**Open Access** **Baghdad Science Journal** **P-ISSN: 2078-8665**
**2020, 17(1) Supplement (March):272-286** **E-ISSN: 2411-7986**

DOI: https://dx.doi.org/10.21123/bsj.2020.17.1(Suppl.).0272

# Synthesis of Six and Seven-membered Heterocyclic Molecules Containing an Adamantyl Fragment and an X-ray Crystal Structure of *(E)-N*-(adamantan-1-yl)-1-(3-nitrophenyl)methanimine

***Shukkur A. Hamed*** [*] ***Ali S. Ismail*** ***Ahmed Dhary Saleh***

Received 7/7/2019, Accepted 24/11/2019, Published 18/3/2020



## Abstract:

Our work included a synthesis of three new imine derivatives—1,3-thiazinan-4-one, 1,3-oxazinan-6-one and 1,3-oxazepin-4,7-dione—which contained an adamantyl fragment. These were produced via the condensation of the Schiff`s base *(E)-N*-(adamantan-1-yl)-1-(3-aryl)methanimine with 3-mercaptopropanoic acid; 3-chloropropanoic acid; and maleic, citraconic anhydride, respectively. These new imines were prepared via the condensation of adamantan-1-ylamine and 3-nitro-, 3-bromobenzaldehyde in *n*-BuOH. We obtained a good yield of products. FTIR, $^{1}$H NMR spectroscopy and C.H.N.S analysis were used to diagnostic the products. The molecular structure of *(E)-N*-(adamantan-1-yl)-1-(3-nitrophenyl)methanimine was confirmed by X-ray crystallography analysis.

**Keywords:** Adamantan-1-ylamine, 1,3-oxazepin-4,7-dione, 1,3-oxazinan-6-one, 1,3-thiazinan-4-one, X-ray crystallography.

## Introduction:

The molecular skeleton of adamantane and its derivative molecules are of current interest to researchers in molecular technology. Adamantan-1-ylamine and its derivatives are amines containing adamantyl fragment in the form of three fused cyclohexane rings in a chair conformation (1), and adamantane is the monomer of the diamond lattice (2). The adamantyl group has been found to be an important component in the development of many drug treatments (3). For example, the addition of adamantyl moiety to an active pharmaceutical molecule leads to improvements in an array of therapeutic drugs (4), and adamantan-1-ylamine was the first anti-viral treatment to be developed (5). This development led to the synthesis and testing of hundreds of adamantylamine derivatives for different bioactivities, especially for cancer drugs. The synthesis and study of the bioactivity of *(E)-N*-(adamantan-1-yl)-1-(3-aryl) methanimine derivatives have been undertaken via the condensation of two components of adamantan-1-ylamine together with various aromatic aldehydes in the presence of acetic acid, and some of the synthesized compounds have been reported to inhibit acetylcholinesterase (ACHE) and to have anti-microbial, anti-cancer impacts in vitro and anti-inflammatory (6-11).

Furthermore, azomethine (imine) compounds are reactive intermediaries for organic synthesis in a number of diverse fields (12, 13).

Thiazine, oxazine and oxazepine have similar structures for six and seven-membered heterocyclic compounds which contain two hetero atoms (S, N) and (O, N), respectively (14-16). Oxazepinone is synthesized via a cyclo-addition reaction (2+5) between imine and anhydride (17-20). Whereas, thiazinanone prepared via the condensation of pyridin-2-ylmethanamine, benzaldehyde derivatives, and 3-mercaptopropanoic acid (14, 20). The reaction between imine and glycolic acid gave oxazinone (21). These three classes of compounds have very great interest in medical treatments such as anti-bacterial, anti-viral and anti-oxidant properties (22-25). Adamantan-1-ylamine derivatives gave a potential value for the development of beneficial bioactivities drugs. This research presents promising synthesis of adamantanylarylmethanimines as predecessors of six and seven-membered heterocyclic molecules containing an adamantyl fragment. The single-crystal structure of *(E)-N*-(adamantan-1-yl)-1-(3-

Department of Chemistry, College of Education for Pure Science, University Of Anbar, Al-Anbar, Iraq
[*] Corresponding author: ahmedsatori73@gmail.com
[*]ORCID ID: 0000-0003-4471-9191

nitrophenyl)methanimine was affirmed by X-ray crystallography analysis.

## Materials and Methods:

All materials and solvents were supplied by Sigma-Aldrich Chemical Co. (Germany) and Romil Co. (UK). Melting point temperatures were measured using the Stuart SMP-10 apparatus. FTIR and $^1$H NMR spectra were recorded using the Bruker-Tensor 27 and Bruker-300 MHz spectrometers, respectively (with DMSO-$d_6$ and $CDCl_3$ as a solvents and TMS as internal standard). Microelemental analysis was performed by using a thermo scientific flash 2000 series analyser, whilst X-ray diffraction was measured using a STOE StadiVari Pilatus100K diffractometer. The progress of reactions were monitored by TLC Silica gel 60G F254 (Sigma-Aldrich) using eluent chloroform/acetone (6:1) and benzene/methanol (7:1) as mobile phase under iodine vapour.

**The general procedure for synthesizing** *(E)-N*-(adamantan-1-yl)**-1-(3-aryl)methanimine (1a,b)**

**1a was synthesized using a simple procedure with comparing (6)**

A solution of 0.013 mol adamantan-1-ylamine in 20 mL butanol was added to a 0.013 mol solution of suitable 3-substituted benzaldehyde in 15 mL butanol. The mixture was heated for 1-1.5 hours with stirring at the boiling point of the solvent. The solvent was evaporated, and the residual product was re-crystallized from *i*-PrOH.

**Description of the properties of (1a and 1b)**

***(E)-N*-(adamantan-1-yl)-1-(3-nitrophenyl)methanimine (1a)**

The reaction of adamantan-1-ylamine (1.96 g, 0.013 mol) and 3-nitrobenzaldehyde (1.96 g, 0.013 mol) gave (1a) as a white crystals, yield 3.4 g, 91%; mp 117–118° C. Found $C_{17}H_{20}N_2O_2$ (%): C 71.17, H 7.68, N 9.50. Calculated (%): C 71.81, H 7.09, N 9.85. $^1$H NMR (300 MHz, DMSO-$d_6$), δ, ppm: 8.58 (1H, s, C<u>H</u>=N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 8.47 (1H, s, <u>$H_2$</u>), 8.27 (1H, d, J=9 Hz, <u>$H_6$</u>), 8.17 (1H, d, J=9 Hz, <u>$H_4$</u>), 7.74 (1H, t, J=9 Hz, <u>$H_5$</u>); adamantyl group: 2.13 (3H, s, 3C<u>H</u>), 1.64-1.78 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3092 (C-$H_{aromatic}$), 2903, 2848 (C-$H_{aliphatic}$), 1638 (C=N), 1522, 1343 (-$NO_2$). Details of the physical properties, C.H.N.S analysis, data of FTIR and $^1$H NMR spectroscopy were determined for products (1a,b-5a,b) and (1a,b-4a,b), respectively, and are displayed in Tables 1-4. X-ray analysis of compound (1a): Single crystal was obtained by allowing *i*-PrOH solution of the compound to stand for one week. The crystallographic data is shown in Tables 5-7.

**Table 1. Physical properties and C.H.N.S analysis of the compounds (1a,b-5a,b).**

| Comp.№ | M. Formula | Color | Solvent of re-cryst. | Yield% | mp° C | C.H.N.S analysis Found (%) / Calculated (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | S |
| 1a | $C_{17}H_{20}N_2O_2$ | White crystals | 2-Propanol | 91 | 117-118 | 71.17<br>71.81 | 7.68<br>7.09 | 9.50<br>9.85 | -<br>- |
| 1b | $C_{17}H_{20}BrN$ | White crystals | 2-Propanol | 94 | 101-102 | 63.85<br>64.16 | 6.10<br>6.33 | 3.92<br>4.40 | -<br>- |
| 2a | $C_{21}H_{22}N_2O_5$ | White powder | 1,4-Dioxane | 65 | 250–251 | 65.58<br>65.96 | 6.10<br>5.80 | 6.92<br>7.33 | -<br>- |
| 2b | $C_{21}H_{22}BrNO_3$ | White powder | 1,4-Dioxane | 69 | 239–240 | 60.09<br>60.59 | 4.95<br>5.33 | 3.70<br>3.36 | -<br>- |
| 3a | $C_{22}H_{24}N_2O_5$ | White powder | 1,4-Dioxane | 77 | 218–219 | 67.10<br>66.65 | 5.31<br>6.10 | 6.52<br>7.07 | -<br>- |
| 3b | $C_{22}H_{24}BrNO_3$ | White powder | 1,4-Dioxane | 74 | 176–177 | 62.10<br>61.40 | 5.15<br>5.62 | 3.78<br>3.25 | -<br>- |
| 4a | $C_{20}H_{24}N_2O_4$ | White powder | Ethanol | 57 | 188–189 | 66.80<br>67.40 | 7.23<br>6.79 | 8.30<br>7.86 | -<br>- |
| 4b | $C_{20}H_{24}BrNO_2$ | White powder | Ethanol | 61 | 174–175 | 61.95<br>61.54 | 6.93<br>6.20 | 3.15<br>3.59 | -<br>- |
| 5a | $C_{20}H_{24}N_2O_3S$ | White powder | Ethanol | 64 | 290 decomp. | 65.15<br>64.49 | 6.93<br>6.49 | 6.85<br>7.52 | 7.84<br>8.61 |
| 5b | $C_{20}H_{24}BrNOS$ | White powder | Ethanol | 68 | 280 decomp. | 60.05<br>59.11 | 6.44<br>5.95 | 3.82<br>3.45 | 8.54<br>7.89 |

***(E)*-*N*-(adamantan-1-yl)-1-(3-bromophenyl)methanimine (1b)**

The reaction of adamantan-1-ylamine (1.96 g, 0.013 mol) and 3-bromobenzaldehyde (2.4 g, 0.013 mol) gave (1b) as a white crystals, yield 3.38 g, 94%; mp 101–102° C. Found $C_{17}H_{20}BrN$ (%): C 63.85, H 6.10, N 3.92. Calculated (%): C 64.16, H 6.33, N 4.40. $^1$H NMR (300 MHz, DMSO-$d_6$), δ, ppm: 8.29 (1H, s, C<u>H</u>=N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 7.94 (1H, s, <u>$H_2$</u>), 7.73 (1H, d, J=6 Hz, <u>$H_6$</u>), 7.61 (1H, d, J=6 Hz, <u>$H_4$</u>), 7.40 (1H, t, J=9 Hz, <u>$H_5$</u>); adamantyl group: 2.12 (3H, s, 3C<u>H</u>), 1.63-1.74 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3052 (C-$H_{aromatic}$), 2906, 2811 (C-$H_{aliphatic}$), 1631 (C=N), 776 (C-Br).

