

Synthesis and spectroscopic studies of some Schiff bases derived from Benzidine and their conversion to 1, 3-oxazepine derivatives throughout [2+5] cycloaddition reactions (II) .

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Abstract:

The present work is oriented towards synthesis of some new series of 1,3-oxazepine derivatives through out two pathways .The first one is reaction of Benzidine with different substituted aldehyde such as (p- hydroxyl , p-methoxy, o -bromo benzaldehyde and vaniline) throughout condensation reaction under refluxing condition in presence of absolute ethanol, acidic to produced imines derivatives (w_5-w_8) .The second one is reactions of the prepared imines (w_5-w_8) with maleic and phthalic anhydride under inert N_2 gas and refluxing conditions to produces a new series of 1,3- oxazepine derivatives ($w_5m -w_8m$) and (w_5ph-w_8ph) respectively . All the preparing compounds well monitored and identified by TLC and spectroscopic tools such as IR,¹H-NMR and Elemental analysis.

Key words: imines, benzylidene and 1, 3-oxazepine-4,7-dione :

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الخلاصة :

البحث موجه باتجاه تحضير سلسلة جديدة من مشتقات 3,1- اوكسازيبين من خلال مسارين , الاول ناتج من تفاعل البنزين غير معوض مع بنزليدهيدات مختلفة مثل (بارا -هيدروكسي , بارا -ميثوكسي , أورثو برومو و الفانيلين) ضمن تفاعلات التكاثر التصعيدية وبوجود الايثانول المطلق وحببيات التجفيف بوسط حمضي ليعطي مشتقات اليمين (w_5-w_8) . والمسار الثاني تفاعل اليمينات المحضرة تصعيديا (w_5-w_8) مع انهيدريد المالك والفتاليك بجو خامل من النتروجين ليعطي سلسلة جديدة من مشتقات 3,1- اوكسازيبين ($w_5m -w_8m$) و ($w_5ph -w_8ph$) على التوالي . تم متابعة وتشخيص جميع المركبات المحضرة بواسطة كروماتوغرافيا الطبقة الرقيقة , طيف الاشعة تحت الحمراء , طيف الرنين النووي المغناطيسي للهيدروجين و التحليل العنصري .

Introduction:

It's well know that azomethine of the general formula ($-C=N-$) has a great attention as precursor in huge organic synthesis and biological applications such as cycloaddition reaction, [Mahrath ,et al,2012 , Altemimy, et al,2010], optoelectronic properties [Issam. et al ,2006],dyes and pharmaceuticals [Noha, et al ,2011] , antimicrobial activity [Anand, et al ,2011] , liquid membrane technology [Shamspur T et al;2003], anti-inflammatory[Singh,W.M, et al;1988] ,anticonvulsant [Hemant,et al;2010] , anti tumor[Zitouni , et al;2007], antihypertensive activity[Sharma, et al ;2010] and anti HIV activities [Tarafder, et al ; 2002].Moreover the reactions of azomethine throughout ring closing to generation a wide range of five , six and seven members ring of heterocyclic organic molecules such as 4 - thiazolidinone derivatives [Sharma, et al;2010] , 1,2-Dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-one derivatives [Ahangar , et al; 2010 , Kategoanar, et al;2010 and Tumtin,et al;2010] and 1,3-oxazepinediones [Yeap, et al ;2010] . All of these derivatives of heterocyclic compounds have an importance as pharmaceutical drugs , active substances in biological systems.[(Aiello et al, 2004, Ott et al, 2004 and Smith et al, 2006] and liquid-crystalline compounds [Yeap et al, 2010] . Therefore the synthesis these kinds of organic compounds have became our interesting .

Experimental:

The characterizations of the prepared compounds were accomplished by FT-IR spectra Perkins Elmer with (KBr) disk and an interval ranging from 450- 4400 cm^{-1} . $^1\text{H-NMR}$ spectra was obtained using Bruker 300 MHz spectrometer in the Jordanian University . The samples were in (DMSO d_6) with tetramethylsilane (TMS) as reference .Elemental analysis was carried out using a EuroEA Elemental Analyzer / university of Kufa . Melting points were recorded on a Stuart Scientific- SMP3 apparatus and are uncorrected.

General procedure and spectroscopy:

The mixture of 1 mmole of Benzidine and 2 mmole of substituted aldehyde were heated in presence of approximately 10-15 ml of absolute ethanol with 2 drops of glacial acetic acid in water bath at 70- 80 C for approximately 30-60 min .The process of reaction was followed by TLC , then filtration or evaporation of the solvent then recrystallized from suitable solvent.[Santosh K,et al,2010].

(I) Synthesis of imines derivatives:

1)Bis (4-methoxybenzylidene)biphenyl-4,4'-diamine (w_5):

2 mmole (0.368 gm) of Benzidine was solvated in absolute ethanol with 4 mmole (0.54gm) of p-methoxy benzaldehyde in presence of drops of glacial acetic acid under refluxing for 60 min, yellow-orange precipitate, after work up of compound the percentage yield was (87%), m.p= (255-256) $^{\circ}\text{C}$. IR spectrum show two adsorption bands appear in the range of 2958.90 and 2839.31 cm^{-1} which belong to C-H aromatic and C-H aliphatic respectively , while (-C=N) appear at 1620 cm^{-1} , (C-O-CH₃) appear in the range 1249.91 cm^{-1} , (-C-N) appear at stretching frequency 1168.90 cm^{-1} , beside that the (aromatic C=C) appear at range 1419 – 1573 cm^{-1} . On the other hands $^1\text{H-NMR}$ in DMSO- d_6 as a solvent showed sharp singlet at $\delta = 8.409$ ppm (s,2H) , (dd,4H) at $\delta = 7.82-7.79$ ppm,(dd,4H) of biphenyl at $\delta = 7.47-7.27$ ppm , (d,4H) at $\delta = 7.22-7.05$ ppm ,(d,4H) at $\delta = 7.06 - 6.67$ ppm and (s,6H, 2CH₃) at $\delta = 3.41$ ppm. The elemental analysis of the molecular formula $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$ (calculated /found): (C, 79.98 / 80.51; H, 5.75 / 6.32; N, 6.66 / 7.47)

2) Bis (4-hydroxybenzylidene) biphenyl-4, 4'-diamine (w_6)

2 mmole (0.368gm) of Benzidine was solvated in absolute ethanol with 4 mmole(0.50g) of p-hydroxyl benzaldehyde in presence of drops of glacial acetic acid under refluxing conditions for about 33 min .Orange-brown color of precipitate was obtained , after filtration and drying the (yield = 68 %) and the m.p = (276-278) $^{\circ}\text{C}$, IR data shows two absorption band at 3355- 3290 cm^{-1} (2OH ,phenolic) ,3032-3010 cm^{-1} (C-H ,aromatic) , 1606 cm^{-1} (C=N-) , 1458- 1589 cm^{-1} (C=C , aromatic) , 1255 cm^{-1} (C – O) , and 1165 cm^{-1} (C-N) . The $^1\text{H-NMR}$ in DMSO- d_6 as solvent showed (s,2H,for OH) at $\delta = 10.13$ ppm also (s,2H ,azomethane) at $\delta = 8.40$ ppm and (d,8H) for biphenyl group at $\delta = 7.63-7.80$ ppm and (d,4H) aromatic at $\delta = 7.90 - 8.0$ ppm while (d,4H) aromatic relatively shielded at $\delta = 7.32-7.42$ ppm, beside the sharp singlet at 2.36 ppm represent DMSO solvent . Elemental analysis of the molecular formula $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$ (calculated /found): C, 79.57 /80.32; H, 5.14 / 5.89; N, 7.14 /7.98) .

