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The Reaction of Carbon Disulfide with Diethyl 3-Amino-2-cyano-2-penten-1,5-dicarboxylate: A Convenient Synthesis of Polyfunctionally Substituted Thiophenes and Their Fused Derivatives

S. M. Sherif[1], N. I. Abdel-Sayed[2], S. M. El-Kousy[3], and R. M. Mohareb[1,*]

[1] Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt
[2] Department of Chemistry, College for Girls, Ain Shams University, Heliopolis, Cairo, Egypt
[3] Department of Chemistry, Faculty of Science, Monoufia University, Sheben El-Koum, Egypt

Summary. Carbon disulfide added to the active methylene group in **1** in basic *DMF* at room temperature to yield the non-isolable 1:1 adduct **2**. *In-situ* cyclization of the latter with some α-bromo compounds afforded the corresponding polyfunctionally substituted thiophenes **5**. The reactivity of **5** towards a variety of reagents was studied. Chemical and spectroscopic evidences for the structure of the new compounds are provided.

Keywords. Thiophene; Thieno[4, 5-c: 2,3-c']dipyrazole; Thieno[3,2-c]pyrazole.

Reaktion von Schwefelkohlenstoff mit 3-Amino-2-cyano-2-penten-1,5-carbonsäurediethylester: Eine einfache Synthese polyfunktionell substituierter Thiophene und ihrer kondensierten Derivate

Zusammenfassung. Die Addition von Schwefelkohlenstoff an die aktive Methylengruppe von **1** in basischem *DMF* bei Zimmertempeatur ergab das nicht isolierbaren 1:1-Addukt **2**. *In situ*-Cyclisierung des letzteren mit einigen α-Brom–Verbindungen führte zu den entsprechenden polyfunktionell substituierten Thiophenen **5**. Die Reaktivität von **5** gegenüber verschiedenen Reagentien wurde untersucht. Die Strukturen der neuen Verbindungen wurden chemisch und spektroskopisch abgesichert.

Introduction

A literature survey reveals that although diethyl 3-amino-2-cyano-2-penten-1,5-dicarboxylate (**1**) [1] has proven to be a valuable synthon for the synthesis of a wide variety of heterocyclic systems [2–6], no reports describe its applicability for the synthesis of thiophenes. As an extension of our efforts directed towards the facile synthesis of heterocyclic ring systems [7–10], we wish to report the reaction of carbon disulfide with **1** followed by heterocyclization of the resulting intermediate adduct with some α-bromo compounds. This synthetic route proved to be an easy and sole approach for the synthesis of hitherto unreported polyfunctionally substituted thiophenes. Moreover, the compounds obtained possess latent functional

substituents which enable its further chemical transformation into 3-thienyl-azoles and azines and fused thiophenes of an expected wide spectrum of biological activity.

Results and Discussion

The carbanion generated *in situ* upon treatment of **1** with KOH in *DMF* at room temperature reacted with equimolar amount of CS_2 to give the intermediate adduct **2**. Treatment of the latter with a two-fold molar equivalent of phenacyl bromide (**3a**) or ethyl bromoacetate (**3b**) furnishes the corresponding thiophene derivatives **5a, b**, in reasonably good yields. Formation of **5** was assumed to proceed *via* the ketene dithioacetals **4**, followed by their subsequent intramolecular cyclization *via* loss of EtOH. The proposed structures **5a, b**, were established by correct analytical and compatible spectral data. Thus, the mass spectrum of **5a**, as an example, revealed a molecular ion peak at $m/e = 492$ (22%). Its ^{1}H NMR spectrum (*DMSO*-d_6) revealed signals at $\delta = 1.16$ (t, 3H, $J = 8.1$ Hz, CH_3), 4.24 (q, 2H, $J = 7.8$ Hz, CH_2), 4.58 (s, 2H, CH_2), 5.21 (s, 2H, NH_2, D_2O-exchangeable), 7.31–7.53 (m, 10H, 2 C_6H_5), and 10.23 (s, 1H, OH, D_2O-exchangeable) ppm.

