Synthetic Manifestation of Nitro Substituted Tetrazole-N-(Hetero)Aryl Derivatives and Energetic Studies


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SUPPORTING INFORMATION

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**General Experimental**

All the reactions were performed in an oven-dried round bottomed flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 or 230-400 Mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber. Proton and carbon nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR) were recorded based on the resonating frequencies as follows: (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) having the solvent resonance as internal standard (¹H NMR, CDCl₃ at 7.26 ppm, DMSO D₆ at 2.50 & 3.50 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm, DMSO D₆ at 44.0 ppm). Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; br s = broad singlet; d = doublet; br d = broad doublet, t = triplet; br t = broad triplet; q = quartet; m = multiplet), coupling constants, J, in (Hz), and integration. Data for ¹³C NMR was reported in terms of chemical shift (ppm). Fluorine nuclear magnetic resonance spectra (¹⁹F NMR) were recorded based on the resonating frequency ¹⁹F NMR, 376 MHz. IR spectra were reported in cm⁻¹. LC-MS spectra were obtained with ionization voltage of 70ev; data was reported in the form of m/z (intensity relative to base peak = 100). Elemental (C, H, N) analysis were carried out using FLASH EA 1112 analyzer. Melting points and decomposition temperatures (DTA) were determined by DSC-TGA measurements. X-ray data was collected at 298K on a SMART APEX CCD and Xcalibur Gemini Eos CCD single crystal diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å).

**Materials:** Unless otherwise noted all the reagents and intermediates were obtained commercially and used without purification. All the starting compounds of substituted N-aryl(hetero) anilines were purchased from Avra Synthesis Pvt Ltd and used as received. Sodium azide, ammonium chloride, aqueous ammonia purchased from Merck Ltd. Triethylorthoformalte, 4-Iodobenzonitrile, β-cyclodextrin were purchased from Alfa Aesar and used as received. Sodium tungstenate hydrate purchased from Finar ltd.

**Caution!** All the 1,2,3,4-tetrazoles derivatives are energetic materials and it tends to explode under certain conditions unpredictably. However, none of the compounds described herein has exploded or detonated in the course of this research. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided. Ignoring safety precautions can lead to serious injuries.
Experimental Procedures:

**General procedure for the synthesis of aryl-tetrazoles (2a-r) (GP-1):** A stirred suspension of the appropriate anilines $1a$−$r$ (1.0 mmol), triethylorthoformate (0.26 mL, 1.6 mmol), and sodium azide (0.097 g., 1.5 mmol) in acetic acid (2-3 mL) were heated at 100 °C in 5−6 h. The mixture was cooled, and the solvent was removed in vacuum. The residue dissolved in a mixture of dichloromethane (50 mL) and 0.1 N aqueous HCl (2-3 mL). The organic phase was washed with water (2-3 mL), brine (2 mL), dried over Na$_2$SO$_4$, and concentrated. The residue was suspended in ethyl ether (5 mL), stirred for 30 min, and filtered to afford the desired product.

**Physical characterization data is exactly matching with the reported values for the respective compounds 2a-2k, 2m-2o.**

1-Phenyl-1H-tetrazole (2a):\[1]

![2a](image)

Following the general procedure GP-1: a mixture of aniline $1a$ (1.00 g, 10.73 mmol), triethylorthoformate (2.85 mL, 17.16 mmol), and sodium azide (1.04 g, 16.0 mmol) in acetic acid (15 mL) was heated at 100 °C in 5−6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product $2a$ (0.950 g) in 60% yield as colorless solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.05 (s, 1H), 7.74−7.72 (m, 2H), 7.62−7.50 (m, 3H); $^{13}$C NMR (127 MHz, CDCl$_3$): $\delta$ 140.6, 133.8, 130.2, 130.1, 121.2.

1-(4-Methylphenyl)-1H-1,2,3,4-triazole (2b):\[2]

![2b](image)

Following the general procedure GP-1: a mixture of 4-methylaniline $1b$ (1.00 g, 9.33 mmol), triethylorthoformate (2.4 mL, 14.88 mmol), and sodium azide (0.90 g, 13.99 mmol) in acetic acid (15 mL) was heated at 100 °C in 5−6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product $2b$ (1.28 g) in 85% yield as light yellow solid.
1H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 8.98 (s, 1H), 7.60 (d, \(J = 8.5\) Hz, 2H), 7.39 (d, \(J = 7.5\) Hz, 2H), 2.47 (s, 3H); \(^{13}\)C NMR (127 MHz, CDCl\textsubscript{3}): \(\delta\) 140.5, 140.4, 131.5, 130.7, 121.1, 21.1.

1-(3-Methylphenyl)-1H-1,2,3,4-tetrazole (2c):\(^{[3]}\)

Following the general procedure (GP-1): a mixture of 3-methylaniline 1c (1.00 g, 9.33 mmol), triethylorthoformate (2.4 mL, 14.93 mmol), and sodium azide (0.91 g, 13.99 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of 2c (1.21 g) in 81% yield as light yellow solid.

1H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 10.07 (s, 1H), 7.73 (s, 1H), 7.69 (d, \(J = 10.0\) Hz, 1H), 7.50 (t, \(J = 8.5\) Hz, 1H), 7.35 (d, \(J = 9.5\) Hz, 1H), 2.40 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 140.7, 140.6, 133.7, 130.7, 129.9, 121.7, 118.1, 21.3.

1-(2-Methylphenyl)-1H-1,2,3,4-triazole (2d):\(^{[3]}\)

Following the general procedure (GP-1): a mixture of 2-methylaniline 1d (3.00 g, 27.99 mmol), triethylorthoformate (7.42 mL, 44.78 mmol), and sodium azide (2.72 g, 41.95 mmol) in acetic acid (45 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (60 mL), stirred for 30 min, and filtered to afford the desired product of 2d (3.49 g) in 77% yield as colorless solid.

1H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.84 (s, 1H), 7.51–7.33 (m, 3H), 7.33–7.27 (m, 1H), 2.18 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) 143.3, 133.6, 132.8, 131.7, 130.8, 127.2, 126.0, 125.8, 17.6.

1-(4-Methoxyphenyl)-1H-1,2,3,4-tetrazole (2e):\(^{[1]}\)

Following the general procedure GP-1: a mixture of 4-methoxyaniline 1e (5.00 g, 40.60 mmol), triethylorthoformate (10.80 mL, 64.96 mmol), and sodium azide (3.95 g, 60.90 mmol) in acetic acid (50
mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (100 mL), stirred for 30 min, and filtered to afford the desired product 2e (5.93 g) in 83% yield as colorless solid.

\[^1\]H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.95 (s, 1H), 7.58 (d, \(J = 8.8\) Hz, 2H), 7.03 (d, \(J = 9.2\) Hz, 2H), 3.85 (s, 3H); \[^13\]C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 160.7, 140.7, 126.9, 122.9, 115.2, 55.7.

**1-(3-Methoxyphenyl)-1H-1,2,3,4-tetrazole (2f):**

Following the general procedure (GP-1): a mixture of 3-methoxyaniline 1f (1.00 g, 8.12 mmol), triethylorthoformate (2.16 mL, 12.99 mmol), and sodium azide (0.791 g, 12.18 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of 2f (1.20 g) in 84% yield as colorless solid.

\[^1\]H NMR (400 MHz, CDCl\(_3\)): \(\delta = \) 9.01 (s, 1H), 7.50 (t, \(J = 8.0\) Hz, 1H), 7.38–7.24 (m, 2H), 7.08 (dd, \(J = 8.4, 2.4\) Hz, 1H), 3.92 (s, 3H); \[^13\]C NMR (101 MHz, CDCl\(_3\)): \(\delta = \) 160.9, 140.6, 134.8, 131.0, 115.7, 112.9, 107.1, 55.8.

