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Synthesis and Characterization Benzimidazole Ring by Using O-phenylinediamine with Different Compounds and Using Mannich reaction for Preparation of Some Derivatives

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ABSTRACT

The research includes synthesis and characterization Benzimidazole rings by using different compounds such as Urea, Thiourea and Carboxylic acid by reactant with O-phenylinediamine, then substitution hydrogen atom with present on nitrogen atom by reactant with primary and secondary amines according to Mannich reaction. Compounds was organized by using F.T.I.R and HNMR spectroscopy.

Keywords: Benzimidazole, O-phenylinediamine, Thiouoria, Amines, Mannich reaction.

INTRODUCTION

Benzimidazole is heterocyclic compound found in many natural and non-natura1 products, such as some vitamins[1]. Therefore, benzimidazole substitutes tooks the attention of differents research groups, especially as compensation or replacement in the position 1,2 is very important sites in the impact of drug effective[2]. In This study reported some of the ways to prepare benzimidazole 2-substitution, for the importance of this compound in the field of antibiotics,such as cancer,angiotensin-II receptor antegonests and antimicrobial properties[3] antifungal, antiparkinson,...etc[4]. The NH group compounds are able to entering into N-alkylation and N-acylation according to Mannich and Michael reaction as in isatin compounds[5], which are similar with benzimidazoles. Mannich reaction very important reaction by converting some of the prepared compounds into other compounds are more important than in the biological field[6].

MATERIALS AND METHODS

1- Melting points were determined by using Melting PointSMP3 apparatus.
2- F.T.I.R. spectra were recorded by using Fourier Transform Infrared Spectrophotometer

(F.T.I.R) 8400 S Shimadzu apparatus.

3- NMR Spectrometer 400 MHz, Avance III 400 Bruker, Germany.

EXPERIMENTAL

Synthesis 1,3-dihydro-benzimidazol-2-subsititution (A and B)

A mixture of o-phenylenediamine with urea to yield (A) and with thiourea to yield (B) in existence of HCl in equal concentrations was heated at 130 ^{0}C under reflux in alcohol solution until the evolution of ammonia ceased[7].

Synthesis 2-Phenol-1H-benzimidazol (C)

A mixture of equal concentration (0.01 mol) of o-phenylenediamine and Salicylic acid in 4N HCl (20 ml) was refluxed for 30 min. then cooled, filtered and recrystallized from absolute alcohol[3].

General procedure for synthesis of compounds (A1) (B1) (C1)

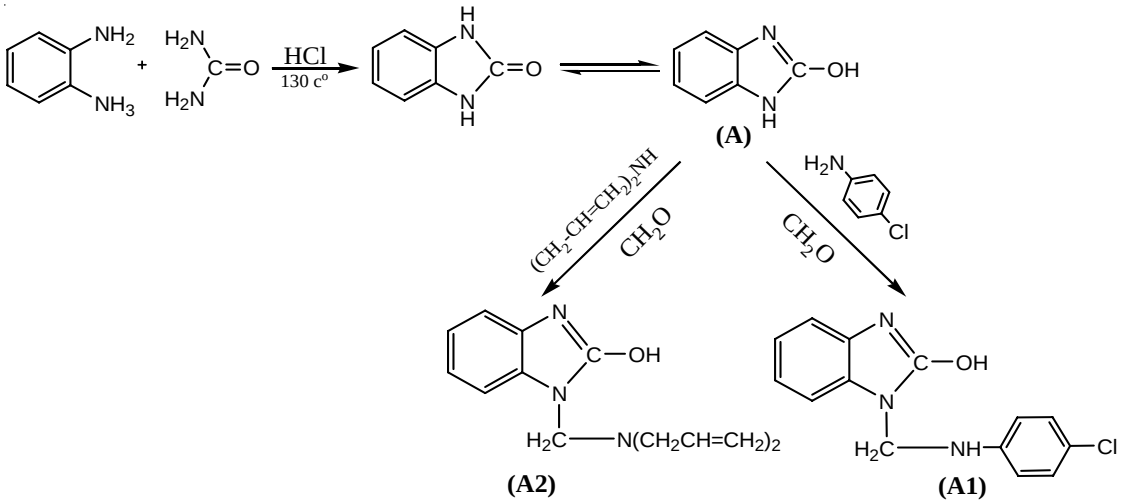
A mixture of alcoholic solution with (A), with (B), with (C) (0.01 mol) and formaldehyde (15 ml, 40 %) was added slowly on alcoholic solution of (4-chloro-aniline) (0.01 mol) the reaction mixture was stirred for three hours at room temperature and kept full night in the fridge. The solid obtained was filtered ,washed with cold ethanol, dried and crystallized form aqueous ethanol to give compounds (A1), (B1), (C1)[8].

