Supporting Information

**The Copper- or Phosphine-Catalyzed Reaction of Alkynes with Isocyanides.
Regioselective Synthesis of Substituted Pyrroles Controlled by the Catalyst**

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Analytical data

2,4-Di(ethoxycarbonyl)-3-methylpyrrole (3a): white solid; ^1H NMR (500 MHz, CDCl_3) δ 1.34 (3H, t, $J = 7.0$ Hz), 1.37 (3H, t, $J = 7.0$ Hz), 2.60 (3H, s), 4.28 (2H, q, $J = 7.0$ Hz), 4.34 (2H, q, $J = 7.0$ Hz), 7.47 (1H, d, $J = 3.5$ Hz), 9.29 (1H, br s: *NH*); ^{13}C NMR (126 MHz, CDCl_3) δ 11.24, 14.41 (x2), 59.70, 60.48, 117.05, 120.86, 126.80, 129.68, 161.55, 164.62; IR (KBr) 3292, 1716, 1666, 1277, 1198, 1070, 1028 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_4$: C, 58.63; H, 6.71; N, 6.21. Found: C, 58.60; H, 6.82; N, 6.15.

2,4-Di(ethoxycarbonyl)-3-(4-hydroxybutyl)pyrrole (3b): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 1.34 (3H, t, $J = 7.0$ Hz), 1.37 (3H, t, $J = 7.0$ Hz), 1.64-1.69 (4H, m), 3.10-3.15 (2H, m), 3.70-3.76 (2H, m), 4.28 (2H, q, $J = 7.0$ Hz), 4.34 (2H, q, $J = 7.0$ Hz), 7.46 (1H, d, $J = 3.5$ Hz), 9.11 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.37, 14.39, 24.13, 26.75, 32.12, 59.75, 60.48, 62.07, 115.91, 120.34, 127.23, 134.62, 161.21, 164.34; IR (neat) 3296, 2936, 1715, 1695, 1416, 1275, 1148, 1094, 1026 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_5$ (M^+) 283.1414. Found 283.1415.

2,4-Di(ethoxycarbonyl)-3-cyclohexylpyrrole (3c): white solid; ^1H NMR (400 MHz, CDCl_3) δ 1.30-1.82 (8H, br m), 1.34 (3H, t, $J = 7.0$ Hz), 1.38 (3H, t, $J = 7.0$ Hz), 2.13 (2H, dq, $J = 3.4, 12.0$ Hz), 3.75 (1H, tt, $J = 12.0, 3.6$ Hz), 4.26 (2H, q, $J = 7.0$ Hz), 4.33 (2H, q, $J = 7.0$ Hz), 7.44 (1H, d, $J = 3.5$ Hz), 9.12 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.44, 14.46, 25.91, 27.21, 30.30, 35.21, 59.80, 60.56, 116.25, 120.01, 127.45, 139.21, 160.92, 164.29; IR (KBr) 3300, 2932, 1715, 1661, 1416, 1263, 1192, 1094, 1026, 962 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_4$ (M^+) 293.1622. Found 293.1624.

2,4-Di(ethoxycarbonyl)-3-(*tert*-butyl)pyrrole (3d): colorless oil; ^1H NMR (400

MHz, CDCl₃) δ 1.33 (3H, t, J = 7.0 Hz), 1.35 (3H, t, J = 7.0 Hz), 1.46 (9H, s), 4.25 (2H, q, J = 7.0 Hz), 4.30 (2H, q, J = 7.0 Hz), 7.11 (1H, d, J = 3.5 Hz), 9.15 (1H, br s: *NH*); ¹³C NMR (100 MHz, CDCl₃) δ 14.25, 14.39, 30.79, 33.12, 60.70, 60.74, 118.69, 120.10, 123.66, 139.65, 160.57, 166.68; IR (neat) 3412, 1707, 1286, 1151, 1042, 959 cm⁻¹; HRMS (EI) Calcd for C₁₄H₂₁NO₄ (M⁺) 267.1465. Found 267.1466.

