Supporting Information(SI)

Constructing high-performance and insensitive energetic salts through increased hydrogen bonds

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Contents

1. Experiment data

General: The compounds in this work are energetic materials that could potentially explode under certain conditions (e.g., impact, friction, or electric discharge). Appropriate safety precautions, such as the use of shields in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves) should be taken at all times when handling these materials.

General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received. ^{1}H and ^{13}C NMR spectra are recorded on a 500 MHz (Bruker AVANCE 500) NMR spectrometer operating at 500 and 125 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter at a heating rate of 5 °C min^{-1}. IR spectra are recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities are determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.01).

3-amino-6-aminomethyl-1,2,4-triazin-5(4H)-one hydrochloride (1) was obtained according to the literature[1].

General procedure for the preparation of energetic salts 2–5

3-amino-6-aminomethyl-1,2,4-triazin-5(4H)-one hydrochloride (0.50 g, 2.82 mmol) was dissolved in a solution of water (15 mL) and followed by adding 1 equiv silver nitrate, silver perchlorate, silver nitro-formate or silver dinitramide. This suspension was stirred for 1 h and then filtered in the dark. The filtrate was concentrated to yield the product.

General procedure for the preparation of energetic salts 7−8

3-Amino-6-(aminomethyl)-1,2,4-triazin-5(4H)-one hydrochloride (0.50 g, 2.82 mmol) was dissolved in methanol (15 mL), followed by the addition of ammonium acetate (1.0 equiv.). The reaction mixture was heated to 90 °C and stirred for 1 h. After cooling to room temperature, the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to afford (3-amino-5-oxo-2,5-dihydro-1,2,4-triazin-6-yl)methanaminium acetate (**6**). Picric acid (PA) or 2,4,6-trinitrobenzene-1,3,5-triol (TNPG) was added to a solution of **6** (0.50 g, 2.49 mmol) in 15 mL of water. The mixtures were continuously stirred for 15 min at 50 °C . The salts **7** and **8** were precipitated from water after the solution was cooled to room temperature and obtained by filtration.

(3-amino-5-oxo-2,5- dihydro-1,2,4-triazin-6-yl)methanaminium perchlorate (2).

Yield: 0.55 g, 81%, Colorless solid. ^{1}H NMR (500 MHz, DMSO-*d₆*): δ = 12.53 (s, 1H), 8.08 (s, 2H), 7.04 (s, 2H), 3.87 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-*d₆*): δ = 162.77, 157.00, 142.13, 38.61 ppm; IR (KBr): ṽ = 3446, 3343, 3234, 1653, 1626, 1566, 1521, 1482, 1426, 1407, 1142, 1053, 890, 774, 618, 573 cm^{-1}; Elemental analysis for $C_4H_8ClN_5O_5$ (241.59): C 19.89, H 3.34, Cl 14.67, N 28.99 %; found: C 20.01, H 3.28, Cl 14.85, N 29.08 %.

(3-amino-5-oxo-2,5- dihydro-1,2,4-triazin-6-yl)methanaminium nitrate (3).

Yield: 0.48 g, 84%, Colorless solid. ^{1}H NMR (500 MHz, DMSO-d6): δ = 12.68 (s, 1H), 8.35 (s, 2H), 8.19 (s, 2H), 3.96 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d6): δ = 156.41, 153.43, 143.77, 37.89 ppm; IR (KBr): ṽ = 2972, 1736, 1691, 1536, 1397, 1269, 1202, 1085, 1042, 1030, 882, 820, 779, 742 cm^{-1}; Elemental analysis for $C_4H_8N_6O_4$ (204.15): C 23.53, H 3.95, N 41.17 %; found: C 24.02, H 3.87, N 41.03 %.

(3-amino-5-oxo-2,5- dihydro-1,2,4-triazin-6-yl)methanaminium nitroformate (4).

Yield: 0.60 g, 73%, yellowish solid. ^{1}H NMR (500 MHz, D_2O): δ = 7.96 (s, 2H), 6.77 (s, 2H), 4.05 (s, 1H), 4.01 (s, 2H) ppm; ^{13}C NMR (125 MHz, D_2O-d6): δ = 164.27, 156.58, 141.03, 139.12, 38.06, 37.39 ppm; IR (KBr): ṽ = 3359, 3314, 3181, 2845, 2630, 2115, 1651, 1537, 1435, 1379, 1357, 1293, 1230, 1136, 1032, 977, 797, 757, 682, 599 cm^{-1}; Elemental analysis for $C_5H_8N_8O_7$ (292.17): C 20.55, H 2.76, N 38.35 %; found: C 20.22, H 2.84, N 38.10 %.

(3-amino-5-oxo-2,5- dihydro-1,2,4-triazin-6-yl)methanaminium dinitramide (5).

Yield: 0.53 g, 76%, yellowish solid. ^{1}H NMR (500 MHz, DMSO-d6): δ = 8.11 (s, 2H), 7.07 (s, 2H), 3.89 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d6): δ = 155.43, 153.73, 144.00, 37.57 ppm; IR (KBr): ṽ = 3359, 3314, 3182, 2846, 2631, 1650, 1568, 1537, 1474, 1444, 1379, 1294, 1230, 1136, 1033, 978, 824, 798, 758 cm^{-1}; Elemental analysis for $C_4H_8N_8O_5$ (248.16): C 19.36, H 3.25, N 45.15 %; found: C 19.52, H 3.17, N 45.27 %.

(3-amino-5-oxo-2,5- dihydro-1,2,4-triazin-6-yl)methanaminium picrate (7).

Yield: 0.75 g, 82%, yellowish solid. ^{1}H NMR (500 MHz, DMSO-d6): δ = 8.60 (s, 1H), 8.10 (s, 2H), 7.07 (s, 2H), 3.88 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d6): δ = 162.49, 161.31, 156.94, 142.25, 142.16, 125.73, 124.80, 38.64 ppm; IR (KBr): ṽ = 3100, 2879, 1708, 1684, 1568, 1525, 1488, 1445, 1320, 1251, 1202, 1160, 1102, 1019, 992, 898, 789, 771 cm^{-1}; Elemental analysis for $C_{10}H_{10}N_8O_8$ (370.24): C 32.44, H 2.72, N 30.27 %; found: C 32.17, H 2.84, N 30.89 %.

(3-amino-5-oxo-2,5-dihydro-1,2,4-triazin-6-yl)methanaminium trinitrophloroglucinate (8).

Yield: 0.74 g, 74%, yellowish solid. ^{1}H NMR (500 MHz, DMSO-d6): δ = 8.09 (s, 2H), 7.06 (s, 2H), 3.87 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d6): δ = 162.58, 156.98, 154.76, 142.15, 38.64 ppm; IR (KBr): ṽ = 3302, 3080, 1677, 1645, 1574, 1553, 1442, 1427, 1362, 1330, 1245, 1154, 1114, 1064, 1018, 981, 940, 868, 789, 778, 745 cm^{-1}; Elemental analysis for $C_{10}H_{10}N_8O_{10}$ (402.24): C 29.86, H 2.51, N 27.86 %; found: C 30.08, H 2.48, N 27.43 %.

2. Crystallographic data

The data for **2,** and **6** were collected with a Bruker D8 VENTURE CCD diffractometer with graphite-monochromated Mo-Ka radiation (λ=0.71073 nm) at 223K or 193 K. The data for **3,** and **4** was collected with a Bruker D8 VENTURE CCD diffractometer with graphite-monochromated Cu-Ka radiation (λ=1.54178 nm) at 223 K or 213K. The data collection and the initial unit cell refinement are performed by using APEX2 (v2010.3-0). Data Reduction is performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections are applied by using the SADABS (v2008/1) program. The structures are solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands are included using a riding model. The crystallographic data and CCDC numbers for these compounds are summarized in Table S1.

Table S1. Crystallographic data for **2**, **3**, **4** and **6.**

Compound	2	3	4	6
CCDC No.	2444771	2444776	2444777	2444772
Empirical Formula	$C_4H_8ClN_5O_5$	$C_4H_8N_6O_4$	$C_5H_8N_8O_7$	$C_6H_{11}N_5O_3$
Formula weight	241.60	204.16	292.19	201.20
Temperature (K)	223.0	223.0	213.0	193.0
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	*Pbca*	$P2_1/n$	$P2_1/n$
a/Å	7.8315(3)	9.9288(4)	7.3547(2)	11.5773(8)
***b*/Å**	8.8391(3)	6.5054(3)	17.5020(4)	6.4537(5)
c/Å	12.7423(5)	24.7500(10)	8.7636(2)	12.6350(9)
α/ °	90	90	90	90
β/ °	92.950(2)	90	109.7340(10)	117.101(2)
γ/ °	90	90	90	90
Volume (Å^3)	880.90(6)	1598.62(12)	1061.82(5)	840.39(11)
Z	4	8	4	4
Density (g cm^{-3})	1.822	1.697	1.828	1.590
μ (mm^{-1})	0.449	1.311	1.494	0.129
F (000)	496.0	848.0	600.0	424
Crystal Size (mm^3)	0.11 × 0.11 × 0.14	0.13 × 0.12 × 0.11	0.15 × 0.12 × 0.11	0.11 × 0.12 × 0.13
Wavelength (Å)	0.71073	1.54178	1.54178	0.71073
2θ range for data collection (°)	5.208 to 54.958	7.144 to 136.924	10.108 to 136.438	3.962 to 55.016

Index ranges	-10≤ h≤ 10, -9 ≤ k ≤ 11, -16 ≤ l ≤ 16	-11≤ h≤ 9, -7 ≤ k ≤ 6, -28 ≤ l ≤ 29	-8 ≤ h ≤ 8, -21 ≤ k ≤ 21, -10 ≤ l ≤ 10	-15≤ h≤ 15, -8 ≤ k ≤ 8, -14 ≤ l ≤ 16
Reflections collected	12120	9854	12759	9437
Independent reflections	2016 [R_{int} = 0.0526, R_{sigma}= 0.0328]	1444 [R_{int} = 0.0535, R_{sigma}= 0.0360]	1925 [R_{int} = 0.0299, R_{sigma} = 0.0199	1944 [R_{int} = 0.0781, R_{sigma} = 0.0549]
Data/restraints/parameters	2016/0/141	1444/0/128	1925/1/183	1944/0/129
Goodness-of-fit on F^2	1.071	1.087	1.076	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 =0.0927	R_1 = 0.0444, wR_2 =0.1202	R_1 = 0.0311, wR_2 =0.0833	R_1 = 0.0565, wR_2 =0.1345
Final R indexes [all data]	R_1 = 0.0446, wR_2 = 0.1005	R_1 = 0.0506, wR_2 = 0.1246	R_1 = 0.0327, wR_2 = 0.0840	R_1 = 0.0821, wR_2 = 0.1657
Largest diff. peak/hole/e Å^{-3}	0.34/-0.45	0.21/-0.20	0.48/-0.44	0.41/-0.33

Table S2. Bond lengths [Å] and angles [°] for **2**.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
Cl1-O2	1.4296(19)	N5-C4	1.333(3)
Cl1-O3	1.4420(17)	N1-H1D	0.9000
Cl1O4	1.407(2)	N1-H1C	0.9000
Cl1-O5	1.4309(17)	N1-H1E	0.9000
O1-C3	1.247(2)	N3-H3	0.80(3)
N1-C1	1.480(2)	N5-H5A	0.8700
N2-N3	1.354(2)	N5-H5B	0.8700
N2-C2	1.286(2)	C1-C2	1.496(2)
N3-C4	1.347(3)	C2-C3	1.476(2)
N4-C4	1.328(2)	C1-H1A	0.9800
N4-C3	1.353(2)	C1-H1B	0.9800

Parameter	Bond angles [°]	**Parameter**	**Bond angles [°]**
O2-Cl1-O5	108.99(11)	C4-N5-H5B	120.00
O3-Cl1-O4	110.50(12)	H5A-N5-H5B	120.00
O3-Cl1-O5	107.88(10)	N1-C1-C2	111.10(14)
O4-Cl1-O5	110.72(12)	N2-C2-C3	122.33(15)
O2-Cl1-O3	109.50(11)	C1-C2-C3	120.01(15)

O2-Cl1-O4	109.22(12)	N2-C2-C1	117.65(15)
N3-N2-C2	116.26(15)	N4-C3-C2	118.21(15)
N2-N3-C4	123.34(16)	O1-C3-N4	121.68(16)
C3-N4-C4	117.34(16)	O1-C3-C2	120.11(15)
H1D-N1-H1E	109.00	N3-C4-N5	117.27(16)
C1-N1-H1C	109.00	N4-C4-N5	120.21(17)
H1C-N1-H1E	109.00	N3-C4-N4	122.52(17)
C1-N1-H1D	109.00	H1A-C1-H1B	108.00
C1-N1-H1E	109.00	N1-C1-H1A	109.00
H1C-N1-H1D	109.00	N1-C1-H1B	109.00
C4-N3-H3	119.9(19)	C2-C1-H1A	109.00
N2-N3-H3	116.4(19)	C2-C1-H1B	109.00
C4-N5H5A	120.00		

Table S3. Hydrogen bonds present in **2**.

