Synthesis and spectroscopic studies of some new oxazepine derivatives throughout [2+5] cycloaddition reactions (IV)

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Abstract:

The present work included Condensation reactions of O-tolidine with different aromatic aldehyde in absolute ethanol to give Schiff bases **(w_{13}-w_{16})**in high yield which on reaction with maleic and phthalic anhydride by [2+5] cycloaddition reactions in presence of suitable solvents give the corresponding [1,3]oxazepine -4,7-dione **(w_{13}m-w_{16}m)** and [1,3] oxazepine -1,5-dione **(w_{13}ph –w_{16}ph)** respectively. The structure of new synthesized compounds were monitored by T.L.C and established on the basis of elemental analysis , FT-IR and ^{1}H-NMR.

Key words: imines, o-Tolidine and[1, 3]-oxazepine-4,7-dione :
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تحضير ودراسة طيفية لبعض مشتقات الاوكسازبين من خلال تفاعلات الإضافة والغلق الحلقي[٢+٥]

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الخلاصة:

تضمن هذا العمل تفاعلات التكاثف لالديهايدات أرومانية مع الاورثوتولدين في الايثانول المطلق كمذيب ليعطي مشتقات لقواعد شيف **(w_{13}-w_{16})** بمنتوج عالي ، والتي تم مفاعلاتها مع انهيدريد ألماليك والفثاليك بوجود مذيبات مناسبة لتعطي مشتقات الاوكسازبين-٧,٤ دايون **(w_{13}m-w_{16}m)** و ٥,١- دايون **(w_{13}ph –w_{16}ph** على التوالي .تمت متابعة المركبات الحديدة المحضرة بواسطة كروموتوعرافيا الطبقة الرقيقة وأثبتت بالاعتماد على تقنيات التحليل العنصري ، الاشعة تحت الحمراء ، والرنين النووي المغناطيسي للهيدروجين .

Introduction:

o-tolidine is the derivatives of benzidine which belong to an important group of aromatic compounds containing methyl group in 3-position of4,4'-diamino biphenyl[1] .o-tolidine was consider a new regent for a simple nephelometric determination of anionic surfactants and chlorine in greywater[2,3] . also used a semiconducting polymers and a precursor of liquid crystal properties [4,5,6] . In particular the formation of imine derivatives which have great interest due to its proceeding in several important path way reactions[7-9]. Moreover the reactions of imine throughout ring closing to generation a wide range of five , six and seven members ring of heterocyclic organic molecules such as 4-thiazolidinone derivatives[10] , 1,2-Dihydro-1-arylnaphtho[1,2][1,3]oxazine-3-one derivatives[11-13] and 1,3- oxazepinediones[14]. In recent years great attention have been reported toward the formation of oxazepine rings[15,16].due to important of these compounds as pharmaceutical drugs and biological system Based on these papers .all of these derivatives have attracted considerable attention as in drug synthesis and a wide range of pharmaceutical activities. for these purpose indicate that the synthesis of these compounds is interesting.

Experimental

Materials and methods:

The chemicals used in this work were obtained from B.D.H. and they were all pure grade reagents. All melting points were determined in an open capillary and are uncorrected. The solvents , ethanol , methanol dichloromethane ,tetrahydrofurane , ether and acetone were purified according to the literature [17]. 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}H-NMR spectra was obtained using Bruker 300 MHz spectrometer in the Jordanian University and Glasgow university . The samples were in (DMSO d_6)and $CDCl_3$ with tetramethylsilane (TMS) as internal reference .Elemental analysis was carried out using a EuroEA Elemental Analyzer / university of Kufa .

1:General procedure for synthesis of imines derivatives by *Schotten-Baumann Reaction)* (w_{13}-w_{16}).

The mixture of 1mmole of o-tolidine (0.21gm) and 2 mmole of substituted aromatic aldehyde (p-chloro ,p-methoy , o-bromo and p-hydroxy benzaldehyde) were heated in presence of approximately (10-15 ml) of absolute ethanol with drops of glacial acetic acid in water bath at 70- 80 C° for approximately 30-40 min .The process of reaction was followed by TLC , then filtration or evaporation of the solvent under reduce pressure followed by recrystalization from suitable solvent[18].

1.1. synthesis of bis (4-chloro benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine (W_{13}).

2mmole,(0.42gm) of O-tolidine in absolute ethanol added to 4 mmole,(0.56 gm) of 4-chloro benzaldehyde in presence of drops of glacial acetic acid under refluxing for 20 min. an solid yellow mixture observed after work up with section filtration yielded 65% with m.p =156-157 C°,IR-spectra show stretching absorption broad band at 3312 cm^{-1} refer to OH group ,3154-2874 cm^{-1} (CH aromatic and alphatic)respectively, while imine band appear in about 1622 cm^{-1} , (C=C)aromatic appear in the range of 1487-1589 cm^{-1}, medium intensity of band appear at 1165 cm^{-1} refer to (C-O) and 1085 cm^{-1} refer to (C-N) and 1012 cm^{-1} belong to (Ar-Cl).On the

other hand ^{1}H-NMR in DMSO-d_6 as a solvent show the chemical shift of compound Y_5 as follows: at δ=8.75-ppm (s,2H ,2CH=N-) , δ= 7.90-8.10 ppm (dd,6H,Ar) , δ = 7.71-7.80 ppm (d,,4H,Ar) , δ = 7.59-7.61 ppm (d , 2H, Ar) , δ =7.29-7.44 ppm (d ,2H ,Ar)and sharp singlet peak close to DMSO at δ=2.45 ppm ,(6H ,2CH_3-Ar).On the other hand Elemental Analysis of the molecular formula $C_{28}H_{22}Cl_2N_2$ (calculated / found) :(C, 73.53/ 74.61; H, 4.85/ 5.26; N, 6.12/ 6.68).

1.2. ***synthesis of bis (4-methoxy benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine(W_{14})***

2 moles (0.42 gm) of o-Tolidine in absolute ethanol was added to 4 mmole (0.48 ml) of p-methoxy benzaldehyde then acidified by glacial acetic acid then refluxing for about 30 min . Direct yellow-greent precipitate observed .Workup of the product with percentage yield = 64 % , m.p = 177-178 C° . IR (KBr) cm^{-1} data, of compound Y_6, shows approximately the same infrared of compound Y_5, such as 3010-2839 cm^{-1} refer to (C-H ,Ar and alphatic) , 1626 cm^{-1} (C=N-) , 1479-1605 cm^{-1} (aromatic C=C),1311 cm^{-1} (C-O-C,) 1161 cm^{-1} (C-N-) . ^{1}H-NMR in DMSO-d_6 as a solvent showed sharp singlet at δ = 8.518 ppm (2H ,s)benzylic , at δ =7.82-7.79 ppm,(dd ,6H,Ar) of , at δ= 7.47-7.27 ppm , (d ,4H, Ar) at δ= 7.22-7.05 ppm ,(dd,2H,Ar) at δ= 7.06 -6.67 ppm(d,2H,Ar), at δ=3.86 ppm (s ,6H, 2CH_3O) and at δ= 3.23 ppm (s ,6H, 2CH_3-Ar) Elemental analysis of the molecular formula **$C_{30}H_{28}N_2O_2$** (calculated / found): (C, 80.33/ 80.91; H, 6.29/ 6.87; N, 6.25/6.65).

1.3. ***synthesis of bis (2-bromo benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine(W_{15})***

2 mmole ,0.42 gm of o-Tolidine and 4mmole, (0.72 gm) of o-bromobenzaldehyde both dissolved in absolute ethanol with drops of glacial acetic acid and molecular sieves then refluxing for 30 min slightly yellow precipitate with m.p = 163-164 C° , yield = 89.3 % , IR (KBr) cm^{-1} data shows , weak absorption band at 3055- 2914 cm^{-1} (C-H, aromatic , alphatic) , 1616 cm^{-1} (C=N-) , 1433-1589 cm^{-1} (aromatic C=C) ,1024 cm^{-1} (C-N) , sharp peak at 762 cm^{-1} (C-Br) .^{1}H-NMR in DMSO-d6 spectra showed δ=8.81 ppm (s,2H,2CH=N-) refer to azomethane proton , at δ= 8.09 -8.11 ppm (d ,2H, ,aromatic) ortho to azomethane , δ= 7.66-7.33 ppm (10H, m ,Ar) , at δ = 7.29 -7.19 ppm (2H,d, Ar) ,at δ=2.32 ppm (s,6H,2CH_3-Ar) . Elemental analysis of the molecular formula **$C_{28}H_{22}Br_2N_2$** (calculated /found) :(C, 61.56 /62.12; H, 4.06/ 4.67; N, 5.13/5.68.

