Supporting Information

Nitrogen-centered Radical Reaction to Energetic Materials: A Mild and Efficient Access to N–N Bridged Compounds

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1. General Methods

Chemical reagents were purchased from Aladdin (iodine), and Bide Pharm (sodium carbonate, 2,6-di-*tert*-butyl-4-methylphenol) in analytical grade and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500 MHz nuclear magnetic resonance spectrometer. DMSO-d_6 was used as solvent and locking solvent. The working frequencies for ^{1}H and ^{13}C are 500.03 MHz and 125.75 MHz, respectively. Chemical shifts were reported relative to tetramethylsilane as internal standard. Decomposition temperature was obtained on a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 ℃ min^{-1}. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were performed on a Vario EL III Analyzer. Impact and friction sensitivities were measured with a BAM fallhammer and friction tester. X-ray intensity data were collected on a Bruker D8 VENTURE PHOTON II system equipped with an Incoatecius 3.0 Microfocus sealed tube. The structure was solved and refined using Bruker SHELXTL Software Package. The data were refined against F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to their parent atoms using a riding model and refined isotropically.

2. Crystallographic data

Table S1. Crystal data and structure refinement for **2**.

Identification code	**2**
CCDC number	2097303
Empirical formula	$C_6H_8N_{10}O_4$
Formula weight	284.22
Temperature/K	170.0
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	21.60(2)
b/Å	4.493(4)
c/Å	12.608(12)
α/°	90
β/°	122.59(2)
γ/°	90
Volume/Å^3	1031.2(17)
Z	4
ρ_{calc} g/cm^3	1.831
μ/mm^{-1}	0.866
F(000)	584.0
Crystal size/mm^3	0.200 × 0.200 × 0.100
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.452 to 102.77
Index ranges	–24 ≤ h ≤ 20, 0 ≤ k ≤ 5, 0 ≤ l ≤ 14
Reflections collected	851
Independent reflections	851 [R_{int} = 0.0000,[a] R_{sigma} = 0.0567]
Data/restraints/parameters	851 / 0 / 91
Goodness-of-fit on F^2	1.121
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0987, wR_2 = 0.2631
Final *R* indexes [all data]	R_1 = 0.1254, wR_2 = 0.2732
Largest diff. peak/hole / e Å^{-3}	0.47/–0.46

[a] R_{int} is unavailable because equivalent points were merged to resolve twinning issues.

Table S2. Bond lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N3	1.244(7)	C1	C3	1.446(9)
N1	N1[a]	1.368(10)	C2	N4	1.326(8)
N1	C2	1.367(7)	N3	O2	1.256(7)
N1	N2	1.436(7)	N2	C3	1.319(8)
C1	C2	1.378(9)	C3	N5	1.326(8)
C1	N3	1.377(8)			

[a]1–X,+Y,3/2–Z.

Table S3. Bond angles for **2**.

Atom	Atom	Atom	Angle/°
N1[a]	N1	N2	117.8(4)
C2	N1	N1[a]	118.2(6)
C2	N1	N2	111.6(5)
C2	C1	N3	125.4(6)
C2	C1	C3	107.5(6)
N3	C1	C3	127.1(6)
N1	C2	C1	105.4(6)
N4	C2	N1	121.9(6)
N4	C2	C1	132.6(6)
O1	N3	C1	118.1(6)
O1	N3	O2	122.6(5)
O2	N3	C1	119.3(6)
C3	N2	N1	104.6(5)
N2	C3	C1	110.2(6)
N2	C3	N5	122.3(6)

[a]1–X,+Y,3/2–Z.

Table S4. Torsion angles for **2**.

Atom	Atom	Atom	Atom	Angle/°
N1[a]	N1	C2	C1	–149.2(4)
N1[a]	N1	C2	N4	31.8(8)
N1[a]	N1	N2	C3	149.9(6)
N1	N2	C3	C1	–5.4(7)
N1	N2	C3	N5	174.1(6)
C2	N1	N2	C3	8.5(7)
C2	C1	N3	O1	4.5(10)
C2	C1	N3	O2	–174.6(6)
C2	C1	C3	N2	0.9(8)
C2	C1	C3	N5	–178.6(6)
N3	C1	C2	N1	–174.1(6)
N3	C1	C2	N4	4.8(12)
N3	C1	C3	N2	179.2(6)
N3	C1	C3	N5	–0.2(11)
N2	N1	C2	C1	–7.9(7)
N2	N1	C2	N4	173.1(6)
C3	C1	C2	N1	4.3(7)
C3	C1	C2	N4	–176.8(7)
C3	C1	N3	O1	–173.6(6)
C3	C1	N3	O2	7.3(10)

[a]1–X,+Y,3/2–Z.

