Synthesis of thieno[3.2-*b*]pyrrolenine derivatives under the Fischer reaction conditions

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The reaction of alkyl 4-(2-acetylhydrazino)-2-methyl-3-thiophenecarboxylates with 3-methylbutan-2-one was carried out under the Fischer reaction conditions. The influence of Lewis acids and solvents on the process was studied. A convenient method for the synthesis of thieno[3.2-*b*]pyrrolenine derivatives was proposed.

Key words: thieno[3,2-*b*]pyrrolenines, 3-methylbutan-2-one, Fischer reaction, β-thienylhydrazine, benzidine rearrangement, Lewis acids.

Thieno[3,2-*b*]pyrrolenines, isosters of indolenines, are of considerable interest as biologically active substances and starting compounds for the preparation of photochromic materials and dyes.[1—4] A number of thienopyrrolenines are known; however, the methods used for their synthesis are labor-consuming.[5,6] Recently, we have developed a more effective approach to the preparation of thieno[3,2-*b*]pyrrolenines,[7] but the use of bultyllithium at the last stage prevents extensive use of this synthesis; this dictates the need for development of more perfect routes to these valuable heterocycles.

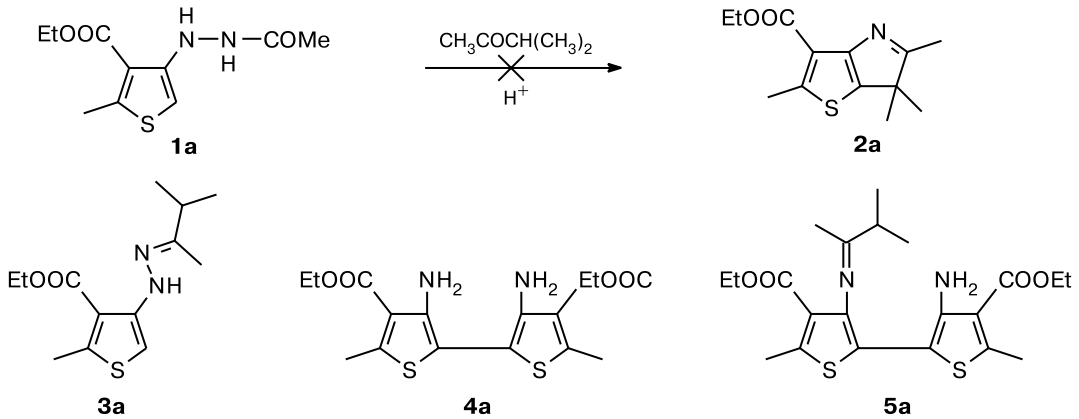
This publication presents a study of the Fischer reaction, which is widely used to prepare indole and indolenine derivatives[8—10] but has not been used so far to construct thieno[3,2-*b*]pyrrolenine derivatives.

We studied the reaction of readily available 4-(2-acetylhydrazino)-2-methylthiophene-3-carboxylate[11] (**1a**) with 3-methylbutan-2-one in various solvents in the presence of Lewis acids (Table 1). Under the Fischer reaction conditions, we expected the formation of product **2a**; however, instead, the reaction gave hydrazone **3a** and the benzidine rearrangement products **4a** and **5a** in various ratios (Scheme 1). The last-mentioned compound has apparently resulted from diamine **4a** condensation

Table 1. Conditions and product yields for the reaction of β-thienylhydrazine **1a** with 3-methylbutan-2-one

Acid	Solvent	Reaction products (%)		
		3a	**4a**	**5a**
TsOH	MeOH	18	22	26
HCl	MeOH	Traces	48	Traces
$ZnCl_2$	MeOH	—	Traces	44
CF_3COOH	EtOH	—	14	40
PPA	$CH_3COCHMe_2$	—	Traces	27

Scheme 1



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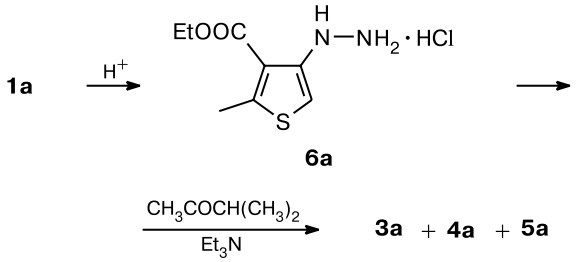
with 3-methylbutan-2-one. It is noteworthy that the benzidine rearrangement product **4a** has also been isolated in a previous work.[11] In all cases, substantial resinification took place.

