Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Synthesis and properties of salts derived from $C_4N_{18}^{2-}$, $C_4N_{18}H^{3-}$ and $C_4N_{18}H_3^-$ anions

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Table of Contents

Experimental Procedures

Cautions! There have been no explosions when dealing with these compounds, but we strongly encourage to take strict precautions because of their high energy and mechanical sensitivity.

General methods

All reagents are purchased from Energy Chemical of analytical grade and were used strictly in accordance with regulations. ^{1}H and ^{13}C NMR were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 500 and 126 MHz, respectively. IR spectra were recorded using KBr pellets with a Thermo Nicolet iS10 sprctrometer. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. The melting and decomposition (onset) points were measured on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1}. Densities were confirmed at room temperature by using the Micromeritics AccuPyc 1340 gas pycnometer. Impact and friction sensitivity were obtained using a standard BAM Fallhammer and a BAM friction tester.

Computations

Computations were performed by using the Gaussian09 suite of programs.[1] The theoretical gas phase enthalpies of formation were calculated used the hybrid DFTB3LYP methods with 6-311++G** basis set[2] based on isodemic reactions (Scheme S1).

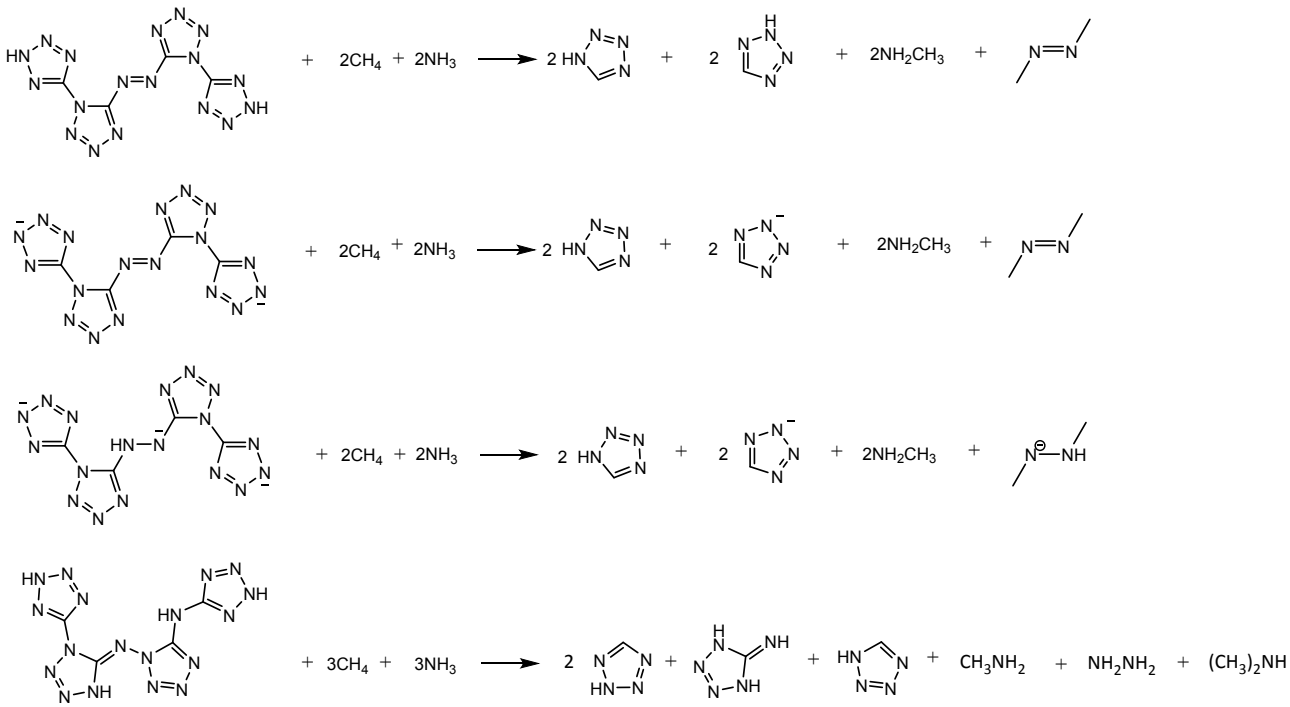
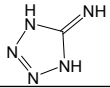


Figure S1 Isodesmic reactions for calculating heats of formation.

Table S1 Calculated total energy (E_0), zero-point energy (ZPE), thermal correction to enthalpy (H_T) and gas phase heats of formation (HOF)

Compound	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
NH_3	-56.5826356	86.27	10.05	-45.9
NH_2CH_3	-95.8938402	160.78	11.64	-22.5
$CH_3NHNCH_3^-$	-189.9085458	236.14	17.28	76.75
$CH_3N{=}NCH_3$	-189.3337358	211.85	16.32	147.85
$(CH_3)_2NH$	-135.1814215	237.51	14.29	-20.60
NH_2NH_2	-111.9105763	134.28	11.16	95.40
tetrazolium	-257.7329825	87.02	11.26	170
tetrazole	-258.2567	123.13	11.83	333.2
2H-tetrazole	-257.7068416	124.96	11.45	318.2
	-313.690963	162.35	15.94	160.74

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Figure S2).[3]

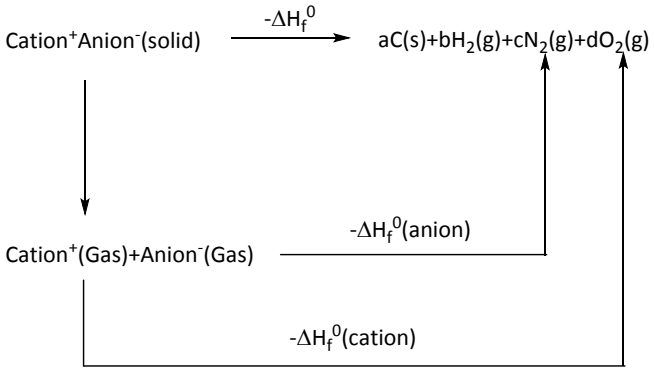


Figure S2 Born-Haber Cycle for the formation of energetic salts.

The number is simplified by equation 1:

ΔH_f^0 (salt, 298 K) = ΔH_f^0 (cation, 298K) + ΔH_f^0 (anion, 298K) – ΔH_L (1)

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]

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

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-}, 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} [Eq. (3)] has the form:

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

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for (g) and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[2]

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,[3] the heat of sublimation can be estimated with Trouton's rule according to supplementary equation (4), where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

ΔH_{sub} = 188/J mol^{-1}K^{-1} × T (4)

Table S2 Densities, calculated lattice energies, and calculated heats of formation

Compound	D[a] (g cm^{-3})	ΔH_{Lat}[b] (kJ mol^{-1})	ΔH_f [c] (kJ mol^{-1}/kJ g^{-1})
2	1.82	-	1557.35/5.15
3	2.03	1292.91	965.16/2.55
4	1.74	1275.21	1241.21/3.69
5	1.71	1092.01	2224.31/4.71
6	1.72	2688.93	1131.43/2.83
7	1.79	-	1402.30/4.61

[a] Density was measured by gas pycnometer at room temperature. [b] Calculated lattice energy. [c] Calculated heat of formation.

Syntheses

1,2-di(2'H-[1,5'-bitetrazol]-5-yl)diazene (2): potassium 5-amino-[1,5'-bitetrazol]-2'-ide[4] (0.44 g, 2.3 mmol) was added slowly to 37% HCl (10 ml) at 0 °C. The solution of potassium permanganate in 20 ml water (0.55 g, 3.45 mmol) was added drop-wise to the mixture. After addition, the suspension was warmed to room temperature and stirred for 2 h, and then treated with 30 % hydrogen peroxide solution, the orange-yellow precipitate was filtered, washed with a small amount of cold water and dried below 35 °C to obtain 0.226 g product in the yield of 65.1 %. **^{1}H NMR** (500 MHz, DMSO) δ 7.07 (s, 2H) ppm. **^{13}C NMR** (126 MHz, DMSO) δ 159.3, 153.9 ppm. **IR** (KBr): ṽ=3022.47, 2187.18, 1567.35, 1494.61, 1465.20, 1408.40, 1343.38, 1232.86, 1170.57, 1149.79, 1126.70, 1094.62, 1027.34, 1012.99, 994.66, 859.95, 753.87, 749.43, 722.14, 702.06, 694.21, 617.71 cm^{-1}. Elemental analysis calcd for $C_4H_2N_{18}$ (302.07): C 15.90, H 0.67, N 83.43 %; found: C 15.97, H 0.66, N 83.35 %.

Dipotassium 5-([1,5'-bitetrazol]-4-ium-2'-id-5-yldiazenyl)-[1,5'-bitetrazol]-2'-ide (3): 0.1122 g KOH (2 mmol) was added to the suspension of 1,2-di(2'H-[1,5'-bitetrazol]-5-yl)diazene (0.302g, 1 mmol) in 10 ml water at 25 °C and stirred for 2 h. The solution was removed on a rotary evaporator to get a yellow solid orange solid 0.359 g, in the yield of 95 %. **^{13}C NMR** (126 MHz, DMSO) δ 159.4, 153.4 ppm. **IR** (KBr): ṽ=3516.26, 3444.77, 1630.66, 1531.95, 1492.34, 1425.51, 1206.97, 1158.88, 1143.83, 1121.51, 1100.94, 1059.98, 1015.03, 998.25, 749.83, 731.08, 701.78, 621.40 cm^{-1}. $C_4N_{18}K_2$ (377.98): C 12.70, N 66.64 %; found: C 12.81, N 66.59 %.

Diammonium 5-([1,5'-bitetrazol]-4-ium-2'-id-5-yldiazenyl)-[1,5'-bitetrazol]-2'-ide (4): compound **2** (0.302 g, 1mmol) was suspended in acetonitrile and the 27 % aqueous ammonia (0.14 ml, 2 mmol) was added drop-wise at room temperature. After stirring 2 h, the precipitate was filtered, washed with acetonitrile and dried in air to get orange

solid 0.30 g in the yield of 89.2 %. **^{1}H NMR** (500 MHz, DMSO) δ (s, 8H) 7.11 ppm. **^{13}C NMR** (126 MHz, DMSO) δ 154.6, 153.7 ppm. **IR** (KBr): ῡ=3169.44, 3043.74, 1636.09, 1532.36, 1472.25, 1422.00, 1164.53, 1126.21, 1091.31, 1018.07, 996.00, 748.23, 731.31, 721.32, 618.48 cm^{-1}. Elemental analysis calcd for $C_4H_8N_{20}$ (336.12): C 14.29, H 2.40, N 83.31 %; found: C 14.25, H 2.47 N 83.25 %.

