Utility of Arylmethylenemalononitriles In Heterocyclic Synthesis : New Synthetic Procedures to Synthesize 4*H*-pyrano[3,2-c] quinoline, Pyrazolo[4,3-*b*] pyridine, 4*H* -Benzo [*b*]pyan , Pyridine and [1,3,4]Thiadiazolo[3,2-*a*] pyridin-2-yl)benzamide Derivatives

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ABSTRACT- 4*H*-pyrano[3,2-*c*]quinolines **7**a,b were prepared *via* reacting arylmethylenemalononitrile **1**a with 3-acetyl-4-hydroxyquinoline **2** or 4-hydroxyquinoline **3**.Pyrazolo[4,3-*b*]pyridines **11**a-f were obtained by reacting **1**a-f with 4-nitrosoantipyrine **8**.Reaction of **1**g with dimedone **12** and the hydrazone **15** resulted in the formation of 4*H*-benzo[*b*]pyran **14** and pyridine **19** respectively. Compound **1** reacted with 1,3,4-thiadiazole **20** to afford [1,3,4]thiadiazolo[3,2-*a*]pyridin-2-yl) benzamides**23**.

Keywords:Arylmethylenemalononitriles,4-hydroxyquinolines ,4*H*-pyrano[3,2-*c*]quinolnes, pyrazolo[4,3-*b*]pyridines,pyridine, 4*H*-benzo[*b*]pyran , [1,3,4]thiadiazolo[3,2-*a*]pyridin-2-yl)benzamides

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1 Introduction

Arylmethylenemalononitriles are versatile reagents which react with nucleophiles under mild conditions[1-4]. In the past decade, we were involved in a program aimed at developing the synthesis of polyfunctionally substituted heterocycles as potential biodegradable agrochemicals [1,2] and antischistosomal agents[5-11]. During this phase of our research, we have been investigated the base catatlysed reactions of cinnamonitriles with active hydrogen reagents.

In connection to this effort, we report here new approach for synthesis of polyfunctionally substituted 4*H*-pyrano[3,2-*c*]quinoline ,pyrazol[4,3-*b*] pyridines ,4*H*-benzo[*b*]pyran and pyridine derivatives ,that have been extensively studied due to their commercial applications in several fields[1-11].

2 EXPERIMENTAL

All melting points are uncorrected and measured on Griffin George MBF 010T (London) apparatus. Recorded yield correspond to the pure products. IR (KBr) spectra were recorded on a Perkin Elmer SP-880 spectrometer and ^{1}H-NMR spectra: were measured on Varian 270 MHz spectrometer on DMSO-d_6 as solvent and TMS an internal standard. Chemical shifts are reported in δ units (ppm). Microanalyses were performed on a LECO CHN-932 elemental analyzer and carried out in the Microanalytical Data Unit at Cairo and Damietta Universities. Mass spectra were recorded on a MS 30(AEI) instrument at 70 eV ionization energy .

Synthesis of pyrano[3,2-c]quinoline derivatives **7**a,b:*General procedure* : *Method* A:

A solution of 3-acetyl-4-hydroxy-2(1*H*)quinolinones **2**a,b (0.0 mole) and (0.0 mole) of 2-(3,4-dimethoxybenzylidene)malononitrile **1**a in ethanol (50 mL) containing few drops of piperidine were refluxed for 15 minutes and then left to cool .The obtained precipitates were collected by filtration and recrystallised from the proper solvents and the identified as **7**a,b.

Method B:

Copmounds **7**a,b were also prepared from 4-hydroxy-2(1*H*)quinolinones **3**a,b (0.01 mole) and (0.01 mole) of 2-(3,4-dimethoxybenzylidene)malononitrile **1**a utilizing the above reaction conditions.

2-Amino-4-(3,4-dimethoxyphenyl)-6-methyl-5-oxo- 5,6-dihydro-4H-pyrano[3,2-c] quinoline-3-carbonitrile **7**a: Formed colorless crystals in 70 % yield , from ethanol / dimethylformamide ,m.p.253-255^{o}C ; IR (ν/cm^{-1}): 3321, 3194(NH_2), 2187(conjugated CN),1672(CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm):3.41 (s,3H, *N*-CH_3) ,3.69(s,3H,OCH_3),3.71(s,3H , OCH_3), 4.49 (s,1H ,pyran H-4),6.66-6.68 (m, 3H,aromatic protons), 7.21 (s, 2H,NH_2)7.39-8.03(m,7H, aromatic protons). *Anal*.Calcd.for $C_{22}H_{19}N_3O_4$ (389.40): C,67.86; H, 4.92; N , 10.79.Found: C,67.67;H,4.76;N,10.62.

2-Amino -4-(3,4-dimethoxyphenyl) -6-ethyl-5-oxo--5,6-dihydro-4H-pyrano[3,2-c] quinoline-3-carbonitrile **7**b : Formed colorless crystals in 75 % yield , from ethanol ,m.p.237-239^{o}C ; IR (ν /cm^{-1}): 3483, 3332 (NH_2) , 2210(conjugated CN),1631(CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 1.19-1.24 (t,J = 7Hz,3H,CH_3) ,3.70(s,3H,OCH_3),3.87(s,3H,OCH_3),4.26-4.29(q,J = 7Hz,2H,CH_2) ,4.5.0 (s,1H,pyranH-4),7.14-8.07 (m,10H, aromatic protons) ,8.82 (s,2H, NH_2).*Anal*.Calcd.for $C_{23}H_{21}N_3O_4$ (403.15): C,68.47; H, 5.25; N , 10.42.Found: C,68.60 ; H,5.36; N,11.33.

