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STUDIES WITH CONDENSED AMINOTHIOPHENES: MICROWAVE ASSISTED CYCLOADDITION REACTIONS OF THIENO[3,4-*d*]-PYRIDAZINONE AND THIENO[3,4-*c*]QUINOLINONE

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Abstract – The arylformazane (**2**) was produced via coupling the α-oxoarylhydrazones (**1**) with aromatic diazonium salts. These formazane condensed readily with ethyl cyanoacetate to yield arylazopyridazinones (**4**) that reacted with sulphur in the presence of piperidine to yield the aminoazothienopyridazinone (**5**), the latter was reacted with electron poor olefins and acetylenes to yield aminoazophthalazines (**8**). Compound (**8**) was reacted with dimethylformamide dimethylacetal to yield amidine (**9**). Similarly aminothienoquinolinone (**17**) was reacted with electron poor olefins and acetylenes to yield aminophthalazines (**20**, **22a**,**b**).

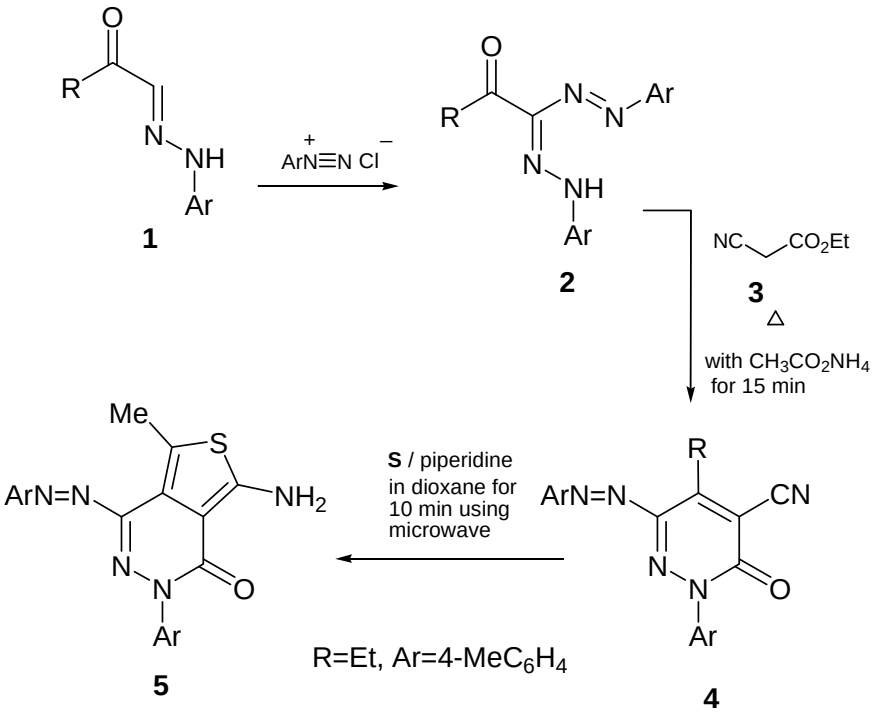
INTRODUCTION

Synthesis of arylazoazoles and arylazoazines is now receiving considerable interest.[1-5] However, to our knowledge, neither arylazopyridazinones nor their benzofused derivatives have yet been synthesized. In conjunction to our interest in chemistry of arylazoazoles and arylazoazines as potential dyes for D2T2 printing, we report here the results of our investigations that aimed at developing routes to these new classes of arylazo derivatives. In the past fifteen years, Elnagdi *et al*.[6-11] have established efficient routes to benzofused phthalazines utilizing alkylpyridazinylcarbonitriles as starting materials. Recently Döpp *et al*.[12,13] reported the preparation of the condensed benzoxepin from the thienocoumarin and 2,3-dichloro-1, 4-naphthoquinone.

RESULTS AND DISCUSSION

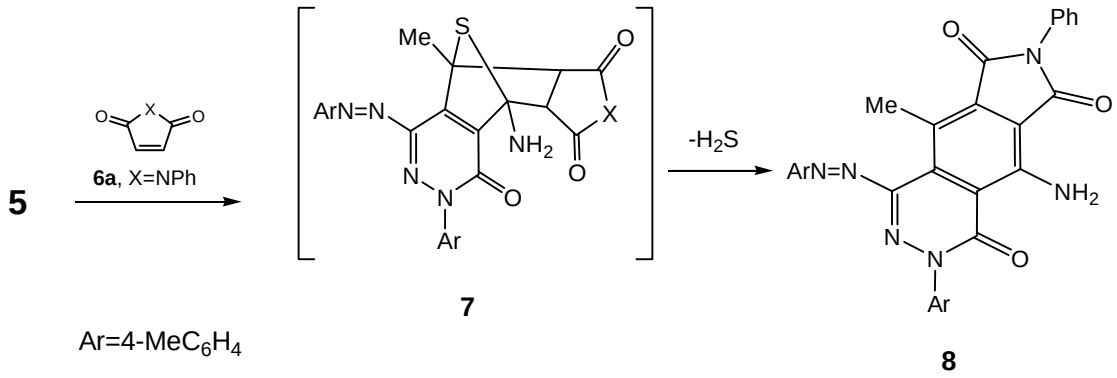
Formazane (**2**) could be readily obtained via coupling the α-oxoarylhydrazone (**1**) with aromatic diazonium salts and could be utilized as starting materials for targeted arylazo pyridazinones. As we have placed emphasis in the last few years on adopting microwave heating as a suitable substitute to

