Supporting Information (SI)

Preparation of Novel Heat-Resistant and Insensitive Fused Ring Energetic Materials

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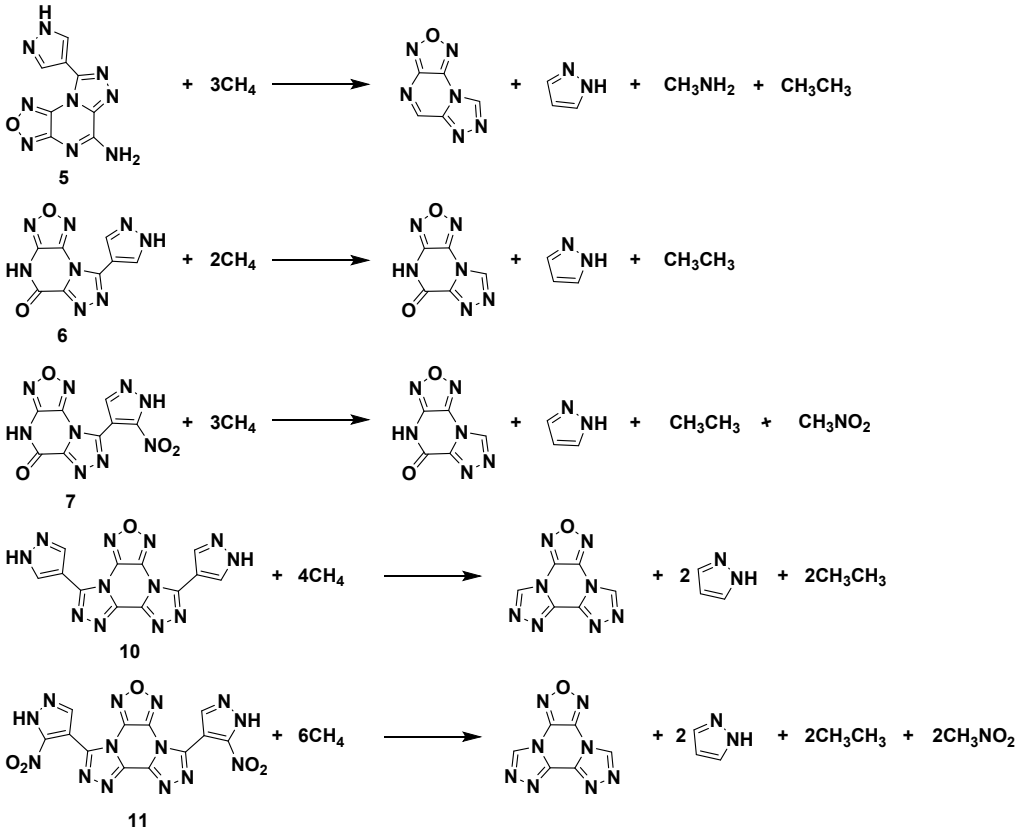
1. Computational details

1.1 Calculations of heats of formation

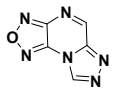
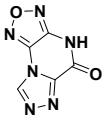
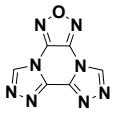
The calculation was performed by using the Gaussian 09 program package[1]. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional[2] with 6-311+G** basis set[3,4]. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heats of formation (HOF) of these compounds were computed through appropriate isodesmic reactions (Scheme S1). Atomization energies were calculated by the CBS-4M[5]. Total energy and heat of formation for the reference compounds are summarized in Table S11. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.



Scheme S1 Isodesmic and tautomeric reactions to compute the HOF.

Table S1 Total energy and heat of formation for the reference compounds

	E_0/a.u.	ZPE / kJ·mol^{-1}	ΔHT / kJ mol^{-1}	HOF / kJ mol^{-1}
5	-875.9390	389.83	37.05	737.04

6	-895.8100	359.23	36.03	552.40
7	-1100.3500	365.53	42.82	590.59
10	-1193.2200	519.63	49.14	1158.08
11	-1602.3100	532.10	62.48	1221.90
CH_4	-40.5339	112.26	10.04	-74.60
CH_3NH_2	-95.8938	160.78	11.64	-22.5
CH_3CH_3	-79.8565	187.31	11.79	-84.01
CH_3NO_2	-245.092	124.93	11.60	-80.80
	-595.4680	216.37	22.09	612.94
	-226.2600	179.20	12.57	177.40
	-670.7390	228.55	25.36	373.01
	-743.0860	258.34	27.33	788.14

References

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(3) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623.

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1.2 Calculations of the extrapolated peak temperature

Table S2 The calculated T_p and T_{p0} values of compound **6, 7, 11,** HNS and TATB at different heating rates

Compound	β / °C·min^{-1}	T_p / °C	T_{p0}/ °C
6	5	377	372
	10	385	
	15	392	
	20	394	
7	5	375	363

	10	384	
	15	390	
	20	393	
11	5	349	335
	10	359	
	15	365	
	20	367	
HNS	5	332	328
	10	340	
	15	351	
	20	364	
TATB	5	368	349
	10	379	
	15	385	
	20	389	

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i = 1,2,3.....N \qquad (1)$$

Note: 1) β is the heating rate of the sample. 2) T_{pi} is the peak temperature of the sample when the heating rate is β. 3) T_{p0} is the peak temperature of the sample when the heating rate approaches zero.

2. The experiment and crystallographic data

Experimental section

Caution! Although we experienced no explosion in handling these energetic materials, the use of small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received. ^{1}H and ^{13}C NMR spectra are recorded on a 500 MHz (Bruker AVANCE 500) NMR spectrometer operating at 500 and 125 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter (METTLER TGA/DSC1) at a heating rate of 5°C min^{-1}. IR spectra are recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities are determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.01). The heat of combustion is tested by Paii 6200 Calorimeter. The samples were dried in a hydrothermal oven at 40°C at least for 24 hours to remove the solvent before all tests. There is no solvent peak in the TG of the dry sample.

X-ray crystallography

The data for **6**·CH_3OH, **7** and **11**·CH_3OH were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-Ka radiation (λ=0.71073 nm) at 170 K. The data collection and the initial unit cell refinement are performed by using APEX2 (v2010.3-0). Data Reduction is performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections are applied by using the SADABS (v2008/1) program. The structures are solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands are included using a riding model. The crystallographic data and CCDC numbers for these compounds are summarized in Table S2

Table S3 Crystallographic Data for **6**·CH_3OH, **7** and **11**·CH_3OH

Compound	**6**·CH_3OH	**7**	**11**·CH_3OH
Empirical formula	$C_9H_8N_8O_3$	$C_8H_3N_9O_4$	$C_{13}H_8N_{14}O_6$
Formula weight	276.23	289.19	456.33
Temperature/K	193.00	170	193.00
Crystal system	monoclinic	trigonal	triclinic
Space group	$P2_1/c$	R-3	P-1
a/Å	8.7309(4)	23.212(3)	7.2696(8)
b/Å	19.6818(10)	23.212(3)	10.8752(12)
c/Å	6.9104(4)	11.2896(19)	12.1046(14)
α/°	90	90	93.652(5)
β/°	105.115(3)	90	102.562(6)
γ/°	90	120	103.331(5)
Volume/Å^3	1146.40(10)	5267.8(15)	902.34(18)
Z	4	18	2
ρ_{calc} g/cm^3	1.600	1.641	1.680
μ/mm^{-1}	1.085	0.137	0.764
F (000)	568.0	2628.0	464.0
Crystal size/mm^3	0.13 × 0.12 × 0.11	0.11 × 0.04 × 0.02	0.11 × 0.1 × 0.08

