A General Synthetic Method for the Formation of Substituted 5-Aminotetrazoles from Thioureas: A Strategy for Diversity Amplification.

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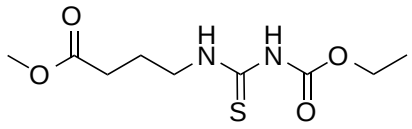
Supporting Information

General. CH_2Cl_2 was distilled from CaH under argon. DMF was distilled from 4 Å molecular sieves under reduced pressure. All other commercial reagents were used as received (Aldrich, Fischer Scientific Ltd. or BDH). All reactions were carried out under an atmosphere of nitrogen. Melting points are uncorrected. ^1H and ^{13}C NMR were recorded at 400 or 300 MHz and 100 or 75 MHz respectively on a Varian Unity 400 or Gemini 300 spectrometer. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ 7.26). Carbon chemical shifts were internally referenced to the dueterated solvent signals in $CDCl_3$ (δ 77.00). Low resolution mass spectra were recorded on a Bell and Howell 21-490 spectrometer, and high resolution spectra were recorded on an AEI MS3074 spectrometer. Flash column chromatography on silica gel (60 Å, 230-400 mesh, obtained from Whatman Company or Toronto Research Chemicals, Inc.) was performed with reagent grade hexanes and ethyl acetate. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel plates, (Alugram SIL G/UV_{254} purchased from Rose Scientific Limited), visualized with a UV_{254} lamp (Spectroline, Longlife Filter) and stained with 20% phosphomolybdic acid in ethanol. Solvent systems associated with R_f values and chromatography are reported as v/v ratios.

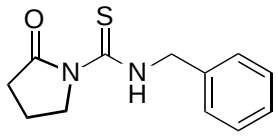
General Procedure for the preparation of Thioureas (5).
To a solution of amine **3** (6.0 mmol, 1.0 equiv) in 15 ml of dry CH_2Cl_2 was treated dropwise with isothiocyanate **4** (6.0 mmol, 1.0 equiv). The resulting solution was stirred at room temperature for 16 h, then diluted with H_2O (50 ml) and extracted with 3 x 15ml of CH_2Cl_2. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by recrystallization (CH_2Cl_2 : Hexanes) or column chromatography through silica gel.

4-(methyl 4-butanoic acid)-3-thio-allophanic acid ethyl ester (table 1, entry 4):



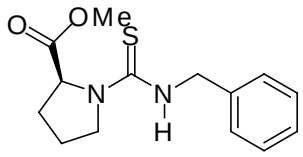
Obtained in 96 % yield as a beige solid; mp = 88-89 °C (EtOAc/hexanes); R_f = 0.43 (50% EtOAc/50% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (1H, bs), 4.23 (2H, q, *J* = 7.2 Hz), 3.75-3.71 (2H, m), 3.69 (3H, s), 2.42 (2H, t, *J* = 7.4 Hz), 2.03 (2H, quintet, *J* = 7.2 Hz), 1.31 (3H, t, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.40, 173.11, 152.66, 62.67, 51.70, 44.58, 31.16, 23.56, 14.11. MS (EI) *m/e* 248 (63, M+), 127 (50), 85 (68), 83 (100), 74 (76), 59 (73); HRMS (EI) *m/e* (M+) calcd. 248.0831, found 248.0828.

2-Oxopyrrolidine-1-carbothioic acid benzylamide (table 2, entry 5):



