

Research article

Rapid And Convenient Microwave-assisted, Regioselective Synthesis and Characterization of a Novel 2,5-Bis(heteroamino)-1,4-Benzoquinones

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Abstract

A series of twenty four 2, 5-Bis (aminoheterocycles) -1,4-benzoquinones were prepared in yields ranging from 95-74% via a reaction between hydroquinone and various heteroamine moiety, in methanolic solution under microwave irradiation, the last was synthesized in three main steps; firstly chalcones produced by the claisen Schmidt condensation of aminoacetophenone with different para substituted benzyldehydes in ethanolic KOH solution under microwave irradiation. These chalcones were further reacted with (semicarbazide, thiosemicarbazide, urea and thiourea), respectively in the presence of base in ethanol, resulted pyrazole and pyrimidine derivatives. Michael 1,4- nucleophilic addition took place between amino heterocycles derivatives and hydroquinone in one pot aerobic oxidation under microwave irradiation resulting in a novel 2,5 Bis (pyrazoleamino)-1,4-benzoquinones and 2,5 Bis (pyrimidineamino)-1,4-benzoquinones. The newly synthesized aminoquinones derivatives were characterized on the basis of their chemical properties and spectroscopic (¹³C NMR, ¹H NMR, FT IR, CHN), all analysis data showed full agreement with the suggested structures. **Copyright © IJACSR, all rights reserved.**

Keywords:

Introduction

Quinones are ubiquitous in nature (1), they are tremendous group of naturally occurring pigments (2). They have captivated human concern for thousands of year, at first in due to their bright colors with possible uses as dyes and drugs. Pigments of diverse colors isolated from different provenances, have been depicted as quinonoid compounds. (3, 4)

These class of compounds are dispersed vastly in nature (5,6) they play pivotal role in biological functions, inclusive biological redox process, their role as electron transfer agents in primary metabolic process such as

photosynthesis and respiration is vital to human.(7) Enormous of benzoquinone derivatives displays eminent pharmacological applications(8) such as antibiotic(9), anticoagulant, antineoplastic antimalarial cancer chemotherapy, for example doxorubicin which has aquinoned moeity being one of the front line cancer chemotherapy treatments in the UK (10- 12).

Quinone analogs create great interest among naturally occurring compounds (13), they are habitual specimen that posses versatile pharmacological activity ranging from antitumor, inhibition of the HIV 1 reverse transcriptase to antibacterial and antiprtozols.(14) The regioselectivity of nucleophilic addition to 1,4-benzoquinones were tremendously studied by means of theory and experiment, results of these studies illustrated the nucleophilic nature that would mainly attack the 5-position of donor substituted 1,4-benzoquinone and 3-position of acceptor –substituted 1,4-benzoquinone. when the nucleophile is nitrogen atom version of the Michael addition is often referred to as the aza-Michael reaction, the inclusion of a nitrogen functionality within, quinones Furnishes to unique systems, as in aminoquinone derivatives, enhances their versatility as building blocks for the construction of biologically (15) compound libraries and qualifies them as potential precursors. its reported the conjugate addition of amines to carbon–carbon double bonds is a useful protocol in synthetic organic chemistry. It is used extensively in the synthesis of pharmaceutical intermediates, peptide analogues, antibiotics, and other biologically active molecules and drugs (16).The nucleophilic addition of amine to 1,4-benzoquinone scaffold afford novel protocol to synthesis aminoquinone analogues with high regioselectivity. . Microwave-assisted chemistry displays modernistic possibilities for the advancement of any chemical reaction that is thermally possible. It typically leads up to prompter reactions, elevates yields and diminishes the formation of by-products.

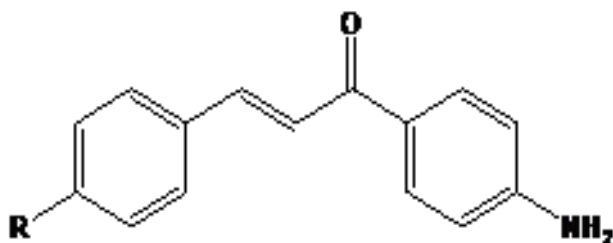
The prominence of these valuable aminoquinones compounds stimulate interest in conducting the present study which was aiming at synthesizing a new analogues of 2,5-diaminoquinones incorporated with two bioactive moiety : quinones unit and pyrazole, using microwave technique.

Synthesis of new compounds:

The synthesis of 2,5-diaminoquinones derivatives consists of three main steps:

i) Synthesis of Chalcones

A mixture of 0.01 mole of p-aminoacetophenone, 0.01mole of substituted benzyldehyde were dissolved in 3ml of ethanol and 0.112gm KOH then irradiated inside microwave oven 115W for 4min. and then it was poured in to crushed ice and acidified with HCL .The solid separated was filtered and recrystallized from ethanol. The physical properties were illustrated in table (1), chalcone can be represented by the following structure.

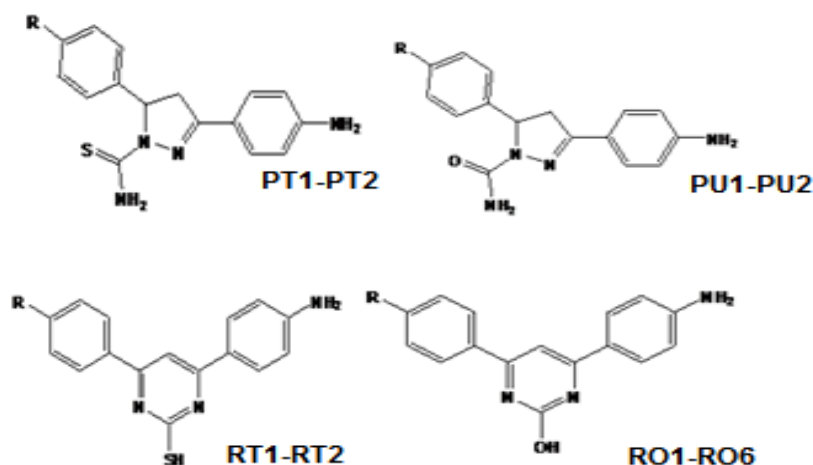


Comp Code	R	Mol Formula	Mol.Wt (gm)	%Yield	M.P c°	Reaction Time (Min) / energy(W)	R _f	appearance
CH-1	-F	C ₁₅ H ₁₂ FNO	241.09	95	152-154	2.5 / 400	0.64	Yellow/powder
CH-2	-Cl	C ₁₅ H ₁₂ ClNO	257.06	88	182-183	2.9 / 400	0.72	Yellow/powder
CH-3	-Br	C ₁₅ H ₁₂ BrNO	302.17	86	212-214	3.5 / 450	0.77	yellow/powder
CH-4	-NO ₂	C ₁₅ H ₁₂ N ₂ O ₃	268.08	96	182-184	4 / 450	0.66	Red orange /powder
CH-5	-OH	C ₁₅ H ₁₃ NO ₂	239.09	84	251-253	6 / 500	0.55	maroon /powder
CH-6	-CH ₃	C ₁₆ H ₁₅ NO	237.12	79	163-165	6 / 500	0.81	cream /powder

Table (1): physical data, percentage of yields, energy and reaction time for chalcones

ii) Synthesis of (pyroazole,pyrimidine) derivatives:

A mixture of (chalcone) (0.01 mole) (semicarbazide,thiosemicarbazide urea,thiourea)respectively (0.02 mole) and KOH (0.02 mole; 1.12 g) in 10 ml ethanol. The contents were thoroughly mixed. The reaction mixture under goes to microwave irradiation in a commercially available IFB domestic microwave oven having a maximum power output of 480W operating at 2450Hz intermittently at 30 seconds intervals for 3-6 min on a completion of reaction as monitored by TLC. It was then cooled and poured in cold water acidified with dil. HCl. Filtered, washed and dried. The product was recrystallized from ethanol to get product. The purity of the compound was checked with TLC. The physical properties of the synthesized compounds were illustrated in tables (2-5), these compounds can be represented by the following structures:



Table(2): physical data ,percentage of yields, energy and reaction time for pyrazole urea

Comp. Code	R	Mol Formula	Mol.Wt (gm)	%Yield	M.P c°	ReactionTime (Min) / energy(W)	R _F	appearance
PU-1	-F	C ₁₆ H ₁₅ FN ₄ O	298.12	92	226-228	3/214	0.59	Browne reddish/powder
PU-2	-Cl	C ₁₆ H ₁₅ ClN ₄ O	314.09	88	235-237	3/214	0.88	Browen/powder
PU-3	-Br	C ₁₆ H ₁₅ BrN ₄ O	359.22	86	234-236	3/214	0.95	dark golden rod/powder
PU-4	-NO ₂	C ₁₆ H ₁₅ N ₅ O ₃	325.32	93	336-337	3/200	0.59	dark orange/powder
PU-5	-OH	C ₁₆ H ₁₆ N ₄ O ₂	296.32	84	204-206	3/315	0.61	Firebrick/powder
PU-6	-CH ₃	C ₁₂ H ₁₈ N ₄ O	294.15	77	239-241	3/310	0.77	Crimson/powder

Table (3): physical data, percentage of yields, energy and reaction time for pyrazole thiourea

Comp Code	R	Mol Formula	Mol.Wt (gm)	%Yield	M.P c°	ReactionTime (Min) / energy(W)	R _F	appearance
PT-1	-F	C ₁₆ H ₁₅ FN ₄ S	314.10	92	263-264	3/214	0.83	Light orange/powder
PT-2	-Cl	C ₁₆ H ₁₅ ClN ₄ S	330.07	88	371-372	3/214	0.75	persimmon/powder
PT-3	-Br	C ₁₆ H ₁₅ BrN ₄ S	375.29	86	277-279	3/214	0.78	Light yellow/powder
PT-4	-NO ₂	C ₁₆ H ₁₅ N ₅ O ₂ S	341.39	93	286-288	3/200	0.61	Orange red/powder

PT-5	-OH	C ₁₆ H ₁₆ N ₄ OS	312.39	84	290-291	3/315	0.53	garnet/powder
PT-6	-CH ₃	C ₁₇ H ₁₈ N ₄ S	310.42	77	273-275	3/310	0.99	Satin gold/powder

Table(4): physical data ,percentage of yields, energy and reaction time for pyrimidine -ol

Comp Code	R	Mol Formula	Mol.Wt (gm)	%Yield	M.P c°	ReactionTime (Min) / energy(W)	R _F	appearance
RO-1	-F	C ₁₆ H ₁₂ FN ₃ O	281.10	92	213-214	3/214	0.72	Light orange/powder
RO-2	-Cl	C ₁₆ H ₁₂ ClN ₃ O	297.07	88	218-220	3/214	0.84	persimmon/powder
RO-3	-Br	C ₁₆ H ₁₂ BrN ₃ O	342.19	86	177-179	3/214	0.77	Light yellow/powder
RO-4	-NO ₂	C ₁₆ H ₁₂ N ₄ O ₃	308.29	93	217-219	3/200	0.68	Orange red/powder
RO-5	-OH	C ₁₆ H ₁₃ N ₃ O ₂	279.29	84	187-188	3/315	0.56	garnet/powder
RO-6	-CH ₃	C ₁₇ H ₁₅ N ₃ O	277.32	77	222-224	3/310	0.92	Satin gold/powder

