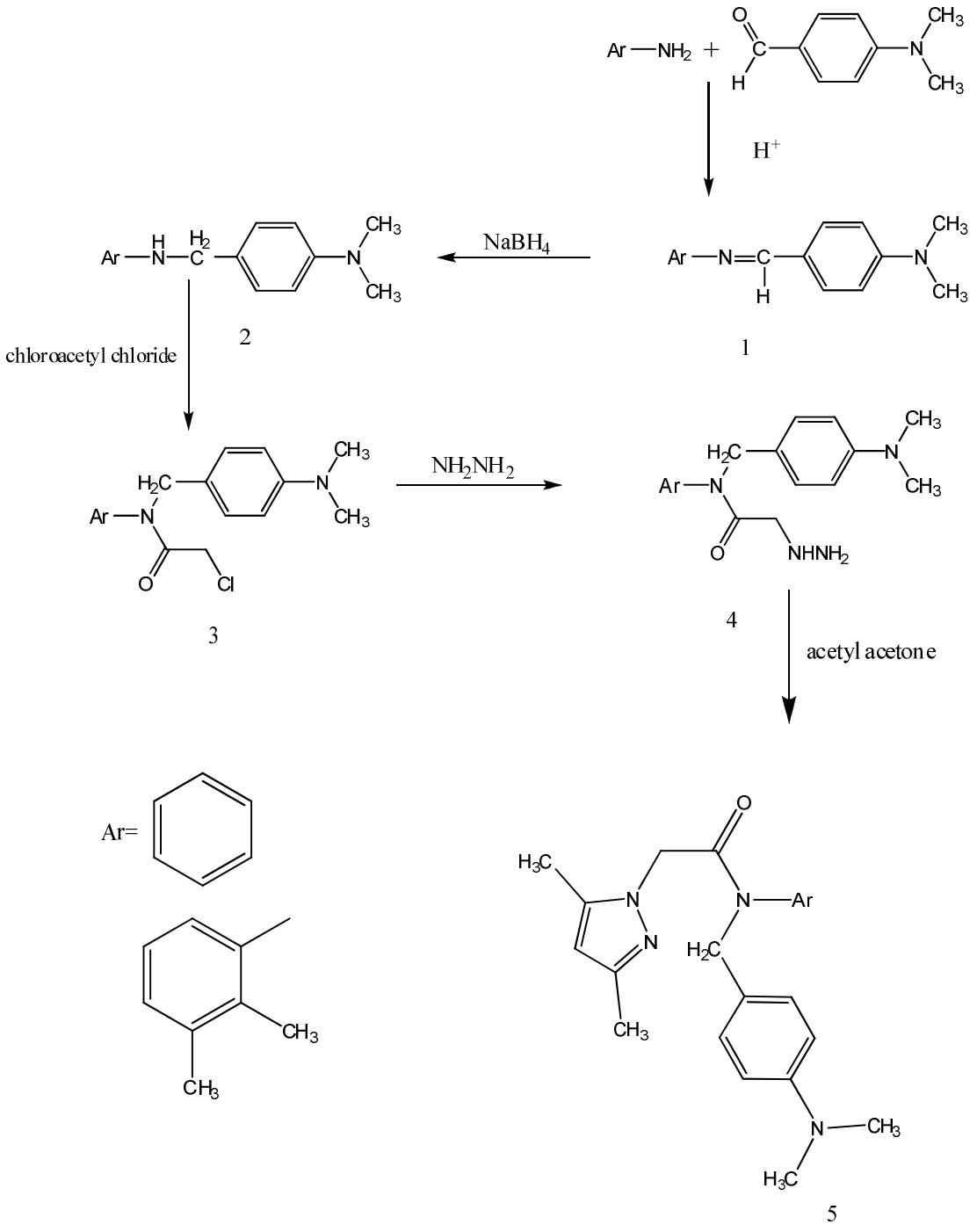


This compound was prepared by the reaction of compound 4 with acetylacetone the compound was identified by TLC and FTIR by the disappearance of NH band at

3200cm^{-1} and appearance of C=N stretching band at 1630 cm^{-1}, and the results of this step were shown in table (1).

