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Synthesis, physicochemical probe and antimicrobial assay of bis-chalcone, pyrazole, amino-pyrimidine and malononitrile derivatives from five and six membered cyclic imides

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Abstract: Heterocyclic imides greately involves in the development of organic synthesis. Coloured flavonoids like bis-chalcones are formed by microwave assisted solvent free route using phenyl succinimide, glutarimide and vanilln. To achieve the pyrazole and amino-pyrimidine derivatives by the cyclization of bis-chalcone with hydrazine hydrate and guanidine nitrate via microwave method. Then dimalononitriles were produced by active methylene group of dinitrile with cyclic imides. Hence the physicodhemical properties and antimicrobial actions persisted by moderate to high potencies.

Keywords: Amino-pyrimidines, Bis-chalcones, Malononitriles, Phenyl glutarimide, Phenyl succinimide, Pyrazoles.

Introduction

Cyclic imides are familiarized with sulphur, oxygen and nitrogen heteroatom performs the vital role in the development of pharmaceutical, biochemical and agricultural extents. Heterocyclic imide shows good CNS and anti-depressive activities [1] as well as cyclic imides [2-3] like succinimides [4-5], maleimides [6], crotonimide-C [7] of glutarimide [8-10], itaconimide and isoindole 1, 3-dione [11] showed the defensive antibacterial, antifungal, anti-proliferative [12] anxiety inhibition and depression disorder [13] activities. Several number of succinimide derivatives showed the seedling growth promoter activities counter to wheat and radish [14].

Certain glutarimides are actively found on the metabolism of spinal neurons and brain [15], anti-muscarinic and nephrotoxic [16], antiviral [17], anticonvulsant [18], anti-mutagenic [19], analgesic [20] activities. The different substituted heterocyclic imides were prepared from cyclic anhydrides [21], baylis-hillmanadducts [22] and tandem process [23], formamide [24], trifluoro-acetylation [25], triethylamine [26], hydroxylamine [27] reagents and bis-heterocyclic derivatives [28] by microwave irradiated method. For the preparation of chalcones; cyclic imides were used as a starting material for further synthesis of heterocyclic entities [29-30]. The bis-chalcones are adaptable precursor of coloured flavonoids having -C=C- bridge between α-β-unsaturated carbonyl carbon and aromatic rings. They are prepared by the condensation of the ketone and aldehyde groups [31]. The chalcones are synthesized by using several types of synthetic routes like solid phase claisen-schemdit, cross-aldol condensation, acid catalyst [32] and microwave assisted methods [33-34]. Some of the chalcone are active against cell line, breast cancer [35] and also acts as antimicrobial agents [36]. The clalconecentered five membered pyrazoles [37] were prepared by the action of -NH_2-NH_2- or C_6H_5-NH_2-NH_2- in presence of sodium acetate [38], acetic

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acid [39] neutral Al_2O_3 [40] catalysts by microwave [41-42], grinding [43], solvent free [44], tandem [45] regio-selective [46] and conventional modes. In a view of the pyrazoline [47] derivatives they are reasonable antibacterial [48], antifungal [49] activities and vanillin based pyrazoline gives important anticancer activities [50]. Certain novel amino-pyrimidines [51], imido-pyrimidines [52], pyrido-pyrimidines [53] and chalcone mediated pyrimidines [54-55] were synthesized by conventional and microwave routes. Chalconecenteredpyrimidines [56] are prepared by guanidine [57], guanidine nitrate [58-59], guanidine hydrochloride [60], thiosemicarbazide [61] by using conventional and microwave assisted solvent free synthesis [62]. Many amino-pyrimidine derivatives showed the substantial antimicrobial [63], antioxidant [64], anticancer [65], analgesic [66] and anti-proliferative activities.

The synthesis of malononitrile groups furnished by knoevenagel condensation reaction utilizing active methylene groups [67] with substituted ketone, aldehydes, hetero-aromatic aldehydes or ketones or diones [68] and indole derivatives. Mostly these are synthesized by aqueous media [69], solvent free method [70], one pot [71], KOH or NaOH [72], ZnO [73] and NH_4COOCH_3 [74] and tamarind juice catalyst[75]. A number of malononitrile derivatives like cyanomethyl [76], cyanoacetanilides [77], benzopyranes [78], cyanohexylidenemalononitrile [79], carbonitriles [80] are simply prepared with active methylene group by conventional, grindstone method [81], solvent free one or multicomponent and microwave assisted solvent free [82] eco-friendly methods.

Result and Discussion

Physicochemical data

The physical properties like melting points, nature of appearance, yield and molecular features of synthesized derivatives note down in the Table **1**.

