Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information-I
NMR Spectral Data

Azide-Acetonitrile "Click" Reaction Triggered by Cs_2CO_3: The Atom-Economic, High-yielding Synthesis of 5-Amino-1,2,3-Triazoles

Patoju M. Krishna, Dhevalapally B. Ramachary,* and Sruthi Peesapati

School of Chemistry, University of Hyderabad, Central University (P.O.), Hyderabad 500 046, India

Email: ramsc@uohyd.ernet.in and ramchary.db@gmail.com

General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed

tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received.

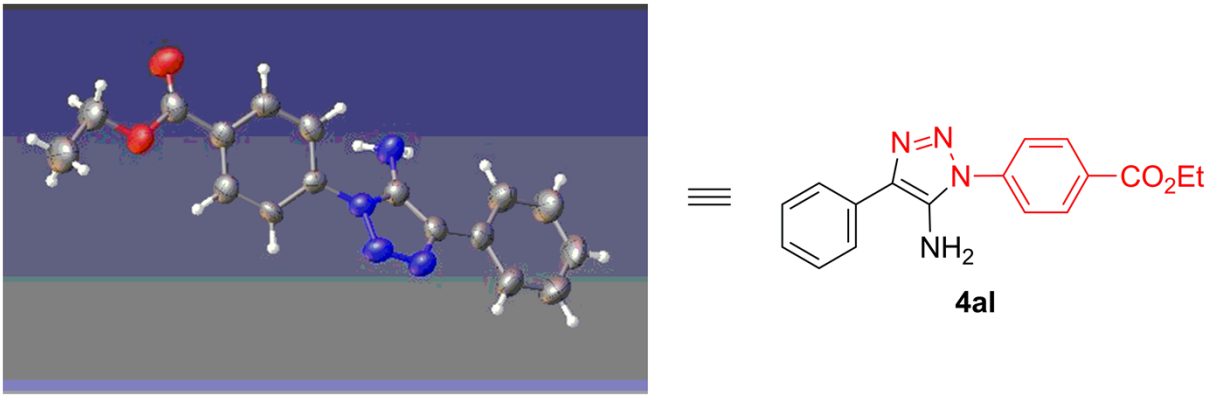


Figure S1. Crystal structure of ethyl 4-(5-amino-4-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (**4al**).

General Experimental Procedures:

Procedure A: General Procedure for the Cs_2CO_3-catalyzed Domino [3+2]-Cycloaddition Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.05 mmol of catalyst **3e** in DMSO+H_2O (7:3; 0.5 M), was added 0.6 mmol of aryl azide **2** and 0.5 mmol of monosubstituted acetonitrile **1** and the reaction mixture was stirred at 25 °C for 0.5-2.0 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure domino products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

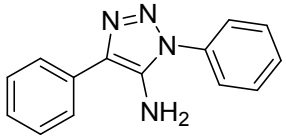
Procedure B: General Procedure for the *t*BuOK-catalyzed Domino [3+2]-Cycloaddition Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.1 mmol of catalyst **3f** in DMSO (0.5 M), was added 0.6 mmol of aryl azide **2** and 0.5 mmol of

monosubstituted acetonitrile **1** and the reaction mixture was stirred at 25 °C for 0.5-2.0 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure domino products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: General Procedure for the DBU-catalyzed Domino [3+2]-Cycloaddition Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.05 mmol of catalyst **3a** in DMSO (0.5 M), was added 0.6 mmol of aryl azide **2** and 0.5 mmol of monosubstituted acetonitrile **1** and the reaction mixture was stirred at 25 °C for 1-2 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure domino products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure D: General Procedure for the Dimroth Rearrangement of Triazoles 4ga and 4ja: 4-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine **4ga** (0.5 mmol) and toluene (2.0 ml) were added in a seal tube and resulting suspension was refluxed at 180 °C for 6 h. Pure product **6ga** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

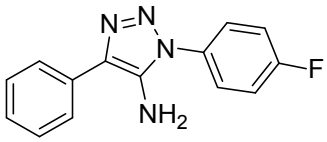
1,4-Diphenyl-1*H*-1,2,3-triazlo-5-amine (4aa):[1] Prepared following the procedure **A** and



4aa

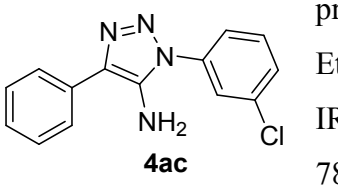
purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 177-178 ˚C [Lit., M.P. 179 °C]; IR (KBr): ν_{max} 3443, 3364, 1600, 1515, 1381, 1270, 1239, 1103, 1070, 969, 763 and 713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.74 (2H, d, J = 7.2 Hz), 7.61-7.55 (4H, m), 7.52-7.51 (1H, m), 7.46 (2H, t, J = 8.0 Hz), 7.31 (1H, t, J = 7.6 Hz), 4.13 (2H, s, NH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 137.4 (C), 135.1 (C), 131.4 (C), 129.9 (2 x CH), 129.8 (C), 129.4 (CH), 129.0 (2 x CH), 127.0 (CH), 125.6 (2 x CH), 124.3 (2 x CH); HRMS m/z 237.1131 ($M + H^+$), calcd for $C_{14}H_{12}N_4H$ 237.1140.

1-(4-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ab): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 132-134 ˚C; IR (neat): ν_{max} 3413, 3320, 1604, 1517, 1440, 1243, 991, 832, 760 and 700 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.87 (2H, br d, *J* = 7.2 Hz), 7.72-7.69 (2H, m), 7.49-7.44 (4H, m), 7.29 (1H, t, *J* = 7.6 Hz), 5.85 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 162.6 (C, d, *J* = 244.0 Hz, *C*-F), 140.0 (C), 132.5 (C), 132.3 (C, d, *J* = 3.0 Hz), 129.2 (2 x CH), 128.2 (C), 127.8 (2 x CH, d, *J* = 9.0 Hz), 126.7 (CH), 125.6 (2 x CH), 117.1 (2 x CH, d, *J* = 23.0 Hz); HRMS m/z 255.1038 (M + H^+), calcd for $C_{14}H_{11}FN_4H$ 255.1046.



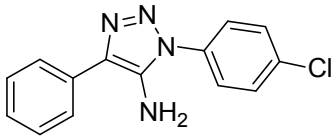
4ab

1-(3-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ac): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 124-126 ˚C; IR (neat): ν_{max} 3294, 1621, 1594, 1425, 1382, 1261, 1221, 1074, 984, 783, 764 and 715 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.81 (2H, d, *J* = 7.5 Hz), 7.74 (1H, m), 7.65-7.61 (3H, m), 7.45 (2H, t, *J* = 8.0 Hz), 7.28 (1H, t, *J* = 7.5 Hz), 5.92 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.9 (C), 137.1 (C), 134.3 (C), 132.2 (C), 131.8 (CH), 129.3 (CH), 129.1 (2 x CH), 128.2 (C), 126.7 (CH), 125.5 (2 x CH), 125.0 (CH), 123.8 (CH); HRMS m/z 271.0735 (M + H^+), calcd for $C_{14}H_{11}ClN_4H$ 271.0750.