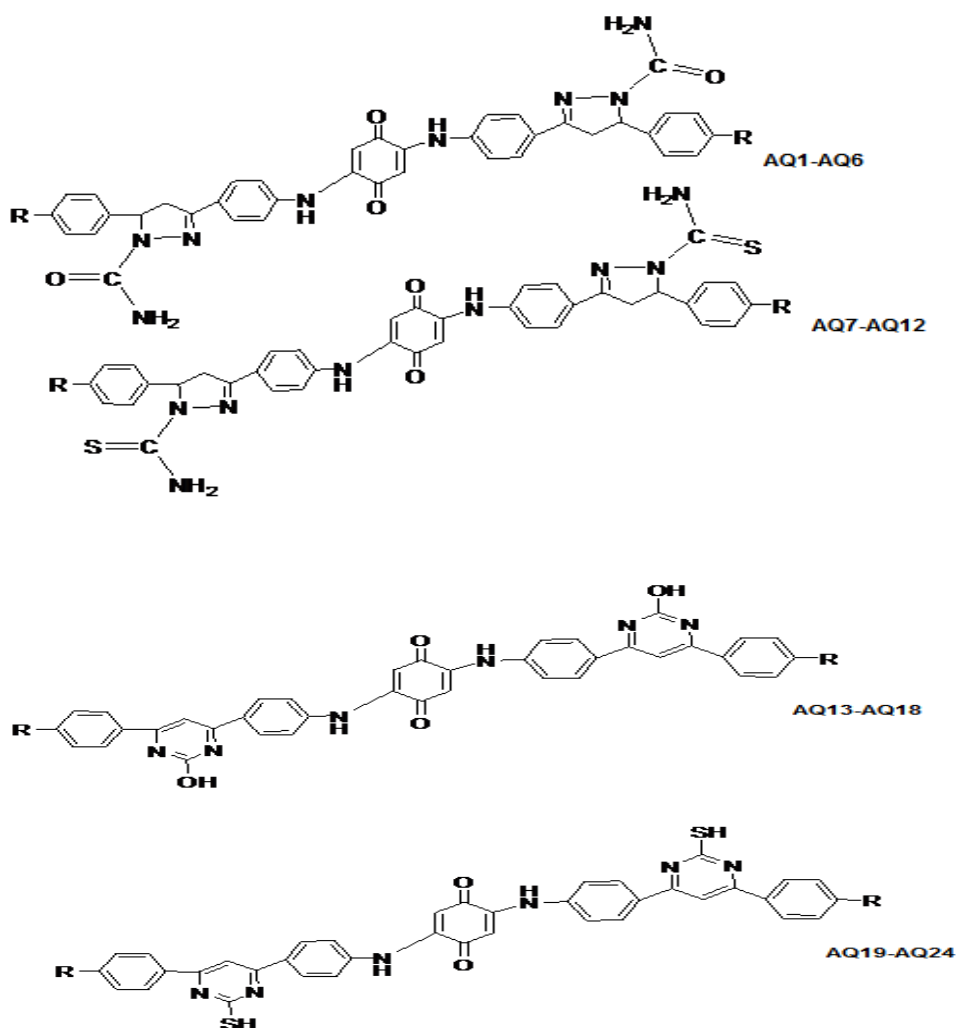
Table(5): physical data ,percentage of yields, energy and reaction time for pyrimidine -thiol

Comp. Code	R	Mol Formula	Mol.Wt (gm)	%Yield	M.P c°	ReactionTime (Min) / energy(W)	R _F	appearance
RT-1	-F	C ₁₆ H ₁₂ FN ₃ S	279.07	92	273-274	3/214	0.62	Light orange/powder

RT-2	-Cl	C ₁₆ H ₁₂ ClN ₃ S	313.80	88	286-287	3/214	0.73	persimmon/powder
RT-3	-Br	C ₁₆ H ₁₂ BrN ₃ S	358.26	86	188-190	3/214	0.78	Light yellow/powder
RT-4	-NO ₂	C ₁₆ H ₁₂ N ₄ O ₂ S	324.36	93	298-299	3/200	0.82	Orange red/powder
RT-5	-OH	C ₁₆ H ₁₃ N ₃ OS	295.08	84	101-103	3/315	0.71	garnet/powder
RT-6	-CH ₃	C ₁₇ H ₁₅ N ₃ S	293.39	77	227-228	3/310	0.89	Satin gold/powder

iii) Synthesis of 2,5-bis amino-p-benzoquinone derivatives:

Methanol solution (10ml) of amine (heterocyclic series) (2.3 mmole) was added to methanol solution (10 ml) of hydroquinones (0.05 mmole). This mixture was irradiated at (320w) for two minutes. The solution was evaporated in room temperature then product was purified by recrystallization from methanol to obtain long crystals with different colors (red, orange, yellow), physical properties were displayed in table(1-6). The structure of final products can be represented by following structures:



Table(6): physical data ,percentage of yields, energy and reaction time for 2,5-diaminoquinone

Comp. Code	R	Mol Formula	Mol.Wt (gm)	%Yield	M.P c°	Reaction Time (Min) / energy(W)	R _f	appearance
AQ-1	-F	C ₃₈ H ₃₀ F ₂ N ₈ O ₄	700.69	78	152-154	3/214	0.72	Light orange/crystal
AQ-2	-Cl	C ₃₈ H ₃₀ Cl ₂ N ₈ O ₄	733.69	83	162-164	3/214	0.61	Dark yellow/crystal
AQ-3	-Br	C ₃₈ H ₃₀ Br ₂ N ₈ O ₄	822.50	80	130-132	3/214	0.63	Light yellow/powder
AQ-4	-NO ₂	C ₃₈ H ₃₀ N ₁₀ O ₈	754.22	92	148-150	3/200	0.54	Orange red/powder
AQ-5	-OH	C ₃₈ H ₃₂ N ₈ O ₆	696.71	86	169-170	3/315	0.81	garnet/powder
AQ-6	-CH ₃	C ₄₀ H ₃₆ N ₈ O ₄	692.29	84	125-124	3/310	0.64	Crimson /powder
AQ-7	-F	C ₃₈ H ₃₀ F ₂ N ₈ O ₂ S ₂	732.19	74	122-123	3/214	0.86	Gold/crystal
AQ-8	-Cl	C ₃₈ H ₃₀ Cl ₂ N ₈ O ₂ S ₂	765.73	89	134-136	3/214	0.68	Light yellow/crystal
AQ-9	-Br	C ₃₈ H ₃₀ Br ₂ N ₈ O ₂ S ₂	854.64	94	186-188	3/214	0.7	Reddish Browne/crystal
AQ-10	-NO ₂	C ₃₈ H ₃₀ N ₁₀ O ₆ S ₂	786.84	94	187-189	3/214	0.49	Red orange/long crystal
AQ-11	-OH	C ₃₈ H ₃₂ N ₈ O ₄ S ₂	728.84	91	144-146	3/200	0.41	Firebrick/crystal
AQ-12	-CH ₃	C ₄₀ H ₃₆ N ₈ O ₂ S ₂	724.90	90	135-136	3/214	0.62	Crimson/crystal
AQ-13	-F	C ₃₈ H ₂₄ F ₂ N ₆ O ₄	666.18	88	176-177	3/200	0.81	Bright yellow/crystal
AQ-14	-Cl	C ₃₈ H ₂₄ Cl ₂ N ₆ O ₄	699.54	91	128-130	3/214	0.92	Yellow/crystal
AQ-15	-Br	C ₃₈ H ₂₄ Br ₂ N ₆ O ₄	788.44	86	97-99	3/310	0.97	Browne/ crystal
AQ-16	-NO ₂	C ₃₈ H ₂₄ F ₂ N ₈ O ₈	720.17	81	176-177	3/200	0.85	Dark orange /crystal
AQ-17	-OH	C ₃₈ H ₂₆ N ₆ O ₆	662.65	91	98-100	3/310	0.79	Reddish brown/ long crystal
AQ-18	-CH ₃	C ₄₀ H ₃₀ N ₆ O ₄	658.70	85	142-144	3/200	0.66	Cream/crystal
AQ-19	-F	C ₃₈ H ₂₄ F ₂ N ₆ O ₂ S ₂	698.76	93	111-113	3/214	0.74	Yellow/crystal
AQ-20	-Cl	C ₃₈ H ₂₄ Cl ₂ N ₆ O ₂ S ₂	731.67	88	148-151	3/200	0.68	Light yellow /crystal

AQ-21	-Br	C ₃₈ H ₂₄ Br ₂ N ₆ O ₂ S ₂	820.57	79	187-189	3/310	0.69	Bright yellow/long crystal
AQ-22	-NO ₂	C ₃₈ H ₂₄ N ₈ O ₆ S ₂	752.78	92	173-175	3/214	0.56	Light orange /long crystal
AQ-23	-OH	C ₃₈ H ₂₆ N ₆ O ₄ S ₂	694.15	95	129-131	3/310	0.41	Maroon/long crystal
AQ-24	-CH ₃	C ₄₀ H ₃₀ N ₆ O ₂ S ₂	690.84	92	164-166	3/214	0.93	Red orange /long crystal

Materials and methods:

Melting points were determined in open capillary tubes and were found uncorrected. The synthesized compounds are characterized and identified by elemental analysis, IR spectra were recorded on FT-IR spectrometer (Perkin Elmer) using KBr disc method, ¹³C spectra were recorded on (Bruker MHz) and ¹H NMR spectra were recorded on ¹H FT-NMR (Bruker AMX 400 MHz) spectrometer in CDCl₃. The FT-IR and melting point measurement were carried out in Iraq, Basrah university, science college, chemistry department. The ¹³C NMR, ¹H NMR and CHN measurement were carried in Iran, Tehran, Tarbiat Modares University.

Results and Discussion

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carboxamide) (AQ1): Yield : (78%), mp(152-154). IR (KBr pellet, cm⁻¹): U(C=O quinone) 1636.59, U(C=O amide) 1650.90, U(C-N) 1284.50, U(C=N) 1594.3, U(C=C) 1600.81, U(C-H aromatic) 30.58.89, U(C-H aliphatic) 2978.53-2891.10. U(NH₂ asym, sym) 3481.70, 3328.98. U(C-F) 1220.86; ¹H NMR (CDCl₃): 4.23(S, 4H -NH₂); 6.306-6.6332(S, 2H -C(1,1')); 2.301(br. S, 2H -NH); 6.722-6.700 [d, J = 8.8 Hz, 4H -C(3,3',3'',3''')]; 7.647-7.626 [d, J = 8.4 Hz, 4H -C(4,4',4'',4''')]; 7.261-7.230 [d, J = 12.4 Hz, 4H -C(5,5',5'',5''')]; 7.331-7.300 [d, J = 12.4 Hz, 4H -C(6,6',6'',6''')]; 3.752-3.717 [m, J = 14 Hz, 4H -C(7,7',8,8')]; 4.121-4.086 [m, J = 14 Hz, 2H -C(9,9')]; ¹³C-NMR (CDCl₃): 181.03 [C(1), C(1')]; 105.39 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.98 [C(4), C(4')]; 116.90-116.88 [C(5), C(5')]; 130.74-130.70 [C(6), C(6')]; 129.60 [C(7), C(7')]; 152.71 [C(8), C(8')]; 39.20 [C(9), C(9')]; 61.09 [C(10), C(10')]; 155.32 [C(11), C(11')]; 140.88 [C(12), C(12')]; 129.28-129.20 [C(13), C(13')]; 115.75-115.73 [C(14), C(14')]; 160.25 [C(15), C(15')]; Anal.(%) for C₃₈H₃₀F₂N₈O₄, Calcd.C, 65.14; H, 4.32; N, 15.99; Found C, 65.16; H, 4.30; N, 15.90.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carboxamide) (AQ2): Yield : (83%), mp. 164-162, IR (KBr pellet, cm⁻¹): U(C=O quinone) 1635.56, U(C=O amide) 1650.91, U(C-N) 1244.28, U(C=N) 1591.33, U(C=C) 1601.58, U(C-H aromatic) 3051.80, U(C-H aliphatic) 2987.28-2811.19. U(NH₂ asym, sym) 3481.73, 3388.94. U(C-Cl) 1100.91; ¹H NMR (CDCl₃): 4.23(S, 4H -NH₂); 6.306-6.6332(S, 2H -C(1,1')); 2.301(br. S, 2H -NH); 6.722-6.700 [d, J = 8.8 Hz, 4H -C(3,3',3'',3''')]; 7.647-7.626 [d, J = 8.4 Hz, 4H -C(4,4',4'',4''')]; 7.311-7.299 [d, J = 4.8 Hz, 4H -C(5,5',5'',5''')]; 7.201-7.191 [d, J = 4.0 Hz, 4H -C(6,6',6'',6''')]; 3.752-3.709 [m, J = 14 Hz, 4H -C(7,7',8,8')]; 4.121-4.086 [m, J = 14 Hz, 2H -C(9,9')]; ¹³C-NMR (CDCl₃): 181.03 [C(1), C(1')]; 105.39 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.98 [C(4), C(4')]; 116.90-116.88 [C(5), C(5')]; 130.74-130.70 [C(6), C(6')]; 129.60 [C(7), C(7')]; 152.71 [C(8), C(8')]; 39.21 [C(9), C(9')]; 60.09 [C(10), C(10')]; 155.32 [C(11), C(11')]; 144.98 [C(12), C(12')]; 127.11-127.10 [C(13), C(13')]; 128.02-128.00 [C(14), C(14')]; 132.26 [C(15), C(15')]; Anal.(%) for C₃₈H₃₀Cl₂N₈O₄, Calcd.C: 62.21; H: 4.12; N: 15.27; Found: C: 62.22, H: 4.19, N: 15.24.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carboxamide) (AQ3): Yield : (80%), mp. 132-130. IR (KBr pellet, cm⁻¹): U(C=O quinone) 1631.59, U(C=O amide) 1650.90, U(C-N) 1284.50, U(C=N) 1589.73, U(C=C) 1600.56, U(C-H aromatic) 3055.62, U(C-H aliphatic) 2987.13-2881.59. U(NH₂ asym, sym) 3481.70, 3328.06. U(C-Br) 1091.12; ¹H NMR (CDCl₃): 4.23(S, 4H -NH₂); 6.306-6.6332(S, 2H -C(1,1')); 2.301(br. S, 2H -NH); 6.722-6.700 [d, J = 8.8 Hz, 4H -C(3,3',3'',3''')]; 7.647-7.626 [d, J = 8.8 Hz, 4H -C(4,4',4'',4''')]; 7.282-7.243 [d, J = 15.6