Radiation	CuKα (λ =1.54178)	MoKα(λ = 0.71073)	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.986 to 135.84	4.138 to 52.71	6.556 to 107.902
Index ranges	-10 ≤ h ≤ 8, -20 ≤ k ≤ 23, -6 ≤ l ≤ 8	21 ≤ h ≤ 28, -28 ≤ k ≤ 28, -12 ≤ l ≤ 14	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	10625	10264	8244
Independent reflections	2076[R_{int} = 0.0440, R_{sigma} = 0.0305]	2389 [R_{int} = 0.0889, R_{sigma} = 0.0788]	3249 [R_{int} = 0.0859, R_{sigma} = 0.0909]
Data/restraints/parameters	2076/0/187	2389/2/198	3249/1/304
Goodness-of-fit on F^2	1.069	1.063	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1047	R_1 = 0.0566, wR_2 = 0.1240	R_1 = 0.0872, wR_2 = 0.2279
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1118	R_1 = 0.1063, wR_2 = 0.1601	R_1 = 0.1205, wR_2 = 0.2455
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.22	0.31/-0.39	0.67/-0.53
CCDC No.	2303258	2303259	2303260

Table S4. Bond lengths [Å] and angles [°] for **6**·CH_3OH.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
O1-C1	1.210(2)	N3-C4	1.293(2)
O2-N2	1.403(2)	N4-C5	1.383(2)
O2-N3	1.385(2)	N4-C3	1.388(2)
O3-C9	1.424(3)	N4-C4	1.391(2)
O3-H3	0.8400	N5-C3	1.308(2)
N1-C2	1.367(2)	N5-N6	1.383(2)
N1-C1	1.373(2)	N6-C5	1.318(2)
N2-C2	1.302(2)	N7-C8	1.333(2)
Parameter	**Bond angles [°]**	**Parameter**	**Bond lengths [Å]**
N2-O2 -N3	111.61(14)	C2-N1 -H1	118.2(16)
C9-O3 -H3	109.00	C1-N1 -H1	120.5(16)
C1-N1 -C2	120.27(16)	N7-N8 -H8	124.00
O2-N2 -C2	104.13(15)	C7-N8 -H8	124.00

O2-N3 -C4	104.10(15)	N1-C1 -C3	115.70(16)
C3-N4 -C4	117.23(14)	O1-C1 -N1	122.92(17)
C4-N4 -C5	137.76(15)	O1-C1 -C3	121.38(16)
C3-N4 -C5	105.01(13)	N1-C2 -N2	126.74(17)
N6-N5 -C3	107.47(14)	N1-C2 -C4	123.97(16)
N5-N6 -C5	108.68(13)	N2-C2 -C4	109.28(16)
N8-N7 -C8	104.77(14)	N5-C3 -C1	126.22(16)
N7-N8 -C7	112.68(15)	N4-C3 -C1	123.80(15)

Table S5. Bond lengths [Å] and angles [°] for **7**.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
O1-N1	1.396(4)	N3-C3	1.369(5)
O1-N2	1.396(3)	N4-C1	1.390(5)
O2-N9	1.227(3)	N4-C4	1.367(4)
O3-N9	1.224(4)	N4-C5	1.377(4)
O4-C3	1.219(4)	N5-N6	1.386(3)
N1-C1	1.294(5)	N6-C5	1.322(5)
N2-C2	1.309(5)	N7-N8	1.353(4)
N3-C2	1.363(5)	N7-C8	1.340(5)
Parameter	**Bond angles [°]**	**Parameter**	**Bond lengths [Å]**
N1-O1 -N2	112.1(3)	O2-N9 -C7	117.4(3)
O1-N1 -C1	103.0(2)	O3-N9 -C7	117.8(3)
O1-N2 -C2	104.3(3)	C2-N3 -H3	124(3)
C2-N3 -C3	120.7(3)	C3-N3 -H3	115(3)
C1-N4 -C4	118.4(3)	N8-N7 -H7	120(2)
C1-N4 -C5	135.8(3)	C8-N7 -H7	127(2)
C4-N4 -C5	105.3(3)	N1-C1 -N4	129.9(3)
N6-N5 -C4	107.2(3)	N1-C1 -C2	112.0(3)
N5-N6 -C5	108.0(3)	N4-C1 -C2	118.1(3)
N8-N7 -C8	113.3(3)	N2-C2 -C1	108.6(3)
N7-N8 -C7	102.8(3)	N3-C2 -C1	123.7(4)
O2-N9 -O3	124.8(3)	N2-C2 -N3	127.7(3)
N1-O1 -N2	112.1(3)	O4-C3 -N3	123.1(3)

Table S6. Bond lengths [Å] and angles [°] for **11**·CH_3OH.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
O1-N1	1.392(4)	N1-C1	1.294(5)
O1-N2	1.398(4)	N2-C2	1.303(5)
O2-N11	1.223(5)	N3-C1	1.396(4)
O3-N11	1.235(5)	N3-C5	1.380(5)

O4-N14	1.216(6)	N3-C4	1.367(4)
O5-N14	1.220(5)	N4-N5	1.395(5)
O6-C13	1.455(8)	N4-C5	1.312(5)
O6-H6	0.8400	N5-C4	1.307(5)
Parameter	**Bond angles [°]**	**Parameter**	**Bond lengths [Å]**
N1-O1 -N2	112.5(3)	N8-N7 -C9	108.4(3)
C13-O6 -H6	110.00	N7-N8 -C3	106.7(3)
O1-N1 -C1	103.8(3)	N10-N9-C7	113.3(3)
O1-N2 -C2	103.3(3)	N9 -N1-C8	103.6(3)
C1-N3 -C5	134.3(3)	O2 -N1-O3	124.1(4)
C4-N3 -C5	105.3(3)	O2 -N1-C8	118.2(3)
C1-N3 -C4	120.3(3)	O3 -N1-C8	117.7(4)
N5-N4 -C5	108.4(3)	N13-N1-C11	112.9(3)
N4-N5 -C4	106.6(3)	N12-N1-C12	103.0(3)
C2-N6 -C3	120.7(3)	O4 -N1-O5	124.1(5)
C2-N6 -C9	134.7(3)	O4 -N1-C12	118.9(4)
C3-N6 -C9	104.4(3)	O5 -N1-C12	117.1(4)

Table S7 Hydrogen bonds of **6**·CH_3OH

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/Å**	**<(DHA)/ °**
N1-H1···O3	0.96(3)	1.72(3)	2.667(2)	178
O3-H3···N7	0.84	1.92	2.7611(19)	177
N8-H8···N5	0.88	2.17	3.053(2)	123
C7-H7···O1	0.95	2.36	2.983(2)	137
C7-H7···N3	0.95	2.23	2.997(2)	145
C9-H9A···O2	0.98	2.49	3.340(3)	178

