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The Conjugate Addition-Cyclization of 3-Oxoacid Thioanilides to β-Nitrostyrenes. An Efficient Synthesis of Functionalized Thiophenes and their Transformation to Pyrroles

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Summary. A new and simple method for synthesis of 2-, 3-, and 4-pyridylcarbonyl-2-aryliminothiophene derivatives based on the conjugate addition-cyclization of 3-oxoacid thioamides to β-nitrostyrenes was developed. Thiophene derivatives in acidic medium undergo ring transformation yielding corresponding pyrroles.

Keywords. 3-Oxoacid thioanilides; β-Nitrostyrene; *Michael* addition; Thiophenes; Pyrroles.

Introduction

The conjugate addition of stabilized carboanions to unsaturated acceptors is one of the fundamental and efficient methods for the formation of carbon–carbon bonds. Among these reactions, additions of nucleophiles to nitro olefins were useful in the synthesis of various heterocyclic systems [1–3]. Most of the reactions reported have focused on the conjugate addition of 1,3-dicarbonyl compounds to nitroalkenes and have been limited to the synthesis of pyrrole or furan derivatives [4–9], which have biological and pharmaceutical activities. We envisioned that this approach could also be applied to the addition of anions derived from 3-oxoacid thioanilides. Previous investigations from our laboratory have shown that cyclic 3-oxoacid thioanilides undergo *Michael* addition to (*E*)-β-nitrostyrenes to give thiophene derivatives with a high degree of diastereoselectivity [10–12]. These results encouraged us to undertake a study on the synthesis of functionalized

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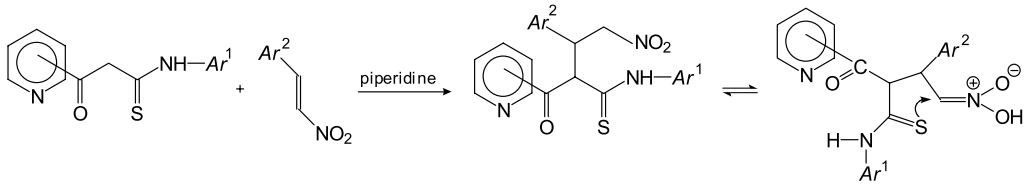
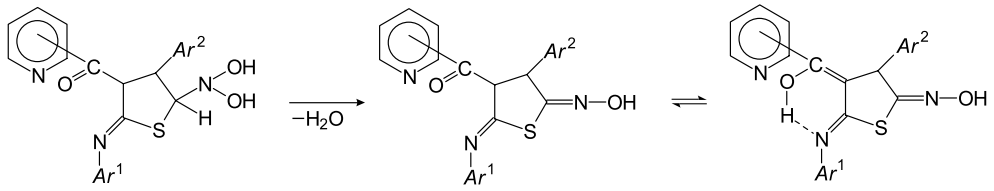
(pyridylcarbonyl)thiophenes and appropriate (pyridylcarbonyl)pyrroles, which might have biological activities.

Results and Discussion

We started our first approach to synthesize polyfunctionalized thiophenes with the preparation of appropriate 3-oxoacid thioanilides **1**, **2**, and **3** containing 2-, 3-, and 4-pyridyl substituents [13]. Reactions of 3-pyridylcarbonyl(thioacetanilides) **2** with (*E*)-β-nitrostyrenes **4** catalyzed by piperidine yielded **7a**–**7e** in excellent yields (Scheme 1). The structures of **7** were deduced from analytical and spectral data. The MS of all products indicated that the *Michael* addition of **2** to **4** was followed



1a-1c **2a-2c** **3a-3c** **4a-4c** **5A** **5B**



5C **6a-6e** **7a-7e** **8a-8e**

					Ar^1	Ar^2
1a	**4a**	**6a**	**10a**	2-*Py*	C_6H_5	C_6H_5
1a	**4b**	**6b**	**10b**	2-*Py*	C_6H_5	4-Cl-C_6H_4
1a	**4c**	**6c**	**10c**	2-*Py*	C_6H_5	4-CH_3-C_6H_4
1b	**4a**	**6d**	**10d**	2-*Py*	4-Cl-C_6H_4	C_6H_5
1c	**4a**	**6e**	**10e**	2-*Py*	4-CH_3-C_6H_4	C_6H_5
2a	**4a**	**7a**	**11a**	3-*Py*	C_6H_5	C_6H_5
2a	**4b**	**7b**	**11b**	3-*Py*	C_6H_5	4-Cl-C_6H_4
2a	**4c**	**7c**	**11c**	3-*Py*	C_6H_5	4-CH_3-C_6H_4
2b	**4a**	**7d**	**11d**	3-*Py*	4-Cl-C_6H_4	C_6H_5
2c	**4a**	**7e**	**11e**	3-*Py*	4-CH_3-C_6H_4	C_6H_5
3a	**4a**	**8a**	**12a**	4-*Py*	C_6H_5	C_6H_5
3a	**4b**	**8b**	**12b**	4-*Py*	C_6H_5	4-Cl-C_6H_4
3a	**4c**	**8c**	**12c**	4-*Py*	C_6H_5	4-CH_3-C_6H_4
3b	**4a**	**8d**	**12d**	4-*Py*	4-Cl-C_6H_4	C_6H_5
3c	**4a**	**8e**	**12e**	4-*Py*	4-CH_3-C_6H_4	C_6H_5