Hydrazones are known to be intermediates in the Fischer indole synthesis;[12–14] therefore, we attempted to prepare hydrazone **3a** according to Scheme 2. Thienylhydrazine hydrochloride **6a**[11] was isolated in 63% yield and hydrazone **3a** was obtained in 42% yield. Compounds **4a** and **5a** were also formed as side products in the second reaction step.

Scheme 2

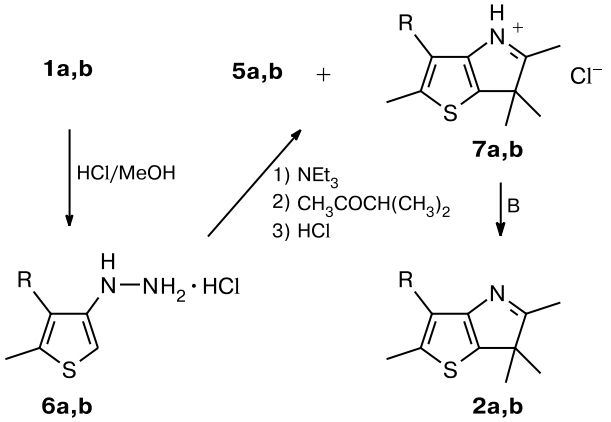


However, further attempts to synthesize thienopyrrolenine by cyclization of hydrazone **3a** under various Fischer reaction conditions have not met with success. For example, refluxing in ethanol with $ZnCl_2$ yields only resinification products and partially recovered starting compound, while in the case of $BF_3 \cdot Et_2O$ in acetic acid, heavy resinification of the reaction mixture is observed and small amounts of compound **5a** are produced.

We assumed that the resinification is due to the instability of thienopyrrolenine as a free base. This may be due to the fact that the thienopyrrolenine system is not aromatic unlike the thienopyrrole system and, hence, it is less stable.

The preparation of the thienopyrrolenine salt in an anhydrous solvent seemed to offer a solution to this problem. To this end, the pre-synthesized hydrazines **6a,b**[11] were refluxed with 3-methylbutan-2-one in benzene in a flow of dry hydrogen chloride for 1 h. Indeed, the reaction gave thienopyrrolenine salts **7a,b**, which are stable on storage in air unlike free thienopyrrolenines **2a,b** (Scheme 3).

Scheme 3



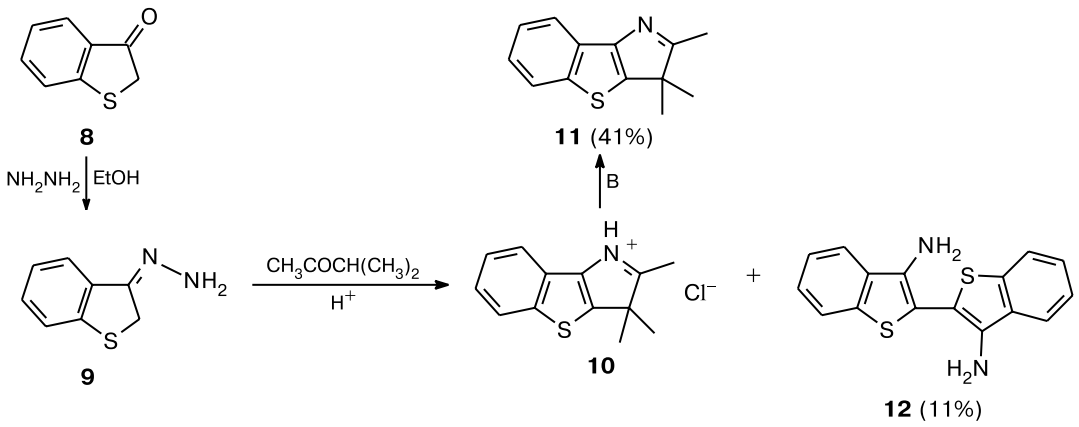
R = EtOOC (**a**), MeOOC (**b**)
B is a base

Using a similar procedure, benzothiophen-3-one (**8**)[14,15] was converted into benzothienopyrrolenine **11** in an overall yield of 35—40% (Scheme 4).