Formation of 6-aryl-1-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo[4,3-*b*] pyridine -5-carbonitriles **11** a-f :

A mixture of arylmethylenemalononitriles **1** (0.01mole) and 1,5-dimethyl-4-nitroso-2-penyl-1*H*-pyrazol-(3(2*H*)-one **8**(0.01mole) in ethanol (50ml),containing few drops of piperidine were refluxed for three hours .The formed solid products were collected by filtration ,recrystallised from the suitable solvents and then identified as **11** a-f .

6-(3,4-Dimethoxyphenyl)-1-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo[4,3-*b*]-5-carbonitrile **11** a : Formed orange crystals in 70 % yield , from ethanol / dimethylformamide,m.p.224-226^{o}C ; IR (ν /cm^{-1}): 2225(conjugated CN),1704(CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.30 (s,3H,*N*-CH_3) ,3.76(s,3H,OCH_3) ,3.87 (s,3H,OCH_3), 7.18-7.64 (m,8H, aromatic protons),8.42(s,1H, pyridine H-4) . *Anal* . Calcd . for $C_{22}H_{18}N_4O_3$ (403.15): C,68.38; H, 4.70; N , 14.50.Found: C,68.60 ; H,4.36; N,14.33.

1-Methyl-3-oxo-6-(3-phenoxyphenyl)-2-phenyl-2,3-dihydro-1*H*-pyrazolo [4,3-*b*]pyridine-5-carbonitrile **11** b : Formed pale yellow crystals in 73 % yield , from ethanol / dimethylformamide,m.p.244-246^{o}C ; IR (ν /cm^{-1}): 2229(conjugated CN),1689 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.34 (s,3H,*N*-CH_3), 7.06-7.67 (m,8H, aromatic protons),8.48(s,1H, pyridine H-4) . *Anal* . Calcd . for $C_{26}H_{18}N_4O_2$ (418.45): C,74.63; H, 4.34; N , 13.39.Found: C,74.70 ; H,4.26; N,13.33.

6-(4-Hydroxy-3-methoxyphenyl)-1-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo[4,3-*b*]-5-carbonitrile **11** c : Formed red crystals in 65 % yield , from ethanol,m.p.260-262^{o}C ; IR (ν /cm^{-1}): 2224(conjugated CN),1661 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.38 (s,3H,*N*-CH_3) ,3.87

(s,3H,OCH_3), 6.97-7.59 (m,8H, aromatic protons),8.37(s,1H, pyridine H-4) ,9.94(s,1H,OH) ; ^{13}C-NMR (DMSO-d_6)(δ,ppm):38.02(*N*-CH_3), 56.32(OCH_3),113.89-148.77(aromatic carbons), 118.79(CN), 158.42 (CO) . *Anal* . Calcd . for $C_{21}H_{16}N_4O_3$ (372.38): C,67.73; H, 4.33; N , 15.05.Found: C,67.83 ; H,4.26; N,15.40.

6-(3-Chlorophenyl)-1-methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo [4,3-*b*]-5-carbonitrile **11** d : Formed yellow crystals in 60 % yield , from ethanol / dimethylformamide,m.p.246-248^{o}C ; IR (ν /cm^{-1}): 2228 (conjugated CN),1695 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.31 (s,3H,*N*-CH_3) , 7.47-7.85 (m,10H, aromatic protons),8.51(s,1H, pyridine H-4) . *Anal* . Calcd . for $C_{20}H_{13}ClN_4O$ (360.80): C,66.58; H, 3.63; N , 15.53.Found: C,66.83 ; H,3.44; N,15.42.

1-Methyl-6-(4-nitrophenyl)-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo [4,3-*b*]-5-carbonitrile **11** e : Formed orange crystals in 65 % yield , from ethanol / dimethylformamide,m.p.>300^{o}C ; IR (ν /cm^{-1}): 2225 (conjugated CN),1701 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.31 (s,3H, *N*-CH_3) , 7.47-7.54 (m,5H, aromatic protons),8.03-8.06 (d,J=7Hz, 2H, aromatic protons),8.46-8.49(d,J=7Hz,2H,aromatic protons), 8.56 (s,1H, pyridine H-4) . *Anal* . Calcd . for $C_{20}H_{13}ClN_4O$ (360.80): C,66.58; H, 3.63; N , 15.53.Found: C,66.83 ; H,3.44; N,15.42.

1-Methyl-6-(4-nitrophenyl)-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo [4,3-*b*]-5-carbonitrile **11** f : Formed yellow crystals in 80 % yield , from ethanol / dimethylformamide,m.p.>300^{o}C ; IR (ν /cm^{-1}): 2225 (conjugated CN),1691 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.35 (s,3H, *N*-CH_3) , 6.97-7.59 (m,7H, aromatic protons), 8.37 (s,1H, pyridine H-4) . *Anal* . Calcd . for $C_{18}H_{11}BrN_4OS$ (411.28): C,52.57; H, 2.70; N , 13.62.Found: C,52.46 ; H,2.54; N,13.42.

Preparation of 2-amino-7,7-dimethyl-4-(4-nitro-1H-pyrrol-2-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **14**:

A suspension of 2-((4-nitro-1*H*-pyrrol-2-yl)methylene)malononitrile **1**g(0.01mole) in ethanol (50ml) containing (0.01mole) of 5,5-dimethylcyclohexane-1,3-dione ,was treated with few drops of triethylamine and heated under reflux for five hours .The precipitate formed was collected by filtration ,recrystallised from ethanol as colorless

crystals,in 60% yield,m.p.218-220^{o}C; IR (ν /cm^{-1}): 3481,3326(NH_2),2196 (conjugated CN); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 0.98(s,3H,CH_3), 1.02 (s,3H,CH_3), 2.18(s,2H,CH_2),3.18(s,2H,CH_2),4.28(s,1H,pyran H-4),6.31-6.32(t,J= 7Hz,1H,aromatic proton),7.06(s,2H,NH_2), 7.70-7.72(t,J= 7Hz, 1H,aromatic proton),11.92(s,1H,NH). *Anal* . Calcd . for $C_{16}H_{16}N_4O_4$ (328.32): C,58.53; H, 4.91; N , 17.06.Found: C,58.65 ; H,4.74; N,17.12.

