Supporting Information (SI)

Benzimidazole Based Low-Sensitivity and Heat-Resistant Energetic Materials: Design and Synthesis

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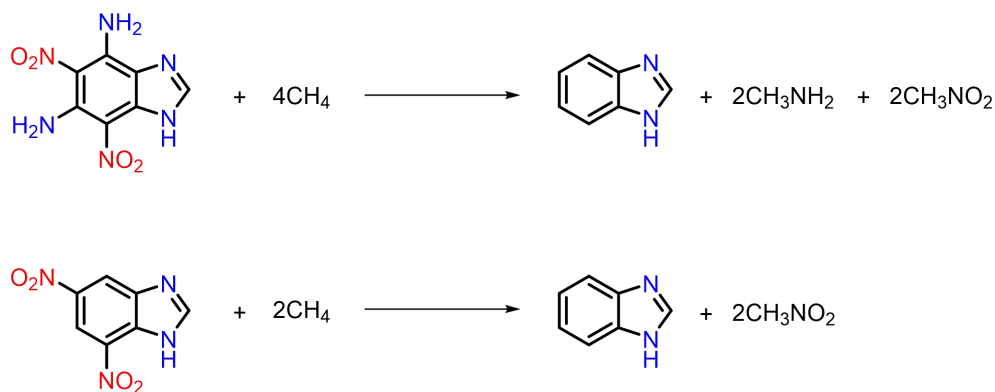
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Content

1. Computational and experimental details

Computational details

The enthalpy of formation of DADNBI and DNBI were directly calculated by the Gaussian 09 program. Gas phase heats of formation of DADNBI and DNBI were computed on an isodesmic reaction (Scheme S1). The enthalpy of reaction was carried out by combining the B3LYP/6-311G** energy difference for the reactions, the total energy (E_0), the scaled zero-point energies (ZPE), values of thermal correction (H_T), and other thermal factors. All optimized structures were characterized to be minima true local energy state without virtual frequencies on the potential energy surface. The enthalpy of formation of the substance at 298 K was calculated according to equation (1) and quation (2).[1,2]

$$\Delta H^0_{298}(g) = \Delta E_0 + \Delta ZPE + \Delta H^0_T + \Delta nRT = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \qquad (1)$$

$$\Delta H^0_{298}(s) = \Delta H^0_{298}(g) - \Delta H^0_{298}(sub) \qquad (2)$$

Scheme S1 Isodesmic reactions to compute the HOF.

Table S1 Calculated total energy (E_0), zero-point energy (ZPE), thermal correctior(H_T), and enthalpy of formation (HOF) of reference compounds

compound	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOF (KJ·mol^{-1})
4,6-diamine-5,7-dinitro-1*H*-benzo[*d*]imidazole	-899.5552224	0.157512	0.013961	26.8
5,7-dinitro-1*H*-benzo[*d*]imidazole	-788.80728	0.122100	0.011944	105.4
1*H*-benzo[*d*]imidazole	-379.960667	0.118009	0.006991	181.7
CH$_4$	-40.5337483	0.044604	0.003812	-74.6
CH$_3$NH$_2$	-245.0816727	0.049631	0.004419	-23
CH$_3$NO$_2$	-95.8884391	0.06381	0.004358	-74.3

Density is another important factor affecting the detonation performance of compounds, which was obtained by the improved density equation.[3] Among them α, β, and γ are the ftting parameters used when calculating the density, and $\upsilon\sigma^2_{Tot}$ represents the electrostatic interaction on the surface of the energetic molecule.[4]

$$\rho = \alpha(\frac{M}{V(0.001)}) + \beta(\upsilon\sigma^2_{Tot})\gamma \tag{3}$$

Detonation performances of the related compound here were calculated using Kamlet-Jacbos (K-J) equations,[5-7]

$$D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \tag{4}$$

$$P = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \tag{5}$$

where P represents the detonation pressure (GPa); D is the detonation velocity (km·s^{-1}); N is the moles of detonation gases per gram explosive; M is the average molecular weight of these gases; Q is the chemical energy of detonation (kJ·g^{-1}); and ρ replaced by the density of explosive (g·cm^{-3}).

This paper calculated the $h_{50\%}$ at 2.5 kg through theoretical computations (B3LYP/6-31G) and selected the balance parameter model to estimate the impact sensitivity $h_{50\%}$.[8]

$$h_{50\%} = a_1 + a_2\exp(a_3\upsilon) \tag{6}$$

In formula (6), a_1, a_2, and a_3 are fitting constants, and υ is the calculated balance of charges.

Experimental section

Caution! Although no explosion is observed with the reagents used, intermediates prepared, and final products during the experiments, the compounds reported in this study are energetic and all operations should be performed in a fume hood equipped with explosion-proof glass, wearing a mask and gloves.

General methods

The main pharmaceuticals, *o*-nitroaniline with a purity of 99% and *N*-chlorosuccinimide with a purity of 98%, were purchased from Macklin; tin (II) chloride dihydrate with a purity of 98% was purchased from Aladdin; other reagents such as sodium hydroxide, anhydrous sodium carbonate, concentrated hydrochloric acid, concentrated sulfuric acid, fuming nitric acid, and other solvents were all analytical grade reagents purchased from chron chemicals. All reagents were analytical grade and were used as received. Single crystal X-ray diffraction was carried out on a Bruker D8 VENTURE diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Integration and scaling of intensity data was performed using the SAINT program. Data were corrected for the effects of absorption using SADABS. The structures were solved by direct method and refined with full-matrix least-squares technique using SHELX-2014 software. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in calculated positions and refined with a riding model. ^{1}H and ^{13}C NMR spectra were recorded on a 600 MHz (Bruker Avance 600) NMR spectrometer operating at 600 and 150 MHz, respectively. The decomposition points

were obtained on a Mettler Toledo TGA/DSC 3+ simultaneous thermal analyzer at a heating rate of 5, 10, 15, and 20 °C·min^{-1}, respectively. IR spectra were recorded on a Shimadzu Corporation-UV-3150 UV-vis spectrophotometer as thin films by using KBr plates.

Synthesis
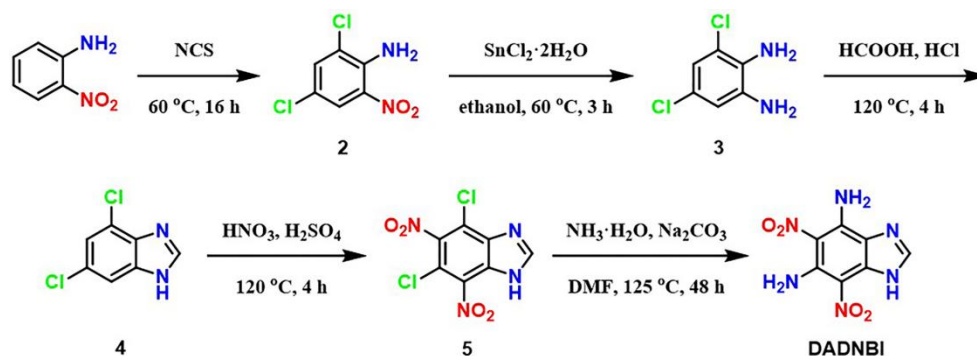
Scheme S2 Synthesis route of DADNBI.

