Supporting Information

Intriguing Rotational Conformations of Energetic 1,2,4-Triazole-pyrazoles: Comparative Insights into Versatile N- Functionalization and Structure-Property Modulation

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1. Experimental Sections

1.1 Safety Precaution

In this work, all new compounds are potential energetic materials that tend to explode under certain external stimuli. Therefore, the whole experimental process should be carried out by using proper safety equipment, such as safety shields, eye protection, and leather gloves.

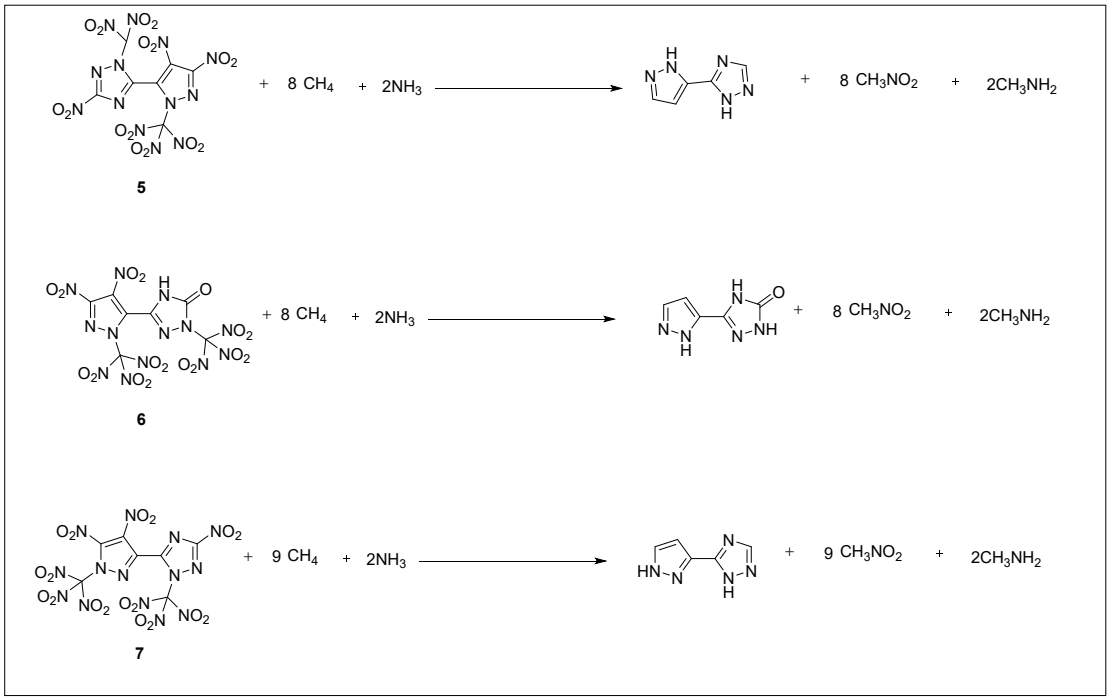
1.2 General methods

^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a Bruker 400 MHz and 125 MHz, respectively, and TMS as internal standard. Chemical shifts were reported in parts per million (ppm). The onset decomposition temperature was measured using a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C min^{-1} under dry nitrogen atmosphere. Infrared spectra (IR) were obtained on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were investigated on a Vario EL III Analyzer. Impact and friction sensitivities were tested by a BAM fallhammer and friction tester. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1340 gas pycnometer. The crystal structures were produced employing Mercury 2021.1.0 software.

2. Computational Details

Theoretical calculations were performed by using the Gaussian 09 E.01 suite of programs [1]. Gas phase heats of formation of the title compounds were computed based on an isodesmic reaction (Scheme S1). The enthalpy of reaction was carried out by combining the M062X/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 further obtained by employing Trouton's rule according to equation 1 (T represents either melting point or decomposition temperature when no melting occurs prior to decomposition) [2].

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



Scheme S1. Isodesmic reactions for **5**, **6** and **7**.

Table S1 The zero point energy (ZPE), temperature correction coefficient (H_T), total energy (E_0), gas phase heat of formation ($\Delta H_{f(g)}$) and heat of sublimation ($\Delta H_{f(S)}$)

Compound	ZPE(a.u)	H_T(a.u)	E_0(a.u)	$\Delta H_{f(g)}$ (kJ mol^{-1})	$\Delta H_{f(S)}$ (kJ mol^{-1})
CH4	0.044558	0.048371	-40.4966719	-74.6	-
NH3	0.034252	0.03807	-56.5405858	-45.9	-
CH3NO2	0.049635	0.054938	-244.9716381	-74.3	-
CH3NH2	0.063782	0.068162	-95.8302896	-23.0	-
Pyrazol-triazole	0.11136	0.119622	-467.2055817	397.4	-
Pyrazol-carbonyl-triazole	0.115534	0.125087	-542.4422682	136.3	-
5	0.18186	0.213958	-2181.487445	655.779213	582.0
6	0.185039	0.21826	-2256.718913	405.402222	325.8
7	0.181889	0.216911	-2385.926857	740.469129	660.9

Table S2 Optimized cartesian coordinates.

5			
O	0.13298	-1.51023	1.810286
N	-0.68408	-1.36104	-1.10818
O	3.53577	-1.04612	2.197753
O	2.545099	4.20461	0.343795

N	1.688736	0.014133	0.205788
N	-1.97862	0.02841	-0.00683
O	2.352412	-1.43236	-1.90327
N	2.715852	0.904892	0.22065
O	-1.19947	2.73428	-1.11581
O	1.551351	-3.16316	1.799574
O	-3.9778	1.553717	-1.0177
O	0.594829	3.749525	-1.81999
N	-2.77774	-1.00412	-0.34579
O	4.140926	3.157649	-0.71994
N	2.098231	-2.14565	-0.96464
N	3.046465	3.23973	-0.20591
N	0.016045	2.879842	-1.20227
N	3.486369	-1.41146	1.050058
N	1.137802	-2.08744	1.45011
N	-2.40944	-3.07713	-1.56274
O	-3.59562	-3.32537	-1.46959
O	4.359794	-1.81902	0.332562
O	-1.54271	-3.76956	-2.06396
O	1.938209	-3.33232	-0.91807
N	-3.57403	1.935425	0.052478
C	-0.70438	-0.20699	-0.48069
C	0.840668	1.895931	-0.53076
C	2.211934	2.023817	-0.21063
C	-1.95914	-1.78997	-0.99876
O	-3.88316	2.932537	0.670575
C	0.510111	0.579753	-0.2614
C	2.035352	-1.3502	0.423258
N	-3.16082	0.491253	2.063128
C	-2.50896	1.08797	0.783667
H	-1.73599	1.769888	1.113179
O	-2.34552	0.120048	2.882738
O	-4.36345	0.438312	2.118254
6			

N	-1.95898	0.556102	0.083605
N	0.897159	-0.14363	-0.07612
O	-0.56022	1.145805	2.241078
N	2.081854	-0.81417	0.11276
O	2.721729	-3.01067	0.691807
N	-3.31188	0.576888	-0.02412
N	-0.3726	1.967011	1.372613
N	0.503181	-2.26079	0.472798
H	-0.03585	-3.0924	0.692815
O	-0.73632	1.277428	-2.12168
N	-0.55199	2.104334	-1.25884
O	-2.69192	3.227131	1.380536
N	-5.10719	-1.00409	-0.10611
O	-1.83322	-3.68186	0.452091
N	-2.64535	-2.99152	-0.16255
C	-0.02283	-1.03762	0.150922
O	-2.78735	3.419183	-0.78818
O	-5.81127	-0.36854	-0.86127
O	0.060011	3.136095	-1.31236
N	3.282483	1.295119	-0.21734
O	0.373925	2.908897	1.373542
N	-2.38609	2.956993	0.246512
C	-1.4445	-0.73195	0.085989
C	-2.56492	-1.54781	-0.02064
N	4.314917	-0.64497	1.080557
O	3.797871	-0.56538	2.16735
C	-3.6715	-0.67171	-0.09168
C	3.339995	-0.2569	-0.1154
C	-1.2979	1.811993	0.105494
C	1.886516	-2.18536	0.462701
O	3.741395	1.92163	0.705293
N	3.995368	-0.7344	-1.47233
O	-5.44299	-1.88115	0.671017
O	-3.52837	-3.41221	-0.87997

