Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information (SI)

Energetic Compounds Featuring Bi(1,3,4-oxadiazole): A New Family of Insensitive Energetic Materials

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1. Experimental Section

General procedure for preparation of the salts (9, 10). Compound **6** (0.5 g, 1.316 mmol) was dissolved in water (20 mL) and silver nitrate (0.447 g, 2.629 mmol) was added to the solution. The mixture was stirred for 2 h, which started instantly to precipitate, was filtered. The wet powder was mixed with water (20 mL) and then the chloride salts (diaminoguanidinium hydrochloride (0.33 g, 2.63 mmol) for **9**, triaminoguanidinium hydrochloride (0.371 g, 2.63 mmol) for **10**) was added. Silver chloride started to precipitate immediately and the mixture was filtered warm under exclusion of light. The solution was evaporated to dryness to obtain yellow solid.

Didiaminoguanidinium 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (9). Yield 0.372 g (88.9%), yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.60 (s, 2H), 7.16 (s, 4H), 4.58 (s, 2H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.76, 159.89, 153.56, 120.84 ppm. IR (KBr): 3460, 3351, 3267, 1681, 1619, 1574, 1499, 1398, 1359, 1321, 1248, 1139, 1063, 995, 957, 816, 748, 611. Elemental analysis calcd (%) for $C_8H_{16}N_{18}O_{10}$ (524.33): C 18.33, H 3.08, N 48.09; found: C 18.50, H 2.89, N 47.88.

Ditriaminoguanidinium 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (10). Yield 0.675 g (92.6%), yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.59 (s, 6H), 4.47 (s, 3H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.75, 159.09, 153.52, 120.78 ppm. IR (KBr): 3595, 3474, 3345, 3252, 1686, 1570, 1498, 1396, 1321,1234, 1125, 1062,957, 820, 748, 607. Elemental analysis calcd (%) for $C_8H_{18}N_{20}O_{10}$ (554.36): C 13.33, H 3.27, N 50.53; found: C 13.42, H 3.41, N 50.22.

Dihydrazinium 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (11). Compound **5** (0.5 g, 1.02 mmol) was dissolved in methanol (10 mL) and 80% hydrazine hydrate (0.2 mL) was added drop wise. The mixture was stirred for 2 h. The precipitate was filtered and washed with methanol. Yield 0.368 g (87.9%), yellow solid. ^{1}H NMR(300 MHz, DMSO-d_6): δ = 6.41 (s, 5H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.75, 153.52, 120.78 ppm. IR (KBr): 3415, 3361,3296, 3157, 1566, 1485, 1413, 1375, 1327, 1257, 1150, 1069, 997, 974, 923, 821, 779, 745, 701, 673. Elemental analysis calcd (%) for $C_6H_{10}N_{12}O_{10}$ (410.22): C 17.57, H 2.46, N 40.97; found: C 15.56, H 2.52, N 40.87.

Dihydroxylammonium 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (12). Compound **5** (0.5 g, 1.02 mmol) was dissolved in acetonitrile (10 mL) and 50% hydroxylamine solution (0.2 mL) was added drop wise. The mixture was stirred for 2 h. The precipitate was filtered and washed with methanol, yield 0.324 g (77.1%), a light yellow product. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.12 (s, 3H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.82, 153.65, 120.94 ppm. IR (KBr): 3302, 3045, 2722, 1574, 1539, 1477, 1366, 1324, 1255, 1147, 1070, 1007, 964, 821, 778, 747, 702, 677. Elemental analysis calcd (%) for $C_6H_8N_{10}O_{12}$ (412.19): C 17.48, H 1.96, N 33.98; found: C 17.56, H 2.01, N 34.15.

Diaminoguanidinium 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (13). Compound **5** (0.5 g, 1.02 mmol) was dissolved in methanol (30 mL) and to this was added aminoguanidine bicarbonate (0.273 g, 2.04 mmol). The mixture was refluxed for 8 h. The solvent was removed in vacuum, left the product as a yellow solid, yield 0.390 g (77.3%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.56 (s, 2H), 7.25 (d, 4H), 4.69 (s, 1H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.74, 158.81, 153.60, 120.82 ppm. IR (KBr): 3444, 3358, 3259, 2493, 1659, 1597, 1561, 1483, 1403, 1325, 1236, 1190, 1141, 1069, 1001, 962, 937, 821, 777, 749, 629. Elemental analysis calcd (%) for $C_8H_{14}N_{16}O_{10}$ (494.30): C 19.44, H 2.85, N 45.34; found: C 19.63, H 2.75, N 45.67.

Didiaminouronium 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (14). Compound **5** (0.5 g, 1.02 mmol) was dissolved in methanol (10 mL) and carbohydrazide (0.183 g, 2.04 mmol) dissolved in water (2 mL) was added drop wise. The mixture was stirred for 2 h. After filtration the solid was obtained as a light yellow solid, yield 0.468 g (87.2%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.99 (s, br, 2H), 3.66 (s, 4H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.77, 159.13, 153.52, 120.78 ppm. IR (KBr): 3354, 3304, 3193, 2968, 2662, 1696, 1624, 1569, 1497, 1400, 1322, 1224, 1141, 1062, 984, 825, 778, 746, 675. Elemental analysis calcd (%) for $C_8H_{14}N_{16}O_{12}$ (526.30): C 18.26, H 2.68, N 42.58; found: C 18.18, H 2.77, N 42.52.

General procedure for preparation of the salts (15-17). Compound **5** (0.5 g, 1.02 mmol) was dissolved in methanol (10 mL) and the triazole (3-amino-1,2,4-triazole (0.141 g, 2.04 mmol) for **15**, 3-amino-1,2,4-triazole (0.172 g, 2.04 mmol) for **16**, 4-amino-1,2,4-triazole (0.172 g, 2.04 mmol) for **17**) was added. The mixture was stirred for 2 h. After filtration, the solid was obtained as a yellow solid.

Di(1,2,4-triazolium) 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (15). Yield 0.364 g (71.7%), yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 13.68 (s, 2H), 9.38 (2, 4H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.81, 153.56, 142.95, 120.87 ppm. IR (KBr): 3147, 3081, 2939, 1688, 1570, 1540, 1494, 1396, 1323, 1240, 1138, 1088, 1059, 1035, 949, 879, 822, 797, 744, 660, 623. Elemental analysis calcd (%) for $C_{10}H_8N_{14}O_{10}$ (484.26): C 24.80, H 1.67, N 40.49; found: C 24.96, H 1.59, N 40.63.

Di(3-amino-1,2,4-triazolium) 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (16). Yield 0.336 g (64.1%), yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.29 (s, 2H), 4.40 (s,2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.77, 153.49, 150.70, 139.11, 120.81 ppm. IR (KBr): 3450, 3323, 3155, 1686, 1536, 1475, 1413, 1369, 1322, 1244, 1210, 1149, 1105, 1080, 952, 830, 782, 750, 707. Elemental analysis calcd (%) for $C_{10}H_{10}N_{16}O_{10}$ (514.29): C 23.35, H 1.96, N 43.58; found: C 23.53, H 1.84, N 43.64.

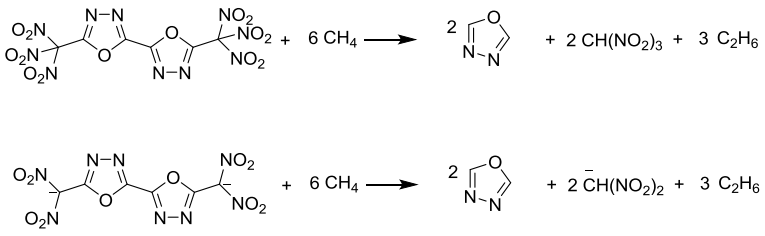
Di(4-amino-1,2,4-triazolium) 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate) (17). Yield 0.403 g (76.9%), yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.53 (s,2H), 9.15 (s, 1H), 8.94 (s,

4H) ppm. ^{13}C NMR(75 MHz, DMSO-d_6): δ = 160.75, 153.56, 144.08, 120.84 ppm. IR (KBr): 3326, 3228, 3127, 2986, 2845, 1637, 1539, 1487, 1413, 1356, 1317, 1238, 1168, 1140, 1075, 1030, 991, 929, 884, 824, 773, 746, 711, 662, 617. Elemental analysis calcd (%) for $C_{10}H_{10}N_{16}O_{10}$ (514.29): C 23.35, H 1.96, N 43.58; found: C 23.66, H 1.98, N 43.45.

2. Computational Details

Calculations were carried by using the Gaussian 09 suite of programs. The geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6-311+G** basis set.[1] All the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

To calculate the heats of formation (HOF), appropriate isodesmic reactions are used. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, are used with the 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 of compound **4** and 5,5'-dinitromethyl-2,2'-bis(1,2,4-oxadiazolyl) anion are shown in Scheme S1.



Scheme S1 Isodemic reactions of compound **4** and 5,5'-dinitromethyl-2,2'-bis(1,2,4-oxadiazolyl) anion.

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

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

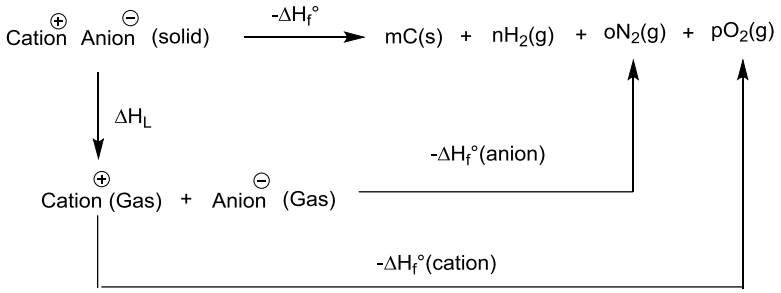
where $\Delta_f H_P$ and $\Delta_f H_R$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression in Equation (2):

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

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 [2,3] or from the high level computing such as CBS-4M.

Based on a Born-Haber energy cycle (Scheme S2), 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 S2 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):

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

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):

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

where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material and the coefficients γ (kJ mol^{-1}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[a]

	E_0/a.u.	ZPE/ kJ mol^{-1}	ΔH_T/ kJ mol^{-1}	HOF/kJ mol^{-1}
CH_4	-40.5339263	112.26	10.04	-74.6[b]
C_2H_6	-79.8565413	187.31	11.79	-84.0[b]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.4[b]
1,3,4-oxadizole	-262.1617961	116.54	11.71	72.2[b]
6 cation	-56.9203229	124.71	9.98	626.4[c]
8 cation	-205.8352836	220.23	2.48	575.9[c]
9 cation	-316.4487748	292.34	15.55	769.0[c]
10 cation	-371.7390268	331.28	17.72	871.5[c]
11 cation	-112.2417207	166.02	9.56	770.0[c]
12 cation	-132.0863677	137.06	8.72	664.4[d]
13 cation	-261.1436758	255.61	14.56	667.4[c]
14 cation	-336.3421325	280.06	19.23	663.4[c]
15 cation	-242.6521743	187.71	10.08	822.2[d]
16 cation	-298.054267	221.04	15.86	826.0[e]
17 cation	-297.9952432	219.72	14.04	913.9[e]

$CH(NO_2)_2^-$	-449.1177648	99.46	18.46	-217.0[e]

[a] E_0 in a.u. ZPE (vibrational zero-point energy) , ΔHT (thermal correction to enthalpy) and HOF are in kJ mol^{-1}. [b] 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.]. [c] Data from Ref.1. [d] Data from Ref.1. [e] Data obtained from CBS-4M calculation in combination with the atomization reaction of the corresponding compound.

3. Single-crystal X-ray Diffraction Analysis of Compound 6

Table S2 Selected bond lengths [Å] and angles [°] for **6**

C(1)-N(1)	1.286(2)	N(3)-O(2)	1.234(2)
C(1)-O(1)	1.348(2)	N(3)-O(3)	1.265(2)
C(1)-C(1)A	1.451(3)	N(4)-O(5)	1.2461(19)
C(2)-N(2)	1.289(2)	N(4)-O(4)	1.2494(19)
C(2)-O(1)	1.377(2)	N(5)-H(5A)	0.888(13)
C(2)-C(3)	1.451(2)	N(5)-H(5B)	0.902(13)
C(3)-N(4)	1.387(2)	N(5)-H(5C)	0.886(13)
C(3)-N(4)	1.390(2)	N(5)-H(5D)	0.875(13)
N(1)-N(2)	1.406(2)		
N(1)-C(1)-O(1)	114.29(16)	O(2)-N(3)-C(3)	123.89(16)
N(1)-C(1)-C(1)A	127.1(2)	O(3)-N(3)-C(3)	114.66(15)
O(1)-C(1)-C(1)A	118.63(19)	O(5)-N(4)-O(4)	121.10(15)
N(2)-C(2)-O(1)	112.15(16)	O(5)-N(4)-C(3)	117.39(15)
N(2)-C(2)-C(3)	128.24(16)	O(4)-N(4)-C(3)	121.49(15)
O(1)-C(2)-C(3)	119.57(15)	H(5A)-N(5)-H(5B)	108.4(13)
N(4)-C(3)-N(3)	122.67(16)	H(5A)-N(5)-H(5C)	110.2(13)
N(4)-C(3)-C(2)	118.99(16)	H(5B)-N(5)-H(5C)	105.9(13)
N(3)-C(3)-C(2)	117.21(16)	H(5A)-N(5)-H(5D)	111.2(13)
C(1)-N(1)-N(2)	105.19(15)	H(5B)-N(5)-H(5D)	108.3(13)
C(2)-N(2)-N(1)	106.69(15)	H(5C)-N(5)-H(5D)	112.7(14)
O(2)-N(3)-O(3)	121.44(15)	C(1)-O(1)-C(2)	101.66(13)

Table S3 Selected torsion angles of for **6** [°]

C(1)-N(1)-N(2)-C(2)	-1.0(2)	O(1)-C(2)-C(3)-N(3)	68.2(2)
O(1)-C(1)-N(1)-N(2)	1.8(2)	N(2)-C(2)-C(3)-N(4)	58.9(3)
O(1)-C(1)-C(1)A-N(1)A	1.9(3)	C(2)-C(3)-N(3)-O(2)	-178.97(16)
N(2)-C(2)-O(1)-C(1)	1.1(2)	N(3)-C(3)-N(4)-O(5)	-177.81(16)
C(3)-C(2)-N(2)-N(1)	177.49(19)	C(1)A-C(1)-O(1)-C(2)	176.54(17)
N(2)-C(2)-C(3)-N(3)	-109.3(2)	O(1)-C(1)-C(1)A-O(1)A	-180.00(17)
N(4)-C(3)-N(3)-O(3)	-168.10(16)	N(1)-C(1)-C(1)A-N(1)A	180.0(2)
N(3)-C(3)-N(4)-O(4)	4.0(3)	O(1)-C(2)-N(2)-N(1)	-0.1(2)
C(2)-C(3)-N(4)-O(5)	14.7(2)	O(1)-C(2)-C(3)-N(4)	-123.69(18)
N(1)-C(1)-O(1)-C(2)	-1.8(2)	N(4)-C(3)-N(3)-O(2)	13.3(3)
C(1)A-C(1)-N(1)-N(2)	-176.37(19)	C(2)-C(3)-N(3)-O(3)	-0.4(2)
N(1)-C(1)-C(1)A-O(1)A	-1.9(3)	C(2)-C(3)-N(4)-O(4)	-163.47(16)
C(3)-C(2)-O(1)-C(1)	-176.74(18)		

Table S4 Hydrogen bonds for **6** [Å and °]

D-H…A	D-H[Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N(5)-H(5A)•••O(4)	0.889(16)	2.082(16)	2.961(2)	169.9(15)
N(5)-H(5A)•••N(2)	0.889(16)	2.626(15)	2.985(2)	105.2(12)
N(5)-H(5B)•••O(3)	0.902(16)	2.225(19)	3.044(2)	150.8(17)
N(5)-H(5C)•••O(2)	0.886(16)	2.133(15)	2.856(2)	138.3(15)
N(5)-H(5C)•••O(4)	0.886(16)	2.131(18)	2.883(2)	142.2(15)
N(5)-H(5D)•••O(5)	0.873(13)	2.194(16)	2.933(2)	142.1(17)
N(5)-H(5D)•••N(1)	0.873(13)	2.472(18)	3.100(2)	129.3(16)