2,4-dichloro-6-nitroaniline (2).[9] *N*-chlorosuccinimide (10.68 g, 79.98 mmol) was dissolved in a mixed solution of dichloromethane (90 mL) and methanol (45 mL), and *o*-nitroaniline (2.76 g, 19.98 mmol) was added, and stirred at 60 °C for 16 h. The reaction was stopped, poured into water, extracted with dichloromethane, and the solvent was removed by vacuum distillation. The product was recrystallized from ethanol to obtain pure product **2** as a yellow solid (3.25 g, 78.5%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.005 (d, *J* = 2.4 Hz, 1H), 7.838 (d, *J* = 3 Hz, 1H), 7.378 (s, 2H) ppm. ESI-MS: m/z calcd for [M-H]$^{-}$: 204.96, found: 205.05. IR (KBr, cm^{-1}): 3850, 3740, 3474, 3363, 2974, 2934, 2346, 2304, 1632, 1508, 1453, 1355, 1258, 1139, 1050, 877, 760, 725, 603, 554.

3, 5-dichloro-1,2-diaminobenzene (3). **2** (1 g, 4.83 mmol) was dissolved in ethanol (60 mL), SnCl$_2$·2H$_2$O (8.8 g, 39.00 mmol) was added, 3 drops of HCl were added, and the mixture was stirred at 60 °C for 3 h. The reaction was stopped, cooled to room temperature, pH was adjusted to 10 with 1 M NaOH, filtered through diatomaceous earth, the solvent was removed by vacuum distillation, extracted with ethyl acetate, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) to obtain pure product **3** as a brown solid (0.73 g, 85.4%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.543 (d, *J* = 2.4 Hz, 1H), 6.505 (d, *J* = 2.4 Hz, 1H), 4.954 (s, 4H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 137.99, 130.61, 120.66, 117.87, 115.92, 112.18 ppm. ESI-MS: m/z calcd for [M+H]$^{+}$: 177.00, found: 177.05. IR (KBr, cm^{-1}): 3347, 2932, 2304, 1628, 1578, 1481, 1421, 1288, 1226, 1062, 931, 846, 721, 646, 571.

5,7-dichloro-1H-benzo[d]imidazole (4). **3** (0.8 g, 4.52 mmol) was dissolved in formic acid (120 mL), 3 drops of HCl were added, and the mixture was stirred at 120 °C for 4 h. The reaction was stopped, cooled to room temperature, pH was adjusted to 5

with 1 M NaOH, and the solid was collected by filtration, dried in a vacuum oven at 45 °C, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 1:3) to obtain pure product **4** as a white solid (0.73 g, 86.7%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.986 (s, 1H), 8.368 (s, 1H), 7.614 (s, 1H), 7.315 (s, 1H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 144.60, 127.02, 121.79 ppm. ESI-MS: m/z calcd for [M-H]$^-$: 184.97, found: 184.95. IR (KBr, cm^{-1}): 3422, 3090, 3030, 2956, 2865, 2762, 2623, 1754, 1620, 1577, 1479, 1411, 1337, 1287, 1187, 1153, 1074, 980, 945, 838, 760, 627, 591, 505.

5,7-dichloro-4,6-dinitro-1H-benzo[d]imidazole (5). **4** (0.8 g, 4.28 mmol) was dissolved in concentrated sulfuric acid (14 mL), placed in an ice bath, fuming nitric acid (14 mL) was added dropwise, the ice bath was removed and switched to the oil bath, and stirred at 120 °C for 4 h. The reaction was stopped, cooled to room temperature, poured into ice water, and the solid was collected by filtration to obtain pure product **5** as a white solid (1.12 g, 94.4%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 14.176 (s, 1H), 8.819 (s, 1H) ppm. ESI-MS: m/z calcd for [M-H]$^-$: 274.94, found: 274.95. IR (KBr, cm^{-1}): 3088, 1619, 1559, 1482, 1394, 1341, 1282, 1206, 1133, 1040, 942, 839, 793, 737, 703, 632, 602, 551, 508.

5,7-diamine-4,6-dinitro-1H-benzo[d]imidazole (DADNBI). Anhydrous sodium carbonate (Na_2CO_3) (0.08 g, 0.75 mmol) was added to a solution of **5** (0.6 g, 2.17 mmol) in DMF (5 mL) and $NH_3 \cdot H_2O$ (1 mL). The reaction mixture was stirred at 125 °C for 48 h. During the reaction, 1 mL $NH_3 \cdot H_2O$ was added every 6 h. Then cool to ambient temperature. The precipitate was obtained by filtration, washed with a large amount of water and ethanol, and dried in vacuum to obtain pure product DADNBI as an orange yellow powder (0.45 g, 86.5%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 12.931 (s, 1H), 10.092 (s, 2H), 8.996-8.807 (m, 2H), 8.013 (s, 1H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 147.46, 147.37, 139.87, 130.31, 122.78, 115.78, 110.33 ppm. ESI-MS: m/z calcd for [M-H]$^-$: 237.04, found: 237.10. IR (KBr, cm^{-1}): 3333, 2346, 1611, 1567, 1528, 1388, 1332, 1266, 1228, 1172, 1085, 942, 880, 783, 696, 624.

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2. The crystallographic data

Table S2 Crystallographic data for DADNBI·DMSO

	DADNBI·DMSO
Empirical formula	$C_9H_{12}N_6O_5S$
Formula weight	316.31
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	C2/c
a/Å	27.756(3)
b/Å	4.6794(5)
c/Å	19.632(2)
α/°	90
β/°	90.257(4)
γ/°	90
Volume/Å^3	2549.8(5)
Z	8
ρ_{calc}g/cm^3	1.648
μ/mm^{-1}	0.290
F(000)	1312.0
Crystal size/mm^3	0.26 × 0.25 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.15 to 52.844
Index ranges	-33 ≤ h ≤ 34, -5 ≤ k ≤ 5, -24 ≤ l ≤ 22
Reflections collected	8229
Independent reflections	2581 [R_{int} = 0.0984, R_{sigma} = 0.1032]
Data/restraints/parameters	2581/178/204
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.1322
Final R indexes [all data]	R_1 = 0.1382, wR_2 = 0.1669
Largest diff. peak/hole / e Å^{-3}	0.37/-0.41
CCDC	2333741

Table S3 Bond distance of compound DADNBI·DMSO

parameter	Å	parameter	Å
S1-O5	1.515(4)	N4-C4	1.393(5)
S1-C8	1.759(4)	N4-C7	1.311(6)
S1-C9	1.759(4)	N5-C5	1.320(6)
O1-N2	1.284(5)	N6-C6	1.420(6)
O2-N2	1.262(5)	C1-C2	1.440(6)
O3-N6	1.231(5)	C1-C6	1.438(6)
O4-N6	1.254(5)	C2-C3	1.421(6)
O5-S1A	1.61(2)	C3-C4	1.370(6)
N1-C1	1.331(5)	C4-C5	1.419(6)
N2-C2	1.374(6)	C5-C6	1.435(6)
N3-C3	1.366(6)	S1A-C8A	1.759(4)
N3-C7	1.360(6)	S1A-C9A	1.759(4)

Table S4 Bond angle of compound DADNBI·DMSO

parameter	°	parameter	°
O5-S1-C8	106.8(3)	N3-C3-C2	132.5(4)

parameter	°	parameter	°
O5-S1-C9	105.5(3)	N3-C3-C4	105.5(4)
C9-S1-C8	98.4(3)	C4-C3-C2	122.0(4)
O1-N2-C2	122.1(4)	N4-C4-C5	125.2(5)
O2-N2-O1	118.6(4)	C3-C4-N4	111.3(4)
O2-N2-C2	119.3(4)	C3-C4-C5	123.5(4)
C7-N3-C3	106.4(4)	N5-C5-C4	118.4(4)
C7-N4-C4	102.9(4)	N5-C5-C6	126.3(4)
O3-N6-O4	119.5(4)	C4-C5-C6	115.3(4)
O3-N6-C6	120.3(4)	N6-C6-C1	119.4(4)
O4-N6-C6	120.2(4)	N6-C6-C5	118.0(4)
N1-C1-C2	118.2(4)	C5-C6-C1	122.6(4)
N1-C1-C6	123.0(4)	N4-C7-N3	113.9(4)
C6-C1-C2	118.8(4)	O5-S1A-C8A	86(3)
N2-C2-C1	123.3(4)	O5-S1A-C9A	129(3)
N2-C2-C3	119.0(4)	O8A-S1A-C9A	107(3)
C3-C2-C1	117.6(4)		

Table S5 Hydrogen atom coordinates ($Å×10^4$) and isotropic displacement parameters ($Å^2×10^3$) for DADNBI·DMSO.