H_z,4 H –C(5,5',5",5""); 7.999-7.961[d, J =15.2 Hz,4 H –C(6,6',6",6""); 3.752-3.717 [m, J =14Hz, 4H –C(7,7',8,8"");4.121-4.086 [m, J =14Hz, 2H –C(9,9""); ¹³ C- NMR(CDCl₃) δ :181.03[C(1), C(1')] ; 105.39 [C(2), C(2')] ; 152.31[C(3), C(3')] ; 142.98[C(4), C(4')] ; 116.90-116.88 [C(5), C(5')] ; 130.74-130.70[C(6), C(6')] ; 129.60 [C(7), C(7')] ; 152.71[C(8), C(8')] ; 39.20 [C(9), C(9')] ; 61.09 [C(10), C(10')] ; 155.32 [C(11), C(11')] ; 145.38 [C(12), C(12')] ; 127.33-127.30 [C(13), C(13')] ; 131.67-131.66 [C(14), C(14')] ; 121.95 [C(15), C(15')] ;Anal.(%) for C₃₈H₃₀Br₂N₈O₄ Calcd. C: 55.49, H: 3.68,N: 13.62,Found: C: 55.56, H: 3.71,N: 13.60.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-nitrophenyl)-4,5-dihydro-1H-pyrazole-1-carboxamide) (AQ4). Yield 92%,mp.148-150,IR (KBr pellet, cm⁻¹):U(C=O quinone) 1639.52, U(C=O amide) 1650.93, U(C-N) 1284.86, U(C=N) 1557.22, U(C= C) 1600.52, U(C- H aromatic) 3052.73, U(C- H aliphatic)2982.16-2886.67. U(NH₂asym, sym) 3483.79, 3328.28; ¹ H NMR(CDCl₃) δ: 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S, 2H –NH);6.695-6.674[d, J =8.4 Hz,4 H –C(3,3',3",3"")] ;7.647-7.626 [d, J =8.4Hz,4 H –C(4,4',4",4"")];7.454-7.415 [d, J =15.6 Hz,4 H –C(5,5',5",5""); 8.339-8.300[d, J =15.6Hz,4 H –C(6,6',6",6""); 3.752-3.717 [m, J =14Hz 4H –C(7,7',8,8"");4.121-4.086 [m, J =14Hz 2H –C(9,9"");¹³ C- NMR (CDCl₃) δ :181.03[C(1), C(1')] ; 105.39 [C(2), C(2')] ; 152.31[C(3), C(3')] ; 142.98[C(4), C(4')] ; 116.90-116.88 [C(5), C(5')] ; 130.74-130.70[C(6), C(6')] ; 129.60 [C(7), C(7')] ; 152.71[C(8), C(8')] ; 39.20 [C(9), C(9')] ; 61.09 [C(10), C(10')] ; 155.32 [C(11), C(11')] ; 147.32 [C(12), C(12')] ; 123.63-123.60 [C(13), C(13')] ; 123.76-123.77 [C(14), C(14')] ; 145.9 [C(15), C(15')] ;Anal.(%) for C₃₈H₃₀N₁₀O₈, Calcd. C:60.47,H:4.01,N: 18.56;Found: . C:60.37, H: 4.03, N: 18.86.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-p-tolyl-4,5-dihydro-1H-pyrazole-1-carboxamide)(AQ5).Yeild 86%, mp.169-171, IR(KBr)pellet, cm⁻¹):U(C=O quinone) 1627.81, U(C=O amide) 1658.61, U(C-N 1238.21, U(C=N) 1569.92, U(C= C) 1595.02, U(C- H aromatic) 3026.11, U(C- H aliphatic) 2910.30-2852.57, U(NH₂asym, sym) 3490.93, 3346.24; ¹ H NMR(CDCl₃) δ: 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S, 2H –NH);6.811-6.814[d, J =1.2 Hz,4 H –C(3,3',3",3"")] ;7.875-7.873 [d, J =0.8 Hz,4 H –C(4,4',4",4"");7.151-7.147 [d, J =1.6Hz,4 H –C(5,5',5",5""); 6.933-6.929[d, J =1.6 Hz,4 H –C(6,6',6",6""); 3.752-3.717 [m, J =14 Hz, 4H –C(7,7',8,8"");4.121-4.086 [m, J =14 Hz, 2H –C(9,9"");2.51[S 6H-CH₃]); ¹³ C- NMR (CDCl₃) δ :181.03[C(1), C(1')] ; 105.39 [C(2), C(2')] ; 152.31[C(3), C(3')] ; 142.98[C(4), C(4')] ; 116.90-116.88 [C(5), C(5')] ; 130.74-130.70[C(6), C(6')] ; 129.60 [C(7), C(7')] ; 152.71[C(8), C(8')] ; 39.20 [C(9), C(9')] ; 61.09 [C(10), C(10')] ; 155.32 [C(11), C(11')] ; 137.42 [C(12), C(12')] ; 125.03-125.00 [C(13), C(13')] ; 128.77-128.73 [C(14), C(14')] ; 138.05 [C(15), C(15')] ; 21.65 [C(16), C(16')] ;Anal.% for C₄₀H₃₆N₈O₄ Calcd. C: 69.34,H: 5.13,N: 16.11; Found: C: 69.35,H: 5.24,N: 16.17.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-hydroxyphenyl)-4,5-dihydro-1H-pyrazole-1-carboxamide) (AQ6).Yeild84%, mp.124-125;IR (KBr pellet, cm⁻¹):U(C=O quinone) 1631.13, U(C=O amide) 1659.11, U(C-N) 1288.36, U(C=N) 1571.88, U(C= C) 1595.02, U(C- H aromatic) 3072.24, U(C- H aliphatic) 2910.30-2852.57. U(NH₂asym, sym) 3490.92, 3355.91, U(O- H) 3222.83; ¹ H NMR (CDCl₃)δ: 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S, 2H –NH);6.722-6.700[d, J =8.8Hz,4 H –C(3,3',3",3"")] ;7.647-7.626 [d, J = 8.4 Hz,4 H –C(4,4',4",4"");7.261-7.241 [d, J =8.00 Hz,4 H –C(5,5',5",5""); 7.321-7.2999[d, J =8.8 Hz,4 H –C(6,6',6",6""); 3.752-3.717[m, J =14 Hz, 4H –C(7,7',8,8"");4.121-4.086 [m, J =14 Hz, 2H –C(9,9""); 9.472[S,2H-C(11,11""); ¹³ C- NMR (CDCl₃) δ :181.03[C(1), C(1')] ; 105.39 [C(2), C(2')] ; 152.31[C(3), C(3')] ; 142.98[C(4), C(4')] ; 116.90-116.88 [C(5), C(5')] ; 130.74-130.70[C(6), C(6')] ; 129.60 [C(7), C(7')] ; 152.71[C(8), C(8')] ; 39.20 [C(9), C(9')] ; 61.09 [C(10), C(10')] ; 155.32 [C(11), C(11')] ; 135.24 [C(12), C(12')] ; 127.44127.42 [C(13), C(13')] ; 115.29-115.27 [C(14), C(14')] ; 156.5 [C(15), C(15')] ;Anal.% for C₃₈H₃₂N₈O₆ Calcd .C: 65.51, H: 4.63,N: 16.08, Found: C,65.56; H, 4.51; N, 15.99.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide) (AQ7): Yield74%, mp.122-123, IR (KBr pellet, cm⁻¹):U(C=O quinone) 1636.13, U(S=O) 1286.43, U(C=N) 1589.23, U(C= C) 1602.74, U(C- H aromatic) 3058.80, U(C- H aliphatic) 2987.53-2891.11 U(NH₂asym, sym) 3483.20, 3328.91, U(C-F) 1225.55; ¹ H NMR(CDCl₃) δ:

4.23(S,4H -NH₂); 6.306-6.6332(S,2H -C(1,1')); 2.301(br. S, 2H -NH);6.722-6.700[d, J = 8.8Hz,4 H -C(3,3',3'',3''')];7.647-7.626 [d, J=8.4 Hz,4 H -C(4,4',4'',4''')];7.332-7.300 [d, J =12.8 Hz,4 H -C(5,5',5'',5''')];7.261-7.230[d, J =12.4Hz,4 H -C(6,6',6'',6''')]; 3.752-3.717 [m, J =14 Hz, 4H -C(7,7',8,8')];4.121-4.086 [m,2H -C(9,9')]; ¹³ C- NMR (CDCl₃) δ : 181.03 [C(1), C(1')]; 105.39 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.98 [C(4), C(4')]; 116.90-116.88 [C(5), C(5')]; 130.74-130.70 [C(6), C(6')]; 129.60 [C(7), C(7')]; 152.71 [C(8), C(8')]; 40.1 [C(9), C(9')]; 66.89 [C(10), C(10')]; 175.62 [C(11), C(11')]; 140.88 [C(12), C(12')]; 129.28-129.20 [C(13), C(13')]; 115.75-115.73 [C(14), C(14')]; 160.25 [C(15), C(15')];Anal.(%) for C₃₈H₃₀F₂N₈O₂S₂,Calcd.C, 62.28; H, 4.13; N, 15.29;

