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An Unexpected Way to Synthesis 1,2,4-Oxadiazolone Derivatives: a class of Insensitive Energetic Materials

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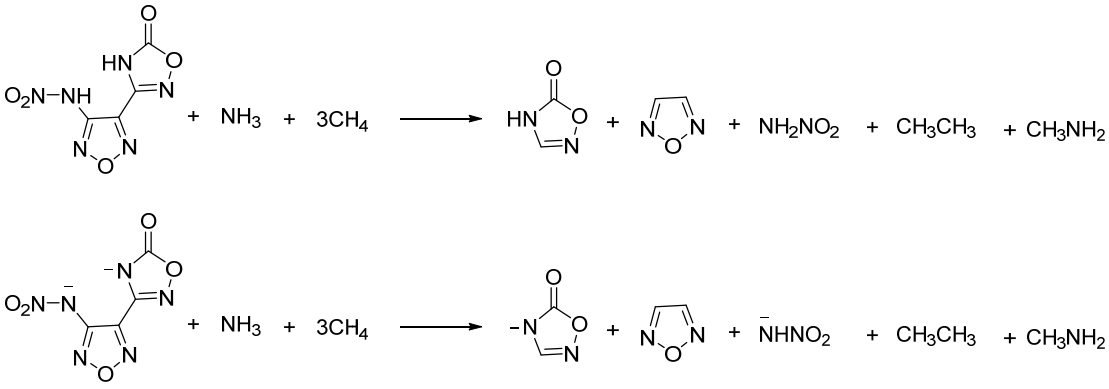
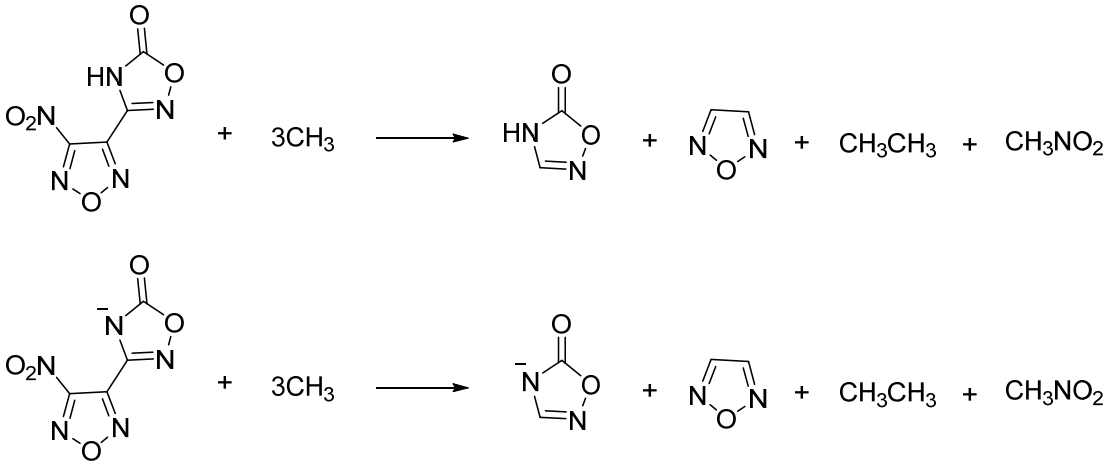
1. Computational Details

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]

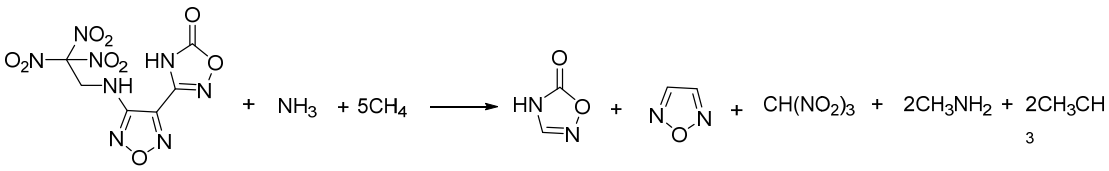
The predictions of heats of formation (HOF) used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (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 **3**-**12** are shown in Scheme S1-Scheme S5.



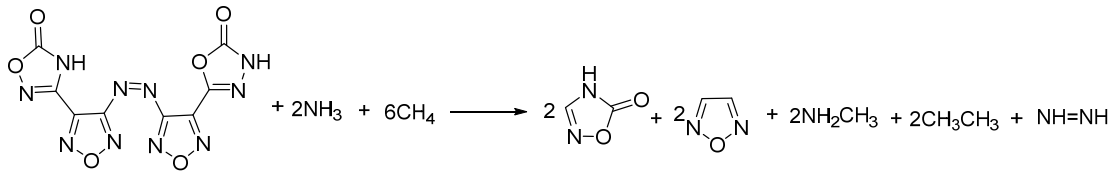
Scheme S1 Isodemic reactions of N-(4-(5-oxo-4,5-dihydro-1,2,4-oxadiazol-3-yl)-1,2,5-oxadiazol-3-yl)nitramide and its anion.



Scheme S2 Isodemic reactions of 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4H)-one and its its anion.



Scheme S3 Isodemic reactions of 3-(4-((2,2,2-trinitroethyl)amino)-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazol-5(4H)-one.



Scheme S4 Isodemic reactions of (Z)-3,3'-(diazene-1,2-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(1,2,4-oxadiazol-5(4H)-one).

The change of enthalpy for the reactions at 298K can be expressed by Equation (1):

$$\Delta H_{298} = \Sigma\Delta_f H_P - \Sigma\Delta_f H_R \qquad (1)$$

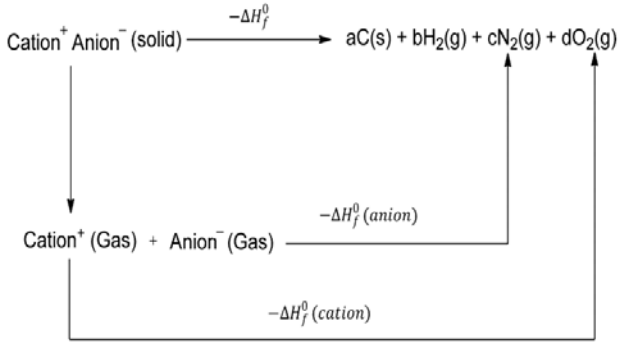
Where $\Sigma\Delta_f H_P$ and $\Sigma\Delta_f H_R$ are the HOF of t,e reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression in Equation (2):

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

where 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 (2), apart from target compound all the others are called reference compounds. The HOF of reference compounds are available either from experiments or from he high level computing such as CBS-4M.

Based on a Born-Haber energy cycle (Scheme S5), the heat of formation of a salt can be simplified by Equation (3):

$$\Delta H_f°(\text{ionic salt, 298 K}) = \Delta H_f°(\text{cation, 298 K}) + \Delta H_f°(\text{anion, 298 K}) - \Delta H_L \qquad (3)$$



Scheme S5 Born–Haber cycle for the formation of energetic salts

where ΔH_L is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al.[4] as given in Equation (4):

$$\Delta H\text{L} = \text{UPOT} + [p(nM/2-2) + q(nX/2-2)]RT \qquad (4)$$

where n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy *U*POT takes the form of equation (5):

$$U\text{POT}(\text{kJ·mol}^{-1}) = \gamma(\rho_m/M_m)1/3 + \delta \qquad (5)$$

where ρ_m is the density (g·cm^{-3}), M_m is the chemical formula mass of the ionic material and the coefficients γ ($\text{kJ·mol}^{-1}\text{cm}$) and δ (kJ·mol^{-1}) are 8375.6 and -178.8, respectively.

Table S1 Total energy and heat of formation for the title compounds at B3LYP/6-311+G** level

Compound	E_0[a]/a.u.	ZPE[b]/kJ mol^{-1}	H_T[c]/ kJ mol^{-1}	HOF[d]/ kJ mol^{-1}
CH_4	-40.5339263	112.26	10.04	-74.6[e]

NH_3	-56.5826356	86.27	10.05	-45.9[e]
CH_3CH_3	-79.8565413	187.31	11.79	-84[e]
CH_3NH_2	-95.8938402	160.78	11.64	-22.5[e]
NH_2NO_2	-261.1248168	98.79	12.39	-3.9[e]
CH_3NO_2	-245.0915559	124.93	11.6	-80.8[e]
CH_3NHCH_3	-135.2095645	231.80	14.35	-18.80[e]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.40[e]
NH=NH	-110.6795238	70.35	10.03	194.97[e]
1,2,4-oxadiazole-5(4H)-one	-337.4295337	128.36	14.48	-128.96[f]
1,2,4-oxadiazole-5(4H)-one$^-$	-336.894443	95.94	13.5	-285.12[f]
1,2,5-oxadizole	-262.1183629	114.62	11.84	215.72[f]
$NHNO_2^-$	-250.5730748	65.76	11.37	-120.22[f]
ammonium	-56.9203229	124.71	9.98	626.4[f]
hydrazinium	-112.2417207	166.02	9.56	770.0[f]
hydroxylammonium	-132.0863677	137.06	8.72	664.4[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] Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL.]. [f] Data obtained from CBS-4M calculation in combination with the atomization reaction of the corresponding compound.

2. Single-crystal X-ray Diffraction Analysis of Compound **2**·H_2O

Table S2 Selected bond lengths [Å] and angles [°] for **2**·H_2O

O1-N1	1.420(2)	N2-C2	1.361(3)
O1-C2	1.368(3)	N3-C3	1.311(3)
O2-N3	1.408(3)	N4-C4	1.301(3)
O2-N4	1.369(3)	N5-C3	1.343(4)
O3-C2	1.206(3)	N2-H2A	0.89(3)
O4-H4C	0.84(3)	N5-H5B	0.87(3)
O4-H4D	0.84(3)	N5-H5A	0.92(3)
N1-C1	1.298(3)	C1-C4	1.449(3)
N2-C1	1.361(3)	C3-C4	1.434(3)
N1 -O1-C2	109.28(16)	N2-C1-C4	126.2(2)
N3 -O2-N4	110.96(16)	N1-C1-N2	112.8(2)
H4C-O4-H4D	107(3)	N1-C1-C4	121.0(2)
O1 -N1-C1	104.39(17)	O1-C2-N2	106.10(19)
C1 -N2-C2	107.4(2)	O1-C2-O3	122.5(2)
O2 -N3-C3	105.16(18)	O3-C2-N2	131.4(2)
O2 -N4-C4	105.71(18)	N3-C3-C4	108.3(2)
C2 -N2-H2A	124.1(16)	N3-C3-N5	124.5(2)
C1 -N2-H2A	128.4(16)	N5-C3-C4	127.3(2)
H5A-N5-H5B	121(3)	C1-C4-C3	127.4(2)
C3 -N5-H5B	119.3(19)	N4-C4-C1	122.7(2)
C3 -N5-H5A	119.0(18)	N4-C4-C3	109.9(2)

Table S3 Selected torsion angles for **2**·H_2O [°]

C2-O1-N1-C1	-0.2(2)	C1-N2-C2-O3	-179.2(3)
N1-O1-C2-O3	179.5(2)	C2-N2-C1-N1	-0.3(3)
N1-O1-C2-N2	0.1(2)	C1-N2-C2-O1	0.1(3)
N4-O2-N3-C3	0.6(2)	O2-N3-C3-N5	178.8(2)
N3-O2-N4-C4	-0.2(2)	O2-N3-C3-C4	-0.7(3)
O1-N1-C1-N2	0.3(3)	O2-N4-C4-C3	-0.3(3)
O1-N1-C1-C4	-178.8(2)	O2-N4-C4-C1	180.0(2)
C2-N2-C1-C4	178.8(2)	N2-C1-C4-C3	-173.5(2)
N2-C1-C4-N4	6.2(4)	N5-C3-C4-C1	1.0(4)
N1-C1-C4-C3	5.4(4)	N3-C3-C4-C1	-179.6(2)
N1-C1-C4-N4	-174.8(2)	N5-C3-C4-N4	-178.8(3)
N3-C3-C4-N4	0.7(3)		

Table S4 Hydrogen bonds for **2**·H_2O [Å and °]

D—H···A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N2-H2A···O4	0.89(3)	1.94(3)	2.800(3)	162(2)
O4-H4C···O4	0.84(3)	2.09(3)	2.885(3)	157(3)
O4-H4D···N3	0.84(3)	2.24(3)	3.023(3)	155(3)
N5-H5A···O1	0.92(3)	2.56(3)	2.939(3)	106(2)
N5-H5A···O3	0.92(3)	1.97(3)	2.876(3)	168(3)
N5-H5B···N1	0.87(3)	2.36(3)	2.952(3)	125(2)
N5-H5B···N1	0.87(3)	2.53(3)	3.158(3)	130(2)

3. Single-crystal X-ray Diffraction Analysis of **4**·H_2O

Table S5 Selected bond lengths [Å] and angles [°] for **4**·H_2O

O1-N1	1.3673	N1-C1	1.2960
O1-N2	1.3790	N2-C2	1.3021
O2-N3	1.2157	N3-C1	1.4592
O3-N3	1.2140	N4-C3	1.2899
O4-N4	1.4265	N5-C4	1.3549
O4-C4	1.3583	N5-C3	1.3615
O5-C4	1.2120	N5-H5	0.9100
O6-H6B	0.8100	C1-C2	1.4206
O6-H6A	0.8200	C2-C3	1.4639
N1-O1-N2	111.36	N1-C1-C2	110.40
N4-O4-C4	109.54	N1-C1-N3	118.94
H6A-O6-H6B	103.00	N3-C1-C2	130.65
O1-N1-C1	104.73	N2-C2-C1	107.69
O1-N2-C2	105.80	N2-C2-C3	118.63
O2-N3-O3	125.96	C1-C2-C3	133.67
O3-N3-C1	116.74	N5-C3-C2	121.69
O2-N3-C1	117.30	N4-C3-N5	113.57