Table S8 Hydrogen bonds of **7**

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/Å**	**<(DHA)/ °**
N7-H7···N5	0.88(3)	2.12(3)	2.997(4)	172(4)
C8-H8···O4	0.95	2.47	2.995(4)	115

Table S9 Hydrogen bonds of **11**·CH_3OH

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/Å**	**<(DHA)/ °**
O6-H6···N8	0.84	2.11	2.933(5)	165
N9-H9···O6	0.91(2)	1.81(2)	2.693(5)	163(4)
N12-H12···N4	0.88	2.12	2.922(5)	151
C7-H7···O2	0.95	2.3	3.126(5)	145
C11-H11···O6	0.95	2.47	3.280(6)	143

C13-H13A···O3	0.98	2.57	3.529(7)	167

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

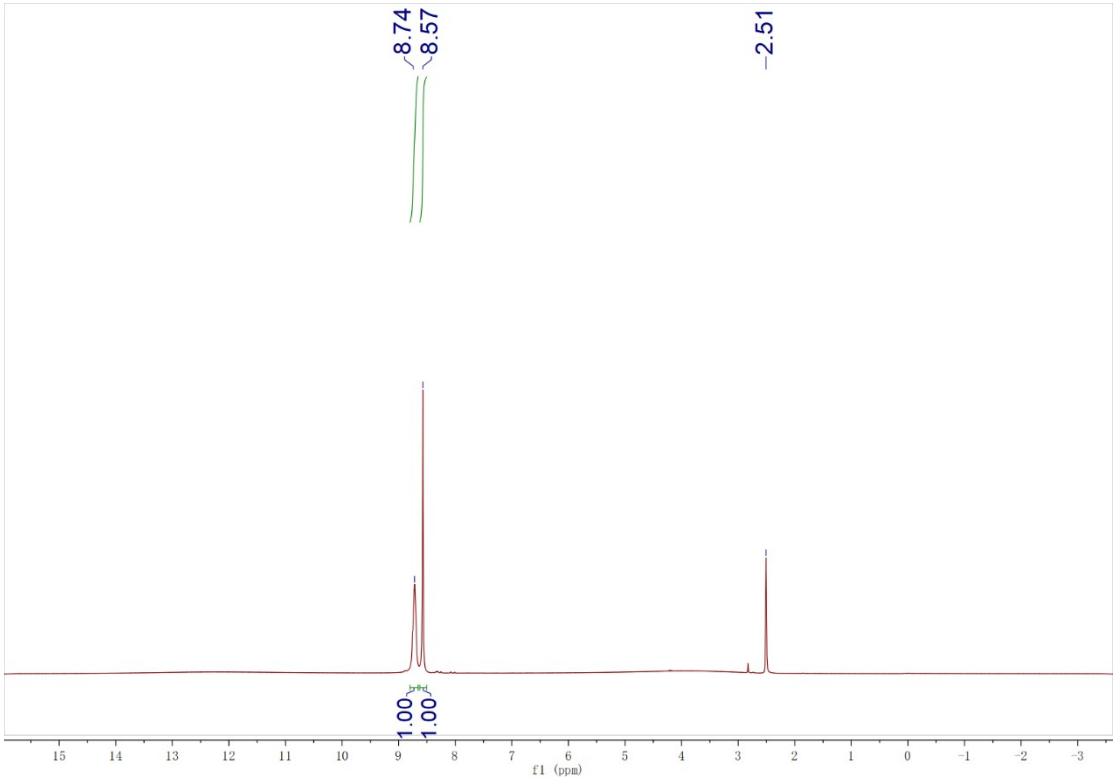


Figure S1 ^{1}H NMR spectra (500 MHz) of **5** in [D_6] DMSO at 25 °C.

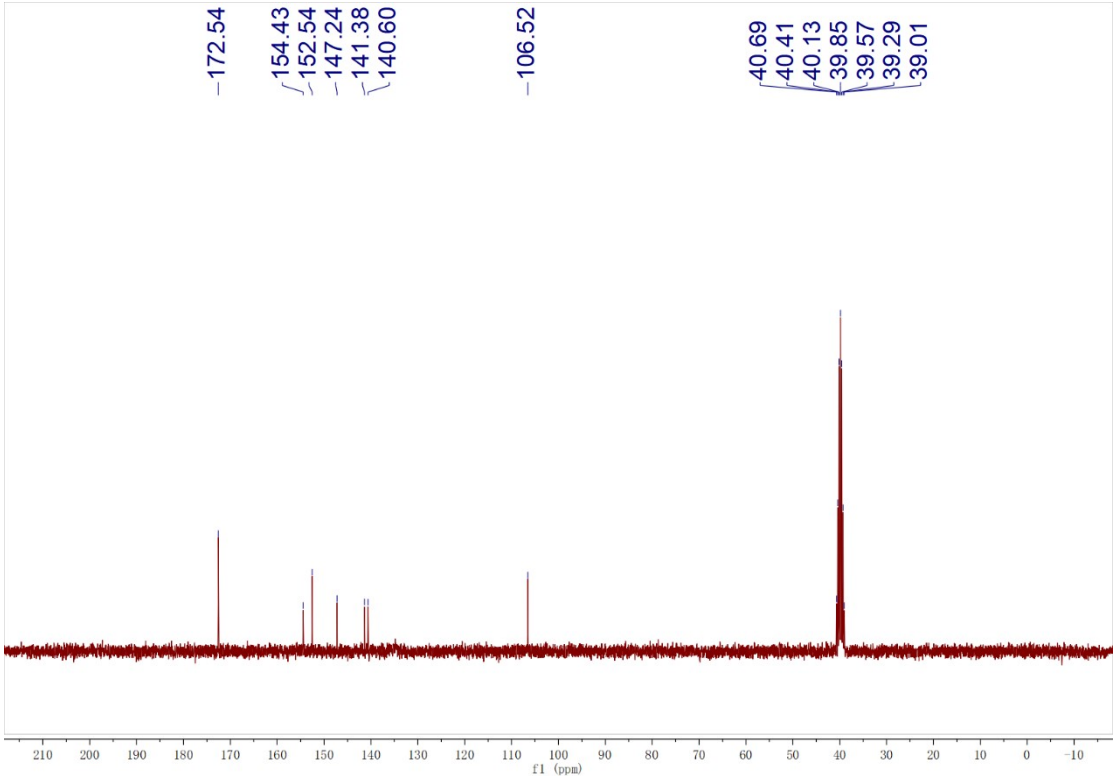


Figure S2 ^{13}C NMR spectra (125 MHz) of **5** in [D6] DMSO at 25 °C.

