Evaluation of Viability of Halogen···O_2N Interactions: Insight from Crystal Packing in a Series of Isomeric Halo and Nitro Substituted Triaryl Compounds with Modular Positioning of Halogen and NO_2 Groups

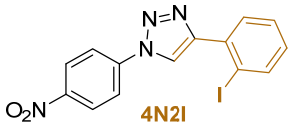
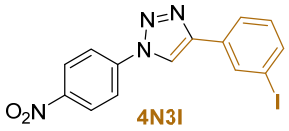
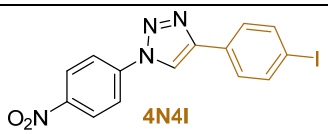
C. V. Ramana,[a,] Yogesh Goriya,[a] Kulbhushan A. Durugkar,[a] Soumitra Chatterjee,[a]*

*Shobhana Krishnaswamy[b] and Rajesh G. Gonnade[b,]**

[a]Division of Organic Chemistry, National Chemical laboratory (CSIR-NCL), Pune, India. Fax: 91 20 2590 2629; Tel: 91 20 2590 2577; E-mail: vr.chepuri@ncl.res.in

[b]Center for Materials Characterization, National Chemical laboratory (CSIR-NCL), Pune, India. Fax: 91 20 2590 2642; Tel: 91 20 2590 2252; E-mail: rg.gonnade@ncl.res.in

Supporting Information

27	 3N4I	^{1}H NMR Spectrum	47
		^{13}C NMR Spectrum	47
		ORTEP (Figure S34)	79
28	 4N2I	^{1}H NMR Spectrum	48
		^{13}C NMR Spectrum	48
		ORTEP (Figure S35)	80
29	 4N3I	^{1}H NMR Spectrum	49
		^{13}C NMR Spectrum	49
		ORTEP (Figure S36)	81
30	 4N4I	^{1}H NMR Spectrum	50
		^{13}C NMR Spectrum	50
		ORTEP (Figure S37)	82

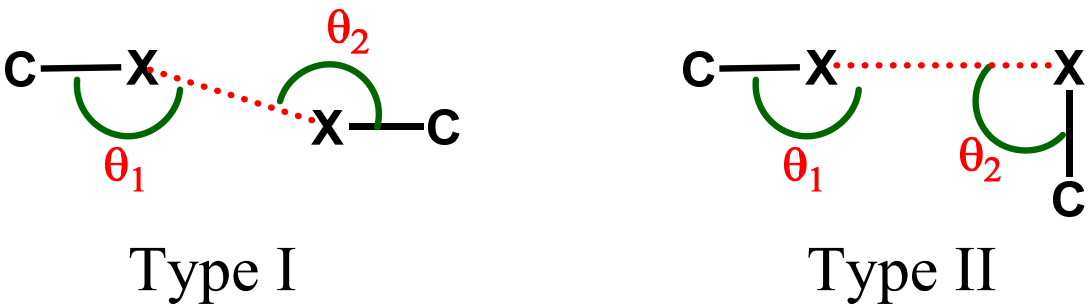


Figure S1. Schematic representation of halogen···halogen interactions.

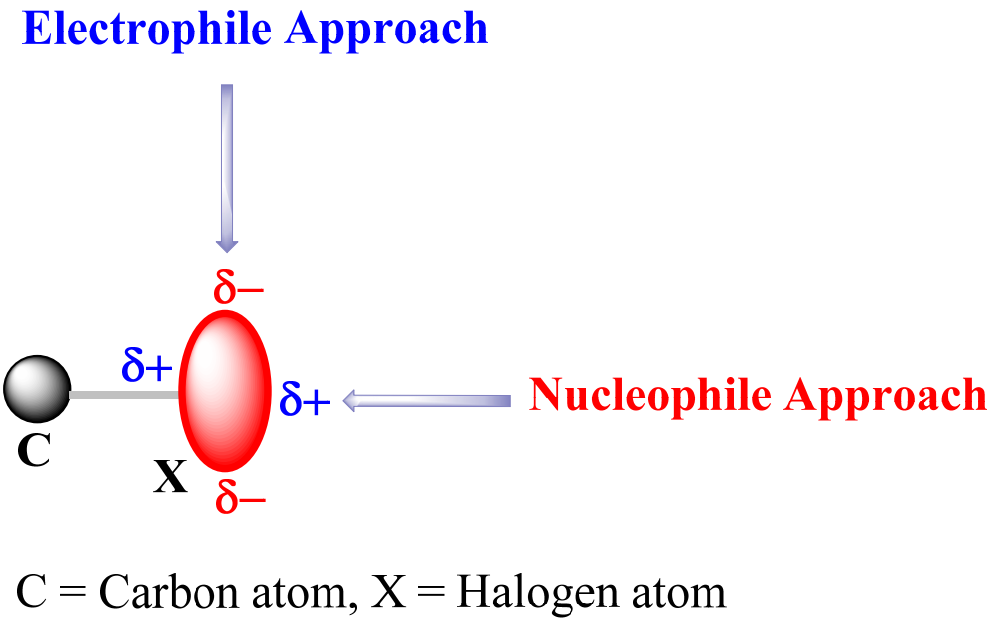


Figure S2. Schematic view of approach of electrophile and nucleophile towards halogen atom.

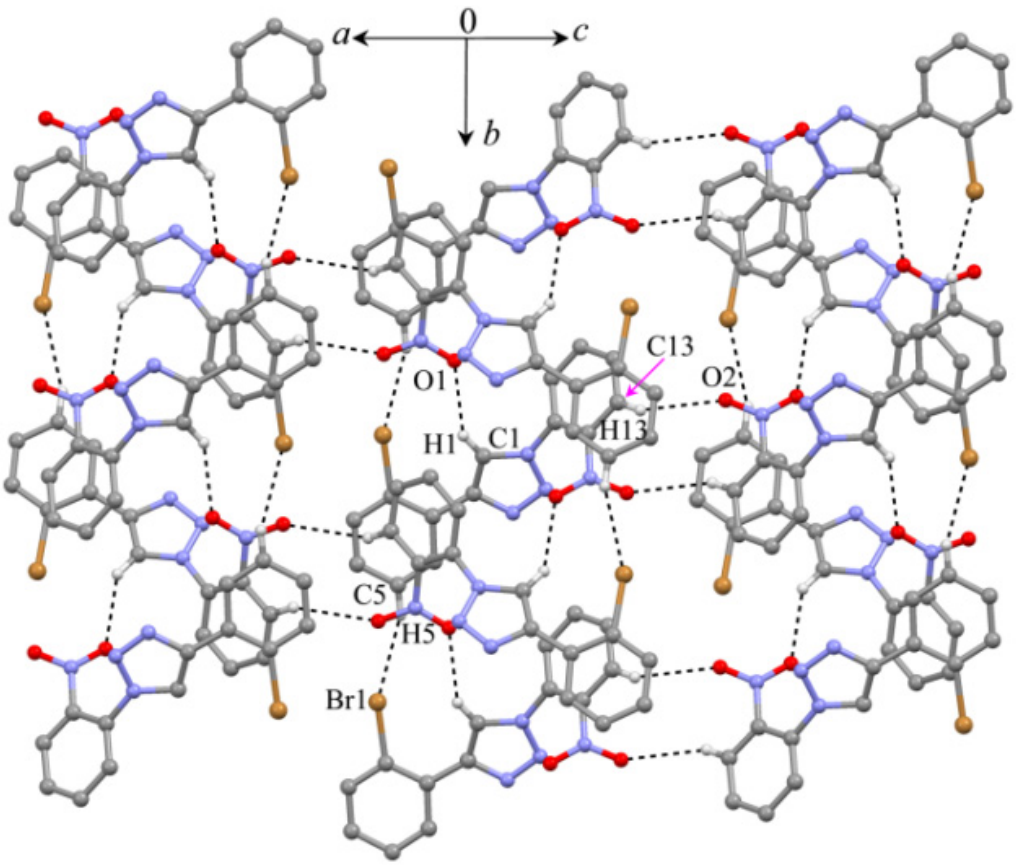


Figure S3. Molecular packing viewed along *ac*-diagonal in **2N2Br**; the structure is isostructural with **2N2Cl**.

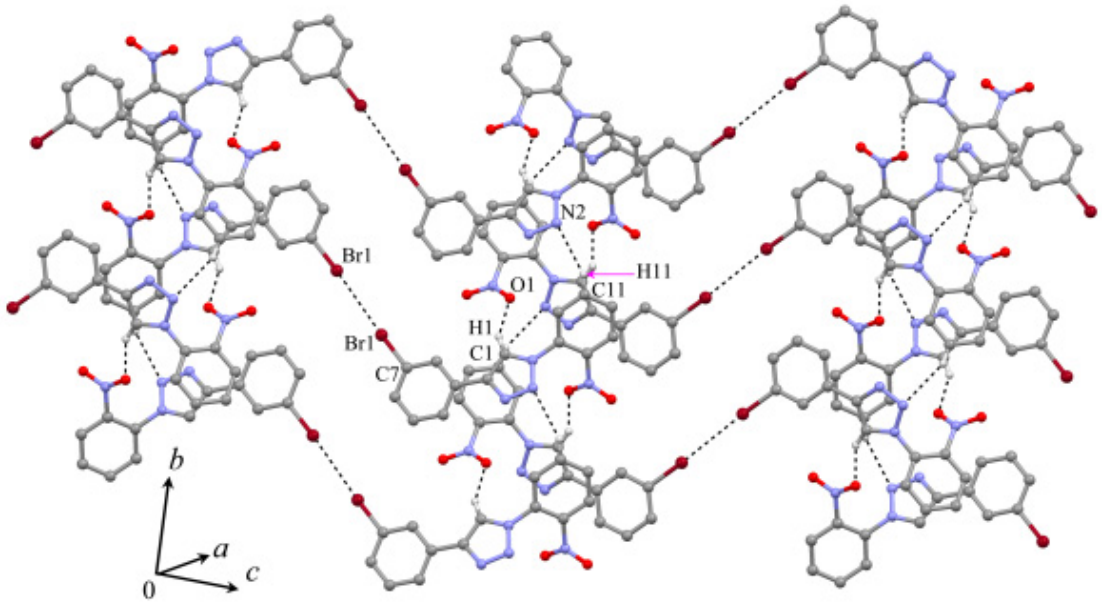


Figure S4. Molecular packing in **2N3Br**; the structure is isostructural with **2N3I**

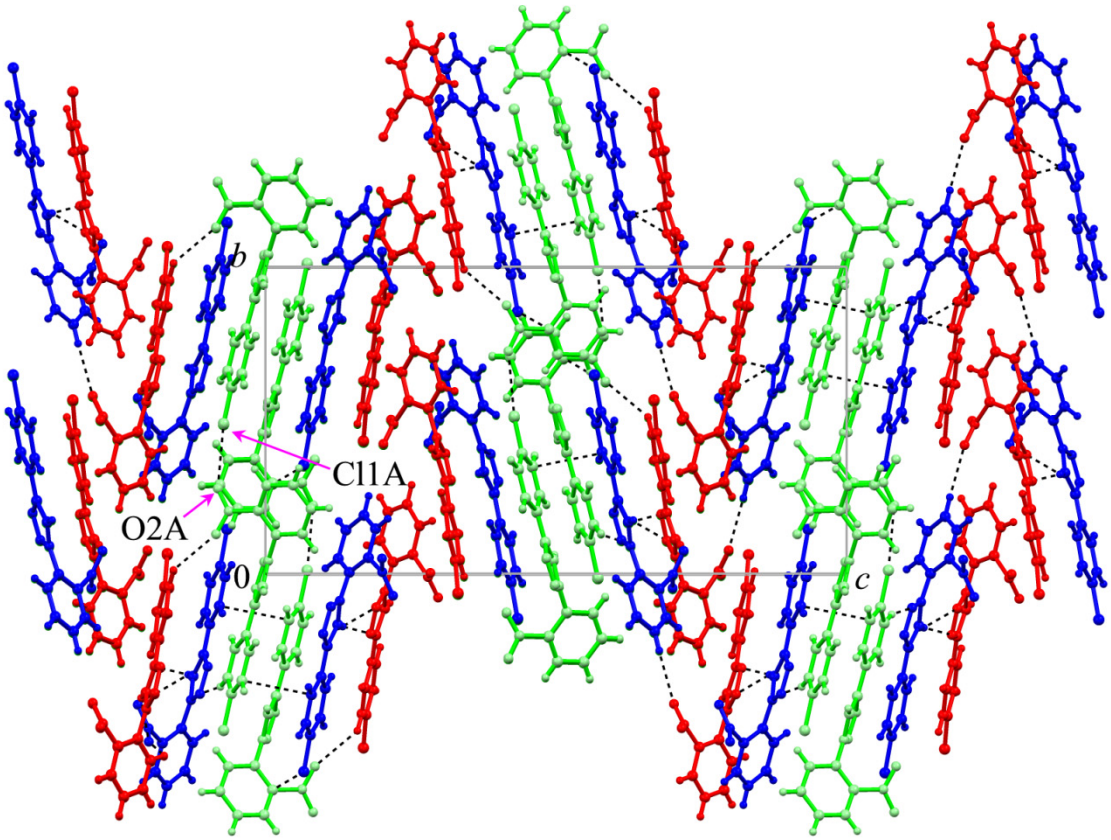
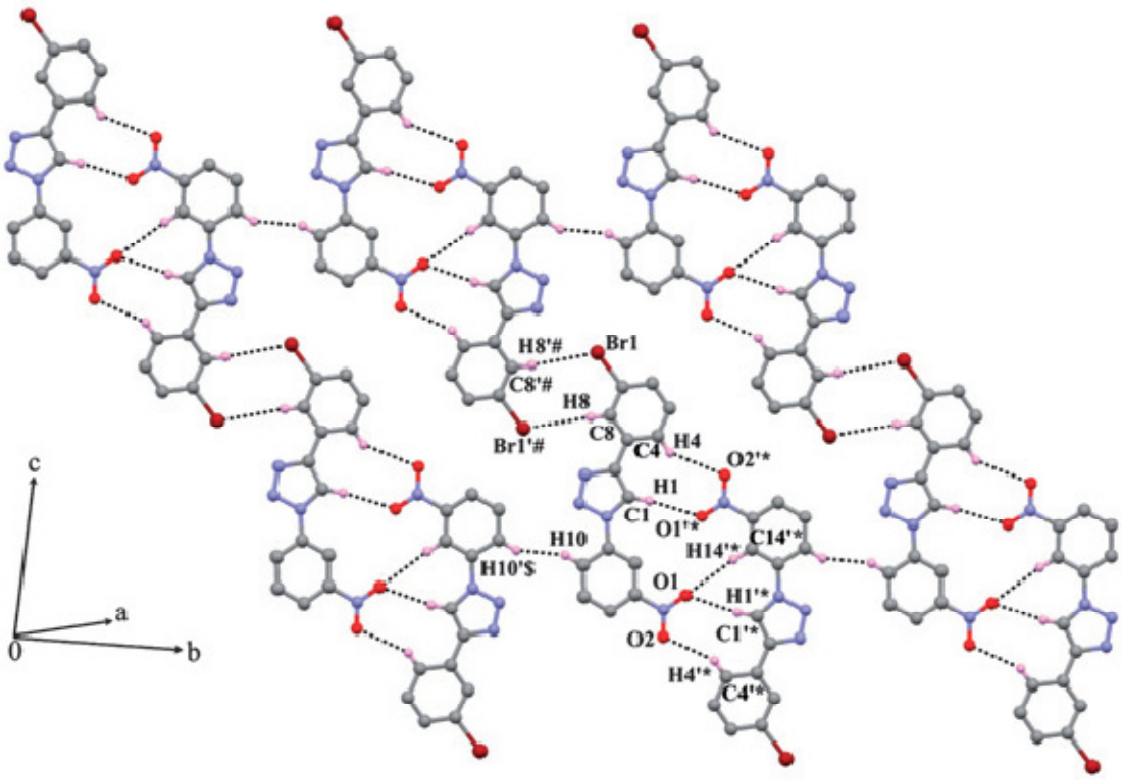


Figure S5. Molecular packing viewed down *a*-axis in **2N4Cl** reveals layered structure of molecules B (blue) and C (red) encapsulating the layers of molecule A (green).



.

Figure S6. Molecular packing in **3N3Br**; **3N3Br** has similar organization as **3N3I**.

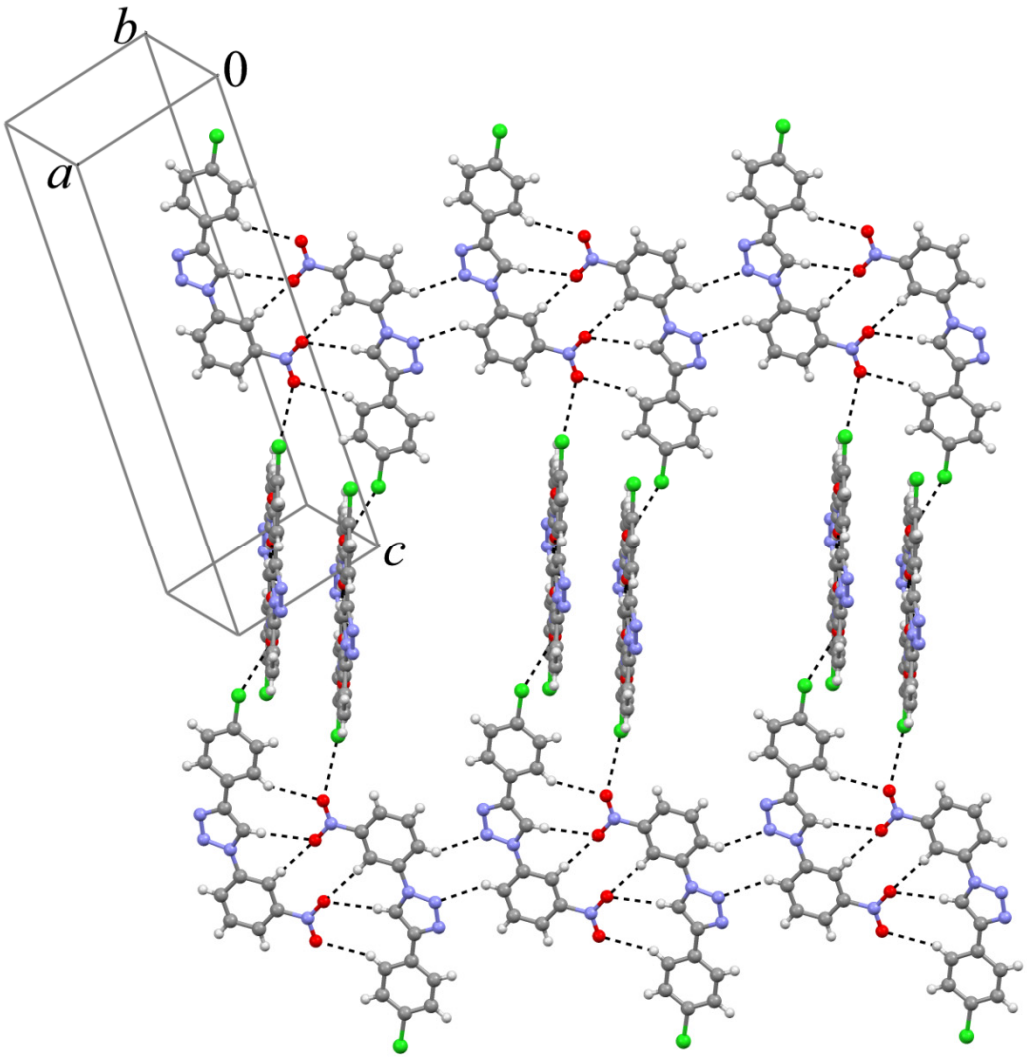


Figure S7. Molecular packing in **3N4Cl**; it has similar organization as **3N** and **3N4Br**.

Experimental:-

A General procedure for cycloaddition reactions with 2/4-nitroflurobenzenes:

Fluoronitrobenzene (100 mg, 0.71 mmol) was mixed with phenyl acetylene (72 mg, 0.71 mmol) in 9:1 DMSO:H_2O (10 mL). To the mixture were added L-proline (16 mg, 0.142 mmol), Na_2CO_3 (15 mg, 0.142 mmol), NaN_3 (55 mg, 0.852 mmol), sodium ascorbate (14 mg, 0.071 mmol), and $CuSO_4.5H_2O$ (9 mg, 0.036 mmol). The mixture was stirred for 24-48 h at 70 °C (bath temperature) and then the mixture was poured into 30 mL of ice-cold water. The solid residue was filtered and crystallized from appropriate solvent systems to procure white to yellow crystalline solids in (57-83%) yield.

B General procedure for cycloaddition reactions with 3-azidobenzene:

A mixture of 3-Azidonitrobenzene (116 mg, 0.71 mmol), phenyl acetylene (72 mg, 0.71 mmol) was taken in 9:1 DMSO:H_2O (10 mL) in a round bottom flask and L-proline (16 mg, 0.142 mmol), Na_2CO_3 (15 mg, 0.142 mmol), sodium ascorbate (14 mg, 0.071 mmol), and $CuSO_4.5H_2O$ (9 mg, 0.036 mmol) were added to that mixture and the complete reaction mixture was heated at 70 ºC (bath temperature) for 24 h with stirring. The reaction mixture was cooled to room temperature and diluted with 30 mL of water and combined water layer was thoroughly extracted with ethyl acetate (3 x 50 mL). Organic layer was dried over sodium sulphate and concentrated under vacuum. The crude solid was purified by column chromatography over 230-400 silica using ethyl acetate-light petroleum (1:4) to obtain white to yellow solids (65-77%). This solid was crystallized from appropriate solvent system.

*1-(2-Nitrophenyl)-4-phenyl-1H-1,2,3-triazole (***2N***)*: mp: 140–141 °C; ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.42–7.56 (m, 3H), 7.83–8.01 (m, 5H), 8.26 (dd, J = 1.1, 8.5 Hz, 1H), 9.20 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 120.7 (d), 125.4 (d, 2C), 125.6 (d), 127.4 (d), 128.5 (d), 129.1 (d, 3C), 129.8 (s), 131.3 (s), 134.5 (s), 144.0 (s), 147.1 (s) ppm; Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04; O, 12.02; Found: C, 62.99; H, 3.67; N, 21.19.

*4-(2-Chlorophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N2Cl***)*: mp: 168–169 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (dt, J = 1.6, 7.8 Hz, 1H), 7.41 (dt, J = 1.2, 7.7 Hz, 1H), 7.48 (dd, J = 0.8, 8.0 Hz, 1H), 7.69–7.73 (m, 2H), 7.82 (dt, J = 1.2, 7.8 Hz, 1H), 8.10 (dd, J = 1.2, 8.1 Hz, 1H), 8.32 (dd, J = 1.2, 7.8 Hz, 1H), 8.53 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.5 (d), 125.6 (d), 127.2 (d), 127.9 (d), 128.4 (s), 129.4 (d), 129.9 (d), 130.1 (s), 130.3 (d), 130.8 (d), 131.3 (s), 133.9 (d), 144.4 (s), 144.5 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.87; H, 2.99; Cl, 11.75; N, 18.59.

*4-(2-Bromophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N2Br***)*: mp: 125–126 °C; ^{1}H (400 MHz, $CDCl_3$): δ 7.24 (dt, J = 1.7, 7.8 Hz, 1H), 7.46 (dt, J = 1.2, 7.8 Hz, 1H), 7.68 (dd, J = 1.0, 8.1 Hz, 1H), 7.73 (br. s, 1H), 7.75 (br. s, 1H), 7.83 (dt, J = 1.6, 8.1 Hz, 1H), 8.12 (dd, J = 1.5, 8.2 Hz, 1H), 8.24 (dd, J = 1.8, 7.8 Hz, 1H), 8.56 (s, 1H); ^{13}C (100 MHz, $CDCl_3$): δ 121.3 (s), 124.3 (d), 125.7 (d, 2C), 127.4 (s), 127.8 (d), 128.1 (s), 129.7 (d), 130.7 (d), 130.9 (d), 133.7 (d, 2C), 142.0 (s), 145.9 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.98; H, 2.39; Br, 23.19; N, 16.51.

*4-(2-Iodophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N2I***)*: mp: 104–105 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.20 (dt, J = 1.7, 7.8 Hz, 1H), 7.55 (dt, J = 1.2, 7.7 Hz, 1H), 7.71 (dd, J = 1.6, 7.7 Hz, 1H), 7.88 (dt, J = 1.5, 7.9 Hz, 1H), 7.93–8.00 (m, 2H), 8.06 (dd, J = 0.8, 8.0 Hz, 1H), 8.27 (dd, J = 1.1, 8.1 Hz, 1H), 9.12 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 97.9 (s), 125.1 (d), 125.8 (d), 127.9 (d), 128.8 (d), 129.2 (s), 130.6 (d), 130.9 (d), 131.5 (d), 134.7 (d), 134.8 (s), 140.3 (d), 144.2 (s), 148.0 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.94; H, 2.44; I, 32.23; N, 14.37.

*4-(3-Chlorophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N3Cl***)*: mp: 128–129 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.45 (ddd, J = 0.9, 1.9, 8.0 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.85–7.89 (m, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.93–8.01 (m, 3H), 8.24 (dd, J = 1.0, 8.3 Hz, 1H), 9.24 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 123.7 (d), 124.1 (d), 125.2 (d), 125.9 (d), 127.6 (d), 128.5 (d), 129.2 (s), 131.3 (d), 131.6 (d), 132.1 (s), 134.1 (s), 134.8 (d), 144.2 (s), 146.0 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.97; H, 2.97; Cl, 11.77; N, 18.67.

*4-(3-Bromophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N3Br***)*: mp: 101–102 °C; ^{1}H (400 MHz, $CDCl_3$): δ 7.02–7.44 (m, 3H), 7.58–7.82 (m, 4H), 7.94–8.04 (m, 2H); ^{13}C (100 MHz, $CDCl_3$): δ 121.4 (d), 123.1 (s), 124.5 (d), 125.7 (d), 126.9 (d), 127.90 (d), 129.0 (d), 130.5 (d), 130.8 (d), 131.5 (d), 131.8 (s), 133.8 (d), 144.4 (s), 146.9 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.76; H, 2.52; Br, 23.42; N, 16.11.

*4-(3-Iodophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N3I***)*: mp: 150–151 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.32 (t, J = 7.9 Hz, 1H), 7.77 (br d, J = 7.9 Hz, 1H), 7.88 (dt, J = 1.7, 7.8 Hz, 1H), 7.95–8.03 (m, 3H), 8.25 (dd, J = 1.1, 8.2 Hz, 1H), 8.30 (br t, J = 1.5 Hz, 1H), 9.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 95.7 (s), 123.6 (d), 124.8 (d), 125.9 (d), 127.6 (d), 129.2 (s), 131.5 (d), 131.6 (d), 132.2 (s), 133.9 (d), 134.8 (d), 137.2 (d), 144.2 (s), 145.7 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.97; H, 2.19; I, 32.43; N, 14.38.

*4-(4-Chlorophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N4Cl***)*: mp: 136–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.4 Hz, 2H), 7.67 (dd, J = 1.2, 7.7 Hz, 1H), 7.72 (dt, J = 1.2, 7.7 Hz, 1H), 7.80–7.84 (m, 3H), 8.08 (s, 1H), 8.10 (dd, J = 1.2, 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 121.1 (d), 125.6 (d), 127.2 (d, 2C), 127.9 (d), 128.2 (s), 129.1 (d, 2C), 130.1 (s), 130.9 (d), 133.9 (d), 134.4 (s), 144.3 (s), 147.3 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.94; H, 2.99; Cl, 11.74; N, 18.60.

*4-(4-Bromophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N4Br***)*: mp: 136–137 °C; ^{1}H (400 MHz, $CDCl_3$): δ 7.40–7.50 (m, 1H), 7.57 (dt, J = 2.2, 8.7 Hz, 1H), 7.65–7.88 (m, 5H),

8.06 (s, 1H), 8.06–8.22 (m, 1H); ^{13}C (100 MHz, $CDCl_3$): δ 121.0 (d), 122.7 (s), 125.6 (d), 127.5 (d, 2C), 127.9 (d), 129.8 (d), 130.8 (d), 132.2 (d, 2C), 132.4 (d), 133.8 (d), 144.4 (s), 147.4 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.44; H, 2.40; Br, 23.11; N, 16.41.

*4-(4-Iodophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (***2N4I***)*: mp: 158–159 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.73–7.75 (m, 2H), 7.86 (dd, J = 1.8, 8.0 Hz, 1H), 7.87–7.89 (m, 2H), 7.96 (dt, J = 1.8, 8.0 Hz, 1H), 8.00 (dt, J = 1.2, 8.0 Hz, 1H), 8.25 (dd, J = 1.2, 8.1 Hz, 1H), 9.21 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 94.6 (s), 123.2 (d), 125.8 (d), 127.5 (d, 2C), 127.6 (d), 129.1 (s), 129.6 (s), 131.5 (d), 134.7 (d), 138.0 (d, 2C), 144.2 (s), 146.4 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.79; H, 2.21; I, 32.23; N, 14.36.

*1-(3-Nitrophenyl)-4-phenyl-1H-1,2,3-triazole (***3N***)*: mp: 204–205 °C; ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.40–7.50 (m, 3H), 7.78 (t, J = 8.21 Hz, 1H), 7.91–7.93 (m, 2H), 8.25–8.33 (m, 2H), 8.30 (s, 1H), 8.65 (t, J = 2.20 Hz, 1H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 115.0 (d), 120.4 (d), 123.5 (d), 125.8 (d, 2C), 126.3 (d), 128.9 (d), 129.5 (d, 2C), 130.2 (s), 132.0 (d), 137.5 (s), 148.1 (s), 148.9 (s) ppm; Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04; O, 12.02; Found: C, 63.06; H, 3.88; N, 20.89.

*4-(2-Chlorophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N2Cl***)*: mp: 149–150 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (dt, J = 1.7, 7.6 Hz, 1H), 7.43 (dt, J = 1.2, 7.6 Hz, 1H), 7.48 (dd, J = 1.0, 8.1 Hz, 1H), 7.70 (t, J = 8.3 Hz, 1H), 8.26 (dd, J = 1.9, 8.1 Hz, 1H), 8.33 (dt, J = 1.7, 7.8 Hz, 2H), 8.69 (t, J = 2.2 Hz, 1H), 8.74 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 115.3 (d), 120.9 (d), 123.3 (d), 126.0 (d), 127.3 (d), 128.3 (s), 129.7 (d), 130.0 (d), 130.4 (d), 131.0 (d), 131.4 (s), 137.7 (s), 145.3 (s), 149.0 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.97; H, 2.97; Cl, 11.73; N, 18.60.

*4-(2-Bromophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N2Br***)*: mp: 131–132 °C. ^{1}H (400 MHz, $CDCl_3$): δ 7.25 (ddd, J = 1.8, 7.4, 9.2 Hz, 1H), 7.46 (dt, J = 1.3, 7.8 Hz, 1H), 7.69 (dd, J = 1.1, 8.1 Hz, 1H), 7.78 (t, J = 8.2 Hz, 1H), 8.20 (dd, J = 1.8, 7.8 Hz, 1H), 8.27 (ddd, J = 1.0, 2.1, 8.2 Hz, 1H), 8.33 (ddd, J = 1.0, 2.1, 8.2 Hz, 1H), 8.66 (t, J = 2.1 Hz,

1H), 8.79 (s, 1H): ^{13}C (100 MHz, $CDCl_3$): δ 115.3 (d), 120.6 (d), 121.3 (s), 123.2 (d), 126.0 (d), 127.9 (d), 129.9 (d), 130.4 (s), 130.8 (d), 131.0 (d), 133.7 (d), 137.8 (s), 146.6 (s), 149.1 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 49.00; H, 2.81; Br, 23.42; N, 16.11.

*4-(2-Iodophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N2I***)*: mp: 122–123 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.22 (dt, J = 1.7, 7.8 Hz, 1H), 7.55 (dt, J = 1.1, 7.6 Hz, 1H), 7.68 (dd, J = 1.6, 7.7 Hz, 1H), 7.95 (t, J = 8.2 Hz, 1H), 8.06 (dd, J = 0.9, 7.9 Hz, 1H), 8.37 (br dd, J = 1.7, 8.3 Hz, 1H), 8.50 (br dd, J = 1.7, 8.2 Hz, 1H), 8.83 (t, J = 2.1 Hz, 1H), 9.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 98.1 (s), 115.1 (d), 122.5 (d), 123.5 (d), 126.4 (d), 128.8 (d), 130.8 (d), 131.0 (d), 131.9 (d), 134.9 (s), 137.3 (s), 140.2 (d), 148.9 (s), 149.0 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.81; H, 2.42; I, 32.27; N, 14.41.

*4-(3-Chlorophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N3Cl***)*: mp: 185–186 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.40 (dd, J = 1.0, 7.7 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.86–7.91 (m, 3H), 8.30 (dd, J = 1.6, 8.3 Hz, 1H), 8.37 (dd, J = 1.4, 8.0 Hz, 1H), 8.68 (t, J = 2.0 Hz, 1H), 9.57 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 114.6 (d), 120.8 (d), 123.4 (d), 124.0 (d), 125.2 (d), 125.9 (d), 128.4 (d), 131.2 (d), 131.8 (d), 132.1 (s), 134.0 (s), 137.2 (s), 146.5 (s), 148.7 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.94; H, 2.99; Cl, 11.80; N, 18.67.

*4-(3-Bromophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N3Br***)*: mp: 195–196 °C; ^{1}H (400 MHz, DMSO-d_6): δ 7.37–7.54 (m, 2H), 7.84–7.99 (m, 2H), 8.14 (t, J = 1.6 Hz, 1H), 8.32 (dd, J = 1.6, 8.3 Hz, 1H), 8.46 (dd, J = 1.6, 8.3 Hz, 1H), 8.86 (t, J = 2.0 Hz, 1H), 9.58 (s, 1H); ^{13}C (100 MHz, DMSO-d_6): δ 112.7 (d), 118.5 (d), 120.7 (s), 121.1 (d), 122.4 (d), 123.8 (d), 126.4 (d), 129.1 (d), 129.2 (d), 129.6 (d), 130.6 (s), 135.6 (s), 144.8 (s), 146.9 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.91; H, 2.83; Br, 23.09; N, 16.06.

*4-(3-Iodophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N3I***)*: mp: 198–199 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.33 (t, J = 7.8 Hz, 1H), 7.77 (br d, J = 8.0 Hz, 1H), 7.94 (t, J = 8.2 Hz, 1H), 8.00 (br d, J = 7.8 Hz, 1H), 8.31 (t, J = 1.5 Hz, 1H), 8.36 (dd, J = 1.8, 8.2 Hz,

1H), 8.45 (dd, *J* = 1.8, 8.1 Hz, 1H), 8.77 (t, *J* = 2.0 Hz, 1H), 9.65 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 95.7 (s), 114.7 (d), 120.9 (d), 123.4 (d), 123.7 (d), 126.1 (d), 131.4 (d), 131.9 (d), 132.3 (s), 133.9 (d), 137.2 (d), 137.3 (s), 146.3 (s), 146.8 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 43.02; H, 2.39; I, 32.48; N, 14.17.