4. Single-crystal X-ray Diffraction Analysis of Compound 9

Table S5 Selected bond lengths [Å] and angles [°] for **9**

C(1)-N(1)	1.293(4)	N(3)-O(3)	1.254(3)
C(1)-O(1)	1.375(3)	N(4)-O(4)	1.249(3)
C(1)-C(3)	1.444(4)	N(4)-O(5)	1.263(3)
C(2)-N(2)	1.284(3)	N(5)-N(6)	1.409(3)

C(2)-O(1)	1.348(3)	N(5)-H(5A)	0.876(17)
C(2)-C(2)A	1.452(5)	N(5)-H(5B)	0.903(17)
C(3)-N(4)	1.362(3)	N(6)-H(6A)	0.870(17)
C(3)-N(3)	1.393(3)	N(7)-N(8)	1.412(3)
C(4)-N(6)	1.312(3)	N(7)-H(7A)	0.901(17)
C(4)-N(7)	1.328(4)	N(8)-H(8A)	0.888(17)
C(4)-N(9)	1.341(4)	N(8)-H(8B)	0.884(17)
N(1)-N(2)	1.402(3)	N(9)-H(9A)	0.881(17)
N(3)-O(2)	1.232(3)	N(9)-H(9B)	0.854(17)
N(1)-C(1)-O(1)	112.4(2)	O(4)-N(4)-C(3)	123.3(2)
N(1)-C(1)-C(3)	129.8(3)	O(5)-N(4)-C(3)	116.2(2)
O(1)-C(1)-C(3)	117.8(3)	N(6)-N(5)-H(5A)	105(2)
N(2)-C(2)-O(1)	114.1(2)	N(6)-N(5)-H(5B)	102.0(18)
N(2)-C(2)-C(2)A	128.3(3)	H(5A)-N(5)-H(5B)	97(3)
O(1)-C(2)-C(2)A	117.6(3)	C(4)-N(6)-N(5)	118.1(2)
N(4)-C(3)-N(3)	123.6(2)	C(4)-N(6)-H(6A)	120.3(19)
N(4)-C(3)-C(1)	119.1(2)	N(5)-N(6)-H(6A)	121.6(19)
N(3)-C(3)-C(1)	117.3(2)	C(4)-N(7)-N(8)	117.7(2)
N(6)-C(4)-N(7)	120.6(3)	C(4)-N(7)-H(7A)	121.2(18)
N(6)-C(4)-N(9)	120.8(3)	N(8)-N(7)-H(7A)	120.3(18)
N(7)-C(4)-N(9)	118.5(3)	N(7)-N(8)-H(8A)	104.7(19)
C(1)-N(1)-N(2)	106.1(2)	N(7)-N(8)-H(8B)	109.6(19)
C(2)-N(2)-N(1)	105.8(2)	H(8A)-N(8)-H(8B)	107(3)
O(2)-N(3)-O(3)	122.4(2)	C(4)-N(9)-H(9A)	114(2)
O(2)-N(3)-C(3)	122.8(2)	C(4)-N(9)-H(9B)	120(2)
O(3)-N(3)-C(3)	114.7(2)	H(9A)-N(9)-H(9B)	121(3)
O(4)-N(4)-O(5)	120.5(2)	C(2)-O(1)-C(1)	101.6(2)

Table S6 Selected torsion angles of for **9** [°]

C(1)-N(1)-N(2)-C(2)	-0.1(3)	O(1)-C(2)-C(2)A-O(1)A	180.0(2)
O(1)-C(1)-N(1)-N(2)	0.1(3)	N(2)-C(2)-C(2)A-N(2)	-180.0(3)
O(1)-C(1)-C(3)-N(4)	-102.9(3)	C(1)-C(3)-N(3)-O(2)	-172.2(2)
N(2)-C(2)-O(1)-C(1)	0.0(3)	N(3)-C(3)-N(4)-O(5)	-173.7(2)
C(2)A-C(2)-N(2)-N(1)	-180.0(2)	C(3)-C(1)-O(1)-C(2)	-179.1(2)
N(2)-C(2)-C(2)A-O(1)A	0.0(4)	O(1)-C(1)-C(3)-N(3)	76.5(3)
N(4)-C(3)-N(3)-O(3)	-173.8(2)	N(1)-C(1)-C(3)-N(4)	78.2(3)
N(3)-C(3)-N(4)-O(4)	7.1(4)	O(1)-C(2)-N(2)-N(1)	0.1(3)
C(1)-C(3)-N(4)-O(5)	5.7(4)	O(1)-C(2)-C(2)A-N(2)A	0.0(4)
N(1)-C(1)-O(1)-C(2)	0.0(3)	N(4)-C(3)-N(3)-O(2)	7.2(4)
C(3)-C(1)-N(1)-N(2)	179.0(2)	C(1)-C(3)-N(3)-O(3)	6.8(4)
N(1)-C(1)-C(3)-N(3)	-102.4(4)	C(1)-C(3)-N(4)-O(4)	-173.5(2)
C(2)A-C(2)-O(1)-C(1)	180.0(2)	O(1)-C(2)-C(2)A-O(1)A	-179.1(2)

Table S7 Hydrogen bonds for **9** [Å and °]

D-H…A	D-H[Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N(5)-H(5A)•••N(2)	0.88(3)	2.30(2)	3.162(3)	168(3)
N(5)-H(5B)•••O(3)	0.91(2)	2.35(2)	3.019(3)	131(2)
N(6)-H(6A)•••N(1)	0.87(2)	2.50(2)	3.306(3)	154(2)
intra N(6)-H(6A)•••N(8)	0.87(2)	2.33(3)	2.655(3)	102.7(19)
N(7)-H(7A)•••O(5)	0.90(2)	2.04(2)	2.924(3)	166(2)
N(8)-H(8A)•••O(5)	0.89(2)	2.31(2)	3.116(4)	151(2)
N(8)-H(8B)•••O(2)	0.88(2)	2.329(19)	3.065(3)	141.0(19)
N(8)-H(8B)•••O(4)	0.88(2)	2.22(3)	2.956(3)	140(2)
intra N(9)-H(9A)•••N(5)	0.88(2)	2.26(3)	2.664(3)	108(2)
N(9)-H(9A)•••N(1)	0.88(2)	2.58(3)	3.333(4)	144(2)
N(9)-H(9B)•••O(4)	0.85(3)	2.23(2)	3.066(3)	166(3)

5. Single-crystal X-ray Diffraction Analysis of Compound 15

Table S8 Selected bond lengths [Å] and angles [°] for **15**

C(1)-N(2)	1.296(3)	C(4)-C(5)	1.450(3)
C(1)-N(3)	1.349(4)	C(5)-N(7)	1.381(3)
C(1)-H(1)	0.9500	C(5)-N(6)	1.388(3)
C(2)-N(1)	1.295(3)	N(1)-N(2)	1.362(3)
C(2)-N(3)	1.308(3)	N(1)-H(1A)	0.90(2)

C(2)-H(2)	0.9500	N(3)-H(3A)	0.88(2)
C(3)-N(4)	1.289(3)	N(4)-N(5)	1.408(3)
C(3)-O(1)	1.349(3)	N(6)-O(2)	1.250(2)
C(3)-C(3)A	1.452(4)	N(6)-O(3)	1.254(2)
C(4)-N(5)	1.289(3)	N(7)-O(4)	1.240(2)
C(4)-O(1)	1.377(3)	N(7)-O(5)	1.265(2)
N(2)-C(1)-N(3)	110.9(3)	C(2)-N(1)-H(1A)	125.5(19)
N(2)-C(1)-H(1)	124.5	N(2)-N(1)-H(1A)	122.5(19)
N(3)-C(1)-H(1)	124.5	C(1)-N(2)-N(1)	103.1(2)
N(1)-C(2)-N(3)	106.7(3)	C(2)-N(3)-C(1)	107.3(2)
N(1)-C(2)-H(2)	126.6	C(2)-N(3)-H(3A)	123.4(19)
N(3)-C(2)-H(2)	126.6	C(1)-N(3)-H(3A)	129.3(19)
N(4)-C(3)-O(1)	114.70(19)	C(3)-N(4)-N(5)	104.8(2)
N(4)-C(3)-C(3)A	127.3(3)	C(4)-N(5)-N(4)	106.78(18)
O(1)-C(3)-C(3)A	118.0(3)	O(2)-N(6)-O(3)	120.5(2)
N(5)-C(4)-O(1)	112.4(2)	O(2)-N(6)-C(5)	122.7(2)
N(5)-C(4)-C(5)	127.8(2)	O(3)-N(6)-C(5)	116.80(19)
O(1)-C(4)-C(5)	119.8(2)	O(4)-N(7)-O(5)	121.37(19)
N(7)-C(5)-N(6)	122.2(2)	O(4)-N(7)-C(5)	123.3(2)
N(7)-C(5)-C(4)	118.2(2)	O(5)-N(7)-C(5)	115.37(19)
N(6)-C(5)-C(4)	118.1(2)	C(3)-O(1)-C(4)	101.37(19)
C(2)-N(1)-N(2)	111.9(2)		

Table S9 Selected torsion angles of for **15** [ ]

C(3)-N(4)-N(5)-C(4)	0.3(3)	O(1)-C(4)-C(5)-N(6)	121.8(3)
O(1)-C(3)-N(4)-N(5)	-0.2(3)	N(5)-C(4)-C(5)-N(7)	110.2(4)
O(1)-C(3)-C(3)A-N(4)A	-0.7(5)	C(4)-C(5)-N(6)-O(2)	169.2(3)
N(5)-C(4)-O(1)-C(3)	0.1(3)	N(6)-C(5)-N(7)-O(5)	162.1(3)
C(5)-C(4)-N(5)-N(4)	177.9(3)	C(3)A-C(3)-O(1)-C(4)	-179.4(3)
N(5)-C(4)-C(5)-N(6)	-56.3(5)	O(1)-C(3)-C(3)A-O(1)A	-180.0(3)
N(7)-C(5)-N(6)-O(3)	176.3(3)	N(4)-C(3)-C(3)A-N(4)A	180.0(3)
N(6)-C(5)-N(7)-O(4)	-17.4(5)	O(1)-C(4)-N(5)-N(4)	-0.3(3)
C(4)-C(5)-N(7)-O(5)	-3.7(4)	O(1)-C(4)-C(5)-N(7)	-71.7(4)
N(4)-C(3)-O(1)-C(4)	0.1(3)	N(7)-C(5)-N(6)-O(2)	3.3(5)
C(3)A-C(3)-N(4)-N(5)	179.1(3)	C(4)-C(5)-N(6)-O(3)	-10.4(5)
N(4)-C(3)-C(3)A-O(1)A	0.7(5)	C(4)-C(5)-N(7)-O(4)	176.7(3)
C(5)-C(4)-O(1)-C(3)	-178.2(3)		

Table S10 Hydrogen bonds for **15** [Å and]

D-H…A	D-H[Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N(1)-H(1A)•••O(2)	0.90(3)	1.92(3)	2.750(3)	152(3)
N(1)-H(1A)•••O(4)	0.90(3)	2.26(3)	2.878(3)	126(2)
N(3)-H(3A)•••O(5)	0.88(3)	2.11(3)	2.922(3)	152(3)
N(3)-H(3A)•••O(3)	0.88(3)	2.59(3)	2.973(3)	107(3)
C(1)-H(1)•••O(3)	0.95	2.55	2.989(3)	108
C(1)-H(1)•••O(5)	0.95	2.4	3.202(4)	142
C(2)-H(2)•••O(4)	0.95	2.54	3.190(4)	126
C(2)-H(2)•••N(4)	0.95	2.52	3.159(4)	124

6. ^{1}H NMR and ^{13}C NMR Spectra of Compounds 3-17.