Table S5. Hydrogen bonds for **2**.

D	H	A	*d*(D–H)/Å	*d*(H–A)/Å	*d*(D–A)/Å	D–H–A/°
N4	H4B	O1	0.88	2.31	2.825(8)	117.1
N4	H4B	O1[a]	0.88	2.20	3.024(7)	156.0
N5	H5A	N2[b]	0.88	2.35	3.076(8)	140.5
N5	H5B	O2	0.88	2.28	2.850(7)	122.1
N5	H5B	O2[c]	0.88	2.24	3.062(8)	154.7

[a]1/2–X,1/2–Y,1–Z; [b]1–X,2–Y,2–Z; [c]1/2–X,1/2+Y,3/2–Z.

Table S6. Crystal data and structure refinement for **3**.

Identification code	**3**
CCDC number	2097304
Empirical formula	$C_{18}H_{27}N_5O_3$
Formula weight	361.44
Temperature/K	188
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1659(10)
b/Å	22.9892(18)
c/Å	9.3626(8)
α/°	90
β/°	102.482(3)
γ/°	90
Volume/Å^3	1926.2(3)
Z	4
ρ_{calc} g/cm^3	1.246
μ/mm^{-1}	0.087
F(000)	776.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.796 to 52.902
Index ranges	$-9 \le h \le 11$, $-28 \le k \le 28$, $-11 \le l \le 11$
Reflections collected	14444
Independent reflections	3875 [R_{int} = 0.0911, R_{sigma} = 0.0870]
Data/restraints/parameters	3875/0/250
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0575, wR_2 = 0.1186
Final R indexes [all data]	R_1 = 0.1097, wR_2 = 0.1463
Largest diff. peak/hole / e Å^{-3}	0.23/–0.23

Table S7. Bond lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.222(3)	C4	C18	1.541(3)
O2	N1	1.258(3)	C5	C6	1.338(3)
O3	N1	1.243(3)	C6	C7	1.493(4)
N1	C2	1.372(3)	C6	C14	1.538(3)
N2	C3	1.343(3)	C7	C8	1.499(3)
N3	C3	1.340(3)	C8	C9	1.330(3)
N3	N4	1.413(3)	C8	C10	1.535(4)
N3	C4	1.474(3)	C10	C11	1.532(4)
N4	C1	1.321(3)	C10	C12	1.534(4)
N5	C1	1.352(3	C10	C13	1.536(4)
C1	C2	1.430(3)	C14	C15	1.523(5)
C2	C3	1.404(3)	C14	C17	1.527(4)
C4	C9	1.495(4)	C14	C16	1.539(4)
C4	C5	1.498(3)			

Table S8. Bond angles for **3**.

Atom	Atom	Atom	Angle/°
O3	N1	O2	121.1(2)
O3	N1	C2	119.4(2)
O2	N1	C2	119.4(2)
C3	N3	N4	112.73(19)
C3	N3	C4	127.02(19)
N4	N3	C4	120.21(18)
C1	N4	N3	104.70(18)
N4	C1	N5	121.9(2)
N4	C1	C2	110.7(2)
N5	C1	C2	127.4(2)
N1	C2	C3	126.8(2)
N1	C2	C1	126.9(2)
C3	C2	C1	106.2(2)
N3	C3	N2	124.9(2)
N3	C3	C2	105.6(2)
N2	C3	C2	129.4(2)
N3	C4	C9	110.04(19)
N3	C4	C5	110.0(2)
C9	C4	C5	112.1(2)
N3	C4	C18	108.39(19)
C9	C4	C18	107.7(2)
C5	C4	C18	108.5(2)
C6	C5	C4	123.6(2)

