Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Triazene Bridged Energetic Materials Based on Nitrotriazole: Synthesis, Characterization and Laser Ignited Combustion Performance

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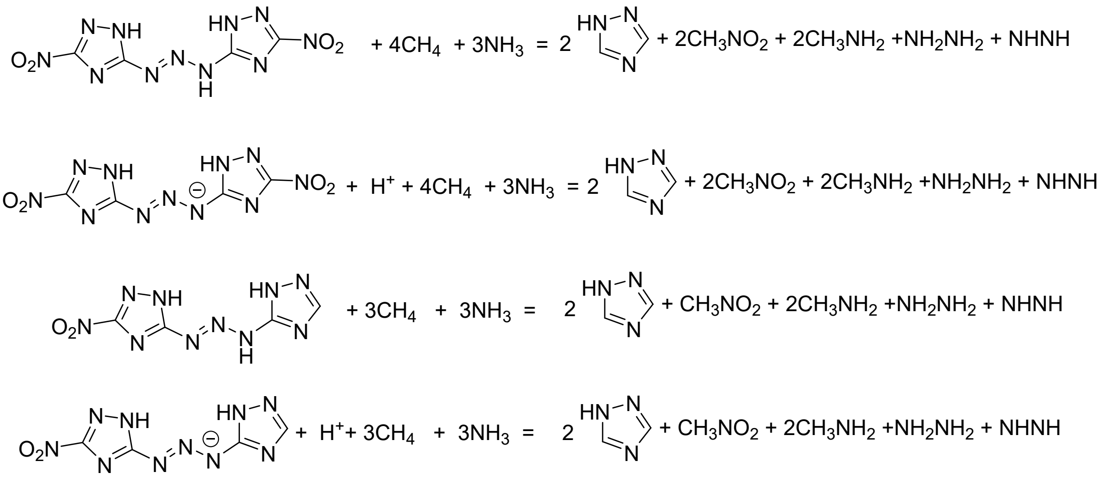
Computation details

1. Heats of formation (HOF)

Computations were carried out by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals[2] with 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. The predictions of heats of formation (HOF) adopt the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of these compounds are in Scheme S1.



Scheme S1. Isodemic reaction for computing the HOF

The change of enthalpy for the reactions at 298 K can be expressed as:

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

Where $\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can be calculated using the following expression:

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

Where E_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 thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq (2) is the PV work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from the experiments[4-6] or from the high level computing like CBS-4M.

For ionic energetic compounds, the HOF can be simplified by eq 3:

$$\Delta H_f^0(\text{salt}, 298\text{ K}) = \Delta H_f^0(\text{cation}, 298\text{ K}) + \Delta H_f^0(\text{anion}, 298\text{ K}) - \Delta H_L \qquad (3)$$

where ΔH_L is the lattice energy of the salts that can be predicted by the formula suggested by Jenkins et al. as：

$$\Delta H_L = U_{POT} + [\, p(nM/2 - 2) + q(nX/2 - 2)]RT \qquad (4)$$

where nM and nX 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 UPOT (kJ mol^{-1}) is as follows:

$$U_{\mathrm{POT}}\ (\mathrm{kJ\ mol^{-1}}) = \gamma\ (\rho_m/M_m)^{1/3} + \delta \quad (5)$$

where ρ (g cm^{-3}) is the density and M (g mol^{-1}) is the chemical formula mass of the ionic material. For 1:1 (charge ratio) salts, the coefficients γ and δ are 1981.2 kJ mol^{-1}·cm and 103.8 kJ mol^{-1}, respectively.[7]

2. Bond dissociation energy (BDE)

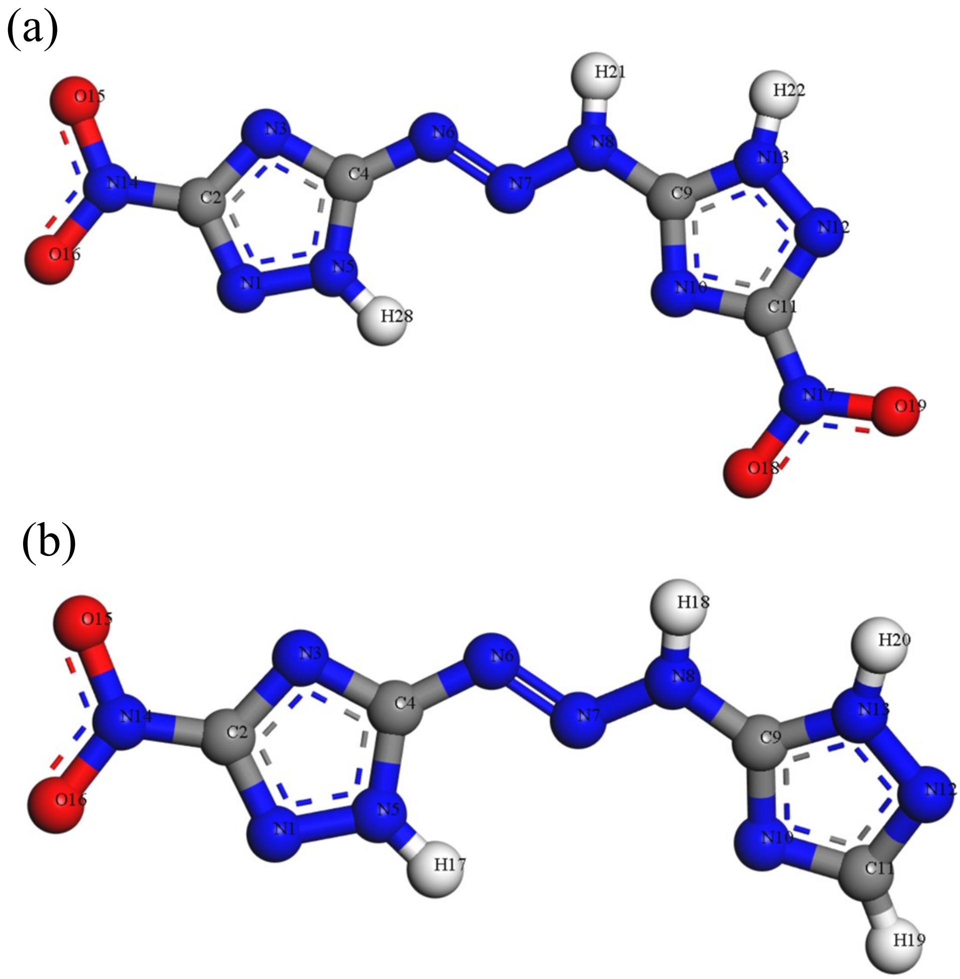


Figure S1. Molecular structures of **1** (a) and **6** (b)

Table S1 Bond orders of compounds **1** and **6**

1		**6**	
N8—H21	0.651924	N8—H18	0.654682
N5—H20	0.682571	N13—H20	0.687594
N13—H22	0.685666	N5—H17	0.688586
C11—N17	0.733126	N12—N13	0.718758
C2—N14	0.739369	C2—N14	0.739399
N12—N13	0.755071	N1—N5	0.817222
N1—N5	0.840481	C11—H19	0.863725
N7—N8	0.903082	N7—N8	0.946384
N14—O16	0.97285	N14—O16	0.962055

N17—O19	0.976253	N8—C9	0.965729
N14—O15	0.979089	N14—O15	0.980818
N17—O18	0.980465	C4—N5	0.996932
N8—C9	0.999195	N10—C11	1.023973
C4—N5	1.001787	C4—N6	1.035579
C4—N6	1.021403	C9—N13	1.039462
C9—N13	1.022193	C2—N3	1.120271
N10—C11	1.076439	N3—C4	1.277199
C2—N3	1.12728	C9—N10	1.296883
N3—C4	1.281321	N1—C2	1.333648
C9—N10	1.295943	N6—N7	1.342435
N1—C2	1.337029	C11—N12	1.363705
N6—N7	1.374392		
C11—N12	1.377606		

Crystallographic Data

Table S2 Crystallographic details of **1** and **2**

Crystals	**1**	**2**
CCDC	2225841	2225842
Formula	$C_4H_7N_{11}O_6$	$C_8H_{14}K_6N_{22}O_{15}$
Formula weight	305.21	893.01
Temperature	146(2) K	150(2) K
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2/c$
ρ/g·cm-1	1.765	1.910
a/Å	10.4637(5)	12.0707(5)
b/Å	16.3279(7)	7.3415(3)
c/Å	6.8604(3)	18.2512(7)
α/(°)	90	90
β/(°)	101.482(2)	106.260(2)
γ/(°)	90	90
Goodness-of-fit on F^2	1.037	1.044
R	0.0376	0.0681
wR	0.0890	0.1312

Table S3 Bond lengths of compounds **1** and **2**

1		**2**	
C1—N2	1.3071(15)	N1—C1	1.332(4)
C1—N3	1.3473(14)	N1—C2	1.351(4)
C1—N1	1.4510(14)	N2—N3	1.373(4)

C2—N3	1.3314(14)	N2—C1	1.326(4)
C2—N4	1.3414(14)	N2—C2	1.352(4)
C2—N5	1.3752(14)	N4—C1	1.437(4)
C3—N10	1.3314(16)	N5—N6	1.301(4)
C3—N8	1.3442(14)	N5—C2	1.392(4)
C3—N7	1.3964(14)	N6—N7	1.305(4)
C4—N9	1.3138(15)	N7—C3	1.395(4)
C4—N10	1.3415(14)	N8—C3	1.353(4)
C4—N11	1.4562(15)	N8—C4	1.342(4)
N1—O2	1.2166(14)	N9—N10	1.370(4)
N1—O1	1.2294(14)	N9—C3	1.341(4)
N2—N4	1.3551(13)	N10—C4	1.324(4)
N5—N6	1.3305(13)	N11—C4	1.426(4)
N6—N7	1.2650(13)	O1—N4	1.229(4)
N8—N9	1.3469(13)	O2—N4	1.245(4)
N11—O4	1.2107(14)	O3—N11	1.233(4)
N11—O3	1.2294(14)	O4—N11	1.239(4)

