Supporting Information

Radical-mediated C–N Bond Activation in 3,5-Diamino-4-nitro-1*H*-pyrazole towards High-energy and Insensitive Energetic Materials

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Table of Contents

1. General Methods S3

2. Crystallographic Data S4

3. Computational Details S16

4. Geometries for Optimized Structures S18

5. NMR Spectra S23

6. DSC Plots S26

7. ESR Measurement S28

8. References S29

1. General Methods

Chemical reagents were purchased from Bide Pharm (*N*-bromosuccinimide, 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. Decomposition temperature was obtained on a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C 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**·DMSO.

CCDC number	2142354
Empirical formula	$C_8H_{12}N_8O_5S$
Formula weight	332.32
Temperature/K	296.15
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	6.973(19)
b/Å	10.12(3)
c/Å	11.10(3)
α/°	70.53(3)
β/°	79.60(3)
γ/°	75.78(3)
Volume/Å^3	711(3)
Z	2
ρ_{calc}/g cm^{-3}	1.552
μ/mm^{-1}	0.267
F(000)	344.0
Crystal size/mm^3	0.160 × 0.150 × 0.130
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.916 to 49.992
Index ranges	–8 ≤ h ≤ 8, –12 ≤ k ≤ 11, –13 ≤ l ≤ 13
Reflections collected	5101
Independent reflections	2477 [R_{int} = 0.0625, R_{sigma} = 0.1057]
Data/restraints/parameters	2477/1/205
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0688, wR_2 = 0.1397
Final R indexes [all data]	R_1 = 0.1361, wR_2 = 0.1626
Largest diff. peak/hole / e Å^{-3}	0.29/–0.33

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

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.531(6)	C3	N5	1.402(6)
S1	C7	1.781(6)	O3	N4	1.248(5)
S1	C8	1.792(6)	C4	N5	1.347(7)
N1	C1	1.348(6)	C4	C5	1.442(7)
C1	N2	1.349(6)	C4	N8	1.330(6)
C1	C2	1.423(7)	C5	N6	1.401(6)
O2	N4	1.240(5)	C5	C6	1.417(7)
N2	N3	1.407(6)	O5	N6	1.255(6)
C2	C3	1.419(7)	N6	O6	1.252(5)
C2	N4	1.400(6)	C6	N7	1.160(6)
C3	N3	1.322(6)			

Table S3. Bond angles for **2**·DMSO.

Atom	Atom	Atom	Angle/°
O1	S1	C7	105.7(3)
O1	S1	C8	106.5(3)
C7	S1	C8	99.1(3)
N1	C1	N2	124.8(5)
N1	C1	C2	130.1(4)
N2	C1	C2	105.1(4)
C1	N2	N3	113.1(4)
C3	C2	C1	105.5(4)
N4	C2	C1	126.7(4)
N4	C2	C3	127.8(4)
N3	C3	C2	112.0(4)
N3	C3	N5	123.0(5)
N5	C3	C2	125.0(4)
C3	N3	N2	104.3(4)
O2	N4	C2	118.6(4)
O2	N4	O3	121.6(4)
O3	N4	C2	119.8(4)
N5	C4	C5	119.8(4)
N8	C4	N5	119.8(4)
N8	C4	C5	120.4(4)
C4	N5	C3	127.9(4)
N6	C5	C4	124.5(4)
N6	C5	C6	114.2(4)
C6	C5	C4	121.3(4)
O5	N6	C5	120.9(4)

Atom	Atom	Atom	Angle/°
O6	N6	C5	117.7(5)
O6	N6	O5	121.4(4)
N7	C6	C5	178.4(5)

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

Atom	Atom	Atom	Atom	Angle/°
N1	C1	N2	N3	178.2(4)
N1	C1	C2	C3	–178.7(5)
N1	C1	C2	N4	0.6(9)
C1	N2	N3	C3	0.8(5)
C1	C2	C3	N3	0.9(6)
C1	C2	C3	N5	–177.6(4)
C1	C2	N4	O2	1.2(7)
C1	C2	N4	O3	–179.4(5)
N2	C1	C2	C3	–0.4(5)
N2	C1	C2	N4	178.9(4)
C2	C1	N2	N3	–0.2(5)
C2	C3	N3	N2	–1.0(5)
C2	C3	N5	C4	178.3(5)
C3	C2	N4	O2	–179.6(5)
C3	C2	N4	O3	–0.1(7)
N3	C3	N5	C4	–0.1(8)
N4	C2	C3	N3	–178.4(4)
N4	C2	C3	N5	3.0(8)
C4	C5	N6	O5	1.1(8)
C4	C5	N6	O6	179.2(5)
N5	C3	N3	N2	177.6(4)
N5	C4	C5	N6	4.0(7)
N5	C4	C5	C6	–178.2(5)
C5	C4	N5	C3	–178.9(4)
C6	C5	N6	O5	–176.8(5)
C6	C5	N6	O6	1.3(7)
N8	C4	N5	C3	1.3(8)
N8	C4	C5	N6	–176.2(4)
N8	C4	C5	C6	1.6(7)

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

D	H	A	d(D–H)/Å	d(H–A)/Å	d(D–A)/Å	D–H–A/°
N1	H1A	O1[1]	0.86	2.30	2.978(9)	136.3
N2	H2	O1	0.86	2.01	2.820(8)	156.8
N5	H5	O3	0.84(5)	2.18(5)	2.834(8)	134(4)
N5	H5	O5	0.84(5)	2.01(5)	2.637(9)	131(4)
C7	H7C	O6[2]	0.96	2.61	3.292(10)	127.9
C8	H8E	O6[3]	0.96	2.50	3.215(9)	131.7
N8	H8A	N3	0.86	2.06	2.717(8)	133.0
N8	H8B	N7[4]	0.86	2.14	2.980(9)	165.2

