Supporting information

1,2,4-Oxadiazole-derived polynitro energetic compounds with sensitivity reduced by methylene bridge

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Contents

1.Experimental section

Caution: all the nitrogen-rich compounds may explode under certain conditions although no explosion was encountered in the procedure of preparing these energetic materials. Thus, it is indispensable to keep safeguard procedures and keep experiments in a small scale at the same time.

General methods：

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (Buruker Avance 400) nuclear magnetic resonance spectrometers operating at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to Me4Si. Differential scanning calorimeter (DSC, Shimadzu TA-60ws) was used to measure the melting temperatures and decomposition temperatures at a heating rate of 10 ^{o}C min^{-1} under argon atmosphere. IR spectra were recorded using KBr pellets for solids on a Bruker ALPHA FT-IR Spektrometer. HRMS was recorded on Bruker Apex IV FTMS. All chemicals were bought from commercial companies and used directly unless otherwise noted. The sensitivities towards impact and friction were determined using a drop hammer and a BAM friction tester.

1 was synthesized according to the literature[S8].

Diethyl 2,2'-(methylenebis(1,2,4-oxadiazole-3,5-diyl)) diacetate (2): To a suspension of (1Z,3Z)-N'1,N'3-dihydroxy-malonimidamide (**1**, 6.61 g, 50 mmol) in 100 mL of CH_3CN was added methyl malonyl chloride (15.81 g, 105 mmol). The mixture was stirred at 0-10 ^{o}C, and the suspension turned into a yellow solution with solids. DBU (22.84 g, 150 mmol) was added in one portion and the reaction mixture was heated to 50 ^{o}C and maintained at this temperature for 6 h. After cooled to room temperature, the solvent was removed under vacuum and the residue was subjected on column chromatography giving **2** (3.21 g, 19.8%) as a colourless solid. Tm (peak) = 44 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.38 (s, 2H, CH_2), 4.28 (s, 4H, CH_2CO), 4.13 (q, 4H, CH_2CH_3), 1.19 (t, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.36 (s, 1C, CH_2CH_3), 23.45 (s, 1C, CCH_2C), 32.94 (s, 1C, CCH_2CO), 61.95 (s, 1C, CH_2CH_3), 166.50 (s, 2C, OCN), 166.74 (s, 2C, COO), 174.46 (s, 2C, NCN) ppm. IR: 2991 (m), 2945 (w), 2906 (w), 1747 (vs), 1589 (vs), 1519 (w), 1475 (m), 1404 (w), 1375 (m), 1301 (w), 1280 (w), 1195 (s), 1172 (s), 1112 (w), 1047 (m), 1025 (m), 939 (s), 893 (m), 813 (m), 761 (m), 719 (w), 677 (w), 628 (w), 580 (m) cm^{-1}.

Bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl)methane (3): NaOH (3.0 M, 4.0 mL) was added to a solution of **2** (648 mg, 2 mmol) in water (6.0 mL). The mixture was stirred for 5 h at ambient temperature, and acidified (pH 3) with hydrochloric acid followed by extraction with ethyl acetate three times. The combined organic phases were washed with aqueous sodium bicarbonate and brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give intermediate 2,2'-(methylenebis(1,2,4-oxadiazole-3,5-diyl))diacetic acid (516 mg, 96.3%) without further purification. It (295 mg, 1.10 mmol) was added in small portions over a period of 15 min to a mixture of fuming HNO_3 (2.0 mL) and 96% H_2SO_4 (5.0 mL) at 0 ^{o}C. The mixture was stirred for 6 h at room temperature and poured into ice water (40 mL). The precipitate was filtered and washed with cold water to afford **3** (156 mg, 31.5% yield) as a white powder. $T_{m\ (peak)}$ = 52 ^{o}C. $T_{d\ (onset)}$ = 117 ^{o}C. ^{1}H NMR (400 MHz, $ClCD_3$): δ = 4.65 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $ClCD_3$): δ = 23.9(s, 1C, CH_2), 116.4 (s, 2C, $C(NO_2)_3$), 162.4 (s, 2C, NCN), 166.2 (s, 2C, OCN) ppm. IR: 2916 (w), 1504 (vs), 1516 (w), 1415 (w), 1338 (w), 1274 (s), 1097 (s), 960 (m), 840 (s), 798 cm^{-1} (vs); HRMS: calc. for $C_7HN_{10}O_{14}$ $[M-H]^-$: 448.9679, found: 448.9672, calc. for $C_7H_2N_9O_{12}$ $[M-NO_2]^-$: 403.9828, found: 403.9827.

Ammonium (methylenebis(1,2,4-oxadiazole-3,5-diyl))bis(di-nitromethanide) (5): Diethyl 2,2'-(methylenebis(1,2,4-oxadiazole-3,5-diyl))diacetate (324 mg, 1 mmol) was dissolved in a solution of 96% H_2SO_4 (2.5 mL) at 0 ^{o}C. After cooling to 0-5 ^{o}C, fuming HNO_3 (1.0 mL) was added dropwise. The reaction mixture was warmed up to room temperature. After stirring for 12 h, it was quenched with ice water followed by extraction with ethyl acetate three times. The combined organic phase was washed with aqueous $NaHCO_3$ and brine, dried over anhydrous sodium sulphate, and evaporated under reduced pressure to obtain the crude product **4** as a yellow oil. Without further purification, **4** was added to a solution of ammonia in methanol at room temperature. After stirring 5 h, the yellow precipitate was collected by filtration, air dried to give **5** (341 mg, 86.5%) as yellow solid. $T_{d\ (onset)}$ = 137 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.42 (s, 2H, CH_2), 7.07 (s, 8H, NH_4) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 24.16 (s, 1C, CH_2), 122.51 (s, 2C, $C(NO_2)_2$), 166.78 (s, 2C, NCN), 171.47 (s, 2C, OCN) ppm. IR: 3226 (s), 3007 (w), 1749 (w), 1591 (s), 1489 (w), 1419 (m), 1247 (vs), 1134 (vs), 1109 (s), 1022 (w), 979 (m), 829 (m), 781 (s), 750 (vs) cm^{-1}; HRMS: calc. for $C_7H_2N_8O_{10}$ $[M - N_2H_8]^{2-}$: 178.9952, found: 178.9959, calc. for $C_7H_3N_8O_{10}$ $[M - N_2H_7]^-$: 358.9978, found: 358.9973.

Bis(5-(fluorodinitromethyl)-1,2,4-oxadiazol-3-yl) methane (6): Compound **5** (47 mg, 0.12 mmol) was diluted in dry CH_3CN (3.0 mL) and Selectfluor® (170 mg, 0.48 mmol) was added at 25 °C. The yellow mixture turned colourless and transparent after stirring for 20 min and additional 3 h. After evaporation of the solvent, extraction with CH_2Cl_2, and column chromatography purification, a pure yellow oil **6** (40 mg, 84.2%) was obtained. $T_{d\ (onset)}$ = 166 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.89 ppm (s, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-*d$_6$*): δ = 23.50(s, CH_2), 110.70(d, $^1J_{C,F}$ = 292.0 Hz, $C(NO_2)_2F$), 163.33 (d, $^2J_{C,F}$ = 27.0 Hz, OCN), 166.13 (NCN) ppm. ^{19}F NMR (376 MHz, DMSO-d$_6$): δ = –103.11 ppm. (s, CF). IR: 2893 (w), 1610 (vs), 1577 (m), 1517 (w), 1415 (m), 1394 (w),1340 (w), 1274 (s), 1240 (m), 1212 (m), 1188 (m), 1099(s), 966 (m), 840 (vs), 796 (vs), 750 (w), 711 (m), 657 (w) cm^{-1}; HRMS: Calc. for $C_7HF_2N_8O_{10}$ $[M - H]^-$: 394.9789, found: 394.9794.

General method for preparing compounds 7–8:

Method A: Hydroxylamine hydrochloride (28 mg, 0.4 mmol) or hydrazine hydrochloride (27 mg, 0.4 mmol) in water (1.0 mL) and **9** (119 mg, 0.2 mmol) in MeOH (2.0 mL) was mixed and stirred. The mixture was filtered and the solution was evaporated to dryness, yielding **7** (18 mg, 21.2%) and **8** (25 mg, 29.4%), respectively.

Method B: To the solution of **4** MeOH (4.0 mL) and 50% hydroxylamine solution (0.12 mL, 2 mmol) or 80% hydrazine hydrate (0.1 mL, 2 mmol) was added. The mixture was stirred for 3 h. The precipitate was filtered and dried in air to give yellow product **7** (210 mg, 49.2%) and **8** (246 mg, 58.0%), respectively.

Hydroxylammonium (methylenebis(1,2,4-oxadiazole-3,5-diyl))bis(dinitromethanide), 7: $T_{d\ (onset)}$ = 175 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.42 (s, 2H, CH_2), 9.89 (s, 2H, OH), 10.09 (s, 6H, NH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 24.26(s, 1C, CH_2), 122.62 (s, 2C, $C(NO_2)_2$), 166.87 (s, 2C, NCN), 171.55 (s, 2C, OCN) ppm. IR: 3344 (w), 3143 (s), 3010 (w), 1593(s), 1521 (w), 1483 (s), 1394 (w), 1363 (w), 1249 (s), 1147 (vs), 1107 (vs), 1020 (w), 981 (s), 911(w), 829 (s), 785 (m), 750 (s), 617 (w) cm^{-1}; HRMS: calc. for $C_7H_2N_8O_{10}$ $[M - N_2H_8]^{2-}$: 178.9952, found: 178.9959, calc. for $C_7H_3N_8O_{10}$ $[M - N_2H_7]^-$: 358.9978, found: 358.9973.

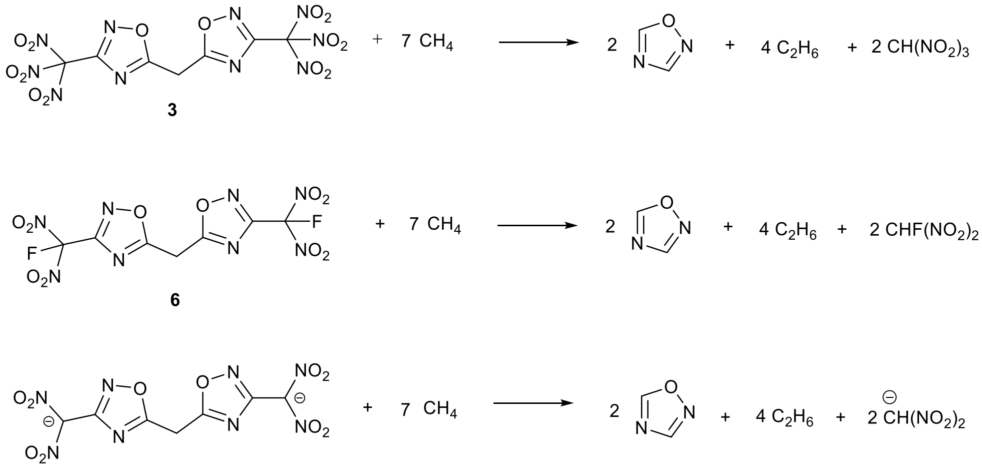
Hydrazinium (methylenebis(1,2,4-oxadiazole-3,5-diyl))-bis(dinitromethanide), 8: $T_{d\ (onset)}$ = 206 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.42 (s, 2H, CH_2), 7.01 (s, 10H, N_2H_5) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 23.40 (s, 1C, CH_2), 121.77 (s, 2C, $C(NO_2)_2$), 166.02 (s, 2C, NCN), 170.70 (s, 2C, OCN) ppm. IR: 3317 (w), 3138 (m), 1589 (s), 1481 (s), 1386 (w), 1301(w), 1251 (m), 1139 (s), 1112 (s), 964 (s), 821 (s), 752 (vs), 723 (w), 646 (w) cm^{-1}; HRMS: calc. for $C_7H_2N_8O_{10}$ $[M - N_2H_8]^{2-}$: 178.9952, found: 178.9959, calc. for $C_7H_3N_8O_{10}$ $[M - N_2H_7]^-$: 358.9978, found: 358.9973.

Silver(I) (methylenebis(1,2,4-oxadiazole-3,5-diyl))bis(dinitro-methanide), 9: $AgNO_3$ (119 mg, 0.70 mmol) was dissolved in water and added to a solution of **5** (138 mg, 0.35 mmol) in water. After stirring for 3 h and filtration the product was obtained as a yellow solid **9** (185 mg, 92.1 %). $T_{d\ (onset)}$ = 133 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.46 (s, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 24.01 (s, CH_2), 122.97 (s, 2C, $C\ (NO_2)_2$), 166.40 (s, 2C, NCN), 171.60 (s, 2C, OCN) ppm. IR: 1587 (m), 1521 (m), 1481 (s), 1396 (s), 1344(m), 1240 (s), 1141 (vs), 1107 (s), 979 (s), 825 (s), 783 (m),746 (vs) cm^{-1}; HRMS: calc. for $C_7H_2N_8O_{10}$ $[M–2Ag]^{2-}$: 178.9952, found: 178.9961, calc. for $C_7H_3N_8O_{10}$ $[M - 2Ag+H]^-$: 358.9978, found: 358.9994.

2.Gaussian Calculations

The density and heats of formation (HOF) of **3**, **5-8** were calculated by the Gaussian09 suite of programs. [S1] First, the geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6-311+G** basis set and optimized structures were used to calculate the density and heats of formation.

The HOF was determined by using an isodesmic reaction (Scheme S1). The HOF of other compounds in Scheme S1 were available in the NIST WebBook[S2] and literature references.[S3]



Scheme S1 Isodesmic reactions for **3**, **6** and for anions of **5, 7-8.**

Compound **3** and **6** are neutral compounds, The change of enthalpy for the reactions at 298K can be expressed by Equation (1):

$$\Delta H_{298K} = \sum H_{f,P} - \sum H_{f,R} \qquad (1)$$

where $H_{f,R}$ and $H_{f,P}$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298K} can also be computed from the Equation (2)[S4]:

$$\Delta H_{298K} = \Delta E_{298K} + \Delta(PV) = \Delta E_0 + \Delta H_{corr} - 0.04\Delta ZPE + \Delta(nRT) \qquad (2)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; For the isodesmic reactions, $\Delta n = 0$. On the left side of Equation (2), the HOF of all the other compound except for target compound are available either from experiments or calculated by G2.

For the ionic salt **5**, **7-8**, the HOF can be simplified by the formula given in Equation (3) based on a Born-Haber energy cycle (Scheme S2),

$$\Delta \mathrm{H}(salts, 298K) = \Delta H(cation, 298K) + \Delta H(anion, 298K) - \Delta H_L \qquad (3)$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al.[S5][Equation (4)]

$$\Delta H_L = U_{pot} + \left[p\left(\frac{n_M}{2} - 2\right) + q\left(\frac{n_X}{2} - 2\right)\right]\mathrm{RT} \quad (4)$$

In this equation, n_{M} and n_{X} depend on the nature of the ions $M_{\mathrm{p+}}$ and $X_{\mathrm{q-}}$, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{pot} [Equation (5)] has the form:

$$U_{pot}[kJ\ mol^{-1}] = \gamma(\rho_m/M_m)^{\frac{1}{3}} + \delta \quad (5)$$

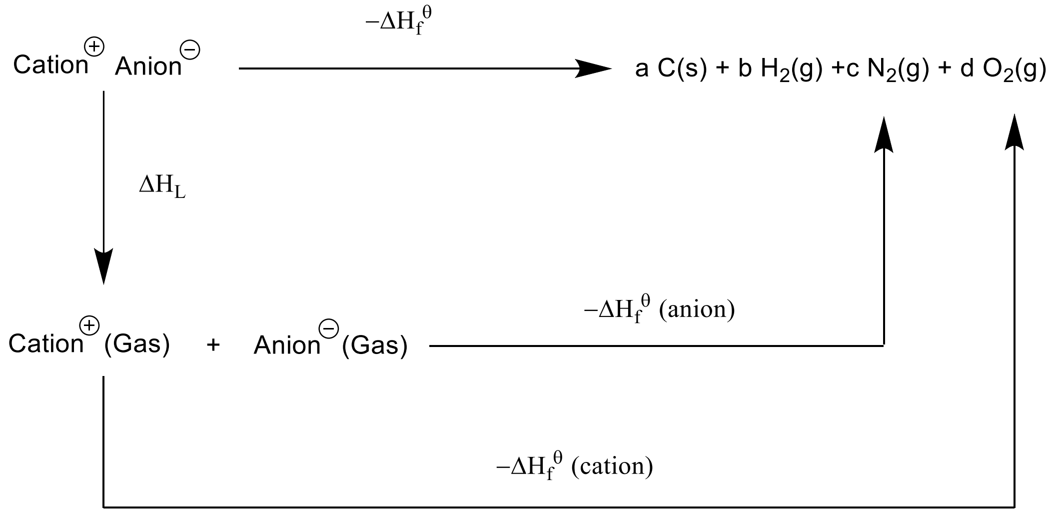
Where values for the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are taken from the literature.[S6]

ρ_{m} [g cm^{-3}] is the density obtained by the formula given in [Equation (6)]. $\mathrm{M_m}$ is the molecular weight, and $\mathrm{V_m}$ is the molar volume of the compound.

$$\rho_m = \frac{M_m}{V_m} \quad (6)$$

For the neutral compound, we directly computed the $\mathrm{V_m}$ with command statement "#B3LYP/6-31+g(d,p) Volume=Tight IOp (6/45=2000)". But for ionic salts with hydrogen atoms, Equation (7) is utilized to get the corrected ionic volume.

$$V_{m(ionic)} = pV_{M+} + qV_{X-} - [0.6763 + 0.9418 \times (no.\ of\ hydrogen\ atoms\ in\ the\ ionic)] \quad (7)$$



Scheme S2. Born-Haber cycle for the formation of energetic salts.

