

UNEXPECTED FORMATION OF PYRROLO[2,1-*b*]THIAZOLES BY REARRANGEMENT OF α -HYDROXYDIHYDRO-1,4-THIAZINES

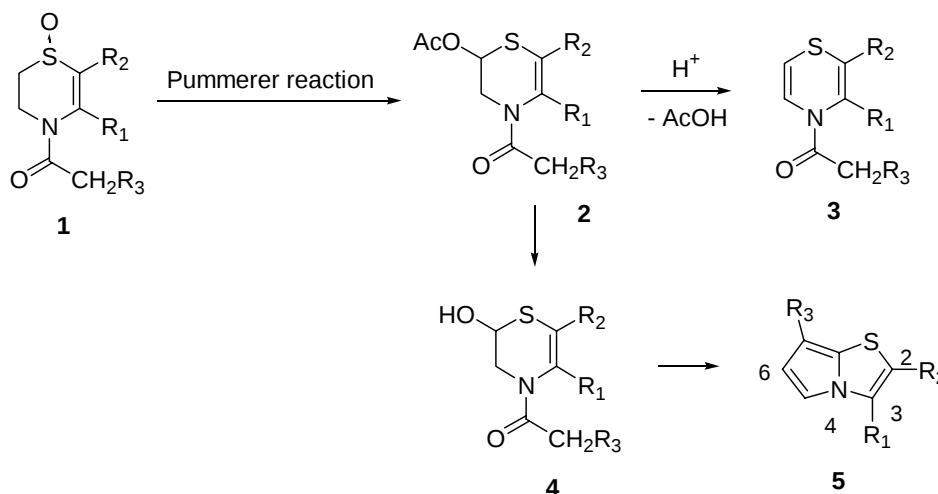
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Abstract - A new synthesis of pyrrolo[2,1-*b*]thiazoles (**5**) is described. Hydrolysis of acetoxy dihydro-1,4-thiazine (**2**) prepared by Pummerer reaction of dihydro-1,4-thiazine sulfoxide gave the intermediate α -hydroxy sulfide (**4**). Dehydration of **4** gave pyrrolo[2,1-*b*]thiazoles (**5**). The reaction mechanism for the formation of **5** including the intermediate thiol (**6**) is discussed.

