Supporting Information

4-Chloro-3,5-Dinitropyrazole: A Precursor for Promising Insensitive Energetic Compounds

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Caution: All of the nitrogen-rich compounds used are energetic materials and may explode under certain conditions. Appropriate safety precautions should be taken when preparing.

General Methods

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^{1}H, and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, and a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz for ^{15}N spectra using DMSO-d_6 as solvent and locking solvent unless otherwise stated. Chemical sifts in ^{13}C and ^{15}N NMR spectra are reported relative to Me_4Si and $MeNO_2$, respectively. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 °C/min. IR spectra were recorded using KBr pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities were determined at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer. The mass spectrum was performed using a Shimadzu GCMS-QP5050A mass spectrometer.

4-Chloro-3,5-dinitropyrazole (1): Prepared from pyrazole in two steps according to the literature.[1-3] A mixture of 3.4 g (50 mmols) pyrazole and 6.7 g (50 mmols) NCS in 100

mL CCl_4 was stirred at room temperature overnight, and the resulting solid was filtered off. The filtrate was washed with 2×20 mL water and dried with Na_2SO_4. After the solvent was removed, the remaining solid was purified by sublimation. 4-Chloropyrazole (4.62 g) was obtained as a colorless solid, and 8.2 g (80 mmols) was then dissolved in 15 mL 20% oleum with cooling. A mixture of 20 mL 100% HNO_3 in 25 mL 65% oleum was slowly added and the solution was maintained at 85 °C for 1 h. After cooling, the precipitate was collected by filtration and recrystallized from water. Compound **1** (14.9 g) was obtained as a white solid in an overall yield of 86%. ^{13}C NMR (CD_3CN): δ 149.0; 103.1; *m/z*: 192 $[M]^+$

General Procedure for 2, 6, 8 and 9: 0.97 g (5 mmol) of **1** and excess of N-nucleophile (50 mmol) was added to a 70 mL steel vessel, then closed and heated at 130 °C for a suitable time (for **2**: 5h, **6** and **8**: overnight). The mixture is poured into ice water after cooling. Compounds **6** and **8** are precipitated as salts. Compounds **2** and **9** were obtained by acidifying the aqueous solution to pH = 1; the resulting solid plus solution was filtered, and the solid remaining on the filter paper was washed with cold water (5 mL × 2), and air dried.

4-Methylamino-3, 5-dinitropyrazole (2):[3] Orange solid, yield 72%. m.p.: 158 °C, T_{dec}: 194 °C, IR (KBr): 3539, 3422, 3379, 3360, 1619, 1524, 1476, 1427, 1377, 1350, 1294, 1040, 985, 841, 746, 722, 611 cm^{-1}; ^1H NMR: δ 3.0 (s, CH_3); 7.8 (br, NH), ^{13}C NMR: δ 33.4; 129.6; 138.8; *m/z*: 187 $[M]^+$.

Ammonium 4-amino-3, 5-dinitropyrazolate monohydrate (6): Orange needles, yield 80%. T_{dec}: 284 °C; IR (KBr): 3610, 1455, 3313, 3229, 2997, 2794, 1695, 1632, 1458, 1425, 1304, 1190, 1131, 931, 833, 758, 687, 532 cm^{-1}; ^1H NMR: δ 7.2 (s, NH_4^+); 6.6 (s, NH_2), ^{13}C NMR: δ 131.8; 143.1;. EA ($C_3H_8N_6O_5$, 208): Calcd, C: 17.31; H: 3.87; N: 40.38; Found, C: 17.39; H: 3.87; N: 40.79.

Guanidinium 4-guanidino-3, 5-dinitropyrazolate (**8**): Red solid, yield 53%. T_{dec}: 245 °C, IR (KBr): 3470, 3424, 3363, 3156, 1663, 1619, 1576, 1479, 1400, 1303, 1175, 1131, 1003, 880, 847, 619 cm^{-1}; ^1H NMR: δ 5.39 (br); 7.8 (br, NH), ^{13}C NMR: δ 123.0; 148.7; 153.3; 157.9. EA ($C_5H_{10}N_{10}O_4$, 274): Calcd, C: 19.36; H: 4.55; N: 45.15; Found, C: 19.14; H: 4.59; N: 43.00.

4-Guanidino-3, 5-dinitropyrazole (9): Yellowish solid, yield: 75%. T_{dec}: 308 °C, IR (KBr): 3468, 3369, 3256, 3146, 2982, 2902, 1659, 1597, 1574, 1483, 1408, 1354, 1312, 1228, 1167, 1117, 1007, 847, 762, 648, 573 cm^{-1}; ^{1}H NMR: δ 7.45 (s); 9.37 (4, NH), ^{13}C NMR: δ 107.6; 150.3; 156.5, ^{15}N NMR: δ -18.8, -55.1; -301.6; -303.0; EA ($C_4H_5N_7O_4$, 215): Calcd, C: 22.33; H: 2.34; N: 45.58; Found, C: 21.95; H: 2.34; N: 44.73, *m/z*: 215 $[M]^+$.

4-(N-methylnitramino)-3,5-dinitropyrazole (3): Using a modified procedure described in the literature.[3] 1 mL 100% HNO_3 was added slowly to a cooled solution of 0.28g (1.5 mmol) of **2** in 3 mL of acetic acid; 0.5 mL acetic anhydride was then added and the mixture stirred for 1.5 h at room temperature. The excess acid was removed under vacuum leaving 0.34 g colourless solid which was pure based on elemental analysis, yield: 95%. m.p.: 157 °C; T_{dec}: 178 °C, IR (KBr): 3332, 1617, 1551, 1494, 1427, 1358, 1319, 1288, 1192, 1103, 1005, 945, 842, 758, 695, 664, 615, 509 cm^{-1}; ^{1}H NMR: δ 3.62 (s, CH_3); 11.8 (br, NH); ^{13}C NMR: δ 40.4; 111.3; 147.7; EA ($C_4H_4N_6O_6$, 232): Calcd, C: 20.70; H: 1.74; N: 36.21; Found, C: 20.69; H: 1.75; N: 35.86; *m/z*: 186 $[M - NO_2]^+$.

Ammonium 4-(N-methylnitramino)-3,5-dinitropyrazolate (4): Excess 20% aqueous ammonia was added to a solution of 0.3 g (1.3 mmol) of **3** in 5 mL ether; the reaction mixture was stirred for 30 min at r.t., and the solvent was removed under vacuum to obtain 0.31 g of **4,** yield: 96%. T_{dec}: 182 °C, IR (KBr): 3232, 3014, 2695, 1678, 1593, 1505, 1458, 1422, 1347, 1297, 1168, 1109, 959, 847, 752, 694, 661, 608 cm^{-1}; ^{1}H NMR: δ 3.65 (s, CH_3); 5.75 (br, NH_4^+) ^{13}C NMR: δ 41.2; 112.1; 150.6. EA ($C_4H_7N_7O_6$, 249): Calcd, C: 19.28; H: 2.83; N: 39.35; Found, C: 19.49; H: 2.85; N: 39.49;

N-Amino-4-(N-methylnitramino)-3,5-dinitropyrazole (5): 0.51g (2 mmol) freshly prepared tosylhydroxylamine[4, 5] in dichloromethane was added to the solution of 0.4 g (1.6 mmole) of **4** in 20 mL CH_3CN. The mixture was stirred overnight; the solvent was removed and the residue was washed with ethyl acetate (15 mL × 3). The filtrate was evaporated and solid obtained was purified by chromatography (EtOAc: DCM=1:10), yield 0.27 g of **5** (68%). M.p. 86 °C, T_{dec}: 176 °C; IR (KBr): 3349, 3285, 1598, 1527, 1458, 1421, 1387, 1337, 1304, 1119, 1077, 984, 945, 883, 787, 733, 677cm^{-1}; ^{1}H NMR: 3.67 (s, CH_3); 8.12 (s, NH_2), ^{13}C NMR 111.7; 135.7 ppm, ^{15}N NMR: δ -27.27, -31.93, -

33.30, -86.15, -163.74, -221.60, -280.92; EA ($C_4H_5N_7O_6$, 247): Calcd, C: 18.76; H: 2.36; N: 38.28; Found: C: 19.05; H: 2.19; N: 38.56; *m/z*: 201 $[M - NO_2]^+$.

1,4-Diamino-3,5-dinitropyrazole (7): Using a method similar to that for preparing **5,** but with **6**, yield: 52%, the product was purified by chromatography (EtOAc: DCM=1:30), crystals suitable for X-ray diffraction were grown from ethyl acetate. M.p. 195 °C, T_{dec}: 241 °C; IR (KBr): 3470, 3348, 3252, 1626, 1559, 1505, 1463, 1439, 1315, 1194, 911, 863, 822, 777, 662, 478 cm^{-1}; ^1H NMR: δ 7.24 (s, C-NH_2); 7.92 (br, N-NH_2), ^{13}C NMR: δ 128.0; 130.2, 134.0, ^{15}N NMR: δ -23.22, -28.83, -85.00, -166.54, -279.74, -314.53; EA ($C_3H_4N_6O_4$, 188): Calcd, C: 19.16; H: 2.14; N: 44.52; Found, C: 19.13; H: 2.08; N: 44.52; *m/z*: 188 $[M]^+$.

1-(3,5-Dinitro-1H-pyrazol-4-yl)-3-nitroguanidine (10): 0.2 g (0.93 mmol) of **9** was slowly added to the mixture of 1 mL 98% H_2SO_4 and 0.5 mL 100% HNO_3 at 0 °C with stirring for 1 h and the solution was poured into 5 g ice water. The resulting white precipitate was filtered and air dried, yield 0.22 g (85%). T_{dec}: 236 °C, , IR (KBr): 3426, 3319, 3252, 3148, 3033,1656, 1621, 1537, 1504, 1468, 1422, 1344, 1266, 1206, 1055, 1008, 953, 841, 785, 754, 702, 675, 647, 579, 483 cm^{-1}; ^1H NMR: δ 8.48 (br); 9.61 (s), ^{13}C NMR: δ 110.2; 145.8; 158.0, EA ($C_4H_4N_8O_6$, 260): Cacld, C: 18.47; H: 1.55; N: 43.08; Found, C: 17.89; H: 1.63; N: 41.76.

N-Methyl-4-chloro-3,5-dinitropyrazole (11): Prepared from **1** using the literature method.[6] ^{13}C NMR (CD_3CN): 148.1; 143.2; 105.9; 43.8, *m/z*: 206 $[M]^+$.

N-Methyl-4-azido-3,5-dinitropyrazole (12): 0.13g (2 mmol) of NaN_3 was added in one portion to the solution of 0.21 g (1 mmol) **11** in 3 mL DMSO; the reaction mixture was stirred 4h at room temperature, and the mixture was poured into 10 g ice water. The precipitate formed was filtered, washed with 5 mL cold water and air dried to obtain 0.2 g pale yellow solid, yield, 92%. M.p.: 98 °C, T_{dec}: 161°C (dec); IR (KBr): 3426, 2137, 1585, 1547, 1511, 1444, 1376, 1332, 1261, 1055, 897, 762, 488 cm^{-1}; ^1H NMR: δ 4.24 (s); ^{13}C NMR: δ 43.0; 116.7, 137.9, 144.0; EA ($C_4H_3N_7O_4$, 213): Calcd, C: 22.54; H: 1.42; N: 46.01; Found, C: 22.48; H: 1.43; N: 45.50; *m/z*: 213 $[M]^+$.

N-Methyl-3-nitro-4-diazo-5-oxide pyrazole (13): 0.32 g (1.5 mmol) **12** in 6 mL acetic acid was heated at 100 °C for 48 h, and the product was purified by chromatography (DCM: Hexane= 10: 1). The crystals were grown from ethyl acetate. M.p. 127°C, T_{dec}:

228°C (dec), IR (KBr): 2155, 1697, 1499, 1444, 1369, 1341, 1271, 1068, 1016, 920, 793, 750, 702, 527 cm^{-1}; ^{1}H NMR (CD_3CN): δ 3.50 (s); ^{13}C NMR (CD_3CN): δ 33.8, 129.9, 162.9, EA ($C_4H_3N_5O_3$, 169): Calcd, C: 28.41; H: 1.79; N: 41.42; Found, C: 28.44; H: 1.81; N: 41.08 ; *m/z*: 169 $[M]^+$.

Hydrazinium 4-methyl-6-nitro-3-oxido-4H-pyrazolo[3,4-d][1,2,3]triazol-ide (14): 0.2 mL (4 mmol) hydrazine monohydrate was added to 0.2 g (0.97 mmol) of **12** in 10 mL ethanol. The mixture was stirred overnight at room temperature. The yellow precipitate was filtered and washed with 5 mL ethanol, and air dried to obtain 0.15 g **14**, yield 71%. T_{dec}: 146°C (dec); IR (KBr): 3324, 3129, 3048, 2860, 2733, 2640, 1614, 1535, 1491, 1439, 1363, 1333,1271, 1229, 1153, 1085, 1034, 968, 818, 756, 602, 426 cm^{-1}; ^{1}H NMR: δ 4.02 (3H, s, CH_3), 7.23 (5H, br, $N_2H_5^+$); ^{13}C NMR: δ 37.0; 132.74, 137.1, 38.0; EA ($C_4H_8N_8O_3$, 216): Calcd, C: 22.23; H: 3.73; N: 51.84; Found, C: 22.16; H: 3.73; N: 51.67; *m/z*: 184.

4-Methyl-6-nitro-1,4-dihydropyrazolo[3,4-d][1,2,3]triazole 3-oxide (15): 0.22g (1 mmol) of **14** in 2 mL H_2O was treated with 10% HCl to pH = 1. The precipitate formed was collected by filtration to obtain a yellowish solid, yield 0.16 g (88%). T_{dec}: 101 °C (dec); IR (KBr): 3451, 2899, 2557, 2440, 1649, 1613, 1538, 1519, 1485, 1398, 1368, 1341, 1267, 1227, 1088, 1043, 968, 941, 816, 758, 623, 583, 462 cm^{-1}; ^{1}H NMR: δ 4.05 (3H, s, CH_3); EA ($C_4H_6N_6O_4$, 202): Calcd, C: 23.77; H: 2.99; N: 41.58; Found, C: 23.69; H: 2.95; N: 41.19; *m/z*: 184 $[M]^+$.

N-Methyl-4-amino-3,5-dinitropyrazole (16): Orange solid obtained by a modified method;[7] 1.05 g (5 mmol) of **11** and 4 mL of aqueous ammonia was heated at 130 °C overnight in a sealed vessel. After cooling, the solvent was removed by air, and a small amount of water (4 mL) was added. The product was collected by filtration, yield 0.64 g (68%). M.p. 159°C, T_{dec}: 270 °C; IR (KBr): 3470, 3360, 1635, 1566, 1475, 1434, 1392, 1345, 1310, 1113, 1043, 888, 830, 784, 754, 666, 619, 471 cm^{-1}; ^{1}H NMR ($CDCl_3$): 4.30 (s, CH_3); 6.32 (s, NH_2); ^{13}C NMR ($CDCl_3$): 43.11; 129.3; 129.7; 131.0; EA ($C_4H_5N_5O_4$, 187): Calcd, C: 25.68; H: 2.69; N: 37.43; Found, C: 25.00; H: 2.69; N: 36.53; *m/z*: 187 $[M]^+$;

N-methyl-3,4,5-trinitropyrazole (17): yellowish solid, prepared according to the literature method.[8] 0.19 g (1 mmol) of **3** was added to 2.6 mL of conc. H_2SO_4 cooled by

ice bath, and then 1.3 mL of 30% H_2O_2 was added drop wise. The mixture was stirred at 0 °C for 3h and the reaction mixture was poured into 10 g ice water. The precipitate was separated by filtration to obtain 0.11g of **17;** the filtrate was extracted with ethyl acetate (10mL × 3) and dried by Na_2SO_4. After removal of the solvent by air, an additional 0.09 g of product was obtained. Yield: 86%. M.p. 90 °C, b.p. 265 °C; T_{dec}: 285 (dec), IR (KBr): 2889, 1539, 1479, 1448, 1339, 1294, 1163, 1103, 1053, 905, 845, 800, 777, 671, 610, 532, 473 cm^{-1}; ^1H NMR ($CDCl_3$): 4.40 (s, CH_3; ^{13}C NMR ($CDCl_3$): 43.2; 123.5; 137.7; 143.0; EA ($C_4H_3N_5O_6$, 217): Cacld, C: 22.13; H: 1.39; N: 32.26; Found, C: 21.69; H: 1.46; N: 31.21. *m/z*: 217 $[M]^+$.

