

1 **Supporting information**

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3 **Thermal Stability of *p*-Dimethylaminophenylpentazole**

4 Yu-zhang Yang^a, Yu-chuan Li^a, Ru-bo Zhang^b, Cheng-hui Sun^a and Si-

5 ping Pang^{a*}

6 ^a School of Materials Science & Engineering, Beijing Institute of Technology, South
7 Street No. 5, Zhongguancun, Haidian District, 100081 Beijing (China)

8 ^b School of Chemistry, Beijing Institute of Technology, South Street No. 5,
9 Zhongguancun, Haidian District, 100081 Beijing (China)

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1 **1. General method**

2 Reagents were purchased from Aladdin and were used as received. ¹H and
3 ¹⁵N NMR spectra were recorded on a 600 MHz (Bruker AVANCE 600)
4 nuclear magnetic resonance spectrometer operating at 75 MHz using
5 CDCl₃ and CD₂Cl₂ as solvent respectively and locking solvent unless
6 otherwise stated. IR spectra were recorded using KBr pellets for solids on
7 a Perkin Elmer Spectrum 400 spectrometer. Gas chromatography mass
8 spectrum (GC-MS) was performed with a Shimadzu GCMS-QP2010
9 Ultra. Melting points were determined on an XT4 microscope melting
10 point apparatus

11

12 **2. Synthesis producers**

13 Caution! Although none of the complexes described herein have exploded
14 or detonated in the course of this research, these materials should be
15 handled with extreme care using the best safety practices.

16 ***p*-Dimethylaminophenylpentazole (1)** : *p*-Dimethylaminophenylamine
17 (0.2 g, 1.47 mmol) was dissolved in methanol (4 ml, cooled to 0 °C). HCl
18 (0.3 ml, 36~38%) was then added. Stirring for 15 min, then water (1 ml)
19 solution of NaNO₂ (0.12 g, 1.617 mmol) was added during 30 min,
20 keeping the temperature of the reaction between 2 and 0 °C. The reaction
21 mixture was then stirred at the same temperature for 1 h. Aether (20 ml, 0
22 °C) was added into the reaction mixture, the precipitate was separated by
23 filtration after stirring 20 min. Pure *p*-dimethylaminophenyldiazonium
24 was obtained by 3 times washing with aether, then dissolved in a mixture
25 of methanol (15 ml) and hexane (5 ml) cooled to -40 °C by an ethanol
26 bath. A saturated solution of NaN₃ (0.13 g, 2 mmol) in aqueous MeOH (5
27 ml, 50%) was added over several minutes. The reaction was stirred
28 vigorously for 1 h. The reaction suspension was filtered in a fridge (-
29 35°C). The precipitated deep green-gray product was diluted with cold
30 methanol (-35 °C 10 ml) for three times. All glass (including filters) and
31 solutions, used in the following work were cooled to between -60 and -50

1 °C by a cold bath of liquid N₂. The filter precipitate dried by a vacuum
2 freezing to yield crude *p*-dimethylaminophenylpentazole (0.125 g, 0.66
3 mmol) as a shiny gray solid with a yield of 45%.