Formation of 6-amino -4-(4-nitro-1H-pyrrol-2-yl)-2oxo-1-((-thiophen-2-yl)ethylidene)amino)-1,2-dihydropyridine-3,5-dicarbonitrile **19** :

A mixture of 2-cyano-*N*'-(1-(thiophene-2-yl)ethylidene)acetohydrazide **15**(0.01mole) and 2-((4-nitro-1*H*-pyrrol-2-yl)methylene)malononitrile **1**g (0.01mole) in ethanol (50ml) containing catalytic amounts of piperidine was refluxed for three hours .The precipitate formed was collected by filtration ,recrystallised from ethanol / dimethylformamide as yellow crystals,in 60% yield,m.p.248-250^{o}C; IR (ν /cm^{-1}): 3447,3150 (NH_2,NH),2211 (conjugated CN),1658(CO); ^{1}H-NMR (DMSO-d_6) (δ,ppm) : 2.42 (s,3H,CH_3), 7.09-7.63(m,7H,aromatic proton) ,8.34(s,2H,NH_2),8.35(s,1H,NH), 12.92(s,1H,NH). *Anal* . Calcd . for $C_{17}H_{11}N_7O_3S$ (393.38): C,51.90; H, 2.82; N , 24.92.Found: C,51.78 ; H,2.76; N,24.87.

Condensation of *N*-(5-cyanomethyl)-1,3,4-thiadiazol-2-yl)benzaminde **20** with aromatic aldehydes:Formation of 2-(4-aryl)vinyl-N-[5-1-cyano) -1,3,4-thiadiazol-2-yl)benzaminde **21**:

Compound **20** (0.01mole) in ethanol(50ml) was treated with (0.01mole) of aromatic aldehydes and few drops of piperidine.The reaction mixture was refluxed for two hours . The solids formed were collected by filtration and purified by recrystallization from the proper solvents then identified as **21**a,b.
(*E*)-*N*-(5-(1-cyano-2-(3,4-dimethoxyphenyl)vinyl)-1,3,4-2-yl)benzamide **21** a : Formed yellow crystals in 70 % yield , from ethanol / dimethylformamide, m.p. > 300^{o}C ; IR (ν /cm^{-1}):3419(NH), 2219 (conjugated CN),1653 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.83 (s,3H, OCH_3) , 3.86 (s,3H, OCH_3) , 7.16-8.15 (m,8H, 7H aromatic protons and 1H CH), 13.29 (s,1H, NH) . *Anal* . Calcd . for $C_{20}H_{16}N_4O_3S$ (392.43): C,61.21; H, 4.11; N , 14.28.Found: C,61.35 ; H,4.23; N,14.40.

(*E*)-*N*-(5-(1-cyano-2-(3-phenoxyphenyl)vinyl)-1,3,4-2-yl)benzamide **21** b : Formed yellow crystals in 70 % yield , from ethanol / dimethylformamide,m.p. > 300^{o}C ; IR (ν /cm^{-1}):3406(NH), 2225 (conjugated CN),1631 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 7.11-8.20 (m,8H, aromatic protons), 9.85 (brs,1H, NH) . *Anal* . Calcd . for $C_{24}H_{16}N_4O_2S$ (424.47): C,67.91; H, 3.80; N , 13.20.Found: C,67.74 ; H,3.65; N,13.40.

Formation of *N*-(6,8-dicyano-7-(aryl)-5-imino-5*H*-[1,3,4]thiadiazolo[3,2-*a*] pyridin-2-yl)benzamides **23** a-c :
Method A:
Equimolecular amounts of **20** (0.01mole) and the appropriate amounts of arylmethylenemalononitriles **1**a,b,f (0.01mole) in absolute ethanol (50ml)and catalytic amount of piperidine were refluxed for three hours.The solid products so formed were filtered off ,recrystallised and then identified as **23** a-c.
Method A:
Compounds **23** a-c were also prepared by reacting equimolecular amounts of **21**and malononitrile using the above reaction conditions.

N-(6,8-dicyano-7-(3,4-dimethoxyphenyl)-5-imino-5*H*-[1,3,4]thiadiazolo [3,2-*a*]pyridin-2-yl)benzamide **23** a : Formed yellow crystals in 73 % yield , from ethanol / dimethylformamide,m. p.162-164^{o}C ; IR (ν /cm^{-1}) :3423(NH), 2215 (conjugated CN),1652 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 3.83(s,3H,OCH_3), 3.83(s,3H,OCH_3),7.14-8.15 (m,9H, 8H aromatic protons and 1H,NH), 13.23 (s,1H, NH) . *Anal* . Calcd . for $C_{24}H_{20}N_6O_3S$ (472.13): C,67.91; H, 3.80; N , 13.20.Found: C,67.74 ; H,3.65; N,13.40.