**1-(2-Methoxyphenyl)-1H-1,2,3,4-tetrazole (2g):**

Following the general procedure (GP-1): a mixture of 2-methoxyaniline 1g (1.00 g, 8.12 mmol), triethylorthoformate (2.16 mL, 12.99 mmol), and sodium azide (0.791 g, 12.18 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product of 2g (1.17 g) in 82% yield as brownish oil.

\[^1\]H NMR (400 MHz, CDCl\(_3\)): \(\delta = \) 9.15 (s, 1H), 7.65 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.45–7.32 (m, 1H), 7.11-6.93 (m, 2H), 3.83 (s, 3H); \[^13\]C NMR (101 MHz, CDCl\(_3\)): \(\delta = \) 150.6, 143.2, 131.0, 124.5, 122.8, 121.3, 112.5, 56.1.
1-(4-(Trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (2h):

Following the general procedure GP-1: a mixture of 4-(trifluoromethoxy)aniline 1h (1.50 g, 8.47 mmol), triethylorthoformate (2.25 mL, 13.54), and sodium azide (0.82 g, 12.70 mmol) in acetic acid (20 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product 2h (1.52 g) in 78% yield as colorless solid.

m.p. 103 °C; R_f = 0.52 (n-hexane/EtOAc, 4:1); ¹H NMR (400 MHz, CDCl₃): δ 9.08 (s, 1H), 7.81 (d, J = 9.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H); ¹³C NMR (127 MHz, CDCl₃): δ 149.9, 140.7, 132.1, 122.8 (d, J = 34 Hz), 121.1, 120.3 (q, J = 259.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ −58.02; IR. (KBr) ν = 3127, 2920, 1680, 1510, 1469, 1210, 859 cm⁻¹; MS (EI) m/z (%) 231 (100) [M⁺+1], 199 (13); elemental analysis calcd (%) for C₈H₅F₃N₄O: C 41.75. H 2.19, N 24.34; Found: C 41.68, H 2.23, N 24.41.

1-(3-(Trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (2i):

Following the general procedure (GP-1): a mixture of 3-(trifluoromethoxy)aniline 1i (3.00 g, 16.93 mmol), triethylorthoformate (4.49 mL, 27.08 mmol), and sodium azide (1.14 g, 25.39 mmol) in acetic acid (40 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (50 mL), stirred for 30 min, and filtered to afford the desired product of 2i (2.98 g) in 76% yield as colorless solid.

m.p. 63 °C; R_f = 0.50 (n-hexane/EtOAc, 4:1); ¹H NMR (400 MHz, CDCl₃): δ 9.29 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ 150.0, 140.8, 134.8, 131.7, 122.1, 120.2 (q, J = 259.2 Hz), 119.2, 114.2; ¹⁹F NMR (376 MHz, CDCl₃): δ −58.02; IR. (KBr) ν = 3121, 2915, 1608, 1500, 1402, 1086, 885 cm⁻¹; MS (EI) m/z (%) 231 (100) [M⁺+1], 199 (13), 184 (5); elemental analysis calcd (%) for C₈H₅F₃N₄O: C 41.75. H 2.19, N 24.34; Found: C 41.65, H 2.23, N 24.38.
1-(4-(Trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (2j): [6]

Following the general procedure GP-1: a mixture of 4-(trifluoromethyl)aniline 1j (1.00 g, 6.20 mmol), triethylorthoformate (1.64 mL, 9.92 mmol), and sodium azide (0.605 g, 9.3 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product of 2j (1.09 g) in 82% yield as colorless solid.

1H NMR (500 MHz, [D_6] DMSO): δ 10.23 (s, 1H), 8.16 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H) ppm; 13C NMR (127 MHz, [D_6] DMSO): δ 142.9, 137.1, 130.1 (q, J = 32.9 Hz), 127.7 (q, J = 3.30 Hz), 124.0 (q, J = 275 Hz), 122.1 ppm; 19F NMR (376 MHz, [D_6] DMSO): δ –61.4;

1-(3-(Trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (2k): [6]

Following the general procedure (GP-1): a mixture of 3-(trifluoromethyl)aniline 1k (1.00 g, 6.206 mmol), triethylorthoformate (1.65 mL, 9.92 mmol), and sodium azide (0.605 g, 9.30 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product of 2k (1.07 g) in 81% yield as colorless solid.

1H NMR (500 MHz, CDCl_3): δ 9.16 (s, 1H), 8.03 (s, 1H), 7.98 (d, J = 9.5 Hz, 1H), 7.84–7.75 (m, 2H); 13C NMR (127 MHz, CDCl_3): δ 140.6, 134.3, 133.4 (q, J = 34.3 Hz ), 131.1, 126.7 (q, J = 2.54 Hz), 124.4, 123.0 (q, J = 276 Hz), 118.3 (q, J = 3.81 Hz); 19F NMR (376 MHz, CDCl_3): δ –62.94;

1-(4-(1H-Pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (2l):

Following the general procedure (GP-1): a mixture of 4-(1H-pyrazol-1-yl)aniline 1l (0.45 g, 2.82 mmol), triethylorthoformate (0.75 mL, 4.51 mmol), and sodium azide (0.274 g, 4.23 mmol) in acetic acid (10 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (25
mL), stirred for 30 min, and filtered to afford the desired product of $2\text{l}$ (0.42 g) in 71% as colorless solid.

$\text{DTA} = 172 \degree\text{C}$ (exotherm); $R_f = 0.57$ ($n$-hexane/EtOAc, 7:3); $^1\text{H}$ NMR (500 MHz, [D$_6$] DMSO): $\delta$ 10.14 (s, 1H), 8.65 (d, $J = 2.5$ Hz, 1H), 8.13 (d, $J = 9.0$ Hz, 2H), 8.05 (d, $J = 9.0$ Hz, 2H), 7.82 (s, 1H), 6.61 (d, $J = 2.0$ Hz, 1H); $^{13}\text{C}$ NMR (127 MHz, [D$_6$] DMSO): $\delta$ 142.7, 142.2, 140.6, 131.8, 128.6, 122.9, 119.9, 109.0; IR (KBr) $\nu =$ 3128, 1605, 1528, 1391, 1336, 1210, 1090, 936 cm$^{-1}$; MS (EI) m/z (%) 213 (100) [M$^+$+1], 186 (7), 129 (15); elemental analysis calcd (%) for C$_{10}$H$_8$N$_6$: C 56.60, H 3.80, N 39.60; Found: C 56.71, H 3.73, N 39.52.

1-(4-Nitrophenyl)-1H-1,2,3,4-tetrazole ($2\text{m}$): [7]

Following the general procedure GP-1: a mixture of 4-nitroaniline $1\text{m}$ (1.00 g, 7.24 mmol), triethylorthoformate (1.92 mL, 11.58 mmol), and sodium azide (0.705 g, 10.86 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of $2\text{m}$ (1.15 g) in 82% yield as yellow solid.

$^1\text{H}$ NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.28 (s, 1H), 8.49 (d, $J = 8.8$ Hz, 2H), 8.23 (d, $J = 8.8$ Hz, 2H);

$^{13}\text{C}$ NMR (101 MHz, [D$_6$] DMSO): $\delta$ 147.9, 143.2, 138.6, 126.1, 122.4.

1-(3-Nitrophenyl)-1H-1,2,3,4-tetrazole ($2\text{n}$): [7]

Following the general procedure (GP-1): a mixture of 3-nitroaniline $1\text{n}$ (1.00 g, 7.24 mmol), triethylorthoformate (1.92 mL, 11.58 mmol), and sodium azide (0.705 g, 10.86 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of $2\text{n}$ (1.20 g) in 86% yield as yellow solid.

$^1\text{H}$ NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.30 (s, 1H), 8.77 (d, $J = 2.0$ Hz, 1H), 8.40 (dd, $J = 7.6$, 1.6, Hz, 2H), 7.95 (t, $J = 8.0$ Hz, 1H); $^{13}\text{C}$ NMR (101 MHz, [D$_6$] DMSO): $\delta$ 148.8, 143.1, 134.9, 132.1, 127.6, 124.5, 116.4.
2-(1H-Tetrazol-1-yl)pyridine (2o):[^8]

Following the general procedure (GP-1): a mixture of pyridin-2-amine 1o (2.00 g, 21.20 mmol), triethylorthoformate (5.6 mL, 33.9 mmol), and sodium azide (2.00 g, 31.8 mmol) in acetic acid (30 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (50 mL), stirred for 30 min, and filtered to afford the desired product of 2o (2.01 g) in 64% yield as colorless solid.

m.p. 127 °C; DTA = 195 °C (exotherm); Rf = 0.50 (n-hexane/EtOAc, 7:3); $^1$H NMR (500 MHz, CDCl$_3$): δ 9.52 (s, 1H), 8.50 (dd, $J = 6.0$, 1.0 Hz, 1H), 8.10–7.92 (m, 2H), 7.48–7.40 (m, 1H); $^{13}$C NMR (127 MHz, CDCl$_3$): δ 149.1, 146.8, 140.1, 139.9, 124.9, 114.3.

