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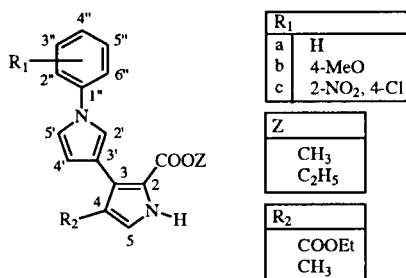
A series of methyl or ethyl 3-(*N*-arylpyrrol-3-yl)-1*H*-pyrrole-2-carboxylates and 2,4-dicarboxylates have been synthesized using an alkyl isocyanides addition-cyclization with *N*-arylpyrrole derivatives such as the carboxaldehydes and nitropropenes.

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The reactive chemical properties of alkyl isocyanides are common knowledge and one can take advantage of this reactivity to synthesize various heterocycles such as oxazoles, pyrroles, imidazoles, *etc.* [1].

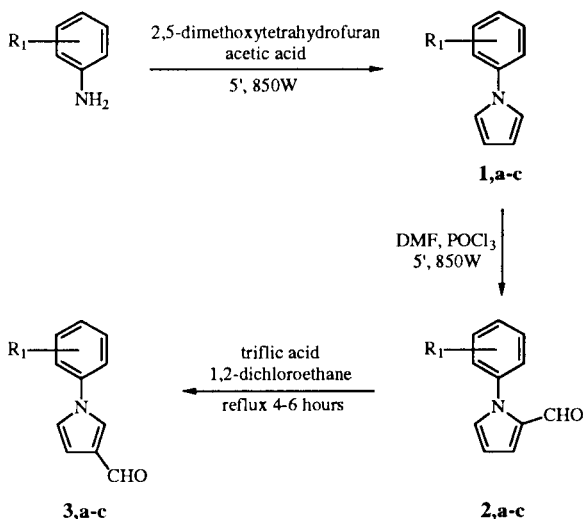
We have described the results of these reagents with several 1-arylpyrroles derivatives in the 2 position of the pyrrole nucleus, especially carboxaldehydes and nitropropene. These allow the synthesis of alkyl 3-(1-arylpyrrol-2-yl)-1*H*-pyrrole-

Scheme 1



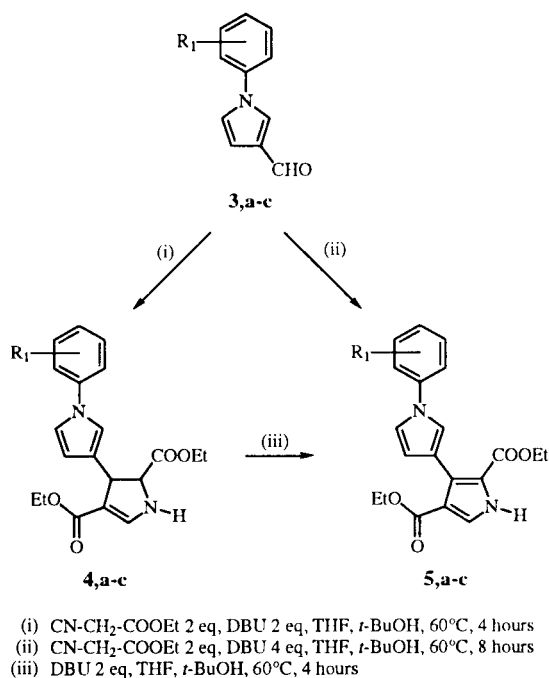
2,4-dicarboxylates and -2-carboxylates [2]. However, we still have to study the reaction of alkyl isocyanides with 1-arylpyrrole derivatives in the 3 position, which allow the synthesis of methyl or ethyl 3-(1-phenylpyrrol-3-yl)-1*H*-pyrrole-2,4-dicarboxylates and -2-carboxylates.