Atom	x	y	z	U(eq)
H1A	6308	3166	2278	35
H1B	6009	5218	2705	35
H3	6276	4919	5334	31
H5A	7514	-2675	4270	33
H5B	7498	-2996	3498	33
H7	6825	1990	5981	32
H8A	5069	6655	5362	58
H8B	4803	9221	5746	58
H8C	4951	6397	6156	58
H9A	5374	9070	7103	71
H9B	5193	11967	6752	71
H9C	5744	11647	6983	71
H8AA	5199	10331	5591	58
H8AB	4938	7307	5499	58
H8AC	5490	7672	5287	58
H9AA	5498	10999	7182	71
H9AB	5031	9138	7358	71
H9AC	5019	11334	6733	71

3. ^{1}H, ^{13}C NMR, MS and IR spectra of 2, 3, 4, 5 and DADNBI
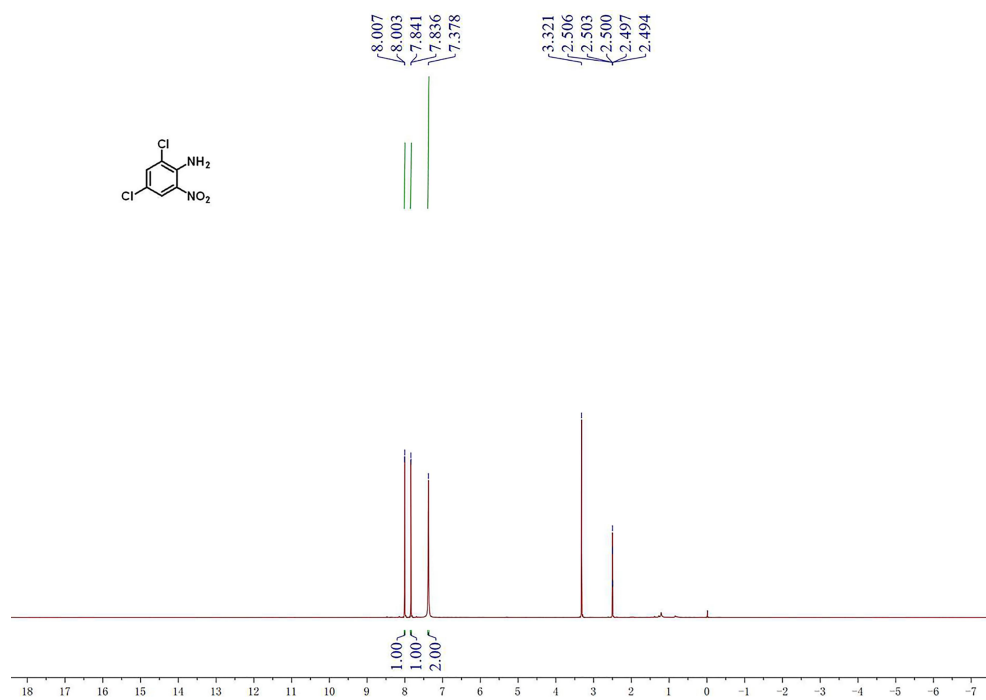
Fig. S1 ^{1}H NMR spectra of **2**.
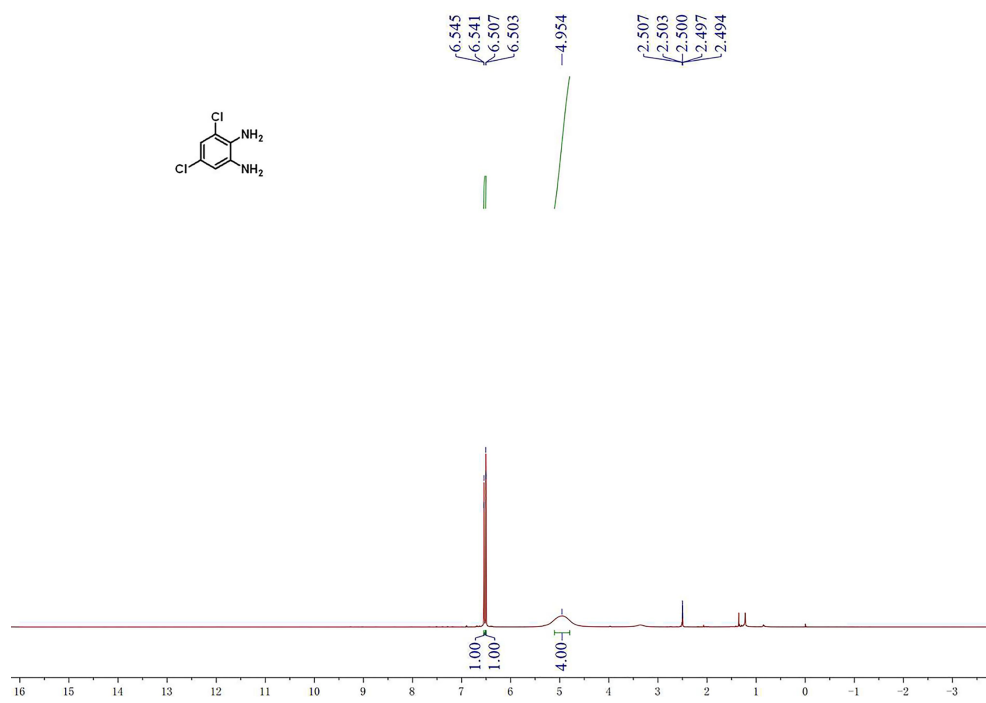
Fig. S2 ^{1}H NMR spectra of **3**.

Fig. S3 ^{13}C NMR spectra of **3**.

Fig. S4 ^{1}H NMR spectra of **4**.

Fig. S5 ^{13}C NMR spectra of **4**.

