SUPPORTING INFORMATION FOR

Indium-Mediated Cleavage of the Trityl Group from Protected 1H-Tetrazoles

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Synthesis of all tetrazoles. General Procedure

The mixture of a nitrile (50 mmol), NaN₃ (65 mmol) and Et₃N.HCl (150 mmol) in toluene (100 mL) was stirred at 110°C for 17-30 h (2b, 2f and 2l for 24 h; 2c and 2d for 17 h; 2e and 2j for 30 h). After cooling to room temperature, the mixture was extracted with water (100 mL). To the aqueous layer, 36% HCl was added dropwise till pH was acidic. After filtration, the solid was washed with water and dried under reduced pressure, yielding the expected tetrazoles 2. The corresponding physical and spectroscopic data for all tetrazoles 2 follow.

5-Phenyl-1H-tetrazole (2a)
White solid; yield: 1.39 g (95%); mp: 215-216°C; ¹H NMR: (300 MHz, DMSO-d₆): δ = 7.55-7.62 (m, 3H), 8.01-8.10 (m, 2H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 124.1 (2×CH), 127.0 (C), 129.4 (CH), 131.3 (2×CH), 155.3 (C).

5-(4'-Methyl-[1,1'-biphenyl]-2-yl)-1H-tetrazole (2b)
Brown solid; yield: 1.84 g (78%); mp: 149-151°C; IR (KBr): 3336, 2974, 2900, 1080, 1046, 879, 755 cm⁻¹; ¹H NMR: (300 MHz, DMSO-d₆): δ = 2.28 (s, 3H), 6.98 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 7.55 (ddd, J = 10.3, 5.8, 1.9 Hz, 2H), 7.63-7.69 (m, 2H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 20.7 (CH₃), 123.4 (CH), 127.6 (CH), 128.7 (2×CH), 128.9 (CH), 130.5 (2×CH), 130.6 (CH), 131.1(C), 136.3 (C), 136.8 (C), 141.5 (C), 155.1 (C); Anal. Calcd for C₁₄H₁₂N₄: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.86; H, 5.17; N, 24.07.

5-Benzyl-1H-tetrazole (2c)
White solid; yield: 1.01 g (63%); mp: 123-124°C; ¹H NMR: (300 MHz, DMSO-d₆): δ = 4.28 (s, 2H), 7.24-7.35 (m, 5H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 29.0 (CH₂), 127.1 (CH), 128.7 (2×CH), 128.8 (2×CH), 136.0 (C), 155.3 (C); Anal. Calcd for C₉H₈N₄: C, 59.99; H, 5.03; N, 34.98. Found: C, 60.05; H, 4.80; N, 36.21.
5-(tert-Butyl)-1H-tetrazole (2d)
White solid; yield: 1.14 g (90%); mp: 208-210°C; IR (KBr): 2977, 2986, 2869, 1717, 1558, 1366, 1066, 1045, 1008 cm⁻¹; ¹H NMR: (300 MHz, DMSO-d₆): δ = 1.35 (s, 9H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 28.9 (3×CH₃), 30.3 (C), 163.4 (C).

5-Undecyl-1H-tetrazole (2e)
Brown solid; yield: 1.28 g (57%); mp: 72-73°C; IR (KBr): 3225, 2914, 2848, 1545, 1471, 1074, 716 cm⁻¹; ¹H NMR: (300 MHz, DMSO-d₆): δ = 0.84 (t, J = 6.8 Hz, 3H), 1.24 (m, 16H), 1.65-1.68 (m, 2H), 2.84 (t, J = 7.6 Hz, 2H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 13.9 (CH₃), 22.2, 22.7, 27.0, 28.3, 28.6, 28.7, 28.9, 29.0 (2C), 31.3 (10×CH₂), 155.9 (C); Anal. Calcd for C₁₂H₂₄N₄: C, 64.24; H, 10.78; N, 24.97. Found: C, 63.97; H, 10.50; N, 26.51.

2-(1H-Tetrazol-5-yl)pyridine (2f)
Brown solid; yield: 1.25 g (85%); mp: 208-210°C; ¹H NMR: (300 MHz, DMSO-d₆): δ = 7.63 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 8.08 (td, J = 7.8, 1.7 Hz, 1H), 8.22 (dt, J = 7.9, 1.0 Hz, 1H), 8.79 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 122.6 (CH), 126.2 (CH), 138.3 (CH), 143.7 (C), 150.1 (C), 154.8 (CH).