Scheme 2

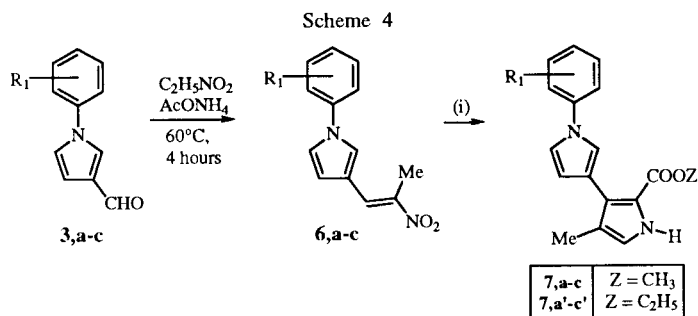


The requisite 1-phenylpyrroles **1a-c** were synthesized from the corresponding anilines *via* the Clauson-Kaas procedure [3], followed by Vilsmeier-Haack formylation to provide the formylated products **2a-c** [4]. The separation of the 3-formylated isomers cannot be achieved in good yields, however we have previously described a convenient acid-mediated rearrangement of 1-phenylpyrrole-2-carboxaldehydes into their 3-isomers [5]. The 1-phenylpyrrole-3-carboxaldehydes **3a-c** were selectively synthesized in high yield by treatment with trifluoromethanesulfonic acid (triflic acid) from **2a-c**. The 1-phenylpyrrole-3-carboxaldehydes **3a-c** reacts with ethyl isocyanide in solution in tetrahydrofuran, in the presence of *tert*-butyl alcohol. With two equivalents of alkyl isocyanide, two equivalents of DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) and a four-hour heating period, the corresponding pyrroline-2,4-dicarboxylates **4a-c** were isolated. If excess base (4 equivalents) was used during an eight-hour heating period, a proton-extracting step occurred and provided the pyrroles-2,4-dicarboxylates **5a-c** [6].

Scheme 3



The arylpyrrolylpyrroles bearing a single ester moiety, **7a-c** were not synthesized directly from **3a-c** but from their corresponding β -nitrostyrene derivatives **6a-c**. These were easily obtained by reaction of nitromethane with **3a-c** in the presence of aqueous alkali, by the Henry reaction [7]. The *E* isomers were always the major products. As usual, 20 minutes at room temperature are required to anionize 1 equivalent of alkyl isocyanide with 1 equivalent of DBU in a mixture of tetrahydrofuran and *tert*-butyl alcohol before heating four hours at 60° [8]. The pyrrole-2-carboxylates **7a-c** were then isolated in good yield.



(i) CN-CH₂-COOZ 1 eq, DBU 1 eq, THF, *t*-BuOH, 60°C, 4 hours

EXPERIMENTAL

General Methods.

Melting points were taken on a Köfler block and are uncorrected. Infrared spectra were recorded on a Philips PU 9716 apparatus and only noteworthy absorptions (reciprocal centimeters) are listed. The nmr spectra were recorded on a Jeol Lambda 400 using TMS as an internal standard. Chemical shifts are reported in ppm downfield (δ) from TMS.

N-Arylpyrrole-3-carboxaldehydes **3a-c**. General Procedure.

Triflic acid (4 equivalents) was added to a solution of the *N*-arylpyrrole-2-carboxaldehyde **2a-c** in 1,2-dichloroethane (20 ml). The reaction mixture was refluxed 3 hours then evaporated to dryness under reduced pressure. The residue was dissolved in diethyl ether and the solution was washed twice with a saturated aqueous sodium bicarbonate solution. The organic layer was separated, dried over magnesium sulfate and evaporated to give predominantly the 3-isomer as a brown oil.

N-Phenylpyrrole-3-carboxaldehyde (**3a**).

This compound was obtained as an oil (93%): ratio **3a:2a**, 100:0; ir (potassium bromide): ν 1660 (CO) cm⁻¹; ¹H-nmr (DMSO-d₆): δ 9.80 (s, 1H, CHO), 8.28 (s, 1H, H₂), 7.44 (d, 1H, J_{H₅H₄} = 1.96 Hz, H₅), 7.38-7.44 (m, 5H, phenyl protons), 6.73 (d, 1H, J_{H₄H₅} = 1.96 Hz, H₄); ms: (m/z, %) 171 (M⁺, 88), 142 (82), 65 (40).

Anal. Calcd. for C₁₁H₉NO: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.01; H, 5.29; N, 8.20.

N-(4-Methoxyphenyl)pyrrole-3-carboxaldehyde (**3b**).

This compound was obtained as an oil (59%): ratio **3b:2b**, 98:2; ir (potassium bromide): ν 1660 (CO) cm⁻¹; ¹H-nmr (deuteriochloroform): δ 9.86 (s, 1H, CHO), 7.98 (s, 1H, H₂),

7.48 (d, 1H, J_{H₅H₄} = 1.98 Hz, H₅), 6.68-7.15 (m, 4H, phenyl protons), 6.76 (d, 1H, J_{H₄H₅} = 1.98 Hz, H₄), 3.73 (s, 3H, OMe); ms: (m/z, %) 201 (M⁺, 76), 172 (53), 65 (41).