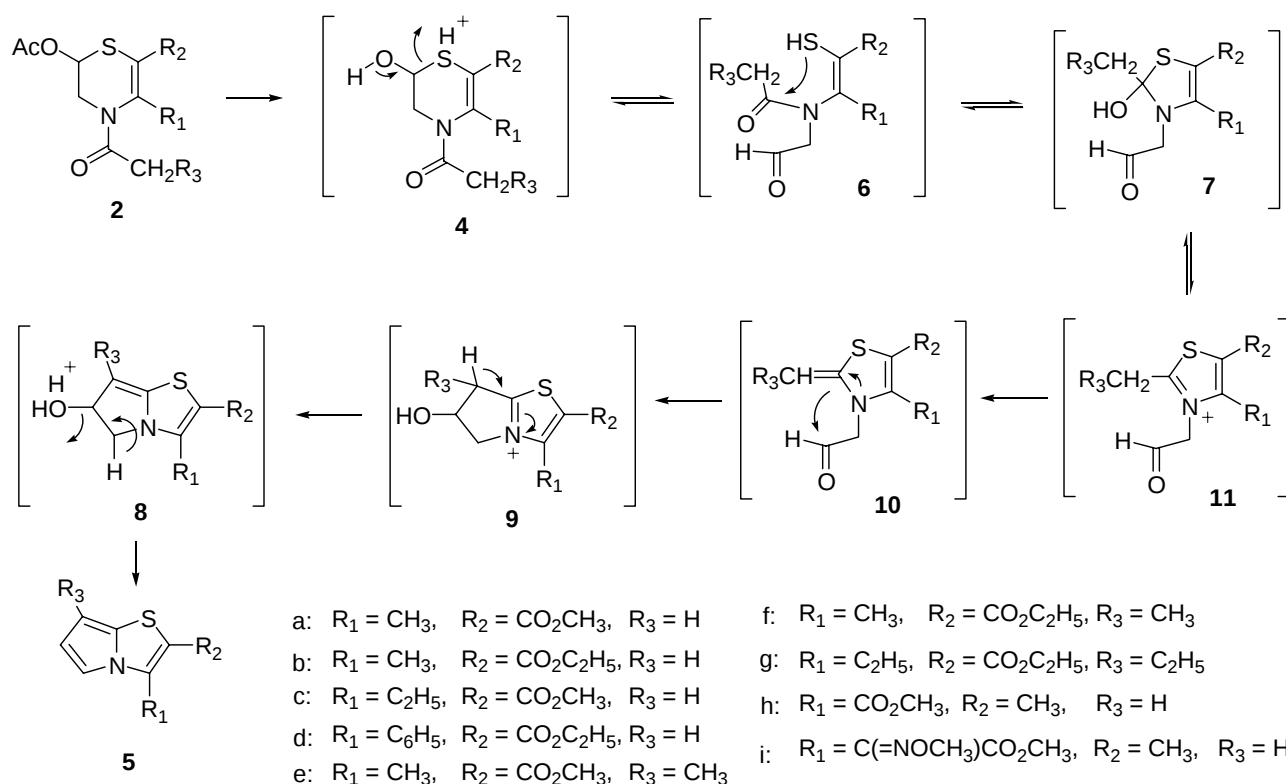
For the purpose of the development of a new class of α,β -unsaturated carboxanilide agrochemical fungicide ¹ we reported a synthesis of 1,4-thiazine carboxanilide (**3**) through Pummerer reaction of dihydro-1,4-thiazine sulfoxide (**1**). ² An unexpected pyrrolo[2,1-*b*]thiazole derivative (**5**) was isolated as a minor product during the final step of the reaction.



This report describes a new synthesis of the pyrrolo[2,1-*b*]thiazole (**5**) from α -hydroxy sulfide (**4**) and the plausible mechanism of the reaction.

Synthesis of the acetoxy-dihydro-1,4-thiazines (**2**) was easily accomplished in two steps, oxidation of

dihydro-1,4-thiazine with aqueous hydrogen peroxide in the presence of benzeneseleninic acid catalyst³ followed by Pummerer reaction of the resultant sulfoxides (**1**) according to the previous report.² Treatment of **2** with *p*-toluenesulfonic acid monohydrate in refluxing toluene gave 1,4-thiazine (**3**). TLC analysis of this elimination reaction indicated the formation of another product. Since acetoxy moiety could be hydrolyzed under acidic conditions, we carried out hydrolysis of acetoxy-dihydro-1,4-thiazines (**2**) by treating with potassium carbonate. The resulting product (**4**) was unstable at room temperature and converted slowly to the compound, which is identical with the minor product described above in the formation of **3**. It was clear that α -hydroxy sulfide (**4**) was initially formed, which was confirmed by analysis of ¹H NMR and IR spectral data of the crude product. Without purification of α -hydroxy sulfide (**4**) the crude product was treated with a catalytic amount of *p*-toluenesulfonic acid in refluxing toluene to afford pyrrolo[2,1-*b*]thiazole (**5**) in moderate yield (see Table 1). Elucidation of the structure (**5**) was achieved by the various spectral, elemental, and X-Ray crystallographic analysis (see Figure 1 for acetylpyrrolo[2,1-*b*]thiazole (**13e**)). In the ¹H NMR spectrum of **5a**, long range coupling (⁴*J* = 1.2 Hz) between C-5 and C-7 proton was found.