3) Bis (3-methoxy-4-hydroxybenzylidene) biphenyl-4, 4'-diamine (w_7)

Benzidine 2 mmole (0.368 gm) was dissolved by absolute ethanol then 4 mmole(0.6 g) of vanillin (3-methoxy -4- hydroxyl benzaldehyde) was added in presence of HOAC glacial . This type of reaction needed more time than the others about 2 hr of refluxing after workup bright yellow precipitation observed with m.p= 226 -228 $^{\circ}\text{C}$ and yield = 75% . IR spectra shows the following bands (broad band with weak intense appear at 3423-3396 cm^{-1} (2OH) , 1624 cm^{-1} (-C=N-) , 1429-1585 cm^{-1} (aromatic C=C) , 1284 cm^{-1} (C-O-CH₃) , 1153-1118 cm^{-1} (C-O) , and 1030 cm^{-1} (C-N). $^1\text{H-NMR}$ in DMSO- d_6 showed (s,2H, OH) of phenolic group deshielded at $\delta = 10.23$ ppm ,(s,2H,azomethane) deshielded at $\delta = 8.42$ ppm ,(dd,14H) aromatic groups at $\delta = 7.79-6.67$ ppm and (s,6H)for methoxy groups in meta position at $\delta = 3.40$ ppm . Elemental analysis of the molecular formula $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$ (calculated /found): C, 74.32 /75.23, H, 5.35 / 5.98; N, 6.19 /6.76).

4) Bis (2-bromobenzylidene) biphenyl-4, 4'-diamine (w_8);

2mmole (0.36 gm) of ortho-bromobenzaldehyde and 1 mmole (0.18 g) of Benzidine were dissolved in absolute ethanol with drops of glacial acetic then refluxing for 35 min slightly yellow precipitate with m.p = 184-186 °C was obtained, (yield = 78 %) , IR data shows , weak absorption band at 3053, 2910 cm^{-1} (C-H, aromatic), 1616 cm^{-1} (C=N-), 1435-1593 cm^{-1} (aromatic C=C) ,1024 cm^{-1} (C-O) , sharp peak at 752 cm^{-1} (C-Br) $^1\text{H-NMR}$ in DMSO- d_6 showed (s,2H) at 8.76 ppm refer to azomethane proton , (d,2H,aromatic) which belong to ortho to azomethane at $\delta=8.19$ -8.21 ppm ,(m,12H,aromatic rings) at the rang between $\delta= 7.64$ -7.43 ppm beside (d,2H,aromatic) at $\delta = 7.19$ -7.16 ppm. Elemental analysis of the molecular formula $\text{C}_{26}\text{H}_{18}\text{N}_2\text{Br}_2$ (calculated /found) : (C, 60.26 /61.12; H, 3.50 /4.21; N, 5.41)

II) Cycloaddition Reaction of the imines derivatives with maleic and phthalic anhydride:

General procedure:

1mmole of desired imine's (w_5 - w_8) was dissolved in suitable solvent under N_2 flow, followed by addition with drop wise the cyclic anhydride under refluxing conditions and monitored with TLC to determine the completion of the reaction. Filtration or evaporation under reduces pressure was done and yielded is dried and recrystallized by a proper solvent.[Mahrath A.J. etal, 2012].

* With maleic anhydride

(1) 3, 3'-(biphenyl-4, 4'-diyl) bis (2-(4-methoxyphenyl) -2, 3-dihydro-1, 3-oxazepine-4, 7-Dione) (w_5m)

reaction of 1mmole (0.42g) of compound w_5 was dissolved in dry THF with 2mmole (0.2 g) maleic anhydride adding with drop wise within N_2 flow and stirring under refluxing condition for about 5 hr ,after evaporating the solvent.the oily product was treated with n-Hexane to obtained orange –yellow precipitate with percentage yield = 81.9 % ,m.p = (112-113)°C ,IR spectra shows the following bands ; two stretching absorption bands at 1718 and 1640 cm^{-1} due to (C=O ,ring) , 1604- 1500 cm^{-1} (C=C, aromatic and alkene's) , 1396 cm^{-1} (CH₃-O-C) , 3010-2877 cm^{-1} (C-H , aromatic and alkene's) . Elemental analysis of the molecular formula $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_8$ of the compound w_5m (calculated /found) C, 70.12 / 70.91; H, 4.58 / 5, 32; N, 4.54 /5.11.

(2) 3, 3'-(biphenyl-4, 4'-diyl) bis (2-(4-hydroxyphenyl)-2, 3-dihydro-1, 3-oxazepine-4, 7-Dione) (w_6m)

1mmole (0.39 g) of w_6 in presence of dichloromethane as solvent was reacted with 2mmole (0.2g) of maleic anhydride under drying and refluxing conditions for about 2-3hr . After work up of the reaction mixture give a yellow precipitate with the percentage yield = 82.7% and m.p = (389-390)°C , IR spectra shows as usual two stretching frequency at 1693 and 1626 cm^{-1} which belong to (C=O ,ring) respectively ,3248 cm^{-1} (OH) , 3182 cm^{-1} (C-H ,azomethane) 3055(C-H ,aromatic) 1558 – 1505 cm^{-1} belong to (C=C ,aromatic and alptic) . Elemental analysis for the molecular formula $\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_8$ of the compound w_6m (calculated /found) C , 69.38 / 70.10 ; H , 4.11 / 4.76 ; N, 4.76 / 5.29 .

(3)3, 3'-(biphenyl-4, 4'-diyl) bis (2-(4-hydroxy-3-methoxyphenyl)-2, 3-dihydro-1, 3-oxazepine-4, 7-Dione) (w_7m)

Reaction of (1mmole , 0.45 g) of the compound w_7 in THF with (2mmole ,0.2 g) of maleic anhydride under drying and refluxing conditions for about 3-4 hr .after work up of the reaction mixture an orange precipitate with the percentage yield = 71.3 % , m.p= (385-387,dec)°C , IR-spectra show two sharp absorption bands in the rang of 1695 & 1627 cm^{-1} (C=O ,ester & amide) respectively .broad band stretching at 3433 cm^{-1} (OH) , 3269-3184 cm^{-1} (C-H-Ar) , 3063-3012 cm^{-1} (C-H , aromatic and alkene's) ,1572-1521 cm^{-1} (C=C ,aromatic & alkene's) , 1393 &1327 cm^{-1} (C-O-C , ether and phenolic) respectively .Elemental Analysis of the molecular formula $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_{10}$ (calculated /found) C, 66.66 /67.21 ; H, 4.35 / 4.92 ; N,4.32 / 4.87 .

(4) 3, 3'-(biphenyl-4, 4'-diyl) bis (2-(2-bromophenyl)-2, 3-dihydro-1, 3-oxazepine-4, 7-Dione) (w_8m).

2.1 mmole (0.20 g) maleic anhydride in 12 ml dichloromethane was added drop wise with stirring to 1 mmole (0.50 g) of w_8 under drying by N_2 flow and refluxing conditions . after 3.5 hr work up the reaction mixture to

obtain a yellow precipitate with percentage yield = 55.7 % ,and m.p = (200-202)C°. From IR spectra two medium sharp bands observed at 1693 and 1627 cm⁻¹ belong to (C=O , ester and amide) respectively , 3055 & 3010 cm⁻¹ (C-H ,aromatic and aliphatic), 1560- 1521 cm⁻¹ (C=C , aromatic and aliphatic) , 1257 cm⁻¹ (C-O) and medium sharp band at 831 cm⁻¹ (C-Br) . on the other hand ¹H-NMR- in (DMSO) solvent showed clearly (d,2H,alkene) at δ= 6.64-6.77 ppm and (d,2H,alkene) at δ= 7.16-7.19 ppm, (s,2H,heterocyclic ring) at 9.82-9.90 ppm beside (m ,6H) aromatic at δ= 7.47 -7.58 ppm, (d,2H) aromatic near C-Br bond appear at δ= 7.61-7.64 ppm and (dd,8H) aromatic appear at δ=7.77- 7.97 ppm and finally sharp singlet peak for DMSO solvent at δ =2.50 -2.54 ppm . Elemental Analysis of the molecular formula C₃₄H₂₂Br₂N₂O₆ (calculated /found) C, 57.17 /57.98; H, 3.10 /4.21; N, 3.92 / 4.55.