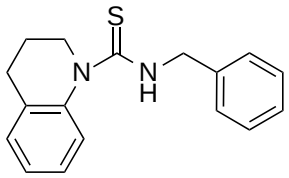
To a flame dried round bottom flask containing sodium hydride (0.026 mol, 1.1 equiv, 60% dispersion in oil) as a slurry in 100 mL THF was added 2-pyrrolidinone (0.024 mol, 1.0 equiv) dropwise over 15 minutes. After the evolution of hydrogen ceased (~ 30 minutes), the flask was cooled to -78 °C and the required isothiocyanate was added (0.026 mol, 1.1 equiv). The reaction was warmed to ambient temperature overnight. The flask was cooled to 0 °C, quenched with sat aq. NH_4Cl and warmed to ambient temeperature. The reaction mixture was concentrated *in vacuo* and purified by recrystalization (20% EtOAc/80% hexanes). Obtained in 92% yield; white solid ; R_f = 0.45 (20% EtOAc/80% hexanes); mp = 88.5-90 °C; IR (KBr) υ 2981, 1696, 1536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (1H, br s), 7.35-7.24 (5H, m), 4.83 (2H, d, *J* = 5.5 Hz), 4.22 (2H, d, *J* = 7.0 Hz), 2.68 (2H, t, *J* = 8.0 Hz), 2.05-1.98 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.80, 176.78, 136.73, 128.89, 127.97, 127.84, 51.34, 49.64, 34.58, 16.98; MS (EI) *m/e* 234 (100, M^+), 148 (19), 106 (94), 91 (66), 86 (55), 64 (20); HRMS (EI) *m/e* (M^+) calcd. 234.0827, found 234.0831.

1-Benzylthiocarbamoyl-(*L*)-proline methyl ester (table 2, entry 6):



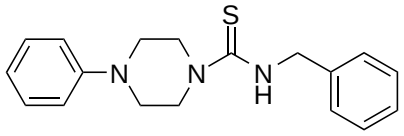
Obtained in 41 % yield. White crystalline solid; mp = 99 - 102 °C (EtOAc/hexanes); R_f = 0.30 (50% EtOAc/50% hexanes); IR (KBr) υ 3283, 2949, 1740, 1533, 1434, 1378, 1203, 916 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.28 (5H, m , aromatics), 5.68 (1H, bs), 5.00 (1H, bd, *J* = 7.1 Hz), 4.89 (1H, dd, *J* = 14.5 Hz, *J* = 5.0 Hz), 4.79 (1H, dd, *J* = 14.5 Hz, *J* = 5.0 Hz), 3.75 (3H, s), 3.67-3.60 (1H, m), 3.51-3.46 (1H, m), 2.27-2.05 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.89, 172.59, 137.86, 128.64, 127.91, 127.56, 63.56, 52.26, 49.75, 47.74, 29.34, 24.27; MS (EI) *m/e* 278 (65, M^+), 246 (35), 130 (19), 128 (47), 106 (48), 91 (64), 86 (36), 84 (49), 70 (100); HRMS (EI) *m/e* (M^+) calcd. 278.1089, found 278.1089. $[\alpha]_D^{20}$ = -0.30 (0.01 g/ml, $CHCl_3$).

3,4-Dihydro-2H-quinoline-1-carbothioic acid phenylamide (table 2, entry 7):



Obtained in 72 % yield. Off-white solid; mp = 100 - 103 °C (CH_2Cl_2:Hexanes); R_f = 0.66 (50% EtOAc/50% hexanes); IR (KBr) υ 3365, 2946, 1598, 1488, 1446, 1361, 1196, 1168, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (1H, bs), 7.40-7.13 (9H, m, aromatics); 4.36 (2H, t, *J* = 6.6 Hz), 2.81 (2H, t, *J* = 6.6 Hz), 2.08 (2H, quintet, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.15, 139.20, 138.62, 134.08, 129.89, 128.70, 126.86, 126.10, 125.69, 124.52, 123.68, 49.30, 26.71, 24.01; MS (EI) *m/e* 268 (54, M^+), 135 (86), 133 (100), 118 (26), 77 (57), 51 (26); HRMS (EI) *m/e* (M^+) calcd. 268.1034, found 268.1037.

4-Phenyl-piperazine-1-carbothioic acid benzylamide (table 2, entry 9):

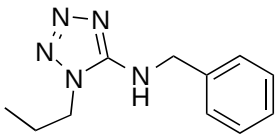


Obtained in 97 % yield. White solid; mp = 182 - 184 °C (CH_2Cl_2:Hexanes); R_f = 0.55 (50% EtOAc/50% hexanes); IR (KBr) υ 3247, 2818, 1549, 1493, 1419, 1381, 1338, 1206, 1162, 1061, 1014, 953 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.25 (7H, m, aromatics), 6.91-6.86 (3H, m, aromatics), 5.71 (1H, bs), 4.89 (2H, d, *J* = 4.8 Hz), 3.99 (4H, t, *J* = 5.2 Hz), 3.28 (4H, t, *J* = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.10, 150.28, 137.74, 129.25, 128.82, 128.13, 127.82, 120.11, 115.80, 50.40, 48.25, 47.12; MS (EI) *m/e* 220 (7.3), 162 (35), 149 (23), 120 (90), 104 (15), 91 (100), 77 (17), 65 (16); HRMS (EI) *m/e* (M^+) calcd. 311.1456, found 311.1452.