Found: C,62.23; H, 4.11; N, 15.34.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide) (AQ8). Yield 89%, mp.134-136 C° .IR (KBr pellet, cm⁻¹):U(C=O quinone) 1635.43, U(S=O) 1289.11, U(C=N) 1589.06, U(C= C) 1602.32, U(C- H aromatic) 3058.87, U(C- H aliphatic) 2987.58-2891.12 U(NH₂asym, sym) 3483.15, 3328.86, U(C-Cl) 1100.91; ¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂); 6.306-6.6332(S,2H -C(1,1')); 2.301(br. S, 2H -NH);6.722-6.700[d, J =8.8 Hz,4 H -C(3,3',3'',3''')];7.647-7.626 [d, J =8.44 Hz,4 H -C(4,4',4'',4''')];7.311-7.299 [d, J =4.8 Hz,4 H -C(5,5',5'',5''')]; 7.201-7.191[d, J =4.00 Hz,4 H -C(6,6',6'',6''')]; 3.752-3.717 [m, J =14 Hz 4H -C(7,7',8,8')];4.121-4.086 [m, J =14 Hz,2H -C(9,9')]; ¹³ C- NMR δ (CDCl₃) : 181.03 [C(1), C(1')]; 105.39 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.98 [C(4), C(4')]; 116.90-116.88 [C(5), C(5')]; 130.74-130.70 [C(6), C(6')]; 129.60 [C(7), C(7')]; 152.71 [C(8), C(8')]; 40.27 [C(9), C(9')]; 66.69 [C(10), C(10')]; 175.22 [C(11), C(11')]; 144.98 [C(12), C(12')]; 127.11-127.10 [C(13), C(13')]; 128.02-128.00 [C(14), C(14')]; 132.26 [C(15), C(15')];Anal.(%) for C₃₈H₃₀Cl₂N₈O₂S₂, Calcd. C, 59.60; H, 3.95; N, 14.63;found: C, 59.66; H: 4.04; N: 14.61.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide) (AQ9).Yeild94%, mp.186-188 ;IR (KBr pellet, cm⁻¹):U(C=O quinone) 1631.67, U(S=O) 1286.43, U(C=N) 1589.23, U(C= C) 1603.67, U(C- H aromatic) 3058.89, U(C- H aliphatic) 2981.50-2891.11 U(NH₂asym, sym) 3492.18, 3328.60, U(C-Br) 1029.92; ¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂); 6.306-6.6332(S,2H -C(1,1')); 2.301(br. S, 2H -NH);6.722-6.700[d, J = 8.8 Hz,4 H -C(3,3',3'',3''')];7.647-7.626 [d, J =8.4 Hz,4 H -C(4,4',4'',4''')];7.282-7.243 [d, J =15.6 Hz,4 H -C(5,5',5'',5''')];7.999-7.961 [d, J =15.2Hz,4 H -C(6,6',6'',6''')]; 3.752-3.717 [m, J =14Hz, 4H -C(7,7',8,8')];4.121-4.086 [m, J =14Hz, 2H -C(9,9')]; ¹³ C- NMR(CDCl₃) δ : 181.03 [C(1), C(1')]; 105.39 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.98 [C(4), C(4')]; 116.90-116.88 [C(5), C(5')]; 130.74-130.70 [C(6), C(6')]; 129.60 [C(7), C(7')]; 152.71 [C(8), C(8')]; 40.28 [C(9), C(9')]; 66.89 [C(10), C(10')]; 175.52 [C(11), C(11')]; 145.38 [C(12), C(12')]; 127.33--127.30 [C(13), C(13')]; 131.67--131.6 [C(14), C(14')]; 121.95 [C(15), C(15')];Anal.(%) for C₃₈H₃₀Br₂N₈O₂S₂, Calcd. C, 53.40; H, 3.54; N, 13.11;found: . C, 53.37; H, 3.59; N,12.99.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-(4-nitrophenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide)(AQ10) .Yield 94%, mp187-189 C°;IR (KBr pellet, cm⁻¹):U(C=O quinone) 1641.60, U(S=O) 1290.22, U(C=N) 1591.19, U(C= C) 1604.12, U(C- H aromatic) 3070.46, U(C- H aliphatic) 2984.67-28890.46, U(NH₂asym,sym) 3483.20, 3384.84. ¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂); 6.306-6.6332(S,2H -C(1,1')); 2.301(br. S, 2H -NH);6.695-6.674[d, J =8.4 Hz,4 H -C(3,3',3'',3''')];7.647-7.626 [d, J =8.4Hz,4 H -C(4,4',4'',4''')];7.454-7.415 [d, J =15.6 Hz,4 H -C(5,5',5'',5''')];8.339-8.300 [d, J = 15.6 Hz,4 H -C(6,6',6'',6''')]; 3.752-3.717 [m, J =14 Hz, 4H -C(7,7',8,8')];4.121-4.086 [m, J =14 Hz, 2H -C(9,9')].¹³ C- NMR (CDCl₃) δ : 181.03 [C(1), C(1')]; 105.39 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.98 [C(4), C(4')]; 116.90-116.88 [C(5), C(5')]; 130.74-130.70 [C(6), C(6')]; 129.60 [C(7), C(7')]; 152.71 [C(8), C(8')]; 40.29 [C(9), C(9')]; 66.59 [C(10), C(10')]; 175.24 [C(11), C(11')]; 147.32 [C(12), C(12')]; 123.63-123.60 [C(13), C(13')]; 123.76-123.77 [C(14), C(14')]; 145.9 [C(15), C(15')]; Anal. (%) forC₃₈H₃₀N₁₀O₆S₂, Calcd. C, 58.01; H, 3.84; N, 17.80;found: C, 57.93; H, 3.87; N, 17.74.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diy)bis(azanediy)bis(4,1-phenylene))bis(5-p-tolyl-4,5-dihydro-1H-pyrazole-1-carbothioamide)(AQ11).Yeild91%,mp144-146C°;IR (KBr pellet, cm⁻¹

):U(C=Oquinone) 1627.81, U(S=O) 1290.29, U(C=N) 1569.95, U(C=C) 1595.02, U(C- Haromatic) 3026.10, U(C- Haliphatic) 2910.38-2852.52, U(NH₂asym, sym) 3490.92,3346.27; ¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1')) ; 2.301(br. S, 2H -NH);6.722-6.700[d, J =8.8 Hz,4 H -C(3,3',3'',3''')] ;7.647-7.626 [d, J =8.4 Hz,4 H -C(4,4',4'',4''')] ;7.261-7.241 [d, J = 8 Hz,4 H -C(5,5',5'',5''')] ;7.321-7.299[d, J = 8.8 Hz,4 H -C(6,6',6'',6''')] ; 3.752-3.717 [m, J = 14 Hz, 4H -C(7,7',8,8')];4.121-4.086 [m., J = 14 Hz, 2H -C(9,9')];2.501[S,3H-CH₃]; ¹³ C- NMR(CDCl₃) δ : 181.03[C(1), C(1')] ; 105.39 [C(2), C(2')] ; 152.31[C(3), C(3')] ; 142.98[C(4), C(4')] ; 116.90-116.88 [C(5), C(5')] ; 130.74-130.70[C(6), C(6')] ; 129.60 [C(7), C(7')] ; 152.71[C(8), C(8')] ; 40.20 [C(9), C(9')] ; 66.85 [C(10), C(10')] ; 175.12 [C(11), C(11')] ; 137.42 [C(12), C(12')] ; 125.03-125.00 [C(13), C(13')] ; 128.77-128.73 [C(14), C(14')] ; 138.21 [C(15), C(15')]; 21.65[C(16), C(16')] ;Anal. (%) for C₄₀H₃₆N₈O₂S₂ Calcd. C, 66.28; H, 5.01; N, 15.46;found: C, 66.22; H, 4.86; N,15.43.

3,3'-(4,4'-(3,6-dioxocyclohexa-1,4-diene-1,4-diyl)bis(azanediy))bis(4,1-phenylene))bis(5-(4-hydroxyphenyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide) (AQ12). Yeild 90%, mp.135-136C°;IR (KBr pellet, cm⁻¹):U(C=Oquinone) 1631.11, U(S=O) 1288.36, U(C=N) 1571.88, U(C= C) 1592.07, U(C- Haromatic) 3019.82, U(C-H aliphatic) 2938.27-2881.03, U(NH₂asym, sym) 3490.90, 3354.93U(O- H) 3222.83; ¹ H NMR (CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1')) ; 2.301(br. S, 2H -NH);6.814-6.811[d, J =1.2 Hz,4 H -C(3,3',3'',3''')] ;7.875-7.873 [d, J =0.8Hz,4 H -C(4,4',4'',4''')] ;7.151-7.147 [d, J =1.6Hz,4 H -C(5,5',5'',5''')] ;6.933-6.929[d, J =1.6 Hz,4 H -C(6,6',6'',6''')] ; 3.752-3.717[m, J =14 Hz, 4H -C(7,7',8,8')];4.121-4.086 [m, J =14 Hz, 2H -C(9,9')];9.472[S,2H-C(11,11')]; ¹³ C- NMR(CDCl₃) δ : 181.03[C(1), C(1')] ; 105.39 [C(2), C(2')] ; 152.31[C(3), C(3')] ; 142.98[C(4), C(4')] ; 116.90-116.88 [C(5), C(5')] ; 130.74-130.70[C(6), C(6')] ; 129.60 [C(7), C(7')] ; 152.71[C(8), C(8')] ; 40.21 [C(9), C(9')] ; 66.19 [C(10), C(10')] ; 175.23 [C(11), C(11')] ; 135.24 [C(12), C(12')] ; 127.44127.42 [C(13), C(13')] ; 115.29-115.27 [C(14), C(14')] ; 138.21 [C(15), C(15')]; 21.65[C(16), C(16')] ;Anal. (%)for C₃₈H₃₂N₈O₄S₂, Calcd. C, 65.51; H, 4.63; N, 16.08;found : C, 65.41; H, 4.69; N, 16.11.

2,5-bis(4-(6-(4-fluorophenyl)-2-hydroxypyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ13) . Yeild 88% ,mp.176-177C°;IR (KBr pellet, cm⁻¹):U(C=O quinone) 1636.59, U(C-O) 1284.50, U(C=N) 1598.74, U(C= C) 1600.39, U(C- H_{aromatic}) 3058.89, , U(NH₂asym,sym) 3446.77, 3446.27, U(C-F) 1220.86. ¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1')) ; 2.301(br. S, 2H -NH);6.892-6.872[d, J = 8 Hz,4 H -C(3,3',3'',3''')] ;7.512-7.492 [d, J = 8 Hz,4 H -C(4,4',4'',4''')] ;8.147-8.116 [d, J = 12.4 Hz,4 H -C(5,5',5'',5''')] ;7.373-7.342[d, J =12.4 Hz,4 H -C(6,6',6'',6''')] ; 7.632 [S, 2H -C(7,7')];11.626 [S,2H -O(8,8')]; ¹³ C- NMR(CDCl₃) δ : 181.6 [C(1) , C(1')] ; 109.37 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.32-129.31 [C(6) , C(6')] ; 125.98 [C(7) , C(7')] ; 162.35 [C(8) , C(8')] ; 93.27 [C(9) , C(9')] ; 155.32 [C(10) , C(10')] ; 160.39 [C(11) , C(11')] ; 131.14 [C(12) , C(12')] ; 130.31-130.30 [C(13) , C(13')] ; 115.95-115.94 [C(14) , C(14')] ; 162.14 [C(15) , C(15')];Anal.(%) for C₃₈H₂₄F₂N₆O₄ ,Calcd. C, 68.46; H, 3.63; N, 12.61;found: C, 68.35; H, 3.57; N, 12.63.