Anal. Calcd. for C₁₂H₁₁NO₂: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.52; H, 5.50; N, 6.95.

N-(2-Nitro-4-chlorophenyl)pyrrole-3-carboxaldehyde (**3c**).

This compound was obtained as oil (66%): ratio **3c:2c**, 95:5; ir (potassium bromide): ν 1670 (CO) cm⁻¹; ¹H-nmr (deuteriochloroform): δ 9.78 (s, 1H, CHO), 8.04 (s, 1H, H₂), 7.83-7.91 (m, 3H, phenyl protons), 7.54 (d, 1H, J_{H₅H₄} = 1.98 Hz, H₅), 6.52 (d, 1H, J_{H₄H₅} = 1.98 Hz, H₄); ms: (m/z, %) 250 (M⁺, 81), 221 (60), 65 (54).

Anal. Calcd. for C₁₁H₇N₂O₃Cl: C, 52.71; H, 2.82; N, 11.18. Found: C, 52.68; H, 2.80; N, 11.18.

Ethyl 3-(*N*-Arylpyrrol-3-yl)-2,3-dihydro-1*H*-pyrrole-2,4-dicarboxylates **4a-c**. General Procedure.

To a solution of the appropriate arylpyrrole-3-carboxaldehyde in tetrahydrofuran (50 ml) and *tert*-butyl alcohol (20 ml) were added DBU (2.1 equivalents) and ethyl isocyanide (2 equivalents). The mixture was stirred for 20 minutes at room temperature then heated for 4 hours at 60°. Concentration of the solvents gave an oil which was washed with water. The oily residue was taken up in diethyl ether. The organic layer was dried over magnesium sulfate and removed under reduced pressure to give **4a-c**.

Ethyl 3-(*N*-Phenylpyrrol-3-yl)-2,3-dihydro-1*H*-pyrrole-2,4-dicarboxylate (**4a**).

This compound was obtained as an oil (62%); ir (potassium bromide): ν 3200 (NH), 1680, 1660 (CO) cm⁻¹; ¹H-nmr (deuteriochloroform): δ 9.45 (s, 1H, NH), 7.47 (s, 1H, H₂), 7.04-7.39 (m, 5H, phenyl protons), 6.93 (s, 1H, H₅), 6.92 (d, 1H, J_{H₅H₄} = 1.97 Hz, H₅), 6.17 (d, 1H, J_{H₄H₅} = 1.97 Hz, H₄), 4.28 (m, 2H, OCH₂), 4.15 (m, 2H, OCH₂), 3.56 (d, 1H, CH), 3.61 (d, 1H, CH), 1.24 (m, 6H, 2 x CH₃); ¹³C-nmr (deuteriochloroform): δ 172.0 (C₂-CO), 164.0 (C₄-CO), 141.3 (C₁'), 140.1 (C₅), 130.1 (C₃' and C₅'), 126.6 (C₄'), 121.2 (C₂' and C₆'), 120.9 (C₃'), 120.5 (C₅'), 119.3 (C₄'), 118.6 (C₂'), 114.5 (C₄'), 60.1 (C₄-COO-CH₂-CH₃), 59.8 (C₂'), 59.3 (C₂-COO-CH₂-CH₃), 45.7 (C₃'), 13.7 (C₄-COO-CH₂-CH₃), 14.3 (C₂-COO-CH₂-CH₃); ms: (m/z, %) 354 (M⁺, 76), 309 (51), 281 (32).

Anal. Calcd. for C₂₀H₂₂N₂O₄: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.76; H, 6.25; N, 7.90.

Ethyl 3-(*N*-(4-Methoxyphenyl)pyrrol-3-yl)-2,3-dihydro-1*H*-pyrrole-2,4-dicarboxylate (**4b**).

