Supporting Information (SI)

Study on the synthesis of 2-fluoro-2,2-dinitromethyl esters as potential melt cast matrix in explosive charges

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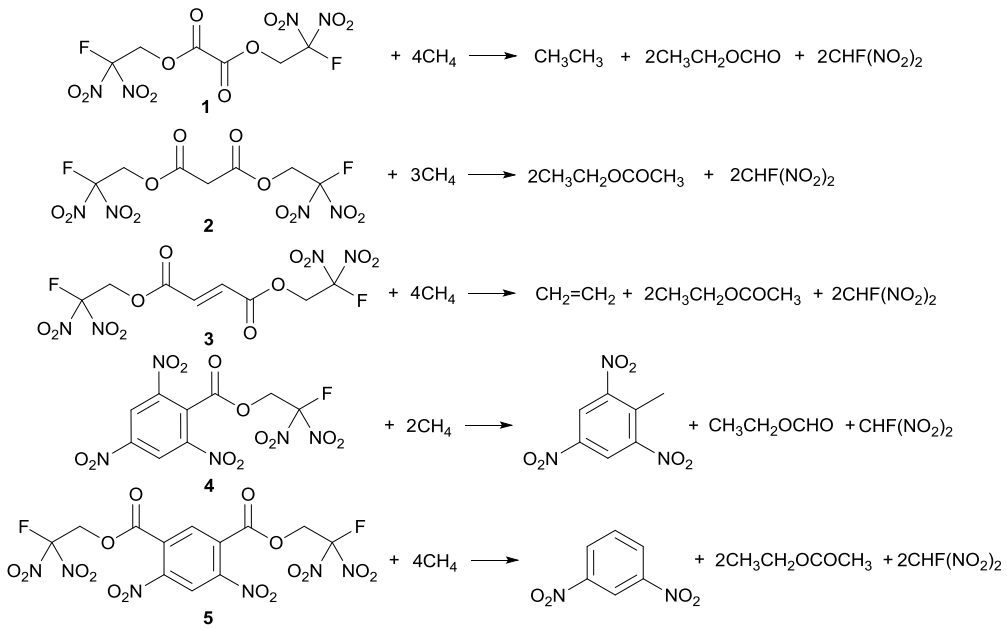
1. Computational data

Computations were performed by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[2] functional with the 6-311+G** basis set.[3] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[4] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The lattice energy of the trinitroethyl derivatives were predicted by using the formula suggested by Jenkins et al.[5]

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of compounds **1-5**, are shown in Scheme S1



Scheme S1. Isodesmic and tautomeric reactions to compute the HOF.

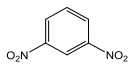
$$\Delta H_{298} = \Sigma\Delta_f HP - \Sigma\Delta_f H_R \quad (1)$$

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression, see Equation (2).

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation [(2)] is the *PV* work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation [(1)], apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from experiments[6,7] or from the high-level computing such as CBS-4M.

Table S1. *Ab initio* computational values of fluorodinitroethyl esters

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
1	-1552.394	387.86	64.85	-917.96
2	-1591.739	460.71	67.46	-972.12
3	-1629.830	473.14	70.49	-880.39
4	-1621.550	437.81	66.79	-335.17
5	-2192.588	601.48	91.23	-719.68
CH_4	-40.534	112.26	10.04	-74.6[e]
CH_2CH_2	-78.614	128.06	10.56	52.4[e]
CH_3CH_3	-79.860	187.31	11.79	-84[e]
CH_3CH_2OCHO	-268.460	234.41	16.12	-381.88[f]
$CH_3CH_2OCOCH_3$	-307.804	296	22.61	-443.6[f]
$CHF(NO_2)_2$	-548.889	111.94	18.81	-212.35[f]
TNT	-885.302	338.50	39.86	24.1[g]
	-641.432	263.43	28.13	53.92[f]

[a] Total energy calculated by B3LYP/6-31+G** method (a.u); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}); [e] Ref. 6; [f] calculated by CBS-4 Enthalpy; [g] Ref 7.

References

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2. Single-crystal X-ray diffraction analysis of compound 1

Table S2. Bond lengths [Å] and angles [°] of compound **1.**

C(1)-O(6)	1.187(2)	C(3)-F(1)	1.326(2)
C(1)-O(1)	1.345(2)	C(3)-N(1)	1.528(2)
C(1)-C(1)#1	1.531(4)	C(3)-N(2)	1.539(3)
C(2)-O(1)	1.443(2)	N(1)-O(2)	1.207(2)
C(2)-C(3)	1.509(3)	N(1)-O(3)	1.2097(19)
C(2)-H(2A)	0.9900	N(2)-O(5)	1.209(2)
C(2)-H(2B)	0.9900	N(2)-O(4)	1.219(2)
O(6)-C(1)-O(1)	126.66(17)	C(2)-C(3)-N(1)	112.31(15)
O(6)-C(1)-C(1)#1	124.7(2)	F(1)-C(3)-N(2)	106.74(15)
O(1)-C(1)-C(1)#1	108.7(2)	C(2)-C(3)-N(2)	111.71(15)

O(1)-C(2)-C(3)	105.10(15)	N(1)-C(3)-N(2)	104.70(14)
O(1)-C(2)-H(2A)	110.7	O(2)-N(1)-O(3)	127.21(17)
C(3)-C(2)-H(2A)	110.7	O(2)-N(1)-C(3)	116.54(15)
O(1)-C(2)-H(2B)	110.7	O(3)-N(1)-C(3)	116.25(15)
C(3)-C(2)-H(2B)	110.7	O(5)-N(2)-O(4)	127.45(19)
H(2A)-C(2)-H(2B)	108.8	O(5)-N(2)-C(3)	117.19(17)
F(1)-C(3)-C(2)	113.39(15)	O(4)-N(2)-C(3)	115.34(16)
F(1)-C(3)-N(1)	107.45(14)	C(1)-O(1)-C(2)	115.85(15)

Table S3. Hydrogen bonds of compound **1** [Å and º]

D-H•••A	d(D-H)/ Å	d(H•••A)/ Å	d(D•••A)/ Å	<(DHA)/ °	comment
C(2)-H(2B)•••O(6)^{i}	0.99	2.41	3.121(3)	128	inter

i:-x,1-y,2-z

3. Single-crystal X-ray diffraction analysis of compound 4

Table S4. Bond lengths [Å] and angles [º] of compound **4**

C(1)-C(6)	1.381(8)	C(8)-H(8A)	0.9900
C(1)-C(2)	1.402(7)	C(8)-H(8B)	0.9900
C(1)-N(1)	1.474(7)	C(9)-F(1)	1.319(7)
C(2)-C(3)	1.397(8)	C(9)-N(2)	1.531(8)
C(2)-C(7)	1.509(8)	C(9)-N(3)	1.541(7)
C(3)-C(4)	1.368(8)	N(1)-O(2)	1.221(6)
C(3)-N(4)	1.485(7)	N(1)-O(1)	1.230(6)
C(4)-C(5)	1.383(7)	N(2)-O(6)	1.207(6)
C(4)-H(4)	0.9500	N(2)-O(5)	1.230(7)
C(5)-C(6)	1.377(8)	N(3)-O(8)	1.199(6)
C(5)-N(5)	1.470(8)	N(3)-O(7)	1.221(6)
C(6)-H(6)	0.9500	N(4)-O(10)	1.221(6)
C(7)-O(4)	1.190(7)	N(4)-O(9)	1.234(6)
C(7)-O(3)	1.344(6)	N(5)-O(11)	1.217(6)
C(8)-O(3)	1.432(7)	N(5)-O(12)	1.229(6)
C(8)-C(9)	1.506(8)		
C(6)-C(1)-C(2)	123.5(5)	C(9)-C(8)-H(8B)	109.9
C(6)-C(1)-N(1)	116.6(5)	H(8A)-C(8)-H(8B)	108.3
C(2)-C(1)-N(1)	119.9(5)	F(1)-C(9)-C(8)	114.5(5)
C(3)-C(2)-C(1)	115.0(6)	F(1)-C(9)-N(2)	107.6(5)
C(3)-C(2)-C(7)	124.5(5)	C(8)-C(9)-N(2)	110.5(5)

