Electronic supplementary information (ESI)

Energetic Triazolotriazines with Trifluoromethyl, Dinitromethyl and Nitroamino Groups: Synthesis, Structure and Properties

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Contents

Experimental Section

Caution! As energetic materials have explosive risks, all operations should be carried out with helmets and behind safety shields. Mechanical actions such as friction and impact, as well as static electricity should be avoided.

3-(Trifluoromethyl)-1H-1,2,4-triazol-5-amine (2)

Aminoguanidine bicarbonate (6.8 g, 0.05 mol) and trifluoroacetic acid (7.5 g, 0.066 mol) were carefully combined under vigorous stirring until the evolution of carbon dioxide ceased completely. Toluene (50 mL) was then added, and the mixture was heated under reflux for 24 hours using a Dean–Stark apparatus to remove water azeotropically. After cooling to room temperature, the precipitated solid was collected by vacuum filtration, washed with cold toluene, and dried to afford 6.16 g of a white waxy solid in 81% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 12.75(s ,1H), 6.46 (s, 1H) ppm.

^{13}C NMR(126 MHz, DMSO-d_6) δ = 158.38, 151.07, 150.34, 149.97, 124.23, 121.56, 118.89, 116.21 ppm.

IR(KBr): v = 3491, 3357, 3264, 3184, 3056, 2920, 2847, 2768, 2712, 1643, 1582, 1550, 1490, 1451, 1363, 1199, 1141, 1108, 1057, 1009, 998, 844, 774, 761, 729, 707, 596, 553, 483 cm^{-1}.

4-Amino-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3-carbonitrile (3)

Compound **2** (4.56 g, 0.03 mol) was dissolved in 10 mL of water and treated with 10 mL of 37% hydrochloric acid. The resulting mixture was cooled to -10 °C. A solution of sodium nitrite (2.3 g, 0.033 mol) in 5 mL of water was added rapidly under vigorous stirring below 0 °C. A large amount of white solid precipitated during the addition. The reaction mixture was maintained at this temperature for 20 minutes. Subsequently, a solution of malononitrile (1.98 g, 0.03 mol) and sodium acetate trihydrate (20 g) in 50 mL of water was added below 5 °C. The system immediately turned bright yellow upon addition. After stirring at 0–5 °C for 1 hour, the mixture was heated to 50 °C and stirred for an additional 40 minutes. The system turned brown with substantial solid precipitation. After cooling to room temperature, the solid was collected by filtration, washed with water, and dried to afford 5.5 g of a white to pale yellow solid in 80% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 10.19 (s, 1H) ppm.

^{13}C NMR(126MHz, DMSO-d_6) δ = 156.05, 145.04, 120.70, 149.97, 124.23, 121.56, 118.89, 116.21 ppm.

IR(KBr): v = 3539, 3451, 2970, 2246, 1692, 1613, 1568, 1507, 1476, 1408, 1369, 1295, 1218, 1177, 986, 780, 762, 708, 666, 552, 483 cm^{-1}.

(Z)-4-Amino-N'-hydroxy-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3-carboximidamide (4)

Compound **3** (2.29 g, 0.01 mol) was dissolved in 30 mL of ethanol. To this solution was added 50% aqueous hydroxylamine solution (0.79 g, 0.012 mol) at room temperature. A yellow-green precipitation of was observed. The mixture was stirred at room temperature for

1 hour, after which the solid was collected by filtration, washed, and dried to afford 1.86 g of a yellow-green powder in 71% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 10.33(s,1H),10.13(s, 1H), 9.64(s, 1H), 6.45(s, 2H) ppm

^{13}C NMR(126MHz, DMSO-d_6) δ = 156.67, 156.28, 156.01, 155.89, 155.51, 151.08, 141.15, 125.11, 123.73, 121.04, 118.34, 115.64 ppm

IR(KBr): v = 3524, 3457, 3411, 3186, 3083, 2921, 2827, 1661, 1631, 1586, 1552, 1523, 1495, 1417, 1364, 1292, 1253, 1224, 1189, 1176, 1114, 976, 834, 775, 710, 576, 549, 517 cm^{-1}.

(Z)-4-Amino-N-hydroxy-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3-carbimidoyl chloride (5)

Compound **4** (2.62 g, 0.01 mol) was suspended in 50 mL of 20% hydrochloric acid. The mixture was cooled to 0 °C, and a solution of sodium nitrite (1.04 g, 0.015 mol) in 5 mL of water was added dropwise under vigorous stirring. A vigorous evolution of gas was observed. After addition completed, the reaction was maintained at 0–5 °C for 3 hours, during which gas evolution ceased completely and the yellow-green slurry turned white. The mixture was then stirred at room temperature for an additional hour. The resulting solid was collected by filtration, washed thoroughly with cold water, and dried to afford 2.11 g of a white solid in 75% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 12.86 (s, 1H), 10.24 (s, 1H), 8.84 (s, 1H) ppm

^{13}C NMR(126MHz, DMSO-d_6) δ = 156.85, 156.46, 156.08, 155.69, 155.65, 141.22, 135.54, 126.68, 123.62, 120.93, 118.23, 115.54 ppm

IR(KBr): v = 3680, 3426, 3254, 3140, 3014, 2887, 2827, 1663, 1600, 1516, 1481, 1415, 1381, 1315, 1286, 1201, 1175, 1157, 1042, 995, 970, 890, 807, 787, 771, 749, 724, 702, 663, 554 cm^{-1}.

Dipotassium 3-(Dinitromethyl)-N-nitro-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amide (6)

Compound **5** (2 g, 7.1 mmol) was added portionwise to a mixture of 5 mL of 95% nitric acid and 16 mL of trifluoroacetic anhydride at 0 °C. The resulting mixture was stirred at 0–5 °C for 12 hours, and then carefully poured into crushed ice to quench the reaction. The product was extracted with dichloromethane (3×30 mL). The combined organic layers were washed quickly with saturated sodium chloride solution (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure, giving a pale yellow residue. To this residue was added a solution of 0.8 g of potassium iodide in 15 mL of anhydrous methanol, upon which the mixture immediately turned dark brown. After standing at room temperature for 24 hours, a precipitate formed. The solid was collected by filtration, washed with a small amount of methanol and ethyl acetate, and dried to yield 0.81 g of a golden-yellow solid in 25% yield.

^{13}C NMR(126MHz, DMSO-d_6) δ = 156.86, 155.97, 155.59, 155.21, 154.83, 139.72, 134.68, 129.39, 123.86, 121.16, 118.48, 115.78 ppm

^{19}F NMR(373MHz, DMSO-d_6) δ = -64.52 ppm

IR(KBr): v =1632, 1558, 1542, 1491, 1470, 1415, 1385, 1353, 1326, 1261, 1214, 1190, 1169,

1143, 1128, 1093, 983, 968, 923, 866, 820, 784 ,775, 759, 736, 705, 676, 546 cm^{-1}.

3-(Dinitromethyl)-N-nitro-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (7)

Compound **6** (0.5 g, 1.17 mmol) was dissolved in 5 mL of water. The solution was cooled to 0 °C, followed by the addition of 4 mL of 37% hydrochloric acid. The mixture was stirred at 0 °C for 30 minutes, during which a white solid precipitated. The solid was quickly collected by filtration, and dried under a stream of air, giving 0.24 g of compound **7** in 63% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 11.22(s, 1H), 9.01 (s, 1H,) ppm

^{13}C NMR(126MHz, DMSO-d_6) δ = 154.92, 154.53, 154.14, 153.75, 148.56, 123.36, 123.05, 120.69, 120.33, 118.00, 117.66, 115.31 ppm

^{19}F NMR(373MHz, DMSO-d_6) δ = -65.14 ppm

IR(KBr): ν = 3165, 3080, 2983, 2959, 2926, 2855, 1654, 1623, 1602, 1590, 1541, 1494, 1435, 1400, 1367, 1327, 1299, 1257, 1220, 1197, 1181, 1157, 1030, 998, 910, 863, 823, 767, 730, 696, 666, 602. cm^{-1}

Diammonium 3-(dinitromethyl)-N-nitro-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amide (8)

Compound **7** (0.35 g, 1 mmol) was dissolved in 15 mL of anhydrous acetonitrile and cooled to –5 °C. Under vigorous stirring, a solution of 2.8 g (containing 2.4 mol of NH_3) of 7 M ammonia in methanol was added dropwise. A golden-yellow precipitation was observed. The solid was collected by filtration, and dried under a stream of air, affording 0.21 g of a golden-yellow solid in 55% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 7.14(s, 1H) ppm

^{13}C NMR(126MHz, DMSO-d_6) δ = 154.72, 153.90, 153.53, 153.16, 152.81, 139.16, 137.64, 132.48, 129.29, 127.24, 119.03, 116.52 ppm

^{19}F NMR(373MHz,DMSO-d_6) δ = -64.60 ppm

IR(KBr) : ν = 3450, 3211, 1638, 1559, 1542, 1491, 1442, 1402, 1350, 1325, 1259, 1212, 1168, 1145, 1126, 1092, 983, 967, 921, 865, 819, 783, 775, 758, 736, 704, 675, 663, 613, 578, 546. $cm^{-1.}$

Ammonium 3-(dinitromethyl)-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (9)

Compound **8** (0.39 g, 1 mmol) was suspended in 15 mL of acetonitrile. To this mixture was added 28% aqueous ammonia 0.061 g (containing 1.2 mmol of NH_3). The reaction vessel was sealed and stirred at room temperature for 12 hours. The volatile components were removed under reduced pressure, and the resulting residue was triturated with 4 mL of ethyl acetate under vigorous stirring to remove impurities. The precipitated solid was collected by filtration and dried to afford compound **8** as a tan solid in 46% yield.

^{1}H NMR(500MHz, DMSO-d_6) δ = 8.87(s, 2H), 7.65(s, 4H) ppm

^{13}CNMR(126MHz, DMSO-d_6) δ = 157.07, 156.69, 156.30, 155.91, 155.73, 141.25, 131.38, 127.57, 123.67, 120.97, 118.28, 115.58 ppm

^{19}F NMR(373MHz, DMSO-d_6) δ = -64.58 ppm

IR(KBr): v = 3442, 3195, 1658, 1538, 1501, 1434, 1329, 1308, 1210, 1127, 1067, 986, 933, 835, 783, 760, 729, 709, 634, 579, 549. cm^{-1} .

(Z)-4-amino-N'-hydroxy-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3-carbimidoyl azide (10)

Compound **5** (0.28 g, 1 mmol) was suspended in 5 mL of anhydrous ethanol. To the suspension was added 2 mL of an aqueous solution of sodium azide (0.13 g, 2 mmol) dropwise under vigorous stirring. After addition, the reaction mixture was heated to 50 °C and stirred for 2 hours. Upon cooled to room temperature, the precipitated solid was collected by filtration, washed with ice-cold water, and dried to afford 0.261 g of a white solid in 90% yield.
^{1}H NMR(500MHz, DMSO-d_6) δ = 12.081(s, 1H), 9.50(s, 2H,) ppm
^{13}C NMR(126MHz, DMSO-d_6) δ = 156.75, 156.35, 155,98, 155.80, 155.60, 141.25, 141.05, 125.80, 123.65, 120.95, 118.26, 115.59 ppm
^{19}F NMR(373 MHz, DMSO-d_6) δ = -64.58 ppm
IR(KBr): v = 3679, 3440, 3221, 3148, 3022, 2859, 2169, 2119, 1643, 1578, 1512, 1482, 1418, 1383, 1351, 1287, 1267, 1210, 1168, 1034, 984, 870, 790, 776, 754, 729, 707, 638, 555, 532.cm^{-1}.

[1-(Chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium] 3-(fluorodinitromethyl)-N-nitro-7-(trifluoromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amide (11)

Compound **6** or **8** (0.5 mmol) was suspended in 5 mL of anhydrous acetonitrile. To this suspension was added Selectfluor (0.354 g, 1 mmol) slowly at room temperature. The resulting mixture was stirred at room temperature for 3 hours. The solvent was then removed under reduced pressure, and the residue was repeatedly extracted with dichloromethane. After removal of dichloromethane, 0.23 g of a pale yellow waxy solid was obtained in 88% yield.
^{1}H NMR(500MHz, DMSO-d_6) δ = 5.31(s, 1H), 3.41(s, 1H), 3.14(s, 1H,) ppm
^{13}C NMR(126MHz, DMSO-d_6) δ = 158.11, 156.12, 155.73, 155.34, 154.95, 138.91, 125.12, 123.49, 122.08, 121.84, 120.70, 118.01, 115.31, 68.04, 51.14, 44.08 ppm
^{19}F NMR(373MHz, DMSO-d_6) δ = -64.58 ppm
IR (KBr): v =2970, 1619, 1549, 1509, 1488, 1461, 1427, 1389, 1364, 1311, 1279, 1227, 1195, 1160, 1095, 1055, 980, 947, 928, 908, 838, 804, 795, 778, 744, 718, 684, 608, 569, 538. cm^{-1}

Computational studies

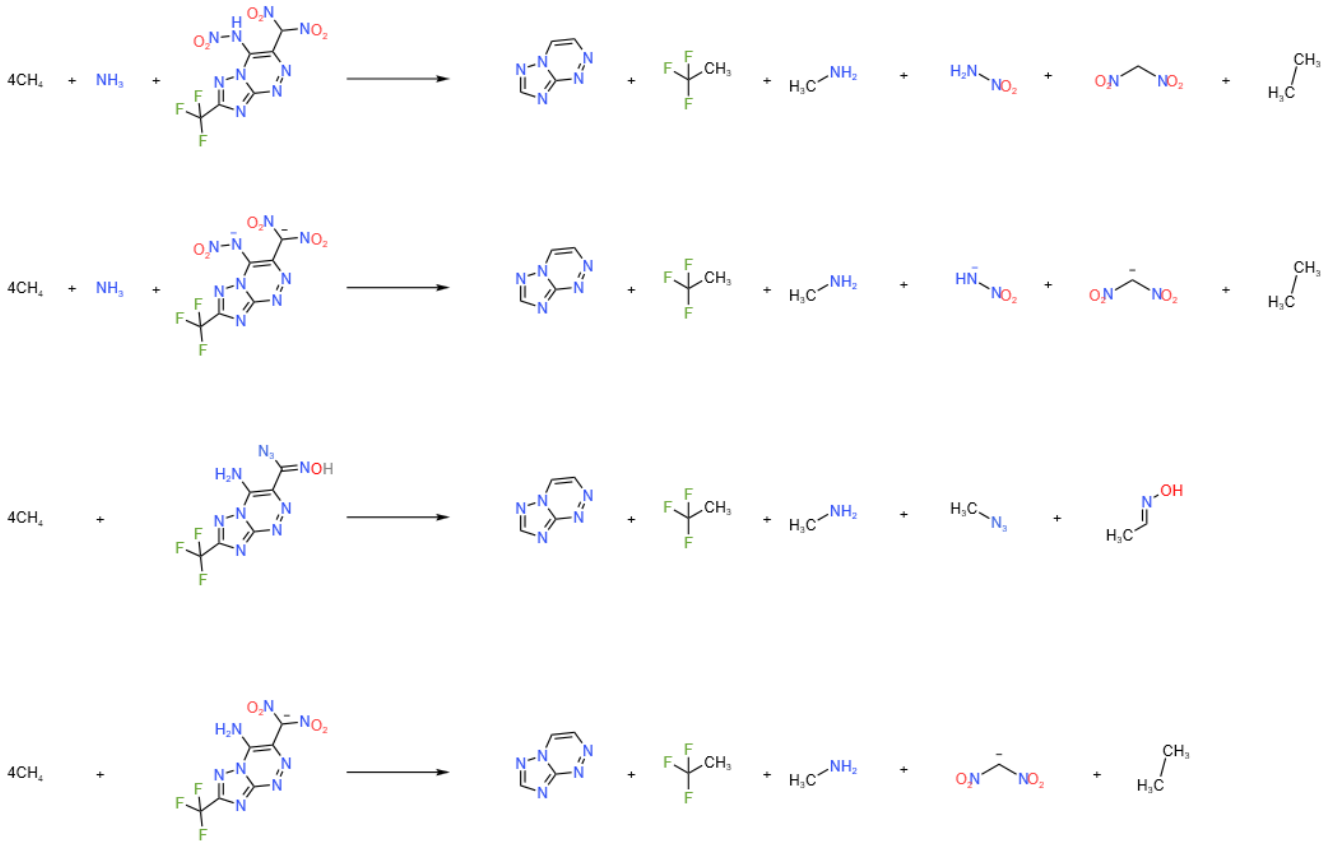


Fig.S1 isodesmic reactions

The predictions of heats of formation (HOF) of compounds used the m062x methods with the 6-311+G(d, p) 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 **Fig. S1**

Table. 1 Thermodynamic parameters calculated based on isodesmic reactions

compounds	E0	ZPE	HF
CH_4	-40.496762	0.045007	0.048819
NH_3	-56.545851	0.034616	0.038432
[1,2,4]triazolo[5,1-c][1,2,4]triazine	-427.86081	0.082917	0.089336
CH_3N_3	-204.05814	0.050899	0.056287
CH_3CF_3	-377.55147	0.057748	0.058692
CH_3NH_2	-95.834736	0.064535	0.068912
$CH(NO_2)_2^-$	-448.93201	0.040832	0.047634
$CH(NO_2)_2F$	-548.67793	0.046505	0.054387
$CH_3CH=NOH$	-209.10457	0.073514	0.079354
$CH_2(NO_2)_2$	-449.43990	0.053852	0.059438
NH_2NO_2	-261.01222	0.040213	0.044792
$NHNO_2^-$	-260.46268	0.027057	0.031275
C_2H_6	-79.797062	0.075096	0.079518
10	-1152.4626	0.134184	0.148948
9 anion	-1268.0439	0.12469	0.141238
6 , 8 anion	-1471.9018	0.115193	0.134943
7	-1472.973	0.142049	0.162062

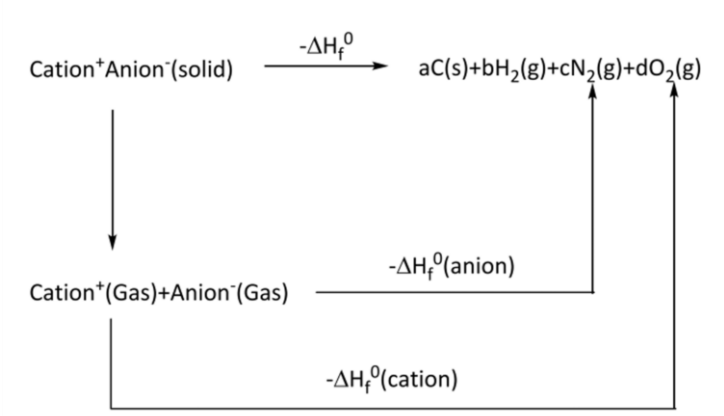


Fig. S2 Born-Haber cycle for the heat of formation of energetic salt

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (**Fig. S2**). The number is simplified by equation[1] :

$$\Delta Hf_0\,(salt,298\ K) = \Delta Hf_0\,(cation,298K) + \Delta Hf_0\,(anion,298K) - \Delta H_L \quad (1)$$

Where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins[2] et al

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

Where n_M and n_X depend on the nature of the ions, n_M and n_X are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The variables q and p represent the charge numbers of the cation and anion, respectively. The equation for lattice potential energy U_{POT} has the form:

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

Where ρ_m [g·cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, the coefficients γ (kJ·mol^{-1}·cm) and δ (kJ·mol^{-1}) are assigned literature values[3].The molar mass of the ionic compound is denoted as M (g/mol).

When the charge ratio q:p = 1:1, the coefficients γ and δ are 1981.2 kJ·mol^{-1} and 103.8 kJ·mol^{-1}, respectively.

When q:p = 1:2, the coefficients γ and δ are 8375.6 kJ·mol^{-1} and -178.8 kJ·mol^{-1}, respectively.

When q:p = 2:1, the coefficients γ and δ are 6764.3 kJ·mol^{-1} and 365.4 kJ·mol^{-1}, respectively.

When q:p = 2:2, the coefficients γ and δ are 6864.0 kJ·mol^{-1} and 732.0 kJ·mol^{-1}, respectively.