****With phthalic anhydride:**

(5) 4, 4'-(biphenyl-4, 4'-diyl) bis (3-(4-methoxyphenyl)-3, 4-dihydrobenzo[e] [1, 3] oxazepine-1, 5-dione) (w₅ph)

Reaction of 1mmole (0.42 g) of compound w₅ with 2mmole (0.3 g) phthalic anhydride in presence of THF as a solvent with stirring and refluxing conditions and dried after 7hr ,work up the reaction mixture ,evaporation of the solvent and treated the oily mixture with dioxin and petroleum ether (40-60C°) directly a precipitate observed with percentage yield = 72.7% , m.p=(82-83)C° ,IR –spectra shown two stretching absorption at 1718 and 1604 cm⁻¹ due to (C=O, ring) of the oxazepine ring , 1522-1505 cm⁻¹ (C=C, aromatic) 2958- 2875 cm⁻¹ (C-H , aromatic and aliphatic),1288-1259 cm⁻¹ (CH₃-O-C , C-O-C) . Elemental analysis of the molecular formula: C₄₄H₃₂N₂O₈ (calculated /found) C, 73.73 / 74.32; H, 4.50 / 4.91; N, 3.91 / 4.25 .

(6) 4,4'-(biphenyl-4,4'-diyl) bis (3-(4-hydroxyphenyl) -3,4-dihydrobenzo [1,3] oxazepine - 1,5-dione) (w₆ph)

Dissolve 1mmole (0.392 gm) of compound w₆ in CH₂Cl₂ ,and 2mmole (0.3 gm) of phthalic anhydride adding drop wise with stirring under refluxing and drying condition for about 5.3 hr , when the reaction completion, work up to produce brown precipitate with percentage yield = 87% and m.p =313-315C°dec.IR spectra showed broad band of (OH) group in the stretching frequency 3352 cm⁻¹ and two absorption bands at 1712 and 1658cm⁻¹ which belong to (C=O ester and amide), 3034 to 2926 cm⁻¹(C-H ,aromatic) ,1597-1502 cm⁻¹ (C=C ,aromatic) , 1301 and 1255 cm⁻¹ (O-C-O and -N-C) , and 1170 cm⁻¹(C-O). Elemental analysis of the molecular formula C₄₂H₂₈N₂O₈ (calculated / found) C, 73.25 / 73.76; H, 4.10 / 4.98; N, 4.07 / 4.31 .

(7) 4, 4'-(biphenyl-4, 4'-diyl) bis (3-(4-hydroxy-3-methoxyphenyl)-3, 4-dihydrobenzo [1, 3] oxazepine-1, 5-dione) (w₇ph)

In 12 ml THF 1mmole (0.45 g) of compound w₇ with stirring then added 2 equivalent mmole of phthalic anhydride (0.3 g) drop wise under refluxing and N₂ drying condition. After 6hr evaporating the solvent directly precipitate observed ,filtration and drying under vacuum to yielded about 57% , m.p= (205-207)C° .IR spectra shown the following bands , broad absorption band at 3396 cm⁻¹ (2OH) phenolic ;1699 and 1606 cm⁻¹ (C=O) ester and amide carbonyl , 3036 cm⁻¹ (C-H) aromatic , 2947-2891 cm⁻¹ (C-H) alkene's , 1500 cm⁻¹(C=C) aromatic , 1332 cm⁻¹ (CH₃-O-C) , on the other hand Elemental analysis of the molecular formula , C₄₄H₃₂N₂O₁₀ (calculated / found) C 70.58 / 71.21; H, 4.31 / 4.76 ; N, 3.74 / 4.13 .

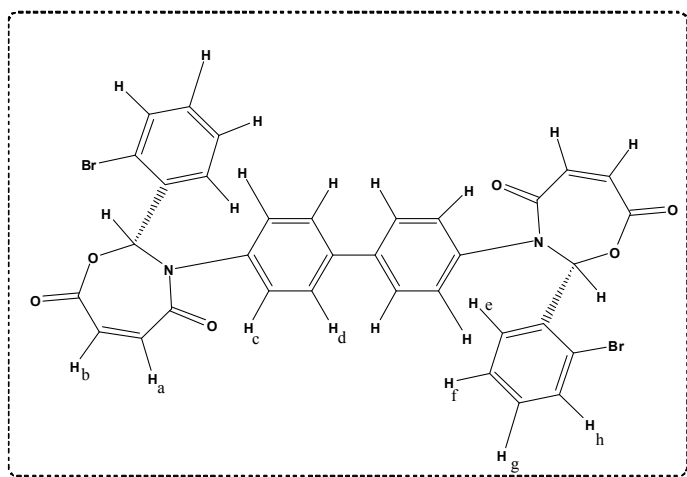
8) 4, 4'-(biphenyl-4, 4'-diyl) bis (3-(2-bromophenyl)-3, 4-dihydrobenzo [1, 3] oxazepine -1, 5- Dione) (w₈ph)

1mmole (0.51g) of compound w₈ dissolved in dioxin with stirring, then adding to 2.0 mmole(0.3 g) phthalic anhydride drop wise under refluxing and N₂ flow condition for about 3hr .after completion of reaction and evaporation of the solvent ,treated the oily compound with n-hexane directly orange – yellow precipitate observed with percentage yield = 68.7% , and m.p=387 C°dec. Infra red spectra showed as usual two stretching absorption bands coupled at 1699 and 1634 cm⁻¹ (C=O, ester and amide) 3059-2926 cm⁻¹ (C-H , aromatic) 1527-1502 cm⁻¹ (C=C ,aromatic) 1321and 1280 cm⁻¹ (C-O-C ,for both side) and 738 cm⁻¹ (C-Br). Elemental

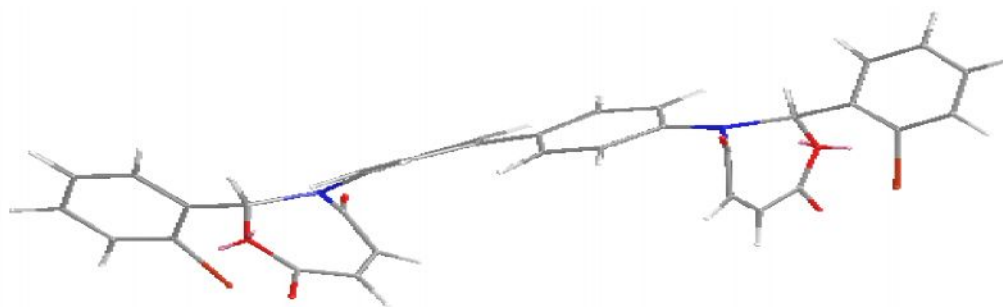
analysis of the molecular formula $C_{42}H_{26}Br_2N_2O_6$ of the compound w_8ph was (calculated / found) C, 61.94 / 62.64; H, 3.22 / 3.87; N, 3.44 / 4.82.