**Table 2. FTIR and $^1$H NMR spectral data for compounds (1a,b).**

| | FTIR data (ν $cm^{-1}$) | | | | | $^1$H NMR chemical shift (DMSO-$d_6$, δ, ppm) | | |
|---|---|---|---|---|---|---|---|---|
| Comp. № | ν C-H aromatic | ν C-H aliphatic | ν C=N | -$NO_2$ | C-Br | C<u>H</u>=N | 4<u>H</u>$_{aromatic}$-phenyl group | (15<u>H</u>-) adamantyl group |
| 1a | 3092 | 2903, 2848 | 1638 | 1522, 1343 | - | 8.58 (s) | 8.47 (1H, s, <u>$H_2$</u>), 8.27 (1H, d, J=9 Hz, <u>$H_6$</u>), 8.17 (1H, d, J=9 Hz, <u>$H_4$</u>), 7.74 (1H, t, J=9 Hz, <u>$H_5$</u>) | 2.13 (3H, s, 3C<u>H</u>), 1.64-1.78 (12H, m, 6C<u>$H_2$</u>) |
| 1b | 3052 | 2906, 2811 | 1631 | - | 776 | 8.29 (s) | 7.94 (1H, s,<u>$H_2$</u>), 7.73 (1H, d, J=6 Hz, <u>$H_6$</u>), 7.61 (1H, d, J=6 Hz, <u>$H_4$</u>), 7.40 (1H, t, J=9 Hz, <u>$H_5$</u>) | 2.12 (3H, s, 3C<u>H</u>), 1.63-1.74 (12H, m, 6C<u>$H_2$</u>) |

**The general procedure for synthesizing 3-(adamantan-1-yl)-2-(3-aryl)-2,3-dihydro-1,3-oxazepin-4,7-dione and 3-(adamantan-1-yl)-6-methyl-2-(3-aryl)-2,3-dihydro-1,3-oxazepin-4,7-dione (2a,b), (3a,b)**

To a hot solution of 0.01 mol compounds 1a,b in 15 mL dry benzene was added to convenient solution of 0.01 mol anhydrides (maleic, citraconic) in 10 mL dry benzene. The mixture was refluxed for 7-10 hours with strong stirring, then the solvent was vaporized. The residual solid was washed with solution 3% $NaHCO_3$ and then three times with water. The product was dried and re-crystallized twice from 1,4-dioxane.

**Description of the properties of (2a,b and 3a,b)**

**3-(adamantan-1-yl)-2-(3-nitrophenyl)-2,3-dihydro-1,3-oxazepin-4,7-dione (2a)**

The reaction of imine (1a) (2.84 g, 0.01 mol) and maleic anhydride (0.98 g, 0.01 mol) gave (2a) as a white powder, yield 2.5 g, 65%; mp 250–251° C. Found $C_{21}H_{22}N_2O_5$ (%): C 65.58, H 6.10, N 6.92. Calculated (%): C 65.96, H 5.80, N 7.33. $^1$H NMR (300 MHz, DMSO-$d_6$), δ, ppm: 10.15 (1H, s, O-C<u>H</u>-N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 8.70 (1H, s, <u>$H_2$</u>), 8.48-8.59 (1H, m, <u>$H_6$</u>), 8.18-8.36 (1H, m, <u>$H_4$</u>), 7.72-7.94 (1H, m, <u>$H_5$</u>), 6.33 (1H, dd, J=6Hz, 12Hz, =C<u>H</u>-CO-N), 4.14 (1H, dd, J=9Hz, 6Hz, =C<u>H</u>-CO-O), adamantyl group: 2.14 (3H, s, 3C<u>H</u>), 1.64-2.03 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3042 (C-$H_{aromatic}$), 2907, 2846 (C-$H_{aliphatic}$), 1728 (C=$O_{lactone}$), 1685 (C=$O_{lactam}$),1524 (C=$C_{aromatic}$), 1436 (CO-N), 1363 (CO-O).

**3-(adamantan-1-yl)-2-(3-bromophenyl)-2,3-dihydro-1,3-oxazepin-4,7-dione (2b)**

The reaction of imine (1b) (3.18 g, 0.01 mol) and maleic anhydride (0.98 g, 0.01 mol) gave (2b) as a white powder, yield 2.8 g, 69%; mp 239–240° C. Found $C_{21}H_{22}BrNO_3$ (%): C 60.09, H 4.95, N 3.70. Calculated (%): C 60.59, H 5.33, N 3.36. $^1$H NMR (300 MHz, DMSO-$d_6$), δ, ppm: 9.86 (1H, s, O-C<u>H</u>-N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 8.21 (1H, s, <u>$H_2$</u>), 7.87-8.11 (1H, m, <u>$H_6$</u>), 7.50-7.65 (1H, m, <u>$H_4$</u>), 7.43-7.60 (1H, m, <u>$H_5$</u>), 6.11 (1H, dd, J=6Hz, 9Hz, =C<u>H</u>-CO-N), 4.12 (1H, dd, J=6Hz, 6Hz, =C<u>H</u>-CO-O), adamantyl group: 2.13 (3H, s, 3C<u>H</u>), 1.63-1.76 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3012 (C-$H_{aromatic}$), 2901, 2817 (C-$H_{aliphatic}$), 1726 (C=$O_{lactone}$), 1665 (C=$O_{lactam}$), 1521 (C=$C_{aromatic}$), 1425 (CO-N), 1353 (CO-O).

**3-(adamantan-1-yl)-6-methyl-2-(3-nitrophenyl)-2,3-dihydro-1,3-oxazepin-4,7-dione (3a)**

The reaction of imine (1a) (2.84 g, 0.01 mol) and citraconic anhydride (1.12 g, 0.01 mol) gave (3a) as a white powder, yield 3 g, 77%; mp 218–219° C. Found $C_{22}H_{24}N_2O_5$ (%): C 67.10, H 5.31, N 6.52. Calculated (%): C 66.65, H 6.10, N 7.07. $^1$H NMR (300 MHz, DMSO-$d_6$), δ, ppm: 10.12 (1H, s, O-C<u>H</u>-N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 8.50 (1H, s, <u>$H_2$</u>), 8.32 (1H, d, J=9Hz, <u>$H_6$</u>), 8.21 (1H, d, J=6Hz, <u>$H_4$</u>), 7.78 (1H, t, J=12Hz, <u>$H_5$</u>), 6.02 (1H, d, J=9Hz, =C<u>H</u>-CO-N), 2.13 (3H, s, C<u>$H_3$</u>), adamantyl group: 2.06 (3H, s, 3C<u>H</u>), 1.53-2.02 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3058 (C-$H_{aromatic}$), 2905, 2816 (C-$H_{aliphatic}$), 1721 (C=$O_{lactone}$),

1673 (C=$O_{lactam}$), 1526 (C=$C_{aromatic}$), 1441 (CO-N), 1351 (CO-O).

**3-(adamantan-1-yl)-2-(3-bromophenyl)-6-methyl-2,3-dihydro-1,3-oxazepin-4,7-dione (3b)**

The reaction of imine (1b) (3.18 g, 0.01 mol) and citraconic anhydride (1.12 g, 0.01 mol) gave (3b) as a white powder, yield 3.1 g, 74%; mp 176–177° C. Found $C_{22}H_{24}BrNO_3$ (%): C 62.10, H 5.15, N 3.78. Calculated (%): C 61.40, H 5.62, N 3.25. $^1$H NMR (300 MHz, DMSO-$d_6$), δ, ppm: 8.58 (1H, s, O-C<u>H</u>-N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 8.48 (1H, s, <u>$H_2$</u>), 8.29 (1H, d, J=6Hz, <u>$H_6$</u>), 8.17 (1H, d, J=9Hz, <u>$H_4$</u>), 7.74 (1H, t, J=9Hz, <u>$H_5$</u>), 6.06 (1H, d, J=9Hz, =C<u>H</u>-CO-N), 2.14 (3H, s, C<u>$H_3$</u>), adamantyl group: 2.09 (3H, s, 3C<u>H</u>), 1.55-2.01 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3019 (C-$H_{aromatic}$), 2908, 2832 (C-$H_{aliphatic}$), 1723 (C=$O_{lactone}$), 1638 (C=$O_{lactam}$), 1531 (C=$C_{aromatic}$), 1447 (CO-N), 1351 (CO-O).

**The general procedure for synthesizing 3-(adamantan-1-yl)-2-(3-aryl)-1,3-oxazinan-6-one (4a,b)**

0.01 mol of compounds 1a and b, in the form of a hot solution, were dissolved in 15 mL dry benzene, then an appropriate solution of 0.01 mol 3-chloropropanoic acid in 15 mL dry benzene was added. The mixture was refluxed at boiling point solvent for 22 hours, and the resulting solvent was vaporized. The residual solid was re-crystallized twice from EtOH.

**Description of the properties of (4a and 4b)**

**3-(adamantan-1-yl)-2-(3-nitrophenyl)-1,3-oxazinan-6-one (4a)**

The reaction of imine (1a) (2.84 g, 0.01 mol) and 3-chloropropanoic acid (1.08 g, 0.01 mol) gave (4a) as a white powder, yield 2 g, 57%; mp 188–189° C. Found $C_{20}H_{24}N_2O_4$ (%): C 66.80, H 7.23, N 8.30. Calculated (%): C 67.40, H 6.79, N 7.86. $^1$H NMR (300 MHz, $CDCl_3$), δ, ppm: 7.93 (1H, s, O-C<u>H</u>-N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 7.44 (1H, d, J=6Hz, <u>$H_2$</u>), 6.67-6.91 (3H, m, <u>$H_4$</u>, <u>$H_5$</u>, <u>$H_6$</u>), 3.65 (2H, br.s, C<u>$H_2$</u>-N), 2.10 (2H, br.s, C<u>$H_2$</u>-CO), adamantyl group: 1.63 (3H, s, 3C<u>H</u>), 0.98-1.36 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3050 (C-$H_{aromatic}$), 2929, 2847 (C-$H_{aliphatic}$), 1722 (C=$O_{lactone}$), 1518 (C=$C_{aromatic}$), 1348 (CO-O).