*4-(4-Chlorophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N4Cl***)*: mp: 223–224 °C; ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.37 (dd, *J* = 2.2, 8.5 Hz, 2H), 7.74–7.88 (m, 3H), 8.17 (dd, *J* = 1.6, 8.0 Hz, 1H), 8.31–8.36 (m, 1H), 8.72 (t, *J* = 2.1 Hz, 1H), 9.37 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 113.2 (d), 118.1 (d), 121.3 (d), 124.1 (d), 125.6 (d, 2C), 127.4 (d, 2C), 127.5 (s), 129.7 (d), 132.1 (s), 136.2 (s), 145.7 (s), 147.3 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.88; H, 2.99; Cl, 11.79; N, 18.69.

*4-(4-Bromophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N4Br***)*: mp: 230–231 °C; ^{1}H (400 MHz, DMSO-d_6): δ 7.46 (br. s, 1H), 7.50 (br. s, 1H), 7.71–7.78 (m, 3H), 8.18 (dd, *J* = 2.1, 8.1 Hz, 1H), 8.30 (dd, *J* = 2.5, 8.2 Hz, 1H), 8.68 (t, *J* = 2.1 Hz, 1H), 9.35 (s, 1H); ^{13}C (100 MHz, DMSO-d_6): δ 112.8 (d), 118.2 (d), 120.0 (s), 121.2 (d), 123.9 (d), 125.1 (d), 125.6 (d), 127.5 (s), 127.7 (d), 129.7 (d), 130.1 (d), 135.7 (s), 145.3 (s), 146.9 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.75; H, 2.81; Br, 23.23; N, 16.30.

*4-(4-Iodophenyl)-1-(3-nitrophenyl)-1H-1,2,3-triazole (***3N4I***)*: mp: 217–218 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.74–7.76 (m, 2H), 7.88–7.90 (m, 2H), 7.94 (t, *J* = 8.2 Hz, 1H), 8.34–8.37 (m, 1H), 8.43–8.46 (m, 1H), 8.77 (t, *J* = 2.1 Hz, 1H), 9.61 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 94.8 (s), 114.8 (d), 120.6 (d), 123.5 (d), 126.2 (d), 127.5 (d, 2C), 129.7 (s), 131.9 (d), 137.3 (s), 138.1 (d, 2C), 147.0 (s), 148.8 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.77; H, 2.42; I, 32.22; N, 14.40.

*1-(4-Nitrophenyl)-4-phenyl-1H-1,2,3-triazole (***4N***)*: mp: 236–238 °C; ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.41–7.56 (m, 3H), 7.93–7.98 (m, 2H), 8.23–8.28 (m, 2H), 8.47–8.51 (m, 2H), 9.48 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 120.1 (d), 120.6 (d, 2C), 125.5 (d,

2C), 125.7 (d, 2C), 128.7 (d), 129.2 (d, 2C), 129.8 (s), 140.9 (s), 146.8 (s), 147.9 (s) ppm; Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04; O, 12.02; Found: C, 63.31; H, 3.53; N, 20.91.

*4-(2-Chlorophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (***4N2Cl***)*: mp: 214–216 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.44–7.52 (m, 2H), 7.62 (d, J = 7.5 Hz, 1H), 8.08 (dd, J = 1.5, 7.5 Hz, 1H), 8.33 (d, J = 8.8 Hz, 2H), 8.45 (d, J = 9.0 Hz, 2H), 9.42 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 120.8 (d, 2C), 122.5 (d), 125.4 (d, 2C), 127.6 (d), 128.3 (s), 130.0 (d), 130.1 (d), 130.3 (d), 130.8 (s), 140.7 (s), 144.4 (s), 146.8 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.97; H, 2.97; Cl, 11.77; N, 18.67.

*4-(2-Bromophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (***4N2Br***)*: mp: 170–171 °C; ^{1}H (400 MHz, $CDCl_3$): δ 7.26 (ddd, J = 1.8, 7.4, 9.2 Hz, 1H), 7.47 (dt, J = 1.2, 7.8 Hz, 1H), 7.69 (dd, J = 1.2, 7.9 Hz, 1H), 8.04 (t, J = 2.6 Hz, 1H), 8.09 (t, J = 2.6 Hz, 1H), 8.2 (dd, J = 1.6, 7.8 Hz, 1H), 8.42 (t, J = 2.6 Hz, 1H), 8.47 (t, J = 2.6 Hz, 1H), 8.79 (s, 1H); ^{13}C (100 MHz, $CDCl_3$): δ 120.5 (d), 121.3 (s), 124.1 (d), 124.9 (d), 125.6 (d), 127.9 (d), 130.0 (d), 130.2 (d), 130.8 (d), 131.9 (s), 133.8 (d), 141.1 (s), 146.7 (s), 147.3 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.57; H, 2.90; Br, 22.89; N, 16.12.

*4-(2-Iodophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (***4N2I***):* mp: 148–149 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.22 (dt, J = 1.7, 7.7 Hz, 1H), 7.55 (dt, J = 1.1, 7.5 Hz, 1H), 7.67 (dd, J = 1.6, 7.7 Hz, 1H), 8.06 (dd, J = 0.9, 7.9 Hz, 1H), 8.29–8.33 (m, 2H), 8.47–8.51 (m, 2H), 9.36 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 98.0 (s), 120.9 (d, 2C), 122.4 (d), 125.8 (d, 2C), 128.7 (d), 130.8 (d), 131.0 (d), 134.8 (s), 140.1 (d), 140.9 (s), 147.0 (s), 149.13 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.96; H, 2.43; I, 32.48; N, 14.17.

*4-(3-Chlorophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (***4N3Cl***)*: mp: 222–223 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40 (dd, J = 0.9, 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.90 (t, J = 1.9 Hz, 1H), 8.15 (d, J = 9.0 Hz, 2H), 8.41 (d, J = 9.0 Hz, 2H), 9.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 120.7 (d, 2C), 120.9 (d), 124.1

(d), 125.3 (d), 125.9 (d, 2C), 128.5 (d), 131.3 (d), 132.0 (s), 134.1 (s), 140.9 (s), 146.7 (s), 147.0 (s) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.87; H, 3.03; Cl, 11.73; N, 18.61.

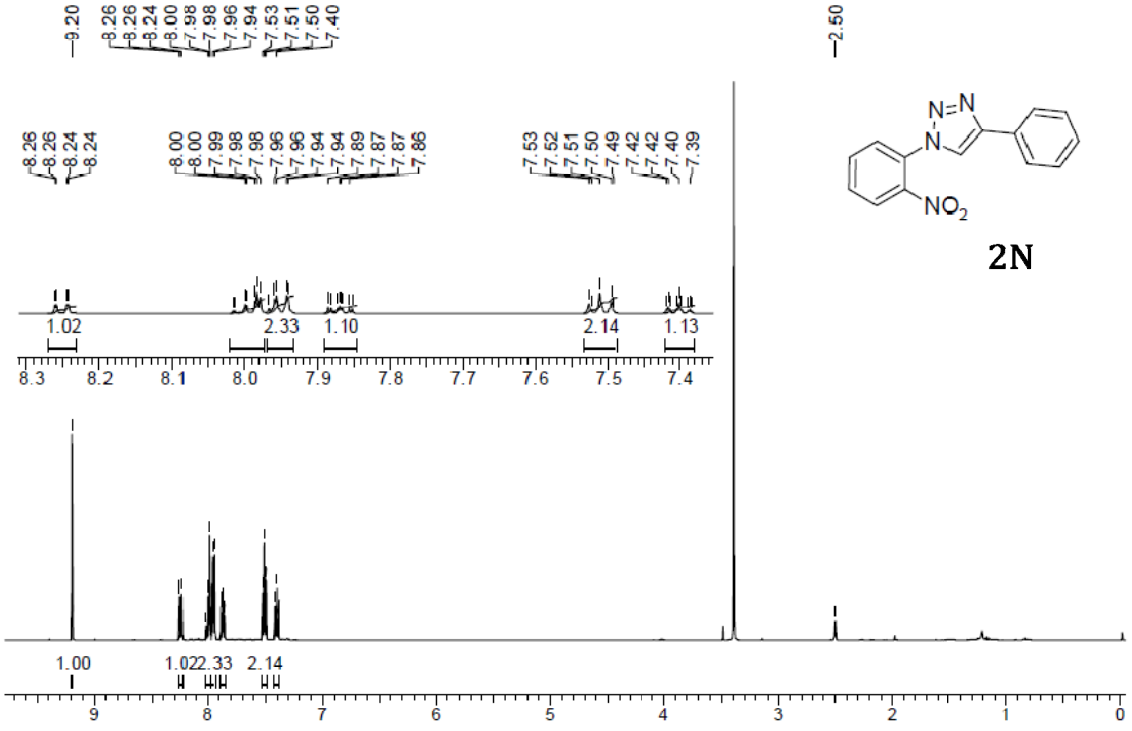
4-(3-Bromophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**4N3Br**): mp: 217–218 °C; ^{1}H (400 MHz, DMSO-d_6): δ 7.36–7.54 (m, 2H), 7.96 (dt, J = 1.8, 7.6 Hz, 1H), 8.14 (t, J = 1.6 Hz, 1+H), 8.26, 8.31, 8.45, 8.51 (4br. m, 4H), 9.47 (s, 1H); ^{13}C (100 MHz, DMSO-d_6): δ 118.6 (d, 2C), 120.8 (d), 122.6 (s), 123.8 (d), 124.1 (d), 126.5 (d), 127.4 (d), 129.1 (d), 129.4 (d), 130.5 (s), 139.3 (s), 145.0 (s), 145.1 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.63; H, 2.88; Br, 23.29; N, 16.48.

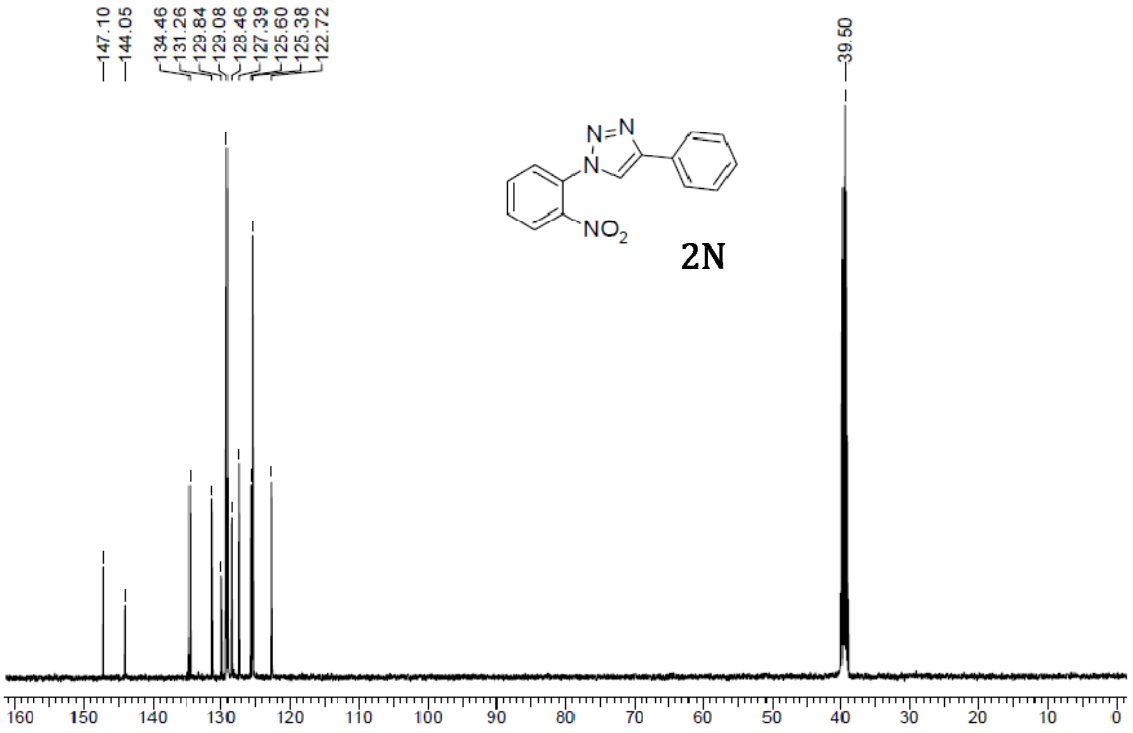
4-(3-Iodophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**4N3I**): mp: 188–189 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.18 (t, J = 7.9 Hz, 1H), 7.63 (dt, J = 1.2, 8.0 Hz, 1H), 7.90–7.92 (m, 1H), 8.17–8.21 (m, 2H), 8.26 (t, J = 1.5 Hz, 1H), 8.36–8.39 (m, 2H), 9.29 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 94.6 (s), 119.6 (d), 120.1 (d, 2C), 124.6 (d), 125.2 (d, 2C), 130.6 +(d), 131.9 (s), 134.0 (d), 136.9 (d), 140.9 (s), 146.5 (s), 146.6 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.74; H, 2.16; I, 32.51; N, 14.46.

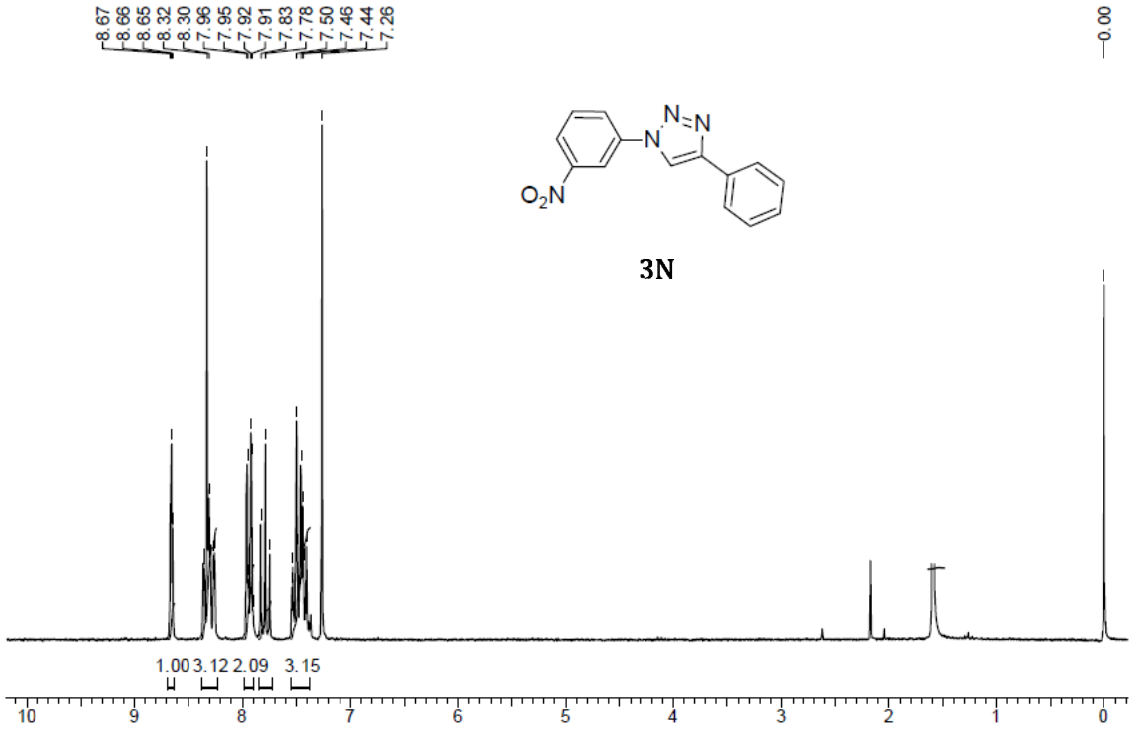
4-(4-Chlorophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**4N4Cl**): mp: 246–248 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.58 (d, J = 5.6 Hz, 2H), 7.95 (d, J = 5.6 Hz, 2H), 8.23 (d, J = 7.0 Hz, 2H), 8.48 (d, J = 7.0 Hz, 2H), 9.53 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 120.5 (d), 120.6 (d, 2C), 125.8 (d, 2C), 127.2 (d, 2C), 128.8 (s), 129.3 (d, 2C), 133.2 (s), 140.9 (s), 146.9 (s, 2C) ppm; Anal. Calcd for $C_{14}H_9ClN_4O_2$: C, 55.92; H, 3.02; Cl, 11.79; N, 18.63; Found: C, 55.87; H, 2.95; Cl, 11.72; N, 18.58.

4-(4-Bromophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**4N4Br**): mp: 149–150 °C; ^{1}H (400 MHz, DMSO-d_6): δ 7.64 (t, J = 2.1 Hz, 1H), 7.77 (t, J = 1.7 Hz, 1H), 7.82 (t, J = 2.3 Hz, 1H), 8.01 (t, J = 2.1 Hz, 1H), 8.06 (t, J = 2.0 Hz, 1H), 8.28 (t, J = 1.8 Hz, 1H), 8.44 (t, J = 1.9 Hz, 1H), 8.48 (t, J = 2.1 Hz, 1H), 9.49 (s, 1H); ^{13}C (100 MHz, DMSO-d_6): δ 118.2 (d), 118.5 (d, 2C), 119.9 (s), 123.7 (d, 2C), 125.5 (d, 2C), 127.3 (s), 130.1 (d, 2C), 139.1 (s), 144.9 (s), 145.2 (s) ppm; Anal. Calcd for $C_{14}H_9BrN_4O_2$: C, 48.72; H, 2.63; Br, 23.15; N, 16.23; O, 9.27; Found: C, 48.70; H, 2.40; Br, 23.43; N, 16.01.

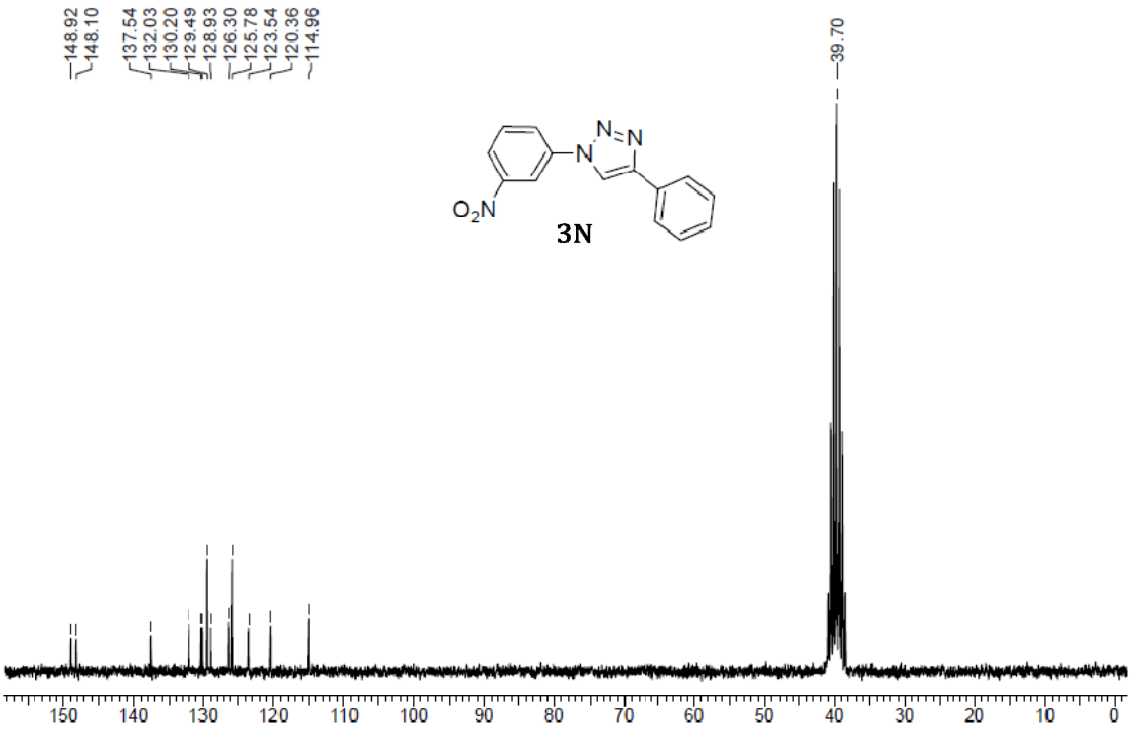
*4-(4-Iodophenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (***4N4I***)*: mp: 248–249 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.76 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H), 8.25 (d, J = 9.1 Hz, 2H), 8.51 (d, J = 9.0 Hz, 2H), 9.59 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 98.0 (s), 120.6 (d), 120.7 (d, 2C), 126.0 (d, 2C), 127.6 (d, 2C), 129.5 (s), 138.1 (d, 2C), 141.0 (s), 146.0 (s), 147.2 (s) ppm; Anal. Calcd for $C_{14}H_9IN_4O_2$: C, 42.88; H, 2.31; I, 32.36; N, 14.29; O, 8.16; Found: C, 42.77; H, 2.17; I, 32.49; N, 14.46.



