Straightforward Entry into 5-Hydroxy-1-aminopyrrolines and the Corresponding Pyrroles from 1,2-Diaza-1,3-butadienes.

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Ethyl (4*S,5*R**)-1-[(aminocarbonyl)amino]-5-hydroxy-2-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5b):** ¹H NMR (DMSO-*d*₆) δ 0.92 (t, *J* = 6.8 Hz, 3 H), 2.12 (d, *J* = 1.2 Hz, 3 H), 3.70 (dq, *J* = 3.6 Hz, *J* = 1.2 Hz, 1 H), 3.85 (q, *J* = 6.8 Hz, 2 H), 4.68 (b.s., 1 H), 5.98 (b.s. 2 H), 6.46 (d, *J* = 7.2 Hz, 1 H), 7.10-7.30 (m, 5 H), 8.14 (b.s., 1 H); ¹³C NMR (DMSO-*d*₆) δ 11.8, 14.1, 54.5, 58.0, 93.5, 99.8, 126.2, 127.7, 128.0, 143.5, 158.4, 159.4, 165.3; IR 3484, 3309, 3196, 1659, 1610 cm⁻¹; MS *m/z* (%) 305 (M⁺, 9), , 287 (100); Anal.Calcd for C₁₅H₁₉N₃O₄: C, 59.01; H, 6.27; N, 13.76; found: C, 58.91; H, 6.18; N, 13.84.

(4*S,5*R**)-1-[(Aminocarbonyl)amino]-5-hydroxy-*N,N*,2-trimethyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxamide (5c):** ¹H NMR (DMSO-*d*₆) δ 1.72 (d, *J* = 1.6 Hz, 3 H), 2.83 (b.s., 6 H), 3.80 (dq, *J* = 7.6 Hz, *J* = 1.6 Hz 1 H), 4.52 (b.s., 1 H), 6.01 (b.s., 2 H), 6.19 (d, *J* = 7.2 Hz, 1 H), 7.10-7.30 (m, 5 H), 7.76 (b.s., 1 H); ¹³C NMR (DMSO-*d*₆) δ 12.2, 36.1, 36.1, 55.7, 99.3, 107.8, 126.6, 128.1, 128.3, 142.0, 146.7, 159.9, 167.6; IR 3399, 3309, 3195, 1676, 1656 cm⁻¹; MS *m/z* (%) 304 (M⁺, 1), 286 (56), 242 (100); Anal.Calcd for C₁₅H₂₀N₄O₃: C, 59.20; H, 6.62; N, 18.41; found: C, 62.14; C, 59.14; H, 6.70; N, 18.45.

Methyl (4*S,5*R**)-1-[(*tert*-butoxycarbonyl)amino]-5-hydroxy-2-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5d):** ¹H NMR (DMSO-*d*₆) δ 1.39 (s, 9 H), 2.10 (s, 3 H), 3.37 (s, 3 H), 3.68 (b.s., 1 H), 4.72 (b.s., 1 H), 6.54 (b.s., 1 H), 7.10-7.30 (m, 5 H), 9.33 (b.s., 1 H); ¹³C NMR (DMSO-*d*₆) δ 11.5, 28.0, 49.8, 54.0, 79.7, 93.5, 98.9, 126.1, 127.3, 128.1, 143.5, 155.0, 158.7, 165.7; IR 3299, 1737, 1693 cm⁻¹; MS *m/z* (%) 348 (M⁺, 4), 330 (30), 274 (100); Anal.Calcd for C₁₈H₂₄N₂O₅: C, 62.05; H, 6.94; N, 8.04; found: C, 61.98; H, 6.92; N, 8.10.

Methyl 1-[(aminocarbonyl)amino]-5-hydroxy-2-methyl-4,4-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5e): m.p. 218-221 °C; ¹H NMR (DMSO-*d*₆) δ 2.15 (s, 3 H), 3.30 (s, 3 H), 5.25 (b.s., 1 H), 5.96 (b.s., 2 H), 6.24 (b.s., 1 H), 7.07-7.50 (m, 10 H), 8.09 (b.s., 1 H); ¹³C NMR (DMSO-*d*₆) δ 12.6, 49.5, 60.5, 94.4, 103.9, 125.4,

125.7, 126.3, 127.2, 128.4, 130.2, 140.7, 146.2, 158.3, 160.3, 165.5; IR 3421, 3328, 3196, 1676, 1612 cm^{-1} ; MS m/z (%) 367 (M^+ , 1), 349 (100); Anal.Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_4$: C, 65.38; H, 5.76; N, 11.44; found: C, 65.29; H, 5.79; N, 11.41.

