



ISSN: 2321-4902

Volume 1 Issue 2

Online Available at [www.chemijournal.com](http://www.chemijournal.com)

## International Journal of Chemical Studies

### Synthesis of some heterocyclic molecules from new benzoxazinones and quinazolinones

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The benzoxazinone **3** was prepared and treated with hydrazine hydrate, hydroxylamine hydrochloride, and *o*-phenylenediamine to give different quinazolinones **4,5** and benzimidazoles **6,7** respectively. Product **4** reacted with different aldehydes forming different Schiff's bases **9,10a\_e**. Also it reacted with different Grignard reagents giving alcohols (**11a,b**) and ketones **11c,d**, according to the bulkiness of the reagent. Finally, dibromo-, monobromoamino- and diamino-quinazolinones **12,13 a-d, & 14 a-d** were prepared upon addition of bromine to **4**, followed by reacting different amines according to their molar ratios. Some benzoxazinone, and quinazolinone derivatives were tested for their antifungal and antibacterial activities and gave promising results.

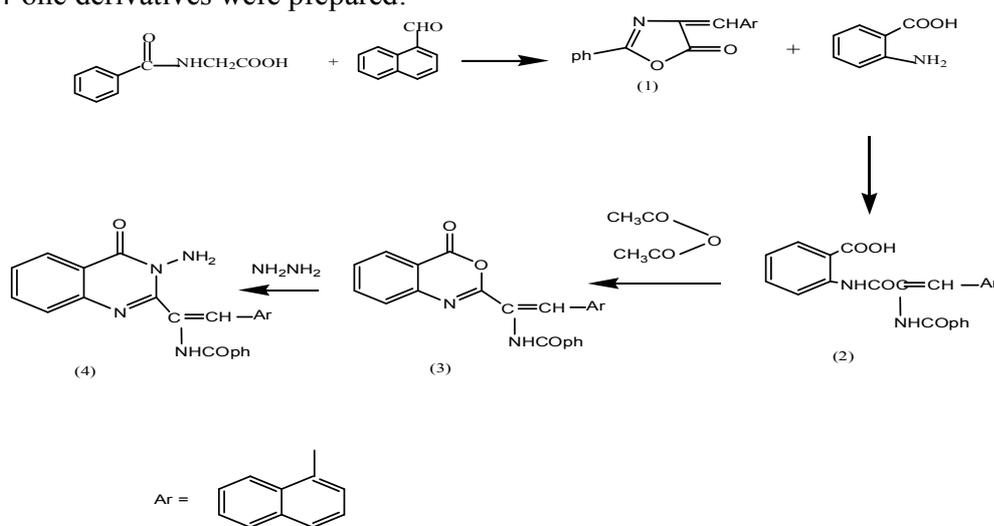
**Keyword:** Quinazolinones, Benzoxazinones, Schiff's Base.

#### 1. Introduction

Many studies have been focused on benzoxazin-4(3)H-one and 3H-quinazolin-4-one and their derivatives since they possess significant activities as antifungal<sup>[1,2]</sup>, antibacterial, and antimetabolic anticancer activity. In the present investigation, new benzoxazin-4(3)-one and 3H-quinazolin-4-one derivatives were prepared.

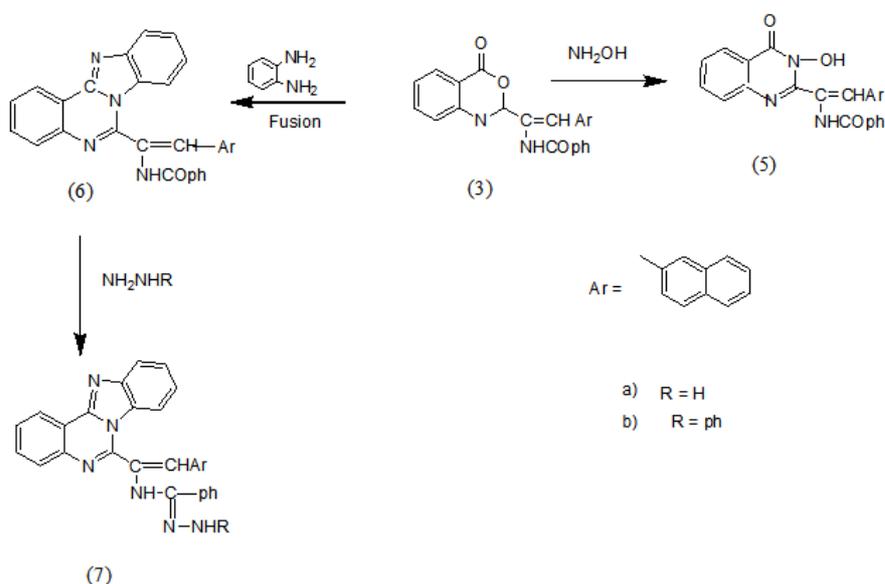
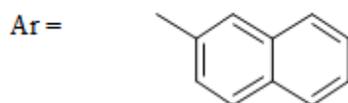
#### 2. Results and Discussion