Atom	Atom	Atom	Angle/°
C5	C6	C7	117.4(2)
C5	C6	C14	122.3(2)
C7	C6	C14	120.1(2)
O1	C7	C6	120.7(2)
O1	C7	C8	120.8(2)
C6	C7	C8	118.5(2)
C9	C8	C7	117.1(2)
C9	C8	C10	122.5(2)
C7	C8	C10	120.1(2)
C8	C9	C4	124.1(2)
C11	C10	C12	108.6(2)
C11	C10	C8	112.8(2)
C12	C10	C8	109.0(2)
C11	C10	C13	107.4(2)
C12	C10	C13	108.2(2)
C8	C10	C13	110.6(2)
C15	C14	C17	109.0(3)
C15	C14	C6	110.7(2)
C17	C14	C6	110.6(2)
C15	C14	C16	108.0(3)
C17	C14	C16	108.9(2)
C6	C14	C16	109.5(2)

Table S9. Torsion angles for **3**.

Atom	Atom	Atom	Atom	Angle/°
O1	C7	C8	C9	157.7(2)
O1	C7	C8	C10	–16.3(3)
O2	N1	C2	C1	–179.4(2)
O2	N1	C2	C3	–2.3(4)
O3	N1	C2	C1	0.8(4)
O3	N1	C2	C3	177.9(2)
N1	C2	C3	N2	5.6(4)
N1	C2	C3	N3	–176.5(2)
N3	N4	C1	N5	–178.2(2)
N3	N4	C1	C2	0.7(2)
N3	C4	C5	C6	–144.8(2)
N3	C4	C9	C8	145.2(2)
N4	N3	C3	N2	177.3(2)
N4	N3	C3	C2	–0.7(3)
N4	N3	C4	C5	–116.9(2)
N4	N3	C4	C9	118.9(2)
N4	N3	C4	C18	1.5(3)
N4	C1	C2	N1	176.4(2)
N4	C1	C2	C3	–1.2(3)
N5	C1	C2	N1	–4.7(4)
N5	C1	C2	C3	177.7(2)
C1	C2	C3	N2	–176.8(2)
C1	C2	C3	N3	1.1(3)
C3	N3	N4	C1	0.0(3)
C3	N3	C4	C5	65.3(3)
C3	N3	C4	C9	–58.8(3)
C3	N3	C4	C18	–176.2(2)
C4	N3	N4	C1	–178.1(2)
C4	N3	C3	N2	–4.8(4)
C4	N3	C3	C2	177.2(2)
C4	C5	C6	C7	1.6(3)
C4	C5	C6	C14	–173.6(2)
C5	C4	C9	C8	22.3(3)
C5	C6	C7	O1	–157.4(2)
C5	C6	C7	C8	20.4(3)
C5	C6	C14	C15	–14.5(4)
C5	C6	C14	C16	104.6(3)
C5	C6	C14	C17	–135.3(2)
C6	C7	C8	C9	–20.1(3)
C6	C7	C8	C10	165.8(2)
C7	C6	C14	C15	170.4(3)

Atom	Atom	Atom	Atom	Angle/°
C7	C6	C14	C16	–70.5(3)
C7	C6	C14	C17	49.6(3)
C7	C8	C9	C4	–2.2(3)
C7	C8	C10	C11	–46.3(3)
C7	C8	C10	C12	74.3(3)
C7	C8	C10	C13	–166.8(2)
C9	C4	C5	C6	–21.9(3)
C9	C8	C10	C11	139.9(2)
C9	C8	C10	C12	–99.4(3)
C9	C8	C10	C13	19.5(3)
C10	C8	C9	C4	171.7(2)
C14	C6	C7	O1	18.0(3)
C14	C6	C7	C8	–164.2(2)
C18	C4	C5	C6	96.8(3)
C18	C4	C9	C8	–96.9(3)

Table S10. Hydrogen bonds for **3**.