C(1)-C(2)-C(7)	120.4(5)	F(1)-C(9)-N(3)	107.2(5)
C(4)-C(3)-C(2)	124.1(6)	C(8)-C(9)-N(3)	110.7(5)
C(4)-C(3)-N(4)	116.5(5)	N(2)-C(9)-N(3)	105.9(5)
C(2)-C(3)-N(4)	119.3(6)	O(2)-N(1)-O(1)	124.4(5)
C(3)-C(4)-C(5)	117.1(5)	O(2)-N(1)-C(1)	118.0(5)
C(3)-C(4)-H(4)	121.4	O(1)-N(1)-C(1)	117.6(5)
C(5)-C(4)-H(4)	121.4	O(6)-N(2)-O(5)	126.4(6)
C(6)-C(5)-C(4)	123.0(6)	O(6)-N(2)-C(9)	117.6(6)
C(6)-C(5)-N(5)	117.8(5)	O(5)-N(2)-C(9)	116.0(5)
C(4)-C(5)-N(5)	119.2(5)	O(8)-N(3)-O(7)	127.8(5)
C(5)-C(6)-C(1)	117.1(5)	O(8)-N(3)-C(9)	117.4(5)
C(5)-C(6)-H(6)	121.4	O(7)-N(3)-C(9)	114.8(5)
C(1)-C(6)-H(6)	121.4	O(10)-N(4)-O(9)	125.0(5)
O(4)-C(7)-O(3)	126.6(6)	O(10)-N(4)-C(3)	117.6(5)
O(4)-C(7)-C(2)	124.0(6)	O(9)-N(4)-C(3)	117.4(5)
O(3)-C(7)-C(2)	109.4(5)	O(11)-N(5)-O(12)	123.3(6)
O(3)-C(8)-C(9)	108.8(5)	O(11)-N(5)-C(5)	119.0(5)
O(3)-C(8)-H(8A)	109.9	O(12)-N(5)-C(5)	117.7(5)
C(9)-C(8)-H(8A)	109.9	C(7)-O(3)-C(8)	115.7(5)

Table S5. Hydrogen bonds of compound **4** [Å and º]

D-H•••A	d(D-H)/ Å	d(H•••A)/	d(D•••A)/ Å	<(DHA)/ °	comment
C(6)-H(6)•••O(7)^{i}	0.95	2.55	3.366(7)	144	inter
C(8)-H(8A)•••O(10)^{ii}	0.99	2.59	3.576(8)	173	inter
C(8)-H(8B)•••O(6)^{iii}	0.99	2.53	3.361(8)	142	inter

i:1+x,y,z; ii:-x,1/2+y,3/2-z; iii:1-x,1/2+y,3/2-z.

