

From Thiourea to Bicyclic Structures: An Original Route to Imidazo[2,1-*b*]thiazoles, 5*H*-Thiazolo[3,2-*a*]pyrimidines, 7*H*-Imidazo[2,1-*b*][1,3]thiazines, and 2*H*,6*H*-Pyrimido[2,1-*b*][1,3]thiazines[†]

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Received March 25, 2003

We report an example of an efficient regioselective synthesis of biheterocyclic compounds using thiourea as starting material. In fact, *N,N'*-bis(dimethylaminomethylene)thiourea (**1**), easily prepared by double condensation of *N,N*-dimethylformamide dimethyl acetal with thiourea, can be reacted with haloketones or acrylic dienophiles to give thiazolic (**2**) and thiazinic (**3**) diazadienes, respectively, themselves undergoing cyclization reactions to yield imidazo[2,1-*b*]thiazoles, 5*H*-thiazolo[3,2-*a*]pyrimidines, 7*H*-imidazo[2,1-*b*][1,3]thiazines, and 2*H*,6*H*-pyrimido[2,1-*b*][1,3]thiazines without any regioisomeric ambiguity. This straightforward route represents an original and unambiguously regioselective pathway to these valuable heterocycles.

Introduction

In recent years, the synthesis of bicyclic compounds possessing an alkylthioamidine central core has been the focus of great interest. This is due, in part, to the broad spectrum of biological properties of these compounds.^{1–4} Imidazo[2,1-*b*]thiazole derivatives are of considerable interest because of their activities as antiarthritic,^{1a,b} immunomodulating,^{1c} herbicidal,^{1d} cardiotonic,^{1e} antiarrhythmic^{1f} and antitumor agents.^{1g,h} One recent paper has shown them to be effective against tuberculosis.¹ⁱ Thiazolo[3,2-*a*]pyrimidines are also of pharmacological

interest due to their antiinflammatory,^{2a,b} psychopharmacological,^{2c} bactericidal,^{2d} and antiviral activity as inhibitors of HIV-1 reverse transcriptase.^{2e} On the other hand, imidazo[2,1-*b*][1,3]thiazines and pyrimido[2,1-*b*][1,3]thiazines have prompted less interest, although some of these compounds proved to be biologically active as benzodiazepine substitutes³ and antiinflammatory agents, respectively.⁴

Numerous methods for the synthesis of these heterocycles involve approaches based on either (i) alkylations of cyclic thioureas by appropriate 1,2- or 1,3-dielectrophiles⁵ or (ii) condensations of 2-aminothiazoles or thiazines with 1,2- or 1,3-difunctionalized units, such as α,β -unsaturated esters or lactam acetals.⁶ Although frequently used, both routes can give mixtures of regioisomers.⁷ Known regioselective syntheses of these structures involve the retrodiene decomposition of the corresponding norbornene-fused derivatives⁸ or the condensation of 2-(cyanoimino)thiazolidine with acyl chlorides,⁹ 2-aminothiazoles with α -halogenoketones,¹⁰ isothiocyanato-2-

[†] Dedicated to the memory of Dr. Alain Reliquet.

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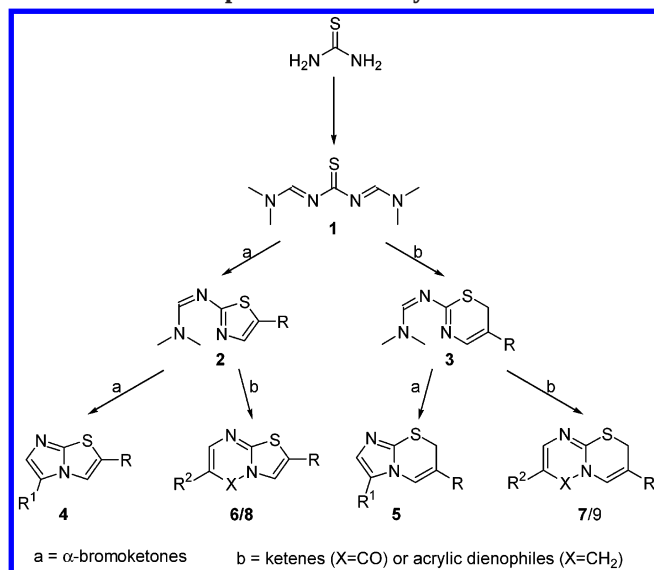
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SCHEME 1. Preparation of Bicyclic Structures



propenium salts with α -aminoketones¹¹ or other specific reactants.¹² The methods mentioned above offer variable versatility and convenience.

