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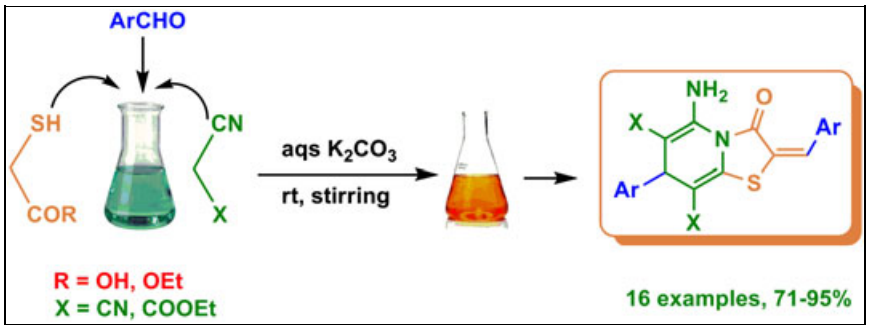
Received August 20, 2011
DOI 10.1002/jhet.1650
Published online 31 October 2013 in Wiley Online Library (wileyonlinelibrary.com).



Facile, three-component domino reactions of readily available thioglycolic acid/ethyl thioglycolate, aromatic aldehydes, and malononitrile/ethyl cyanoacetate in aqueous potassium carbonate at room temperature afforded thiazolo[3,2-*a*]pyridine derivatives chemoselectively in good to excellent yield. All the formed 4*H*-chromenes were characterized by spectral and X-ray methods.

J. Hetercyclic Chem., **51**, 244 (2014).

INTRODUCTION

Under green chemical protocol, the destructive volatile organic solvents normally employed in organic synthesis are to be replaced by nontoxic, nonvolatile media such as ionic liquids, polyethylene glycol, and water [1]. In recent years, many organic transformations have been effected using water as the solvent with notable success [2].

Thiazolopyridine moiety was found in wide range of biologically active compounds. Thiazolo[3,2-*a*]pyridine derivatives are found to exhibit a broad spectrum of potent anticancer activity and are useful for chemotherapy of various cancers, such as leukemia, lung cancer, and melanoma [3–5]. Also thiazolo[3,2-*a*]pyridines have many important bioactivities such as beta-amyloid production inhibitor [6], potent CDK2-cyclin A inhibitor [7], potential uterus stimulant [8], coronary dilator, antihypertensive, muscle relaxant [9], antibacterial, and antifungal [10]. These derivatives have been found to scavenge free radicals [11]. Some biologically active compounds with this nucleus are shown in Figure 1 [12–14]. Obviously, the synthesis of many new compounds of this class of compound may give a library of compounds as possible candidates for different biological activities. This article describes the synthesis of a set of densely substituted thiazolopyridine derivatives with cyano/carbethoxy, amino, aryl, and arylidene groups over the periphery of the basic nucleus.

RESULTS AND DISCUSSION

The synthesis of thiazolopyridine skeleton has earlier been achieved by a multistep reaction. The reaction of benzylidene malononitrile with N-substituted thiocarbamoylacetamides and methyl 2-chloroacetate using piperidine as catalyst in methanol has yielded the required heterocyclic moiety [15]. Recently, from thioglycolic acid, aromatic aldehyde, and malononitrile, with the use of microwave irradiation at an elevated temperature, a set of thiazolo[3,2-*a*]pyridines has been prepared, and their antioxidant and cytotoxic activities have been studied [11]. In the present work, the scope of this reaction has been widened. It is found that this water-mediated reaction can be effected even at room temperature without the use of microwave irradiation. It is also noticed that the reaction is very much accommodative and more productive with thioglycolic ester in the place of thioglycolic acid. In addition, the reaction has gone with all ease, when ethyl cyanoacetate has been employed instead of malononitrile. This has led to more products with carbetoxy-substituted thiazolo[3,2-*a*]pyridines, although in the original work, only the cyano-substituted thiazolo[3,2-*a*]pyridines alone have been synthesized [11].