Ethyl 1-[(aminocarbonyl)amino]-5-hydroxy-2-methyl-4,4-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (5f): m.p. 153-156 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 0.83 (t, $J = 7.2$ Hz, 3 H), 2.17 (s, 3 H), 3.76 (q, $J = 7.2$ Hz, 2 H), 5.28 (b.s., 1 H), 5.98 (b.s., 2 H), 6.26 (b.s., 1 H), 7.10-7.50 (m, 10 H), 8.11 (s, 1 H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 12.8, 14.0, 58.0, 60.6, 94.9, 103.4, 125.6, 125.9, 126.5, 127.4, 128.7, 130.5, 140.8, 146.4, 158.3, 160.6, 165.3; IR 3534, 3411, 3172, 1700, 1661 cm^{-1} ; MS m/z (%) 381 (M^+ , 3), 363 (100); Anal.Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_4$: C, 66.13; H, 6.08; N, 11.02; found: C, 66.13; H, 6.08; N, 11.02.

Methyl 1-[(methoxycarbonyl)amino]-5-hydroxy-2-methyl-4,4-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (5g): m.p. 129-134 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 2.13 (s, 3 H), 3.32 (s, 3 H), 3.62 (s, 3 H), 5.31 (b.s., 1 H), 6.53 (d, $J = 5.6$ Hz, 1 H), 7.09-7.42 (m, 10 H), 9.63 (b.s., 1 H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 12.6, 49.7, 52.1, 60.2, 93.9, 104.0, 125.4, 125.7, 126.2, 127.2, 128.1, 130.0, 140.6, 145.9, 156.1, 159.1, 165.1; IR 3296, 3244, 1757, 1648 cm^{-1} ; MS m/z (%) 382 (M^+ , 14), 364 (46), 322 (28), 292 (89), 278 (50), 264 (67), 248 (52), 231 (100); Anal.Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_5$: C, 65.96; H, 5.80; N, 7.33; found: C, 65.91; H, 5.73 N, 7.26.

Ethyl 1-[(ethoxycarbonyl)amino]-5-hydroxy-2-methyl-4,4-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (5h): m.p. 111-115 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 0.86 (t, $J = 6.8$ Hz, 3 H), 1.19 (t, $J = 6.8$ Hz, 3 H), 2.15 (s, 3 H), 3.77 (q, $J = 6.8$ Hz, 2 H), 4.06 (q, $J = 6.8$ Hz, 2 H), 5.33 (b.s., 1 H), 6.51 (d, $J = 6.4$ Hz, 1 H), 7.10-7.42 (m, 10 H), 9.54 (b.s., 1 H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 12.4, 14.0, 14.6, 58.0, 60.2, 60.8, 94.0, 104.2, 125.3, 125.7, 126.1, 127.1, 128.3, 130.1, 140.6, 146.0, 155.6, 159.2, 164.8; IR 3330, 1719, 1643 cm^{-1} ; MS m/z (%) 410 (M^+ , 12), 392 (75), 363 (12), 336 (28), 306 (60), 292 (51), 276 (27), 264 (73), 248 (70), 231 (100); Anal.Calcd for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_5$: C, 67.30; H, 6.38; N, 6.82; found: C, 67.19; H, 6.33; N, 6.87.