Table S4 Bond angles of compounds **1** and **2**

1		**2**	
N2—C1—N3	118.20(10)	C1—N1—C2	99.4(3)
N2—C1—N1	120.50(10)	C1—N2—N3	103.7(3)
N3—C1—N1	121.30(10)	C2—N3—N2	105.5(3)
N3—C2—N4	111.64(10)	O1—N4—O2	123.7(3)
N3—C2—N5	124.94(10)	O1—N4—C1	117.9(3)
N4—C2—N5	123.40(10)	O2—N4—C1	118.4(3)
N10—C3—N8	110.69(10)	N6—N5—C2	111.0(3)
N10—C3—N7	129.23(10)	N5—N6—N7	112.1(3)
N8—C3—N7	120.07(10)	N6—N7—C3	111.7(3)
N9—C4—N10	117.91(11)	C4—N8—C3	98.6(3)
N9—C4—N11	119.69(10)	C3—N9—N10	105.7(3)
N10—C4—N11	122.39(10)	C4—N10—N9	103.7(2)
O2—N1—O1	125.34(10)	O3—N11—O4	123.6(3)
O2—N1—C1	118.24(10)	O3—N11—C4	117.3(3)
O1—N1—C1	116.42(10)	O4—N11—C4	119.1(3)
C1—N2—N4	101.18(9)	N1—C1—N4	121.5(3)
C2—N3—C1	99.80(9)	N2—C1—N1	117.4(3)
C2—N4—N2	109.17(9)	N2—C1—N4	121.1(3)
N6—N5—C2	114.81(9)	N1—C2—N3	114.1(3)
N7—N6—N5	112.77(10)	N1—C2—N5	126.6(3)
N6—N7—C3	109.81(10)	N3—C2—N5	119.3(3)
C3—N8—N9	109.99(10)	N8—C3—N7	126.9(3)

C4—N9—N8	100.91(9)	N9—C3—N7	118.4(3)
C3—N10—C4	110.51(9)	N9—C3—N8	114.7(3)
C4—N11—O3	125.93(11)	N10—C4—N8	117.4(3)
C4—N11—C4	117.46(10)	N10—C4—N11	121.5(3)
C3—N11—C4	116.61(10)		

Table S5 The torsion angles of compounds **1** and **2**

1		**2**	
C1—N2—N4—C2	-0.21(12)	O1—N4—C1—N1	-4.6(5)
C2—N5—N6—N7	177.89(10)	O1—N4—C1—N2	176.6(3)
N5—N6—N7—C3	178.40(9)	O2—N4—C1—N1	175.2(3)
C3—N8—N9—C4	0.05(12)	O2—N4—C1—N2	-3.6(5)
N2—C1—N1—O1	-178.94(11)	O3—N11—C4—N8	-1.1(5)
N2—C1—N1—O2	0.58(17)	O3—N11—C4—N10	-177.4(3)
N3—C1—N1—O1	0.96(17)	O4—N11—C4—N8	-179.7(3)
N3—C1—N1—O2	-179.52(11)	O4—N11—C4—N10	1.9(5)
N1—C1—N2—N4	179.98(12)	N2—N3—C2—N1	-0.3(4)
N3—C1—N2—N4	0.08(13)	N2—N3—C2—N5	-178.5(3)
N1—C1—N3—C2	-179.83(11)	N3—N2—C1—N1	0.9(4)
N2—C1—N3—C2	0.07(14)	N3—N2—C1—N4	179.7(3)
N4—C2—N3—C1	-0.21(13)	N5—N6—N7—C3	-177.5(3)
N5—C2—N3—C1	178.35(11)	N6—N5—C2—N1	15.2(5)
N3—C2—N4—N2	0.28(14)	N6—N5—C2—N3	-166.8(3)
N5—C2—N4—N2	-178.30(11)	N6—N7—C3—N8	16.2(5)
N3—C2—N5—N6	-175.76(11)	N6—N7—C3—N9	-164.8(3)
N4—C2—N5—N6	2.64(16)	N9—N10—C4—N8	0.2(4)
N8—C3—N7—N6	175.79(10)	N9—N10—C4—N11	178.8(3)
N10—C3—N7—N6	-5.67(17)	N10—N9—C3—N7	179.5(3)
N7—C3—N8—N9	178.64(100	N10—N9—C3—N8	-1.4(4)
N10—C3—N8—N9	-0.15(14)	C1—N1—C2—N3	0.8(4)
N7—C3—N10—C4	-178.48(12)	C1—N1—C2—N5	178.8(4)
N8—C3—N10—C4	0.16(12)	C1—N2—N3—C2	-0.3(4)
N10—C4—N9—N8	0.05(14)	C2—N1—C1—N2	-1.1(4)
N11—C4—N9—N8	179.07(10)	C2—N1—C1—N4	-179.9(3)
N9—C4—N10—C3	-0.14(14)	C2—N5—N6—N7	-175.1(3)
N11—C4—N10—C3	-179.13(11)	C3—N8—C4—N10	-1.0(4)
N9—C4—N11—O3	1.27(17)	C3—N8—C4—N11	-179.5(3)
N9—C4—N11—O4	-178.92(11)	C3—N9—N10—C4	0.6(3)
N10—C4—N11—O3	-179.76(11)	C4—N8—C3—N7	-179.6(3)
N10—C4—N11—O4	0.05(18)	C4—N8—C3—N9	1.4(4)

Table S6 Hydrogen bonds of compound **1**

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N4—H4⋯O6	0.88	1.80	2.6807(13)	175
N5—H5⋯O5	0.88	1.83	2.6904(15)	165
O5—H5A⋯O1	0.85	2.16	2.9456(12)	153
O5—H5B⋯O3	0.86	2.33	3.1280(15)	155
O5—H5B⋯N9	0.86	2.24	2.8923(13)	132
O6—H6A⋯N10	0.85	2.18	2.9871(13)	159
O6—H6B⋯N2	0.85	2.13	2.9374(14)	158
N8—H8⋯O1	0.88	2.51	3.2134(15)	138
N8—H8⋯N3	0.88	2.14	2.9363(15)	151

Table S7 Hydrogen bonds of compound **2**

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
O5—H5A⋯N5	0.87	2.20	2.853(4)	132
O5—H5B⋯O6	0.87	2.48	2.890(8)	109
O5—H5B⋯N9	0.87	2.56	2.942(4)	108
O6—H6A⋯O5	0.87	2.08	2.890(8)	154
O6—H6B⋯O9	0.87	2.01	2.821(7)	155
O7—H7⋯N7	0.85	2.01	2.865(3)	176
O8—H8A⋯N9	0.87	2.07	2.942(6)	180
O8—H8B⋯N7	0.87	2.22	3.091(6)	175
O9—H9⋯N3	0.87	2.08	2.893(3)	156

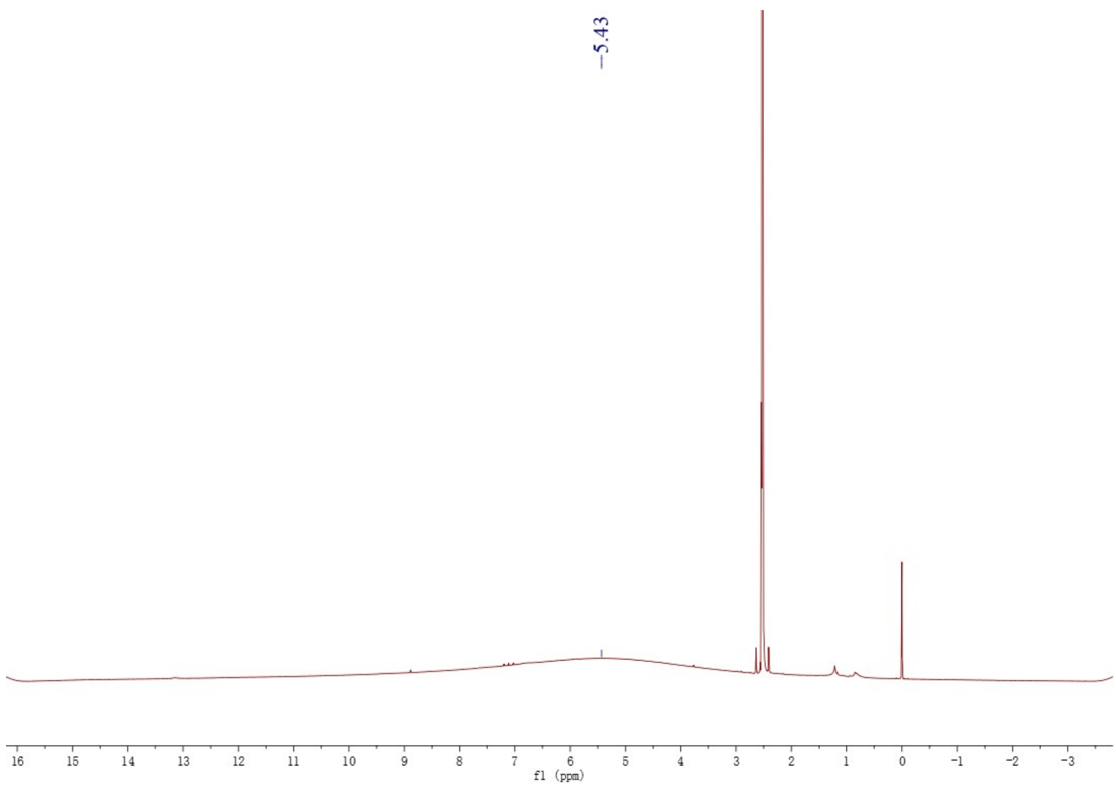


Figure S2. ^{1}H NMR of **1** (d_6-DMSO)

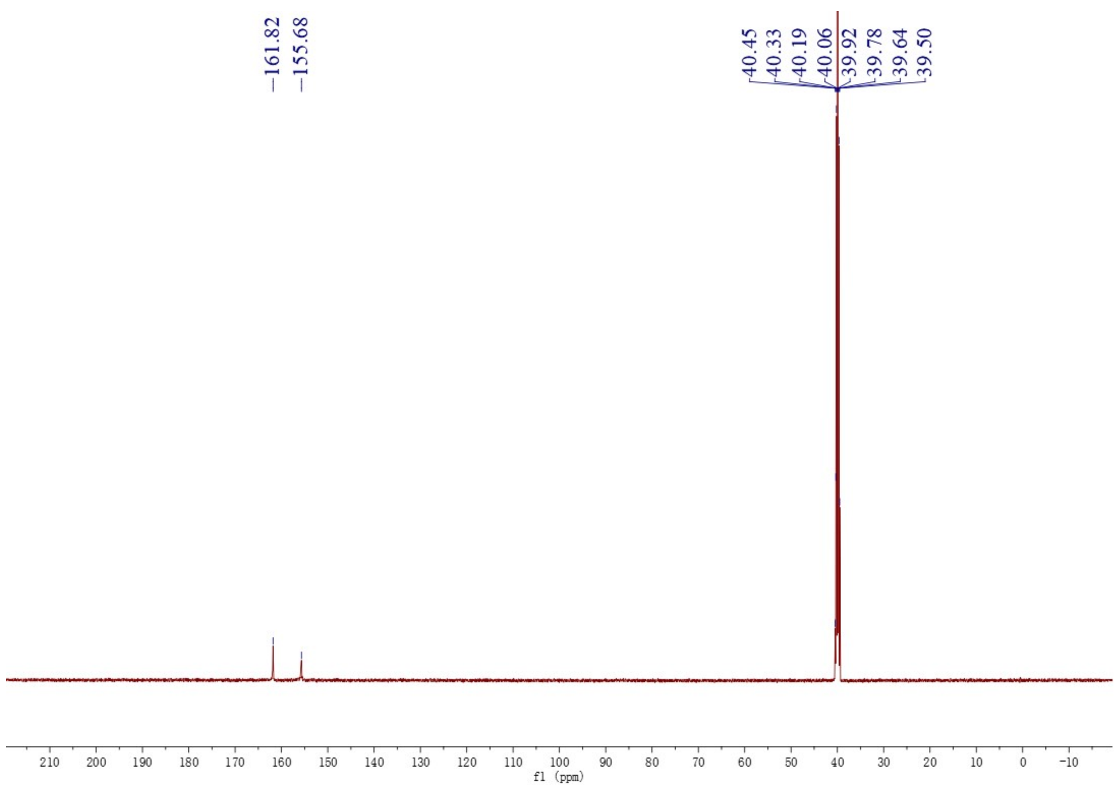


Figure S3 ^{13}C NMR of **1** (d_6-DMSO)

