Supporting Information (SI)

Synthesis and characterization of a new family of energetic salts based on guanidinium cation containing furoxanyl functionality

Bo Wu,[a] Zhixin Wang, [a] Hongwei Yang,*[a] Qiuhan Lin,[a,b] Xuehai Ju, [a] Chunxu, Lu [a] and Guangbin Cheng*[a]

a: School of Chemical Engineering, Nanjing University of Science and Technology Nanjing 210094, P. R. China

b: School of Materials Science & Engineering, Beijing Institute of Technology

Beijing 100081, P. R. China.

Email: hyang@mail.njust.edu.cn
gcheng@mail.njust.edu.cn

Table of Contents

1. Computational Details

Method of calculated densities

One of the most important physical properties of an energetic material is its density. The theoretical detonation parameters were calculated with the density from theoretical calculation. For an ionic crystal with formula unit M_pX_q, their volumes are simply the sum of the volumes of the ions contained in the formula unit:[1]

$$V = pV_{M+} + qV_{X-} \quad (1)$$

where M denotes the cation and X denotes the anion. Because the volumes of individual ions able to be evaluated using the DFT procedure, equation (1) was used to calculate formula unit volumes for ionic crystal. For those salts that contain hydrogen atoms, a "correct" molecular volume using a molecular structure optimized at the DFT level can be calculated using:

$$V_{(\text{corrected})\text{Opt}} = V_{(\text{uncorrected})\text{Opt}} - [0.6763 + 0.9418 \times(\text{no. of hydrogen atoms in the ion})] \quad (2)$$

$$\rho\ (\text{g}\cdot\text{cm}^{-3}) = M_m/V_{(\text{corrected})\text{Opt}} \quad (3)$$

Heat of formation

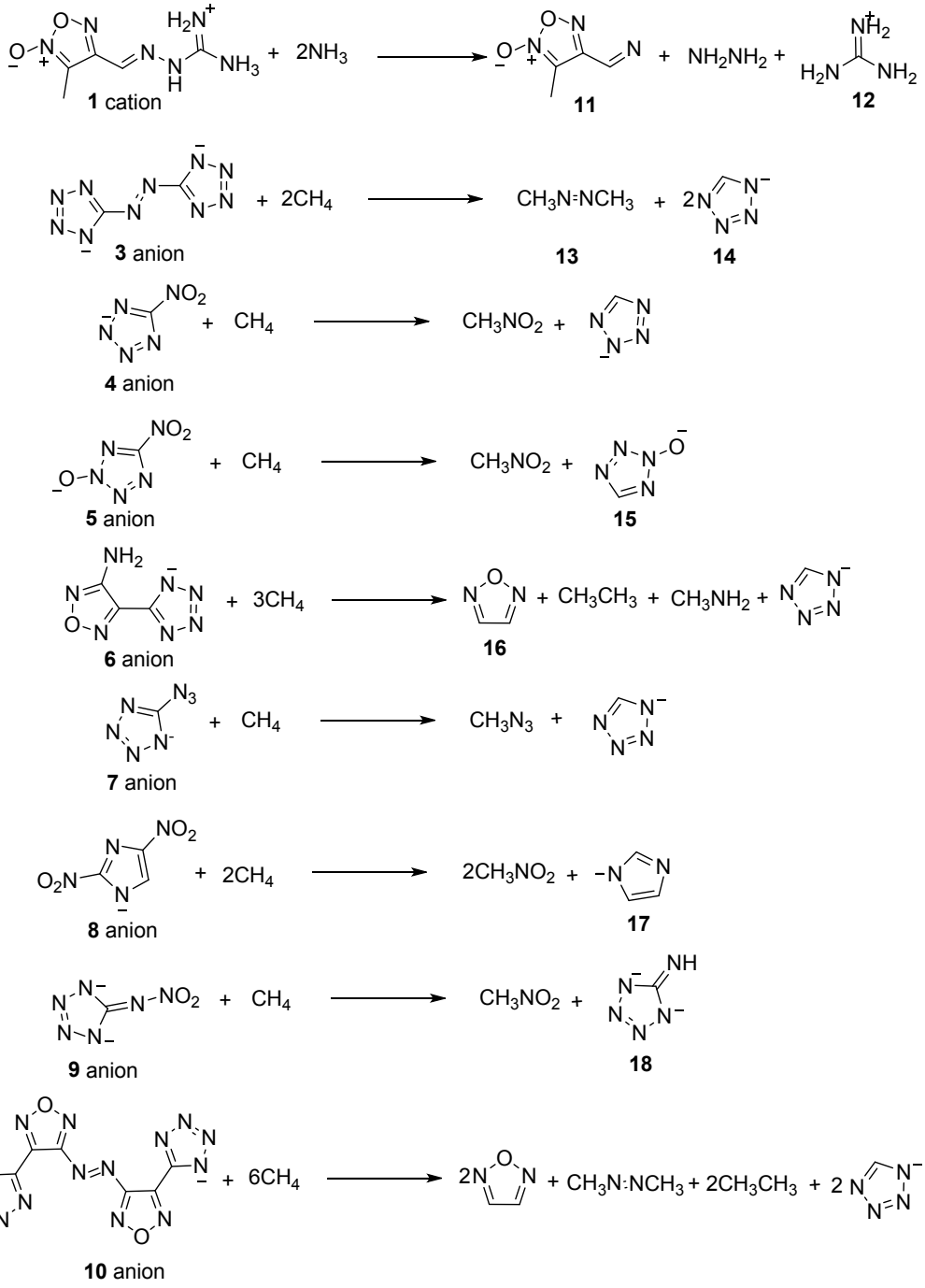
Calculations were performed by using the Gaussian 09 suite of programs. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional[1] with 6-311+G** basis set,[2] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heats of formation (HOF) of the furoxanyl fuctionalized guanidinium cation (FAG cation) and anions were computed through appropriate isodesmic reactions (Scheme S1). The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title compounds are in Scheme S1. The change of enthalpy for the reactions at 298 K can be expressed as

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

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

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq (2) is the PV work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from the experiments[3-5] or from the high level computing like CBS-4M.



Scheme S1. Isodesmic reactions for the furoxanyl fuctionalized guanidinium cation (FAG cation) and anions.

Based on Born-Haber energy cycles, the heat of formation of a salt can be simplified and expressed as Equation (3), in which ΔH_L is the lattice energy of the salt. This quantity could be predicted by the formula suggested by Jenkins et al (Equation (4)), in which n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for the lattice potential energy, U_{POT}, takes the form of equation (5), where ρ_m (g cm^{-3}) is the density, M_m (g) is the chemical formula mass of the ionic material and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[6]

$$\Delta H_f^o(\text{salt},298\text{ K}) = \Delta H_f^o(\text{cation},298\text{ K}) + \Delta H_f^o(\text{anion},298\text{ K}) - \Delta H_L \quad (3)$$

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

$$U_{POT}\ (\text{kJ}\cdot\text{mol}^{-1}) = \gamma\,(\rho_m/M_m)^{1/3} + \delta \quad (5)$$

Table S1 Total energy and heat of formation for the title compounds at B3LYP/6-311+G** level[a]

	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	-74.60[b]
NH_3	-56.5826356	86.27	10.05	-45.90[b]
H_2N-NH_2	-111.9105763	134.28	11.16	95.40[b]
CH_3NO_2	-245.0915559	124.93	11.60	-80.80[b]
CH_3CH_3	-79.8565413	187.31	11.79	-84.00[b]
CH_3NH_2	-95.8938402	160.78	11.64	-22.50[b]
CH_3N_3	-204.153351	126.22	14.41	302.30[c]
1cation	-674.7098601	418.16	38.90	961.93
3 anion	-623.787668	144.11	25.27	788.47
4 anion	-462.3675686	90.67	17.74	112.01
5 anion	-537.5669458	101.24	19.85	57.84
6 anion	-574.1182105	191.70	22.33	331.55
7 anion	-421.4323947	93.13	18.05	485.83
8 anion	-634.8962488	157.74	25.06	-129.87
9 anion	-517.0464687	100.91	19.95	402.04
10 anion	-1145.654207	273.34	45.46	1200.14
11	-470.112577	248.22	25.28	257.97[c]
12	-205.8352863	220.21	15.56	565.59[d]
13	-189.3337358	211.85	16.32	147.85[c]
14	-257.7887821	84.91	11.26	175.75[d]
15	-332.9899087	96.05	13.15	117.33[d]
16	-262.1183629	114.62	11.84	215.72[c]
17	-225.7140337	144.06	12.04	60.08[d]
18	-312.4067394	93.18	13.81	617.14[d]

[a] E0 in a.u. ZPE (vibrational zero-point energy)，ΔH_T (thermal correction to enthalpy) and HOF are in kJ mol^{-1}. [b] 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.]. [c] Data obtained from CBS-4M calculation in combination with the atomization reaction of the corresponding compound. [d] Data from Ref.[4].