Discussion :

It's well known that 1,3-oxazepine-4,7-dione is a seven-member ring containing nitrogen, oxygen and two carbonyl groups. In previous work a series of 1,3-oxazepine derivatives were prepared from substituted imines with maleic and phthalic anhydride throughout concerted reaction of the type (2+5) cyclization reaction [Mahrath et al, 2012]. In the same manner a new series of imines were prepared via condensation reaction of Benzidine with substituted aromatic aldehyde in presence of absolute ethanol and glacial acetic acid (w_5-w_8) (*scheme 1*). The prepared compounds in *scheme 1* were reacted with each of maleic and phthalic anhydride to forming seven member ring of oxazepine derivatives (w_5m-w_8m) and (w_5ph-w_8ph) respectively (*scheme 2*). The structures of the prepared compounds were determined on the basis of their FT-IR, 1H -NMR and Elemental analysis data. Recall to the generation of azomethine derivatives (w_5-w_8). IR-spectra of compounds showed appearance of azomethane group in the range of $1616 - 1624\text{ cm}^{-1}$ and disappearance of (NH_2) absorption bands in the range $3460-3250\text{ cm}^{-1}$ which were belonging to asymmetric and symmetric stretching frequency of NH_2 . beside to the presence of OH group in case of w_6 and w_7 which appear clearly in the range of $3419-3424\text{ cm}^{-1}$ (**figure 2**). On the other hand 1H -NMR spectra confirmed the chemical structure azomethine compounds. such as for compound ($w_5, w_6, w_7, \text{and } w_8$) in the (**figure 2-6**). For instance 1H -NMR in $DMSO-d_6$ of compound w_6 shows sharp singlet peak in 10.10 ppm which belong to two (OH) phenolic groups which clearly deshielded and disappearance when D_2O was used leading to exchangeable (O-H to O-D). Also the singlet peak at 8.45 ppm is assigned to the proton of azomethine (CH=N-) group [Issam, 2006,]. The azomethine group appeared at higher field, i.e deshielded because the nitrogen atom is bonded to an aromatic ring and the nitrogen has a lone pair of electrons that enables it to delocalize into the aromatic ring. On the other hand reaction of azomethine with cyclic anhydride goes through out cycloaddition reaction between imine ($-N=C-$) and five membered ring of the maleic anhydride, i.e (2+5) concerted cyclization reaction [Cary, etal, 2007]. IR spectra of these compounds (w_5m-w_8m) showed clearly disappearance of stretching absorption bands of imine groups at $1616-1624\text{ cm}^{-1}$ and appearance of two sharp (medium-strong) stretching absorption bands at range of $1626 - 1718\text{ cm}^{-1}$ which belong to (C=O) for amide and ester in the seven membered oxazepine ring, **figure (7,8, and 9)**. also the 1H -NMR spectra clarified the formation of oxazepine ring as example formation of compound w_8m , **figure (10)** showed clearly (d,2H) of alkene type H_a in the two rings appear at $\delta = 6.64-6.77\text{ ppm}$ and another (d,2H) of alkene type H_b in the two rings which appear at $\delta = 7.16-7.19\text{ ppm}$. On the other hand sharp singlet peak of two protons of chiral center of oxazepine rings appear at $\delta = 9.84-9.90\text{ ppm}$ which clearly deshielded beside the rest of peaks (m,6H) aromatic at $\delta = 7.47-7.58\text{ ppm}$, (d,2H) aromatic H_h appear at $\delta = 7.61-7.64\text{ ppm}$ and (dd,8H) H_d, H_c aromatic appear at $\delta = 7.77-7.97\text{ ppm}$. unfortunately the rest of 1H -NMR spectra of other compound are not reach yet.

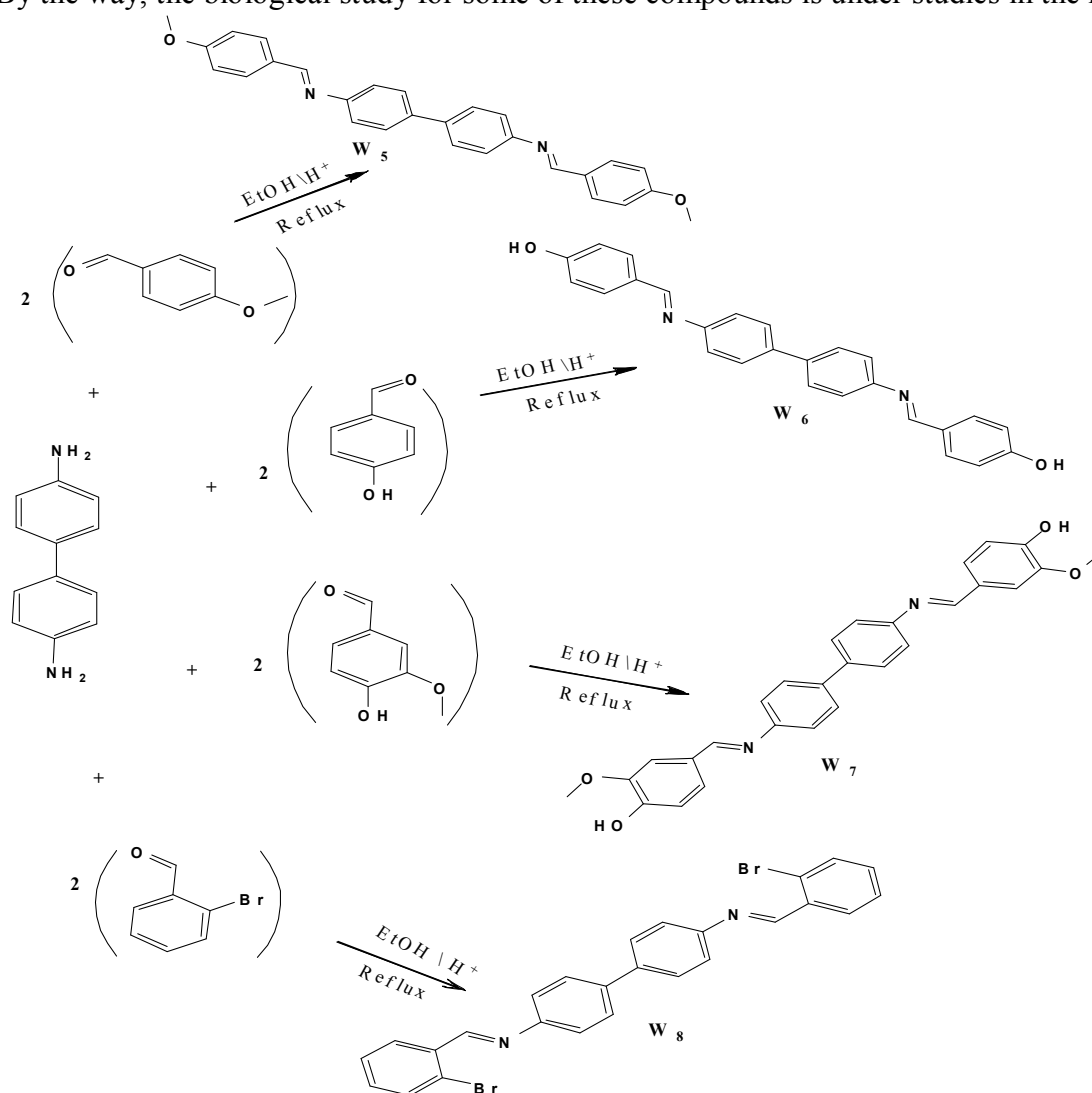


Compound (w_8m)

