

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 (**w₁₃-w₁₆**) 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_{13m}-w_{16m}**) and [1,3] oxazepine -1,5-dione (**w_{13ph} – w_{16ph}**) respectively. The structure of new synthesized compounds were monitored by T.L.C and established on the basis of elemental analysis, FT-IR and ¹H-NMR.

Key words: imines, o-Tolidine and [1, 3]-oxazepine-4,7-dione :

Introduction:

o-tolidine is the derivatives of benzidine which belong to an important group of aromatic compounds containing methyl group in 3-position of 4,4'-diamino biphenyl⁽¹⁾. o-tolidine was consider a new reagent 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, tetrahydrofuran, 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. ¹H-NMR spectra was obtained using Bruker 300 MHz spectrometer in the Jordanian University and Glasgow university. The samples were in (DMSO d₆) and CDCl₃ 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* (W₁₃-W₁₆).

The mixture of 1mmole of o-tolidine (0.21gm) and 2 mmole of substituted aromatic aldehyde (p-chloro ,p-methoxy , 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 recrystallization from suitable solvent⁽¹⁸⁾.

1.1. synthesis of bis (4-chloro benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine (W₁₃).

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 ¹H-NMR in DMSO-d₆ as a solvent show the chemical shift of compound Y₅ 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 ,2CH₃-Ar).On the other hand Elemental Analysis of the molecular formula C₂₈H₂₂Cl₂N₂ (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(W₁₄)

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-green precipitate observed .Workup of the product with percentage yield = 64 % , m.p = 177-178 C° . IR (KBr) cm⁻¹ data, of compound Y₆, shows approximately the same infrared of compound Y₅, 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-). ¹H-NMR in DMSO-d₆ 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, 2CH₃O) and at δ= 3.23 ppm (s , 6H, 2CH₃-Ar) Elemental analysis of the molecular formula C₃₀H₂₈N₂O₂ (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(W₁₅)

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) .¹H-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 $\delta = 7.29 - 7.19$ ppm (2H, d, Ar), at $\delta = 2.32$ ppm (s, 6H, 2CH₃-Ar). Elemental analysis of the molecular formula C₂₈H₂₂Br₂N₂ (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(W₁₆)

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 W₁₆, shows approximately the same infrared of compound W₁₄, such as 3067-2918 cm⁻¹ refer to (C-H, Ar and aliphatic), 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 C₂₈H₂₂Br₂N₂ (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 (W₁₃-W₁₆) mentioned in part one was dissolved in suitable solvent under N₂ 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 reduced pressure and yielded was dried and recrystallized 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) (W₁₃M)

reaction of 1mmole (0.47 g) of compound W₁₃ with 2 mmole (0.20 g) maleic anhydride in dry THF adding with drop wise within N₂ flow and stirring under refluxing condition for about 3.5 hr, after cooling the reaction mixture a 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 aliphatic'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 C₃₆H₂₆Cl₂N₂O₆ of the compound W₁₃M (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) (W₁₄M)

reaction of 1mmole (0.44 g) of compound W₁₄ with 2 mmole (0.20 g) maleic anhydride in dry dichloromethane adding with drop wise within N₂ flow and stirring under refluxing condition for about 4.0 hr, after cooling the reaction mixture a yellow precipitate observed, section filtration yielded 60 % with m.p = 212-214 C°. 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), 1410-1580 cm⁻¹ (C=C, aromatic and alkene's), 3051-2910 cm⁻¹ (C-H, aromatic and aliphatic's) in addition to stretching frequency at 3192 cm⁻¹ (CH, chiral) in addition to (C-O-C) at 1307 cm⁻¹.

¹H-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 Y₆M (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) (W₁₅M).

reaction of 1mmole (0.51 g) of compound W₁₅ with 2 mmole (0.20 g) maleic anhydride in dry dichloromethane adding with drop wise within N₂ 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 1327cm⁻¹. ¹H-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 W₁₅M (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)(W₁₆M).

reaction of 1mmole (0.54 g) of compound W₁₆ with 2 mmole (0.20 g) maleic anhydride in dry dichloromethane adding with drop wise within N₂ 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 Y₅M (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 (W₁₃.W₁₆) mentioned in part one were dissolved in suitable solvent under N₂ 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) (W₁₃Ph).

reaction of 1mmole (0.47 g) of compound W₁₃ with 2 mmole (0.30 g) phthalic anhydride in dry THF adding with drop wise within N₂ 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 $\text{C}_{44}\text{H}_{30}\text{Cl}_2\text{N}_2\text{O}_6$ of the compound **W₁₃Ph** (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) (W₁₄Ph)

reaction of 1mmole (0.44 g) of compound **W₁₅** 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 $\text{C}_{46}\text{H}_{36}\text{N}_2\text{O}_8$ of the compound **W₁₄Ph** (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) (W₁₅Ph).

reaction of 1mmole (0.51 g) of compound **W₁₅** 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 3061 cm^{-1} (CH, chiral) in addition to (C-Br,ortho) at 738 cm^{-1} . ^1H -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 $\text{C}_{44}\text{H}_{30}\text{Br}_2\text{N}_2\text{O}_6$ of the compound **W₁₅Ph** (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).(W₁₆Ph).

reaction of 1mmole (0.54 g) of compound **W₁₆** 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) . ^1H -NMR-DMSO- d_6 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 ,2CH₃-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 C₃₆H₂₆Br₂N₂O₆of the compound **W₁₆Ph** (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-dihydrobenzo[1,3]oxazepine-1,5-dione .many researchers have investigated these types of Heterocyclic compounds due to their important