O4-N4-C3	117.30	N4-C3-C2	124.74
C3-N5-C4	106.94	O4-C4-O5	123.33
C3-N5-H5	130.00	O4-C4-N5	106.40
C4-N5-H5	124.00	O5-C4-N5	130.27

Table S6 Selected torsion angles for **4**·H_2O [°]

N2-O1-N1-C1	1.35	O3-N3-C1-C2	27.68
N1-O1-N2-C2	-1.57	O4-N4-C3-N5	0.18
C4-O4-N4-C3	0.74	O4-N4-C3-C2	179.86
N4-O4-C4-N5	-1.35	C4-N5-C3-C2	179.29
N4-O4-C4-O5	178.46	C3-N5-C4-O4	1.42
O1-N1-C1-C2	-0.63	C3-N5-C4-O5	-178.38
O1-N1-C1-N3	178.77	C4-N5-C3-N4	-1.03
O1-N2-C2-C3	179.97	N3-C1-C2-C3	1.75
O1-N2-C2-C1	1.11	N1-C1-C2-N2	-0.32
O2-N3-C1-N1	28.16	N1-C1-C2-C3	-178.94
O3-N3-C1-N1	-151.58	N3-C1-C2-N2	-179.63
O2-N3-C1-C2	-152.58	N2-C2-C3-N4	165.39
C1-C2-C3-N4	-16.11	C1-C2-C3-N5	163.54
N2-C2-C3-N5	-14.96		

Table S7 Hydrogen bonds for **4**·H_2O [Å and °]

D—H···A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N5-H5···O6	0.9100	1.7900	2.6905	167.00
O6-H6A···O5	0.8200	2.0600	2.8672	165.00
O6-H6B···O5	0.8100	1.9800	2.7825	167.00

4. Single-crystal X-ray Diffraction Analysis of Compound 7

Table S8 Selected bond lengths [Å] and angles [°] for **7**

O1-N1	1.408(4)	N6-C3	1.365(5)
O1-N2	1.378(4)	N6-C4	1.330(4)
O2-N4	1.238(4)	N7-H7B	0.960(18)
O3-N4	1.253(4)	N7-H7C	0.938(19)
O4-N5	1.416(4)	N7-H7A	0.934(17)
O4-C4	1.372(4)	N7-H7D	0.95(3)
O5-C4	1.248(4)	N8-H8B	0.944(19)
N1-C1	1.316(4)	N8-H8C	0.94(2)
N2-C2	1.301(4)	N8-H8A	0.949(16)
N3-N4	1.329(4)	N8-H8D	0.95(2)
N3-C1	1.374(4)	C1-C2	1.440(5)
N5-C3	1.297(4)	C2-C3	1.462(4)
N1 -O1-N2	111.3(2)	H8A-N8-H8C	110(2)
N5 -O4-C4	107.6(2)	H8C-N8-H8D	110(2)
O1 -N1-C1	104.8(3)	H8A-N8-H8D	109(2)

O1 -N2-C2	105.5(3)	H8B-N8-H8C	111(2)
N4 -N3-C1	117.0(3)	H8B-N8-H8D	110(2)
O2 -N4-O3	121.4(3)	N1 -C1-C2	108.5(3)
O2 -N4-N3	124.7(3)	N3 -C1-C2	120.1(3)
O3 -N4-N3	114.0(3)	N1 -C1-N3	131.4(3)
O4 -N5-C3	102.5(3)	N2 -C2-C1	109.9(3)
C3 -N6-C4	103.2(3)	N2 -C2-C3	120.9(3)
H7B-N7-H7C	109(2)	C1 -C2-C3	129.3(3)
H7B-N7-H7D	107(2)	N5 -C3-N6	116.4(3)
H7C-N7-H7D	110(2)	N6 -C3-C2	122.9(3)
H7A-N7-H7C	111(2)	N5 -C3-C2	120.7(3)
H7A-N7-H7D	111(2)	O4 -C4-N6	110.3(3)
H7A-N7-H7B	109(2)	O5 -C4-N6	131.9(3)
H8A-N8-H8B	108(2)	O4 -C4-O5	117.8(2)

Table S9 Selected torsion angles of for **7** [°]

N2-O1-N1-C1	0.6(4)	O4-N5-C3-N6	0.1(4)
N1-O1-N2-C2	-1.1(4)	O4-N5-C3-C2	178.0(3)
N5-O4-C4-N6	1.4(4)	C4-N6-C3-C2	-177.1(3)
C4-O4-N5-C3	-0.9(3)	C3-N6-C4-O4	-1.3(4)
N5-O4-C4-O5	-176.8(3)	C3-N6-C4-O5	176.6(4)
O1-N1-C1-C2	0.1(4)	C4-N6-C3-N5	0.8(4)
O1-N1-C1-N3	180.0(3)	N3-C1-C2-C3	0.2(5)
O1-N2-C2-C3	-179.6(3)	N1-C1-C2-N2	-0.8(4)
O1-N2-C2-C1	1.1(4)	N1-C1-C2-C3	-180.0(3)
C1-N3-N4-O3	179.0(3)	N3-C1-C2-N2	179.3(3)
C1-N3-N4-O2	-1.5(5)	N2-C2-C3-N5	179.2(3)
N4-N3-C1-N1	-0.8(5)	C1-C2-C3-N5	-1.8(6)
N4-N3-C1-C2	179.1(3)	C1-C2-C3-N6	176.0(3)
N2-C2-C3-N6	-3.1(5)		

Table S10 Hydrogen bonds for **7** [Å and °]

D—H···A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N7-H7A···N3	0.934(17)	2.201(18)	3.123(4)	169(2)
N7-H7A···N5	0.934(17)	2.47(2)	2.975(4)	113.9(19)
N7-H7B···O5	0.960(18)	1.883(18)	2.842(4)	178.0(17)
N7-H7C···O3	0.938(19)	2.498(18)	3.265(4)	139(2)
N7-H7C···N3	0.938(19)	2.24(2)	3.153(4)	166(2)
N7-H7C···N4	0.938(19)	2.62(2)	3.512(4)	159(2)
N7-H7D···N1	0.95(3)	2.11(3)	3.026(4)	162(2)
N8-H8A···O5	0.949(16)	2.047(18)	2.932(4)	154(2)
N8-H8B···O3	0.944(19)	1.94(2)	2.856(4)	164(2)
N8-H8C···O4	0.94(2)	2.49(2)	3.056(4)	119(2)
N8-H8C···O5	0.94(2)	2.09(2)	3.010(4)	166(2)

5. ^{1}H NMR and ^{13}C NMR Spectra of Compounds 2-12.