Table(I): FTIR spectrum of the prepared compounds(1-5)
(Robert M. Selvirstine 2005)

Product	IR(KBr) cm^{-1}
1 a,b	ν CH 3002 (s) ν C=N group 1640 (s)
2 a,b	ν NH 3398 (s) ν C=C 1569(m)
3 a,b	ν C=O amide 1640(m) ν C=C 1581 (m)
4 a,b	ν NH_2 3263 (s) ν C=O amide 1604(s) ν C=C 1506 (m)
5 a,b	ν C=N 1650 (m) ν C=O amide 1740(m) ν C=C 1606 (m)



Scheme (1) show the steps of the prepared compounds

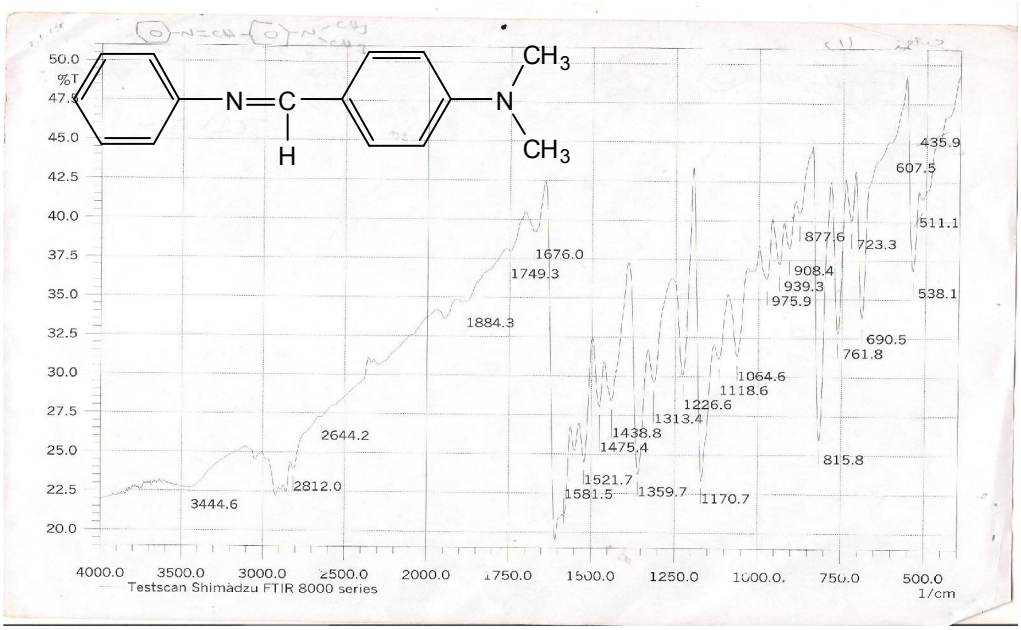


Fig. (1) : FTIR Spectra of compound1a

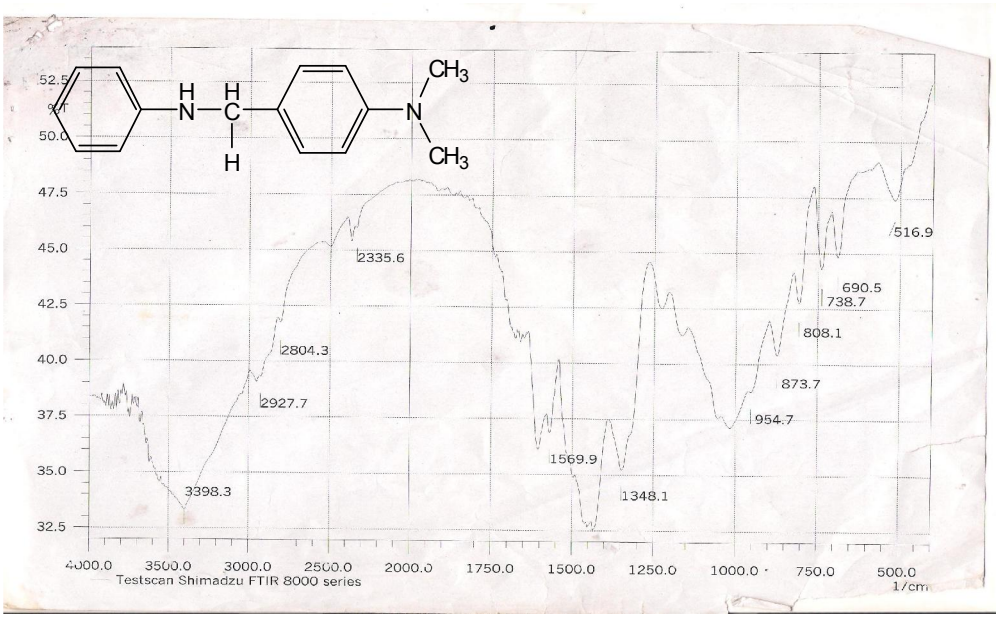


Fig (2) ftir spectra of compound 1b

Fig. (3) : FTIR Spectra of compound 2a