O	3.457238	-1.67361	-2.01038
O	2.773489	1.703471	-1.23525
O	5.443036	-0.94572	0.790771
O	4.960515	-0.10446	-1.82904
7			
N	2.354273	1.899333	-0.2429
N	2.440001	-0.28087	0.026683
O	-3.0016	3.561513	0.586674
N	-0.61017	-0.17748	-0.12968
O	4.577227	3.452608	-0.61617
N	3.734315	0.116478	-0.10901
O	-4.18037	1.846005	-0.07071
N	-1.88376	0.255109	-0.03847
N	4.797651	2.270456	-0.4394
O	1.053515	-1.05525	2.158535
O	-2.38452	-2.60064	-1.39391
O	0.287444	3.701334	1.443812
O	1.412534	-1.48408	-2.0653
O	5.879343	1.714861	-0.39646
O	-1.96582	-2.60337	0.745823
N	-0.14876	3.440799	0.340795
N	-3.13489	2.409982	0.227808
O	-3.18587	0.175472	-2.32462
N	-2.36768	-2.12677	-0.28758
N	-3.80411	-0.40437	-1.46384
C	1.614957	0.832004	-0.06973
O	-0.22928	4.169096	-0.62545
C	3.610646	1.409614	-0.25723
C	-0.62305	2.058479	0.157494
O	-4.92227	-0.83652	-1.4853
O	-4.69504	-1.57647	1.139063
N	1.408458	-2.0039	1.4942
C	0.162649	0.89026	-0.00831
C	-1.92022	1.625628	0.130359

O	4.055193	-2.46736	1.290514
O	-3.55232	0.055717	2.020965
N	-3.8438	-0.72584	1.145403
N	1.358562	-2.20404	-1.09625
N	3.517616	-2.46294	0.213421
C	-2.95299	-0.67341	-0.14829
C	2.161225	-1.661	0.161966
O	1.286467	-3.17811	1.72722
O	3.862828	-2.96889	-0.82328
O	0.822134	-3.27232	-0.97213

Table S3 Molecular Simulations of **5-7**.

Compound	**5**	**6**	**7**
BDE of $C-NO_2$(kJ mol^{-1})	199.65	188.84	193.79
longest C-NO_2 bonds(Å)	C7-N6:1.544(6)	C7-N11:1.551(8)	C7-N3:1.562(8)

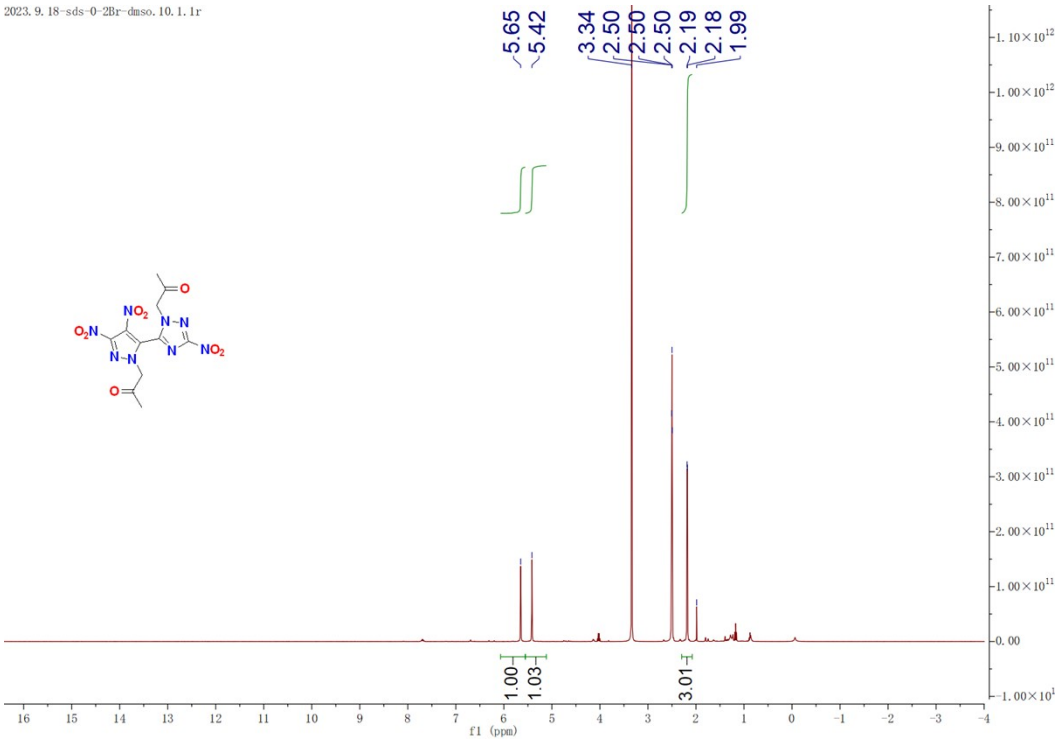
3. Crystallographic data

	3	**4**	**7（100K）**
CCDC No.	2383267	2383268	2383263
Empirical Formula	$C_{11}H_{10}N_8O_8$	$C_{11}H_{10}N_8O_8$	$C_7N_{14}O_{18}$
Formula Weight	382.27	382.27	568.21
Temperature (K)	100	300	100
Crystal System	monoclinic	Triclinic	monoclinic
Space group	*P2₁/c*	*P-1*	*P2₁/c*
Unit cell dimensions			
a (Å)	9.4589(4)	4.7235(13)	7.2676(5)
b (Å)	19.5048(7)	9.109(3)	27.6444(17)
c (Å)	8.4757(3)	19.068(6)	9.5690(6)
α (°)	90	91.415(15)	90
β (°)	92.997(2)	93.630(14)	92.166(2)
γ (°)	90	98.321(14)	90
Volume (Å^3)	1561.58(10)	809.7(4)	1921.1(2)
Z	4	2	4
Density (g cm^{-3}) (calculated)	1.626	1.568	1.965
F(000)	784.0	392	1136.0
Crystal size (mm^3)	0.09 x 0.03 x 0.01	0.120 x 0.100 x 0.08	0.12 x 0.08 x 0.05
Goodness-of-fit on F^2	1.038	1.087	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0462, wR_2 = 0.1221	R_1 = 0.1236, wR_2 = 0.2408	R_1 = 0.0539, wR_2 = 0.1058
Final R indexes [all data]	R_1 = 0.0560, wR_2 = 0.1292	R_1 = 0.2448, wR_2 = 0.2736	R_1 = 0.1046, wR_2 = 0.1301