Similarly, treatment of the intermediate adduct **2** with bromomalononitrile (**3c**) or ethyl bromocyanoacetate (**3d**) furnishes the corresponding thiophene derivatives **5c** and **5d**, respectively. Formation of **5c, d** was assumed to proceed *via* **4**, followed by hydrolysis of the CN group into COOH decarboxylation and subsequent cyclization. Similar phenomena have been reported previously [11]. The identity of the product was established on the basis of elemental analyses and spectral background in each case.

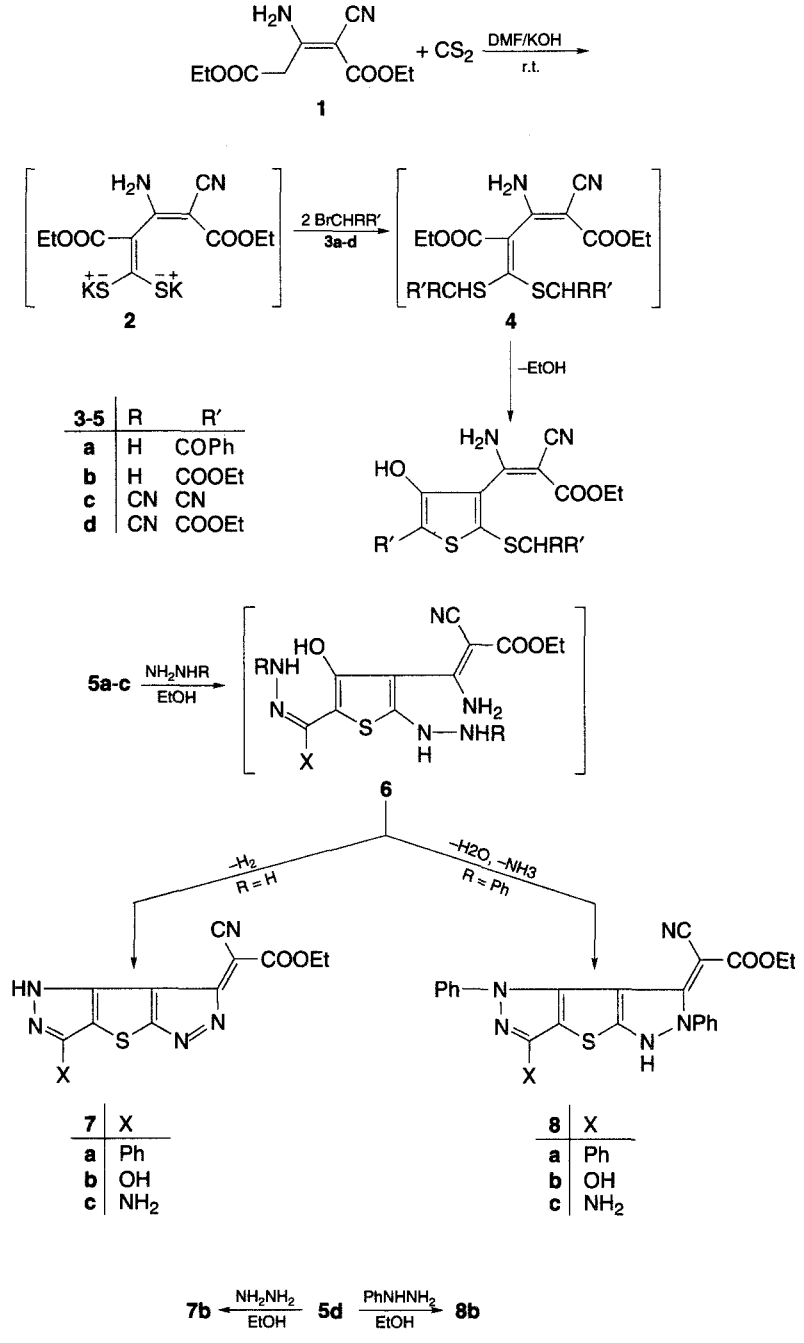
Next, we investigated the applicability of **5** to be annelated to provide fused thiophenes. No identifiable products were isolated from the reaction of **5** with equimolar equivalent of hydrazines. However, compounds **5a–c** reacted with a two-fold molar equivalent of hydrazine hydrate in EtOH under reflux to yield the corresponding thieno[4,5-c:2,3-c′]dipyrazole derivatives **7a–c**, a new ring system. Formation of **7** was assumed to proceed *via* intermediate formation of the acyclic structure, cyclization *via* elimination of ammonia and water and subsequent autoxidation. Similar phenomena have been reported previously [12, 13]. Similarly, **5a–c** reacted with a two-fold equivalent of phenylhydrazine to afford the corresponding thieno[4,5-*c*:2,3-*c*′]dipyrazole derivatives **8a–c**. Alternatively, **5d** reacted with hydrazine hydrate and phenylhydrazine under the same experimental conditions to afford a single product, in each case, in all aspects (m.p., mixed m.p. and IR data) identical with **7b** and **8b**, respectively. The proposed structures of **7** and **8** were confirmed on the basis of elemental analyses and spectral data (cf. Experimental).