This compound was obtained as an oil (64%); ir (potassium bromide): ν 3200 (NH), 1680, 1660 (CO) cm⁻¹; ¹H-nmr (deuteriochloroform): δ 9.56 (s, 1H, NH), 6.97 (s, 1H, H₂), 6.90 (s, 1H, H₅), 6.63-7.18 (m, 4H, phenyl protons), 6.58 (d, 1H, J_{H₅H₄} = 1.99 Hz, H₅), 6.18 (d, 1H, J_{H₄H₅} = 1.99 Hz, H₄), 4.24 (m, 2H, OCH₂), 4.14 (m, 2H, OCH₂), 3.75 (s, 3H, OMe), 3.58 (d, 1H, CH), 3.56 (d, 1H, CH), 1.22 (m, 6H, 2 x CH₃); ¹³C-nmr (deuteriochloroform): δ 171.8 (C₂-CO), 164.2 (C₄-CO), 159.6 (C₄'), 139.7 (C₅'), 132.9 (C₁'), 121.6 (C₂' and C₆'), 121.0 (C₃'), 120.2 (C₅'), 119.5 (C₄'), 117.9 (C₂'), 114.6 (C₃' and C₅'), 114.3 (C₄'), 60.1 (C₄-COO-CH₂-CH₃), 59.7 (C₂'), 59.3 (C₂-COO-CH₂-CH₃), 56.0 (OCH₃), 45.6 (C₃'), 13.6 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃); ms: (m/z, %) 384 (M⁺, 71), 339 (54), 311 (48).

Anal. Calcd. for C₂₁H₂₄N₂O₅: C, 65.61; H, 6.29; N, 7.29. Found: C, 65.58; H, 6.28; N, 7.30.

Ethyl 3-(*N*-(4-Chloro-2-nitrophenyl)pyrrol-3-yl)-2,3-dihydro-1*H*-pyrrole-2,4-dicarboxylate (**4c**).

This compound was obtained as an oil (51%); ir (potassium bromide): ν 3200 (NH), 1670, 1660 (CO) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 9.56 (s, 1H, NH), 7.73 (s, 1H, H^{2'}), 7.30-7.58 (m, 3H, phenyl protons), 7.28 (s, 1H, H⁵), 7.01 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.97 \text{ Hz}$, H^{5'}), 6.52 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.97 \text{ Hz}$, H^{4'}), 4.21 (m, 2H, OCH₂), 4.13 (m, 2H, OCH₂), 3.51 (d, 1H, CH), 3.13 (d, 1H, CH), 1.26 (m, 6H, 2 x CH₃); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 171.9 (C₂-CO), 164.8 (C₄-CO), 141.6 (C_{2''}), 139.6 (C₅), 135.9 (C_{5''}), 133.6 (C_{1''}), 131.0 (C_{4''}), 124.2 (C_{3''}), 122.5 (C_{6''}), 120.4 (C₃), 120.1 (C₅), 119.3 (C₄), 117.7 (C₂), 114.2 (C_{4'}), 60.0 (C₄-COO-CH₂-CH₃), 59.8 (C₂), 59.5 (C₂-COO-CH₂-CH₃), 45.7 (C₃), 13.6 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃); ms: (m/z, %) 433 (M⁺, 71), 388 (62), 360 (58).

Anal. Calcd. for C₂₀H₂₀N₃O₆Cl: C, 55.37; H, 4.65; N, 9.69. Found: C, 55.34; H, 4.64; N, 9.68.

Ethyl 3-(*N*-Arylpyrrol-3-yl)-1*H*-pyrrole-2,4-dicarboxylates **5a-c**. General Procedure.

If using a large excess of DBU (4 equivalents at least) in the reaction described above and heating for 8 hours at 60°, the pyrroline ring undergoes a proton-extracting step to give the pyrrole. Poured into water, the (*N*-arylpyrrol-3-yl)pyrrolyldicarboxylate compounds are extracted with ethyl ether. The organic layer is dried over magnesium sulfate, passed through a silica gel pad and removed *in vacuo* to give **5a-c** as oils.

Ethyl 3-(*N*-Phenylpyrrol-2-yl)-1*H*-pyrrole-2,4-dicarboxylate (**5a**).