Thus the synthesis of thiazolo[3,2-*a*]pyridines (**4a–p**) via tandem cyclization in 5% aqueous potassium carbonate has been achieved at room temperature by the reaction of thioglycolic acid or ethyl thioglycolate (**1**) and malononitrile

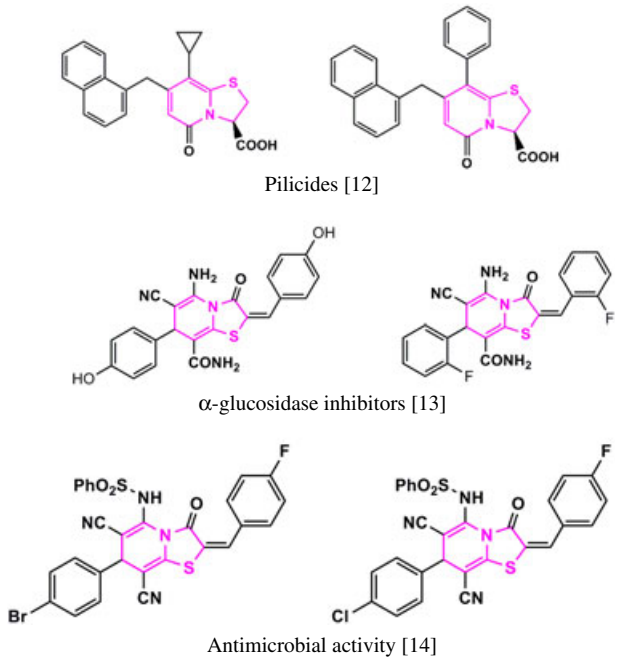


Figure 1. Selected examples of thiazolopyridines with biological and pharmacological activities. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

or ethyl cyanoacetate (**2**) with variety of aldehydes (**3**) in 1:2:2 ratio in the presence of tetrabutyl ammonium bromide. The purification is not tedious as mere water wash followed by recrystallization from 3:2 chloroform/ethanol mixtures gave quantitative yield of the products (**4a–p**) (71–95%; Table 1, Scheme 1). All the synthesized thiazolo[3,2-*a*] pyridines derivatives (**4a–p**) have been completely characterized by spectral and single crystal X-ray analysis. The complete assignment of signals and 2D connectivities for a representative case **4e** is shown in Figure 2. Although some cyano-substituted thiazolopyridines of the type **4** have been reported [11], all the compounds reported in the present work are new and hitherto unreported.

When the reaction was carried out in the presence of thioglycolate instead of the respective acid, the yield was enhanced and the reaction time was appreciably reduced, suggesting that the former is the candidate of choice for this reaction. Between malononitrile and ethyl cyanoacetate, it can be noticed that the reaction is sluggish with cyanoacetate taking nearly 4 h for completion, whereas with malononitrile, less than half an hour is sufficient for completion of the reaction, although there is no apparent difference in the yield. The mechanism of the reaction is well documented [11].

From the crystal structure of **4e** (CCDC number 840149) (Figure 3), it is clear that the pyridine, thiazole, and arylidene rings are in the same plane and the aryl ring present as the substituent in the pyridine ring goes out of plane from the rest of the molecule. The pyridine ring has a half-chair conformation. The spectral data also support the assigned structure.

EXPERIMENTAL

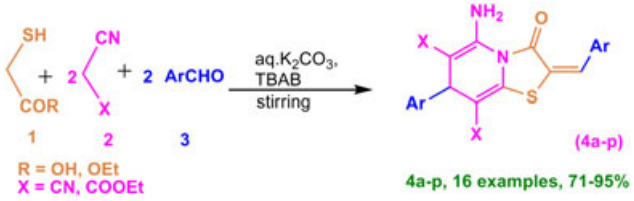
All chemicals used in this investigation were of reagent-grade quality and used without further purification. All melting points were recorded in open capillaries and are uncorrected. The ^{1}H and ^{13}C nmr spectra were recorded on a Bruker 300-MHz spectrometer (Bruker, Fallanden, Switzerland) at 300 and 75 MHz, respectively, in $CDCl_3$/DMSO-d_6 using TMS as internal standard. The chemical shifts are presented in δ scale. Microanalyses were carried out on a PerkinElmer (PerkinElmer, Lv Venlo, The Netherlands) instrument.