General procedure for the synthesis of compounds (A2) (B2) (C2)

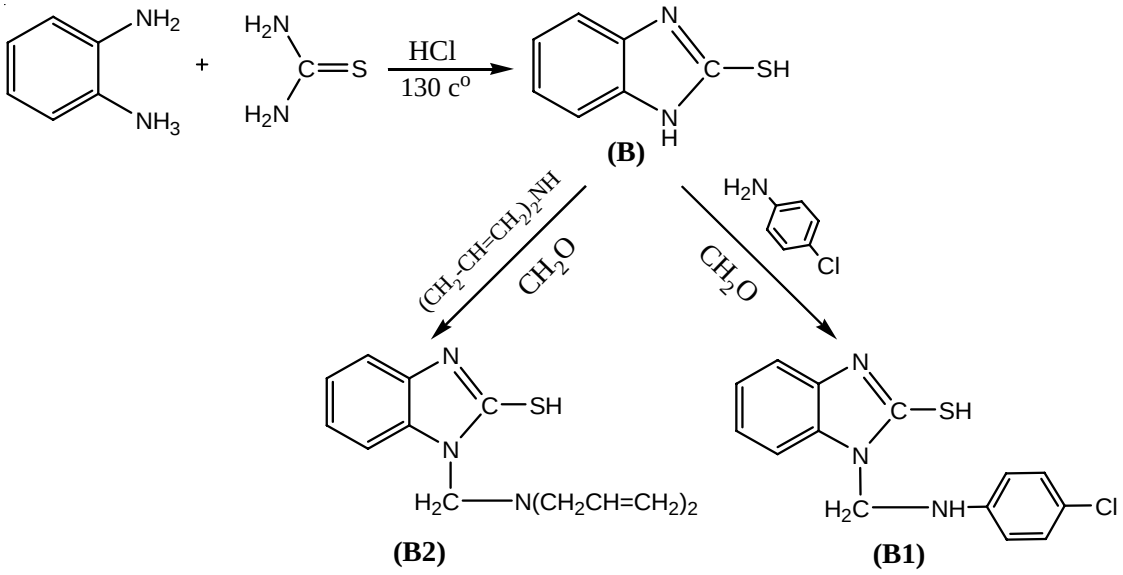
A mixture equimolar of (A), (B), (C) with Diallylamine in presence formaldehyde were carried out 0-5 ^{o}C by stirring with magnetic stirrer[9].

Table. 1: show physical properties of compounds

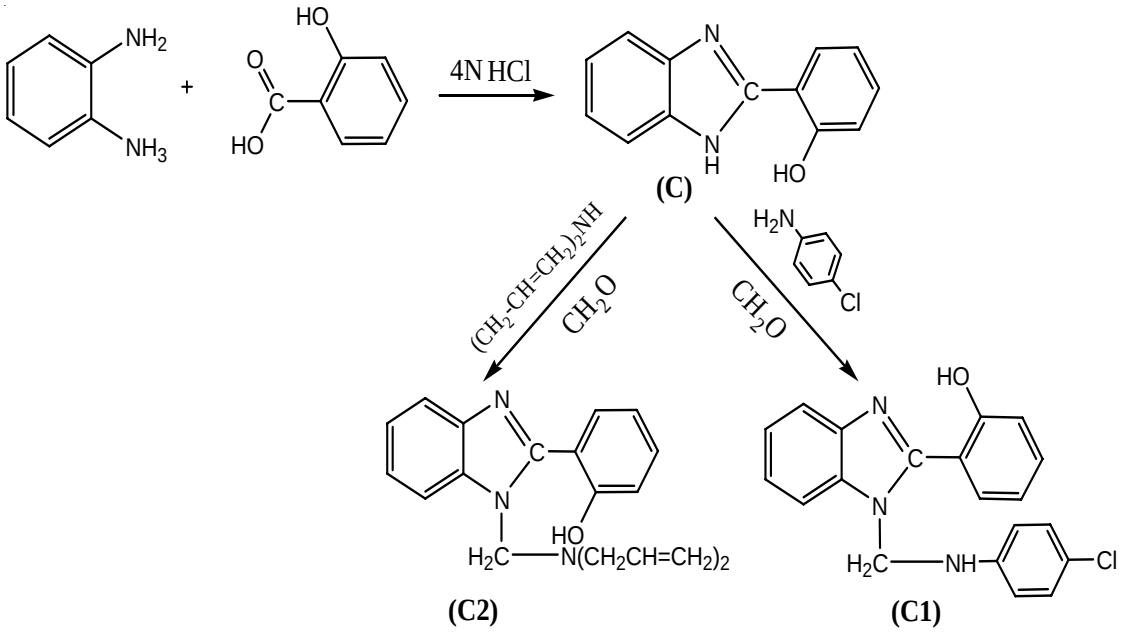
Compound	Molecular formula	Solvent	Yield %	m.p. C^o	Color
A	$C_7H_6N_2O$	Ethanol	94	275-279	Yellow
B	$C_7H_6N_2S$	Ethanol	66	114-118	Violet
C	$C_{13}H_{10}N_2O$	Ethanol	72	155-161	Violet
A1	$C_{21}H_{18}N_4OCl$	Ethanol	63	Oil	Yellow
B1	$C_{14}H_{12}N_3ClS$	Ethanol	62	Oil	Nutty
C1	$C_{20}H_{16}N_3ClO$	Ethanol	64	Oil	Nutty
A2	$C_{21}H_{28}N_4O$	Ethanol	70	Oil	Yellow
B2	$C_{14}H_{17}N_3S$	Ethanol	73	Oil	Nutty
C2	$C_{20}H_{21}N_3O$	Ethanol	76	Oil	Nutty



Scheme 1



Scheme 2



Scheme 3

RESULT AND DISCUSSION

The aim of the research is to synthesis mannich bases from different Benzimidazole rings with primary and secondary amines by using formaldehyde as catalyst.

