A convenient synthesis of 3-cyano-4-imino-2-methylthio-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole and its reactions with selected nucleophiles

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Abstract

2-Amino benzothiazole **(1)** and 2-amino-6-methyl benzothiazole **(4)** in *N*, *N*′-dimethyl formamide (DMF) and anhydrous potassium carbonate reacted with bis(methylthio)methylene malononitrile **(2)** to afford 3-cyano-4-imino-2-methylthio-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole **(3)** and 3-cyano-4-imino-2- methylthio-8-methyl-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole **(5)**, respectively. The latter were further reacted with selected N–, O– and C– nucleophiles such as aryl and hetaryl amines, substituted phenols and compounds with an active methylene group.

Keywords: 2-Amino-*6H*-methylbenzothiazole, bis(methylthio)methylenemalononitrile, 3-cyano-4-imino-2-methylthio-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole

Introduction

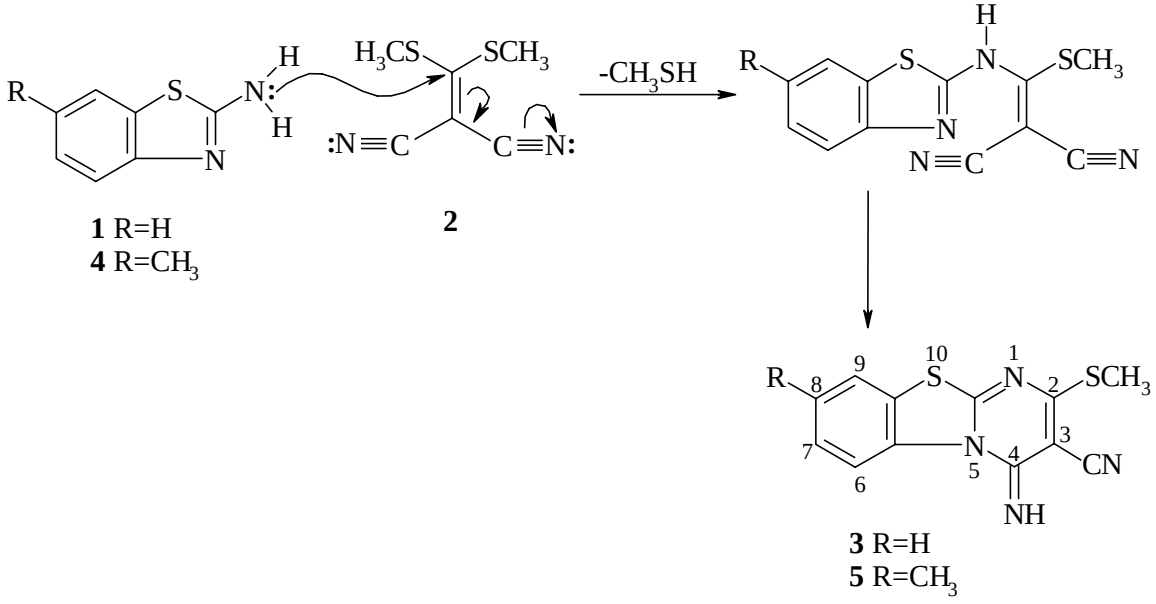
A survey of the literature reveals that few references are available on the synthesis and biological activity of heterocycles containing a benzothiazole fused with the pyrimidine ring[1-15]. In our recent publications[16-19], we have outlined convenient synthesis of new fused heterocyclic systems like pyrimidobenzothiazoles[16-17], pyrazolopyrimido benzothiazoles[18] and bezothiazolotriazepines and studies on their biological activities[19]. Further, there are few references available on the synthesis of heterocycles fused with an iminopyrimidine ring. Yoshihisa Okamoto and et. al.[20] reported the synthesis of 4-imino-*4H* pyrido [1,2-*a*] pyrimidine-3-carbonitirile and ethyl 4-imino-*4H*-thiozolo[1,2-*a*] pyrimidine-3-carboxylate. Benjaman Podanyi and et. al.[21] reported the synthesis and ring chain tautomerism of [(α-aza arylamino)methylene] malononitriles. Patrick Jimonet and his research group[22] reported the synthesis and pharmacological activity of 3-

