

## Reactions of 6,8-dibromo-2-(3,5-dinitrophenyl)-4*H*-Benzo[*d*] [1,3]oxazin-4-one with Nitrogen and Carbon Nucleophiles

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**Abstract:** The hitherto unknown 6,8-dibromo-2-(3,5-dinitrophenyl)-4*H*-benzo [*d*] [1,3] oxazin-4-one **1** was constructed and its proclivity with some nitrogen and carbon nucleophiles was studied. Compound **1** was utilized as scaffold for novel quinazolinone derivatives **8-10** and **12**. Novel heterocycles **11,13-15** were also constructed from benzoxazinone **1**. All the newly synthesized compounds were characterized by physical and chemical tools.(I.R, <sup>1</sup>HNMR and MASS spectra).

**Key words:** 4*H*-benzo[*d*][1,3]oxazin-4-one • Quinazolinone-4(3*H*)-one • Benzo [*d*] imidazol • Quinoline-3-carboxylic acid and quinoline-3-carbonitrile

### INTRODUCTION

Benzoxazines and their derivatives have been received great attention, some of them proved to be of special importance in medicine as antifungal, anticoagulant, antispasmodic and antiallergic agents [1]. 2-(4-Toluenesulphonyloxy phenyl 3,1-benzoxazine-4-one was prepared and reacted with some nitrogen nucleophiles, the antimicrobial antifungal activity of all the products were evaluated [2]. A series of 2,8-disubstituted benzoxazinones were synthesized and subjected to anti-platelet aggregation, inhibition of superoxide anion generation and inhibition of neutrophil elastase release assays [3].

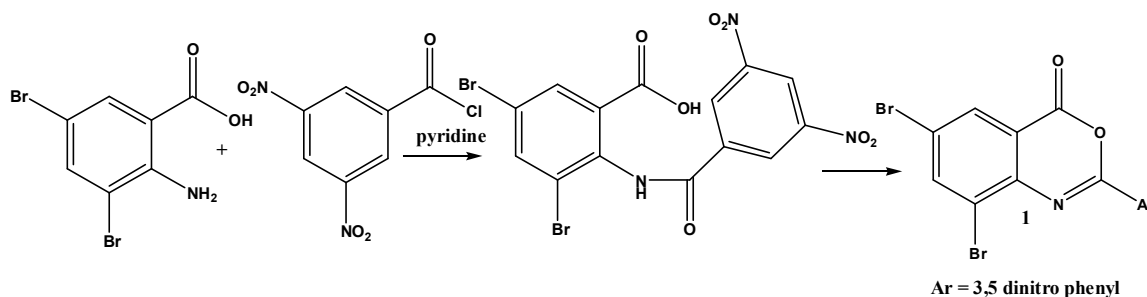
One-pot montmorillonite K-10 clay-supported three-component reactions of substituted salicylaldehydes, ribosyl/deoxyribosylureas and ammonium acetate expeditiously yield the novel *N*-nucleosides, 4-amino-3,4-dihydro-3-(*b*-D-ribo- or *b*-D-20-deoxyribofuranosyl)- 2*H*-benz [*e*]-1,3-oxazin-2-ones; via cycloisomerisation of an aldimine intermediate under solvent-free microwave irradiation conditions [4]. A series of 2-substituted benzoxazinones were synthesized and subjected to anti-human coronavirus and ICAM-1 expression inhibition assays [5].

A new method has been designed to prepare the known benzoxazinone derivative 2-(*N*-phthaloylmethyl)-4*H*-3,1-benzoxazin-4-one. The acyl chloride derivative

*N*-phthaloylglycine reacts with anthranilic acid in chloroform; in the presence of triethylamine, to give an intermediate that is then reacted with cyanuric chloride, used as a cyclization agent; to produce the benzoxazinone derivative [6]. A new series of 6-iodo-2-undecylquinazolin-4(3*H*)-ones were prepared via reaction of 6-iodo-2-undecyl-4*H*-benzoxazin-4-one with nitrogen nucleophiles, namely, primary amines, 4-amino antipyrine, hydrazine hydrate, diamines, ethanol amine and/or hydrazide derivatives and screened for their antitumor activity in vitro against a panel of three human tumor cell lines namely; hepatocellular carcinoma (liver) HepG2; colon cancer HCT-116; and mammary gland breast MCF-7 [7].

6,8-Dibromo-(4*H*)-3,1-benzoxazinone was synthesized and allowed to react with some nitrogen nucleophiles [8]. A series of benzoxazinones were synthesized *via* reaction of anthranilic acid with various substituted benzoyl chlorides in the presence of triethylamine in chloroform, showed a good inhibition of  $\alpha$ -chymotrypsin with IC<sub>50</sub>  $\pm$  SEM values between 6.5 and 341.1  $\mu$ M [9].