conventional heating in an oil bath,[14-16] we have utilized heating in a direct beam microwave oven in this work whenever it looked feasible. Heating (**2**) with ethyl cyanoacetate at 200 ºC for 15 min in presence of ammonium acetate has afforded (**4**) in 71% yield. The arylazopyridazinone (**4**) readily reacted with elemental sulphur in the presence of piperidine on heating in focused microwave at 190 ºC for 10 min adopting MORE (Microwave Organic Reactions Enhancement) technology[17] in dioxane as reaction medium to yield arylazoaminothienopyridazine (**5**) in 88% yield (Scheme 1).



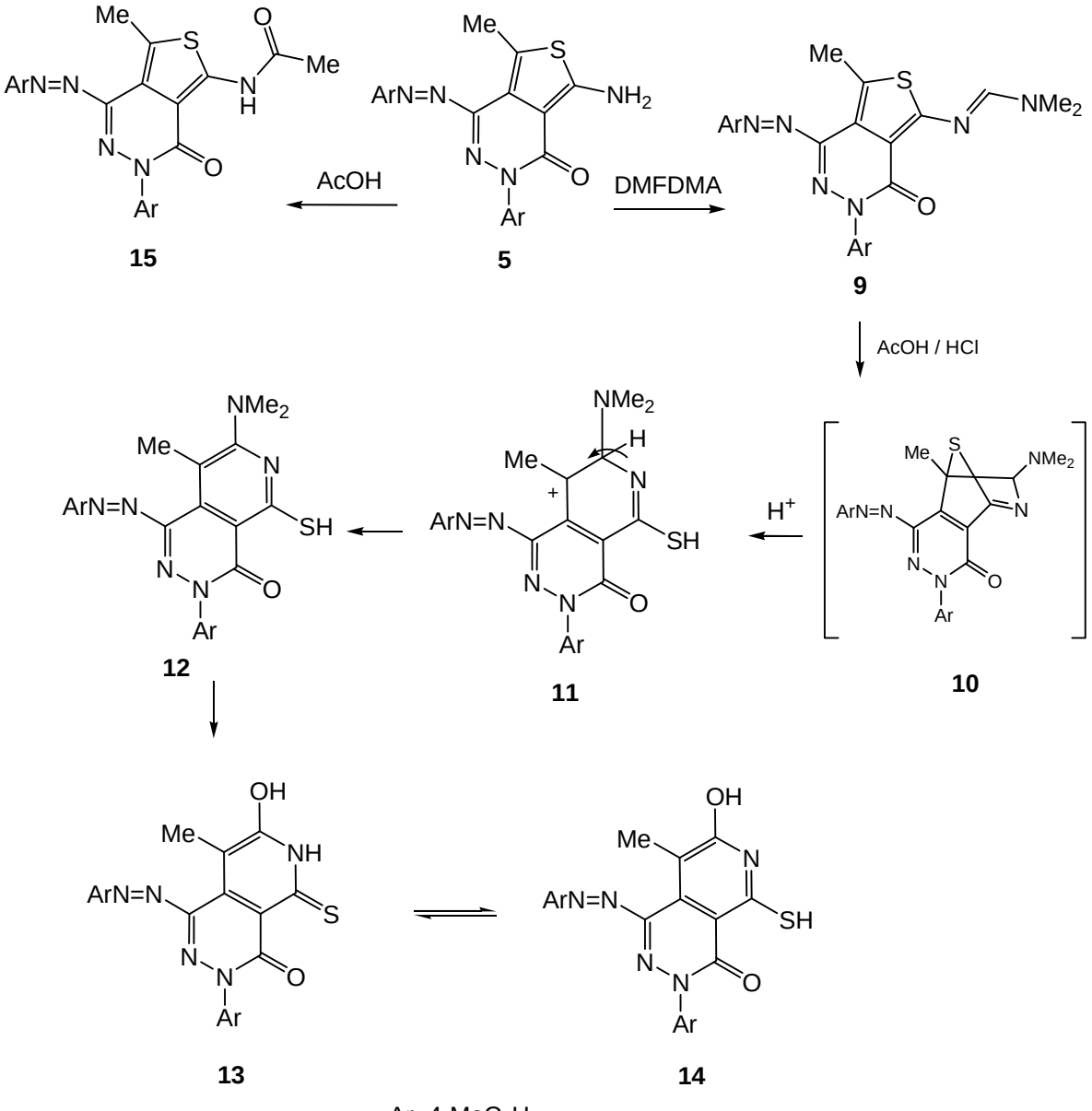
Scheme 1

Typical to the established behavior of thienopyridazines compound (**5**) reacted readily with *N*-phenylmaleimide in a mixture of acetic acid and dioxane to yield (**8**) *via* intermediary of [4+2] cycloadducts (**7**) that could not be isolated but a well accepted intermediate in this type of reactions[13] (Scheme 2).



