Supporting Information

for

Achieving the highest density and energy within diazo-oxide compounds

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1. General Methods

All reagents were purchased from Energy Chemical of analytical grade and were used as supplied, if not stated otherwise. The melting points and decomposition temperatures were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 mL min^{-1}.

2. Safety Precautions

All the new pyrazole compounds in this manuscript are powerful explosives, and should be handled with extreme care using the best safety practices.

3. Spectrum Analysis

3.1 ^{1}H and ^{13}C NMR Spectra
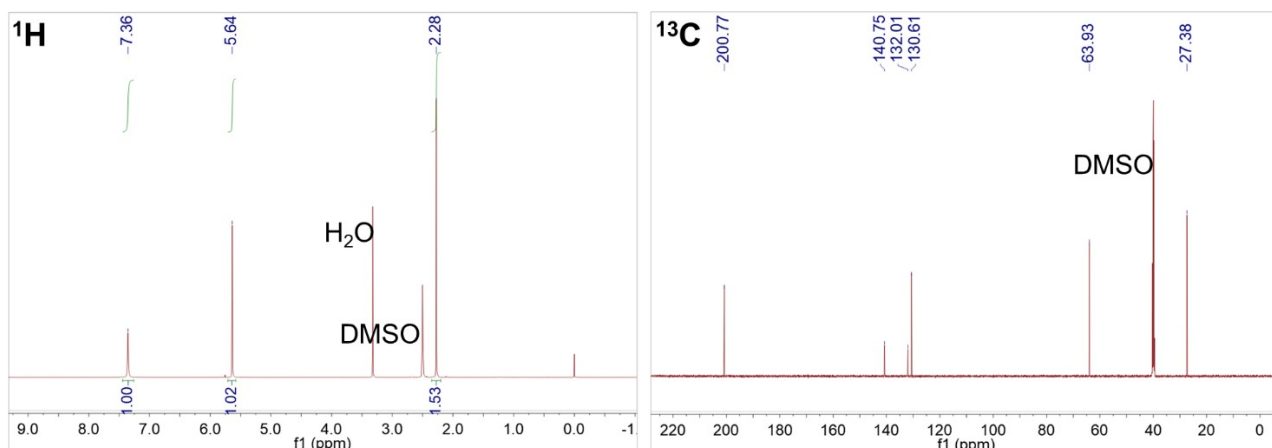

Figure S1. ^{1}H and ^{13}C NMR of compound **1** in DMSO-d$_6$.