New routes to these structures would be of great interest, and recently we published efficient synthetic procedures involving heterocyclic diazadienes.^{13e,f} We showed that such amidines, prepared by condensation of 2-aminothiazoline or 2-amino-4,6,6-trimethyl-6H-1,3-thiazine with *N,N*-dimethylacetamide or formamide dimethyl acetal, were useful building blocks for the regioselective synthesis of these heterocycles. As part of our continuing study on the reactivity of polyheteropolynes,¹³ we now report that title compounds can be conveniently prepared in three steps starting from thiourea. By this method, we recently described a novel access to thiazolopyrimidine and imidazo-1,3-thiazine derivatives involving compound **1**.^{13j} Our method utilizes *N,N'*-bis(dimethylaminomethylene)thiourea (**1**) as a common intermediate, undergoing cyclization reactions to afford either five- (**2**) or six-membered-ring (**3**) monocyclic diazadienes, themselves being precursors to the bicyclic structures (Scheme 1).

Results and Discussion

Compound **1** was easily prepared in 95% yield by double condensation of commercially available *N,N'*-

TABLE 1. Yields of Compounds **2a–d** and **3a,b**

compd	R	yield (%)
2a	COOCH ₃	81
2b ^{13j}	COC ₆ H ₄ Br- <i>p</i>	74
2c	COC ₆ H ₄ Cl- <i>p</i>	82
2d	COC ₆ H ₄ CH ₃ - <i>p</i>	72
3a	CHO	48
3b ^{13j}	COCH ₃	45

dimethylformamide dimethyl acetal and thiourea in dichloromethane. It is worth noting that monocondensation was favored when methanol was employed as the solvent.^{13c}

With gram quantities of precursor (**1**) in hand, initial work focused on exploring its reactivity toward various electrophiles. First, treatment of *N,N'*-bis(dimethylaminomethylene)thiourea (**1**) with α -bromoketones or methyl bromoacetate gave nonisolated *S*-alkyl salts, which underwent cyclization when treated with a base via condensation of the generated enolate with one of the amidinium moieties. Spontaneous deamination of the intermediary cycloadduct afforded *N,N*-dimethyl-*N'*-(thiazol-2-yl)amidines (**2**) in high yields (Table 1, Scheme 2). This mirrors work described by Knoll and Liebscher;¹⁴ however, these authors did not make any attempts toward further cyclizations.

We then decided to investigate the feasibility of a reaction between *N,N'*-bis(dimethylaminomethylene)thiourea (**1**) and acrylic dienophiles. This reaction gave *N,N*-dimethyl-*N'*-(6H-1,3-thiazin-2-yl)formamidines (**3**) in only moderate yields after loss of dimethylamine (Table 1, Scheme 2). In accordance with the literature, we assume that the reaction proceeds by a classical hetero-Diels–Alder reaction rather than a conjugate addition/alkylation.¹⁵ When acrolein was used as the dienophile, partial degradation (20–30%) of the product amidine side chain was observed during the workup procedure, leading to the undesired 5-formyl-2-formylamino-6H-1,3-thiazine. Whereas with methyl vinyl ketone the main problem was double condensation resulting from second [4 + 2] cycloaddition between this dienophile and the resulting thiazine **3b**, occurring before complete consumption of the starting material. Consequently bicycle **9c** was observed as a major side product (15%). Compounds **3** were unambiguously characterized by spectroscopy techniques. The proof of the thiazine structure, so the total regioselectivity, was given by the ¹H NMR spectra where we observed the loss of dimethylamino group and the presence of two singlets (3.68 and 7.52 for S-CH₂ and N-CH, respectively).