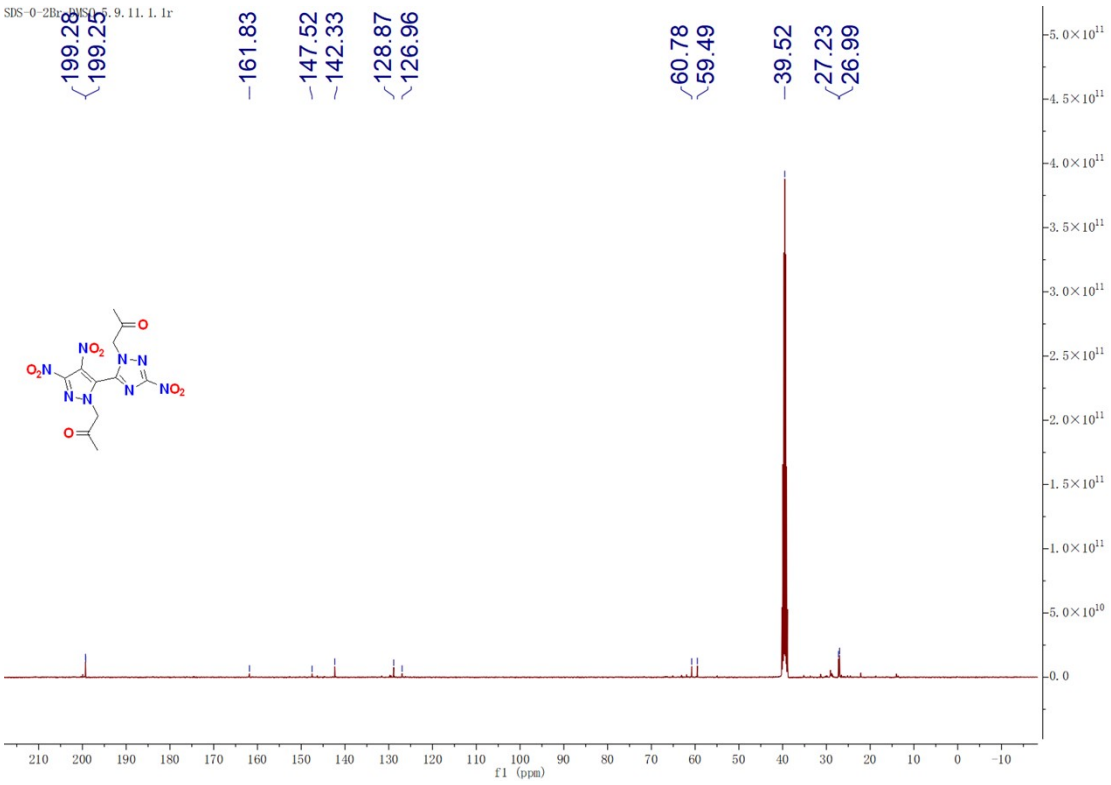
	5	**6**	**7**
CCDC No.	2345886	2345888	2345923
Empirical Formula	$C_7HN_{13}O_{16}$	$C_7HN_{13}O_{17}$	$C_7N_{14}O_{18}$
Formula Weight	523.21	539.21	568.21
Temperature (K)	296	296	296
Crystal System	monoclinic	monoclinic	monoclinic
Space group	*P2₁/n*	*P2₁/n*	*P2₁/c*
Unit cell dimensions			
a (Å)	11.024(4)	16.353(5)	7.373(6)
b (Å)	8.252(3)	6.658(2)	28.46(3)
c (Å)	20.514(9)	17.976(6)	9.683(7)
α (°)	90	90	90
β (°)	105.522(14)	104.968(10)	92.772(19)
γ (°)	90	90	90

Volume ($Å^3$)	1798.1(13)	1890.6(11)	2030(3)
Z	4	4	4
Density (g cm^{-3}) (calculated)	1.933	1.894	1.860
F(000)	1048.0	1080.0	1136.0
Crystal size (mm^3)	0.08 x 0.05 x 0.05	0.12 x 0.06 x 0.05	0.12 x 0.05 x 0.03
Goodness-of-fit on F^2	1.011	1.055	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0650, wR_2 = 0.1411	R_1 = 0.0870, wR_2 = 0.1527	R_1 = 0.0740, wR_2 = 0.1662
Final R indexes [all data]	R_1 = 0.1408, wR_2 = 0.1848	R_1 = 0.1978, wR_2 = 0.2092	R_1 = 0.1596, wR_2 = 0.2114

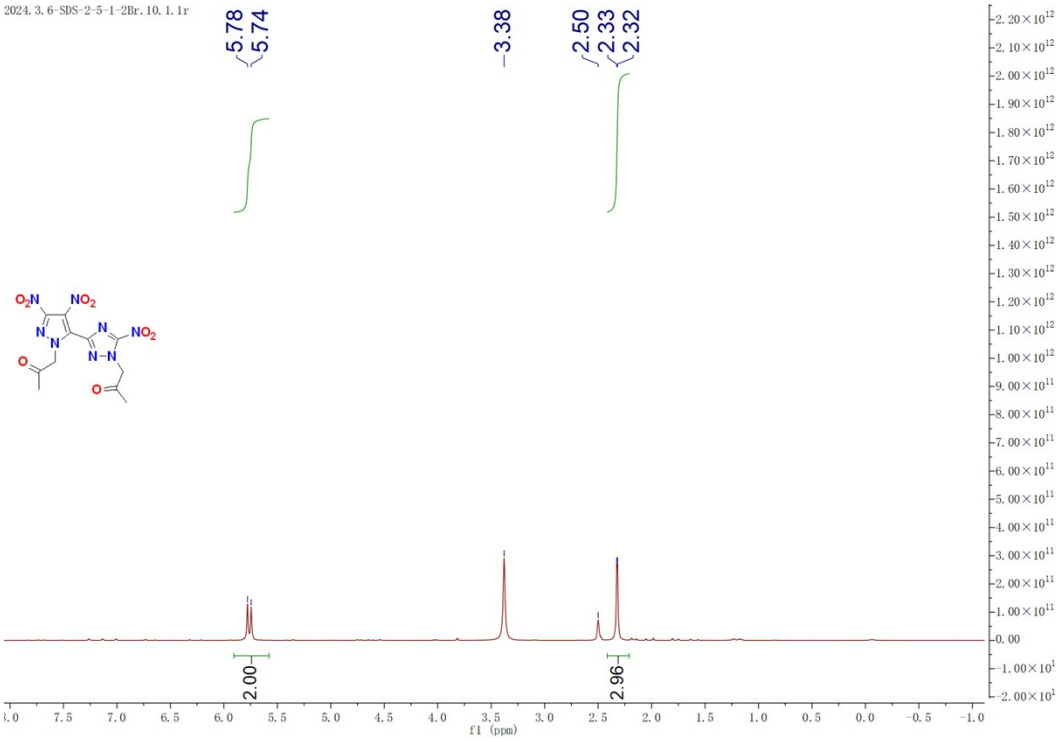
4. ^{1}H and ^{13}C NMR spectra



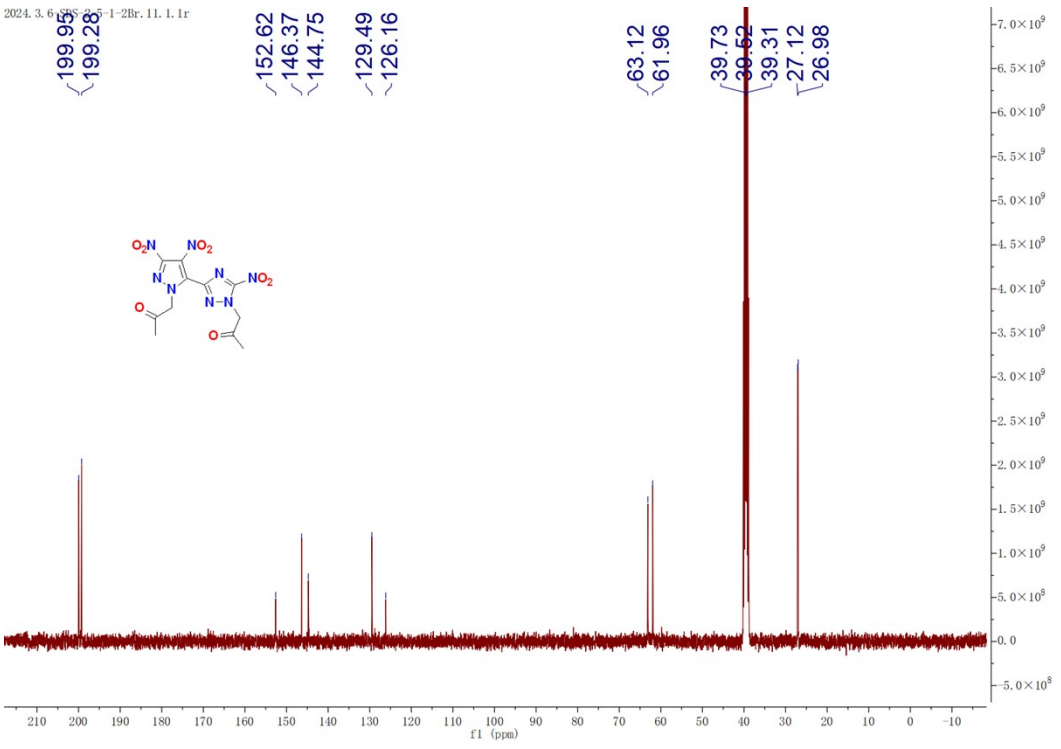
^{1}H NMR spectrum of **2** in d_6-DMSO.