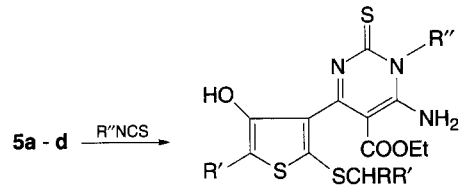
A literature search indicated that the NH_2 groups of the enaminonitrile moiety in compounds having a somewhat similar structure to **5** are generally inactive due to their presence in the anionic enaminonitrile form [3, 14]. However, compounds **5a–d** reacted with equimolar amounts of the appropriate isothiocyanate reagent in refluxing dioxane containing a few drops of triethylamine to the corresponding 4-(thiophen-3′-yl)-pyrimidine-2-thione derivatives **9a–e**, respectively. The identity of the products was established on the basis of elemental analyses and spectral data.

Reaction of **5d** with hydroxylamine hydrochloride in EtOH/AcONa provided the isoxazole derivative **10**. Treatment of **10** with a two-fold molar equivalent of

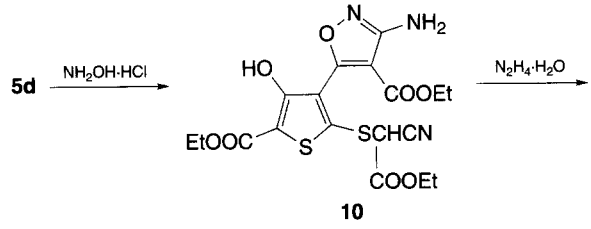
hydrazine hydrate in refluxing EtOH afforded the corresponding thieno[3,2-*c*]-pyrazole derivative **11**. Formation of **11** was assumed to be achieved *via* nucleophilic substitution of the SCH(CN)COOEt moiety, hydrazide formation at the thiophene-C_5, cyclization to the pyrazole ring *via* water elimination, and subsequent autoxidation [12, 13]. Compound **11** was characterized by analytical and spectroscopic data (cf. Experimental).

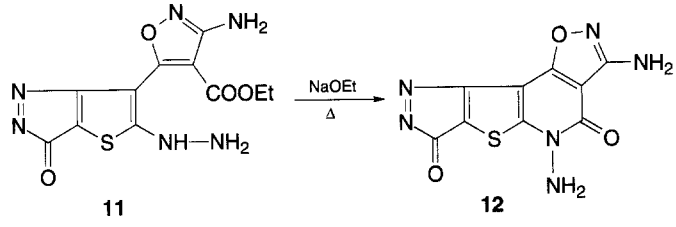
Cyclization of **11** to the corresponding pyrazoloisoxazolothienopyridine derivative **12** was achieved in good yield upon refluxing of **11** in sodium ethoxide solution.