Bis(5-amino-1H-tetrazol-4-ium) (*E*)-5,5''-(diazene-1,2-diyl)bis(([1,5'-bitetrazol]-2'-ide)) (5): compound **2** (0.604g, 2 mmol) was suspended in 15 ml water at 60 °C. 5-amino-1H-tetrazole (0.3403 g, 4 mmol) was added in one portion and the mixture was stirred at this temperature for 6 h. Then the solution was cooled to 25 °C and left overnight. The solid was filtered, washed with acetonitrile and dried in air to get 0.63 g compound 5 in the yield of 66.7%. **^{1}H NMR** (500 MHz, DMSO) δ 6.16 (s, 8H) ppm. **^{13}C NMR** (126 MHz, DMSO) δ 159.4, 155.7, 153.8 ppm. **IR** (KBr): ῡ=3625.22, 3370.21, 3171.75, 2999.95, 2848.45, 2720.91, 1071.89, 1463.48, 1541.15, 1490.34, 1424.57, 1326.53, 1259.23, 1165.29, 1154.95, 1126.21, 1087.66, 1031.31, 987.68, 841.25, 748.37, 728.63, 718.20, 666.74, 618.41, 565.75. Elemental analysis calcd for $C_6H_8N_{28}$ (472.15): C 15.26, H 1.71, N 83.04 %; found: C 15.41, H 1.66, N 82.89 %.

Trihydrazinium (5,5''-(hydrazine-1-id-1,2-diyl)bis(([1,5'-bitetrazol]-2'-ide))) (6): compound **2** (0.302 g, 1mmol) was suspended in 20 ml acetonitrile and the 85 % hydrazine hydrate (0.5 g, 10 mmol) was added drop-wise at room temperature and stirred for 4 h. The precipitate was filtered was washed with acetonitrile and dried in air to get pale pink solid 0.34 g in the yield of 92.8 %. **^{1}H NMR** (500 MHz, DMSO) δ 6.23 (s, 16H) ppm. **^{13}C NMR** (126 MHz, DMSO) δ 155.6, 154.7 ppm. **IR** (KBr): ῡ= 3319.84, 3270.29, 2613.14, 1655.45, 1580.03, 1539.52, 1472.55, 1458.96, 1335.72, 1311.26, 1210.45, 1162.54, 1122.64, 1090.86, 1072.96, 1041.50, 1018.22, 976.71, 959.10, 898.61, 770.84, 736.64, 712.94, 660.49, 632.44 cm^{-1}. Elemental analysis calcd for $C_4H_{16}N_{24}$ (400.02): C 12.0, H 4.03, N 83.97 %; found: C 11.89, H 4.11, N 83.98 %.

(*E*)-1-(2'H-[1,5'-bitetrazol]-5(4H)-ylideneamino)-N-(2H-tetrazol-5-yl)-1H-tetrazol-5-amine (7): the 0.2 ml 37 % HCl was added to the solution of compound **5** (0.602g, 2 mmol) in 10ml water, the mixture was stirred for 2 h at room temperature. The solid was filtered, washed with water, acetontrile and dried in air to obtain white production 0.51 g in the yield of 83.9 %. **^{1}H NMR** (500 MHz, DMSO) δ 8.12 (br, 1H) 2.06 (s, 1H) ppm. **^{13}C NMR** (126 MHz, DMSO) δ 154.0, 153.7, 151.6, 150.2 ppm. **IR** (KBr): ῡ=3131.29, 2177.11, 2139.04, 1604.12, 1569.73, 1503.38, 1472.75, 1456.61, 1397.40, 1347.90, 1248.71, 1187.53, 1106.40, 694.80, 680.63, 664.32, 636.47. Elemental analysis calcd for $C_4H_4N_{18}$ (304.09): C 15.79, H 1.33, N 82.88 %; found: C 15.83, H 1.28, N 82.82 %.

Dimethylammonium (*E*)-5-((5-((2H-tetrazol-5-yl)amino)-1H-tetrazol-1-yl)imino)-4,5-dihydro-[1,5'-bitetrazol]-2'-ide (8): 0.304 g compound **7** (1 mmol) was dissolved in 0.2 ml DMF for 14 days at room temperature to get colourless crystal. **^{1}H NMR** (500 MHz, DMSO) δ 8.25 (s, 1H) 4.61 (s, 6H) ppm. **^{13}C NMR** (126 MHz, DMSO) δ 154.7, 153.4, 152.2, 150.5, 34.6 ppm.

Results and Discussion

Table S3. Crystallographic data for **2**, **3**·$2H_2O$, **4**·$2H_2O$, **5**·$2H_2O$, **6**, and **8**·H_2O.

Compd	**2**	**3**·$2H_2O$	**4**·$2H_2O$	**5**·$2H_2O$	**6**	**8**·H_2O
Empirical formula	$C_4H_2N_{18}$	$C_4H_2KN_{18}\cdot 2H_2O$	$C_4H_8N_{20}\cdot 2H_2O$	$C_6H_8N_{28}\cdot 4H_2O$	$C_4H_{16}N_{24}$	$C_6H_{10}N_{19}\cdot 4H_2O$
Formula weight	302.24	414.46	372.34	544.47	400.41	367.35
Temperature/K	296	296	296	296	296	296
Crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1	$P2_1/c$	P-1	P-1
a/Å	6.7578	6.7396	6.6694	23.398	7.1132	8.2241
b/Å	7.7273	7.7275	7.5568	5.4052	10.6476	8.4195
c/Å	10.6046	8.6497	8.9249	18.155	10.9222	12.477
α/°	90	100.429	114.559	90	83.385	107.695
β/°	93.283	107.356	96.129	101.790	72.037	91.553
γ/°	90	114.906	107.120	90	79.277	111.931
Volume/ $Å^3$	552.86(15)	364.70(4)	377.16(14)	2247.7	771.69(15)	753.8(2)
Z	2	2	1	4	2	2
ρ_{calc}/g cm^{-3}	1.816	1.887	1.639	1.609	1.723	1.619
F(000)	304	208	192	1120	416	380
θ range[°]	3.264-	2.638-27.638	2.601-27.634	0.889-24.998	1.964-	2.704-27.476

Index ranges	-7 ≤ h ≤ 8 -180 ≤ k ≤10 -12 ≤ l ≤ 13	-8 ≤ h ≤8 -10≤ k ≤9 -11 ≤ l ≤11	-8 ≤ h ≤ 8 -9 ≤ k ≤ 8 0 ≤ l ≤ 11	-25 ≤ h ≤ 27 -6 ≤ k ≤ 5 -21 ≤ l ≤ 21	-9 ≤ h ≤ 9 -13 ≤ k ≤ 13 -14 ≤ l ≤ 14	-10≤ h ≤ 10 -10≤ k ≤ 10 -16≤ l ≤ 16
Data/restraints/ parameters	1257/0/100	1679/0/124	1745/13/136	3958/0/355	3520/0/256	3417/0/237
GOF on F^2	1.037	1.024	1.066	1.012	1.052	1.061
$R[F^2 > 2\sigma(F^2)]$	0.0349	0.0293	0.0673	0.0574	0.0526	0.0398
$wR(F^2)$	0.0868	0.0724	0.1332	0.0152	0.1450	0.0936
CCDC number	2008382	2013111	2013110	2015888	2020075	2020073

Table S4 Bond lengths (Å) for **2**.

C1-N1	1.3116(17)	N2-N3	1.2985(19)
C1-N4	1.3256(19)	N2-H2	0.8600
C1-N8	1.4098(15)	N3-N4	1.3228(16)
C2-N7	1.3104(16)	N5-N6	1.2929(15)
C2-N8	1.3441(15)	N5-N8	1.3508(15)
C2-N9	1.4028(17)	N6-N7	1.3579(16)
N1-N2	1.3161(15)	N9-N9	1.245(2)

Table S5 Bond angles (°) for **2**.

N1-C1-N4	114.86(12)	N2-N3-N4	106.02(11)
N1-C1-N8	122.46(12)	N3-N4-C1	104.32(12)
N4-C1-N8	122.69(12)	N6-N5-N8	105.91(10)
N7-C2-N8	108.82(11)	N5-N6-N7	111.39(11)
N7-C2-N9	130.25(11)	C2-N7-N6	105.64(11)
N8-C2-N9	120.85(11)	C2-N8-N5	108.23(10)
C1-N1-N2	99.74(11)	C2-N8-C1	130.03(11)
N3-N2-N1	115.06(11)	N5-N8-C1	121.72(10)
N3-N2-H2	122.5	N9-N9-C2	111.22(13)
N1-N2-H2	122.5		

Table S6. Hydrogen bonds in **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...N7	0.86	2.10	2.8483(16)	145.6

Table S7 Bond lengths (Å) for **3·2H_2O**.

C1-N4	1.3172(19)	K1-N8	3.0541(14)
C1-N1	1.3235(19)	K1-N4	3.2994(14)
C1-N5	1.4140(19)	K1-K1	4.1741(7)
C2-N8	1.316(2)	N1-N2	1.350(2)
C2-N5	1.3481(18)	N2-N3	1.307(2)

C2-N9	1.3987(19)	N3-N4	1.3538(19)
K1-O1	2.8174(15)	N5-N6	1.3466(17)
K1-O1	2.8408(14)	N6-N7	1.3015(19)
K1-N2	2.9046(14)	N7-N8	1.3505(18)
K1-N7	2.9964(14)	N9-N9	1.236(2)
K1-N1	3.0256(14)	O1-H1A	0.79(3)
K1-N6	3.0289(13)	O1-H1B	0.84(3)

Table S8 Bond angles (°) for **3·2H$_2$O**.

N4-C1-N1	114.73(13)	N2-K1-K1	123.08(3)
N4-C1-N5	123.97(13)	N7-K1-K1	65.44(3)
N1-C1-N5	121.29(13)	N1-K1-K1	109.65(3)
N8-C2-N5	109.51(13)	N6-K1-K1	56.14(3)
N8-C2-N9	129.37(13)	N8-K1-K1	141.83(3)
N5-C2-N9	121.10(13)	N4-K1-K1	96.79(3)
O1-K1-O1	84.93(4)	C1-N1-N2	102.75(13)
O1-K1-N2	85.33(4)	C1-N1-K1	116.38(10)
O1-K1-N2	151.98(4)	N2-N1-K1	132.46(10)
O1-K1-N7	69.97(4)	N3-N2-N1	109.95(12)
O1-K1-N7	74.27(4)	N3-N2-K1	128.06(10)
N2-K1-N7	77.71(4)	N1-N2-K1	114.66(10)
O1-K1-N1	94.27(4)	N2-N3-N4	109.69(13)
O1-K1-N1	114.85(4)	C1-N4-N3	102.87(12)
N2-K1-N1	92.04(4)	C1-N4-K1	132.95(10)
N7-K1-N1	161.62(4)	N3-N4-K1	107.69(9)
O1-K1-N6	63.43(4)	N6-N5-C2	107.26(12)
O1-K1-N6	67.96(4)	N6-N5-C1	120.31(12)
N2-K1-N6	129.09(4)	C2-N5-C1	132.40(12)
N7-K1-N6	121.17(4)	N7-N6-N5	106.71(11)
N1-K1-N6	54.69(4)	N7-N6-K1	130.64(9)
O1-K1-N8	145.47(4)	N5-N6-K1	115.92(9)
O1-K1-N8	109.76(4)	N6-N7-N8	111.16(12)
N2-K1-N8	66.93(4)	N6-N7-K1	103.61(8)
N7-K1-N8	83.81(4)	N8-N7-K1	144.73(10)
N1-K1-N8	106.37(4)	C2-N8-N7	105.36(12)
N6-K1-N8	150.78(4)	C2-N8-K1	117.69(10)
O1-K1-N4	127.60(4)	N7-N8-K1	118.39(9)
O1-K1-N4	64.44(4)	N9-N9-C2	111.99(16)
N2-K1-N4	139.55(4)	K1-O1-K1	95.07(4)
N7-K1-N4	131.18(4)	K1-O1-H1A	117.1(18)

N1-K1-N4	65.83(4)	K1-O1-H1A	112.4(18)
N6-K1-N4	65.86(4)	K1-O1-H1B	118.3(16)
N8-K1-N4	86.55(4)	K1-O1-H1B	108.4(17)
O1-K1-K1	42.68(3)	H1A-O1-H1B	105(2)
O1-K1-K1	42.25(3)		

Table S9. Hydrogen bonds in **3·2H$_2$O**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1A...N4	0.79(3)	2.32(3)	3.0827(19)	163(2)
O1-H1B...N3	0.84(3)	2.19(3)	2.938(2)	149(2)

Table S10 Bond lengths (Å) for **4·2H$_2$O**.