Scheme 1

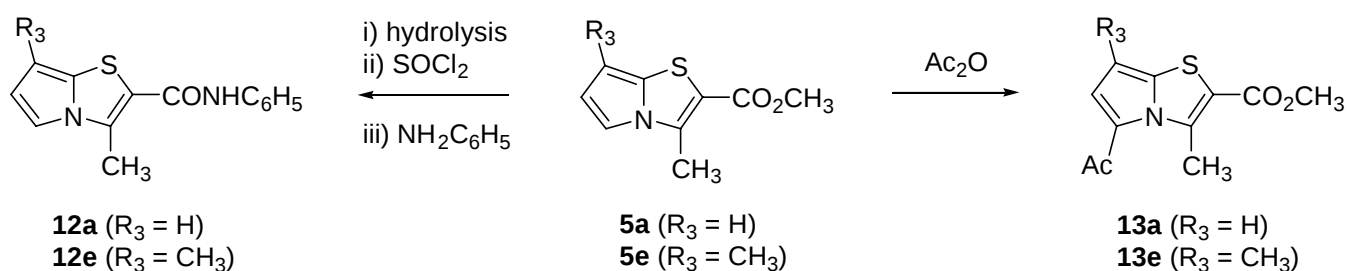
The plausible reaction mechanism is proposed for the rearrangement of **2** to **5** (Scheme 1). Hydrolysis of the acetoxy group of **2** afforded a hemithioacetal which is in equilibrium with thiol compound (**6**) in the

presence of acid.⁴ Internal nucleophilic attack of sulfur to the carbonyl group of **6** would give hemithioketal intermediate, *tert*-alcohol (**7**) which is in equilibrium with **11**. Deprotonation of **11** followed by cyclization of **10** assisted by lone pair electron of nitrogen would result in **5** after dehydration.

Table 1. Pyrrolo[2,1-*b*]thiazoles (**5**)

Compounds	R ₁	R ₂	R ₃	yields(%) ^a
5a	CH ₃	CO ₂ CH ₃	H	50
5b	CH ₃	CO ₂ C ₂ H ₅	H	29
5c	C ₂ H ₅	CO ₂ CH ₃	H	76
5d	C ₆ H ₅	CO ₂ C ₂ H ₅	H	16
5e	CH ₃	CO ₂ CH ₃	CH ₃	71
5f	CH ₃	CO ₂ C ₂ H ₅	CH ₃	23
5g	C ₂ H ₅	CO ₂ CH ₃	CH ₃	62
5h	CO ₂ CH ₃	CH ₃	H	51
5i	C(=NOCH ₃)CO ₂ CH ₃	CH ₃	H	38

^a The reactions were not optimized.



Scheme 2

As an extension of our study for development of new agrochemical fungicide which has α,β -unsaturated carboxanilide with pyrrolo[2,1-*b*]thiazole scaffold we performed acetylation and hydrolysis of **5a** and **5e** (Scheme 2). Hydrolysis of **5a** and **5e** followed by coupling with aniline afforded the corresponding pyrrolo[2,1-*b*]thiazolecarboxanilides (**12a**) and (**12e**) respectively. Treatment of **5a** and **5e** in refluxing acetic anhydride gave the corresponding **13a** and **13e** (Figure 1 for the X-Ray crystallographic analysis).

Their spectral data including ^1H , ^{13}C NMR, MS spectra, elemental analyses agreed with their structures.