substituted-2-imino benzothiazolines. These compounds were found to be three times more potent than 6-(trifluoromethoxy)-2-benzothiazolamine (Riluzole), a blocker of excitatory amino acid mediated neurotransmission. These observations have stimulated considerable interest to explore the synthesis of new compounds in which the iminopyrimidine ring is fused through the nitrogen atom with another biologically active nucleus such as benzothiazole. In the present work, we report the one pot synthesis of new heterocyclic compounds, 3-cyano-4-imino-2-methylthio-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole **(3)** and 3-cyano-4-imino-2-methylthio-8-methyl-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole **(5)** and preparation of their 2-substituted derivatives.

Results and Discussion

Compounds **3** and **5** were prepared from the reaction of bis(methylthio)methylene malononitrile **(2)** with 2-amino benzothiazole **(1)** and 2-amino-6-methyl benzothiazole **(4)** independently in the presence of *N,N'*- dimethyl formamide and a catalytic amount of anhydrous potassium carbonate, respectively. Gompper and Topfl[23] reported the preparation of compound **5** by refluxing 2-amino-6-methyl benzothiazole in triethyl amine and ethanol with bis(methylthio)methylene malononitrile for 30 minutes. The resulting product was crystallized from n-butanol with m. p. 260 – 265 °C and yield of only 13 %. The structure was established on the basis of elemental analysis only. However, in the present investigation we report the preparation of compound **5** with a 50 % yield. The structure of this compound with m. p. 220 °C was confirmed on the basis of elemental analysis, IR, PMR and mass spectral data. Spectral studies of compounds **3** and **5** show that these compounds are stable and do not exhibit any tautomerism.

Scheme 1 represents a tentative mechanism pathway for the formation of compounds **3** and **5**.