C1-N4	1.309(3)	N6-N7	1.292(3)
C1-N1	1.318(3)	N7-N8	1.351(3)
C1-N5	1.413(3)	N9-N9	1.216(4)
C2-N8	1.310(3)	N10-H10A	0.899(14)
C2-N5	1.349(3)	N10-H10B	0.937(14)
C2-N9	1.401(3)	N10-H10C	0.883(14)
N1-N2	1.350(3)	N10-H10D	0.897(14)
N2-N3	1.301(3)	O1-H1A	0.879(18)
N3-N4	1.348(3)	O1-H1B	0.873(18)
N5-N6	1.352(3)		

Table S11 Bond angles (°) for **4·2H$_2$O**.

N4-C1-N1	114.5(2)	N6-N5-C1	120.38(18)
N4-C1-N5	123.5(2)	N7-N6-N5	106.47(18)
N1-C1-N5	122.0(2)	N6-N7-N8	111.5(2)
N8-C2-N5	109.4(2)	C2-N8-N7	105.4(2)
N8-C2-N9	129.4(2)	N9-N9-C2	113.4(3)
N5-C2-N9	121.1(2)	H10A-N10-H10B	104.8(18)
C1-N1-N2	102.9(2)	H10A-N10-H10C	109.3(18)
N3-N2-N1	109.8(2)	H10B-N10-H10C	107.6(18)
N2-N3-N4	109.5(2)	H10A-N10-H10D	114.2(18)
C1-N4-N3	103.3(2)	H10B-N10-H10D	107.3(17)
C2-N5-N6	107.17(19)	H10C-N10-H10D	113.1(19)
C2-N5-C1	132.5(2)	H1A-O1-H1B	107(2)

Table S12 Hydrogen bonds in **4·2H$_2$O**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N10-H10A...N3	0.899(14)	2.670(19)	3.376(3)	136.1(18)
N10-H10A...N4	0.899(14)	2.017(15)	2.893(3)	165(2)
N10-H10B...O1	0.937(14)	1.954(14)	2.881(3)	170(2)

N10-H10C...N3	0.883(14)	2.316(17)	3.096(3)	147(2)
N10-H10C...N8	0.883(14)	2.48(2)	2.976(3)	116.2(18)
N10-H10D...O1	0.897(14)	2.012(15)	2.892(3)	167(2)
O1-H1A...N1	0.879(18)	2.061(19)	2.923(3)	166(4)
O1-H1B...N2	0.873(18)	2.14(2)	2.975(3)	160(3)

Table S13 Bond lengths (Å) for **5·2H$_2$O**.

C1-N1	1.304(4)	N12-N13	1.346(4)
C1-N4	1.322(4)	N14-N15	1.358(3)
C1-N5	1.414(4)	N15-N16	1.301(3)
C2-N8	1.310(4)	N16-N17	1.360(3)
C2-N5	1.353(4)	N18-N18	1.265(5)
C2-N9	1.414(4)	N19-H19A	0.8600
C3-N10	1.315(4)	N19-H19B	0.8600
C3-N13	1.325(4)	N20-N21	1.362(4)
C3-N14	1.410(4)	N20-H20	0.8600
C4-N17	1.324(4)	N21-N22	1.271(4)
C4-N14	1.348(4)	N22-N23	1.360(4)
C4-N18	1.404(4)	N23-H23	0.8600
C5-N19	1.289(4)	N25-H25A	0.8600
C5-N23	1.338(4)	N25-H25B	0.8600
C5-N20	1.339(4)	N27-N28	1.271(4)
C6-N25	1.309(4)	N27-N30	1.355(4)
C6-N29	1.332(4)	N28-N29	1.357(4)
C6-N30	1.341(4)	N29-H29	0.8600
N1-N2	1.348(4)	N30-H30	0.8600
N2-N3	1.313(3)	O1-H1A	0.8501
N3-N4	1.337(3)	O1-H1B	0.8499
N5-N6	1.352(3)	O2-H2A	0.8498
N6-N7	1.300(4)	O2-H2B	0.8500
N7-N8	1.358(3)	O3-H3A	0.8501
N9-N9	1.257(5)	O3-H3B	0.8501
N10-N11	1.349(3)	O4-H4A	0.8501
N11-N12	1.310(3)	O4-H4B	0.8501

Table S14 Bond angles (°) for **5·2H$_2$O.**

N1-C1-N4	114.0(3)	C4-N14-N15	107.6(3)
N1-C1-N5	124.4(3)	C4-N14-C3	133.7(3)
N4-C1-N5	121.5(3)	N15-N14-C3	118.7(3)

N8-C2-N5	109.1(3)	N16-N15-N14	106.6(2)
N8-C2-N9	129.8(3)	N15-N16-N17	111.1(2)
N5-C2-N9	121.1(3)	C4-N17-N16	105.6(3)
N10-C3-N13	113.8(3)	N18-N18-C4	112.0(3)
N10-C3-N14	125.0(3)	C5-N19-H19A	120.0
N13-C3-N14	121.2(3)	C5-N19-H19B	120.0
N17-C4-N14	109.2(3)	H19A-N19-H19B	120.0
N17-C4-N18	129.5(3)	C5-N20-N21	111.0(3)
N14-C4-N18	121.3(3)	C5-N20-H20	124.5
N19-C5-N23	128.3(3)	N21-N20-H20	124.5
N19-C5-N20	128.7(3)	N22-N21-N20	107.3(3)
N23-C5-N20	103.1(3)	N21-N22-N23	108.0(3)
N25-C6-N29	128.3(3)	C5-N23-N22	110.7(3)
N25-C6-N30	128.1(3)	C5-N23-H23	124.7
N29-C6-N30	103.6(3)	N22-N23-H23	124.7
C1-N1-N2	103.4(3)	C6-N25-H25A	120.0
N3-N2-N1	109.8(3)	C6-N25-H25B	120.0
N2-N3-N4	108.9(3)	H25A-N25-H25B	120.0
C1-N4-N3	103.9(2)	N28-N27-N30	108.2(3)
N6-N5-C2	107.3(2)	N27-N28-N29	107.5(3)
N6-N5-C1	119.1(3)	C6-N29-N28	110.6(3)
C2-N5-C1	133.6(3)	C6-N29-H29	124.7
N7-N6-N5	106.9(2)	N28-N29-H29	124.7
N6-N7-N8	110.5(2)	C6-N30-N27	110.0(3)
C2-N8-N7	106.2(3)	C6-N30-H30	125.0
N9-N9-C2	111.5(3)	N27-N30-H30	125.0
C3-N10-N11	103.5(2)	H1A-O1-H1B	104.5
N12-N11-N10	109.7(2)	H2A-O2-H2B	104.5
N11-N12-N13	109.4(2)	H3A-O3-H3B	104.5
C3-N13-N12	103.6(3)	H4A-O4-H4B	104.5

Table S15. Hydrogen bonds in **5·2H$_2$O**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N19-H19A...O4	0.86	1.94	2.789(4)	168.8
N19-H19B...N4	0.86	2.05	2.906(4)	177.0
N20-H20...O3	0.86	1.89	2.736(4)	166.2
N23-H23...N2	0.86	1.98	2.823(4)	167.5
N25-H25A...N13	0.86	2.13	2.981(4)	168.4
N25-H25B...O1	0.86	1.94	2.780(3)	166.4

N29-H29...O2	0.86	2.01	2.763(4)	146.2
N30-H30...N11	0.86	2.05	2.897(4)	169.5

Table S16 Bond lengths (Å) for **6**.

C1-N1	1.324(2)	N13-N14	1.3751(19)
C1-N4	1.325(2)	N15-N16	1.350(2)
C1-N5	1.3872	N16-N17	1.308(2)
C2-N9	1.317(2)	N17-N18	1.350(2)
C2-N8	1.355(2)	N19-N20	1.441(2)
C2-N5	1.368(2)	N19-H19A	0.8900
C3-N10	1.326(2)	N19-H19B	0.8900
C3-N11	1.329(2)	N20-H20A	0.8900
C3-N14	1.359(2)	N20-H20B	0.8900
C4-N18	1.320(2)	N20-H20C	0.8900
C4-N15	1.321(2)	N21-N22	1.445(2)
C4-N14	1.397(2)	N21-H21A	0.8900
N1-N2	1.3584(19)	N21-H21B	0.8900
N2-N3	1.302(2)	N22-H22A	0.8900
N3-N(4	1.340(2)	N22-H22B	0.8900
N5-N6	1.3904(19)	N22-H22C	0.8900
N6-N7	1.277(2)	N23-N24	1.430(2)
N7-N8	1.363(2)	N23-H23A	0.8900
N9-N10	1.4119(19)	N23-H23B	0.8900
N10-H10	0.8600	N23-H23C	0.8900
N11-N12	1.366(2)	N24-H24A	0.8900
N12-N13	1.278(2)	N24-H24B	0.8900

Table S17 Bond angles (°) for **6**.

