

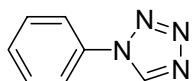
SUPPORTING INFORMATION

Title: A Facile Synthesis of 1-Substituted-1*H*-1,2,3,4-Tetrazoles Catalyzed by Ytterbium Triflate Hydrate

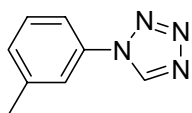
Author(s): Wei-Ke Su,* Zhi Hong, Wei-Guang Shan, Xing-Xian Zhang

Ref. No.: O200600007

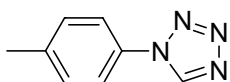
^1H NMR, ^{13}C NMR, IR and MS data of products are listed here.



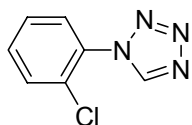
1-phenyl-1H-1,2,3,4-tetrazole (2a): Yield: 124 mg (85%). mp. 64-65 °C (lit.^[3f] 65-66 °C). pale yellow needle crystal. ^1H NMR (400 MHz, CDCl_3): δ = 7.62-7.53 (m, 3H), 7.75-7.72 (m, 2H), 9.09 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 119.00, 121.16, 123.30, 129.32, 149.24 ppm. IR (KBr): ν = 1681, 1587, 1489, 1322, 1209 cm^{-1} . MS (EI): m/z (%) = 147 (100).



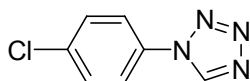
1-(3-methylphenyl)-1H-1,2,3,4-tetrazole (2b): Yield: 143 mg (89%). mp 53-54 °C (lit.^[3d] 53-54 °C). pale yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 2.48 (s, 3H), 7.35 (d, J = 7.6 Hz, 1H), 7.55-7.44 (m, 3H), 9.02 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.20, 118.07, 121.60, 129.80, 130.62, 133.58, 140.53 ppm. IR (KBr): ν = 1494, 1482, 1376, 1224, 1189, 1176, 1176, 1167, 1097 cm^{-1} . MS (EI): m/z (%) = 161 (100).



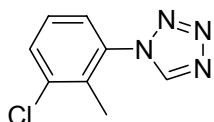
1-(4-methylphenyl)-1H-1,2,3,4-tetrazole (2c): Yield: 146 mg (91%). mp 93-94 °C (lit.^[3f] 93-94 °C); colorless needle crystal. ^1H NMR (400 MHz, CDCl_3): δ = 2.46 (s, 3H), 7.39-7.37 (m, 2H), 7.61-7.58 (m, 2H), 9.01 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.39, 121.35, 130.89, 131.71, 140.65, 140.76 ppm. IR (KBr): ν = 1517, 1467, 1391, 1214, 1204, 1176, 1094, 1047, 999, 822 cm^{-1} . MS (EI): m/z (%) = 161 (100).



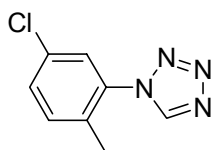
1-(2-chlorophenyl)-1H-1,2,3,4-tetrazole (2d): Yield: 148 mg (82%). mp 87-88 °C (lit.^[3d] 86-87 °C); colorless needle crystal. ¹H NMR (400 MHz, CDCl₃): δ = 7.67-7.51 (m, 4H), 9.08 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 127.81, 128.59, 128.96, 131.27, 131.80, 132.08, 143.50 ppm. IR (KBr): ν = 1494, 1461, 1204, 1174, 1090, 993, 888, 761 cm⁻¹. MS (EI): m/z (%) = 180 (100).



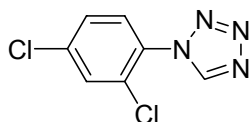
1-(4-chlorophenyl)-1H-1,2,3,4-tetrazole (2e): Yield: 159 mg (88%). mp 157-158 °C (lit.^[3f] 155-156 °C); colorless needle crystal. ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (d, J = 8.8Hz, 2H), 7.70 (d, J = 8.8Hz, 2H), 9.04 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 122.74, 130.73, 132.55, 136.35, 140.76 ppm. IR (KBr): ν = 1504, 1385, 1215, 1205, 1175, 1088, 996, 826 cm⁻¹. MS (EI): m/z (%) = 180 (100).