1H-Tetrazol-5-amine (2g)
White solid; yield: 0.79 g (93%); mp: 212-214°C; IR (KBr): 3399, 3192, 1636, 1263, 1044 cm⁻¹; ¹H NMR: (300 MHz, MeOD-d₄): δ = 6.56 (s, 2H); ¹³C NMR: (75 MHz, MeOD-d₄): δ = 158.2 (C); Anal. Calcd for CH₂N₅: C, 14.12; H, 3.55; N, 82.33. Found: C, 14.59; H, 3.92; N, 79.46.
3,3-Dimethyl-1-(1H-tetrazol-5-yl)butan-2-one (2j)
Orange solid; yield: 1.43 g (85%); mp: 152-154°C; IR (KBr): 2973, 2322, 1716, 1365, 1048, 1007, 728 cm⁻¹; ¹H NMR: (300 MHz, DMSO-d₆): δ = 1.18 (s, 9H), 4.41 (s, 2H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 25.8 (3×CH₃), 32.2 (CH₂), 44.0 (C-C=O), 128.2 (C), 209.3 (C=O); Anal. Calcd for C₇H₁₂N₄O: C, 49.99; H, 7.19; N, 33.31. Found: C, 49.96; H, 6.61; N, 31.52.

5-Benzhydryl-1H-tetrazole (2k)
White solid; yield: 1.70 g (72%); mp: 165-166°C; IR (KBr): 3264, 2917, 1560, 1446, 743, 695, 632 cm⁻¹; ¹H NMR: (300 MHz, MeOD-d₄): δ = 5.85 (s, 1H), 7.14-7.30 (m, 10H); ¹³C NMR: (75 MHz, MeOD-d₄): δ = 40.8 (CH), 128.6 (2×CH), 129.6 (4×CH), 129.9 (4×CH), 140.8 (C), 160.0 (2×C); Anal. Calcd for C₁₄H₁₂N₄: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.86; H, 5.17; N, 24.07.

5-(Anthracen-9-yl)-1H-tetrazole (2l)
Green solid; yield: 1.85 g (75%); mp: 215-216°C; IR (KBr): 2987, 2900, 1578, 1053, 735 cm⁻¹; ¹H NMR: (300 MHz, DMSO-d₆): δ = 7.45 (d, J = 8.6 Hz, 2H), 7.56-7.63 (m, 4H), 8.23-8.31 (m, 2H), 8.94 (s, 1H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 120.6 (2×CH), 124.8 (2×CH), 126.4 (2×C), 128.2 (CH), 129.2 (C), 130.8 (2×CH), 131.0 (2×CH), 138.3 (2×C), 150.1 (C); Anal. Calcd for C₁₅H₁₀N₄: C, 73.16; H, 4.09; N, 22.75. Found: C, 72.80; H, 4.18; N, 22.75.
Tritylation of 5-Substituted Tetrazoles. General Procedure

A solution of the corresponding tetrazole (10.0 mmol) in CH₂Cl₂ (5 mL) was added to a solution of trityl chloride (3.1 g, 11.0 mmol), triethylamine (2.5 mL, 17.6 mmol) and 4-(dimethylamino)pyridine (92 mg, 0.4 mmol) in CH₂Cl₂ (10 mL) at room temperature and the mixture was stirred overnight. The reaction was then quenched with water (5 mL) and extracted with ethyl acetate (3 × 15 mL) and the combined organic phases were washed with brine (5 mL) and dried over sodium sulfate. After evaporation of the solvents (15 Torr), the resulting residue was purified by column chromatography (deactivated silica gel, hexane/ethyl acetate) affording the expected tetrazoles 1a-1f and 1i-1l.

For the preparation of the double tritylated compound 1g the amounts of the reagents and solvent used were double the ones indicated above. Compound 1g was separated by column chromatography [deactivated silica gel, hexane/ethyl acetate]. The corresponding physical, spectroscopic and analytical data for the tritylated tetrazoles follow.

FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer using KBr pellets. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ¹H and 75 MHz for ¹³C) using CDCl₃, DMSO-d₆, MeOD-d₄ as solvents and TMS (0.00 ppm, ¹H) and CDCl₃ (77.0 ppm, ¹³C), DMSO-d₆ (2.50 ppm, ¹H and 39.75 ppm, ¹³C), MeOD-d₄ (4.87 ppm, ¹H and 49.0 ppm, ¹³C) as internal standards; chemical shifts are given in δ (ppm) and coupling constants (J) in Hz. Elemental analysis were measured by the Technical Services of the University of Alicante. Column chromatography was performed using silica gel 60 (35-70 mesh) or basic aluminium oxide (50-160 µm particle size). When mentioned, deactivated silica gel means that it was treated with 5% triethylamine in hexane and the column was eluted with the same solvent mixture until the coming eluent was basic according to pH paper. All reagents used for the synthesis of N-trityltetrazoles 1.