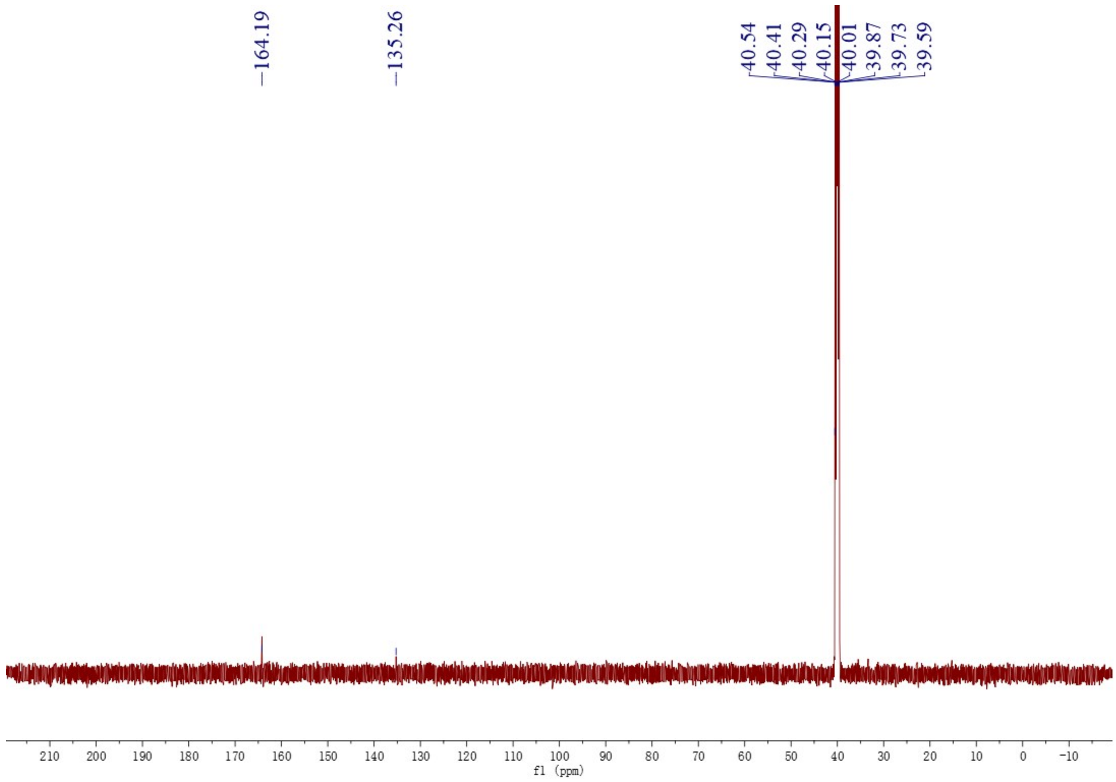


Figure S4 ^{13}C NMR of **2** (d_6-DMSO)

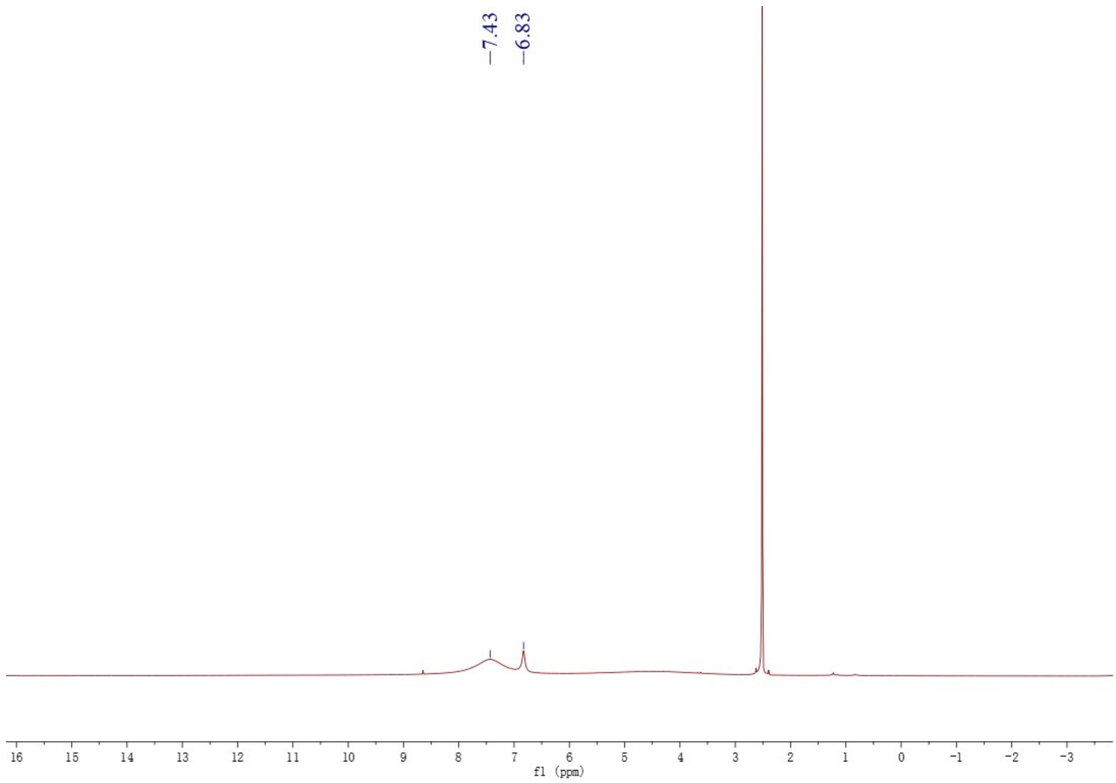


Figure S5 ^{1}H NMR of **3** (d_6-DMSO)

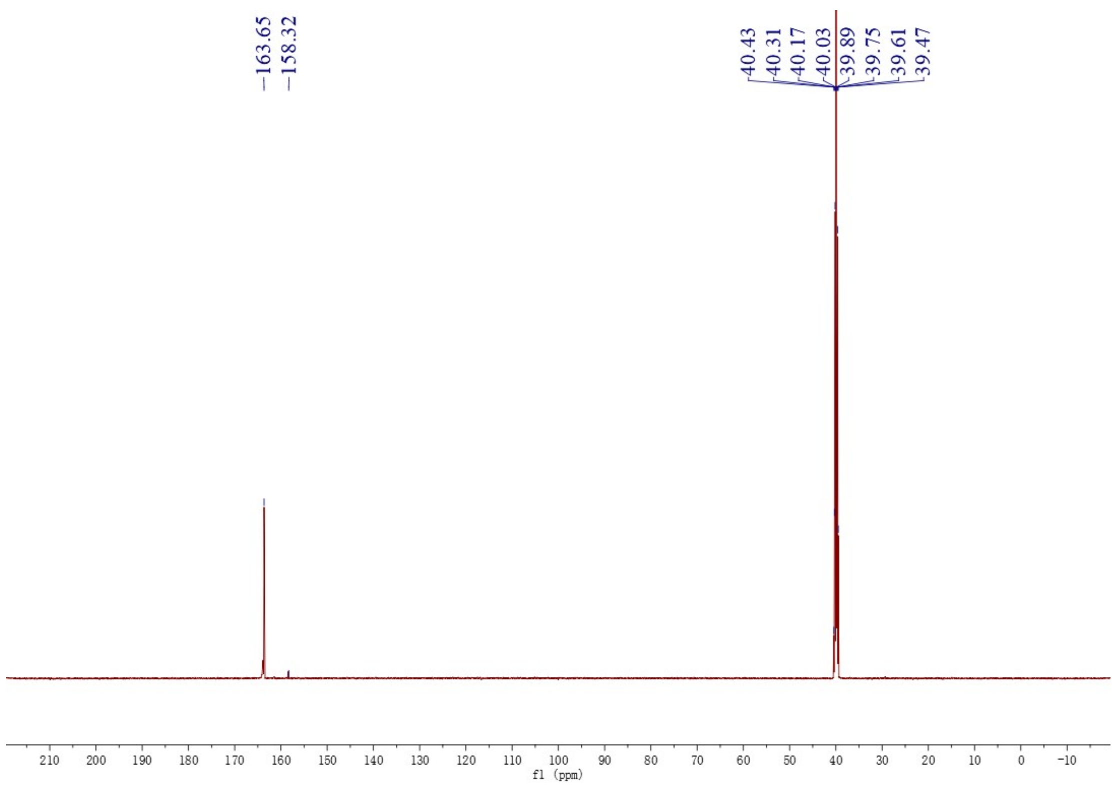


Figure S6 ^{13}C NMR of **3** (d_6-DMSO)