The benzoxazin-4-one **3** was prepared and treated with hydrazine hydrate affording the 3H-quinazolin-4-one following the reaction sequence depicted in Scheme 1.



Scheme 1

Previously<sup>[3]</sup>, it was reported that the 4H-3,1-benzoxazinone derivatives gave the corresponding 3-quinazolin-4-one when reacted with hydroxylamine hydrochloride. Thus, in our case when the benzoxazinone **3** was treated with hydroxylamine hydrochloride, the 3-hydroxyquinazolin-4-one derivative **5** was obtained. In spite of correct analytical data and I.R., the structure of **5** was also proved by C<sup>13</sup> NMR



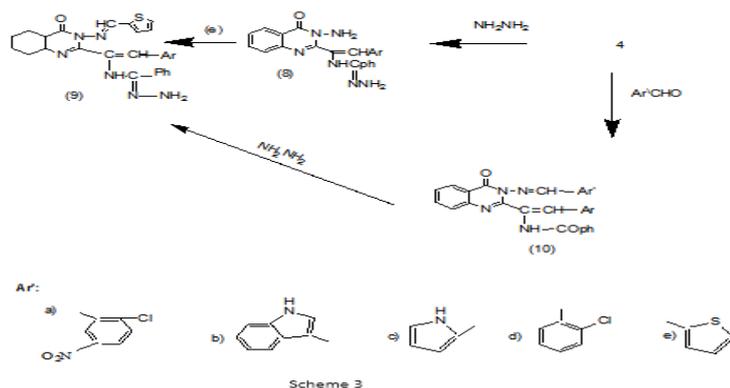
Scheme 2

Owing to the great importance of the Schiff's bases as possessing antimicrobial and antibacterial activities<sup>[5]</sup> the authors focused their attention on preparing new Schiff's bases bearing quinazoline moiety. Thus refluxing **4** with hydrazine hydrate in n-butanol, gave the hydrazino derivative **8** which undergoes condensation with thiophene-2-carboxaldehyde giving the Schiff's base **9**. In spite of all analytical and spectral data for proving the structure of **9**, an authentic reaction was done by refluxing **10e** with hydrazine hydrate giving **9** in good yield.

Also **4** reacted with different aldehydes namely 2-chloro-5-nitrobenzaldehyde, indole-3-carboxaldehyde, 2-chlorobenzaldehyde, and

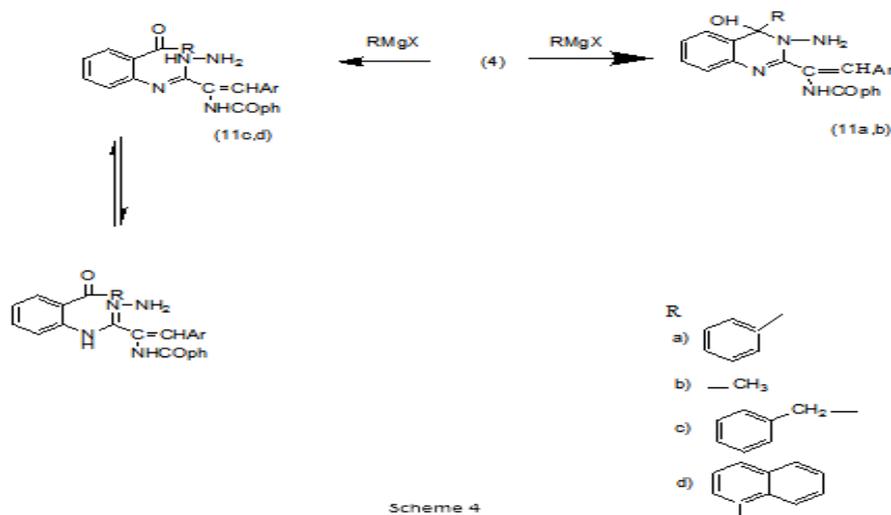
It has been reported<sup>[4]</sup> that the condensation of 2-aryl(alkyl)benzoxazinone with o-phenylenediamine gave the corresponding 2-aryl-3-hetaryl-4H3,1 quinazolinones, however in our study, by fusion of **3** with o-phenylenediamine, the heterocyclic benzimidazole derivative **6** was formed. Furthermore on treating **6** with hydrazine hydrate or phenyl hydrazine in n-butanol, the corresponding hydrazino or phenylhydrazino derivatives **7 a,b** were respectively obtained (c.f. scheme 2). The structures of **3**, **4**, **6**, & **7** were confirmed from analytical as well as spectral data.

thiophene-2-carboxaldehyde (c.f. Scheme 3), to give the Schiff's bases **10a-e**.



