Supporting Information

Direct catalytic synthesis of densely substituted 3-formylpyrroles from imines and 1,4-ketoaldehydes

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**General Experimental Methods:**

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on SiO$_2$ gel F-254 plates. Unless otherwise noted all reactions have been carried out with distilled and dried solvents. Oven (120 °C) dried glassware were used. All work up and purification were carried out with reagent grade solvents in air. The normal column chromatography was performed on silica gel (100-200 mesh) and Flash column chromatography was performed on silica gel (230-400 meshes) using the mixture of Hexane-EtOAc as eluting solvent. All reagents were of analytical grade and used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a BRUKER-AV400 (400 MHz and 75 MHz) spectrometer in CDCl$_3$ solution and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. High resolution mass spectra were recorded using quadrupole electrospray ionization (ESI) technique. Infrared (FT-IR) spectra were recorded on a ABB Bomen MB 3000 FTIR Spectrophotometer system using KBr pellets. Melting points were recorded in open glass capillary tubes on a MPA 120-automated melting point apparatus and are uncorrected.

**General Experimental procedure for the synthesis of Hydroxy Ketones from Lactones**$^{(1)}$:

**Synthesis of 4-Hydroxy-1-phenylbutan-1-one:**

Bromobenzene (1.81 g, 11.6 mmol, 1.0 equiv.) in dry THF (10.0 mL) was added drop wise with the help of syringe to a stirred solution of crushed magnesium turnings (0.56 g, 23.2 mmol, 2.0 equiv.) in dry THF (10 mL, freshly distilled from sodium/benzophenone) at room temperature for one hour under inert atmosphere. This prepared Grignard reagent solution was cooled at 0 °C and then added drop wise through canula to the stirred solution of butyrolactone (1.0 g, 11.6 mmol, 1 equiv.) in THF (10 mL) at 0 °C over 30 minutes. The combined reaction mixture was stirred at 0 °C for additional 2 h and then quenched by NH$_4$Cl (15 mL, saturated) and organic
layer was separated. The aqueous layer was again extracted with EtOAc (2 x 10 mL). The combined extracts were washed by brine (15 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography (Hexane: EtOAc, 20:1 to 5:1) to give the desired keto-alcohol as white semi solid (1.30 g, 68% yield).

White semi solid, ¹H NMR (400 MHz, CDCl₃) δ 1.89-1.96 (m, 2H), 3.05 (t, J = 7.0 Hz, 2H), 3.65 (t, J = 6.2 Hz, 2H), 3.98 (bs, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.92 (d, J = 7.2 Hz, 2H);

**General Experimental procedure for the synthesis of 4-Oxo-4-phenylbutanal (2a):**

4-Hydroxy-1-phenylbutan-1-one (0.5 g, 3.0 mmol, 1 equiv.) solution in dichloromethane (2.5 mL) was added to a stirred solution of PCC (0.98 g, 4.6 mmol, 1.5 equiv.) and celite (0.25 g) in dichloromethane (2.5 mL) and stirred for 3 hrs at room temperature. The reaction was monitored by TLC till completion. Filter the reaction mixture over a pad of Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane: EtOAc = 90:10 to 70:30) to give the desired product 2a as a yellow oily liquid (0.272 g, 55% yield).

Yellow oily liquid, ¹H NMR (400 MHz, CDCl₃) δ 2.79-2.97 (m, 2H), 3.31 (t, J = 6.3Hz, 2H), 7.40-7.48 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.98 (d, J = 7.6 Hz, 2H), 9.90 (s, 1H) ; ¹³C NMR (75 MHz, CDCl₃) δ 30.97, 37.54, 128.00 (2C), 128.60 (2C), 133.27, 136.37, 197.83, 200.70; IR (KBr)/cm⁻¹ 2923,1728, 1681, 1211, 979, 694; HRMS (ESI): Calcd for C₁₀H₁₀O₂ (M+H⁺) 163.0759; Found 163.0763.

Typical procedure for the synthesis of 2,5-diaryl pyrrole-3-carboxaldehydes (4):

4-Oxo-4-phenylbutanal 2a (0.9 mmol, 3M solution) was added to a mixture of preformed N-PMP aldimine 3c (0.3 mmol) and L-proline (0.06 mmol) in DMSO (3.0 mL) at room temperature. The reaction mixture was stirred at room temperature until the aldimine was consumed as monitored by TLC. The reaction was quenched with cold water (10 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification through silica gel column chromatography by eluting the mixture of EtOAc/Hexane to give 2,5-diaryl pyrrole 3-carboxaldehydes 4 with high yields (70%). In almost all the cases, we also obtained about ≤10% of aromatic aldehyde due to cleavage of corresponding imine under these conditions.