In continuation of our efforts towards construct heterocyclic compounds and evaluate their pharmaceutical importance [10-28], the present work deals with synthesis of new benzoxazinone derivative bearing a bulky moiety at position 2, in order to study the stability and reactivity of benzoxazinone nucleus toward some different nucleophilic reagents.

Scheme 1: Formation of 6,8-dibromo-2-(3,5-dinitrophenyl)-4H-benzo[*d*][1,3] oxazin-4-one

## RESULTS AND DISCUSSION

The hitherto unknown 6,8-dibromo-2-(3,5-dinitrophenyl)-4H-benzo[*d*][1,3] oxazin-4-one **1** was constructed in situ from the reaction of 3,5-dibromoanthranic acid and 3,5-dinitrobenzoyl chloride in the presence of dry pyridine as a solvent. (Scheme 1).

The structure assignment of compound **1** was substantiated from its correct elemental analysis (c.f. experimental section). I.R of compound **1** showed absorption bands at  $\nu$  1766 $\text{cm}^{-1}$  (lactonic C=O),  $\nu$  1621 $\text{cm}^{-1}$  (C=N), The EI-MS of **1** showed the correct molecular ion peak at  $m/z=469$  (28.6%) together with [M+2] and [M+4] peaks at  $m/z=471$  (54.6%), 473 (30%) respectively and the base peak at  $m/z=75$  (100%).  $^1\text{H-NMR}$  spectrum (DMSO- $d_6$ ) of **1** revealed a signals at  $\delta$  ppm. 9.10-9.05 (m, 2H<sub>arom</sub>), 8.55-8.29 (m, 3H<sub>arom</sub>).

In this work the proclivity of benzoxazinones with some nitrogen and carbon nucleophiles was studied, Indeed compound **1** was allowed to react with primary and secondary amines under different conditions, (in ethanol and in n-butanol as a solvent) in mild conditions, ethanol as low B.P solvent the amides **2-7** were produced, where as in n-butanol as high B.P solvent the quinazolinones **8-10** were performed. The structures of compound **2-7** were confirmed from their I.R. spectra exhibited a strong absorption band at  $\nu$  3424-3181 $\text{cm}^{-1}$  corresponding to the amide NH functions and  $\nu$  1680-1656 $\text{cm}^{-1}$  for the carbonyl groups and the  $^1\text{H-NMR}$  spectrum (DMSO- $d_6$ ) of **2** revealed a signals at  $\delta$  ppm. 12.3-10.78 (br.s, 1H, NH, exchangeable with D<sub>2</sub>O), (c.f. the experimental section).

Reaction of compound **1** with ammonia derivatives such as benzyl amine, hydrazine hydrate, benzoyl hydrazine and guanidine in boiling ethanol afforded 2-(3,5-dinitrobenzoylamino)-3,5-dibromo-*N*-substituted benzamides **2-5**, their structures were confirmed from correct elemental and spectral analysis. However,

reaction of compound **1** with secondary amines for instance, morpholine and piperidine afforded the benzamides **6** and **7**.