Table S1 The molar volume, molecular weight and calculated densities for the title compounds at B3LYP/6-311+G** level

	V_{M+} [cm^3 mol^{-1}]	V_{X-} [cm^3 mol^{-1}]	V_m [cm^3 mol^{-1}]	M [g mol^{-1}]	ρ_m [g cm^{-3}]
3	-	-	236.137	450.15	1.906
5	18.272	201.942	228.3917	394.22	1.726
6	-	-	211.169	396.14	1.876
7	26.118	201.942	244.0837	426.22	1.746
8	28.492	201.942	246.9481	424.25	1.718

Table S2 Total energy and heat of formation for the title compounds at B3LYP/6-311+G** level

	E_0[a] [hartree]	ZPE[b] [hartree]	H_{corr}[c] [hartree]	HOF[d] [kJ·mol-1]
CH_4	-40.3984876	0.044793	0.048605	-74.6[e]
C_2H_6	-79.6094381	0.074599	0.079027	-84.0[e]
$CH(NO_2)_2$ anion	-448.164078	0.039729	0.046609	-217.0[f]
$CH(NO_2)_3$	-652.8416073	0.054458	0.064315	-13.4[e]
$CHF(NO_2)_2$	-547.788867	0.044535	0.051715	-238.1[g]
1,2,4-oxadiazole	-261.5727899	0.046538	0.050909	75.0[e]
5, **7-8** anion	-1455.156971	0.141113	0.163058	-208.3
5 cation	-	-	-	626.4
7 cation	-	-	-	669.5
8 cation	-	-	-	770
3	-1864.519309	0.168189	0.196249	174.2
6	-1654.415321	0.149181	0.173519	-272.7

[a] Total energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method; [b] Zero-point correction; [c] Thermal correction to enthalpy; [d] Heat of formation (1 hartree = 2625.499748 kJ·mol^{-1}). [e]Data are from Ref. [D. R. Lide, ed., *CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008*), CRC Press/Taylor and Francis, Boca Raton, FL.].[f]Data from Ref.[S7]. [g]Data calculated from G2 calculation.

3. References

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4. Screening of Reaction Conditions for 2

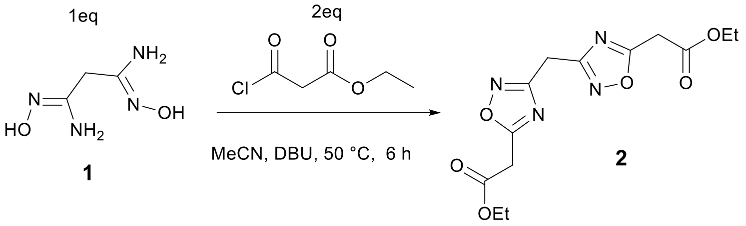

Table S3 Screening of Reaction Conditions for **2**.

entry	solvent	base	temperature	time	Yield (%) of **2**
1	MeCN	-	25	6h	No reaction
2	MeCN	Cs_2CO_3(4eq)	25	6h	0
3	MeCN	Cs_2CO_3(4eq)	50	15h	10
4[a]	MeCN	Cs_2CO_3(8eq)	50	15h	5
5	toluene	-	50	6h	0
6	toluene	Cs_2CO_3(4eq)	50	6h	trace
7	DME	pyridine	50	6h	trace
8	MeCN	K_2CO_3(4eq)	50	24h	2
9	MeCN	DMAP(4eq)	50	6h	trace
10	MeCN	DABCO(4eq)	50	6h	trace
11	MeCN	DBU(4eq)	50	6h	15
12	MeCN	DBU(3eq)	50	6h	20
13	MeCN	DBU(3eq)	50	12h	18
14[b]	MeCN	DBU(3eq)	50	6h	21

[a] Reaction was carried out with 4eq methyl malonyl chloride compared with **1**. [b] Reaction was carried out in argon atmosphere with anhydrous acetonitrile.

5. X-ray Diffraction

Table S4 Crystallographic data for **2**, **5**·H_2O.

Compd.	**2**	**5**·H_2O
Formula	$C_{13}H_{16}N_4O_6$	$C_7H_{12}N_{10}O_{11}$
Mw[g mol^{-1}]	324.30	412.27
T[K]	296(2)	296(2)
Crystal size[mm^3]	0.200 ×0.150 × 0.100	0.200 ×0.150 × 0.100
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1/n$
a[Å]	15.5467(9)	14.2662(6)
b[Å]	7.7138(5)	7.0922(3)
c[Å]	13.3519(8)	15.6154(6)

α[°]	90	90
β[°]	107.417(2)	90.9520(10)
γ[°]	90	90
V[Å^3]	1527.80(16)	1579.73(11)
Z	4	4
ρ_{calc}[g cm^{-3}]	1.410	1.733
μ[mm^{-1}]	0.113	0.162
F[000]	680	848
θ range[°]	2.746-28.281	1.918 -28.286
Reflections collected	9020 / 1901	18880 / 3920
Index ranges	-20<=h<=20, -10<=k<=10, -17<=l<=17	-19<=h<=18, -9<=k<=9, -20<=l<=20
R_{int}	0.0181	0.0300
Data/restraints/parameters	1901 / 0 / 105	3920 / 0 / 293
Final *R* index[$I > 2\sigma(I)$]	R_1 = 0.0340, wR_2 = 0.0988	R1 = 0.0461, wR2 = 0.1130
Final *R* index[all data]	R_1 =0.0392, wR_2 = 0.1040	R1 = 0.0542, wR2 = 0.1193
GOF on F^2	1.036	1.075
CCDC	1876731	1876622

$R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. $wR_2 = [(w(F_o^2 - F_c^2)^2)/w(F_o^2)^2]^{1/2}$.

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(3)	6410(1)	726(1)	5064(1)	46(1)
O(1)	6911(1)	5119(1)	7339(1)	61(1)
N(1)	5521(1)	5499(1)	6347(1)	40(1)
O(2)	6013(1)	1149(1)	6524(1)	58(1)
C(2)	5699(1)	6453(1)	7257(1)	39(1)

C(1)	5000	7563(2)	7500	46(1)
N(2)	6506(1)	6291(2)	7880(1)	60(1)
C(3)	6279(1)	4734(1)	6447(1)	40(1)
C(5)	6283(1)	1689(1)	5836(1)	39(1)
C(4)	6525(1)	3546(1)	5700(1)	46(1)
C(6)	6244(1)	-1125(1)	5118(1)	51(1)
C(7)	6293(1)	-1916(2)	4117(1)	65(1)

Table S6. Bond lengths [A] and angles [deg] for **2**.

O(3)-C(5)	1.3326(12)
O(3)-C(6)	1.4567(13)
O(1)-C(3)	1.3314(13)
O(1)-N(2)	1.4172(13)
N(1)-C(3)	1.2876(14)
N(1)-C(2)	1.3754(12)
O(2)-C(5)	1.1935(12)
C(2)-N(2)	1.2875(14)
C(2)-C(1)	1.4935(13)
C(1)-C(2)#1	1.4934(13)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(3)-C(4)	1.4864(14)
C(5)-C(4)	1.5055(15)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(6)-C(7)	1.4916(18)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(5)-O(3)-C(6)	116.03(8)
C(3)-O(1)-N(2)	106.02(8)
C(3)-N(1)-C(2)	102.59(8)
N(2)-C(2)-N(1)	114.71(9)
N(2)-C(2)-C(1)	123.16(8)
N(1)-C(2)-C(1)	122.12(8)
C(2)#1-C(1)-C(2)	110.07(11)
C(2)#1-C(1)-H(1A)	109.6
C(2)-C(1)-H(1A)	109.6
C(2)#1-C(1)-H(1B)	109.6

C(2)-C(1)-H(1B)	109.6
H(1A)-C(1)-H(1B)	108.2
C(2)-N(2)-O(1)	103.20(8)
N(1)-C(3)-O(1)	113.47(9)
N(1)-C(3)-C(4)	128.61(9)
O(1)-C(3)-C(4)	117.90(9)
O(2)-C(5)-O(3)	124.69(10)
O(2)-C(5)-C(4)	125.64(10)
O(3)-C(5)-C(4)	109.67(8)
C(3)-C(4)-C(5)	112.46(8)
C(3)-C(4)-H(4A)	109.1
C(5)-C(4)-H(4A)	109.1
C(3)-C(4)-H(4B)	109.1
C(5)-C(4)-H(4B)	109.1
H(4A)-C(4)-H(4B)	107.8
O(3)-C(6)-C(7)	107.43(9)
O(3)-C(6)-H(6A)	110.2
C(7)-C(6)-H(6A)	110.2
O(3)-C(6)-H(6B)	110.2
C(7)-C(6)-H(6B)	110.2
H(6A)-C(6)-H(6B)	108.5
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table S7. Anisotropic displacement parameters (A^2 x 10^3) for **2**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(3)	58(1)	40(1)	46(1)	1(1)	24(1)	0(1)
O(1)	41(1)	80(1)	55(1)	-17(1)	2(1)	1(1)
N(1)	44(1)	42(1)	33(1)	-3(1)	9(1)	1(1)
O(2)	74(1)	59(1)	52(1)	6(1)	34(1)	0(1)
C(2)	50(1)	34(1)	32(1)	0(1)	14(1)	-8(1)
C(1)	69(1)	32(1)	42(1)	0	24(1)	0
N(2)	55(1)	73(1)	48(1)	-20(1)	7(1)	-6(1)

C(3)	41(1)	41(1)	37(1)	1(1)	12(1)	-5(1)
C(5)	34(1)	46(1)	37(1)	4(1)	11(1)	5(1)
C(4)	50(1)	45(1)	48(1)	0(1)	24(1)	0(1)
C(6)	58(1)	40(1)	56(1)	7(1)	17(1)	2(1)
C(7)	84(1)	45(1)	69(1)	-6(1)	27(1)	3(1)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2**.

	x	y	z	U(eq)
H(1A)	5281	8300	8097	55
H(1B)	4719	8300	6903	55
H(4A)	7168	3625	5803	55
H(4B)	6216	3911	4988	55
H(6A)	5653	-1321	5203	61
H(6B)	6694	-1639	5710	61
H(7A)	6186	-3140	4128	98
H(7B)	5844	-1399	3537	98
H(7C)	6880	-1716	4042	98

Table S9. Selected torsion angles [deg] for **2**.

-0.18 (0.11)	C3 - N1 - C2 - N2
-179.28 (0.09)	C3 - N1 - C2 - C1
-108.45 (0.10)	N2 - C2 - C1 - C2_$1
70.57 (0.08)	N1 - C2 - C1 - C2_$1
0.02 (0.12)	N1 - C2 - N2 - O1
179.10 (0.09)	C1 - C2 - N2 - O1
0.15 (0.12)	C3 - O1 - N2 - C2
0.29 (0.12)	C2 - N1 - C3 - O1
-178.22 (0.10)	C2 - N1 - C3 - C4
-0.29 (0.13)	N2 - O1 - C3 - N1
178.39 (0.09)	N2 - O1 - C3 - C4
-3.11 (0.14)	C6 - O3 - C5 - O2
177.21 (0.08)	C6 - O3 - C5 - C4
-86.58 (0.13)	N1 - C3 - C4 - C5
94.97 (0.11)	O1 - C3 - C4 - C5
-7.69 (0.15)	O2 - C5 - C4 - C3
171.99 (0.08)	O3 - C5 - C4 - C3
171.95 (0.09)	C5 - O3 - C6 - C7

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **5·H$_2$O**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(4)	-3250(1)	1927(2)	4079(1)	26(1)
N(1)	-1206(1)	-92(2)	3646(1)	27(1)
O(3)	-3791(1)	2792(2)	4542(1)	39(1)
O(1)	-1835(1)	1536(2)	2582(1)	36(1)
O(5)	-1086(1)	4353(2)	4166(1)	39(1)
O(10)	4287(1)	421(2)	3961(1)	42(1)
N(5)	1391(1)	-1557(2)	2740(1)	28(1)
N(8)	3529(1)	-1461(2)	2550(1)	30(1)
O(9)	2901(1)	744(2)	4482(1)	40(1)
O(8)	4387(1)	-1347(2)	2526(1)	53(1)
O(2)	-3486(1)	486(2)	3674(1)	35(1)
N(7)	3433(1)	102(2)	3931(1)	28(1)
C(2)	-926(1)	-768(2)	2862(1)	25(1)
C(5)	629(1)	-2168(2)	3174(1)	26(1)
O(4)	-2404(1)	5241(2)	4730(1)	44(1)
C(3)	-1756(1)	1279(2)	3430(1)	24(1)
C(7)	3022(1)	-944(2)	3266(1)	24(1)
C(6)	2046(1)	-1457(2)	3322(1)	24(1)
N(2)	-1271(1)	135(2)	2210(1)	37(1)
N(3)	-1949(1)	4078(2)	4306(1)	29(1)
O(7)	3068(1)	-2071(2)	1924(1)	55(1)
C(4)	-2326(1)	2489(2)	3966(1)	25(1)
C(1)	-312(1)	-2454(2)	2761(1)	29(1)
O(6)	1735(1)	-1957(3)	4090(1)	64(1)
N(6)	776(1)	-2421(4)	3980(1)	66(1)
N(9)	5813(1)	2543(2)	9602(1)	38(1)
O(11)	8922(1)	-2(2)	8954(1)	44(1)
N(10)	9450(1)	2187(2)	610(1)	33(1)

Table S11. Bond lengths [A] and angles [deg] for **5·H$_2$O**.

N(4)-O(3)	1.2303(16)
N(4)-O(2)	1.2449(16)
N(4)-C(4)	1.3905(18)
N(1)-C(3)	1.2907(19)
N(1)-C(2)	1.3795(17)
O(1)-C(3)	1.3386(17)

O(1)-N(2)	1.4102(17)
O(5)-N(3)	1.2693(16)
O(10)-N(7)	1.2391(17)
N(5)-C(6)	1.2945(18)
N(5)-C(5)	1.3614(18)
N(8)-O(8)	1.2277(17)
N(8)-O(7)	1.2461(18)
N(8)-C(7)	1.3911(18)
O(9)-N(7)	1.2423(17)
N(7)-C(7)	1.3973(18)
C(2)-N(2)	1.294(2)
C(2)-C(1)	1.492(2)
C(5)-N(6)	1.285(2)
C(5)-C(1)	1.4931(19)
O(4)-N(3)	1.2472(17)
C(3)-C(4)	1.4570(19)
C(7)-C(6)	1.4429(19)
C(6)-O(6)	1.3348(17)
N(3)-C(4)	1.3529(19)
O(6)-N(6)	1.4156(19)

O(3)-N(4)-O(2)	122.67(12)
O(3)-N(4)-C(4)	122.47(13)
O(2)-N(4)-C(4)	114.86(12)
C(3)-N(1)-C(2)	102.33(12)
C(3)-O(1)-N(2)	105.74(11)
C(6)-N(5)-C(5)	103.97(12)
O(8)-N(8)-O(7)	120.80(13)
O(8)-N(8)-C(7)	122.59(14)
O(7)-N(8)-C(7)	116.60(12)
O(10)-N(7)-O(9)	121.26(13)
O(10)-N(7)-C(7)	121.67(13)
O(9)-N(7)-C(7)	117.04(12)
N(2)-C(2)-N(1)	114.44(13)
N(2)-C(2)-C(1)	121.98(13)
N(1)-C(2)-C(1)	123.53(13)
N(6)-C(5)-N(5)	114.41(13)
N(6)-C(5)-C(1)	122.35(14)
N(5)-C(5)-C(1)	123.21(13)
N(1)-C(3)-O(1)	113.76(12)
N(1)-C(3)-C(4)	129.48(13)
O(1)-C(3)-C(4)	116.67(12)
N(8)-C(7)-N(7)	121.31(12)
N(8)-C(7)-C(6)	119.78(12)
N(7)-C(7)-C(6)	118.90(12)
N(5)-C(6)-O(6)	111.72(12)
N(5)-C(6)-C(7)	131.15(13)

O(6)-C(6)-C(7)	117.12(12)
C(2)-N(2)-O(1)	103.73(11)
O(4)-N(3)-O(5)	120.25(13)
O(4)-N(3)-C(4)	123.56(13)
O(5)-N(3)-C(4)	116.18(12)
N(3)-C(4)-N(4)	124.05(12)
N(3)-C(4)-C(3)	119.61(12)
N(4)-C(4)-C(3)	116.33(12)
C(2)-C(1)-C(5)	111.73(12)
C(6)-O(6)-N(6)	106.66(12)
C(5)-N(6)-O(6)	103.24(13)

Table S12. Anisotropic displacement parameters (A^2 x 10^3) for **$5\cdot H_2O$**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
N(4)	24(1)	29(1)	23(1)	2(1)	2(1)	2(1)
N(1)	26(1)	36(1)	21(1)	-2(1)	1(1)	7(1)
O(3)	29(1)	47(1)	43(1)	-6(1)	14(1)	2(1)
O(1)	46(1)	41(1)	21(1)	2(1)	3(1)	15(1)
O(5)	27(1)	44(1)	46(1)	-5(1)	6(1)	-9(1)
O(10)	28(1)	50(1)	49(1)	-5(1)	-9(1)	-8(1)
N(5)	23(1)	41(1)	21(1)	1(1)	0(1)	-2(1)
N(8)	28(1)	31(1)	32(1)	-3(1)	8(1)	-5(1)
O(9)	42(1)	49(1)	30(1)	-12(1)	0(1)	5(1)
O(8)	28(1)	75(1)	57(1)	-16(1)	16(1)	-9(1)
O(2)	34(1)	34(1)	39(1)	-4(1)	-1(1)	-6(1)
N(7)	29(1)	28(1)	26(1)	2(1)	-5(1)	1(1)
C(2)	19(1)	33(1)	23(1)	-4(1)	2(1)	-2(1)
C(5)	21(1)	35(1)	24(1)	-3(1)	2(1)	2(1)
O(4)	41(1)	37(1)	54(1)	-19(1)	10(1)	-1(1)
C(3)	24(1)	30(1)	19(1)	-1(1)	1(1)	-1(1)
C(7)	22(1)	29(1)	23(1)	0(1)	0(1)	-1(1)
C(6)	23(1)	30(1)	19(1)	1(1)	1(1)	2(1)
N(2)	44(1)	43(1)	23(1)	-3(1)	6(1)	11(1)
N(3)	28(1)	30(1)	28(1)	-1(1)	3(1)	-1(1)
O(7)	42(1)	90(1)	34(1)	-27(1)	13(1)	-18(1)
C(4)	23(1)	28(1)	24(1)	-2(1)	2(1)	2(1)
C(1)	20(1)	36(1)	32(1)	-10(1)	1(1)	2(1)
O(6)	30(1)	136(2)	26(1)	27(1)	-6(1)	-26(1)
N(6)	27(1)	142(2)	31(1)	21(1)	-2(1)	-27(1)

N(9)	38(1)	42(1)	35(1)	4(1)	8(1)	8(1)
O(11)	44(1)	54(1)	33(1)	13(1)	3(1)	9(1)
N(10)	35(1)	33(1)	31(1)	3(1)	4(1)	1(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **5·H$_2$O**.