D-H···A	**d(D-H)/Å**	**d(H···A)/Å**	**d(D···A)/Å**	**<(DHA)/°**
N1-H1C···O1	0.9000	1.9700	2.855(2)	169.00
N1-H1D···O1	0.9000	2.1000	2.951(2)	157.00
N1-H1E···O3	0.9000	2.3000	3.106(2)	149.00
N1-H1E···O5	0.9000	2.5800	2.875(2)	100.00
N3-H3···O3	0.80(3)	2.17(3)	2.968(2)	176(2)
N3-H3···O5	0.80(3)	2.57(3)	3.069(2)	122(3)
N5-H5A···O2	0.8700	2.0300	2.897(2)	175.00
N5-H5B···O4	0.8700	2.1400	2.938(3)	152.00
C1-H1B···O2	0.9800	2.4000	3.298(3)	152.00

Table S4. Torsion angles of compound **2**.

parameter	**Å**	**parameter**	**Å**
C2-N2-N3-C4	0.4(3)	C4-N4-C3-C2	-0.6(2)
N3-N2-C2-C3	-0.8(2)	C4-N4-C3-O1	178.74(16)
N3-N2-C2-C1	177.58(14)	N1-C1-C2-C3	177.85(14)
N2-N3-C4-N5	-179.41(16)	N1-C1-C2-N2	-0.6(2)
N2-N3-C4-N4	-0.1(3)	C1-C2-C3-N4	-177.41(15)
C3-N4-C4-N5	179.51(16)	N2-C2-C3-O1	-178.38(16)
C3-N4-C4-N3	0.2(2)	N2-C2-C3-N4	1.0(2)
C1-C2-C3-O1	3.2(2)		

Table S5. Bond lengths [Å] and angles [°] for **3**.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
O1-C2	1.248(2)	N1-H1B	0.8700
O2-N6	1.252(2)	N1-H1A	0.8700
O3-N6	1.258(2)	N3-H3	0.8700
O4-N6	1.236(2)	N5-H5C	0.9000
N1-C1	1.315(3)	N5-H5B	0.9000
N2-C1	1.339(2)	N5-H5A	0.9000
N2-C2	1.347(2)	C2-C3	1.474(3)
N3-C1	1.357(2)	C3-C4	1.500(3)
N3 -N4	1.354(2)	C4-H4A	0.9800
N4-C3	1.286(2)	C4-H4B	0.9800
N5-C4	1.469(3)		

Parameter	Bond angles [°]	**Parameter**	**Bond angles [°]**
C1-N2-C2	118.08(16)	O2-N6-O3	119.61(17)
N4-N3-C1	123.74(16)	N1-C1-N3	117.75(17)
N3-N4-C3	116.48(16)	N1-C1-N2	121.10(17)
C1-N1-H1A	120.00	N2-C1-N3	121.15(17)
C1-N1-H1B	120.00	O1-C2-N2	121.68(18)
H1A-N1 -H1B	120.00	N2-C2-C3	118.43(17)
C1-N3 -H3	118.00	O1-C2-C3	119.90(18)
N4-N3-H3	118.00	C2-C3-C4	118.50(17)
C4-N5-H5B	109.00	N4-C3-C4	119.38(17)
C4-N5-H5C	109.00	N4-C3-C2	122.13(18)
C4-N5-H5A	109.00	N5-C4-C3	112.32(17)
H5A-N5-H5C	109.00	N5-C4-H4B	109.00
H5B-N5-H5C	109.00	H4A-C4-H4B	108.00
H5A-N5-H5B	109.00	C3-C4 -H4A	109.00
O3-N6-O4	120.08(16)	C3-C4 -H4B	109.00
O2-N6-O4	120.29(18)	N5-C4-H4A	109.00

Table S6. Hydrogen bonds present in **3**

D-H···A	**d(D-H)/Å**	**d(H···A)/Å**	**d(D···A)/Å**	**<(DHA)/°**
N1-H1A···O2	0.8700	2.1700	2.882(2)	139.00
N1-H1B···O1	0.8700	2.0000	2.871(2)	174.00
N3-H3···N2	0.8700	2.0100	2.867(2)	169.00
N5-H5A··· O1	0.9000	2.2800	3.046(2)	143.00

N5-H5A···O3	0.9000	2.3800	2.979(3)	124.00
N5-H5B···O3	0.9000	2.0600	2.927(2)	162.00
N5- H5B···O4	0.9000	2.5200	3.028(2)	116.00
N5-H5C···O2	0.9000	1.9200	2.807(2)	168.00
N5-H5C···O4	0.9000	2.5900	3.060(2)	114.00
C4-H4A··· O3	0.9800	2.4100	3.296(3)	150.00
C4-H4B···O1	0.9800	2.4200	2.822(2)	104.00
C4-H4B···O4	0.9800	2.4600	3.083(3)	121.00

Table S7. Torsion angles of compound **3**.

parameter	**Å**	**parameter**	**Å**
C2-N2-C1-N1	179.76(19)	N3-N4-C3-C2	0.0(3)
C2-N2-C1-N3	-0.8(3)	N3-N4-C3-C4	179.70(19)
C1-N2-C2-O1	-179.5(2)	O1-C2-C3-N4	179.9(2)
C1-N2-C2-C3	0.3(3)	O1-C2-C3-C4	0.2(3)
C1-N3-N4-C3	-0.4(3)	N2-C2-C3-N4	0.1(3)
N4-N3-C1-N1	-179.7(2)	N2-C2-C3-C4	-179.66(19)
N4-N3-C1-N2	0.9(3)	N4-C3-C4-N5	-37.7(3)
C2-C3-C4-N5	142.03(18)		

Table S8. Bond lengths [Å] and angles [°] for **4**.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
O1-C3	1.2393(18)	N1-H1C	0.9000
O2-N6	1.2489(17)	N1-H1D	0.9000
O3-N6	1.2333(16)	N1-H1E	0.9000
O4-N7	1.2305(17)	N3-H3	0.8700
O5-N7	1.2553(18)	N5-H5A	0.8700
O6-N8	1.2134(14)	N5-H5B	0.8700
O7-N8	1.2184(16)	N6-C5	1.377(2)
N1-C1	1.4795(19)	N7-C5	1.386(2)
N2-N3	1.3543(17)	N8-C5	1.4435(18)
N2-C2	1.2845(18)	C1-C2	1.498(2)
N3-C4	1.3440(17)	C2-C3	1.4667(19)
N4-C3	1.3557(19)	C1-H1B	0.9800
N4-C4	1.3339(18)	C1-H1A	0.9800
N5-C4	1.3314(19)		

Parameter	Bond angles [°]	**Parameter**	**Bond angles [°]**

N3-N2-C2	116.33(11)	O7-N8-C5	119.34(12)
N2-N3-C4	123.25(12)	O6-N8-O7	123.59(12)
C3-N4-C4	117.86(11)	N1-C1-C2	110.91(12)
H1D-N1-H1E	109.00	C1-C2-C3	118.42(12)
C1-N1-H1D	109.00	N2-C2-C1	118.68(12)
C1-N1-H1E	109.00	N2-C2-C3	122.89(12)
C1-N1-H1C	109.00	N4-C3-C2	117.53(12)
H1C-N1-H1E	109.00	O1-C3-N4	121.63(13)
H1C-N1-H1D	109.00	O1-C3-C2	120.83(13)
C4-N3-H3	118.00	N4-C4-N5	119.91(12)
N2-N3-H3	118.00	N3-C4-N5	118.06(13)
C4-N5-H5B	120.00	N3-C4-N4	122.03(13)
H5A-N5-H5B	120.00	N1-C1-H1B	109.00
C4-N5-H5A	120.00	N1-C1-H1A	109.00
O3-N6-C5	120.98(13)	H1AC1-H1B	108.00
O2-N6-C5	117.42(12)	C2-C1-H1A	109.00
O2-N6-O3	121.59(13)	C2-C1-H1B	109.00
O4-N7-C5	120.41(13)	N6-C5-N7	125.16(13)
O5-N7-C5	116.90(12)	N6-C5-N8	117.76(12)
O4-N7-O5	122.65(13)	N7-C5-N8	117.07(13)
O6-N8-C5	117.08(11)		

Table S9. Hydrogen bonds present in **4.**

D-H···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
N1-H1C···O5	0.9000	2.1900	3.0109(17)	151.00
N1-H1C···O6	0.9000	2.3800	3.0728(15)	134.00
N1-H1D···O2	0.9000	2.2000	2.9397(17)	140.00
N1-H1D···O7	0.9000	2.2900	3.0487(17)	142.00
N1-H1E···N4	0.9000	1.9700	2.8531(16)	165.00
N3-H3···O7	0.8700	2.5400	2.9717(15)	111.00
N3- H3···O1	0.8700	1.9500	2.7914(17)	164.00
N5- H5A···O6	0.8700	2.3900	3.2545(16)	177.00
N5-H5A···O2	0.8700	2.5800	3.0051(18)	111.00
N5-H5B···O1	0.8700	2.4600	3.1747(17)	140.00
N5-H5B···O3	0.8700	2.4700	3.2117(19)	144.00

Table S10. Torsion angles of compound **4**.

parameter	Å	parameter	Å

C2-N2-N3-C4	0.91(19)	O7-N8-C5-N6	-55.82(18)
N3-N2-C2-C3	0.03(19)	O6-N8-C5-N6	123.89(14)
N3-N2-C2-C1	179.10(11)	O6-N8-C5-N7	-57.68(17)
N2-N3-C4-N5	-179.60(12)	O7-N8-C5-N7	122.62(15)
N2-N3-C4-N4	0.6(2)	N1-C1-C2-C3	-174.10(12)
C3-N4-C4-N5	177.15(12)	N1-C1-C2-N2	6.78(18)
C3-N4-C4-N3	-3.09(19)	N2-C2-C3O1	177.20(13)
C4-N4-C3-C2	3.81(18)	N2-C2-C3-N4	-2.4(2)
C4-N4-C3-O1	-175.81(13)	C1-C2-C3-O1	-1.9(2)
O2-N6-C5-N8	6.92(19)	C1-C2-C3-N4	178.50(12)
O3-N6-C5-N7	9.9(2)	O5-N7-C5-N8	-12.04(19)
O2-N6-C5-N7	-171.38(13)	O5-N7-C5-N6	166.26(13)
O3-N6-C5-N8	-171.84(12)	O4-N7-C5-N6	-11.6(2)
O4-N7-C5-N8	170.15(13)		

Table S11. Bond lengths [Å] and angles [°] for **6**.

