Chapter 1

Synthesis of 2-substituted-benzo[d][1,3]oxazin-4-ones and Quinazoline-4(3H)-ones

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1.1 General Remarks:

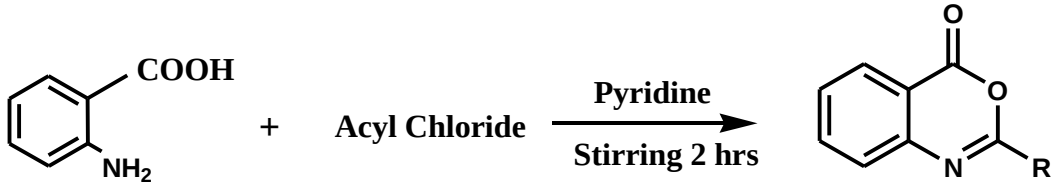
The commercially available aldehydes, ketones, acyl chlorides and amines needed for ligand synthesis were used without further purification and were procured from Merck. Other reagents were purchased from the companies Across, Sigma-Aldrich, Merck and Thomas Baker. ^{1}H and spectra were recorded on a *Bruker Avance* 300 spectrophotometer (300MHz). C NMR spectra were recorded on a *Bruker Avance* 300 spectrometer (75 MHz) Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. Coupling patterns are described by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet). Solvents are specified in each case. The NMR peak assignments have been done by using TOCSY, COSY, HSQC and HMBC. The electrospray mass spectra were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. The ESI capillary was set at 3.5 kV and cone voltage was 40 V. The DART-MS was recorded on a JEOL-AccuTOF JMS-T100LC Mass spectrometer. Dry Helium was used with 4 LPM flow rate for ionization at 350 ^{o}C. Infrared spectra were recorded on a FTIR-8300 SHIMADZU spectrophotometer in the 4000-400 cm^{-1} region as KBr pellets. Only characteristics absorption bands are reported. Absorptions are given in wave number (cm^{-1}); abbreviations: s= strong, m= medium, w= weak, b= broad. UV/VIS spectra were taken on a JASCO V-530 UV/VIS spectrophotometer. A thermostatic controlled water bath was attached to the spectrophotometer to carry out temperature dependent spectra. DSC studies were carried out in the 30-230^{o}C temperature range at a heating range of 5^{o}C per min on a Perkin Elmer Pyris D6 Differential Scanning Calorimeter. The phase contrast microscopic images were carried out in OLYMPUS CK – 40. The curve fitting for the studies were done using ORIGIN 6.1, owned by

Department of Physics, North Bengal University. Quantum mechanical calculations have been carried out on a Desk Top PC with an intel Pentium IV Core 2 Duo processor. The semi empirical program package MOPAC 2000 (Fujitsu) program, in Chem 3D Ultra 8.0 Graphic interface under CambridgeSoft software Chem Office 3D Ultra 8.0 Graphic interface under CsmbridgeSoft software Chem Office Ultra 2004 was used for visualization. For each compound, computations were carried out with the PM3 method. The semi-empirical (MOPAC) method for the quantum mechanical calculations was. The molecular structures obtained in this were used in a configurational interaction calculation to compute dipole moments, bond orders, and electronic transition energy.

1.2. General Synthetic Procedures and Analytical Data:

1.2.1 General procedure for the synthesis of 2-substituted-benzo[d] [1, 3] oxazin-4-ones (1a-1d)

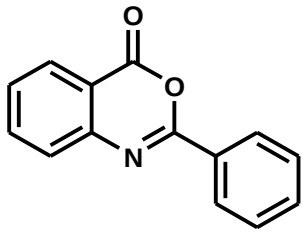
The synthesis of 2-substituted-benzo[d] [1, 3] oxazin-4-ones was carried out by following the previous reported methods. (Niementowski, 1895; Bain & Smalley, 1968).