1H-benzimidazole-2-ol (A)

Infrared spectroscopy of this compound showed a broadband at 3348-3433 cm^{-1} refers to O-H group, as well as the emergence of weak peak at 1739 cm^{-1} indicate that O-H group turn to C=O

group by resonance between O-H and N atom , the spectroscopy showed too other peaks at 3132-3178cm^{-1} refers to N-H group and at 3024 cm^{-1} to C-H aromatic. Table (2) shows other peaks to this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar(6.97 Hz 1H),OH(5.45 Hz 1H),NH(5.45 Hz 1H)

1-{[(4-chlorophenyl)amino]methyl}-1H-benzimidazol-2-ol (A1)

Infrared spectroscopy showed overlap of (O-H) peak with (N-H) peaks at 3261-3481 cm^{-1} after substitution (H) atom by compound (4-chloro aniline), also emergence absorption peak at 2921-2979 cm^{-1} refers to (C-H) aliphatic. Table (2) shows the other peaks for this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar (7.09,7.10 Hz and 7.25), OH(5.24Hz), CH2(5.77-5.81Hz), NH(3.84-3.88Hz).

1-[(diallyl-amino)methyl]-1*H*-benzimidazol-2-ol (A2)

Infrared measurements of this compound showed disappearance (N-H) peak duo to substitution H atom by compound (diallyl amine) and emergence new peak at 2908-2958 cm^{-1} refers to (C-H) and (CH=CH) respectively in addition to (O-H) group in 3355-3394 cm^{-1}. Table. (2) shows other peaks to this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar (7.18,7.19 Hz and 7.32 Hz), OH(4.89 Hz), CH_2 (4.76 Hz), CH=(5.87 Hz), CH2 (3.41 Hz), =CH2(5.30 and 5.43 Hz).

1H-Benzimidazole-2-thiol (B)

Infrared spectrum for this compound showed absorption peaks sharp at 3379 cm^{-1} indicate to (N-H) group, also appearance absorption peak at 2360 cm^{-1} indicate to (S-H) group. Table. (2) shows other absorption peaks for this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar (broad 7.19-7.28Hz 2H) and (broad 7.64-7.73 Hz 2H),

1-{[(4-chlorophenyl)amino]methyl}-Benzimidazole-2-thiol (B1)

Infrared spectrum showed stay of absorption peaks of (N-H) group at 3224 cm^{-1} after substitution of (H) atom by compound (4-chloroaniline) and emergence absorption peak at 2923 cm^{-1} indicate to (C-H) aliphatic. Table. (2) shows other absorption peaks for this compound.

1-[(diprop-2-en-1-ylamino)methyl]-1Hbenzimidazole-2-thiol (B2)

Infrared spectrum showed disappearance absorption peak of (N-H) after substitution of (H) atom by compound (Diallylamine) and appearance absorption peak at 2950 cm^{-1} indicated to (C-H) aliphatic. Table. (2) shows other absorption peaks for this compound. ^{1}HNMR (400 MHz, DMSO) δ(ppm) Ar(7.27,7.31 and 7.72 Hz), SH(2.54 Hz 1H), CH2(4.70 2H), CH2-CH= (3.51-3.52 Hz 4H), CH= (5.07 Hz 2H) , =CH2(4.85-4.95Hz 4H).

2-(2-hydroxyphenyl)-1H-Benzimidazol (Compound)

Infrared spectrum showed broadband at 3402-3421cm^{-1} indicated to (OH) group and absorption peak at 3236 cm^{-1} indicated to (NH) group. Table. (2) shows other absorption peaks for this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar(7.23,7.24 and 7.77 Hz) and (6.77, 6.89 and 7.05), OH(6.74Hz), NH(6.77Hz).

2-(2-hydroxyphenyl)-1-{[(4-chlorophenyl) amino]methyl}-1*H*-Benzimidazol (Compound 1)

Infrared spectrum showed appearance broadband at 3317-3417 cm^{-1} indicated to (OH) group and absorption peak at 3186 cm^{-1} indicated to (NH) group and new absorption peak at 2981cm^{-1} indicated to (C-H) aliphatic. Table. (2) shows other absorption peaks for this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar(7.03),(7.19-7.21), (7.76, 7.39) and (6.76, 6.86Hz), OH(4.97Hz 1H), CH2 (5.49 Hz), NH(4.14 - 4.17Hz 1H).

2-(2-hydroxyphenyl)-1-[(diprop-2-enamino) methyl]-1*H*-Benzimidazol (Compound 2)

Infrared spectrum showed survival of broadband for (OH) group at 3398 cm^{-1} and disappearance absorption peak of (N-H) for Benzimidazole ring duo to substitution hydrogen atom by formaldehyde and secondary amine and new absorption peaks at 2800-2977 cm^{-1} indicated to C-H aliphatic in propene. Table. (2) shows other absorption peaks for this compound. ^{1}HNMR (400 MHz , DMSO) δ(ppm) Ar(7.25-7.29Hz) and (7.32,7.44 , 7.70 , 7.79Hz), OH(4.79Hz) , CH2(4.68Hz) , =CH(5.49-5.55Hz) , CH2-CH= (3.67-369Hz), =CH2(5.16-5.18 Hz).

