Synthesis of 5-Acylethynylpyrrole-2-carbaldehydes via Transition Metal-Free Ethynylation of the Pyrrole Moiety with Acylbromoacetylenes on Al₂O₃

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Supplementary Material

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General information

IR spectra were obtained with a Bruker Vertex 70 spectrometer (400–4000 cm^{-1} , KBr pellets). ^1H (400.13 MHz) and ^{13}C NMR (100.61 MHz) spectra were recorded with a Bruker DPX-400 instrument. Elemental analyses were recorded with an EA FLASH 1112 Series (CHN Analyzer) instrument. The determination of the unit cell and the data collection for 4-[3-(furan-2-yl)-3-oxoprop-1-yl]-1*H*-pyrrole-2-carbadehyde (**4b**) was performed on a Bruker D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_α radiation ($\lambda = 0.71073$) at 100(2) K using the ω – 2θ scan technique. A specimen of $\text{C}_{12}\text{H}_7\text{N}_1\text{O}_3$, approximate dimensions 0.118 x 0.145 x 0.282 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell with $\text{P2}_1/\text{n}$ space group yielded a total of 38567 reflections to a maximum θ angle of 30.09° (0.71 Å resolution), of which 2894 were independent (average redundancy 13.327, completeness = 99.9%, $R_{\text{int}} = 7.06\%$, $R_{\text{sig}} = 3.47\%$) and 2162 (74.71%) were greater than $2\sigma(\text{F}^2)$. The final cell constants of $\underline{a} = 6.4543(3)$ Å, $\underline{b} = 13.5519(7)$ Å, $\underline{c} = 11.5474(5)$ Å, $\beta = 101.922(2)^\circ$, volume = $988.24(8)$ Å³, are based upon the refinement of the XYZ-centroids of 9923 reflections above $20\ \sigma(\text{I})$ with $4.693^\circ < 2\theta < 59.68^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.905. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9710 and 0.9880. The structure was solved and refined using the Bruker SHELXTL Software Package.¹

I. Analytical data of compounds

Synthesis of ethynylpyrroles 5a-f. General Procedure.

Acetal **3a,b** (1.821 mmol) and acylbromoacetylene **2a-c** (1.821 mmol) were carefully grinded together with alumina (10-fold amount by weight) for 5 min and allowed to stay at rt for 6 hours. Then the solid reaction mixture was placed on the top of an Al₂O₃-packed column and successively eluted with *n*-hexane and systems of *n*-hexane with diethyl ether (hexane/diethyl ether with gradient from 3:1, 1:1, 1:3) to afford ethynylpyrroles **5a-f**.

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrrol-2-yl]-1-phenylprop-2-yn-1-one (**5a**)

Yield: 304 mg (54%); grey needles; mp 141–143 °C. Anal. Calcd for C₁₉H₁₉NO₃: C, 73.77; H, 6.19; N, 4.53%. Found: C, 73.48; H, 6.16; N, 4.51. IR (KBr): 3314 (NH), 2174 (C≡C), 1625 (CO) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): δ = 9.09 (1H, br. s, NH), 8.18–8.16 (2H, m, *Ho* Ph), 7.63–7.59 (1H, m, *Hp* Ph), 7.52–7.48 (2H, m, *Hm* Ph), 6.82 (1H, dd, *J* = 2.7, 3.4 Hz, H-3), 6.29 (1H, dd, *J* = 2.9, 3.4 Hz, H-4), 5.50 (1H, s, O-CH-O), 3.76 (2H, d, *J* = 11.2 Hz, CH₂), 3.64 (2H, d, *J* = 11.2 Hz, CH₂), 1.26 (3H, s, Me), 0.81 (3H, s, Me). ¹³C NMR (100.6 MHz, CDCl₃): δ = 177.7 (C=O), 137.0 (C_i), 134.6 (C-5), 134.0 (C_p), 129.5 (C_o), 128.7 (C_m), 121.1 (C-3), 109.8 (C-2), 108.5 (C-4), 96.1 (O-CH-O), 91.9 (≡C), 88.1 (C≡), 77.5 (CH₂-O), 30.5 (Me₂C), 23.1 (Me), 22.0 (Me).