Scheme 1.1: 2-Substituted benzo[d] [1, 3] oxazin-4-ones.[R=phenyl(1a); p-Me-phenyl(1b); p-Cl-phenyl(1c); methyl(1d)]

1.2.1.1 Synthesis of 2-phenyl benzo[d] [1, 3] oxazin-4-one (1a).

A mixture of anthranilic acid (2-aminobenzoic acid) MW- 113.14 (0.03 mole i.e 4.01g) and benzoyl chloride (0.06 mole, 8.4 g) was dissolved in pyridine (60 ml). The mixture was stirred for 2 hours with occasional cooling. The mixture was diluted with water (300ml) when light brown solid separates out. It was filtered and washed. The product was dried and recrystallized from ethanol.



(1)

Yield 78%; Light Yellow solid; m.p. 120^{o}C

Anal. Calcd for ($C_{14}H_9NO_2$): C, 75.33; H, 4.06; N, 6.27. Found: C, 75.86; H, 4.23; N, 6.02

^{1}HNMR (300 MHz, $CDCl_3$): δ 8.33 (5-H); δ 8.31 (7-H); δ 7.84 (8-H); δ 7.72 (6-H); δ 7.56 (2'-H); δ 7.51 (3'-H); δ 7.26 (4'-H).

^{13}CNMR (300 MHz, $CDCl_3$): 158.78 (C-4); 156.35 (C-2); 146.20 (C-8b); 136.79 (C-7); 132.65 (C-5); 129.98 (C-4'); 128.93 (C-1'); 128.52 (C-2'); 127.99 (C-3'); 127.74 (C-6); 126.85 (C-8); and 116.86 (C-5a).

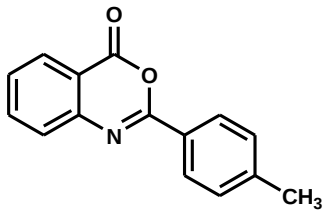
m/z found for ($C_{14}H_9NO_2$): 224(M+1), 246 (M+Na), 469 (2M+Na).

1.2.1.2 Synthesis of 2-p-tolyl-benzo[d] [1, 3] oxazin-4-one (1b).

The toulic acid MW- 136.15 (0.11 mole) was taken in a round bottom flask and thionyl chloride was added in a less amount to dissolve the toulic acid. During the addition of thionyl chloride, HCl fumes released. When the fumes became less, the solution was heated until it dissolved. Following dissolution, the solution was refluxed for 30 minutes at low temperatures because at high temperature solution churns to brown colour. After reflux, the excess solvent was distilled out and the remaining liquid tolyl chloride in round flask was collected.

The stirred solution of anthranilic acid (0.11mole) in pyridine (60ml), tolyl chloride was added dropwise, maintaining the temperature near 0-5 ^{o}C for 1 hour. The reaction mixture was stirred for another 2h at room temperature until a solid product was

formed. The reaction mixture was neutralized with $NaHCO_3$ solution and the pale yellow solid, which separated, was filtered. Finally the product was recrystallized from ethanol after washing with water



(2)

Yield 82%; Light Yellow solid; m.p. 152.7^{o}C

Anal. Calcd for ($C_{15}H_{11}NO_2$): C, 75.94; H, 4.67; N, 5.90. Found: C, 75.36; H, 4.84; N, 5.54

^{1}HNMR (300 MHz, $CDCl_3$): δ 8.25 (5-H); δ 8.19 (7-H); δ 7.85 (8-H); δ 7.79 (6-H); δ 7.69 & δ 7.52 (2'-Hs); δ 7.33 & δ 7.26 (3'-Hs); δ 2.45 (CH_3);

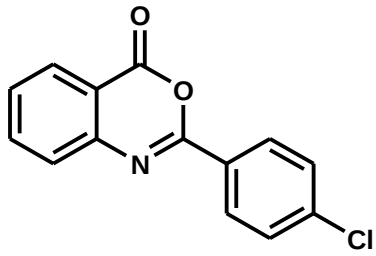
^{13}CNMR (300 MHz, $CDCl_3$): 159.71 (C-4); 157.37 (C-2); 147.16 (C-8b); 143.44 (C-4'); 136.53 (C-7); 129.53 (C-5); 128.59 (C-3'); 128.35 (C-2'); 128.02 (C-6); 127.46 (C-1'); 127.10 (C-8); 116.96 (C-5a) and 21.70 (CH_3).

m/z found for $C_{15}H_{11}NO_2$: 238(M+1), 260 (M+Na), 497 (2M+Na).