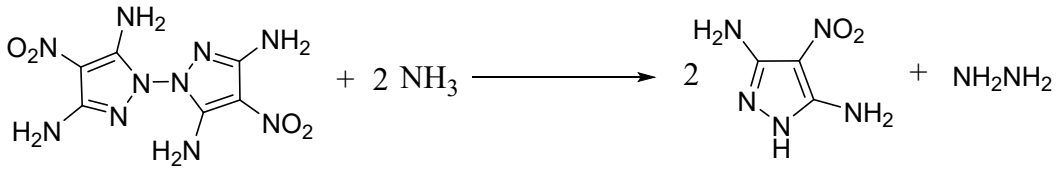
D	H	A	*d*(D–H)/Å	*d*(H–A)/Å	*d*(D–A)/Å	D–H–A/°
N2	H2A	O2[a]	0.88	2.62	3.376(3)	144.5
N2	H2B	O2	0.88	2.30	2.845(3)	120.2
N5	H5B	O1[b]	0.84(3)	2.26(3)	3.040(3)	153(2)
N5	H5B	O3	0.84(3)	2.26(3)	2.830(3)	125(2)

[a]1/2+X,3/2–Y,1/2+Z; [b]–1+X,+Y,–1+Z.

3. Computational methods

Gas phase heats of formation were calculated based on an isodesmic reaction (Scheme S1). The enthalpy of reaction was obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid state heats of formation were calculated with Trouton's rule according to equation 1 (*T* represents either melting point or decomposition temperature when no melting occurs prior to decomposition).[1]

$$\Delta H_{sub} = 188/J\ mol^{-1}K^{-1} \times T \qquad (1)$$



2 **1**

Scheme S1. Isodesmic reaction for **2.**

Table S11. Calculated zero point energy (*ZPE*), values of the correction (H_r), total energy (E_0) and heats of formation (*HOF*) in gas state.

Species	*ZPE*	H_r	E_0	corrected E_0	*HOF*(kJ mol^{-1})
2	0.194636	0.213261	–1079.176625	–1078.971149	301.06
1	0.107276	0.117201	–540.1924739	–540.07956	110.74
NH_2NH_2	0.05331	0.057521	–111.5836915	–111.52830	95.4[2]
NH_3	0.034384	0.038203	–56.4154647	–56.37864	–45.9[2]

4. ESR measurement

Room temperature ESR spectra of sample powder were obtained using a JEOL JES FA200 ESR spectrometer (9.1GHz, X-band). Conditions of ESR measurements were as follows: microwave power (2 mW), sweep width (321mT to 328.5mT), modulation frequency (100 kHz), time constant (0.1 s) and measure time (2 min). The simulation of the hyperfine structure on the free radical was taken by the Easyspin and metlab software. Based on the measured spectra and references,[3] a nitrogen-centered radical was found as described in the paper.

5. NMR Spectra

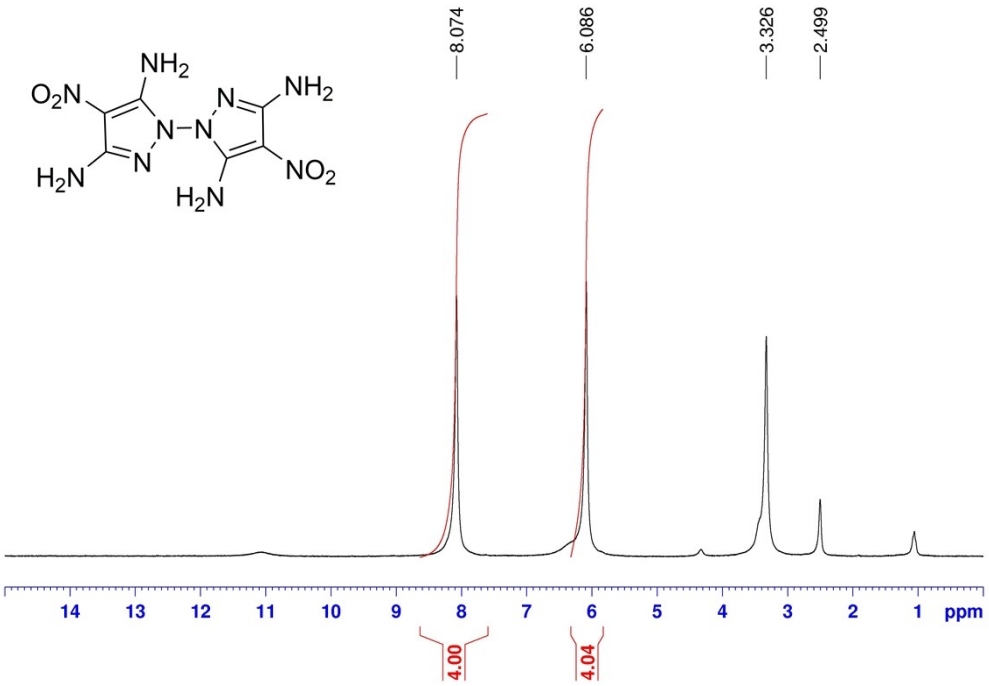


Figure S1 ^{1}H NMR spectrum of **2**.