4. ^{1}H NMR and ^{13}C NMR spectra of compounds 1-5

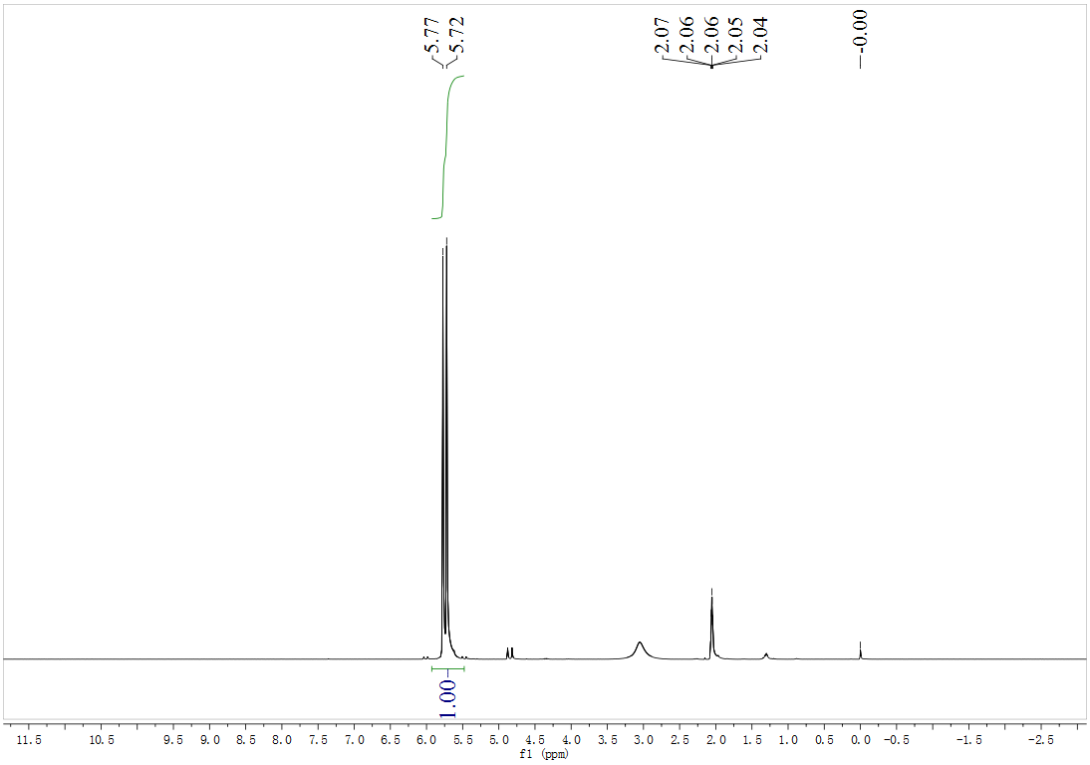

Fig. S1 ^{1}H-NMR spectra (300 MHz) of **1** in acetone-d_6 at 25 ℃

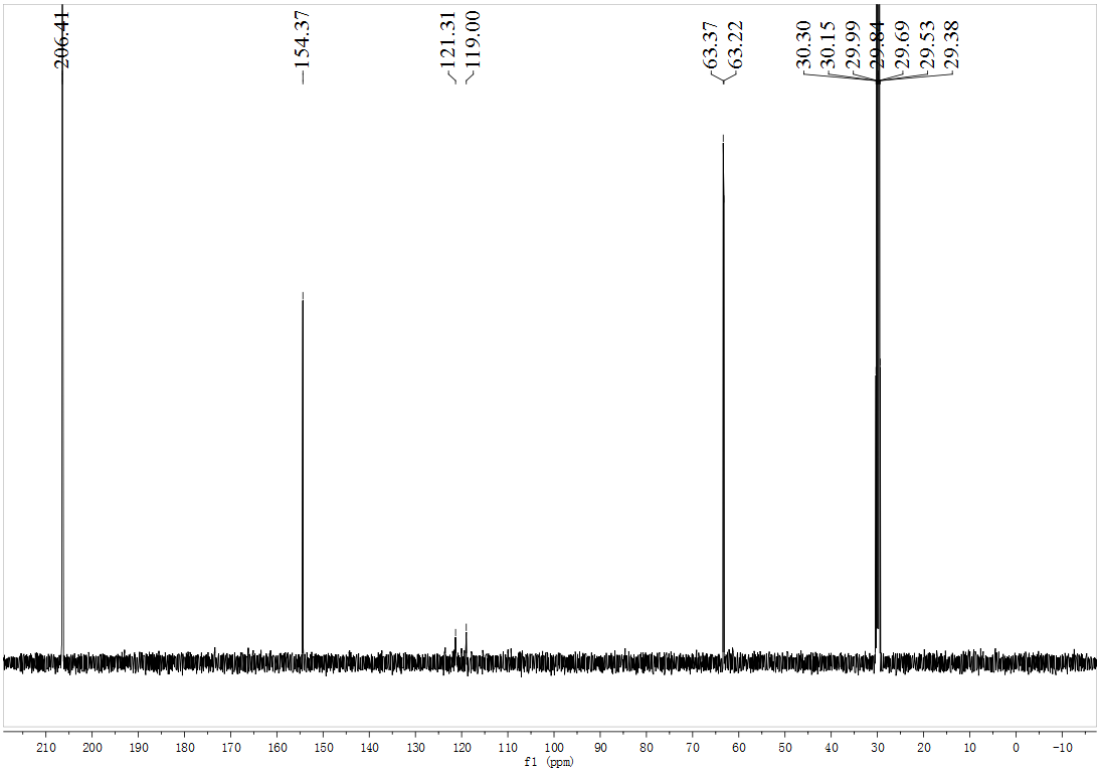

Fig. S2 ^{13}C-NMR spectra (126 MHz) of **1** in acetone-d_6 at 25 ℃

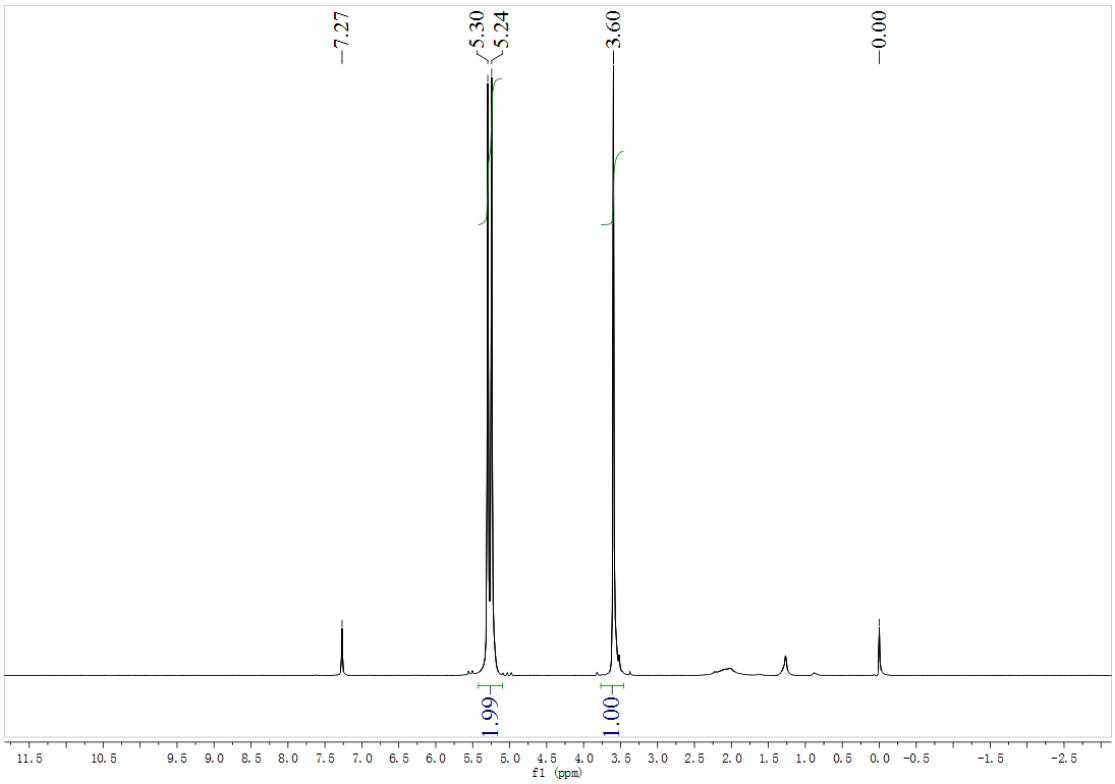

Fig. S3 ^{1}H-NMR spectra (300 MHz) of **2** in $CDCl_3$-d_6 at 25 ℃