Figure S2. ^{1}H and ^{13}C NMR of compound **2** in CD$_3$CN-d$_3$.
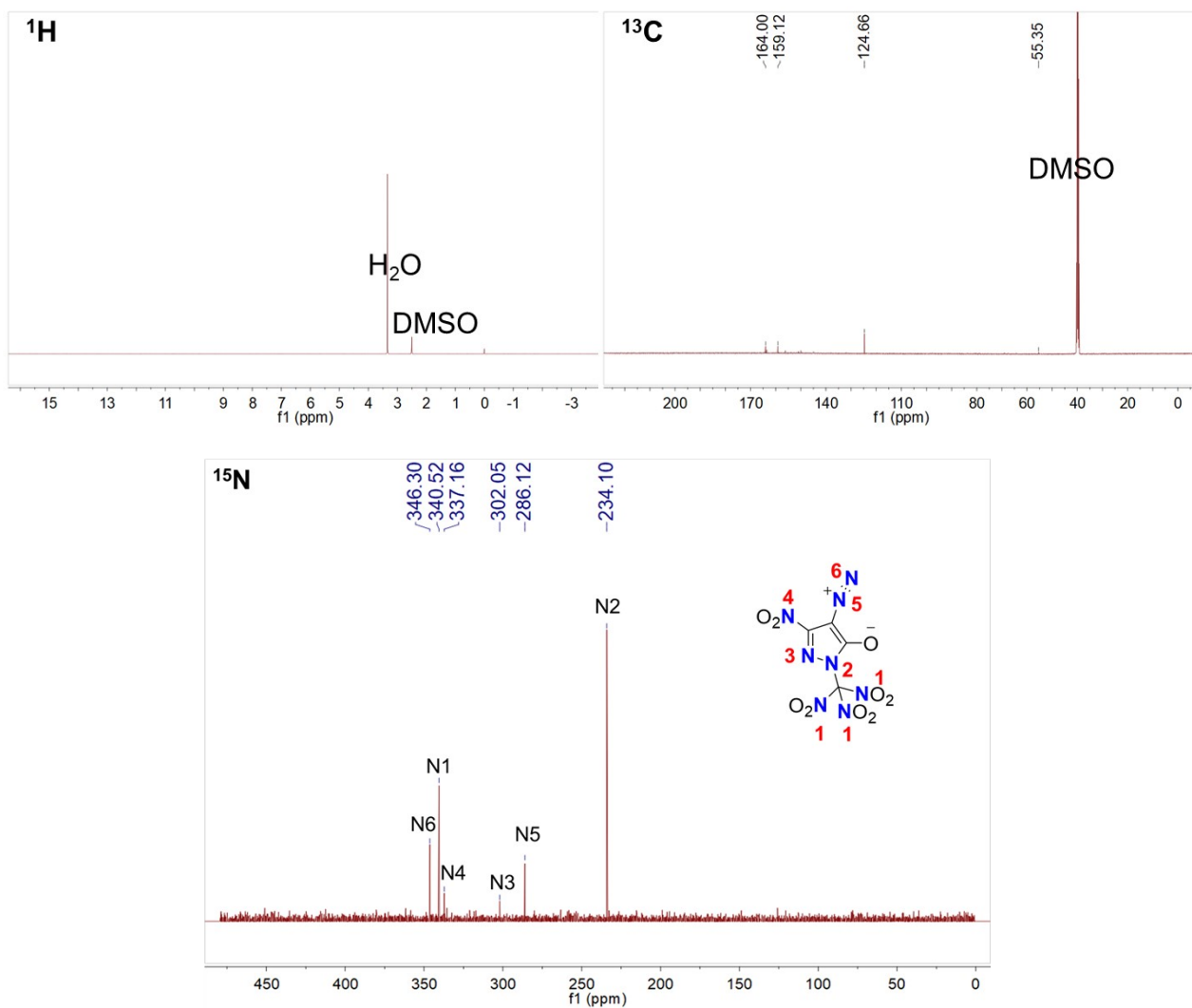
Figure S3. ^1H and ^{13}C NMR of compound **3** in DMSO-d_6 and ^{15}N NMR in CH_2Cl_2 (NH_3 as external standard).
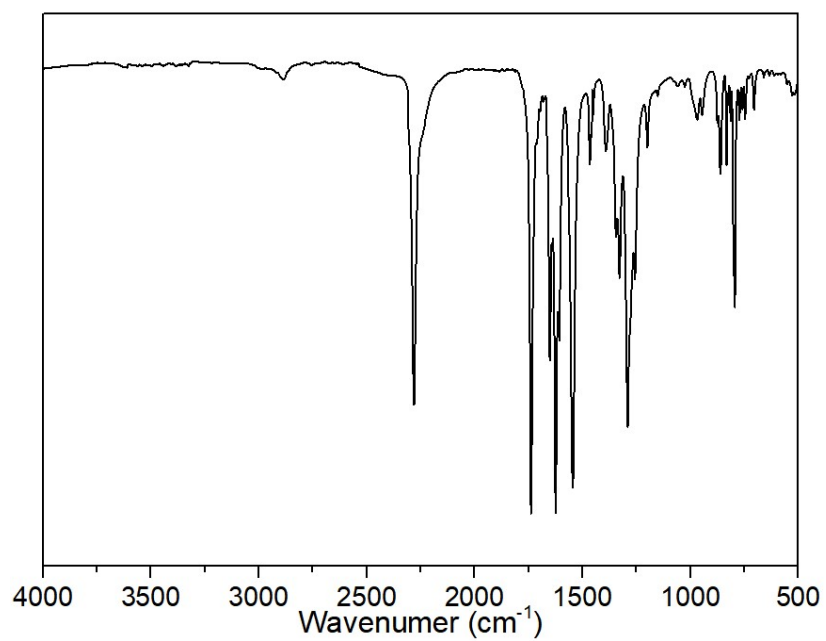
3.2 IR Spectra

