

**A SYNTHESIS OF HETEROCYCLIC RING SYSTEMS.
PYRIDO[3',2':4,5]THIENO[2,3-*b*]PYRROLIZINE AND PYRIDO-
[6',5':4,5][3',2':4,5]DITHIENO[2,3-*b*':2,3-*b*]DIPYRROLIZINE**

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Abstract - A synthesis for two new polycyclic heterocyclic ring systems is reported. Cyclization of pyrrolidinocarboxamide derivatives of ethyl 3-(pyrrol-1-yl)thieno[2,3-*b*]pyridine-2-carboxylate (**4**) and ethyl 3,5-di(pyrrol-1-yl)dithieno[3',2'-*e*:2,3-*b*]pyridine-2,6-dicarboxylate (**11**) afford iminium salts that were transformed into the new heteropolycyclic compounds (**6**) and (**13**), respectively.

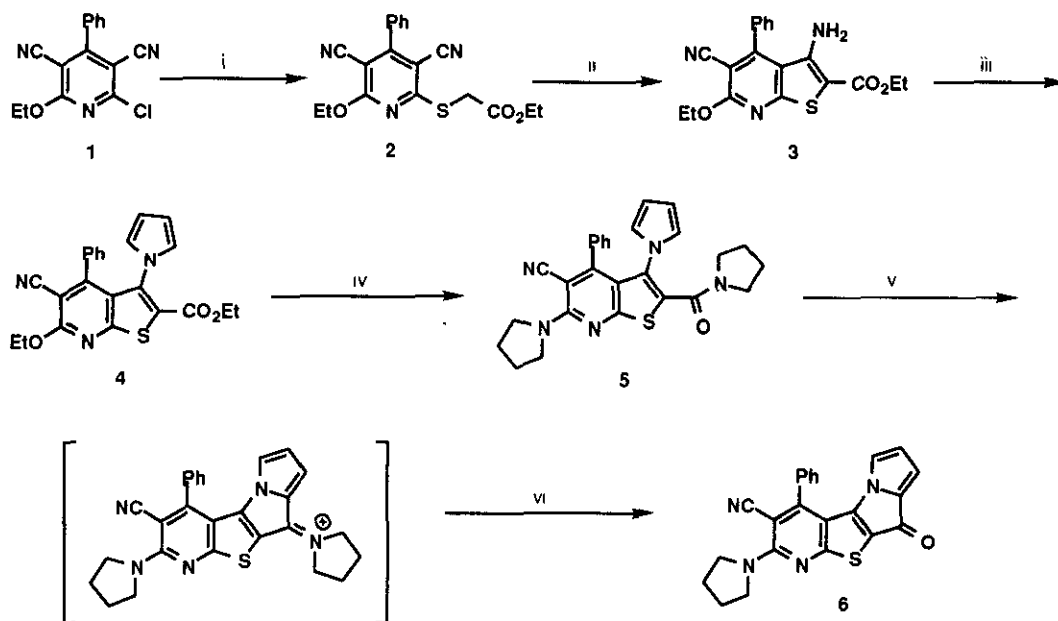
As a part of our research programme¹ aimed at the preparation of novel thiophene-fused heterocycles of therapeutical significance, we report on the synthesis of two heteropolycyclic compounds including a new ring system, namely pyrido[3',2':4,5]thieno[2,3-*b*]pyrrolizine and pyrido[6',5':4,5][3',2':4,5]dithieno[2,3-*b*':2,3-*b*]dipyrrolizine (**6** and **13**, respectively).

Recently, thiophene derivatives, which are both commercially available drugs and agents under clinical investigation, were the subject of a comprehensive review.² Many compounds containing the pyridothieno ring system are known to have interesting pharmacological properties. Such derivatives possess antianaphilactic,³ antiinflammatory,⁴ analgesic,⁵ antipyretic,⁶ hypocholesterolemic,⁷ antibacterial⁸ or antiallergic⁹ activity. In addition, some of them have good vasodilating and hypotensive properties,¹⁰ inhibit platelet aggregation¹¹ or possess potential antineoplastic activity.¹² On the other hand, a number of heterocyclic compounds containing the pyrrolo moiety reportedly exhibit major pharmacological activity especially as antitumour¹³ and anxiolytic and antipsychotic¹⁴ agents. All these properties aroused our interest in synthesising new heterocyclic compounds including both pyridothieno and pyrrolo moieties. With suitable substituents, these structures allow different derivatives related to compounds of biological and pharmacological interest to be obtained.