	x	y	z	U(eq)
H(1)	-235	-2710	2156	35
H(2)	-612	-3541	3015	35
H(9)	9990(20)	1560(40)	824(17)	75(8)
H(11)	8770(20)	430(40)	8480(20)	83(9)
H(5)	5910(30)	1390(60)	9920(20)	116(12)
H(7)	9460(20)	2480(40)	40(20)	86(9)
H(10)	9380(20)	3290(50)	900(20)	98(10)
H(6)	5930(20)	3550(50)	9880(20)	106(12)
H(8)	8980(20)	1560(50)	717(19)	86(10)
H(3)	6120(20)	2510(50)	9050(20)	114(12)
H(4)	5220(30)	2420(50)	9500(20)	102(11)
H(12)	8430(20)	-180(50)	9243(19)	87(10)

Table S14. Selected torsion angles [deg] for **5·H$_2$O**

-0.60 (0.18)	C3 - N1 - C2 - N2
176.62 (0.13)	C3 - N1 - C2 - C1
-0.86 (0.21)	C6 - N5 - C5 - N6
-178.56 (0.14)	C6 - N5 - C5 - C1
0.80 (0.17)	C2 - N1 - C3 - O1
-175.62 (0.14)	C2 - N1 - C3 - C4
-0.72 (0.17)	N2 - O1 - C3 - N1
176.19 (0.12)	N2 - O1 - C3 - C4
-13.74 (0.23)	O8 - N8 - C7 - N7
166.84 (0.15)	O7 - N8 - C7 - N7
167.61 (0.15)	O8 - N8 - C7 - C6
-11.81 (0.22)	O7 - N8 - C7 - C6
8.67 (0.21)	O10 - N7 - C7 - N8
-169.48 (0.14)	O9 - N7 - C7 - N8
-172.67 (0.13)	O10 - N7 - C7 - C6
9.18 (0.19)	O9 - N7 - C7 - C6
0.40 (0.19)	C5 - N5 - C6 - O6
-178.31 (0.15)	C5 - N5 - C6 - C7
36.32 (0.24)	N8 - C7 - C6 - N5
-142.36 (0.16)	N7 - C7 - C6 - N5

-142.33 (0.16)	N8 - C7 - C6 - O6
38.99 (0.21)	N7 - C7 - C6 - O6
0.19 (0.18)	N1 - C2 - N2 - O1
-177.08 (0.13)	C1 - C2 - N2 - O1
0.29 (0.16)	C3 - O1 - N2 - C2
2.74 (0.23)	O4 - N3 - C4 - N4
-177.64 (0.13)	O5 - N3 - C4 - N4
-175.79 (0.14)	O4 - N3 - C4 - C3
3.83 (0.20)	O5 - N3 - C4 - C3
4.16 (0.22)	O3 - N4 - C4 - N3
-175.77 (0.13)	O2 - N4 - C4 - N3
-177.27 (0.13)	O3 - N4 - C4 - C3
2.80 (0.18)	O2 - N4 - C4 - C3
-87.87 (0.20)	N1 - C3 - C4 - N3
95.79 (0.17)	O1 - C3 - C4 - N3
93.49 (0.19)	N1 - C3 - C4 - N4
-82.85 (0.17)	O1 - C3 - C4 - N4
-120.91 (0.16)	N2 - C2 - C1 - C5
62.07 (0.19)	N1 - C2 - C1 - C5
-82.38 (0.22)	N6 - C5 - C1 - C2
95.14 (0.17)	N5 - C5 - C1 - C2
0.12 (0.23)	N5 - C6 - O6 - N6
179.03 (0.17)	C7 - C6 - O6 - N6
0.91 (0.25)	N5 - C5 - N6 - O6
178.64 (0.16)	C1 - C5 - N6 - O6
-0.61 (0.25)	C6 - O6 - N6 - C5.

Table S15. Hydrogen bonds for **5·H_2O**. [A and deg.].

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C1-H1	0.970	2.441	156.54	3.354	O5 [x, y+1, z]
C1-H2	0.970	2.589	145.15	3.430	O10 [-x+3/2, y+1/2, -z+3/2]
C1-H2	0.970	2.563	119.64	3.157	O2 [-x+5/2, y+1/2, -z+3/2]
N10-H9	0.945	1.933	168.36	2.865	O11 [-x, -y+2, -z+1]
O11-H11	0.830	2.071	171.84	2.895	N5 [-x+1, -y+2, -z+1]
N9-H5	0.962	2.048	166.23	2.991	O5 [-x+3/2, y+1/2, -z+1/2]
N9-H5	0.962	2.336	123.01	2.972	O4 [-x+3/2, y+1/2, -z+1/2]
N9-H5	0.962	2.510	152.11	3.390	N3 [-x+3/2, y+1/2, -z+1/2]
N10-H7	0.907	2.265	151.00	3.090	O10 [x-1/2, -y+3/2, z+1/2]
N10-H7	0.907	2.556	118.90	3.098	O11 [x, y, z+1]
N10-H10	0.911	2.433	119.31	2.986	O10 [-x+1/2, y-1/2, -z+3/2]
N10-H10	0.911	2.129	148.40	2.943	O2 [-x+3/2, y-1/2, -z+3/2]
N9-H6	0.850	2.523	144.24	3.250	N1 [-x+3/2, y-1/2, -z+1/2]
N10-H8	0.828	2.519	150.25	3.264	O4 [-x+3/2, y+1/2, -z+3/2]
N10-H8	0.828	2.570	121.35	3.083	N2 [x-1, y, z]
N9-H3	0.972	2.665	158.49	3.587	N8 [-x+1, -y+2, -z+1]
N9-H3	0.972	1.954	167.16	2.909	O7 [-x+1, -y+2, -z+1]
N9-H4	0.867	2.295	152.36	3.090	O5 [x-1/2, -y+3/2, z-1/2]
O11-H12	0.848	2.212	157.92	3.015	O4 [-x+3/2, y+1/2, -z+1/2]

6. Copies of Spectrum

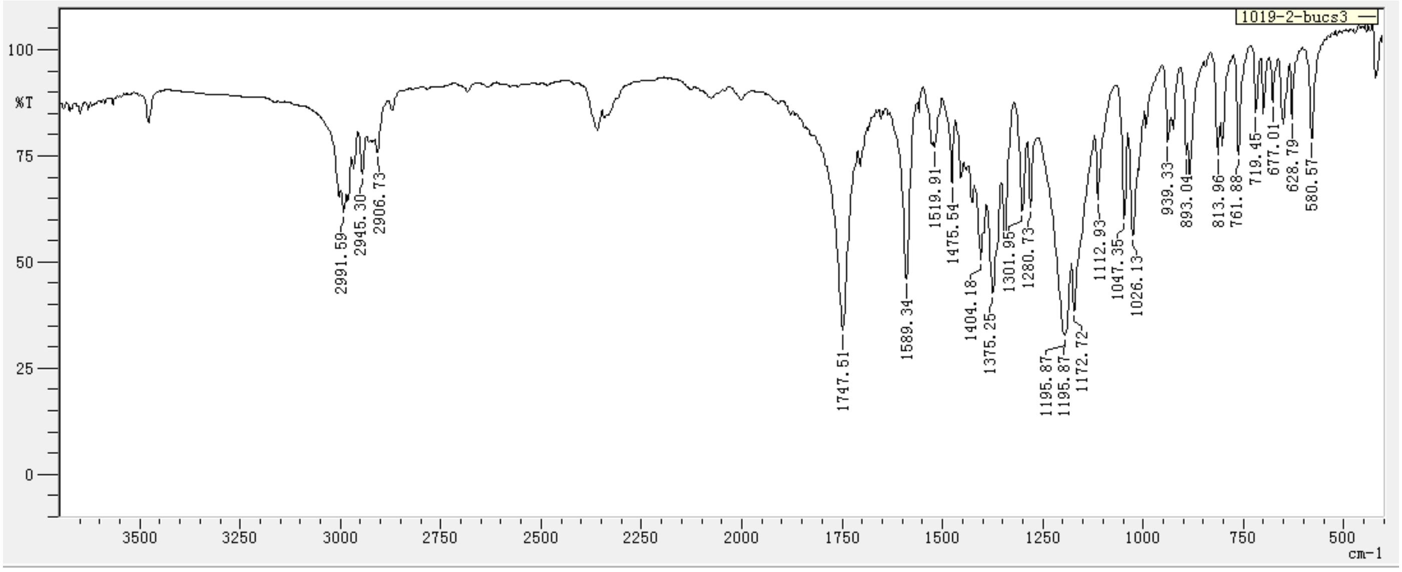

Figure S1 IR spectrum of **2**.

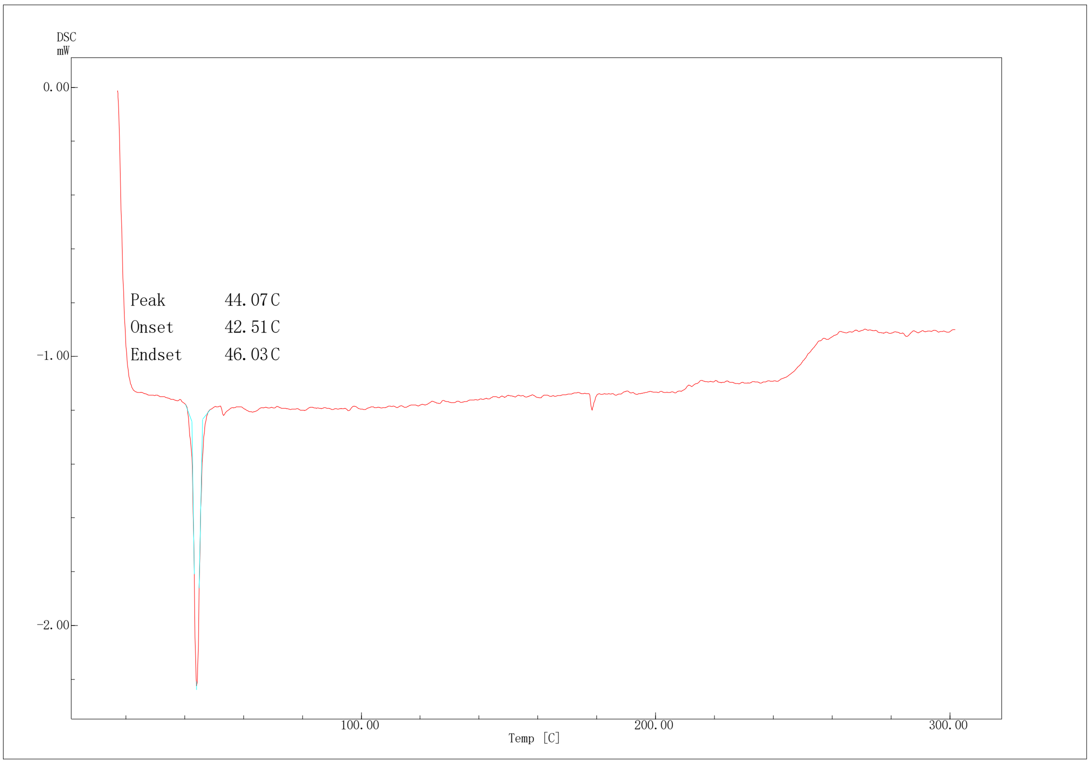

Figure S2 DSC curve of **2** (10 ºC min^{-1}).

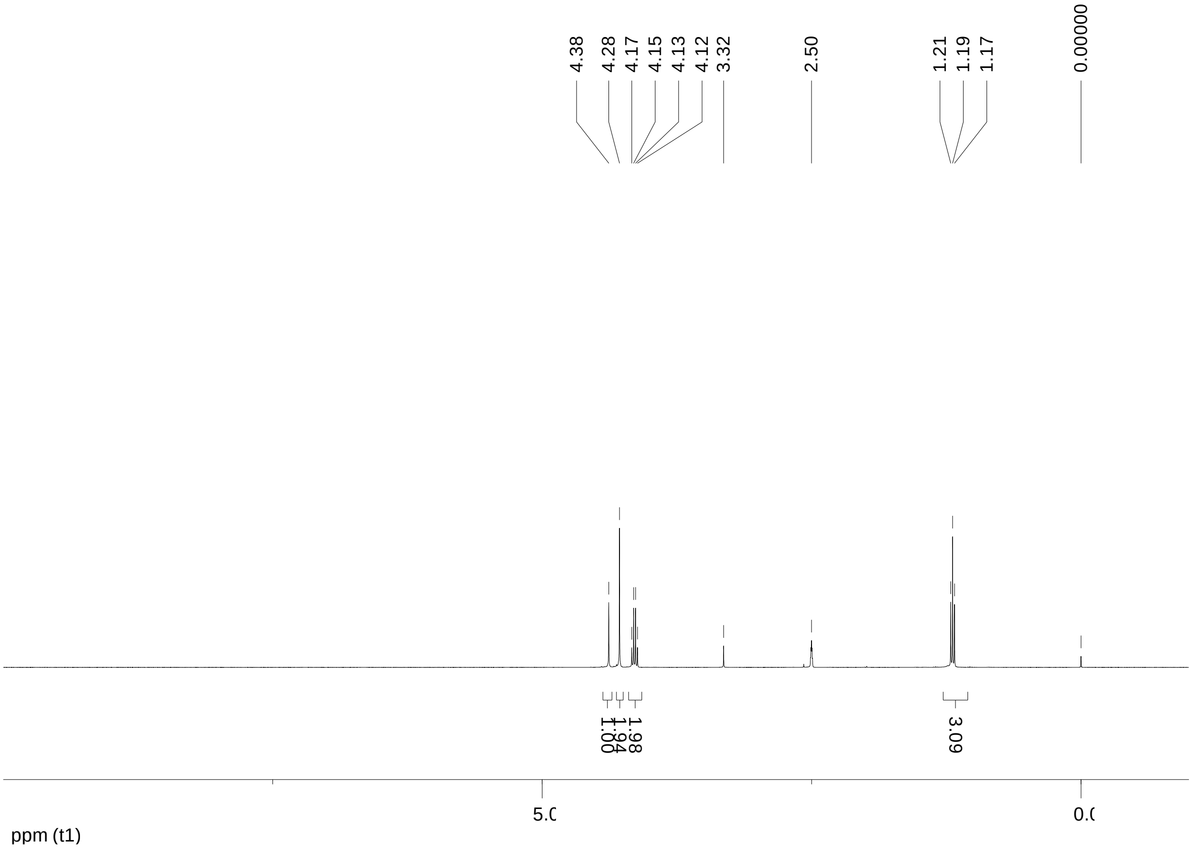

Figure S3 ^{1}H NMR spectrum of **2**.

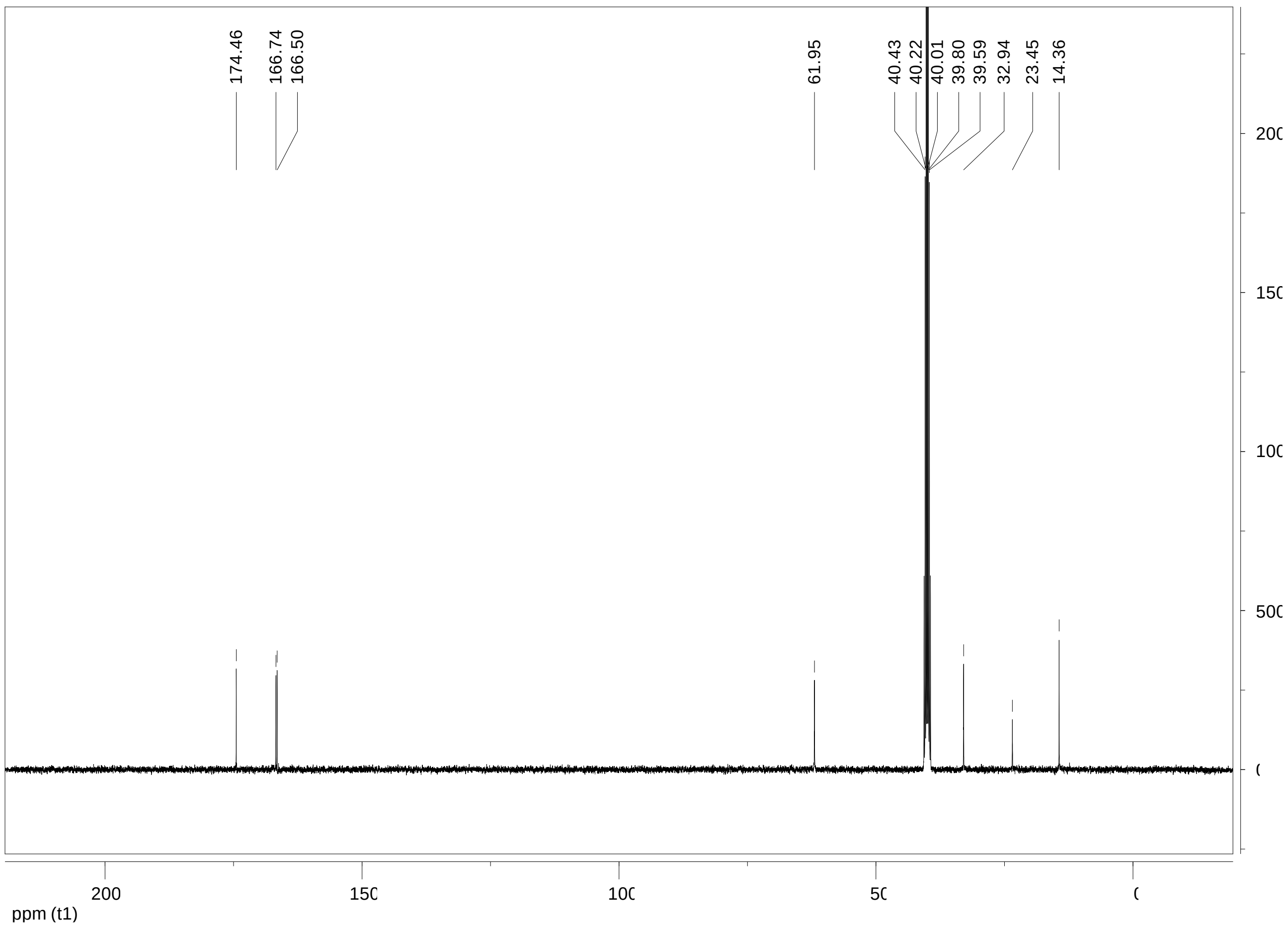

Figure S4 ^{13}C NMR spectrum of **2**.

