Supporting information

Previously furnished.

General Procedures. Column chromatography was conducted on silica gel 60 (40-63 m), available from E. Merck. Thin layer chromatographies were performed on 0.5 mm 20 cm 20 cm E. Merck silica gel plates (60 F-254). Melting points measured were uncorrected. The ^{13}C and ^{1}H NMR spectra were recorded at room temperature at 50 and 200 MHz respectively. Chemical shifts ( ) are given in ppm downfield from tetramethylsilane as internal standard. All chemicals were reagent grade and used without further purification. Tetrahydrofuran was freshly distilled from Na/benzophenone ketyl, while dichloromethane was distilled over CaH_2. All reactions were carried in a N_2 atmosphere.

Experimental procedures.

***N,N'*-Bis(dimethylaminomethylene)thiourea (1).** *N,N*-dimethylformamide dimethylacetal (30 mmol) was added to a suspension of thiourea (10 mmol) in dichloromethane (10 mL). The reaction mixture was refluxed for 4 hours then the solvent was evaporated. Compound **1** was recrystallized from ether as yellow crystals (Yield: 95%). Mp: 138-140 °C. IR (KBr): 2920, 2360, 1646, 1606, 1416, 1333, 1258, 1228, 1102, 975 cm^{-1}. ^{1}H NMR (DMSO-d_6): 3.00 (s, 6H), 3.15 (s, 6H), 8.68 (s, 2H). ^{13}C NMR (DMSO-d_6): 35.4(2), 40.9(2), 161.3(2), 207.6. MS *m/z*: 115 (20), 99 (24), 71 (39). Anal. calcd for $C_7H_{14}N_4S$: C, 45.14; H, 7.58; N, 30.08. Found: C, 45.38; H, 7.87; N, 29.89.

Imidazo[2,1-*b*]thiazoles (4). A solution of -bromoketone (2.2 mmol) (*p*-chlorophenacyl bromide for **4a,d**, *p*-bromophenacyl bromide for **4b**, *p*-toluoylacyl bromide for **4c,e**) and thiazolylamidine **2** (2 mmol) in tetrahydrofuran (10 mL) was heated under reflux for 20 hours. After cooling to room temperature, triethylamine (4.4 mmol) was added and the mixture was

stirred for a further 24 hours. The solvent was evaporated and the residue, diluted with dichloromethane, was purifed by chromatography (elution dichloromethane/ethyl acetate 19/1). Compounds **4** were recrystallized from ether.

2*H*,6*H*-Pyrimido[2,1-*b*][1,3]thiazin-6-ones (7).

Method A: Ketene (CAUTION), produced by cracking of acetone, was passed through a solution of amidine **3b** (1 mmol) in dichloromethane (100 mL) until complete consumption of the starting material, as monitored by TLC. The solvent was then evaporated, the resulting residue diluted with dichloromethane and purifed by chromatography (elution dichloromethane/ethyl acetate 5/1). Compound **7a** was recrystallized from ether.

Method B: Ethyl malonyl chloride (1.2 mmol) was added to a solution of amidine **3** (1 mmol) in dichloromethane (10 mL). After 6 hours of stirring at room temperature, the reaction mixture was cooled to 0 °C and triethylamine (2.4 mmol) was added. The mixture was stirred at room temperature for a further 16 hours then the solvent was evaporated. The residue was diluted with dichloromethane and purifed by chromatography (elution dichloromethane/ethyl acetate 5/1). Compounds **7b,c** were recrystallized from ether.

Spectroscopic data

***N'*-(5-*p*-Bromobenzoylthiazol-2-yl)-*N,N*-dimethylformamidine (2b).** Yellow crystals (Yield: 74%). Mp: 162-164 °C. IR (KBr): 2917, 1626, 1608, 1453, 1393. ^{1}H NMR ($CDCl_3$): 3.15 (s, 3H), 3.18 (s, 3H), 7.65-7.69 (m, 4H), 7.81 (s, 1H), 8.36 (s, 1H). ^{13}C NMR ($CDCl_3$): 35.3, 41.2, 126.8, 130.3(2), 131.7(2), 132.0, 137.2, 149.2, 156.5, 181.2, 186.0. MS *m/z*: 339/337 (63/60, M^+), 306/304 (19/19), 155 (32), 154 (100), 98 (28). Anal. calcd for $C_{13}H_{12}BrN_3OS$: C, 46.17; H, 3.58; N, 12.42. Found: C, 46.42; H, 3.83; N, 12.57.