N-(6,8-dicyano-7-(3-phenoxyphenyl)-5-imino-5*H*-[1,3,4]thiadiazolo [3,2-*a*]pyridin-2-yl)benzamide **23** b : Formed orange crystals in 73 % yield , from ethanol / dimethylformamide,m. p.167-169^{o}C ; IR (ν /cm^{-1}) :3423(NH), 2227 (conjugated CN),1659 (CO); ^{1}H-NMR (DMSO-d_6)(δ,ppm): 7.09-8.15 (m,13H, aromatic protons), 8.29(s,1H,NH),13.36 (s,1H, NH) . *Anal* . Calcd . for $C_{27}H_{16}N_6O_2S$ (488.52): C,66.38; H, 3.30; N , 17.20.Found: C,66.46 ; H,3.54; N,17.40.

N-(6,8-dicyano-7-(5-bromothiophen-2-yl)-5-imino-5*H*-[1,3,4]thiadiazolo [3,2-*a*] pyridin-2-yl)benzamide **23** c : Formed yellow crystals in 73 %

yield , from ethanol / dimethylformamide,m. p. > 300^{o}C ; IR (ν /cm^{-1}) :3447(NH), 2220 (conjugated CN),1623 (CO); ^{1}H-NMR (DMSO-d$_6$) (δ,ppm): 7.46-7.73 (m,6H ,5H, aromatic protons and 1H ,NH),8.11-8.13(d,J =7Hz , 2H , aromatic protons), 8.48(s,1H,NH); ^{13}C-NMR (DMSO-d$_6$) (δ,ppm): 99.52,121.02, 128.96,129.17,132.30, 133.65, 138.46,138.64,140.07,143.81(aromatic carbons),116.22(CN), 166.04 (C=NH),190.24(C=O). *Anal* . Calcd . for $C_{19}H_9BrN_6OS2$ (481.25): C,47.41; H, 1.88; N , 17.46.Found: C,47.65 ; H,2.02; N,17.35.

3.RESULTS AND DISCUSSIN

It has been found that ,the reaction of 3-acetyl-4-hydroxyquinolin-2(1*H*)-ones **2**a,b with arylmethylenenitriles **1a** in ethanol and in the presence of catalytic amounts of piperidine ,resulted in the formation ,2-amino-4-aryl-6-(4-hydroxy-2-oxo-1,2-dihydroquinolin-yl)-3-substituuted -4*H*-pyran derivatives **4** and 2-amino-4-aryl-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline derivatives **7**. Structures **4** were readily ruled out by analytical and spectral data of the reaction products.Thus, structures **7** were established for the reaction products based on ^{1}H-NMR spectra which revealed the presence of pyran-4*H* protons at δ = 4.5-5.0 ppm. Compounds **7** were assumed to be formed *via* addition of quinolinyl C-3 to the π-deficient center in **2** to give the adduct **5** , which hyrolysed and readily eliminate its acetyl group under the reaction conditions to give the intermediates **6**.These were cyclised to **7**.Elimination of the acetyl groups in this reactions parallels the reported deacetylation of similar systems under similar conditions [1,2]. Compounds **2** may be existing as 4-quinolone[1,2] , at which quinolin-3-position becomes more acidic than its acetyl group.Moreover,the steric effect in the intermediates **5** facilitate deacetylation process .The structures of compounds **7** were also confirmed by synthesizing them from reaction of 4-hydroxyquinolin-2(1*H*)-ones **3**a,b under the same reaction conditions(*c.f.*Scheme 1).

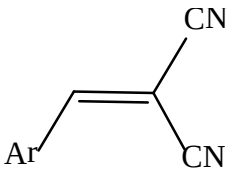
Also, we have found that, arylidenemalononitriles **1**a-f reacted readily with 1,2-dihydro-2,3-dimethyl-4-nitroso-1-phenylpyrazol-5-one **8** to give products *via* hydrogen cyanide and water elimination. 6-Aryl-1-methyl-3-oxo-1,2,3-trihydro-2-phenylpyrazolo[4,3-*b*]pyridine-5-carbonitriles **11**a-f structures were assigned as reaction products based on their elemental analysis and spectral data. Also, IR spectra of **11**a-f showed absorption bands corresponding to the cyano and carbonyl groups of phenazonyl moieties. Compounds **11** were assumed to be formed *via* addition of the

methyl group in **8** to the activated double bond in **1** to give the adducts **9** which cyclized to give the intermediates **10**. The later aromatized through elimination of hydrogen cyanide or ethyl formate and water to give**11** . Similar sequence for the formation of similar systems has been reported before [2] (*c.f.* Scheme 2).