9	R	R'	R''
a	H	PhCO	Ph
b	H	PhCO	PhCO
c	H	COOEt	Ph
d	CN	CN	Ph
e	CN	COOEt	Ph





Experimental

Melting points are uncorrected; IR spectra (KBr): Pye Unicam SP-1000, cm^{-1}; ^1H NMR spectra (*DMSO*-d_6): Varian Gemini 200 MHz spectrometer, *TMS* as internal standard, chemical shifts in δ (ppm); mass spectra: AEI MS 30 mass spectrometer operating at 70 eV; microanalytical data: Microanalytical Data Unit at Cairo University.

Ethyl 3-Amino-2-cyano-3-(2',5'-disubstituted-4'-hydroxy-3'-thienyl)-acrylates (**5a–d**), *general procedure*

To a cold suspension of powdered KOH (0.025 mol) in *DMF* (30 ml), compound **1** (0.025 mol) and subsequently carbon disulfide (0.025 mol) were added. The mixture was stirred at room temperature for 24 h, then treated with the appropriate α-bromo compound **3a–d** (0.05 mol) and left aside at room temperature for additional 24 h. The reaction mixture was triturated with cold H_2O (30 ml) and neutralized with dilute HCl (*pH* = 7). The resulting precipitated solid was filtered off and crystallized from the proper solvent.

Ethyl 3-Amino-2-cyano-3-(5'-benzoyl-4'-hydroxy-2'-phenacylthio-3'-thienyl)acrylate (**5a**)

Pale yellow crystals from EtOH, yield 62%, m.p. 181 °C; $C_{25}H_{20}N_2O_5S_2$ (492.56); calc.: C 60.96, H 4.09, N 5.68, S 13.02; found: C 60.8, H 4.0, N 5.6, S 12.8; IR: 3580–3320 (OH, NH_2), 2220 (CN), 1700, 1690, 1670 (3C=O); ^{1}H NMR: 1.16 (t, 3H, $J = 8.1$ Hz, CH_3), 4.24 (q, 2H, $J = 7.8$ Hz, CH_2), 4.58 (s, 2H, CH_2), 5.21 (s, 2H, NH_2, D_2O-exchangeable), 7.31–7.53 (m, 10H, 2 C_6H_5), 10.23 (s, 1H, OH, D_2O-exchangeable).

Ethyl 3-Amino-2-cyano-3-(5'-ethoxycarbonyl-2'-ethoxycarbonylmethylthio-4'-hydroxy-3'-thienyl)-acrylate (**5b**)

Yellow crystals from EtOH, yield 58%, m.p. 95 °C; $C_{17}H_{20}N_2O_7S_2$ (428.27); calc.: C 47.65, H 4.70, N 6.53, S 14.96; found: C 47.6, H 4.5, N 6.5, S 14.8; IR: 3585–3330 (OH, NH_2), 2220 (CN), 1710, 1705, 1690 (3C=O); ^{1}H NMR: 1.15–1.34 (m, 9H, $3CH_3$), 4.19–4.30 (m, 6H, 3 CH_2), 4.53 (s, 2H, CH_2), 5.38 (s, 2H, NH_2, D_2O-exchangeable), 10.20 (s, 1H, OH, D_2O-exchangeable).

Ethyl 3-Amino-2-cyano-3-(5'-cyano-2'-dicyanomethylthio-4'-hydroxy-3'-thienyl)-acrylate (**5c**)

Pale yellow crystals from EtOH, yield 60%, m.p. 166 °C; $C_{14}H_9N_5O_3S_2$ (359.38); calc.: C 46.79, H 2.52, N 19.48, S 17.84; found: C 46.7, H 2.5, N 19.3, S 17.7; IR: 3575–3340 (OH, NH_2), 2225, 2220, 2215 (3CN), 1690 (C=O); ^{1}H NMR: 1.13 (t, 3H, $J = 8.0$ Hz, CH_3), 4.24 (q, 2H, $J = 7.9$ Hz, CH_2), 4.89 (s, 2H, NH_2, D_2O-exchangeable), 5.23 (s, 1H, CH), 10.39 (s, br, 1H, OH, D_2O-exchangeable).

