Synthesis and Properties of Gem-dinitro Energetic Salts Based on 1,2,4-Oxadiazole with Low Impact Sensitivity

Tian Lu,[a] He Yuna,[a] Song Jia,[a] Zhengwen Hou, [a] Hongquan Yin,[a] Guijuan Fan,[b] and Fu-Xue Chen[a*]

a. School of Chemistry & Chemical Engineering, Beijing Institute of Technology (Liangxiang Campus), No. 8 Liangxiang east road, Fangshan district, Beijing 102488, China. E-mail: fuxue.chen@bit.edu.cn

b. Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621050, Sichuan, China.

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 ^{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 Me_4Si. Differential scanning calorimeter (DSC, Shimadzu TA-60ws) was used to measure the melting temperatures and decomposition temperatures at a heating rate of 10 °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.

Compound **1** was synthesized according to the literature.[S1]

***N*-Hydroxy-5-methyl-1,2,4-oxadiazole-3-carbimidoyl chloride** (**2**): To a solution of N'-Hydroxy-5-methyl-1,2,4-oxadiazole-3-carboximidamide (**1**, 2.63 g, 18.50 mmol) in a mixture of concentrated HCl (9.2 mL) and water (30.0 mL) was added the solution of sodium nitrite (1.40 g, 20.40 mmol) in 5.00 mL water while always keeping the temperature between 0-5 °C. The reaction mixture was stirred for 8 h with the temperature warming up to ambient temperature. The solid was collected by filtration, washed with ice-water, and dried in air to give **2** as a white solid (2.55 g, 85.34%). $T_{m\,(peak)}$ = 156.20 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.65 (s, 3H, CH_3), 13.42 (s, 1H, NOH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.55 (s, 1C, CH_3), 125.82 (s, 1C, CCl), 164.20 (s, 1C, NCN), 178.91 (s, 1C, OCN) ppm. IR: 3213 (m), 3155 (m), 3092 (m), 2989 (w), 2924 (w), 2858 (m), 1578 (vs), 1506 (s), 1422 (m), 1383 (m), 1277(m), 1078(vs), 1018 (vs), 937 (s), 829 (w), 783(w), 719 (w), 654(w), 472(m) cm^{-1}; HRMS: calc. for $C_4H_5ClN_3O_2$ $[M + H]^+$: 162.0065, found: 162.0065.

3-(Chlorodinitromethyl)-5-methyl-1,2,4-oxadiazole (**3**): **2** (161.50 mg, 1.00 mmol) was added dropwise to a stirred mixture of fuming HNO_3 (0.8 mL) and trifluoroacetic acid anhydride (1.4 mL) at 0 °C. The mixture was allowed to warm slowly to room temperature and stirred for 8 h. It was poured into ice water (30.0 mL) and filtered to give **3** as a white solid (96.00 mg, 43.13%), which was dissolved in the mixture of petroleum ether and ethyl acetate (2:1) and evaporating slowly at 4 °C to give colorless block crystal suitable for X-ray diffraction. $T_{m\,(peak)}$ = 65.03 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.78 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.89 (s, 1C, CH_3), 161.95 (s, 1C, NCN), 181.98 (s, 1C, OCN) ppm. IR: 2926 (s), 1610 (vs),1580 (vs), 1514 (m), 1384 (m), 1300 (m), 1261(s), 1093(vs), 975 (m), 918 (w), 824 (vs), 792(vs), 709 (m), 698(m), 644(w) cm^{-1}.

Potassium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**4**): **3** (400.00 mg, 1.80 mmol) was dissolved in methanol (16.0 mL) and then the solution of potassium iodide (598.00 mg, 3.60 mmol) in methanol (8.0 mL) was added dropwise and the reaction mixture turn to reddish brown immediately. Keep stirring for 12 h at 25 °C followed by filtration and washed with cold methanol (3.0 mL) to give precipitate **3** (343.00 mg, 84.69%). $T_{d(onset)}$ = 178.20 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 2H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.44 (s, CH_3), 123.32 (s, 1C, C $(NO_2)_2$), 163.45 (s, 1C, NCN), 176.98 (s, 1C, OCN) ppm. IR: 1585 (m), 1541 (s), 1472 (s), 1391 (m), 1371 (w), 1232(vs), 1138 (vs), 827 (m), 785 (w),754 (s) cm^{-1}; HRMS: $C_4H_3N_4O_5$ $[M - K]^-$: 187.0109, found: 187.0105.

General method for preparing compounds 5–11:

Concentrated hydrochloric acid was added dropwise to the suspension of potassium salt **3** (163.00 mg, 0.72 mmol) in water (10.0 mL) while keep stirring at 0 °C. Then it was extracted with ethyl acetate (3 × 10.0 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and then concentrated under vacuum to obtain a yellow oil which was dissolved in MeOH (4.0 mL). Subsequently, various bases include ammonia in methanol (7 M, 0.3 mL, 2.00 mmol), 50% hydroxylamine solution (0.12 mL, 2.00 mmol), 80% hydrazine hydrate (0.1 mL, 2.00 mmol), 3-amino-1,2,4-triazole (60.40 mg, 0.72 mmol), 1,3-diaminourea (64.00 mg, 0.72 mmol),

aminoguanidinium carbonate (98.00 mg, 0.72 mmol) and guanidinium carbonate (64.00 mg, 0.72 mmol) was added. The mixture was stirred at ambient temperature for 8 h. The precipitate was filtered and dried in air to give yellow product **5-11**, respectively.

Ammonium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**5**): (119.00 mg, 80.80%) $T_{d(onset)}$ = 160.64 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 3H, CH_3), 7.06 (s, 4H, NH_4) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.44 (s, 1C, CH_3), 123.27 (s, 1C, $C(NO_2)_2$), 163.43 (s, 1C, NCN), 176.98 (s, 1C, OCN) ppm. IR: 3226 (s), 3041(w), 2968(w), 2843 (w), 1579 (s), 1545 (vs), 1481 (m), 1456 (w), 1348(m), 1263(vs), 1139 (vs), 1115 (vs), 1041 (w), 970 (m), 897 (s), 818(vs), 744 (s), 700(m), 498(vs) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - NH_4]^-$: 187.0109, found: 187.0106.

Hydroxylammonium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**6**): (103.00 mg, 64.65%) $T_{d(onset)}$ = 147.74 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 3H, CH_3), 8.55 (br, 4H, NH_3 OH)ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.39(s, 1C, CH_3), 123.27 (s, 1C, $C(NO_2)_2$), 163.31 (s, 1C, NCN), 177.12 (s, 1C, OCN) ppm. IR: 3429(m), 3055 (m), 2937 (w), 2713 (w), 1581 (w), 1550(s), 1477 (s), 1361 (w), 1261(s), 1117 (vs), 979 (m), 893(w), 817 (s), 752 (s) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - NH_3OH]^-$: 187.0109, found: 187.0106.

Hydrazinium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**7**): (123.00 mg, 77.60%) $T_{d\ (onset)}$ = 165.53 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 2H, CH_3), 6.98 (br, s, 5H, N_2H_5) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.44 (s, 1C, CH_3), 123.23 (s, 1C, $C(NO_2)_2$), 163.42 (s, 1C, NCN), 176.99 (s, 1C, OCN) ppm. IR: 3373 (s), 3307 (m), 2933 (m), 2713 (w), 2612 (w), 1548 (s), 1473 (s), 1361 (w), 1301(w), 1257 (s), 1143 (m), 1117 (s), 977 (s), 889 (s), 819 (vs), 752 (s) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - N_2H_7]^-$: 187.0109, found: 187.0119.

5-Amino-1H-1,2,4-triazol-2-ium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**8**): (143.00 mg, 72.97%) $T_{d\ (onset)}$ = 107.98 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 3H, CH_3), 8.25(s, 2H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.44 (s, 1C, CH_3), 123.22 (s, 1C, $C(NO_2)_2$), 140.33 (s, 1C, NCNH), 151.71(s, 1C, $NC(NH)NH_2$), 163.43 (s, 1C, NCN), 178.97 (s, 1C, OCN) ppm. IR: 3410 (vs), 3317 (s), 2965 (m), 1687(vs), 1577 (s), 1510 (vs), 1477 (s), 1419 (m), 1350 (vs), 1203 (vs), 1114 (m), 1045 (m), 945 (m), 908 (m), 866 (m), 750 (s), 711 (s), 513 (w) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - C_2N_4H_5]^-$: 187.0109, found: 187.0119.

Diaminouronium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**9**): (172.00 mg, 85.87%) $T_{d\ (onset)}$ = 136.60 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 3H, CH_3), 8.35(br, s, 6H, NH_2, NH_2, NH_2,) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 11.89 (s, 1C, CH_3), 122.73 (s, 1C, $C(NO_2)_2$), 159.02(s, 1C, $NH_{1C}ONH$), 162.90 (s, 1C, NCN), 176.41 (s, 1C, OCN) ppm. IR: 3294 (s), 3145 (w), 2951 (m), 2671 (w), 1685(w), 1645 (s), 1581(m), 1550 (m), 1472 (vs), 1357 (s), 1246 (vs), 1136 (s), 1112 (s), 896 (m), 819 (vs), 748 (vs) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - CON_4H_7]^-$: 187.0109, found: 187.0103.

Aminoguanidinium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**10**): (122.00 mg, 64.63%) $T_{d\ (onset)}$ = 146.78 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 2H, CH_3), 4.67(s, 2H, NH_2), 7.20 (br, s, 5H, NH_2, NH_2, H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 11.88 (s, 1C, CH_3), 122.67 (s, 1C, $C(NO_2)_2$), 158.67(s, 1C, $C(NH_2)_2$), 162.89 (s, 1C, NCN), 176.40 (s, 1C, OCN) ppm. IR: 3452 (m), 3425 (m), 3374 (w), 3283 (w), 3076(w), 2974 (w), 1663(vs), 1579 (m), 1543 (s), 1475 (vs), 1354 (m), 1255 (vs), 1143 (vs), 1114 (s), 962 (w), 906 (m), 821 (s), 750 (s), 648 (m), 482 (m) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - CN_4H_7]^-$: 187.0109, found: 187.0106.

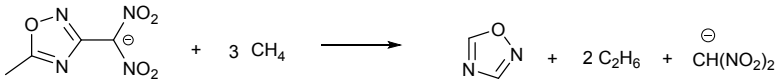
Guanidinium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**11**): (124.00 mg, 69.68%) $T_{d\ (onset)}$ = 185.20 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 2.61 (s, 2H, CH_3), 6.89(s, 6H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 12.43 (s, 1C, CH_3), 123.20 (s, 1C, $C(NO_2)_2$), 158.33(s, 1C, $C(NH_2)_3$), 163.44 (s, 1C, NCN), 176.95 (s, 1C, OCN) ppm. IR: 3455 (s), 3418 (s), 3350 (s), 3269 (m), 3211(m), 3045(w), 2935 (w), 1654(vs), 1583 (m), 1535 (s), 1474 (vs), 1375 (m), 1265 (vs), 1149 (m), 1111 (s), 964 (w), 918 (m), 823 (s), 750 (s), 555 (m) cm^{-1}; HRMS: calc. for $C_4H_3N_4O_5$ $[M - CN_4H_7]^-$: 187.0109, found: 187.0105.

2.Gaussian Calculations

The density and heats of formation (HOF) of **4-11** were calculated by the Gaussian09 suite of programs.[S2]

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[S3] and literature references.[S4]



Scheme S1 Isodesmic reactions for anions of **4-11**.

For the ionic salt **4-11**, the HOF can be simplified by the formula given in Eq (1) based on a Born-Haber energy cycle (Scheme S2),

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

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al [Eq (2)].[S5]

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

In this equation, n_M and n_X depend on the nature of the ions M_{p+} and X_{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} [Eq (3)] has the form:

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

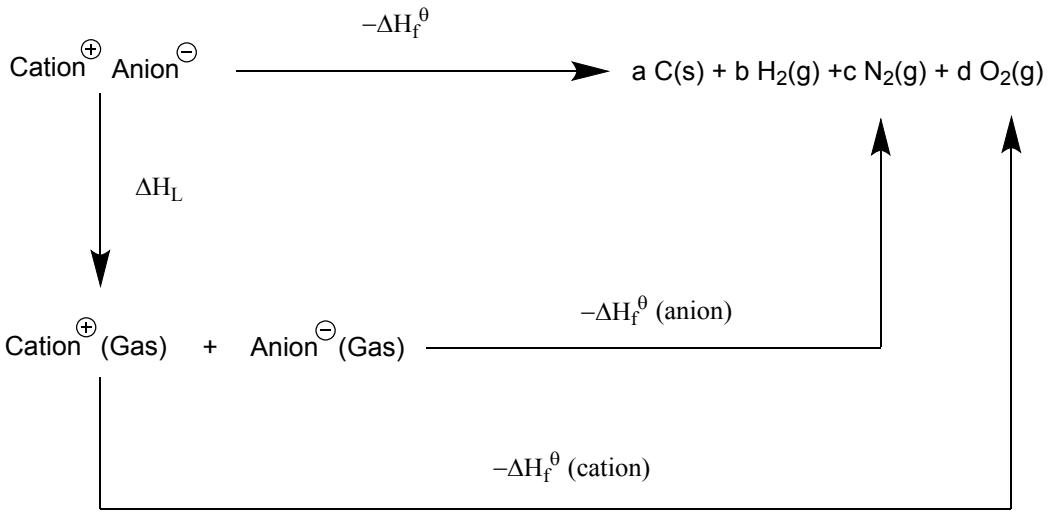
Where values for the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are taken from the literature.[S6]

ρ_m [g cm^{-3}] is the density obtained by the formula given in [Eq (4)]. M_m is the molecular weight, and V_m is the molar volume of the compound.

$$\rho_m = \frac{M_m}{V_m} \quad (4)$$

For ionic salts with hydrogen atoms, Eq (5) is utilized to get the corrected ionic volume. We can get a correction factor by the density of crystal to get the more accurate volume of anion.

$$V_{m(ionic)} = pV_{M+} + qV_{X-} - [0.6763 + 0.9418 \times (no.\ of\ hydrogen\ atoms\ in\ the\ ionic)] \quad (5)$$



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}]
5	18.272	111.542	122.545	205.13	1.674
6	26.118	111.542	130.391	221.129	1.696
8	58.934	111.542	162.265	272.181	1.677
9	65.286	111.542	166.734	278.185	1.668
10	57.165	111.542	158.613	262.186	1.653
11	48.543	111.542	147.165	247.171	1.680

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]
1,2,4-oxadiazole	−261.5727899	0.046538	0.050909	75.0[e]
anion	−747.7975938	0.093718	0.106033	−193.2 [f]
5 cation	-	-	-	626.4 [f]
6 cation	-	-	-	664.4 [f]
7 cation	-	-	-	770.0 [f]
8 cation	-	-	-	826.0 [f]
9 cation	-	-	-	663.4 [f]
10 cation	-	-	-	667.4 [f]
11 cation	-	-	-	575.9 [f]

[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].

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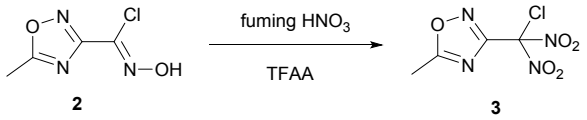
4. Screening of Reaction Time for 3



2 **3**

Table S3 Screening of Reaction Time for **3**.

Entry[a]	Time (h)	Yield (%) of **3**
1	4	31.5
2	8	43.1
3	10	41.0
4	12	41.7
5	16	38.6
6	18	38.4
7	24	38.6

[a] All Reactions was carried out in the same conditions except reaction time with the scale of 1mmol **2** and 0.8ml HNO_3, 1.4ml TFAA.

5. X-ray Diffraction

Table S4 Crystallographic data for **3**, **4**, **7**.

Compd.	**3**	**4**	**7**
Formula	$C_4H_3ClN_4O_5$	$C_{12}H_9K_3N_{12}O_{15}$	$C_4H_8N_6O_5$
Mw[g mol^{-1}]	222.55	678.61	220.16
T[K]	296(2)	170	293(2)
Crystal size[mm^3]	0.700 ×0.40 × 0.300	0.230 ×0.160 × 0.070	0.800×0.600 × 0.500
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2(1)/c	Pbca	P2(1)/c
a[Å]	8.898(3)	7.9304(2)	8.2956(7)
b[Å]	15.100(5)	15.4465(5)	8.4968(7)
c[Å]	6.171(2)	39.4906(13)	12.4697(11)
α[°]	90	90	90
β[°]	97.794(9)	90	95.072(3)
γ[°]	90	90	90
V[Å^3]	821.5(5)	4837.5(3)	875.50(13)
Z	4	8	4
ρ_{calc}[g cm^{-3}]	1.799	1.864	1.670

μ[mm^{-1}]	0.471	0.664	0.151
F[000]	448	2736	456
θ range[°]	2.310-28.294	2.637-27.111	2.465-28.451
Reflections collected	9114 / 2032	72661 / 5335	10429 / 2190
Index ranges	-11<=h<=11, -19<=k<=20, -8<=l<=8	-10<=h<=9, -19<=k<=19, -50<=l<=50	-11<=h<=11, -11<=k<=11, -16<=l<=16
R_{int}	0.0281	0.0447	0.0302
Data/restraints/parameters	2032 / 0 / 128	5335 / 0 / 382	2190 / 0 / 137
Final R index[$I > 2\sigma(I)$]	R1 = 0.0293, wR_2 = 0.0888	R1 = 0.0275 wR_2 = 0.0636	R1 =0.0984 wR_2 = 0.2562
Final R index[all data]	R_1 =0.0311, wR_2 = 0.0905	R_1 =0.0342 wR_2 = 0.0677	R_1 = 0.1019 wR_2 = 0.2576
GOF on F^2	1.066	1.079	1.275
CCDC	2018730	2038764	2018495

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

Table S5. Displacement parameters (A^2 x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	7054(1)	5943(1)	12203(1)	24(1)
O(2)	9664(1)	6387(1)	9990(2)	30(1)
O(5)	5289(1)	7096(1)	9013(2)	26(1)
N(3)	5685(1)	6418(1)	8209(2)	18(1)
O(4)	5111(1)	6058(1)	6536(2)	27(1)
N(2)	8018(1)	4922(1)	6690(2)	18(1)
C(3)	7108(1)	5948(1)	9424(2)	15(1)
O(3)	8221(1)	7002(1)	7294(2)	30(1)
O(1)	7137(1)	3675(1)	7904(2)	22(1)
C(2)	7291(1)	5048(1)	8481(2)	15(1)
N(4)	8461(1)	6513(1)	8861(2)	18(1)
N(1)	6749(1)	4342(1)	9312(2)	21(1)
C(1)	7890(2)	4065(1)	6415(2)	19(1)
C(4)	8478(2)	3500(1)	4763(3)	31(1)

Table S6. Bond lengths [A] and angles [deg] for **3**.