This compound was obtained as an oil (78%); ir (potassium bromide): ν 3200 (NH), 1680, 1670 (CO) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 9.51 (s, 1H, NH), 7.21 (s, 1H, H^{2'}), 6.95-7.16 (m, 5H, phenyl protons), 7.01 (s, 1H, H⁵), 6.91 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.96 \text{ Hz}$, H^{5'}), 6.40 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.96 \text{ Hz}$, H^{4'}), 4.24 (m, 2H, OCH₂), 4.18 (m, 2H, OCH₂), 1.26 (m, 6H, 2 x CH₃); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 164.0 (C₄-CO), 159.0 (C₂-CO), 140.4 (C_{1''}), 130.1 (C_{3''} and C_{5''}), 126.6 (C_{4''}), 123.1 (C₅), 121.8 (C₂), 121.2 (C_{2''} and C_{6''}), 120.1 (C₂ and C₅), 115.6 (C₃), 111.2 (C_{3'} and C_{4'}), 109.3 (C₄), 59.4 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃), 13.6 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃); ms: (m/z, %) 352 (M⁺, 92), 262 (61), 206 (52).

Anal. Calcd. for C₂₀H₂₀N₂O₄: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.15; H, 5.71; N, 7.95.

Ethyl 3-(*N*-(4-Methoxyphenyl)pyrrol-3-yl)-1*H*-pyrrole-2,4-dicarboxylate (**5b**).

This compound was obtained as an oil (78%); ir (potassium bromide): ν 3250 (NH), 1680, 1660 (CO) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 9.52 (s, 1H, NH), 7.56 (s, 1H, H^{2'}), 7.05 (s, 1H, H⁵), 6.73-7.18 (m, 4H, phenyl protons), 6.41 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.98 \text{ Hz}$, H^{5'}), 6.28 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.98 \text{ Hz}$, H^{4'}), 4.22 (m, 2H, OCH₂), 4.18 (m, 2H, OCH₂), 3.74 (s, 3H, OMe), 1.25 (m, 6H, 2 x CH₃); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 164.8 (C₄-CO), 159.1 (C₂-CO), 158.4 (C_{4''}), 133.1 (C_{1''}), 122.9 (C₅), 122.1 (C₂), 121.6 (C_{2''} and C_{6''}), 120.2 (C₂ and C₅), 115.1 (C₃), 114.6 (C_{3''} and C_{5''}), 110.2 (C₃ and C_{4'}), 109.9 (C₄), 59.2 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃), 13.5 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃); ms: (m/z, %) 382 (M⁺, 71), 292 (58), 236 (44).

Anal. Calcd. for C₂₁H₂₂N₂O₅: C, 65.96; H, 5.80; N, 7.33. Found: C, 65.94; H, 5.78; N, 7.32.

Ethyl 3-(*N*-(4-Chloro-2-nitrophenyl)pyrrol-3-yl)-1*H*-pyrrole-2,4-dicarboxylate (**5c**).

This compound was obtained as an oil (76%); ir (potassium bromide): ν 3300 (NH), 1680, 1665 (CO) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 9.58 (s, 1H, NH), 7.81 (s, 1H, H^{2'}), 7.66 (s, 1H, H⁵), 7.31-7.60 (m, 3H, phenyl protons), 7.24 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.98 \text{ Hz}$, H^{5'}), 6.78 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.98 \text{ Hz}$, H^{4'}), 4.20 (m, 2H, OCH₂), 4.17 (m, 2H, OCH₂), 1.27 (m, 6H, 2 x CH₃); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 165.2 (C₄-CO), 159.3 (C₂-CO), 141.4 (C_{2''}), 135.7 (C_{5''}), 133.9 (C_{5''}), 132.1 (C_{4''}), 124.6 (C_{3''}), 123.2 (C₅), 122.5 (C_{6''}), 122.1 (C₂), 119.2 (C₂ and C₅), 115.2 (C₃), 110.1 (C_{3'} and C_{4'}), 109.9 (C₄), 59.1 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃), 13.6 (C₂-COO-CH₂-CH₃ and C₄-COO-CH₂-CH₃); ms: (m/z, %) 431 (M⁺, 81), 341 (70), 285 (64).

Anal. Calcd. for C₂₀H₁₈N₃O₆Cl: C, 55.63; H, 4.20; N, 9.73. Found: C, 55.61; H, 4.19; N, 9.71.

(*E*)-1-(*N*-Arylpyrrol-3-yl)-2-nitroprop-2-enes **6a-c**. General Procedure.

To a suspension of ammonium acetate (2.5 equivalents) in nitroethane (50 ml) is added a solution of the appropriate *N*-phenylpyrrolicarboxaldehyde in nitroethane (100 ml). The mixture is heated for 4 hours at 60° after which the solvent is evaporated. The oily residue is washed with water and taken up in diethyl ether. The organics are dried over magnesium sulfate then removed under reduced pressure to give analytically pure **6a-c**:

(*E*)-2-Nitro-1-(*N*-phenylpyrrol-3-yl)prop-2-ene (**6a**).