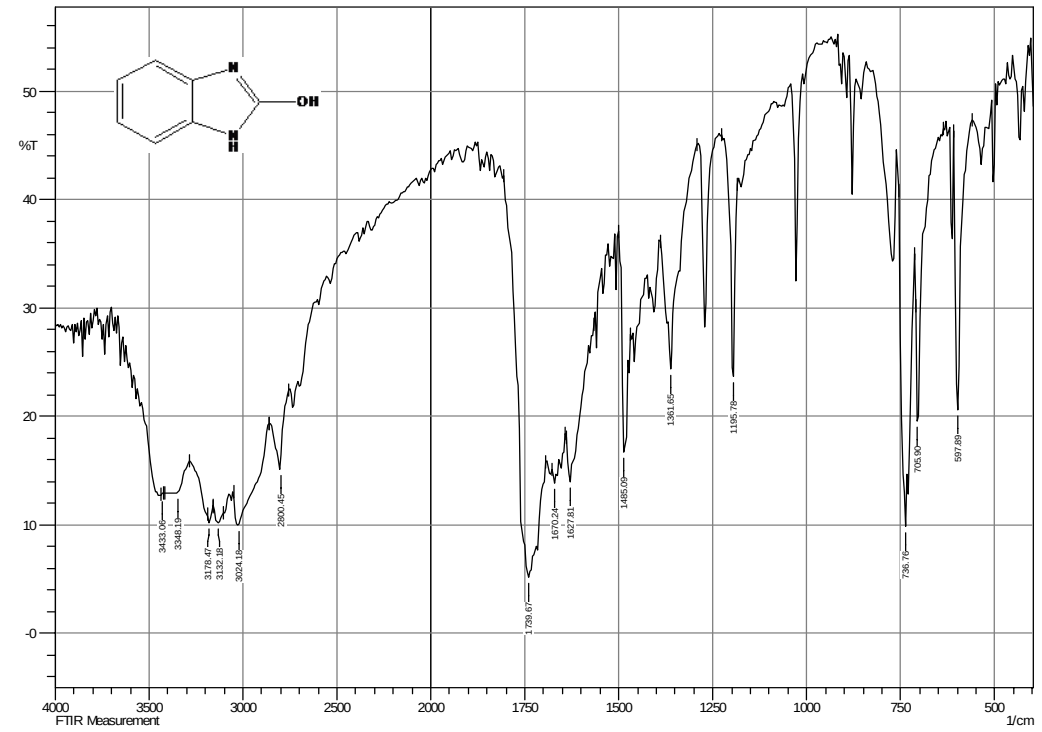


Fig. 1. F.T.I.R Spectroscopy of Compound (A)

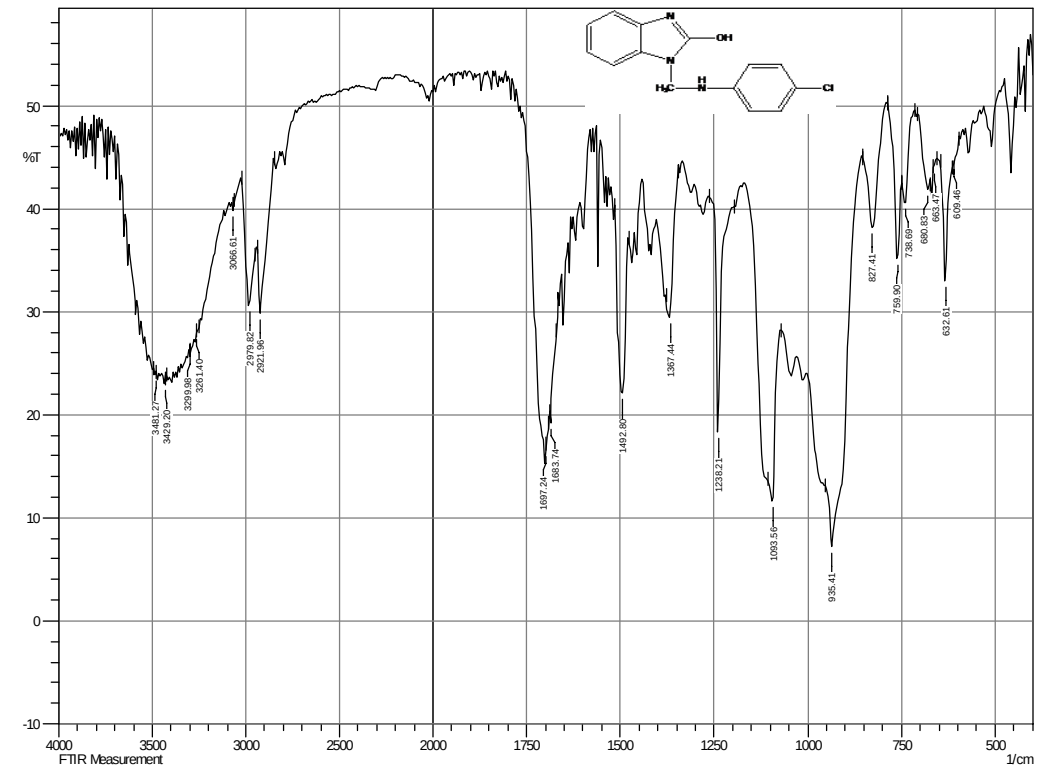


Fig. 2. F.T.I.R Spectroscopy of Compound (A1)