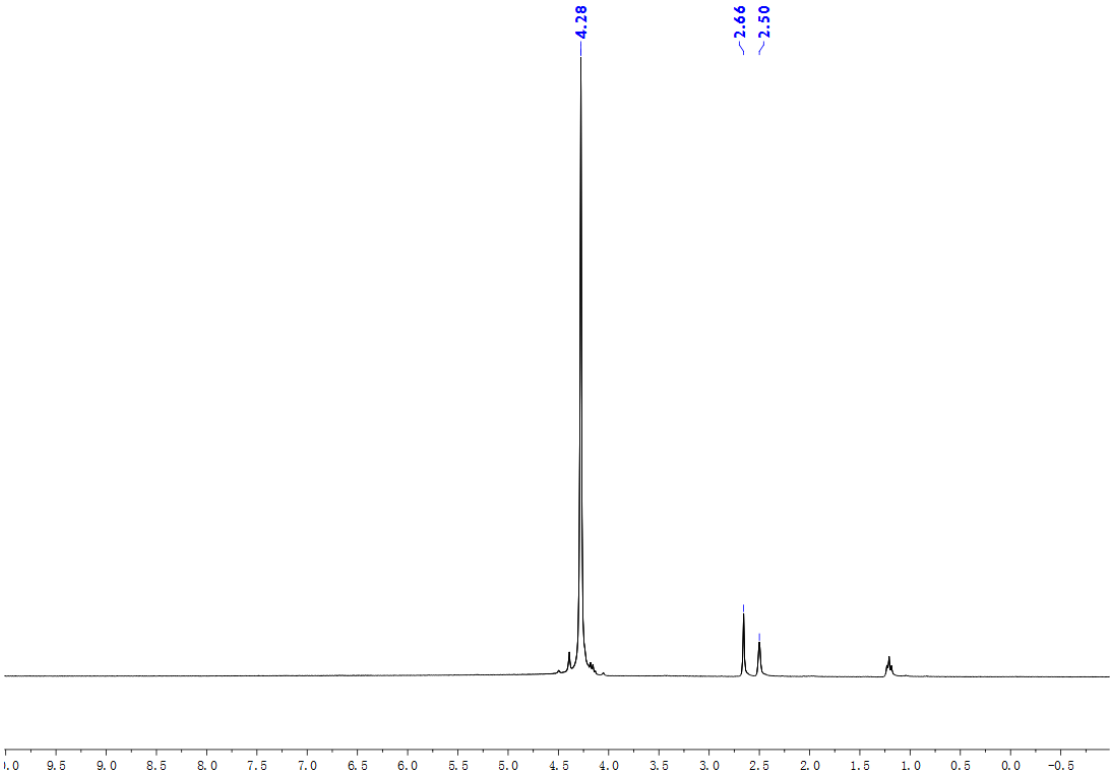


Figure S1 ^{1}H NMR spectrum of **3** in DMSO-d_6

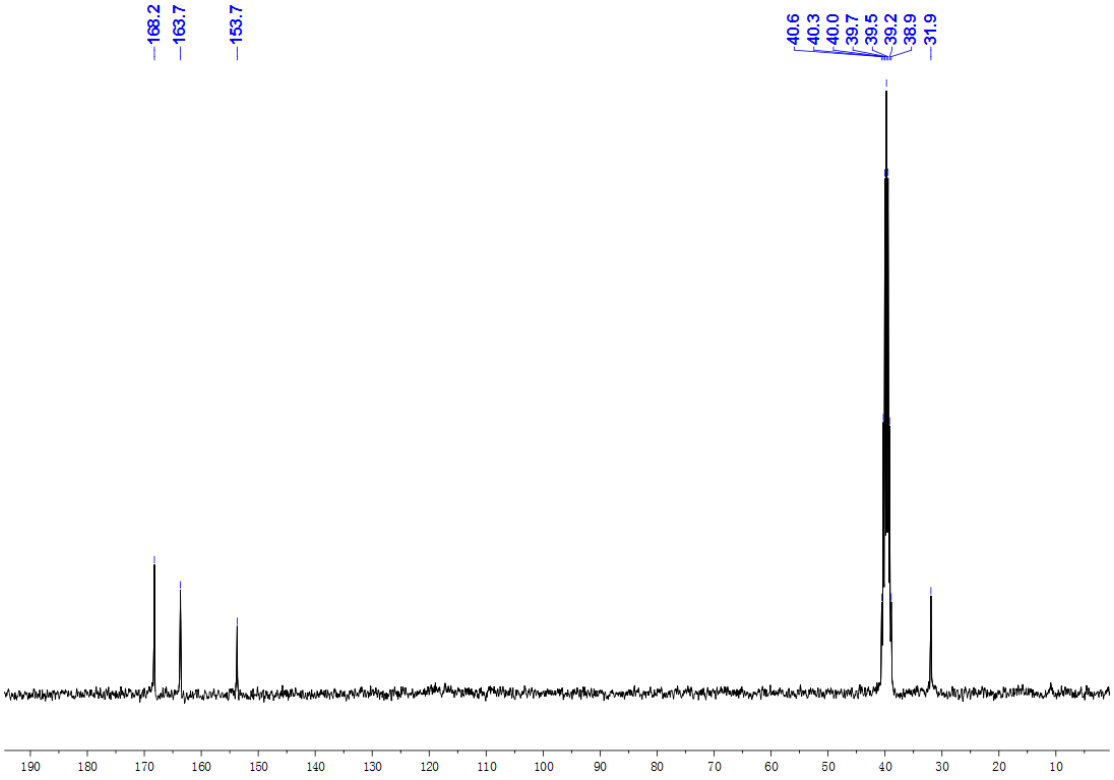


Figure S2 ^{13}C NMR spectrum of **3** in DMSO-d_6

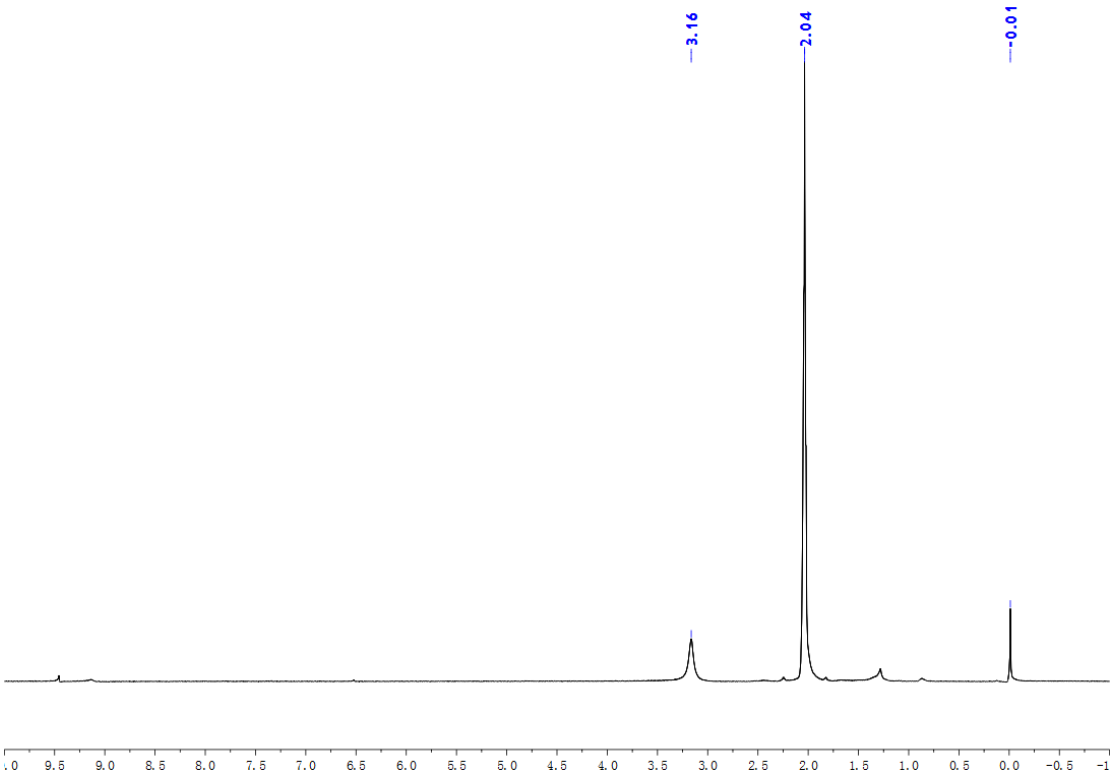


Figure S3 ^{1}H NMR spectrum of **4** in Acetone-d_6

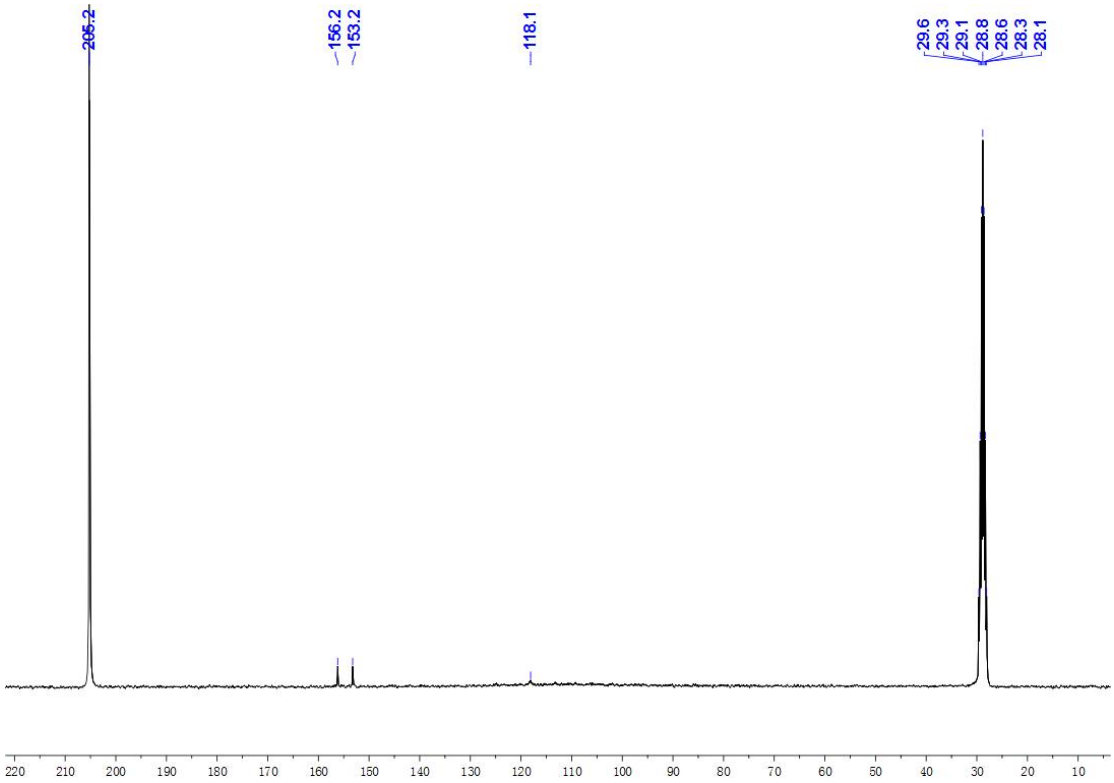


Figure S4 ^{13}C NMR spectrum of 4 in Acetone-d_6

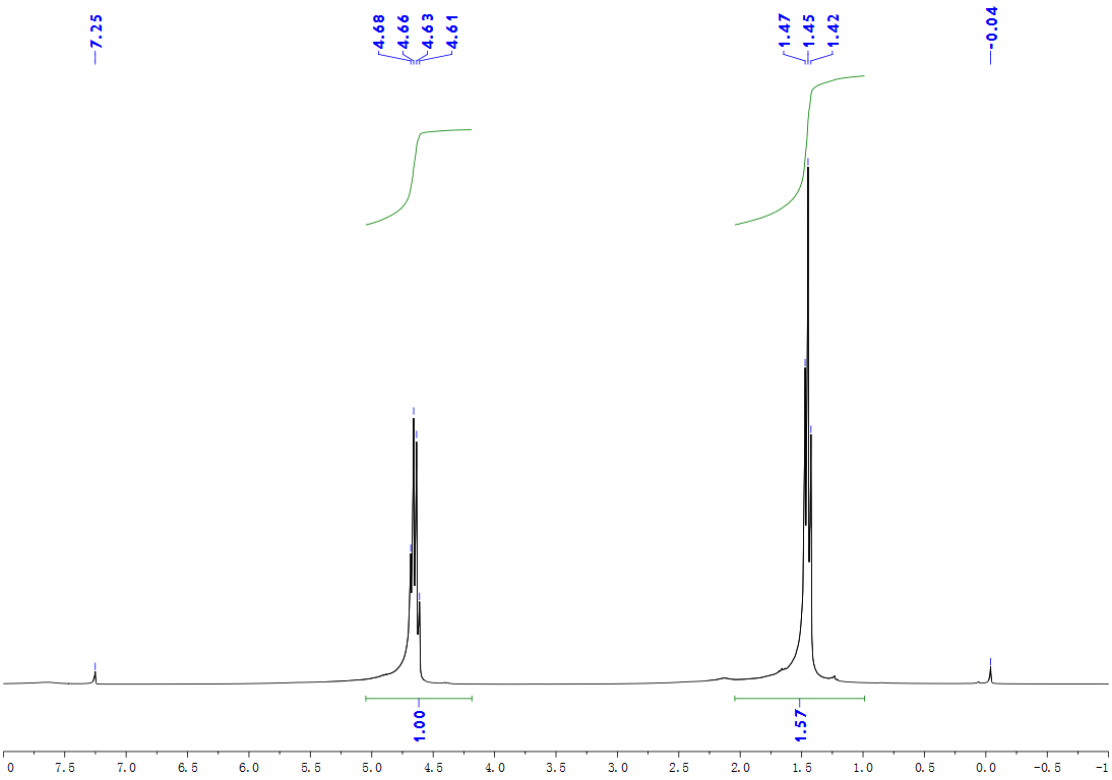


Figure S5 ^{1}H NMR spectrum of **5** in $CDCl_3$

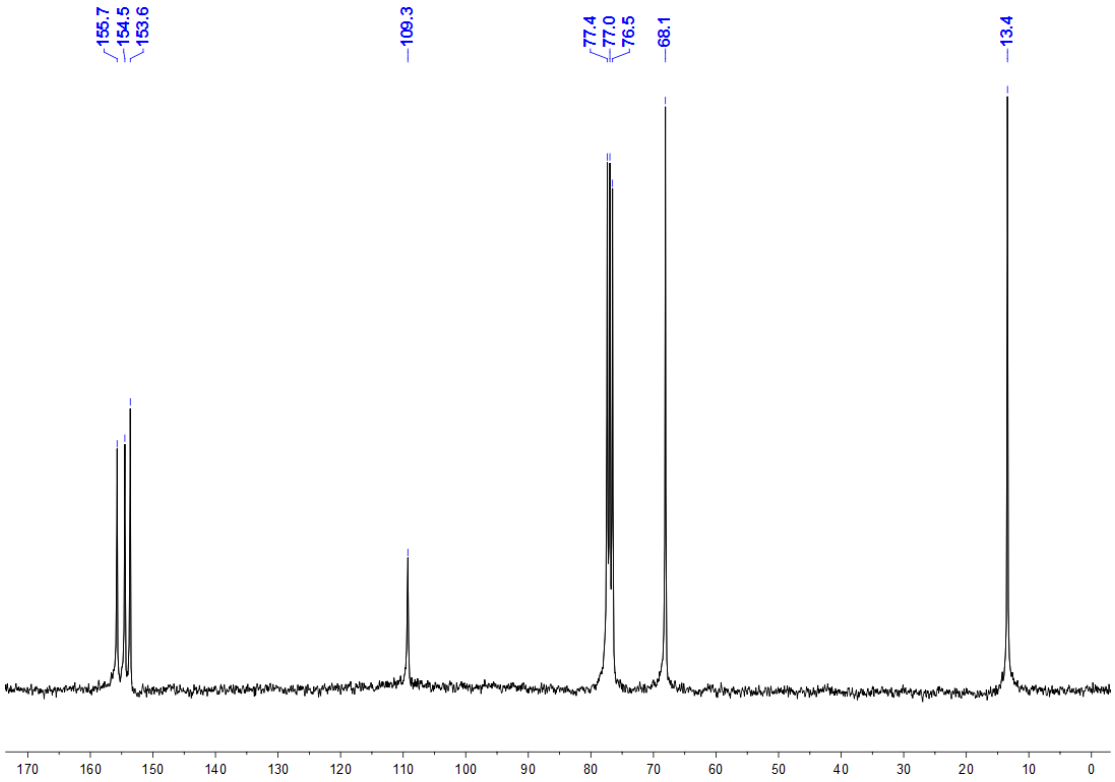


Figure S6 ^{13}C NMR spectrum of **5** in $CDCl_3$

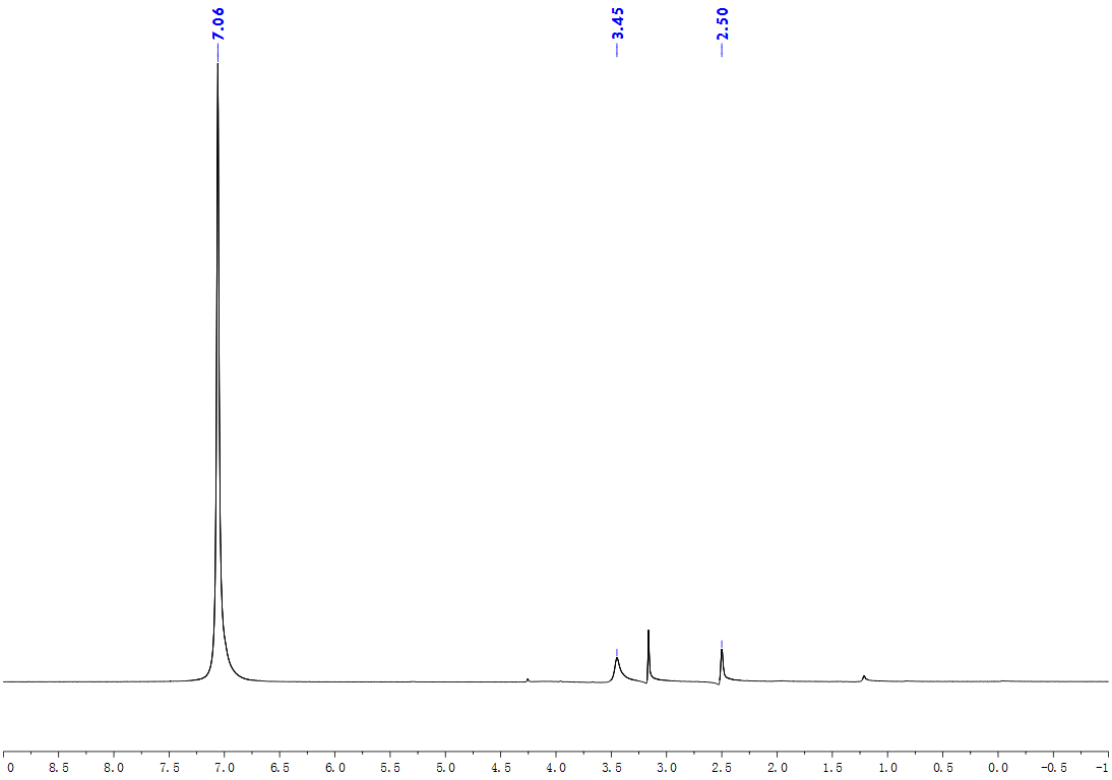


Figure S7 ^{1}H NMR spectrum of **6** in DMSO-d_6