This compound was obtained as an oil (78%); $^1\text{H-nmr}$ (deuteriochloroform): δ 7.61 (d, 1H, CH), 7.35-7.48 (m, 5H, phenyl protons), 7.41 (s, 1H, H²), 7.11 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.98 \text{ Hz}$, H⁵), 6.54 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.98 \text{ Hz}$, H⁴), 2.48 (s, 3H, Me); ms: (m/z, %) 228 (M⁺, 64), 143 (48), 77 (37).

Anal. Calcd. for C₁₃H₁₂N₂O₂: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.38; H, 5.29; N, 12.28.

(*E*)-2-Nitro-1-(*N*-(4-methoxyphenyl)pyrrol-3-yl)prop-2-ene (**6b**).

This compound was obtained as yellow crystals (diethyl ether/petroleum ether) (76%), mp 78°; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.58 (d, 1H, CH), 7.36 (s, 1H, H²), 7.02-7.24 (m, 4H, phenyl protons), 7.16 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.97 \text{ Hz}$, H⁵), 6.80 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.97 \text{ Hz}$, H⁴), 3.71 (s, 3H, OMe), 2.54 (s, 3H, Me); ms: (m/z, %) 258 (M⁺, 63), 173 (51), 141 (48).

Anal. Calcd. for C₁₄H₁₄N₂O₃: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.08; H, 5.45; N, 10.84.

(*E*)-2-Nitro-1-(*N*-(4-chloro-2-nitrophenyl)pyrrol-3-yl)prop-2-ene (**6c**).

This compound was obtained as yellow crystals (diethyl ether/petroleum ether) (64%), mp 98°; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.81 (d, 1H, CH), 7.79 (s, 1H, H²), 7.31-7.76 (m, 3H, phenyl protons), 6.94 (d, 1H, $J_{\text{H}^5 \text{H}^4} = 1.96 \text{ Hz}$, H⁵), 6.64 (d, 1H, $J_{\text{H}^4 \text{H}^5} = 1.96 \text{ Hz}$, H⁴), 2.56 (s, 3H, Me); ms: (m/z, %) 307 (M⁺, 58), 222 (41), 190 (33).

Anal. Calcd. for C₁₃H₁₀N₃O₄Cl: C, 50.75; H, 3.28; N, 13.66. Found: C, 50.73; H, 3.27; N, 13.64.

Alkyl 4-Methyl-3-(*N*-arylpyrrol-3-yl)-1*H*-pyrrole-2-carboxylates **7a-c** and **7a'-c'**. General Procedure.

To a solution of the appropriate nitrovinylarylpyrrole derivative in tetrahydrofuran (50 ml) and *tert*-butyl alcohol (20 ml) were added DBU (1.1 equivalents) and alkyl isocyanide methyl to give **7a-c** or ethyl to give **7a'-c'**, (1 equivalent). The mixture was stirred for 20 minutes at room temperature then heated for 4 hours at 60°. Concentration of the solvents gave an oil which

was washed with water. The oily residue was taken up in diethyl ether. The organic layer was dried over magnesium sulfate and removed under reduced pressure.

Methyl-4-Methyl-3-(*N*-phenylpyrrol-3-yl)-1*H*-pyrrole-2-carboxylate (**7a**).

This compound was obtained as an oil (68%); ir (potassium bromide): ν 3400 (NH), 1680 (CO) cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): δ 11.35 (s, 1H, NH), 7.48 (s, 1H, H $2'$), 7.51-7.68 (m, 5H, phenyl protons), 7.39 (s, 1H, H $5'$), 6.84 (d, 1H, $J_{\text{H}5' \text{H}4'} = 1.98$ Hz, H $5'$), 6.49 (d, 1H, $J_{\text{H}4' \text{H}5'} = 1.98$ Hz, H $4'$), 3.72 (s, 3H, OMe), 2.10 (m, 3H, Me); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.3 (CO), 140.6 (C $1''$), 129.4 (C $3''$ and C $5''$), 125.4 (C $4''$), 123.1 (C 2), 121.8 (C 5), 120.3 (C $2'$ and C $6''$), 120.1 (C 4), 119.6 (C 3), 119.2 (C $2'$ and C 5), 110.3 (C $3'$ and C $4'$), 50.3 (OCH $_3$), 12.6 (CH $_3$); ms: (m/z, %) 280 (M $^+$, 100), 249 (98), 221 (48).