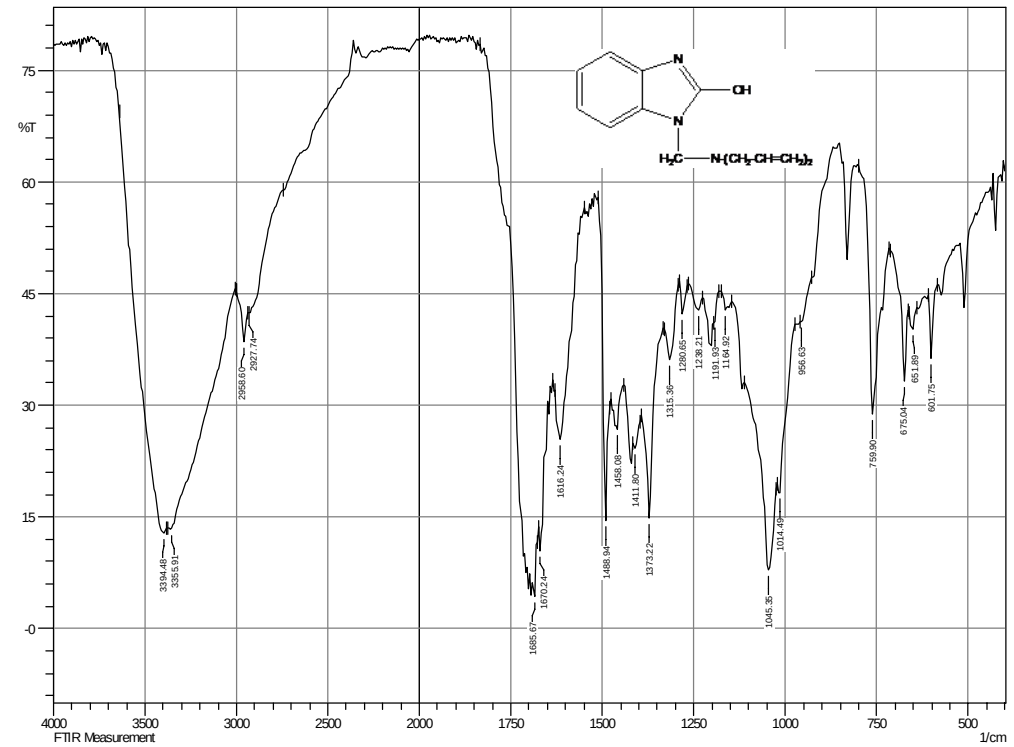


Fig. 3. F.T.I.R Spectroscopy of compound (A1)

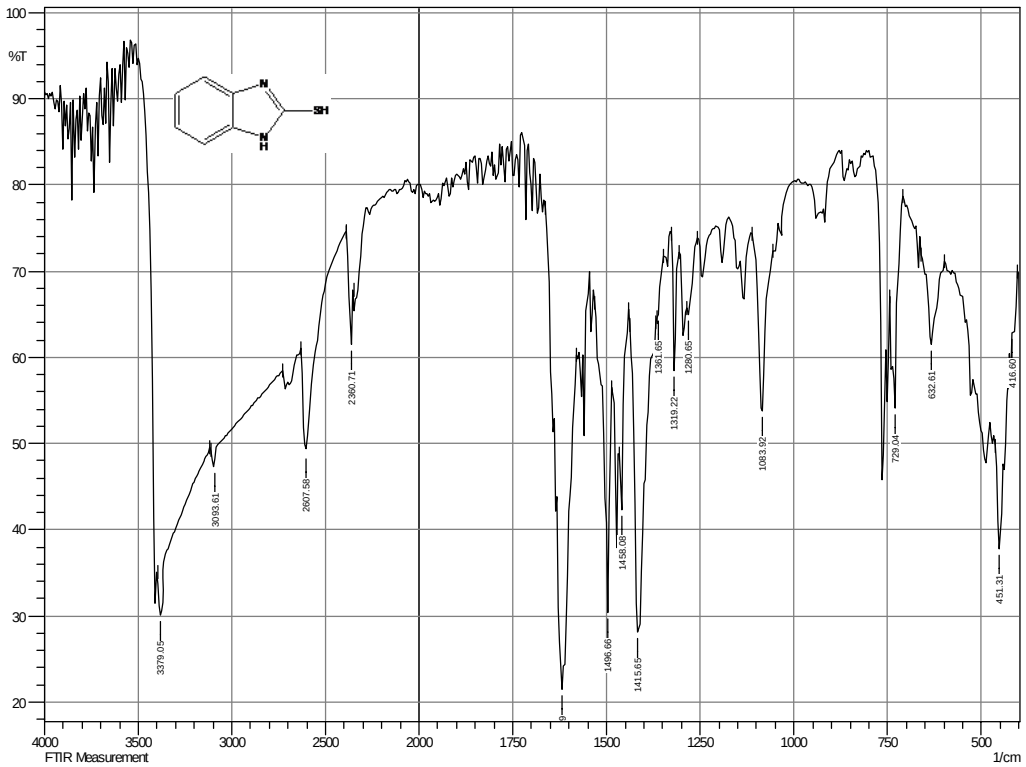


Fig. 4. F.T.I.R Spectroscopy of compound (B)