The synthesis of the title compound (**6**) was accomplished by starting from 2-chloro-3,5-dicyano-6-ethoxy-4-phenylpyridine (**1**)¹⁵ and using the procedure summarized in the Scheme 1. The thiophene ring was added on the pyridine ring by condensing **1** with ethyl 2-mercaptoacetate in

the presence of an equimolecular amount of potassium carbonate in refluxing ethanol to give the 2-ethoxycarbonylmethylthiopyridine-3-carbonitrile (**2**), which, on refluxing with ethanol in the presence of excess anhydrous potassium carbonate, underwent Thorpe-Ziegler cyclization to yield ethyl 3-aminothieno[2,3-*b*]pyridine-2-carboxylate (**3**). This amine (**3**) was also obtained directly from **1** and ethyl 2-mercaptoacetate using excess of potassium carbonate.

Scheme 1

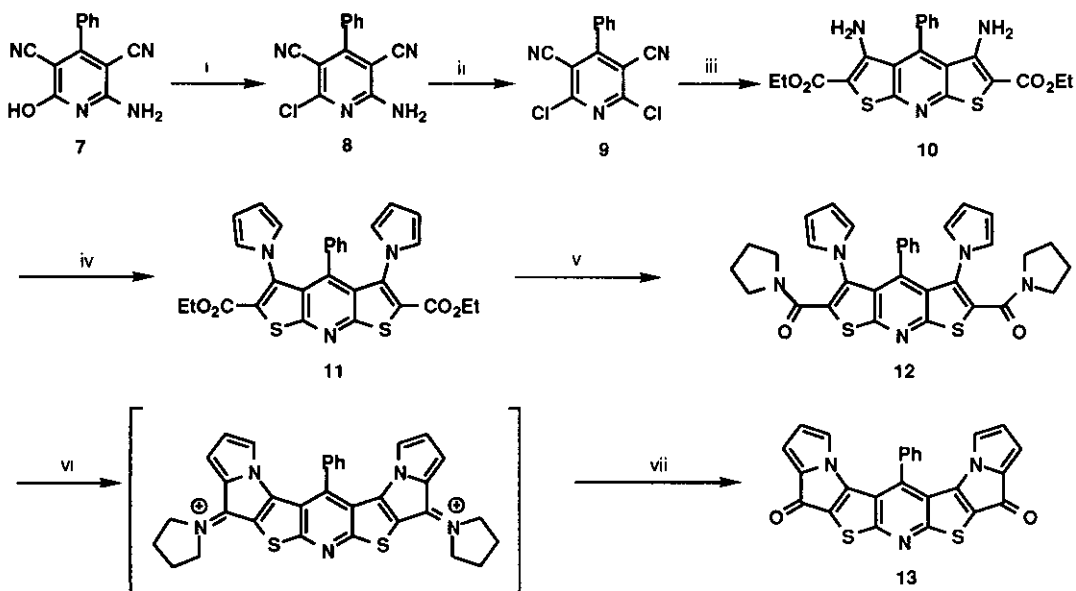


Reagents: i: HSCH₂CO₂Et, K₂CO₃, EtOH, reflux, 30 min. ii: K₂CO₃, EtOH, reflux, 1 h. iii: DMTHF, AcOH, reflux, 30 min. iv: Pyrrolidine, reflux, 24 h. v: POCl₃, CH₂Cl₂, reflux, 3.5 h. vi: KOH

Reaction of ethyl 3-aminothieno[2,3-*b*]pyridine-2-carboxylate (**3**) with 2,5-dimethoxytetrahydrofuran in acetic acid according to the Clauson-Kaas method¹⁶ gave ethyl 3-(pyrrol-1-yl)thieno[2,3-*b*]pyridine-2-carboxylate (**4**), which, on prolonged refluxing in pyrrolidine,¹⁷ afforded the *N*-pyrrolidinoamide (**5**). A concomitant displacement of the ethoxy substituent by the pyrrolidine moiety in the resulting product (**5**) was also observed. Bischler-Napieralski cyclization of this compound in boiling phosphorus oxychloride yielded an iminium salt that was hydrolyzed to the expected tetracyclic ketone (**6**) by the action of aqueous sodium hydroxide according to the Rault procedure.¹⁸ The starting material for the synthesis of the desired heteropolycyclic compound pyrido[6',5':4,5][3',2':4,5]dithieno[2,3-*b*:2,3-*b'*]dipyrrolizine (**13**) was 2,6-dichloro-3,5-dicyano-4-phenylpyridine (**9**) which was synthesized as shows in Scheme 2.