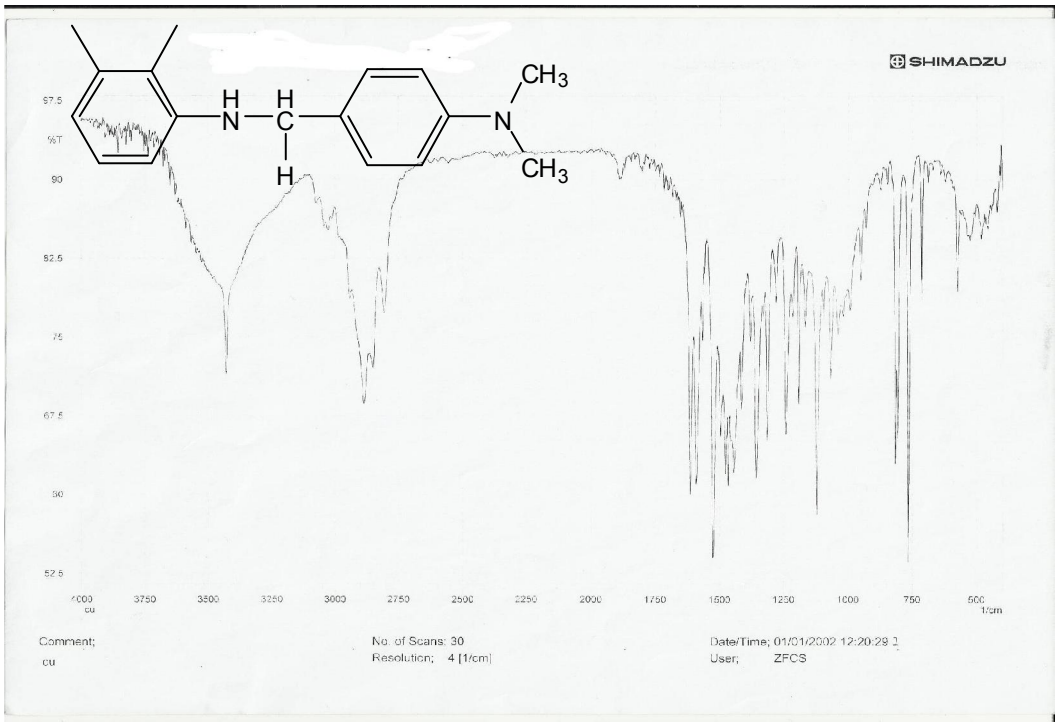


Fig. (4) : FTIR Spectra of compound 2b

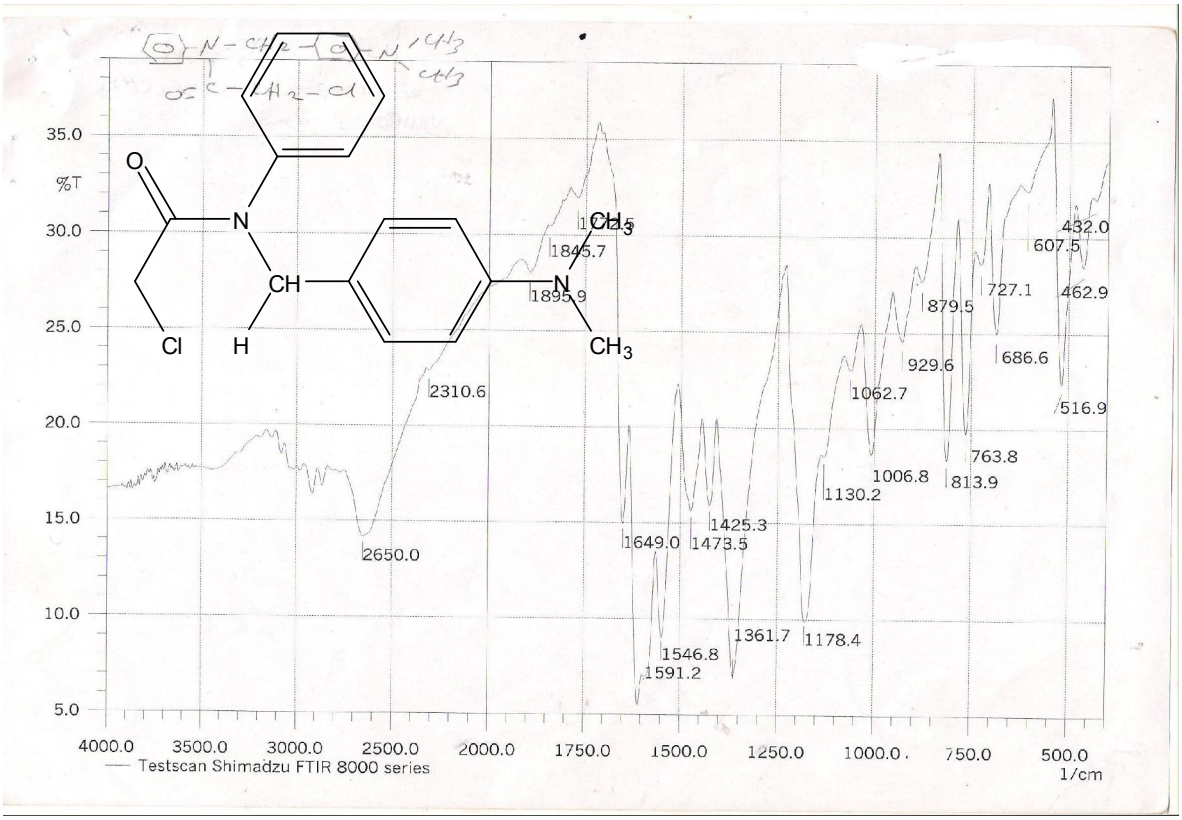


Fig. (5) : FTIR Spectra of compound 3a

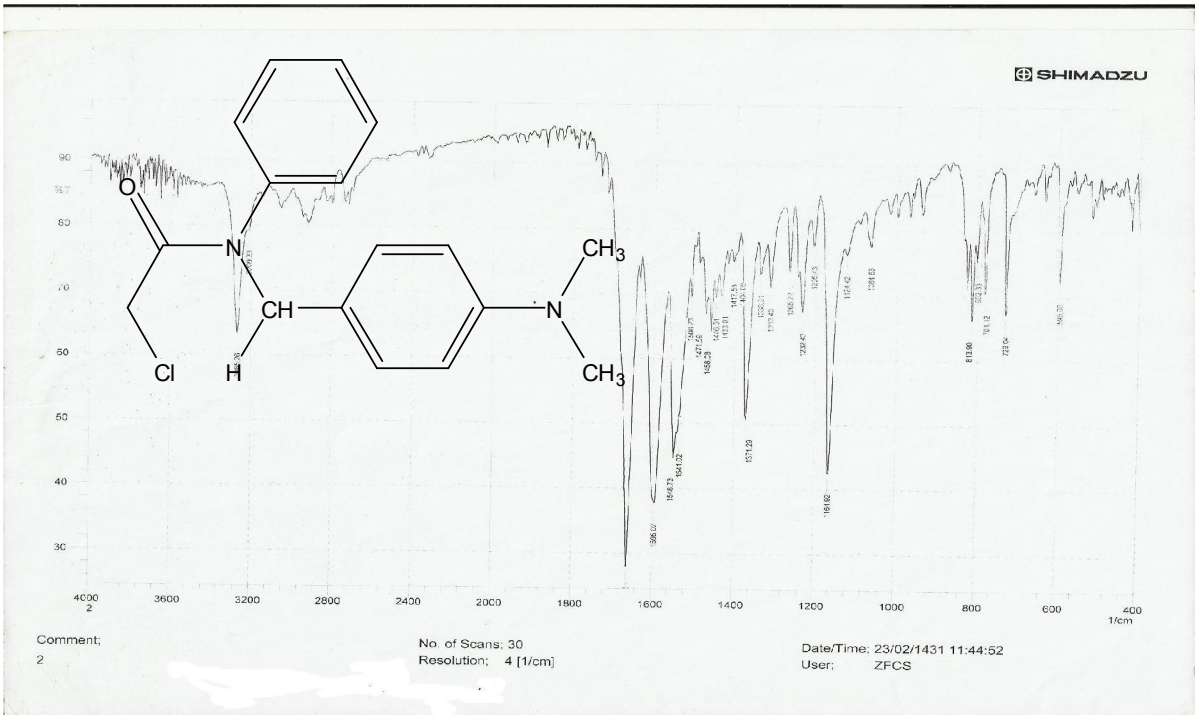


