Supporting Information

Site-Selective Electrochemical Synthesis of Nitrogen-Enriched Bis-Pyrazole Derivatives: A Sustainable Approach for N-N versus N=N bond Formation

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1. Experimental Section

1.1 General Methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer. Chemical shifts are reported in relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Densities were determined at room temperature with a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses of C/H/N were performed on a Vario EL III Analyzer. Impact and friction sensitivities were measured by a BAM fallhammer and friction tester, respectively. X-ray intensity data were collected on a Bruker D8 VENTURE PHOTON II system equipped with an Incoatecius 3.0 Microfocus sealed tube. The crystal structures were refined by Bruker SHELXTL software Package. The data were refined against F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined isotropically. CV and electrolysis experiments were performed using an CorrTest CS Electrochemical Workstation.

1.2 Synthesis

3,5-Diamino-4-cyanopyrazole (**1**) was prepared according to a literature method.

Synthesis of (E)-3,3'-(diazene-1,2-diyl)bis(5-amino-1H-pyrazole-4-carbonitrile) (2)

1 (2.0 mmol, 0.2462 g) in 20 mL of 0.5 M NaOH (aq) was electrolyzed at 2.4 V for 3 h in a single compartment cell using a 2.0 x 2.0 x 0.3 cm^3 graphite plate working electrode and a 2.0 x 2.0 x 0.3 cm^3 graphite plate counter electrode. After the reaction was completed, the pH of the reaction solution was adjusted to acidic levels using a 10 wt% hydrochloric acid solution, resulting in the observation of solid precipitation. Then the precipitate was filtered, washed with water and air-dried to give the compound **2** (0.2083g, 86%) as a red solid.

$T_{d(}$onset$_{)}$: 357 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 12.85 ppm (s, 2H), 6.76 ppm (s, 4H). ^{13}C NMR (DMSO-d_6, 76 MHz) δ: 160.58, 155.22, 114.79, 61.54 ppm. IR (KBr, v): 3386, 3312, 3149, 2212, 1652, 1594, 1514, 1473, 1353, 1267, 1191, 1147, 1049, 871, 822, 733, 680, 568, 552 cm^{-1}. Anal. Calc. for $C_8H_6N_{10}$: C 39.67%, H 2.50%, N 57.83%; Found: C 39.53%, H 2.46%, N 57.64%. high resolution mass spectrum (Electrosprayionization) m/z: [M-H]$^-$ calcd for $C_8H_5N_{10}^-$: 241.0704; Found 241.0701.

Synthesis of 3,3',5,5'-tetraamino-[1,1'-bipyrazole]-4,4'-dicarbonitrile (3)

1 (2.0 mmol, 0.2462 g) in 20 mL of 0.2 M NH_4OAc (aq) was electrolyzed at 2.4 V for 6 h in a single compartment cell using a 2.0 x 2.0 x 0.3 cm^3 graphite plate working electrode and a 1.0 x 1.0 x 0.02 cm^3 platinum plate counter electrode. Solid precipitation was produced during the reaction. After the reaction was completed, the precipitate was filtered, washed with water and air-dried to give the compound **3** (0.1905g, 78%) as a dark yellow solid.

$T_{d(}$onset$_{)}$: 178 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 7.04 ppm (s, 4H), 5.37 ppm (s, 4H). ^{13}C NMR (DMSO-d_6, 76 MHz) δ: 155.32, 154.01, 115.09, 60.74 ppm. IR (KBr, ν): 3456, 3350, 3190, 2217, 1656, 1613, 1583, 1560, 1498, 1360, 1144, 1105, 1020, 796, 730 cm^{-1}. Anal. Calc. for $C_8H_8N_{10}$: C 39.34%, H 3.30%, N 57.35%; Found: C 39.27%, H 3.29%, N 57.21%. high resolution mass spectrum (Electrosprayionization) m/z: [M-H]$^-$ calcd for $C_8H_7N_{10}^-$: 243.0861; Found 243.0857.

Synthesis of (E)-5,5'-(diazene-1,2-diyl)bis(4-oxo-4,7-dihydro-3H-pyrazolo[3,4-d][1,2,3] triazine 2-oxide) (4)

2 (0.50 g, 1.51 mmol) was added into a mixture of concentrated sulfuric acid (5 mL) and KNO_3 (1.0 g), and reacted for 5 h at 25 °C. The mixture was poured into ice water, filtered, washed with cold water and dried in air to obtain **4** (0.4887 g, 71%) as orange powder.

T_d(onset): 265 °C. ^{13}C NMR (DMSO-d_6, 76 MHz) δ: 160.14, 156.20, 155.64, 90.80 ppm. IR (KBr, ν): 3056, 2659, 1583, 1361, 1294, 1183, 1107, 904, 849, 783, 760, 703, 635, 590 cm^{-1}. Anal. Calc. for $C_8H_4N_{12}O_4$: C 28.92%, H 1.21%, N 50.60% O 19.26%; Found: C 28.89%, H 1.13%, N 50.48%, O 19.05%. high resolution mass spectrum (Electrosprayionization) m/z: [M-H]$^-$ calcd for $C_8H_3N_{12}O_4^-$: 331.0406; Found 331.0400.

1.3 General procedure for CV tests

Cyclic voltammetry was conducted at room temperature using a three-electrode electrochemical cell. The working electrode was a stable platinum-carbon electrode, the counter electrode was a graphite electrode, and the reference electrode was an Ag/AgCl electrode immersed in a saturated KCl aqueous solution. The electrolytic cell was filled with 20 mL of water containing either ammonium acetate (2.0 mmol) or sodium hydroxide (2.0 mmol). Compound **1** (0.10 mmol) was added and fully dissolved before testing. The scan rate was set to 100 mV/s, with a potential range of 0 V to 2.5 V.