Methyl 1-[(*tert*-butoxycarbonyl)amino]-5-hydroxy-2-methyl-4,4-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5i): m.p. 69-73 °C; ^1H NMR (DMSO- d_6) δ 1.40 (s, 9 H), 2.12 (s, 3 H), 3.31 (s, 3 H), 5.27 (s, 1 H), 6.46 (s, 1 H), 7.04-7.40 (m, 10 H), 9.24 (s, 1 H); ^{13}C NMR (DMSO- d_6) δ 12.5, 28.1, 49.6, 60.3, 79.8, 94.2, 104.0, 125.5, 125.8, 127.4, 128.4, 130.2, 141.0, 146.2, 154.9, 159.8, 165.5; IR 3302, 1693, 1688 cm^{-1} ; MS m/z (%) 424 (M^+ , 3), 406 (11), 368 (39), 350 (47), 292 (100); Anal.Calcd for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_5$: C, 67.91; H, 6.65; N, 6.60; found: C, 67.89; H, 6.61; N, 6.53.

Methyl (4*S,5*R**)-3-acetyl-1-[(aminocarbonyl)amino]-5-hydroxy-2-methyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5j):** ^1H NMR (DMSO- d_6) δ 2.07 (s, 3 H), 2.10 (s, 3 H), 3.42-3.55 (m, 4 H), 4.87 (b.s., 1 H), 6.04 (b.s., 2 H), 6.68 (d, $J = 7.6$ Hz, 1 H), 8.23 (b.s., 1 H); ^{13}C NMR (DMSO- d_6) δ 11.8, 28.4, 50.4, 61.1, 88.0, 94.8, 158.4, 160.8, 165.5, 207.3; IR 3448, 3334, 1700, 1710, 1690, 1661 cm^{-1} ; MS m/z (%) 257 (M^+ , 4), 239 (21), 224 (16), 207 (100); Anal.Calcd for $\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_5$: C, 46.69; H, 5.88; N, 16.33; found: C, 46.56; H, 5.95; N, 16.27.

Ethyl (4*S,5*R**)-3-acetyl-1-[(aminocarbonyl)amino]-5-hydroxy-2-methyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5k):** ^1H NMR (DMSO- d_6) δ 1.14 (t, $J = 7.2$ Hz, 3 H), 2.02 (s, 3 H), 2.29 (s, 3 H), 3.52 (b.s., 1 H), 4.00 (q, $J = 7.2$ Hz, 2 H), 4.86 (b.s., 1 H), 6.04 (b.s., 2 H), 6.66 (b.s., 1 H), 8.22 (b.s., 1 H); ^{13}C NMR (DMSO- d_6) δ 11.7, 14.4, 28.4, 58.6, 61.0, 87.7, 94.9, 158.5, 160.7, 165.0, 207.4; IR 3436, 3315, 1708, 1698, 1674 cm^{-1} ; MS m/z (%) 271 (M^+ , 7), 253 (30), 238 (16), 207 (100); Anal.Calcd for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}_5$: C, 48.70; H, 6.32; N, 15.49; found: C, 48.68; H, 6.44; N, 15.37.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (6b): m.p. 180-183 °C; ^1H NMR (DMSO- d_6) δ 1.07 (t, $J = 7.2$ Hz, 3 H), 2.28 (s, 3 H), 4.05 (q, $J = 7.2$ Hz, 2 H), 6.28 (s, 2 H), 6.74 (s, 1 H), 7.17-7.31 (m, 5 H), 9.36 (s, 1 H); ^{13}C NMR (DMSO- d_6) δ 10.4, 14.0, 58.8, 107.9, 121.3, 122.8, 125.8, 127.4, 128.8, 135.2, 137.3, 157.2, 164.5; IR 3411, 3304, 3196, 1680 cm^{-1} ; MS m/z (%) 287 (M^+ , 100); Anal.Calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3$: C, 62.71; H, 5.96; N, 14.62; found: C, 62.64; H, 5.84; N, 14.53.

1-[(Aminocarbonyl)amino]-*N,N*,2-trimethyl-4-phenyl-1*H*-pyrrole-3-carboxamide (6c): m.p. 225-230 °C; ¹H NMR (DMSO-*d*₆) δ 1.97 (s, 3 H), 2.64 (s, 3 H), 2.89 (s, 3 H), 6.19 (s, 2 H), 6.96 (s, 1 H), 7.10-7.30 (m, 5 H), 9.25 (s, 1 H); ¹³C NMR (DMSO-*d*₆) δ 9.2, 34.2, 37.6, 112.8, 119.1, 119.3, 125.6, 125.8, 128.5, 129.2, 135.1, 157.6, 167.5; IR 3443, 3324, 3205, 1705, 1690 cm⁻¹; MS *m/z* (%) 286 (M⁺, 58), 242 (100); Anal.Calcd for C₁₅H₁₈N₄O₂: C, 62.92; H, 6.34; N, 19.57; found: C, 63.01; H, 6.39; N, 19.44.