1 R=H
4 R=CH_3

2

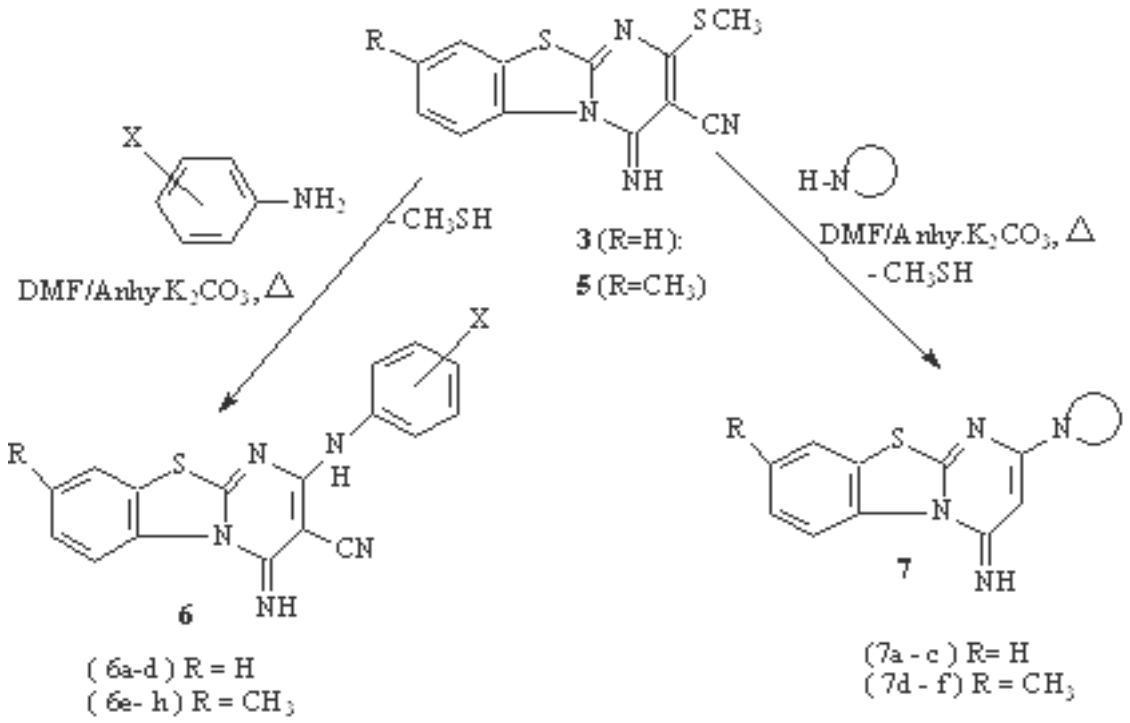
3 R=H
5 R=CH_3

Scheme 1

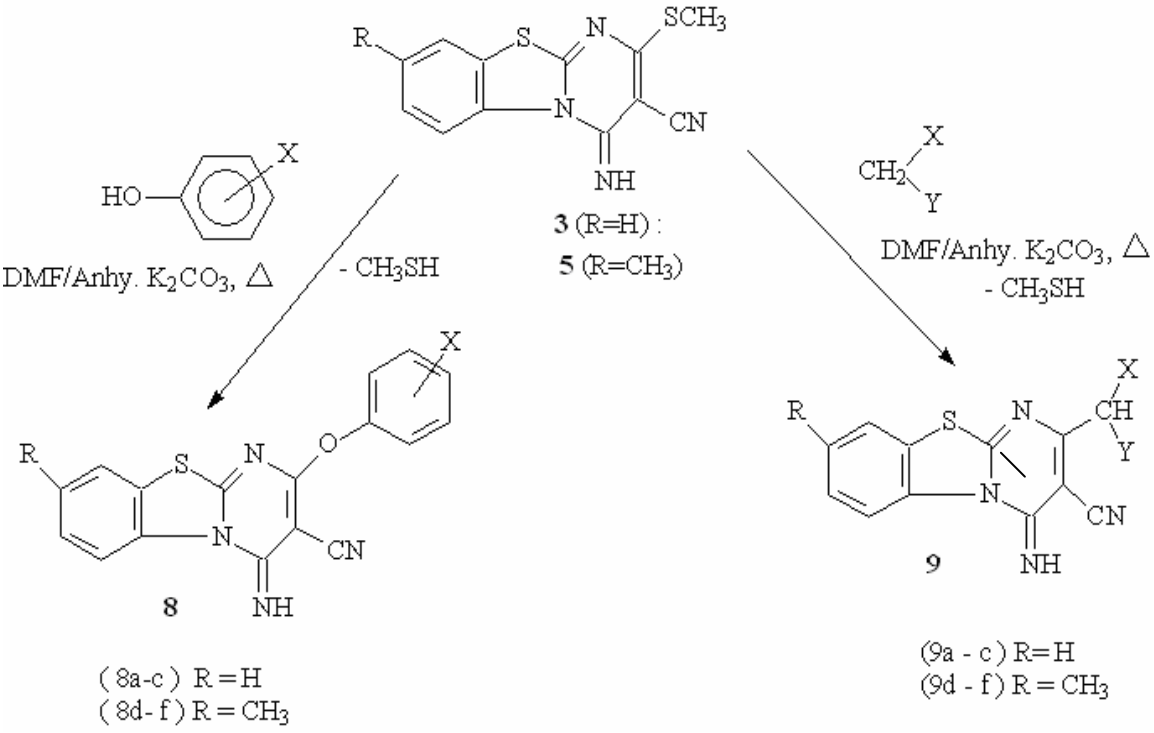
Compounds **3** and **5** possess a replaceable active methylthio group at the 2-position, which is activated by the ring 1-nitrogen atom and the electron withdrawing 3-cyano group. Compounds **3** and **5** were reacted with selected N-, O- and C- nucleophiles like arylamines, hetaryl amines, substituted phenols and compounds containing an active methylene group, respectively. These reactions resulted in the formation of 2,3-disubstituted derivatives of 4-imino-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole and 4-imino-8-methyl-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazole. According to this method, compounds **3** and **5** independently, on reaction with p-chloroaniline, p-methoxyaniline, p-methylaniline and p-nitroaniline in *N*, *N*'- dimethyl formamide and a catalytic amount of anhydrous potassium carbonate, afforded 3-cyano-4-imino-*8H* / 8-methyl-2- (4'-chloroanilino / 4'-methoxyanilino / 4'-methylanilino / 4'-nitroanilino)-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazoles **(6a-6h)**; respectively **(Scheme 2)**. Under similar experimental conditions, compounds **3** and **5** reacted independently with morpholine, piperidine and pyrrolidine to yield 3-cyano-4-imino-*8H* / 8-methyl-2-morpholino / piperidino / pyrrolidino-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazoles **(7a-7f)**; respectively.