Anal. Calcd. for C $_{17}\text{H}_{16}\text{N}_2\text{O}_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.82; H, 5.74; N, 10.01.

Ethyl 4-Methyl-3-(*N*-phenylpyrrol-3-yl)-1*H*-pyrrole-2-carboxylate (**7a'**).

This compound was obtained as an oil (69%); ir (potassium bromide): ν 3400 (NH), 1670 (CO) cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): δ 11.34 (s, 1H, NH), 7.48 (s, 1H, H $2'$), 7.48-7.67 (m, 5H, phenyl protons), 7.41 (s, 1H, H $5'$), 6.83 (ds 1H, $J_{\text{H}5' \text{H}4'} = 1.98$ Hz, H $5'$), 6.48 (d, 1H, $J_{\text{H}4' \text{H}5'} = 1.98$ Hz, H $4'$), 3.93 (m, 2H, OCH $_2$ ester), 2.09 (m, 3H, Me), 1.36 (m, 3H, CH $_3$ ester); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.1 (CO), 140.5 (C $1''$), 129.1 (C $3''$ and C $5''$), 125.2 (C $4''$), 123.1 (C 2), 121.7 (C 5), 120.3 (C $2'$ and C $6''$), 119.9 (C 4), 119.3 (C 3), 119.0 (C $2'$ and C 5), 111.1 (C $3'$ and C $4'$), 59.6 (OCH $_3$), 13.6 (O-CH $_2$ -CH $_3$), 12.3 (CH $_3$); ms: (m/z, %) 294 (M $^+$, 100), 249 (86), 221 (42).

Anal. Calcd. for C $_{18}\text{H}_{18}\text{N}_2\text{O}_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.43; H, 6.15; N, 9.52.

Methyl 4-Methyl-3-(*N*-(4-methoxyphenyl)pyrrol-3-yl)-1*H*-pyrrole-2-carboxylate (**7b**).

This compound was obtained as yellow crystals (petroleum ether) (45%); ir (potassium bromide): ν 3300 (NH), 1680 (CO) cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): δ 11.24 (s, 1H, NH), 7.51 (s, 1H, H $2'$), 7.46 (s, 1H, H $5'$), 6.94-7.42 (m, 4H, phenyl protons), 6.72 (d, 1H, $J_{\text{H}5' \text{H}4'} = 1.97$ Hz, H $5'$), 6.38 (d, 1H, $J_{\text{H}4' \text{H}5'} = 1.97$ Hz, H $4'$), 3.81 (s, 3H, OMe ester), 3.71 (s, 3H, OMe), 2.01 (m, 3H, Me); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.1 (CO), 158.6 (C $4''$), 132.5 (C $1''$), 123.4 (C 2), 122.1 (C 4), 121.4 (C $2'$ and C $6''$), 120.2 (C 4), 119.8 (C 3), 118.6 (C $2'$ and C 5), 114.8 (C $3''$), 110.3 (C $3'$ and C $4'$), 56.1 (O-CH $_3$), 50.3 (COO-CH $_3$), 12.4 (CH $_3$); ms: (m/z, %) 310 (M $^+$, 100), 279 (94), 251 (64).

Anal. Calcd. for C $_{18}\text{H}_{18}\text{N}_2\text{O}_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.66; H, 5.84; N, 9.01.

Ethyl 4-Methyl-3-(*N*-(4-methoxyphenyl)pyrrol-3-yl)-1*H*-pyrrole-2-carboxylate (**7b'**).