5-Phenyl-1-trityl-1H-tetrazole (1a)

White solid; yield: 3.69 g (95%); mp: 156-158°C; IR (KBr): 1491, 1447, 1189, 1026, 762, 747, 729, 693 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 7.13-7.47 (m, 18H), 8.12-8.16 (m, 2H); ¹³C NMR: (75 MHz, CDCl₃): δ = 83.3 (C), 127.2 (2×CH), 127.7 (3×CH), 127.9 (6×CH), 128.9 (C), 130.5 (6×CH), 141.5 (CH), 145.3 (2×CH), 150.8 (3×C), 164.2 (C); Anal. Calcd for C₂₆H₂₀N₄: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.09; H, 5.66; N, 13.92.
5-(4'-Methyl-[1,1'-biphenyl]-2-yl)-1-trityl-1H-tetrazole (1b)
White solid; yield: 3.21 g (67%); mp: 180-184°C; IR (KBr): 3056, 1445, 1028, 748, 698, 640 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 2.19 (s, 3H), 6.82-6.95 (m, 9H), 7.17-7.40 (m, 13H), 7.81-7.84 (m, 1H); ¹³C NMR: (75 MHz, CDCl₃): δ = 21.3 (CH₃), 83.0 (C), 126.6, 127.4, 127.7, 128.1, 128.2, 128.3 (4C), 129.2, 129.3 (6C), 129.4, 130.4, 130.5, 130.8, 136.5 (23×CH), 138.3 (C), 141.4 (C), 142.4 (C), 147.0 (C), 154.1 (3×C), 164.3 (C); Anal. Calcd for C₃₃H₂₆N₄: C, 82.82; H, 5.48; N, 11.71. Found: C, 82.37; H, 5.46; N, 11.42.

5-Benzyl-1-trityl-1H-tetrazole (1c)
White solid; yield: 3.54 g (88%); mp: 160-164°C; IR (KBr): 1530, 1252, 1073, 889, 733, 694 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 4.28 (s, 2H), 7.08-7.12 (m, 6H), 7.23-7.37 (m, 14H); ¹³C NMR: (75 MHz, CDCl₃): δ = 32.0 (CH₂), 83.0 (C), 126.8 (CH), 127.8 (3×CH), 128.1 (6×CH), 128.8 (2×CH), 129.1 (2×CH), 130.0 (6×CH), 137.0 (C), 141.5 (3×C), 164.6 (C); Anal. Calcd for C₂₇H₂₂N₄: C, 80.57; H, 5.51; N, 13.92. Found: C, 80.30; H, 5.52; N, 14.84.

5-(tert-Butyl)-1-trityl-1H-tetrazole (1d)
White solid; yield: 2.54 g (69%); mp: 132-136°C; IR (KBr): 3005, 2922, 2850, 1493, 1444, 747, 698 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 1.34 (s, 9H), 1.27 (m, 16H), 1.72-1.79 (m, 2H), 2.90 (t, J = 7.6 Hz, 2H), 7.01-7.26 (m, 15H); ¹³C NMR: (75 MHz, CDCl₃): δ = 14.3 (CH₃), 22.8, 29.2, 29.4, 29.7, 29.8, 32.2, 39.7 (C), 82.7 (C), 127.9 (5×CH), 128.2, 128.4, 129.1 (2×CH), 130.3 (6×CH), 141.5 (3×C), 162.1 (C); Anal. Calcd for C₂₄H₂₄N₄: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.58; H, 8.14; N, 13.46.

1-Trityl-5-undecyl-1H-tetrazole (1e)
Brown solid; yield: 3.87 g (83%); mp: 76-80°C; IR (KBr): 2922, 2850, 1493, 1444, 747, 698 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 0.87 (t, J = 6.8 Hz, 3H), 1.27 (m, 16H), 1.72-1.79 (m, 2H), 2.90 (t, J = 7.6 Hz, 2H), 7.07-7.36 (m, 15H); ¹³C NMR: (75 MHz, CDCl₃): δ = 14.3 (CH₃), 22.8, 29.2, 29.4, 29.7, 29.8, 32.2, 39.7 (C), 82.7 (C), 127.9 (5×CH), 128.2, 128.4,
128.7, 129.9, 130.3 (6×CH), 141.6 (3×C), 166.2 (C); Anal. Calcd for C₃₁H₃₈N₄: C, 79.79; H, 8.21; N, 12.01. Found: C, 80.06; H, 8.14; N, 13.46.

2-(1-Trityl-1H-tetrazol-5-yl)pyridine (1f)
Pink solid; yield: 3.31 g (85%); mp: 126-128°C; IR (KBr): 1489, 1446, 1072, 747, 698 cm⁻¹; ¹H NMR: (300 MHz, DMSO-d₆): δ = 6.79-6.94 (m, 15H), 7.17-7.21 (m, 1H), 7.64 (td, J = 7.8, 1.6 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 8.36 (d, J = 4.4 Hz, 1H); ¹³C NMR: (75 MHz, DMSO-d₆): δ = 51.6 (C), 86.4 (CH), 122.6 (CH), 126.1 (CH), 127.0 (3×CH), 127.9 (6×CH), 128.2 (6×CH), 137.0 (3×C), 138.2 (C), 143.6 (C), 150.1 (CH); Anal. Calcd for C₂₅H₁₉N₅: C, 77.10; H, 4.92; N, 17.98. Found: C, 77.00; H, 5.57; N, 17.41.