Scheme 2

Reaction of compound (**5**) with dimethylformamide dimethylacetal (DMFDMA) in microwave oven at 180 °C for 15 min afforded the corresponding amidine (**9**), no trace of C-1 alkylation product was observed. Compounds (**9**) upon heated with ammonium acetate in presence of few drops of acetic acid in microwave oven at 140 °C for 25 min afforded the pyridopyridazine derivatives (**13**). This is assumed to be formed via initial intramoleulr [4+2] cycloaddition of amidine moiety to the diene system in the thiophene ring yielding (**10**). This readily undergoes ring opening to yield carbocation (**11**) that is then deprotonated yielding (**12**). Hydrolysis of dimethylamino moiety in the latter product afforded the final product (**13**). Although it is difficult to rule out completely isomeric form (**14**), a simulated spectra led us to assume structure (**13**) for the product as the simulated spectra of this compound best fits measured one (Scheme 3).

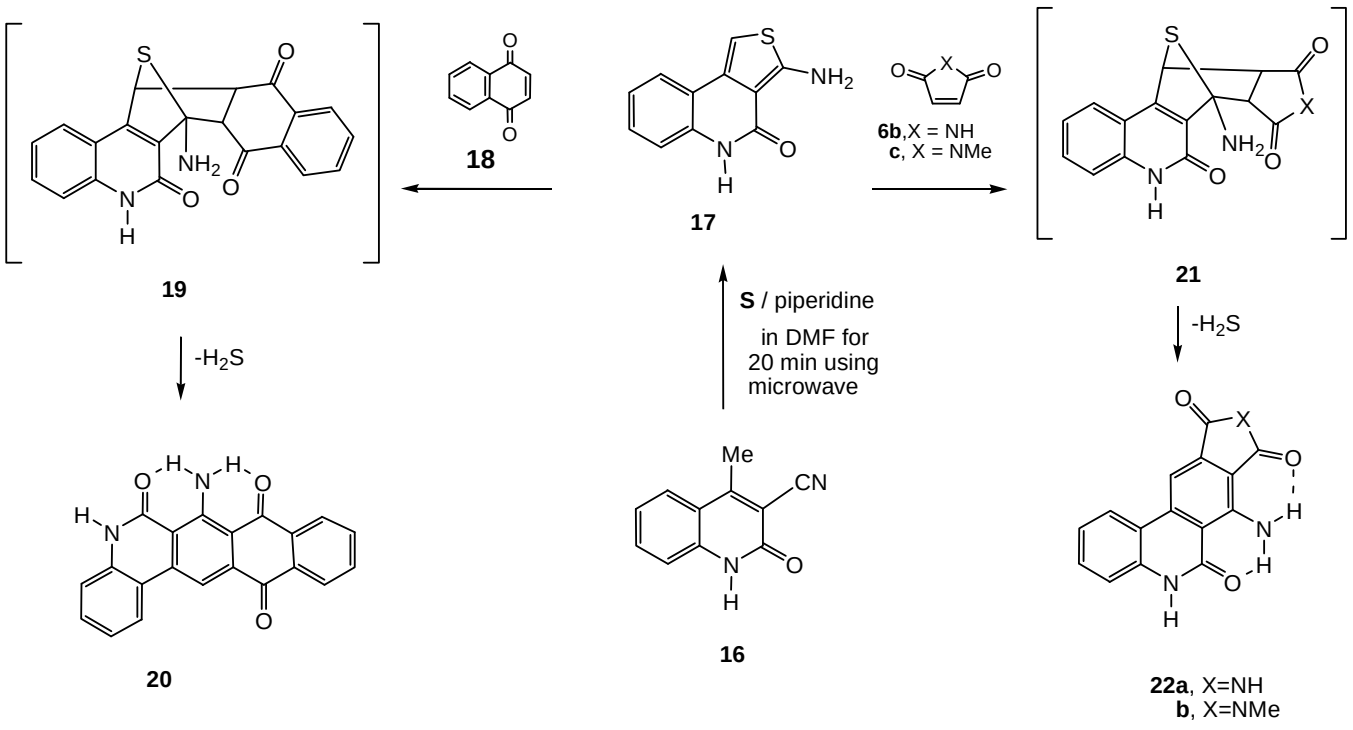


Scheme 3

Acylating (**5**) by heating in the microwave oven at 150 °C for 20 min with acetic acid resulted in the formation of acetylamino derivative (**15**) in 81% yield. This however proved completely inert as diene in the Diels-Alder reaction. It can thus be concluded that the presence of an amino function that donates electrons to C-5 is essential to maintain reactivity of the system. These reactions are really looked at to be dipolar non-concerted reactions. In support of this view Elnagdi *et al*.[7] and more recently Döpp *et al*.[18] have shown that the reaction of condensed aminothiophenes as well as 2-aminothiophenes with electron poor olefins and acetylenes results in the formation of C-1 alkylation products.

Treatment of 2-aminoacetophenone with ethyl cyanoacetate in microwave oven at 200 °C for 5 min in presence of ammonium acetate has afforded (**16**), that readily reacted with elemental sulphur in presence of piperidine on heating in focused microwave at 180 °C for 20 min, adopting MORE technology[17] in DMF as the reaction medium to yield arylaminothienoquinolinone (**17**) (Scheme 4).