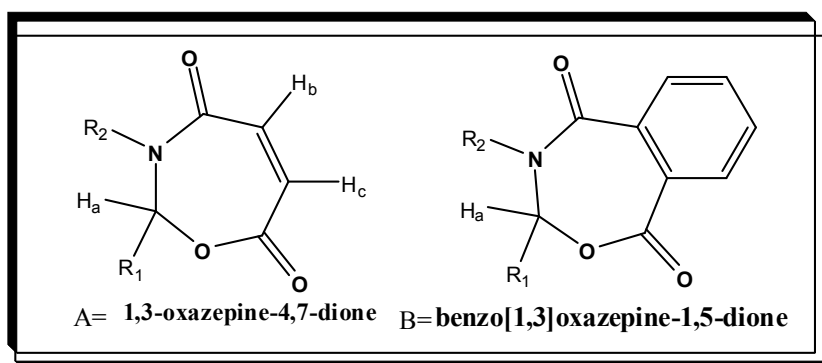
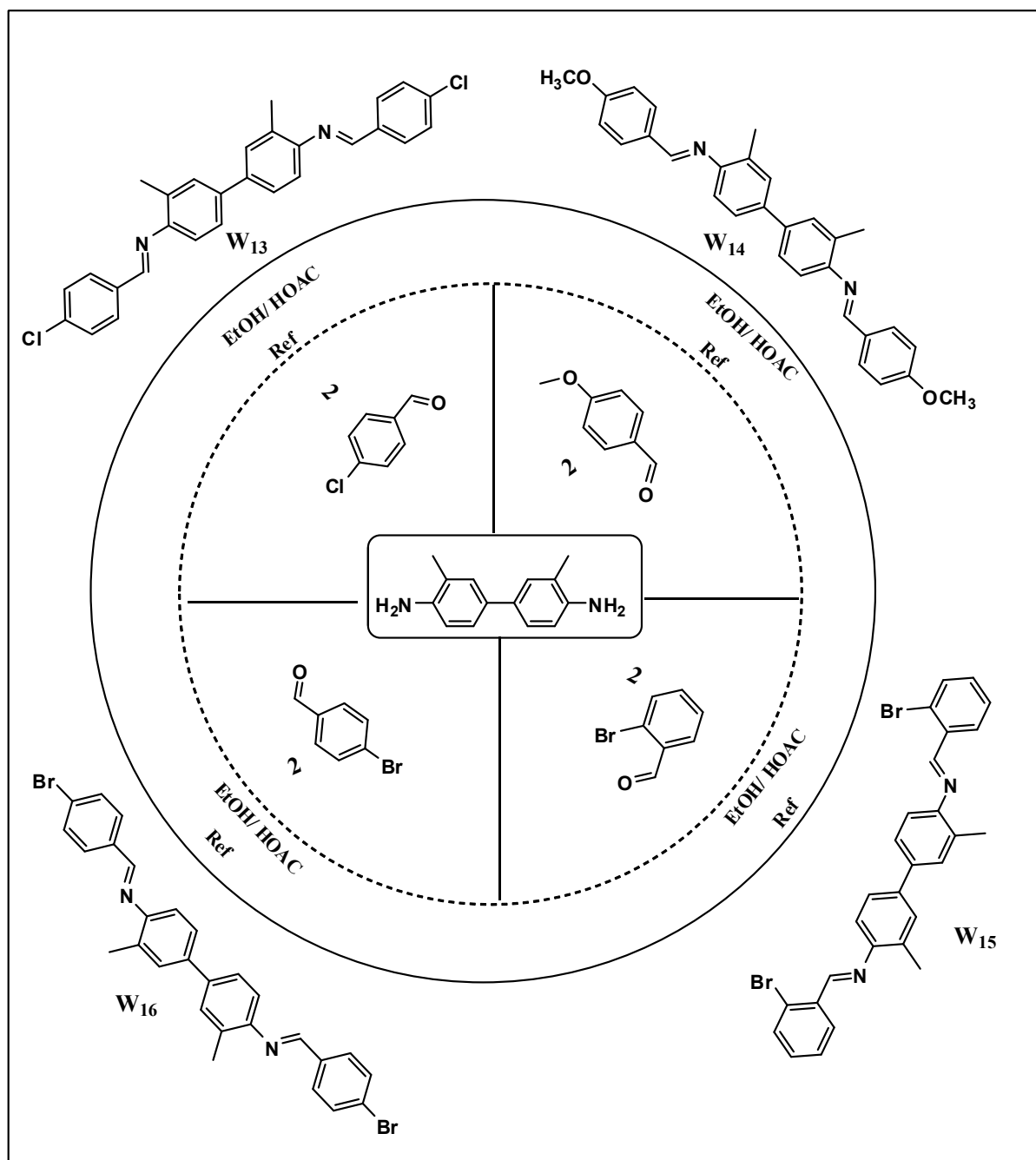


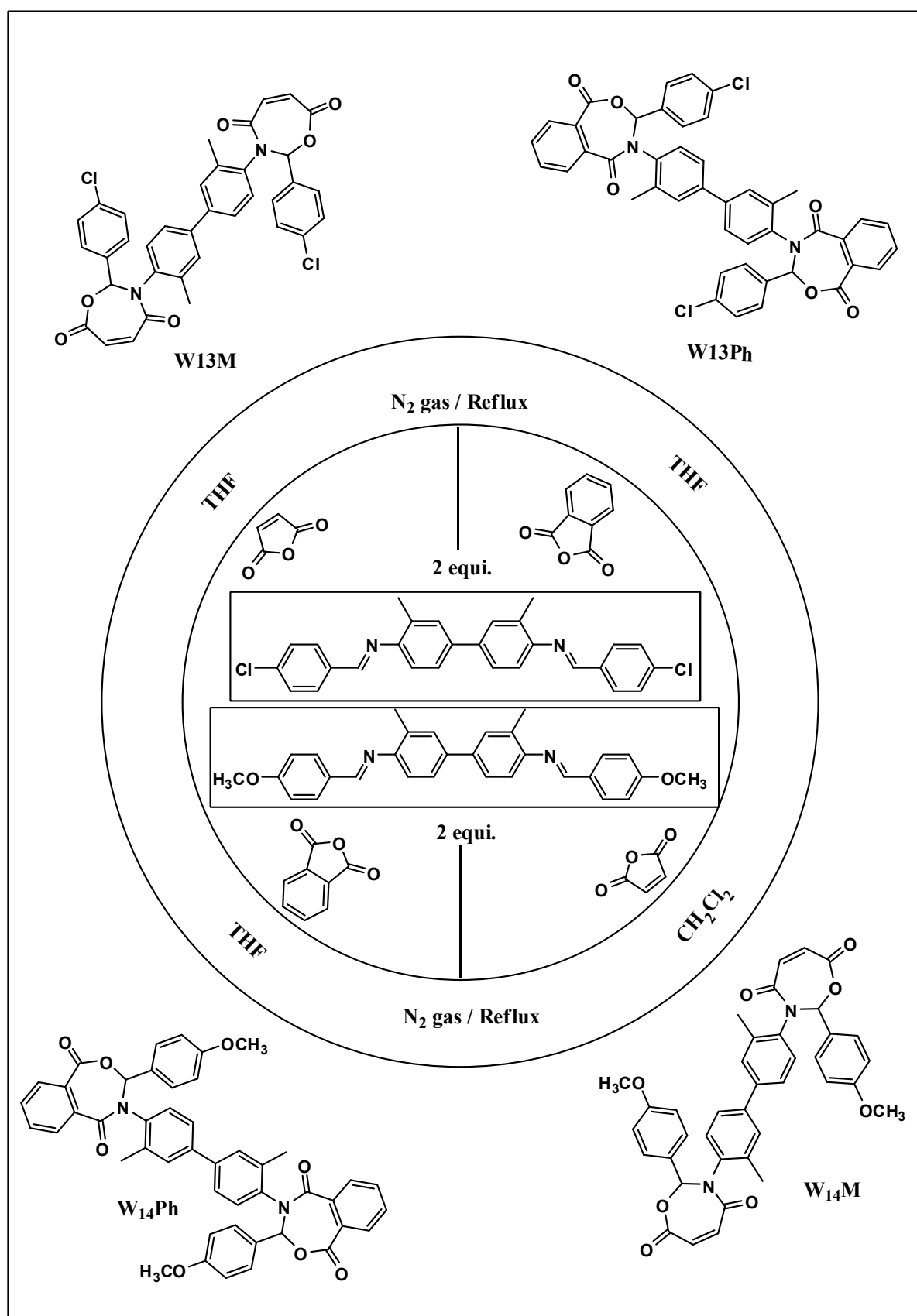
Figure (1): Two types A and B of [1,3] oxazepine – dione .