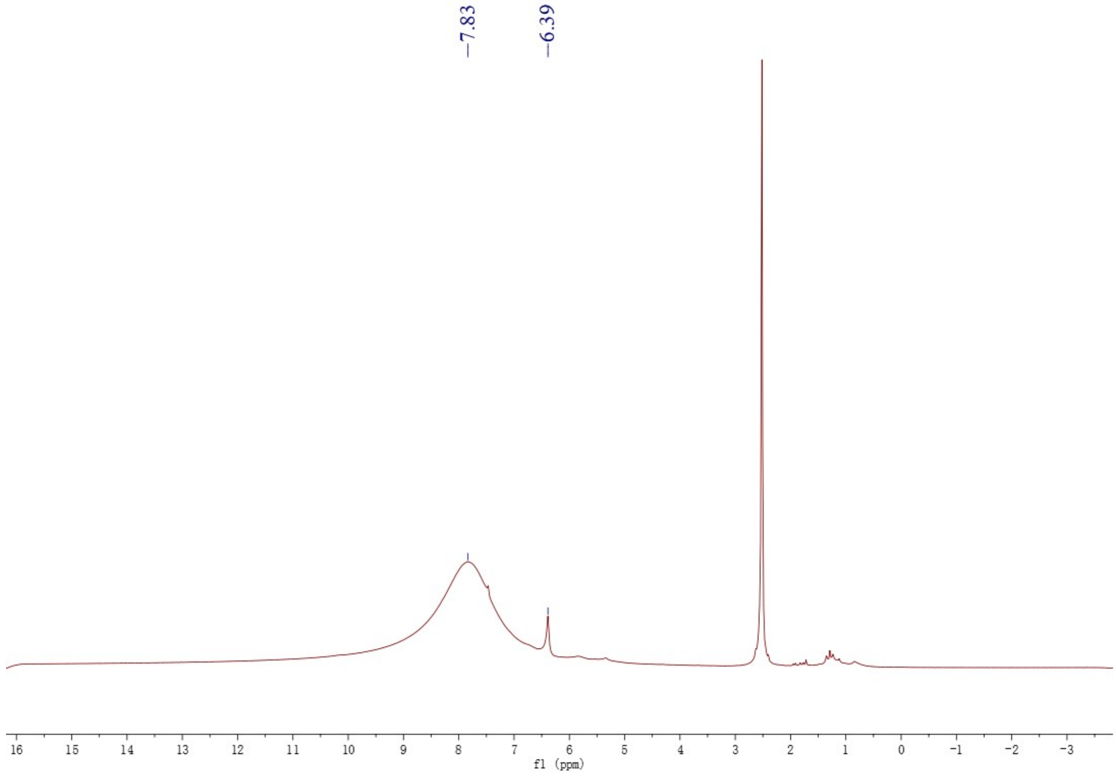


Figure S7 ^{1}H NMR of **4** (d_6-DMSO)

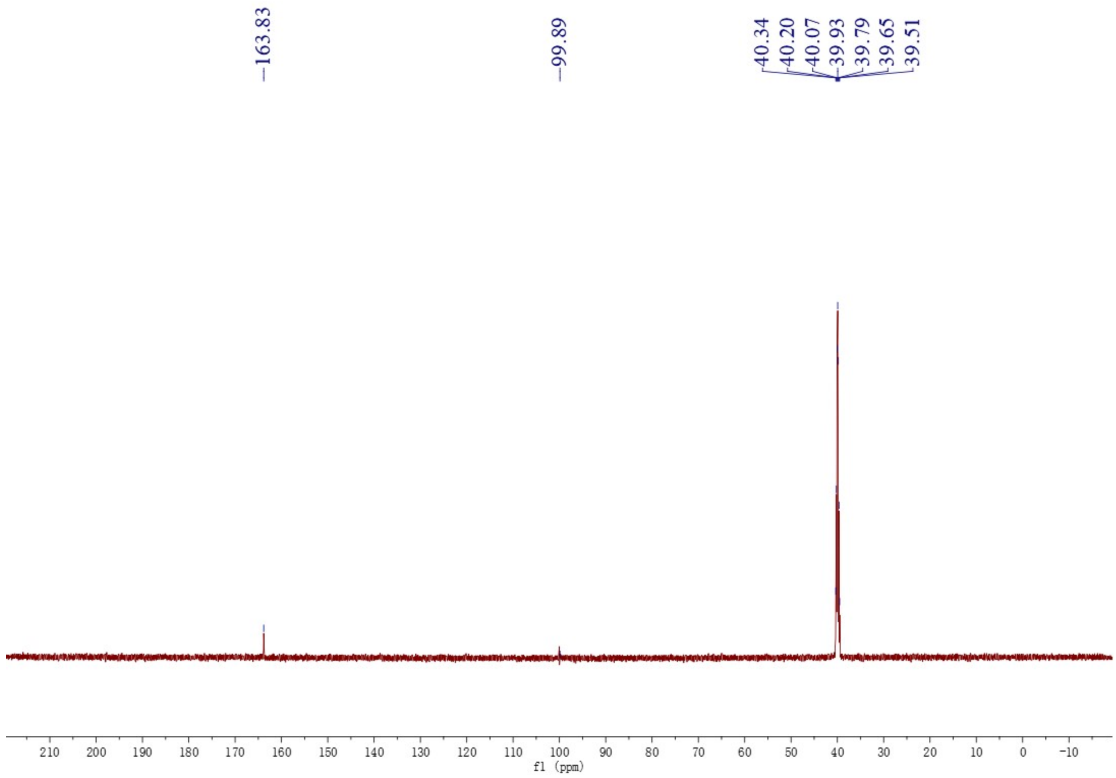


Figure S8 ^{13}C NMR of **4** (d_6-DMSO)

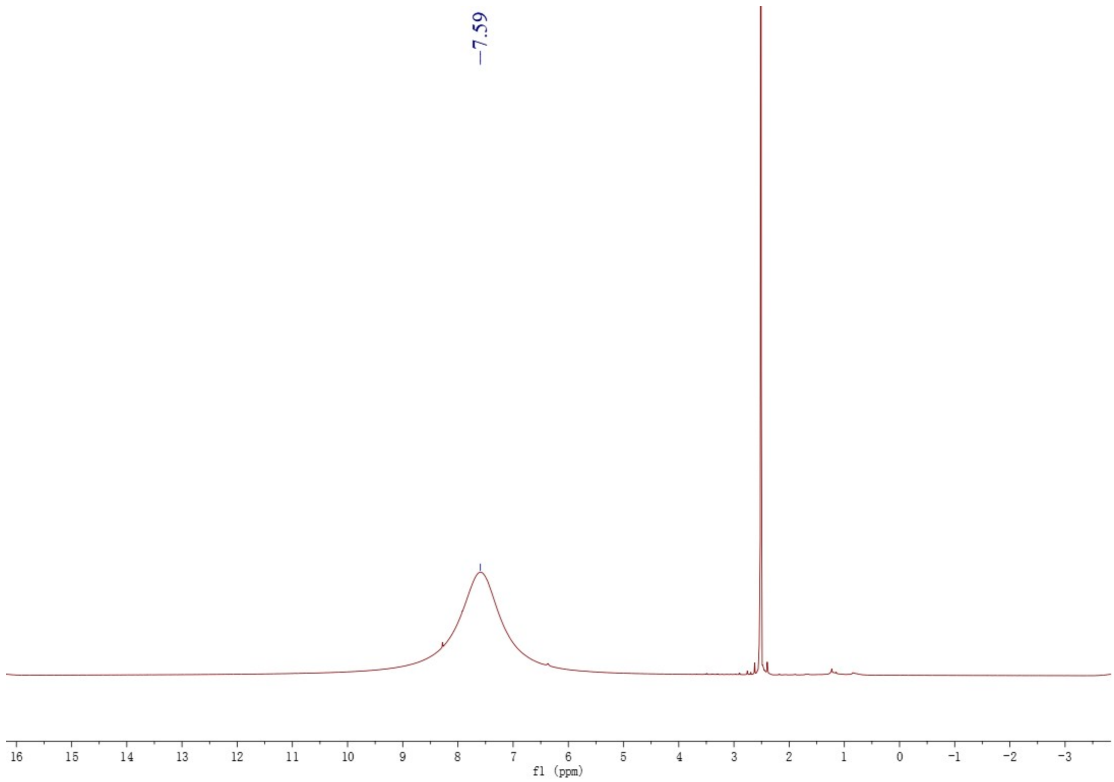


Figure S9 ^{1}H NMR of **5** (d_6-DMSO)

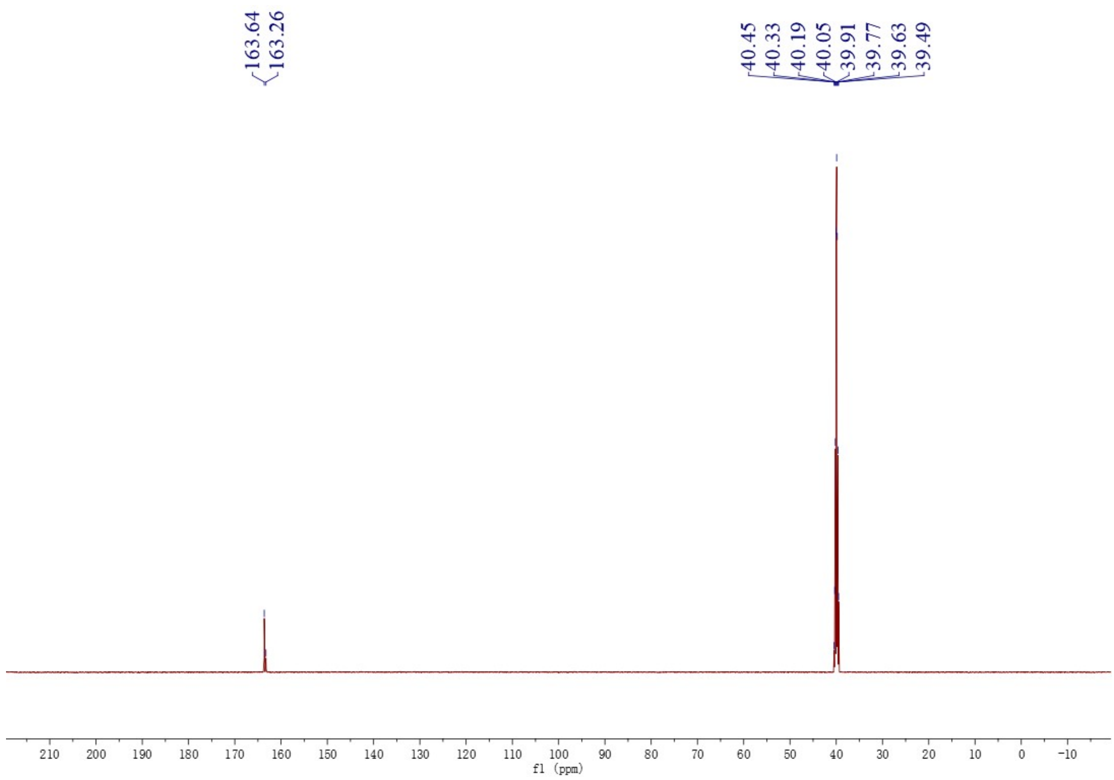


Figure S10 ^{13}C NMR of **5** (d_6-DMSO)

