SUPPORTING INFORMATION

TRIAZENE-BRIDGED NITROGEN-RICH HETEROCYCLIC ENERGETIC COMPOUNDS 4,4'-(TRIAZ-1-ENE-1,3-DIYL)BIS(1,2,5-OXADIAZOL-3-AMINE) - SYNTHESIS, CHARACTERIZATION AND PROPERTIES

Jin Zhu, Qian-xiong Chen, Su-ming Jing*, Ke-yao Li, Zhi-neng Wang, Yuan-yuan Wang, Jia-hao Deng

Author’s address and e-mail address : Jin Zhu, Lead-Author, Department of Environmental and Safety Engineering, North University of China, Taiyuan, Shanxi, China. zhujinzbdx@foxmail.com. Su-ming Jing, Corresponding author, Department of Environmental and Safety Engineering, North University of China, Taiyuan, Shanxi, China. j782855067@163.com

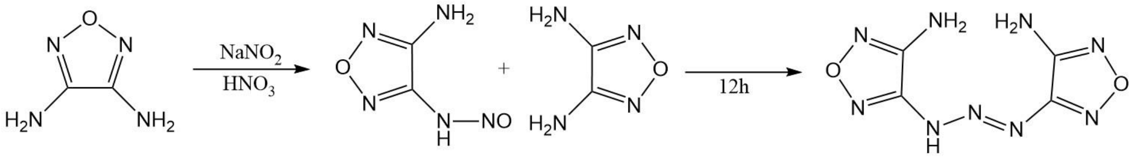
EXPERIMENTAL SECTION

Caution: Although we have not experienced any difficulties in preparing and handling these new energetic materials, proper protective precautions must be used. All compounds should be handled with care using the best safety practices.

GENERAL METHODS.

All reagents were obtained from HuBei JuSheng Technology Co.LTD and were used as received. Bruker AVANCE 300 nuclear magnetic resonance spectrometer operating at 500, and 150 MHz were used to collect ^{1}H and ^{13}C spectra. DMSO-d_6 was employed as solvent and locking solvent. Chemical shifts are given relative to Me_4Si for ^{1}H and ^{13}C spectra. Melting and decomposition (onset) points were measured by a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets for solids on a Nicolet Thermo model AVATAR 370 spectrometer. Densities were determined at room temperature by a Micromeritics AccuPyc 1340 gas pycnometer. Elemental analyses were determined using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were tested by using a standard BAM Fall hammer and a BAM friction tester. Packing coefficients were calculated using SHELXTL, whereas crystal structures were generated by Ortep 3.0

4,4'-(triaz-1-ene-1,3-diyl)bis(1,2,5-oxadiazol-3-amine)(8) At low temperature (0° C) with stirring, 5 ml of distilled water was poured into a 25 ml three-necked flask and 3,4-diaminofurazan (0.1 g 0.001 mol) was added to form a suspension. Nitric acid solution of sodium nitrite ($NaNO_2$ 0.42g 0.00061mol; 98% nitric acid 0.5ml; water 2ml) was prepared and slowly added to the suspension. The temperature was then raised to 25° C and the reaction was kept at temperature for 12 hours. At the end of the reaction, yellow particles were obtained by filtration in 81.3% yield. **IR** cm^{-3}: 3462, 3350, 2872, 1638, 1598, 1561, 1494, 1440, 1415, 1337, 1231, 1121, 1001, 932, 873, 743, 669, 607. **^{1}H NMR**(500MHz, DMSO-d6, 25°C, ppm) δ: 6.81, 13.85-14.57. **^{13}C NMR**(150MHz, DMSO-d6, 25°C, ppm): 150.76、151.12. **Elemental analysis for $C_4H_5N_9O_2$**, Calcd(%): C 22.75 H 2.39 N 59.70 O 15.15; Found(%): C 22.73 H 2.29 N 59.58.