Parameter	**Bond lengths [Å]**	**Parameter**	**Bond lengths [Å]**
O1-C3	1.242(3)	N1-H1C	0.9100
O2-C5	1.269(3)	N3-H3	0.8800
O3-C5	1.252(3)	N5-H5B	0.8800
N1-C1	1.486(3)	N5-H5A	0.8800
N2-N3	1.355(3)	C1-C2	1.501(3)
N2-C2	1.291(4)	C2-C3	1.480(3)
N3-C4	1.344(3)	C1-H1E	0.9900
N4-C4	1.339(3)	C1-H1D	0.9900
N4-C3	1.351(3)	C5-C6	1.507(4)
N5-C4	1.325(3)	C6-H6A	0.9800
N1-H1A	0.9100	C6-H6B	0.9800
N1-H1B	0.9100	C6-H6C	0.9800

Parameter	Bond angles [°]	**Parameter**	**Bond angles [°]**
N3-N2-C2	116.7(2)	O1-C3-N4	122.4(2)
N2-N3-C4	122.9(2)	O1-C3-C2	119.8(2)
C3-N4-C4	117.6(2)	N3-C4-N5	118.4(2)
H1B-N1-H1C	109.00	N4-C4-N5	118.9(2)
C1-N1-H1B	109.00	N3-C4-N4	122.7(2)
C1-N1-H1C	110.00	N1-C1-H1D	109.00
C1-N1-H1A	109.00	N1-C1-H1E	109.00
H1A-N1-H1C	109.00	C2-C1-H1D	109.00
H1A-N1-H1B	109.00	C2-C1-H1E	109.00

C4-N3-H3	119.00	H1D-C1-H1E	108.00
N2-N3-H3	119.00	O2-C5-O3	124.6(2)
C4-N5-H5B	120.00	O2-C5-C6	117.0(2)
H5A-N5-H5B	120.00	O3-C5-C6	118.4(2)
C4-N5-H5A	120.00	C5-C6-H6A	109.00
N1-C1-C2	111.7(2)	C5-C6-H6B	109.00
N2-C2-C1	118.4(2)	C5-C6-H6C	109.00
N2-C2-C3	122.3(2)	H6A-C6-H6B	109.00
C1-C2-C3	119.3(2)	H6A-C6-H6C	109.00
N4-C3-C2	117.8(2)	H6B-C6-H6C	109.00

Table S12. Hydrogen bonds present in **6**.

D-H···A	**d(D-H)/Å**	**d(H···A)/Å**	**d(D···A)/Å**	**<(DHA)/°**
N1-H1A···N4	0.9100	2.0900	2.946(3)	156.00
N1-H1B···O1	0.9100	1.9400	2.818(3)	162.00
N1-H1C···O3	0.9100	1.9800	2.861(3)	163.00
N3-H3···O2	0.8800	1.7800	2.658(3)	172.00
N5-H5A···O2	0.8800	2.0200	2.865(3)	159.00
N5-H5B···O3	0.8800	2.0200	2.901(3)	175.00
C1-H1D···O1	0.9900	2.3900	2.841(3)	107.00
C6-H6A···N5	0.9800	2.5900	3.564(4)	171.00
C6-H6B···O1	0.9800	2.5100	3.228(4)	130.00

Table S13. Torsion angles of compound **6**.

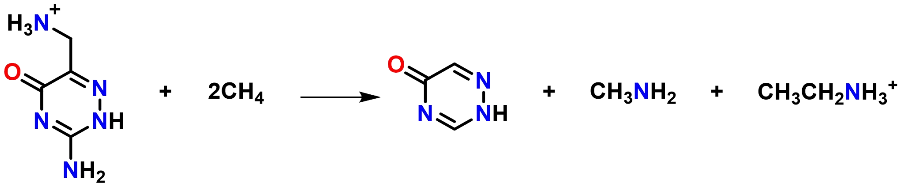
parameter	**Å**	**parameter**	**Å**
C2-N2-N3-C4	-0.3(3)	C1-C2-C3-N4	-178.8(2)
N3-N2-C2-C1	179.6(2)	C3-N4-C4-N5	-178.7(2)
N3-N2-C2-C3	1.2(3)	N1-C1-C2-N2	53.4(3)
N2-N3-C4-N4	-1.4(4)	N1-C1-C2-C3	-128.2(2)
N2-N3-C4-N5	179.4(2)	N2-C2-C3-O1	179.1(2)
C4-N4-C3-O1	179.3(2)	N2-C2-C3-N4	-0.5(4)
C4-N4-C3-C2	-1.1(3)	C1-C2-C3-O1	0.8(4)
C3-N4-C4-N3	2.1(4)		

3. Theoretical calculation

Heat of formation

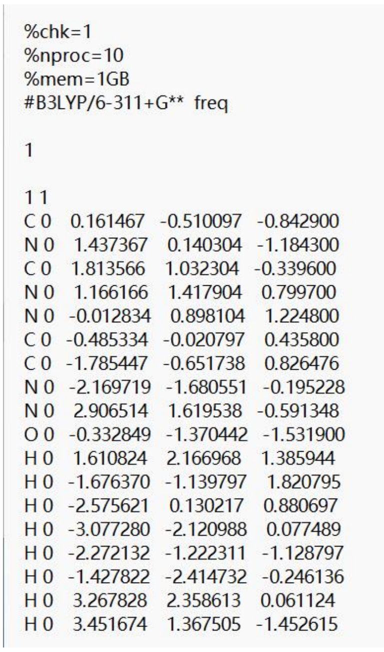
Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs[2]. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[3] functional with the 6-311+G** basis set[4]. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M[5]. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies[6].

The predictions of heat 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 ΔH_f of the title compounds are in Fig. S1. In addition, the detailed information (such as *ZPE*, E_0 and ΔH_T) of the related small molecules is provided in Table S14.



1$^+$

Fig. S1. Isodesmic reactions for compounds **1**$^+$.



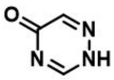
```
%chk=1
%nproc=10
%mem=1GB
#B3LYP/6-311+G** freq

1

1 1
C 0   0.161467  -0.510097  -0.842900
N 0   1.437367   0.140304  -1.184300
C 0   1.813566   1.032304  -0.339600
N 0   1.166166   1.417904   0.799700
N 0  -0.012834   0.898104   1.224800
C 0  -0.485334  -0.020797   0.435800
C 0  -1.785447  -0.651738   0.826476
N 0  -2.169719  -1.680551  -0.195228
N 0   2.906514   1.619538  -0.591348
O 0  -0.332849  -1.370442  -1.531900
H 0   1.610824   2.166968   1.385944
H 0  -1.676370  -1.139797   1.820795
H 0  -2.575621   0.130217   0.880697
H 0  -3.077280  -2.120988   0.077489
H 0  -2.272132  -1.222311  -1.128797
H 0  -1.427822  -2.414732  -0.246136
H 0   3.267828   2.358613   0.061124
H 0   3.451674   1.367505  -1.452615
```

Fig. S2. Calculation code for enthalpy of formation of compound **1**$^+$.

Table S14. Calculated zero-point energy (*ZPE*), thermal correction to enthalpy (ΔH_T), total energy(E_0) and heats of formation (ΔH_f) for related small molecules

Compound	E_0^{a}（kJ/mol）	ZPE^b（kJ/mol）	H_T^{c}（kJ/mol）	ΔH_f^{d}（kJ/mol）
1^+	-506.09	377.62	29.87	740.79
CH_4	-40.53	112.26	10.04	-74.60
CH_3NH_2	-95.89	160.78	11.64	-22.50
$CH_3CH_2N^+H_3$	-135.58	268.77	12.61	564.56
	-355.66	171.54	15.82	110.19

[a] Total energy calculated by B3LYP/6-311+G** method (a.u). [b] zero-point correction (kJ mol^{-1}). [c] thermal correction to enthalpy (kJ mol^{-1}). [d] heat of formation (kJ mol^{-1}, gas).

The change of enthalpy for the reactions at 298 K can be expressed as Equation 1

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

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

$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$ (Equation 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 thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation 2 is the PV work term. It equals $\Delta(nRT)$ for the reactions of ideal gas. For the isodesmic reaction, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation 1, apart from target compound, all the others are called reference compounds. The HOF of reference compounds is available either from the experiments or from the high-level computing such as CBS-4M[5].

For energetic salts (**2 - 8**), the solid-phase enthalpy of formation is obtained using a Born−Haber energy cycle[6-10].

the solid-phase heat of formation is calculated by the following equation:

$\Delta H_{f,\,salt} = \Delta H_{f,cation} + \Delta H_{f,anion} - \Delta H_L$ (Equation 5)

Where ΔHL is the lattice energy of the salts, which could be obtained with the following formula proposed by Jenkins et al[9] .

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

Where nM and nX depend on the nature of the ions, Mp+ and Xq- , and are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The following is the equation for lattice potential energy U_{POT} :

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

Where ρ_m is the density of the salt, M_m is the chemical formula mass of the ionic material. The value of coefficient γ and δ are acquired from relevant literature.

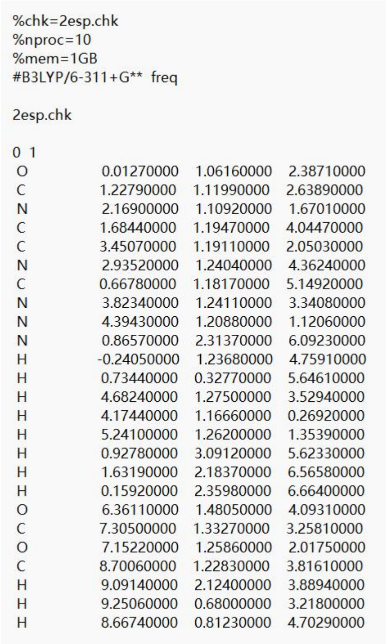
Table S15. Calculated heat of formation of cation ($\Delta H_{f,cation}$), heat of formation of anion ($\Delta H_{f,anion}$), lattice energy (ΔH_L) and solid phase heats of formation ($\Delta H_{f,salt}$).

Compound	$\Delta H_{f,cation}$/kJ·mol^{-1}	$\Delta H_{f,anion}$/kJ·mol^{-1}	ΔH_L/kJ·mol^{-1}	$\Delta H_{f,salt}$/kJ·mol^{-1}
2	740.79	-277.80	496.424	-33.44
3	740.79	-307.90	508.82	-75.94
4	740.79	540.56	484.75	796.60
5	740.79	-182.74	472.29	85.76
7	740.79	-783.02	438.14	-480.37
8	740.79	-843.57	432.76	-535.54

The electrostatic potential surface analysis (ESP) and non-covalent interactions (NCI) analysis

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs[2]. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[3] functional with the 6-311+G** basis set[4]. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies[6].

The electrostatic potential surface analysis (ESP) is a 3D surface representation constructed by calculating the critical points (maxima and minima) of positive and negative charge distributions on a molecular surface. This calculation was performed using Gaussian 09 software with specific input parameters, as exemplified by the computational code for Compound **2** shown in Fig. S3.



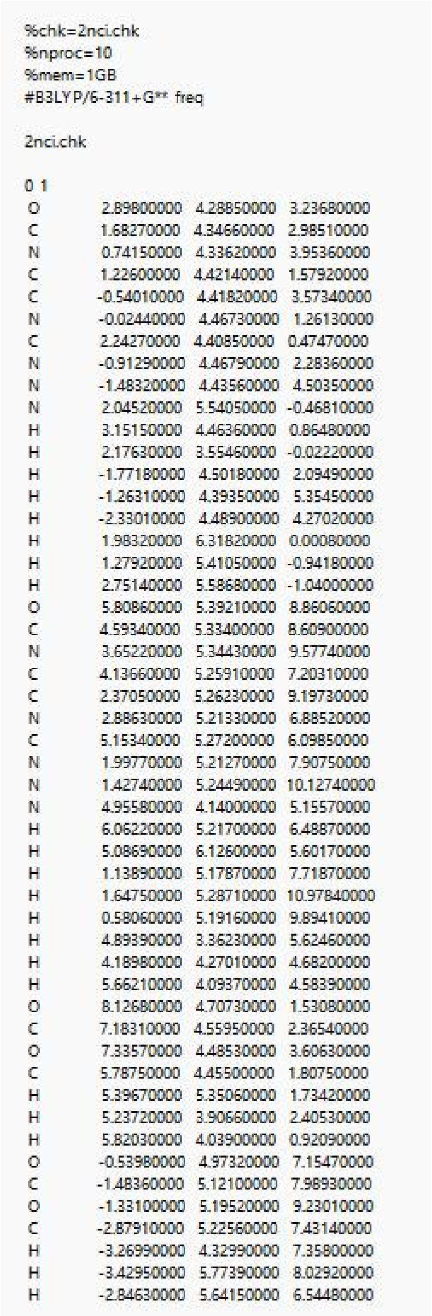
```
%chk=2esp.chk
%nproc=10
%mem=1GB
#B3LYP/6-311+G**  freq

2esp.chk

0  1
 O              0.01270000   1.06160000   2.38710000
 C              1.22790000   1.11990000   2.63890000
 N              2.16900000   1.10920000   1.67010000
 C              1.68440000   1.19470000   4.04470000
 C              3.45070000   1.19110000   2.05030000
 N              2.93520000   1.24040000   4.36240000
 C              0.66780000   1.18170000   5.14920000
 N              3.82340000   1.24110000   3.34080000
 N              4.39430000   1.20880000   1.12060000
 N              0.86570000   2.31370000   6.09230000
 H             -0.24050000   1.23680000   4.75910000
 H              0.73440000   0.32770000   5.64610000
 H              4.68240000   1.27500000   3.52940000
 H              4.17440000   1.16660000   0.26920000
 H              5.24100000   1.26200000   1.35390000
 H              0.92780000   3.09120000   5.62330000
 H              1.63190000   2.18370000   6.56580000
 H              0.15920000   2.35980000   6.66400000
 O              6.36110000   1.48050000   4.09310000
 C              7.30500000   1.33270000   3.25810000
 O              7.15220000   1.25860000   2.01750000
 C              8.70060000   1.22830000   3.81610000
 H              9.09140000   2.12400000   3.88940000
 H              9.25060000   0.68000000   3.21800000
 H              8.66740000   0.81230000   4.70290000
```

Fig. S3. Calculation code for ESP of compound **2**.