**3-(adamantan-1-yl)-2-(3-bromophenyl)-1,3-oxazinan-6-one (4b)**

The reaction of imine (1b) (3.18 g, 0.01 mol) and 3-chloropropanoic acid (1.08 g, 0.01 mol) gave (4b) as a white powder, yield 2.3 g, 61%; mp 174–175° C. Found $C_{20}H_{24}BrNO_2$ (%): C 61.95, H 6.93, N 3.15. Calculated (%): C 61.54, H 6.20, N 3.59. $^1$H NMR (300 MHz, $CDCl_3$), δ, ppm: 7.74 (1H, s, O-C<u>H</u>-N); phenyl group ($H_2$, $H_4$, $H_5$, $H_6$ aromatic): 6.94 (1H, d, J=9Hz, <u>$H_2$</u>), 6.56-6.61 (3H, m, <u>$H_4$</u>, <u>$H_5$</u>, <u>$H_6$</u>), 3.06 (2H, br.s, C<u>$H_2$</u>-N), 2.09 (2H, br.s, C<u>$H_2$</u>-CO), adamantyl group: 1.42 (3H, s, 3C<u>H</u>), 0.96-1.26 (12H, m, 6C<u>$H_2$</u>). FTIR (ν $cm^{-1}$): 3030 (C-$H_{aromatic}$), 2912, 2825 (C-$H_{aliphatic}$), 1719 (C=$O_{lactone}$), 1523 (C=$C_{aromatic}$), 1340 (CO-O).

**The general procedure for synthesizing 3-(adamantan-1-yl)-2-(3-aryl)-1,3-thiazinan-4-one (5a,b)**

A 0.01 mol solution of compound 1a and b was mixed with 15 mL dry 1,4-dioxane, and a convenient solution of 0.01 mol 3-mercaptopropanoic acid in 10 mL dry 1,4-dioxane in the presence of a small portion of anhydrous $ZnCl_2$. This was then refluxed for 22-24 hours with vigorous stirring. The solvent was vaporized and the residual solid was washed with a 5% solution $NaHCO_3$ and then with distilled water. The obtained product was dried and re-crystallized from EtOH.

**Description of the properties of (5a and 5b)**

**3-(adamantan-1-yl)-2-(3-nitrophenyl)-1,3-thiazinan-4-one (5a)**

The reaction of imine (1a) (2.84 g, 0.01 mol) and 3-mercaptopropanoic acid (1.06 g, 0.01 mol) gave (5a) as a white powder, yield 2.3 g, 64%; mp 290° C (decomp.). Found $C_{20}H_{24}N_2O_3S$ (%): C 65.15, H 6.93, N 6.85, S 7.84. Calculated (%): C 64.49, H 6.49, N 7.52, S 8.61. FTIR (ν $cm^{-1}$): 3085 (C-$H_{aromatic}$), 2939, 2813 (C-$H_{aliphatic}$), 1709 (C=$O_{lactam}$), 1549 (C=$C_{aromatic}$), 832 (C-S-C).

**3-(adamantan-1-yl)-2-(3-bromophenyl)-1,3-thiazinan-4-one (5b)**

The reaction of imine (1b) (3.18 g, 0.01 mol) and 3-mercaptopropanoic acid (1.06 g, 0.01 mol) gave (5b) as a white powder, yield 2.7 g, 68%; mp 280° C (decomp.). Found $C_{20}H_{24}BrNOS$ (%): C 60.05, H 6.44, N 3.82, S 8.54. Calculated (%): C 59.11, H 5.95, N 3.45, S 7.89. FTIR (ν $cm^{-1}$): 3059 (C-$H_{aromatic}$), 2931, 2849 (C-$H_{aliphatic}$), 1705 (C=$O_{lactam}$), 1564 (C=$C_{aromatic}$), 883 (C-S-C).

**Table 3. FTIR spectral data (ν, $cm^{-1}$) for compounds (2a,b-5a,b)**

| Comp. № | ν C-H aromatic | ν C-$H_{aliphatic}$ | ν C=O lactone | ν C=O lactam | ν C=C aromatic | ν (CO)-N | ν (CO)-O | ν C-S-C |
|---|---|---|---|---|---|---|---|---|
| 2a | 3042 | 2907, 2846 | 1728 | 1685 | 1524 | 1436 | 1363 | - |
| 2b | 3012 | 2901, 2817 | 1726 | 1665 | 1521 | 1425 | 1353 | - |
| 3a | 3058 | 2905, 2816 | 1721 | 1673 | 1526 | 1441 | 1351 | - |
| 3b | 3019 | 2908, 2832 | 1723 | 1638 | 1531 | 1447 | 1351 | - |
| 4a | 3050 | 2929, 2847 | 1722 | - | 1518 | - | 1348 | - |
| 4b | 3030 | 2912, 2825 | 1719 | - | 1523 | - | 1340 | - |
| 5a | 3085 | 2939, 2813 | - | 1709 | 1549 | - | - | 832 |
| 5b | 3059 | 2931, 2849 | - | 1705 | 1564 | - | - | 883 |

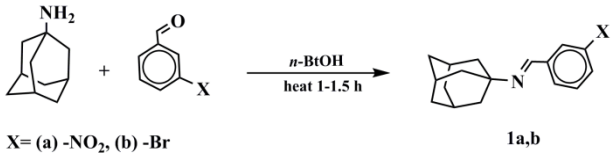
**Table 4. $^1$H NMR chemical shift (DMSO-$d_6$ and $CDCl_3$*, δ, ppm) for compounds (2a,b-4a,b)**

| Comp.№ | O-C<u>H</u>-N | 4<u>H</u>-phenyl group | (15<u>H</u>-) adamantyl group (3H,3C<u>H</u>), (12H,6C$\underline{H_2}$) | =C<u>H</u>CO-N | =C<u>H</u>-CO-O | (3H, C$\underline{H_3}$) | C$\underline{H_2}$-N | C$\underline{H_2}$-CO |
|---|---|---|---|---|---|---|---|---|
| 2a | 10.15 (s) | 8.70 (1H, s, $\underline{H_2}$), 8.48-8.59 (1H, m, $\underline{H_6}$), 8.18-8.36 (1H, m, $\underline{H_4}$), 7.72-7.94 (1H, m, $\underline{H_5}$), | 2.14 (s), 1.64-2.03 (m) | 6.33 (1H, dd, J=6Hz, 12Hz,) | 4.14 (1H, dd, J=9Hz, 6Hz,) | - | - | - |
| 2b | 9.86 (s) | 8.21 (1H, s, $\underline{H_2}$), 7.87-8.11 (1H, m, $\underline{H_6}$), 7.50-7.65 (1H, m, $\underline{H_4}$), 7.43-7.60 (1H, m, $\underline{H_5}$) | 2.13 (s), 1.63-1.76 (m) | 6.11 (1H, dd, J=6Hz, 9Hz) | 4.12 (1H, dd, J=6Hz, 6Hz) | - | - | - |
| 3a | 10.12 (s) | 8.50 (1H, s, $\underline{H_2}$), 8.32 (1H, d, J=9Hz, $\underline{H_6}$), 8.21 (1H, d, J=6Hz, $\underline{H_4}$), 7.78 (1H, t, J=12Hz, $\underline{H_5}$) | 2.06 (s), 1.53-2.02 (m) | 6.02 (1H, d, J=9Hz) | - | 2.13 (s) | - | - |
| 3b | 8.58 (s) | 8.48 (1H, s, $\underline{H_2}$), 8.29 (1H, d, J=6Hz, $\underline{H_6}$), 8.17 (1H, d, J=9Hz, $\underline{H_4}$), 7.74 (1H, t, J=9Hz, $\underline{H_5}$) | 2.09 (s), 1.55-2.01 (m) | 6.06 (1H, d, J=9Hz) | - | 2.14 (s) | - | - |
| 4a* | 7.93 (s) | 7.44 (1H, d, J=6Hz, $\underline{H_2}$), 6.67-6.91 (3H, m, $\underline{H_4}$, $\underline{H_5}$, $\underline{H_6}$) | 1.63 (s), 0.98-1.36 (m) | - | - | - | 3.65 (2H, br.s) | 2.10 (2H, br.s) |
| 4b* | 7.74 (s) | 6.94 (1H, d, J=9Hz, $\underline{H_2}$), 6.56-6.61 (3H, m, $\underline{H_4}$, $\underline{H_5}$, $\underline{H_6}$) | 1.42 (s), 0.96-1.26 (m) | - | - | - | 3.06 (2H, br.s) | 2.09 (2H, br.s) |

## Results and Discussion:

The routes of the reactions are shown in reaction equation 1 and scheme 2. The reaction schemes included the synthesis of two new Schiff bases—*(E)-N*-(adamantan-1-yl)-1-(3-aryl)methanimine) (1a,b)—which are essential for the dependent synthesis of three new imine derivatives—1,3-thiazinan-4-one, 1,3-oxazinan-6-one and 1,3-oxazepin-4,7-dione (2a,b-5a,b)—which contain an adamantyl fragment as a result of the condensation of compounds (1a,b) with 3-mercaptopropanoic acid, 3-chloropropanoic acid and maleic, citraconic anhydride, respectively. The structures of the intermediate and final products were determined by FTIR, $^1$H NMR, C.H.N.S analysis, and single-crystal X-ray diffraction analysis for 1a. Details of the spectral data FTIR and $^1$H NMR for products (1a,b-5a,b) and (1a,b-4a,b), respectively are displayed in Tables 2-4. An outline of the range of FTIR and $^1$H NMR data will

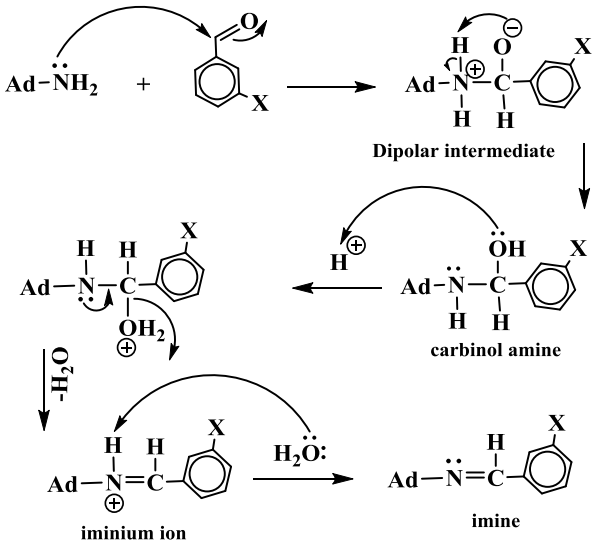
also be provided in the following reaction equation 1.