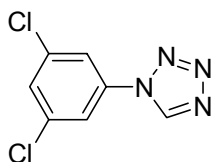
1-(3-chloro-2-methylphenyl)-1H-1,2,3,4-tetrazole (2f): Yield: 146 mg (75%). colorless needle crystal. mp 95-96 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.20 (s, 3H), 7.27 (d, J = 8.0Hz, 1H), 7.37 (t, J = 8.0Hz, 1H), 7.63 (d, J = 8.0Hz, 1H), 8.84 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 15.18, 124.69, 127.47, 131.80, 132.87, 133.87, 136.40, 143.18 ppm. IR (KBr): ν = 1597, 1581, 1482, 1459, 1385, 1233, 1191, 1177, 1097, 1056, 993 cm⁻¹. MS (EI): m/z (%) = 194 (15), 165 (100). C₈H₇ClN₄ (195): calcd. C 49.37, H 3.63, N 28.79; found C 49.41, H 3.66, N 28.75.



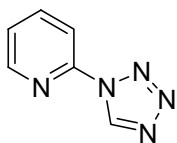
1-(5-chloro-2-methylphenyl)-1H-1,2,3,4-tetrazole (2g): Yield: 152 mg (78%). colorless needle crystal. mp 54-55 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.20 (s, 3 H), 7.40-7.38 (m, 2H), 7.50-7.47 (m, 1H), 8.87 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 17.65, 126.18, 131.23, 132.53, 132.92, 133.18, 133.81, 143.19 ppm. IR (KBr): ν = 1601, 1578, 1502, 1472, 1386, 1216, 1179, 1135, 1091, 1034, 1001, 962 cm⁻¹. MS (EI): m/z (%) = 165 (100). C₈H₇ClN₄ (195): calcd. C 49.37, H 3.63, N 28.79; found C 49.42, H 3.59, N 28.84.



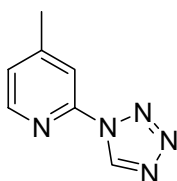
1-(2, 4-dichlorophenyl)-1H-1,2,3,4-tetrazole (2h): Yield: 174 mg (81%). colorless needle crystal. mp 146 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.63 (dd, J = 2.8 Hz and 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 2.4 Hz, 1H), 9.07 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 120.45, 123.34, 132.25, 133.00, 134.81, 134.89, 140.69 ppm. IR (KBr): ν = 1580, 1492, 1428, 1249, 1214, 1034, 875 cm^{-1} . MS (EI): m/z (%) = 219 (9), 217 (53), 215 (100). $\text{C}_7\text{H}_4\text{Cl}_2\text{N}_4$ (215): calcd. C 39.09, H 1.87, N 26.06; found C 39.14, H 1.83, N 26.11.



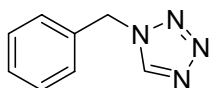
1-(3, 5-dichlorophenyl)-1H-1,2,3,4-tetrazole (2i): Yield: 181 mg (84%). colorless needle crystal. mp 128 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.55 (t, J = 1.6 Hz, 1H), 7.70 (t, J = 1.6 Hz, 2H), 9.07 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 119.66, 130.11, 135.01, 136.85, 140.35 ppm. IR (KBr): ν = 1588, 1477, 1428, 1068, 1007, 854, 665 cm^{-1} . MS (EI): m/z (%) = 219 (10), 217 (58), 215 (100). $\text{C}_7\text{H}_4\text{Cl}_2\text{N}_4$ (215): calcd. C 39.09, H 1.87, N 26.06; found C 39.14, H 1.84, N 26.13.



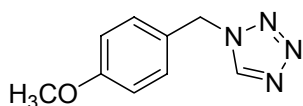
1-(2-pyridine)-1H-1,2,3,4-tetrazole (2j): Yield: 131 mg (89%). mp 129-130 °C (lit.^[9] 125-126 °C). colorless needle crystal. ^1H NMR (400 MHz, CDCl_3): δ = 7.51-7.47 (m, 1H), 8.06-8.01 (m, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 9.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 114.58, 125.05, 140.05, 140.30, 147.07, 149.28 ppm. IR (KBr): ν = 1597, 1576, 1472, 1391, 1212, 1182, 1151, 1090, 1006 cm^{-1} . MS (EI): m/z (%) = 118 (100).