The non-covalent interactions (NCI) arise from weak intermolecular forces (e.g., van der Waals, hydrogen bonding), calculated using Gaussian 09 software with specific input parameters, as exemplified by the computational code for Compound **2** shown in Fig. S4.



```
%chk=2nci.chk
%nproc=10
%mem=1GB
#B3LYP/6-311+G** freq

2nci.chk

0 1
 O          2.89800000   4.28850000   3.23680000
 C          1.68270000   4.34660000   2.98510000
 N          0.74150000   4.33620000   3.95360000
 C          1.22600000   4.42140000   1.57920000
 C         -0.54010000   4.41820000   3.57340000
 N         -0.02440000   4.46730000   1.26130000
 C          2.24270000   4.40850000   0.47470000
 N         -0.91290000   4.46790000   2.28360000
 N         -1.48320000   4.43560000   4.50350000
 N          2.04520000   5.54050000  -0.46810000
 H          3.15150000   4.46360000   0.86480000
 H          2.17630000   3.55460000  -0.02220000
 H         -1.77180000   4.50180000   2.09490000
 H         -1.26310000   4.39350000   5.35450000
 H         -2.33010000   4.48900000   4.27020000
 H          1.98320000   6.31820000   0.00080000
 H          1.27920000   5.41050000  -0.94180000
 H          2.75140000   5.58680000  -1.04000000
 O          5.80860000   5.39210000   8.86060000
 C          4.59340000   5.33400000   8.60900000
 N          3.65220000   5.34430000   9.57740000
 C          4.13660000   5.25910000   7.20310000
 C          2.37050000   5.26230000   9.19730000
 N          2.88630000   5.21330000   6.88520000
 C          5.15340000   5.27200000   6.09850000
 N          1.99770000   5.21270000   7.90750000
 N          1.42740000   5.24490000  10.12740000
 N          4.95580000   4.14000000   5.15570000
 H          6.06220000   5.21700000   6.48870000
 H          5.08690000   6.12600000   5.60170000
 H          1.13890000   5.17870000   7.71870000
 H          1.64750000   5.28710000  10.97840000
 H          0.58060000   5.19160000   9.89410000
 H          4.89390000   3.36230000   5.62460000
 H          4.18980000   4.27010000   4.68200000
 H          5.66210000   4.09370000   4.58390000
 O          8.12680000   4.70730000   1.53080000
 C          7.18310000   4.55950000   2.36540000
 O          7.33570000   4.48530000   3.60630000
 C          5.78750000   4.45500000   1.80750000
 H          5.39670000   5.35060000   1.73420000
 H          5.23720000   3.90660000   2.40530000
 H          5.82030000   4.03900000   0.92090000
 O         -0.53980000   4.97320000   7.15470000
 C         -1.48360000   5.12100000   7.98930000
 O         -1.33100000   5.19520000   9.23010000
 C         -2.87910000   5.22560000   7.43140000
 H         -3.26990000   4.32990000   7.35800000
 H         -3.42950000   5.77390000   8.02920000
 H         -2.84630000   5.64150000   6.54480000
```

Fig. S4. Calculation code for NCI of compound **2**.

4. TGA-DSC curves

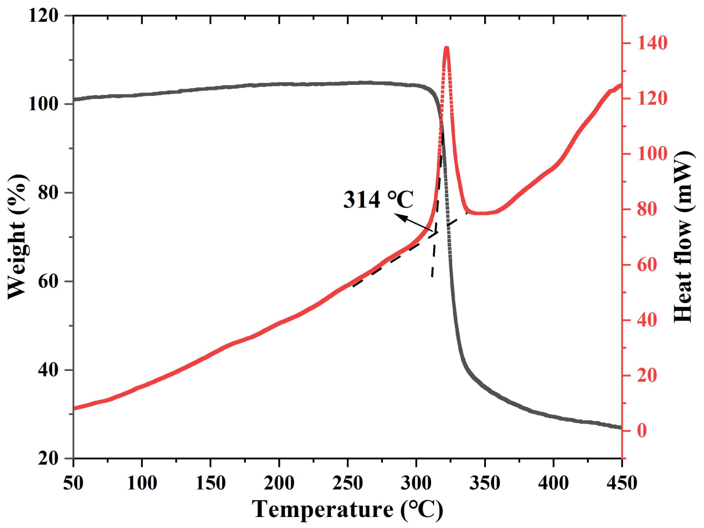


Fig. S5. TGA-DSC of investigated compounds **2**.

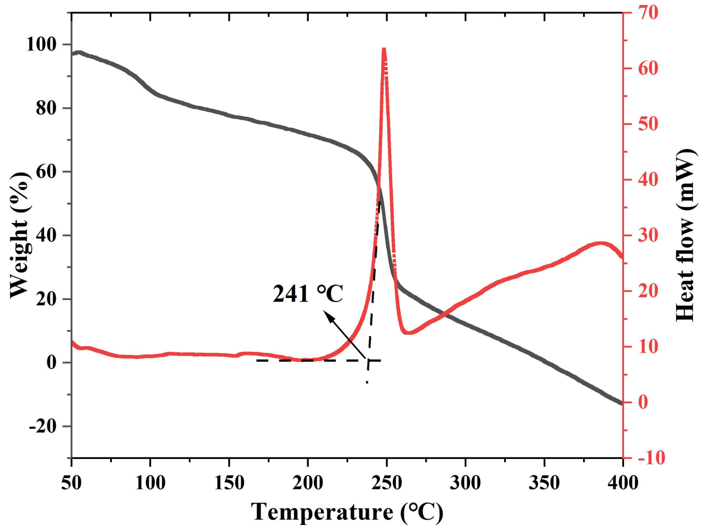


Fig. S6. TGA-DSC of investigated compounds **3**.

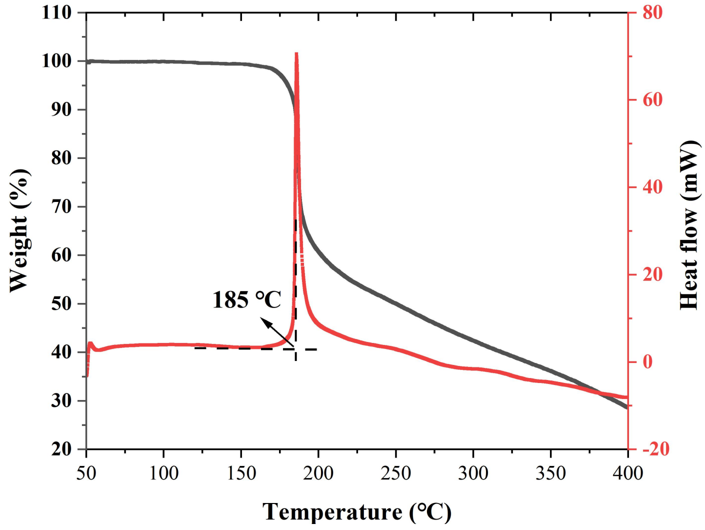


Fig. S7. TGA-DSC of investigated compounds **4**.

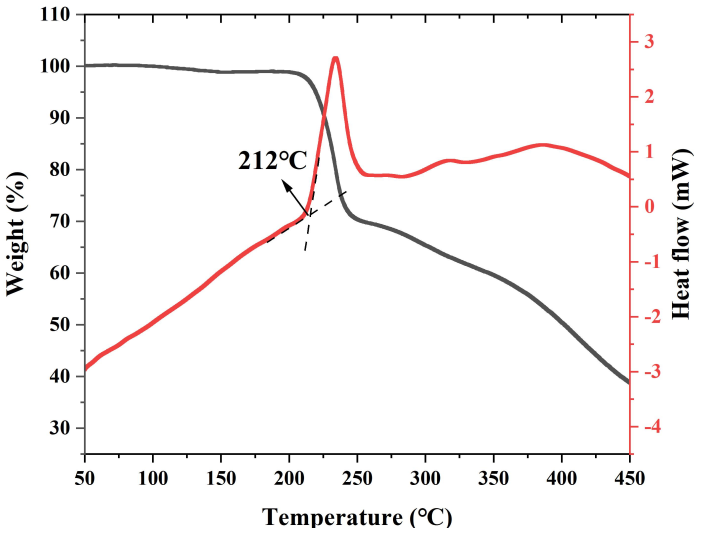


Fig. S8.TGA-DSC of investigated compounds **5**.

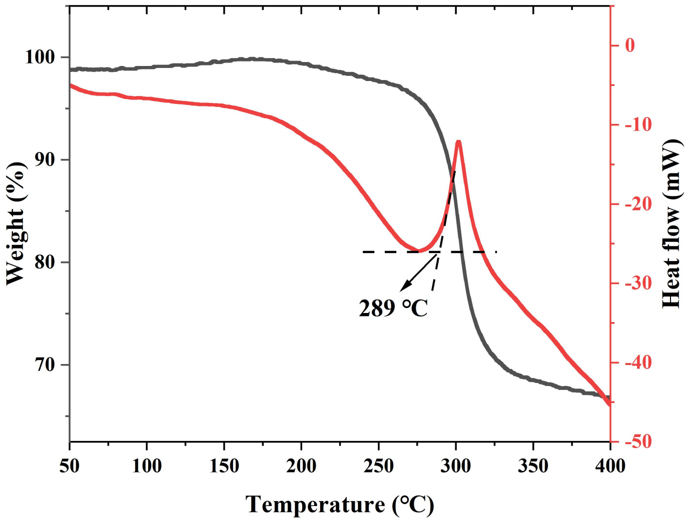


Fig. S9.TGA-DSC of investigated compounds **7**.

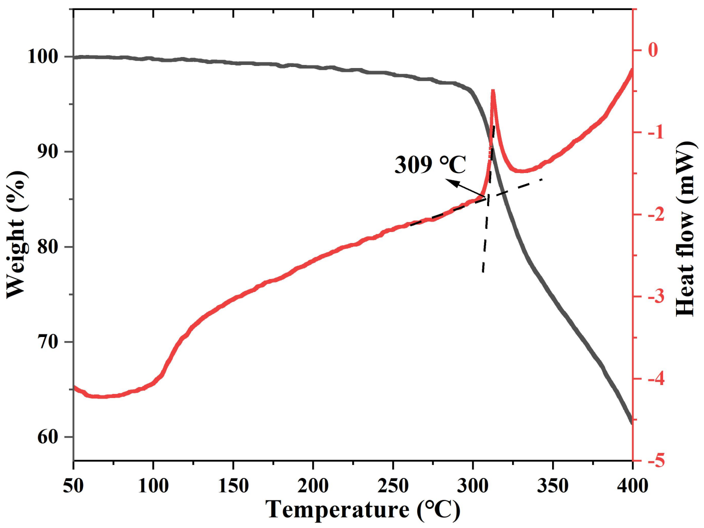


Fig. S10. TGA-DSC of investigated compounds **8**.