Straightforward application of Elnagdi's synthesis of fused pyridazinones from aminothienopyridazinones;[10] aminothienoquinolinone (**17**) was reacted with maleimide and N-methylmaleimide in a mixture of acetic acid and dioxane, in focused microwave at 170 °C for 30 min to yield phthalazines (**22a,b**). We have traced the elimination of H_2S during the reaction process by lead acetate paper. We have also investigated the possible adoption of other routes, also explored by Elnagdi *et al*.,[9] and Döpp *et al*.[13] for the synthesis of phthalazines. Typical to these reports, aminothienoquinolinone (**17**) reacted with 1,4-naphthoquinone to yield arylphthalazinone (**20**). This is a further extension to our established phthalazine synthesis, which is believed to proceed via intermediacy of (**19**) (Scheme 4).



Scheme 4

CONCLUSION

In summary, arylazopyridazines and condensed phthalazines could be prepared via procedures similar to our previously described ones. We could show that the condesed aminothiophenes, are highly active toward maleimides and naphthoquinone, so long as the amino function donates electrons to thiophene ring.
In absence of this effect the system is rather inert.

EXPERIMENTAL

Melting points are uncorrected. All the reactions were conducted under microwave irradiation in heavy-walled Pyrex tubes (capacity 10 mL) fitted with PCS cap. Microwave heating was carried out with a single mode cavity Explorer Microwave Synthesizer (CEM Corporation, NC, USA), producing continuous irradiation and equipped with simultaneous external air-cooling system. IR spectra were recorded in KBr disks using a Perkin-Elmer System 2000 FT-IR spectrophotometer. UV/Vis spectral data were recorded on UV/Vis spectrophotometer (Carry-Varian 5). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX 400, super-conducting NMR spectrometer in $CDCl_3$ or DMSO as solvent and TMS as internal standard; chemical shifts were reported in δ units (ppm). Mass spectra were measured on a VG Autospec-Q (high resolution, high performance, tri-sector GC/MS/MS). Microanalyses were performed on a LECO CHNS-932 Elemental Analyzer.

1-(*p*-Tolylhydrazono)butan-2-one (1).

A mixture of KOH (3.5 g, 0.053 mol) in water (100 mL), ethyl acetoacetate or methyl propionyl acetate (6.5 g, 0.05 mol) was allowed to stir at rt for 24 h. The solution of KOAc was cooled to 0 °C and concentrated hydrochloric acid (4.5 mL) in ice-water (15 mL) was added slowly with stirring, this mixture was then gradually treated under stirring with a solution of aryldiazonium chloride (prepared from the corresponding aromatic amine (0.01 mol) and the appropriate quantities of both hydrochloric acid and $NaNO_2$. The mixture is made basic by addition of NaOAc (8.2 g) dissolved in water (30 mL). The solid product, so formed, was collected by filtration and crystallized from toluene. Compound (**1**) was obtained as orange crystals. Yield (1.26 g, 66%), mp 134-136 ºC, IR (KBr) ν 3236 (NH), 1651(CO) cm^{-1}; UV/Vis at λ_{max} ($CHCl_3$) = 347 nm.^{1}H NMR (DMSO-d_6) δ 1.01 (t, 3H, J = 7.4 Hz, CH_3), 2.24 (s, 3H, CH_3), 2.75 (q, 2H, J = 7.4 Hz, CH_2), 7.05 (d, 2H, J = 8.4 Hz, *p*-tolyl-H), 7.10 (d, 2H, J = 8.4 Hz, *p*-tolyl-H), 7.21 (s, 1H, imine-H), 11.21 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ 200.0 (CO), 142.0, 134.3, 131.4, 130.4, 114.4, 30.0 (CH_2), 21.3 (CH_3), 9.5 (CH_3). MS (EI) *m/z* = 190 (M^+, 100), 106 (60), 79 (15), 57 (22). Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.56; H, 7.34; N, 14.73.

1-[-2-(4-Methylphenyl)-1-diazenyl]-1-[-2-(4-methylphenyl)hydrazono]butan-2-one (2).

A solution of aryldiazonium chloride (prepared from the corresponding aromatic amine (0.01 mol) and the appropriate quantities of both hydrochloric acid and $NaNO_2$ (0.01 mol) at 0 °C was added to a

solution of compound (**1**) (0.01 mol) in EtOH (50 mL) containing NaOAc (2 g). The reaction mixture was stirred at rt for 1 h. The solid product, so formed, was collected by filtration and crystallized from EtOH. Compound (**2**) was obtained as wine red crystals. Yield (1.84 g, 60%), mp 142-144 ºC, IR (KBr) ν 3423 (NH), 1681 (CO) cm^{-1}; UV/Vis at λ_{max} ($CHCl_3$) = 455 nm. ^{1}H NMR (DMSO-d_6) δ 1.09 (t, 3H, *J* = 7.2 Hz, CH_3), 2.36 (s, 6H, *p*-tolyl-CH_3), 2.99 (q, 2H, *J* = 7.2 Hz, CH_2), 7.32 (d, 4H, *J* = 7.8 Hz, *p*-tolyl-H), 7.72 (d, 4H, *J* = 7.8 Hz, *p*-tolyl-H), 14.93 (s, 1H, NH, D_2O exchangeable). ^{13}C NMR (DMSO-d_6) δ 196.5 (CO), 145.7, 141.2, 139.5, 131.0, 120.4, 31.9 (CH_2), 21.9 (*p*-tolyl-CH_3), 9.5 (CH_3). MS (EI) *m/z*= 308 (M^+, 36), 132 (20), 106 (100), 91 (42). Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 70.10; H, 6.54; N, 18.12.