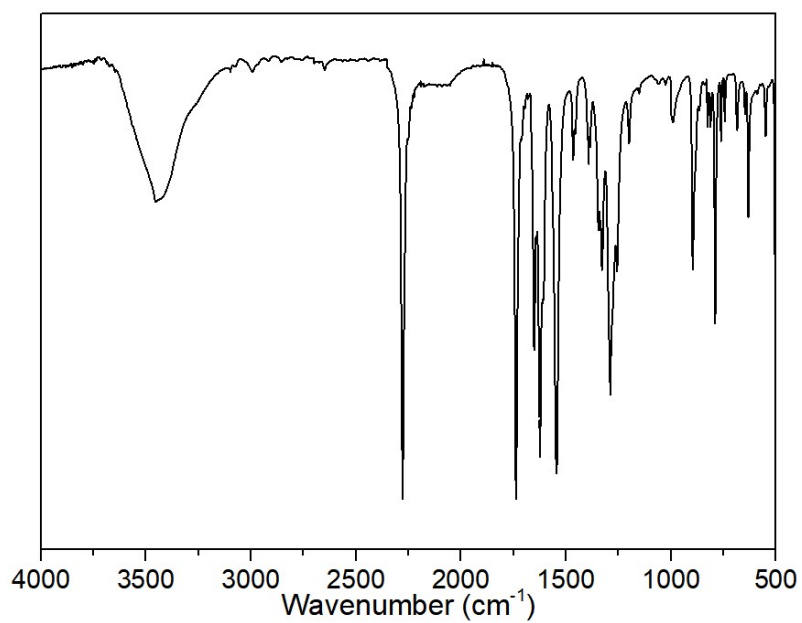**Figure S4.** IR spectrum of **2**.

Figure S5. IR spectrum of **3**.

4. Crystal Structures

4.1 X-ray crystallography details

A yellow block crystal (**1**) of dimensions 0.20×0.20×0.20 mm^3, a colorless block crystal (**2**) of dimensions 0.20×0.20×0.20 mm^3 and a colorless block crystal (**3**) of dimensions 0.20×0.20×0.20 mm^3 were mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 296 K. Corrections for Lorentz and polarization effects and for absorption (ψ scan) were applied. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares calculation on F2 with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they were attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

Table S1. Crystallographic data for **1**, **2**, and **3**.

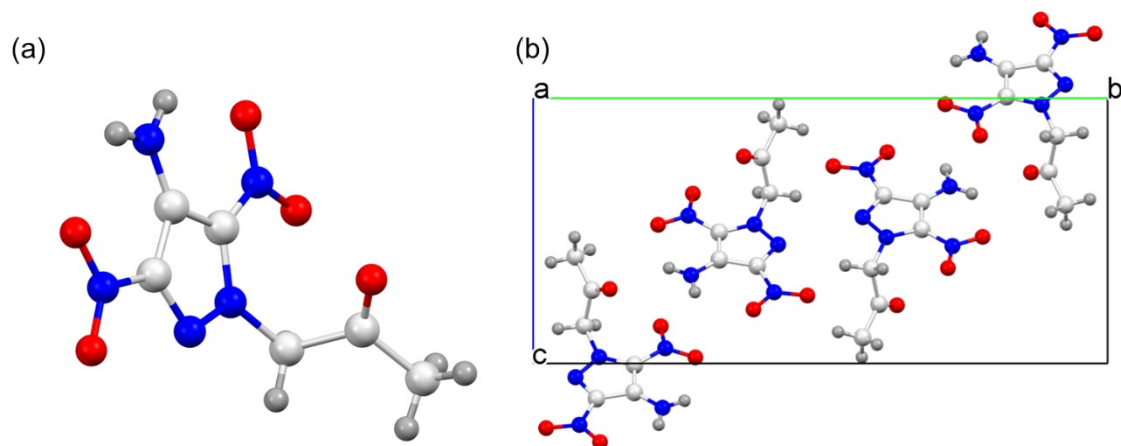| Compound	1	2	3
Formula	$C_6H_7N_5O_5$	$C_4HN_7O_7$	$C_4N_8O_9$
M_w	229.17	259.12	304.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	4.554(2)	5.5251(5)	10.250(3)
b [Å]	21.006(11)	13.8205(13)	10.283(3)
c [Å]	9.757(5)	12.4504(11)	11.223(3)
α[°]	90	90	90
β[°]	96.452(9)	93.952(2)	117.014(5)
γ[°]	90	90	90
V [Å^3]	927.5(8)	948.45(15)	1053.9(5)
Z	4	4	4
T [K]	296	296	296
λ [Å]	0.71073	0.71073	0.71073
P_{calcd}[g cm^{-3}]	1.641	1.815	1.917
μ [mm^{-1}]	0.144	0.173	0.188
F(000)	472	520	608
θ range[°]	2.86-25.00	2.95-24.98	2.84-20.85
Index ranges	-5 ≤ h ≤ 5	-6 ≤ h ≤ 6	-12 ≤ h ≤ 12
	-24 ≤ k ≤ 24	-16 ≤ k ≤ 16	-12 ≤ k ≤ 12
	-11 ≤ l ≤ 10	-14 ≤ l ≤ 13	-13 ≤ l ≤ 13
Data/restraints/parameters	1619/0/146	1667/0/163	1842/0/190
GOF on F2	1.090	1.037	1.032
R[F^2> 2σ(F^2)]	0.1068	0.0518	0.0451
wR(F^2)	0.1983	0.1324	0.1212

4.2 Bond lengths and angles

(a)

(b)

Figure S1. (a) Crystal structure of **1**; (b) Packing diagram of **1**.

Table S2. Bond lengths (Å) and bond angles (°) for **2**.

Bond lengths		
C6 H6A 0.9600	C1 N2 1.336(7)	C4 C5 1.512(8)
C6 H6B 0.9600	C1 C2 1.410(8)	C4 H4A 0.9700
C6 H6C 0.9600	C1 N1 1.436(8)	C4 H4B 0.9700
N1 O2 1.223(6)	C2 N4 1.344(7)	C5 O3 1.199(7)
N1 O1 1.236(6)	C2 C3 1.382(8)	C5 C6 1.504(8)
N2 N3 1.325(6)	C3 N3 1.370(7)	N5 O5 1.235(6)
N4 H4C 0.8600	C3 N5 1.408(7)	N5 O4 1.238(6)
N4 H4D 0.8600	C4 N3 1.472(7)	
Bond angles		
N2 C1 C2 114.0(5)	N3 C4 C5 111.0(5)	C5 C6 H6A 109.5
N2 C1 N1 119.4(5)	N3 C4 H4A 109.4	C5 C6 H6B 109.5
C2 C1 N1 126.6(6)	C5 C4 H4A 109.4	H6A C6 H6B 109.5
N4 C2 C3 129.2(6)	N3 C4 H4B 109.4	C5 C6 H6C 109.5
N4 C2 C1 129.6(6)	C5 C4 H4B 109.4	H6A C6 H6C 109.5
C3 C2 C1 101.2(5)	H4A C4 H4B 108.0	H6B C6 H6C 109.5
N3 C3 C2 109.1(5)	O3 C5 C6 123.5(6)	O2 N1 O1 124.7(6)
N3 C3 N5 123.7(5)	O3 C5 C4 121.6(6)	O2 N1 C1 118.9(6)
C2 C3 N5 127.2(6)	C6 C5 C4 114.9(6)	O1 N1 C1 116.4(6)

N3 N2 C1 104.5(4)	O5 N5 O4 123.9(5)	C2 N4 H4C 120.0
N2 N3 C3 111.2(5)	O5 N5 C3 116.9(5)	C2 N4 H4D 120.0
N2 N3 C4 117.2(5)	O4 N5 C3 119.3(5)	H4C N4 H4D 120.0
C3 N3 C4 130.1(5)		