5. ^{1}H and ^{13}C NMR spectra for all new compounds

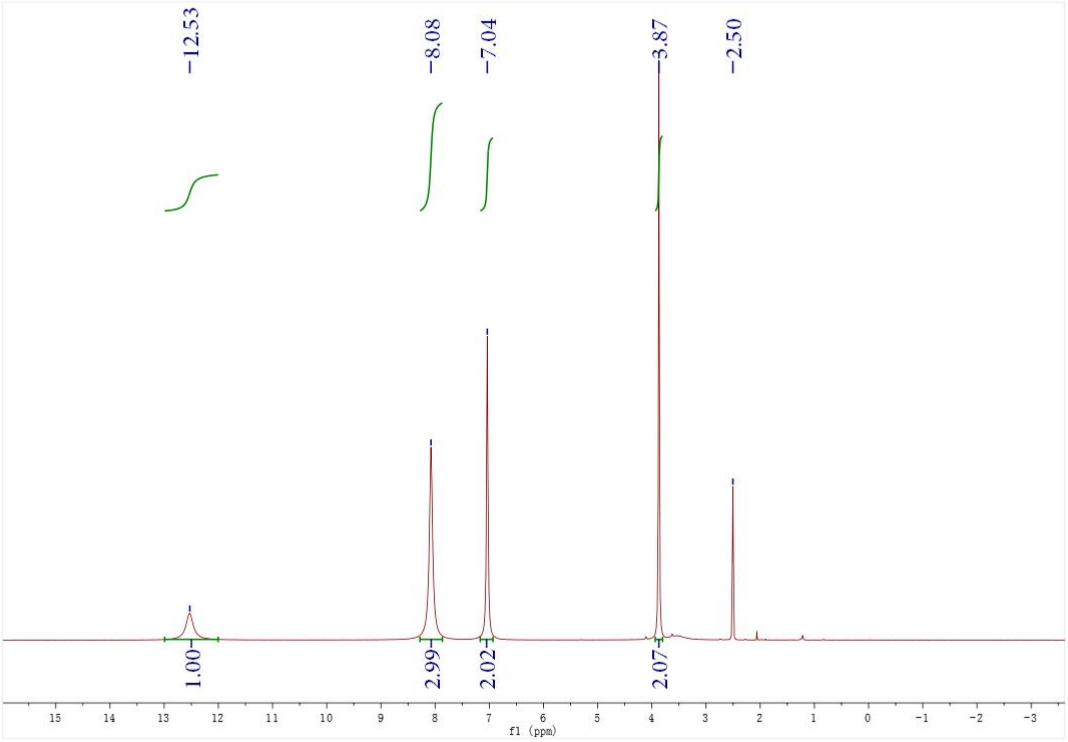


Fig. S11. ^{1}H NMR spectrum of **2** in DMSO-d_6.

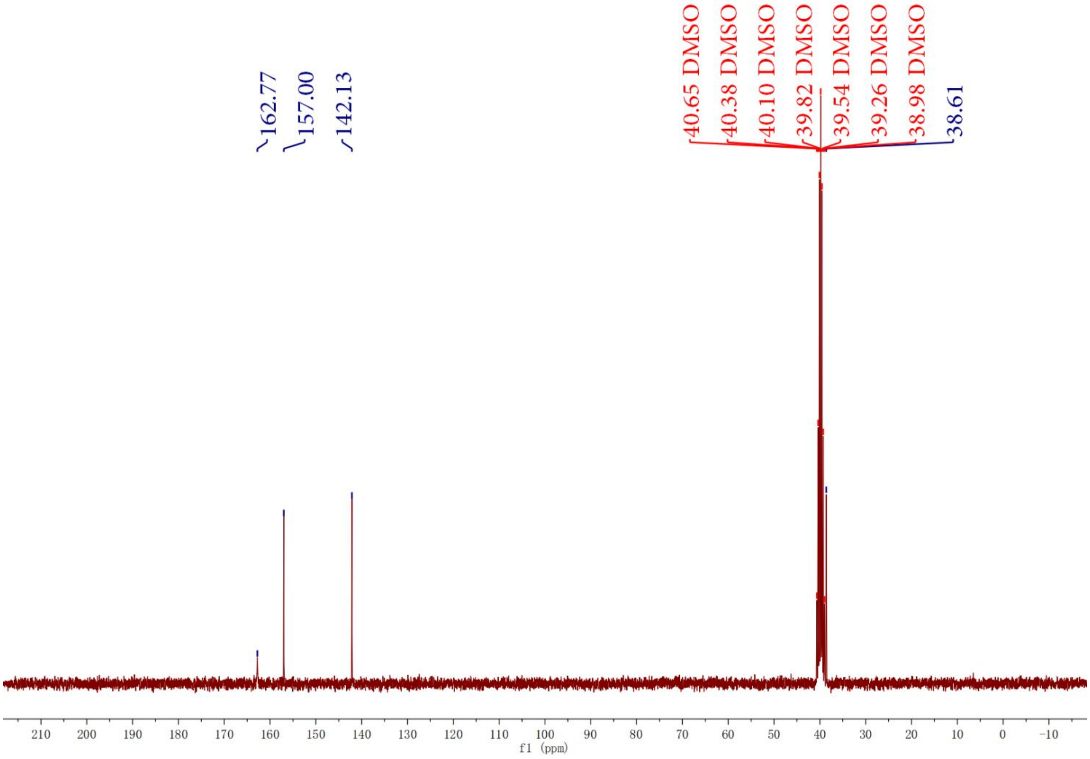


Fig. S12. ^{13}C NMR spectrum of **2** in DMSO-*d*$_6$.

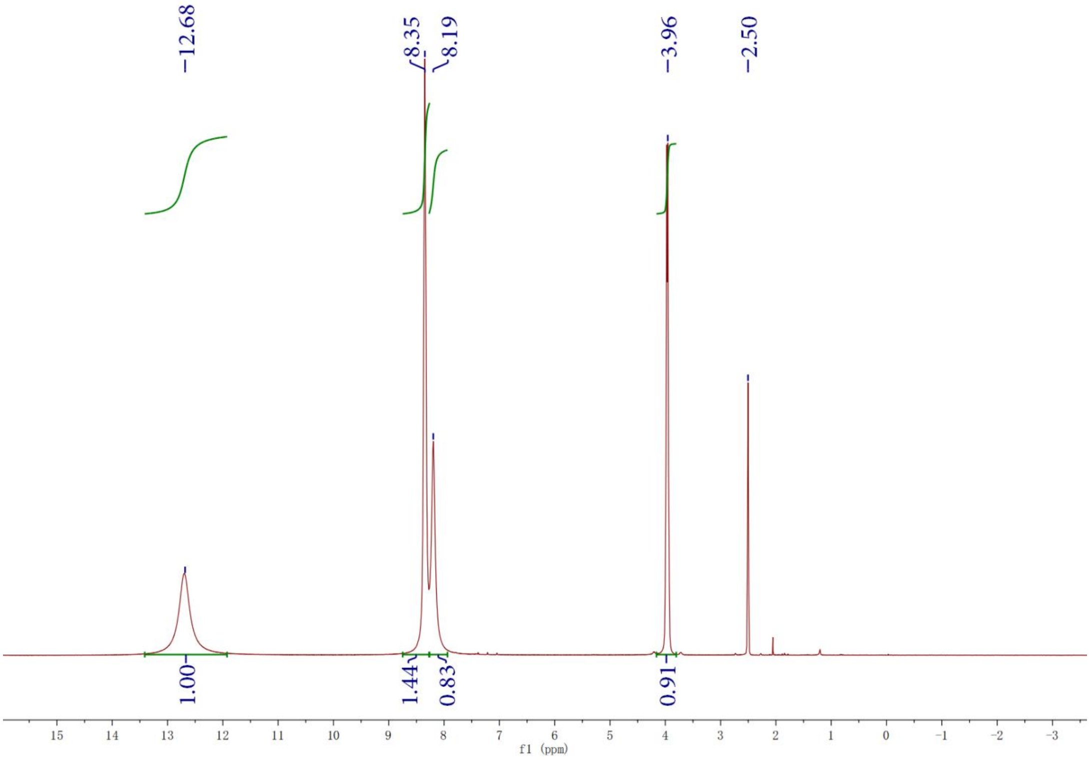


Fig. S13. ^{1}H NMR spectrum of **3** in DMSO-*d*$_6$.

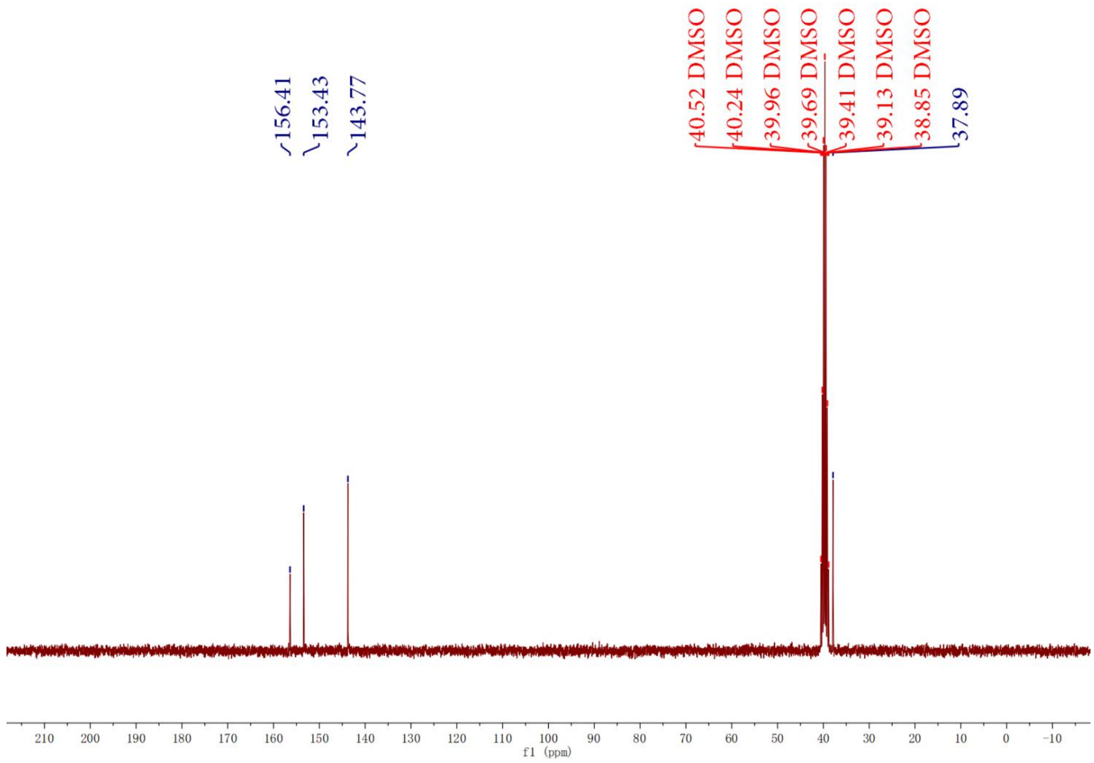


Fig. S14. ^{13}C NMR spectrum of **3** in DMSO-d_6.

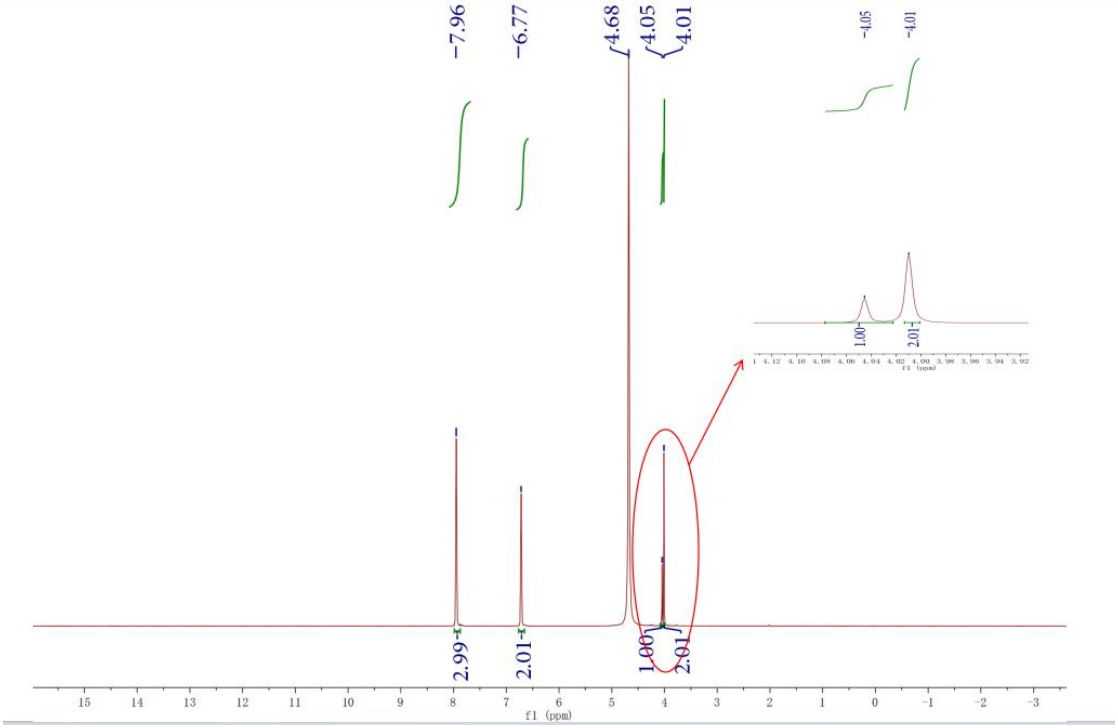


Fig. S15. ^{1}H NMR spectrum of **4** in D$_2$O.