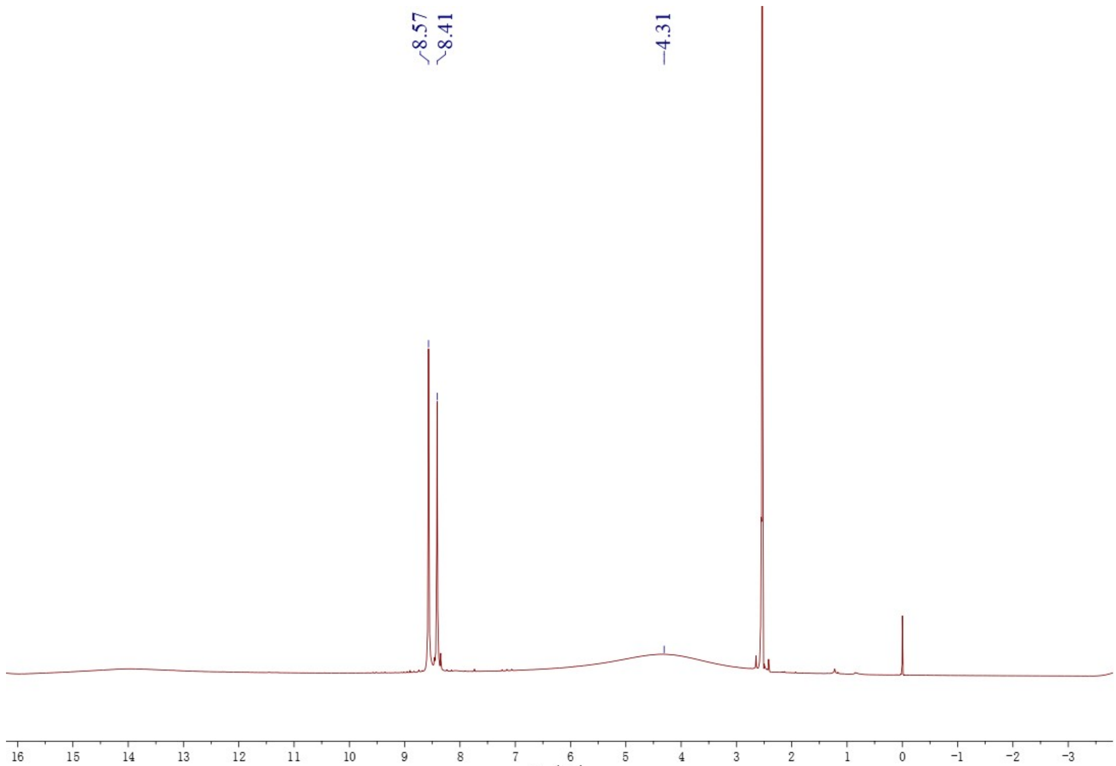


Figure S11 ^{1}H NMR of **6** (d_6-DMSO)

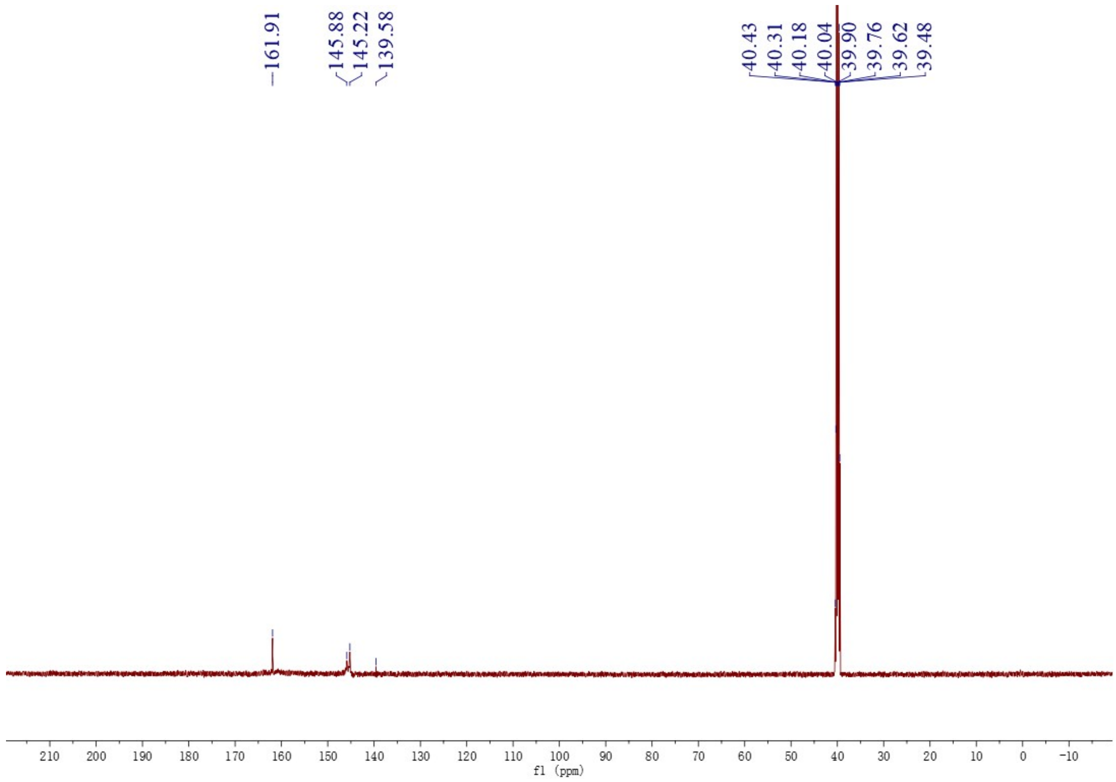


Figure S12 ^{13}C NMR of **6** (d_6-DMSO)

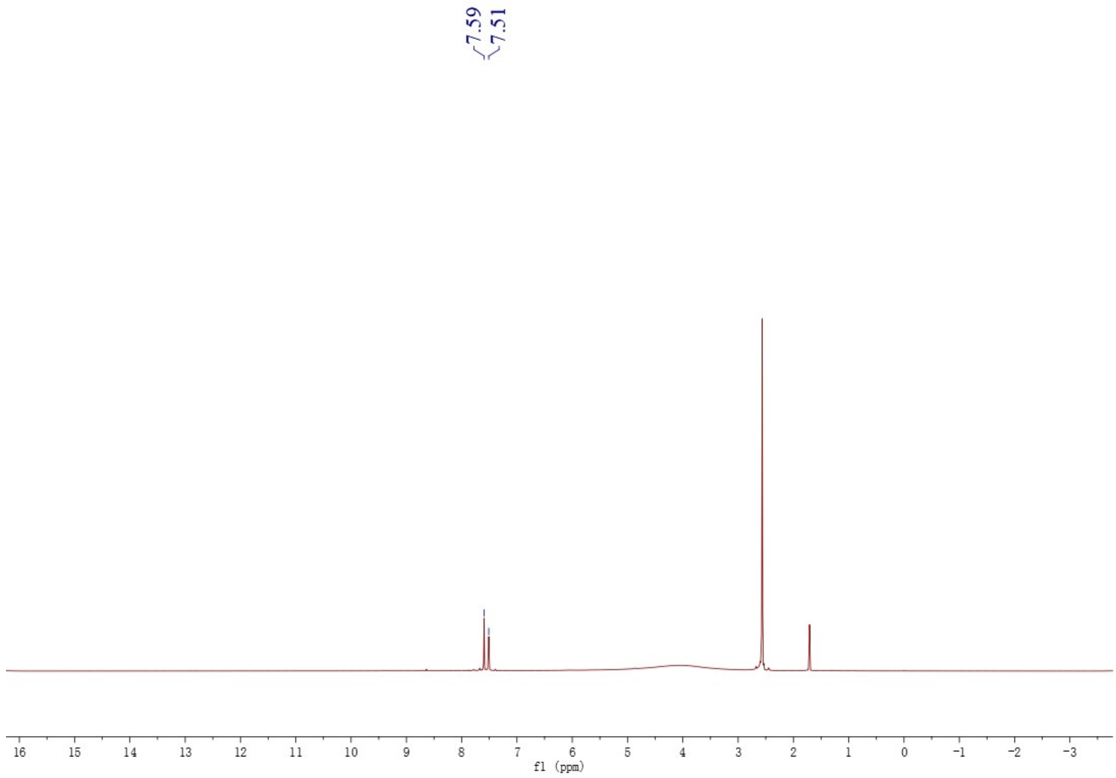


Figure S13 ^{1}H NMR of **7** (d_6-DMSO)

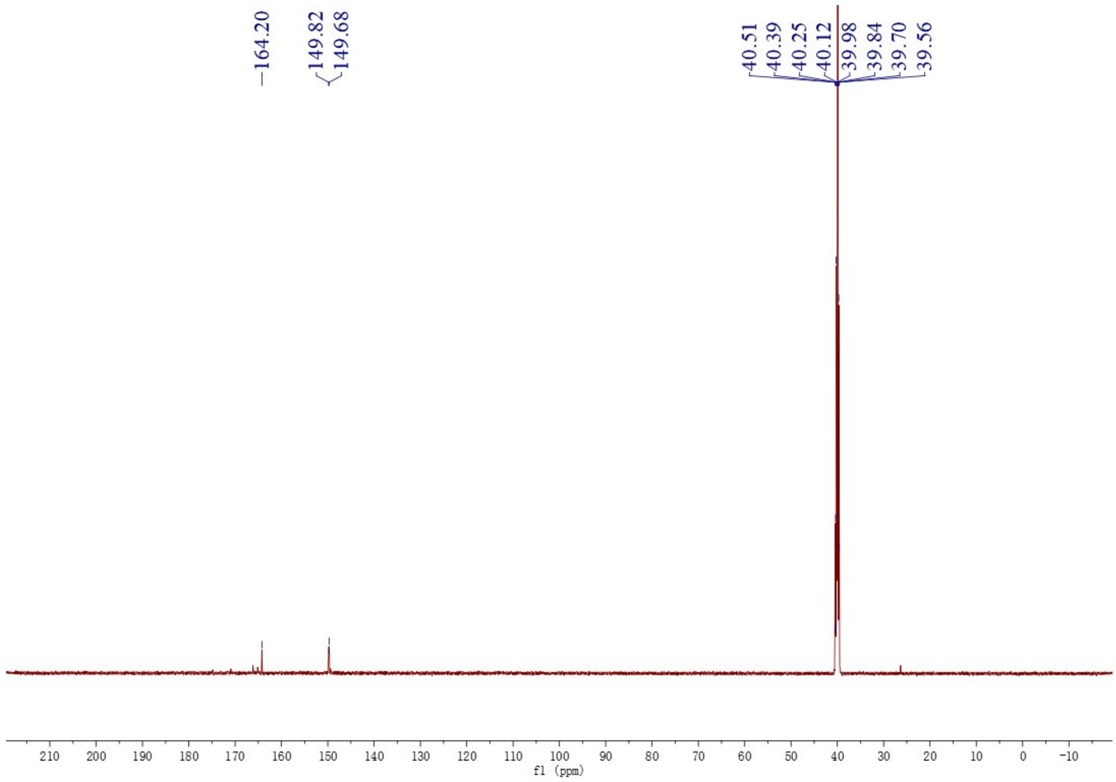


Figure S14 ^{13}C NMR of **7** (d_6-DMSO)