5-Ethyl-3-oxo-2-*p*-tolyl-6-*p*-tolylazo-2,3-dihydropyridazine-4-carbonitrile (4).

A mixture of compound (**2**) (3.08 g, 0.01mol), ethyl cyanoacetate (1.13 g, 0.01 mol), ammonium acetate (2 g) was heated with stirring at 200 ºC for 15 min. After cooling, the formed precipitate was washed with EtOH and filtered off and crystallized from dioxane to afford product (**4**). Compound (**4**) was obtained as buff crystals. Yield (2.28 g, 64%), mp 194-196 °C, IR (KBr) ν 2234 (CN), 1675 (CO) cm^{-1}; UV/Vis at λ_{max} ($CHCl_3$) = 325 nm. ^{1}H NMR (DMSO-d_6) δ 1.26 (t, 3H, *J* = 7.3 Hz, CH_3), 2.38 (s, 3H, *p*-tolyl-CH_3), 2.42 (s, 3H, *p*-tolyl-CH_3), 3.02 (q, 2H, *J* = 7.0 Hz, CH_2), 7.34 (d, 2H, *J* = 8.0 Hz, *p*-tolyl-H), 7.43-7.49 (m, 4H, *p*-tolyl-H), 7.84 (d, 2H, *J* = 8.0 Hz, *p*-tolyl-H). ^{13}C NMR (DMSO-d_6) δ 157.6 (CO), 155.7, 151.3, 150.1, 145.2, 139.8, 138.9, 131.3, 130.3, 126.6, 124.5, 114.8, 114.3, 25.3 (CH_2), 22.2 (*p*-tolyl-CH_3), 14.4 (*p*-tolyl-CH_3), 9.0 (CH_3). MS (EI) *m/z* = 357 (M^+, 33), 342 (15), 91 (100), 65 (17). Anal. Calcd for $C_{21}H_{19}N_5O$: C, 70.57; H, 5.36; N, 19.59. Found: C, 70.57; H, 5.38; N, 19.59.

7-Amino-5-methyl-2-*p*-tolyl-4-*p*-tolylazo-2*H*-thieno[3,4-*d*]pyridazin-1-one (5).

A dried heavy-walled Pyrex tube containing a small stir bar was charged with compounds (**4**) (0.01 mol), and elemental sulphur (032 g, 0.01 mol)) in dioxane (2 mL) and few drops of piperidine were added. The tube containing the reaction mixture was fitted with PCS cap and then it was exposed to an automated microwave irradiation at 190 °C for 10 min. The build-up pressure in the closed reaction vessel was carefully monitored and was found to be typically in the range of 170-180 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The crude product was poured onto water, the solid product, so formed, was collected by filtration and crystallized from EtOH. Compound (**5**) was obtained as wine red crystals. Yield (3.43 g, 88%), mp 208-209 °C, IR (KBr) ν 3322, 3278 (NH_2), 1642 (CO) cm^{-1}; UV/Vis at λ_{max} ($CHCl_3$) = 453 nm. ^{1}H NMR (DMSO-d_6) δ 2.33 (s, 3H, CH_3), 2.41 (s, 3H, *p*-tolyl-CH_3), 2.45 (s, 3H, *p*-tolyl-CH_3), 7.22 (d, 2H, *J* = 7.6 Hz, *p*-tolyl-H), 7.37 (d, 2H, *J* = 7.7 Hz, *p*-tolyl-H), 7.41 (d, 2H, *J* = 7.9 Hz, *p*-tolyl-H), 7.51 (s, 2H, NH_2, D_2O exchangeable), 7.81 (d, 2H, *J* = 7.7 Hz, *p*-tolyl-H). ^{13}C NMR (DMSO-d_6) δ 161.2 (CO), 159.9, 150.5, 150.4, 144.2, 139.1, 137.1, 131.0, 129.6, 126.7, 124.1, 122.5,

116.6, 105.0, 22.0 (*p*-tolyl-CH_3), 21.5 (*p*-tolyl-CH_3), 15.2 (CH_3). MS (EI) *m/z*= 389 (M^+, 100), 270 (30), 106 (60), 91 (80); Anal. Calcd for $C_{21}H_{19}N_5OS$: C, 64.76; H, 4.92; N, 17.98; S, 8.23. Found: C, 65.08; H, 5.06; N, 17.91; S, 8.22.

9-Amino-5-methyl-7-phenyl-2-*p*-tolyl-4-*p*-tolylazo-2*H*-pyrrolo[3,4-*g*]phthalazine-1,6,8-trione (8).