In this work, on the basis of Gaussian 16 C.021 packages, all the sample structures were fully optimized by ωB97XD with 6-31G+(d) basis set basis set. The Independent Gradient Model based on Hirshfeld partition (IGMH) were calculated by the Multiwfn 3.8(dev). The distributions of IGM pictures were obtained from VMD 1.9.3 program (**Fig. S3**).

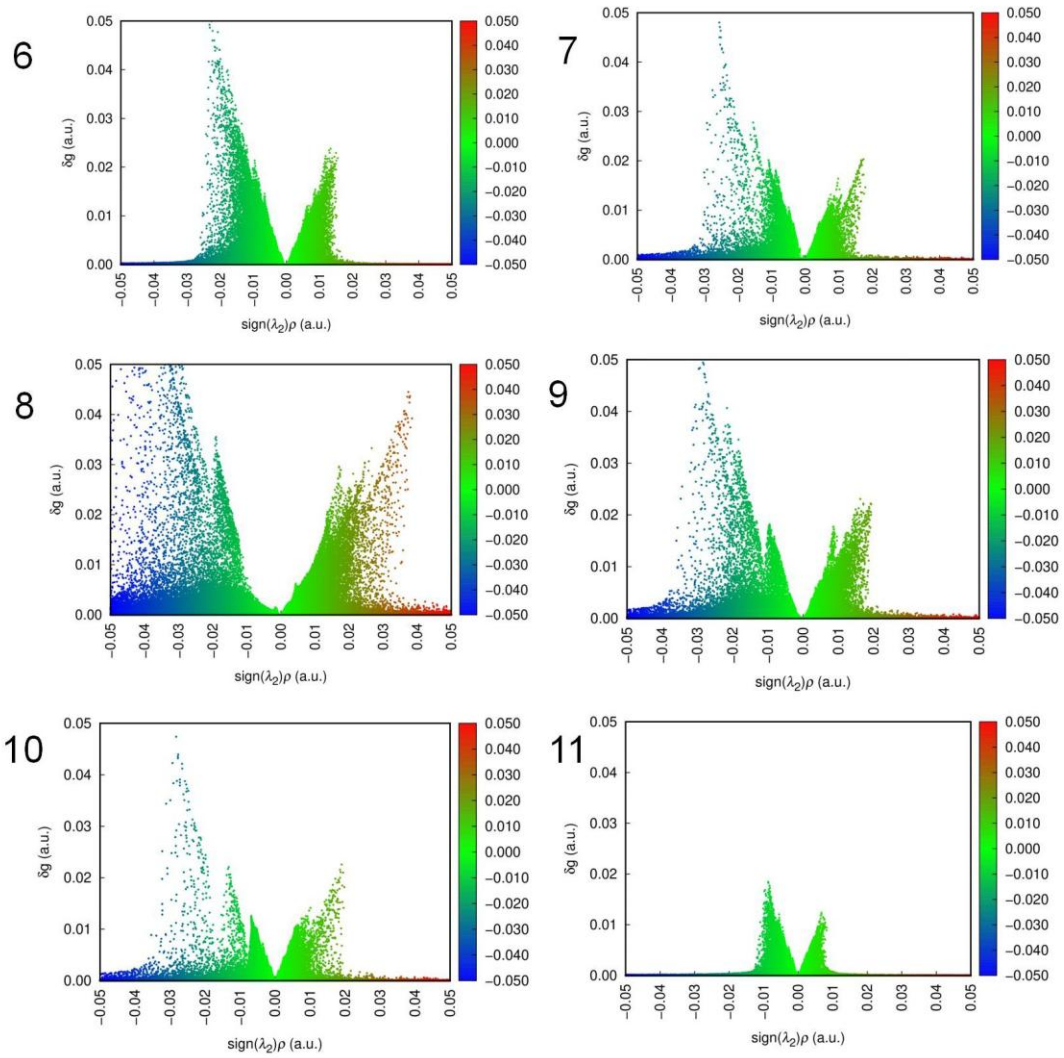


Fig. S3 NCI Scatter Plots of Compounds **6**, **7**, **8**, **9**, **10**, and **11**

Crystallographic data

Crystallographic data for **9**.

Table. 2 Crystal data and structure refinement for **9·H_2O**.	
Identification code	9·H2O
Empirical formula	$C_6H_8F_3N_9O_5$
Formula weight	343.21
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.0942(14)
b/Å	13.4468(18)
c/Å	10.1321(15)
α/°	90
β/°	92.162(6)
γ/°	90
Volume/$Å^3$	1238.2(3)
Z	4
$\rho_{calc}g/cm^3$	1.841
μ/mm^{-1}	0.183
F(000)	696.0
Crystal size/mm^3	0.24 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.482 to 52.796
Index ranges	$-11 \le h \le 9$, $-15 \le k \le 16$, $-12 \le l \le 12$
Reflections collected	8515
Independent reflections	2506 [R_{int} = 0.0956, R_{sigma} = 0.0936]
Data/restraints/parameters	2506/205/232
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0768, wR_2 = 0.1652
Final R indexes [all data]	R_1 = 0.1223, wR_2 = 0.1919
Largest diff. peak/hole / e $Å^{-3}$	0.73/-0.41

Table 3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F3	6148(15)	3796(19)	6430(30)	27.8(16)
O2	4356(3)	10131(2)	3326(3)	23.4(7)
O1	4298(3)	8523(2)	3032(3)	23.6(7)
F2	7154(17)	3401(12)	4658(14)	33.3(18)
O3	6891(3)	10843(2)	4246(3)	25.1(7)
F1	8350(12)	3983(11)	6695(10)	32.7(16)
O4	8578(3)	9727(2)	4667(3)	34.1(8)
O5	10327(4)	7776(3)	6057(4)	37.7(9)
N8	4975(4)	9312(2)	3398(3)	17.8(7)
N3	6903(4)	6573(2)	4933(3)	19.1(7)
N4	5488(4)	7760(3)	5932(3)	23.3(8)
N2	6512(4)	5787(3)	5703(4)	22.6(8)
N1	8157(4)	5307(3)	4159(4)	22.0(7)
N7	7293(4)	9957(3)	4272(3)	20.1(7)
N6	8401(4)	6901(3)	3106(4)	24.1(8)
N5	7885(4)	7835(3)	3132(3)	22.3(8)
N9	11064(5)	6149(3)	7867(4)	32.4(10)
C6	6385(4)	9170(3)	3896(4)	18.7(8)
C5	6943(4)	8149(3)	4011(4)	18.3(8)
C3	6386(4)	7518(3)	5018(4)	17.6(8)
C4	7880(4)	6280(3)	3999(4)	20.5(8)
C2	7303(4)	5074(3)	5174(4)	20.6(8)
C1	7275(5)	4035(3)	5713(5)	26.1(7)
F1A	8485(12)	3770(11)	6396(10)	32.7(16)

Table 3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F3A	5995(15)	3917(19)	6320(30)	27.8(16)
F2A	7495(17)	3325(12)	4848(15)	33.3(18)

Table. 4 Anisotropic Displacement Parameters (Å2×103) for 1_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F3	30(2)	17(5)	37(3)	10(2)	8(2)	9(2)
O2	22.2(15)	15.5(12)	32.5(16)	1.0(12)	0.5(13)	5.6(10)
O1	19.5(15)	18.5(12)	32.8(17)	-4.5(12)	2.5(12)	-1.5(11)
F2	44(5)	16(2)	40(3)	1(3)	7(2)	12(3)
O3	24.8(16)	14.6(12)	36.1(18)	-0.3(12)	4.0(14)	0.7(10)
F1	30(2)	30(5)	39(4)	6(3)	4(3)	17.0(19)
O4	17.1(13)	29.2(17)	55(2)	-4.3(16)	-7.0(13)	1.7(11)
O5	37(2)	32(2)	44(2)	-8.7(17)	7.9(17)	6.7(15)
N8	16.4(13)	13.8(12)	23.5(17)	1.2(12)	4.6(12)	1.0(9)
N3	17.0(16)	15.0(12)	25.5(16)	2.2(11)	3.0(12)	2.9(11)
N4	24.9(19)	15.6(17)	29.9(18)	4.4(14)	7.9(13)	6.8(14)
N2	23.5(18)	14.2(13)	30.5(18)	2.8(12)	7.0(13)	3.4(12)
N1	20.3(17)	15.9(13)	30.1(18)	-0.2(12)	3.7(13)	3.5(12)
N7	16.9(13)	16.3(12)	27.4(18)	-1.7(13)	2.4(12)	0.5(10)
N6	24.0(19)	18.4(14)	30.5(18)	1.9(12)	9.2(14)	3.7(12)
N5	19.9(17)	16.5(14)	30.9(18)	0.4(13)	5.7(13)	0.9(12)
N9	26(2)	36(2)	35(2)	2(2)	5.0(19)	4.7(18)

Table. 4 Anisotropic Displacement Parameters (Å2×103) for 1_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	16.1(14)	14.6(13)	26(2)	1.2(13)	3.4(13)	0.3(10)
C5	14.6(17)	15.9(13)	24.2(18)	1.1(12)	0.2(13)	0.9(12)
C3	15.1(18)	13.6(13)	24.0(17)	-1.0(12)	0.3(12)	0.0(12)
C4	16.2(19)	16.8(14)	29.0(19)	0.1(13)	5.2(13)	2.6(13)
C2	17.7(19)	16.3(12)	27.7(18)	-0.2(12)	0.8(13)	2.7(12)
C1	28.1(15)	16.6(14)	34.1(17)	3.8(11)	5.9(11)	7.9(13)
F1A	30(2)	30(5)	39(4)	6(3)	4(3)	17.0(19)
F3A	30(2)	17(5)	37(3)	10(2)	8(2)	9(2)
F2A	44(5)	16(2)	40(3)	1(3)	7(2)	12(3)

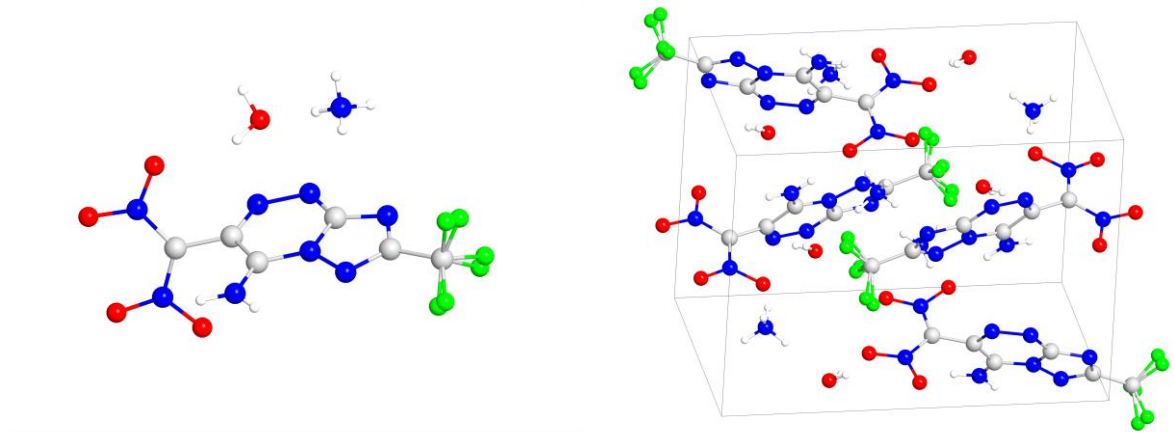


Fig. S4 Crystal Packing of Crystal **9·H₂O**

Crystallographic data for **10·1/2DMF·1/2H₂O**

Table. 5 Crystal data and structure refinement for **10·1/2DMF·1/2H₂O**.	
Identification code	10·1/2DMF·1/2H₂O
Empirical formula	$C_{15}H_{15}F_6N_{21}O_4$
Formula weight	667.48
Temperature/K	170.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	8.1445(6)
b/Å	10.7710(7)
c/Å	15.6123(12)
α/°	86.096(2)
β/°	79.109(3)
γ/°	86.365(2)
Volume/Å^3	1340.00(17)
Z	2
ρ_{calc}g/cm^3	1.654
μ/mm^{-1}	0.154
F(000)	676.0
Crystal size/mm^3	0.24 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.796 to 52.784
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 11, -19 ≤ l ≤ 19
Reflections collected	14988
Independent reflections	5461 [R_{int} = 0.0931, R_{sigma} = 0.1165]
Data/restraints/parameters	5461/396/464
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0788, wR_2 = 0.1530
Final R indexes [all data]	R_1 = 0.1608, wR_2 = 0.1917
Largest diff. peak/hole / e Å^{-3}	0.39/-0.43

Table. 6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Y1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O2	10019(4)	7544(3)	6408.6(19)	28.3(8)
F2	5340(20)	4410(30)	1750(30)	50(6)
O3	5797(4)	3202(3)	7170(2)	33.3(8)
O4	3837(4)	1433(3)	7110(2)	34.1(8)
O1	11072(4)	6951(3)	2276(2)	35.2(8)
N2	7758(4)	5226(3)	3826(2)	19.3(8)
F1	7880(40)	4990(30)	1280(20)	50(4)
N5	6950(4)	4575(3)	5522(2)	22.0(8)
F3	7830(40)	3222(17)	1600(30)	58(5)
N10	9485(4)	6771(3)	3995(2)	23.2(8)
N9	9515(4)	7032(3)	5710(2)	24.4(9)
N14	3759(5)	1320(3)	6240(2)	27.3(9)
N18	4427(4)	1896(3)	4508(2)	24.2(9)
N13	3142(4)	621(3)	3735(2)	23.9(8)
N3	6268(5)	3776(3)	3455(2)	25.9(9)
N4	6331(5)	3912(3)	4981(2)	25.7(9)
F4	4560(30)	1516(18)	1210(30)	63(5)
N1	7972(5)	5379(3)	2940(2)	24.9(8)
N20	1746(4)	-741(3)	5141(2)	26.3(9)
N19	1460(5)	-1053(3)	4372(2)	28.0(9)
N7	8314(5)	6007(4)	7445(3)	29.9(9)
N11	2142(5)	-463(3)	2828(3)	31.8(9)

Table. 6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Y1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
N6	7914(5)	5616(4)	6779(2)	34.7(10)
N12	3773(5)	1159(3)	2933(2)	29.4(9)
N16	1876(5)	-276(4)	7547(3)	39.7(11)
N15	1956(5)	-393(4)	6747(3)	39.0(11)
F6	4670(40)	-230(30)	1140(40)	80(6)
F5	2220(40)	530(30)	1080(30)	76(6)
C4	8454(5)	5914(4)	4365(3)	19.3(9)
C3	6744(5)	4260(4)	4131(3)	21.7(9)
C8	8538(5)	6127(4)	5949(3)	21.0(9)
C5	7946(5)	5528(4)	5254(3)	19.3(9)
C14	3453(5)	961(4)	4511(3)	22.6(9)
C12	2668(5)	216(4)	5236(3)	23.6(10)
N00Z	10843(6)	7367(5)	862(3)	48.3(12)
C2	7049(6)	4491(4)	2776(3)	26.1(10)
N8	8502(6)	6178(4)	8122(3)	44.8(12)
C13	2829(5)	441(4)	6133(3)	25.4(10)
C11	2169(5)	-355(4)	3670(3)	25.5(10)
C10	3117(6)	456(4)	2436(3)	30.5(11)
N17	1612(7)	-338(5)	8284(3)	60.7(15)
C16	10244(7)	7287(4)	1702(3)	36.5(12)
C1	6925(7)	4252(5)	1864(3)	36.3(11)
C9	3512(7)	627(5)	1466(3)	44.1(12)
C15	12586(8)	7033(8)	527(4)	82(2)
C6	9768(9)	7747(8)	242(4)	88(3)

Table. 6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Y1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
F6A	4250(40)	-380(30)	1090(40)	80(6)
F4A	4120(30)	1729(16)	1190(30)	58(5)
F5A	2130(40)	910(30)	1150(30)	76(6)
F3A	7430(40)	3077(15)	1680(30)	50(5)
F2A	5380(20)	4100(30)	1740(30)	47(5)
F1A	7470(40)	5200(30)	1300(20)	60(7)

Table. 7 Anisotropic Displacement Parameters (Å2×103) for Y1_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O2	30.3(19)	26.5(18)	31.3(18)	-7.2(14)	-7.9(14)	-12.2(15)
F2	48(5)	72(17)	40(7)	-22(11)	-20(4)	-14(5)
O3	36(2)	29.7(19)	37(2)	2.4(15)	-9.8(16)	-16.0(16)
O4	40(2)	30.3(19)	34.6(19)	-3.4(15)	-7.7(16)	-16.7(16)
O1	39(2)	41(2)	27.0(18)	1.0(15)	-6.5(15)	-18.2(17)
N2	23.5(19)	15.9(17)	19.6(18)	-0.8(14)	-5.9(15)	-5.7(15)
F1	62(9)	62(8)	29(5)	-1(5)	-10(5)	-32(8)
N5	21.4(19)	17.6(18)	28(2)	-2.7(15)	-4.7(16)	-6.2(15)
F3	66(12)	62(6)	45(9)	-25(7)	-3(9)	-5(7)
N10	27(2)	18.7(19)	25(2)	-0.5(15)	-6.8(16)	-7.6(16)
N9	25(2)	17.8(18)	33(2)	-6.6(16)	-9.6(17)	-6.9(16)
N14	29(2)	23(2)	31(2)	-4.4(16)	-9.1(17)	-4.1(17)
N18	23(2)	19.8(19)	31(2)	-2.5(16)	-5.0(16)	-8.8(16)
N13	23(2)	18.1(18)	32(2)	-4.8(15)	-6.6(16)	-3.1(16)

Table. 7 Anisotropic Displacement Parameters (Å2×103) for Y1_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N3	28(2)	25(2)	26(2)	-1.7(16)	-5.0(16)	-9.3(17)
N4	28(2)	24(2)	28(2)	-2.7(16)	-8.7(17)	-8.6(17)
F4	70(11)	81(9)	39(6)	4(9)	-4(9)	-39(9)
N1	29(2)	21.7(19)	24(2)	-0.7(15)	-5.2(16)	-6.6(17)
N20	24(2)	20.5(19)	35(2)	-3.0(16)	-6.7(17)	-2.8(16)
N19	29(2)	24(2)	34(2)	-2.1(16)	-9.1(17)	-7.3(17)
N7	29(2)	29(2)	32(2)	-1.1(18)	-4.4(18)	-8.4(18)
N11	34(2)	25(2)	39(2)	-1.9(17)	-10.6(18)	-4.7(18)
N6	46(3)	38(2)	23(2)	-1.7(17)	-8.2(18)	-22(2)
N12	31(2)	27(2)	32(2)	-0.4(16)	-9.1(17)	-4.5(18)
N16	46(3)	32(2)	41(2)	-1(2)	-2(2)	-20(2)
N15	50(3)	35(2)	33(2)	-2.4(18)	-3(2)	-24(2)
F6	127(13)	65(6)	43(5)	-18(5)	-6(11)	12(9)
F5	73(4)	114(17)	50(7)	22(12)	-32(5)	-35(7)
C4	17(2)	14(2)	27(2)	-1.5(17)	-3.3(17)	-3.2(17)
C3	19(2)	16(2)	32(2)	0.6(17)	-7.8(18)	-4.9(18)
C8	20(2)	18(2)	26(2)	2.0(17)	-3.5(18)	-5.0(18)
C5	21(2)	13(2)	25(2)	-0.8(16)	-6.0(18)	-3.9(17)
C14	17(2)	13(2)	38(2)	-4.1(17)	-3.9(18)	0.3(17)
C12	19(2)	17(2)	35(2)	-2.7(18)	-6.5(19)	-5.5(18)
N00Z	58(3)	62(3)	24(2)	3(2)	-6(2)	-7(3)
C2	26(2)	27(2)	26(2)	-0.1(18)	-3.7(19)	-9(2)
N8	56(3)	52(3)	28(2)	-7(2)	-8(2)	-18(2)
C13	20(2)	17(2)	40(3)	-3.3(18)	-3.9(19)	-3.6(18)