Table 1

Synthesis of thiazolopyridines **4**.

			1 (R = OH)		**1** (R = OEt)	
Entry	Aryl in **3**	X in **2**	Time (h)	Yield (%)	Time (h)	Yield (%)
4a	Phenyl	COOEt	24	80	4	92
4b	4-Chlorophenyl	COOEt	24	76	4	83
4c	2,4-Chlorophenyl	COOEt	24	78	4	85
4d	4-Methylphenyl	COOEt	24	80	4	94
4e	4-Methoxyphenyl	COOEt	24	71	4	90
4f	2-Methoxyphenyl	COOEt	24	76	4	95
4g	2,5-Methoxyphenyl	COOEt	24	72	4	93
4h	3,5-Methoxyphenyl	COOEt	24	75	4	92
4i	Phenyl	CN	8	78	0.5	95
4j	4-Chlorophenyl	CN	8	73	0.5	91
4k	2,4-Chlorophenyl	CN	8	75	0.5	89
4l	4-Methylphenyl	CN	8	80	0.5	92
4m	4-Methoxyphenyl	CN	8	71	0.5	94
4n	2-Methoxyphenyl	CN	8	74	0.5	93
4o	2,5-Methoxyphenyl	CN	8	77	0.5	90
4p	3,5-Methoxyphenyl	CN	8	75	0.5	93

Scheme 1



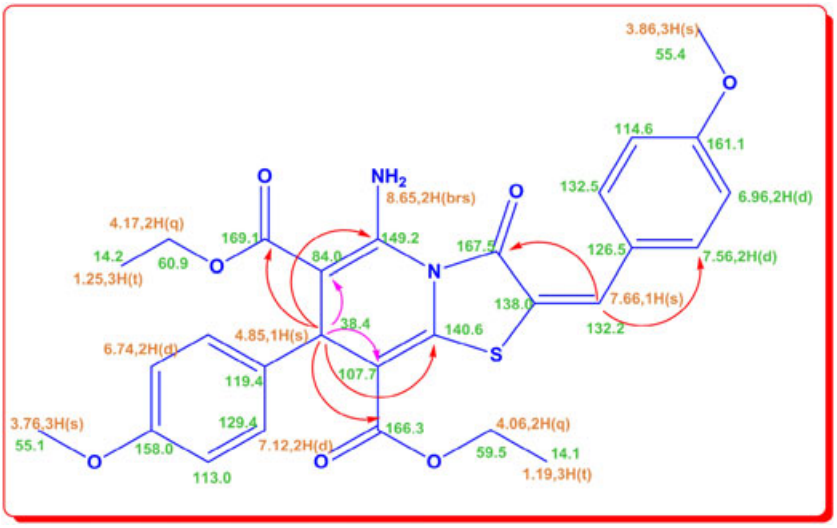


Figure 2. HMBC correlation with ^{1}H and ^{13}C nmr of **4e**. Rose and red arrows show two and three bond connectivities, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

General procedure for the synthesis of thiazolo[3,2-*a*] pyridines (4). To a mixture of arylaldehyde (2.1 mmol) and malononitrile/ethyl cyanoacetate (2.1 mmol), ethyl thioglycolate/ethyl thioglycolic acid (1 mmol) was added and stirred at room temperature. The reaction mass was thoroughly mixed with 5% potassium carbonate (25 mL) at room temperature, and then the reaction mixture was stirred for their optimal condition. Quantitative amount of thiazolo[3,2-*a*]pyridines were deposited in a solution, which was filtered and thoroughly washed with water. The crude thiazolo[*3*,2-*a*]pyridines were recrystallized from 3:2 mixture of chloroform/ethanol.