The readily available 2-amino-3,5-dicyano-5-hydroxy-4-phenylpyridine (**7**)¹⁵ was transformed into the corresponding chloroderivative (**8**) by using phosphoryl chloride. Treatment of **8** with isoamyl

Scheme 2



Reagents: i: PCl_5 , POCl_3 , reflux, 24 h. ii: CuCl_2 , *t*-Amyl Nitrite, CH_3CN , r.t., 12 h. iii: $\text{HSCH}_2\text{CO}_2\text{Et}$, K_2CO_3 , EtOH, reflux, 48 h. iv: DMTHF, AcOH, reflux, 3 h. v: Pyrrolidine, reflux, 1.5 h. vi: POCl_3 , reflux, 36 h. vii: KOH.

nitrite and copper(II) chloride in acetonitrile at 65°C yielded the desired 2,6-dichloro derivative (**9**). Reaction of this compound with ethyl 2-mercaptoacetate and subsequent base-promoted intramolecular ring formation afforded the *ortho*-aminothiopyridinecarboxylate (**10**) in 81% yield. Condensation of this compound with 2,5-dimethoxytetrahydrofuran in acetic acid under reflux, gave ethyl 3,5-di(pyrrol-1-yl)dithieno[3',2'-*e*:2,3-*b*]pyridine (**11**) as the main compound. After removal of acetic acid, treatment of **11** with pyrrolidine gave the amide (**12**). Cyclization with phosphoryl chloride and subsequent hydrolysis of the intermediate iminium salt with aqueous sodium hydroxide afforded the desired polycyclic derivative (**13**). The reactions involved and results obtained are shown in Scheme 2.

The presence of the pyrrolizidine moiety makes pyridothienopyrrolizine derivatives (**6** and **13**) interesting as potential antitumour agents. In fact, several natural substances belonging to the pyrrolizidine class^{19,20} and other related heteropolycyclic compounds of pharmaceutical interest are antineoplastic agents that may be selective for hypoxic cells in solid tumours.²¹

EXPERIMENTAL SECTION

All reagents used were commercial grade chemicals from freshly opened containers. Melting points were determined on a Buchi 510 apparatus and are reported uncorrected. Ir spectra were recorded on potassium bromide disks on a Perkin-Elmer 383 spectrophotometer. ^1H and ^{13}C nmr spectra were obtained on a Bruker AC200F instrument at room temperature. Mass spectra were

obtained at 70 eV by using a VG4 spectrometer. The silica gel 60 HF₂₅₄₊₃₆₆ used for analytical thin layer chromatography and the silica gel 60 (230-400 mesh) employed for medium-pressure chromatography (mpc) were purchased from Merck. Microanalyses for C, H, and N were performed by the Elemental Analyses General Service of the University of La Coruña.

6-Ethoxy-2-ethoxycarbonylmethylthio-4-phenylpyridine-3,5-dicarbonitrile (2)