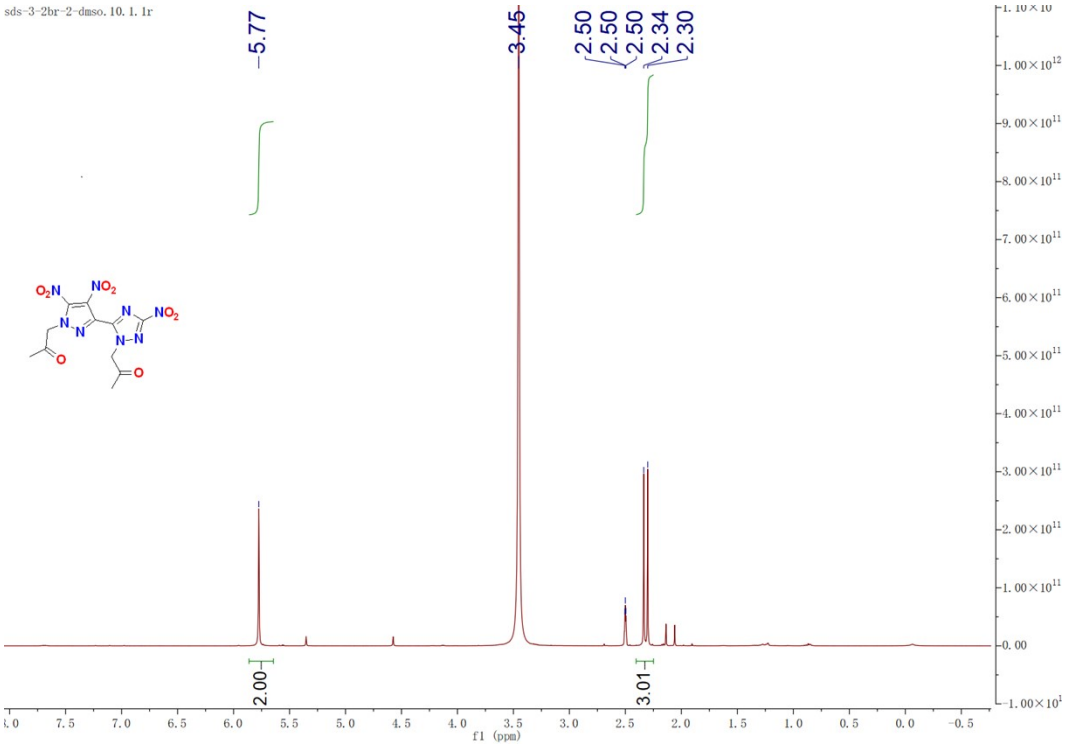
^{13}C NMR spectrum of **2** in d_6-DMSO.



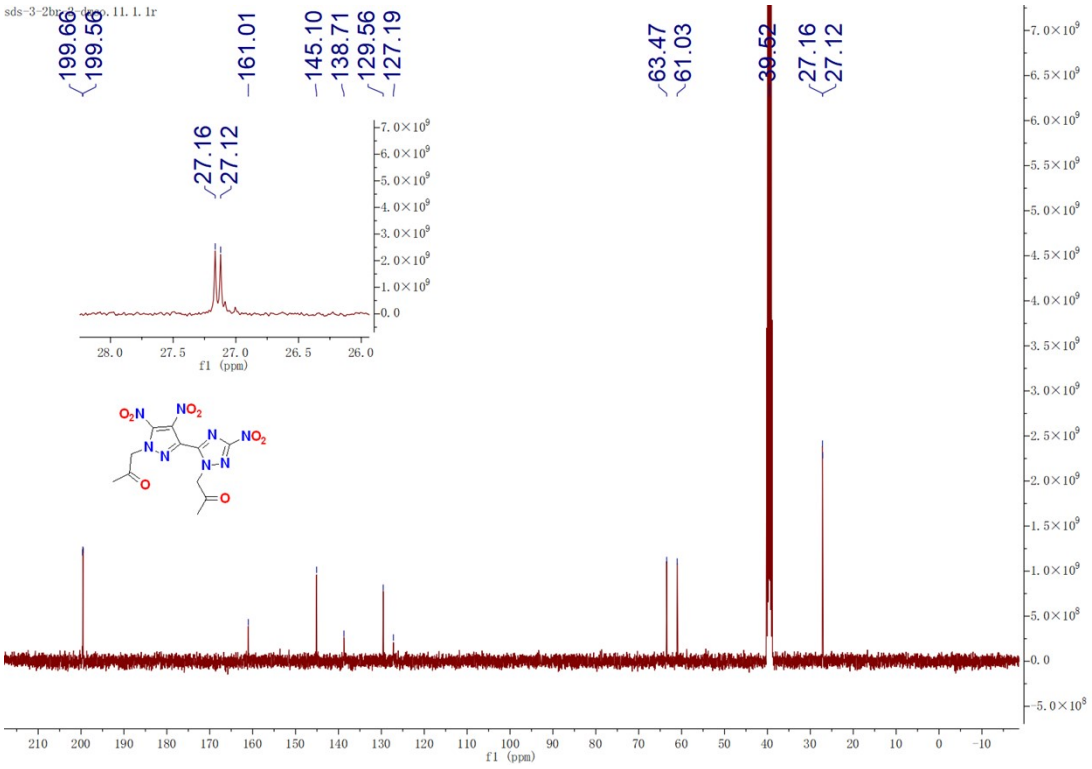
^{1}H NMR spectrum of **3** in d_6-DMSO.



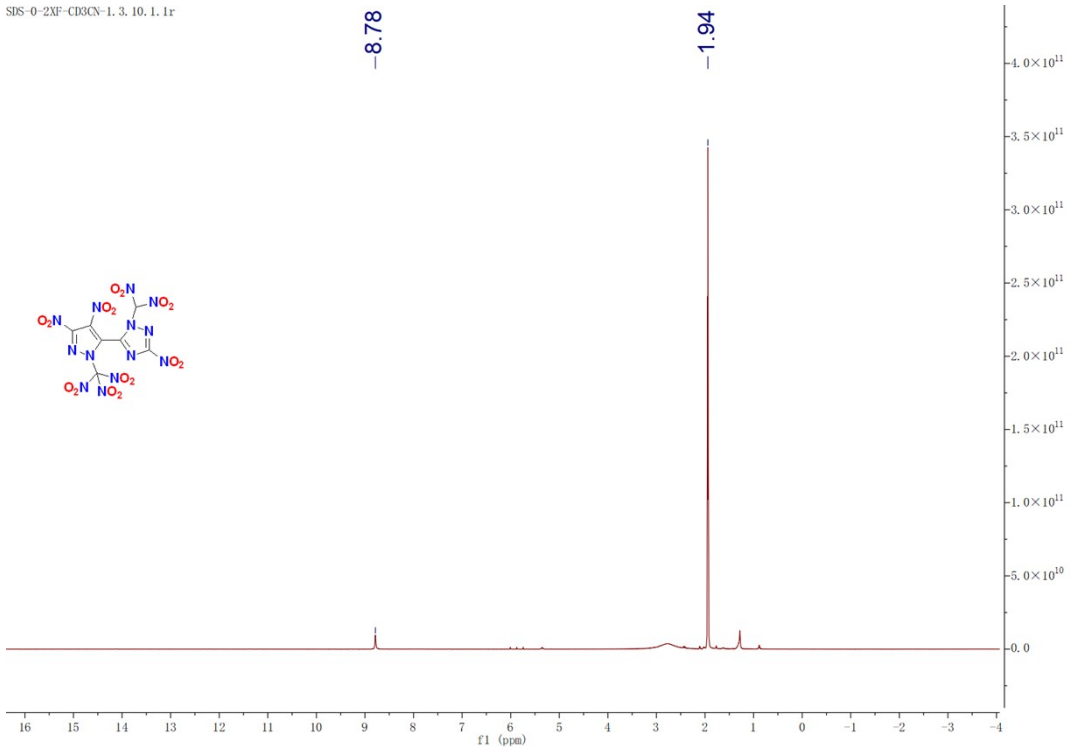
^{13}C NMR spectrum of **3** in d_6-DMSO.