1.2.1.3 Synthesis of 2-p-chlorophenyl-benzo[d] [1, 3] oxazin-4-one (1c).

The thionyl chloride was added in a less amount to p-chlorobenzoic acid MW-156.56 (0.11 mole). The p-chlorobenzoic acid was dissolved in thionyl chloride after heating. The solution was then refluxed for 30 minutes at low temperatures. The excess solvent was distilled out after reflux and the remaining liquid p-chloro benzoyl chloride was collected. The stirred solution of anthranilic acid (0.11mole) in pyridine (60ml), p-chloro benzoyl chloride was added dropwise, maintaining the temperature near 0-5 ^{o}C for 1 h. The reaction mixture was stirred for another 2 hours at room temperature until a solid

product was formed. The reaction mixture was neutralized with $NaHCO_3$ solution and the pale yellow solid, which separated was filtered. Finally it was recrystallized from ethanol after washing with water.



(3)

Yield 79%; Light Yellow solid; m.p.- 188.8^{o}C

Anal. Calcd for ($C_{14}H_8ClNO_2$): C, 65.26; H, 3.13; N, 5.44. Found: C, 65.73; H, 3.89; N, 5.03

^{1}HNMR (300 MHz, $CDCl_3$): δ 8.20 (5-H); δ 8.18 (7-H); δ 8.15 (8-H); δ 7.96 (6-H); δ 7.74 & δ 7.70 (2'-Hs); δ 7.66 (3'-H) & δ 7.64 (3'-Hs);

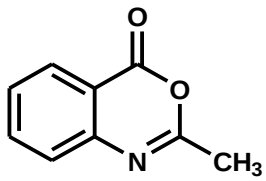
^{13}CNMR (300 MHz, $CDCl_3$): 158.61 (C-4); 155.51 (C-2); 146.02 (C-8b); 137.47 (C-4'); 136.83 (C-7); 129.50 (C-3'); 129.11 (C-2'); 128.91 (C-1'); 128.69 (C-5); 128.02 (C-6); 126.86 (C-8) and 116.90(C-5a).

m/z found for ($C_{14}H_8ClNO_2$): 258 (M+1), 280 (M+Na), 537 (2M+Na).

1.2.1.4 Synthesis of 2-methyl benzo[d] [1, 3] oxazin-4-one (1d)

A solution of anthranilic acid and acetic anhydride (1mole in 0.5L) was refluxed for 2hrs. The excess solvent was removed by distillation. The residual brown gummy slurry when subjected to vacuum distillation in the range of 120^{o}C-130^{o}C at about 8mmHg pressure; the slurry melted and white needle shaped crystals are deposited throughout the condenser and the receiving flask. Yield was about 85%.The solid was recrystallized from dry hexane as long white dense needle. In a separate batch of

preparation it was resublimed in vacuum to get the needle shaped crystals (m.p- 81.9°C, lit mp-81-82°C).



(4)

Yield 84%; White solid; m.p.- 81.9°C

Anal. Calcd for ($C_9H_7NO_2$): C, 67.07; H, 4.38; N, 8.69. Found: C, 67.56; H, 3.98; N, 8.33.

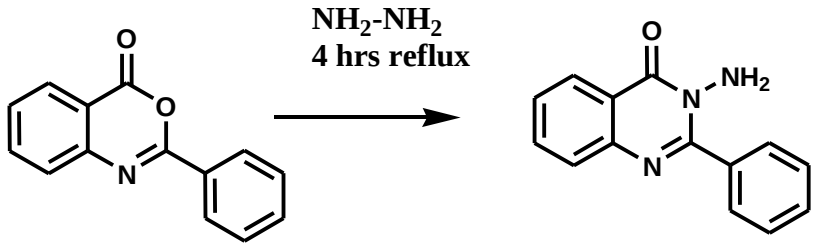
^{1}HNMR (300 MHz, $CDCl_3$): δ 8.73 (5-H); δ 8.12 (7-H); δ 7.60 (8-H); δ 7.14 (6-H); δ 2.27(CH_3);