A solution of 2-chloro-6-ethoxy-4-phenylpyridine-3,5-dicarbonitrile (1, 1.20 g, 4.23 mmol), ethyl 2-mercaptoacetate (0.55 ml, 5.07 mmol) and Na₂CO₃ in ethanol (40 ml) was refluxed for 10 min. After cooling, the solid was filtered off and recrystallized from ethanol/acetone to yield **2** (0.91 g, 70%); mp 132-134 °C. ¹H Nmr (CDCl₃) δ: 1.28 (t, 3H, J = 7.1 Hz, CH₃); 1.47 (t, 3H, J = 7.1 Hz, CH₃); 3.99 (s, 2H, SCH₂); 4.26 (q, 2H, J = 7.1 Hz, OCH₂); 4.56 (q, 2H, J = 7.1 Hz, OCH₂); 7.50-7.58 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 14.0 (CH₃); 14.2 (CH₃); 32.9 (SCH₂); 62.1 (OCH₂); 65.0 (OCH₂); 92.6, 99.6 (C-3, C-5); 113.3 (CN); 113.8 (CN); 128.4, 129.0, 131.1, 132.3 (C₆H₅); 159.4 (C-2); 164.3; 166.8, 167.8. Ir (KBr): 2220 (CN); 1750 (CO); 1550; 1340. Ms (DEI, 70eV) m/z (%): 367 (M⁺, 32); 338 (30); 320 (15); 294 (18); 266 (100); 165 (43). Anal. Calcd for C₁₉H₁₇N₃O₃S: C, 62.11; H, 4.66; N, 11.43. Found: C, 62.23; H, 4.54; N, 11.50

Ethyl 3-amino-5-cyano-6-ethoxy-4-phenylthieno[2,3-b]pyridine-2-carboxylate (3)

A solution of **2** (0.40 g, 1.1 mmol) and K₂CO₃ (0.18 g, 1.3 mmol) in ethanol (10 ml) was refluxed for 1 h. The solid was filtered off and recrystallized from ethanol/acetone to yield **3** (0.36, 90%), mp 244-246 °C. ¹H Nmr (CDCl₃) δ: 1.36 (t, 3H, J = 7.1 Hz, CH₃); 1.50 (t, 3H, J = 7.1 Hz, CH₃); 4.30 (q, 2H, J = 7.1 Hz, OCH₂); 4.61 (q, 2H, J = 7.1 Hz, OCH₂); 5.50 (br s, 2H, exchangeable with D₂O, NH₂); 7.42-7.64 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 14.2 (CH₃); 14.4 (CH₃); 60.5 (OCH₂); 64.2 (OCH₂); 95.3 (C-5); 114.2 (CN); 116.9 (C-3a), 128.2, 129.4, 130.5, 133.1 (C₆H₅); 147.5 (C-3), 153.6 (C-7a), 162.8, 163.6, 165.1 (C-4, C-6, CO). Ir (KBr): 3380 (NH); 3500 (NH); 2220 (CN); 1660 (CO); 1600; 1550; 1340. Ms (DEI, 70eV) m/z (%): 367 (M⁺, 65); 339 (17); 320 (15), 292 (100); 264 (29); 236 (12). Anal. Calcd for C₁₉H₁₇N₃O₃S: C, 62.11; H, 4.66; N, 11.43. Found: C, 62.29; H, 4.45; N, 11.40

Ethyl 5-cyano-6-ethoxy-4-phenyl-3-(pyrrol-1-yl)thieno[2,3-b]pyridine-2-carboxylate (4)

A solution of **3** (1.02 g, 2.72 mmol) and 2,5-dimethoxytetrahydrofuran (0.53 ml, 4.08 mmol) in acetic acid (11 ml) was refluxed for 30 min. After cooling, the solid was filtered off and recrystallized from ethanol to yield **4** (0.90 g, 78%), mp 168-170 °C. ¹H Nmr (CDCl₃) δ: 1.18 (t, 3H, J = 7.1 Hz, CH₃); 1.51 (t, 3H, J = 7.0 Hz, CH₃); 4.49 (q, 2H, J = 7.1 Hz, OCH₂); 4.64 (q, 2H, J = 7.0 Hz, OCH₂); 5.78 (t, 2H, J = 2.1 Hz, Hpyrrol); 6.22 (t, 2H, J = 2.2 Hz, Hpyrrol); 7.01-7.30 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 13.9 (CH₃); 14.3 (CH₃); 61.9 (OCH₂); 64.5 (OCH₂); 97.7 (C-5); 109.1 (CH); 114.2 (CN); 121.6 (C-3a), 122.0 (NCH), 125.4 (C-2); 127.2, 128.1, 129.0, 132.1 (C₆H₅), 136.8 (C-3); 155.2 (C-7a); 160.3, 161.4, 162.5 (CO, C-4, C-6). Ir (KBr): 2220 (CN), 1700 (CO), 1550; 1480, 1340. Ms (DEI, 70 eV) m/z (%): 417 (M⁺, 100); 344 (38); 317 (59); 316 (67); 286 (42); 272 (13). Anal. Calcd for C₂₃H₁₉N₃O₃S: C, 66.17; H, 4.59; N, 10.07. Found: C, 66.32; H, 4.42; N, 10.15.