References

1 (a) A. D. Becke, *J. Phys. Chem.*, 1993, **98**, 5648; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem*., 1994, **98**, 11623.
2 P. C.Hariharan and J. A. Pople, *Theoretica Chimica Acta*, 1973, **28**, 213.
3 D. R. Lide, CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL, 2007-2008.
4 N. Fischer, T. M. Klapötke and J. Stierstorfer, *Z. Anorg. Allg. Chem*., 2009, **635**, 271.
5 Y. -H. Joo, J. H. Chung, S. G. Cho and E. M. Goh, *New J. Chem.*, 2013, **37**, 1180.
6 H. D. B. Jenkins, D. Tudela and L. Glasser. Inorg. Chem., 2002, 41, 2364.

2. Crystal data and structure refinement details of 1, 4, 5 and 6. Their selected bond lengths [Å], angles [°] and hydrogen bonds details.

Table S2. Crystal data and structure refinement details of **1**, **4**, **5** and **6**.

Crystal	**1**	**4**	**5**	**6**
formula	$C_5H_9ClN_6O_2$	$C_6H_{10}N_{11}O_4$	$C_6H_9N_{11}O_5$	$C_8H_{13}N_{13}O_4$
T/ K	173(2)	173(2)	173(2)	173(2)
λ/ Å	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/ Å	5.8923(5)	10.9990(8)	11.3383(10)	9.3457(6)
b/ Å	11.4413(9)	6.3838(4)	6.2879(5)	25.7804(17)
c/ Å	7.6951(7)	18.1184(10)	18.1702(12)	13.4303(9)
α/°	90	90	90	90
β/°	112.239(3)	104.323(2)	104.761(3)	109.4145(19)
γ/°	90	90	90	90
V/ Å^3	480.18(7)	1232.65(14)	1252.67(17)	3051.8(3)
Z	2	4	4	8
ρ/ g cm^{-3}	1.526	1.612	1.672	1.547
F(000)	228	616	648	1472
□ range for data collection/ ∘	3.37 to 25.03	3.35 to 26.02	3.44 to 25.37	3.22 to 25.98
Limiting	-7<=h<=7, -	-	-13<=h<=13,	-

indices	13<=k<=13, -9<=l<=9	13<=h<=13, -7<=k<=7, -21<=l<=22	-7<=k<=7, -21<=l<=21	11<=h<=11, -31<=k<=31, -16<=l<=16
GOF on F^2	1.006	1.017	1.033	1.021
Final R indices [I>2σ(I)]	R_1 = 0.0507, wR_2 = 0.1002	R_1 = 0.0356, wR_2 = 0.0864	R_1 = 0.0412, wR_2 = 0.0877	R_1 = 0.0461, wR_2 = 0.0879
R indices (all data)	R_1 = 0.0785, wR_2 = 0.1137	R_1 = 0.0540, wR_2 = 0.0948	R_1 = 0.0796, wR_2 = 0.1008	R_1 = 0.1013, wR_2 = 0.0981
CCDC	996724	1017968	1017969	1017970

Table S3. Selected bond lengths [Å] and angles [°] of salt **1**

Parameter	Å	Parameter	°
C(1)-N(1)	1.312(6)	N(1)-C(1)-C(2)	106.3(4)
C(1)-C(2)	1.413(7)	N(1)-C(1)-C(3)	120.2(4)
C(1)-C(3)	1.478(7)	C(2)-C(1)-C(3)	133.5(4)
C(2)-N(2)	1.317(6)	N(2)-C(2)-C(1)	112.0(4)
C(2)-C(4)	1.445(6)	N(2)-C(2)-C(4)	119.0(4)
C(4)-N(3)	1.277(6)	C(1)-C(2)-C(4)	129.0(4)
C(5)-N(6)	1.317(6)	N(3)-C(4)-C(2)	119.4(4)
C(5)-N(5)	1.322(6)	N(6)-C(5)-N(5)	121.2(4)
C(5)-N(4)	1.337(6)	N(6)-C(5)-N(4)	118.4(4)
N(1)-O(2)	1.237(5)	N(5)-C(5)-N(4)	120.3(4)
N(1)-O(1)	1.464(5)	O(2)-N(1)-C(1)	136.0(5)
N(2)-O(1)	1.368(5)	O(2)-N(1)-O(1)	115.9(4)
N(3)-N(4)	1.367(5)	C(1)-N(1)-O(1)	107.9(4)
		C(2)-N(2)-O(1)	107.0(4)
		C(4)-N(3)-N(4)	115.9(4)
		C(5)-N(4)-N(3)	119.2(4)
		N(2)-O(1)-N(1)	106.8(3)

Table S4. Hydrogen bonds present in salt **1**.

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment

N(4) —H(4A) •••Cl(1) [i]	0.88	2.20	3.048(4)	163	inter
N(5) —H(5A) •••Cl(1) [i]	0.88	2.40	3.196(4)	151	inter
N(5) —H(5B) •••Cl(1) [ii]	0.88	2.76	3.346(4)	125	inter
N(5) —H(5B) •••N(3)	0.88	2.36	2.676(5)	102	intra
N(5) —H(5B) •••O(1)[iii]	0.88	2.60	3.007(5)	110	inter
N(6) —H(6A) •••Cl(1)[iii]	0.88	2.54	3.303(4)	145	inter
N(6) —H(6B) •••O(2)[iv]	0.88	2.29	2.919(6)	129	inter
N(6) —H(6B) •••Cl(1)[i]	0.88	2.77	3.495(4)	141	inter
C(3) —H(3A) •••O(2)	0.98	2.59	2.977(8)	104	intra
C(3) —H(3A) ••• Cl(1) [ii]	0.98	2.70	3.669(5)	172	inter

i: 1-x,1/2+y,-z; ii: -1+x,y,z; iii: -x,-1/2+y,1-z; iv: 1+x,y,-1+z

Table S5. Selected bond lengths [Å] and angles [°] of salt **4**

Parameter	Å	Parameter	°
C(1)-N(4)	1.320(2)	N(4)-C(1)-N(1)	114.24(14)
C(1)-N(1)	1.322(2)	N(4)-C(1)-N(5)	122.71(15)
C(1)-N(5)	1.445(2)	N(1)-C(1)-N(5)	123.05(13)
C(2)-N(6)	1.315(2)	N(6)-C(2)-C(3)	106.07(15)
C(2)-C(3)	1.415(2)	N(6)-C(2)-C(4)	121.35(16)
C(2)-C(4)	1.479(3)	C(3)-C(2)-C(4)	132.43(17)
C(3)-N(7)	1.312(2)	N(7)-C(3)-C(2)	112.04(15)
C(3)-C(5)	1.456(2)	N(7)-C(3)-C(5)	118.59(15)
C(5)-N(8)	1.277(2)	C(2)-C(3)-C(5)	129.35(15)
C(6)-N(11)	1.315(2)	N(8)-C(5)-C(3)	119.00(15)
C(6)-N(10)	1.321(2)	N(11)-C(6)-N(10)	122.98(15)
C(6)-N(9)	1.348(2)	N(11)-C(6)-N(9)	119.57(15)
N(1)-N(2)	1.3423(19)	N(10)-C(6)-N(9)	117.44(14)
N(2)-N(3)	1.3186(19)	C(1)-N(1)-N(2)	103.41(13)
N(3)-N(4)	1.343(2)	N(3)-N(2)-N(1)	109.35(14)
N(5)-O(2)	1.2225(19)	N(2)-N(3)-N(4)	109.83(13)
N(5)-O(1)	1.2232(18)	C(1)-N(4)-N(3)	103.17(13)
N(6)-O(4)	1.2372(19)	O(2)-N(5)-O(1)	124.45(15)
N(6)-O(3)	1.4583(19)	O(2)-N(5)-C(1)	117.89(13)
N(7)-O(3)	1.3677(18)	O(1)-N(5)-C(1)	117.64(14)
N(8)-N(9)	1.3731(18)	O(4)-N(6)-C(2)	135.08(16)
		O(4)-N(6)-O(3)	117.11(14)
		C(2)-N(6)-O(3)	107.82(13)
		C(3)-N(7)-O(3)	106.98(13)

	C(5)-N(8)-N(9)	114.98(14)
	C(6)-N(9)-N(8)	118.71(13)
	N(7)-O(3)-N(6)	107.04(11)

Table S6. Hydrogen bonds present in salt **4**.