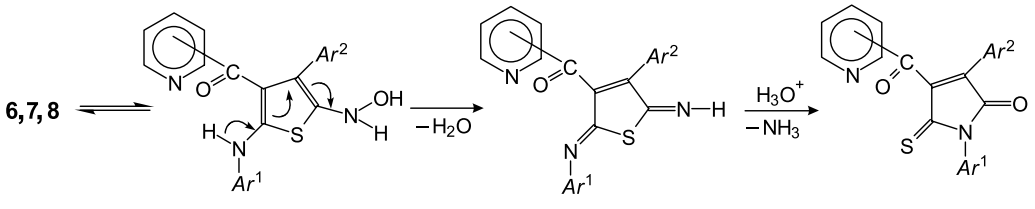
Scheme 1

by elimination of water. The IR spectra of **7** showed the characteristic broad band of hydroxyl groups at 3422 cm^{-1}. These data combined with ^1H and ^{13}C NMR spectra allowed to establish the constitution of **7a**–**7e** as thiophene derivatives. *E.g.*, the ^1H NMR spectrum of **7d** revealed a singlet at $\delta = 5.55$ ppm of one proton attached to C-4 of thiophene ring. Aromatic protons of 3-pyridyl group resonated at $\delta = 7.23$ (m), 7.68 (m), and 8.45 (m) ppm. Other aromatic protons appeared at $\delta = 6.92$ (m), 7.08 (m), 7.50 (m), and 7.53 (m) ppm. Two singlets at $\delta = 11.70$ and 12.57 ppm were assigned to protons of two hydroxyl groups of oxime and enol. Thus, the molecule of **7d** in $CDCl_3$ solution exists in a keto-enol equilibrium, which is entirely shifted towards the enolic form.

In a similar way we synthesized thiophenes **6** and **8** bearing 2- and 4-pyridylcarbonyl groups (Scheme 1). All compounds exhibited similar spectral features to those of **7**. Comparison of three series of the above reactions showed that the rate of reactions and yields of products were influenced by character of substrates. The thioanilides containing the 3-pyridyl group were more reactive towards (*E*)-β-nitrostyrenes than those substituted by 2- and 4-pyridyl residues because the reaction of the former with (*E*)-β-nitrostyrenes yielded **7** in very good yields (70–79%), whereas yields of **6** and **8** were lower (40–55, 59–70%). Moreover, the presence of methyl or chlorine substituents in the thioanilide fragments of substrates increased the yields of products. Formation of all products can be rationalized as shown in Scheme 1.

The conjugate addition of the anion of the thioanilides **1**–**3**, generated in basic medium, to (*E*)-β-nitrostyrenes **4** involves the *Michael* adduct **5A**, which undergoes S-ring closure by nucleophilic attack of the sulfur atom on the α-carbon atom of the tautomeric form of the nitroethane fragment **5B**. Elimination of water from **5C** occurred smoothly yielding the thiophene derivatives **6**–**8**.

The high degree of functionalization of the obtained thiophenes suggested that they ought to react with acidic reagents on any of two exocyclic C=N bonds. Our attention was turned to the *Beckmann* rearrangement or to hydrolysis of the oxime function. *E.g.*, when an ethanolic suspension of **7** was heated with a few drops of conc. HCl we observed dissolution and slow change of the colour of the solution from yellow to dark-green. Work-up of the mixture gave dark-green crystalline products **11** (Scheme 2). The MS spectrum of **11d** ($m/z = 404$) suggested that in acidic medium the oxime function of **7d** was hydrolysed and moreover, the molecule was dehydrogenated. The IR spectrum of **11d** displayed two strong carbonyl



Labels of substituents are given in Scheme 1

Scheme 2

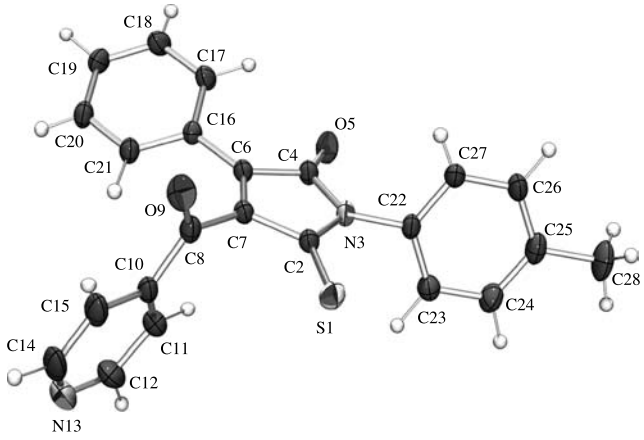


Fig. 1. A perspective view of **12e** with the crystallographic atom numbering scheme; atomic displacement ellipsoids are drawn at 30% probability

bands at $\bar{\nu} = 1740$ and $1668\,cm^{-1}$. Its ^1H NMR spectrum showed only aromatic protons in the range of $\delta = 7.32$–9.04 ppm. The ^{13}C NMR spectrum revealed three signals at $\delta = 195.34$ ppm (C=S) and $\delta = 190.68$ and 170.60 ppm (C=O). In a similar way compounds **6** and **8** were converted into the pyrroles **10** and **12**. Their spectral features and analytical data were similar to those of **11**. The final structure assignment of products **10**, **11**, and **12** was performed by X-ray analysis of **12e**. A perspective view of the molecule with the atomic numbering scheme is given in Fig. 1.

Although **12e** has no chiral centers, the compound crystallizes in a chiral space group *Cc* (monoclinic system). The absolute structure was determined through the refinement of the *Flack* parameter [14], which converged to $-0.02(5)$ indicating the correctness of absolute structure assignment. The crystal packing is dominated by the *van der Waals* interactions, since there are only two intramolecular short contacts involving oxygen atoms of the carbonyl groups: C15–H15 $\cdots$ O9 (2.824(1)Å, 95.3(1)°) and C17–H17 $\cdots$ O5 (3.006(1)Å, 118.67(1)°).

The reaction pathways of the transformation of **6**, **7**, and **8** in acidic medium can be rationalized by water elimination from **6**–**8** leading to the imine intermediate **9**, and its subsequent hydrolysis to a carbonyl group followed by a *Dimroth* ring transformation to 5-thioxopyrrol-2-ones **10**–**12**. The suggested mechanism is outlined in Scheme 2.

In conclusion, the present study demonstrates that the tandem conjugate addition-cyclization strategy affords a facile and efficient route to thiophene and pyrrole systems bearing various substituents. The obtained compounds may be useful in medicinal chemistry since pyridine, thiophene, and pyrrole moieties display a broad range of biological activities and have been widely used as pharmaceuticals.