***(E)*-Diethyl 5-amino-2-benzylidene-3-oxo-7-phenyl-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4a).** This compound was obtained as a yellow solid, mp 263–264 (62)°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.20 (m, 6H), 4.04 (q, J = 13.4 Hz, 2H), 4.17 (q, J = 13.4 Hz, 2H), 4.89 (s, 1H), 7.12–7.22 (m, 5H), 7.41 (m, 3H), 7.60 (d, J = 7.5, 2H), 7.71 (s, 1H), 8.66 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.0, 14.1, 39.3, 59.6, 61.0, 83.8, 107.9, 122.4, 126.2, 127.6, 128.4, 129.0, 130.0, 130.5, 132.3, 133.6, 140.6, 145.4, 149.1, 166.1, 167.2, 169.0.

Anal. Calcd for $C_{26}H_{24}N_2O_5S$: C, 65.53; H, 5.08; N, 5.88%. Found: C, 65.47; H, 4.96; N, 5.83%.

***(E)*-Diethyl 5-amino-2-(4-chlorobenzylidene)-7-(4-chlorophenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4b).** This compound was obtained as a yellow solid, mp 272–274°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.18 (m, 6H), 4.15 (m, 4H), 5.24 (s, 1H) 7.14 (d, J = 7.2 Hz, 2H), 7.37 (m, 4H), 7.58 (d, J = 7.2 Hz, 2H), 7.73 (s, 1H), 8.71, (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.3, 14.5, 38.9, 60.1, 61.7, 82.5, 107.0, 124.9, 126.8, 127.3, 128.2, 129.5, 130.3, 130.4, 132.8, 133.0, 133.2, 134.5, 136.7, 142.1, 142.3, 150.0, 166.3, 166.8, 169.2.

Anal. Calcd for $C_{26}H_{22}Cl_2N_2O_5S$: C, 57.25; H, 4.07; N, 5.14%. Found: C, 57.21; H, 4.01; N, 5.12%.

***(E)*-Diethyl 5-amino-2-(2,4-dichlorobenzylidene)-7-(2,4-dichlorophenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4c).** This compound was obtained as a yellow solid, mp 251–252°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.19 (m, 6H), 4.13 (m, 4H), 5.25 (s, 1H) 7.13 (s, 2H), 7.32 (m, 2H), 7.50 (s, 1H), 7.59 (d, J = 7.8 Hz 1H), 8.01 (s, 1H), 8.80 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.3, 14.5, 38.9, 60.1, 61.7, 82.5, 107.0, 124.9, 126.8, 127.3, 128.2, 129.5, 130.3, 130.4, 132.8, 133.0, 133.2, 134.5, 136.7, 142.1, 142.3, 150.0, 166.3, 166.8, 169.2.

Anal. Calcd for $C_{26}H_{20}Cl_4N_2O_5S$: C, 50.83; H, 3.28; N, 4.56%. Found: C, 50.79; H, 3.25; N, 4.51%.

***(E)*-Diethyl 5-amino-2-(4-methylbenzylidene)-3-oxo-7-p-tolyl-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4d).** This compound was obtained as a yellow solid, mp 266–267°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.21 (m, 6H), 2.27 (s, 3H), 2.39 (s, 3H), 4.06 (q, J = 14.4 Hz, 2H), 4.17 (q, J = 14.4 Hz, 2H), 4.86 (s, 1H) 7.00 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 7.2 Hz 1H), 7.68 (s, 1H), 8.63 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.4, 14.6, 21.4, 21.9, 39.3, 60.0, 61.4, 84.5, 108.4, 121.7, 128.8,

