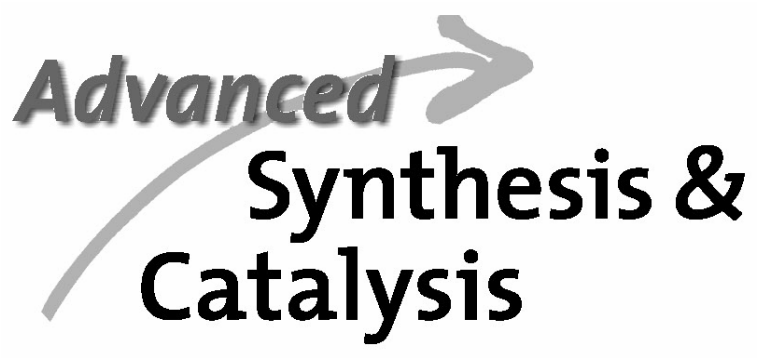

Supporting Information

Improved Synthesis of Pyrroles and Indoles *via* Lewis Acid-Catalyzed Mukaiyama-Michael type Addition/Heterocyclization of Enolsilyl Derivatives on 1,2-Diaza-1,3-Butadienes. Role of the Catalyst in the Reaction Mechanism

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SUPPORTING INFORMATION

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Experimental

During the course of the reactions, the following work-up, and the long standing, compounds **3a-f** give a partial transformation to the relevants **4a-d**.

4-Ethyl 1-methyl 2,2-dimethyl-3-[1-(2-{[(1,1,1-trimethylsilyl)amino]carbonyl}hydrazono) ethyl]succinate (3a): oil; ^{1}H NMR ($CDCl_3$): d 0.25 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 3H), 1.30 (s, 3H), 1.84 (s, 3H), 3.61 (s, 3H), 3.77 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.78 (s, 1H), 9.25 (s, 1H); ^{13}C NMR ($CDCl_3$): d -0.6, 14.2, 16.2, 22.1, 25.0, 43.4, 52.1, 60.4, 61.1, 142.6, 159.7, 170.5, 177.5.

Methyl 3-[(dimethylamino)carbonyl]-2,2-dimethyl-4-(2-{[(1,1,1-trimethylsilyl)amino] carbonyl}hydrazono)pentanoate (3b): oil; ^{1}H NMR ($CDCl_3$): d 0.21 (s, 9H), 1.25 (s, 3H), 1.28 (s, 3H), 1.83 (s, 3H), 2.92 (s, 3H), 3.00 (s, 3H), 3.62 (s, 3H), 3.94 (s, 1H), 5.75 (s, 1H), 9.62 (s, 1H); ^{13}C NMR ($CDCl_3$): d -0.6, 15.8, 23.0, 24.4, 35.8, 37.7, 44.9, 51.9, 57.2, 144.2, 159.7, 170.3, 177.9.

1-Ethyl 4-methyl 2-{1,2-({[1-(*tert*-butyl)-1,1-dimethylsilyl]amino}carbonyl)hydrazono]ethyl} succinate (3c): oil; ^{1}H NMR ($CDCl_3$): d 0.20 (s, 6H), 0.93 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.95 (s, 3H), 2.77 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 2.85 (dd, *J* = 16.4 Hz, *J* = 7.6 Hz, 1H),3.65 (s, 3H), 3.73 (dd, *J* = 7.6 Hz, *J* = 7.2 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 5.78 (s, 1H), 9.51 (s, 1H); ^{13}C NMR ($CDCl_3$): d -5.0, 14.0, 15.8, 17.3, 26.1, 33.7, 49.8, 51.9, 61.4, 143.9, 159.8, 170.9, 171.9.