Table1: Physical data of the synthesized derivative **1a-10a.**

Entry	Molecular Formula	Molecular Weight	Yield (%)	Physical Appearance	Nature of Crystal	Melting Point (ºC)
1a	$C_{10}H_9NO_2$	175.06	79.91%	White	Needle	154-156 ºC
2a	$C_{11}H_{11}NO_2$	189.21	77.92%	White	Needle	120-122 ºC
3a	$C_{26}H_{21}NO_6$	443.45	84.56%	Yellowish	Needle	112-114 ºC
4a	$C_{27}H_{23}NO_6$	457.47	79.91%	Whitish Yellow	Amorphous	78-80 ºC
5a	$C_{26}H_{25}N_5O_4$	471.51	91.48%	Yellowish Mud	Flakes	172-174 ºC
6a	$C_{27}H_{27}N_5O_4$	485.53	82.57%	Brownish	Lumps	151-153 ºC
7a	$C_{28}H_{23}N_7O_4$	521.53	92.30%	Yellowish White	Granular	179-181 ºC
8a	$C_{29}H_{25}N_7O_4$	535.55	80.45%	Brownish Yellow	Granular	89-91 ºC
9a	$C_{16}H_9N_5$	271.28	55.55%	Coffee Colour	Fluffy	138-140 ºC
10a	$C_{17}H_{11}N_5$	285.30	61.40%	Coffee Colour	Needle	97-99 ºC

Note: *All the compounds are found in solid states*

Antimicrobial assay

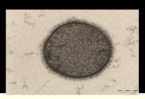
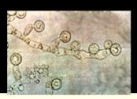
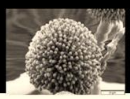
All the compounds were evaluated their antibacterial actions counter to the gram positive *Bacillus subtilis* (MCMB-310) and gram negative *Escherichia coli* (MCMB-301) bacterial strains *in-vitro*at the concentrations of 100µg/mL by bore plate method using DMF solvent. Ampicillin was used as standard drug for antibacterial activities. And *in-vitro* antifungal potency against *Candida albicans*(NICM-3471) and*Aspergillusniger*(NICM-545) fungal strains at the concentration 100µg/mL per disc employing the paper disc diffusion method using DMSO solvent. Amphotericin-B was used as standard drug for antifungal activities. Zone of inhibition measured by digital vernier caliper and readings are noted in the Table **2.**

Chemistry

Cyclic imides **1a**, **2a** were prepared by conventional routes. Thereby eco-friendly microwave assisted solvent-free methods with neutral corundum (Al_2O_3) catalyst were practiced for further derivatives. Bis-chalcones**3a**, **4a** derived from cyclic imides were prepared with vanillin and imides. Then pyrazoles **5a**,

6a synthesized by the cyclization of chalcones with hydrazine hydrate and amino-pyrimidine **7a**, **8a** persisted the cyclization with bis-chalcones and guanidine nitrate. The dimalononitriles**9a**, **10a** are afforded from cyclic imides. Physicochemical data and spectral anal of all the synthesized compounds were verified.

Table 2: Zone of inhibition calculated by Mean±SD method

Entry	Zone diameter in mm (100 µg/mL)			
	Bacillus Subtilis 	*Escherichia Coli* 	*Candida albicans* 	*Aspergillus niger* 
1a	…	…	9.63±0.23**	12.62±0.33*
2a	4.66±4.04****	4.66±4.04****	…	…
3a	8.33±0.57****	8.33±0.57****	11.94±0.09	…
4a	…	…	16.31±0.33****	16.46±0.27****
5a	7.33±0.57****	7.33±0.57****	…	…
6a	7.33±1.15****	7.33±1.15****	…	…
7a	6.66±0.57****	6.66±0.57****	11.48±0.10	…
8a	6.33±0.57****	6.33±0.57****	…	10.23±0.38
9a	7.33±0.57****	7.33±0.57****	13.83±0.05	…
10a	…	7.33±0.57****	…	…
Std	24.33±0.57	24.33±0.57	12.40 ± 0.43	10.45 ± 0.11
***Note: '…'** means no zone of inhibition*				

Statistical Analysis

Antimicrobial results of 1a-10a derivatives were calculated by Mean±SD by triplicate (N=3) method. Two ways ANOVA with Dunnett multiple comparison tests was performed by standard drugs against synthesized compounds. P value P<0.05 was considered as statistically significant which is represented by p<0.05=*, p<0.01=**, p<0.001=*** and p<0.0001**** practiced with standard drugs as shown in the Figure **1**.