2,5-bis(4-(6-(4-fluorophenyl)-2-mercaptopyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ14). Yeild 91% ,mp.128-130;IR (KBr pellet, cm⁻¹):U(C=Oquinone) 1636.88, U(C-N) 1292.22, U(C= N) 1544.88, U(C= C) 1600.81, U(C- H_{aromatic}) 3234.40, , U(NH) 3357.84, U(C-F) 1220.86, U(S-H) 2360.71,U(C-F) 1220.86. ¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1')) ; 2.301(br. S, 2H -NH);6.892-6.872[d, J =8 Hz,4 H -C(3,3',3'',3''')] ;7.512-7.492 [d, J =8 Hz,4 H -C(4,4',4'',4''')] ;8.147-8.116 [d, J =12.4 Hz,4 H -C(5,5',5'',5''')] ;7.342-7.334[d, J =12.4 Hz,4 H -C(6,6',6'',6''')] ; 8.479 [S, 2H -C(7,7')];12.126 [S,2H -S(8,8')]; ¹³ C- NMR(CDCl₃) δ : 181.39 [C(1) , C(1')] ; 109.37 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.32-129.31 [C(6) , C(6')] ; 125.98 [C(7) , C(7')] ; 169.63 [C(8) , C(8')] ; 109.32 [C(9) , C(9')] ; 166.32 [C(10) , C(10')] ; 181.06 [C(11) , C(11')] ; 131.14 [C(12) , C(12')] ; 130.31-130.30 [C(13) , C(13')] ; 115.95-115.94 [C(14) , C(14')] ; 162.14 [C(15) , C(15')] ;Anal (%) for C₃₈H₂₄F₂N₆O₄ ,Calcd. C, 65.32; H, 3.46; N, 12.03;found: C, 65.41; H,3.41; N, 12.00.

2,5-bis(4-(6-(4-chlorophenyl)-2-hydroxypyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ15). Yeild86%,mp97-99C°;IR (KBr pellet, cm⁻¹):U(C=Oquinone) 1635.59, U(C-N) 1273.51, U(C= N) 1573.34, U(C= C) 1600.71, U(C- H_{aromatic}) 3054.83, , U(NH) 3443.76, U(C-Cl) 1101.98, U(O-H) 3342.24;¹ H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1')) ; 2.301(br. S, 2H -NH);6.692-6.672 d, J =8

Hz,4 H –C(3,3',3",3''')]; 7.526-7.506 [d, $J = 8$ Hz,4 H –C(4,4',4",4''')]; 7.987-7.956 [d, $J = 12.4$ Hz,4 H –C(5,5',5",5''')]; 7.558-7.527 [d, $J = 12.4$ Hz,4 H –C(6,6',6",6''')]; 7.632 [S, 2H –C(7,7')]; 11.337 [S,2H –O(8,8')]; ¹³C- NMR(CDCl₃) δ : 181.06 [C(1) , C(1')] ; 101.30 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 128.41-128.39 [C(6) , C(6')] ; 125.69 [C(7) , C(7')] ; 162.35 [C(8) , C(8')] ; 93.27 [C(9) , C(9')] ; 155.32 [C(10) , C(10')] ; 160.39 [C(11) , C(11')] ; 133.19 [C(12) , C(12')] ; 129.31-129.30 [C(13) , C(13')] ; 129.33-129.32 [C(14) , C(14')] ; 135.14 [C(15) , C(15')]; Anal. (%) for C₃₈H₂₄Cl₂N₆O₄ Calcd . C, 65.24; H, 3.46; N, 12.01; found: C, 65.23; H, 3.51; N, 11.98.

2,5-bis(4-(6-(4-chlorophenyl)-2-mercaptopyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-

dione(AQ16). Yeild 81% ,mp.176-177C° ,IR (KBr pellet, cm⁻¹):U(C=O_{quinone}) 1635.74, U(C-N) 1285.62, U(C= N) 1596.95, U(C= C) 1606.59, U(C- H_{aromatic}) 3066.43, , U(NH) 3357.84, U(S-H) 2553.58,U(C-Cl) 1108.34.. ¹H NMR(CDCl₃) δ : 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S , 2H –NH);6.692-6.672 d, $J = 8$ Hz,4 H –C(3,3',3",3''')]; 7.526-7.506 [d, $J = 8$ Hz,4 H –C(4,4',4",4''')];7.987-7.956 [d, $J = 12.4$ Hz,4 H –C(5,5',5",5''')];7.558-7.527[d, $J = 12.4$ Hz,4 H –C(6,6',6",6''')]; 8.158 [S, 2H –C(7,7')];12.187 [S,2H –S(8,8')]; ¹³C- NMR(CDCl₃) δ : 181.09 [C(1) , C(1')] ; 101.33 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 128.41-128.39 [C(6) , C(6')] ; 125.63 [C(7) , C(7')] ; 167.98 [C(8) , C(8')] ; 109.37 [C(9) , C(9')] ; 164.94 [C(10) , C(10')] ; 181.06 [C(11) , C(11')] ; 133.19 [C(12) , C(12')] ; 129.31-129.30 [C(13) , C(13')] ; 129.33-129.32 [C(14) , C(14')] ; 135.14 [C(15) , C(15')]; Anal.(%) for C₃₈H₂₄Cl₂N₆O₂S₂ ,Calcd. C, 62.38; H, 3.31; N, 11.49; found: . C, 65.23; H, 3.28; N, 11.52.

2,5-bis(4-(6-(4-bromophenyl)-2-hydroxypyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-

dione(AQ17).Yeild 91% ,mp.98-100C° ,IR (KBr pellet, cm⁻¹):U(C=O_{quinone}) 1631.55, U(C-N) 1284.50, U(C= N) 1591.54, U(C= C) 1600.13, U(C- H_{aromatic}) 3054.87, , U(NH) 3447.73, U(CBr) 1025.91, U(O-H) 3464.27; ¹H NMR(CDCl₃) δ : 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S , 2H –NH);7.294-7.268 d, $J = 10.4$ Hz,4 H –C(3,3',3",3''')]; 7.598-7.572[d, $J = 10.4$ Hz,4 H –C(4,4',4",4''')];7.692-7.656 [d, $J = 14.4$ Hz,4 H –C(5,5',5",5''')];7.647-7.6612[d, $J = 14.0$ Hz,4H–C(6,6',6",6''')];7.598 [S, 2H –C(7,7')];11.626 [S,2H –O(8,8')]; ¹³C- NMR(CDCl₃) δ : 181.06 [C(1) , C(1')] ; 101.34 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 93.27 [C(9) , C(9')] ; 155.32 [C(10) , C(10')] ; 160.39 [C(11) , C(11')] ; 134.11 [C(12) , C(12')] ; 129.32-129.31 [C(13) , C(13')] ; 133.54-133.52 [C(14) , C(14')] ; 123.34 [C(15) , C(15')] ; Anal.(%) for C₃₈H₂₄Br₂N₆O₄ ,Calcd.C, 57.89; H, 3.07; N, 10.66; found: C,57.92; H, 3.13; N,10.60.

2,5-bis(4-(6-(4-bromophenyl)-2-mercaptopyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-

dione(AQ18). Yeild 85% ,mp.142-144C° .IR (KBr pellet, cm⁻¹):U(C=O_{quinone}) 1631.61, U(C-N) 1280.65, U(C= N) 1591.72, U(C= C) 1606.59, U(C- H_{aromatic}) 3069.01, , U(NH) 3352.88, U(S-H) 2553.55,U(C-Br) 1091.12. ¹H NMR(CDCl₃) δ : 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S , 2H –NH);7.294-7.268 d, $J = 10.4$ Hz,4 H –C(3,3',3",3''')]; 7.598-7.572 [d, $J = 10.4$ Hz,4 H –C(4,4',4",4''')];7.692-7.656 [d, $J = 14.4$ Hz,4 H –C(5,5',5",5''')];7.647-7.6612[d, $J = 14.0$ Hz,4 H –C(6,6',6",6''')]; 8.402 [S, 2H –C(7,7')];12.124 [S,2H –S(8,8')]; ¹³C- NMR δ : 181.09 [C(1) , C(1')] ; 101.18 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 128.91-128.90 [C(6) , C(6')] ; 125.54 [C(7) , C(7')] ; 169.50 [C(8) , C(8')] ; 109.37 [C(9) , C(9')] ; 165.38 [C(10) , C(10')] ; 181.06[C(11) , C(11')] ; 134.11 [C(12) , C(12')] ; 129.32-129.31 [C(13) , C(13')] ; 133.54-133.52 [C(14) , C(14')] ; 123.34 [C(15) , C(15')] ; Anal. (%) for C₃₈H₂₄Br₂N₆O₂S₂ ,Calcd. C, 55.62; H, 2.95; N, 10.24; found: C, 55.65; H, 3.01; N, 10.22.

2,5-bis(4-(2-mercapto-6-(4-nitrophenyl)pyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-

dione(AQ19). Yeild 93% ,mp.111-113C° ,IR (KBr pellet, cm⁻¹):U(C=O_{quinone}) 1639.52, U(C-N) 1290.29, U(C= N) 1591.16, U(C= C) 1600.38, U(C- H_{aromatic}) 3070.46, , U(NH) 3483.20, 3384.84 U(S-H) 2228.62, 1091.12; ¹H NMR(CDCl₃) δ : 4.23(S,4H –NH₂) ; 6.306-6.6332(S,2H –C(1,1')) ; 2.301(br. S , 2H –NH);6.722-6.700 d, $J = 8.8$ Hz,4 H –C(3,3',3",3''')]; 7.519-7.497 [d, $J = 8.8$ Hz,4 H –C(4,4',4",4''')];8.043-8.004 [d, $J = 15.6$ Hz,4 H –C(5,5',5",5''')];8.237-8.198[d, $J = 15.6$ Hz,4 H –C(6,6',6",6''')];8.543 [S, 2H –C(7,7')];12.340[S,2H –S(8,8')]; ¹³C- NMR δ (CDCl₃) : 181.06 [C(1) , C(1')] ; 101.37 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.35-129.33 [C(6) , C(6')] ; 125.34 [C(7) , C(7')] ; 165.65 [C(8) , C(8')] ; 109.87 [C(9) , C(9')] ; 164.62 [C(10) , C(10')] ; 181.03C(11) , C(11')] ; 141.12 [C(12) , C(12')] ;

126.51-126.50 [C(13) , C(13')] ; 124.34--124.30 [C(14) , C(14')] ; 149.64 [C(15) , C(15')];Anal.(%) for $C_{38}H_{24}N_8O_6S_2$,Calcd. C, 63.33; H, 3.36; N: 15.55;found : C, 63.35; H, 3.26; N: 15.51.

2,5-bis(4-(2-hydroxy-6-(4-nitrophenyl)pyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ20) . Yeild 88% ,mp.148-151C°,IR (KBr pellet, cm^{-1}):U(C=O_{quinone}) 1638.74, U(C-N) 1292.22, U(C= N) 1544.88, U(C= C) 1600.81, U(C- H_{aromatic}) 3056.40, , U(NH) 3378.05, 3234.40, U(O-H) 2360.71; ¹H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1') ; 2.301(br. S , 2H -NH);6.722-6.700 d, J =8.8 Hz,4 H -C(3,3',3'',3''')] ;7.519-7.497 [d, J =8.8 Hz,4 H -C(4,4',4'',4''')];8.043-8.004 [d, J = 15.6 Hz,4 H -C(5,5',5'',5''')];8.237-8.198[d, J =15.6Hz,4 H -C(6,6',6'',6''')];8.543 [S, 2H -C(7,7')];11.340[S,2H -O(8,8')];¹³C-NMR(CDCl₃) δ : 181.8 [C(1) , C(1')] ; 101.37 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.35-129.33 [C(6) , C(6')] ; 125.34 [C(7) , C(7')] ; 162.35 [C(8) , C(8')] ; 93.27 [C(9) , C(9')] ; 155.32 [C(10) , C(10')] ; 160.39C(11) , C(11')] ; 141.12 [C(12) , C(12')] ; 126.51-126.50 [C(13) , C(13')] ; 124.34--124.30 [C(14) , C(14')] ; 149.64 [C(15) , C(15')] ;Anal. (%) for $C_{38}H_{24}N_8O_8$,Calcd.C, 60.63; H, 3.21; N, 14.89;found: C,60.53; H, 3.22; N, 14.88.