Methyl 4-[2-({[(1-*tert*-butyl)-1,1-dimethylsilyl]amino}carbonyl)hydrazono]-3-[(dimethylamino)carbonyl]pentanoate (3d): oil; ^{1}H NMR ($CDCl_3$): d 0.19 (s, 6H), 0.91 (s, 9H), 1.85 (s, 3H), 2.53 (dd, *J* = 16.4 Hz, *J* = 5.2 Hz, 1H), 2.94 (s, 3H), 3.00 (dd, *J* = 16.4 Hz, *J* = 9.6 Hz, 1H), 3.07 (s, 3H), 3.65 (s, 3H), 4.00 (dd, *J* = 9.6 Hz, *J* = 5.2 Hz, 1H), 5.80 (s, 1H), 9.57 (s, 1H); ^{13}C NMR ($CDCl_3$): d -5.0, -4.9, 13.7, 17.2, 26.1, 34.2, 36.0, 37.2, 47.5, 51.9, 145.2, 159.7, 169.8, 172.4.

1-Ethyl 4-methyl 2-[1-(2-{[(1,1,1-trimethylsilyl)amino]carbonyl}hydrazono)ethyl]succinate (3e): oil; ^{1}H NMR ($CDCl_3$): d 0.27 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.89 (s, 3H), 2.80 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 2.84 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H),3.67 (s, 3H), 3.76 (t, *J* = 7.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.72 (s, 1H), 8.01 (s, 1H); ^{13}C NMR ($CDCl_3$): d -0.5, 14.1, 15.2, 33.8, 49.9, 51.9, 61.5, 143.5, 159.0, 170.9, 171.9.

4-Ethyl 1-methyl 3-{1[2-({[1-(*tert*-butyl)-1,1-dimethylsilyl]amino}carbonyl)hydrazono]ethyl}-2,2-dimethylsuccinate (3f): oil; ^{1}H NMR ($CDCl_3$): d 0.24 (s, 6H), 0.95 (s, 9H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.29 (s, 3H), 1.31 (s, 3H), 1.85 (s, 3H), 3.62 (s, 3H), 3.77 (s, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 5.76 (s, 1H), 8.95 (s, 1H); ^{13}C NMR ($CDCl_3$): d -5.0, 14.2, 16.5, 17.5, 22.4, 24.7, 43.5, 52,1, 60.2, 61.1, 142.5, 159.5, 170.5, 177.4.

4-Ethyl 1-methyl 3-{1-[2-(aminocarbonyl)hydrazono]ethyl}-2,2-dimethylsuccinate (4a): mp: 138-142 °C; ^{1}H NMR ($CDCl_3$): d 1.28 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 6H), 1.92 (s, 3H), 3.64 (s, 3H), 3.80 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 6.16 (s, 1H), 6.59 (s, 1H), 8.85 (brs, 1H); ^{13}C NMR ($CDCl_3$): d 14.2, 15.9, 22.0, 25.2, 43.5, 52.2, 60.4, 61.2, 143.9, 158.1, 170.2, 177.7; IR (nujol): 3502, 3374, 1734, 1714, 1680, 1576 cm^{-1}; EIMS *m/z* (%): 287 (M^+, 6), 187 (37), 139 (33), 98 (100). HRMS Calcd for $C_{12}H_{21}N_3O_5$: 287.1481. Found: 287.1480.

Methyl 4-[2-(aminocarbonyl)hydrazono]-3-[(dimethylamino)carbonyl]-2,2-dimethyl pentanoate (4b): mp: 183-187 °C; ^{1}H NMR (DMSO-d_6): d 1.13 (s, 3H), 1.17 (s, 3H), 1.69 (s, 3H), 2.79 (s, 3H), 2.92 (s, 3H), 3.51 (s, 3H), 3.92 (s, 1H), 6.23 (brs, 2H), 9.11 (s, 1H); ^{13}C NMR (DMSO-d_6): d 15.7, 22.7, 24.7, 35.2, 37.1, 44.1, 51.6, 56.7, 143.7, 157.2, 169.9, 177.1; IR (nujol): 3470, 3353, 1719, 1693, 1647, 1586 cm^{-1}; EIMS *m/z* (%): 242 (M^+-44, 34), 199 (64), 139 (100). Anal. Calcd for $C_{12}H_{22}N_4O_4$: C, 50.34; H, 7.77; N, 19.57. Found: C, 50.19; H, 7.62; N, 19.69.