2,4-Di(ethoxycarbonyl)-3-phenylpyrrole (3e): white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.08 (3H, t, J = 7.0 Hz), 1.11 (3H, t, J = 7.0 Hz), 4.11 (2H, q, J = 7.0 Hz), 4.13 (2H, q, J = 7.0 Hz), 7.30-7.35 (5H, m), 7.57-7.60 (1H, m), 9.34 (1H, br s: *NH*); ¹³C NMR (75.5 MHz, CDCl₃) δ 13.80, 13.98, 59.75, 60.53, 117.21, 120.95, 126.81, 126.92, 127.05, 130.11, 132.33, 133.74, 161.03, 163.83; IR (KBr) 3292, 1688, 1285, 1267, 1176, 1120, 1028, 762, 700 cm⁻¹; Anal. Calcd for C₁₆H₁₇NO₄: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.58; H, 6.06; N, 4.83; HRMS (EI) Calcd for C₁₆H₁₇NO₄ (M⁺) 287.1152. Found 287.1156.

2,4-Di(ethoxycarbonyl)pyrrole (3f): white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.35 (3H, t, J = 7.0 Hz), 1.36 (3H, t, J = 7.0 Hz), 4.30 (2H, q, J = 7.0 Hz), 4.33 (2H, q, J = 7.0 Hz), 7.30 (1H, dd, J = 2.5, 1.5 Hz), 7.53 (1H, dd, J = 3.0, 1.5 Hz), 9.26 (1H, br s: *NH*); ¹³C NMR (75.5 MHz, CDCl₃) δ 14.25, 14.31, 60.07, 60.82, 115.88, 118.11, 123.68, 127.18, 161.16, 164.12; IR (KBr) 3277, 1697, 1290, 1204, 1092, 1020 cm⁻¹; Anal. Calcd for C₁₀H₁₃NO₄: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.60; H, 6.13; N, 6.57; HRMS (EI) Calcd for C₁₀H₁₂NO₄ (M⁺) 211.0839. Found 211.0837.

2,3,4-Tri(ethoxycarbonyl)pyrrole (3g): white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.32 (3H, t, J = 7.0 Hz), 1.35 (3H, t, J = 7.0 Hz), 1.40 (3H, t, J = 7.0 Hz), 4.29 (2H, q, J = 7.0 Hz), 4.33 (2H, q, J = 7.0 Hz), 4.40 (2H, q, J = 7.0 Hz), 7.47-7.49 (1H, m), 9.30 (1H, br s: *NH*); ¹³C NMR (75.5 MHz, CDCl₃) δ 14.08 (x2), 14.19, 60.48, 61.40, 61.70, 116.32, 121.06, 123.21, 126.18, 159.81, 162.63, 165.36; IR (KBr) 3269, 1742, 1717, 1688, 1288, 1209, 1177, 1022 cm⁻¹; Anal. Calcd for C₁₃H₁₇NO₆: C, 55.12; H, 6.05; N, 4.95. Found: C, 54.93; H, 6.04; N, 4.94; HRMS (EI) Calcd for C₁₃H₁₇NO₆ (M⁺) 283.1050. Found 283.1051.

4-Acyl-2-ethoxycarbonyl-3-phenylpyrrole (3h): white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.05 (3H, t, J = 7.0 Hz), 2.03 (3H, s), 4.12 (2H, q, J = 7.0 Hz), 7.29-7.39 (5H, m), 7.57-7.59 (1H, m), 9.35 (1H, br s: *NH*); ¹³C NMR (75.5 MHz, CDCl₃) δ 13.75,

29.18, 60.53, 121.28, 126.25, 126.82, 127.42, 127.53, 128.31, 129.91, 131.21, 131.76, 134.35, 161.07, 194.48; IR (KBr) 3167, 1701, 1653, 1269, 1186, 1151, 1024, 764, 700 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$ (M^+) 257.1046. Found 257.1051.

4-Diethylcarbamoyl-2-ethoxycarbonyl-3-phenylpyrrole (3i): yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 0.70 (3H, br s), 0.98 (3H, br s), 1.23 (3H, t, $J = 7.0$ Hz), 2.94 (2H, br s), 3.37 (2H, br s), 4.23 (2H, q, $J = 7.0$ Hz), 7.11 (1H, d, $J = 3.0$ Hz), 7.27-7.45 (5H, m), 9.27 (1H br s: *NH*); ^{13}C NMR (67.8 MHz, CDCl_3) δ 12.26, 13.43, 14.07, 38.64, 42.66, 60.45, 118.41, 121.01, 122.56, 127.31, 127.50, 128.78, 130.18, 133.13, 168.89, 166.45; IR (KBr) 3146, 3138, 3126, 1720, 1593, 1267, 1150, 766, 704 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$ (M^+) 314.1468. Found 314.1625.

