ISSN: 0067-2904

Synthesis and Characterization of Some New Tropylidene Derivatives and Studying their Biological Activities

Muath Jabbar Tarfa Al-Abbasee[1*], Ahmood khalaf jebur[2], Afraa Sabir Shihab[2]
[1]Chemistry Department, College of Education, University of Samara, Samara, Iraq
[2]Chemistry Department, College of Science, University of Tikrit, Tikrit, Iraq

Received: 17/9/2020 Accepted: 9/4/2021

Abstract

Some new tropylidene derivatives were prepared in this work and their *in vitro* antibacterial and antifungal activities were studied. All the prepared compounds were characterized by their physical properties, such as melting point and color, and chemical properties, using the techniques of FT-IR, ^{1}H-NMR and ^{13}C-NMR.

Keywords: tropylated azomethines, halopyridines, 1,3,5-cyclo- heptatriene moiety, antibacterial, anti-fungal.

تحضير وتشخيص بعض المشتقات الجديدة لحلقة التروبيليدين ودراسة فعاليتها الحيوية

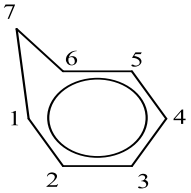
معاذ جبار طرفه العباسي[1*] ، حمود خلف جبر[2] ، عفراء صابر شهاب [2]
[1]كلية التربية ، جامعة سامراء ، صلاح الدين ، العراق
[2]كلية العلوم ، جامعة تكريت ، صلاح الدين ، العراق

الخلاصة

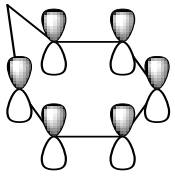
تهدف الدراسة الحالية الى تخليق مشتقات جديدة لحلقة التروبيليدين واختبار فعاليتها كمضادات للبكتريا وللفطريات. شخّصت جميع المركبات المحضّرة بوساطة درجات الانصهار واللون ومطيافية الاشعة تحت الحمراء وشخّص بعضها بوساطة مطيافية الرنين النووي المغناطيسي للبروتون وللكاربون.

1. Introduction

Tropylidene ring is one of the important compounds that possess many uses in laboratory industry and medicine. This homoaromatic cation has a pivotal role as benzene component in the field of aromatic systems. The configuration of the ring consists of 6 π electrons conjugated throughout seven cyclic carbons. In spite of the presence of a hindrance in the π frame, it contributes to a set of chemical and physical characteristics of the tropylidene cation that distinguish it as a real aromatic structure [1].



1



2

*Email maath52@uosamarra.edu.iq

Tropylium ion salts are a kind of charged, non-benzenoid aromatic species obeying Huckel's rule. The chemistry of these species has obtained high attention by many researches [2]. Moreover, tropylium tetrafluoroborate is considered as one of the most interesting compounds in several fields [3].

Tropylium salts are employed in organic synthesis as reagents [4], via the functionalization of cyclic olefins with aromatic aldehydes [5]. Tropylium salts are also utilized as typical reagents in the synthesis of N-tropylanilines [6]. This tropylium salt can be easily obtained by hydride elimination from cycloheptatriene, either by triphenylcarbenium tetrafluoroborate [7] or by phosphorus (V) chloride and tetrafluoroboric acid solution [8] **.**

Nitrogen-including derivatives with the 1,3,5-cyclo- heptatriene moiety have various biological activities [9, 10]. Tropylated anilines and their substituents are biogenic molecules. Some of them have been utilized for the functionalization of calixarenes [11], as well as being promising models of enzymes used in nanomedicine and mesomorphism researches [12]. The tropylium ring participates in several biologically active natural molecules (e.g. colchamine and colchicine) that are utilized to handle oncological diseases [13].

In addition, tropylidene ring demonstrates antimicrobial reactivity to a broad scale of bacteria [14-16], such as *Staphylococcus aureus* and *Candida albicans* strains, which makes it of distinct interest in treating microbial diseases, such as eczema [17].

The purpose of our work is to produce a newly cycloheptatriene derivative by two ways; the first way is via azomethines (A_1-A_{10}) by utilizing 1,3,5-cycloheptatrienyl tetrafluoroborate.

2. Materials and Methods

2.1 Materials

Melting points of the synthesized compounds were measured by open capillaries and were uncorrected. All the compounds were purified by recrystallization in hexane and the completion of the products was recognized by Thin Layer Chromatography (TLC). The spectral identification of the compounds was performed using FT-IR, ^{1}H-NMR and ^{13}C-NMR. Some of the prepared compounds were studied for biological activity.

2.2.1. Preparation of tropylium tetrafluroborate (A) [18 , 19]

Cycloheptatriene (1.8 mmole , 1.9 ml) and triphenylcarbenium tetrafluoroborate (6 g , 1.8 mmole) were placed into a 250 ml round bottom flask with magnetic stirring, with dropwise adding acetonitrile by a minimal amount to the reaction flask until all the solid material was converted to a solution. Once the solution has formed, about it was left a few minutes for the reaction to be complete and then the solvent was removed under reduced pressure by rotatory evaporator. The produced dense white precipitate is the tropylium tetrafluroborate, which was isolated by Buchner suction filtration and washed with small portions of cold ethanol followed by cold ether, yield crystals (78%, 2.5 g) that were decomposed at 198 °C.

2.2.2. General procedure for the preparation of tropylidine azomethine derivatives (A_1-A_{10}) [20]

An equimolar mixture of acetophenone substituents, tropylium tetrafluoroborate, and aniline in tetrahydrofuran was taken into a 100 ml round bottom flask with magnetic stirring. The mixture was stirred for (3 hr) at room temperature. The product solution was neutralized with 10% ammonia and then recrystallized in hexane. The physical properties of the compounds (A_1-A_{10}) are shown in table (1).

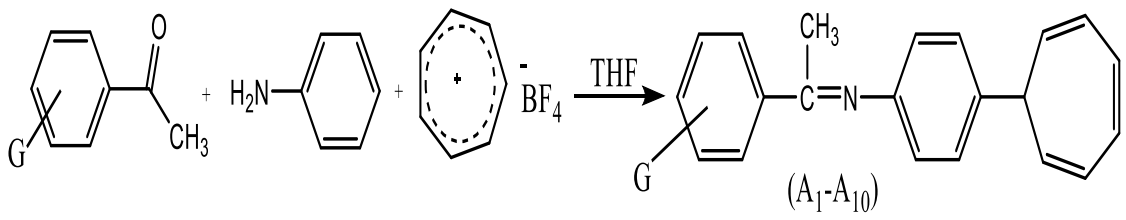
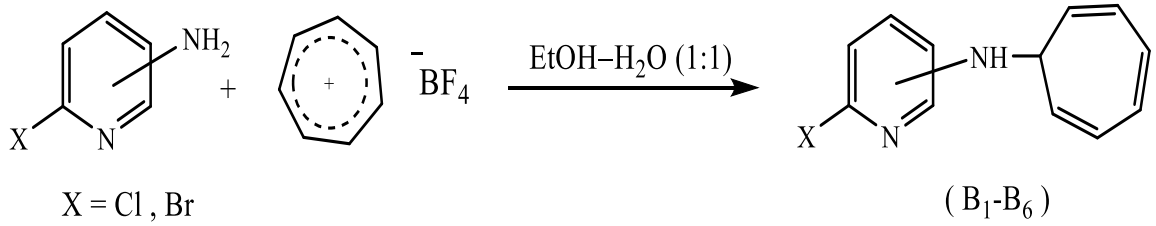


Table 1-Physical properties of the synthesized compounds (A_1-A_{10})

Compound No.	G (A_1-A_{10})	Nomenclature for compounds	Chemical formula	Colour	Melting point °C	Yield %
A_1	H	N-(4-(2,4,6-cycloheptatrienyl)phenyl)-1-phenylethan-1-imine	$C_{21}H_{19}N$	white	66-68	51
A_2	4-OMe	N-(4-(2,4,6-cycloheptatrienyl)phenyl)-1-(4-methoxyphenyl)ethan-1-imine	$C_{22}H_{21}NO$	off white	72-74	66
A_3	4-OH	4-(1-((4-(2,4,6-cycloheptatrienyl)phenyl)imino) ethyl)phenol	$C_{21}H_{19}NO$	white	110-112	72
A_4	4-NMe_2	4-(1-((4-(2,4,6-cycloheptatrienyl)phenyl)imino) ethyl)-N,N-dimethylaniline	$C_{23}H_{24}N$	pale yellow	80-82	69
A_5	4-NO_2	N-(4-(2,4,6-cycloheptatrienyl)phenyl)-1-(4-nitrophenyl)ethan-1-imine	$C_{21}H_{18}N_2O_2$	yellow	104-106	38
A_6	3-NO_2	N-(4-(2,4,6-cycloheptatrienyl)phenyl)-1-(3-nitrophenyl)ethan-1-imine	$C_{21}H_{18}N_2O_2$	yellow-orange	100-102	35
A_7	2-NO_2	N-(4-(2,4,6-cycloheptatrienyl)phenyl)-1-(2-nitrophenyl)ethan-1-imine	$C_{21}H_{18}N_2O_2$	bright yellow	90-92	33
A_8	4-Br	1-(4-bromophenyl)-N-(4-(2,4,6-cycloheptatrienyl)phenyl)ethan-1-imine	$C_{21}H_{18}BrN$	white	89-91	40
A_9	4-Cl	1-(4-chlorophenyl)-N-(4-(2,4,6-cycloheptatrienyl)phenyl)ethan-1-imine	$C_{21}H_{18}ClN$	white	74-76	42
A_{10}	4-acetyl	N-(4-(2,4,6-cycloheptatrienyl)phenyl)-1-(4-acetylphenyl)ethan-1-imine	$C_{22}H_{21}NO$	yellow	oily	35