Fig. S6 ^{1}H NMR spectra of **5**.
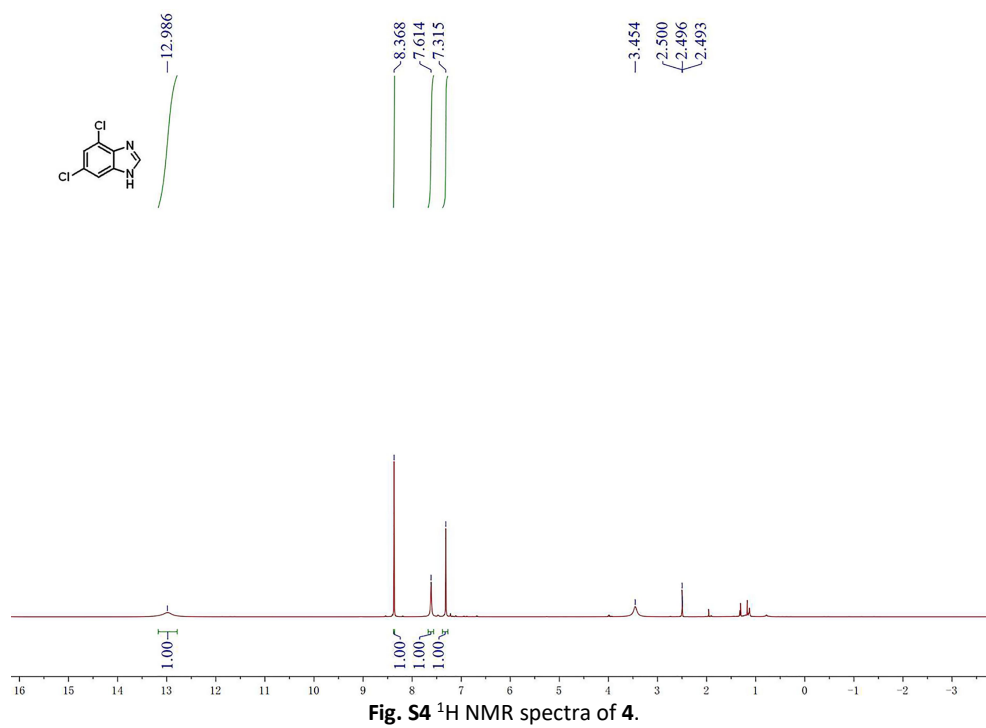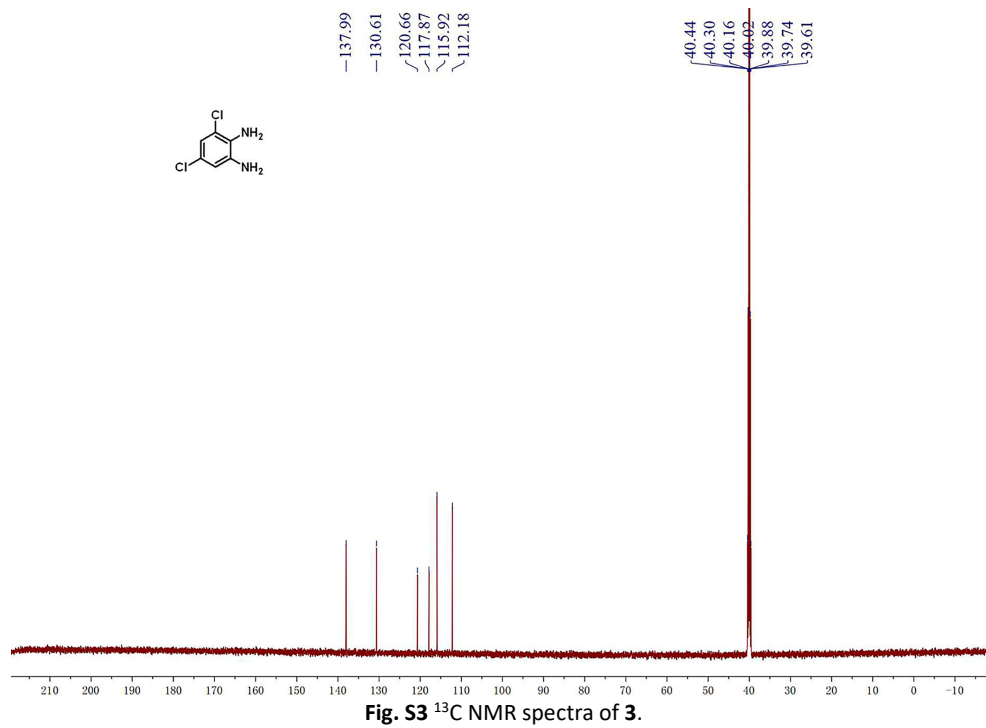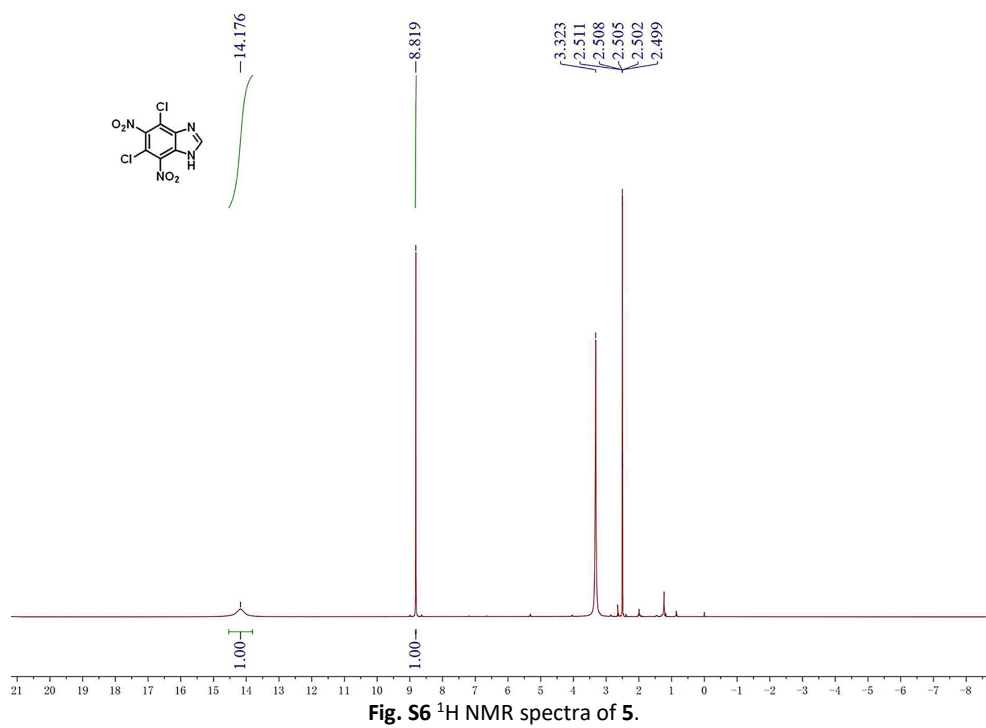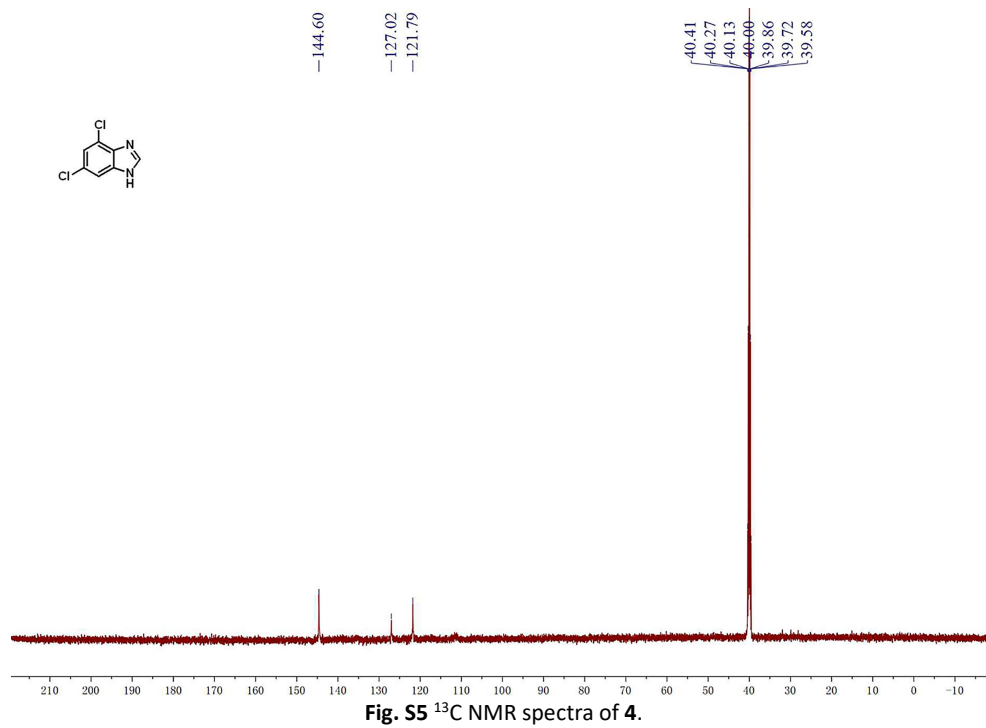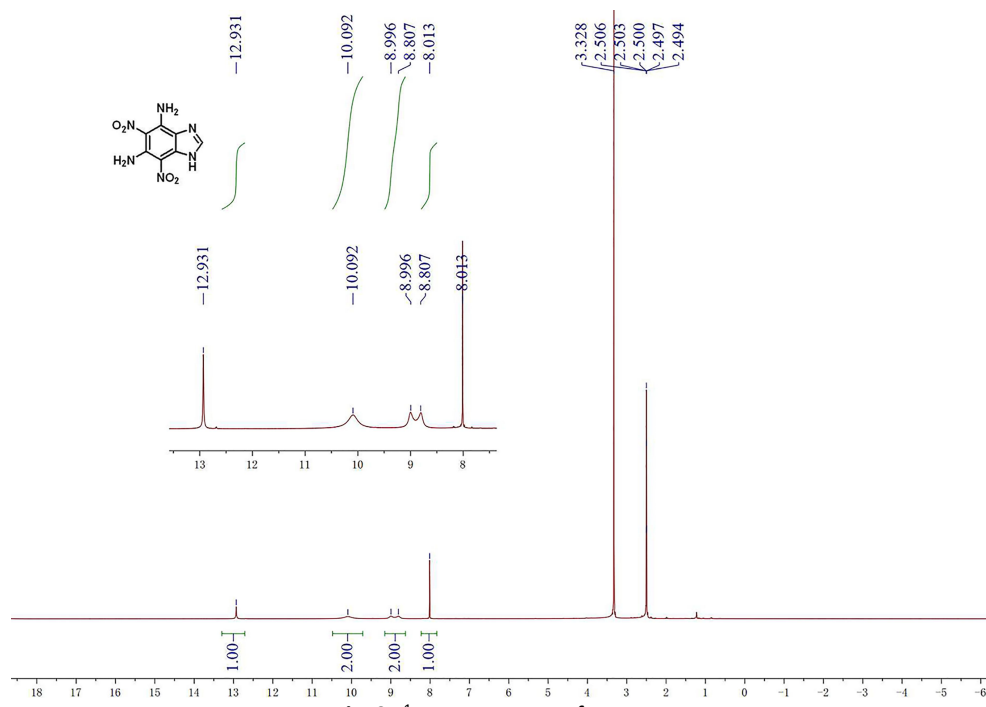
Fig. S7 ^{1}H NMR spectra of DADNBI.
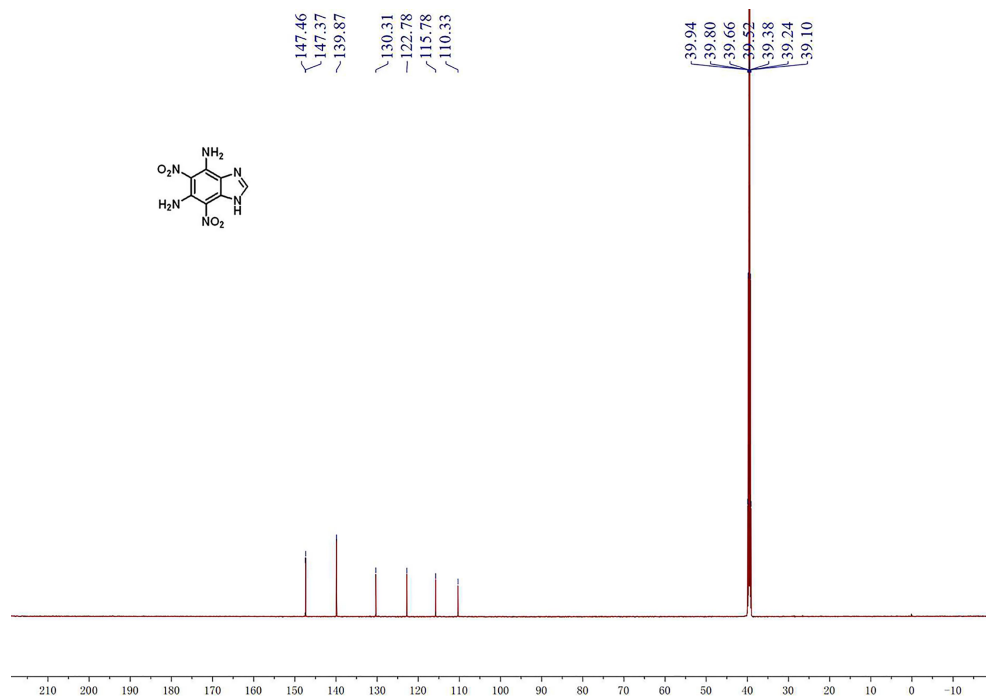
Fig. S8 ^{13}C NMR spectra of DADNBI.