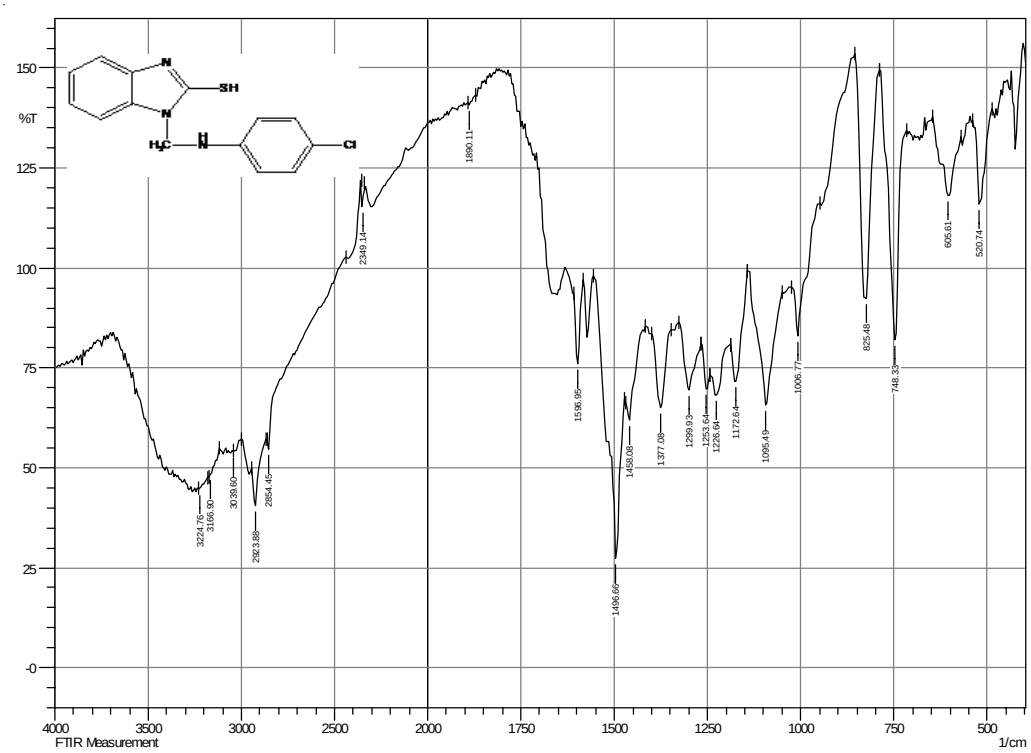


Fig. 5. F.T.I.R Spectroscopy of compound (B1)

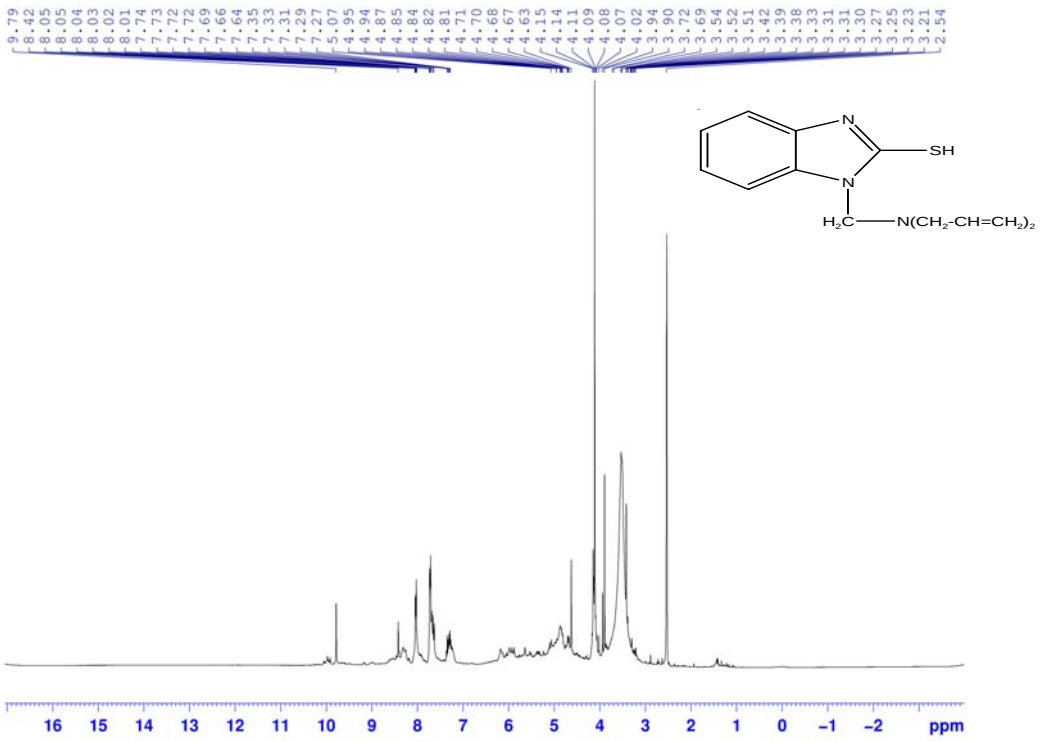


Fig. 6. H-NMR Spectroscopy of compound (B2)