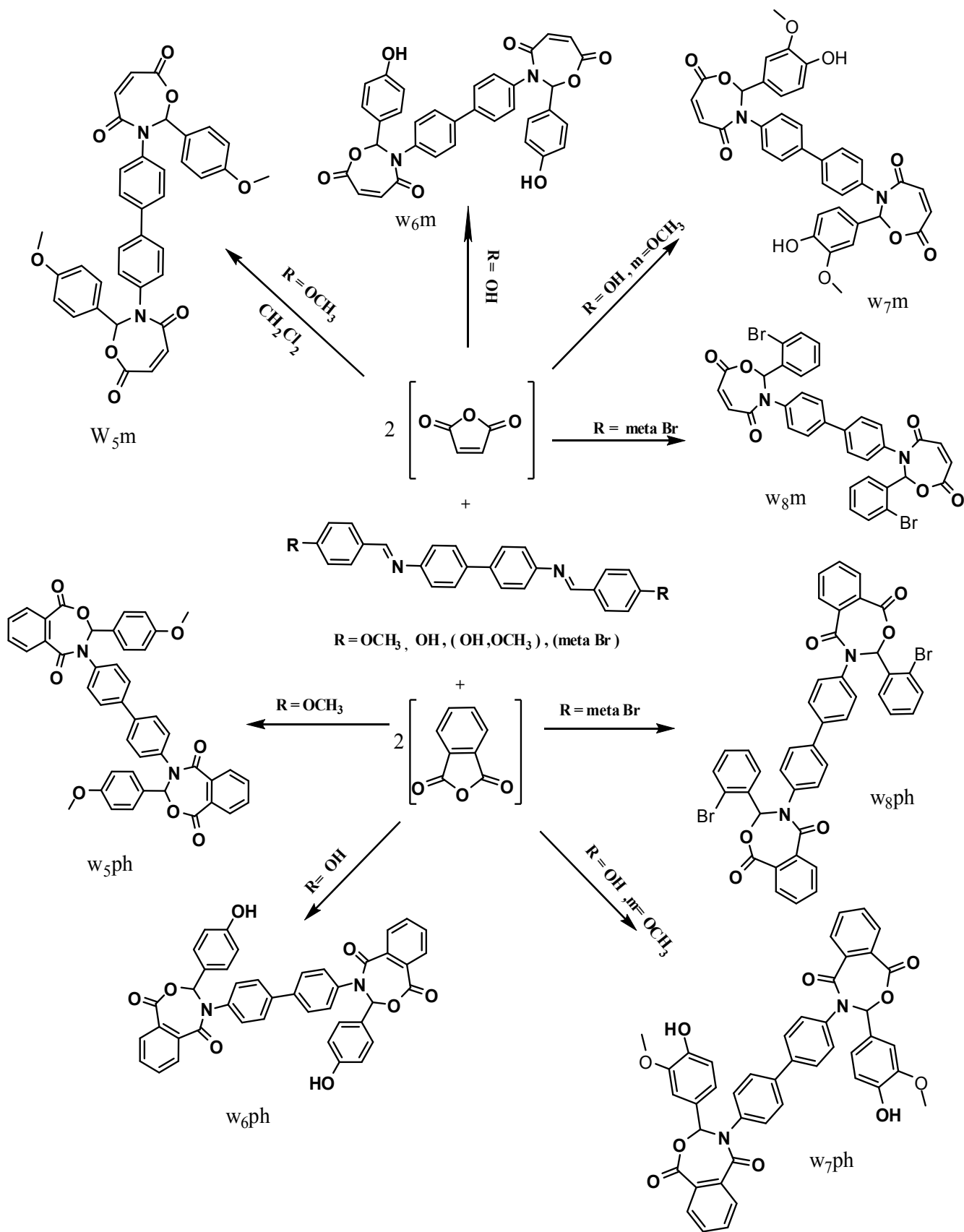


(3D view of compound w_8m)

Also elemental analysis of the prepared compounds were agreement with calculated value .on the other hand the default structure of (w_8m)compound in 3D view shows the orientation of oxazepine rings in perpendicular of plane of the symmetry of biphenyl molecule which give an indication that there is no steric factor between Br atom and proton of oxazepine ring.The only disadvantage was long time of reaction and low percentage yield. By the way, the biological study for some of these compounds is under studies in the near future.



(Scheme 1: Generation of imine derivatives (w_5 - w_8))



(Scheme 2: Generation of Oxazepine derivatives w_5m-w_8m and w_5ph-w_8ph)

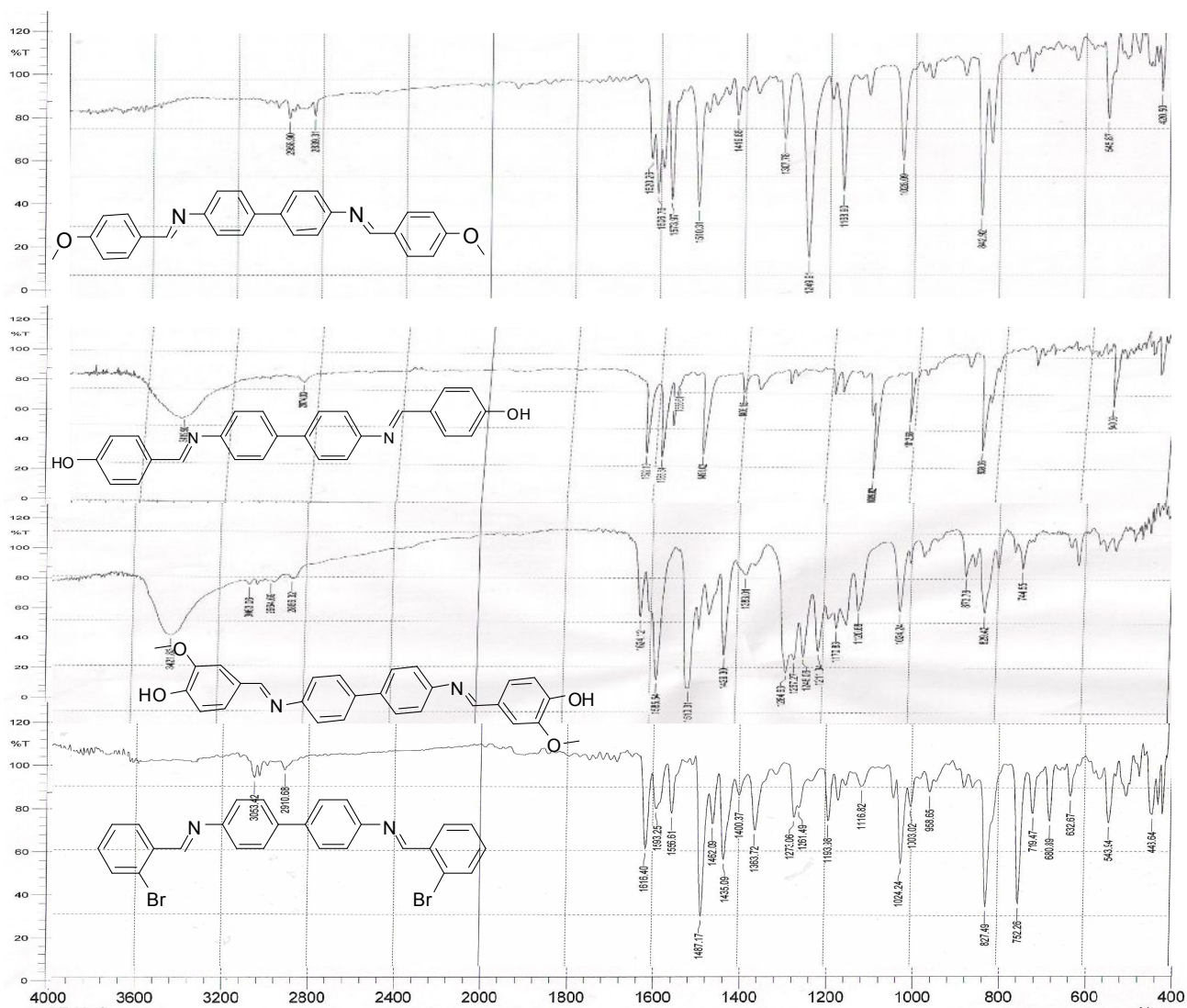


Figure (1) IR-spectrum of compounds (w₅-w₈)

W₅ : bis(4-methoxybenzylidene)biphenyl-4,4'-diamine .