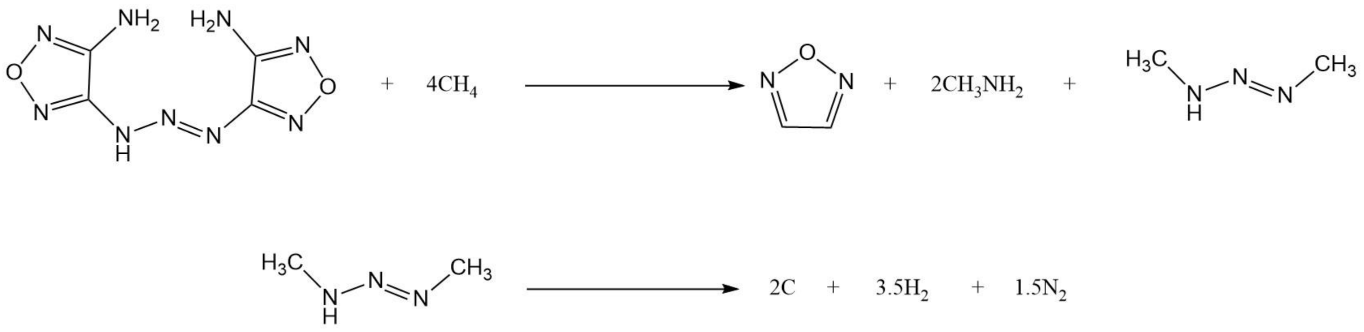
9 10 8

Scheme 1 Synthesis route for 8

THEORETICAL CALCULATIONS

HEAT OF FORMATION (HOF)

Optimization and frequency calculation of the 8 structure for the B3PW91/6-311G* basis set under the Gaussian09W program[1]. Then, isobond reactions were designed to predict the theoretical enthalpy of production of 8, Scheme 2.



Scheme 2

The heat generation equation for 8:

$$\Delta H_{298} = \sum H_{\mathrm{f,p}} - \sum H_{\mathrm{f,R}} \tag{2-1}$$

Here, $\sum H_{\mathrm{f,p}}$ and $\sum H_{\mathrm{f,R}}$ are the sum of the enthalpies of production of the products and reactants at 298 K.

Energetic materials usually exist in the solid state at room temperature, so it is the enthalpy of solid phase formation that has practical significance and can be calculated according to Gaius' law[2]:

$$\Delta H_{\mathrm{f,solid}} = \Delta H_{\mathrm{f,gas}} - \Delta H_{\mathrm{sub}} \tag{2-2}$$

Here, $\Delta H_{\mathrm{f,solid}}$ is the enthalpy of solid phase formation; $\Delta H_{\mathrm{f,gas}}$ is the enthalpy of gas phase formation; ΔH_{sub} is the sublimation enthalpy. The enthalpy of sublimation can be calculated according to Equations 2-3 proposed by Politzer[3]:

$$\Delta_{\mathrm{s}} H^0 = 0.000267 s^2 + 1.650087 \times (\nu\sigma_1^2)^{0.5} - 2.966078 \tag{2-3}$$

Here, S is the total molecule surface area (Å^2), $\nu\sigma_1^2$ is the product of the electrostatic equilibrium coefficient and the total variance of the electrostatic potential (kcal^2•mol^{-2}).

Table1 Calculated zero point energy (ZPE), values of the correction (HT), total energy (E0) and heats of formation (HOF)

Compound	ZPE	HT	E0	ΔH(kJ/mol)	HOF(g, kJ/mol)	HOF(s, kJ/mol)
8	0.139933	0.011992	-797.851483	-170.3660695	950.8	926.3
CH_4	0.045078	0.003812	-40.46362	-	-74.6	-
furazan	0.04622	0.004381	-261.903388	-	196.3	-
CH_3NH_2	0.038833	0.004314	-260.885164	-	-22.5	-
$CH_3NHN_2CH_3$	0.102337	0.007213	-244.43205	-	134.4	-