1.4. synthesis of bis (4-bromo benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine(W_{16})

2 moles (0.42 gm) of o-Tolidine in absolute ethanol was added to 4 mmole (0.74 gm)of p-bromobenzaldehyde then acidified by glacial acetic acid then refluxing for about 20 min . Direct yellow light precipitate observed .Workup of the product with percentage yield = 91 % , m.p = 163-165 C° . IR data, of compound W_{16}, shows approximately the same infrared of compound W_{14}, such as 3067-2918 cm^{-1} refer to (C-H ,Ar and alphatic) , 1624 cm^{-1} (C=N-), 1485-1583 cm^{-1} (aromatic C=C), 1166 cm^{-1} (C-N-) except stretching absorption at 1008 cm^{-1} which belong to (Ar-Br). Elemental analysis of the molecular formula **$C_{28}H_{22}Br_2N_2$** (calculated / found) C, 61.56 /62.21; H, 4.06/ 4.59; N, 5.13/ 5.62).

Cycloaddition Reaction of the Imines Derivatives Derived From o-Tolidine With Maleic and Phthalic Anhydride:

- With Maleic Anhydride

General procedure :

1mmole of desired imine's **(W_{13}-W_{16})** mentioned in part one was dissolved in suitable solvent under N_2 flow, followed by addition with drop wise the cyclic anhydride (maleic anhydride) under refluxing conditions and monitored with TLC to determine the completion of

the reaction.Filtration or evaporation under reduces pressure and yielded was dried and recrystilized by a proper solvent [8]. The equation in the scheme (5) represent the following general reactions .

2.1.Synthesis of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-chlorophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione) ($W_{13}M$)

reaction of 1mmole (0.47 g) of compound **W_{13}** with 2 mmole (0.20 g) maleic anhydride in dry THF adding with drop wise within N_2 flow and stirring under refluxing condition for about 3.5 hr ,after cooling the reaction mixture an yellow precipitate observed ,section filtration yielded 65 % with m.p =**202-204** C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1712 and 1627 cm^{-1} due to (2 C=O ,ring) , 1450-1575 cm^{-1} (C=C, aromatic and alkene's), 3037-2993 cm^{-1} (C-H , aromatic and alphatic's) in addition to stretching frequency at 3250 cm^{-1} (CH, chiral) in addition to 1126 cm-1 refer to (Ar-Cl) .Mass spectrum shown the molecular ion peak in intensity of (M^+) = 653 (70%) with m/z= 623 ,584 , 407 ,362 ,246 , 133 , 90 ,69(100%) . Elemental analysis of the molecular formula **$C_{36}H_{26}Cl_2N_2O_6$** of the compound $W_{13}M$ (calculated /found) = C, 66.16 / 66.62; H, 4.01/ 4.59; N, 4.29 / 4.82.).

2.2. Synthesis of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-methoxyphenyl) -2,3 -dihydro -1,3-oxazepine-4,7-dione) ($W_{14}M$)

reaction of 1mmole (0.44 g) of compound **W_{14}** with 2 mmole (0.20 g) maleic anhydride in dry dichloromethane adding with drop wise within N_2 flow and stirring under refluxing condition for about 4.0 hr ,after cooling the reaction mixture an yellow precipitate observed ,section filtration yielded 60 % with m.p =212-214C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1712 and 1629 cm^{-1} due to (2 C=O ,ring) , 1410-1580cm^{-1} (C=C, aromatic and alkene's), 3051-2910 cm^{-1} (C-H , aromatic and alphatic's) in addition to stretching frequency at 3192 cm^{-1} (CH, chiral) in addition to (C-O-C) at 1307$cm^{-1.}$ ^{1}H-NMR-DMSO-d6 shown the following peaks at δ =9.57 ppm (s, 2H, chiral ,2CH, oxazepine) , at δ = 7.79- 7.83 ppm (d,2H, Ar) ,at δ = 7.50-7.70 ppm (d,8H, Ar) , at δ = 7.22-7.28 ppm (d ,2H, Ar) , at δ = 6.76 -6.84 ppm (t ,2H, Ar) , at δ = 6.59- 6.71 ppm (d ,4H,2CH=CH-, alkene) at δ = 6.33- 6.36 ppm (d, 4H, 2CH=CH- ,alkene). Mass spectrum shown the molecular ion peak is not observed (M^+) while m/z=629, 573 ,483 ,393,313,217,147, 103,73(100%), 55. Elemental analysis of the ,molecular formula **$C_{38}H_{32}N_2O_8$**of the compound Y_6M (calculated /found) = C, 70.80/ 71.49; H, 5.00/ 5.61; N, 4.35/4.65.

2.3. Synthesis of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(2-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione) ($W_{15}M$).

reaction of 1mmole (0.51 g) of compound **W_{15}** with 2 mmole (0.20 g) maleic anhydride in dry dichloromethane adding with drop wise within N_2 flow and stirring under refluxing condition for about 4.0 hr ,after cooling the reaction mixture an yellow precipitate observed ,section filtration yielded 50 % with m.p = > 250 C° dec .. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1717 and 1621cm^{-1} due to (2 C=O ,ring) , 1430-1589cm^{-1} (C=C, aromatic and alkene's), 3049-2908 cm^{-1} (C-H , aromatic and alphatic's) in addition to stretching frequency at 3215 cm^{-1} (CH, chiral) in addition to (C-O-C) at 1327$cm^{-1.}$ ^{1}H-NMR-DMSO-d6 shown the following peaks at δ =9.27 ppm (s, 2H, chiral ,2CH, oxazepine) , at δ = 7.89- 7.99 ppm (d,2H, Ar) ,at δ = 7.52-7.61 ppm (t, 6H, Ar) , at δ = 7.12-7.23 ppm (t ,6H, Ar) , at δ = 6.55 -6.66 ppm (d ,4H,2CH=CH-, alkene) at δ = 6.29- 6.35 ppm (d, 4H, 2CH=CH- ,alkene). Elemental analysis of the ,molecular formula **$C_{36}H_{26}Br_2N_2O_6$**of the compound $W_{15}M$ (calculated /found) = C, 58.24 /58.76; H, 3.53/4.21; N, 3.77 /4.31.

2.4. Synthesis of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione)($W_{16}M$).

reaction of 1mmole (0.54 g) of compound **W_{16}** with 2 mmole (0.20 g) maleic anhydride in dry dichloromethane adding with drop wise within N_2 flow and stirring under refluxing condition for about 3.0 hr ,after cooling the reaction mixture an yellow precipitate observed ,section filtration yielded 72 % with m.p =220-222 C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1701 and 1627 cm^{-1} due to (2 C=O ,ring) , 1458-1587 cm^{-1} (C=C, aromatic and alkene's), 3049-2903 cm^{-1} (C-H , aromatic and alphatic's) in addition to stretching frequency at 3217 cm^{-1} (CH, chiral) in addition to 825 cm^{-1} refer to (Ar-Br) . .Mass spectrum shown the molecular ion peak is not observed (M^+) , while m/z= 563, 438 ,336 , 256,191 ,121(100%), 105 , 84 . Elemental analysis of the molecular formula **$C_{36}H_{26}Br_2N_2O_6$**of the compound Y_5M (calculated /found) = C, 58.24 /58.81; H, 3.53/ 4.12; N, 3.77/ 4.32).

- **With Phthalic Anhydride :**

General procedure :

1mmole of desired imine's **(W_{13}-W_{16})** mentioned in part one were dissolved in suitable solvent under N_2 flow, followed by addition with drop wise the cyclic anhydride (phthalic anhydride) under refluxing conditions and monitored with TLC to determine the completion of the reaction. Filtration or evaporation under reduces pressure and yielded was dried and recrystilized by a proper solvent [8].

2.5. Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(4-chlorophenyl)-3,4-dihydro benzo [1,3]oxazepine-1,5-dione) (W_{13}Ph).

reaction of 1mmole (0.47 g) of compound **W_{13}** with 2 mmole (0.30 g) phthalic anhydride in dry THF adding with drop wise within N_2 flow and stirring under refluxing condition for about 4.5 hr ,after cooling the reaction mixture an yellow precipitate observed ,section filtration yielded 52 % with m.p =**196-198** C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 171207 and 1656 cm^{-1} due to (2 C=O ,ring) , 1452-1590 cm^{-1} (C=C, aromatic and alkene's), 3012-2956 cm^{-1} (C-H , aromatic and alphatic's) in addition to stretching frequency at 3252 cm^{-1} (CH, chiral) in addition to 1072 cm^{-1} refer to (Ar-Cl) .Mass spectrum shown the molecular ion peak in low intensity of (M^+) = 752 with m/z= 694 ,629 , 564 ,492 ,377 ,261 , 171(100%) ,131 and 91 . Elemental analysis of the molecular formula **$C_{44}H_{30}Cl_2N_2O_6$** of the compound **W_{13}Ph** (calculated /found) = C, 70.12/ 70.69; H, 4.01/4.76 ; N, 3.72/ 4.32.