1.4 Radical scavenger trapping experiments

Radical scavenger trapping experiments in N=N coupling reaction

1 (2.0 mmol, 1 equiv.) and **BHT** (4.0 mmol, 2 equiv.) in 20 mL of 0.5 M NaOH (aq) was electrolyzed at 2.4 V for 3 h in a single compartment cell using a 2.0 x 2.0 x 0.3 cm^3 graphite plate working electrode and a 2.0 x 2.0 x 0.3 cm^3 graphite plate counter electrode. After the reaction was completed, the pH of the reaction solution was adjusted to acidic levels using a 10 wt% hydrochloric acid solution. The target product was not obtained

Radical scavenger trapping experiments in N-N coupling reaction

1 (2.0 mmol, 1 equiv.) and **BHT** (4.0 mmol, 2 equiv.) in 20 mL of 0.2 M NH_4OAc (aq) was electrolyzed at 2.4 V for 6 h in a single compartment cell using a 2.0 x 2.0 x 0.3 cm^3 graphite plate working electrode and a 1.0 x 1.0 x 0.02 cm^3 platinum plate counter electrode. White solid precipitation was produced during the reaction. After the completion of the reaction, BHT was removed with ethanol, and the white solid was filtered and dried to obtain **1-BHT**.

2. Crystallographic Data

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

CCDC number	2368736
Empirical formula	$C_8H_8N_{10}O$
Formula weight	260.24
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1$/n (14)
a/Å	3.616 (2)
b/Å	16.677 (11)
c/Å	17.954 (11)
α/°	90
β/°	95.76(2)
γ/°	90
Volume/Å^3	1077.2(11)
Z	4
ρ_{calc}/g cm^{-3}	1.605
μ/mm^{-1}	1.024
F(000)	536
Radiation	CuK$_\alpha$ (λ = 1.54178 Å)
2Θ range for data collection/°	7.25 to 128.48 (0.86 Å)
Index ranges	$-4 \leq h \leq 4$ $-16 \leq k \leq 19$ $-20 \leq l \leq 20$
Reflections collected	7126
Independent reflections	1779 R_{int} = 0.1214 R_{sigma} = 0.0982
Data/restraints/parameters	1779/13/190
Goodness-of-fit on F^2	1.061
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0715, wR_2 = 0.1773
Final R indexes [all data]	R_1 = 0.1346, wR_2 = 0.2104
Largest diff. peak/hole / e Å^{-3}	0.29/-0.33

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

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C (1A)	C (3A)	1.387(7)	C (3A)	N (5A)	1.339(6)
C (1A)	C (4A)	1.398(7)	C (3A)	N (2A)	1.345(6)
C (1A)	C (2A)	1.422(7)	C (4A)	N (3A)	1.155(6)
C (2A)	N (1A)	1.316(6)	N (1A)	N (2A)	1.356(5)
C (2A)	N (4A)	1.393(6)	N (4A)	N (4A)	1.261(8)

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

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C (3A)	C (1A)	C (4A)	124.1(4)	N (5A)	C (3A)	C (1A)	130.5(4)
C (3A)	C (1A)	C (2A)	105.0(4)	N (2A)	C (3A)	C (1A)	105.7(4)
C (4A)	C (1A)	C (2A)	130.8(5)	N (3A)	C (4A)	C (1A)	175.9(5)
N (1A)	C (2A)	N (4A)	116.4(4)	C (2A)	N (1A)	N (2A)	105.0(4)
N (1A)	C (2A)	C (1A)	111.0(4)	C (3A)	N (2A)	N (1A)	113.2(4)
N (4A)	C (2A)	C (1A)	132.5(5)	N (4)	N (4A)	C (2A)	112.6(5)
N (5A)	C (3A)	N (2A)	123.8(4)				

Table S4. Hydrogen bonds for **2**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	O1	0.88	2.18	2.864(6)	134.6
N5	H3	N1^1	0.90	2.06	2.928(6)	162.0
O1	H1	N3^2	0.85	2.10	2.923(6)	163.0

^{1}-1/2+X,1/2-Y,1/2+Z; ^{2}1/2+X,1/2-Y,-1/2+Z;

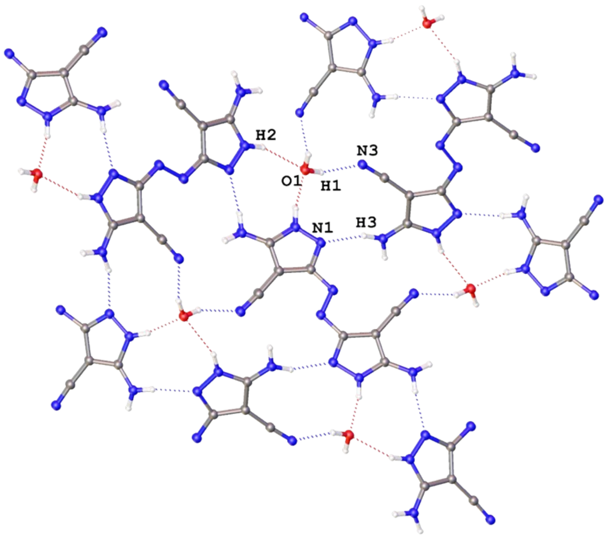


Fig.S1. Intermolecular hydrogen bond interactions of **$2\cdot H_2O$**.