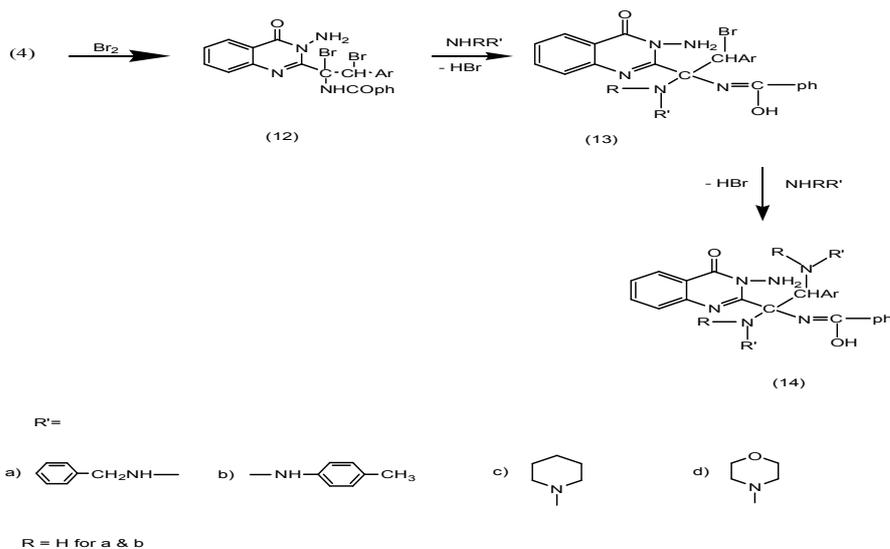
When different Grignard reagents namely phenylmagnesium bromide, methylmagnesium iodide, benzylmagnesium bromide, and naphthylmagnesium bromide reacted with the quinazolinone **4**, different products were achieved according to the reagent (c.f. Scheme 4). Thus in the case of non-bulky reagent, a 4-substituted quinazolinol derivatives **11a,b** were obtained,

while with a bulky reagent, ketones **11c,d** were formed<sup>[6,7]</sup>. Thus, the reaction products depend on the bulkiness of the reagent which causes steric hindrance at position 4. The product's structures (**11c,d**) were confirmed from IR showing new ketonic group  $\gamma\text{C}=\text{O}$  at 1735 & 1750 cm.



Finally, addition of liquid bromine to **3**, gave the dibromo derivative **12** which, on turn reacted with different amines namely benzylamine, 4-methyl aniline, piperidine, and morpholine in molar ratios giving the monobromoamino

derivatives **13** and the diamino derivatives **14** in good yield (c.f. Scheme 5). All the structures of the previous products were inferred from their analytical data as well as spectral data.



Scheme 5

**Table:** Results of the biological activities for antibacterial & antifungal agents

Compound	Bacteria				Fungi			
	Gram+( <i>Bacillus subtilis</i> )		Gram-( <i>E-Coli</i> )		<i>Aspergillus niger</i>		<i>Fusarium spp.</i>	
	10 ppm	100 ppm	10 ppm	100 ppm	10 ppm	100 ppm	10 ppm	100 ppm
1	-	-	-	-	+	+	+	+
2	-	+	-	+	-	+	-	+
3	-	+	-	+	-	-	-	-
8	-	-	-	+	+	++	+	++
9	-	-	-	-	+	++	+	++
10e	-	-	-	+	-	++	-	+
11a	-	+	-	-	+	+	-	-
11b	-	+	-	-	-	+	-	-
13b	-	+	-	+	-	+	-	-
13c	-	-	-	-	+	++	+	++

Antimicrobial: Nizo-arm    Antifungal: Penicillin

### 3. Experimental

All melting points are uncorrected. IR spectra were recorded in on Pye-Unicam SP 1200 spectrophotometer using KBr wafer technique. The  $^1\text{H-NMR}$  spectra were determined on Varian Gemini 200 MHz, using TMS as internal standard (chemical shifts in  $\delta$ -scale). EI-MS were measured on Shimadzu-GC-MS operating at 70 eV.  $^{13}\text{C-NMR}$  spectra were measured on JOEL 75 MHz. Elemental analysis were carried out at the Micro-analytical Center at Cairo University. TLC on silica gel plates (Merk 60,F254) was used to monitor the reaction and for testing the purity of the products.