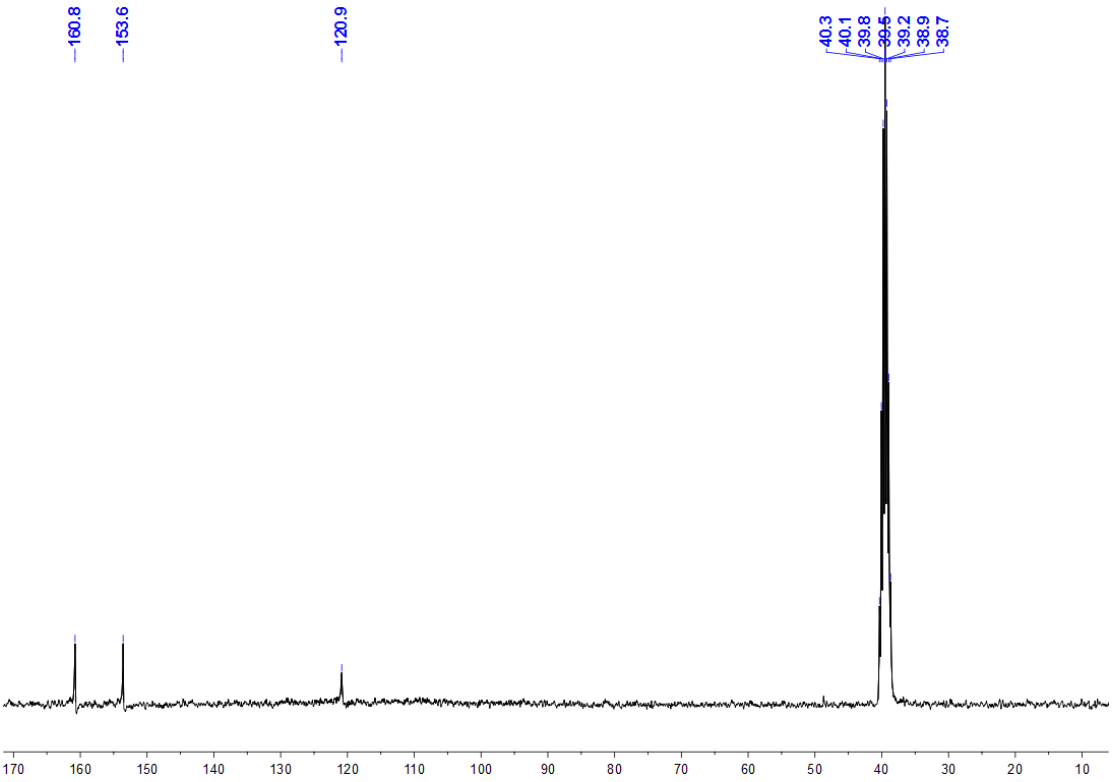


Figure S8 ^{13}C NMR spectrum of **6** in DMSO-d_6

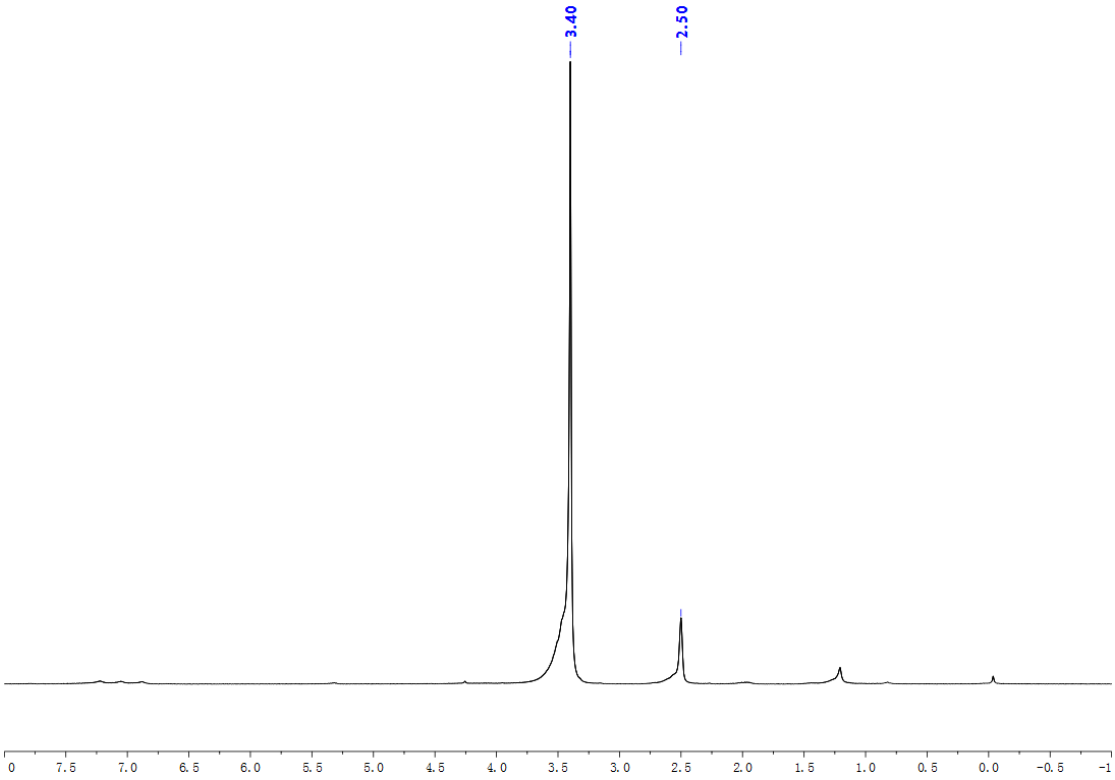


Figure S9 ^{1}H NMR spectrum of **7** in DMSO-d_6

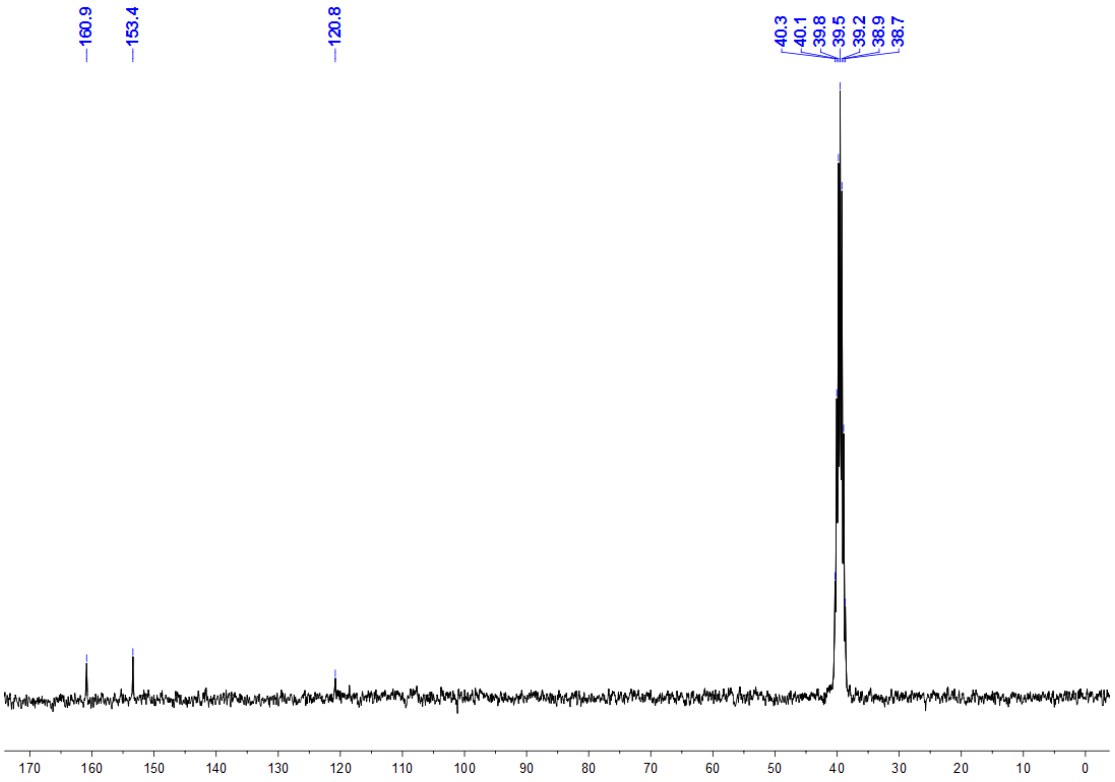


Figure S10 ^{13}C NMR spectrum of **7** in DMSO-d_6

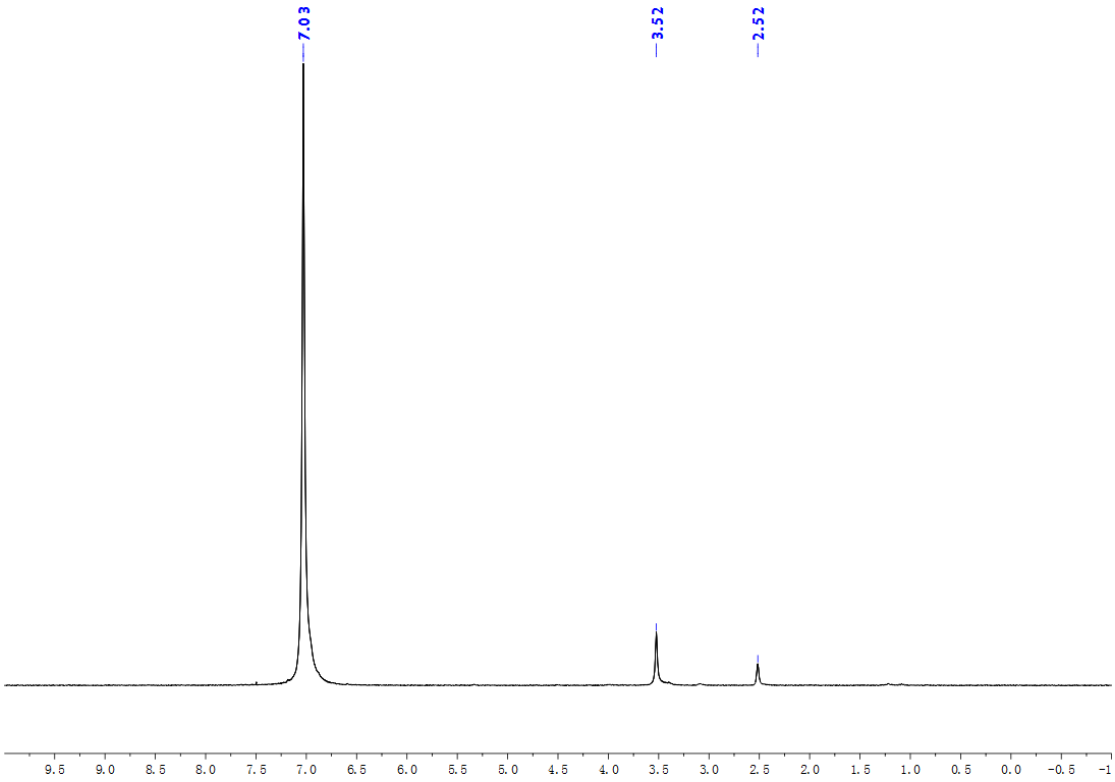


Figure S11 ^{1}H NMR spectrum of **8** in DMSO-d_6

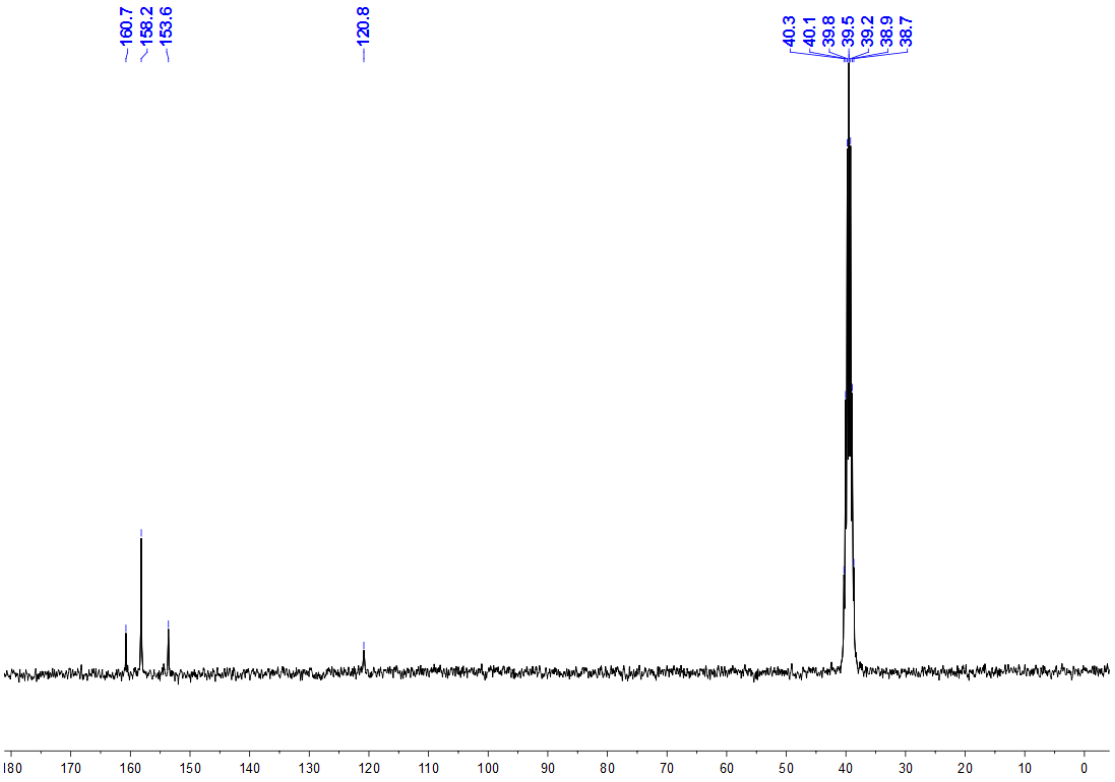


Figure S12 ^{13}C NMR spectrum of **8** in DMSO-d_6

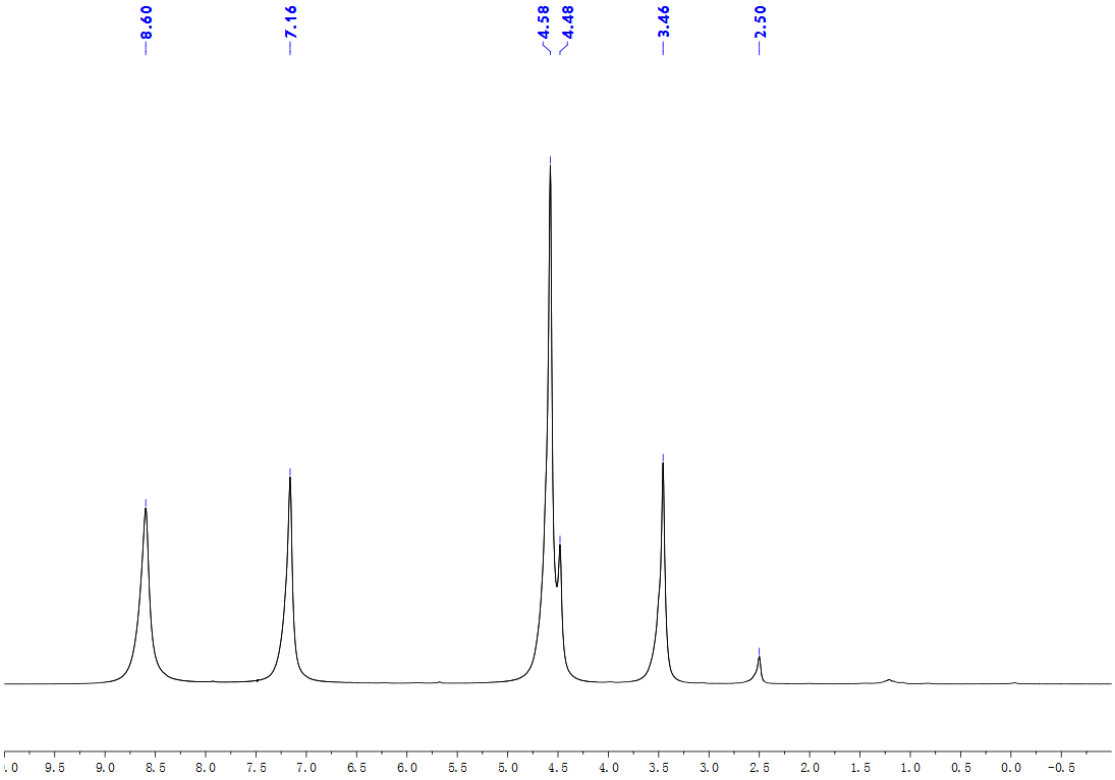


Figure S13 ^{1}H NMR spectrum of **9** in DMSO-d_6

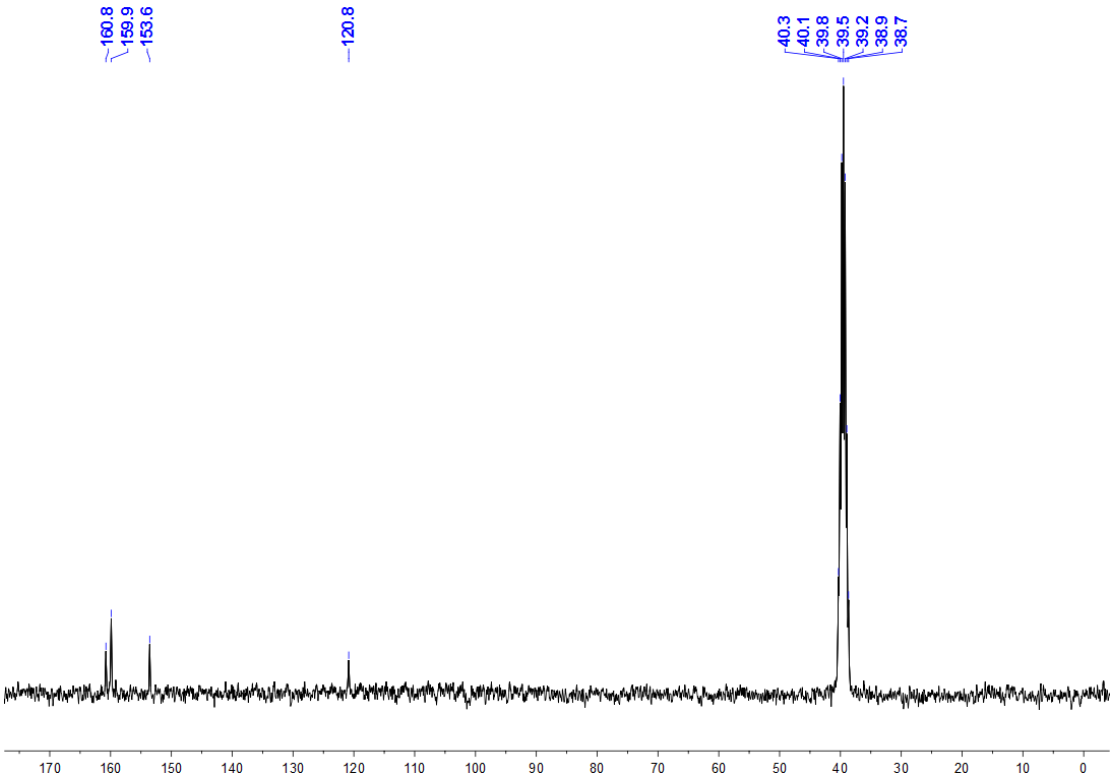


Figure S14 ^{13}C NMR spectrum of **9** in DMSO-d_6