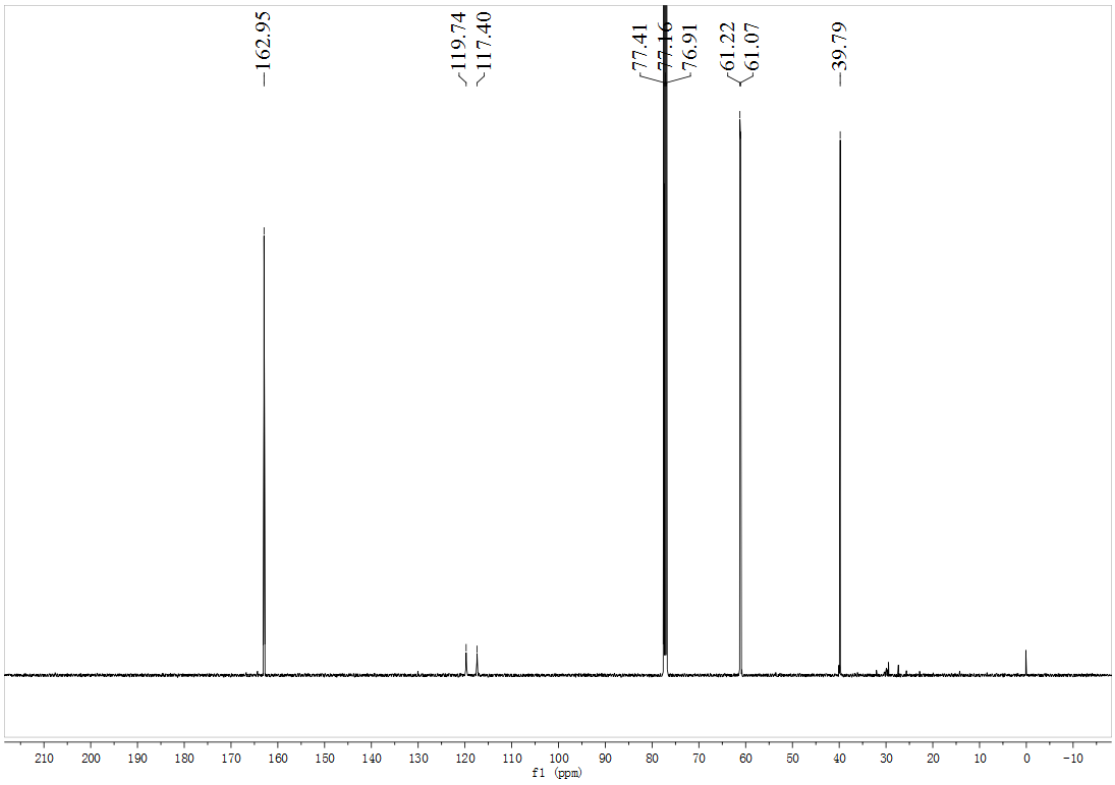

Fig. S4 ^{13}C-NMR spectra (126 MHz) of **2** in $CDCl_3$-d_6 at 25 ℃

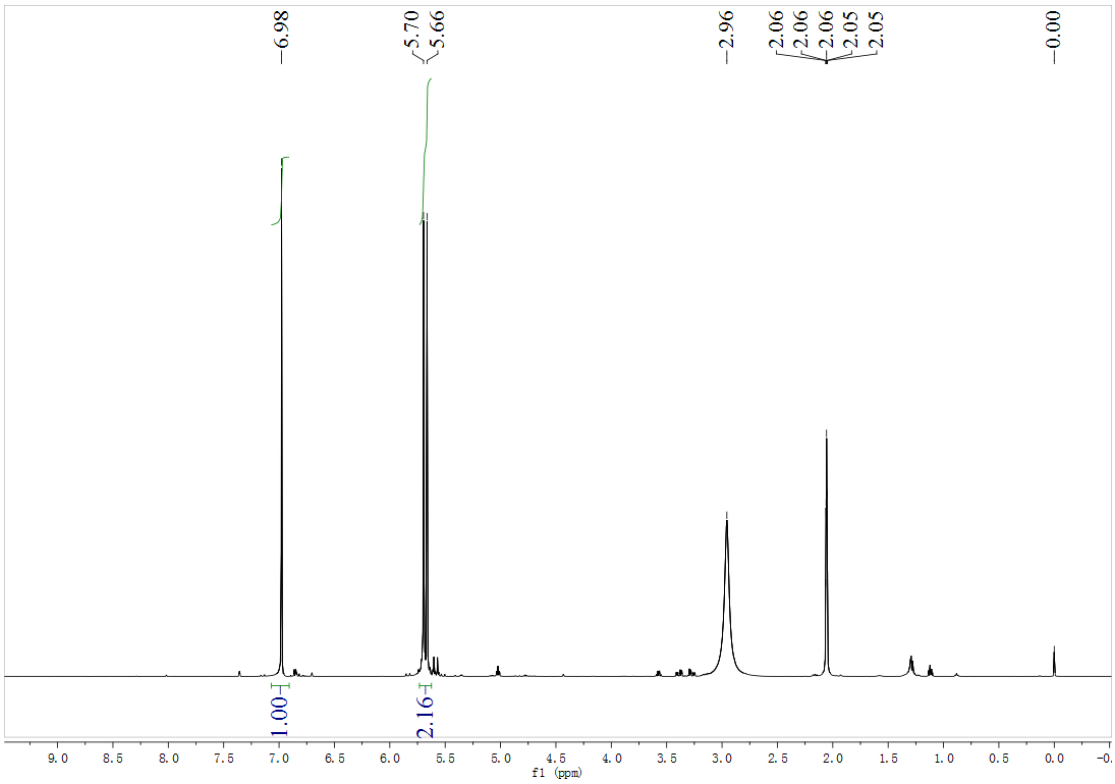

Fig. S5 ^{1}H-NMR spectra (300 MHz) of **3** in acetone-d_6 at 25 ℃

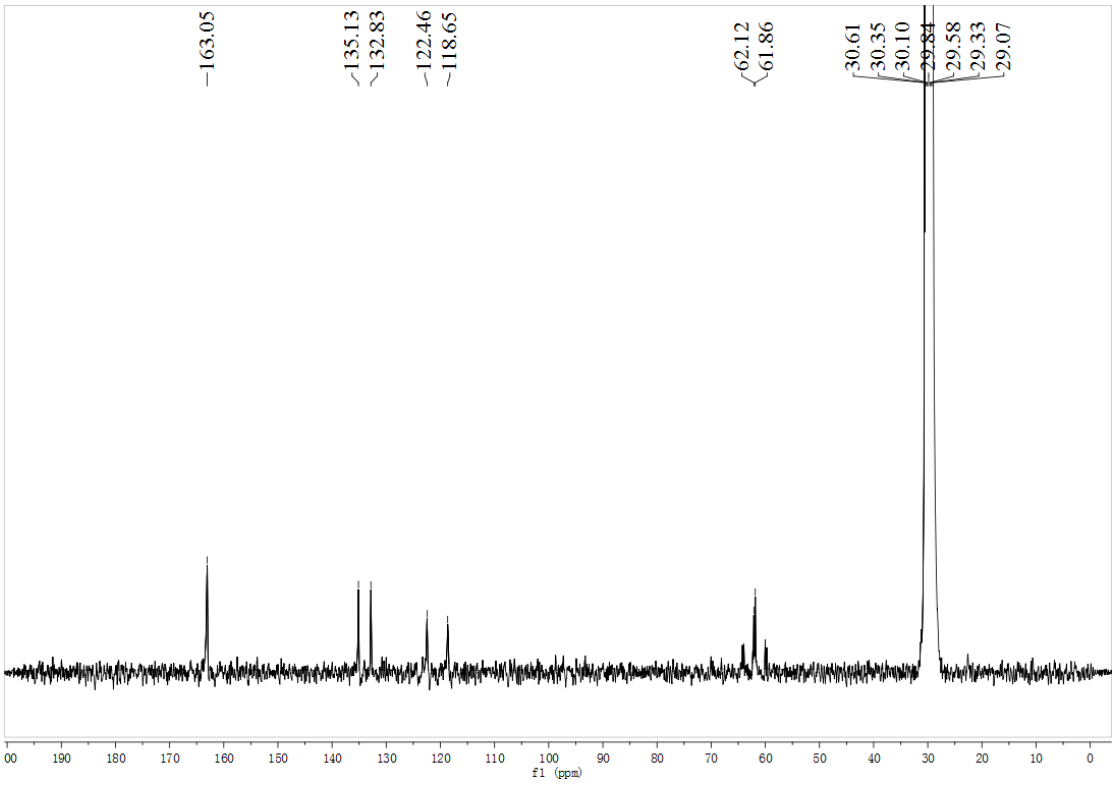

Fig. S6 ^{13}C-NMR spectra (75 MHz) of **3** in acetone-d_6 at 25 ℃

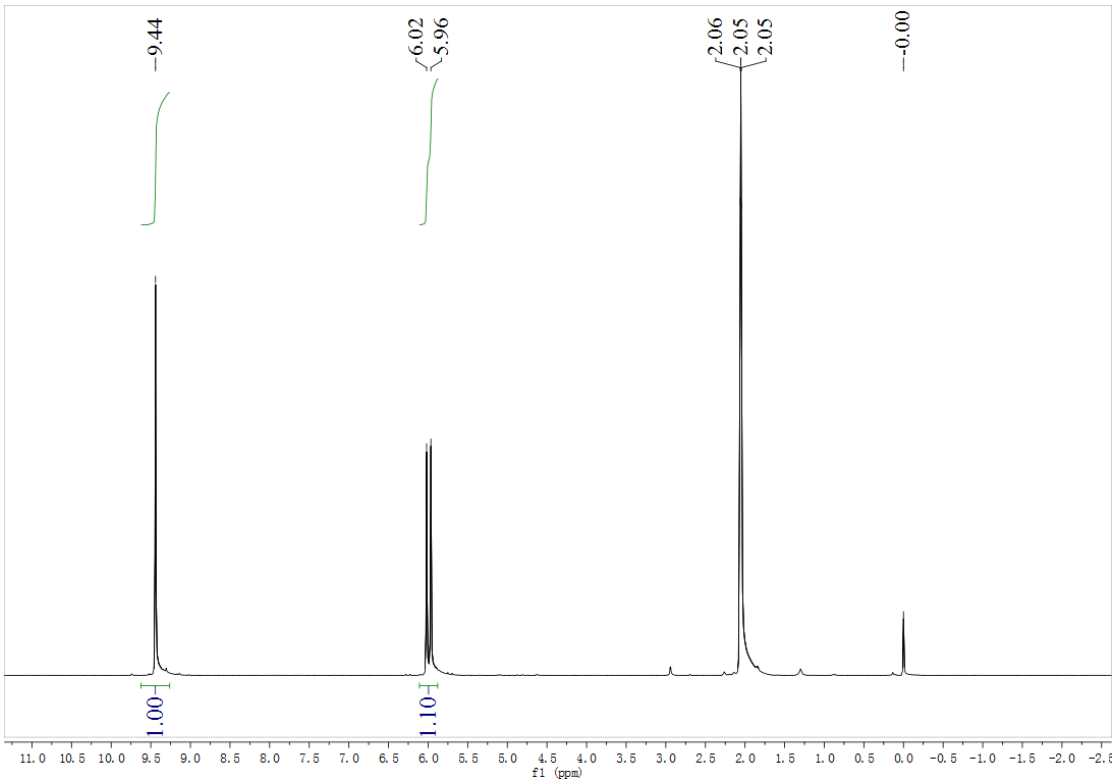