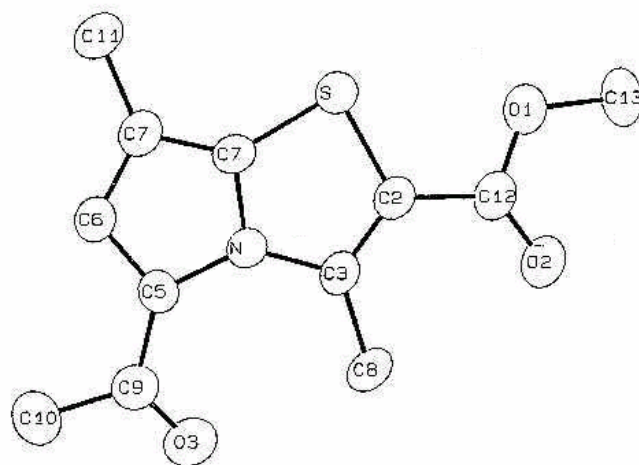


Figure 1. ORTEP plots of pyrrolo[2,1-*b*]thiazole (**13e**).⁵

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. All ^1H NMR (300 MHz) and ^{13}C NMR (78.5 MHz) spectra were recorded on a Varian Gemini 300 spectrometer in CDCl_3 . Chemical shift (δ) are given in ppm and the coupling constants (J) in Hz. IR spectra were obtained on a Perkin-Elmer 16F-PC FT-IR and are reported in cm^{-1} . MS spectra were recorded on a Hewlett Packard 5890 series GC/MSD. HRMS were obtained on a Finnigan MAT95S. Elemental analysis was performed using a Fisons EA1108 analyzer. All chromatographic isolation was accomplished on silica gel GF₂₅₄ (230-400 mesh). All the crystalline products reported in this paper were recrystallized from ethyl acetate and *n*-hexane.

Preparation of methyl 3-methylpyrrolo[2,1-*b*]thiazole-2-carboxylate (**5a**) (General Procedure)

A solution of methyl 6-acetoxy-4-acetyl-3-methyl-1,4-thiazine-2-carboxylate (15.0 g, 54.87 mmol) and potassium carbonate (15.15 g, 110 mmol) in 50% aqueous methanol (40 mL) was stirred for 30 min. The solvent was evaporated under reduced pressure. The residue was dissolved in methylene chloride (100 mL), washed with water, and then dried (MgSO_4). Evaporation of the solvent gave oily residue (12.24 g). To a solution of this residue in toluene (150 mL) was added *p*-toluenesulfonic acid monohydrate (521 mg). The reaction mixture was refluxed for 3 h with Dean-Stark water trap. The reaction mixture was cooled, washed with aqueous saturated sodium bicarbonate solution, water and then dried (MgSO_4). Evaporation of the solvent gave light brown oily residue (12.07 g). Flash chromatography on silica gel (GF₂₅₄, 230-400 mesh) using ethyl acetate and *n*-hexane (1:4) as an eluent afforded **5a** (5.13 g, 50%, R_f

0.4). mp 106-107 °C; ^1H NMR 2.68 (s, 3H, 3-CH₃), 3.83 (s, 3H, 2-OCH₃), 6.15 (dd, $J_{5,7} = 1.2$, $J_{6,7} = 3.6$, 1H, 7-CH), 6.64 (dd, $J_{6,7} = 3.6$, $J_{5,6} = 2.8$, 1H, 6-CH), 7.07 (dd, $J_{5,7} = 1.2$, $J_{5,6} = 2.8$, 1H, 5-CH); ^{13}C NMR 12.60, 52.13, 98.14, 109.63 113.09, 116.82, 128.70, 137.87, 163.23; IR (KBr) 1700 (C=O), 1592 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 195 (M^+ , 100), 180 ($\text{M}^+ - \text{CH}_3$, 22), 164 ($\text{M}^+ - \text{OCH}_3$, 32), 136 ($\text{M}^+ - \text{CO}_2\text{CH}_3$); HRMS for C₉H₉NO₂S Calcd 195.0354. Found 195.0354; *Anal.* Calcd for C₉H₉NO₂S: C, 55.37, H, 4.65, N, 7.17. Found, C, 55.36, H, 4.65, N, 7.17.