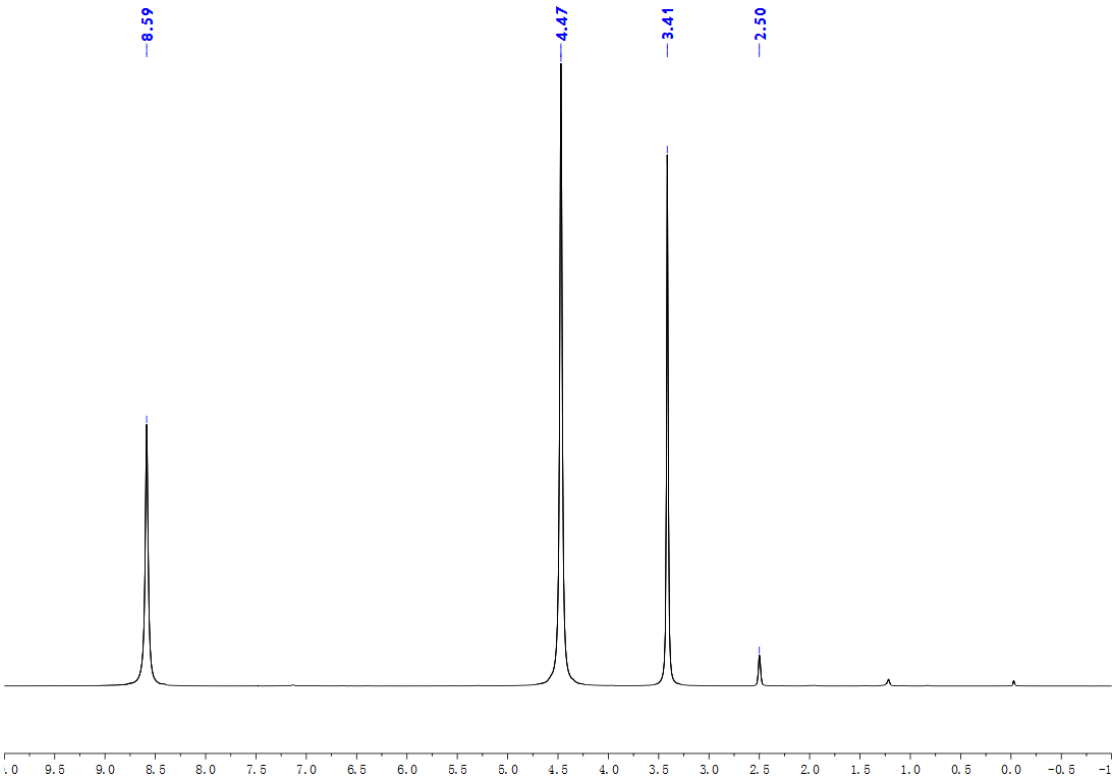


Figure S15 ^{1}H NMR spectrum of **10** in DMSO-d_6

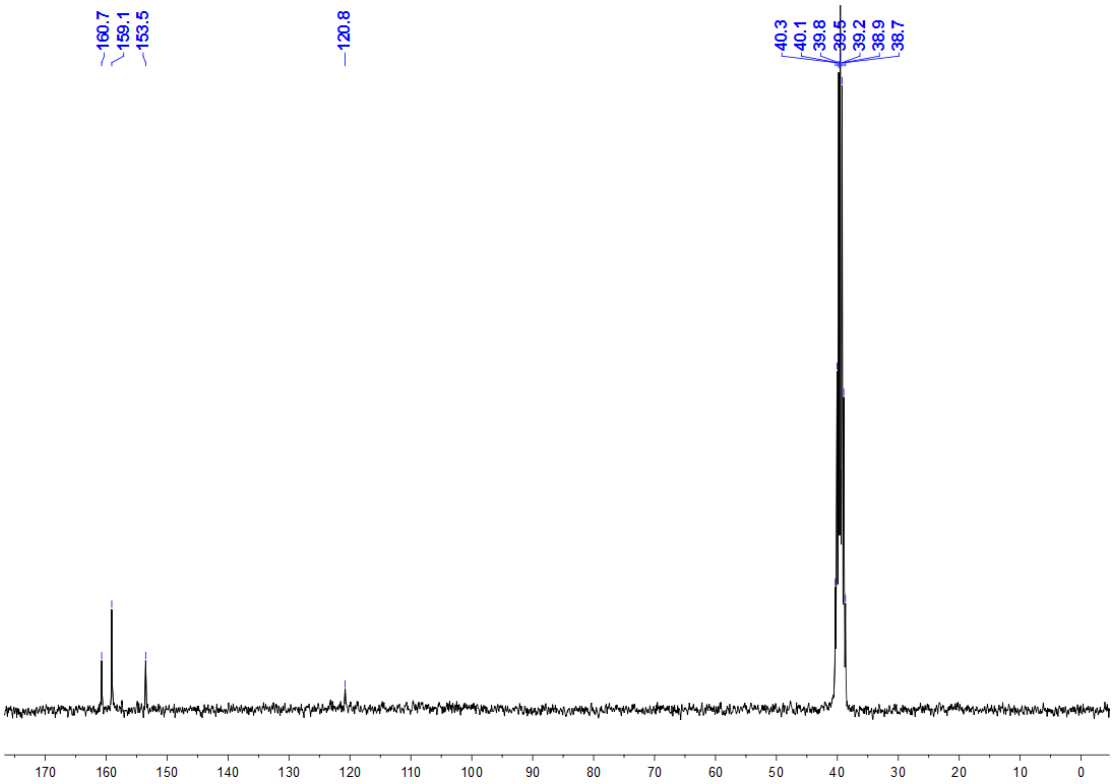


Figure S16 ^{13}C NMR spectrum of **10** in DMSO-d_6

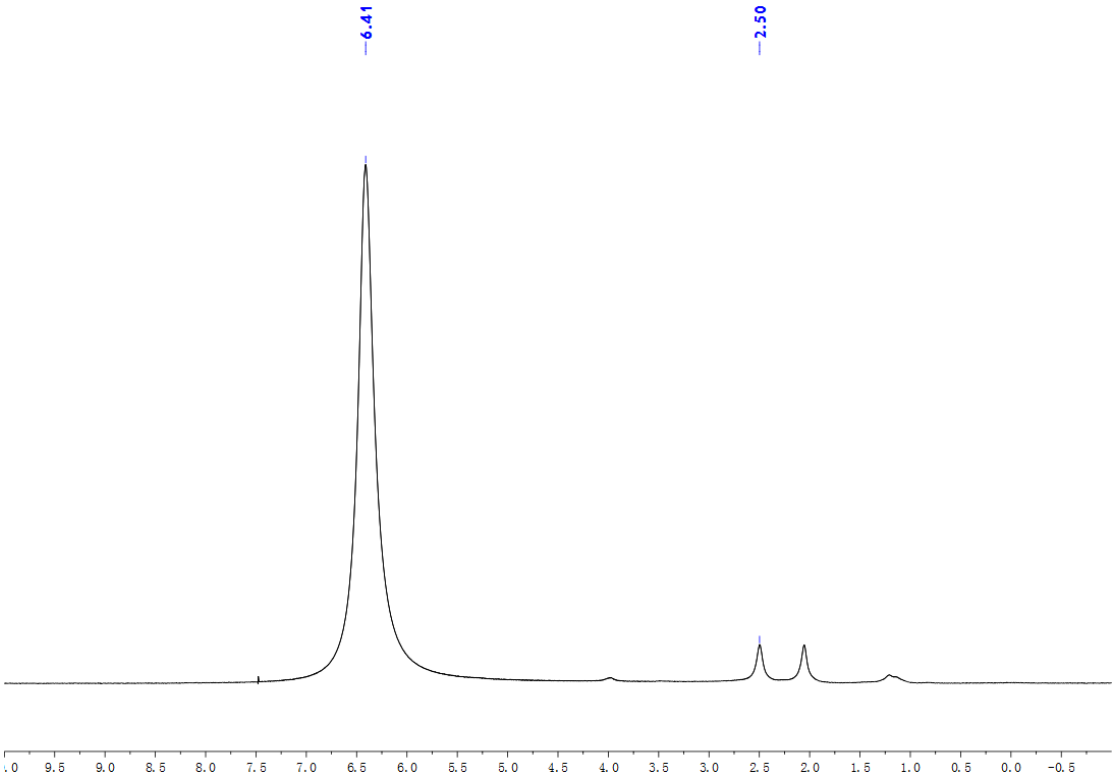


Figure S17 ^{1}H NMR spectrum of **11** in DMSO-d_6

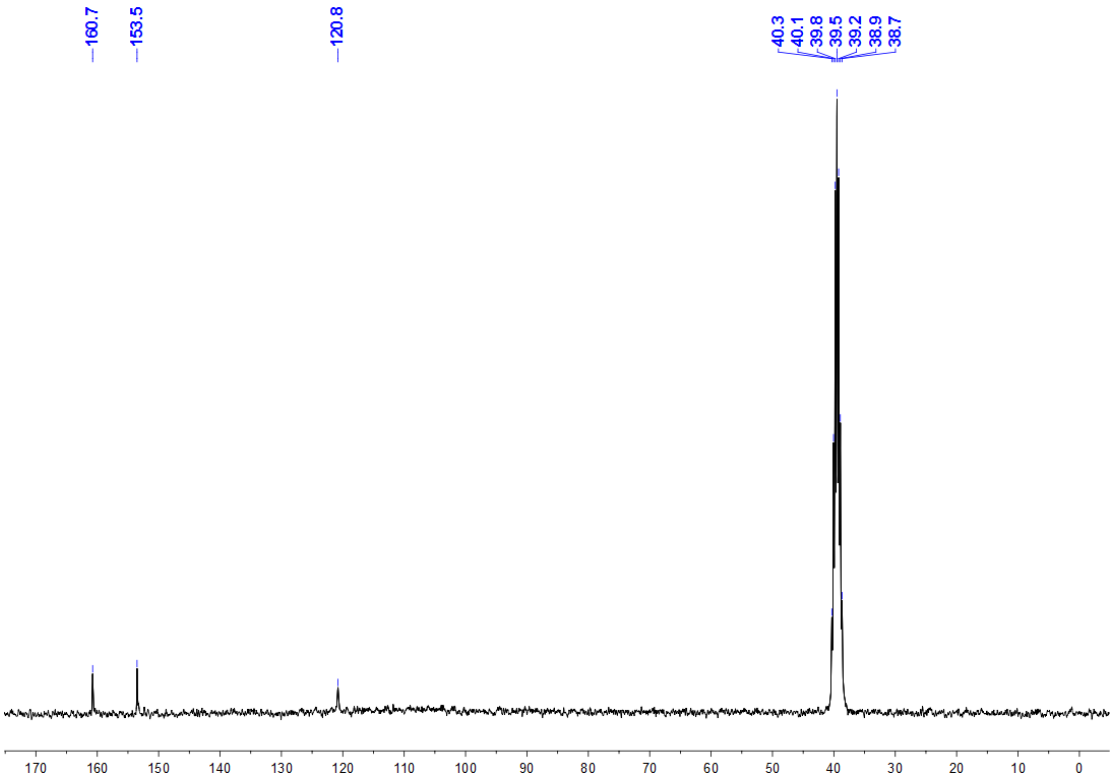


Figure S18 ^{13}C NMR spectrum of **11** in DMSO-d_6

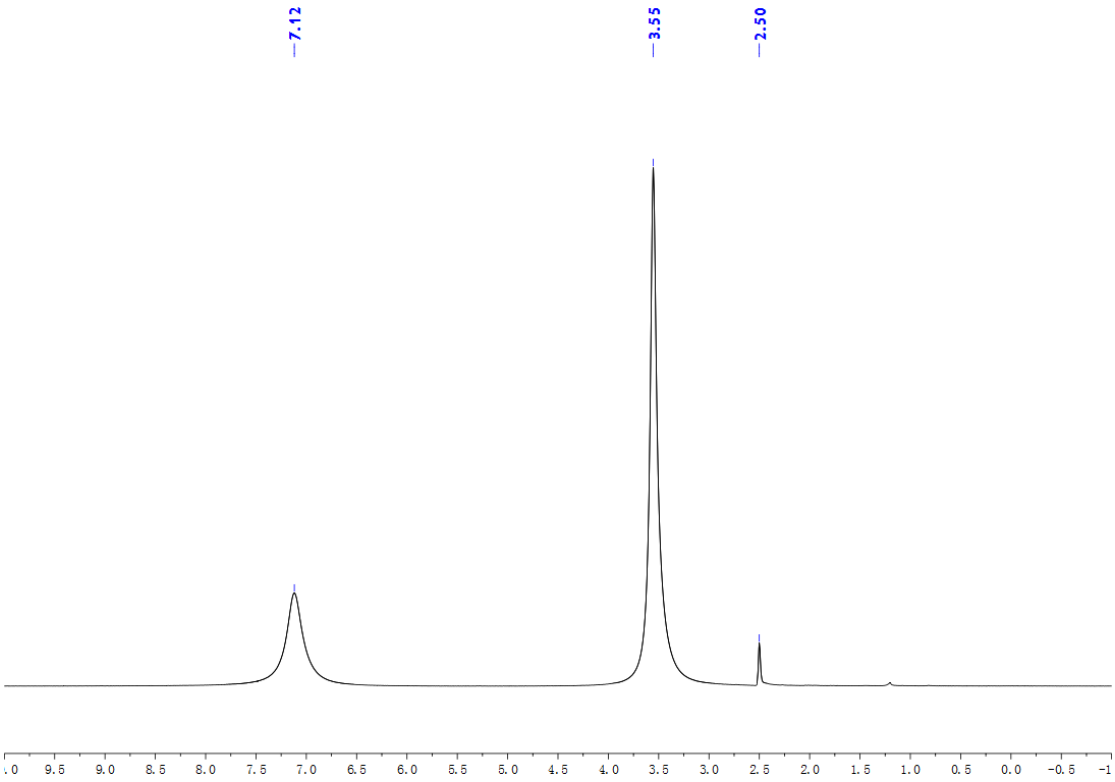


Figure S19 ^{1}H NMR spectrum of **12** in DMSO-d_6

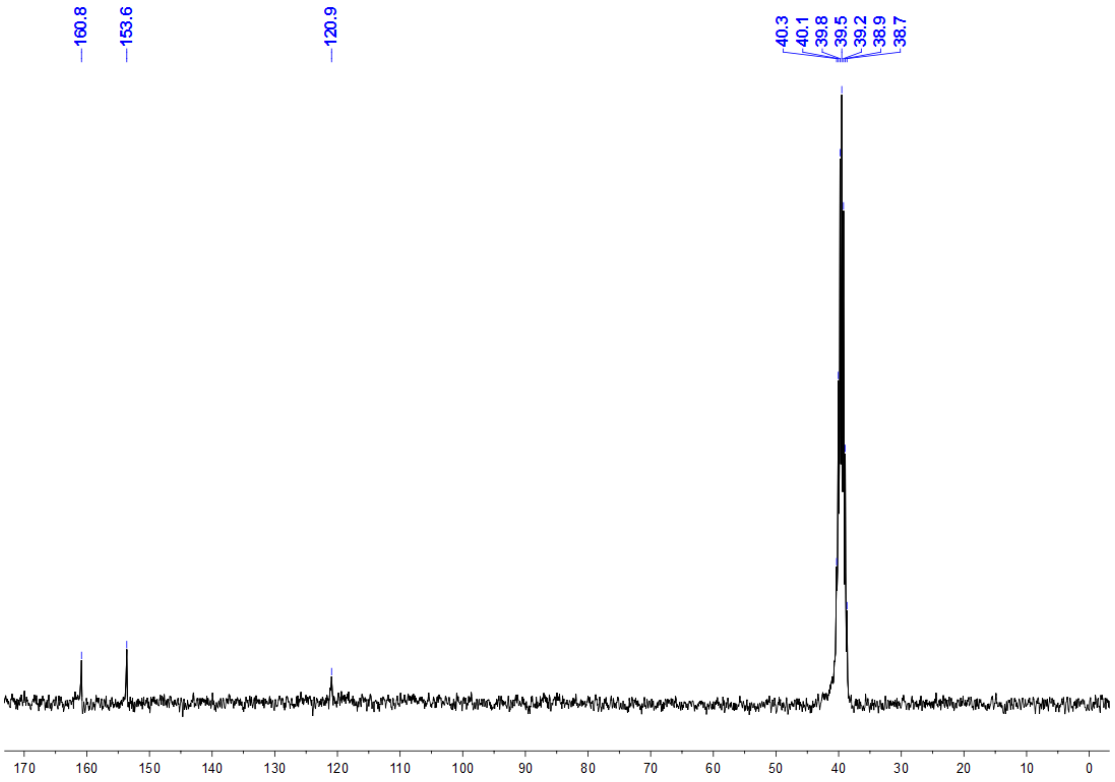


Figure S20 ^{13}C NMR spectrum of **12** in DMSO-d_6

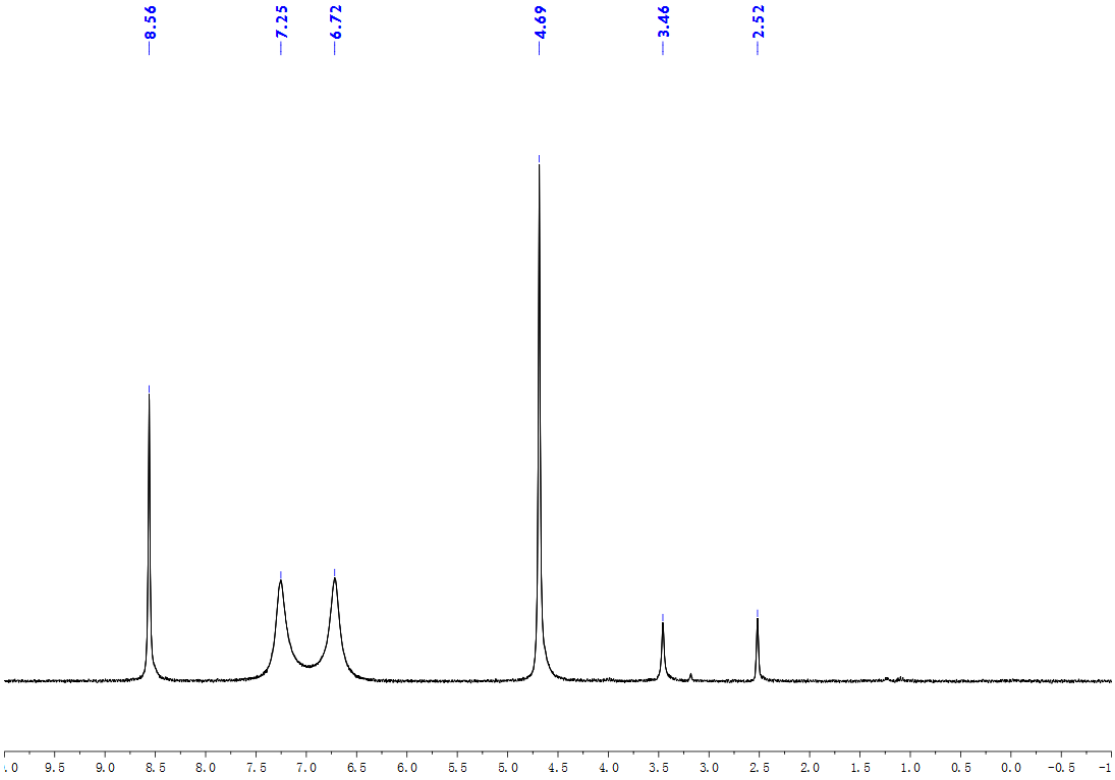


Figure S21 ^{1}H NMR spectrum of **13** in DMSO-d_6