Fig. S7 ^{1}H-NMR spectra (300 MHz) of **4** in acetone-d_6 at 25 ℃

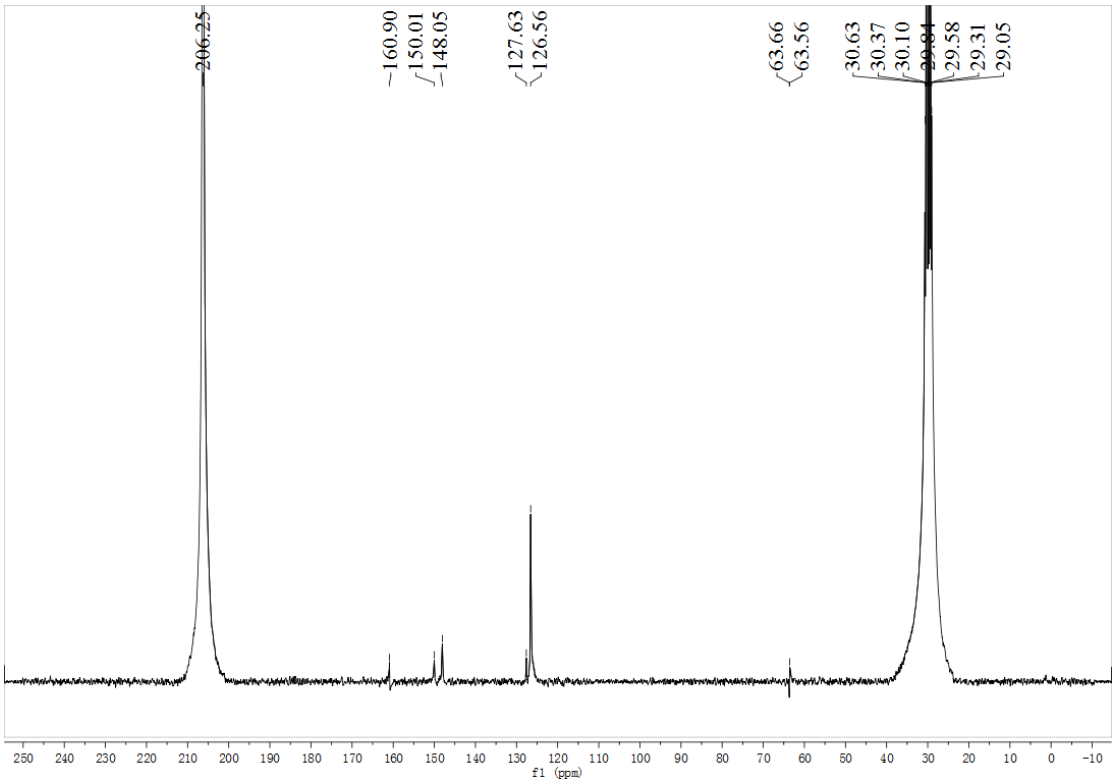

Fig. S8 ^{13}C-NMR spectra (75 MHz) of **4** in acetone-d_6 at 25 ℃

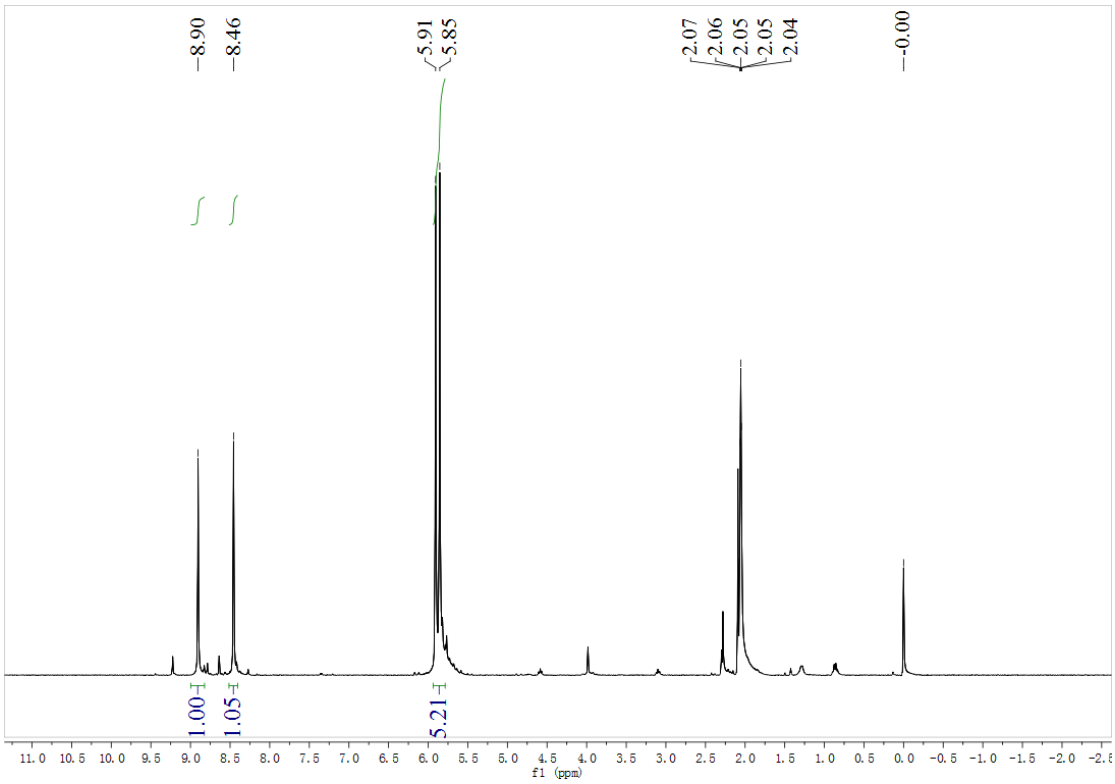

Fig. S9 ^{1}H-NMR spectra (300 MHz) of **5** in acetone-d_6 at 25 ℃

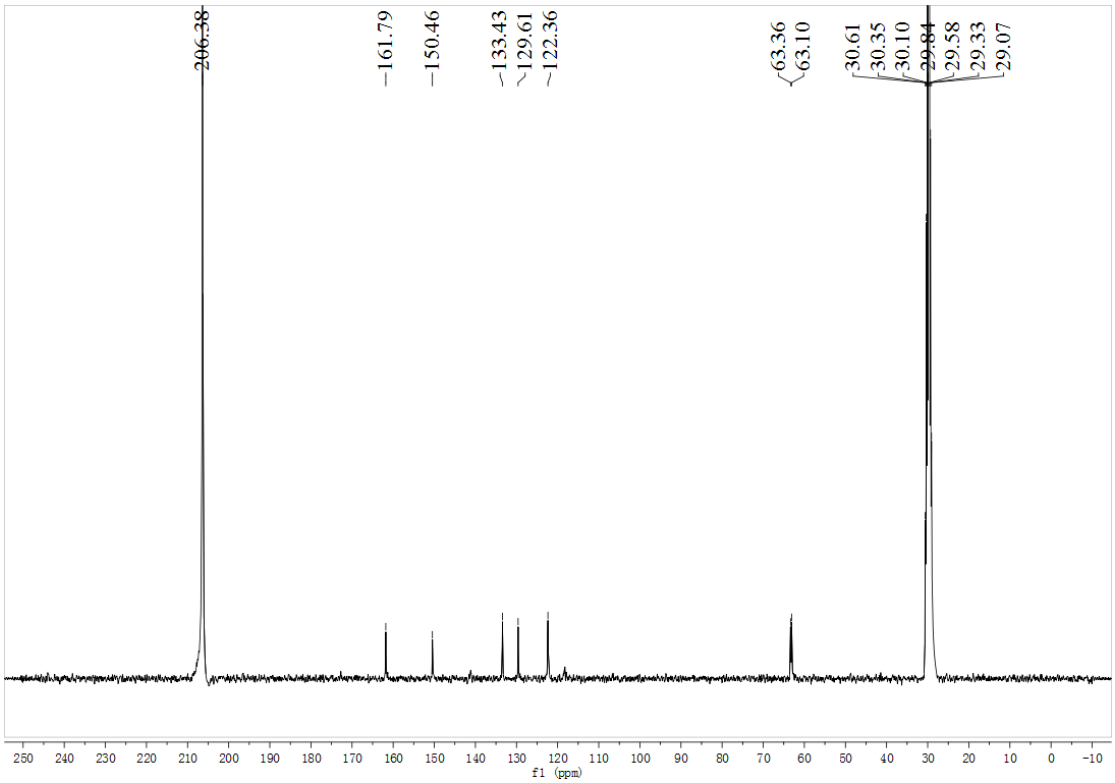

Fig. S10 ^{13}C-NMR spectra (75 MHz) of **5** in acetone-d_6 at 25 ℃