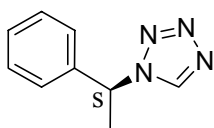
4-methyl-2-(1H-1,2,3,4-tetrazol-1-yl)pyridine (2k): Yield: 140 mg (87%). pink needle crystal. mp 130 °C. ^1H NMR (400 MHz, CDCl_3): δ = 2.50 (s, 3H), 7.25-7.24 (m, 1H), 7.89 (s, 1H), 8.37 (d, J = 5.2 Hz, 1H), 9.52 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.02, 115.17, 126.05, 140.44, 147.18, 148.86, 152.09 ppm. IR (KBr): ν = 1617, 1476, 1450, 1239, 1174, 1091, 995, 952, 838 cm^{-1} . MS (EI): m/z (%) = 162 (45), 134 (100). $\text{C}_7\text{H}_7\text{N}_5$ (161): calcd. C 52.16, H 4.38, N 43.46; found C 52.22, H 4.42, N 43.41.



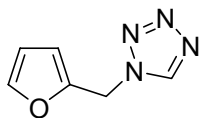
1-benzyl-1H-1,2,3,4-tetrazole (2l): Yield: 127 mg (79%). mp 57-58 °C (lit.^[3e] 58-59 °C). white solid. ^1H NMR (400 MHz, CDCl_3): δ = 5.61 (s, 2H), 7.40-7.28 (m, 5H), 8.61 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 51.93, 128.15, 129.09, 129.16, 132.80, 142.51 ppm. IR (KBr): ν = 1494, 1476, 1457, 1436, 1422, 1244, 1163, 1104 cm^{-1} .



1-(4-methoxybenzyl)-1H-1,2,3,4-tetrazole (2m): Yield: 143 mg (75%). mp 67-68 °C (lit.^[3e] 68-69 °C). colorless needle crystal. ^1H NMR (400 MHz, CDCl_3): δ = 3.82 (s, 3H), 5.53 (s, 2H), 6.93-6.91 (m, 2H), 7.27 (d, J = 8.8 Hz, 2H), 8.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 51.41, 54.98, 114.37, 124.30, 129.59, 141.87, 159.94 ppm. IR (KBr): ν = 1611, 1514, 1253, 1163, 1033 cm^{-1} . MS (EI): m/z (%) = 121 (100).



(s)-1-(1-phenylethyl)-1H-1,2,3,4-tetrazole (2n): Yield: 125 mg (72%). colorless crystal. mp 72-73 °C. $[\alpha]_{\text{D}}^{17.4}$ = +23.04 (c = 0.1, methanol). ^1H NMR (400 MHz, CDCl_3): δ = 2.04 (m, 3H), 5.86 (m, 1H), 7.42-7.29 (m, 5H), 8.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.20, 59.18, 126.09, 126.51, 129.07, 129.22, 138.16, 141.61 ppm. IR (KBr): ν = 1495, 1467, 1456, 1425, 1383, 1258, 1208, 1163, 1112, 1097, 1069, 1051, 1027 cm^{-1} . MS (EI): m/z (%) = 117 (40), 105 (100). $\text{C}_9\text{H}_{10}\text{N}_4$ (174): calcd. C 62.04, H 5.79, N 32.17; found C 61.99, H 5.73, N 32.24.



1-(2-furylmethyl)-1H-1,2,3,4-tetrazole (2o): Yield: 107 mg (71%). colorless needle crystal. mp 85 °C. ^1H NMR (400 MHz, CDCl_3): δ = 5.64 (s, 2H), 6.42-6.41 (m, 1H), 6.56-6.55 (m, 1H), 7.46-7.45 (m, 1H), 8.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 44.96, 111.24, 111.43, 142.69, 144.39, 145.79 ppm. IR (KBr): ν = 1506, 1476, 1430, 1354, 1260, 1165, 1154, 1104, 1016 cm^{-1} . MS (EI): m/z (%) = 151 (100). $\text{C}_6\text{H}_6\text{N}_4\text{O}$ (150): calcd. C 47.99, H 4.03, N 37.32; found C 48.07, H 3.99, N 37.38.