***N'*-(5-Acetyl-6*H*-1,3-thiazin-2-yl)-*N,N*-dimethylformamidine (3b).** Yellow oil (Yield: 45%). $R_{f\ (acetone)}$ = 0.5. IR: 1642, 1625, 1377, 1468, 1296, 1236, 1206, 1120. ^{1}H NMR ($CDCl_3$): 2.37 (s, 3H), 3.15 (s, 3H), 3.18 (s, 3H), 3.67 (s, 2H), 7.81 (s, 1H), 8.32 (s, 1H). ^{13}C NMR ($CDCl_3$): 22.9, 25.0, 35.6, 41.4, 114.1, 150.1, 157.3, 169.4, 195.9. MS (IC) *m/z*: 212 (62, M + H^+), 144 (74), 104 (91), 88 (100). Anal. calcd for $C_9H_{13}N_3OS$: C, 51.16; H, 6.20; N, 19.89. Found: C, 51.02; H, 6.11; N, 19.97.

6-Acetyl-3-*p*-bromobenzoyl-7*H*-imidazo[2,1-*b*][1,3]thiazine (5b). Colourless crystals (Yield: 49%). Mp: 202-204 °C. IR (KBr): 1671, 1638, 1579, 1526, 1417, 1368, 1165, 1003, 893, 753. ^{1}H NMR ($CDCl_3$): 2.50 (s, 3H), 3.91 (d, 2H, *J* = 0.9 Hz), 7.63 (s, 1H), 7.64-7.75 (m, 4H), 8.66 (t, 1H, *J* = 0.9 Hz). ^{13}C NMR ($CDCl_3$): 21.4, 25.2, 119.6, 128.0, 129.7, 136.5, 130.2(2), 132.0(2), 134.8, 142.4, 150.3, 182.9, 194.4. MS *m/z*: 364/362 (43/39, M^+), 296/294 (100/91), 185/183 (46/46), 157/155 (39/41). Anal. calcd for $C_{15}H_{11}BrN_2O_2S$: C, 49.60; H, 3.05; N, 7.71. Found: C, 49.47; H, 2.95; N, 7.83.

5-Acetyl-2-*p*-bromobenzoyl-5*H*-thiazolo[3,2-*a*]pyrimidine (8a). Yellow crystals (Yield: 47%). Mp: 232-235 °C. IR (KBr): 1618, 1589, 1493, 1410, 1327, 1249, 1180, 854, 757. ^{1}H NMR (CF_3CO_2D): 2.57 (s, 3H), 5.29 (s, 2H), 7.79 (s, 1H), 7.82 (s, 4H), 8.11 (s, 1H). ^{13}C NMR (CF_3CO_2D): 25.1, 48.8, 115.3, 132.3(2), 135.2(2), 133.5, 133.8, 134.8, 136.0, 138.6, 165.6, 188.3, 201.7. MS *m/z*: 364/362 (100/97, M^+), 349/347 (16/16), 321/319 (13/13), 282 (9), 185/183 (25/23), 157/155 (17/17). Anal. calcd for $C_{15}H_{11}BrN_2O_2S$: C, 49.60; H, 3.05; N, 7.71. Found: C, 49.85; H, 3.21; N, 7.49.

3,7-Diacetyl-2*H*,6*H*-pyrimido[2,1-*b*][1,3]thiazine (9c). Yellow crystals (Yield: 52%). Mp: 234-237 °C. IR (KBr): 1664, 1648, 1502, 1397, 1244, 1148. ^{1}H NMR ($CDCl_3$): 2.31 (s, 3H), 2.35 (s, 3H), 3.71 (d, 2H, J = 0.9 Hz), 4.49 (d, 2H, J = 1.2 Hz), 6.99 (t, 1H, J = 0.9 Hz), 7.36 (t, 1H, J = 1.2 Hz). ^{13}C NMR (DMSO-d_6): 21.2, 24.7, 25.0, 47.4, 117.0, 117.2, 143.6, 144.7, 159.4, 193.9, 194.8. MS *m/z*: 236 (63, M^+), 219 (5), 193 (15), 151 (13), 43 (100). Anal. calcd for $C_{11}H_{12}N_2O_2S$: C, 55.92; H, 5.12; N, 11.86. Found: C, 56.06; H, 4.98; N, 11.82.