Cl(1)-C(3)	1.7219(14)
O(2)-N(4)	1.2103(16)
O(5)-N(3)	1.2102(15)
N(3)-O(4)	1.2166(16)
N(3)-C(3)	1.5523(16)
N(2)-C(1)	1.3077(18)
N(2)-C(2)	1.3675(16)
C(3)-C(2)	1.4967(17)
C(3)-N(4)	1.5530(16)
O(3)-N(4)	1.2117(16)
O(1)-C(1)	1.3443(17)
O(1)-N(1)	1.4043(15)
C(2)-N(1)	1.3027(17)
C(1)-C(4)	1.4786(19)
O(5)-N(3)-O(4)	127.82(12)
O(5)-N(3)-C(3)	116.89(11)
O(4)-N(3)-C(3)	115.28(10)
C(1)-N(2)-C(2)	101.53(11)
C(2)-C(3)-N(3)	110.60(10)
C(2)-C(3)-N(4)	106.46(10)
N(3)-C(3)-N(4)	104.30(9)
C(2)-C(3)-Cl(1)	113.72(9)
N(3)-C(3)-Cl(1)	110.62(8)
N(4)-C(3)-Cl(1)	110.64(8)
C(1)-O(1)-N(1)	107.20(10)
N(1)-C(2)-N(2)	116.47(11)
N(1)-C(2)-C(3)	121.59(11)
N(2)-C(2)-C(3)	121.93(11)
O(2)-N(4)-O(3)	126.98(12)
O(2)-N(4)-C(3)	115.90(11)
O(3)-N(4)-C(3)	117.05(11)
C(2)-N(1)-O(1)	101.98(10)
N(2)-C(1)-O(1)	112.81(12)
N(2)-C(1)-C(4)	128.88(14)
O(1)-C(1)-C(4)	118.30(13)

Table S7. Anisotropic displacement parameters (A^2 x 10^3) for **3**. 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
Cl(1)	34(1)	26(1)	12(1)	0(1)	5(1)	-4(1)
O(2)	18(1)	37(1)	34(1)	-2(1)	-3(1)	-4(1)
O(5)	26(1)	19(1)	34(1)	-1(1)	9(1)	5(1)
N(3)	16(1)	18(1)	19(1)	3(1)	5(1)	1(1)
O(4)	24(1)	33(1)	21(1)	-2(1)	-4(1)	5(1)
N(2)	21(1)	19(1)	16(1)	1(1)	4(1)	2(1)
C(3)	16(1)	16(1)	13(1)	2(1)	3(1)	-1(1)
O(3)	27(1)	26(1)	38(1)	15(1)	12(1)	1(1)
O(1)	24(1)	16(1)	27(1)	-1(1)	3(1)	-1(1)
C(2)	15(1)	16(1)	14(1)	1(1)	1(1)	0(1)
N(4)	17(1)	16(1)	23(1)	-1(1)	5(1)	-2(1)
N(1)	24(1)	16(1)	23(1)	0(1)	6(1)	-2(1)
C(1)	19(1)	20(1)	19(1)	0(1)	-1(1)	4(1)
C(4)	34(1)	29(1)	29(1)	-9(1)	3(1)	11(1)

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

	x	y	z	U(eq)
H(4A)	8505	3834	3445	46
H(4B)	7827	2996	4457	46
H(4C)	9483	3304	5316	46

Table S9. Displacement parameters (A^2 x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
K1	1603.6(5)	1394.0(2)	4314.6(2)	22.44(8)
K2	4099.9(4)	3721.1(2)	3789.0(2)	19.04(8)
K3	8956.5(4)	4016.9(2)	2236.6(2)	21.16(8)
O1	-225.1(15)	2117.3(7)	2459.5(3)	25.0(2)
O2	2848.3(14)	2611.9(7)	3232.8(3)	24.1(2)
O3	3004.3(14)	1859.8(7)	3695.7(3)	23.4(2)

O4	936.4(15)	539.5(7)	3730.7(3)	23.8(2)
O5	-280.3(14)	194.8(7)	3255.7(3)	22.7(2)
O6	385.2(15)	4102.5(9)	5598.7(3)	32.9(3)
O7	2166(2)	2446.5(8)	4855.2(3)	42.4(4)
O8	3568.3(17)	2917.8(8)	4418.2(3)	29.3(3)
O9	3738.0(18)	4607.4(7)	4387.7(3)	30.3(3)
O10	3353.2(15)	5267.6(7)	4866.2(3)	25.8(3)
O11	9907.7(16)	3211.9(9)	4161.4(3)	34.2(3)
O12	6481.5(14)	3228.6(7)	3293.4(3)	23.2(2)
O13	7368.5(14)	3876.8(8)	2839.2(3)	24.5(3)
O14	11640.7(14)	4439.6(8)	3338.5(3)	24.1(2)
O15	10542.7(13)	4242.8(8)	2841.6(3)	21.8(2)
N1	1339.9(17)	1033.8(8)	2643.3(3)	20.0(3)
N2	-187.4(19)	2192.3(9)	2817.1(3)	25.5(3)
N3	2401.7(16)	1976.8(8)	3407.8(3)	17.8(3)
N4	637.8(16)	696.6(8)	3427.1(3)	17.8(3)
N5	2996.0(18)	3691.7(9)	5494.0(3)	23.3(3)
N6	590.3(19)	4140.1(11)	5242.2(4)	33.4(4)
N7	2880.3(19)	3049.9(9)	4698.8(3)	26.8(3)
N8	3349.0(17)	4589.9(8)	4694.2(3)	20.9(3)
N9	7889.0(16)	3929.7(9)	3903.8(3)	20.8(3)
N10	10324(2)	3213.9(11)	3812.8(4)	35.9(4)
N11	7599.4(16)	3641.5(8)	3136.8(3)	17.5(3)
N12	10444.6(15)	4182.7(8)	3154.9(3)	16.8(3)
C1	868(2)	1188.5(11)	2018.0(4)	25.2(4)
C2	704.8(19)	1415.3(10)	2381.6(4)	19.4(3)
C3	767.4(19)	1549.6(10)	2906.6(4)	17.7(3)
C4	1241(2)	1417.4(10)	3262.3(4)	18.3(3)
C5	1994(2)	3741.4(13)	6098.7(4)	33.2(4)
C6	1866(2)	3829.1(11)	5725.0(4)	23.4(3)
C7	2141(2)	3894.4(10)	5199.4(4)	21.7(3)
C8	2865(2)	3841.4(10)	4857.7(4)	22.8(3)
C9	7742(2)	3748.2(13)	4533.8(4)	32.5(4)
C10	8455(2)	3647.4(10)	4190.8(4)	20.3(3)
C11	9097.1(19)	3650.6(10)	3677.6(4)	17.6(3)
C12	9050.0(18)	3837.4(10)	3314.7(4)	17.1(3)

Table S10. Bond lengths [A] and angles [deg] for **4.**

K1 K2	4.5986(5)	O2 N3	1.2511(16)
K1 O3	2.7793(11)	O3 N3	1.2467(16)

K1	O4	2.7093(11)	O4	N4	1.2458(16)
K1	O6[1]	3.1143(13)	O5	N4	1.2606(16)
K1	O7	2.7202(13)	O6	N6	1.4183(18)
K1	O8	2.8522(13)	O6	C6	1.344(2)
K1	O9[2]	2.7879(12)	O7	N7	1.2533(18)
K1	O10[2]	2.7881(12)	O8	N7	1.2521(18)
K1	O11[3]	3.1717(13)	O9	N8	1.2493(16)
K1	N5[4]	2.9621(14)	O10	N8	1.2481(16)
K1	N7	3.1416(14)	O11	N10	1.4154(17)
K1	N8[2]	3.1645(13)	O11	C10	1.339(2)
K2	O2	2.9574(11)	O12	N11	1.2552(16)
K2	O3	3.0259(12)	O13	N11	1.2435(16)
K2	O4[5]	2.8183(12)	O14	N12	1.2582(16)
K2	O5[5]	3.2396(12)	O15	N12	1.2433(16)
K2	O8	2.8090(12)	N1	C2	1.292(2)
K2	O9	2.7470(11)	N1	C3	1.387(2)
K2	O12	2.8242(11)	N2	C3	1.298(2)
K2	O14[3]	2.8637(11)	N3	C4	1.3870(19)
K2	N3	3.3674(13)	N4	C4	1.376(2)
K2	N4[5]	3.3759(13)	N5	C6	1.296(2)
K2	N9	3.0559(14)	N5	C7	1.383(2)
K2	N10[3]	3.0966(17)	N6	C7	1.298(2)
K3	O1[6]	3.1314(11)	N7	C8	1.374(2)
K3	O2[7]	2.9862(11)	N8	C8	1.379(2)
K3	O5[8]	2.8621(11)	N9	C10	1.295(2)
K3	O12[7]	3.1421(12)	N9	C11	1.3790(19)
K3	O13	2.7013(11)	N10	C11	1.299(2)
K3	O13[7]	2.7309(11)	N11	C12	1.3815(19)
K3	O14[9]	2.9928(12)	N12	C12	1.3805(19)
K3	O15[9]	2.7471(11)	C1	C2	1.483(2)
K3	O15	2.7226(11)	C3	C4	1.468(2)
K3	N1[8]	3.1601(13)	C5	C6	1.486(2)
K3	N11[7]	3.2949(13)	C7	C8	1.469(2)
K3	N12[9]	3.1957(13)	C9	C10	1.476(2)
O1	N2	1.4171(16)	C11	C12	1.462(2)
O1	C2	1.3470(19)			

O3	K1	K2	39.53(2)	O13	K3	O12[7]	148.53(3)
O3	K1	O6[1]	77.03(3)	O13[7]	K3	O12[7]	42.68(3)
O3	K1	O8	72.19(3)	O13	K3	O13[7]	123.52(3)
O3	K1	O9[2]	112.71(4)	O13[7]	K3	O14[9]	122.83(3)
O3	K1	O10[2]	147.53(4)	O13	K3	O14[9]	113.58(3)
O3	K1	O11[3]	76.85(3)	O13	K3	O15[9]	69.49(3)

O3	K1	N5^{4}	128.46(4)	O13	K3	O15	56.80(3)
O3	K1	N7	94.88(4)	O13^{7}	K3	O15^{9}	166.96(3)
O3	K1	N8^{2}	129.77(4)	O13^{7}	K3	N1^{8}	99.69(4)
O4	K1	K2	94.63(3)	O13	K3	N1^{8}	84.95(4)
O4	K1	O3	57.02(3)	O13^{7}	K3	N11^{7}	21.29(3)
O4	K1	O6^{1}	99.31(4)	O13	K3	N11^{7}	142.09(3)
O4	K1	O7	172.40(4)	O13	K3	N12^{9}	91.51(3)
O4	K1	O8	129.11(4)	O13^{7}	K3	N12^{9}	144.77(3)
O4	K1	O9^{2}	65.59(3)	O14^{9}	K3	O1^{6}	123.02(3)
O4	K1	O10^{2}	111.31(3)	O14^{9}	K3	O12^{7}	88.29(3)
O4	K1	O11^{3}	100.72(3)	O14^{9}	K3	N1^{8}	81.56(3)
O4	K1	N5^{4}	90.38(4)	O14^{9}	K3	N11^{7}	103.70(3)
O4	K1	N7	150.54(4)	O14^{9}	K3	N12^{9}	23.16(3)
O4	K1	N8^{2}	88.65(3)	O15^{9}	K3	O1^{6}	110.79(3)
O6^{1}	K1	K2	80.07(3)	O15	K3	O1^{6}	77.15(3)
O6^{1}	K1	O11^{3}	130.34(4)	O15^{9}	K3	O2^{7}	74.49(3)
O6^{1}	K1	N7	80.62(4)	O15	K3	O2^{7}	140.70(4)
O6^{1}	K1	N8^{2}	73.72(4)	O15	K3	O5^{8}	110.19(3)
O7	K1	K2	79.42(3)	O15^{9}	K3	O5^{8}	101.80(3)
O7	K1	O3	118.02(4)	O15	K3	O12^{7}	109.86(3)
O7	K1	O6^{1}	84.43(4)	O15^{9}	K3	O12^{7}	127.05(3)
O7	K1	O8	45.94(4)	O15	K3	O13^{7}	69.43(3)
O7	K1	O9^{2}	121.76(4)	O15^{9}	K3	O14^{9}	44.13(3)
O7	K1	O10^{2}	75.98(4)	O15	K3	O14^{9}	157.14(4)
O7	K1	O11^{3}	71.95(4)	O15	K3	O15^{9}	122.52(3)
O7	K1	N5^{4}	89.14(4)	O15^{9}	K3	N1^{8}	79.53(4)
O7	K1	N7	23.29(4)	O15	K3	N1^{8}	77.07(4)
O7	K1	N8^{2}	98.78(4)	O15^{9}	K3	N11^{7}	146.74(3)
O8	K1	K2	35.37(2)	O15	K3	N11^{7}	90.58(3)
O8	K1	O6^{1}	70.21(4)	O15	K3	N12^{9}	144.78(3)
O8	K1	O11^{3}	61.86(4)	O15^{9}	K3	N12^{9}	22.57(3)
O8	K1	N5^{4}	121.87(4)	N1^{8}	K3	N11^{7}	107.81(3)
O8	K1	N7	23.48(3)	N1^{8}	K3	N12^{9}	85.92(3)
O8	K1	N8^{2}	130.72(4)	N12^{9}	K3	N11^{7}	124.18(3)
O9^{2}	K1	K2	149.57(3)	N2	O1	K3^{3}	102.00(8)
O9^{2}	K1	O6^{1}	80.70(4)	C2	O1	K3^{3}	143.47(9)
O9^{2}	K1	O8	148.78(4)	C2	O1	N2	106.38(11)
O9^{2}	K1	O10^{2}	45.79(3)	K2	O2	K3^{9}	86.63(3)
O9^{2}	K1	O11^{3}	148.75(4)	N3	O2	K2	97.99(8)
O9^{2}	K1	N5^{4}	80.53(4)	N3	O2	K3^{9}	174.84(9)
O9^{2}	K1	N7	141.93(4)	K1	O3	K2	104.69(4)
O9^{2}	K1	N8^{2}	23.14(3)	N3	O3	K1	133.35(9)
O10^{2}	K1	K2	146.63(3)	N3	O3	K2	94.78(8)

O10^{2}	K1	O6^{1}	75.44(3)	K1	O4	K2^{2}	114.71(4)
O10^{2}	K1	O8	113.34(3)	N4	O4	K1	139.58(9)
O10^{2}	K1	O11^{3}	134.97(3)	N4	O4	K2^{2}	105.71(8)
O10^{2}	K1	N5^{4}	77.56(4)	K3^{10}	O5	K2^{2}	83.62(3)
O10^{2}	K1	N7	97.28(3)	N4	O5	K2^{2}	85.18(8)
O10^{2}	K1	N8^{2}	23.11(3)	N4	O5	K3^{10}	122.94(9)
O11^{3}	K1	K2	53.45(2)	N6	O6	K1^{4}	103.28(9)
N5^{4}	K1	K2	124.46(3)	C6	O6	K1^{4}	136.32(10)
N5^{4}	K1	O6^{1}	153.00(4)	C6	O6	N6	106.32(13)
N5^{4}	K1	O11^{3}	71.26(4)	N7	O7	K1	97.58(9)
N5^{4}	K1	N7	102.97(4)	K2	O8	K1	108.64(4)
N5^{4}	K1	N8^{2}	81.45(4)	N7	O8	K1	91.34(9)
N7	K1	K2	56.14(3)	N7	O8	K2	140.93(10)
N7	K1	O11^{3}	60.53(4)	K2	O9	K1^{5}	114.48(4)
N7	K1	N8^{2}	118.97(3)	N8	O9	K1^{5}	95.61(8)
N8^{2}	K1	K2	153.77(3)	N8	O9	K2	148.08(10)
N8^{2}	K1	O11^{3}	151.05(4)	N8	O10	K1^{5}	95.62(8)
O2	K2	O3	42.50(3)	N10	O11	K1^{6}	95.08(9)
O2	K2	O5^{5}	91.21(3)	C10	O11	K1^{6}	142.47(10)
O2	K2	N3	21.59(3)	C10	O11	N10	106.50(12)
O2	K2	N4^{5}	103.29(3)	K2	O12	K3^{9}	86.05(3)
O2	K2	N9	120.08(3)	N11	O12	K2	132.61(9)
O2	K2	N10^{3}	63.35(4)	N11	O12	K3^{9}	85.69(8)
O3	K2	O5^{5}	132.18(3)	K3	O13	K3^{9}	111.04(4)
O3	K2	N3	21.65(3)	N11	O13	K3^{9}	105.82(8)
O3	K2	N4^{5}	145.58(3)	N11	O13	K3	141.93(9)
O3	K2	N9	113.61(3)	K2^{6}	O14	K3^{7}	88.22(3)
O3	K2	N10^{3}	59.05(4)	N12	O14	K2^{6}	138.53(9)
O4^{5}	K2	O2	120.88(3)	N12	O14	K3^{7}	87.50(8)
O4^{5}	K2	O3	159.07(3)	K3	O15	K3^{7}	109.90(4)
O4^{5}	K2	O5^{5}	41.36(3)	N12	O15	K3^{7}	99.44(8)
O4^{5}	K2	O12	102.63(3)	N12	O15	K3	146.61(9)
O4^{5}	K2	O14^{3}	63.64(3)	C2	N1	K3^{10}	122.74(10)
O4^{5}	K2	N3	139.18(3)	C2	N1	C3	102.14(13)
O4^{5}	K2	N4^{5}	20.81(3)	C3	N1	K3^{10}	115.44(9)
O4^{5}	K2	N9	85.24(4)	C3	N2	O1	102.78(12)
O4^{5}	K2	N10^{3}	104.17(4)	O2	N3	K2	60.42(7)
O5^{5}	K2	N3	112.77(3)	O2	N3	C4	116.58(12)
O5^{5}	K2	N4^{5}	21.85(3)	O3	N3	K2	63.57(7)
O8	K2	O2	110.53(3)	O3	N3	O2	120.60(12)
O8	K2	O3	69.20(3)	O3	N3	C4	122.81(13)
O8	K2	O4^{5}	120.73(3)	C4	N3	K2	161.62(10)
O8	K2	O5^{5}	158.25(3)	O4	N4	K2^{2}	53.48(7)

O8	K2	O12	126.47(4)	O4	N4	O5	120.45(13)
O8	K2	O14^{3}	128.21(4)	O4	N4	C4	123.15(13)
O8	K2	N3	88.97(3)	O5	N4	K2^{2}	72.98(8)
O8	K2	N4^{5}	141.53(3)	O5	N4	C4	116.38(12)
O8	K2	N9	93.61(4)	C4	N4	K2^{2}	155.58(10)
O8	K2	N10^{3}	73.52(4)	C6	N5	K1^{1}	119.71(11)
O9	K2	O2	153.24(4)	C6	N5	C7	102.48(14)
O9	K2	O3	123.25(3)	C7	N5	K1^{1}	134.30(10)
O9	K2	O4^{5}	64.70(3)	C7	N6	O6	103.06(13)
O9	K2	O5^{5}	103.86(3)	O7	N7	K1	59.12(8)
O9	K2	O8	56.17(3)	O7	N7	C8	115.64(14)
O9	K2	O12	143.18(4)	O8	N7	K1	65.18(8)
O9	K2	O14^{3}	105.69(4)	O8	N7	O7	120.78(14)
O9	K2	N3	137.88(4)	O8	N7	C8	123.57(14)
O9	K2	N4^{5}	85.43(3)	C8	N7	K1	160.37(12)
O9	K2	N9	85.56(4)	O9	N8	K1^{5}	61.25(8)
O9	K2	N10^{3}	89.94(4)	O9	N8	C8	122.73(13)
O12	K2	O2	63.49(3)	O10	N8	K1^{5}	61.27(7)
O12	K2	O3	81.47(3)	O10	N8	O9	120.57(13)
O12	K2	O5^{5}	62.96(3)	O10	N8	C8	116.68(13)
O12	K2	O14^{3}	97.43(3)	C8	N8	K1^{5}	164.48(11)
O12	K2	N3	75.06(3)	C10	N9	K2	115.80(10)
O12	K2	N4^{5}	84.77(3)	C10	N9	C11	102.77(13)
O12	K2	N9	58.23(3)	C11	N9	K2	123.65(10)
O12	K2	N10^{3}	126.84(4)	O11	N10	K2^{6}	104.81(10)
O14^{3}	K2	O2	62.26(3)	C11	N10	K2^{6}	125.48(12)
O14^{3}	K2	O3	95.57(3)	C11	N10	O11	103.08(13)
O14^{3}	K2	O5^{5}	61.35(3)	O12	N11	K3^{9}	71.98(8)
O14^{3}	K2	N3	76.11(3)	O12	N11	C12	116.66(12)
O14^{3}	K2	N4^{5}	55.15(3)	O13	N11	K3^{9}	52.88(7)
O14^{3}	K2	N9	136.13(4)	O13	N11	O12	120.68(13)
O14^{3}	K2	N10^{3}	57.20(4)	O13	N11	C12	122.63(13)
N3	K2	N4^{5}	123.95(3)	C12	N11	K3^{9}	156.81(10)
N9	K2	O5^{5}	74.82(3)	O14	N12	K3^{7}	69.33(7)
N9	K2	N3	122.95(3)	O14	N12	C12	117.55(12)
N9	K2	N4^{5}	84.66(3)	O15	N12	K3^{7}	57.99(7)
N9	K2	N10^{3}	166.66(4)	O15	N12	O14	120.19(12)
N10^{3}	K2	O5^{5}	118.48(4)	O15	N12	C12	122.26(12)
N10^{3}	K2	N3	54.86(4)	C12	N12	K3^{7}	152.67(10)
N10^{3}	K2	N4^{5}	107.52(4)	O1	C2	C1	117.33(13)
O1^{6}	K3	O12^{7}	72.07(3)	N1	C2	O1	113.44(13)
O1^{6}	K3	N1^{8}	153.76(3)	N1	C2	C1	129.23(15)
O1^{6}	K3	N11^{7}	77.24(3)	N1	C3	C4	123.63(13)

O1[6]	K3	N12[9]	113.07(3)	N2 C3 N1	115.24(13)
O2[7]	K3	O1[6]	63.55(3)	N2 C3 C4	121.08(14)
O2[7]	K3	O12[7]	59.50(3)	N3 C4 C3	118.65(13)
O2[7]	K3	O14[9]	60.46(3)	N4 C4 N3	122.61(13)
O2[7]	K3	N1[8]	141.98(3)	N4 C4 C3	118.44(13)
O2[7]	K3	N11[7]	81.51(3)	O6 C6 C5	117.20(15)
O2[7]	K3	N12[9]	60.10(3)	N5 C6 O6	113.23(14)
O5[8]	K3	O1[6]	135.28(3)	N5 C6 C5	129.56(16)
O5[8]	K3	O2[7]	98.53(3)	N5 C7 C8	124.69(15)
O5[8]	K3	O12[7]	63.91(3)	N6 C7 N5	114.91(14)
O5[8]	K3	O14[9]	64.60(3)	N6 C7 C8	120.41(15)
O5[8]	K3	N1[8]	60.17(3)	N7 C8 N8	121.99(14)
O5[8]	K3	N11[7]	59.09(3)	N7 C8 C7	118.20(14)
O5[8]	K3	N12[9]	86.57(3)	N8 C8 C7	119.50(14)
O12[7]	K3	N1[8]	121.97(3)	O11 C10 C9	117.54(14)
O12[7]	K3	N11[7]	22.32(3)	N9 C10 O11	113.04(13)
O12[7]	K3	N12[9]	105.32(3)	N9 C10 C9	129.41(15)
O13	K3	O1[6]	76.93(3)	N9 C11 C12	123.74(13)
O13[7]	K3	O1[6]	75.59(4)	N10 C11 N9	114.60(13)
O13	K3	O2[7]	110.57(4)	N10 C11 C12	121.65(14)
O13[7]	K3	O2[7]	99.55(3)	N11 C12 C11	118.46(13)
O13[7]	K3	O5[8]	67.20(3)	N12 C12 N11	121.28(13)
O13	K3	O5[8]	145.12(4)	N12 C12 C11	120.24(13)