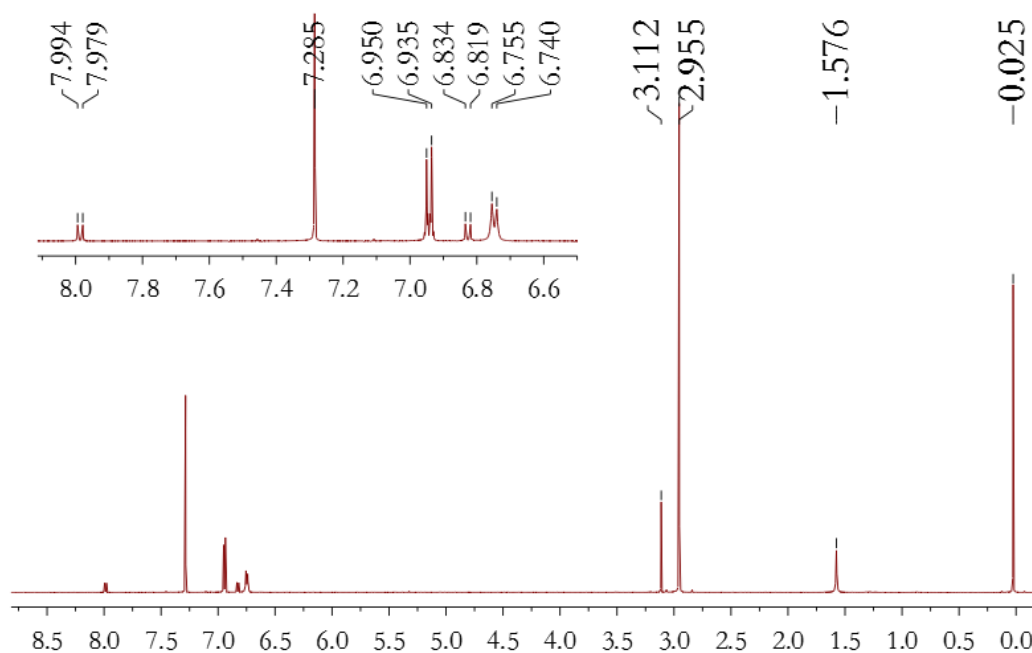
4 Crude **1** was dissolved in dichloromethane for saturated solution in a
5 glass bottle. Double ether was added slowly along the wall of bottle by a
6 syringe. The bottle was sealed and sat at -35 °C. Dark yellow needle crystal
7 was obtained after 48 h. after methanol washing and vacuum drying, the
8 pure pale yellow crystal **1** was obtained. This step was carried out at least
9 2 times, and the bright yellow needle for testing was obtained in a NMR
10 tube (d = 2.5 mm) with the method above.

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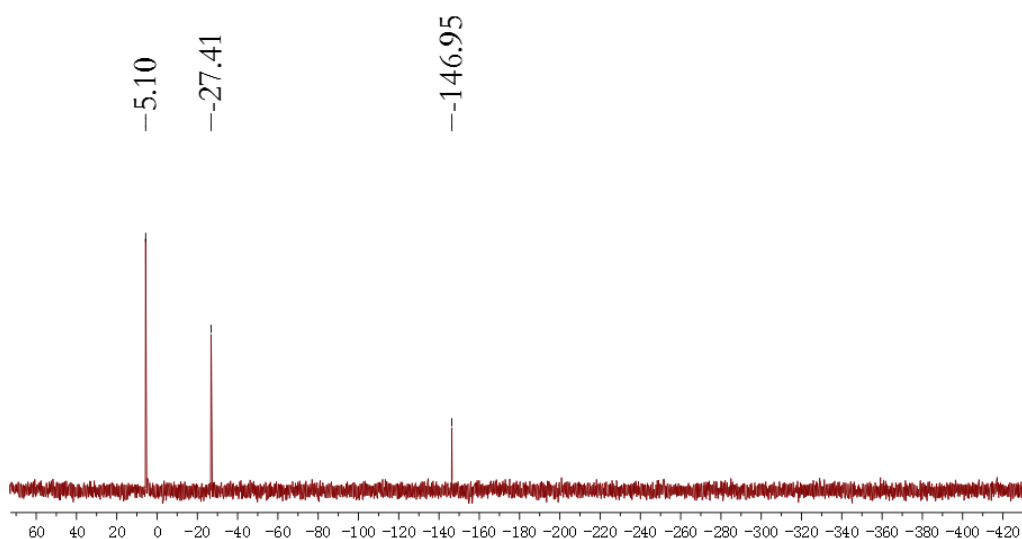
12 ***p*-Dimethylaminophenylazide (2)** : 0.1 g (0.53 mmol) of Crystal **1** was
13 preserved in a unsealed flask at room temperature, silver paper was
14 surrounded the flask for avoiding light. 0.08 g (0.48 mmol) dark green
15 powder was obtained after a week, yield: 91%, M.p.: 42 °C, *T*_{dec}: 156 °C.

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17 **3. NMR**



18 **Figure S1.** ¹H NMR spectrum of mixture of **1** and **2** at room temperature.