We have previously demonstrated 4,5-dihydrothiazole amidines to be useful heterodienes.^{13e} It therefore seemed reasonable to investigate the feasibility of cycloadducts **2** to act as heterodienes, their aromaticity being clearly decreased by the presence of an electron-withdrawing group in the 5-position. Moreover, the same consideration

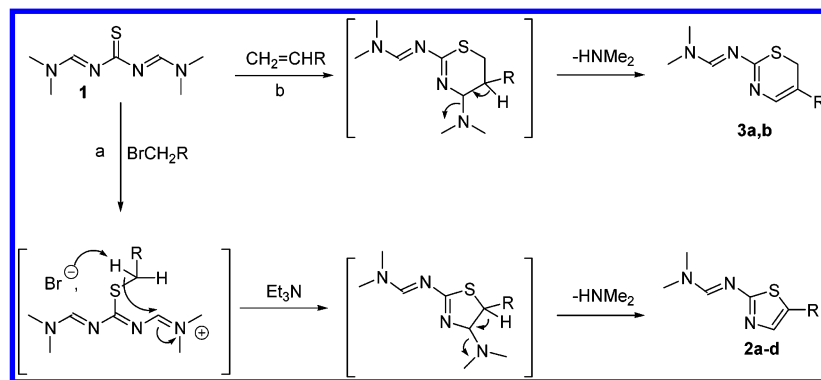
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SCHEME 2. Synthesis of **2** and **3**^a

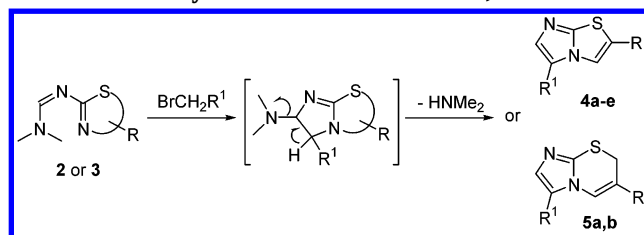
^a Reagents and conditions: (a) CH₂Cl₂, rt, 15 min then TEA, rt, 20 h; (b) CH₂Cl₂, rt, 18 h.

TABLE 2. Yields of Compounds **4a–e** and **5a,b**

compd	R	R ¹	yield (%)
4a	CO ₂ CH ₃	COC ₆ H ₄ Cl- <i>p</i>	68
4b	COC ₆ H ₄ Br- <i>p</i>	COC ₆ H ₄ Br- <i>p</i>	74
4c	COC ₆ H ₄ Br- <i>p</i>	COC ₆ H ₄ CH ₃ - <i>p</i>	73
4d	COC ₆ H ₄ CH ₃ - <i>p</i>	COC ₆ H ₄ Cl- <i>p</i>	87
4e	COC ₆ H ₄ Cl- <i>p</i>	COC ₆ H ₄ CH ₃ - <i>p</i>	82
5a	CHO	COC ₆ H ₄ Br- <i>p</i>	41
5b ^{13j}	COCH ₃	COC ₆ H ₄ Br- <i>p</i>	49

TABLE 3. Yields of Compounds **6a–e** and **7a–c**

compd	R	R ²	yield (%)
6a	COC ₆ H ₄ Cl- <i>p</i>	H	55
6b	COC ₆ H ₄ Br- <i>p</i>	CO ₂ CH ₃	77
6c	COC ₆ H ₄ Cl- <i>p</i>	CO ₂ CH ₃	86
6d	COC ₆ H ₄ CH ₃ - <i>p</i>	CO ₂ CH ₃	65
6e	COC ₆ H ₄ Cl- <i>p</i>	CO ₂ C ₂ H ₅	63
7a	COCH ₃	H	58
7b	CHO	CO ₂ C ₂ H ₅	51
7c	COCH ₃	CO ₂ C ₂ H ₅	59

SCHEME 3. Synthesis of **4a–e** and **5a,b**^a

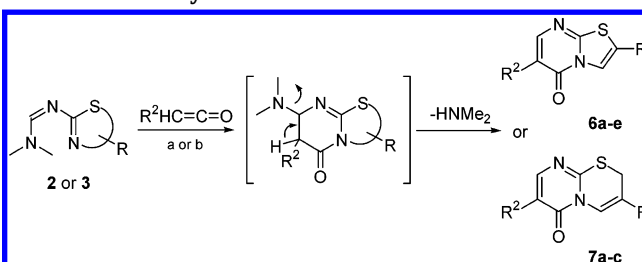
^a Reagents and conditions: THF, reflux, 6 or 20 h then TEA, rt, 24 h.

could be applied to compounds **3**, which should react in a similar way as the thiazine amidines previously studied by our group.^{13f}

Initially the reaction of amidines **2** and **3** with α -bromoketones was examined. As expected, the resulting *N*-alkyl salts, whose isolations were not encouraged, were converted in situ by addition of triethylamine, leading after spontaneous deamination to the corresponding imidazo[2,1-*b*]thiazoles (**4**) and 7*H*-imidazo[2,1-*b*][1,3]-thiazines (**5**) (Table 2, Scheme 3).