Figure 1: Plausible mechanism of the cascade [4+2] annulation reaction
1-(4-methoxyphenyl)-2-(2-nitrophenyl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4aa):

Yellow pasty liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.68 (s, 3H), 6.67 (s, 1H), 6.76 (d, $J$ = 8.8 Hz, 2H), 6.92-6.95 (m, 2H), 6.98 (d, $J$ = 8.8 Hz, 2H), 7.02-7.05 (m, 3H), 7.26-7.30 (m, 2H), 7.68-7.73 (m, 2H), 9.86 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.41, 109.30, 114.61 (2C), 122.32, 125.96, 126.95, 128.03 (2C), 128.11 (2C), 128.31 (2C), 128.54 (2C), 129.35 (2C), 129.60, 131.80, 133.15, 136.14, 142.28, 159.58, 185.93; IR (KBr)/cm$^{-1}$ 2932, 1674, 1512, 1250, 1173; HRMS (ESI): Calcd for C$_{24}$H$_{18}$N$_2$O$_4$ (M+H$^+$) 399.1346; Found 399.1348.

1-(4-methoxyphenyl)-2-(3-nitrophenyl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4ab):

Reddish brown solid (M.P = 154-155 °C), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.75 (s, 3H), 6.74 (d, $J$ = 8.8 Hz, 2H), 6.91 (d, $J$ = 8.8 Hz, 2H), 6.98 (s, 1H), 7.10-7.12 (m, 2H), 7.20-7.25 (m, 3H), 7.41 (d, $J$ = 7.7 Hz, 1H) 7.53-7.57 (m, 1H), 8.05-8.11 (m, 1H), 8.14-8.22 (m, 1H), 9.73 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.33, 107.97, 114.33 (2C), 123.20, 124.39, 125.76, 125.93, 127.54, 128.21(2C), 128.75 (2C), 129.07, 129.56 (2C), 131.17, 131.33, 136.83, 137.63, 140.24, 147.65, 159.23, 185.98; IR (KBr)/cm$^{-1}$ 2932, 2854, 1666, 1512, 1342, 1172; HRMS (ESI): Calcd for C$_{24}$H$_{18}$N$_2$O$_4$ (M+H$^+$) 399.1346; Found 399.1342.

1-(4-methoxyphenyl)-2-(4-nitrophenyl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4ac):

Yellow solid (M.P = 163-164 °C), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.77 (s, 3H), 6.75 (d, $J$ = 8.9 Hz, 2H), 6.89 (d, $J$ = 8.8 Hz, 2H), 7.09-7.11 (m, 2H), 7.23 (t, $J$ = 3.5 Hz, 3H), 7.37 (d, $J$ = 8.6 Hz, 2H), 8.15 (d, $J$ = 8.7 Hz, 2H), 9.75 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.35,
108.33, 114.35 (2C), 123.18 (2C), 124.57, 127.59, 127.97, 128.22 (2C), 128.78 (2C), 129.46 (2C), 131.81 (2C), 133.04, 133.23, 137.91, 140.19, 147.28, 159.25, 186.04; IR (KBr)/cm\(^{-1}\): 2924, 2854, 1674, 1596, 1342, 1172; HRMS (ESI): Calcd for C\(_{24}\)H\(_{18}\)N\(_2\)O\(_4\) (M+H\(^+\)) 399.1346; Found 399.1338.

2-(2-fluorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1\(H\)-pyrrole-3-carbaldehyde (4ad):

Reddish solid (M.P = 145-146 °C) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.73 (s, 3H), 6.69 (d, \(J = 8.3\) Hz, 2H), 6.92 (d, \(J = 6.2\) Hz, 2H), 6.97 (s, 1H), 7.01 (t, \(J = 8.8\) Hz, 1H) 7.12 (m, 3H), 7.20 (m, 4H), 7.34 (m, 1H), 9.62 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.26, 107.29, 113.81, 115.66, 123.78, 123.81, 124.63, 127.26, 128.13 (2C), 128.64 (2C), 129.10, 129.95, 131.16, 131.22, 131.58, 133.30, 137.43, 138.03, 158.90, 161.33, 186.36; IR (KBr)/cm\(^{-1}\) 2932, 2854, 1659, 1250, 1180, 1026; HRMS (ESI): Calcd for C\(_{24}\)H\(_{18}\)FNO\(_2\) (M+H\(^+\)) 372.1400; Found 372.1409.

2-(3-fluorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1\(H\)-pyrrole-3-carbaldehyde (4ae):

Yellow liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.76 (s, 3H), 6.73 (d, \(J = 8.9\) Hz, 2H), 6.88-6.91 (m, 3H), 6.96 (s, 1H), 6.99-7.05 (m, 2H), 7.09-7.11 (m, 2H), 7.20-7.24 (m, 3H), 7.42 (d, \(J = 7.3\) Hz, 1H), 9.71 (s, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.34, 107.36, 114.14 (2C), 124.18, 125.36 (2C), 127.08, 127.34, 128.15, 128.58 (2C), 128.79, 129.50, 129.64, 129.75, 131.55, 137.13, 159.07, 163.30, 186.63; IR (KBr)/cm\(^{-1}\) 2908, 1680, 1247, 1174; HRMS (ESI): Calcd for C\(_{24}\)H\(_{18}\)FNO\(_2\) (M+H\(^+\)) 372.1400; Found 372.1395.