General Procedure for the preparation of 5-Aminotetrazoles (1).

To a suspension of thiourea **5** (1.25 mmol, 1.0 equiv), sodium azide (244 mg, 3.75 mmol, 3.0 equiv) and mercuric chloride (373 mg, 1.38 mmol, 1.1 equiv) in 5 ml of dry DMF was added triethylamine (503 μm, 3.75 mmol, 3.0 equiv). The resulting suspension was stirred for 3 h at room temperature or until TLC indicated complete consumption of starting material. The suspension was filtered through a pad of celite, washing with CH_2Cl_2. The filtrate was diluted with water, extracted with 3 x 15ml of CH_2Cl_2, the combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography.

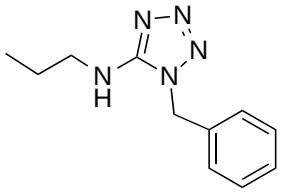
Benzyl-(1-propyl-1H-tetrazol-5-yl)-amine (table 1, entry 2):



Obtained in 45 % yield. White solid; mp = 117 - 118 °C (EtOAc/hexanes); R_f = 0.36 (50% EtOAc/50% hexanes); IR (KBr) υ 3267, 2972, 1614, 1451, 1366, 1070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.27 (5H, m, aromatics), 5.14 (1H, t, *J* = 5.7 Hz), 4.58 (2H, d, *J* = 5.7 Hz), 4.00 (2H, t, *J* = 7.3 Hz), 1.83 (2H, six, *J* = 7.4 Hz), 0.92 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.28, 137.87, 128.63, 127.83, 127.73, 48.31, 46.94, 22.02, 10.91; MS

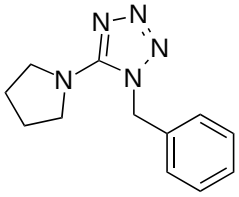
(EI) *m/e* 217 (21, M^+), 160 (44), 131 (18), 106 (39), 91 (100), 65 (22); HRMS (EI) *m/e* (M^+) calcd. 217.1327, found 217.1320.

(1-Benzyl-1H-tetrazol-5-yl)-propyl-amine (table 1, entry 2):



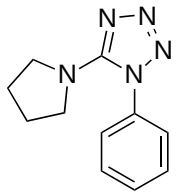
Obtained in 44 % yield. While solid; mp = 92 - 94 °C (EtOAc/hexanes); R_f = 0.35 (50% EtOAc/50% hexanes); IR (KBr) υ 3274, 2931, 1608, 1454, 1260, 1143, 1102 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.37 (3H, m, aromatics), 7.23-7.20 (2H, m, aromatics), 5.32 (2H, s), 3.74 (1H, bs), 3.31 (2H, dt, *J* = 7.3 Hz, *J* = 7.0 Hz), 1.51 (2H, six, *J* = 7.3 Hz), 0.79 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.41, 132.73, 129.41, 129.01, 127.37, 49.31, 46.12, 22,60, 10.85; MS (EI) *m/e* 217 (9, M^+), 174 (16), 104 (12), 91 (100), 65 (19); HRMS (EI) *m/e* (M^+) calcd. 217.1327, found 217.1324.