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrrol-2-yl]-1-(furan-2-yl)prop-2-yn-1-one (**5b**).

Yield: 223 mg (41%); yellow crystals; mp 142–146 °C. Anal. Calcd for C₁₇H₁₇NO₄: C, 68.21; H, 5.72; N, 4.68%. Found: C, 68.48; H, 5.56; N, 4.61. IR (KBr): 3206 (NH), 2174 (C≡C), 1612 (CO) cm⁻¹. ¹H NMR (400.1 MHz, C₆D₆): δ = 8.72 (1H, br. s, NH), 7.05 (1H, dd, *J* = 0.7, 3.5 Hz, H-5 furan), 6.90 (1H, dd, *J* = 0.7, 1.7 Hz, H-3 furan), 6.66 (1H, dd, *J* = 1.6, 3.6 Hz, H-3), 6.29 (1H, dd, *J* = 1.7, 3.5 Hz, 1H, H-4 furan), 5.83 (1H, dd, *J* = 1.6, 3.6 Hz, H-4), 5.09 (1H, s, O-CH-O), 3.39 (2H, d, *J* = 10.8 Hz, CH₂), 3.15 (2H, d, *J* = 10.8 Hz, CH₂), 1.05 (3H, s, Me), 0.33 (3H, s, Me). ¹³C NMR (100.6 MHz, C₆D₆): δ = 164.5 (C=O), 153.9 (C-2 furan), 147.0 (C-5 furan), 135.1 (C-5), 120.8 (C-3 furan), 118.9 (C-3), 112.4 (C-4 furan), 110.0 (C-2), 108.5 (C-4), 96.3 (O-CH-O), 91.7 (≡C), 86.8 (C≡), 77.0 (CH₂-O), 30.1 (Me₂C), 23.0 (Me), 21.6 (Me).

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrrol-2-yl]-1-(thiophen-2-yl)prop-2-yn-1-one (**5c**).

Yield: 247 mg (43%); yellow crystals; mp 141–143 °C. Anal. Calcd for C₁₇H₁₇NO₃S: C, 64.74; H, 5.43; N, 4.44; S, 10.17%. Found: C, 64.58; H, 5.66; N, 4.21; S, 10.01. IR (KBr): 3314 (NH), 2175 (C≡C), 1605 (CO) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): δ = 8.97 (1H, br. s, NH), 7.94 (1H, dd, *J* = 1.2, 3.8 Hz, H-3 thiophene), 7.70 (1H, dd, *J* = 1.2, 4.9 Hz, H-5 thiophene), 7.18 (1H, dd, *J* = 3.8, 4.9 Hz, 1H, H-4 thiophene), 6.79 (1H, dd, *J* = 2.4, 3.8 Hz, H-4), 6.28 (1H, dd, *J* = 2.4, 3.8 Hz, H-3), 5.49 (1H, s, O-CH-O), 3.75 (2H, d, *J* = 10.8 Hz, CH₂), 3.63 (2H, d, *J* = 10.8 Hz, CH₂), 1.26 (3H, s, Me), 0.81 (3H, s, Me). ¹³C NMR (100.6 MHz, CDCl₃): δ = 168.6 (C=O), 144.0 (C-2 thiophene), 133.8 (C-5 thiophene), 133.7 (C-3 thiophene), 133.6 (C-5), 127.4 (C-4 thiophene), 120.0 (C-3), 108.7 (C-2), 107.4 (C-4), 95.0 (O-CH-O), 90.2 (≡C), 86.0 (C≡), 76.5 (CH₂-O), 29.5 (Me₂C), 22.1 (Me), 21.0 (Me).