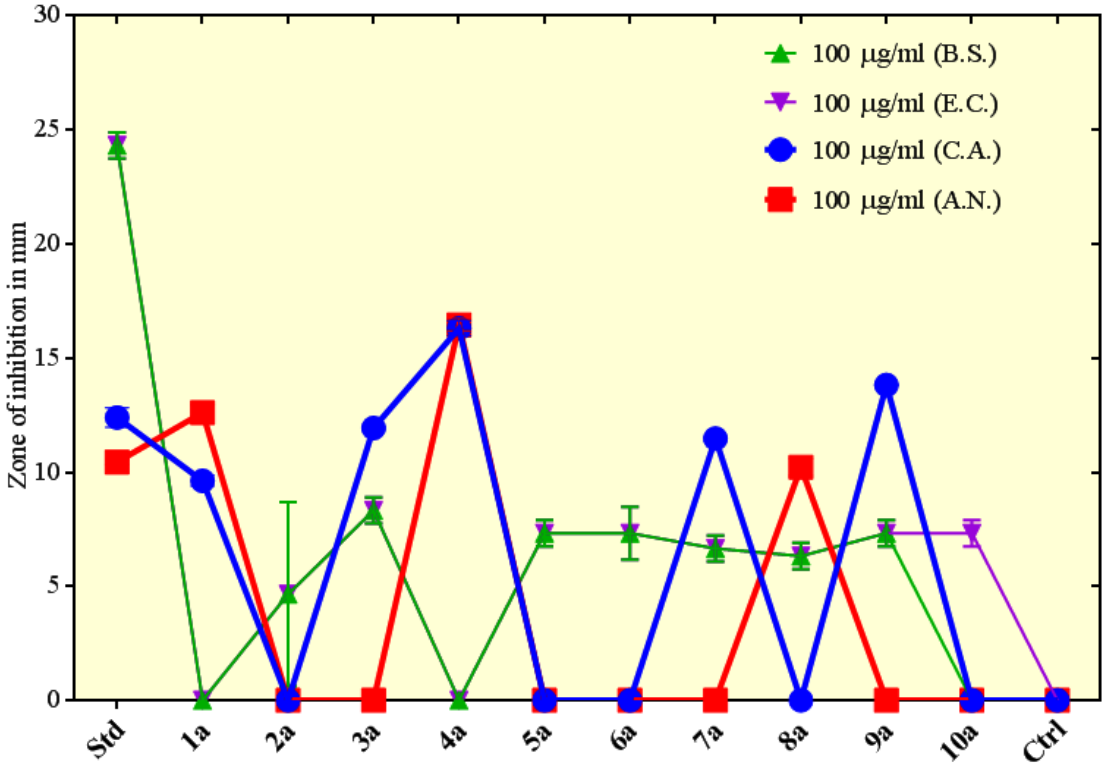
In the antibacterial frame of references, almost all the prepared derivatives are moderately active against gram positive Bacillus subtilis bacteria except **1a**, **4a**, **10a** and gram negative Escherichia colibacteria except **1a**, **4a** as compared to standard drug ampicillin. Prospectively the antifungal potencies, very few compounds **3a**, **4a**, **7a**, **9a** showed superior potency against Candida albicans and**1a**, **4a**, **8a** are very active against Aspergillusniger fungal strains.

Conclusions

At the end of the line, bis-chalcones, bi-pyrazoles, amino-pyrimidines and dimalononitriles derived from cyclic imides as a starting components were synthesized by eco-friendly microwave system. These derivatives are mildly active against bacterial strains. A few derivatives are highly potent against fungal species as compare with the standard drug except bi-pyrazoles. According to solvent free microwave route of the synthesis and antifungal efficacies, they might be used for different substituted heterocyclic, antioxidant and anticancer offshoots.

Experimental

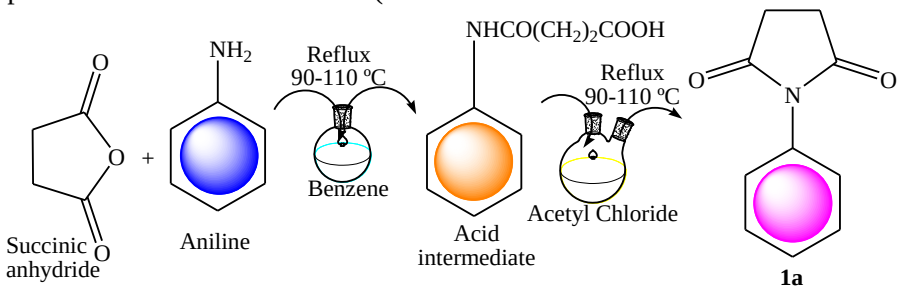
All the compounds were synthesized in hours from the commercially purchased aniline, succinic anhydride, glutaric anhydride, vanillin, guanidine nitrate, hydrazine hydrate, dicyanomethane, acetyl chloride, neutral alumina, benzene and ethanol. Melting points are ensured and note down by open-glass capillary and were uncorrected. IR spectra in KBr pallets were verified on Shimadzu-FTIR: 8400S and ATR Brucker alpha FTIR spectrophotometer. ^{1}H NMR spectra were recorded by 200.13 MHz, 300.06 MHz, and 500.13 MHz using Brucker spectrophotometer. The reaction was monitored by TLC and performed using pre-coated silica-gel aluminium sheets.