4-Cyano-2-ethoxycarbonyl-3-phenylpyrrole (3j): white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.21 (3H, t, $J = 7.0$ Hz), 4.25 (2H, q, $J = 7.0$ Hz), 7.38-7.53 (6H, m), 9.48 (1H, br s: *NH*); ^{13}C NMR (75.5 MHz, CDCl_3) δ 13.91, 61.20, 96.90, 115.08, 119.80, 127.89, 128.16, 128.39, 129.92, 131.00, 133.73, 160.30; IR (KBr) 3271, 2239, 1732, 1269, 1250, 1165, 1128, 1030, 758, 685 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.79; H, 5.20; N, 11.58; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ (M^+) 240.0893. Found 240.0894.

2-Ethoxycarbonyl-4-phenylsulfonyl-3-phenylpyrrole (3k): white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.00 (3H, t, $J = 7.0$ Hz), 4.08 (2H, q, $J = 7.0$ Hz), 7.05-7.44 (10H, m), 7.73 (1H, d, $J = 3.0$ Hz), 9.59 (1H, br s: *NH*); ^{13}C NMR (67.8 MHz, CDCl_3) δ 13.79, 60.88, 121.98, 125.60, 126.48, 127.07, 127.36, 127.67, 128.32, 129.61, 130.46, 130.91, 132.46, 141.51, 160.42; IR (KBr) 3260, 1676, 1385, 1308, 1271, 1231, 1184, 1150, 1086, 768, 729, 689 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_4\text{S}$ (M^+) 355.0873. Found 355.0873.

1,4-Bis(2,4-di(ethoxycarbonyl)pyrrolyl)benzene (3l): white solid; ^1H NMR (400 MHz, CDCl_3) δ 1.14 (6H, t, $J = 7.0$ Hz), 1.15 (6H, t, $J = 7.0$ Hz), 4.13 (4H, q, $J = 7.0$ Hz), 4.16 (4H, q, $J = 7.0$ Hz), 7.31 (4H, s), 7.60 (2H, d, $J = 3.5$ Hz), 9.37 (2H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 13.97, 14.13, 59.77, 60.63, 117.46, 120.98, 126.71, 128.92, 132.19, 132.39, 161.08, 163.70; IR (KBr) 3300, 1726, 1699, 1659, 1526, 1410, 1267, 1182, 1026, 785 cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_8$: C, 62.90; H, 5.68; N, 5.64. Found: C, 62.66; H, 5.75; N, 5.58.

4-Ethoxycarbonyl-2-methoxycarbonyl-3-methylpyrrole (3m): white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.35 (3H, t, $J = 7.0$ Hz), 2.60 (3H, s), 3.88 (3H, s), 4.29 (2H, q, $J = 7.0$ Hz), 7.48 (1H, d, $J = 3.0$ Hz), 9.18 (1H, br s: *NH*); ^{13}C NMR (75.5 MHz, CDCl_3) δ 11.22, 14.34, 51.43, 59.68, 116.85, 120.56, 127.21, 129.87, 162.06, 164.65; IR (KBr) 3354, 1699, 1682, 1271, 1232, 1178, 1067 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_4$ (M^+) 211.0839. Found 211.0838.

2-(*tert*-Butoxycarbonyl)-4-ethoxycarbonyl-3-methylpyrrole (3n): white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.34 (3H, t, $J = 7.0$ Hz), 1.58 (9H, s), 2.57 (3H, s), 4.28 (2H, q, $J = 7.0$ Hz), 7.44 (1H, d, $J = 3.0$ Hz), 9.31 (1H, br s: *NH*); ^{13}C NMR (75.5 MHz, CDCl_3) δ 11.28, 14.33, 28.36 (x3), 59.54, 81.55, 116.59, 122.00, 126.65, 128.79, 161.51, 164.80; IR (KBr) 3296, 1715, 1693, 1684, 1668, 1281, 1234, 1169, 1142, 1067 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.88; H, 7.64; N, 5.35; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_4$ (M^+) 253.1309. Found 253.1311.