1-Benzyl-5-pyrrolidin-1-yl-1H-tetrazole (table 2, entry 1):



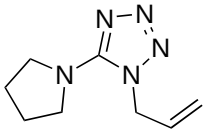
Obtained in 89 % yield. Beige solid; mp = 95 - 99 °C (EtOAc/hexanes); R_f = 0.20 (50% EtOAc/50% hexanes); IR (KBr) υ 2978, 2872, 1599, 1452, 1421, 1281, 1093, 1002, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (3H, m, aromatics), 7.12-7.11 (2H, m, aromatics), 5.51 (2H, s), 3.49 (4H, t, *J* = 6.6 Hz), 1.93-1.89 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.05, 135.35, 128.99, 128.22, 126.24, 50.21, 49.45, 25.52; MS (EI) *m/e* 229 (37, M^+), 173 (22), 172 (20), 91 (100), 65 (21), 55 (60); HRMS (EI) *m/e* (M^+) calcd.229.1327, found 229.1325.

1-Phenyl-5-pyrrolidin-1-yl-1H-tetrazole (table 2, entry 2):



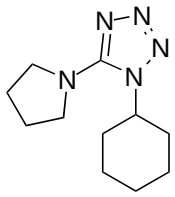
Obtained in 92 % yield. Off-white solid; mp = 133 - 136 °C (EtOAc/hexanes); R_f = 0.26 (50% EtOAc/50% hexanes); IR (KBr) υ 2977, 2874, 1604, 1504, 1431, 1141, 1088, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (5H, m, aromatics), 3.30-3.26 (4H, m), 1.91-1.88 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.67, 134.63, 129.73, 129.18, 126.19, 49.83, 25.52; MS (EI) *m/e* 215 (59, M^+), 190 (69), 186 (47), 158 (82), 132 (42), 118 (42), 98 (100), 91 (84), 77 (83), 55 (68); HRMS (EI) *m/e* (M^+) calcd. 215.1171, found 215.1174.

1-Allyl-5-pyrrolidin-1-yl-1H-tetrazole (table 2, entry 3):



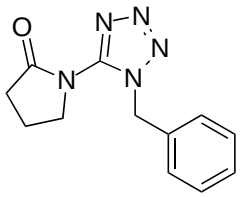
Obtained in 52 % yield. Light yellow oil; R_f = 0.16 (50% EtOAc/50% hexanes); IR (film) υ 3281, 2955, 2877, 1728, 1594, 1546, 1451, 1418, 1356, 1234, 1093, 991, 929 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.99 (1H, m), 5.29 (1H, d, *J* = 10.4 Hz), 5.07 (1H, d, *J* = 17.2 Hz), 4.93-4.91 (2H, m), 3.59-3.55 (4H, m), 2.01-1.98 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.32, 131.66, 118.24, 49.45, 48.96, 25.57; MS (EI) *m/e* 179 (60, M^+), 138 (36), 137 (31), 110 (18), 97 (18), 70 (56), 55(100); HRMS (EI) *m/e* (M^+) calcd.179.1171, found 179.1177.

1-Cyclohexyl-5-pyrrolidin-1-yl-1H-tetrazole (table 2, entry 4):



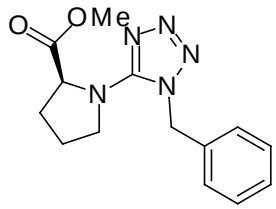
Obtained in 83 % yield. White crystalline solid; mp = 110 - 112 °C (EtOAc/hexanes); R_f = 0.27 (50% EtOAc/50% hexanes); IR (KBr) υ 2933, 2867, 1585, 1454, 1422, 1350, 1156, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.23-4.16 (1H, m), 3.60-3.49 (4H, m), 2.06-1.92 (10H, m), 1.76-1.73 (1H, m), 1.43-1.25 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.22, 57.18, 49.86, 32.85, 25.38, 25.31, 24.78; MS (EI) *m/e* 221 (30, M^+), 140 (35), 111 (64), 86 (22), 84 (38), 82 (41), 55 (100); HRMS (EI) *m/e* (M^+) calcd. 221.1640, found 221.1646.