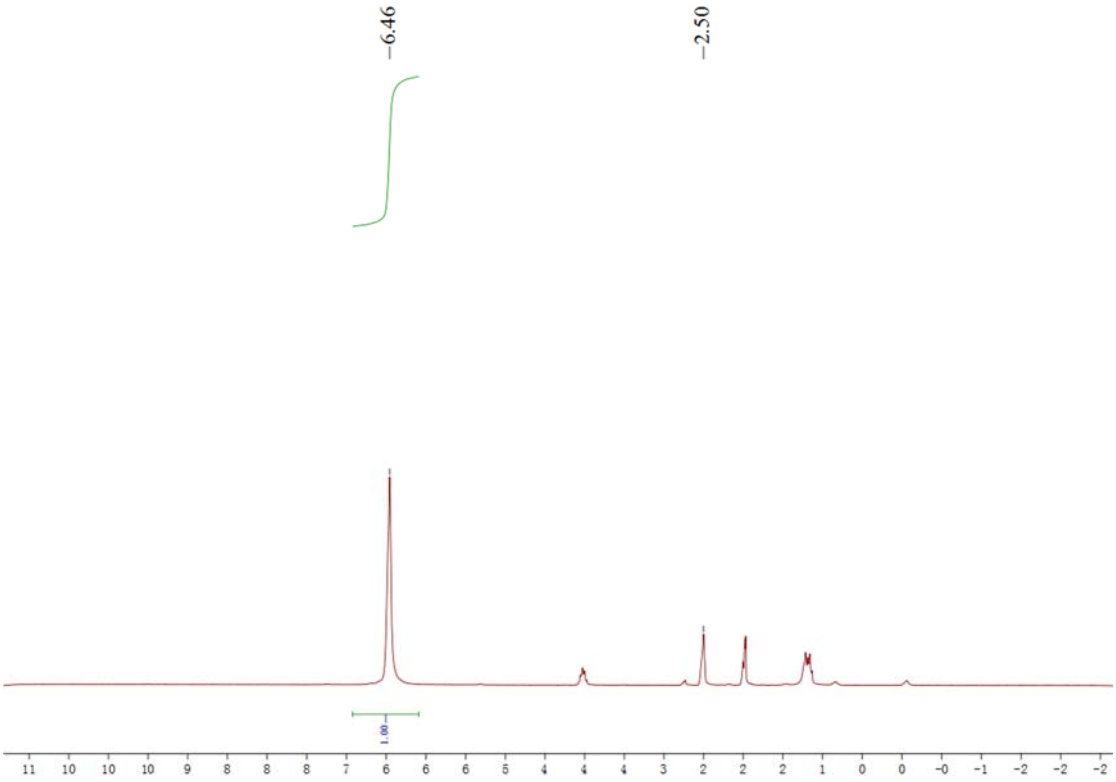


Figure S1 ^{1}H NMR spectrum of **2** in DMSO-d_6

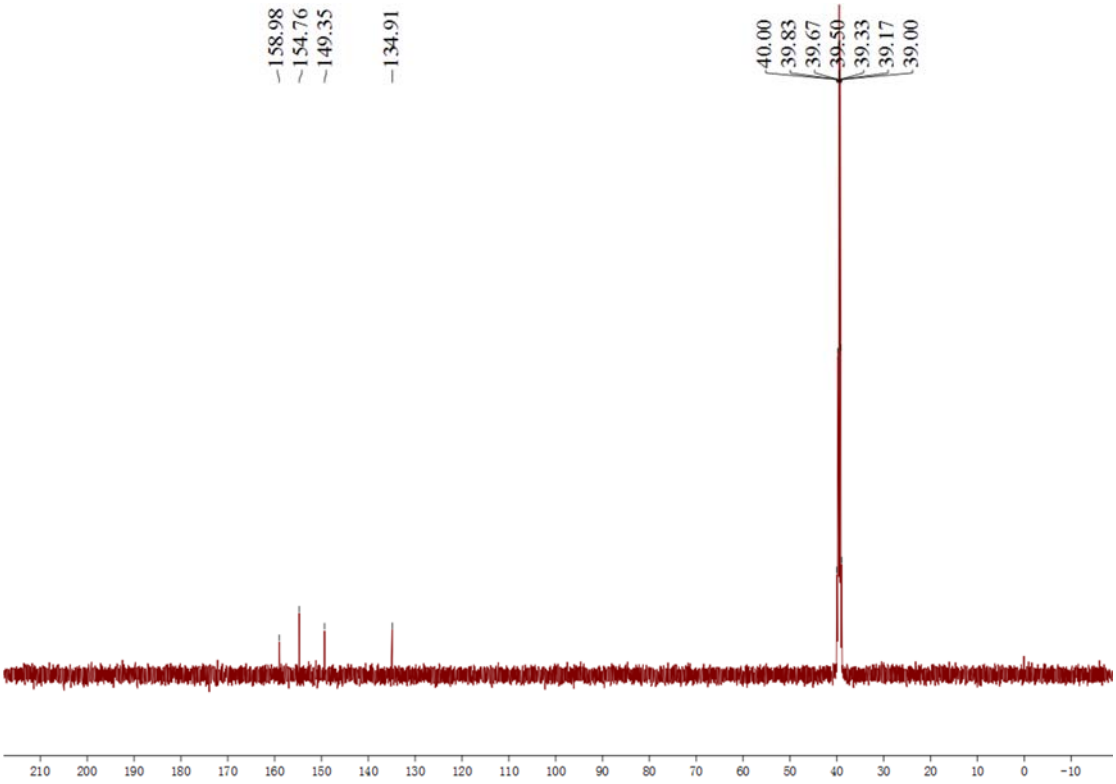


Figure S2 ^{13}C NMR spectrum of **2** in DMSO-d_6

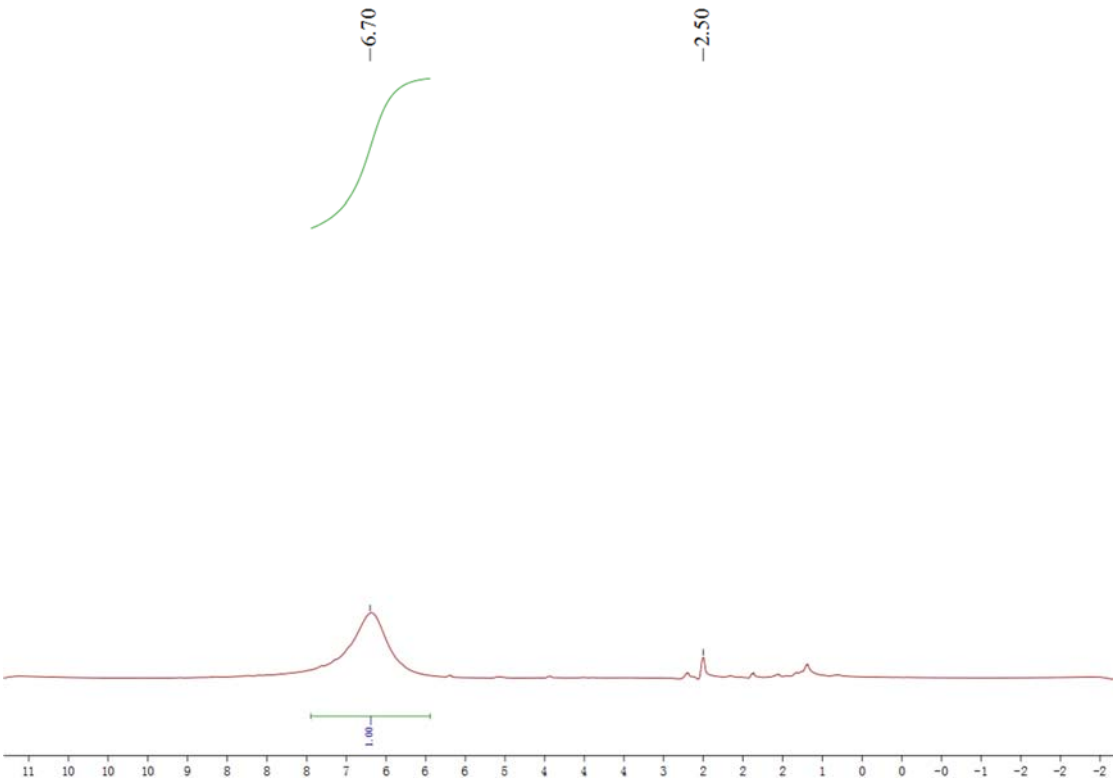


Figure S3 ^{1}H NMR spectrum of **3** in DMSO-d_6

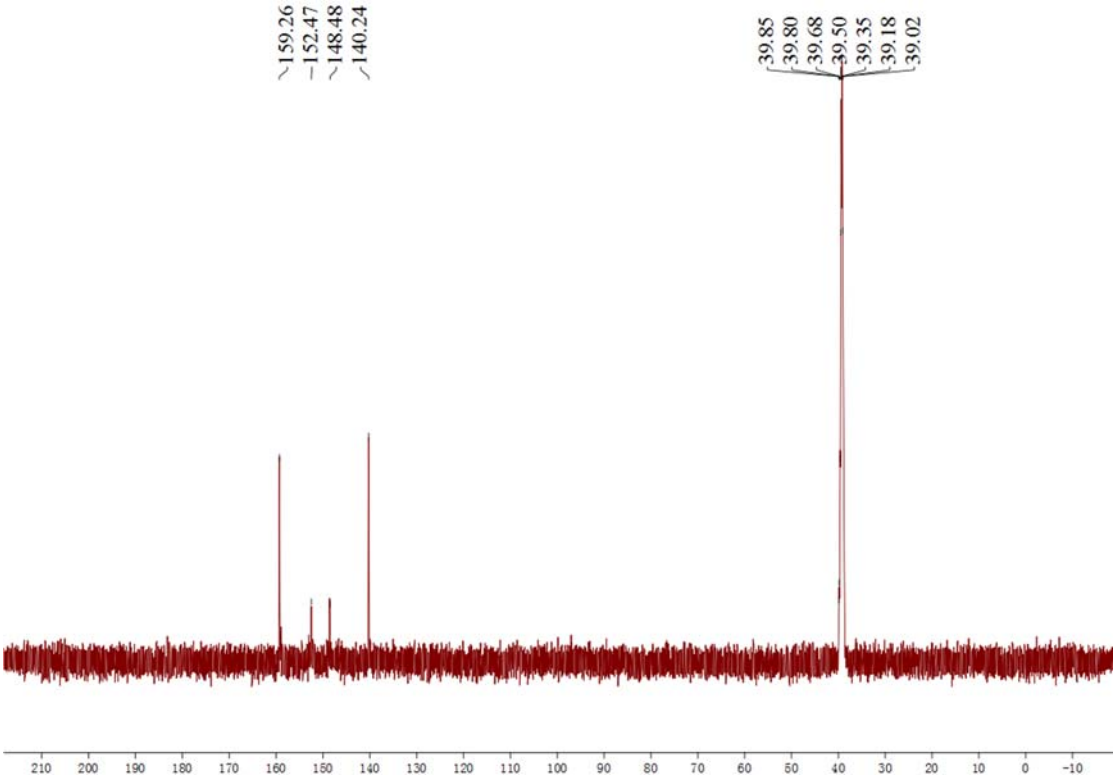


Figure S4 ^{13}C NMR spectrum of **3** in DMSO-d_6

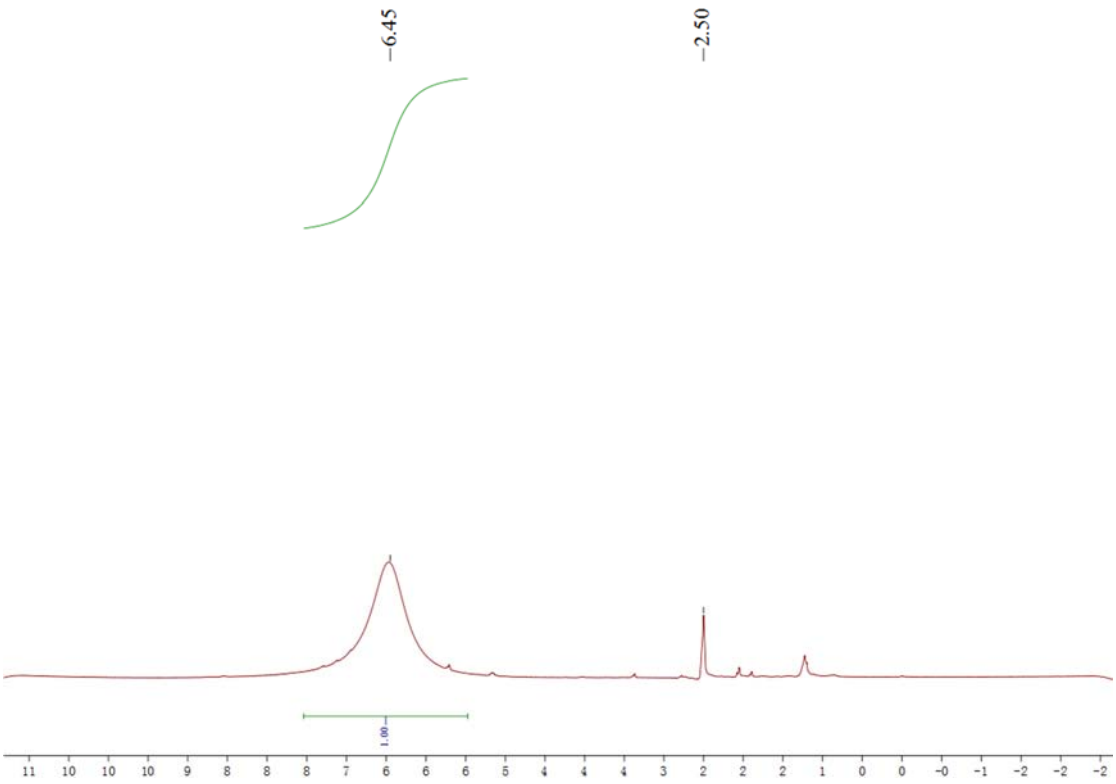


Figure S5 ^{1}H NMR spectrum of **4** in DMSO-d_6

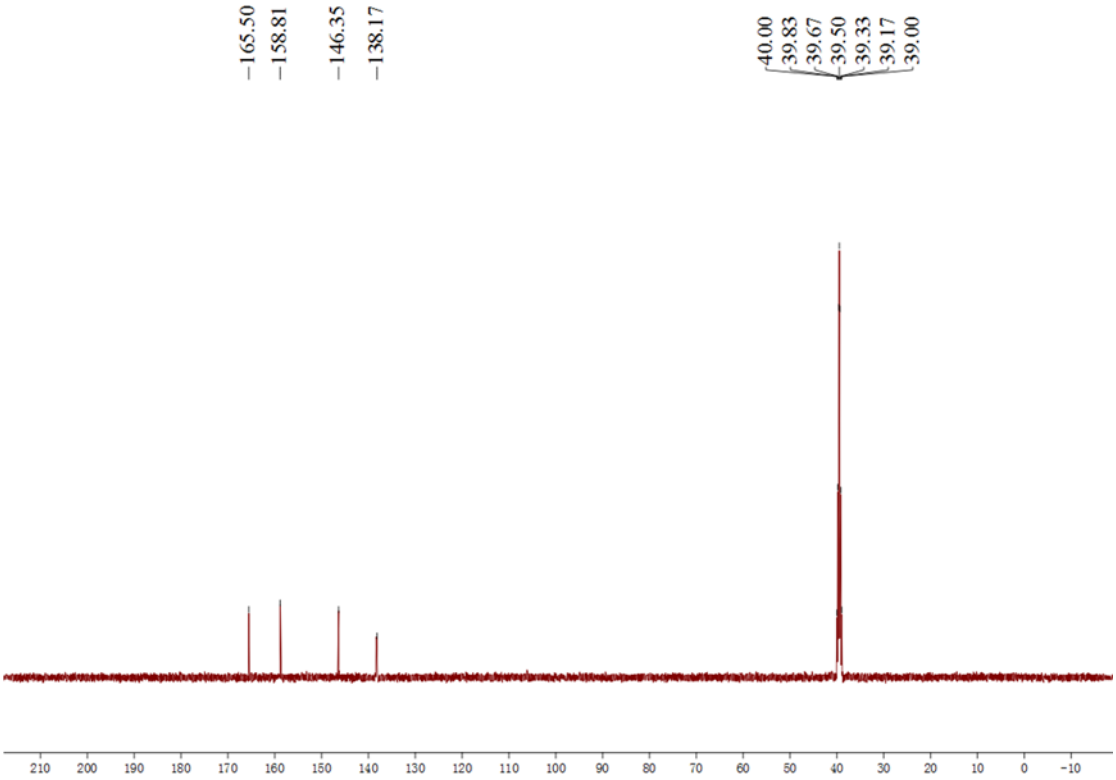