Table S11. Anisotropic displacement parameters (A^2 x 10^3) for **4**. 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
K1	28.80(18)	19.98(17)	18.54(16)	-1.17(13)	0.36(14)	-3.01(14)
K2	20.23(16)	20.45(16)	16.45(16)	-1.15(12)	0.53(12)	-0.15(13)
K3	14.82(15)	32.59(19)	16.08(16)	2.23(13)	0.06(12)	0.65(13)
O1	33.2(6)	23.1(6)	18.6(5)	0.7(4)	-4.8(5)	6.9(5)
O2	27.5(6)	22.0(6)	22.7(6)	0.9(4)	2.9(5)	-8.4(5)
O3	23.0(6)	27.7(6)	19.4(5)	-0.9(5)	-4.8(4)	-0.8(5)
O4	34.8(6)	22.1(6)	14.7(5)	1.2(4)	-0.1(5)	-1.0(5)
O5	24.2(6)	19.3(5)	24.6(6)	-3.7(4)	-1.5(5)	-4.7(5)
O6	25.0(6)	48.2(8)	25.4(6)	7.3(6)	4.2(5)	0.9(6)
O7	83.2(11)	23.9(6)	20.0(6)	3.0(5)	0.4(7)	-19.9(7)

O8	44.6(7)	23.0(6)	20.2(6)	-2.9(5)	0.3(5)	0.0(5)
O9	53.4(8)	22.2(6)	15.5(6)	0.2(4)	8.2(5)	-0.3(6)
O10	36.7(7)	19.0(6)	21.7(6)	-4.0(4)	5.1(5)	-0.3(5)
O11	31.6(7)	54.3(8)	16.7(6)	11.0(5)	3.6(5)	18.5(6)
O12	19.4(5)	27.2(6)	22.9(6)	-3.5(5)	6.1(4)	-7.7(5)
O13	16.6(5)	41.9(7)	15.1(5)	2.4(5)	-0.9(4)	2.7(5)
O14	18.6(5)	31.3(6)	22.5(6)	1.1(5)	-6.3(4)	-6.9(5)
O15	18.0(5)	33.1(6)	14.3(5)	2.9(4)	2.0(4)	-2.2(5)
N1	23.6(7)	19.6(6)	17.0(6)	-1.0(5)	-1.2(5)	2.0(5)
N2	33.7(8)	25.3(7)	17.4(6)	-2.3(5)	-2.8(6)	7.1(6)
N3	17.3(6)	18.7(6)	17.3(6)	-2.8(5)	1.7(5)	1.7(5)
N4	18.8(6)	16.9(6)	17.6(6)	-1.5(5)	1.1(5)	2.2(5)
N5	25.7(7)	27.9(7)	16.2(6)	1.9(5)	-1.4(5)	-2.3(6)
N6	29.2(8)	48.8(10)	22.2(7)	8.6(7)	-1.3(6)	-1.1(7)
N7	42.2(9)	21.4(7)	16.7(6)	1.7(5)	-5.3(6)	-4.1(6)
N8	25.8(7)	20.3(7)	16.4(6)	-0.6(5)	0.1(5)	1.0(5)
N9	20.7(7)	27.6(7)	14.2(6)	0.0(5)	2.4(5)	4.4(5)
N10	34.8(8)	55.1(10)	18.0(7)	10.1(7)	8.4(6)	21.4(8)
N11	14.7(6)	21.8(6)	15.9(6)	-3.0(5)	3.9(5)	1.3(5)
N12	14.8(6)	19.1(6)	16.6(6)	1.1(5)	-0.8(5)	1.5(5)
C1	33.2(9)	24.6(8)	17.8(8)	0.4(6)	-2.4(7)	-0.2(7)
C2	20.6(7)	17.0(7)	20.5(8)	0.3(6)	-0.5(6)	-2.5(6)
C3	18.4(7)	16.6(7)	18.1(7)	-0.5(6)	0.2(6)	-1.7(6)
C4	21.1(7)	17.6(7)	16.2(7)	-0.6(6)	-0.4(6)	-1.1(6)
C5	33.0(10)	49.1(11)	17.4(8)	1.7(8)	2.2(7)	-7.8(8)
C6	24.0(8)	25.3(8)	21.0(8)	2.0(6)	-0.9(6)	-6.3(7)
C7	26.4(8)	20.9(8)	17.9(7)	1.2(6)	-2.0(6)	-5.3(6)
C8	32.9(9)	19.8(8)	15.7(7)	0.3(6)	-1.3(6)	-3.7(7)
C9	37.2(10)	45.0(11)	15.3(8)	-0.5(7)	3.5(7)	2.9(8)
C10	21.2(8)	23.0(8)	16.7(7)	-0.8(6)	1.4(6)	1.5(6)
C11	17.1(7)	19.3(7)	16.4(7)	0.0(6)	1.4(6)	0.4(6)
C12	14.3(7)	22.4(8)	14.6(7)	0.0(6)	0.9(5)	0.0(6)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **4**.

	x	y	z	U(eq)
H1A	-191.91	935.92	1937.43	38
H1B	1782.61	768.1	1989.26	38
H1C	1122.1	1711.68	1887.22	38

H5A	2325.4	4298.11	6197.36	50
H5B	2842.5	3302.67	6154.46	50
H5C	898.92	3565.48	6190.77	50
H9A	7276.3	3193.56	4609.83	49
H9B	6844.46	4184.32	4529.07	49
H9C	8630.62	3933.67	4690.16	49

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5467(4)	6588(4)	1019(3)	44(1)
O(2)	1300(4)	11760(4)	381(3)	43(1)
O(3)	2560(5)	10445(5)	1696(3)	46(1)
O(4)	1174(5)	10363(5)	-1499(3)	49(1)
O(5)	2362(6)	8097(5)	-1507(3)	54(1)
N(1)	5038(5)	8058(5)	535(4)	43(1)
N(2)	2823(4)	6746(5)	972(3)	34(1)
N(4)	2089(4)	10590(5)	716(3)	30(1)
N(5)	1991(5)	9310(5)	-1016(3)	36(1)
C(4)	2508(5)	9373(5)	65(3)	29(1)
C(3)	3468(5)	8075(5)	532(3)	28(1)
C(2)	4085(5)	5908(6)	1247(3)	30(1)
C(1)	4200(7)	4349(6)	1756(4)	45(1)
N(6)	774(8)	15(9)	3907(5)	79(2)
N(7)	513(5)	1427(6)	3358(4)	50(1)

Table S14. Bond lengths [A] and angles [deg] for **7**.

O(1)-C(2)	1.336(5)
O(1)-N(1)	1.419(6)
O(2)-N(4)	1.242(5)
O(3)-N(4)	1.256(5)
O(4)-N(5)	1.245(6)
O(5)-N(5)	1.252(6)
N(1)-C(3)	1.303(6)
N(2)-C(2)	1.288(6)
N(2)-C(3)	1.384(6)
N(4)-C(4)	1.378(6)

N(5)-C(4)	1.378(5)
C(4)-C(3)	1.452(6)
C(2)-C(1)	1.468(7)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
N(6)-N(7)	1.389(8)
N(6)-H(6B)	0.8900
N(6)-H(6A)	0.8898
N(7)-H(7A)	0.8900
N(7)-H(7B)	0.8898
N(7)-H(7C)	0.8900

C(2)-O(1)-N(1)	106.5(3)
C(3)-N(1)-O(1)	103.0(4)
C(2)-N(2)-C(3)	102.9(4)
O(2)-N(4)-O(3)	121.0(4)
O(2)-N(4)-C(4)	123.7(4)
O(3)-N(4)-C(4)	115.3(4)
O(4)-N(5)-O(5)	120.1(4)
O(4)-N(5)-C(4)	123.7(4)
O(5)-N(5)-C(4)	116.2(4)
N(4)-C(4)-N(5)	122.1(4)
N(4)-C(4)-C(3)	119.4(4)
N(5)-C(4)-C(3)	118.4(4)
N(1)-C(3)-N(2)	114.3(4)
N(1)-C(3)-C(4)	121.5(4)
N(2)-C(3)-C(4)	124.2(4)
N(2)-C(2)-O(1)	113.4(4)
N(2)-C(2)-C(1)	129.4(4)
O(1)-C(2)-C(1)	117.2(4)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(7)-N(6)-H(6B)	109.1
N(7)-N(6)-H(6A)	109.1
H(6B)-N(6)-H(6A)	109.7
N(6)-N(7)-H(7A)	109.1
N(6)-N(7)-H(7B)	110.3
H(7A)-N(7)-H(7B)	109.4
N(6)-N(7)-H(7C)	109.0
H(7A)-N(7)-H(7C)	109.5

H(7B)-N(7)-H(7C)	109.5

Symmetry transformations used to generate equivalent atoms:

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

Table S15. Anisotropic displacement parameters (A^2 x 10^3) for **7**. 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(1)	30(2)	40(2)	65(2)	7(2)	10(2)	2(2)
O(2)	45(2)	39(2)	45(2)	5(2)	5(2)	11(2)
O(3)	53(2)	57(2)	26(2)	-6(2)	1(1)	12(2)
O(4)	57(2)	52(2)	35(2)	8(2)	-11(2)	-6(2)
O(5)	80(3)	53(2)	31(2)	-9(2)	4(2)	-1(2)
N(1)	30(2)	38(2)	63(3)	8(2)	12(2)	-3(2)
N(2)	28(2)	42(2)	33(2)	5(2)	3(1)	-6(2)
N(4)	26(2)	37(2)	28(2)	2(2)	4(1)	-2(2)
N(5)	39(2)	43(2)	27(2)	-1(2)	4(2)	-10(2)
C(4)	29(2)	32(2)	25(2)	2(2)	5(2)	-4(2)
C(3)	26(2)	34(2)	23(2)	-1(2)	4(1)	-2(2)
C(2)	32(2)	33(2)	25(2)	-5(2)	4(2)	-2(2)
C(1)	51(3)	38(3)	45(3)	7(2)	1(2)	3(2)
N(6)	78(4)	84(5)	77(4)	19(4)	19(3)	22(4)
N(7)	38(2)	65(3)	46(2)	-24(2)	7(2)	0(2)

Table S16. Displacement parameters (A^2 x 10^3) for **7**.

	x	y	z	U(eq)
H(1A)	3318	3704	1464	67
H(1B)	4151	4460	2519	67
H(1C)	5207	3865	1618	67
H(6B)	334	−765	3505	95
H(6A)	1834	−143	4034	95
H(7A)	986	2203	3749	59
H(7B)	926	1385	2724	59
H(7C)	−547	1605	3257	59

Table S17. Selected torsion angles [deg] for **7**.

C(2)-O(1)-N(1)-C(3)	−0.1(5)
O(2)-N(4)-C(4)-N(5)	−4.1(6)
O(3)-N(4)-C(4)-N(5)	175.7(4)
O(2)-N(4)-C(4)-C(3)	178.5(4)
O(3)-N(4)-C(4)-C(3)	−1.7(6)
O(4)-N(5)-C(4)-N(4)	3.2(7)
O(5)-N(5)-C(4)-N(4)	−175.5(4)
O(4)-N(5)-C(4)-C(3)	−179.4(4)
O(5)-N(5)-C(4)-C(3)	1.9(6)
O(1)-N(1)-C(3)-N(2)	0.1(5)
O(1)-N(1)-C(3)-C(4)	−177.9(4)
C(2)-N(2)-C(3)-N(1)	0.0(5)
C(2)-N(2)-C(3)-C(4)	177.8(4)
N(4)-C(4)-C(3)-N(1)	−94.2(5)
N(5)-C(4)-C(3)-N(1)	88.4(5)
N(4)-C(4)-C(3)-N(2)	88.1(5)
N(5)- C(4)-C(3)-N(2)	−89.3(5)
C(3)-N(2)-C(2)-O(1)	0.0(5)
C(3)-N(2)-C(2)-C(1)	−179.7(5)
N(1)-O(1)-C(2)-N(2)	0.1(5)
N(1)-O(1)-C(2)-C(1)	179.8(4)

6. Copies of Spectrum

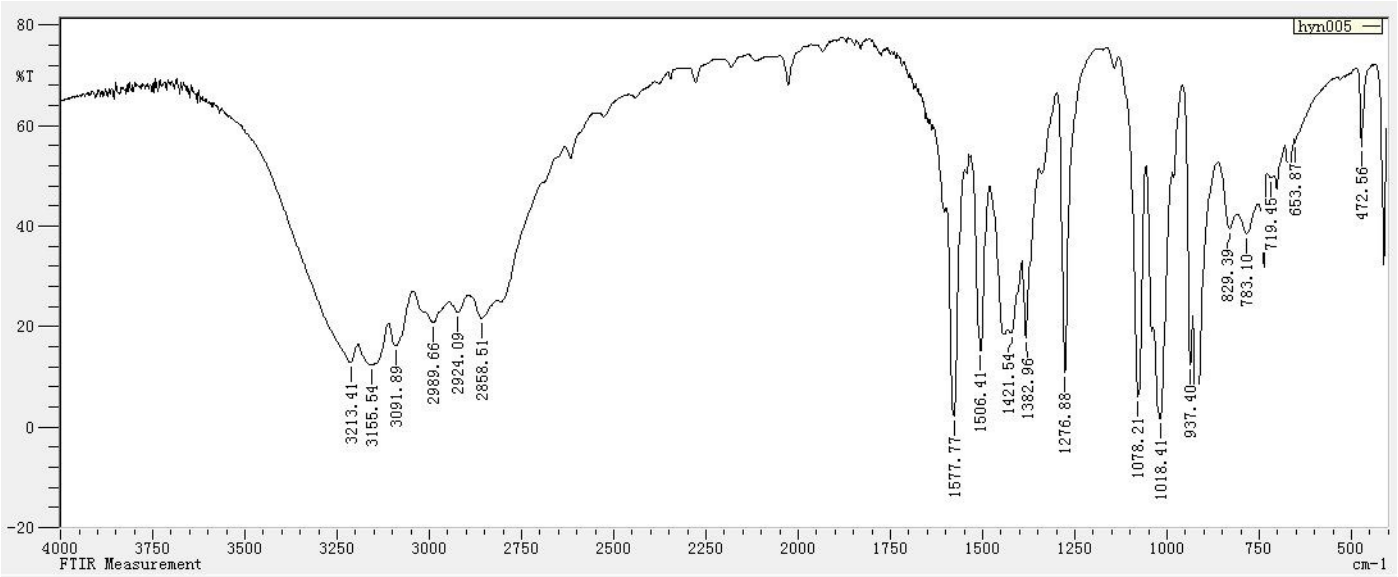


Figure S1 IR spectrum of **2**.

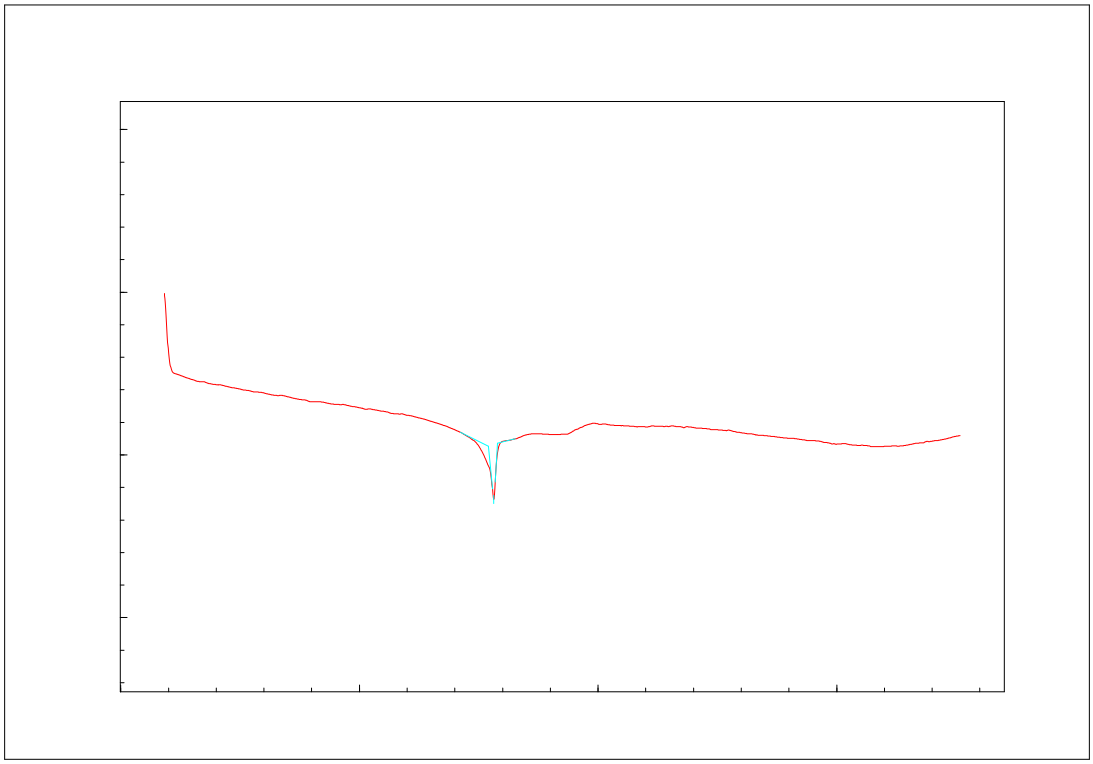


Figure S2 DSC curve of **2** (10 ºC min^{-1}).

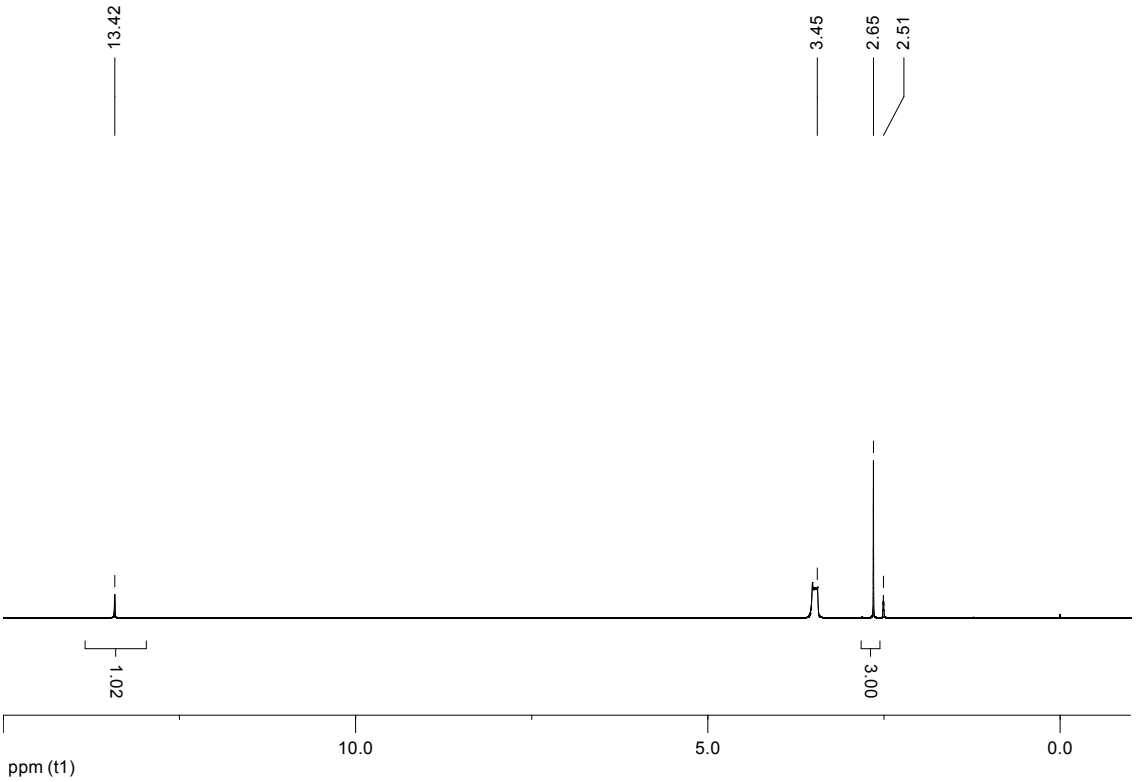


Figure S3 ^{1}H NMR spectrum of **2**.

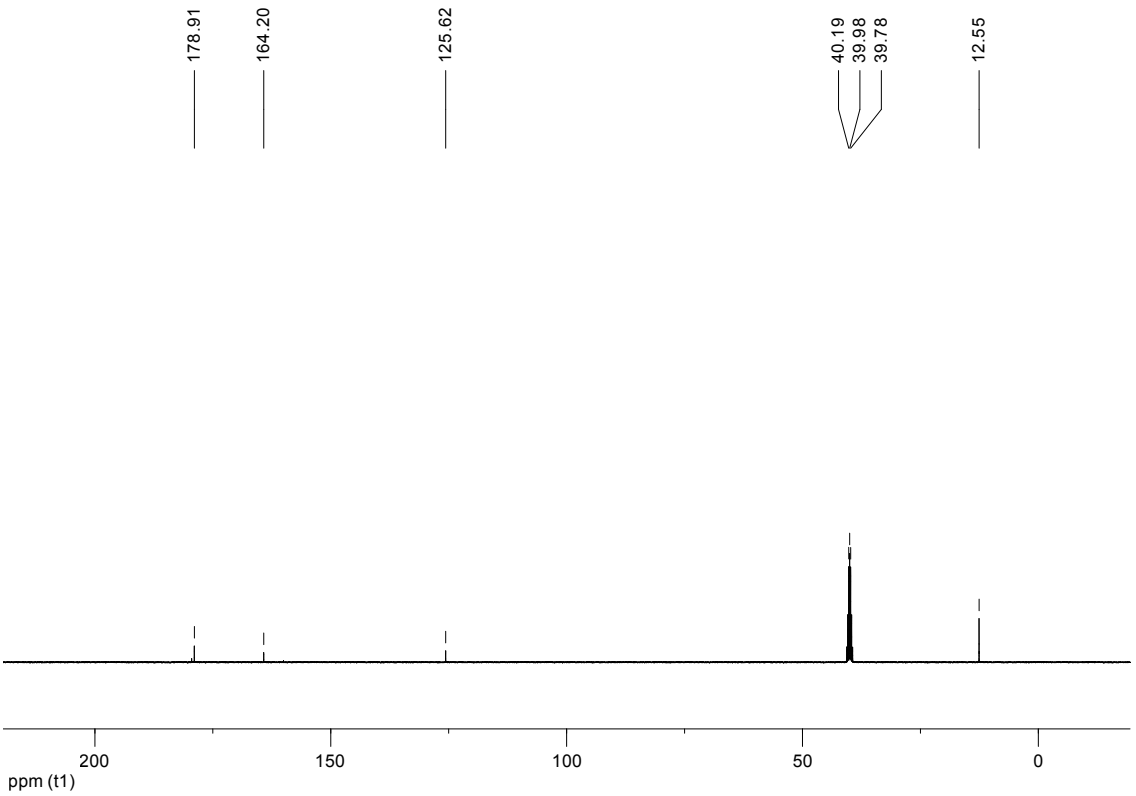


Figure S4 ^{13}C NMR spectrum of **2**.