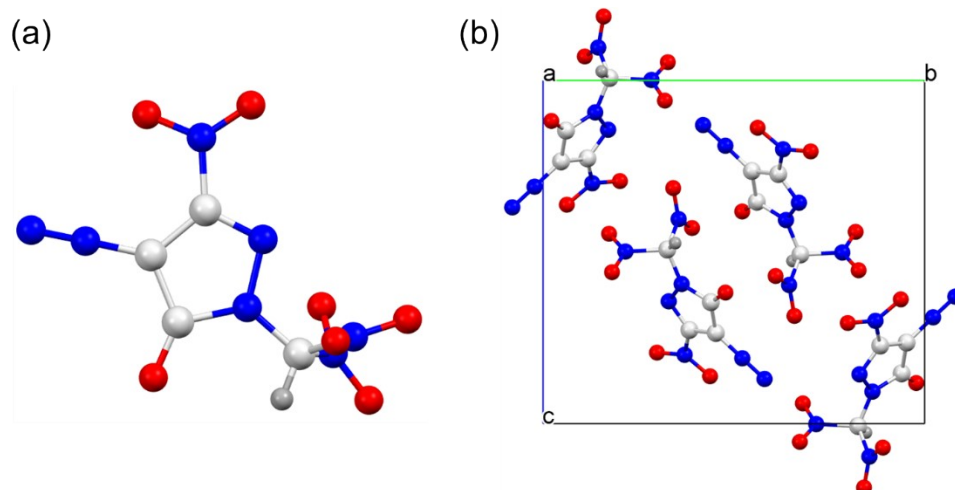(a)   (b)

Figure S2. (a) Crystal structure of **2**; (b) Packing diagram of **2**.

Table S3. Bond lengths (Å) and bond angles (°) for **2**.

Bond lengths		
N1 O1 1.203(4)	C1 N2 1.285(4)	C3 N3 1.394(3)
N1 O2 1.221(3)	C1 C4 1.402(4)	C3 N4 1.516(4)
N2 N3 1.387(3)	C1 N1 1.444(4)	C3 N5 1.518(4)
N4 O4 1.195(3)	C2 O3 1.205(3)	C3 H3 0.9800
N4 O5 1.194(3)	C2 N3 1.406(4)	C4 N6 1.333(4)
N5 O7 1.198(3)	C2 C4 1.438(4)	N6 N7 1.106(4)
N5 O6 1.206(3)		
Bond angles		
N2 C1 C4 113.4(2)	C3 N3 C2 126.1(2)	N5 C3 H3 109.3
N2 C1 N1 119.9(3)	O4 N4 O5 126.0(3)	O1 N1 O2 125.7(3)
C4 C1 N1 126.7(3)	O4 N4 C3 114.7(3)	O1 N1 C1 119.1(3)
O3 C2 N3 126.0(3)	O5 N4 C3 119.3(3)	O2 N1 C1 115.2(3)

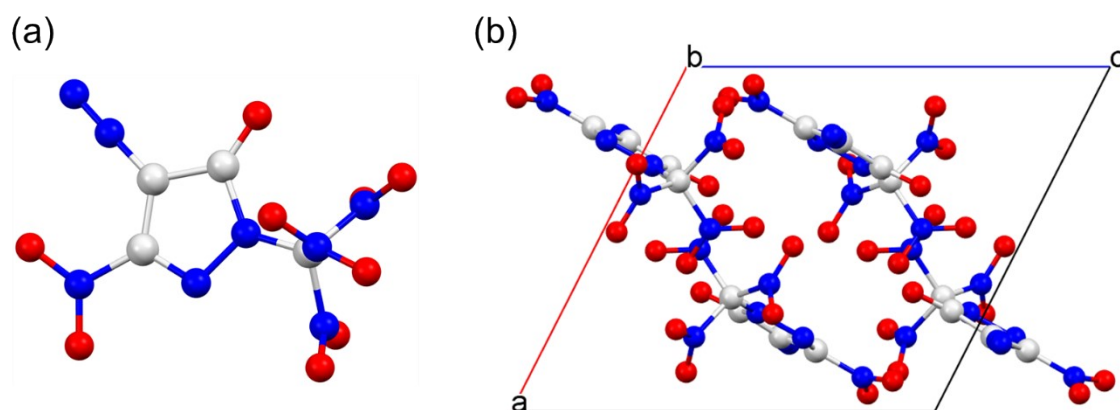|		
O3 C2 C4 134.2(3)	O7 N5 O6 126.1(3)	C1 N2 N3 103.9(2)
N3 C2 C4 99.8(2)	O7 N5 C3 116.1(3)	N2 N3 C3 118.6(2)
N3 C3 N4 109.0(2)	O6 N5 C3 117.8(3)	N2 N3 C2 115.1(2)
N3 C3 N5 113.2(2)	N6 C4 C1 128.3(3)	N7 N6 C4 179.2(4)
N4 C3 N5 106.8(2)	N6 C4 C2 124.0(3)	N4 C3 H3 109.3
N3 C3 H3 109.3	C1 C4 C2 107.7(2)	