class which have varieties of biological applications⁽¹⁹⁻²¹⁾. Our interesting were to modification of oxazepine rings throughout changing the R₁ and R₂ 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 ,¹H-NMR and Elemental Analysis. Recall to FT-IR in (KBr) disk .In the first step: the imines derivatives (W₁₃-W₁₆)which formed by condensation reaction were proved according to disappearance of (NH₂) 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 ¹H-NMR in DMSO-d₆ as a solvent confirmed the generation of these compounds, .For compound **W₁₃** its obvious sharp singlet peak appear at δ = 8.32 ppm which belong to 2CH of azomethane groups ,this proton was deshielded 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 (**W₁₃- W₁₆**). 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 \geq 3200 cm⁻¹ ,**figure (3a,3band 4a)**, secondly: In ¹H-NMR- in DMSO-d₆

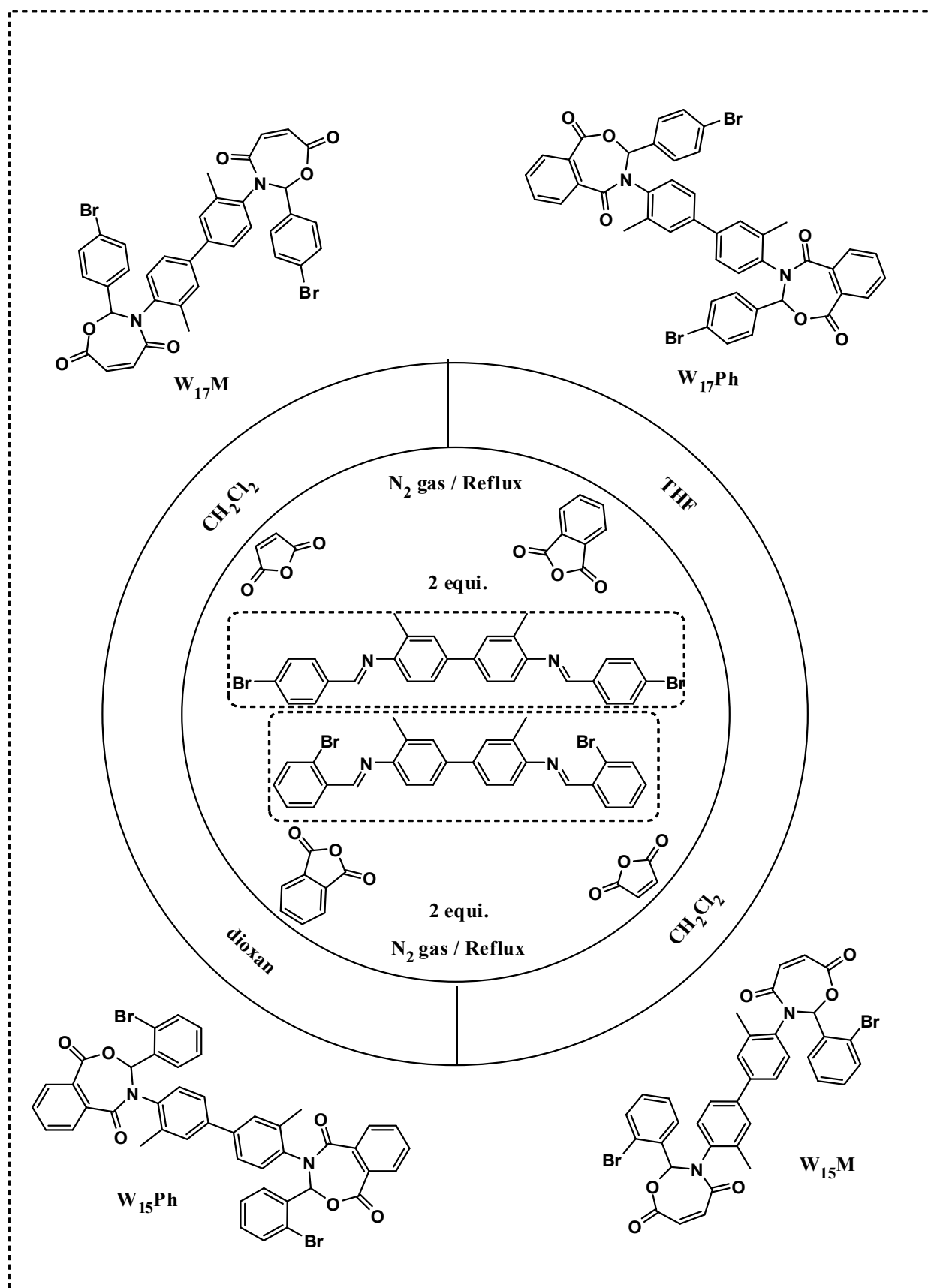
there are more than one proton can be distinguished, highly deshielding protons of charily ring **figure (1, H_a)** observed singlet peak at chemical shift $\delta \geq 8.50$ ppm. and alkene's protons in the same **figure 1 (H_b, and H_c)** in **1,3-oxazepine 4,7-dione** observed in lower chemical shift than aromatic protons (as doublet to doublet signal at approximately $\delta=6.34- 6.53$ ppm) **figure (5a,5b)** ⁽²²⁾. Also in compounds (**W₁₅Ph and W₁₆Ph**) the CH chiral of oxazepine rings appear at $\delta= 9.16$ 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 (**W₁₃M –W₁₆M**) and (**W₁₃Ph-W₁₆Ph**) were agreement relatively with calculated value. On the other hand mass spectra confirm the formation of the compounds (**W₁₃M, W₁₆M, W₁₃Ph and W₁₄Ph**) 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 (**W₁₃-W₁₆**).