Graph 1: Antimicrobial Activities of 1a-10a (Mean±SD)

General procedure for the preparation of 1-Phenyl succinimide and glutarimide:

The mixture of benzene and 1mole succinic anhydride heated under reflux condition with constant stirring at 90-110 ºC for 15 to 20 minutes till the clear solution formed. Then 1mole of aniline with 5ml benzene was slowly poured into the solution constantly stirred for 15 to 20 minutes turns homogeneous solution. Upon evaporation of benzene the 3-(1-phenyl) propanoic acid intermediate was obtained. Thereafter the mixture of 3-(1-phenyl) propanoic acid refluxed with 9mole acetyl chloride by constant stirring at the same time and temperature with the complete liberation of HCl gas. Then the mixture was cooled at room temperature which accomplished the solid products 1-Phenyl succinimide or 1-phenylpyrrolidine-2, 5-dione (**1a**) as shown in the scheme **1.**



Scheme - 1: Synthesis of phenylpyrrolidine-2, 5-dione **(1a)**

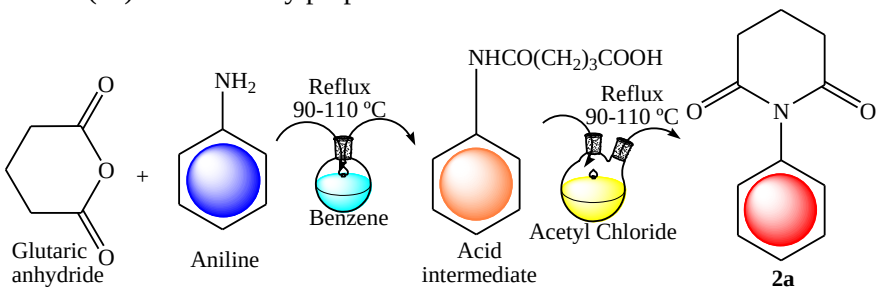
Same procedure was applied for the preparation of 1-Phenyl glutarimide; glutaric anhydride (1mole) was refluxed with aniline (1mole) which form 3-(1-phenyl) butanoic acid and then refluxed with acetyl chloride (9mole) by constant stirring at the similar time and temperature, the 1-phenylpiperidine-2, 6-dione (**2a**) solid product was obtained in the scheme **2.**

General procedure for the preparation of Bis-chalcones:

The bis-chalcones was synthesized by the mixture of 0.01mole of phenyl succinimide (1a) and 0.02mole of 4-hydroxy-3-methoxy-benzaldehyde or vanillin in 2 gm of neutral Al_2O_3 under microwave assisted solvent free conditions at 640W power for 5-8 minutes which

form coloured compound 3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-pyrrolidine-2,5-dione (**3a**) as shown in the reaction scheme **3**.

The 3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-piperidine-2,6-dione(4a) was similarly prepared by the mixture of 0.01mole of phenyl glutarimide **2a** and 0.02mole of vanillin in 2 gm of neutral Al_2O_3 under microwave on 640W powers for 3-6 minutes scheme **4**.



Scheme - 2: Synthesis of 1-phenylpiperidine-2, 6-dione **(2a)**

General procedure for the preparation of Pyrazoles:

The pyrazole derivatives were synthesized by the mixture of 0.02mole of 3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-pyrrolidine-2,5-dione **3a**and 0.04mole of hydrazine hydrate with 2 gm of neutral Al_2O_3 under microwave assisted solvent free conditions on 640 W power for 4-7 minutes. The afforded colored compound (3Z,4Z)-3,4-bis-(4-hydroxy-3-methoxy-benzylidene)-7-(1-phenyl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c,5,4-c] dipyrazole(**5a**) was recovered by ethyl acetate shown in scheme **5**.

Correspondingly the compound (3Z,4Z)-3,4-bis-(4-hydroxy-3-methoxy-benzylidene)-7-(1-phenyl)-3,3a,3b ,4,5,7-hexahydro-2H-piperidine- [2,3-c,5,4-c] dipyrazole(6a) was synthesized by 0.02mole of **3a** and 0.04mole of hydrazine hydrate with 2 gm of neutral Al_2O_3 under microwave on the same condition for 3-6 minutes represent in the scheme **6**.

General procedure for the preparation of Amino-pyrimidines:

Amino-pyrimidine derivatives were synthesized by the mixture of 0.02mole of afforded bis-chalcone**3a** and 0.04mole of guanidine nitrate with 2 gm of neutral Al_2O_3 under microwave assisted solvent free conditions on 640W power for 4-7 minutes. Whitish yellow 9-(1-phenyl)-4,5-(2",'"-methoxyphenol)-9H-1,3,6,8,9-penta-azo-fluorene-2,7-diamine (**7a)** product obtained in the scheme **7**.

Likewise the 9-(1-phenyl)-4,5-(2",'"-methoxyphenol)-9H-1,3,6,8,9-hexa-azo-fluorene-2,7-diamine (8a) derivative was synthesized by the mixture of 0.02mole of afforded bis-chalcone**4a** and 0.04mole of guanidine nitrate with neutral Al_2O_3 by solvent free microwave condition on same watt power and time as shown in the scheme **8**.