Experimental

Melting points were determined on a *Boetius* hot stage apparatus. IR spectra: Bruker IFS 48 in KBr pellets, Nujol mulls, or HCB. NMR spectra: Bruker AMX 500 (^1H: 500.14 MHz ^{13}C:

125.76 MHz) in *DMSO*-d_6 or $CDCl_3$ with *TMS* as an internal standard. Mass spectra: Finningan Mat 95 (EI, 70 eV). Microanalyses were performed with a Euro EA 3000 Elemental Analyzer; their results agreed satisfactorily with the calculated values. 2,3,4-Pyridylcarbonyl thioanilides **1**, **2**, and **3** were obtained according to Ref. [14]. Silica gel 60, 0.063–0.2 mm was used for column chromatography.

*General Procedure for the Synthesis of **6–8***

A solution of thioanilide **1**, **2**, or **3** (**1a–3a**: 2.56 g, 10 mmol) and the appropriate (*E*)-*β*-nitrostyrene **4** (**4a**: 1.49 g, 10 mmol) in 50 cm^3 anhydrous ethanol was refluxed with a few drops of piperidine for 3 h. The precipitate was filtered off and washed with 10 cm^3 ethanol. Products were crystallized from methanol.

5-Hydroxyimino-4-phenyl-2-phenylimino-3-(2-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**6a**, $C_{22}H_{17}N_3O_2S$)

Yellow crystals; mp 201–202°C; yield 55%; IR (KBr): $\bar{\nu} = 3416$ (OH), 1641 (C=N), 960 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 6.23$ (s, CH), 7.01–7.03 (m, 3H arom), 7.04–7.11 (m, 2H arom), 7.32–7.37 (m, 2H arom), 7.49–7.50 (m, 5H arom), 7.70–7.74 (td, $J = 7.6$, 1.8 Hz, 1CH pyridyl), 8.56–8.57 (ddd, $J = 4.8$, 1.8, 1.0 Hz, 1CH pyridyl), 11.64 (s, OH-oxime), 13.04 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 52.08$ (C-4), 105.71 (C-3), 122.51, 123.11, 124.94, 126.35, 126.39, 126.81, 127.94, 129.49, 136.83, 139.17, 142.83, 147.67, 153.29 (17C arom), 156.32, 164.03 (C=N), 183.52 (C–OH enol) ppm; MS: m/z (%) = 387 (22, $[M]^{+\bullet}$), 370 (9), 281 (100).

4-(4-Chlorophenyl)-5-hydroxyimino-2-phenylimino-3-(2-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**6b**, $C_{22}H_{16}ClN_3O_2S$)

Yellow crystals; mp 188–189°C; yield 52%; IR (KBr): $\bar{\nu} = 3384$ (OH), 1627 (C=N), 950 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 6.24$ (s, CH), 7.07–7.09 (m, 2H arom), 7.15–7.17 (m, 2H arom), 7.33–7.39 (m, 2H arom), 7.47–7.56 (m, 5H arom), 7.74–7.77 (td, $J = 7.6$, 1.6 Hz, 1CH pyridyl), 8.55–8.56 (ddd, $J = 4.8$, 1.8, 1.0 Hz, 1CH pyridyl), 11.70 (s, OH-oxime), 13.07 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 51.59$ (C-4), 105.17 (C-3), 122.58, 123.18, 125.06, 126.49, 127.92, 128.71, 129.49, 130.86, 136.94, 139.09, 141.95, 147.69, 152.88 (17C arom), 156.10, 164.30 (C=N), 183.21 (C–OH enol) ppm; MS: m/z (%) = 421 (19, $[M]^{+\bullet}$), 404 (15), 315 (100).

5-Hydroxyimino-4-(4-methylphenyl)-2-phenylimino-3-(2-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**6c**, $C_{23}H_{19}N_3O_2S$)

Yellow crystals; mp 192–193°C; yield 41%; IR (KBr): $\bar{\nu} = 3263$ (OH), 1627 (C=N), 949 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 2.13$ (s, CH_3), 6.23 (s, CH), 6.90–6.91 (m, 4H arom), 7.31–7.37 (m, 2H arom), 7.46–7.53 (m, 5H arom), 7.72–7.75 (td, $J = 7.6$, 1.6 Hz, 1CH pyridyl), 8.56–8.58 (ddd, $J = 4.8$, 1.6, 0.8, 1CH pyridyl), 11.60 (s, OH-oxime), 13.04 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 20.36$ (CH_3), 51.66 (C-4), 105.80 (C-3), 122.58, 123.04, 124.98, 126.34, 126.65, 128.53, 129.49, 135.36, 136.84, 139.18, 139.90, 147.67, 153.45 (17C arom), 156.32, 163.95 (C=N), 183.43 (C–OH enol) ppm; MS: m/z (%) = 401 (23, $[M]^{+\bullet}$), 384 (10), 295 (100).

2-(4-Chlorophenylimino)-5-hydroxyimino-4-phenyl-3-(2-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**6d**, $C_{22}H_{16}ClN_3O_2S$)

Yellow crystals; mp 215–216°C; yield 53%; IR (KBr): $\bar{\nu} = 3214$ (OH), 1624 (C=N), 952 (N–O oxime) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 6.23$ (s, CH), 7.00–7.04 (m, 3H arom), 7.08–7.10 (m, 2H arom), 7.34–7.37 (m, 1H arom), 7.48–7.56 (m, 5H arom), 7.70–7.74 (td, $J = 7.8$, 1.8 Hz, 1CH pyridyl), 8.56–8.58 (ddd, $J = 4.8$, 1.8, 1.0 Hz, 1CH pyridyl), 11.66 (s, OH-oxime), 12.92 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 52.15$ (C-4), 106.17 (C-3), 122.52, 124.98, 126.37, 126.83, 127.95, 129.34, 130.51, 136.86, 138.29, 142.71, 147.70, 153.07 (17C arom), 156.16, 163.61 (C=N), 183.46 (C–OH enol) ppm; MS: m/z (%) = 421 (23, $[M]^{+\bullet}$), 404 (4), 315 (100).