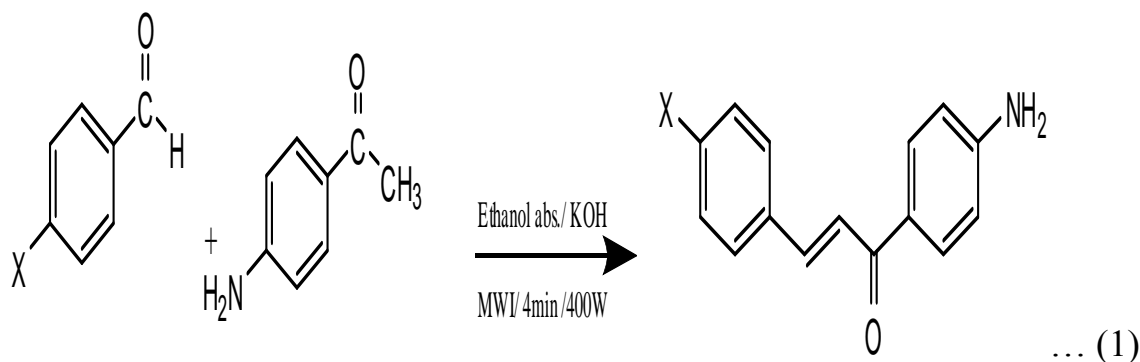
2,5-bis(4-(2-hydroxy-6-p-tolylpyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione: (AQ21). Yeild 79% ,mp187-189C°,IR (KBr pellet, cm^{-1}):U(C=O_{quinone}) 1627.81, U(C-N) 1290.22, U(C= N) 1569.92, U(C= C) 1595.02, U(C- H_{aromatic}) 3026.11, U(C- H_{aliphatic}) 2910.30, 2852.57, U(NH) 3440.77, 3234.40, U(O-H) 3461.27;¹H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1') ; 2.301(br. S , 2H -NH);6.722-6.700 d, J =8.8 Hz,4 H -C(3,3',3'',3''')] ;7.512-7.7.492 [d, J =8 Hz,4 H -C(4,4',4'',4''')];7.671-7.632 [d, J =15.6 Hz,4 H -C(5,5',5'',5''')];7.294-7.255[d, J =15.6 Hz,4 H -C(6,6',6'',6''')];7.671 [S, 2H -C(7,7')];11.342[S,2H -O(8,8')]; 2.337[S,3H-C(10,10')]; ¹³C- NMR(CDCl₃) δ : 181.06 [C(1) , C(1')] ; 101.37 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.35-129.33 [C(6) , C(6')] ; 125.51 [C(7) , C(7')] ; 162.35 [C(8) , C(8')] ; 93.27 [C(9) , C(9')] ; 155.32 [C(10) , C(10')] ; 160.39C(11) , C(11')] ; 131.11 [C(12) , C(12')] ; 123.01-123.00 [C(13) , C(13')] ; 129.32-129.31 [C(14) , C(14')] ; 132.54 [C(15) , C(15')] ; 23.87[C(16) , C(16')];Anal. (%) for $C_{40}H_{30}N_6O_4$,Calcd. C, 72.94; H, 4.59; N, 12.76;found: C,72.96; H, 4.52; N, 12.79.

2,5-bis(4-(2-mercapto-6-p-tolylpyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ22) Yeild 92% ,mp.(173-175), IR (KBr pellet, cm^{-1}):U(C=O_{quinone}) 1625.88, U(C-N) 1292.22, U(C= N) 1544.88, U(C= C) 1600.81, U(C- H_{aromatic}) 3019.05, U(C- H_{aliphatic}) 2911.42, 2867.09, U(NH) 3461.99, 3344.34 U(S-H) 2360.71; ¹H NMR(CDCl₃) δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1') ; 2.301(br. S , 2H -NH);6.722-6.700 d, J =8.8Hz,4 H -C(3,3',3'',3''')] ;7.512-7.7.492 [d, J =8 Hz,4 H -C(4,4',4'',4''')];7.671-7.632 [d, J = 15.6 Hz,4 H -C(5,5',5'',5''')];7.294-7.255[d, J =15.6 Hz,4 H -C(6,6',6'',6''')];8.181 [S, 2H -C(7,7')];12.184[S,2H -S(8,8')]; 2.337[S,3H-C(10,10')]; ¹³C- NMR(CDCl₃) δ : 181.60 [C(1) , C(1')] ; 101.01 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.35-129.33 [C(6) , C(6')] ; 125.51 [C(7) , C(7')] ; 165.36 [C(8) , C(8')] ; 109.37 [C(9) , C(9')] ; 165.32 [C(10) , C(10')] ; 181.5C(11) , C(11')] ; 132.54 [C(12) , C(12')] ; 123.01-123.00 [C(13) , C(13')] ; 129.32-129.31 [C(14) , C(14')] ; 131.11 [C(15) , C(15')] ; 23.87[C(16) , C(16')];Anal.(%) for $C_{40}H_{30}N_6O_2S_2$,Calcd. C, 69.54; H, 4.38; N, 12.17;found: C,69.56; H, 4.30; N, 12.19.

2,5-bis(4-(2-hydroxy-6-(4-hydroxyphenyl)pyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ23) .Yeild 95% ,mp.129-131C°,IR (KBr pellet, cm^{-1}):U(C=O_{quinone}) 1630.67, U(C-N) 1290.35, U(C= N) 1511.06, U(C= C) 16006.81, U(C- H_{aromatic}) 3013.72, , U(NH) 3340.88, 3217.93, U(O-H) Me.Wi NH₂ . ¹H NMR δ : 4.23(S,4H -NH₂) ; 6.306-6.6332(S,2H -C(1,1') ; 2.301(br. S , 2H -NH);6.722-6.700 d, J = Hz,4 H -C(3,3',3'',3''')] ;7.503-7.481 [d, J = Hz,4 H -C(4,4',4'',4''')];7.416-7.378 [d, J = Hz,4 H -C(5,5',5'',5''')];6.843-6.804 [d, J = Hz,4 H -C(6,6',6'',6''')];7.615 [S, 2H -C(7,7')];11.339[S,2H -O(8,8')]; 9.386[S,2H-O(10,10')];¹³C- NMR (CDCl₃) δ : 181.60 [C(1) , C(1')] ; 109.37 [C(2) , C(2')] ; 152.31 [C(3) , C(3')] ; 142.20 [C(4) , C(4')] ; 114.48-114.50 [C(5) , C(5')] ; 129.35-129.33 [C(6) , C(6')] ; 125.51 [C(7) , C(7')] ; 162.35 [C(8) , C(8')] ; 93.27 [C(9) , C(9')] ; 155.32 [C(10) , C(10')] ; 160.39C(11) , C(11')] ; 128.74 [C(12) , C(12')] ; 128.42-128.40 [C(13) , C(13')] ; 116.39-116.38 [C(14) , C(14')] ; 158.36 [C(15) , C(15')];Anal.(%) for $C_{38}H_{26}N_6O_6$ Calcd.C: 68.88; H, 3.95; N, 12.68;found: 68.78; H, 3.95; N, 12.77.

2,5-bis(4-(6-(4-hydroxyphenyl)-2-mercaptopyrimidin-4-yl)phenylamino)cyclohexa-2,5-diene-1,4-dione(AQ24). Yield 92%, mp. 164-166°C. IR (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{O}_{\text{quinone}})$ 1630.19, $\nu(\text{C}-\text{N})$ 1290.29, $\nu(\text{C}=\text{N})$ 1571.88, $\nu(\text{C}=\text{C})$ 1595.02, $\nu(\text{C}-\text{H}_{\text{aromatic}})$ 3004.95, $\nu(\text{C}-\text{H}_{\text{aliphatic}})$ 2911.42, 2867.09, $\nu(\text{NH})$ 3340.48, 3213.19, $\nu(\text{S}-\text{H})$ 2601.79 $\nu(\text{O}-\text{H})$ Me.Wi NH_2 ; $^1\text{H NMR}$ (CDCl_3) δ : 4.23 (s, 4H $-\text{NH}_2$); 6.306-6.6332 (s, 2H $-\text{C}(1,1')$); 2.301 (br. s, 2H $-\text{NH}$); 6.722-6.700 d, $J=8.8$ Hz, 4H $-\text{C}(3,3',3'',3''')$]; 7.503-7.481 [d, $J=8.8$ Hz, 4H $-\text{C}(4,4',4'',4''')$]; 7.416-7.378 [d, $J=15.2$ Hz, 4H $-\text{C}(5,5',5'',5''')$]; 6.843-6.804 [d, $J=15.6$ Hz, 4H $-\text{C}(6,6',6'',6''')$]; 8.435 [s, 2H $-\text{C}(7,7')$]; 12.339 [s, 2H $-\text{O}(8,8')$]; 9.386 [s, 2H $-\text{O}(10,10')$]; $^{13}\text{C-NMR}$ (CDCl_3) δ : 181.62 [C(1), C(1')]; 101.08 [C(2), C(2')]; 152.31 [C(3), C(3')]; 142.20 [C(4), C(4')]; 114.48-114.50 [C(5), C(5')]; 129.35-129.33 [C(6), C(6')]; 125.51 [C(7), C(7')]; 165.25 [C(8), C(8')]; 109.37 [C(9), C(9')]; 165.12 [C(10), C(10')]; 181.5 [C(11), C(11')]; 128.74 [C(12), C(12')]; 128.42-128.40 [C(13), C(13')]; 116.39-116.38 [C(14), C(14')]; 158.36 [C(15), C(15')]; Anal. (%) for $\text{C}_{38}\text{H}_{26}\text{N}_6\text{O}_4\text{S}_2$ Calcd. C, 65.69; H, 3.77; N, 12.10; found: C, 65.66; H, 3.70; N, 12.00.

A series of chalcones were prepared according to Claisen Schmidt condensation, of variously substituted aromatic aldehydes with Para amino acetophenone by using base catalyzed, under microwave irradiation to give corresponding chalcones. The reactions were monitored for its completion by TLC at 30 seconds intervals for (1-6) minutes depending on substituent's of benzaldehyde. The reaction is presented in equation 1.[17]