W₆: Bis (4-hydroxybenzylidene) biphenyl-4, 4'-diamine .

W₇ : Bis (3-methoxy-4-hydroxybenzylidene) biphenyl-4, 4'-diamine .

W₈ : Bis (2-bromobenzylidene) biphenyl-4, 4'-diamine .

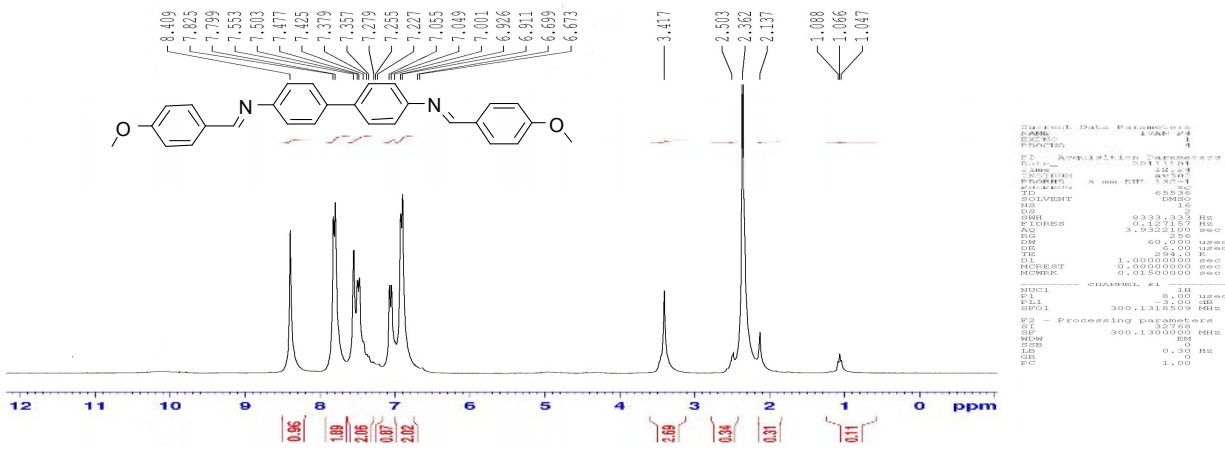


Figure (2) : ¹H-NMR spectrum of bis(4-methoxybenzylidene)biphenyl-4,4'-diamine (**w₅**) in DMSO solvent

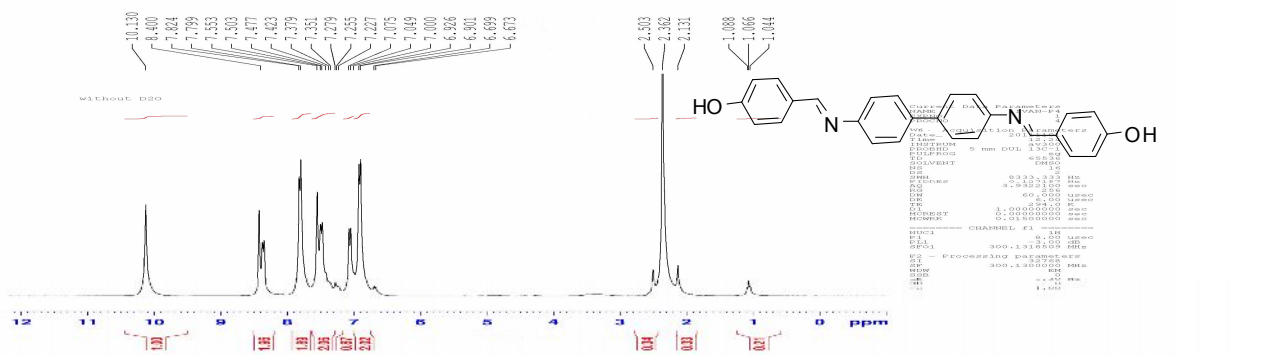


Figure 3: ¹H-NMR-spectra of Bis (4-hydroxybenzylidene) biphenyl -4, 4'-diamine in DMSO-d₆ solvent (**w₆**)

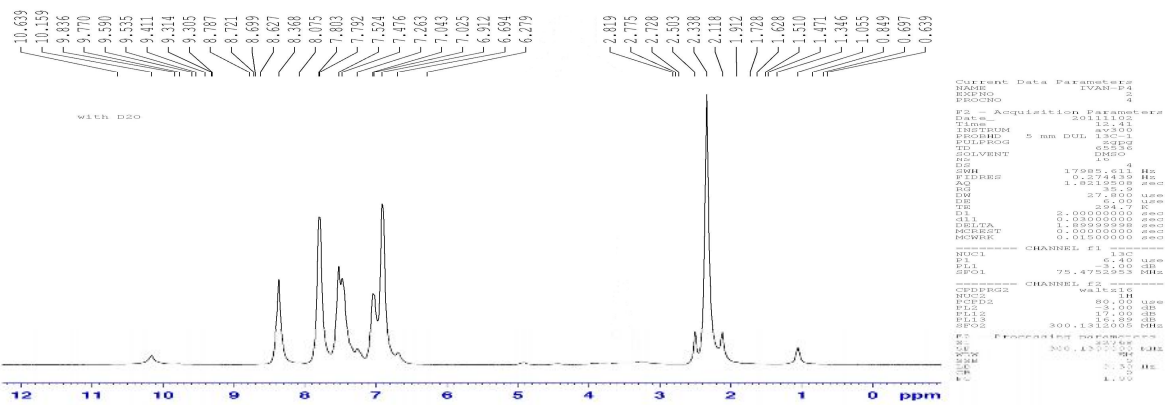


Figure 4: ¹H-NMR-spectra of Bis (4-hydroxybenzylidene) biphenyl -4, 4'-diamine of (**w₆**) with D₂O