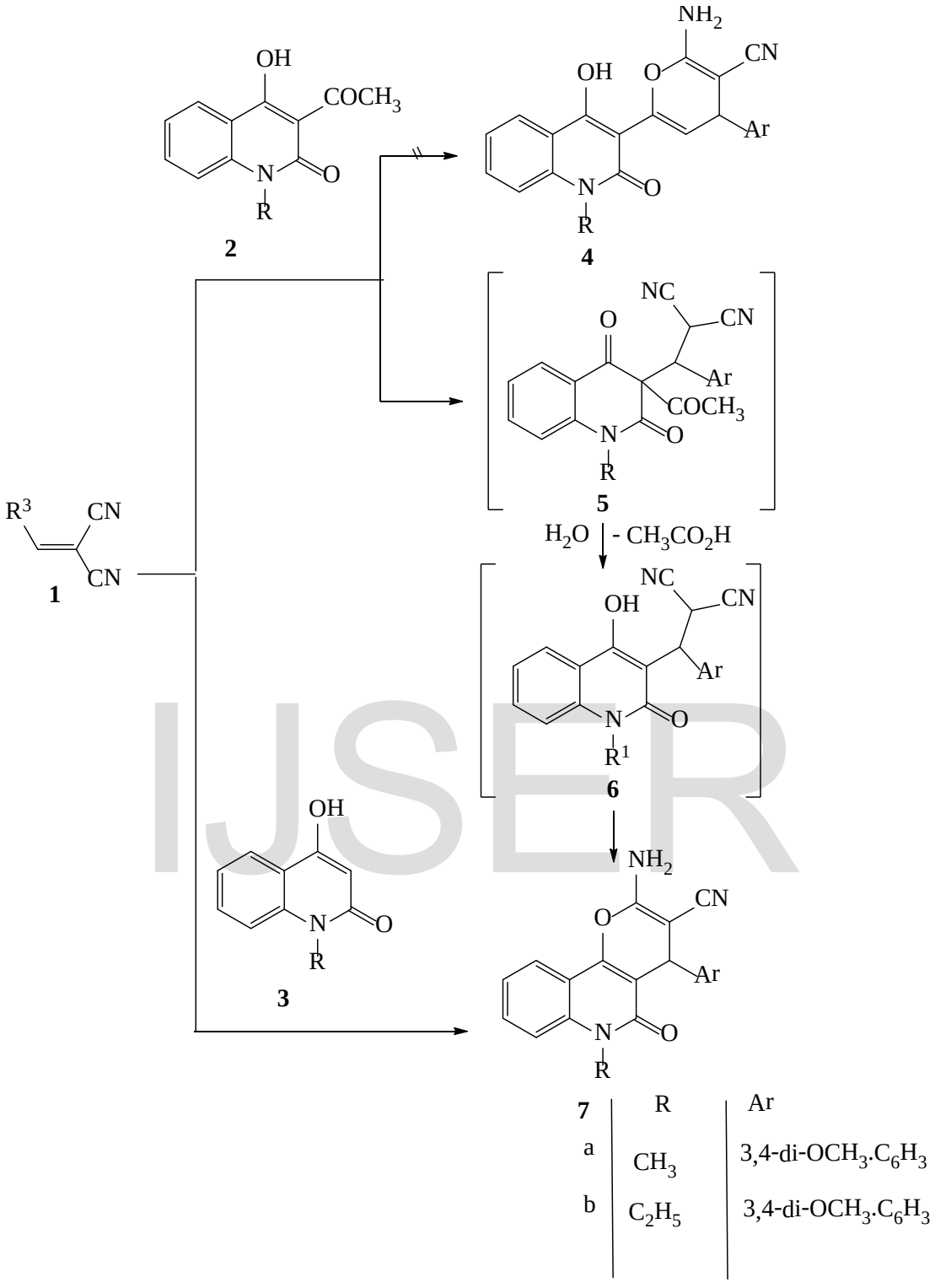
In addition ,5,5-dimethylcyclohexan-1,3-dione **12** reacted with 2-((4-nitro-1*H*-pyrrol-2-yl)methylene)malononitrile **1**g in ethanolic / triethylamine to afford 1:1 adduct .This adduct was formulated as 2-amino-7,7-dimethyl-4-(4-nitro-1*H*-pyrryl-2-yl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile **14**.

2-Cyano-*N*'-(1-(thiophene-2-yl)ethylidene)acetohydrazide **15** reacted with 2-((4-nitro-1*H*-pyrrol-2-yl)methylene)malononitrile **1**g in ethanol catalysed by piperidine to give either 2-cyano-*N*-(3-cyano-2-imino-5-methyl-6-(4-nitro-1*H*-pyrrol-2-yl)-4-(thiophen-2-yl)pyridine-1(2*H*)-yl)acetamide **17** or 6-amino-4-(4-nitro-1*H*-pyrrol-2-yl)-2-oxo-1-((1-thiophen-2-yl)ethylidene)amino)-1,2-dihydropyridine-3,5-dicarbonitrile **19**.Structure **17** was excluded by ^{1}H-NMR spectrum which clearly indicates the absence of methylene protons at $\delta = 4.5$ ppm.Thus, structure **19** was was elucidated as a reaction product from its analytical and spectral data(*c.f.*experimantal).Compound **19** was suggested to be obtained *via* addition of the activated the active methylene group in **15** to the *pi*-deficient carbon in 2-((4-nitro-1*H*-pyrrol-2-yl)methylene) malononitrile **1**g to give the adduct **18** which cyclised and dehydrogenated to give **19** (*c.f.*scheme 3).