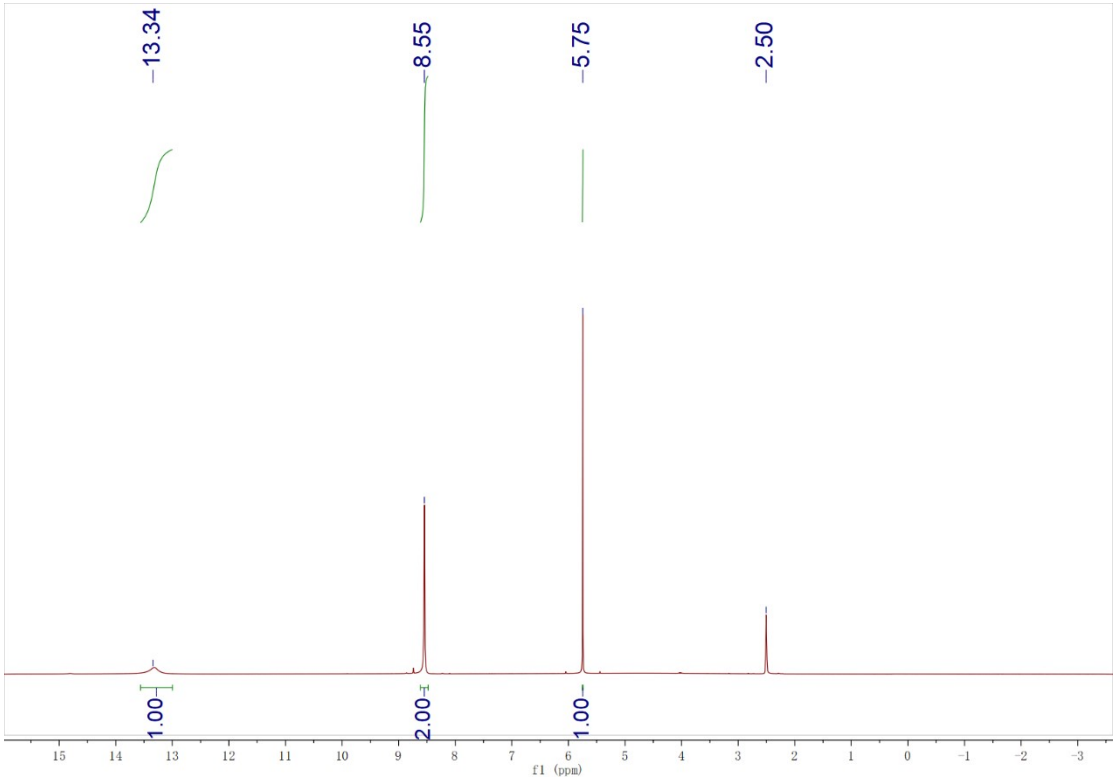


Figure S3 ^{1}H NMR spectra (500 MHz) of **6** in [D_6] DMSO at 25 °C.

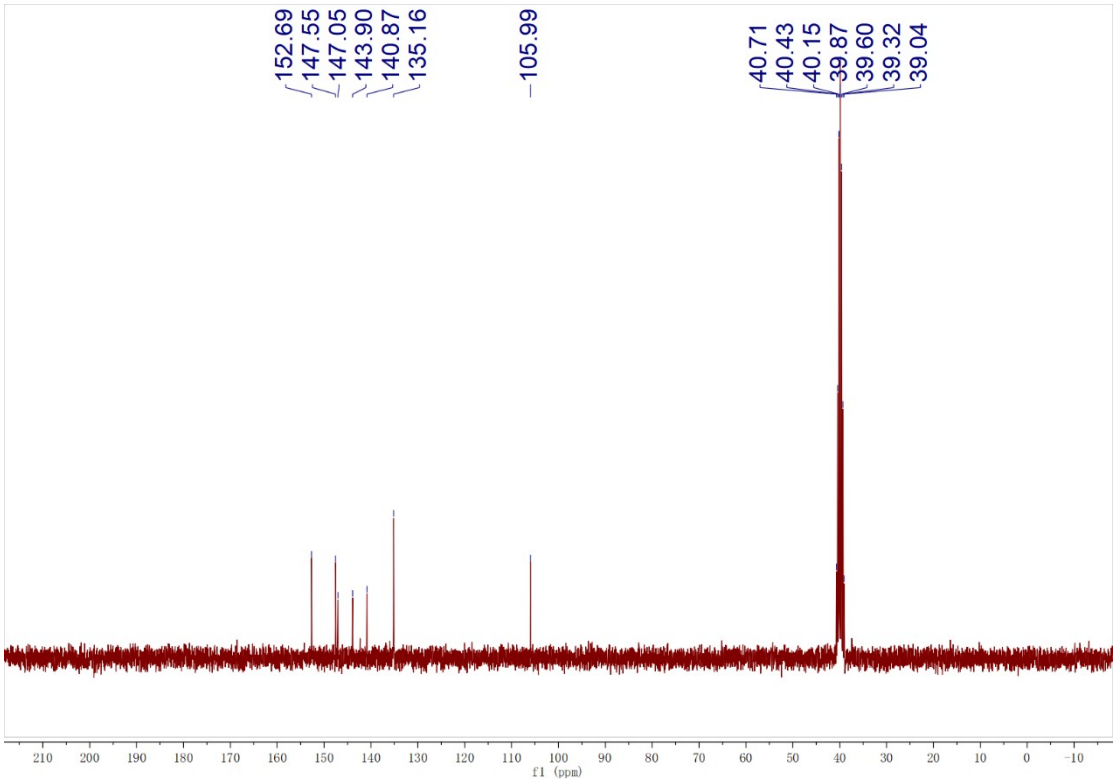


Figure S4 ^{13}C NMR spectra (125 MHz) of **6** in [D6] DMSO at 25 °C.

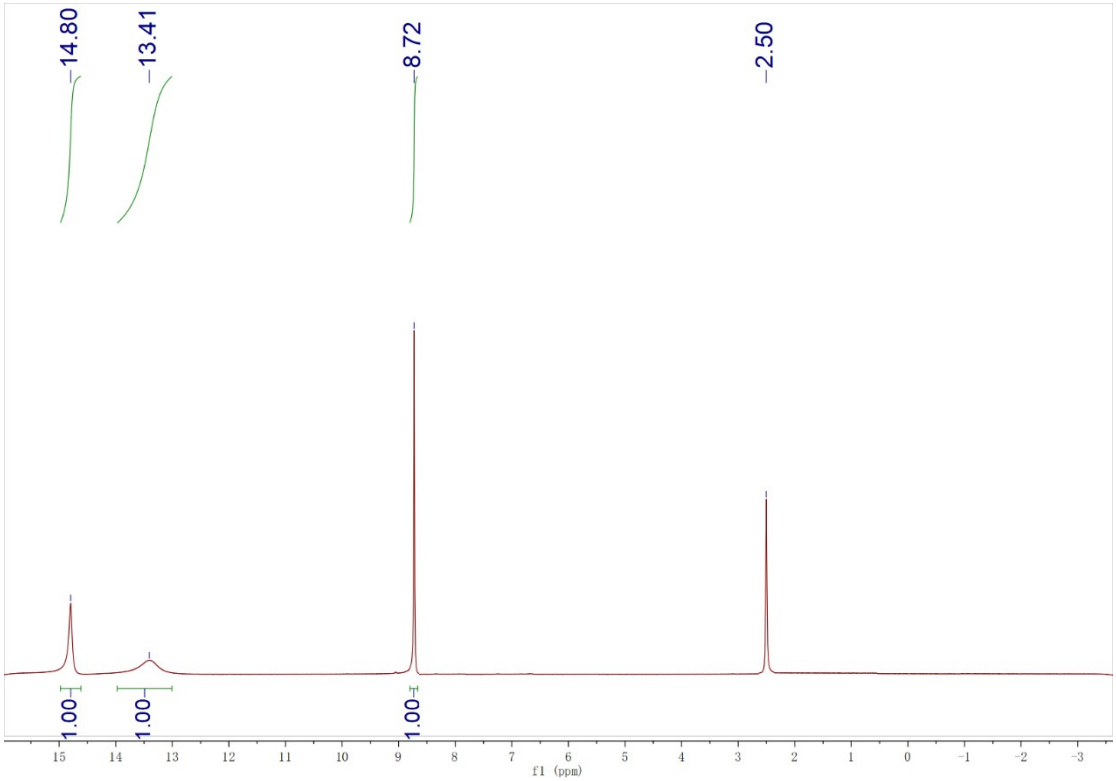


Figure S5 ^{1}H NMR spectra (500 MHz) of **7** in [D_6] DMSO at 25 °C.

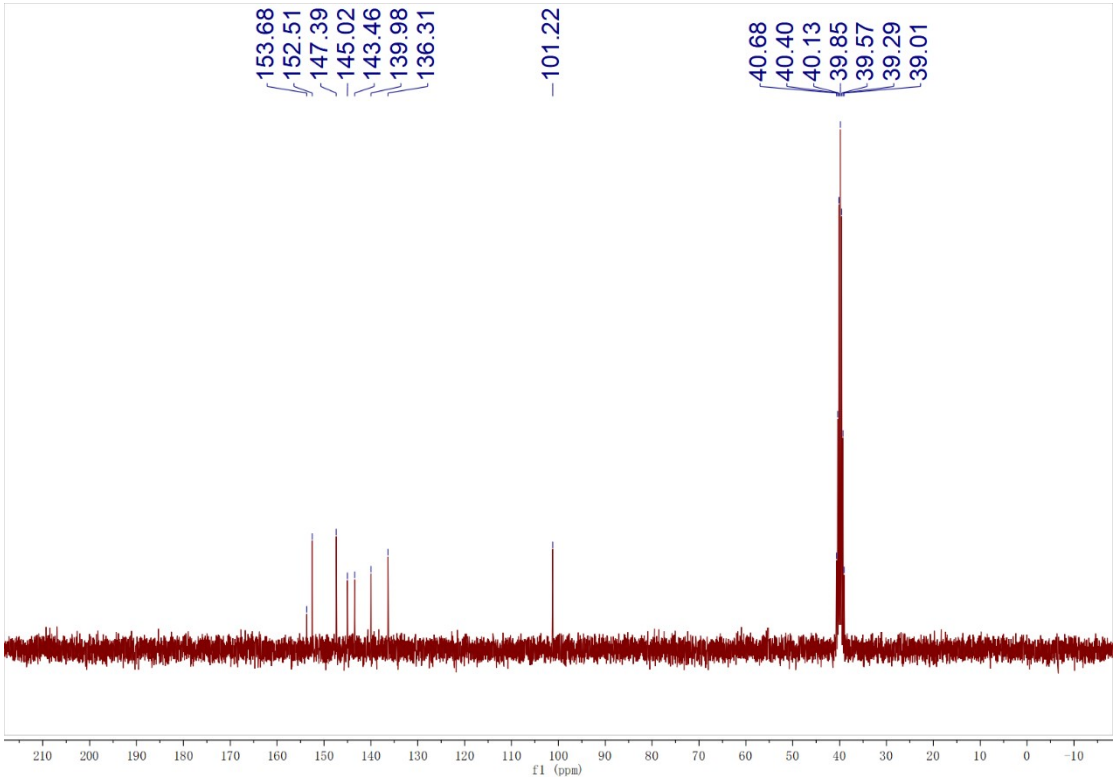


Figure S6 ^{13}C NMR spectra (125 MHz) of **7** in [D6] DMSO at 25 °C.

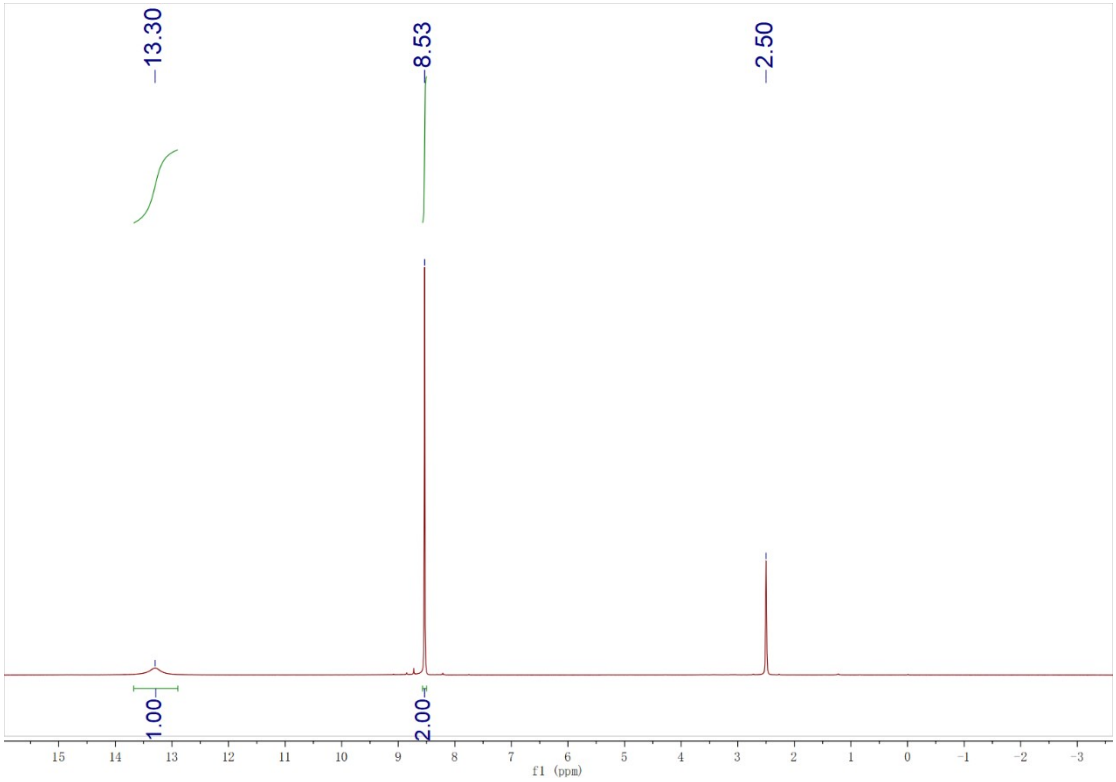


Figure S7 ^{1}H NMR spectra (500 MHz) of **10** in [D_6] DMSO at 25 ^{o}C.

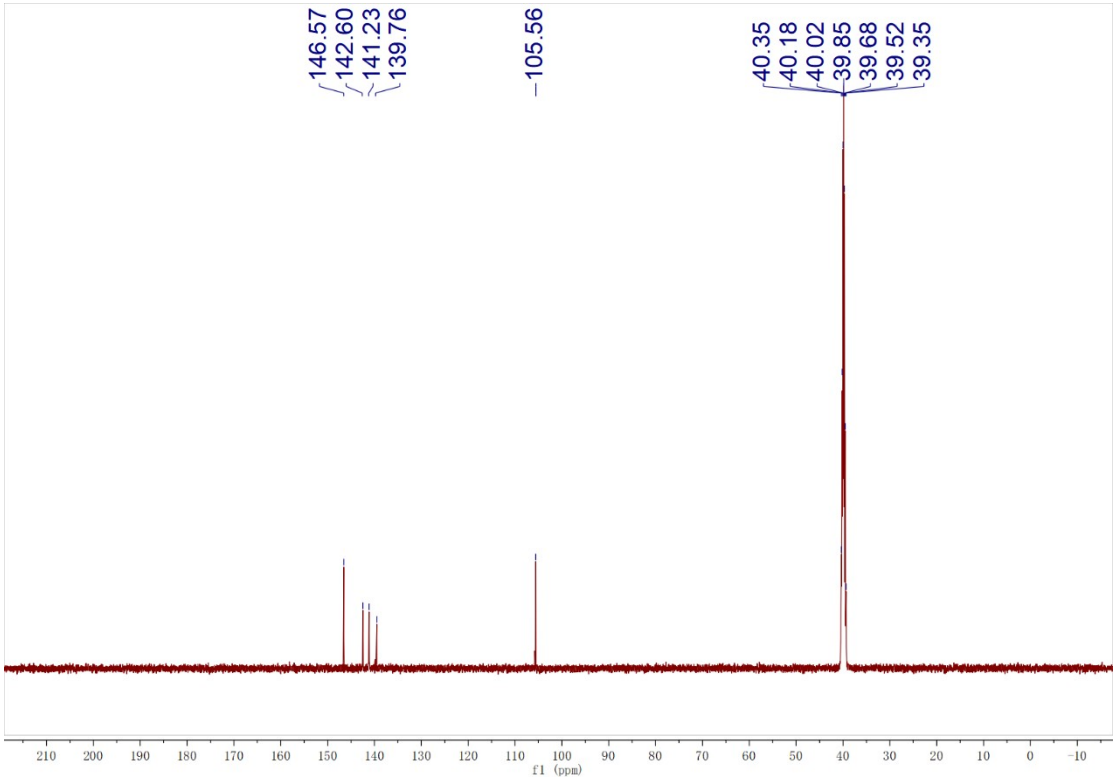


Figure S8 ^{13}C NMR spectra (125 MHz) of **10** in [D6] DMSO at 25 ^{o}C.

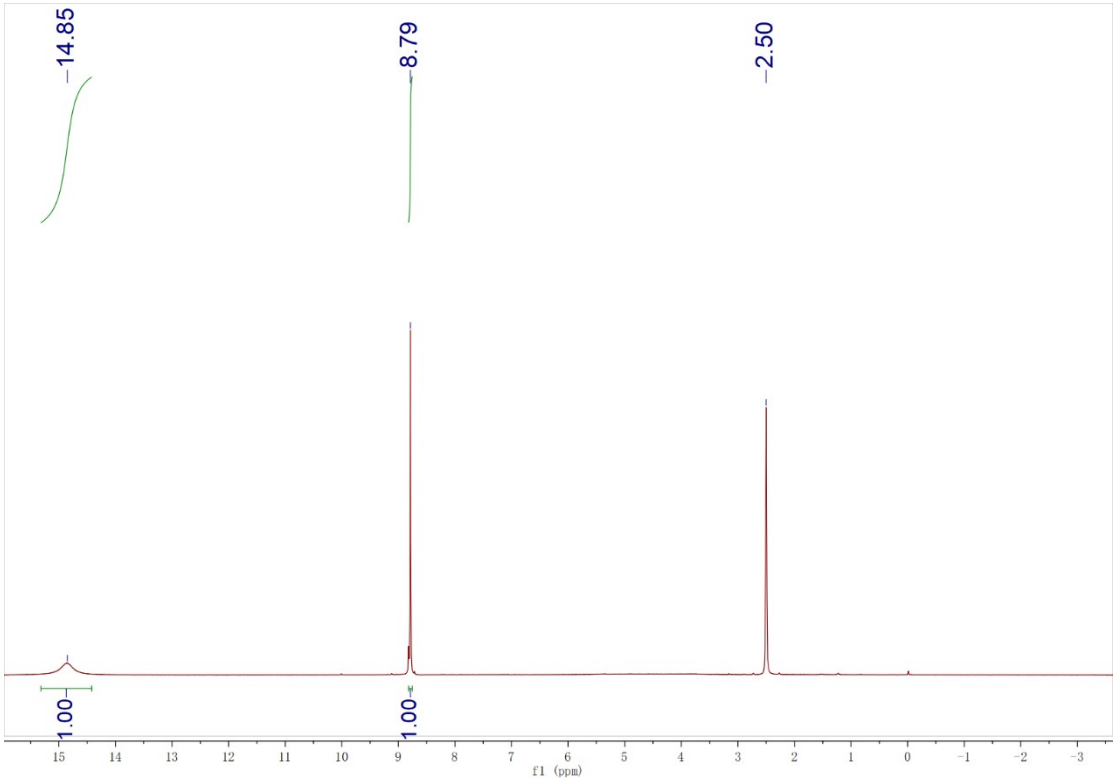


Figure S9 ^{1}H NMR spectra (500 MHz) of **11** in [D_6] DMSO at 25 °C.

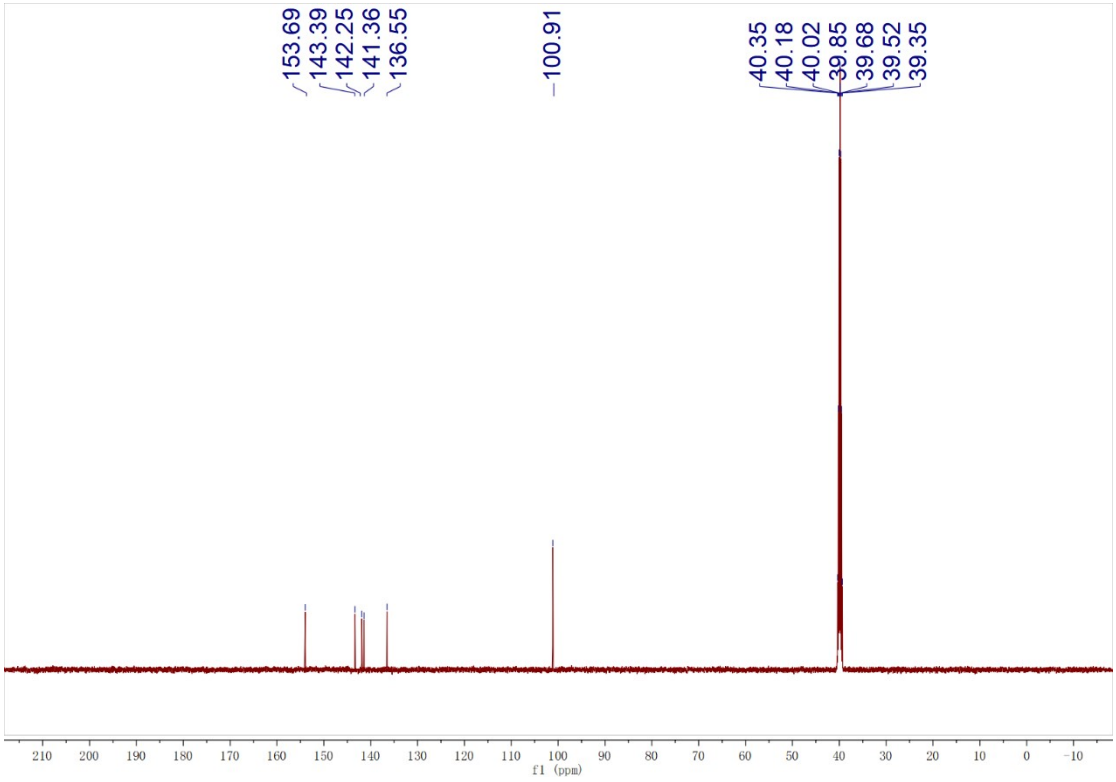


Figure S10 ^{13}C NMR spectra (125 MHz) of **11** in [D6] DMSO at 25 °C.