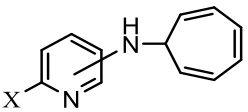
2.2.3. General procedure for the preparation of halo cycloheptatrienyl amino pyridine derivatives (B_1-B_6) [21]

Tropylium tetrafluoroborate (1.4 mmole , 0.25 g) was dissolved in a mixture of 5 ml of distilled water and 5 ml of ethanol. Substituted amino pyridine (1.4 mmole , 0.13 g) was added at room temperature. The collected mixture was mechanically stirred for 30 minutes, followed by TLC (n-hexane 4:1 ethylacetate), and then neutralized with 10% solution of NH_4OH to pH = 7 and allowed for crystallization. The produced crystals were collected, washed, dried, and recrystalized from hexane. The physical properties and yield for the synthesized compounds (B_1-B_6) are listed in Table-2.



X = Cl , Br (B_1-B_6)

Table 2-Physical properties for the synthesized compounds (B_1-B_6)

Compound no.	 (B_1-B_6) X = Cl , Br	Chemical formula	Colour	Melting point ℃	Yield %
B_1	2-chloro-N-(cyclohepta-2,4,6-trien-1-yl)pyridin-4-amine	$C_{12}H_{11}ClN_2$	white	103-105	66
B_2	2-bromo-*N*-(cyclohepta-2,4,6-trien-1-yl)pyridin-4-amine	$C_{12}H_{11}BrN_2$	pale-yellow	116-118	60
B_3	6-chloro-*N*-(cyclohepta-2,4,6-trien-1-yl)pyridin-2-amine	$C_{12}H_{11}ClN_2$	white	-7977	68
B_4	6-bromo-*N*-(cyclohepta-2,4,6-trien-1-yl)pyridin-2-amine	$C_{12}H_{11}BrN_2$	yellow	75-77	63
B_5	6-chloro-*N*-(cyclohepta-2,4,6-trien-1-yl)pyridin-3-amine	$C_{12}H_{11}ClN_2$	yellow	93-95	78
B_6	6-bromo-*N*-(cyclohepta-2,4,6-trien-1-yl)pyridin-3-amine	$C_{12}H_{11}BrN_2$	light-yellow	98-100	70

3. Biological activity of the produced compounds

The antibacterial and antifungal activities of the gained compounds were measured by using the plates' method.

3.1Standard solutions

The stock solution was prepared according to the USP (United States Pharmacopeia) as in Table-3. They were stored at 20-80 ℃ and used within the period indicated. Gradually increased concentrations were made from the stock solution, often in the ratio of 1:1.25 (Table-3).

Table 3- Data of standard antibiotics

Antibiotic	Stock solutions				
	First solvent	First concentration	Further diluent	Eventual concentration	Used for
Neomycin	B3	-	-	1 mg / mL	14 days

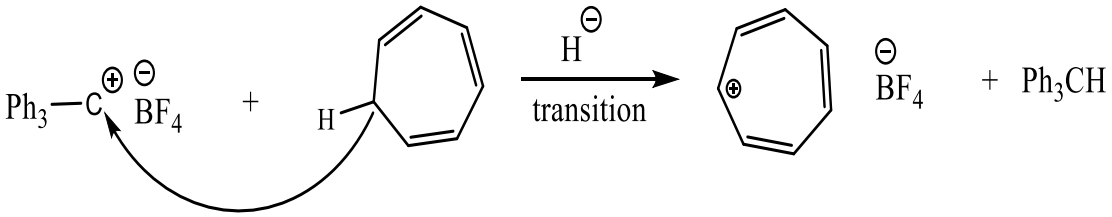
Media and solutions

The media were prepared depending on the tables listed below. Buffer solutions were prepared as described in Table-4.

Table 4-Buffers

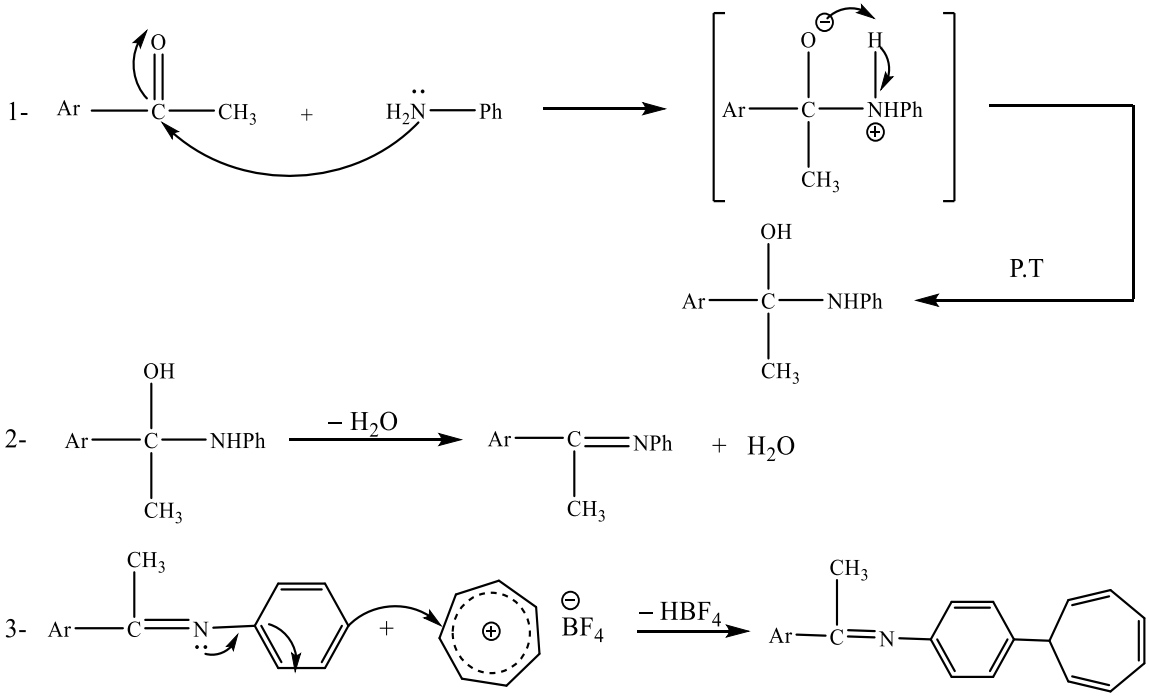
Buffer	Concentration of dibasic potassium phosphate (g/L)	Concentration of monobasic potassium phosphate (g/L)	Volume of 10 N potasium hydroxide (ml)	pH after sterilization
Buffer B.3 (0.1 M , pH 8.0)	16.73	0.523	-	8.0 ± 0.1
Buffer B.6 (10% , pH 6.0)	20	80	-	6.0 ± 0.05
pH adjusted with 18 N phosphoric acid or 10 N potassium hydroxide				

4. **Results and Discussion**



Tropylium tetrafluroborate (1) was prepared by the reaction of tritylium tetrafluoroborate with cycloheptatriene.

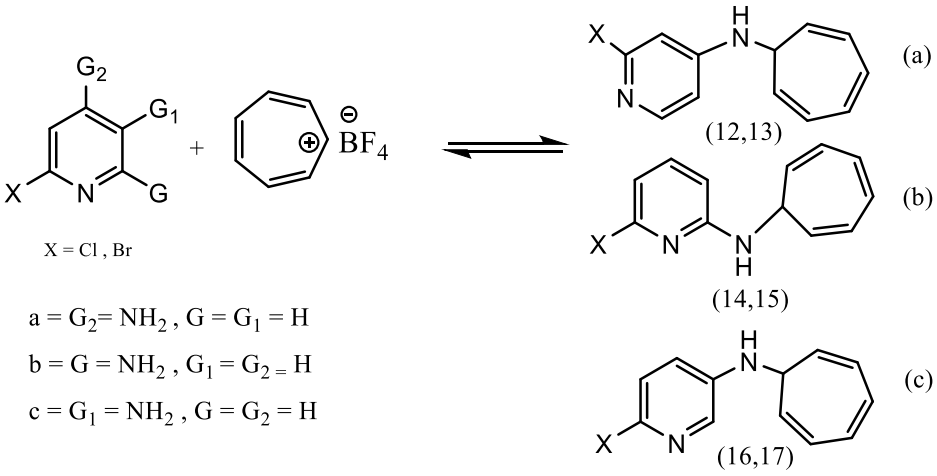
Tropylation of the produced Schiff-bases was prepared according to the following mechanism:



Ar = H , p-OMe , p-OH , p-NMe_2 , p-NO_2 , m-NO_2 , o-NO_2 , p-Br , p-Cl , p-COMe

Modification of a simple protocol was applied to synthesize a new haloaminopyridine containing cycloheptatriene moiety in a good yield (B_1-B_6).