2-Diethylcarbamoyl-4-ethoxycarbonyl-3-methylpyrrole (3o): white solid; ^1H NMR (400 MHz, CDCl_3) δ 1.18 (6H, t, $J = 7.0$ Hz), 1.33 (3H, t, $J = 7.0$ Hz), 2.30 (3H, s), 3.51 (4H, q, $J = 7.0$ Hz), 4.26 (2H, q, $J = 7.0$ Hz), 7.42 (1H, d, $J = 3.0$ Hz), 9.45 (1H, br s: *NH*); ^{13}C NMR (67.8 MHz, CDCl_3) δ 11.70, 13.48 (x2, br s), 14.37, 41.11 (x2, br s), 59.27, 114.50, 120.45, 124.44, 125.84, 165.06, 165.19; IR (KBr) 3221, 1699, 1593, 1240, 1177, 1063 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_3$ (M^+) 252.1468. Found 252.1470.

2-Diethoxyphosphoryl-4-ethoxycarbonyl-3-methylpyrrole (3p): white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.32 (6H, dt, $J = 0.5, 7.0$ Hz), 1.34 (3H, t, $J = 7.0$ Hz), 2.43 (3H, d, $J = 2.0$ Hz), 3.95-4.18 (4H, m), 4.28 (2H, q, $J = 7.0$ Hz), 7.55 (1H, dd, $J = 5.0, 3.0$ Hz), 9.97 (1H, br s: *NH*); ^{13}C NMR (75.5 MHz, CDCl_3) δ 11.17, 14.41, 16.12 (x2, $^3J(\text{C},\text{P}) = 6.8$ Hz), 59.50, 62.17 (x2, $^2J(\text{C},\text{P}) = 4.4$ Hz), 115.79 ($J(\text{C},\text{P}) = 226.35$ Hz), 116.48 ($J(\text{C},\text{P}) = 15.54$ Hz), 128.82 ($J(\text{C},\text{P}) = 11.85$ Hz), 131.00 ($J(\text{C},\text{P}) = 17.43$ Hz), 164.82 ($^4J(\text{C},\text{P}) = 2.49$ Hz); IR (KBr) 3188, 1709, 1242, 1165, 1086, 1028 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{20}\text{NO}_5\text{P}$ (M^+) 289.1274. Found 289.1073.

4-Ethoxycarbonyl-3-methyl-2-phenylpyrrole (3q): white solid; ^1H NMR (270 MHz, CDCl_3) δ 1.36 (3H, t, $J = 7.0$ Hz), 2.43 (3H, s), 4.30 (2H, q, $J = 7.0$ Hz), 7.28-7.48 (6H,

m), 8.35 (1H, br s: *NH*); ^{13}C NMR (67.8 MHz, CDCl_3) δ 11.22, 14.54, 59.45, 116.15, 117.37, 123.88, 126.77, 127.23, 128.59, 130.03, 132.56, 165.53; IR (KBr) 3317, 3287, 1678, 1234, 1175, 1084, 762, 727, 698, 677 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.22; H, 6.79; N, 6.03; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ (M^+) 229.1097. Found 229.1098.

2,3-Di(ethoxycarbonyl)-4-methylpyrrole (4a): colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 1.32 (3H, t, $J = 7.2$ Hz), 1.35 (3H, t, $J = 7.2$ Hz), 2.14 (3H, d, $J = 0.6$ Hz), 4.30 (2H, q, $J = 7.2$ Hz), 4.33 (2H, q, $J = 7.2$ Hz), 6.65 (1H, dd, $J = 2.8, 0.8$ Hz), 9.29 (1H, br s: *NH*); ^{13}C NMR (75.5 MHz, CDCl_3) δ 10.87, 14.24 (x2), 60.66, 60.79, 120.09, 120.55, 121.79, 122.11, 160.19, 165.56; IR (neat) 3308, 1705, 1699, 1279, 1259, 1194, 1126, 1078, 1036 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_4$ (M^+) 225.099. Found 225.099.