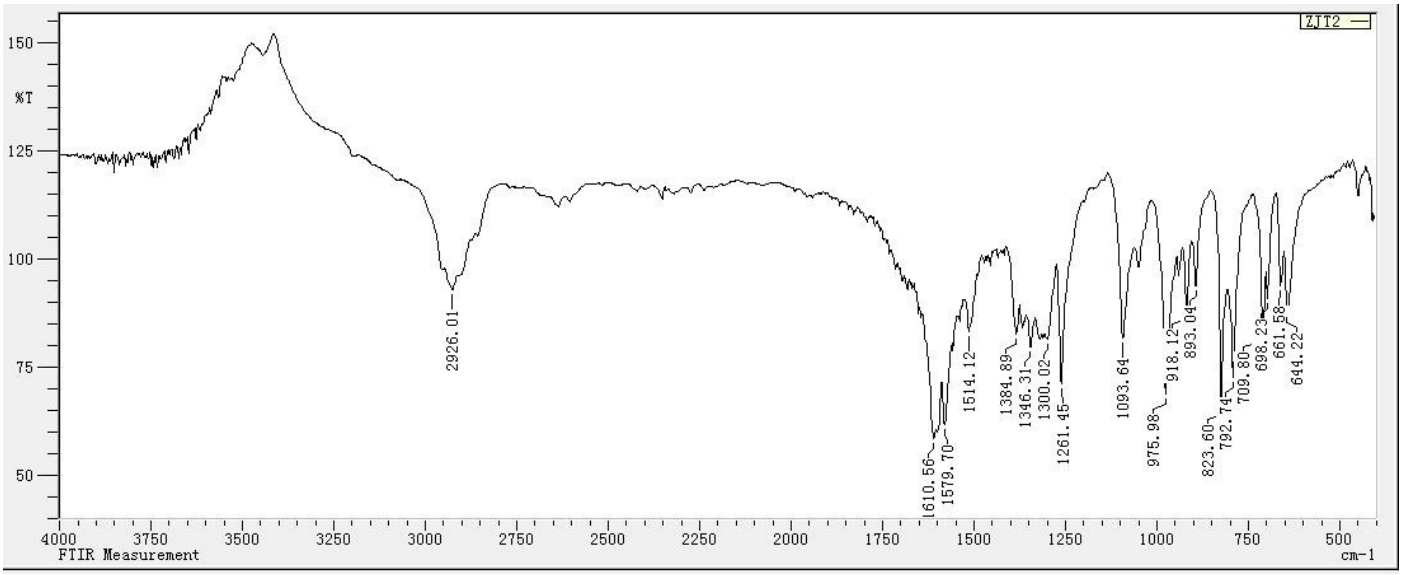


Figure S5 IR spectrum of **3**.

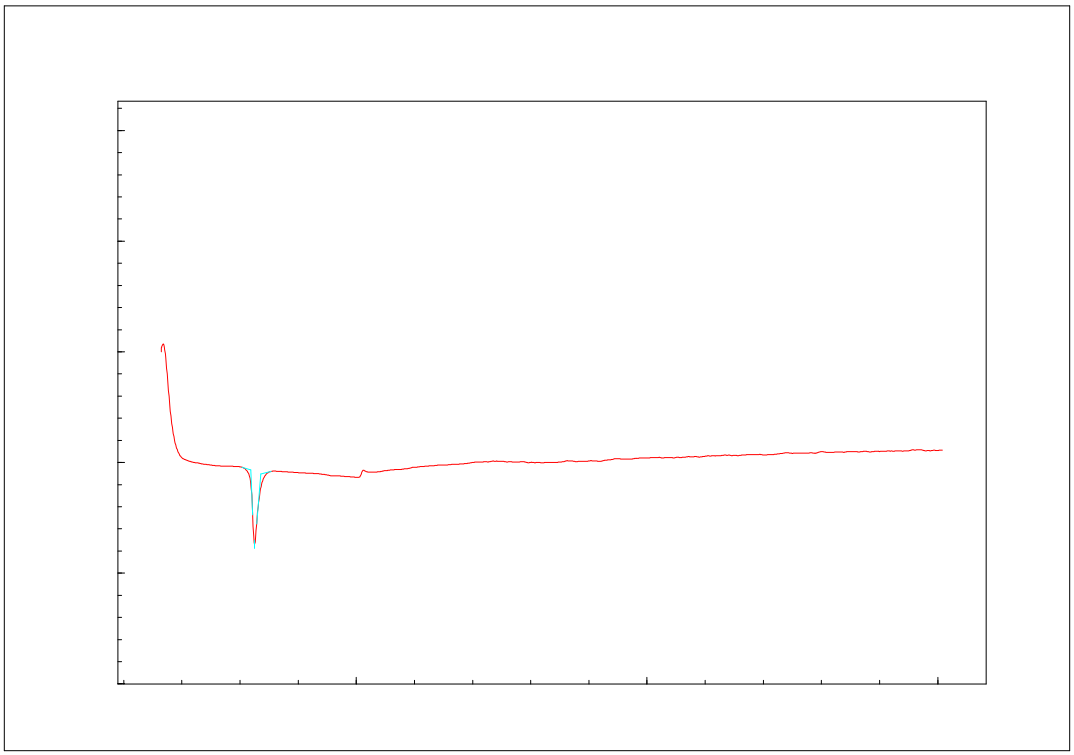


Figure S6 DSC curve of **3** (10 ℃ min^{-1})

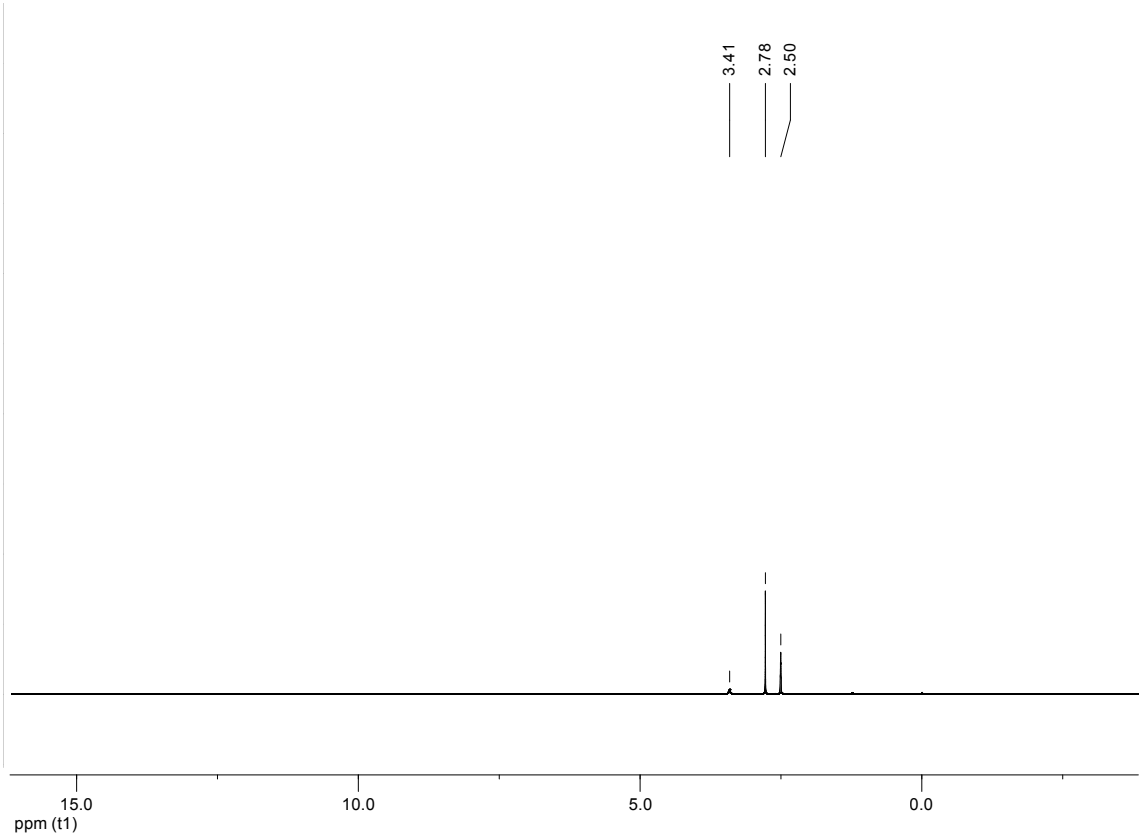


Figure S7 ^{1}H NMR spectrum of **3**.

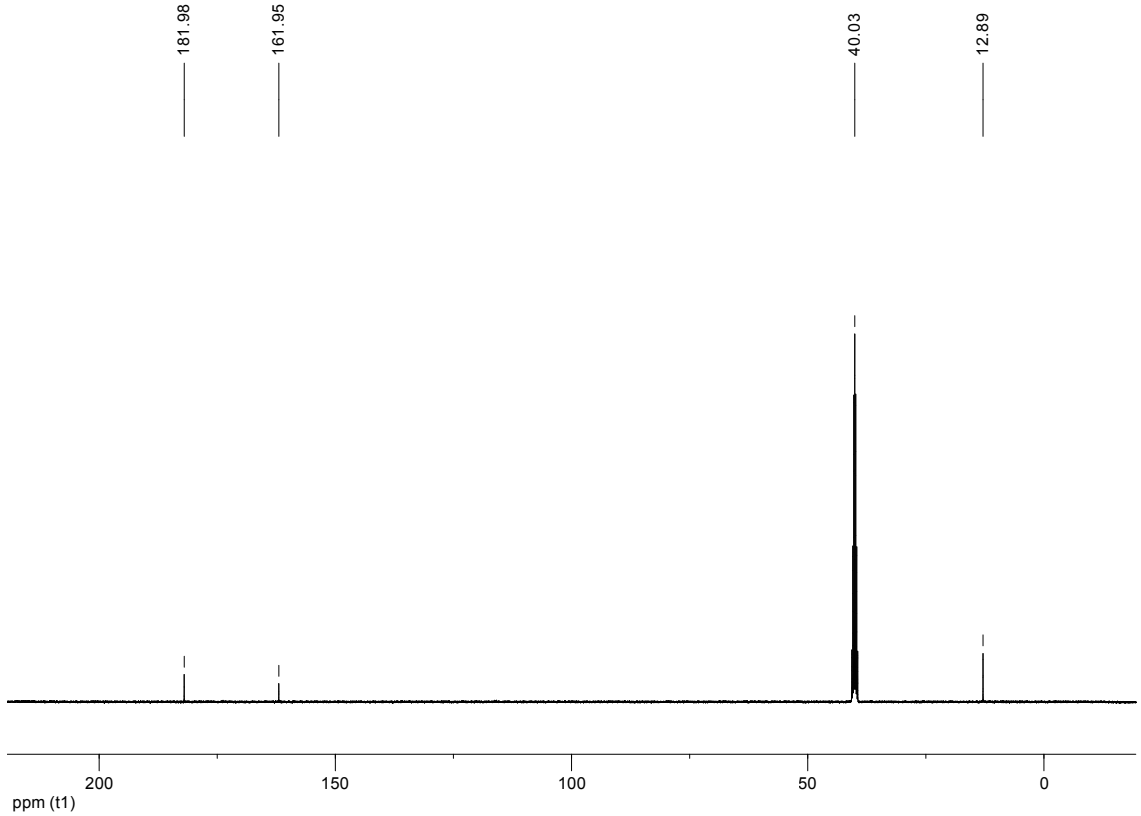


Figure S8 ^{13}C NMR spectrum of **3**.

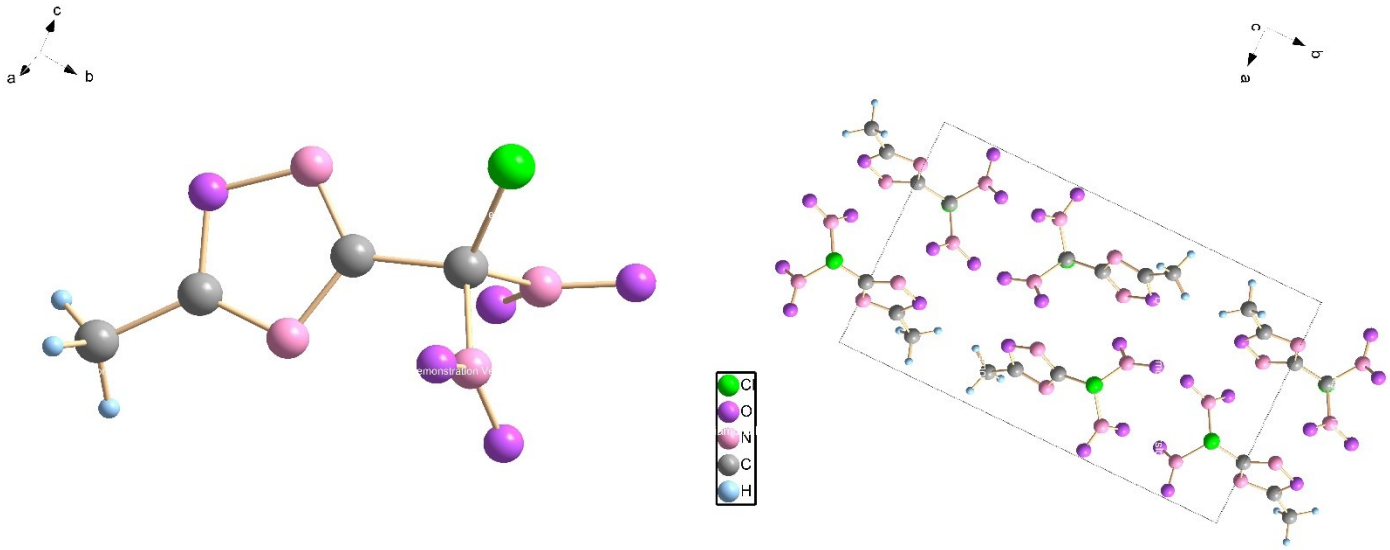


Figure S9 X-ray crystal structure of **3**

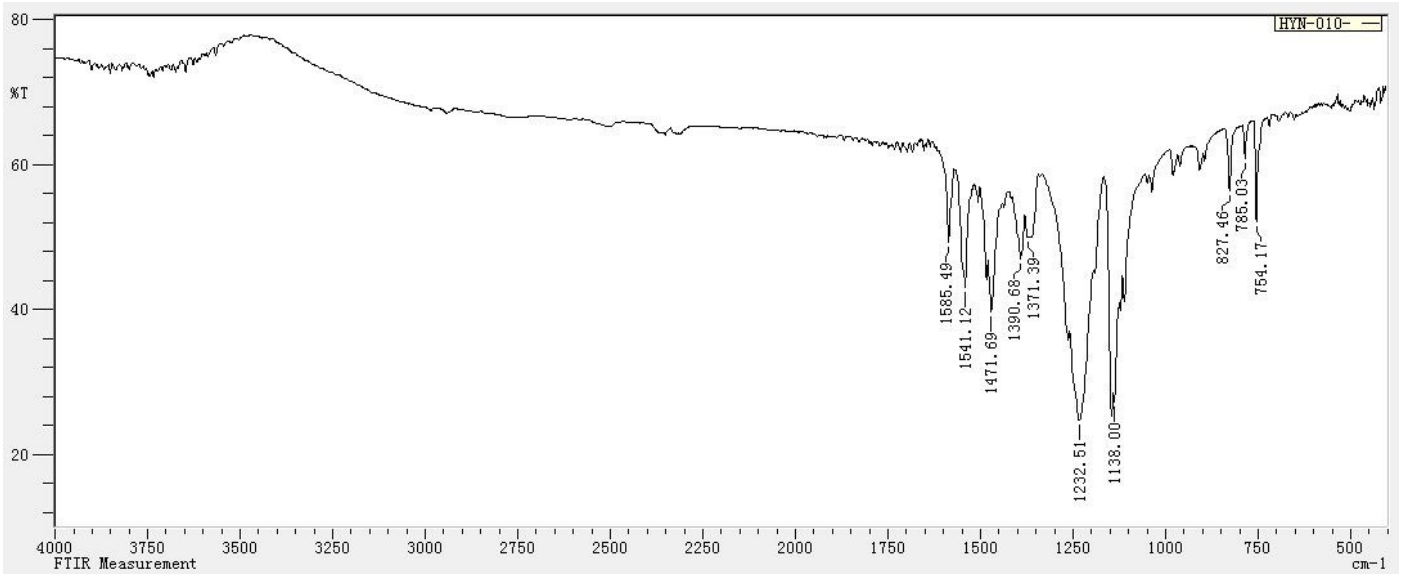


Figure S10 IR spectrum of **4**.

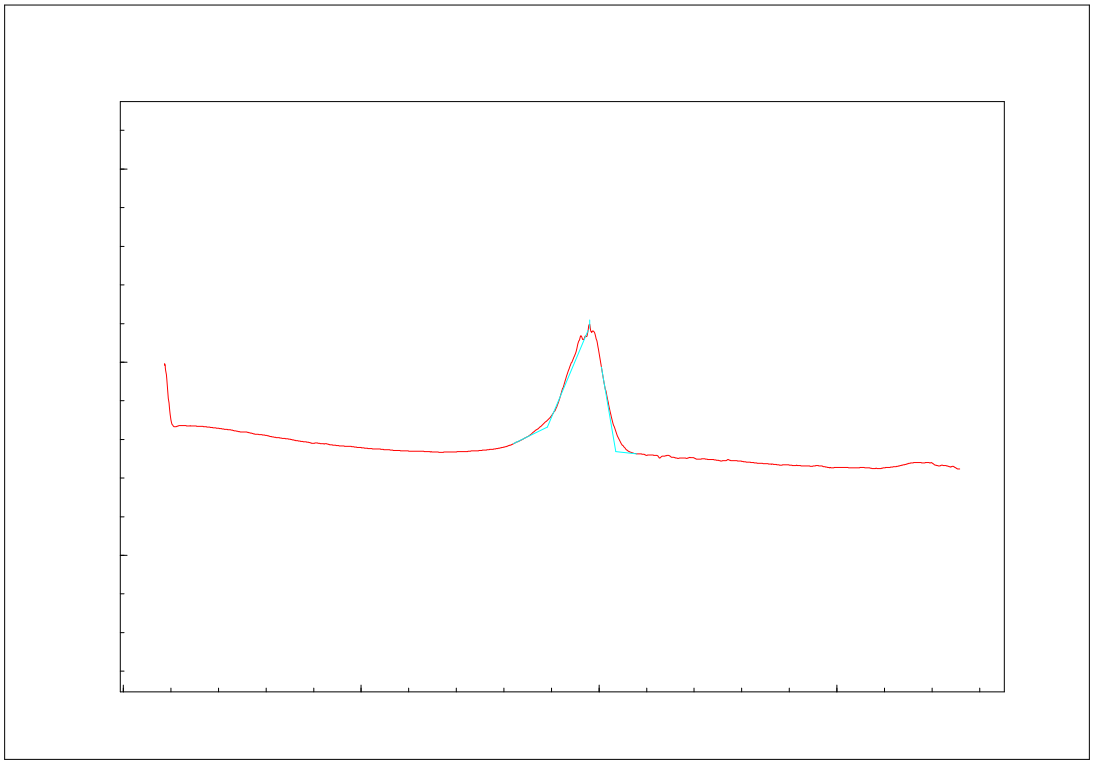


Figure S11 DSC curve of **4** (10 ºC min^{-1})

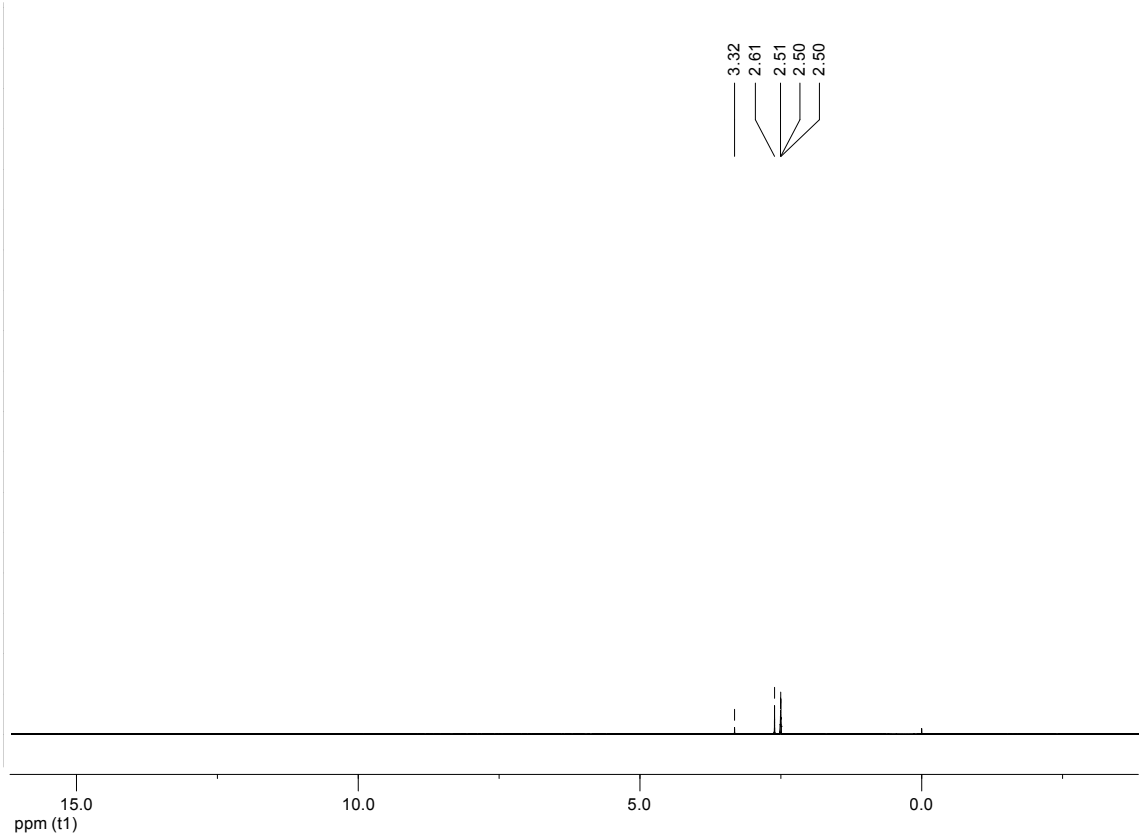


Figure S12 ^{1}H NMR spectrum of **4**.