[1]-X,1-Y,-Z; [2]-1+X,1+Y,-1+Z; [3]+X,1+Y,-1+Z; [4]2-X,-Y,1-Z

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

CCDC number	2142355
Empirical formula	$C_6H_6N_8O_4$
Formula weight	254.19
Temperature/K	307.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.484(9)
b/Å	7.966(11)
c/Å	18.00(4)
α/°	90
β/°	91.59(4)
γ/°	90
Volume/Å^3	929(3)
Z	4
ρ_{calc}/g cm^{-3}	1.816
μ/mm^{-1}	1.353
F(000)	520.0
Crystal size/mm^3	0.15 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.828 to 133.334
Index ranges	$-7 \le h \le 7$, $-9 \le k \le 9$, $-21 \le l \le 21$
Reflections collected	6115
Independent reflections	1623 [R_{int} = 0.1203, R_{sigma} = 0.0910]
Data/restraints/parameters	1623/5/169
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1561
Final R indexes [all data]	R_1 = 0.1494, wR_2 = 0.2217
Largest diff. peak/hole / e Å^{-3}	0.32/–0.31

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

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N3	1.244(6)	N3	C3	1.407(8)
C1	C3	1.382(8)	O4	N5	1.242(6)
C1	N6	1.372(7)	C4	C5	1.442(7)
C1	N8	1.332(7)	C4	N8	1.360(8)
O2	N3	1.238(6)	N5	C5	1.438(8)
N2	C4	1.324(7)	C5	C6	1.411(8)
C2	C3	1.438(8)	N6	C6	1.390(8)
C2	N7	1.352(7)	N6	N7	1.397(6)
C2	N9	1.338(8)	C6	N10	1.324(6)
O3	N5	1.233(6)			

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

Atom	Atom	Atom	Angle/°
N6	C1	C3	104.0(5)
N8	C1	C3	132.8(5)
N8	C1	N6	123.1(5)
N7	C2	C3	110.0(5)
N9	C2	C3	127.1(6)
N9	C2	N7	122.8(5)
O1	N3	C3	120.2(5)
O2	N3	O1	121.5(5)
O2	N3	C3	118.3(5)
C1	C3	C2	108.0(5)
C1	C3	N3	128.1(5)
N3	C3	C2	123.9(6)
N2	C4	C5	122.5(6)
N2	C4	N8	115.8(5)
N8	C4	C5	121.7(5)
O3	N5	O4	120.4(5)
O3	N5	C5	120.5(5)
O4	N5	C5	119.0(5)
N5	C5	C4	121.2(5)
C6	C5	C4	120.0(5)
C6	C5	N5	118.8(5)
C1	N6	C6	123.4(5)
C1	N6	N7	114.4(5)
C6	N6	N7	122.2(4)
N6	C6	C5	114.4(4)
N10	C6	C5	129.0(6)
N10	C6	N6	116.6(5)

Atom	Atom	Atom	Angle/°
C2	N7	N6	103.5(4)
C1	N8	C4	117.3(4)

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

Atom	Atom	Atom	Atom	Angle/°
O1	N3	C3	C1	–175.4(6)
O1	N3	C3	C2	4.7(9)
C1	N6	C6	C5	–2.4(7)
C1	N6	C6	N10	–179.8(5)
C1	N6	N7	C2	0.3(6)
O2	N3	C3	C1	5.6(9)
O2	N3	C3	C2	–174.2(5)
N2	C4	C5	N5	–2.8(9)
N2	C4	C5	C6	177.2(6)
N2	C4	N8	C1	–179.7(5)
O3	N5	C5	C4	–4.3(8)
O3	N5	C5	C6	175.7(5)
C3	C1	N6	C6	–179.0(5)
C3	C1	N6	N7	0.0(6)
C3	C1	N8	C4	178.8(6)
C3	C2	N7	N6	–0.5(6)
O4	N5	C5	C4	179.1(5)
O4	N5	C5	C6	–0.9(8)
C4	C5	C6	N6	4.7(7)
C4	C5	C6	N10	–178.3(5)
N5	C5	C6	N6	–175.3(5)
N5	C5	C6	N10	1.7(9)
C5	C4	N8	C1	2.1(8)
N6	C1	C3	C2	–0.4(6)
N6	C1	C3	N3	179.7(5)
N6	C1	N8	C4	0.3(8)
C6	N6	N7	C2	179.4(5)
N7	C2	C3	C1	0.6(7)
N7	C2	C3	N3	–179.5(5)
N7	N6	C6	C5	178.6(4)
N7	N6	C6	N10	1.2(8)
N8	C1	C3	C2	–179.1(6)
N8	C1	C3	N3	1.0(11)
N8	C1	N6	C6	–0.1(8)
N8	C1	N6	N7	178.9(5)
N8	C4	C5	N5	175.2(5)
N8	C4	C5	C6	–4.8(8)

Atom	Atom	Atom	Atom	Angle/°
N9	C2	C3	C1	178.8(6)
N9	C2	C3	N3	–1.3(10)
N9	C2	N7	N6	–178.9(5)

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	O3	0.903(18)	2.01(4)	2.612(8)	123(4)
N2	H2B	N8[1]	0.894(18)	2.27(2)	3.166(7)	177(6)
N9	H9A	N7[2]	0.86	2.43	3.271(7)	165.7
N9	H9B	O1	0.86	2.20	2.774(7)	124.0
N9	H9B	O4[3]	0.86	2.52	3.094(10)	125.4
N10	H10A	O4[4]	0.86	2.49	3.088(7)	127.7
N10	H10B	O1[5]	0.86	2.55	3.226(8)	136.2
N10	H10B	O2[5]	0.86	2.52	3.267(10)	146.4
N10	H10B	O4	0.86	2.02	2.610(8)	124.5

[1]2-X,1-Y,1-Z; [2]-X,-Y,1-Z; [3]-1/2+X,1/2-Y,1/2+Z; [4]1/2-X,-1/2+Y,1/2-Z; [5]-1/2+X,1/2-Y,-1/2+Z

Table S11. Crystal data and structure refinement for **4**·CH_3OH.