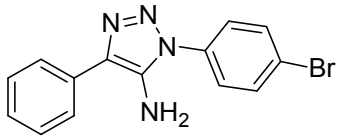
4ac

1-(4-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ad):[5] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 180-182 ˚C [Lit., M.P. 181-182 °C]; IR (neat): ν_{max} 3419, 3323, 1612, 1498, 1444, 1407, 1382, 1259, 1093, 982, 819, and 769 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.81 (2H, d, *J* = 7.5 Hz), 7.68 (4H, m), 7.45 (2H, t, *J* = 7.5 Hz), 7.28 (1H, t, *J* = 7.5 Hz), 5.86 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.9 (C), 134.7 (C), 133.9 (C), 132.3 (C), 130.2 (2 x CH), 129.1 (2 x CH), 128.2 (C), 127.0 (2 x CH), 126.7 (CH), 125.5 (2 x CH); HRMS m/z 271.0750 (M + H^+), calcd for $C_{14}H_{11}ClN_4H$ 271.0750.



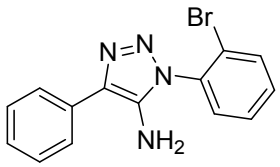
4ad

1-(4-Bromophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ae):[5] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 185-187 ˚C [Lit., M.P. 185-187 °C]; IR (neat): ν_{max} 3314, 2920, 2851, 1610, 1508, 1444, 1259, 1070, 980, 908, 832, 815, 769 and 716 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.81 (2H, br d, *J* = 7.2 Hz), 7.79 (2H, br d, *J* = 7.2 Hz), 7.60 (2H, br d, *J* = 8.8 Hz), 7.44 (2H, t, *J* = 8.0 Hz), 7.27 (1H, t, *J* = 7.2 Hz), 5.86 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.8 (C), 135.1 (C), 133.1 (2 x CH), 132.2 (C), 129.1 (2 x CH), 128.2 (C), 127.2 (2 x CH), 126.6 (CH), 125.5 (2 x CH), 122.3 (C); HRMS m/z 315.0249 (M + H^+), calcd for $C_{14}H_{11}BrN_4H$ 315.0245.



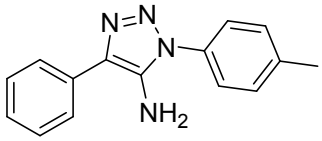
4ae

1-(2-Bromophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 120-122 ˚C; IR (neat): ν_{max} 3402, 3161, 3073, 1599, 1561, 1467, 1308, 1265, 1020, 991, 914 and 739 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.91 (1H, br d, *J* = 7.6 Hz), 7.83 (2H, br d, *J* = 7.2 Hz), 7.65-7.54 (3H, m), 7.43 (2H, t, *J* = 7.6 Hz), 7.25 (1H, t, *J* = 7.2 Hz), 5.82 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 140.9 (C), 134.6 (C), 134.1 (CH), 132.7 (CH), 132.6 (C), 130.8 (CH), 129.6 (CH), 129.1 (2 x CH), 126.5 (C), 126.3 (CH), 125.0 (2 x CH), 122.3 (C); HRMS m/z 315.0249 (M + H^+), calcd for $C_{14}H_{11}BrN_4H$ 315.0245.



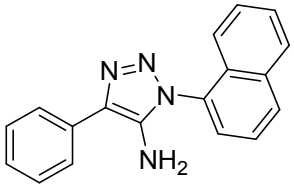
4af

4-Phenyl-1-(p-tolyl)-1*H*-1,2,3-triazol-5-amine (4ag):[6] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 172-174 ˚C [Lit., M.P. 176 °C]; IR (Neat): ν_{max} 3375, 3282, 1600, 1517, 1441, 1260, 1106, 986, 832, 772, 695 and 498 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.83 (2H, d, *J* = 7.2 Hz), 7.51-7.41 (6H, m), 7.27 (1H, t, *J* = 7.2 Hz), 5.72 (2H, s, N*H*$_2$), 3.43 (3H, s, Ar-C*H*$_3$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.7 (C), 139.1 (C), 133.3 (C), 132.5 (C), 130.6 (2 x CH), 129.1 (2 x CH), 128.1 (C), 126.6 (CH), 125.5 (2 x CH), 125.1 (2 x CH), 21.3 (CH_3); HRMS m/z 251.1290 (M + H^+), calcd for $C_{15}H_{14}N_4H$ 251.1297.



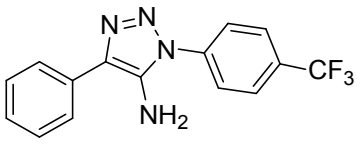
4ag

1-(Naphthalen-1-yl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a semi solid; IR (neat): ν_{max} 3315, 3194, 1625, 1606, 1508, 1404, 1264, 1023, 991, 803, 770, 733 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.21 (1H, d, *J* = 7.6 Hz), 8.13 (1H, d, *J* = 7.6 Hz), 7.89 (2H, d, *J* = 7.2 Hz), 7.75-7.69 (2H, m), 7.67-7.635 (1H, m), 7.63-7.58 (1H, m), 7.46 (2H, t, *J* = 7.6 Hz), 7.33-7.26 (2H, m), 5.72 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 141.5 (C), 134.5 (C), 132.7 (C), 131.6 (C), 130.9 (CH), 130.0 (C), 129.2 (2 x CH), 128.9 (CH), 128.2 (CH), 127.5 (CH), 126.8 (C), 126.6 (CH), 126.5 (CH), 126.4 (CH), 125.3 (2 x CH), 123.0 (CH); HRMS m/z 287.1288 (M + H^+), calcd for $C_{18}H_{14}N_4H$ 287.1297.



4ah

1-(4-Methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ai):[6] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a white solid. Mp 162-164 ˚C [Lit., M.P. 163-164 °C]; IR (neat): ν_{max} 3458, 3305, 2851, 1623, 1507, 1463, 1440, 1248, 1036, 979, 908, 832 and 771 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.79 (2H, d, *J* = 7.6 Hz), 7.50 (2H, d, *J* = 8.8 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 7.26 (1H, t, *J* = 7.2 Hz), 7.15 (2H, d, *J* = 9.2 Hz), 5.64 (2H, s, N*H*$_2$), 3.85 (3H, s, OC*H*$_3$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 160.1 (C), 139.8 (C), 132.5 (C), 129.1 (2 x CH), 128.6 (C), 127.8 (C), 127.0 (2 x CH), 126.5 (CH), 125.4 (2 x CH), 115.3 (2 x CH), 56.1 (CH_3); HRMS m/z 267.1240 (M + H^+), calcd for $C_{15}H_{14}N_4OH$ 267.1246.