5-Hydroxyimino-2-(4-methylphenylimino)-4-phenyl-3-(2-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**6e**, $C_{23}H_{19}N_3O_2S$)
Yellow crystals; mp 203–204°C; yield 40%; IR (KBr): $\bar{\nu} = 3445$ (OH), 1634 (C=N), 958 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 2.35$ (s, CH_3), 6.22 (s, CH), 7.00–7.04 (m, 3H arom), 7.07–7.10 (m, 2H arom), 7.29–7.37 (m, 5H arom), 7.48–7.50 (m, 1H arom), 7.69–7.73 (td, $J = 7.6$, 1.8 Hz, 1CH pyridyl), 8.55–8.56 (ddd, $J = 4.8$, 1.8, 1.0 Hz, 1CH pyridyl), 11.61 (s, OH-oxime), 12.97 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 20.41$ (CH_3), 52.13 (C-4), 105.31 (C-3), 122.47, 123.22, 124.86, 126.31, 126.81, 127.92, 129.90, 136.03, 136.64, 136.78, 142.92, 147.64, 153.36 (17C arom), 156.40, 164.51 (C=N), 183.37 (C–OH enol) ppm; MS: m/z (%) = 401 (26, $[M]^{+\bullet}$), 384 (2), 295 (100), 169 (85).

5-Hydroxyimino-4-phenyl-2-phenylimino-3-(3-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**7a**, $C_{22}H_{17}N_3O_2S$)
Pale yellow prisms; mp 231–232°C; yield 74%; IR (KBr): $\bar{\nu} = 3446$ (OH), 1644 (C=N), 965 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 5.60$ (s, CH), 6.93–6.95 (m, 2H arom), 7.14–7.16 (m, 2H arom), 7.24–7.27 (m, 1H arom), 7.32–7.36 (m, 1H arom), 7.46–7.52 (m, 5H arom), 7.71–7.73 (dt, $J = 7.8$, 3.6, 1.8 Hz, 1CH pyridyl), 8.49–8.51 (m, 2CH pyridyl), 11.73 (s, OH-oxime), 12.71 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 51.67$ (C-4), 105.66 (C-3), 122.83, 123.09, 126.47, 128.06, 128.76, 129.46, 131.13, 133.57, 136.49, 138.89, 140.89, 146.72, 149.94 (17C arom), 152.28, 163.17 (C=N), 185.87 (C–OH enol) ppm; MS: m/z (%) = 387 (73, $[M]^{+\bullet}$), 370 (32), 281 (100).

4-(4-Chlorophenyl)-5-hydroxyimino-2-phenylimino-3-(3-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**7b**, $C_{22}H_{16}ClN_3O_2S$)
Pale yellow prisms; mp 221–222°C; yield 79%; IR (KBr): $\bar{\nu} = 3431$ (OH), 1646 (C=N), 966 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 5.60$ (s, CH), 6.93–6.95 (m, 2H arom), 7.14–7.16 (m, 2H arom), 7.24–7.27 (m, 1H arom), 7.32–7.35 (m, 1H arom), 7.46–7.52 (m, 4H arom), 7.71–7.73 (dt, $J = 7.8$, 3.8, 1.8 Hz, 1CH pyridyl), 8.46–8.48 (m, 2H pyridyl), 11.73 (s, OH-oxime), 12.70 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 51.67$ (C-4), 105.68 (C-3), 122.85, 123.11, 126.49, 128.07, 128.77, 129.49, 131.13, 133.60, 136.50, 138.90, 140.90, 146.73, 149.95 (17C arom), 152.29, 163.17 (C=N), 185.89 (C–OH enol) ppm; MS: m/z (%) = 421 (48, $[M]^{+\bullet}$), 404 (45), 315 (75), 106 (100).

5-Hydroxyimino-4-(4-methylphenyl)-2-phenylimino-3-(3-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**7c**, $C_{23}H_{19}N_3O_2S$)
Colourless prisms; mp 217–218°C; yield 70%; IR (KBr): $\bar{\nu} = 3445$ (OH), 1648 (C=N), 965 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 2.15$ (s, CH_3), 5.50 (s, CH), 6.80–6.82 (m, 2H arom), 6.90–6.92 (m, 2H arom), 7.23–7.26 (m, 1H arom), 7.32–7.35 (m, 1H arom), 7.46–7.51 (m, 4H arom), 7.71–7.73 (dt, $J = 7.8$, 4.0, 1.8 Hz, 1CH pyridyl), 8.46–8.47 (m, 2CH pyridyl), 11.65 (s, OH-oxime), 12.73 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 20.40$ (CH_3), 52.00 (C-4), 106.08 (C-3), 122.81, 123.03, 126.39, 126.73, 128.70, 129.50, 133.65, 135.66, 136.55, 138.94, 138.99, 146.83, 149.92 (17C arom), 152.80, 162.99 (C=N), 185.93 (C–OH enol) ppm; MS: m/z (%) = 401 (54, $[M]^{+\bullet}$), 384 (50), 383 (100), 295 (98).

2-(4-Chlorophenylimino)-5-hydroxyimino-4-phenyl-3-(3-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**7d**, $C_{22}H_{16}ClN_3O_2S$)
Colourless prisms; mp 223–224°C; yield 71%; IR (KBr): $\bar{\nu} = 3422$ (OH), 1603 (C=N), 972 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): $\delta = 5.55$ (s, CH), 6.91–6.93 (m, 2H arom), 7.04–7.11 (m, 3H arom), 7.22–7.24 (m, 1H arom), 7.49–7.55 (m, 4H arom), 7.67–7.70 (dt, $J = 7.8$, 4.0, 1.8 Hz, 1CH pyridyl), 8.44–8.46 (m, 2CH pyridyl), 11.70 (s, OH-oxime), 12.57 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 52.46$ (C-4), 106.65 (C-3), 122.81, 124.92, 126.61, 126.94, 128.13, 129.34, 130.51,

133.63, 136.44, 138.10, 141.77, 146.77, 149.96 (17C arom), 152.48, 162.49 (C=N), 186.00 (C–OH enol) ppm; MS: m/z (%) = 421 (65, $[M]^{+\bullet}$), 420 (100), 404 (47), 316 (87).