#### 3.1. 5-naphthylidene 2-phenyloxazol-4-one (1)

A mixture of hippuric acid(0.01 mole), naphthaldehyde(0.01mole),sodium acetate(anhydrous)(0.03moles) and acetic anhydride was heated on a water bath for two hrs.The reaction mixture was cooled and poured into cold water to separate(1) m.p.166-167 °C (60% yield)which was filtered off and crystallized from ethanol.IR( $\text{cm}^{-1}$ ):1770(C=O),1636(C=N).Anal.\Cald. for  $\text{C}_{20}\text{H}_{13}\text{NO}_2$ ,(299) :C,80.3;H,4.3;N,4.7.Found:C,80.7;H,4.4;N,4.3.

### 3.2. 2-( $\alpha$ -Benzoylamino- $\beta$ -2-naphthylacrylamido)benzoic acid (2)

A mixture of (1)(0.01mole) and anthranilic acid (0.01mole) was refluxed in 20ml of acetic acid for 6 hrs, cooled and poured into cold water. A yellow ppt. was formed, m.p. 219 °C (75%yield) and crystallized from benzene. IR( $\gamma\text{cm}^{-1}$ ): 3600-3200(NH), 1710-1650(C=O), 1600-1580(NH). Anal. Calcd. for  $\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}_4$ , (436): C, 74.3; H, 4.6; N, 6.4. Found: C, 74.5; H, 5.0; N, 6.3.

### 3.3. 2-( $\alpha$ -benzoylamino- $\beta$ -2-naphthylacrylamido-4H-3,1-benzoxazin-4one (3)

A mixture of (2)(0.01mole) and acetic anhydride(25ml) was refluxed at 150-170 °C using "Water Separator System" for one hr. The mixture was left under hood system for half an hr., a yellow solid was separated, filtered off and crystallized from pet. ether giving (3) m.p. 156 °C (90%yield). IR( $\gamma\text{cm}^{-1}$ ): 3300-3200(NH), 1750-1710(C=O), 1630-1590(C=N), 1130, 1150(C-O). Anal. Calcd. for  $\text{C}_{27}\text{H}_{18}\text{N}_2\text{O}_3$ , (418): C, 77.5; H, 4.3; N, 6.65. Found: C, 77.6; H, 4.1; N, 6.5.

### 3.4. 2(Z or E)[2'-benzamido- $\alpha$ -naphthylidene methyl] 3-amino-4-H-3,1-quinazolin-4-one (4)

A solution of (3)(0.01mole) and hydrazine hydrate(0.01mole) in 50 ml n-butanol was refluxed for 3 hrs. A yellow solid was separated (80%yield), m.p. 75 °C and crystallized from diethyl ether. IR( $\gamma\text{cm}^{-1}$ ): 3600-3200(NH), 1699-1655(C=O), 1560(C=N);  $^1\text{H-NMR}$ (DMSO- $d_6$ ) $\delta$ (ppm): 10.9-9(s, 2H, enolic form), 9.7(s, 1H, NH exchangeable with  $\text{D}_2\text{O}$ ), 8.9-7.4(m, 16H, aromatic protons), 4.1(s, 2H,  $\text{NH}_2$  exchangeable with  $\text{D}_2\text{O}$ ). Anal. Calcd. for  $\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_2$ , (432): C, 75; H, 4.6; N, 12.9. Found: C, 75.3; H, 5; N, 12.9.

### 3.5. 2(Z/E)[2'-benzamido- $\alpha$ -naphthylidene methyl]3-amino-4-H-3,1-quinazolin-4-ol (5)

A solution of (3)(0.01mole) and hydroxylamine hydrochloride(0.015mole) in 30ml ethyl alcohol was heated under reflux for 3 hrs. An orange solid was formed, crystallized from benzene, (90%yield) and has m.p. 165 °C -166 °C. IR

( $\gamma\text{cm}^{-1}$ ): 3700-3200(NH), 1689, 1645(C=O), 1578(C=N). Anal. Calcd. for  $\text{C}_{27}\text{H}_{19}\text{N}_3\text{O}_3$ , (433): C, 74.8; H, 4.4; N, 9.7. Found: C, 74.6; H, 4.6; N, 9.9.