1-Ethyl 4-methyl 2-{1-[2-(aminocarbonyl)hydrazono]ethyl}succinate (4c): mp: 123-127 °C; ^{1}H NMR (DMSO-d_6): d 1.52 (t, *J* = 7.2 Hz, 3H), 1.81 (s, 3H), 2.77 (dd, *J* = 16.8 Hz, *J* = 6.4 Hz, 1H), 2.79 (dd, *J* = 16.8 Hz, *J* = 8.4 Hz, 1H), 3.56 (s, 3H), 3.63 (dd, *J* = 8.4 Hz, *J* = 6.4 Hz, 1H), 4.08 (dq, *J* = 7.2 Hz, *J* = 2.0 Hz, 2H), 6.20 (brs, 2H), 9.21 (s, 1H); ^{13}C NMR (DMSO-d_6): d 13.9, 15.3, 33.3, 49.4, 51.4, 60.7, 143.9, 157.0, 170.7, 171.7; IR (nujol): 3470, 3190, 1729, 1693, 1581, 1444 cm^{-1}; EIMS *m/z* (%): 259 (M^+, 33), 213 (11), 200 (15), 185 (40), 170 (75), 157 (18), 138 (43), 111 (100). HRMS Calcd for $C_{10}H_{17}N_3O_5$: 259.1168. Found: 259.1169.

Methyl 4-[2-(aminocarbonyl)hydrazono]-3-[(dimethylamino)pentanoate (4d): mp: 155-159 °C; ^{1}H NMR (DMSO-d_6): d 1.68 (s, 3H), 2.54 (dd, *J* = 16.4 Hz, *J* = 5.8 Hz, 1H), 2.79 (dd, *J* = 16.4 Hz, *J* = 9.0 Hz, 1H), 2.80 (s, 3H), 3.02 (s, 3H), 3.54 (s, 3H), 3.97 (dd, *J* = 9.0 Hz, *J* = 5.8 Hz, 1H), 6.22 (brs, 2H), 9.15 (s, 1H); ^{13}C NMR (DMSO-d_6): d 13.7, 33.9, 35.4, 37.0, 46.6, 145.0, 157.2, 169.7, 172.0; IR (nujol): 3393, 3188, 1723, 1694, 1456 cm^{-1}; EIMS *m/z* (%): 259 (M^++1, 2), 214 (72), 199 (13), 184 (40), 171 (100). Anal. Calcd for $C_{10}H_{18}N_4O_4$: C, 46.50; H, 7.02; N, 21.69. Found: C, 46.64; H, 7.11; N, 21.56

2-{2-[(Dimethylamino)carbonyl]-1-methyl-4-oxo-4-phenylbutylidene}-1-hydrazine carboxamide (4e): mp:151-155 °C; ^{1}H NMR (DMSO-d_6): d 1.78 (s, 3H), 2.79 (s, 3H), 3.07 (s, 3H), 3.15 (dd, *J* = 17.8 Hz, *J* = 3.6 Hz, 1H), 3.68 (dd, *J* = 17.8 Hz, *J* = 10.0 Hz, 1H), 4.16 (dd, *J* = 10.0 Hz, *J* = 3.6 Hz, 1H), 6.24 (brs, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 9.18 (s, 1H); ^{13}C NMR (DMSO-d_6): d 13.9, 35.4, 37.0, 38.6, 46.1, 128.0, 128.7, 133.3, 136.4, 145.9, 157.2, 170.1, 198.0; IR (nujol): 3427, 3241, 1693, 1683, 1647 cm^{-1}; EIMS *m/z* (%): 260 (M^+-44, 15), 217 (62), 105 (100). Anal. Calcd for $C_{15}H_{20}N_4O_3$: C, 59.20; H, 6.62; N, 18.41. Found: C, 59.31; H, 6.56; N, 18.30.