2-(4-fluorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1\(H\)-pyrrole-3-carbaldehyde (4af):

Yellow liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.76 (s, 3H), 6.73 (d, \(J = 8.9\) Hz, 2H), 6.87 (d, \(J = 8.9\) Hz, 2H), 6.95 (s, 1H), 6.99 (t, \(J = 8.7\) Hz, 2H), 7.09-7.11 (m, 2H), 7.16-7.22 (m, 5H), 9.68 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.33, 107.21, 114.08 (2C), 115.17, 115.35, 124.02,
127.28, 128.14 (2C), 128.78 (2C), 129.56 (2C), 129.79, 131.58, 132.90, 132.96, 136.88, 142.96 (2C), 158.93, 176.15, 186.76; IR (KBr)/cm⁻¹ 2924, 2854, 1659, 1218, 1157, 1049; HRMS (ESI): Calcd for C₂₄H₁₈FNO₂ (MH⁺) 372.1400; Found 372.1397.

2-(2-chlorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4ag):

Red oily liquid, ¹H NMR (400 MHz, CDCl₃) δ 3.72 (s, 3H), 6.67 (d, J = 9.1 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 6.96 (s, 1H), 7.11-7.14 (m, 2H), 7.19-7.23 (m, 4H), 7.27-7.31 (m, 2H), 7.37 (d, J = 8.2 Hz, 1H), 9.53 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 55.26, 106.98, 113.80 (2C), 124.39, 126.25 (2C), 127.20 (2C), 129.11 (2C), 129.30, 129.51 (2C), 129.96, 135.53 (2C), 131.65, 133.49, 135.57, 136.96, 141.26, 158.89, 186.21; IR (KBr)/cm⁻¹ 2924, 1666, 1250, 1180; HRMS (ESI): Calcd for C₂₄H₁₈CINO₂ (M+H⁺) 388.1104; Found 388.1106.

2-(3-chlorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4ah):

Brownish red oily liquid, ¹H NMR (400 MHz, CDCl₃) δ 3.75 (s, 3H), 6.72 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.94 (s, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.09 (dd, J = 7.0 Hz, 5.9 Hz, 2H), 7.17-7.24 (m, 6H), 9.69 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 55.38, 107.43, 114.18 (2C), 124.28, 127.36, 127.88 (2C), 128.16 (2C), 128.80 (2C), 129.23, 129.31, 129.57 (2C), 131.14, 131.34, 131.56, 134.00, 137.21, 143.03, 159.13 , 186.53; IR (KBr)/cm⁻¹ 2932, 1666, 1250, 1165, 1034; HRMS (ESI): Calcd for C₂₄H₁₈CINO₂ (M+H⁺) 388.1104; Found 388.1094.

2-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4ai):

Yellow viscous oily liquid, ¹H NMR (400 MHz, CDCl₃) δ 3.76 (s, 3H), 6.74 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 6.96 (s, 1H), 7.08-7.11 (m, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.19-7.24 (m, 3H), 7.27-7.30 (m, 3H) 9.70 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 55.31, 107.42, 114.14 (2C), 124.08, 127.30, 128.12 (2C), 128.34 (2C), 128.75 (2C), 129.54 (2C), 129.72,
131.53, 132.32 (2C), 134.70, 137.08, 142.68, 152.98, 159.02, 186.55; IR (KBr)/cm$^{-1}$ 2924, 2854, 1659, 1250, 1157, 1088; HRMS (ESI): Calcd for C$_{24}$H$_{18}$ClNO$_2$ (M+H$^+$) 388.1104; Found 388.1103.

2-(2-bromophenyl)-1-(4-methoxyphenyl)-5-phenyl-1$H$-pyrrole-3-carbaldehyde (4aj):

Reddish viscous oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.69 (s, 3H), 6.64 (d, $J$ = 9.1 Hz, 2H), 6.93 (m, 3H), 7.07-7.12 (m, 2H), 7.15-7.21 (m, 4H), 7.22-7.25 (m, 2H), 7.53 (d, $J$ = 8.0 Hz, 1H), 9.50 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.22, 106.78, 113.74 (2C), 124.12, 125.89, 126.78, 127.15, 128.12 (2C), 128.48 (2C), 129.14 (2C), 129.84, 130.63, 131.32, 131.57, 132.58, 133.48, 136.74, 142.89, 158.82, 186.22; IR (KBr)/cm$^{-1}$ 2924, 2854, 1674, 1242, 1173, 1034; HRMS (ESI): Calcd for C$_{24}$H$_{18}$BrNO$_2$ (M+H$^+$) 432.0599; Found 432.0605.