Ethyl 3-methylpyrrolo[2,1-*b*]thiazole-2-carboxylate (5b). mp 62 °C; ^1H NMR 1.32 (t, $J = 7.1$, 3H, ethyl CH₃), 2.62 (s, 3H, 3-CH₃), 4.27 (q, $J = 7.1$, 2H, ethyl CH₂), 6.12 (d, $J = 3.8$, 1H, 7-CH), 6.64 (dd, $J = 3.8$, $J = 3.0$, 1H, 6-CH), 7.07 (d, $J = 3.0$, 1H, 5-CH); ^{13}C NMR 12.52, 14.39, 61.18, 98.07, 109.58, 113.51, 116.69, 128.68, 137.57, 162.76; IR (KBr) 1696 (C=O), 1598 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 209 (M^+ , 86), 181 ($\text{M}^+ - \text{C}_2\text{H}_5$, 100), 164 ($\text{M}^+ - \text{OC}_2\text{H}_5$, 21), 136 ($\text{M}^+ - \text{CO}_2\text{C}_2\text{H}_5$, 23); HRMS for C₁₀H₁₁NO₂S Calcd 209.0510. Found 209.0509; *Anal.* Calcd for C₁₀H₁₁NO₂S: C, 57.39, H, 5.30, N, 6.69. Found, C, 57.66, H, 5.26, N, 6.77.

Methyl 3-ethylpyrrolo[2,1-*b*]thiazole-2-carboxylate (5c). mp 46-47 °C; ^1H NMR 1.31 (t, $J = 7.5$, 3H, 3-CH₃), 3.23 (q, $J = 7.5$, 2H, 3-CH₂), 3.87 (s, 3H, 2-OCH₃), 6.17 (dd, $J_{5,7} = 1.2$, $J_{6,7} = 3.6$, 1H, 7-CH), 6.66 (dd, $J_{6,7} = 3.6$, $J_{5,6} = 2.8$, 1H, 6-CH), 7.15 (dd, $J_{5,7} = 1.2$, $J_{5,6} = 2.8$, 1H, 5-CH); IR (KBr) 1714 (C=O), 1592 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 209 (M^+ , 100), 178 ($\text{M}^+ - \text{OCH}_3$, 13), 164 ($\text{M}^+ - \text{C}_2\text{H}_5$, 48); HRMS for C₁₀H₁₁NO₂S: Calcd 209.0510, found 209.0511; *Anal.* Calcd for C₁₀H₁₁NO₂S: C, 57.39, H, 5.30, N, 6.69. Found, C, 57.68, H, 5.22, N, 6.72.

Ethyl 3-phenylpyrrolo[2,1-*b*]thiazole-2-carboxylate (5d). mp 91-92 °C; ^1H NMR 1.20 (t, $J = 7.1$, 3H, ethyl CH₃), 4.20 (q, $J = 7.1$, 2H, ethyl CH₂), 6.22 (dd, $J_{5,7} = 1.0$, $J_{6,7} = 3.5$, 1H, 7-CH), 6.61 (dd, $J_{5,6} = 2.5$, $J_{6,7} = 3.5$, 1H, 6-CH), 6.93 (2d, $J_{5,7} = 1.0$, $J_{5,6} = 2.5$, 1H, 5-CH), 7.54 (s, 5H, 3-ArH); IR (KBr) 1716 (C=O), 1576 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 271 (M^+ , 76), 243 (100), 226 (16) 198 (41); HRMS for C₁₅H₁₃NO₂S: Calcd 271.0667. Found 271.0667; *Anal.* Calcd for C₁₅H₁₃NO₂S: C, 66.40, H, 4.83, N, 5.16. Found, C, 66.26, H, 4.72, N, 5.43.

Methyl 3,7-dimethylpyrrolo[2,1-*b*]thiazole-2-carboxylate (5e). mp 112 °C; ^1H NMR 2.17 (s, 3H, 7-CH₃), 2.70 (s, 3H, 3-CH₃), 3.87 (s, 3H, CO₂CH₃), 6.49 (s, 1H, 6-CH), 7.06 (br s, 1H, 5-CH); ^{13}C NMR 11.56, 12.39, 52.08, 107.9, 108.9, 112.5, 118.1, 125.5, 138.3, 163.4; IR (KBr) 1630 (C=O), 1580 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 209 (M^+ , 85), 208 (100), 194 ($\text{M}^+ - \text{CH}_3$, 4), 178 ($\text{M}^+ - \text{OCH}_3$, 10), 150 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 32); HRMS for C₁₀H₁₁NO₂S: Calcd 209.0510. Found 209.0510; *Anal.* Calcd for C₁₀H₁₁NO₂S: C, 57.39, H, 5.30, N, 6.69. Found, C, 57.46, H, 5.41, N, 6.77.