CCDC number	2142356
Empirical formula	$C_7H_8N_8O_7$
Formula weight	316.21
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.849(5)
b/Å	9.328(4)
c/Å	12.780(6)
α/°	90
β/°	110.352(7)
γ/°	90
Volume/Å^3	1212.6(9)
Z	4
ρ_{calc}/g cm^{-3}	1.732
μ/mm^{-1}	0.155
F(000)	648.0
Crystal size/mm^3	0.16 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.256 to 54.968
Index ranges	–13 ≤ h ≤ 14, –12 ≤ k ≤ 11, –16 ≤ l ≤ 16
Reflections collected	7211
Independent reflections	2759 [R_{int} = 0.0590, R_{sigma} = 0.0707]
Data/restraints/parameters	2759/0/200
Goodness-of-fit on F^2	0.990
Final R indexes [I>=2σ (I)]	R_1 = 0.0580, wR_2 = 0.1578
Final R indexes [all data]	R_1 = 0.1010, wR_2 = 0.1949
Largest diff. peak/hole / e Å^{-3}	0.27/–0.33

Table S12. Bond lengths for **4**·CH_3OH.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N4	1.211(3)	N3	C3	1.315(3)
O2	N4	1.215(4)	N3	C4	1.361(4)
O3	N5	1.220(3)	N4	C1	1.465(3)
O4	N5	1.235(3)	N5	C2	1.399(3)
O5	C7	1.405(4)	N6	C4	1.316(3)
O6	N7	1.226(3)	N7	C5	1.414(4)
O7	N7	1.250(3)	N8	C6	1.299(3)
N1	N2	1.377(3)	C1	C2	1.403(4)
N1	C1	1.308(4)	C2	C3	1.410(4)
N2	C3	1.380(3)	C4	C5	1.435(4)
N2	C6	1.366(3)	C5	C6	1.408(4)

Table S13. Bond angles for **4**·CH_3OH.

Atom	Atom	Atom	Angle/°
C1	N1	N2	102.2(2)
N1	N2	C3	114.3(2)
C6	N2	N1	121.9(2)
C6	N2	C3	123.8(2)
C3	N3	C4	116.5(2)
O1	N4	O2	126.2(3)
O1	N4	C1	117.8(3)
O2	N4	C1	115.9(3)
O3	N5	O4	124.5(2)
O3	N5	C2	118.2(3)
O4	N5	C2	117.3(2)
O6	N7	O7	120.8(2)
O6	N7	C5	120.7(3)
O7	N7	C5	118.5(2)
N1	C1	N4	116.6(2)
N1	C1	C2	115.2(2)
C2	C1	N4	128.0(3)
N5	C2	C1	128.5(3)
N5	C2	C3	127.0(2)
C1	C2	C3	104.3(2)
N2	C3	C2	104.0(2)
N3	C3	N2	123.6(2)
N3	C3	C2	132.4(2)
N3	C4	C5	121.7(2)
N6	C4	N3	113.5(2)
N6	C4	C5	124.8(3)

Atom	Atom	Atom	Angle/°
N7	C5	C4	120.7(2)
C6	C5	N7	118.7(2)
C6	C5	C4	120.7(2)
N2	C6	C5	113.7(2)
N8	C6	N2	115.6(2)
N8	C6	C5	130.7(3)

Table S14. Torsion angles for **4**·CH_3OH.

Atom	Atom	Atom	Atom	Angle/°
O1	N4	C1	N1	–62.2(4)
O1	N4	C1	C2	123.1(4)
O2	N4	C1	N1	115.8(3)
O2	N4	C1	C2	–59.0(4)
O3	N5	C2	C1	–3.2(5)
O3	N5	C2	C3	170.1(3)
O4	N5	C2	C1	178.2(3)
O4	N5	C2	C3	–8.6(4)
O6	N7	C5	C4	5.4(4)
O6	N7	C5	C6	–174.4(3)
O7	N7	C5	C4	–174.5(3)
O7	N7	C5	C6	5.6(4)
N1	N2	C3	N3	–179.9(3)
N1	N2	C3	C2	–0.2(3)
N1	N2	C6	N8	1.8(4)
N1	N2	C6	C5	–178.9(2)
N1	C1	C2	N5	173.9(3)
N1	C1	C2	C3	–0.5(3)
N2	N1	C1	N4	–175.1(2)
N2	N1	C1	C2	0.4(3)
N3	C4	C5	N7	179.6(3)
N3	C4	C5	C6	–0.5(4)
N4	C1	C2	N5	–11.2(5)
N4	C1	C2	C3	174.3(3)
N5	C2	C3	N2	–174.2(3)
N5	C2	C3	N3	5.5(5)
N6	C4	C5	N7	0.7(4)
N6	C4	C5	C6	–179.4(3)
N7	C5	C6	N2	–179.7(2)
N7	C5	C6	N8	–0.5(5)
C1	N1	N2	C3	–0.1(3)
C1	N1	N2	C6	177.9(2)
C1	C2	C3	N2	0.4(3)

Atom	Atom	Atom	Atom	Angle/°
C1	C2	C3	N3	–179.9(3)
C3	N2	C6	N8	179.5(3)
C3	N2	C6	C5	–1.2(4)
C3	N3	C4	N6	–179.6(3)
C3	N3	C4	C5	1.3(4)
C4	N3	C3	N2	–2.1(4)
C4	N3	C3	C2	178.2(3)
C4	C5	C6	N2	0.4(4)
C4	C5	C6	N8	179.6(3)
C6	N2	C3	N3	2.2(4)
C6	N2	C3	C2	–178.1(2)

Table S15. Hydrogen bonds for **4**·CH_3OH.