It is noteworthy that under these conditions, the benzidine rearrangement products **5a,b** and **12** are also formed, but now in low yields.

Salts **7a,b** and **10** were not characterized in a pure state due to the difficulty of their purification. As noted

Scheme 4



B is a base

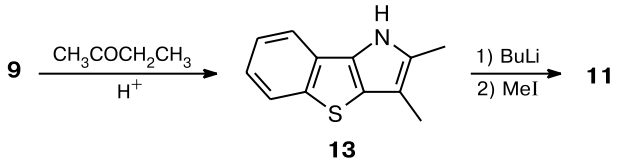
above, thienopyrrolenines are unstable under ambient conditions but can be stored at a temperature of −10 to −12 °C for several months.

The structures of thienopyrrolenines **2a,b** and **11** were proved by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry and confirmed by elemental analysis. A typical feature of the ^{13}C NMR spectra of compounds **2a,b** and **11** is the presence of signals at 190 and 54 ppm, corresponding to the imine and quaternary carbon atoms of the pyrrolenine ring. The ^{1}H NMR spectra of compounds **11—13** exhibit signals for the ABCD system of the benzene ring (*cf.* Ref. 17).

The proposed method for the synthesis of thieno[3,2-*b*]pyrrolenines has a number of advantages over known methods. Indeed, according to published data,[6] the total yields of thienopyrrolenines do not exceed 5%, whereas the yields for **2a,b** and **11** are 25—30%. In addition, this approach is based on the use of readily available starting compounds.

The method we have developed previously[7] and give here for comparison (Scheme 5) is also inferior to the methods depicted in Schemes 3 and 4. The yield of product **11** according to Scheme 5 is not more than 7% in relation to the starting hydrazone **9**; in addition, this method involves BuLi, which restricts substantially its scope.

Scheme 5



Thus, we proposed a convenient approach to the synthesis of thieno[3,2-*b*]pyrrolenine derivatives.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker AM-300 spectrometers in $CDCl_3$; mass spectra (EI) were run on a Kratos instrument (70 eV) with direct sample injection into the ion source. The melting points were measured on a Boetius hot stage and not corrected. The reaction completion was indicated by TLC (Silufol UV-254, elution with a petroleum ether (60—80 °C)—ethyl acetate mixture, 6 : 1). Column chromatography was carried out with silica gel Acros (C.A.S.-7631-86-9) (0.060—0.200). Ethyl 4-(2-acetylhydrazino)-2-methylthiophene-3-carboxylate (**1a**)[11] 4-hydrazino-2-methylthiophene-3-carboxate hydrochlorides **6a,b**,[11] and benzothiophenone **8**[15] were prepared by known procedures. Commercially available (Merck, Acros, Aldrich) butan-2-one, 3-methylbutan-2-one, trifluoroacetic acid, and *p*-toluenesulfonic acid samples, a 15% solution of butyllithium in hexane, anhydrous (99.9%) zinc chloride, methanol, and benzene were used.

The reaction of ethyl 4-(2-acetylhydrazino)-2-methylthiophene-3-carboxylate (1a) with 3-methylbutan-2-one under the Fischer reaction conditions. Lewis acid (2 mmol) was added to a solution of ethyl 4-(2-acetylhydrazino)-2-methylthiophene-3-carboxylate (**1a**) (0.24 g, 1 mmol) and 3-methylbutan-2-one (0.11 mL, 1.05 mmol) in 5 mL of the solvent (see Table 1) and the mixture was refluxed for 4 h. After completion of the reaction (TLC monitoring), the reaction mixture was poured in water, the product was extracted with ethyl acetate, the organic layer was concentrated, and the residue was chromatographed on silica gel (elution with petroleum ether—ethyl acetate, 6 : 1). (In the case of TsOH, HCl, and $ZnCl_2$ catalysts, compound **4a** crystallized on cooling the reaction mixture.) The product yields and the reaction conditions are summarized in Table 1.