### 3.6. 2-(Z \E)-(1-naphthyl-1-benzo[d]-imidazo[1,2-c]quinazolin-6-yl)ethen-1-yl-benzamide (6)

A mixture of (3) (0.01mole) and o-phenylenediamine(0.01mole) was fused in an oil bath at 150 °C -160 °C for about 4 hrs. The obtained brown solid was crystallized from pet. ether m.p. 78 °C -79 °C (85%yield). IR( $\gamma\text{cm}^{-1}$ ): 3652-3250(NH), 1657(C=O), 1597(C=N).  $^1\text{H-NMR}$ (DMSO- $d_6$ ) $\delta$ (ppm): 10.1(s, 1H, NH exchangeable with  $\text{D}_2\text{O}$ ), 8.2-7.1(m, 20 H, aromatic protons), 2.5(s, 1H, CH=C). MS m/z(%): 494 ( $\text{M}^+$ ), 272(25%), 151(32%), 145(36%), 105(34%), 68(79), 56(100). Anal. Calcd. for  $\text{C}_{33}\text{H}_{22}\text{N}_4\text{O}$ , (490): C, 80.8; H, 4.5; N, 11.4. Found: C, 80.7; H, 4.7; N, 11.2.

### 3.7. Action of hydrazine hydrate or phenylhydrazine on (6); formation of hydrazine or phenylhydrazino derivatives of (7)

A solution of (6)(0.01mole) and hydrazine hydrate or phenylhydrazine(0.01mole) in 50ml n-butanol was refluxed for 4 hrs. A solid was separated and crystallized from the proper solvent. (7 a) (40% yield), m.p. 78 °C - 80 °C, brown solid, crystallized from benzene. IR( $\gamma\text{cm}^{-1}$ ): 3650-3200(NH), 1662(C=N). Anal. Calcd. for  $\text{C}_{33}\text{H}_{24}\text{N}_6$ , (486): C, 78.6; H, 4.8; N, 16.7. Found: C, 78.2; H, 5.2; N, 16.1. (7 b) (50% yield), m.p. 85 °C -87 °C, reddish brown ppt., crystallized from benzene. IR( $\gamma\text{cm}^{-1}$ ): 3650-3200(NH), 1662, 1599(C=N).  $^1\text{H-NMR}$ (DMSO- $d_6$ ) $\delta$ (ppm): 8.2-7(m, 25H, aromatic protons), 2.6(s, 1H, CH=C). MS m/z(%): 578 ( $\text{M}^+$ ), 243(33%), 151(42%), 65(100%), 55(82%) Anal. Calcd. for  $\text{C}_{39}\text{H}_{26}\text{N}_6$ , (578): C, 80.7; H, 4.8; N, 14.5. Found: C, 80.5; H, 5; N, 14.3.

### 3.8. Schiff's Base Formation (8)

A solution of (4) (0.01 mole) and hydrazine hydrate (0.01 mole) in 50 ml n-butanol was refluxed for 3 hrs. A yellow solid was formed, crystallized from diethyl ether, m.p. 86 °C (85% yield). IR ( $\gamma\text{cm}^{-1}$ ): 3759-3200(NH), 1651(C=O), 1564(C=N). Anal. Calcd for  $\text{C}_{27}\text{H}_{22}\text{N}_6\text{O}$  (424): C, 72.6; H, 4.9; N, 18.8. Found: C, 72.5; H, 5.1; N, 18.7.

### 3.9. Condensation of (8) with aldehydes; formation of Schiff's base (9)

A solution of (8) (0.01 mole) and thiophene-2-carboxaldehyde in 50 ml ethanol and few drops of piperidine was refluxed for 4 hrs. The solid formed was washed with water and HCl, crystallized from butanol, m.p. 190 °C (75% yield). IR ( $\gamma\text{cm}^{-1}$ ): 3700-3200(NH), 1629(C=O), 1588(C=N). MS  $m/z$  (%):  $\text{M}^+$  542(1), 445(1.4), 247(100), 171(48), 83(13). Anal. Calcd for  $\text{C}_{32}\text{H}_{24}\text{N}_6\text{OS}$  (540): C, 71.1; H, 4.4; N, 15.5. Found: C, 70.9; H, 4.6; N, 15.4.

### 3.10. Authentic Method for the Formation of (9)

A solution of (10<sub>e</sub>) (0.01 mole) and hydrazine hydrate (0.01 mole) in 50 ml n-butanol was heated under reflux for 3 hrs. After evaporation of the solvent, a solid was separated on cooling which was crystallized from ethanol m.p. 190 °C, 90% yield.