2-(3-bromophenyl)-1-(4-methoxyphenyl)-5-phenyl-1$H$-pyrrole-3-carbaldehyde (4ak):

Slight yellow solid (M.P = 170-171 °C) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.73 (s, 3H), 6.75 (d, $J$ = 8.8 Hz, 2H), 6.92 (d, $J$ = 8.9 Hz, 2H), 7.02 (s, 1H), 7.11-7.17 (m, 5H), 7.20-7.24 (m, 4H), 9.76 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.11, 107.17, 113.99 (2C), 121.76, 124.05, 124.83, 127.18, 127.80, 127.97 (2C), 128.07, 128.14, 128.55 (2C), 129.31, 129.37 (2C), 129.53, 131.28, 133.74 137.01, 158.94, 186.16; IR (KBr)/cm$^{-1}$ 2924, 2854, 1659, 1250, 1157, 1041; HRMS (ESI): Calcd for C$_{24}$H$_{18}$BrNO$_2$ (M+H$^+$) 432.0599; Found 432.0602.

2-(4-bromophenyl)-1-(4-methoxyphenyl)-5-phenyl-1$H$-pyrrole-3-carbaldehyde (4al):

White solid (M.P = 167-168 °C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.61 (s, 3H), 6.58 (d, $J$ = 8.9 Hz, 2H), 6.72 (d, $J$ = 8.9 Hz, 2H), 6.80 (s, 1H), 6.91 (d, $J$ = 8.4 Hz, 2H), 6.94 (dd, $J$ = 6.6, 3.0 Hz, 2H), 7.00-7.08 (m, 3H), 7.27 (d, $J$ = 8.3 Hz, 2H), 9.54 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$)
δ 55.31, 107.42, 114.13 (2C), 122.99, 124.00, 125.31, 127.30, 127.83, 128.12 (2C), 128.54, 128.73 (2C), 129.51 (2C), 131.27 (2C), 132.55 (2C), 137.07, 142.65, 158.97, 186.57; IR (KBr)/cm\(^{-1}\) 2932, 2847, 1666, 1250, 1168, 1034; HRMS (ESI): Calcd for C\(_{24}\)H\(_{18}\)BrNO\(_2\) (M+H\(^+\)) 432.0599; Found 432.0595.

2-(3-bromo-4-fluorophenyl)-1-(4-methoxyphenyl)-5-phenyl-1\(H\)-pyrrole-3-carbaldehyde (4am):

Yellow liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 3.77 (s, 3H), 6.75 (d, \(J = 8.9\) Hz, 2H), 6.89 (d, \(J = 8.9\) Hz, 2H), 6.95 (s, 1H), 7.00-7.11 (m, 4H), 7.20-7.23 (m, 3H), 7.46 (dd, 6.5, 2.0 Hz, 1H), 9.70 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 55.38, 107.42, 108.91, 114.22 (2C), 116.06, 116.24, 124.22, 127.40, 128.17 (2C), 128.73 (2C), 129.52 (2C), 131.36, 131.65, 131.71, 136.08, 137.19, 142.94, 159.11, 176.12, 186.30; IR (KBr)/cm\(^{-1}\) 2924, 2854, 1666, 1250, 1157, 1041; HRMS (ESI): Calcd for C\(_{24}\)H\(_{17}\)BrFNO\(_2\) (M+H\(^+\)) 450.0505; Found 450.0511.

1-(4-methoxyphenyl)-5-phenyl-2-(4-(trifluoromethyl)phenyl)-1\(H\)-pyrrole carbaldehyde (4an):

Yellow oily liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 3.75 (s, 3H), 6.72 (d, \(J = 8.9\) Hz, 2H), 6.87 (d, \(J = 8.9\) Hz, 2H), 6.97 (s, 1H), 7.04-7.15 (m, 2H), 7.15-7.23 (m, 3H), 7.26 (d, \(J = 6.3\) Hz, 2H), 7.54 (d, \(J = 8.1\) Hz, 2H), 9.70 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 55.32, 107.68, 114.20 (2C), 124.32, 124.94, 124.97, 127.41, 127.84 (2C), 128.16 (2C), 128.77(2C), 129.49 (2C), 131.37 (2C), 133.17, 137.38, 141.85, 142.94 (2C), 159.06, 186.41; IR (KBr)/cm\(^{-1}\) 2924, 2854, 1674, 1250, 1118; HRMS (ESI): Calcd for C\(_{25}\)H\(_{18}\)F\(_3\)NO\(_2\) (M+H\(^+\)) 422.1368; Found 422.1374.

1-(4-methoxyphenyl)-2,5-diphenyl-1\(H\)-pyrrole-3-carbaldehyde (4ao):
Yellow viscous liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.75 (s, 3H), 6.71 (d, $J = 8.9$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 6.96 (s, 1H), 7.11 (dd, $J = 7.4$ Hz, 5.9 Hz, 2H), 7.18-7.22 (m, 5H), 7.27-7.32 (m, 3H), 9.69 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.32, 107.17, 114.00 (2C), 123.98, 123.37 (2C), 127.20, 127.88, 128.42, 128.59 (2C), 128.80 (2C), 129.45, 129.65 (2C), 130.06, 131.20 (2C), 131.77, 136.81, 158.89, 187.11; IR (KBr)/cm$^{-1}$ 2924, 2854, 1666, 1242, 1165, 1034; HRMS (ESI): Calcd for C$_{24}$H$_{19}$NO$_2$ (M+H$^+$) 354.1494; Found 354.1498.