Figure S3. (a) Crystal structure of **3**; (b) Packing diagram of **3**.
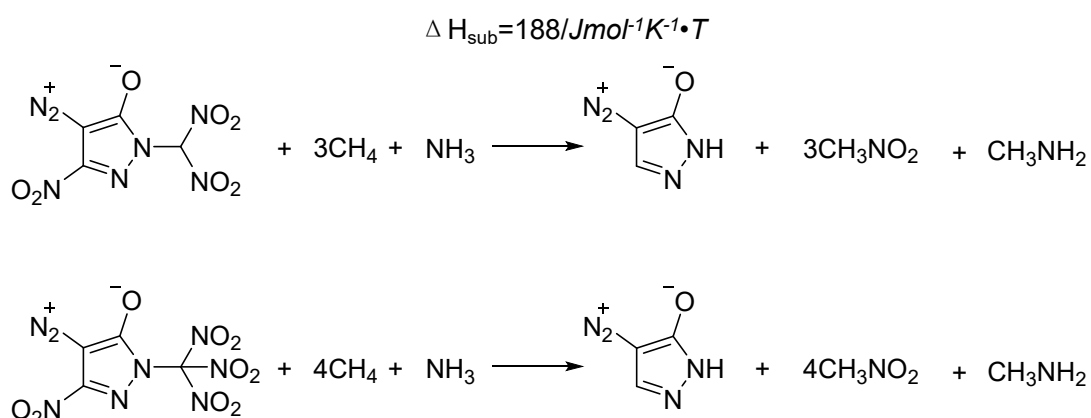
Table S4. Bond lengths (Å) and bond angles (°) for **3**.

Bond lengths		
C1 O7 1.203(3)	N3 O5 1.184(3)	C3 N5 1.289(3)
C1 N4 1.416(3)	N3 O6 1.188(3)	C3 C4 1.398(4)
C1 C4 1.434(4)	N4 N5 1.390(3)	C3 N9 1.446(3)
C2 N4 1.380(3)	C4 N7 1.335(4)	N2 O2 1.189(3)
C2 N1 1.537(3)	N7 N8 1.101(3)	N2 O1 1.199(3)
C2 N3 1.554(3)	N9 O9 1.206(3)	N1 O4 1.193(3)
C2 N2 1.556(3)	N9 O8 1.219(3)	N1 O3 1.199(3)
Bond angles		
O7 C1 N4 125.4(2)	N5 N4 C1 114.5(2)	N5 C3 N9 120.6(3)
O7 C1 C4 134.4(2)	C3 N5 N4 103.8(2)	C4 C3 N9 125.7(3)
N4 C1 C4 100.2(2)	N7 C4 C3 127.3(2)	O2 N2 O1 128.0(3)