2-[3-(Dimethylamino)-1-methyl-3-oxo-2-(2-oxo-3-cyclohexenyl)propylidene]-hydrazine carboxamide (4f): Compound **4f** was obtained as isomeric mixture in 55:45 ratio by using DMSO-d_6 as a solvent (determined by ^{1}H-NMR). For clarity sake the NMR values are given separately for each isomer. Major component **4f**: ^{1}H NMR (DMSO-d_6): d 1.50 (m, 1H), 1.59 (m, 1H), 1.68 (s, 3H), 2.33 (m, 1H), 2.45 (m, 1H), 2.79 (s, 3H), 3.04 (s, 3H), 3.19 (m, 1H), 3.66 (d, J = 10.0 Hz, 1H), 5.84 (m, 1H), 6.31 (s, 2H), 7.01 (m, 1H), 9.09 (s, 1H); ^{13}C NMR (DMSO-d_6): d 12.5, 25.8, 26.2, 35.4, 36.8, 46.5, 50.3, 128.3, 145.1, 150.7, 157.1, 169.9, 199.6; minor component **4f**: ^{1}H NMR (DMSO-d_6): d 1.71 (m, 2H), 1.75 (s, 3H), 2.04 (m, 1H), 2.31 (m, 1H), 2.78 (s, 3H), 2.91 (m, 1H), 2.96 (s, 3H), 3.98 (d, J = 8.4 Hz, 1H), 5.84 (m, 1H), 6.15 (bs, 2H), 7.02 (m, 1H), 9.11 (s, 1H); ^{13}C NMR (DMSO-d_6): d 14.3, 24.5, 24.9, 35.2, 37.0, 46.4, 49.6, 128.8, 145.9, 150.5, 157.0, 169.2, 199.0; IR (nujol): 3401, 3176, 1696, 1666, 1631, 1467 cm^{-1}; EIMS *m/z* (%): 280 (M^+, 1), 262 (13), 236 (58), 193 (100). Anal. Calcd for $C_{13}H_{20}N_4O_3$: C, 55.70; H, 7.19; N, 19.99. Found: C, 55.61; H, 7.28; N, 20.21.

Ethyl 1-[(aminoycarbonyl)amino]-2,4,4-trimethyl-5-oxo-4,5-dihydro-1*H*-3-pyrrolecarboxylate (5a): mp: 195-199 °C; ^{1}H NMR (DMSO-d_6): d 1.22 (s, 6H), 1.23 (t, J = 7.2 Hz, 3H), 2.20 (s, 3H), 4.12 (q, J = 7.2 Hz, 2H), 6.31 (brs, 2H), 8.56 (brs, 1H); ^{13}C NMR (DMSO-d_6): d 11.5, 14.2, 22.3, 22.6, 43.5, 59.0, 110.2, 154.5, 157.2, 163.4, 180.3; IR (nujol): 3428, 3342, 1691 cm^{-1}; EIMS *m/z* (%): 255 (M^+, 4), 212 (13), 197 (16), 169 (44), 155 (66), 151 (61), 139 (100). HRMS Calcd for $C_{11}H_{17}N_3O_4$: 255.1219. Found: 255.1216.

***N*3,*N*3,2,4,4-Pentamethyl-1-[(aminocarbonyl)amino]-5-oxo-4,5-dihydro 1*H*-3-pyrrolecarboxamide (5b):** mp: 193-197 °C; ^{1}H NMR (DMSO-d_6): d 1.14 (s, 6H), 1.74 (s, 3H), 2.90 (s, 6H), 6.22 (brs, 2H), 8.39 (brs, 1H); ^{13}C NMR (DMSO-d_6): d 10.9, 22.4, 23.0, 35.9, 45.3, 113.8, 138.7, 157.5, 165.6, 180.1; IR (nujol): 3421, 3340, 3252, 1723, 1600 cm^{-1}; EIMS *m/z* (%): 254 (M^+, 6), 210 (16), 167 (32), 151 (24), 139 (100). HRMS Calcd for $C_{11}H_{18}N_4O_3$: 254.1378. Found: 254.1381.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-1*H*-3-pyrrolecarboxylate (6a): mp: 184-188 °C; ^{1}H NMR (DMSO-d_6): d 1.23 (t, J = 7.2 Hz, 3H), 2.26 (s, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.21 (brs, 2H), 6.27 (d, J = 3.2 Hz, 1H), 6.63 (d, J = 3.2 Hz, 1H), 9.32 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.0, 14.4, 58.8, 106.7, 109.4, 122.0, 136.6, 157.2, 164.3; IR (nujol): 3426, 3306, 1676 cm^{-1}; EIMS *m/z* (%): 211 (M^+, 46), 166 (33), 152 (100). Anal. Calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found: C, 51.26; H, 6.25; N, 19.95.