1-(4-methoxyphenyl)-2-(naphthalen-1-yl)-5-phenyl-1$H$-pyrrole-3-carbaldehyde (4ap):

Deep red pasty liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.62 (s, 3H), 6.51 (d, $J = 8.2$ Hz, 2H), 6.82 (d, $J = 8.2$ Hz, 2H), 7.05 (s, 1H), 7.15-7.17 (m, 2H), 7.21-7.24 (m, 3H), 7.38-7.46 (m, 4H), 7.70 (d, $J = 8.9$ Hz, 1H), 7.81-7.85 (m, 2H), 9.39 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.16, 106.86, 113.68 (2C), 124.64, 125.34, 125.80, 126.15, 126.81, 127.16, 127.28, 128.18 (2C), 128.58 (2C), 128.87, 129.53, 130.21, 130.46, 131.82, 133.13, 133.76, 137.01, 143.11, 157.68, 157.87, 158.64, 186.79; IR (KBr)/cm$^{-1}$ 3016, 1658, 1512, 1249, 1172; HRMS (ESI): Calcd for C$_{28}$H$_{21}$NO$_2$ (M+H$^+$) 404.1650; Found 404.1654.

1-(4-methoxyphenyl)-2-(naphthalen-2-yl)-5-phenyl-1$H$-pyrrole-3-carbaldehyde (4aq):

White solid (M.P = 176-177 $^\circ$C) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.72 (s, 3H), 6.68 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 7.01 (s, 1H), 7.12 - 7.15 (m, 3H), 7.22-7.24 (m, 3H), 7.52 (dd, $J = 6.1$ Hz, 3.3 Hz, 2H), 7.68 ( d, $J = 8.5$ Hz, 1H), 7.81 (dd, $J = 6.0$, 3.4 Hz, 2H), 7.84 (s, 1H), 9.75 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.29, 107.33, 114.07 (2C), 124.25, 126.61, 126.89, 127.24, 127.60, 127.66, 127.81, 127.88, 128.15 (2C), 128.20, 128.81 (2C), 129.60 (2C), 130.06, 131.19, 131.74, 132.60, 132.69, 136.94, 139.28, 158.86, 187.24; IR (KBr)/cm$^{-1}$ 2922, 2916, 2854, 1666, 1512, 1435, 1373, 1249, 1172; HRMS (ESI): Calcd for C$_{28}$H$_{21}$NO$_2$ (M+H$^+$) 404.1650; Found 404.1648.
1-(4-methoxyphenyl)-5-phenyl-2-(pyridin-2-yl)-1H-pyrrole-3-carbaldehyde (4ar):

Reddish brown pasty liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.76 (s, 3H), 6.73 (d, $J = 8.9$ Hz, 2H), 6.96 (d, $J = 8.9$ Hz, 2H), 6.98 (s, 1H), 7.05 (d, $J = 7.9$ Hz, 1H), 7.08-7.11 (m, 2H), 7.18-7.22 (m, 4H), 7.55 (t, $J = 7.8$, 1.8 Hz, 1H), 8.62 (d, $J = 4.1$, 1H), 9.91 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.33, 107.78, 114.00 (2C), 122.60, 125.10, 126.10, 127.30, 128.11 (2C), 128.89 (2C), 129.51 (2C), 130.19, 131.64, 135.73, 137.23, 141.75, 149.24, 149.53, 158.97, 187.58; IR (KBr)/cm$^{-1}$ 2932, 1659, 1250, 1173; HRMS (ESI): Calcd for C$_{23}$H$_{18}$N$_2$O$_2$ (M+H$^+$) 355.1446; Found 355.1442.

1-(4-methoxyphenyl)-5-phenyl-2-(pyridin-3-yl)-1H-pyrrole-3-carbaldehyde (4as):

Reddish brown pasty liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.76 (s, 3H), 6.73 (d, $J = 8.9$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 6.99 (s, 1H), 7.10-7.12 (m, 2H), 7.22 (t, $J = 3.3$ Hz, 4H), 7.49-7.52 (m, 1H), 8.49 (s, 1H), 8.55 (d, $J = 3.9$ Hz, 1H), 9.71 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.33, 107.83, 114.31 (2C), 122.90, 124.69, 126.06, 127.47, 128.18 (2C), 128.77 (2C), 129.35, 129.63 (2C), 131.33, 137.71, 138.39, 139.72, 149.08, 150.93, 159.22, 186.12; IR (KBr)/cm$^{-1}$ 2932, 1666, 1250, 1180, 1026; HRMS (ESI): Calcd for C$_{23}$H$_{18}$N$_2$O$_2$ (M+H$^+$) 355.1446; Found 355.1448.