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-ethyl-1H-pyrrol-2-yl]-1-phenylprop-2-yn-1-one (5d).

Yield: 331 mg (54%); yellow crystals; mp 70–72 °C. Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15%. Found: C, 74.62; H, 6.98; N, 4.18. IR (KBr): 2171 ($C\equiv C$), 1624 (CO) cm^{-1} . 1H NMR (400.1 MHz, $CDCl_3$): δ = 8.17 (2H, m, *Ho* Ph), 7.63–7.59 (1H, m, *Hp* Ph), 7.52–7.49 (2H, m, *Hm* Ph), 6.78 (1H, d, J = 4.0 Hz, H-3), 6.30 (1H, d, J = 4.0 Hz, H-4), 5.47 (1H, s, O-CH-O), 4.39 (2H, q, J = 7.2 Hz, NCH_2), 3.78 (2H, d, J = 10.8 Hz, CH_2), 3.62 (2H, d, J = 10.8 Hz, CH_2), 1.48 (3H, t, J = 7.2 Hz, $\underline{Me}CH_2$), 1.30 (3H, s, Me), 0.81 (3H, s, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 177.4 (C=O), 137.3 (*ci*), 134.4 (C-5), 133.8 (*Cp*), 129.3 (*Co*), 128.7 (*Cm*), 120.4 (C-3), 113.5 (C-2), 109.8 (C-4), 97.1 (O-CH-O), 94.8 ($\equiv C$), 87.5 ($C\equiv$), 78.0 (CH_2 -O), 41.7 (NCH_2), 30.3 (Me_2C), 23.3 (Me), 22.0 (Me), 16.7 ($\underline{Me}CH_2$).

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-ethyl-1H-pyrrol-2-yl]-1-(furan-2-yl)prop-2-yn-1-one (5e).

Yield: 298 mg (50%); yellow crystals; mp 68–70 °C. Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N 4.28%. Found: C, 69.79; H, 6.67; N, 4.20. IR (KBr): 2177 ($C\equiv C$), 1626 (CO) cm^{-1} . 1H NMR (400.1 MHz, $CDCl_3$): δ = 7.65 (1H, dd, J = 0.7, 1.7 Hz, H-5 furan), 7.32 (1H, dd, J = 0.7, 3.5 Hz, H-3 furan), 6.75 (1H, d, J = 3.4 Hz, H-3), 6.59 (1H, dd, J = 1.7, 3.5 Hz, H-4 furan), 6.28 (1H, d, J = 3.4 Hz H-4), 5.46 (1H, s, O-CH-O), 4.36 (2H, q, J = 7.0 Hz, NCH_2), 3.77 (2H, d, J = 10.8 Hz, CH_2), 3.63 (2H, d, J = 10.8 Hz, CH_2), 1.46 (3H, t, J = 7.0 Hz, $\underline{Me}CH_2$), 1.30 (3H, s, Me), 0.81 (3H, s, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 164.6 (C=O), 153.4 (C-2 furan), 147.5 (C-5 furan), 134.5 (C-5), 120.3 (C-3), 119.3 (C-3 furan), 113.3 (C-2), 112.6 (C-4 furan), 109.8 (C-4), 97.1 (O-CH-O), 93.9 ($\equiv C$), 86.6 ($C\equiv$), 78.0 (CH_2 -O), 41.6 (NCH_2), 30.3 (Me_2C), 23.3 (Me), 22.0 (Me), 16.7 (CH_2Me).

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-ethyl-1H-pyrrol-2-yl]-1-(thiophen-2-yl)prop-2-yn-1-one (5f).