5-Hydroxyimino-2-(4-methylphenylimino)-4-phenyl-3-(3-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**7e**, $C_{23}H_{19}N_3O_2S$)
Yellow crystals; mp 214–215°C; yield 71%; IR (KBr): $\bar{\nu}$ = 3445 (OH), 1655 (C=N), 968 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 2.35 (s, CH_3), 5.53 (s, CH), 6.89–6.91 (m, 2H arom), 7.03–7.10 (m, 3H arom), 7.21–7.23 (m, 1H arom), 7.29–7.31 (m, 2H arom), 7.35–7.37 (m, 2H arom), 7.66–7.68 (dt, J = 7.8, 3.8, 2.0 Hz, 1CH pyridyl), 8.43–8.44 (m, 2CH pyridyl), 11.65 (s, OH-oxime), 12.66 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 20.41 (CH_3), 52.39 (C-4), 105.65 (C-3), 122.79, 123.22, 126.56, 126.89, 128.11, 129.91, 133.55, 136.10, 136.45, 136.65, 141.97, 146.72, 149.79 (17C arom), 152.73, 163.59 (C=N), 185.83 (C–OH enol) ppm; MS: m/z (%) = 401 (81, $[M]^{+\bullet}$), 384 (51), 295 (100).

5-Hydroxyimino-4-phenyl-2-phenylimino-3-(4-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**8a**, $C_{22}H_{17}N_3O_2S$)
Yellow crystals; mp 214–215°C; yield 61%; IR (KBr): $\bar{\nu}$ = 3457 (OH), 1641 (C=N), 964 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 5.47 (s, CH), 6.89–6.91 (m, 2H arom), 7.05–7.11 (m, 3H arom), 7.17–7.18 (d, J = 6.0 Hz, 2CH pyridyl), 7.33–7.36 (m, 1H arom), 7.47–7.52 (m, 4H arom), 8.41–8.43 (d, J = 6.0 Hz, 2CH pyridyl), 11.70 (s, OH-oxime), 12.67 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 52.12 (C-4), 105.54 (C-3), 120.16, 123.24, 126.60, 126.99, 128.11, 129.51, 138.86, 141.81, 147.62, 149.32 (17C arom), 152.63, 163.68 (C=N), 186.03 (C–OH enol) ppm; MS: m/z (%) = 387 (59, $[M]^{+\bullet}$), 370 (35), 281 (100).

4-(4-Chlorophenyl)-5-hydroxyimino-2-phenylimino-3-(4-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**8b**, $C_{22}H_{16}ClN_3O_2S$)
Pale yellow prisms; mp 232–233°C; yield 60%; IR (KBr): $\bar{\nu}$ = 3431 (OH), 1634 (C=N), 969 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 5.53 (s, CH), 6.92–6.94 (m, 2H arom), 7.14–7.15 (m, 2H arom), 7.21–7.22 (d, J = 5.8 Hz, 2CH pyridyl), 7.33–7.37 (m, 1H arom), 7.47–7.52 (m, 4H arom), 8.44–8.45 (d, J = 5.8 Hz, 2CH pyridyl), 11.75 (s, OH-oxime), 12.65 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 51.44 (C-4), 105.09 (C-3), 120.16, 123.31, 126.69, 128.06, 128.88, 129.51, 131.17, 138.79, 140.83, 147.56, 149.43 (17C arom), 152.26, 163.82 (C=N), 185.92 (C–OH enol) ppm; MS: m/z (%) = 421 (73, $[M]^{+\bullet}$), 404 (33), 315 (100).

5-Hydroxyimino-4-(4-methylphenyl)-2-phenylimino-3-(3-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**8c**, $C_{23}H_{19}N_3O_2S$)
Pale yellow prisms; mp 242–243°C; yield 59%; IR (KBr): $\bar{\nu}$ = 3452 (OH), 1641 (C=N), 965 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 2.16 (s, CH_3), 5.43 (s, CH), 6.77–6.79 (m, 2H arom), 6.89–6.91 (m, 2H arom), 7.19–7.20 (d, J = 5.8 Hz, 2CH pyridyl), 7.32–7.36 (m, 1H arom), 7.46–7.52 (m, 4H arom), 8.43–8.44 (d, J = 5.8 Hz, 2CH pyridyl), 11.66 (s, OH-oxime), 12.68 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 20.41 (CH_3), 51.75 (C-4), 105.51 (C-3), 120.22, 123.19, 126.56, 126.81, 128.67, 129.50, 135.68, 138.87, 147.60, 149.35 (17C arom), 152.75, 163.62 (C=N), 185.94 (C–OH enol) ppm; MS: m/z (%) = 401 (61, $[M]^{+\bullet}$), 384 (34), 295 (100).

2-(4-Chlorophenylimino)-5-hydroxyimino-4-phenyl-3-(4-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**8d**, $C_{22}H_{16}ClN_3O_2S$)
Yellow crystals; mp 216–217°C; yield 70%; IR (KBr): $\bar{\nu}$ = 3434 (OH), 1594 (C=N), 971 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 5.47 (s, CH), 6.89–6.91 (m, 2H arom), 7.07–7.09 (m, 3H arom), 7.16–7.17 (d, J = 5.5 Hz, 2CH pyridyl), 7.50–7.56 (m, 4H arom), 8.42–8.43 (d, J = 5.5 Hz, 2CH pyridyl), 11.71 (s, OH-oxime), 12.53 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 52.20 (C-4), 105.99 (C-3), 120.14, 125.14, 126.63, 127.01, 128.11, 129.35, 130.72, 137.96, 141.69, 147.50, 149.34,

(17C arom), 152.42, 163.19 (C=N), 186.09 (C–OH enol) ppm; MS: m/z (%) = 421 (89, $[M]^{+\bullet}$), 404 (42), 315 (100).