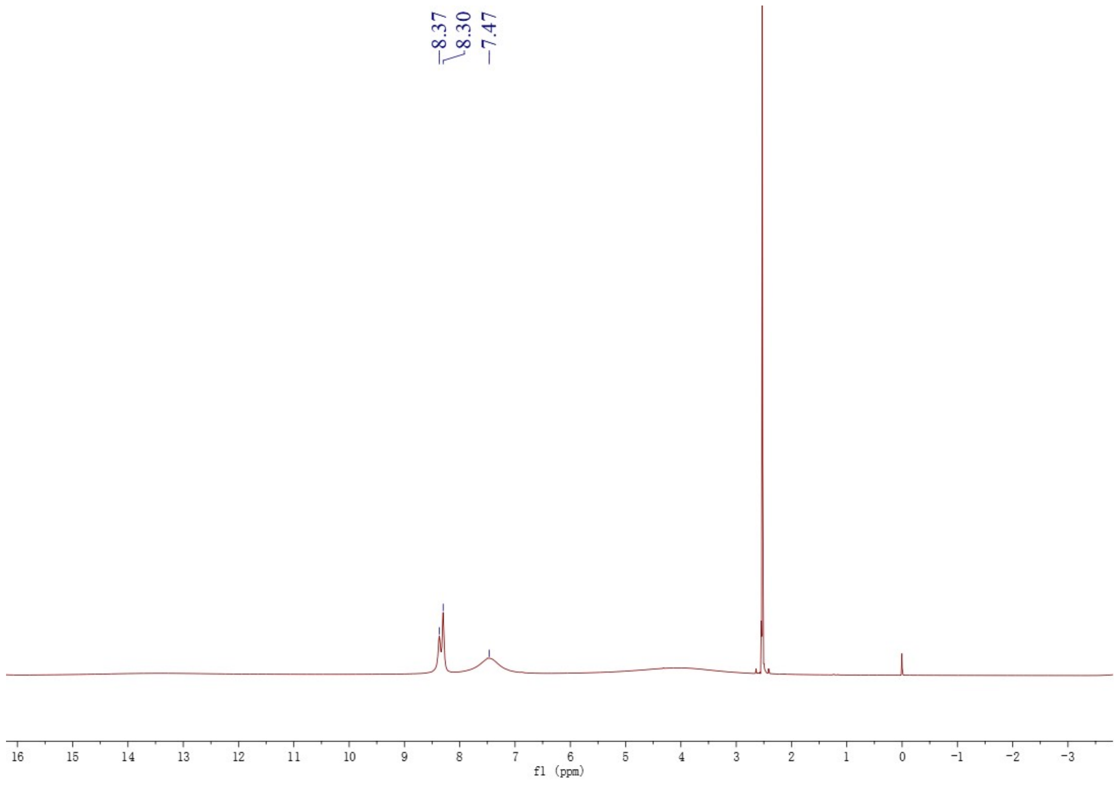


Figure S15 ^{1}H NMR of **8** (d_6-DMSO)

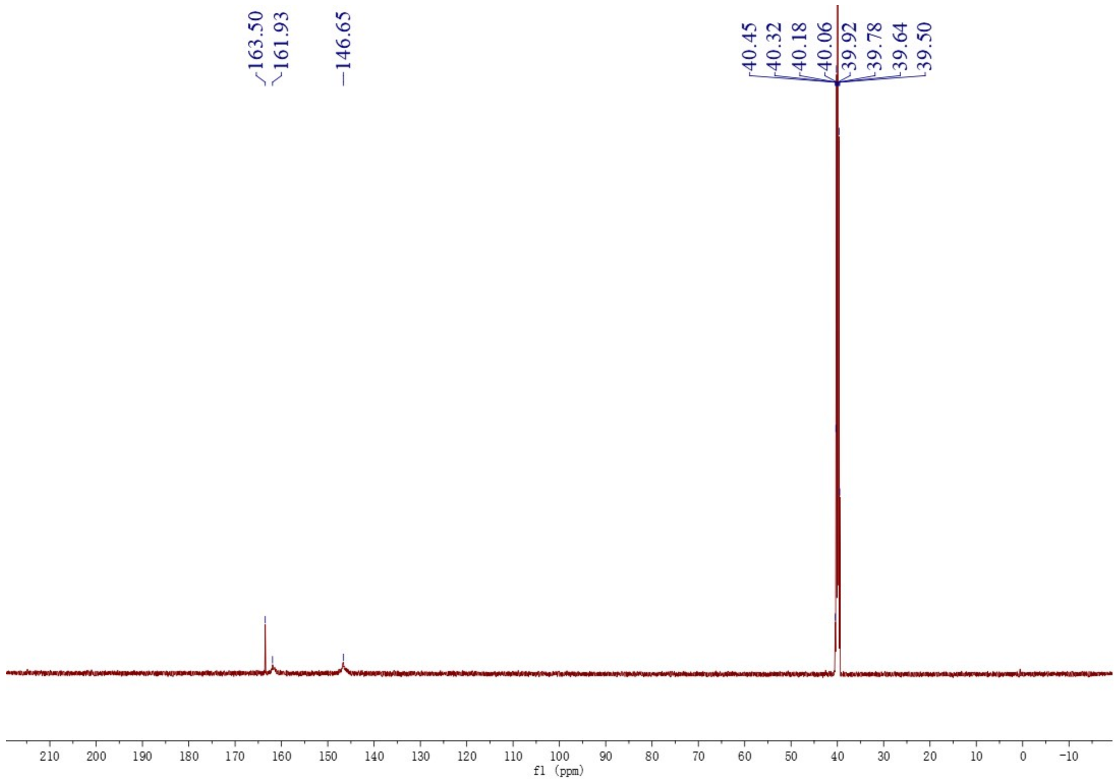


Figure S16 ^{13}C NMR of **8** (d_6-DMSO)

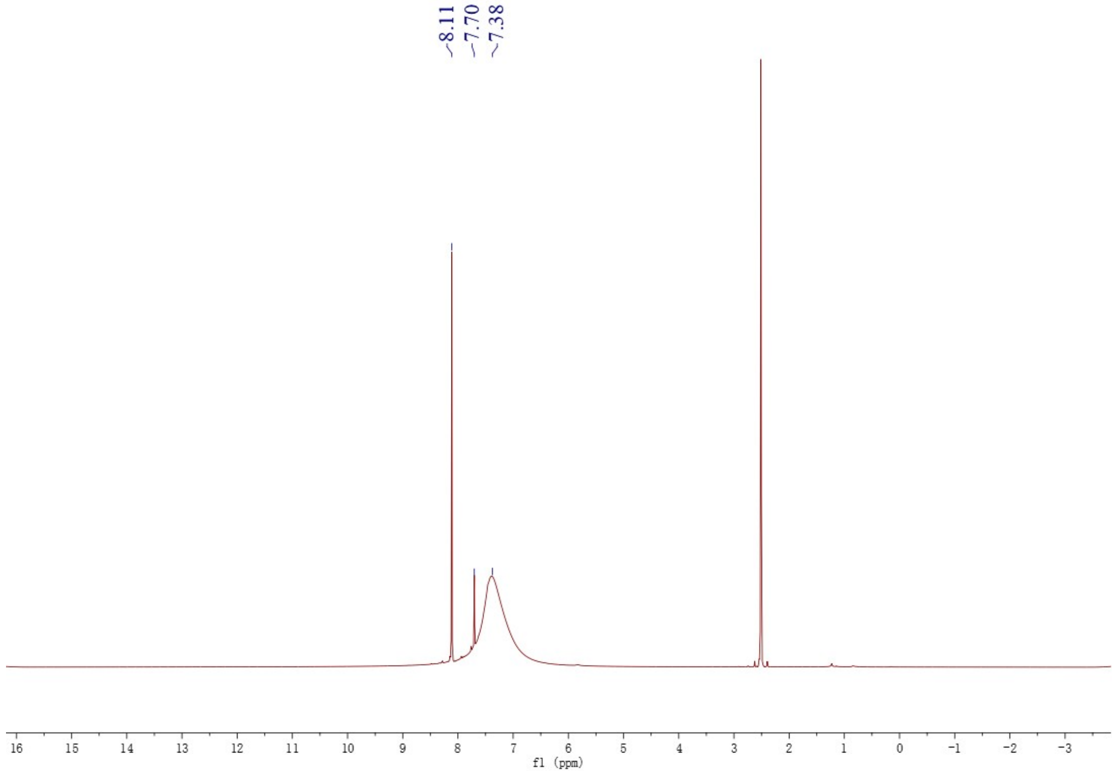


Figure S17 ^{1}H NMR of **9** (d_6-DMSO)

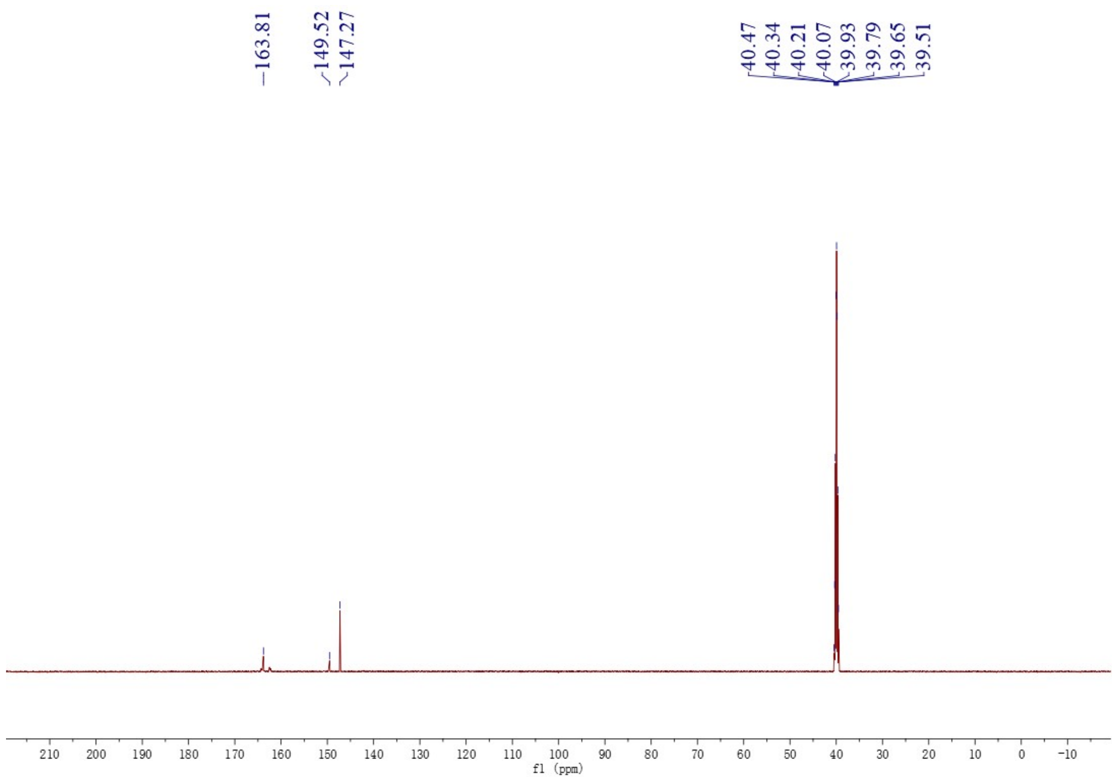


Figure S18 ^{13}C NMR of **9** (d_6-DMSO)