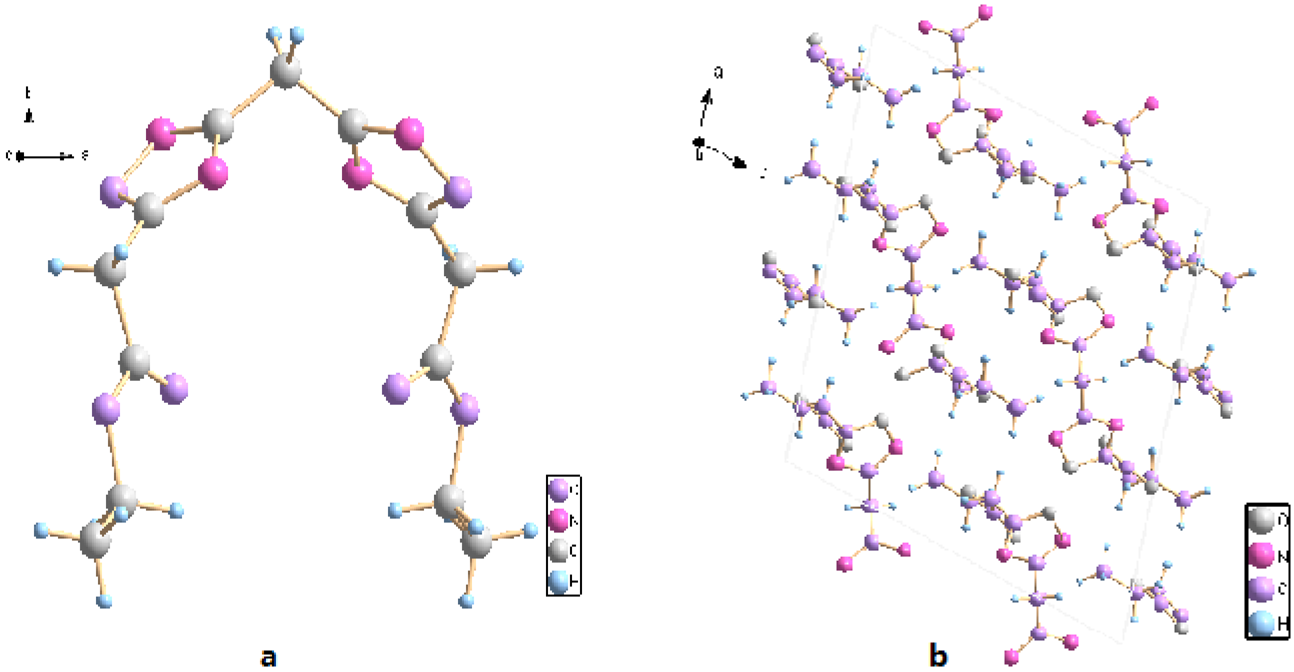

Figure S5 X-ray crystal structure of **2**.

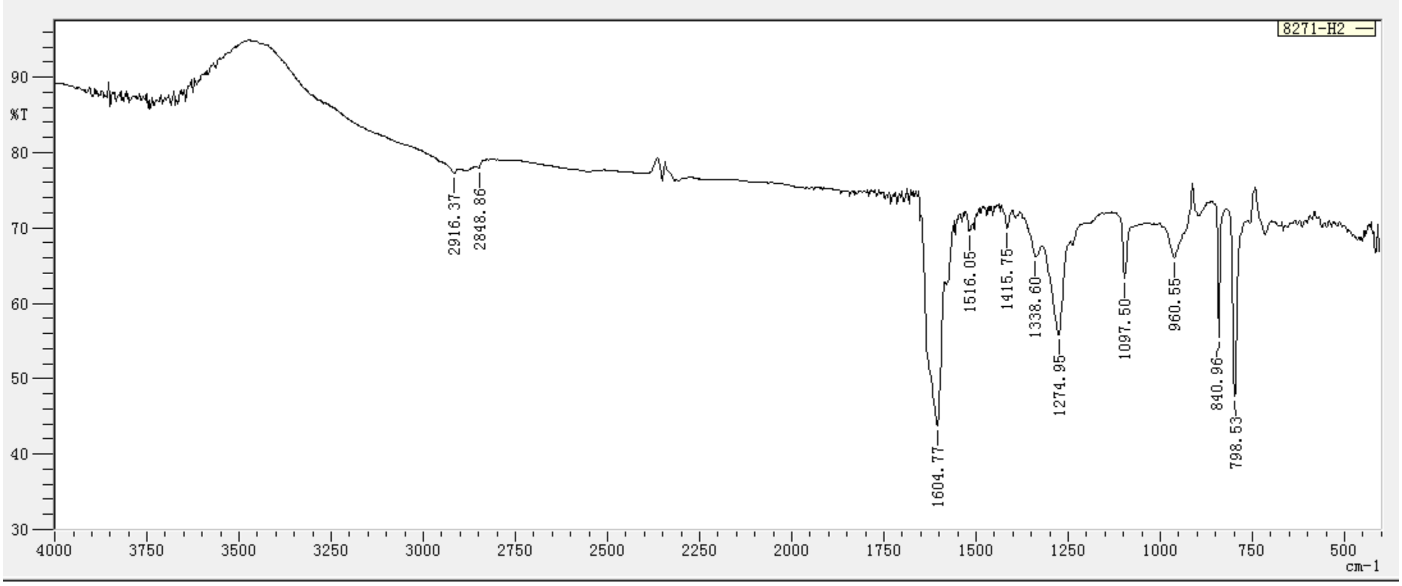

Figure S6 IR spectrum of **3**.

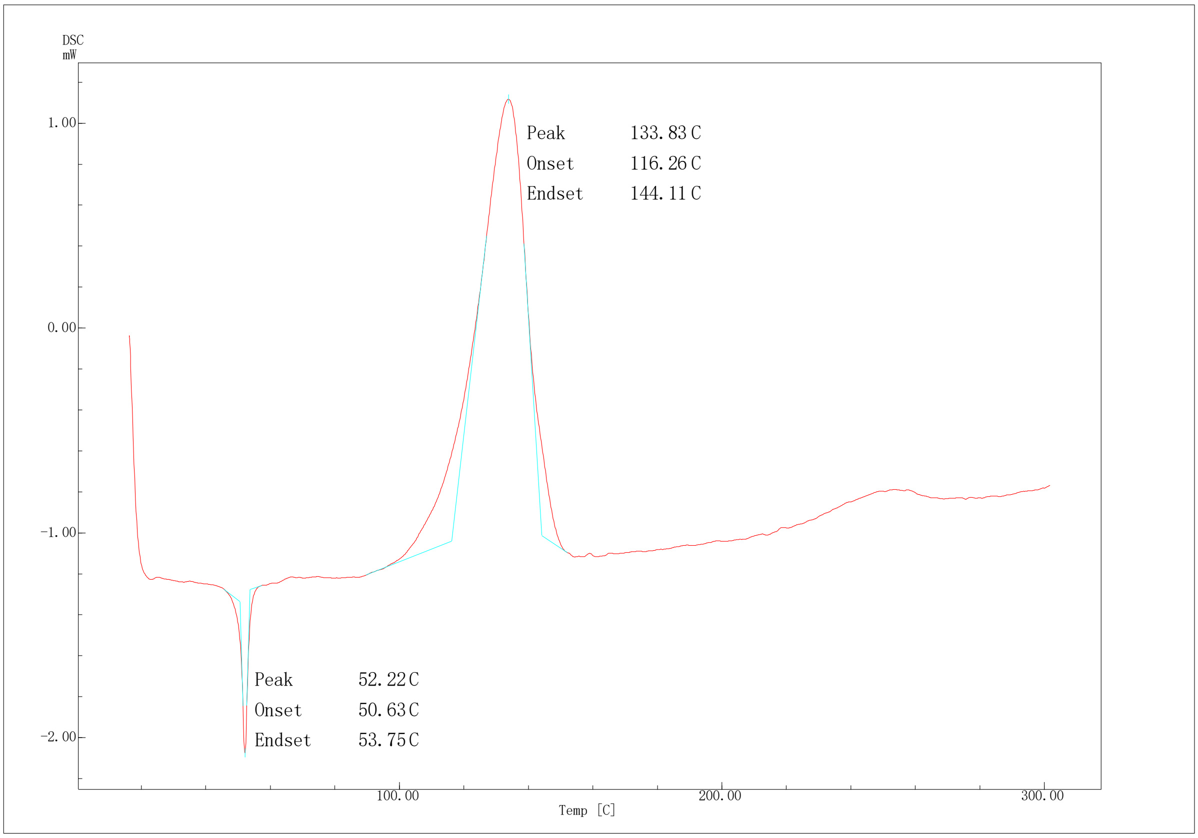

Figure S7 DSC curve of **3** (10 ºC min^{-1})

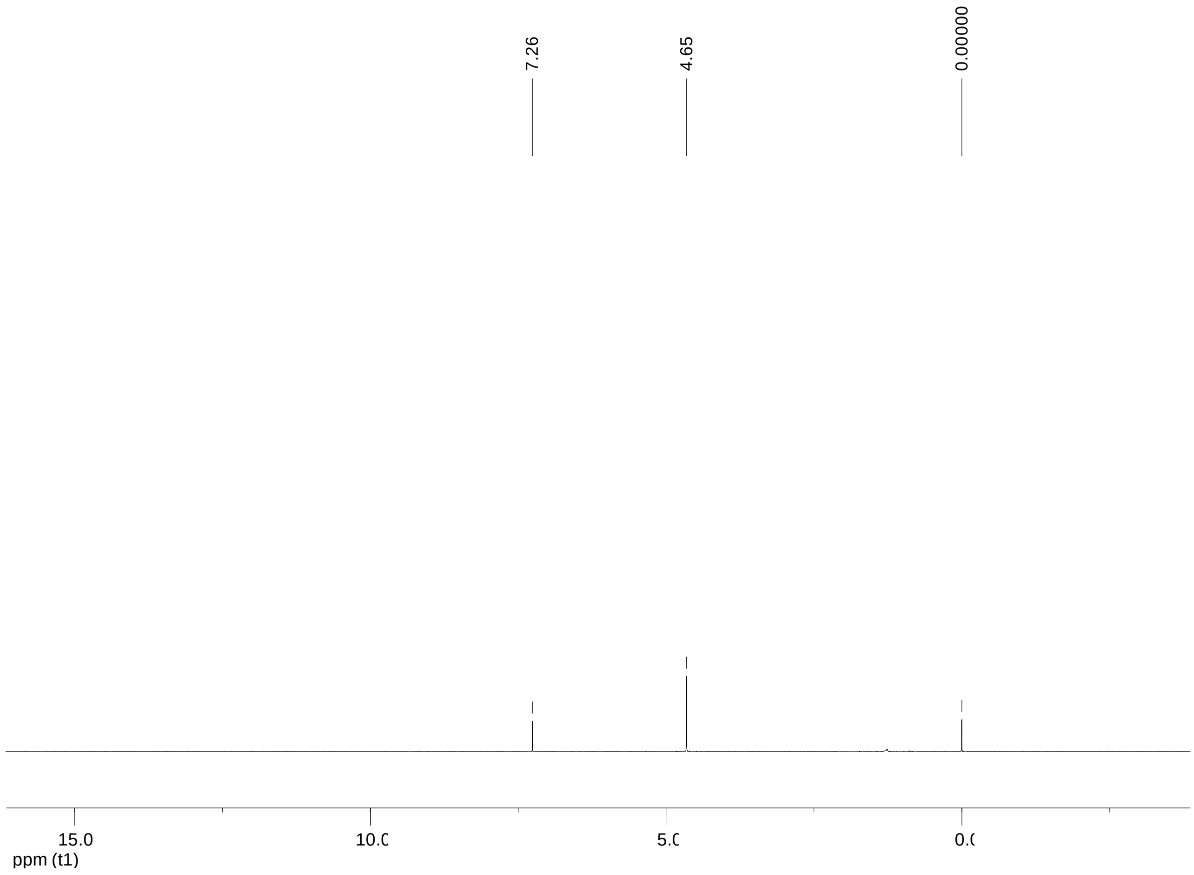

Figure S8 ^{1}H NMR spectrum of **3**.

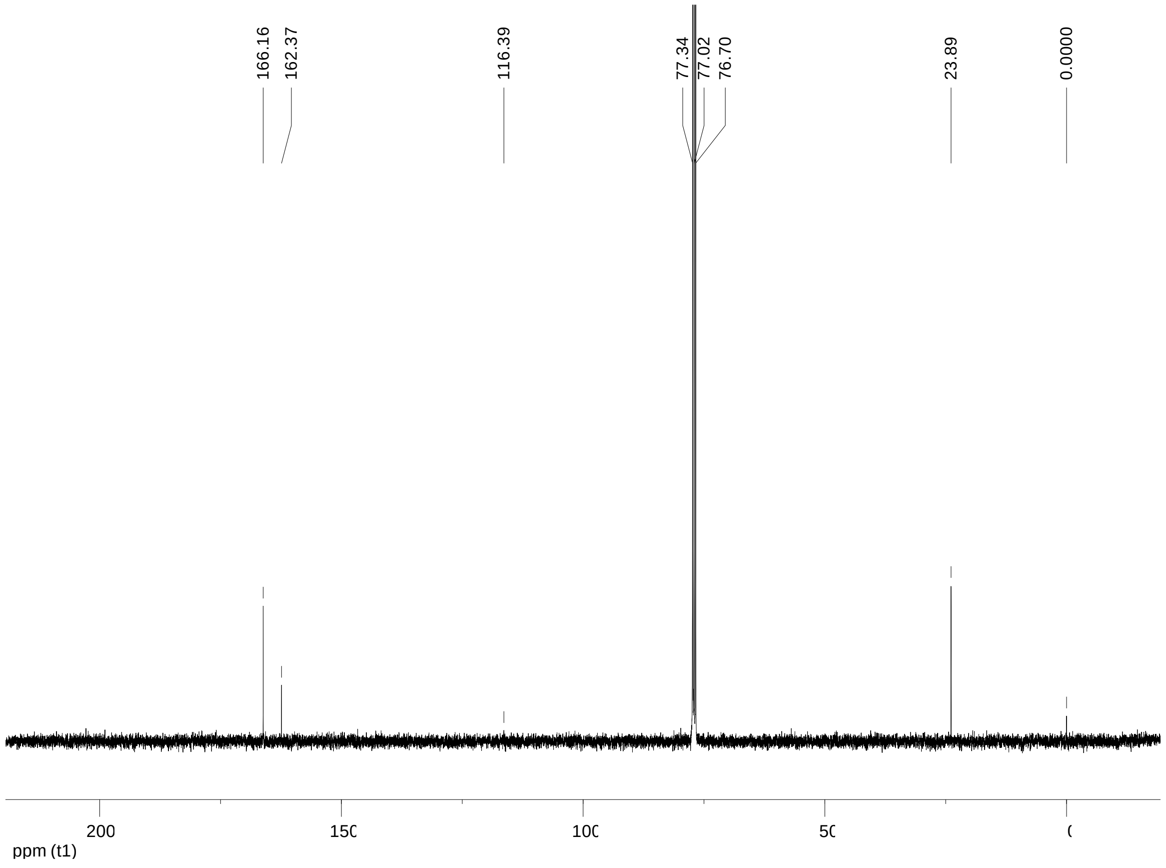

Figure S9 ^{13}C NMR spectrum of **3**.

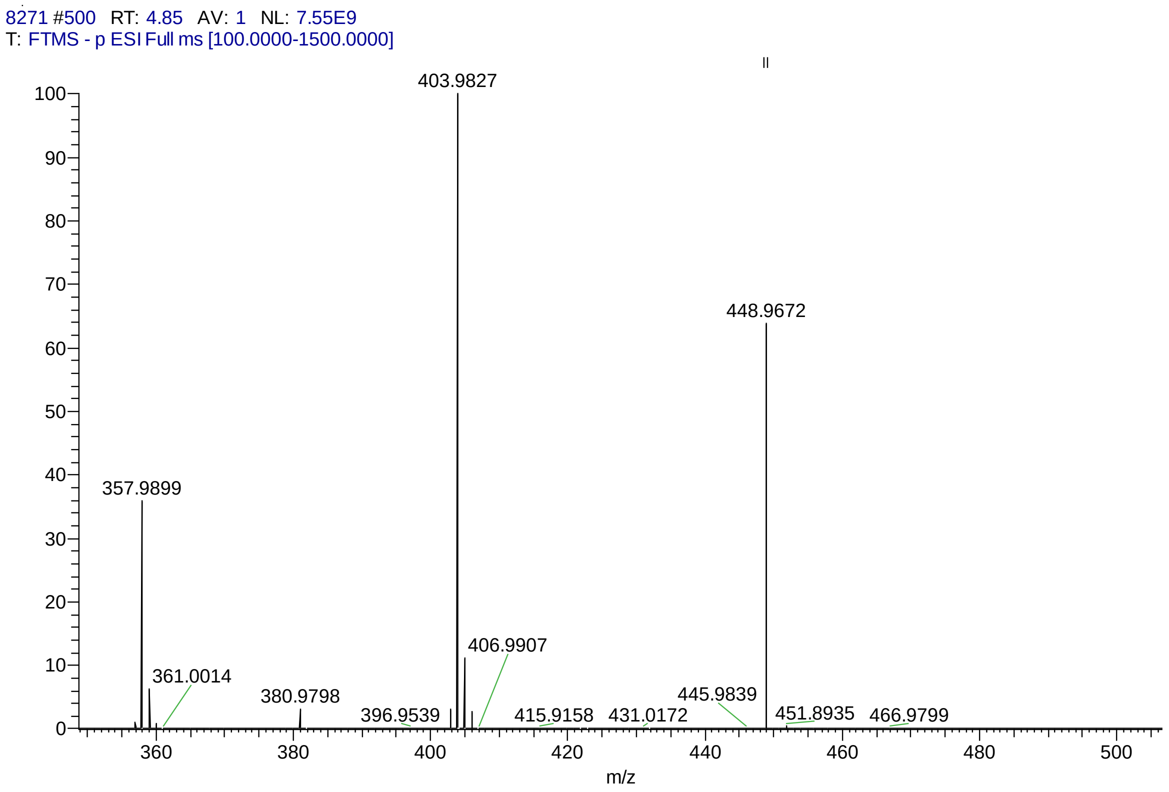

Figure S10 HRMS spectrum of **3**

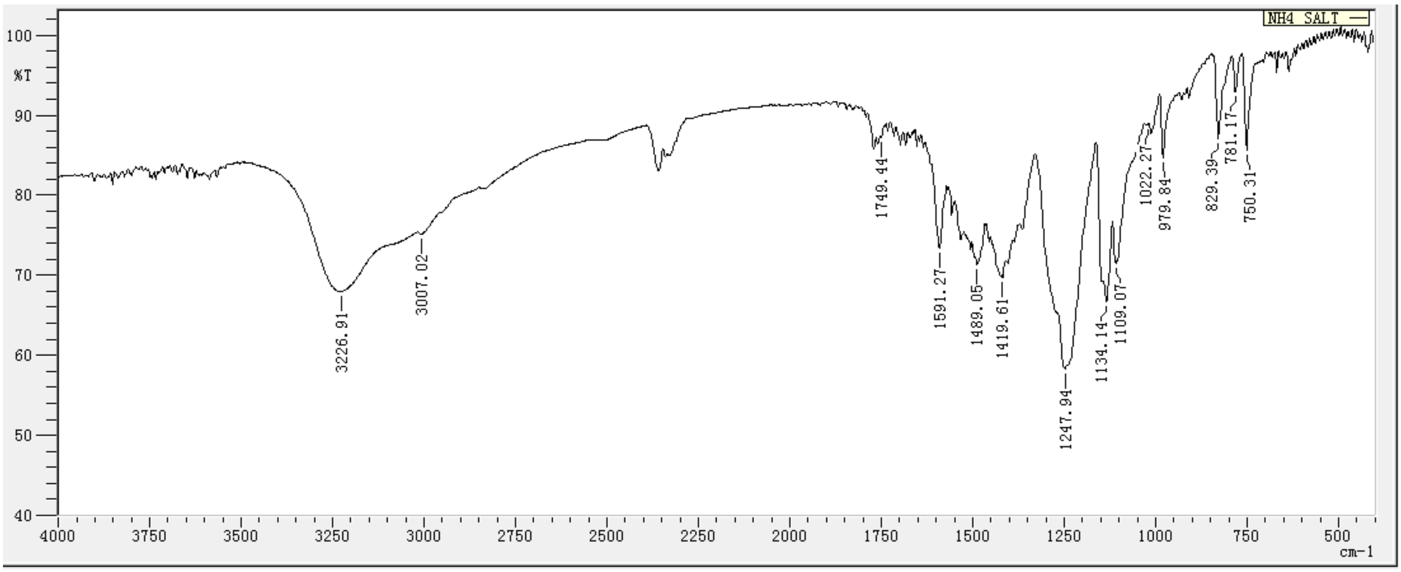

Figure S11 IR spectrum of **5**.