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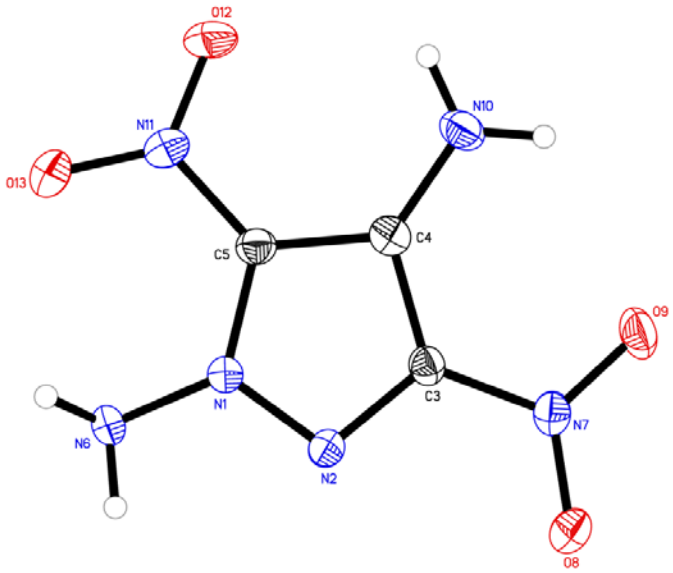
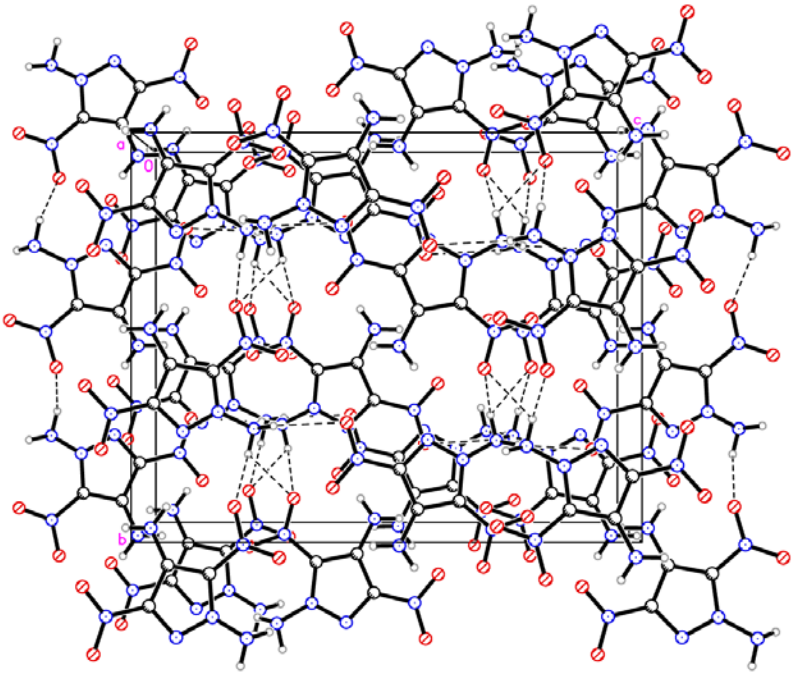
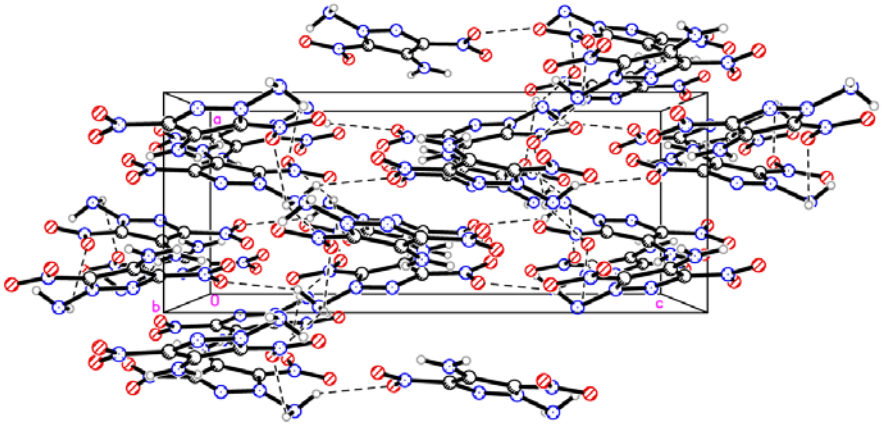
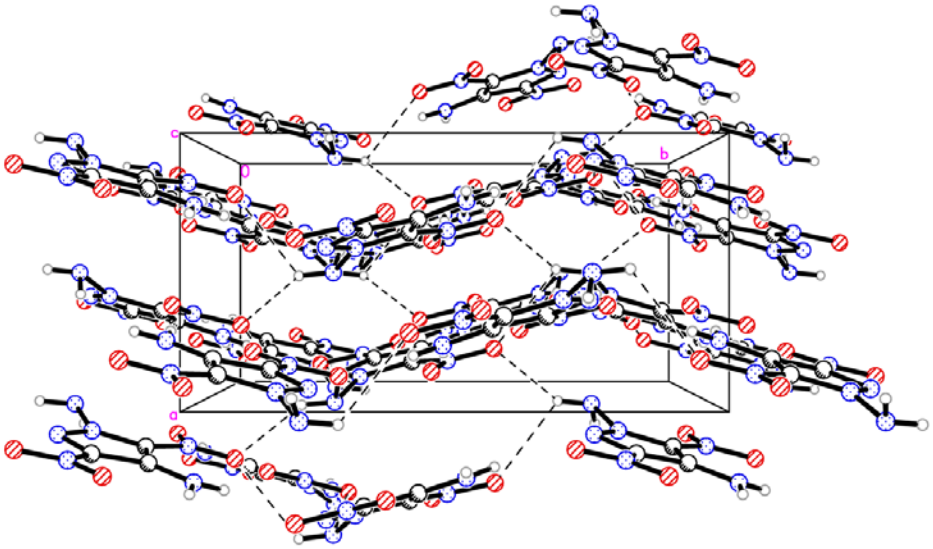
X-ray crystallography

Compound 7

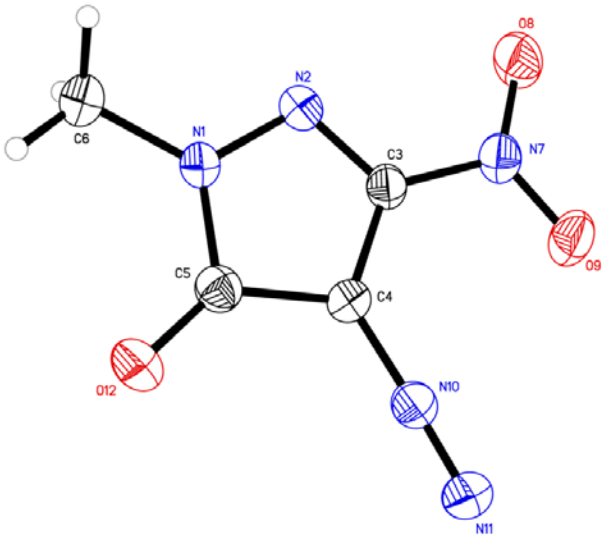


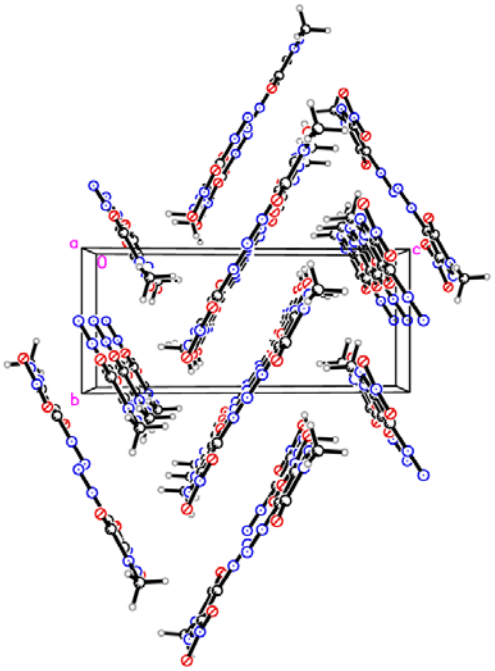


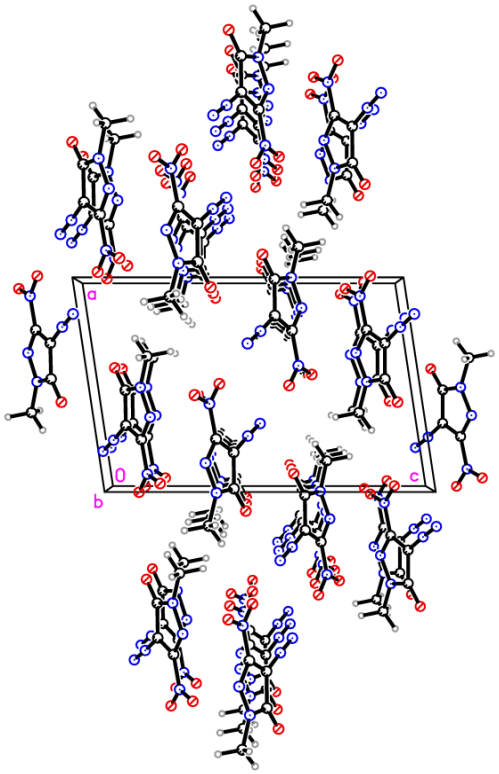


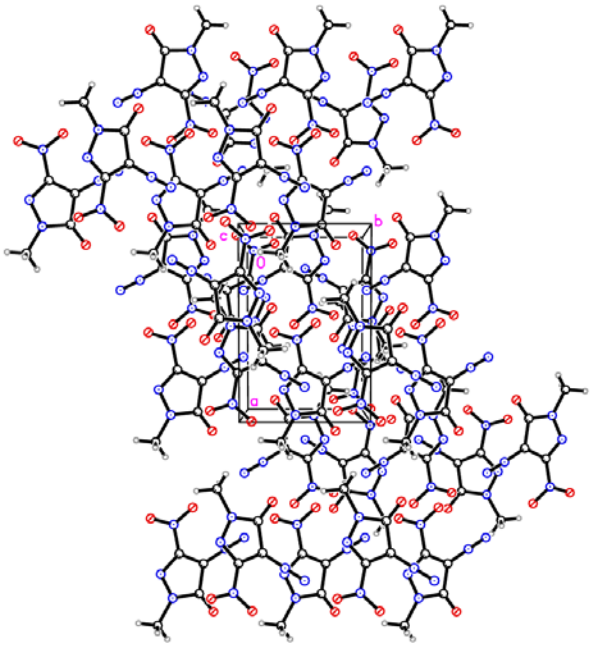


Compound 13









Single-crystal X-ray Diffraction Analysis of compound 7 (CCDC 906540)

$C_3H_4N_6O_4$, FW = 188.12, Orthorhombic, Pbca, a = 6.4359(4) Å, b= 12.7184(7) Å, c = 15.8769(10) Å, α = 90°, β = 90°, γ = 90°, V = 1299.59(14) Å^3, Z = 8, ρ_{calc} = 1.923 Mg/m^3, μ = 0.175 mm^{-1}, *F*(000) = 768, R_1 = 0.0286 for 1246 observed (I > 2σI) reflections and 0.0304 for all 1333 reflections, Goodness-of-fit = 1.063, 130 parameters.

An orange plate of dimensions 0.44 x 0.32 x 0.14 mm^2 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2010.3-0].[1] Data reduction was performed using *SAINT* [v7.68A][2] and *XPREP* [v2008/2][3]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[4] The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v2008/4] system of programs.[5] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Single-crystal X-ray Diffraction Analysis of 13 (CCDC 906539).

$C_4H_3N_5O_3$, FW = 169.11, Monoclinic, $P2_1/n$, a = 8.7709(12) Å, b= 5.7826(8) Å, c = 13.3180(18) Å, α = 90°, β = 98.504(6)°, γ = 90°, V = 668.04(16) Å^3, Z = 4, ρ_{calc} = 1.681 Mg/m^3, μ = 0.146 mm^{-1}, *F*(000) = 344, R_1 = 0.0422 for 804 observed (I > 2σI) reflections and 0.0989 for all 1375 reflections, Goodness-of-fit = 1.022, 110 parameters.

A yellow plate of dimensions 0.32 x 0.08 x 0.01 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 293(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2010.3-0].[1] Data Reduction was performed using *SAINT* [v7.68A][2] and *XPREP* [v2008/2][3]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[4] The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v2008/4] system of programs.[5] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

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Table S1. Crystal data and structure refinement for **7** and **13**.

	7	**13**
Empirical formula	$C_3H_4N_6O_4$	$C_4H_3N_5O_3$
Formula weight	188.12	169.11
Temperature	150(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	$P2_1/n$
Unit cell dimensions	a = 6.4359(4) Å = 90°.□	a = 8.7709(12) Å a= 90°.
	b = 12.7184(7) Å = 90°.□	b = 5.7826(8) Å b= 98.504(6)°.
	c = 15.8769(10) Å = 90°.□	c = 13.3180(18) Å g = 90°.
Volume	1299.59(14) $Å^3$	668.04(16) $Å^3$
Z	8	4
Density (-123ºC)	1.923 Mg/m^3	1.681 Mg/m^3
Density (20ºC)	1.874 Mg/m^3	
Absorption coefficient	0.175 mm^{-1}	0.146 mm^{-1}
F(000)	768	344
Crystal size	0.44 x 0.32 x 0.14 mm^3	0.32 x 0.08 x 0.01 mm^3
Theta range for data collection	2.57 to 26.53°.	2.61 to 26.55°.
Index ranges	-8<=h<=8, -15<=k<=15, -19<=l<=18	-10<=h<=10, -7<=k<=7, -16<=l<=15
Reflections collected	11406	6049
Independent reflections	1333 [R_{int} = 0.0199]	1375 [R_{int} = 0.0482]
Completeness to theta = 26.53°	99.5 %	98.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9759 and 0.9269	0.9985 and 0.9549
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1333 / 6 / 130	1375 / 0 / 110
Goodness-of-fit on F^2	1.063	1.022
Final R indices [I>2sigma(I)]	R_1 = 0.0286, wR_2 = 0.0768	R_1 = 0.0422, wR_2 = 0.0848
R indices (all data)	R_1 = 0.0304, wR_2 = 0.0784	R_1 = 0.0989, wR_2 = 0.1037
Largest diff. peak and hole	0.287 and -0.225 $e.Å^{-3}$	0.154 and -0.149 $e.Å^{-3}$
CCDC	906539	906540

Table S2. Hydrogen bonds for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...O(8)#1	0.856(9)	2.405(12)	3.1591(14)	147.4(16)
N(6)-H(6B)...O(12)#2	0.860(9)	2.443(14)	2.9920(13)	122.3(13)
N(10)-H(10A)...O(9)	0.850(9)	2.293(15)	2.8235(15)	120.7(14)
N(10)-H(10B)...O(12)	0.842(9)	2.300(15)	2.8147(15)	119.7(14)

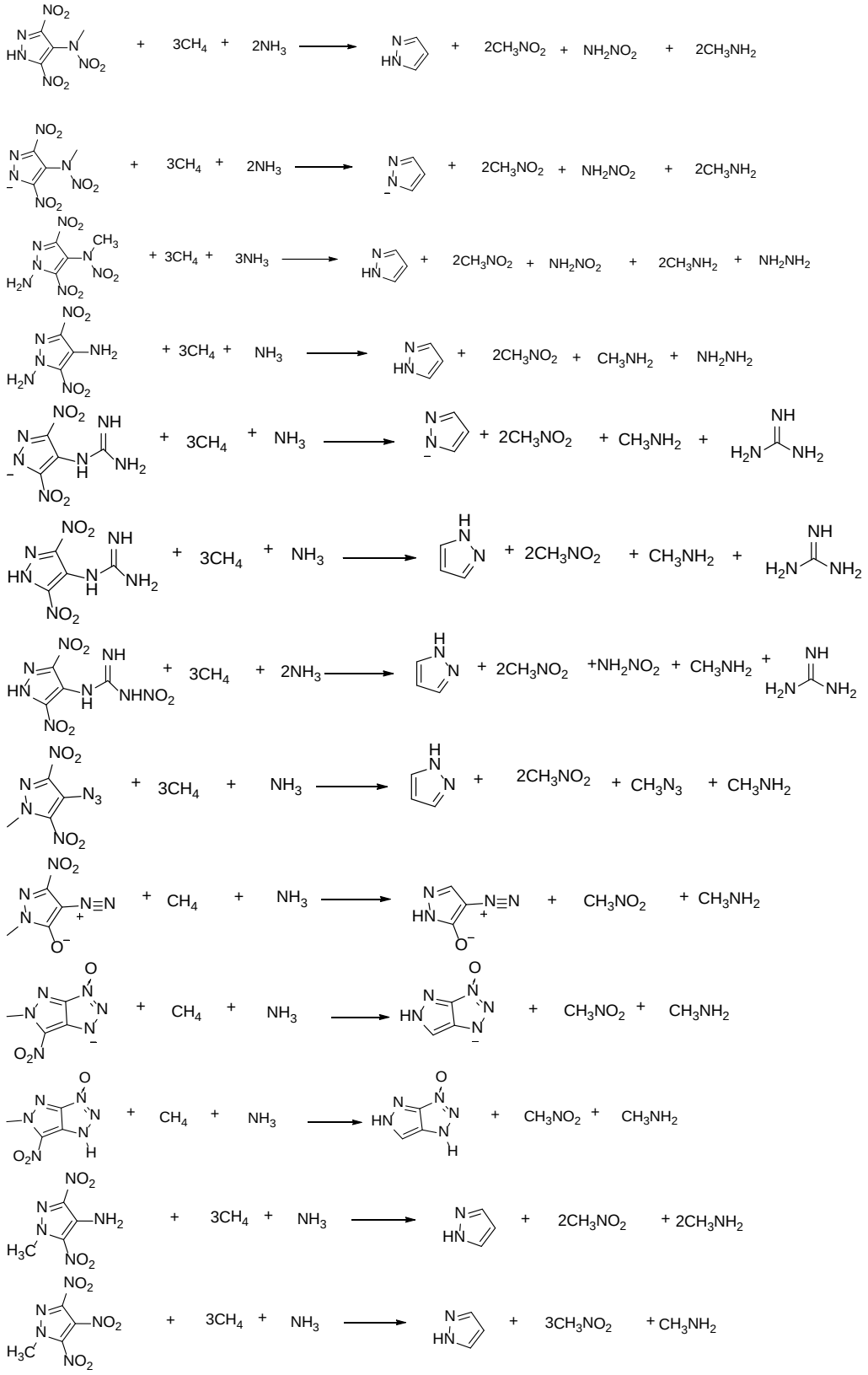
Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z-1/2 #2 -x,y+1/2,-z+1/2

Table S3. Bond lengths [Å] and angles [°] for **7** and **13**.