Scheme (2) : [2+5] Cycloaddition Reactions of Imine Derivative (**W13**, **W14**) with Maleic and Phthalic anhydride to afford (**W13M**, **W13Ph**, **W14M** and **W14Ph**).



Scheme (3): [2+5] Cycloaddition Reaction of Imine Derivatives (**W₁₄**, **W₁₅**) with Maleic and Phthalic anhydride to afford (**W₁₄M**, **W₁₄Ph**, **W₁₅M**, and **W₁₅Ph**).

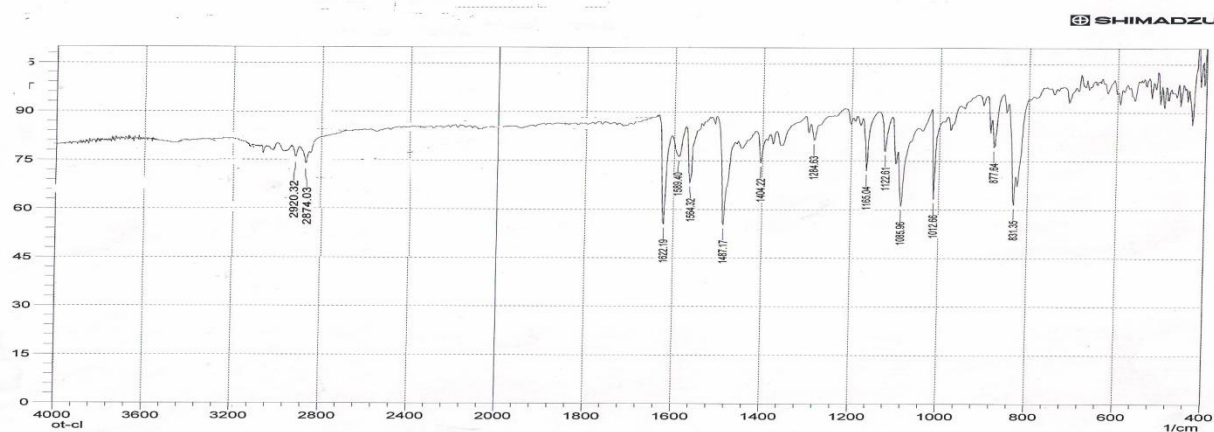


Figure (2a): FT-IR spectra of bis (*p*-chloro benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine (W_{13})

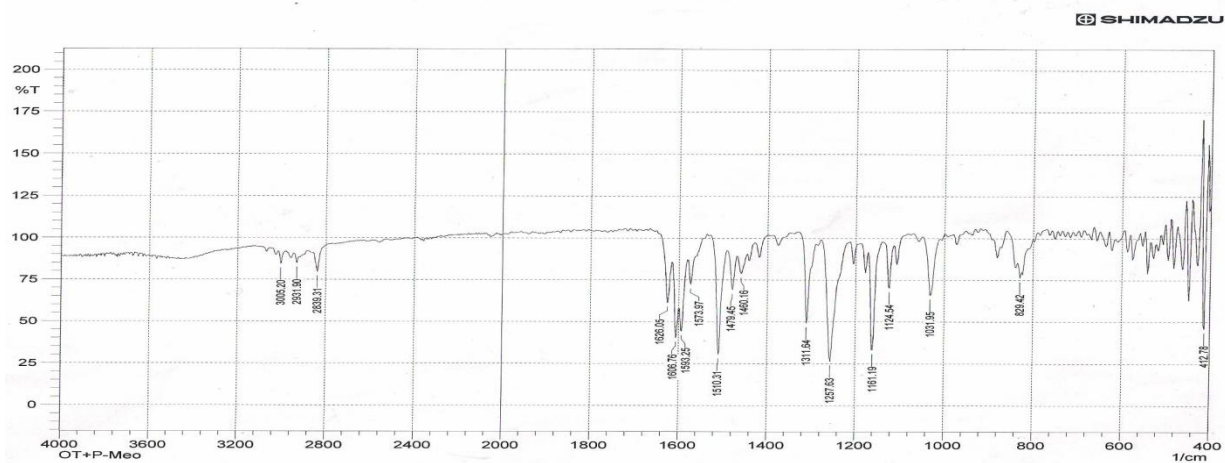


Figure (2b): FT-IR spectra of bis (*p*-methoxy benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine (W_{14}).