2,3-Di(ethoxycarbonyl)-4-hexylpyrrole (4b): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 0.86(3H, t, $J = 7.0$ Hz), 1.22-1.35 (8H, m), 1.32 (3H, t, $J = 7.0$ Hz), 1.36 (3H, t, $J = 7.0$ Hz), 2.53 (2H, t, $J = 7.5$ Hz), 4.30 (2H, q, $J = 7.0$ Hz), 4.33 (2H, q, $J = 7.0$ Hz), 6.67 (1H, d, $J = 3.0$ Hz), 8.99 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.08, 14.26, 14.27, 22.60, 25.57, 29.02, 30.56, 31.65, 60.72, 60.73, 119.66, 120.26, 121.26, 127.01, 160.21, 165.76; IR (neat) 3312, 2930, 1697, 1406, 1283, 1248, 1196, 1072 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_4$ (M^+) 295.1778. Found 295.1782.

2,3-Di(ethoxycarbonyl)-4-(4-hydroxybutyl)pyrrole (4c): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 1.31 (3H, t, $J = 7.0$ Hz), 1.35 (3H, t, $J = 7.0$ Hz), 1.50-1.67 (4H, m), 2.57 (2H, br t, $J = 7.2$ Hz), 3.64 (2H, br t, $J = 5.8$ Hz), 4.29 (2H, q, $J = 7.0$ Hz), 4.33 (2H, q, $J = 7.0$ Hz), 6.67 (1H, d, $J = 7.0$ Hz), 9.20 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.22, 14.25, 25.14, 26.65, 32.14, 60.77, 60.80, 62.39, 119.83, 120.02, 121.40, 126.48, 160.25, 165.89; IR (neat) 3319, 2937, 1699, 1406, 1285, 1252, 1196, 1084 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_5$ (M^+) 283.1414. Found 283.1417.

4-Cyclohexyl-2,3-di(ethoxycarbonyl)pyrrole (4d): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 1.15-1.42 (5H, m), 1.33 (3H, t, $J = 7.0$ Hz), 1.38 (3H, t, $J = 7.0$ Hz), 1.67-1.96 (5H, m), 2.65(1H, tt, $J = 11.6, 3.3$ Hz), 4.30 (2H, q, $J = 7.0$ Hz), 4.36 (2H, q, $J = 7.0$ Hz), 6.67 (1H, d, $J = 3.0$ Hz), 9.00 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.21, 14.26, 26.13, 26.67, 34.31, 35.19, 60.69, 60.79, 118.12, 119.81, 120.81, 160.28, 166.13; IR (neat) 3315, 2926, 2851, 1705, 1699, 1406, 1273, 1248, 1192, 1070, 773 cm^{-1} .

¹; HRMS (EI) Calcd for C₁₆H₂₃NO₄ (M⁺) 293.1622. Found 293.1622.

2,3-Di(ethoxycarbonyl)-4-phenylpyrrole (4f): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.28 (3H, t, *J* = 7.0 Hz), 1.36 (3H, t, *J* = 7.0 Hz), 4.31 (2H, q, *J* = 7.0 Hz), 4.34 (3H, t, *J* = 7.0 Hz), 7.02 (1H, d, *J* = 3.0 Hz), 7.25- 7.42 (5H, m), 9.21(1H, br s: *NH*); ¹³C NMR (100 MHz, CDCl₃) δ 14.02, 14.23, 60.97, 61.32, 120.04, 120.27, 121.23, 125.90, 126.75, 127.32, 128.35, 133.42, 160.11, 166.36; IR (neat) 3300, 2982, 1717, 1379, 1190, 1130, 1051, 777, 698 cm⁻¹; HRMS (EI) Calcd for C₁₆H₁₇NO₄ (M⁺) 287.1152. Found 287.1155.