Table. 7 Anisotropic Displacement Parameters (Å2×103) for Y1_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	24(2)	19(2)	37(2)	-1.6(18)	-11(2)	-3.7(19)
C10	23(2)	26(2)	42(3)	-3(2)	-6(2)	-5(2)
N17	85(4)	59(3)	38(3)	-2(2)	1(3)	-39(3)
C16	48(3)	32(3)	29(3)	2(2)	-5(2)	-10(2)
C1	39(3)	40(3)	31(3)	-3(2)	-6(2)	-14(2)
C9	55(3)	40(3)	40(3)	-3(2)	-12(2)	-14(2)
C15	53(4)	148(8)	41(4)	-10(4)	3(3)	-7(4)
C6	87(5)	136(7)	42(4)	18(4)	-26(4)	1(5)
F6A	127(13)	65(6)	43(5)	-18(5)	-6(11)	12(9)
F4A	79(11)	44(5)	48(7)	5(4)	-1(10)	-18(6)
F5A	73(4)	114(17)	50(7)	22(12)	-32(5)	-35(7)
F3A	67(12)	44(4)	41(8)	-17(5)	-6(9)	-4(6)
F2A	39(4)	60(13)	46(7)	-20(9)	-13(4)	-11(4)
F1A	85(16)	68(9)	28(6)	13(7)	-8(8)	-41(10)

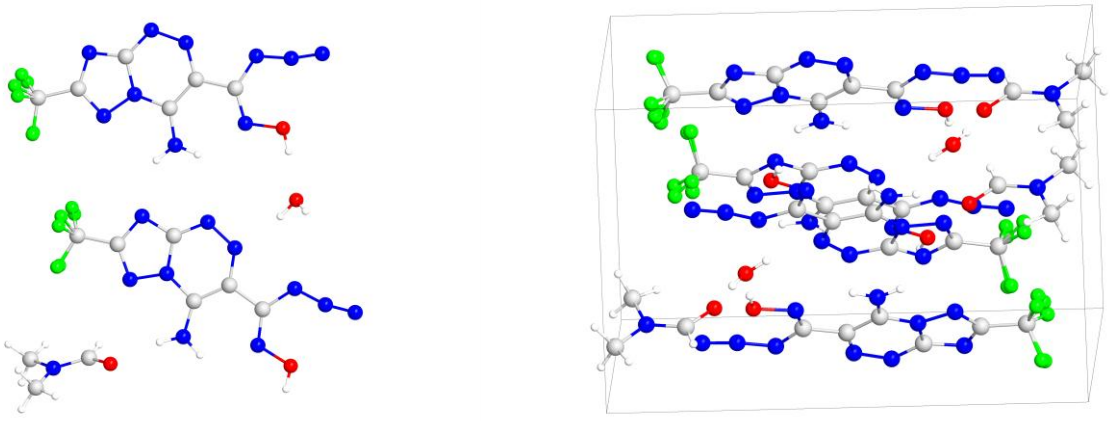


Fig. S5 Crystal Packing of Crystal **10·1/2DMF·1/2H₂O**

Crystallographic data for **11**

Table. 8 crystal data and structure refinement for **11**.	
Identification code	11
Empirical formula	$C_{13}H_{14}ClF_4N_{11}O_6$
Formula weight	531.80
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.0309(3)
b/Å	7.8291(2)
c/Å	23.1989(6)
α/°	90
β/°	92.1040(10)
γ/°	90
Volume/Å^3	2002.15(9)
Z	4
P_{calc}g/cm^3	1.764
μ/mm^{-1}	0.290
F(000)	1080.0
Crystal size/mm^3	0.26 × 0.25 × 0.2
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.15 to 52.766
Index ranges	$-13 \le h \le 13$, $-9 \le k \le 9$, $-28 \le l \le 28$
Reflections collected	22408
Independent reflections	4078 [R_{int} = 0.0684, R_{sigma} = 0.0439]
Data/restraints/parameters	4078/0/316
Goodness-of-fit on F^2	1.048
Final r indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0914
Final r indexes [all data]	R_1 = 0.0510, wR_2 = 0.0990
Largest diff. Peak/hole/e Å^{-3}	0.29/-0.28

Table. 9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for dhxg1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	3426.1(5)	9282.1(7)	9389.7(2)	36.65(15)
F4	6043.3(10)	3705.2(14)	4917.2(5)	26.5(3)
F3	7803.2(11)	10657.7(18)	7366.4(6)	44.4(4)
O3	7618.8(12)	2022.1(17)	6066.1(6)	26.8(3)
F1	6392.0(15)	9976(2)	7930.0(6)	52.9(4)
O4	7867.0(13)	1910.5(18)	5139.1(7)	31.8(3)
F2	6036.8(14)	11714.8(17)	7240.5(7)	52.5(4)
O5	5218.4(14)	724.3(18)	5898.1(7)	33.8(4)
O1	8184.3(15)	8474.7(18)	5533.0(7)	36.0(4)
O6	4329.9(14)	1707(2)	5117.5(7)	38.1(4)
N3	6372.6(13)	6943.5(18)	6387.3(6)	16.0(3)
N5	4794.9(14)	4390.8(19)	6160.4(7)	19.7(3)
N2	7042.2(13)	8262.9(19)	6619.8(7)	18.3(3)
N11	3836.4(13)	6663.8(19)	8664.4(7)	18.4(3)
N1	5211.1(14)	8033(2)	7051.6(7)	20.6(3)
N6	7749.2(14)	5722.7(19)	5715.6(7)	21.0(3)
N8	7307.5(14)	2260.6(19)	5565.4(7)	20.8(3)
N7	8520.2(14)	7148.0(19)	5753.9(7)	21.4(3)
O2	9527.6(14)	6891(2)	5965.5(9)	44.9(4)
N4	4463.1(14)	5549(2)	6542.1(7)	22.0(3)
N9	5113.5(14)	1709(2)	5497.1(7)	24.0(4)
N10	2888.3(15)	4243(2)	8058.9(8)	27.7(4)

Table. 9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for dhxg1_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C3	6738.7(16)	5789(2)	5981.5(7)	16.1(4)
C2	5843.2(15)	4482(2)	5901.3(8)	16.4(4)
C4	5279.5(15)	6800(2)	6657.8(8)	17.8(4)
C5	6283.8(16)	8832(2)	7003.7(8)	18.7(4)
C1	6065.4(16)	3139(2)	5465.5(8)	18.8(4)
C10	4805.7(17)	5723(3)	8345.1(9)	26.7(4)
C11	4199.1(19)	4272(3)	7991.6(9)	29.1(5)
C7	4453.8(18)	8052(3)	9007.8(9)	26.2(4)
C6	6633.5(18)	10304(2)	7386.2(9)	24.9(4)
C8	2928.1(19)	7377(3)	8224.1(9)	29.2(5)
C12	3231(2)	5395(3)	9048.4(9)	30.5(5)
C13	2648(2)	3995(3)	8670.5(10)	30.4(5)
C9	2388(2)	5884(3)	7869.4(11)	36.2(5)

Table. 10 Anisotropic Displacement Parameters (Å2×103) for dhxg1_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
Cl1	44.1(3)	31.7(3)	35.1(3)	-10.4(2)	15.3(2)	-3.4(2)
F4	35.5(6)	26.0(6)	17.6(6)	3.4(5)	-2.4(5)	2.7(5)
F3	28.6(7)	50.6(8)	54.8(9)	-31.3(7)	10.3(6)	-13.7(6)
O3	26.5(7)	25.1(7)	28.2(8)	4.3(6)	-5.6(6)	3.5(6)
F1	80.4(11)	57.6(9)	21.7(7)	-14.4(6)	13.6(7)	-32.2(8)

Table. 10 Anisotropic Displacement Parameters (Å2×103) for dhxg1_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
O4	34.1(8)	26.6(7)	35.5(9)	-5.1(6)	14.2(7)	4.9(6)
F2	65.1(10)	27.3(7)	64.0(10)	-19.3(7)	-10.8(8)	13.4(7)
O5	36.0(8)	27.3(8)	38.1(9)	5.1(7)	0.5(7)	-8.9(6)
O1	55.0(10)	19.0(7)	33.8(9)	5.7(6)	-2.7(7)	-4.0(7)
O6	28.4(8)	41.9(9)	42.8(9)	-10.7(7)	-13.2(7)	-4.1(7)
N3	16.5(7)	16.0(7)	15.4(7)	-0.8(6)	0.3(6)	0.3(6)
N5	17.5(7)	21.8(8)	19.5(8)	0.2(6)	-0.4(6)	0.2(6)
N2	20.4(8)	15.7(7)	18.9(8)	-2.5(6)	1.3(6)	-0.9(6)
N11	17.0(7)	20.7(8)	17.7(8)	0.6(6)	2.1(6)	0.1(6)
N1	17.6(7)	21.9(8)	22.3(8)	-3.2(6)	0.5(6)	2.3(6)
N6	22.2(8)	16.9(7)	24.4(9)	-4.3(6)	6.9(6)	-4.2(6)
N8	22.0(8)	13.4(7)	27.2(9)	-1.2(6)	2.7(7)	0.2(6)
N7	23.2(8)	18.5(8)	22.9(8)	-2.6(7)	7.5(7)	-3.6(6)
O2	25.3(8)	31.8(8)	76.7(13)	-9.3(8)	-10.8(8)	0.7(7)
N4	19.2(8)	24.4(8)	22.7(8)	-3.7(7)	3.2(6)	-0.9(6)
N9	22.2(8)	21.2(8)	28.3(9)	-8.1(7)	-0.7(7)	-1.0(6)
N10	27.2(9)	25.3(9)	30.2(9)	-0.8(7)	-4.6(7)	-1.5(7)
C3	19.5(9)	15.3(8)	13.4(9)	0.5(7)	-1.3(7)	2.6(7)
C2	16.8(8)	15.9(8)	16.6(9)	1.3(7)	-1.5(7)	0.4(7)
C4	14.5(8)	22.3(9)	16.7(9)	1.5(7)	1.0(7)	3.5(7)
C5	20.5(9)	18.7(9)	16.7(9)	-0.5(7)	0.2(7)	3.4(7)
C1	20.9(9)	18.9(9)	16.5(9)	1.9(7)	-2.3(7)	-0.2(7)

Table. 10 Anisotropic Displacement Parameters (Å2×103) for dhxg1_0m. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
C10	19.6(9)	27.9(10)	33.1(11)	-3.0(9)	8.1(8)	2.5(8)
C11	33.1(11)	30.9(11)	23.7(11)	-4.2(9)	3.9(9)	2.5(9)
C7	24.8(10)	27.8(10)	26.3(11)	-5.0(8)	5.3(8)	-5.6(8)
C6	25.8(10)	25.3(10)	23.8(10)	-5.7(8)	5.3(8)	-1.0(8)
C8	29.5(11)	25.2(10)	32.2(11)	2.2(9)	-9.0(9)	7.0(8)
C12	33.8(11)	34.4(11)	23.6(11)	5.2(9)	6.1(9)	-10.4(9)
C13	31.5(11)	24.8(10)	35.4(12)	0.7(9)	7.7(9)	-5.7(8)
C9	37.2(12)	30.5(11)	39.6(13)	-0.4(10)	-16.9(10)	2.0(9)

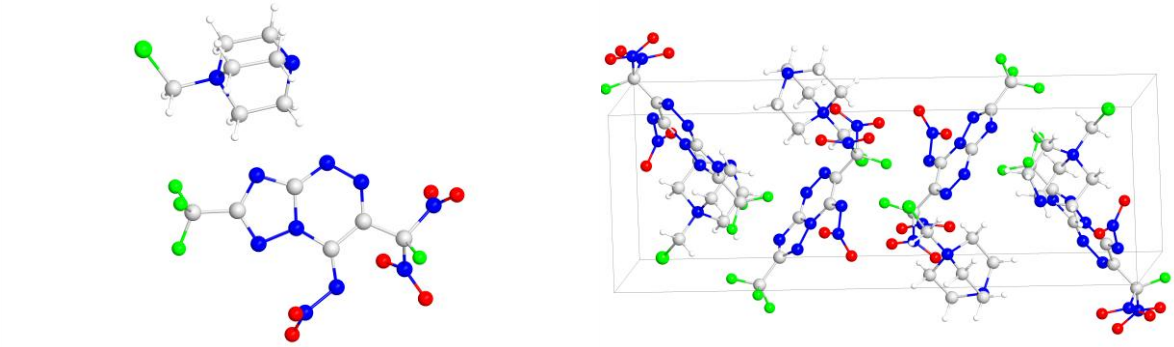
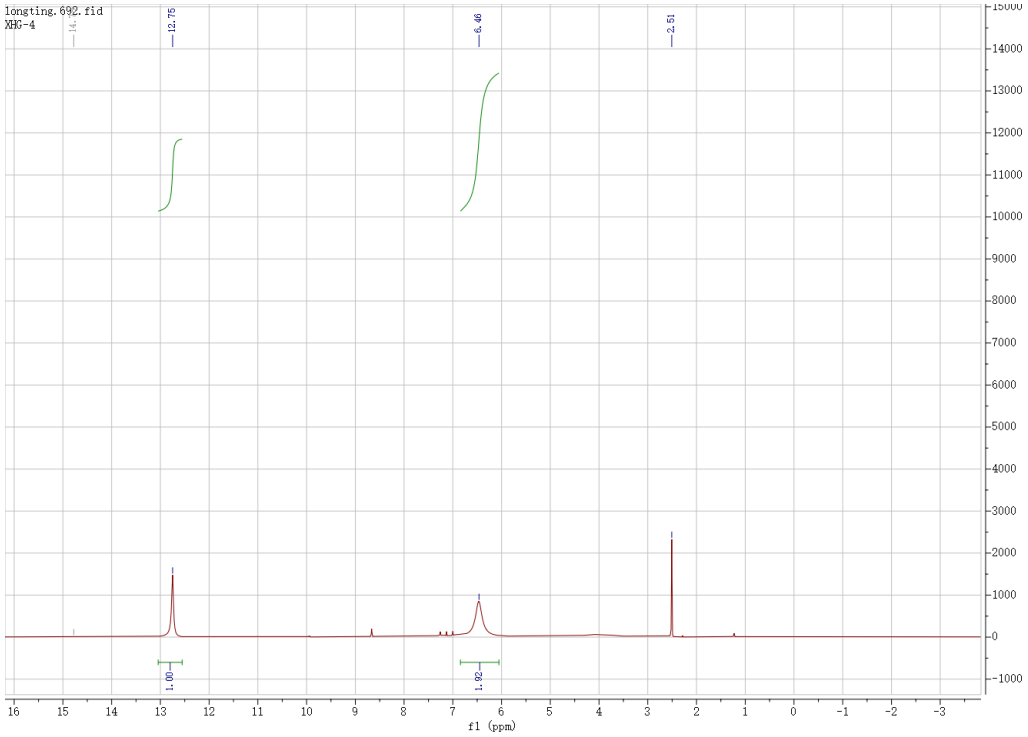


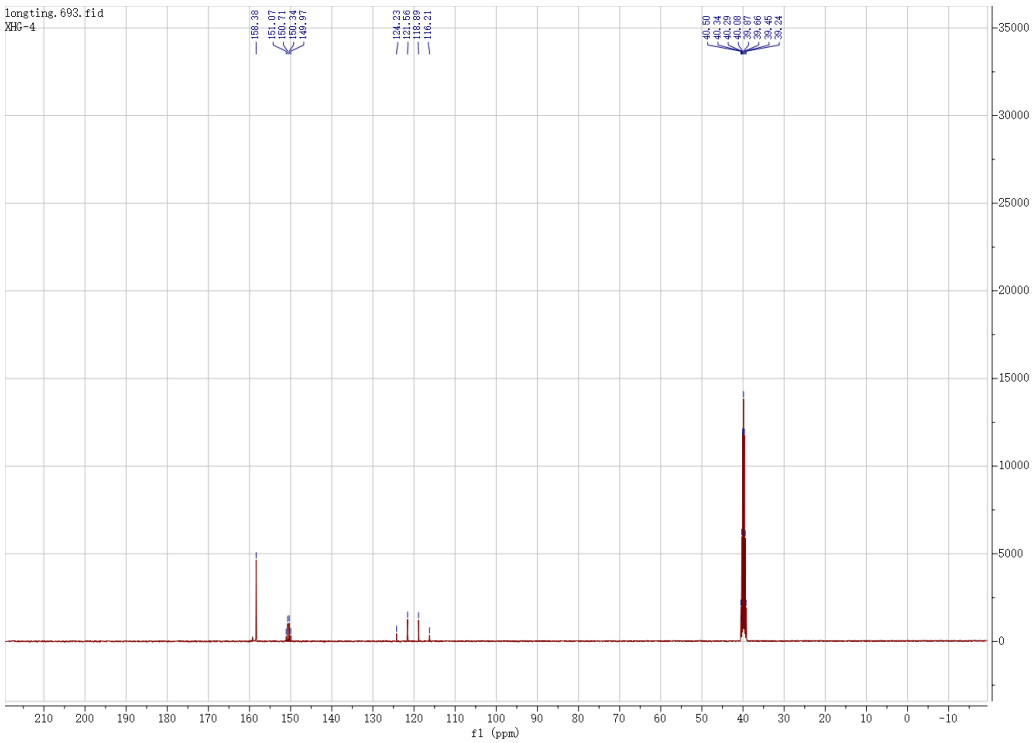
Fig. S6 Crystal Packing of Crystal **11**

Structural Analysis

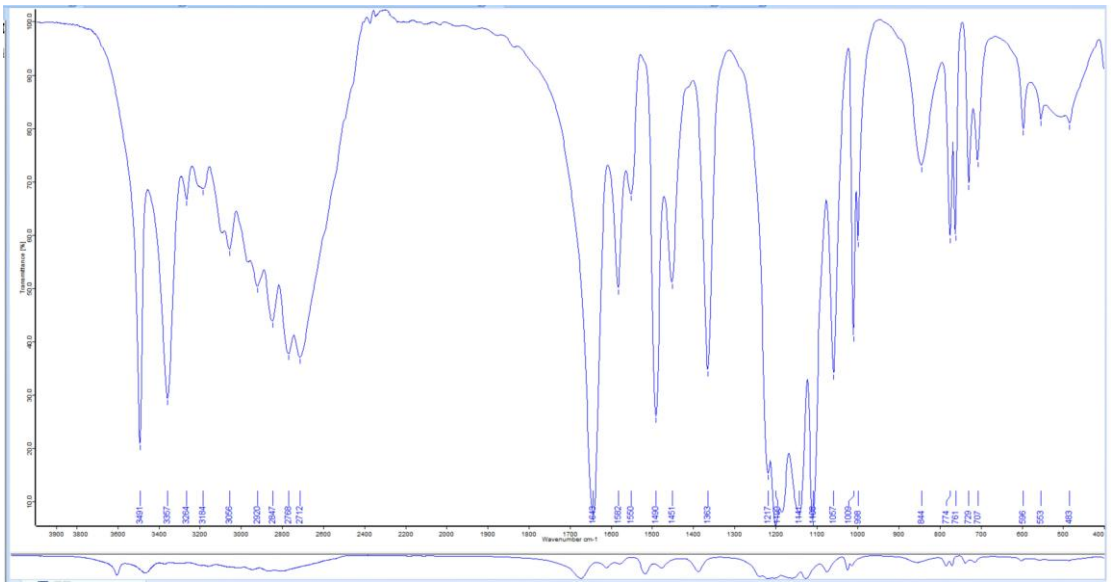
^{1}H NMR spectra in DMSO-d_6 for compound **2**