A solution of compound (**5**) (3.89 g, 0.01 mol) and N-phenylmaleimide (1.73 g, 0.01mol), in dioxane (10 mL) and few drops of acetic acid was refluxed for 8 h. The solvent was evaporated and then the residue was washed with EtOH. The solid products, so formed, were collected by filtration and crystallized from DMF. Compound (**8**) was obtained as orange crystals. Yield (4.06 g, 77%), mp 300-302 °C, IR (KBr) ν 3436, 3310 (NH_2),1752, 1704, 1648 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 2.48 (s, 3H, *p*-tolyl-CH_3), 2.80 (s, 3H, *p*-tolyl-CH_3), 7.36 (d, 2H, *J* = 7.8 Hz, *p*-tolyl-H), 7.52 (d, 4H, *J* = 8.1 Hz, *p*-tolyl-H), 7.57-7.64 (m, 5H, phenyl-H), 7.94 (d, 2H, *J* = 7.7 Hz, *p*-tolyl-H), 9.47 (s, 2H, NH_2). MS (EI) *m/z*= 528 (M^+, 85), 422 (90), 91 (95). Anal. Calcd for $C_{31}H_{24}N_6O_3$: C, 70.44; H, 4.58; N, 15.90. Found: C, 70.00; H, 4.53; N, 15.92.

***N*,*N*-Dimethyl-*N*'-(7-methyl-4-oxo-3-*p*-tolyl-1-*p*-tolylazo-3,4-dihydrothieno[3,4-*d*]pyridazin-5-yl)-formamidine** (**9**).

A mixture of (**5**) (3.89 g, 0.01 mol) and DMFDMA (1.19 g, 10 mmol) in the presence of a few drops of dimethylformamide was irradiated in a microwave oven at 180 °C for 15 min. The build-up of pressure in the closed reaction vessel was carefully monitored. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 ^{o}C. The crude product was washed with EtOH. The solid product, so formed, was collected by filtration and crystallized from DMF. Compound (**9**) was obtained as wine red crystals. Yield (4.04 g, 91%), mp 203-205 °C, IR (KBr) ν 1642 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ = 2.34 (s, 3H, CH_3), 2.42 (s, 3H, *p*-tolyl-CH_3), 2.56 (s, 3H, *p*-tolyl-CH_3), 2.98 (s, 3H, NCH_3), 3.07 (s, 3H, NCH_3), 7.23 (d, 2H, *J* = 7.6 Hz, *p*-tolyl-H), 7.34 (d, 2H, *J* = 7.5 Hz, *p*-tolyl-H), 7.42 (d, 2H, *J* = 7.6 Hz, *p*-tolyl-H), 7.83 (d, 2H, *J* = 7.5 Hz, *p*-tolyl-H), 7.99 (s, 1H, amidine-H). ^{13}C NMR (DMSO-d_6) δ 164.4 (CO), 158.1, 157.8, 151.1, 150.4, 144.4, 139.9, 137.5, 131.2, 129.8, 127.4, 125.7, 124.6, 124.3, 113.4, 35.2 (NCH_3), 22.1 (*p*-tolyl-CH_3), 21.6 (*p*-tolyl-CH_3), 16.4 (CH_3). MS (EI) *m/z*= 444 (M^+, 100), 388 (10), 324 (25), 91 (40). Anal. Calcd for $C_{24}H_{24}N_6OS$: C, 64.84; H, 5.44; N, 18.90; S, 7.21. Found: C, 64.60; H, 5.58; N, 18.75; S, 7.20.

7-Hydroxy-8-methyl-5-thioxo-3-*p*-tolyl-1-*p*-tolylazo-5,6-dihydro-3*H*-pyrido[3,4-*d*]pyridazin-4-one (**13**).

A mixture of (**9**) (4.44 g, 0.01 mol) and ammonium acetate (4 g) in the presence of a few drops of acetic acid was irradiated in a microwave oven at 140 °C for 25 min. The build-up pressure in the closed reaction vessel was carefully monitored. After the irradiation, the reaction tube was cooled with

high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The crude product was poured onto water, the solid product, so formed, was collected by filtration and crystallized from dioxane/EtOH (3:1). Compound (**13**) was obtained as orange crystals. Yield (2.66 g, 64%), mp 295-297 °C, IR (KBr) ν 3444 (OH), 3271 (NH), 1674, 1641 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ = 2.37 (s, 3H, CH_3), 2.43 (s, 3H, *p*-tolyl-CH_3), 2.66 (s, 3H, *p*-tolyl-CH_3), 7.29 (d, 2H, *J* = 7.8 Hz, *p*-tolyl-H), 7.44 (t, 4H, *J* = 7.4 Hz, *p*-tolyl-H), 7.87 (d, 2H, *J* = 7.8 Hz, *p*-tolyl-H), 8.61 (s, 1H, NH), 11.7 (s, 1H, OH).^{13}C NMR (DMSO-d_6) δ 157.8, 151.3, 151.0, 144.4, 141.1, 138.4, 138.2, 130.6, 130.2, 130.0, 129.6, 126.4, 125.6, 124.5, 120.2, 22.3 (*p*-tolyl-CH_3), 21.8 (*p*-tolyl-CH_3), 15.7 (CH_3). MS (EI) *m/z*= 417 (M^+, 85), 389 (75), 356 (10), 270 (40), 91 (100). Anal. Calcd for $C_{22}H_{19}N_5O_2S$: C, 63.29; H, 4.59; N, 16.78; S, 7.68. Found: C, 63.26; H, 4.78; N, 16.75; S, 7.56.