2.6. Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(4-methoxyphenyl)-3,4-dihydro benzo[1,3]oxazepine-1,5-dione) (W_{14}Ph)

reaction of 1mmole (0.44 g) of compound **W_{15}** with 2 mmole (0.30 g) phthalic anhydride in dry THF adding with drop wise within N_2 flow and stirring under refluxing condition for about 6.0 hr ,after cooling the reaction mixture an oily .when work up hexane –petroleum ether a brown precipitate observed ,section filtration yielded 69% with m.p =149-150 C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1720 and 1680 cm^{-1} due to (2 C=O ,ring) , 1444 -1529 cm^{-1} (C=C, aromatic and alkene's), 2960-2874 cm^{-1} (C-H , aromatic and alphatic's) at stretching frequency at 3092 cm^{-1} (CH, chiral) in addition to (C-O-C) at 1269 cm^{-1} .Mass spectrum shown the molecular ion peak is not observed (M^+) while ,m/z= 629, 573 ,483 ,393,313,217,147, 103,73(100%), 55. Elemental analysis of the ,molecular formula

$C_{46}H_{36}N_2O_8$ of the compound **W_{14}Ph** (calculated /found) = C, 74.18 / 74.43; H, 4.87/ 5.25; N, 3.76 /4.19 .

2.7. Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(2-bromophenyl)-3,4-dihydro benzo[1,3]oxazepine-1,5-dione) (W_{15}Ph).

reaction of 1mmole (0.51 g) of compound **W_{15}** with 2 mmole (0.30 g) phthalic anhydride in dry dioxan adding with drop wise within N_2 flow and stirring under refluxing condition for about 3.0 hr ,after cooling the reaction mixture an oily .when work up hexane an orange –yellow precipitate observed ,section filtration yielded 68 % with m.p =245-246 C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1702and 1664 cm^{-1} due to (2 C=O ,ring) , 1504-1589 cm^{-1} (C=C, aromatic), 2928-2956 cm^{-1} (C-H , aromatic) at stretching frequency at 3061cm^{-1} (CH, chiral) in addition to (C-Br,ortho) at 738 cm^{-1}. ^{1}H-NMR-DMSO-d_6 shown the following peaks at δ =9.16 ppm (s, 2H, chiral ,2CH, oxazepine) , at δ = 8.20- 8.24 ppm (d,2H, Ar-phath.) ,at δ = 7.78-7.85 ppm (d,6H, Ar) , at δ = 7.47-7.65 ppm (m ,10H, Ar) , at δ = 7.15 -7.25 ppm (t ,4H, Ar) .Elemental analysis of the ,molecular formula **$C_{44}H_{30}Br_2N_2O_6$** of the compound **W_{15}Ph** (calculated /found) = C, 62.72/ 63.21; H, 3.593.78; N, 3.32/3.50.

2.8. Synthesis of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(4-bromophenyl)-3,4-dihydro benzo[1,3]oxazepine-1,5-dione).(W_{16}Ph).

reaction of 1mmole (0.54 g) of compound **W_{16}** with 2 mmole (0.30 g) phthalic anhydride in dry THF adding with drop wise within N_2 flow and stirring under refluxing condition for about 4.3 hr ,after evapouration of the reaction mixture an oily product observed ,after work up with petroleum ether 40-60 C° an yellow –orange precipitate observed ,section filtration yielded 63 % with m.p =287-289 C°. IR (KBr) cm^{-1} spectra shows the following bands ; two stretching strong absorption bands at 1716 and 1653 cm^{-1} due to (2 C=O ,ring) , 1442-1579 cm^{-1} (C=C, aromatic and alkene's), 3008-2916 cm^{-1} (C-H , aromatic and alphatic's) in addition to stretching frequency at 3271 cm^{-1} (CH, chiral) in addition to 817 cm^{-1} refer to (Ar-Br) . ^{1}H-NMR-DMSO-d6 shown at δ= 9.82 ppm (s ,2H,2CH, oxazepine ring) ,at δ= 8.43-8.51 ppm (d ,2H, Ar) ,at δ= 7.97- 7.99 ppm (d, 4H ,Ar) , at δ= 7.49 -7.84 ppm(m, 8H ,Ar) ,at δ= 7.05 -7.14 ppm (d,8H, Ar) ,and at δ= 2.26ppm (s ,6H ,2CH_3-Ar). Mass spectrum shown the molecular ion peak is not observed (M^+) = ? while m/z= 563, 438 ,336 , 256,191 ,121(100%), 105 , 84 . Elemental analysis of the molecular formula **$C_{36}H_{26}Br_2N_2O_6$**of the compound **W_{16}Ph** (calculated /found) = C, 62.72 /63.34 ; H, 3.59/ 4.19; N, 3.32/ 3.7).

Discussion :

It's well known that [1,3] oxazepine -4,7-dione or 1,5- dione figure (1) are a heterocyclic seven membered ring containing nitrogen , oxygen and two carbonyl groups.when R1 and R2 = H the component (**A**) known 2,3-dihydro-1,3- oxazepine -4,7-dione whilst (**B)** known 3,4-dihydrobenzo1,3-oxazepine-1,5-dione .many researchers have investigated these types of Heterocyclic compounds due to their important

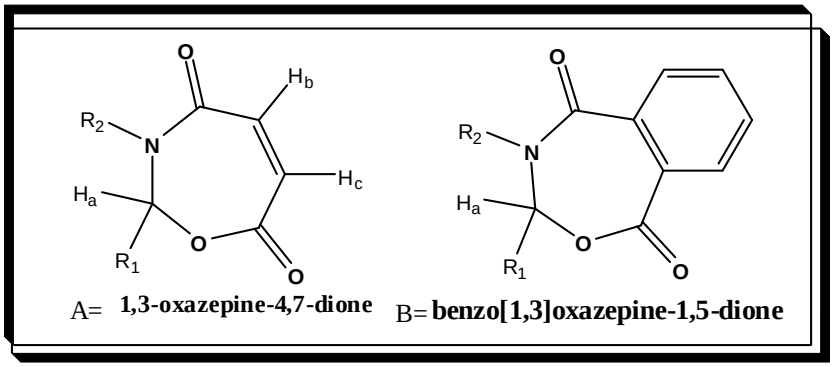
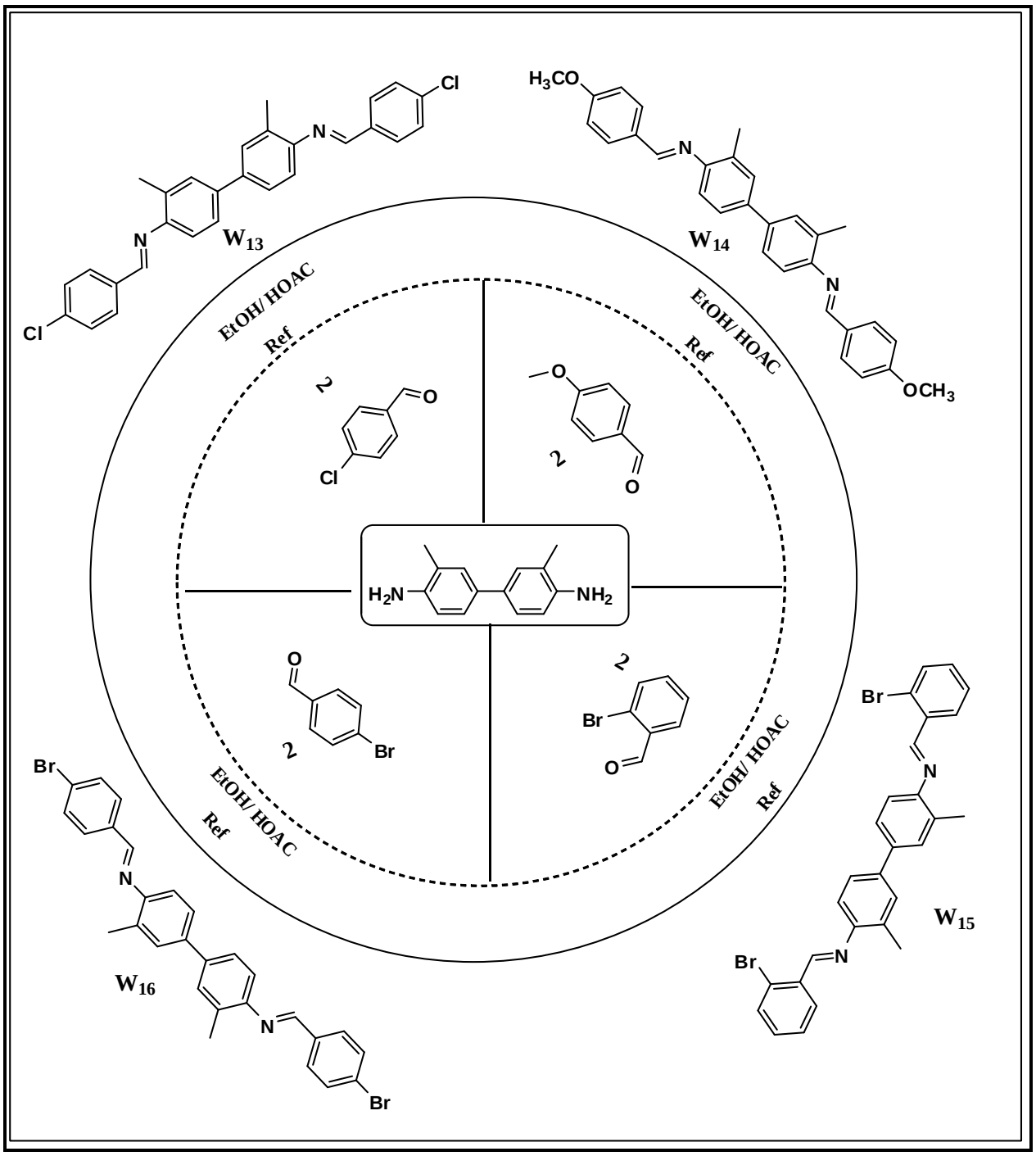
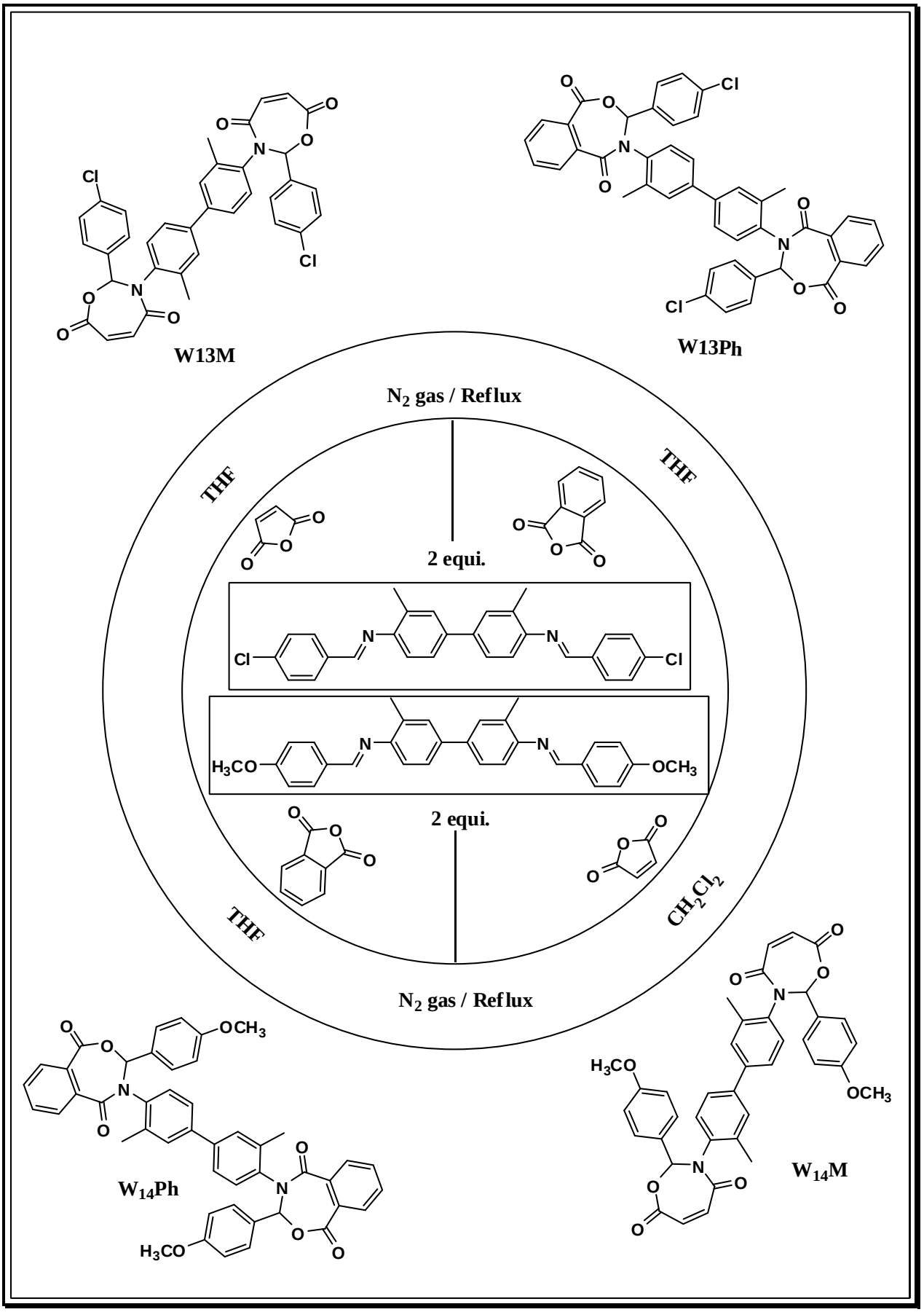