### 3.11. Condensation of (4) with different aldehydes; formation of different Schiff's bases (10a-e)

A solution of (4) (0.01 mole) and different aromatic aldehydes namely 2-chloro-5-nitrobenzaldehyde, indole-3-carboxaldehyde, 2-chlorobenzaldehyde, and thiophene-2-carboxaldehyde (c.f. Scheme 3) in 50 ml ethanol with few drops of piperidine was refluxed for 4 hrs. The solid formed was washed with water and HCl and crystallized from the proper solvent.

(10a): m.p. 95-96 °C (85% yield), yellow solid crystallized from benzene. IR ( $\gamma\text{cm}^{-1}$ ): 3500-3200(NH), 1720-1652(C=O), 1600(C=N). Anal. Calcd for

$\text{C}_{34}\text{H}_{22}\text{N}_5\text{O}_4\text{Cl}$  (601.5): C, 68; H, 3.7; N, 11.7. Found: C, 67.8; H, 4; N, 11.5.

(10b): m.p. 223-225 °C (90% yield), brown solid crystallized from benzene. IR ( $\gamma\text{cm}^{-1}$ ): 3600-3200(NH), 1715, 1650(C=O), 1589(C=N). Anal. Calcd for  $\text{C}_{36}\text{H}_{25}\text{N}_5\text{O}_2$  (559): C, 77.3; H, 4.5; N, 12.5. Found: C, 76.9; H, 4.8; N, 12.4.

(10c): m.p. 209-210 °C (75% yield), grey solid crystallized from benzene. IR ( $\gamma\text{cm}^{-1}$ ): 3600-3200(NH), 1740, 1650(C=O), 1550(C=N). Anal. Calcd for  $\text{C}_{32}\text{H}_{23}\text{N}_5\text{O}_2$  (509): C, 75.4; H, 4.5; N, 13.8. Found: C, 75.2; H, 4.6; N, 13.5.

(10d): m.p. 99-100 °C (85% yield), greenish yellow solid crystallized from benzene. IR ( $\gamma\text{cm}^{-1}$ ): 3600-3200(NH), 1730, 1660(C=O), 1588(C=N). Anal. Calcd for  $\text{C}_{34}\text{H}_{23}\text{N}_4\text{O}_2\text{Cl}$  (556.5): C, 73.6; H, 4.1; N, 10.1. Found: C, 74; H, 4.3; N, 9.9.

(10e) m.p. 199-200 °C (90% yield), brown ppt. crystallized from benzene. IR ( $\gamma\text{cm}^{-1}$ ): 3600-3200(NH), 1669, 1650(C=O), 1589(C=N). MS  $m/z$  (%):  $\text{M}^+$  526(56), 256(56), 418(100), 151(75), 127(45). Anal. Calcd for  $\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_2\text{S}$  (526): C, 73; H, 4.2; N, 10.6. Found: C, 72.9; H, 4.3; N, 10.4.

### 3.12. Addition of Grignard reagent to (4); formation of 4-(phenyl or methyl-2(Z/E)[2-benzamido- $\alpha$ -naphthylidene methyl]3-amino 3,1 quinazolin-4-ol) (11a,b) and N-(Z/E)-3-hydrazinyl-1-naphthalen-1-yl-3-[2-(phenylacetyl or naphthyl) phenylimino] prop-1-ene-2-yl benzamide (11c,d)

To a suspension of (4) (0.01 mole) in dry ether, an ethereal solution of Grignard reagents (0.03 moles), namely phenylmagnesium bromide, methylmagnesium iodide, benzylmagnesium bromide, and naphthylmagnesium bromide (c.f. scheme 4) were added. The reaction mixture was refluxed on a water bath for 4 hrs, poured on crushed ice and HCl, a solid was separated which was crystallized from the proper solvent to give (11a-d).

(11a) m.p. 88-89 °C, greenish yellow solid, crystallized from ethanol, (35% yield). IR ( $\gamma\text{cm}^{-1}$ ): 3700-

3200(NH), (OH), 1659(C=O), 1600(C=N). MS  
m/z(%): M<sup>+</sup> 510(12), 151(82), 127(18), 105(19), 74(100). Anal.\Calcd for

C<sub>33</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>(510): C, 77.6; H, 5.1; N, 10.9. Found: C, 77.4; H, 5; N, 11.1

(11b) m.p. 108 °-109 °C, dark yellow solid, crystallized from ethanol, (60% yield). IR(γcm<sup>-1</sup>) 3700-3200(NH), (OH), 1675(C=O), 1600(C=N).