^{13}CNMR (300 MHz, $CDCl_3$): 171.47 (C-2); 169.43 (C-4); 142.04 (C-8b); 135.64 (C-7); 131.72 (C-5); 122.73 (C-6); 120.53 (C-8); 113.78 (C-5a) and 25.52 (-CH_3).

m/z found for ($C_9H_7NO_2$): 160(M), 161(M+1), 162(M+2), 180($M+H_2O+H^+$), 359($2M+2H_2O+H^+$).

1.2.2 Synthesis of 3-amino-2-phenyl-quinazoline-4(3H)-one (2a):

To an ethanolic solution of 2-phenyl-3,1-benzoxazin-4-(3H)-one (1gm, 4.22 mmole), hydrazine hydrate 98% (1.5ml) was added and the mixture was heated in a water bath for about 3 hours. The flask containing the reaction mixture was cooled and the solid thus formed was filtered and washed with water. The air dried product was recrystallized from ethanol. Purity of the compound was checked by TLC using benzene and ethyl acetate as mobile phase in ratio of 7:3.



Scheme 1.2: Synthesis of 3-amino-2-phenyl-quinazoline-4(3H)-one

Yield 76%; Brownish Yellow solid; m.p.- 220 °C;

Anal. Calcd for ($C_{20}H_{16}N_2O_4$): C, 68.96; H, 4.63; N, 8.04. Found: C, 68.44; H, 4.92; N, 7.89.

^{1}HNMR (300 MHz, $CDCl_3$): δ 8.73 (5-H); δ 8.12 (7-H); δ 7.60 (8-H); δ 7.14 (6-H); δ 2.27(CH_3);

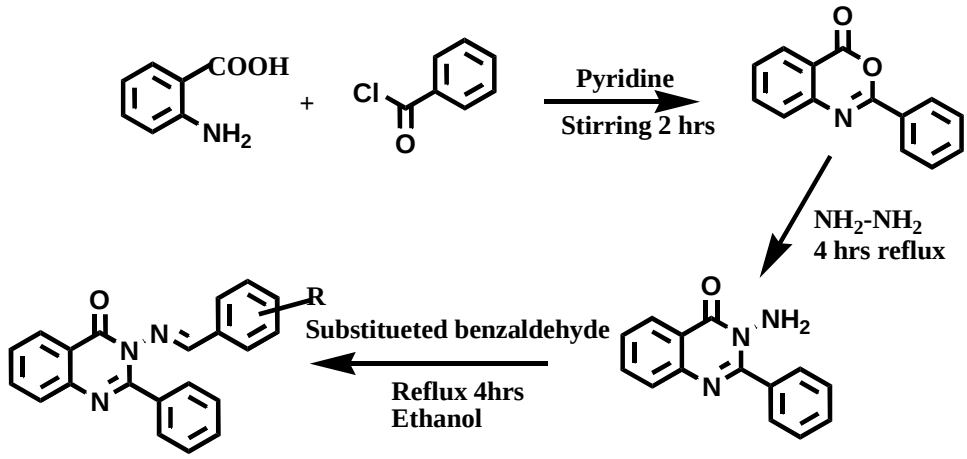
^{13}CNMR (300 MHz, $CDCl_3$): 171.47 (C-2); 169.43 (C-4); 142.04 (C-8b); 135.64 (C-7); 131.72 (C-5); 122.73 (C-6); 120.53 (C-8); 113.78 (C-5a) and 25.52 (-CH_3).