N,1-Ditrityl-1H-tetrazol-5-amine (1g)
White solid; yield: 1.42 g (25%); mp: 220-222°C; IR (KBr): 1560, 1493, 1446, 1184, 881, 743, 696, 632 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 6.82 (s, 1H), 6.84-7.40 (m, 30H); ¹³C NMR: (75 MHz, CDCl₃): δ = 71.7 (C), 82.1 (C), 125.9, 126.4, 126.8, 127.6, 127.8, 127.9, 128.0 (5C), 128.4 (6C), 129.0 (5C), 129.6 (6C), 130.1, 141.5 (30×CH), 144.8 (3×C), 147.8 (3×C), 165.1 (C); Anal. Calcd for C₃₉H₃₁N₅: C, 82.22; H, 5.48; N, 12.27. Found: C, 82.22; H, 5.46; N, 11.42.

3,3-Dimethyl-1-(1-trityl-1H-tetrazol-5-yl)butan-2-one (1j)
Pink solid; yield: 2.55 g (62%); mp: 190-194°C; IR (KBr): 1714, 1445, 1057, 882, 752, 697 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 1.22 (s, 9H), 4.17 (s, 2H), 7.10-7.35 (m, 15H); ¹³C NMR: (75 MHz, CDCl₃): δ = 25.8 (3×CH₃), 32.2 (CH₂), 44.0 (C-C=O), 82.8 (C), 127.4 (3×CH), 127.8 (6×CH), 130.3 (6×CH), 141.5 (3×C), 162.1 (C), 209.3 (C=O); Anal. Calcd for C₂₆H₂₆N₄O: C, 76.07; H, 6.38; N, 13.65. Found: C, 75.09; H, 5.57; N, 17.41.

5-Benzydryl-1-trityl-1H-tetrazole (1k)
Yellow solid; yield: 2.92 g (61%); mp: 164-166°C; IR (KBr): 1492, 1445, 1048, 748, 697, 639 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 5.88 (s, 1H), 7.13-7.38 (m, 25H); ¹³C NMR: (75 MHz, CDCl₃): δ = 50.9 (CH), 82.1 (C), 125.9, 126.4, 126.8, 127.4 (2C), 127.6 (4C), 127.8 (3C), 127.9, 128.1, 128.4 (6C), 129.0, 129.6, 130.1, 141.5, 144.0 (25×CH),
144.8 (C), 147.0 (2×C), 165.1 (3×C); Anal. Calcd for C33H26N4: C, 82.82; H, 5.48; N, 11.71. Found: C, 82.37; H, 5.46; N, 11.42.

5-(Anthracen-9-yl)-1-trityl-1H-tetrazole (11)
Green solid; yield: 3.47 g (71%); mp: 170-172°C; IR (KBr): 1491, 1447, 1189, 876, 762, 747, 694 cm⁻¹; ¹H NMR: (300 MHz, CDCl₃): δ = 7.23-7.45 (m, 21H), 7.70-7.73 (m, 1H), 8.03 (dd, J = 4.8, 4.2 Hz, 1H), 8.57 (s, 1H); ¹³C NMR: (75 MHz, CDCl₃): δ = 83.7 (C), 125.6 (2×CH), 126.8 (2×C), 127.4 (2×C), 128.0 (3×CH), 128.1 (CH), 128.2 (6×CH), 128.6 (2×CH), 128.7 (2×CH), 130.4 (6×CH), 131.3 (C), 141.6 (2×C), 147.0 (3×C), 162.6 (C); Anal. Calcd for C₃₄H₂₄N₄: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.05; H, 5.34; N, 8.79.
NMR spectra for compounds 1 and 2
75 MHz, CDCl₃
$75$ MHz, CDCl$_3$
75 MHz, CDCl₃
$300 \text{ MHz, DMSO-}d_6$
$2\text{d}$

$300 \text{ MHz, DMSO-}d_6$
$^{75}\text{MHz, DMSO-d}_6$
75 MHz, MeOD-d$_4$
75 MHz, MeOD-d₄
300 MHz, DMSO-d$_6$
$^{1}H NMR\, DMSO-d_6$
75 MHz, DMSO-d$_6$
75 MHz, MeOD-d₄
75 MHz, DMSO-d$_6$
300 MHz, MeOD-d₄