Yield: 256 mg (41%); yellow crystals; mp 88–90 °C. Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N 4.08; S, 9.34%. Found: C, 66.18; H, 6.12; N, 4.20; S, 9.02. IR (KBr): 2175 ($C\equiv C$), 1610 (CO) cm^{-1} . 1H NMR (400.1 MHz, $CDCl_3$): δ = 7.92 (1H, dd, J = 1.2, 3.8 Hz, H-3 thiophene), 7.69 (1H, dd, J = 1.2, 4.9 Hz, H-5 thiophene), 7.17 (1H, dd, J = 3.8, 4.9 Hz, H-4 thiophene), 6.77 (1H, d, J = 3.8 Hz, H-3), 6.29 (1H, d, J = 3.8 Hz H-4), 5.46 (1H, s, O-CH-O), 4.38 (2H, q, J = 7.0 Hz, NCH_2), 3.78 (2H, d, J = 10.8 Hz, CH_2), 3.63 (2H, d, J = 10.8 Hz, CH_2), 1.48 (3H, t, J = 7.0 Hz, $\underline{Me}CH_2$), 1.30 (3H, s, Me), 0.81 (3H, s, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.2 (C=O), 145.1 (C-2 thiophene), 134.5 (C-3 thiophene), 134.4 (C-5), 133.8 (C-5 thiophene), 128.3 (C-4 thiophene), 120.4 (C-3), 113.2 (C-2), 109.8 (C-4), 97.0 (O-CH-O), 94.0 ($\equiv C$), 86.0 ($C\equiv$), 77.9 (CH_2 -O), 41.6 (NCH_2), 30.3 (Me_2C), 23.2 (Me), 21.9 (Me), 16.8 (CH_2Me).

Synthesis of 5-ethynylpyrrole-2-carbaldehydes 4a-f. General Procedure.

Solution of pyrrole **5a-f** (2.295 mmol) in acetone (30 ml) was added to 4M solution of HCl (9.5 ml) in acetone (20 ml) and the mixture was stirred at room temperature for 1 h. Then diethyl ether was added (50 ml) and resulted solution was washed twice by saturated NaCl and 5% $NaHCO_3$ solutions, dried over K_2CO_3 . Residue after removing solvent was purified by flash chromatography on Al_2O_3 (eluent: *n*-hexane, hexane/diethyl ether with gradient from 3:1, 1:1, 1:3) to give pyrroles **4a-f**.

5-(3-Oxo-3-phenylprop-1-ynyl)-1H-pyrrole-2-carbaldehyde (4a).

Yield: 394 mg (77%); grey solid; mp 197–199 °C. Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27%. Found: C, 75.56; H, 4.19; N, 6.09. IR (KBr): 3230 (NH), 2194 ($C\equiv C$), 1662 (HCO), 1630 (COPh) cm^{-1} . 1H NMR (400.1 MHz, acetone- d_6): δ = 12.06 (1H, br. s, NH), 9.66 (1H, s, HC=O), 8.22–8.21 (2H, m, *Ho* Ph), 7.72–7.69 (1H, m, *Hp* Ph), 7.59–7.56 (2H, m, *Hm* Ph), 7.09 (1H, dd, J = 2.7, 3.4 Hz, H-4), 6.98 (1H, dd, J = 2.9, 3.4 Hz, H-3). ^{13}C NMR (100.6 MHz, acetone- d_6): δ = 180.5 (HC=O), 177.5 (C=O), 137.7 (Ci), 136.8 (C-2), 135.4 (Cp), 130.3 (Co, C-3), 129.9 (Cm), 121.7 (C-4), 120.6 (C-5), 91.6 ($\equiv C$), 85.3 (C $\equiv$).

5-[3-(Furan-2-yl)-3-oxoprop-1-ynyl]-1H-pyrrole-2-carbaldehyde (4b).