The electron-withdrawing chloro and bromo substituents reduced the yield of the related products in comparison with a previous study.



a = G_2= NH_2 , G = G_1 = H

b = G = NH_2 , G_1 = G_2 = H

c = G_1 = NH_2 , G = G_2 = H

FT-IR Spectra

FT-IR stretching bands for compound (A_1) indicated the appearance of aromatic (-C-H) at 3044 cm^{-1}, aliphatic (-C-H) at 2984 cm^{-1}, (-C=N) at 1650 cm^{-1} and aromatic (-C=C-) at 1600-1510 cm^{-1}, as shown in Table-5 and in Figure-1. The FT-IR spectrum of compound (A_3) showed the appearance of broad (-OH) at 3348 cm^{-1} , aromatic (-C-H) at 3100 cm^{-1}, aliphatic (-C-H) at 2983 cm^{-1}, (-C=N) at 1666 cm^{-1} and aromatic (-C=C-) at 1666-1604 cm^{-1}, as demonstrated in Table-5 and in Figure-2. The FT-IR spectrum of compound (A_5) showed the appearance of aromatic (-C-H) at 3083 cm^{-1}, aliphatic (-C-H) at 2979 cm^{-1}, (-C=N) at 1662 cm^{-1} , and aromatic (-C=C-) at 1600-1580 cm^{-1}, as well as the absorption of two bands for the nitro group at 1510 and 1394 cm^{-1}, as shown in Table-5 and Figure-3 [22, 23].

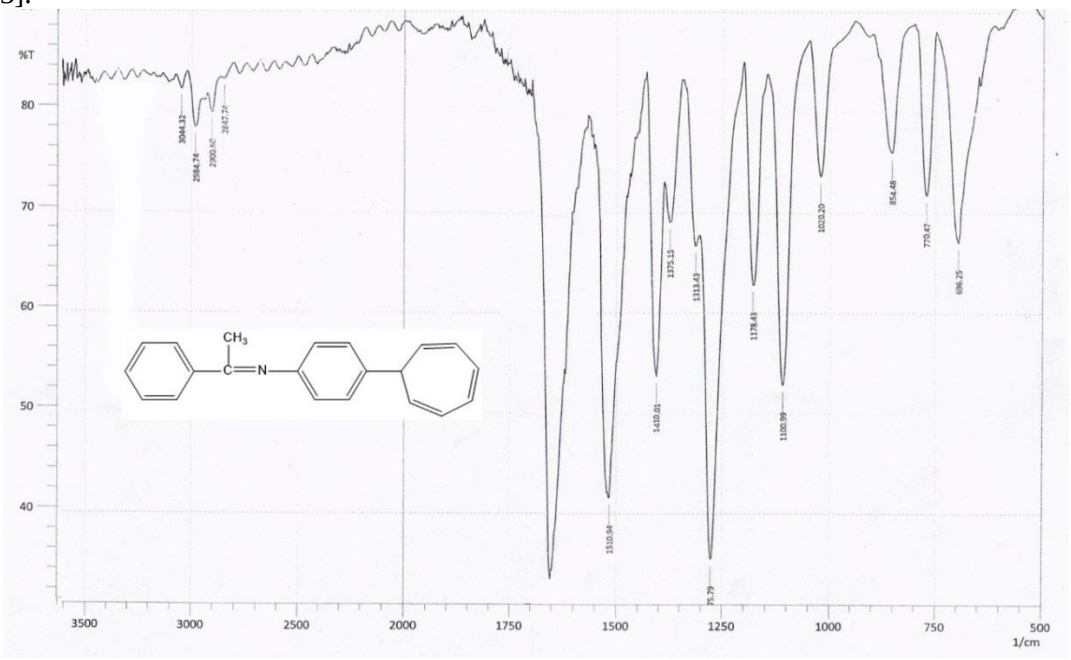


Figure 1- IR spectrum of compound (A_1)

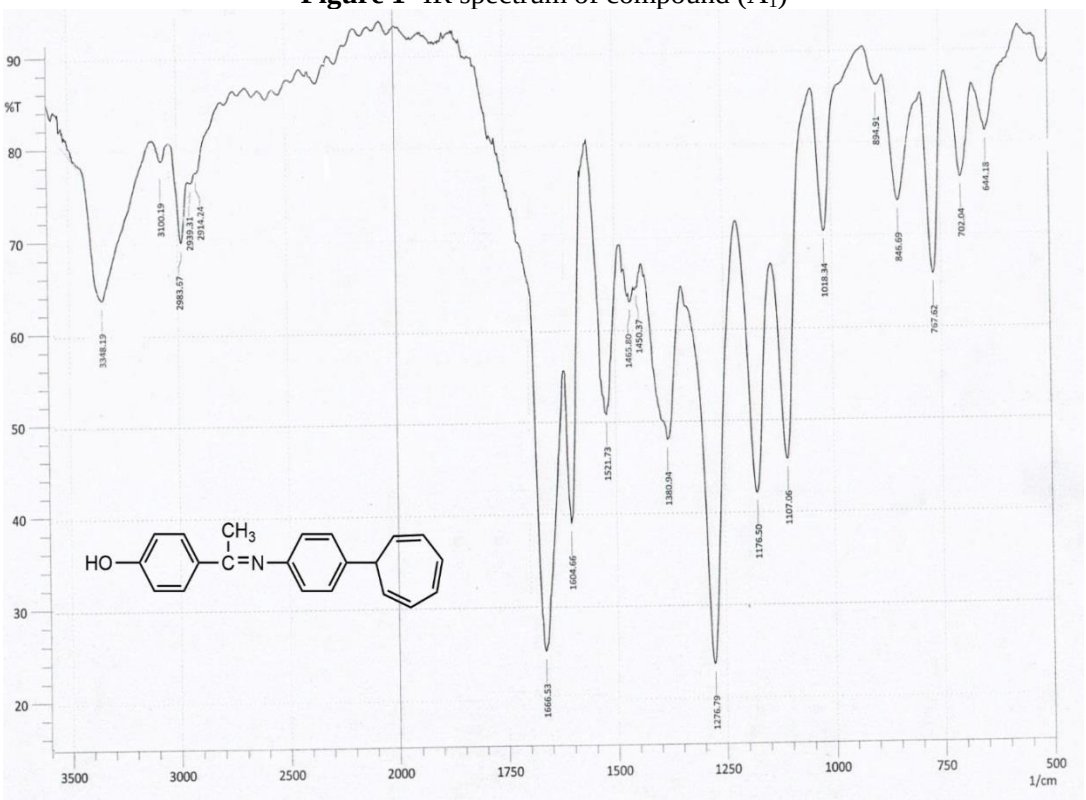


Figure 2- IR spectrum of compound (A_3)