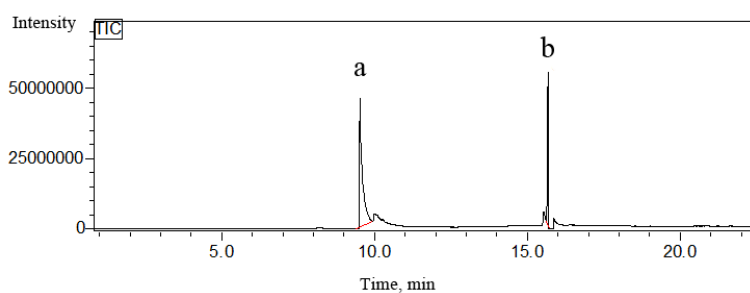
1 **Figure S2.** ^{15}N NMR spectrum of **1** and **2** at $-20\text{ }^\circ\text{C}$.

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3 **4. Mass spectra**

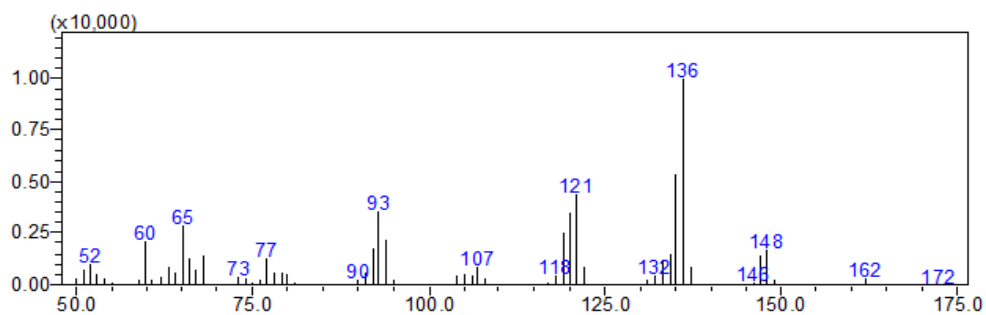
4 The initial oven temperature was $30\text{ }^\circ\text{C}$ (held for 3 min), and then
 5 increased to $70\text{ }^\circ\text{C}$ at the rate of $20\text{ }^\circ\text{C}/\text{min}$, held for 3 min, then
 6 increased to $300\text{ }^\circ\text{C}$ at the rate of $25\text{ }^\circ\text{C}/\text{min}$, held for 3 min. The total run
 7 time was 20 min. Mass spectra were performed with a Agilent 6120
 8 LCMS instrument.

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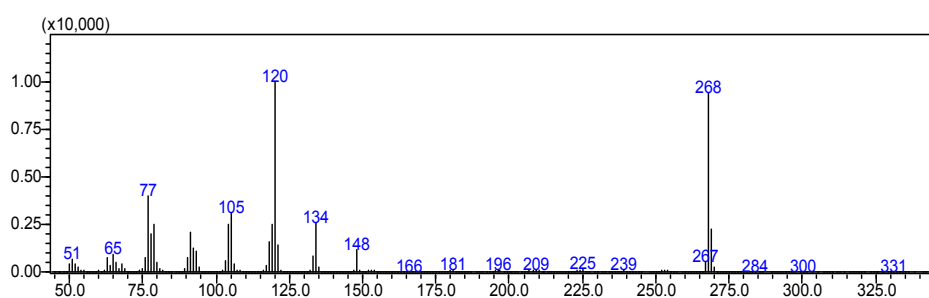


10 **Figure S3.** Chromatograms of GC/MS

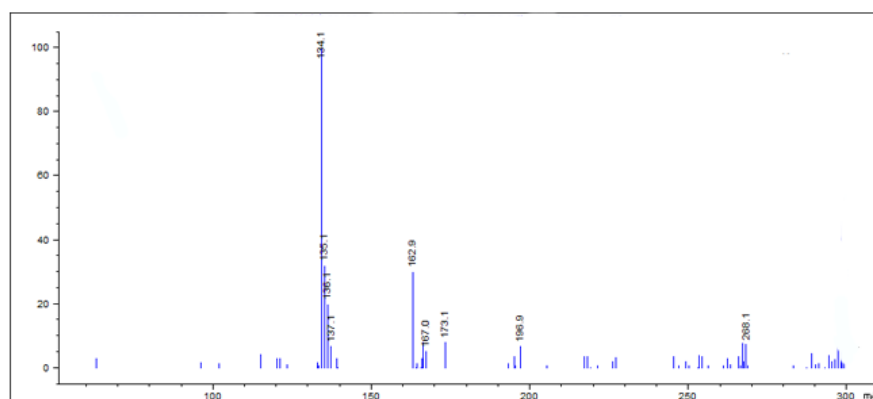
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1 **Figure S4.** Mass spectrum of *a* in figure S2.