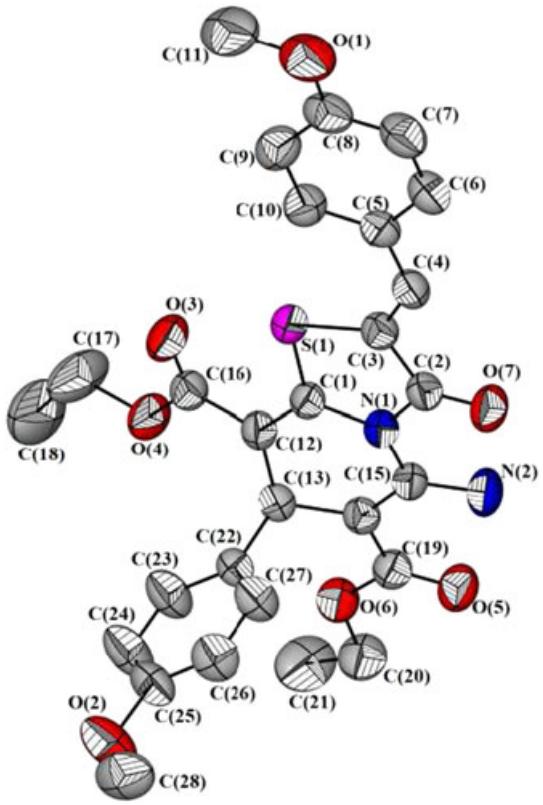


Figure 3. ORTEP diagram of compound **4e**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

130.2, 131.0, 131.4, 132.8, 136.1, 141.0, 141.1, 143.0, 149.6, 166.6, 167.8, 169.5.

Anal. Calcd for $C_{28}H_{28}N_2O_5S$: C, 66.65; H, 5.59; N, 5.55%. Found: C 66.62; H, 5.54; N, 5.49%.

***(E)*-Diethyl 5-amino-2-(4-methoxybenzylidene)-7-(4-methoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4e)**. This compound was obtained as a yellow solid, mp 277–278°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.22 (m, 6H), 3.75 (s, 3H), 3.85 (s, 3H), 4.05–4.21 (m, 4H), 4.85 (s, 1H), 6.74 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 9.00 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 9.00 Hz 1H), 7.66 (s, 1H), 8.65 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.1, 14.2, 55.1, 55.4, 59.5, 60.9, 84.0, 107.7, 113.0, 114.6, 119.4, 126.5, 129.4, 132.2, 132.5, 138.0, 140.6,149.2, 158.0, 161.1, 166.3, 167.5, 169.1.

Anal. Calcd for $C_{28}H_{28}N_2O_7S$: C, 62.67; H, 5.26; N, 5.22%. Found: C, 62.64; H, 5.21; N, 5.19%.

***(E)*-Diethyl 5-amino-2-(2-methoxybenzylidene)-7-(2-methoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*] pyridine-6,8-dicarboxylate (4f)**. This compound was obtained as a yellow solid, mp 257–258°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.20 (m, 6H), 3.65 (s, 3H), 3.90 (s, 3H), 4.01–4.16 (m, 4H), 4.98 (s, 1H), 6.79 (m, 2H), 6.92 (d, J = 8.10 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 8.17 (s, 1H), 8.68 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.0, 14.1, 37.3, 55.3, 55.5, 59.3, 60.7, 81.5, 105.4, 110.8, 111.0, 119.4, 120.8, 122.1, 122.9, 126.8, 127.5, 129.6, 131.2, 131.5, 132.4, 142.0, 150.3, 158.1, 158.3, 166.6, 167.4, 169.4.

Anal. Calcd for $C_{28}H_{28}N_2O_7S$: C, 62.67; H, 5.26; N, 5.22%. Found: C, 62.65; H, 5.23; N, 5.17%.