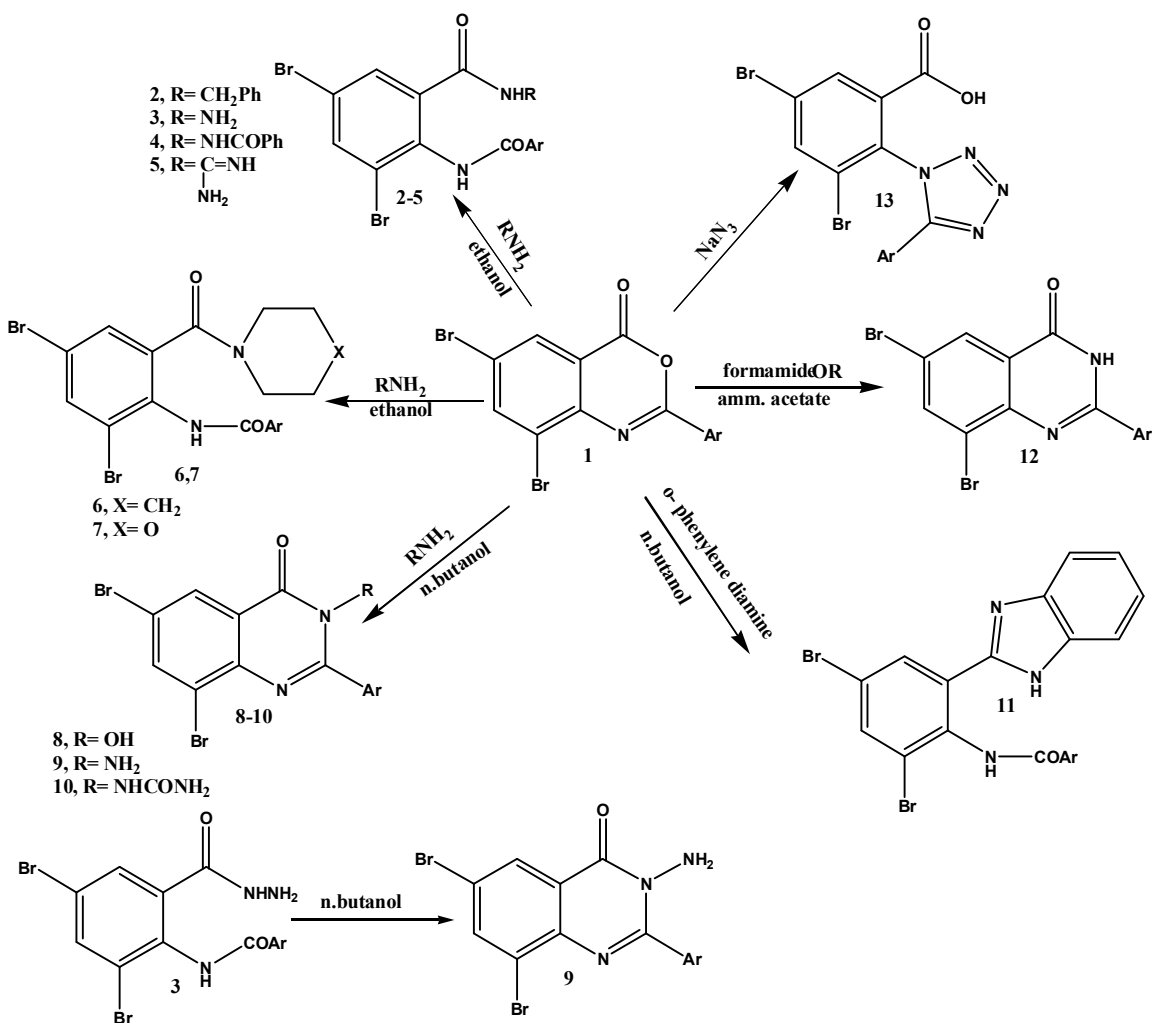
6,8-dibromo-2-(3,5-dinitrophenyl)-*N*-substituted quinazolin-4-ones **8-10** were constructed from the reaction of compound **1** with hydroxylamine hydrochloride, hydrazine hydrate and semicarbazide hydrochloride in n-butanol as a solvent. The structure assignment of compounds **8-10** was substantiated from their I.R spectra which exhibited no signal corresponding the lactonic carbonyl at  $\nu$  1766  $\text{cm}^{-1}$  and showed a signal at  $\nu$  1691-1660  $\text{cm}^{-1}$  for the lactam carbonyl of quinazolines.

As a chemical evidence of the structures of compound **2-10**, Compound **3** was underwent ring closure on boiling in n-butanol to compound **9** (Scheme 2).

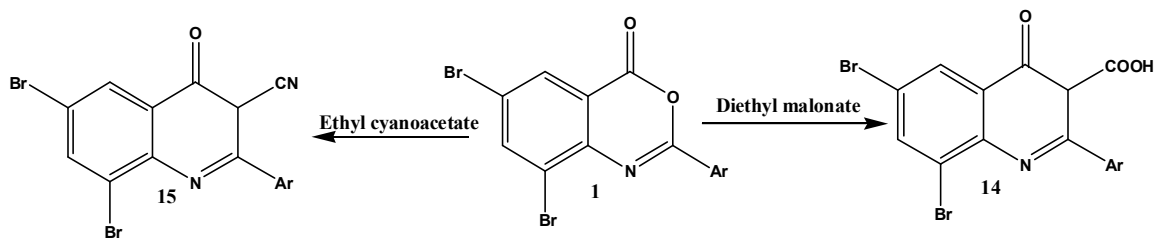
On the other hand *o*-phenylene diamine reacted with benzoxazinone **1** in boiling n-butanol afforded the *N*-(2-(1H-benzo[*d*]imidazol-2-yl)-4,6-dibromophenyl)-3,5-dinitrobenzamide **11** which structure was proved from the I.R spectrum which displayed a strong absorption band at  $\nu$  1662  $\text{cm}^{-1}$  (C=O), 1625  $\text{cm}^{-1}$  (C=N) and 3230  $\text{cm}^{-1}$  (NH), the mass spectrum confirms the structure of compound **11**, showed the correct molecular ion peak at  $m/z=559$  (14.6%) together with [M+2] and [M+4] peaks at  $m/z=561$  (27.6%), 563 (15%) respectively and the base peak at  $m/z=75$  (100%).