2-(1H-Tetrazol-1-yl)pyrimidine (2p):

Following the general procedure (GP-1): a mixture of pyrimidin-2-amine 1p (1.00 g, 10.51 mmol), triethylorthoformate (2.79 mL, 16.8 mmol), and sodium azide (1.02 g, 15.76 mmol) in acetic acid (15 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product 2p (0.912 g) in 58% as colorless solid.

m.p. 142 °C; DTA = 194 °C (exotherm); Rf = 0.52 (n-hexane/EtOAc, 7:3); $^1$H NMR (400 MHz, CDCl$_3$): δ 9.58 (s, 1H), 8.92 (d, $J = 4.8$ Hz, 2H), 7.53 (t, $J = 2.5$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 159.8, 152.8, 141.7, 122.0, 117.0; IR (KBr) ν = 3106, 1720, 1589, 1463, 1424, 1380, 997 cm$^{-1}$; MS (EI) m/z (%) 149 (100) [$M^+1$]; elemental analysis calcd (%) for C$_5$H$_4$N$_6$: C 40.54, H 2.72, N 56.74; Found: C 40.61, H 2.78, N 56.85.

2-(1H-Tetrazol-1-yl)pyrazine (2q):

Following the general procedure (GP-1): a mixture of pyrazin-2-amine 1q (2.00 g, 21.05 mmol), triethylorthoformate (5.5 mL, 33.63 mmol), and sodium azide (2.05 g, 31.57 mmol) in acetic acid (30 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (50
mL), stirred for 30 min, and filtered to afford the desired product of 2q (1.92 g) in 61% as colorless solid.

m.p. 127 °C; DTA = 177 °C (exotherm); $R_f = 0.54$ (n-hexane/EtOAc, 7:3); $^1$H NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.28 (d, $J = 1.2$ Hz, 1H), 9.37 (s, 1H), 8.91 (s, 1H), 8.78 (s, 1H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): $\delta$ 146.4, 143.8, 143.7, 142.7, 137.6; IR (KBr) ν = 3134, 3084, 1589, 1479, 1216, 865 cm$^{-1}$; MS (EI) m/z (%) 149 (100) [M$^+$+1]; elemental analysis calcd (%) for C$_5$H$_4$N$_6$: C 40.54, H 2.72, N 56.74; Found: C 40.38, H 2.65, N 56.62.

2,6-di(1H-Ttetrazol-1-yl)pyridine (2r): Following the general procedure (GP-1): a mixture of 2,6-diamino pyridine 1r (1.00 g, 9.16 mmol), triethylorthoformate (4.87 mL, 29.31 mmol), and sodium azide (1.78 g, 27.48 mmol) in acetic acid (15 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product 2r (0.356 g) in 18% as colorless solid.

DTA = 224 °C (sharp exotherm); $R_f = 0.55$ (n-hexane/EtOAc, 1:1); $^1$H NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.51 (s, 2H), 8.51 (t, $J = 8.4$ Hz, 1H), 8.23 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): $\delta$ 145.6, 145.5, 142.5, 115.3; IR (KBr) ν = 3134, 3117, 3046, 1605, 1583, 1490, 1424, 1282, 1210, 1095, 1008, 947 cm$^{-1}$; MS (EI) m/z (%) 216 (100) [M$^+$+1], 199 (2), 157 (6), elemental analysis calcd (%) for C$_7$H$_5$N$_9$: C 39.07, H 2.34, N 58.59; Found: C 39.15, H 2.26, N 58.42.

**General procedure for the synthesis of 3-5 (GP-2):** A mixture of 98% sulphuric acid (5.0 mL) and 95% nitric acid (2.5 mL) was added to 2 (1.0 mmol) at 0 °C. The reaction was conducted at the respective conditions shown in Table 2 (Manuscript). Upon completion, the reaction mixture was cooled by the addition of ice and neutralized with saturated aqueous solution of NaHCO$_3$. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with water (2 × 20 mL), brine (25 mL), and dried over Na$_2$SO$_4$. Solvent was filtered and evaporated under vacuum. The crude residue was purified using column chromatography on silica gel to afford the desired nitration products in overall good yields.
Preparation of 2m from 2a:
Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-Phenyl-1H-tetrazole (2a; 1.00 g, 6.84 mmol) at 0 °C and stirred RT for 24 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 2m (1.02 g) in 78% yield as light yellow color solid.

1-(4-Methyl-3-nitrophenyl)-1H-1,2,3,4-tetrazole (3b):

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(4-methylphenyl)-1H-1,2,3,4-triazole (2b; 0.250 g, 1.56 mmol) at 0 °C and stirred RT for 2 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 3b (0.276 g) in 86% as light yellow color solid.

m.p. 104 °C; DTA = 193 °C (exotherm); $R_f = 0.48$ (n-hexane/EtOAc, 7:3); $^1$H NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.19 (s, 1H), 8.55 (s, 1H), 8.18 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 7.6$ Hz, 1H), 2.58 (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): $\delta$ 149.6, 143.0, 134.9, 134.5, 132.7, 125.8, 117.4, 19.7; IR. (KBr) $\nu$ = 3111, 1722, 1536, 1360, 1221, 1086, 833 cm$^{-1}$; MS (EI) m/z (%) 206 (100) [M$^+$+1] elemental analysis calcd (%) for C$_8$H$_7$N$_5$O$_2$: C 46.83, H 3.44, N 34.13; Found: C 46.75, H 3.51, N 34.07.

1-(4-Methyl-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4b):

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (16 mL) and 95% nitric acid (8 mL) was added to 1-(4-methylphenyl)-1H-1,2,3,4-triazole (2b; 0.378 g, 2.36 mmol) at 0 °C and stirred 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 4b (0.486 g) in 82% as light yellow color solid.

DTA = 178 °C (exotherm); $R_f = 0.47$ (n-hexane/EtOAc, 4:1); $^1$H NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.25 (s, 1H), 8.88 (s, 2H), 2.53 (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): $\delta$ 151.8, 143.4, 132.9, 127.5, 117.4.
120.8, 14.9; IR (KBr) ν = 3452, 3113, 1633, 1547, 1504, 1344, 1219, 1174, 1089, 1012, 893, 713 cm⁻¹; MS (EI) m/z (%) 251 (100) [M⁺+1], 169 (15), 137(8); elemental analysis calcd (%) for C₈H₆N₆O₄: C 38.41, H 2.42, N 33.59; Found: C 38.51, H 2.49, N 33.48.

1-(3-Methyl-4-nitrophenyl)-1H-1,2,3,4-tetrazole (3c):

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (6 mL) and 95% nitric acid (3 mL) was added to 1-(3-methylphenyl)-1H-1,2,3,4-triazole (2c; 0.273 g, 1.70 mmol) at 0 °C and stirred RT for 2 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 3c (0.291 g) in 83% as light yellow color solid.

m.p. 163 °C; DTA = 192 °C (exotherm); δf = 0.52 (n-hexane/EtOAc, 1:3); ¹H NMR (400 MHz, [D₆] DMSO): δ 10.20 (s, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.13 (s, 1H), 8.02 (dd, J = 7.2, 2.0 Hz, 1H), 2.63 (s, 3H); ¹³C NMR (101 MHz, [D₆] DMSO): δ 149.0, 142.8, 136.9, 135.9, 127.0, 124.8, 119.7, 20.1; IR. (KBr) ν = 3134, 3094, 1616, 1585, 1521, 1340, 1222, 1174, 879 cm⁻¹; MS (EI) m/z (%) 100 [M⁺+1], 171 (6), 167 (18); elemental analysis calcd (%) for C₈H₇N₅O₂: C 46.83, H 3.44, N 34.13; Found: C 46.94, H 3.48, N 34.07.