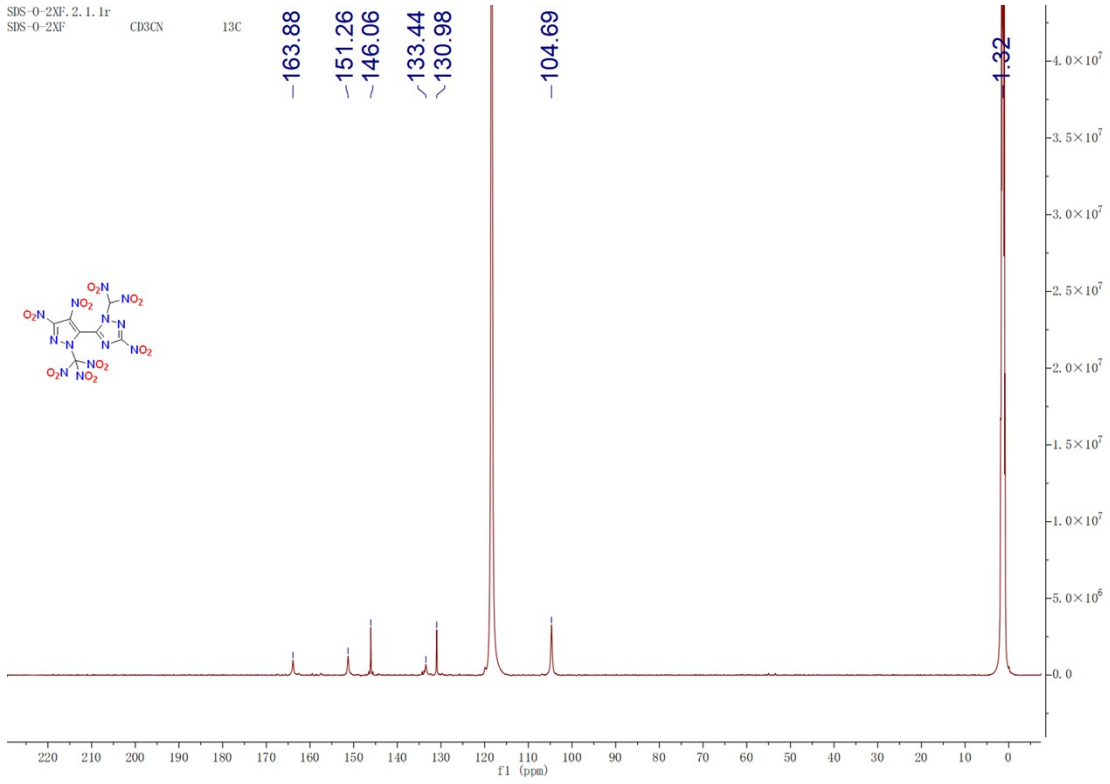
^{1}H NMR spectrum of **4** in d_6-DMSO.



^{13}C NMR spectrum of **4** in d_6-DMSO.



^{1}H NMR spectrum of **5** in d_3-CD_3CN.



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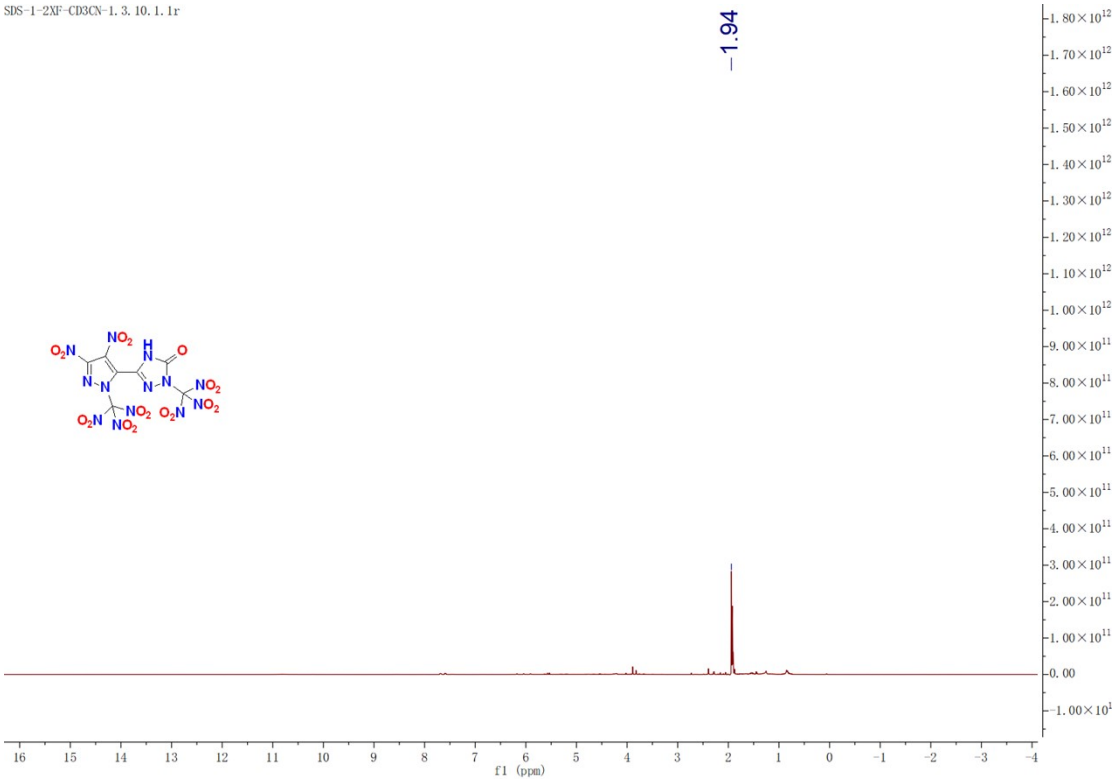
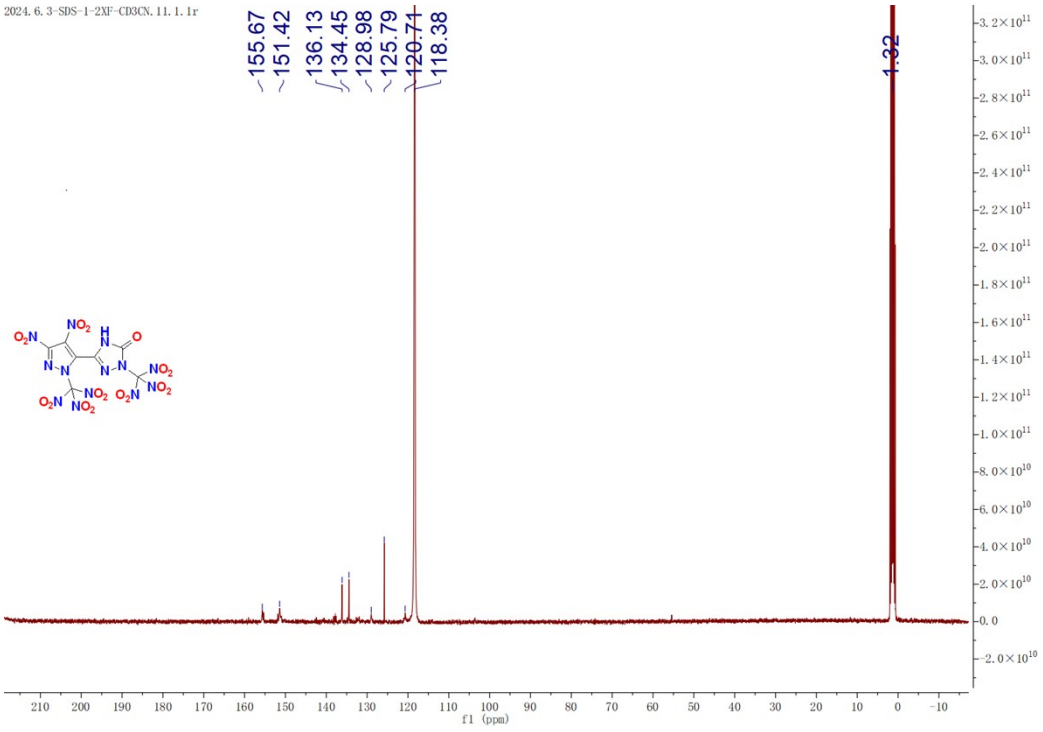