Fusion of benzoxazinone **1** with formamide and/or ammonium acetate yielded 6,8-dibromo-2-(3,5-dinitrophenyl)quinazolin-4(3H)-one **12**. The structure of quinazolin-4-on derivative **12** was elucidated from the following data, IR ( $\nu$   $\text{cm}^{-1}$ ): 3174, (NH/OH), 1671  $\text{cm}^{-1}$  (C=O), 1608  $\text{cm}^{-1}$  (C=N).  $^1\text{H-NMR}$  (DMSO- $d_6$ ) of **12**  $\delta$  ppm. 10.01 (s, 1H, NH), disappeared by D<sub>2</sub>O 9.02-8.81 (m, 2H<sub>arom</sub>), 8.75-8.69 (m, 3H<sub>arom</sub>).

Ring opening of compound **1** with hydrazoic acid gave 3,5-dibromo-2-(5-(3,5-dinitrophenyl)-1H-tetrazol-1-yl)benzoic acid **13**.



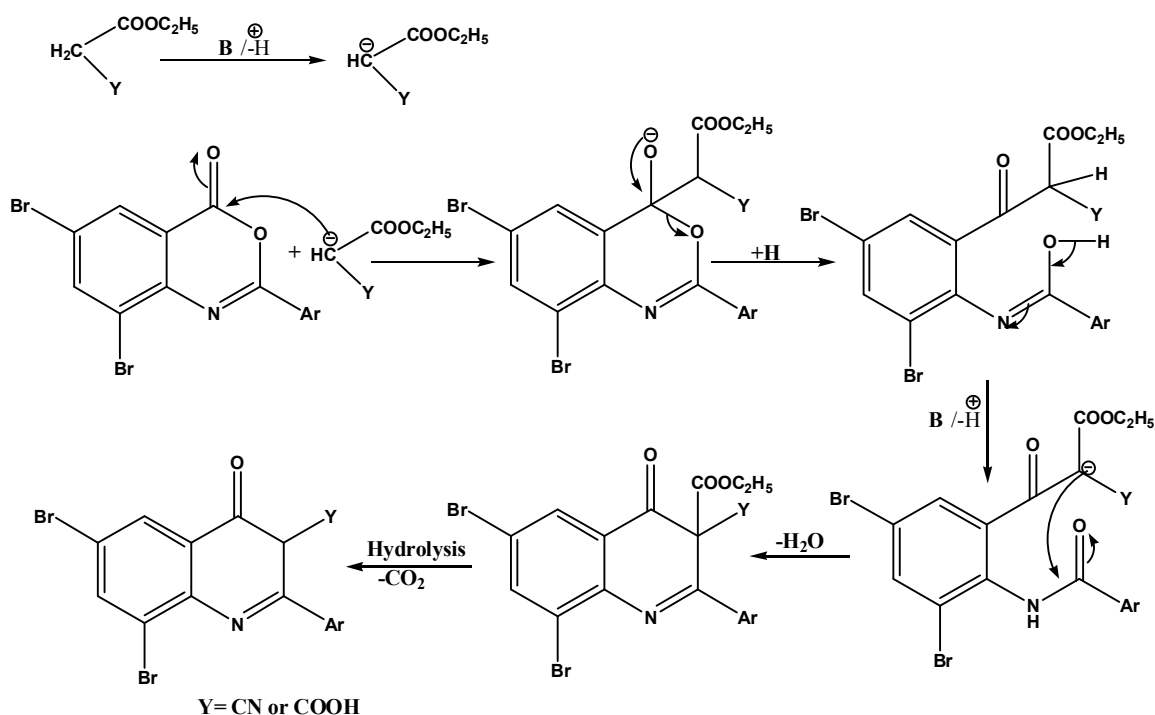
Scheme 2: Reaction of benzoxazinone **1** with some nitrogen nucleophiles.



Scheme 3: Reaction of benzoxazinone **1** with carbon nucleophiles.