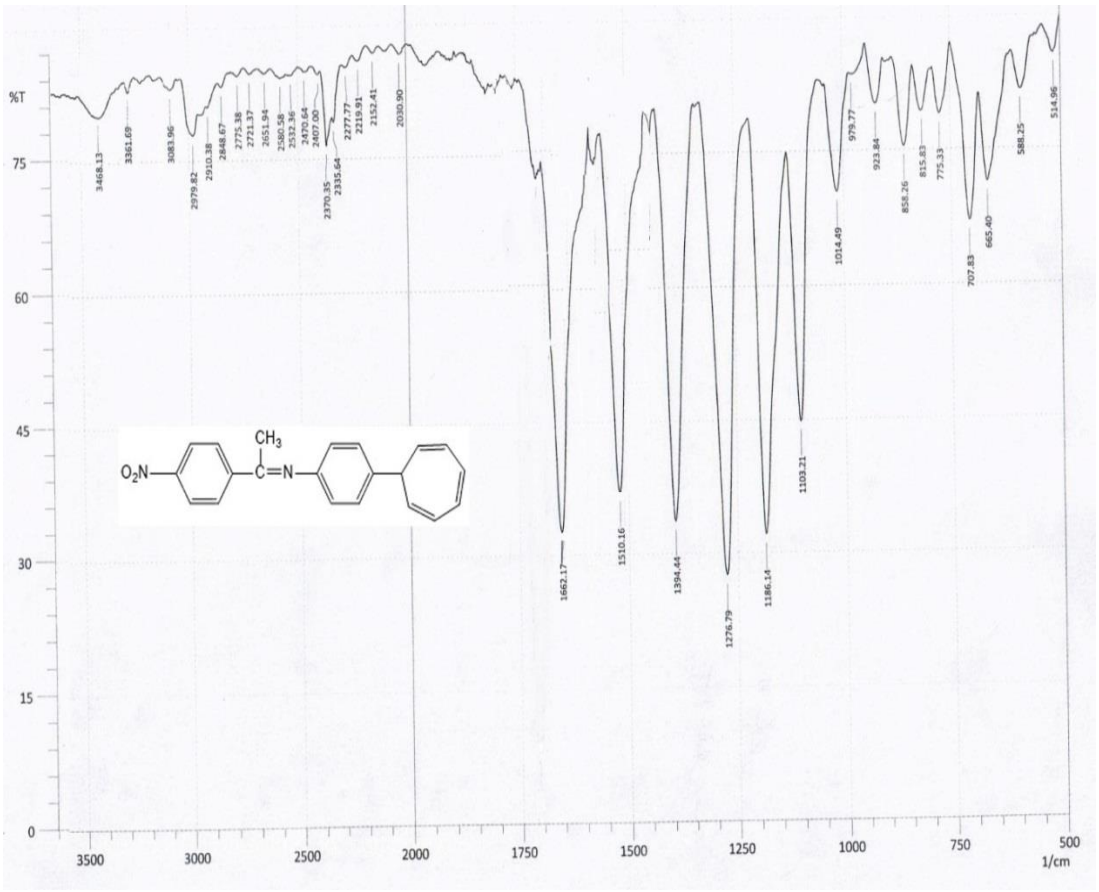


Figure 3- IR spectrum of compound (A_5)

Table 5- The FT-IR characteristic bands and their location for compounds (A_1-A_{10})

IR(KBr) , γ (cm^{-1})							
Comp. No.	Functional group						
	γ NO_2	γ C=C	γ C=N	γ C=O	γ C-H aliphatic	γ C-H aromatic	γ OH
A_1	----	1600-1573	1652	----	2920	3029	---
A_2	---	1610-1570	1650	----	2912	3025	---
A_3	---	1666-1604	1666	----	2983	3100	3348
A_4	---	1615-1590	1659	----	2950	3040	----
A_5	1510,1394	1600-1580	1662	----	2979	3083	---
A_6	1550-1340	1610-1585	1645	----	2970	3050	---
A_7	1540-1350	1608-1575	1640	----	2960	3033	---
A_8	---	1610-1580	1635	----	2965	3020	---
A_9	---	1615-1570	1620	----	2966	3045	---
A_{10}	---	1610-1600	1662	1710	2910	3010	----

Table 6- The FT-IR characteristic bands and their location for compounds (B_1-B_6)

IR(KBr) , γ (cm^{-1})					
Comp. No.	Functional group				
	γ C=C	γ C=N	γ C-H aliphatic	γ C-H aromatic	γ NH

B_1	1515-1600	1650	2981	3047	3323
B_2	1520-1615	1640	2970	3050	3318
B_3	1535-1605	1630	2960	3025	3320
B_4	1531-1612	1650	2945	3041	3311
B_5	1533-1600	1650	2943	3043	3315
B_6	1525-1610	1625	2985	3050	3335

Results of ^{1}HNMR and ^{13}C-NMR analyses for the produced compounds

The ^{1}HNMR spectrum of compound (B_1) (in DMSO as a solvent) showed the following characteristic chemical shifts: a triplet signal δ (3.7 ppm) ascribed to proton, pointed as (a) in Figure-4, a quartet signal at δ (4.15 ppm) ascribed to protons, pointed as (b) in Figure- 4, a singlet signal at δ (6 ppm) ascribed to protons, pointed as (c) in Figure- 4, a multiplet signal at δ (6.09 ppm) ascribed to protons, pointed as (d) in Figure- 4, a singlet signal at δ (6.57 ppm) ascribed to protons, pointed as (e) in Figure- 4, a quartet signal at δ (7.26 ppm) ascribed to protons, pointed as (f) in Figure- 4, and a doublet two signals at δ (7.48, 7.53 ppm) ascribed to protons, pointed as g ,and h, respectively, in Figure- 4 [24].

The ^{13}C-NMR spectrum of compound (A_1) revealed CH_3 at δ 39 ppm (pointed as a in Figure-5), cyclic (-CH) at δ 60 ppm (b), a signal at δ 117 ppm ascribed to carbons (c), a signal at δ 120 ppm ascribed to carbons (d), a signal at δ 122.9 ppm ascribed to carbons (e), a signal at δ 123 ppm ascribed to carbons (f), a signal at δ 127 ppm ascribed to carbons (g), a signal at δ 130 ppm ascribed to carbons (h), a signal at δ 136 ppm ascribed to carbon (i), a signal at δ 157 ppm ascribed to carbon (k), a signal at δ 166 ppm ascribed to carbon (L) and a signal at δ 170 ppm ascribed to C=N (m), as shown in in Figure-5 [24].

The ^{13}C-NMR spectrum of compound (A_3) revealed CH_3 at δ 34.8 ppm (a), cyclic (-CH) at δ 60 ppm (b), a signal at δ 117 ppm ascribed to carbons (c), a signal at δ 120 ppm ascribed to carbons (d), a signal at δ 122.6 ppm ascribed to carbons (e), a signal at δ 124.5 ppm ascribed to carbons (f), a signal at δ 127 ppm ascribed to carbons (g), a signal at δ 130.3 ppm ascribed to carbons (h), a signal at δ 131 ppm ascribed to carbon (i), a signal at δ 134 ppm ascribed to carbon (j), a signal at δ 141.8 ppm ascribed to carbon (k), a signal at δ 165 ppm ascribed to carbon (L) and a signal at δ 170 ppm ascribed to carbon (m), as shown in Figure-6 [24].

The ^{13}C-NMR spectrum of compound (A_4) revealed CH_3 at δ 30.9 ppm (a), cyclic (-CH) at δ 55.6 ppm (b), N-Methyl protons at δ 56.5 ppm (c), a signal at δ 115.4 ppm ascribed to carbons (d), a signal at δ 118.2 ppm ascribed to carbons (e), a signal at δ 129.1 ppm ascribed to carbons (f), a signal at δ 129.4 ppm ascribed to carbons (g), a signal at δ 157.5 ppm ascribed to carbons (h), a signal at δ 158.3 ppm ascribed to carbons (i), a signal at δ 159 ppm ascribed to carbons (j), a signal at δ 166.9 ppm ascribed to carbons (k), a signal at δ 171.3 ppm ascribed to carbons (L) and a signal at δ 173.1 ppm ascribed to carbons (m), as shown in Figure-7 [24].

The ^{13}C-NMR spectrum of compound (A_5) revealed CH_3 at δ 30 ppm (marked as a in Figure-8, cyclic (-CH) at δ 54.4 ppm (b), a signal at δ 101.7 ppm ascribed to carbons pointed as (c), a signal at δ 121.1 ppm ascribed to carbons (d), a signal at δ 122.5 ppm ascribed to carbons (e), a signal at δ 128.6 ppm ascribed to carbons (f), a signal at δ 129 ppm ascribed to carbons (g), a signal at δ 131.7 ppm ascribed to carbons (h), a signal at δ 132 ppm ascribed to carbons (i), a signal at δ 132.8 ppm ascribed to carbons (j), a signal at δ 134.2 ppm ascribed to carbons (k), a signal at δ 143.6 ppm ascribed to carbons (L) and a signal at δ 175.7 ppm ascribed to carbons (m), as shown in Figure-8 [24].