***N*-(7-Methyl-4-oxo-3-*p*-tolyl-1-*p*-tolylazo-3,4-dihydrothieno[3,4-*d*]pyridazin-5-yl)acetamide** (**15**).

A solution of (**5**) (3.89 g, 0.01 mol) in acetic acid (3 mL) was irradiated in a microwave oven at 150 °C for 20 min. The build-up pressure in the closed reaction vessel was carefully monitored. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The crude product was washed with EtOH. The solid product, so formed, was collected by filtration and crystallized from dioxane. Compound (**15**) was obtained as brown crystals. Yield (3.50 g, 81%), mp 207-209 °C, IR (KBr) ν 3269 (NH), 1680, 1640 (CO) cm^{-1}.^1H NMR (DMSO-d_6) δ= 2.30 (s, 3H,$COCH_3$), 2.36 (s, 3H, *p*-tolyl-CH_3), 2.42 (s, 3H, *p*-tolyl-CH_3), 2.63 (s, 3H, CH_3), 7.28 (d, 2H, *J* = 7.8 Hz, *p*-tolyl-H), 7.44-7.46 (m, 4H, *p*-tolyl-H), 7.85 (d, 2H, *J* = 7.8 Hz, *p*-tolyl-H), 11.00 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ 168.4 (CO), 158.3, 150.6, 149.9, 144.2, 142.8, 138.4, 137.5, 130.7, 129.4, 128.2, 126.5, 123.8, 120.8, 112.2, 23.1 (*p*-tolyl-CH_3), 21.1 (*p*-tolyl-CH_3), 18.9 (CH_3), 14.9 (CH_3). MS (EI) *m/z*= 431 (M^+, 100), 389 (40), 270 (25), 91 (80). Anal. Calcd for $C_{23}H_{21}N_5O_2S$: C, 64.02; H, 4.91; N, 16.23; S, 7.43. Found: C, 63.94; H, 4.95; N, 16.33; S, 7.38.

4-Methyl-2-oxo-1,2-dihydroquinoline-3-carbonitrile (**16**).

A dried heavy-walled Pyrex tube containing a small stir bar was charged with 2-aminoacetophenone (1.35 g, 0.01 mol), ethyl cyanoacetate (1.13 g, 0.01 mol) and ammonium acetate (2 g). The tube containing the reaction mixture was fitted with PCS cap and then it was exposed to an automated microwave irradiation at 200 °C for 5 min. The build-up of pressure in the closed reaction vessel was carefully monitored and was found to be typically in the range of 190-195 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The crude product was washed with EtOH. The solid product, so formed, was collected by filtration and crystallized from DMF. Compound (**16**) was obtained as white crystals. Yield (0.95 g, 52%), mp 329-330 °C (lit.,[11] 320 °C) IR (KBr) ν 2222 (CN), 1660 (CO) cm^{-1}.^1H NMR (DMSO-d_6) δ = 2.71 (s, 3H, CH_3), 7.28-7.35 (m, 2H, quinolinyl-H), 7.22 (t, 1H, *J* = 7.9 Hz, quinolinyl-H), 7.37 (d, 1H, *J* = 8.0 Hz,

quinolinyl-H), 12.31 (s, 1H, NH), MS (EI) *m/z*= 184 (M^+, 100), 156 (85), 128 (30), 77 (17). Anal. Calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.66; H, 4.39; N, 15.21.

3-Amino-5*H*-thieno[3,4-*c*]quinolin-4-one (**17**).[11]

A dried heavy-walled Pyrex tube containing a small stir bar was charged with compounds (**16**) (1.84 g, 0.01 mol), elemental sulphur (0.32 g, 0.01 mol)) in DMF (2 mL) and few drops of piperidine were added. The tube containing the reaction mixture was fitted with PCS cap and then it was exposed to an automated microwave irradiation at 170 ºC for 30 min. The build-up pressure in the closed reaction vessel was carefully monitored and was found to be typically in the range of 75 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The crude product was poured onto water, the solid product, so formed, was collected by filtration and crystallized from DMF. Compound (**17**) was obtained as gray crystals. Yield (0.70 g, 56%), mp 200-202 °C, IR (KBr) ν 3410, 3298, 3175 (NH_2, NH), 1649 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ = 6.81 (s, 1H, thiophenyl-H), 7.01 (t, 1H, *J* = 7.1 Hz, quinolinyl-H), 7.10 (d, 1H, *J* = 7.90 Hz, quinolinyl-H), 7.24 (t, 1H, *J* = 8.1 Hz, quinolinyl-H), 7.40 (s, 2H, NH_2), 7.80 (d, 1H, *J* = 7.6 Hz, quinolinyl-H), 10.44 (s, 1H, NH), MS (EI) *m/z*= 216 (M^+, 45), 184 (100), 156 (70), 128 (30); 105 (42), 77 (28).