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment
N(9) —H(9) ••• N(4) [i]	0.88	1.96	2.8290(19)	170	inter
N(10)—H(10A)••• N(2) [ii]	0.88	2.23	2.988(2)	145	inter
N(10)—H(10A)••• O(1) [iii]	0.88	2.52	3.1199(19)	126	inter
N(10) —H(10B) •••N(3)[i]	0.88	2.21	3.060(2)	164	inter
N(11) —H(11A)•••N(1)[iii]	0.88	2.09	2.959(2)	172	inter
N(11) —H(11B) •••N(8)	0.88	2.32	2.657(2)	103	intra
C(4) —H(4C) •••O(1)[iii]	0.98	2.43	3.360(3)	159	inter
C(5) —H(5) •••O(2)[i]	0.95	2.51	3.448(2)	170	inter

i: 1-x,1-y,-z; ii: x,-1+y,z; iii: 1-x,-1/2+y,1/2-z

Table S7. Selected bond lengths [Å] and angles [°] of salt **5**

Parameter	Å	Parameter	°
C(1)-N(4)	1.314(3)	N(4)-C(1)-N(1)	115.61(19)
C(1)-N(1)	1.329(3)	N(4)-C(1)-N(5)	121.63(19)
C(1)-N(5)	1.438(3)	N(1)-C(1)-N(5)	122.72(18)
C(2)-N(6)	1.322(3)	N(6)-C(2)-C(3)	106.08(19)
C(2)-C(3)	1.414(3)	N(6)-C(2)-C(4)	120.8(2)
C(2)-C(4)	1.479(3)	C(3)-C(2)-C(4)	133.1(2)
C(3)-N(7)	1.309(3)	N(7)-C(3)-C(2)	112.11(19)
C(3)-C(5)	1.455(3)	N(7)-C(3)-C(5)	118.82(19)
C(5)-N(8)	1.275(3)	C(2)-C(3)-C(5)	129.0(2)
C(6)-N(11)	1.313(3)	N(8)-C(5)-C(3)	118.8(2)
C(6)-N(10)	1.319(3)	N(11)-C(6)-N(10)	122.5(2)
C(6)-N(9)	1.345(3)	N(11)-C(6)-N(9)	119.53(19)
N(1)-N(2)	1.334(2)	N(10)-C(6)-N(9)	118.0(2)
N(2)-O(1)	1.269(2)	C(1)-N(1)-N(2)	99.40(16)
N(2)-N(3)	1.329(2)	O(1)-N(2)-N(3)	122.23(18)
N(3)-N(4)	1.335(3)	O(1)-N(2)-N(1)	123.28(18)
N(5)-O(3)	1.219(2)	N(3)-N(2)-N(1)	114.48(18)
N(5)-O(2)	1.229(2)	N(2)-N(3)-N(4)	105.35(17)
N(6)-O(5)	1.233(2)	C(1)-N(4)-N(3)	105.16(18)
N(6)-O(4)	1.456(2)	O(3)-N(5)-O(2)	124.8(2)
N(7)-O(4)	1.370(2)	O(3)-N(5)-C(1)	118.03(18)

N(8)-N(9)	1.367(2)	O(2)-N(5)-C(1)	117.17(19)
		O(5)-N(6)-C(2)	135.0(2)
		O(5)-N(6)-O(4)	117.41(17)
		C(2)-N(6)-O(4)	107.56(17)
		C(3)-N(7)-O(4)	107.00(17)
		C(5)-N(8)-N(9)	116.19(17)
		C(6)-N(9)-N(8)	118.33(17)
		N(7)-O(4)-N(6)	107.17(14)

Table S8. Hydrogen bonds present in salt **5**.

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment
N(9) —H(9) ••• N(1) [i]	0.88	2.20	3.080(3)	174	inter
N(10)—H(10A)••• O(2) [ii]	0.88	2.54	3.206(3)	133	inter
N(10)—H(10A)••• O(1) [iii]	0.88	2.43	2.930(3)	117	inter
N(10) —H(10B) ••• O(1)[i]	0.88	1.91	2.784(3)	172	inter
N(11) —H(11A)••• N(4)[ii]	0.88	2.09	2.956(3)	169	inter
N(11) —H(11B) ••• O(2)[ii]	0.88	2.44	3.140(3)	137	inter
N(11) —H(11B) •••N(8)	0.88	2.30	2.641(3)	103	intra
C(4) —H(4A) •••O(2) [ii]	0.98	2.37	3.296(3)	157	inter
C(5) —H(5) •••O(3)[i]	0.95	2.49	3.398(3)	159	inter

i: -1/2-x, -3/2+y, 1/2-z; ii: 1/2+x, 1/2-y, 1/2+z; iii: x, -1+y, z; iv: x, -1+y,z; v: 1/2+x, 1/2-y, 1/2+z

Table S9. Selected bond lengths [Å] and angles [°] of salt **6**

Parameter	Å	Parameter	°
C(1)-N(1)	1.309(3)	N(1)-C(1)-N(3)	123.9(2)
C(1)-N(3)	1.350(3)	N(1)-C(1)-C(2)	108.63(19)
C(1)-C(2)	1.440(3)	N(3)-C(1)-C(2)	127.43(19)
C(2)-N(2)	1.303(3)	N(2)-C(2)-C(1)	108.73(18)
C(2)-C(3)	1.450(3)	N(2)-C(2)-C(3)	122.44(19)
C(3)-N(4)	1.335(3)	C(1)-C(2)-C(3)	128.82(19)
C(3)-N(7)	1.351(2)	N(4)-C(3)-N(7)	112.55(18)
C(4)-N(8)	1.311(3)	N(4)-C(3)-C(2)	122.59(18)
C(4)-N(10)	1.349(3)	N(7)-C(3)-C(2)	124.86(19)
C(4)-C(5)	1.425(3)	N(8)-C(4)-N(10)	124.8(2)
C(5)-N(9)	1.300(3)	N(8)-C(4)-C(5)	109.26(19)
C(5)-C(6)	1.465(3)	N(10)-C(4)-C(5)	125.9(2)
C(6)-N(14)	1.335(3)	N(9)-C(5)-C(4)	109.51(19)
C(6)-N(11)	1.337(3)	N(9)-C(5)-C(6)	123.54(19)

C(7)-N(15)	1.321(3)	C(4)-C(5)-C(6)	126.95(19)
C(7)-C(8)	1.415(3)	N(14)-C(6)-N(11)	112.51(18)
C(7)-C(9)	1.481(3)	N(14)-C(6)-C(5)	125.55(19)
C(8)-N(16)	1.316(2)	N(11)-C(6)-C(5)	121.94(18)
C(8)-C(10)	1.457(3)	N(15)-C(7)-C(8)	105.68(18)
C(10)-N(17)	1.274(3)	N(15)-C(7)-C(9)	120.86(19)
C(11)-N(21)	1.323(3)	C(8)-C(7)-C(9)	133.42(19)
C(11)-C(12)	1.420(3)	N(16)-C(8)-C(7)	112.53(18)
C(11)-C(13)	1.476(3)	N(16)-C(8)-C(10)	117.26(19)
C(12)-N(22)	1.318(3)	C(7)-C(8)-C(10)	130.20(19)
C(12)-C(14)	1.448(3)	N(17)-C(10)-C(8)	121.49(19)
C(14)-N(23)	1.281(3)	N(21)-C(11)-C(12)	106.3(2)
C(15)-N(26)	1.309(3)	N(21)-C(11)-C(13)	120.6(2)
C(15)-N(25)	1.319(3)	C(12)-C(11)-C(13)	133.1(2)
C(15)-N(24)	1.347(3)	N(22)-C(12)-C(11)	112.2(2)
C(23)-N(20)	1.312(3)	N(22)-C(12)-C(14)	118.2(2)
C(23)-N(19)	1.321(3)	C(11)-C(12)-C(14)	129.7(2)
C(23)-N(18)	1.350(3)	N(23)-C(14)-C(12)	120.4(2)
N(1)-O(1)	1.401(2)	N(26)-C(15)-N(25)	121.6(2)
N(2)-O(1)	1.374(2)	N(26)-C(15)-N(24)	118.6(2)
N(4)-N(5)	1.346(2)	N(25)-C(15)-N(24)	119.8(2)
N(5)-N(6)	1.328(2)	N(20)-C(23)-N(19)	121.54(19)
N(6)-N(7)	1.345(2)	N(20)-C(23)-N(18)	118.76(19)
N(8)-O(2)	1.408(2)	N(19)-C(23)-N(18)	119.68(19)
N(9)-O(2)	1.375(2)	C(1)-N(1)-O(1)	105.70(16)
N(11)-N(12)	1.348(2)	C(2)-N(2)-O(1)	106.70(16)
N(12)-N(13)	1.322(2)	C(3)-N(4)-N(5)	104.05(16)
N(13)-N(14)	1.341(2)	N(6)-N(5)-N(4)	110.02(16)
N(15)-O(4)	1.238(2)	N(5)-N(6)-N(7)	109.37(16)
N(15)-O(3)	1.457(2)	N(6)-N(7)-C(3)	104.02(17)
N(16)-O(3)	1.376(2)	C(4)-N(8)-O(2)	104.51(17)
N(17)-N(18)	1.377(2)	C(5)-N(9)-O(2)	105.83(17)
N(21)-O(6)	1.234(2)	C(6)-N(11)-N(12)	104.11(16)
N(21)-O(5)	1.466(2)	N(13)-N(12)-N(11)	109.40(17)
N(22)-O(5)	1.377(2)	N(12)-N(13)-N(14)	109.68(16)
N(23)-N(24)	1.376(2)	C(6)-N(14)-N(13)	104.30(17)
		O(4)-N(15)-C(7)	134.55(19)
		O(4)-N(15)-O(3)	117.23(16)
		C(7)-N(15)-O(3)	108.21(16)
		C(8)-N(16)-O(3)	106.64(16)
		C(10)-N(17)-N(18)	114.87(17)
		C(23)-N(18)-N(17)	118.86(17)
		O(6)-N(21)-C(11)	136.1(2)
		O(6)-N(21)-O(5)	116.37(18)

	C(11)-N(21)-O(5)	107.56(18)
	C(12)-N(22)-O(5)	106.78(19)
	C(14)-N(23)-N(24)	115.81(19)
	C(15)-N(24)-N(23)	118.35(18)
	N(2)-O(1)-N(1)	110.22(14)
	N(9)-O(2)-N(8)	110.90(15)
	N(16)-O(3)-N(15)	106.93(13)
	N(22)-O(5)-N(21)	107.17(15)

Table S10. Hydrogen bonds present in salt **6**.