**Reaction equation 1. For synthesis compounds (1a,b)**

**FTIR and $^1$H NMR data for compounds (1a,b) is shown in Figs. 1, 2, 3 and 4.**

FTIR: all spectra exhibited evanescence in the stretching vibration bands of groups -$NH_2$ and C=O for amine and aldehydes, respectively with characteristic stretching vibration bands of the azomethine group (C=N) at 1638 and 1631 $cm^{-1}$, stretching vibration bands at range 3052 and 3092 $cm^{-1}$ for C-$H_{aromatic}$, and stretching vibration bands at range 2811-2906 $cm^{-1}$ for C-$H_{aliphatic}$. $^1$H NMR data: all spectra exhibited singlet and multiplet signals of the adamantyl group (3H, s, 3C<u>H</u>), (12H, m, 6C<u>$H_2$</u>) at the range δ 1.63-2.13 ppm, and protons for the CH=N group displayed a singlet signal at δ 8.29 and 8.58 ppm, and displayed singlet, doublet , doublet and triplet of protons (<u>$H_2$</u>, <u>$H_6$</u>, <u>$H_4$</u>, <u>$H_5$</u> aromatic), respectively in an phenyl group at the range δ 7.40-8.47 ppm. The forming imine derivatives (1a,b) was carried out according to mechanism in literature (19). The nitrogen of amine attacks to the carbonyl group by nucleophilic addition to produce hemi-aminal and then the leaving of a water molecule to give the target compound. See Scheme 1.




**Scheme 1. The suggested mechanism of the forming imine derivatives (1a,b)**

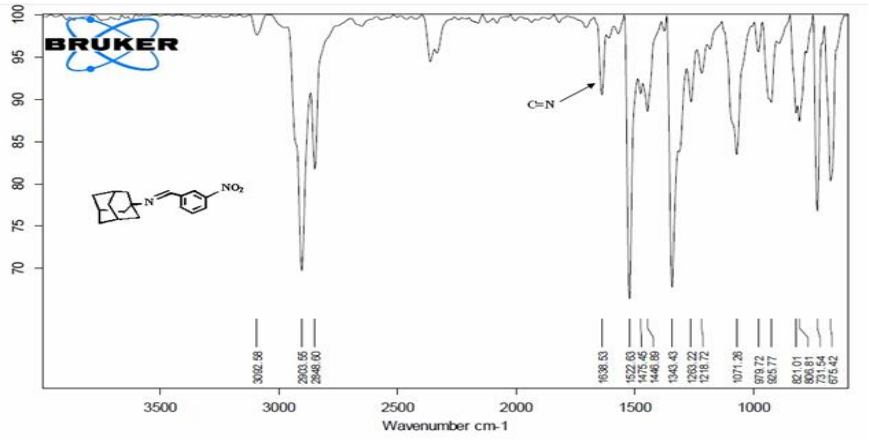



**Figure 1. FTIR spectrum of compound (1a)**

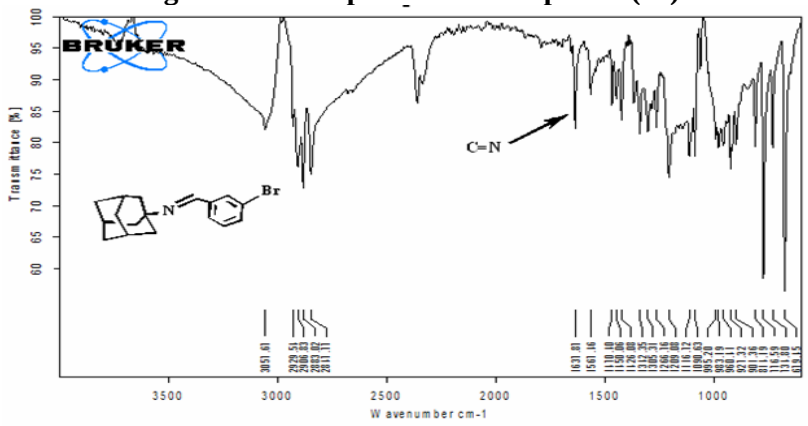



**Figure 2. FTIR spectrum of compound (1b)**

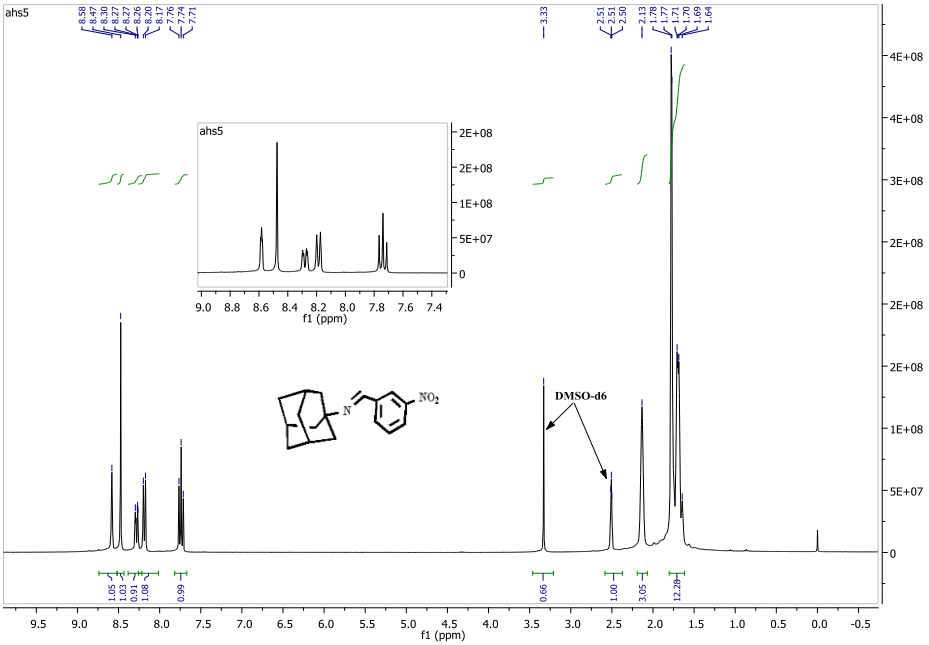



**Figure 3. $^{1}$H NMR spectrum of compound (1a)**

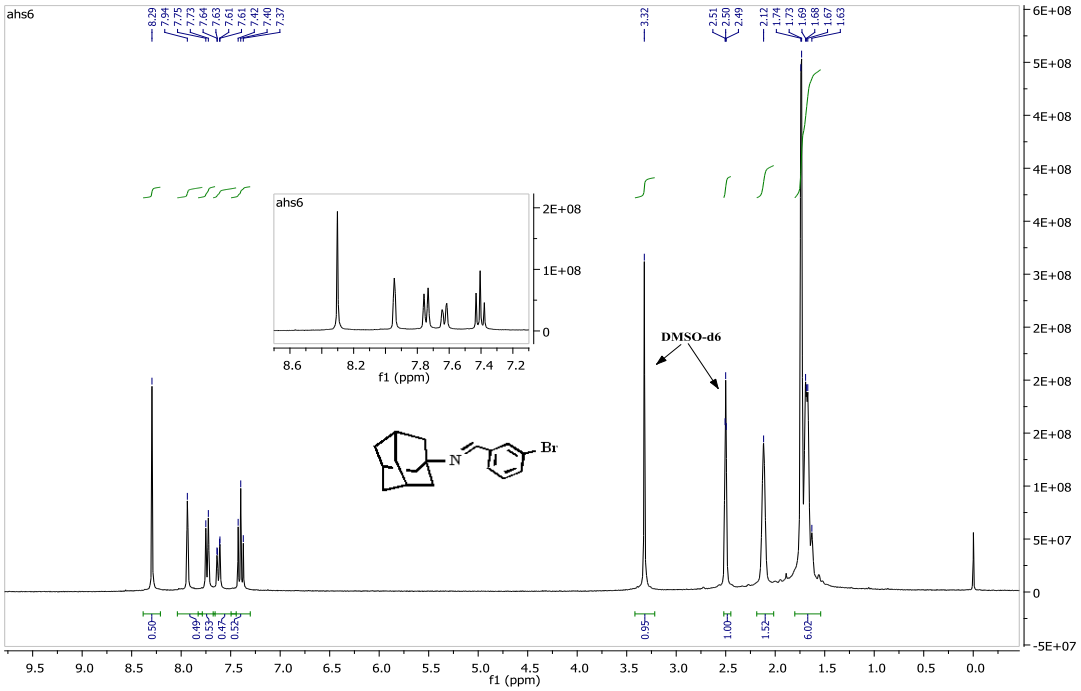
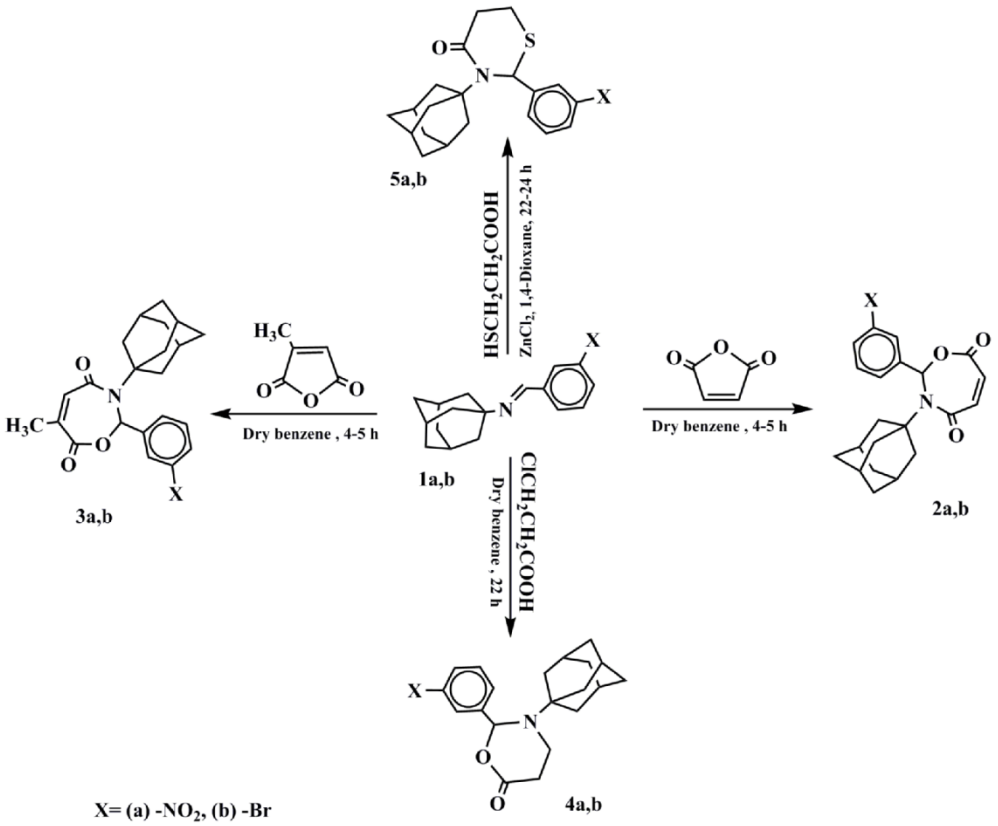
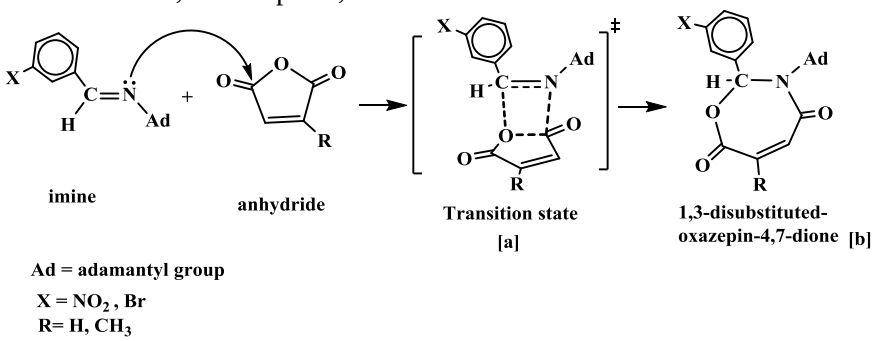