5-Hydroxyimino-2-(4-methylphenylimino)-4-phenyl-3-(4-pyridylcarbonyl)-2,3,4,5-tetrahydrothiophene (**8e**, $C_{23}H_{19}N_3O_2S$)
Pale yellow prisms; mp 224–225°C; yield 62%; IR (KBr): $\bar{\nu}$ = 3438 (OH), 1595 (C=N), 968 (N–O oxime) cm^{-1}; ^1H NMR (*DMSO*-d_6): δ = 2.35 (s, CH_3), 5.46 (s, CH), 6.88–6.90 (m, 2H arom), 7.07–7.09 (m, 3H arom), 7.16–7.17 (d, J = 5.8 Hz, 2CH pyridyl), 7.29–7.31 (m, 2H arom), 7.35–7.37 (m, 2H arom), 8.41–8.42 (d, J = 5.8 Hz, 2CH pyridyl), 11.67 (s, OH-oxime), 12.61 (s, OH-enol) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 20.42 (CH_3), 52.17 (C-4), 105.12 (C-3), 120.16, 123.34, 126.57, 126.97, 128.09, 129.91, 136.26, 141.90, 147.70, 149.30 (17C arom), 152.68, 164.16 (C=N), 185.85 (C–OH enol) ppm; MS: m/z (%) = 401 (99, $[M]^{+\bullet}$), 384 (48), 295 (100).

*General Procedure for the Synthesis of **10–12***
A suspension of **6**, **7**, and **8** (**6a**–**8a**: 1.93 g, 5 mmol) in 40 cm^3 anhydrous ethanol was treated with 5 cm^3 conc. HCl. The mixture was refluxed for 2 h to dissolve the substrate. The ethanolic solution was concentrated and the residue was poured into ice/H_2O. The precipitate was separated, washed with H_2O, dried, and purified by column chromatography on silica gel using $CHCl_3$ as the eluent. Products were crystallized from methanol.

1,3-Diphenyl-4-(2-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one (**10a**, $C_{22}H_{14}N_2O_2S$)
Brown crystals; mp 130–131°C; yield 29%; IR (Nujol): $\bar{\nu}$ = 1732 (C=O), 1179 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.08–7.51 (m, 12H arom), 8.01–8.03 (m, 2H arom) ppm; ^{13}C NMR ($CDCl_3$): δ = 128.34, 128.59, 128.75, 129.12, 129.85, 130.97, 131.15, 133.33 (17C arom), 136.11 (C-3), 137.15 (C-4), 149.47, 171.61 (C=O), 198.97 (C=S) ppm; MS: m/z (%) = 370 (92, $[M]^{+\bullet}$), 313 (22), 265 (100), 236 (58).

3-(4-Chlorophenyl)-1-phenyl-4-(2-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**10b**, $C_{22}H_{13}ClN_2O_2S$)
Brown crystals; mp 199–200°C; yield 87%; IR (Nujol): $\bar{\nu}$ = 1733, 1691 (C=O), 1137 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.32–7.34 (m, 2H arom), 7.38–7.40 (m, 2H arom), 7.44–7.53 (m, 4H arom), 7.67–7.69 (m, 2H arom), 7.89–7.92 (td, J = 7.8, 1.6 Hz, 1CH pyridyl), 8.16–8.18 (d, J = 7.8 Hz, 1CH pyridyl), 8.61–8.62 (ddd, J = 4.8, 1.6, 0.8 Hz, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): δ = 122.85, 126.51, 128.03, 128.35, 128.95, 129.16, 129.21, 131.06, 132.13, 132.86, 137.13, 137.23, 140.47 (17C arom), 149.50 (C-3), 153.04 (C-4), 171.05, 192.73 (C=O), 196.33 (C=S) ppm; MS: m/z (%) = 404 (68, $[M]^{+\bullet}$), 299 (100), 264 (54).

3-(4-Methylphenyl)-1-phenyl-4-(2-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**10c**, $C_{23}H_{16}N_2O_2S$)
Brown crystals; mp 207–208°C; yield 34%; IR (Nujol): $\bar{\nu}$ = 1736, 1687 (C=O), 1132 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.32 (s, CH_3), 7.14–7.16 (m, 2H arom), 7.39–7.53 (m, 6H arom), 7.63–7.64 (m, 2H arom), 7.88–7.91 (td, J = 7.8, 1.6 Hz, 1CH pyridyl), 8.16–8.18 (d, J = 7.8 Hz, 1CH pyridyl), 8.70–8.71 (ddd, J = 4.8, 1.6, 0.8 Hz, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.52 (CH_3), 122.84, 125.20, 127.81, 128.43, 128.81, 129.09, 129.65, 129.86, 133.05, 133.37, 137.12, 139.60, 141.38 (17C arom), 149.48 (C-3), 153.24 (C-4), 171.33, 193.13 (C=O), 196.80 (C=S) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 327 (26), 218 (22).

1-(4-Chlorophenyl)-3-phenyl-4-(2-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**10d**, $C_{22}H_{13}ClN_2O_2S$)
Brown needles; mp 194–195°C; yield 59%; IR (Nujol): $\bar{\nu}$ = 1731, 1691 (C=O), 1140 (C=S) cm^{-1}; UV (Ethanol): λ_{max} (log ε) = 206 (4.39), 232 (4.33), 346 (4.17) nm; ^1H NMR ($CDCl_3$): δ = 7.33–7.39

(m, 5H arom), 7.46–7.49 (m, 3H arom), 7.69–7.71 (m, 2H arom), 7.88–7.92 (td, $J = 8.0$, 2.0 Hz, 1CH pyridyl), 8.16–8.18 (d, $J = 8$ Hz, 1CH pyridyl), 8.60–8.62 (ddd, $J = 4.8$, 2.0, 0.8 Hz, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 122.85$, 127.88, 127.94, 128.85, 129.39, 129.66, 129.82, 130.79, 131.39, 133.41, 134.80, 137.19, 140.58 (17C arom), 149.47 (C-3), 153.08 (C-4), 170.97, 192.66 (C=O), 196.25 (C=S) ppm; MS: m/z (%) = 404 (100, $[M]^{+\bullet}$), 347 (20), 238 (22).

1-(4-Methylphenyl)-3-phenyl-4-(2-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**10e**, $C_{23}H_{16}N_2O_2S$)
Brown needles; mp 218–219°C; yield 65%; IR (KBr): $\bar{\nu} = 1738$, 1684 (C=O), 1140 (C=S) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.32$ (s, CH_3), 7.27–7.38 (m, 7H arom), 7.45–7.48 (m, 1H arom), 7.70–7.72 (m, 2H arom), 7.87–7.90 (td, $J = 8.0$, 2.0 Hz, 1CH pyridyl), 8.16–8.17 (d, $J = 8.0$ Hz, 1CH pyridyl), 8.61–8.62 (m, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.26$ (CH_3), 122.81, 127.84, 128.12, 128.77, 129.83, 130.32, 130.61, 133.32, 137.12, 138.97, 140.34 (17C arom), 149.45 (C-3), 153.17 (C-4), 171.29, 192.90 (C=O), 196.79 (C=S) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 218 (173).