NMR Spectra

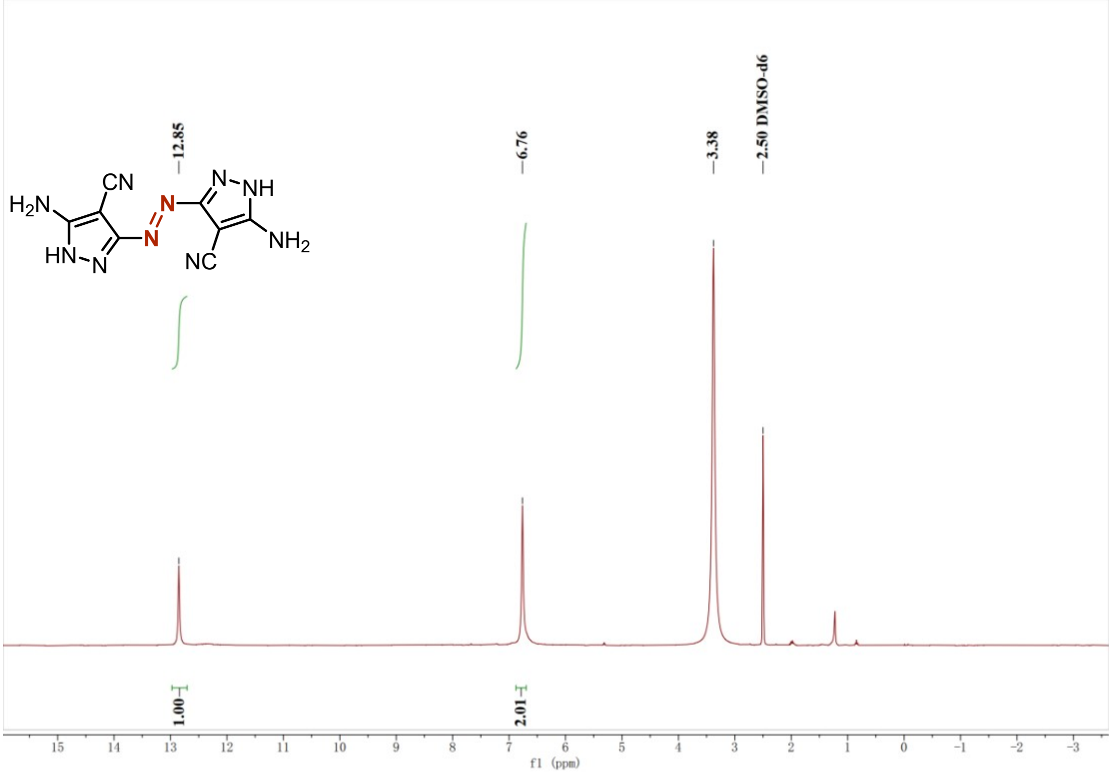


Figure S2. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2**.

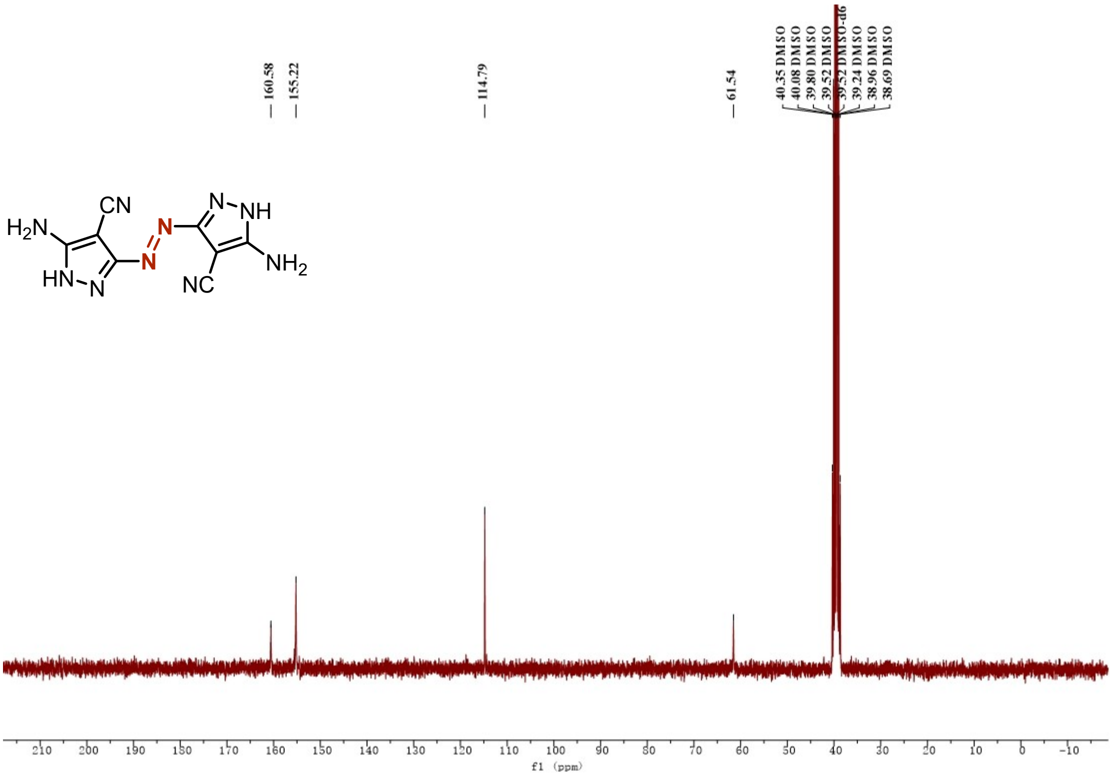


Figure S3. ^{13}C NMR spectrum (76 MHz, DMSO-d_6) of **2**.