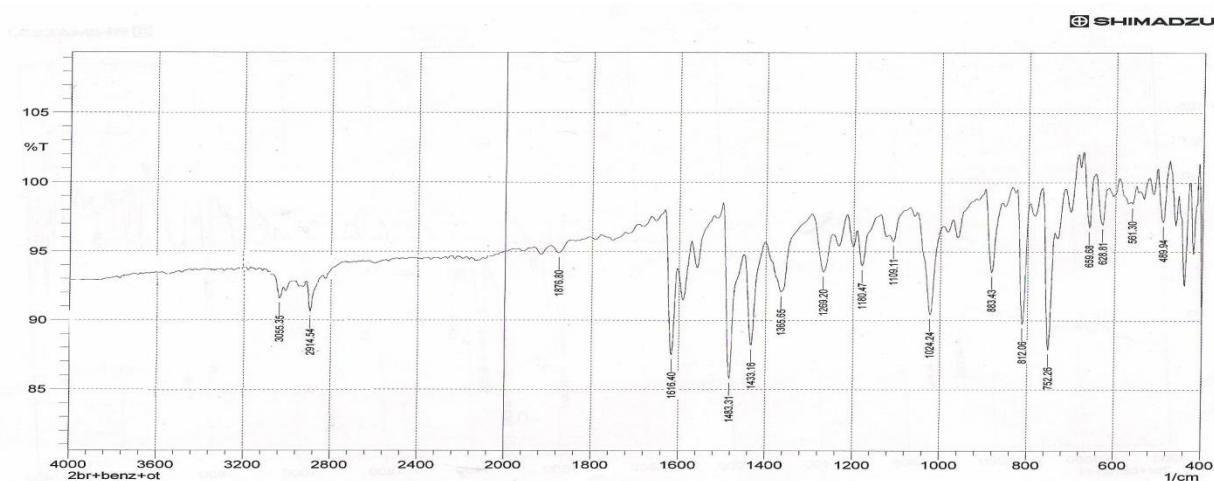


Figure (2c): FT-IR spectra of bis (*2*-bromo benzylidene) 3,3'dimethyl biphenyl-4,4'-diamine (W_{15}).

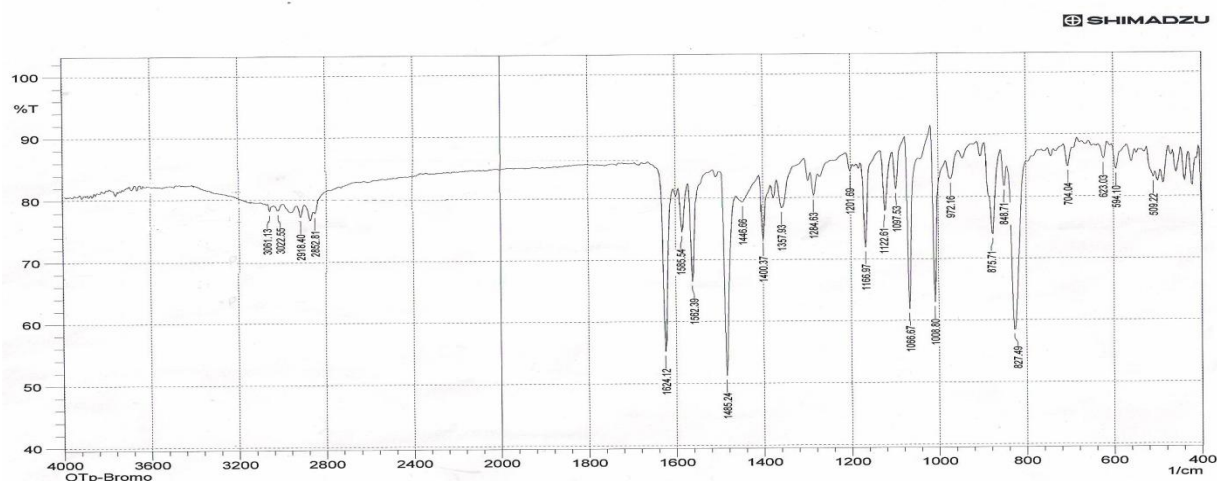


Figure (2d): FT-IR spectra of bis (p-bromo benzyldiene) 3,3'dimethyl biphenyl-4,4'-diamine (W₁₆)

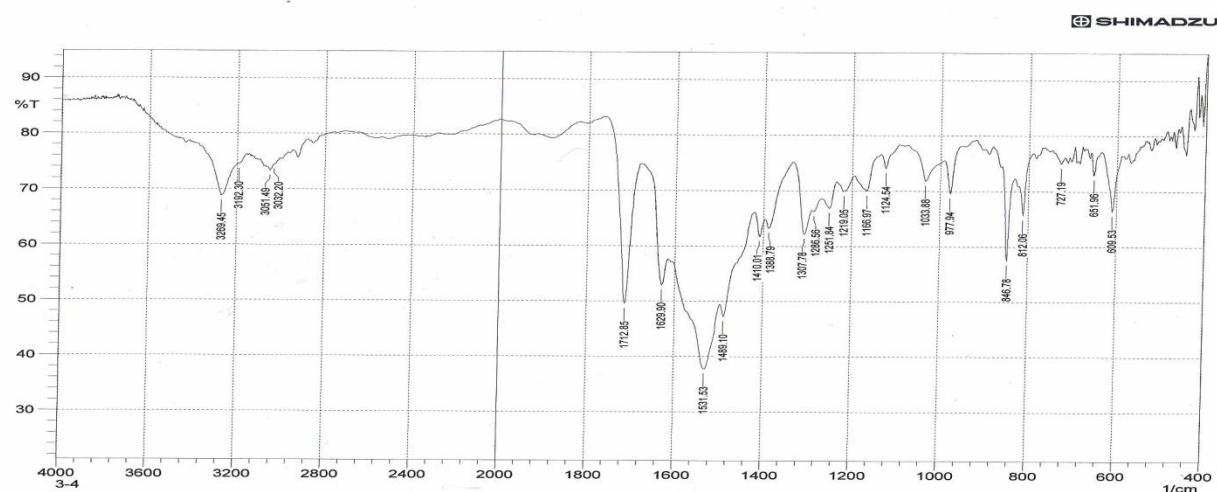


Figure (3a) : FT-IR spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-methoxy phenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione (W_{14M}).