1-(1-Benzyl-1H-tetrazol-5-yl)-pyrrolidine-2-one (table 2, entry 5):



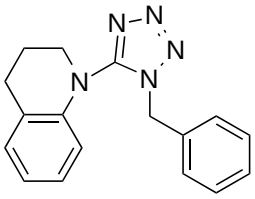
Obtained in 54 % yield, along with 26 % recovered starting material. Yellow oil; R_f = 0.24 (50% EtOAc/50% hexanes); IR (film) υ 3441, 2986, 2899, 1720, 1555, 1461, 1377, 1238, 1090, 1019, 927 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (3H, m, aromatics), 7.15-7.12 (2H, m, aromatics), 5.71 (2H, s), 3.68 (2H, t, *J* = 7.1 Hz), 2.44 (2H, t, *J* = 7.8 Hz), 2.01 (2H, tt, *J* = 7.8 Hz, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.22, 149.88, 133.14, 128.78, 128.67, 127.66, 52.50, 48.82, 30.60, 18.89; MS (EI) *m/e* 244 (5, M^+), 214 (100), 111 (22), 104 (23), 91 (86), 83 (27), 69 (26), 65 (30); HRMS (EI) *m/e* (M^+) calcd. 244.1198, found 244.1995.

1-(1-Benzyl-1H-tetrazole-5-yl)-(*L*)-proline methyl ester (table 2, entry 6):



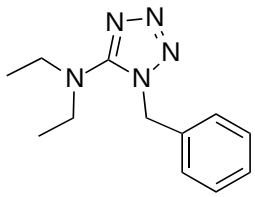
Obtained in 87 % yield. Off-white solid; mp = 118 - 120 °C (EtOAc/hexanes); IR (KBr) υ 2960, 1740, 1585, 1448, 1351, 1261, 1172, 1089, 1009 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (3H, m, aromatics), 7.13-7.11 (2H, m , aromatics), 5.53 (2H, s), 4.61 (1H, dd, *J* = 3.7 Hz, *J* = 8.3 Hz), 3.74-3.70 (1H, m), 3.68 (3H, s), 3.49-3.43 (1H, m), 2.28-2.17 (1H, m), 2.08-1.93 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.61, 155.40, 135.11, 129.05, 128.31, 126.18, 62.38, 52.35, 50.27, 49.25, 29.82, 24.53; MS (EI) *m/e* 287 (9, M^+), 228 (59), 159 (19), 97 (34), 91 (100), 70 (26); HRMS (EI) *m/e* (M^+) calcd. 287.1382, found 287.1395; $[\alpha]_D^{20}$ = -0.83 (0.01g/ml, $CHCl_3$).

1-(1-Phenyl-1H-tetrazol-5-yl)-1,2,3,4-tetrahydro-quinoline (table 2, entry 7):



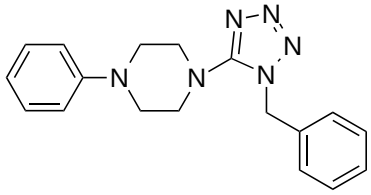
Obtained in 80 % yield; Yellow-beige solid; mp = 142 - 145 °C (EtOAc/hexanes); R_f = 0.57 (50% EtOAc/50% hexanes); IR (KBr) υ 3070, 2925, 2871, 1595, 1538, 1497, 1454, 1419, 1301, 1265, 1114, 1023 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.36 (5H, m, aromatics), 7.06-7.03 (1H, m, aromatic), 6.85-6.77 (2H, m, aromatics), 6.53-6.50 (1H, m, aromatic), 3.66 (2H, t, *J* = 5.9 Hz); 2.83 (2H, t, *J* = 6.6 Hz), 2.03 (2H, tt, *J* = 5.9Hz, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.07, 138.83, 134.16, 129.38, 129.33, 129.09, 126.52, 126.44, 122.70, 122.03, 117.12, 49.17, 26.67, 22.34; MS (EI) *m/e* 277 (39, M^+), 249 (46), 248 (59), 132 (100), 130 (43), 117 (56), 91 (24), 77 (36); HRMS (EI) *m/e* (M^+) calcd. 277.1327, found 277.1327.

(1-Benzyl-1H-tetrazol-5-yl)-diethyl-amine (table 2, entry 8):



Obtained in 78 % yield. Light yellow oil; R_f = 0.36 (50% EtOAc/50% hexanes); IR (film) υ 2923, 1734, 1576, 1437, 1168, 1092, 1017 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.31 (3H, m, aromatics), 7.20-7.17 (2H, m, aromatics), 5.40 (1H, s), 3.25 (4H, q, *J* = 7.1 Hz), 1.07 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.78, 134.22, 128.75, 128.15, 126.50, 50.23, 45.45, 12.64; MS (EI) *m/e* 231 (30, M^+), 160 (12), 91 (100), 72 (28), 65 (24), 56 (93); HRMS (EI) *m/e* (M^+) calcd. 231.1484, found 231.1490.