Figure (1): Two types A and B of [1,3] oxazepine – dione .

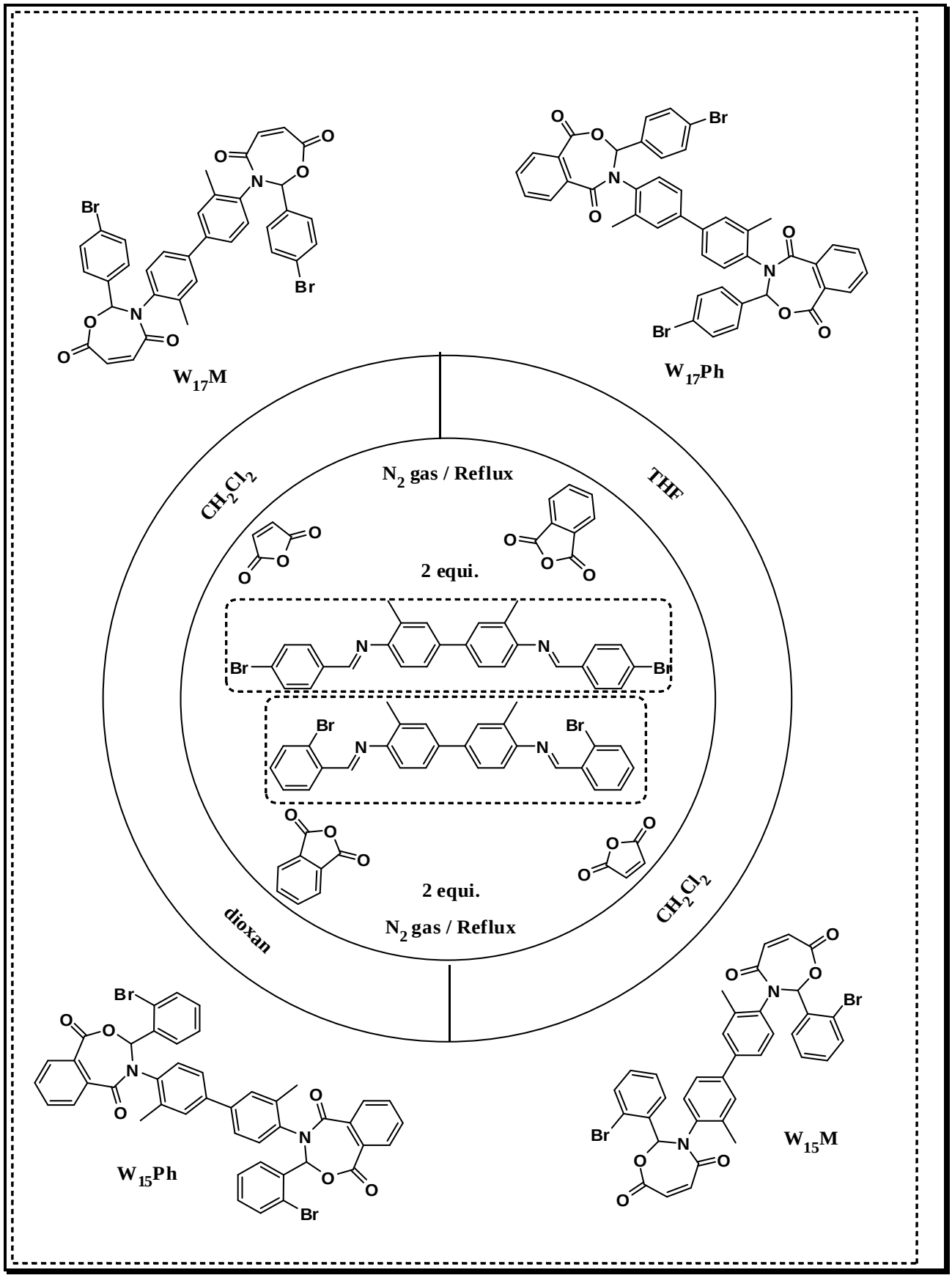
class which have varieties of biological applications [19-21]. Our interesting were to modification of oxazepine rings throughout changing the R_1 and R_2 in 2 and 3 positions and these changing might be make variation in their biological applications. Therefore we starting to create an imine derivatives by using selective aldehyde with O-tolidine under *Schotten-Baumann* reaction **scheme (1)**. All the imines derivatives were monitored by TLC and identified by FT-IR ,^{1}H-NMR and Elemental Analysis. Recall to FT-IR in (KBr) disk .In the first step: the imines derivatives (w_{13}-w_{16})which formed by condensation reaction were proved according to disappearance of (**NH_2**) absorption bands in the range 3462-3255 cm^{-1} which were belonging to asymmetric and symmetric stretching frequency and appearance sharp (strong –medium) intense of azomethane (C=N-) group in the stretching frequency range at 1608 – 1626 cm^{-1}. For instance **figure (2a to 2d) scheme (1)** . On the other hand ^{1}H-NMR in DMSO-d_6 as a solvent confirmed the generation of these compounds, .For compound **W_{13}** its obvious sharp singlet peak appear at δ= 8.32 ppm which belong to 2CH of azomethane groups ,this proton was deshilded due to the effect of nitrogen azomethane and aromatic ring[9]. Also, Elemental analysis gave matching values for calculated and found molecular formula of each compound of **(W_{13}- W_{16}).** The second step involved coupling reaction between azomethane group(imines' derivatives)and two carbonyl groups throughout [2+5] cycloaddition reaction (concerted reaction**) scheme (2&3)**. This type of reaction afforded a seven membered ring **of 1,3-oxazepine -4,7-dione and 1,3-oxazepine -1,5-dione derivatives , figure (1).** These molecules identified easily by two major important things : firstly in FT-IR data: two different stretching frequency of (C=O,lacton and lactam) groups in oxazepine ring which appear approximately at 1716 and 1642 cm^{-1} respectively , and(CH, chiral) appear at ≥ 3200 cm^{-1} ,**figure (3a,3band 4a)**, secondly: In ^{1}H-NMR- in DMSO-d_6 there are more than one proton can be distinguished , highly deshielding protons of charily ring **figure (1, H_a)** observed singlet peak at chemical shift δ ≥8.50 ppm. and alkene's protons in the same **figure 1 (H_b,and H_c)** in **1,3-oxazepine 4,7-dione** observed in lower chemical shift than aromatic protons **(a**s doublet to doublet signal at approximately δ=6.34- 6.53 ppm) **figure (5a,5b)** [22] **.** Also in compounds **(W_{15}Ph and W_{16}Ph)** the **CH** chiral of oxazepine rings appear at at δ= 9.16 and 9.82 ppm as sharp signal and highly deshielded due to the effect of oxygen ,nitrogen and aromatic ring on it.Elemental analysis of the prepared compounds **(W_{13}M –W_{16}M)** and **(W_{13}Ph-W_{16}Ph)** were agreement relatively with calculated value. On the other hand mass spectra confirm the formation of the compounds (**W_{13}M ,W_{16}M ,W_{13}Ph and W_{14}Ph)** by presence of molecular ion peak **(m/z), figure (7a,b,c and d).**all the oxazepine derivatives are new molecules[23] and they tested now infield of biological applications.