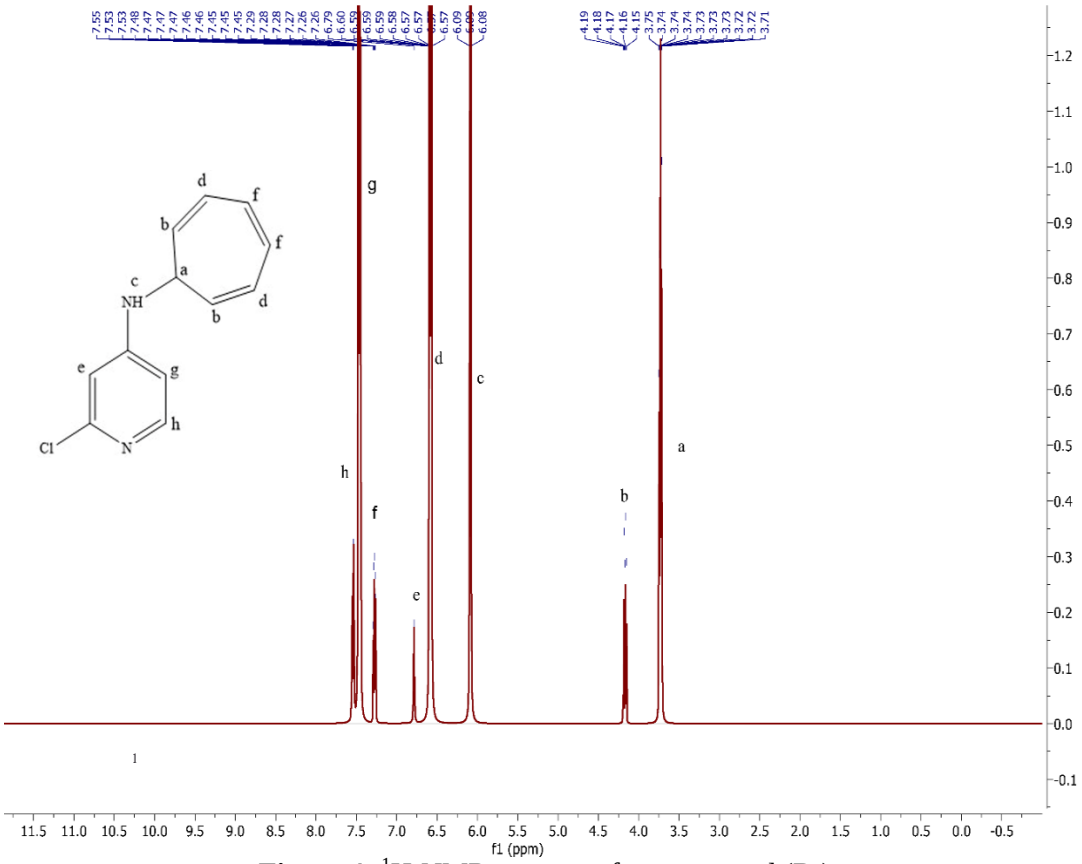


Figure 4- ^{1}H-NMR spectrum for compound (B_1)

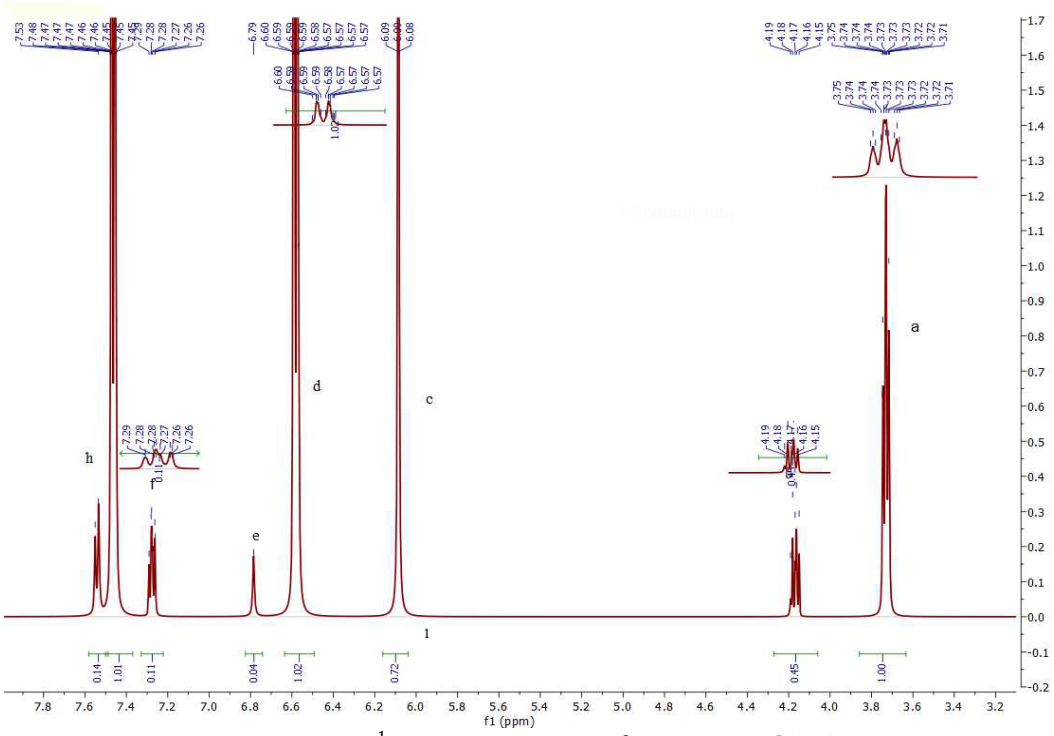


Figure 5- ^{1}H-NMR expansion for compound (B_1)

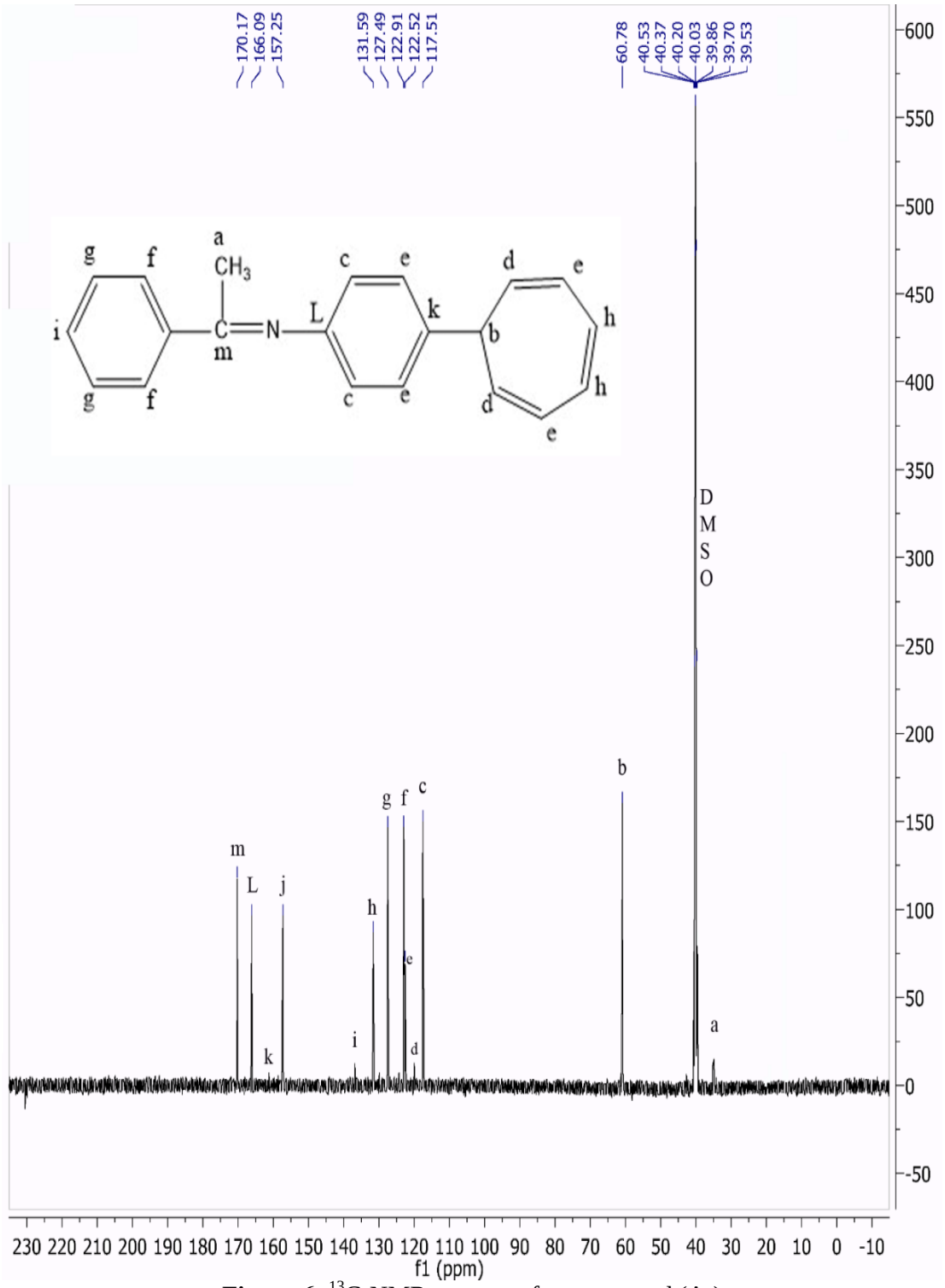


Figure-6- ^{13}C-NMR spectrum for compound (A_1)