D	H	A	d(D–H)/Å	d(H–A)/Å	d(D–A)/Å	D–H–A/°
N6	H6A	O6	0.91	2.03	2.623(4)	121.6
N6	H6B	O5	1.00	1.95	2.937(4)	168.4
N8	H8A	O2[1]	0.93	2.21	3.117(3)	166.3
N8	H8B	O4[2]	0.87	2.27	3.002(3)	142.4
N8	H8B	O7	0.87	1.99	2.612(3)	128.0
O5	H5	O7[3]	1.02	2.12	3.097(3)	158.3

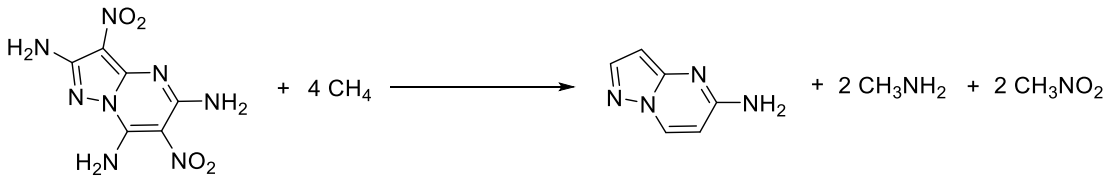
[1]3/2-X,-1/2+Y,1/2-Z; [2]+X,-1+Y,+Z; [3]+X,1+Y,+Z

3. Computational Details

DFT calculations were accomplished with Gaussian 09 Rev. D.01 suite of package[1] and ORCA 5.0.2.[2] All species in the mechanism study were optimized to either minimum or transition state with ωB97X-D functional and 6-311G(d,p) basis set. Frequency calculations at the same level of theory were carried out to further characterize each species and to obtain the thermodynamic corrections to Gibbs free energy. Intrinsic reaction coordinate (IRC) was calculated to confirm the connection between the transition state and the corresponding reactant/product.[3] Single-point energies were calculated at DLPNO-CCSD(T1)/cc-pVTZ level with cc-pVTZ/C as an auxiliary basis set. The Gibbs free energies were calculated in the gas phase at 298.15 K, 1 atm.

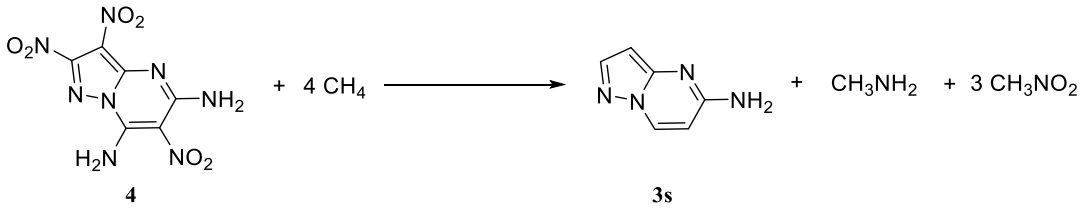
Gas phase heats of formation were calculated based on an isodesmic reaction (Scheme S1 and Scheme S2). The enthalpy of reaction was obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal 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).[4]

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



3 **3s**

Scheme S1. Isodesmic reaction for **3**.



4 **3s**

Scheme S2. Isodesmic reaction for **4**.

Table S16. 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})
3	0.159908	0.176342	–968.7802711	–968.610325	221.31
4	0.146538	0.163865	–1117.629137	–1117.47113	265.91
3s	0.121701	0.129571	–450.0928666	–449.968164	292.68[a]
CH_4	0.044793	0.048605	–40.3796224	–40.332810	–74.6[5]
CH_3NH_2	0.064030	0.068401	–95.5938410	–95.528000	–23.0[5]
CH_3NO_2	0.049840	0.055138	–244.4784821	–244.42534	–74.3[5]

[a] Data obtained from G2.

4. Geometries for Optimized Structures

Table S17. Geometries for **1**.

Atom	*x*	*y*	*z*
N	0.269180	–2.441129	0.069622
H	0.874002	–3.136945	–0.331522
H	–0.726838	–2.572688	–0.042149
C	0.651790	–1.142824	0.014904
C	–0.129334	0.019027	0.055465
N	–1.524462	0.060426	–0.000717
O	–2.138938	–1.007361	0.002349
O	–2.074278	1.154425	–0.055664
C	0.796685	1.111514	0.021555
N	0.478830	2.433096	0.086474
H	1.194802	3.076818	–0.203668
H	–0.477349	2.661031	–0.134218
N	2.032140	0.672027	–0.033183
N	1.912243	–0.706321	–0.037385
H	2.750749	–1.257722	–0.007143

Table S18. Geometries for **A**.

Atom	*x*	*y*	*z*
N	–0.452087	2.396797	0.000529
H	–1.202396	3.066669	–0.000906
H	0.515940	2.679160	0.000087
C	–0.741554	1.101938	0.000235
C	0.131171	0.000297	0.000651
N	1.524818	0.001768	0.000000
O	2.101450	1.086645	–0.000661
O	2.103621	–1.081861	0.000071
C	–0.739009	–1.103611	0.000047
N	–0.446122	–2.397725	0.000353
H	–1.194884	–3.069519	–0.001555
H	0.522356	–2.678133	0.000348
N	–2.040017	–0.660135	–0.000452
N	–2.041626	0.655268	–0.000266

Table S19. Geometries for **B**.

Atom	*x*	*y*	*z*
N	0.251095	2.347377	–0.000005
H	–0.310390	3.182298	0.000062
H	1.260548	2.375376	0.000264
C	–0.341645	1.168767	–0.000084
C	0.127114	–0.109979	–0.000041
N	1.497699	–0.462586	–0.000027
O	2.298934	0.476394	0.000462
O	1.807373	–1.631636	–0.000571
C	–1.050296	–0.959480	0.000102
N	–1.196866	–2.209208	0.000404
H	–2.195432	–2.425247	0.000431
N	–2.191988	–0.031433	–0.000131
N	–1.790830	1.143515	–0.000204

Table S20. Geometries for **IM-1**.

Atom	*x*	*y*	*z*
N	–0.302884	2.313934	–0.000002
H	–1.034672	3.004710	0.000016
H	0.674304	2.568338	–0.000518
C	–0.619016	1.033084	0.000162
C	0.131292	–0.105756	–0.000092
N	1.542766	–0.163429	0.000039
O	2.129238	0.919842	–0.000709
O	2.082138	–1.247856	0.000963
C	–0.814092	–1.203653	–0.000201
N	–0.715024	–2.448440	–0.000688
N	–2.155724	–0.559780	0.000080
N	–2.014812	0.673290	0.000466

Table S21. Geometries for **TS-1**.