3-Cyano-4-imino-2-(4'-chlorophenoxy / 4'-chloro-3'-methylphenoxy / 4'-nitrophenoxy)-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazoles **(8a-8c)** and 3-cyano-4-imino-8-methyl-2-(4'-chlorophenoxy / 4'-chloro-3'-methylphenoxy / 4'-nitrophenoxy)-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazoles **(8d-8f)** were obtained by the condensation of compounds **3** or **5** independently with p-chlorophenol, *p*-chloro-*m*-methylphenol and *p*-nitrophenol in N, N'- dimethyl formamide and a catalytic amount of anhydrous potassium carbonate **(Scheme 3)**. Compounds **3** and **5** on reaction independently with ethyl acetoacetate, diethyl malonate and ethyl cyanoacetate in the presence of dimethyl formamide and a catalytic amount of anhydrous potassium carbonate yielded compounds, characterized on the basis of their analytical and spectral data as 3-cyano-4-imino-*8H*-2- ethylacetoacetyl / diethylmalonyl / ethyl cyanoacetyl-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazoles **(9a-9c)** and 3-cyano-4-imino-8-methyl-2- ethylacetoacetyl / diethylmalonyl / ethyl cyanoacetyl-*4H*-pyrimido [2,1-*b*] [1,3] benzothiazoles **(9d-9f)**; respectively **(Scheme 3)**.

Compounds **6a-h**, **7a-f**, **8a-f** and **9a-f** show absorption bands in their IR spectra in the range of 3350cm^{-1} to 3450 cm^{-1} and 2200 cm^{-1} to 2230 cm^{-1} due to =NH stretching and CN stretching; respectively. ^{1}H NMR and mass spectral data are also in agreement with the structures assigned to compounds **6a-h**, **7a-f**, **8a-f** and **9a-f**.



Scheme 2



Scheme 3

Experimental Section

General Procedures. Melting points were determined in open capillary tubes and were uncorrected. All the reactions were monitored by Thin Layer Chromatography, carried out on 0.2mm Silica gel-G plates using iodine vapour for detection. Infrared spectra were recorded in Nujol / or as Potassium bromide pellets on a Bomen MB 104 FT Infrared Spectrophotometer. Nuclear Magnetic Resonance spectra were obtained on a Gemini 200 MHz Spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded on a FT VG-7070 H Mass spectrophotometer using the EI technique at 70 eV. All reactions were carried out under ambient atmosphere. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

General Procedure

3-Cyano-4-imino-2-methylthio-*8H* / 8-methyl-*4H*-pyrimido[2,1-*b*][1,3]benzothiazoles (3 and **5).** A mixture of 2-aminobenzothiazole **(1)** / 2-amino-6-methylbenzothiazole **(4)** (0.01 mol) and bis(methylthio)methylene malononitrile **(2)** (0.01 mol) in 15 mL of N, N'- dimethyl formamide and anhydrous potassium carbonate (10mg) was refluxed for 5 hours. The reaction mixure was cooled to room temperature and poured into ice cold water. The separated solid product was filtered, washed with water and recrystallized from a N, N'- dimethyl formamide- ethanol mixture to give pure **3** and **5**.