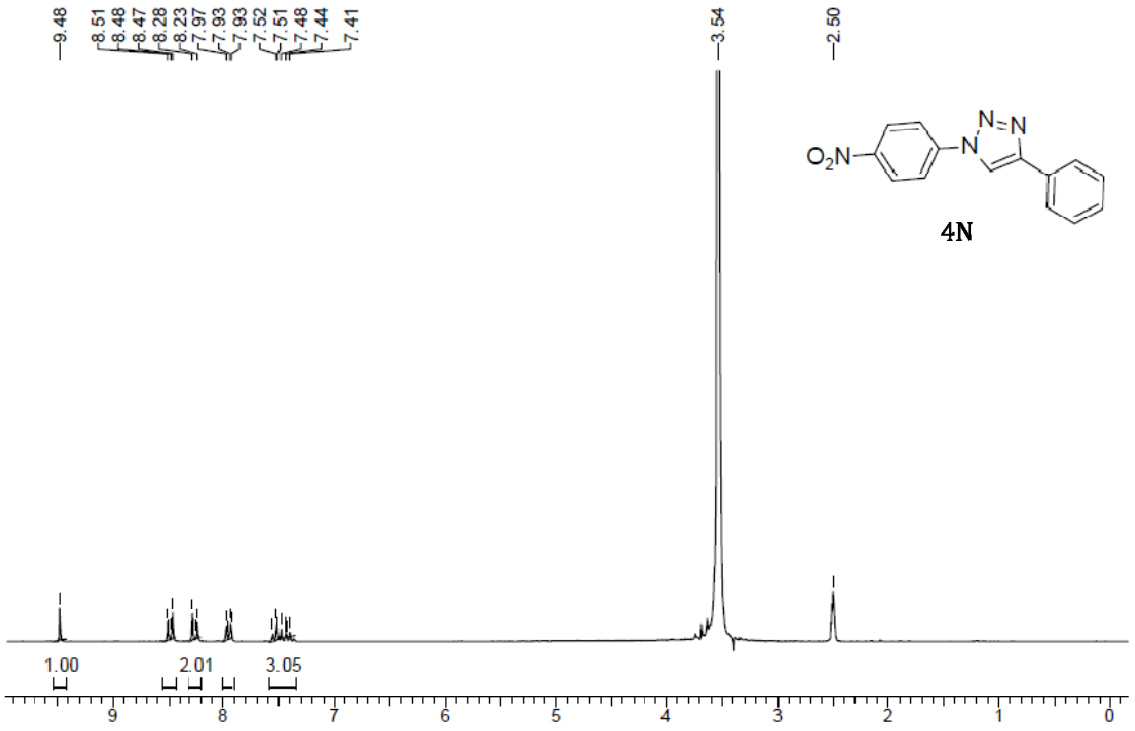


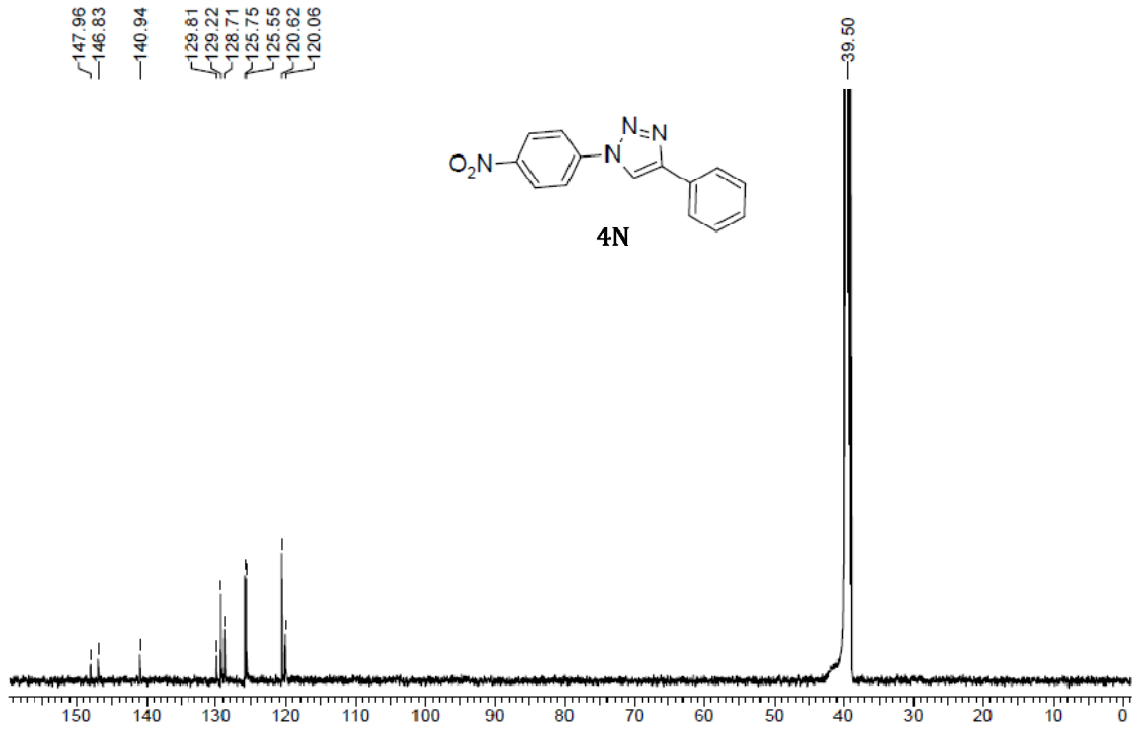


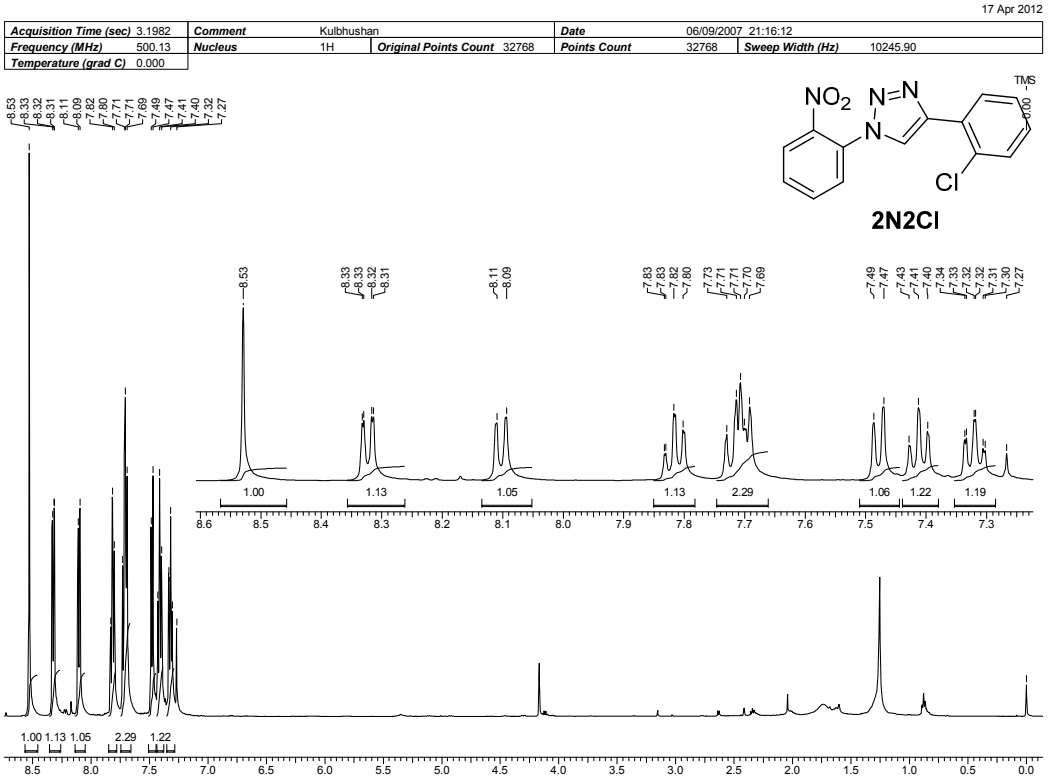
3N

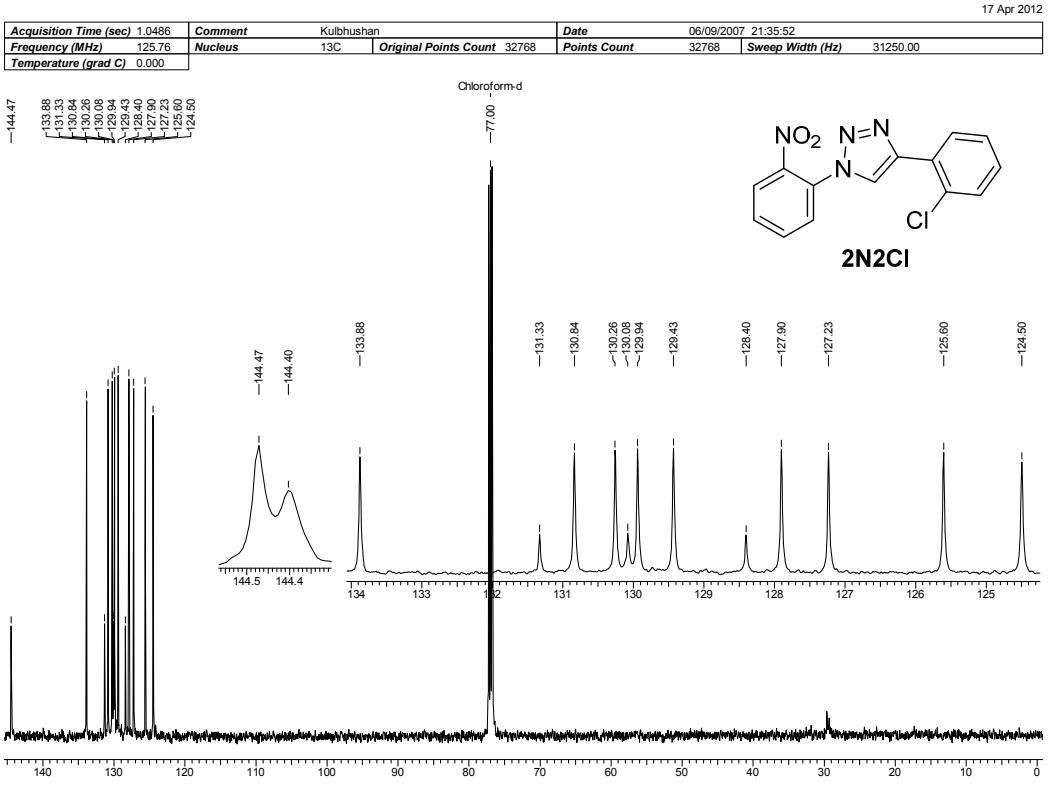


3N

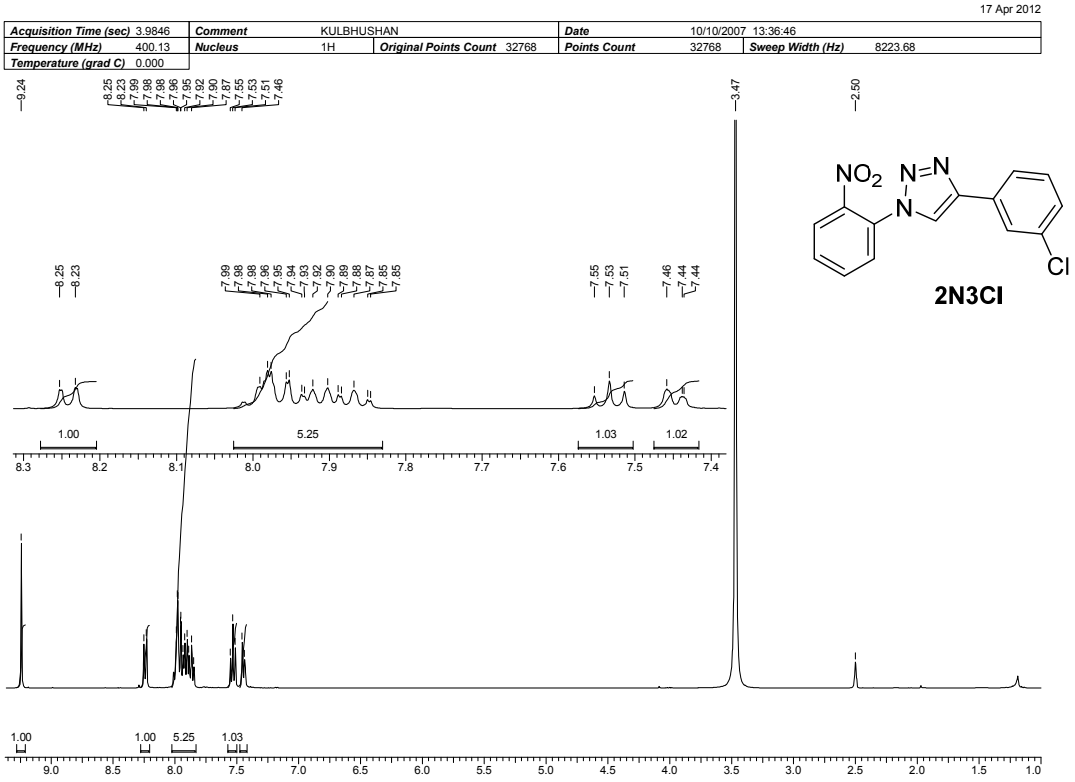

9.48
8.51
8.48
8.47
8.28
8.23
7.97
7.93
7.93
7.52
7.51
7.48
7.44
7.41
3.54
2.50
1.00
2.01
3.05
4N

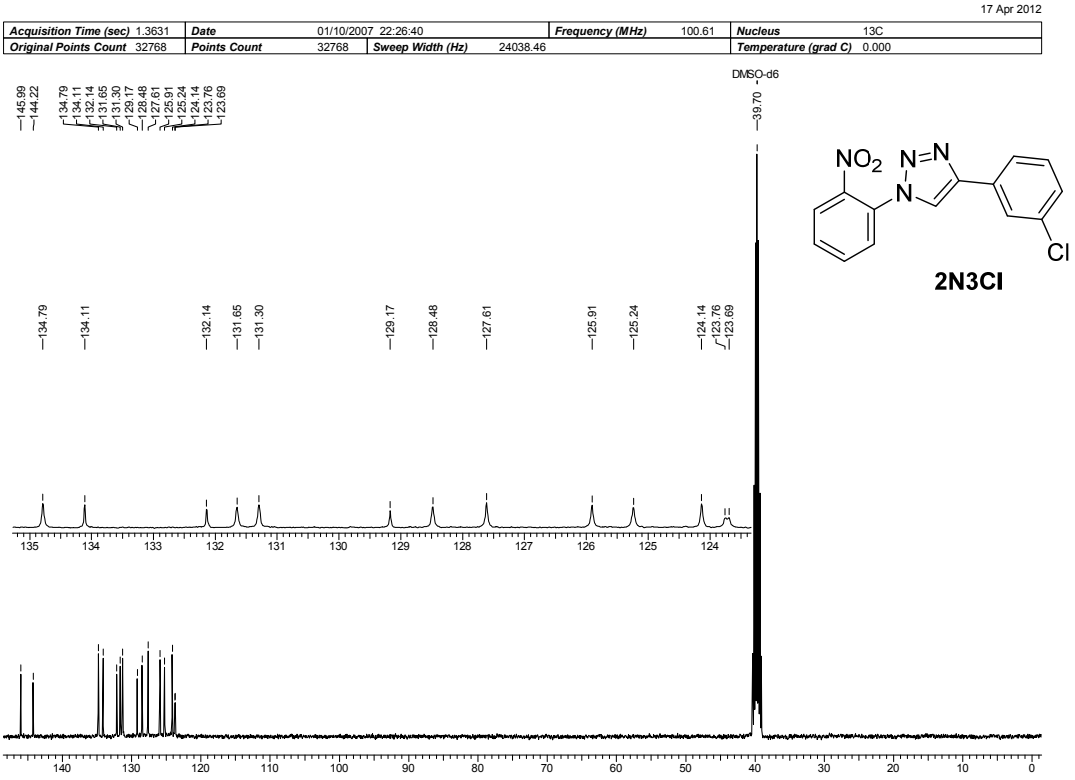

147.96
146.83
140.94
129.81
129.22
128.71
125.75
125.55
120.62
120.06
39.50
4N

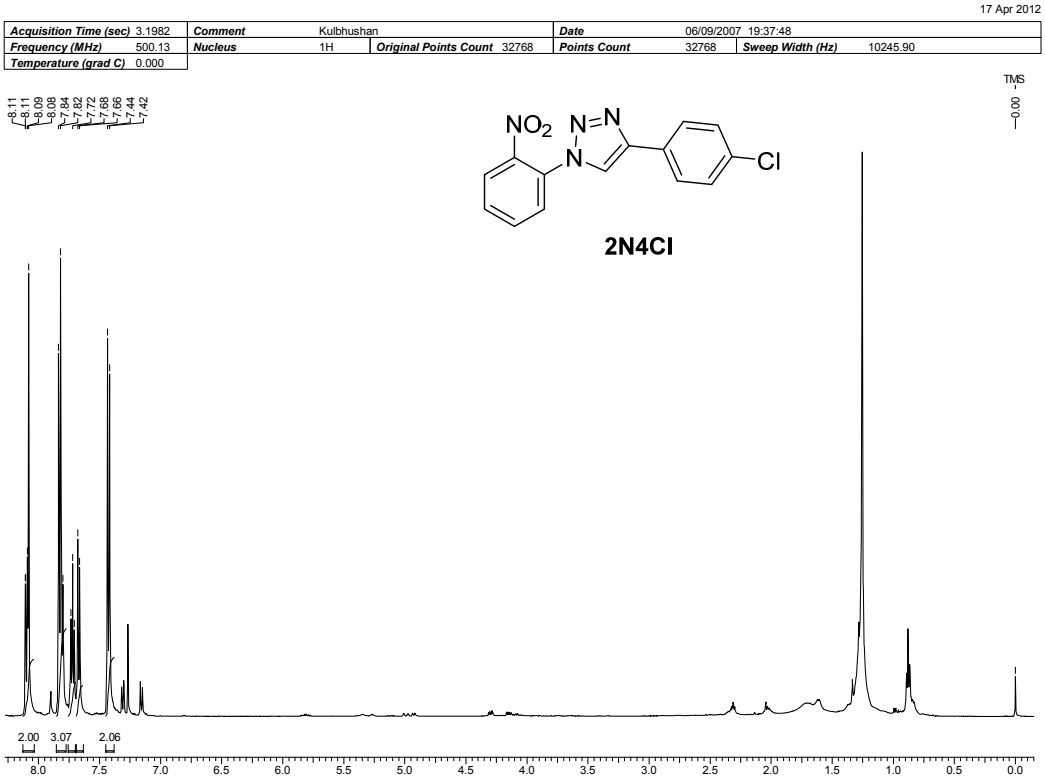

17 Apr 2012
Acquisition Time (sec) 3.1982
Comment Kulbhushan
Date 06/09/2007 21:16:12
Frequency (MHz) 500.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 10245.90
Temperature (grad C) 0.000
TMS
NO2
N=N
N
Cl
2N2Cl
8.53
8.33
8.32
8.31
8.11
8.09
7.83
7.82
7.80
7.73
7.71
7.70
7.69
7.49
7.47
7.43
7.41
7.40
7.34
7.33
7.32
7.31
7.30
7.27
1.00 1.13 1.05 2.29 1.22
1.00 1.13 1.05 1.13 2.29 1.06 1.22 1.19

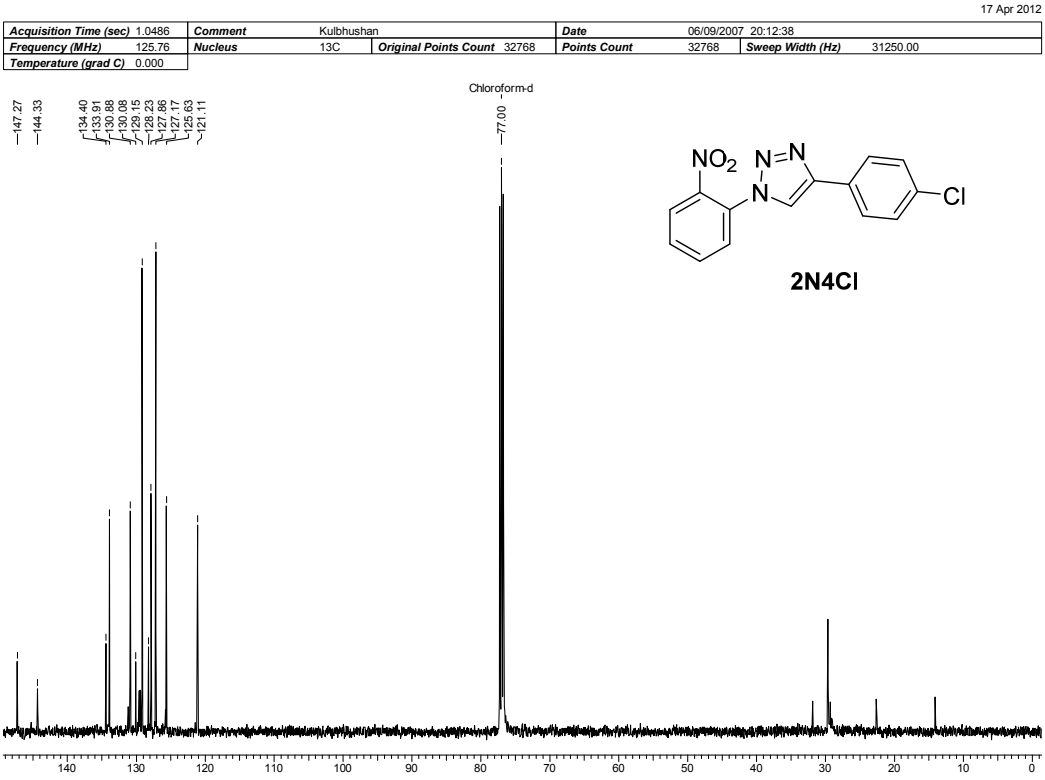

17 Apr 2012
Acquisition Time (sec) 1.0486
Comment Kulbhushan
Date 06/09/2007 21:35:52
Frequency (MHz) 125.76
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 31250.00
Temperature (grad C) 0.000
Chloroform-d
77.00
NO2
N=N
N
Cl
2N2Cl
144.47
144.40
133.88
131.33
130.84
130.26
130.08
129.94
129.43
128.40
127.90
127.23
125.60
124.50

Supporting Information

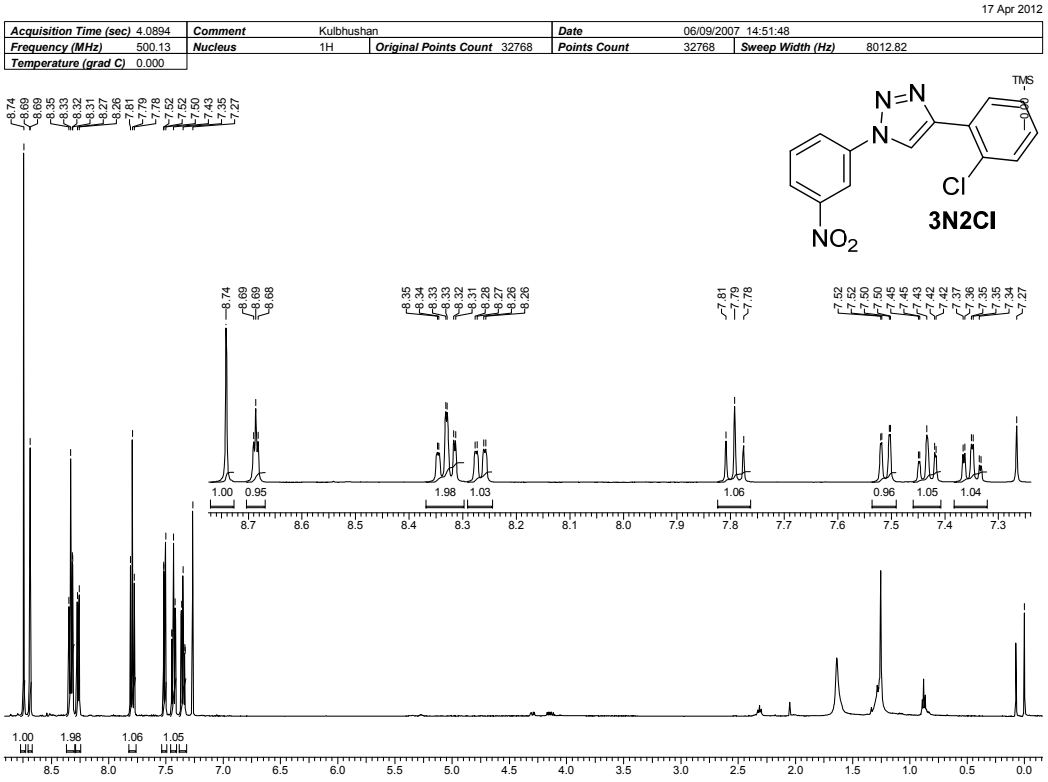


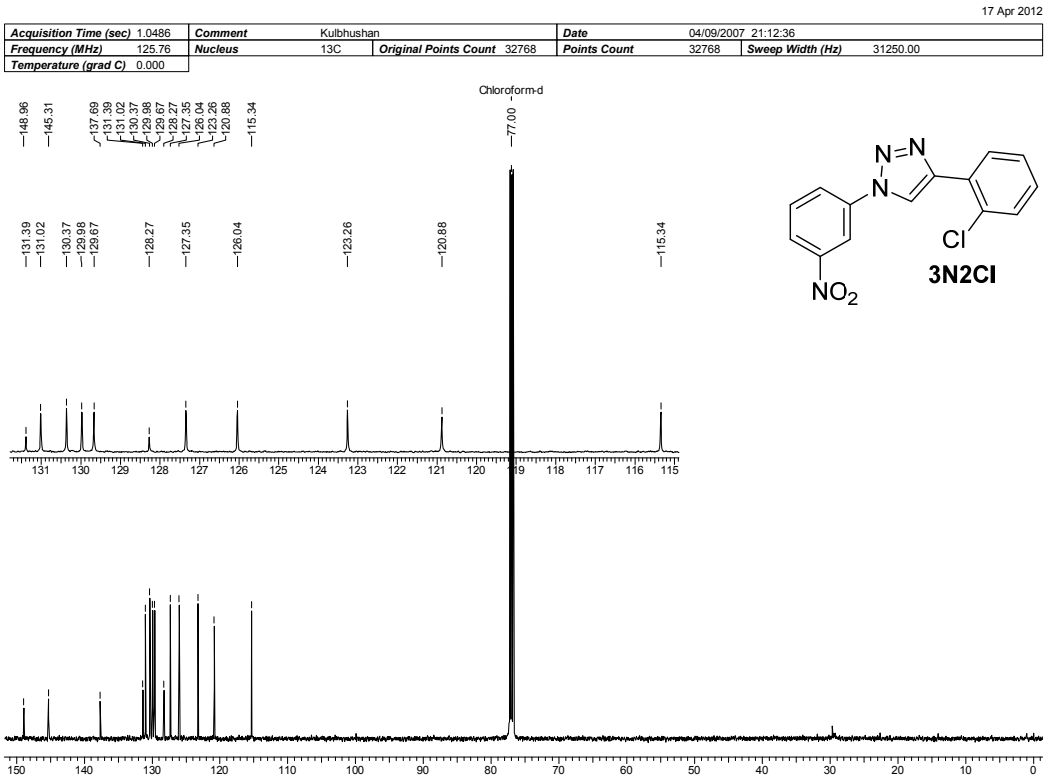


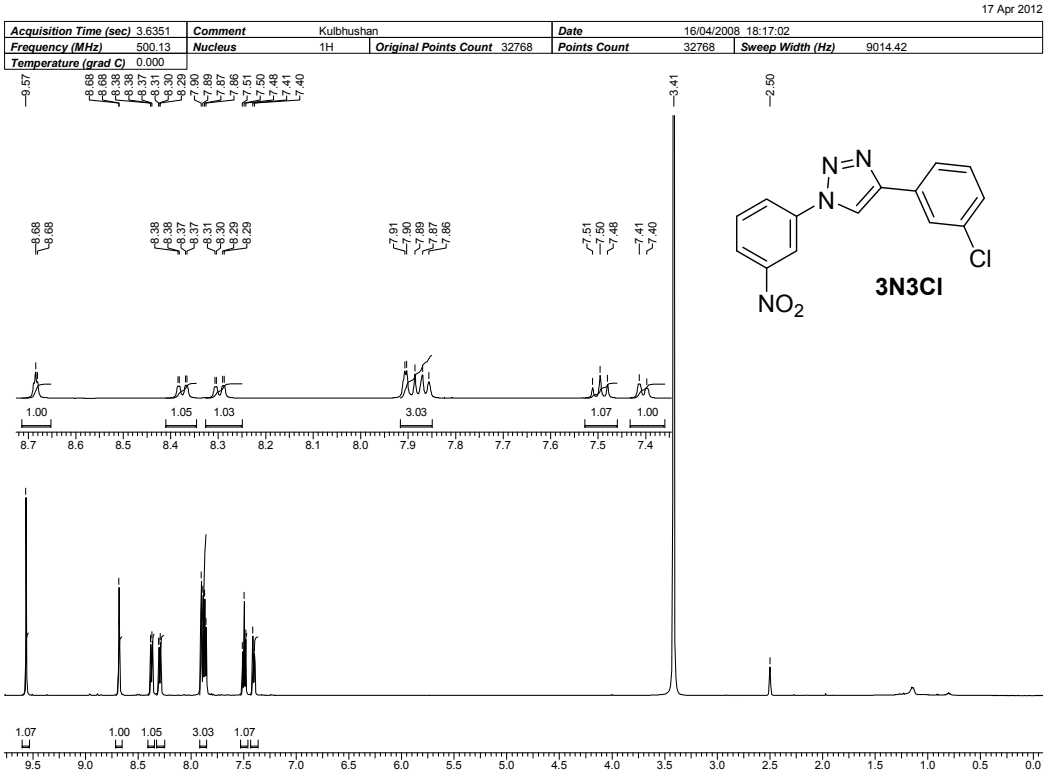

17 Apr 2012
Acquisition Time (sec) 3.1982
Comment Kulbhushan
Date 06/09/2007 19:37:48
Frequency (MHz) 500.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 10245.90
Temperature (grad C) 0.000
8.11
8.11
8.09
8.08
7.84
7.82
7.72
7.68
7.66
7.44
7.42
TMS
0.00
NO2
N=N
N
Cl
2N4Cl
2.00
3.07
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

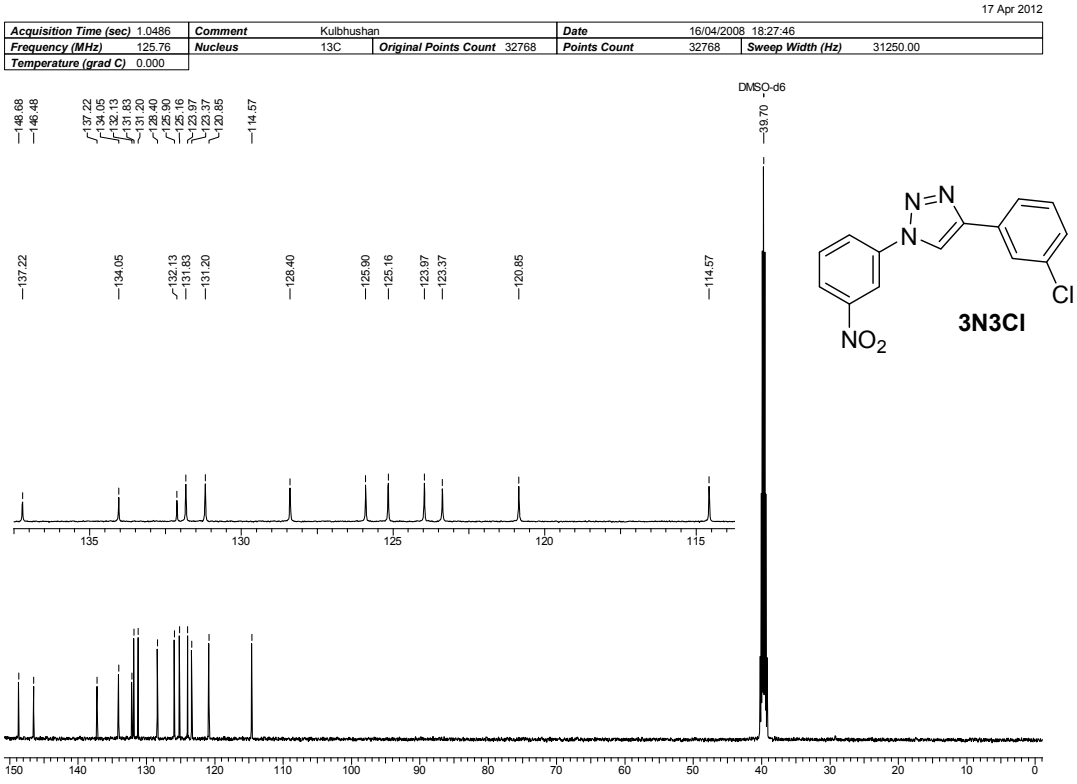

17 Apr 2012
Acquisition Time (sec) 1.0486
Comment Kulbhushan
Date 06/09/2007 20:12:38
Frequency (MHz) 125.76
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 31250.00
Temperature (grad C) 0.000
Chloroform-d
147.27
144.33
134.40
133.91
130.88
130.06
129.15
128.23
127.86
127.17
125.63
121.11
77.00
NO2
N=N
N
Cl
2N4Cl
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Supporting Information

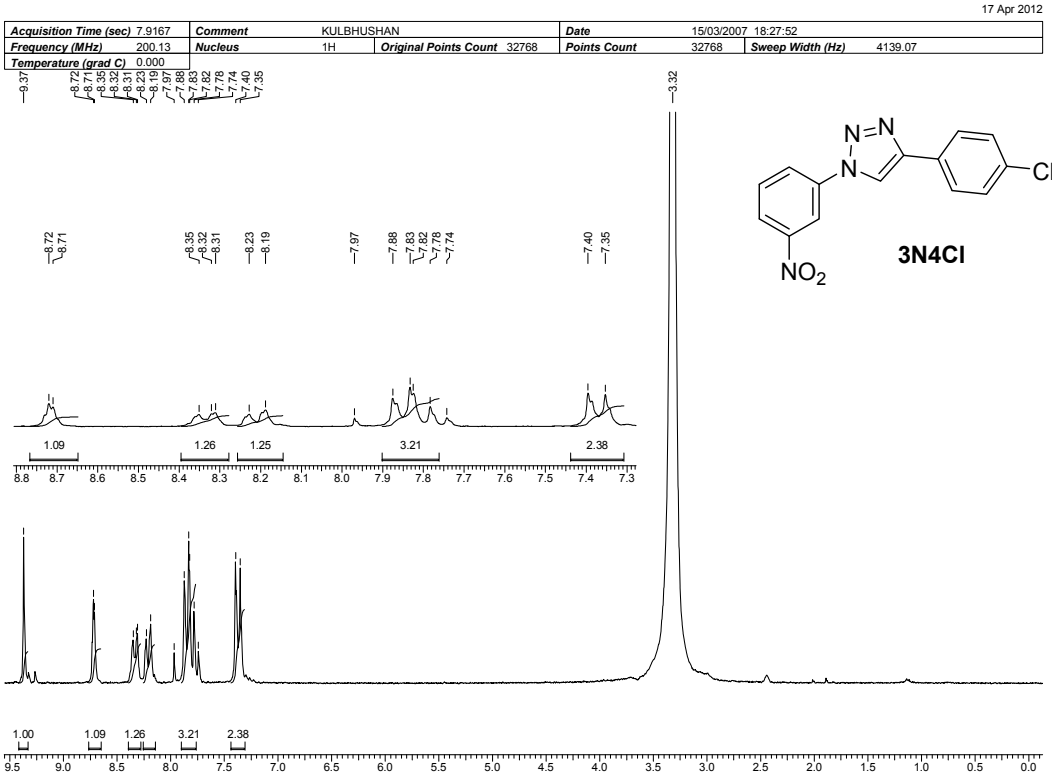


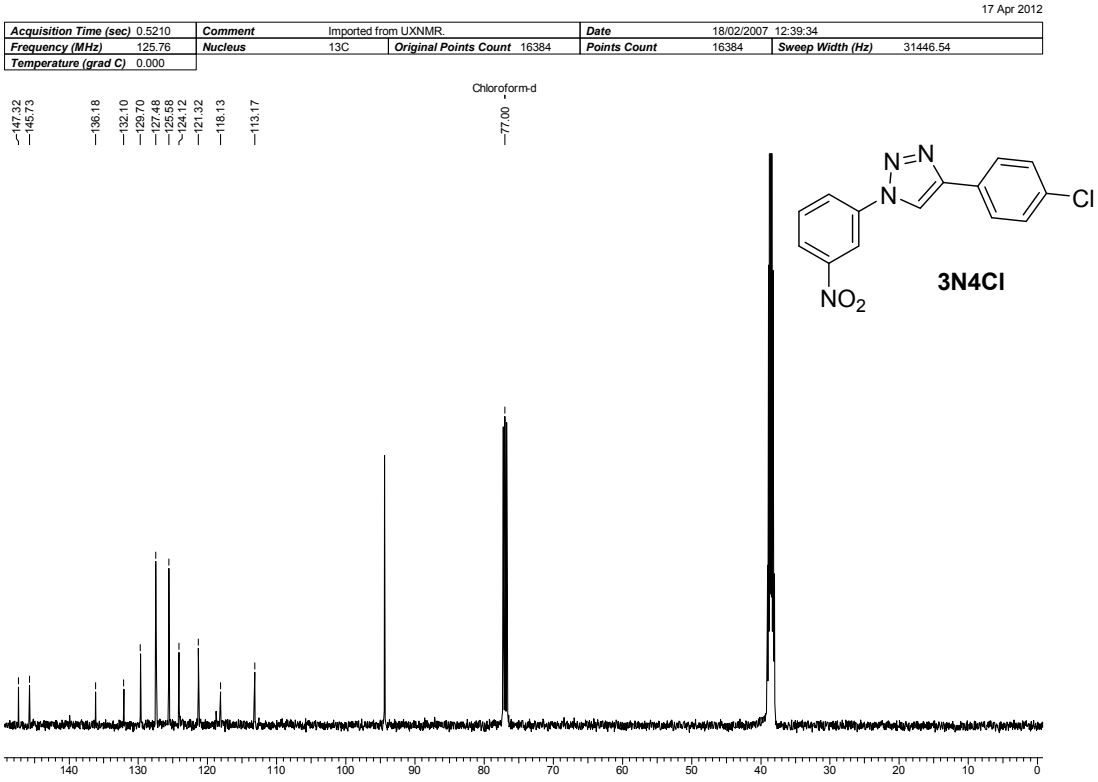


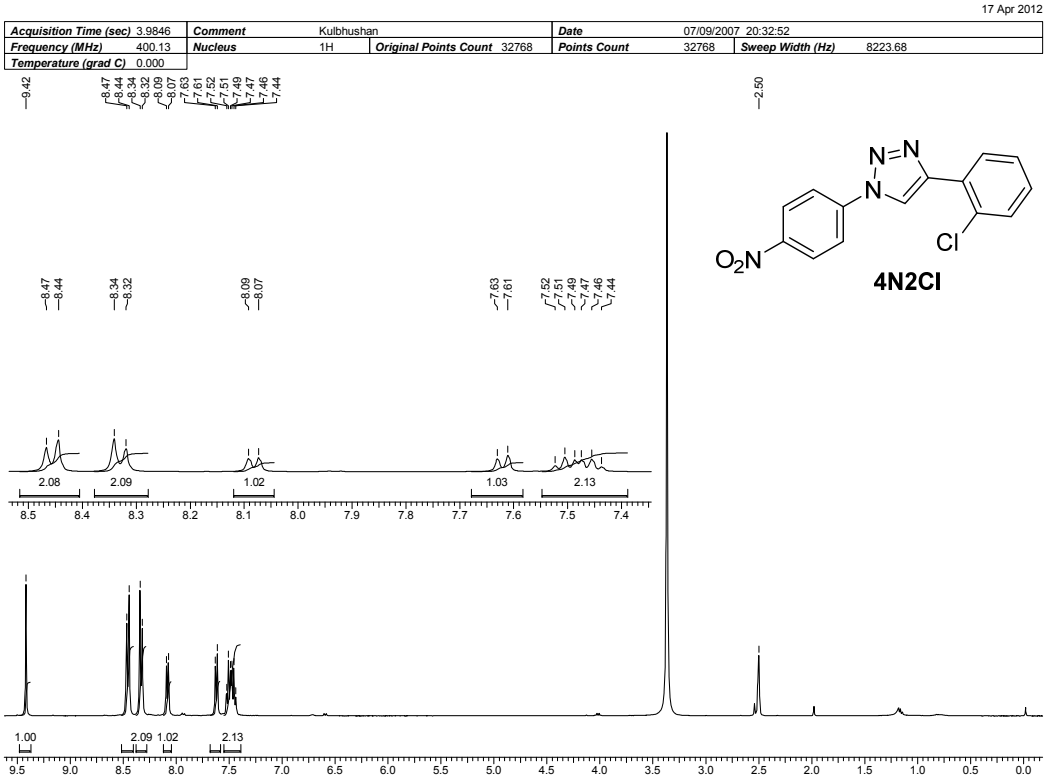

17 Apr 2012
Acquisition Time (sec) 3.6351
Comment Kulbhushan
Date 16/04/2008 18:17:02
Frequency (MHz) 500.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 9014.42
Temperature (grad C) 0.000
9.57
8.68
8.38
8.37
8.31
8.30
8.29
7.90
7.89
7.87
7.86
7.51
7.50
7.48
7.41
7.40
3.41
2.50
1.00
1.05
1.03
3.03
1.07
1.00
N
N
Cl
NO2
3N3Cl

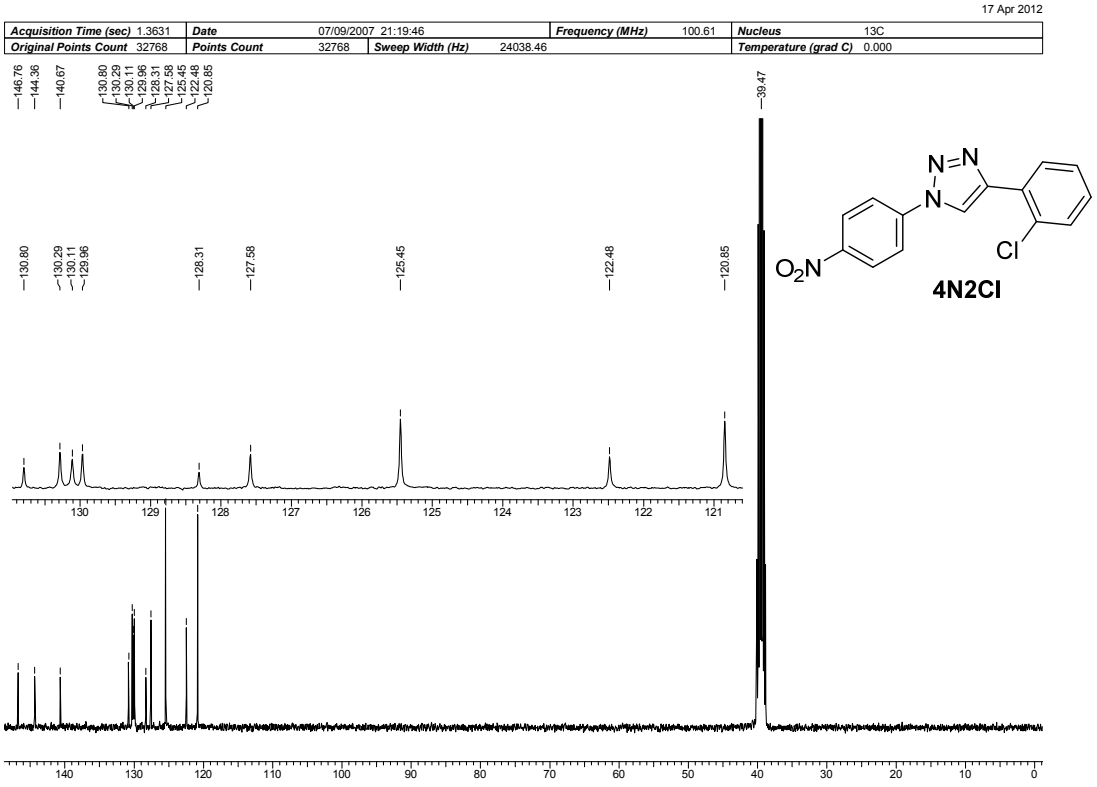

17 Apr 2012
Acquisition Time (sec) 1.0486
Comment Kulbhushan
Date 16/04/2008 18:27:46
Frequency (MHz) 125.76
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 31250.00
Temperature (grad C) 0.000
DMSO-d6
148.68
146.48
137.22
134.05
132.13
131.83
131.20
128.40
125.90
125.16
123.97
123.37
120.85
114.57
39.70
N
N
Cl
NO2
3N3Cl