2 **Figure S5.** Mass spectrum of *b* in figure S2.

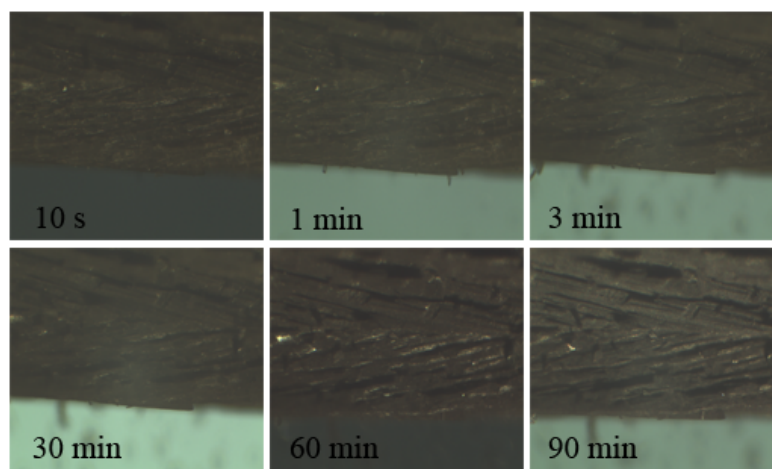


3 **Figure S6.** Mass Spectrum of photolysis product of **2**.

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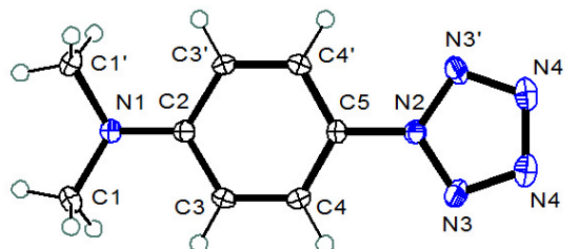
1 5. Decomposition observation



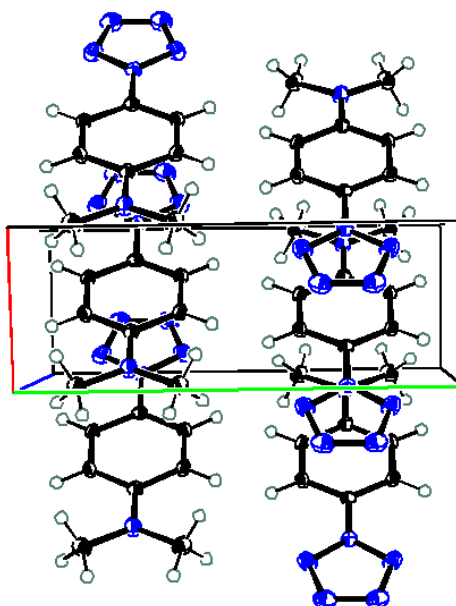
2 **Figure S7.** Microscope images of decomposition process of **1** at room
3 temperature.