7	Bond length [Å]	**13**	Bond length [Å]
N(1)-N(2)	1.3059(14)	N(1)-N(2)	1.363(2)
N(1)-C(5)	1.3758(15)	N(1)-C(5)	1.386(3)
N(1)-N(6)	1.3912(14)	N(1)-C(6)	1.451(3)
N(2)-C(3)	1.3534(15)	N(2)-C(3)	1.297(3)
C(3)-N(7)	1.4053(15)	C(3)-C(4)	1.407(3)
C(3)-C(4)	1.4074(16)	C(3)-N(7)	1.429(3)
C(4)-N(10)	1.3363(16)	C(4)-N(10)	1.323(3)
C(4)-C(5)	1.4028(17)	C(4)-C(5)	1.446(3)
C(5)-N(11)	1.3979(15)	C(5)-O(12)	1.218(2)
N(6)-H(6A)	0.856(9)	C(6)-H(6A)	0.9600
N(6)-H(6B)	0.860(9)	C(6)-H(6B)	0.9600
N(7)-O(8)	1.2373(14)	C(6)-H(6C)	0.9600
N(7)-O(9)	1.2416(13)	N(7)-O(8)	1.220(2)
N(10)-H(10A)	0.850(9)	N(7)-O(9)	1.224(2)
N(10)-H(10B)	0.842(9)	N(10)-N(11)	1.116(2)
N(11)-O(13)	1.2340(14)		
N(11)-O(12)	1.2404(14)		
7	angles [°]	**13**	angles [°]
N(2)-N(1)-C(5)	112.41(9)	N(2)-N(1)-C(5)	114.47(17)
N(2)-N(1)-N(6)	120.20(9)	N(2)-N(1)-C(6)	120.27(19)
C(5)-N(1)-N(6)	126.32(10)	C(5)-N(1)-C(6)	125.24(18)
N(1)-N(2)-C(3)	104.66(9)	C(3)-N(2)-N(1)	105.64(17)
N(2)-C(3)-N(7)	119.65(10)	N(2)-C(3)-C(4)	112.02(19)
N(2)-C(3)-C(4)	113.61(10)	N(2)-C(3)-N(7)	121.40(19)
N(7)-C(3)-C(4)	126.66(10)	C(4)-C(3)-N(7)	126.59(19)
N(10)-C(4)-C(5)	128.81(11)	N(10)-C(4)-C(3)	128.8(2)
N(10)-C(4)-C(3)	129.87(11)	N(10)-C(4)-C(5)	124.71(19)
C(5)-C(4)-C(3)	101.31(10)	C(3)-C(4)-C(5)	106.49(17)
N(1)-C(5)-N(11)	124.10(11)	O(12)-C(5)-N(1)	126.1(2)
N(1)-C(5)-C(4)	107.99(10)	O(12)-C(5)-C(4)	132.5(2)
N(11)-C(5)-C(4)	127.91(11)	N(1)-C(5)-C(4)	101.37(18)
N(1)-N(6)-H(6A)	108.1(12)	N(1)-C(6)-H(6A)	109.5
N(1)-N(6)-H(6B)	105.6(11)	N(1)-C(6)-H(6B)	109.5
H(6A)-N(6)-H(6B)	111.7(14)	H(6A)-C(6)-H(6B)	109.5
O(8)-N(7)-O(9)	123.55(10)	N(1)-C(6)-H(6C)	109.5
O(8)-N(7)-C(3)	119.68(10)	H(6A)-C(6)-H(6C)	109.5
O(9)-N(7)-C(3)	116.78(10)	H(6B)-C(6)-H(6C)	109.5
C(4)-N(10)-H(10A)	119.2(11)	O(8)-N(7)-O(9)	124.52(19)
C(4)-N(10)-H(10B)	119.9(12)	O(8)-N(7)-C(3)	119.46(19)
H(10A)-N(10)-H(10B)	119.7(16)	O(9)-N(7)-C(3)	116.0(2)
O(13)-N(11)-O(12)	124.25(10)	N(11)-N(10)-C(4)	177.7(2)
O(13)-N(11)-C(5)	119.70(10)		
O(12)-N(11)-C(5)	116.05(10)		

Table S4 Calculated (B3LYP/6-31+G**// MP2/6-311++G**) total energy(E0), zero-point energy (*ZPE*), values of the correction (Hr), and heats of formation (HOF) of **3**-**17**

Entry	E_0	*ZPE*	H_r	HOF [kJ/mol]
3	-932.3127103	0.122934	0.137988	137.0
4(anion)	-931.8181065	0.109339	0.124162	472.8
5	-987.5012822	0.139063	0.155599	220.7
7	-744.2440734	0.109627	0.121794	166.0
8(anion)	-836.9996673	0.119235	0.132653	491.0
9	-837.5020045	0.132976	0.146643	182.6
10	-1041.5729831	0.134501	0.150874	236.6
12	-744.2440734	0.109627	0.121794	436.0
13	-652.0221153	0.091789	0.105122	177.0
14(anion)	-706.6515601	0.096885	0.108238	549.6
15	-707.1647594	0.110579	0.122264	414.4
16	-728.2485174	0.121063	0.133433	64.5
17	-877.0963389	0.105894	0.119874	109.1