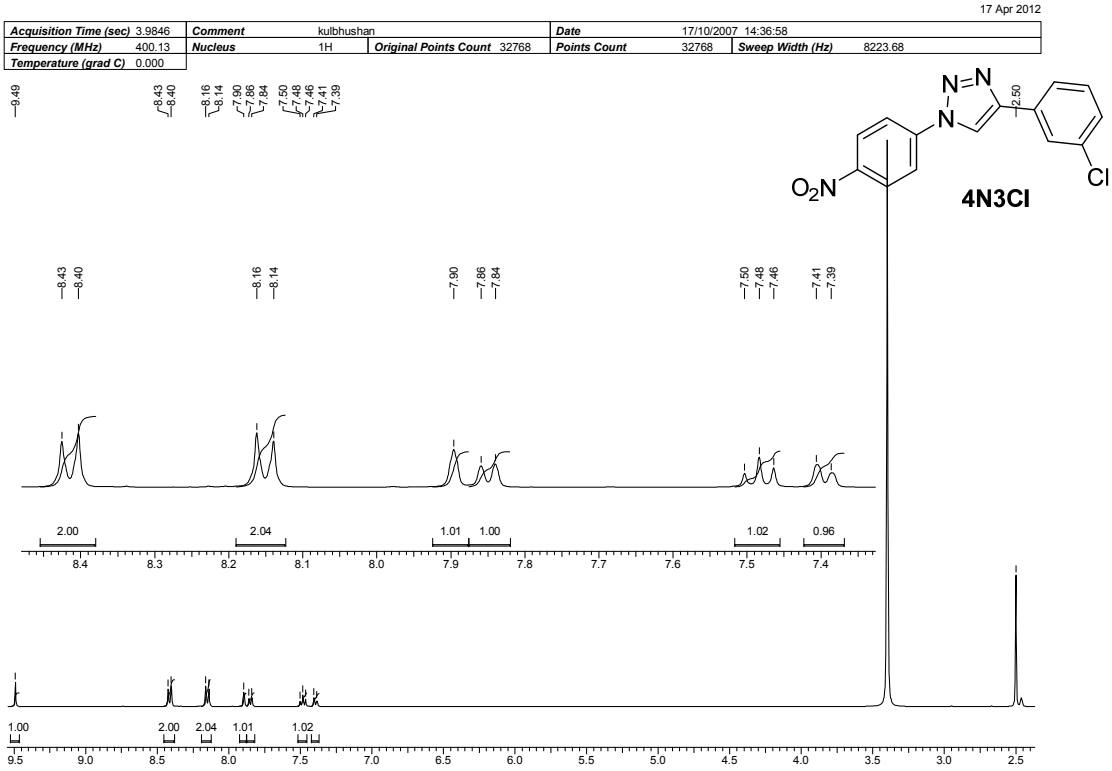
Supporting Information

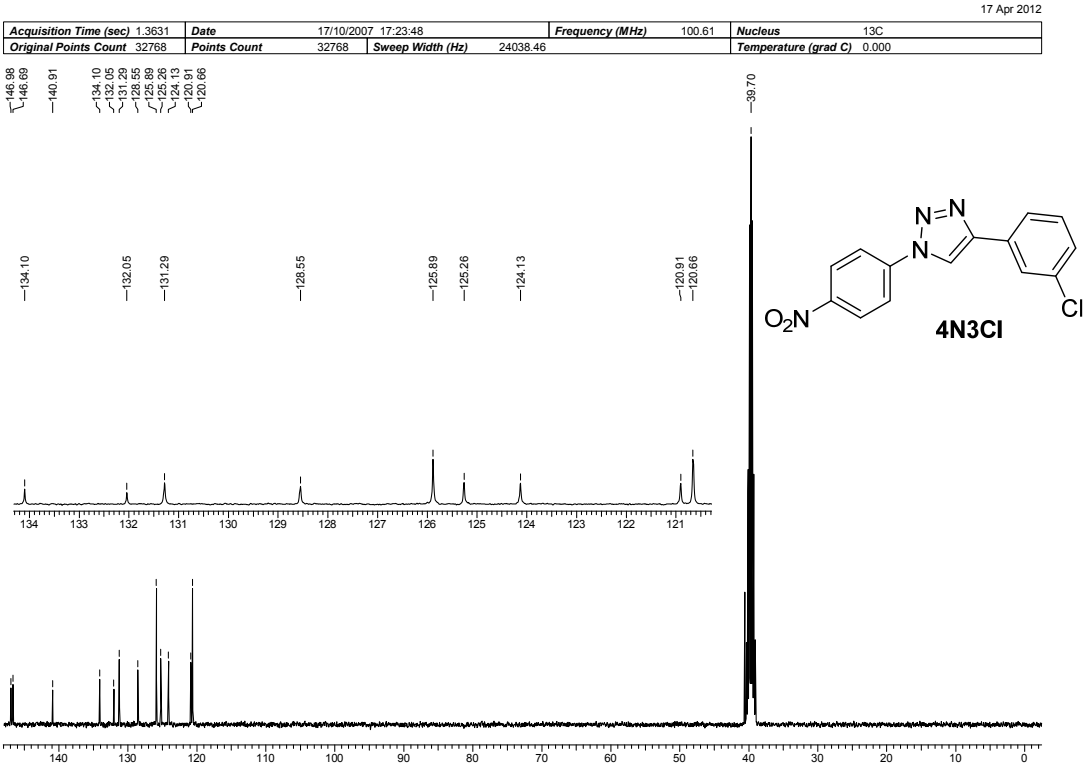


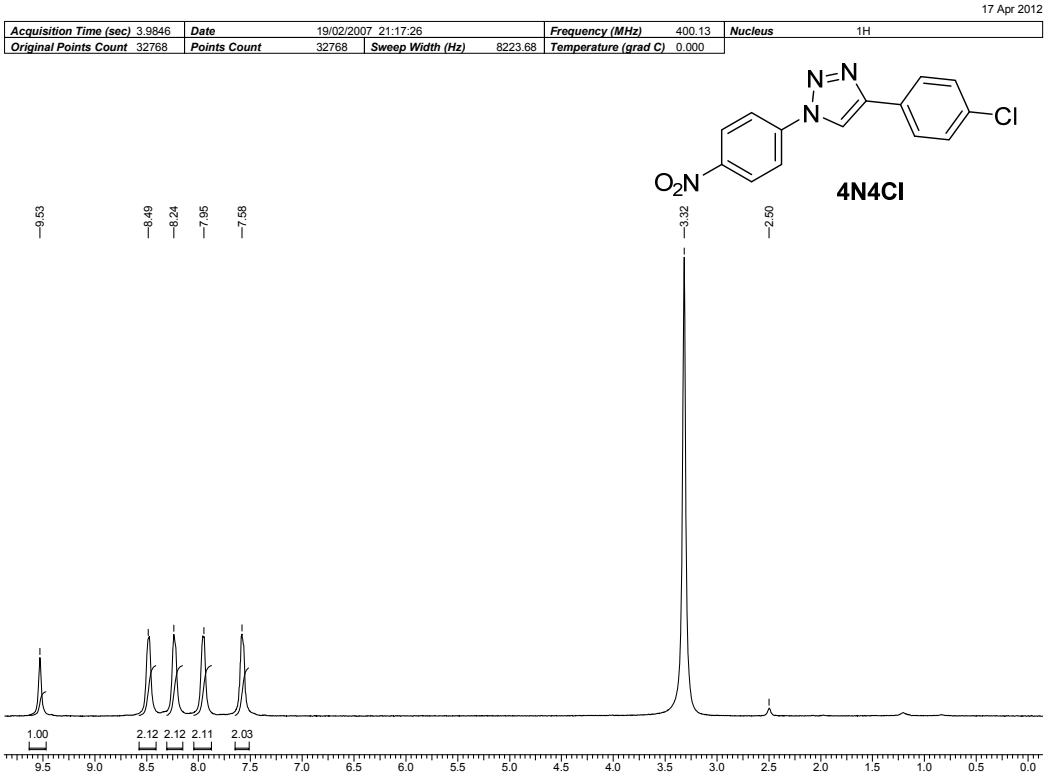


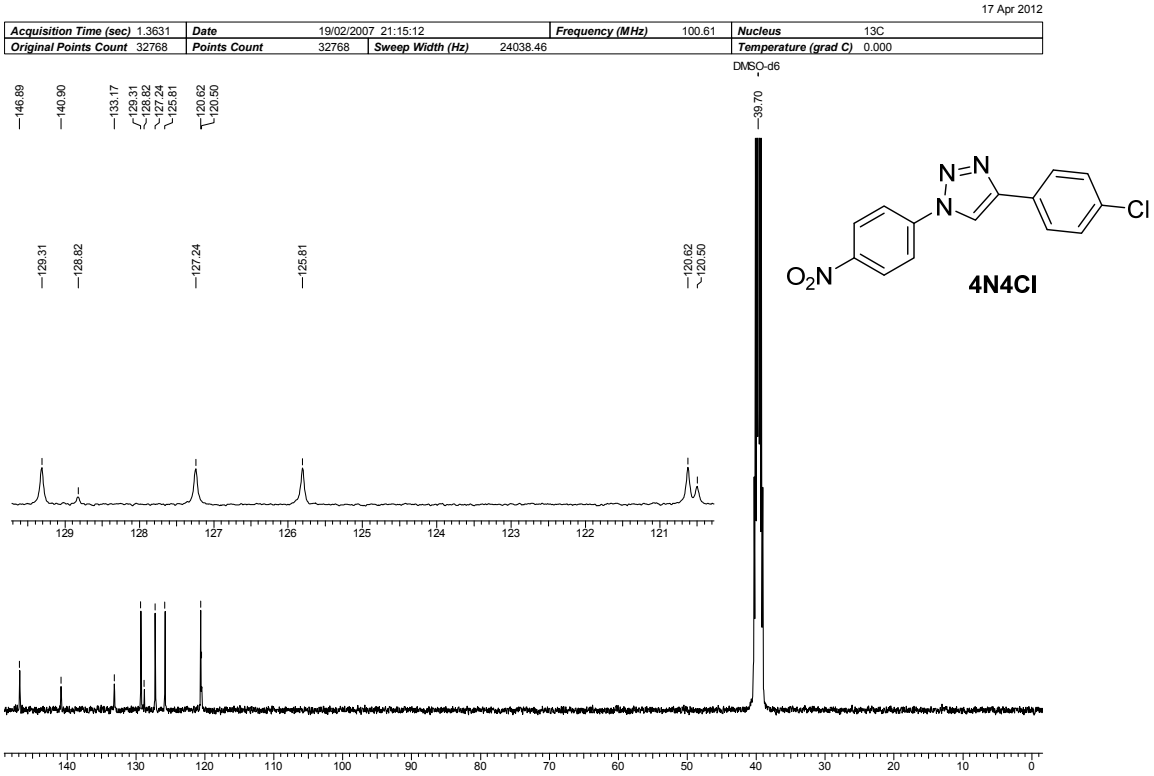

17 Apr 2012
Acquisition Time (sec) 3.9846
Comment Kulbhushan
Date 07/09/2007 20:32:52
Frequency (MHz) 400.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 8223.68
Temperature (grad C) 0.000
9.42
8.47
8.44
8.34
8.32
8.09
8.07
7.63
7.61
7.52
7.51
7.49
7.47
7.46
7.44
2.50
4N2Cl
2.08
2.09
1.02
1.03
2.13
1.00
2.09
1.02
2.13

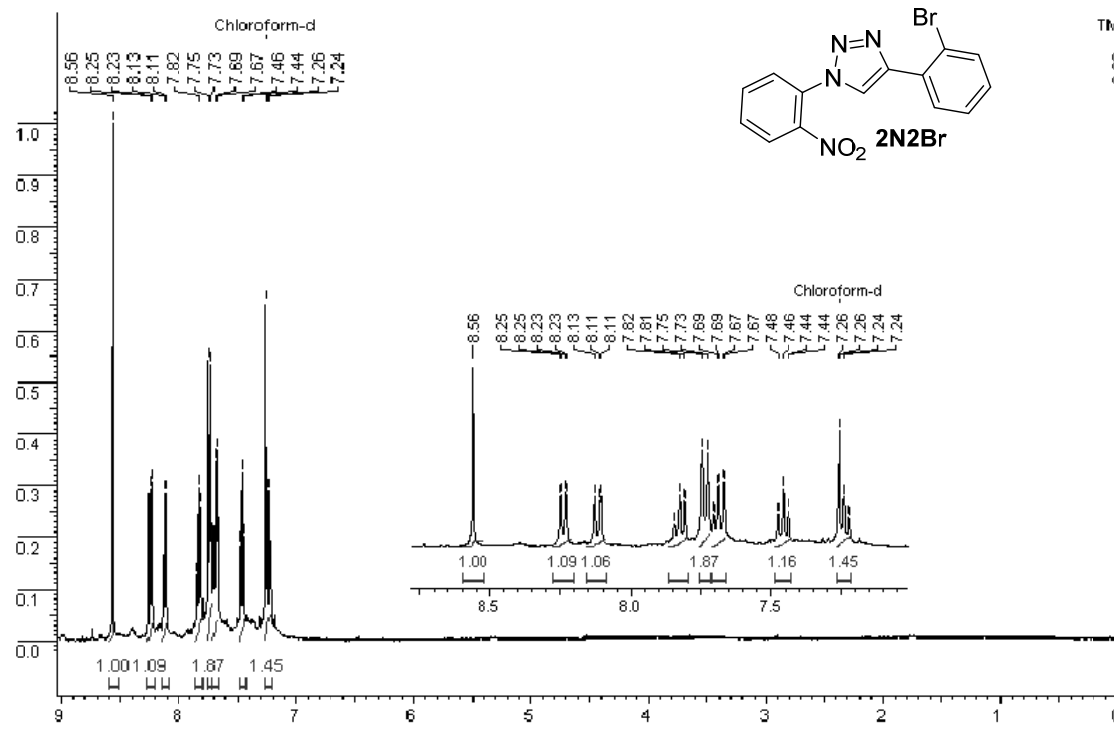

17 Apr 2012
Acquisition Time (sec) 1.3631
Date 07/09/2007 21:19:46
Frequency (MHz) 100.61
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 24038.46
Temperature (grad C) 0.000
146.76
144.36
140.67
130.80
130.29
130.11
129.96
128.31
127.58
125.45
122.48
120.85
39.47
4N2Cl

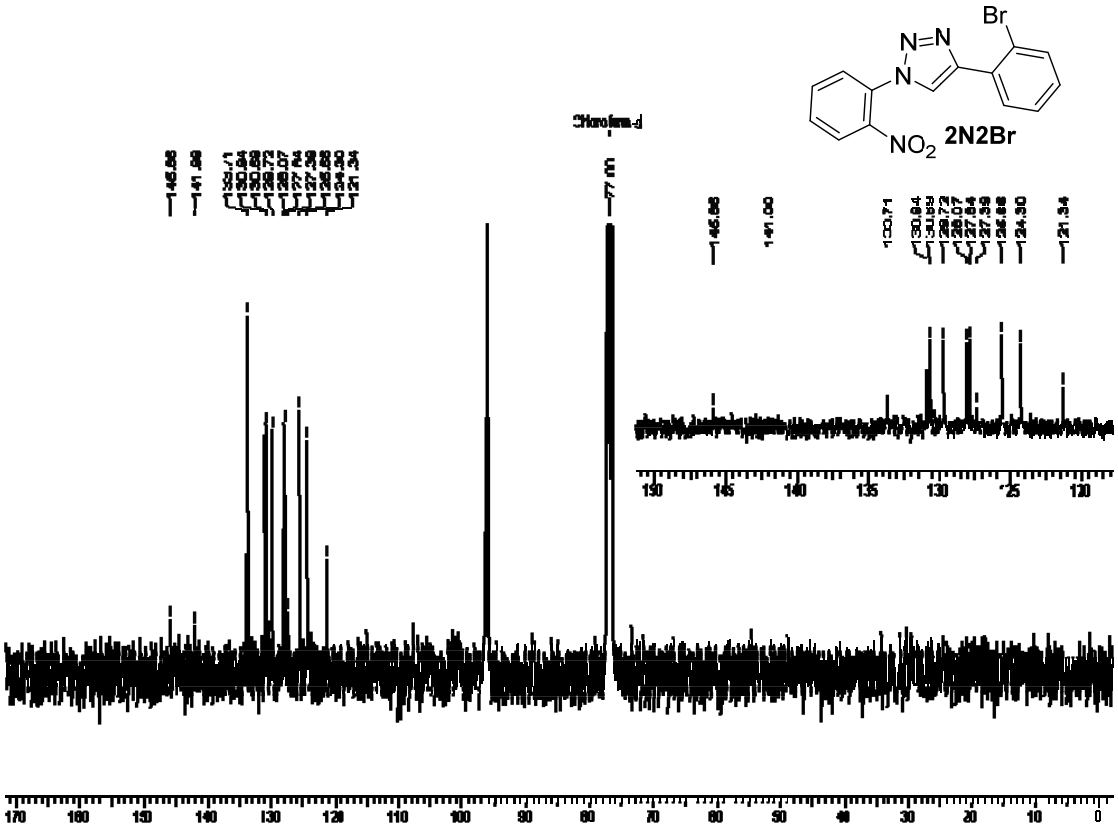

17 Apr 2012
Acquisition Time (sec) 3.9846
Comment kulbhushan
Date 17/10/2007 14:36:58
Frequency (MHz) 400.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 8223.68
Temperature (grad C) 0.000
9.49
8.43
8.40
8.16
8.14
7.90
7.86
7.84
7.50
7.48
7.46
7.41
7.39
2.50
4N3Cl

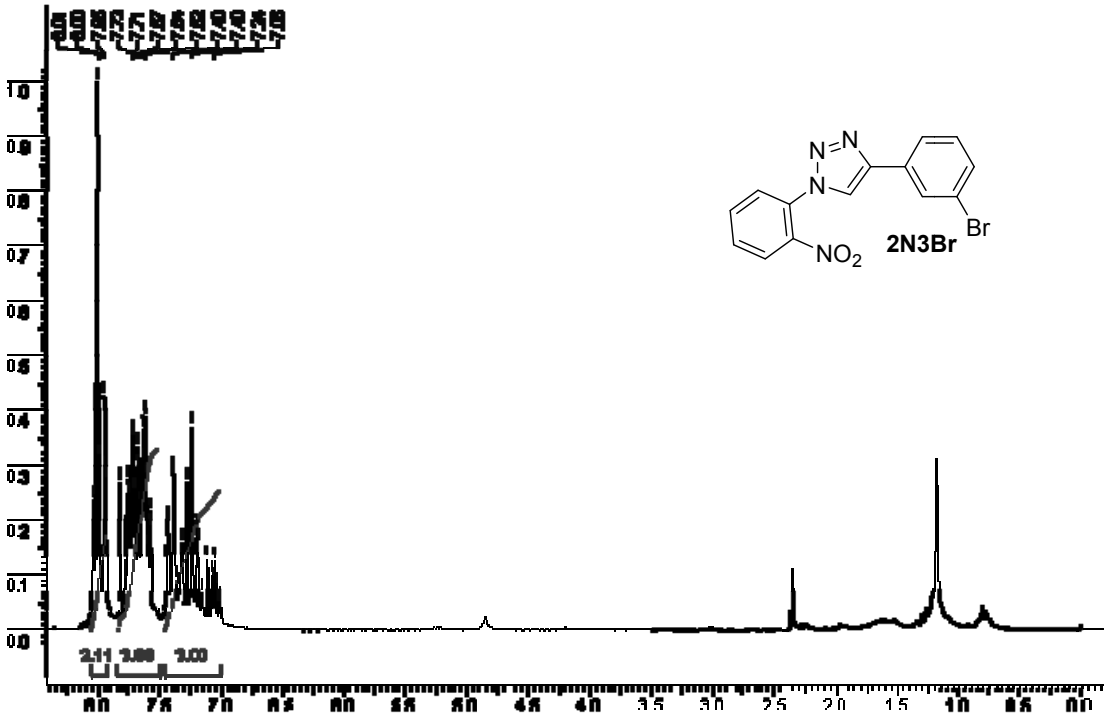

17 Apr 2012
Acquisition Time (sec) 1.3631
Date 17/10/2007 17:23:48
Frequency (MHz) 100.61
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 24038.46
Temperature (grad C) 0.000
146.98
146.69
140.91
134.10
132.05
131.29
128.55
125.89
125.26
124.13
120.91
120.66
39.70
4N3Cl

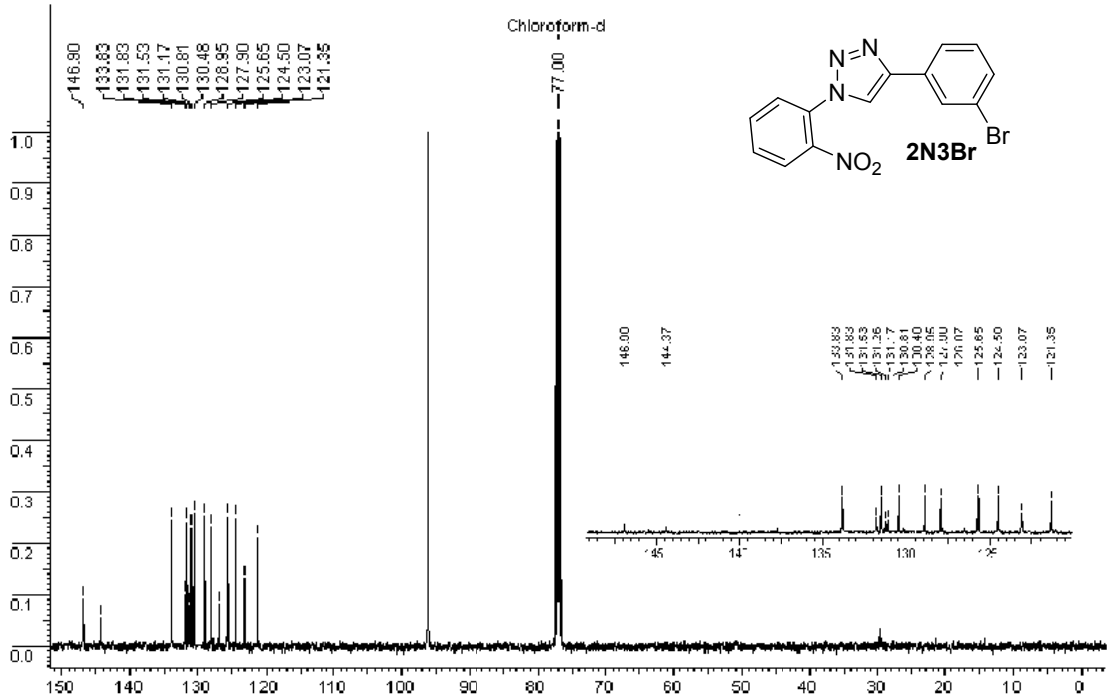

17 Apr 2012
Acquisition Time (sec) 3.9846
Date 19/02/2007 21:17:26
Frequency (MHz) 400.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 8223.68
Temperature (grad C) 0.000
4N4Cl
9.53
8.49
8.24
7.95
7.58
3.32
2.50
1.00
2.12
2.12
2.11
2.03

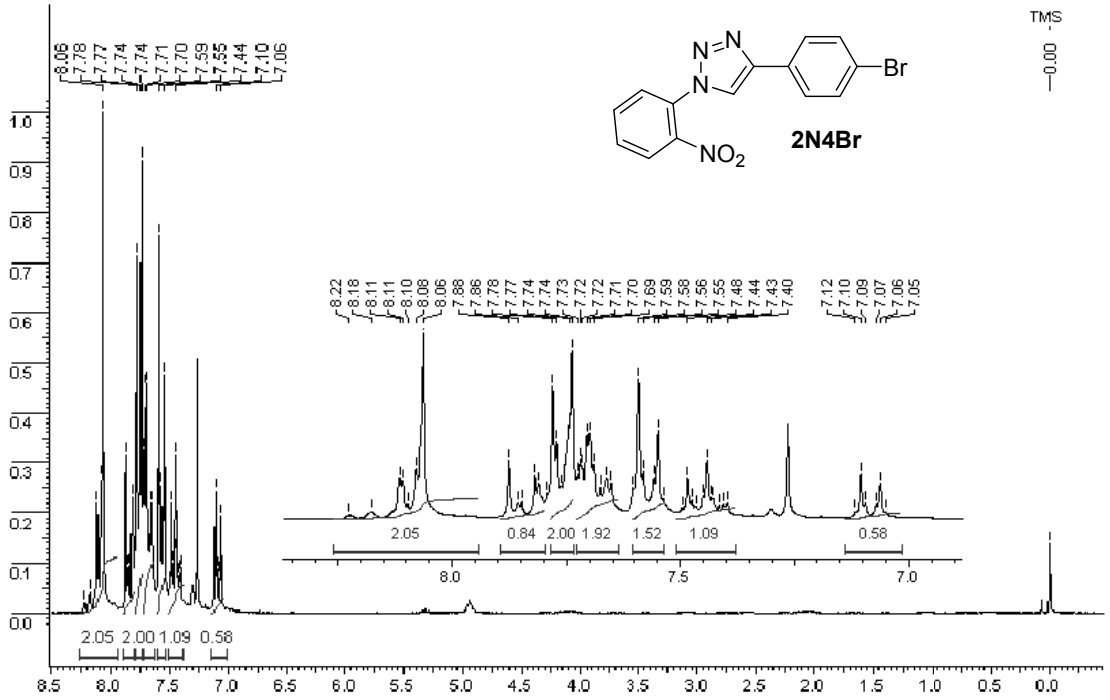

17 Apr 2012
Acquisition Time (sec) 1.3631
Date 19/02/2007 21:15:12
Frequency (MHz) 100.61
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 24038.46
Temperature (grad C) 0.000
DMSO-d6
4N4Cl
146.89
140.90
133.17
129.31
128.82
127.24
125.81
120.62
120.50
39.70