Treatment of compounds **2** and **3** with a range of ketenes led to a [4 + 2] cyclocondensation which gave 5*H*-thiazolo[3,2-*a*]pyrimidin-5-ones (**6**) and 2*H*,6*H*-pyrimido[2,1-*b*][1,3]thiazin-6-ones (**7**), respectively, by loss of dimethylamine (Table 3, Scheme 4). Our pathway excludes any regioisomeric ambiguity: indeed, the ¹H NMR deshielding effect observed for the proton signal in position 3 (for **6a–e**) or 4 (for **7a–c**) is unambiguously attributed to the proximity of the carbonyl function of pyrimidinic ring. Moreover, the final step that consisted of deamination of the supposed intermediary cycloadduct was not possible for the unlikely isomer.

Finally, to complete this study, we decided to investigate the behavior of amidines **2** and **3** with acrylic dienophiles (either as neat liquids or in chloroform). The

SCHEME 4. Synthesis of **6a–e** and **7a–c**^a

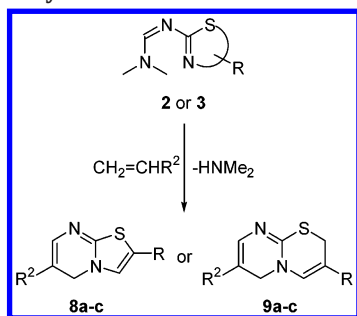
^a Reagents and conditions: (a) R² = H, CH₂Cl₂, rt, 1 h; (b) R² ≠ H, CH₂Cl₂, rt, 4 h, then TEA, 0 °C → rt, 16 h.

TABLE 4. Yields of Compounds **8a–c** and **9a–c**

compd	R	R ²	yield (%)
8a ^{13j}	COC ₆ H ₄ Br- <i>p</i>	COCH ₃	47
8b	COC ₆ H ₄ Cl- <i>p</i>	COCH ₃	53
8c	COC ₆ H ₄ CH ₃ - <i>p</i>	COCH ₃	46
9a	CHO	COCH ₃	48
9b	COCH ₃	CHO	53
9c ^{13j}	COCH ₃	COCH ₃	52

tandem [4 + 2] cycloaddition/deamination process occurred as expected, furnishing 5*H*-thiazolo[3,2-*a*]pyrimidines (**8**) and 2*H*,6*H*-pyrimido[2,1-*b*][1,3]thiazines (**9**) respectively, albeit in moderate yields (Table 4, Scheme 5). It is worth noting that this synthetic sequence makes it possible to obtain regioisomers **9a** and **9b**, both bearing an acetoxy and a formyl group, in a regiocontrolled manner. Similarly, the expected derivatives **8** and **9** were obtained with an absolute regioselectivity. The ¹H NMR spectra of **8a–c** and **9a–c** showed a singlet due to the methylene group in position 5 or 6, respectively, and thus excluded the regioisomeric substituted structure.

In conclusion, we have demonstrated *N,N'*-bis(dimethylaminomethylene)thiourea **1** to be a suitable building

SCHEME 5. Synthesis of 8a–c and 9a–c^a

^a Reagents and conditions: neat or CHCl₃, reflux, 6 h or 4 days.

block for the synthesis of imidazo[2,1-*b*]thiazoles (**4**), 5*H*-thiazolo[3,2-*a*]pyrimidines (**6** and **8**), 7*H*-imidazo[2,1-*b*]-[1,3]thiazines (**5**) and 2*H*,6*H*-pyrimido[2,1-*b*] [1,3]thiazines (**7** and **9**). This straightforward route represents an original and unambiguously regioselective pathway to these valuable heterocycles.