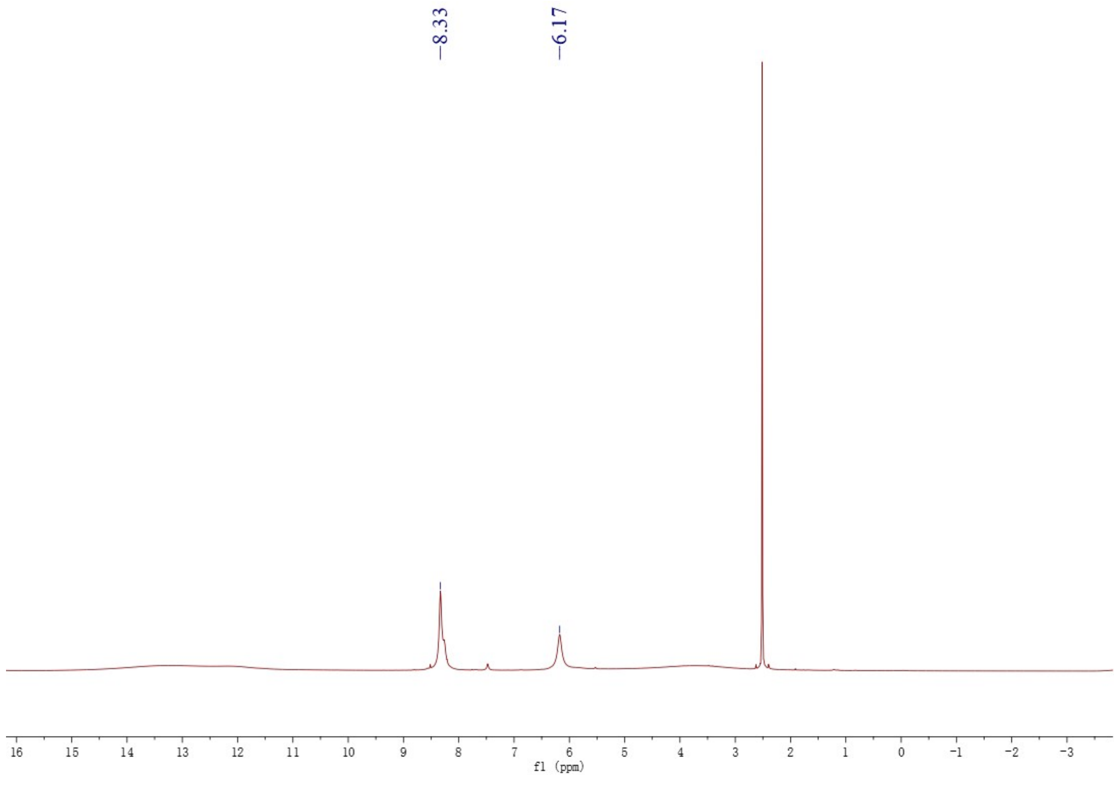


Figure S19 ^{1}H NMR of **10** (d_6-DMSO)

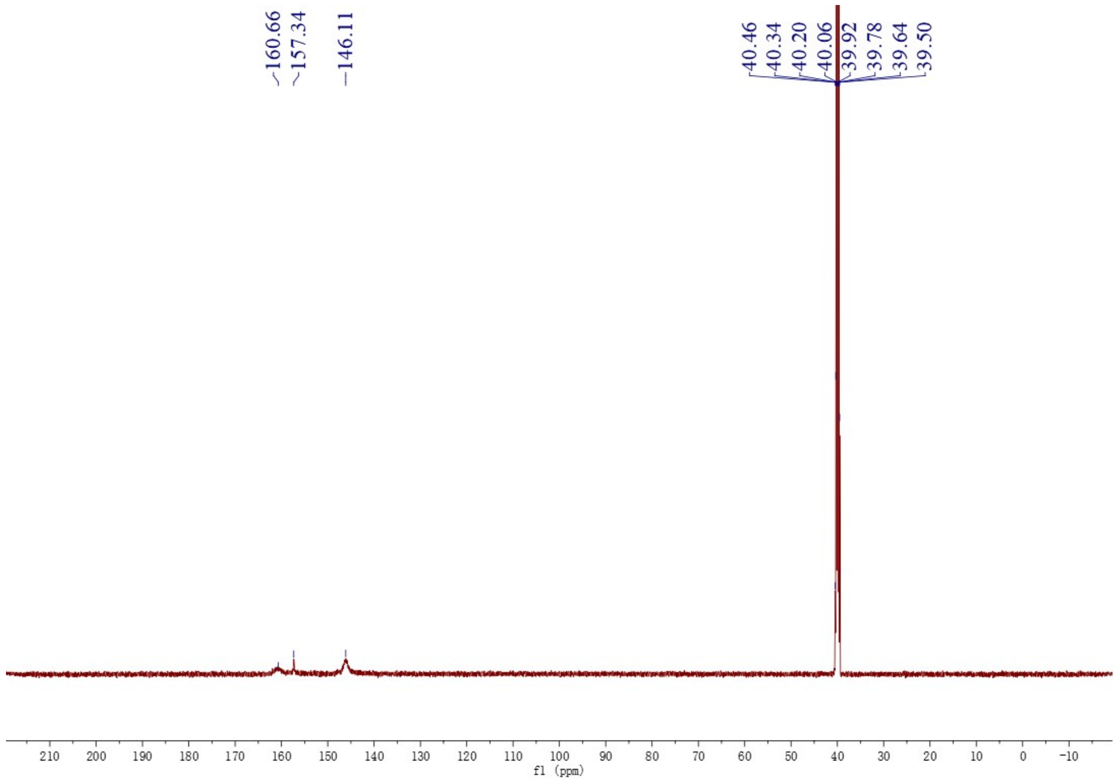


Figure S20 ^{13}C NMR of **10** (d_6-DMSO)