Scheme (1): condensation reaction of o-tolidine via aromatic aldehyde in presence of absolute ethanol and glacial acetic acid under refluxing condition to afforded **(W_{13}-W_{16}).**



Scheme (2) :[2+5] Cycloaddition Reactions of Imine Derivative (**W_{13},W_{14}**) with Maleic and Phthalic anhydride to afforded **(W_{13}M ,W_{13}Ph ,W_{14}M and W_{14}Ph).**



Scheme (3): [2+5] Cycloadditin Reaction of Imine Derivatives **(W_{14},W_{15})**with Maleic and Phthalic anhydride to afforded (**W_{14M} ,W_{14}Ph ,W_{15}M , and W_{15}Ph)** .

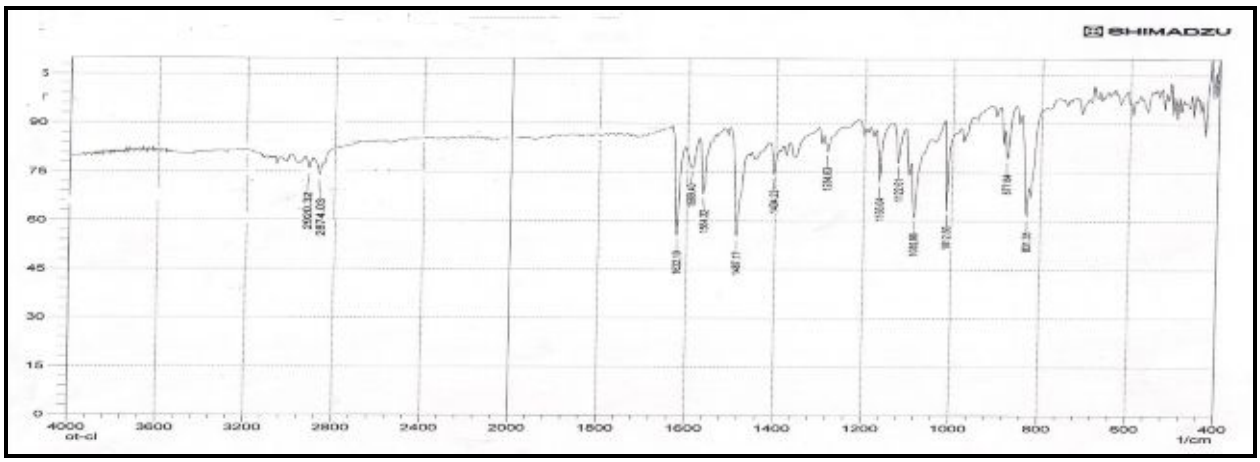


Figure (2a): *FT-IR spectra of bis (p-chloro benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine* ***(W_{13})***

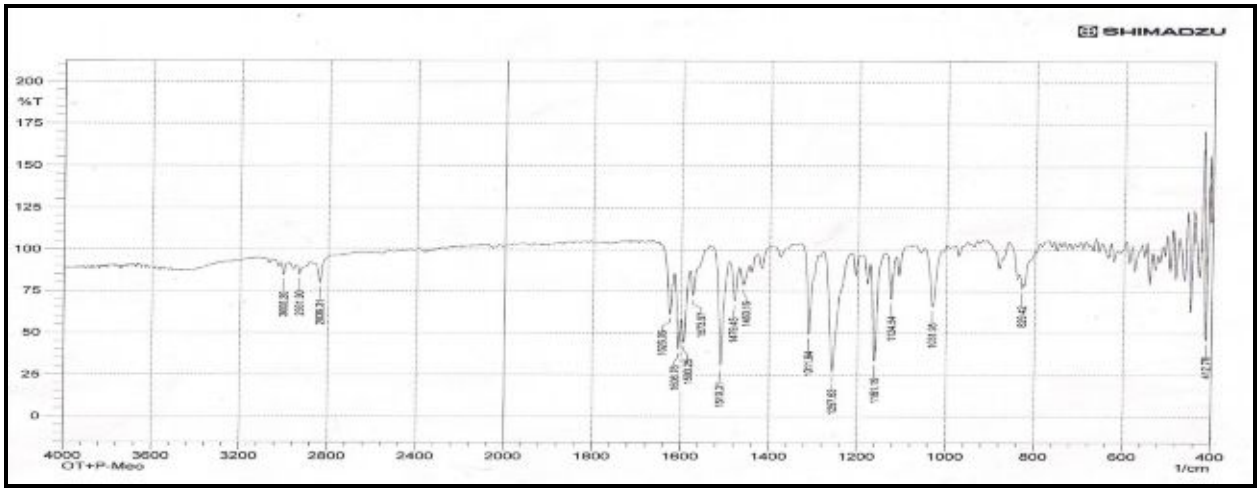


Figure (2b): *FT-IR spectra of bis (p-methoxy benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine* ***(W_{14}).***

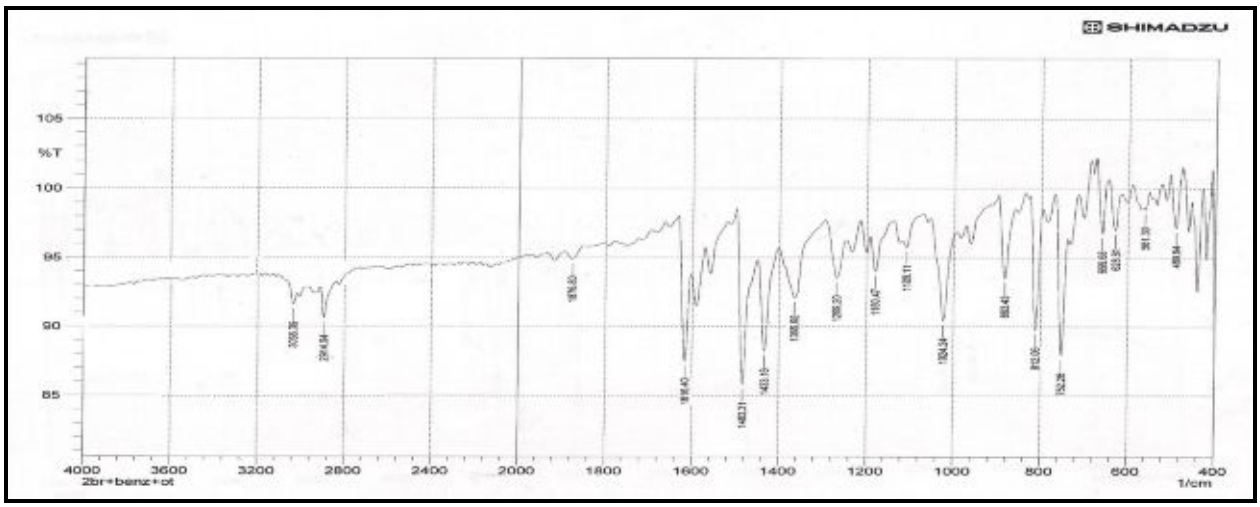


Figure (2c): FT-IR spectra of *bis (2-bromo benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine* ***(W_{15}).***