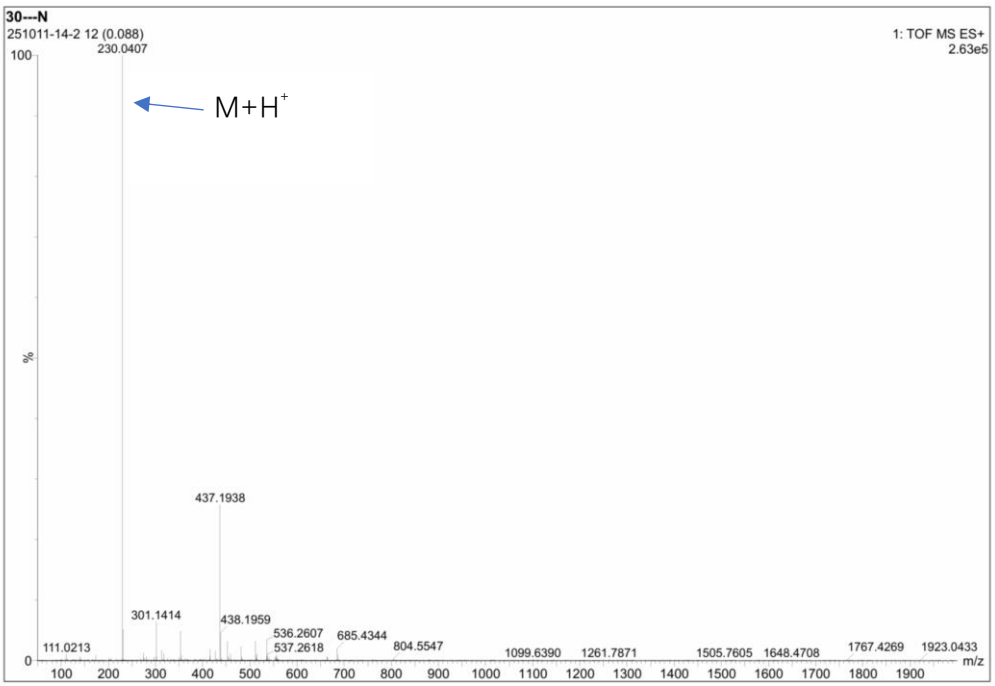
^{13}C NMR spectra in DMSO-d_6 for compound **2**



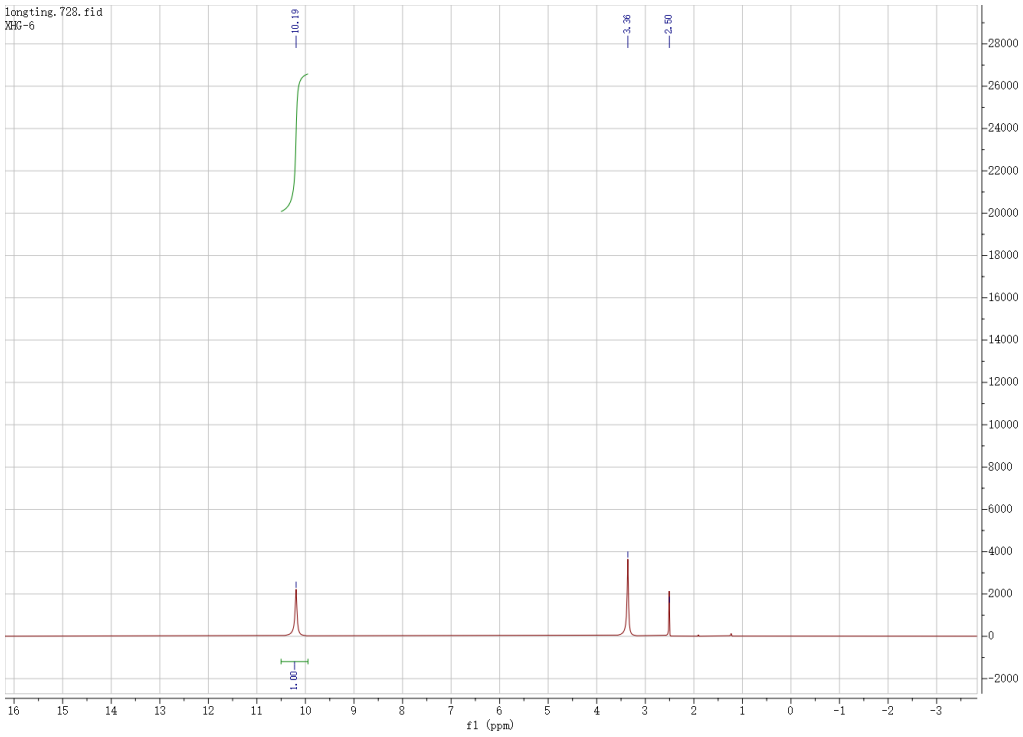
IR spectra for compound **2**



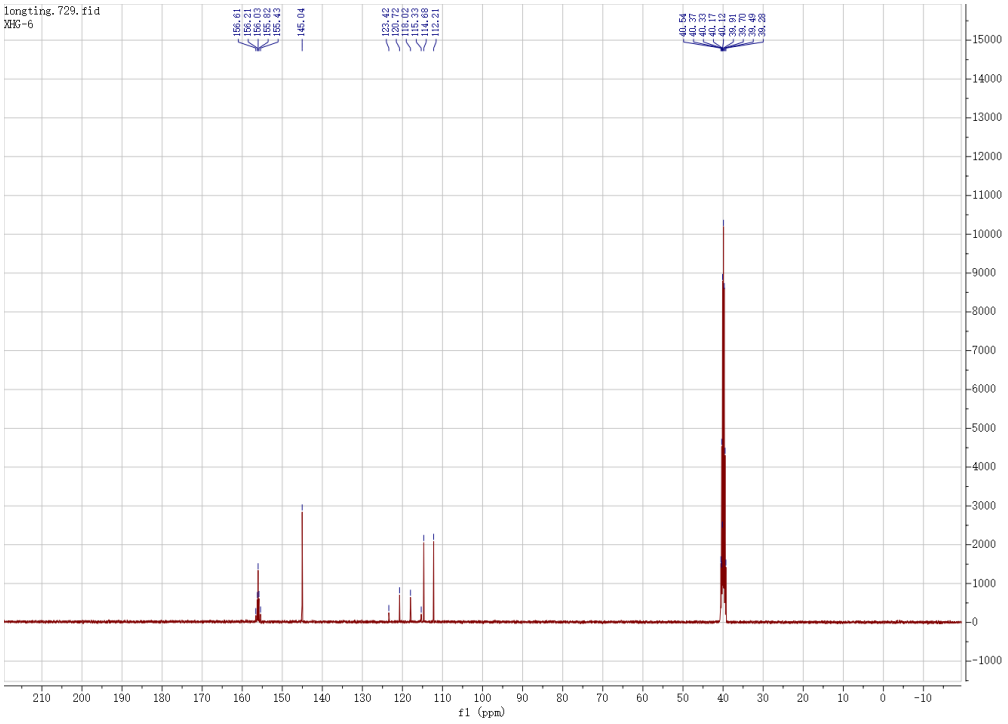
ESI-MS spectrum of **3**



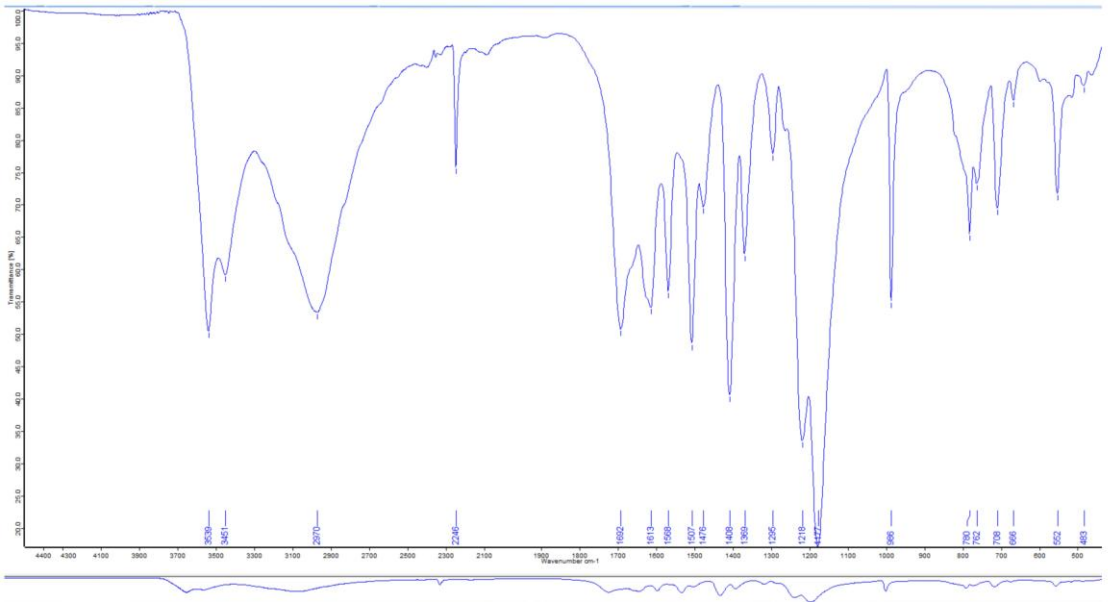
^{1}H NMR spectra in DMSO-*d*$_6$ for compound **3**



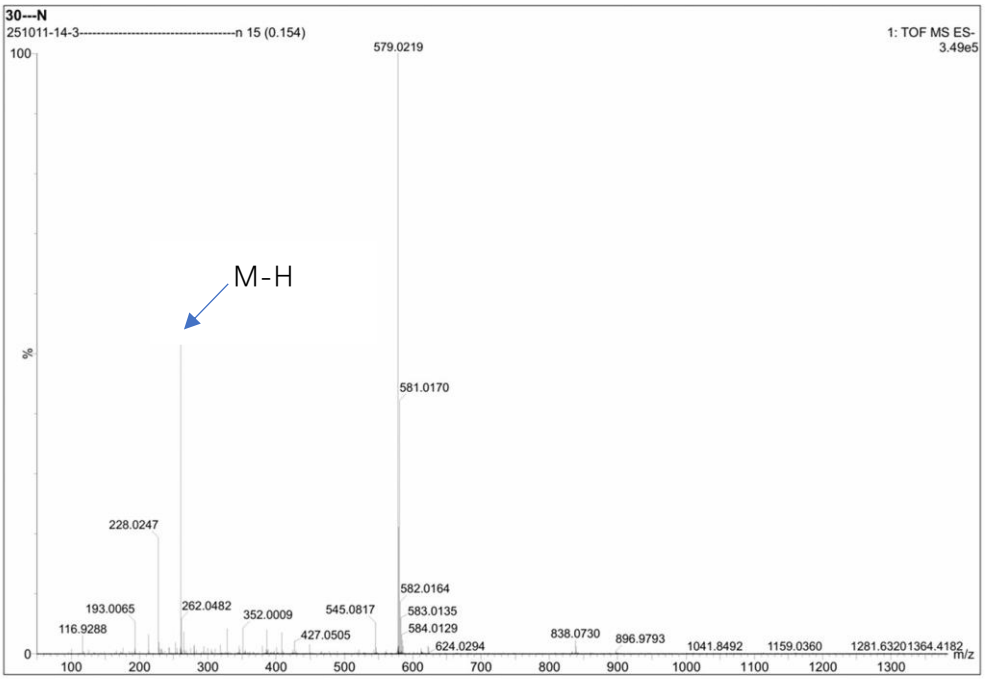
^{13}C NMR spectra in DMSO-d$_6$ for compound **3**



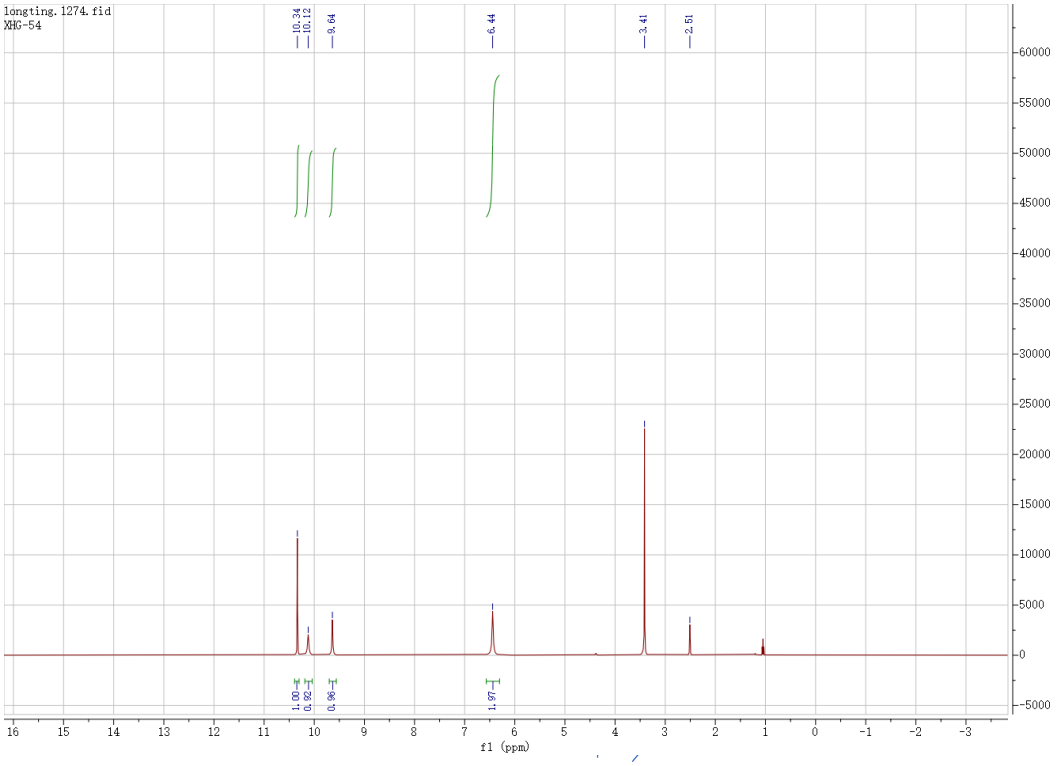
IR spectra for compound **3**



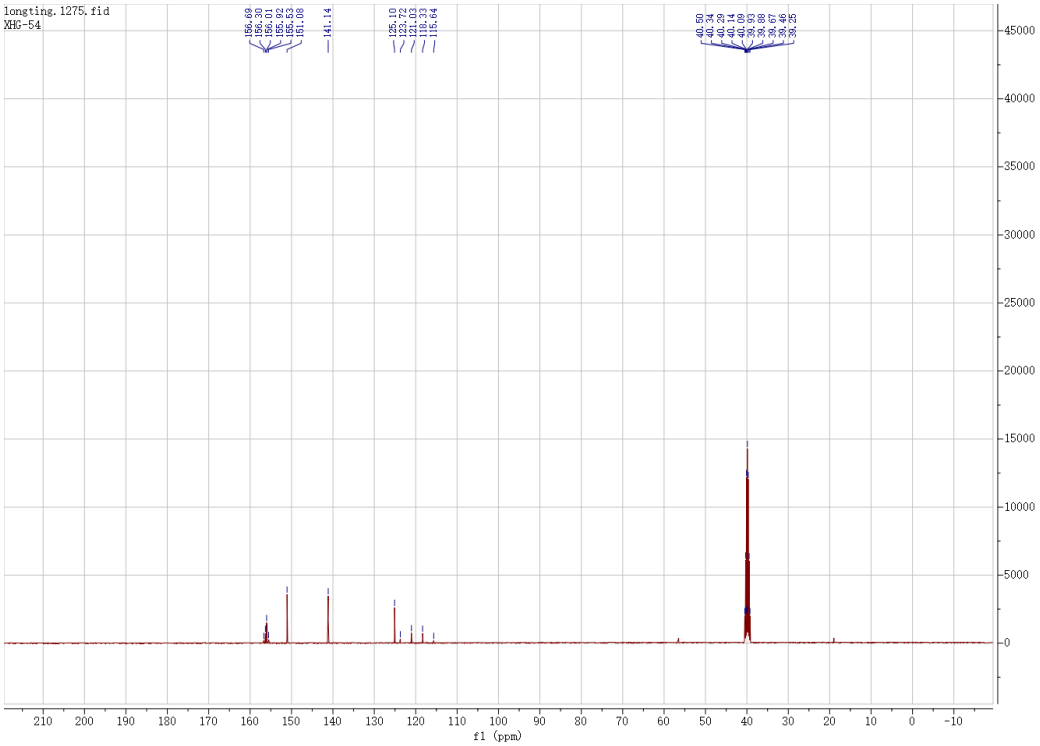
ESI-MS spectrum of **4**



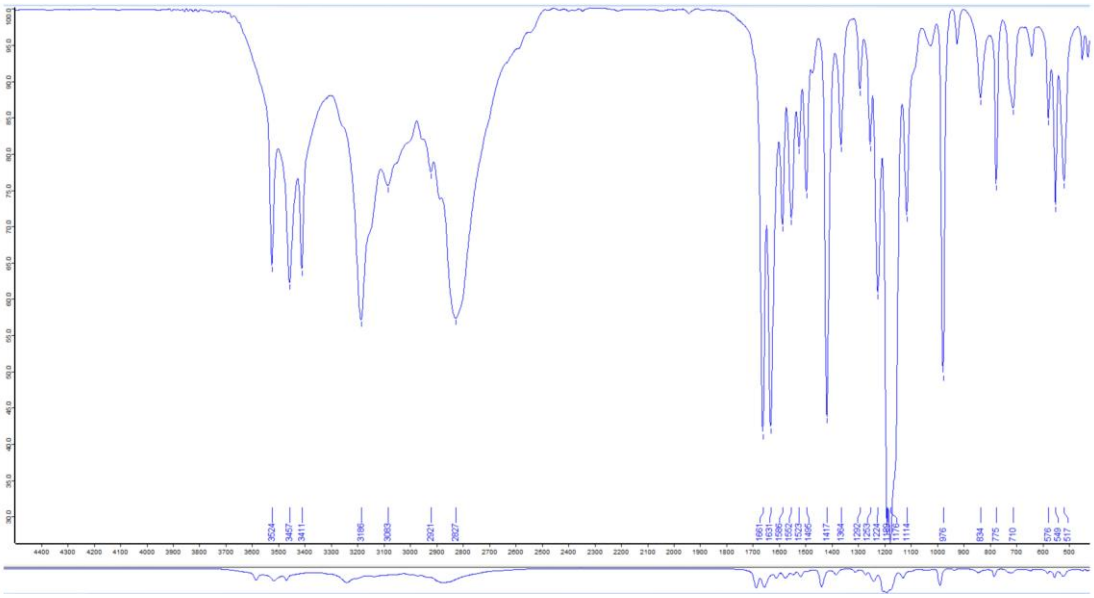
^{1}H NMR spectra in DMSO-d_6 for compound **4**



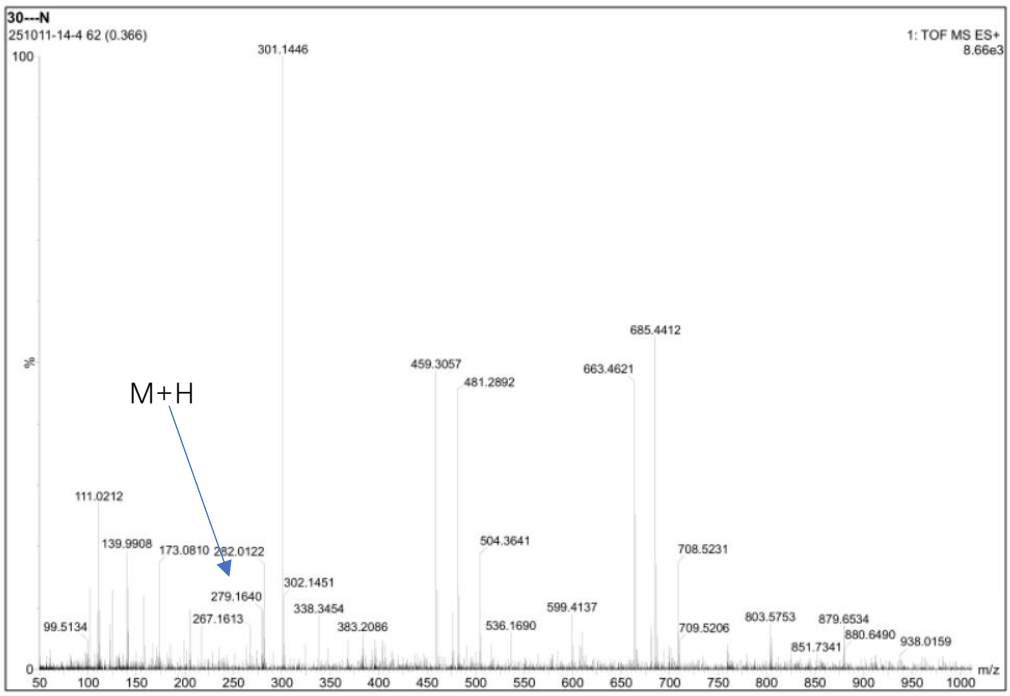
^{13}C NMR spectra in DMSO-d_6 for compound **4**