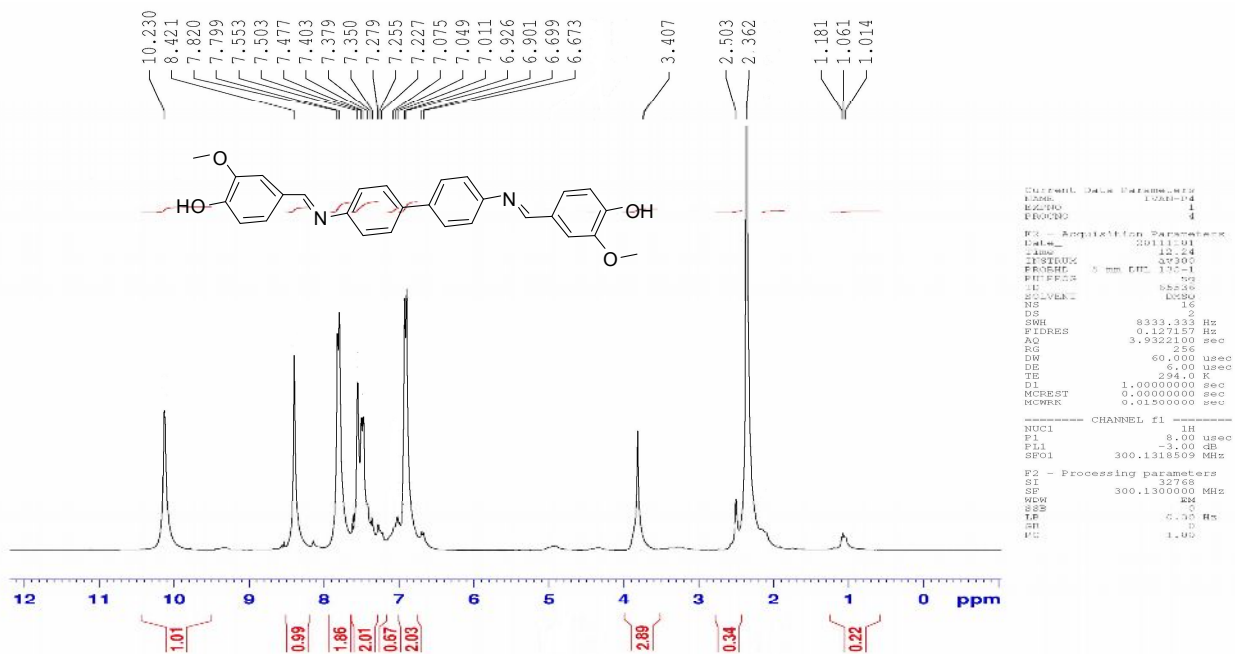


Figure (5) ; ¹H-NMR spectrum of Bis (3-methoxy-4-hydroxybenzylidene) biphenyl-4, 4'-diamine (**w7**) in DMSO-d₆ .

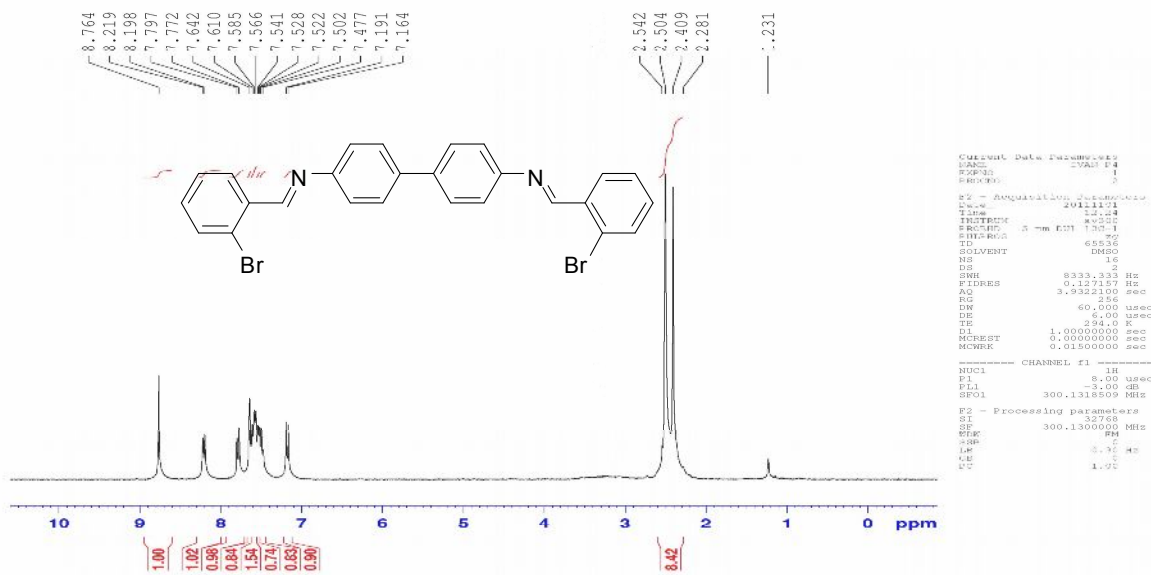


Figure (6) : ¹H-NMR spectrum of Bis (2-bromobenzylidene) biphenyl-4, 4'-diamine (**w8**) in DMSO.

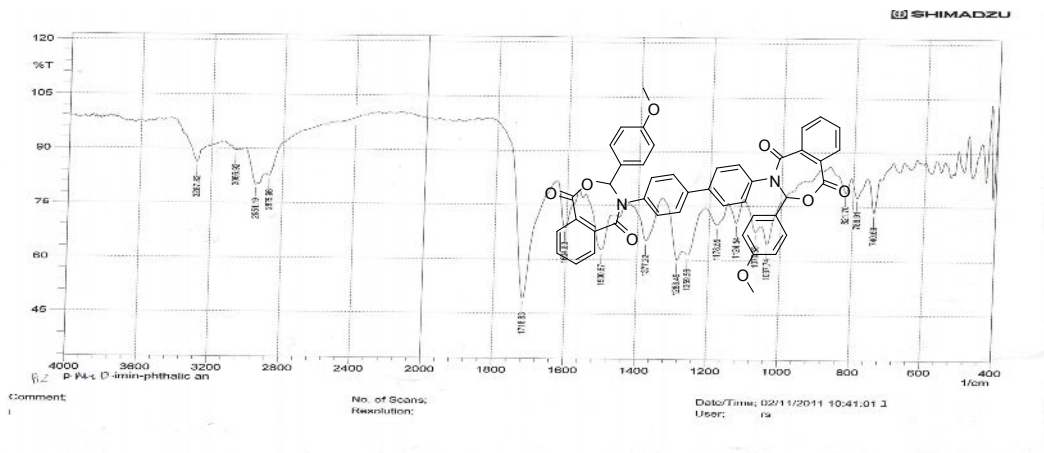


Figure (7) : IR-spectrum of 4,4'-(biphenyl-4,4'-diyl)bis[3-(4-methoxyphenyl)-3,4-dihydrobenzo(1,3) oxazepine-1,5-dione] w_{5ph}

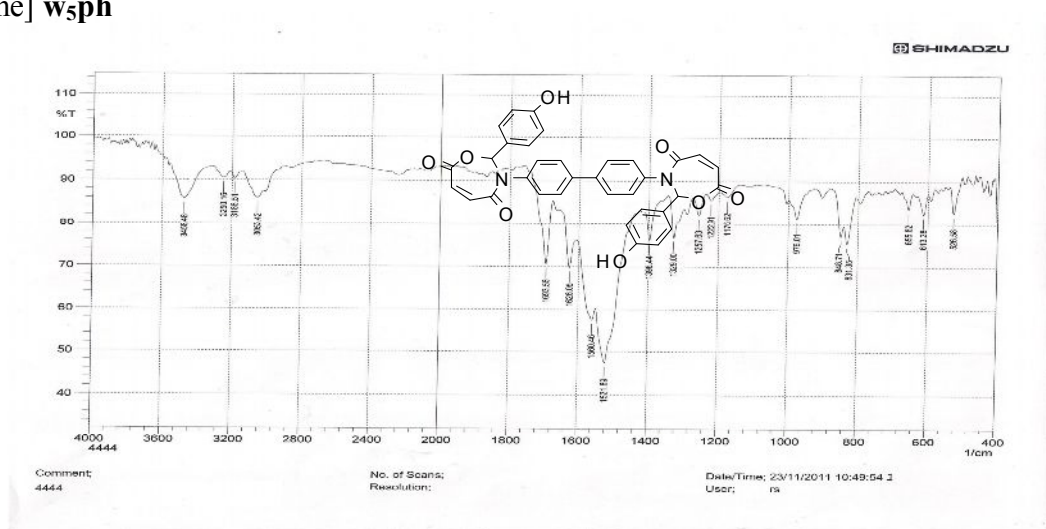


Figure (8) :IR spectrum of 3,3'-(biphenyl-4,4'-diyl)bis(2-(4-hydroxyphenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione) w_{6m}