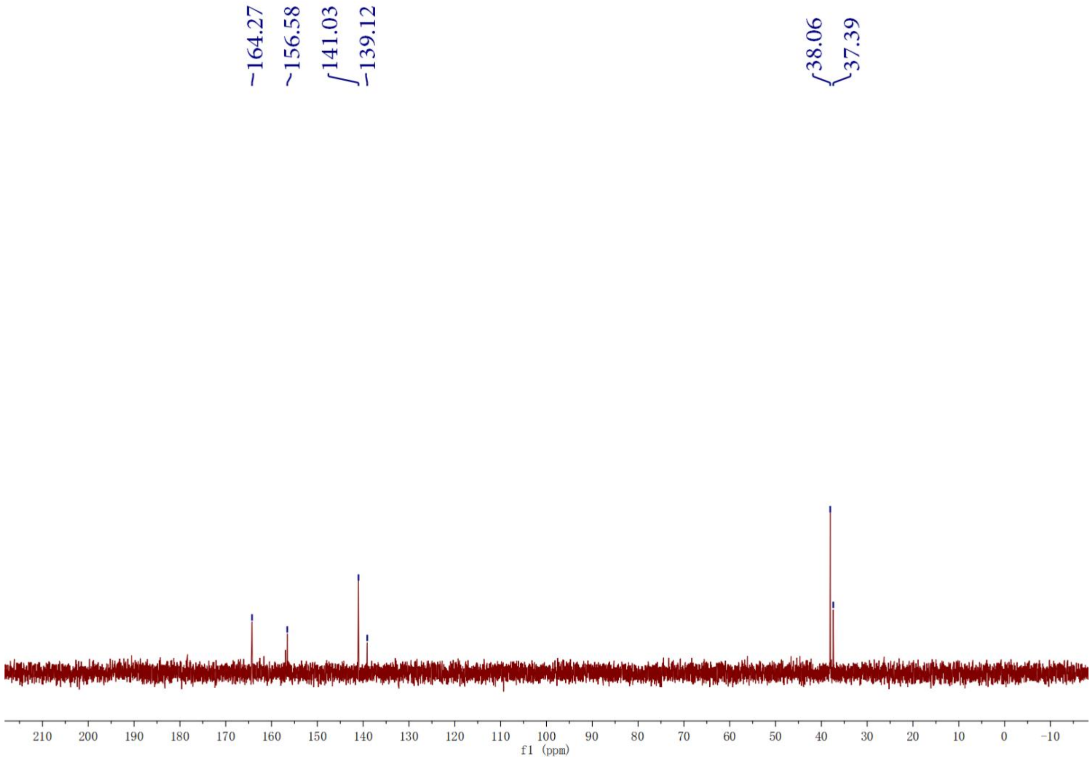


Fig. S16. ^{13}C NMR spectrum of **4** in D_2O.

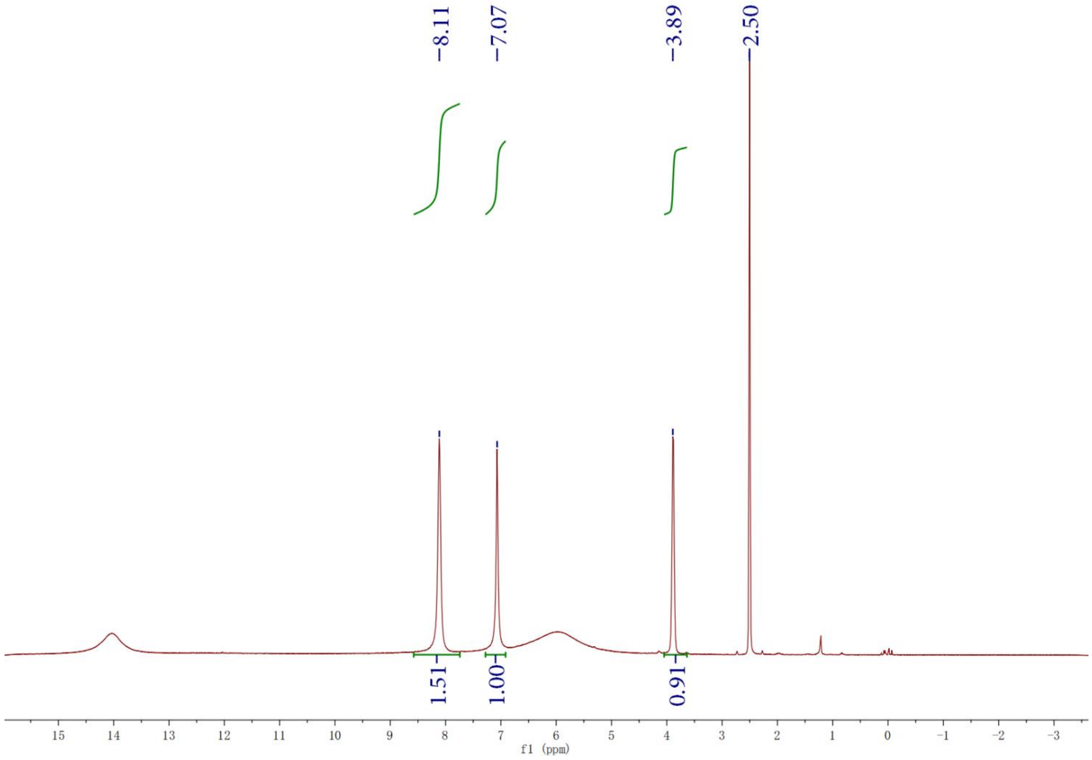


Fig. S17. ^{1}H NMR spectrum of **5** in DMSO-d_6.

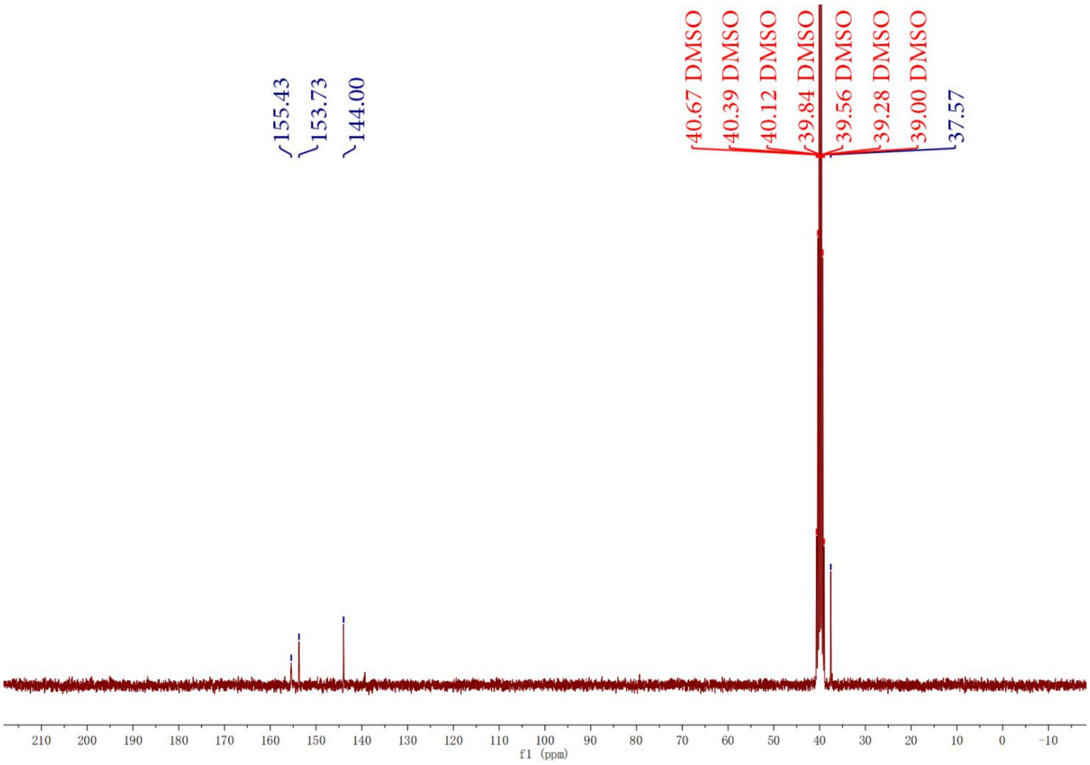


Fig. S18. ^{13}C NMR spectrum of **5** in DMSO-d_6.

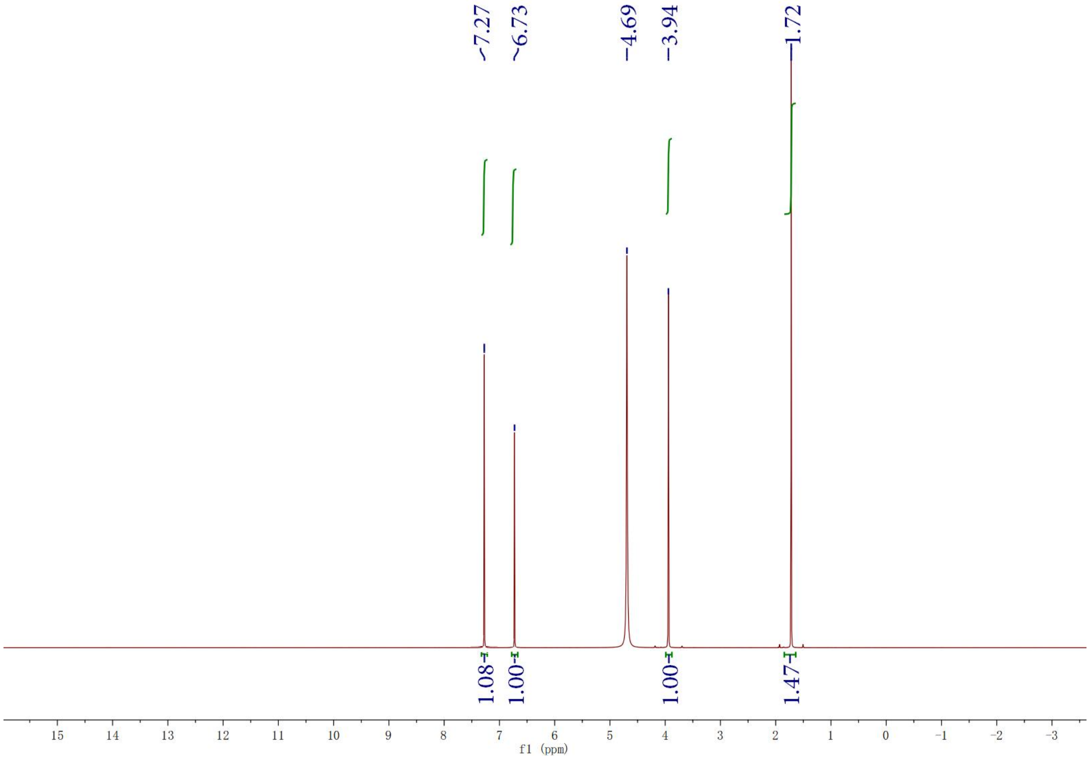


Fig. S19. ^{1}H NMR spectrum of **6** in D_2O.