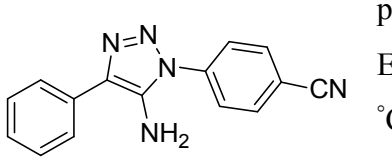
4ai

4-Phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-5-amine (4aj): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 170-172 ˚C; IR (neat): 3079, 2920, 2859, 1714, 1643, 1467, 1380, 1319, 991, 914 and 722 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.00 (2H, d, *J* = 8.4 Hz), 7.92 (2H, d, *J* = 8.4 Hz), 7.83 (2H, d, *J* = 7.6 Hz), 7.46 (2H, t, *J* = 7.6 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 6.00 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 140.0 (C), 139.3 (C), 132.2 (C), 129.5 (C, q, *J* = 32.0 Hz), 129.2 (2 x CH), 128.6 (C), 127.3 (2 x CH, q, *J* = 4.0 Hz), 126.8

4aj

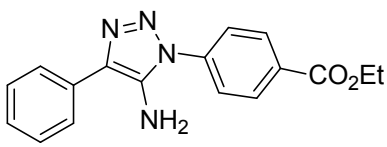
(CH), 125.7 (2 x CH), 125.5 (2 x CH), 124.5 (CF_3, q, J = 270.0 Hz); HRMS m/z 305.1002 ($M + H^+$), calcd for $C_{15}H_{11}F_3N_4H$ 305.1014.

4-(5-Amino-4-phenyl-1*H*-1,2,3-triazol-1-yl)benzonitrile (4ak): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 150-152 °C; IR (neat): ν_{max} 3409, 3320, 2233, 1609, 1516, 1444, 1413, 1381, 1262, 1128, 1070, 982, 847, and 771 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.10 (2H, br d, J = 8.4 Hz), 7.90 (2H, br d, J = 8.4 Hz), 7.81 (2H, br d, J = 7.2 Hz), 7.46 (2H, br t, J = 8.0 Hz), 7.29 (1H, br t, J = 7.2 Hz), 6.02 (2H, s, NH_2); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.9 (C), 139.6 (C), 134.4 (2 x CH), 132.0 (C), 129.2 (2 x CH), 128.6 (C), 126.9 (CH), 125.7 (2 x CH), 125.4 (2 x CH), 118.8 (C), 111.7 (C); HRMS m/z 262.1095 ($M + H^+$), calcd for $C_{15}H_{11}N_5H$ 262.1093.



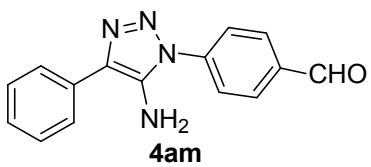
4ak

Ethyl 4-(5-amino-4-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (4al): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 110-112 °C; IR (neat): ν_{max} 3413, 3320, 2920, 1715, 1621, 1419, 1271, 1106, 865, 772, 695 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.18 (2H, br d, J = 8.0 Hz), 7.82 (2H, br d, J = 8.0 Hz), 7.80 (2H, br d, J = 8.0 Hz), 7.45 (2H, br t, J = 7.6 Hz), 7.28 (1H, br t, J = 7.2 Hz), 5.95 (2H, s, NH_2), 4.37 (2H, q, J = 6.8 Hz), 1.35 (3H, t, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 165.6 (C, *C*=O), 139.9 (C), 139.6 (C), 132.2 (C), 131.2 (2 x CH), 130.3 (C), 129.2 (2 x CH), 128.5 (C), 126.8 (CH), 125.7 (2 x CH), 124.8 (2 x CH), 61.7 (CH_2), 14.7 (CH_3); HRMS m/z 309.1346 ($M + H^+$), calcd for $C_{17}H_{16}N_4O_2H$ 309.1352.



4al

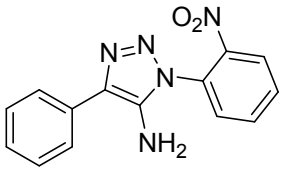
4-(5-Amino-4-phenyl-1*H*-1,2,3-triazol-1-yl)benzaldehyde (4am): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as a White solid. Mp 120-122 °C; IR (neat): ν_{max} 3385, 3277, 1705, 1603, 1578, 1514, 1443, 1420, 1375, 1302, 1203, 1167, 1023, 982, 829 and 766 cm^{-1}; ^1H NMR (DMSO-d6, 500 MHz) δ 10.13 (1H, s, C*H*O), 8.15 (2H, d, J = 8.5 Hz), 7.91 (2H, d, J = 8.0 Hz), 7.80 (2H, d, J = 7.5 Hz), 7.46 (2H, t, J = 7.5 Hz), 7.29 (1H, t, J = 7.5 Hz), 6.00 (2H, s, NH_2); ^{13}C



4am

NMR (DMSO-d_6, 100 MHz) δ 193.0 (*C*HO, C), 140.5 (C), 139.9 (C), 136.1 (C), 132.1 (C), 131.4 (2 x CH), 129.2 (2 x CH), 128.5 (C), 126.8 (CH), 125.6 (2 x CH), 125.0 (2 x CH); HRMS m/z 265.1078 ($M + H^+$), calcd for $C_{15}H_{12}N_4OH$ 265.1089.

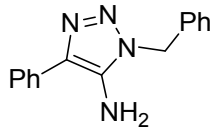
1-(2-Nitrophenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4an): Prepared following the procedure



4an

A and purified by column chromatography using EtOAc/hexane and isolated as a White solid. Mp 135-137 °C; IR (neat): ν_{max} 3303, 3150, 1615, 1588, 1522, 1440, 1347, 1270, 1139, 980, 766, 739 and 700 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.28 (1H, dd, *J* = 8.0, 1.2 Hz), 7.98 (1H, dt, *J* = 7.6, 1.2 Hz), 7.89-7.81 (4H, m), 7.45 (2H, t, *J* = 7.6 Hz), 7.28 (1H, t, *J* = 7.2 Hz), 6.06 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 145.8 (C), 141.2 (CH), 135.3 (CH), 132.2 (C), 131.8 (C), 130.3 (CH), 129.1 (2 x CH), 128.3 (C), 127.1 (C), 126.5 (CH), 126.1 (CH), 125.2 (2 x CH); LCMS m/z 282.40 ($M + H^+$), calcd for $C_{14}H_{11}N_5O_2H$ 282.0991.