Figure S6 ^{13}C NMR spectrum of **4** in DMSO-d_6

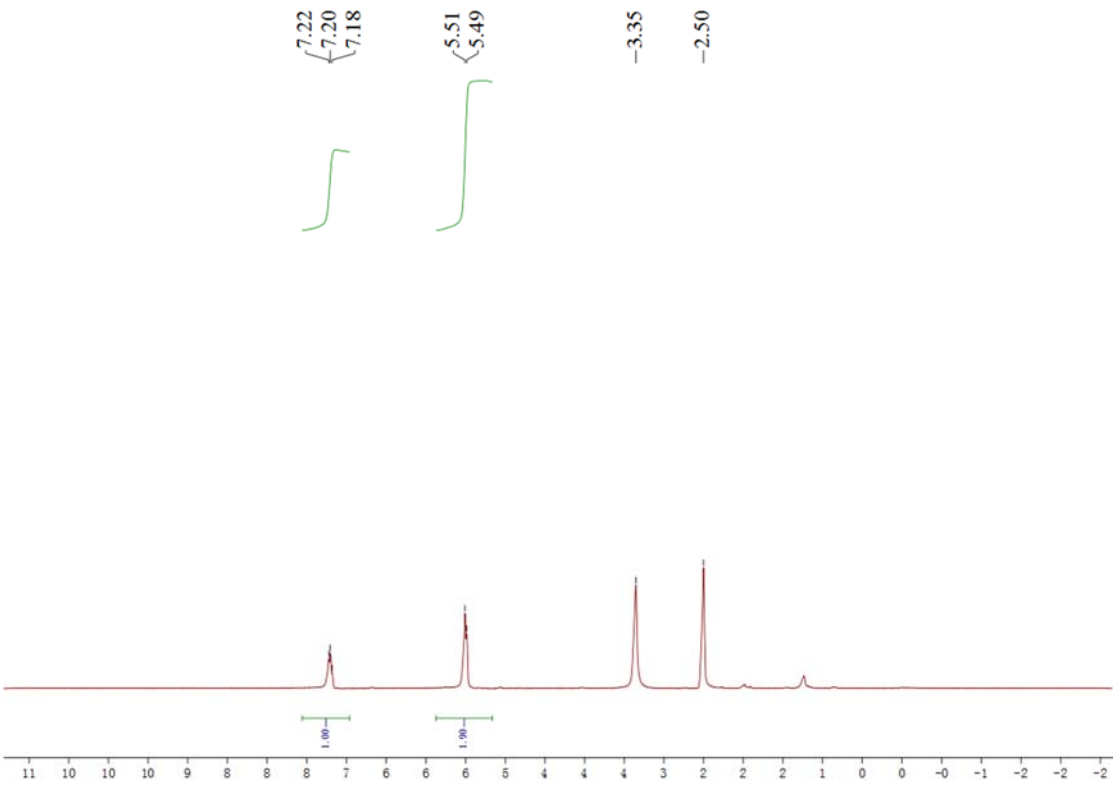


Figure S7 ^{1}H NMR spectrum of **5** in DMSO-d_6

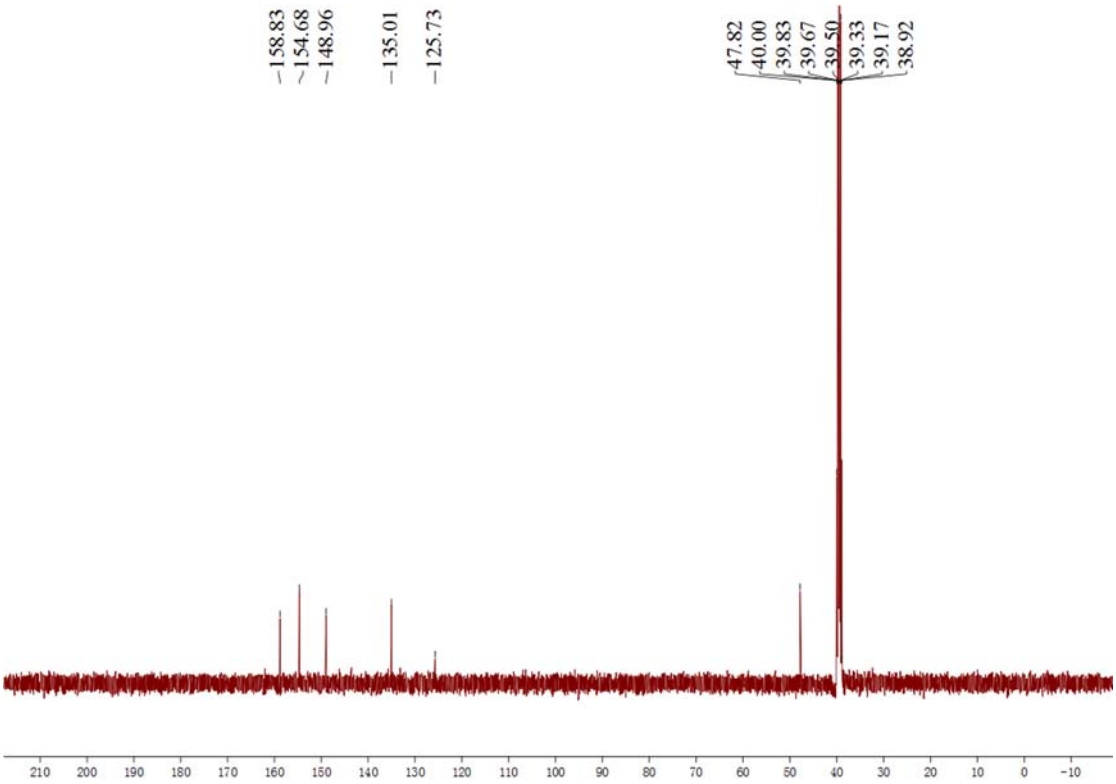


Figure S8 ^{13}C NMR spectrum of **5** in DMSO-d_6

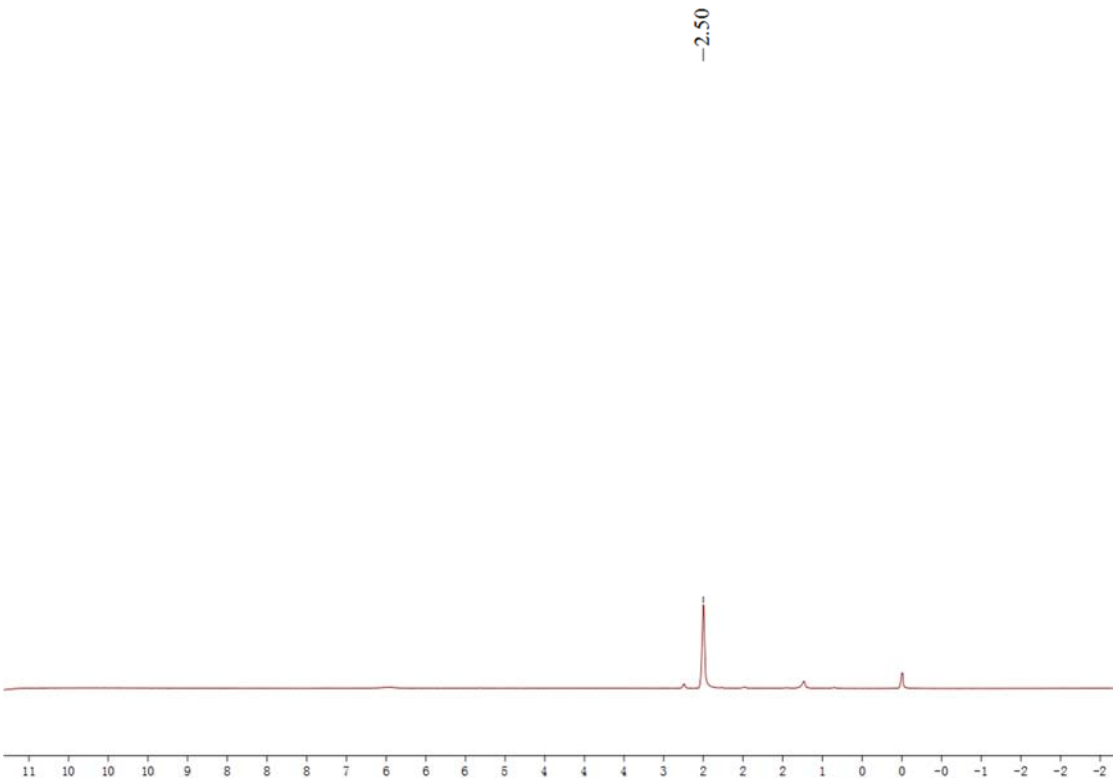


Figure S9 ^{1}H NMR spectrum of **6** in DMSO-d_6

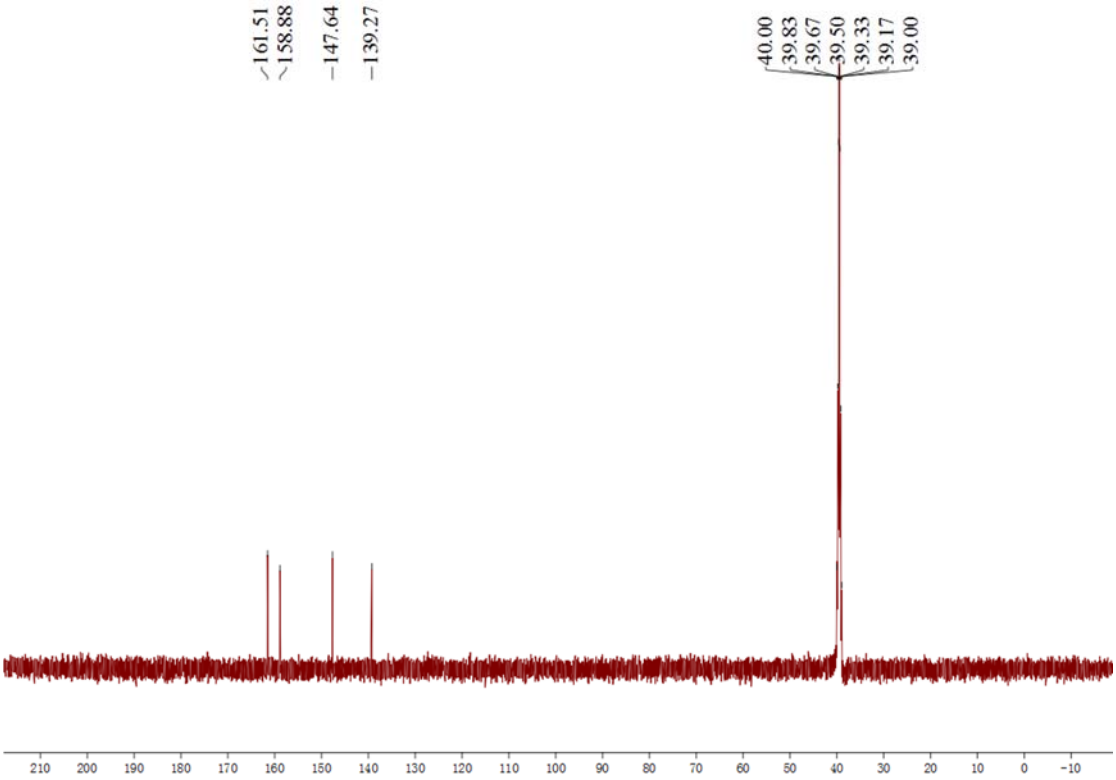


Figure S10 ^{13}C NMR spectrum of **6** in DMSO-d_6

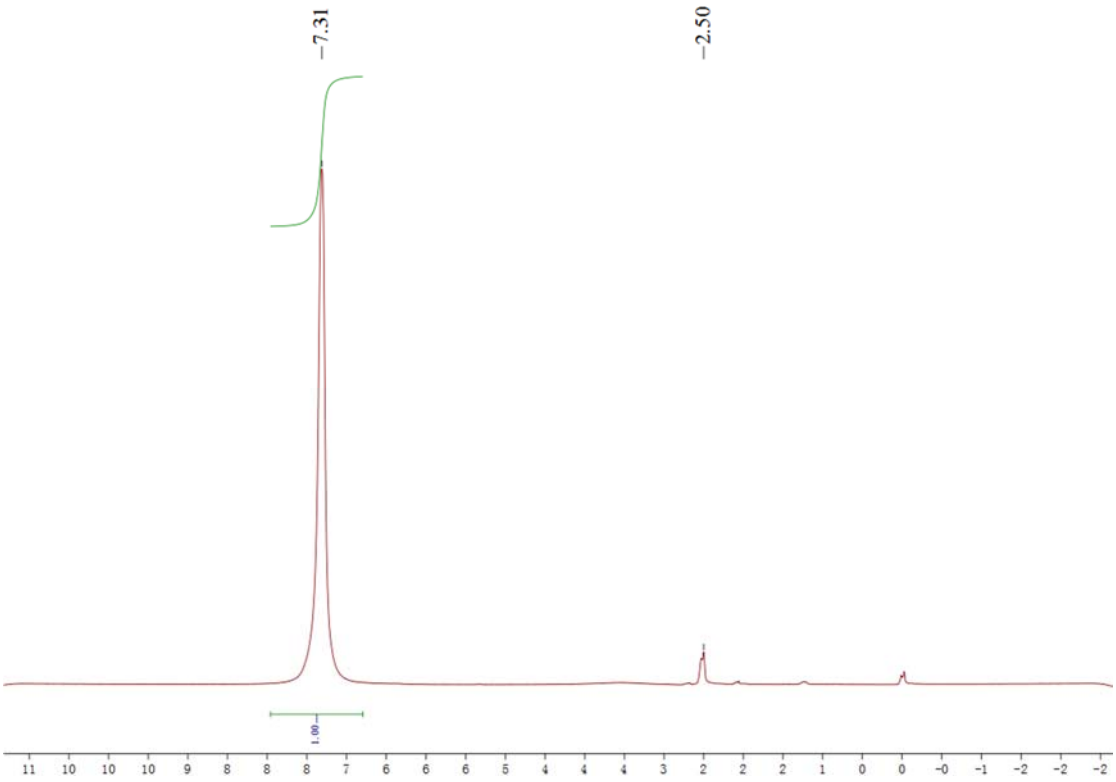