4-Phenyl-2-(pyrrolidine-1-carbonyl)-6-(pyrrolidin-1-yl)-3-(pyrrol-1-yl)thieno[2,3-b]pyridine-5-carbonitrile (5)

A solution of **4** (1.02 g, 2.44 mmol) in pyrrolidine (8.5 ml) was refluxed for 24 h. The solvent was removed under reduced pressure and purified by mpc using CH₂Cl₂/EtOH (99:1) as eluent to yield **5** (1.01 g, 89%), mp 237-239 °C. ¹H Nmr (CDCl₃) δ: 1.52-1.77 (m, 4H, CH₂CH₂CH₂CH₂); 1.98-2.04 (m, 4H, CH₂CH₂CH₂CH₂); 2.65 (t, 2H, J = 6.5 Hz, N-CH₂); 3.41 (t, 2H, J = 7.0 Hz, N-CH₂); 3.81-3.88 (m, 4H, N-CH₂); 5.69 (t, 2H, J = 2.1 Hz, Hpyrrol); 6.20 (t, 2H, J = 2.0 Hz, Hpyrrol); 7.02-7.25 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 24.0 (CH₂); 25.5 (CH₂); 25.6 (CH₂); 45.8 (CH₂); 47.3 (CH₂); 49.9 (CH₂); 91.4 (C-5), 109.2 (CH); 116.2 (CN); 117.7, 125.4, 129.2 (C-2, C-3, C-3a);

121.0 (NCH); 127.9, 128.9, 133.6 (C₆H₅); 153.9 (C-6); 155.6 (C-7a); 161.1, 163.2 (CO, C-4) Ir (KBr): 2220 (CN); 1630 (CO); 1550; 1480; 1430. Ms (DEI, 70 eV) m/z (%): 467 (M⁺, 38); 398 (62); 369 (44), 341 (26). Anal. Calcd for C₂₇H₂₅N₅OS: C, 69.35; H, 5.39; N, 14.98. Found: C, 69.50; H, 5.51; N, 15.14.

3-Cyano-9-oxo-4-phenyl-2-(pyrrolidin-1-yl)pyrido[3',2':4,5]thieno[2,3-b]pyrrolizine (6)

A solution of 5 (0.32 g, 0.68 mmol), POCl₃ (2 ml, 7.8 mmol) in CH₂Cl₂ (5 ml) was refluxed for 3.5 h. The reaction mixture was allowed to stand overnight at room temperature. The mixture was cooled, following the addition of CH₂Cl₂ (10 ml) and then poured into 50 ml of 25% aqueous KOH. The mixture was extracted twice with 30 ml portions of CH₂Cl₂ and the organic layer was washed with water and 10% HCl, then was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and purified by mpic using CH₂Cl₂ as eluent to yield 6 (0.21 g, 83%), mp >300°C. ¹H Nmr (CDCl₃) δ: 2.04 (m, 4H, Hpyrrolidine); 3.89 (m, 4H, Hpyrrolidine); 4.06 (d, 1H, J = 2.8 Hz, H-8); 5.63 (dd, 1H, J = 3.7, J = 2.8 Hz, H-7); 6.52 (dd, 1H, J = 3.7, J = 0.9 Hz, H-6); 7.41-7.64 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 25.6 (CH₂); 50.0 (CH₂); 92.1 (C-3); 111.3 (CN); 113.0 (CH); 115.7 (CH); 117.0; 118.8; 123.3 (CH); 128.2, 130.0, 130.5, 134.5 (C₆H₅); 136.0; 146.1; 153.0 (C-10a); 154.5 (C-2); 170.2, 175.2 (CO, C-4) Ir (KBr): 2220 (CN), 1670 (CO); 1550; 1440. Ms (DEI, 70 eV) m/z (%): 396 (M⁺, 100); 395 (47); 368 (25); 341 (12). Anal. Calcd for C₂₃H₁₆N₄OS: C, 69.68; H, 4.07; N, 14.13. Found: C, 69.58; H, 3.91; N, 13.98.