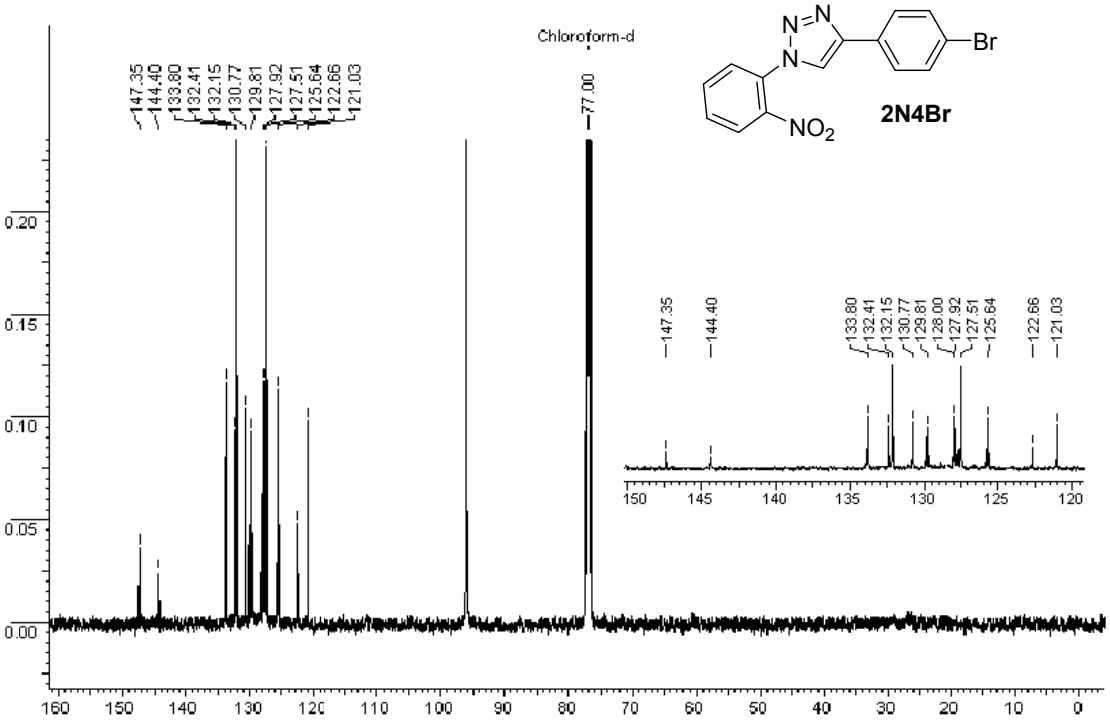


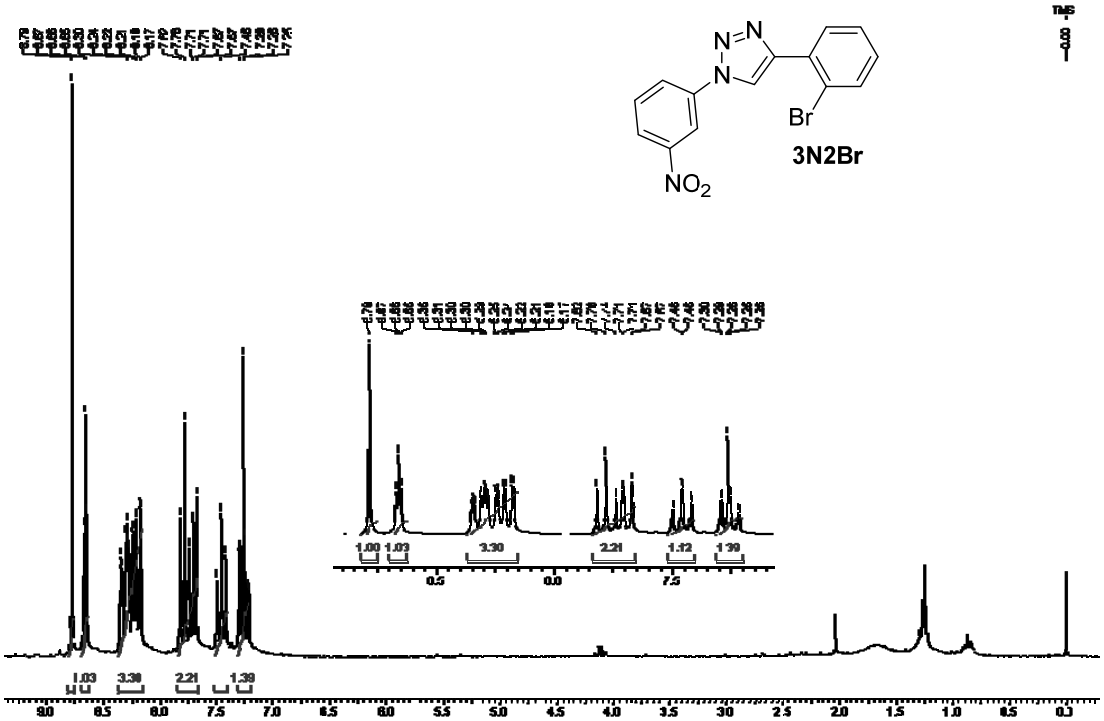


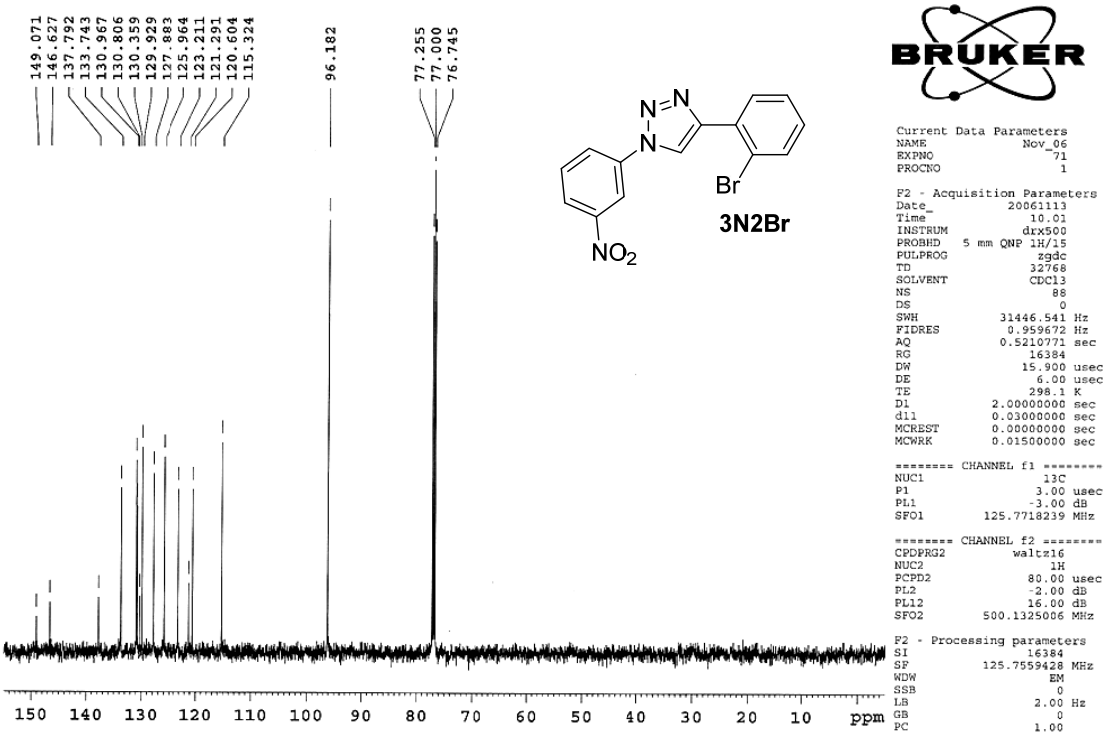


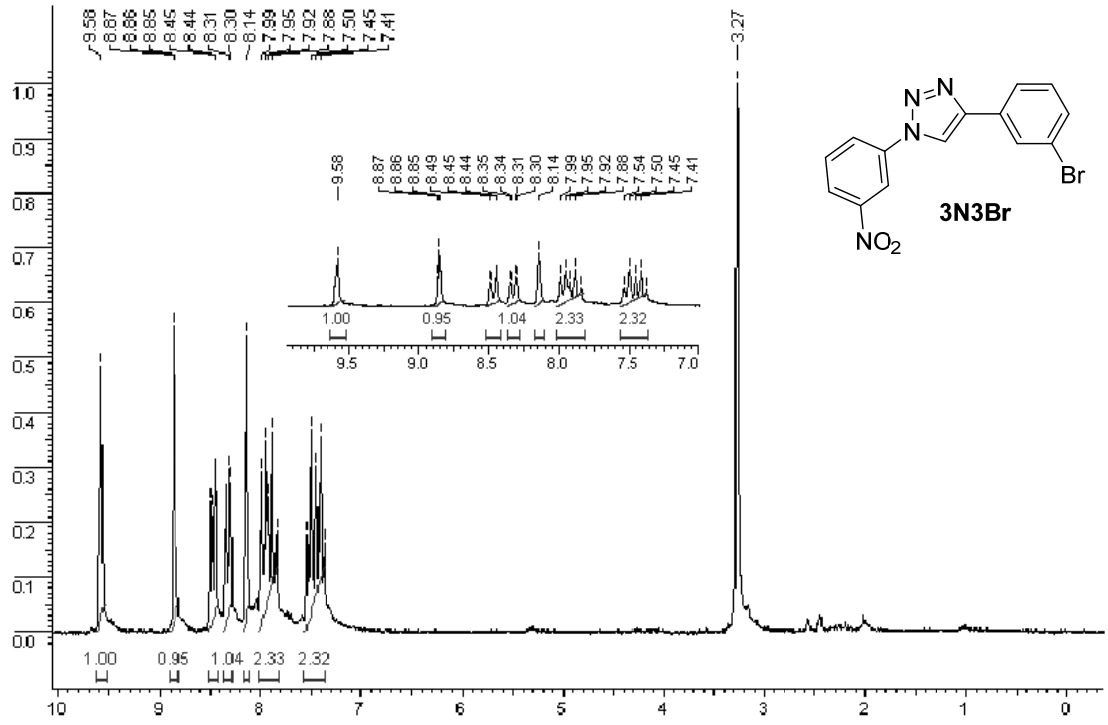


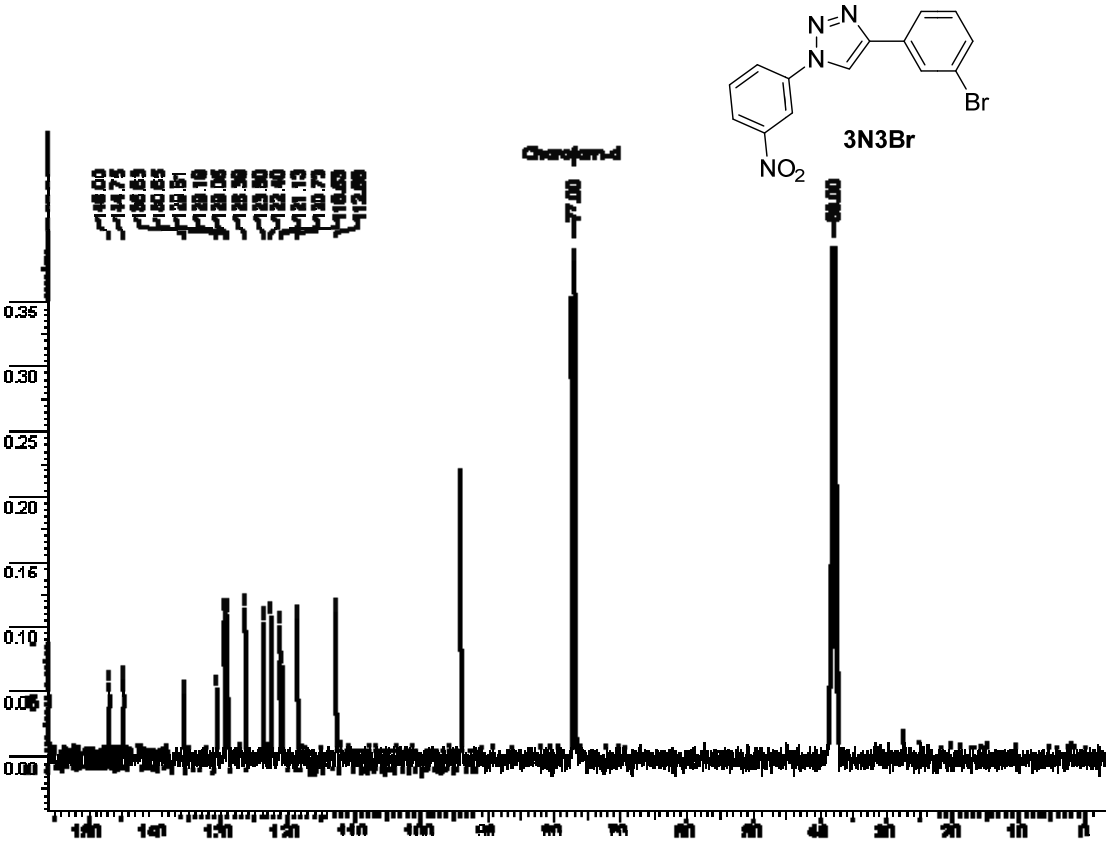


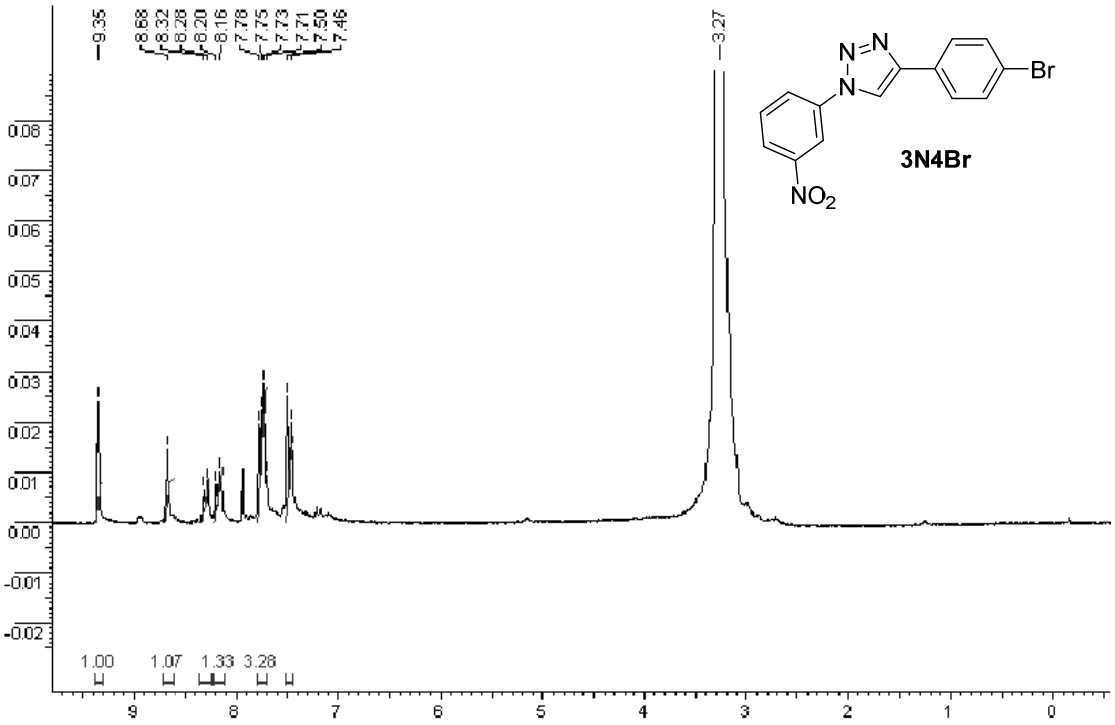


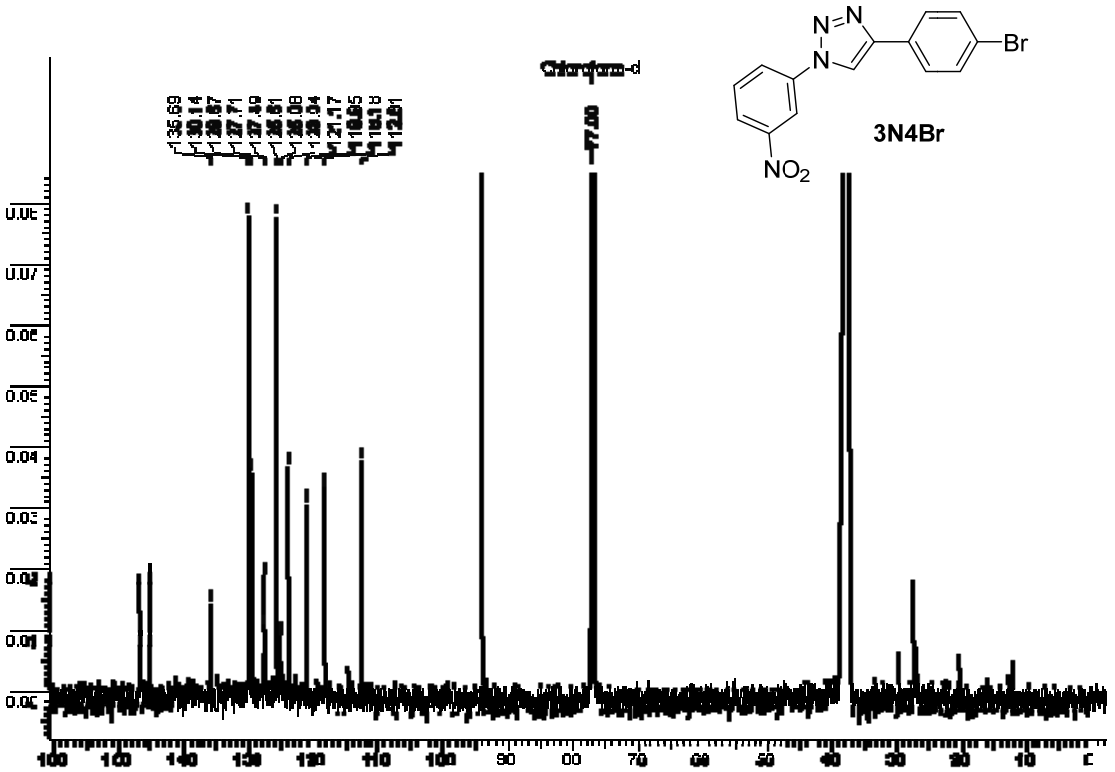


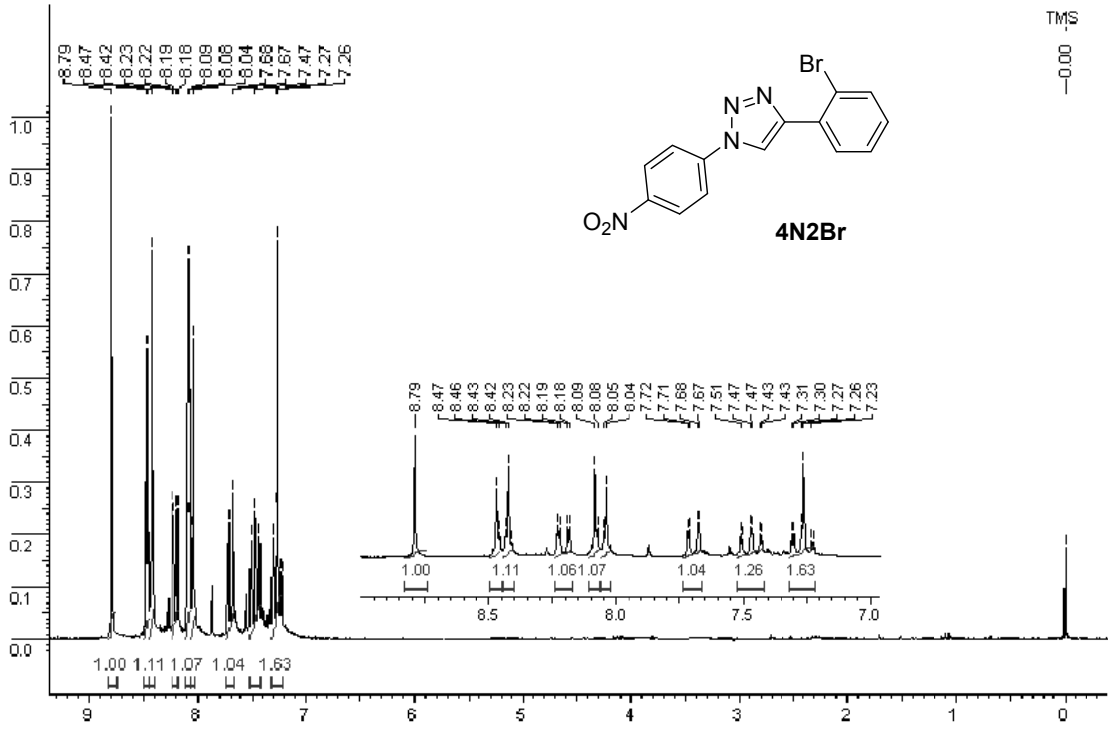


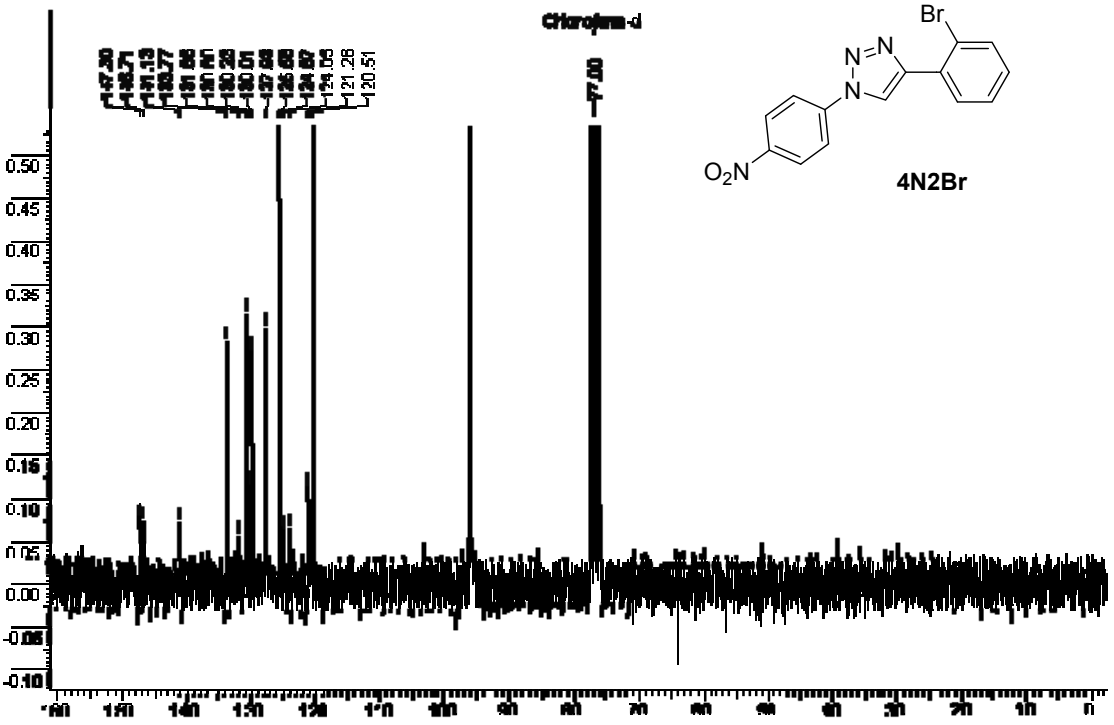


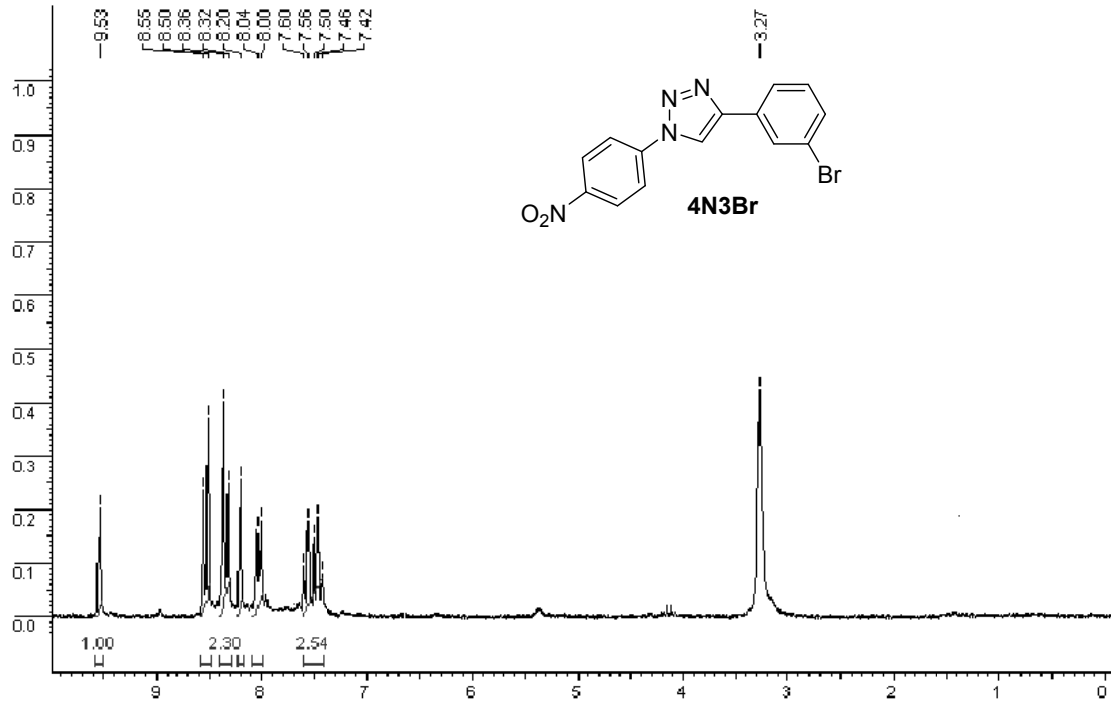


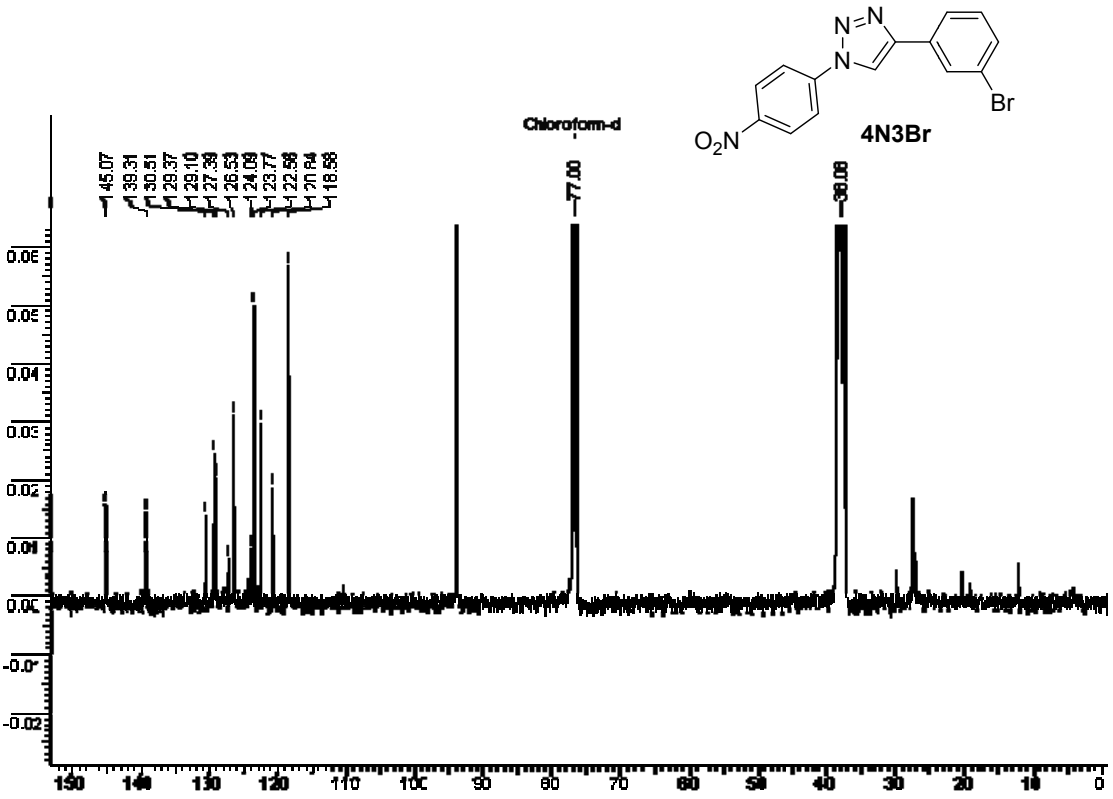


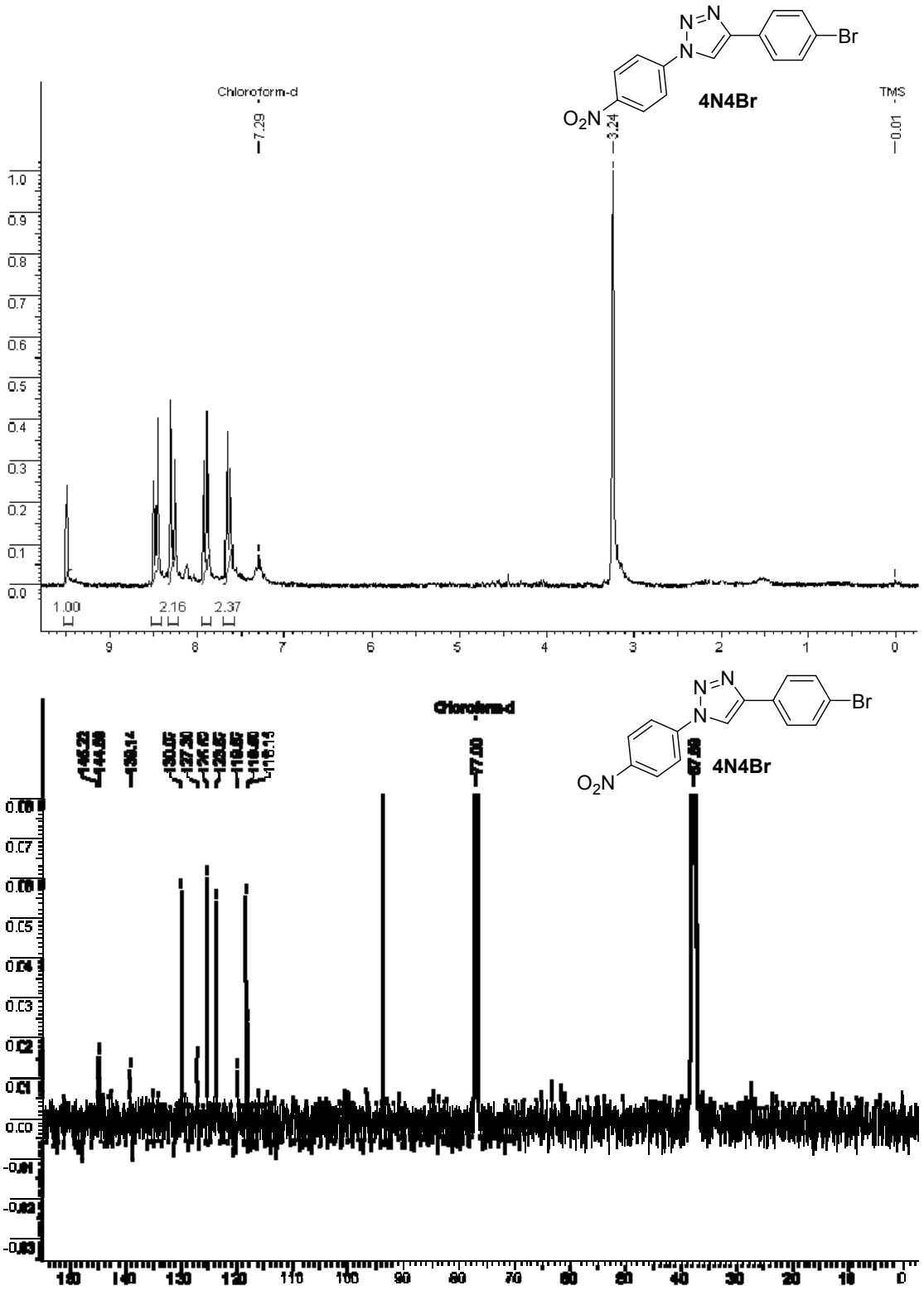






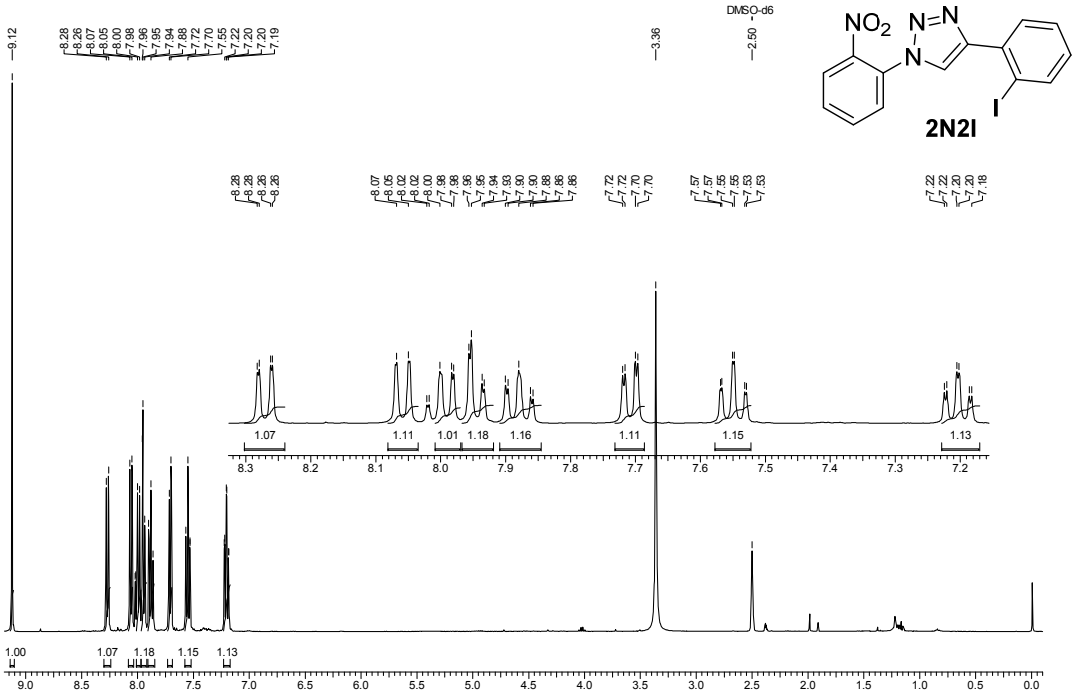





Chloroform-d
7.29
3.24
TMS
0.01
4N4Br
1.00
2.16
2.37
Chloroform-d
77.00
4N4Br

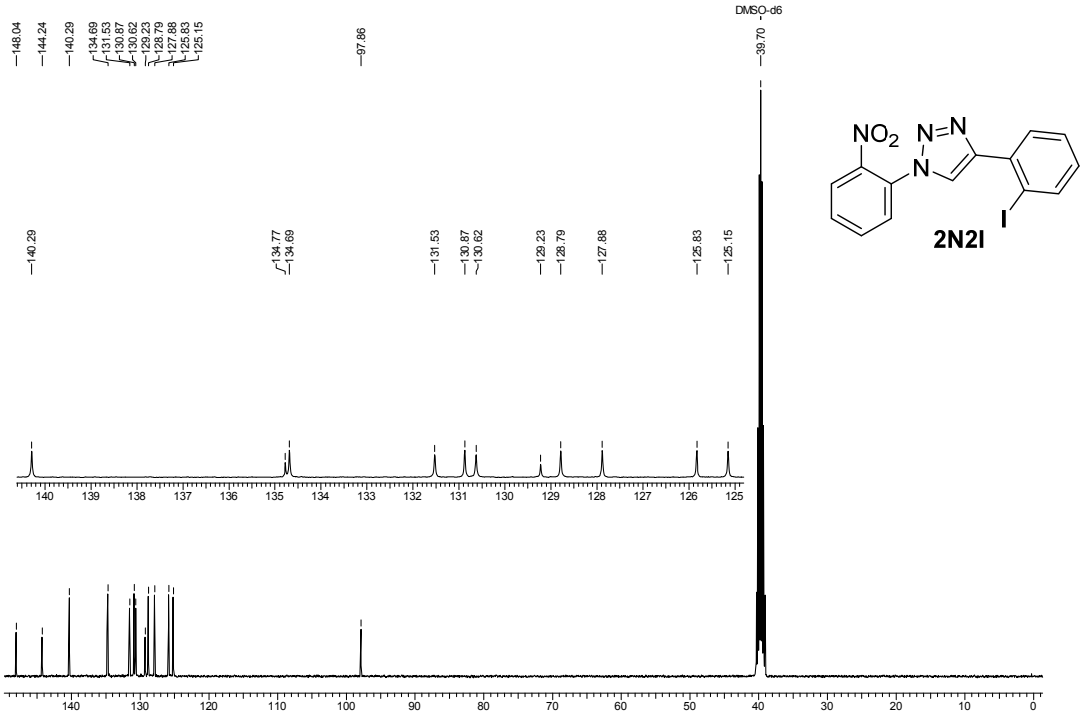
17 Apr 2012

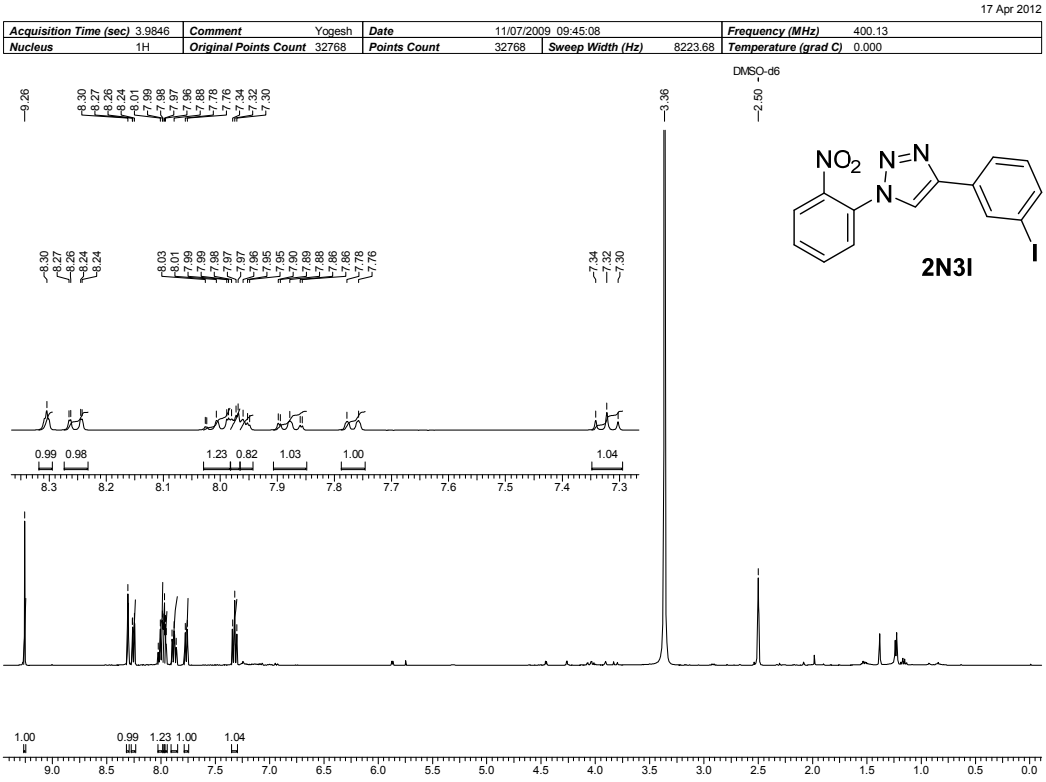
Acquisition Time (sec)	3.9846	**Comment**	Yogesh	**Date**	27/07/2009 18:09:10	**Frequency (MHz)**	400.13
Nucleus	1H	**Original Points Count**	32768	**Points Count**	32768 **Sweep Width (Hz)** 8223.68	**Temperature (grad C)**	0.000

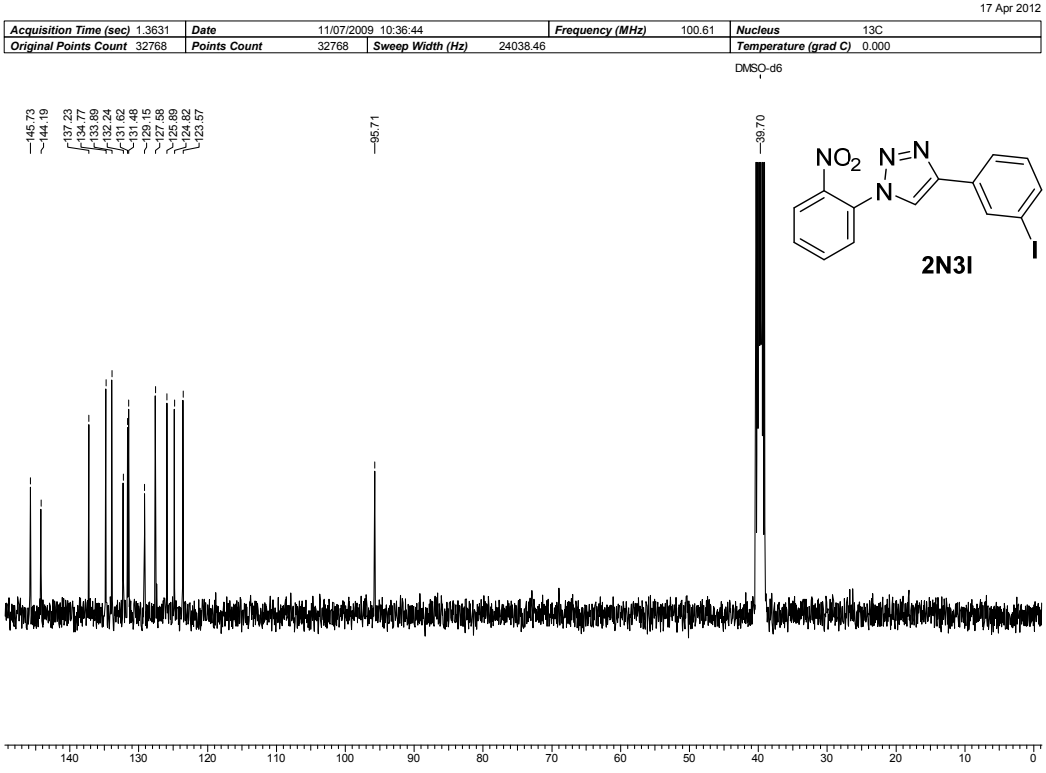


17 Apr 2012

Acquisition Time (sec)	1.3631	**Date**	27/07/2009 20:11:34			**Frequency (MHz)**	100.61	**Nucleus**	13C
Original Points Count	32768	**Points Count**	32768	**Sweep Width (Hz)**	24038.46			**Temperature (grad C)**	0.000

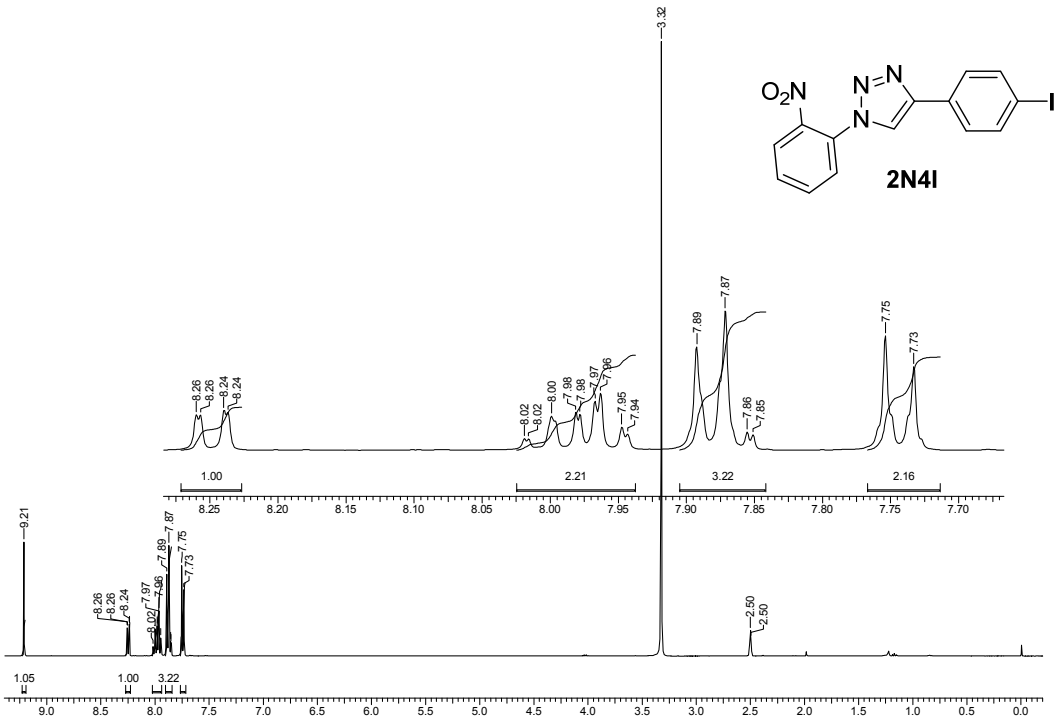



17 Apr 2012
Acquisition Time (sec) 3.9846
Comment Yogesh
Date 11/07/2009 09:45:08
Frequency (MHz) 400.13
Nucleus 1H
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 8223.68
Temperature (grad C) 0.000
DMSO-d6
9.26
8.30
8.27
8.26
8.24
8.01
7.99
7.98
7.97
7.96
7.88
7.78
7.76
7.34
7.32
7.30
3.36
2.50
NO2
N=N
N
I
2N3I
0.99 0.98 1.23 0.82 1.03 1.00 1.04
1.00 0.99 1.23 1.00 1.04


17 Apr 2012
Acquisition Time (sec) 1.3631
Date 11/07/2009 10:36:44
Frequency (MHz) 100.61
Nucleus 13C
Original Points Count 32768
Points Count 32768
Sweep Width (Hz) 24038.46
Temperature (grad C) 0.000
DMSO-d6
145.73
144.19
137.23
134.77
134.69
132.24
131.62
131.48
129.15
127.58
125.89
124.82
123.57
95.71
39.70
NO2
N=N
N
I
2N3I