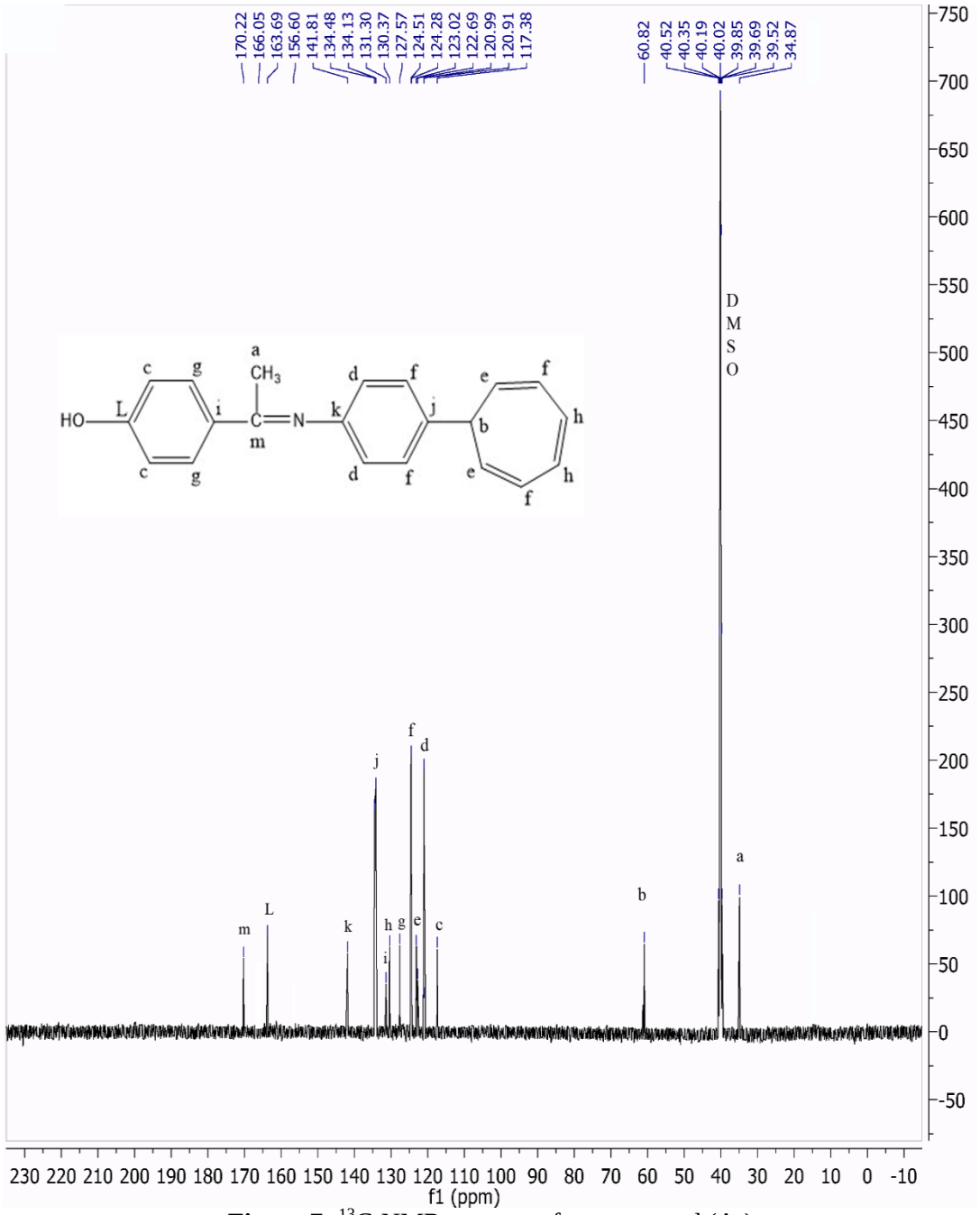


Figure 7- ^{13}C-NMR spectrum for compound (A_3)

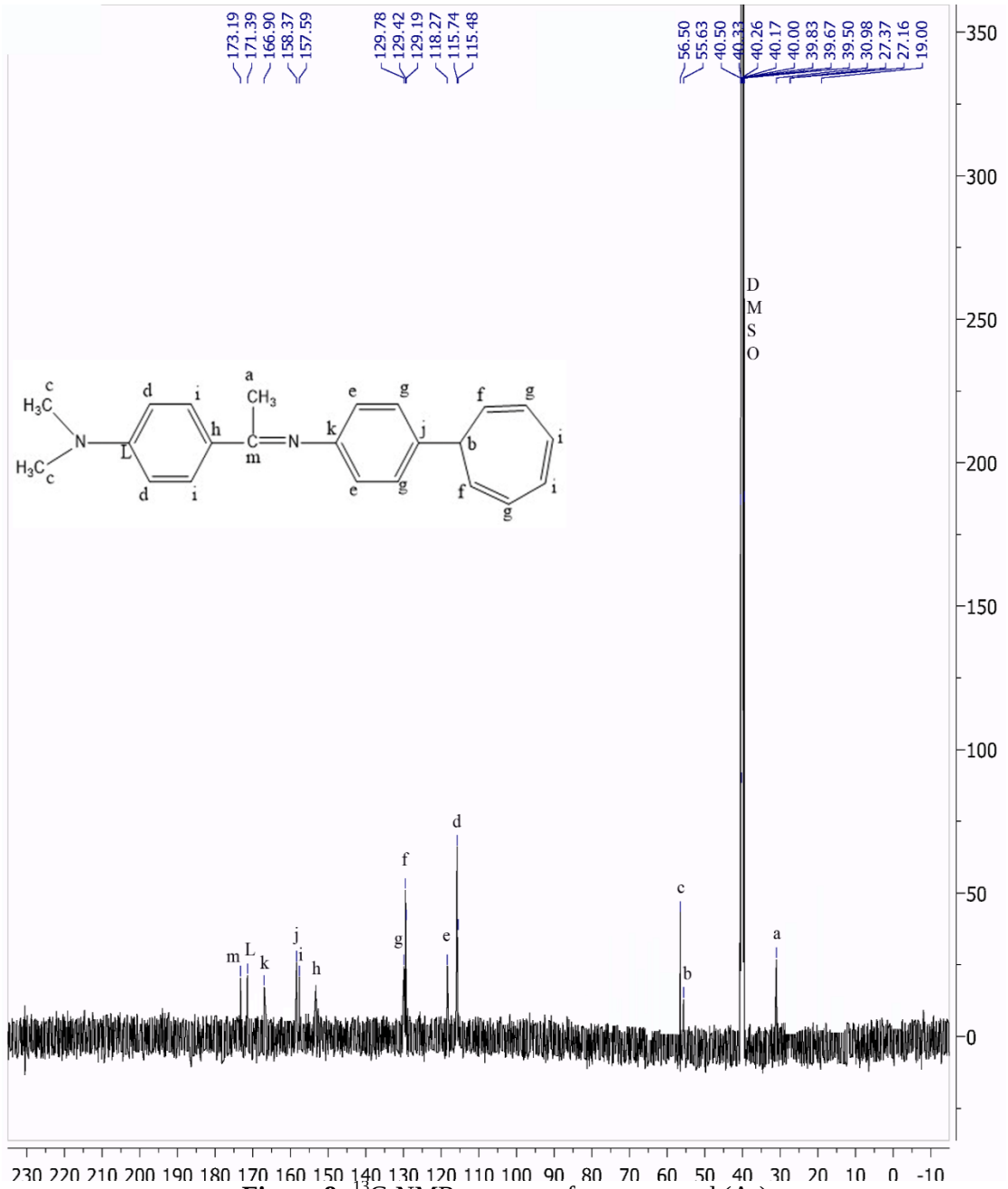


Figure 8- ^{13}C-NMR spectrum for compound (A_4)