Methyl 1-[(*tert*-butoxycarbonyl)amino]-2-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (6d): m.p. 138-142 °C; ¹H NMR (DMSO-*d*₆) δ 1.44 (s, 9 H), 2.27 (s, 3 H), 3.56 (s, 3 H), 6.82 (s, 1 H), 7.15-7.31 (m, 5 H), 10.47 (b.s., 1 H); ¹³C NMR (DMSO-*d*₆) δ 10.9, 28.6, 51.1, 81.6, 108.6, 121.8, 123.6, 126.7, 128.3, 129.3, 135.5, 137.4, 155.0, 165.6; IR 3274, 1724, 1700, 1685 cm⁻¹; MS *m/z* (%) 330 (M⁺, 30), 274 (100); Anal.Calcd for C₁₈H₂₂N₂O₄: C, 65.44; H, 6.71; N, 8.48; found: C, 65.38; H, 6.74; N, 8.39.

Methyl 4-acetyl-1-[(aminocarbonyl)amino]-2-methyl-1*H*-pyrrole-3-carboxylate (6e): m.p. 192-195 °C; ¹H NMR (DMSO-*d*₆) δ 2.10 (s, 3 H), 2.29 (s, 3 H), 3.66 (s, 3 H), 6.38 (s, 2 H), 7.45 (s, 1 H), 9.47 (s, 1 H); ¹³C NMR (DMSO-*d*₆) δ 9.5, 28.3, 51.2, 109.8, 122.0, 128.6, 136.5, 157.1, 165.3, 192.2; IR 3397, 3265, 3196, 1715, 1680 cm⁻¹; MS *m/z* (%) 239 (M⁺, 39), 224 (16), 207 (100); Anal.Calcd for C₁₀H₁₃N₃O₄: C, 50.21; H, 5.48; N, 17.56; found: C, 50.37; H, 5.54; N, 17.47.

Ethyl 4-acetyl-1-[(aminocarbonyl)amino]-2-methyl-1*H*-pyrrole-3-carboxylate (6f): m.p. 178-180 °C; ¹H NMR (DMSO-*d*₆) δ 1.21 (t, *J* = 7.2 Hz, 3 H), 2.11 (s, 3 H), 2.29 (s, 3 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 6.37 (s, 2 H), 7.44 (s, 1 H), 9.44 (s, 1 H); ¹³C NMR (DMSO-*d*₆) δ 10.2, 14.7, 29.1, 60.4, 110.8, 122.7, 129.1, 137.0, 157.8, 165.4, 192.8; IR 3367, 3250, 3206, 1685, 1671 cm⁻¹; MS *m/z* (%) 253 (M⁺, 35), 238 (19), 207 (100); Anal.Calcd for C₁₁H₁₅N₃O₄: C, 52.17; H, 5.97; N, 16.59; found: C, 52.08; H, 5.99; N, 16.63.

Dimethyl 1-[(aminocarbonyl)amino]-2-methyl-1H-pyrrole-3,4-dicarboxylate (6g): m.p. 185-189 °C; ^1H NMR (DMSO- d_6) δ 2.13 (s, 3 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 6.37 (s, 2 H), 7.21 (s, 1 H), 9.44 (s, 1 H); ^{13}C NMR (DMSO- d_6) δ 9.6, 51.2, 110.1, 112.1, 127.6, 136.6, 157.0, 163.5, 164.6; IR 3397, 3240, 3181, 1759, 1690 cm^{-1} ; MS m/z (%) 255 (M^+ , 19), 223 (100); Anal.Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_5$: C, 47.06; H, 5.13; N, 16.46; found: C, 47.12; H, 5.07; N, 16.51.