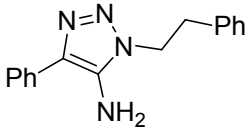
1-Benzyl-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ao):[7] Prepared following the procedure **B** and



4ao

purified by column chromatography using EtOAc/hexane and was isolated as a White solid. Mp 155-156 °C [Lit., M.P. 156 °C]; IR (neat): ν_{max} 3314, 3203, 1637, 1605, 1586, 1518, 1496, 1445, 1368, 1251, 1225, 1114, 1073, 993, 803, 767 and 718 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.18 (2H, br d, *J* = 6.4 Hz), 6.85-6.78 (4H, m), 6.75-6.64 (4H, m), 5.31 (2H, s, N*H*$_2$), 4.91 (2H, s, NC*H*$_2$Ph); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.7 (C), 136.8 (C), 132.8 (C), 129.1 (2 x CH), 129.0 (2 x CH), 128.1 (CH), 127.9 (2 x CH), 127.7 (C), 126.2 (CH), 125.0 (2 x CH), 48.9 (CH_2); HRMS m/z 251.1299 ($M + H^+$), calcd for $C_{15}H_{14}N_4H$ 251.1297.

1-Phenethyl-4-phenyl-1*H*-1,2,3-triazol-5-amine (4ap): Prepared following the procedure **B**

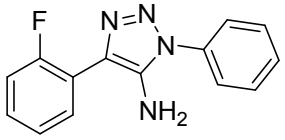


4ap

and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 126-128 °C; IR (neat): ν_{max} 3298, 3177, 1632, 1582, 1528, 1445, 1265, 1073, 1007, 760, and 706 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.74 (2H, br d, *J* = 7.2 Hz), 7.41 (2H, br t, *J* = 7.6 Hz), 7.32-7.31 (4H, m), 7.25-7.21 (2H, m), 5.80 (2H, s, N*H*$_2$), 4.41 (2H, t, *J* = 8.0 Hz), 3.10 (2H, t, *J* = 8.0 Hz); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.4 (C), 138.4 (C), 132.9

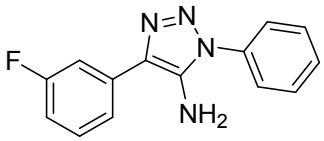
(C), 129.4 (2 x CH), 129.0 (2 x CH), 128.8 (2 x CH), 127.7 (C), 126.9 (CH), 126.1 (CH), 125.0 (2 x CH), 46.9 (CH_2), 35.0 (CH_2); LCMS m/z 265.00 ($M + H^+$), calcd for $C_{16}H_{16}N_4H$ 265.1453.

4-(2-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 132-134 ˚C; IR (neat): ν_{max} 3352, 1606, 1512, 1451, 1374, 1222, 1197, 1106, 979, 820 and 760 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.70-7.61 (5H, m), 7.54 (1H, tt, *J* = 7.0, 1.2 Hz), 7.43-7.39 (1H, m), 7.32-7.29 (2H, m), 5.65 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 159.4 (C, d, *J* = 245.0 Hz, *C*-F), 140.8 (C), 136.0 (C), 130.7 (CH, d, *J* = 3.0 Hz), 130.2 (2 x CH), 129.5 (CH, d, *J* = 8.0 Hz), 129.3 (CH), 125.1 (CH), 124.8 (2 x CH), 123.8 (C), 119.9 (C, d, *J* = 14.0 Hz), 116.4 (CH, d, *J* = 21.0 Hz); HRMS m/z 255.1037 ($M + H^+$), calcd for $C_{14}H_{11}FN_4H$ 255.1046.



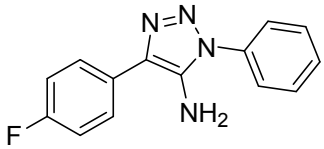
4ba

4-(3-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 152-154 ˚C; IR (neat): 3401, 3330, 1161, 1500, 1434, 1383, 1278, 1263, 1191, 1161, 1024, 987, 869, and 756 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.70 (1H, d, *J* = 8.0 Hz), 7.64-7.63 (5H, m), 7.58-7.55 (1H, m), 7.48 (1H, q, *J* = 8.0 Hz), 7.09 (1H, t, *J* = 8.5 Hz), 5.95(2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 163.0 (C, d, *J* = 240 Hz), 140.1 (C), 135.6 (C), 134.7 (C, d, *J* = 12.5 Hz), 131.0 (CH, d, *J* = 8.75 Hz), 130.2 (2 x CH), 129.5 (CH), 126.9 (C), 125.2 (2 x CH), 121.3 (CH, d, *J* = 2.5 Hz), 113.0 (CH, d, *J* = 21.25 Hz); 111.7 (CH, d, *J* = 22.5 Hz); LRMS m/z 255.00 ($M + H^+$), calcd for $C_{14}H_{11}FN_4H$ 255.1046.



4ca

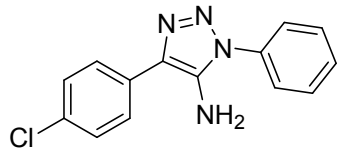
4-(4-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4da):[2] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 188-190 ˚C [Lit., M.P. 192 °C]; IR (neat): ν_{max} 3286, 3192, 1612, 1576, 1517, 1452, 1381, 1221, 1091, 983, 909, 835 and 816 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.84 (2H, m), 7.63-7.62 (4H, m), 7.56 (1H, m), 7.28 (2H, br t, *J* = 9.0 Hz), 5.79 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 161.2 (C, d, *J* = 241 Hz), 139.5 (C), 135.8 (C), 130.2 (2 x CH), 129.4 (CH), 128.9 (C, d, *J* = 2.5 Hz), 127.5 (C), 127.4 (2 x CH, d, *J* =



4da

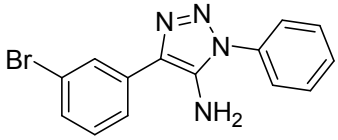
8.75 Hz), 125.1 (2 x CH), 115.9 (2 x CH, d, J = 21.25 Hz); HRMS m/z 255.1047 (M + H^+), calcd for $C_{14}H_{11}FN_4H$ 255.1046.

4-(4-Chlorophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4ea):[2] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow solid. Mp 188-190 °C [Lit., M.P. 189 °C]; IR (Neat): νmax 3398, 3280, 1623, 1509, 1454, 1402, 1380, 1257, 1093, 986, 910, 832, 823, 768, 750, and 720 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.83 (2H, d, J = 8.5 Hz), 7.65-7.61 (4H, m), 7.57-7.55 (1H, m), 7.49 (2H, d, J = 9.0 Hz), 5.87 (2H, s, NH_2); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.9 (C), 135.7 (C), 131.3 (C), 130.8 (C), 130.2 (2 x CH), 129.5 (CH), 129.0 (2 x CH), 127.0 (2 x CH, C), 125.2 (2 x CH); HRMS m/z 271.0743 (M + H^+), calcd for $C_{14}H_{11}ClN_4H$ 271.0750.