1-(1-Benzyl-1H-tetrazol-5-yl)-4-phenyl-piperazine (table 2, entry 9):



Obtained in 66 % yield. Beige solid; mp = 128 - 131 °C (EtOAc/hexanes); R_f = 0.45 (50% EtOAc/50% hexanes); IR (KBr) υ 3032, 2918, 2849, 1597, 1549, 1498, 1452, 1234, 1144, 946 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.20 (7H, m, aromatics), 6.92-6.87 (3H, m, aromatics), 5.43 (2H, s), 3.38-3.35 (4H, m), 3.21-3.18 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.55, 150.68, 133.61, 129.11, 129.06, 128.58, 126.94, 120.44, 116.37, 50.49, 49.72, 48.62; MS (EI) *m/e* 320 (67 M^+), 295 (16), 188 (48), 160 (18), 145 (50), 133 (99), (132 (99), 120 (73), 104 (56), 91 (100); HRMS (EI) *m/e* (M^+) calcd. 320.1749, found 320.1743.

X-Ray Crystal Data for 1-Benzyl-5-pyrrolidin-1-yl-1H-tetrazole (table 2, entry 1)

Table 1. Crystal data and structure refinement for k99259a.

Identification code	k99259a	
Empirical formula	C12 H15 N5	
Formula weight	229.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 8.1926(3) Å	α= 90°.
	b = 12.2982(4) Å	β= 90°.
	c = 11.3204(5) Å	γ = 90°.
Volume	1140.58(8) $Å^3$	
Z	4	
Density (calculated)	1.335 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	488	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.99 to 30.06°.	
Index ranges	-11<=h<=11, -17<=k<=17, -15<=l<=15	
Reflections collected	7222	
Independent reflections	3122 [R(int) = 0.034]	
Completeness to theta = 30.06°	99.8 %	
Absorption correction	multi-scan (Denzo-SMN)	
Max. and min. transmission	0.9872 and 0.9788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3122 / 1 / 156	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.0986	
R indices (all data)	R1 = 0.0771, wR2 = 0.1094	
Absolute structure parameter	0(2)	
Extinction coefficient	0.008(2)	
Largest diff. peak and hole	0.183 and -0.183 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for k99259a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3766(2)	4982(1)	8464(1)	19(1)
N(2)	4559(2)	4673(1)	7451(1)	24(1)
N(3)	4930(2)	5557(1)	6902(1)	26(1)
N(4)	4415(2)	6458(1)	7496(1)	23(1)
N(5)	2991(2)	6732(1)	9283(1)	22(1)
C(1)	3690(2)	6083(1)	8474(2)	18(1)
C(2)	3175(2)	7918(1)	9136(2)	24(1)
C(3)	2477(2)	8366(2)	10284(2)	25(1)
C(4)	2863(2)	7486(1)	11195(2)	24(1)
C(5)	2603(2)	6430(2)	10513(2)	21(1)
C(6)	3171(2)	4121(1)	9254(2)	20(1)
C(7)	1327(2)	4070(1)	9352(2)	20(1)
C(8)	657(2)	3636(2)	10380(2)	23(1)
C(9)	-1021(2)	3513(2)	10485(2)	29(1)
C(10)	-2036(2)	3835(2)	9569(2)	31(1)
C(11)	-1380(2)	4281(2)	8549(2)	28(1)
C(12)	301(2)	4397(1)	8442(2)	23(1)

Table 3. Bond lengths [Å] and angles [°] for k99259a.