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment
N(3)—H(3A)•••N(8)^{i}	0.88	2.40	3.217(3)	155	inter
N(3)—H(3B)•••N(4)	0.88	2.46	3.047(3)	125	intra
O(7)—H(7A)•••N(14)^{ii}	0.840(16)	1.994(17)	2.823(2)	169(3)	inter
O(7)—H(7B)•••O(4)^{i}	0.83(2)	2.18(2)	2.914(3)	148(2)	inter
O(8)—H(8A)•••N(13)^{iii}	0.83(2)	2.10(2)	2.896(3)	160.2(19)	inter
O(8)—H(8B)•••O(7)^{iii}	0.823(17)	2.033(17)	2.852(3)	174(2)	inter
N(10)—H(10A)•••N(1)^{i}	0.88	2.08	2.919(3)	159	inter
N(10)—H(10B)•••N(11)	0.88	2.33	2.940(3)	127	intra
N(18)—H(18)•••N(12)^{i}	0.88	2.08	2.946(2)	167	inter
N(19)—H(19A)•••N(6)^{iv}	0.88	2.20	3.056(3)	165	inter
N(19)—H(19B)•••N(17)	0.88	2.33	2.669(2)	103	intra
N(20)—H(20A)•••N(5)^{iv}	0.88	2.01	2.875(3)	166	inter
N(20)—H(20B)•••O(8)^{v}	0.88	2.01	2.845(3)	158	inter
N(24)—H(24)•••N(7)^{v}	0.88	2.07	2.949(3)	174	inter
N(25)—H(25A)•••N(13)^{vi}	0.88	2.38	3.126(3)	143	inter
N(25)—H(25B)•••N(23)	0.88	2.32	2.657(3)	103	intra
N(25)—H(25B)•••O(8) ^{vii}	0.88	2.37	3.000(3)	129	inter
N(26)—H(26A)•••O(7)^{i}	0.88	1.94	2.821(3)	173	inter
N(26)—H(26B)•••N(2)^{i}	0.88	2.07	2.924(3)	164	inter
C(10)—H(10)•••N(11)^{i}	0.95	2.31	3.255(3)	175	inter

C(10)—H(10)•••N(12)^{i}	0.95	2.59	3.405(3)	144	inter

i: 1-x, 1-y, 1-z; ii: 1-x, -1/2+y, 1/2-z; iii: 1-x, 1-y, -z; iv: -1+x, y, 1+z; v: x, y, 1+z; vi: x, 3/2-y, 1/2+z; vii: 1-x, 1/2+y, 1/2-z

3. Figure S1-S4 Crystal structure of salts 1 and 5.

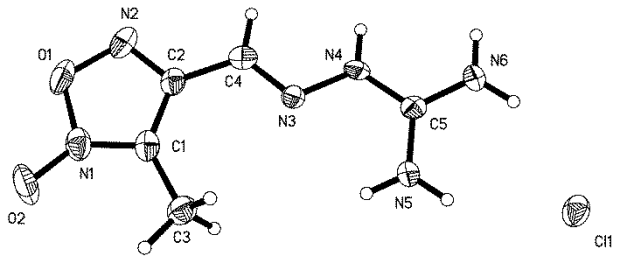


Figure S1. Molecular structure of **1**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.

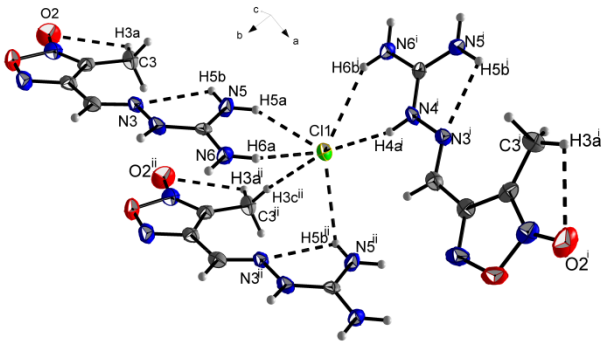


Figure S2. View of the hydrogen bonds of one chloride anion in the structure of **1**. Thermal ellipsoids represent the 50% probability level. Symmetry operators: (i) 1-x, -0.5+y, -z; (ii) 1+x, y, z.

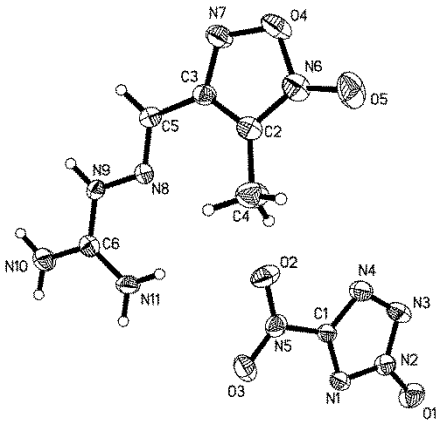


Figure S3. Molecular structure of **5**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.

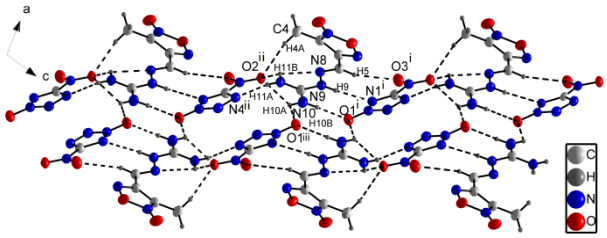


Figure S4. View along the *b* axes in the structure of **5**.