2-Amino-6-chloro-4-phenylpyridine-3,5-dicarbonitrile (8)

A solution of 7 (1.0 g, 1.29 mmol), PCl₅ (0.27 g, 1.29 mmol) in POCl₃ (20 ml) was refluxed for 24 h. The solvent was removed under reduced pressure following the addition of ice (200 g). The solid was filtered off and purified by mpic using CH₂Cl₂ as eluent to yield 8 (0.3 g, 33%), mp 194-196°C. ¹H Nmr (CDCl₃) δ: 7.56 (s, 5H, C₆H₅); 8.35 (br s, 2H, NH₂) ppm. ¹³C NMR (CDCl₃) δ: 89.7 (C-CN); 114.4 (CN); 115.0 (CN); 128.4, 128.8, 130.7, 133.6 (C₆H₅); 155.3 (C-6); 160.3; 160.5 Ir (KBr): 3400 (NH); 3200 (NH); 2220 (CN); 1650. Ms (DEI, 70 eV) m/z (%): 254 (M⁺, 100); 219 (40); 192 (11); 165 (59). Anal. Calcd for C₁₃H₇N₄Cl: C, 61.31; H, 2.77; N, 21.99. Found: C, 61.20; H, 2.96; N, 22.11.

2,6-Dichloro-4-phenylpyridine-3,5-dicarbonitrile (9)

To a rapidly stirred mixture of anhydrous copper(II) chloride (0.19 g, 1.41 mmol), *i*-amyl nitrite (0.21 g, 1.79 mmol) in anhydrous acetonitrile (20 ml) 8 (0.3 g, 1.18 mmol) was added. The reaction was heated at 65°C for 5 h. After the mixture was cooled, the reaction solution was poured into 30 ml of 20% aqueous hydrochloric acid. The solid was filtered off and purified by MPLC using CH₂Cl₂ as eluent to yield 9 (0.2 g, 63%), mp 204-206°C. ¹H Nmr (CDCl₃) δ: 7.54-7.68 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 110.0 (C-3); 112.4 (CN); 128.5, 129.5, 131.1, 132.2 (C₆H₅); 156.0 (C-2); 161.1 (C-4). Ir (KBr): 2220 (CN), 1530; 1350; 1100. Ms (DEI, 70 eV) m/z (%): 273 (M⁺, 100); 238 (30); 237 (90); 211 (10); 202 (52). Anal. Calcd for C₁₃H₅N₃Cl₂: C, 56.94; H, 1.84; N, 15.33. Found: C, 57.13; H, 1.70; N, 15.45.

Ethyl 3,5-diamino-4-phenylthieno[3',2'-e:2,3-b]pyridine-2,6-dicarboxylate (10)

A solution of 9 (4.0 g, 14.6 mmol), ethyl-2-mercaptoacetate (3.15 ml, 32.1 mmol) and Na₂CO₃ (3 g, 29.2 mmol) in ethanol/THF (2:1, 150 ml) was refluxed for 48 h. After cooling, the solid was filtered off and recrystallized from ethanol/CH₂Cl₂ to yield 10 (5.2 g, 81%); mp >300°C. ¹H Nmr (CDCl₃) δ: 1.35 (t, 6H, J = 7.2 Hz, 2CH₃); 4.31 (q, 4H, J = 7.2 Hz, 2OCH₂); 5.42 (br s, 4H, 2NH₂); 7.54-7.68 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 14.4 (CH₃); 60.5 (OCH₂); 96.2 (C-2), 119.6 (C-3a); 128.4, 129.6, 130.5, 133.0 (C₆H₅); 143.0, 148.1 (C-3, C-

7a); 162.1, 165.5 (C-4, CO). Ir (KBr): 3495 (NH), 3400 (NH); 1680 (CO); 1600; 1530; 1350. Ms (DEI, 70 eV) m/z (%): 441 (M⁺, 100); 413 (13); 395 (14); 394 (46), 366 (12), 294 (11). Anal. Calcd for C₂₁H₁₉N₃O₄S₂: C, 57.11; H, 4.33; N, 9.52. Found: C, 57.02; H, 4.19; N, 9.41.