IR (KBr, cm^{-1}): 2944, 1760, 1750, 1645, 1605, 1472, 1464, 1320, and 1008

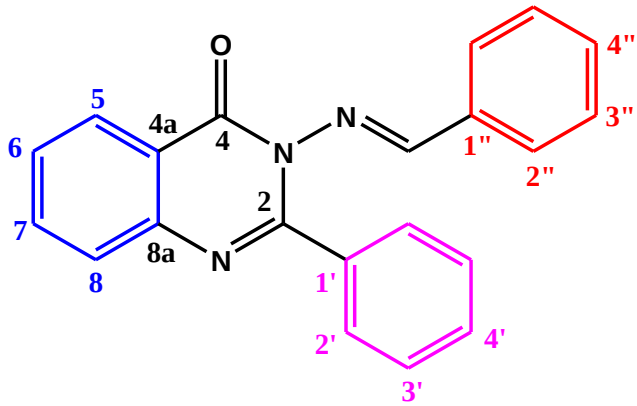
m/z found for ($C_{20}H_{16}N_2O_4$): 349(M+1), 350(M+2), 407(M+2H_2O+Na).

1.2.3 Synthesis of 3-(Arylideneamino)-2-phenylquinazoline-4(3*H*)-ones (3a-j):

A mixture of 3-amino-2-phenylquinazolin-4(3H)-one (0.01 mole), appropriate aromatic aldehyde (0.01 mole) and ethanol (20 mL) was refluxed for 4-6 hours. The resulting mixture was cooled and poured into ice water. The separated solid was filtered, washed with water and recrystallized from ethanol.



Scheme 1.3: Synthesis of the 3-(Arylideneamino)-2-phenylquinazoline-4(3H)-ones



3-(Arylideneamino)-2-phenylquinazoline-4(3H)-one

(5)

3-{[(2-Hydroxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3a)**

Yield 76%; mp- 144 ^{o}C; R_f 0.77;

^{1}**H-NMR:** 6.69 (H- 5”), 6.9 (H-3”), 7.35 (H-4”), 7.35 (H-6”), 7.4 (H-4’), 7.48 (H-3’), 7.56 (H-6), 7.6 (H-8), 7.6 (H-7), 7.81 (H-2’), 8.36 (H-5), 9.19 (s, 1H, H-C=N), 9.99 (OH, H-bonded), 7.8 Hz (J_{56});

^{13}**C-NMR:** 116.42 (C-1”), 117.50 (C-3’’), 119.69 (C-5”), 121.46 (C-4a), 127.32 (C-8), 127.39 (C-6), 128.00 (C-2’),128.97 (C-5), 130.34 (C-3’), 132.5 (C-6”), 133.33 (C-4’), 134.19 (C-4”), 134.84 (C-7), 146.37 (C-8a), 153.63 (C-2), 159.14 (C-4), 159.74 (=C(OH)-, C-2”), 164.75 (H-C=N), C-1’ quaternary peak not observed;

IR (KBr, cm^{-1}) : 3200-3100, 1681.8, 1604.7, 1467.7;

m/z found for ($C_{21}H_{15}N_3O_2$): 342 (M+1);

Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.89%; H, 4.45%; N, 12.31%; found: C, 74.10%; H, 4.45%; N, 12.28%.

3-{[(4-Methoxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3b)**

Yield 75%; m.p. 140°C; R_f 0.75;

^{1}HNMR: 3.84 (s, 3H, methoxy protons), 7.37 (H-3'/ H-4'), 7.40 (H-3"), 7.46 (H-8), 7.53 (H-6), 7.78 (H- 2"), 7.80 (H-7), 7.84 (H-2'), 8.36 (H-5), 8.87 (1H, s, H-C=N-N);

^{13}C-NMR: 55.40 (-O-CH_3), 114.34 (C-3"), 121.48 (C-4a), 125.89 (C-1"), 126.90 (C-8), 127.26 (C-2'), 127.70 (C-6), 127.88 (C-5), 129.89 (C-2"), 129.90 (C-4'), 130.75 (C-3'), 134.39 (C-7), 134.67 (C-1'), 146.50 (C-8a), 159.40 (C-4), 163.08 (=C(OCH_3)-,C-4"), 164.0 (C-2), 166.55 (H-C=N);

m/z found for ($C_{22}H_{17}N_3O_2$): 356(M+1)

IR (KBr, cm^{-1}): 1679.9, 1602.7, 1448.4, 1494.7, 1257.5, 1170.7

Anal. Calcd. for $C_{22}H_{17}N_3O_2$: C, 74.35%, H, 4.82%, N, 11.82%; found: C, 74.40%, H, 4.90%, N, 11.78%.