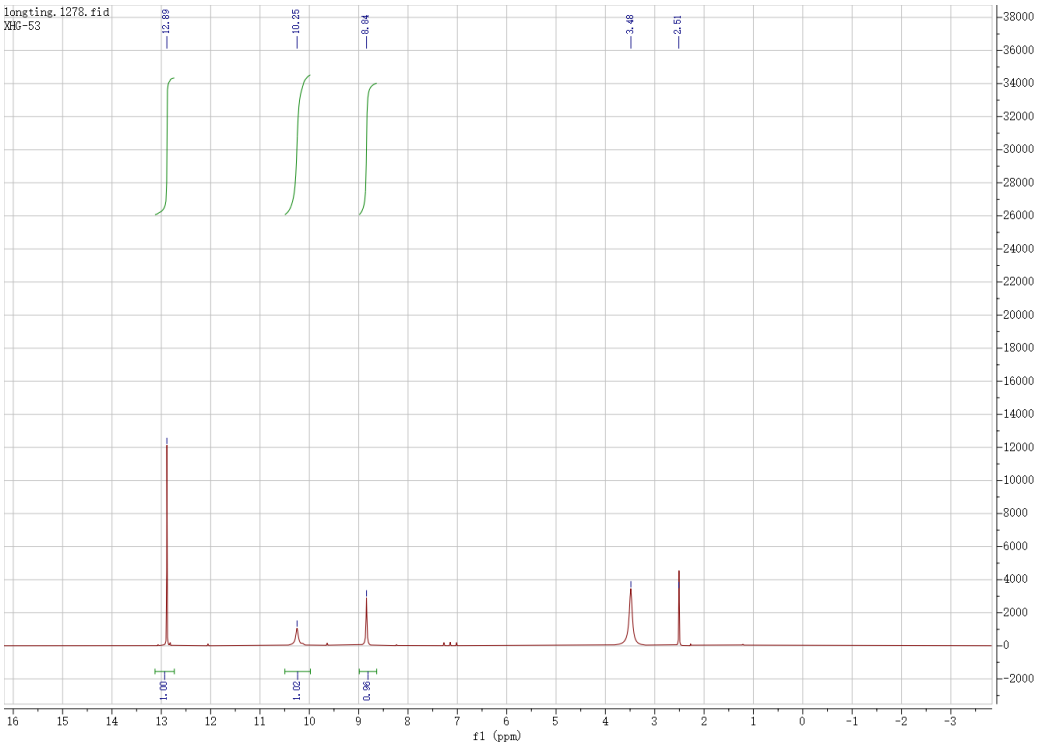
IR spectra for compound **4**



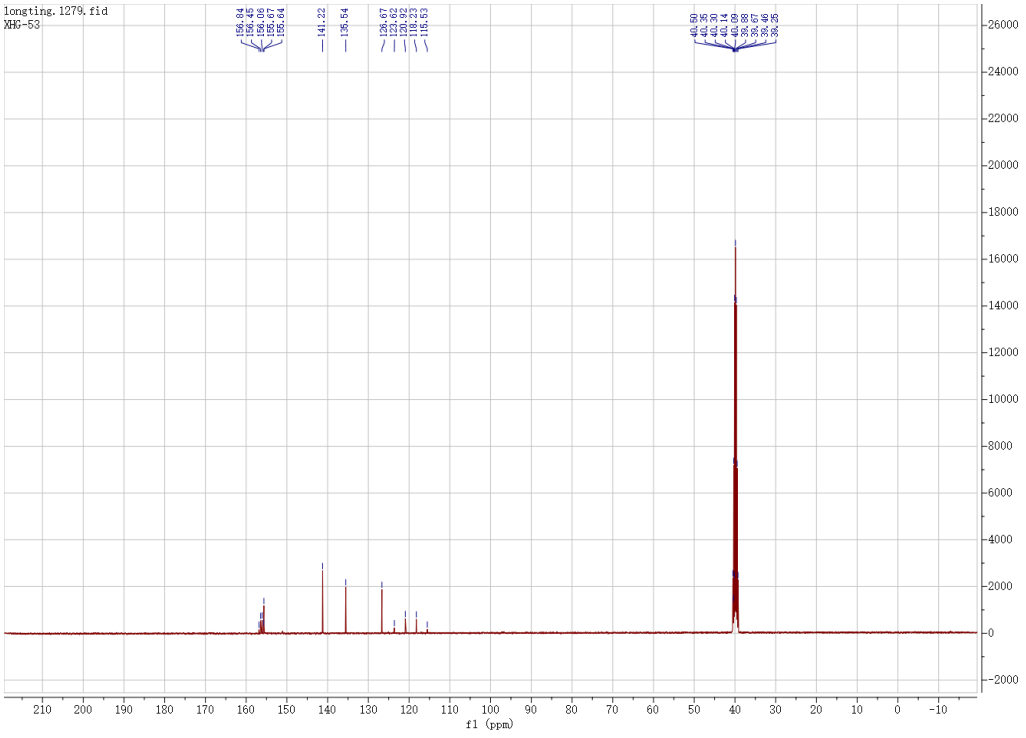
ESI-MS spectrum of **5**



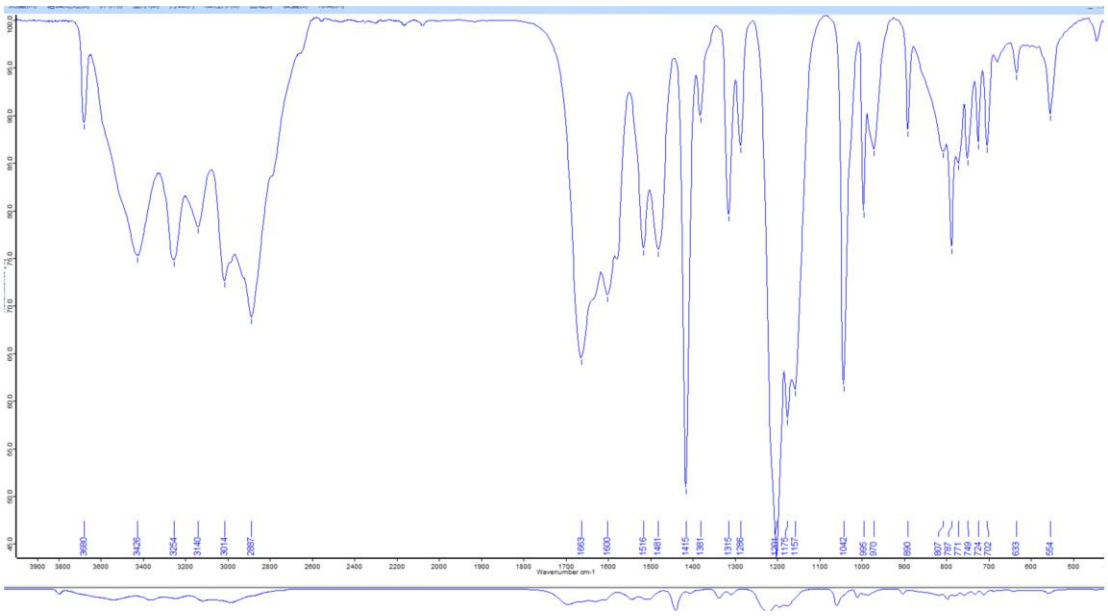
^{1}H NMR spectra in DMSO-d_6 for compound **5**



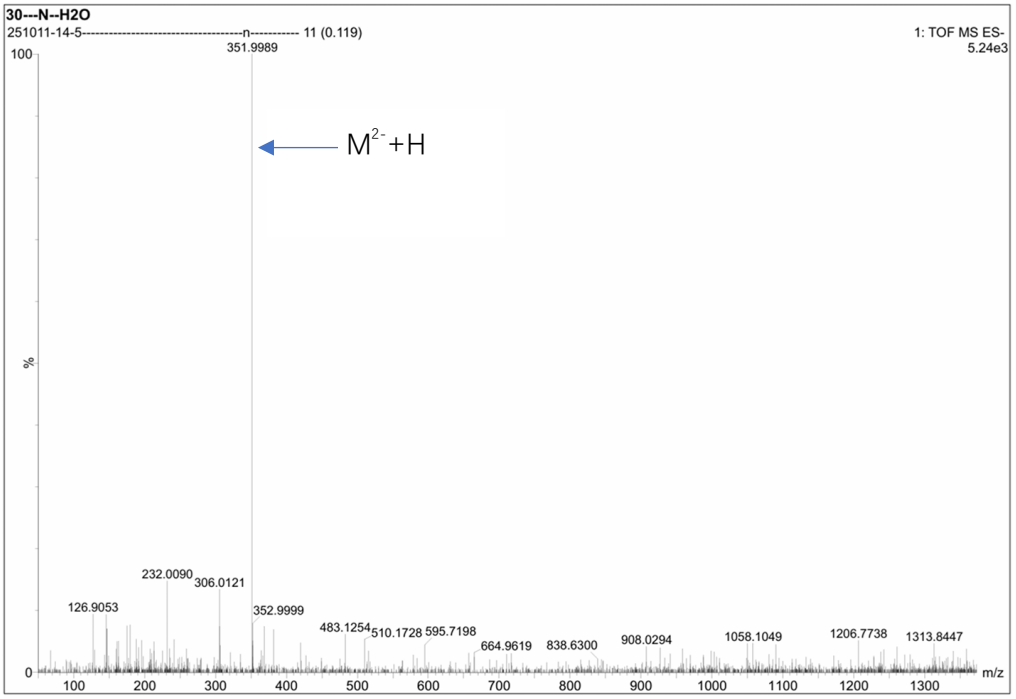
^{13}C NMR spectra in DMSO-d_6 for compound **5**



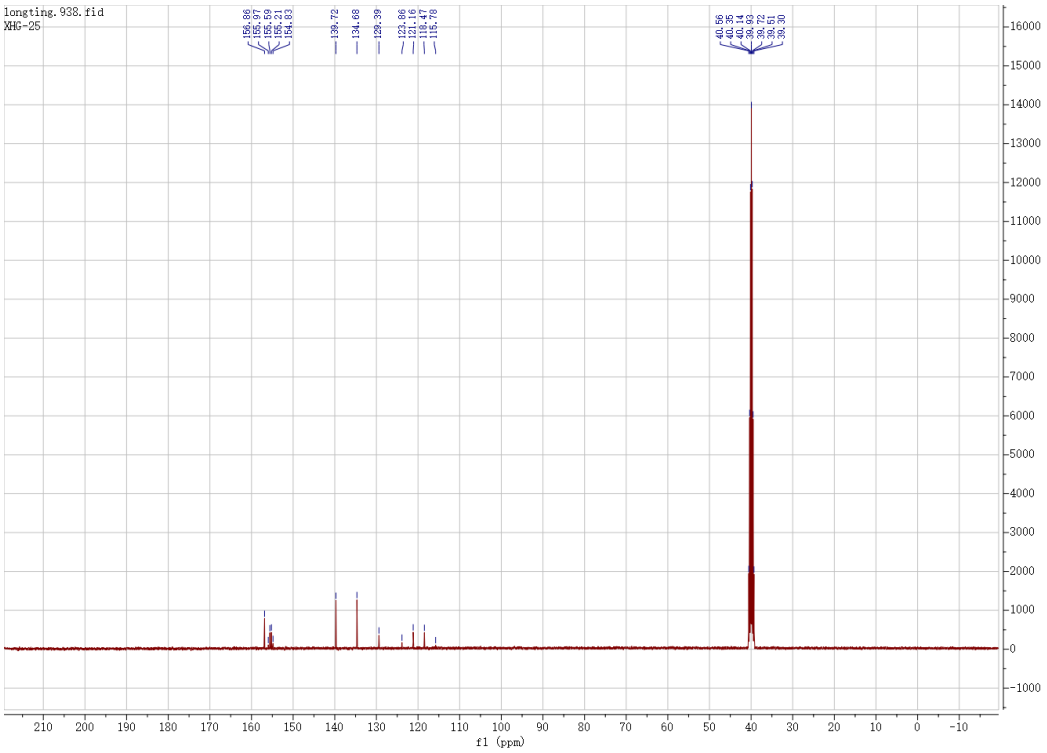
IR spectra for compound **5**



ESI-MS spectrum of **6**



^{13}C NMR spectra in DMSO-d_6 for compound **6**



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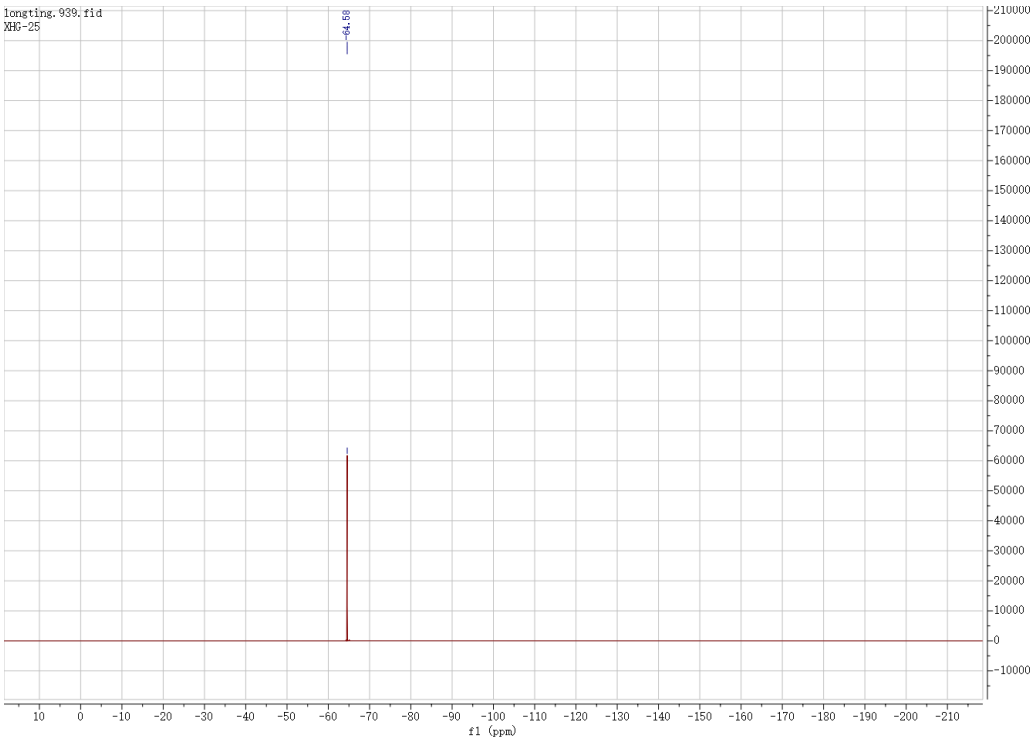
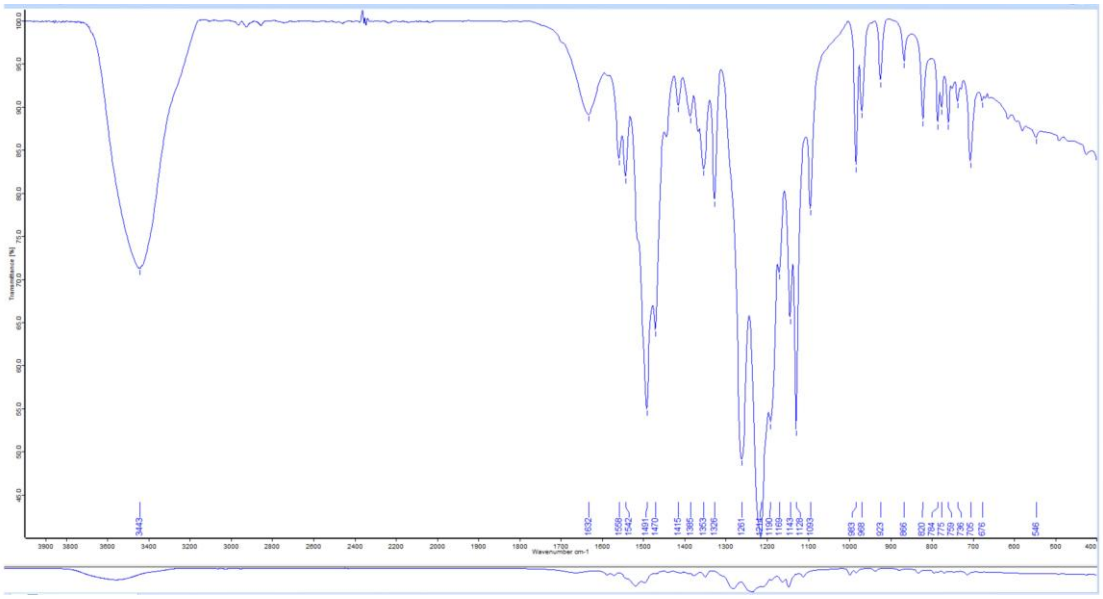
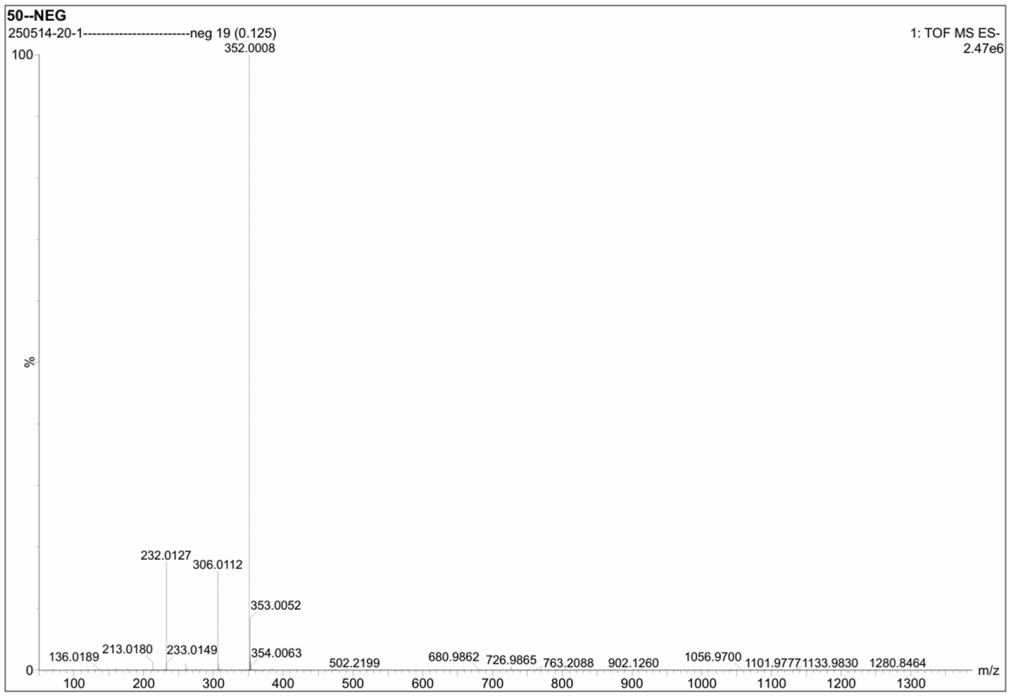
^{19}F NMR spectra in DMSO-d_6 for compound **6**