Yield: 425 mg (87%); yellow crystals; mp 168–170 °C. Anal. Calcd for $C_{12}H_7NO_3$: C, 67.61; H, 3.31; N, 6.57%. Found: C, 67.29; H, 3.07; N, 6.34. IR (KBr): 3240 (NH), 2207 ($C\equiv C$), 1658 (HCO), 1628 (CO) cm^{-1} . 1H NMR (400.1 MHz, $CDCl_3$): δ = 9.69 (1H, br. s, NH), 9.61 (1H, s, HC=O), 7.72 (1H, dd, J = 0.8, 1.7 Hz, H-5 furan), 7.43 (1H, dd, J = 0.8, 3.6 Hz, H-3 furan), 6.98 (1H, dd, J = 2.5, 4.0 Hz, H-4), 6.85 (1H, dd, J = 2.4, 4.0 Hz, H-3), 6.64 (1H, dd, J = 1.7, 3.6 Hz, H-4 furan). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 179.5 (HC=O), 163.0 (C=O), 153.1 (C-2 furan), 148.4 (C-5 furan), 134.9 (C-2), 121.2 (C-3 furan), 120.8 (C-3), 120.4 (C-4), 117.2 (C-5), 113.0 (C-4 furan), 91.0 ($\equiv C$), 82.9 (C $\equiv$).

5-[3-Oxo-3-(thiophen-2-yl)prop-1-ynyl]-1H-pyrrole-2-carbaldehyde (4c).

Yield: 394 mg (75%); yellow solid; mp 185 °C. Anal. Calcd for $C_{12}H_7NO_2S$: C, 62.87; H, 3.08; N, 6.11; S, 13.99%. Found: C, 62.69; H, 3.11; N, 6.24; S, 14.15. IR (KBr): 3251 (NH), 2195 ($C\equiv C$), 1658 (HCO), 1617 (CO) cm^{-1} . 1H NMR (400.1 MHz, acetone- d_6): δ = 12.02 (1H, br. s, NH), 9.65 (1H, s, H-CO), 8.17 (1H, dd, J = 1.0, 3.8 Hz, H-3 thiophene), 8.02 (1H, dd, J = 1.0, 4.9 Hz, H-5 thiophene), 7.28 (1H, dd, J = 3.8, 4.9 Hz, H-4 thiophene), 7.09 (1H, d, J = 3.9 Hz, H-4), 6.94 (1H, d, J = 3.9 Hz, H-3). ^{13}C NMR (100.6 MHz, acetone- d_6): δ = 180.5 (HC=O), 169.4 (C=O), 145.6 (C-2 thiophene), 137.0 (C-3,5 thiophene), 136.8 (C-2), 129.7 (C-4 thiophene), 121.6 (C-3), 120.5 (C-4), 117.3 (C-5), 90.9 ($\equiv C$), 83.7 (C $\equiv$).

1-Ethyl-5-(3-oxo-3-phenylprop-1-ynyl)-1H-pyrrole-2-carbaldehyde (4d).

Yield: 484 mg (84%); yellow solid; mp 84–86 °C. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57%. Found: C, 76.19; H, 5.30; N, 5.21. IR (KBr): 2183 ($C\equiv C$), 1662 (HCO), 1634 (CO) cm^{-1} . 1H NMR (400.1 MHz, $CDCl_3$): δ = 9.65 (1H, s, H-CO), 8.18–8.16 (2H, m, *Ho* Ph), 7.68–7.64 (1H, m, *Hp* Ph), 7.56–7.52 (2H, m, *Hm* Ph), 6.95 (1H, d, J = 4.0 Hz, H-4), 6.81 (1H, d, J = 4.0 Hz, H-3), 4.62 (2H, q, J = 7.2 Hz, CH_2), 1.45 (3H, t, J = 7.2 Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 179.8 (HC=O), 177.2 (C=O), 136.8 (Ci), 134.5 (Cp), 133.6 (C-2), 129.5 (Co), 128.9 (Cm), 123.2 (C-3), 120.8 (C-5), 119.7 (C-4), 94.9 ($\equiv C$), 83.0 (C $\equiv$), 42.7 (CH_2), 16.6 (CH_3).

1-Ethyl-5-[3-(furan-2-yl)-3-oxoprop-1-ynyl]-1H-pyrrole-2-carbaldehyde (4e).

