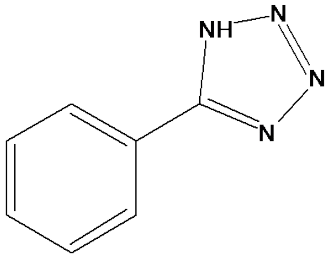
Microwave assisted synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition over heterogeneous Cu based catalyst: Application to the preparation of ^{13}N-labelled tetrazoles

S. M. Joshi,[a] R. B. Mane[b], V. Gómez-Vallejo,[c] J. Llop[a,†] and Chandrashekhar Rode.[b,*]

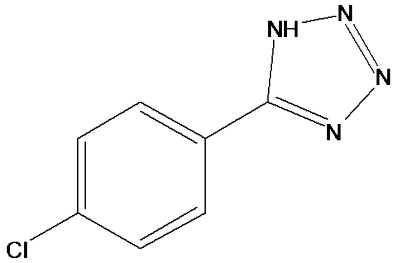
Characterization of compounds 2a-2k

Phenyltetrazole (2a):



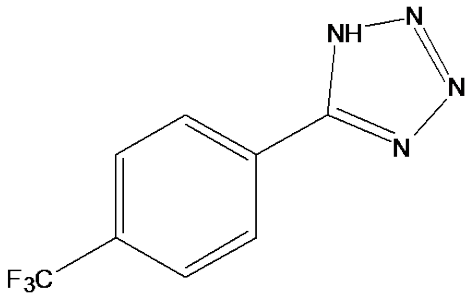
^{1}HNMR (400 MHz, DMSO-d_6) δ 7.55-7.60 (m, *3H*, aromatic), 8.01-8.05 (m, *2H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 154.5 (tetrazole ring), 131.0, 130.2, 127.2, 124.4; LCMS: calculated for $C_7H_6N_4$ (MH^+): 147.149; found: 147.054.

5-(4'-Chlorophenyl)tetrazole (2b):



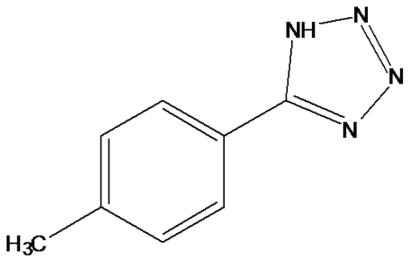
^{1}HNMR (400 MHz, DMSO-d_6) δ 8.02 (d, J = 8.4 Hz, *2H*, aromatic), 7.65 (d, J = 8.4 Hz, *2H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6): d =155.6, 135.2, 129.5, 128.2, 124.4; LCMS calculated for $C_7H_5ClN_4$ (MH+): 181.594; found: 181.006.

5-(4'-(Trifluoromethyl)phenyl)tetrazole (2c):



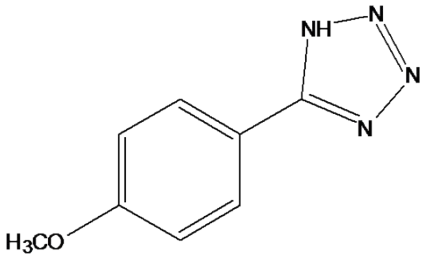
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21(d, J = 8.1 Hz, *2H*, aromatic), 7.92 (d, J = 8.1 Hz, *2H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6): d =155.2, 131.2, 128.3, 127.6, 126.2, 123.7; LCMS calculated for $C_8H_5F_3N_4$ (MH+): 215.147; found: 215.021.

5-(4'-Tolyl)tetrazole (2d):



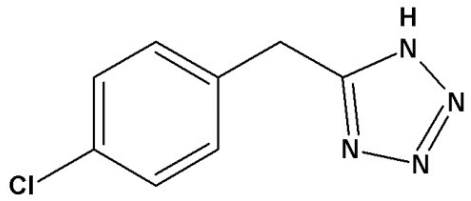
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96(d, J = 8.0 Hz, *2H*, aromatic), 7.48 (d, J = 8.0 Hz, *2H*, aromatic), 2.30 (s, *3H*, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 154.8, 139.4, 130.4, 126.6, 121.4, 21.1; LCMS calculated for $C_8H_8N_4$ (MH+): 161.175; found: 161.067.

5-(4'-Methoxyphenyl)tetrazole (2e):



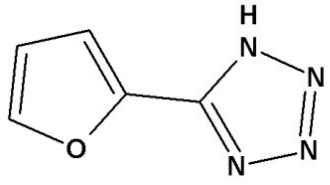
^{1}HNMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 9.0 Hz, *2H*, aromatic), 7.13 (d, J = 9.0 Hz, *2H*, aromatic), 3.82 (s, *3H*, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 161.6, 154.4, 128.4, 116.4, 114.6, 55.2; LCMS calculated for $C_8H_8N_4O$(MH+): 177.175; found: 177.053.

5-((4'-Chlorophenyl)methyl)tetrazole (2f):



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (d, J = 8.4 Hz, *2H*, aromatic), 7.27 (d, J = 8.4 Hz, *2H*, aromatic), 4.36 (s, *2H*, CH_2); ^{13}C-NMR (125 MHz, DMSO-d_6, δ, ppm): 154.4, 134.5, 131.2, 130.2, 128.2, 27.4; LCMS calculated for $C_8H_7ClN_4$ (MH+): 195.620; Found: 195.508.

5-(2-Furyl)tetrazole (2g):



^{1}H NMR (400 MHz, DMSO-d_6) δ 6.73-6.78 (m, *1H*, aromatic), 7.25 (bd, J = 3.5 Hz, *1H*, aromatic), 8.02-8.06 (m, *1H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 148.6, 146.3, 140.2, 113.5, 112.7; LCMS calculated for $C_5H_5N_4O$ (MH+): 137.111; found: 137.040.

5-(2-Naphthyl)tetrazole (2h):

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62-8.59 (m, *1H*, aromatic), 8.18-8.00 (m, *3H*, aromatic), 8.05-7.97 (m, *1H*, aromatic), 7.67-7.59 (m, *2H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 155.7, 134.00, 132.80, 129.30, 128.70, 127.78, 127.80, 127.25, 127.10, 123.68, 121.55; LCMS calculated for $C_{11}H_9N_4$ (MH+): 197.082; found: 197.082.

5-(4-Hydroxyphenyl)tetrazole (2i):

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (br, *1H*), 7.84 (d, J=8.5 Hz, aromatic), 6.93 (d, J=8.5 Hz, *2H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 161.22, 153.7, 127.89, 115.81, 113.89; LCMS calculated for $C_7H_7N_4O$ (MH+): 163.061; found: 163.061.

5-(3-Nitrophenyl)tetrazole (2j):

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (s, *1H*, aromatic), 8.40−8.47 (m, *2H*, aromatic), 7.90 (t, J =8.1 Hz, *1H*, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 155.4, 148.6, 133.4, 131.6, 126.5, 126.9, 122.3; LCMS calculated for $C_7H_6N_5O_2$ (MH+): 192.141; found: 192.190.

5-t-Butyltetrazole (2k):

^{1} H NMR (400 MHz, DMSO-d_6) δ 1.34 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 164.01, 30.41, 29.12. LCMS calculated for $C_5H_{11}N_4$ (MH+): 127.159; found: 127.148.

Figure 1S. Reusability of the 30%Cu-Cr-Al catalyst for the synthesis of **2a**