4. TG and DSC of new compounds

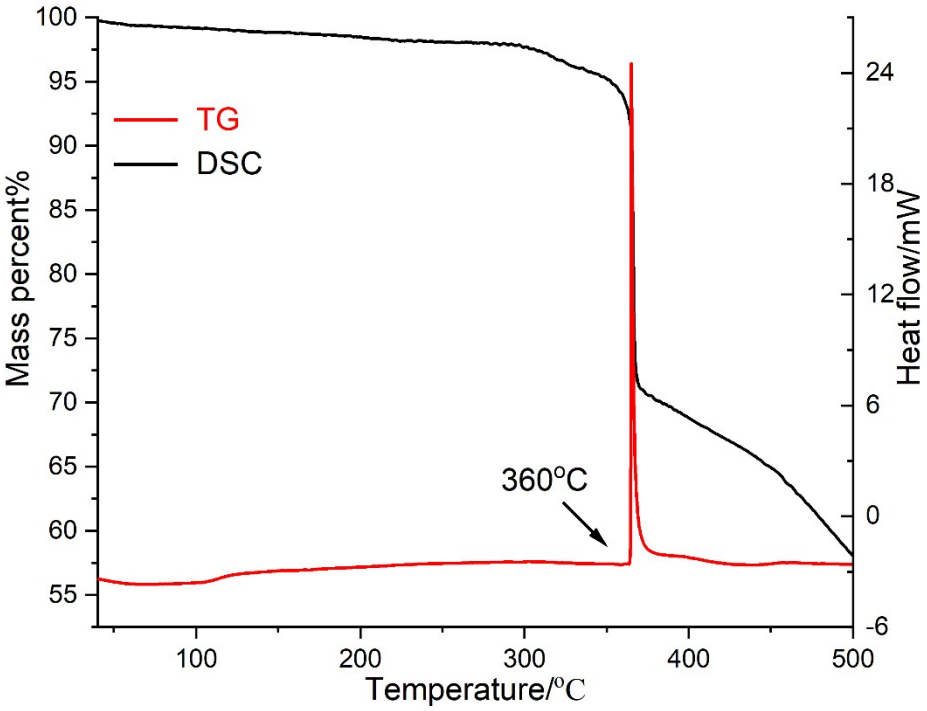


Figure S11 TG and DSC of **5**

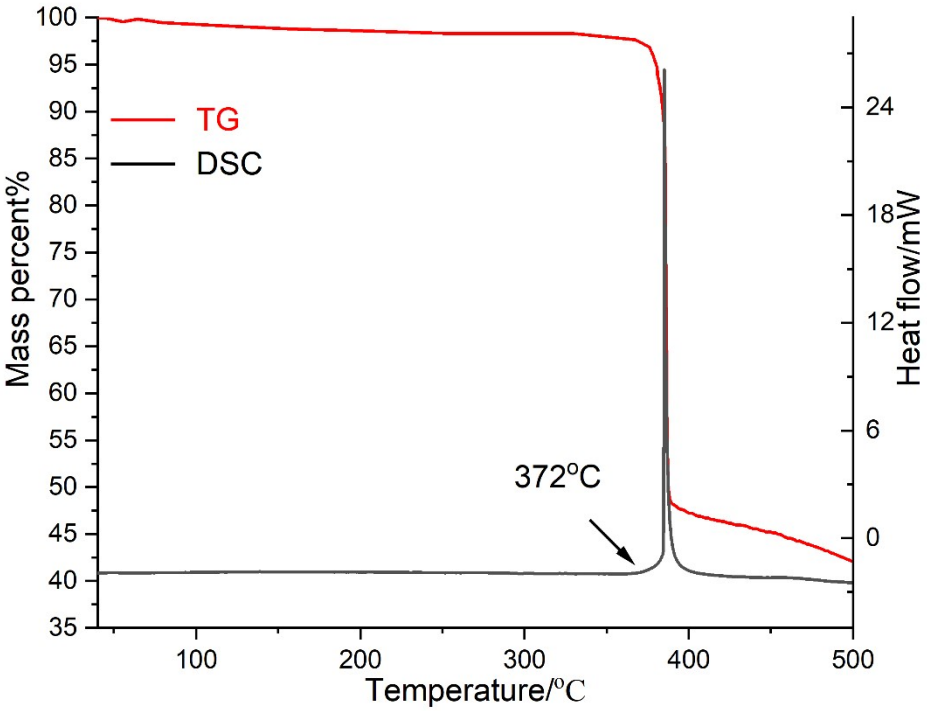


Figure S12 TG and DSC of **6**

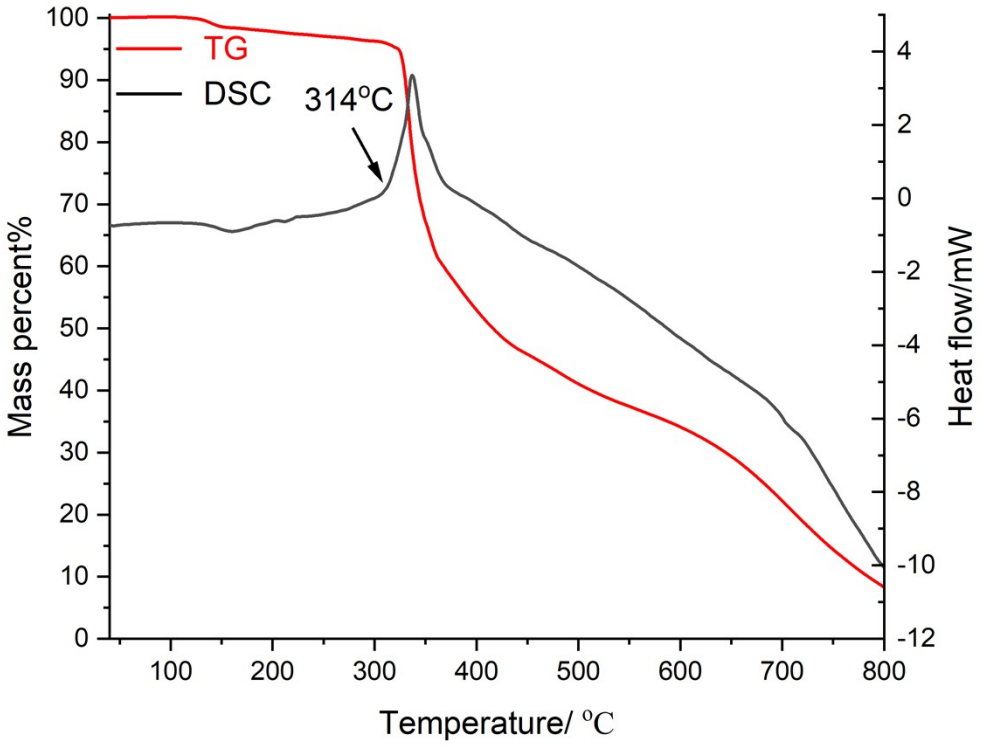


Figure S13 TG and DSC of **7**

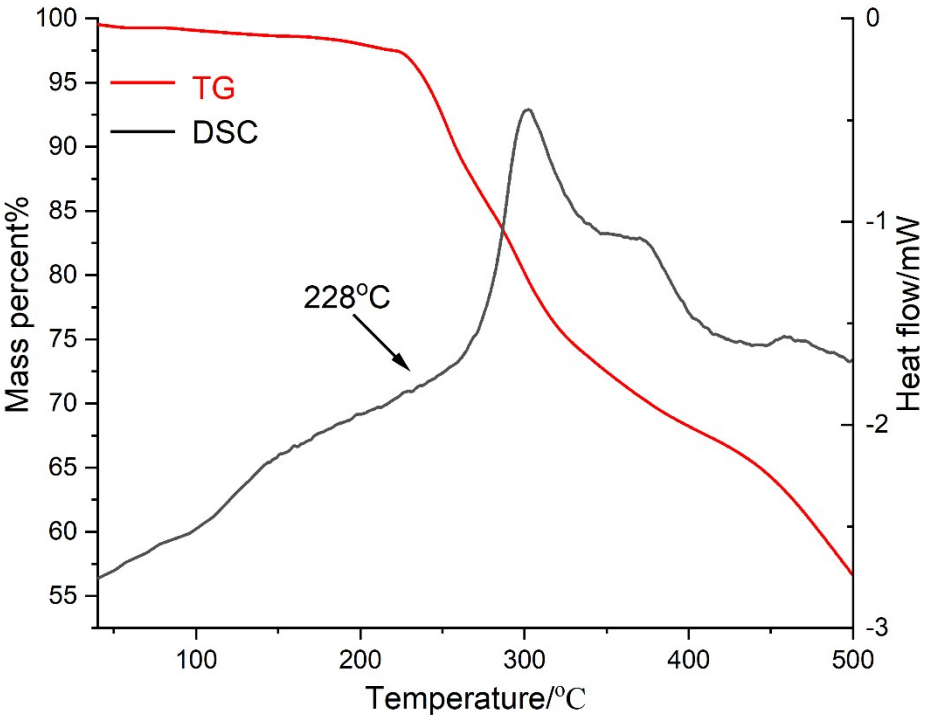


Figure S14 TG and DSC of **10**

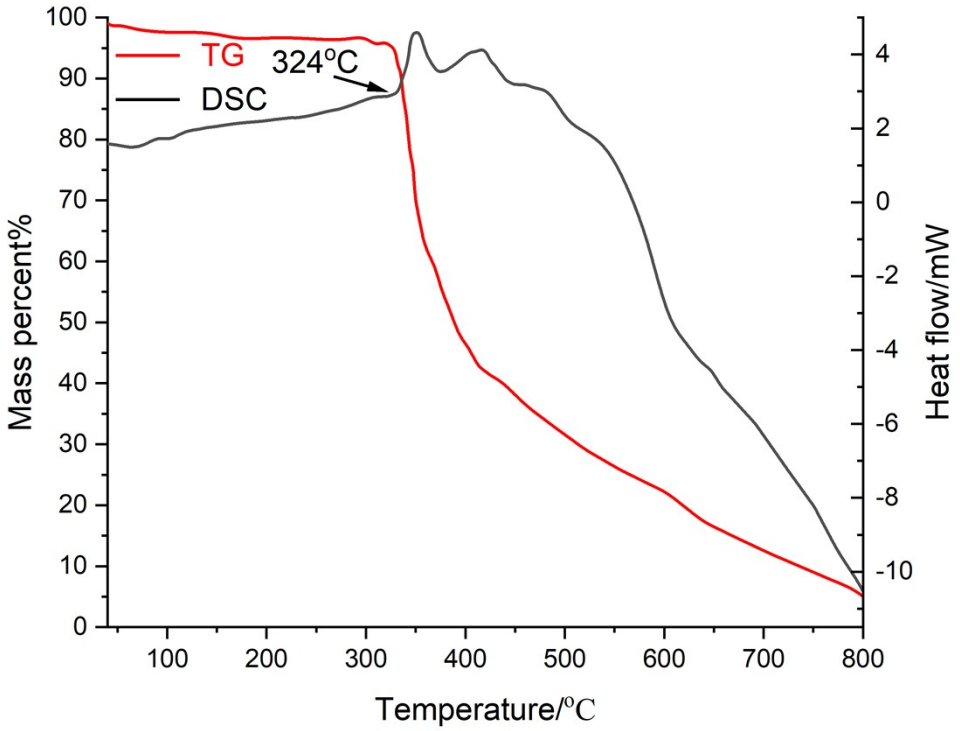
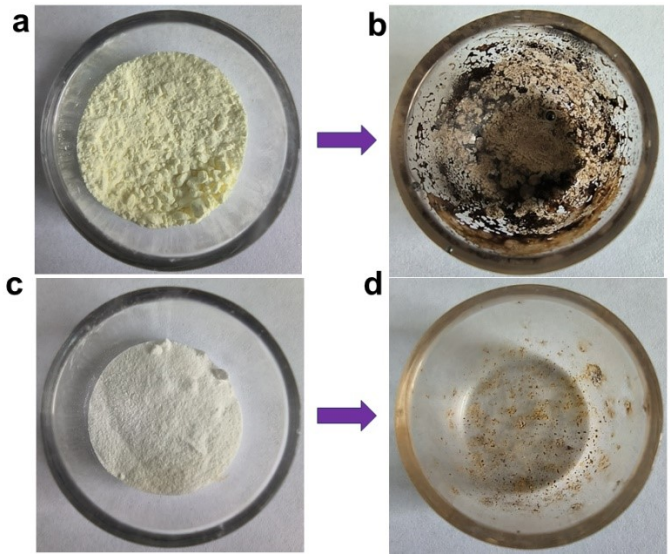


Figure S15 TG and DSC of **11**

5. The heat of combustion test of compounds 7 and 11.



Scheme 2 a, **c:** the the sample of **7** and **11**; **b**, **d:** the residue of the sample **7** and **11** after the heat of combustion test

Compound	pre-test mass/g	residual mass/g	mass reduction/%	heat of combustion value/ kJ mol^{-1}	$\Delta_f H_m$ kJ mol^{-1}/ kJ g^{-1}
7	0.6447	0.0074	98.85	4149.38	572.6/1.98
11	0.6893	0.0032	99.54	6456.25	1162.5/2.74

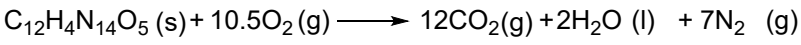


Table S10 the sample mass and heat of combustion value of **7** and **11**