***N*3,*N*3,2-Trimethyl-1-[(aminocarbonyl)amino]-1*H*-3-pyrrolecarboxamide (6b):** mp: 173-177 °C; ^{1}H NMR (DMSO-d_6): d 2.04 (s, 3H), 2.94 (brs, 6H), 6.01 (s, 1H), 6.14 (brs, 2H), 6.58 (s, 1H), 9.24 (s, 1H); ^{13}C NMR (DMSO-d_6): d 9.8, 38.9, 105.7, 113.3, 120.7, 131.6, 157.6, 167.2; IR (nujol): 3475, 3414, 1688 cm^{-1}; EIMS *m/z* (%): 210 (M^+, 26), 180 (100). Anal. Calcd for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; N, 26.65. Found: C, 51.57; H, 6.65; N, 26.52.

Ethyl 1-[(aminocarbonyl)amino]-2,5-dimethyl-1*H*-3-pyrrolecarboxylate (6c): mp: 209-213 °C; ^{1}H NMR (DMSO-d_6): d 1.21 (t, J = 7.6 Hz, 3H), 1.99 (s, 3H), 2.26 (s, 3H), 4.12 (q, J = 7,6 Hz, 2H), 6.05 (s, 1H), 6.20 (brs, 2H), 9.10 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.5, 14.5, 58.7, 104.4, 108.1, 127.7, 135.9, 157.3, 164.4; IR (nujol): 3369, 3175, 1683 cm^{-1}; EIMS *m/z* (%): 225 (M^+, 47), 179 (33), 166 (100). HRMS Calcd for $C_{10}H_{15}N_3O_3$: 225.1113. Found: 225.1111.

***N*3,*N*3,2,5-Tetramethyl-1-[(aminocarbonyl)amino]-1*H*-3-pyrrolecarboxamide (6d):** mp: 197-201 °C; ^{1}H NMR (DMSO-d_6): d 2.00 (s, 3H), 2.05 (s, 3H), 2.93 (brs, 6H), 5.80 (s, 1H), 6.14 (brs, 2H), 8.99 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.1, 10.7, 39.1, 103.4, 111.9, 127.2, 130.6, 157.5, 167.3; IR (nujol): 3404, 3185, 1719 cm^{-1}; EIMS *m/z* (%): 224 (M^+, 52), 330 (85), 180 (86), 163 (100). HRMS Calcd for $C_{10}H_{16}N_4O_2$: 224.1273. Found: 224.1270.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-5-phenyl-1*H*-3-pyrrolecarboxylate (6e): mp: 229-233 °C; ^{1}H NMR (DMSO-d_6): d 1.25 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.26 (brs, 2H), 6.50 (s, 1H), 7.25-7.47 (m, 5H), 9.33 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.4, 14.4, 59.0, 106.3, 109.4, 127.0, 127.4, 128.3, 131.1, 133.0, 138.4, 157.0, 164.2; IR (nujol): 3386, 3279, 1691, 1677 cm^{-1}; EIMS *m/z* (%): 287 (M^+, 100). HRMS Calcd for $C_{15}H_{17}N_3O_3$: 287.1269. Found: 287.1266.