1-(4-methoxyphenyl)-5-phenyl-2-(pyridin-4-yl)-1H-pyrrole-3-carbaldehyde (4at):

Yellow pasty liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.76 (s, 3H), 6.74 (d, $J = 8.9$ Hz, 2H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.97 (s, 1H), 7.07-7.09 (m, 4H), 7.21 (m, 3H), 8.55 (bs, 2H), 9.75 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.31, 108.03, 114.25 (2C), 124.41, 125.41, 127.50 (2C), 128.18 (2C), 128.73 (2C), 129.24, 129.38 (2C), 131.08, 137.57, 137.83, 139.88, 149.32 (2C), 159.19, 186.07; IR (KBr)/cm$^{-1}$ 2931, 1674, 1250, 1173, 1026; HRMS (ESI): Calcd for C$_{23}$H$_{18}$N$_2$O$_2$ (M+H$^+$) 355.1446; Found 355.1444.
1-(4-methoxyphenyl)-5-phenyl-2-(thiophen-2-yl)-1H-pyrrole-3-carbaldehyde (4au):

Yellowish orange pasty liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.78 (s, 3H), 6.78 (d, \(J = 8.9\) Hz, 2H), 6.96-7.00 (m, 5H), 7.11-7.13 (m, 2H), 7.21 (t, \(J = 3.7\) Hz, 4H), 9.86 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.36, 89.71, 107.40, 114.08 (2C), 121.88, 126.81, 127.38, 127.88 (2C), 128.15 (2C), 128.73 (2C), 129.87 (2C), 130.81, 131.50, 137.70, 142.99, 159.38, 186.90; IR (KBr)/cm\(^{-1}\) 2924, 2854, 1666, 1242, 1173 1034; Found 356.0295. HRMS (ESI): Calcd for C\(_{22}\)H\(_{17}\)NO\(_2\)S (M+H\(^{+}\)) 360.1058; Found 360.1064.

1-(4-methoxyphenyl)-5-phenyl-2-(p-tolyl)-1H-pyrrole-3-carbaldehyde (4av):

Brown pasty liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.33 (s, 3H), 3.76 (s, 3H), 6.72 (d, \(J = 8.5\) Hz, 2H), 6.88 (d, \(J = 8.4\) Hz, 2H), 6.95 (s, 1H), 7.08 (m, 5H), 7.20 (m, 2H), 7.35 (t, \(J = 7.3\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 9.69 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 22.67, 55.34, 107.09, 113.97 (2C), 123.88, 125.34, 126.41, 127.12, 127.86, 128.08, 128.57, 128.75 (2C), 129.62, 130.16, 131.03 (2C), 131.84, 136.69, 138.36, 143.00, 144.79, 158.84, 187.16; IR (KBr)/cm\(^{-1}\) 2914, 1668, 1248, 1178; HRMS (ESI): Calcd for C\(_{25}\)H\(_{21}\)NO\(_2\) (M+H\(^{+}\)) 368.1650; Found 368.1648.

1-(4-methoxyphenyl)-2-(4-nitrophenyl)-5-(p-tolyl)-1H-pyrrole-3-carbaldehyde (4bc):

Yellow solid, (M.P = 156-157 °C) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.30 (s, 3H), 3.77 (s, 3H), 6.75 (d, \(J = 8.8\) Hz, 2H), 6.99 (d, \(J = 8.8\) Hz, 2H), 6.95 (s, 1H), 6.98 (d, \(J = 8.1\) Hz, 2H), 7.04 (d, \(J = 8.1\) Hz, 2H), 7.36 (d, \(J = 8.6\) Hz, 2H), 8.14 (d, \(J = 8.7\) Hz, 2H), 9.74 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 21.15, 55.37, 107.98, 114.34 (2C), 123.19 (2C), 124.55, 128.12, 128.67 (2C), 128.98 (2C), 129.49 (2C), 130.17, 131.82 (2C), 136.26, 137.53, 138.08, 140.08, 147.27, 159.22, 186.14;
IR (KBr)/cm\(^{-1}\) 2936, 2862, 1782, 1234; HRMS (ESI): Calcd for C\(_{25}\)H\(_{20}\)N\(_2\)O\(_4\) (M+H\(^+\)) 413.1501; Found 413.1505.

5-(3-methoxyphenyl)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1\(H\)-pyrrole-3-carbaldehyde (4cc):

![Structure of 5-(3-methoxyphenyl)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1\(H\)-pyrrole-3-carbaldehyde (4cc)](image)

Yellow liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.65 (s, 3H), 3.77 (s, 3H), 6.64-6.69 (m, 2H), 6.75-6.79 (m, 3H), 6.90 (d, \(J = 8.9\) Hz, 2H), 7.00 (s, 1H), 7.13 (t, \(J = 8.0\) Hz, 1H), 7.38 (d, \(J = 8.8\) Hz, 2H), 8.15 (d, \(J = 8.8\) Hz, 2H), 9.75 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.09, 55.43, 108.50, 113.70, 114.08, 114.42 (2C), 121.28, 123.21 (2C), 124.63, 129.27, 129.44, 129.50 (2C), 131.86 (2C), 132.40, 136.24, 137.80, 140.29, 147.40, 159.26, 159.39, 186.00; IR (KBr)/cm\(^{-1}\) 2962, 2823, 1666, 1519,1342, 1234; HRMS (ESI): Calcd for C\(_{25}\)H\(_{20}\)N\(_2\)O\(_4\) (M+H\(^+\)) 429.1450; Found 429.1454.