H<sup>1</sup>-NMR(DMSO-d<sub>6</sub>)δ(ppm) 10(s, 1H, OH), 9.9(s, 1H, NH exchangeable with D<sub>2</sub>O), 8.9-7.4(m, 16H, aromatic protons), 4.2(s, 2H, NH<sub>2</sub> exchangeable with D<sub>2</sub>O), 2.5(s, 1H, CH=), 1.7(s, 3H, CH<sub>3</sub>) MS m/z(%): M<sup>+</sup>

448(2), 374(2), 176(20), 127(16) (Anal.\Calcd for C<sub>28</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>(448): C, 75; H, 5.4; N, 12.5. Found: C, 74.9; H, 5.9; N, 12.3.

(11c) m.p. 59 °-62 °C, reddish brown solid, crystallized from ethanol, (40% yield). IR(γcm<sup>-1</sup>)

3600-3200(NH), 1735, 1672(C=O), 1587(C=N) H<sup>1</sup>-NMR(DMSO-d<sub>6</sub>)δ(ppm) 10(s, 2H), 9.74, 9.72(s, 2H, 2 NH exchangeable with D<sub>2</sub>O), 7.9-7.4(m, 21H, aromatic protons) 4.3(s, 2H, NH<sub>2</sub> exchangeable with D<sub>2</sub>O), 2.5(2, 1H, CH=C), 1.8(s, 2H, CH<sub>2</sub>). Anal.\Calcd for

C<sub>34</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>(524): C, 77.8; H, 5.3; N, 10.7.

Found: C, 77.7; H, 5.5; N, 10.5.

(11d) m.p. 97 °-98 °C, brown solid, crystallized from ethanol, (50% yield). Anal.\Calcd for C<sub>37</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>(560): C, 79.3; H, 5; N, 10. Found: C, 79.2; H, 5.2; N, 9.9.

### 3.13. Addition of bromine to (4); formation of the dibromoquinazolin-4-one derivative (12)

To a solution of (4) (0.01 mole) in 30ml chloroform, liquid bromine (30ml) was added dropwise over a period of 2 hrs. A reddish brown solid was separated, filtered off, crystallized from benzene, m.p. 64 °-66 °C (80% yield). IR(γcm<sup>-1</sup>) 3750-

3200(NH), 1715, 1680(C=O), 1600(C=N), 530(C-Br). Anal.\Calcd for C<sub>27</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>Br<sub>2</sub>(592): C, 54.7; H, 3.4; N, 9.5. Found: 54.9; H, 3.7; N, 9.4.

### 3.14 Action of amines on the dibromide(12); formation of monoaminosubstituted derivatives of (4), (13a-d)

To a mixture of (0.01 mole) of (12) in 30ml ethanol, the amines namely benzylamine, 4-methyl aniline, piperidine, and morpholine (c.f. scheme 5) were added. The reaction mixture was refluxed for 3 hrs. A solid was separated and crystallized from the proper solvent giving (13a-d).

(13a) m.p. 108 °-109 °C, grey ppt. crystallized from pet. ether (66% yield). IR(γcm<sup>-1</sup>) 3650-3200(NH), 1665(C=O), 1591(C=N). Anal.\Calcd for C<sub>34</sub>H<sub>28</sub>N<sub>5</sub>O<sub>2</sub>Br(618)

: C, 66; H, 4.5; N, 11.3. Found: C, 66.1; H, 4.7; N, 11.2.

(13b) m.p. 79 °-81 °C, brown ppt. crystallized from pet. ether (71% yield). IR(γcm<sup>-1</sup>) 3675-3200(NH), 1667(C=O), 1602(C=N). Anal.\Calcd.

for C<sub>34</sub>H<sub>28</sub>N<sub>5</sub>O<sub>2</sub>Br(618): C, 66; H, 4.5; N, 11.3. Found: C, 66.1; H, 4.7; N, 11.2.

(13c) m.p. 69 °-70 °C, dark grey ppt. crystallized from pet. ether 69 (% yield). IR(γcm<sup>-1</sup>) 3675-3195(NH), 1670(C=O), 1597(C=N) H<sup>1</sup>-NMR(DMSO-

d<sub>6</sub>)δppm) 10.2, 10.1(s, 2H), 9.7(s, H, NH exchangeable with D<sub>2</sub>O), 8.3-6.3(m, 16H, aromatic protons), 4.4(s, 2H, NH<sub>2</sub> exchangeable with D<sub>2</sub>O), 2.2(s, 1H, CH), 1.6-

0.98(t, 4H, 2CH<sub>2</sub> m, 6H, 3 CH<sub>2</sub>), Anal.\Calcd for C<sub>32</sub>H<sub>30</sub>N<sub>5</sub>O<sub>2</sub>Br(596): C, 64.4; H, 5; N, 11.7. Found: C, 64.8; H, 5.2; N, 11.9.