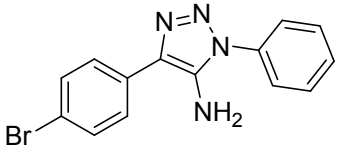
4ea

4-(3-Bromophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. Mp 112-114 °C; IR (neat): ν_{max} 3348, 1601, 1574, 1510, 1452, 1410, 1379, 1278, 1254, 1122, 1068, 993, 983, 877, 787, 767, 752 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.98 (1H, t, J = 2.0 Hz), 7.83 (1H, td, J = 8.0, 1.0 Hz), 7.65-7.61 (4H, m), 7.58-7.55 (1H, m), 7.46-7.44 (1H, m), 7.41-7.38 (1H, t, J = 8.0 Hz), 5.96 (2H, s, NH_2); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 140.2 (C), 135.6 (C), 134.8 (C), 131.2 (CH), 130.2 (2 x CH), 129.6 (CH), 129.1 (CH), 127.6 (CH), 126.6 (C), 125.3 (2 x CH), 124.1 (CH), 122.7 (C); HRMS m/z 315.0239 (M + H^+), calcd for $C_{14}H_{11}BrN_4H$ 315.0245.



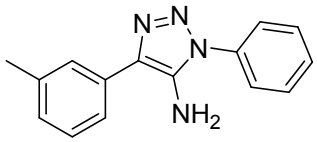
4fa

4-(4-Bromophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4ga):[3] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a solid; Mp 188-190 °C [Lit., M.P. 191 °C]; IR (KBr): 3364, 3298, 1616, 1512, 1457, 1402, 1265, 1073, 1002, 832, 767 and 701 cm-1; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.80 (2H, d, J = 8.5 Hz), 7.63-7.62 (6H, m), 7.56 (1H, m), 5.91 (2H, s, NH_2); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.9 (C), 135.7 (C), 131.9 (2 x CH), 131.6 (C), 130.2 (2 x CH), 129.5 (CH), 127.4 (2 x CH), 127.1 (C), 125.1 (2 x CH), 119.3 (C); HRMS m/z 315.0246 (M + H^+), calcd for $C_{14}H_{11}BrN_4H$ 315.0245.



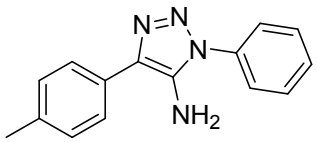
4ga

1-Phenyl-4-(m-tolyl)-1*H*-1,2,3-triazol-5-amine (4ha): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as a White solid. Mp 113-114 °C; IR (neat): νmax 3298, 3208, 1631, 1598, 1515, 1455, 1369, 1270, 1044, 980, 916, 854, 781 and 722 cm-1; ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 7.64-7.61 (6H, m), 7.58-7.53 (1H, m), 7.33 (1H, t, *J* = 7.6 Hz), 7.09 (1H, br d, *J* = 7.6 Hz), 5.76 (2H, s, N*H*$_2$), 2.38 (3H, s, Ar-C*H*$_3$) ; ^{13}C NMR (DMSO-d$_6$, DEPT-135) δ 139.6 (C), 138.2 (C), 135.9 (C), 132.3 (C), 130.2 (2 x CH), 129.4 (CH), 129.0 (CH), 128.2 (C), 127.3 (CH), 126.1 (CH), 125.0 (2 x CH), 122.7 (CH), 21.7 (CH$_3$); LCMS m/z 249.10 (M - H$^+$), calcd for $C_{15}H_{13}N_4$ 249.1140.



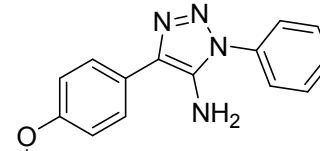
4ha

1-Phenyl-4-(p-tolyl)-1*H*-1,2,3-triazol-5-amine (4ia):[5] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow solid. Mp 180-182 °C [Lit., M.P. 179-181 °C]; IR (neat): νmax 3274, 3195, 1616, 1594, 1579, 1518, 1503, 1452, 1378, 1245, 980 and 708 cm-1; ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 7.69 (2H, br d, *J* = 8.0 Hz), 7.63-7.61 (4H, m), 7.57-7.53 (1H, m), 7.25 (2H, br d, *J* = 7.6 Hz), 5.66 (2H, s, N*H*$_2$), 2.34 (3H, s, Ar-C*H*$_3$); ^{13}C NMR (DMSO-d$_6$, DEPT-135) δ 139.4 (C), 135.9 (C), 135.8 (C), 130.2 (2 x CH), 129.7 (2 x CH), 129.6 (C), 129.4 (CH), 128.4 (C), 125.5 (2 x CH), 125.1 (2 x CH), 21.3 (CH$_3$); HRMS m/z 251.1294 (M + H$^+$), calcd for $C_{15}H_{14}N_4H$ 251.1297.



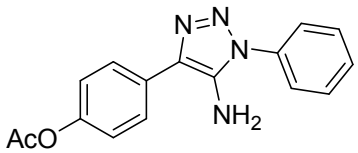
4ia

4-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4ja):[2] Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 162-164 °C [Lit., M.P. 164 °C]; IR (KBr): νmax 3362, 1599, 1565, 1509, 1453, 1382, 1237, 1105, 1026, 833 and 771cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 500 MHz) δ 7.44 (2H, d, *J* = 8.5 Hz), 7.33-7.31 (4H, m), 7.26-7.24 (1H, m), 6.73 (2H, d, *J* = 8.5 Hz), 5.34 (2H, s, N*H*$_2$), 3.50 (3H, s, Ar-OC*H*$_3$); ^{13}C NMR (DMSO-d$_6$, DEPT-135) δ 158.2 (C), 138.9 (C), 135.9 (C), 130.1 (2 x CH), 129.3 (CH), 128.5 (C), 127.0 (2 x CH, C), 124.9 (2 x CH), 114.5 (2 x CH), 55.6 (CH$_3$); HRMS m/z 267.1244 (M + H$^+$), calcd for $C_{15}H_{14}N_4OH$ 267.1246.