General procedure for the preparation of malononitriles:

Malononitrile derivatives were synthesized by eco-friendly system. The mixture of 0.02mole of afforded 1-phenyl succinimides **1a** and 0.04mole of dicyanomethane in 2 gm of neutral Al_2O_3 irradiated by microwave in solvent free state on 640W power for 4-7 minutes accomplished the 2,2'-(1-phenylpyrrolidine-2,5-diylidene) dimalononitrile (**9a**) in the scheme **9**.

By practicing same approach the 2,2'-(1-phenylpiperidine-2,6-diylidene)dimalononitrile (10a) derivative was synthesized by 0.02mole of afforded 1-phenyl glutarimides **2a** and 0.04mole of dicyanomethane in 2 gm of neutral Al_2O_3 by microwave supported solvent free state on same watt power and time as shown in the reaction scheme **10.**

Spectral analysis:

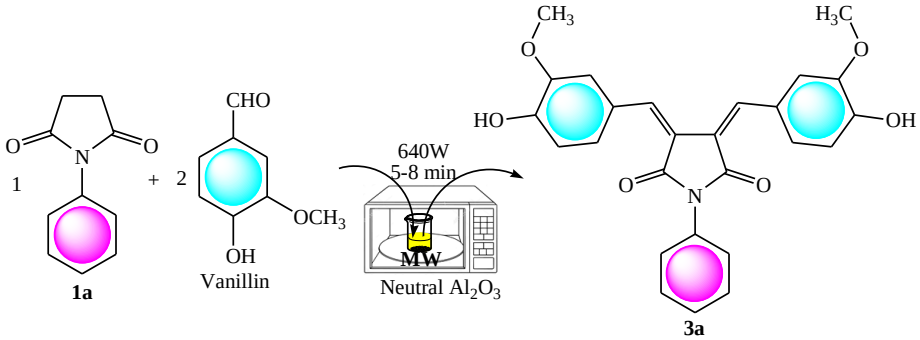
*1-phenylpyrrolidine-2, 5-dione **(1a):***

M.F.: $C_{10}H_9NO_2$, C,H,N Observed: C, 68.15; H, 4.10; N, 8.50, FTIR (KBr): >C=O (2-Peaks): 1708cm^{-1} and 1774cm^{-1}, cyclic CH_2-CH_2: 2937 cm^{-1}, cyclic imines 1291cm^{-1}, Ar (3-Peaks): 1457cm^{-1}, 1502cm^{-1} and 1595 cm^{-1}, ^{1}H NMR-(300.06 MHz, $CDCl_3$, δ ppm) : 7.45-7.25 (m, 4H, Ar-H), 2.92 (s, 4H, imide)

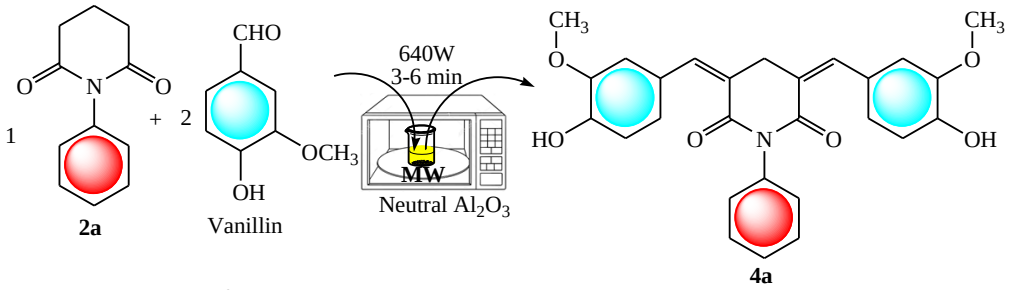
*1-phenylpiperidine-2, 6-dione **(2a):***

M.F.: $C_{11}H_{11}NO_2$, C,H,N Observed:C, 69.89; H, 5.46; N, 7.49, FTIR (ATR):>C=O (2-Peaks): 1694cm^{-1} and 1770cm^{-1}, cyclic CH_2-CH_2-CH_2: 2971cm^{-1}, cyclic imines 1314cm^{-1}, Ar (3-Peaks): 1499cm^{-1}, 1535cm^{-1} and 1598cm^{-1}, ^{1}H NMR-(300.06 MHz, $CDCl_3$, δ ppm)