(13d) m.p. 102 °-105 °C dark green ppt. crystallized from pet. ether (57% yield). IR(γcm<sup>-1</sup>) 3700-

3250(C=N), 1669(C=O), 1598(C=N). Anal.\calcd for C<sub>31</sub>H<sub>28</sub>N<sub>5</sub>O<sub>3</sub>Br(578): C, 62.2; H, 4.7; N, 11.7. Found: C, 62.5; H, 4.9; N, 11.8.

### 3.15 Action of amines on (13a-d); formation of diamino derivatives of (4): (14a-d)

To a mixture of (0.01 mole) of (13a-d) in 30ml ethanol, the amines namely benzylamine, 4-methyl aniline, piperidine, and morpholine (c.f. scheme 5) were added. The reaction mixture was refluxed for 6 hrs. A solid was separated and crystallized from the proper solvent giving (14a-d).

(14a) m.p. 89 °-91 °C, brown ppt., crystallized from pet .ether(60%yield) IR(  $\gamma\text{cm}^{-1}$ ) 3650-3250(NH), 1656(C=O), 1602(C=N). Anal.\Calcd for  $\text{C}_{41}\text{H}_{36}\text{N}_6\text{O}_2(644)$ : C, 76.4; H, 5.6; N, 13. Found: C, 76.1; H, 5.8; N, 12.8.

(14b) m.p. 75 °-77 °C, brown ppt., crystallized from pet .ether(63%yield). IR(  $\gamma\text{cm}^{-1}$ ) 3672-3200(NH), 1674(C=O), 1603(C=N). Anal.\Calcd for  $\text{C}_{41}\text{H}_{36}\text{N}_6\text{O}_2(644)$ : C, 76.4; H, 5.6; N, 13. Found: C, 76.2; H, 5.8; N, 13.1

(14c) m.p. 140 °-142 °C, dark green ppt., crystallised from pet .ether(55%yield). IR(  $\gamma\text{cm}^{-1}$ ) 3750-3200(NH), 1668(C=O), 1596(C=N). MS m/z(%) 600(15), 352(17), 315(21), 195(25), 160(26), 105(87), 83(100). Anal.\Calcd for  $\text{C}_{37}\text{H}_{40}\text{N}_6\text{O}_2(600)$ : C, 74; H, 6.7; N, 14. Found C, 74.2; H, 6.9; N, 13.9.

(14d) m.p. 118 °-119 °C, dark grey ppt., crystallised from pet .ether). I.R.(  $\gamma\text{cm}^{-1}$ ) 3652-3250(NH), 1668(C=O), 1597(C=N). Anal.\Calcd for  $\text{C}_{35}\text{H}_{36}\text{N}_6\text{O}_4(604)$ : C, 69.5; H, 5.9; N, 13.9. Found: C, 69.4; H, 6.1; N, 13.5.

#### 4. References

1. Lopez, S.E.; Rosales, M.E. Canelon, C.E.; Valverode, E .A.; Narvaez, R.C.; Charris, J.E.; Giannini, F.A.; Enriz, R.D.; Carrasco, M.; Zacchino, S. Heterocycl. Commun. 2001, 7, 473.
2. Farghaly, A.O.; Moharram, A.M. Boll. Chim. Farm. 1999, 138, 280.
3. D'Rozario, A.P.; Derekj, G.; Robert, H. and Andrew, W., J. Chem. Soc. Perkin Tans. (3), 590, 1981.
4. Dash, B.; Dora, E.K. and Panda, C.S., J. Ind. Chem. Soc. 57 (8), 835, (1980).
5. T. Daniel Thangadurai and Son-Ki Ihm, J. Ind. Eng. Chem., Vol 9, No. 5, (2003) 569-575.
6. Fahmy, A.F.M.; El-Hashash, M.A.; Habashy, M.M. and El-Wannise, S.A., J. Rev. Roum. de Chim., 23, (11), 567, (1978).
7. Soliman, F.M.A.; Islam, I.; Souka, L. and Dawood, N., J. Chem. Soc. Pak. 15 (2), 149, (1993)