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Fig. S9 Mass spectra (MS) of **2**.

Fig. S10 Mass spectra (MS) of **3**.
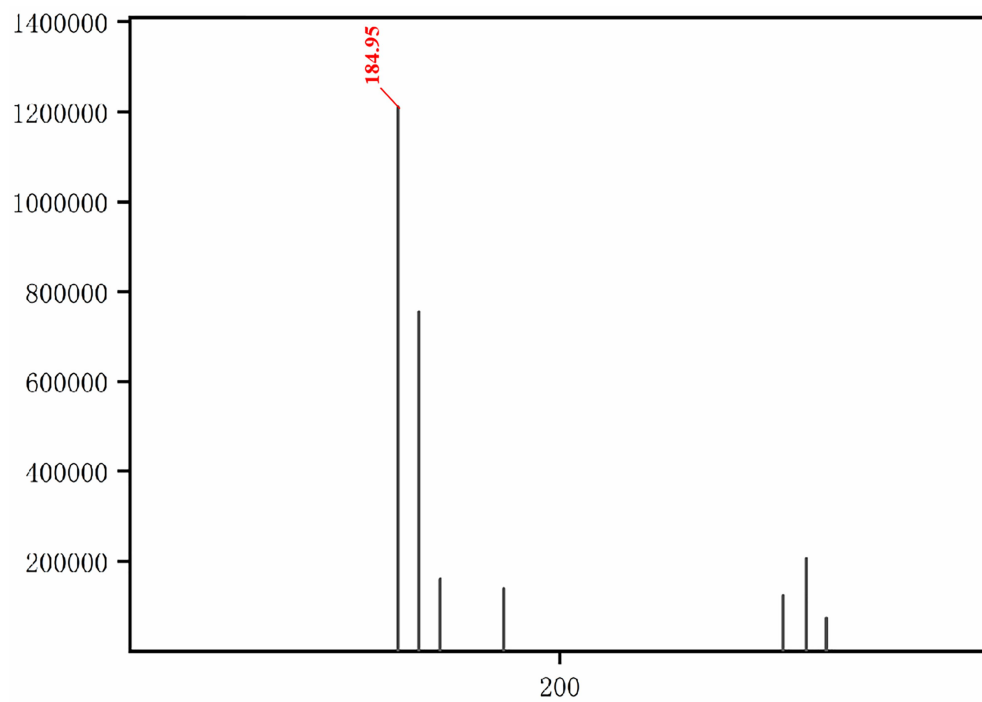
Fig. S11 Mass spectra (MS) of **4**.
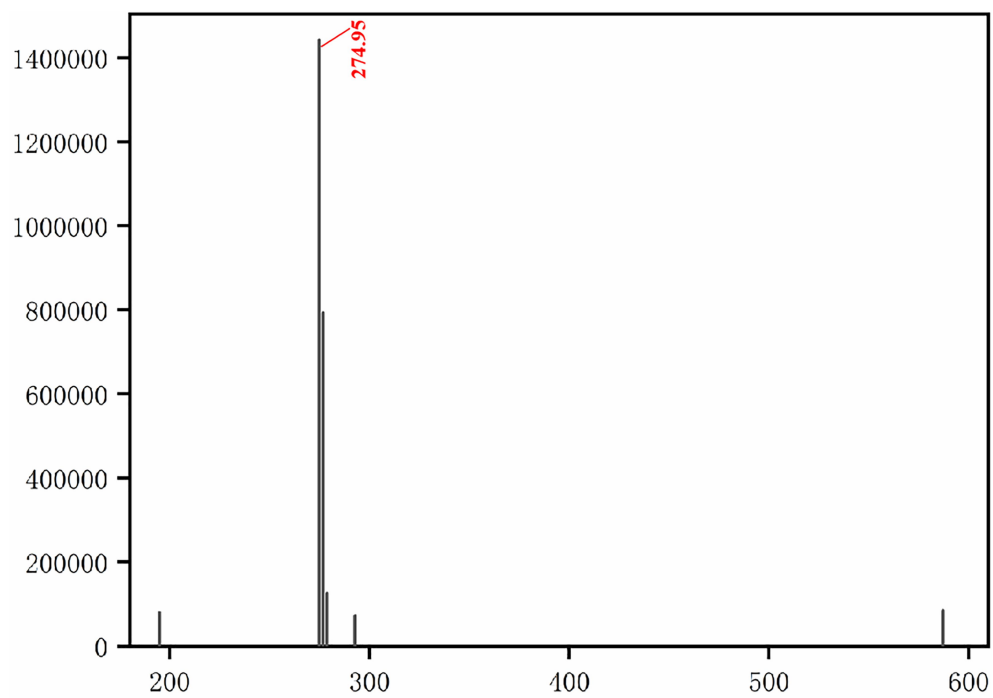
Fig. S12 Mass spectra (MS) of **5**.