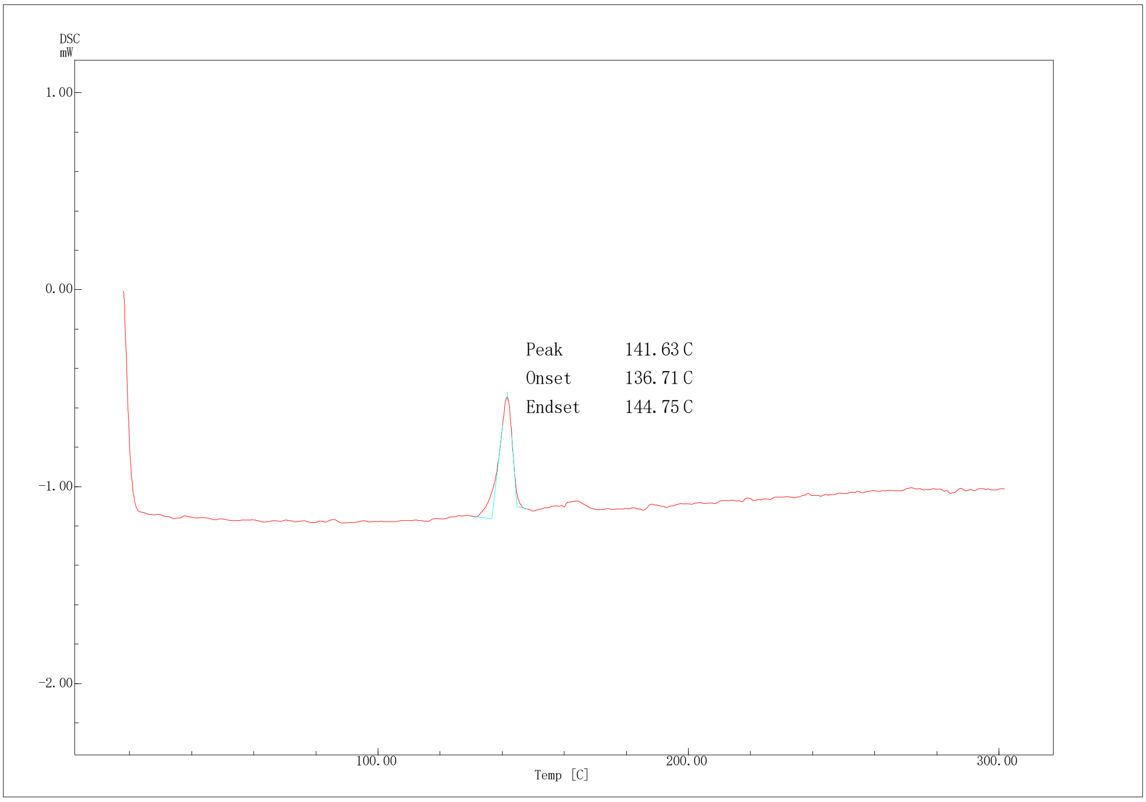

Figure S12 DSC curve of **5** (10 ºC min^{-1})

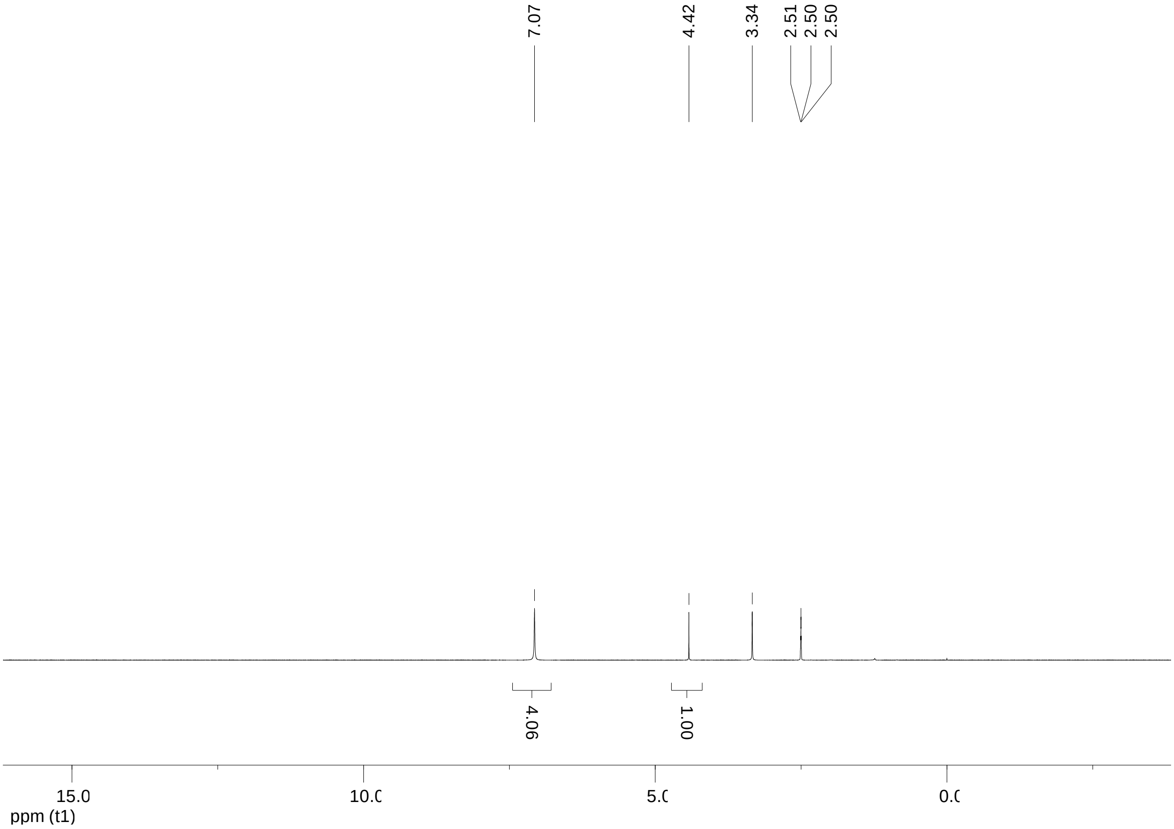

Figure S13 ^{1}H NMR spectrum of **5**.

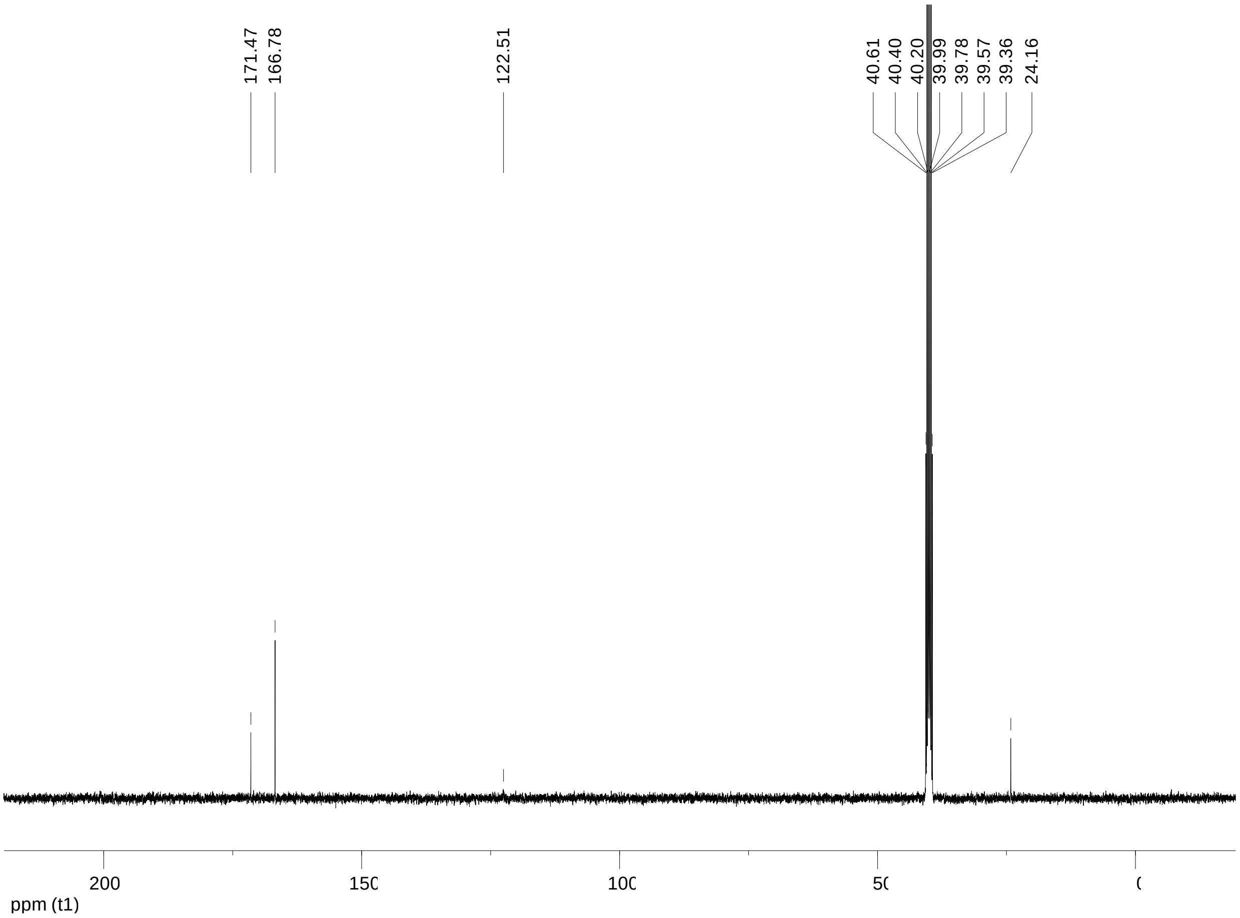

Figure S14 ^{13}C NMR spectrum of **5**.

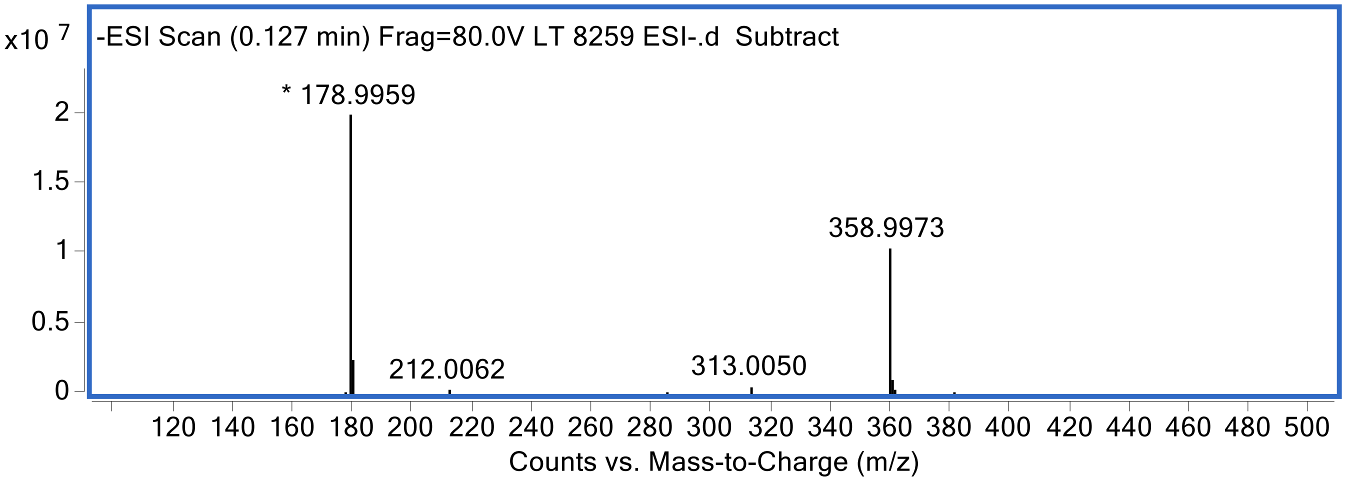

Figure S15 HRMS spectrum of **5**.

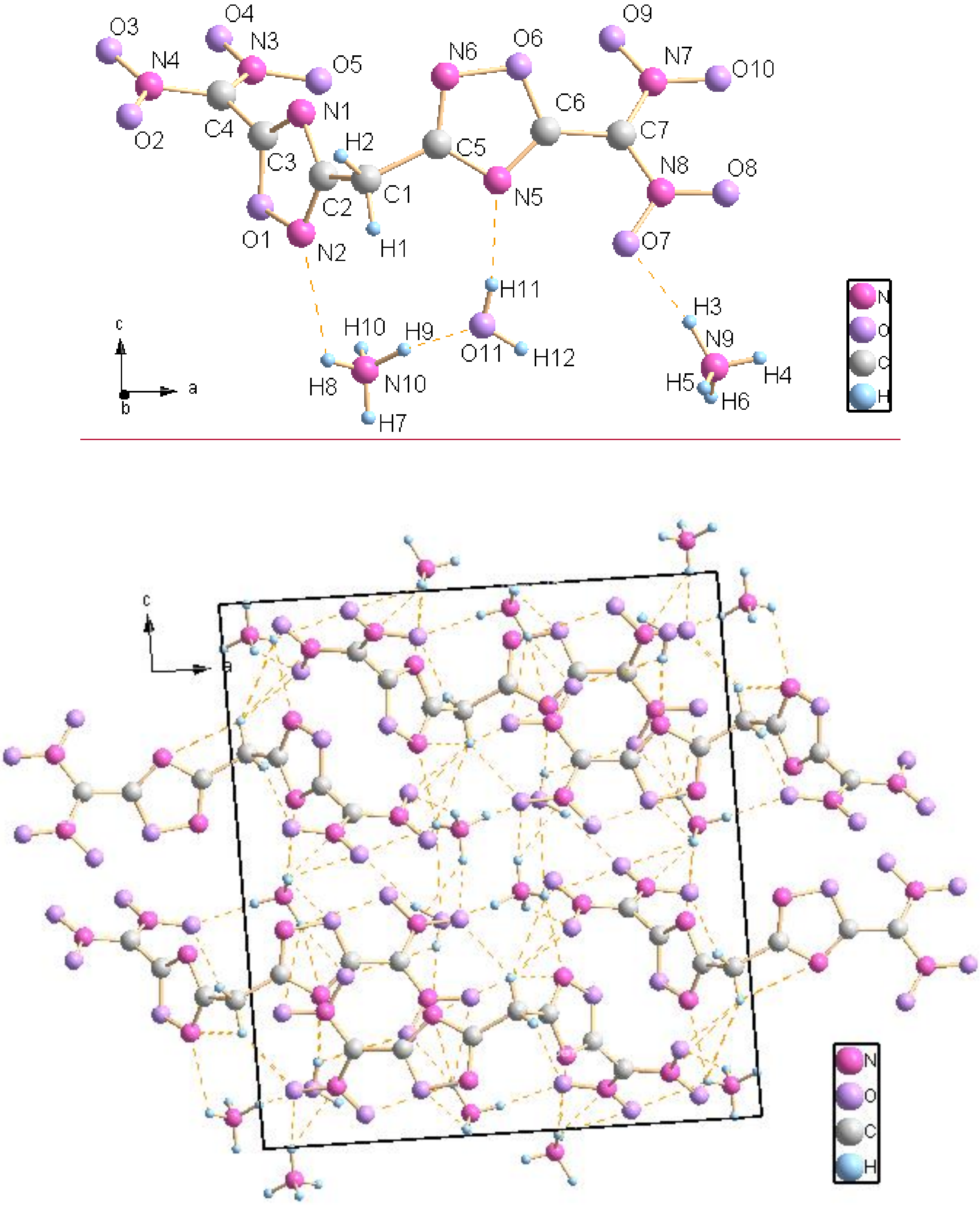

Figure S16 X-ray crystal structure of **5 • H_2O**

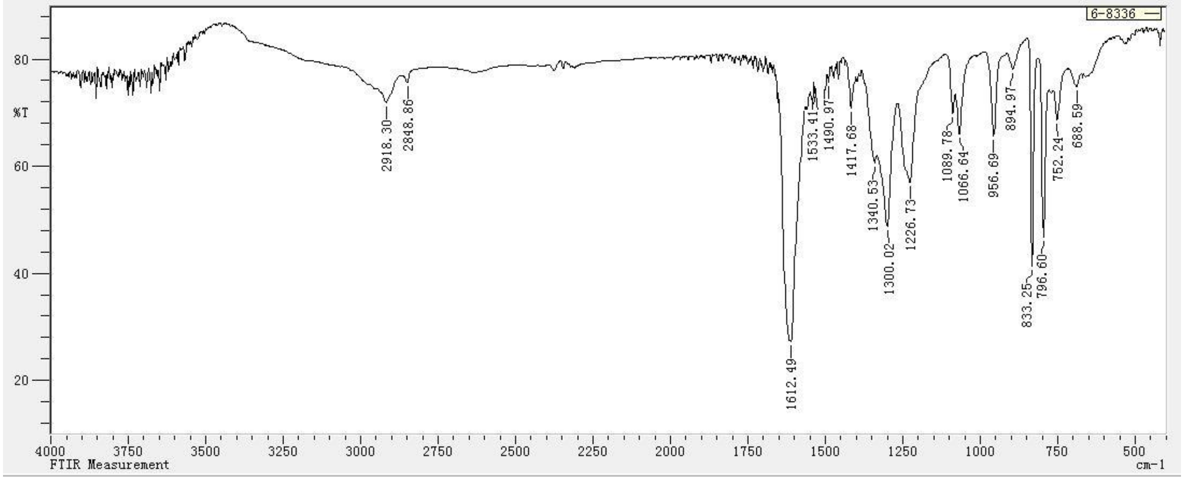

Figure S17 IR spectrum of **6**

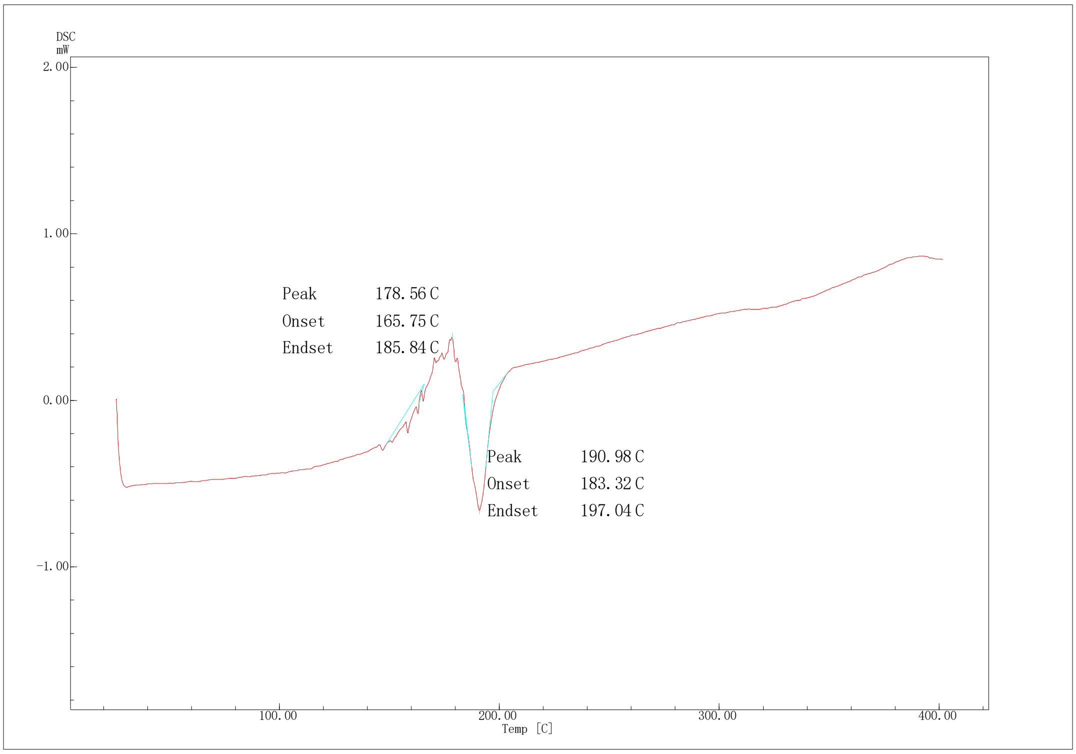

Figure S18 DSC curve of **6** (10 ºC min^{-1})

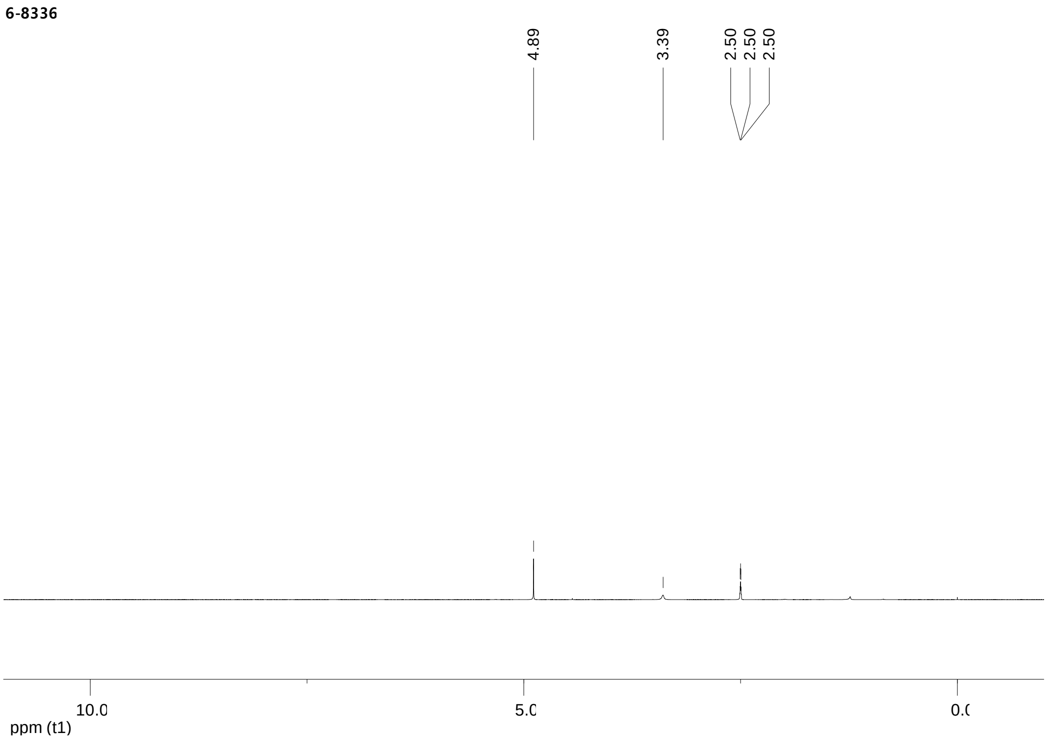

Figure S19 ^{1}H NMR spectrum of **6**

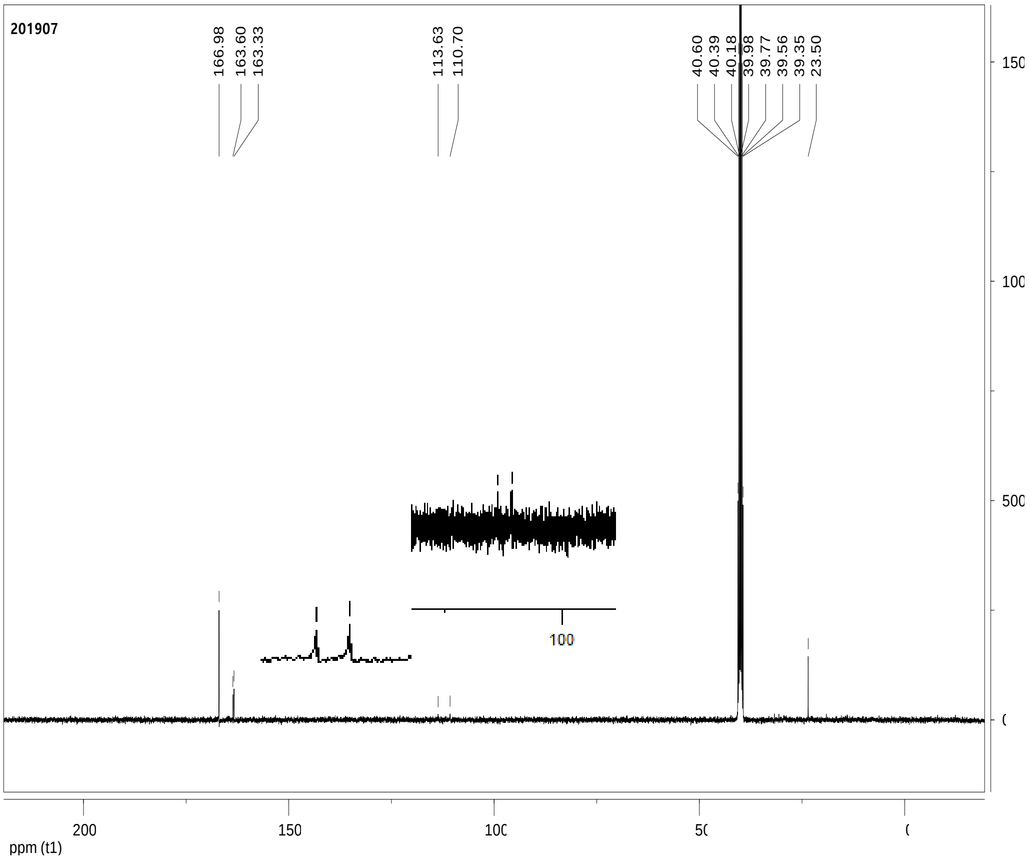

Figure S20 ^{13}C NMR spectrum of **6**.

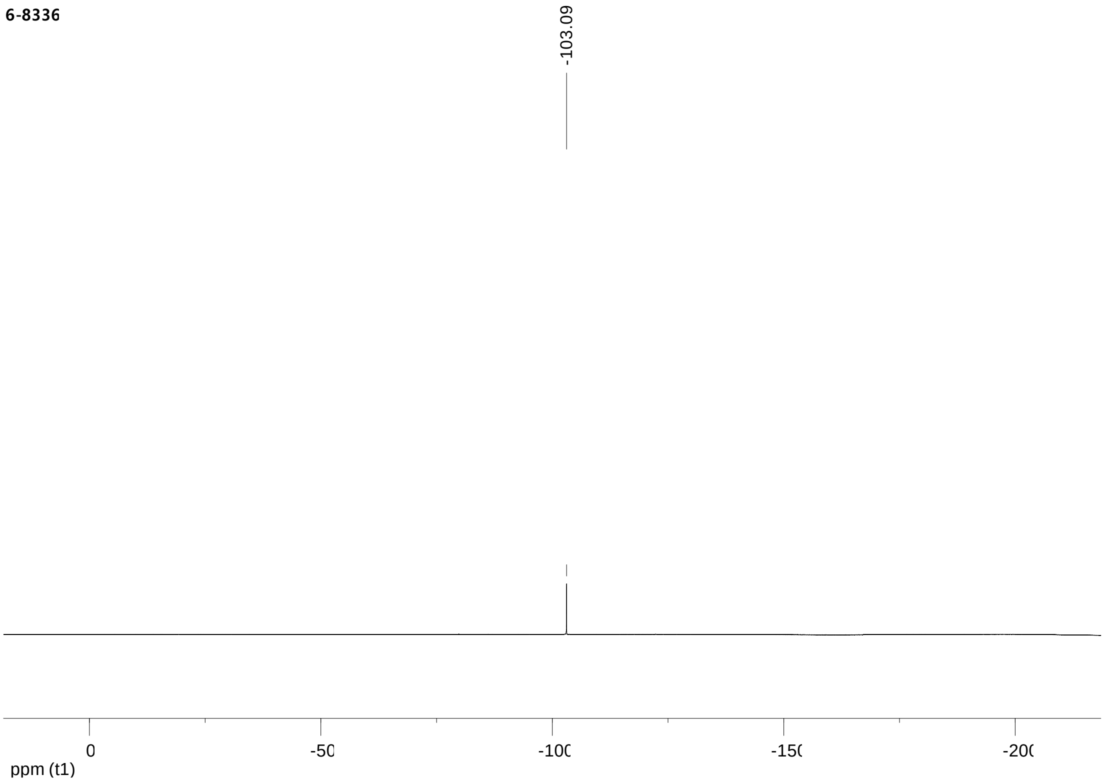

Figure S21 ^{19}F NMR spectrum of **6**

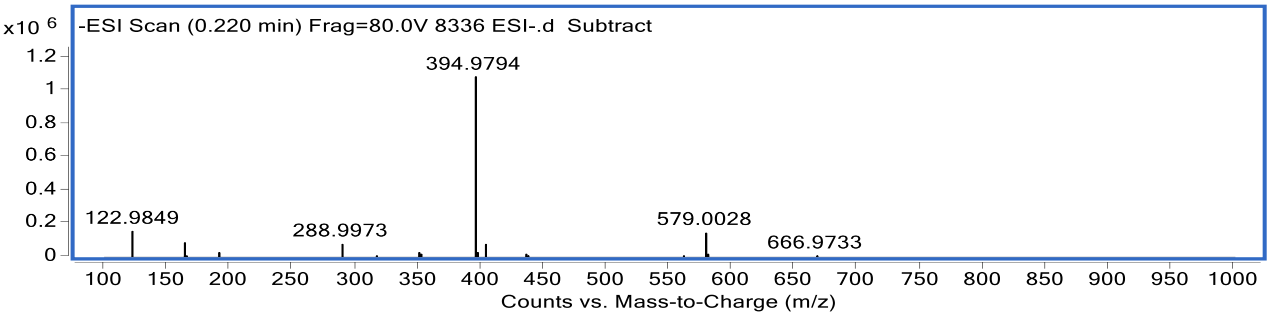

Figure S22 HRMS spectrum of **6**

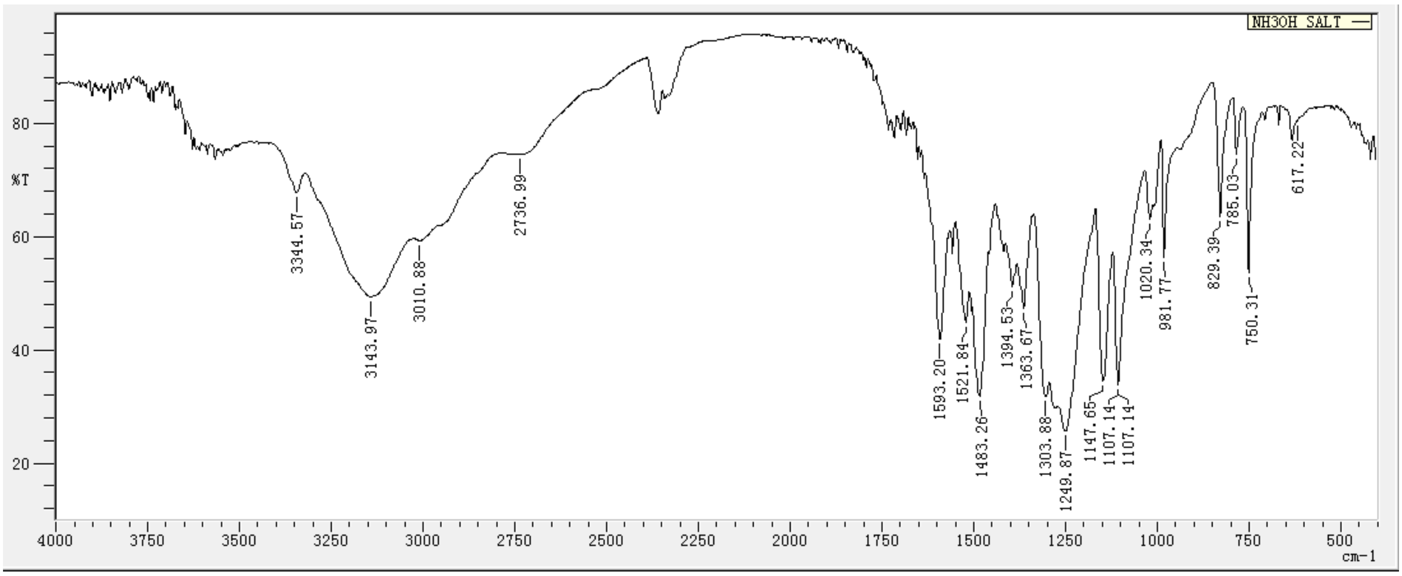

Figure S23 IR spectrum of **7**.