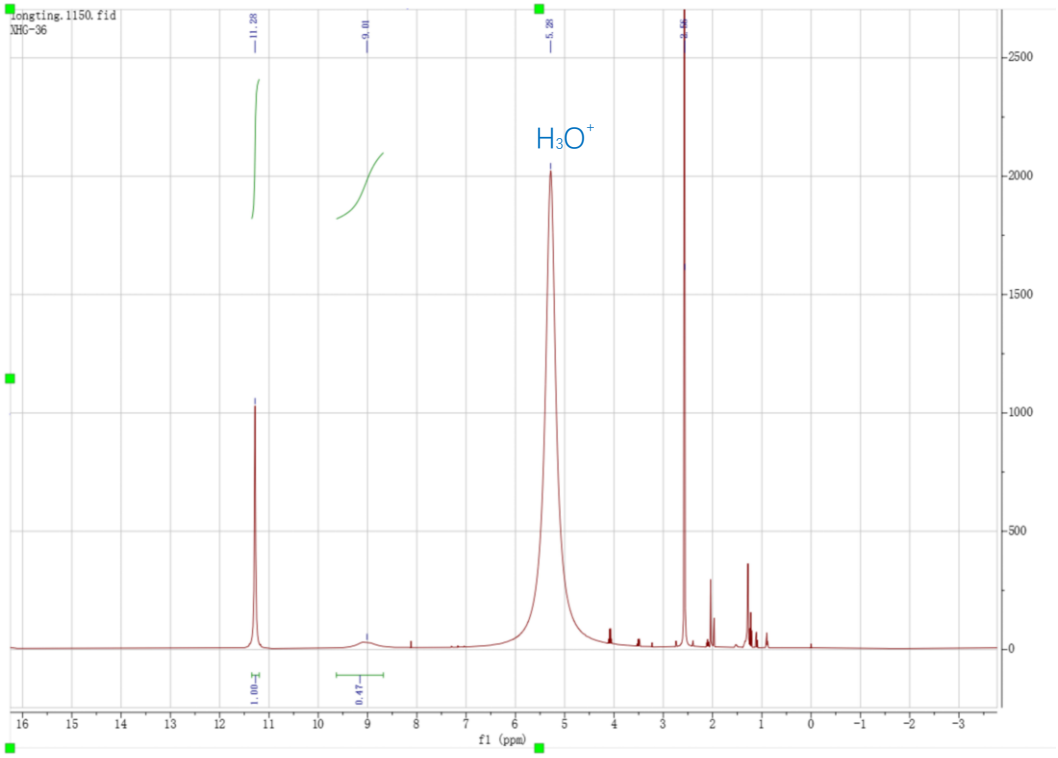
IR spectra for compound **6**



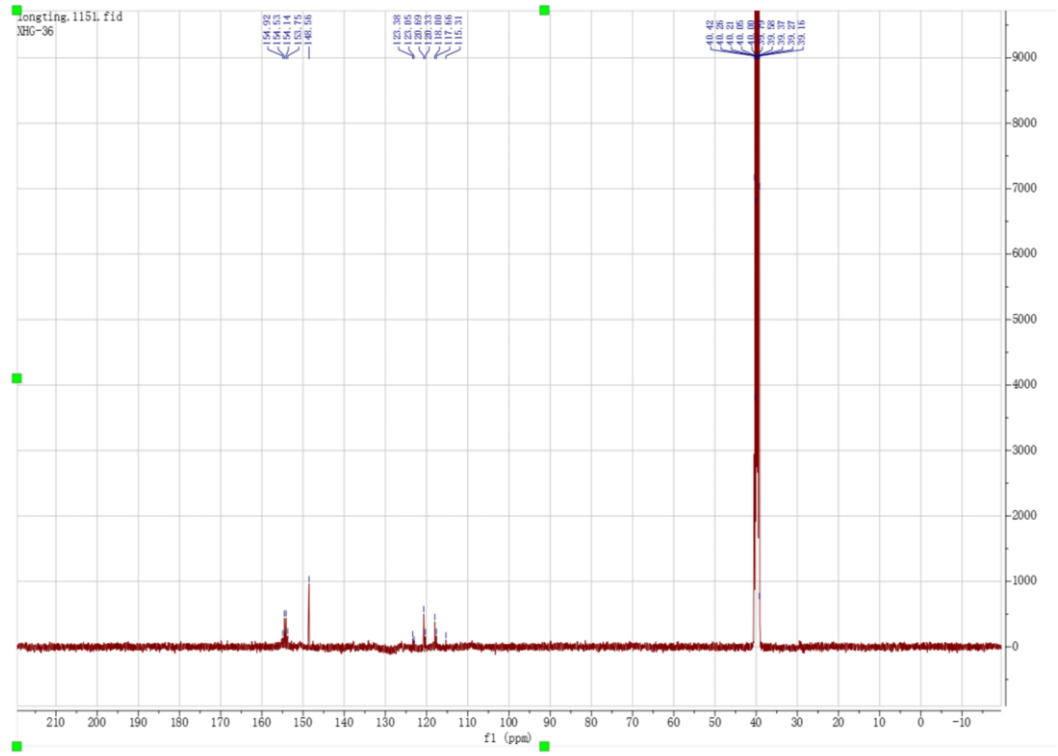
ESI-MS spectrum of **7**



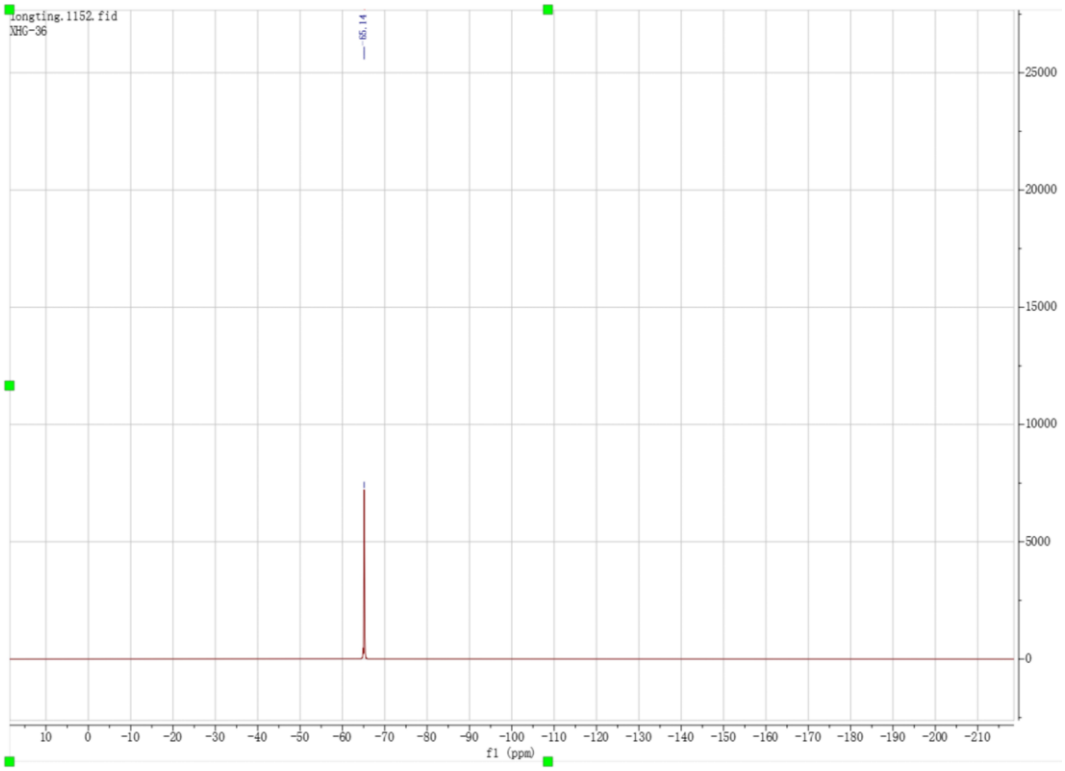
^{1}H NMR spectra in DMSO-d_6 for compound **7**



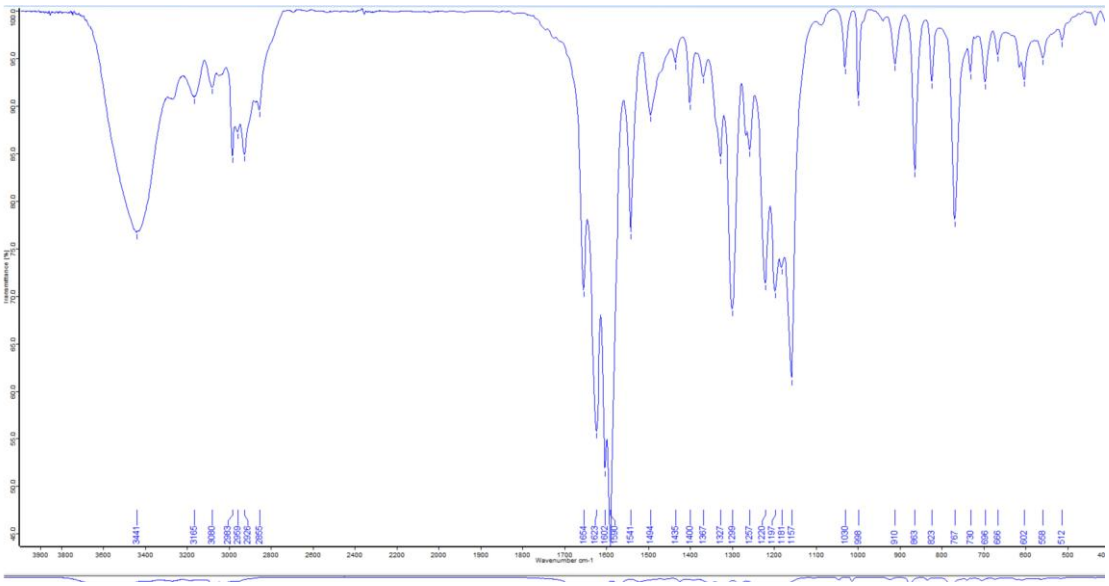
^{13}C NMR spectra in DMSO-d_6 for compound **7**



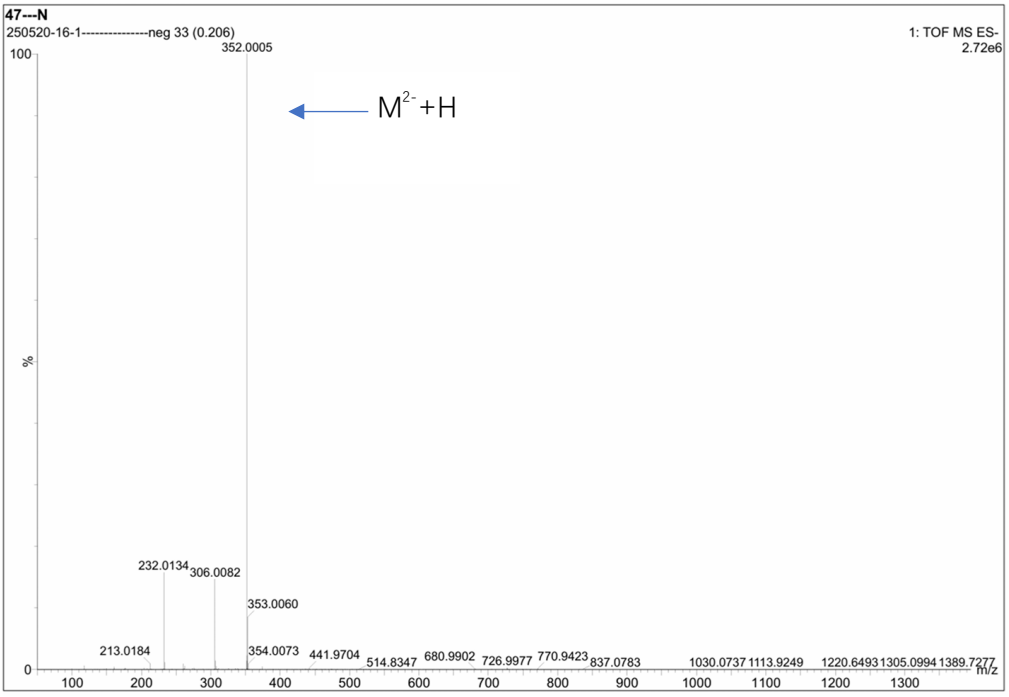
^{19}F NMR spectra in DMSO-d_6 for compound **7**



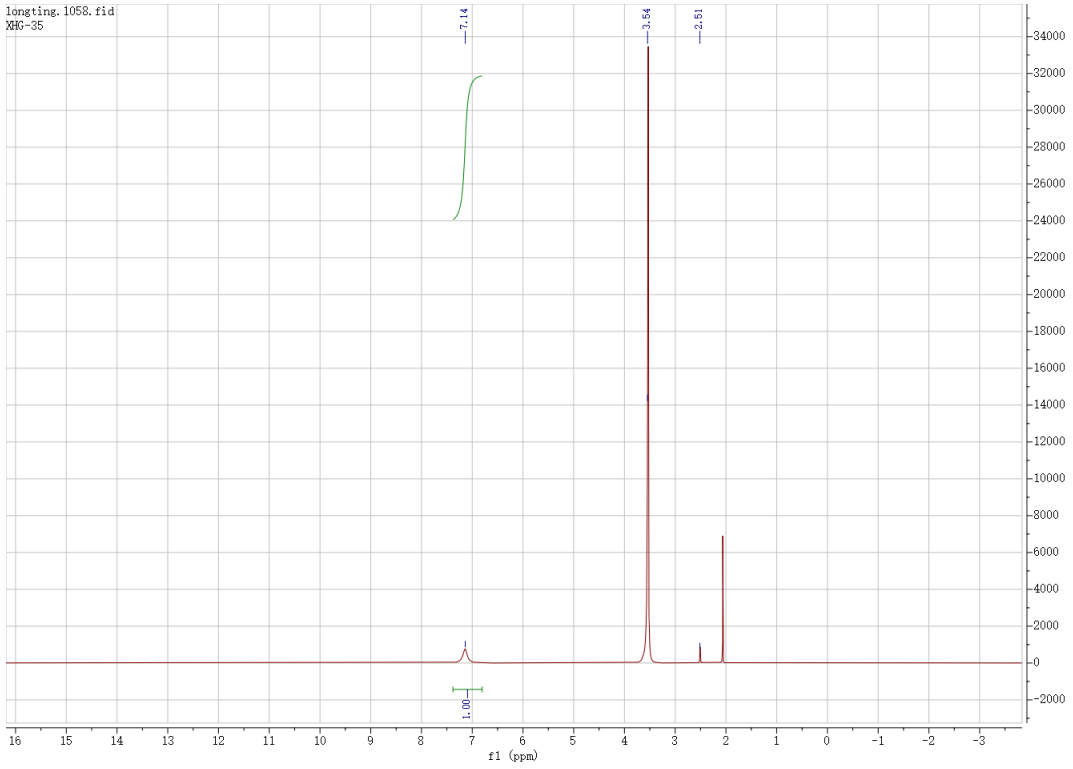
IR spectra for compound **7**



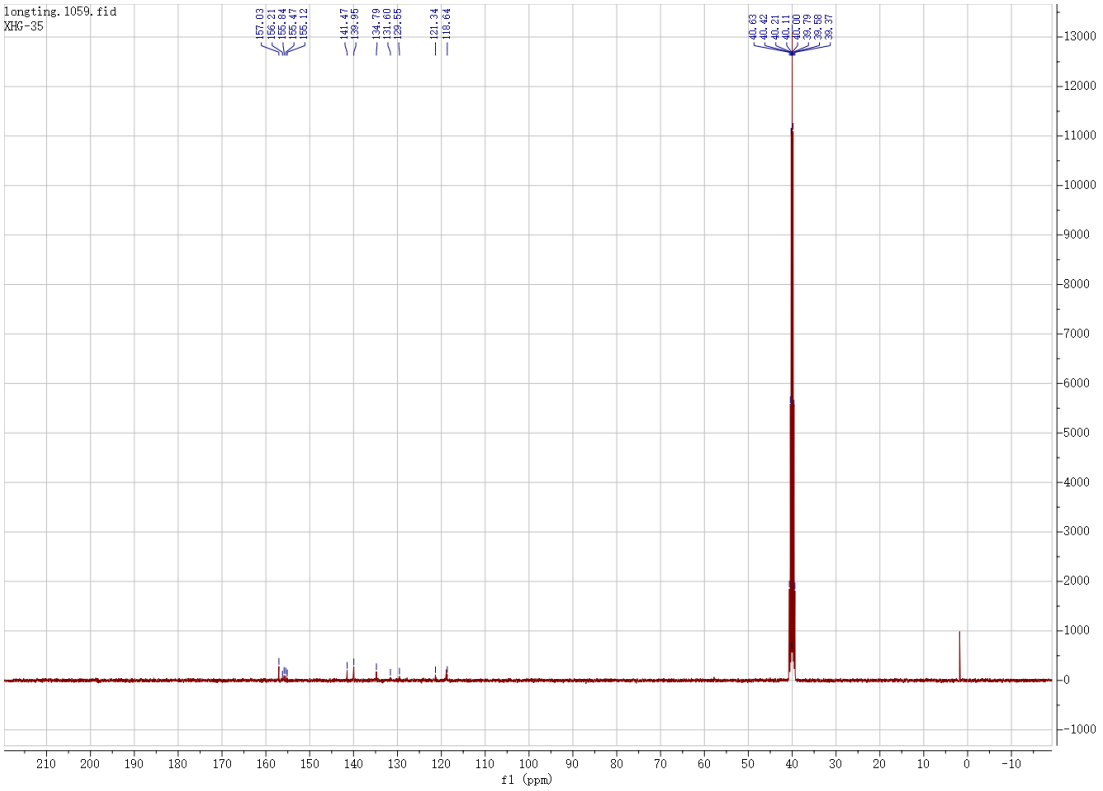
ESI-MS spectrum of **8**



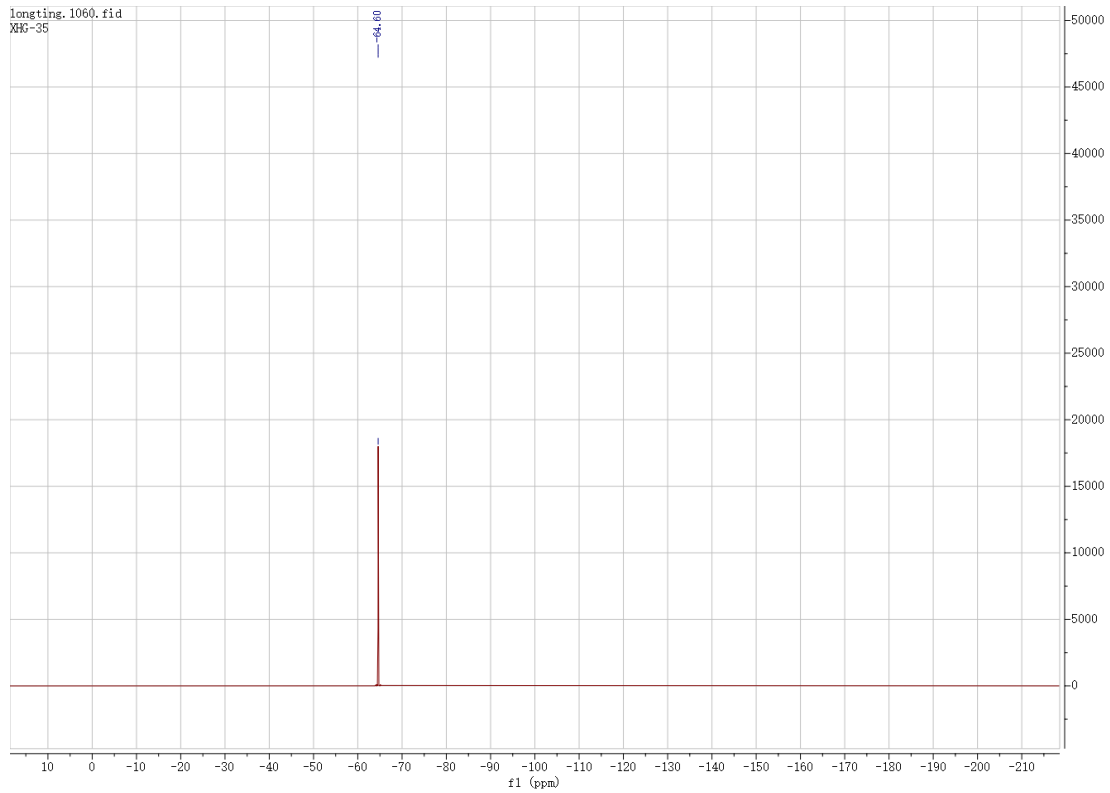
1H NMR spectra in DMSO-d_6 for compound **8**