1-(5-Methyl-2,4-dinitrophenyl)-1H-1,2,3,4-tetrazole (4c):

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) was added to 1-(3-methylphenyl)-1H-1,2,3,4-triazole (2c; 1.00 g, 6.24 mmol) at 0 °C and stirred 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 4c (1.217 g) 78% as light yellow color solid.

m.p. 135 °C; DTA = 168 °C (exotherm); δf = 0.55 (n-hexane/EtOAc, 6:4); ¹H NMR (400 MHz, [D₆] DMSO): δ 10.05 (s, 1H), 8.95 (s, 1H), 8.26 (s, 1H), 2.71 (s, 3H); ¹³C NMR (101 MHz, [D₆] DMSO): δ 149.5, 145.3, 141.5, 141.2, 133.4, 129.2, 123.2, 20.0; IR (KBr) ν = 3134, 1600, 1534, 1353, 1090, 958

S12
1-(2-Methyl-5-nitrophenyl)-1H-1,2,3,4-tetrazole (3d):

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(2-methylphenyl)-1H-1,2,3,4-triazole (2d; 0.660 g, 4.12 mmol) at 0 °C and stirred room temperature for 2 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 3d (0.691 g) in 82% as yellow solid.

m.p. 143 °C; DTA = 187 °C (exotherm); $R_f = 0.55$ ($n$-hexane/EtOAc, 7:3); $^1$H NMR (400 MHz, [D$_6$] DMSO): $\delta$ 9.91 (s, 1H), 8.51 (d, $J = 2.4$ Hz, 1H), 8.39 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 2.31 (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): $\delta$ 146.6, 145.2, 142.2, 133.8, 133.3, 125.5, 122.0, 18.2; IR (KBr) $\nu = 3123, 2849, 1517, 1347, 1090, 849$ cm$^{-1}$; MS (EI) m/z (%) 204 (100) [$M^{+}$−1], 191 (3); elemental analysis calcd (%) for C$_8$H$_7$N$_5$O$_2$: C 46.83, H 3.44, N 34.13; Found: C 46.75, H 3.37, N 34.26.

(2-Methyl-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4d):

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) was added to 1-(2-methylphenyl)-1H-1,2,3,4-triazole (2d; 1.00 g, 6.25 mmol) at 0 °C and stirred 80 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 4d (1.181 g) in 75% as yellow solid.

m.p. 141 °C; DTA = 194 °C (exotherm); $R_f = 0.50$ ($n$-hexane/EtOAc, 4:1); $^1$H NMR (500 MHz, [D$_6$] DMSO): $\delta$ 9.95 (s, 1H), 9.02 (d, $J = 1.6$ Hz, 1H), 8.91 (d, $J = 2.0$ Hz, 1H), 2.29 (s, 3H); $^{13}$C NMR (127 MHz, [D$_6$] DMSO): $\delta$ 151.0, 146.1, 145.8, 136.6, 135.6, 126.2, 121.8, 15.1; IR (KBr) $\nu = 3128, 3084,
2920, 1534, 1347, 1090, 909 cm$^{-1}$; MS (EI) m/z (%) 251 (100) [$M^+1$], 169 (15), 137 (11), 115 (5); elemental analysis calcd (%) for C$_8$H$_6$N$_6$O$_4$: C 38.41, H 2.42, N 33.59; Found: C 38.56, H 2.37, N 33.45.

1-(4-Methoxy-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4e):

![Diagram of 4e]

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (60 mL) and 95% nitric acid (30 mL) was added to 1-(4-methoxyphenyl)-1H-1,2,3,4-triazole (2e; 5.6 g, 31.78 mmol) at 0 °C and stirred at room temperature for 1h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 4e (7.45 g) in 88% yield as colorless solid.

m.p. 106 °C; DTA = 156 °C (exotherm); $R_f$ = 0.54 (n-hexane/EtOAc, 4:1); $^1$H NMR (400 MHz, [D$_6$] DMSO): $\delta$ 10.20 (s, 1H), 8.94 (s, 2H), 4.02 (s, 3H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): $\delta$ 147.0, 145.3, 143.4, 129.4, 122.9, 65.2; IR (KBr) v = 3138, 3043, 1630, 1543, 1352, 1211, 1184, 898 cm$^{-1}$; MS (EI) m/z (%) 265 (100) [$M^+1$], 254 (12), 237(10); elemental analysis calcd (%) for C$_8$H$_6$N$_6$O$_5$: C 36.10, H 2.27, N 31.57; Found: C 36.19, H 2.21, N 31.68.

Nitration of 2f for the preparation of 4f and 4f$'$:

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (16 mL) and 95% nitric acid (8 mL) was added to 1-(3-methoxyphenyl)-1H-1,2,3,4-tetrazole (2f; 0.5 g, 2.84 mmol) at 0 °C and stirred at RT for 3 h. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford 4f (0.138 g ; 18%) and 4f$'$ (0.487 g ; 64%) as yellow color solids.

However, nitration of 2f (0.5 g, 2.84 mmol) at 80 °C for 6 h exclusively produced 4f$'$ (0.592 g) in 78% yield as yellow color solid.

1-(3-Methoxy-2,4-dinitrophenyl)-1H-tetrazole (4f):

![Diagram of 4f]
DTA = 154 °C (exotherm); \( R_f = 0.61 \) (n-hexane/EtOAc, 7:3); \(^1\)H NMR (400 MHz, [D\(_6\)] DMSO): \( \delta 10.03 \) (s, 1H), 8.74 (d, \( J = 8.0 \) Hz, 1H), 7.94 (d, \( J = 8.0 \) Hz, 1H), 4.16 (s, 3H); \(^{13}\)C NMR (101 MHz, [D\(_6\)] DMSO): \( \delta 155.6, 146.4, 137.6, 136.5, 130.8, 121.7, 117.9, 59.2 \); IR (KBr) \( \nu = 3134, 3073, 1621, 1528, 1331, 1084 \) cm\(^{-1}\); MS (EI) m/z (%): 267 \(^{100}\), 265 (48), 239 (9), 238 (53), 105 (9); elemental analysis calcd (%) for C\(_8\)H\(_6\)N\(_6\)O\(_5\): C 36.10, H 2.27, N 31.57; Found: C 36.21, H 2.23, N 31.45.

1-(5-Methoxy-2,4-dinitrophenyl)-1H-1,2,3,4-tetrazole (4f\(^f\)):

\[
\begin{align*}
\text{DTA} &= 177 °C (exotherm); \ R_f = 0.64 \ (n\text{-hexane/EtOAc}, 3:1); \ ^1H \text{ NMR} (400 MHz, [D}_6) \text{ DMSO): } \delta 9.97 \ (s, 1H), 8.98 \ (s, 1H), 8.06 \ (s, 1H), 4.10 \ (s, 3H); \ ^{13}C \text{ NMR} (101 MHz, [D}_6) \text{ DMSO): } \delta 156.3, 145.3, 139.2, 135.7, 131.5, 124.4, 116.1, 59.4; \ IR (KBr) \nu = 3136, 3076, 2924, 1618, 1601, 1525, 1338, 1089, 997, 833 \text{ cm}^{-1}; \ MS (EI) \text{ m/z } (%): 265 \ (100) [\text{M}+1], 254 \ (13), 237 \ (12); \text{ elemental analysis calcd } (\%) \text{ for C}_8\text{H}_6\text{N}_6\text{O}_5: \text{C } 36.10, \text{ H} 2.27, \text{ N} 31.57; \text{ Found: C } 36.27, \text{ H} 2.21, \text{ N} 31.68.
\end{align*}
\]

Nitration of 2g for the preparation of 3g and 4g:

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (8 mL) and 95% nitric acid (4 mL) was added to 1-(2-methoxyphenyl)-1H-1,2,3,4-tetrazole (2g; 0.378 g, 1.70 mmol) at 0 °C and stirred at room temperature 30 min. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford 3g (0.074 g; 29%) and 4g (0.161 g; 55%) as yellow color solids. Whereas nitration of 2g (0.720 g, 4.11 mmol) at room temperature for 6 h produced 4g (0.894 g) in 82% as yellow color solid.

1-(2-Methoxy-5-nitrophenyl)-1H-1,2,3,4-tetrazole (3g):

\[
\text{m.p. 123 °C; DTA = 217 °C (exotherm); } \ R_f = 0.68 \ (n\text{-hexane/EtOAc}, 4:1); \ ^1H \text{ NMR} (400 MHz, [D}_6) \text{ DMSO): } \delta 9.89 \ (s, 1H), 8.62 \ (d, \ J = 2.8 \ Hz, 1H), 8.50 \ (dd, \ J = 9.6, 2.8 \ Hz, 1H), 7.59 \ (d, \ J = 9.2 \ Hz, 1H), 4.01 \ (s, 3H); \ ^{13}C \text{ NMR} (101 MHz, [D}_6) \text{ DMSO): } \delta 157.5, 145.3, 140.9, 127.8, 122.9, 122.3, 114.2, 58.1;
\]
IR (KBr) ν = 3139, 3101, 3052, 2871, 1616, 1605, 1550, 1347, 1276, 1123, 1084, 958 cm⁻¹; MS (EI) m/z (%) 220 (100) [M⁺–1], 205 (8), 177 (8); elemental analysis calcd (%) for C₈H₇N₅O₃: C 43.44, H 3.19, N 31.66; Found: C 43.27, H 3.26, N 31.86.