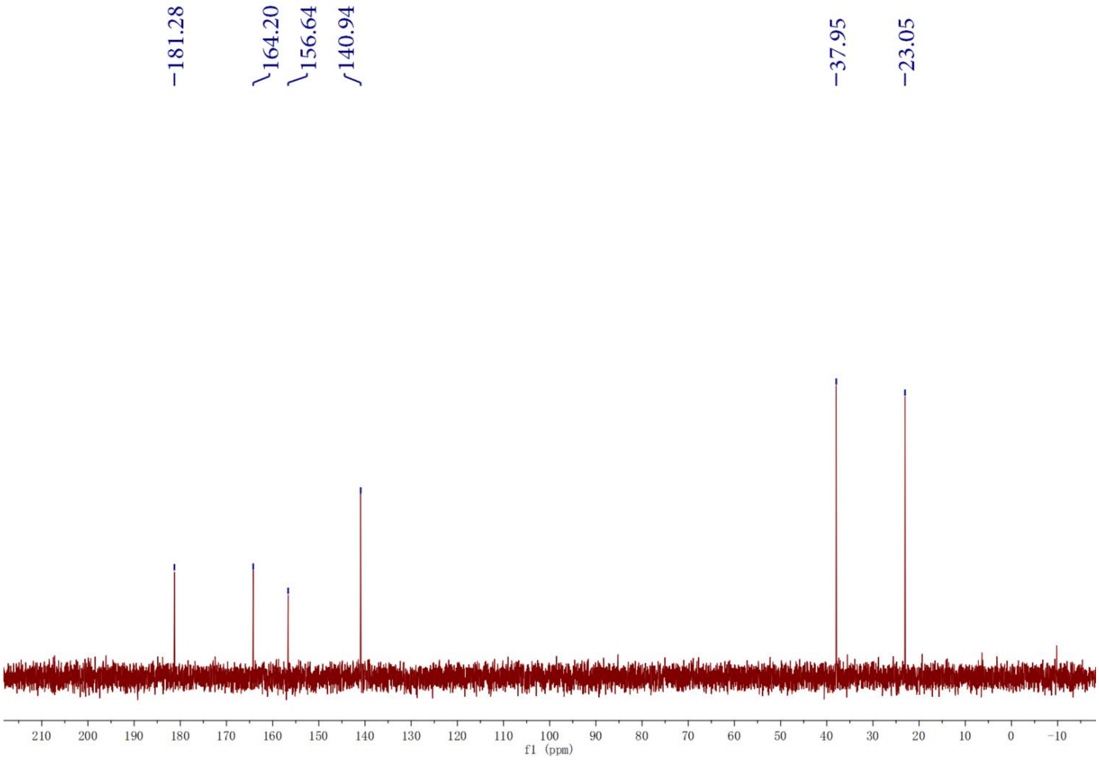


Fig. S20. ^{13}C NMR spectrum of **6** in D_2O.

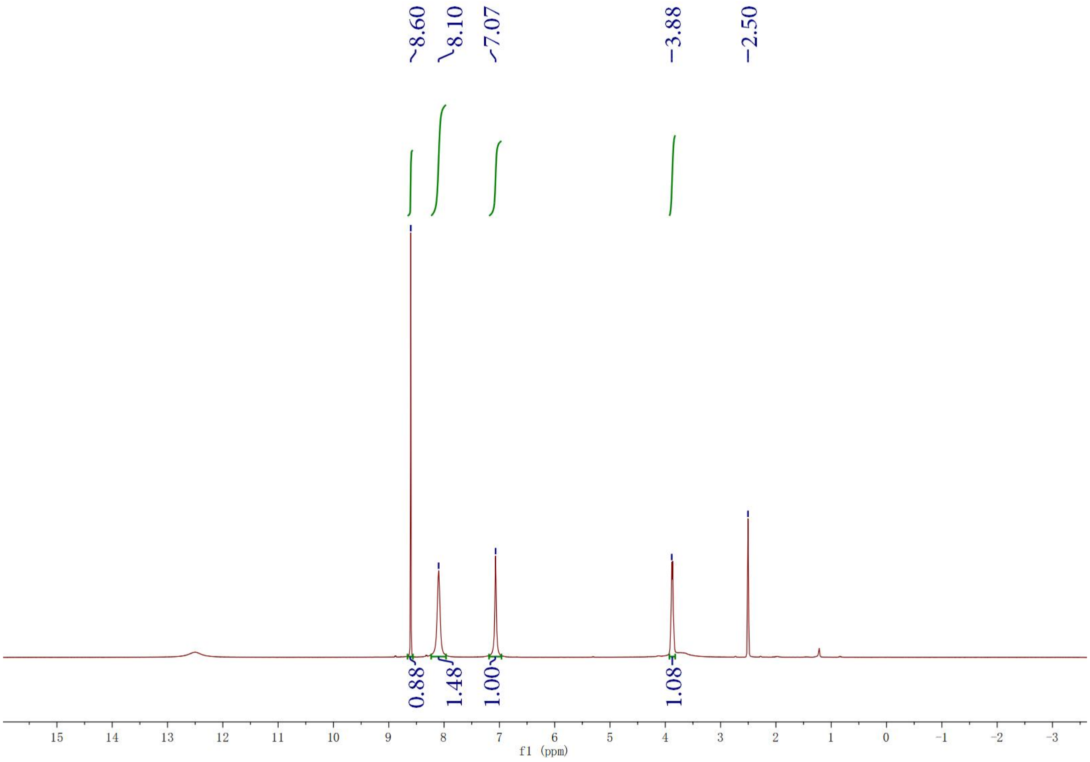


Fig. S21. ^{1}H NMR spectrum of **7** in DMSO-d_6.

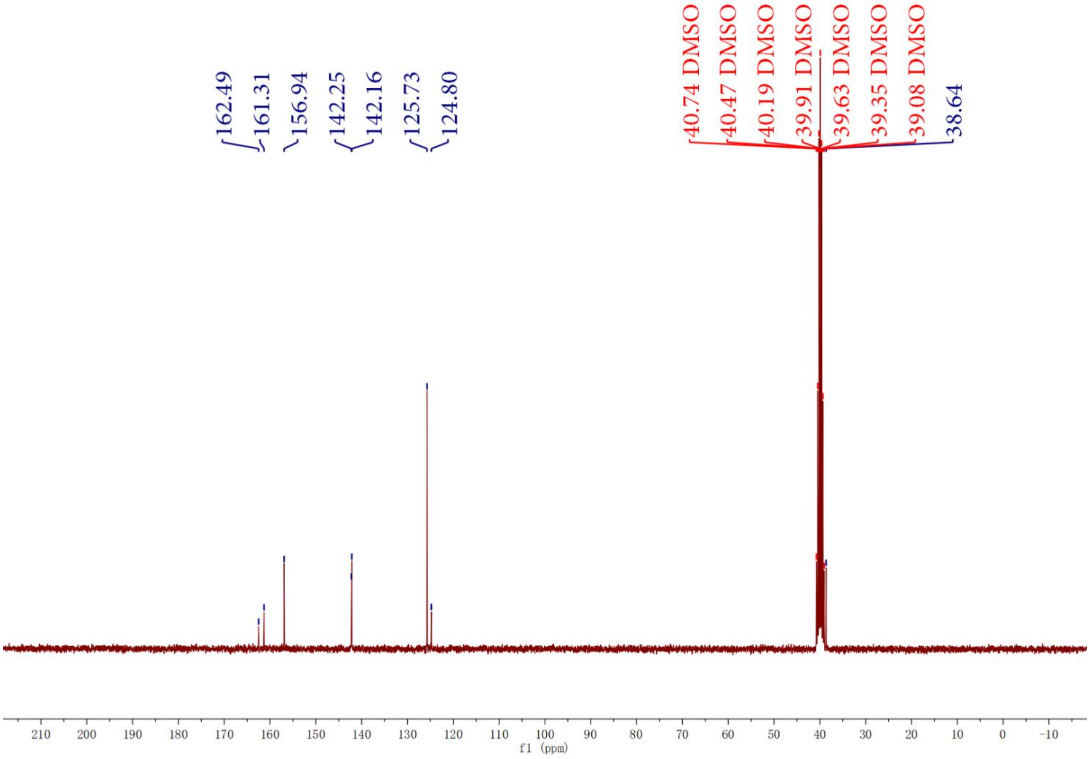


Fig. S22. ^{13}C NMR spectrum of **7** in DMSO-d_6.

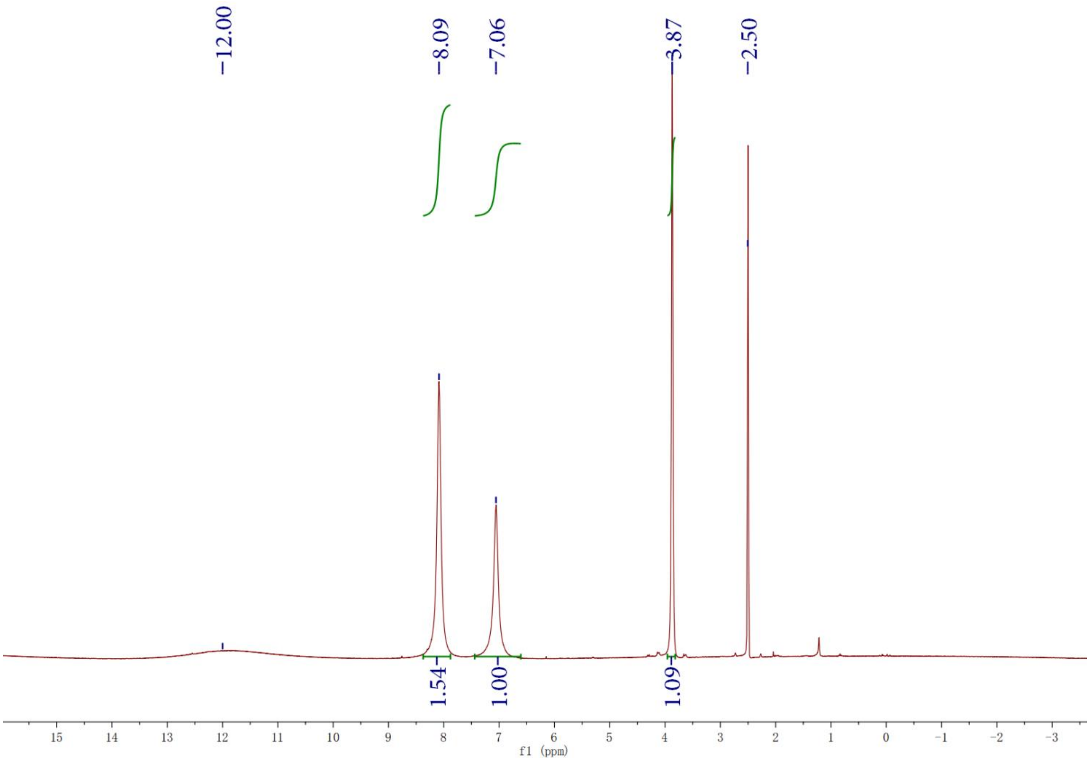


Fig. S23. ^{1}H NMR spectrum of **8** in DMSO-d_6.

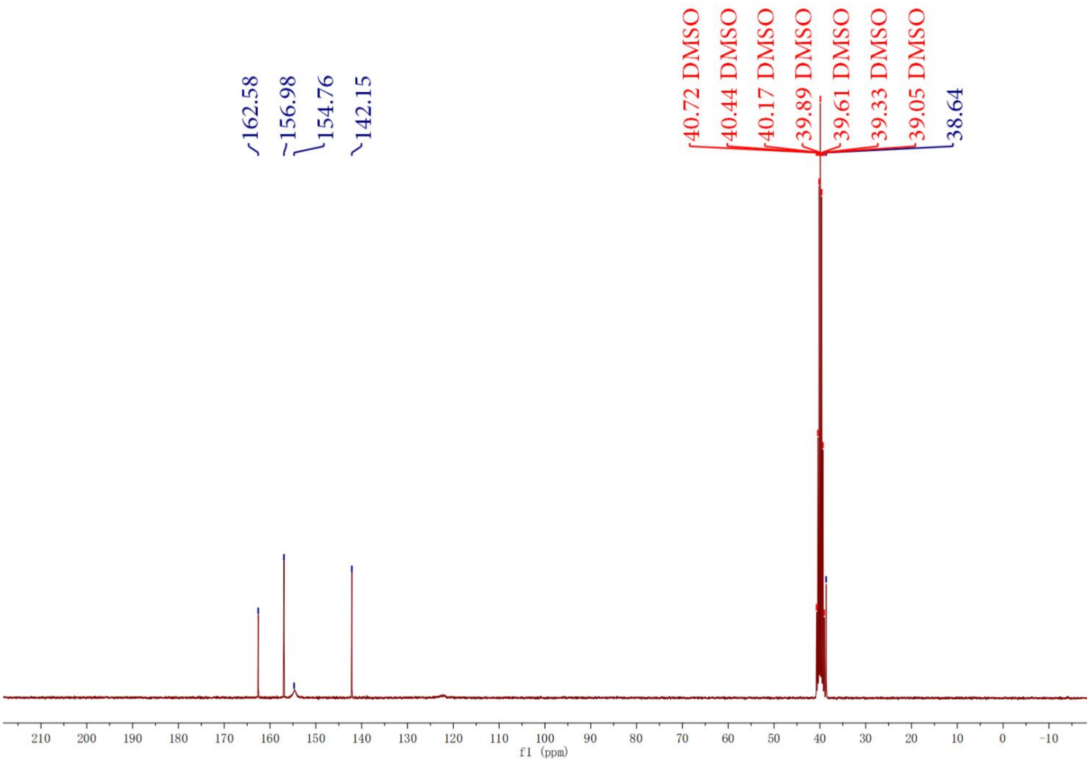


Fig. S24. ^{13}C NMR spectrum of **8** in DMSO-d_6.