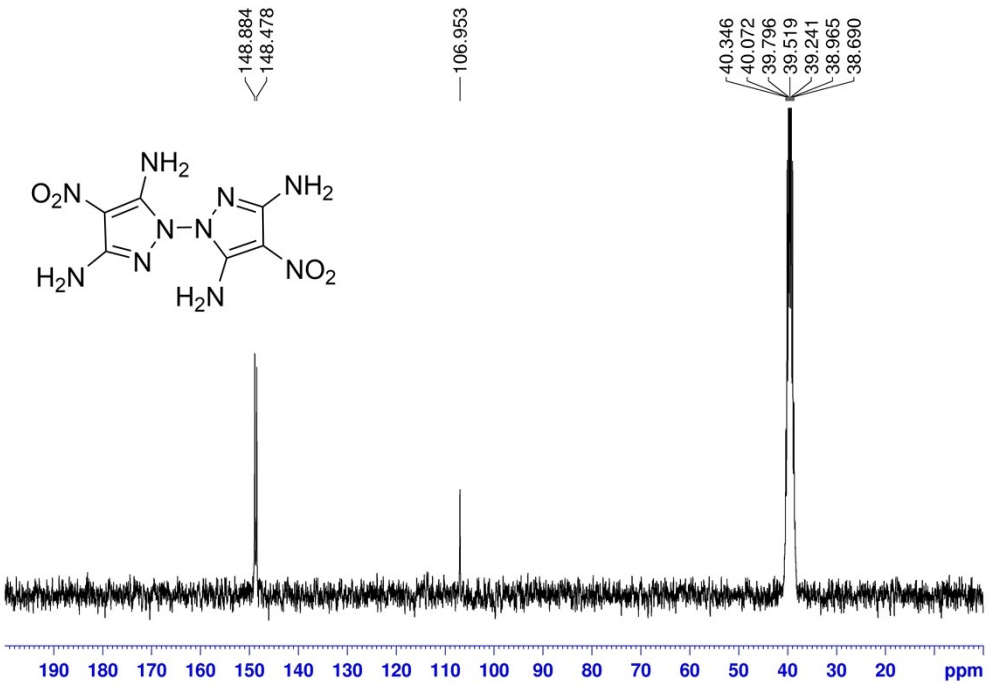


Figure S2 ^{13}C NMR spectrum of **2**.