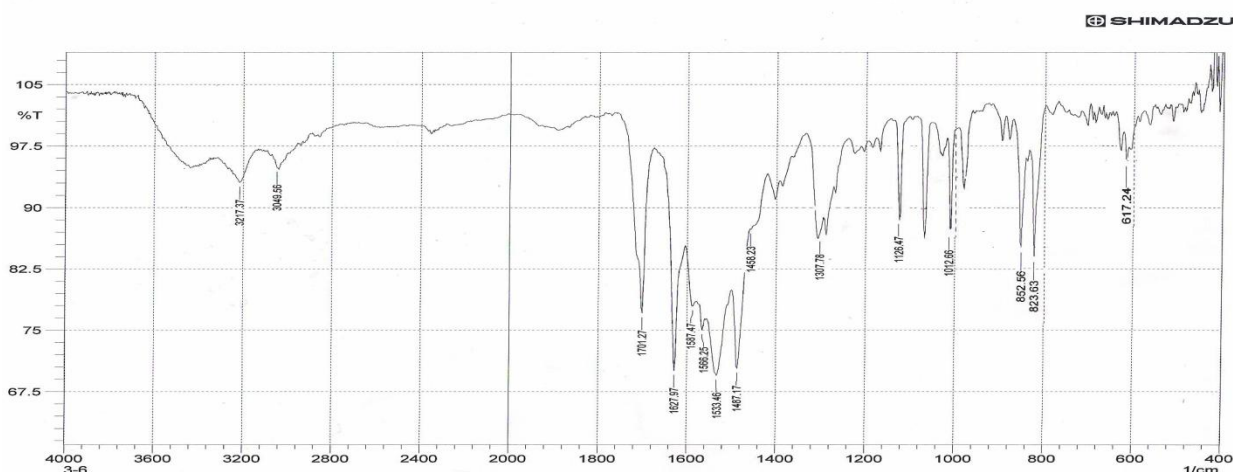


Figure (3b) : FT-IR spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione (W_{16M}).

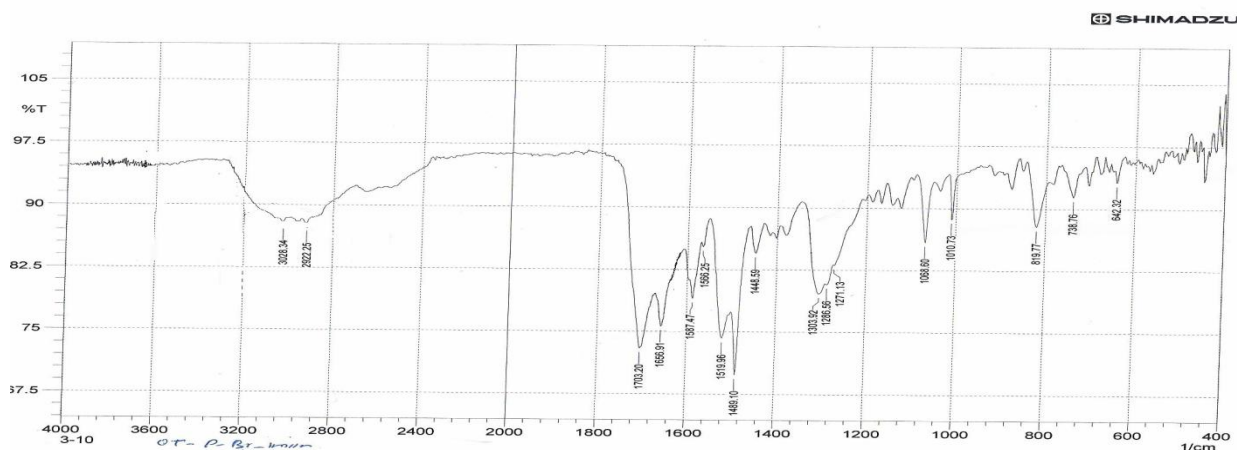


Figure (4a) : FT-IR spectra of of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(4-bromophenyl) -3,4-dihydro benzo[1,3]oxazepine-1,5-dione)(W₁₆Ph).

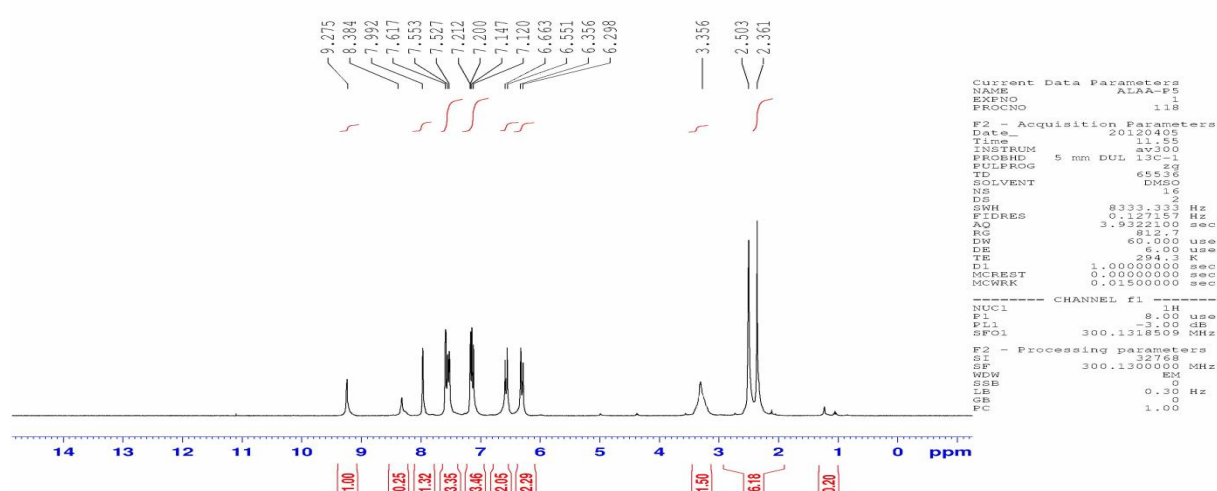


Figure (5a):¹H-NMR spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(2-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione) (W₁₅M).

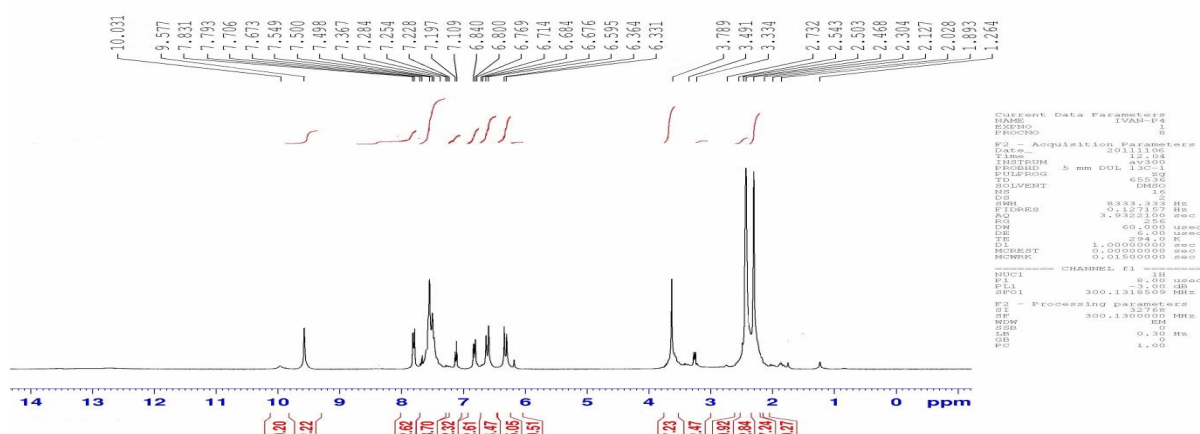


Figure (5b):¹H-NMR spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(p-methoxy phenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione)(W₁₄M).