Figure S11 ^{1}H NMR spectrum of **7** in DMSO-d_6

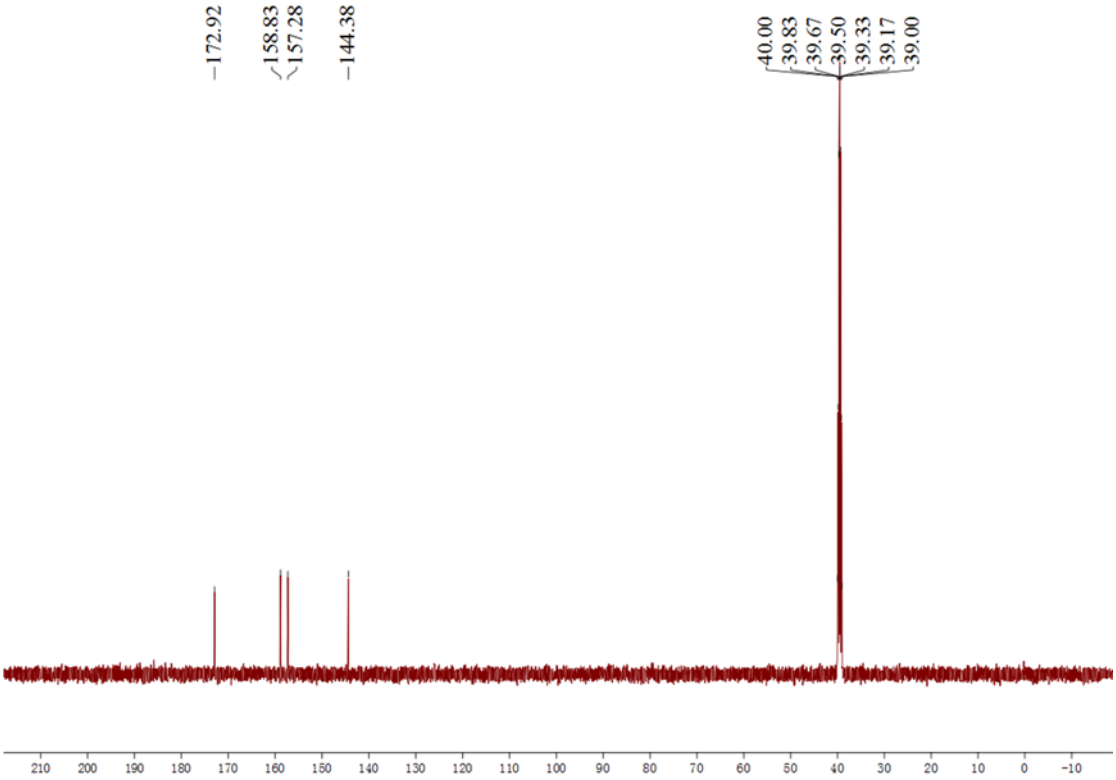


Figure S12 ^{13}C NMR spectrum of **7** in DMSO-d_6

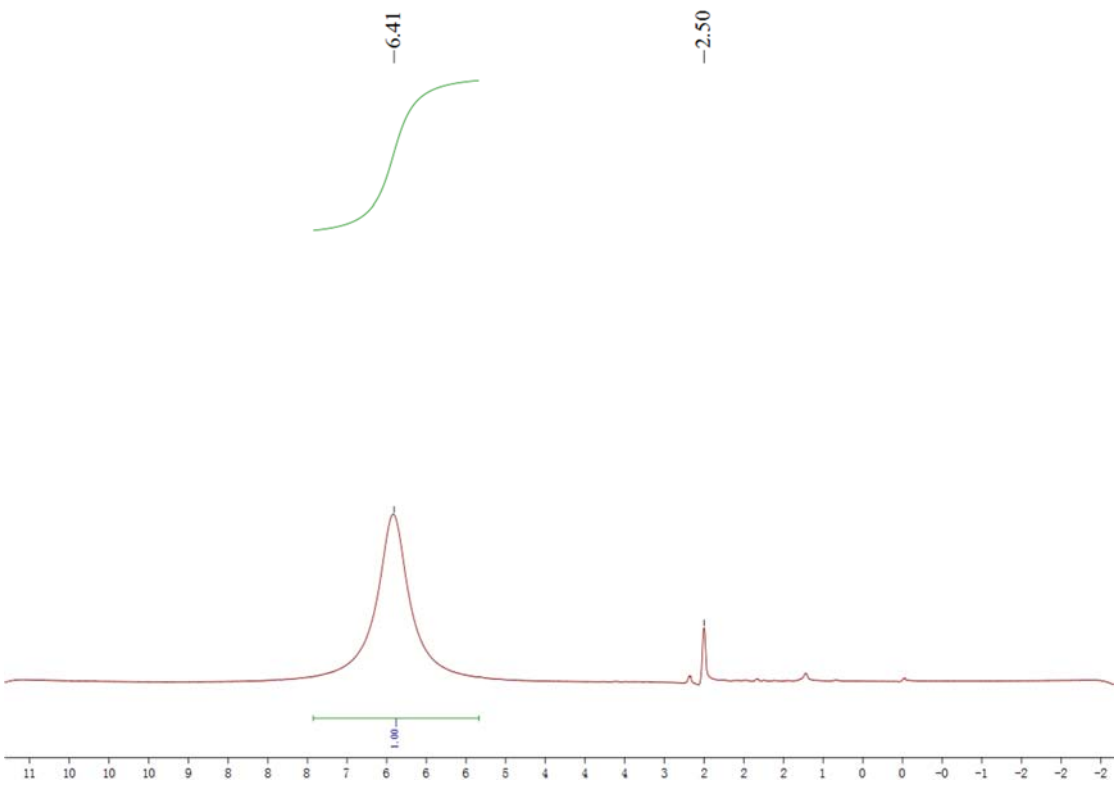


Figure S13 ^{1}H NMR spectrum of **8** in DMSO-d_6

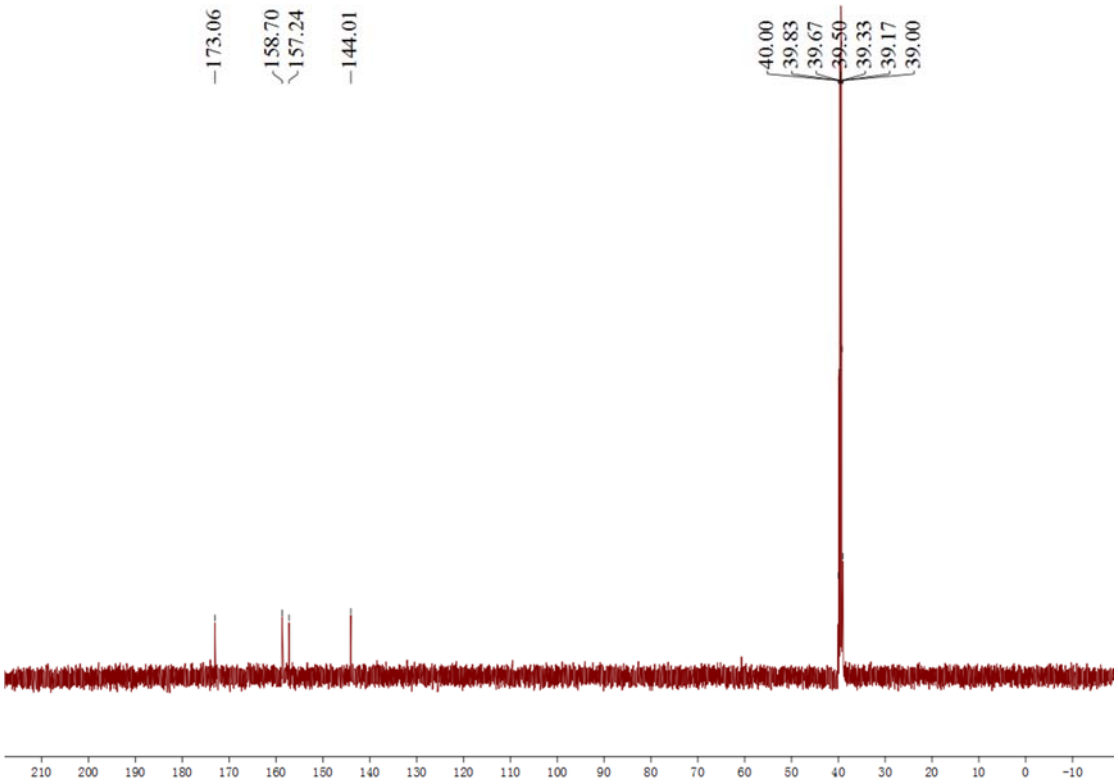


Figure S14 ^{13}C NMR spectrum of **8** in DMSO-d_6

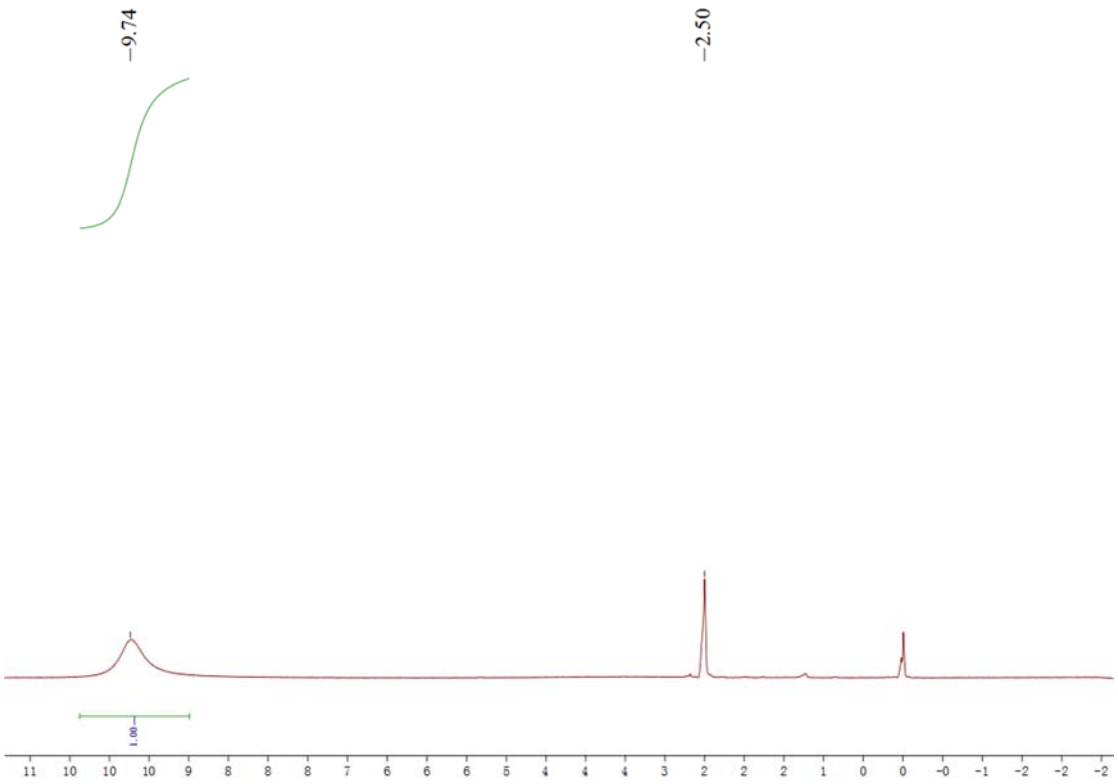


Figure S15 ^{1}H NMR spectrum of **9** in DMSO-d_6

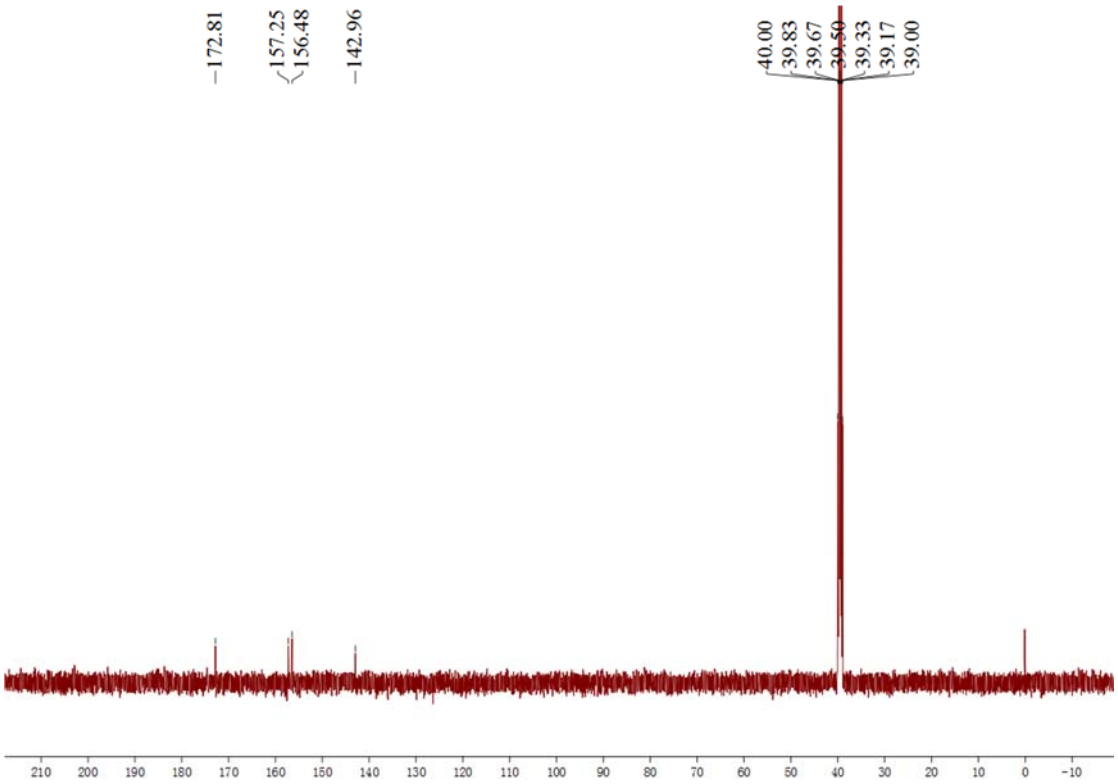