Fig. (6) : FTIR Spectra of compound 3b

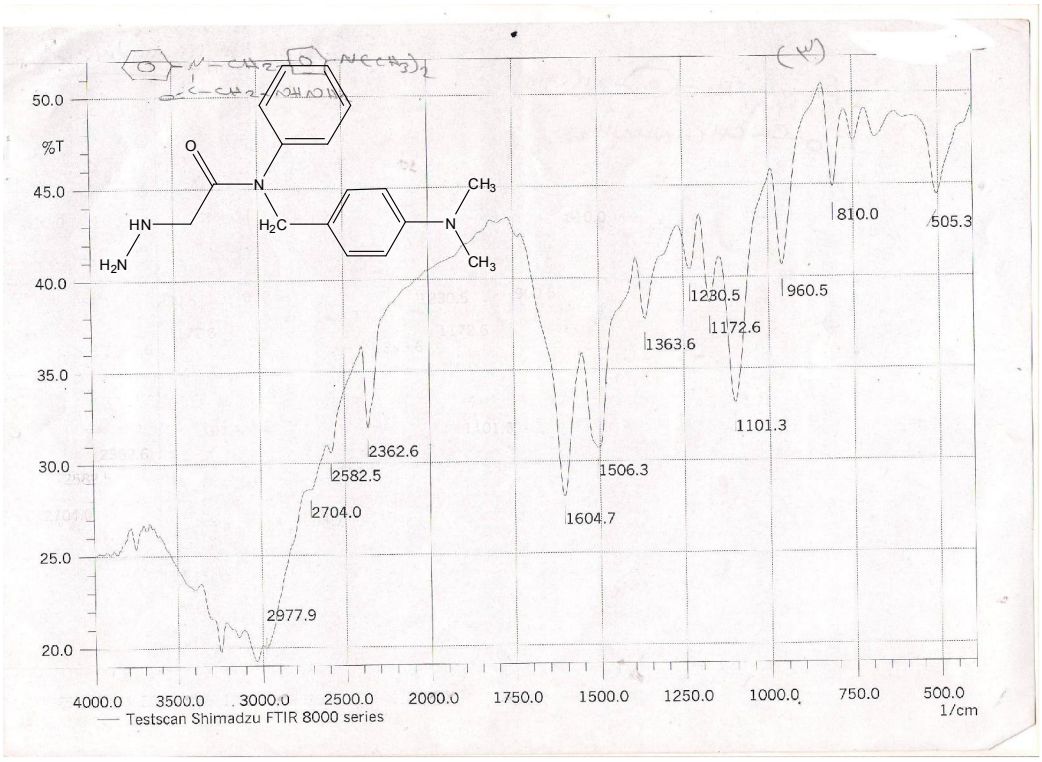


Fig. (7) : FTIR Spectra of compound 4a

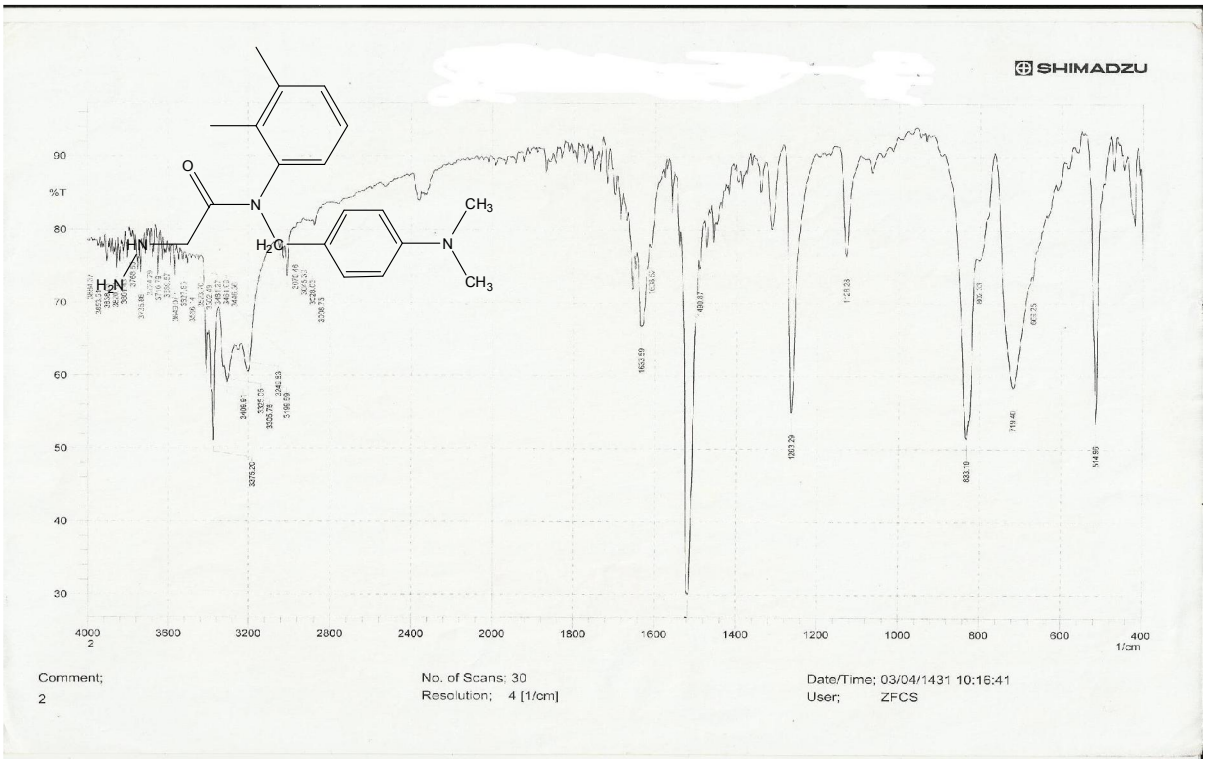


Fig. (8) : FTIR Spectra of compound 4b