N1-C1-N4	113.50(14)	C4-N15-N16	102.94(15)
N1-C1-N5	124.29(15)	N17-N16-N15	110.04(14)
N4-C1-N5	122.20(14)	N16-N17-N18	109.38(15)
N9-C2-N8	128.80(15)	C4-N18-N17	103.34(14)
N9-C2-N5	124.63(14)	N20-N19-H19A	109.4
N8-C2-N5	106.56(14)	N20-N19-H19B	109.4
N10-C3-N11	127.55(15)	H19A-N19-H19B	109.5
N10-C3-N14	123.75(15)	N19-N20-H20A	109.5
N11-C3-N14	108.68(14)	N19-N20-H20B	109.5
N18-C4-N15	114.29(15)	H20A-N20-H20B	109.5
N18-C4-N14	121.02(15)	N19-N20-H20C	109.5
N15-C4-N14	124.68(15)	H20A-N20-H20C	109.5

C1-N1-N2	102.86(13)	H20B-N20-H20C	109.5
N3-N2-N1	110.08(13)	N22-N21-H21A	109.1
N2-N3-N4	109.49(14)	N22-N21-H21B	109.3
C1-N4-N3	104.07(14)	H21A-N21-H21B	109.5
C2-N5-C1	131.03(14)	N21-N22-H22A	109.5
C2-N5-N6	108.55(13)	N21-N22-H22B	109.5
C1-N5-N6	119.72(13)	H22A-N22-H22B	109.5
N7-N6-N5	105.89(14)	N21-N22-H22C	109.5
N6-N7-N8	112.58(14)	H22A-N22-H22C	109.5
C2-N8-N7	106.42(14)	H22B-N22-H22C	109.5
C2-N9-N10	108.12(13)	N24-N23-H23A	109.5
C3-N10-N9	118.69(14)	N24-N23-H23B	109.5
C3-N10-H10	120.7	H23A-N23-H23B	109.5
N9-N10-H10	120.7	N24-N23-H23C	109.5
C3-N11-N12	104.88(13)	H23A-N23-H23C	109.5
N13-N12-N11	112.96(14)	H23B-N23-H23C	109.5
N12-N13-N14	105.66(13)	N23-N24-H24A	109.3
C3-N14-N13	107.79(13)	N23-N24-H24B	109.3
C3-N14-C4	128.33(14)	H24A-N24-H24B	109.5
N13-N14-C4	123.88(14)		

Table S18. Hydrogen bonds in **6**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N24-H24B...N17	0.89	2.51	3.175(2)	131.6
N24-H24A...N18	0.89	2.31	3.102(2)	148.1
N24-H24A...N17	0.89	2.35	3.222(2)	165.7
N23-H23C...N19	0.89	2.06	2.901(2)	156.7
N23-H23C...N11	0.89	2.63	3.094(2)	113.5
N23-H23B...N8	0.89	1.99	2.842(2)	158.9
N23-H23A...N9	0.89	2.66	3.141(2)	115.1
N23-H23A...N1	0.89	2.16	3.012(2)	160.1
N22-H22C...N24	0.89	2.03	2.919(2)	177.2
N22-H22B...N3	0.89	2.63	3.307(2)	133.4
N22-H22B...N2	0.89	2.06	2.918(2)	161.3
N22-H22A...N9	0.89	2.03	2.910(2)	169.4
N21-H21B...N11	0.89	2.41	3.218(2)	151.3
N21-H21A...N3	0.89	2.59	3.238(2)	130.3
N20-H20C...N21	0.89	2.11	2.940(2)	155.0
N20-H20C...N13	0.89	2.66	3.088(2)	110.6

N20-H20B...N4	0.89	1.94	2.831(2)	176.7
N20-H20A...N12	0.89	2.11	2.944(2)	156.4
N20-H20A...N11	0.89	2.68	3.306(2)	128.0
N19-H19B...N15	0.89	2.34	3.190(2)	159.7
N19-H19A...N16	0.89	2.18	3.055(2)	168.0
N10-H10...N18	0.86	2.23	2.828(2)	127.0

Table S19 Bond lengths (Å) for **8·H_2O**.

C1-N4	1.3185(16)	N1-N2	1.3533(15)
C1-N1	1.3185(17)	N2-N3	1.3032(17)
C1-N5	1.4018(16)	N3-N4	1.3458(16)
C2-N(9	1.2959(17)	N5-N6	1.3777(16)
C2-N8	1.3593(17)	N6-N7	1.2642(17)
C2-N5	1.3754(15)	N7-N8	1.3549(17)
C3-N13	1.3239(16)	N8-H8	0.8600
C3-N10	1.3421(16)	N9-N10	1.3854(14)
C3-N14	1.3541(17)	N10-N11	1.3596(15)
C4-N15	1.3258(17)	N11-N12	1.2941(16)
C4-N18	1.3415(18)	N12-N13	1.3607(16)
C4-N14	1.3778(17)	N14-H14	0.8600
C5-N19	1.467(2)	N15-N16	1.3328(16)
C5-H5A	0.9600	N16-N17	1.3028(17)
C5-H5B	0.9600	N16-H16	0.8600
C5-H5C	0.9600	N17-N18	1.3223(17)
C6-N19	1.466(2)	N19-H19A	0.8900
C6-H6A	0.9600	N19-H19B	0.8900
C6-H6B	0.9600	O1-H1B	0.9269
C6-H6C	0.9600	O1-H1A	0.9159

Table S20 Bond angles (°) for **8·H_2O**.

N4-C1-N1	113.91(11)	N6-N5-C1	118.02(10)
N4-C1-N5	120.58(11)	N7-N6-N5	107.72(11)
N1-C1-N5	125.50(11)	N6-N7-N8	109.00(11)
N9-C2-N8	134.25(12)	N7-N8-C2	111.13(11)
N9-C2-N5	123.78(11)	N7-N8-H8	124.4
N8-C2-N5	101.97(11)	C2-N8-H8	124.4
N13-C3-N10	108.48(11)	C2-N9-N10	114.37(10)
N13-C3-N14	128.75(12)	C3-N10-N11	108.52(10)
N10-C3-N14	122.76(11)	C3-N10-N9	124.03(10)

N15-C4-N18	113.26(12)	N11-N10-N9	127.37(10)
N15-C4-N14	125.91(12)	N12-N11-N10	105.87(10)
N18-C4-N14	120.82(11)	N11-N12-N13	111.43(11)
N19-C5-H5A	109.5	C3-N13-N12	105.70(11)
N19-C5-H5B	109.5	C3-N14-C4	122.78(11)
H5A-C5-H5B	109.5	C3-N14-H14	118.6
N19-C5-H5C	109.5	C4-N14-H14	118.6
H5A-C5-H5C	109.5	C4-N15-N16	100.62(11)
H5B-C5-H5C	109.5	N17-N16-N15	114.37(11)
N19-C6-H(6A	109.5	N17-N16-H16	122.8
N19-C6-H6B	109.5	N15-N16-H16	122.8
H6A-C6-H6B	109.5	N16-N17-N18	106.44(11)
N19-C6-H6C	109.5	N17-N18-C4	105.31(11)
H6A-C6-H6C	109.5	C6-N19-C5	113.96(13)
H6B-C6-H6C	109.5	C6-N19-H19A	108.8
C1-N1-N2	103.39(11)	C5-N19-H19A	108.8
N3-N2-N1	109.34(11)	C6-N19-H19B	108.8
N2-N3-N4	109.95(11)	C5-N19-H19B	108.8
C1-N4-N3	103.40(11)	H19A-N19-H19B	107.7
C2-N5-N6	110.18(10)	H1B-O1-H1A	106.0
C2-N5-C1	131.80(11)		

Table S21. Hydrogen bonds in **8·H_2O**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C5-H5B...O1	0.96	2.49	3.395(2)	156.0
N19-H19A...N4	0.89	2.05	2.9209(17)	164.4
N19-H19B...N13	0.89	2.19	2.9125(17)	138.1
N19-H19B...N15	0.89	2.28	2.9992(17)	137.5
C6-H6C...N17	0.96	2.66	3.373(2)	131.8
N8-H8...N11	0.86	2.16	2.6829(16)	118.4
N8-H8...N2	0.86	2.23	2.9044(17)	135.6
N14-H14...O1	0.86	1.98	2.8043(15)	159.8
N16-H16...N3	0.86	2.04	2.8720(17)	164.0
O1-H1A...N12	0.92	2.29	3.1847(17)	164.1
O1-H1B...N1	0.93	1.96	2.8805(16)	175.6

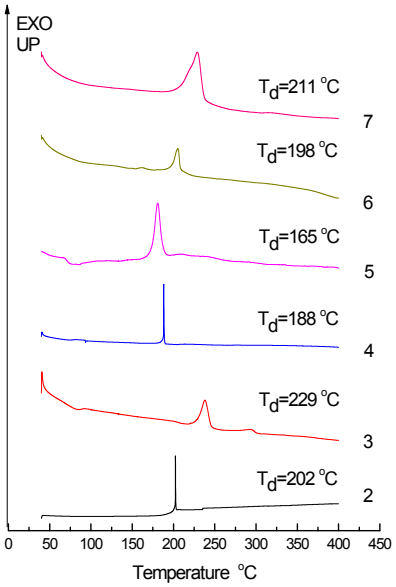


Figure S3 DSC plots for compounds **2**-**7**.

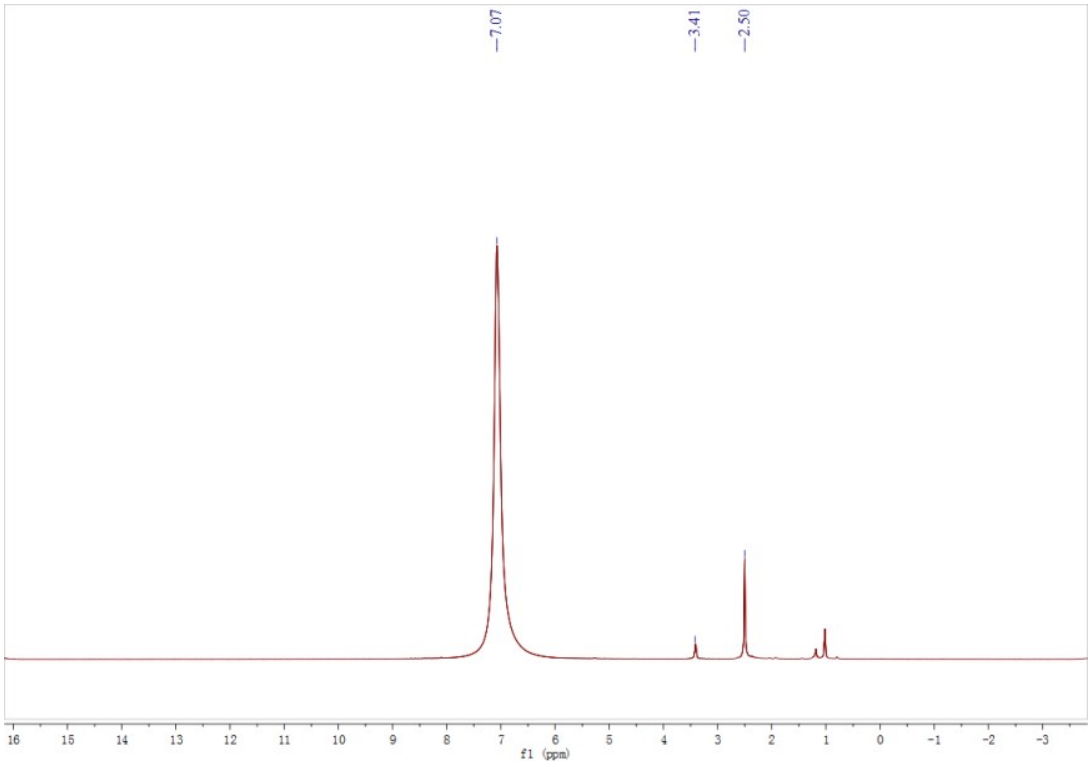


Figure S4 ^{1}HNMR spectra for compounds **2**.