2,3-Di(ethoxycarbonyl)-4-(4-methoxyphenyl)pyrrole (4g): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (3H, t, *J* = 7.0 Hz), 1.35 (3H, t, *J* = 7.0 Hz), 3.82 (3H, s), 4.31 (2H, q, *J* = 7.0 Hz), 4.34 (2H, q, *J* = 7.0 Hz), 6.87-6.91 (2H, m), 6.96 (1H, d, *J* = 3.0 Hz), 7.31-7.35 (2H, m), 9.16(1H, br s: *NH*); ¹³C NMR (100 MHz, CDCl₃) δ 14.06, 14.23, 55.20, 60.89, 61.27, 113.83, 119.69, 120.11, 121.04, 125.61, 125.97, 128.53, 158.51, 160.11, 166.47; IR (neat) 3300, 2982, 1713, 1283, 1258, 1180, 1128, 1051, 835, 734 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₉NO₅ (M⁺) 317.1258. Found 317.1260.

2,3-Di(ethoxycarbonyl)-4-(4-trifluoromethylphenyl)pyrrole (4h): light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (3H, t, *J* = 7.0 Hz), 1.36 (3H, t, *J* = 7.0 Hz), 4.33 (2H, q, *J* = 7.0 Hz), 4.36 (2H, q, *J* = 7.0 Hz), 7.07 (1H, d, *J* = 3.0 Hz), 7.49-7.63 (4H, m), 9.30 (1H, br s: *NH*); ¹³C NMR (100 MHz, CDCl₃) δ 14.08, 14.30, 61.25, 61.57, 120.15, 120.29, 121.95, 122.79, 124.75, 125.35, 125.39, 125.42, 125.47, 127.59, 128.74, 129.06, 137.11, 137.12, 159.90, 165.90; IR (KBr) 3314, 1693, 1327, 1198, 1167, 1126, 864 cm⁻¹; Anal. Calcd for C₁₇H₁₆NO₄F₃: C, 57.47; H, 4.54; N, 3.94. Found: C, 57.24; H, 4.65; N, 4.03.

2,3-Di(ethoxycarbonyl)-4-isopropenylpyrrole (4i): yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.33 (3H, t, *J* = 7.0 Hz), 1.38 (3H, t, *J* = 7.0 Hz), 2.03 (3H, dd, *J* = 1.6, 0.8 Hz), 4.31 (2H, q, *J* = 7.0 Hz), 4.36 (2H, q, *J* = 7.0 Hz), 4.95 (1H, dq, *J* = 1.2, 1.4 Hz), 5.08 (1H, br m), 6.88 (1H, d, *J* = 3.0 Hz), 9.05 (1H, br s: *NH*); ¹³C NMR (100 MHz, CDCl₃) δ 14.13, 14.30, 22.77, 60.96, 61.47, 111.85, 119.54, 119.82, 120.95, 126.14, 135.76, 159.93, 166.91; IR (neat) 3321, 1732, 1715, 1634, 1294, 1259, 1188, 1067 cm⁻¹; HRMS (ESI) Calcd for C₁₃H₁₇NO₄Na ([M+Na]⁺) 274.1050. Found 274.1050.

3-Acyl-2-ethoxycarbonyl-4-phenylpyrrole (4l): white solid; ¹H NMR (500 MHz,

CDCl_3) δ 1.35 (3H, t, $J = 7.0$ Hz), 2.45 (3H, s), 4.35 (2H, q, $J = 7.0$ Hz), 7.00 (1H, d, $J = 3.0$ Hz), 9.37 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.16, 32.62, 61.04, 119.77, 120.37, 125.33, 126.79, 127.58, 128.49, 129.44, 133.44, 160.19, 201.93; IR (KBr) 3209, 1709, 1676, 1381, 1254, 1186, 1051, 777, 760 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.26; H, 6.01; N, 5.26; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$ (M^+) 257.1046. Found 257.1048.

3-Diethylcarbamoyl-2-ethoxycarbonyl-4-phenylpyrrole (4m): white solid; ^1H NMR (400 MHz, CDCl_3) δ 0.80 (3H, t, $J = 7.0$ Hz), 1.20 (3H, t, $J = 7.0$ Hz), 1.33 (3H, t, $J = 7.0$ Hz), 2.98-3.15 (2H, m), 3.41-3.50 (1H, m), 3.57-3.66 (1H, m), 4.24-4.40 (2H, m), 7.11 (1H, d, $J = 3.0$ Hz), 7.21-7.49 (5H, m), 9.16 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 12.53, 13.50, 14.41, 39.04, 43.06, 60.75, 119.82, 119.90, 123.47, 124.49, 126.61, 126.82, 128.51, 133.62, 160.38, 166.44; IR (KBr) 3199, 2986, 1703, 1601, 1379, 1288, 1169, 1121, 777 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$: C, 68.77; H, 7.05; N, 8.91. Found: C, 68.56; H, 7.02; N, 8.80; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$ (M^+) 314.1625. Found 314.1627.