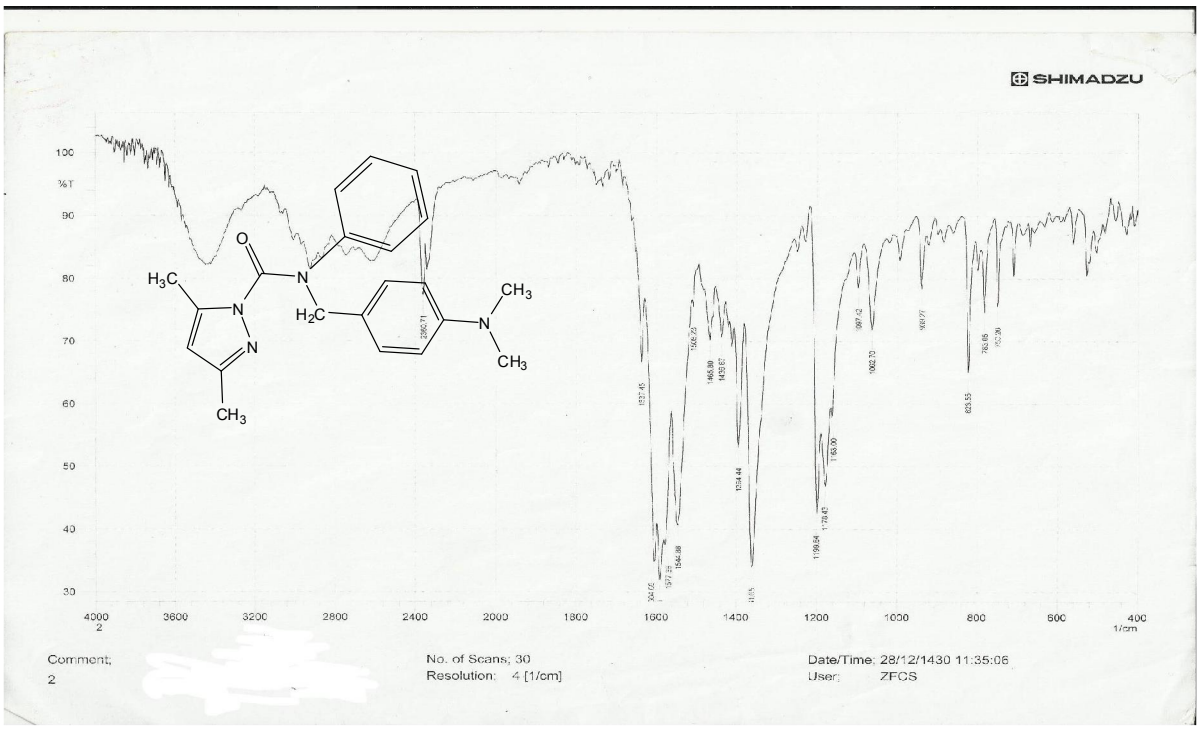


Fig. (10) : FTIR Spectra of compound 5a

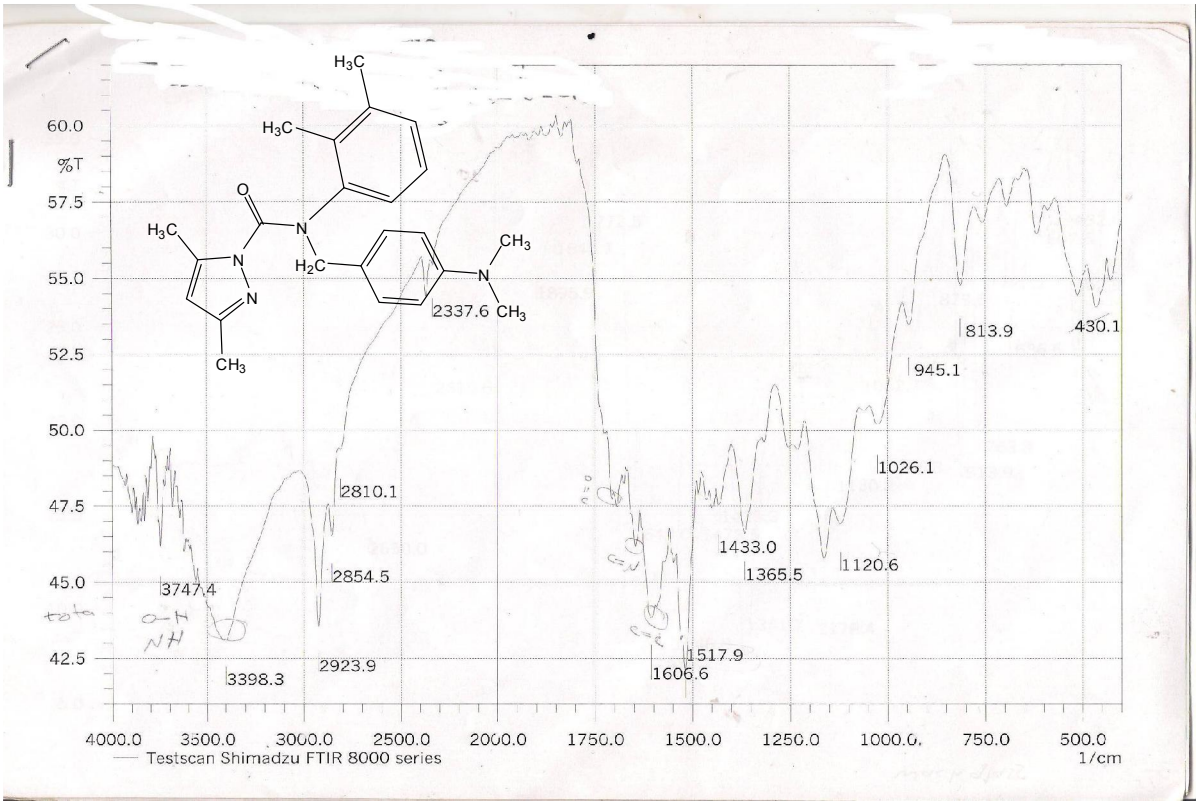


Fig. (10) : FTIR Spectra of compound 5b

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