Scheme S1. Isodesmic reactions

^{1}H, ^{13}C and ^{15}N NMR Spectra

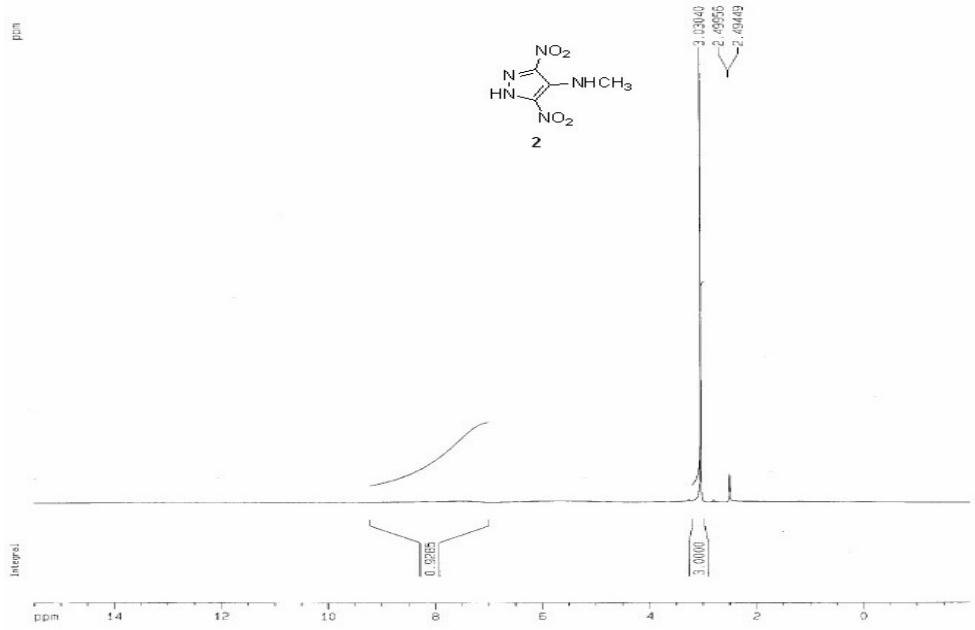


Figure S1

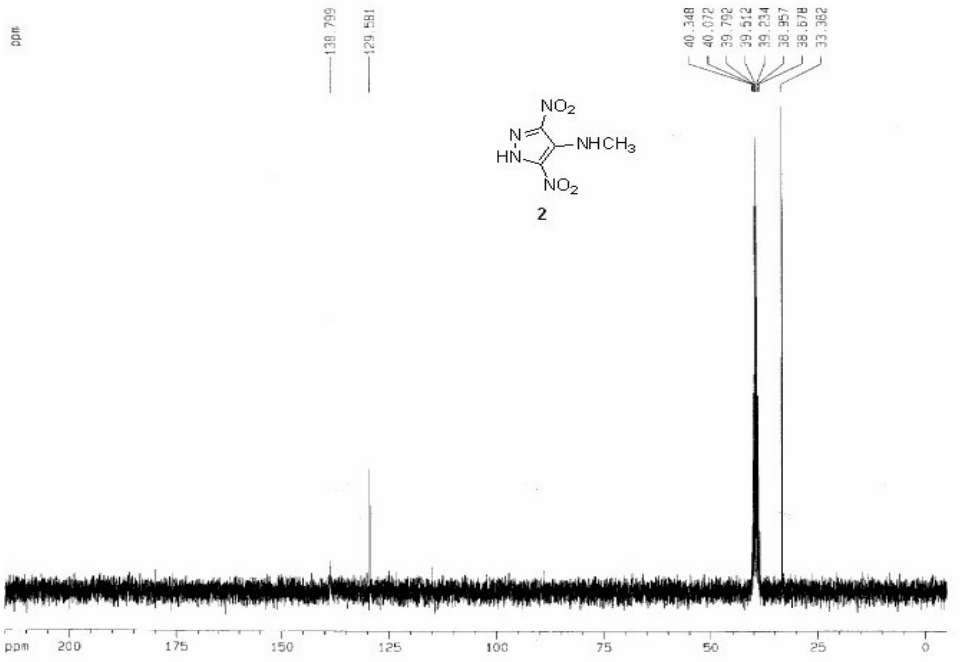


Figure S2

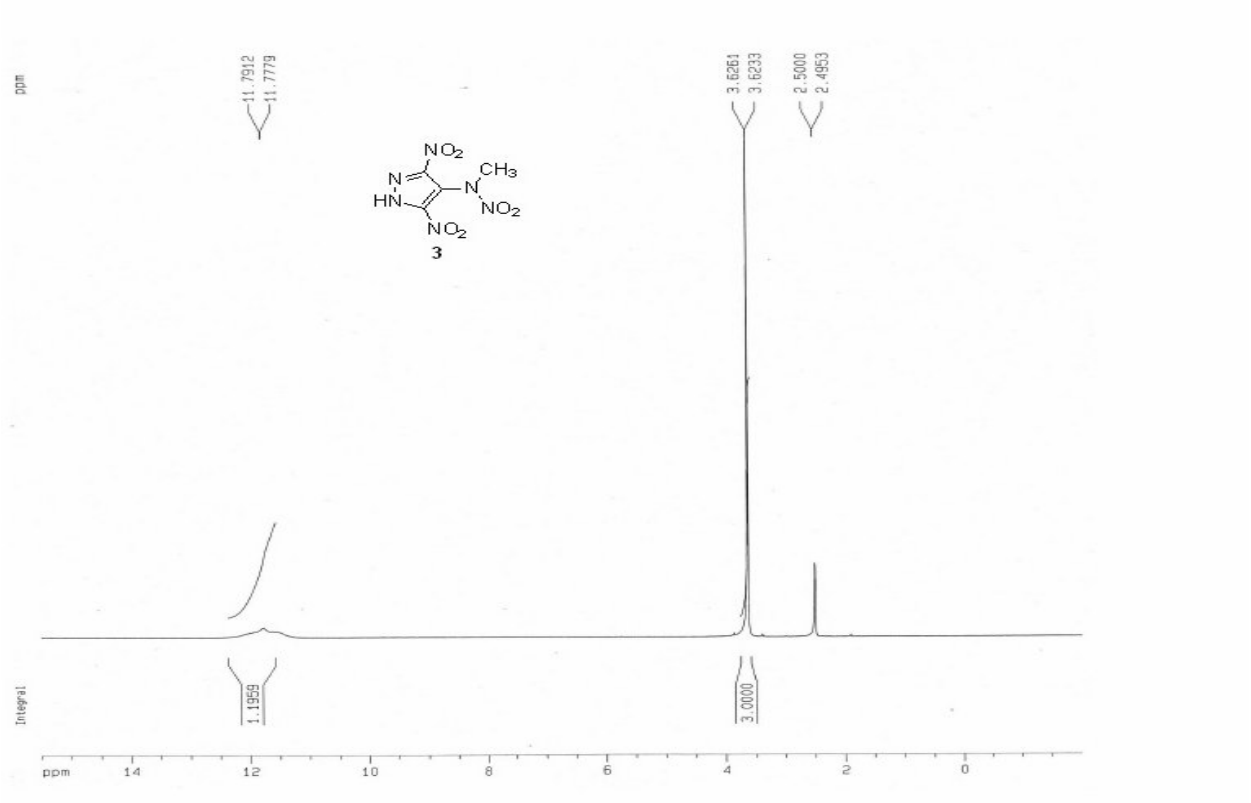


Figure S3

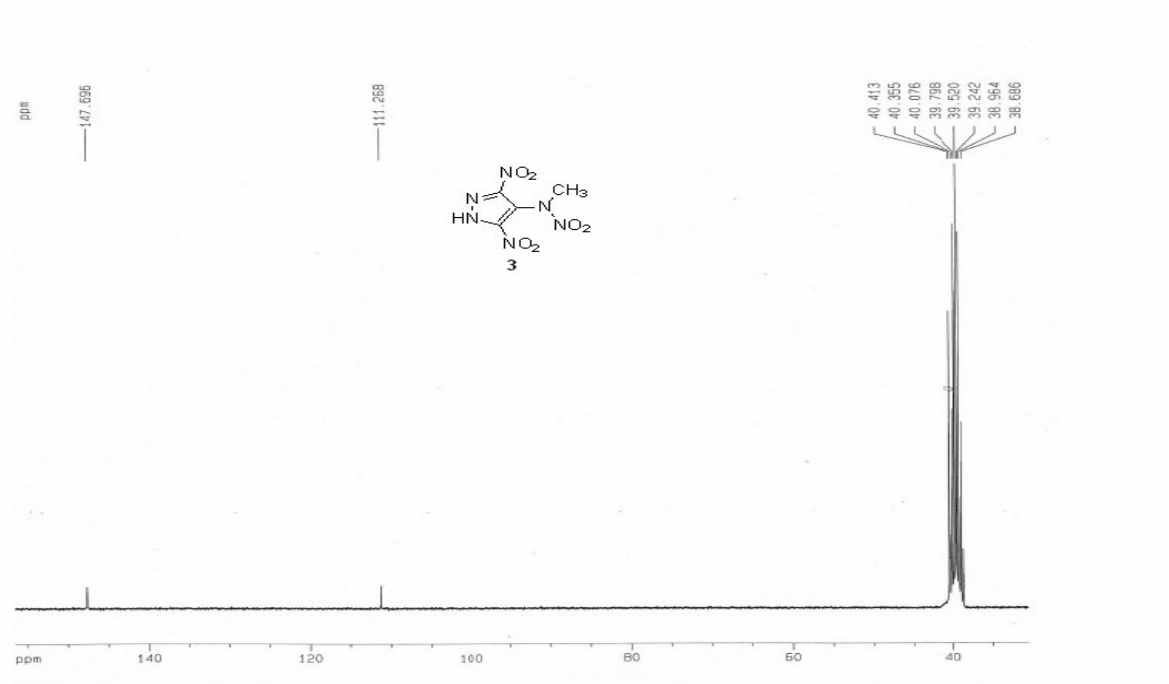


Figure S4

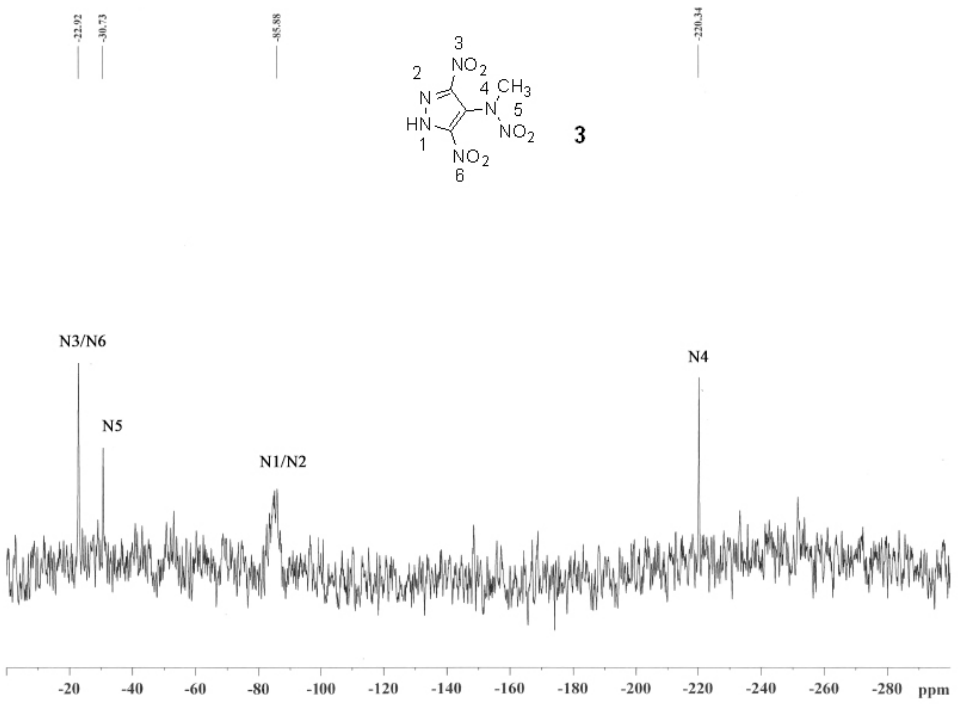


Figure S5

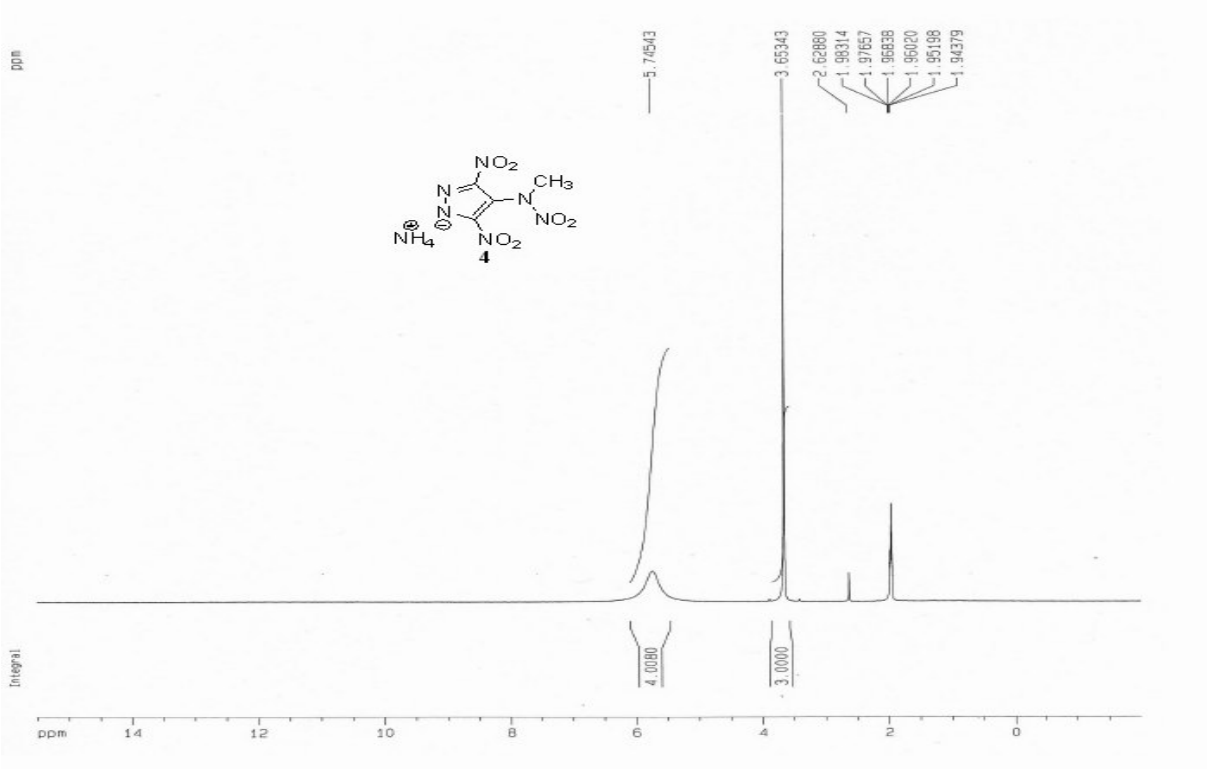


Figure S6

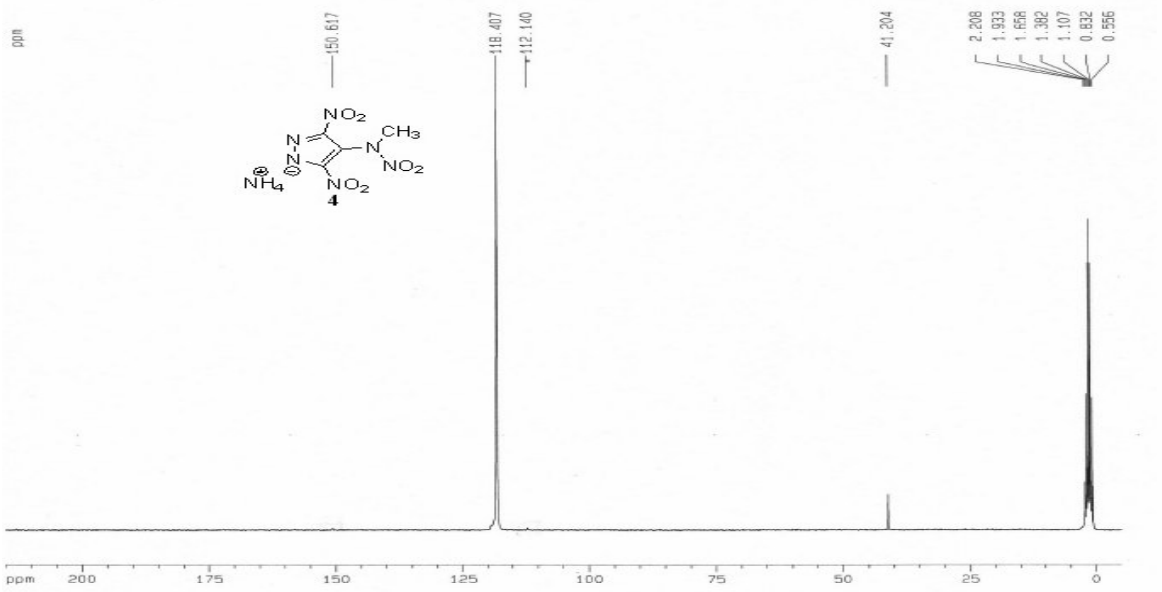


Figure S7

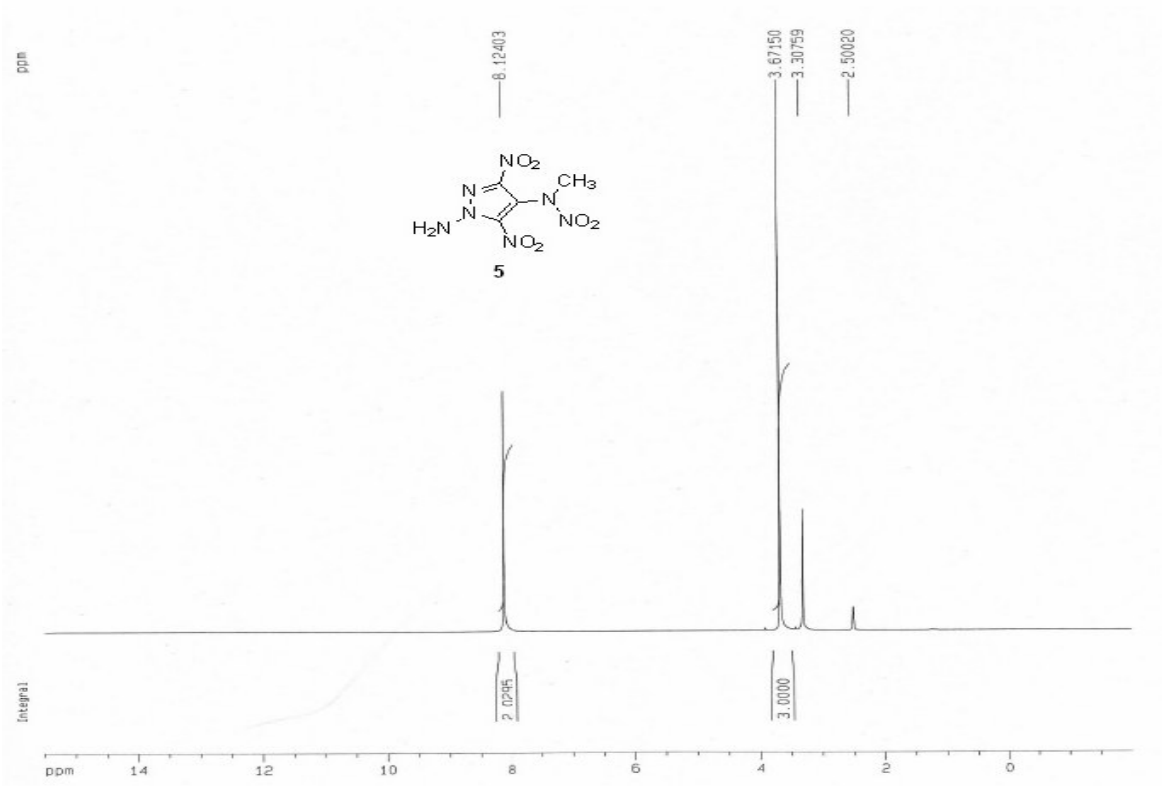


Figure S8

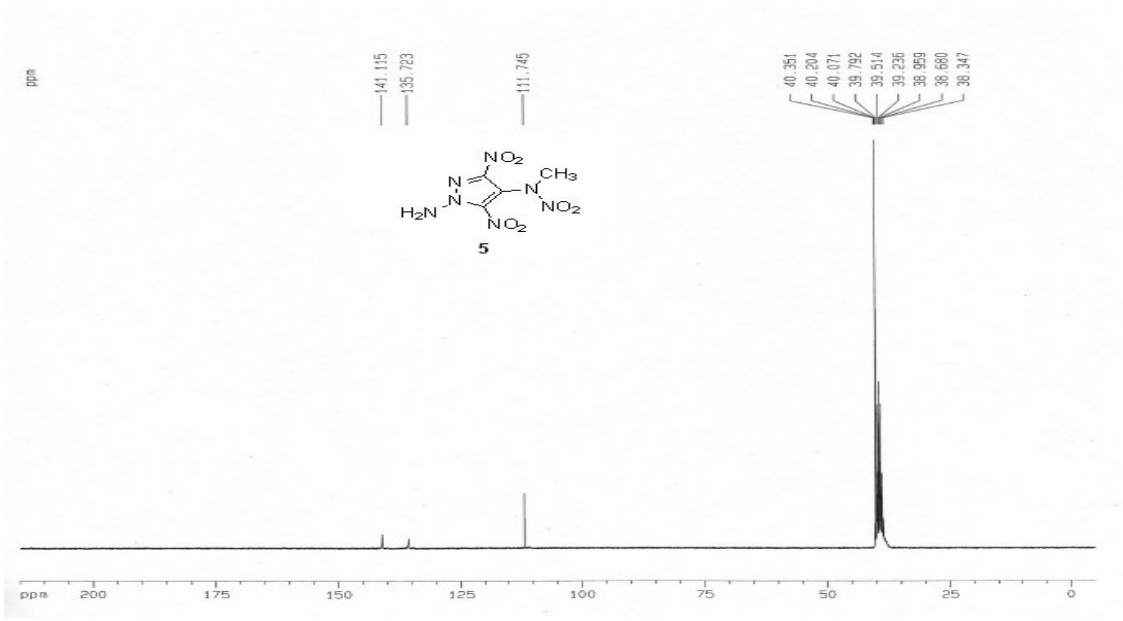


Figure S9

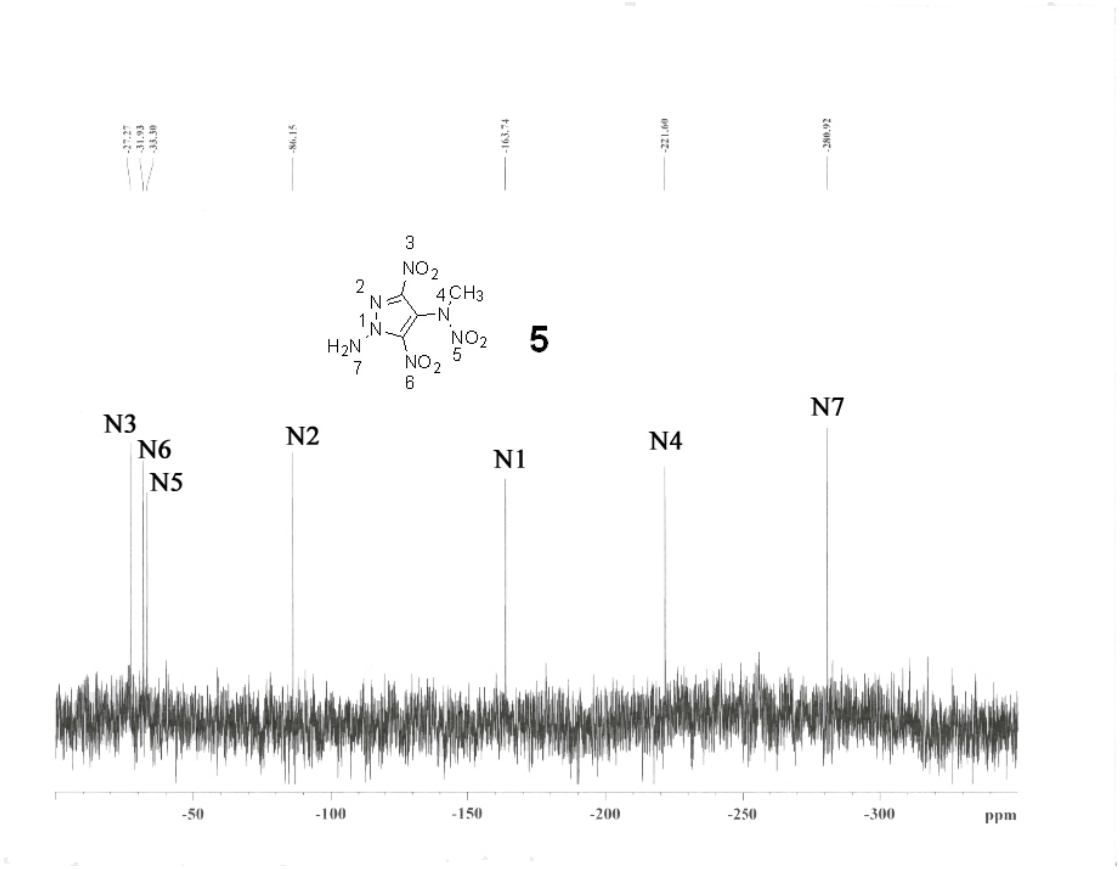


Figure S10

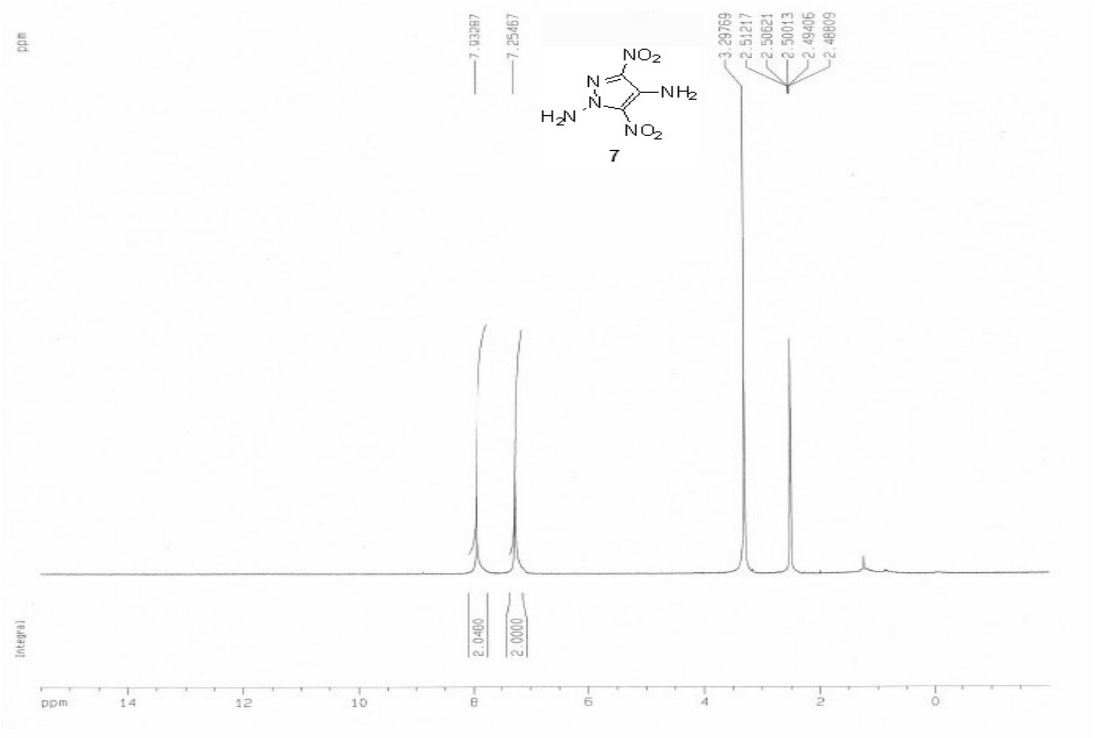


Figure S11

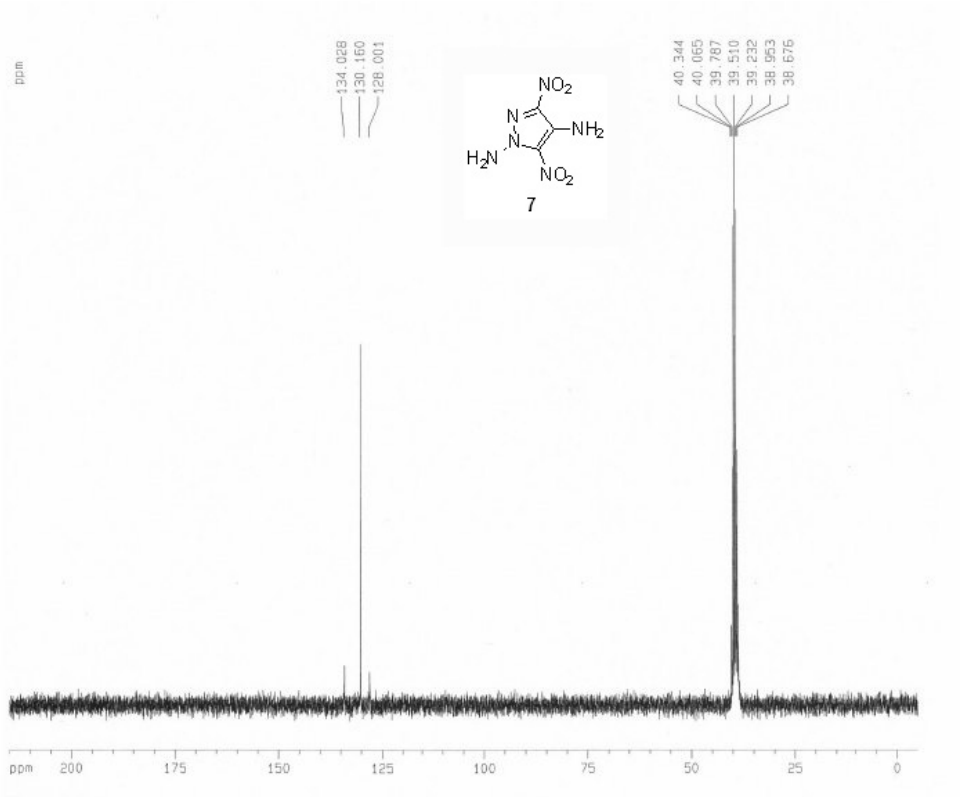


Figure S12

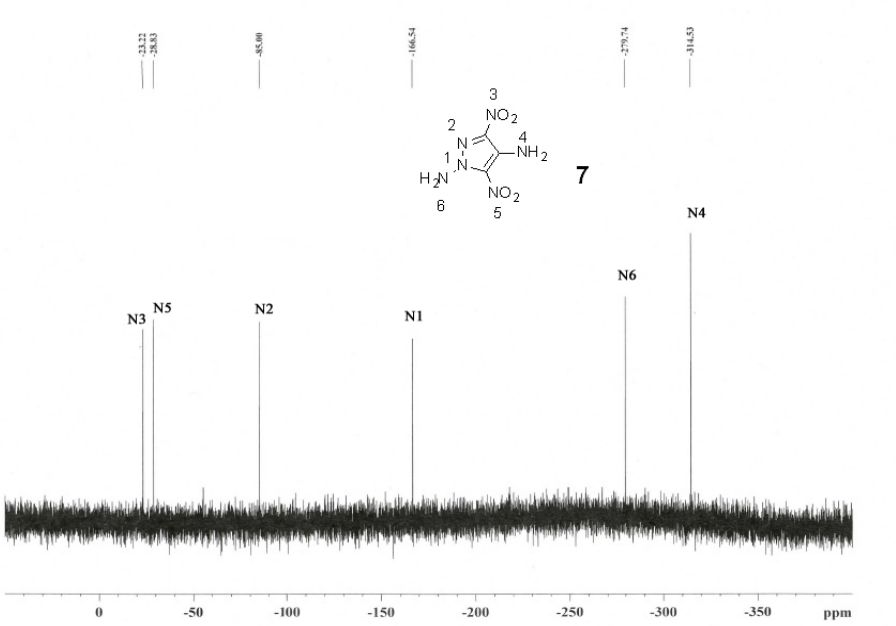


Figure S13

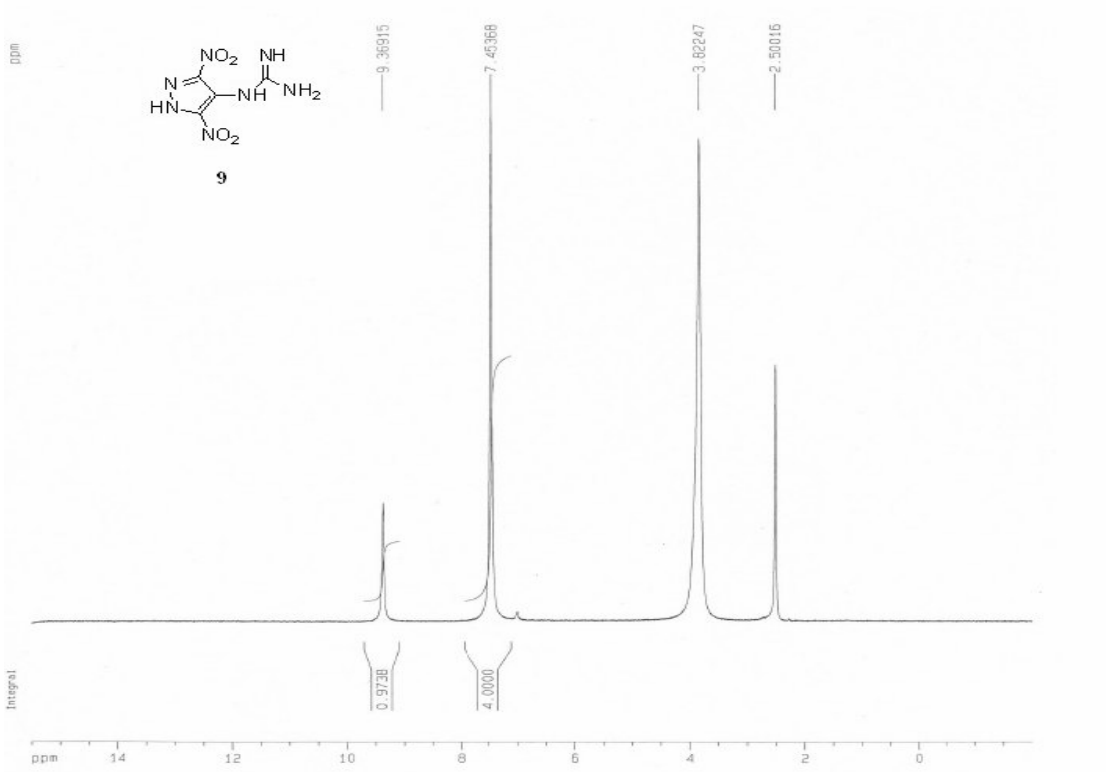


Figure S14

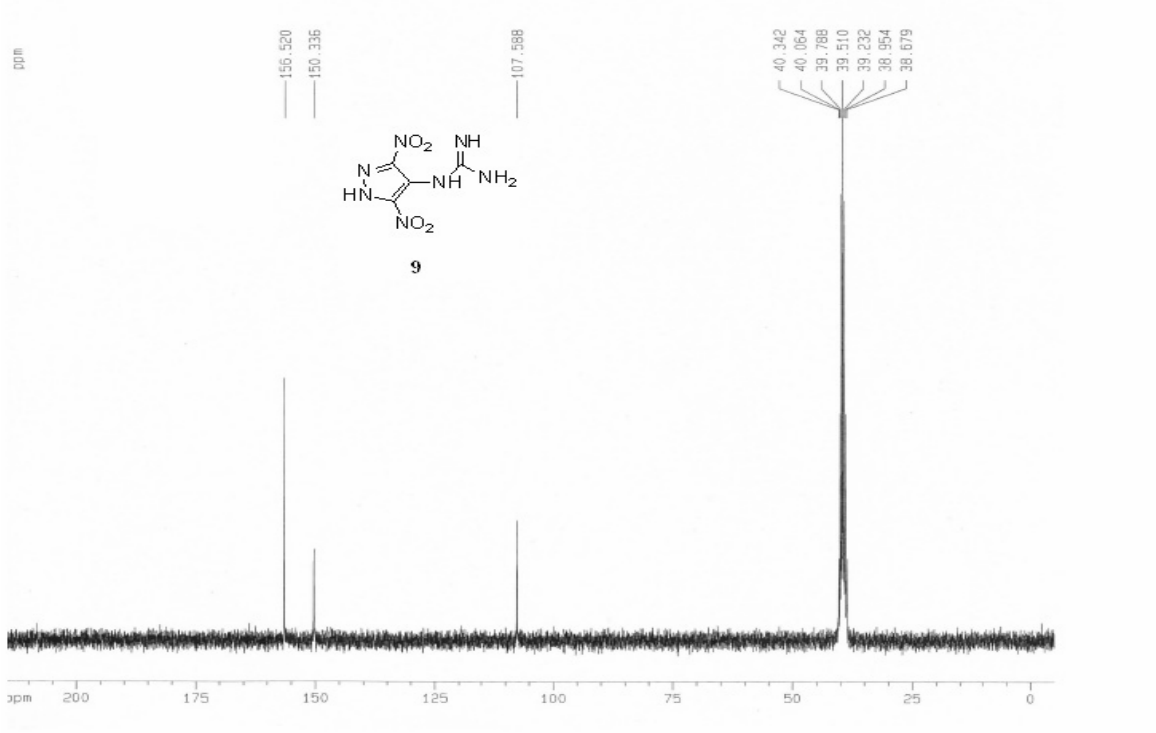


Figure S15

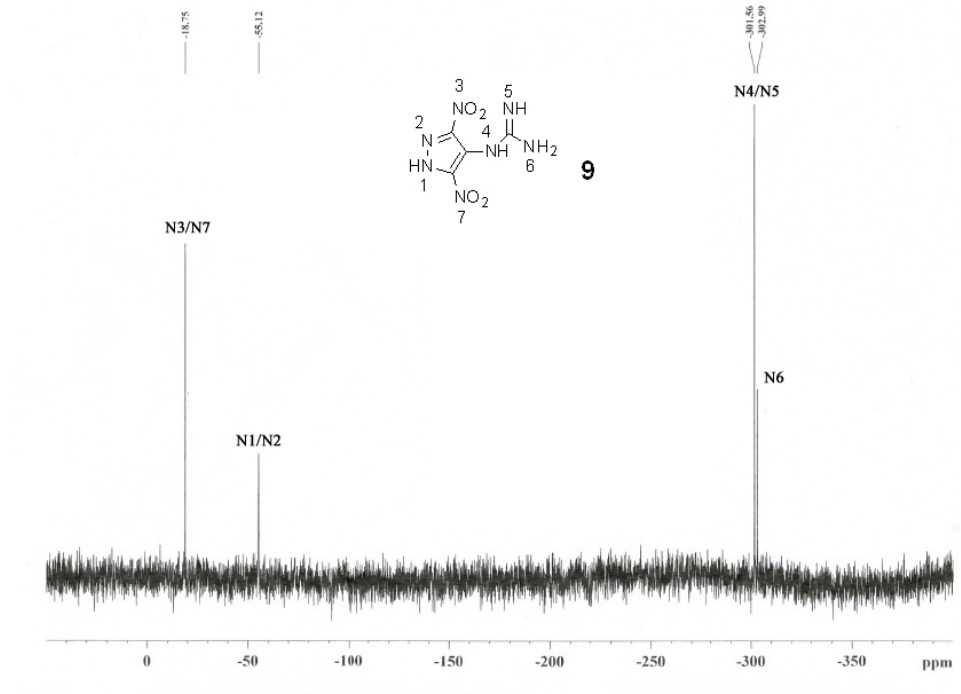
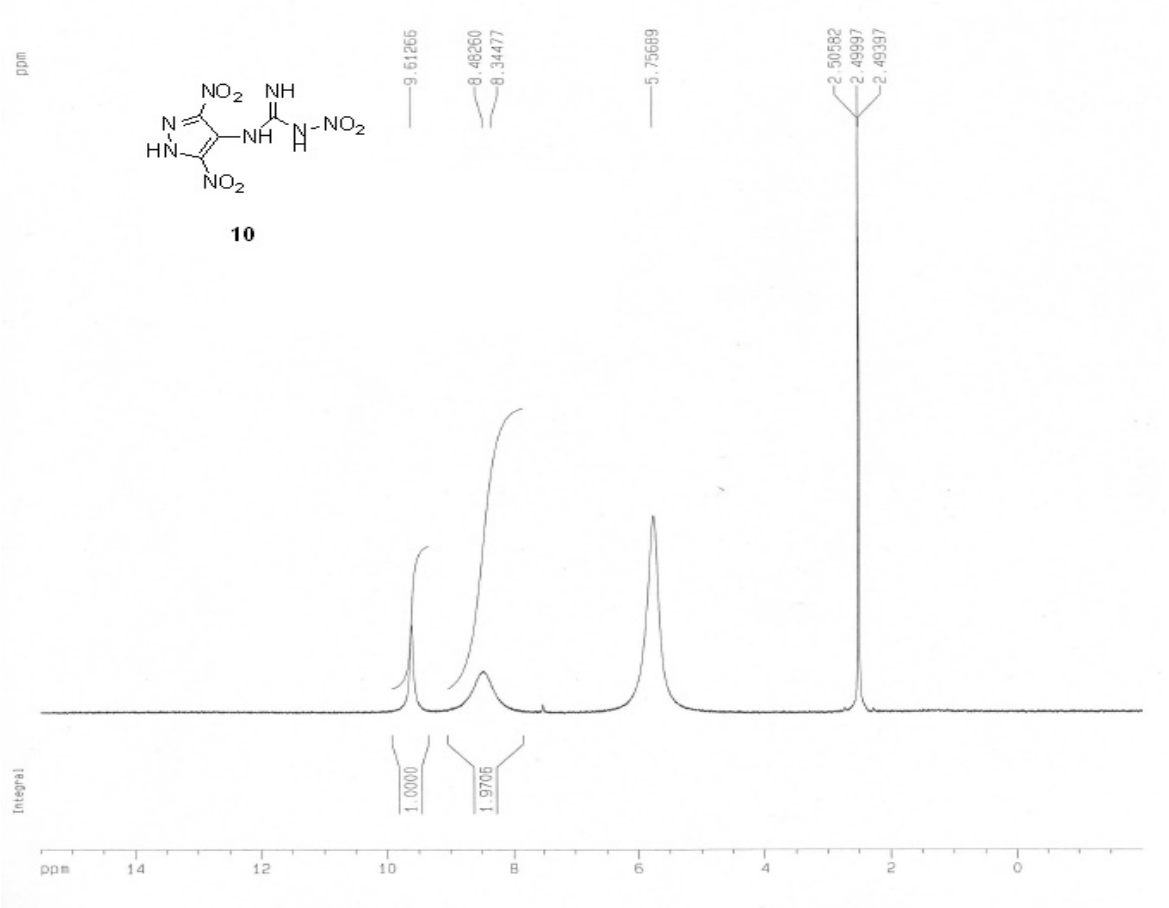


Figure S16



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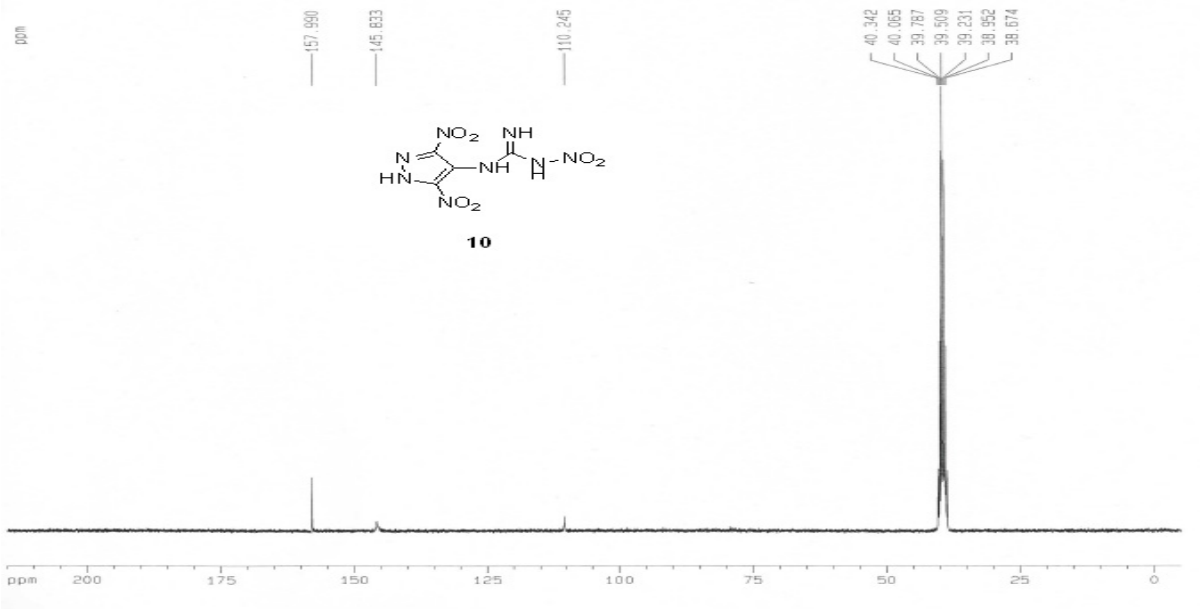
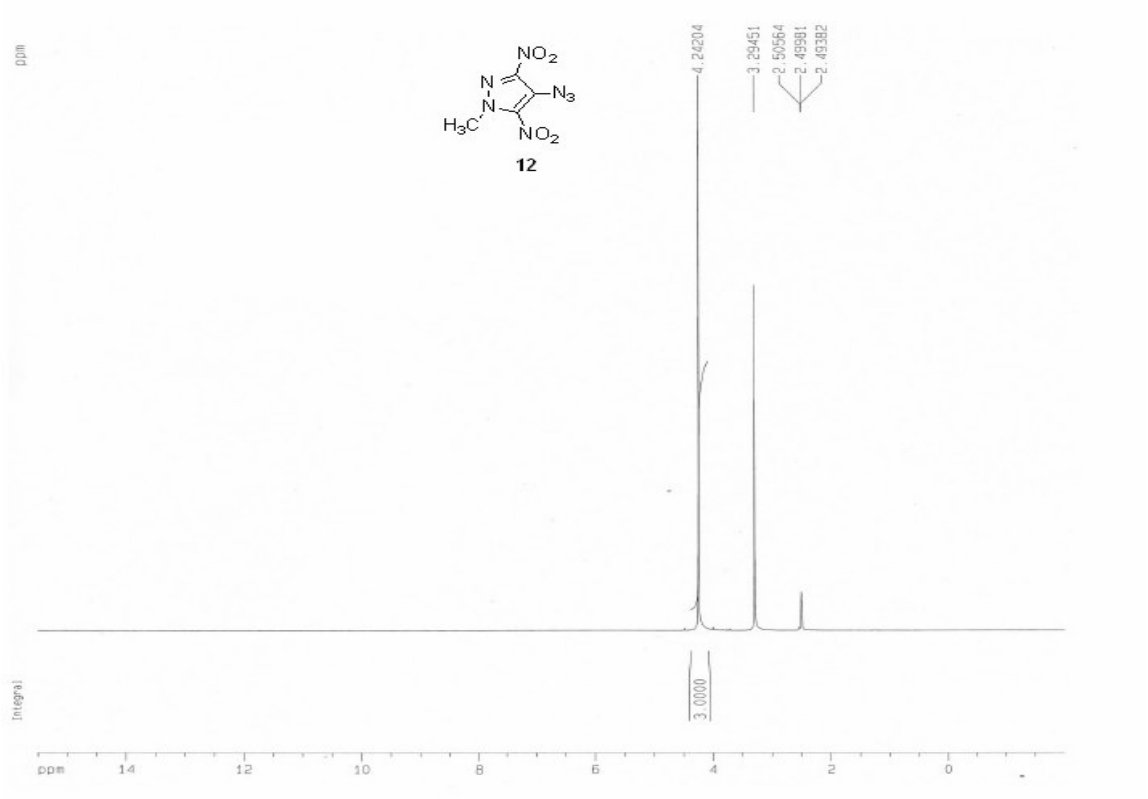


Figure S18



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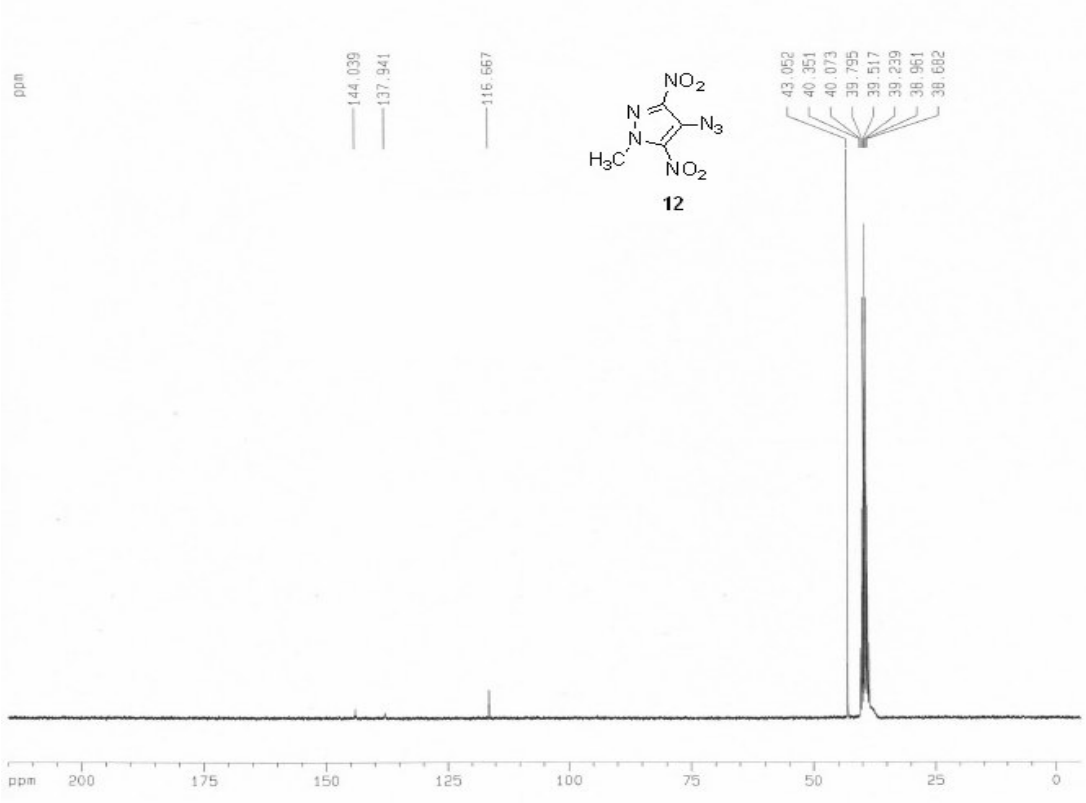


Figure S20

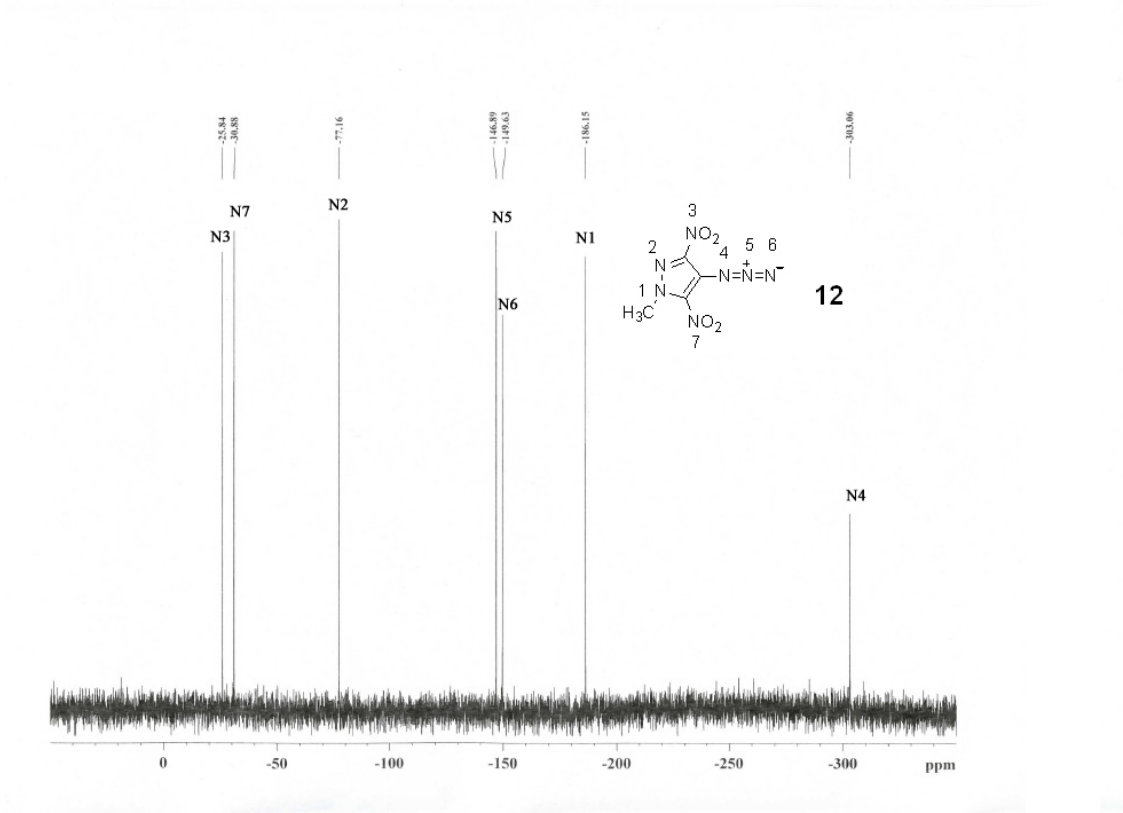
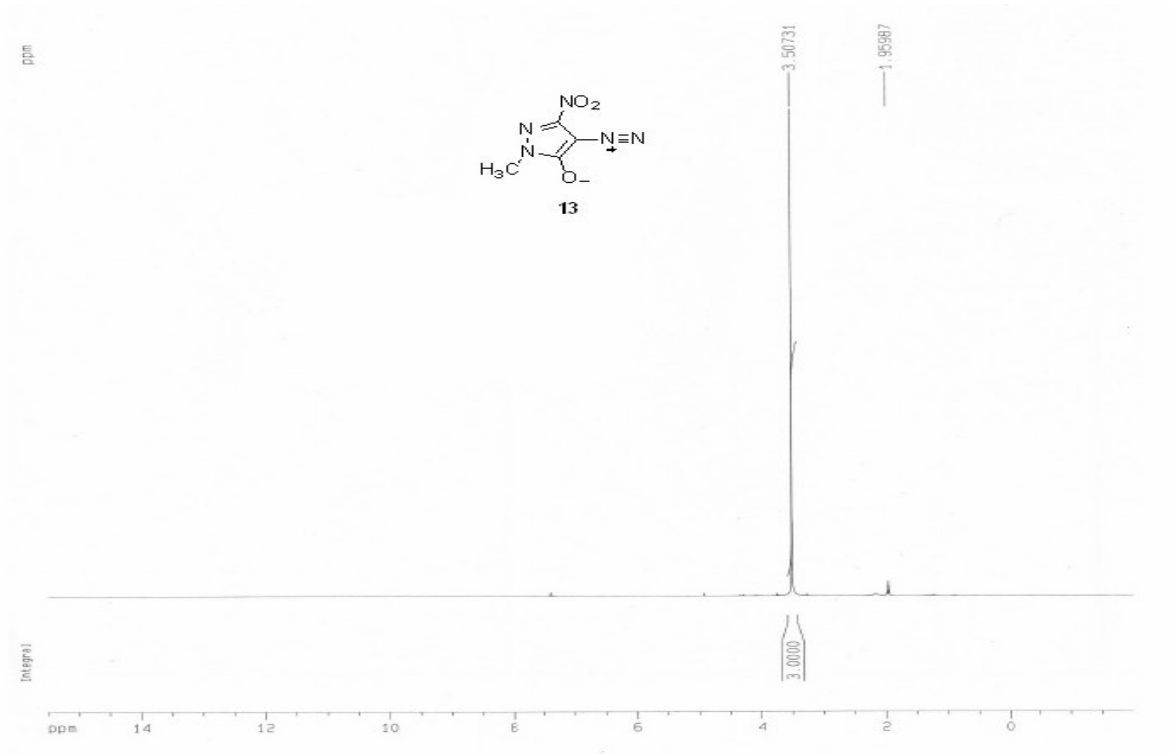


Figure S21



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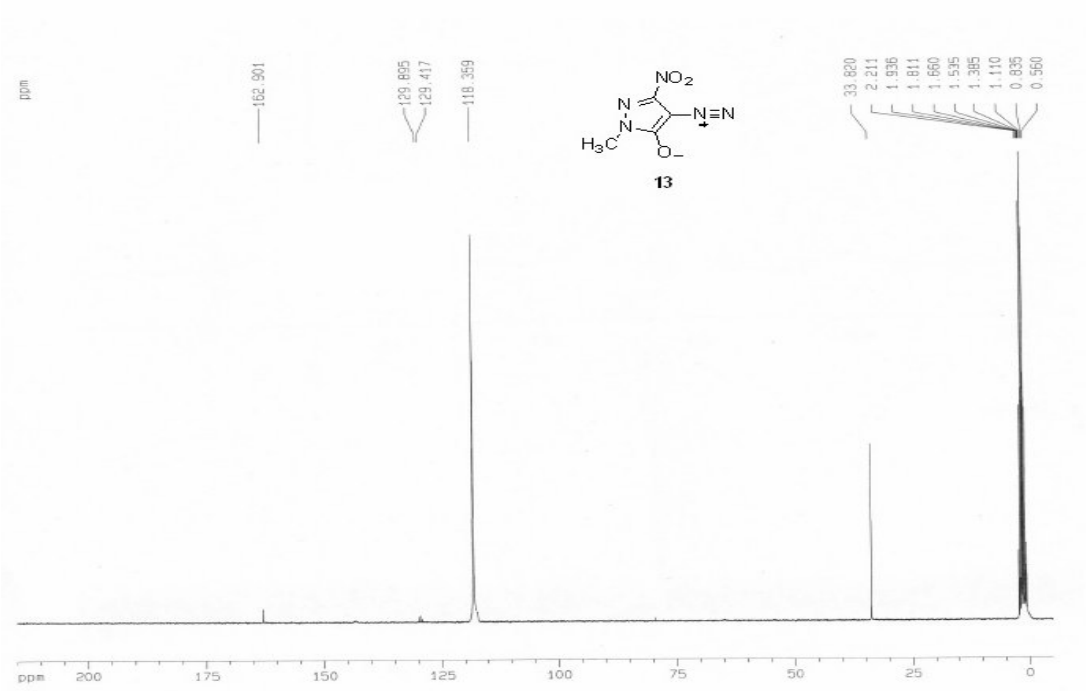