**Figure 4. $^{1}$H NMR spectrum of compound (1b)**




**Scheme 2. Pathways for synthesis compounds (2a,b -5a,b)**

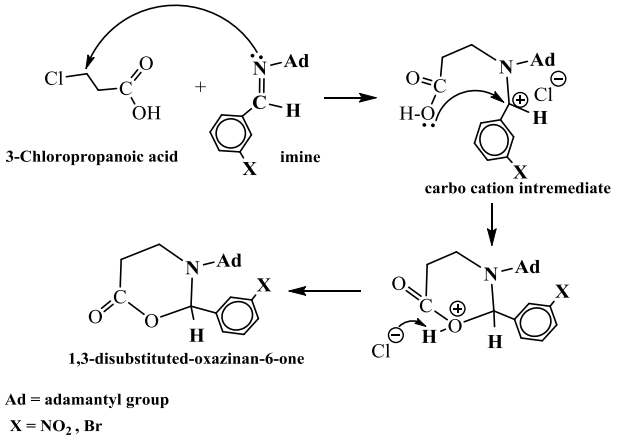
FTIR spectra of compounds (2a,b-5a,b) revealed the disappearance of absorption bands of -C=N azomethines and C=O anhydrides, and the appearance of a stretching vibrations of C-H aromatic at 3010-3085 $cm^{-1}$ and C-$H_{aliphatic}$ at 2811-2915 $cm^{-1}$. The stretching vibrations of the C=$O_{lactone}$ and C=$O_{lactam}$ groups were confirmed by a strong absorption band observed at the ranges 1722-1730 $cm^{-1}$ and 1663-1704 $cm^{-1}$ respectively, whilst the stretching vibrations of the CO-N, CO-O and C-S-C groups appeared at the frequency ranges of 1490-1529 $cm^{-1}$, 1332-1340 $cm^{-1}$ and 832-883 $cm^{-1}$, respectively. These data was displayed selective spectra in Figs. 5, 6 and 7. The proposed mechanisms of formation 1,3-oxazepin-4,7-one (2a,b and 3a,b), 1,3-oxazinan-6-one (4a,b) and 1,3-thiazinan-4-one (5a,b) derivatives were explained in literatures (16, 21, 24). The forming mechanism (2a,b and 3a,b) compounds included a cyclo-addition reaction (2+5) to produce cyclic seven membered by nucleophilic acts of the ion pair of electrons in an imine group towards the electrophilic center of carbonyl group of the cyclic anhydride to make cyclic four and five membered as a transition state [a] which was recycled intramolecular by concerted, breaking and forming cyclic seven membered to make the target compound [b] without forming intermediate. See Scheme 3.




**Scheme 3. The suggested mechanism of the forming 1,3-oxazepin-4,7-one derivatives (2a,b and 3a,b)**

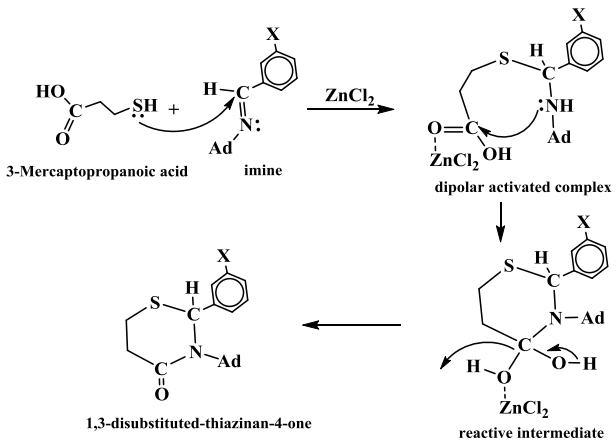
While the mechanism forming compound (4a,b) may occur by concerting dipolar cyclo-addition, which involves a Nucleophilic attack of the unshared electron pair-nitrogen atom of the azomethine group (-C=N-) towards a carbon atom of 3-chloropropanoic acid to which the chlorine

atom binds to form an intermediate (carbocation), which recycled intramolecular to give the final product. See Scheme 4.




**Scheme 4. The suggested mechanism of the forming 1,3-oxazinan-6-one derivatives (4a,b)**

Whilst the mechanism forming compound (5a,b) may be occurred by addition anhydrous $ZnCl_2$ as catalyst which may activate the acid group by forming O...Zn bonding with oxygen carbonyl group, thereafter accelerate to promote nucleophilicity of mercapto group of 3-mercaptopropanoic acid causing its superficial addition on the imine. Then a nucleophile attacks of the electron pair-nitrogen atom towards the carbon atom of the carboxyl group. Afterwards support the intramolecular cyclo-addition to form intermediate and then the leaving water molecule. See Scheme 5.