N4 C2 N1 114.4(2)	N7 C4 C1 124.6(2)	O2 N2 C2 116.8(2)
N4 C2 N3 109.2(2)	C3 C4 C1 107.7(2)	O1 N2 C2 115.2(2)
N1 C2 N3 108.1(2)	N8 N7 C4 179.1(3)	O4 N1 O3 127.6(3)
N4 C2 N2 110.1(2)	O9 N9 O8 126.4(3)	O4 N1 C2 117.6(3)
N1 C2 N2 106.6(2)	O9 N9 C3 118.7(3)	O3 N1 C2 114.8(3)
N3 C2 N2 108.2(2)	O8 N9 C3 115.0(3)	O5 N3 O6 128.2(3)
N5 C3 C4 113.7(2)	C2 N4 N5 118.5(2)	O5 N3 C2 115.8(3)
O6 N3 C2 115.9(2)	C2 N4 C1 126.5(2)	

5. Heat of formation

The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S2). The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (H_{corr}), and other thermal factors. The heats of formation for the diazo-oxide pyrazole were obtained by an atomization approach using G2 ab initio method. The heats of formation of other compounds in Scheme S2 were obtained from the NIST WebBook. The solid state heats of formation were calculated with Trouton's rule according to the following equation (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).

$$\Delta H_{sub}=188/Jmol^{-1}K^{-1} \cdot T$$

Scheme S1. Isodesmic reactions for calculating heats of formation for **2** and **3**, respectively.

Table S5. Calculated Total Energy (E_0), Zero Point Energy (ZPE) and values of Thermal Correction (H_{corr}) of the compounds.

Compound	ZPE/a.u.	H_{corr}/a.u.	E_0/a.u.
2	0.097201	0.108071	-1060.195476
3	0.098487	0.111628	-1264.257444
CH_4	0.044793	0.048605	-40.3796224
NH_3	0.034372	0.03819	-56.4154644
diazo-oxide pyrazole	0.064026	0.068877	-408.7261129
CH_3NH_2	0.064026	0.068401	-95.5938452
CH_3NO_2	0.049856	0.055129	-244.4784875

6. Thermal stability

Differential scanning calorimetry (DSC/TG) showed that **3** possessed a higher thermal stability with a decomposition temperature of 130 $^{\circ}$C, while the decomposition temperature of **2** was 116 $^{\circ}$C.
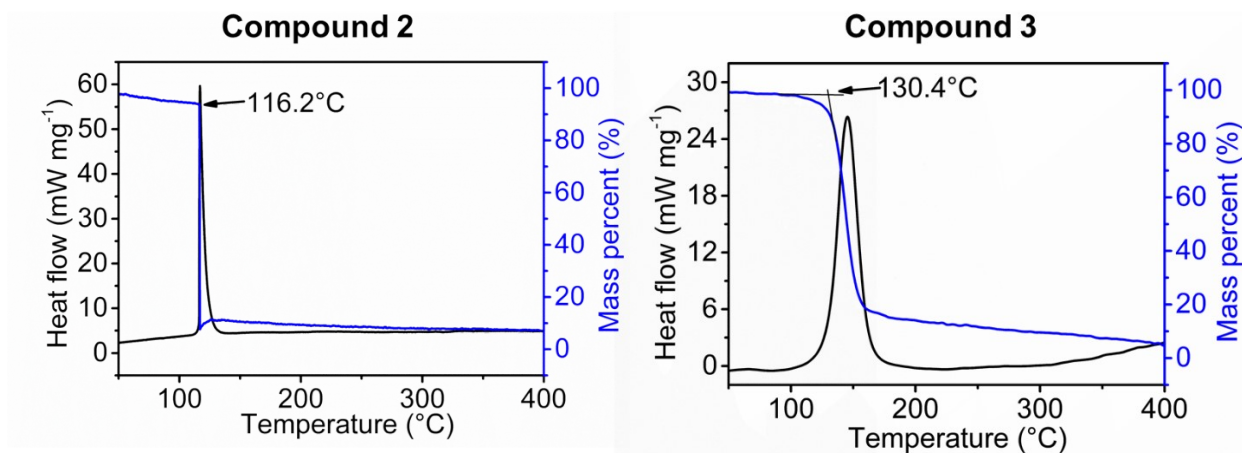

Figure S4. Differential scanning calorimetry and thermal gravimetric analyzer (TG-DSC) plots: (left) **2** and (right) **3**.