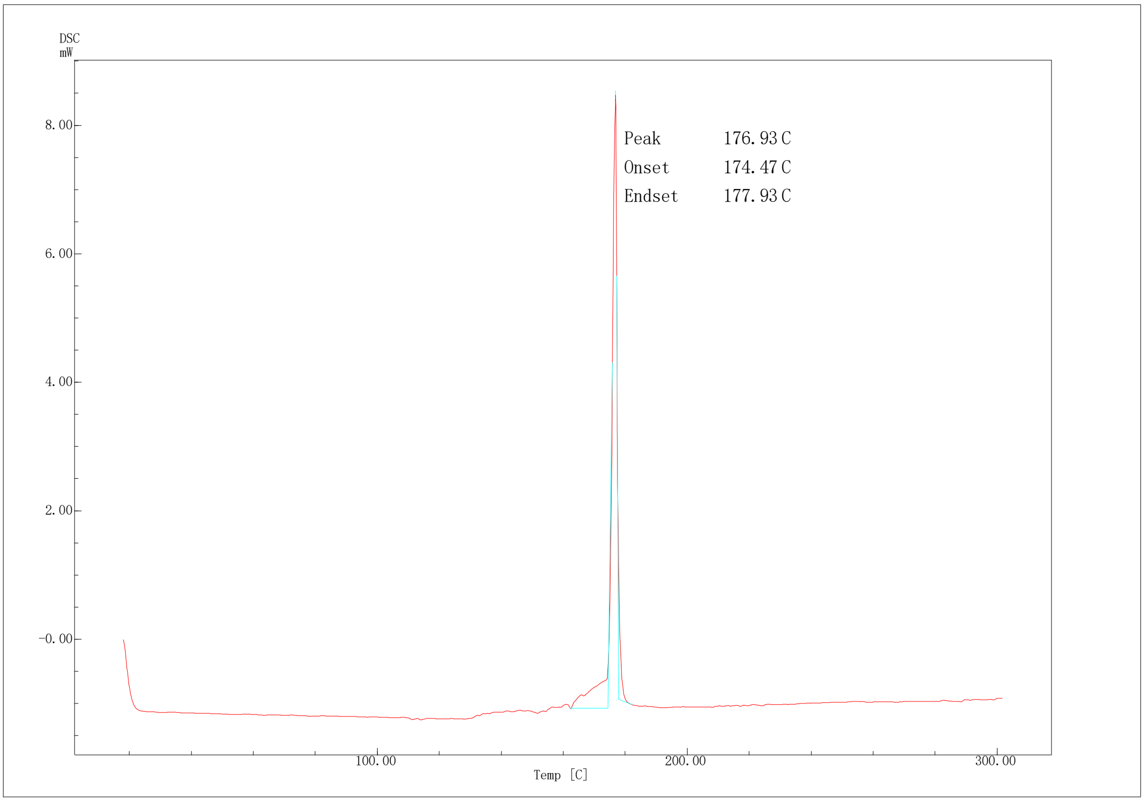

Figure S24 DSC curve of **7** (10 ºC min^{-1})

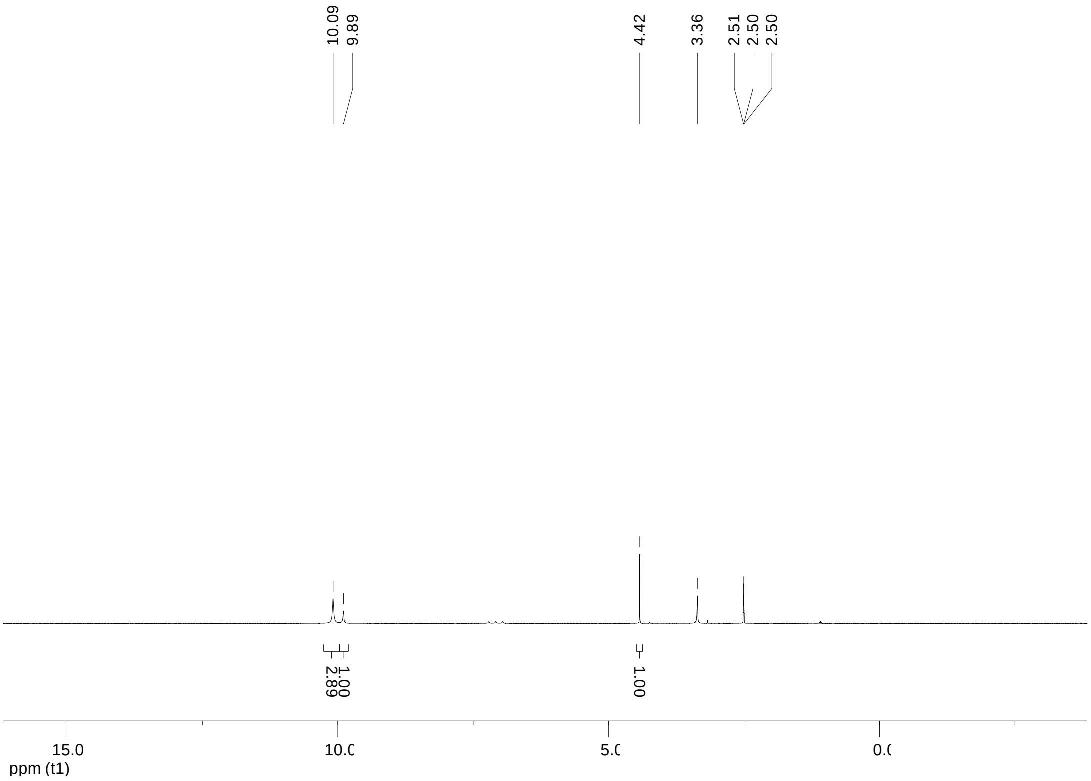

Figure S25 ^{1}H NMR spectrum of **7**

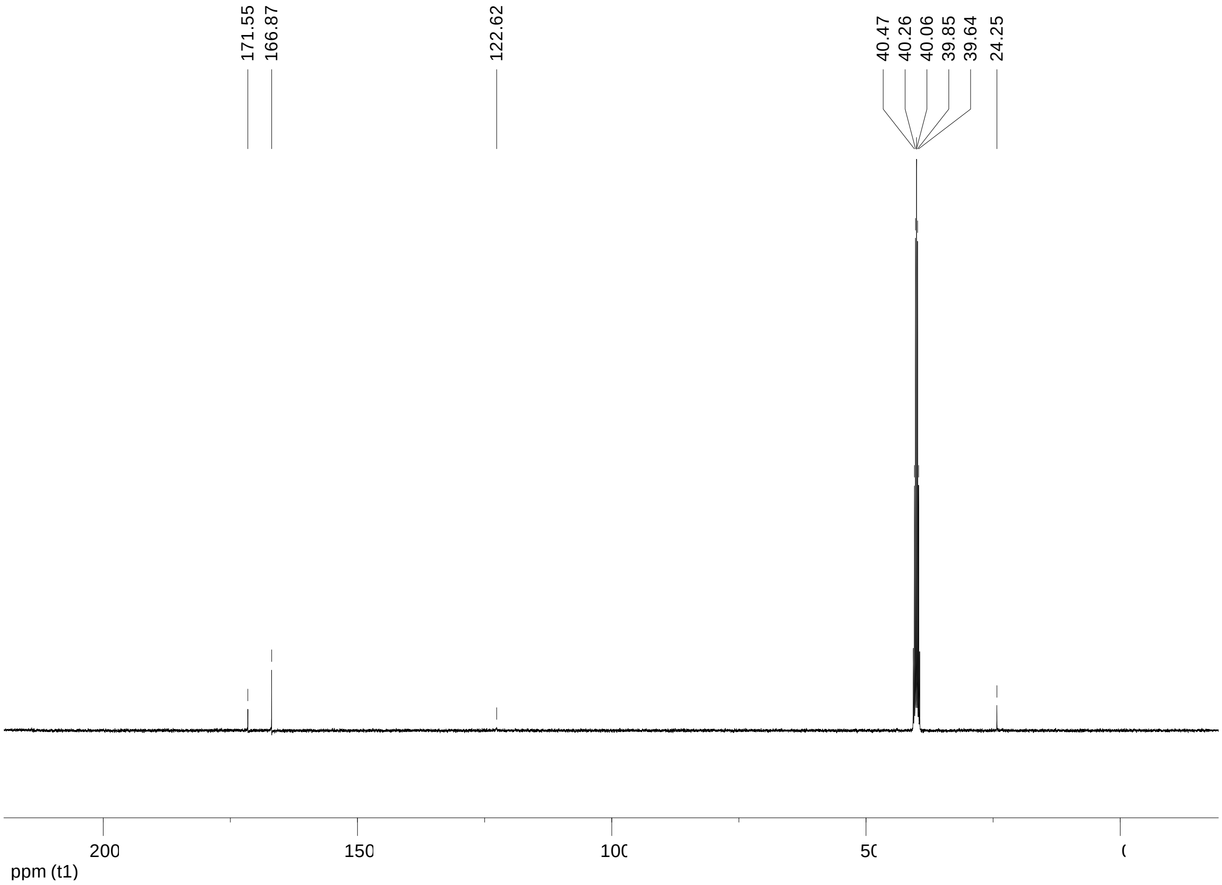

Figure S26 ^{13}C NMR spectrum of **7**.

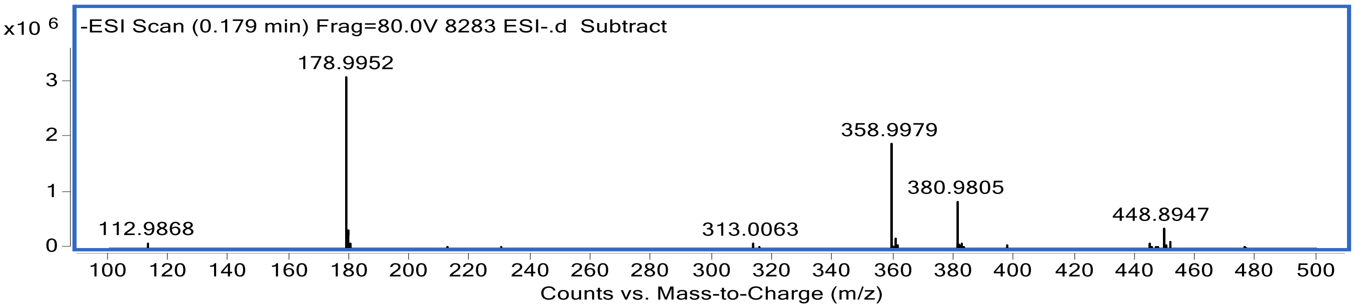

Figure S27 HRMS spectrum of **7**

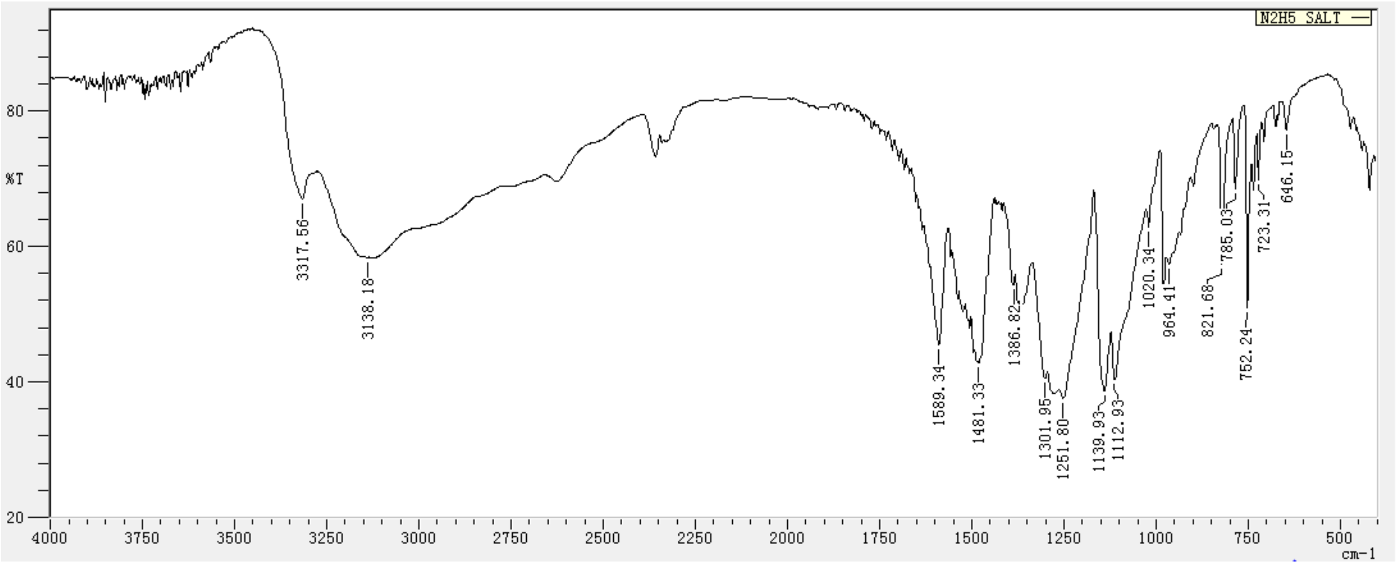

Figure S28 IR spectrum of **8**.

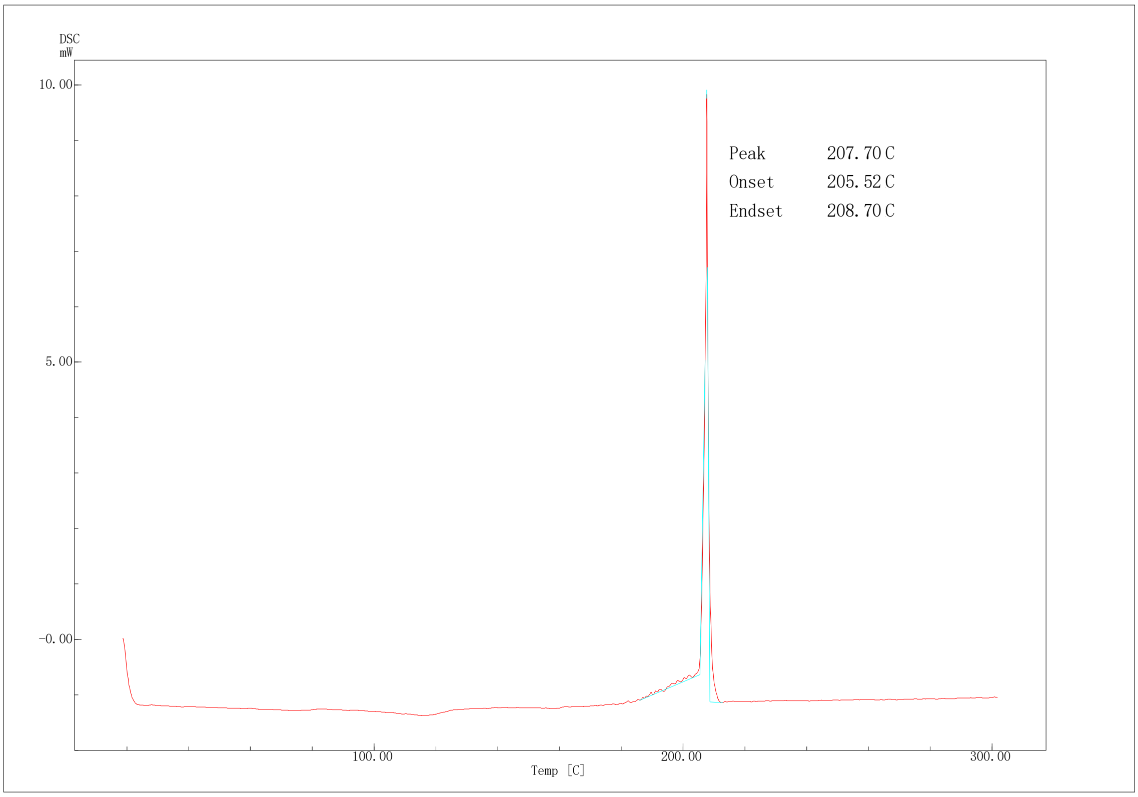

Figure S28 DSC curve of **8** (10 ºC min^{-1})

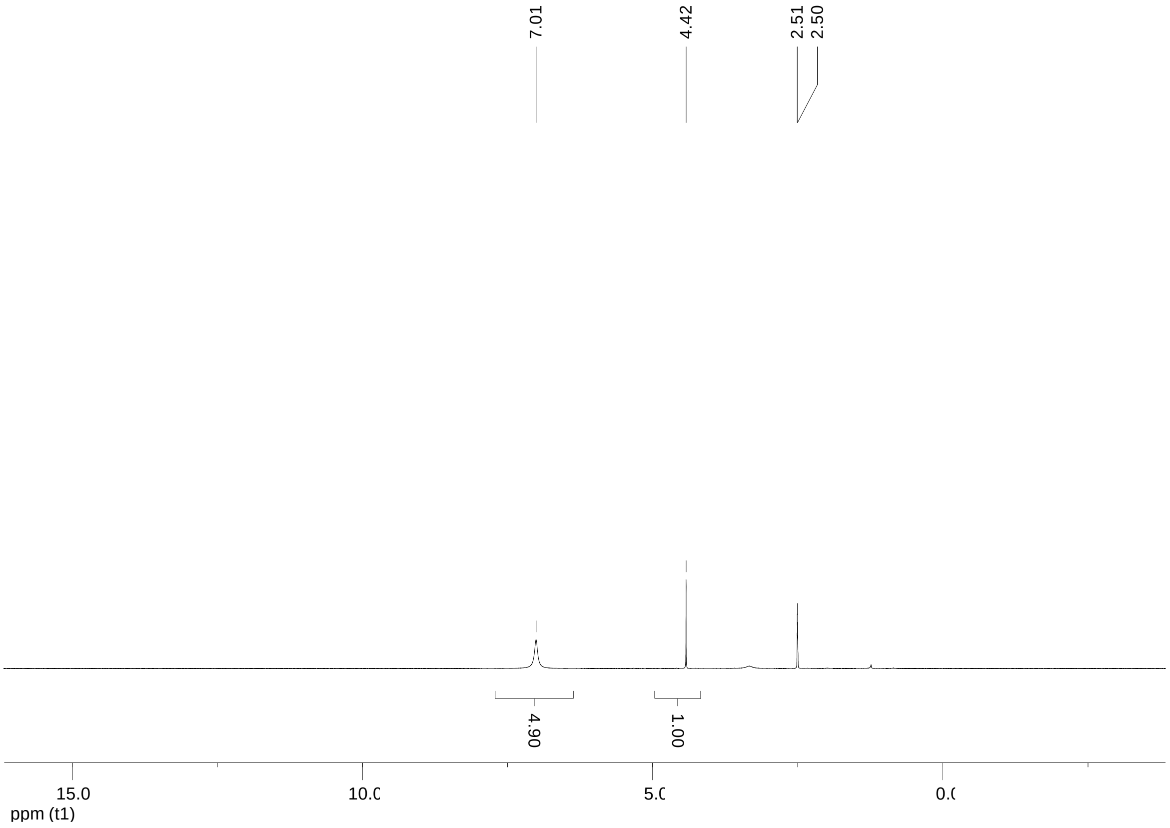

Figure S29 ^{1}H NMR spectrum of **8**

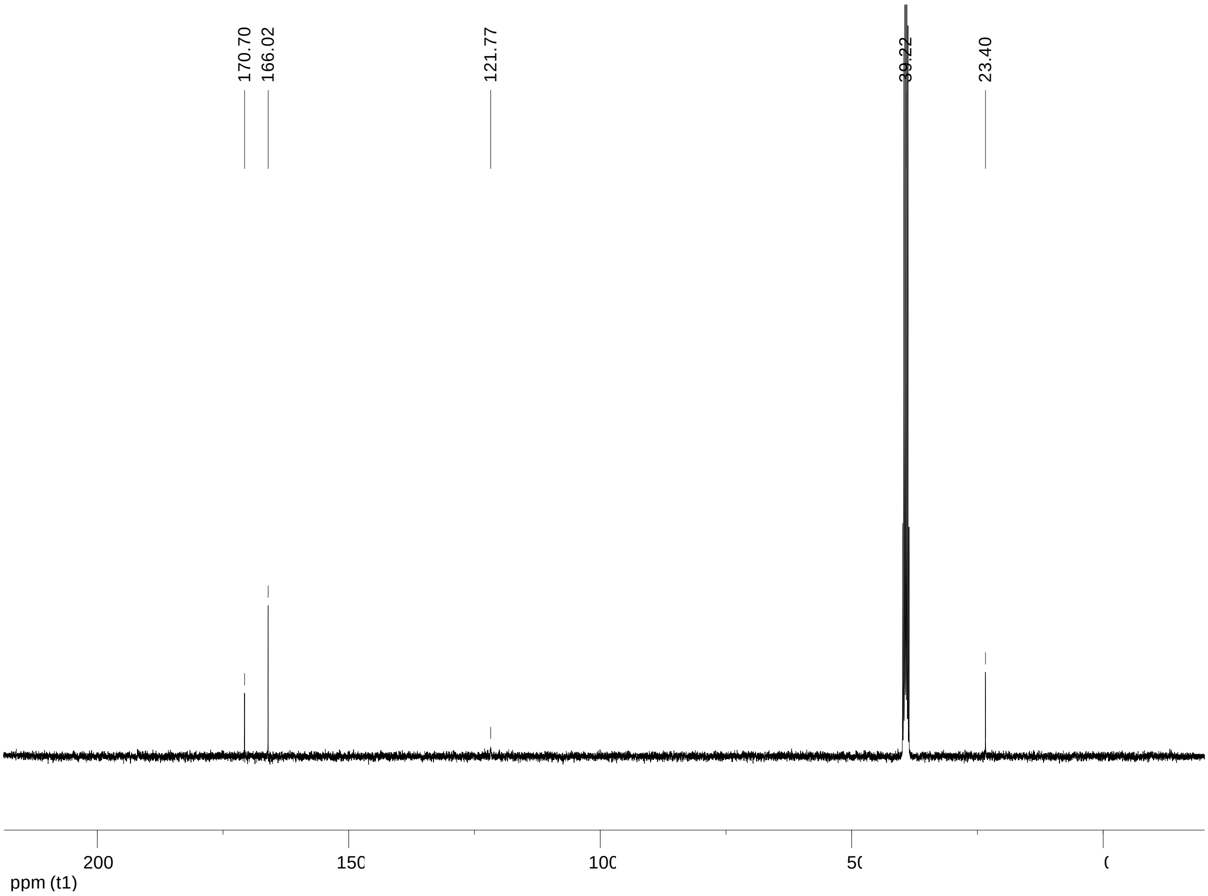

Figure S30 ^{13}C NMR spectrum of **8**.