By studying the reaction of benzoxazinone **1** with active methylene compounds as carbon nucleophiles, compound **1** was allowed to react with diethyl malonate and /or ethyl cyanoacetate in the presence of dry pyridine as a catalyst base the reaction occurred via heterocyclic ring opening at position -4- by carbanion of active methyleneto form firstly an open adduct as an

intermediate which cyclized to form afforded 6,8-dibromo-2-(3,5-dinitrophenyl)-4-oxo-3,4-dihydroquinoline-3-carboxylic acid, **14** and 6,8-dibromo-2-(3,5-dinitrophenyl)-4-oxo-3,4-dihydroquinoline-3-carbonitrile **15** (Scheme 3). The structure assignment of compounds **14** and **15** were substantiated from its correct elemental and spectral data (I.R, <sup>1</sup>HNMR and MASS).



Scheme 4: The mechanism of the reaction on benzoxazinone with active methylene compounds

The mechanism of formation of 14 and 15 was discussed in the following scheme (scheme 4).

**Experimental:** Melting points are uncorrected and were measured by an electric melting point apparatus (G-K). The IR spectra were recorded on a Pye-Unicam SP1200 spectrophotometer using KBr Wafer technique. The  $^1\text{H-NMR}$  spectra were determined on a Varian GEMINI 200 MHz NMR spectrophotometer using  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  as solvent and TMS as an internal standard. All chemical shifts are in ppm downfield from TMS. The elemental analysis were carried out in faculty of Science, Ain Shams University. MS were recorded on Shimadzu GC-MS QP1000EX instrument in micro analytical lab, Cairo University. The monitoring of the progress of all reactions and homogeneity of the synthesized compound was carried out by TLC.

**6,8-dibromo-2-(3,5-dinitrophenyl)-4H-benzo[d][1,3]oxazin-4-one (1):** To a solution of 3,5-dibromoanthranilic acid (0.01mol) in dry pyridine (50ml), 3,5-dinitrobenzoyl chloride (0.01mol) in dry diethyl ether (30ml) was added dropwise with stirring. The reaction mixture was heated on water bath for 2 hours, poured on ice cold water and HCl. The solid separated was filtered off dried and recrystallized from benzene/ethano mixture to

give **1** as pale yellow crystals, m.p: 238-240°C. Yield (80%). Anal. Calcd.: for  $\text{C}_{14}\text{H}_5\text{Br}_2\text{N}_3\text{O}_6$  (471): C, 35.66; H, 1.06; N, 8.91 Found: C, 35.26; H, 1.02; N, 8.73; IR ( $\text{cm}^{-1}$ ): 1766 $\text{cm}^{-1}$  (lactonic C=O), 1621 $\text{cm}^{-1}$  (C=N). MS m/z (%) m/z= 469 (28.6%) together with [M+2] and [M+4] peaks at m/z= 471 (54.6%), 473 (30%) respectively and the base peak at m/z= 75 (100%).  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) of t  $\delta$  ppm. 9.10-9.05 (m, 2 $\text{H}_{\text{arom}}$ ), 8.55-8.29 (m, 3 $\text{H}_{\text{arom}}$ ).

**General Procedure For The Synthesis of Compounds 2-7:** A mixture of benzoxazinone **1** (0.01mol) and primary amines and/or secondary amines namely benzyl amine, hydrazine, benzoyl hydrazine, guanidine hydrochloride, piperidine and morpholine (0.01mol) in ethanol (50ml) was refluxed for four hours. The solid obtained was filtered off dried and recrystallized from proper solvent.

**N-benzyl-3,5-dibromo-2-(3,5-dinitrobenzamido) benzamid (2):** Recrystallized from dioxane. m.p: 260-262°C. Yield (68%). Anal. Calcd.: for  $\text{C}_{21}\text{H}_{14}\text{Br}_2\text{N}_4\text{O}_6$  (578): C, 43.60; H, 2.42; N, 9.68. Found: C, 43.35; H, 2.22; N, 9.56; IR ( $\text{cm}^{-1}$ ): 3426 and 3419 (NH/OH), 1656 $\text{cm}^{-1}$  (C=O), 1630 $\text{cm}^{-1}$  (C=N). MS m/z (%) m/z= 578 (18.6%) together with [M+2] and [M+4] peaks at m/z= 581 (34.6%), 583 (30%) respectively and the base peak at m/z= 75 (100%).  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) of t  $\delta$  ppm. 11.02 (s, 1H, NH), 10.76 (s, 1H, NH), 9.10-9.05

(m, 2H<sub>arom</sub>), 8.55-8.29 (m, 3H<sub>arom</sub>), 8.05(m,5H<sub>arom</sub>) and 1.98 (s, 2H, CH<sub>2</sub>).