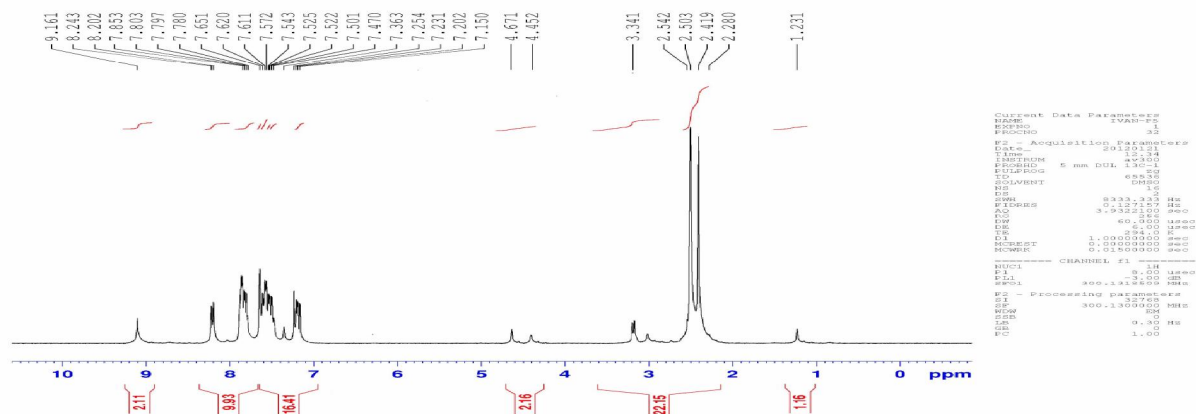


Figure (6a) : ^1H -NMR spectra of of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(2-bromo phenyl) -3,4-dihydro benzo[1,3]oxazepine-1,5-dione. (**W₁₅Ph**).

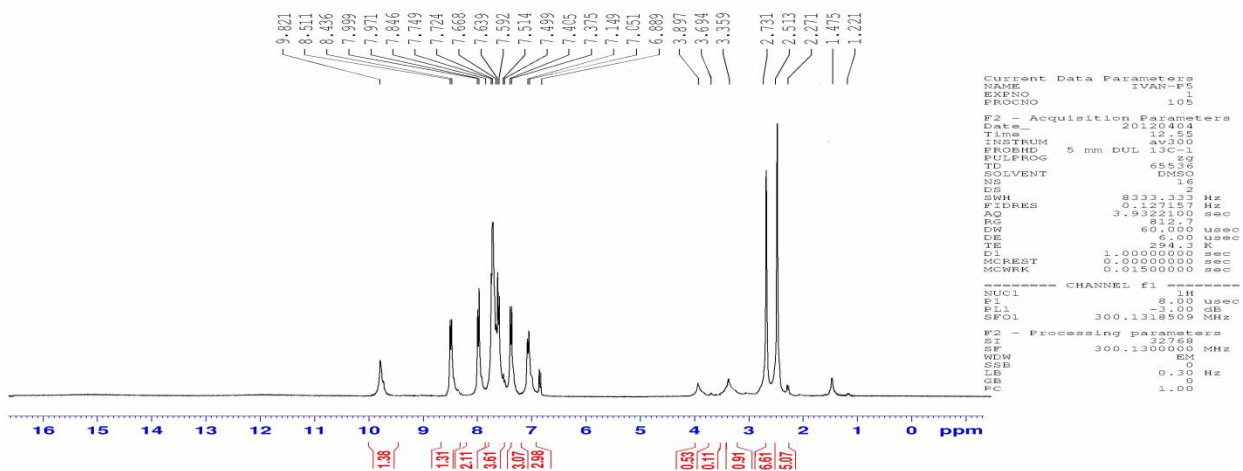


Figure (6b) : ^1H -NMR spectra of of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(p-bromo phenyl) -3,4-dihydro benzo[1,3]oxazepine-1,5-dione.(W₁₆Ph).

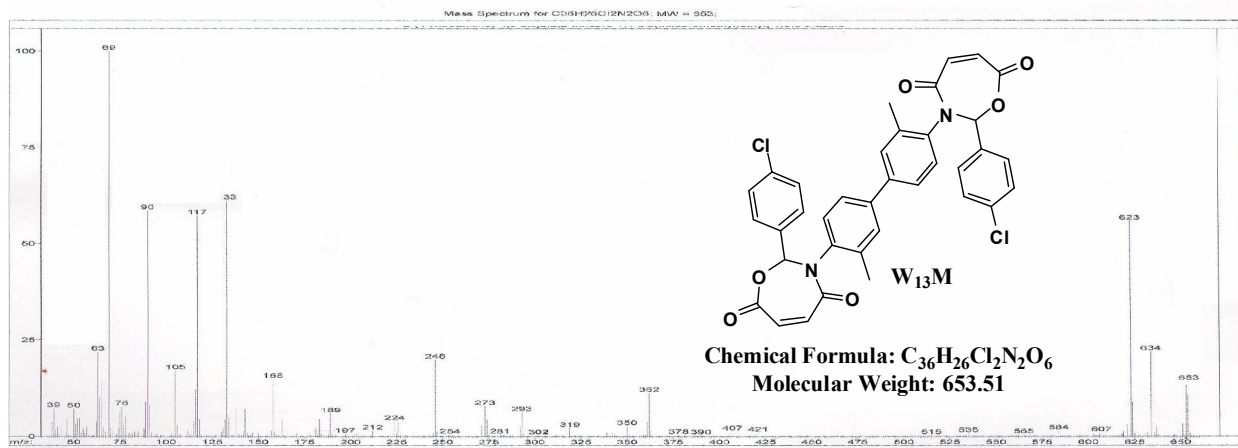


Figure (7a) : Mass spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-chlorophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione.(W₁₃M).