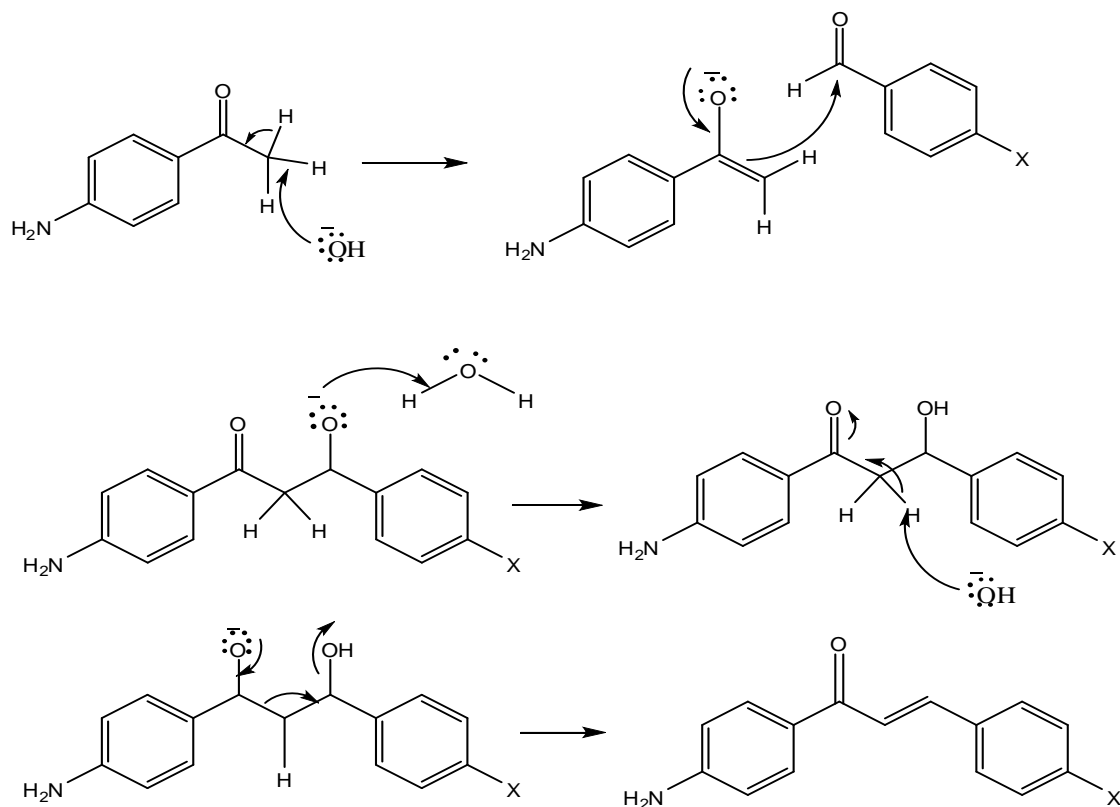


X: F, Cl, Br, NO_2 , OH, CH_3

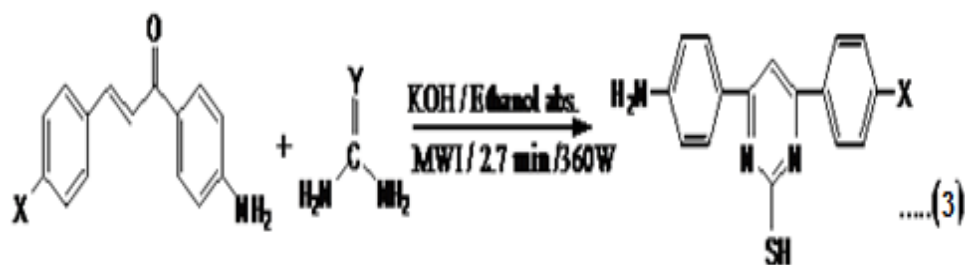
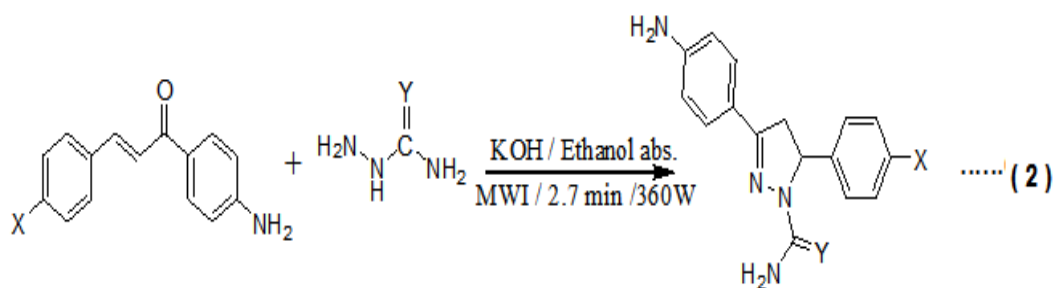
The synthesized chalcones showed different yields depending on the substituent groups as they were electron withdrawing group or electron donating group. Aldehydes with electron donating groups led to increasing the electron density on the carbon atom of carbonyl group, resulting in enhancing their electronic properties which subsequently decreasing the yield of the products. In contrast those with electron withdrawing groups resulted in increasing the yield as the electron densities on carbon atom of carbonyl were decreased.

The mechanism of reaction can be explained in scheme (1) which showed the nucleophilic attack of enolate anion at carbon atom of carbonyl related to benzaldehyde with elimination of water at end of reaction.

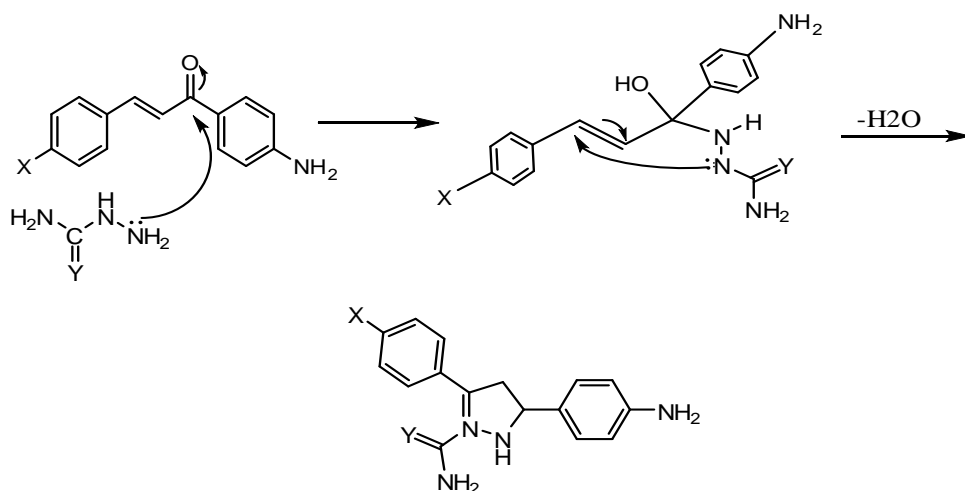
Then these chalcones were mixed with (semicarbazide, thiosemicarbazide, urea, thiourea) respectively with equal molar in presence of KOH, the mixture dissolved in absolute ethanol and irradiated in microwave as shown in equation (2). It was found that the yield of products related to the ability of substituent group on drawing electrons.



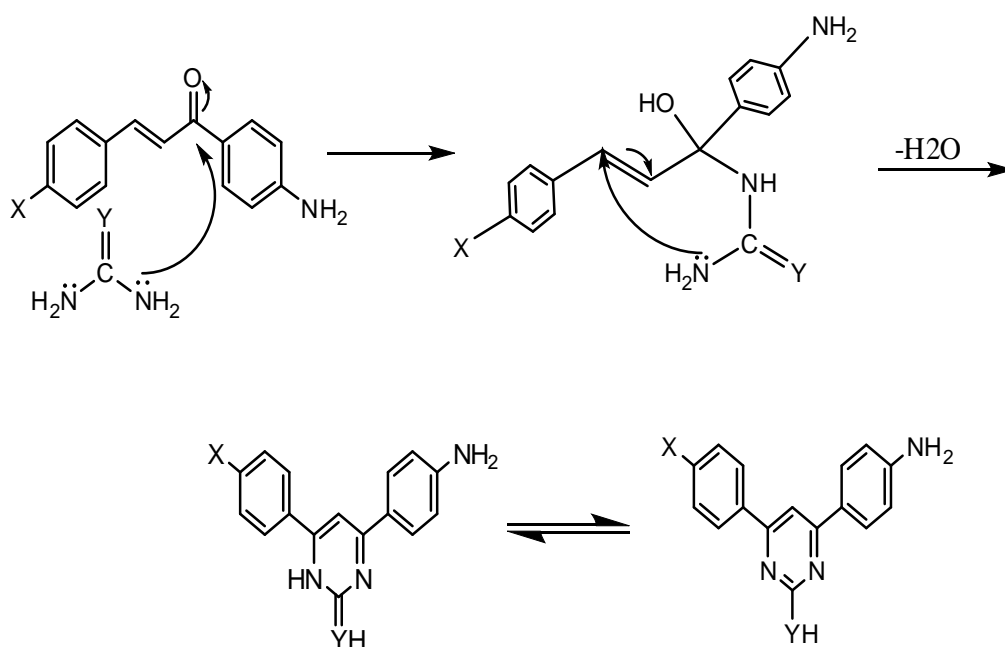
Scheme (1): mechanism of chalcone synthesis



The mechanism of reactions [18], [19] can be explained by means of nucleophilic attack of amino group related to (semicarbazide, thiosemicarbazide) followed by cyclization, as described in scheme 2,3 respectively :

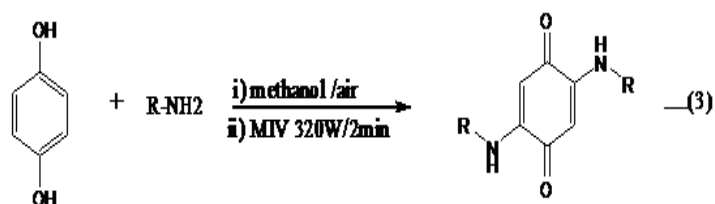


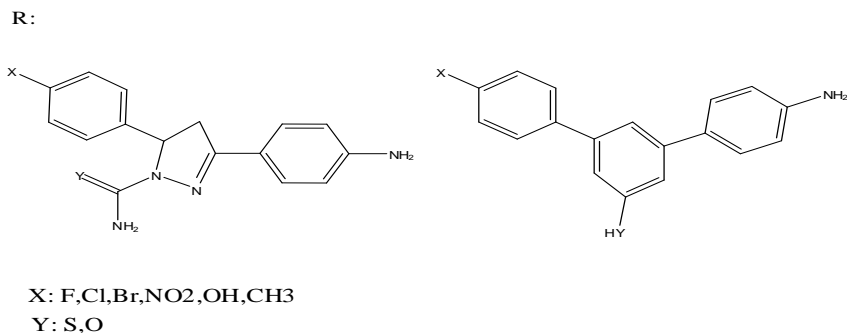
Scheme (2): mechanism of pyrazole synthesis



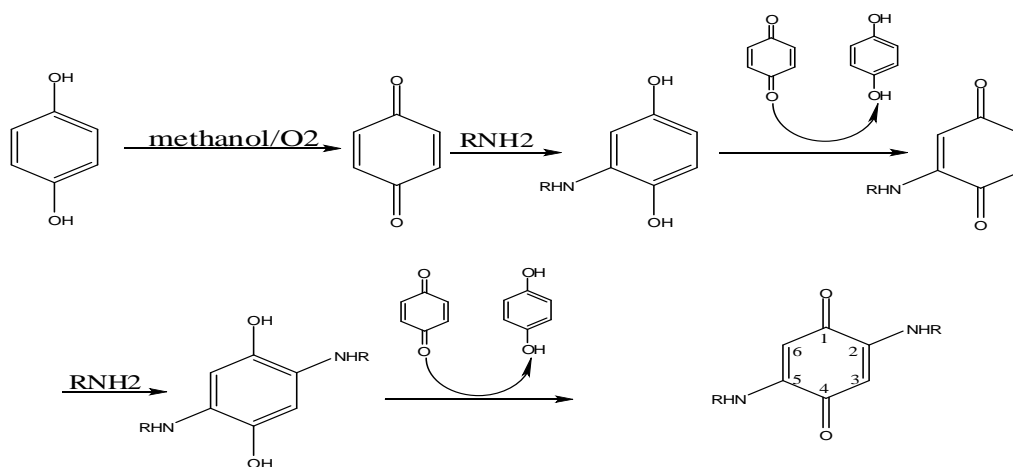
Scheme (3)

To synthesis 2,5-bis aminoquinone deritvetives, (10ml) Methanol solution of amine (hetrocyclic series)(2.3 mmole) was added to methanol solution (10 ml) of hydroquinones (0.05 mmole).This mixture was irradiated at (320w) for two minutes .the solution was evaporated in room temperature then product was purified by recrystalization from methanol to obtain long crystals with different colors (red, orange, yellow) .As displayed in equation(3)