Ethyl 3-Amino-2-cyano-3-(2'-cyanoethoxycarbonylmethylthio-5'-ethoxycarbonyl-4'-hydroxy-3'-thienyl)-acrylate (**5d**)

Pale brown crystals from methanol, yield 46%, m.p. 65 °C; $C_{18}H_{19}N_3O_7S_2$ (453.48); calc.: C 47.67, H 4.22, N 9.26, S 14.14; found: C 47.5, H 4.0, N 9.1, S 14.0, IR: 3580–3320 (OH, NH_2), 2225, 2220 (2CN), 1690–1670 (3C=O).

Thieno[4,5-c:2,3-c']dipyrazoles (**7a–c** *and* **8a–c**) *general procedure*

To a solution of **5a–c** (0.005 mol) in EtOH (30 ml), hydrazine hydrate or phenylhydrazine (0.01 mol) was added. The mixute was heated under reflux for 6 h. The solid product formed upon dilution with H_2O containing a few drops of HCl ($pH = 6$) was collected and crystallized from the proper solvent.

6-Cyanoethoxycarbonylmethylidene-3-phenyl-1H-thieno[4,5-c:2,3-c']dipyrazole (**7a**)

Pale yellow crystals from EtOH, yield 52%, m.p. 123 °C; $C_{17}H_{11}N_5O_2S$ (349.36); calc.: C 58.44, H 3.17, N 20.04, S 9.17; found: C 58.3, H 3.1 N 20.0 S 8.9; IR: 3450–3380 (NH), 2220 (CN), 1690 (C=O); ^{1}H NMR: 1.16 (t, 3H, $J = 8.2$ Hz, CH_3), 3.32 (s, 1H, NH, D_2O-exchangeable), 4.42 (q, 2H, $J = 7.9$ Hz, CH_2), 7.32–7.49 (m, 5H, C_6H_5).

6-Cyanoethoxycarbonylmethylidene-3-hydroxy-1H-thieno[4,5-c:2,3-c']dipyrazole (**7b**)

Yellow crystals from dioxane, yield 63%, m.p. 225 °C; $C_{11}H_7N_5O_3S$ (289.26); calc: C 45.67, H 2.43, N 24.21, S 11.08; found: C 45.5, H 2.4, N 24.0, S 10.9; IR: 3540–3300 (OH, NH), 2220 (CN), 1690 (C=O); ^{1}H NMR: 1.16 (t, 3H, $J = 8.0$ Hz, CH_3), 3.23 (s, 1H, NH, D_2O-exchangeable), 4.29 (q, 2H, $J = 8.2$ Hz, CH_2), 10.21 (s, 1H, OH, D_2O-exchangeable).

The same product (m.p., mixed m.p., and IR spectrum), yield 54%, was obtained upon reacting **5d** (0.005 mol) with hydrazine hydrate following the experimental procedure described above for the preparation of **7a–c**.

3-Amino-6-cyanoethoxycarbonylmethylidene-1H-thieno[4,5-c:2,3-c']dipyrazole (**7c**)

Orange crystals from dioxane, yield 59%, mp. 207 °C; $C_{11}H_8N_6O_2S$ (288.28); calc.: C 45.83, H 2.79, N 29.15, S 11.12; found: C 45.7, H 2.7, N 29.0, S 11.1; IR: 3460–3350 (NH), 2220 (CN), 1695 (C=O); ^{1}H NMR: 1.13 (t, 3H, $J = 7.9$ Hz, CH_3), 3.89 (s, 1H, NH, D_2O-exchangeable), 4.29 (q, 2H, $J = 8.0$ Hz, CH_2), 4.89 (s, 2H, NH_2, D_2O-exchangeable).