Ethyl 2-methyl-4-(3-methyl-2-butylidenehydrazino)-thiophene-3-carboxylate (3a). Light yellow oil. ^{1}H NMR, δ: 1.13 (d, 6 H, $CH(C\underline{H}_3)_2$, J = 6.6 Hz); 1.40 (t, 3 H, $CO_2CH_2C\underline{H}_3$, J = 7.2 Hz); 1.85 (s, 3 H, $C\underline{H}_3C$=N); 2.56 (m, 1 H, $C\underline{H}Me_2$); 2.66 (s, 3 H, Me); 4.35 (q, 2 H, $CO_2C\underline{H}_2CH_3$, J = 7.2 Hz); 6.35 (s, 1 H, $C_{thioph}H$); 9.05 (br.s, 1 H, NH). MS, m/z: 268 $[M]^+$. Found (%): C, 58.40; H, 7.70; S, 11.60. $C_{13}H_{20}N_2O_2S$. Calculated (%): C, 58.18; H, 7.51; S, 11.95.

Diethyl 3,3′-diamino-5,5′-dimethyl-2,2′-bithiophene-4,4′-dicarboxylate (4a). M.p. 145—147 °C. (Ref. 11: 144—146 °C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.40 (t, 6 H, $CO_2CH_2C\underline{H}_3$, J = 7.36 Hz); 2.64 (s, 6 H, 2 Me); 4.36 (q, 4 H, $CO_2C\underline{H}_2CH_3$, J = 7.36 Hz); 4.97 (br.s, 4 H, 2 NH_2). MS, m/z: 368 $[M]^+$.

Diethyl 3-amino-5,5′-dimethyl-3′-(3-methyl-2-butylideneamino)-2,2′-bithiophene-4,4′-dicarboxylate (5a). M.p. 151—153 °C. ^{1}H NMR, δ: 0.95 (d, 6 H, $CH(C\underline{H}_3)_2$, J = 6.9 Hz); 1.36 (s, 3 H, $C\underline{H}_3C$=N); 1.39 (t, 6 H, $CO_2CH_2C\underline{H}_3$, J = 7.3 Hz); 2.09 (m, 1 H, $C\underline{H}(Me)_2$); 2.62 (s, 6 H, 2Me); 4.35 (q, 4 H, $CO_2C\underline{H}_2CH_3$, J = 7.3 Hz); 7.09 (br.s, 2 H, NH_2). MS, m/z: 436 $[M]^+$. Found (%): C, 57.67; H, 6.65; S, 14.44. $C_{21}H_{28}N_2O_4S_2$. Calculated (%): C, 57.77; H, 6.46; S, 14.69.

4-(2-Acetylhydrazino)-3-methoxycarbonyl-2-methylthiophene (1b). Compound **1b** was synthesized similarly to **1a** by a known procedure.[11] Dimethyl 3,3′-diamino-5,5′-dimethyl-2,2′-bithiophene-4,4′-dicarboxylate (**4b**) was formed as a by-product (5%).

Yield 44%. M.p. 134—136 °C. ^{1}H NMR, δ: 2.03, 2.09 (both s, 3 H, COMe); 2.61, 2.64 (both s, 3 H, 2-Me); 3.85, 3.88 (both s, 3 H, CO_2Me); 5.95 (s, 1 H, CH); 7.05 (br.s, 1 H, NH); 7.70, 7.81 (both br.s, 1 H, NH). MS, m/z: 228 $[M]^+$. Found (%): C, 47.28; H, 5.20; S, 13.81. $C_9H_{12}N_2O_3S$. Calculated (%): C, 47.36; H, 5.30; S, 14.05.