DETONATION PERFORMANCE

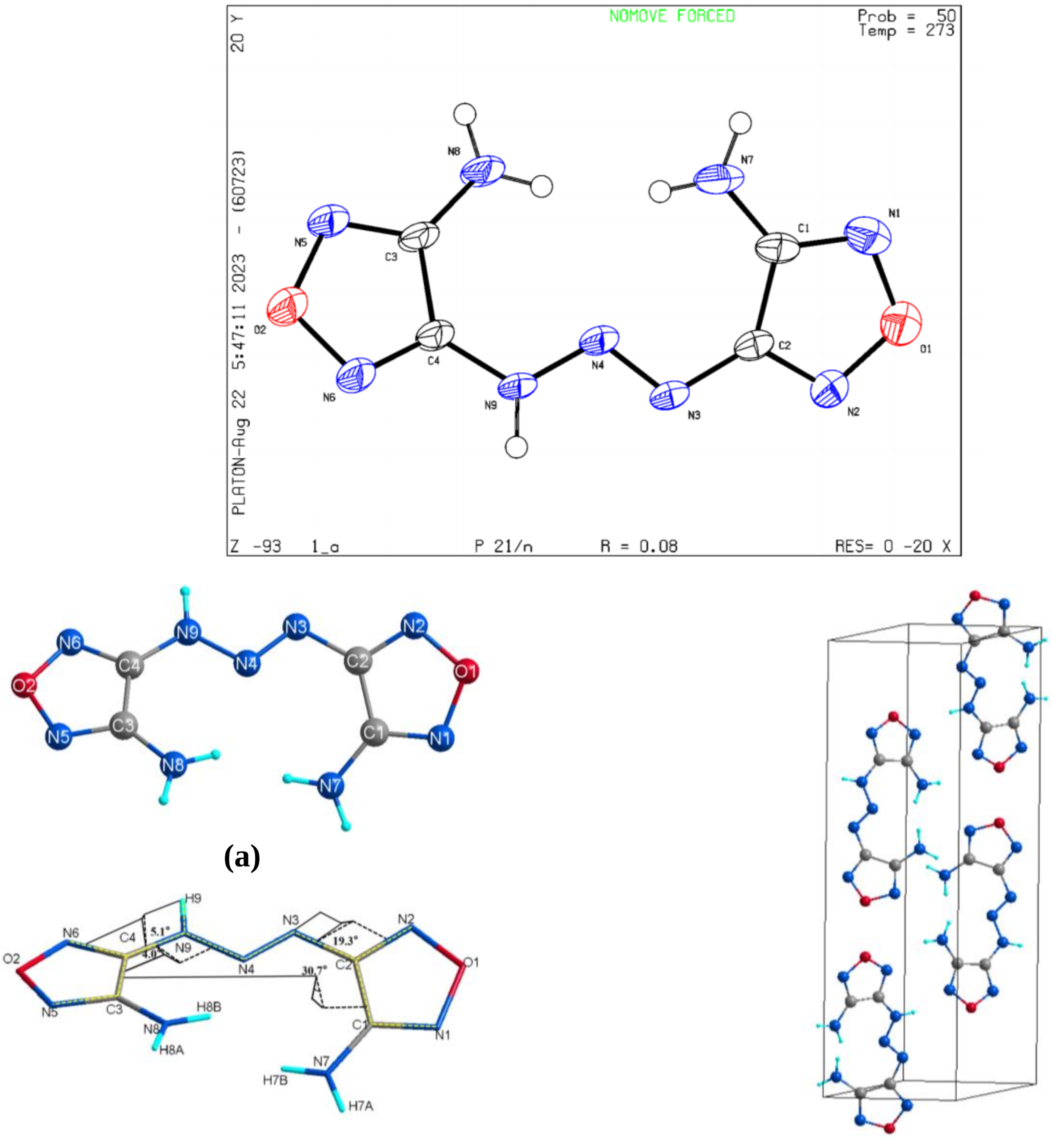
The study mainly use the Kamlet-Jacobs formula [4] to calculate the Detonation performance. Because DFTNP contains F, an expanded form of the K-J formula was used[5], it is assumed that the explosive detonation still follows the K-J formula for N,$\overline{\mathrm{M}}$,Q calculation, H atoms first react with F atoms to generate HF, the rest then react with oxygen atoms to generate H_2O, if the remaining O will first oxidize C to CO_2, if C is not enough to be fully oxidized then in the form of solid C, N still exists in the form of N_2.