Figure S16 ^{13}C NMR spectrum of **9** in DMSO-d_6

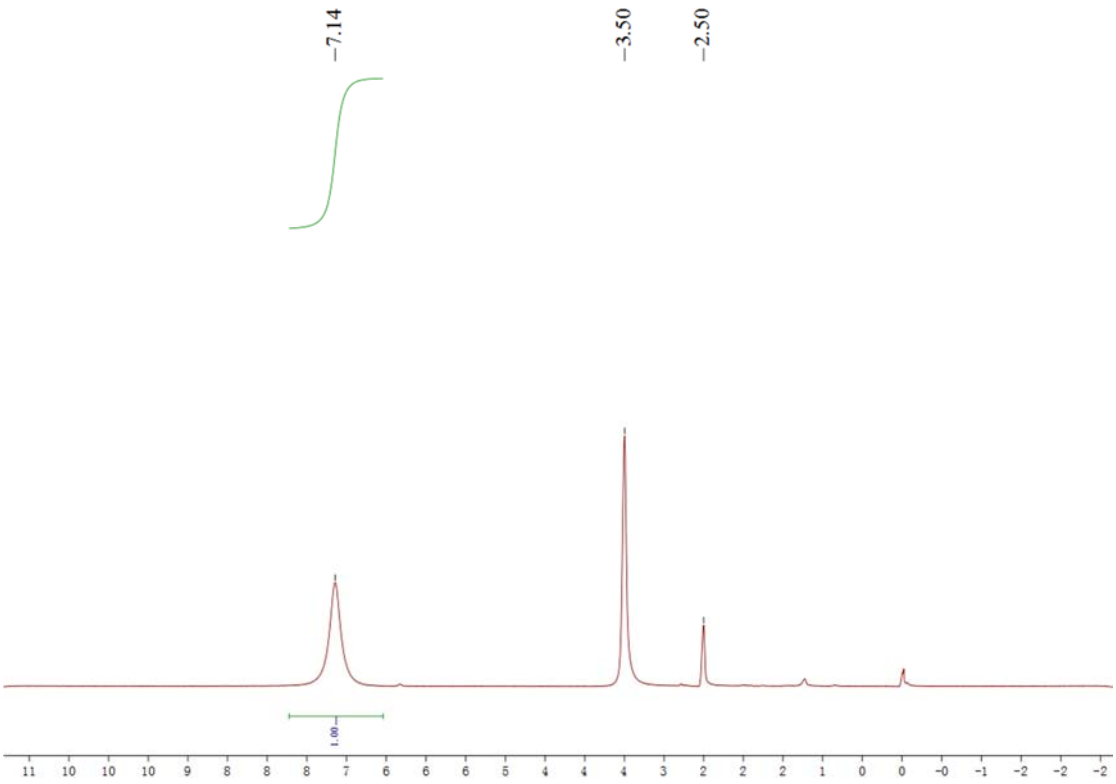


Figure S17 ^{1}H NMR spectrum of **10** in DMSO-d_6

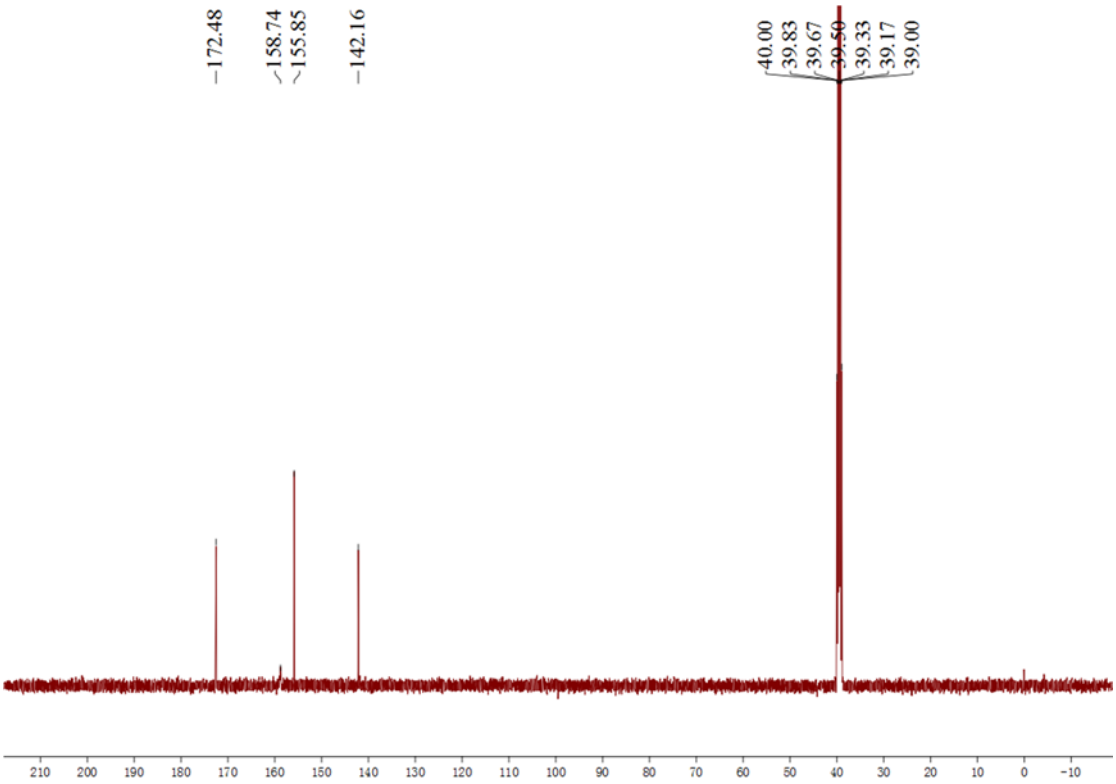


Figure S18 ^{13}C NMR spectrum of **10** in DMSO-d_6

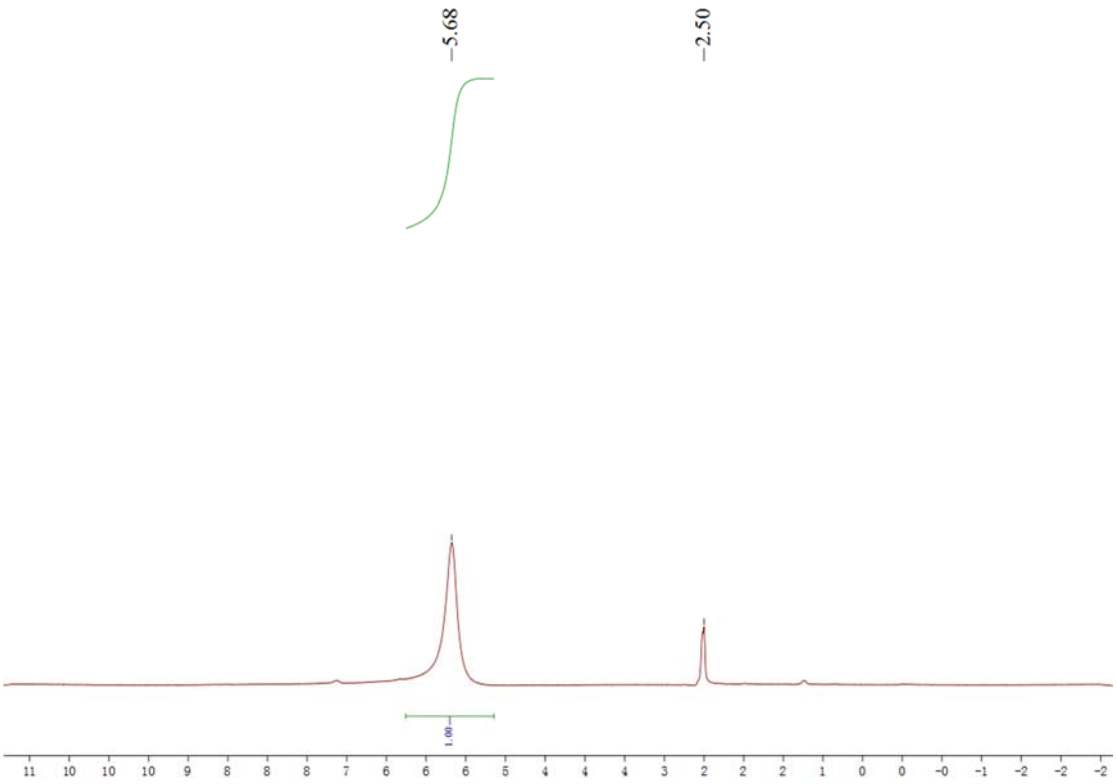


Figure S19 ^{1}H NMR spectrum of **11** in DMSO-d_6

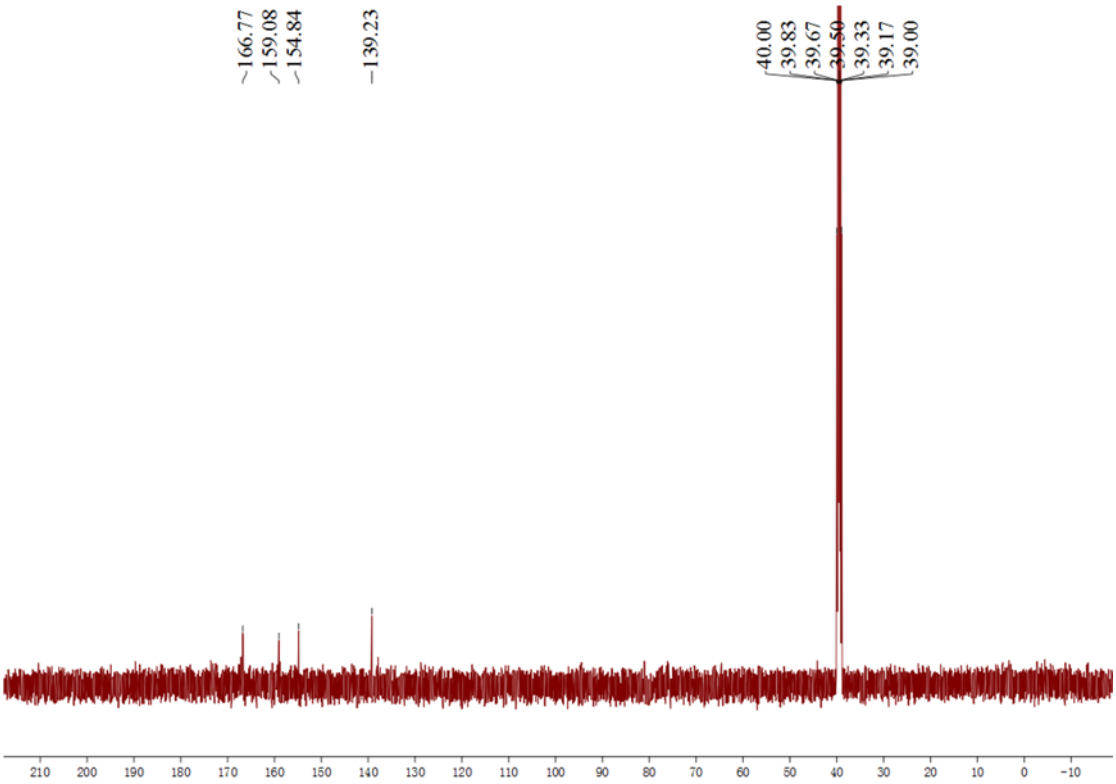


Figure S20 ^{13}C NMR spectrum of **11** in DMSO-d_6

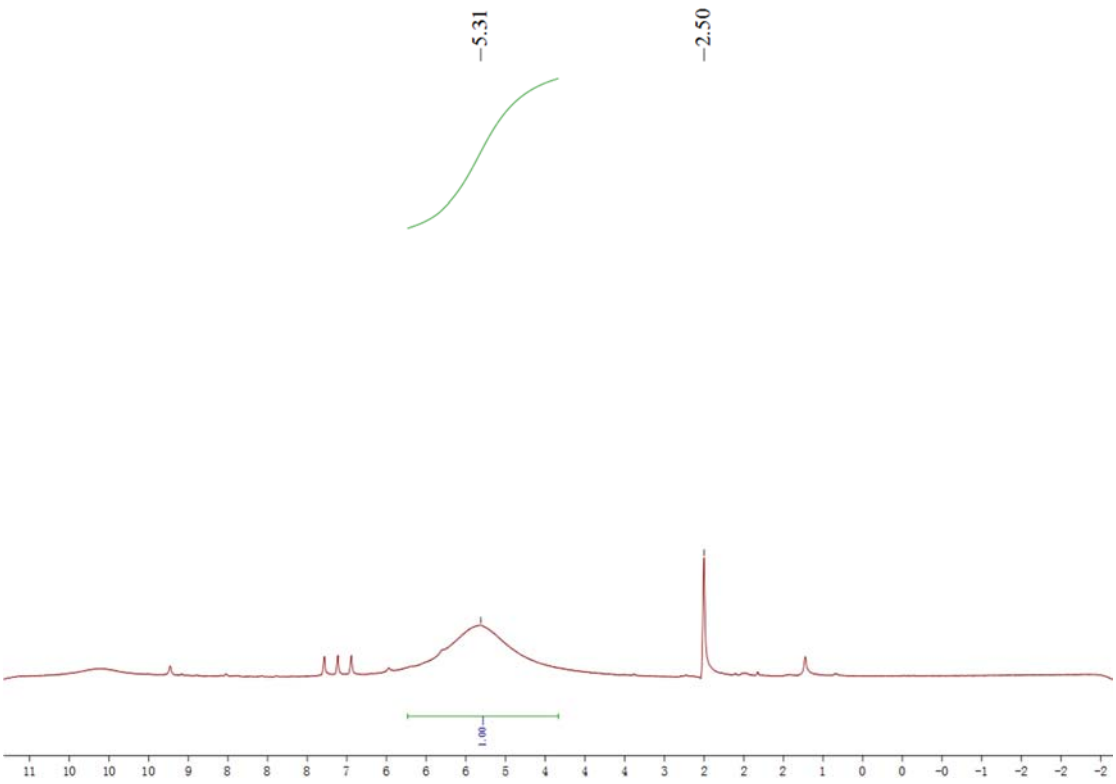


Figure S21 ^{1}H NMR spectrum of **12** in DMSO-d_6