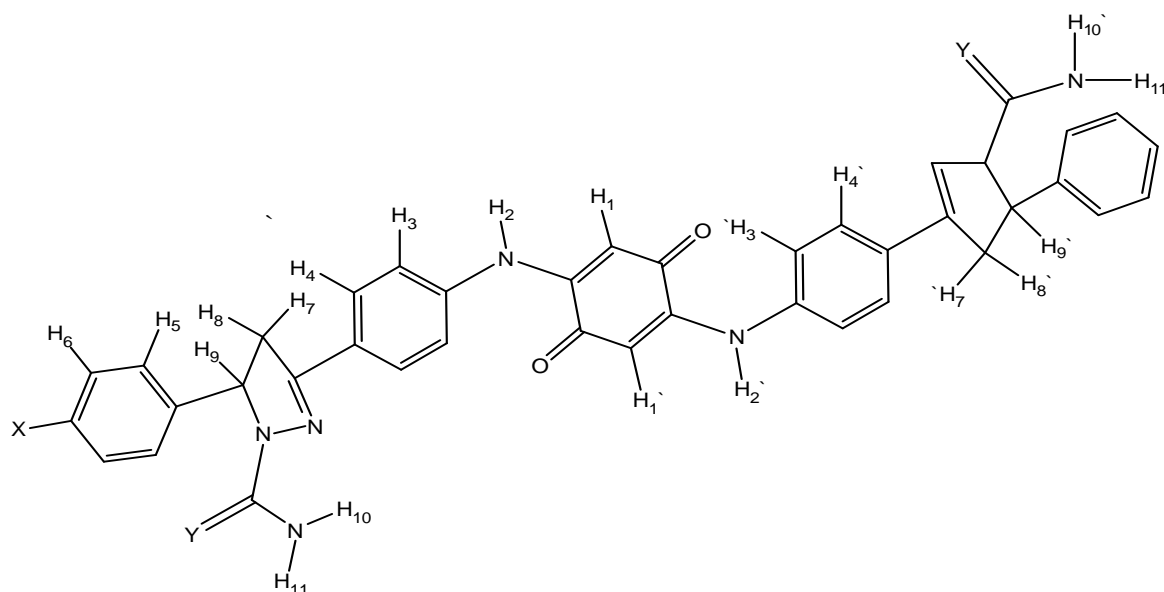


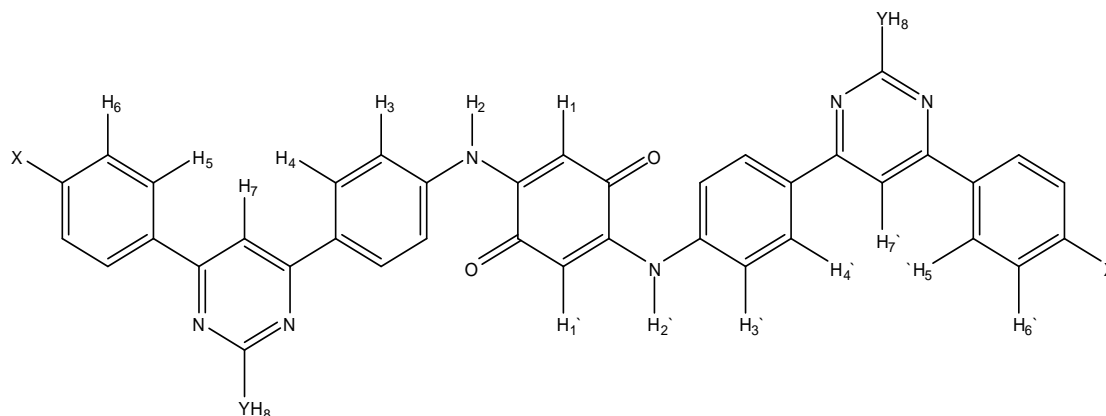
Mechanism of reaction [19] can be explained by nucleophilic attack of amino group according to 1, 4- addition (Michael addition) or conjugate addition.as illustrated in scheme (3).



Scheme (3): mechanism of 2,5Diaaminoquinone derivative synthesis

The structure of final products can be illustrated in the following structures:



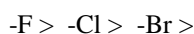


X: -F, -Cl, -Br, -NO₂, -OH, -CH₃. Y: OH, SH

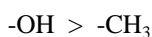
The purity of compounds was determined by TLC and elemental analysis. Spectral data (IR, ¹H NMR, ¹³C NMR) of all the newly synthesized compounds were in full agreement with proposed structures.

The infrared of all aminoquinone derivatives have common strong to medium absorption in the region (1637-1641cm⁻¹) due to the (C=O) stretching which they were characteristic to quinone moiety. Peaks with variable intensity appeared in the range (3100-3050 cm⁻¹) were accounted to aromatic stretching vibration while weak bands were observed in the range (2856-2928cm⁻¹) related to (C-H), (CH₂), (CH₃) groups. Stretching of primary and secondary amine as well as alcoholic groups bands were appeared in the range (3310-3485 cm⁻¹). Two strong peaks indicate aromatic double bond (C=C) stretching (1600-1590 cm⁻¹) and (1471-1479 cm⁻¹).

It was found from spectra that carbonyl group absorption correlated with the electronic properties of substituent whether it was electron withdrawing groups or electron donating groups, as described in the following arrangement:



Their absorption were: (163.59 cm⁻¹), (1635.74 cm⁻¹), (1631.67 cm⁻¹) respectively.



Their absorption were (1630.67 cm⁻¹), (1627.81 cm⁻¹) respectively.

In the region (1220 cm⁻¹), (1109cm⁻¹), (1092cm⁻¹) strong peaks appeared related to stretching of (C-F), (C-Cl), (C-Br) respectively.

¹H NMR of all spectra displayed strong singlet peak at (6.332-6.300) ppm and medium singlet peak at (4.203-4.187) ppm related to quinonoid protons (H₁, H_{1'}) and secondary amine protons (H₂, H_{2'}) respectively.

Multiple peaks appeared at the region (3.709-4.121) ppm related to heterocyclic protons (H₇, H₈, H₉) in the compounds (AQ1- AQ12). Singlet broad peak appeared at (2.301) ppm due to primary amine protons (H₁₀, H₁₁) in the compounds (AQ1- AQ6) but the same peak shifted to lower magnetic field (4.752) ppm. The aromatic system classified into two groups A and B. Protons of B ring (H₅, H₆) showed AX system in all compounds while protons of A ring showed both AX and AB system depending on the substituent's on para position.

Ratio of chemical shift differences to coupling constant was calculated, and found to be smaller than 10 for the compounds (AQ1, AQ2, AQ5, AQ7, AQ8, AQ11, AQ17, AQ18) which indicates AB system for these compounds while others displayed AX system since value of () more than 10. ¹³C NMR related to All spectra showed peaks at (181.8-181.06), (109.37-101.18), (152.31), (142.20), (114.48-114.50), (129.32-129.31) - (128.41-128.39), (125.69) related to carbon (C₁, C₂, C₃, C₄, C₅, C₆, C₇) respectively.

It was observed that chemical shift for C₁₂ decreased by the presence of electron withdrawing groups in para position.[20]-[24].

Conclusion

The 2,5-Bis(heteroamino)-1,4-benzoquinone derivatives, were synthesized successfully throughout aerobic oxidation of hydroquinone followed by conjugate addition of primary amine according to Michael addition protocol under microwave irradiation. All spectral data improved the full agreement of the chemical structure for synthesized compounds.

References List

- [1] N. Chairungsi, K. Jumpatong, P. Suebsakwong, W Sengpracha, W. Phutdhawong, and D. Buddhasukh. 2006. Electrocoagulation of Quinone Pigments Molecules. 11, 514-522.
- [2] I. Abraham, R.Joshi, P. Pardasani and R.T. Pardasani. 2011. Recent advances in 1,4-benzoquinone Chemistry. J. Braz. Chem. Soc., vol.22(3):385-421.
- [3] B.M. Mabla. 2011. Synthesis of Quinone Natural Product and Analogues. PhD Dissertation, College of Science, Universiteit Gent. Belgium.
- [4] R. OJANI, J.B. RAOOF, R. H.ZADEH and A. ALINEZHAD. 2008. Electrochemical Oxidation of Catechol in the Presence of Dimethyl Chloromalonate and its Digital Simulation. Asian Journal of Chemistry Vol. 20(8): 5863-5872.
- [5] B. Sun, J. Hoshino, K. Jermihovc, L. Marlerb, J. M. Pezzutob, Andrew D. Mesecarc, and M. Cushmana. 2010. Design, Synthesis, and Biological Evaluation of Resveratrol Analogues as Aromatase and Quinone Reductase 2 Inhibitors for Chemoprevention of Cancer. Bioorg Med Chem. 18(14): 5352–5366.
- [6] T. Mukherjee. 2000. Photo and Radiation Chemistry of Quinones. PINS, 66, A, no.:239-265.
- [7] A. Emadi, J.S. Harwood, S. Kohanim, K.W. Stagliano. 2002. Regio controlled synthesis of the trimeric quinone framework of concurvone. Org Lett. 21;4(4):521-4.
- [8] J. Koyama. 2006. Anti-Infective Quinone Derivatives of Recent Patents. Recent Patents on Anti-Infective Drug Discovery, 1, 113-125.
- [9] J. A. Valderrama, A. Ibacache, J. A. Rodriguez, C. Theoduloz, and J. Benites. 2011. Studies on quinones. Part 47. Synthesis of novel phenylaminophenanthridinequinones as potential antitumor agents. European Journal of Medicinal Chemistry 46,: 3398-3409.
- [10] F. C. C. Lam, A. N. Pearce, S. H. Tan, M. Kaiser and B. R. Copp. 2013. Discovery and Evaluation of Thiazinoquinones as Anti-Protozoal Agents Mar. Drugs, 11, 3472-3499.
- [11] A. Naeem, O. M. Alakloby, S.H. M. Aljabre, A. R. M. Alqurashi; M. A. Randhawa. 2007. Comparison of Antifungal Activity of Thymoquinone and Amphotericin B Against *Fusarium solani* in-vitro. Scientific Journal of King Faisal University (Basic and Applied Sciences) .Vol. 8 (2): 137-145.
- [12] S. Al-Jabre, OM Al-Akloby, A.R. Al-Qurashi, N. Akhtar, A. Al-Dossary, M.A.Randhawa. 2003. Thymoquinone, an active principle of *Nigella sativa*, inhibited *Aspergillus niger*. Pakistan J. Med. Res. Vol. 42 (3):1-4pages.
- [13] A. Salim, L. Zeenelabdin, S. Mohan, R. Othman, S. I. Abdelwahab B. Kamalidehghan, B. Y. Sheikh and M. Yousif Ibrahim. 2013. Thymoquinone Induced Mitochondria –Mediated Apoptosis in Acute Lymphoblastic Leukaemia in Vitro. Molecules, 18, 11219-11240.

- [14] M.B. Carriere. 1998. Synthesis and Reactions of Quinons with some possible biological applications. Msc. Thesis, College of Science, University of Waterloo, Ontario-Canda.
- [15] A. Ying, L. Wang, H. Deng, J.Chen, X. Chen, and W. Yeb. 2009. Green and efficient aza-Michael additions of aromatic amines to α,β -unsaturated ketones catalyzed by DBU based task-specific ionic liquids without solvent, ARKIVOC 288-298.
- [16] L. Huang.2010. STUDIES IN HETEROCYCLIC SYNTHESIS, dissertation, University of Florida, Chemistry, 166 pp.
- [17] S. Z. angade, S. Mokle, A Vibhute, Y Vibhute. 2011. An efficient and operationally simple synthesis of some new chalcones by using grinding technique, chemical sciences journal, vol: CSJ-13.
- [18] A. R. Trivedi, D.K. Dodiya, N. R. Ravat, and V. H. Shah 2008.synthesis and biological evaluation of some new pyrimines via a novel chalcone series, ARKIVOC:131-141.
- [19] L. C. A. Barbosa, U. A. Pereira, C.R.A. Maltha, R. R. Teixeira, V.M.M. Valente, J.R.O. Ferreira, L.V.C.Lotufo, M.O.Moraes and C.Pessoa.2010. Synthesis and Biological Evaluation of 2,5-Bis(alkylamino)-1,4-benzoquinones.Molecules 15:5629-5643.
- [20] Z.L. You, D.M.Xian, M. Zhang, X.S.Cheng, X.F.Li. 2012. Synthesis, biological evaluation, and molecular docking studies of 2,5-substituted-1,4-benzoquinone as novel urease inhibitors, Bioorganic & Medicinal Chemistry , 20:4889–4894.