^{1}H NMR spectrum of **6** in d_3-CD_3CN.



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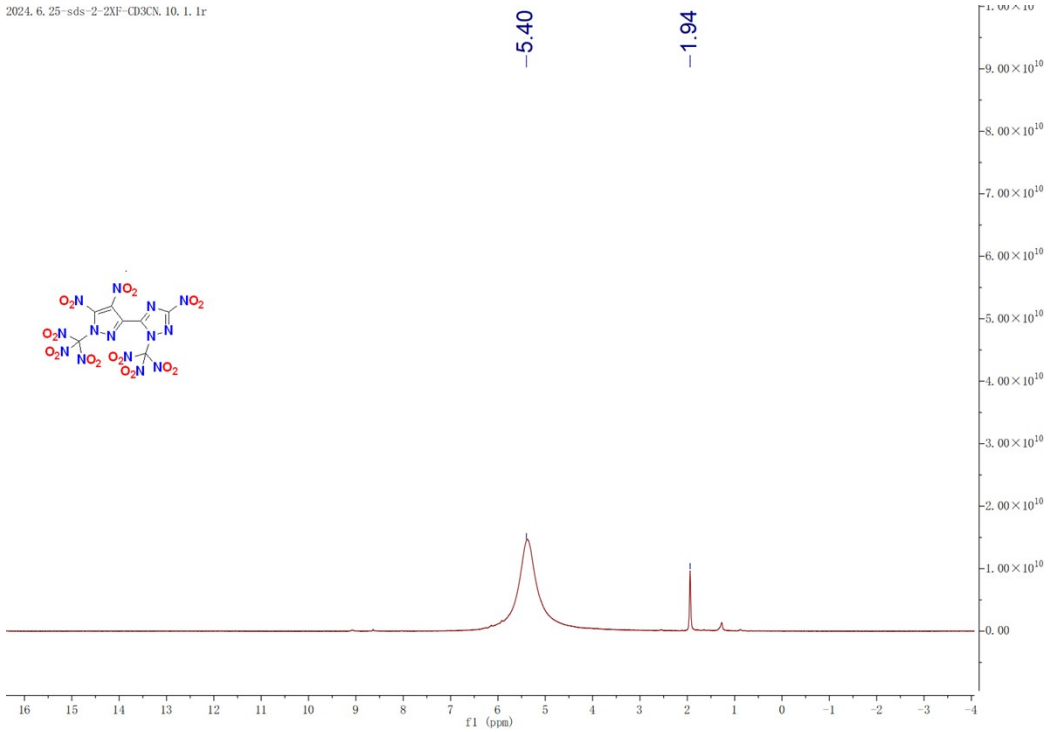
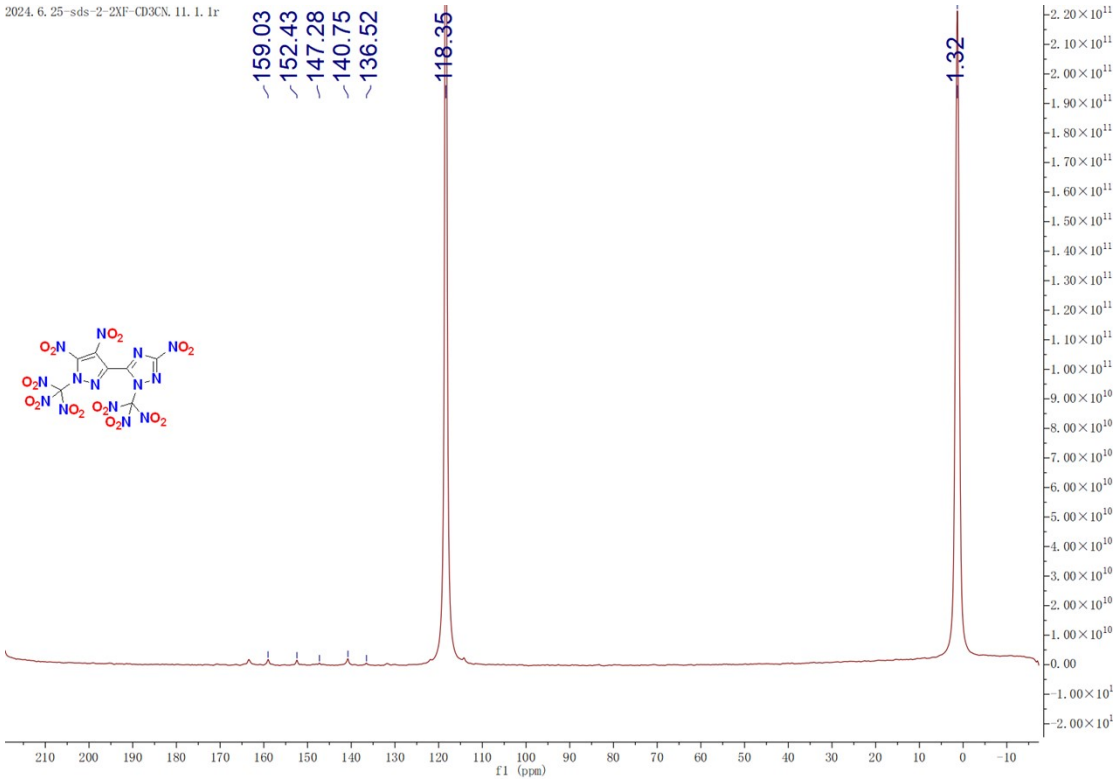
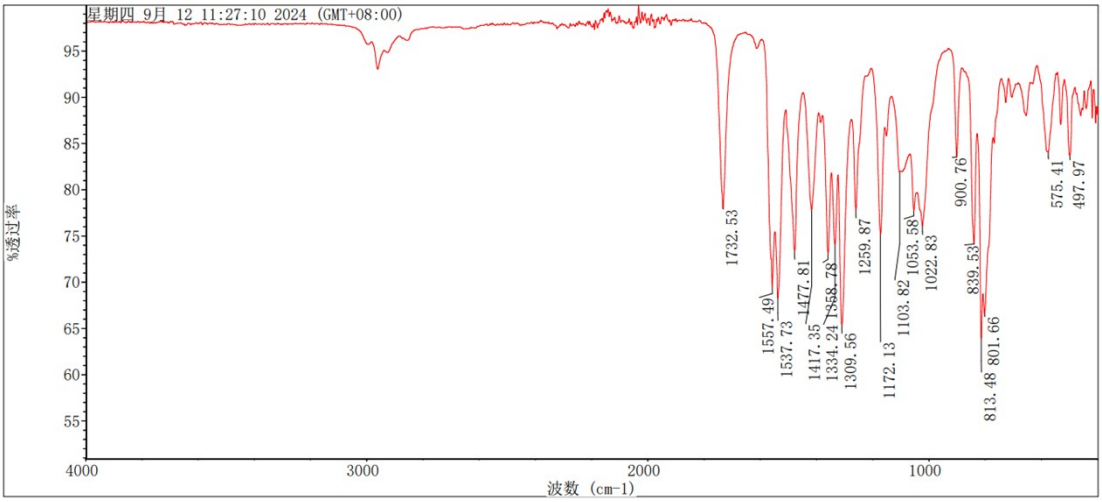


^{1}H NMR spectrum of **7** in d_3-CD_3CN.