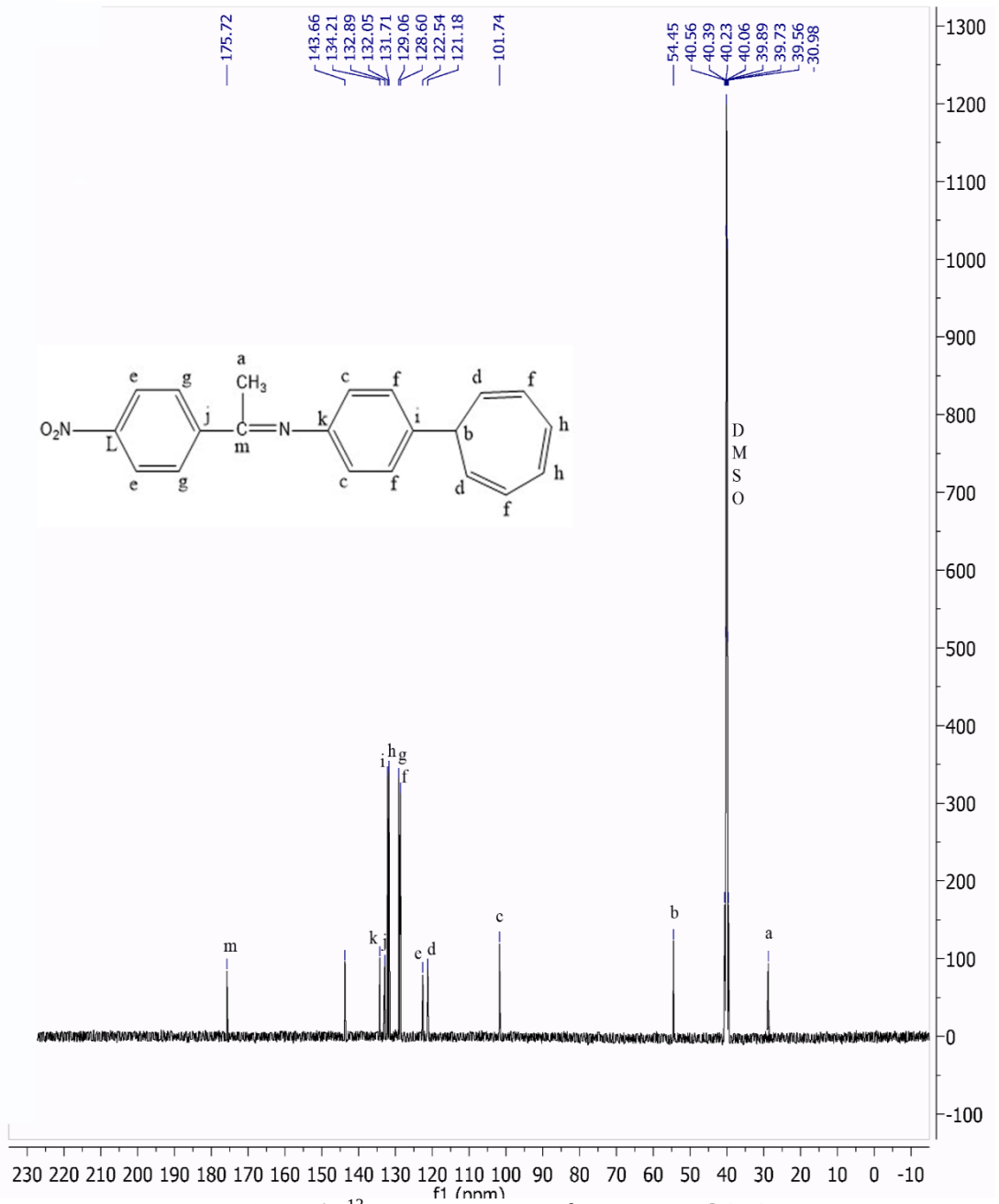


Figure 9- ^{13}C-NMR spectrum for compound (A_5)

5. Biological activities of the produced compounds

In our work, the new series of tropylated azomethines derivatives revealed powerful antibacterial and antifungal activities when compared with those of the standard drug Neomycin.

The minimum inhibition value by using the gained tropylated azomethine (A_3) was 10 mg/ml against *Bacillus subtilis* (image 1), while the maximum inhibition was 18 mg/ml against *Staphylococcus aureus* (image 2) and 17 mg/ml against *Candida albicans* (image 3).

The minimum inhibition value for the gained tropylated azomethine (A_4) was 11 mg/ml against *Bacillus subtilis* (image 4), while the maximum inhibition was 17 mg/ml against ***S**taphylococcus **a**ureus* (image 5) and 14 mg/ml against *Candida albicans* (image 6). The minimum inhibition for the gained tropylated azomethine (A_5) was 10 mg/ml against *Bacillus pumilus* (image 7) while the maximum inhibition was 14 mg/ml against *Staphylococcus aureus* (image 8) and 18 mg/ml against *Candida albicans* (image 9).

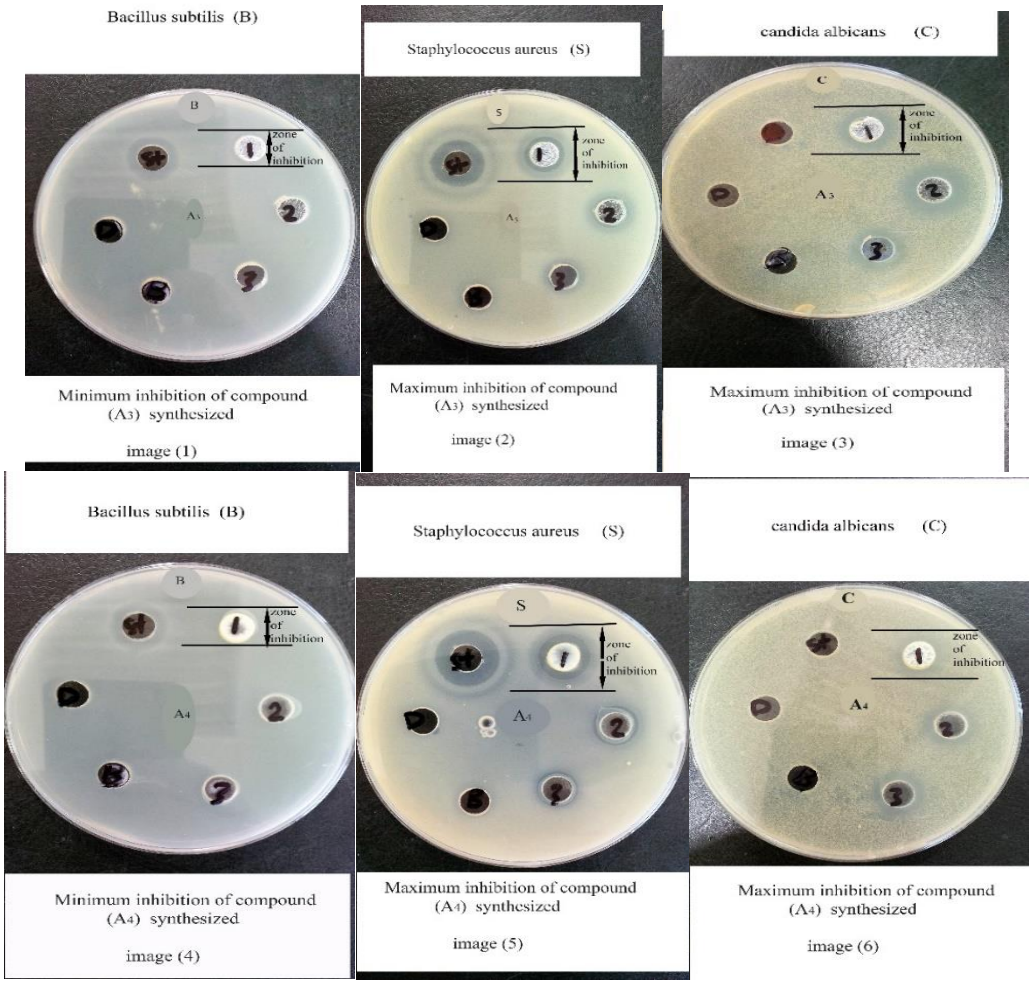
Tropylated azomethine (A_6) was inactive against *Bacillus subtilis* (image 10) while the maximum

inhibition was 17 mg/ml against *Staphylococcus aureus* (image 11) and 12 mg/ml against *Candida albicans* (image 12).

Table 7- Results of antibacterial and antifungal activity for the synthesized compounds (A_3-A_6)

Compound no.	Bacillus subtilis (B)				Bacillus pumilus (E)				Staphylococcus aureus (S)				Candida albicans (C)			
	st. 0.1 mg/mL	25 mg/mL	15 mg/mL	5 mg/mL	st. 0.1 mg/mL	25 mg/mL	15 mg/mL	5 mg/mL	st. 0.1 mg/mL	25 mg/mL	15 mg/mL	5 mg/mL	St.	25 mg/mL	15 mg/mL	5 mg/mL
A_3	15	10	/	/	16	11	10	6	14	18	13	11	/	17	16	11
A_4	15	11	/	/	16	12	8	/	14	17	12	10	/	14	12	11
A_5	15	11	/	/	16	10	9	7	14	14	11	10	/	18	9	9
A_6	15	/	/	/	16	10	8	6	14	17	11	7	/	12	10	7

-Inhibition zone in mm.
- St. is "References Standard USP" = Neomycin (as Sulfate).