N(1)-C(1)	1.356(2)
N(1)-N(2)	1.372(2)
N(1)-C(6)	1.469(2)
N(2)-N(3)	1.288(2)
N(3)-N(4)	1.363(2)
N(4)-C(1)	1.338(2)
N(5)-C(1)	1.343(2)
N(5)-C(5)	1.476(2)
N(5)-C(2)	1.476(2)
C(2)-C(3)	1.523(3)
C(3)-C(4)	1.527(3)
C(4)-C(5)	1.526(2)
C(6)-C(7)	1.516(2)
C(7)-C(12)	1.389(3)
C(7)-C(8)	1.393(3)
C(8)-C(9)	1.389(3)
C(9)-C(10)	1.386(3)
C(10)-C(11)	1.387(3)
C(11)-C(12)	1.390(3)
C(1)-N(1)-N(2)	107.77(14)
C(1)-N(1)-C(6)	134.37(15)
N(2)-N(1)-C(6)	117.84(14)
N(3)-N(2)-N(1)	106.33(14)
N(2)-N(3)-N(4)	112.02(15)
C(1)-N(4)-N(3)	105.41(14)
C(1)-N(5)-C(5)	125.84(15)
C(1)-N(5)-C(2)	117.84(14)
C(5)-N(5)-C(2)	112.14(14)
N(4)-C(1)-N(5)	123.27(15)
N(4)-C(1)-N(1)	108.47(15)
N(5)-C(1)-N(1)	128.24(16)
N(5)-C(2)-C(3)	102.91(14)
C(2)-C(3)-C(4)	103.97(15)

C(5)-C(4)-C(3)	103.51(16)
N(5)-C(5)-C(4)	103.47(14)
N(1)-C(6)-C(7)	113.86(14)
C(12)-C(7)-C(8)	119.45(15)
C(12)-C(7)-C(6)	122.50(16)
C(8)-C(7)-C(6)	117.99(15)
C(9)-C(8)-C(7)	120.24(17)
C(10)-C(9)-C(8)	119.93(18)
C(9)-C(10)-C(11)	120.19(17)
C(10)-C(11)-C(12)	119.81(18)
C(7)-C(12)-C(11)	120.38(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for k99259a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	21(1)	21(1)	16(1)	0(1)	1(1)	0(1)
N(2)	24(1)	29(1)	18(1)	-4(1)	4(1)	1(1)
N(3)	27(1)	30(1)	20(1)	-1(1)	3(1)	0(1)
N(4)	24(1)	26(1)	19(1)	2(1)	1(1)	-1(1)
N(5)	30(1)	15(1)	19(1)	1(1)	3(1)	1(1)
C(1)	15(1)	21(1)	17(1)	2(1)	-3(1)	-1(1)
C(2)	31(1)	16(1)	25(1)	3(1)	-1(1)	0(1)
C(3)	31(1)	20(1)	24(1)	1(1)	3(1)	2(1)
C(4)	31(1)	21(1)	20(1)	0(1)	3(1)	2(1)
C(5)	27(1)	20(1)	16(1)	1(1)	4(1)	-1(1)
C(6)	23(1)	18(1)	20(1)	2(1)	-2(1)	0(1)
C(7)	22(1)	16(1)	22(1)	-5(1)	-1(1)	1(1)
C(8)	29(1)	18(1)	24(1)	-1(1)	0(1)	0(1)
C(9)	32(1)	20(1)	36(1)	-2(1)	12(1)	-2(1)
C(10)	23(1)	22(1)	48(1)	-10(1)	5(1)	-3(1)
C(11)	25(1)	25(1)	34(1)	-8(1)	-7(1)	4(1)
C(12)	28(1)	20(1)	21(1)	-6(1)	-2(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for k99259a.

	x	y	z	U(eq)
H(2A)	2551	8183	8445	29
H(2B)	4337	8122	9042	29
H(3A)	1285	8483	10218	30
H(3B)	3006	9063	10499	30
H(4A)	4002	7547	11477	29
H(4B)	2115	7533	11880	29
H(5A)	3344	5852	10801	25
H(5B)	1461	6176	10584	25
H(6A)	3635	4239	10052	24
H(6B)	3577	3411	8964	24
H(8A)	1351	3424	11011	28
H(9A)	-1474	3209	11183	35
H(10A)	-3184	3750	9641	37
H(11A)	-2077	4506	7925	34
H(12A)	751	4702	7744	27

ORTEP PLOT with 30% thermal ellipsoids: