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Supporting Information

Synthesis, Characterization and Properties of Heat-resistant Explosive Materials: Polynitroaromatic Substituted Difurazano[3,4-*b*:3'4'-*e*]pyrazines

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1. X-ray crystallogray

Crystal of **2** was obtained from the solution in MeCN at -18°C. Bond lengths, bond angles and dihedral angles of the data collection and refinement are given in Table S1 and S2. The CIF file has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication 955441.

Table S1. Bond lengths[Å] for the structure of **2**.

N(1)-O(2)	1.210(2)	C(1)-C(2)	1.382(2)
N(1)-O(1)	1.2147(19)	C(1)-C(6)	1.387(2)
N(1)-C(3)	1.4691(19)	C(1)-H(1)	0.9300
N(2)-O(3)	1.2187(16)	C(2)-C(3)	1.379(2)
N(2)-O(4)	1.2208(17)	C(2)-H(2A)	0.9300
N(2)-C(5)	1.4732(18)	C(3)-C(4)	1.375(2)
N(3)-C(7)	1.3881(18)	C(4)-C(5)	1.381(2)
N(3)-C(8)	1.3910(18)	C(4)-H(4)	0.9300
N(3)-C(6)	1.4285(18)	C(5)-C(6)	1.398(2)
N(4)-C(7)#1	1.2955(19)	C(7)-N(4)#1	1.2956(19)
N(4)-O(5)	1.4040(16)	C(7)-C(8)#1	1.4282(19)
N(5)-C(8)	1.2904(18)	C(8)-C(7)#1	1.4282(19)
N(5)-O(5)	1.3991(17)		

Table S2. Bond angles [deg] and dihedral angles [deg] for the structure of **2**.

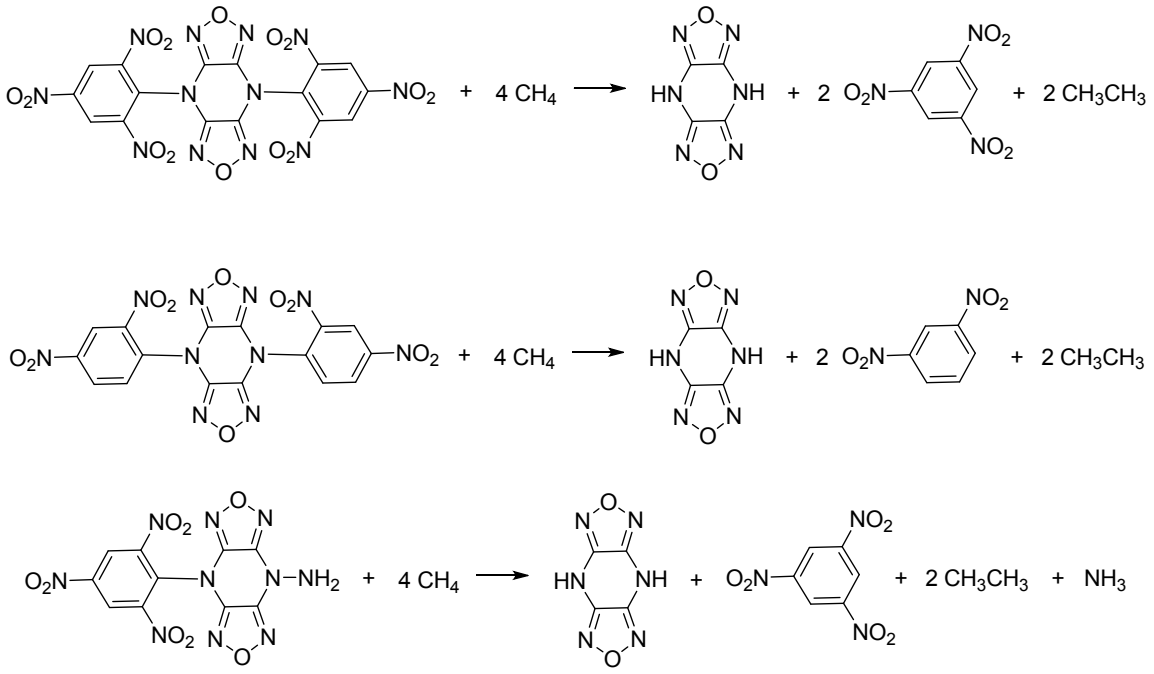
O(2)-N(1)-O(1)	123.98(15)	C(8)-N(5)-O(5)-N(4)	0.07(16)
O(2)-N(1)-C(3)	117.89(14)	C(7)#1-N(4)-O(5)-N(5)	0.30(16)
O(1)-N(1)-C(3)	118.11(15)	C(6)-C(1)-C(2)-C(3)	-1.5(2)
O(3)-N(2)-O(4)	124.10(14)	C(1)-C(2)-C(3)-C(4)	1.7(2)
O(3)-N(2)-C(5)	118.22(12)	C(1)-C(2)-C(3)-N(1)	-179.79(14)
O(4)-N(2)-C(5)	117.52(13)	O(2)-N(1)-C(3)-C(4)	-14.7(2)
C(7)-N(3)-C(8)	113.74(11)	O(1)-N(1)-C(3)-C(4)	166.46(15)
C(7)-N(3)-C(6)	122.84(11)	O(2)-N(1)-C(3)-C(2)	166.77(18)
C(8)-N(3)-C(6)	122.55(11)	O(1)-N(1)-C(3)-C(2)	-12.1(2)
C(7)#1-N(4)-O(5)	104.40(11)	C(2)-C(3)-C(4)-C(5)	0.5(2)
C(8)-N(5)-O(5)	104.62(11)	N(1)-C(3)-C(4)-C(5)	-177.99(13)
N(5)-O(5)-N(4)	111.06(10)	C(3)-C(4)-C(5)-C(6)	-3.0(2)
C(2)-C(1)-C(6)	121.05(14)	C(3)-C(4)-C(5)-N(2)	172.17(12)
C(2)-C(1)-H(1)	119.5	O(3)-N(2)-C(5)-C(4)	28.78(19)
C(6)-C(1)-H(1)	119.5	O(4)-N(2)-C(5)-C(4)	-146.74(14)
C(3)-C(2)-C(1)	118.39(14)	O(3)-N(2)-C(5)-C(6)	-156.12(14)
C(3)-C(2)-H(2A)	120.8	O(4)-N(2)-C(5)-C(6)	28.4(2)
C(1)-C(2)-H(2A)	120.8	C(2)-C(1)-C(6)-C(5)	-0.8(2)
C(4)-C(3)-C(2)	122.70(13)	C(2)-C(1)-C(6)-N(3)	176.70(13)
C(4)-C(3)-N(1)	117.87(14)	C(4)-C(5)-C(6)-C(1)	3.1(2)
C(2)-C(3)-N(1)	119.42(14)	N(2)-C(5)-C(6)-C(1)	-171.71(13)
C(3)-C(4)-C(5)	117.91(13)	C(4)-C(5)-C(6)-N(3)	-174.27(12)
C(3)-C(4)-H(4)	121	N(2)-C(5)-C(6)-N(3)	10.9(2)
C(5)-C(4)-H(4)	121	C(7)-N(3)-C(6)-C(1)	47.69(19)
C(4)-C(5)-C(6)	121.35(13)	C(8)-N(3)-C(6)-C(1)	-121.01(15)
C(4)-C(5)-N(2)	116.06(12)	C(7)-N(3)-C(6)-C(5)	-134.92(14)
C(6)-C(5)-N(2)	122.40(12)	C(8)-N(3)-C(6)-C(5)	56.38(19)
C(1)-C(6)-C(5)	118.50(13)	C(8)-N(3)-C(7)-N(4)#1	-177.97(14)
C(1)-C(6)-N(3)	118.91(13)	C(6)-N(3)-C(7)-N(4)#1	12.4(2)
C(5)-C(6)-N(3)	122.54(12)	C(8)-N(3)-C(7)-C(8)#1	0.7(2)
N(4)#1-C(7)-N(3)	127.03(13)	C(6)-N(3)-C(7)-C(8)#1	-168.87(13)

N(4)#1-C(7)-C(8)#1	109.84(12)	O(5)-N(5)-C(8)-N(3)	178.27(13)
N(3)-C(7)-C(8)#1	123.11(12)	O(5)-N(5)-C(8)-C(7)#1	-0.39(16)
N(5)-C(8)-N(3)	126.77(13)	C(7)-N(3)-C(8)-N(5)	-179.22(14)
N(5)-C(8)-C(7)#1	110.08(12)	C(6)-N(3)-C(8)-N(5)	-9.6(2)
N(3)-C(8)-C(7)#1	123.14(12)	C(7)-N(3)-C(8)-C(7)#1	-0.7(2)
		C(6)-N(3)-C(8)-C(7)#1	168.91(13)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z

2. Theoretical study

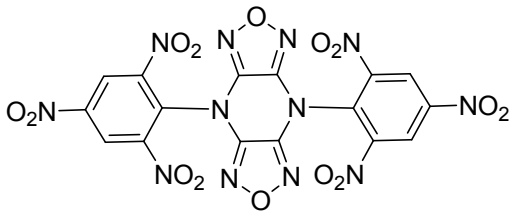
Calculations were carried out by using the Gaussian 09 (Revision B. 01) suite of programs.[1] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G**basis set, and single-point energies were calculated at the MP2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Isodesmic reactions of all compounds are given in Scheme S1.



Scheme S1

Geometry coordinates

The optimized structure of **1**



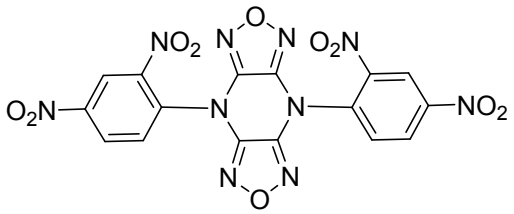
1

Table S3. Geometry coordinates of **1**.

N	7.170174	0.00043	0.000292
N	2.965435	2.467514	0.547355
N	1.473518	-0.000322	-0.000329
N	-1.145723	1.448956	-1.902593
N	1.145536	1.448535	-1.903024
O	7.728982	-1.078172	-0.176899
O	7.728664	1.079154	0.17775
O	3.531905	3.484572	0.165188
O	1.930663	2.423073	1.206016
O	-0.000123	1.92177	-2.521741
C	3.627549	-1.178801	-0.219714
C	5.017193	-1.199682	-0.190413
H	5.557515	-2.126532	-0.336981
C	5.688917	0.000244	0.000109
C	5.016842	1.200002	0.190482
H	5.556905	2.12698	0.337189
C	3.6272	1.178761	0.219476
C	2.889108	-0.000116	-0.000204
C	0.716475	-0.714342	0.920185
C	0.716393	0.713983	-0.920547
N	-7.170176	-0.000152	0.000025
N	-2.965707	-2.467574	-0.547539
N	-1.47352	0.000195	0.000209
N	1.145718	-1.449058	1.902494
N	-1.14554	-1.448639	1.902922
O	-7.728881	1.078479	0.177361
O	-7.728768	-1.078834	-0.177366
O	-3.53216	-3.48458	-0.165211
O	-1.931093	-2.423244	-1.206453
O	0.000119	-1.921859	2.521652
C	-3.627439	1.178786	0.219718
C	-5.017082	1.199783	0.190562
H	-5.557315	2.126674	0.337202
C	-5.688918	-0.000084	0.00007
C	-5.016957	-1.199888	-0.190413

H	-5.557109	-2.126816	-0.337106
C	-3.627314	-1.178763	-0.219544
C	-2.889111	0.000052	0.000125
C	-0.716479	0.714227	-0.920294
C	-0.716396	-0.714097	0.920439
N	2.966216	-2.467762	-0.5477
O	1.931641	-2.423668	-1.206671
O	3.532885	-3.484634	-0.16531
N	-2.965934	2.467668	0.547644
O	-1.931203	2.423423	1.206361
O	-3.532617	3.484616	0.165471

The optimized structure of **2**



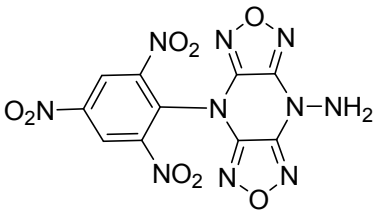
2

Table S4. Geometry coordinates of **2**.

N	7.12471	0.58755	0.224042
N	3.152223	-2.041484	-0.94033
N	1.460175	0.178799	0.107488
N	-1.024468	-1.964223	1.463896
N	1.246803	-1.685714	1.62347
O	7.593836	1.648568	0.631215
O	7.779282	-0.385672	-0.142284
O	3.84087	-3.052718	-0.863835
O	2.059038	-1.968505	-1.502878
O	0.14924	-2.418794	2.046472
C	3.48687	1.432066	0.544515
H	2.85657	2.245664	0.884649
C	4.872657	1.557159	0.578745
H	5.348729	2.463919	0.930766
C	5.650883	0.475959	0.172029
C	5.08903	-0.709872	-0.284146
H	5.710989	-1.536935	-0.601183
C	3.702459	-0.802797	-0.347606
C	2.882583	0.256909	0.086849
C	0.656844	0.981694	-0.694531

C	0.764179	-0.809487	0.792789
N	-7.124881	-0.58702	-0.223535
N	-3.151724	2.041114	0.940674
N	-1.460248	-0.179115	-0.108134
N	1.024345	1.964094	-1.464329
N	-1.246927	1.685569	-1.623901
O	-7.594228	-1.647854	-0.630898
O	-7.779224	0.38614	0.143309
O	-3.840348	3.052413	0.864831
O	-2.058352	1.967847	1.502825
O	-0.149375	2.418707	-2.046843
C	-3.487227	-1.431924	-0.545163
H	-2.857104	-2.245485	-0.885718
C	-4.87304	-1.556812	-0.579107
H	-5.349324	-2.463389	-0.931316
C	-5.651026	-0.475644	-0.171839
C	-5.088893	0.709954	0.284607
H	-5.710662	1.537003	0.602052
C	-3.702296	0.802666	0.347761
C	-2.882678	-0.257013	-0.087229
C	-0.656936	-0.981916	0.693996
C	-0.764273	0.809253	-0.79333

The optimized structure of **3**



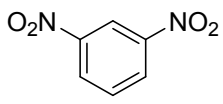
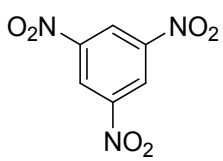
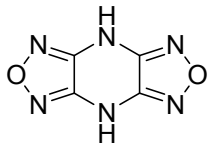
3

Table S5. Geometry coordinates of **3**.

N	4.930311	-0.010326	0.002542
N	0.731852	2.255528	1.137283
N	-0.76368	0.002199	0.0003
N	-3.36164	1.921459	-1.483581
N	-1.063129	1.895646	-1.461036
O	5.487946	-1.01556	-0.429313
O	5.491616	0.992957	0.434088
O	1.297857	3.335206	1.015602
O	-0.29992	2.052208	1.771592

O	-2.196382	2.525051	-1.946421
C	1.386238	-1.094891	-0.494707
C	2.775742	-1.124768	-0.471803
H	3.314765	-1.988848	-0.839105
C	3.450134	-0.007696	0.00284
C	2.779738	1.111561	0.47832
H	3.321759	1.973609	0.846079
C	1.39034	1.086408	0.5012
C	0.648492	-0.002464	0.002558
C	-1.523381	-0.923006	0.705816
C	-1.514001	0.935669	-0.712395
N	-1.102671	-1.890333	1.463186
N	-3.401091	-1.875407	1.447923
O	-2.255317	-2.501589	1.933237
C	-2.951028	0.946063	-0.724709
C	-2.958561	-0.908998	0.695296
N	-5.094384	0.048849	-0.039993
H	-5.445832	-0.831591	-0.411241
H	-5.445436	0.180501	0.906602
N	-3.696722	0.017406	-0.016679
N	0.723983	-2.264211	-1.126701
O	1.290246	-3.344187	-1.006622
O	-0.311961	-2.062413	-1.754606

Table S6. Ab Initio computional data.

Compound	E_0 (hartree)	H_T (hartree)	ZPE (hartree)	HOF ^{Exp} (kJ/mol)	HOF ^{Calcd} (kJ/mol)
1	-2321.235360	0.031485	0.188976	—	894.1
2	-1912.288151	0.028812	0.187609	—	782.6
3	-1532.104412	0.023060	0.185683	—	845.6
CH_4	-40.481351	0.003812	0.044793	-74.6[2]	—
CH_3CH_3	-79.767042	0.004428	0.074599	-84[2]	—
	-641.175553	0.010328	0.105242	-27[2]	—
	-845.671111	0.013008	0.107081	-37.7[2]	—
	-632.345929	0.009156	0.084082	674.1[3]	—
NH_3	-56.532613	0.003818	0.034372	-45.9[2]	—

References:

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3. ^{1}H and ^{13}C NMR spectra of compounds 1-3