4. ^{1}H and ^{13}C NMR spectra of compounds 1-10

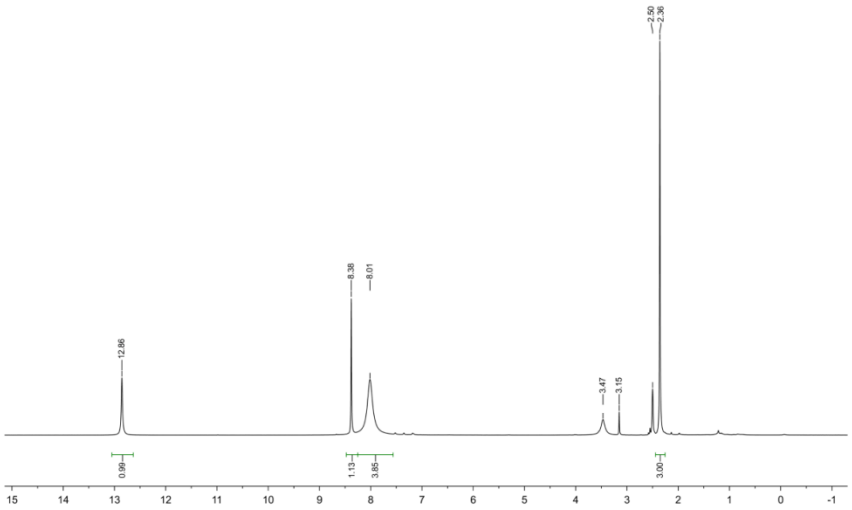


Figure S5 ^{1}H NMR spectra (300 MHz) of **1** in [D_6]DMSO at 25 ^{o}C

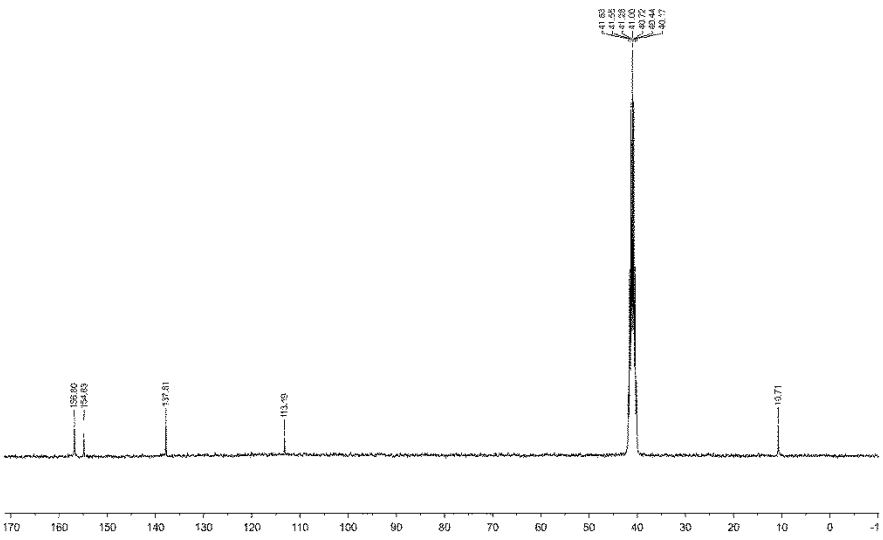


Figure S6 ^{13}C NMR specta (75 MHz) of **1** in [D_6]DMSO at 25 ^{o}C

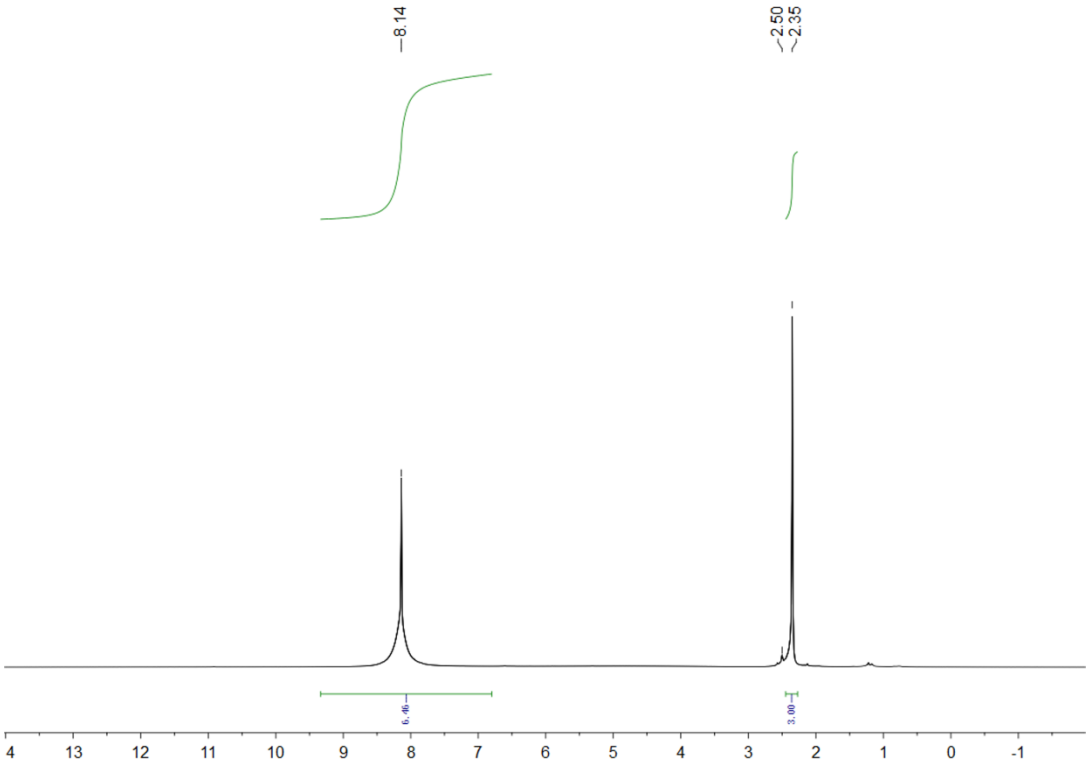


Figure S7 ^{1}H NMR spectra (300 MHz) of **2** in [D_6]DMSO at 25 ^{o}C

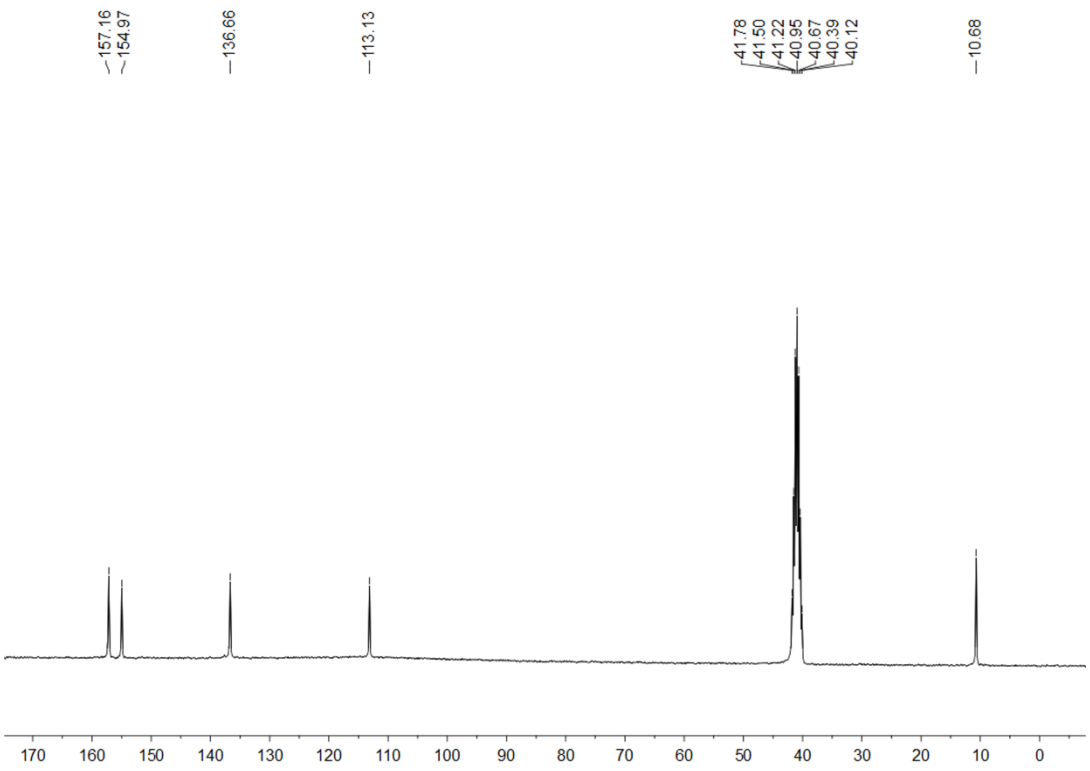