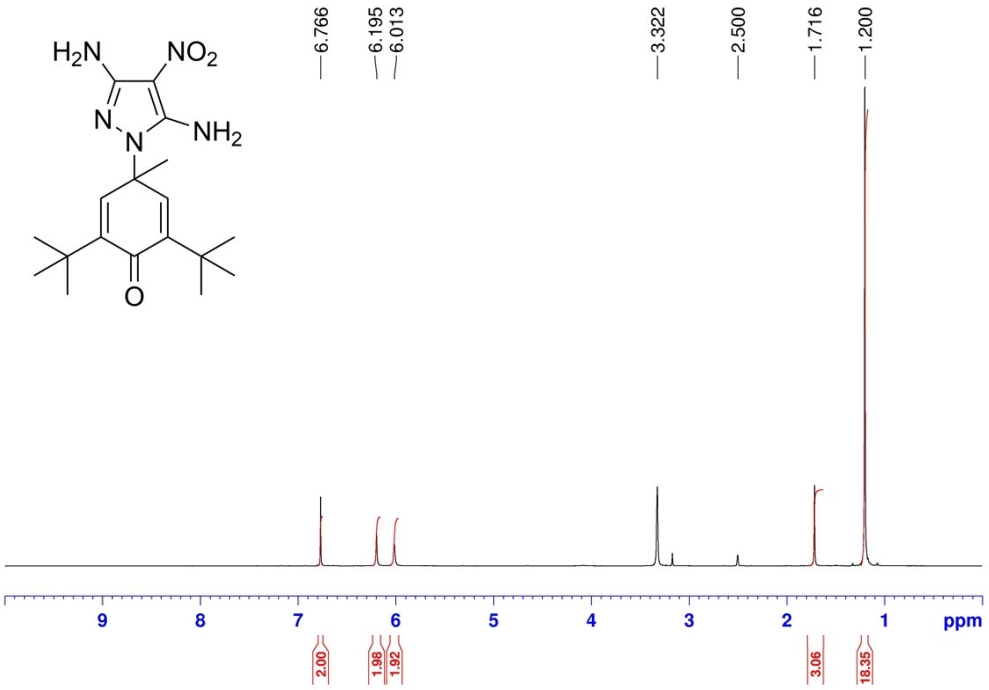


Figure S3 ^{1}H NMR spectrum of **3**.

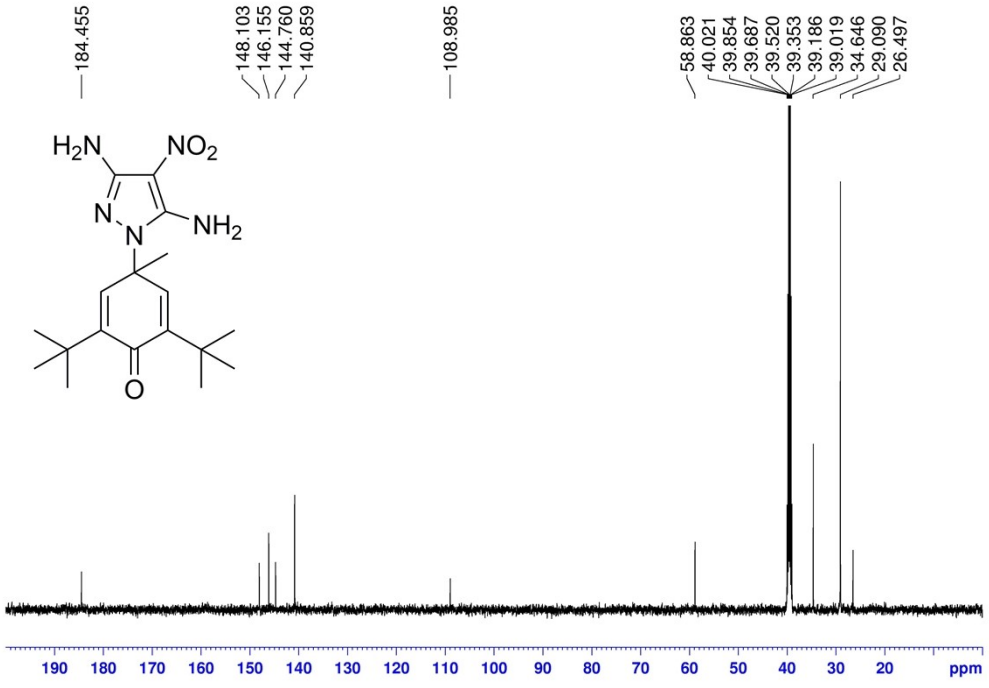


Figure S4 ^{13}C NMR spectrum of **3**.