1-(2-Methoxy-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4g):

```
N N
N
4g
O Me
O
2
N
O
2
N
```
m.p. 132 °C; DTA = 171 °C (exotherm); Rᵣ = 0.59 (n-hexane/EtOAc, 4:1); ¹H NMR (400 MHz, [D₆] DMSO): δ 9.96 (s, 1H), 9.05 (d, J = 2.8 Hz, 1H), 9.00 (d, J = 2.8 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (101 MHz, [D₆] DMSO): δ 152.0, 145.6, 143.4, 142.2, 129.3, 126.7, 123.3, 64.02; IR (KBr) ν = 3139, 3095, 1600, 1556, 1342, 958 cm⁻¹; MS (EI) m/z (%) 265 (100) [M⁺–1], 254 (13), 237 (12); elemental analysis calcd (%) for C₈H₆N₆O₅: C 36.10, H 2.27, N 31.57; Found: C 36.23, H 2.21, N 31.45.

1-(2-Nitro-4-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (3h):

```
F-CO- phenyl
```
Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(4-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (2h; 0.378 g, 1.64 mmol) at 0 °C and stirred at room temperature for 6 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 3h (0.352 g) in 78% yield as yellow color solid.
m.p. 63 °C; DTA = 161 °C (exotherm); Rᵣ = 0.63 (n-hexane/EtOAc, 3:1); ¹H NMR (400 MHz, [D₆] DMSO): δ 10.09 (s, 1H), 8.75 (s, 1H), 8.51 (br d, J = 7.2 Hz, 1H), 8.30 (br d, J = 6.8 Hz, 1H); ¹³C NMR (101 MHz, [D₆] DMSO): δ = 145.2, 144.2, 132.4 (q, J = 34.3 Hz), 132.2, 130.4, 129.8, 124.0, 122.9 (q, J = 274 Hz); ¹⁹F NMR (376 MHz, [D₆] DMSO): δ = -57.1 ; IR (KBr) ν = 3134, 3057, 1556, 1353, 1287, 1090, 893 cm⁻¹; MS (EI) m/z (%) 276 (100) [M⁺+1], 251 (3), 236 (5); elemental analysis calcd (%) for C₈H₄F₃N₅O₃: C 34.92, H 1.47, N 25.45; Found: C 34.85, H 1.41, N 25.32.
Nitration of 2i for the preparation of 3i and 3i':

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (10 mL) and 95% nitric acid (5 mL) was added to 1-(3-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (2i; 0.3 g, 1.30 mmol) at 0 °C and stirred at room temperature for 6 h. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford 3i (0.194 g; 54%) and 3i' (0.115 g; 32%) as yellow color solids.

1-(2-Nitro-5-(trifluoromethoxy)phenyl)-1H-tetrazole (3i):

\[ \text{m.p. 58 °C; DTA = 169 °C (exotherm); } R_f = 0.40 \text{ (n-hexane/EtOAc, 7:3); } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 9.10 \text{ (br s, 1H), 8.33 (d, } J = 8.8 \text{ Hz, 1H), 7.63 (d, } J = 8.8 \text{ Hz, 1H), 7.51 (s, 1H); } ^{13}\text{C NMR (101 MHz, CDCl}_3\text{): } \delta 152.5, 141.4, 128.8, 128.5, 123.9, 123.0, 120.6, 120.0 (q, } J = 263.2); ^{19}\text{F NMR (376 MHz, CDCl}_3\text{): } \delta -57.9; \text{ IR (KBr) } \nu = 3139, 1610, 1539, 1347, 1090, 953 \text{ cm}^{-1}; \text{ MS (EI) m/z (%)} 277 (100) [M]+1; \text{ elemental analysis calcd (%) for C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_3\text{: C 34.92, H 1.47, N 25.45; Found: C 35.12, H 1.41, N 25.36.} \]

1-(4-Nitro-3-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (3i'):

\[ \text{m.p. 114 °C; DTA = 173 °C (exotherm); } R_f = 0.55 \text{ (n-hexane/EtOAc, 7:3); } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 9.13 \text{ (s, 1H), 8.32 (d, } J = 9.2 \text{ Hz, 1H), 7.65 (dd, } J = 8.0, 2.0 \text{ Hz, 1H), 7.54 (br d, } J = 2.0 \text{ Hz, 1H); } ^{13}\text{C NMR (101 MHz, CDCl}_3\text{): } \delta 152.4, 143.7, 141.3, 128.6, 128.5, 123.0, 120.6, 119.9 (q, } J = 263 \text{ Hz); } ^{19}\text{F NMR (376 MHz, CDCl}_3\text{): } \delta -57.5; \text{ IR (KBr) } \nu = 3134, 2920, 1599, 1462, 1293, 1161, 1090, 947 \text{ cm}^{-1}; \text{ MS (EI) m/z (%)} 276 (100) [M]+1; \text{ elemental analysis calcd (%) for C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_3\text{: C 34.92, H 1.47, N 25.45; Found: C 34.83, H 1.51, N 25.32.} \]
1-(2-Nitro-4-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (3j):

\[
\begin{array}{c}
\text{F}_3\text{C}-\text{NO}_2-\text{N}^\ast-\text{N}^\ast-\text{N}^\ast \\
\text{3j}
\end{array}
\]

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (10 mL) and 95% nitric acid (5 mL) was added to 1-(4-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (2j; 0.214 g, 1.00 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 3j (0.178 g) in 68% yield as yellow color solid.

m.p. 73 °C; DTA = 158 °C (exotherm); \( R_f = 0.52 \) (n-hexane/EtOAc, 3:1); \(^1\)H NMR (400 MHz, [D\(_6\)] DMSO): \( \delta \) 10.07 (s, 1H), 8.74 (d, \( J = 1.2 \) Hz, 1H), 8.50 (d, \( J = 8.0 \) Hz, 1H), 8.28 (d, \( J = 8.4 \) Hz, 1H); \(^1^3\)C NMR (101 MHz, [D\(_6\)] DMSO): \( \delta \) 145.2, 144.2, 143.4, 132.4 (q, \( J = 33.3 \) Hz), 132.2, 130.4, 129.8, 124.0 (q, \( J = 4.0 \) Hz), 122.9 (q, \( J = 274 \) Hz); \(^1^9\)F NMR (376 MHz, [D\(_6\)] DMSO): \( \delta \) −61.6; IR (KBr) \( \nu = 3150, 2915, 1627, 1550, 1473, 1326, 1271, 860 \) cm\(^{-1}\); MS (EI) m/z (%): 260 (100) [M\(^+\) + 1], 163 (5); elemental analysis calcd (%) for C\(_8\)H\(_4\)F\(_3\)N\(_5\)O\(_2\): C 37.08, H 1.56, N 27.02; Found: C 37.16, H 1.61, N 27.15.

1-(4-Nitro-3-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (3k):

\[
\begin{array}{c}
\text{NO}_2-\text{F}_3\text{C}-\text{N}^\ast-\text{N}^\ast-\text{N}^\ast \\
\text{3k}
\end{array}
\]

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(3-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (2k; 0.368 g, 1.72 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 3k (0.322 g) in 72% yield as yellow color solid.

m.p. 97 °C; DTA = 203 °C (exotherm); \( R_f = 0.52 \) (n-hexane/EtOAc, 3:2); \(^1\)H NMR (400 MHz, [D\(_6\)] DMSO): \( \delta \) 10.36 (s, 1H), 8.61 (s, 1H), 8.65 (d, \( J = 8.8 \) Hz, 1H), 8.48 (d, \( J = 8.8 \) Hz, 1H); \(^1^3\)C NMR (101 MHz, [D\(_6\)] DMSO): \( \delta \) 147.2, 143.4, 137.1, 128.2, 126.8, 123.7 (q, \( J = 34.4 \) Hz), 121.9 (q, \( J = 276 \) Hz), 121.2 (q, \( J = 4.0 \) Hz); \(^1^9\)F NMR (376 MHz, [D\(_6\)] DMSO): \( \delta \) −60.3; IR (KBr) \( \nu = 3134, 2904, 1605, 1539, \)
Nitration of 2l for the preparation of 4l and 5l:

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (8 mL) and 95% nitric acid (4 mL) was added to 1-(4-(1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (2l; 0.186 g, 0.877 mmol) at 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford 4l (0.11 g; 42%) as orange color solid and 5l (0.069 g; 20%) as yellow color semi solid.