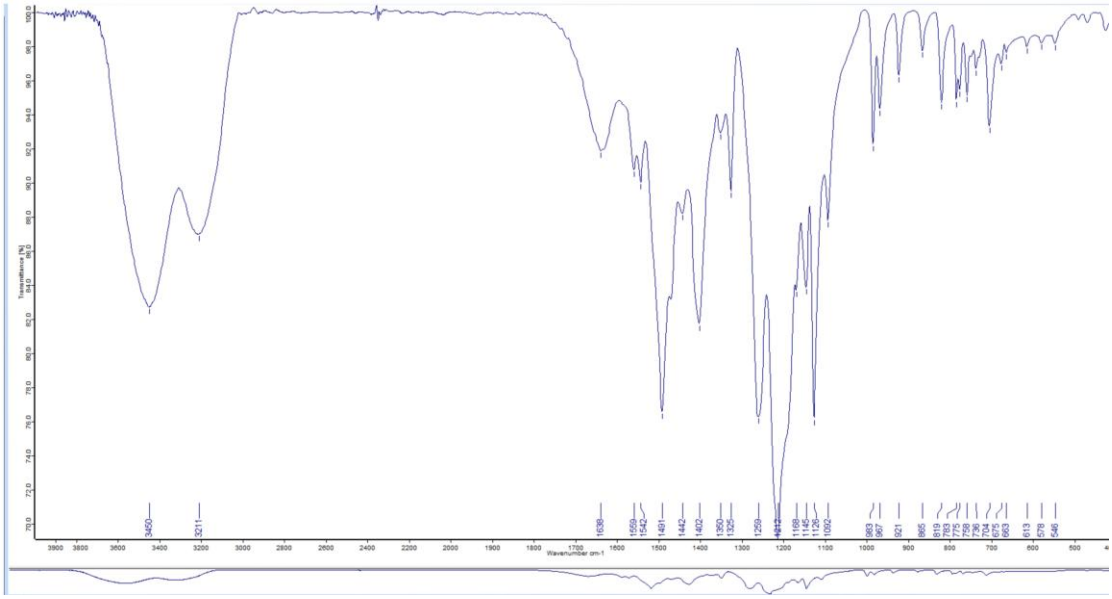
^{13}C NMR spectra in DMSO-d_6 for compound **8**



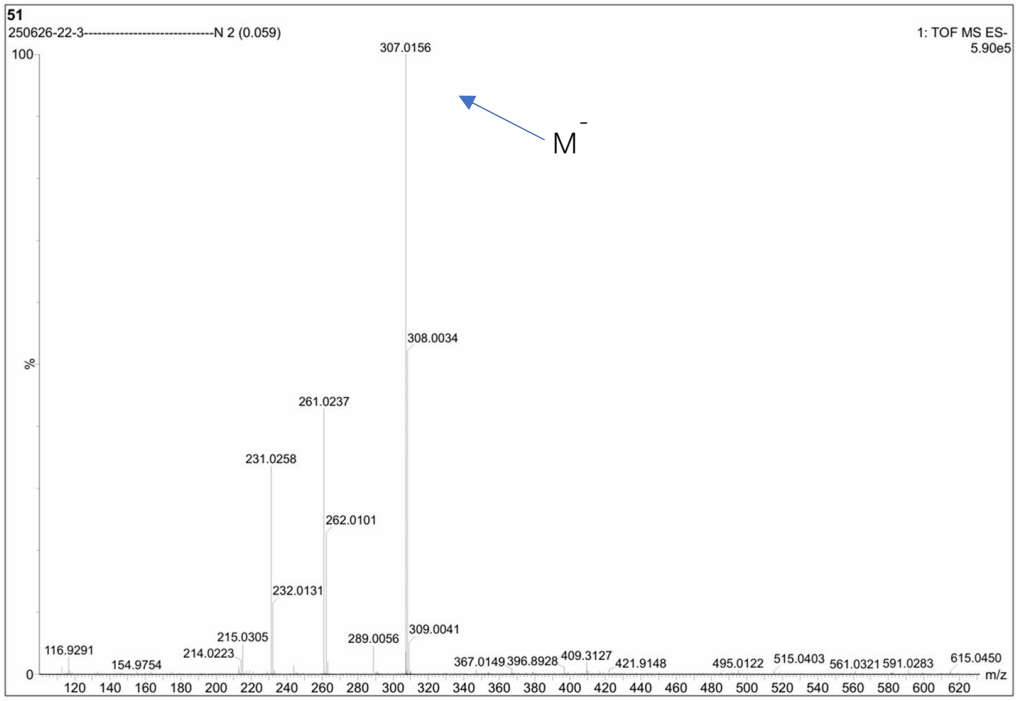
^{19}F NMR spectra in DMSO-d_6 for compound **8**



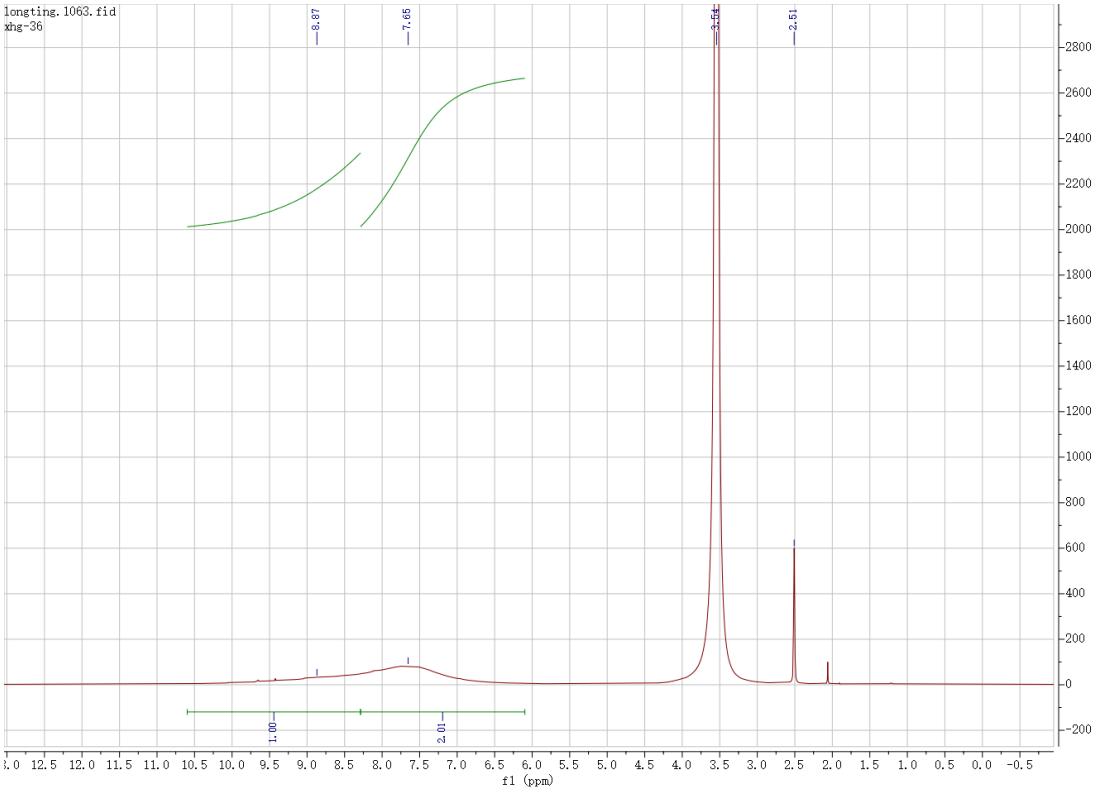
IR spectra for compound **8**



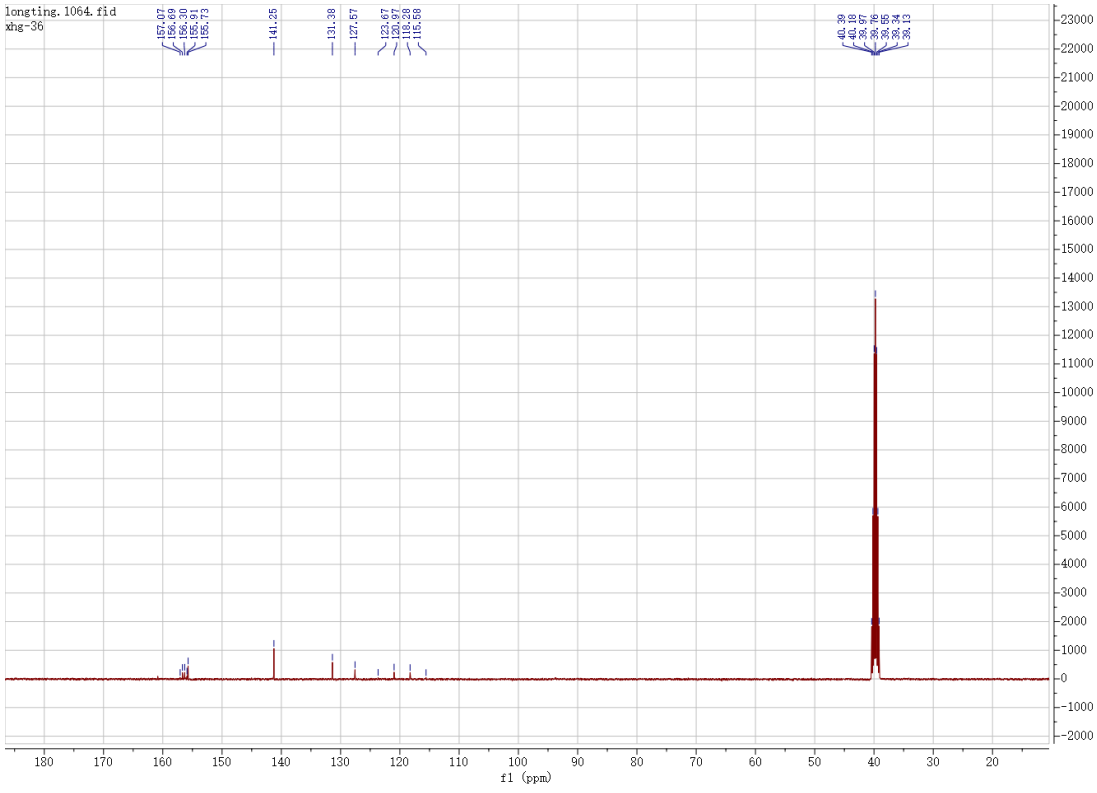
ESI-MS spectrum of **9**



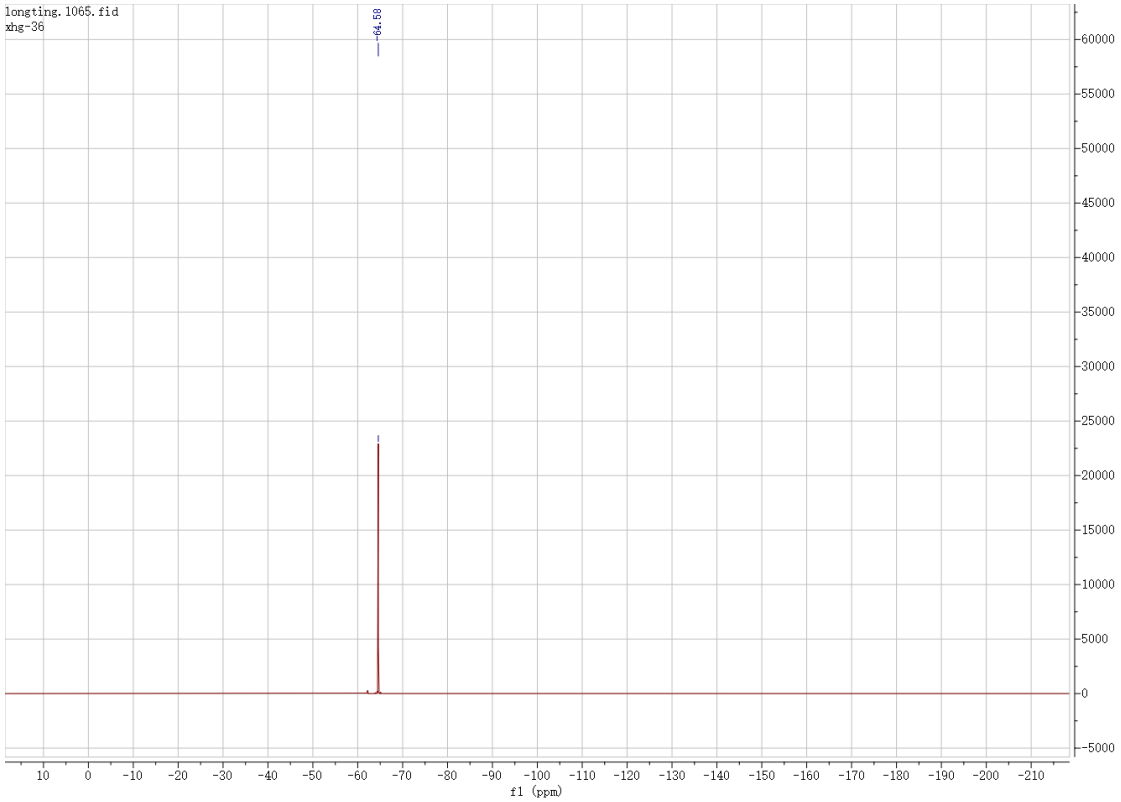
H NMR spectra in DMSO-d_6 for compound **9**



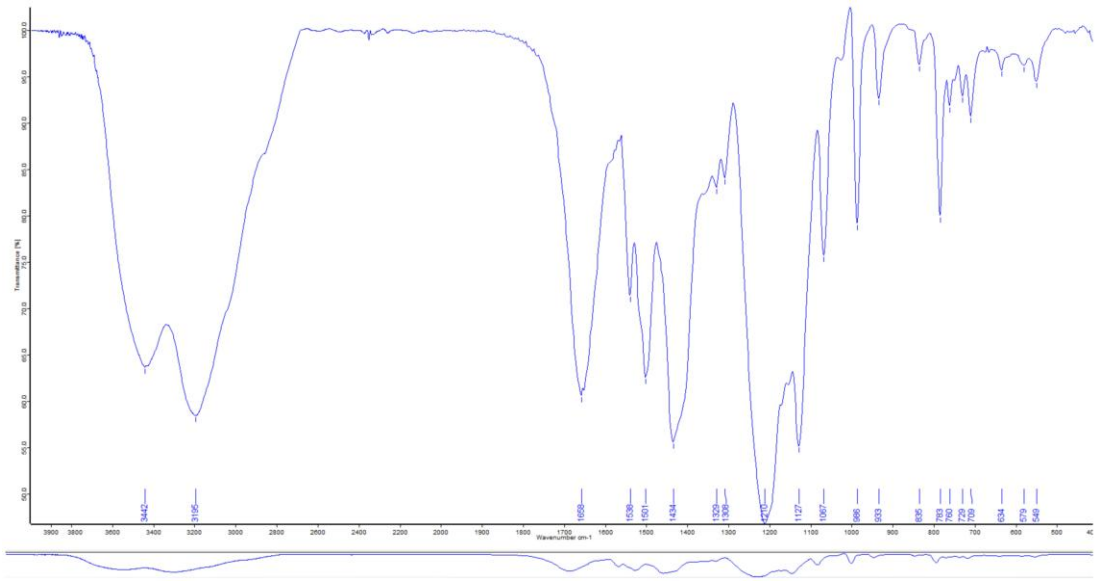
^{13}C NMR spectra in DMSO-d_6 for compound **9**



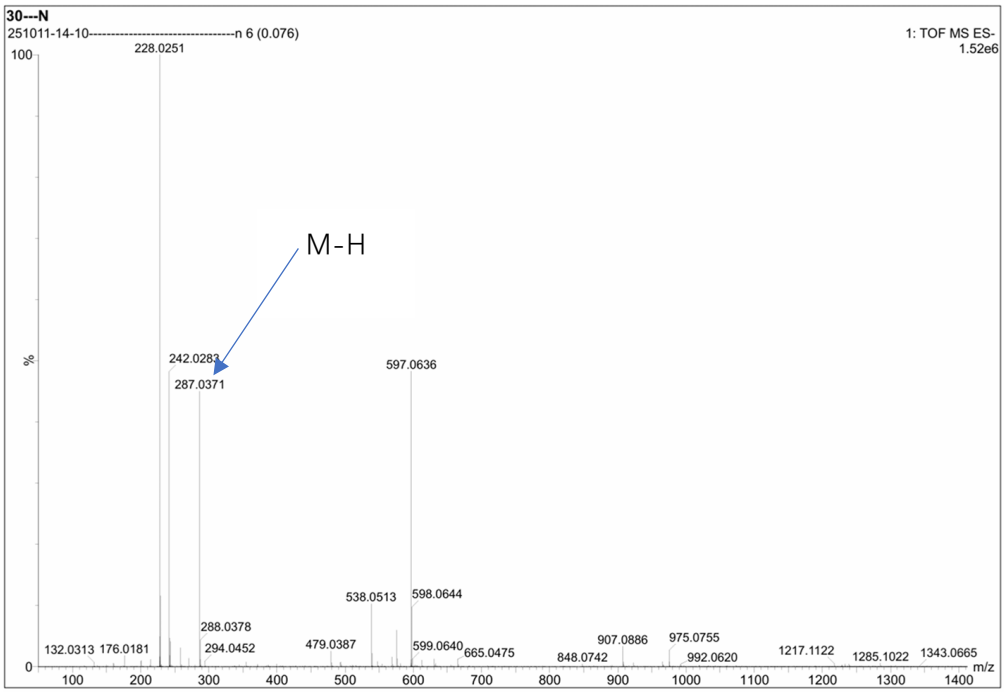
^{19}F NMR spectra in DMSO-d_6 for compound **9**