***N*3,*N*3,2-Trimethyl-1-[(aminocarbonyl)amino]-5-phenyl-1*H*-3-pyrrolecarboxamide (6f):** mp: 230-234 °C; ^{1}H NMR (DMSO-d_6): d 2.12 (s, 3H), 2.99 (brs, 6H), 6.21 (brs, 2H), 6.29 (s, 1H), 7.22-7.48 (m, 5H), 9.22 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.1, 37.5, 105.5, 113.4, 126.6, 127.1, 128.2, 131.5, 131.7, 133.4, 157.3, 166.9; IR (nujol): 3435, 3214, 1721, 1705, 1589 cm^{-1}; EIMS *m/z* (%): 286 (M^+, 83), 242 (100). HRMS Calcd for $C_{15}H_{18}N_4O_2$: 286.1429. Found: 286.1426.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-4,5,6,7-tetrahydro-1*H*-3-indolecarboxylate (6g): mp: 188-192 °C; ^{1}H NMR (DMSO-d_6): d 1.23 (t, J = 7.2 Hz, 3H), 1.64 (m, 4H), 2.19-2.20 (m, 2H), 2.26 (s, 3H), 2.52 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 6.15 (brs, 2H), 8.99 (s, 1H); ^{13}C NMR (DMSO-

d_6): d 10.3, 14.4, 20.1, 22.1, 22.9, 23.1, 58.3, 106.9, 114.9, 128.1, 135.4, 157.3, 165.0; IR (nujol): 3391, 3178, 1682 cm^{-1}; EIMS *m/z* (%): 265 (M^+, 68), 206 (100). HRMS Calcd for $C_{13}H_{19}N_3O_3$: 265.1426. Found: 265.1427.

***N*3,*N*3,2-Trimethyl-1-[(aminocarbonyl)amino]-4,5,6,7-tetrahydro-1*H*-3-indolecarboxamide (6h):** mp: 144-148 °C; ^{1}H NMR (DMSO-d_6): d 1.62 (m, 4H), 1.95 (s, 3H), 2.30 (m, 4H), 2.89 (s, 6H), 6.06 (brs, 2H), 8.84 (s, 1H); ^{13}C NMR (DMSO-d_6): d 9.7, 20.3, 21.6, 22.3, 23.1, 36.1, 112.0, 112.5, 126.8, 126.9, 157.7, 167.6; IR (nujol): 3423, 3169, 1716, 1584 cm^{-1}; EIMS *m/z* (%): 264 (M^+, 56), 220 (69), 205 (100). HRMS Calcd for $C_{13}H_{20}N_4O_2$: 264.1586. Found: 264.1583.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-4,5-dihydro-1*H*-3-indolecarboxylate (6i): mp: 204-208 °C; ^{1}H NMR (DMSO-d_6): d 1.24 (t, J = 7.2 Hz, 3H), 2.20 (m, 5H), 2.75 (t, J = 9.2 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H), 5.64 (dt, J = 9.6 Hz, J = 4.8 Hz, 1H), 6.12 (dt, J = 9.6 Hz, J = 2.0 Hz, 1H), 6.22 (brs, 2H), 9.14 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.3, 14.4, 20.8, 23.7, 58.7, 107.3, 114.8, 115.9, 122.8, 128.3, 136.0, 157.3, 164.8; IR (nujol): 3374, 3190, 1685 cm^{-1}; EIMS *m/z* (%): 263 (M^+, 100). HRMS Calcd for $C_{13}H_{17}N_3O_3$: 263.1269. Found: 260.1268.

***N*3,*N*3,2-Trimethyl-1-[(aminocarbonyl)amino]-1*H*-3-indolecarboxamide (7a):** mp: 150-154 °C; ^{1}H NMR (DMSO-d_6): d 2.24 (s, 3H), 2.97 (s, 6H), 6.37 (s, 2H), 7.00-7.20 (m, 3H), 7.37 (d, *J* = 7.6 Hz, 1H), 9.31 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.3, 36.7, 58.7, 106.7, 108.9, 119.0, 120.5, 121.5, 125.3, 135.7, 138.6, 157.6, 166.5; IR (nujol): 3496, 3185, 1698, 1459 cm^{-1}; EIMS *m/z* (%): 260 (M^+, 45), 216 (M^+, 100). HRMS Calcd for $C_{13}H_{16}N_4O_2$: 260.1273. Found: 260.1269.