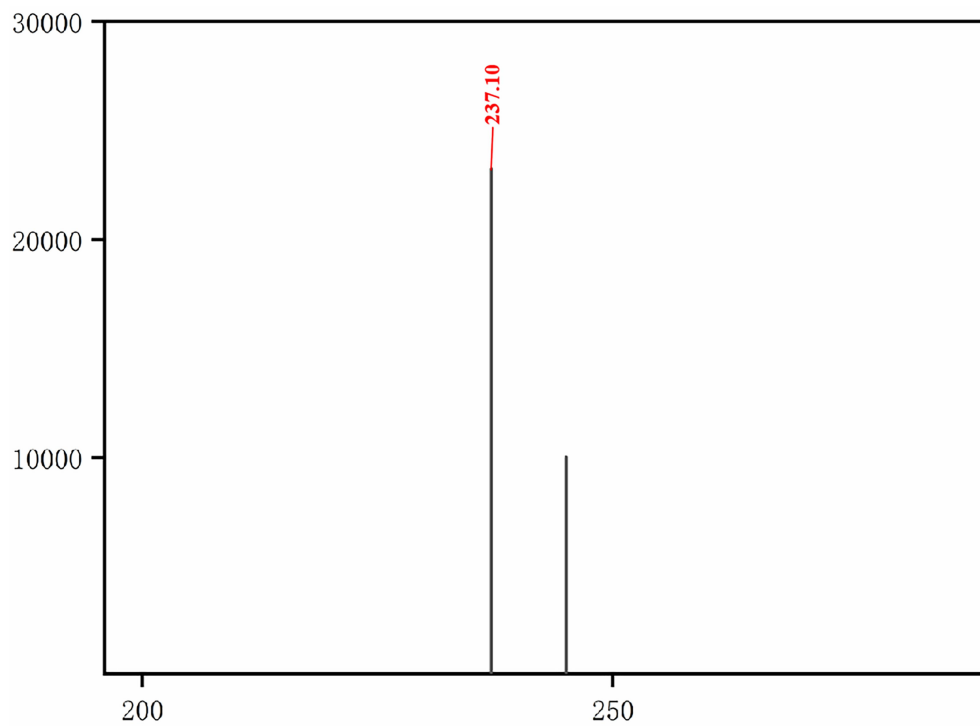
Fig. S13 Mass spectra (MS) of DADNBI.
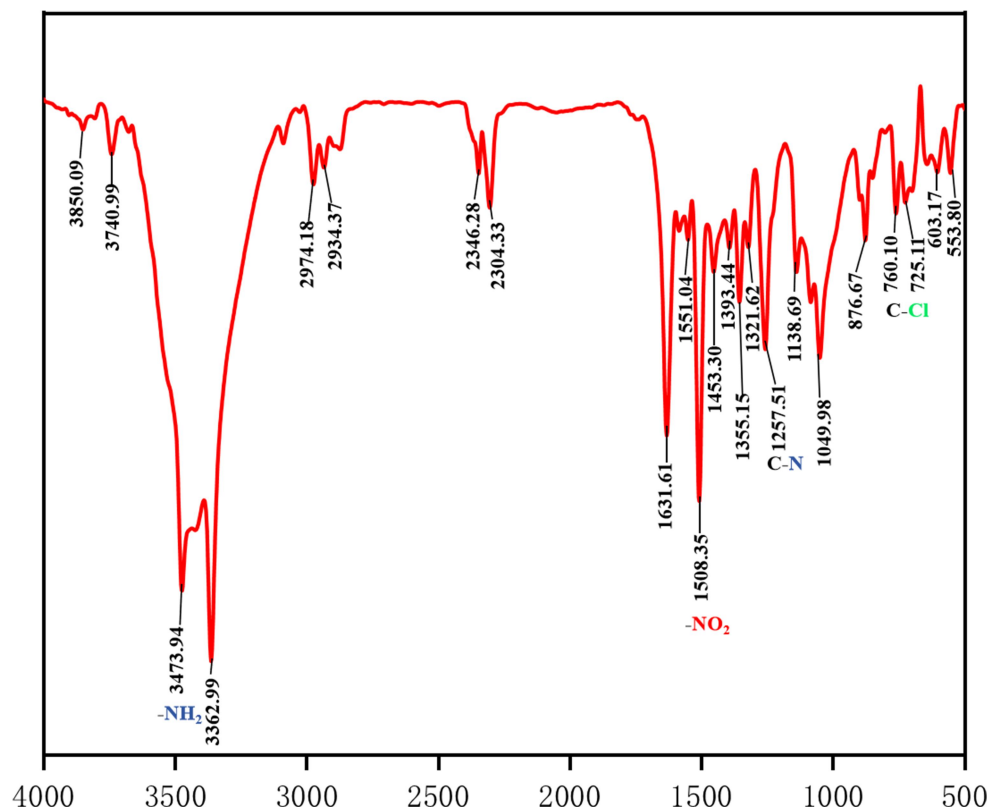
Fig. S14 Infrared spectra (IR) of **2**.
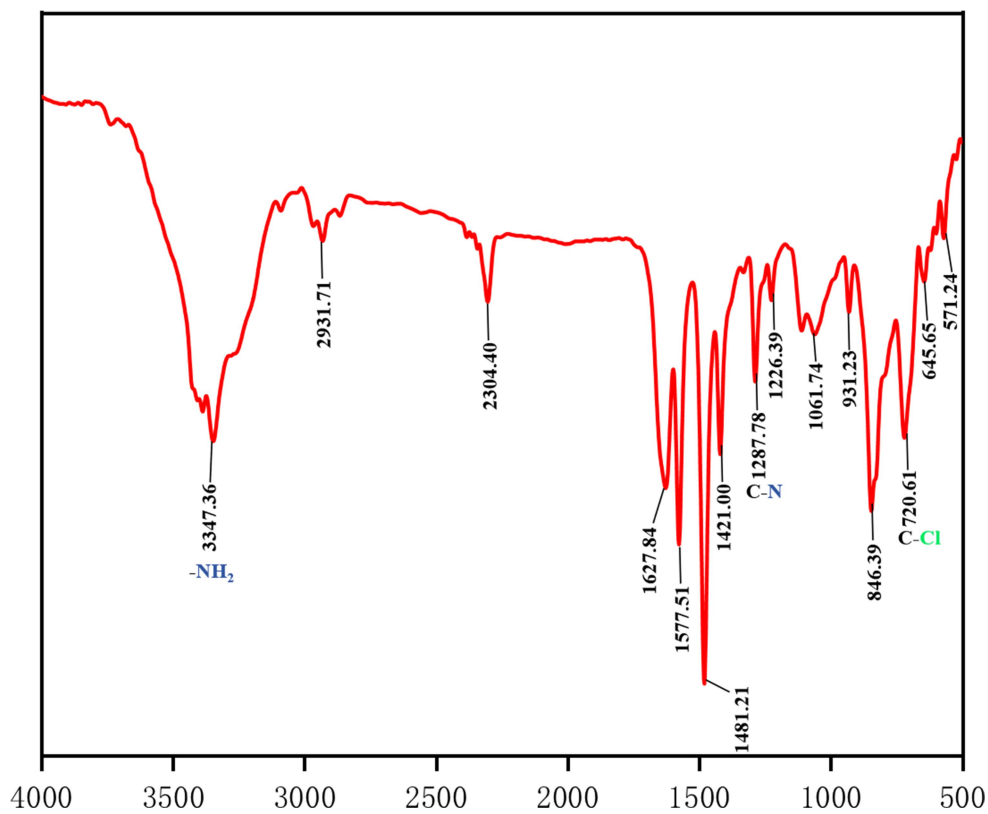
Fig. S15 Infrared spectra (IR) of **3**.
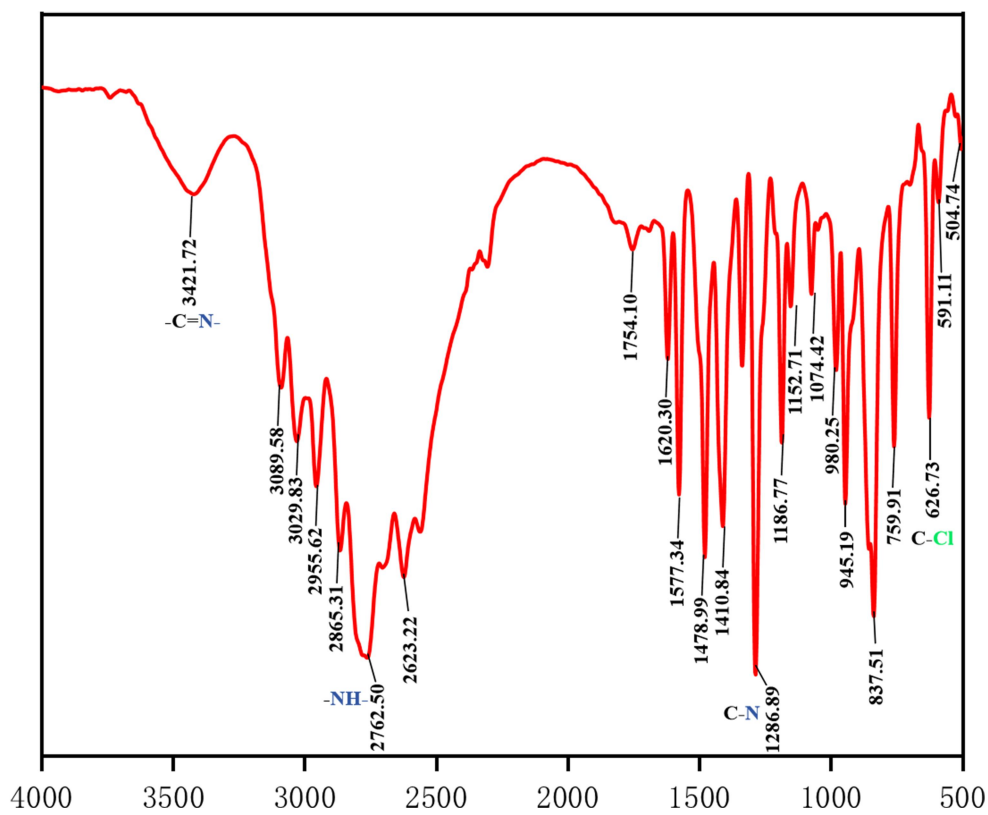