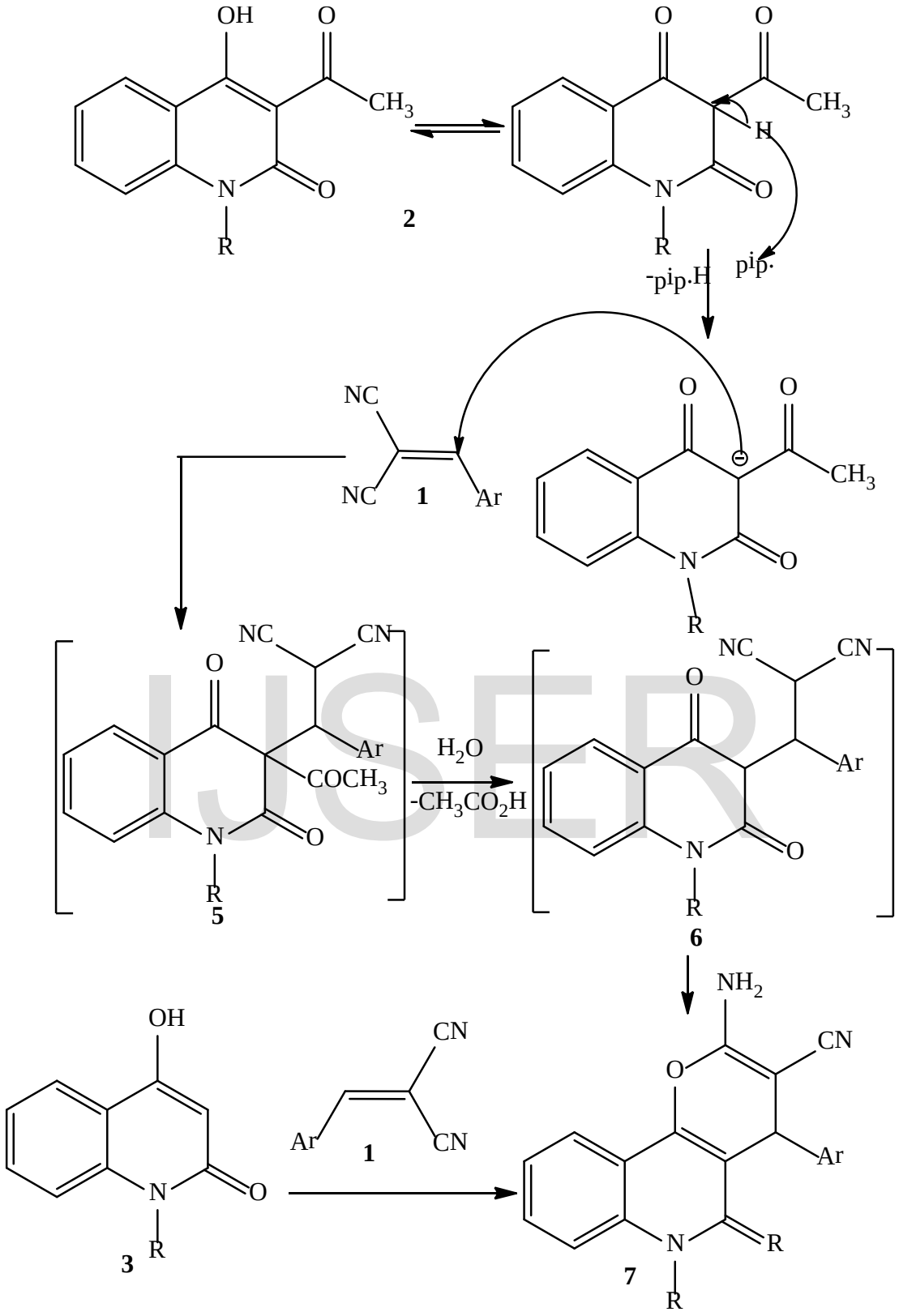
We have also investigated the reactivity of arylmethylenemalononitriles **1** towards alkylheterocycles .Thus,we have found that, arylmethylenemalononitriles **1**a,b,f reacted readily with *N*-(5-(cyanomethyl)-1,3,4-thiadiazol-2-yl)benzamide **20** in ethanolic / piperidine to yield either *N*-(6,8-dicyano-7-(aryl)-5-imino-5*H*-[1,3,4] thiadiazolo[3,2-*a*]pyridin-2-yl)benzamides **23** or *N*-(5-amino-7-aryl-6,8-dicyano-7H-[1,3,4]thiadizolo[3,2-*a*]pyridine-2-yl)benzamides **24**. ^{1}H-NMR spectra of the reaction products revelead no signals at $\delta \approx 4.5$-5.0 ppm for one proton linked to sp^3 carbon corresponding to pyridine H-4 protons.Consequently,Structures **23** were elucidated as reaction products.The formation of **23** was assumed to proceed *via* Michael type addition of the active methylene group in *N*-(5-(cyanomethyl)-1,3,4-thiadiazol-2-yl)benzamide **20** to the activated double bonds in the arylmethylenemalononitriles **1** to give Michael adducts **22** ,which readily cyclised and dehydrogenated to afford the final isolable products **23** (*c.f.*scheme 4).