***(E)*-Diethyl 5-amino-2-(2,5-dimethoxybenzylidene)-7-(2,5-dimethoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4g)**. This compound was obtained as a yellow solid, mp 257–258°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.22 (m, 6H), 3.60 (s, 3H), 3.76 (s, 3H), 3.82 (s, 3H), 3.85 (s, 3H), 4.04–4.14 (m, 4H), 4.90 (s, 1H), 6.66 (s, 2H), 6.86 (m, 3H), 7.16 (d, J = 2.7 Hz, 1H), 8.09 (s, 1H), 8.68 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.5, 14.7, 38.1, 56.0, 56.3, 56.5, 56.5, 59.8, 61.1, 81.8, 105.7, 112.5, 112.9, 114.9, 117.6, 119.0, 122.7, 123.0, 123.9, 127.3, 132.8, 142.3, 150.8, 153.1, 153.2, 153.3, 153.9, 166.8, 167.7, 169.8.

Anal. Calcd for $C_{30}H_{32}N_2O_9S$: C, 60.39; H, 5.41; N, 5.70%. Found: C, 60.34; H, 5.37; N, 5.65%.

***(E)*-Diethyl 5-amino-2-(3,5-dimethoxybenzylidene)-7-(3,5-dimethoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarboxylate (4h)**. This compound was obtained as a yellow solid, mp 255–256°C; ^{1}H nmr ($CDCl_3$, 300 MHz): δ 1.21 (m, 6H), 3.58 (s, 3H), 3.74 (s, 3H), 3.80 (s, 3H), 3.83 (s, 3H), 4.07–4.16 (m, 4H), 4.87 (s, 1H), 6.22 (s, 2H), 6.43 (s, 2H), 7.98 (s, 2H), 8.12 (s, 1H), 8.67 (bs, 2H); ^{13}C nmr ($CDCl_3$, 75 MHz): δ 14.3, 14.4, 38.3, 55.8, 56.1, 56.3, 56.6, 59.5, 60.9, 82.7, 104.8, 111.9, 112.3, 113.9, 115.6, 119.0, 122.5, 123.4, 123.7, 127.1, 132.5, 141.9, 150.4, 155.6, 155.9, 160.9, 167.6, 167.9, 170.0.

Anal. Calcd for $C_{30}H_{32}N_2O_9S$: C, 60.39; H, 5.41; N, 5.70%. Found: C, 60.36; H, 5.35; N, 5.67%.

***(E)*-5-Amino-2-benzylidene-3-oxo-7-phenyl-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4i)**. This compound was obtained as a yellow solid, mp 243–244°C; ^{1}H nmr (DMSO-d_6, 300 MHz): δ 4.56 (s, 1H), 7.35–7.65 (m, 12H), 7.83 (s, 1H); ^{13}C nmr ($CDCl_3$, 75 MHz): 41.9, 64.6, 88.6, 116.7, 119.5, 128.9, 128.9, 129.7, 130.3, 131.0, 131.5, 132.7, 133.6, 142.5, 143.6, 148.6, 166.1.

Anal. Calcd for $C_{22}H_{14}N_4OS$: C, 69.09; H, 3.69; N, 14.65%. Found: C, 68.97; H, 3.65; N, 14.59%.

***(E)*-5-Amino-2-(4-chlorobenzylidene)-7-(4-chlorophenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4j)**. This compound was obtained as a yellow solid, mp 283–284°C; ^{1}H nmr (300 MHz, DMSO-d_6): 4.64 (s, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.59–7.62 (m, 6H), 7.73 (d, J = 8.2 Hz, 2H), 7.74 (s, 1H), ^{13}C nmr (75 MHz, DMSO-d_6): δ 40.8, 62.1, 87.0, 115.6, 118.3, 119.5, 120.9, 123.7, 129.7, 130.5, 131.2, 131.6, 132.0, 132.4, 132.7, 140.8, 142.9, 146.5, 165.8.

Anal. Calcd for $C_{22}H_{12}Cl_2N_4OS$: C, 58.55; H, 2.68; N, 12.41%. Found: C, 58.52; H, 2.61; N, 12.37%.

***(E)*-5-Amino-2-(2,4-dichlorobenzylidene)-7-(2,4-dichlorophenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4k)**. This compound was obtained as a yellow solid, mp 261–262°C; ^{1}H nmr (300 MHz, DMSO-d_6): δ 4.89 (s, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.22 (m, 4H), 7.43 (s, 1H), 7.48 (s, 1H), 7.55 (d, J = 7.2 Hz 1H), 8.01 (s, 1H).