Ethyl 3,7-dimethylpyrrolo[2,1-*b*]thiazole-2-carboxylate (5f). mp 68 °C; ^1H NMR 1.39 (t, $J = 7.1$, 3H, ethyl CH₃), 2.18 (s, 3H, 7-CH₃), 2.69 (s, 3H, 3-CH₃), 4.34 (q, $J = 7.1$, 2H, ethyl CH₂), 6.48 (d, $J = 2.8$, 1H,

6-CH), 7.00 (d, $J = 2.8$, 1H, 5-CH); IR (KBr) 1694 (C=O), 1596 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 223 (M^+ , 56), 194 ($M^+ - C_2H_5$, 100), 178 ($M^+ - OC_2H_5$, 3); HRMS for $C_{11}H_{13}NO_2S$: Calcd 223.0667, found 223.0669; *Anal.* Calcd for $C_{11}H_{13}NO_2S$: C, 59.17, H, 5.87, N, 6.27. Found, C, 59.45, H, 5.86, N, 6.38.

Methyl 7-ethyl-3-methyl-pyrrolo[2,1-*b*]thiazole-2-carboxylate (5g). mp 96-97 °C; 1H NMR 1.25 (t, $J = 7.5$, 3H, ethyl CH_3), 2.57 (q, $J = 7.5$, 2H, ethyl CH_2), 2.67 (s, 3H, 3- CH_3), 3.86 (s, 3H, 2- OCH_3), 6.49 (d, $J = 2.9$, 1H, 6-CH), 7.02 (d, $J = 2.9$, 1H, 5-CH); IR (KBr) 1700 (C=O), 1592 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 223 (M^+ , 58), 208 ($M^+ - CH_3$, 100), 192 ($M^+ - OCH_3$, 31); HRMS for $C_{11}H_{13}NO_2S$: Calcd 223.0667, found 223.0667; *Anal.* Calcd for $C_{11}H_{13}NO_2S$: C, 59.17, H, 5.87, N, 6.27. Found, C, 59.25, H, 5.65, N, 6.28.

Methyl 2-methylpyrrolo[2,1-*b*]thiazole-3-carboxylate (5h). oil; 1H NMR 2.66 (s, 3H, 2- CH_3), 3.96 (s, 3H, 3- $COCH_3$), 6.18 (br s, 1H, 7-CH), 6.52 (s, 1H, 6-CH), 7.78 (br s, 1H, 5-CH); IR (KBr) 1706 (C=O), 1580 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 195 (M^+ , 100), 180 ($M^+ - CH_3$, 35); HRMS for $C_9H_9NO_2S$: Calcd 195.0354, found 195.0354; *Anal.* Calcd for $C_9H_9NO_2S$: C, 55.37, H, 4.65, N, 7.17. Found, C, 55.86, H, 4.35, N, 6.97.

Methyl methoxyimino(2-methylpyrrolo[2,1-*b*]thiazol-3-yl)acetate (5i). mp 92 °C; 1H NMR 2.22 (s, 3H, 2- CH_3), 3.89 (s, 3H, 3- CO_2CH_3), 4.15 (s, 3H, $NOCH_3$), 6.14 (dd, $J_{5,7} = 1.0$, $J_{6,7} = 3.5$, 1H, 7-CH), 6.44 (dd, $J_{5,6} = 2.5$, $J_{6,7} = 3.5$, 1H, 6-CH), 6.72 (dd, $J_{5,7} = 1.0$, $J_{5,6} = 2.5$, 1H, 5-CH); IR (KBr) 1736 (C=O), 1624 (C=N), 1590 (C=C) cm^{-1} ; MS (70 eV) m/z (relative intensity) 252 (M^+ , 64), 189 (28), 162 ($M^+ - OCH_3$ and CO_2CH_3 , 100) 149 (32); HRMS for $C_{11}H_{12}N_2O_3S$: Calcd 252.0569. Found 252.0569; *Anal.* Calcd for $C_{11}H_{12}N_2O_3S$: C, 52.37, H, 4.79, N, 11.10. Found, C, 52.46, H, 4.85, N, 11.45.