**3,5-dibromo-2-(3,5-dinitrobenzamido)benzohydrazide (3)**  
Recrystallized from dimethylformamide. m.p: 272-274°C. Yield (61%). Anal. Calcd.: for C<sub>14</sub>H<sub>9</sub>Br<sub>2</sub>N<sub>5</sub>O<sub>6</sub> (503): C, 33.40; H, 1.78; N, 13.91. Found: C, 33.23; H, 1.69; N, 13.72; IR (ν cm<sup>-1</sup>): 3232, 3380-3454 (NH/OH), 1654 cm<sup>-1</sup> (C=O), 1620 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 10.02 (s, 1H, NH), 9.76 (s, 1H, NH), disappeared by D<sub>2</sub>O 9.09-9.01 (m, 2H<sub>arom</sub>), 8.65-8.39 (m, 3H<sub>arom</sub>) and 6.98 (s, 2H, NH<sub>2</sub>). disappeared by D<sub>2</sub>O.

**N-benzoylamino-3,5-dibromo-2-(3,5-dinitrobenzamido)Benzamid (4)**: Recrystallized from dioxane. m.p: 255-257. Yield (58%). Anal. Calcd.: for C<sub>21</sub>H<sub>13</sub>Br<sub>2</sub>N<sub>5</sub>O<sub>7</sub> (607): C, 41.50; H, 2.14; N, 11.50. Found: C, 41.23; H, 2.01; N, 11.32; IR (ν cm<sup>-1</sup>): 3235 (NH/OH), 1656 cm<sup>-1</sup> (C=O), 1610 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 10.02 (s, 1H, NH), 9.76 (s, 1H, NH), 9.52 (s, 1H, NH) disappeared by D<sub>2</sub>O 9.02-8.91 (m, 2H<sub>arom</sub>), 8.85-8.39 (m, 3H<sub>arom</sub>) and 7.98 (s, 5H<sub>arom</sub>).

**N-(2,4-dibromo-6-(guanidinocarbonyl)phenyl)-3,5-dinitrobenzamide (5)**: Recrystallized from dioxane. m.p: 240-242°C. Yield (72%). Anal. Calcd.: for C<sub>15</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>6</sub> (530): C, 33.96; H, 1.88; N, 15.84. Found: C, 33.89; H, 1.59; N, 15.78; IR (ν cm<sup>-1</sup>): 3262, 3424 (NH/OH), 1680 cm<sup>-1</sup> (C=O), 1620 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 9.92 (s, 1H, NH), 9.16 (s, 1H, NH), disappeared by D<sub>2</sub>O 8.92-8.81 (m, 2H<sub>arom</sub>), 8.75-8.69 (m, 3H<sub>arom</sub>) and 6.92 (s, 2H, NH<sub>2</sub>), 3.16 (s, 1H, NH), disappeared by D<sub>2</sub>O.

**N-(2,4-dibromo-6-(piperidine-1-carbonyl)phenyl)-3,5-dinitrobenzamide(6)**: Recrystallized from dimethylformamide. m.p: 230-232°C. Yield (48%). Anal. Calcd.: for C<sub>19</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>7</sub> (556): C, 41.00; H, 2.87; N, 10.07. Found: C, 39.68; H, 2.67; N, 9.92; IR (ν cm<sup>-1</sup>): 3181, 3442 (NH/OH), 1677 cm<sup>-1</sup> (C=O), 1608 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 10.22 (s, 1H, NH), disappeared by D<sub>2</sub>O 8.92-8.81 (m, 2H<sub>arom</sub>), 8.75-8.69 (m, 3H<sub>arom</sub>) and 4.92 (m, 10H, CH<sub>2</sub>). MS m/z (%) m/z= 556 (30.6%) together with [M+2] and [M+4] peaks at m/z= 558 (60.6%), 562 (30%) respectively, m/z=232 (4.8%), m/z=234 (12.8%), m/z=236 (7.8%), m/z=193 (13.8%) and the base peak at m/z= 74 (100%).

**N-(2,4-dibromo-6-(morpholine-4-carbonyl)phenyl)-3,5-dinitrobenzamide(7)**: Recrystallized from dimethylformamide. m.p: 240-242°C. Yield (45%). Anal.

Calcd.: for C<sub>18</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>7</sub> (558): C, 38.71; H, 2.51; N, 10.03. Found: C, 38.68; H, 2.34; N, 9.98; IR (ν cm<sup>-1</sup>): 3212, 3448 (NH/OH), 1679 cm<sup>-1</sup> (C=O), 1614 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 9.92 (s, 1H, NH), disappeared by D<sub>2</sub>O 8.82-8.78 (m, 2H<sub>arom</sub>), 8.71-8.62 (m, 3H<sub>arom</sub>) and 4.62 (m, 8H, CH<sub>2</sub>).