Anal. Calcd for $C_{22}H_{10}Cl_4N_4OS$: C, 50.79; H, 1.94; N, 10.77%. Found: C, 50.73; H, 1.89; N, 10.71%.

***(E)*-5-Amino-2-(4-methylbenzylidene)-3-oxo-7-p-tolyl-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4l)**. This compound was obtained as a yellow solid, mp 265–266°C; ^{1}H nmr (300 MHz, DMSO-d_6): δ 2.19 (s, 3H), 2.25 (s, 3H), 4.63 (s, 1H), 7.09 (s, 2H), 7.12–7.20 (m, 6H), 7.41 (d, J = 7.5 Hz, 2H), 7.71 (s, 1H).

Anal. Calcd for $C_{24}H_{18}N_4OS$: C, 70.72; H, 4.42; N, 13.65%. Found: C, 70.67; H, 4.39; N, 13.61%.

***(E)*-5-Amino-2-(4-methoxybenzylidene)-7-(4-methoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4m)**. This compound was obtained as a yellow solid, mp 279–280°C;

^{1}H nmr (300 MHz, DMSO-d_6): δ 3.81 (s, 3H), 3.88 (s, 3H), 4.54 (s, 1H), 7.00 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.57 (s, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.83 (s, 1H).

Anal. Calcd for $C_{24}H_{18}N_4O_3S$: C, 65.14; H, 4.10; N, 12.66%. Found: C, 65.10; H, 3.99; N, 12.54%.

***(E)*-5-Amino-2-(2-methoxybenzylidene)-7-(2-methoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4n)**. This compound was obtained as a yellow solid, mp 279–280°C; ^{1}H nmr (300 MHz, DMSO-d_6): δ 3.84 (s, 3H), 3.91 (s, 3H), 4.87 (s, 1H), 6.91–7.12 (m, 5H), 7.21–7.46 (m, 5H), 7.79 (s, 1H).

Anal. Calcd for $C_{24}H_{18}N_4O_3S$: C, 65.14; H, 4.10; N, 12.66%. Found: C, 65.09; H, 4.07; N, 12.61%.

***(E)*-5-Amino-2-(2,5-dimethoxybenzylidene)-7-(2,5-dimethoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4o)**. This compound was obtained as a yellow solid, mp 259–260°C; ^{1}H nmr (300 MHz, DMSO-d_6): δ 3.76 (s, 3H), 3.80 (s, 3H), 3.88 (s, 3H), 3.97 (s, 3H), 4.81 (s, 1H), 6.80–7.01 (m, 6H), 7.42 (s, 2H), 7.92 (s, 1H).

Anal. Calcd for $C_{24}H_{22}N_4O_5S$: C, 62.14; H, 4.41; N, 11.15%. Found: C, 62.09; H, 4.38; N, 11.11%.

***(E)*-5-Amino-2-(3,5-dimethoxybenzylidene)-7-(3,5-dimethoxyphenyl)-3-oxo-3,7-dihydro-2*H*-thiazolo[3,2-*a*]pyridine-6,8-dicarbonitrile (4p)**. This compound was obtained as a yellow solid, mp 278–279°C; ^{1}H nmr (300 MHz, DMSO-d_6): δ 3.73 (s, 3H), 3.78 (s, 3H), 3.82 (s, 3H), 3.90 (s, 3H), 4.83 (s, 1H), 6.96–7.83 (m, 6H), 7.95 (s, 2H), 7.99 (s, 1H).

Anal. Calcd for $C_{24}H_{22}N_4O_5S$: C, 62.14; H, 4.41; N, 11.15%. Found: C, 62.10; H, 4.36; N, 11.09%.

Acknowledgment. The authors thank the DST, New Delhi, for the assistance under the IRHPA program for the NMR facility. One of the authors (M. B.) thanks the UGC for a research fellowship.

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