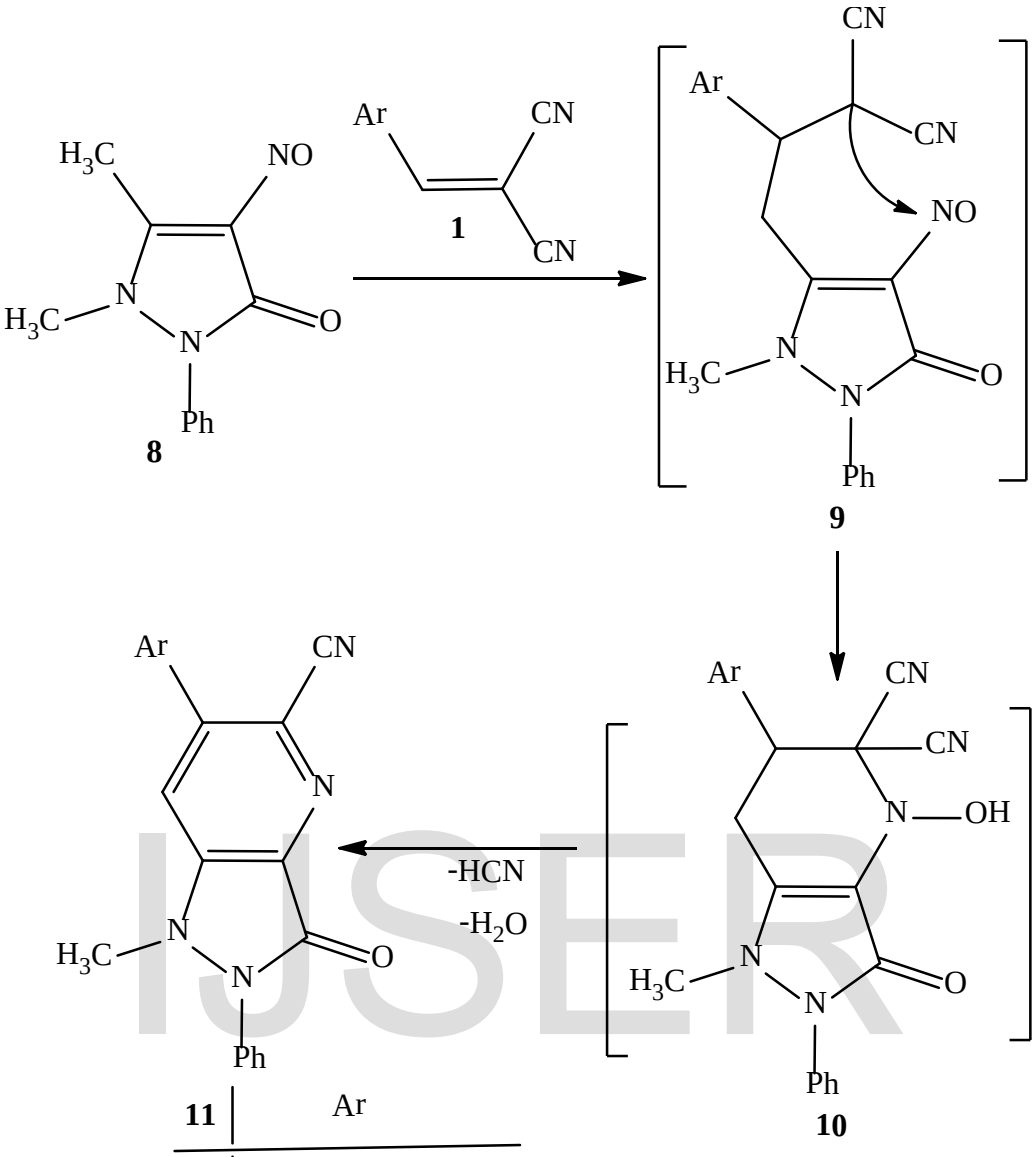
1	Ar
a	3,4-di-$OCH_3.C_6H_3$
b	3-$OPh.C_6H_4$
c	4OH,3-$OCH_3.C_6H_3$
d	3-$Cl.C_6H_4$
e	4-$NO_2.C_6H_4$
f	5-bromo-2-thien$_y$l
g	4-nitro-2-py^{rr}$_y$l