1-(4-(4-Nitro-1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (4l):

\[
\begin{align*}
\text{m.p.} & \quad 130 ^\circ C; \quad \text{DTA} = 167 ^\circ C \text{ (exotherm)}; \quad R_f = 0.40 (n\text{-hexane/EtOAc, 3:2}); \\
^1H \text{ NMR} (500 MHz, [D_6]DMSO): & \quad \delta 10.30 (s, 1H), 9.69 (s, 1H), 8.82 (d, J = 2.5 Hz, 1H), 8.66 (s, 1H), 8.52 (dd, J = 8.5, 2.0 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H); \\
^{13}C \text{ NMR} (127 MHz, [D_6]DMSO): & \quad \delta 144.7, 143.4, 138.4, 137.5, 134.9, 132.4, 131.5, 129.2, 126.4, 118.9; \quad \text{IR (KBr)} \nu = 3139, 2958, 1545, 1512, 1413, 1331, 1221, 1084, 947 \text{ cm}^{-1}; \quad \text{MS (EI) m/z (}% \rightleftharpoons 303 (100) [M^+1], 282 (12), 215 (10); \quad \text{elemental analysis calcd (}% \rightleftharpoons 39.74, H 2.00, N 37.08; \quad \text{Found: C 39.65, H 2.10, N 37.21.}
\end{align*}
\]

1-(4-(4,5-Dinitro-1H-pyrazol-1-yl)-3-nitrophenyl)-1H-1,2,3,4-tetrazole (5l):

\[
\begin{align*}
R_f & = 0.55 (n\text{-hexane/EtOAc, 3:2}); \quad ^1H \text{ NMR} (500 MHz, [D_6]DMSO): \delta 10.35 (s, 1H), 9.90 (s, 1H), 8.94 (d, J = 2.5 Hz, 1H), 8.61 (dd, J = 8.5, 2.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H); \quad ^{13}C \text{ NMR} (127 MHz, [D_6]DMSO): \delta 148.9, 144.4, 143.5, 136.5, 136.0, 130.9, 130.6 128.1, 127.0, 119.2; \quad \text{IR (KBr)} \nu = 3402, 2920, 2252, 2126, 1649, 1545, 1331, 1221, 1030, 860 \text{ cm}^{-1}; \quad \text{MS (EI) m/z}
\end{align*}
\]
(%) 348 (100) [M′+1], 303 (16), 271(12); elemental analysis calcd (%) for C_{10}H_{5}N_{9}O_{6}: C 34.59, H 1.45, N 36.31; Found: C 34.48, H 1.51, N 36.45.

**Preparation of 2,6-dinitro-4-(1H-tetrazol-1-yl)aniline (6):**

![Image of 6]

An aqueous solution of ammonia (6.0 mL) was added to a solution of compound 4e (6.00 g, 22.54 mmol) in acetonitrile (120.0 mL). The resulting solution was refluxed for 8 h. Upon completion, the reaction mixture was cooled to RT. The reaction mixture was precipitated during cooling, the solid was filtered and washed with diethylether and dried in air to afford 6 (4.76 g) in 84% yield as orange color solid.

DTA = 223 °C (sharp exotherm); R_f = 0.52 (n-hexane/EtOAc, 3:2); \(^1\)H NMR (400 MHz, [D_6] DMSO): \(\delta\) 10.13 (s, 1H), 8.97 (s, 2H), 8.60 (s, 2H); \(^{13}\)C NMR (101 MHz, [D_6] DMSO): \(\delta\) 143.1, 141.2, 135.3, 127.1, 120.2; IR (KBr) \(\nu = 3466, 3356, 1541, 1342, 1078, 773 \text{ cm}^{-1}\); MS (EI) m/z (%) 252 (100) [M′+1], 212 (9), 91 (7); elemental analysis calcd (%) for C_{7}H_{5}N_{7}O_{4}: C 33.47, H 2.01, N 39.04; Found: C 33.52, H 2.12, N 39.15.

**Preparation of N-(2,6-dinitro-4-(1H-tetrazol-1-yl)phenyl)nitramide (7):**

![Image of 7]

To an ice-cold fuming nitric acid (10 mL), was added 6 (0.8 g, 3.18 mmol) in small portions and the reaction mixture was stirred at 0–5 °C for 15-20 minutes. Then the resulting mixture was poured into crushed ice. The solid was collected by suction filtration and washed with cold water and dried under vaccum. The solid was further wased with triflouroacetic acid to afford 7 (0.72 g) in 76% yield as yellow color solid.

DTA = 175 °C (sharp exotherm); R_f = 0.50 (n-hexane/EtOAc, 1:4); \(^1\)H NMR (400 MHz, [D_6] DMSO): \(\delta\) 10.2 (s, 1H), 9.43 (br s; 1H), 8.84 (s, 2H); \(^{13}\)C NMR (101 MHz, [D_6] DMSO): \(\delta\) 145.9, 143.4, 130.3,129.9, 121.4; IR (KBr) \(\nu = 3512, 3150, 1567, 1347, 1002, 723 \text{ cm}^{-1}\); MS (EI) m/z (%) 297 (100)
[M$^+$+1], 281 (18), 251 (5), 223 (5); elemental analysis calcd (%) for C$_7$H$_3$N$_7$O$_6$: C 28.39, H 1.36, N 37.84; Found: C 28.31, H 1.31, N 37.92.

**Preparation of 1-(3,4,5-trinitrophenyl)-1H-tetrazole (8):**

![Diagram of 8]

Compound 6 (1.00 g, 3.98 mmol) was dissolved in sulphuric acid (100 mL), and Na$_2$WO$_4$·2H$_2$O (0.987 g, 2.98 mmol) was subsequently added to the mixture at 0 °C. Hydrogen peroxide (30%, 7 mL) was then added dropwise to the reaction mixture and the resulting mixture was stirred at RT for 18 h and then poured into ice cold water. The precipitate was filtered off, washed with cold water and recrystallized from ethylacetate to afford 8 (0.831 g) in 74% as yellow color solid.

DTA = 175 °C (sharp exotherm); $R_f$ = 0.54 (n-hexane/EtOAc, 3:1); $^1$H NMR (500 MHz, [D$_6$] DMSO): δ 10.08 (s, 1H), 8.71 (s, 2H); $^{13}$C NMR (127 MHz, [D$_6$] DMSO): δ 147.5, 143.2, 141.1, 123.6, 123.2; IR (KBr) ν = 3134, 1556, 1336, 1073, 991 cm$^{-1}$; MS (EI) m/z (%) 282 (100) [M$^+$+1], 256 (11), 206 (7), 157 (11), 111 (28), 79 (36); elemental analysis calcd (%) for C$_7$H$_3$N$_7$O$_6$: C 29.90, H 1.08, N 34.87; Found: C 30.07, H 1.16, N 34.75.

**Preparation of 1-(4-azido-3,5-dinitrophenyl)-1H-tetrazole (9):**

![Diagram of 9]

Trimethylsilyl azide (0.654g, 5.69 mmol) was added to a solution of 8 (0.80 g, 2.84 mmol) in dimethyl formamide (8.0 mL). The reaction mixture was stirred at ambient temperature for 2 h. The reaction mixture was poured into ice. The colorless solid was collected by suction filtration and was washed with cold water and the solid was dried under vacuum to afford 9 (0.61 g) in 77% yield as colorless solid.

DTA = 223 °C (sharp exotherm); $R_f$ = 0.54 (n-hexane/EtOAc, 7:3); $^1$H NMR (400 MHz, [D$_6$] DMSO): δ 10.27 (s, 1H), 9.0 (s, 2H); $^{13}$C NMR (101 MHz, [D$_6$] DMSO): δ 144.9, 143.4, 130.2, 128.7, 122.1; IR (KBr) ν = 3156, 2180, 2142, 1534, 1358, 1084, 904 cm$^{-1}$; MS (EI) m/z (%) 278 (100) [M$^+$+1], 123 (5); elemental analysis calcd (%) for C$_7$H$_5$N$_7$O$_4$: C 30.33, H 1.09, N 45.48; Found: C 30.41, H 1.13, N 45.36.
X-ray crystallography: X-ray reflections for 3d, 4c, 4e, 6, 7 and 9 were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). Data integration was done using SAINT.\textsuperscript{[9]} Intensities for absorption were corrected using SADABS.\textsuperscript{[10]} Structure solution and refinement were carried out using Bruker SHELX-TL.\textsuperscript{[11]} X-ray reflections for 4b, 4g, 4f' and 8 were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-Kα, radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). OLEX2-1.0\textsuperscript{[12]} and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C–H hydrogens were fixed.