5. Mass spectra of compounds 1-5

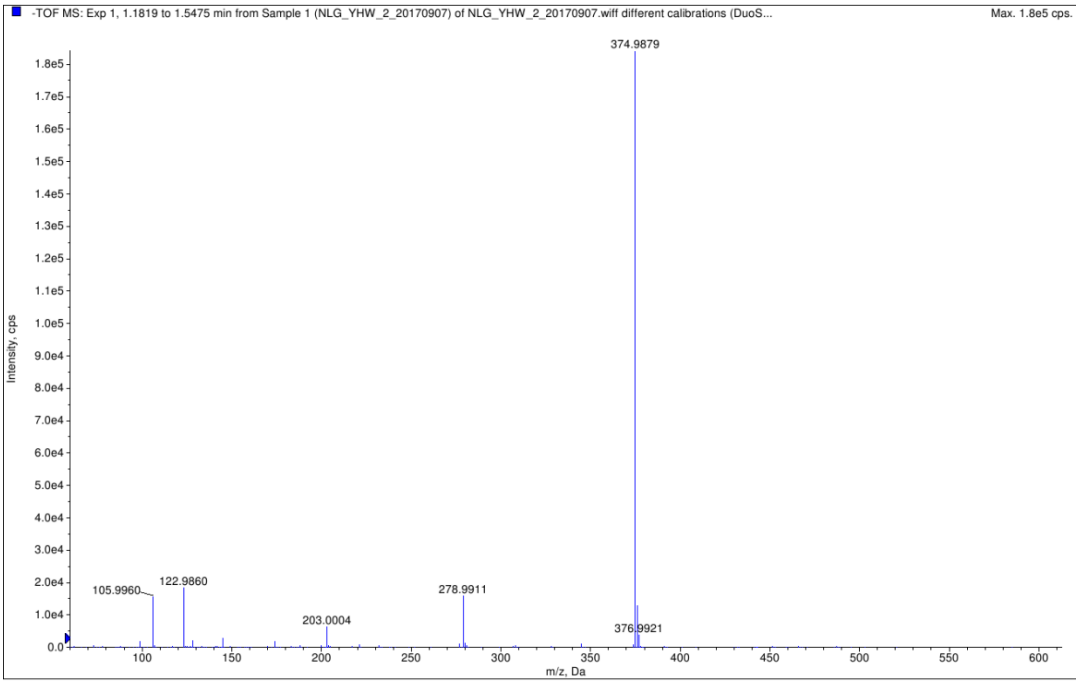

Fig. S11 Mass spectrum of **2**

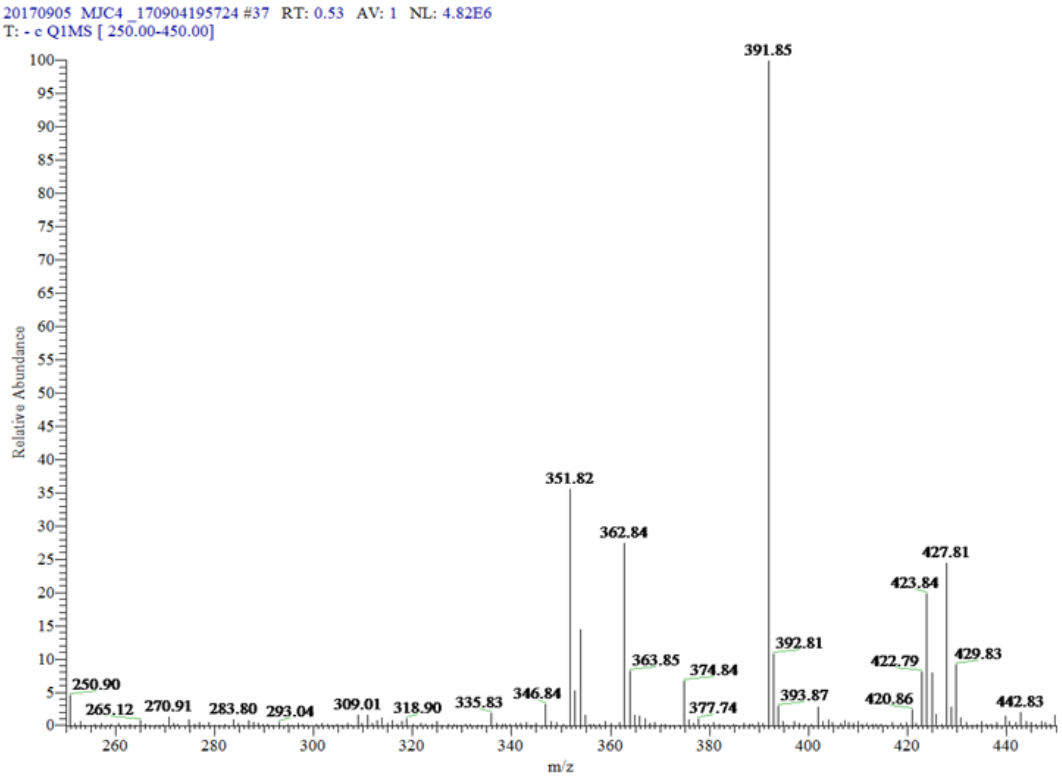

Fig. S12 Mass spectrum of **4**

6. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) curves of compounds 1-5

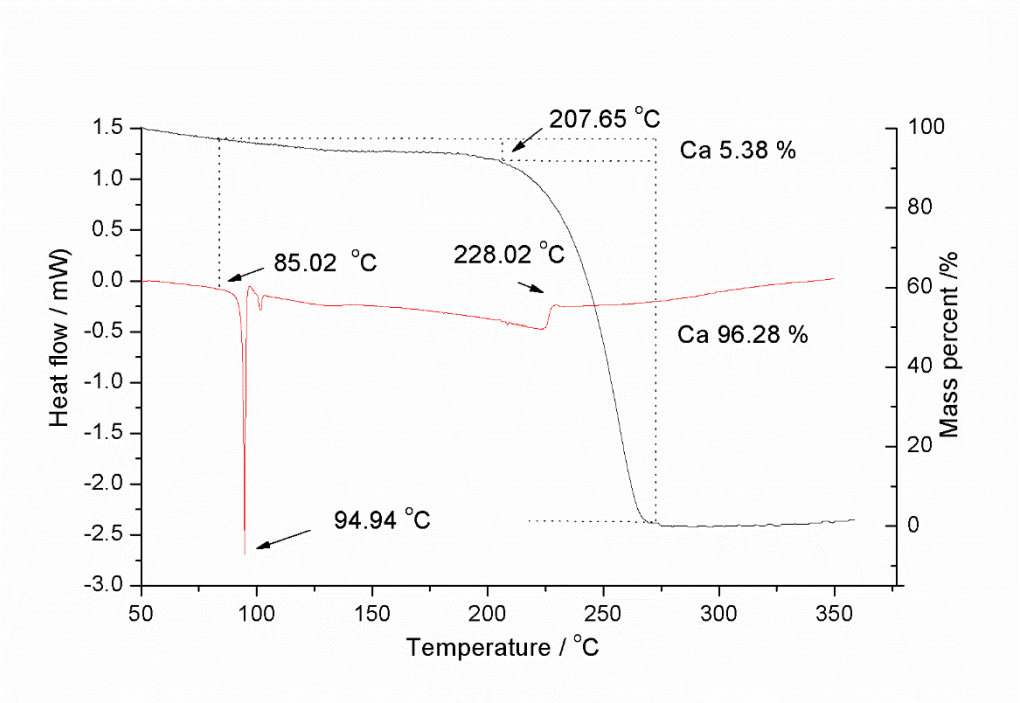

Fig. S13 TG and DSC curves of **1** under nitrogen with a heating rate of 5 °C min^{-1}.