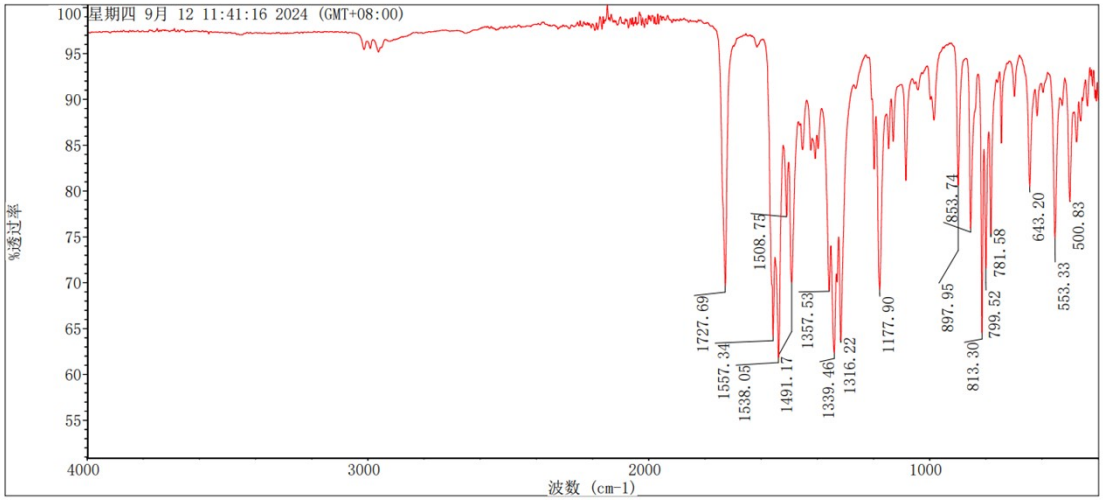


^{13}C NMR spectrum of **7** in d_3-CD_3CN.

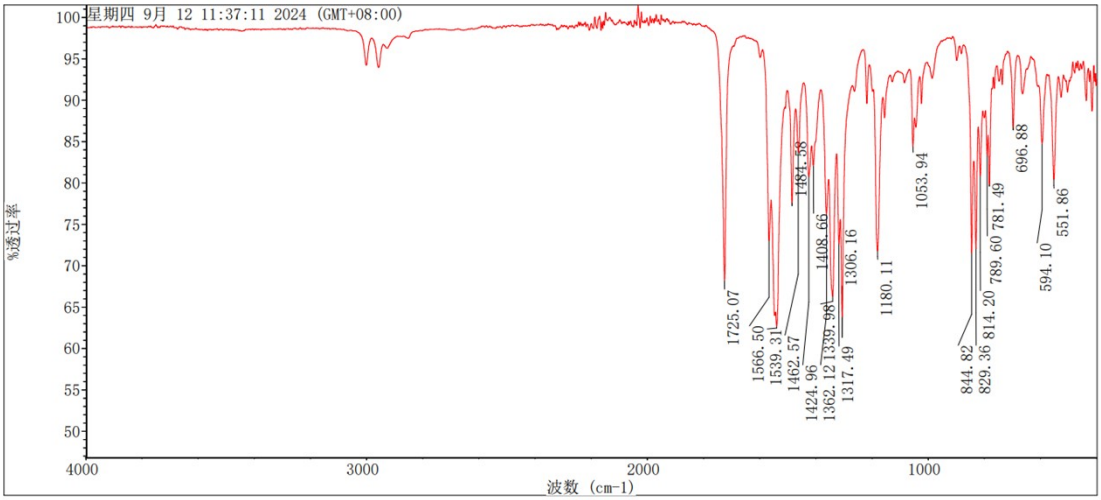
5. IR spectra



IR spectrum of compound **2**



IR spectrum of compound **3**



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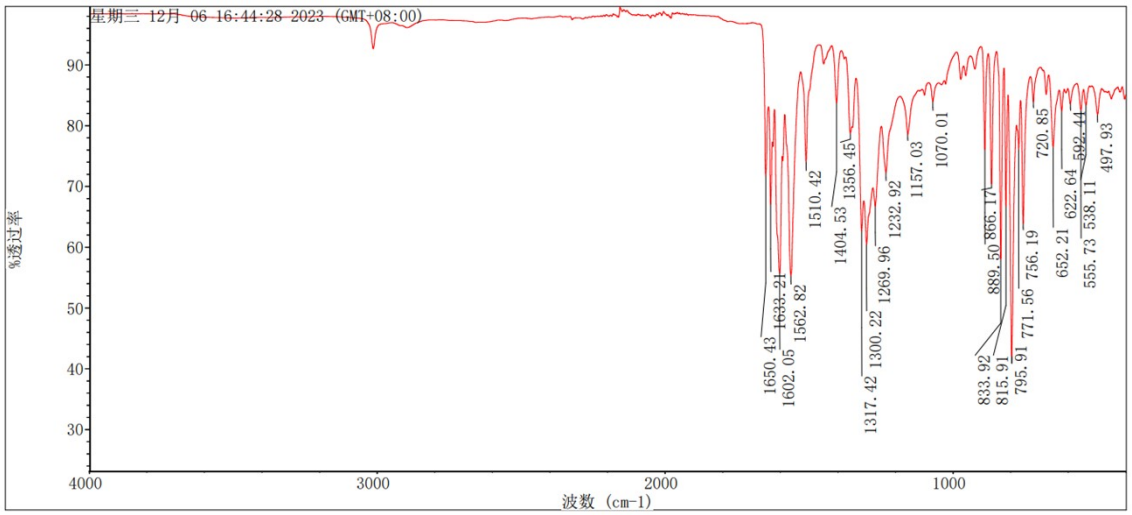
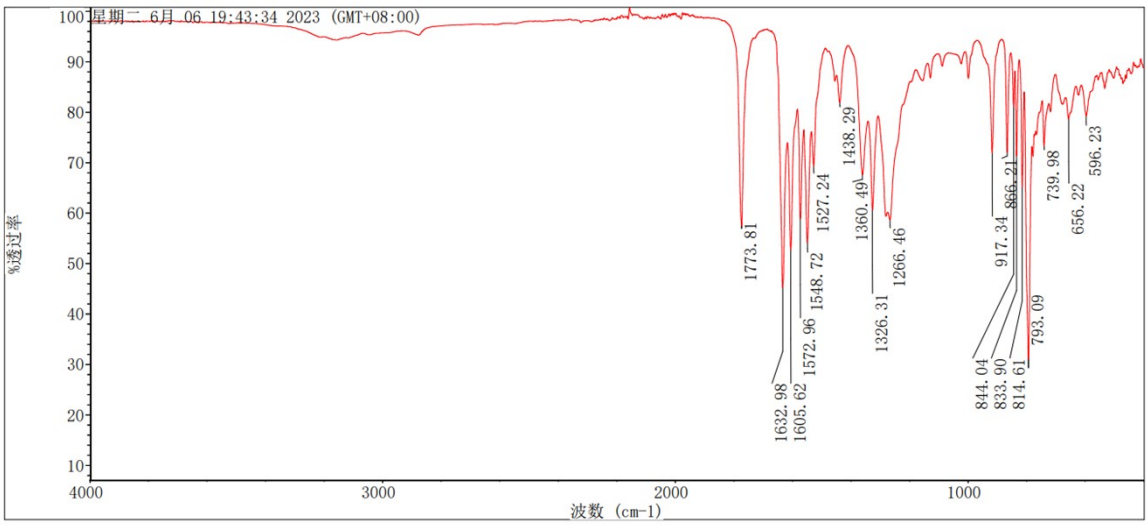
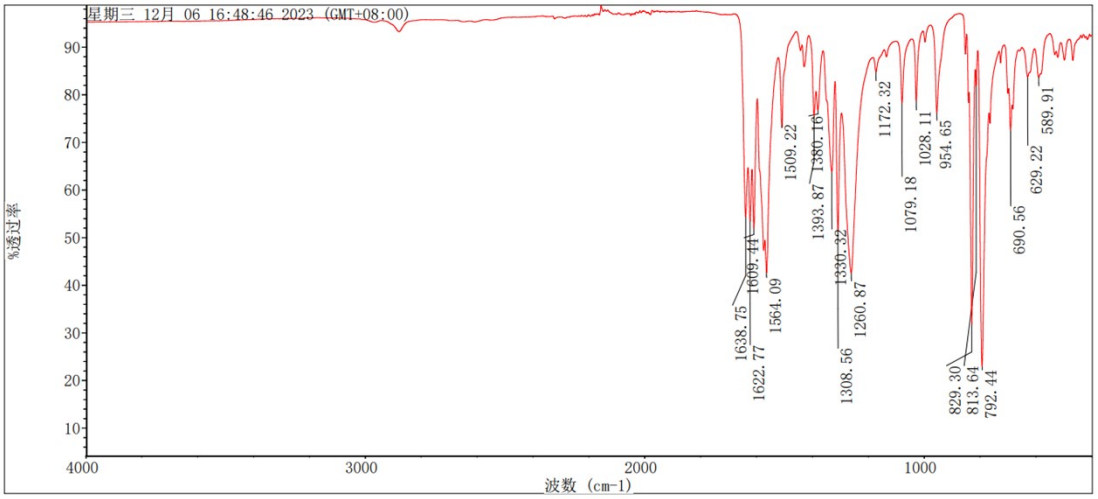