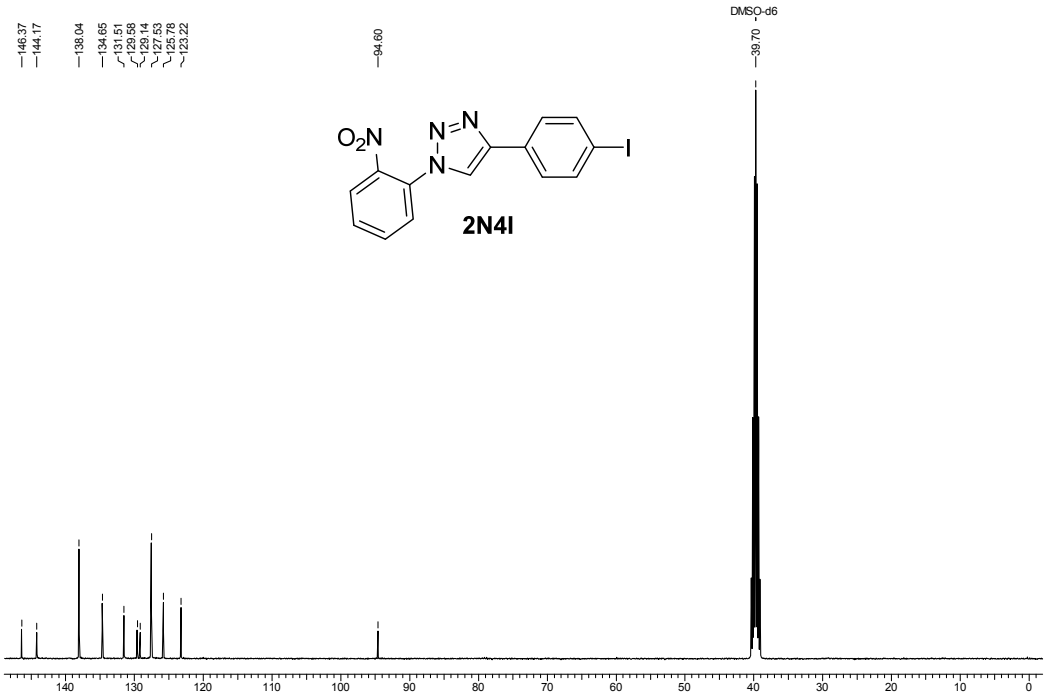
17 Apr 2012

Acquisition Time (sec)	3.9846	*Comment*	Yogesh	*Date*	02/08/2009 16:50:44	*Frequency (MHz)*	400.13
Nucleus	1H	*Original Points Count*	32768	*Points Count*	32768	*Sweep Width (Hz)*	8223.68	*Temperature (grad C)*	0.000



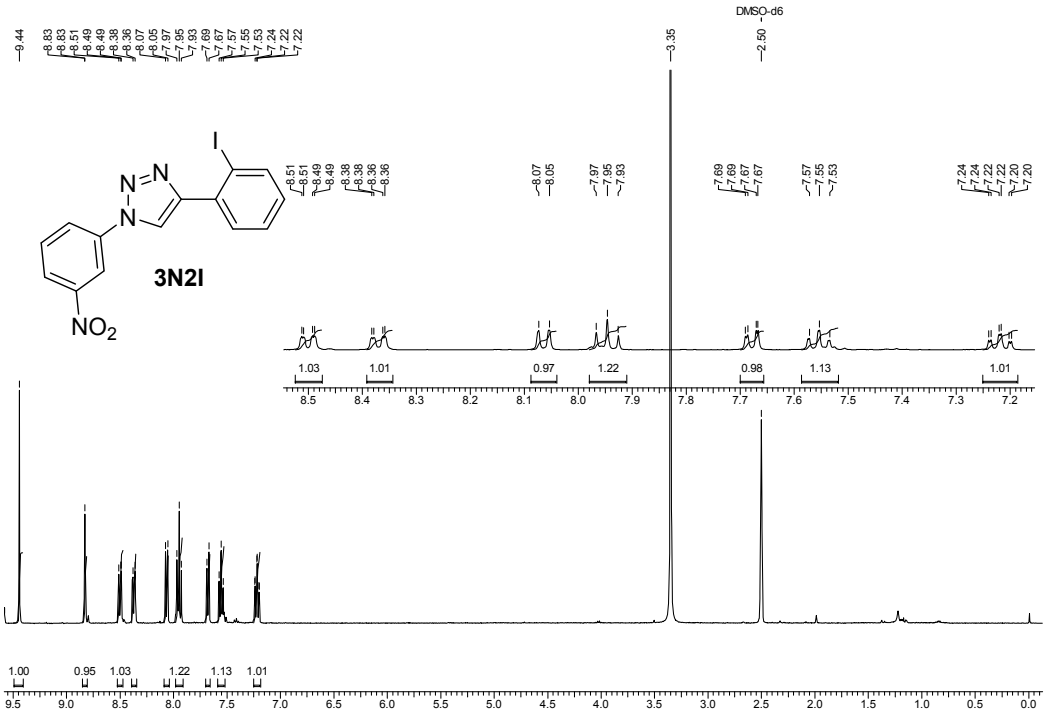
17 Apr 2012

Acquisition Time (sec)	1.3631	*Date*	02/08/2009 19:24:54	*Frequency (MHz)*	100.61	*Nucleus*	13C
Original Points Count	32768	*Points Count*	32768	*Sweep Width (Hz)*	24038.46	*Temperature (grad C)*	0.000



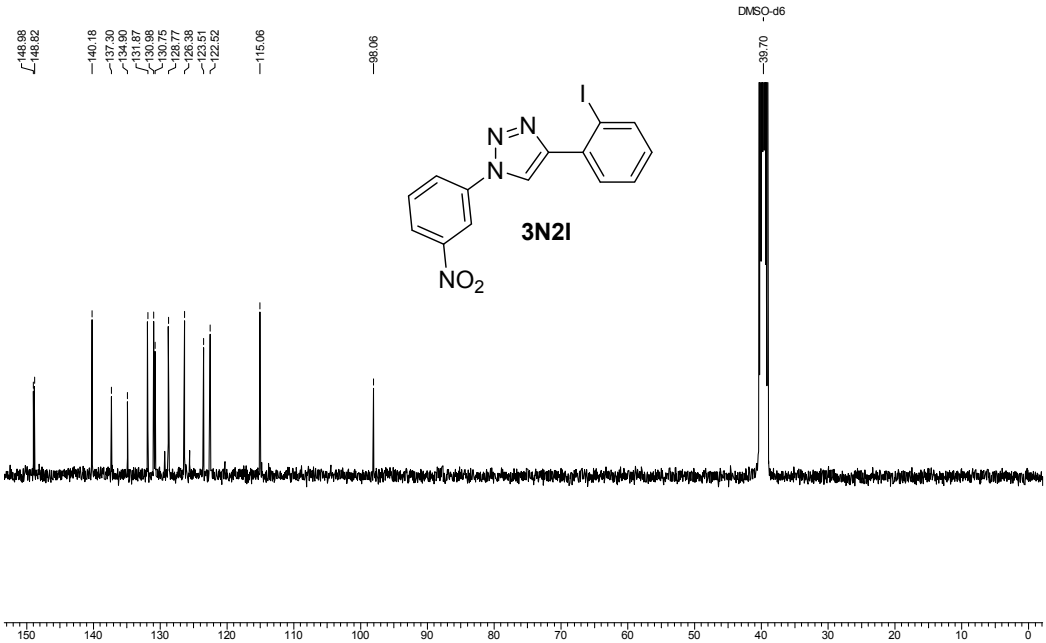
17 Apr 2012

Acquisition Time (sec) 3.9846	*Comment* Yogesh	*Date* 27/07/2009 13:12:32				*Frequency (MHz)* 400.13	
Nucleus 1H	*Original Points Count* 32768	*Points Count* 32768	*Sweep Width (Hz)* 8223.68			*Temperature (grad C)* 0.000	



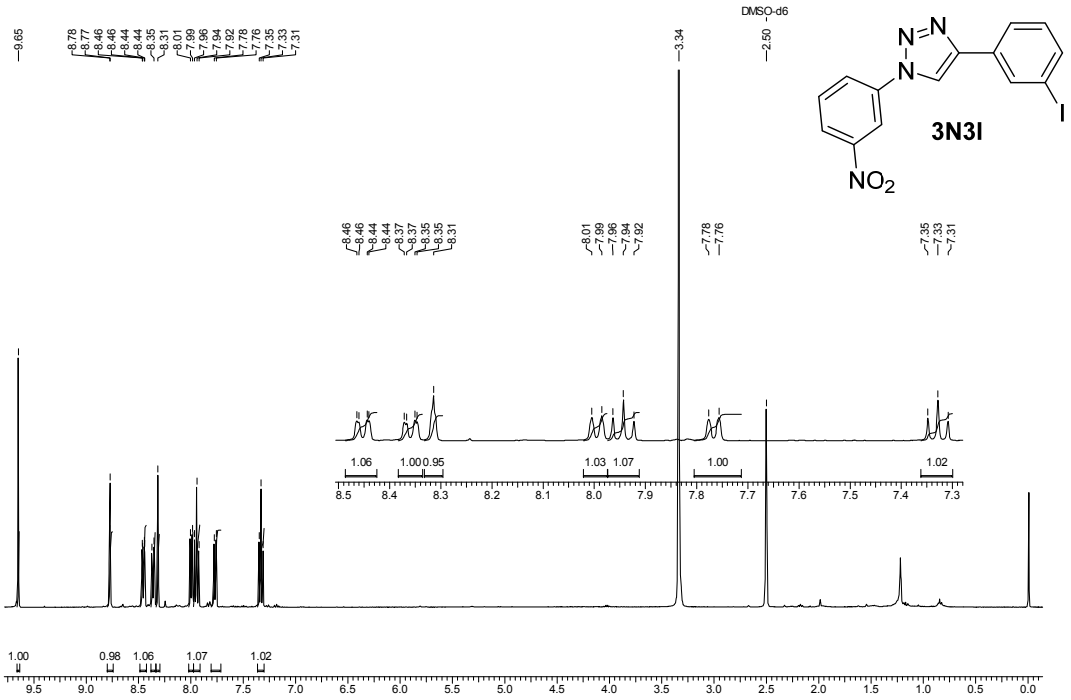
17 Apr 2012

Acquisition Time (sec) 1.3631	*Date* 27/07/2009 17:00:30		*Frequency (MHz)* 100.61	*Nucleus* 13C	
Original Points Count 32768	*Points Count* 32768	*Sweep Width (Hz)* 24038.46		*Temperature (grad C)* 0.000	



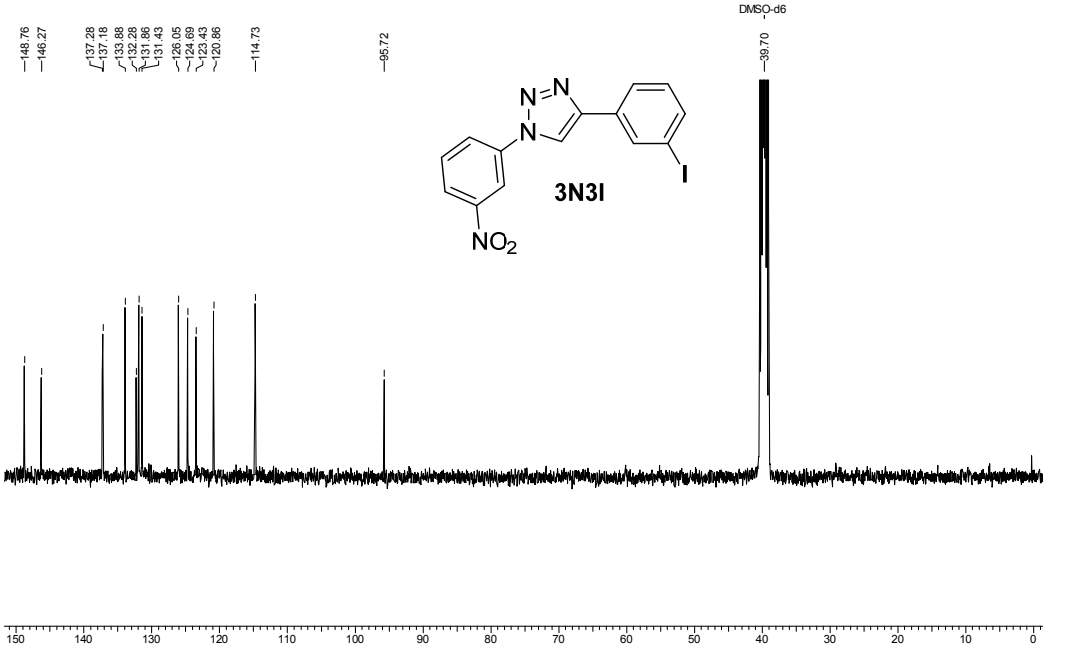
17 Apr 2012

Acquisition Time (sec)	3.9846	***Comment***	Yogesh	***Date***	18/07/2009 14:44:32	***Frequency (MHz)***	400.13
Nucleus	1H	***Original Points Count***	32768	***Points Count***	32768	***Sweep Width (Hz)***	8223.68	***Temperature (grad C)***	0.000



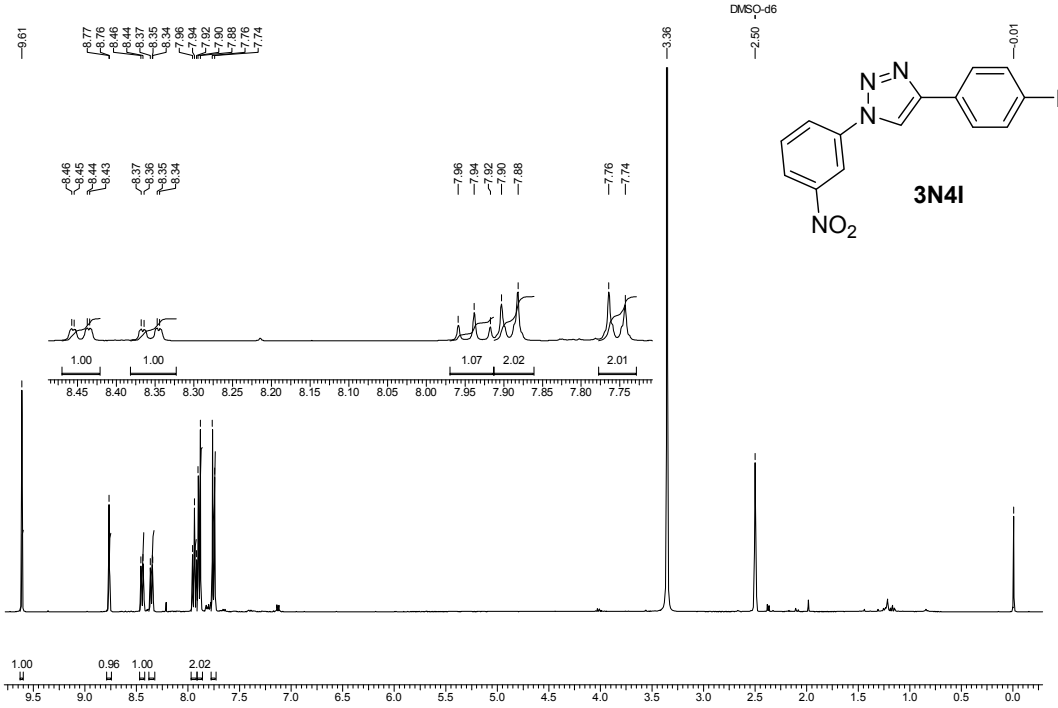
17 Apr 2012

Acquisition Time (sec)	1.3631	***Date***	18/07/2009 20:28:56			***Frequency (MHz)***	100.61	***Nucleus***	13C
Original Points Count	32768	***Points Count***	32768	***Sweep Width (Hz)***	24038.46			***Temperature (grad C)***	0.000



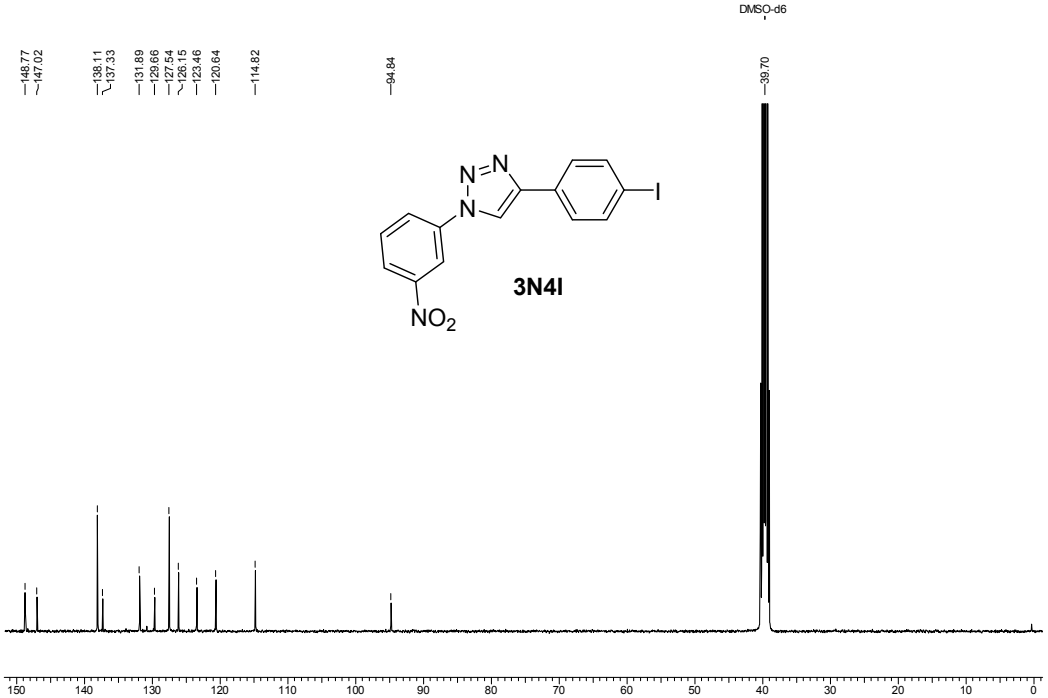
17 Apr 2012

Acquisition Time (sec)	3.9846	*Comment*	Yogesh	*Date*	25/07/2009 08:36:36	*Frequency (MHz)*	400.13
Nucleus	1H	*Original Points Count*	32768	*Points Count*	32768	*Sweep Width (Hz)*	8223.68	*Temperature (grad C)*	0.000



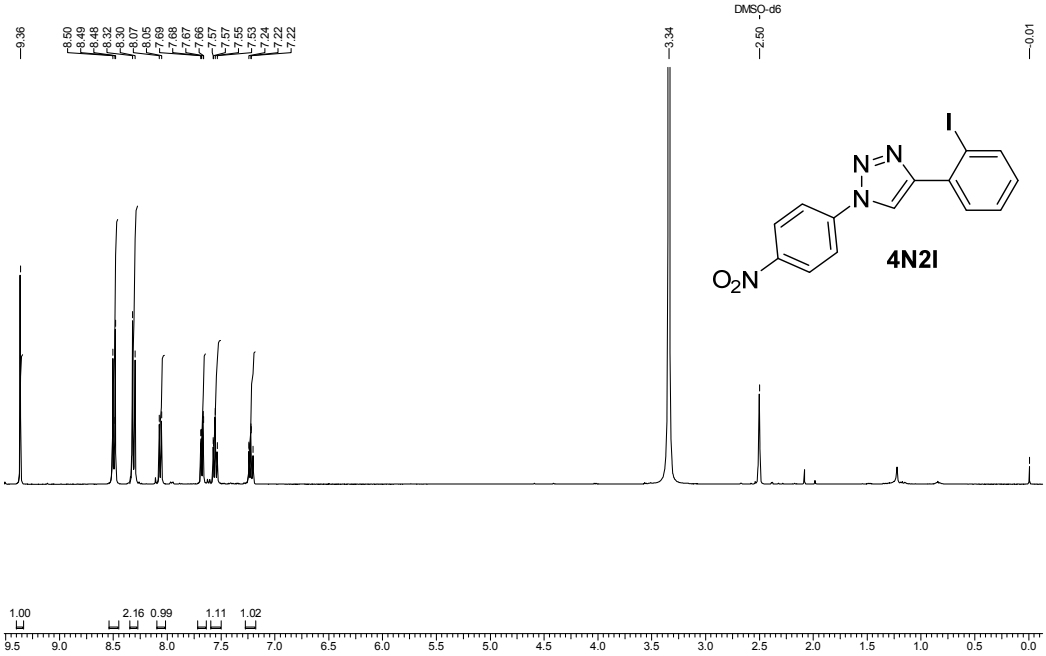
17 Apr 2012

Acquisition Time (sec)	1.3631	*Date*	25/07/2009 08:37:20	*Frequency (MHz)*	100.61	*Nucleus*	13C
Original Points Count	32768	*Points Count*	32768	*Sweep Width (Hz)*	24038.46	*Temperature (grad C)*	0.000



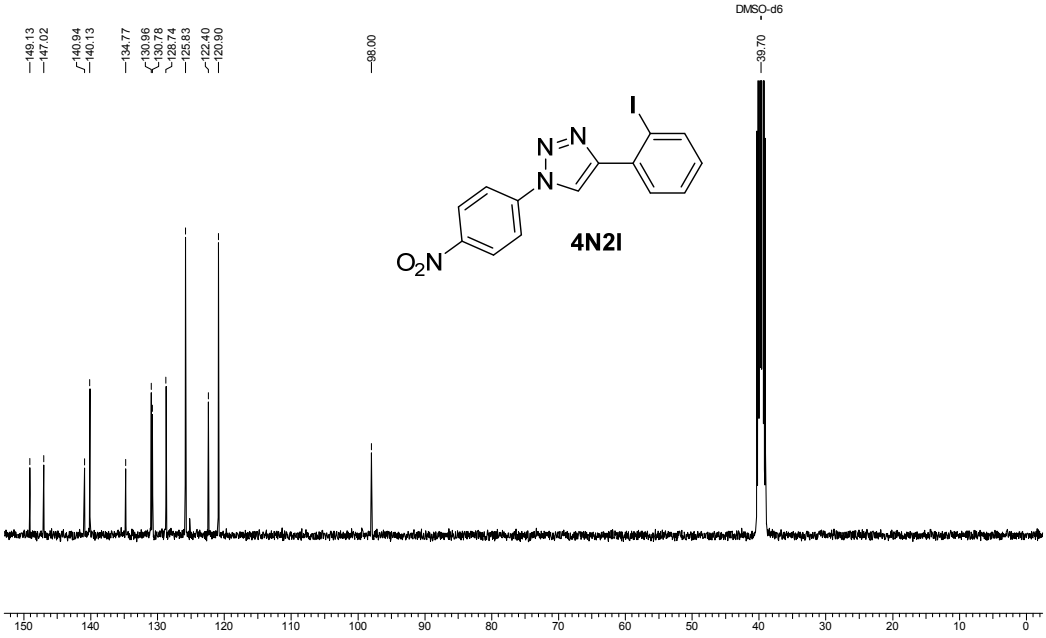
17 Apr 2012

Acquisition Time (sec)	3.9846	***Comment***	Yogesh	***Date***	01/08/2009 15:25:56			***Frequency (MHz)***	400.13
Nucleus	1H	***Original Points Count***	32768	***Points Count***	32768	***Sweep Width (Hz)***	8223.68	***Temperature (grad C)***	0.000



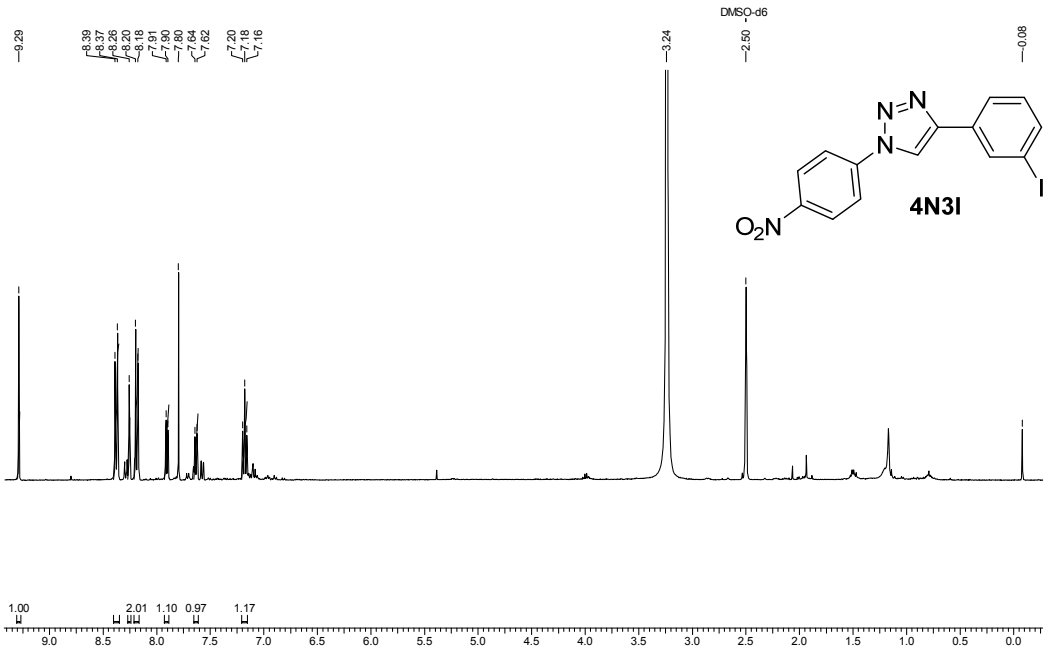
17 Apr 2012

Acquisition Time (sec)	1.3631	***Date***	01/08/2009 19:31:38			***Frequency (MHz)***	100.61	***Nucleus***	13C
Original Points Count	32768	***Points Count***	32768	***Sweep Width (Hz)***	24038.46			***Temperature (grad C)***	0.000



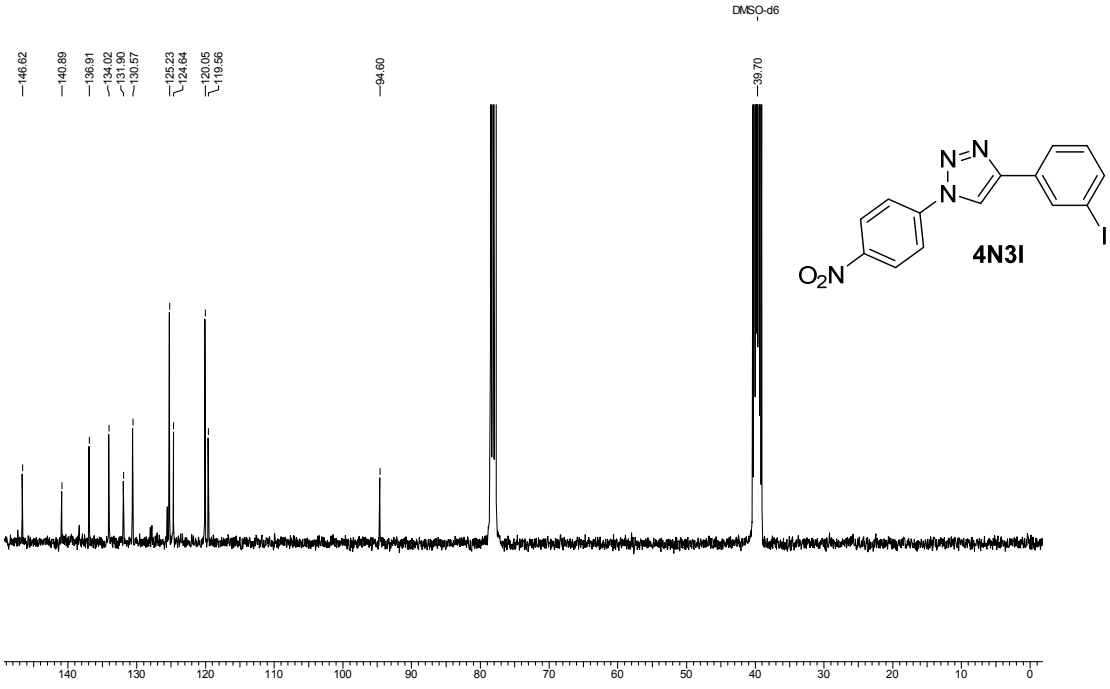
17 Apr 2012

Acquisition Time (sec)	3.9846	***Comment***	Yogesh	***Date***	08/07/2009 19:04:32			***Frequency (MHz)***	400.13
Nucleus	1H	***Original Points Count***	32768	***Points Count***	32768	***Sweep Width (Hz)***	8223.68	***Temperature (grad C)***	0.000



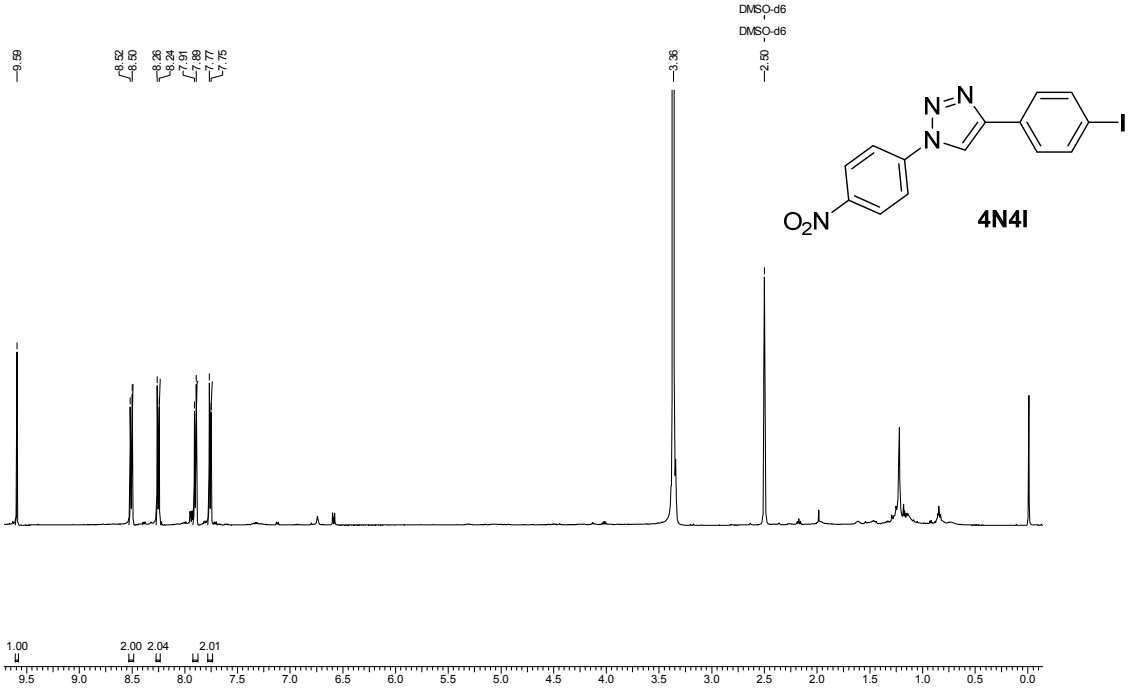
17 Apr 2012

Acquisition Time (sec)	1.3631	***Date***	09/07/2009 08:56:10			***Frequency (MHz)***	100.61	***Nucleus***	13C
Original Points Count	32768	***Points Count***	32768	***Sweep Width (Hz)***	24038.46			***Temperature (grad C)***	0.000



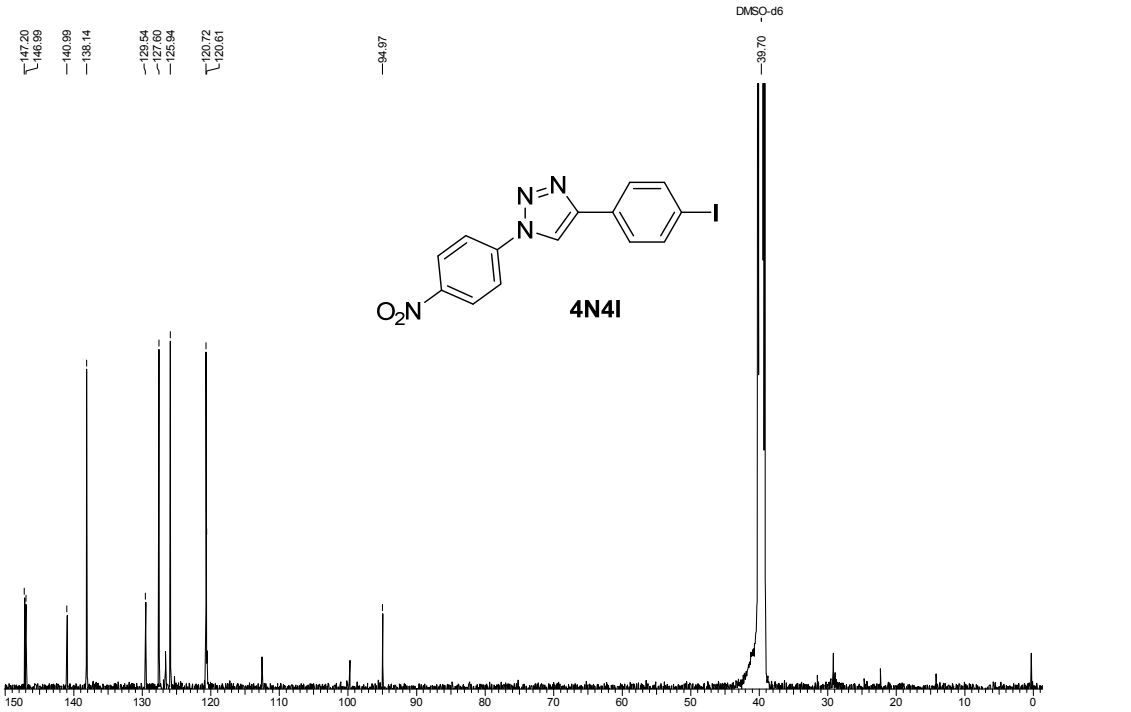
17 Apr 2012

Acquisition Time (sec) 3.6351	***Comment*** Yogesh	***Date*** 18/07/2009 13:44:50				***Frequency (MHz)*** 500.13	
Nucleus 1H	***Original Points Count*** 32768	***Points Count*** 32768		***Sweep Width (Hz)*** 9014.42		***Temperature (grad C)*** 0.000	



17 Apr 2012

Acquisition Time (sec) 1.0486	***Date*** 18/07/2009 14:39:24			***Frequency (MHz)*** 125.76		***Nucleus*** 13C	
Original Points Count 32768	***Points Count*** 32768	***Sweep Width (Hz)*** 31250.00				***Temperature (grad C)*** 0.000	



Crystallographic details

Crystal structure analysis of non-halo (**2N**, **3N** and **4N**) and bromo derivatives (**2N2Br**, **2N3Br**, **2N4Br**, **3N2Br**, **3N3Br**, **3N4Br**, **4N2Br**, **4N3Br** and **4N4Br**) have been reported earlier from our group (C. V. Ramana, S. Chatterjee, K. A. Durugkar and R. G. Gonnade, *CrystEngComm* 2009, **11**, 143). These data were directly used in the analysis without further refinement. The crystal structure data for these compounds is given in Table S1, for ready reference.