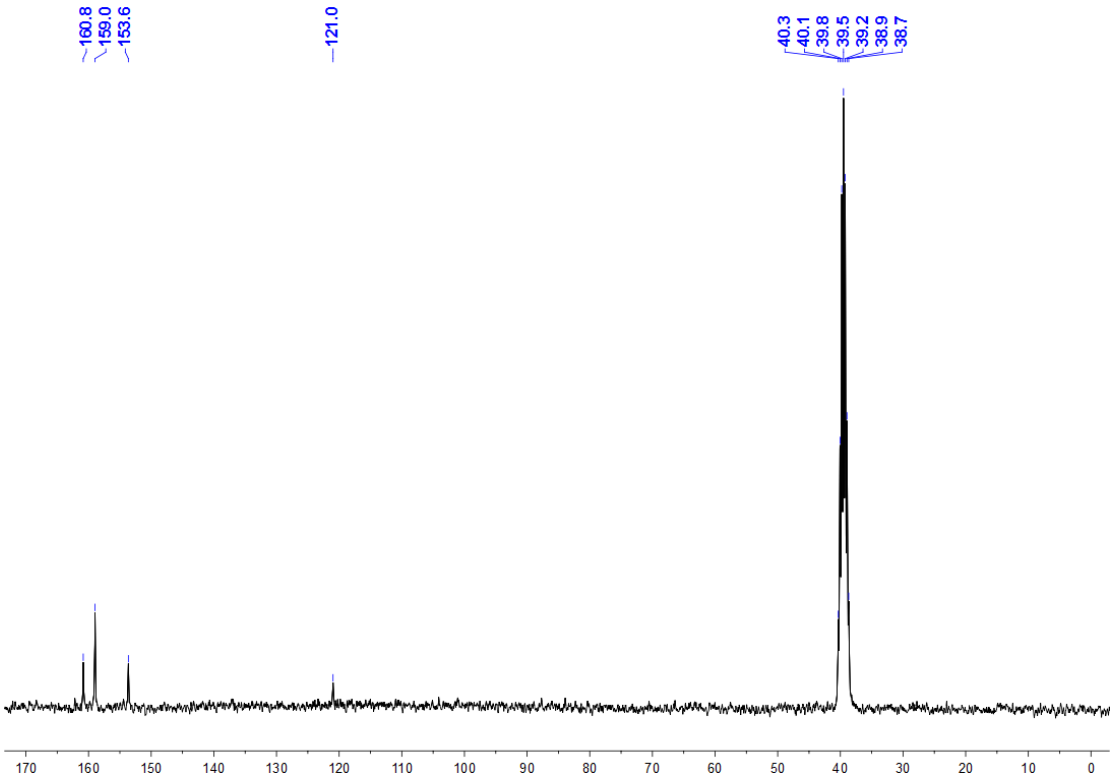


Figure S22 ^{13}C NMR spectrum of **13** in DMSO-d_6

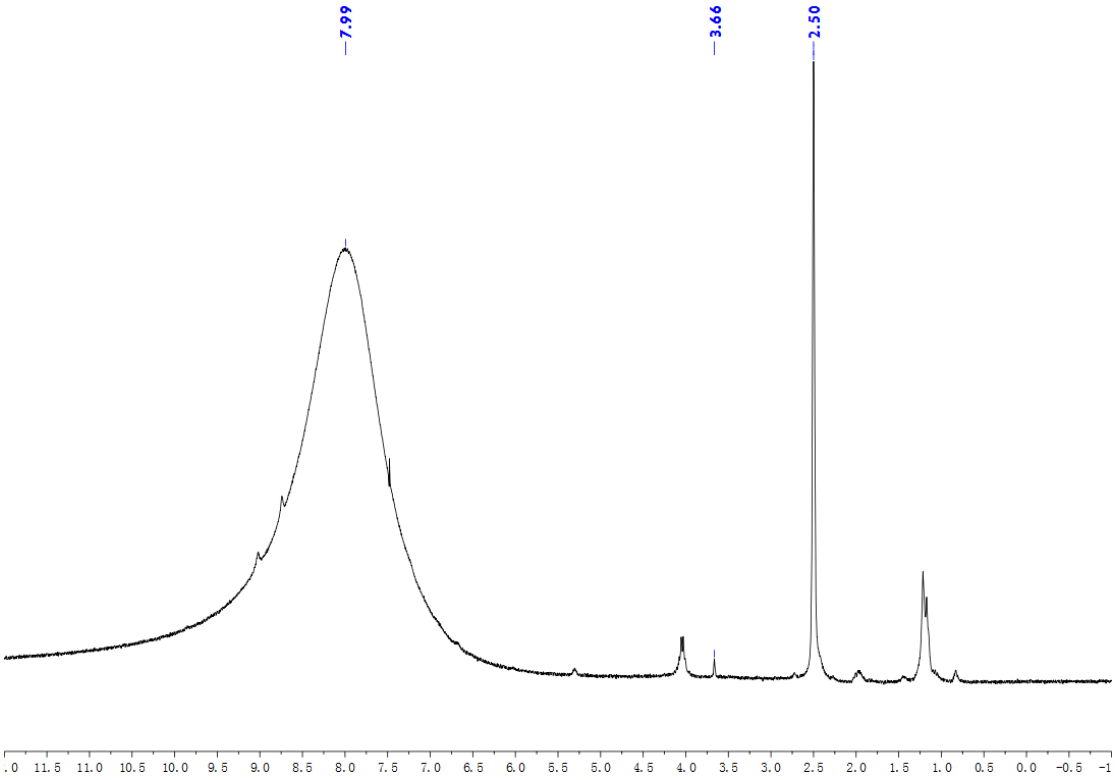


Figure S23 ^{1}H NMR spectrum of **14** in DMSO-d_6

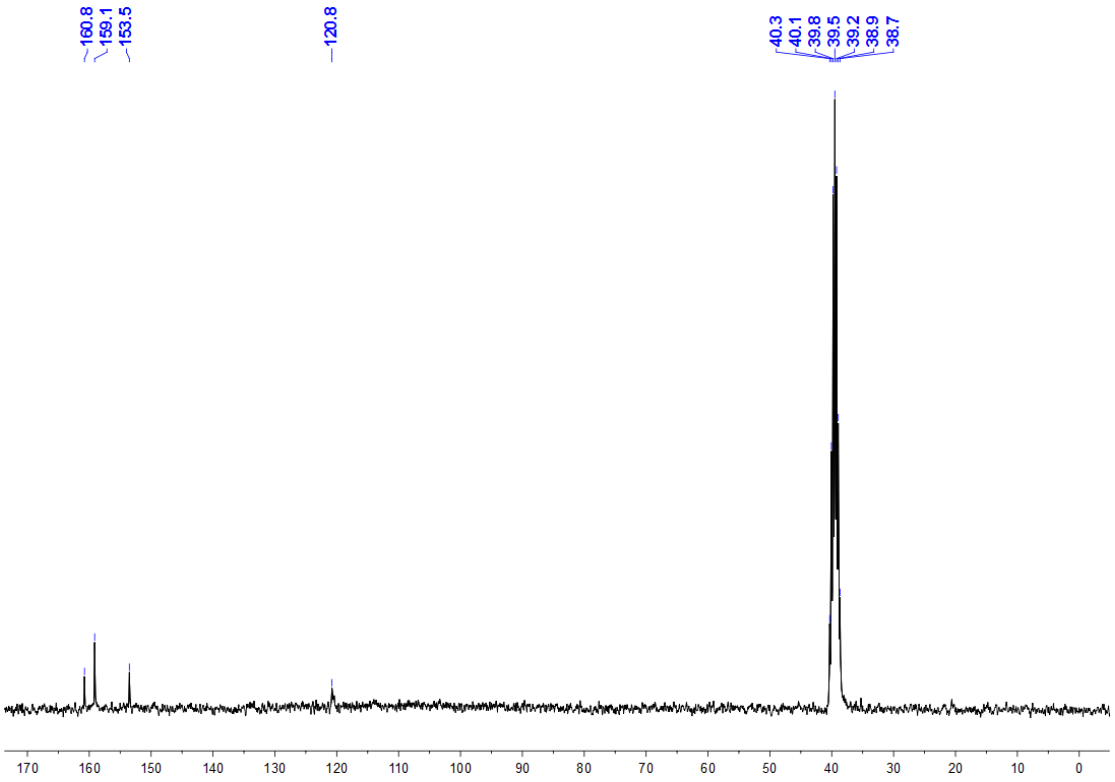


Figure S24 ^{13}C NMR spectrum of **14** in DMSO-d_6

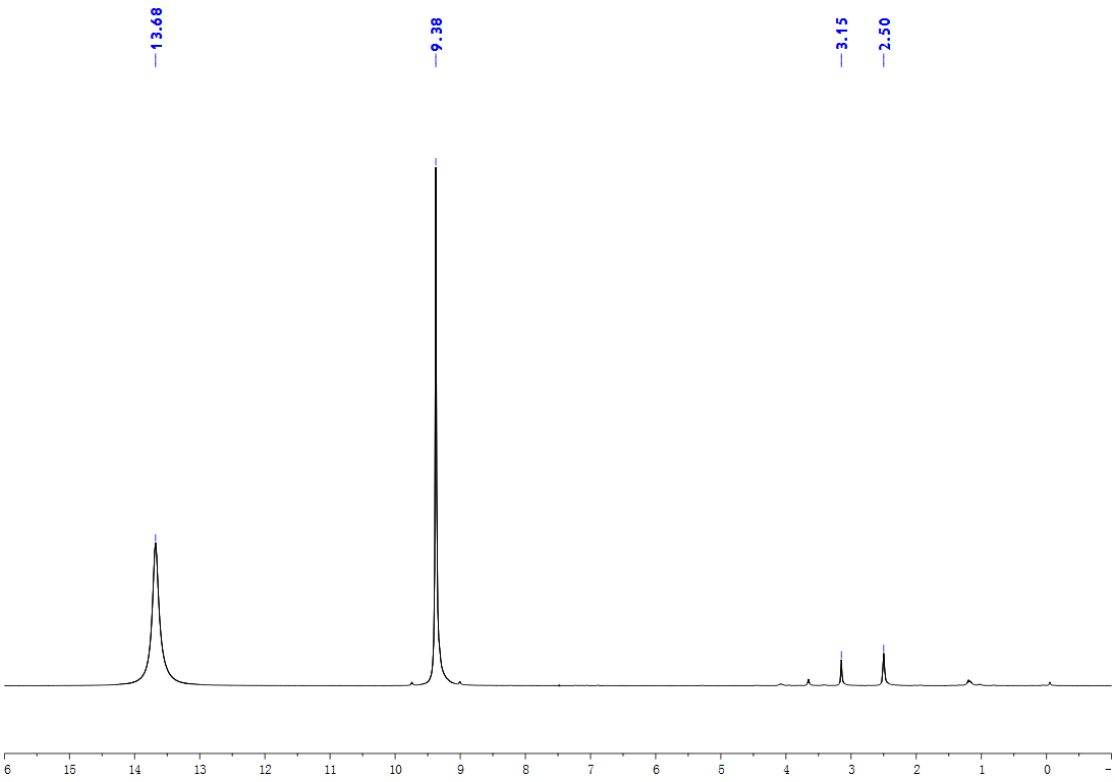


Figure S25 ^{1}H NMR spectrum of **15** in DMSO-d_6

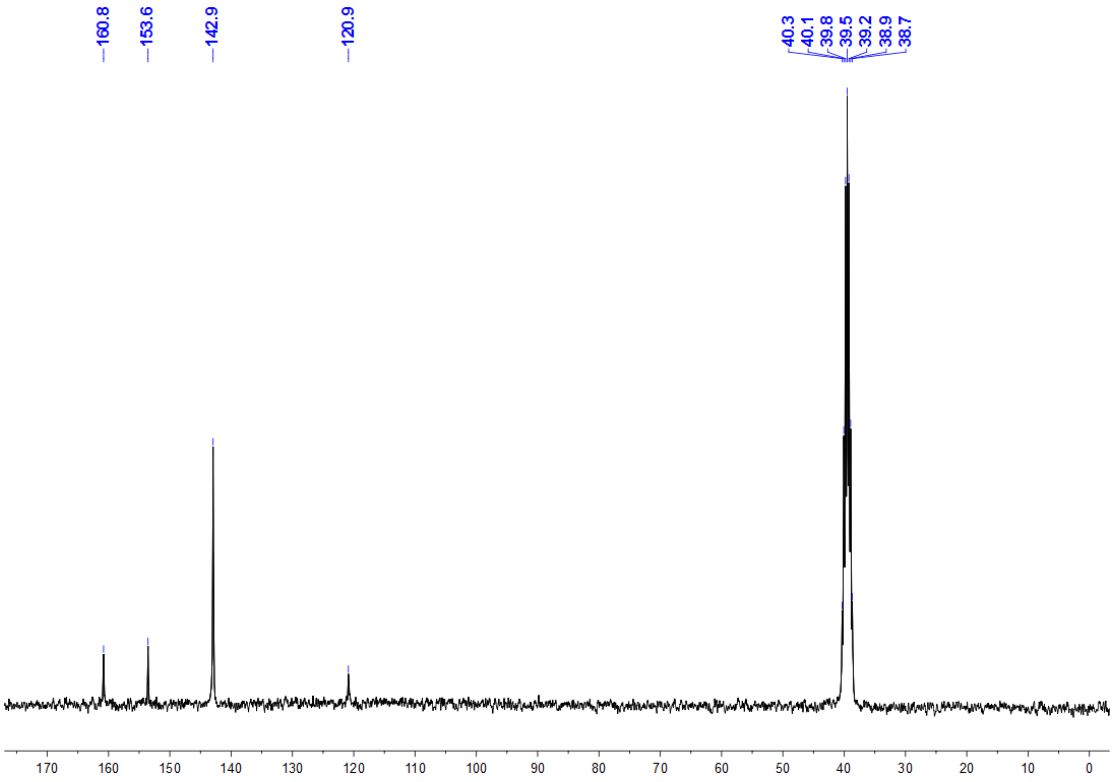


Figure S26 ^{13}C NMR spectrum of **15** in DMSO-d_6

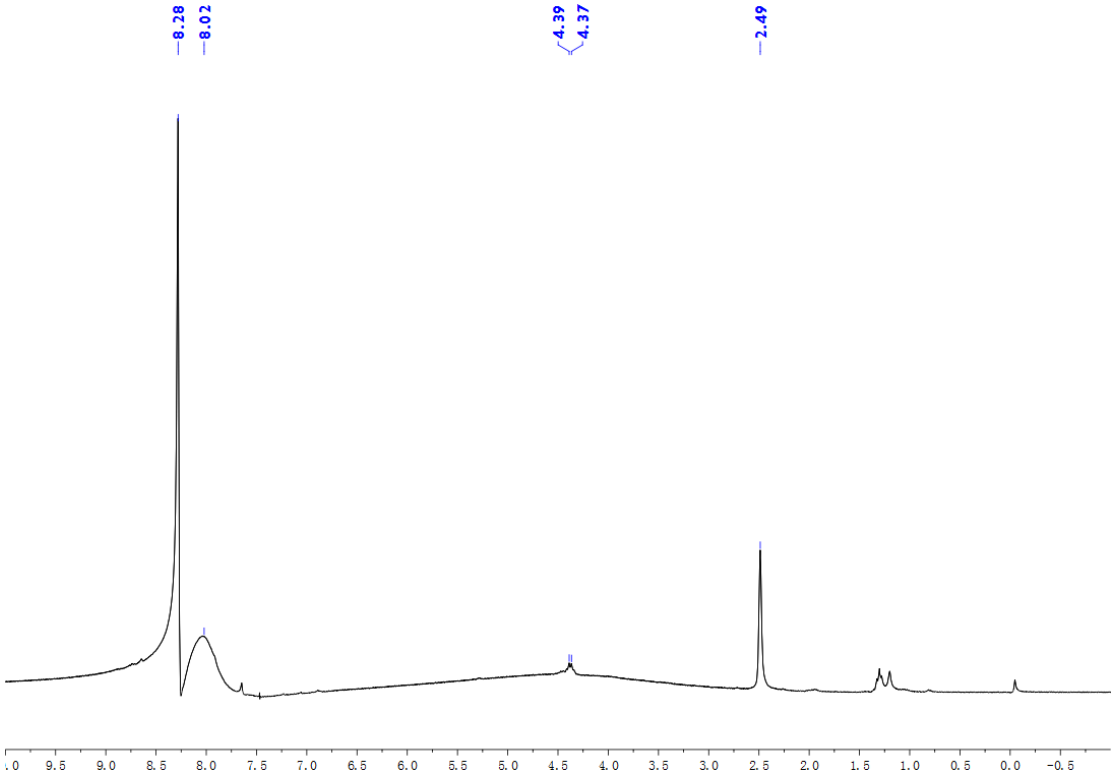


Figure S27 ^{1}H NMR spectrum of **16** in DMSO-d_6

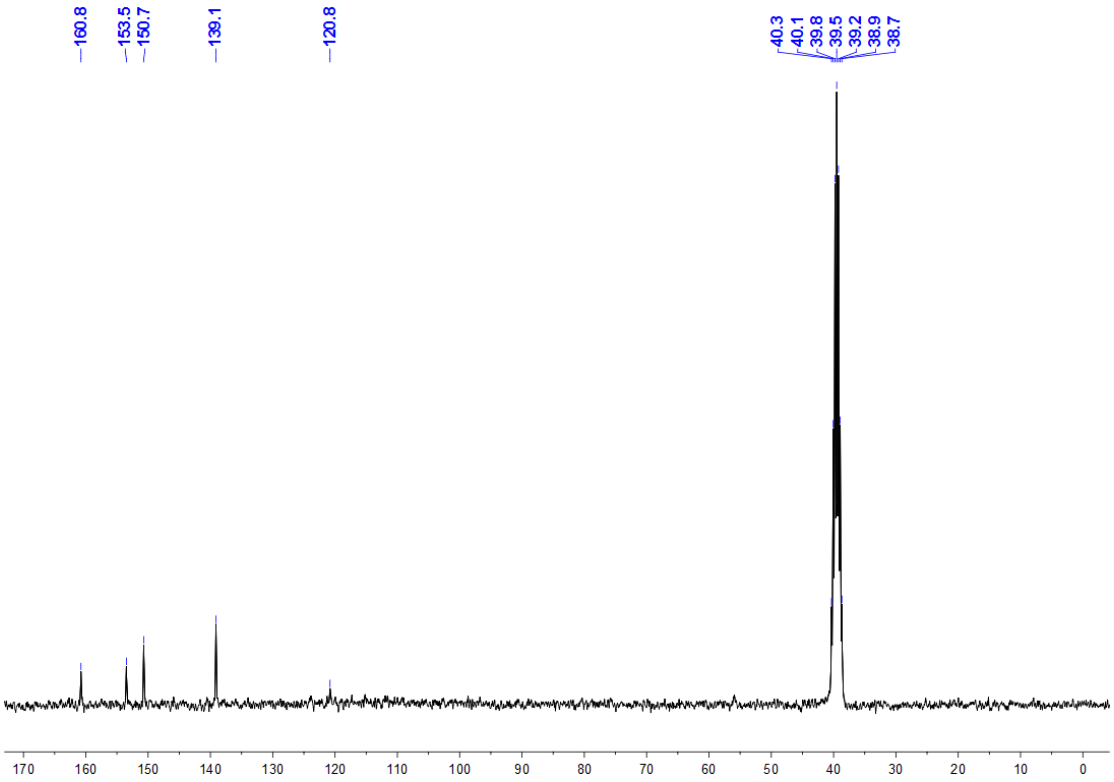


Figure S28 ^{13}C NMR spectrum of **16** in DMSO-d_6