IR spectrum of compound **5**

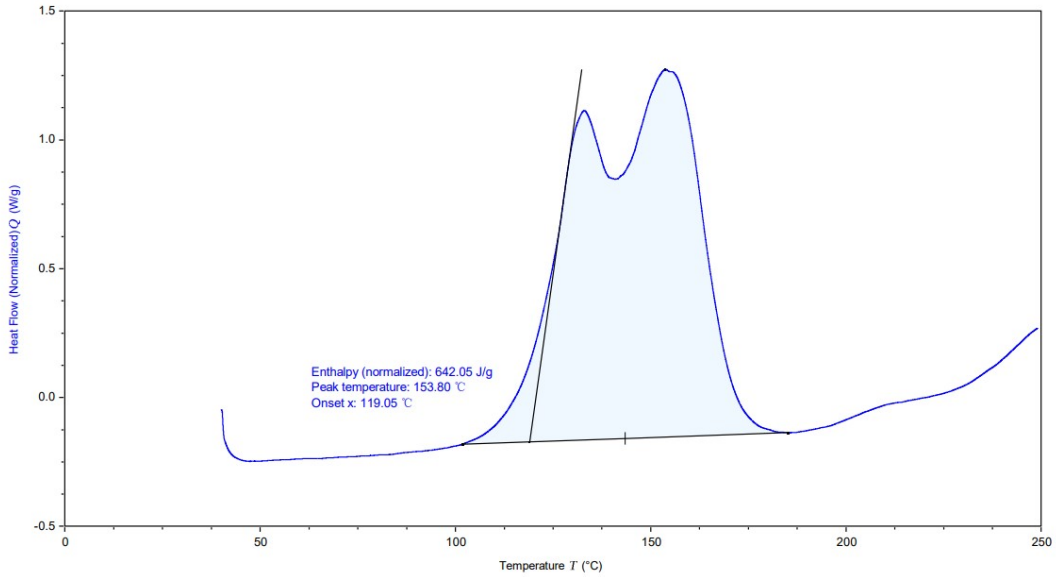


IR spectrum of compound **6**

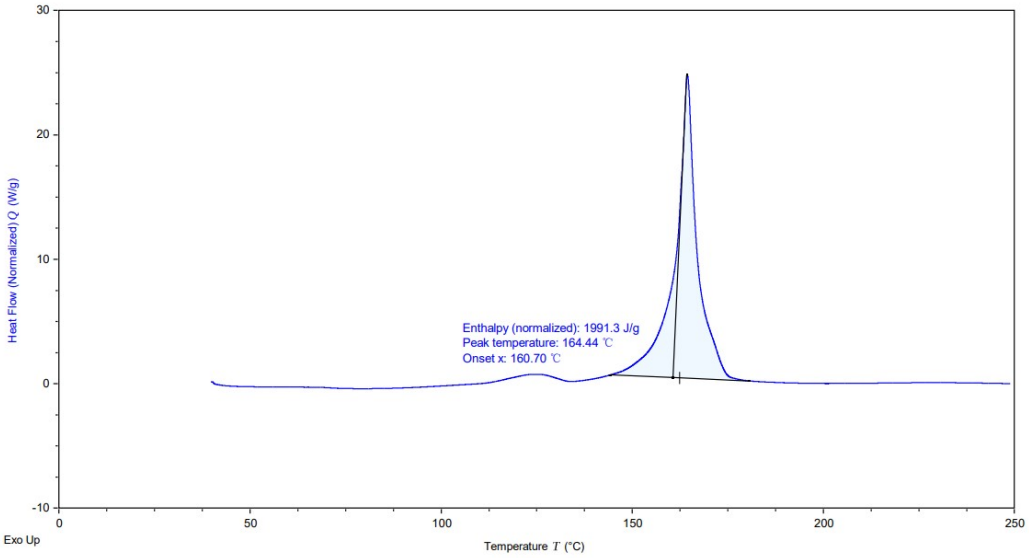


IR spectrum of compound **7**

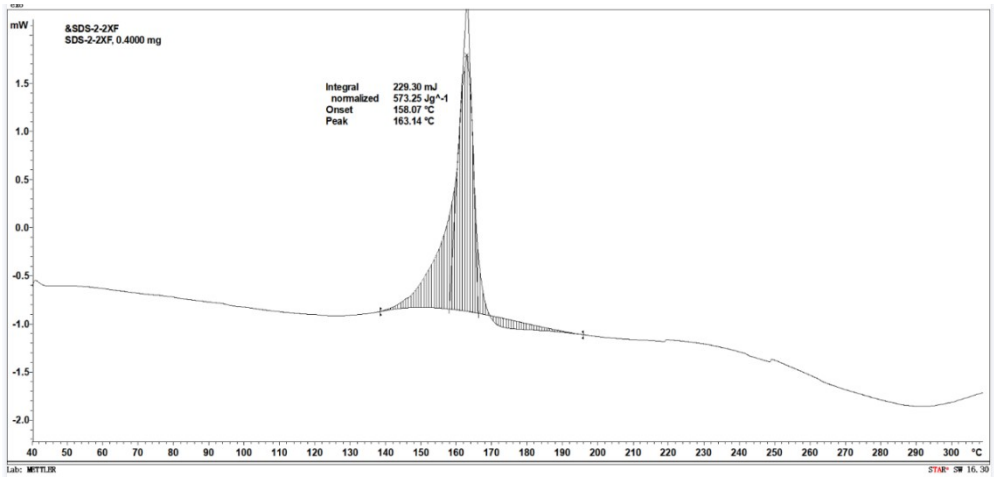
6. DSC curve of 5, 6 and 7



DSC curve of compound **5** at 5 °C min^{-1}



DSC curve of compound **6** at 5 °C min^{-1}



DSC curve of compound **7** at 5 °C min^{-1}

References

1 (a) A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 1993, **98**, 5648-5652; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, *J. Phys. Chem.* 1994, **98**, 11623-11627.

2 M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, Empirical Correlations between Thermodynamic Properties and Intermolecular Forces, *J. Am. Chem. Soc.* 1995, **117**, 5013-5015.