**Scheme 5. The suggested mechanism of the forming 1,3-thiazinan-4-one derivatives (5a,b)**

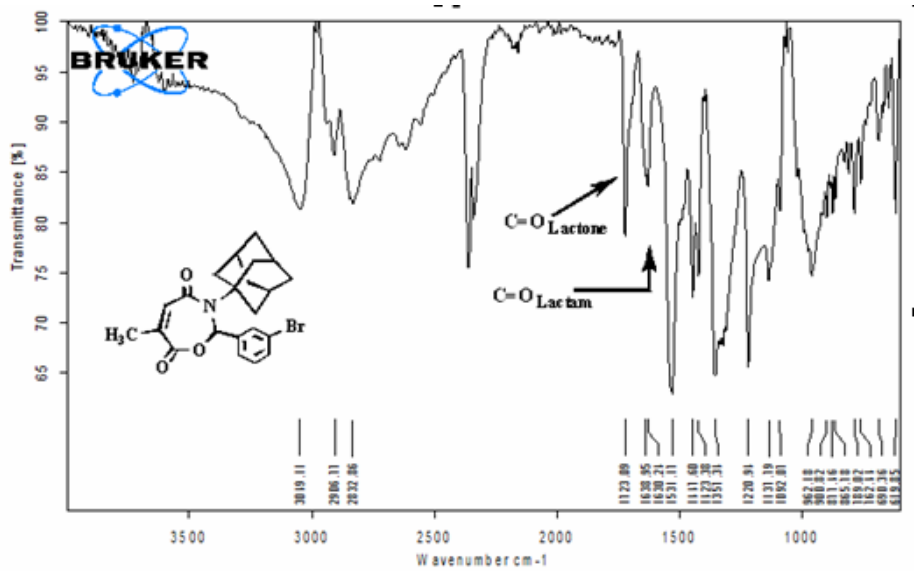



**Figure 5. FTIR spectrum of compound (3b)**

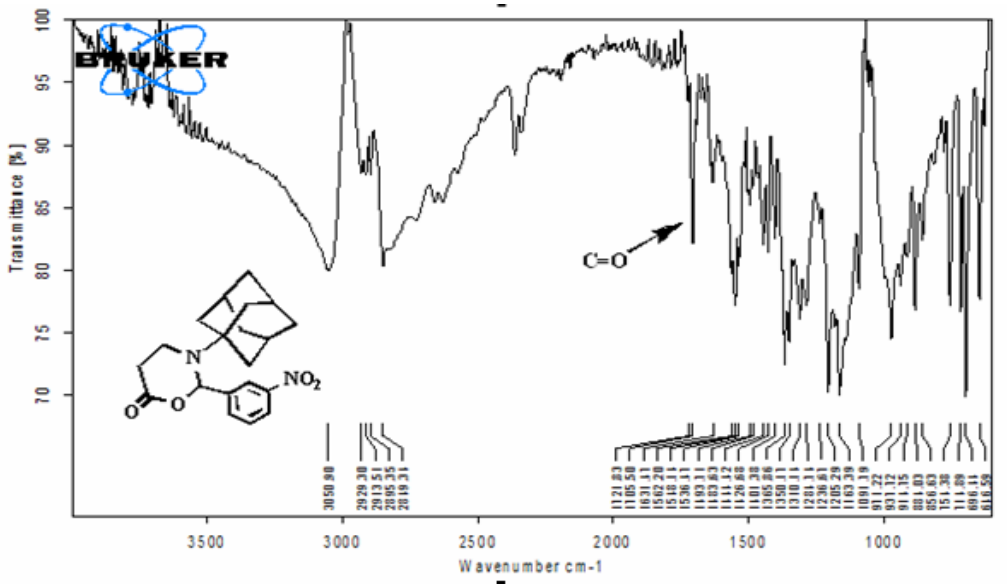



**Figure 6. FTIR spectrum of compound (4a)**

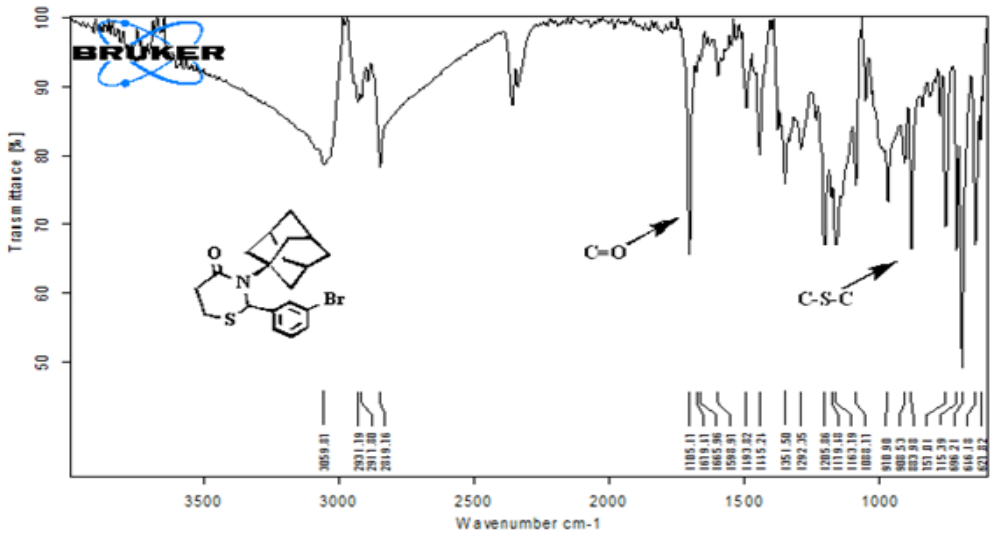



**Figure 7. FTIR spectrum of compound (5b)**

The $^{1}$H NMR spectra of compounds (2a,b-4a,b) showed singlet and multiplet signals of the adamantyl group (3H, s, 3CH), (12H, m, 6$CH_2$) at the range δ 0.96-2.14 ppm, and protons for the O-CH-N group displayed a singlet signal at range δ 7.74 -10.15 ppm, whilst protons of the phenyl group ($H_2$, $H_6$, $H_4$, $H_5$ $_{aromatic}$) of compounds (2a,b-4a,b) showed different signals (s, m, m, m; s, d, d, t; d, m), respectively at a range of δ 6.56-8.70 ppm. The protons of the (=CHCO-N) and (=CH-CO-O) groups in compounds 2a,b were observed as doublet- doublet signals at ranges of 6.11-6.33 ppm and 4.12-4.14 ppm, respectively. Whilst protons of the (=CHCO-N) group in compounds 3a,b were observed as doublet signal at range of 6.02-6.06 ppm, the protons of the methyl group showed singlet signal at δ 2.13 and 2.14 ppm. The protons of the ($CH_2$-N) and ($CH_2$-CO) groups in compounds 4a,b displayed a broad singlet signals at ranges of 3.06-3.65 ppm and 2.09-2.10 ppm, respectively. These data was displayed selective spectra in Figs. 8, 9 and 10.

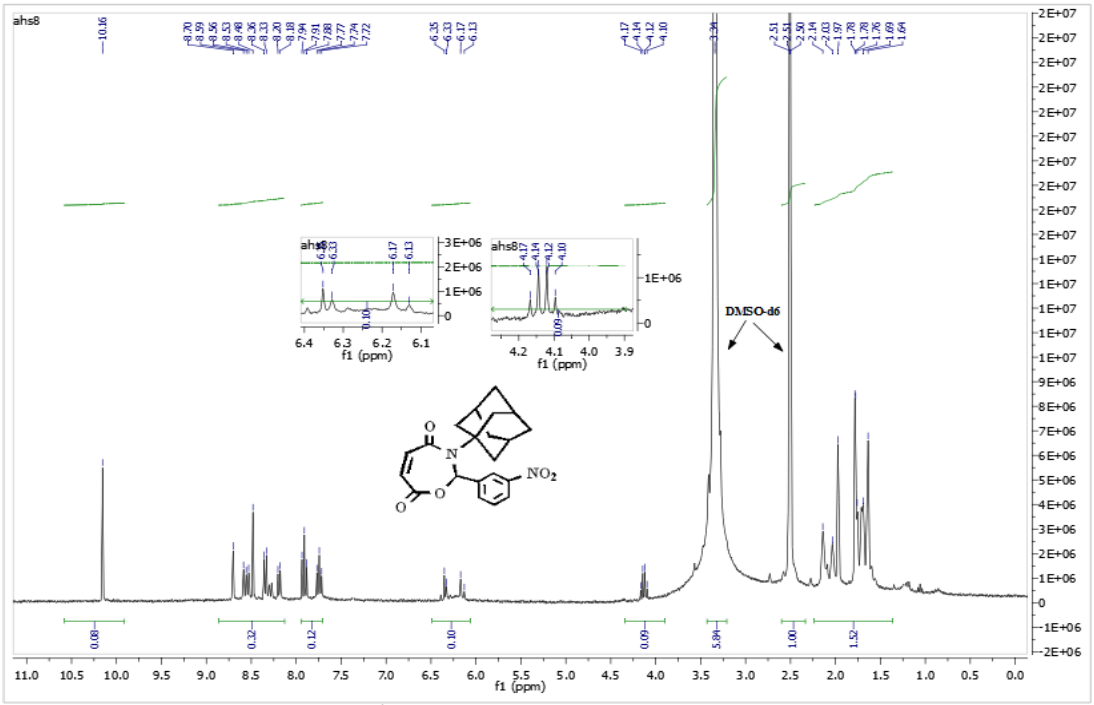



**Figure 8. $^{1}$H NMR spectrum of compound (2a)**

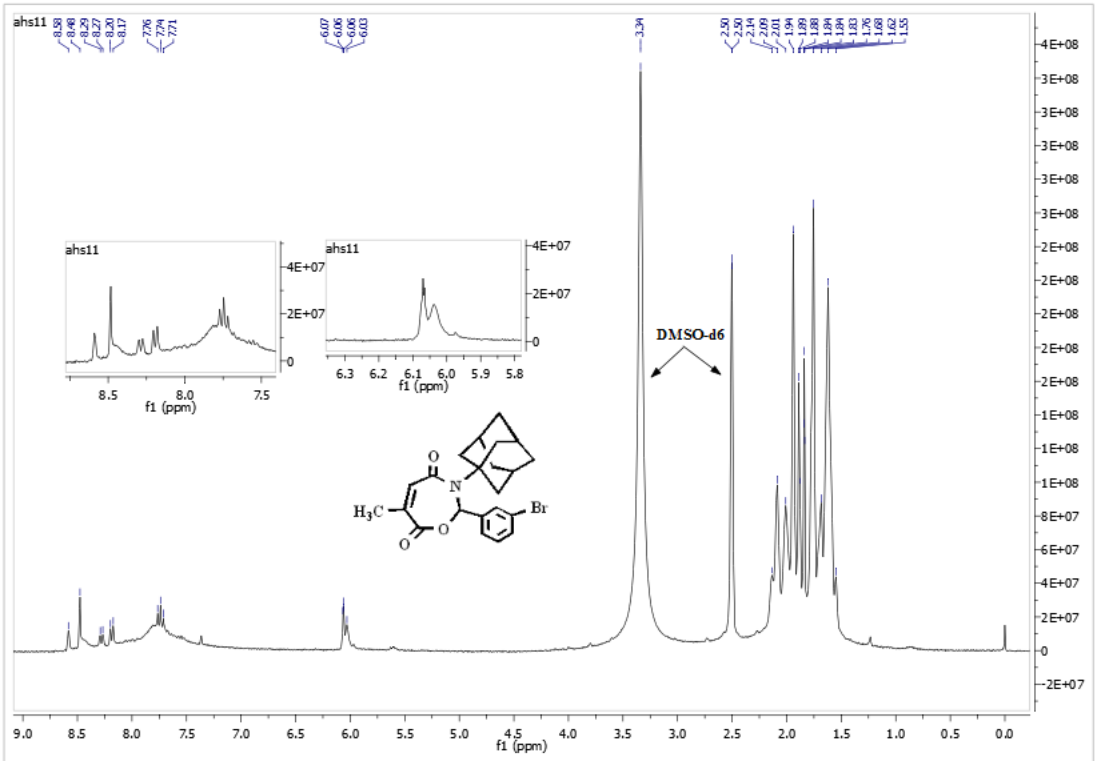



**Figure 9. $^{1}$H NMR spectrum of compound (3b)**

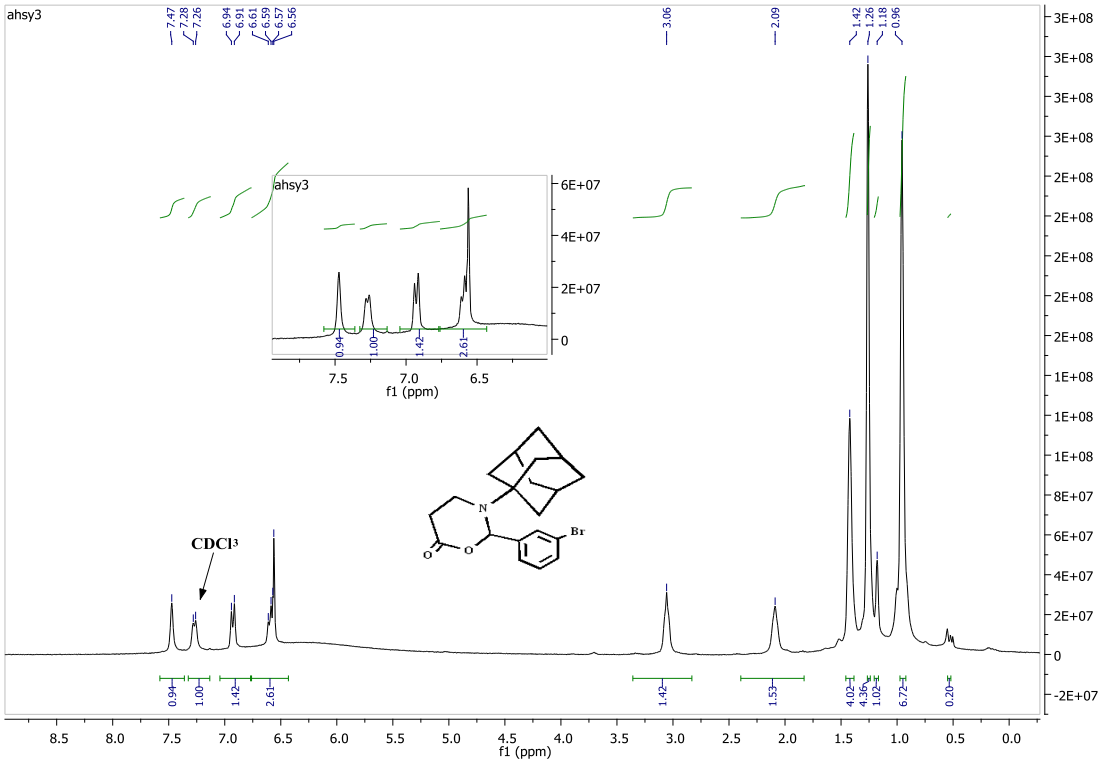



**Figure 10. $^{1}$H NMR spectrum of compound (4b)**

## Crystallographic Study

The molecular structure of compound (1a) was displayed in Fig. 11. The crystalline data for (1a) was as follows: $C_{17}H_{20}N_2O_2$, MW= 284.35 g.mol$^{-1}$, Orthorhombic, space group (Pnma), a= 24.7642(7) Å, b= 6.8123(2) Å, c= 17.5235(5) Å, α= 90°, β= 90°, γ= 90°, *V* =2956.24(15) Å$^3$, Z= 8, Crystal dimensions, mm (0.10 x 0.10 x 0.10), D*x*= 1.278 g.cm$^{-3}$.