Fig. S16 Infrared spectra (IR) of **4**.
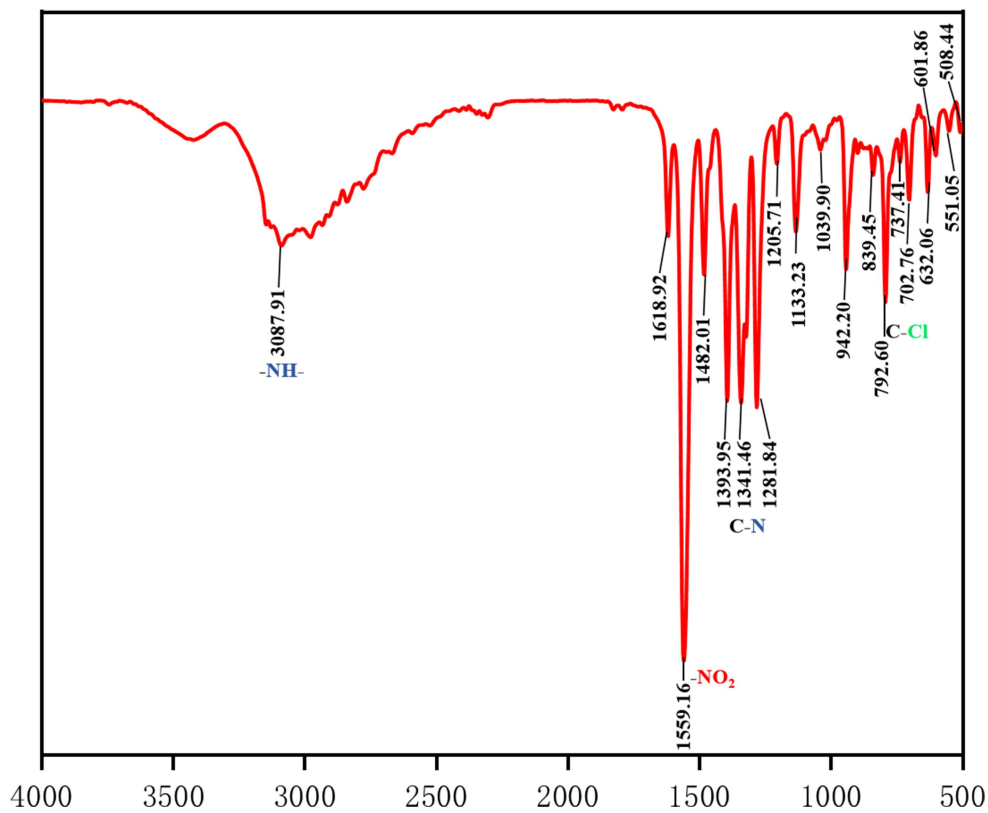
Fig. S17 Infrared spectra (IR) of **5**.
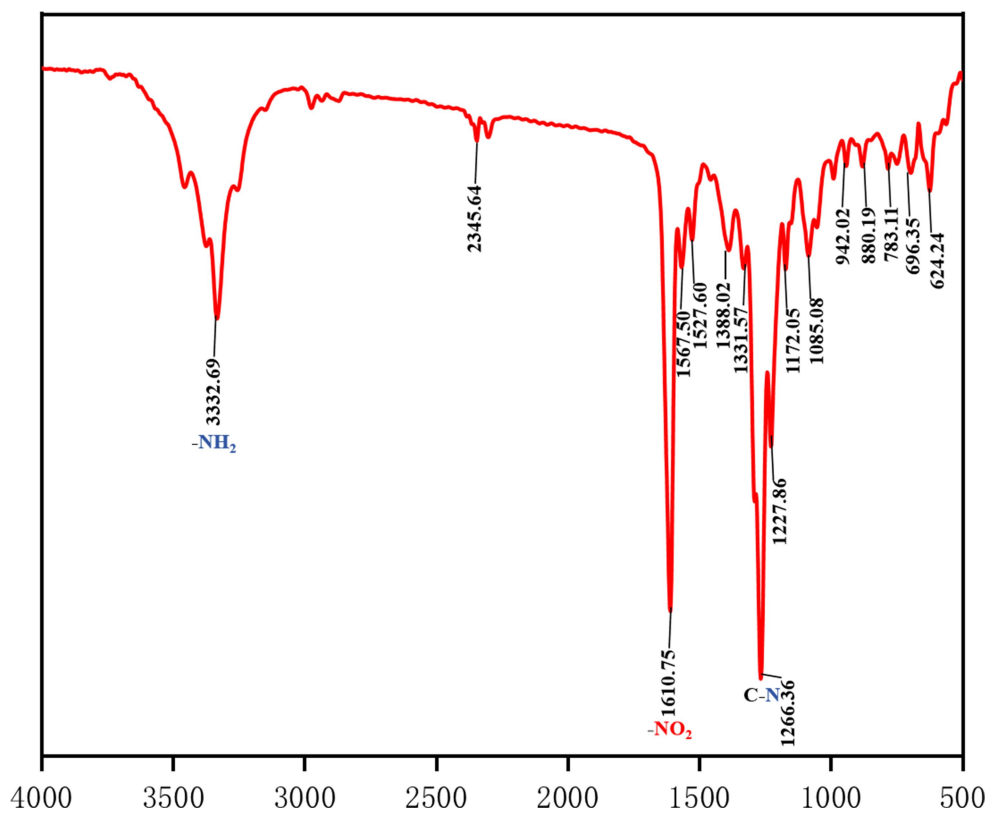
Fig. S18 Infrared spectra (IR) of DADNBI.
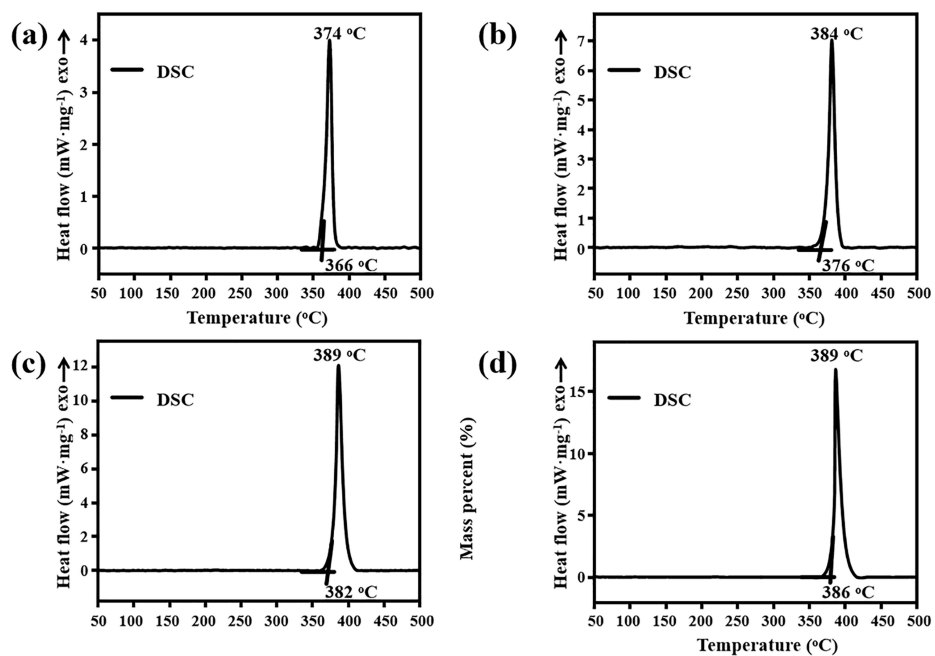
4. TG-DSC curves of DADNB