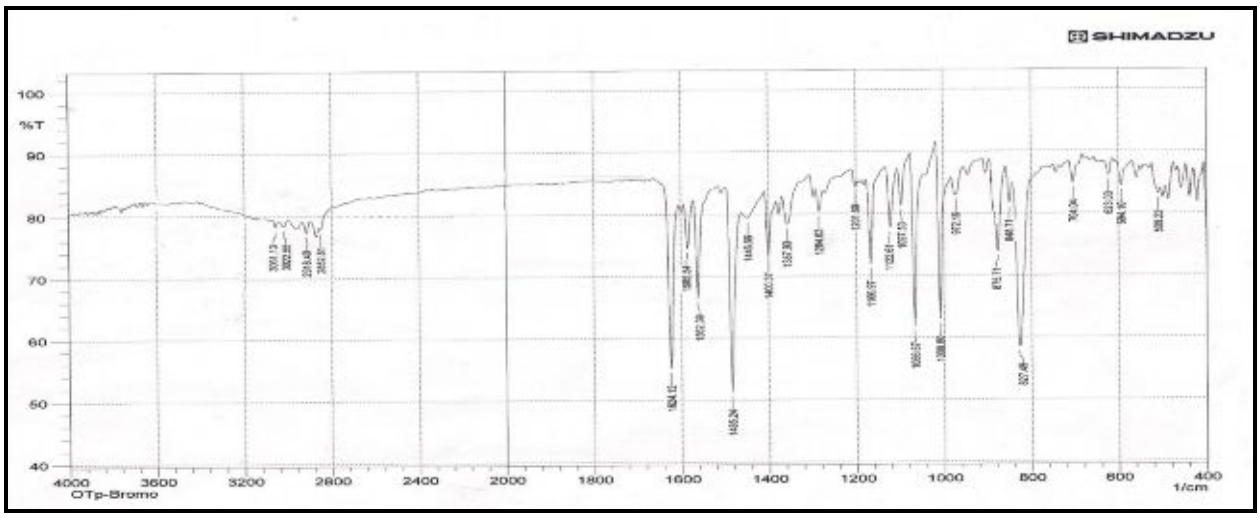


Figure (2d): FT-IR spectra of *bis (p-bromo benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine* ***(W_{16})***

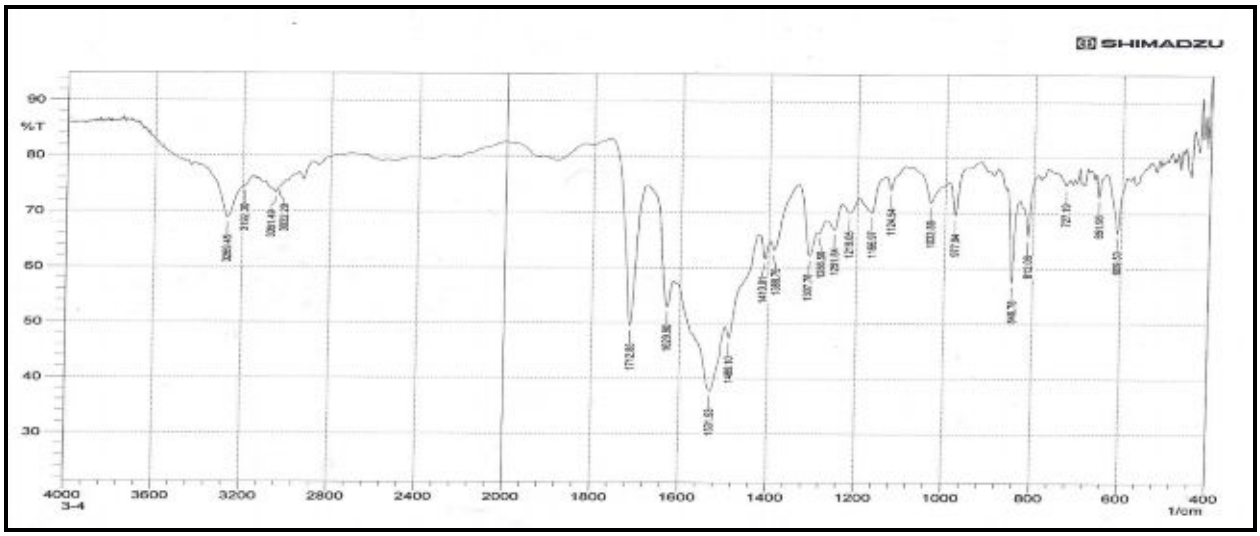


Figure (3a) *: FT-IR spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-methoxy phenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione.* ***(W_{14}M).***

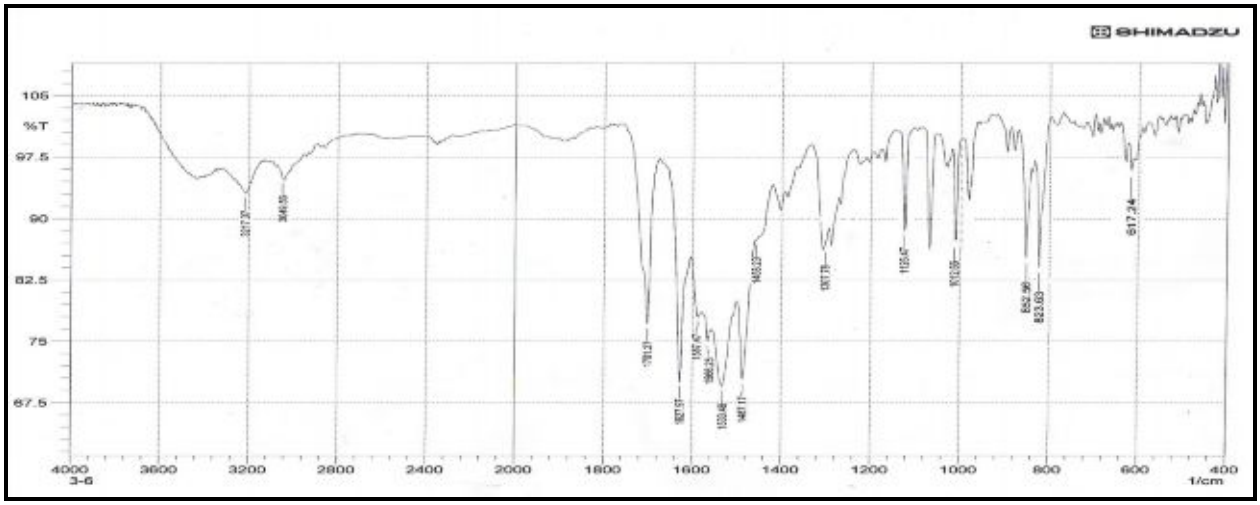


Figure (3b) *: FT-IR spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione* ***(W_{16}M)***.

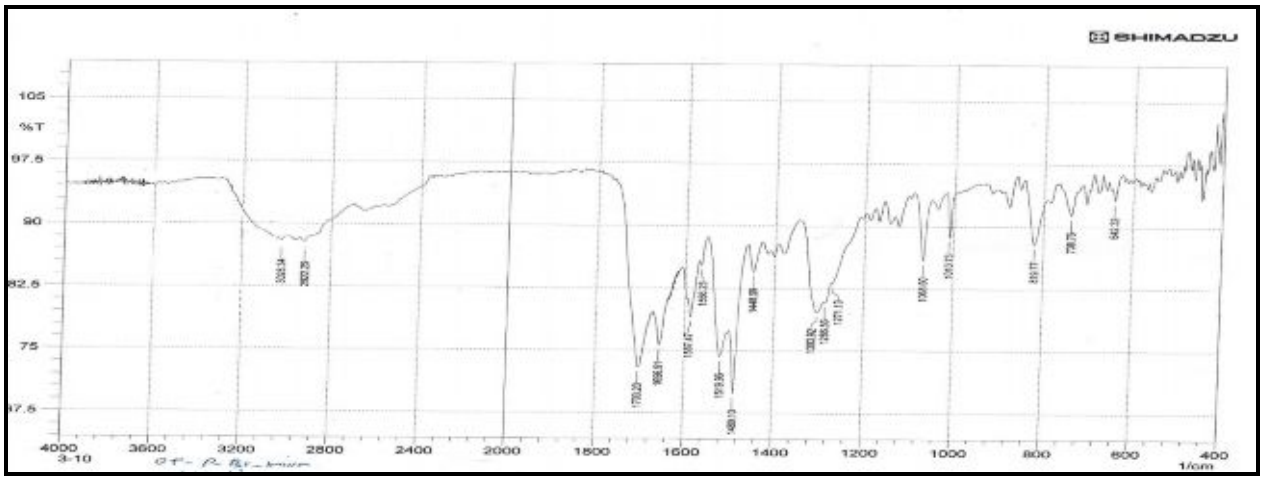


Figure (4a)** : FT-IR spectra of of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(4-bromophenyl) -3,4-dihydro benzo[1,3]oxazepine-1,5-dione)**(W_{16}Ph).