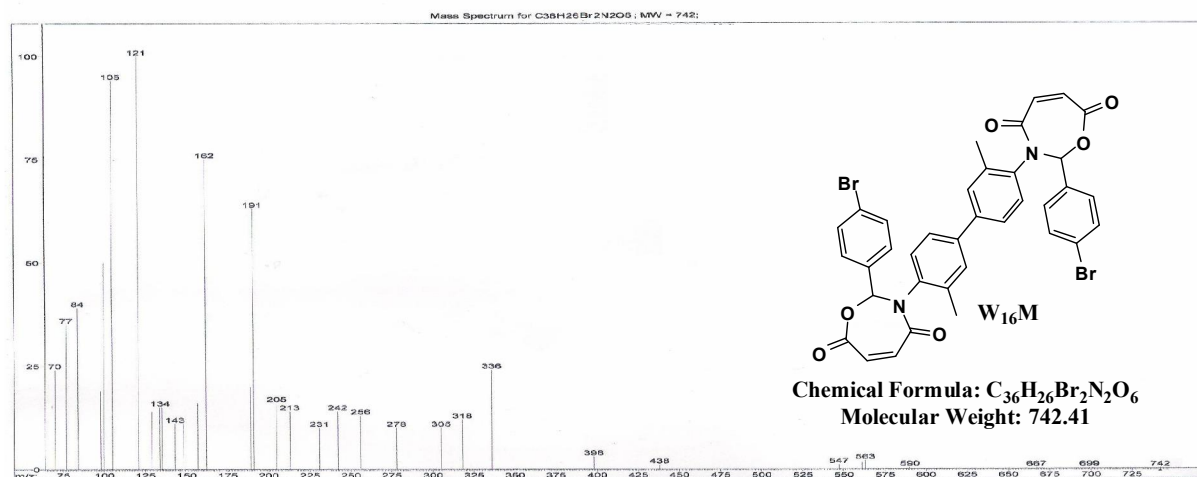


Figure (7b): Mass spectra of 3,3'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(2-(4-bromophenyl)-2,3-dihydro-1,3-oxazepine-4,7-dione (**W₁₆M**).

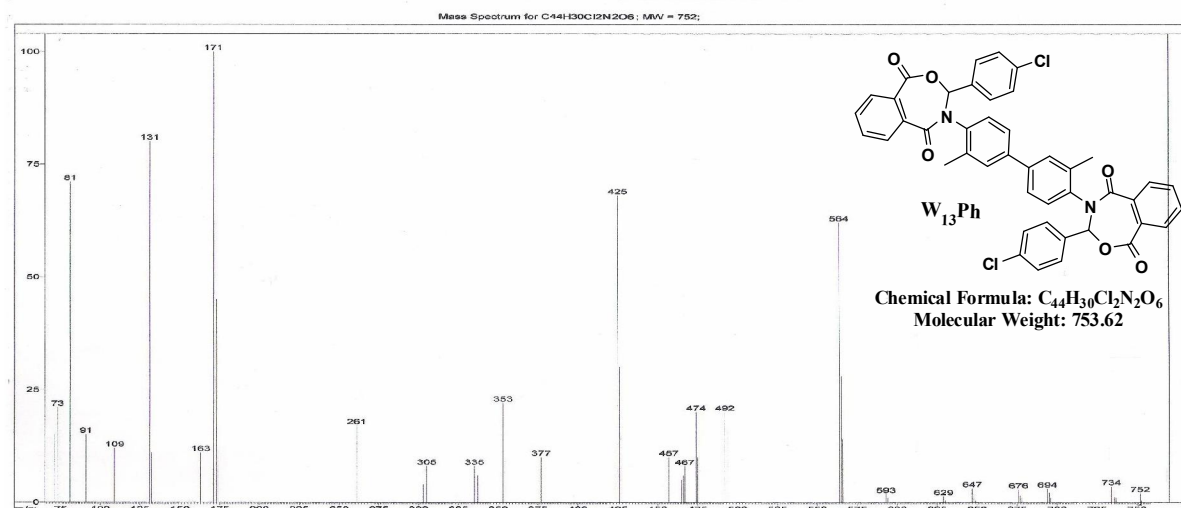


Figure (7c): Mass spectra of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(p-chlorophenyl)-3,4-dihydro benzo[1,3]oxazepine-1,5-dione (**W₁₃Ph**).

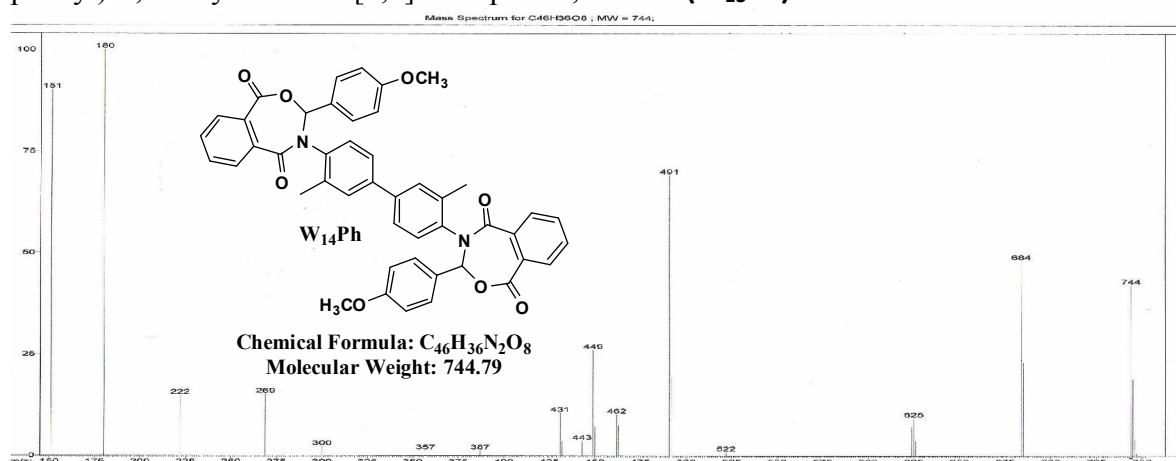


Figure (7d): Mass spectra of 4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(3-(p-methoxyphenyl)-3,4-dihydro benzo[1,3]oxazepine-1,5-dione (**W₁₄Ph**).

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