**General Procedure For The Synthesis of Compounds 8-10**: A mixture of primary amines namely hydroxyl amine hydrochloride, hydrazine hydrate and semicarbazide hydrochloride (0.01mol) in n-butanol (50ml) was refluxed for four hours the solid obtained after evaporating the solvent was filtered off, dried and recrystallized from suitable solvent.

**6,8-dibromo-2-(3,5-dinitrophenyl)-3-hydroxyquinazolin-4(3H)-one (8)**: Recrystallized from dimethylformamide. m.p: 250-252°C. Yield (68%). Anal. Calcd.: for C<sub>14</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>6</sub> (486): C, 34.60; H, 1.24; N, 11.53. Found: C, 34.35; H, 1.12; N, 11.35; IR (ν cm<sup>-1</sup>): 3442, (NH/OH), 1691 cm<sup>-1</sup> (C=O), 1602 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 9.82 (s, 1H, OH), disappeared by D<sub>2</sub>O 8.92-8.81 (m, 2H<sub>arom</sub>), 8.75-8.69 (m, 3H<sub>arom</sub>).

**3-amino-6,8-dibromo-2-(3,5-dinitrophenyl)quinazolin-4(3H)-one (9)**: Recrystallized from dioxane. m.p: 245-247°C. Yield (58%). Anal. Calcd.: for C<sub>14</sub>H<sub>7</sub>Br<sub>2</sub>N<sub>5</sub>O<sub>5</sub> (486): C, 34.63; H, 1.44; N, 11.53. Found: C, 34.35; H, 1.32; N, 11.35; IR (ν cm<sup>-1</sup>): 3180-3291, (NH<sub>2</sub>), 1696 cm<sup>-1</sup> (C=O), 1610 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 8.72-8.51 (m, 2H<sub>arom</sub>), 8.45-8.29 (m, 3H<sub>arom</sub>) and 6.32 (s, 2H, NH<sub>2</sub>), disappeared by D<sub>2</sub>O.

**1-(6,8-dibromo-2-(3,5-dinitrophenyl)-4-oxoquinazolin-3(4H)-yl)urea (10)**: Recrystallized from ethano/dioxane. m.p: 222-224°C. Yield (84). Anal. Calcd.: for C<sub>15</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>6</sub> (528): C, 34.10; H, 1.51; N, 15.90. Found: C, 33.95; H, 1.42; N, 15.35; IR (ν cm<sup>-1</sup>): 3100, (NH), 3291-3320 (NH<sub>2</sub>), 1680, 1660, cm<sup>-1</sup> (C=O), 1604 cm<sup>-1</sup> (C=N). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) of t δ ppm. 10.92 (s, 1H, NH), disappeared by D<sub>2</sub>O 8.92-8.81 (m, 2H<sub>arom</sub>), 8.75-8.69 (m, 3H<sub>arom</sub>) and 6.92 (s, 2H, NH<sub>2</sub>), disappeared by D<sub>2</sub>O.

**N-(2-(1H-benzo[d]imidazol-2-yl)-4,6-dibromophenyl)-3,5-dinitrobenzamide (11)**: A mixture of benzoxazinone **1** (0.01mol) and *o* phenylene diamine (0.01mol) in ethano was refluxed for four hours. The solid obtained after evaporating the solvent was filtered off, dried and recrystallized from dioxane to give **11** as white crystals.

m.p: 280-282°C. Yield (78%). Anal. Calcd.: for  $C_{20}H_{11}Br_2N_5O_5$  (561): C, 42.78; H, 1.96; N, 12.47. Found: C, 42.63; H, 1.88; N, 12.32; IR ( $\nu$   $cm^{-1}$ ): 3477, (OH), 3477, 3230, (NH), 1662  $cm^{-1}$  (C=O), 1625  $cm^{-1}$  (C=N).  $^1H$ -NMR (DMSO- $d_6$ ) of t  $\delta$  ppm. 10.02 (s, 1H, NH), disappeared by  $D_2O$  8.92-8.81 (m, 2 $H_{arom}$ ), 8.75-8.69 (m, 3 $H_{arom}$ ) and 7.92 (m, 4 $H_{arom}$ ), 3.16 (s, 1H, NH), disappeared by  $D_2O$ .