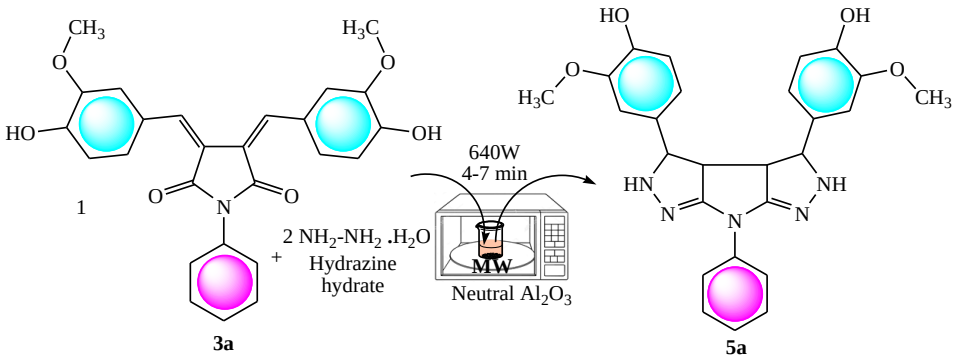
:7.92-7.33 (d, 4H, Ar-H), 1.80 (m, 2H, $–CH_2$-CH_2- CH_2–), 2.27 (t, 4H, imide).



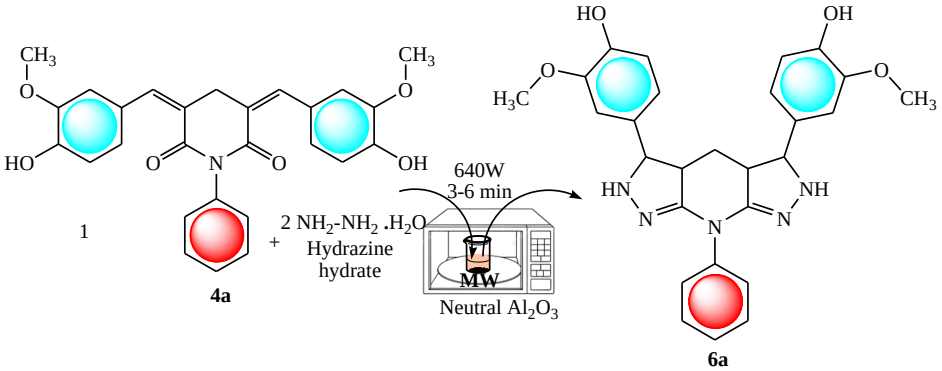
Scheme - 3: Synthesis of 3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-pyrrolidine-2,5-dione **(3a)**



Scheme - 4: Synthesis of 3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-piperidine-2,6-dione **(4a)**



Scheme - 5: Synthesis of (3Z,4Z)-3,4-bis-(4-hydroxy-3-methoxy-benzylidene)-7-(1-phenyl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo[2,3-c,5,4-c] dipyrazole **(5a)**

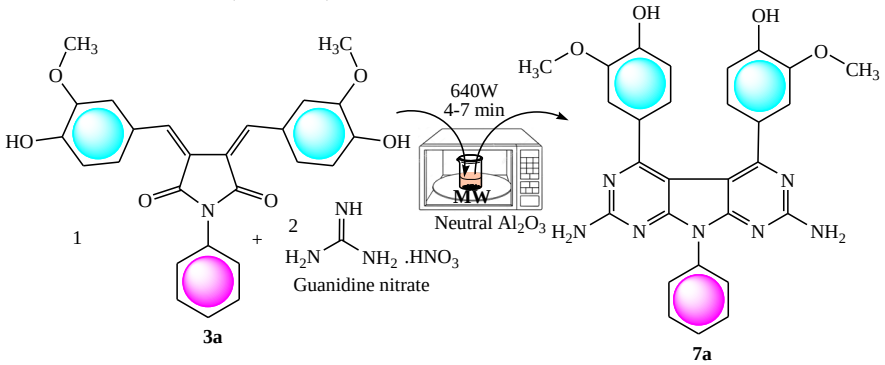


Scheme -6: Synthesis of (3Z,4Z)-3,4-bis-(4-hydroxy-3-methoxy-benzylidene)-7-(1-phenyl)-3,3a,3b,4,5,7-hexahydro-2H- piperidine-[2,3-c,5,4-c] dipyrazole **(6a)**

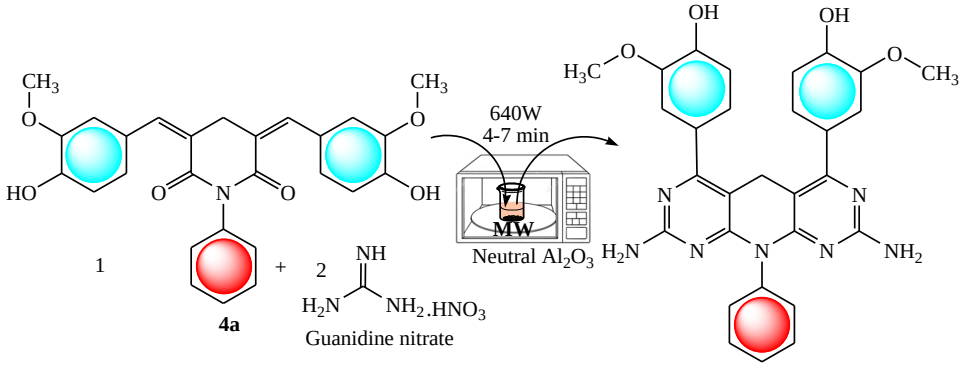
3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-pyrrolidine-2,5-dione(3a):