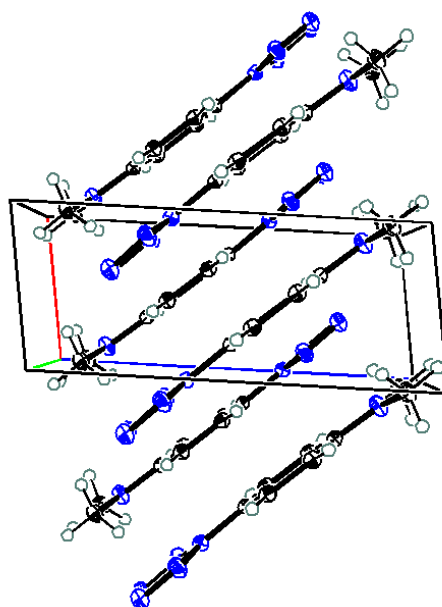
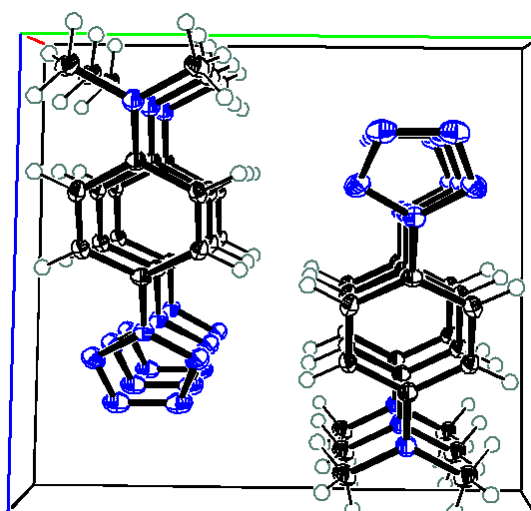
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5 6. Single-crystal X-ray diffraction



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2 **Figure S8.** Crystal structure of **1**.

3

Empirical formula	C ₈ H ₁₀ N ₆
Formula weight	190.22 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic, P 2 ₁ /m
Space-group	P2 ₁ /m
Unit cell demensions	$a=4.0830(12)$ Å $\alpha=90^\circ$ $b=10.953(3)$ Å $\beta=98.431(6)^\circ$ $c=10.082(3)$ Å $\gamma=90^\circ$
Cell ratio	$a/b=0.3728$ $b/c=1.864$ $c/a=2.4693$
Cell volume	446.01(20) Å ³
Z	2
Cal. density	1.41635 g/cm ³
Absorption coefficient	0.097 mm ⁻¹
F(000)	200

Crystal size	0.500 x 0.360 x 0.170 mm
Theta range for data collection	2.042 to 27.431 °
Limiting indices	-5<=h<=5, -13<=k<=14, -13<=l<=7
Reflections collected / unique	3000 / 1075 [R(int) = 0.0192]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.75 and 0.69
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1075 / 0 / 71
Goodness-of-fit on F ²	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0956
R indices (all data)	R1 = 0.0455, wR2 = 0.1016
Extinction coefficient	n/a
Largest diff. peak and hole	0.301 and -0.189 e.Å ⁻³
Empirical formula	C8 H10 N6
Formula weight	190.22 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic, P 21/m
Space-group	P2 ₁ /m
Unit cell demensions	a=4.0830(12) Å alpha=90 ° b=10.953(3) Å beta=98.431(6) ° c=10.082(3) Å gamma=90 °
Cell ratio	a/b=0.3728 b/c=1.864 c/a=2.4693
Cell volume	446.01(20) Å ³
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R indices (all data)	R1 = 0.0455, wR2 = 0.1016
Extinction coefficient	n/a
Largest diff. peak and hole	0.301 and -0.189 e.Å ⁻³

1 **Table S1.** Crystal data and structure refinement for **1**.

2

3

4

Bond length	(Å)	Bond length	(Å)
N1-C2	1.368(2)	C1-H1b	0.9800
N1-C1	1.4560(13)	C1-H1c	0.9800
N1-C1'	1.4560(13)	C2-C3	1.4197(12)
N2-N3	1.3262(12)	C2-C3'	1.4197(12)
N2-N3'	1.3262(12)	C3-C4	1.3819(16)
N2-C5	1.4333(15)	C3-H3	0.9500
N3-N4	1.3111(15)	C4-C5	1.3914(13)
N4-N4'	1.344(2)	C4-H4	0.9500
C1-H1a	0.98000	C5-C4'	1.3914(13)

1 **Table S2.** Bond length (Å) in crystal for **1**.