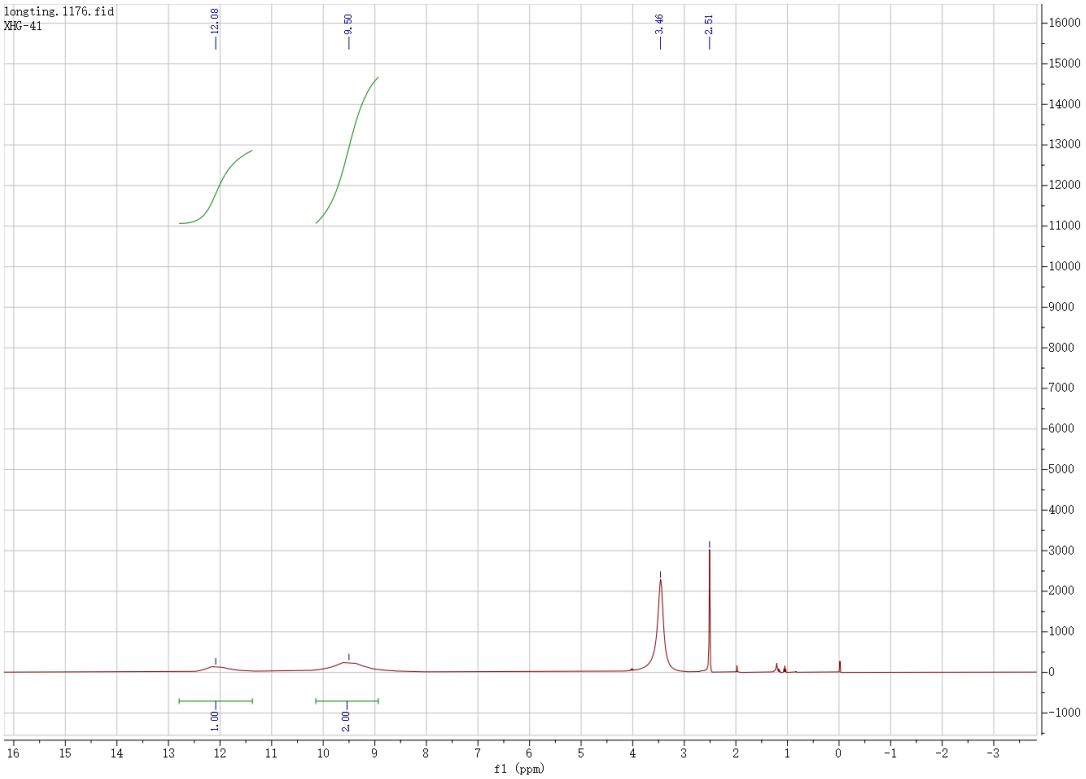
IR spectra for compound **9**



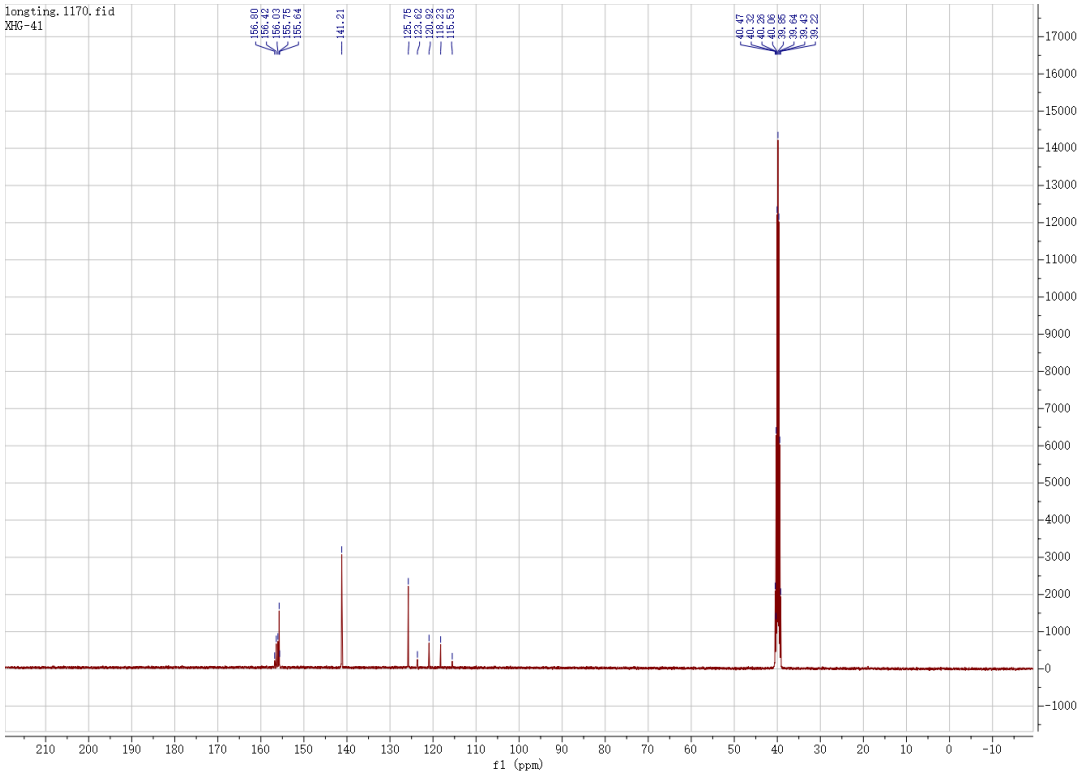
ESI-MS spectrum of **10**



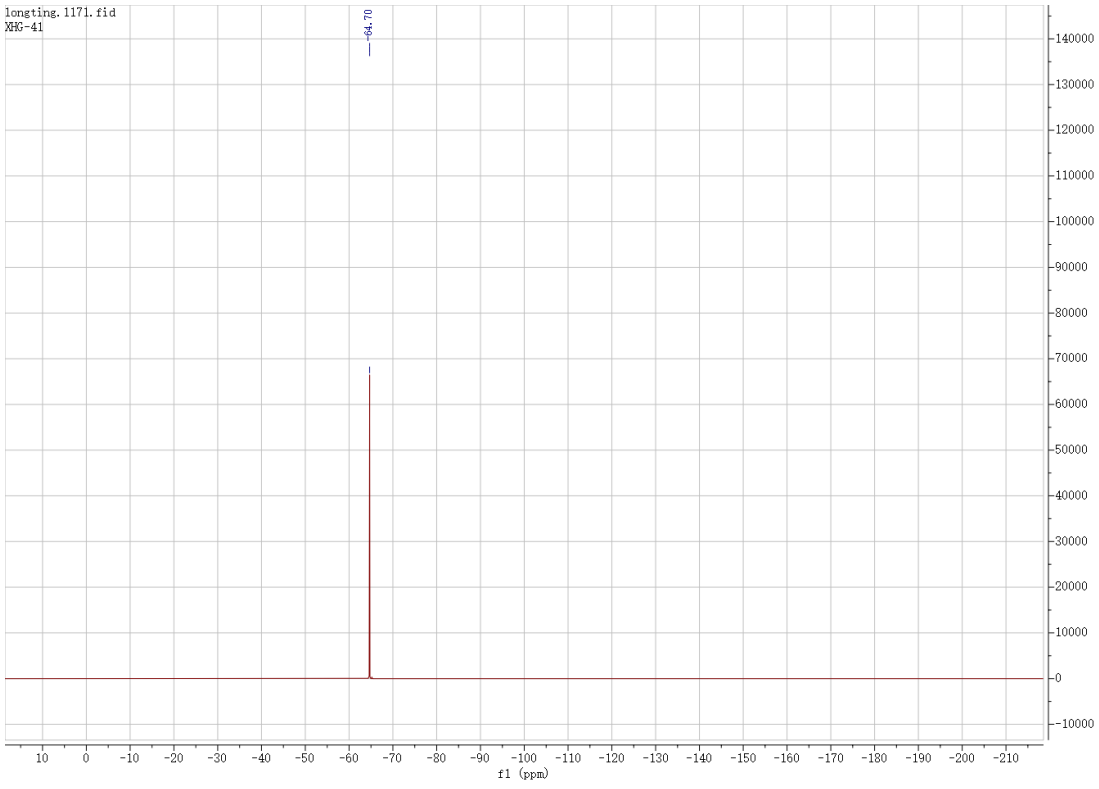
^{1}H NMR spectra in DMSO-d_6 for compound **10**



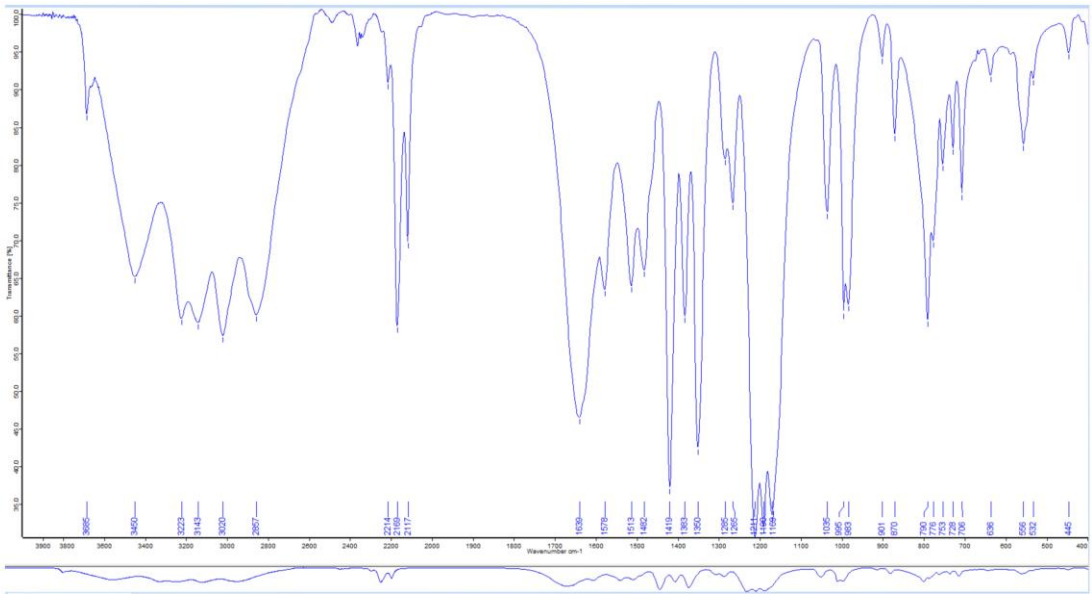
^{13}C NMR spectra in DMSO-d_6 for compound **10**



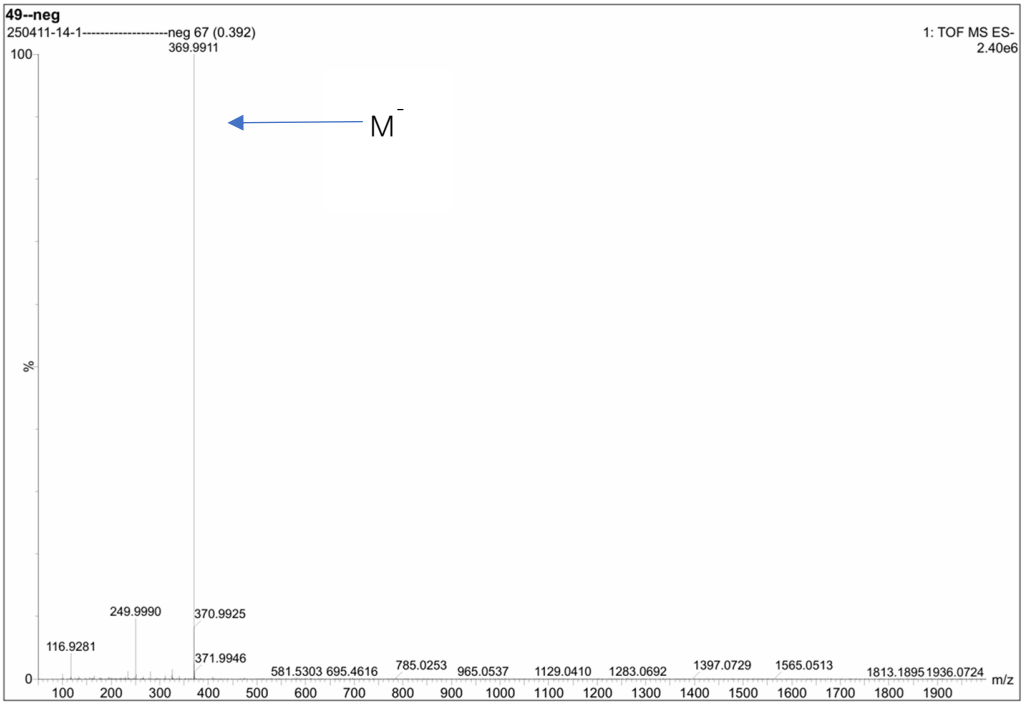
^{19}F NMR spectra in DMSO-d_6 for compound **10**



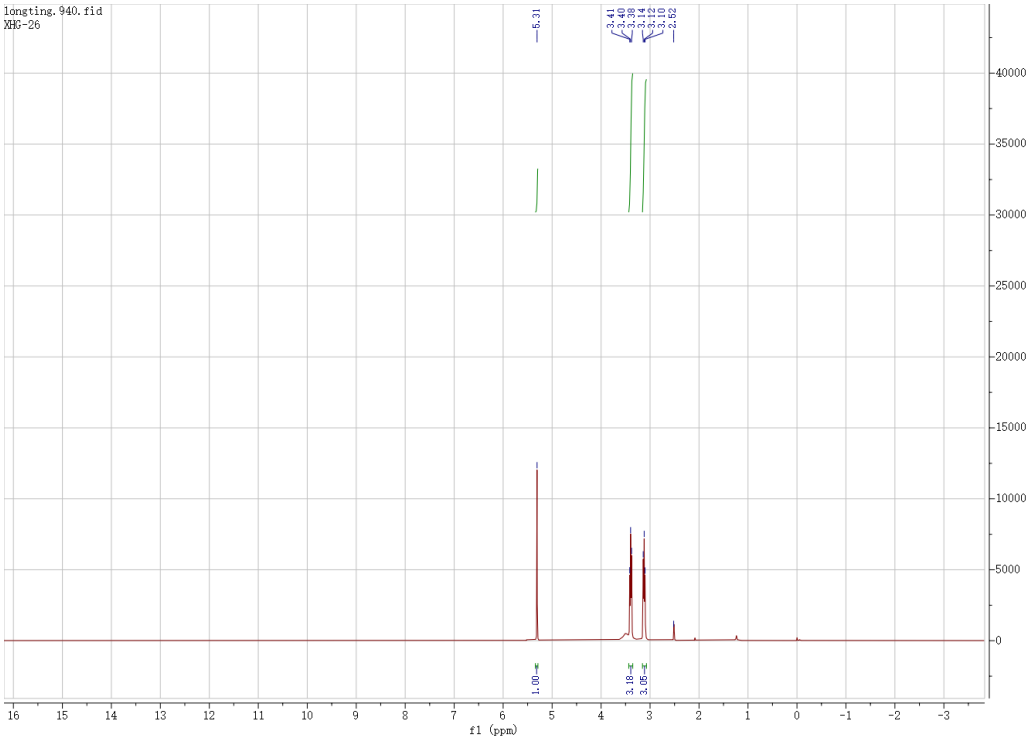
IR spectra for compound **10**



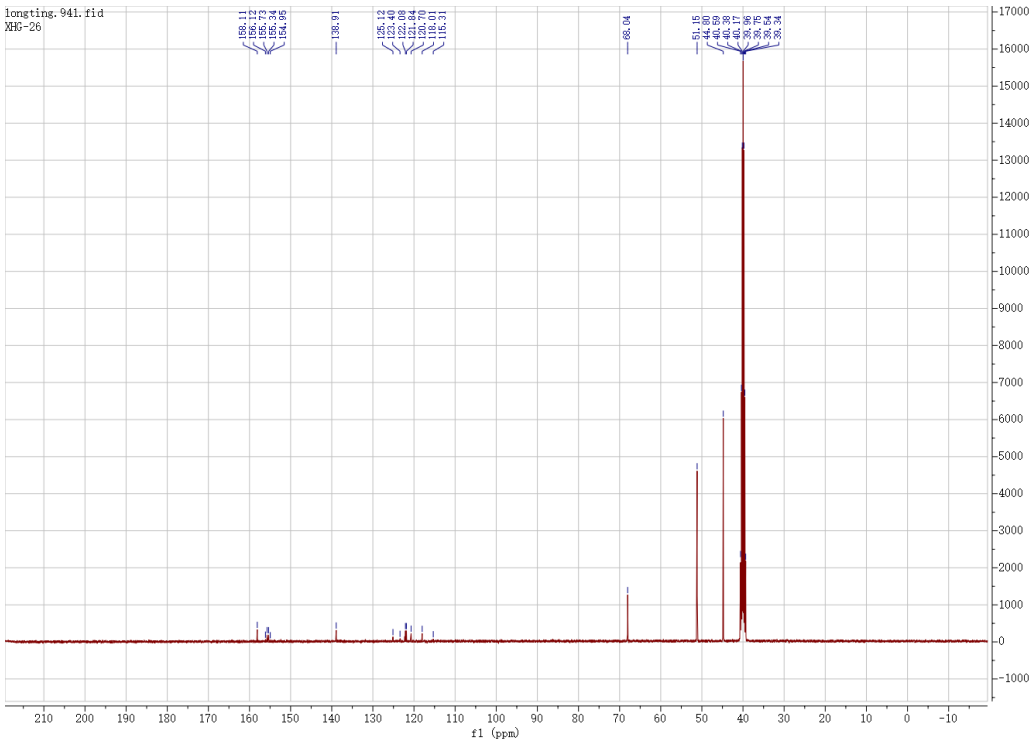
ESI-MS spectrum of **11**



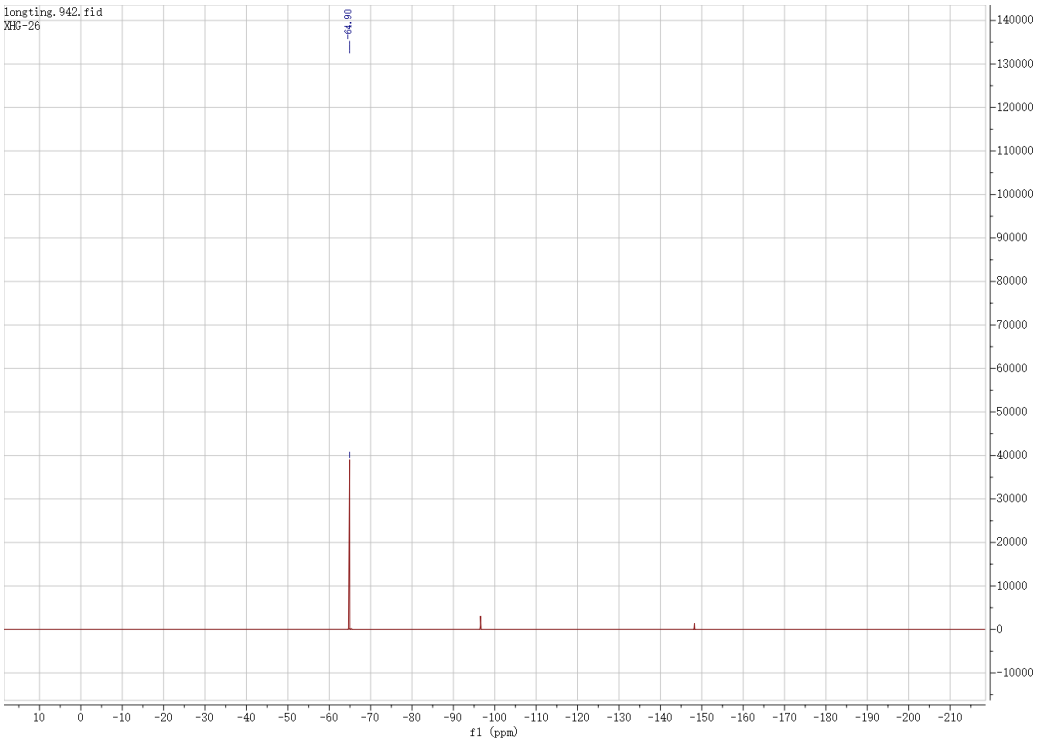
^{1}H NMR spectra in DMSO-d_6 for compound **11**



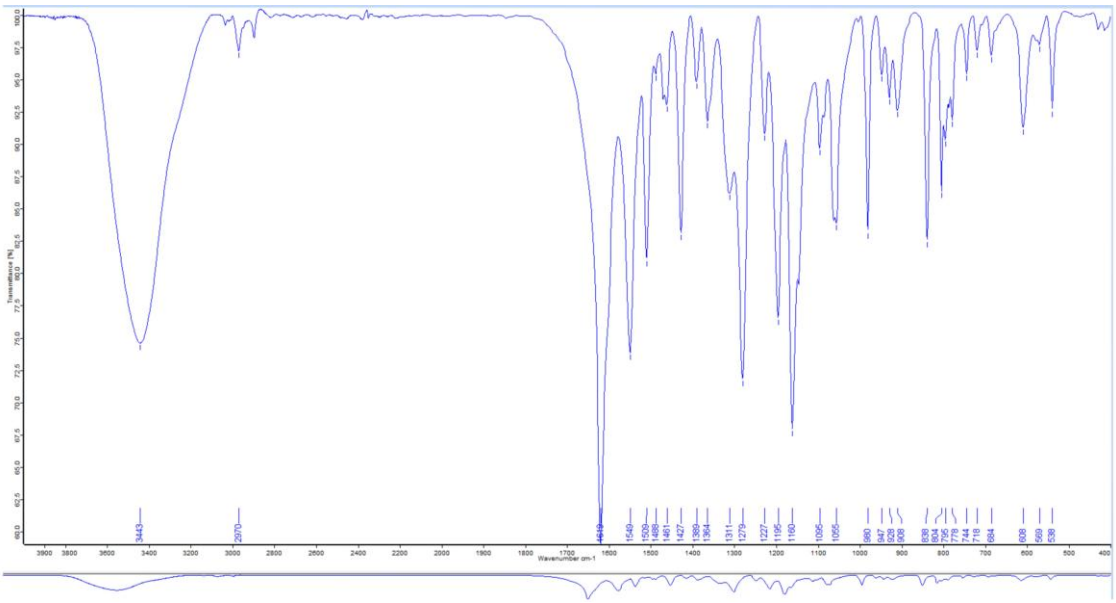
^{13}C NMR spectra in DMSO-d_6 for compound **11**



^{19}F NMR spectra in DMSO-d_6 for compound **11**



IR spectra for compound **11**



References

1. L. He, G.-H. Tao, D. A. Parrish and J. n. M. Shreeve, Inorganic Chemistry, 2011, 50, 679-685
2. R. Wang, H. Gao, C. Ye, B. Twamley and J. n. M. Shreeve, Inorganic chemistry, 2007, 46, 932-938.
3. H. D. B. Jenkins, D. Tudela and L. Glasser, Inorganic Chemistry, 2002, 41, 2364-2367.