3-Methyl-*N*-phenylpyrrolo[2,1-*b*]thiazole-2-carboxamide (12a). A mixture of **5a** (2.01 g, 10.3 mmol) and sodium hydroxide (3.0 g, 75 mmol) in water (50 mL) was refluxed for 40 min. The reaction mixture was cooled to rt, and washed with ethyl ether. The aqueous layer was acidified (pH = 2-3) with 3N hydrochloric acid. The light brown precipitate was collected by filtration. The filtrate was extracted with methylene chloride and evaporated. The residue were combined with the precipitate, and crystallized from ethanol to give 3-methylpyrrolo[2,1-*b*]thiazole-2-carboxylic acid (1.40 g, 75%, mp 198-200 °C). To a suspension of this acid (1.0 g, 5.52 mmol) in dried benzene (10 mL) was added thionyl chloride (0.44 mL, 6.07 mmol) and the reaction mixture was refluxed for 30 min. The reaction mixture was cooled to rt and triethylamine (8.5 mL) and aniline (0.5 mL, 5.52 mmol) were added sequentially and then stirred at the same temperature for 2 h. The reaction mixture was washed with aqueous saturated sodium bicarbonate solution, 0.5 N hydrochloric acid, and then water. The organic layer was dried ($MgSO_4$) and evaporated to give light blue solid (1.25 g). Flash chromatography on silica gel using a mixture of ethyl

acetate and *n*-hexane (1:9) as an eluent afforded **12a** (1.10 g, 78 %, R_f 0.2). mp 167 °C; ^1H NMR 2.72 (s, 3H, 3-CH₃), 6.23 (dd, $J_{5,7} = 1.2$, $J_{6,7} = 2.8$, 1H, 7-CH), 6.67 (dd, $J_{6,7} = 2.8$, $J_{5,6} = 3.6$, 1H, 6-CH), 7.12-7.54 (m, 6H, 5-vinyl CH and ArH), 7.39 (br s, 1H, NH); IR (KBr) 1640 (C=O), 1598 (C=C) cm⁻¹; MS (70 eV) m/z (relative intensity) 256 (M^+ , 57), 164 ($\text{M}^+ - \text{NHC}_6\text{H}_5$, 100); HRMS for C₁₄H₁₂N₂OS: Calcd 256.0670, found 256.0669; *Anal.* Calcd for C₁₄H₁₂N₂OS: C, 65.60, H, 4.72, N, 10.93. Found, C, 65.66, H, 4.75, N, 10.86.

3,7-Dimethyl-*N*-phenylpyrrolo[2,1-*b*]thiazole-2-carboxamide (12b). yield 36 %, mp 110-114 °C; ^1H NMR 2.15 (s, 3H, 7-CH₃), 2.68 (s, 3H, 3-CH₃), 6.44 (d, $J = 2.7$, 1H, 6-CH), 7.03 (d, $J = 2.7$, 1H, 5-CH), 7.08-7.51 (m, 5H, ArH), 7.63 (br s, 1H, NH), IR (KBr) 3425 (NH), 1648 (C=O) cm⁻¹; MS (70 eV) m/z (relative intensity) 270 (M^+ , 92), 178 ($\text{M}^+ - \text{NHC}_6\text{H}_5$, 100), 150 ($\text{M}^+ - \text{C}_6\text{H}_5\text{NHCO}$, 48); HRMS for C₁₅H₁₄N₂OS: Calcd 270.0827. Found 270.0828; *Anal.* Calcd for C₁₅H₁₄N₂OS: C, 65.64, H, 5.22, N, 10.36. Found, C, 65.76, H, 5.33, N, 10.28.