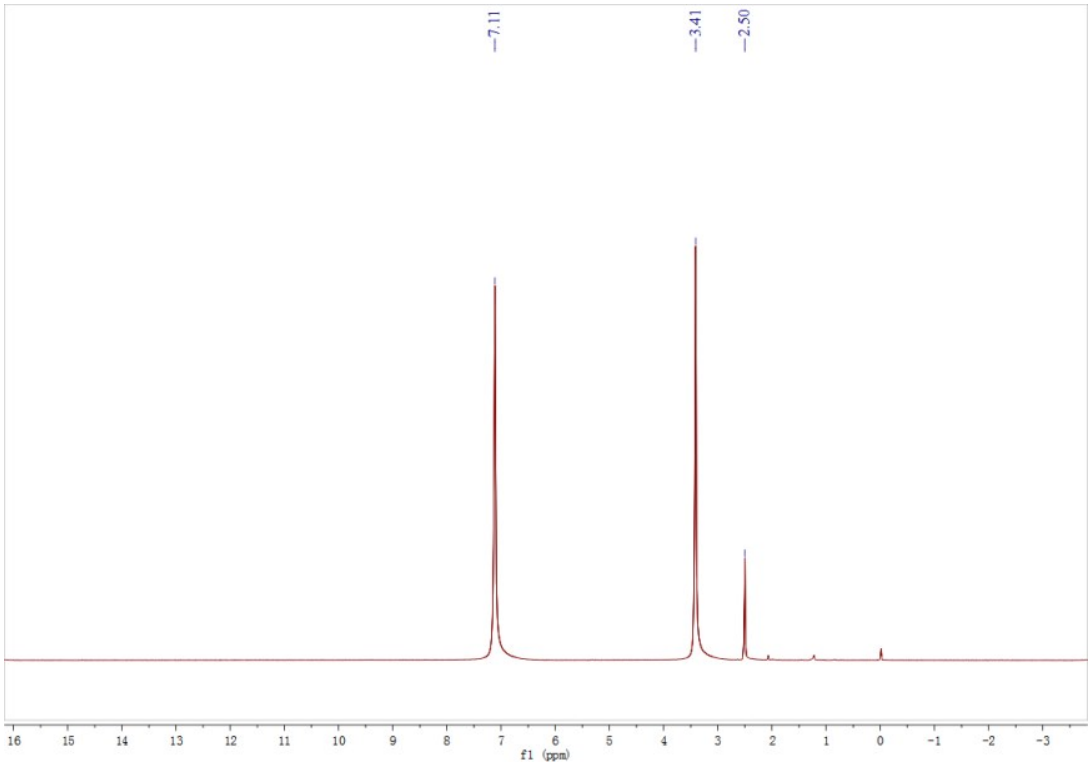


Figure S5 [1]HNMR spectra for compounds **4**.

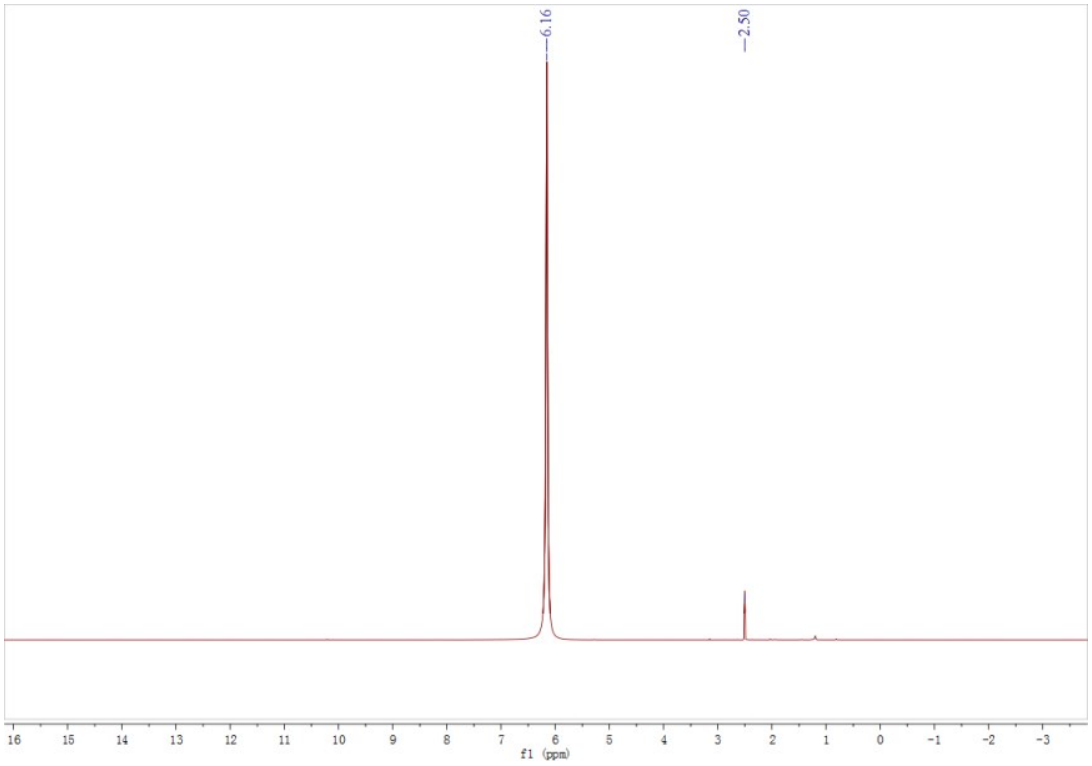


Figure S6 [1]HNMR spectra for compounds **5**.

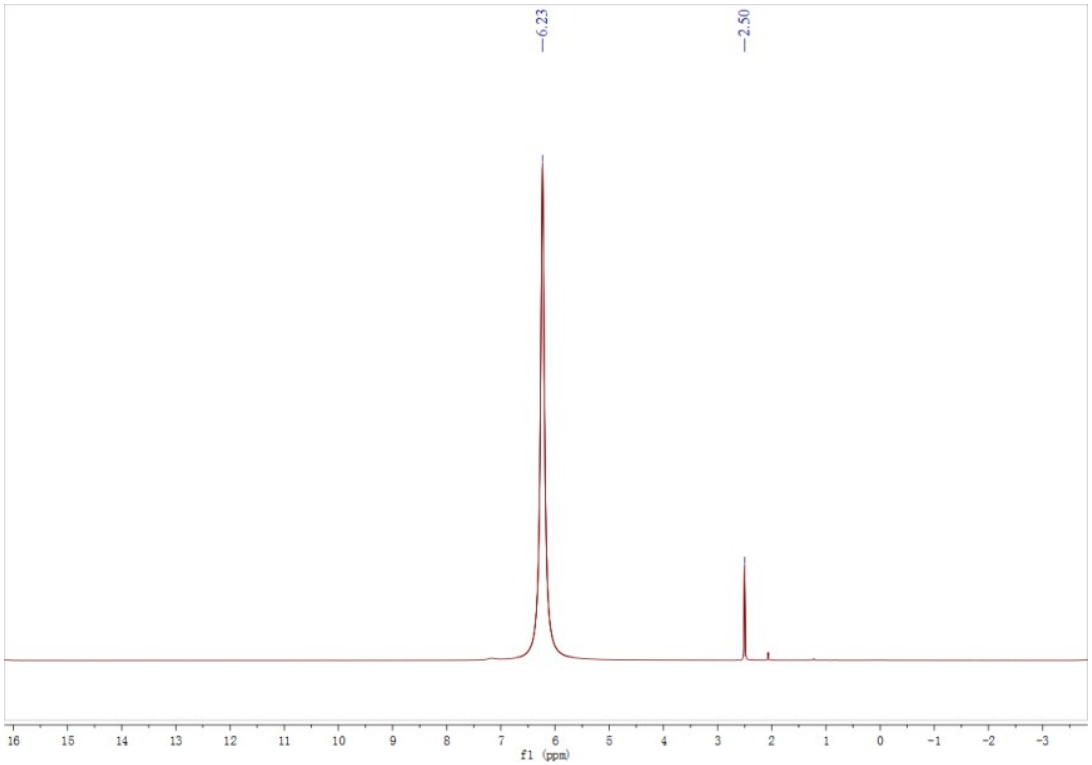


Figure S7 ^{1}HNMR spectra for compounds **6**.

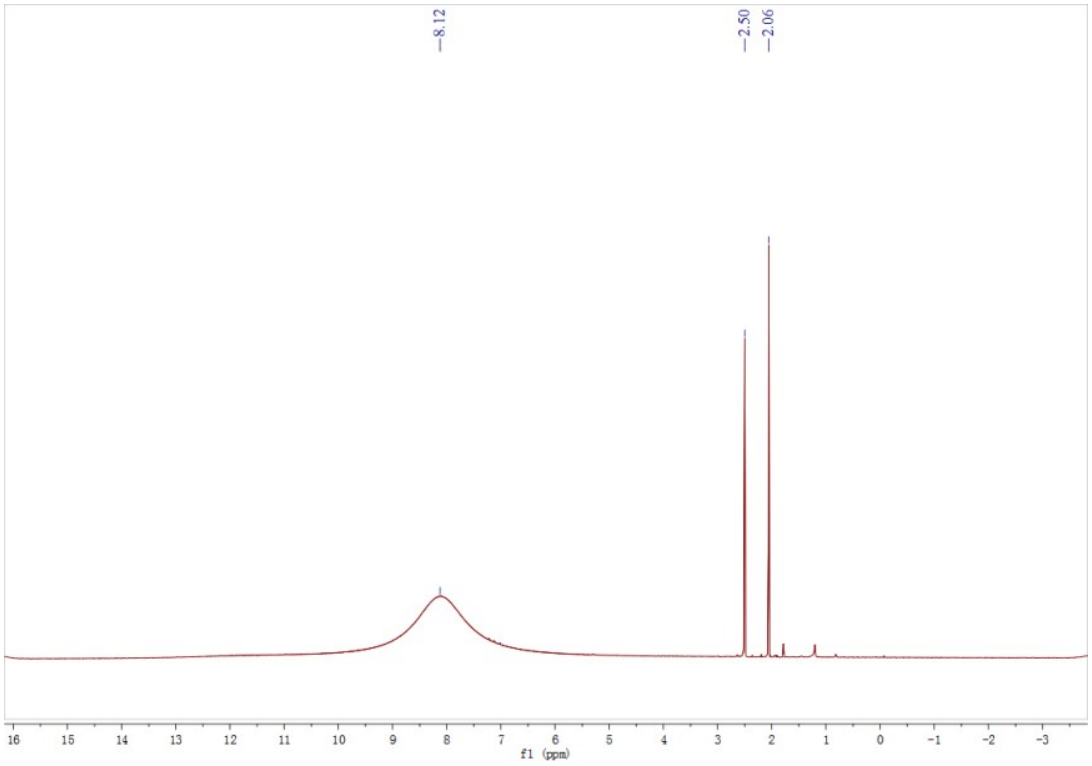


Figure S8 ^{1}HNMR spectra for compounds **7**.