4ja

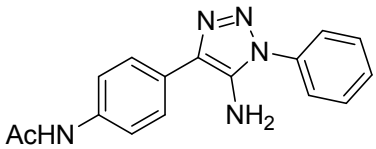
4-(5-Amino-1-phenyl-1*H*-1,2,3-triazol-4-yl)phenyl acetate (4ka): Prepared following the procedure **A** and purified by column chromatography using



4ka

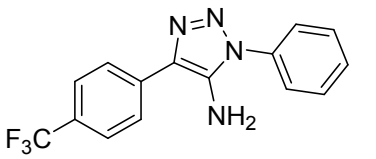
EtOAc/hexane and was isolated as a oily liquid; IR (Neat): ν_{max} 3430, 3331, 1751, 1620, 1515, 1370, 1274, 1217, 1190, 983, 911, 851, 767 and 718 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.81 (2H, br d, *J* = 8.8 Hz), 7.63-7.62 (4H, m), 7.57-7.54 (1H, m), 7.19 (2H, br d, *J* = 8.4 Hz), 5.78 (2H, s, N*H*$_2$), 2.29 (3H, s, Ar-OCOC*H*$_3$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 169.8 (C, O-*C*=O), 149.2 (C), 139.7 (C), 135.8 (C), 130.2 (2 x CH), 130.0 (C), 129.5 (CH), 127.6 (C), 126.5 (2 x CH), 125.1 (2 x CH), 122.5 (2 x CH), 21.4 (CH_3); HRMS m/z 295.1188 ($M + H^+$), calcd for $C_{16}H_{14}N_4O_2H$ 295.1195.

N-(4-(5-Amino-1-phenyl-1*H*-1,2,3-triazol-4-yl)phenyl)acetamide (4la): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a semi solid; IR (neat): ν_{max} 3575, 3301, 2923, 1661, 1601, 1514, 1442, 1408, 1373, 1318, 1286, 1110, 1019, 909, 810, 752, 694 and 653 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.00 (1H, s), 7.72 (2H, d, *J* = 8.5 Hz), 7.66 (2H, d, *J* = 8.5 Hz), 7.63-7.62 (4H, m), 7.55 (1H, m), 5.69 (2H, s, N*H*$_2$), 2.07 (3H, s, Ar-NHCOC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.6 (NH-*C*=O, C), 139.1 (C), 138.0 (C), 135.9 (C), 130.1 (2 x CH), 129.3 (CH), 128.2 (C), 127.1 (C), 125.8 (2 x CH), 125.0 (2 x CH), 119.6 (2 x CH), 24.5 (CH_3); HRMS m/z 294.1353 ($M + H^+$), calcd for $C_{16}H_{15}N_5OH$ 294.1355.



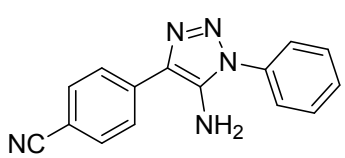
4la

1-Phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-5-amine (4ma): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 168-170 °C; IR (neat): ν_{max} 3435, 3326, 1617, 1506, 1453, 1412, 1318, 1280, 1239, 1166, 1072, 982, 840, 736 and 712 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.03 (2H, d, *J* = 8.5 Hz), 7.77 (2H, d, *J* = 8.0 Hz), 7.66-7.61 (4H, m), 7.59-7.56 (1H, m), 6.05 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 140.0 (C), 139.3 (C), 132.2 (C), 129.5 (C, q, *J* = 32.5 Hz), 129.2 (2 x CH), 128.6 (C), 127.4 (2 x CH, q, *J* = 3.75 Hz), 126.9 (CH), 125.7 (2 x CH), 125.5 (2 x CH), 124.5 (C, q, *J* = 270 Hz); HRMS m/z 305.1016 ($M + H^+$), calcd for $C_{15}H_{11}F_3N_4H$ 305.1014.



4ma

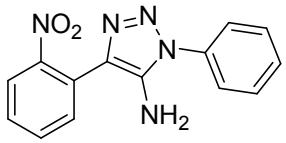
4-(5-Amino-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzonitrile (4na): Prepared following the procedure **A** and purified by column chromatography using



4na

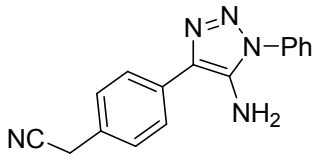
EtOAc/hexane and was isolated as a semi solid; IR (neat): ν_{max} 3405, 3282, 2229, 1613, 1503, 1452, 1408, 1260, 1226, 1128, 1047, 1024, 984, 909, 844 and 759 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.00 (2H, br d, *J* = 8.4 Hz), 7.86 (2H, br d, *J* = 8.4 Hz), 7.66-755 (5H, m), 6.15 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 141.1 (C), 137.1 (C), 135.4 (C), 133.1 (2 x CH), 130.3 (2 x CH), 129.7 (CH), 126.2 (C), 125.43 (2 x CH), 125.38 (2 x CH), 119.7 (C), 108.2 (C, *C*N); LCMS m/z 262.25 ($M + H^+$), calcd for $C_{15}H_{11}N_5H$ 262.1093.

4-(2-Nitrophenyl)-1-phenyl-1*H*-1,2,3-triazol-5-amine (4oa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 185-187 ˚C; IR (KBr): ν_{max} 3450, 3354, 1625, 1524, 1494, 1358, 1307, 1268, 1219, 1073, 983, 951, 855, 781, 768, 733 and 718 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 7.96 (1H, dd, *J* = 8.0, 1.0 Hz), 7.77-7.11 (2H, m), 7.65-7.63 (4H, m), 7.58-7.55 (2H, m), 6.00 (2H, s, N*H*$_2$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 148.6 (C), 140.8 (C), 135.7 (C), 133.0 (CH), 130.8 (CH), 130.2 (2 x CH), 129.4 (CH), 128.5 (CH), 125.4 (C), 124.7 (2 x CH), 124.7 (CH), 124.1 (C); HRMS m/z 282.0992 ($M + H^+$), calcd for $C_{14}H_{11}N_5O_2H$, 282.0991.



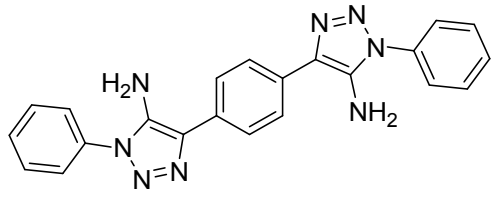
4oa

2-(4-(5-Amino-1-phenyl-1*H*-1,2,3-triazol-4-yl)phenyl)acetonitrile (4pa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow solid. Mp 146-148 ˚C; IR (neat): ν_{max} 3463, 3377, 1603, 1416, 1262, 1235, 1117, 971, 827, 728, 711 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.82 (2H, br d, *J* = 8.0 Hz), 7.63-7.61 (4H, m), 7.58-7.54 (1H, m), 7.41 (2H, br d, *J* = 8.4 Hz), 5.82 (2H, s, N*H*$_2$), 4.07 (2H, s, Ar-C*H*$_2$CN); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.8 (C), 135.8 (C), 131.8 (C), 130.2 (2 x CH), 129.5 (CH), 129.3 (C), 128.9 (2 x CH), 127.5 (C), 125.9 (2 x CH), 125.2 (2 x CH), 119.9 (C), 22.6 (CH_2, Ar-*C*H$_2$CN); LCMS m/z 276.15 ($M + H^+$), calcd for $C_{16}H_{13}N_5H$ 276.1249.