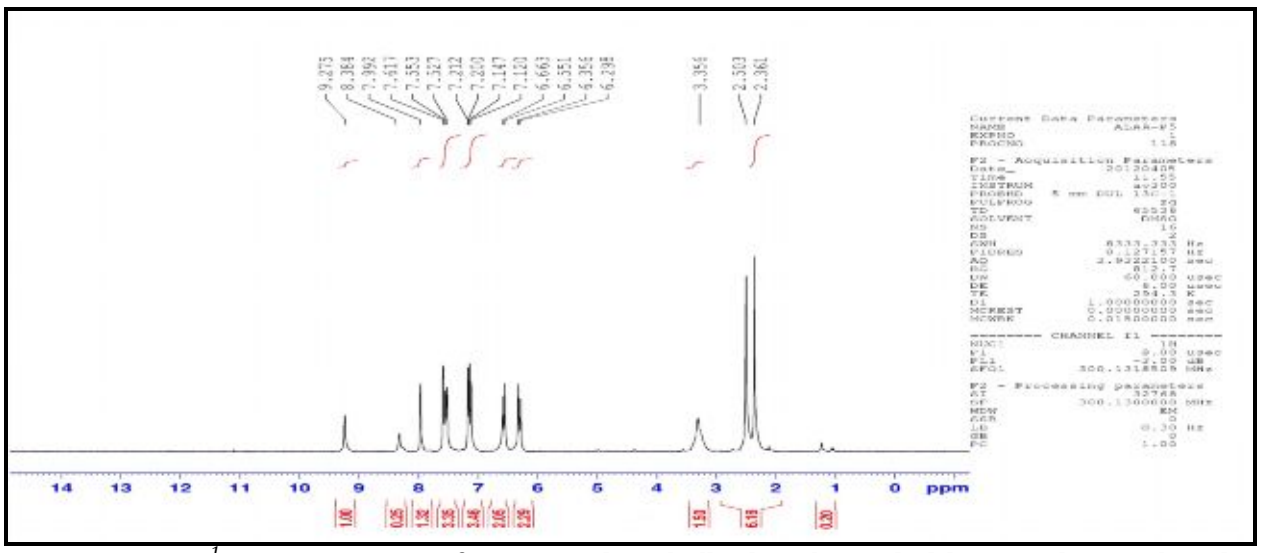


***Figure (5a)** : ^{1}H-NMR spectra of* 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(2-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione**) (W_{15}M).**

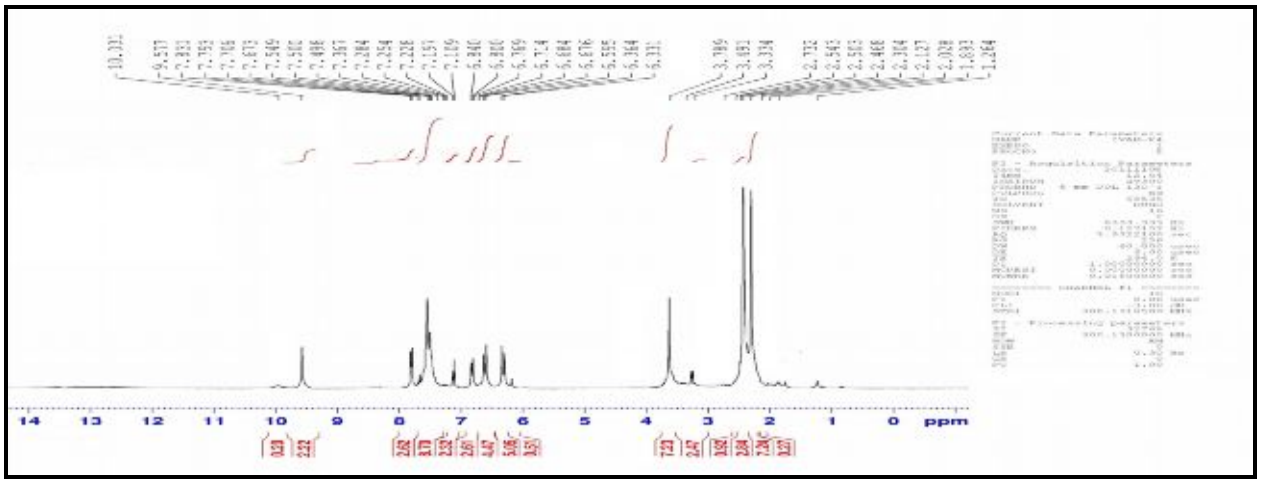


***Figure (5b)** : ^{1}H-NMR spectra of* 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(p-methoxy phenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione)**(W_{14}M)**.

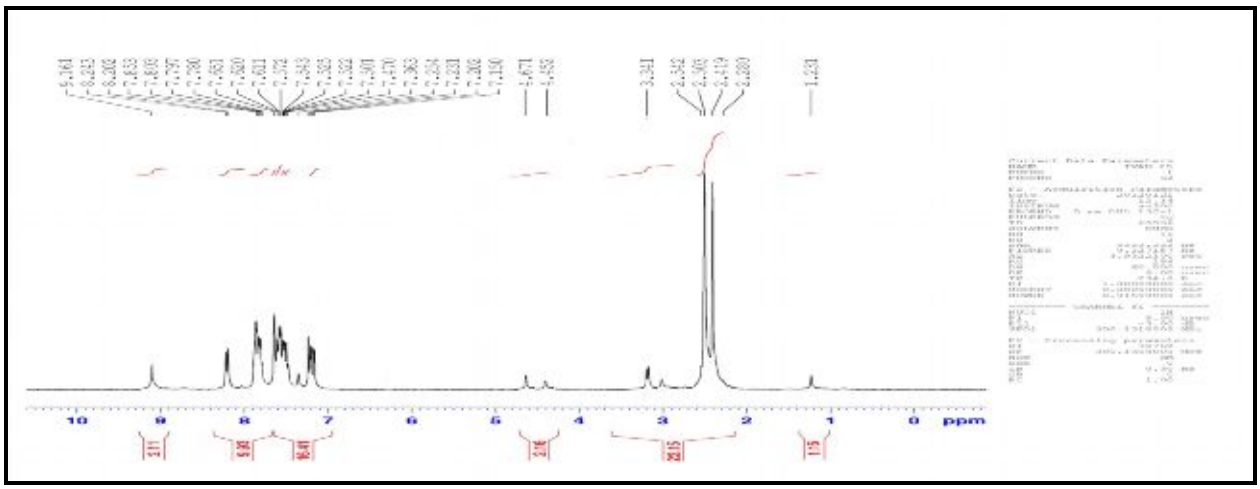


Figure (6a) : *^{1}H-NMR spectra of of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(2-bromo phenyl) -3,4-dihydro benzo[1,3]oxazepine-1,5-dione.($W_{15}Ph$).*

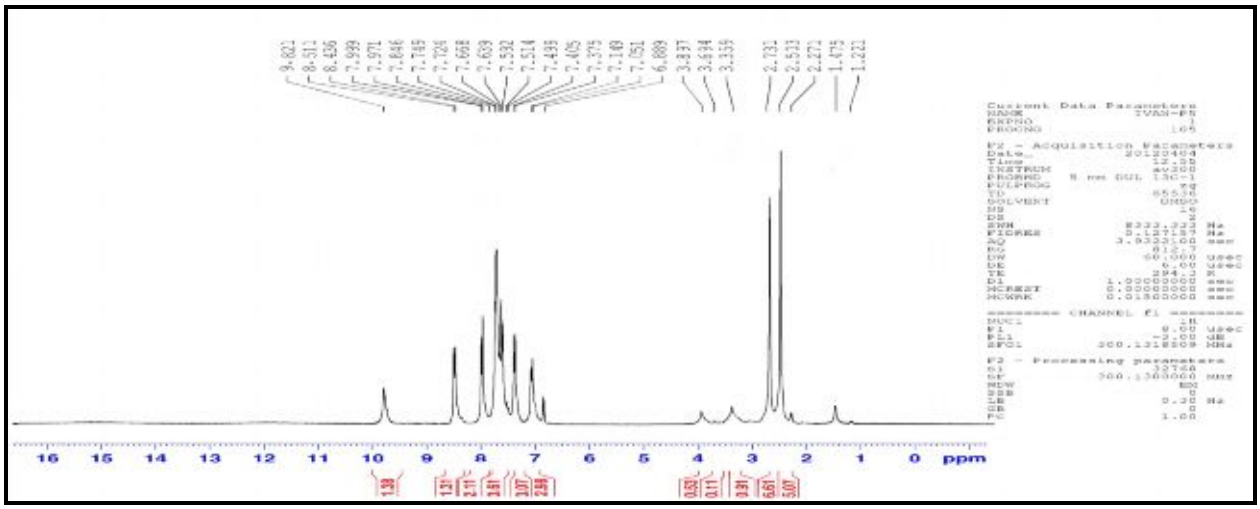


Figure (6b) : *^{1}H-NMR spectra of of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(p-bromo phenyl) -3,4-dihydro benzo[1,3]oxazepine-1,5-dione.($W_{16}Ph$).*