The X-ray diffraction intensity for compound 1a was measured using a *STOE StadiVari Pilatus100K* diffractometer (26), *λ(CuKα)* = 1.5418 Å, using the *ω*-scanning technique. The data for the X-ray diffraction were processed by the *WinGX* suite (27), with the *SHELX-97* program package being used to perform all subsequent calculations (28). The crystal structure was determined using the direct method, then refined with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were placed geometrically and refined isotropically using a riding model. The drawing of the structure was prepared using the *MERCURY CSD 3.1* program (29). The bond length for (N1-C11) is 1.258 (3) Å, which is normal for double bond of (N=C), and the arrangement around this bond is trans (30). The structure displayed no hydrogen bonds. The details of the crystal data are provided in Tables 5-7.

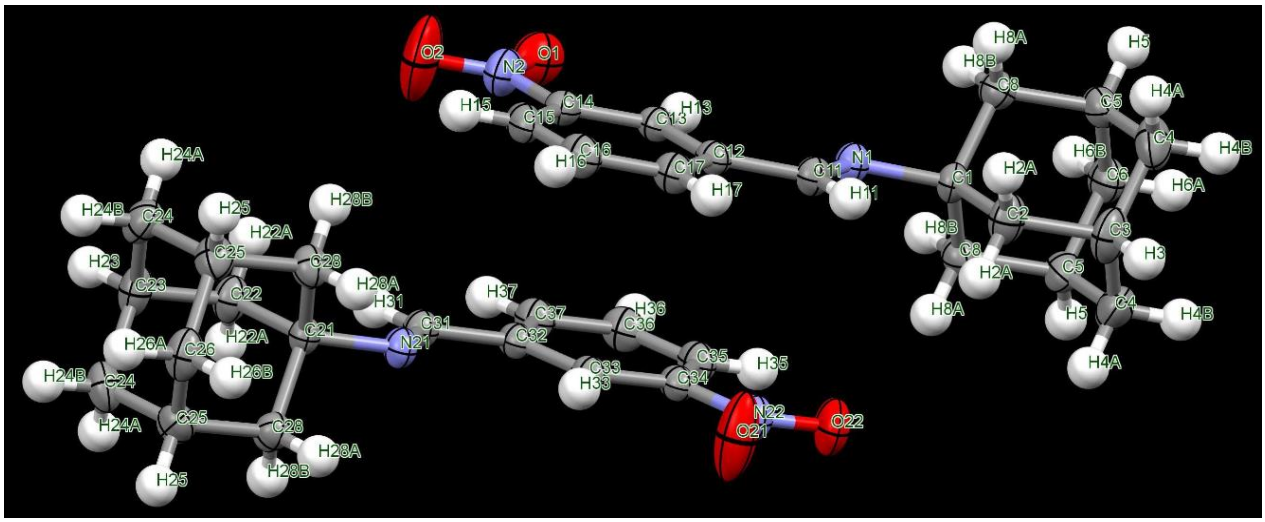


**Figure 11. The molecular structure, showing the atomic numbering of compound 1a**

**Table 5. Crystal data and refinement details for compound 1a**

| | |
|---|---|
| Formula | $C_{17}H_{20}N_2O_2$ |
| MW | 284.35 g.mol$^{-1}$ |
| Crystal system | Orthorhombic |
| Space Group | Pnma |
| a, Å | 24.7642(7) |
| b, Å | 6.8123(2) |
| c, Å | 17.5235(5) |
| α, ° | 90 |
| β, ° | 90 |
| γ, ° | 90 |
| V, Å$^3$ | 2956.24(15) |
| Z | 8 |
| Dx, g/cm$^3$ | 1.278 |
| Radiation | Cu $K_\alpha$ |
| $\mu(K_\alpha)$, mm$^{-1}$ | 0.675 |
| θ range, ° | 3.569-72.124 |
| h, k, l range | -30≤h≤30 -8≤k≤2 -21≤l≤21 |
| Crystal dimensions, mm | 0.10 x 0.10 x 0.10 |
| Total reflections | 30628 |
| Reflections/parameters | 3114 / 236 |
| GooF | 0.956 |
| $R_1$ [I≥ 2σ(I)] | 0.0394 |
| $\Delta\rho_{max}/\Delta\rho_{min}$, e/Å$^3$ | 0.207/ -0.159 |

**Table 6. Bond lengths d (Å) for compound 1a**

| Bond | *d (Å)* | Bond | *d (Å)* |
|---|---|---|---|
| O1-N2 | 1.212(3) | O21-N22 | 1.196(3) |
| O2-N2 | 1.209(4) | O22-N22 | 1.207(3) |
| N1-C11 | 1.258(3) | N21-C31 | 1.258(3) |
| N1-C1 | 1.466(3) | N21-C21 | 1.467(3) |
| N2-C14 | 1.470(4) | N22-C34 | 1.466(3) |
| C1-C2 | 1.522(4) | C21-C22 | 1.524(3) |
| C1-C8 | 1.530(2) | C21-C28 | 1.529(2) |
| C2-C3 | 1.524(4) | C22-C23 | 1.525(4) |
| C2-H2A | 0.9700 | C22-H22A | 0.9700 |
| C2-H2B | 0.9700 | C22-H22B | 0.9700 |
| C3-C4 | 1.519(3) | C23-C24 | 1.518(3) |
| C3-H3 | 0.9800 | C23-H23 | 0.9800 |
| C4-C5 | 1.511(3) | C24-C25 | 1.514(3) |
| C4-H4A | 0.9700 | C24-H24A | 0.9700 |
| C4-H4B | 0.9700 | C24-H24B | 0.9700 |
| C5-C6 | 1.519(2) | C25-C26 | 1.517(2) |
| C5-C8 | 1.528(2) | C25-C28 | 1.530(2) |
| C5-H5 | 0.9800 | C25-H25 | 0.9800 |
| C6-H6A | 0.9700 | C26-H26A | 0.9700 |
| C6-H6B | 0.9700 | C26-H26B | 0.9700 |
| C8-H8A | 0.9700 | C28-H28A | 0.9700 |
| C8-H8B | 0.9700 | C28-H28B | 0.9700 |
| C11-C12 | 1.464(3) | C31-C32 | 1.464(3) |
| C11-H11 | 0.9300 | C31-H31 | 0.9300 |
| C12-C17 | 1.385(3) | C32-C33 | 1.390(3) |
| C12-C13 | 1.393(3) | C32-C37 | 1.392(3) |
| C13-C14 | 1.368(3) | C33-C34 | 1.369(3) |
| C13-H13 | 0.9300 | C33-H33 | 0.9300 |
| C14-C15 | 1.379(4) | C34-C35 | 1.382(4) |
| C15-C16 | 1.370(4) | C35-C36 | 1.374(4) |
| C15-H15 | 0.9300 | C35-H35 | 0.9300 |
| C16-C17 | 1.372(4) | C36-C37 | 1.377(4) |
| C16-H16 | 0.9300 | C36-H36 | 0.9300 |
| C17-H17 | 0.9300 | C37-H37 | 0.9300 |

**Table 7. Bond angles *ω*° for compound 1a.**

| Angle | *ω*,° | Angle | *ω*,° |
|---|---|---|---|
| C11-N1-C1 | 121.5(2) | C16-C17-C12 | 121.7(3) |
| O2-N2-O1 | 123.3(3) | C31-N21-C21 | 121.7(2) |
| O2-N2-C14 | 117.4(3) | O21-N22-O22 | 122.1(3) |
| O1-N2-C14 | 119.3(3) | O21-N22-C34 | 118.5(2) |
| N1-C1-C2 | 116.6(2) | O22-N22-C34 | 119.5(2) |
| N1-C1-C8 | 107.06(13) | N21-C21-C22 | 116.8(2) |
| C2-C1-C8 | 108.77(13) | N21-C21-C28 | 107.16(13) |
| N1-C1-C8 | 107.06(13) | C22-C21-C28 | 108.49(13) |
| C2-C1-C8 | 108.77(13) | C28-C21-C28 | 108.5(2) |
| C8-C1-C8 | 108.3(2) | C21-C22-C23 | 110.2(2) |
| C1-C2-C3 | 109.9(2) | C24-C23-C24 | 109.5(2) |
| C4-C3-C4 | 109.5(3) | C24-C23-C22 | 109.81(15) |
| C4-C3-C2 | 109.83(16) | C25-C24-C23 | 109.28(16) |
| C5-C4-C3 | 109.30(17) | C24-C25-C26 | 109.58(17) |
| C4-C5-C6 | 109.34(18) | C24-C25-C28 | 109.43(16) |
| C4-C5-C8 | 109.45(16) | C26-C25-C28 | 109.25(16) |
| C6-C5-C8 | 109.79(16) | C25-C26-C25 | 109.7(2) |
| C5-C6-C5 | 109.3(2) | C21-C28-C25 | 110.43(14) |
| C5-C8-C1 | 110.25(14) | N21-C31-C32 | 122.6(2) |
| N1-C11-C12 | 122.9(2) | C33-C32-C37 | 118.1(2) |
| C17-C12-C13 | 118.5(2) | C33-C32-C31 | 121.6(2) |
| C17-C12-C11 | 121.0(2) | C37-C32-C31 | 120.3(2) |
| C13-C12-C11 | 120.5(2) | C34-C33-C32 | 119.2(2) |
| C14-C13-C12 | 118.9(2) | C33-C34-C35 | 123.1(3) |
| C13-C14-C15 | 122.5(2) | C33-C34-N22 | 118.3(2) |
| C13-C14-N2 | 118.2(3) | C35-C34-N22 | 118.6(2) |
| C15-C14-N2 | 119.3(3) | C36-C35-C34 | 117.4(2) |
| C16-C15-C14 | 118.6(2) | C35-C36-C37 | 120.7(3) |
| C15-C16-C17 | 119.9(3) | C36-C37-C32 | 121.3(3) |

## Conclusion:

From the research undertaken here, two new starting materials (imines) of *(E)-N*-(adamantan-1-yl)-1-(3-aryl) methanimine were produced, with a yields of (91 and 94%) being obtained. These are precursors for the synthesis of three new imine derivatives—1,3-thiazinan-4-one, 1,3-oxazinan-6-one and 1,3-oxazepin-4,7-dione—which included an adamantyl fragment. All products were identified by $^1$H NMR , FTIR spectra and C.H.N.S analysis, and the molecular structure of *(E)-N*-(adamantan-1-yl)-1-(3-nitrophenyl) methanimine was affirmed by X-ray crystallography.