4pa

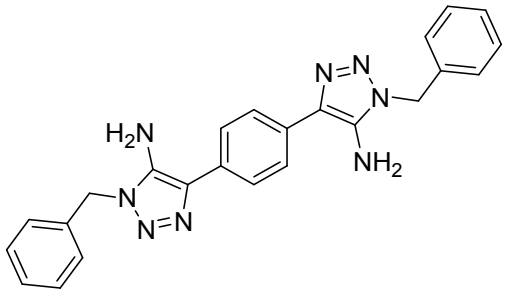
4,4'-(1,4-Phenylene)bis(1-phenyl-1*H*-1,2,3-triazol-5-amine) (5pa): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and was isolated as a white solid. Mp 200-202 ˚C; IR (neat): ν_{max} 3402, 3319, 1617, 1523, 1505, 1451, 1413, 1378, 1294, 1256, 1242, 1132, 1052, 982, 907, 839 and 754 cm^{-1}; ^1H NMR (DMSO-d_6, 400



5pa

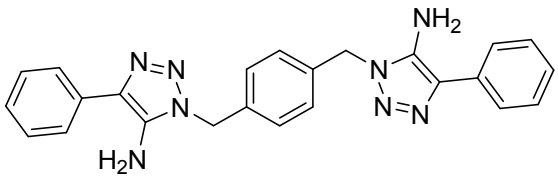
MHz) δ 7.89 (4H, s), 7.65-7.64 (8H, m), 7.57 (2H, m), 5.79 (4H, s, 2 x NH_2); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.5 (2 x C), 135.8 (2 x C), 130.2 (4 x CH), 130.1 (2 x C), 129.4 (2 x CH), 128.1 (2 x C), 125.6 (4 x CH), 125.1 (4 x CH); HRMS m/z 395.1744 (M + H^+), calcd for $C_{22}H_{19}N_8H$ 395.1733.

4,4'-(1,4-Phenylene)bis(1-benzyl-1*H*-1,2,3-triazol-5-amine) (5po): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 220-222 °C; IR (neat): νmax 3390, 3326, 3210, 1640, 1588, 1538, 1361, 1251, 1117, 848 and 731 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.78 (4H, s), 7.39-7.35 (4H, m), 7.32-7.26 (6H, m), 5.85 (4H, s, 2 x NH_2), 5.48 (4H, s, 2 x ArCH_2N); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.5 (2 x C), 136.8 (2 x C), 130.2 (2 x C), 129.0 (4 x CH), 128.1 (2 x CH), 127.9 (4 x CH), 127.8 (2 x C), 125.0 (4 x CH), 48.9 (2 x CH_2); LRMS m/z 423.65 (M + H^+), calcd for $C_{24}H_{22}N_8H$ 423.2046.



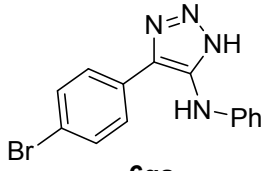
5po

1,1'-(1,4-Phenylenebis(methylene))bis(4-phenyl-1*H*-1,2,3-triazol-5-amine) (5ar): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and was isolated as a yellow solid. Mp 220-222 ˚C; IR (neat): ν_{max} 3321, 3213, 1644, 1589, 1548, 1521, 1273, 1254, 1120, 989, 910, 833, 800, 764, 752 and 716 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.74 (4H, d, *J* = 7.6 Hz), 7.39 (4H, t, *J* = 7.6 Hz), 7.25-7.20 (6H, m), 5.84 (4H, s, 2 x NH_2), 5.46 (4H, s, 2 x ArCH_2N); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.6 (2 x C), 136.2 (2 x C), 132.8 (2 x C), 128.9 (4 x CH), 128.1 (4 x CH), 127.8 (2 x C), 126.2 (2 x CH), 125.0 (4 x CH), 48.6 (2 x CH_2); HRMS m/z 423.2044 (M + H^+), calcd for $C_{24}H_{22}N_8H$ 423.2046.



5ar

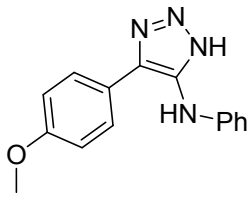
4-(4-Bromophenyl)-N-phenyl-1*H*-1,2,3-triazol-5-amine (6ga):[4] Prepared following the procedure **D** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 140-142 ˚C; IR (neat): ν_{max} 3391, 3161, 2920, 1610, 1545, 1501, 1402, 1315, 1068,



6ga

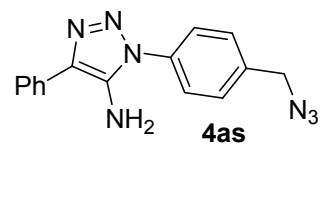
1019, 986, 827, 756, 695 cm^{-1}; ^1H NMR (DMSO-d_6 + TFA (three drops), 400 MHz) δ 7.74 (2H, d, *J* = 8.4 Hz), 7.61 (2H, d, *J* = 8.8 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 6.91 (2H, d, *J* = 7.6 Hz), 6.72 (1H, t, *J* = 7.2 Hz); ^{13}C NMR (DMSO-d_6 + TFA (three drops), DEPT-135) δ 145.4 (C), 143.5 (C), 135.3 (C), 132.2 (2 x CH), 130.1 (C), 129.5 (2 x CH), 128.8 (2 x CH), 121.5 (C), 119.3 (CH), 115.2 (2 x CH); HRMS m/z 315.0230 (M + H^+), calcd for $C_{14}H_{11}BrN_4H$ 315.0245.

4-(4-Methoxyphenyl)-N-phenyl-1*H*-1,2,3-triazol-5-amine (6ja): Prepared following the procedure **D** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 160-162 ˚C; IR (neat): ν_{max} 3409, 3168, 1598, 1552, 1497, 1463, 1322, 1252, 1181, 1020, 982, 837, 744 cm^{-1}; ^1H NMR (DMSO-d_6 + TFA (three drops), 400 MHz) δ 7.72 (2H, d, *J* = 8.4 Hz), 7.12 (2H, t, *J* = 7.6 Hz), 6.98 (2H, d, *J* = 8.4 Hz), 6.86 (2H, d, *J* = 7.6 Hz), 6.70 (1H, t, *J* = 7.2 Hz), 3.76 (3H, s, Ar-OC*H*$_3$); ^{13}C NMR (DMSO-d_6 + TFA (three drops), DEPT-135) δ 159.5 (C), 145.9 (C), 142.5 (C), 136.0 (C), 129.4 (2 x CH), 128.1 (2 x CH), 122.8 (C), 118.8 (CH), 114.8 (2 x CH), 114.6 (2 x CH), 55.6 (CH_3); HRMS m/z 267.1237 (M + H^+), calcd for $C_{15}H_{14}N_4OH$ 267.1246.