Atom	*x*	*y*	*z*
O	2.127998	–1.196129	0.000070
O	2.092650	0.967839	–0.000070
N	–0.692615	–2.515124	–0.000026
N	–2.276846	–0.486436	–0.000004
N	–2.031320	0.693898	0.000009
N	1.546396	–0.137504	–0.000001
C	–0.696869	–1.313492	–0.000014
C	–0.623580	1.010862	0.000008
C	0.123202	–0.130938	–0.000006
N	–0.295269	2.289615	0.000033
H	0.686117	2.529307	–0.000017
H	–1.020239	2.987273	0.000016

Table S22. Geometries for **IM-2**.

Atom	*x*	*y*	*z*
O	2.397613	0.808838	–0.046827
O	1.929685	–1.296172	–0.073224
N	–0.407197	2.704613	0.106828
N	–2.732383	0.352088	–0.382594
N	–2.148686	–0.437967	0.255104
N	1.611894	–0.107766	–0.036383
C	–0.121503	1.590046	0.061917
C	–0.744016	–0.782068	0.067763
C	0.203960	0.211397	0.018416
N	–0.563079	–2.093116	0.047065
H	0.384431	–2.442080	–0.019679
H	–1.357298	–2.700457	0.161365

Table S23. Geometries for **TS-2**.

Atom	*x*	*y*	*z*
O	–2.489226	0.682947	–0.046400
O	–1.882639	–1.390415	–0.036691
N	0.278367	2.736210	0.051138
N	3.083094	0.215223	–0.077195
N	2.018253	–0.202844	–0.039063
N	–1.637867	–0.179117	–0.022593
C	–0.016104	1.621150	0.039536
C	0.778551	–0.694719	0.023514
C	–0.276804	0.235147	0.025779
N	0.673064	–2.042843	0.129177
H	–0.278305	–2.381970	0.036065
H	1.434983	–2.614158	–0.194561

Table S24. Geometries for **IM-3**.

Atom	*x*	*y*	*z*
O	2.397792	0.808212	0.047477
O	1.929409	–1.296637	0.072945
N	–0.405889	2.704881	–0.107005
N	–2.732699	0.352915	0.382511
N	–2.149088	–0.437696	–0.254560
N	1.611882	–0.108155	0.036396
C	–0.121041	1.590055	–0.062201
C	–0.744200	–0.781876	–0.067938
C	0.204002	0.211340	–0.018772
N	–0.563604	–2.092988	–0.047194
H	0.383812	–2.442266	0.018945
H	–1.358196	–2.700137	–0.159897

Table S25. Geometries for **TS-3**.

Atom	*x*	*y*	*z*
N	1.087265	–1.745571	0.000049
H	2.055098	–2.034995	0.000028
H	0.330561	–2.419568	0.000040
C	0.784230	–0.472312	0.000052
C	–0.374708	0.228164	0.000033
N	–1.641456	–0.480056	–0.000018
O	–1.592360	–1.707870	–0.000001
O	–2.657594	0.170853	–0.000072
C	–0.424943	1.645568	0.000025
N	–0.441194	2.796619	0.000015
N	3.262105	0.051904	–0.000171
N	2.262778	0.568844	0.000104

Table S26. Geometries for **C**.

Atom	*x*	*y*	*z*
N	–2.106263	–1.245330	0.019961
H	–2.672735	–1.979330	–0.374398
H	–2.553878	–0.403547	0.372394
C	–0.809719	–1.256943	–0.107877
C	0.196848	–0.371623	–0.026941
N	–0.099904	1.062942	–0.010823
O	–1.275939	1.378103	0.122056
O	0.822783	1.832377	–0.122204
C	1.561481	–0.754639	0.029367
N	2.657624	–1.103574	0.081704

5. NMR Spectra

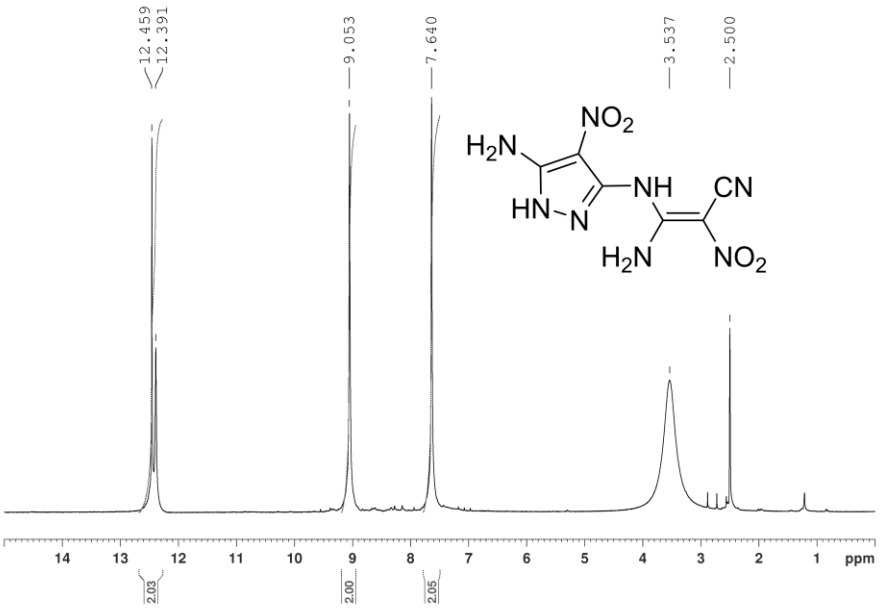


Figure S1. ^{1}H NMR spectrum of **2**.