Experimental Section

***N,N*-Dimethyl-*N'*-(thiazol-2-yl)amidines (**2**).** The α -carbonylated bromide (5 mmol) (methyl bromoacetate for **2a**, *p*-bromophenacyl bromide for **2b**,^{13j} *p*-chlorophenacyl bromide for **2c**, *p*-toluoylacyl bromide for **2d**) was added to a solution of *N,N'*-bis(dimethylaminomethylene)thiourea **1** (5 mmol) in dichloromethane (10 mL). After 15 min of stirring at room temperature, the triethylamine (10 mmol) was added. The reaction mixture was further stirred for 20 h, and then the solvent was evaporated. The residue, diluted with dichloromethane, was purified by chromatography (elution dichloromethane/ethyl acetate 1/9 for **2a**, 4/1 for **2b**, 3/2 for **2c**, 3/1 for **2d**). Compounds **2** were recrystallized from ether.

***N'*-(5-Methoxycarbonylthiazol-2-yl)-*N,N*-dimethylformamidine (**2a**).** Yellow crystals (yield 81%). Mp: 104.5–105.5 °C. IR (KBr): 3087, 1703, 1621, 1401, 1318, 1249 cm⁻¹. ¹H NMR (CDCl₃) δ : 3.11 (s, 3H), 3.14 (s, 3H), 3.85 (s, 3H), 7.98 (s, 1H), 8.35 (s, 1H). ¹³C NMR (CDCl₃) δ : 34.9, 40.9, 51.7, 120.9, 147.0, 156.0, 162.4, 179.7. MS *m/z*: 213 (52, M⁺), 153 (86), 42 (100). Anal. Calcd for C₈H₁₁N₃O₂S: C, 45.06; H, 5.20; N, 19.70. Found: C, 44.87; H, 5.06; N, 19.53.

***N'*-(5-*p*-Chlorobenzoylthiazol-2-yl)-*N,N*-dimethylformamidine (**2c**).** Yellow crystals (yield 82%). Mp: 159–160 °C. IR (KBr): 2918, 1632, 1608, 1448 cm⁻¹. ¹H NMR (CDCl₃) δ : 3.15 (s, 3H), 3.17 (s, 3H), 7.44–7.78 (m, 4H), 7.81 (s, 1H), 8.36 (s, 1H). ¹³C NMR (CDCl₃) δ : 35.0, 40.9, 128.7 (2), 130.1 (2), 131.9, 136.6, 138.1, 149.0, 156.4, 181.1, 185.8. MS *m/z*: 295/293 (40/100, M⁺), 154 (87). Anal. Calcd for C₁₃H₁₂ClN₃OS: C, 53.15; H, 4.12; N, 14.30. Found: C, 53.01; H, 3.91; N, 14.15.

***N,N*-Dimethyl-*N'*-(5-*p*-toluoylthiazol-2-yl)formamidine (**2d**).** Yellow crystals (yield 72%). Mp: 146–148 °C. IR (KBr): 1610, 1442, 1371, 1283, 1100 cm⁻¹. ¹H NMR (CDCl₃) δ : 2.44 (s, 3H), 3.14 (s, 3H), 3.17 (s, 3H), 7.26–7.76 (m, 4H), 7.84 (s, 1H), 8.35 (s, 1H). ¹³C NMR (CDCl₃) δ : 21.5, 35.2, 41.1, 128.9 (2), 129.1 (2), 132.5, 135.6, 142.6, 148.6, 156.4, 180.1, 187.0. MS *m/z*: 273 (100, M⁺), 154 (59), 119 (41). Anal. Calcd for C₁₄H₁₅N₃OS: C, 61.52; H, 5.53; N, 15.37. Found: C, 61.40; H, 5.76; N, 15.51.

***N,N*-Dimethyl-*N'*-(5-formyl-6*H*-1,3-thiazin-2-yl)formamidine (**3a**).** The *N,N'*-bis(dimethylaminomethylene)thiourea **1** (4 mmol) was added to a solution of acroleine (20 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 18 h at room temperature, diluted with acetone (80 mL), and filtered through a short pad of Celite. The solvent was evaporated, and the residue was diluted with dichloromethane.