2-Substituted derivatives of 3-cyano-4-imino-2-methylthio-*8H* / 8-methyl-*4H*-pyrimido[2,1-*b*][1,3]benzothiazoles (6a-h, 7a-f, 8a-f and **9a-f).** A mixture of **3** or **5** (0.001 mol) and, independently, various aromatic amines, hetaryl amines, substituted phenols or compounds containing an active methylene group (0.001 mol) in N, N'- dimethyl formamide (10 mL) and anhydrous potassium carbonate (10mg) was refluxed for 4 to 6 hours. The reaction mixture was cooled to room temperature and poured into ice cold water. The separated solid product was filtered, washed with water and recrystallized from a N, N'- dimethyl formamide-ethanol mixture to give pure **6a-h, 7a-f, 8a-f** and **9a-f**.

3-cyano-4-Imino-2-methylthio-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (3). Yellow powder, yield 55 %, mp 240 °C (dec.). IR (KBr / cm^{-1}) 3350 (=NH), 2225 (CN); ^{1}H NMR (60MHz, DMSO-d_6) δ 2.6 (s, 3H, SCH_3), 7.6-8.7 (m, 4H), 9.4 (br s, 1H, =NH). EI-MS (m/z: RA %): 272 ($M^{+\cdot}$, 100%), 255 (35), 239 (20), 225 (62), 207 (10), 192 (8). Anal. Calcd. For $C_{12}H_8N_4S_2$: C, 52.94; H, 2.94; N, 20.58. Found: C, 52.90; H, 2.90; N, 20.54.

3-Cyano-4-imino-2-methylthio-8-methyl-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (5). Yellow powder, yield 50 %, mp 220 °C (dec.). IR (KBr / cm^{-1}) 3380 (=NH), 2210 (CN); ^{1}H NMR (60MHz, DMSO-d_6) δ 2.4 (s, 3H, Ar-CH_3), 2.6 (s, 3H, SCH_3), 7.3-7.7 (m, 3H), 9.3 (br s, 1H, =NH). EI-MS (m/z: RA %): 286 ($M^{+\cdot}$, 100%), 269 (35), 253 (20), 239 (72), 227 (8), 221 (10), 195 (12). Anal. Calcd. For $C_{13}H_{10}N_4S_2$: C, 54.54; H, 3.50; N, 19.58. Found: C, 54.34; H, 3.19; N, 19.40.

3-Cyano-4-imino-2-(4'-chloroanilino)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (6a). Yellow powder, yield 40 %, mp 140 °C (dec.). IR (KBr / cm^{-1}) 3380 (NH), 3300 (=NH), 2220 (CN); ^{1}H NMR (60MHz, DMSO-d_6) δ 4.1 (br s, 1H,-NH), 7-7.8 (m, 8H, Ar-H), 9.48 (br s, 1H, =NH). EI-

MS (m/z: RA %): 355 ($M^{+\bullet}$, 60%), 357 (20). Anal. Calcd. For $C_{17}H_{10}N_5SCl$: C, 57.79; H, 2.83; N, 19.83. Found: C, 57.74; H, 2.80; N, 19.75.

3-Cyano-4-imino-2-(4'-methoxyanilino)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (6b). Yellow powder, yield 72 %, mp 220 °C (dec.). IR (KBr / cm^{-1}) 3297 (NH), 3275 (=NH), 2199 (CN); Anal. Calcd. For $C_{18}H_{13}N_5OS$: C, 61.89; H, 3.72; N, 20.05. Found: C, 61.82; H, 3.70; N, 20.00.