Dimethyl 3,3′-diamino-5,5′-dimethyl-2,2′-bithiophene-4,4′-dicarboxylate (4b). M.p. 150—152 °C. ^{1}H NMR (300 MHz), $CDCl_3$, δ: 2.64 (s, 6 H, 2 Me); 3.90 (s, 6 H, CO_2Me). MS, m/z: 340 $[M]^+$. Found (%): C, 49.18; H, 4.53; S, 18.55. $C_{14}H_{16}N_2O_4S_2$. Calculated (%): C, 49.40; H, 4.74; S, 18.84.

Ethyl 2-methyl-4-(3-methyl-2-butylidenehydrazino)thiophene-3-carboxylate (3a). A solution of ethyl 4-hydrazino-2-methylthiophene-3-carboxylate hydrochloride (**6a**) (380 mg, 1.61 mmol), 3-methylbutanone (170 mg, 2 mmol), and triethylamine (170 mg, 1.7 mmol) in 10 mL of ethanol was stirred for 1 h at room temperature. After completion of the reaction, the solvent was evaporated and the residue was washed with ether and filtered to remove $NEt_3 \cdot HCl$. Diethyl ether was evapo-

rated, the residue was chromatographed on silica gel using a 6 : 1 petroleum ether (60—80 °C)—ethyl acetate mixture as the eluent to give 180 mg (42%) of **3a**, 50 mg (17%) of **4a**, and 80 mg (23%) of **5a**.

Esters of 2,5,6,6-tetramethyl-6*H*-thieno[3,2-*b*]pyrrolenine-3-carboxylic acid (2a,b). A solution of methyl or ethyl 4-hydrazino-2-methylthiophene-3-carboxylate hydrochloride **6a** or **6b** (30 mmol), 3-methylbutanone (4.3 mL, 40 mmol), and triethylamine (5.6 mL, 40 mmol) in 130 mL of ethanol was stirred for 1 h at room temperature. The compound **5a** (or **5b**) was filtered off, the mother liquor was concentrated, and the residue was extracted with diethyl ether. Diethyl ether was evaporated and the residue was dissolved in 150 mL of anhydrous benzene and refluxed for 30 min. Then, while continuing refluxing, hydrogen chloride gas was passed through the solution. The solution darkened and a solid precipitated. The reaction mixture was refluxed for 1 h and cooled to room temperature, the hydrogen chloride supply was terminated, ethyl acetate (100 mL) was added, and the mixture was washed with a solution of sodium bicarbonate and dried over magnesium sulfate. The solvent was evaporated, the residue was chromatographed on silica gel using a 2 : 3 $CHCl_3$—ethyl acetate mixture as the eluent.

Ethyl 2,5,6,6-tetramethyl-6*H*-thieno[3,2-*b*]pyrrolenine-3-carboxylate (2a). Yield 2.0 g (26%). M.p. 91—93 °C. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.25 (s, 6 H, CMe_2); 1.35 (t, 3 H, $CO_2CH_2C\underline{H}_3$, J = 7.35 Hz); 2.21 (s, 3 H, 5-Me); 2.67 (s, 3 H, 2-Me); 4.36 (q, 2 H, $CO_2C\underline{H}_2CH_3$, J = 7.35 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ: 14.48, 15.94, 17.00, 23.48, 23.78, 54.19 ($\underline{C}Me_2$), 60.63, 119.89, 138.54, 150.51, 155.91, 163.34, 190.69 (C=N). MS, m/z: 251 $[M]^+$. Found (%): C, 62.36; H, 7.04; S, 12.48. $C_{13}H_{17}NO_2S$. Calculated (%): C, 62.12; H, 6.82; S, 12.76.

Methyl 2,5,6,6-tetramethyl-6*H*-thieno[3,2-*b*]pyrrolenine-3-carboxylate (2b). Yield 1.7 g (23%). M.p. 125—127 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 1.32 (s, 6 H, CMe_2); 2.28 (s, 3 H, 5-Me); 2.75 (s, 3 H, 2-Me); 3.94 (s, 3 H, CO_2Me). MS, m/z: 237 $[M]^+$. Found (%): C, 60.90; H, 6.45; S, 13.29. $C_{12}H_{15}NO_2S$. Calculated (%): C, 60.73; H, 6.37; S, 13.11.