1, 5-bis (4-methoxyphenyl)-2-(4-nitrophenyl)-1\(H\)-pyrrole-3-carbaldehyde (4dc):

![Structure of 1, 5-bis (4-methoxyphenyl)-2-(4-nitrophenyl)-1\(H\)-pyrrole-3-carbaldehyde (4dc)](image)

Yellow solid (M.P = 145-146 \(^\circ\)C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.77 (s, 6H), 6.75 (dd, \(J = 8.3\) Hz, 8.6 Hz, 4H), 6.86 (s, 1H), 6.90 (d, \(J = 8.8\) Hz, 2H), 7.01 (d, \(J = 8.7\) Hz, 2H), 7.35 (d, \(J = 8.6\) Hz, 2H), 8.14 (d, \(J = 8.6\) Hz, 2H), 9.74 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.36, 55.37, 107.60, 113.69 (2C), 114.34 (2C), 123.18 (2C), 124.54, 126.78, 129.38, 129.52 (2C), 130.12 (2C), 131.82 (2C), 136.29, 137.91, 139.88, 147.25, 159.06, 159.21, 186.10; IR (KBr)/cm\(^{-1}\) 2924, 2854, 1776, 1250, 1165, 1034; HRMS (ESI): Calcd for C\(_{25}\)H\(_{20}\)N\(_2\)O\(_5\) (M+H\(^+\)) 429.1450; Found 429.1452.

5-(4-fluorophenyl)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1\(H\)-pyrrole-3-carbaldehyde (4ec):

![Structure of 5-(4-fluorophenyl)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1\(H\)-pyrrole-3-carbaldehyde (4ec)](image)

Yellowish oily liquid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.78 (s, 3H), 6.75 (d, \(J = 8.9\) Hz, 2H), 6.86-6.90 (m, 3H), 7.05-7.14 (m, 4H), 7.35 (d, \(J = 8.8\) Hz, 2H), 8.14 (d, \(J = 8.6\) Hz, 2H), 9.74 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 55.09, 55.43, 108.50, 113.70, 114.08, 114.42 (2C), 121.28, 123.21 (2C), 124.63, 129.27, 129.44, 129.50 (2C), 131.86 (2C), 132.40, 136.24, 137.80, 140.29, 147.40, 159.26, 159.39, 186.00; IR (KBr)/cm\(^{-1}\) 2962, 2823, 1666, 1519,1342, 1234; HRMS (ESI): Calcd for C\(_{25}\)H\(_{20}\)N\(_2\)O\(_4\) (M+H\(^+\)) 413.1501; Found 413.1505.
7.36 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 9.75 (s, 1H); 13C NMR (75 MHz, CDCl3) δ 54.40, 107.34, 113.47 (2C), 114.29, 114.46, 122.25 (2C), 128.09, 128.48 (2C), 128.60, 129.44, 129.51, 129.58, 129.63, 130.51, 131.82 (2C), 135.11, 135.60, 135.94, 158.37, 185.00; IR (KBr)/cm⁻¹ 2962, 2885, 1782, 1342, 1172; HRMS (ESI): Calcd for C24H17FN2O4 (MH⁺) 417.1250; Found 417.1257.

**Typical procedure for the synthesis of (4-fluorophenyl)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1H-pyrrole-3-carbaldehyde (5):**

N- Bromosuccinimide (NBS) (22 mg, 0.125 mmol) was added to the stirred solution of pyrrole 4ec (50 mg, 0.125 mmol) in CH₃CN (4.0 mL) at rt and further heated at 80 °C for 4 hrs. The reaction was cooled to room temperature and solvent was evaporated under reduced pressure. The crude material was taken in saturated NaHCO₃ solution and extracted with ethyl acetate (2 x 5 mL), the combined organic layer was washed with brine and dried over Na₂SO₄ and concentrated under vacuo. Corresponding intermediate bromo compound (80 mg, 68%), was obtained as reddish oily liquid after simple chromatographic purification using EtOAc/hexane.

To the stirred solution of crude bromo compound (78 mg, 0.15 mmol) in DMF (3.0 mL) were added PhB(OH)₂ (1.5 equiv, 28 mg, 0.23 mmol), Pd (PPh₃)₄ (10 mol%, 18 mg, 0.015 mmol) and K₂CO₃ (2M solution, 78 μL, 0.15 mmol) under inert atmosphere. The reaction was then heated to 110 °C for 4 hrs. After complete consumption of the intermediate bromo compound on TLC, reaction was cooled and filtered through celite. After standard work up and chromatographic purification using (Hexane : EtOAc = 20:1) gave compound 5 (55 mg, 72%), as a yellow oily liquid.