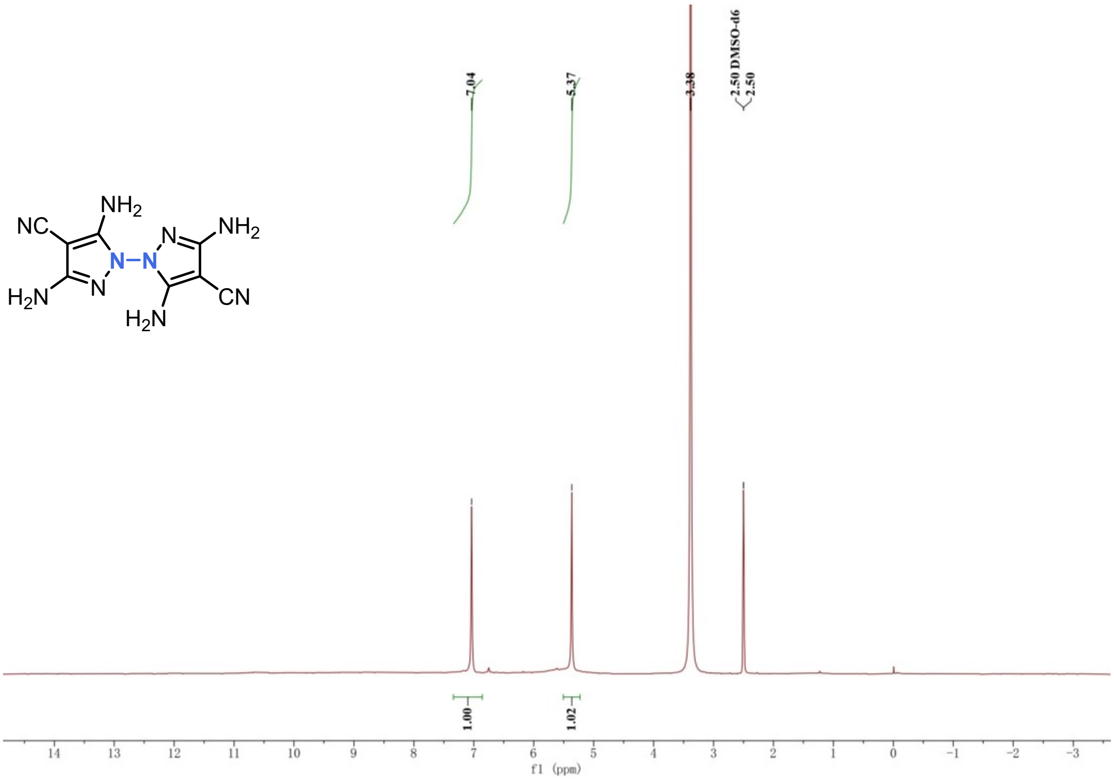


Figure S4. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3**.

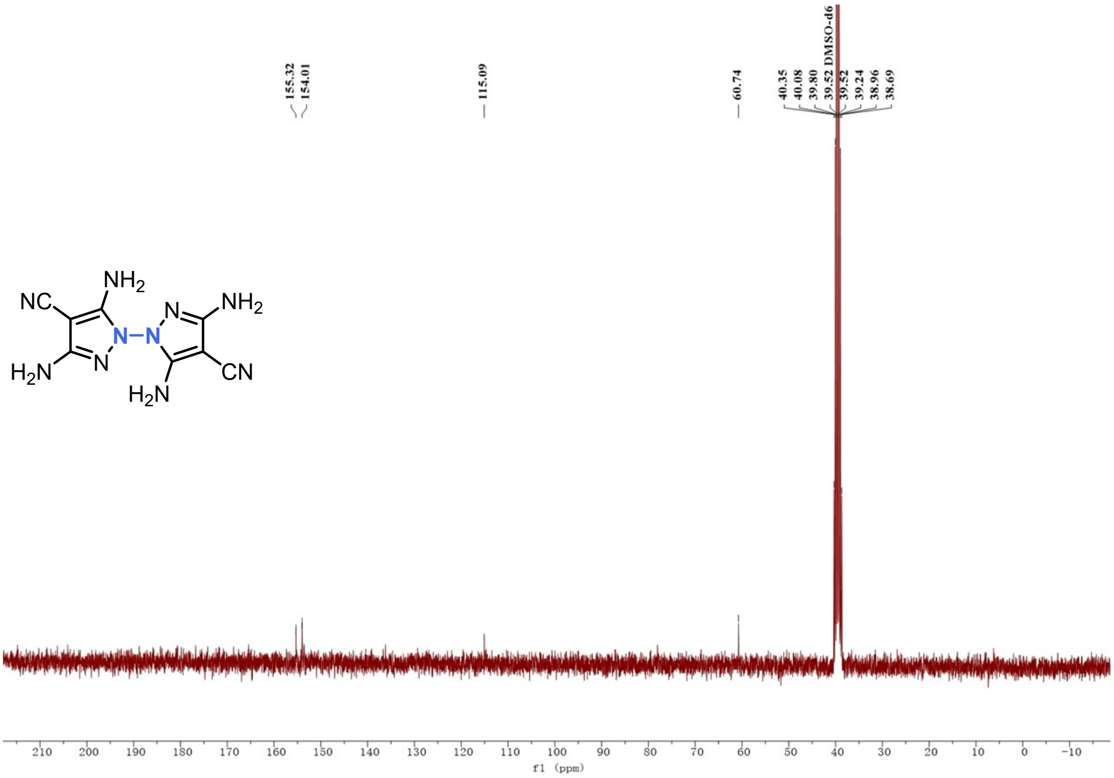


Figure S5. ^{13}C NMR spectrum (76 MHz, DMSO-d_6) of **3**.