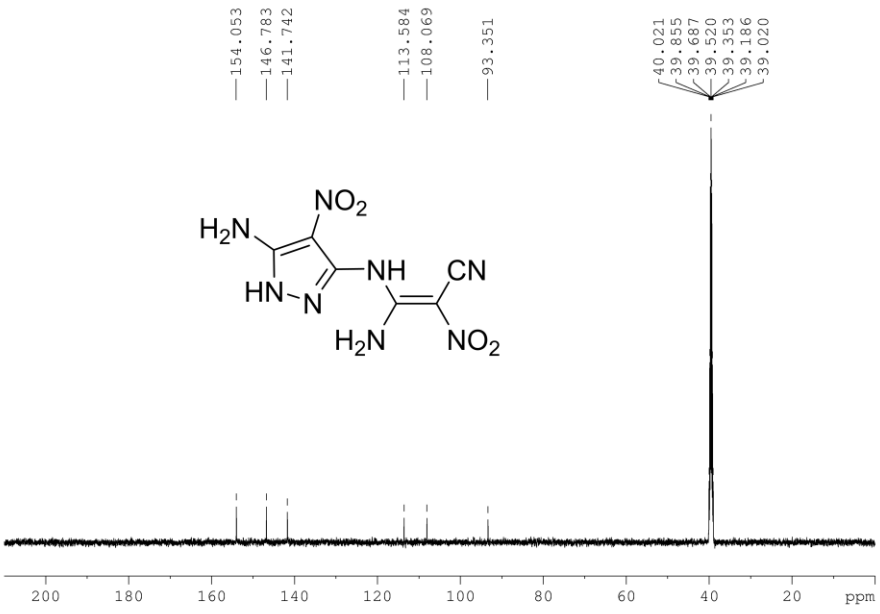


Figure S2. ^{13}C NMR spectrum of **2**.

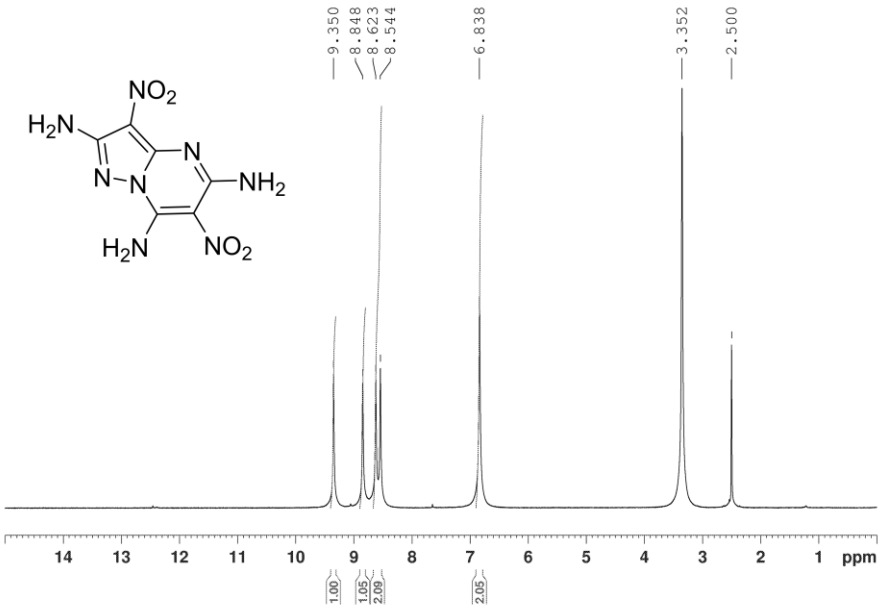


Figure S3. ^{1}H NMR spectrum of **3**.

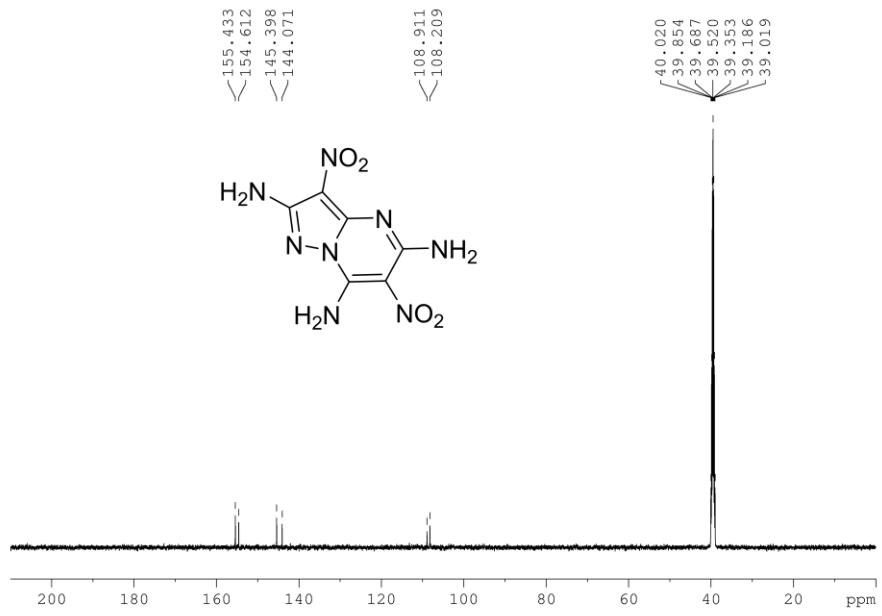


Figure S4. ^{13}C NMR spectrum of **3**.

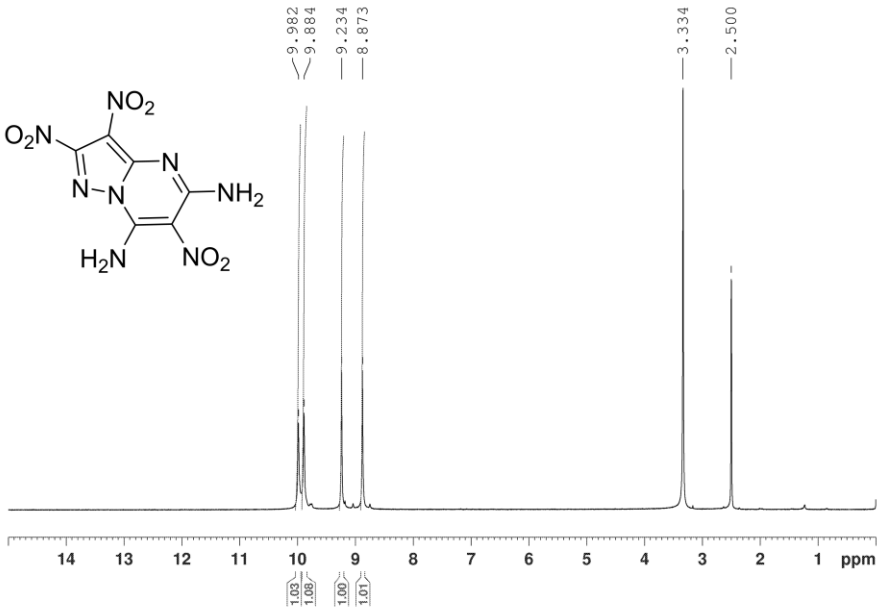


Figure S5. ^{1}H NMR spectrum of **4**.