3-{[(4-Fluorophenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3c)**

Yield 68%; m.p. 166°C; R_f0.73;

^{1}H-NMR: 7.1 (H-4"), 7.41 (H-3'), 7.45 (H-4'), 7.49 (H-6), 7.53 (H-8), 7.54 (H-2"), 7.7 (H- 2'), 7.8 (H-7), 8.3 (H-5), 9.04 (s, 1H, H-C=N); 7.8 Hz (J_{56}), 0.9 Hz (J_{57}), 0Hz (J_{58}), 6.3 Hz (J_{67}), 1.8 Hz (J_{68}), 8.7 Hz ($J_{2"3"}$);

^{13}C-NMR: 166.30 (=C(F)-, C-4"), 164.84 (H-C=N), 153.97 (C-4), 153.90 (C-2), 146.60 (C-8a), 134.55 (C-1'), 134.15 (C-7), 131.00 (C-2"), 130.89 (C-4'), 130.50 (C-1"), 129.30 (C- 2'), 128.98 (C-3'), 127.68 (C-6), 127.20 (C-5), 126.79 (C-8), 121.50 (C-4a), 116.33 (C-3");

m/z found for *($C_{21}H_{14}N_3OF$):* 344(M+1);

IR (KBr, cm^{-1}): 1674.1, 1614.3, 1593.1, 1554.5, 1537.2, 1469.7, 1373.2, 1184.2;

Anal. Calcd. for $C_{21}H_{14}N_3OF$: C, 73.46%, H, 4.11%, N, 12.24%; found: C, 73.50%, H, 4.10%, N, 12.18%.

3-{[4-Dimethylaminophenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3d)**

Yield 70%; m.p. 178°C; R_f 0.8;

^{1}H-NMR: 3.04 (-N-CH_3), 6.66 (H-3"), 7.40 (H-3' and H-4'), 7.58 (H-6 and H-2"), 7.79 (H-8 and H-2'), 7.80 (H-7), 8.36 (H-5), 8.67 (s, 1H. H-C=N); 8.7 Hz (J_{56}), 0.9 Hz (J_{57}), 0 Hz (J_{58}), 7.5 Hz (J_{67}), 9.0 Hz ($J_{2"3"}$);

^{13}C-NMR: 187.65 (H-C=N), 159.80 (C-4), 154.07 (C-2), 153.06 (=C($N(CH_3)_2$), C-4"), 146.66 (C-8a), 134.80 (C-1'), 134.15 (C-7), 130.72 (C-2"), 129.70 (C-4'), 129.30 (C-2'), 127.89 (C-3'), 127.68 (C-3), 127.20 (C-5), 126.79 (C-8), 121.58 (C-1"), 120.30 (C-4a), 111.52 (C-3"), 40.13 (-N-CH3);

IR (KBr, cm^{-1}): 1681.8, 1589.2, 1556.4, 1508.2, 1456.2, 1375.2, 1328.9, 1313.4;

m/z found for (*$C_{23}H_{20}N_4O$*): 344(M+1)

Anal. Calcd. for C23H20N4O: C, 74.98%, H, 5.47%, N, 15.2%; found: C, 74.99%, H, 5.50%, N, 15.13%.

3-{[4-Chloroyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3e)**

Yield 72%; m.p. 162°C; R_f 0.81;

^{1}H-NMR: 7.37 (H-3'), 7.42 (H-4'), 7.49 (H-6), 7.53 (H-8), 7.54 (H-3"), 7.68 (H-2"), 7.80 (H-7), 7.82 (H-2'), 8.36 (H-5), 9.10 (s, 1H, H-C=N);

^{13}C-NMR: 121.47 (C-4a), 127.16 (C-8), 127.33 (C-2'), 127.88 (C-6), 127.93 (C-5), 129.24 (C-3'), 129.77 (C-3"), 129.92 (C-4'), 130.00 (C-2"), 131.36 (C-1"), 134.36 (C-1"), 134.78 (C 7), 138.46 (=C(Cl)-, C-4"), 146.47 (C-8a), 154.00 (C-2), 159.22 (C-4), 164.40 (H-C=N);