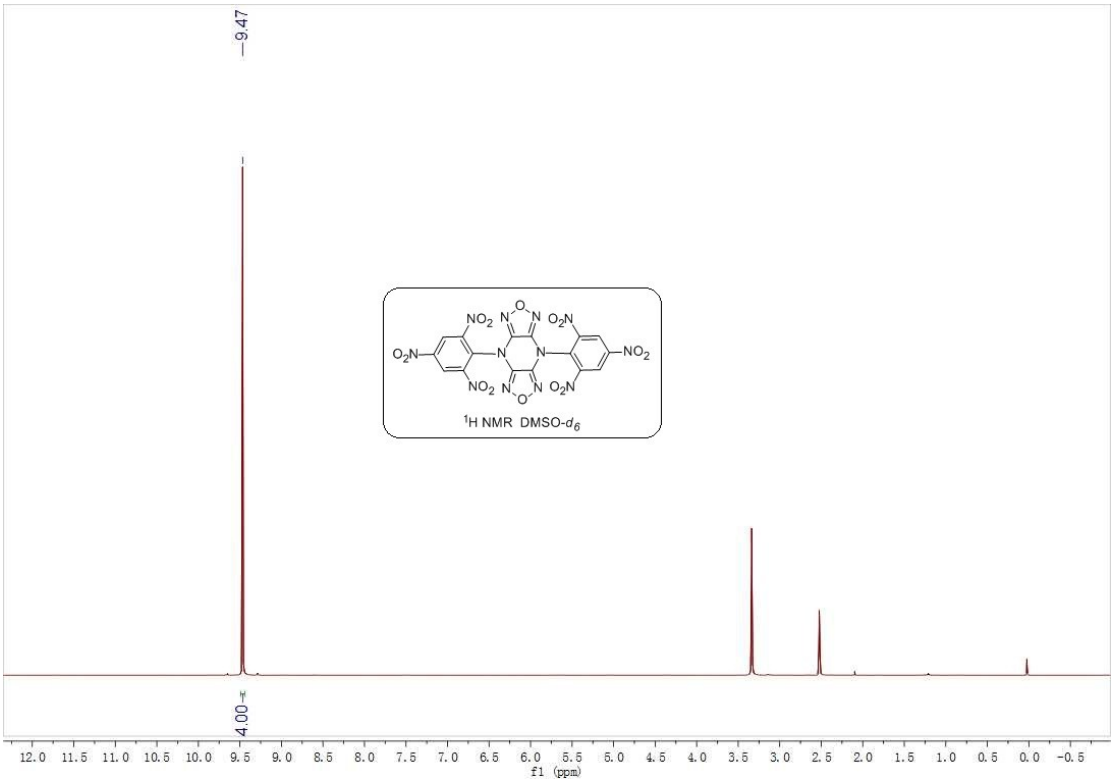

Fig. S1 ^{1}H NMR spectrum of **1** in DMSO-d_6

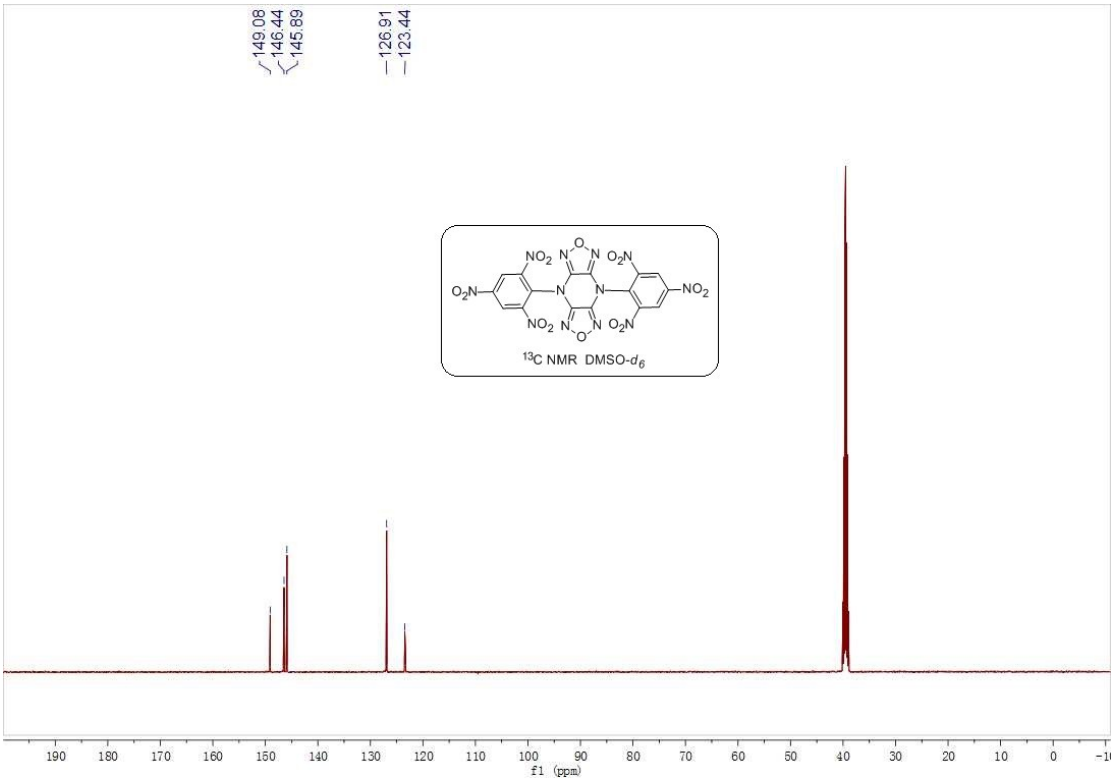

Fig. S2 ^{13}C NMR spectrum of **1** in DMSO-d_6

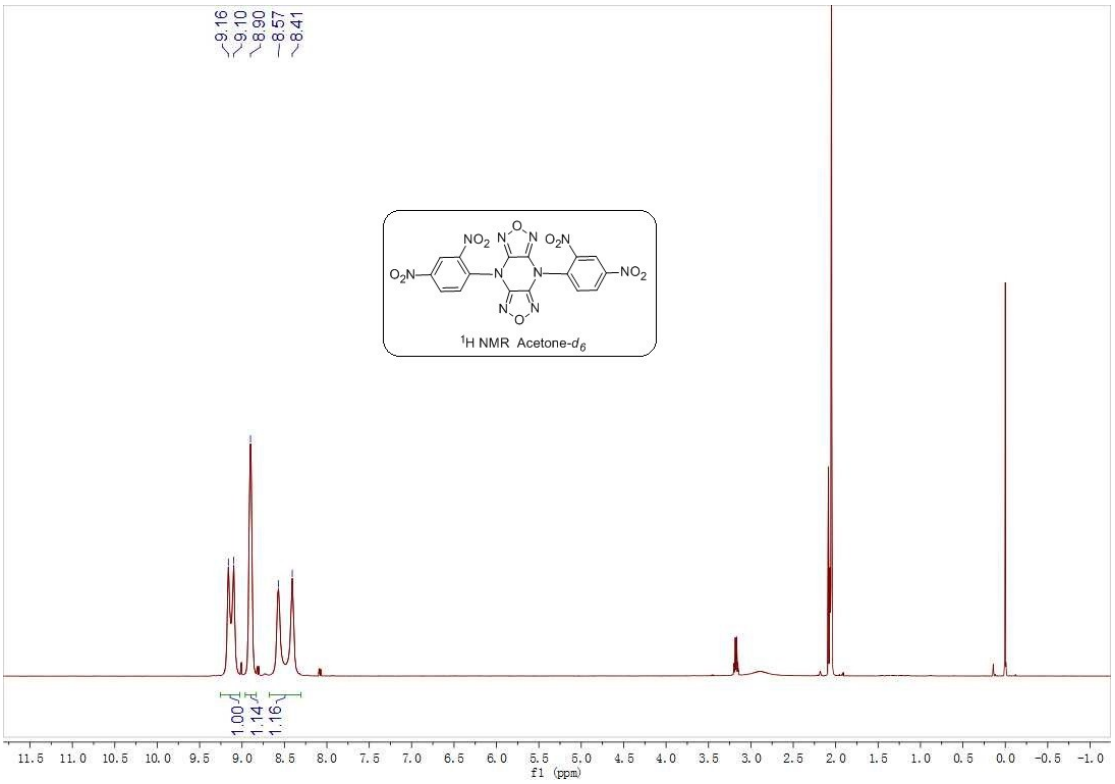

Fig. S3 ^{1}H NMR spectrum of **2** in Acetone-d_6

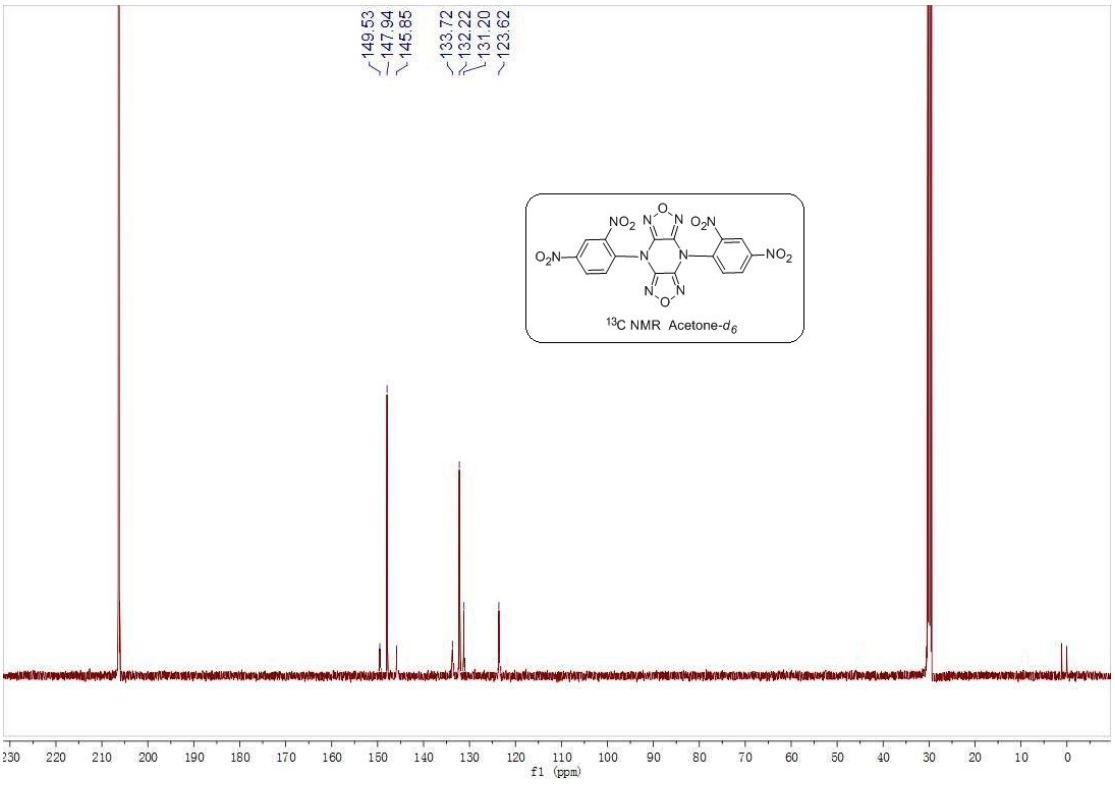

Fig. S4 ^{13}C NMR spectrum of **2** in Acetone-d_6

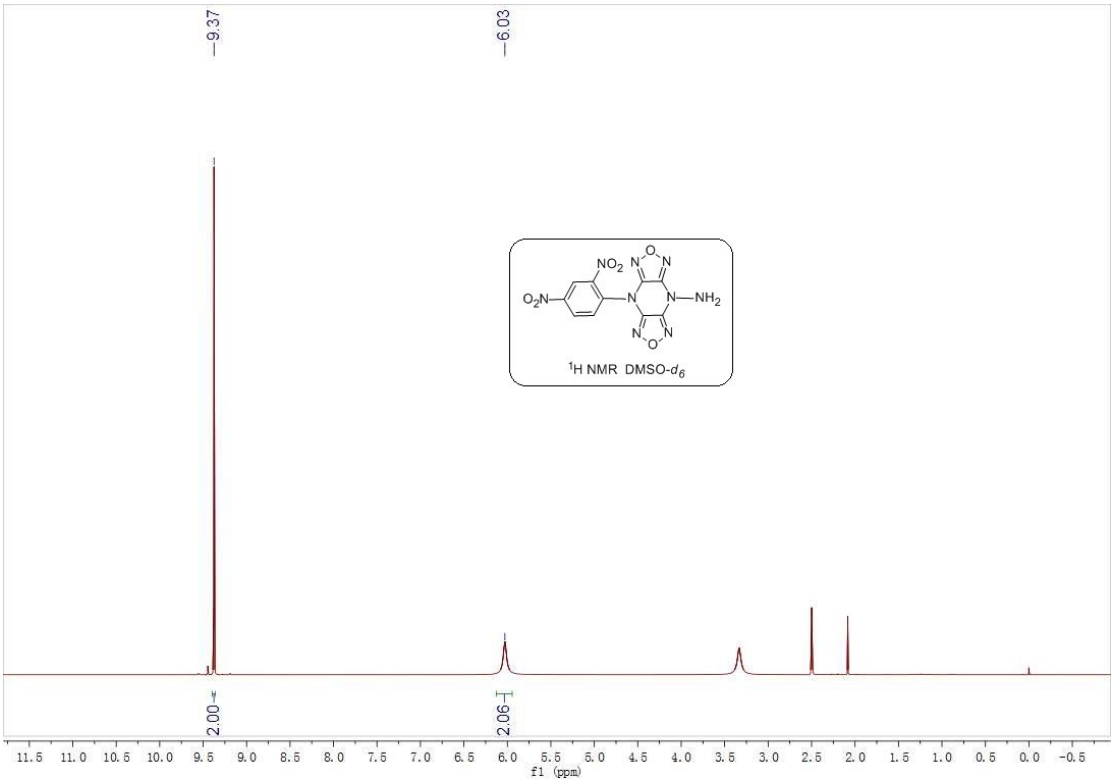

Fig. S5 ^{1}H NMR spectrum of **3** in DMSO-d_6

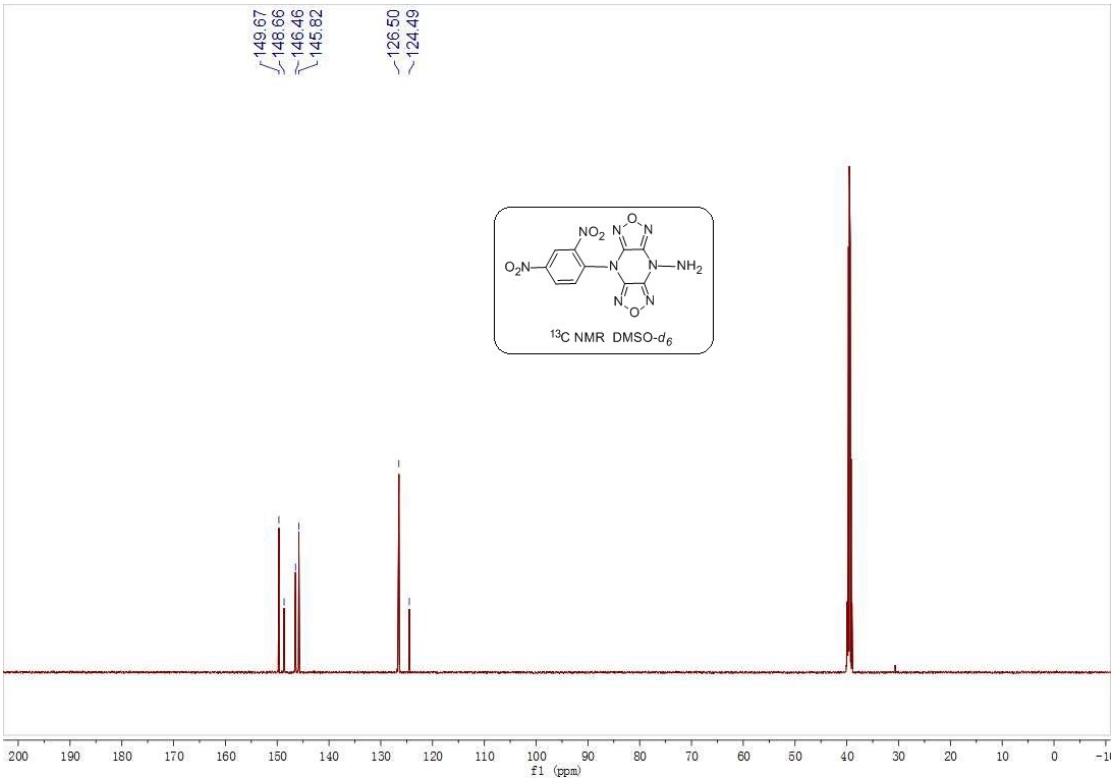

Fig. S6 ^{13}C NMR spectrum of **3** in DMSO-d_6