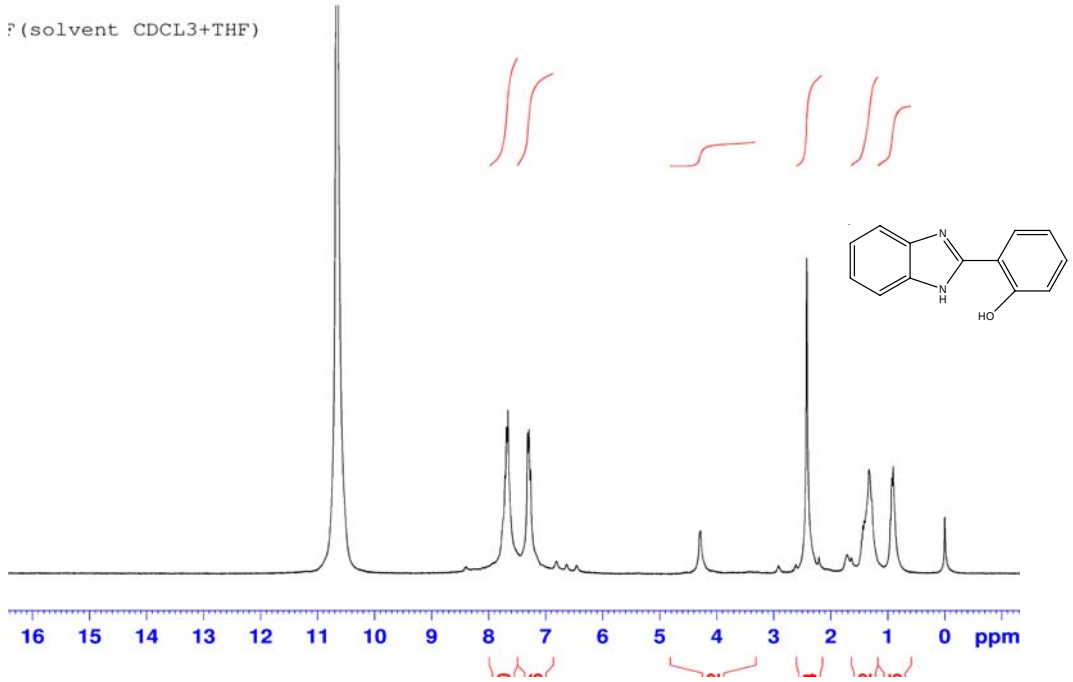


Fig. 7. H-NMR Spectroscopy of compound (C)