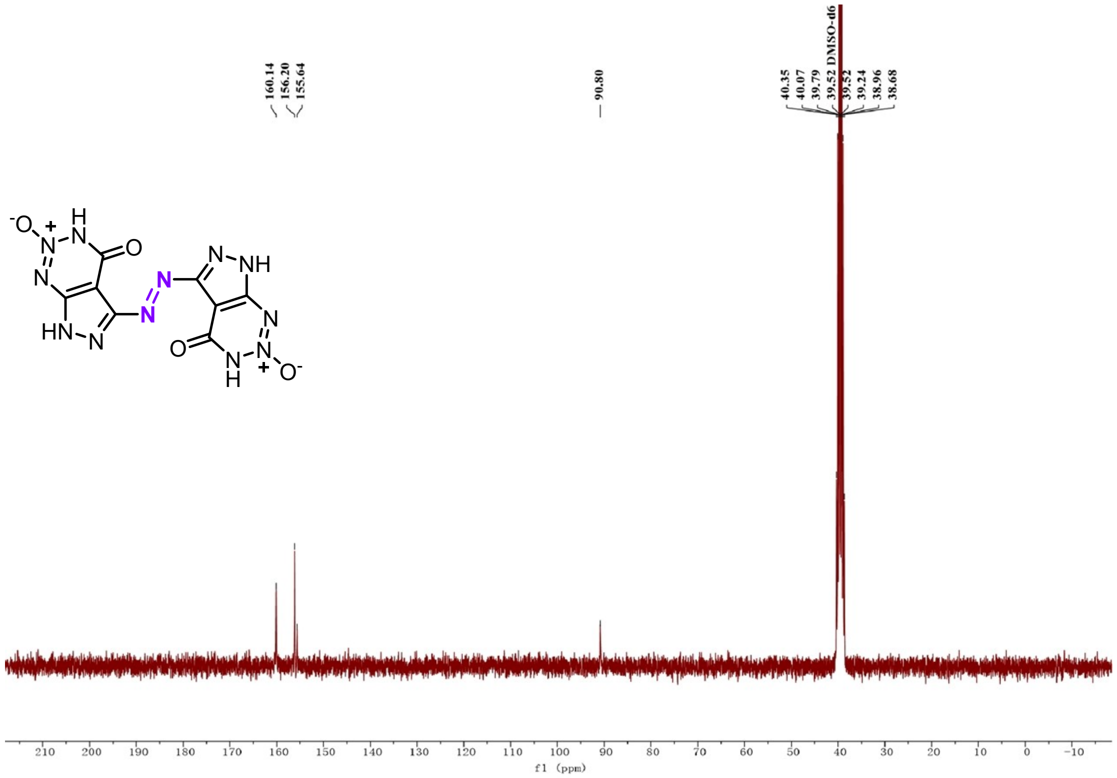


Figure S6. ^{13}C NMR spectrum (76 MHz, DMSO-*d*$_6$) of **4**.

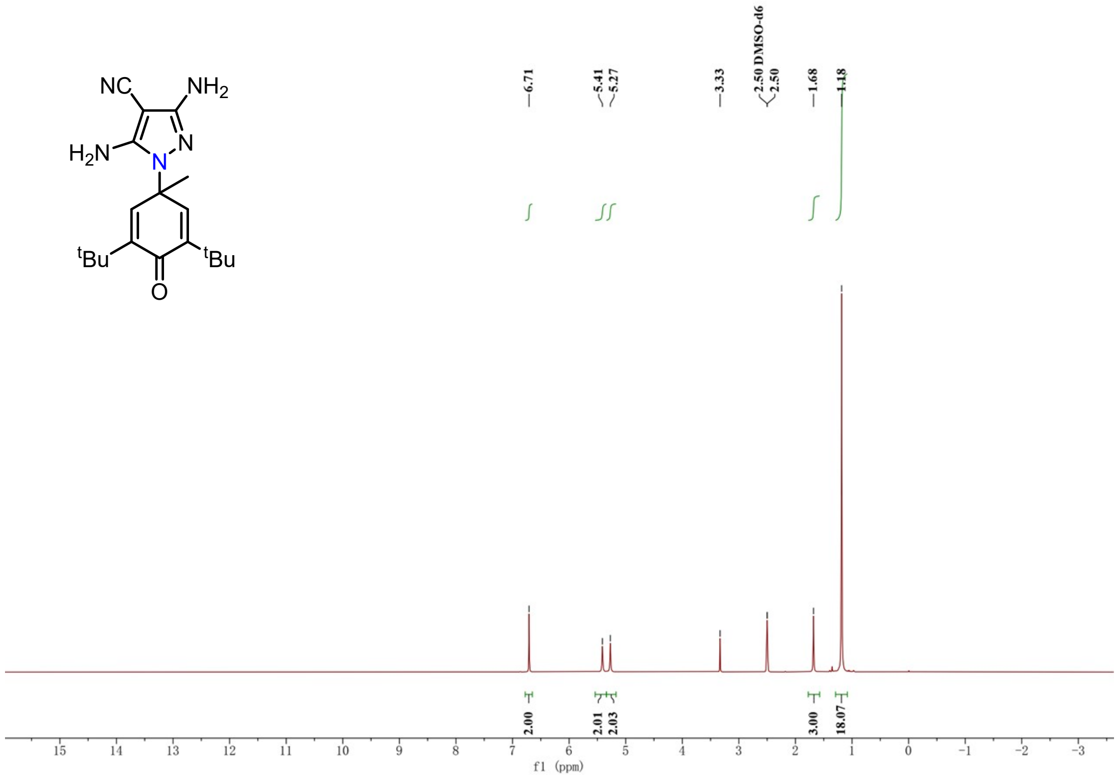


Figure S7. ^{1}H NMR spectrum (300 MHz, DMSO-*d*$_6$) of **1-BHT**.