6. DSC Plots

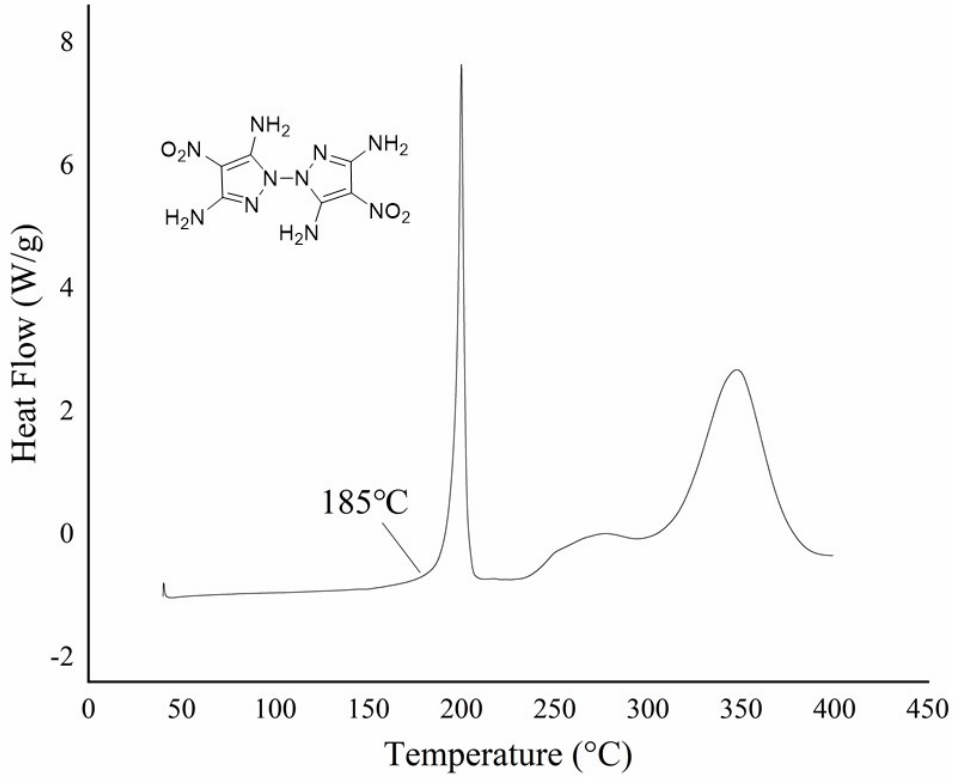


Figure S5 DSC plot of **2**.

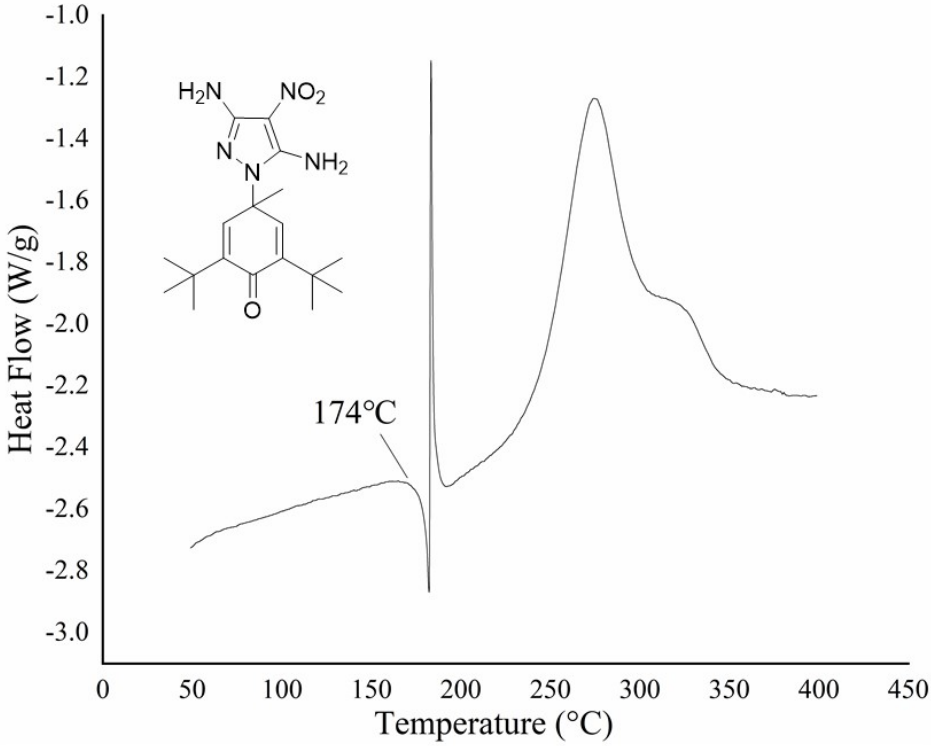


Figure S6 DSC plot of **3**.

7. References

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3. (*a*) M. Jiang, H. Yang and H. Fu, *Org. Lett.* **2016**, *18*, 5248–5251; (*b*) J. Su, B. Wang, D. Liu, L. Du, Y. Liu, J. Su and W. Zheng, *Chem. Commun*. **2015**, *51*, 12680–12683; (*c*) M. Jiang, H. Li, H. Yang and H. Fu, *Angew. Chem. Int. Ed*. **2017**, *56*, 874–879.