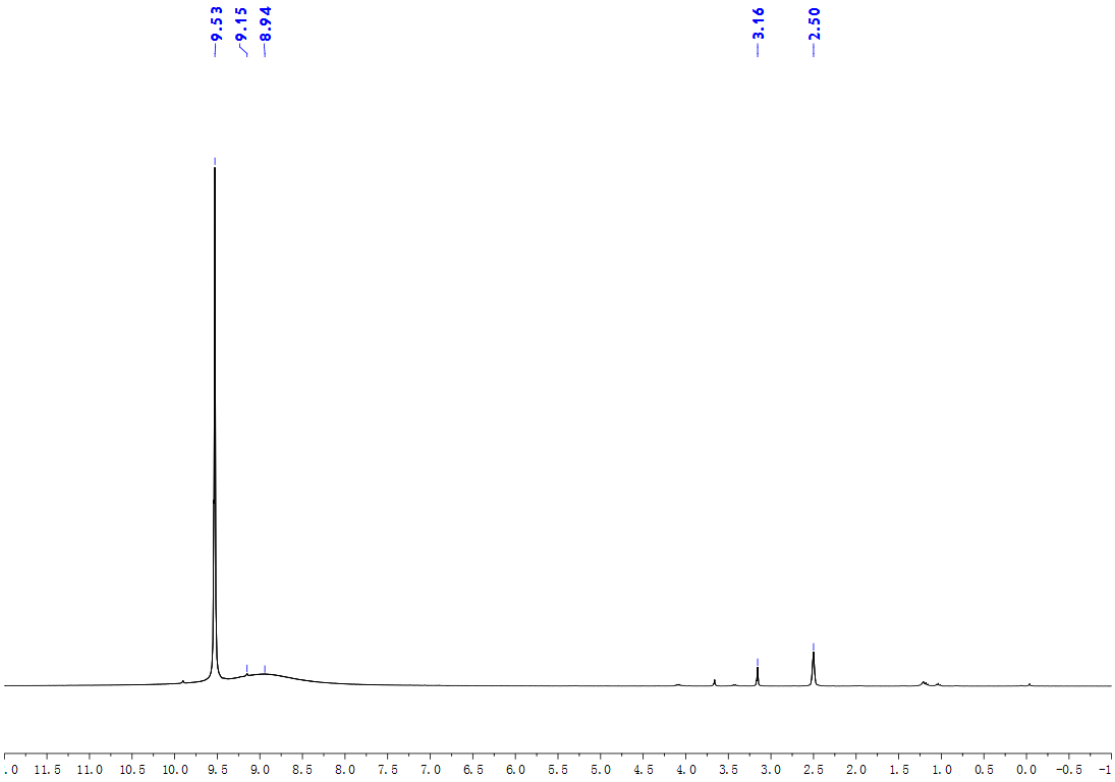


Figure S29 ^{1}H NMR spectrum of **17** in DMSO-d_6

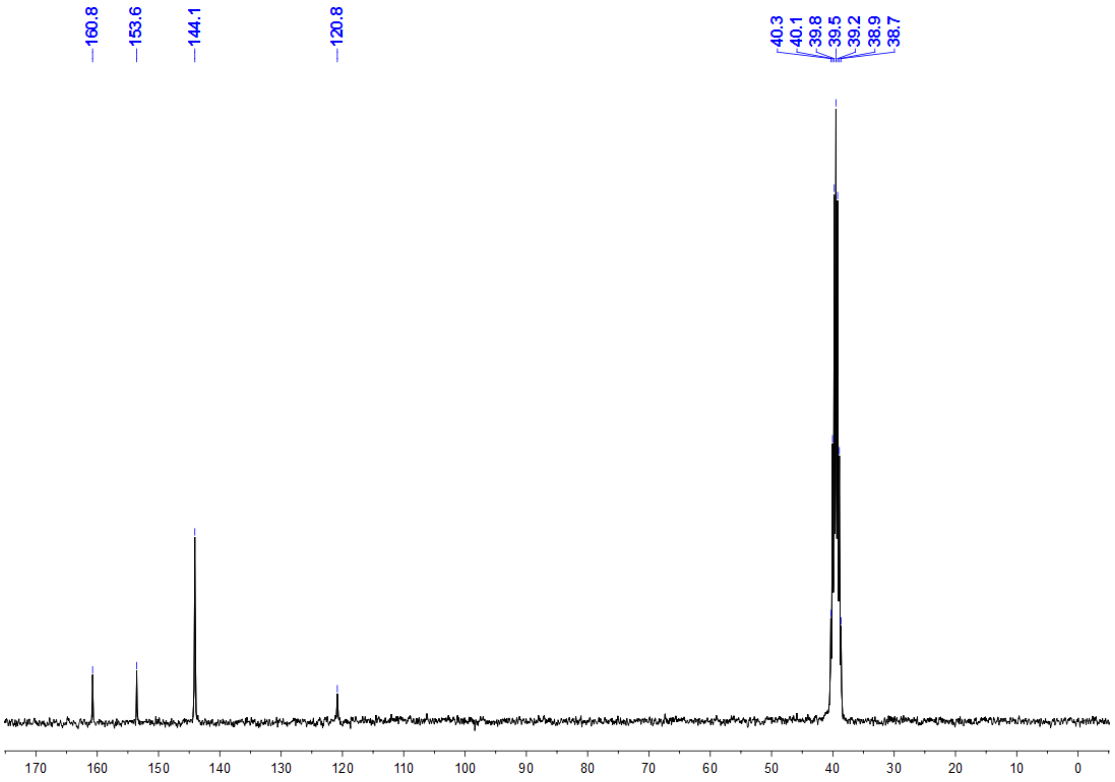


Figure S30 ^{13}C NMR spectrum of **18** in DMSO-d_6

7. Figure S31-S42 DSC and TG Plots of Compound 4 and The Salts (6, 8-17).

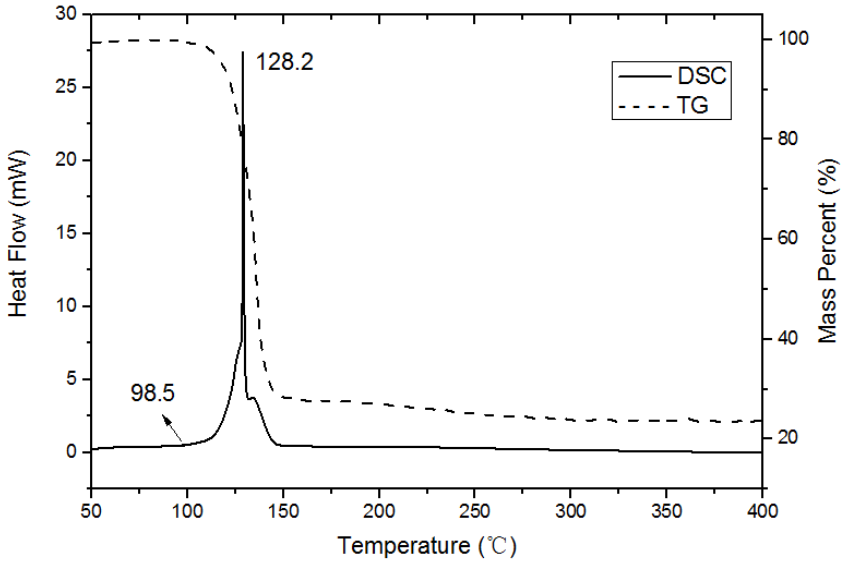


Figure S31 The DSC and TG plots of **4**

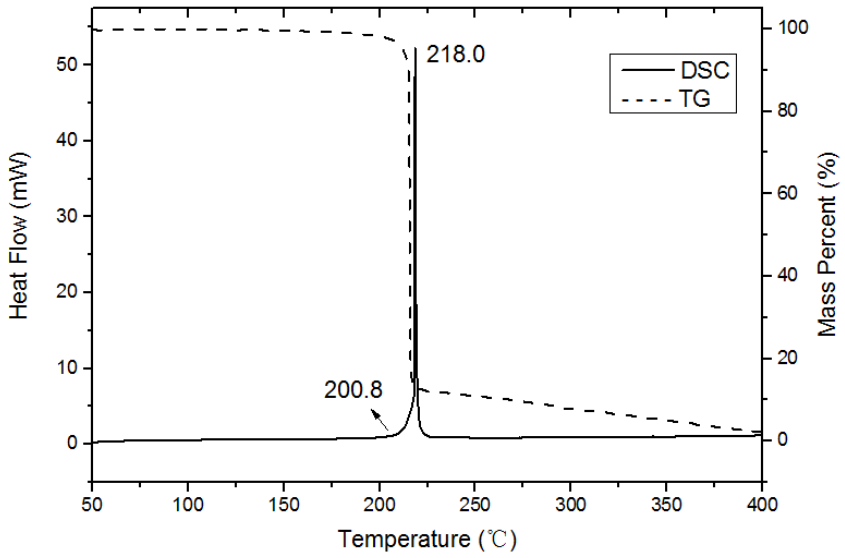


Figure S32 The DSC and TG plots of **6**

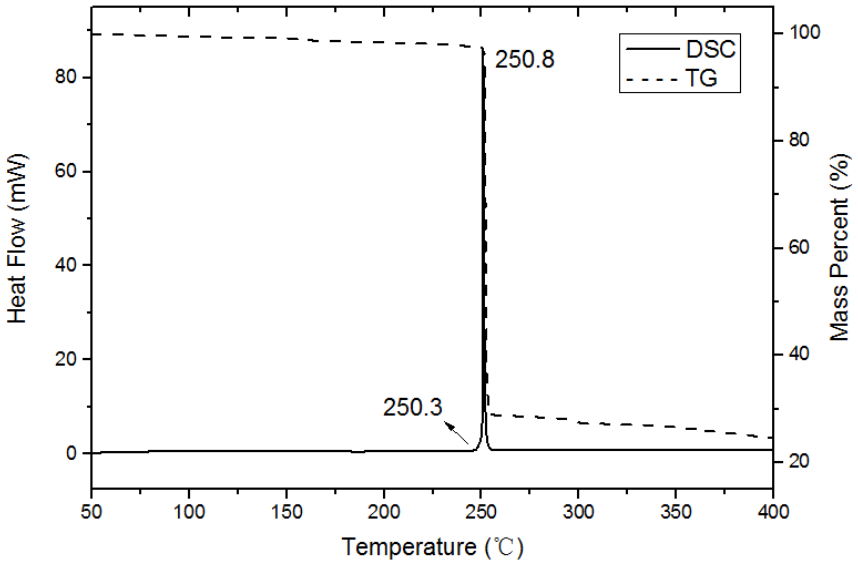


Figure S33 The DSC and TG plots of **8**

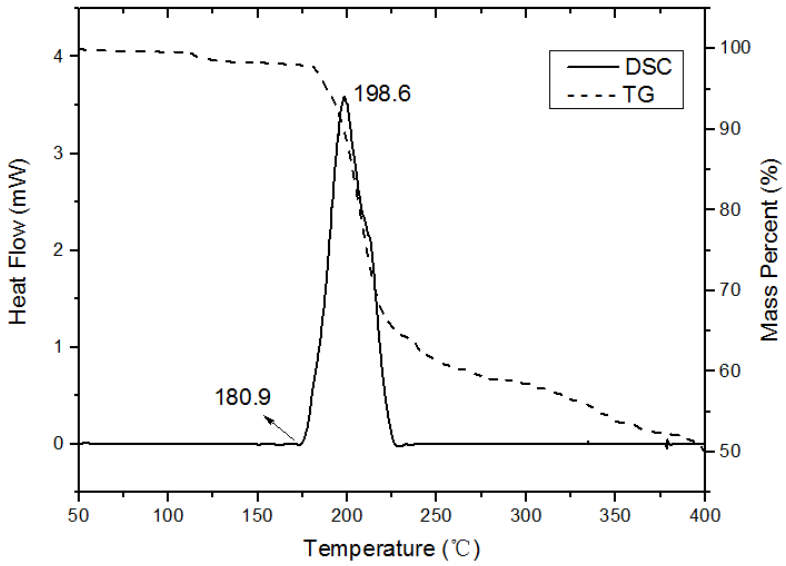


Figure S34 The DSC and TG plots of **9**

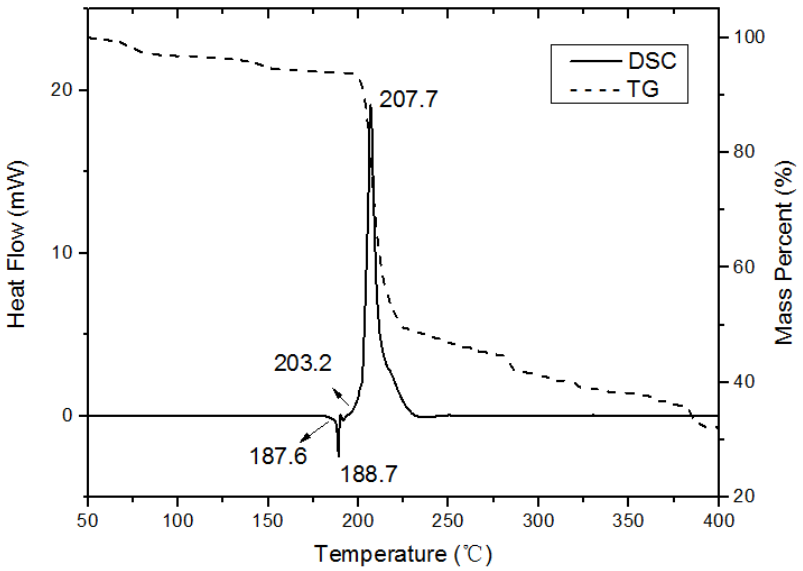


Figure S35 The DSC and TG plots of **10**