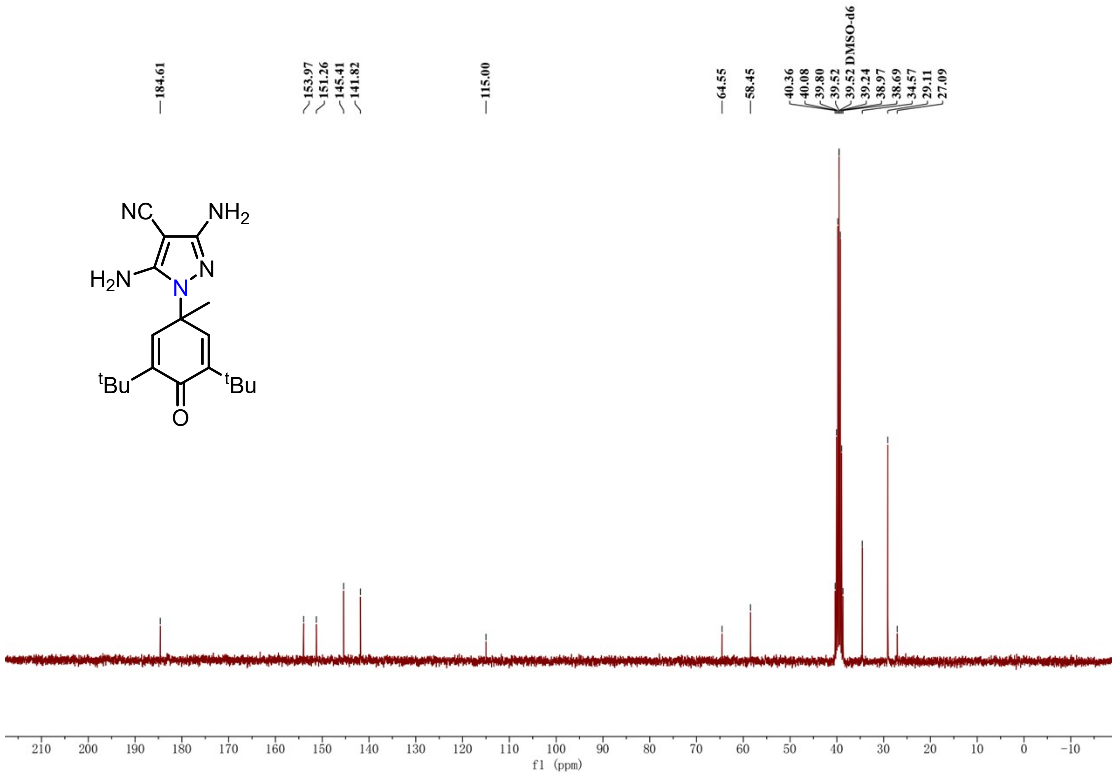


Figure S8. ^{13}C NMR spectrum (76 MHz, DMSO- d_6) of **1-BHT**.

4. High Resolution Mass Spectrum

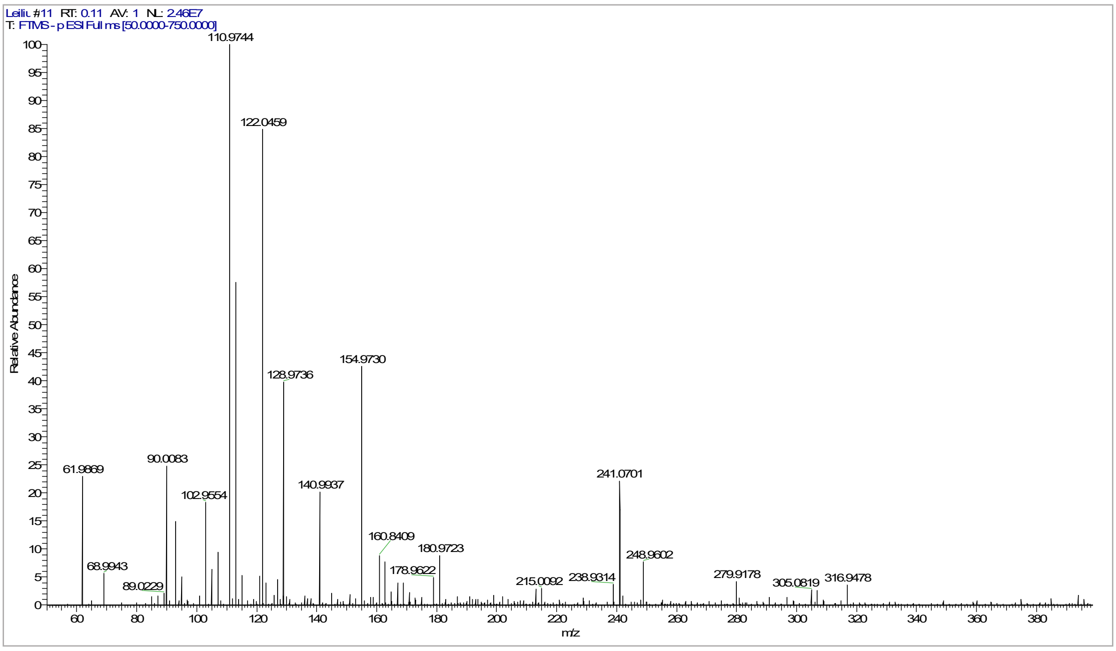


Figure S9. High resolution mass spectrum of **2**.