M.F.: $C_{26}H_{21}NO_6$, C,H,N Observed: C, 69.85; H, 4.50; N, 3.34, FTIR (KBr) : >C=O (2-Peaks): 1661cm^{-1} and 1700cm^{-1}, =C-H : 3000cm^{-1}, Ar (3-Peaks): 1453cm^{-1}, 1501cm^{-1} and 1590cm^{-1}, Ar-OCH_3: 1296cm^{-}

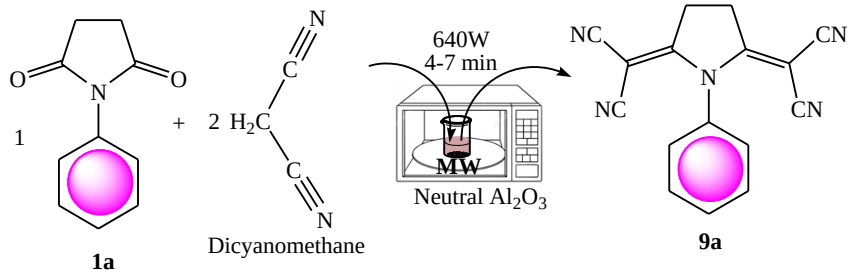
[1], Ar-OH: 3400cm^{-1}, ^{1}H NMR-(300.06 MHz, $CDCl_3$, δ ppm) : 7.42-6.80 (m, 8H, Ar-H and =CH), 9.77 (s, 1H, -OH), 3.86 (s, 3H, $-OCH_3$).



Scheme - 7: Synthesis of 9-(1-phenyl)-4,5-(2",'"-methoxyphenol)-9H-1,3,6,8,9-penta-azo-fluorene-2,7-diamine **(7a)**



Scheme - 8: Synthesis of 9-(1-phenyl)-4,5-(2",'"-methoxyphenol)-9H-1,3,6,8,9-hexa-azo-fluorene-2,7-diamine **(8a)**



Scheme - 8: Synthesis of 2,2'-(1-phenylpyrrolidine-2,5-diylidene)dimalononitrile **(9a)**

3,5-bis((Z)-4-hydroxy-3-methoxybenzylidene)-1-phenyl-piperidine-2,6-dione(4a):

M.F.: $C_{27}H_{23}NO_6$, C,H,N Observed:C, 71.06; H, 6.98; N, 3.24, FTIR (KBr) : >C=O (2-Peaks): 1595cm^{-1} and 1672cm^{-1}, =C-H: 2968cm^{-1}, Ar (3-Peaks): 1455cm^{-1}, 1513cm^{-1} and 1541cm^{-1}, Ar-OCH_3: 1157cm^{-1}, Ar-OH: 3320cm^{-1}, ^{1}H NMR-(200.13 MHz; $CDCl_3$; δ ppm) : 7.40-6.26 (m, 8H, Ar-H and =CH), 9.87 (s, 1H, -OH), 3.70 (s, 3H, $-OCH_3$), 2.46 (s, 2H, $-CH_2$).

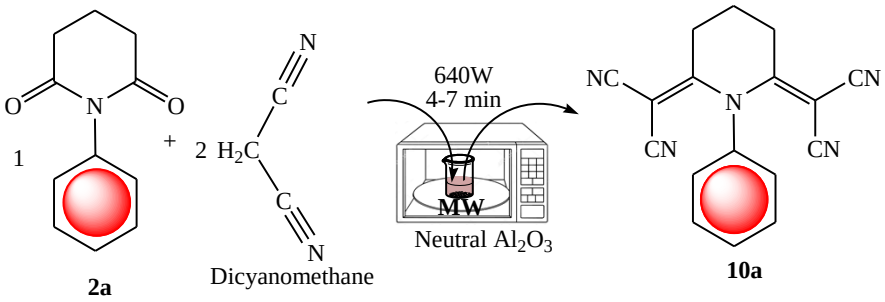
(3Z,4Z)-3,4-bis-(4-hydroxy-3-methoxy-benzylidene)-7-(1-phenyl)-3,3a,3b,4,5,7-hexahydro-2H-pyrrolo [2,3-c,5,4-c] dipyrazole(5a) :

M.F.: $C_{26}H_{25}N_5O_4$, C,H,N Observed:C, 66.38; H, 5.44; N, 14.79, FTIR (KBr) : -NH (1-Peak): 3292cm^{-1}, Ar (3-Peaks): 1507cm^{-1}, 1597 cm^{-1} and 1643cm^{-1}, Ar-OCH_3: 1271cm^{-1}, Ar-OH: 3600cm^{-1}, ^{1}H NMR-(300.06 MHz; DMSO-d_6; δ ppm): 7.57-6.39 (m, 8H, Ar-H), 8.56 (s, 1H, -NH), 9.93 (s, 1H, -OH), 3.34 (d, 1H, -CH), 2.32-2.23 (d, 1H, -CH), 3.74 (s, 3H, $-OCH_3$).