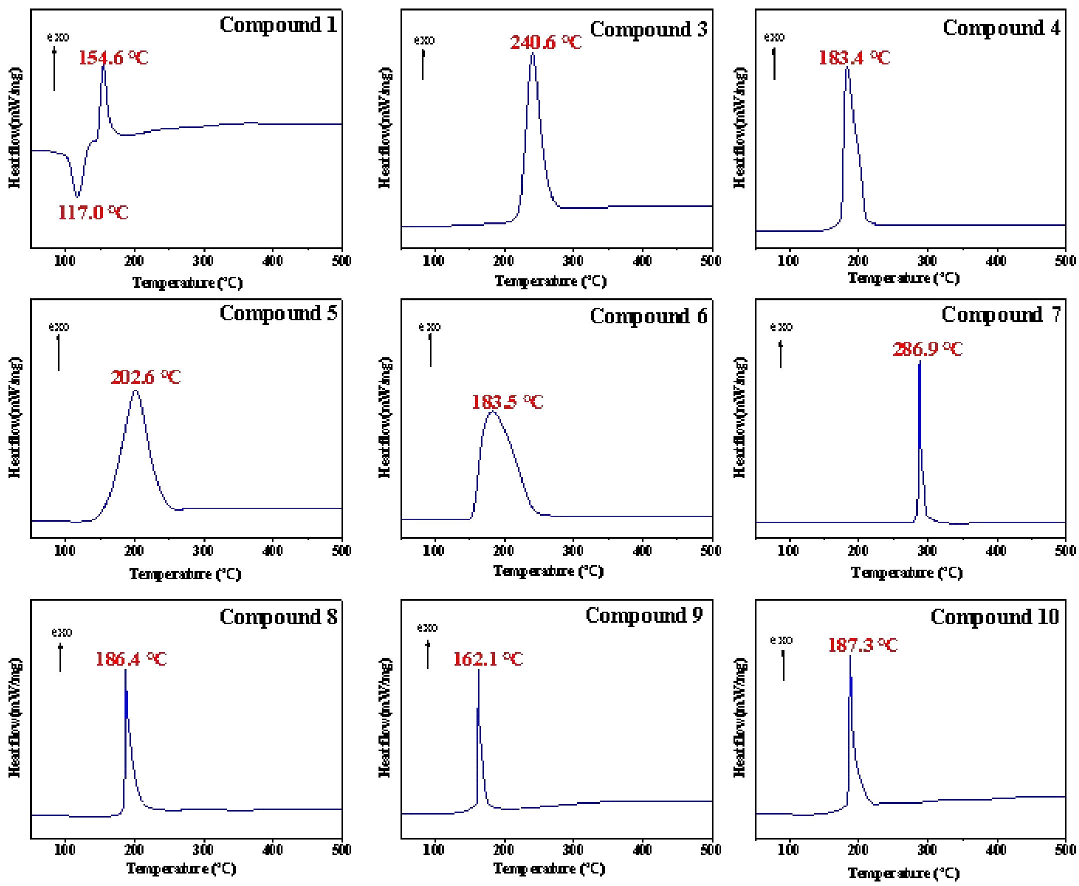


Figure S21 DSC curves of compounds **1** and **3-10**

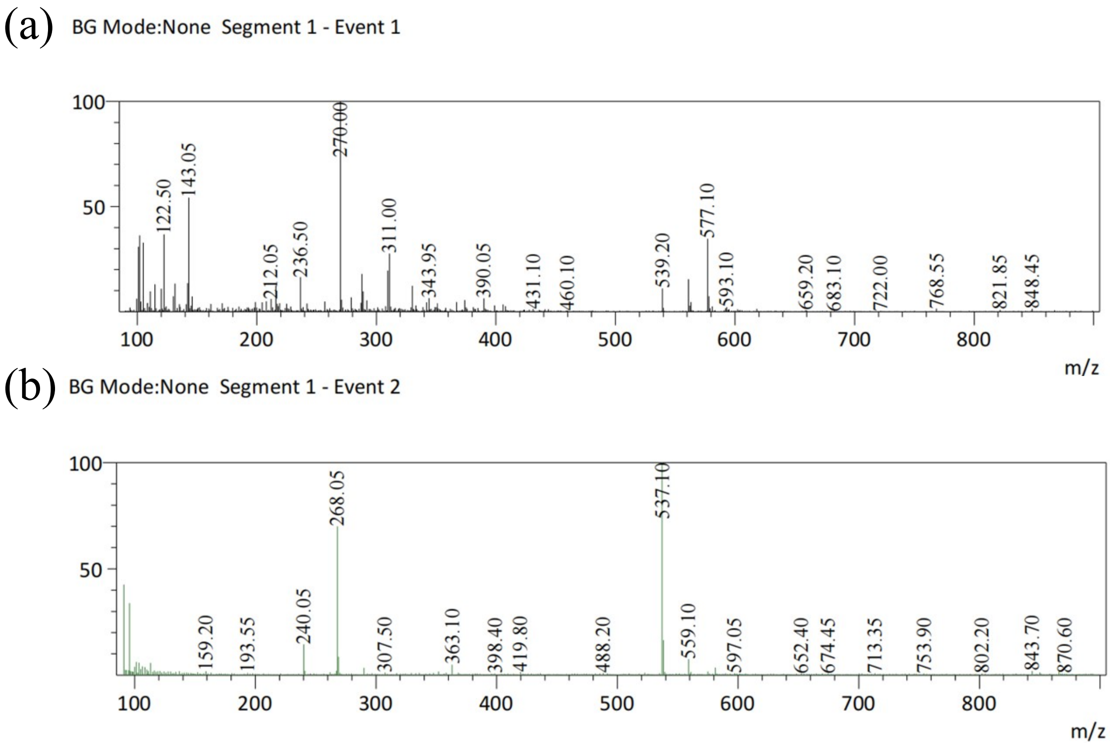


Figure S22 MS spectrum of compound **1** (a) ESI positive, (b) ESI negative

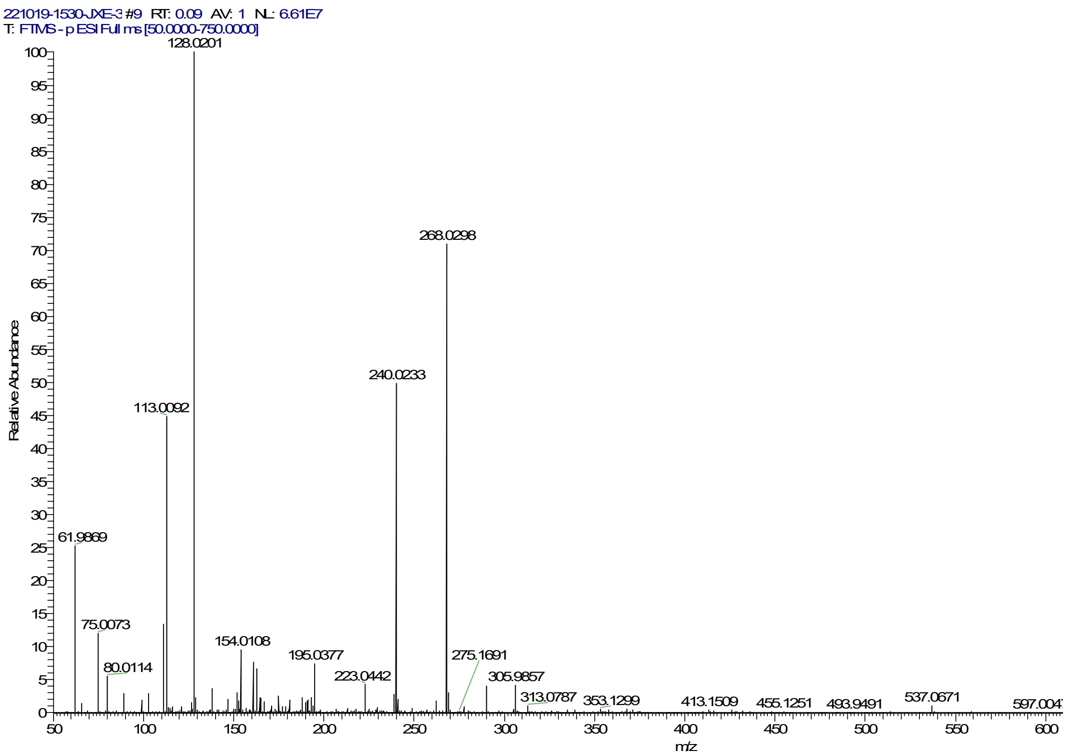


Figure S23 MS spectrum of compound **4**

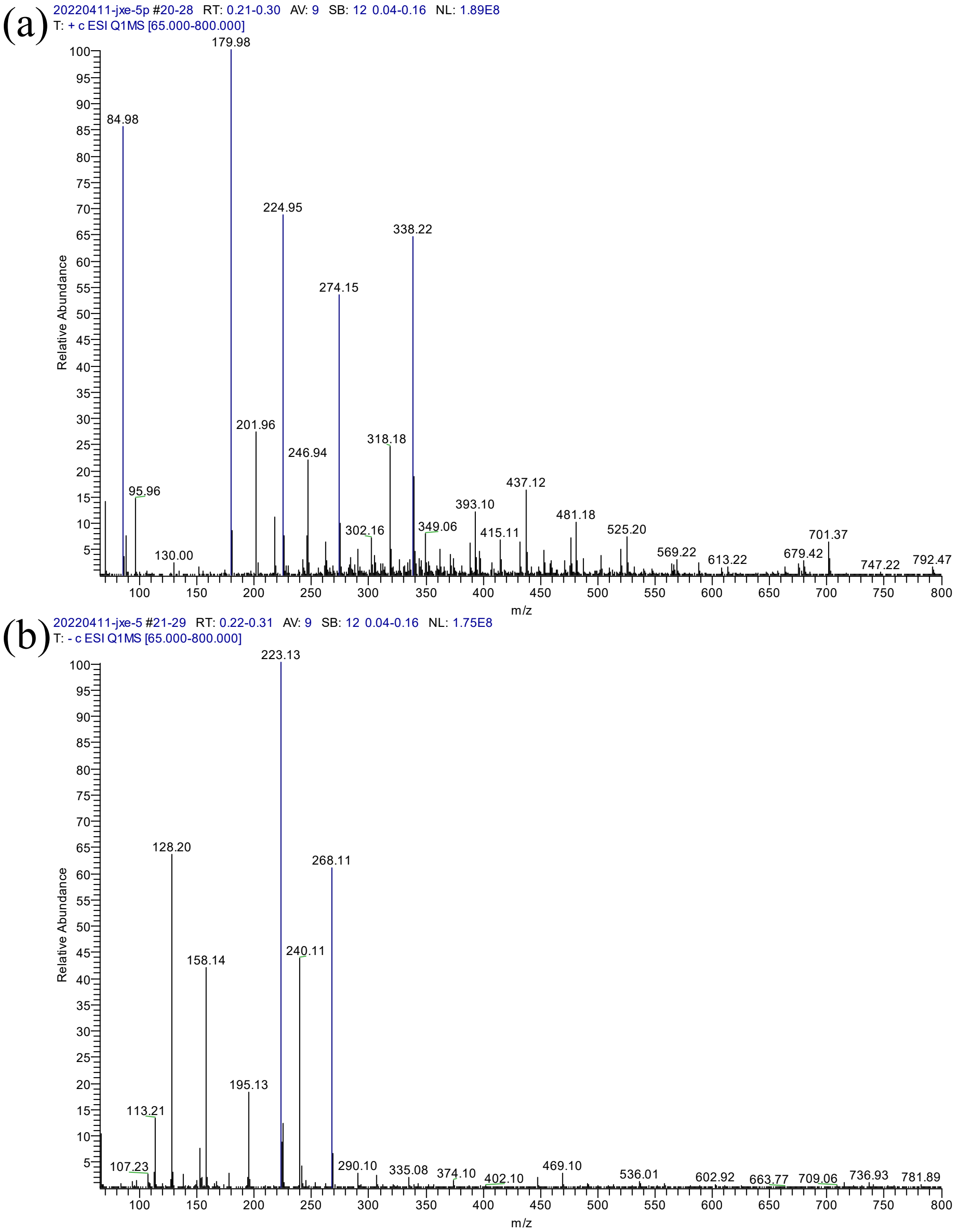


Figure S24 MS spectrum of compound **6** (a) ESI positive, (b) ESI negative

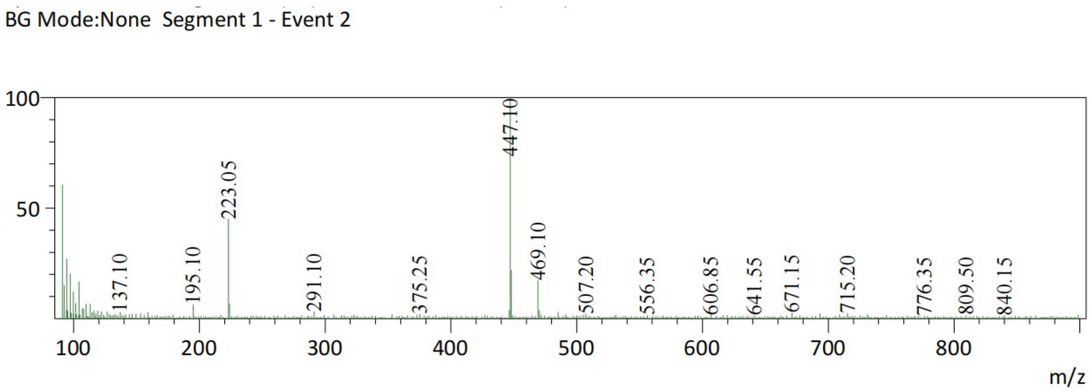


Figure S25 MS spectrum of compound **7**

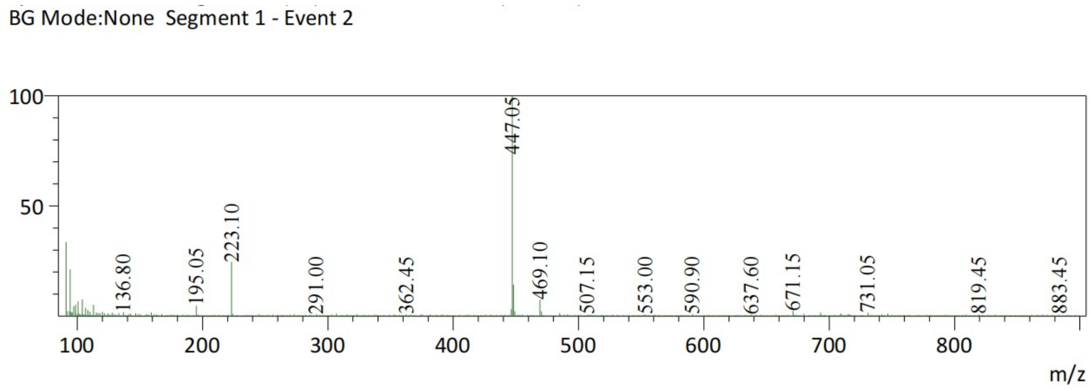


Figure S26 MS spectrum of compound **8**

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