Figure S23

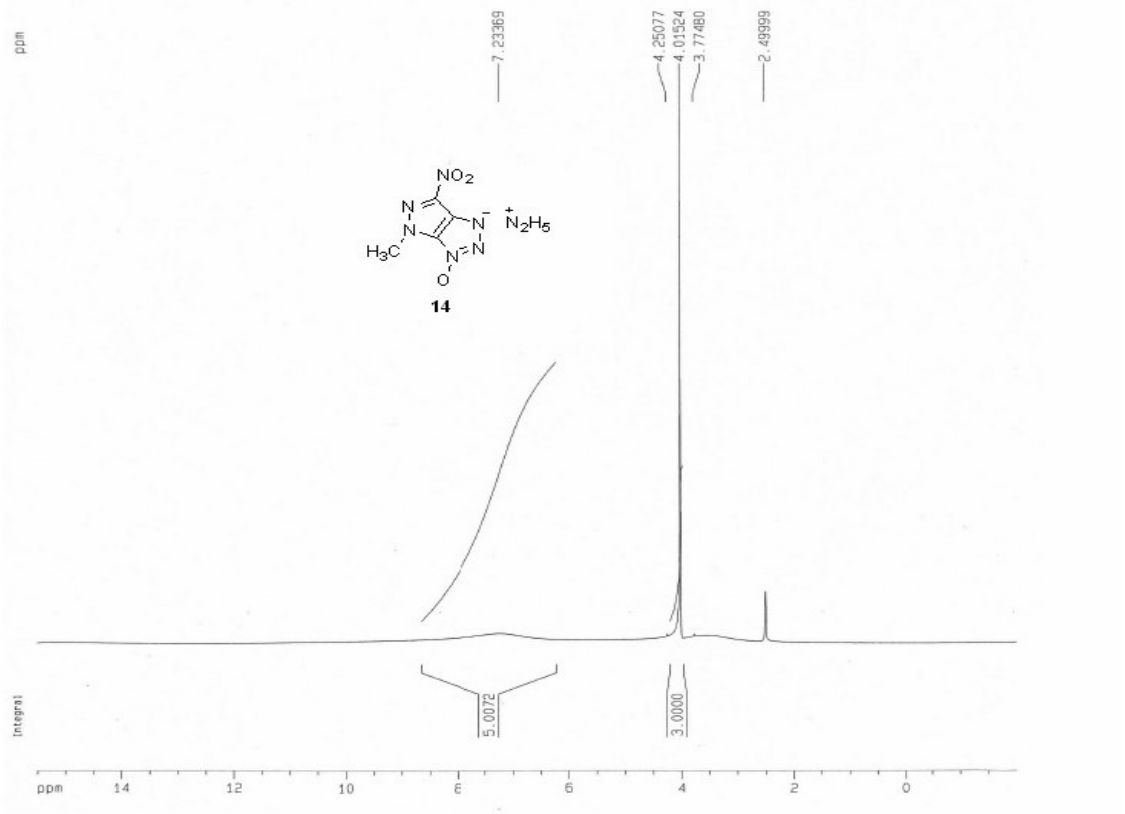

Figure S24

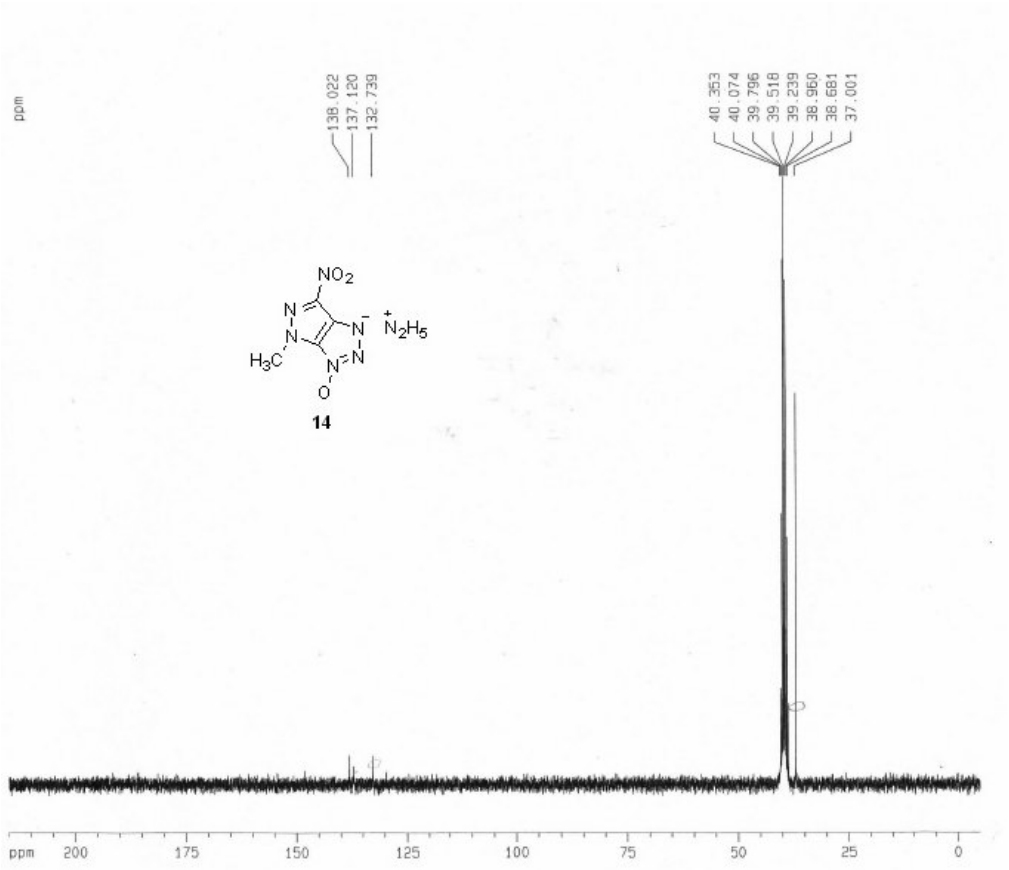

Figure S25

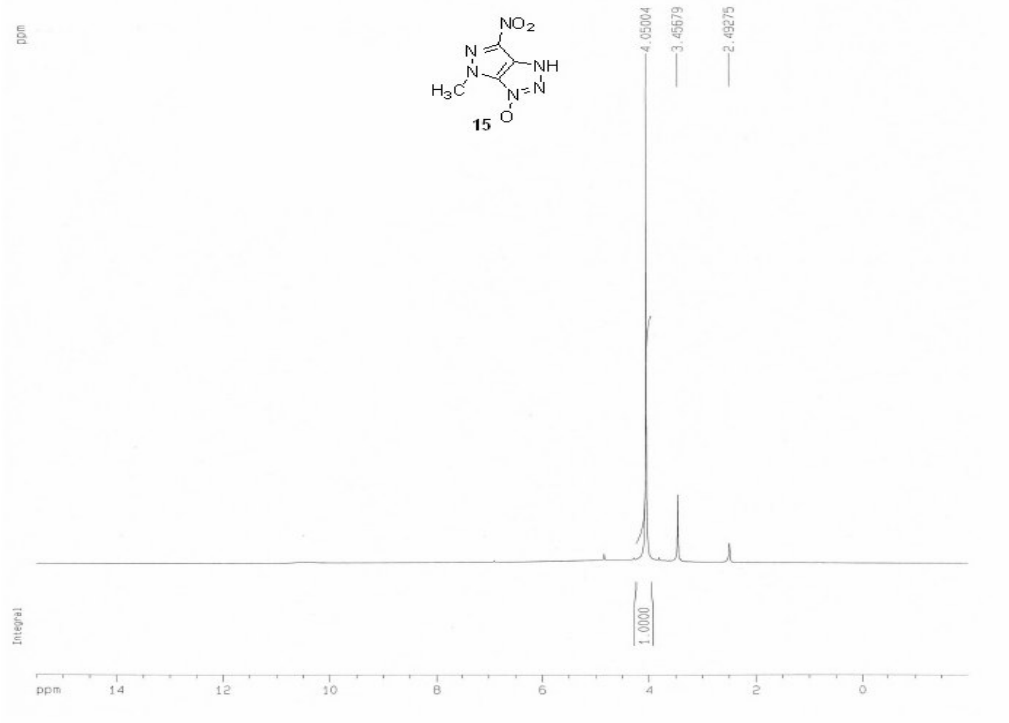

Figure S26

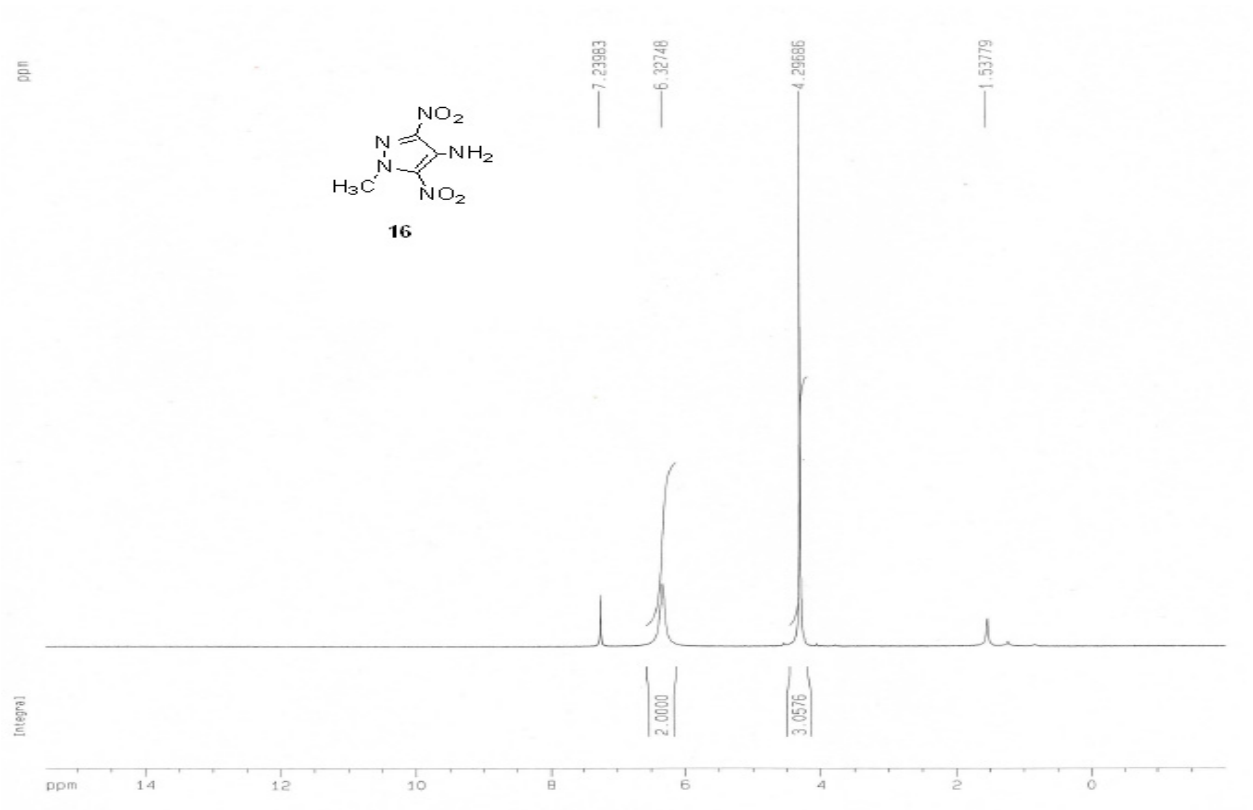

Figure S27

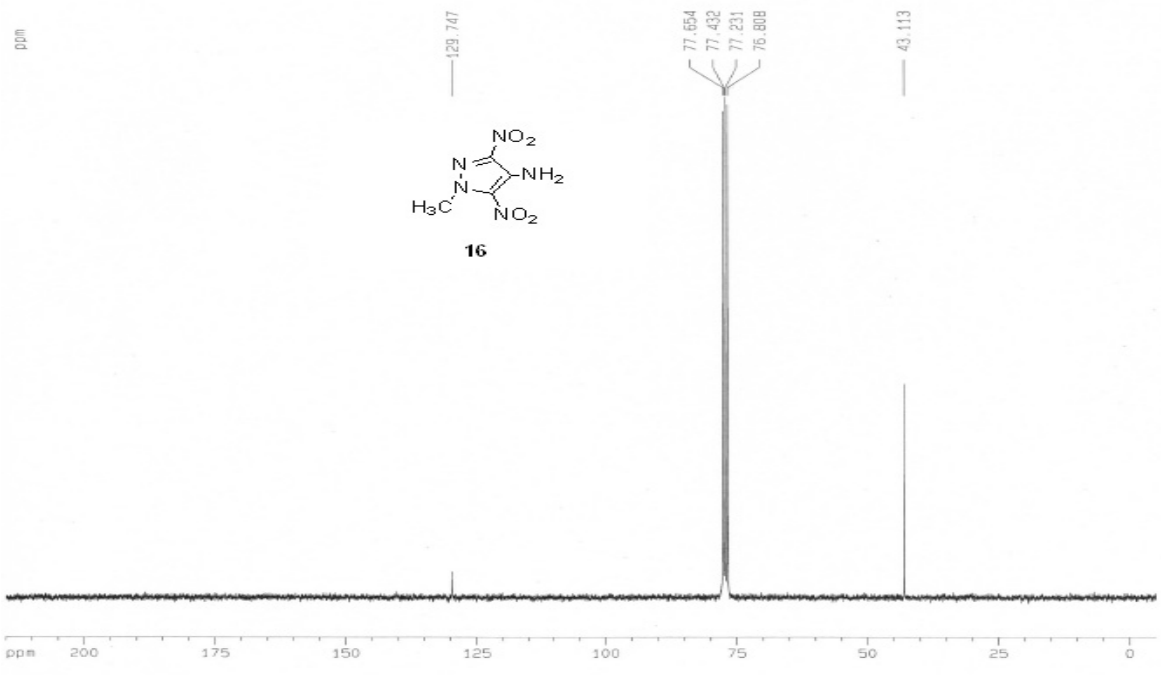

Figure S28

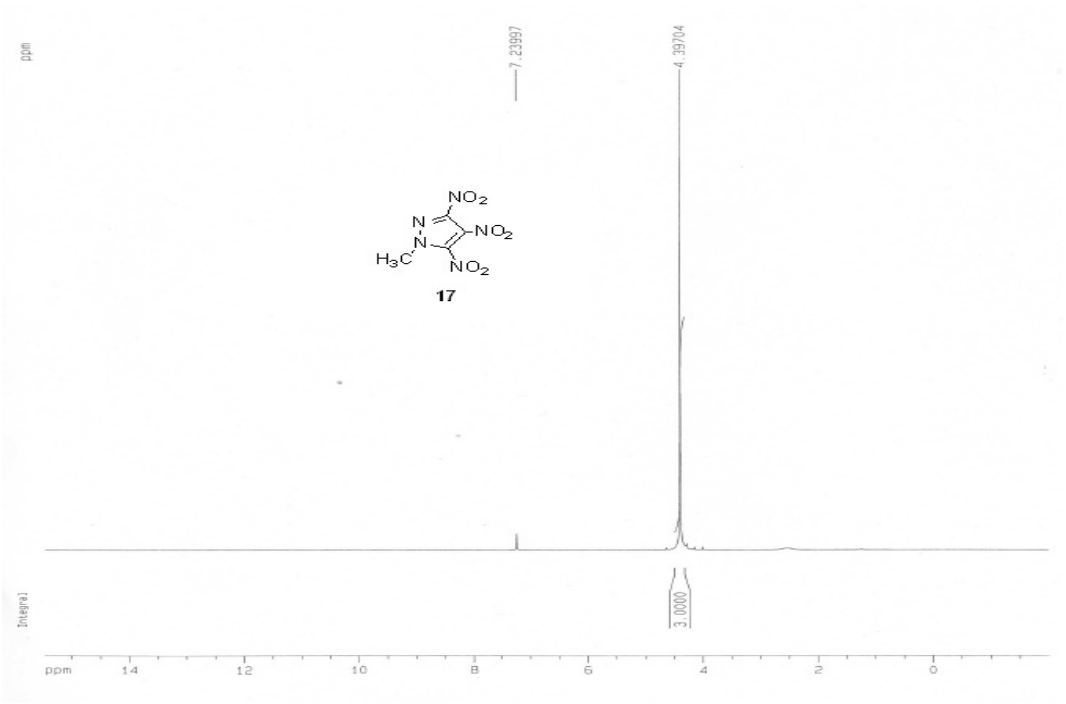

Figure S29

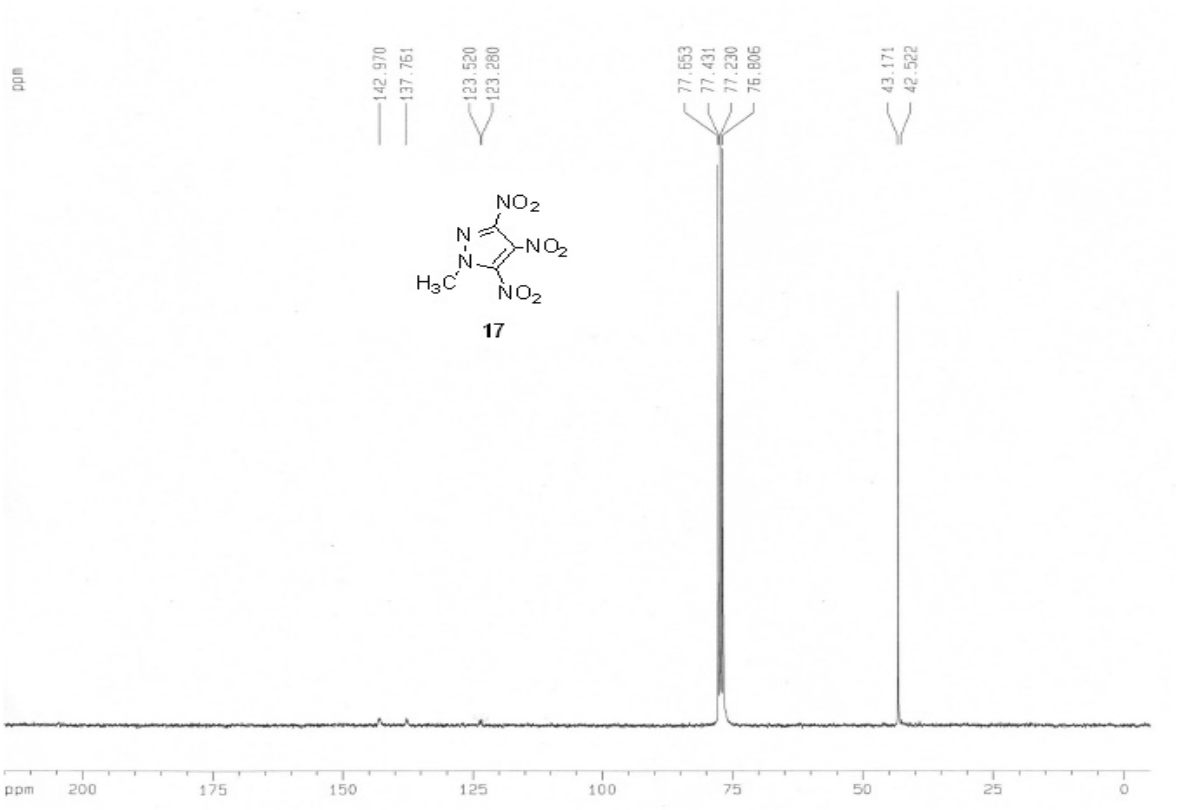

Figure S30

DSC Figures

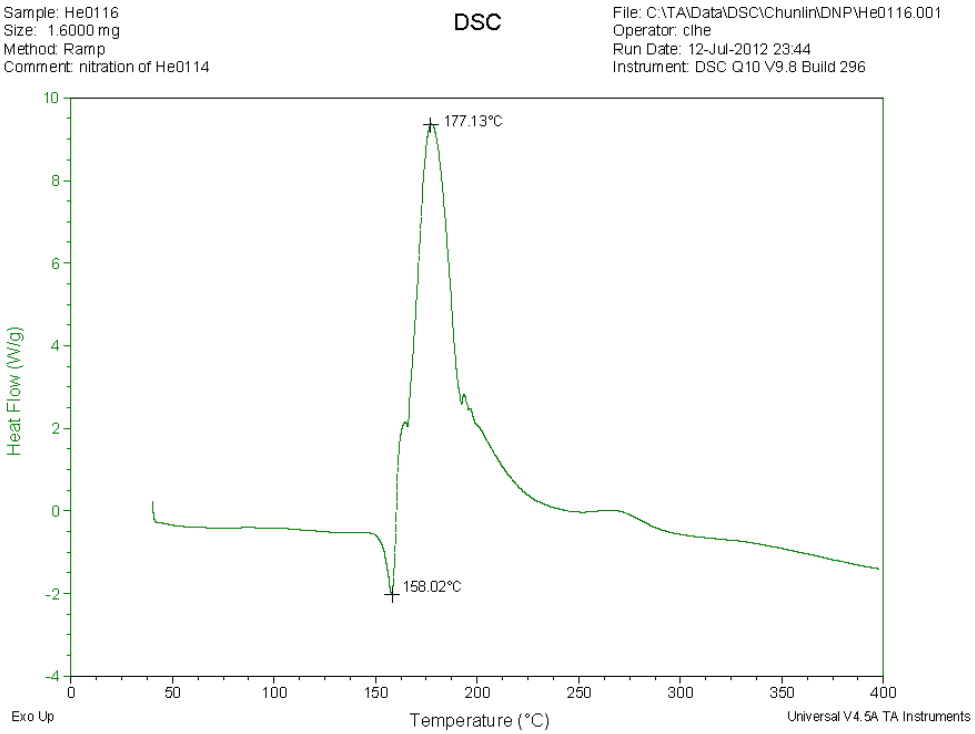

Figure S31 DSC figure of compound 3

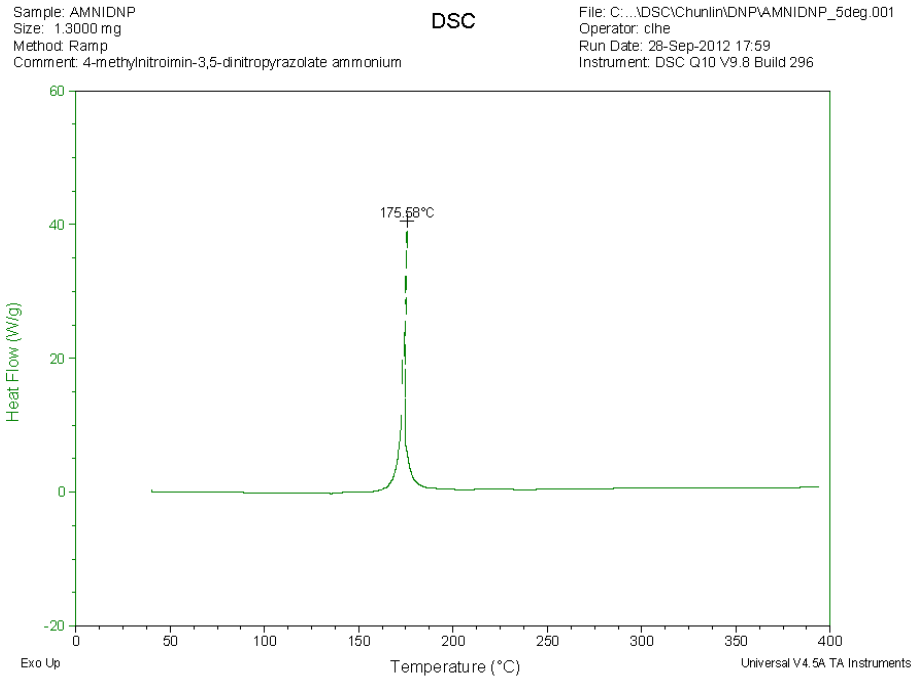

Figure S32 DSC figure of compound 4

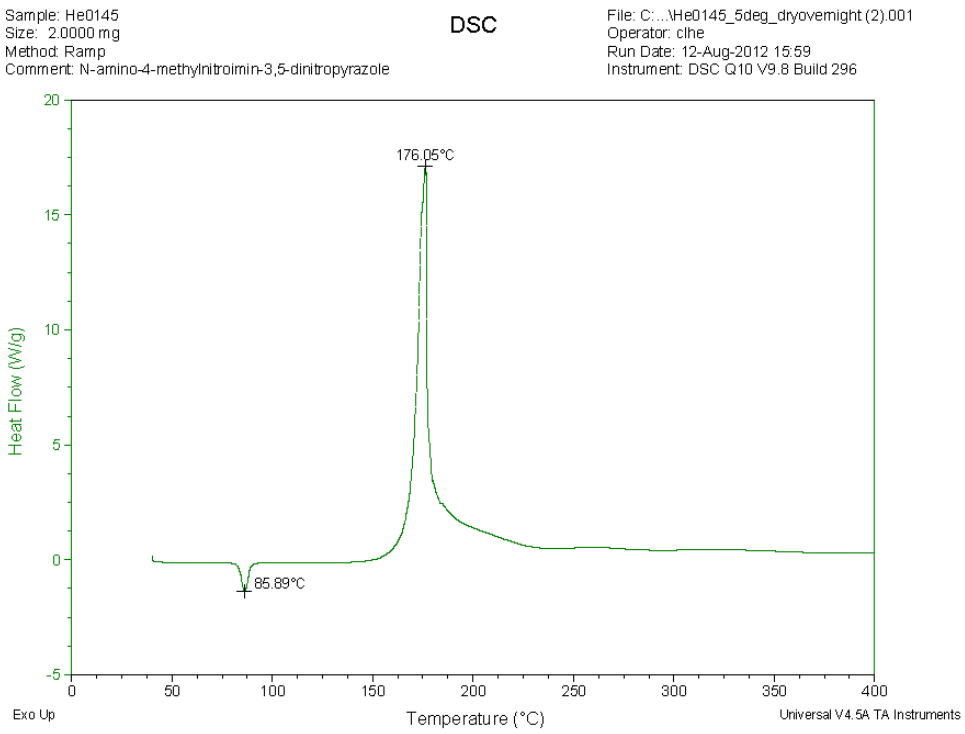

Figure S33 DSC figure of compound 5

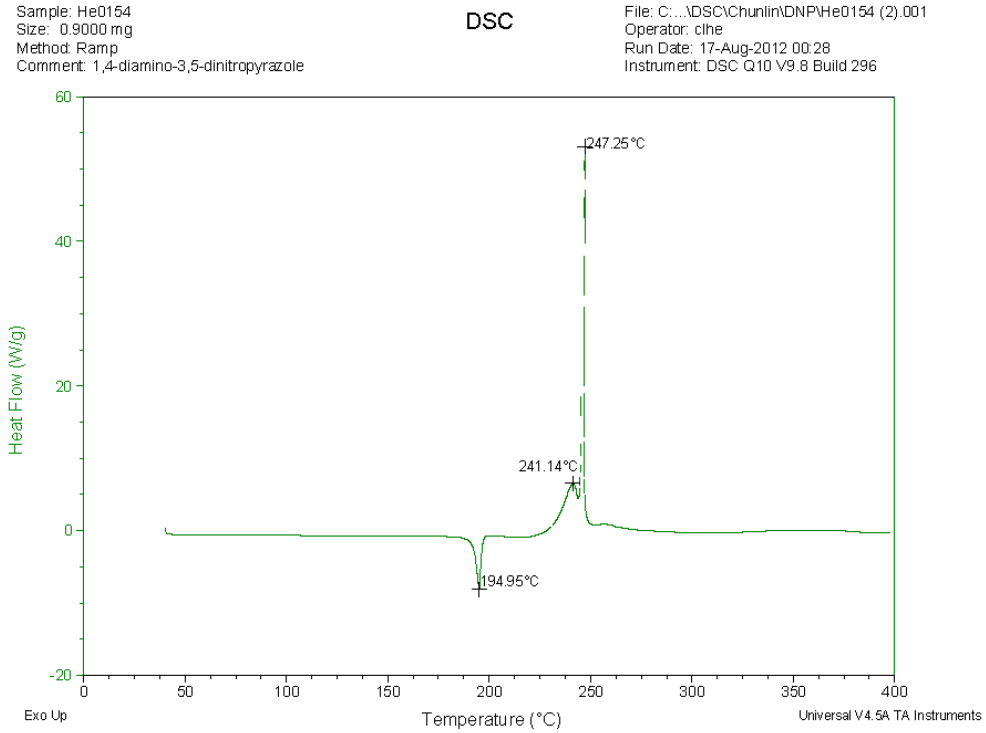

Figure S34 DSC figure of compound 7