Diethyl 3-amino-5,5′-dimethyl-3′-(3-methyl-2-butylideneamino)-2,2′-bithiophene-4,4′-dicarboxylate (5a). Yield 1.8 g (28%). M.p. 150—152 °C.

Dimethyl 3-amino-5,5′-dimethyl-3′-(3-methyl-2-butylideneamino)-2,2′-bithiophene-4,4′-dicarboxylate (5b). Yield 2.0 g (31%). M.p. 128—130 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 0.97 (d, 6 H, $CH(C\underline{H}_3)_2$, J = 6.61 Hz); 1.36 (s, 3 H, $C\underline{H}_3C$=N); 2.10 (m, 1 H, $C\underline{H}(Me)_2$); 2.61 (s, 6 H, 2-Me); 3.87 (s, 6 H, CO_2CH_3); 7.09 (br.s, 2 H, NH_2). MS, m/z: 408 $[M]^+$. Found (%): C, 56.01; H, 5.95; S, 15.44. $C_{19}H_{24}N_2O_4S_2$. Calculated (%): C, 55.86; H, 5.92; S, 15.70.

Benzo[*b*]thiophen-3(2*H*)-one hydrazone (9) *p*-Toluenesulfonic acid (0.86 g, 5 mmol) and hydrazine hydrate 15 mL (0.3 mol) were added with stirring to a solution of benzothiophen-3-one (**8**) (9.6 g, 0.05 mol) in 15 mL of ethanol. The solution immediately became dark. The mixture was refluxed for 1 h and during this period, the solution became light. The reaction mixture was kept for 3—4 h at room temperature, and the precipitate was filtered off and dried in air. Yield 5.8 g (71%). M.p. 110—112 °C. ^{1}H NMR, δ: 3.91 (s, 2 H, CH_2); 5.25 (br.s, 2 H, NH_2); 7.11 (m, 1 H, H_{arom}), 7.24—7.27 (m, 2 H, 2 H_{arom}); 7.65 (d, 1 H, H_{arom}, J = 7.35 Hz). MS, m/z: 164 $[M]^+$. Found (%): C, 58.79; H, 4.93; N, 16.91; S, 19.07. $C_8H_8N_2S$. Calculated (%): C, 58.51; H, 4.91; N, 17.06; S, 19.53.

2,3,3-Trimethylbenzo[*b*]thieno[3,2-*b*]pyrrolenine (11). ***A.*** 3-Methylbutan-2-one (2.2 mL, 20 mmol) was added to a suspension of benzothiophen-3-one hydrazone **9** (3 g, 18 mmol) in 30 mL of anhydrous benzene. The reaction mixture was refluxed for 15 min during which the precipitate dissolved. While continuing refluxing, hydrogen chloride gas was passed through the solution, the solution darkened, and a solid precipitated. The reaction mixture was refluxed for 1 h and cooled to room temperature, the supply of hydrogen chloride was terminated, the precipitate was filtered off, and the filtrate was poured into 200 mL of water and extracted with 3×50 mL of ethyl acetate. The organic fractions were combined, washed with water, and concentrated under reduced pressure. After solvent evaporation, the residue was chromatographed on silica gel using a 3 : 1 CH_2Cl_2—ethyl acetate mixture as the eluent to give 3.5 g (41%) of 2,3,3-trimethylbenzo[*b*]thieno[3,2-*b*]pyrrolenine (**11**) and 0.31 g (11%) of 3,3′-diamino-2,2′-bibenzo[*b*]thiophene (**12**).