6ja

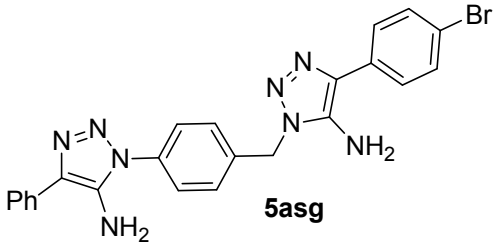
1-(4-(Azidomethyl)phenyl)-4-phenyl-1*H*-1,2,3-triazol-5-amine (4as): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 125-127 °C; IR (neat): ν_{max} 3435, 3347, 3068, 2926, 2849, 2093, 1627, 1523, 1419, 1342, 986, 827, 767, 695 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 7.81 (2H, br d, *J* = 7.2 Hz), 7.67 (2H, d, *J* = 8.4 Hz), 7.62 (2H, d, *J* = 8.4 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 7.27 (1H, t, *J* = 7.6 Hz), 5.82 (2H, s, N*H*$_2$), 4.60 (2H, s, Ar-C*H*$_2$N$_3$); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 139.7 (C), 137.0 (C), 135.5 (C), 132.3 (C), 130.0 (2 x CH), 129.1 (2 x CH), 128.2 (C), 126.6 (CH), 125.5 (2 x CH), 125.2 (2 x CH), 53.5 (CH_2); HRMS m/z 292.1301 (M + H^+), calcd for $C_{15}H_{13}N_7H$ 292.1311.



4as

1-(4-((5-Amino-4-(4-bromophenyl)-1*H*-1,2,3-triazol-1-yl)methyl)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (5asg):

Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and was isolated as a light yellow solid. Mp 180-182 °C; IR



5asg

(neat):ν_{max} 3384(br), 1636, 1603, 1519, 1374, 1270, 1175, 1048, 1023, 995, 823, 761 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.80 (2H, d, *J* = 7.6 Hz), 7.74 (2H, d, *J* = 8.4 Hz), 7.65 (2H, d, *J* = 8.0 Hz), 7.60 (2H, d, *J* = 8.0 Hz), 7.52 (2H, d, *J* = 8.0 Hz), 7.44 (2H, t, *J* = 7.6 Hz), 7.27 (1H, t, *J* = 7.2 Hz), 6.08 (2H, s, NH_2), 5.80 (2H, s, NH_2), 5.62 (2H, s, Ar-CH_2N); ^{13}C NMR (DMSO-d_6, DEPT-135) δ 140.1 (C), 139.7 (C), 137.4 (C), 135.3 (C), 132.3 (C), 132.0 (C), 131.9 (2 x CH), 129.3 (2 x CH), 129.1 (2 x CH), 128.1 (C), 127.0 (2 x CH), 126.8 (C), 126.6 (CH), 125.5 (2 x CH), 125.3 (2 x CH), 119.0 (C), 48.5 (CH_2); HRMS m/z 487.0983 ($M+H^+$), calcd for $C_{23}H_{19}N_8BrH$ 487.0994.

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Table S1: Compound Characterization Checklist.

Entry	Compound	New/Known	M.P	Reference
1	**4aa**	known	177-178 °C [Lit., M.P. 179 °C]	(a)
2	**4ab**	new	132-134 °C	_
3	**4ac**	new	124-126 °C	_
4	**4ad**	known	180-182 °C [Lit., M.P. 181-182 °C]	(b)
5	**4ae**	known	185-187 °C [Lit., M.P. 185-187 °C]	(b)
6	**4af**	new	120-122 °C	_
7	**4ag**	known	172-174 °C [Lit., M.P. 176 °C]	(c)
8	**4ah**	new	Semi solid	_
9	**4ai**	known	162-164 °C [Lit., M.P. 163-164 °C]	(c)
10	**4aj**	new	170-172 °C	_
11	**4ak**	new	150-152 °C	_
12	**4al**	new	110-112 °C	_
13	**4am**	new	120-122 °C	_
14	**4an**	new	135-137 °C	_
15	**4ao**	known	155-156 °C [Lit., M.P. 156 °C]	(d)
16	**4ap**	new	126-128 °C	_
17	**4ba**	new	132-134 °C	_
18	**4ca**	new	152-154 °C	_
19	**4da**	known	188-190 °C [Lit., M.P. 192 °C]	(e)
20	**4ea**	known	188-190 °C [Lit., M.P. 189 °C]	(e)
21	**4fa**	new	112-114 °C	_
22	**4ga**	known	188-190 °C [Lit., M.P. 191 °C]	(e)
23	**4ha**	new	113-114 °C	_
24	**4ia**	known	180-182 °C [Lit., M.P. 179-181 °C]	(b)
25	**4ja**	known	162-164 °C [Lit., M.P. 164 °C]	(e)
26	**4ka**	new	Oily liquid	_
27	**4la**	new	Semi solid	_
28	**4ma**	new	168-170 °C	_
29	**4na**	new	Semi solid	_
30	**4oa**	new	185-187 °C	_
31	**4pa**	new	146-147 °C	_
32	**5pa**	new	200-202 °C	_
33	**5po**	new	220-222 °C	_
34	**5ar**	new	220-222 °C	_
35	**6ga**	new	140-142 °C	_
36	**6ja**	new	160-162 °C	_
37	**4as**	new	125-127 °C	_
38	**5asg**	new	180-182 °C	_

[a] E. Lieber, T. S. Chao and C. N. R. Rao, *Org. Synth.*, **1957**, *37*, 26; [b] Zhao Xu et al, *Chem. Res. Chinese U.*, **2012**, *28*, 424-429; [c] 1) Zhao Qian et al, *Gaodeng Xuexiao Huaxue Xuebao*, **2011**, *32*, 2806-2811; 2) E. Lieber, T. -S. Chao, and C. N. R. Rao, *J. Org. Chem.* **1957**, *22*, 654; [d] A. C. Tome, *Science of Synthesis*, **2004**, *13*, 415-601; [e] P. A. S. Smith, J. J. Friar, W. Resemann and A. C.Watson, *J. Org. Chem.*, **1990**, *55*, 3351-3362.