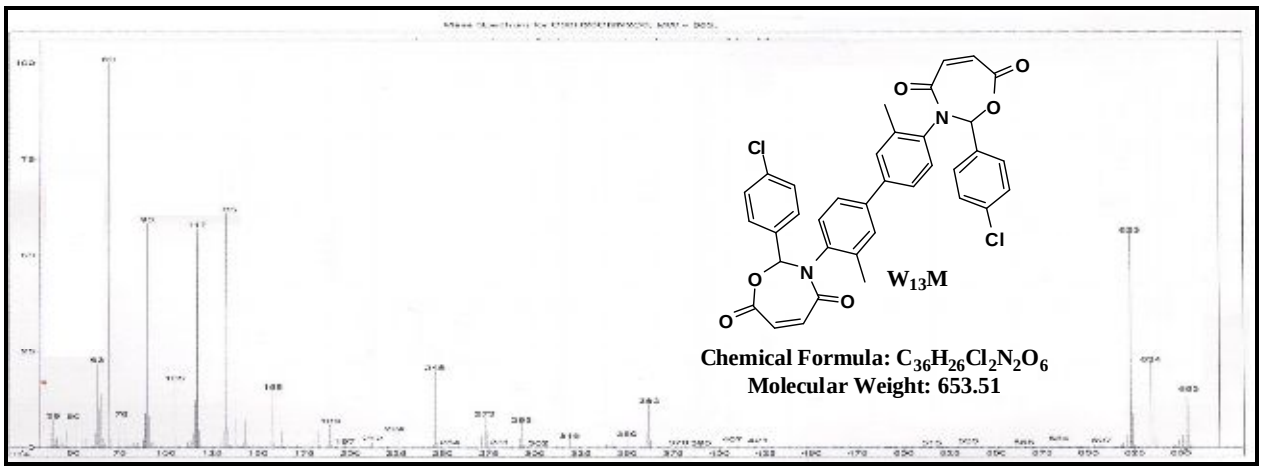


Figure (7a) : *Mass spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-chlorophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione.**($W_{13}M$).***

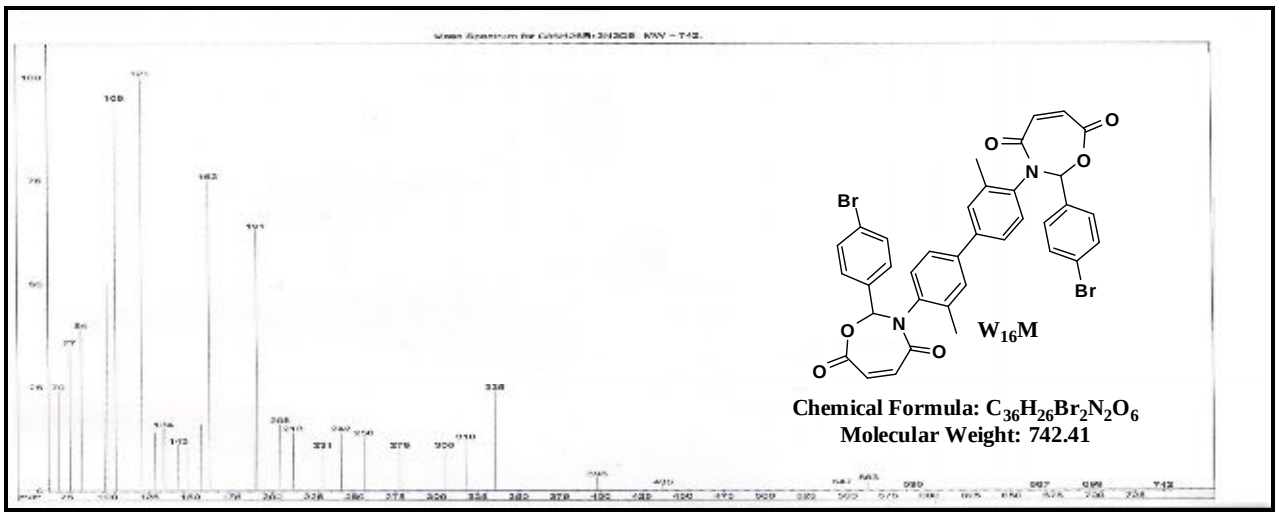


Figure (7b): Mass spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-bromophenyl)-2,3-dihydro -1,3-oxazepine-4,7-dione ($W_{16}M$).

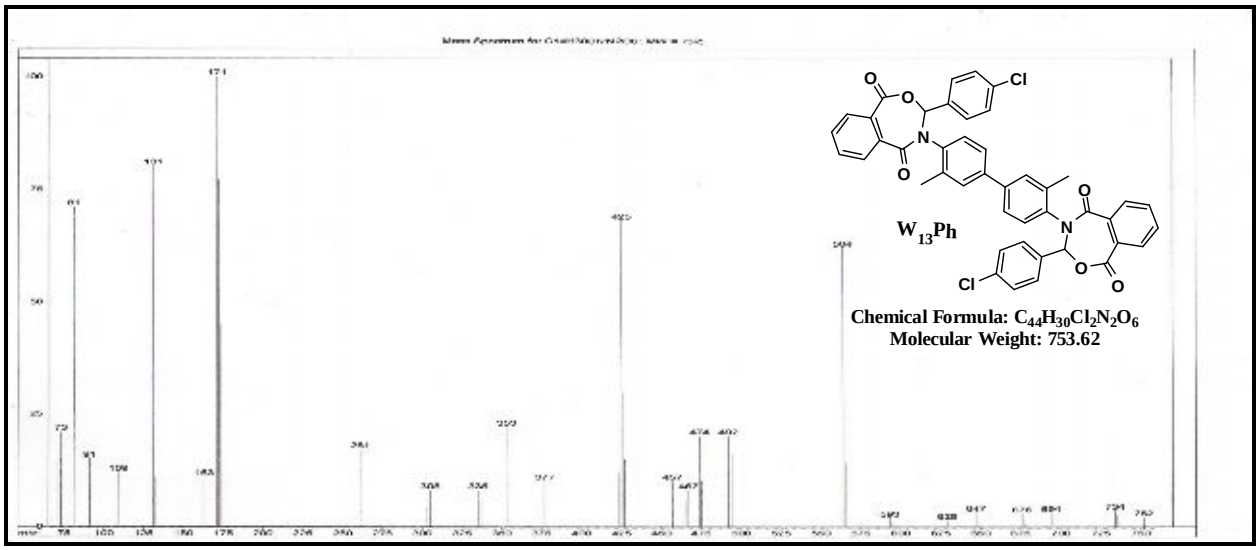


Figure (7c): *Mass spectra of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(p-chloro phenyl)-3,4-dihydro benzo[1,3]oxazepine-1,5-dione.($W_{13}Ph$).*

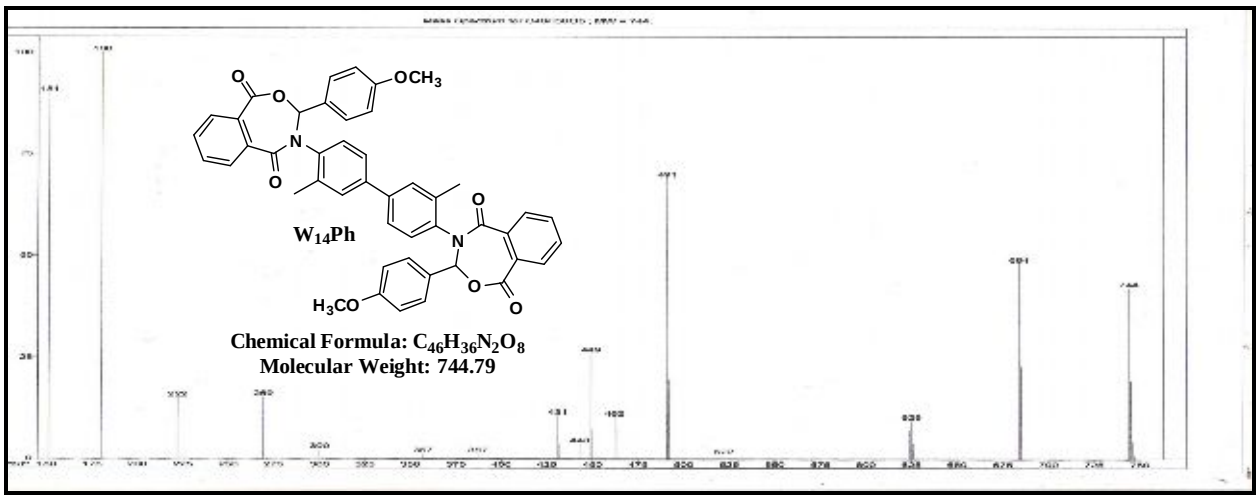


Figure (7d)*: Mass spectra of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(p-methoxyphenyl) -3,4- dihydro benzo[1,3]oxazepine-1,5-dione ($W_{14}Ph$).*

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