**(4-fluorophenyl)-1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1H-pyrrole-3-carbaldehyde (5):**
Yellowish pasty liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.74 (s, 3H), 6.79 (d, $J = 8.8$ Hz, 2H), 6.79 (t, $J = 8.7$, 3H), 6.84 (d, $J = 8.8$ Hz, 2H), 6.90 (dd, $J = 8.8$ Hz, 5.4 Hz 2H), 7.04 (t, $J = 8.6$ Hz, 1H), 7.29 (m, 2H), 7.36 (dd, $J = 8.9$ Hz, 5.2 Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 2H), 8.13 (d, $J = 8.8$ Hz, 2H) 9.85 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 55.33, 114.15 (2C), 115.18, 115.69, 122.97 (2C), 125.74, 127.08, 127.19, 127.26, 128.07 (2C), 129.01, 129.65 (2C), 130.86 (2C), 132.06 (2C), 132.60, 132.82, 132.89, 133.58, 136.98, 137.29, 147.22, 159.15, 162.95, 186.91; IR (KBr)/cm$^{-1}$ 2923, 1728, 1512, 1350, 1226; HRMS (ESI): Calcd for C$_{30}$H$_{21}$F$_{2}$N$_{2}$O$_{4}$ (MH$^+$) 493.1563; Found 493.1567.
Crystal structure of 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)-5-phenyl-1H-pyrrole-3-carbaldehyde (4aq):

[CCDC - 1007133]

The title compound, 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)-5-phenyl-1H-pyrrole-3-carbaldehyde, crystallizes in the monoclinic space group P2_1/c with the following unit-cell parameters: a = 12.6491(8), b = 7.9932(4), c = 21.9541(13) Å, β= 105.450(7), Z = 4. The crystal structure was solved by direct methods using single-crystal X-ray diffraction data and refined by full-matrix least-squares procedures to a final R-value of 0.0489 for 2249 observed reflections.

X-ray intensity data of 7999 reflections (of which 4184 unique) were collected at room temperature on a CCD area-detector diffractometer (X’calibur system – Oxford diffraction make, U.K.) equipped with graphite monochromated MoKα radiation (λ=0.71073 Å). The crystal used for data collection was of dimensions 0.30 x 0.20 x 0.20 mm. The intensities were measured by ω scan mode for 0 ranges 3.77 to 26.0°. 2249 reflections were treated as observed (I > 2σ(I)). Data were corrected for Lorentz and polarisation factors. The structure was solved by direct methods using SHELXS97.(1) All non-hydrogen atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using SHELXL97 [1 All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-hydrogen atoms with C-H= 0.93-0.96 Å, and Uiso = 1.5Ueq of the attached C atom for methyl H atoms and 1.2 Ueq for other H atoms. The final refinement cycles converged to an R = 0.0489 and wR (F^2) = 0.1114 for the observed data. Residual electron densities ranged from -0.172 to 0.158 eÅ^3. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1. CCDC - 1007133 contains the supplementary crystallographic data for this paper.

Results and discussion
An ORTEP view of the title compound with atomic labeling is shown in Fig.1. The geometry of the molecule was calculated using the WinGX and PARST software's.

References


Table 1  Crystal and experimental data

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<td>Crystal description</td>
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<td>Formula weight</td>
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<td>Radiation, Wavelength</td>
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<tr>
<td>Crystal system</td>
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<td>Unit cell volume</td>
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</tbody>
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Density (calculated)  
1.253 Mgm$^{-3}$

No. of molecules per unit cell, Z  
4

Temperature  
273(2) K

Absorption coefficient($\mu$)  
0.078 mm$^{-1}$

F (000)  
848

Scan mode  
omega scan

$\theta$ range for entire data collection  
3.77$< \theta < 26.00$°

Reflections collected / unique  
7999/4184

Reflections observed (I > 2$\sigma$(I))  
2249

Structure determination  
Direct methods

Refinement  
Full-matrix least-squares on F$^2$

No. of parameters refined  
280

Final R  
0.0489

wR(F$^2$)  
0.1114

Weight  
\[1/[\sigma^2(F_o^2)+(0.0277P)^2+0.00P]\]

where P=[F_o^2+2F_c^2]/3

Goodness-of-fit  
0.918

( $\Delta$ /$\sigma$ )$_{\text{max}}$ in the final cycle  
0.008

Final residual electron density  
-0.172 $< \Delta \rho < 0.158$ eÅ$^{-3}$
Measurement

$X'calibur$ system – Oxford diffraction make,  U.K.

Software for structure solution:  SHELXS97 (Sheldrick, 1997)

Software for refinement:  SHELXL97 (Sheldrick, 1997)

Software for molecular plotting:  ORTEP-3 (Farrugia, 1997) PLATON (Spek, 2003)

Software for geometrical calculation  PLATON (Spek, 2003) PARST (Nardelli, 1995)

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**Figure 1**  *ORTEP* view of the molecule with displacement ellipsoids drawn at 40%. H atoms are shown as small spheres of arbitrary radii.

CCDC- 1007133  contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).