Yield: 448 mg (81%); yellow solid; mp 82-84 °C. Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81%. Found: C, 69.58; H, 4.88; N, 5.47. IR (KBr): 2178 ($C\equiv C$), 1659 (HCO), 1620 (CO) cm^{-1} . 1H NMR (400.13 MHz, $CDCl_3$): δ = 9.63 (1H, s, H-CO), 7.71 (1H, dd, J = 0.7, 1.7 Hz, H-5 furan), 7.38 (1H, dd, J = 0.7, 3.5 Hz, H-3 furan), 6.93 (1H, d, J = 4.2 Hz, H-4), 6.77 (1H, d, J = 4.2 Hz, H-3), 6.63 (1H, dd, J = 1.7, 3.5 Hz, H-4 furan), 4.59 (2H, q, J = 7.2 Hz, CH_2), 1.42 (3H, t, J = 7.2 Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 179.7 (HC=O), 164.0 (C=O), 153.1 (C-2 furan), 148.2 (C-5 furan), 133.6 (C-2), 123.1 (C-3), 120.6 (C-5), 120.4 (C-4), 119.6 (C-3 furan), 113.0 (C-4 furan), 94.0 ($\equiv C$), 82.2 (C $\equiv$), 42.6 (CH_2), 16.6 (CH_3).

1-Ethyl-5-[3-oxo-3-(thiophen-2-yl)prop-1-ynyl]-1H-pyrrole-2-carbaldehyde (4f).

Yield: 525 mg (89%); yellow solid; mp 90-92 °C. Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; S, 12.46%. Found: C, 65.21; H, 4.28; N, 5.15; S, 12.08. IR (KBr): 2181 ($C\equiv C$), 1663 (HCO), 1604 (CO) cm^{-1} . 1H NMR (400.13 MHz, $CDCl_3$): δ = 9.65 (1H, s, H-CO), 7.96 (1H, dd, J = 1.0, 3.8 Hz, H-3 thiophene), 7.77 (1H, dd, J = 1.0, 4.9 Hz, H-5 thiophene), 7.22 (1H, dd, J = 3.8, 4.9 Hz, H-4 thiophene), 6.94 (1H, d, J = 4.2 Hz, H-4), 6.79 (1H, d, J = 4.2 Hz, H-3), 4.61 (2H, q, J = 7.2 Hz, CH_2), 1.44 (3H, t, J = 7.2 Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 179.7 (HC=O), 168.7 (C=O), 144.5 (C-2 thiophene), 135.6 (C-3 thiophene), 134.6 (C-5 thiophene), 133.5 (C-2), 128.6 (C-4 thiophene), 123.1 (C-3), 120.6 (C-5), 119.7 (C-4), 94.3 ($\equiv C$), 81.6 (C $\equiv$), 42.6 (CH_2), 16.6 (CH_3).

Data of X-Ray analysis of 4-[3-(furan-2-yl)-3-oxoprop-1-yl]-1H-pyrrole-2-carbadehyde (4b).

Figure 1. X-ray determined unit cell of 4-[3-(furan-2-yl)-3-oxoprop-1-yl]-1H-pyrrole-2-carbadehyde (**4b**).

The final anisotropic full-matrix least-squares refinement on F^2 with 145 variables converged at $R1 = 4.30\%$, for the observed data and $wR2 = 11.07\%$ for all data. The goodness-of-fit was 1.018. The largest peak in the final difference electron density synthesis was $0.310 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.258 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.054 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.433 g/cm^3 and $F(000)$, 440 e^- .

Figure 2. X-ray structure of 4-[3-(furan-2-yl)-3-oxoprop-1-yl]-1H-pyrrole-2-carbadehyde (**4b**).

Figure 3. The structure of $C_{12}H_7N_1O_3$ is almost planar. The nonplanarity of formyl group in according to heterocyclic frame is about 12° . The going out of the carbonyl oxygen from the plane is about 0.6 Å.