2

Bong angles	(°)	Bong angles	(°)
C2-N1-C1	120.36(7)	H1b-C1-H1c	109.500
C2-N1-C1'	120.35(7)	N1-C2-C3'	121.32(7)
C1'-N1-C1	119.02(13)	N1-C2-C3	121.30(7)
N3'-N2-N3	111.72(13)	C3'-C2-C3	117.39(14)
N3'-N2-C5	124.13(6)	C4-C3-C2	123.14(10)
N3-N2-C5	124.13(6)	C4-C3-H3	119.400
N4-N3-N2	105.2(1)	C2-C3-H3	119.400
N3-N4-N4'	108.95(7)	C3-C4-C5	119.83(10)
N1-C1-H1a	109.500	C3-C4-H4	120.100
N1-C1-H1b	109.500	C5-C4-H4	120.100
N1-C1-H1c	109.500	C4-C5-C4'	120.68(14)
H1a-C1-H1b	109.500	C4-C5-N2	119.64(7)
H1a-C1-H1c	109.500	C4'-C5-N2	119.64(7)

3 **Table S3.** Bond angles (°) in crystal for **1**.

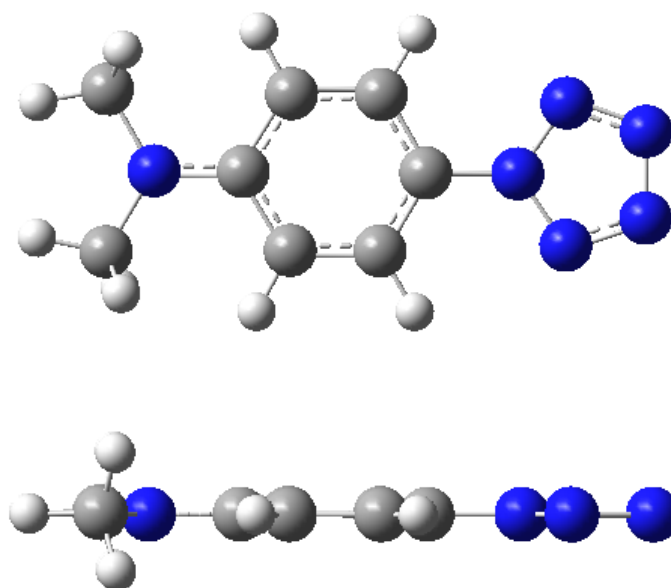
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1 **7. Calculation detail**



2 **Figure S9.** Theoretical optimized geometry of **1**.

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Bond length	(Å)	Bond length	(Å)
N1-C2	1.3778	C1-H1b	1.0909
N1-C1	1.4537	C1-H1c	1.0994
N1-C1'	1.4537	C2-C3	1.4173
N2-N3	1.3319	C2-C3'	1.4173
N2-N3'	1.3319	C3-C4	1.3868
N2-C5	1.4229	C3-H3	1.0827
N3-N4	1.3031	C4-C5	1.3967
N4-N4'	1.3443	C4-H4	1.0839
C1-H1a	1.0985	C5-C4'	1.3967

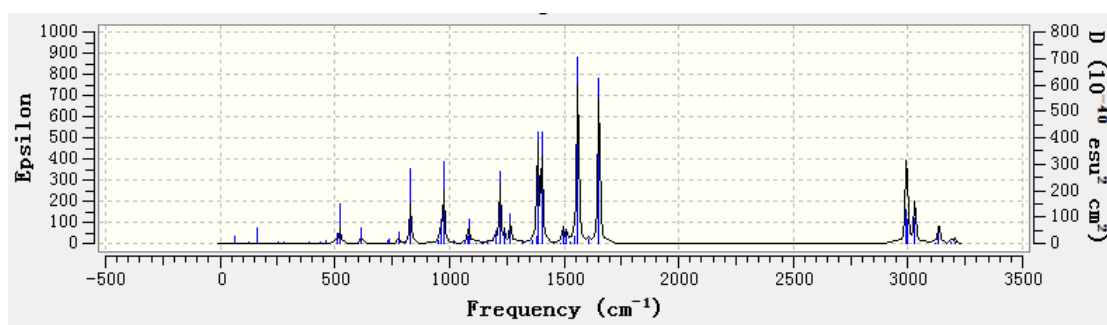
4 **Table S4.** Bond length (Å) by DFT method B3LYP/6-31G(d) level.