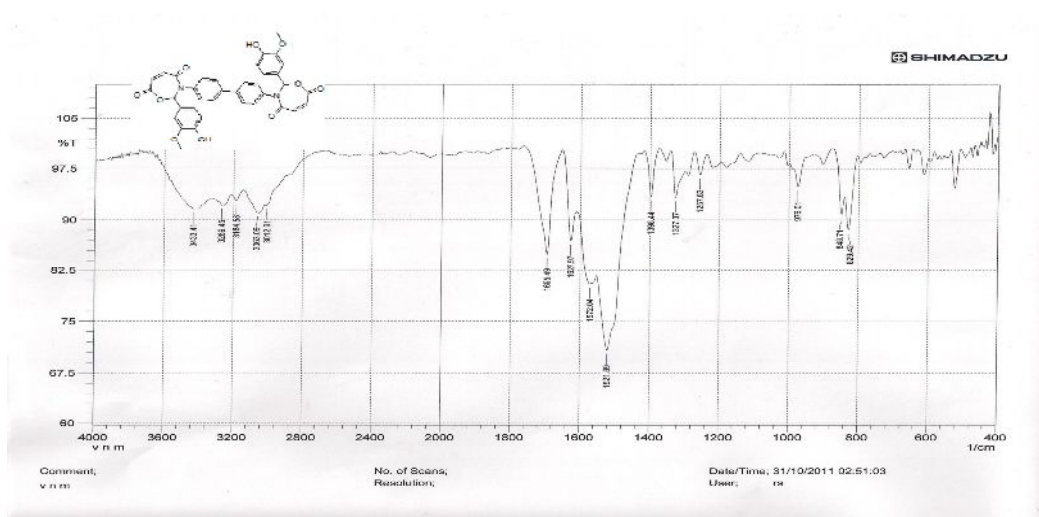


Figure (9): IR-spectrum 3,3'-(biphenyl-4,4'-diyl)bis[2-(4-hydroxy-3-methoxyphenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione] w_{7m} .

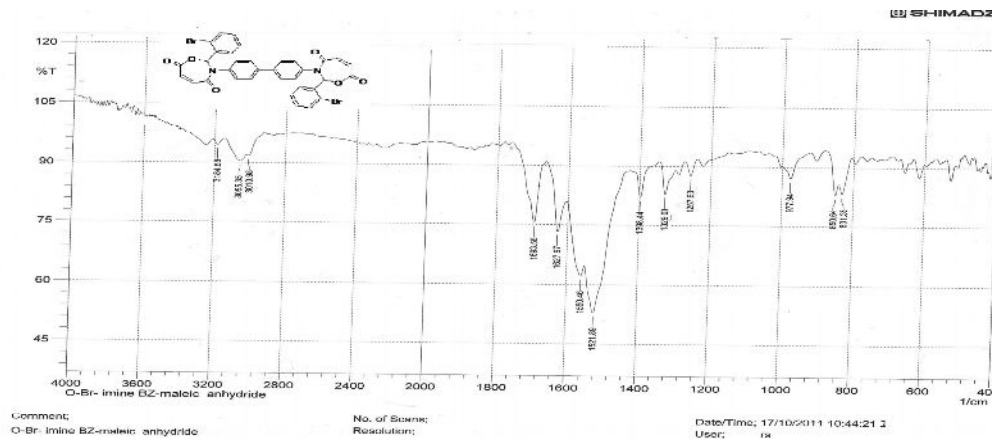
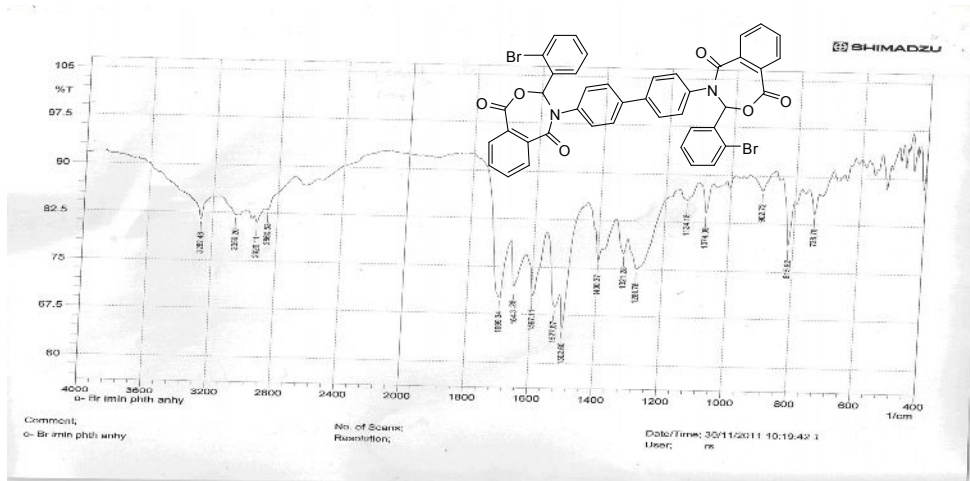


Figure (10): IR-spectrum of 3,3'-(biphenyl-4,4'-diyl)bis[2-(2-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione] w₈m



Figure(11):IR-spectrum of 4,4'-(biphenyl-4,4'-diyl)bis[3-(2-bromophenyl)-3,4- dihydrobenzo (1,3) oxazepine-1,5-dione] w₈ph

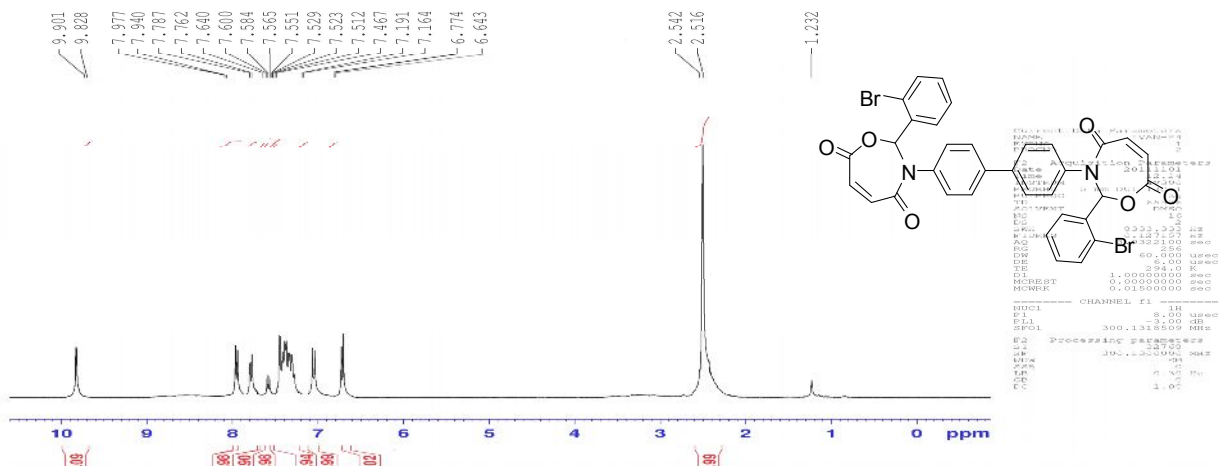


Figure (12):¹H-NMR spectra of 3,3'-(biphenyl-4,4'-diyl)bis[2-(2-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione] in DMSO-d₆ .(w₈m)

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