CCDC-1515416 (3d), CCDC-1515420 (4b), CCDC-1515419 (4c), CCDC-1515414 (4e), CCDC-1515422 (4f'), CCDC-1515413 (4g), CCDC-1515415 (6), CCDC-1515417 (7), CCDC-1515421 (8), and CCDC-1515418 (9) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Figure 1.** Molecular structures of compounds 3d thermal ellipsoids are set at 30% probability and hydrogen atoms are labelled for clarity.
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### Table S2. Crystallographic data for compounds 4g, 6, 7, 8 and 9.

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Theoretical study: All the calculations were performed using the Gaussian 03 program suite.[13, 14] The geometric optimization of the structures and frequency analyses were carried out using B3PW91 functional with 6-31G (d, p) basis set. The zero point energies (ZPEs) and the corresponding thermal corrections ($H^0_T$) to the enthalpy at 298.15 K were obtained from frequency calculations and were subsequently added to the electronic energies. All the optimized structures were characterized to be true local energy minima on the potential energy. The method of isodesmic reactions has been employed to calculate HOF from total energies obtained from DFT calculations. Crystal packing density was predicted by the molecular packing calculations using CVFF force field in the polymorph module of Material Studio Suite.[15] Based on the predicted densities and HOFs, using Explo5 version 6.02,[16] the detonation velocity ($D$) and detonation pressure ($P$) for the energetic materials are calculated.

Table S3. The energetic properties of 2m-2q, 3b-d, 3g, 3h, 3i, 3i', 3j and 3k.

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<td>-98.8</td>
<td>1.72</td>
<td>7120</td>
<td>18.72</td>
<td>73</td>
<td>152</td>
<td>-214.30</td>
</tr>
<tr>
<td>3k</td>
<td>-98.8</td>
<td>1.75</td>
<td>7295</td>
<td>19.68</td>
<td>97</td>
<td>195</td>
<td>-215.85</td>
</tr>
</tbody>
</table>

[a] Oxygen balance; [b] Calculated density; the crystal density is shown in parenthesis. [c] Detonation velocity (calculated with Explo5 version 6.02).[16] [d] Detonation pressure (calculated with Explo5 version 6.02).[e] Thermal melting ($T_m$) point and thermal decomposition ($T_d$) temperature under nitrogen gas (10 °C min$^{-1}$) [f] Heat of formation
Molecular Electrostatic Potentials

The effect of substituents on nitration reactions was supported by the electrostatic potential surface graphs (Figure 2) of N-aryl-tetrazole derivatives. These graphs revealed the possibility of the occurrence of electrophilic substitution on aryl ring. The electrostatic potential surface graphs of all the N-aryl-tetrazole derivatives (2a–n) are obtained through DFT calculations at the [B3PW91/6-31G (d,p)] level with the electronegative and electropositive regions and 0.001 au (electrons/Bohr$^3$) contour is the surface of the electron density, proposed by Bader et al.$^{[17]}$ The electrostatic potential of aryl ring in 2a is neutral, marked with green color as shown in Figure 2; as a result mono-nitration product is exclusively obtained. Whereas the electrostatic potential of aryl ring in the electron donating groups (–Me and –OMe, pyrazole) containing N-aryl tetrazole derivatives 2b, 2c, 2d, 2e, 2f, 2g and 2l showed negative potential (Figure 2). As a result nitration of –Me and –OMe and pyrazole substituted N-aryl-tetrazoles delivered mono as well as dinitration products 3b, 3c, 3d, 3g, 4b, 4c, 4d, 4e, 4f, 4f', 4g, 4l, and 5l (tri-nitro product). In case of –OCF$_3$ and –CF$_3$ substituted N-aryl-tetrazoles 2h, 2i, 2j and 2k the electrostatic potential of aryl ring has become neutral with green color (Figure 2), which in turn delivers the mono-nitration products (3h, 3i, 3i', 3j and 3k). Positive electrostatic potential (blue color) was observed in the aryl-ring for the strong electron withdrawing –NO$_2$ substituted N-aryl-tetrazoles 2m & 2n, (Figure 2). As a consequence, electrophilic substitution was not feasible on –NO$_2$ substituted N-aryl-tetrazoles.

![Graphs of Molecular Electrostatic Potentials](image-url)
Figure 2. Optimized structures and electrostatic potential surface graphs of compounds 2a–n (B3PW91/6-31G (d, p), 0.001 electron/bohr$^3$ isosurface. The red regions represent electron-rich sites and the blue regions represent electron-deficient sites. Gray = carbon; white = hydrogen; blue = nitrogen; red = oxygen; skyblue = fluorine.
Isodesmic Reactions for the Prediction of Heat of Formation:

\[
\begin{align*}
\text{N-N} & + \text{N-N-N} + \text{CH}_3\text{NH}_2 \quad \rightarrow \quad \text{N=N-N} + \text{CH}_4 + \text{NH}_3 \\
\text{N-N} & + \text{N-N-N} + \text{CH}_3\text{NH}_2 \quad \rightarrow \quad \text{N=N-N} + \text{CH}_4 + \text{NH}_3 \\
\text{N=N} & + \text{N-N-N} + \text{CH}_3\text{NH}_2 \quad \rightarrow \quad \text{N=N-N} + \text{CH}_4 + \text{NH}_3 \\
\text{N-N} & + 2 \text{N-N} + 2\text{CH}_3\text{NH}_2 \quad \rightarrow \quad \text{N=N-N} + 2\text{CH}_4 + 2\text{NH}_3 \\
\text{N=N} & + \text{N-N-N} + \text{CH}_3\text{CH}_3 + \text{CH}_3\text{NH}_2 + \text{CH}_3\text{NO}_2 \quad \rightarrow \quad \text{Me-O=N-N} + 2\text{CH}_4 + \text{NH}_3 \\
\text{N=N} & + \text{N-N-N} + \text{CH}_3\text{CH}_3 + \text{CH}_3\text{NH}_2 + 2\text{CH}_3\text{NO}_2 \quad \rightarrow \quad \text{H_3C-O=N-N} + 3\text{CH}_4 + \text{NH}_3 \\
\text{N=N} & + \text{N-N-N} + \text{CH}_3\text{CH}_3 + \text{CH}_3\text{NH}_2 + \text{CH}_3\text{NO}_2 \quad \rightarrow \quad \text{Me-O=N-N} + 2\text{CH}_4 + \text{NH}_3 \\
\text{N=N} & + \text{N-N-N} + \text{CH}_3\text{CH}_3 + \text{CH}_3\text{NH}_2 + 2\text{CH}_3\text{NO}_2 \quad \rightarrow \quad \text{Me-O=N-N} + 3\text{CH}_4 + \text{NH}_3 \\
\text{N=N} & + \text{N-N-N} + \text{CH}_3\text{CH}_3 + \text{CH}_3\text{NH}_2 + \text{CH}_3\text{NO}_2 \quad \rightarrow \quad \text{Me-O=N-N} + 2\text{CH}_4 + \text{NH}_3
\end{align*}
\]
References:

11. G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany, **1997**.
13. Heat of formation calculated in gaseous state (Gaussian 03) with isodesmic approach.


kn8-32-(2)
FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data.exe
Sample ID: KN6-143 (# 22)
Analysis type: Unknown
Chromatogram filename: UNK-06122016-2.dat
Sample weight: 2.672

![Chemical Structure]

Element Name | Element % | Ret. Time
--- | --- | ---
Nitrogen | 24.41 | 0.79
Carbon | 41.68 | 1.15
Hydrogen | 2.396 | 4.56
Element Name | Element % | Ret. Time  
---|---|---
Nitrogen | 24.38 | 0.74
Carbon | 41.65 | 1.11
Hydrogen | 2.23 | 4.61
**FLASH EA 1112 SERIES CHN REPORT**

**THERMO FINNIGAN**

Method filename: 
Sample ID: KN8-29 (# 9)
Analysis type: Unkn
Chromatogram filename: UNK-18082014-9.dat
Sample weight: 1.008

---

![Chemical structure](image)

---

**Element** | **Name** | **Element %** | **Ret. Time**
--- | --- | --- | ---
Nitrogen | 39.52 | 0.75
Carbon | 56.71 | 1.17
Hydrogen | 3.73 | 3.93

S98
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN8-152 (# 49)
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-9.dat
Sample weight: 1.315