6. IR Spectrum of the prepared compounds

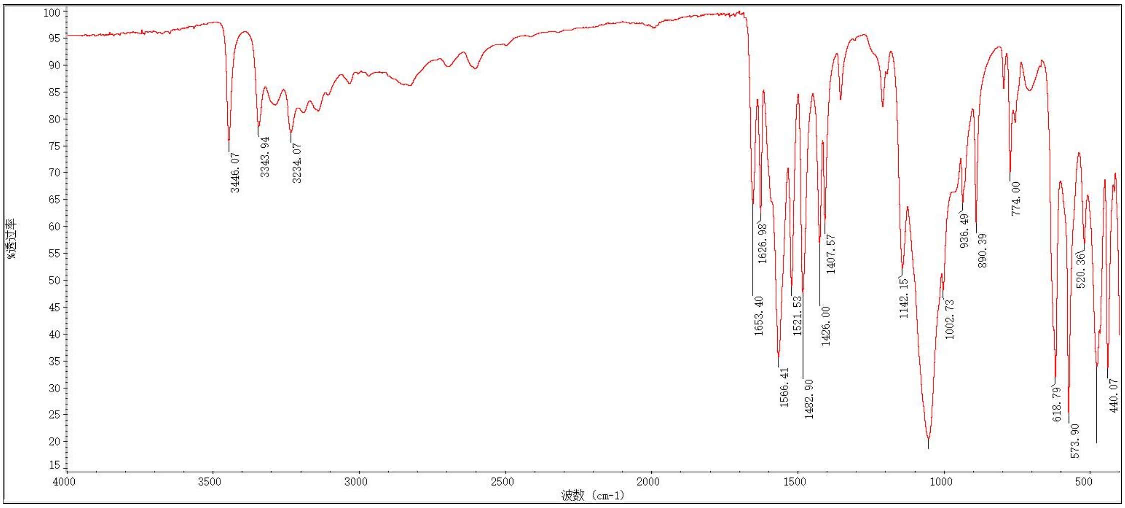


Fig. S25. IR Spectrum of **2**.

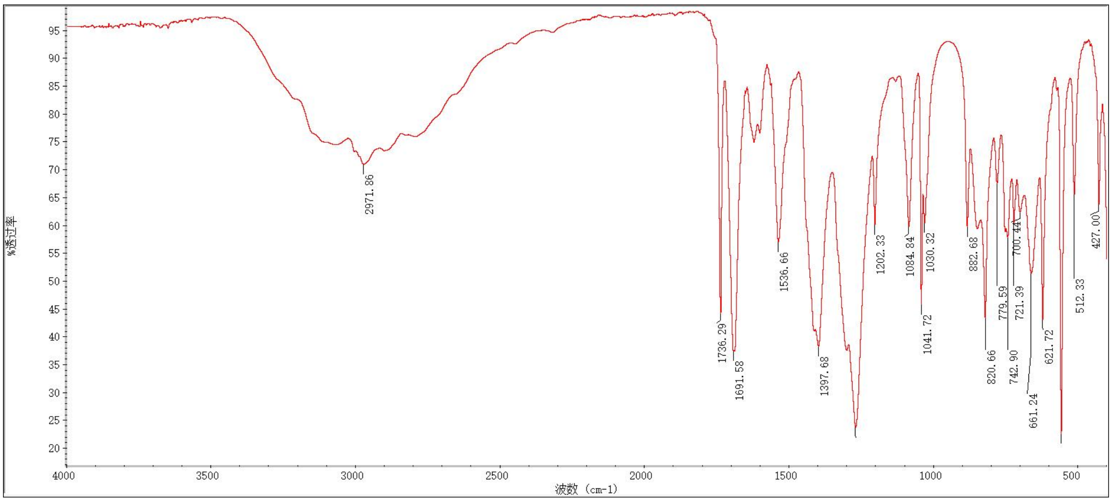


Fig. S26. IR Spectrum of **4**.

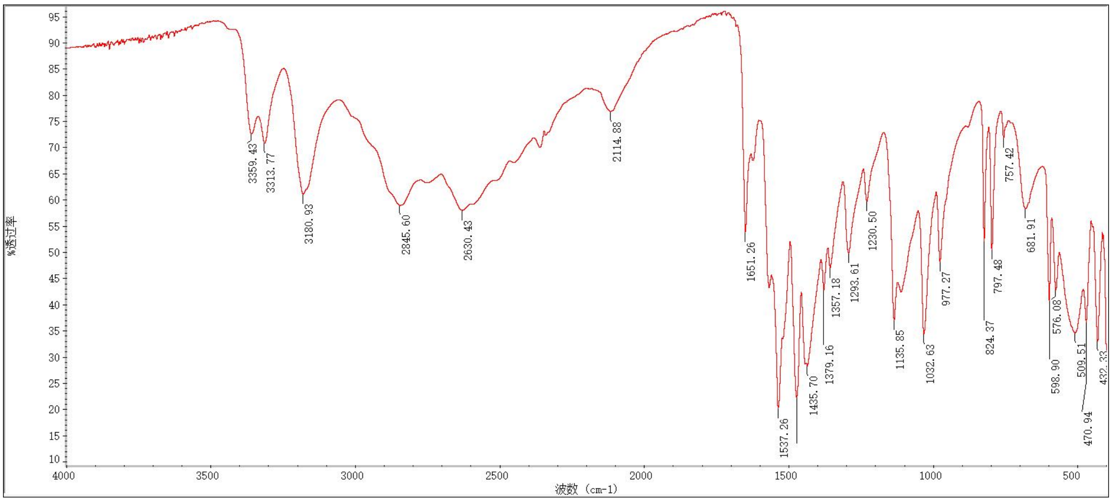


Fig. S27. IR Spectrum of **5**.

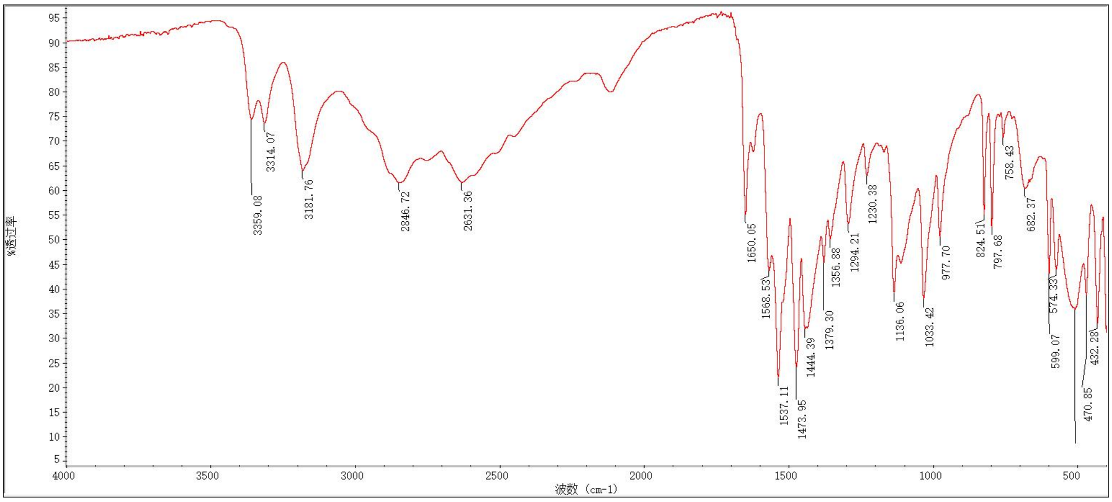


Fig. S28. IR Spectrum of **6**.

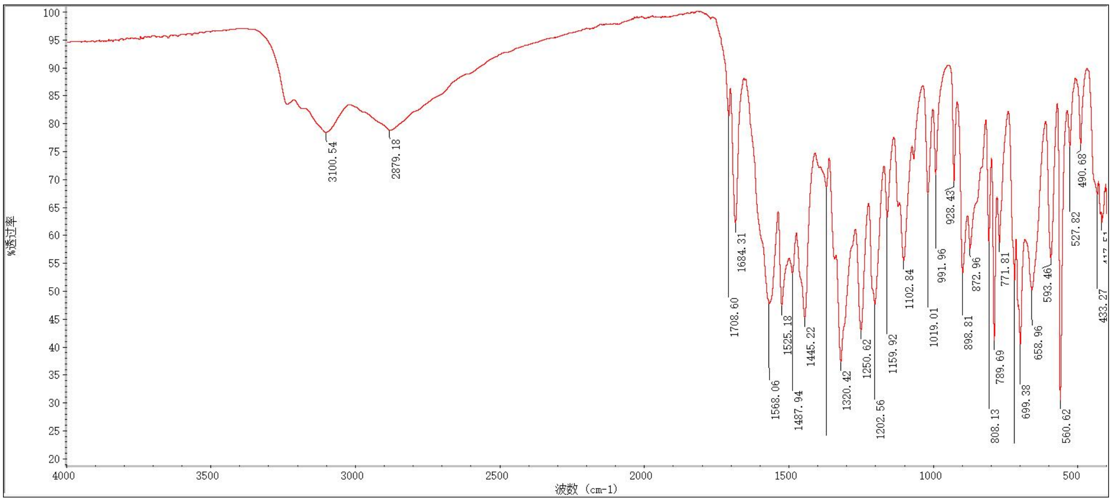


Fig. S29. **IR** Spectrum of **7**.

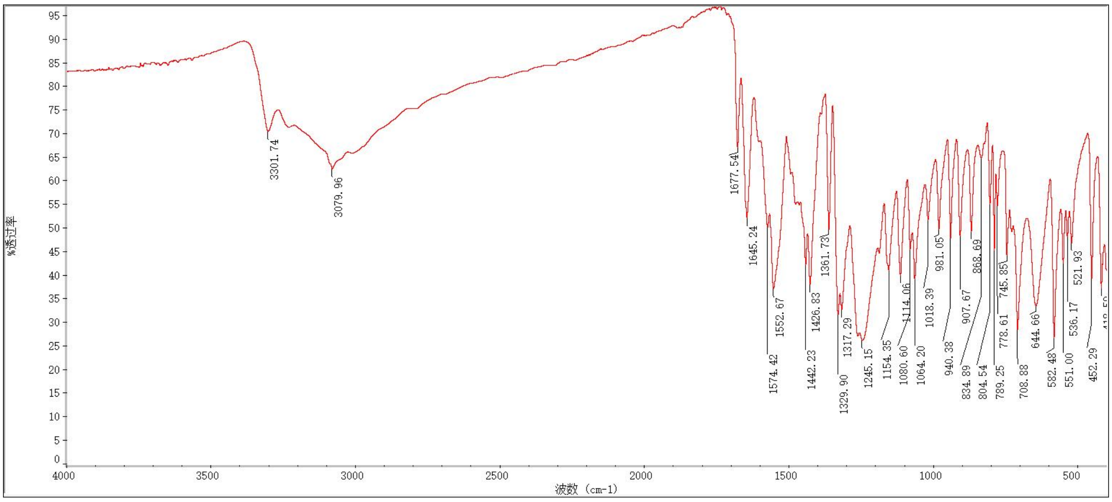


Fig. S30. **IR** Spectrum of **8**.

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