Ethyl 1-[(aminocarbonyl)amino]-2-methyl-1*H*-3-indolecarboxylate (7b): mp: 242-246 °C; ^{1}H NMR (DMSO-d_6): d 1.34 (t, *J* = 7.2 Hz, 3H), 2.54 (s, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.42 (s, 2H), 7.15-7.25 (m, 3H), 7.94-7.98 (m, 1H) 9.42 (s, 1H); ^{13}C NMR (DMSO-d_6): d 10.9, 14.4, 59.0, 101.6, 109.1, 120.5, 121.8, 122.3, 123.9, 136.1, 146.4, 157.2, 164.8; IR (nujol): 3384, 3183, 1713, 1680, 1470 cm^{-1}; EIMS *m/z* (%): 261 (M^+, 100). HRMS Calcd for $C_{13}H_{15}N_3O_3$: 261.1113. Found: 261.1112.

Computational method

All structures discussed are computed with Gaussian 03 programs (Revision C.02) by:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

Energies of stationary points

	Energy	
molecule	hartree	kcal/mol
E-X	-958.713673	0.0
E-Y	-958.724789	-6.98
Z-X	-958.712949	0.45
Z-Y	-958.721609	-4.98

Geometries of stationary points (Cartesian coordinates in Å)

E-X

```
34
scf done:  -958.713673
 C -1.031269 1.656224 -0.865463
 O -2.226003 1.968302 -1.036604
 N -0.698185 0.388464 -0.414790
 N 0.689807 0.194789 -0.104770
 C 1.307137 -0.720357 -0.768097
 C 0.755067 -1.588469 -1.868601
 H 0.679570 -2.629576 -1.533682
 H -0.226270 -1.247613 -2.198011
 H 1.445928 -1.579635 -2.718951
 C 2.771173 -0.930389 -0.427359
 H 2.910683 -1.981540 -0.137509
 H 3.366361 -0.763711 -1.333209
 C 3.290151 -0.005332 0.671875
 O 3.909951 1.012827 0.384076
 C 3.065736 -0.430197 2.104160
 H 3.306746 0.386479 2.787469
 H 2.033007 -0.756519 2.255457
 H 3.715068 -1.287480 2.325252
 N 0.003442 2.505778 -1.175170
 H -0.271609 3.482470 -1.271972
 H 0.902314 2.342155 -0.731093
 Si -1.999954 -0.582953 0.402978
 C -3.234882 -1.203515 -0.870482
 H -4.019971 -1.786845 -0.373124
 H -3.708462 -0.369969 -1.396927
 H -2.759785 -1.854631 -1.613015
 C -2.836045 0.442768 1.739444
 H -2.104524 0.827215 2.459894
 H -3.378591 1.291730 1.315109
 H -3.550623 -0.179996 2.292139
 C -1.132495 -2.041499 1.220865
 H -0.385079 -1.719331 1.953630
 H -1.884891 -2.630902 1.760100
 H -0.646186 -2.715907 0.508863
```

***E*-Y**

```
34
scf done: -958.724798
 C -0.210588 2.804379 0.548766
```

```
 O 0.664379 3.599360 0.183276
 N 0.082631 1.522226 1.016924
 N 1.372624 1.066778 0.945394
 C 1.637097 -0.115371 1.385478
 C 0.634877 -1.059698 2.005199
 H 0.082052 -0.570085 2.817358
 H -0.096058 -1.406464 1.263806
 H 1.126906 -1.943486 2.416378
 C 3.074732 -0.557307 1.272785
 H 3.699109 0.288119 0.957283
 H 3.460553 -0.875870 2.252636
 C 3.307581 -1.699035 0.283918
 O 2.408371 -2.137702 -0.424559
 C 4.716243 -2.251272 0.225244
 H 4.798537 -2.997531 -0.567237
 H 5.437298 -1.444106 0.052709
 H 4.975598 -2.709301 1.187332
 N -1.548509 3.115613 0.550713
 H -2.187159 2.379684 0.872459
 H -0.692666 0.886004 1.210842
Si -2.201273 4.701030 0.040495
 C -1.524494 6.062440 1.146741
 H -1.932748 7.037546 0.853364
 H -1.788747 5.890577 2.196613
 H -0.433486 6.117122 1.075561
 C -4.062032 4.520778 0.262851
 H -4.470640 3.721042 -0.366266
 H -4.328445 4.301941 1.303738
 H -4.569504 5.451445 -0.017592
 C -1.775768 5.026992 -1.761547
 H -2.169681 4.237725 -2.412343
 H -2.205578 5.980349 -2.093092
 H -0.691774 5.075928 -1.905530
```