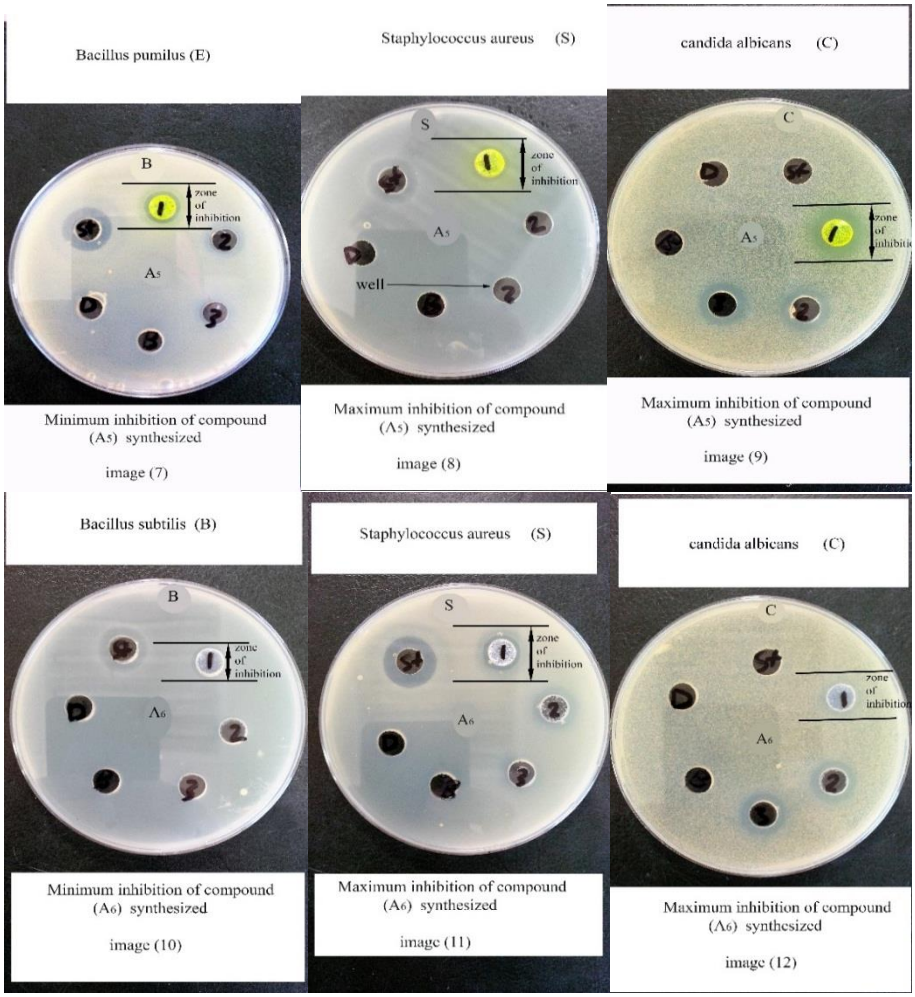


Figure 10-Images showing the biological activities of the synthesized compounds (A_3-A_6)

6. Conclusions

In conclusion, we developed a simple, effective, and attractive protocol to synthesize a new series of tropylated azomethines and tropylated haloaminopyridines in a good yield by simple stirring, short reaction time, and ease of workup. The synthesized tropylated azomethines were characterized by melting point, FT-IR, ^{1}H-NMR and ^{13}C-NMR tests. The compounds (A_3-A_6) were examined for their antibacterial and antifungal activities by the cylinder-plate method against various Gram positive bacteria and fungi (*Candida albicans*). Some of the gained tropylated azomethines revealed significant activities against *Bacillus pumilus* and powerful activities against *Candida albicans* and *Staphylococcus aureus*, in comparison with the effects of the standard drug (Neomycin) at the concentrations employed.

We conclude that azomethines were produced in the first stage and subsequently tropylated, since the compound 4-(cyclohepta-2,4,6-trien-1-yl)aniline could not be isolated and, as a result, aniline could not react with tropylium tetrafluoroborate at the first stage in tetrahydrofuran.

7. Acknowledgements

The authors are thankful to The State Company for Drugs Industry and Medical Appliances, Samarra – Iraq (Sdi) for financial support and provision of reagents.

8. References

1. C. Ronald F. Michael J. McGlinchey, and A. Varadarajan. **1984**."Ring currents, NMR chemical shifts, and homoaromaticity: the homotropylium ion revisited. *Journal of the American Chemical Society*, **106**(20): 5974-5978.
2. J. V .CRIVELLO. **1973**. A Novel and Convenient Preparation of Tropylium Ion Salts. *Synthetic Communications*, **3**(1): 9-12.

3. G. Picotin. **1988**. Synthesis of 7-alkyl-cycloheptatrienes from allylic silanes and tropylium tetrafluoroborate. *Tetrahedron letters* , **29**(46): 5897-5898.

4. L.Yunnikova, P. V. Esenbaeva. **2019**. Modification of Monocarboxylic Acid Hydrazides with Tropylium Salts. *Russian Journal of Organic Chemistry*, **55**(12): 1982-1984.

5. T.Uyen, et al. **2018**. Tropylium-promoted carbonyl–olefin metathesis reactions. *Chemical science*, **9**(23): 5145-5151.

6. L.P.Yunnikova, T. A. Akent'eva, and V.V. Esenbaeva. **2015**. Tropylation of Arylamines and Antimicrobial Activity of 4-(7-Cyclohepta-1,3,5-Trienyl)-*N*-(1-Cyclohepta-2,4,6-Trienyl)Aniline. *Pharm. Chem. J.*, **49**: 243. 2015

7. L. Yunnikova, T. Akentieva and T. Makhova. **2013**. One-Pot Three- Component Synthesis of N-Arylmethyl-4-(7-cyclohepta-1,3,5- trienyl) anilines, *International Journal of Organic Chemistry*, **3**(2): 148-150.

8. G. Picotin and Ph. Miginiac. **1988**. Synthesis of 7-alkyl-cycloheptatrienes from allylic silanes and Tropylium tetrafluoroborate. *Tetrahedron Letters*, **29**(46): 5897-5898.

9. L. P. Yunnikova, T. A. Akentieva, T. V. Makhova and G. A. Aleksandrova. **2012**. "4-(7-Cyclohepta-1,3,5-trienyl)aniline and Derivatives Featured by Antimycobacterial Action, *Butlerov Communications*, **32**(10): 22-26.

10. L. P. Yunnikova, T. A. Akentieva, T. V. Makhova and G. A. Aleksandrova. **2012**. "Synthesis and Antimicrobial Activity of Amines and Imines with a Cycloheptatriene Fragment. *Pharmaceutical Chemistry Journal*, **46**(12): 106-108.

11. M.Fehlinger, W.Abraham. Calix [4] arenes bearing a tropylium substituent as hosts for organic cations. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **58**(3-4): 263-274.

12. L.Yunnikova, P. Likhareva, T. A. Akent'eva. **2017**. Electrophilic tropylation of 2-aminopyridine. *Russian Journal of General Chemistry*, **87**(2): 347-349.

13. M. D. Mashkovskii. Synthesis. **2002**. Antiinflammatory and Analgesic Activity of 4-Antipyrine Derivatives. *Drugs [in Russian]*, Vol. 2, Novaya Volna, Moscow, pp. 432 – 433. 2002

14. E. Matsumura, T. Okabe, T. Fukui, T. Ohe, , N. Ishida, and Y. Inamori, *Biol.* **2004.** Electrophilic Tropylation of Aminopyridines and 4-Aminoquinoline. *Pharm. Bull.* , **27**(10): 1666.

15. S. Marian, H. Marcin, K. Sirichai. **2014**. The Biological Activities of Troponoids and Their Use in Agriculture A Review. *Journal of Horticultural Research*, **22**(1): 5-19.

16. P. Lidia ,Yunnikova, V. Victoria, Esenbaeva. **2018**. Tropylium and tritylium salts in reactions with 2-amino-4, 6-disubstituted pyrimidines. **61**(8): 47-52.

17. L. P. Yunnikova, Yu. E. Likhareva, M. K. Islyaykin, and E. A. Danilova. **2020**. Xanthylium, Thioxanthylium, and Tropylium Salts in Reactions with Imidazole and Benzimidazole. *Russian Journal of Organic Chemistry*. **56**(5): 828–832.

18. B. Steven, R. Boudjouk. **1992**. Trityl tetrakis [3, 5-bis (trifluoromethyl) phenyl] borate: a new hydride abstraction reagent. *The Journal of Organic Chemistry*, **57**(20): 5545-5547.

19. G. Connelly, E .Geiger. **1996**. Chemical redox agents for organometallic chemistry. *Chemical Reviews* , 96.2: 877-910,1996

20. T. A. Akent'eva and R. R. Makhmudov. **2017**. One-Pot Multicomponent Synthesis of 4-(7-Cyclohepta-1,3,5-trienyl)aniline Derivatives. *Russian Journal of General Chemistry.* **87**(7): 1631–1633.

21. L. P. Yunnikova, Yu. E. Likhareva, and V. V. Esenbaeva. **2019**. Electrophilic Tropylation of Aminopyridines and 4-Aminoquinoline. *Russian Journal of General Chemistry*. **89**(9): 1927–1930.

22. R.M. Silverstein, F. X. Webster, D. Kiemle, BryceDL. **2005**. *Spectrometric identification of organic compounds*. 7thed., John Wiley and Sons. New York, US.

23. H.H. Mihsen, S. K. Abass, M. T. Alhasan. **2020**. Synthesis, Characterization and Antimicrobial Activities of Mixed Ligand Complexes of Fe (II), Co(II), Ni(II) and Cu (II) Ions Derived from Imine of Benzidine and o-phenylenediammine. *Iraqi Journal of Science*. **61**(11): 2762-2775.

24. Z. A. Sallal, H. Th. Ghanem. **2018**. Synthesis and Identification of New Oxazepine Derivatives bearing Azo group in their structures. *Iraqi Journal of Science*. **59**(1A): 1-8.