Figure S8 ^{13}C NMR specta (75 MHz) of **2** in [D_6]DMSO at 25 ^{o}C

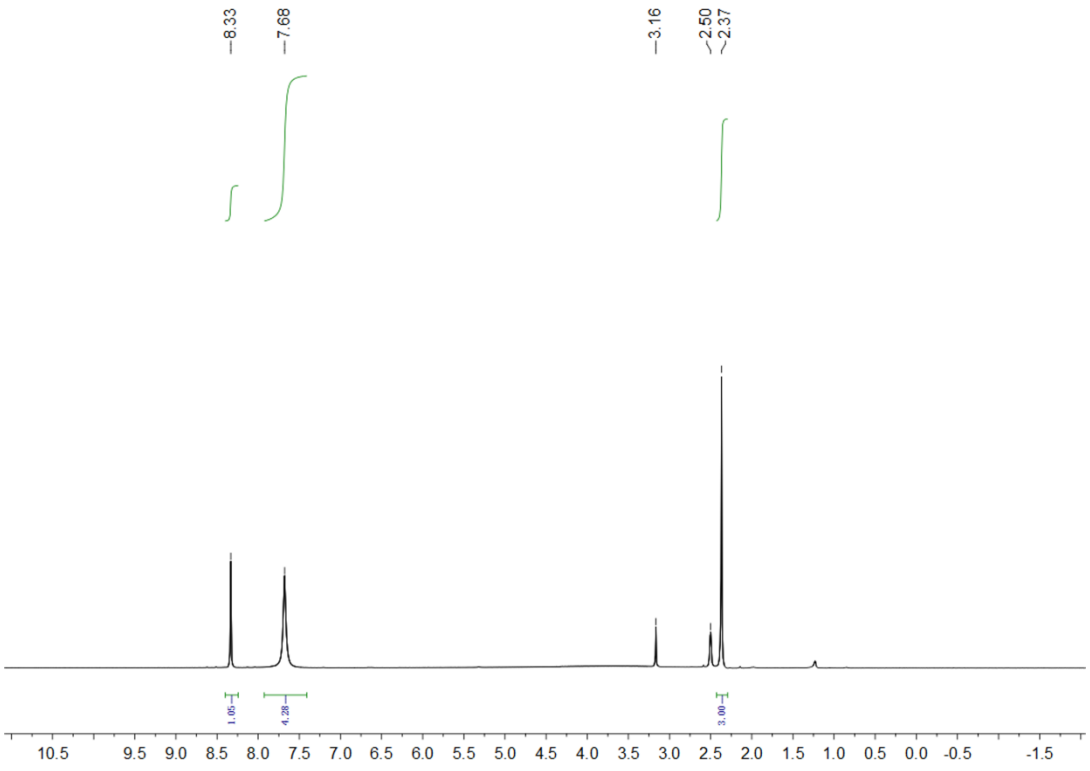


Figure S9 ^{1}H NMR spectra (300 MHz) of **3** in [D_6]DMSO at 25 ^{o}C

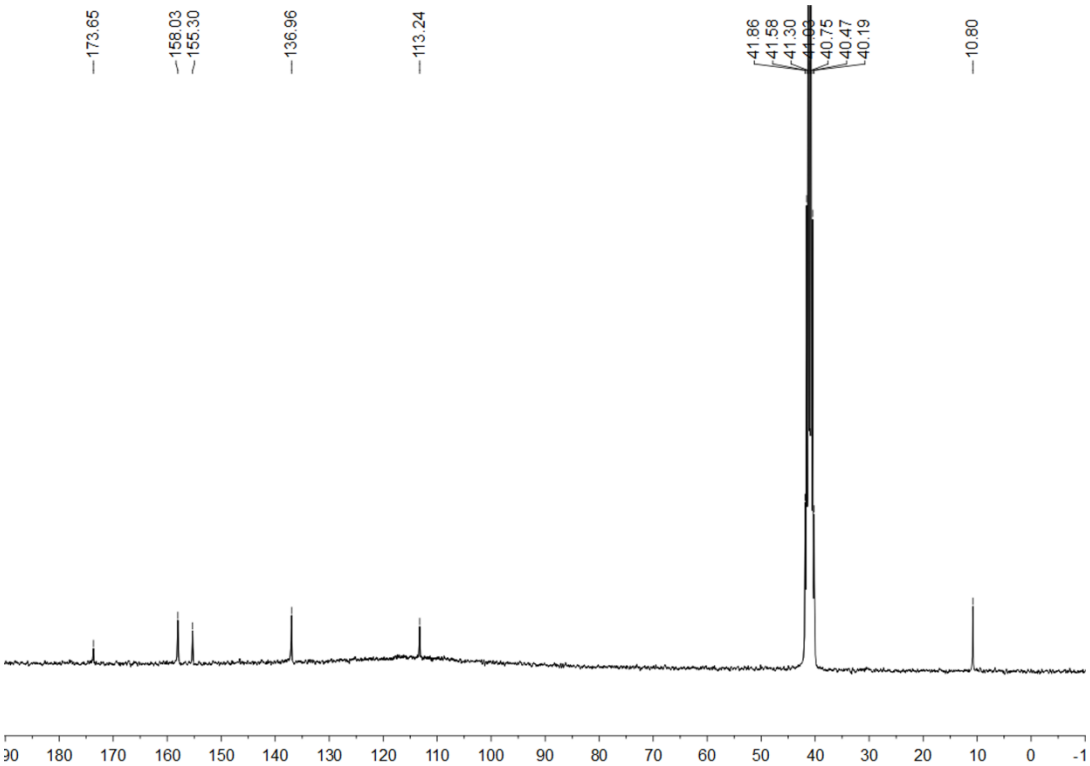


Figure S10 ^{13}C NMR specta (75 MHz) of **3** in [D_6]DMSO at 25 ^{o}C

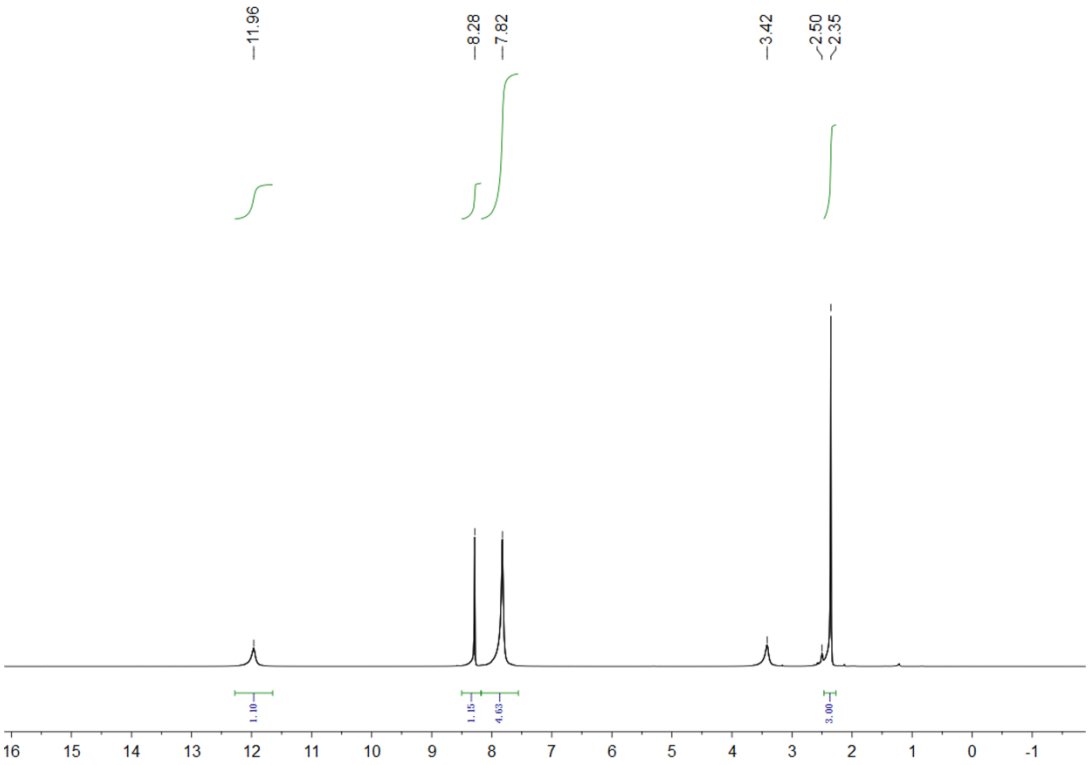


Figure S11 ^{1}H NMR spectra (300 MHz) of **4** in [D_6]DMSO at 25 ^{o}C

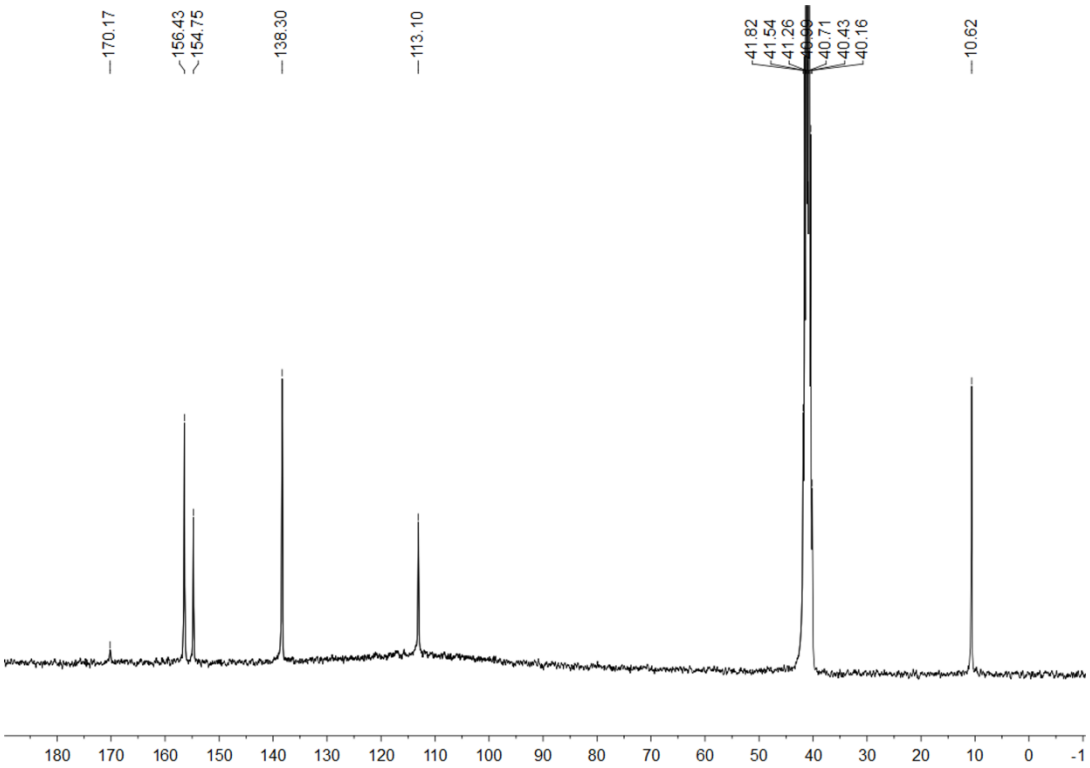