$$D = 1.01(N\overline{M}^{0.5}Q^{0.5})^{0.5}(1 + 1.3\rho) \tag{2-6}$$

$$P = 1.558\rho^2 N\overline{M}^{0.5}Q^{0.5} \tag{2-7}$$

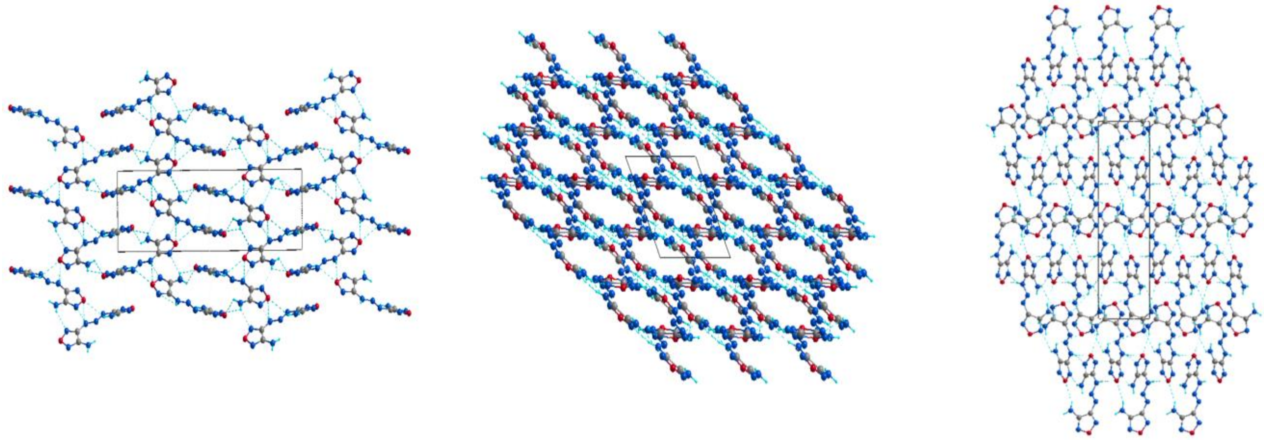
Here, N is the number of moles of gas produced by the explosion of a unit mass of explosive(mol·g $^{-1}$); $\overline{M}$ is the average molar mass of the gas product(g·mol $^{-1}$) ; Q is the explosive heat of the compound(J·g $^{-1}$)。

X-RAY CRYSTALLOGRAPHY OF 8



(a) (b) (c)

Fig 1 X-ray structures (single crystal) of 8(a). Torsion angle of 8(b). A cell of 8(c)



(a) (b) (c)

Fig 2 8 Molecular stacking at different angles

Table 2 Crystal data and structure refinement for crystals

4,4'-(triaz-1-ene-1,3-diyl)bis(1,2,5-oxadiazol-3-amine)(8)			
Moiety formula	$C_4H_5N_9O_2$	γ [°]	90
Formula weight	211.17	V [Å^3]	834.18(14)
T[K]	273	Z	4
ρ. [g/cm^3]	1.681	μ [mm^{-1}]	1.212
Crystal description	monoclinic system	F000	432.0
Space group	P 21/n	h，k，lmax	7, 25, 8
a [Å]	6.1615(6)	Tmin，Tmax	0.865, 0.908
b [Å]	21.2629(19)	θ(max)	66.782
c [Å]	7.0630(6)	R	0.0802(1178)
α [°]	90	wR2	0.2083(1484)
β [°]	115.645	CCDC number	2290524

Table 3 Bond length of 8

Bond	Selected distances	Bond	Selected distances
C1-N7	1.355(4)	N2-O1	1.367(3)
C1-C2	1.447(3)	N3-N4	1.264(3)
C1-N1	1.306(4)	N4-N9	1.322(3)
C2-N3	1.389(3)	N5-O2	1.399(3)
C2-N2	1.298(3)	N6-O2	1.381(3)
C3-N5	1.300(4)	N7-H7A	0.86
C3-N8	1.341(4)	N7-H7B	0.86
C3-C4	1.451(3)	N8-H8A	0.86
C4-N9	1.371(3)	N8-H8B	0.86
C4-N6	1.291(4)	N9-H9	0.86
N1-O1	1.408(3)		