Table S1: Summary of crystallographic data for non-halo and bromo derivatives

	2N	**2N2Br**	**2N3Br**	**2N4Br**	**3N**	**3N2Br**
Chemical formula	$C_{14}H_{10}N_4O_2$	$C_{14}H_9BrN_4O_2$	$C_{14}H_9BrN_4O_2$	$C_{14}H_9BrN_4O_2$	$C_{14}H_{10}N_4O_2$	$C_{14}H_9BrN_4O_2$
M_r	266.26	345.16	345.16	345.16	266.26	345.16
Crystal Size	0.43×0.41×0.26	0.77×0.68×0.54	0.51×0.23×0.13	0.68×0.25×0.20	0.31×0.22×0.20	0.76×0.07×0.06
Temp. (K)	297(2)	297(2)	297(2)	297(2)	297(2)	297(2)
Crystal system	monoclinic	monoclinic	Monoclinic	Monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	12.180(4)	12.388(13)	9.2835(11)	5.4468(9)	8.502(3)	7.228(7)
b/Å	7.501(3))	8.051(9)	7.2943(9)	20.778(3)	5.3559(18)	13.308(13)
c/Å	14.277(5)	14.256(15)	20.794(2)	12.482(2)	27.363(9)	14.521(15)
α/°	90	90	90	90	90	90
β/°	100.286(7)	103.305(18)	97.444(2)	102.427(3)	95.564(6)	93.675(19)
γ/°	90	90	90	90	90	90
V/Å^3	1283.5(8)	□□□□□□□□139	1396.2(3)	1379.6(4)	1240.1(7)	1394(2)
Z, D_{calc}/g cm^{-3}	4, 1.378	4, 1.657	4, 1.642	4, 1.662	4, 1.426	4, 1.645
□/mm^{-1}	0.097	2.981	2.954	2.989	0.100	2.959
F(000)	552	688	688	688	552	688
θ max/°	26.0	25.0	25.0	25.0	25.0	25.0
Absor. Correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
T_{min}	0.960	0.207	0.314	0.236	0.970	0.212
T_{max}	0.975	0.296	0.700	0.586	0.980	0.852
Reflections collected	9605	6344	8147	6843	5402	9670
Unique reflections	2513	2419	2448	2427	2170	2455
Observed reflections	1661	1685	1881	1896	1779	1522
h, *k*, *l* (min, max)	(-14, 15), (-9, 9), (-17, 17)	(-12, 14), (-7, 9), (-16, 16)	(-11, 10), (-8, 8), (-24, 24)	(-6, 6), (-22, 24), (-9, 14)	(-10, 10), (-6, 6), (-32, 25)	(-8, 8), (-15, 13), (-17, 17)
R_{int}	0.0446	0.052	0.024	0.0221	0.036	0.0269
Number of parameters	221	190	190	226	181	379
R_1_obs, R_1_all	0.062, 0.0.0100	0.047, 0.070	0.0369, 0.0518	0.0361, 0.0503	0.0525, 0.0655	0.0342, 0.0492
wR_2_obs, wR_2_all	0.130, 0.148	0.124, 0.138	0.0876, 0.0942	0.0823, 0.0889	0.1260, 0.1328	0.0785, 0.0847
GoF	1.098	0.96	1.03	1.045	1.038	1.023
$\Delta\rho_{max}$,$\Delta\rho_{min}$/eÅ^{-3}	0.16, –0.15	0.92, –0.28	0.57, –0.39	0.66, –0.51	0.17, –0.15	0.44, –0.29
CCDC No.	679556	679554	679558	679559	679560	679561

	3N3Br	**3N4Br**	**4N**	**4N2Br**	**4N3Br**	**4N4Br**
Chemical formula	$C_{14}H_9BrN_4O_2$	$C_{14}H_9BrN_4O_2$	$C_{14}H_{10}N_4O_2$	$C_{14}H_9BrN_4O_2$	$C_{14}H_9BrN_4O_2$	$C_{14}H_9BrN_4O_2$
M_r	266.26	345.16	266.26	345.16	266.26	345.16
Crystal Size	0.33×0.26×0.09	0.37×0.32×0.03	0.69×0.52×0.08	0.68×0.25×0.20	0.88×0.13×0.08	0.82×0.43×0.12
Temp. (K)	297(2)	297(2)	297(2)	297(2)	297(2)	297(2)
Crystal system	Triclinic	Monoclinic	triclinic	Monoclinic	monoclinic	Triclinic
Space group	*P*-1	$P2_1/n$	*P*-1	*C*2/*c*	$P2_1/c$	*P*-1
a/Å	7.4402(6)	8.667(3)	5.757(2)	29.52(2)	7.5222(8)	9.6141(15)
b/Å	12.4535(10)	5.2323(18)	7.198(3)	7.057(5)	14.1697(15)	12.0915(19)
c/Å	14.6016(12)	30.304(11)	14.862(6)	13.022(9)	13.0479(14)	12.900(2)
α/°	91.2720(10)	90	101.081(6)	90	90	87.535(2)
β/°	98.9940(10)	96.248(6)	99.217(6)	97.405(12)	90.391(2)	71.407(2)
γ/°	96.3090(10)	90	90.859(6)	90	90	76.183(2)
V/Å^3	1327.14(19)	1366.0(8)	595.8(4)	2690(3)	1390.7(3)	1379.3(4)
Z, D_{calc}/g cm^{-3}	4, 1.727	4, 1.678	2, 1.484	8, 1.705	4, 1.649	4, 1.662
μ/mm^{-1}	3.107	3.019	2.104	3.066	2.965	2.990
F(000)	688	688	276	1376	688	688
θ max/°	25.0	25.0	26.0	25.0	25.0	25.0
Absor. Correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
T_{min}	0.427	0.401	0.932	0.230	0.180	0.193
T_{max}	0.767	0.915	0.992	0.580	0.789	0.715
Reflections collected	12926	6524	4652	6468	7835	13109
Unique reflections	4654	2403	2296	2377	2434	4834
Observed reflections	3565	1718	2006	1764	1859	3401
h, *k*, *l* (min, max)	(-8, 8), (-14, 14), (-17, 17)	(-9, 10), (-6, 5), (-36, 27)	(-7, 7), (-8, 8), (-16, 18)	(-34, 28), (-5, 8), (-15, 15)	(-8, 8), (-16, 14), (-15, 15)	(-11, 11), (-14,14), (-15, 15)
R_{int}	0.0269	0.029	0.0181	0.0378	0.026	0.0356
Number of parameters	379	226	221	199	190	379
R_1_obs, R_1_all	0.0342, 0.0492	0.0459, 0.0675	0.0363, 0.0414	0.0385, 0.0556	0.0387, 0.0547	0.0429, 0.0674
wR_2_obs, wR_2_all	0.0785, 0.0847	0.1064, 0.1186	0.0996, 0.1042	0.0953, 0.1037	0.0958, 0.1033	0.1159, 0.1284
GoF	1.023	1.034	1.060	1.010	1.041	1.019
$\Delta\rho_{max}$,$\Delta\rho_{min}$/eÅ^{-3}	0.44, –0.29	0.65, –0.54	0.20, –0.17	0.31, –0.23	0.49, –0.44	0.86, –0.47
CCDC No.	679562	679563	679564	679565	679566	679567

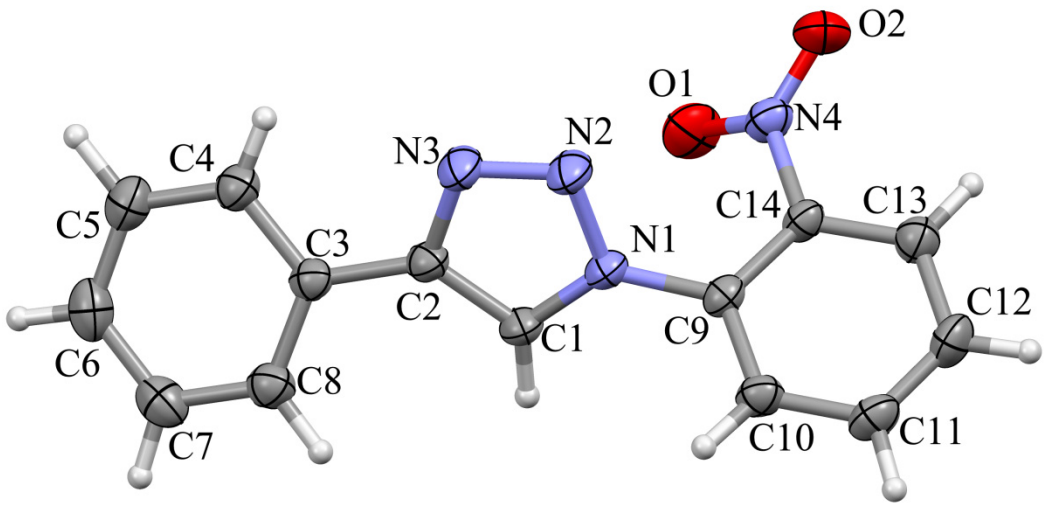


Figure S8. ORTEP of molecule in crystals of **2N**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

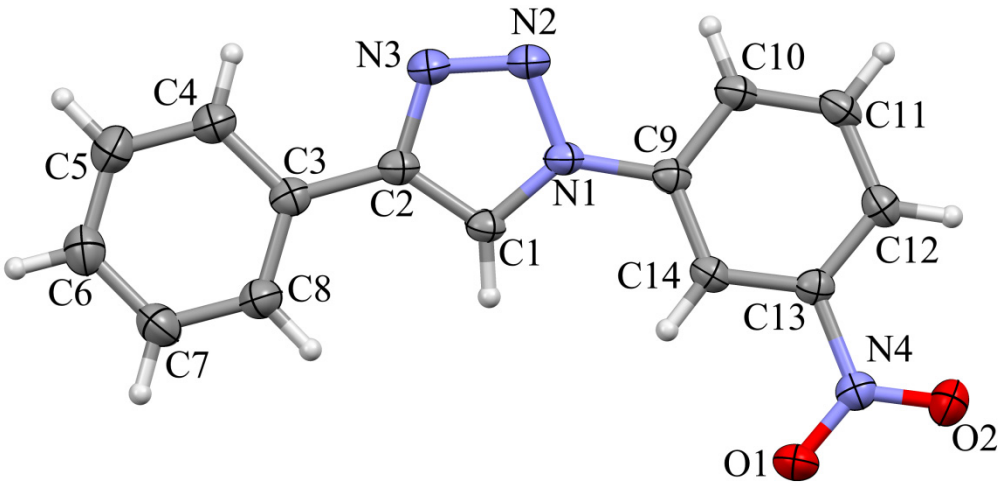


Figure S9. ORTEP of molecule in crystals of **3N**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

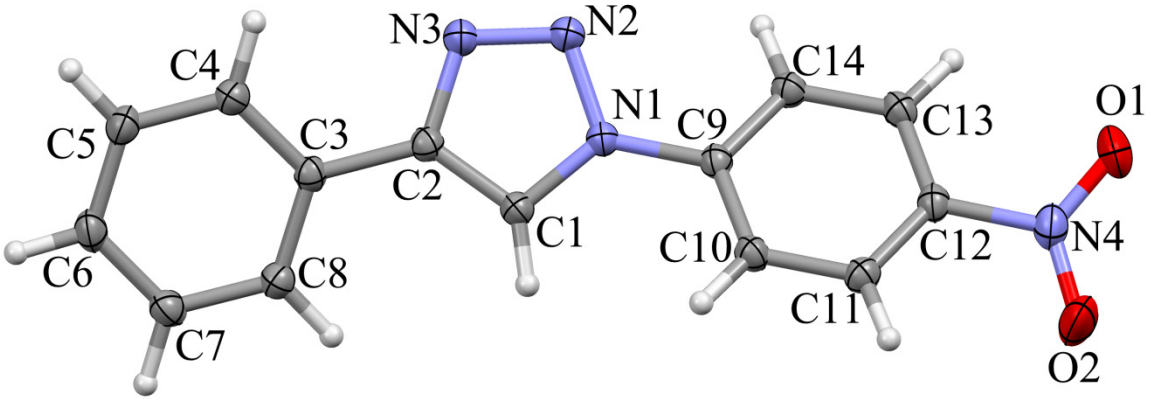


Figure S10. ORTEP of molecule in crystals of **4N**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

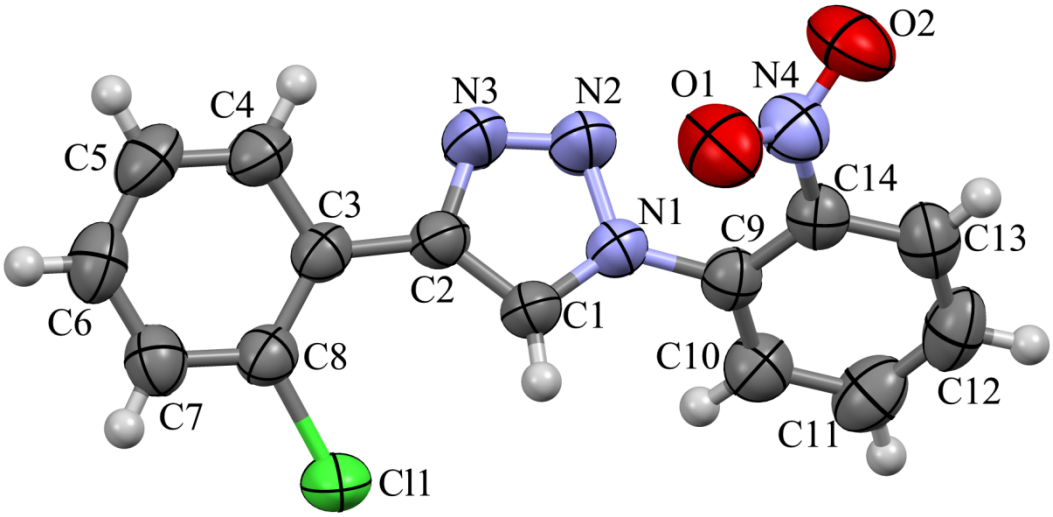


Figure S11. ORTEP of molecule in crystals of **2N2Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

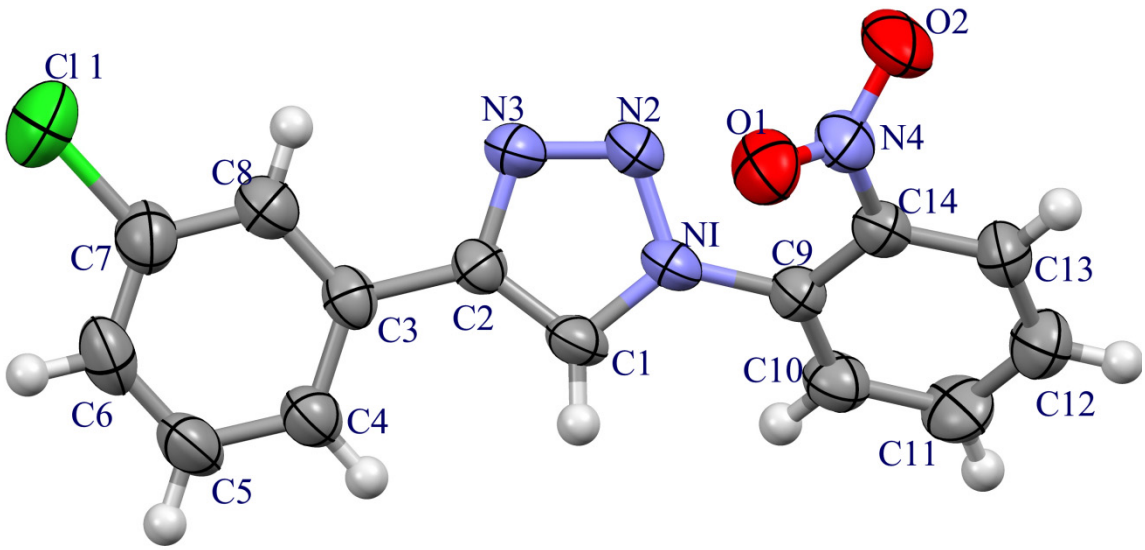


Figure S12. ORTEP of molecule in crystals of **2N3Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

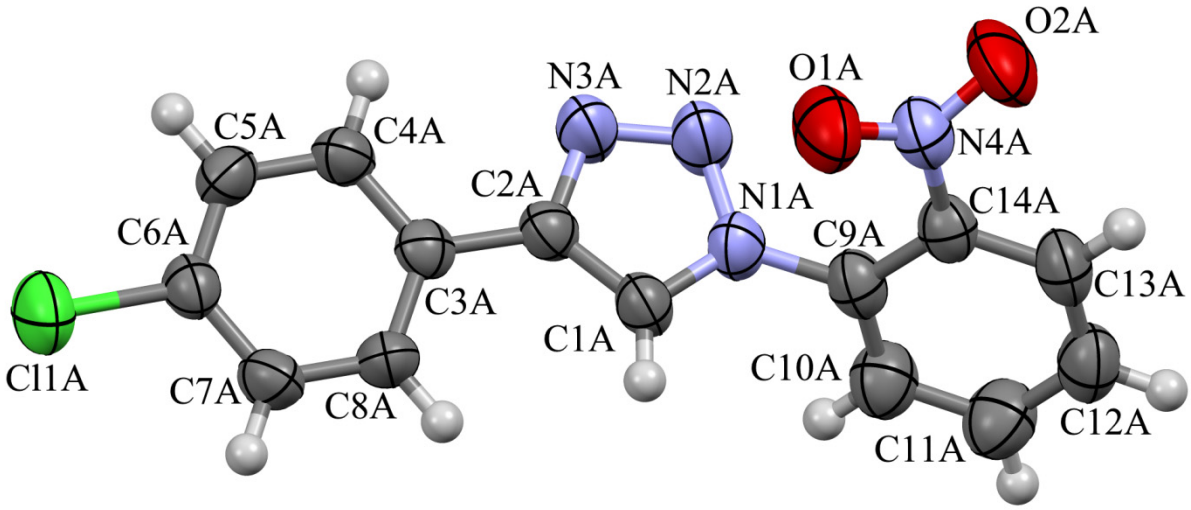


Figure S13. ORTEP of molecule in crystals of **2N4Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

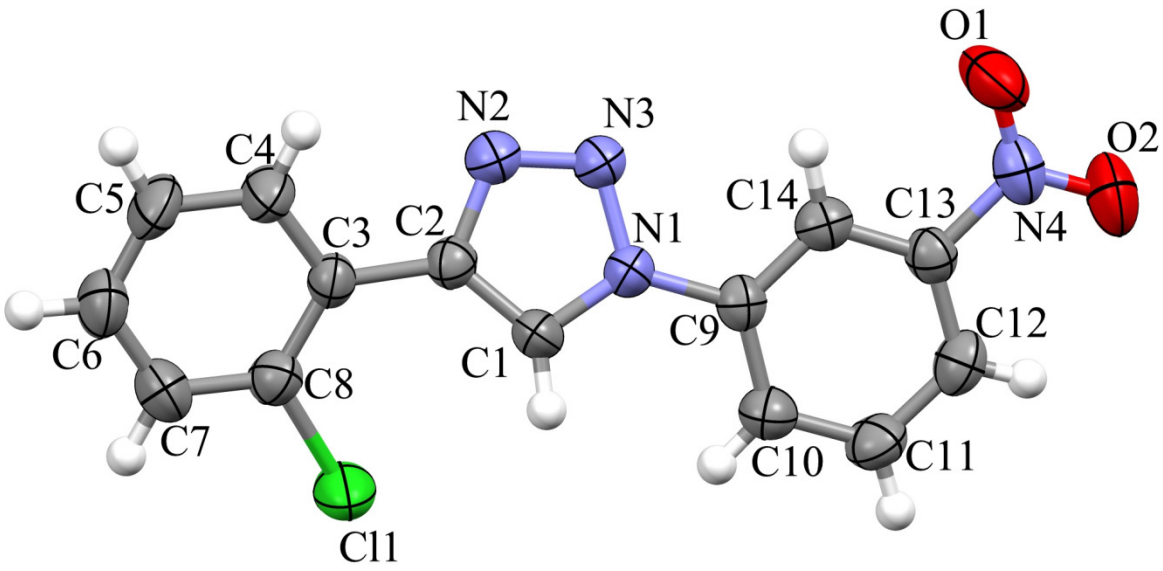


Figure S14. ORTEP of molecule in crystals of **3N2Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

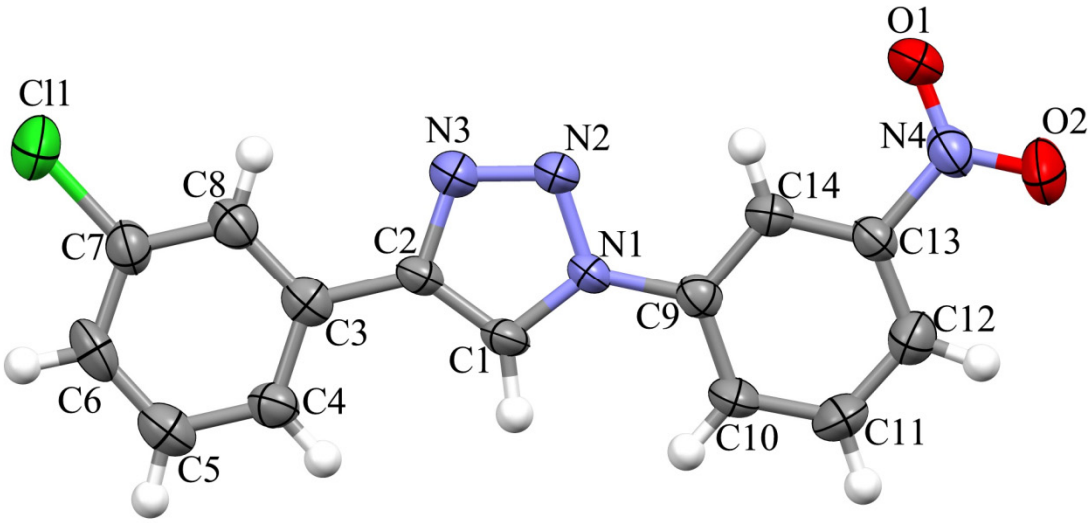


Figure S15. ORTEP of molecule in crystals of **3N3Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

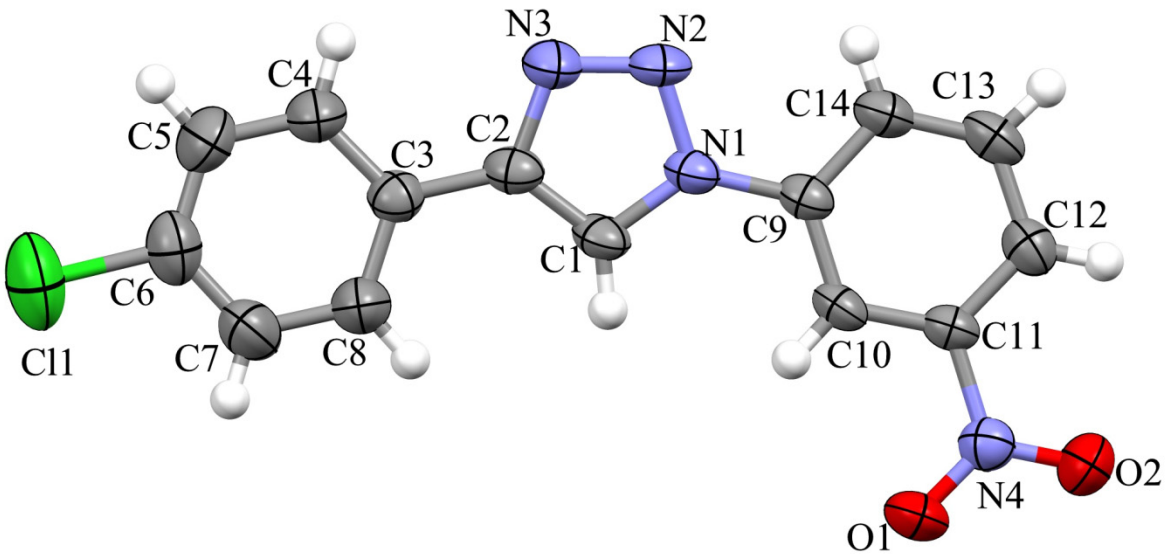


Figure S16. ORTEP of molecule in crystals of **3N4Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

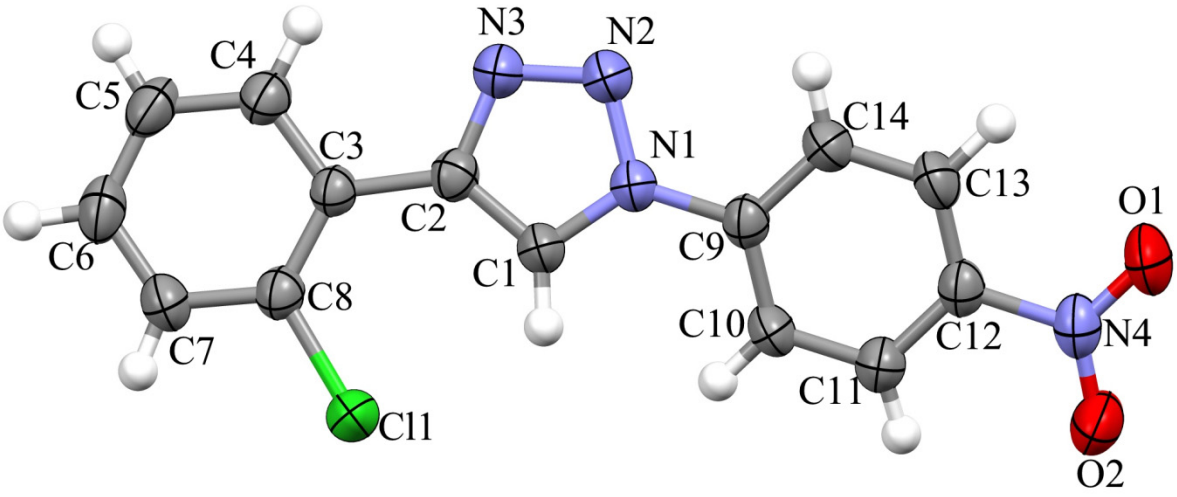


Figure S17. ORTEP of molecule in crystals of **4N2Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

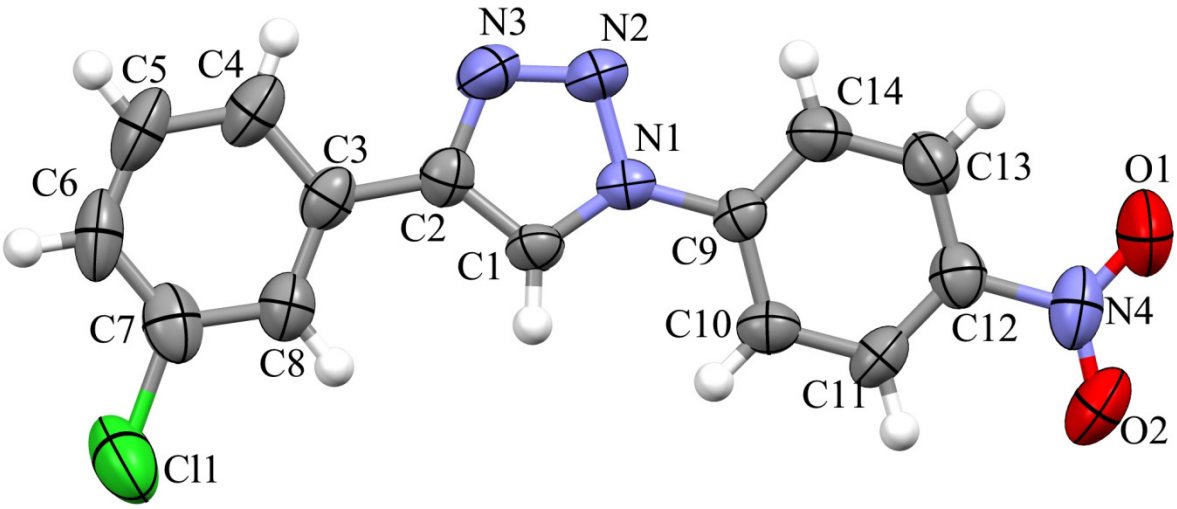


Figure S18. ORTEP of molecule in crystals of **4N3Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

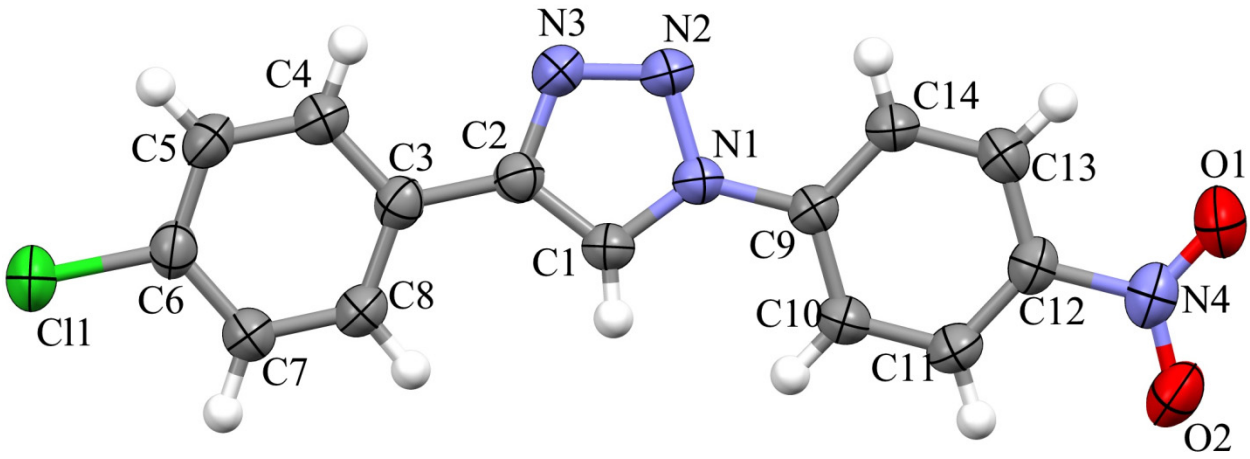


Figure S19. ORTEP of molecule in crystals of **4N4Cl**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

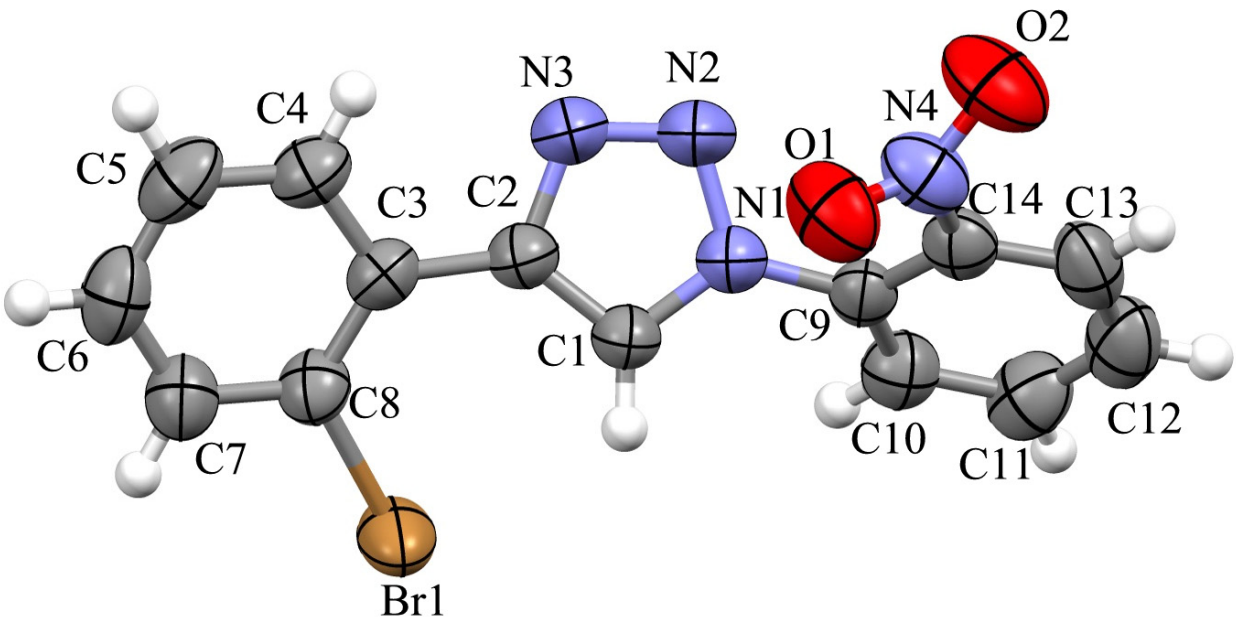


Figure S20. ORTEP of molecule in crystals of **2N2Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

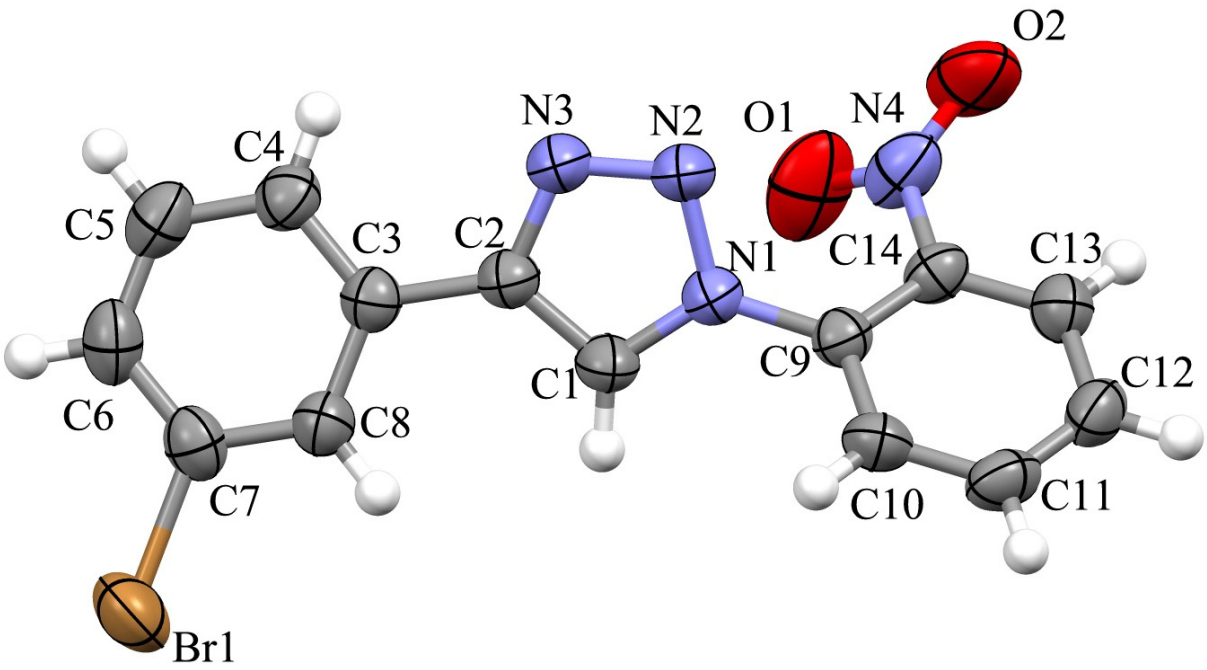


Figure S21. ORTEP of molecule in crystals of **2N3Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