3-Cyano-4-imino-2-(4'-methylanilino)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (6c). Yellow powder, yield 65 %, mp 250 °C (dec.). IR (KBr / cm^{-1}) 3365 (NH), 3302 (=NH), 2207 (CN); Anal. Calcd. For $C_{18}H_{13}N_5S$: C, 64.86; H, 3.90; N, 21.02. Found: C, 64.81; H, 3.85; N, 21.00.

3-Cyano-4-imino-2-(4'-nitroanilino)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole(6d). Yellow powder, yield 50 %, mp 130 °C (dec.). IR (KBr / cm^{-1}) 3370 (NH), 3293 (=NH), 2210 (CN); Anal. Calcd. For $C_{17}H_{10}N_6O_2S$: C, 55.49; H, 2.74; N, 23.07. Found: C, 55.47; H, 2.71; N, 23.01.

3-Cyano-4-imino-8-methyl-2-(4'-chloroanilino)-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (6e). Yellow powder, yield 50 %, mp 155 °C (dec.). IR (KBr / cm^{-1}) 3370 (NH), 3296 (=NH), 2218 (CN); Anal. Calcd. For $C_{18}H_{12}N_5SCl$: C, 57.44; H, 3.19; N, 22.34; Found: C, 57.41; H, 3.14; N, 22.30.

3-Cyano-4-imino-8-methyl-2-(4'-methoxyanilino)-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (6f). Yellow powder, yield 65 %, mp 180 °C (dec.). IR (KBr / cm^{-1}) 3380 (NH), 3302 (=NH), 2205 (CN); Anal. Calcd. For $C_{19}H_{15}N_5OS$: C, 63.15; H, 4.15; N, 19.39; Found: C, 63.10; H, 4.11; N, 19.33.

3-Cyano-4-imino-8-methyl-2-(4'-methylanilino)-*4H*-pyrimido[2,1-*b*][1,3]benzothia- zole (6g). Yellow powder, yield 70 %, mp 190 °C (dec.). IR (KBr / cm^{-1}) 3396 (NH), 3315 (=NH), 2210 (CN); Anal. Calcd. For $C_{19}H_{15}N_5S$: C, 66.08; H, 4.34; N, 20.28; Found: C, 66.03; H, 4.30; N, 20.23.

3-Cyano-4-imino-8-methyl-2-(4'-nitroanilino)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (6h). Yellow powder, yield 65 %, mp 250 °C (dec.). IR (KBr / cm^{-1}) 3300 (NH), 3297 (=NH), 2199 (CN); EI-MS (m/z: RA %): 376 ($M^{+\bullet}$, 25%), 332 (8), 286 (45), 239 (35), 140 (20), 138 (100), 65 (96); Anal. Calcd. For $C_{18}H_{12}N_6O_2S$: C, 59.17; H, 3.28; N, 19.17; Found: C, 59.14; H, 3.21; N, 19.15.

3-Cyano-4-imino-2-morpholino-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (7a). Yellow powder, yield 68 %, mp 120 °C (dec.). IR (KBr / cm^{-1}) 3410 (=NH), 2970 (-CH_2), 2210 (CN), 1232 (OCH_2); ^{1}H NMR (60MHz, DMSO-d_6) δ 2.6 (t, 4H), 3.8 (t, 4H), 7.2-7.7 (m, 4H), 9.3 (br s, 1H). EI-MS (m/z: RA %): 311 (70), 286 (40), 225 (32), 124 (96), 65 (100); Anal. Calcd. for $C_{15}H_{13}N_5OS$: C, 57.50; H, 4.15; N, 22.36; Found: C, 57.46; H, 4.12; N, 22.31.