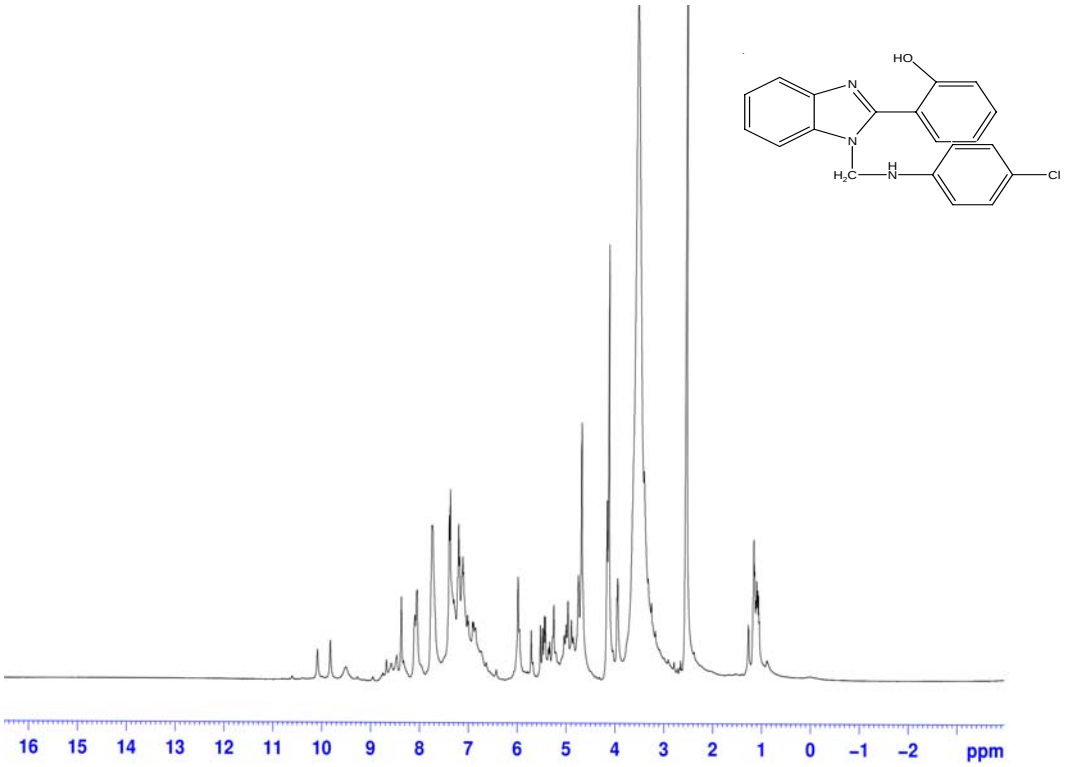


Fig. 8. H-NMR Spectroscopy of compound (C1)

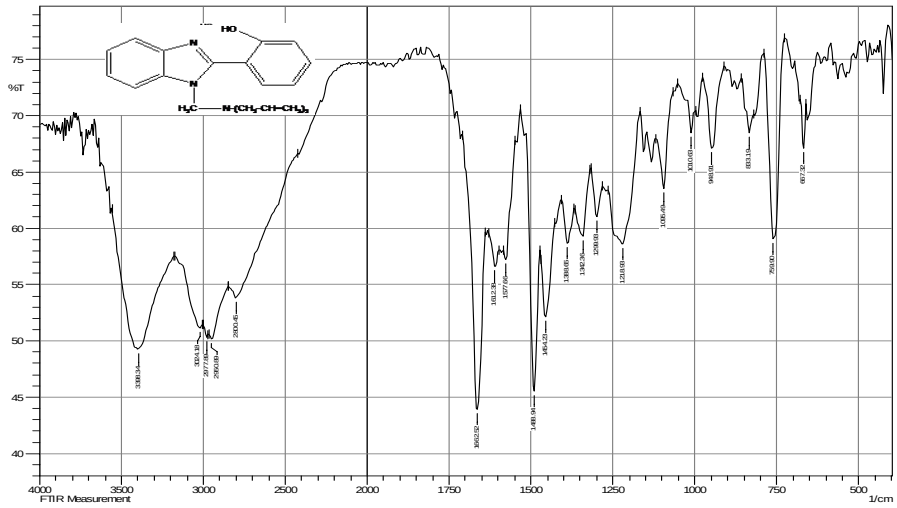
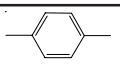


Fig. 9. F.T.I.R Spectroscopy of compound (C2)

Table. 2: Show F.T.I.R absorption packs of compounds

Compounds	C-H aryl	C=CC=N	C-N	C-O	C-S	C-Cl		
A	3024	1670-1627	1361	1195	—	—	—	705-736
B	3093	1620-1496	1280	—	1890	—	—	729
C	3055	1654-1612	1249	1157	—	—	—	759
A1	3066	1697-1683	1238	1093	—	632	827	759
B1	3039	1630-1596	1377	—	1890	605	825	748
C1	3066	1666-1573	1584	1091	—	632	848	763
A2	3058	1685-1670	1375	1045	—	—	—	759
B2	3055	1616-1542	1272	—	1747	—	—	756
C2	3024	1662-1577	1218	1095	—	—	—	759

CONCLUSION

In this study I am reported synthesis of many Benzimidazol rings from o-phenylinediamineas starting material with different compounds by using HCl as catalyst in all synthesis works and note the higher of percentage ratio for the results, then using Mannich reaction to prepared derivatives of the Benzimidazol rings were prepared. These derivatives confirmed from spectral data analysis; F.T.I.R and H-NMR.

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REFERENCE

1. Ramanatham V., Sanjay D. V., Bobba. V. S. Kumar, Umesh N. B., Shekar B. B., and Uday C.Mashelkar. *ARKIVOC*., **2008** *10*(4), 27-49.
2. Shaimaa Adnan, Kasim Hassan and Hassan Thamer, *Iraqi National Journal of Chemistry.,* **2014**,*53*, 66-75.
3. Panneer Selvam, T. , P. P. Radhika, S. Janagaraj1, A. Siva Kumar, *Research in Biotechnology.,*ISSN: 2229-791X, **2011**, *2*(3):50-57.
4. Mohan Babu Maradolla, Sunil Kumar Allam, Amaravathi Mandha, and G. V. P.Chandramouli, *ARKIVOC.,* **2008** *10*(5) 42-46.
5. Khalaf Ahmed Jasim AL- Bayati, Tikrit *Journal of Pure Science.,* **2012,** *17*(2), ISSN: 1813 – 1662.
6. Suad M.Al-Araji and Rana A.Ali, *Baghdad Science Journal.,* **2012,** *9*(1).
7. John B. Wright THF: Rsesarch Laboratories, The Upjohn Company, Kalamazoo, Michigan., **1951**, 446 – 454.
8. Badie A. Ahmed and Salem J. Mohammed. *Iraqi National Journal of Chemistry.,* **2011**, *44*, 582- 589.
9. V. Ravichandran, S. Mohan, and K. Suresh Kumar. *ARKIVOC.,* **2007,** *10*(4), 51-57.