(3Z,4Z)-3,4-bis-(4-hydroxy-3-methoxy-benzylidene)-7-(1-phenyl)-3,3a,3b,4,5,7-hexahydro-2H-piperidine-[2,3-c,5,4-c] dipyrazole(6a):

M.F.: $C_{27}H_{27}N_5O_4$, C,H,N Observed:C, 66.98; H, 5.76; N, 14.86, FTIR (KBr): -NH (1-Peak): 3218cm^{-1}, Ar (3-Peaks): 1511cm^{-1}, 1600cm^{-1} and 1651cm^{-1}, Ar-

OCH_3: 1280cm^{-1}, Ar-OH: 3482cm^{-1}, ^{1}H NMR-(500.13 MHz; DMSO-d_6; δ ppm): 7.64-6.74 (m, 5H, Ar-H and =CH), 8.58 (s, 1H, -NH), 10.06 (s, 1H, -OH), 3.45 (d, 1H, -CH), 2.38-2.27 (m, 1H, -CH), 2.05-1.81 (m, 2H, -CH_2), 3.77 (s, 3H, -OCH_3).



Scheme - 9: Synthesis of 2,2'-(1-phenylpiperidine-2,6-diylidene)dimalononitrile **(10a)**

9-(1-phenyl)-4,5-(2","'-methoxyphenol)-9H-1,3,6,8,9-penta-azo-fluorene-2,7-diamine(7a) :

M.F.: $C_{28}H_{23}N_7O_4$, C,H,N Observed: C, 64.83; H, 4.73; N, 19.10, FTIR (ATR) : -NH_2 (2-Peaks): 3194cm^{-1}and 3315cm^{-1}, Ar (3-Peaks): 1500cm^{-1}, 1578cm^{-1} and 1662cm^{-1}, Ar-OCH_3: 1182cm^{-1}, Ar-OH: 3400cm^{-1}, ^{1}H NMR-(300.06 MHz; DMSO-d_6; δ ppm) : 7.41-7.02 (m, 8H, Ar-H), 3.56 (s, 3H, OCH_3), 9.73 (s, 2H, -NH_2), 10.25 (s, 1H, -OH).

9-(1-phenyl)-4,5-(2","'-methoxyphenol)-9H-1,3,6,8,9-hexa-azo-fluorene-2,7-diamine(8a) :

M.F.: $C_{29}H_{25}N_7O_4$, C,H,N Observed: C, 65.19; H, 4.71; N, 18.95, FTIR (KBr): -NH_2 (2-Peaks): 3303cm^{-1}and 3365cm^{-1}, Ar (3-Peaks): 1532cm^{-1}, 1595cm^{-1} and 1665cm^{-1}, Ar-OCH_3: 1293cm^{-1}, Ar-OH: 3509cm^{-1}, ^{1}H NMR-(500.13 MHz; DMSO-d_6; δ ppm): 7.56-6.98 (m, 5H, Ar-H), 9.77 (s, 2H, -NH_2), 10.27 (s, 1H, -OH), 3.80 (s, 3H, OCH_3), 3.41 (s, 2H, CH_2).

2,2'-(1-phenylpyrrolidine-2,5-diylidene) dimalononitrile (9a):

M.F.: $C_{16}H_9N_5$, C,H,N Observed: C, 71.34; H, 3.68; N, 25.98, FTIR (ATR): -C≡N (1-Peak): 2194cm^{-1}, cyclic CH_2-CH_2: 2918cm^{-1}, cyclic imines 1379cm^{-1}, Ar (3-Peaks): 1499cm^{-1}, 1550cm^{-1} and 1683cm^{-1}, ^{1}H NMR-(300.06 MHz; DMSO-d_6; δ ppm): 2.76 (s, 4H, imide), 7.47-7.27 (m, 5H, Ar-H).

2,2'-(1-phenylpiperidine-2,6-diylidene) dimalononitrile(10a):

M.F.: $C_{17}H_{11}N_5$, C,H,N Observed: C, 71.84; H, 4.42; N, 24.78, FTIR (KBr): -C≡N (1-Peak): 2338cm^{-1}, cyclic CH_2-CH_2-CH_2: 2962cm^{-1}, cyclic imines 1317cm^{-1}, Ar (3-Peaks): 1501 cm^{-1}, 1541 cm^{-1} and 1602 cm^{-1}, ^{1}H NMR-(500.13 MHz; DMSO-d_6; δ ppm): 1.81 (m, 2H, imide), 2.28 (m, 4H, imide), 7.58-7.02 (m, 5H, Ar-H)**.**

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