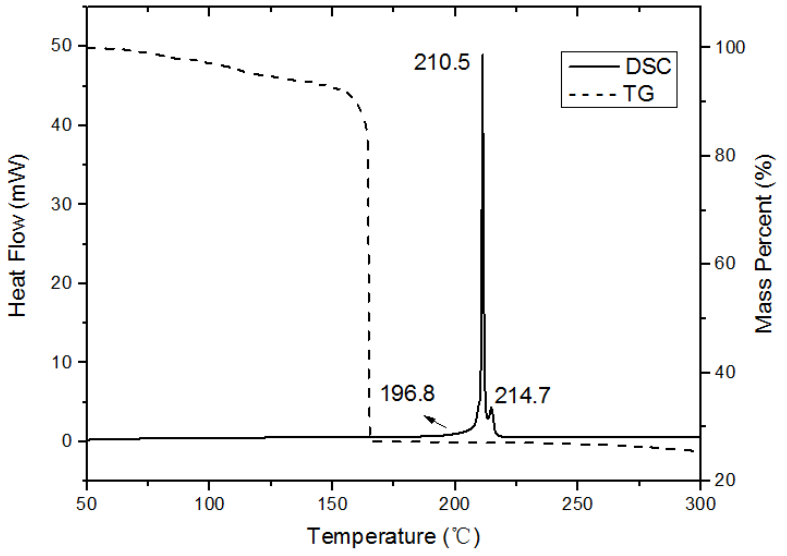


Figure S36 The DSC and TG plots of **11**

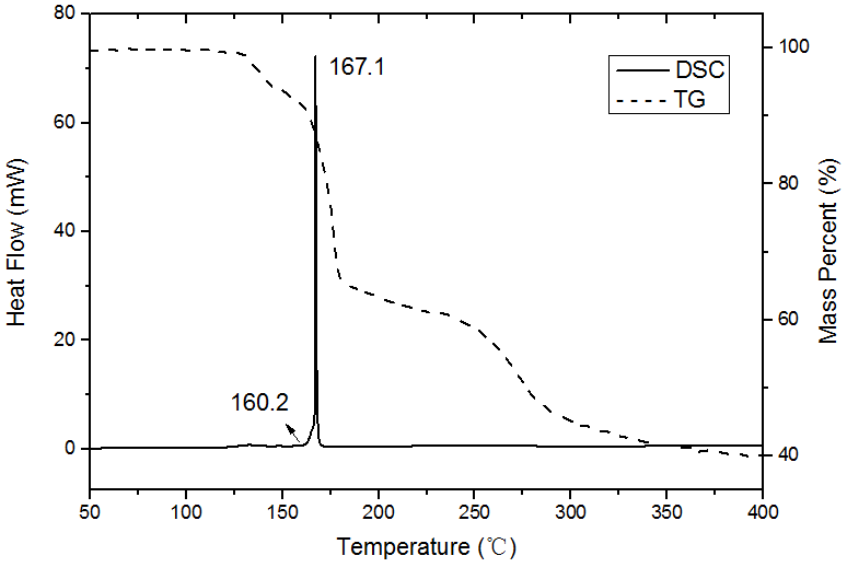


Figure S37 The DSC and TG plots of **12**

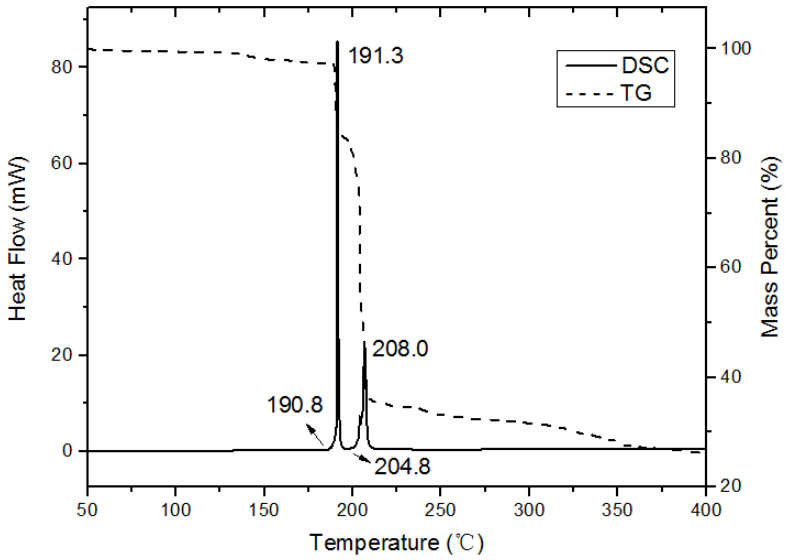


Figure S38 The DSC and TG plots of **13**

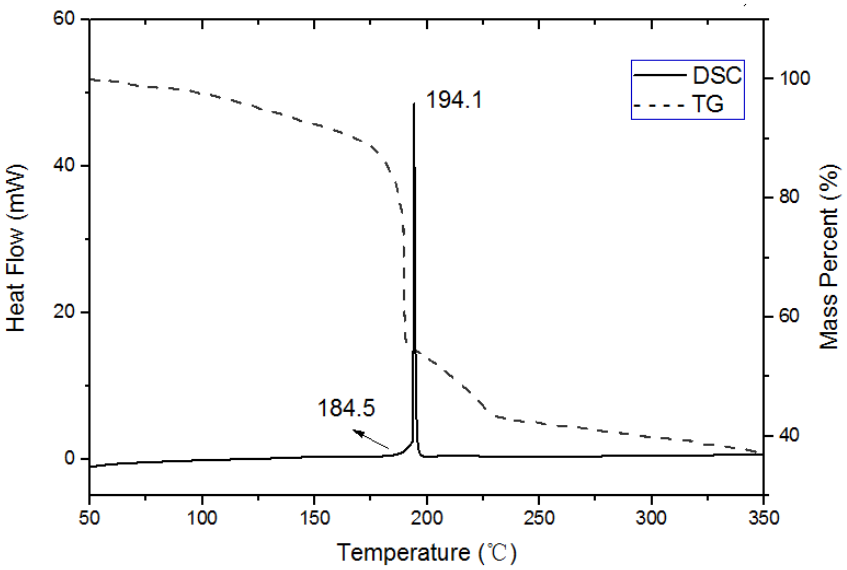


Figure S39 The DSC and TG plots of **14**

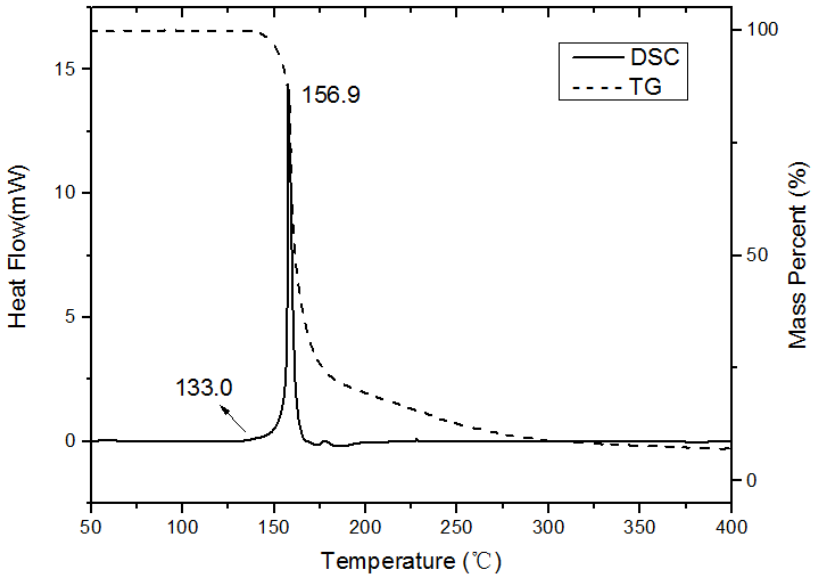


Figure S40 The DSC and TG plots of **15**

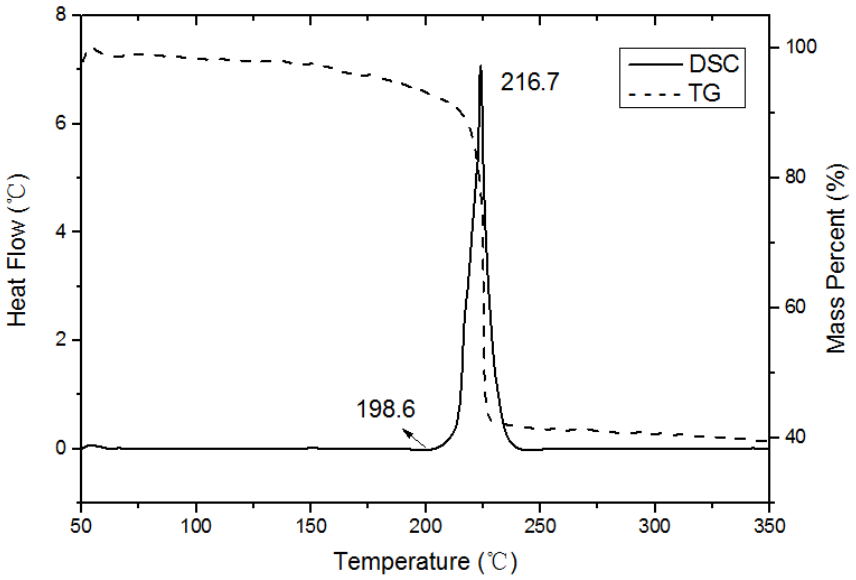


Figure S41 The DSC and TG plots of **16**

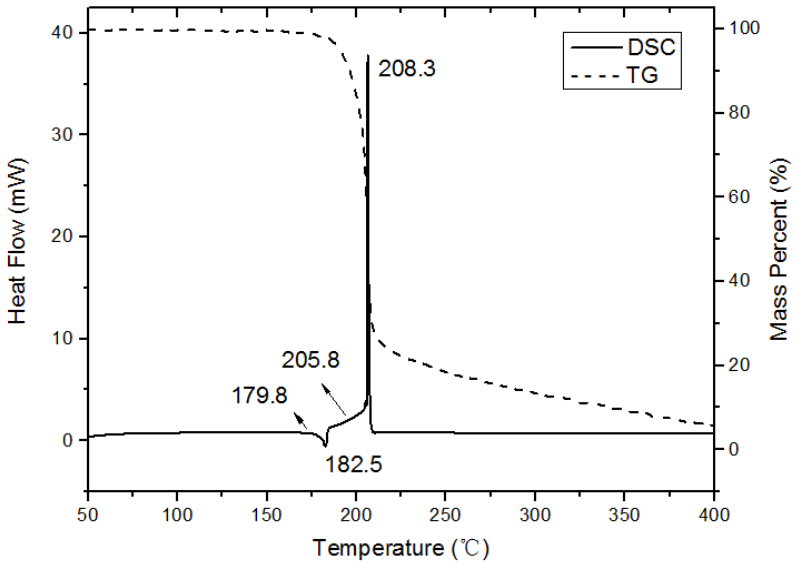


Figure S42 The DSC and TG plots of **17**

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