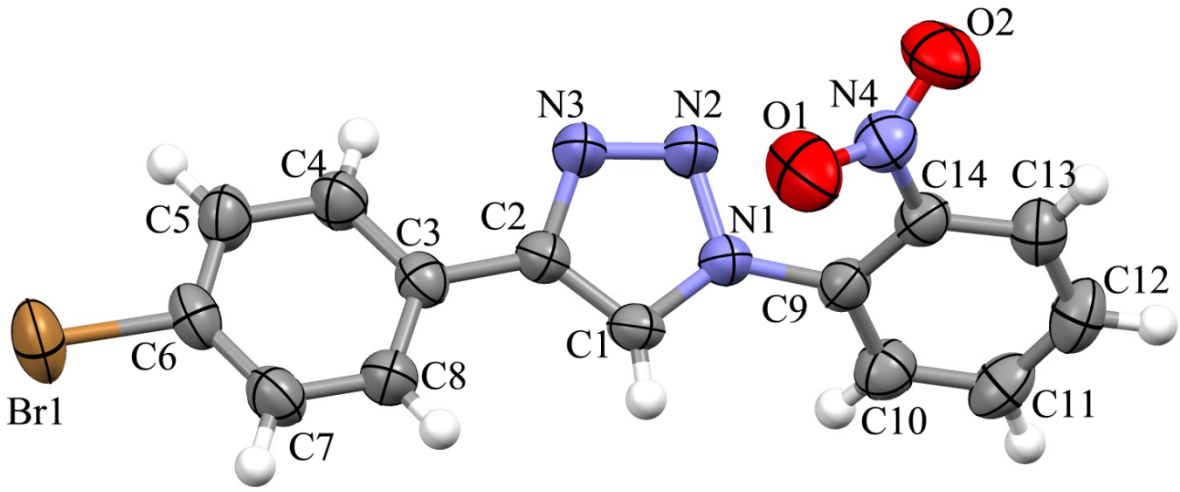


Figure S22. ORTEP of molecule in crystals of **2N4Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

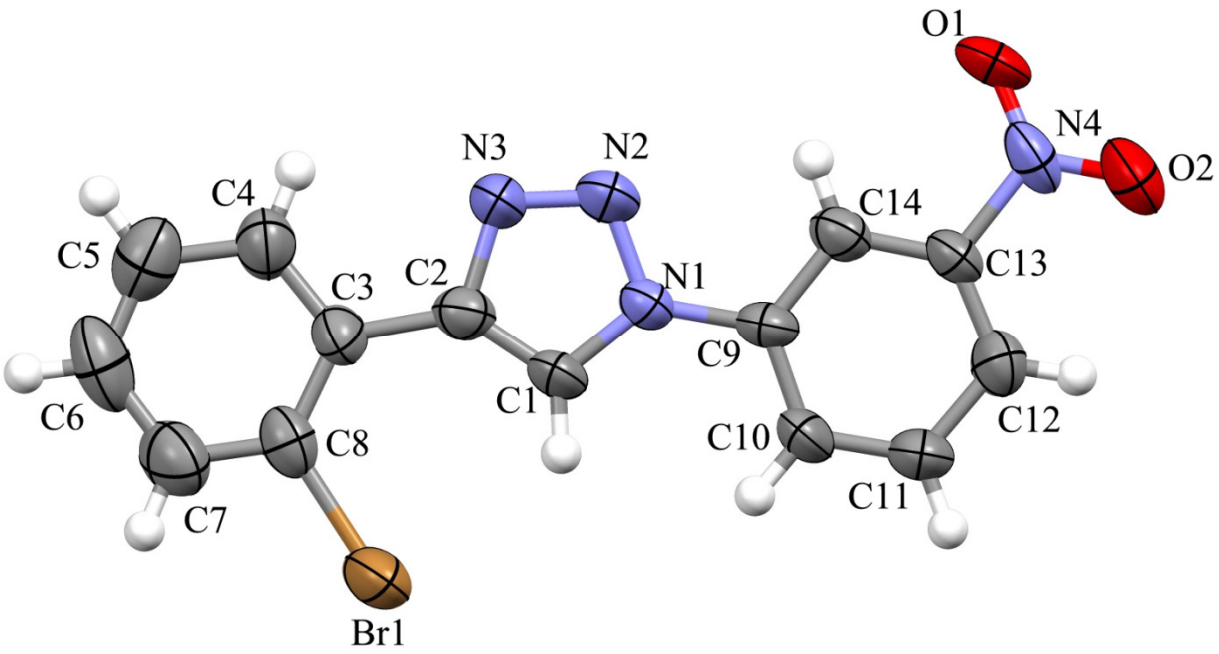


Figure S23. ORTEP of molecule in crystals of **3N2Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

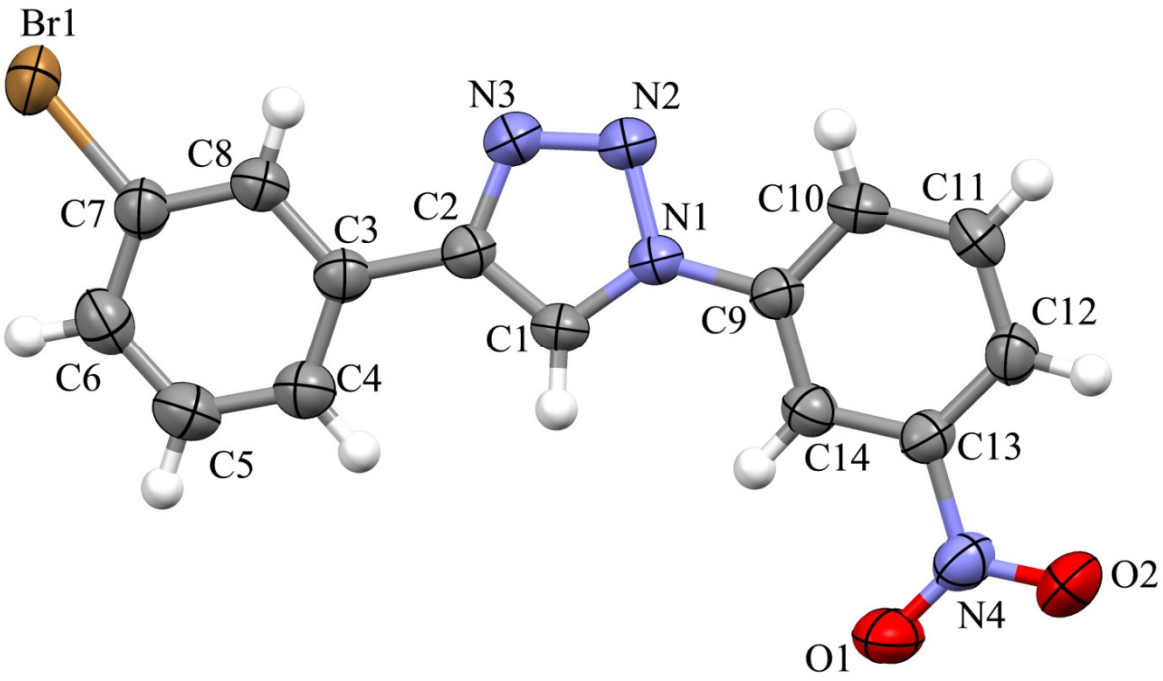


Figure S24. ORTEP of molecule in crystals of **3N3Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

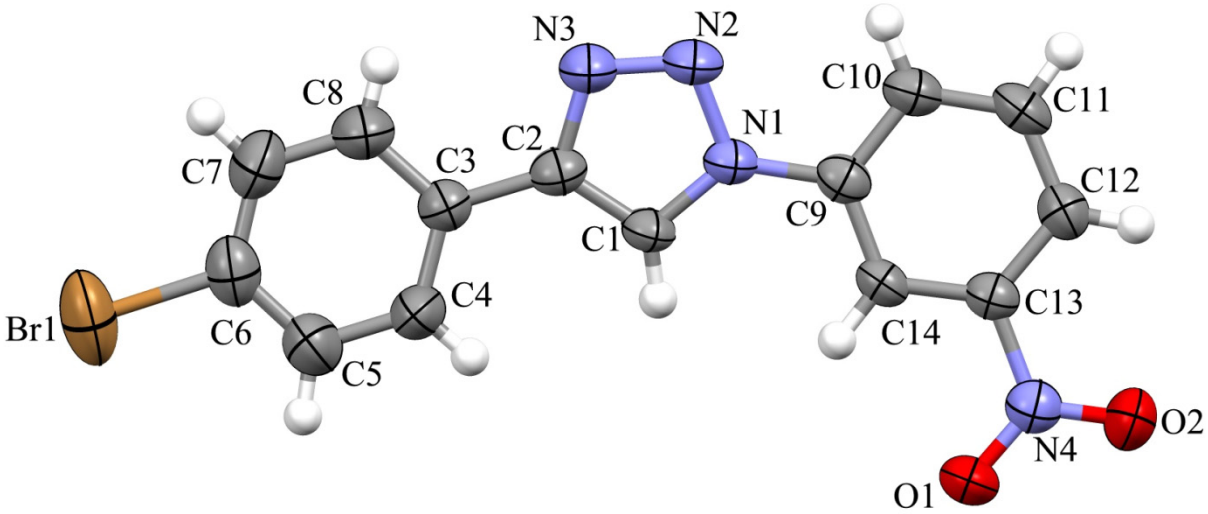


Figure S25. ORTEP of molecule in crystals of **3N4Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

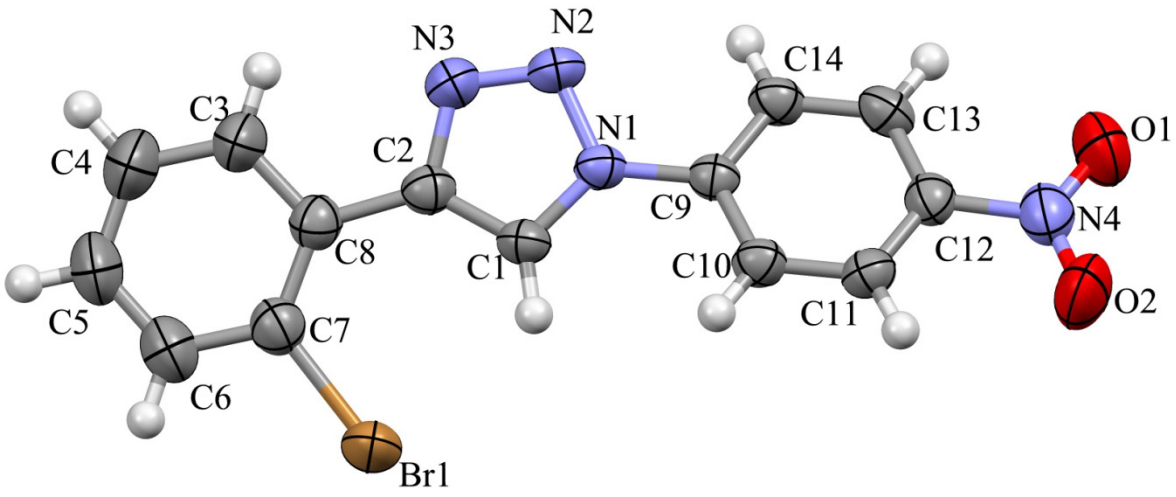


Figure S26. ORTEP of molecule in crystals of **4N2Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

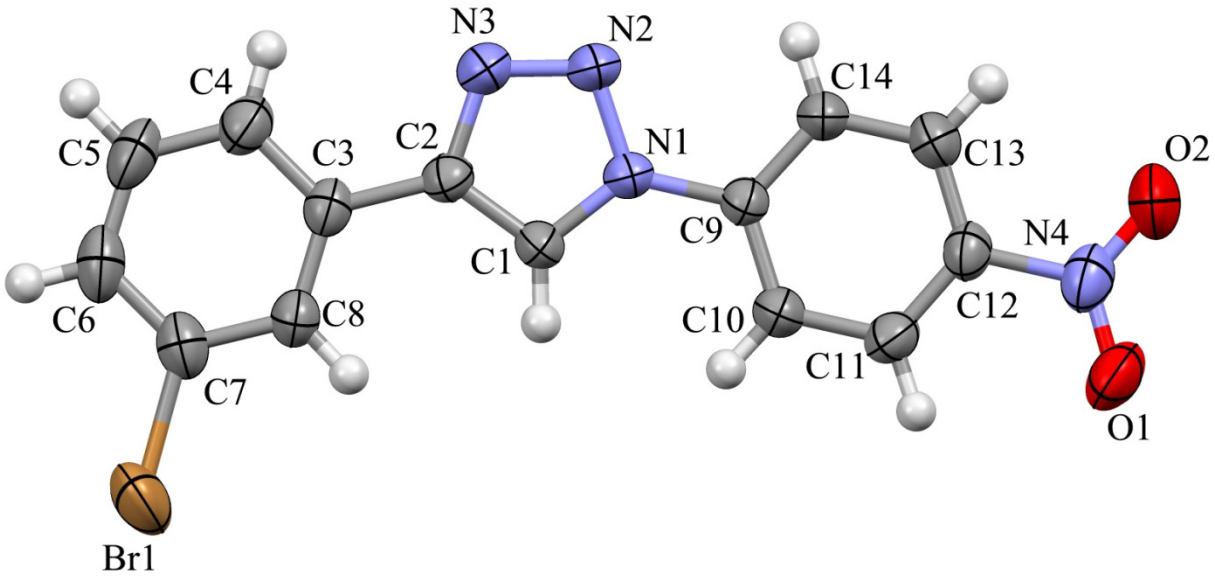


Figure S27. ORTEP of molecule in crystals of **4N3Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

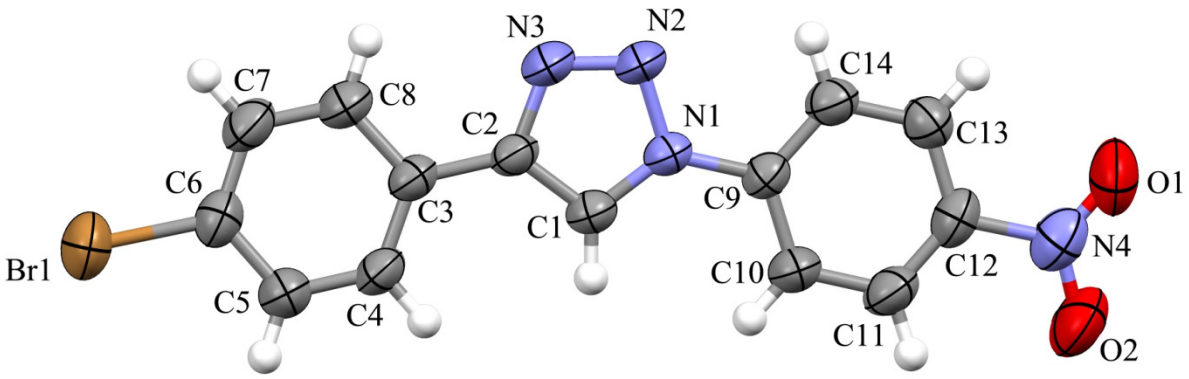


Figure S28. ORTEP of molecule in crystals of **4N4Br**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

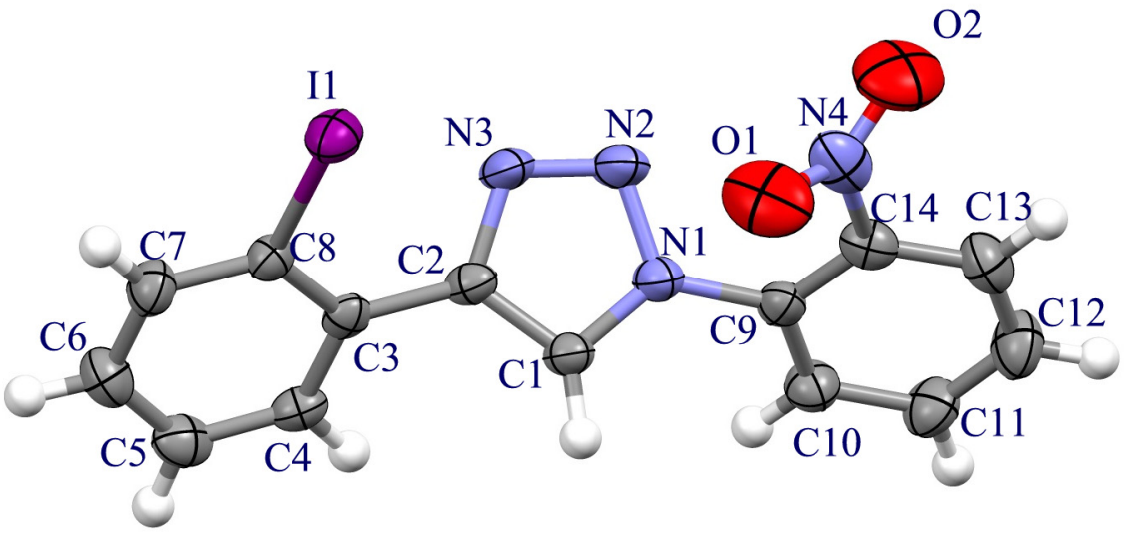


Figure S29. ORTEP of molecule in crystals of **2N2I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

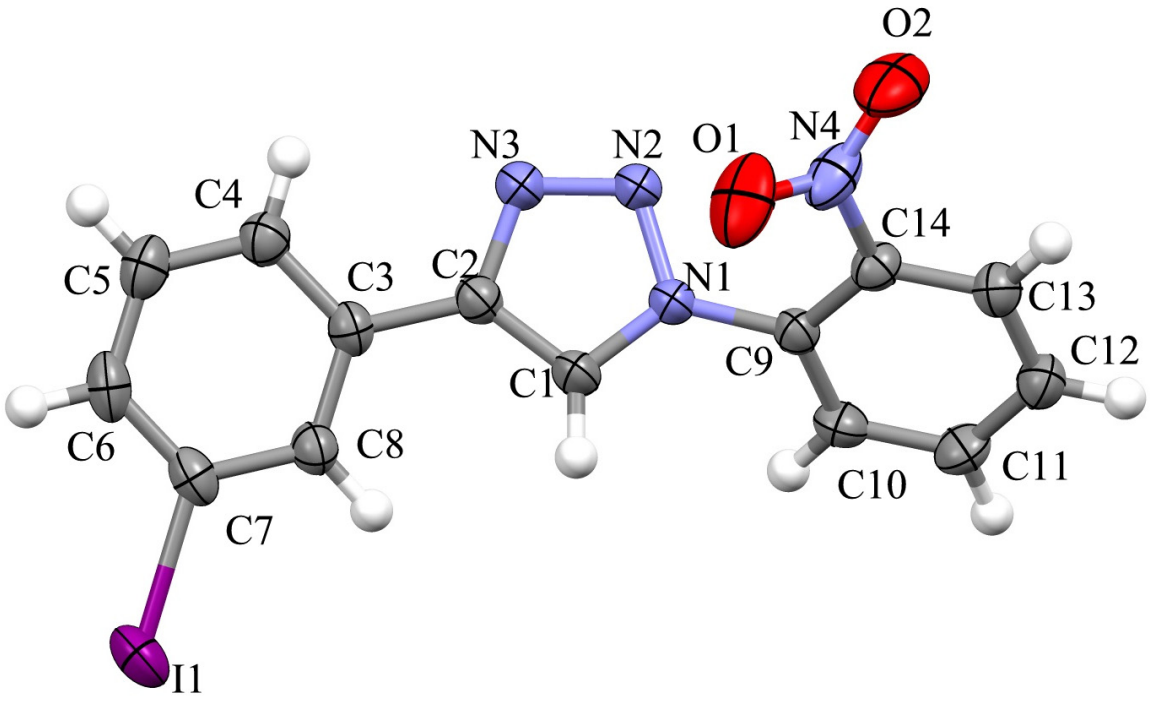


Figure S30. ORTEP of molecule in crystals of **2N3I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

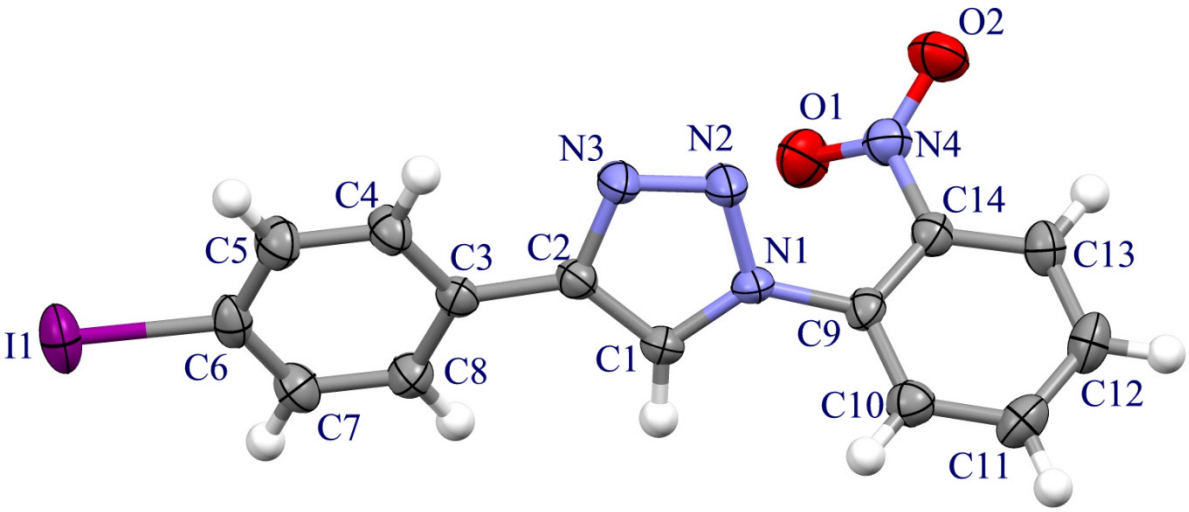


Figure S31. ORTEP of molecule in crystals of **2N4I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

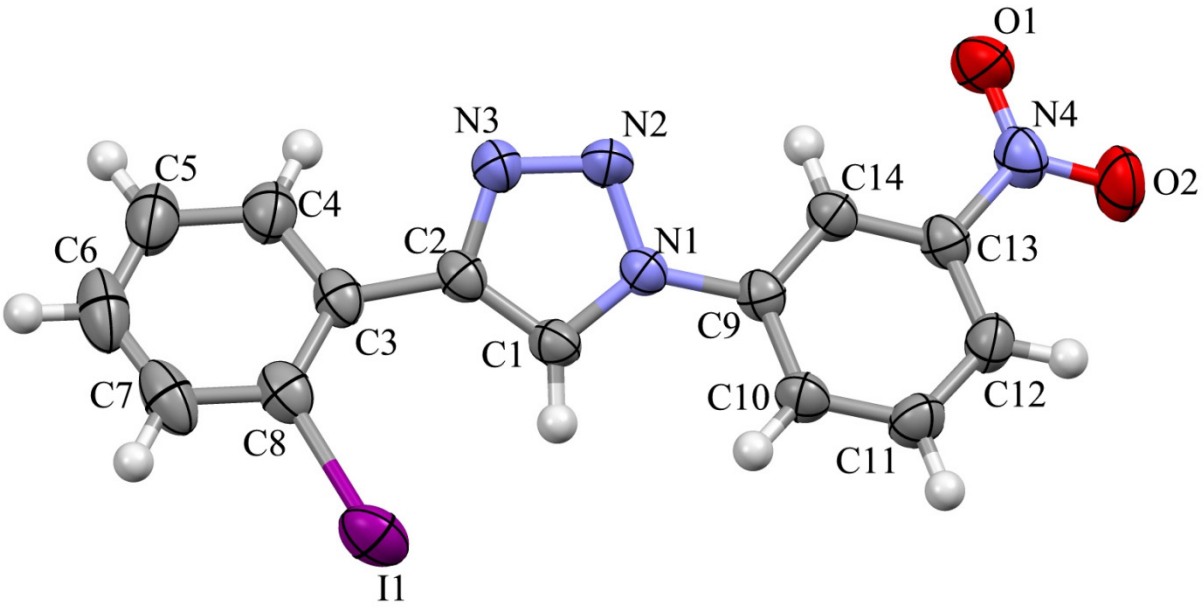


Figure S32. ORTEP of molecule in crystals of **3N2I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

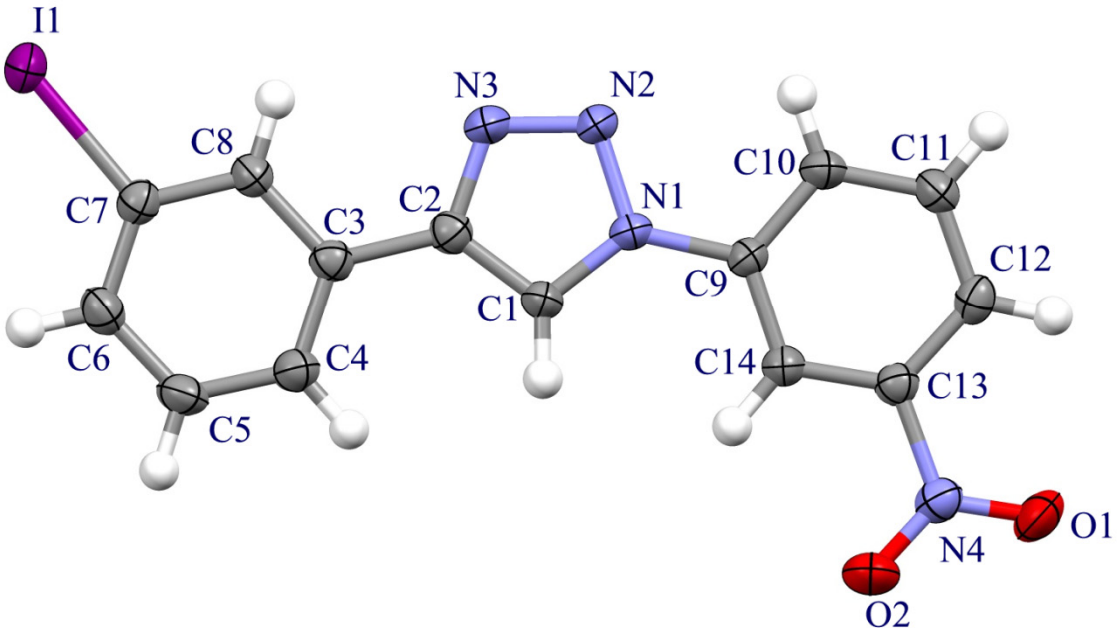


Figure S33. ORTEP of molecule in crystals of **3N3I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

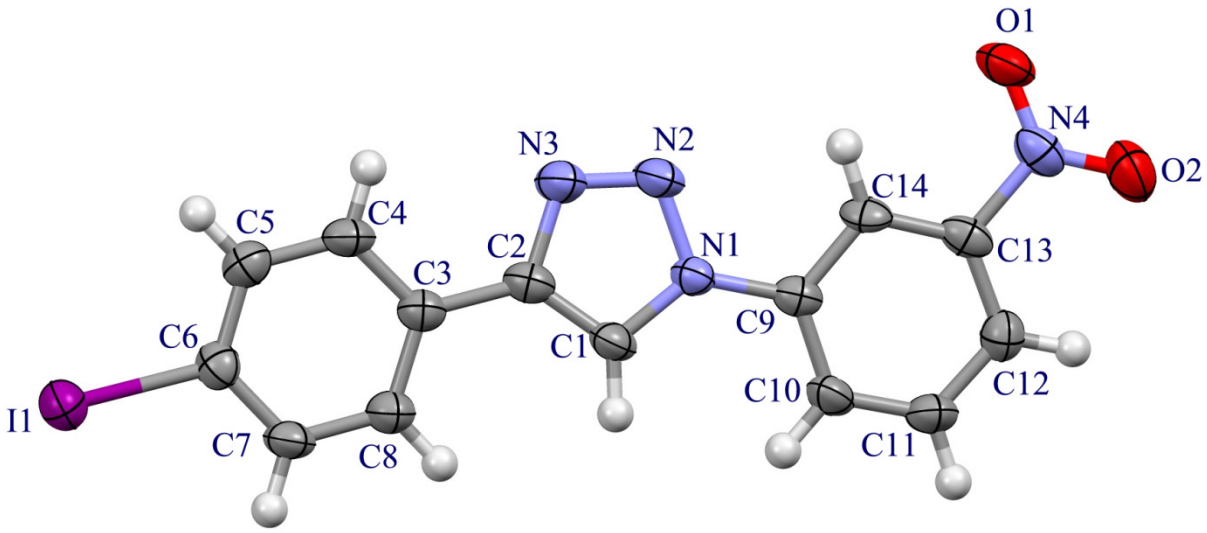


Figure S34. ORTEP of molecule in crystals of **3N4I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

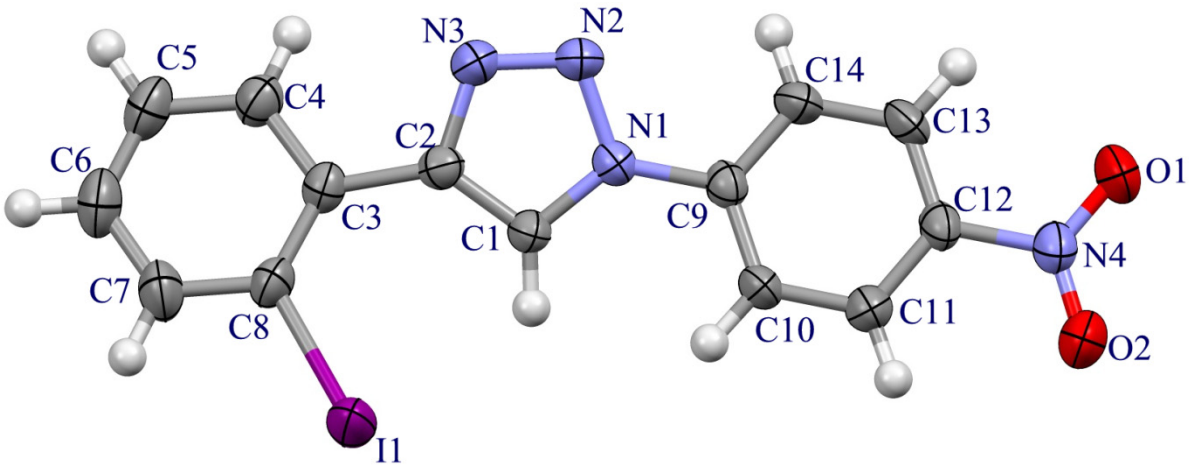


Figure S35. ORTEP of molecule in crystals of **4N2I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

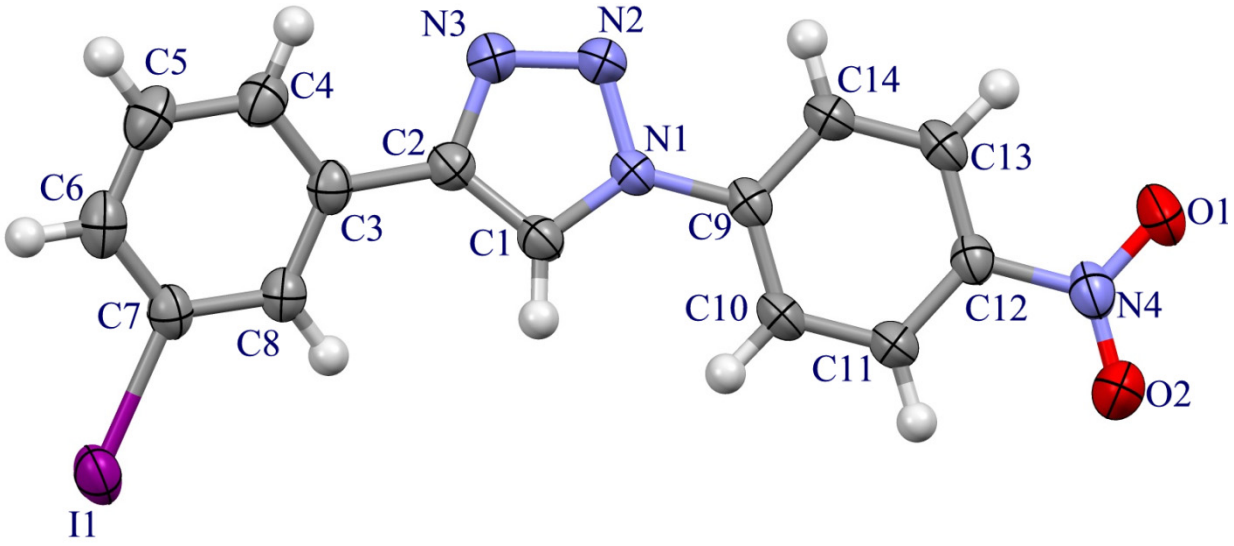


Figure S36. ORTEP of molecule in crystals of **4N3I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.

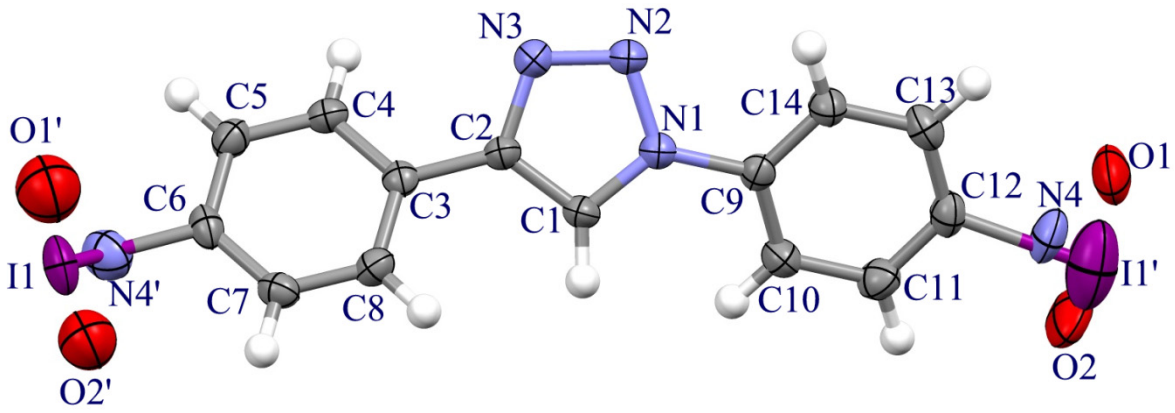


Figure S37. ORTEP of molecule in crystals of **4N4I**. Thermal ellipsoids are drawn at 50% probability level and H-atoms are depicted as spheres of arbitrary radii.