Compounds **3a** was isolated as a yellow oil by chromatography (elution ethyl acetate/acetone 3/2) (yield 48%). *R*_f (acetone) = 0.2. IR: 2928, 1618, 1453, 1108 cm⁻¹. ¹H NMR (CDCl₃) δ : 3.16 (s, 3H), 3.20 (s, 3H), 3.68 (s, 2H), 7.52 (s, 1H), 8.40 (s, 1H), 9.46 (s, 1H). ¹³C NMR (CDCl₃) δ : 21.9, 35.7, 41.7, 114.5, 157.3, 158.3, 171.7, 190.1. MS *m/z*: 197 (52, M⁺), 168 (100), 115 (64). Anal. Calcd for C₈H₁₁N₃OS: C, 48.71; H, 5.62; N, 21.30. Found: C, 48.63; H, 5.76; N, 21.18.

Imidazo[2,1-*b*]thiazoles (4**).** Compounds **4** were prepared using the same procedure described above for the synthesis of **2**.

5-*p*-Chlorobenzoyl-2-methoxycarbonylimidazo[2,1-*b*]thiazole (4a**).** Colorless crystals (yield 68%). Mp: 180.5–181.5 °C. IR (KBr): 1726, 1264 cm⁻¹. ¹H NMR (CDCl₃) δ : 3.98 (s, 3H), 7.50–7.88 (m, 4H), 7.97 (s, 1H), 9.12 (s, 1H). ¹³C NMR (CDCl₃) δ : 53.2, 124.5, 127.3, 129.2 (2), 130.1 (2), 136.0, 139.2, 145.0 (2), 156.5, 161.2, 181.7. MS *m/z*: 322/320 (39/100, M⁺), 209 (76), 141/139 (12/37), 113/111 (16/51). Anal. Calcd for C₁₄H₉ClN₂O₃S: C, 52.43; H, 2.83; N, 8.73. Found: C, 52.61; H, 3.02; N, 8.58.

2,5-Bis(*p*-bromobenzoyl)imidazo[2,1-*b*]thiazole (4b**).** Colorless crystals (yield 74%). Mp: 253–255 °C. IR (KBr): 2362, 1629, 1618, 1585, 1438, 1400 cm⁻¹. ¹H NMR (CDCl₃) δ : 7.67–7.83 (m, 8H), 8.01 (s, 1H), 8.95 (s, 1H). ¹³C NMR (CDCl₃) δ : 127.5, 127.9, 129.3 (2), 130.1 (2), 130.4 (2), 130.7 (2), 134.3, 134.4, 134.9, 135.1, 144.2, 145.0, 156.4, 181.9, 182.6. MS *m/z*: 492/490/488 (52/92/46, M⁺), 335/333 (35/36), 185/183 (95/100), 157/155 (70/73). Anal. Calcd for C₁₉H₁₀Br₂N₂O₂S: C, 46.56; H, 2.06; N, 5.72. Found: C, 46.77; H, 2.14; N, 5.59.

2-*p*-Bromobenzoyl-5-*p*-toluoylimidazo[2,1-*b*]thiazole (4c**).** Colorless crystals (yield 73%). Mp: 193–196 °C. IR (KBr): 1632, 1620, 1587, 1380 cm⁻¹. ¹H NMR (CDCl₃) δ : 2.47 (s, 3H), 7.33–7.84 (m, 8H), 8.03 (s, 1H), 8.97 (s, 1H). ¹³C NMR (CDCl₃) δ : 21.6, 127.1, 128.1, 128.7 (2), 129.5 (2), 130.2 (2), 132.3 (2), 129.5, 134.2, 134.6, 135.1, 143.7, 145.0, 156.2, 182.8, 186.1. MS *m/z*: 426/424 (63/59, M⁺), 185/183 (47/48), 119 (66), 91 (100). Anal. Calcd for C₂₀H₁₃BrN₂O₂S: C, 56.48; H, 3.08; N, 6.59. Found: C, 56.27; H, 3.22; N, 6.38.

5-*p*-Chlorobenzoyl-2-*p*-toluoylimidazo[2,1-*b*]thiazole (4d**).** Colorless crystals (yield 87%). Mp: 184.5–185.5 °C. IR (KBr): 2358, 1652, 1645, 1373, 897 cm⁻¹. ¹H NMR (CDCl₃) δ : 2.49 (s, 3H), 7.36–7.88 (m, 8H), 8.00 (s, 1H), 8.96 (s, 1H). ¹³C NMR (CDCl₃) δ : 21.6, 126.7, 127.5, 129.0 (2), 129.1 (2), 129.7 (2), 129.9 (2), 133.6, 135.1, 135.7, 139.1, 144.4, 145.2, 156.7, 181.6, 186.6. MS *m/z*: 382/380 (31/70, M⁺), 269 (19), 119 (100), 91 (74). Anal. Calcd for C₂₀H₁₃ClN₂O₂S: C, 63.08; H, 3.44; N, 7.36. Found: C, 63.25; H, 3.29; N, 7.54.