Figure S12 ^{13}C NMR specta (75 MHz) of **4** in [D_6]DMSO at 25 ^{o}C

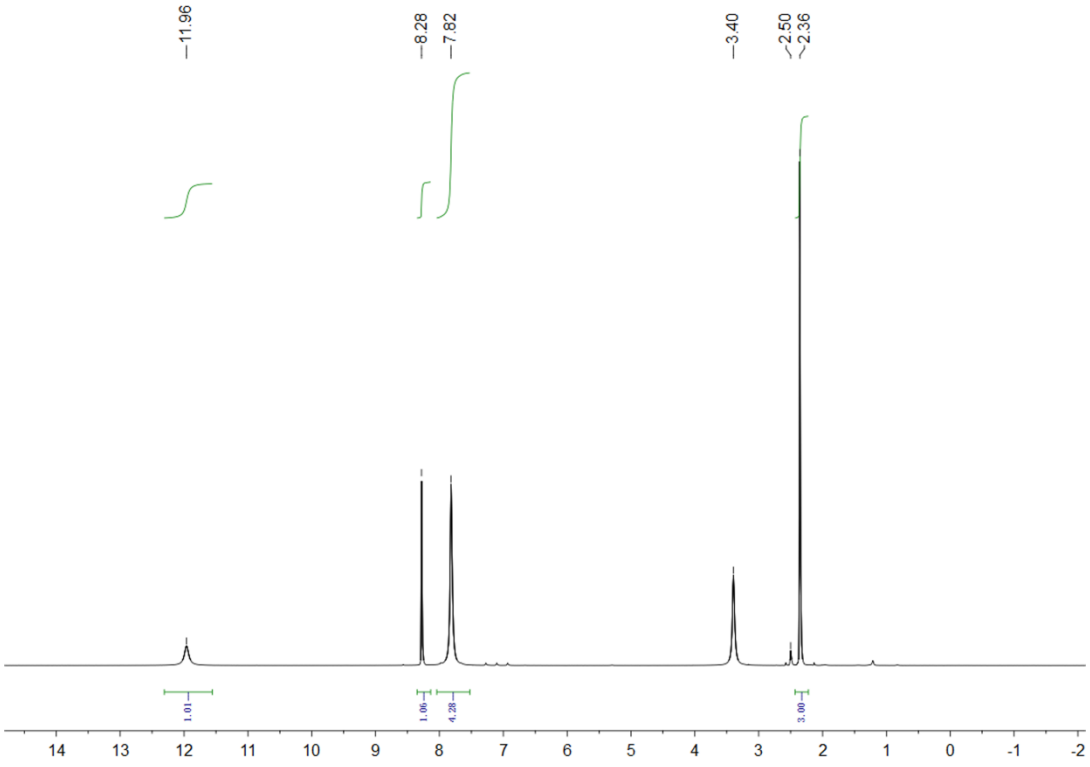


Figure S13 ^{1}H NMR spectra (300 MHz) of **5** in [D_6]DMSO at 25 ^{o}C

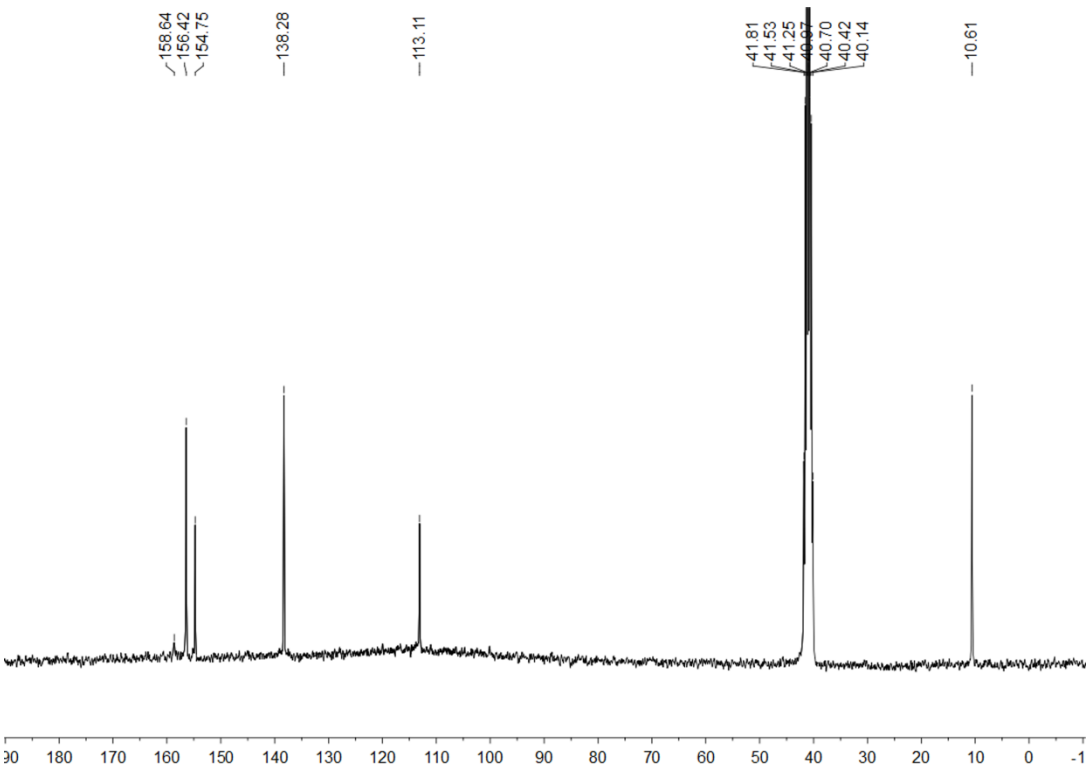


Figure S14 ^{13}C NMR specta (75 MHz) of **5** in [D_6]DMSO at 25 ^{o}C

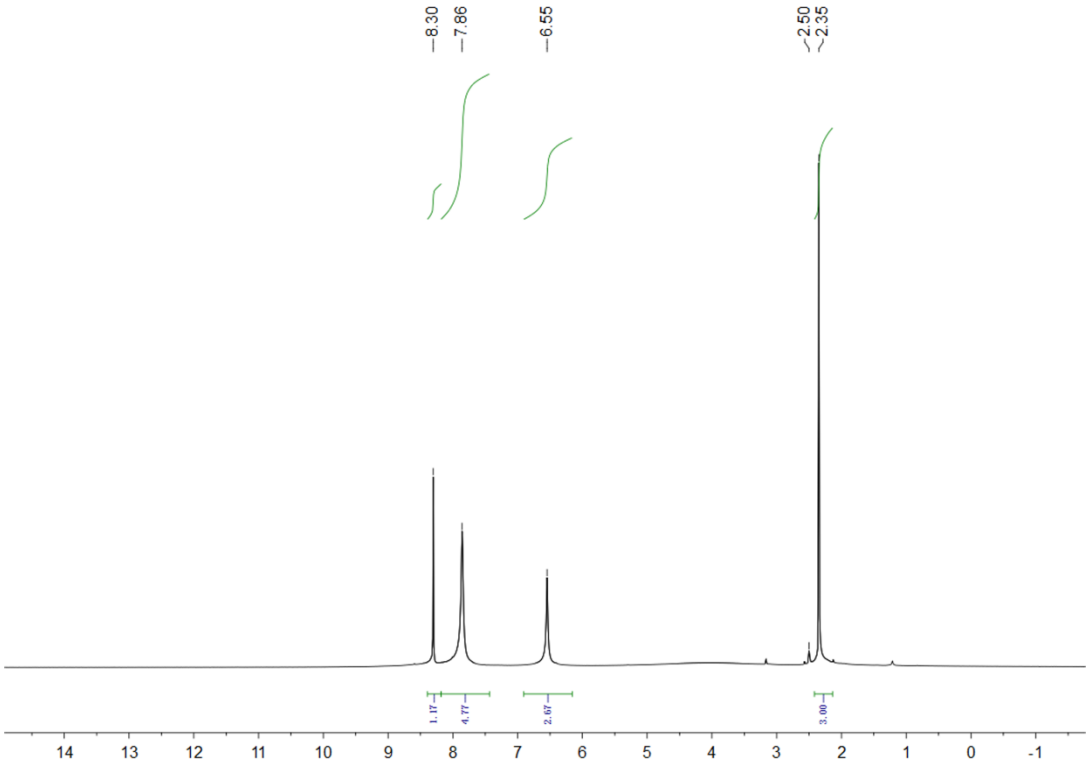


Figure S15 ^{1}H NMR spectra (300 MHz) of **6** in [D_6]DMSO at 25 ^{o}C