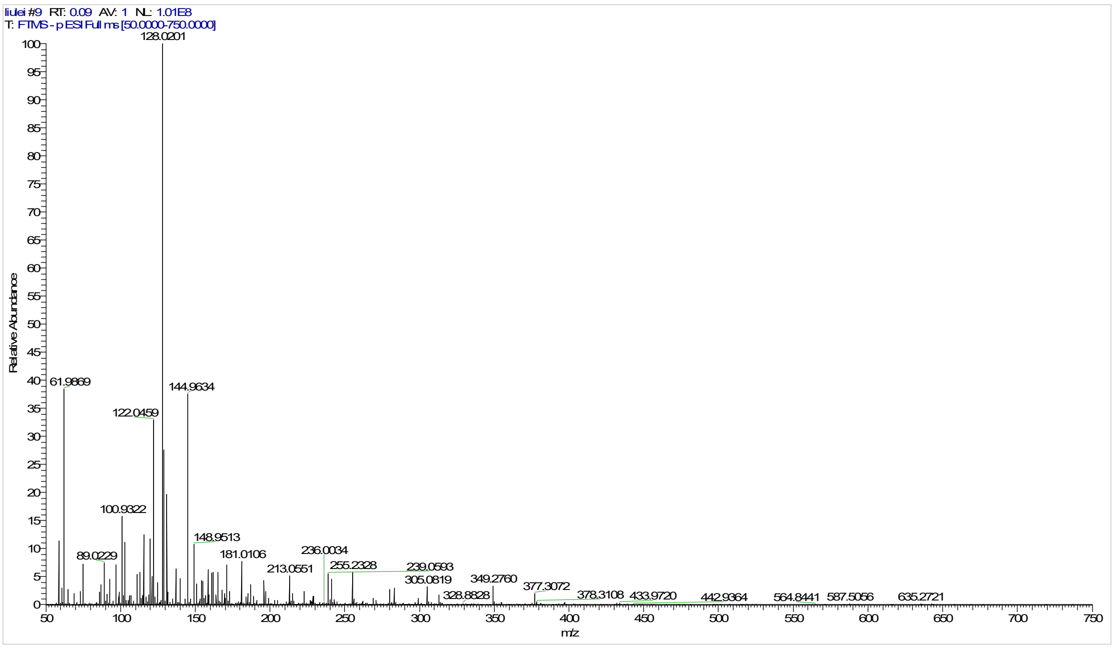


Figure S10. High resolution mass spectrum of **3**.

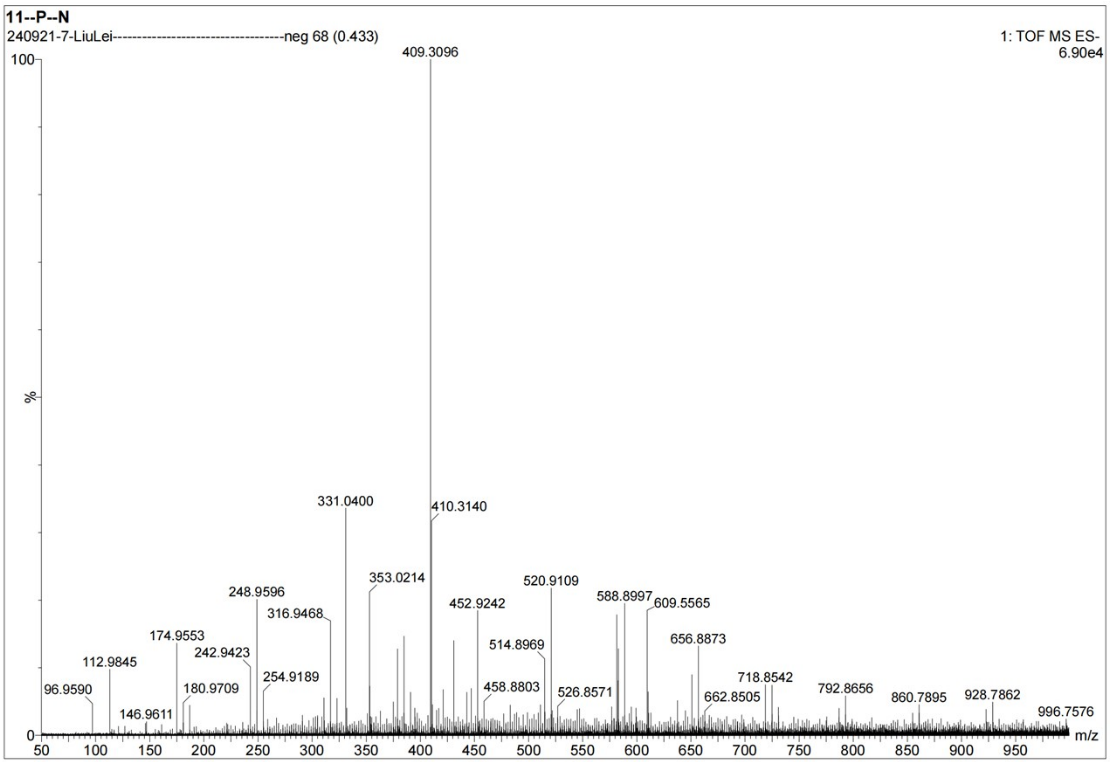


Figure S11. High resolution mass spectrum of **4**.