IR (KBr, cm^{-1}): 1679.9, 1591.2, 1554.5, 1377.1;

m/z found for (*$C_{21}H_{14}N_3OCl$*): 360(M+1);

Anal. Calcd. for $C_{21}H_{14}N_3OCl$: C, 70.10%; H, 3.92%; N, 11.68%; found: C, 70.20%; H, 4.10%; N, 11.62%.

3-{[3-Methoxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3f)**

Yield 75%; m.p. 134°C; Rf 0.67;

Anal. Calcd. for $C_{22}H_{17}N_3O_2$: C, 74.35%; H, 4.28%; N, 11.82%; found: C, 74.45%; H, 4.35%; N, 11.78%.

^{1}HNMR: 3.74 (s, 3H, methoxy protons), 7.30 (H-4"), 7.40 (H-2"), 7.43 (H-3'), 7.45 (H-4'), 7.55 (H-5"/ H-6"), 7.62 (H-6), 7.69 (H-8), 7.72 (H-7), 7.82 (H-2'), 8.37 (H-5), 9.09 (s, 1H, H-C=N-N);
^{13}C-NMR: 111.74 (C-2"), 119.15 (C-4"), 121.56 (C-4a), 121.76 (C-6"), 122.33 (C-8), 127.08 (C-6), 127.31 (C- 5), 127.87 (C-2'), 128.17 (C-5"), 128.18 (C-3'), 129.84 (C-4'), 134.22 (C-1'), 134.51 (C-7), 134.88 (C-1"), 146.51 (C-8a), 154.13 (C-2), 159.27 (C-4), 159.86 (=C(OCH3), C-3"), 165.52 (H-C=N);
IR (KBr, cm^{-1}): 1679.9, 1575.7, 1465.8, 1367.4, 1317.3, 1276.8;
m/z found for ($C_{22}H_{17}N_3O_2$): 356(M+1);

3-{[(4-Hydroxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3g)**
Yield 76%; m.p. 167°C; Rf 0.63;
Anal. Calcd. For $C_{21}H_{15}N_3O_2$: C, 73.89%; H, 4.43%; N, 12.31%; found: C, 73.99%; H, 4.49%; N, 12.30%.
^{1}H-NMR: 5.03 (-OH), 7.42 (H-3"/H-5"), 7.50 (H-3'/H-4'), 7.52 (H-6), 7.68 (H-2"/H-6"), 7.78 (H-7), 7.80 (H-8), 7.82 (H-2'), 8.29 (m, H-5), 9.16 (s, 1H, H-C=N-N);
^{13}C-NMR: 110.00 (C- 3"), 120.10 (C-4a), 126.61 (C-8), 127.08 (C-6), 127.79 (C-5), 128.20 (C-2'), 129.28 (C-3'), 130.29 (C-4'), 133.94 (C-2"), 134.50 (C-7), 134.52 (C-1"), 143.12 (C-8a), 149.00 (C-2), 149.88 (-CH=N-), 155.00 (C-4), 161.54 (=C(OH)-, C-4"), C-1' quaternary peak not observed;
IR (KBr, cm^{-1}): 3307.7, 3213.2, 1668.2, 1645.2, 1604.7, 1554.5, 1375.2, 1338.5;
m/z found for ($C_{21}H_{15}N_3O_2$) : 342(M+1)

3-{[(4-Hydroxy-3-methoxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one **(3h).** Yield 74%; m.p. 155°C; Rf 0.62;
Anal. Calcd. for $C_{22}H_{17}N_3O_3$: C, 71.15%; H, 4.61%; N, 11.31%; found: C, 71.25%; H, 4.65%; N, 11.26%.