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<th>Element %</th>
<th>Ret. Time</th>
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<tbody>
<tr>
<td>Nitrogen</td>
<td>56.85</td>
<td>0.87</td>
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<tr>
<td>Carbon</td>
<td>40.61</td>
<td>1.43</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.78</td>
<td>4.93</td>
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</tbody>
</table>
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data.exe
Sample ID: KN8-150 (# 48)
Analysis type: Unknown
Chromatogram filename: UNK-20012015-8.dat
Sample weight: .648

<table>
<thead>
<tr>
<th>Element Name</th>
<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>56.62</td>
<td>0.82</td>
</tr>
<tr>
<td>Carbon</td>
<td>40.38</td>
<td>1.24</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.65</td>
<td>4.18</td>
</tr>
</tbody>
</table>
Element Name | Element % | Ret. Time
--- | --- | ---
Nitrogen | 58.42 | 1.28
Carbon | 39.15 | 2.22
Hydrogen | 2.26 | 9.15
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-19 (# 42)
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-2.dat
Sample weight: 1.186

Element Name | Element % | Ret. Time
--- | --- | ---
Nitrogen | 34.07 | 0.88
Carbon | 46.75 | 1.41
Hydrogen | 3.51 | 4.92

3b
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-17 (# 16)
Analysis type: UnkNown
Chromatogram filename: UNK-17112014-16.dat
Sample weight: 1.412

<table>
<thead>
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<th>% Element</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>33. 48</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>38. 51</td>
<td>1.36</td>
<td></td>
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<tr>
<td>Hydrogen</td>
<td>2. 49</td>
<td>4.82</td>
<td></td>
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</table>

S103
FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-18 (# 62)
Analysis type: UnkNown
Chromatogram filename: UNK-01112016-2.dat
Sample weight: 1.261

<table>
<thead>
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<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
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<tr>
<td>Hydrogen</td>
<td>3.48</td>
<td>5.04</td>
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</table>

S104
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-34 (# 45)
Analysis type: Unknown
Chromatogram filename: UNK-20012015-5.dat
Sample weight: 1.215

<table>
<thead>
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<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>33.45</td>
<td>0.88</td>
</tr>
<tr>
<td>Carbon</td>
<td>38.56</td>
<td>1.41</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.36</td>
<td>4.92</td>
</tr>
</tbody>
</table>
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-19 (# 114)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-14.dat
Sample weight: 1.261

![Chemical Structure](image)

### Chromatogram

<table>
<thead>
<tr>
<th>Element</th>
<th>Name</th>
<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>34. 26</td>
<td>0. 73</td>
<td></td>
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<tr>
<td>Carbon</td>
<td>46. 75</td>
<td>1. 14</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3. 37</td>
<td>3. 92</td>
<td></td>
</tr>
</tbody>
</table>

S106
### Analysis Details

- **Method filename:** C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
- **Sample ID:** MBR-39-1 (# 52)
- **Analysis type:** UnkNown
- **Chromatogram filename:** UNK-20012015-12.dat
- **Sample weight:** 1.206 g

### Chromatogram

![Chromatogram Graph](image)

### Element Analysis

<table>
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<tr>
<th>Element Name</th>
<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>33.45</td>
<td>0.74</td>
</tr>
<tr>
<td>Carbon</td>
<td>38.56</td>
<td>1.16</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.37</td>
<td>3.88</td>
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</table>
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-21 (# 116)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-16.dat
Sample weight: 1.296

![Chemical Structure](image)

<table>
<thead>
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<th>Element</th>
<th>Name</th>
<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td></td>
<td>31.68</td>
<td>0.88</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>36.19</td>
<td>1.41</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>2.21</td>
<td>4.94</td>
</tr>
</tbody>
</table>

S108
**Eleme**| **Name**| **Element %**| **Ret. Time**
---|---|---|---
Nitrogen| 31.45| 0.78
Carbon| 36.21| 1.18
Hydrogen| 2.23| 4.32
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-2-2 (# 17)
Analysis type: Unknown
Chromatogram filename: UNK-17112014-17.dat
Sample weight: 1.173

Element | Name   | Element % | Ret. Time |
---------|--------|-----------|-----------|
Nitrogen | 31.68  |           | 0.87      |
Carbon   | 36.27  |           | 1.38      |
Hydrogen | 2.21   |           | 4.78      |
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN5-176-2 (# 115)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-15.dat
Sample weight: 1.312

<table>
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<tr>
<td>Nitrogen</td>
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<td>0.88</td>
</tr>
<tr>
<td>Carbon</td>
<td>43.27</td>
<td>1.38</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.26</td>
<td>4.93</td>
</tr>
</tbody>
</table>
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex KN5-176-1 (# 21)
Sample ID: UnkNown
Analysis type: UNK-13042015-1.dat
Chromatogram filename: 1.132
Sample weight: 4g

<table>
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<th>Element Name</th>
<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>31.45</td>
<td>0.78</td>
</tr>
<tr>
<td>Carbon</td>
<td>36.23</td>
<td>1.18</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.21</td>
<td>4.29</td>
</tr>
</tbody>
</table>
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-145 (# 111)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-11.dat
Sample weight: 1.291

<table>
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<th>Element %</th>
<th>Ret. Time</th>
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</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td></td>
<td>25.32</td>
<td>0.73</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>34.85</td>
<td>1.16</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>1.41</td>
<td>3.97</td>
</tr>
</tbody>
</table>

[Diagram of chemical structure]

S113
FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:
Sample ID:
Analysis type:
Chromatogram filename:
Sample weight:

C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
MBR-38-1ST (# 22)
UnkNown
UNK-13042015-2.dat
1.113

<table>
<thead>
<tr>
<th>Element</th>
<th>Name</th>
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<th>Ret. Time</th>
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<tbody>
<tr>
<td>Nitrogen</td>
<td></td>
<td>25.36</td>
<td>0.78</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>35.12</td>
<td>1.20</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>1.41</td>
<td>4.27</td>
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</table>
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-38-2 (# 57)
Analysis type: Unknown
Chromatogram filename: UNK-20012015-17.dat
Sample weight: 1.276

Element | Name     | Element % | Ret. Time
---------|----------|-----------|------------
Nitrogen  |          | 25.32     | 0.77       |
Carbon    |          | 34.83     | 1.18       |
Hydrogen  |          | 1.51      | 4.28       |
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN5-162 (# 112)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-12.dat
Sample weight: 1.283

![Chemical Structure](image)

3k

<table>
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<th>Element %</th>
<th>Ret. Time</th>
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<tr>
<td>Nitrogen</td>
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</tr>
<tr>
<td>Carbon</td>
<td>37.21</td>
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<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.61</td>
<td>3.97</td>
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S117
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN8-32-1 (# 120)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-20.dat
Sample weight: 1.293

<table>
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<td>Nitrogen</td>
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<tr>
<td>Carbon</td>
<td>39.65</td>
<td>1.18</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.10</td>
<td>4.12</td>
</tr>
</tbody>
</table>
Element | Name     | Element % | Ret. Time |
---------|----------|-----------|-----------|
Nitrogen |          | 36.45     | 0.87      |
Carbon   |          | 34.48     | 1.43      |
Hydrogen |          | 1.51      | 4.93      |
Element Name | Element % | Ret. Time
---|---|---
Nitrogen | 39.15 | 0.75
Carbon | 33.52 | 1.19
Hydrogen | 2.12 | 4.14
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-2-196 (# 76)
Analysis type: UnkNown
Chromatogram filename: UNK-19052016-6.dat
Sample weight: 1.215

<table>
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<th>Element %</th>
<th>Ret. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
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<td>0.75</td>
</tr>
<tr>
<td>Carbon</td>
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<td>1.19</td>
</tr>
<tr>
<td>Hydrogen</td>
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<td>4.14</td>
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</table>

![Chemical Structure](image)
FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_e
Sample ID: RAVI-6 (# 7)
Analysis type: UnkNown
Chromatogram filename: UNK-13042015-7.dat
Sample weight: 2.412

![Graph with retention times and peak heights]

<table>
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<th>Ret. Time</th>
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<tr>
<td>Carbon</td>
<td>30.07</td>
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</tr>
<tr>
<td>Hydrogen</td>
<td>1.16</td>
<td>4.53</td>
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S122
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-2-195 (# 75)
Analysis type: Unknown
Chromatogram filename: UNK-19052016-5.dat
Sample weight: 1.512

![Chemical Structure Image]

<table>
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<tbody>
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</tr>
<tr>
<td>Carbon</td>
<td>30.41</td>
<td>1.19</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.13</td>
<td>4.32</td>
</tr>
</tbody>
</table>

S123