3-Cyano-2-ethoxycarbonyl-4-phenylpyrrole (4n): white solid; ^1H NMR (400 MHz, CDCl_3) δ 1.45 (3H, t, $J = 7.0$ Hz), 4.46 (2H, q, $J = 7.0$ Hz), 7.15 (1H, d, $J = 3.0$ Hz), 7.33-7.66 (5H, m), 9.57 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.22, 62.01, 95.83, 114.87, 120.13, 126.82, 127.81, 128.05, 128.86, 130.34, 131.59, 159.26; IR (KBr) 3817, 3132, 2231, 1709, 1452, 1379, 1176, 1130, 1065, 773 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ (M^+) 240.0893. Found 240.0892.

2-(tert-butoxycarbonyl)-3-ethoxycarbonyl-4-phenylpyrrole (4o): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 1.26 (3H, t, $J = 7.0$ Hz), 1.55 (9H, s), 4.29 (2H, q, $J = 7.0$ Hz), 6.98 (1H, d, $J = 3.0$ Hz), 7.25-7.41 (5H, m), 9.13 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 14.02, 28.20, 61.18, 82.03, 119.54, 119.83, 122.43, 125.63, 126.64, 127.31, 128.30, 133.65, 169.76, 166.49; IR (neat) 3296, 2979, 1705, 1387, 1288, 1163, 1130, 1049 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_4$ (M^+) 315.1465. Found 315.1470.

2-Diethylcarbamoyl-3-ethoxycarbonyl-4-phenylpyrrole (4p): yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 1.06-1.35 (6H, br s), 1.16 (3H, t, $J = 7.0$ Hz), 3.24-3.68 (4H, br s), 4.16 (2H, q, $J = 7.0$ Hz), 6.69 (1H, d, $J = 3.0$ Hz), 7.25-7.42 (5H, m), 10.30 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 12.53, 13.86, 14.09, 39.53, 43.44, 59.73, 110.59, 118.70, 126.23, 126.36, 127.52, 129.41, 130.99, 134.71, 164.16, 165.22; IR (neat) 3190,

2980, 1715, 1699, 1614, 1456, 1286, 1119, 752 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$ (M^+) 314.1625. Found 314.1623.

2-Diethoxyphosphoryl-3-ethoxycarbonyl-4-phenylpyrrole (4q): colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.19 (3H, t, $J = 7.0$ Hz), 1.33 (6H, t, $J = 7.0$ Hz), 4.06-4.24 (6H, m), 6.99 (1H, m), 7.24-7.40 (5H, m), 9.69 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 13.96, 16.25, 16.32, 60.35, 62.82, 62.87, 120.19, 120.33, 122.36, 122.47, 126.65, 127.73, 128.79, 128.91, 128.96, 134.20, 164.17; IR (neat) 3163, 1717, 1271, 1234, 1130, 1024, 762, 698 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_5\text{P}$ (M^+) 351.1230. Found 351.1233.

3-Ethoxycarbonyl-4-phenyl-2-(toluenesulfonyl)pyrrole (4r): white solid; ^1H NMR (400 MHz, CDCl_3) δ 1.06(3H, t, $J = 7.0$ Hz), 2.43 (3H, s), 4.14 (2H, q, $J = 7.0$ Hz), 6.98 (1H, d, $J = 3.0$ Hz), 7.25-7.35 (7H, m), 7.93 (2H, m), 9.59 (1H, br s: *NH*); ^{13}C NMR (100 MHz, CDCl_3) δ 13.80, 21.69, 60.92, 117.48, 120.48, 127.10, 127.83, 127.88, 128.73, 128.97, 129.46, 129.70, 133.32, 138.06, 144.32, 163.03; IR (neat) 3296, 1717, 1327, 1283, 1205, 1148, 1284, 1240 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_4\text{S}$ (M^+) 369.1029. Found 369.1033.