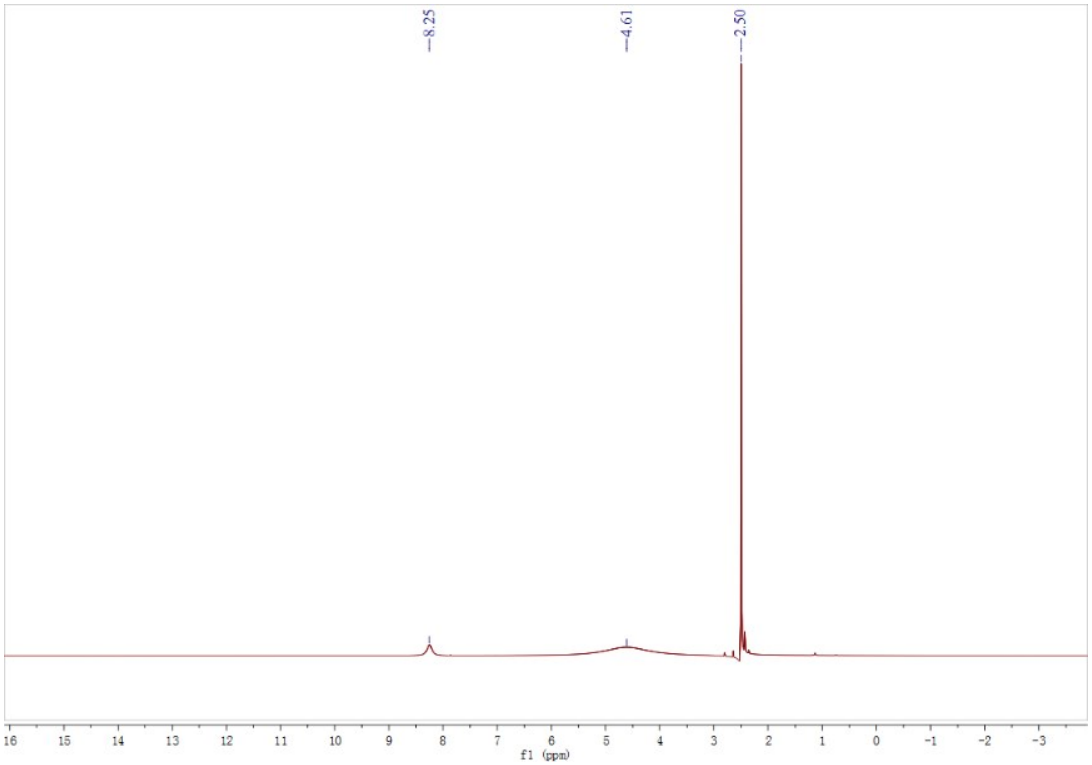


Figure S9 [1]HNMR spectra for compounds **8**.

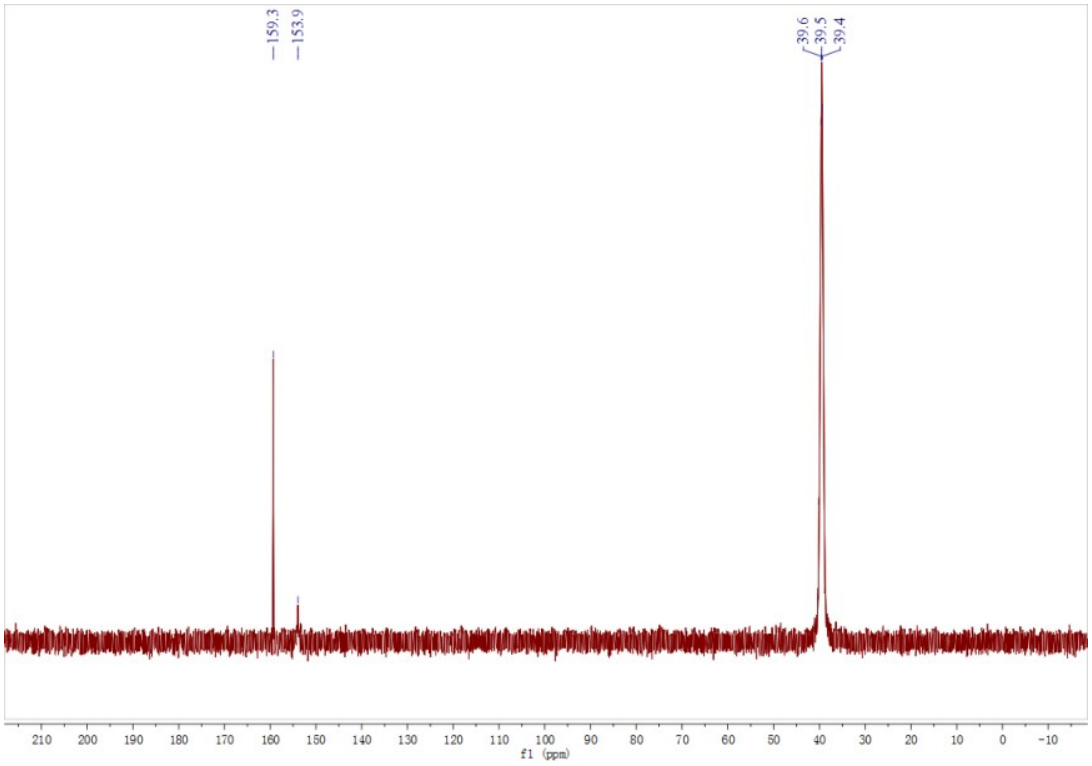


Figure S9 [13]CNMR spectra for compounds **2**.

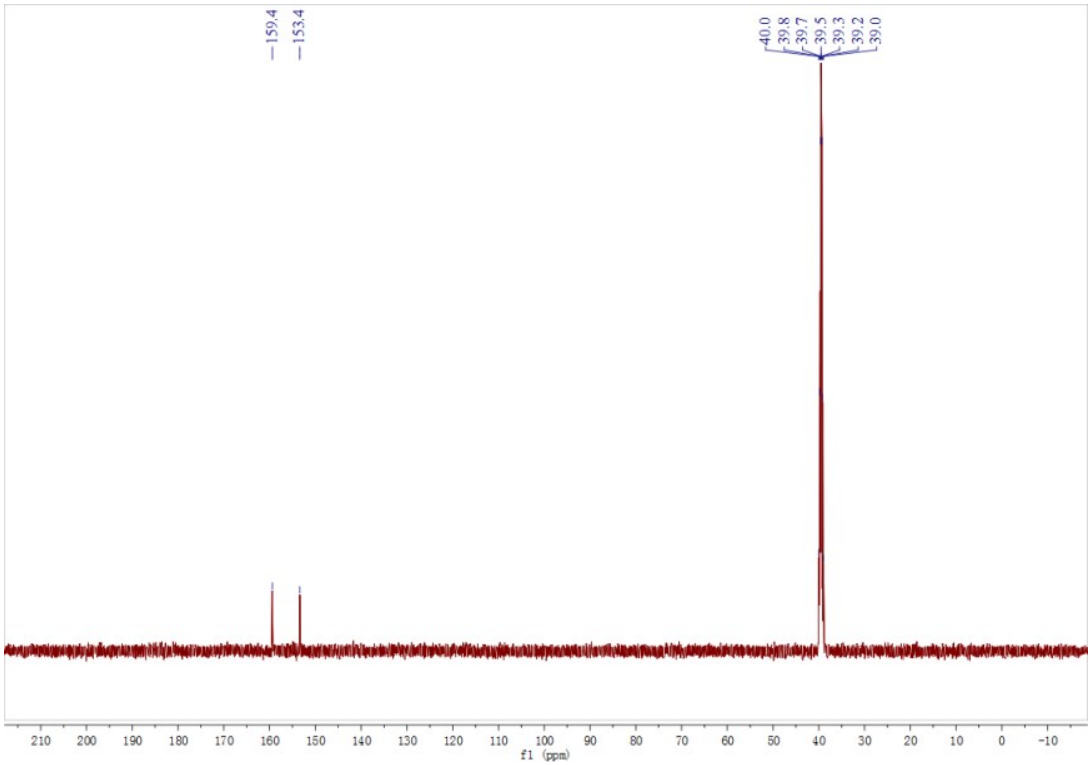


Figure S10 ^{13}CNMR spectra for compounds **3**.

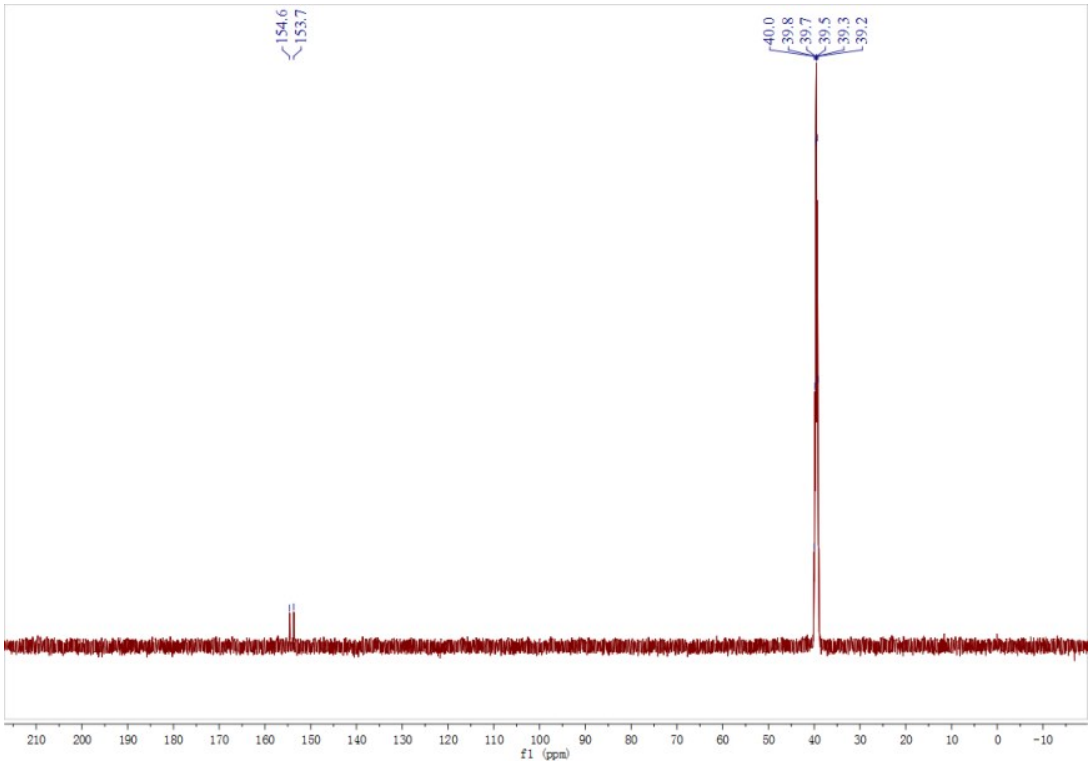


Figure S11 ^{13}CNMR spectra for compounds **4**.