2-*p*-Chlorobenzoyl-5-*p*-toluoylimidazo[2,1-*b*]thiazole (4e**).** Colorless crystals (yield 82%). Mp: 160.5–161.5 °C. IR (KBr): 1636, 1620, 1380, 1302, 899 cm⁻¹. ¹H NMR (CDCl₃) δ : 2.47 (s, 3H), 7.33–7.80 (m, 8H), 8.02 (s, 1H), 8.97 (s, 1H). ¹³C NMR (CDCl₃) δ : 21.5, 127.0, 128.1, 128.3 (2), 128.4 (2), 130.1 (2), 130.1, 134.1, 134.6, 139.8, 143.7, 145.0, 156.1, 182.7, 185.8. MS *m/z*: 382/380 (42/100, M⁺), 291/289 (9/22), 141/139 (16/52), 119 (45), 91 (59). Anal. Calcd for C₂₀H₁₃ClN₂O₂S: C, 63.08; H, 3.44; N, 7.36. Found: C, 63.21; H, 3.63; N, 7.60.

3-*p*-Bromobenzoyl-6-formyl-7*H*-imidazo[2,1-*b*][1,3]-thiazine (5a**).** The *p*-bromophenacyl bromide (1.1 mmol) was added to a solution of amidine **3** (1 mmol) in tetrahydrofuran (10 mL). The reaction mixture was refluxed for 6 h. After the mixture was cooled to room temperature, triethylamine (2.2 mmol) was added. The mixture was further stirred for 24 h. The solvent was then evaporated, and the residue, diluted with dichloromethane, was purified by chromatography (elution dichloromethane/ethyl acetate 9/1). Compound **5** was recrystallized from ether. Colorless crystals (yield 41%). Mp: 144–146 °C. IR (KBr): 1685, 1646, 1623, 1422, 1336, 894 cm⁻¹. ¹H NMR (CDCl₃) δ : 3.88 (d, 2H, *J* = 0.9 Hz), 7.63 (s, 1H), 7.64–7.76 (m, 4H), 8.50 (t, 1H, *J* = 0.9 Hz), 9.65 (s, 1H). ¹³C NMR

C₁₀H₁₀N₂O₂S: C, 54.04; H, 4.53; N, 12.60. Found: C, 54.26; H, 4.61; N, 12.48.

7-Formyl-3-acetyl-2*H*,6*H*-pyrimido[2,1-*b*][1,3]-thiazine (9b). Yellow crystals (yield 53%). Mp: 159.5–160.5 °C. IR (KBr): 1653, 1472, 1223 cm⁻¹. ¹H NMR (CDCl₃) δ: 2.37 (s, 3H), 3.72 (d, 2H, *J* = 0.9 Hz), 4.52 (d, 2H, *J* = 1.2 Hz), 6.97 (t, 1H, *J* = 0.9 Hz), 7.22 (t, 1H, *J* = 1.2 Hz), 9.44 (s, 1H). ¹³C NMR (CDCl₃) δ: 21.9, 25.1, 48.1, 118.2, 119.0, 141.6, 151.6, 162.2, 188.8, 193.4. MS *m/z*: 222 (100, M⁺), 43 (69). Anal. Calcd for C₁₀H₁₀N₂O₂S: C, 54.04; H, 4.53; N, 12.60. Found: C, 53.87; H, 4.63; N, 12.52.

Acknowledgment. We are grateful to the French Ministry of Education and the CNRS for financial support.

Supporting Information Available: General procedures, detailed experimental procedures for compounds **1**, **4**, and **7**, spectroscopic data for **1**, **2b**, **3b**, **5b**, **8a**, and **9c**, and copies of ¹H and ¹³C NMR for all compounds (except ¹H for **8b** and ¹³C for **4b**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO034381L