1,3-Diphenyl-4-(3-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one (**11a**, $C_{22}H_{14}N_2O_2S$)
Brown needles; mp 217–218°C; yield 69%; IR (HCB): $\bar{\nu} = 1749$, 1669 (C=O), 1170 (C=S) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.35$–7.43 (m, 6H arom), 7.47–7.49 (m, 1H arom), 7.52–7.55 (m, 2H arom), 7.72–7.74 (m, 2H arom), 8.22–8.25 (dt, $J = 8.0$, 4.0, 1.8 Hz, 1CH pyridyl), 8.77–8.78 (m, 1H arom), 9.0 (s, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 123.88$, 127.25, 128.29, 129.15, 129.28, 129.97, 131.41, 132.74, 133.41, 136.17, 137.55 (17C arom), 151.12 (C-3), 154.63 (C-4), 170.84, 190.86 (C=O), 195.74 (C=S) ppm; MS: m/z (%) = 370 (100, $[M]^{+\bullet}$), 313 (27), 204 (80).

3-(4-Chlorophenyl)-1-phenyl-4-(3-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**11b**, $C_{22}H_{13}ClN_2O_2S$)
Green needles; mp 219–220°C; yield 78%; IR (KBr): $\bar{\nu} = 1743$, 1670 (C=O), 1138 (C=S) cm^{-1}; UV (Ethanol): λ_{max} (log ε) = 206 (4.43), 232 (4.35), 350 (4.24) nm; ^{1}H NMR ($CDCl_3$): $\delta = 7.36$–7.38 (m, 4H arom), 7.42–7.49 (m, 2H arom), 7.15–7.55 (m, 2H arom), 7.68–7.71 (m, 2H arom), 8.22–8.24 (dt, $J = 8.0$, 4.0, 2.0 Hz, 1CH pyridyl), 8.79–8.81 (m, 1H arom), 9.0 (s, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 123.97$, 125.69, 128.24, 129.21, 129.31, 129.58, 131.18, 131.34, 132.25, 132.59, 136.12, 137.58, 138.02 (17C arom), 151.12 (C-3), 154.83 (C-4), 170.66, 190.71 (C=O), 195.47 (C=S) ppm; MS: m/z (%) = 404 (100, $[M]^{+\bullet}$), 376 (8), 238 (70).

3-(4-Methylphenyl)-1-phenyl-4-(3-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**11c**, $C_{23}H_{16}N_2O_2S$)
Brown needles; mp 239–240°C; yield 72%; IR (HCB): $\bar{\nu} = 1748$, 1670 (C=O), 1170 (C=S) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.21$ (s, CH_3), 7.06–7.08 (m, 2H arom), 7.26–7.44 (m, 6H arom), 7.53–7.55 (m, 2H arom), 8.11–8.13 (dt, $J = 8.0$, 4.0, 2.0 Hz, 1CH pyridyl), 8.66–8.67 (m, 1H arom), 8.9 (s, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.57$ (CH_3), 123.89, 124.41, 128.30, 129.08, 129.25, 129.99, 131.44, 132.78, 133.42, 136.21, 136.68, 142.36 (17C arom), 151.13 (C-3), 154.59 (C-4), 170.96, 191.16 (C=O), 195.88 (C=S) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 368 (26), 218 (79).

1-(4-Chlorophenyl)-3-phenyl-4-(3-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**11d**, $C_{22}H_{13}ClN_2O_2S$)
Brown needles; mp 186–187°C; yield 83%; IR (HCB): $\bar{\nu} = 1741$, 1668 (C=O), 1170 (C=S) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.32$–7.44 (m, 6H arom), 7.49–7.52 (m, 2H arom), 7.71–7.72 (m, 2H arom), 8.22–8.24 (dt, $J = 8.0$, 4.0, 1.8 Hz, 1CH pyridyl), 8.77–8.79 (m, 1H arom), 9.0 (s, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 123.93$, 127.07, 129.21, 129.54, 129.95, 131.09, 131.32, 131.56, 133.48, 135.12, 136.15, 137.64 (17C arom), 151.11 (C-3), 154.71 (C-4), 170.60, 190.68 (C=O), 195.34 (C=S) ppm; MS: m/z (%) = 404 (85, $[M]^{+\bullet}$), 347 (17), 238 (100).

1-(4-Methylphenyl)-3-phenyl-4-(3-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**11e**, $C_{23}H_{16}N_2O_2S$)
Green powder; mp 163–164°C; yield 81%; IR (HCB): $\bar{\nu} = 1731$, 1667 (C=O), 1173 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.43$ (s, CH_3), 7.26–7.28 (m, 2H arom), 7.73–7.39 (m, 4H arom), 7.41–7.45 (m, 2H arom), 7.73–7.75 (m, 2H arom), 8.23–8.25 (dt, $J = 8.0$, 4.0, 1.8 Hz, 1CH pyridyl), 8.78–8.79 (m, 1H arom), 9.0 (s, 1CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.28$ (CH_3), 123.89, 127.27, 128.00, 129.14, 129.96, 130.00, 131.37, 133.40, 136.18, 137.48, 139.32 (17C arom), 151.13 (C-3), 154.63 (C-4), 170.93, 190.92 (C=O), 195.90 (C=S) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 368 (13), 218 (61).

1,3-Diphenyl-4-(4-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one (**12a**, $C_{22}H_{14}N_2O_2S$)
Green needles; mp 163–164°C; yield 72%; IR (KBr): $\bar{\nu}$=1731, 1678 (C=O), 1138 (C=S) cm^{-1}; UV (Ethanol): λ_{max} (log ε) = 208 (4.39), 224 (4.38), 346 (4.25) nm; ^1H NMR ($CDCl_3$): $\delta = 7.36$–7.39 (m, 4H arom), 7.42–7.49 (m, 2H arom), 7.52–7.55 (m, 2H arom), 7.68–7.69 (d, $J = 6$ Hz, 2CH pyridyl), 7.70–7.71 (m, 2H arom), 8.79–8.81 (d, $J = 6$ Hz, 2CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 121.72$, 127.12, 128.23, 129.19, 129.28, 129.94, 131.55, 132.61, 133.80, 137.26 (17C arom), 141.50 (C-3), 151.18 (C-4), 170.71, 191.59 (C=O), 195.54 (C=S) ppm; MS: m/z (%) = 370 (100, $[M]^{+\bullet}$), 313 (27), 204 (47).

3-(4-Chlorophenyl)-1-phenyl-4-(4-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**12b**, $C_{22}H_{13}ClN_2O_2S$)
Green needles; mp 175–176°C; yield 79%; IR (KBr): $\bar{\nu} = 1729$, 1685 (C=O), 1138 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.35$–7.37 (m, 4H arom), 7.46–7.55 (m, 3H arom), 7.66–7.67 (m, 2H arom), 7.68–7.69 (d, $J = 6$ Hz, 2CH pyridyl), 8.82–8.83 (d, $J = 6$ Hz, 2CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 121.65$, 125.55, 128.18, 129.25, 129.33, 129.63, 131.15, 132.47, 132.64, 137.30, 138.17 (17C arom), 141.38 (C-3), 151.28 (C-4), 170.54, 191.51 (C=O), 195.29 (C=S) ppm; MS: m/z (%) = 404 (100, $[M]^{+\bullet}$), 238 (52).

3-(4-Methylphenyl)-1-phenyl-4-(4-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**12c**, $C_{23}H_{16}N_2O_2S$)
Green needles; mp 148–149°C; yield 86%; IR (KBr): $\bar{\nu} = 1729$, 1676 (C=O), 1188 (C=S) cm^{-1}; UV (Ethanol): λ_{max} (log ε) = 206 (4.45), 226 (4.41), 358 (4.25) nm;^1H NMR ($CDCl_3$): $\delta = 2.33$ (s, CH_3), 7.17–7.19 (m, 2H arom), 7.37–7.39 (m, 2H arom), 7.45–7.54 (m, 3H arom), 7.61–7.63 (m, 2H arom), 7.68–7.69 (d, $J = 6$ Hz, 2CH pyridyl), 8.79–8.80 (d, $J = 6$ Hz, 2CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.57$ (CH_3), 121.75, 124.29, 128.25, 129.09, 129.24, 129.97, 130.02, 132.67, 133.80, 136.39, 141.55 (17C arom), 142.51 (C-3), 151.16 (C-4), 170.81, 191.84 (C=O), 195.68 (C=S) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 327 (34), 218 (76).

1-(4-Chlorophenyl)-3-phenyl-4-(4-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**12d**, $C_{22}H_{13}ClN_2O_2S$)
Green needles; mp 157–158°C; yield 42%; IR (KBr): $\bar{\nu} = 1729$, 1689 (C=O), 1142 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.32$–7.35 (m, 2H arom), 7.36–7.39 (m, 2H arom), 7.42–7.46 (m, 1H arom), 7.50–7.52 (m, 2H arom), 7.67–7.68 (d, $J = 6$ Hz, 2CH pyridyl), 7.69–7.70 (m, 2H arom), 8.79–8.80 (d, $J = 6$ Hz , 2CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 121.69$, 126.98, 129.25, 129.50, 129.58, 129.94, 131.01, 131.69, 133.89, 135.17, 137.40 (17C arom), 141.44 (C-3), 151.21 (C-4), 170.49, 191.42 (C=O), 195.17 (C=S) ppm; MS: m/z (%) = 404 (100, $[M]^{+\bullet}$), 347 (18), 238 (51).

1-(4-Methylphenyl)-3-phenyl-4-(4-pyridylcarbonyl)-5-thioxopyrrol-2(5H)-one
(**12e**, $C_{23}H_{16}N_2O_2S$)
Brown needles; mp 162–163°C; yield 80%; IR (KBr): $\bar{\nu} = 1734$, 1682 (C=O), 1133 (C=S) cm^{-1}; UV (Ethanol): λ_{max} (log ε) = 208 (4.38), 224 (4.39), 348 (4.21) nm; ^1H NMR ($CDCl_3$): $\delta = 2.34$ (s, CH_3), 7.17–7.19 (m, 2H arom), 7.24–7.30 (m, 4H arom), 7.33–7.36 (m, 1H arom), 7.59–7.61 (d, $J = 6.2$ Hz,

2CH pyridyl), 7.62–7.63 (m, 2H arom), 8.71–8.72 (d, $J = 6.2$ Hz, 2CH pyridyl) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.25$ (CH_3), 121.70, 127.14, 127.93, 129.14, 129.91, 129.97, 130.27, 131.47, 133.76, 137.20, 139.33 (17C arom), 141.49 (C-3), 151.15 (C-4), 170.78, 191.62 (C=O), 195.70 (C=S) ppm; MS: m/z (%) = 384 (100, $[M]^{+\bullet}$), 369 (19), 218 (50).

Crystal structure analysis: Compound **12e** crystallizes in the monoclinic system, space group *Cc*, with unit cell parameters $a = 17.1791(2)$, $b = 12.8014(2)$, $c = 10.8984(1)$ Å, $\beta = 126.109(1)^\circ$, $V = 1936.32(3)$ Å^3, $Z = 4$. A total of 4437 independent reflections (R(int) = 0.0162) were collected on a sample (size $0.3 \times 0.2 \times 0.1$ mm^3) using MoKα radiation, up to $\theta = 27.56^\circ$ with data completeness of 99.98%. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using SHELX-97 program system [15]. Final R indices for $I > 2\sigma(I)$ were $R1 = 0.0285$ and $R1 = 0.0311$, w$R2 = 0.0781$ for all data. The final difference *Fourier* map of electron density revealed the largest peak and hole with 0.126 and -0.014 e.Å^{-3}. The structural data were deposited at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) under reference number CCDC 272451.

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