Compound **11**. M.p. 86—88 °C (Ref. 6: 121—123 °C). ^{1}H NMR, δ: 1.40 (s, 6 H, CMe_2); 2.33 (s, 3 H, 5-Me); 7.30 (t, 1 H, ABCD, H_{arom}, part C, J_{CB} = 7.4 Hz, $J_{C,D}$ = 8.1 Hz); 7.43 (t, 1 H, ABCD, H_{arom}, part B, J_{BC} = 7.4 Hz, $J_{B,A}$ = 8.1 Hz); 7.81 (d, 1 H, ABCD, H_{arom}, part D, J_{DC} = 8.1 Hz); 8.07 (d, 1 H, ABCD, H_{arom}, part A, J_{AB} = 8.1 Hz). ^{13}C NMR, δ: 15.68 ($\underline{C}H_3$—C=N); 23.27 ($\underline{C}H_3)_2$—C); 54.68 (Me_2—$\underline{C}$); 120.97, 123.74, 123.78, 124.73, 130.38, 143.40, 143.48, 150.44 ($C_{arom.}$); 189.91 (C=N). MS, m/z: 215 $[M]^+$. Found (%): C, 72.53; H, 6.38; N, 6.50. $C_{13}H_{13}NS$. Calculated (%): C, 72.52; H, 6.09; N, 6.51.

Compound **12**. M.p. 237—239 °C. ^{1}H NMR, δ: 4.17 (br.s, 4 H, 2 NH_2); 7.35—7.42 (m, 4 H, ABCD, H_{arom}, parts B, C, J_{BA} = 6.6 Hz, J_{BC} = 7.2 Hz, J_{CB} = 7.2 Hz, J_{CD} = 6.6 Hz); 7.60 (d, 2 H, ABCD, H_{arom}, part A, J_{AB} = 6.6 Hz); 7.77 (d, 2 H, ABCD, H_{arom}, part D, J_{DC} = 6.6 Hz). MS, m/z: 296 $[M]^+$. Found (%): C, 64.74; H, 3.97; N, 9.29; S, 21.53. $C_{16}H_{12}N_2S_2$. Calculated (%): C, 64.83; H, 4.08; N, 9.45; S, 21.64.

B. A 15% solution of butyllithium in hexane (5.5 mL, 8.8 mmol) was added at −78—90 °C under argon over a period of 1 h to a solution of 2,3-dimethylbenzo[*b*]thieno[3,2-*b*]pyrrole **13** (0.82 g, 4 mmol) in 15 mL of anhydrous tetrahydrofuran. The mixture was kept for 45 min at −75—85 °C and cooled to −80 °C. Methyl iodide (0.55 mL, 8.8 mmol) was added and the mixture was kept for 1.5 h at −70 °C and slowly warmed-up to 15 °C. The solution was poured into water and extracted with ether and the residue was chromatographed on silica gel using a 7 : 1 petroleum ether—ethyl acetate mixture as the eluent to give 0.18 g (20%) of compound **11**.

2,3-Dimethyl-1*H*-benzo[*b*]thieno[3,2-*b*]pyrrole (13). Butan-2-one (20 mol) was added to a suspension of benzothiophen-3-one hydrazone **9** (3 g, 18 mmol) in 40 mL of anhydrous methanol. The mixture was refluxed for 15 min, while the precipitate dissolved. Concentrated HCl (1.8 mL, 20 mmol) was added and the solution immediately became dark. The solution was refluxed for 1 h, cooled, poured into cold water, and extracted with ethyl acetate. After evaporation of the solvent, the residue was chromatographed on silica gel using a 10 : 1 petroleum ether—ethyl acetate mixture as the eluent to give 1.5 g (40%) of compound **13**. M.p. 132—134 °C (heptane). ^{1}H NMR, δ: 2.20 (s, 3 H, 3-Me); 2.37 (s, 3 H, 2-Me); 7.18 (t, 1 H, ABCD, H_{arom},

part C, J_{CB} = 7.2 Hz, J_{CD} = 7.8 Hz); 7.32 (m, 1 H, ABCD, H_{arom}, part B, J_{BC} = 7.2 Hz, J_{BA} = 7.9 Hz); 7.59 (d, 1 H, ABCD, H_{arom}, part D, J_{DC} = 7.9 Hz); 7.80 (d, 1 H, ABCD, H_{arom}, part A, J_{AB} = 7.9 Hz); 8.16 (br.s, 1 H, NH). MS, *m/z*: 201 $[M]^+$. Found (%): C, 70.63; H, 5.67; N, 6.74; S, 15.69. $C_{12}H_{11}NS$. Calculated (%): C, 71.60; H, 5.51; N, 6.96; S, 15.93.

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