Fig. S19 (a) DSC curves of DADNBI (5 °C·min⁻¹). (b) DSC curves of DADNBI (10 °C·min⁻¹). (c) DSC curves of DADNBI (15 °C·min⁻¹). (d) DSC curves of DADNBI (20 °C·min⁻¹).
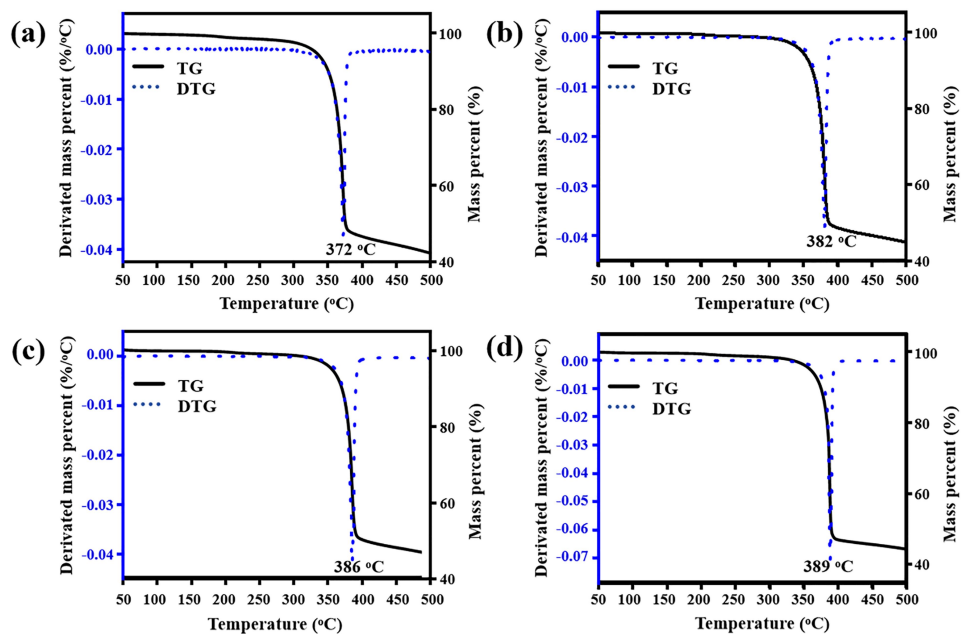

Fig. S20 (a) TG-DTG curves of DADNBI (5 °C·min⁻¹). (b) TG-DTG curves of DADNBI (10 °C·min⁻¹). (c) TG-DTG curves of DADNBI (15 °C·min⁻¹). (d) TG-DTG curves of DADNBI (20 °C·min⁻¹).