3-Ethyl 4-methyl-1-[(aminocarbonyl)amino]-2-methyl-1H-pyrrole-3,4-dicarboxylate (6h): m.p. 187-190 °C; ^1H NMR (DMSO- d_6) δ 1.22 (t, $J = 7.2$ Hz, 3 H), 2.14 (s, 3 H), 3.66 (s, 3 H), 4.16 (q, $J = 7.2$ Hz, 2 H), 6.35 (s, 2 H), 7.20 (s, 1 H), 9.42 (s, 1 H); ^{13}C NMR (DMSO- d_6) δ 9.6, 14.1, 51.1, 59.6, 110.3, 112.2, 127.3, 136.4, 157.0, 163.6, 164.0; IR 3426, 3260, 3201, 1729, 1680 cm^{-1} ; MS m/z (%) 269 (M^+ , 20), 237 (7), 223 (100); Anal.Calcd for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_5$: C, 49.07; H, 5.62; N, 15.61; found: C, 49.06; H, 5.51; N, 15.54.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-4,5-diphenyl-1H-pyrrole-3-carboxylate (7b): m.p. 186-189 °C; ^1H NMR (DMSO- d_6) δ 0.94 (t, $J = 7.2$ Hz, 3 H), 2.36 (s, 3 H), 3.95 (q, $J = 7.2$ Hz, 2 H), 6.20 (s, 2 H), 7.00-7.22 (m, 10 H), 9.17 (s, 1 H); ^{13}C NMR (DMSO- d_6) δ 10.8, 13.9, 58.7, 108.4, 120.4, 125.6, 126.9, 127.0, 127.5, 130.1, 130.2, 130.4, 131.0, 135.3, 136.7, 156.9, 164.2; IR 3410, 3306, 3197, 1695, 1667 cm^{-1} ; MS m/z (%) 364 ($\text{M}^+ + 1$, 25), 363 (M^+ , 100); Anal.Calcd for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_3$: C, 69.41; H, 5.82; N, 11.56; found: C, 69.37; H, 5.89; N, 11.47.

Methyl 1-[(methoxycarbonyl)amino]-2-methyl-4,5-diphenyl-1H-pyrrole-3-carboxylate (7c): m.p. 158-162 °C; ^1H NMR (DMSO- d_6) δ 2.37 (s, 3 H), 3.51 (s, 3 H), 3.61 (s, 3 H), 6.99-7.23 (m, 10 H), 10.66 (s, 1 H); ^{13}C NMR (DMSO- d_6) δ 10.7, 50.5, 52.7, 108.7, 120.8, 125.8, 127.0, 127.3, 127.8, 129.6, 130.0, 130.2, 130.8, 134.6, 136.0, 155.6, 164.5; IR 3230, 1728, 1709; 1676 cm^{-1} ; MS m/z (%) 365 ($\text{M}^+ + 1$, 24), 364 (M^+ , 100); Anal.Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4$: C, 69.22; H, 5.53; N, 7.69; found: C, 69.23; H, 5.58; N, 7.75.

Ethyl 1-[(ethoxycarbonyl)amino]-2-methyl-4,5-diphenyl-1*H*-pyrrole-3-carboxylate (7d): m.p. 161-164 °C; ¹H NMR (DMSO-*d*₆) δ 0.95 (t, *J* = 7.2 Hz, 3 H), 1.11 (t, *J* = 7.2 Hz, 3 H), 2.37 (s, 3 H), 3.96 (q, *J* = 7.2 Hz, 2 H), 4.06 (q, *J* = 7.2 Hz, 2 H), 7.00-7.23 (m, 10 H), 10.56 (s, 1 H); ¹³C NMR (DMSO-*d*₆) δ 10.6, 13.9, 14.4, 58.8, 61.4, 108.9, 120.8, 125.7, 127.0, 127.3, 127.7, 129.7, 130.0, 130.3, 130.6, 134.9, 135.9, 155.1, 164.0; IR 3282, 1719, 1691 cm⁻¹; MS *m/z* (%) 393 (M⁺+1, 25), 392 (M⁺, 100); Anal.Calcd for C₂₃H₂₄N₂O₄: C, 70.39; H, 6.16; N, 7.14; found: C, 70.43; H, 6.12; N, 7.11.