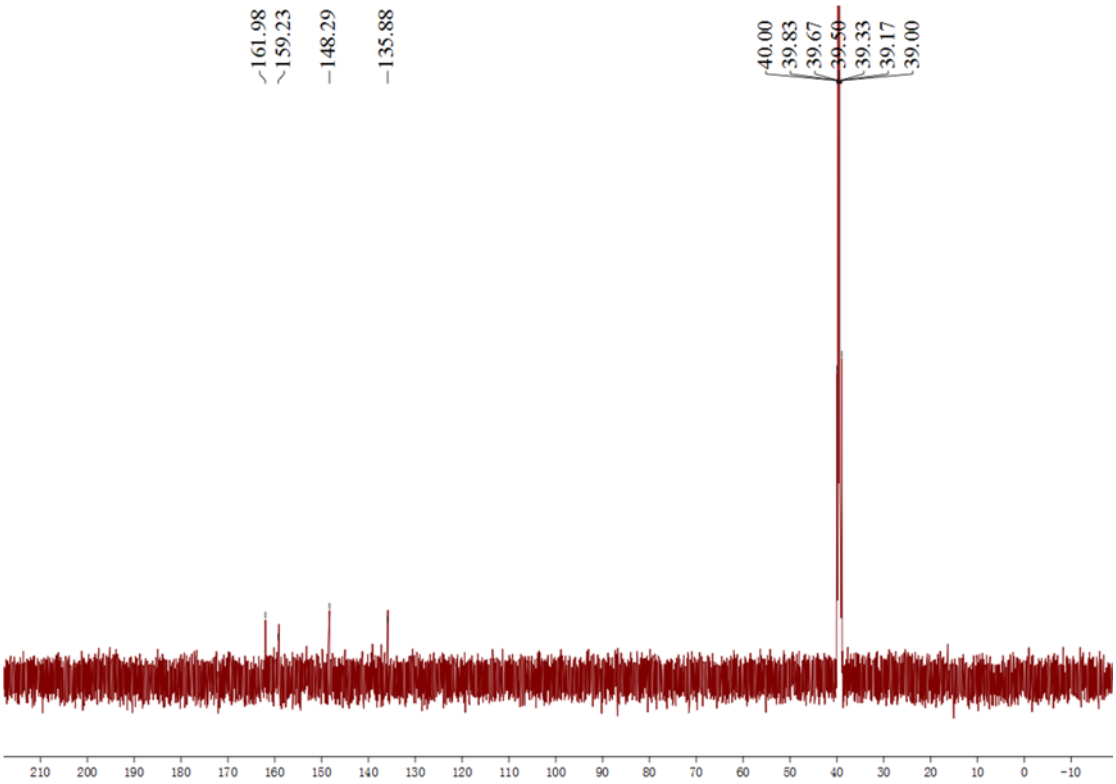


Figure S22 ^{13}C NMR spectrum of **12** in DMSO-d_6

6. Figure S23-S32 DSC Plot of Compound 3-12.

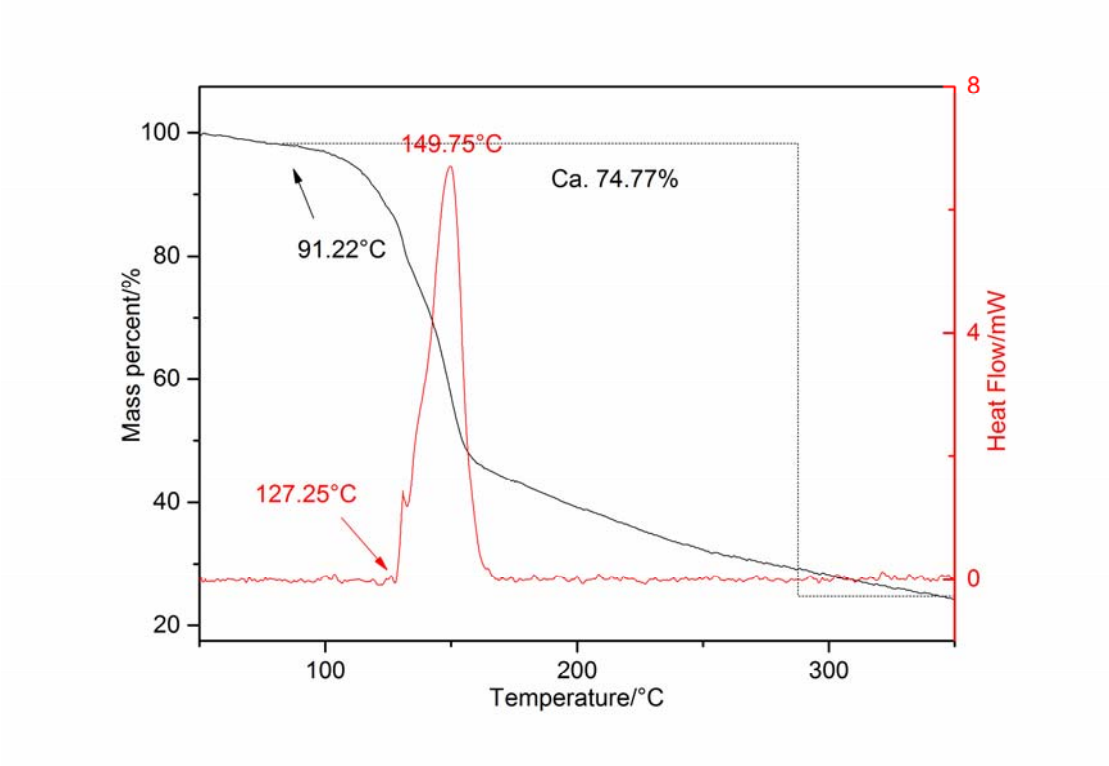


Figure S23 The DSC plot of **3**

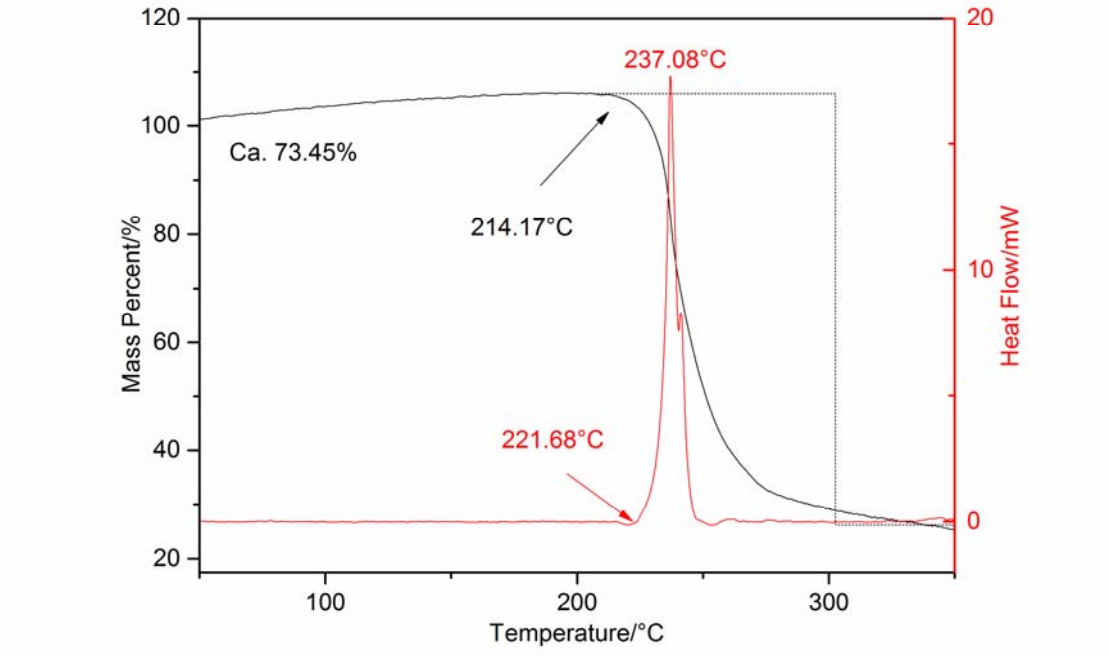


Figure S24 The DSC plot of **4**

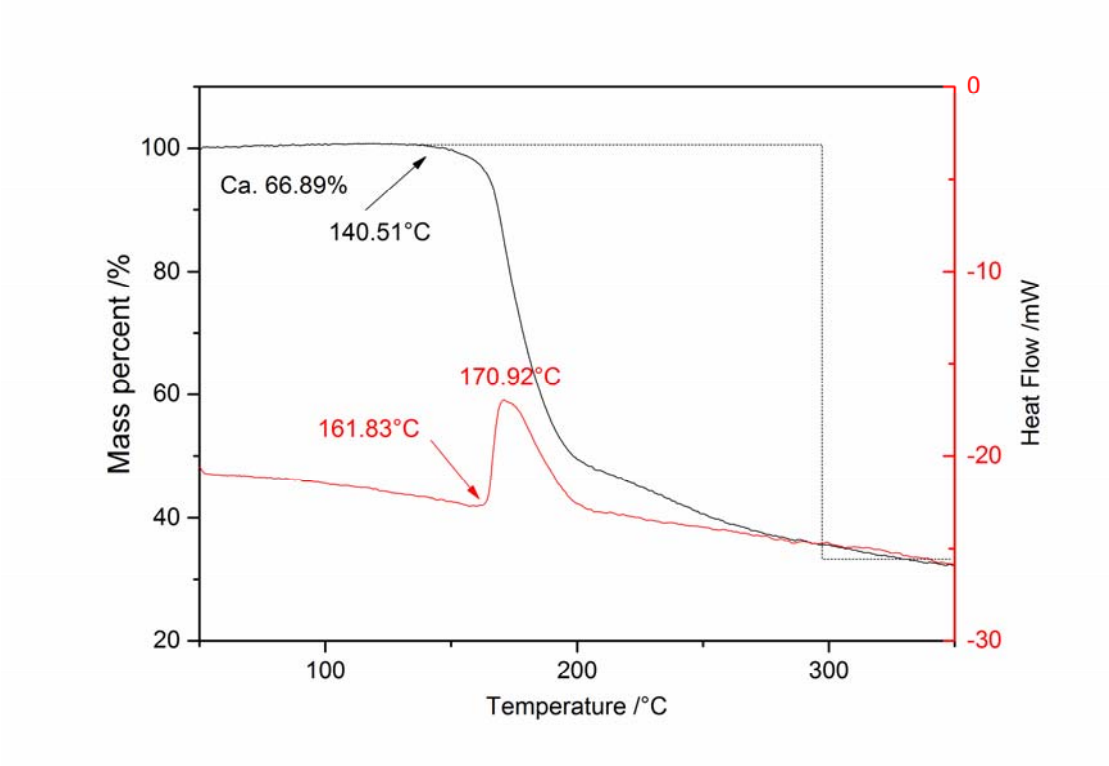


Figure S25 The DSC plot of **5**

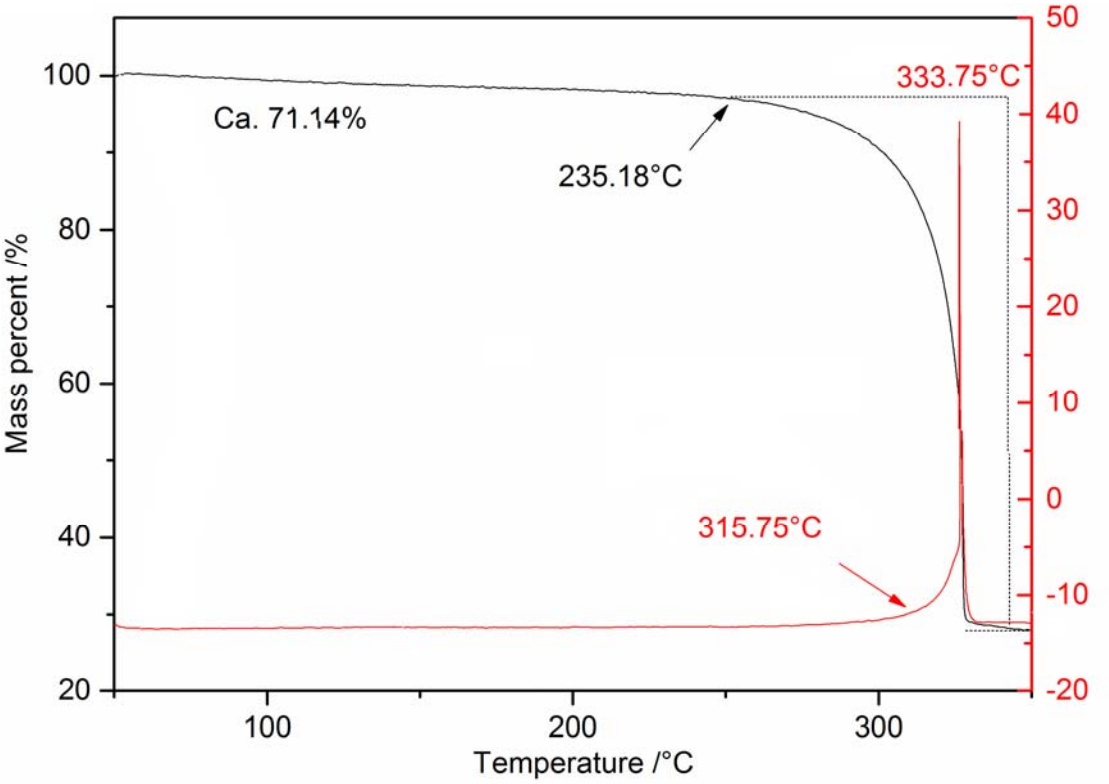


Figure S26 The DSC plot of **6**

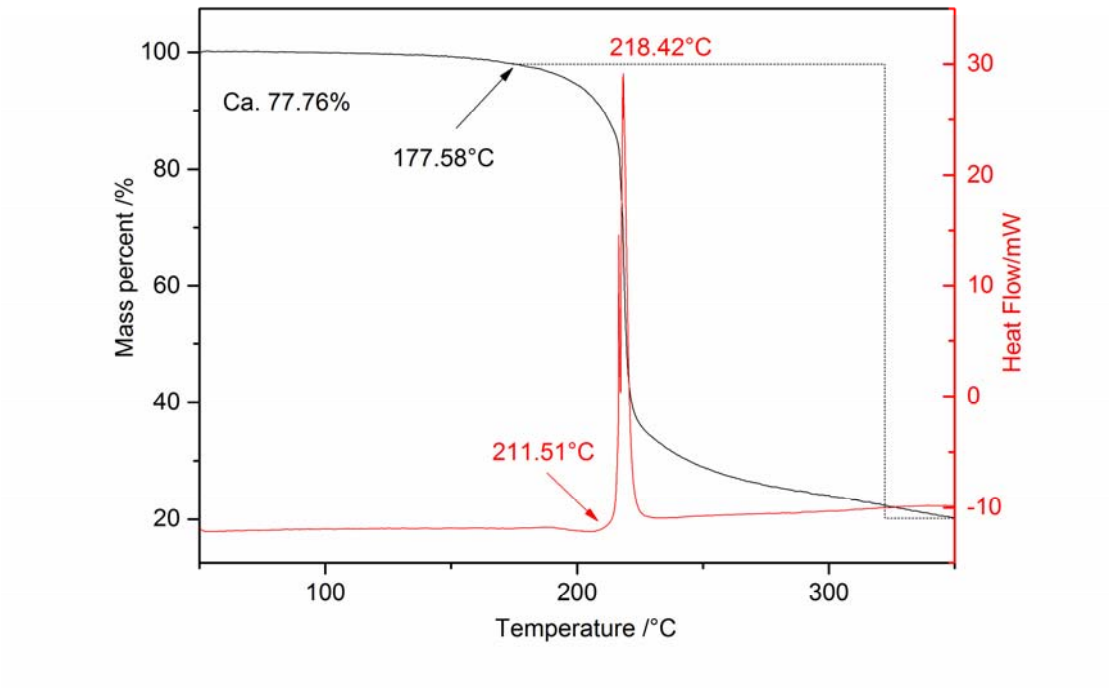