3-Cyano-4-imino-2-piperidino-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (7b). Yellow powder, yield 75 %, mp 110 °C (dec.). IR (KBr / cm^{-1}) 3386 (=NH), 2980 (-CH_2-), 2206 (CN); Anal. Calcd. for $C_{16}H_{15}N_5S$: C, 61.73; H, 4.82; N, 22.36; Found: C, 61.70; H, 4.79; N, 22.31.

3-Cyano-4-imino-2-pyrrolidino-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (7c). Yellow powder, yield 72 %, mp 118 °C (dec.). IR (KBr / cm^{-1}) 3340 (=NH), 2970 (CH_2), 2200 (CN); Anal. Calcd. for $C_{15}H_{13}N_5S$: C, 60.60; H, 4.38; N, 23.57; Found: C, 60.55; H, 4.33; N, 23.53.

3-Cyano-4-imino-2-morpholino-8-methyl-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (7d). Yellow powder, yield 70 %, mp 180 °C (dec.). IR (KBr / cm^{-1}) 3296 (=NH), 2985 (-CH_3), 2196 (CN), 1271 (OCH_2-); ^{1}H NMR (60MHz, DMSO-d_6) δ 1.3 (s, 3H), 2.8 (t, 4H), 3.5 (t, 4H), 7.3-7.9 (m, 3H), 9.4 (br s, 1H). EI-MS (m/z: RA %): 325 ($M^{+\cdot}$, 70%), 286 (100), 239 (82), 231 (15), 149 (75), 93 (35), 45 (32);Anal. Calcd. for $C_{16}H_{15}N_5OS$: C, 59.07; H, 4.61; N, 21.53; Found: C, 59.00; H, 4.57; N, 21.50.

3-Cyano-4-imino-2-piperidino-8-methyl-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (7e). Yellow powder, yield 70 %, mp 140 °C (dec.). IR (KBr / cm^{-1}) 3370 (=NH), 2990 (-CH_2), 2197 (CN); Anal. Calcd. for $C_{17}H_{17}N_5S$: C, 63.15; H, 5.26; N, 9.90; Found: C, 63.11; H, 5.21; N, 9.85.

3-Cyano-4-imino-2-pyrrolidino-8-methyl-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (7f). Yellow powder, yield 68 %, mp 120 °C (dec.). IR (KBr / cm^{-1}) 3400 (=NH), 3050 (CH_2), 2260 (CN); Anal. Calcd. for $C_{16}H_{15}N_5S$: C, 62.13; H, 4.85; N, 22.65; Found: C, 62.08; H, 4.80; N, 22.60.

3-Cyano-4-imino-2-(4'-chlorophenoxy)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (8a). Yellow powder, yield 45 %, mp 262 °C (dec.). IR (KBr / cm^{-1}) 3310 (=NH), 2195 (CN); Anal. Calcd. for $C_{16}H_9N_3OSCl$: C, 65.19; H, 3.05; N, 14.26; Found: C, 65.16; H, 3.01; N, 14.23.

3-Cyano-4-imino-2-(4'-chloro-3'-methylphenoxy)-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (8b). Yellow powder, yield 50 %, mp 108 °C (dec.). IR (KBr / cm^{-1}) 3351 (=NH), 2200 (CN); EI-MS (m/z: RA %): 368 (M+2, 8 %), 366 ($M^{+\cdot}$, 25%), 272 (100), 225 (75), 135 (85), 108 (20); Anal. Calcd. for $C_{18}H_{11}N_4OSCl$: C, 63.25; H, 3.41; N, 17.36; Found: C, 63.23; H, 3.39; N, 17.32.

3-Cyano-4-imino-2-(4'-nitrophenoxy)-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (8c). Yellow powder, yield 60 %, mp 110 °C (dec.). IR (KBr / cm^{-1}) 3301 (=NH), 2190 (CN), 1570 (-NO_2); Anal. Calcd. for $C_{17}H_9N_5O_3S$: C, 56.19; H, 2.47; N, 19.28; Found: C, 56.16; H, 2.45; N, 19.26.