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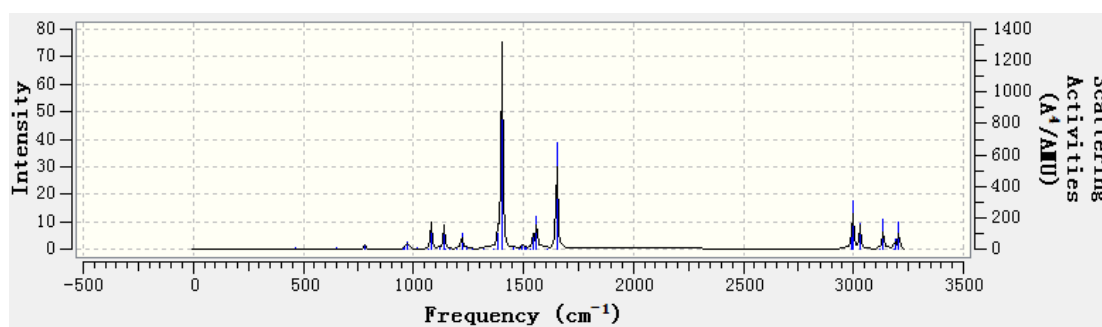
Bong angles	(°)	Bong angles	(°)
C2-N1-C1	120.90	H1b-C1-H1c	107.98
C2-N1-C1'	120.90	N1-C2-C3'	121.34
C1'-N1-C1	119.73	N1-C2-C3	121.34
N3'-N2-N3	111.41	C3'-C2-C3	117.32

N3'-N2-C5	124.30	C4-C3-C2	128.26
N3-N2-C5	124.30	C4-C3-H3	120.39
N4-N3-N2	105.11	C2-C3-H3	120.39
N3-N4-N4'	109.19	C3-C4-C5	119.90
N1-C1-H1a	111.66	C3-C4-H4	120.21
N1-C1-H1b	109.15	C5-C4-H4	119.89
N1-C1-H1c	111.99	C4-C5-C4'	120.19
H1a-C1-H1b	107.85	C4-C5-N2	119.91
H1a-C1-H1c	108.06	C4'-C5-N2	119.91

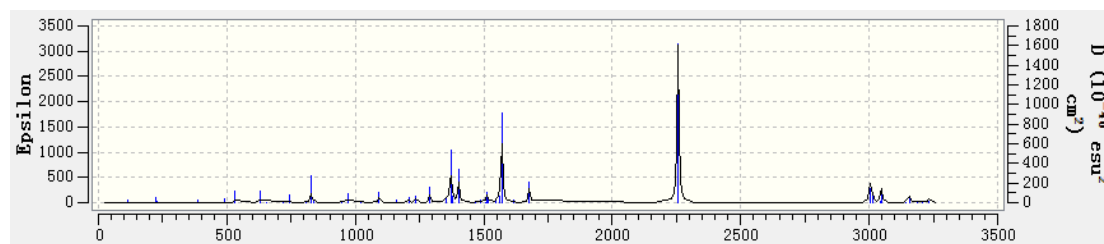
1 **Table S5.** Bond angles ($^{\circ}$) by DFT method B3LYP/6-31G(d) level.



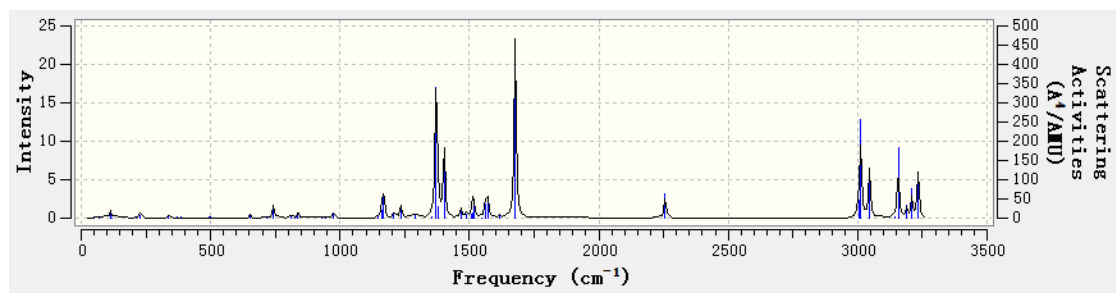
2 **Figure S10.** Simulated IR spectrum of **1**.



3 **Figure S11.** Simulated Raman spectrum of **1**.



4 **Figure S12.** Simulated IR spectrum of **2**.



1 **Figure S13.** Simulated Raman spectrum of **2**.