Figure S27 The DSC plot of **7**

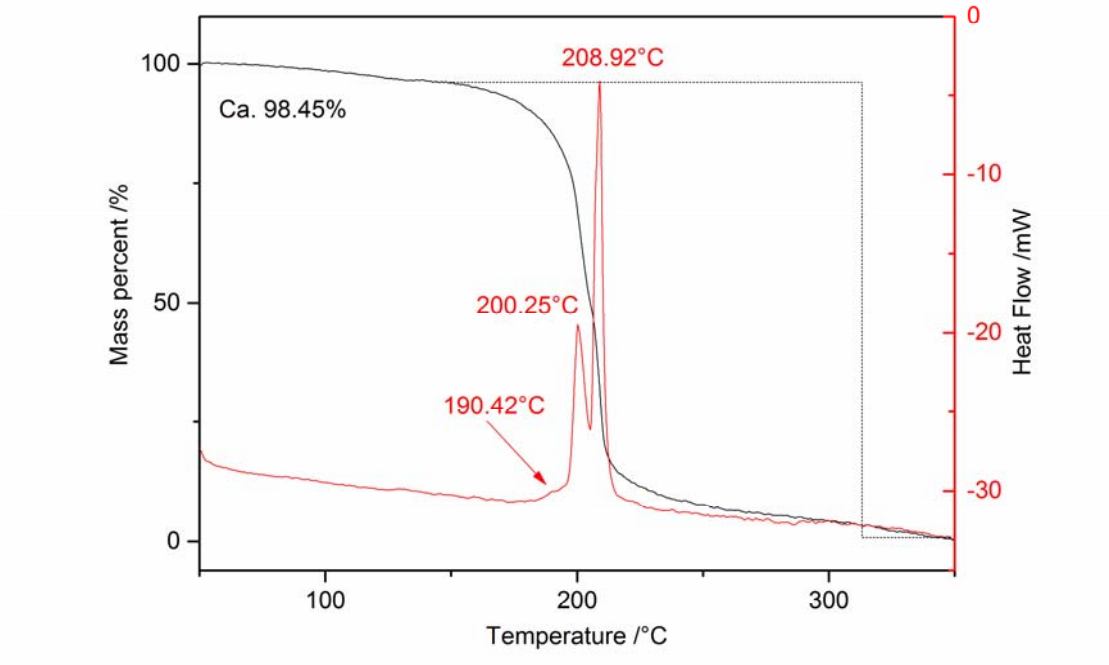


Figure S28 The DSC plot of **8**

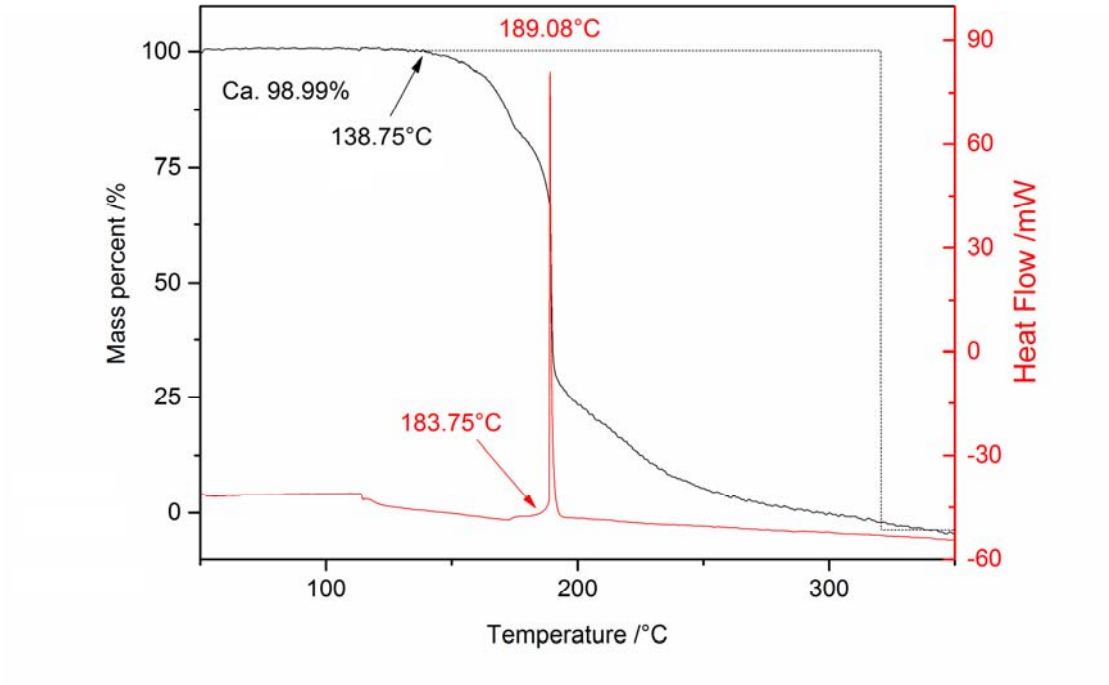


Figure S29 The DSC plot of **9**

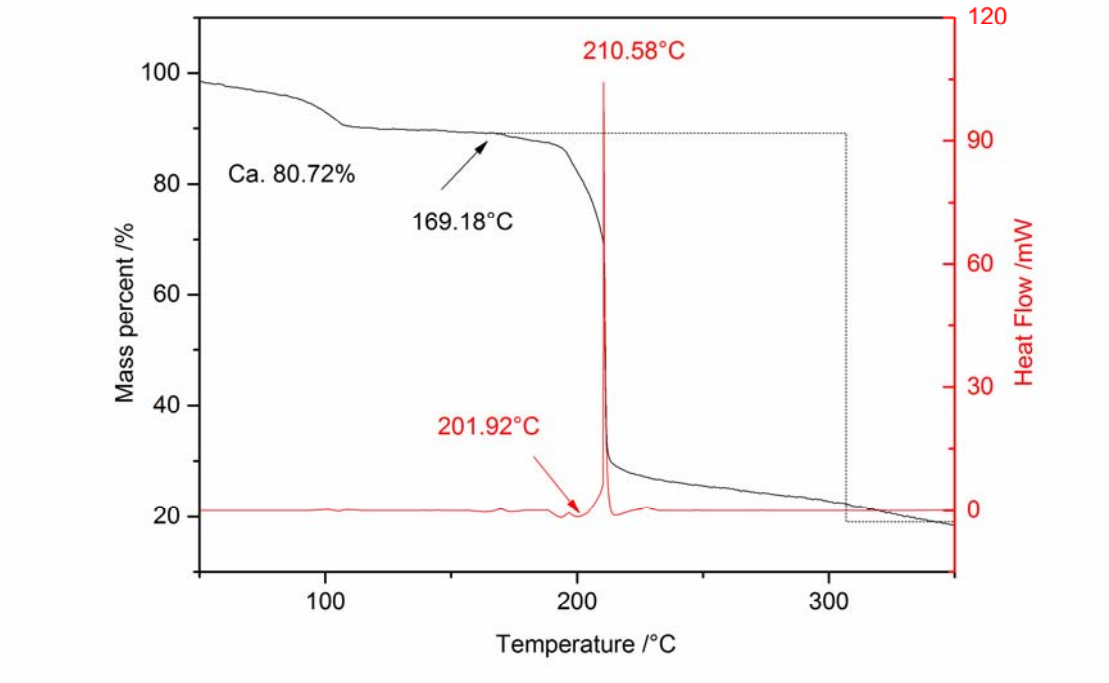


Figure S30 The DSC of plot **10**

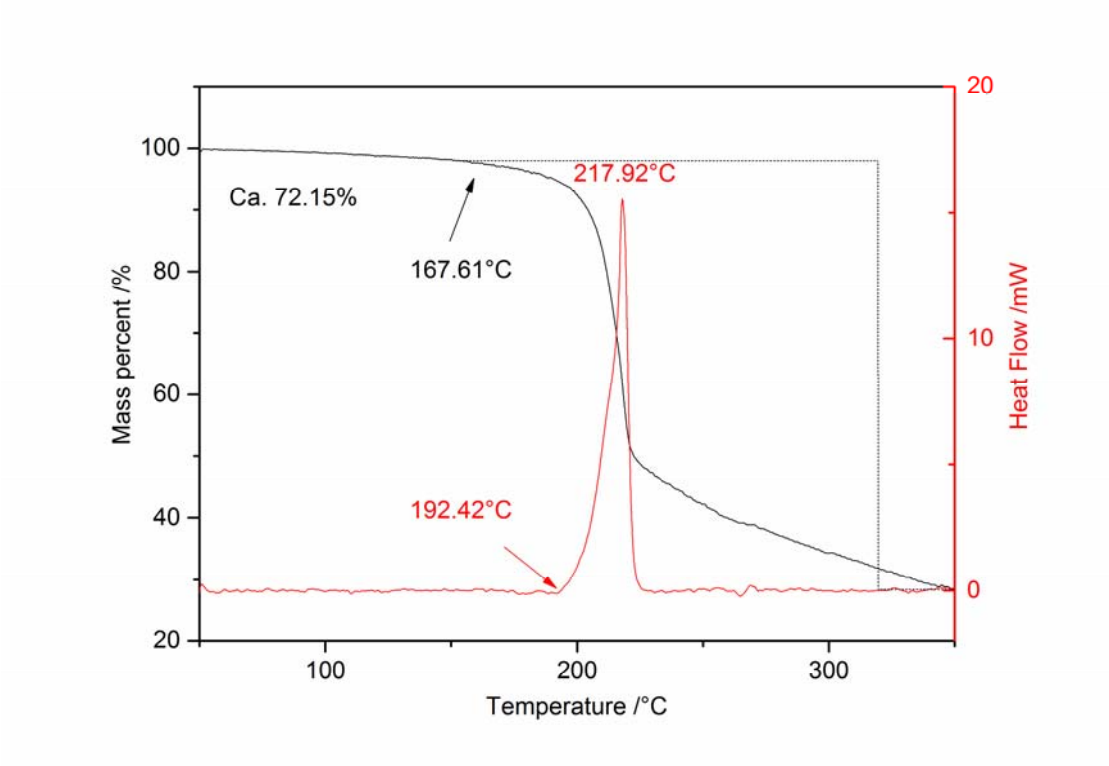


Figure S31 The DSC plot of **11**

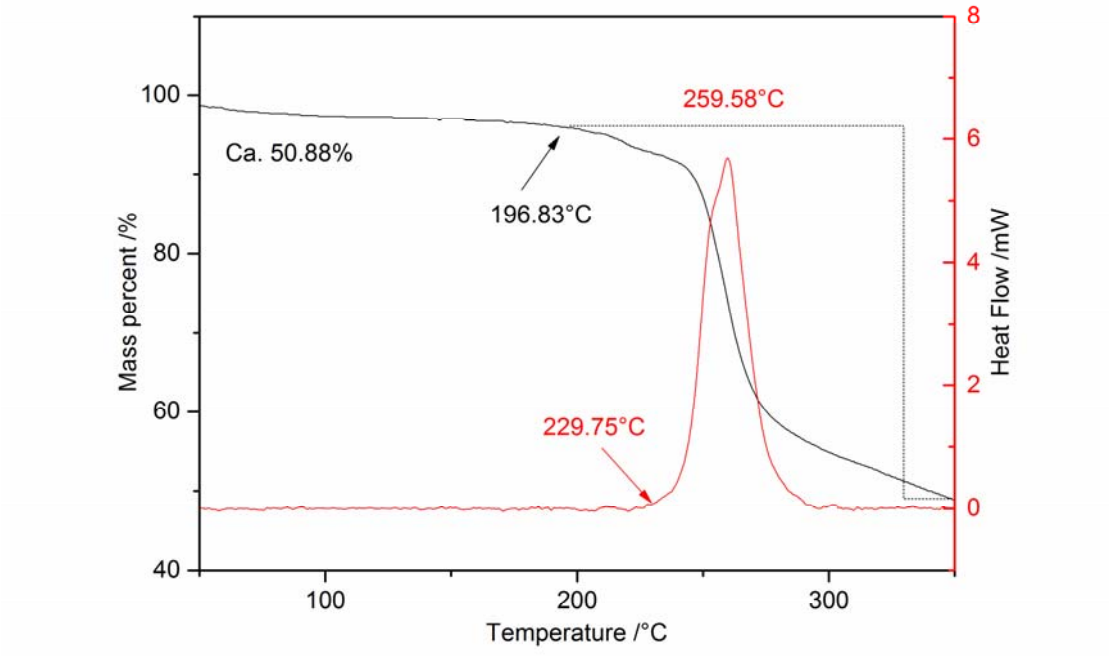


Figure S32 The DSC plot of **12**

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