3-Cyano-4-imino-2-(4'-chlorophenoxy)-8-methyl-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (8d). Yellow powder, yield 50 %, mp 155 °C (dec.). IR (KBr / cm^{-1}) 3300, (=NH), 2195 (CN); Anal. Calcd. for $C_{18}H_{11}N_4OSCl$: C, 59.01; H, 3.00; N, 15.30; Found: C, 59.99; H, 2.98; N, 15.07.

3-Cyano-4-imino-2-(4'-chloro-3'-methylphenoxy)-8-methyl-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (8e). Yellow powder, yield 65 %, mp 194 °C (dec.). IR (KBr / cm^{-1}) 3380 (=NH), 2220 (CN), Anal. Calcd. for $C_{19}H_{12}N_4OSCl$: C, 60.00; H, 3.42; N, 14.73; Found: C, 59.93; H, 3.39; N, 14.70.

3-Cyano-2-(α-ethyl acetoacetyl)-4-imino-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (9a). Yellow powder, yield 50 %, mp 220 °C (dec.). IR (KBr / cm^{-1}) 3447 (=NH), 2226 (CN), 1768 (C=O); Anal. Calcd. for $C_{17}H_{15}N_4O_3S$: C, 57.46; H, 4.22; N, 15.77; Found: C, 57.43; H, 4.19; N, 15.73.

3-Cyano-2-(α-diethyl malonyl)-4-imino-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (9b). Yellow powder, yield 65 %, mp 165 °C (dec.). IR (KBr / cm^{-1}) 3303 (=NH), 2202 (CN), 1730 (C=O); Anal. Calcd. for $C_{18}H_{14}N_4OS$: C, 56.54; H, 3.66; N, 14.65; Found: C, 56.51; H, 3.62; N, 14.62.

3-Cyano-2-(α-ethyl cyanoacetyl)-4-imino-*4H*-pyrimido[2,1-*b*][1,3]benzothiazole (9c). Yellow powder, yield 72 %, mp 110 °C (dec.). IR (KBr / cm^{-1}) 3400 (NH), 2227 (CN), 2215 (CN), 1744 (CO); EI-MS (m/z: RA %): 384 ($M^{+\cdot}$, 43%), 374 (25), 309 (10), 272 (60), 225 (55), 150 (80), 73 (92), 57 (90); Anal. Calcd. for $C_{16}H_{11}N_5O_2S$: C, 56.97; H, 3.26; N, 20.77; Found: C, 56.95; H, 3.22; N, 20.74.

3-Cyano-2-(α-ethyl acetoacetyl)-4-imino-8-methyl-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (9d). Yellow powder, yield 60 %, mp 165 °C (dec.). IR (KBr / cm^{-1}) 3420 (NH), 2226 (CN), 1758 (CO); Anal. Calcd. for $C_{18}H_{16}N_4O_3S$: C, 57.30; H, 4.49; N, 15.73; Found: C, 57.21; H, 4.42; N, 15.70.

3-Cyano-2-(α-diethyl malonyl)-4-imino-8-methyl-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (9e). Yellow powder, yield 65 %, mp 195 °C (dec.). IR (KBr / cm^{-1}) 3298 (=NH), 2202 (CN), 1735 (CO); Anal. Calcd. for $C_{19}H_{18}N_4O_4S$: C, 57.28; H, 2.52; N, 14.07; Found: C, 57.20; H, 2.40; N, 14.01.

3-Cyano-2-(α-ethyl cyanoacetyl)-4-imino-8-methyl-*4H*-pyrimido[2,1-*b*][1,3] benzothiazole (9f). Yellow powder, yield 72 %, mp 110 °C (dec.). IR (KBr / cm^{-1}) 3397 (=NH), 2199 (CN),1728 (CO); Anal. Calcd. for $C_{17}H_{13}N_5O_2S$: C, 58.11; H, 3.70; N, 19.94; Found: C, 58.02; H, 3.69; N, 19.88.

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