7-Amino-5*H*-5-aza-benzo[*a*]naphthacene-6,8,13-trione (**20**).

A solution of (**17**) (1.26 g, 0.01 mol), and naphthoquinone (1.54 g, 0.01 mol) in DMF (2 mL) was irradiated in a microwave oven at 140 °C for 25 min. The build-up pressure in the closed reaction vessel was carefully monitored and was found to be typically in the range of 100 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 °C. The crude product was washed with EtOH. The solid product, so formed, was collected by filtration and crystallized from DMF. Compound (**20**) was obtained as wine red crystals. Yield (3.09 g, 91%), mp > 300 °C, IR (KBr) ν 3449, 3347, 3239 (NH_2, NH), 1663, 1602 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ = 7.32-7.39 (m, 2H, Ar-H), 7.59 (t, 1H, *J* = 7.7 Hz, Ar-H), 7.83 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.90-8.00 (m, 1H, Ar-H), 8.14-8.22 (m, 3H, Ar-H), 8.35 (d, 1H, *J* = 8.2 Hz, Ar-H), 10.09 (s, 1H, NH, D_2O exchangeable), 10.48 (s, 1H, NH, D_2O exchangeable), 12.04 (s, 1H, NH, D_2O exchangeable). MS (EI) *m/z*= 340 (M^+, 100), 295 (35), 282 (15), 221 (25); 99 (10), 76 (27). Anal. Calcd for $C_{21}H_{12}N_2O_3$: C, 74.11; H, 3.55; N, 8.23. Found: C, 72.67; H, 3.75; N, 8.25.

General Procedure for The Preparation of Compounds (**22a,b**)**.**

A dried heavy-walled Pyrex tube containing a small stir bar was charged with each of maleimide, or *N*-methylmaleimide (0.01 mol), compounds (**17**) (1.26 g, 0.01 mol) in dioxane (2 mL) and few drops of AcOH were added. The tube containing the reaction mixture was fitted with PCS cap and then it was exposed to an automated microwave irradiation at 170 °C for 30 min. The build-up of pressure in the

closed reaction vessel was carefully monitored and was found to be typically in the range of 50-75 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50 ºC. The solvent was evaporated then washed with EtOH. The solid products, so formed, were collected by filtration and crystallized from dioxane.

7-Amino-5*H*-pyrrolo[3,4-*j*]phenanthridine-6,8,10-trione (**22a**).

Compound (**22a**) was obtained as buff crystals. Yield (1.81 g, 65%), mp > 300 °C, IR (KBr) ν 3466, 3323 (NH_2), 3169 (NH), 3123 (NH), 1759, 1686, 1650 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ = 7.10 (s, 1H, NH, D_2O exchangeable), 7.25 (t, 1H, *J* = 7.3 Hz, Ar-H), 7.35 (d, 1H, *J* = 8.1 Hz, Ar-H), 7.55 (t, 1H, *J* = 7.7 Hz, Ar-H), 7.89 (s, 1H, Ar-H), 8.44 (d, 1H, *J* = 8.2 Hz, Ar-H), 9.28 (s, 1H, NH, D_2O exchangeable), 11.19 (s, 1H, NH, D_2O exchangeable), 11.92 (s, 1H, NH, D_2O exchangeable), ^{13}C NMR (DMSO-d_6) δ = 171.5 (CO), 169.6 (CO), 164.3 (CO), 149.8, 143.9, 138.1, 137.7, 132.3, 125.9, 123.8, 118.6, 116.9, 113.5, 109.0, 104.3. MS (EI) *m/z*= 279 (M^+, 100), 208 (65), 179 (22), 153 (15), 126 (12), 76 (15). Anal. Calcd for $C_{15}H_9N_3O_3$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.08; H, 3.27; N, 15.13.

7-Amino-9-methyl-5*H*-pyrrolo[3,4-*j*]phenanthridine-6,8,10-trione (**22b**).

Compound (**22b**) was obtained as brown crystals. Yield (1.75 g, 60%), mp > 300 °C, IR (KBr) ν 3440, 3323 (NH_2), 3171 (NH), 1754, 1688 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ = 3.03 (s, 3H, CH_3), 7.12 (s, 1H, NH, D_2O exchangeable), 7.26 (t, 1H, *J* = 7.8 Hz, Ar-H), 7.36 (d, 1H, *J* = 8.1 Hz, Ar-H), 7.54 (t, 1H, *J* = 7.9 Hz, Ar-H), 7.97 (s, 1H, Ar-H), 8.49 (d, 1H, *J* = 8.3 Hz, Ar-H), 9.31 (s, 1H, NH, D_2O exchangeable), 11.96 (s, 1H, NH, D_2O exchangeable). ^{13}C NMR (DMSO-d_6) δ = 169.0 (CO), 167.4 (CO), 163.2 (CO), 148.4, 142.9, 137.1, 135.9, 131.3, 125.1, 122.8, 117.6, 115.9, 112.6, 107.1, 103.7, 23.5 (CH_3). MS (EI) *m/z*= 293 (M^+, 100), 208 (95), 179 (75), 152 (55); 126 (36), 76 (52). Anal. Calcd for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.78; N, 14.33. Found: 64.98; H, 3.75; N, 14.34.

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