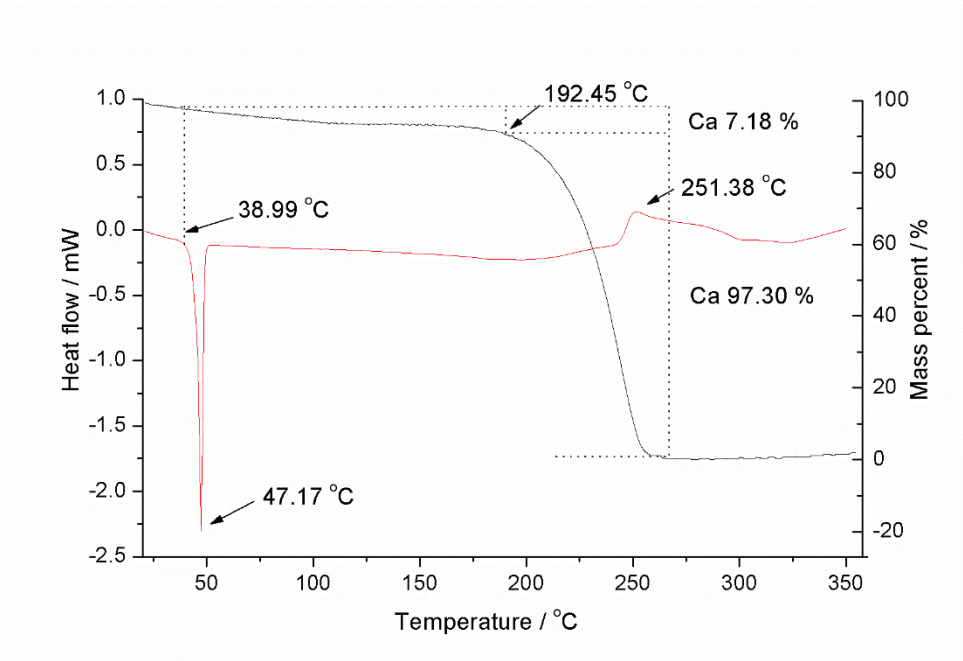

Fig. S14 TG and DSC curves of **2** under nitrogen with a heating rate of 5 °C min^{-1}.

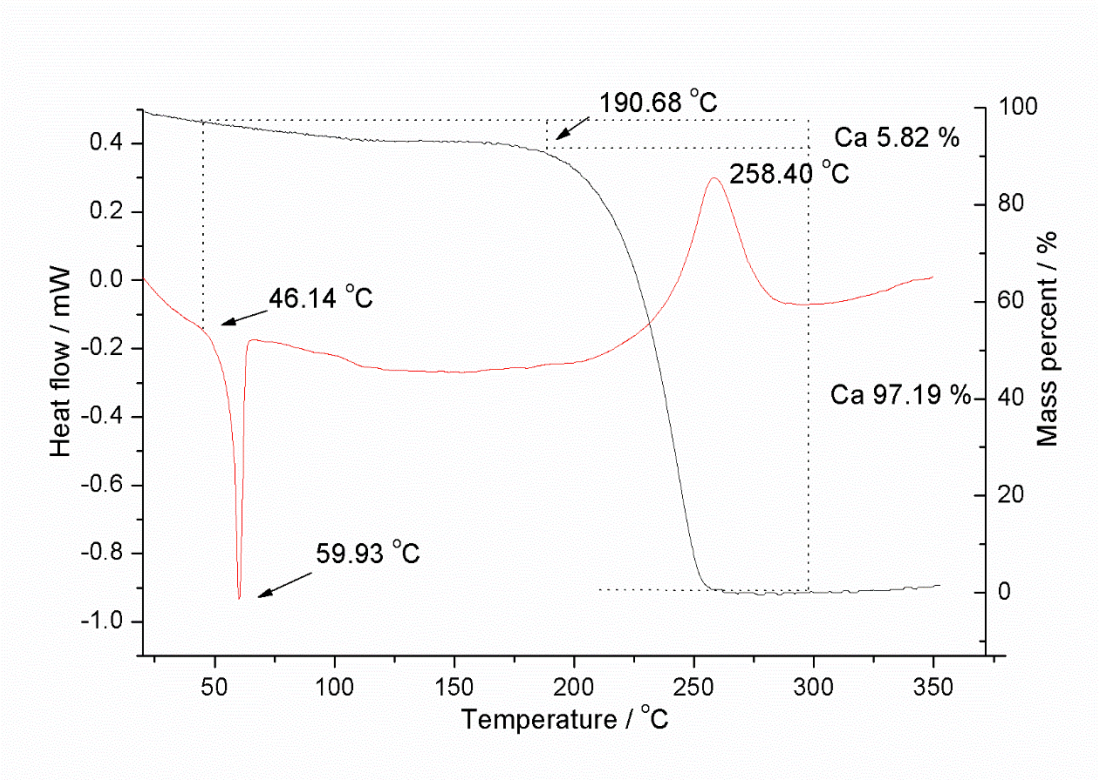

Fig. S15 TG and DSC curves of **3** under nitrogen with a heating rate of 5 °C min^{-1}.

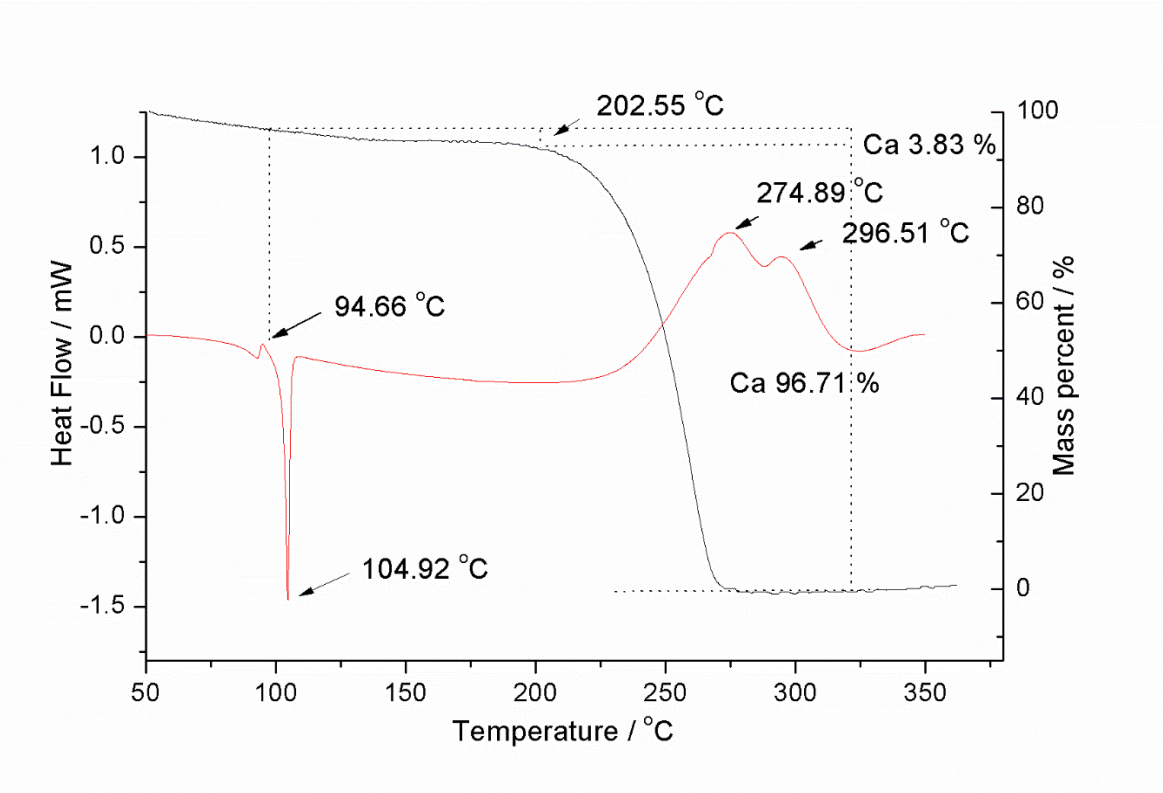

Fig. S16 TG and DSC curves of **4** under nitrogen with a heating rate of 5 °C min^{-1}.