**6,8-dibromo-2-(3,5-dinitrophenyl)quinazolin-4(3H)-one (12):** A mixture of benzoxazinone **1** (0.01 mol) and 20 ml formamide and/or (0.01) mol amm. Acetate was refluxed on oil bath at 220°C for three hours. the reaction mixture was poured onto cold water and the solid separated was filtered off, dried and recrystallized from dimethylformamide, to give **12** as pale yellow crystals. m.p: over 300°C. Yield (78%). Anal. Calcd.: for  $C_{14}H_6Br_2N_4O_5$  (470): C, 35.74; H, 1.27; N, 11.91. Found: C, 34.23; H, 1.19; N, 11.78; IR ( $\nu$   $cm^{-1}$ ): 3174, (NH/OH), 1671  $cm^{-1}$  (C=O), 1608  $cm^{-1}$  (C=N).  $^1H$ -NMR (DMSO- $d_6$ ) of t  $\delta$  ppm. 10.01 (s, 1H, NH), disappeared by  $D_2O$  9.02-8.81 (m, 2 $H_{arom}$ ), 8.75-8.69 (m, 3 $H_{arom}$ ). MS m/z (%) m/z= 468 (28.6%) together with [M+2] and [M+4] peaks at m/z= 471 (54.6%), 472 (30%) respectively, m/z=388 (4.8%), m/z=275 (30.8%), m/z=377 (52.8%), m/z=379 (29.8%) and the base peak at m/z= 167 (100%).

**3,5-dibromo-2-(5-(3,5-dinitrophenyl)-1H-tetrazol-1-yl)benzoic acid (13):** A mixture of benzoxazinone **1** (0.01 mol) and sod. azide (0.20) mol in acetic acid was refluxed on oil bath at 220°C for six hours. the reaction mixture was cooled. The solid separated was filtered off, washed with water, dried and recrystallized from benzene, to give **13** as pale yellow crystals. m.p: 202-204°C. Yield (87%). Anal. Calcd.: for  $C_{14}H_6Br_2N_6O_6$  (514): C, 32.68; H, 1.16; N, 16.34. Found: C, 32.59; H, 1.09; N, 16.24; IR ( $\nu$   $cm^{-1}$ ): 3445, (OH), 1690  $cm^{-1}$  (C=O).  $^1H$ -NMR (DMSO- $d_6$ ) of t  $\delta$  ppm. 12.01 (s, 1H, COOH), disappeared by  $D_2O$  9.02-8.81 (m, 2 $H_{arom}$ ), 8.75-8.69 (m, 3 $H_{arom}$ ).

**General Procedure For The Reaction of Benzoxazinone With Active Methylene Compounds:** A mixture of benzoxazinone **1** (0.01 mol) and active methylene compounds namely diethyl malonate and/or ethyl cyanoacetate (0.01 mol) in dry pyridine (30 ml) was refluxed for ten hours. The reaction mixture was poured onto crushed ice and acidified with 10% cold HCl (20 ml). The formed precipitate was filtered off, washed with water, dried and recrystallized from benzene/ethanol mixture to give **14** and **15** as yellow crystals.

**6,8-dibromo-2-(3,5-dinitrophenyl)-4-oxo-3,4-dihydroquinoline-3-carboxylic acid (14):** m.p: 210-212°C. Yield (40%). Anal. Calcd.: for  $C_{16}H_7Br_2N_5O_7$  (513): C, 37.42; H, 1.36; N, 8.18. Found: C, 37.23; H, 1.29; N, 8.02; IR ( $\nu$   $cm^{-1}$ ): 3452, (OH), 1690  $cm^{-1}$  (C=O), 1604  $cm^{-1}$  (C=N).  $^1H$ -NMR (DMSO- $d_6$ ) of t  $\delta$  ppm. 10.92 (s, 1H, COOH), 8.92-8.81 (m, 2 $H_{arom}$ ), 8.75-8.69 (m, 3 $H_{arom}$ ) and 5.16 (s, 1H, CH).

**6,8-dibromo-2-(3,5-dinitrophenyl)-4-oxo-3,4-dihydroquinoline-3-carbonitrile (15):** m.p: 220-222°C. Yield (38%). Anal. Calcd.: for  $C_{16}H_6Br_2N_4O_5$  (494): C, 38.86; H, 1.21; N, 11.33. Found: C, 38.76; H, 1.12; N, 11.20; IR ( $\nu$   $cm^{-1}$ ): 2212, (CN), 1680  $cm^{-1}$  (C=O), 1604  $cm^{-1}$  (C=N).  $^1H$ -NMR (DMSO- $d_6$ ) of t  $\delta$  ppm. 8.92-8.81 (m, 2 $H_{arom}$ ), 8.75-8.69 (m, 3 $H_{arom}$ ). 4.96 (s, 1H, CH).

## CONCLUSION

During the current investigation, we synthesized a new building block; namely 6,8-dibromo-2-(3,5-dinitrophenyl)-4H-benzo[d][1,3]oxazin-4-one and its proclivity with nitrogen and carbon nucleophiles was studied. From that compound, a series of different quinazolinone and quinoline derivatives were synthesized and their structural and spectral data were elucidated.

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