6-Cyanoethoxycarbonylmethylidene-1,3,5-triphenyl-4H-thieno[4,5-c:2,3-c']dipyrazole (**8a**)

Brown crystals from *DMF*, yield 60%, m.p. 263 °C; $C_{29}H_{21}N_5O_2S$ (503.57); calc.: C 69.16, H 4.20, N 13.90, S 6.36; found: C 69.0, H 4.0, N 13.7, S 6.3; IR: 3460–3350 (NH), 2220 (CN), 1690 (C=O); ^{1}H NMR: 1.14 (t 3H, $J = 7.9$ Hz, CH_3), 4.29 (q, 2H, $J = 8.1$ Hz, CH_2), 7.30–7.49 (m, 15H, 3 C_6H_5), 8.21 (s, 1H, NH, D_2O-exchangeable).

6-Cyanoethoxycarbonylmethylidene-1,5-diphenyl-3-hydroxy-4H-thieno[4,5-c: 2,3-c']dipyrazole (**8b**)

Orange crystals from dioxane, yield 62%, m.p. 177 °C; $C_{23}H_{17}N_5O_3S$ (443.47); calc.: C 62.29, H 3.86, N 15.79, S 7.23; found: C 62.0, H 3.8, N 15.6, S 7.2; IR: 3565–3320 (OH, NH), 2215 (CN), 1695 (C=O); ^{1}H NMR: 1.14 (t, 3H, $J = 8.0$ Hz, CH_3). 4.24 (q, 2H, $J = 8.2$ Hz, CH_2), 7.32–7.51 (m, 10H, 2 C_6H_5), 8.29 (s, 1H, NH, D_2O-exchangeable) 10.29 (s, 1H, OH, D_2O-exchangeable).

The same product (m.p., mixed m.p., and IR spectrum), yield 51%, was obtained upon reacting **5d** (0.005 mol) with phenylhydrazine following the experimental procedure described above for the preparation of **8a–c.**

*3-Amino-6-cyanoethoxycarbonylmethylidene-1,5-diphenyl-4H-thieno[4,5-c: 2,3-c']*dipyrazole (**8c**)

Brown crystals from EtOH, yield 52%, m.p. 111 °C; $C_{23}H_{18}N_6O_2S$ (442.49); calc: C 62.43, H 4.09, N 18.99, S 7.24; found C 62.4, H 3.9 , N 18.8, S 7.0; IR: 3460–3325 (NH_2, NH), 2215 (CN), 1690 (C=O); ^{1}H NMR: 1.13 (t, 3H, $J = 8.0$ Hz, CH_3), 4.25 (q, 2H, J = 7.9 Hz, CH_2), 4.82 (s, 2H, NH_2, D_2O-exchangeable), 7.32–7.53 (m, 10H, 2 C_6H_5), 8.23 (s, 1H, NH, D_2O-exchangeable).

6-Amino-5-ethoxycarbonyl-4-(3'-thienyl-)-pyrimidine-2-thiones (**9a, c–e**), *general procedure*

To a solution of **5a–d** (0.005 mol) in dioxane (30 ml) containing Et_3N (4 drops), phenyl isothiocyanate (0.005 mol) was added. The reaction mixture was heated under reflux for 4 h and then left overnight at room temperature. The mixture was triturated with H_2O (30 ml) and acidified with HCl (pH = 6.5). The solid product was filtered off and crystallized from the proper solvent.

6-Amino-4-(5'-benzoyl-4'-hydroxy-2'-phenacylthio-3'-thienyl)-5-ethoxycarbonyl-1-phenylpyrimidine-2-thione (**9a**)

Yellow crystals from dioxane, yield 54%, m.p. 223 °C; $C_{32}H_{25}N_3O_5S_3$ (627.75); calc.: C 61.22, H 4.01, N 6.69, S 15.32; found: C 61.0, H 3.9, N 6.6, S 15.3; IR: 3560–3320 (OH, NH_2). 1700, 1690–1675 (3C=O); ^{1}H NMR: 1.16 (t, 3H, $J = 8.0$ Hz, CH_3) 4.24 (q, 2H, $J = 8.2$ Hz, CH_2), 4.43 (s, 2H, CH_2), 5.21 (s, 2H, NH_2, D_2O-exchangeable), 7.32–7.48 (m, 15H, 3 C_6H_5), 10.23 (s, 1H, OH, D_2O-exchangeable).