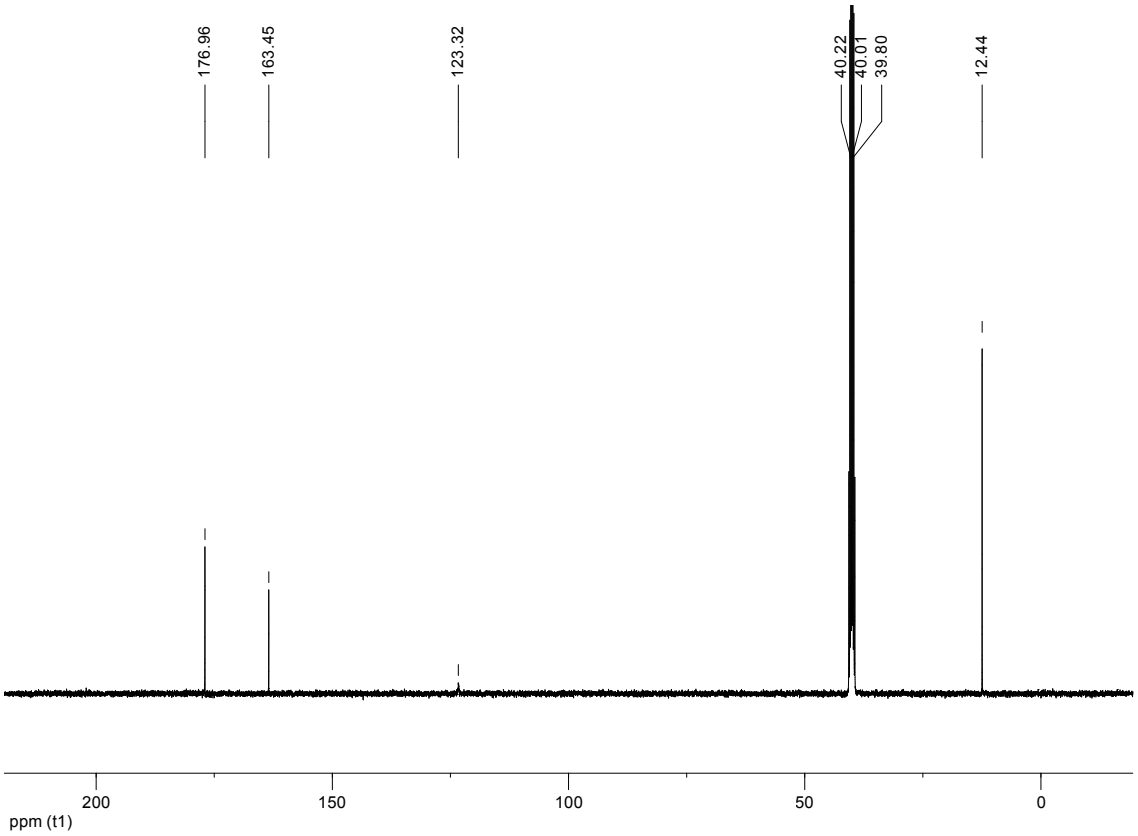


Figure S13 ^{13}C NMR spectrum of **4**.

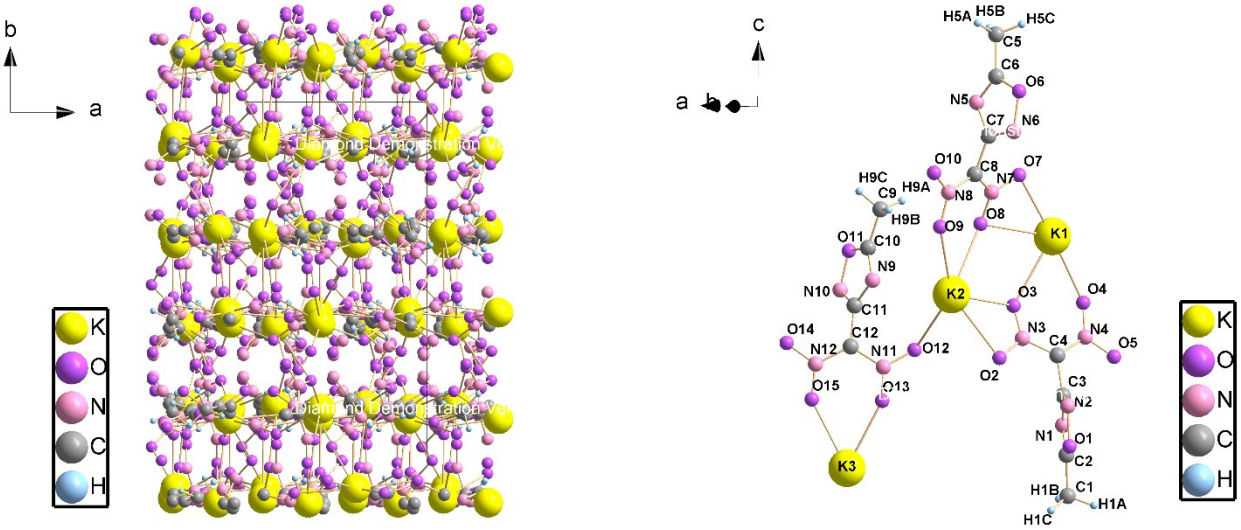


Figure S14 X-ray crystal structure of **4**

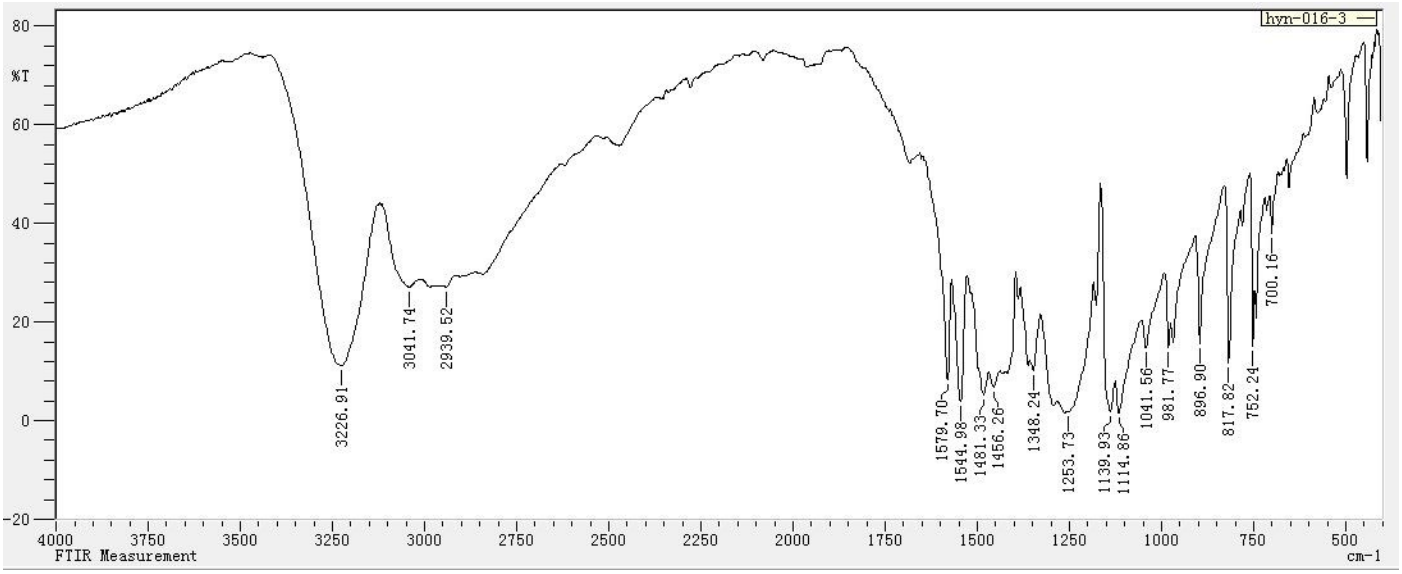


Figure S15 IR spectrum of **5**

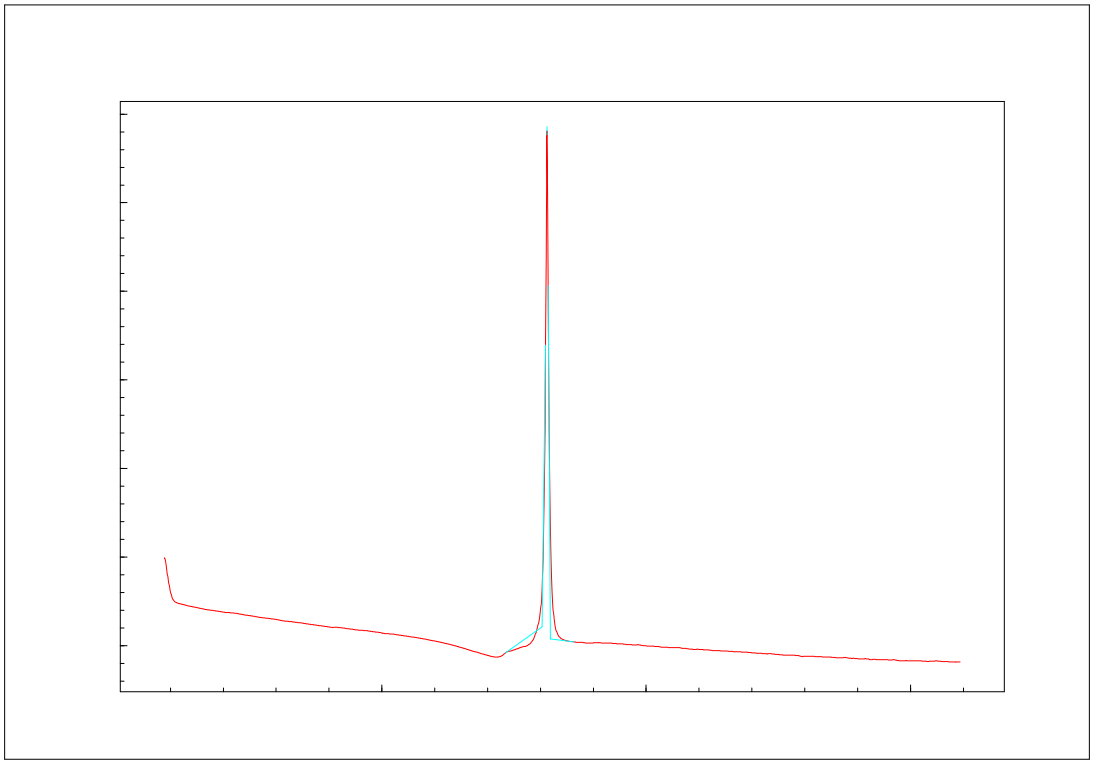


Figure S16 DSC curve of **5** (10 ºC min^{-1})

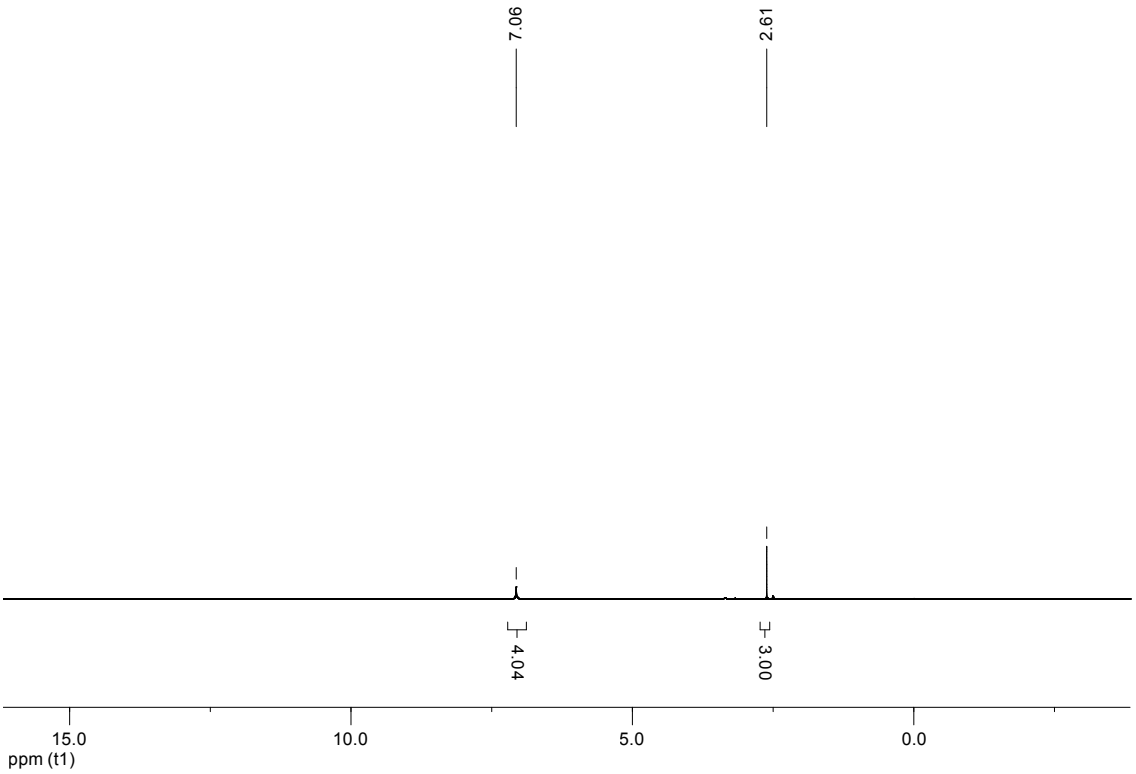


Figure S17 ^{1}H NMR spectrum of **5**

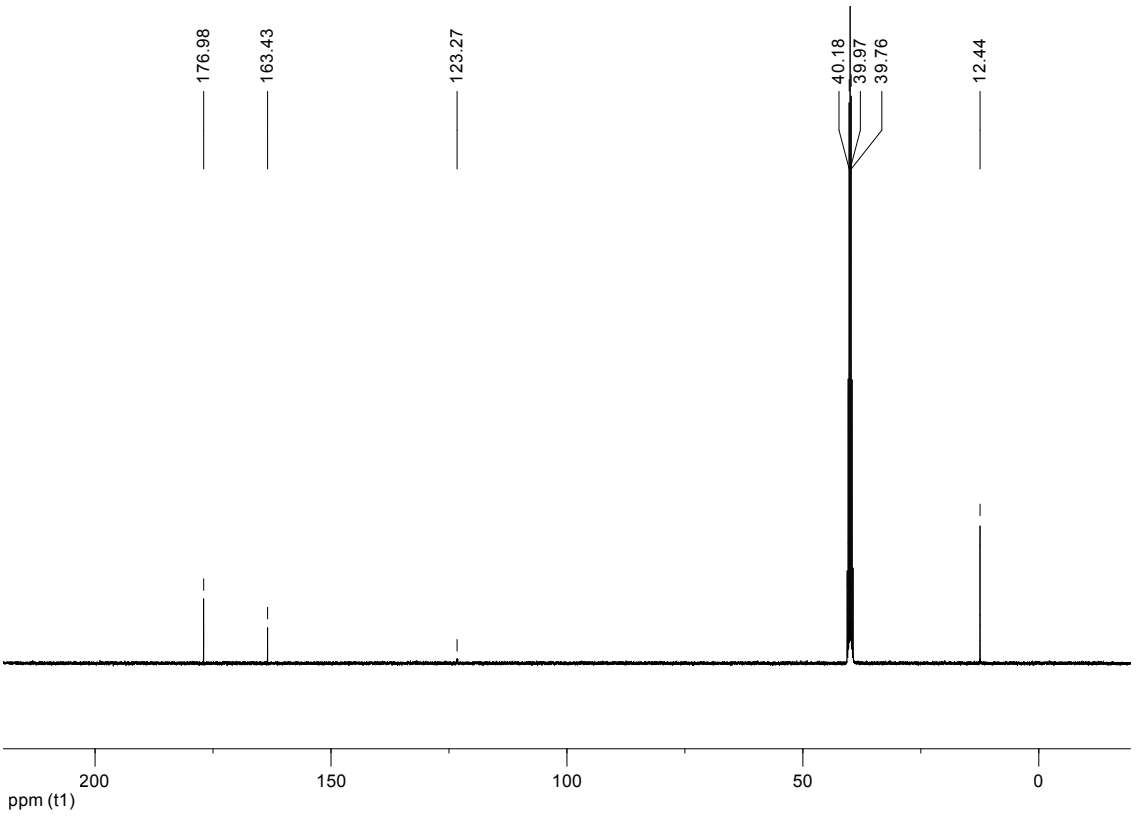


Figure S18 ^{13}C NMR spectrum of **5**.

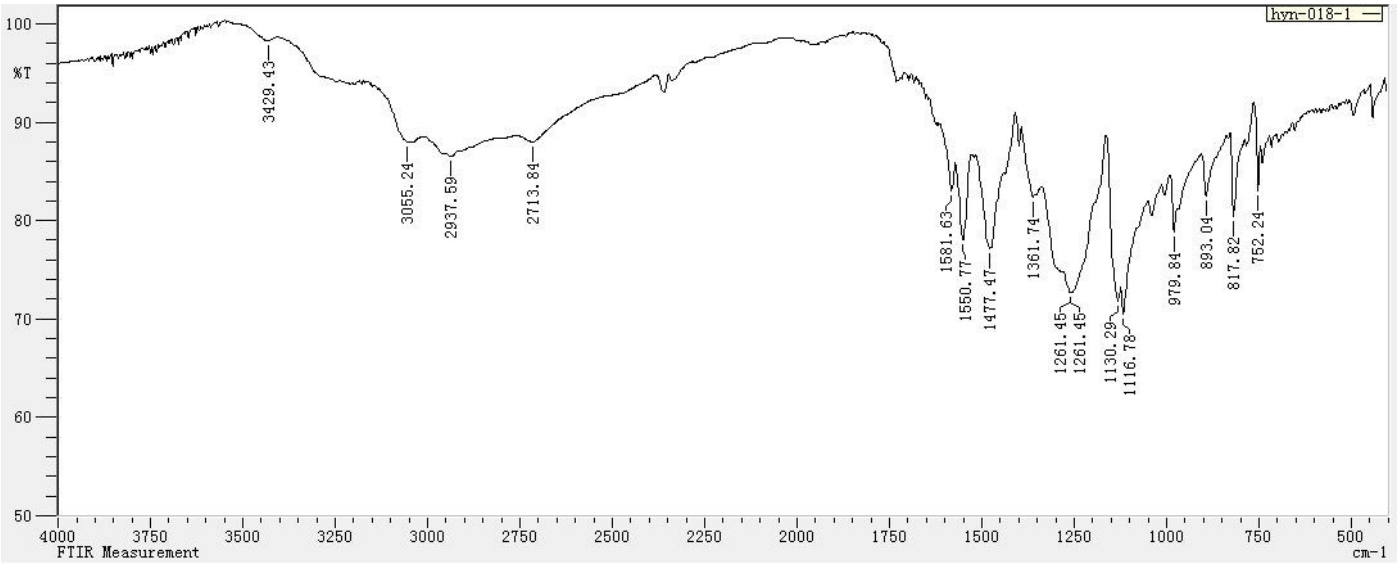


Figure S19 IR spectrum of **6**.