Table 4 Partial bond angle of 8

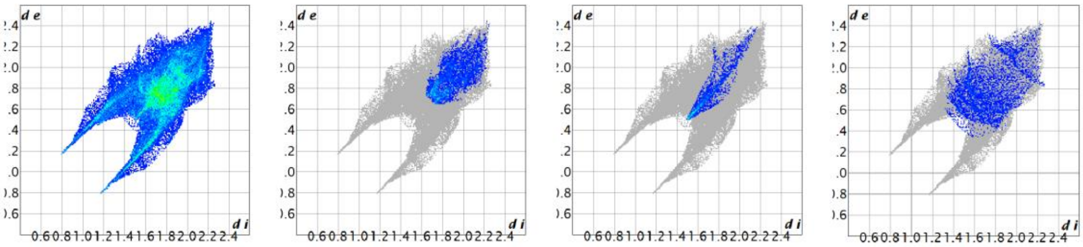
Bond	angles [°]	Bond	angles [°]
N1-C1-N7	124.2(2)	N3-N4-N9	112.77(19)
N1-C1-C2	108.2(2)	C3-N5-O2	106.81(19)
N7-C1-C2	127.6(3)	C4-N6-O2	105.89(19)
N2-C2-N3	118.8(2)	C1-N7-H7A	120
N2-C2-C1	109.2(2)	C1-N7-H7B	120
N3-C2-C1	132.0(2)	H7A-N7-H7B	120
N5-C3-N8	124.6(2)	C3-N8-H8A	120
N5-C3-C4	107.1(2)	C3-N8-H8B	120
N8-C3-C4	128.2(2)	H8A-N8-H8B	120
N6-C4-N9	120.6(2)	N4-N9-C4	119.0(2)
N6-C4-C3	110.1(2)	N4-N9-H9	120.5
N9-C4-C3	129.3(2)	C4-N9-H9	120.5
C1-N1-O1	105.6(2)	N2-O1-N1	110.5(2)

C2-N2-O1	106.6(2)	N6-O2-N5	110.07(19)
N4-N3-C2	111.35(19)		

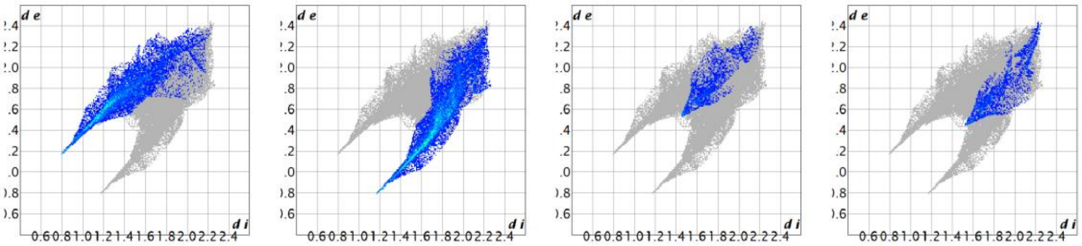
Table 5 Hydrogen bonds for DFTNP[Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(9)-H(9)...N(5)	0.86	2.10	2.93	160.02
N(8)-H(8a)...N(6)	0.86	2.55	3.34	154.30
N(8)-H(8a)...N(1)	0.86	2.68	3.18	117.48
N(7)-H(7a)...N(2)	0.86	2.38	3.22	167.47
N(9)-H(9)...O(2)	0.86	2.96	3.80	164.19
N(7)-H(7b)...O(2)	0.86	2.72	3.44	141.19
N(8)-H(8b)...O(1)	0.86	2.90	4.05	80.83