6-Amino-5-ethoxycarbonyl-4-(5'-ethoxycarbonyl-2'-ethoxycarbonylmethylthio-4'-hydroxy-3'-thienyl)-1-phenylpyrimidine-2-thione (**9c**)

Yellow crystals from EtOH, yield 42%, m.p. 145 °C; $C_{24}H_{25}N_3O_7S_3$ (563.66); calc.: C 51.14, H 4.47, N 7.45, S 17.06; found: C 51.0, H 4.3, N 7.3, S 17.0; IR: 3560–3385 (OH, NH_2), 1710, 1690–1675 (3C=O), 1200 (C=S).

6-Amino-4-(5'-cyano-2'-dicyanomethylthio-4'-hydroxy-3'-thienyl)-5-ethoxycarbonyl-1-phenylpyrimidine-2-thione (**9d**)

Yellow crystals from dioxane, yield 59%, m.p. 212 °C; $C_{21}H_{14}N_6O_3S_3$ (494.56); calc.: C 51.00, H 2.85, N 16.99, S 19.44; found: C 50.8, H 2.8, N 16.9, S 19.4; IR: 3590–3320 (OH, NH_2), 2225, 2220, 2215 (3CN), 1690 (C=O); ^{1}H NMR: 1.17 (t, 3H, J = 8.1 Hz, CH_3), 4.29 (q, 2H, J = 8.3 Hz, CH_2), 4.89 (s, 2H, NH_2, D_2O-exchangeable), 5.23 (s, 1H, CH), 7.32–7.45 (m, 5H, C_6H_5), 10.25 (s, 1H, OH, D_2O-exchangeable).

6-Amino-4-(2'-cyanoethoxycarbonylmethylthio-5'-ethoxycarbonyl-4'-hydroxy-3'-thienyl)-5-ethoxycarbonyl-1-phenylpyrimidine-2-thione (**9e**)

Brown crystals from dioxane, yield 55%, m.p. 193 °C; $C_{23}H_{19}N_5O_5S_3$ (541.62); calc.: C 51.00, H 3.52, N 12.92, S 17.16; found: C 50.9, H 3.5, N 12.8, S 17.0; IR: 3585–3330 (OH, NH_2), 2220, 2215 (2CN), 1690, 1685 (2C=O), 1200 (C=S); ^{1}H NMR: 1.13, 1.15 (2 t, 6H, 2 CH_3), 4.22, 4.25 (2 q, 4H, 2CH_2), 4.85 (s, 2H, NH_2 D_2O-exchangeable), 5.31 (s, 1H, CH), 7.31–7.45 (m, 5H, C_6H_5), 10.32 (s, 1H, OH, D_2O-exchangeable).

6-Amino-1-benzoyl-4-(5'-benzoyl-4'-hydroxy-2'-phenacylthio-3'-thienyl)-5-ethoxycarbonylpyrimidine-2-thione (**9b**)