Figure 4. The space orientation of molecules is appropriate to form an intermolecular hydrogen bond N-H...O type and formation of molecular dimers.

Figure 5. The distance between O...H is 1.989 Å. In the crystal lattice the orientation of molecules have a parquet structure.

II. Selected of ^1H , ^{13}C NMR spectra

Ethynylpyrroles **5a-f**.

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrrol-2-yl]-1-phenylprop-2-yn-1-one (**5a**)

^1H spectrum of **5a** (400.13 MHz, CDCl_3)

^{13}C spectrum of **5a** (100.61 MHz, CDCl_3)

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrrol-2-yl]-1-(furan-2-yl)prop-2-yn-1-one (5b**).**

¹H spectrum of **5b** (400.13 MHz, C₆D₆)

¹³C spectrum of **5b** (100.61 MHz, C₆D₆)

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrrol-2-yl]-1-(thiophen-2-yl)prop-2-yn-1-one (5c).

¹H spectrum of **5c** (400.13 MHz, CDCl₃)

¹³C spectrum of **5c** (100.61 MHz, CDCl₃)

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-ethyl-1*H*-pyrrol-2-yl]-1-phenylprop-2-yn-1-one (5d**).**

¹H spectrum of **5d** (400.13 MHz, CDCl₃)

¹³C spectrum of **5d** (100.61 MHz, CDCl₃)

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-ethyl-1H-pyrrol-2-yl]-1-(furan-2-yl)prop-2-yn-1-one (5e).

¹H spectrum of **5e** (400.13 MHz, CDCl₃)

¹³C spectrum of **5e** (100.61 MHz, CDCl₃)

3-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-ethyl-1H-pyrrol-2-yl]-1-(thiophen-2-yl)prop-2-yn-1-one (5f).

^1H spectrum of **5f** (400.13 MHz, CDCl_3)

^{13}C spectrum of **5f** (100.61 MHz, CDCl_3)

5-Ethynylpyrrole-2-carbaldehydes 4a-f.

5-(3-Oxo-3-phenylprop-1-ynyl)-1H-pyrrole-2-carbaldehyde (4a).

¹H spectrum of **4a** (400.13 MHz, acetone-d₆)

¹³C spectrum of **4a** (100.61 MHz, acetone-d₆)

5-[3-(Furan-2-yl)-3-oxopropyn-1-ynyl]-1*H*-pyrrole-2-carbaldehyde (**4b**).

¹H spectrum of **4b** (400.13 MHz, CDCl₃)

¹³C spectrum of **4b** (100.61 MHz, CDCl₃)

5-[3-Oxo-3-(thiophen-2-yl)prop-1-ynyl]-1*H*-pyrrole-2-carboxaldehyde (4c).

¹H spectrum of **4c** (400.13 MHz, acetone-d₆)

¹³C spectrum of **4c** (100.61 MHz, acetone-d₆)

1-Ethyl- 5-(3-oxo-3-phenylprop-1-ynyl)-1*H*-pyrrole-2-carbaldehyde (4d).

¹H spectrum of **4d** (400.13 MHz, CDCl₃)

¹³C spectrum of **4d** (100.61 MHz, CDCl₃)

1-Ethyl-5-[3-(furan-2-yl)-3-oxoprop-1-ynyl]-1*H*-pyrrole-2-carbaldehyde (4e).

¹H spectrum of **4e** (400.13 MHz, CDCl₃)

¹³C spectrum of **4e** (100.61 MHz, CDCl₃)

1-Ethyl-5-[3-oxo-3-(thiophen-2-yl)prop-1-ynyl]-1H-pyrrole-2-carbaldehyde (4f).

¹H spectrum of **4f** (400.13 MHz, CDCl₃)

¹³C spectrum of **4f** (100.61 MHz, CDCl₃)

References

- (1) Sheldrick, G. M. *Acta Crystallogr A* **2008**, *64*, 112–122.