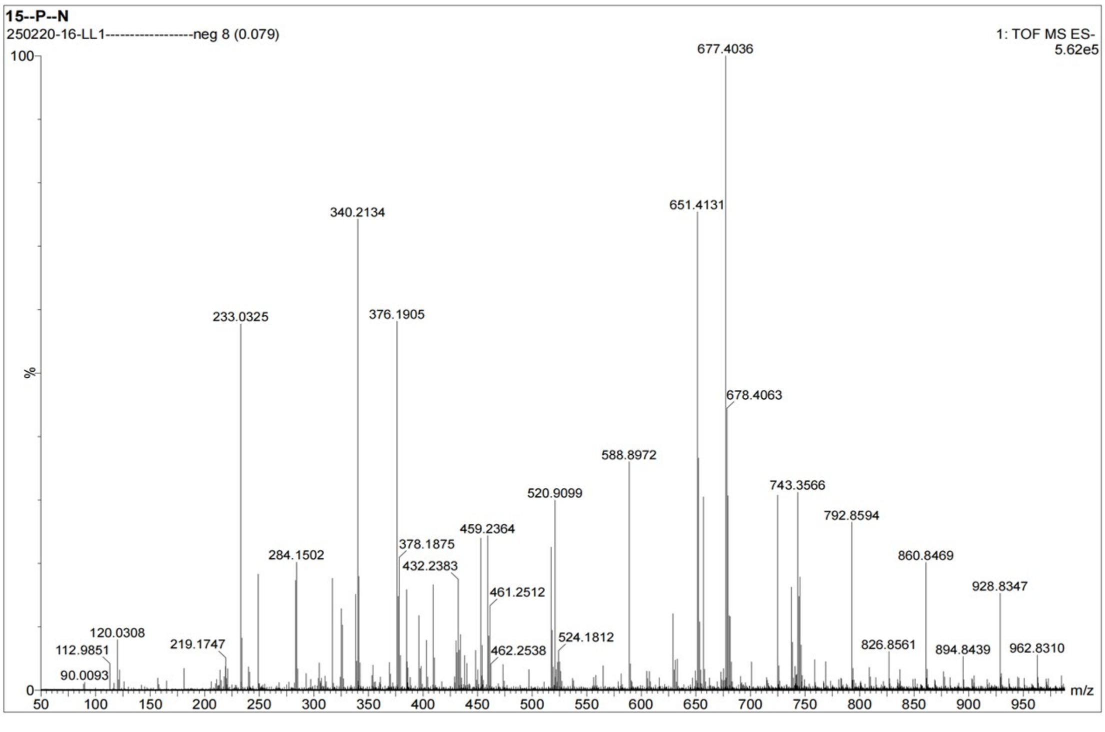
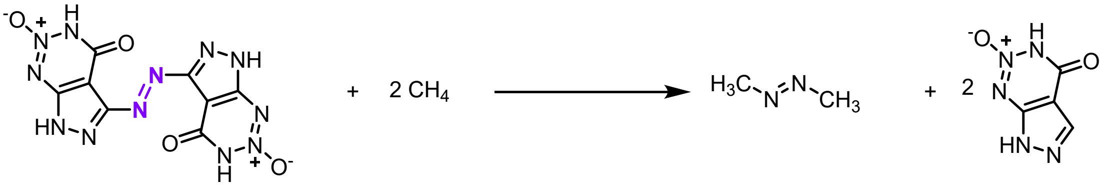


Figure S12. High resolution mass spectrum of **1-BHT**.

5. Computational Details (ΔH_f)

Theoretical calculations were performed using the Gaussian 09 program package. The gas phase heats of formation were calculated based on an isodesmic reaction (Scheme S1). The enthalpy of reaction was obtained by combining the MP2/6311++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 further computed with Trouton's rule according to equation 1 (*T* represents either melting point or decomposition temperature when no melting occurs prior to decomposition).

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



4 **4a** **4b** **4c**

Scheme S1. Isodesmic reaction for **4**.

Table S5. Calculated heats of formation (HOF) in gas state.

Species	ZPE[a]	Hr[b]	E_0[c]	corrected E	HOF[d]
4	0.1719	0.1906	-1262.02	-1261.84	943.67
4a	0.0448	0.0486	-40.38	-40.33	-77.72[e]
4b	0.0832	0.0881	-188.77	-188.68	152.09[e]
4c	0.1008	0.1087	-577.00	-576.89	273.11[e]

[a] ZPE (hartree): zero-point energy. [b] Hr (hartree): values of the correction. [c] E_0 (kJ mol^{-1}): total energy. [d] HOF (kJ mol^{-1}): heats of formation. [e] data obtained from G2.

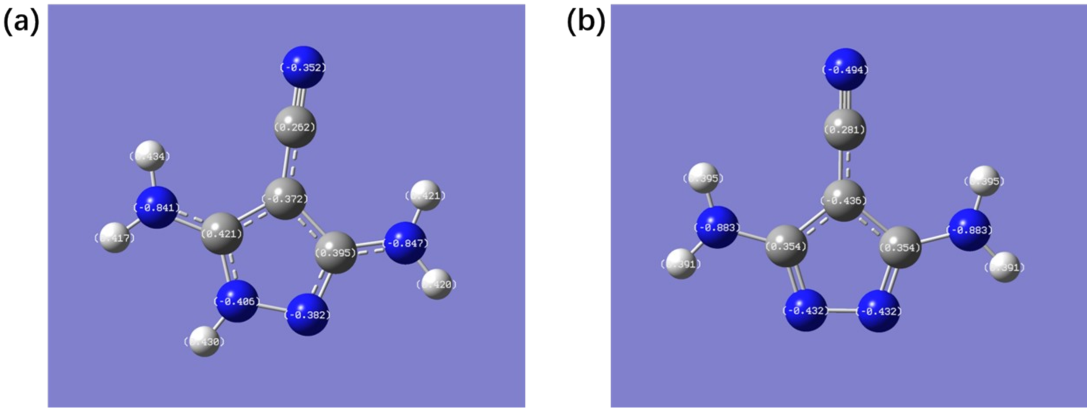


Figure S13. Natural bond orbital (NBO) charge distribution analysis plots of **1**.