Scheme 1:Formation of 4H-pyrano[3,2-c]quinolines **7**

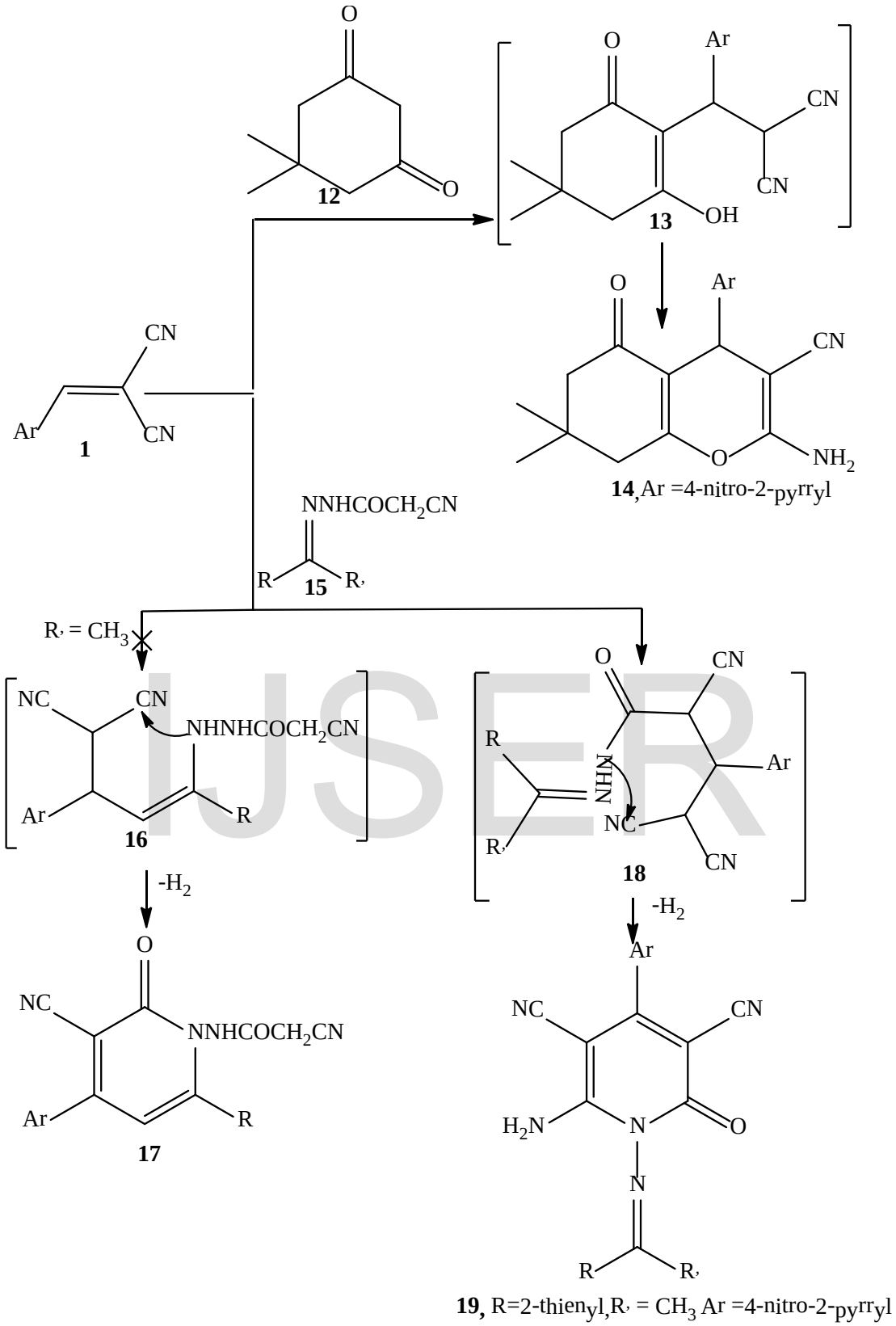


Mechanim for formation of compounds **7**

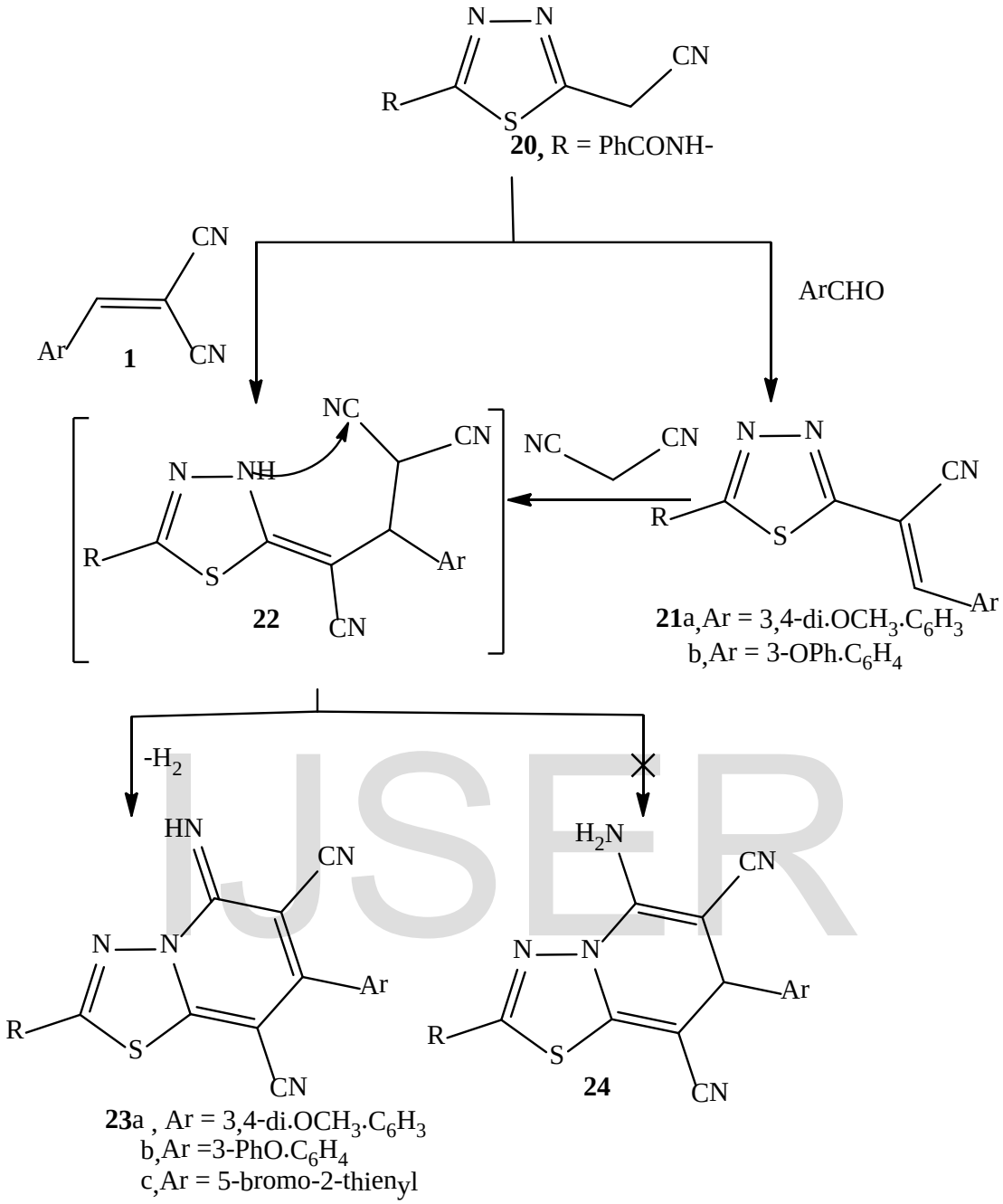


11	Ar
a	3,4-di-$OCH_3.C_6H_3$
b	3-$OPh.C_6H_3$
c	4-OH,3-$OCH_3.C_6H_3$
d	3-$Cl.C_6H_4$
e	4-$NO_2.C_6H_4$
f	5-bromo-2-thienyl

Scheme 2 :Formation of pyrazolo[4,3-b]pyridines **11**



Scheme 3 :Formation of benzo[b]pyrans **14** and pyridine **19**



Scheme 4 : Formation of 1,3,4-thiadiazolo[2,3-*b*]pyridines **23**

Conclusion

We conclude that,several new 4*H*-pyrano[3,2-*c*]quinoline,pyrazolo[4,3-*b*] pyridine,4*H*-benzo[*b*]pyran , pyridine and thiadiazolo[3,2-*a*]pyridine derivatives were prepared *via* reacting active hydrogen reagents with arylmethylenemalononitriles as readily obtainable starting materials that could be useful for biological evaluation studies.

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