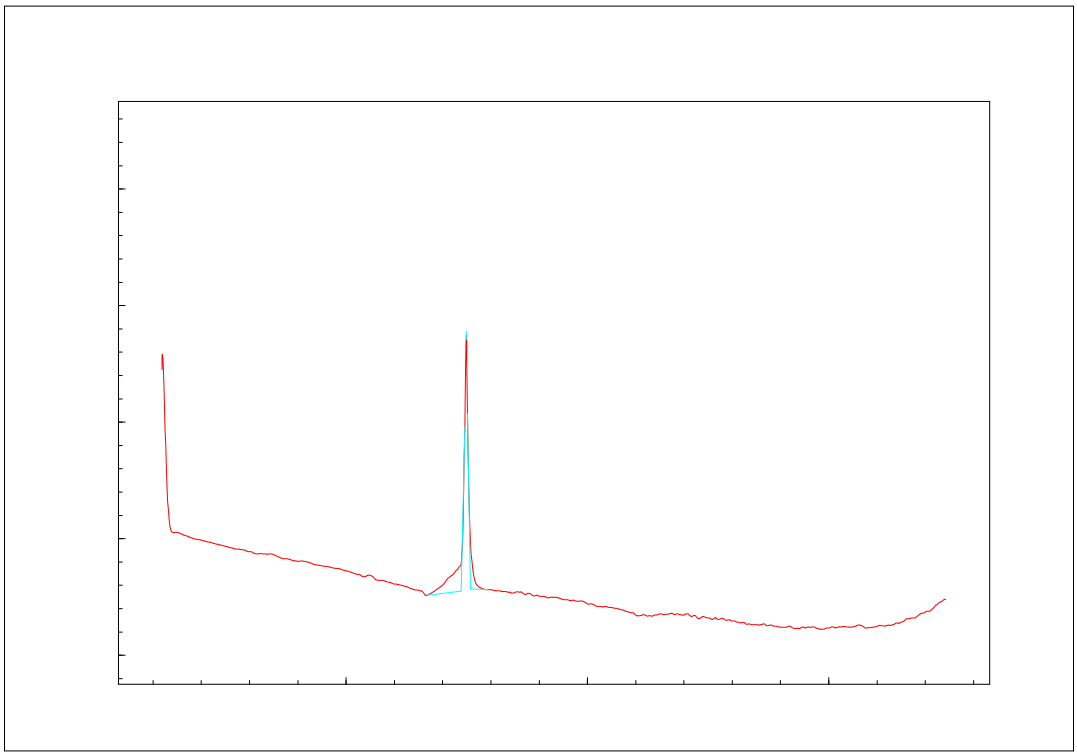


Figure S20 DSC curve of **6** (10 ºC min^{-1})

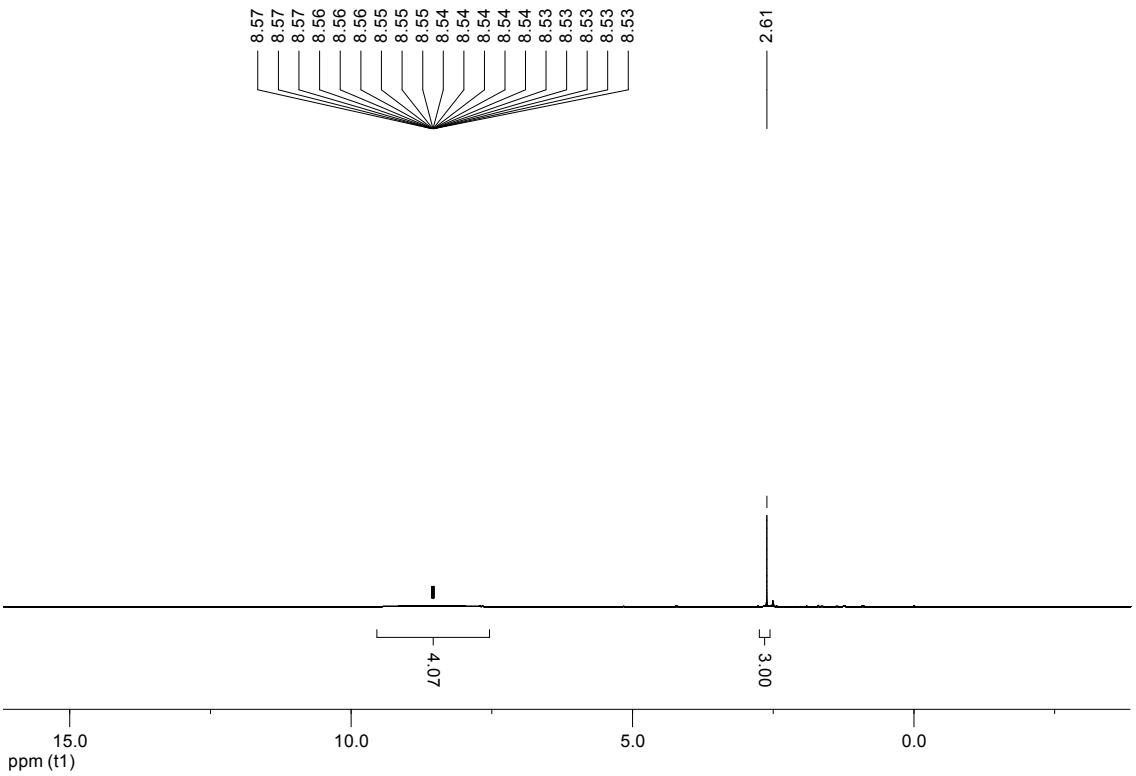


Figure S21 ^{1}H NMR spectrum of **6**

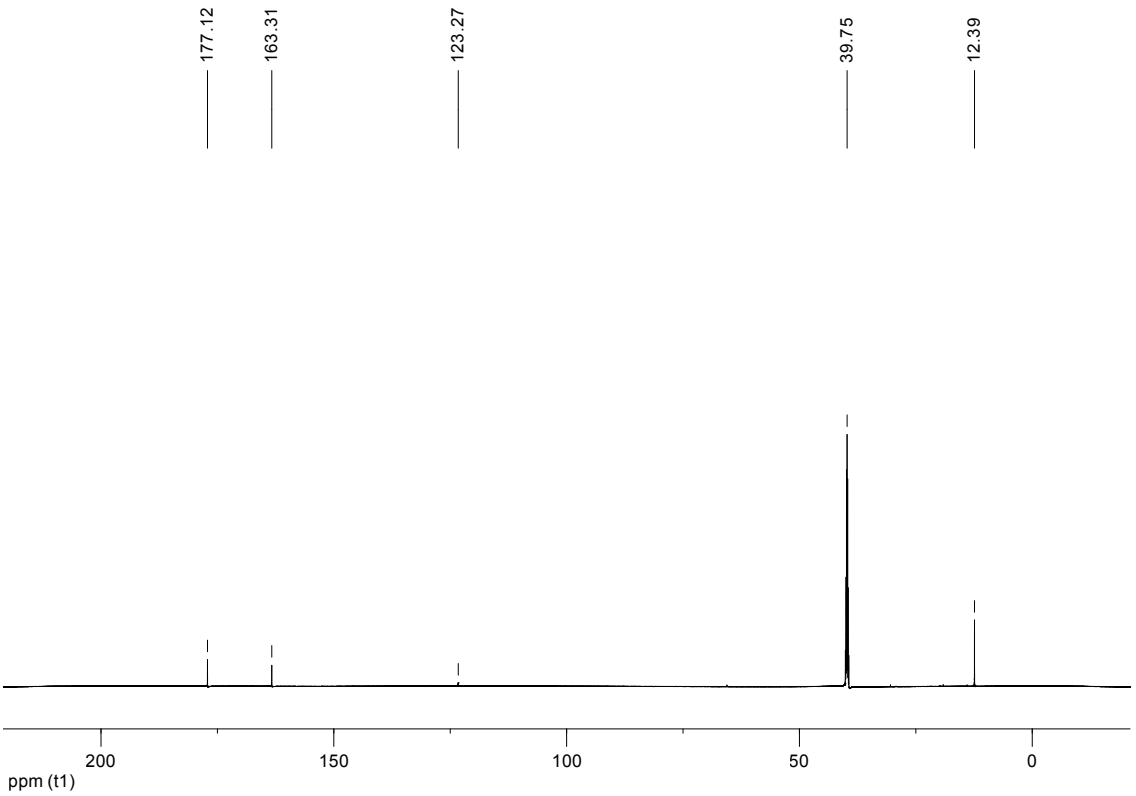


Figure S22 ^{13}C NMR spectrum of **6**.

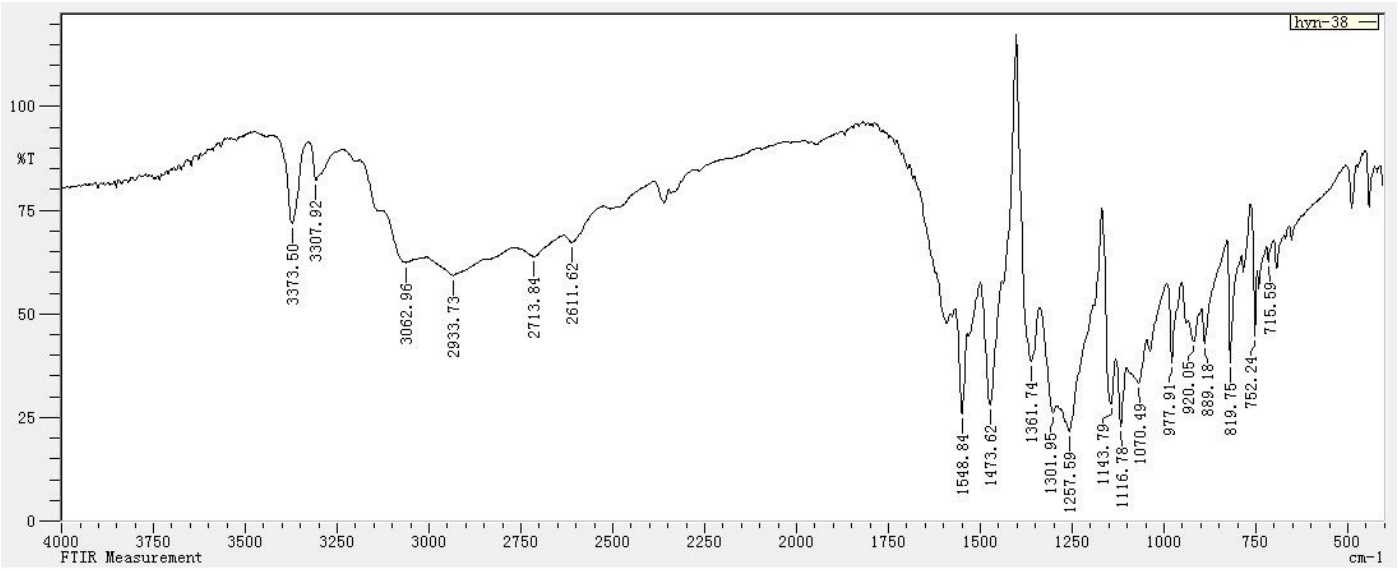


Figure S23 IR spectrum of **7**.

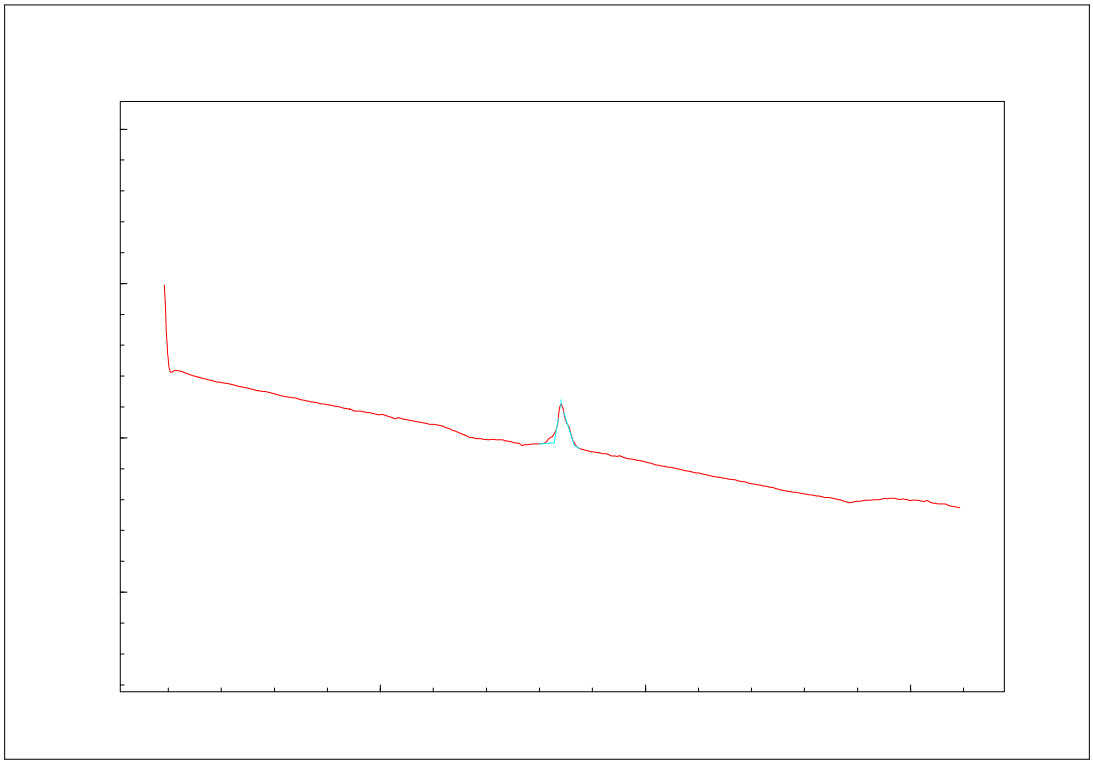


Figure S24 DSC curve of **7** (10 ºC min^{-1})

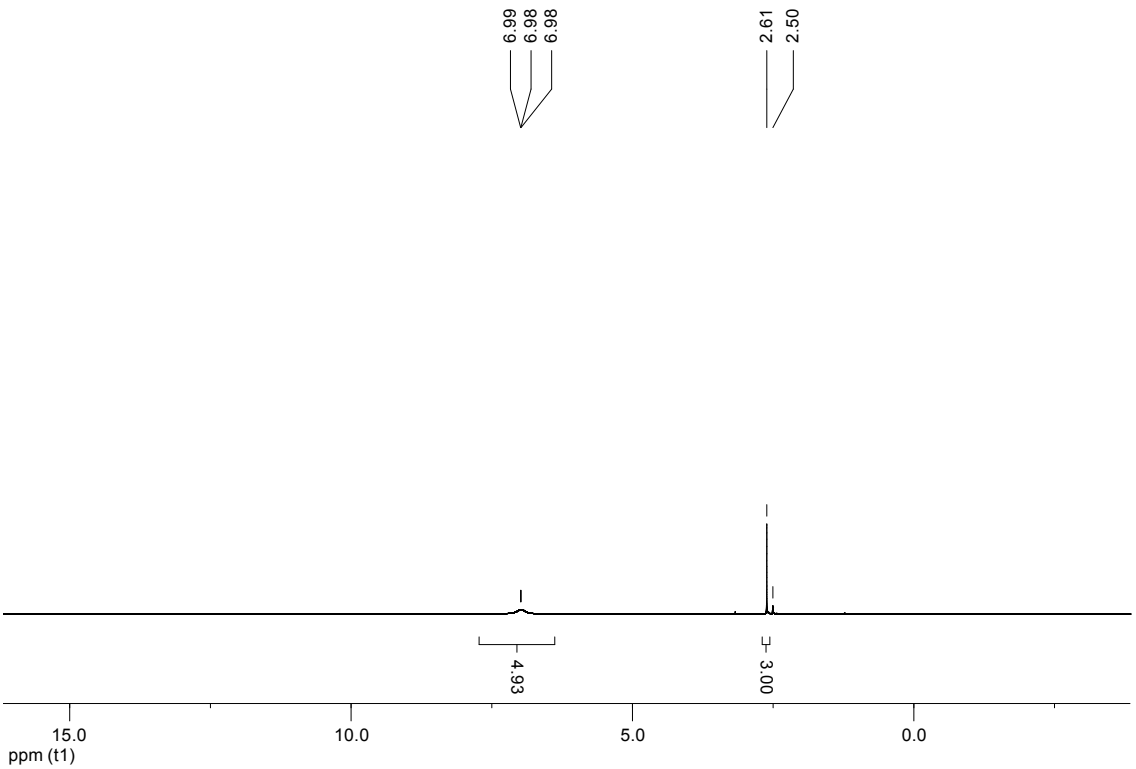


Figure S25 ^{1}H NMR spectrum of **7**

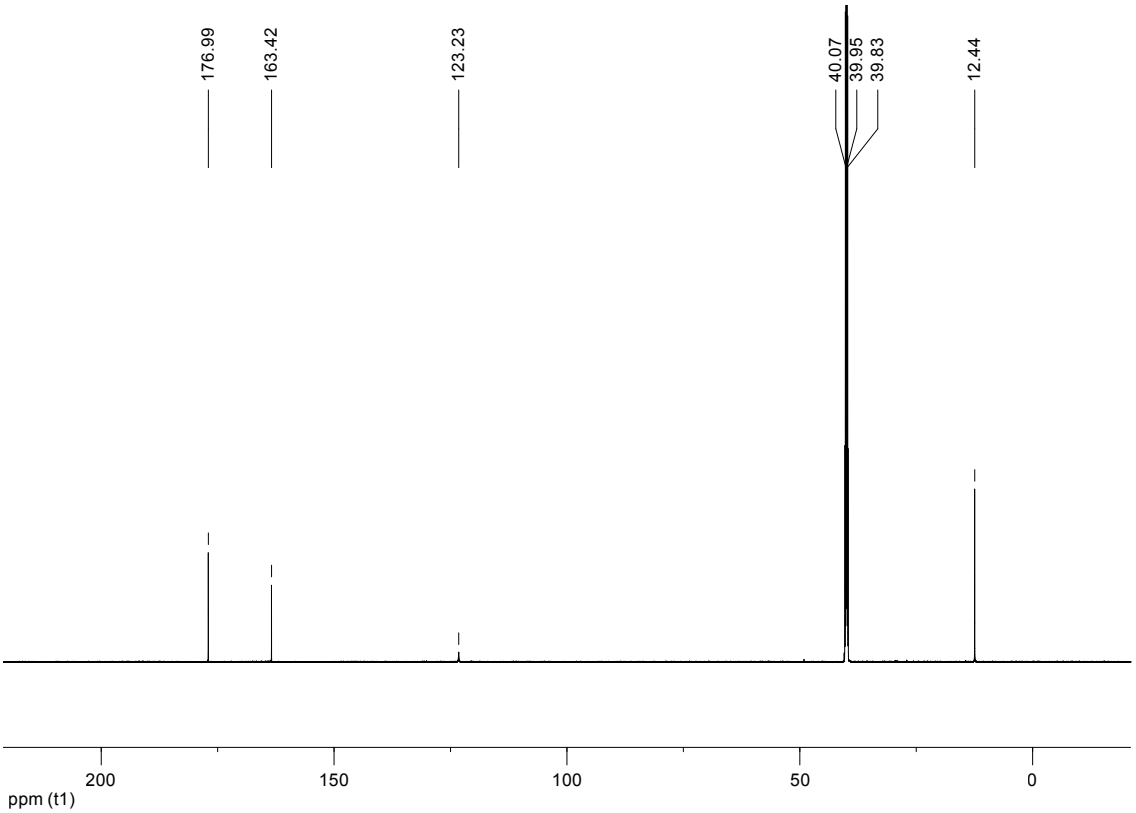


Figure S26 ^{13}C NMR spectrum of **7.**

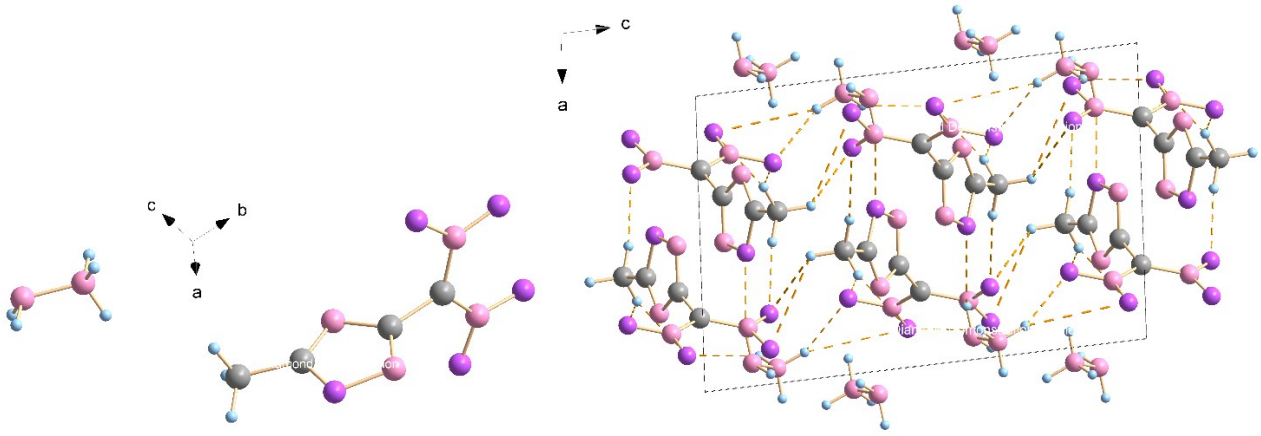


Figure S27 X-ray crystal of **7**

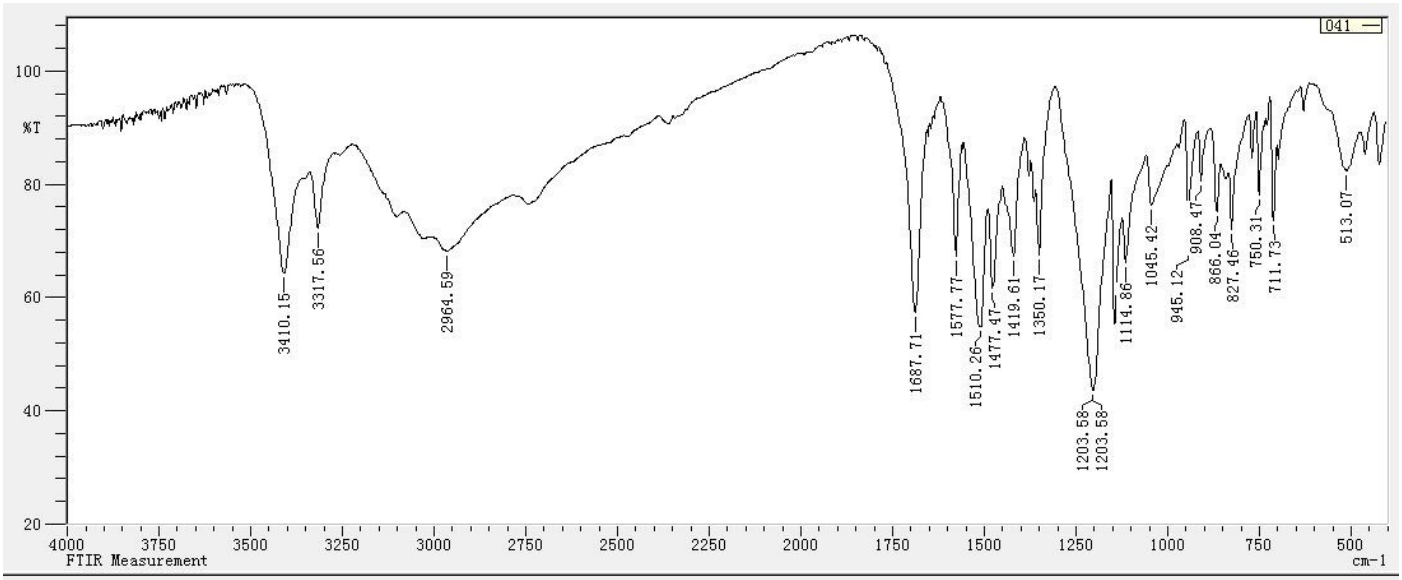


Figure S28 IR spectrum of **8**.