## Acknowledgment:

We are grateful to Mr. Jalal al-Heeti (University of Ankara–Faculty of Science–Chemistry Department- Turkey) and Prof. Dmitry V. Albov (Chemistry Department, Moscow State University, Russian Federation, email:

dmitryalbov@mail.ru) for their support in performing the (C.H.N.S and $^1$H NMR) analysis and the X-ray crystallography analysis.

## Conflicts of Interest: None.

## References:

1. Fort RC. Adamantane, The Chemistry of Diamond Molecules, Studies in Organic Chemistry. 5th ed. Marcel Dekker: New York, USA; 1976.
2. Fort RC, Schleyer PVR. Adamantane, Consequences of the Diamondoid Structure. Chem. Rev. 1964; 64: 277-300.
3. Raupp-Barcaro IF, Vital MA, Galduróz JC, Andreatini R. Potential Anti-depressant effect of amantadine: A review of preclinical studies and clinical trials. Braz J Psychiatry. 2018; 40(4): 449-458
4. Al-Abdullah ES, Al-Tuwaijri HM, Hassan HM, Al-Alshaikh MA, Habib EE, El-Emam AA. Synthesis, Anti-microbial and hypoglycemic activities of novel N-(1-adamantyl)carbothioamide derivatives. Molecules. 2015; 20(5): 8125-8143.
5. Stetter H. Advances in the chemistry of organic ring systems with Adamantine Type structures. Angewante Chemie International Edition in English. 1962; 1(6): 286-298.
6. Pham VH, Vu BD, Cao DN, Nguyen VT, Phan TPD, Nguyen QH, et al. Synthesis and bioactivity screening of some novel N-(adamantan-1yl)-1-aryl-methanimines, J mil pharm med. 2019; 2: 88-94.
7. Davies W, Grunert RR, Haff RF, Mcgahen JW, Neumayer EM, Paulshock EM, et al. Anti-viral Activity of 1-Adamantanamine (Amantadine). Science. 1964; 144: 862-863.
8. Whitley RJ, Alford CA. Developmental aspects of selected anti-viral chemotherapeutic agents. Annu Rev Microb. 1978; 32: 285-300.
9. Al-Wahaibi L, Hassan H, Abo-Kamar A, Ghabbour H, El-Emam A. Adamantane-Isothiourea Hybrid Derivatives: Synthesis, Characterization, In Vitro Anti-microbial, and In Vivo Hypoglycemic Activities. Molecules. 2017; 22(5): 710.
10. Kapitsa IG, Suslov EV, Teplov GV, Korchagina DV, Komarova NI, Volcho KP, et al. Synthesis and anxiolytic activity of 2-aminoadamantane derivatives containing Mono terpene fragments. Pharm Chem J. 2012; 46(5): 263-265.
11. Kumar CS, Kwong HC, Mah SH, Chia TS, Loh WS, Quah CK, et al. Synthesis and Crystallographic Insight into the Structural Aspects of Some Novel Adamantane Based Ester Derivatives. Molecules. 2015; 20(10): 18827-18846.
12. Kshash AH, Mokhlef MG. Synthesis, Characterization and DFT Study of 4,4′-Oxydianiline Imines as Precursors of Tetrahalo-1,3-oxazepin-1,5-dione. Indones J Chem. 2017; 17 (2): 330-335.
13. Al-Sultani KTA. Synthesis, Identification and Evaluation the Biological Activity for Some New Heterocyclic Compounds Derived from Schiff Bases. J Appl Chem. 2016; 9(5): 1-11.
14. Bosenbecker J, Bareño VDO, Difabio R, Vasconcellos FA, Dutra FSP, Oliveira PS, et al. Synthesis and anti-oxidant activity of 3- (pyridin-2-ylmethyl)-1,3-thiazinane(thiazolidine)-4-ones. J Biochem Mol Toxicol. 2014; 28(9): 425-432.
15. Aljamali NM. Synthesis and identification of oxazepine, diazepine compounds via pericyclic reactions. J Chem & Cheml Sci. 2013; 3(2): 64-69.
16. Sallal ZA, Ghanem HT. Synthesis of New 1,3-Oxazepine Derivatives Containing Azo Group. J Kufa Chem Sci. 2011; (2): 11-23.
17. Younus AAQ, Jber NR. Synthesis and characterization new 1,3-oxazepine compounds from new bis-4-amino-3-mercapto-1,2,4-triazol derivatives. OCAIJ. 2016; 12(2): 1-12.
18. Mohammad AKT, Yeap GY, Osman H. Synthesis, characterization and theoretical study of new liquid crystal compound with an oxazepine core. J Mol Struct. 2015; 1087: 88-96.
19. Abid OH, Ahmed KR. Preparation and Identification of 1,3-Oxazepine Derivatives from Selected Carboxylic Acid Anhydrides with Imines Derived from 4-methyl aniline. Al-Must J Sci. 2018; 29(2): 93-100.
20. Gouvea DP, Bareno VDO, Bosenbecker J, Drawanz BB, Neuenfeldt PD, Siqueira GM, et al. Ultrasonic promoted synthesis of thiazolidinones from 2-aminopyridine and 2-picolylamine. Ultrason Sonochem. 2012; 19: 1127-1131.
21. Abid OH, Abbass HH. Synthesis and Characterization of New Oxazolidine-4-one Derivatives via the Reaction of Various Some Imines with Glycolic Acid. J Uni Anb Pure Sci. 2017; 11(2): 41-48.
22. Alexander AK, Joseph L, George M. Synthesis of Novel 5,6-Benz-1,3-Oxazepin-4,7-dione Derivatives and Screening For Anti-bacterial, Anti-oxidant and Anti-inflammatory Activities. EJPMR. 2016; 3(7): 330-336.
23. Naeem IK, Zimam EH. Synthesis, Characterization and Study Anti-bacterial Activity of some New 1,3-oxazepine and 1,3-diazepine Derivatives. Der Pharm Chem. 2017. 9(21): 86-93.
24. Pang HX, Hui YH, Fan K, Xing XJ , Wu Y, Yang JH, et al. A catalysis study of mesoporous MCM-41 supported Schiff base and $CuSO_4.5H_2O$ in highly regioselective synthesis of 4-thiazolidinone derivatives from cyclo-condensation of mercaptoacetic acid. Chin Chem Lett. 2016; 27: 335–339.
25. Zebardast T, Zarghi A, Daraie B, Hedayati M, Dadrass OG. Design and synthesis of 3-alkyl-2-aryl-1,3-thiazinane-4-one derivatives as selective cyclooxygenase (COX-2) inhibitors. Bioorg Med Chem Lett. 2009; 19: 3162-3165.
26. Stoe C. X-AREA, X-RED32. Stoe C. Darmstadt: Germany; 2012.
27. Farrugia LJ. WinGX and ORTEP for Windows. J Appl Crystallogr. 2012; 45: 849-854.
28. Sheldrick GM. A short history of SHELX. Acta Crystallogr. 2015; C71: 3-8.
29. Macrae CF, Edington PR, McCabe P, Pidcock E,

Shields GP, Taylor R. et al. Mercury: visualization and analysis of crystal structures. J Appl Crystallogr. 2006; 39: 453-457.
30. Al-Wahaibi LH, Hassan HM, Abo-Kamar AM, Ghabbour HA, El-Emam AA. Crystal structure of 4-bromobenzyl (Z)-N′-(adamantan-1-yl)-4-phenylpiperazin-1-carbothioimidate $C_{28}H_{34}BrN_3S$. Z Kristallogr, NCS. 2017; 232(2): 189-191.

# تحضير جزيئات سداسية وسباعية حلقية غير متجانسة حاوية على جزء الادامنتيل والاشعة السينية للتركيب البلوري لمركب *(E)*-*N*-(ادامنتان-1-يل)-1-(3-نايتروفينيل)ميثانيمين

**أحمد حمد شكر** **علي سامي اسماعيل** **أحمد ضاري صالح**

قسم الكيمياء، كلية التربية للعلوم الصرفة، جامعة الانبار، الانبار، العراق.

**الخلاصة:**

تضمن عملنا تحضير ثلاث مشتقات ايمينية جديدة- 1،3- ثيازينان -4-ون ، 1،3- أوكسازينان-6-ون و 1،3- أوكسازيبين-4، 7-دايون والتي احتوت جزء الادامنتيل. وانتجت المركبات من خلال تفاعل تكثيف قاعدة شيف N-(ادامنتان-1-يل)-1-(3-اريل)ميثانيمين مع 3-مركبتوحامض البروبانويك، 3-كلوروحامض البروبانويك، ومالیك، سيتراكونك انهيدرايد، على التوالي. حضرت الايمينات الجديدة من خلال تفاعل التكثيف للادامنتان-1-يل امين و3-نايترو، 3-بروموبنزالديهايد في البيوتانول الاعتيادي. وحصلنا على نواتج جيدة، وشخص تركيبها باستخدام مطيافية الاشعة تحت الحمراء، الرنيين النووي المغناطيسي البروتوني، والتحليل الدقيق للعناصر (C.H.N.S). اثبت التركيب الجزيئي للمركب *(E)*-*N*-(ادامنتان-1-يل)-1-(3-نايتروفينيل)ميثانيمين باستخدام تحليل الاشعة السينية للبلورات.

**الكلمات المفتاحية:** ادامنتان-1-يل امين، 1،3- أوكسازيبين-4، 7-دايون، 1،3- أوكسازينان-6-ون، 1،3- ثيازينان -4-ون، الاشعة السينية للبلورات.