This compound was obtained as yellow crystals (petroleum ether) (52%), mp 65 $^\circ$; ir (potassium bromide): ν 3300 (NH), 1670 (CO) cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): δ 11.26 (s, 1H, NH), 7.50 (s, 1H, H $2'$), 7.45 (s, 1H, H $5'$), 6.96-7.38 (m, 4H, phenyl protons), 6.68 (d, 1H, $J_{\text{H}5' \text{H}4'} = 1.97$ Hz, H $5'$), 6.40 (d, 1H, $J_{\text{H}4' \text{H}5'} = 1.97$ Hz, H $4'$), 3.87 (m, 2H, OCH $_2$ ester), 3.68 (s, 3H, OMe), 1.98 (m, 3H, Me), 1.34 (m, 3H, CH $_3$ ester); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.1 (CO), 158.6 (C $4''$), 132.5 (C $1''$), 123.4 (C 2), 122.6 (C 5), 121.7 (C $2'$ and C $6''$), 120.2 (C 4), 120.0 (C 3), 119.6

(C $2'$ and C $5'$), 115.8 (C $3''$ and C $4''$), 110.3 (C $3'$ and C $4'$), 59.9 (COO-CH $_2$ -CH $_3$), 56.3 (OCH $_3$), 13.7 (COO-CH $_2$ -CH $_3$), 12.4 (CH $_3$); ms: (m/z, %) 324 (M $^+$, 100), 279 (96), 251 (54).

Anal. Calcd. for C $_{19}\text{H}_{20}\text{N}_2\text{O}_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.34; H, 6.20; N, 8.66.

Methyl 4-Methyl-3-(*N*-(4-chloro-2-nitrophenyl)pyrrol-3-yl)-1*H*-pyrrole-2-carboxylate (**7c**).

This compound was obtained as an oil (62%); ir (potassium bromide): ν 3300 (NH), 1670 (CO) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 11.17 (s, 1H, NH), 7.53-7.71 (m, 3H, phenyl protons), 7.45 (s, 1H, H $2'$), 7.36 (s, 1H, H $5'$), 6.78 (d, 1H, $J_{\text{H}5' \text{H}4'} = 1.96$ Hz, H $5'$), 6.51 (d, 1H, $J_{\text{H}4' \text{H}5'} = 1.96$ Hz, H $4'$), 3.71 (s, 3H, OMe ester), 1.98 (m, 3H, Me); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.1 (CO), 141.6 (C $2''$), 135.6 (C $5''$), 134.6 (C $1''$), 132.6 (C $4''$), 126.7 (C $3''$), 123.2 (C 2), 122.9 (C $6''$), 121.8 (C 5), 120.5 (C 4), 119.3 (C 3), 119.1 (C $2'$ and C 5), 110.1 (C $3'$ and C $4'$), 50.2 (OCH $_3$), 12.4 (CH $_3$); ms: (m/z, %) 359 (M $^+$, 100), 328 (75), 300 (48).

Anal. Calcd. for C $_{17}\text{H}_{14}\text{N}_3\text{O}_4\text{Cl}$: C, 56.76; H, 3.92; N, 11.68. Found: C, 56.74; H, 3.91; N, 11.67.

Ethyl 4-Methyl-3-(*N*-(4-chloro-2-nitrophenyl)pyrrol-3-yl)-1*H*-pyrrole-2-carboxylate (**7c'**).

This compound was obtained as yellow crystals (diethyl ether/petroleum ether) (69%); mp 56 $^\circ$; ir (potassium bromide): ν 3300 (NH), 1680 (CO) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 11.14 (s, 1H, NH), 7.48-7.69 (m, 3H, phenyl protons), 7.46 (s, 1H, H $2'$), 7.38 (s, 1H, H $5'$), 6.78 (d, 1H, $J_{\text{H}5' \text{H}4'} = 1.97$ Hz, H $5'$), 6.54 (d, 1H, $J_{\text{H}4' \text{H}5'} = 1.97$ Hz, H $4'$), 4.01 (m, 2H, OCH $_2$ ester), 1.97 (m, 3H, Me), 1.28 (m, 3H, CH $_3$ ester); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 159.1 (CO), 141.6 (C $2''$), 135.6 (C $5''$), 134.6 (C $1''$), 132.6 (C $4''$), 126.7 (C $3''$), 123.2 (C 2), 122.9 (C $6''$), 121.8 (C 5), 120.5 (C 4), 119.3 (C 3), 119.1 (C $2'$ and C 5), 110.1 (C $3'$ and C $4'$), 59.4 (COO-CH $_2$ -CH $_3$), 13.8 (COO-CH $_2$ -CH $_3$), 12.4 (CH $_3$); ms: (m/z, %) 373 (M $^+$, 98), 328 (81), 300 (54).

Anal. Calcd. for C $_{18}\text{H}_{16}\text{N}_3\text{O}_4\text{Cl}$: C, 57.84; H, 4.31; N, 11.24. Found: C, 57.81; H, 4.30; N, 11.25.

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