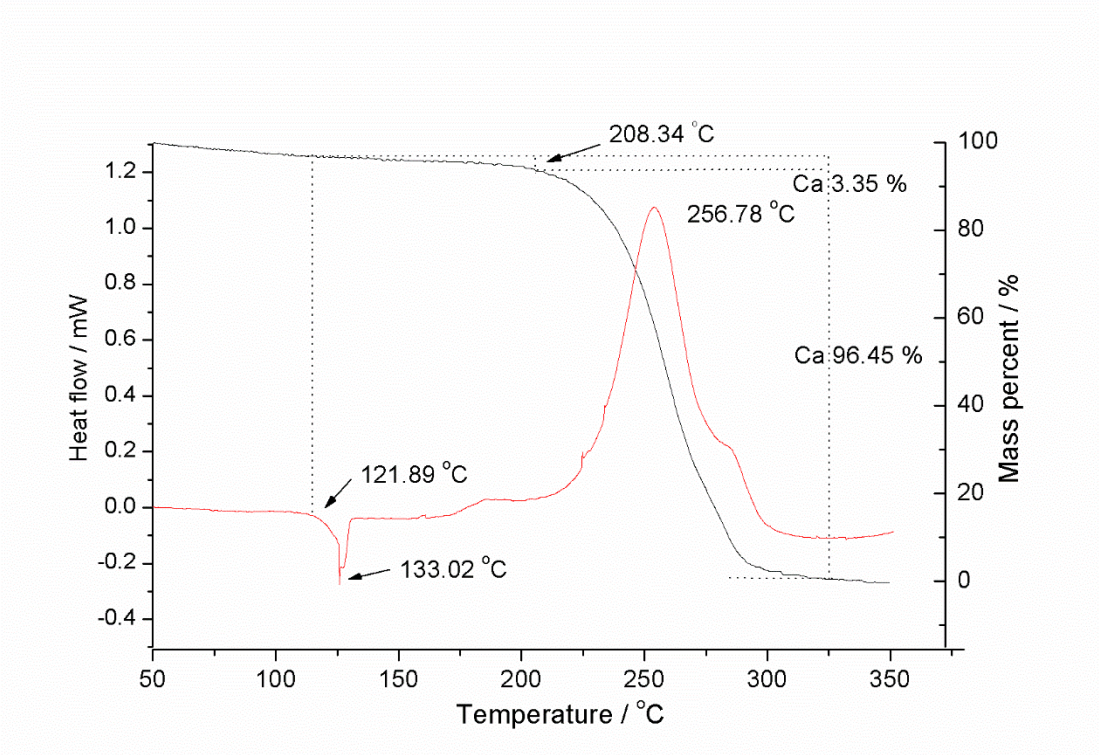

Fig. S17 TG and DSC curves of **5** under nitrogen with a heating rate of 5 °C min^{-1}.

Table S6 Rate of evaporation of compound **1-5** calculated based on the TG curves

Compound	Weight loss[%]	T_m[°C]	T_{dec}[°C]	Time[min]	Rate of evaporation[%/min]
1	5.38	85.0	207.7	24.5	0.22
2	7.18	39.0	192.5	30.7	0.23
3	5.82	46.1	190.7	28.9	0.20
4	3.83	94.7	202.6	21.6	0.18
5	3.35	121.9	208.3	17.3	0.19

7. Compatibility of compound 1 & 4 with RDX

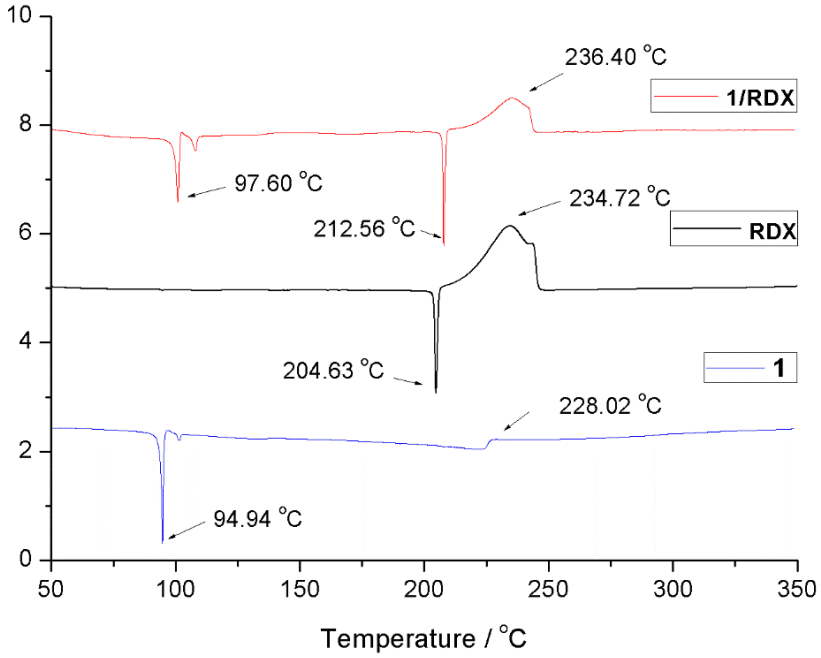

Fig. S18 DSC curves of single and mixture systems

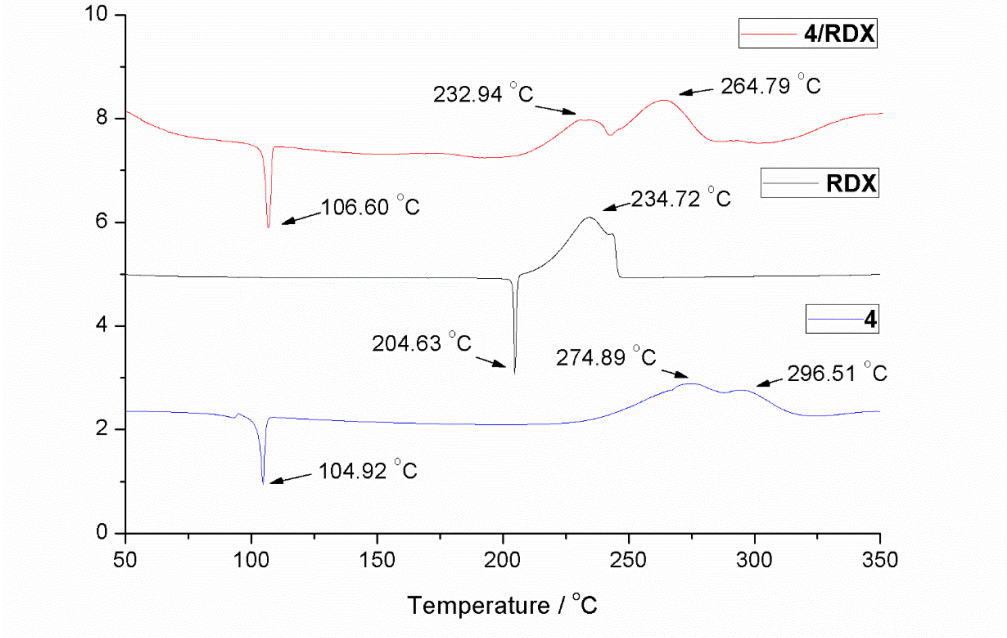

Fig. S19 DSC curves of single and mixture systems

Table S7 Evaluation standards of the compatibility for explosives and contacted material

Criteria ΔT_p [^oC]	Rating	Note
≤ 2	A---Compatible or good compatibility	Safe for use in any explosive
3-5	B---Slightly sensitized or fair compatibility	Safe for use in testing, when the device will be used in a very short period of time; not to be used as a binder material, or when long-term storage is desired
6-15	C---Sensitized or poor compatibility	Not recommended for use with explosive items
>15	D---Hazardous or bad compatibility	Hazardous. Do not use under any conditions