To a solution of **5a** (0.005 mol) in dioxane (30 ml) containing Et_3N (4 drops), benzoyl isothiocyanate (0.005 mol), prepared by adding ammonium thiocyanate (0.005 mol) to benzoyl chloride (0.005 mol) in dioxane (30 mol) was added. The reaction mixture was heated under reflux for 4 h, left at room temperature overnight, and then poured onto ice. The precipitated solid product was collected by filtration and crystallized from dioxane to afford orange crystals. Yield 61%, m.p. 151 °C; $C_{33}H_{25}N_3O_6S_3$ (655.76); calc.: C 60.44, H 3.84, N 6.41, S 14.66; found: C 60.3, H 3.8, N 6.2, S 14.5; IR: 3590–3320 (OH, NH_2), 1700, 1695–1680 (4C=O), 1200 (C=S); ^{1}H NMR: 1.13 (t, 3H, J = 8.0 Hz, CH_3), 4.23 (q, 2H, J = 7.9 Hz, CH_2), 4.65 (s, 2H, NH_2, D_2O-exchangeable), 3.81 (s, 2H, CH_2), 7.32–7.48 (m, 15H, 3 C_6H_5), 10.39 (s, 1H, OH D_2O-exchangeable).

3-Amino-5-(2'-cyanoethoxycarbonylmethylthio-5'-ethoxycarbonyl-4'-hydroxy-3'-thienyl)-4-ethoxycarbonyl-isoxazole (**10**)

To a solution of **5d** (0.01 mol) in EtOH (30 ml) containing AcONa (2 g), hydroxylamine hydrochloride (0.01 mol) was added. The reaction mixture was heated under reflux for 6 h and then poured into an ice/H_2O mixture. The solid product formed was filtered off and crystallized from dioxane. Yield 68%, m.p. 187 °C; $C_{18}H_{19}N_3O_8S_2$ (469.48); calc.: C 46.05, H 4.07, N 8.94, S 13.65; found: C 46.0, H 3.8, N 8.9, S 13.5; IR: 3540–3320 (OH, NH_2), 2220 (CN), 1690, 1680–1670 (3C=O); ^{1}H NMR: 1.13–1.45 (m, 9H, 3 CH_3), 4.20–4.41 (m, 6H, 3 CH_2), 4.85 (s, 2H, NH_2, D_2O-exchangeable), 5.21 (s, 1H, CH), 10.23 (s, 1H, OH, D_2O-exchangeable).

6-(3'-Amino-4'-ethoxycarbonyl-isoxazol-5'-yl)-5-hydrazino-3-oxo-thieno[3,2-c]pyrazole (**11**)

To a solution of **10** (0.01 mol) in EtOH (30 ml), hydrazine hydrate (0.02 mol) was added. The reaction mixture was heated under reflux for 8 h. The solid product formed upon dilution with H_2O and acidification with dilute HCl (pH = 6.5) was collected by filtration and crystallized from dioxane. Yield 62%, m.p. 198 °C; $C_{11}H_{10}N_6O_4S$ (322.29); calc.: C 40.99, H 3.12, N 26.07, S 9.94; found: C 40.9, H 3.0, N 25.9, S 9.8; IR: 3455–3320 (NH_2, NH), 1695 (C=O); ^{1}H NMR: 1.13 (t, 3H, J = 8.0 Hz, CH_3), 3.22 (s, 2H, NH_2, D_2O-exchangeable), 4.25 (q, 2H, J = 7.9 Hz, CH_2), 4.68 (s, 1H, NH, D_2O-exchangeable), 5.34 (s, 2H, NH_2, D_2O-exchangeable).

Pyrazolo[3',4':4'',5'']isoxazolo[4',5':2'',3'']thieno[2,3-b]pyridine derivative (**12**)

A solution of **11** (0.01 mol) in sodium ethoxide (0.01 mol), prepared by adding sodium metal (0.23 g, 0.01 g atom) to absolute ethanol (40 ml) was heated, under reflux for 1 h and then left to cool to room temperature. The mixture was poured into ice/water and acidified with dilute HCl. The solid product was collected by filtration and crystallized from *DMF*. Yield 52%, m.p. > 300 °C; $C_9H_4N_6O_3S$ (276.22); calc.: C 39.13, H 1.46, N 30.42, S 11.61; found: C 39.0, H 1.4, N 30.3, S 11.6; IR: 3480–3320 (NH_2), 1695, 1690 (2C=O); ^1H NMR: 4.82, 5.21 (2s, 4H, $2NH_2$, D_2O-exchangeable).

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