^{1}H-NMR: 3.81 (s, 3H, methoxy protons), 5.03 (-OH), 6.92 (H-5"), 7.20 (H- 2"), 7.32 (H-6"), 7.50 (H-3'/H-4'), 7.52 (H-6), 7.76 (H-7), 7.78 (H-8), 7.83 (H-2'), 8.3 (m, H-5), 8.90 (s,1H, H-C=N-N);

^{13}C-NMR: 55.95 (-O-CH3), 108.67 (C-2"), 114.46 (C-5"), 125.40 (C-6"), 126.40 (C-4a), 126.63 (C-8), 127.08 (C-1"), 127.27 (C-2'), 127.77 (C-6), 128.20 (C-5), 129.31 (C-1'), 129.93 (C-3'), 130.32 (C-4'), 134.50 (C-7), 143.23 (C-8a), 146.72 (=C(OH)-, C-4"), 147.28 (=C(OCH3)-, C- 3"), 154.40 (C-4), 159.82 (-CH=N-);

IR (KBr, cm^{-1}): 3305.8, 3215.1, 1749.3, 1712.7, 1664.5, 1575.7, 1467.7, 1377.1;

m/z found for ($C_{22}H_{17}N_3O_3$): 372 (M+1);

***3-{[(3-Nitrophenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one* (3i).**

Yield 78%; m.p. 248°C; Rf 0.53;

Anal. Calcd. for $C_{21}H_{14}N_4O_3$: C, 68.10%; H, 3.84%; N, 15.15%; found: C, 68.15%; H, 3.81%; N, 15.13%

^{1}H-NMR ($CDCl_3$ + DMSO-d6): 7.22 (H-7), 7.30 (H-3'), 7.62 (H-6), 7.63 (H-4'/ H-4"), 7.9 (H-8), 8.02 (H-2'), 8.26 (H- 5"/ H-6"), 8.54 (H-5), 9.58 (H-2"), 8.59 (s, 1H, H-C=N);

^{13}C-NMR ($CDCl_3$ + DMSO-d6): 118.29 (C- 4a), 120.65 (C-4"), 122.30 (C-8), 122.33 (C-2"), 126.90 (C-5"), 127.27 (C-5), 127.97 (C-6"), 128.17 (C-2'), 128.28 (C-6), 130.00 (C-7), 131.50 (C-3'), 132.40 (C-4'), 133.47 (C-1"), 134.09 (=C(NO3)-, C- 3"), 139.82 (C-8a), 161.65 (-CH=N-), 164.88 (C-2), 165.50 (C-4), C-1' quaternary peak not observed;

IR (KBr, cm^{-1}): 1674.1, 1641.3, 1500, 1456.2, 1344.3;

m/z found for *($C_{21}H_{14}N_4O_3$)* : 371(M+1);

***3-{[(Pheny)lmethylene]amino}-2-phenylquinazolin-4(3H)-one* (3j)**

Yield 80%; m.p. 196°C; R_f 0.68;

Anal. Calcd. for $C_{21}H_{15}N_3O$: C, 77.52%; H, 4.65%; N, 12.91%; found: C, 77.54%; H, 4.71%; N, 12.85%.

^{1}H-NMR ($CDCl_3$ + DMSO-d6): 6.98 (H-7), 7.40 (H-3'), 7.41 (H-4'), 7.45 (H-6), 7.49 (H-3"), 7.55 (H-4"), 7.67 (H-8), 7.81 (H-2'), 8.05 (H-2"), 8.47 (s, 1H, H-C=N), 8.62 (H-5);

^{13}C-NMR ($CDCl_3$ + DMSO-d_6): 119.83 (C- 4a), 121.62 (C-5), 122.82 (C-2"), 127.47 (C-2'), 127.72 (C-6), 127.84 (C-8), 128.66 (C-3'), 128.82 (C- 3"), 130.62 (C-4"), 132.10 (C-4'), 132.72 (C-7), 133.65 (C-1'), 134.31 (C-1"), 139.79 (C-8a), 149.98 (-CH=N-), 165.77 (C-4), 166.03 (C-2);

IR (KBr, cm^{-1}): 1662.52, 1647.1, 1645.2, 1556.4, 1454.2;

m/z found for ($C_{21}H_{15}N_3O$): 326(M+1);