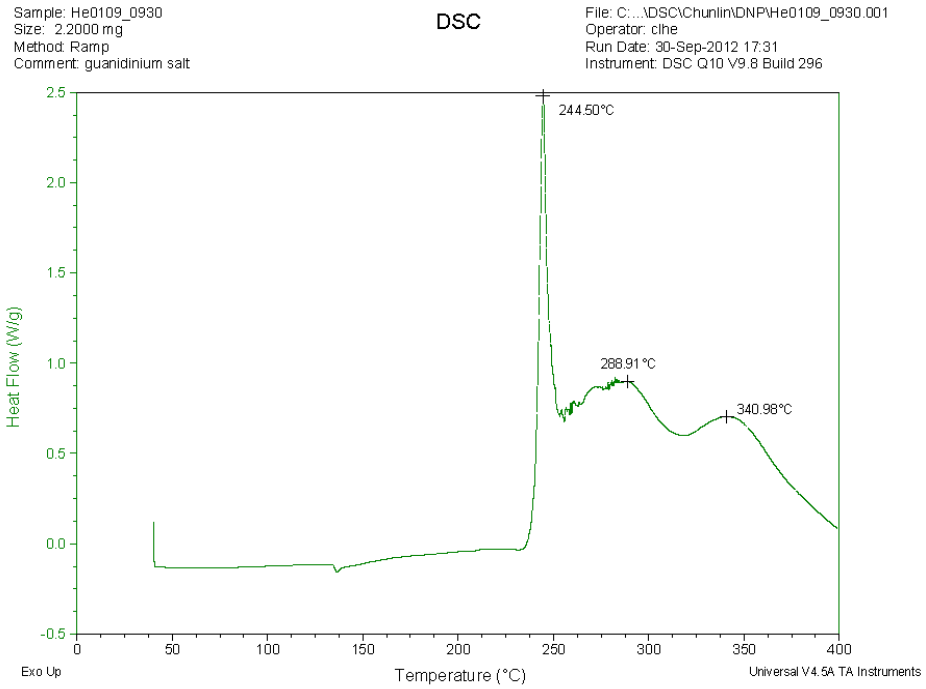

Figure S35 DSC figure of compound 8

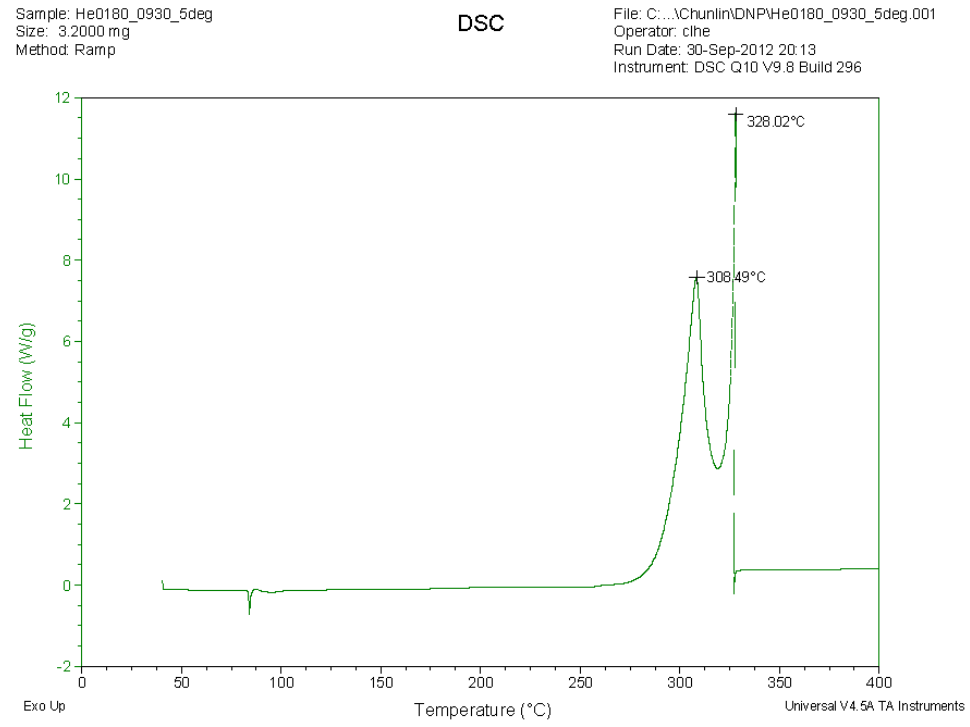

Figure S36 DSC figure of compound 9

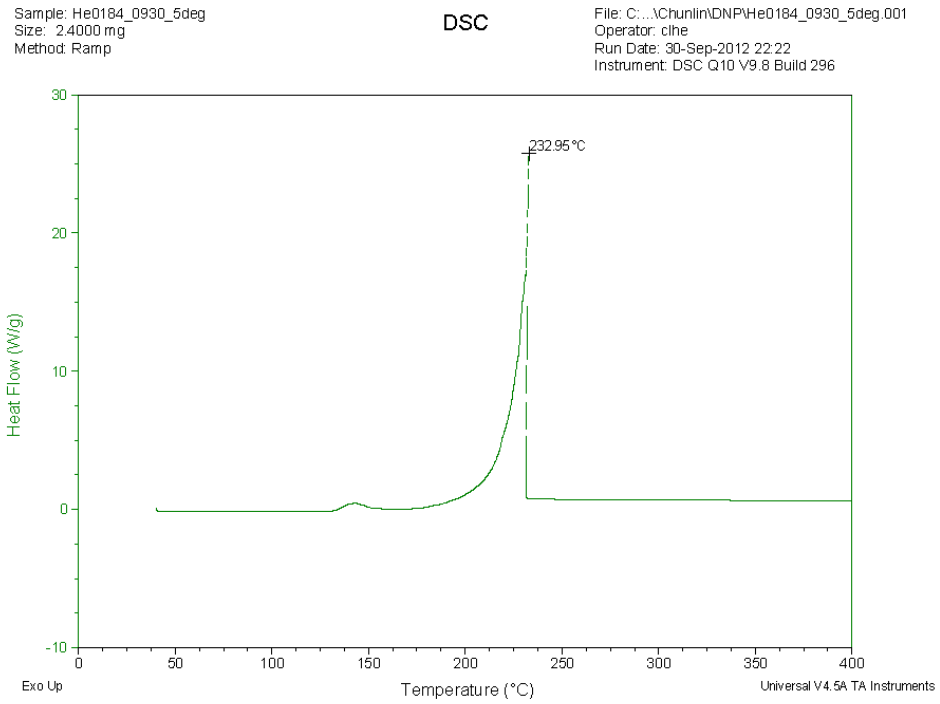

Figure S37 DSC figure of compound 10

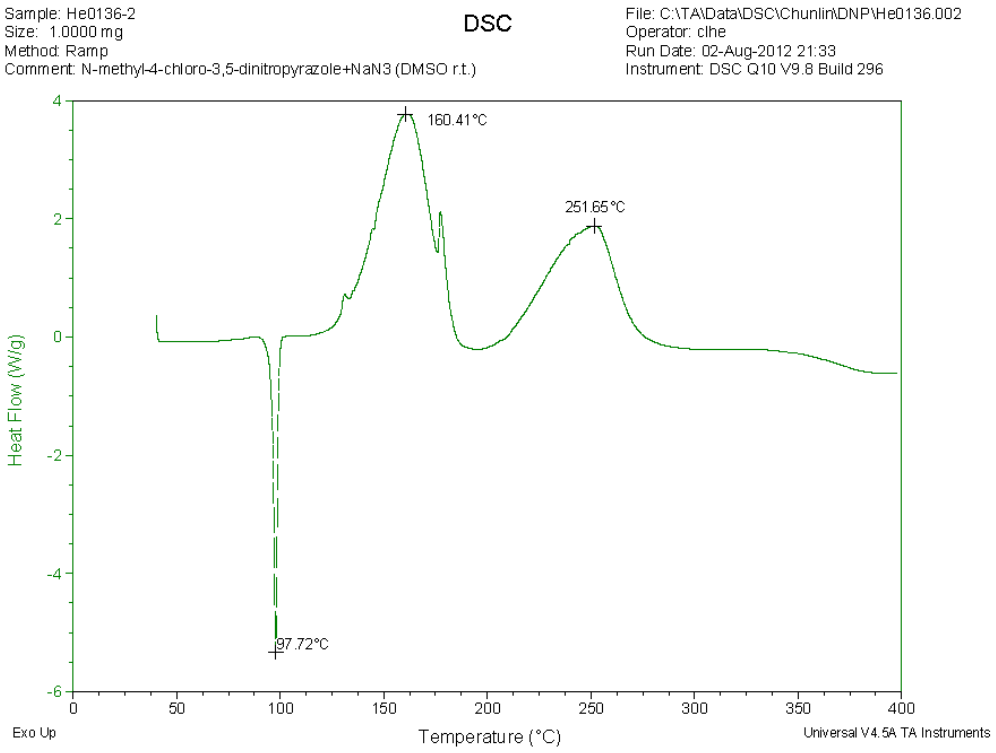

Figure S38 DSC figure of compound 12

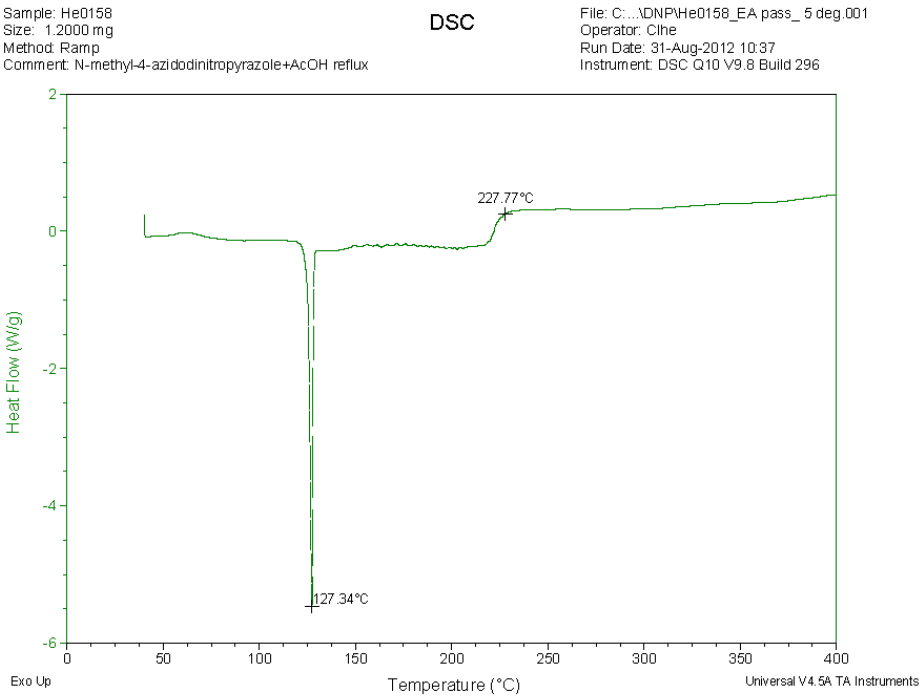

Figure S39 DSC figure of compound 13

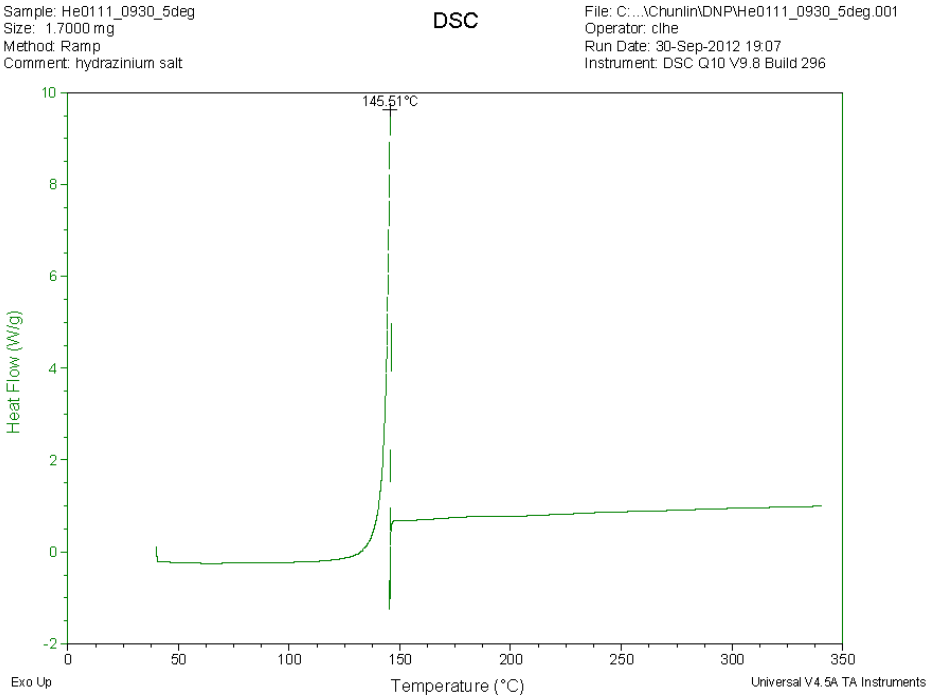

Figure S40 DSC figure of compound 14

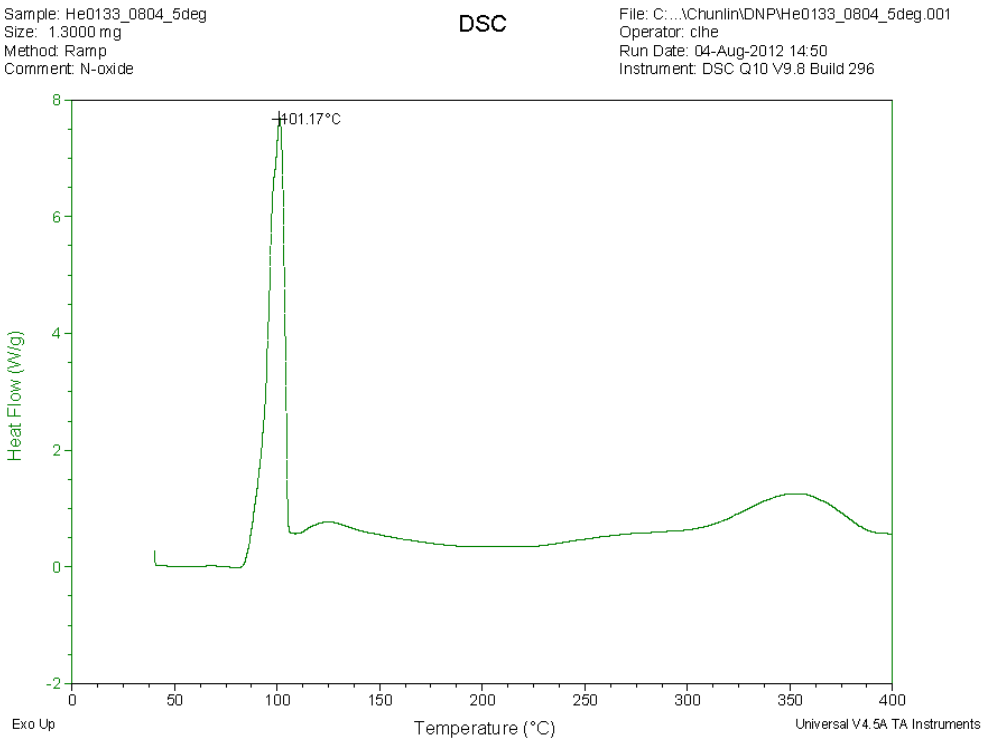

Figure S41 DSC figure of compound 15

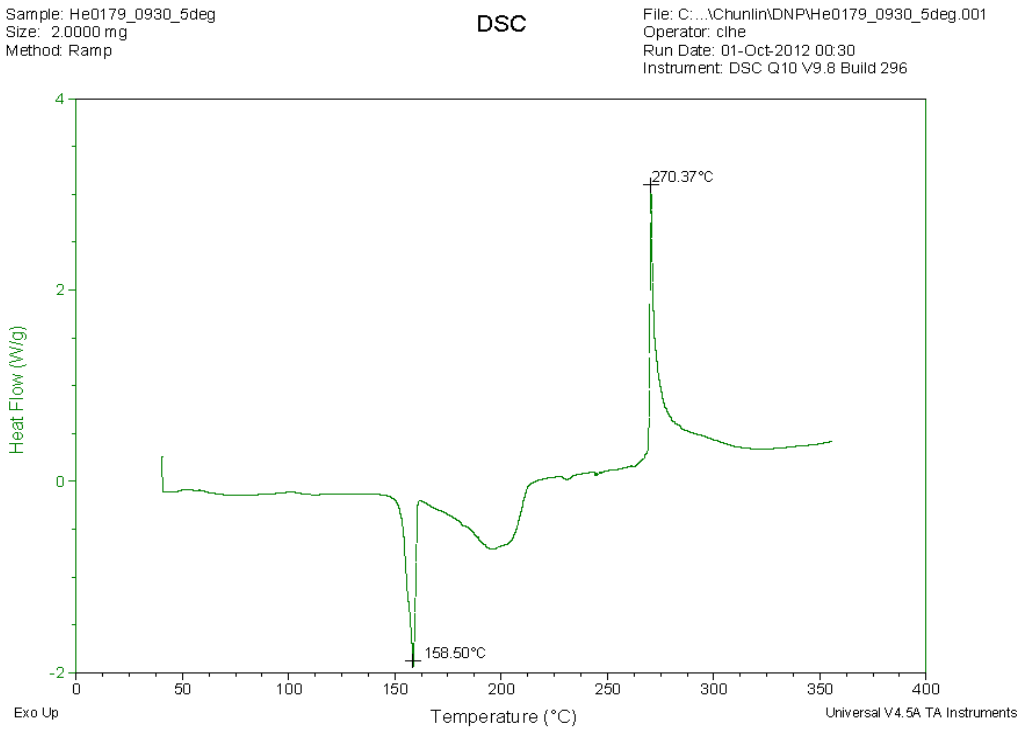

Figure S42 DSC figure of compound 16

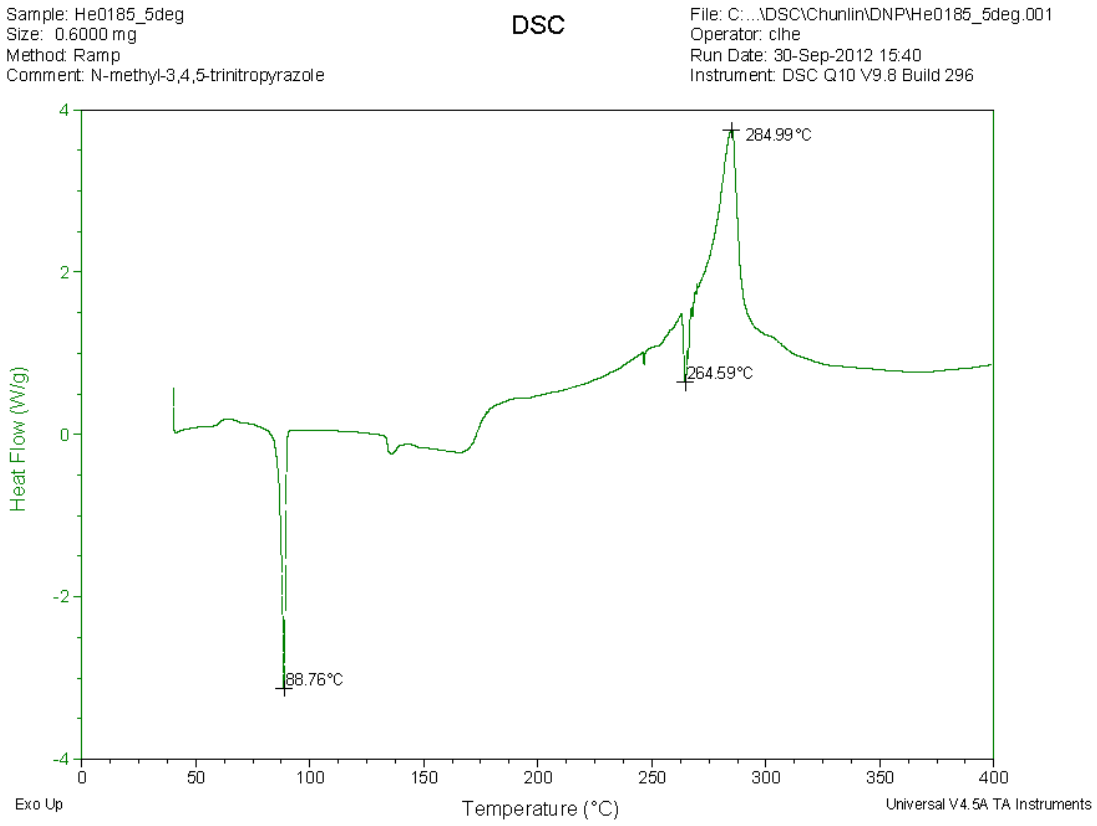

Figure S43 DSC figure of compound 17