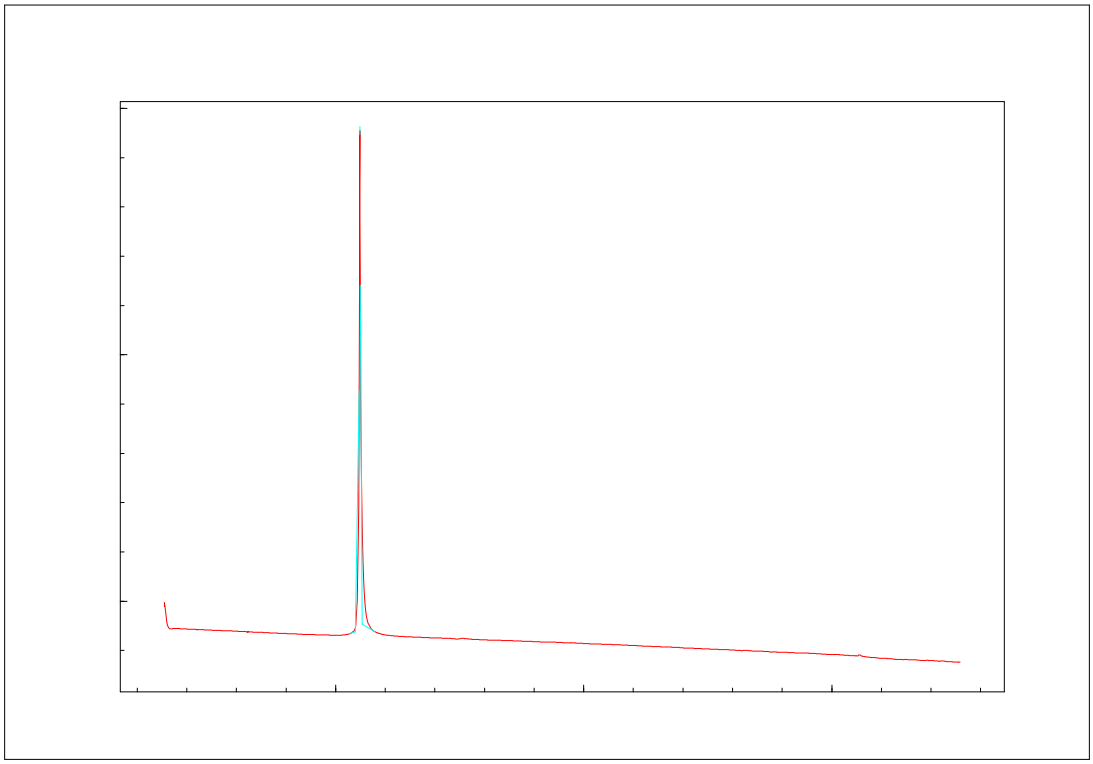


Figure S29 DSC curve of **8** (10 ºC min^{-1})

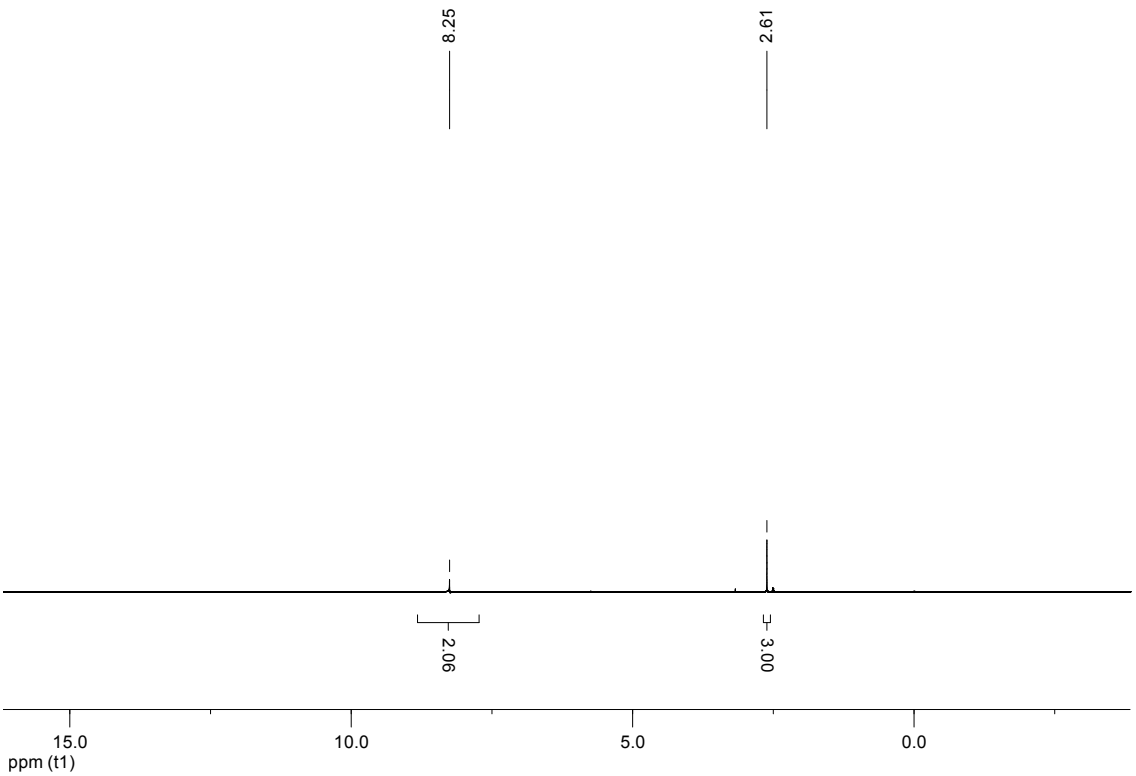


Figure S30 ^{1}H NMR spectrum of **8**

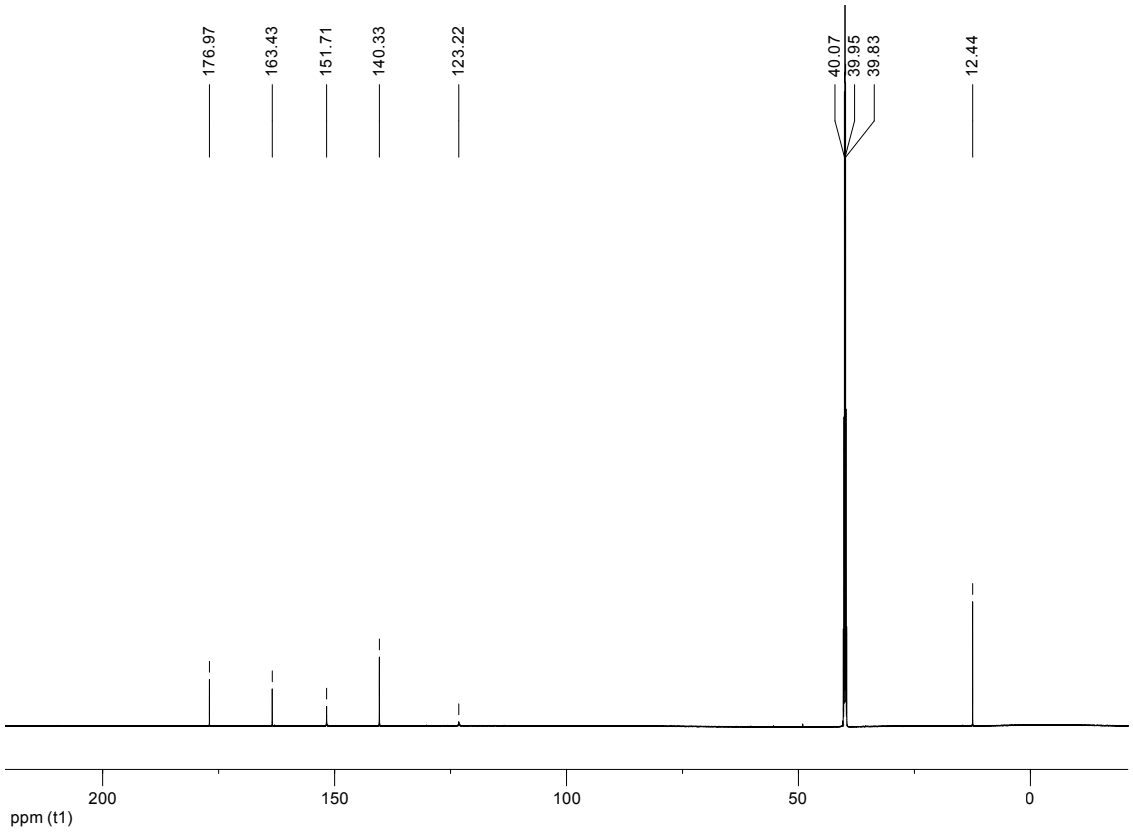


Figure S31 ^{13}C NMR spectrum of **8**.

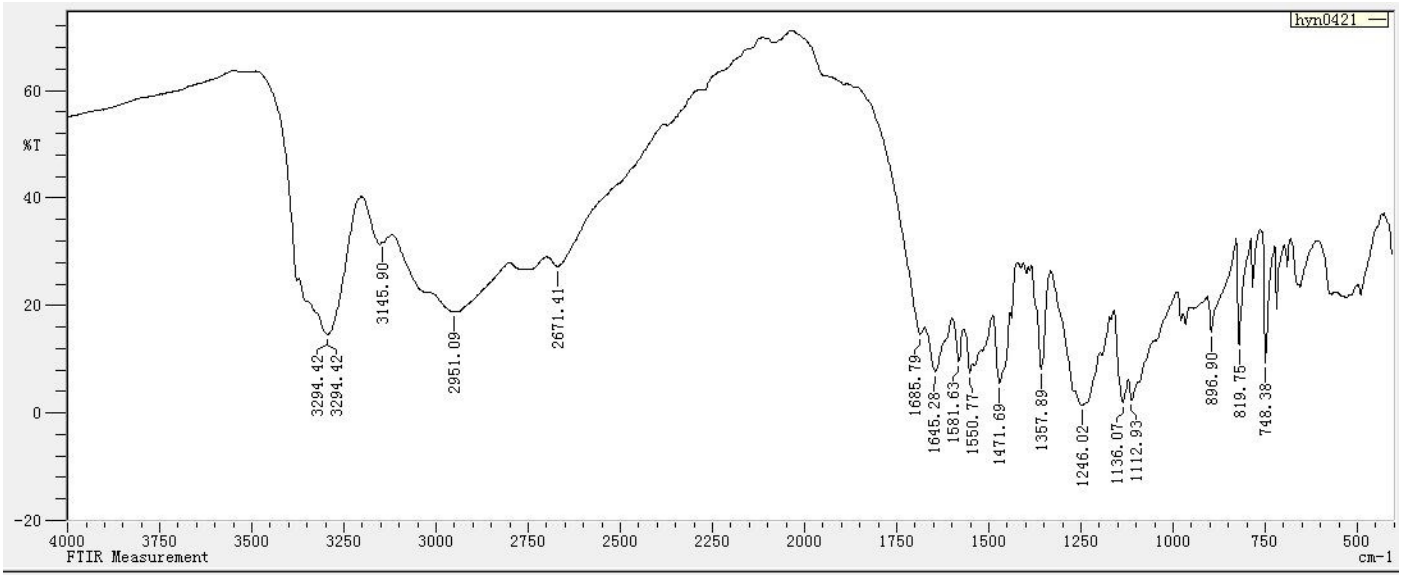


Figure S32 IR spectrum of **9**.

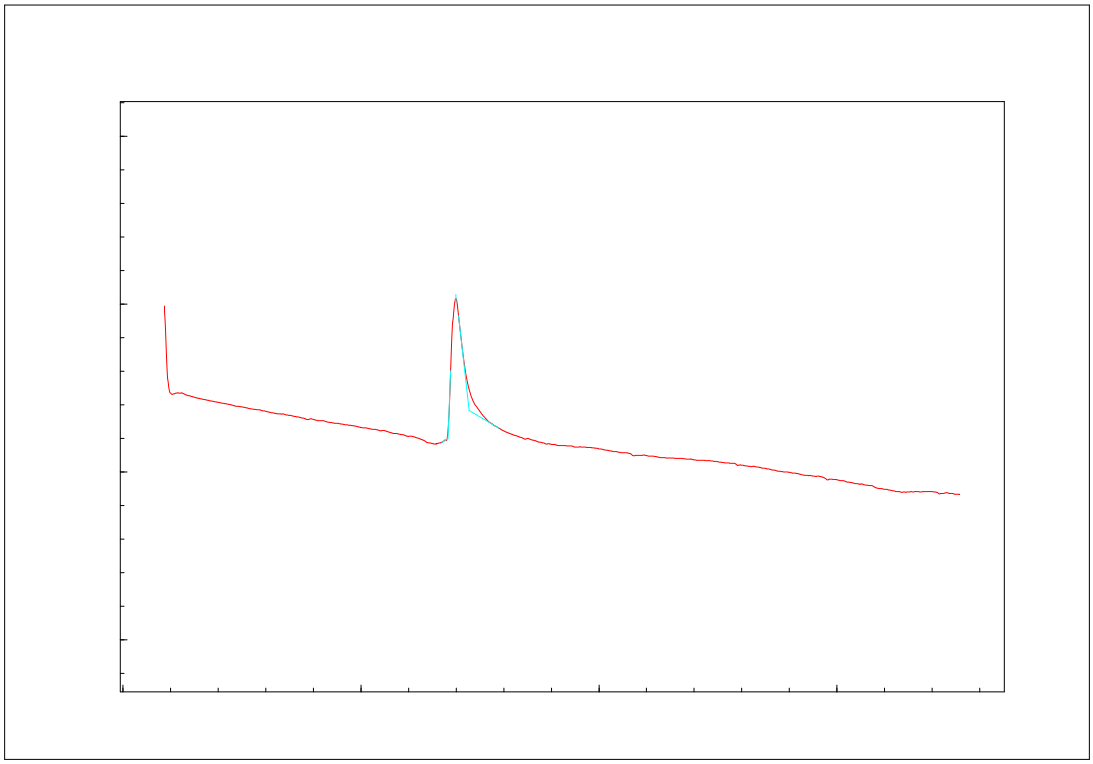


Figure S33 DSC curve of **9** (10 ºC min^{-1})

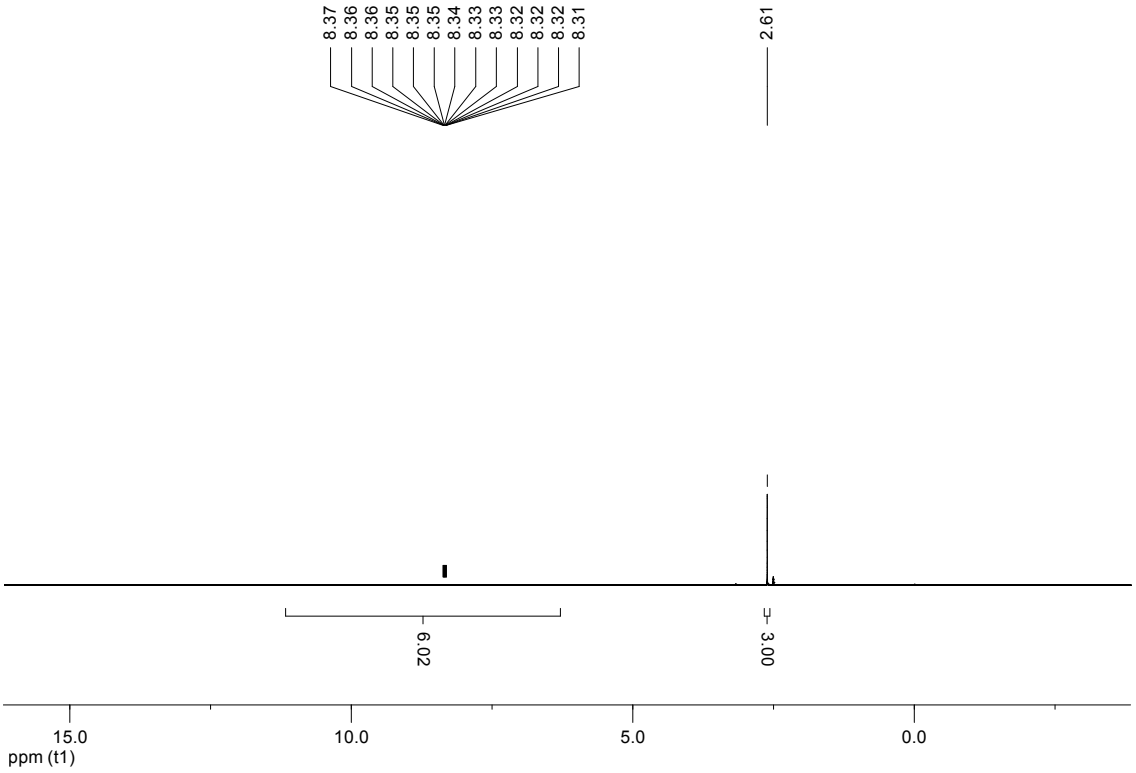


Figure S34 ^{1}H NMR spectrum of **9**

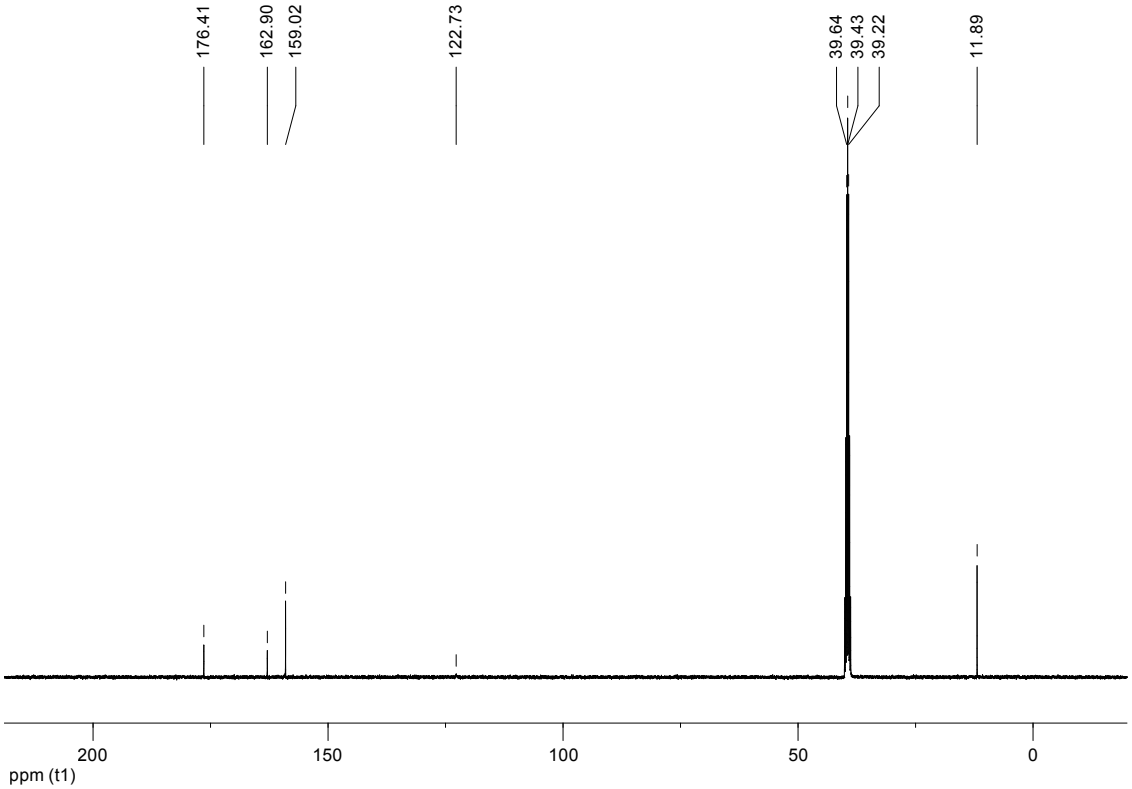


Figure S35 ^{13}C NMR spectrum of **9**.