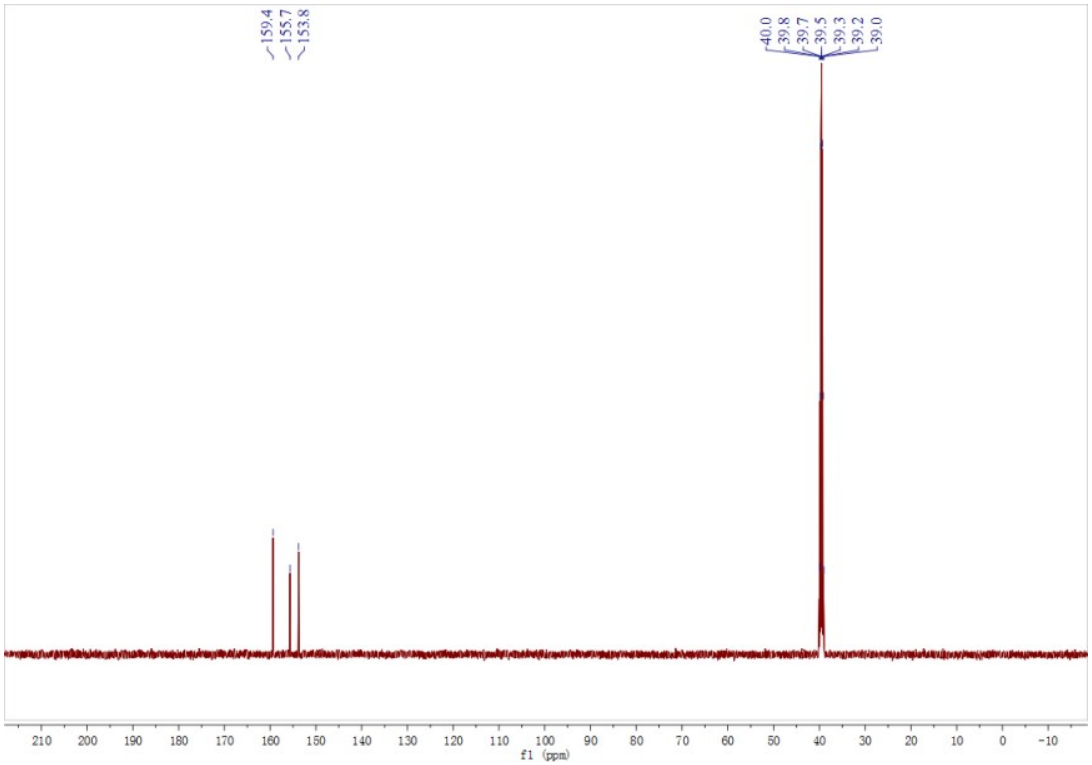


Figure S12 ^{13}CNMR spectra for compounds **5**.

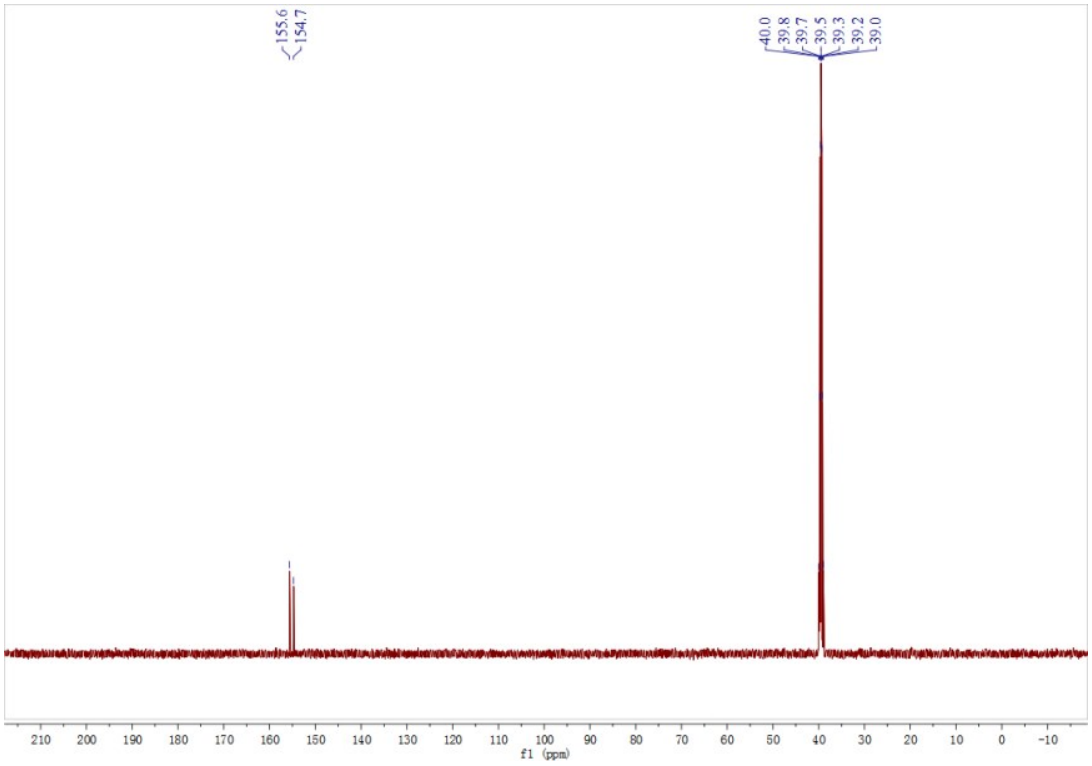


Figure S13 ^{13}CNMR spectra for compounds **6**.

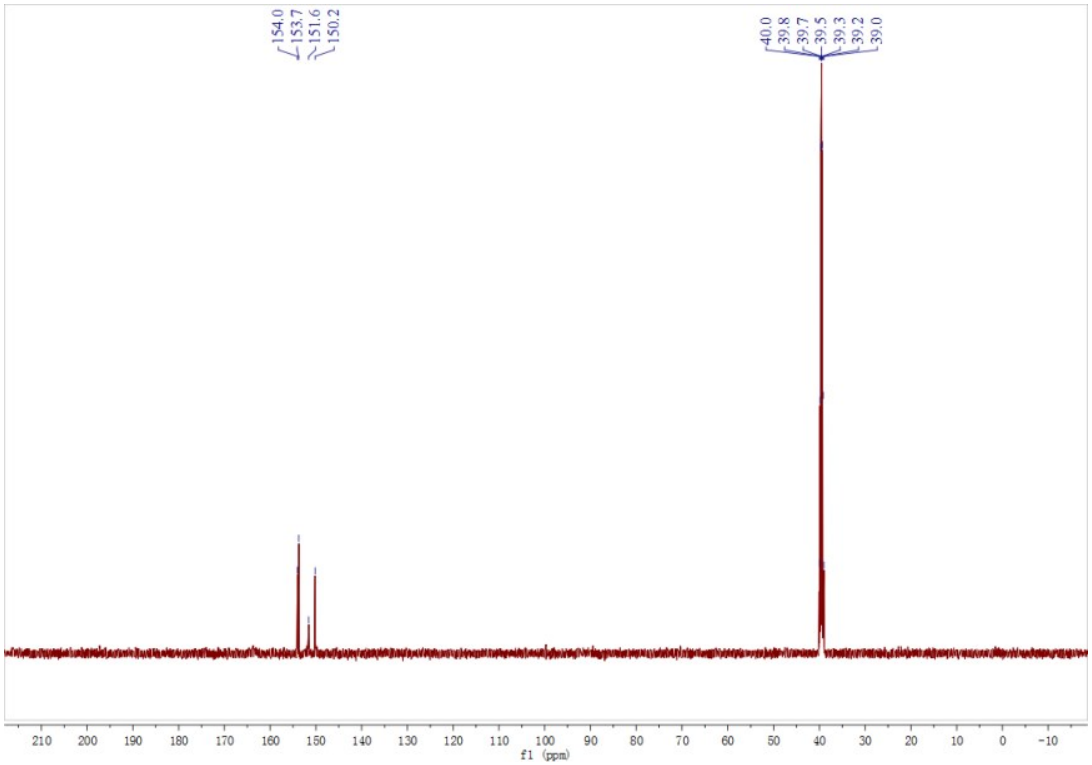


Figure S14 ^{13}CNMR spectra for compounds **7**.

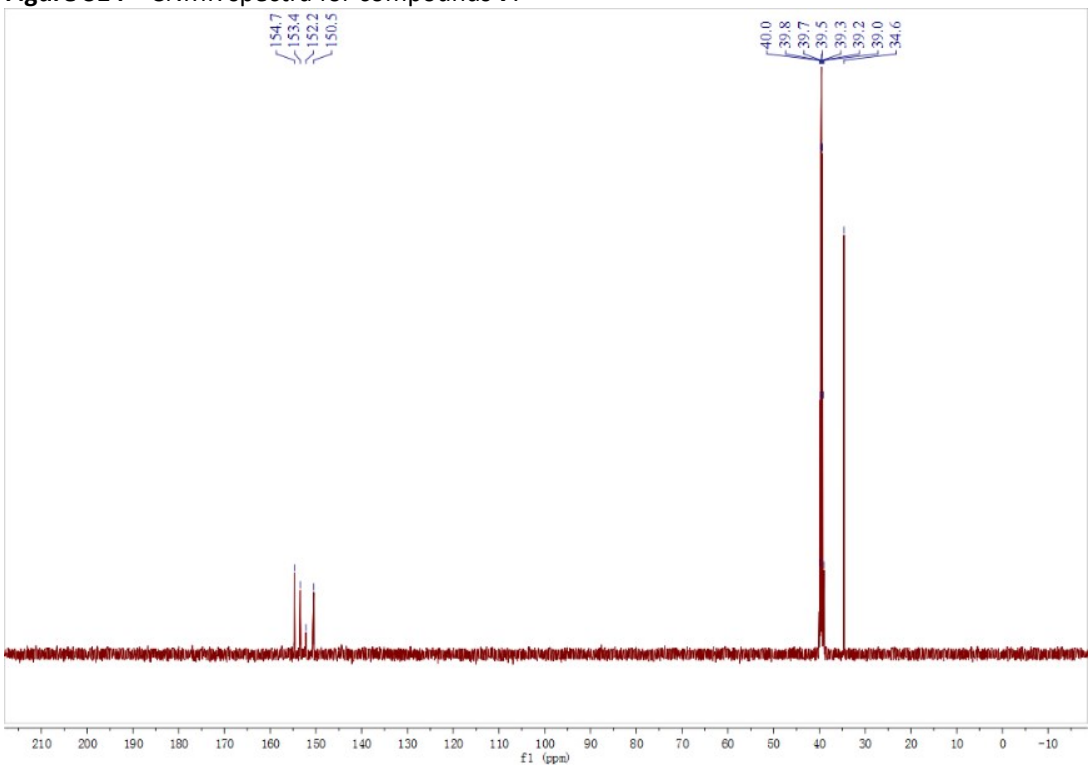


Figure S15 ^{13}CNMR spectra for compounds **8**.