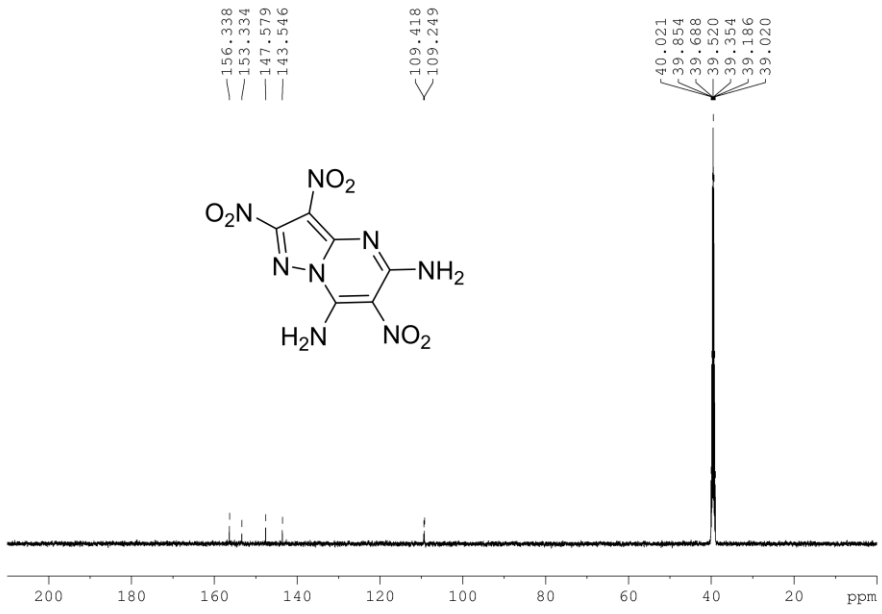


Figure S6. ^{13}C NMR spectrum of **4**.

6. DSC Plots

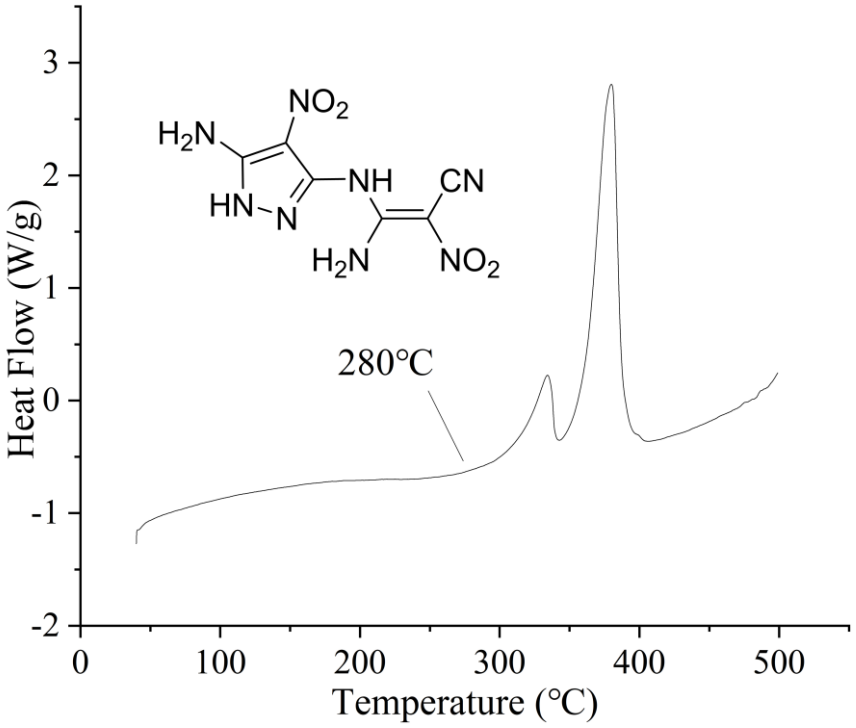


Figure S7. DSC plot of **2**.

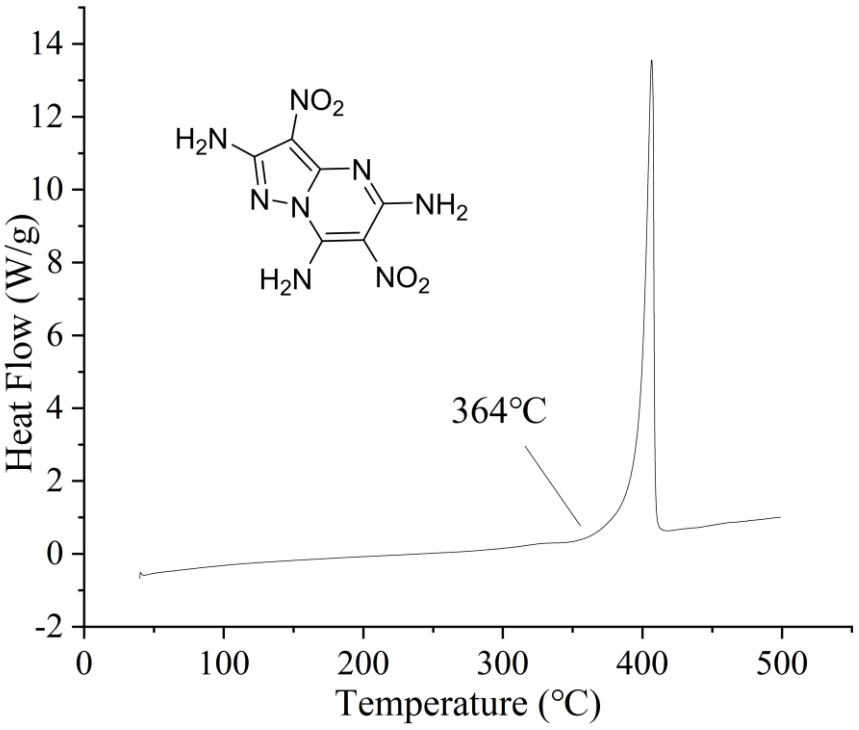


Figure S8. DSC plot of **3**.