Ethyl 3,5-di(pyrrol-1-yl)-4-phenyldithieno[3',2'-e:2,3-b]pyridine-2,6-dicarboxylate (11)

A solution of **10** (0.2 g, 0.45 mmol) and 2,5-dimethoxytetrahydrofuran (0.17 ml, 1.36 mmol) in acetic acid (30 ml) was refluxed for 3 h. After cooling, the solid was filtered off and recrystallized from ethanol/CH₂Cl₂ to yield **11** (0.24 g, 98%), mp 276-277°C. ¹H Nmr (CDCl₃) δ: 1.17 (t, 6H, J = 7.2 Hz, 2CH₃); 4.19 (q, 4H, J = 7.2 Hz, 2OCH₂); 5.74 (t, 4H, J = 2.0 Hz, 4Hpyrrol); 6.13 (t, 4H, J = 2.1 Hz, 4Hpyrrol); 6.69-6.94 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 13.8 (CH₃); 62.0 (OCH₂); 109.0 (CH); 122.3 (NCH), 125.5 (C-2); 127.1, 127.2, 129.3, 130.1 (C₆H₅), 137.0 (C-3), 146.7 (C-7a); 159.8 (CO); 160.6 (C-4). Ir (KBr): 1730 (CO). Ms (DEI, 70 eV) m/z (%): 541 (M⁺, 98); 422 (10); 397 (20); 393 (17); 224 (13). Anal. Calcd for C₂₉H₂₃N₃O₄S₂: C, 64.31; H, 4.28; N, 7.76. Found: C, 64.19; H, 4.35; N, 7.67.

4-Phenyl-2,6-di(pyrrolidine-1-carbonyl)-3,5-di(pyrrol-1-yl)dithieno[3',2'-e:2,3-b]pyridine (12)

A solution of **11** (0.12 g, 0.22 mmol) in pyrrolidine (6 ml) was refluxed for 1.5 h. After cooling, the solid was filtered off and recrystallized from ethanol/CH₂Cl₂ to yield **12** (0.13 g, 95%), mp >300°C. ¹H Nmr (CDCl₃) δ: 1.54-1.74 (m, 8H, 2CH₂-CH₂); 2.82 (t, 4H, J = 6.5 Hz, N-CH₂), 3.40 (t, 4H, J = 6.9 Hz, N-CH₂), 5.66 (t, 4H, J = 2.1 Hz, 4Hpyrrol), 6.16 (t, 4H, J = 2.1 Hz, 4Hpyrrol); 6.63-6.97 (m, 5H, C₆H₅). ¹³C Nmr (CDCl₃) δ: 24.0 (CH₂); 25.3 (CH₂); 45.7 (CH₂); 47.6 (CH₂); 109.0 (CH); 121.2 (NCH); 122.8, 129.2, 132.2 (C-2, C-3, C-3a); 126.9, 127.1, 127.3, 131.3 (C₆H₅); 142.9 (C-7a); 158.2 (CO); 160.8 (C-4). Ir (KBr): 1620 (CO); 1555; 1525; 1480; 1440. Ms (DEI, 70 eV) m/z (%): 591 (M⁺, 13); 522 (8); 453 (15); 396 (10). Anal. Calcd for C₃₃H₂₉N₅O₂S₂: C, 66.98; H, 4.94; N, 11.83. Found: C, 67.05; H, 4.74; N, 11.72.

10,13-Dioxo-5-phenylpyrido[6',5':4,5][3',2':4,5]dithieno[2,3-b':2,3-b]dipyrrolizine (13)

A solution of **12** (0.1 g, 0.16 mmol) in POCl₃ (5 ml) was refluxed for 36 h. The solvent was removed under reduced pressure following the addition of CH₂Cl₂ (10 ml) and ice (100 g), then poured into 25 ml of 25% aqueous KOH. The mixture was extracted twice with 30 ml portions of CH₂Cl₂ and the organic layer was washed with water and 10% HCl, then was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and purified by MPLC using CH₂Cl₂ as eluent to yield **13** (0.03 g, 42%) mp >300°C. Ir (KBr): 1700 (CO); 1550, 1450. Ms (DEI, 70 eV) m/z (%): 449 (M⁺, 100), 419 (7). Anal. Calcd for C₂₅H₁₁N₃O₂S₂: C, 66.80; H, 2.47; N, 9.35. Found: C, 66.92; H, 2.59; N, 9.55.

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