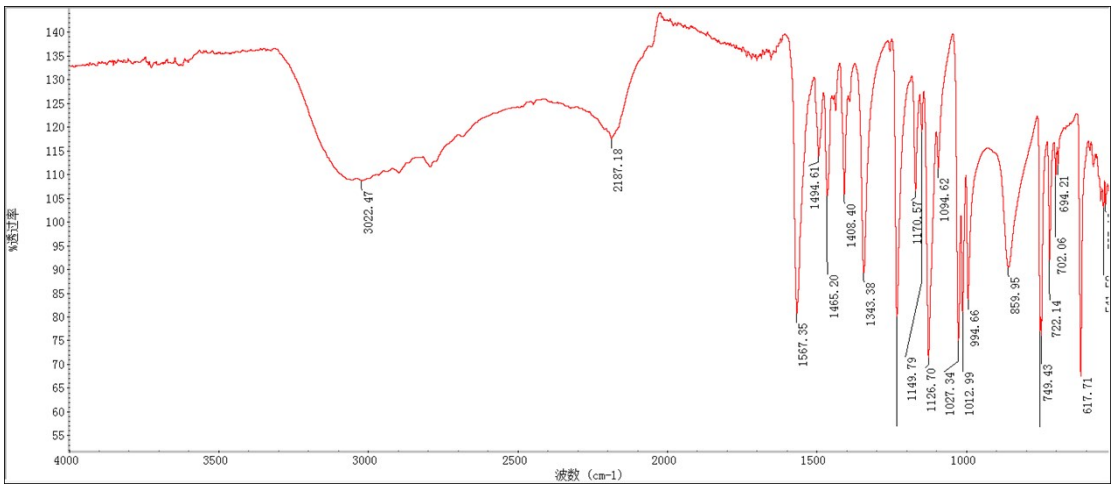


Figure S16 IR spectra for **2**.

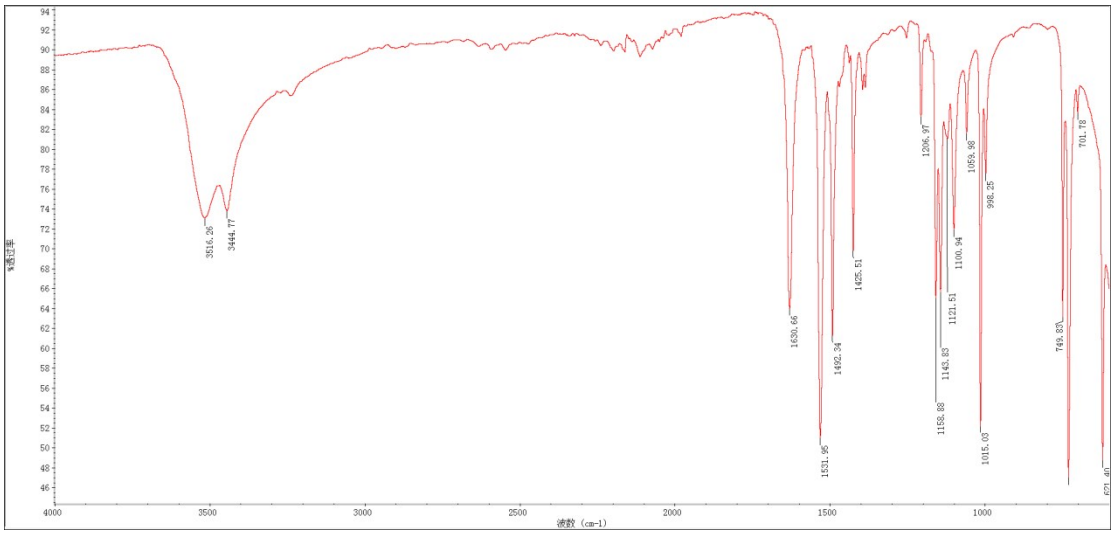


Figure S17 IR spectra for **3**.

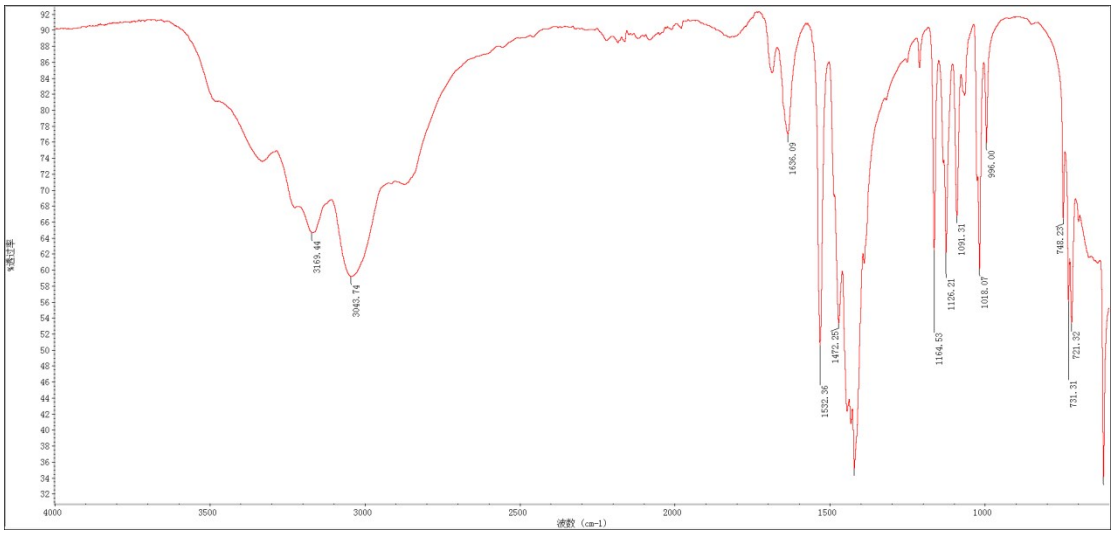


Figure S18 IR spectra for **4**.

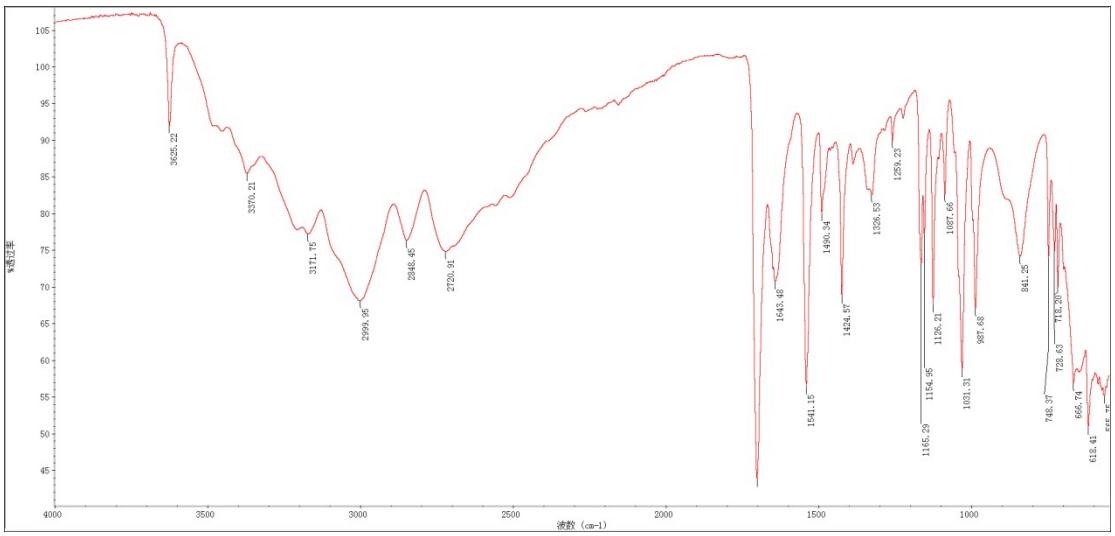


Figure S19 IR spectra for **5**.

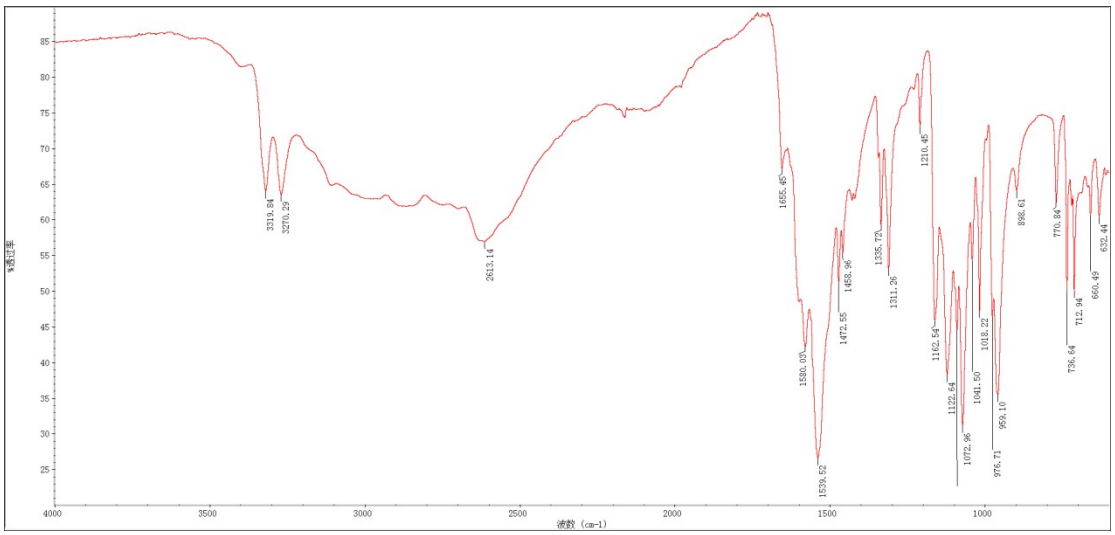


Figure S20 IR spectra for **6**.

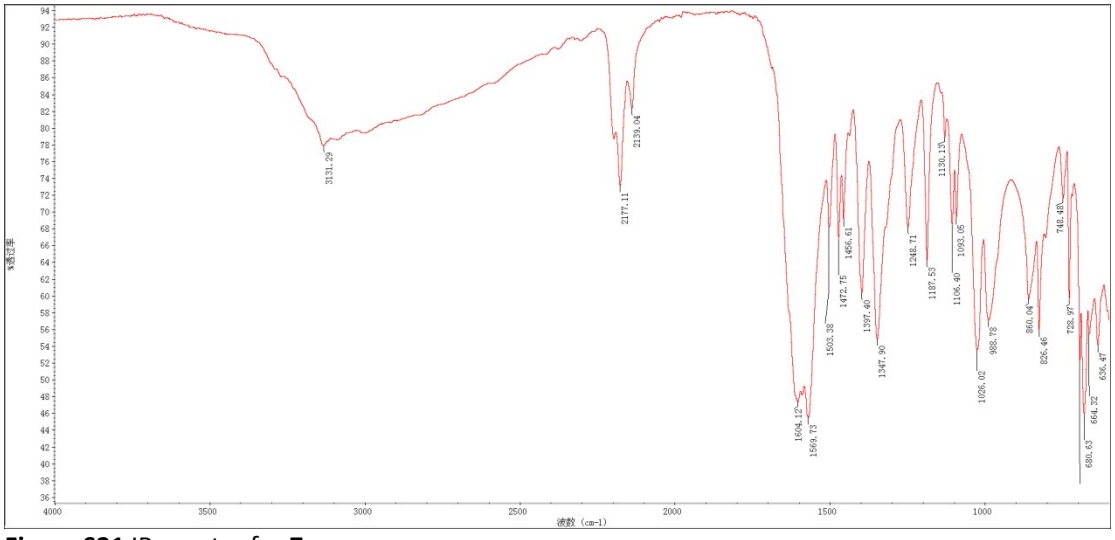


Figure S21 IR spectra for **7**.

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