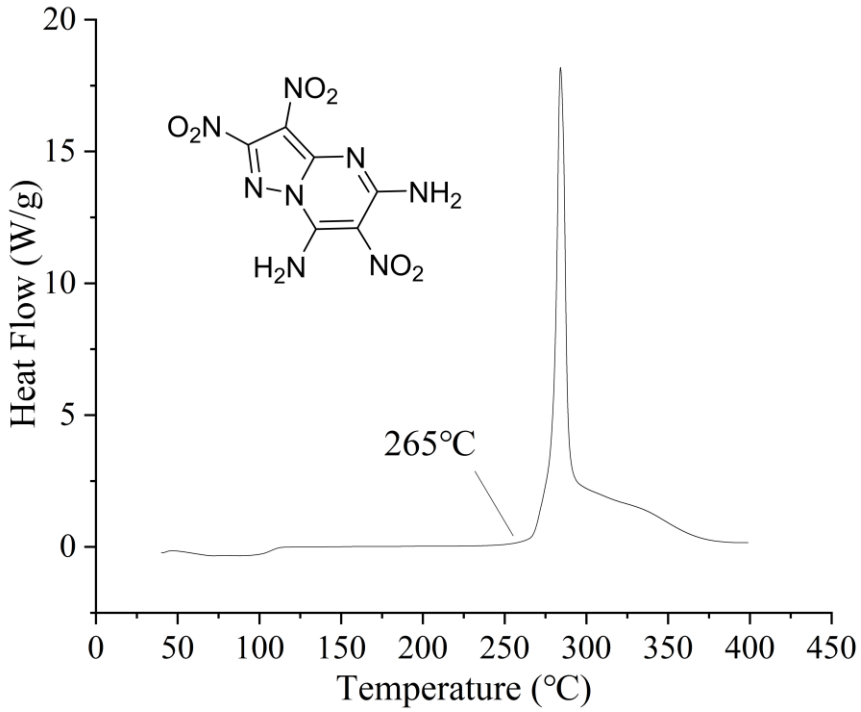


Figure S9. DSC plot of **4**.

7. ESR Measurement

Electron spin resonance (ESR) spectroscopy was investigated through the reaction of **1**, NBS in DMF, together with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a radical trap. ESR spectra were recorded and given in Figure S10 (a). Twenty signals with a g-value of 2.003 were observed. This is another direct proof of the existence of nitrogen-centered radical. In addition, theoretical spectra were simulated and shown in Figure S10 (b). By comparing experimental and simulated plots, the simulated spectra of the hyperfine structure on the free radical are in good agreement with experimental results. Based on the measured spectra and references,[6] the nitrogen-centered radical pathway was further confirmed.

Room temperature ESR spectra of sample powder were obtained using a JEOL JES FA200 ESR spectrometer (9.1GHz, X-band). Microwave power employed was 2 mW, sweep width ranged from 320 to 330 mT, modulation frequency was 100 kHz, time constant was 0.1 s and measure time was 2 min, respectively. The simulation of the hyperfine structure on the radical was taken by the Easyspin and metlab software.

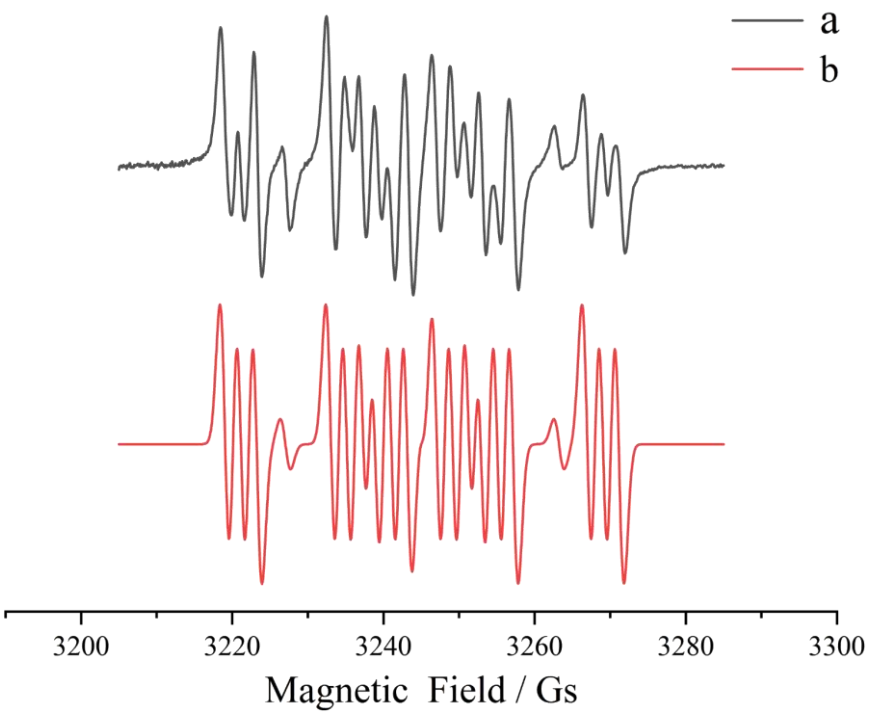


Figure S10. X-band ESR spectra from radical experiment (a) and simulation (b).

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