Methyl 5-acetyl-3-methylpyrrolo[2,1-*b*]thiazole-2-carboxylate (13a). A solution of **5a** (300 mg, 1.54 mmol) in acetic anhydride (5 mL) was refluxed for 20 h. Evaporation of the reaction mixture gave light brown solid, which was crystallized from ethyl acetate and petroleum ether afforded acetylated pyrrolothiazole (**13a**) (113 mg, 31%). mp 128-129 °C; ^1H NMR 2.49 (s, 3H, 5-Ac), 3.06 (s, 3H, 3-CH₃), 3.89 (s, 3H, OCH₃), 6.27 (d, $J = 4.4$, 1H, 7-CH), 7.39 (d, $J = 4.4$, 1H, 6-CH); ^{13}C NMR 15.85, 27.34, 52.38, 99.56, 115.25, 127.65, 128.75, 140.27, 143.48, 162.41, 184.25; IR (KBr) 1717 (acetyl C=O), 1656 (ester C=O), 1584 (C=C) cm⁻¹; MS (70 eV) m/z (relative intensity) 237 (M^+ , 58), 222 ($\text{M}^+ - \text{CH}_3$, 100), 206 ($\text{M}^+ - \text{OCH}_3$, 6), 194 ($\text{M}^+ - \text{COCH}_3$, 32); HRMS for C₁₁H₁₁NO₃S: Calcd 237.0460. Found 237.0460; *Anal.* Calcd for C₁₁H₁₁NO₃S: C, 55.68, H, 4.67, N, 5.90. Found, C, 55.41, H, 4.70, N, 5.88.

Methyl 5-acetyl-3,7-dimethylpyrrolo[2,1-*b*]thiazole-2-carboxylate (13e). yield 13 %; mp 187-188 °C; ^1H NMR 2.16 (s, 3H, 7-CH₃), 2.45 (s, 3H, 5-Ac), 2.70 (s, 3H, 3-CH₃), 3.89 (s, 3H, CO₂CH₃), 7.21 (s, 1H, 6-CH); ^{13}C NMR 11.13, 15.89, 27.26, 52.32, 109.25, 114.88, 126.89, 129.07, 138.49, 144.13, 162.58, 183.81; IR (KBr) 1714 (acetyl C=O), 1652 (ester C=O), 1588 (C=C) cm⁻¹; MS (70 eV) m/z (relative intensity) 251 (M^+ , 62), 236 ($\text{M}^+ - \text{CH}_3$, 100), 220 ($\text{M}^+ - \text{OCH}_3$, 5), 208 ($\text{M}^+ - \text{COCH}_3$, 8), 193 (6); HRMS for C₁₂H₁₃NO₃S: Calcd 251.0616. Found 251.0614; *Anal.* Calcd for C₁₂H₁₃NO₃S: C, 57.35, H, 5.21, N, 5.57. Found, C, 57.51, H, 5.23, N, 5.58.

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5. The X-Ray analysis was performed with the methyl 5-acetyl-3,7-dimethylpyrrolo[2,1-*b*]thiazole-2-carboxylate (**13e**). The data was collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-Ray tube and a graphite monochromator. Orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 7.569(3) \text{ \AA}$, $b = 8.813(2) \text{ \AA}$, $c = 21.273(5) \text{ \AA}$, $V = 1419.0(4) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.509 \text{ gcm}^{-3}$, $\mu = 0.255 \text{ mm}^{-1}$. A total of 1138 independent absorption-corrected reflections were collected. The structure was solved using SHELXS86 and SHELXL93 programs. The resulting structural parameters were refined to convergence of $R_1 = 0.0398$ for 1138 independent reflections with $I > 2\sigma(I)$ using full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms.