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1-Aryl-5-methoxy-pyrrolones as Synthons for 1,3-Dipolar Cycloadditions

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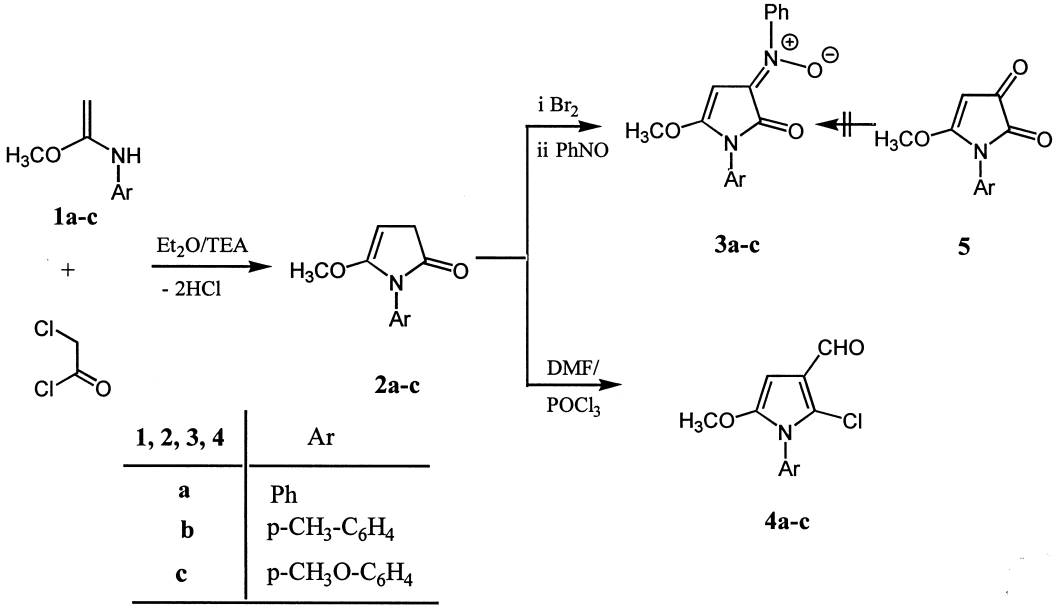
Abstract—A general method is described to convert the title compound into more complex nitrogen heterocyclic systems in a short and attractive pathway. Spiroisoxazolidine **6** was obtained from the reaction of nitrone **3** with ethyl vinyl ether. Chloroformylation of pyrrolone **2** gave 1-aryl-2-chloro-5-methoxy-pyrrol-3-carbaldehyde **4**. Substitution of chlorine atom with unsaturated nucleophiles **8a**,**b** and then modifying the aldehyde function into 1,3-dipoles **10** and **14** furnished tricyclic heterocycles **11**, **12** and **15** via intramolecular 1,3-dipolar cycloaddition reaction.

Introduction

The chemistry of monocyclic heterocyclic 2,3-diones has in general been widely explored during the last few decades. In particular, derivatives of such structures have been found to serve as versatile synthons in (a) thermolysis reactions[1] (b) cycloaddition reactions[2] and (c) reactions with nucleophiles.[3] Several attempts to change functional groups in pyrrole- or furan-2,3-diones and related systems have been reported.[4] In an effort to explore the scope of these reactions, a number of new pyrrole substrates bearing a 1,3-dipole unit was prepared and tested for cycloaddition reactions. The model compounds of type **4** are interesting starting materials for two reasons: firstly, the chlorine atom is easily substituted by unsaturated nucleophiles; and secondly the aldehyde function is ideally suited for conversion into 1,3-dipoles (nitrone and nitrile oxide). By incorporating an internal 1,3-dipole tethered to a dipolarophile, construction



Scheme 1.

Keywords: 1,3-dipolar cycloaddition; nitrones; nitrile oxide; pyrrolones.

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of spiro and more complex nitrogen heterocyclic systems has been performed in a short and attractive pathway, starting from simple pyrrolone **2**. With this goal in mind, some model studies were undertaken to determine the facility of intramolecular cyclization of 1,3-dipoles **3**, **10** and **14**.

Thus, 1-aryl-5-methoxy-pyrrol-2-one **2a–c** were easily synthesized, in 74–82% yield, from the reaction of *N*-aryl-acetimidic ester[5] with chloroacetyl chloride as outlined in Scheme 1. Bromination of pyrrolone **2** followed by treatment with nitrosobenzene at room temperature furnished the heterocyclic aryl nitrones **3** in 62–73% yield. Several trials to get **3** from pyrrol-2,3-diones **5**[1b] and phenyl hydroxylamine were unsuccessful. On the other hand, conversion of pyrrolone **2** into 1-aryl-2-chloro-5-methoxypyrrol-3-carbaldehyde **4** can be achieved by chloroformylation of pyrrolone **2** (see Experimental) in a similar way for chloroformylation of 3-methyl-1-phenyl-pyrazol-5-one.[6]

The structural conformation of **3a–c** was accomplished on the basis of the analytical data and spectroscopic properties: the IR spectrum of **3a** showed a characteristic absorption band at 1710 cm^{-1} for the C=O group. The ^1H NMR showed a singlet at 4.45 ppm for 1H at pyrrole C-4 and a singlet at 3.80 for 3H of OMe, 7.30–8.59 (10H, m, 2 Ph).

The nitrones **3** exist in *E* or *Z* isomeric forms. The *E* isomer has two protons (*ortho*) deshielded by the ring carbonyl but owing to the lack of these signals all nitrones are presumably formed in the *Z* configuration only (Fig. 1).

The reactivity of nitrone **3a–c** was examined by allowing it to react with ethyl vinyl ether, which is known to be a good dienophile for α,β-unsaturated carbonyl compounds[7] and a useful dipolarophile with 1,3-dipoles[8] (Scheme 2). The IR spectra of the formed product showed a C=O band but at frequency higher than that of the starting nitrones which is attributed to relief of conjugation. This assumption allows us to exclude the heterodienic product **7** and hence the reaction must be regarded as a 1,3-dipolar cycloaddition.

On the other hand, the ^{13}C NMR spectrum of **6a** shows signal at 55.27 which was assigned to the spiro carbon atom in addition 63.72 for OCH_2 which act as strong evidence for the proposed structure. The ^1H NMR spectra are consistent with the spiroisoxazolidino heterocyclic structures (see Experimental).

The reaction of 1-aryl-2-chloro-5-methoxypyrrol-3-carbaldehyde **4** with alkenylamine **8**a in refluxing ethanol gave the corresponding 2-alkenylamino derivatives **9a–c**, while substitution with allenethiolate, generated by basic decomposition of the allylisothiourea salt, furnished the 2-(allylsulfanyl)pyrrol-3-carbaldehyde **9d–f** as shown in Scheme 3. Treatment of **9a–f** with freshly prepared phenyl hydroxylamine, in refluxing ethanol for 3 h, gave nitrones intermediates **10** which underwent intramolecular cyclization to furnish the fused tricyclic system **11** in a good to excellent yield. None of the isomeric bridged product **12** is produced despite the preference for that regio-chemistry in the intermolecular reaction.[9] The structures of **11** was confirmed beside the elemental analysis by spectroscopic data (see Experimental).

Finally the aldehydes **9a–f** were converted into more reactive nitrile oxides **14**, which were generated in situ by formation of the oxime **13** which were then oxidized with sodium hypochlorite.[10] Nitrile oxide **14** cyclized spontaneously to the dihydroisooxazole **15a–f** in quantitative yield at room temperature. The oximes **13** were prepared and characterized in the customary way (see Experimental).

Conclusion

In summary, we have demonstrated that 1-aryl-5-methoxy-2-pyrrolone **2** are potential candidates for several fused heterocycles systems via intramolecular 1,3-dipolar

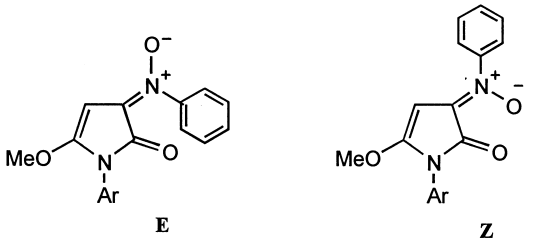
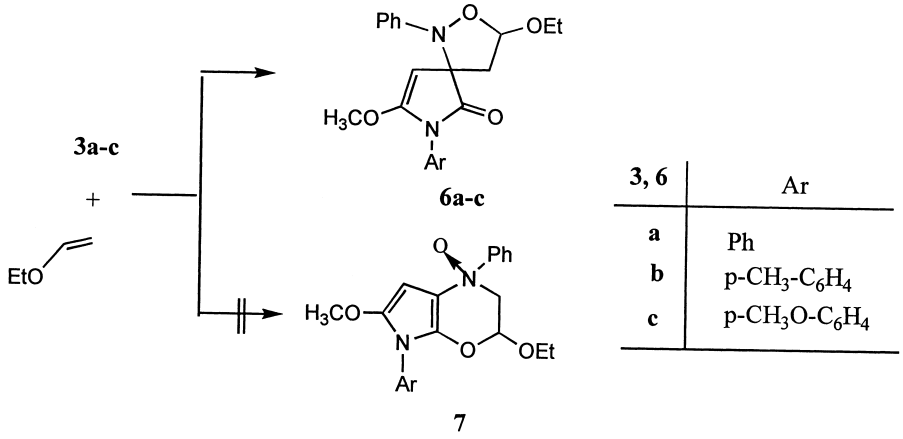
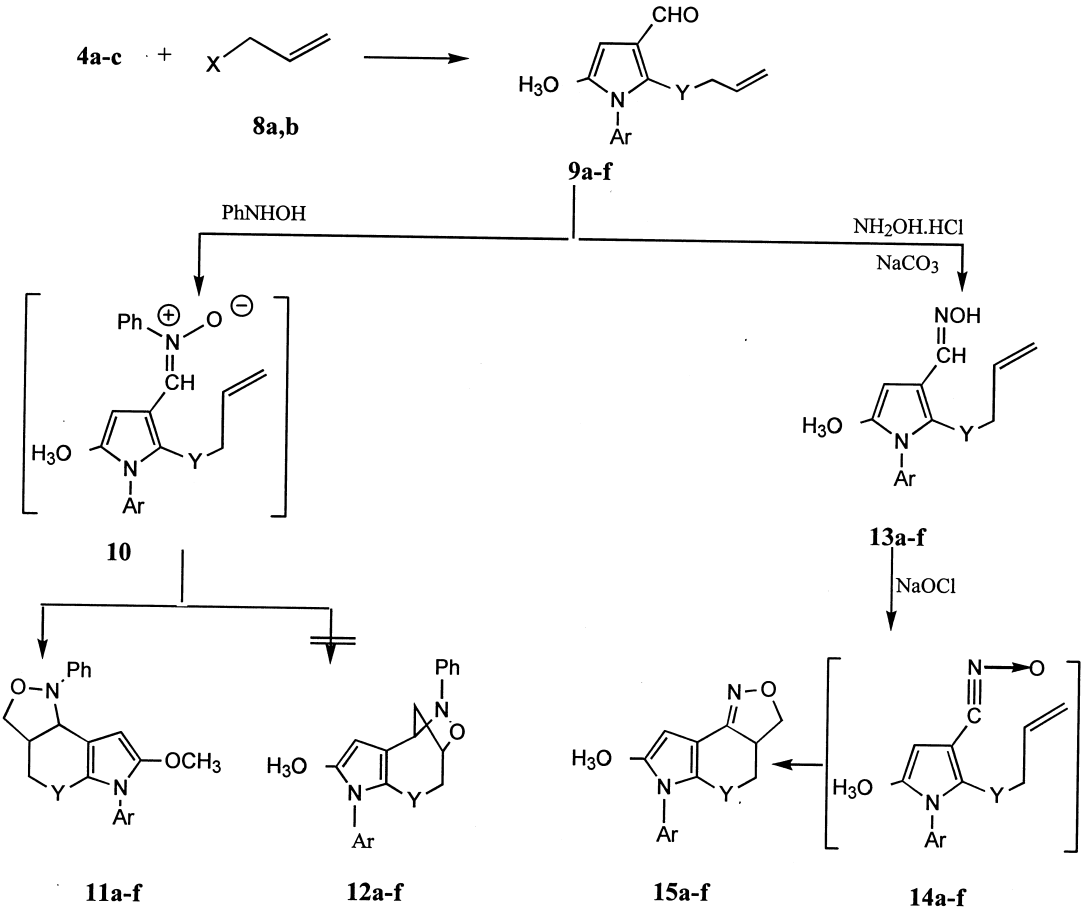


Figure 1.



Scheme 2.



8	X
a	$NHCH_3$
b	SH

9, 11, 12, 13, 15	Y	Ar
a	NCH_3	Ph
b	NCH_3	p-CH_3-C_6H_4
c	NCH_3	p-CH_3O-C_6H_4
d	S	Ph
e	S	p-CH_3-C_6H_4
f	S	p-CH_3O-C_6H_4

Scheme 3.

cycloaddition reactions. Incorporation of the 1,3-dipole unit on the tether can be achieved by two ways: (a) bromination of pyrrolone **2** followed by treatment with nitrosobenzene furnishes heteroaromatic nitrones **3**; (b) chloroformylation of **2** gave 1-aryl-2-chloro-5-methoxypyrrole-3-carbaldehyde **4**. By introducing an unsaturated nucleophile at position **2** and converting the aldehyde function into a 1,3-dipole (nitrone or nitrile oxide), construction of spiro and fused tricyclic systems has been performed in a simple and short way.

Experimental

All melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Infra-red spectra were measured with a Perkin–Elmer Model 298 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer with $CDCl_3$ as solvent and TMS as internal reference, chemical shifts are expressed as δ ppm. Analytical data were performed on C,H,N-Elemental analyzer Carlo Erba 1106. Silica gel 60 (Merck, 230–400 mesh) was used for flash chromatography.

1-Aryl-5-methoxy-2,3-dihydro-1H-2-pyrrolone 2a–c

General procedure: A solution of the corresponding *N*-aryl-acetimidic ester **1** (0.1 mmol) obtained by heating equimolar mixtures of alkyl orthoacetate and primary aromatic amine,[5] and dry triethylamine (2.02 g, 0.2 mmol) in dry Et_2O (50 mL) is maintained at 0°C. A solution of chloroacetyl chloride (1.34 g, 0.12 mmol) in dry Et_2O (10 mL) is added

dropwise during 30 min with vigorous stirring. After 2 h at 0°C, *n*-hexane (50 mL) is added, and stirring continued for 30 min. at room temperature. The precipitate is filtered and washed rapidly with ice water (2×30 mL) to remove the ammonium salt. Recrystallization of the crude colorless product from ethanol afforded **2** in 74–82% yield.

5-Methoxy-1-phenyl-2,3-dihydro-1H-2-pyrrolone (2a) (1.4 g, 74%) as colorless needles, mp 112–114°C; [Found: C, 69.71; H, 5.82; N, 7.32. $C_{11}H_{11}NO_2$ requires C, 69.83; H, 5.86; N, 7.40%]; R_f (toluene/acetone 10: 2) 0.42; ν_{max} (KBr) 1710 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.25–7.78 (5H, m, Ph), 3.80 (3H, s, O*Me*), 3.52 (1H, t, *J*=6.7 Hz, C4-*H*), 3.01 (2H, d, *J*=6.7 Hz, C3-*H*); δ_C (100.6 MHz, $CDCl_3$) 171.82, 152.89, 134.78, 131.27, 127.06, 120.52, 92.62, 54.37, 36.77.

5-Methoxy-1-(4-methyl phenyl)-2,3-dihydro-1H-2-pyrrolone (2b) (1.6 g, 78%) as colorless needles, mp 139–140°C; [Found: C, 70.78; H, 6.32; N, 6.77. $C_{12}H_{13}NO_2$ requires C, 70.92; H, 6.45; N, 6.89%]; R_f (toluene/acetone 10: 2) 0.53; ν_{max} (KBr) 1715 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.15–7.58 (4H, m, Ph), 3.77 (3H, s, O*Me*), 3.50 (1H, t, *J*=6.7 Hz, C4-*H*), 3.15 (2H, d, *J*=6.7 Hz, C3-*H*), 2.28 (3H, s, CH_3); δ_C (100.6 MHz, $CDCl_3$) 170.95, 152.8, 135.85, 132.99, 131.53, 126.92, 92.81, 54.72, 36.75, 21.16.

5-Methoxy-1-(4-methoxy phenyl)-2,3-dihydro-1H-2-pyrrolone (2c) (1.8 g, 82%) as colorless needles, mp 152–153°C; [Found: C, 65.68; H, 5.87; N, 6.32. $C_{12}H_{13}NO_3$ requires C, 65.74; H, 5.98; N, 6.39%]; R_f (toluene/acetone 10: 2) 0.47; ν_{max} (KBr) 1715 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.20–7.65 (4H, m, Ar), 3.77 (3H, s, O*Me*), 3.69 (3H, s, O*Me*), 3.50 (1H, t, *J*=6.7 Hz, C4-*H*), 3.01 (2H, d, *J*=6.7 Hz, C3-*H*).

Arylnitrones 3a–c

General procedure: Saturated solution of 1-aryl-3-bromo-5-methoxypyrrol-2-one (0.05 mmol), was obtained in quantitative yield by brominating of **2** with one mole of bromine in acetic acid (40 mL) at room temperature. The clear solution was poured into water (50 mL) to give a white solid which can be used as or can be crystallized from EtOH, and nitrosobenzene (5.35 g, 0.05 mmol) in EtOH (10 mL) are mixed and stirred at room temperature for 6 h. The product was collected by suction to give 62–73% yield of **3a–c**, which recrystallize from benzene.

[5-Methoxy-2-oxo-1-phenyl-2,3-dihydro-1H-3-pyrrolyldine](phenyl)ammoniumolate 3a (1.82 g, 62%) as colorless needles, mp 168–170°C; [Found: C, 69.11; H, 4.70; N 9.49. $C_{17}H_{14}N_2O_3$ requires C, 69.38; H, 4.79; N, 9.52%]; R_f (toluene/acetone 10: 2) 0.35; ν_{max} (KBr) 1710 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.27–8.61 (10H, m, 2Ph), 4.46 (1H, s, C4-*H*), 3.80 (3H, s, O*Me*); δ_C (100.6 MHz, $CDCl_3$) 165.98, 158.07, 156.94, 147.45, 138.91, 132.08, 129.22, 128.33, 127.29, 121.65, 120.55, 86.18, 54.47.

[5-Methoxy-1-(4-methylphenyl)-2-oxo-2,3-dihydro-1H-3-pyrrolyldine](phenyl)ammoniumolate 3b (2.1 g, 68%) as colorless needles, mp 178°C; [Found: C, 69.97; H, 5.05; N, 8.95. $C_{18}H_{16}N_2O_3$ requires C, 70.12; H, 5.23; N 9.09%]; R_f (toluene/acetone 10: 2) 0.40; ν_{max} (KBr) 1705 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.12–8.60 (9H, m, Ph and Ar), 4.46 (1H, s, C4-*H*), 3.80 (3H, s, O*Me*), 2.28 (3H, s, *Me*); δ_C (100.6 MHz, $CDCl_3$) 166.64, 166.42, 157.21, 147.45, 139.98, 135.20, 131.54, 130.61, 129.22, 127.29, 120.55, 86.42, 54.47, 21.01.

[5-Methoxy-1-(4-methoxyphenyl)-2-oxo-2,3-dihydro-1H-3-pyrrolyldine](phenyl)ammoniumolate 3c (2.36 g, 73%) as colorless needles, mp 158°C; [Found: C, 66.37; H, 4.82; N, 8.45. $C_{18}H_{16}N_2O_4$ requires C, 66.66; H, 4.97; N 8.64%]; R_f (toluene/acetone 10: 2) 0.45; ν_{max} (KBr) 1705 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.79–7.82 (9H, m, Ph and Ar), 4.46 (1H, s, C4-*H*), 3.80 (3H, s, O*Me*), 3.69 (3H, s, O*Me*); δ_C (100.6 MHz, $CDCl_3$) 167.42, 167.24, 157.63, 147.45, 134.01, 131.93, 130.61, 129.22, 127.29, 120.55, 118.89, 87.52, 57.30, 54.47.

1-Aryl-2-chloro-5-methoxy-1H-3-pyrrolcarbaldehyde 4a–c

General method: A similar way for chloroformylation of 3-methyl-1-phenyl-pyrazol-5-one[7] was used.

2-Chloro-5-methoxy-1-phenyl-1H-3-pyrrolcarbaldehyde 4a (1.34 g, 57%) as colorless needles, mp 163°C; [Found: C, 60.97; H, 4.06; Cl, 14.79; N, 5.89. $C_{12}H_{10}ClNO_2$ requires C, 61.16; H, 4.28; Cl, 15.04; N, 5.94%]; R_f (toluene/acetone 10: 2) 0.37; ν_{max} (KBr) 1675 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 10.24 (1H, s, C*H*O), 6.28–7.24 (5H, m, Ph), 6.26 (1H, s, C4-*H*), 3.90 (3H, s, O*Me*); δ_C (100.6 MHz, $CDCl_3$) 183.92, 158.37, 136.24, 134.13, 130.63, 127.67, 120.61, 111.90, 92.43, 56.80.

2-Chloro-5-methoxy-1-(4-methylphenyl)-1H-3-pyrrolcarbaldehyde 4b (1.62 g, 65%) as colorless needles, mp 178°C; [Found: C, 62.50; H, 4.82; Cl, 13.95; N, 5.44. $C_{13}H_{12}ClNO_2$ requires C, 62.53; H, 4.84; Cl, 14.20; N 5.61%]; R_f (toluene/acetone 10: 2) 0.39; ν_{max} (KBr) 1670 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 10.32 (1H, s, C*H*O), 6.67–7.28 (4H, m, Ar), 6.30 (1H, s, C4-*H*), 3.80 (3H, s, O*Me*), 2.38 (3H, s, *Me*); δ_C (100.6 MHz, $CDCl_3$) 184.32, 158.82, 140.65, 136.74, 135.21, 132.38, 120.26, 112.21, 93.03, 56.18, 21.01.

2-Chloro-5-methoxy-1-(4-methoxyphenyl)-1H-3-pyrrolcarbaldehyde 4c (1.83 g, 69%) as colorless needles, mp 211°C; [Found: C, 58.69; H, 4.52; Cl, 13.10; N, 5.22. $C_{13}H_{12}ClNO_3$ requires C, 58.77; H, 4.55; Cl, 13.34; N, 5.27%]; R_f (toluene/acetone 10: 2) 0.44; ν_{max} (KBr) 1670 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 10.08 (1H, s, C*H*O), 6.71–7.78 (4H, m, Ar), 6.35 (1H, s, C4-*H*), 3.80 (3H, s, O*Me*), 3.77 (3H, s, O*Me*); δ_C (100.6 MHz, $CDCl_3$) 183.72, 159.08, 145.71, 137.01, 134.82, 129.23, 122.94, 112.87, 92.70, 57.90, 55.78.

Spiroisoxazolidino-heterocyles 6a–c

General method: A mixture of nitrones **3a–c** (1 mmol) and ethylvinyl ether (7.2 g, 0.1 mol) was allowed to react at room temperature until the T.L.C. showed the disappearance of the starting nitrone (about 48 h). The excess of vinylether was evaporated, the residue was simply crystallized from the EtOH and the spiroisoxazolidino-heterocyles **6a–c** were obtained in nearly quantitative yield, which recrystallized from EtOH.

3-Ethoxy-8-methoxy-1,7-diphenyl-2-oxa-1,7-diazaspiro-[4.4]non-8-en-6-one 6a (2.38 g, 65%) as colorless prisms, mp 167°C; [Found: C, 68.95; H, 6.25; N, 7.73. $C_{21}H_{22}N_2O_4$ requires C, 68.84; H, 6.05; N, 7.65%]; R_f (toluene/acetone 10: 2) 0.67; ν_{max} (KBr) 3100, 2890, 1725 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.29–7.84 (10H, m, 2 Ph), 5.69 (1H, dd, *J*=3, 6 Hz, C3-*H*), 3.77 (3H, s, O*Me*), 3.68 (1H, s, C9-*H*), 3.52 (2H, q, *J*=7 Hz, ester CH_2), 2.79–2.94 (2H, dd, *J*=3, 6 Hz, CH_2), 1.10 (3H, t, *J*=7 Hz, *Me*); δ_C (100.6 MHz, $CDCl_3$) 171.95, 151.63, 144.82, 134.92, 130.54, 129.67, 127.29, 126.74, 121.29, 120.52, 101.51, 89.59, 63.72, 55.27, 54.77, 41.21, 14.73.

3-Ethoxy-8-methoxy-7-(methylphenyl)-1-phenyl-2-oxa-1,7-diazaspiro[4.4]non-8-en-6-one 6b (2.46 g, 70%) as colorless prisms, mp 152°C; [Found: C, 69.21; H, 6.24; N, 7.28. $C_{22}H_{24}N_2O_4$ requires C, 69.46; H, 6.36; N, 7.36%]; R_f (toluene/acetone 10: 2) 0.70; ν_{max} (KBr) 3100, 2890, 1720 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.21–7.89 (9H, m, Ph and Ar), 5.73 (1H, dd, J=3, 6 Hz, C3-*H*), 3.79 (s, 3H, O*Me*), 3.72 (1H, s, C9-*H*), 3.52 (2H, q, *J*=7 Hz, ester CH_2), 2.80–2.94 (2H, dd, *J*=3, 6 Hz,CH_2), 2.20 (3H, s, *Me*), 1.15 (3H, t, *J*=7 Hz, *Me*); δ_C (100.6 MHz, $CDCl_3$) 172.75, 151.23, 145.82, 135.72, 130.22, 129.16, 127.29, 126.97, 121.59, 120.45, 96.89, 91.34, 63.52, 56.07, 54.97, 39.57, 21.65, 14.73.

3-Ethoxy-8-methoxy-7-(methoxyphenyl)-1-phenyl-2-oxa-1,7-diazaspiro[4.4]non-8-en-6-one 6c (2.97 g, 75%) as colorless prisms, mp 183°C; [Found: C, 66.48; H, 6.10; N, 7.13. $C_{22}H_{24}N_2O_5$ requires C, 66.65; H, 6.10; N, 7.07%]; R_f (toluene/acetone 10: 2) 0.72; ν_{max} (KBr) 3100, 2900, 1720 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.79–7.35 (9H, m, Ph and Ar), 5.68 (1H, dd, *J*=3, 6 Hz, C3-*H*), 3.75 (3H, s, OCH_3), 3.70 (1H, s, C9-*H*), 3.69 (3H, s, O*Me*), 3.52 (2H, q, *J*=7 Hz, ester CH_2), 2.82–2.90 (2H, dd, *J*=3, 6 Hz, CH_2), 1.25 (3H, t, *J*=7 Hz, *Me*); δ_C (100.6 MHz, $CDCl_3$) 173.59, 152.03, 147.62, 136.44, 131.24, 129.86, 128.12, 126.07, 122.32, 121.11, 96.05, 90.07, 63.45, 57.30, 55.25, 54.62, 40.15, 14.33.

General method for 9a–c

A mixture of chloroaldehyde **4** (13 mmol) and diallylamine **8a** (2.49 g, 35 mmol) in ethanol (40 mL) was refluxed for 12 h. The ethanol was removed in vacuo and the residue was poured into water, then extracted with chloroform (25 mL×3). The organic layer was dried and the chloroform was evaporated off. The residue was purified by flash chromatography (*n*-hexane:chloroform 5:1) to give **9a–c** in 70–83% yield.

2-[Allyl(methyl)amino]-5-methoxy-1-phenyl-1H-3-pyrrolecarbaldehyde 9a (1.89 g, 70%) as light yellow needles, mp 142°C; [Found: C, 70.88; H, 6.51; N, 10.18. $C_{16}H_{18}N_2O_2$ requires C, 71.09; H, 6.71; N, 10.36%]; R_f (toluene/acetone 10: 2) 0.71; ν_{max} (KBr) 1670 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.88 (s, 1H, C*H*O), 6.58–7.37 (5H, m, Ph), 5.82 (1H, m, C*H*=CH_2), 5.24 (1H, s, C4-*H*), 5.14, 4.85 (2H, dd, *J*=18, 5 Hz, CH=CH_2), 4.26 (2H, d, *J*=6.6 Hz, CH_2), 3.93 (3H, s, O*Me*), 3.02 (3H, s, N*Me*); δ_C (100.6 MHz, $CDCl_3$) 184.92, 149.99, 145.14, 134.86, 131.34, 129.91, 126.67, 133.22, 118.49, 103.26, 90.12, 56.98, 55.46, 39.14.

2-[Allyl(methyl)amino]-5-methoxy-1-(4-methylphenyl)-1H-3-pyrrolecarbaldehyde 9b (2.13 g, 75%) as light yellow needles, mp 167°C; [Found: C, 71.64; H, 6.91; N, 9.65. $C_{17}H_{20}N_2O_2$ requires C, 71.81; H, 7.09; N, 9.85%]; R_f (toluene/acetone 10: 2) 0.75; ν_{max} (KBr) 1665 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.88 (1H, s, C*H*O), 6.68–7.21 (4H, m, Ar), 5.82 (1H, m, C*H*=CH_2), 5.35 (1H, s, C4-*H*), 5.09, 4.95 (2H, dd, *J*=17, 5 Hz, CH=CH_2), 4.35 (2H, d, *J*=6.6 Hz, CH_2), 3.87 (3H, s, O*Me*), 3.02 (3H, s, N*Me*), 2.35 (3H, s, *Me*).

2-[Allyl(methyl)amino]-5-methoxy-1-(4-methoxyphenyl)-1H-3-pyrrolecarbaldehyde 9c (2.49 g, 83%) as light yellow needles, mp 189°C; [Found: C, 67.79; H, 6.55; N, 9.12. $C_{17}H_{20}N_2O_3$ requires C, 67.98; H, 6.71; N, 9.33%]; R_f (toluene/acetone 10: 2) 0.77; ν_{max} (KBr) 1665 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.78 (1H, s, C*H*O), 6.74–7.32 (4H, m, Ar), 5.90 (1H, m, C*H*=CH_2), 5.25 (1H, s, C4-*H*), 5.15, 5.04 (2H, dd, *J*=16, 5 Hz, CH=CH_2), 4.25 (2H, d, *J*=7 Hz, CH_2), 3.85 (3H, s, O*Me*), 3.72 (3H, s, O*Me*), 3.12 (3H, s, N*Me*).

General method for 9d–f

A solution of allyl bromide (6.0 g, 0.05 mol) and thiourea (3.81 g, 0.05 mol) in ethanol (60 mL) was refluxed for 1 h then a solution of ethanolic NaOH (4 g in 100 mL) was added and reflux was continued for a further 1 h. The chloroaldehyde **4** (34 mmol) was added to the mixture which was then refluxed for 30 min. After addition of water (75 mL) to the mixture it was extracted with diethylether (3×70 mL), dried ($MgSO_4$) and evaporated to give **9d–f** in 60–74% yield which was crystallized from ethanol.

2-(Allylsulfanyl)-5-methoxy-1-phenyl-1H-3-pyrrolecarbaldehyde 9d (1.63 g, 60%) as light yellow needles, mp 89°C; [Found: C, 65.78; H, 5.43; N, 4.98; S, 11.89. $C_{15}H_{15}NO_2S$ requires C, 65.91; H, 5.53; N, 5.12; S, 11.73%]; R_f (toluene/acetone 10: 2) 0.70; ν_{max} (KBr) 1670 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 10.08 (1H, s, C*H*O), 7.38–7.57 (5H, m, Ph), 5.75 (1H, m, C*H*=CH_2), 5.60 (1H, s, C4-*H*), 4.95, 4.85 (2H, dd, *J*=16, 4, CH=CH_2), 3.80 (3H, s, O*Me*), 3.48 (2H, d, *J*=7 Hz, CH_2S); δ_C (100.6 MHz, $CDCl_3$) 185.20, 158.32, 157.22, 135.65, 129.81, 129.61, 126.81, 121.39, 120.87, 112.87, 89.72, 56.66, 33.98.

2-(Allylsulfanyl)-5-methoxy-1-(4-methylphenyl)-1H-3-pyrrolecarbaldehyde 9e (1.86 g, 65%) as light yellow needles, mp 113°C; [Found: C, 66.92; H, 6.03; N, 4.99; S, 11.23. $C_{16}H_{17}NO_2S$ requires C, 66.87; H, 5.96; N, 4.87; S 11.16%]; R_f (toluene/acetone 10: 2) 0.74; ν_{max} (KBr) 1665 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.91 (1H, s, C*H*O), 7.01–7.35 (4H, m, Ar), 5.80 (1H, m, C*H*=CH_2), 5.65 (1H, s, C4-H), 4.80, 4.60 (2H, dd, *J*=17, 6 Hz, CH=CH_2), 3.85 (3H, s, O*Me*), 3.25 (2H, d, *J*=7 Hz, CH_2S), 2.38 (3H, s, *Me*).

2-(Allylsulfanyl)-5-methoxy-1-(4-methoxyphenyl)-1H-3-pyrrolecarbaldehyde 9f (2.25g, 74%) as light yellow needles, mp 132°C; [Found: C, 63.12; H, 5.44; N, 4.43; S, 10.33. $C_{16}H_{17}NO_3S$ requires C, 63.35; H, 5.65; N, 4.62; S, 10.57%]; R_f (toluene/acetone 10: 2) 0.80; ν_{max} (KBr)

1675 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.94 (1H, s, C*H*O), 7.21–7.45 (4H, m, Ar), 5.65 (1H, s, C4-H), 5.55 (1H, m, C*H*=CH_2), 5.05, 4.75 (2H, dd, *J*=17, 5 Hz, CH=CH_2), 3.90 (3H, s, O*Me*), 3.18 (2H, d, *J*=7 Hz, CH_2S), 3.65 (3H, s, O*Me*).

1-Aryl-7-methoxy-6-phenyl-3,3a,4,5,6,8b-hexahydro-1H-isoxazolo[3,4-d]pyrolo[2,3-b]pyridine 11a–f

General method: To a stirred solution of aldehyde **9** (1 mmol) in absolute EtOH (15 mL) is added dropwise a solution of phenylhydroxylamine freshly prepared (109 mg 1 mmol). The mixture is then refluxed gently for 3 h. The solid was filtered off, washed with EtOH and dried to give **11a–f** in 60–80% yield.

7-Methoxy-5-methyl-1,6-diphenyl-3,3a,4,5,6,8b-hexahydro-1H-isoxazolo[3,4-d]pyrolo[2,3-b]pyridine 11a (2.86 g, 79%) as pale yellow prisms, mp 214–215°C; [Found: C, 73.28; H, 6.62; N, 11.89. $C_{22}H_{23}N_3O_2$ requires C, 73.11; H, 6.41; N, 11.63%]; R_f (toluene/acetone 10: 2) 0.45; ν_{max} (KBr) 3050, 2980 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.84–7.75 (10H, m, 2Ph), 4.18 (1H, d, *J*=5 Hz, C9-*H*), 3.93 (1H, dd, *J*=16, 7 Hz, C3-*H*), 3.88 (1H, s, C8-*H*), 3.83 (1H, dd, *J*=16, 7 Hz, C3-*H*), 3.80 (3H, s, O*Me*), 3.67 (1H, dd, *J*=12, 6 Hz, C4-*H*), 3.60 (1H, dd, *J*=12, 6 Hz, C4-*H*), 3.29 (3H, s, N*Me*), 2.75 (1H, m, C3a-*H*).

7-Methoxy-5-methyl-6-(4-methylphenyl)-1-phenyl-3,3a,4,5,6,8b-hexahydro-1H-isoxazolo[3,4-d]pyrolo-[2,3-b]pyridine 11b (3 g, 80%) as pale yellow prisms, mp 225–226°C; [Found: C, 73.78, H, 6.81; N, 11.39. $C_{23}H_{25}N_3O_2$ requires C, 73.58; H, 6.71; N, 11.19%]; R_f (toluene/acetone 10: 2) 0.47; ν_{max} (KBr) 3050, 2980 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.95–7.82 (9H, m, Ph and Ar), 4.32 (1H, d, *J*=5 Hz, C9-*H*), 4.23 (1H, s, C8-*H*), 3.97 (1H, dd, *J*=16, 7 Hz, C3-*H*), 3.83 (3H, s, O*Me*), 3.78 (1H, dd, *J*=12, 6 Hz, C4-*H*), 3.76 (1H, dd, *J*=16, 7 Hz, C3-*H*), 3.71 (1H, dd, *J*=12, 6 Hz, C4-*H*), 3.35 (3H, s, N*Me*), 2.75 (1H, m, C3a-*H*), 2.32 (3H, s, *Me*).

7-Methoxy-6-(4-methoxyphenyl)-5-methyl-1-phenyl-3,3a,4,5,6,8b-hexahydro-1H-isoxazolo[3,4-d]pyrolo-[2,3-b]-pyridine 11c (3.12 g, 80%) as pale yellow prisms, mp 205–206°C; [Found: C, 70.51; H, 6.40; N, 10.70. $C_{23}H_{25}N_3O_3$ requires C, 70.57; H, 6.44; N, 10.73%]; R_f (toluene/acetone 10: 2) 0.43; ν_{max} (KBr) 3050, 2980 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.85–7.75 (9H, m, Ph and Ar), 4.41 (1H, d, *J*=5 Hz, C9-H), 4.29 (1H, s, C8-*H*), 3.91 (1H, dd, *J*=16, 7 Hz, C3-*H*), 3.86 (3H, s, O*Me*), 3.80 (1H, dd, *J*=16, 7 Hz, C3-*H*), 3.75 (3H, s, O*Me*), 3.69 (1H, dd, *J*=12, 6 Hz, C4-*H*), 3.67 (1H, dd, *J*=12, 6 Hz, C4-*H*), 3.47 (3H, s, N*Me*), 2.62 (1H, m, C3a-*H*).

7-Methoxy-1,6-diphenyl-3a,4,6,8b-tetrahydro-1H,3H-pyrrolo[3′,2′:5,6]thiopyrano[4,3-c]isoxazole 11d (2.2 g, 60%) as pale yellow prisms, mp 182–184°C; [Found: C, 68.95; H, 5.45; N, 7.55; S, 8.69. $C_{21}H_{20}N_2O_2S$ requires C, 69.21; H, 5.53; N, 7.69; S, 8.80%]; R_f (toluene/acetone 10: 2) 0.38; ν_{max} (KBr) 3040, 2980 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.57–7.55 (10H, m, 2Ph), 4.65 (1H, d, *J*=6 Hz, C9-*H*), 4.56 (1H, s, C8-*H*), 4.0 (2H, dd, *J*=13, 7.5 Hz, C3-*H*), 3.85 (3H, s, OMe), 3.30 (2H, m, CH_2S), 2.50 (1H, m, C3a-*H*); δ_C (100.6 MHz, $CDCl_3$) 158.30, 149.61, 146.32, 139.01, 129.52, 129.23, 127.43, 126.82, 132.90, 122.11, 120.55, 108.28, 71.31, 61.76, 55.98, 40.00, 29.71.

7-Methoxy-6-(4-methylphenyl)-1-phenyl-3a,4,6,8b-tetrahydro-1H,3H-pyrrolo[3′,2′:5,6]thiopyrano[4,3-c]isoxazole 11e (2.46 g, 65%) as pale yellow prisms, mp 168–169°C; [Found: C, 69.66; H, 5.76; N, 7.32; S, 8.31. $C_{22}H_{22}N_2O_2S$ requires C, 69.82; H, 5.86; N, 7.40; S, 8.45%]; R_f (toluene/acetone 10: 2) 0.41; ν_{max} (KBr) 3040, 2980 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.75–7.55 (9H, m, Ph and Ar) 4.69 (1H, d, *J*=6 Hz, C9-*H*), 4.50 (1H, s, C8-*H*), 4.12 (2H, dd, *J*=13, 8 Hz, C3-*H*), 3.90 (3H, s, OMe), 3.24–3.30 (2H, m, CH_2S), 2.45 (1H, m, C3a-*H*), 2.38 (3H, s, *Me*).

7-Methoxy-6-(4-methoxyphenyl)-1-phenyl-3a,4,6,8b-tetrahydro-1H,3H-pyrrolo[3′,2′:5,6]thiopyrano[4,3-c]isoxazole 11f (2.64 g, 67%) as pale yellow prisms, mp222–223°C; [Found: C, 66.80; H, 5.52; N, 7.12; S, 8.01. $C_{22}H_{22}N_2O_3S$ requires C, 66.98; H, 5.62; N, 7.10; S, 8.13%]; R_f (toluene/acetone 10: 2) 0.40; ν_{max} (KBr) 3040, 2980 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.76–7.50 (9H, m, Ph and Ar), 4.68 (1H, d, *J*=6 Hz, C9-*H*), 4.50 (1H, s, C8-*H*), 4.17 (2H, dd, *J*=13, 8 Hz, C3-*H*), 3.88 (3H, s, O*Me*), 3.20–3.28 (2H, m, CH_2S), 2.53 (1H, m, C3a-*H*), 3.77 (3H, s, O*Me*).

1-Aryl-2-[allyl(methyl)amine]-5-methoxy-1H-3-pyrrolecarbaldehydeoxime 13a–f

General Method: A solution of the aldehyde **9** (4 mmol) in ethanol (20 mL) was treated with aqueous $NH_2OH.HCl$ and $NaHCO_3$ (8 mmol each in 10 mL) and stirred overnight at room temperature. The mixture was extracted with dichloromethane (3×25 mL) and the combined extracts were washed with water (3×25 mL), dried ($MgSO_4$) and evaporated, the residue was crystallized from ethanol to give 65–70% yield from oxime **13a–f**.

2-[Allyl(methyl)amine]-5-methoxy-1-Phenyl-1H-3-pyrrolecarbaldehydeoxime 13a (1.97 g, 69%) as colorless needles, mp 125°C; [Found: C, 67.11; H, 6.52, N, 14.59. $C_{16}H_{19}N_3O_2$ requires C, 67.35; H, 6.71; N, 14.73%]; R_f (toluene/acetone 10: 2) 0.75; ν_{max} (KBr) 3400–3200, 1640 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 10.76 (1H, bs, O*H*), 7.23–7.30 (5H, m, Ph), 7.47 (1H, s, C*H*=N), 5.94 (1H, m, C*H*=CH_2), 5.02, 5.12 (2H, dd, *J*=10, 5 Hz, CH=CH_2), 4.93 (1H, s, C4-*H*), 3.90 (2H, d, *J*=7 Hz, CH_2), 3.90 (3H, s, O*Me*), 3.04 (3H, s, N*Me*), δ_C (100.6 MHz, $CDCl_3$) 149.95, 146.55, 145.58, 135.83, 133.02, 130.52, 128.55, 126.67, 118.79, 113.67, 89.92, 59.10, 53.30, 40.85.

2-[Allyl(methyl)amine]-5-methoxy-1-(4-methylphenyl)-1H-3-pyrrolecarbaldehydeoxime 13b (2.16 g, 72%) as colorless needles, mp 167°C; [Found: C, 67.93; H, 6.96; N, 13.89. $C_{17}H_{21}N_3O_2$ requires C, 68.21; H, 7.07; N, 14.04%]; R_f (toluene/acetone 10: 2) 0.77; ν_{max} (KBr) 3400–3200, 1635 cm^{-1}.

2-[Allyl(methyl)amine]-5-methoxy-1-(4-methoxyphenyl)-1H-3-pyrrolecarbaldehydeoxime 13c (2.06 g, 65%) as colorless needles, mp 181°C; [Found: C, 64.53; H, 6.63; N, 13.18. $C_{17}H_{21}N_3O_3$ requires C, 64.74; H, 6.71; N, 13.32%]; R_f (toluene/acetone 10: 2) 0.80; ν_{max} (KBr) 3400–3200, 1635 cm^{-1}.

2-(Allylsulfanyl)-5-methoxy-1-phenyl-1H-3-pyrrolecarbaldehydeoxime 13d (1.7 g, 59%) as colorless needles, mp 142°C; [Found: C, 62.53; H, 5.60; N, 9.80; S, 10.89. $C_{15}H_{16}N_2O_2S$ requires C, 62.48; H, 5.59; N, 9.71; S, 11.12%]; R_f (toluene/acetone 10: 2) 0.68; ν_{max} (KBr) 3400–3200, 1640 cm^{-1}.

2-(Allylsulfanyl)-5-methoxy-1-(4-methylphenyl)-1H-3-pyrrolecarbaldehydeoxime 13e (1.79g, 59%) as colorless needles, mp 165°C; [Found: C, 63.42; H, 5.92; N, 9.03; S, 10.47. $C_{16}H_{18}N_2O_2S$ requires C, 63.55; H, 6.00; N, 9.26; S, 10.60%]; R_f (toluene/acetone 10: 2) 0.70; ν_{max} (KBr) 3400–3200, 1640 cm^{-1}.

2-(Allylsulfanyl)-5-methoxy-1-(4-methoxyphenyl)-1H-3-pyrrolecarbaldehydeoxime 13f (2.17g, 68%) as colorless needles, mp 133°C; [Found: C, 60.21; H, 5.43; N, 8.89; S, 9.89. $C_{16}H_{18}N_2O_3S$ requires C, 60.36; H, 5.70; N, 8.80; S, 10.07%]; R_f (toluene/acetone 10: 2) 0.73; ν_{max} (KBr) 3400–3200, 1640 cm^{-1}.

Aqueous NaOCl (13%, 4 mol) was added dropwise at 0°C to a vigorously stirred solution of the oxime **13** (2.75 mmol) in chloroform (30 mL). After the mixture had been stirred overnight at room temperature the organic phase was separated, dried ($MgSO_4$), and evaporated, the crude product **15a–f** in nearly quantitative yield which then was crystallized from cyclohexane/chloroform (3:1).

7-Methoxy-5-methyl-6-phenyl-3a,4,5,6-tetrahydro-3H-isoxazolo[3,4-d]pyrrolo[2,3-b]pyridine 15a (2.64 g, 93%) as colorless prisms, mp 155°C; [Found: C, 67.63; H, 5.89; N, 14.68. $C_{16}H_{17}N_3O_2$ requires C, 67.83; H, 6.05; N, 14.83%]; R_f (toluene/acetone 10: 2) 0.47; ν_{max} (KBr) 1610 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.28–7.75 (5H, m, Ph), 4.95 (1H, s, C8-*H*), 4.68 (2H, dd, *J*=14, 8 Hz, C3-*H*), 3.95 (3H, s, O*Me*), 3.65 (1H, m, C3a-*H*), 3.30 (3H, s, N*Me*), 3.27 (2H, dd, *J*=8, 3 Hz, C4 -*H*), δ_C (100.6 MHz, $CDCl_3$) 152.08, 150.47, 146.10, 140.55, 137.74, 129.10, 126.52, 120.61, 104.27, 72.73, 55.98, 53.42, 43.89, 38.45.

7-Methoxy-5-methyl-6-(4-methylphenyl)-3a,4,5,6-tetrahydro-3H-isoxazolo[3,4-d]pyrrolo[2,3-b]pyridine 15b (2.74 g, 92%) as colorless prisms, mp 179°C; [Found: C, 68.52, H, 6.29; N, 14.00. $C_{17}H_{19}N_3O_2$ requires C, 68.67; H, 6.44; N, 14.13%]; R_f (toluene/acetone 10: 2) 0.50; ν_{max} (KBr) 1610 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.42–7.75 (4H, m, Ar), 4.90 (1H, s, C8-*H*), 4.68 (2H, dd, *J*=14, 7 Hz, C3-H), 3.90 (3H, s, O*Me*), 3.69 (1H, m, C3a-*H*), 3.30 (3H, s, N*Me*), 3.27 (2H, dd, *J*=8, 3 Hz, C4-*H*), 2.38 (3H, s, *Me*).

7-Methoxy-6-(4-methoxyphenyl)-5-methyl-3a,4,5,6-tetrahydro-3H-isoxazolo[3,4-d]pyrrolo[2,3-b]pyridine 15c (2.98 g, 95%) as colorless prisms, mp 203°C; [Found: C, 64.89; H, 5.95; N, 13.20. $C_{17}H_{19}N_3O_3$ requires C, 65.16; H, 6.11; N, 13.41%]; R_f (toluene/acetone 10: 2) 0.43; ν_{max} (KBr) 1610 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.40–7.70 (4H, m, Ar), 4.90 (1H, s, C8-*H*), 4.65 (2H, dd, *J*=14, 8 Hz, C3-*H*), 3.90 (3H, s, O*Me*), 3.75 (3H, s, O*Me*), 3.69 (1H, m, C3a-*H*), 3.32 (3H, s, N*Me*), 3.27 (2H, dd, *J*=8, 4 Hz, C4-*H*).

7-Methoxy-6-phenyl-3a,4-dihydro-3H,6H-pyrrolo[3′,2′:5,6]-thiopyrano[4,3-c]isoxazole 15d (2.69 g, 94%) as colorless prisms, mp 212°C; [Found: C, 62.73; H, 4.79; N, 9.80; S, 10.95. $C_{15}H_{14}N_2O_2S$ requires C, 62.92; H, 4.93; N, 9.78; S, 11.20%]; R_f (toluene/acetone 10: 2) 0.37; ν_{max} (KBr) 1610 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.64–7.42 (5H, m, Ph), 5.48 (1H, s, C8-*H*), 4.83 (1H, d, *J*=4 Hz, C3-*H*), 4.75 (1H, d, *J*=9 Hz, C3-*H*), 4.03 (1H, m, C3a-*H*), 3.95 (3H, s, O*Me*), 3.61 (1H, d, *J*=14 Hz, C4-*H*), 3.45 (1H, d, *J*=6 Hz, C4-*H*); δ_C (100.6 MHz, $CDCl_3$) 152.40, 151.48, 151.40, 145.76, 137.70, 129.10, 128.92, 125.87, 121.43, 66.52, 56.30, 47.81, 24.65.

7-Methoxy-6-(4-methylphenyl)-3a,4-dihydro-3H,6H-pyrrolo[3′,2′:5,6]thiopyrano[4,3-c]isoxazole 15e (2.85 g, 95%) as colorless prisms, mp 185°C; [Found: C, 63.86; H, 5.22; N, 9.28; S, 10.52. $C_{16}H_{16}N_2O_2S$ requires C, 63.98; H, 5.37; N, 9.33; S, 10.67%]; R_f (toluene/acetone 10: 2) 0.43; ν_{max} (KBr) 1615 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.10–7.40 (4H, m, Ar), 5.50 (1H, s, C8-*H*), 4.85 (1H, d, *J*=4 Hz, C3-*H*), 4.70 (1H, d, *J*=9 Hz, C3-*H*), 4.13 (1H, m, C3a-*H*), 3.90 (3H, s, O*Me*), 3.55 (1H, d, *J*=14 Hz, C4-*H*), 3.40 (1H, d, *J*=6 Hz, C4-*H*), 2.38 (3H, s, *Me*); δ_C (100.6 MHz, $CDCl_3$) 153.45, 152.32, 150.30, 147.60, 136.18, 135.47, 131.16, 129.42, 121.50, 66.30, 55.90, 47.75, 24.65, 21.01.

7-Methoxy-6-(4-methoxyphenyl)-3a,4-dihydro-3H,6H-pyrrolo[3′,2′:5,6]thiopyrano[4,3-c]isoxazole 15f (3.04 g, 96%) as colorless prisms, mp 258°C; [Found: C, 60.54; H, 4.96; N, 8.80; S, 9.85. $C_{16}H_{16}N_2O_3S$ requires C, 60.74; H, 5.10; N, 8.85; S, 10.13%]; R_f (toluene/acetone 10: 2) 0.47; ν_{max} (KBr) 1615 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.88–7.22 (4H, m, Ar), 5.55 (1H, s, C8-*H*), 4.85 (1H, d, *J*=4 Hz, C3-*H*), 4.70 (1H, d, *J*=9 Hz, C3-*H*), 4.15 (1H, m, C3a-*H*), 3.95 (3H, s, O*Me*), 3.80 (3H, s, O*Me*), 3.68 (1H, d, *J*=14 Hz, C4-H), 3.50 (1H, d, *J*=6 Hz, C4-H); δ_C (100.6 MHz, $CDCl_3$) 153.09, 152.67, 151.88, 147.64, 139.56, 130.88, 126.87, 126.72, 123.32, 68.82, 55.85, 48.25, 25.20.

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