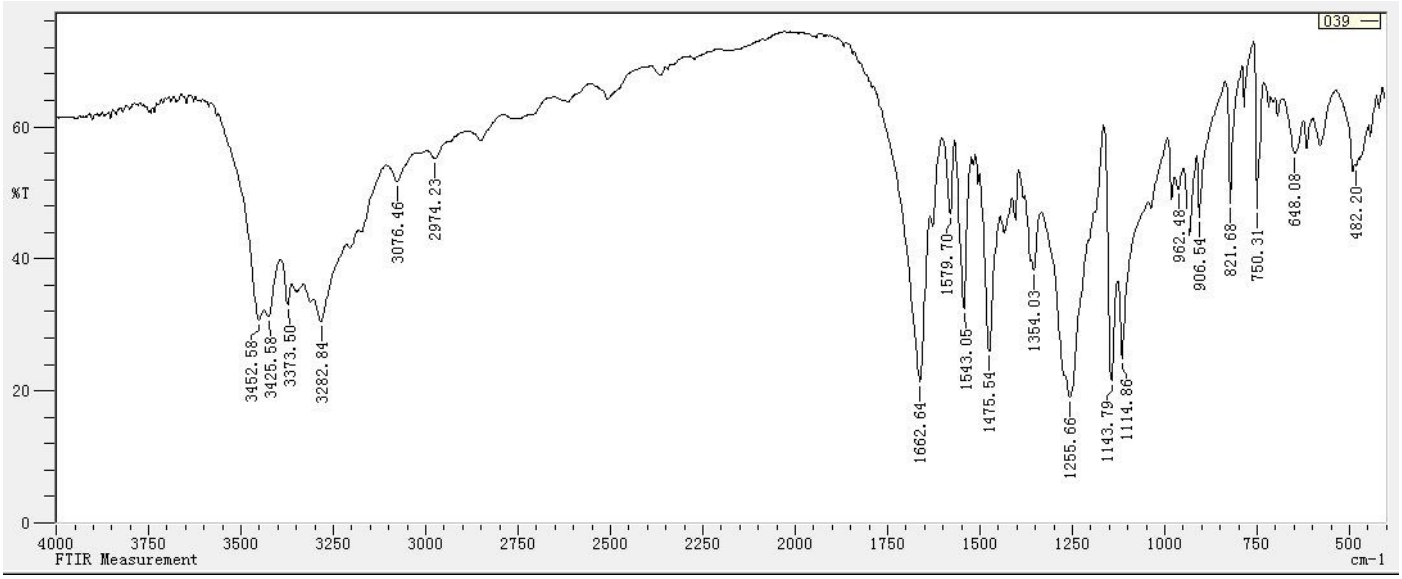


Figure S36 IR spectrum of **10**.

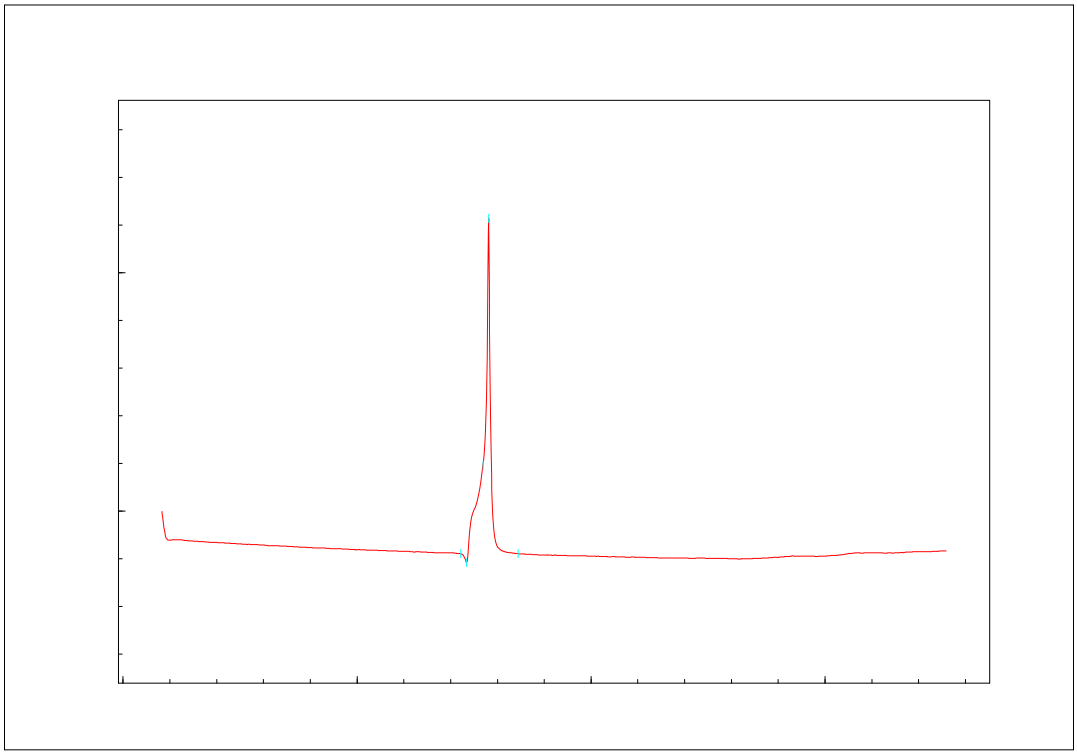


Figure S37 DSC curve of **10** (10 ºC min^{-1})

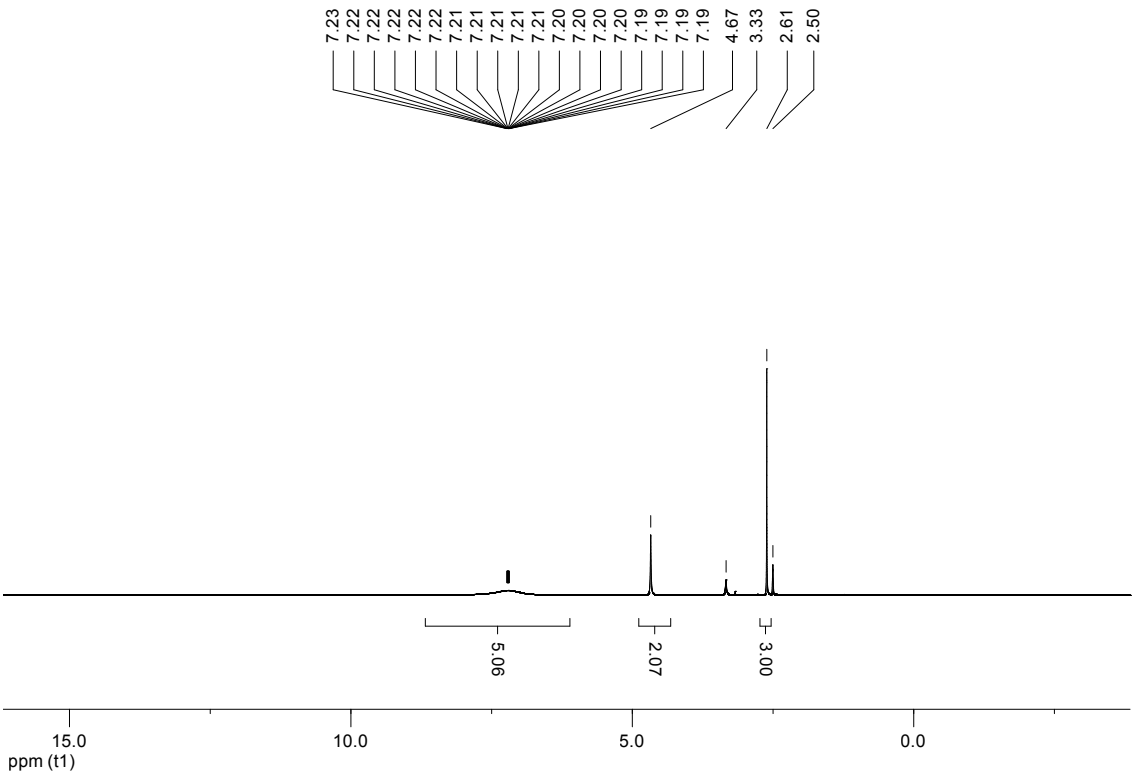


Figure S38 ^{1}H NMR spectrum of **10**

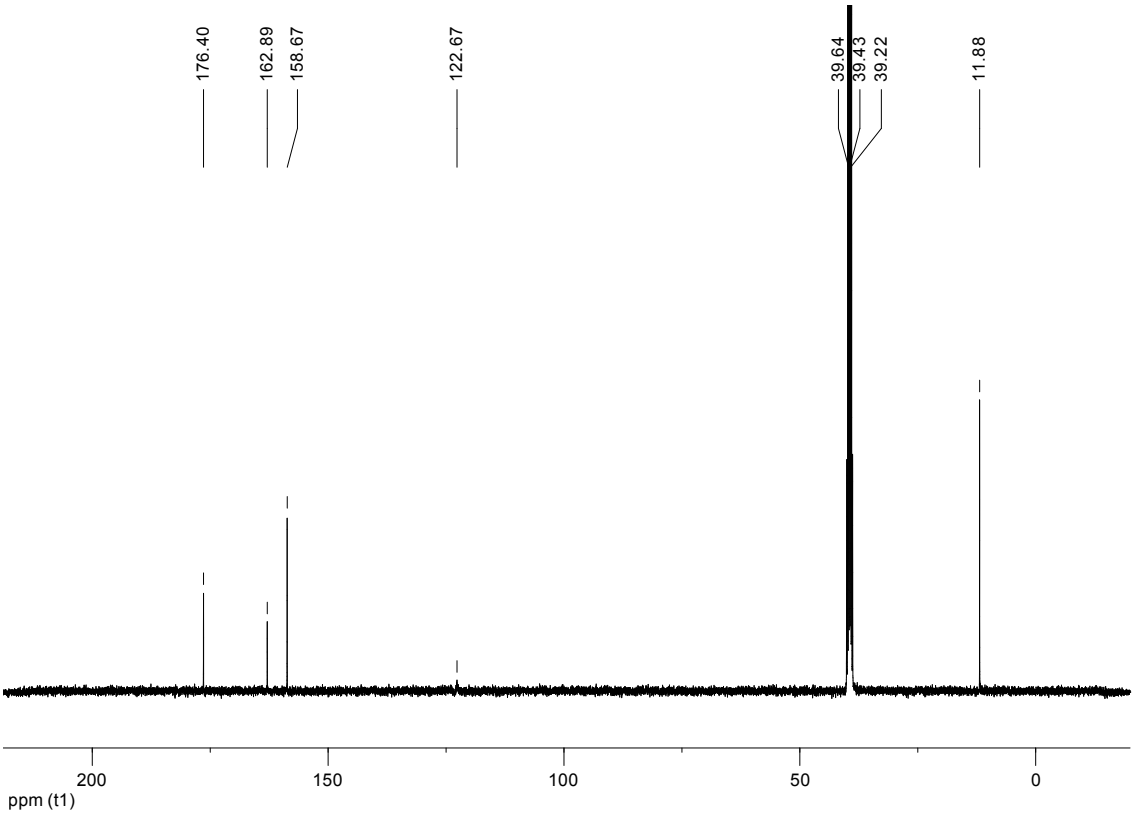


Figure S39 ^{13}C NMR spectrum of **10**.

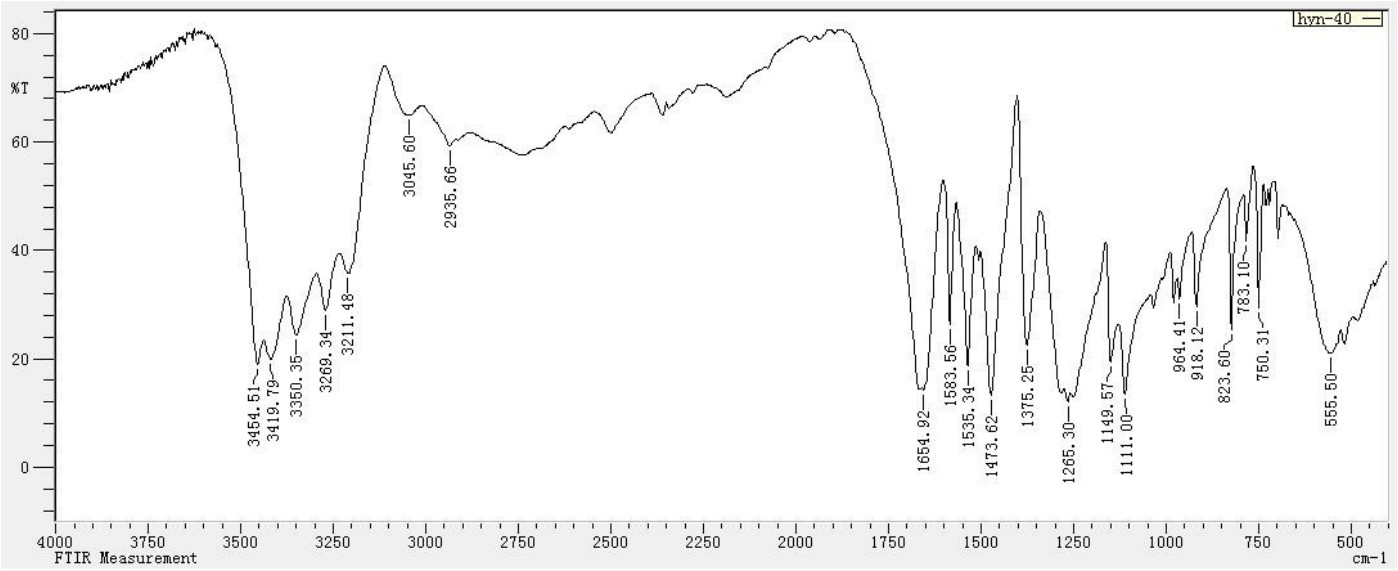


Figure S40 IR spectrum of **11**.

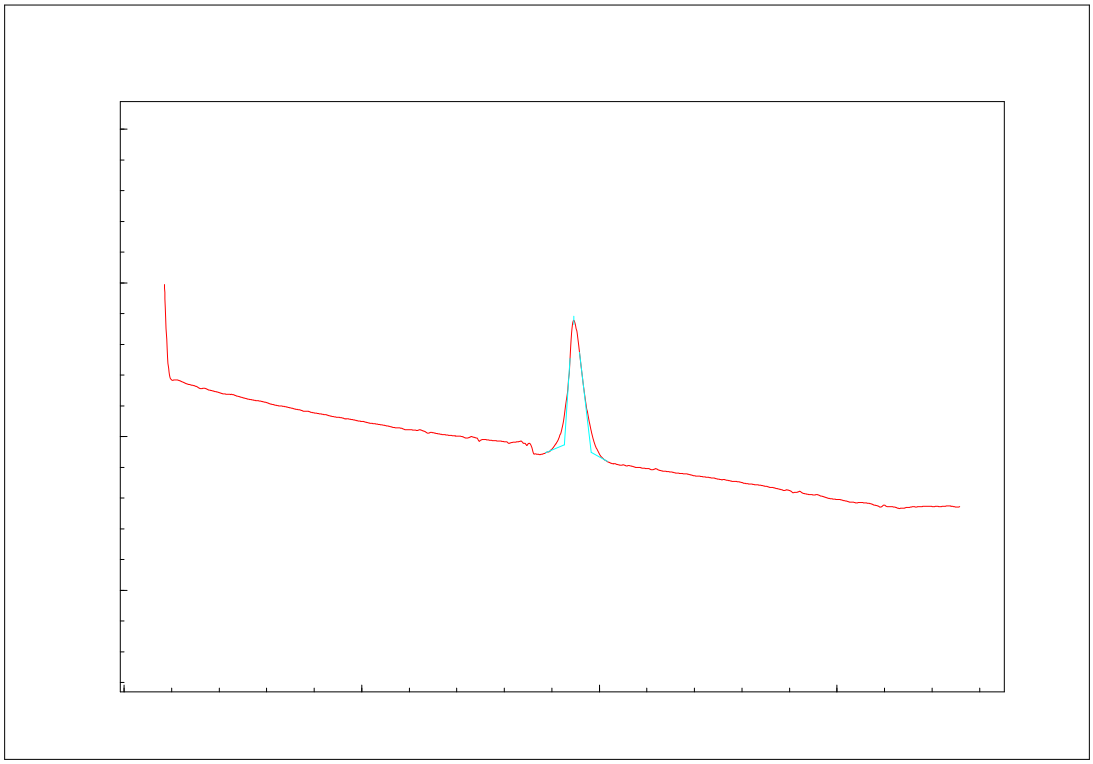


Figure S41 DSC curve of **11** (10 ºC min^{-1})

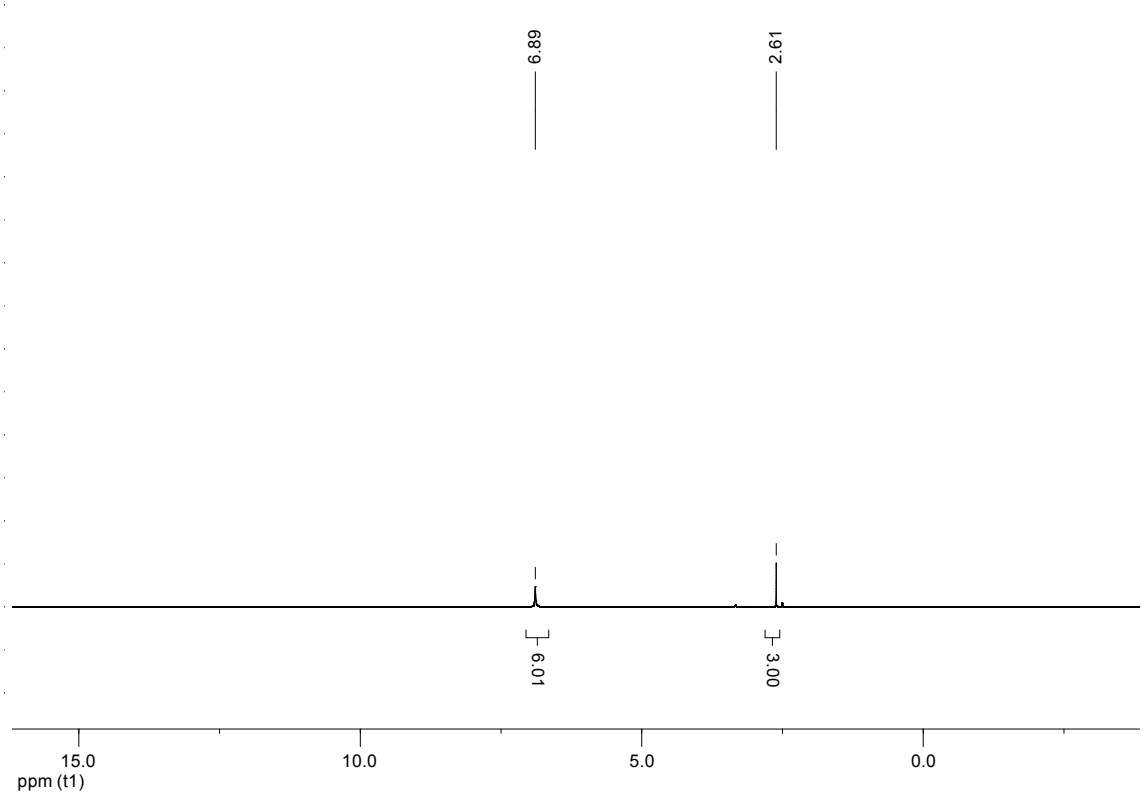


Figure S42 ^{1}H NMR spectrum of **11**

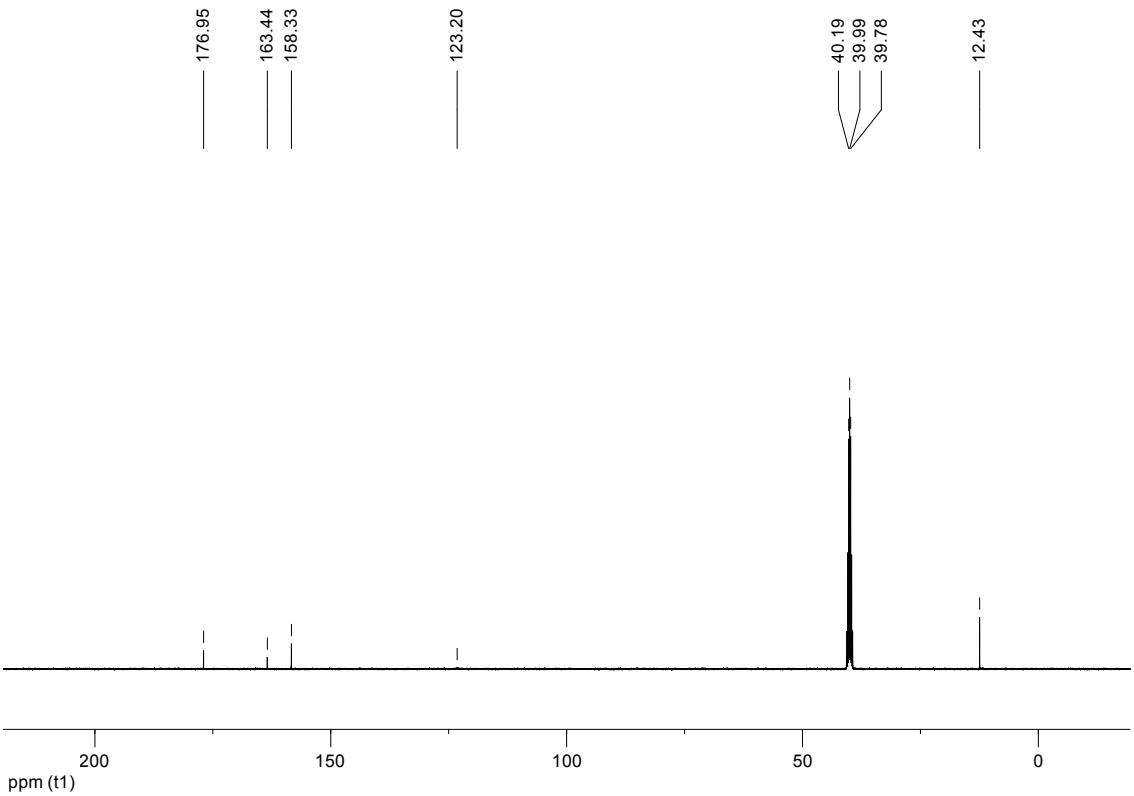


Figure S43 ^{13}C NMR spectrum of **11**.