***Z*-X**

```
   34
scf done:  -958.712949
 C -1.354217 1.893341 -0.426256
 O -2.575338 2.144416 -0.393473
 N -0.901769 0.595565 -0.247299
 N 0.527123 0.443357 -0.110370
 C 1.114305 -0.204703 -1.056754
 C 2.601781 -0.390405 -0.944017
 H 3.088281 0.015843 -1.837507
 H 2.991466 0.103416 -0.051649
 H 2.844547 -1.459312 -0.902463
 C 0.436236 -0.768796 -2.293132
 H 1.005694 -1.636313 -2.650648
 H -0.579367 -1.096009 -2.076436
 C 0.425590 0.241721 -3.455176
 O 1.439790 0.849700 -3.771132
 C -0.883763 0.412733 -4.186574
 H -0.760525 1.075893 -5.044795
 H -1.261418 -0.562823 -4.515851
 H -1.631871 0.827665 -3.501229
 N -0.414902 2.855591 -0.710382
 H -0.760616 3.810828 -0.626333
 H 0.540810 2.705468 -0.394803
Si -1.998570 -0.567503 0.623371
 C -3.438587 -1.034377 -0.491166
 H -4.105556 -1.730228 0.033274
 H -4.017030 -0.151380 -0.775574
 H -3.098703 -1.532702 -1.406723
 C -2.581209 0.186855 2.244162
 H -1.730251 0.459656 2.879279
 H -3.184359 1.083181 2.074307
 H -3.191727 -0.535900 2.799637
 C -0.948481 -2.088945 0.981629
 H -0.082160 -1.852337 1.608013
 H -1.561371 -2.819672 1.524224
 H -0.585740 -2.582939 0.073356
```

***Z*-Y**

```
34
scf done:  -958.721609
 C -0.309330 2.554021 0.213956
 O 0.598350 3.385832 0.099824
 N -0.078604 1.179798 0.338876
 N 1.214325 0.727377 0.228317
```

```
C 1.443616 -0.537542 0.306228
C 2.871101 -1.001213 0.172407
H 2.980459 -1.703857 -0.663899
H 3.536395 -0.151746 0.003422
H 3.192170 -1.533055 1.077158
C 0.383824 -1.610839 0.554575
H 0.871576 -2.517183 0.923929
H -0.317305 -1.261182 1.324522
C -0.429276 -1.916043 -0.704493
O -1.271061 -1.112288 -1.101634
C -0.152745 -3.209063 -1.427925
H -0.741658 -3.273637 -2.344756
H 0.915758 -3.293086 -1.660859
H -0.395588 -4.053221 -0.770073
N -1.639156 2.902547 0.249742
H -2.296240 2.161929 0.516231
H -0.840287 0.546524 0.085747
Si -2.207314 4.590827 0.075968
C -1.565147 5.653724 1.489003
H -1.934921 6.682536 1.396685
H -1.893810 5.265308 2.460249
H -0.470763 5.684259 1.488507
C -4.084670 4.469536 0.148450
H -4.485709 3.853840 -0.665400
H -4.431385 4.043280 1.097645
H -4.527418 5.468583 0.056079
C -1.654554 5.275883 -1.585227
H -2.044312 4.671672 -2.412819
H -2.019522 6.302015 -1.717390
H -0.562714 5.291992 -1.660760
```