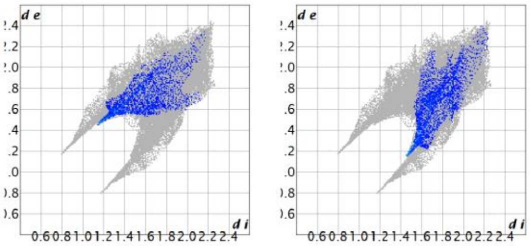
2D fingerprint plots for 8



All weak interaction **N...N** **O...O** **H...H**



H...N **N...H** **O...N** **N...O**



H...O **O...H**

Fig 3 2D fingerprint plots for 8

NMR AND FTIR

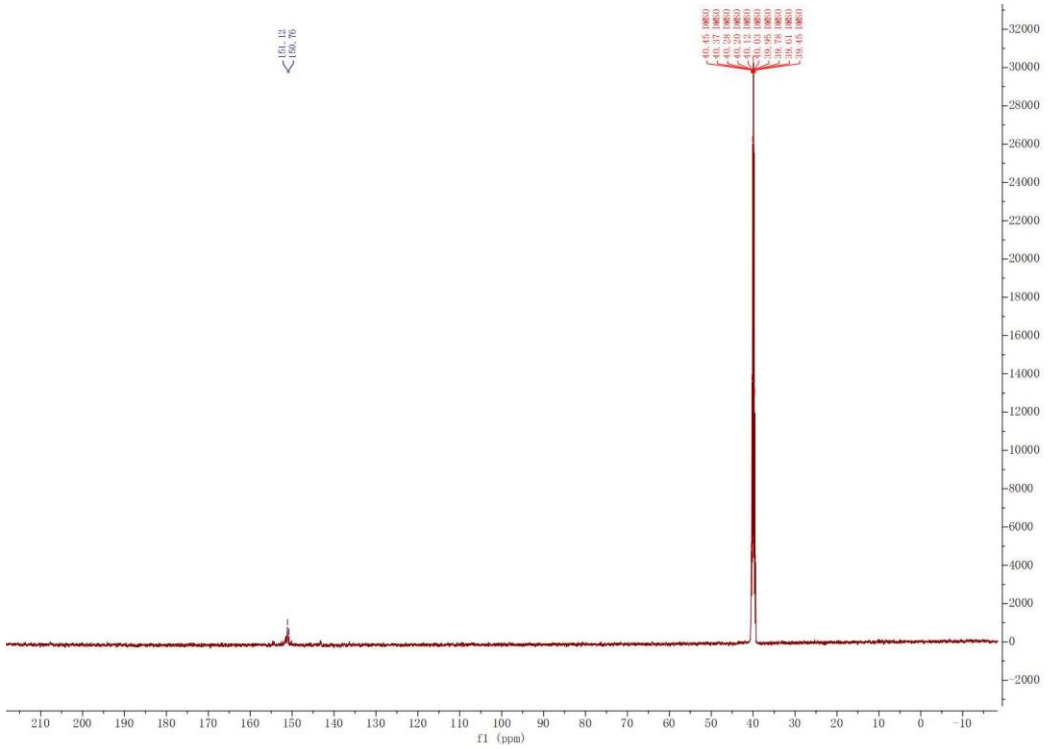


Figure 4 ^{13}C NMR of 8

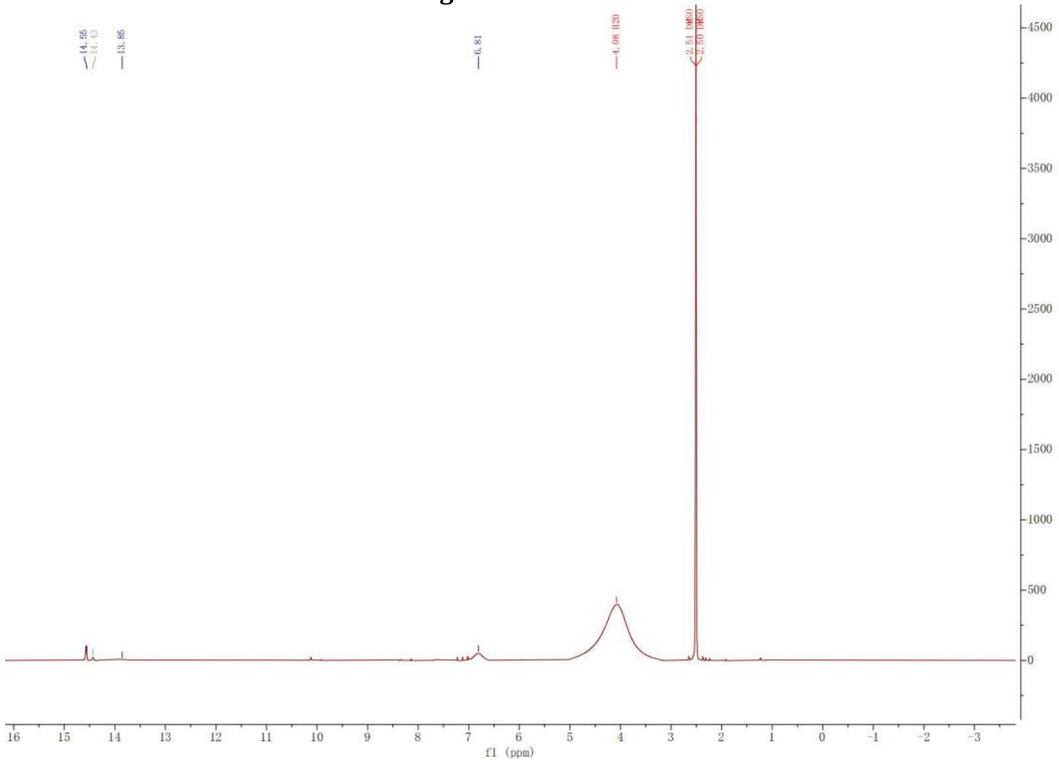


Figure 5 ^{1}H NMR of 8

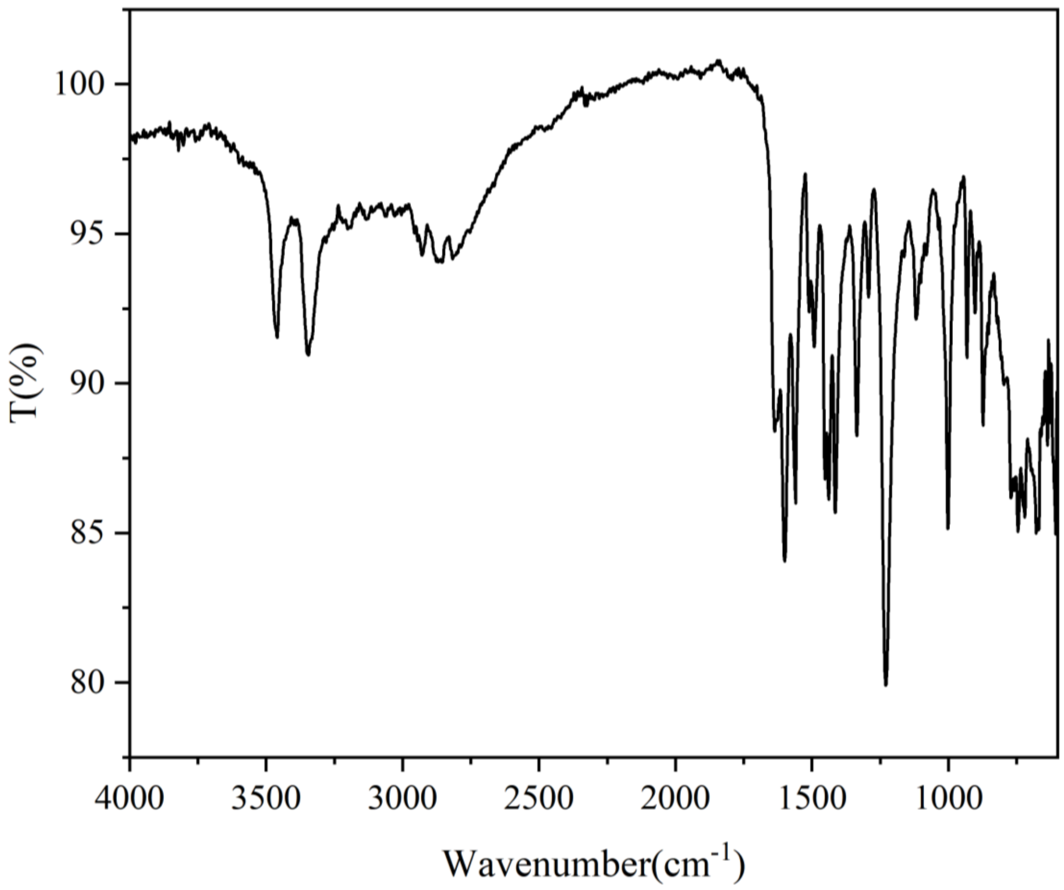


Figure 6. FTIR of **8**

References

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