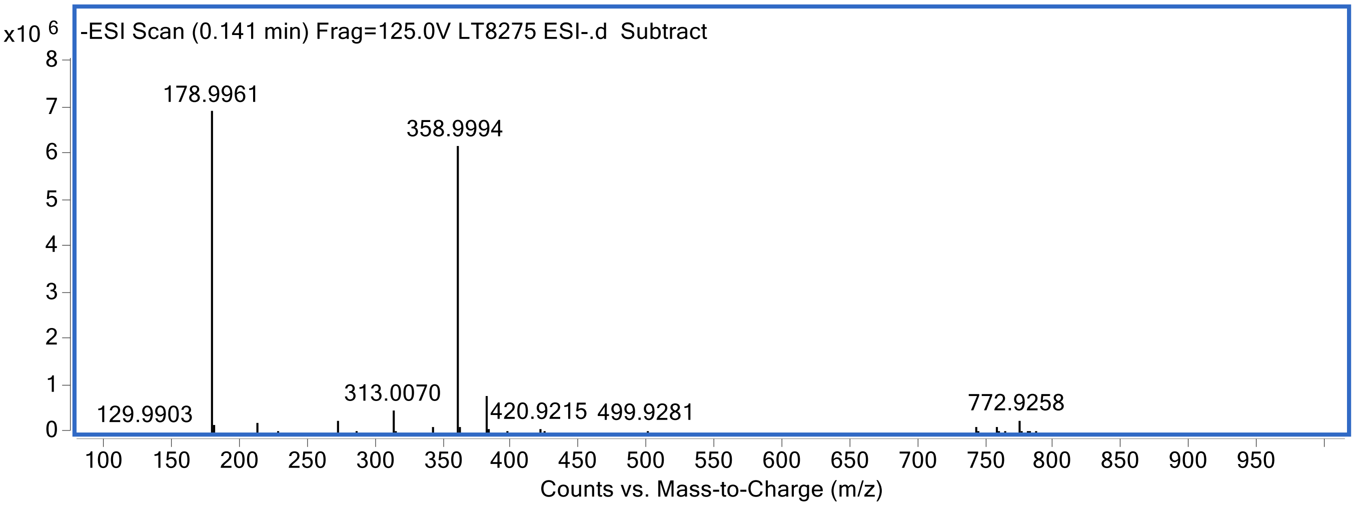

Figure S31 HRMS spectrum of **8**

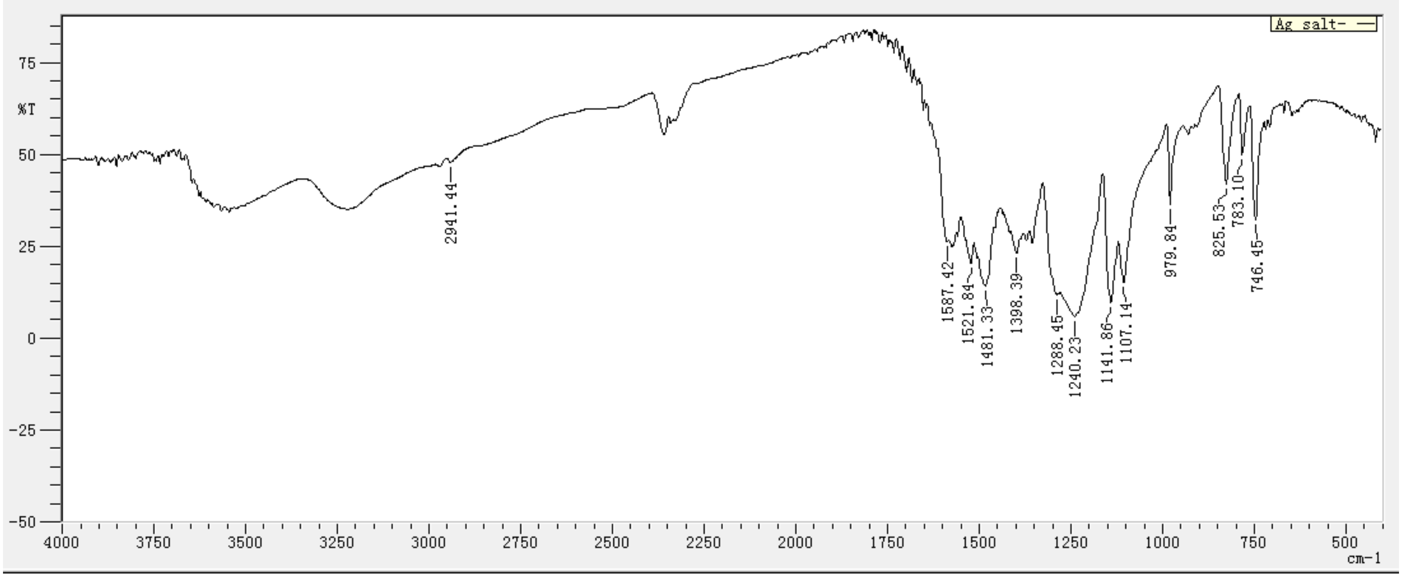

Figure S32 IR spectrum of **9**.

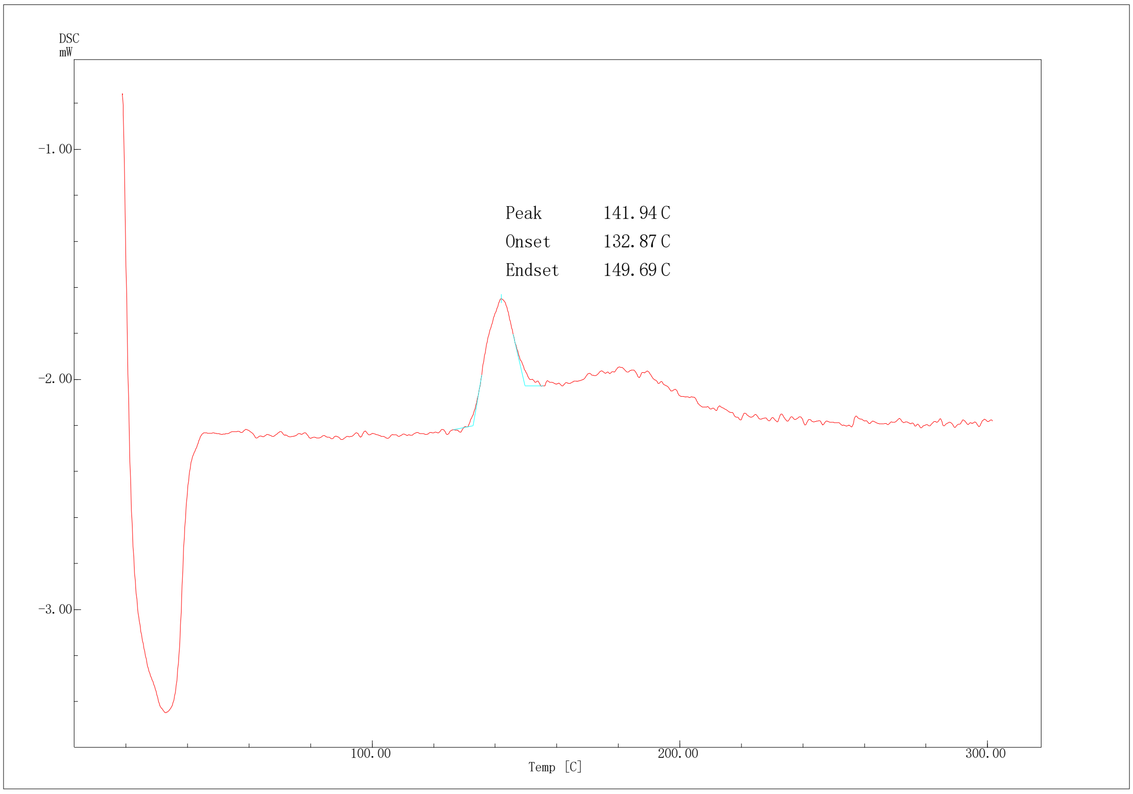

Figure S33 DSC curve of **9** (10 ºC min^{-1})

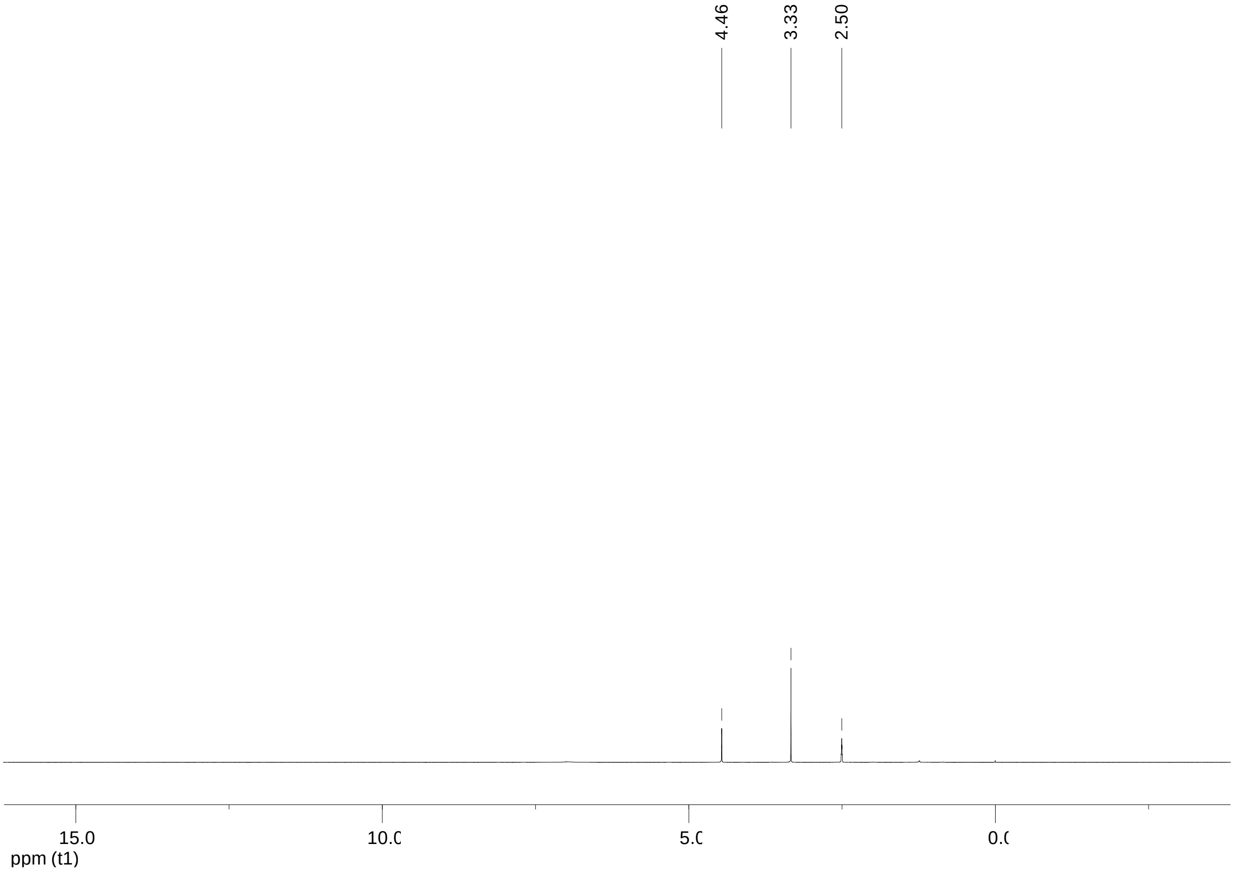

Figure S34 ^{1}H NMR spectrum of **9**

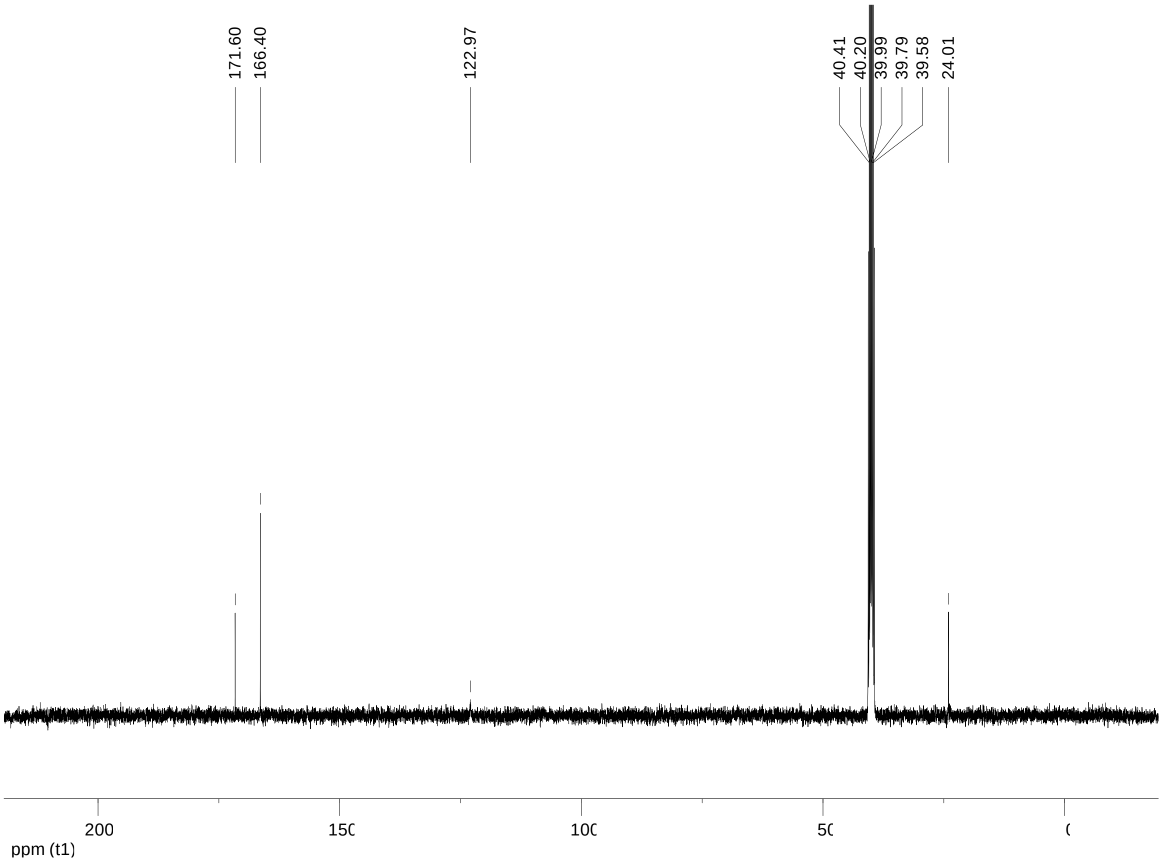

Figure S35 ^{13}C NMR spectrum of **9**.

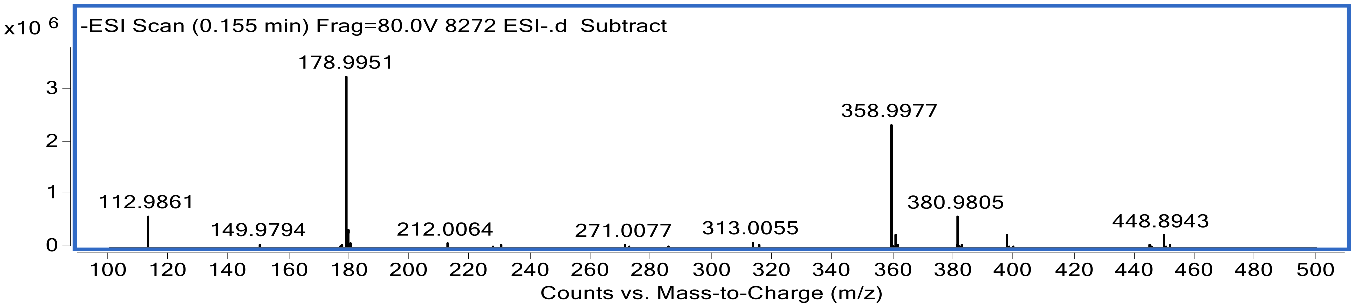

Figure S36 HRMS spectrum of **9**