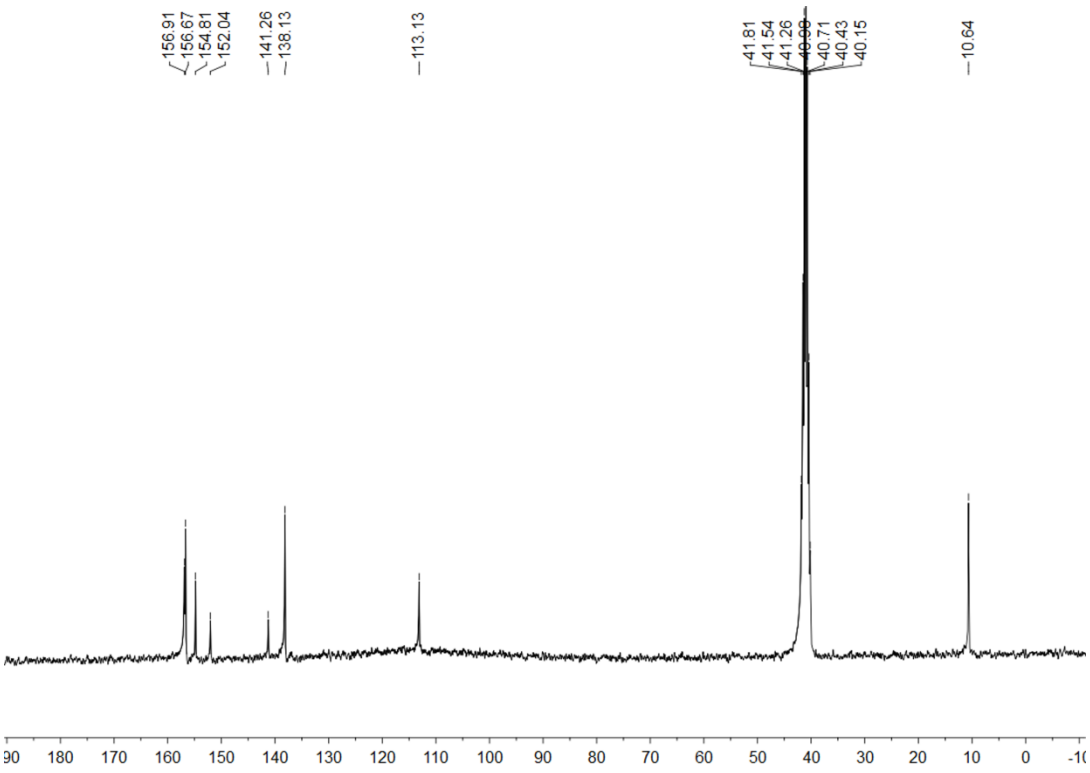


Figure S16 ^{13}C NMR specta (75 MHz) of **6** in [D_6]DMSO at 25 ^{o}C

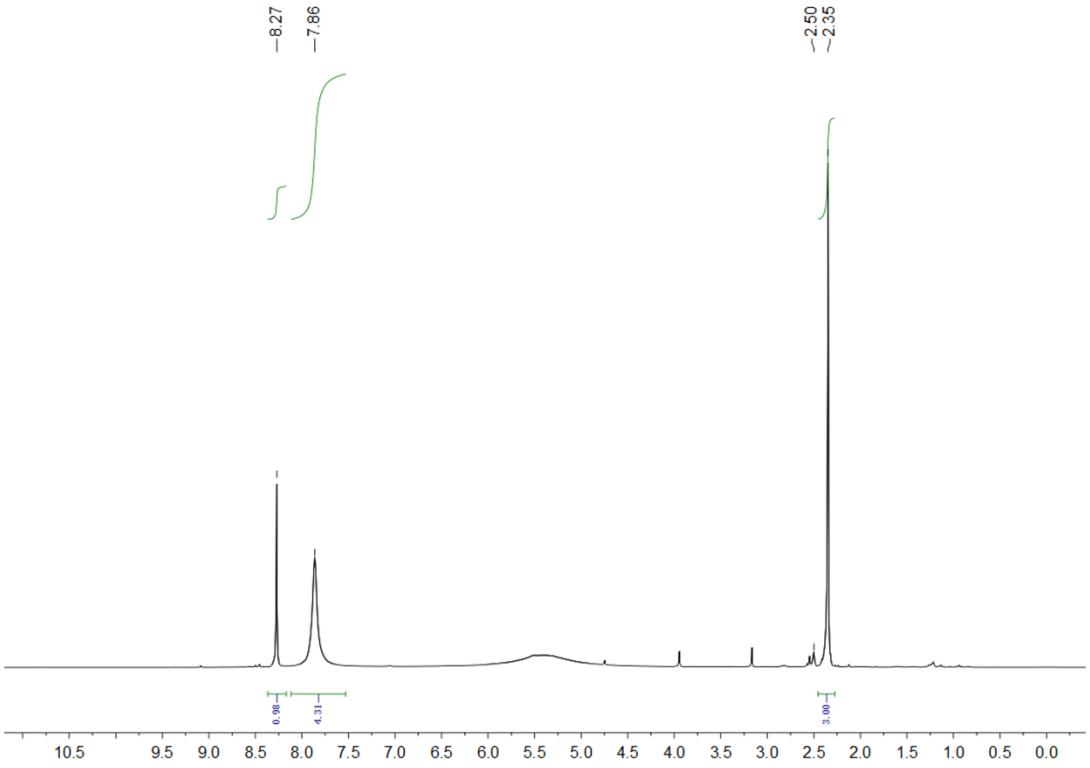


Figure S17 ^{1}H NMR spectra (300 MHz) of **7** in [D_6]DMSO at 25 ^{o}C

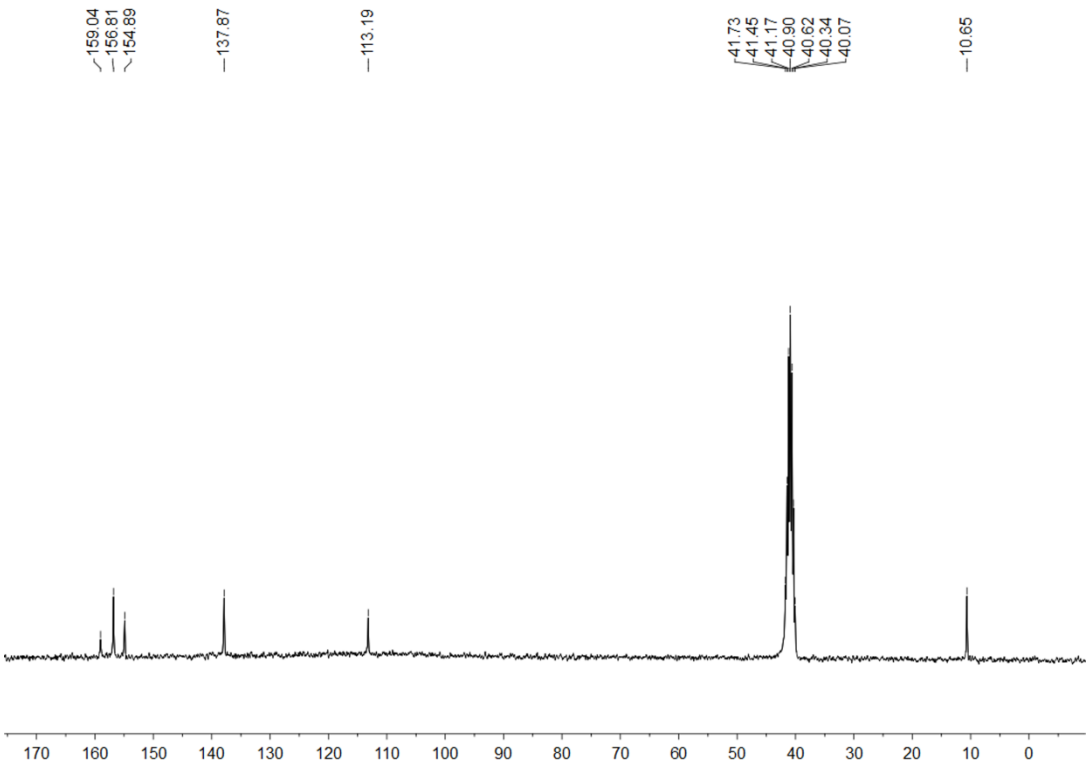


Figure S18 ^{13}C NMR specta (75 MHz) of **7** in [D_6]DMSO at 25 ^{o}C

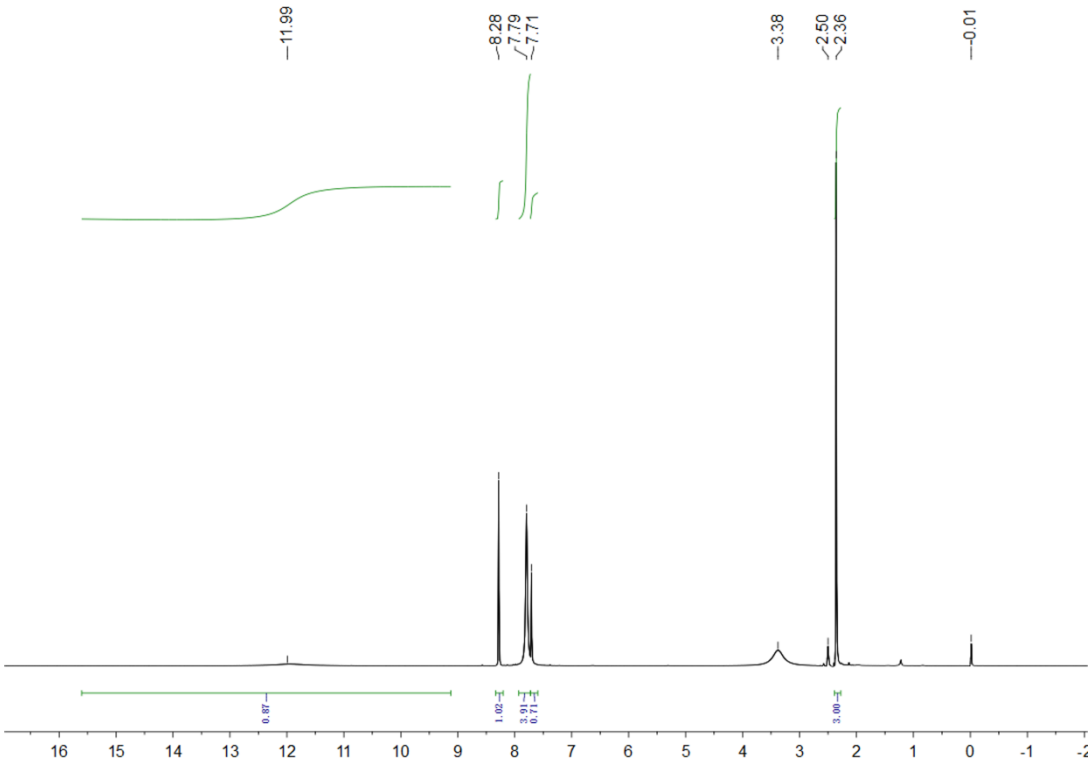


Figure S19 ^{1}H NMR spectra (300 MHz) of **8** in [D_6]DMSO at 25 ^{o}C

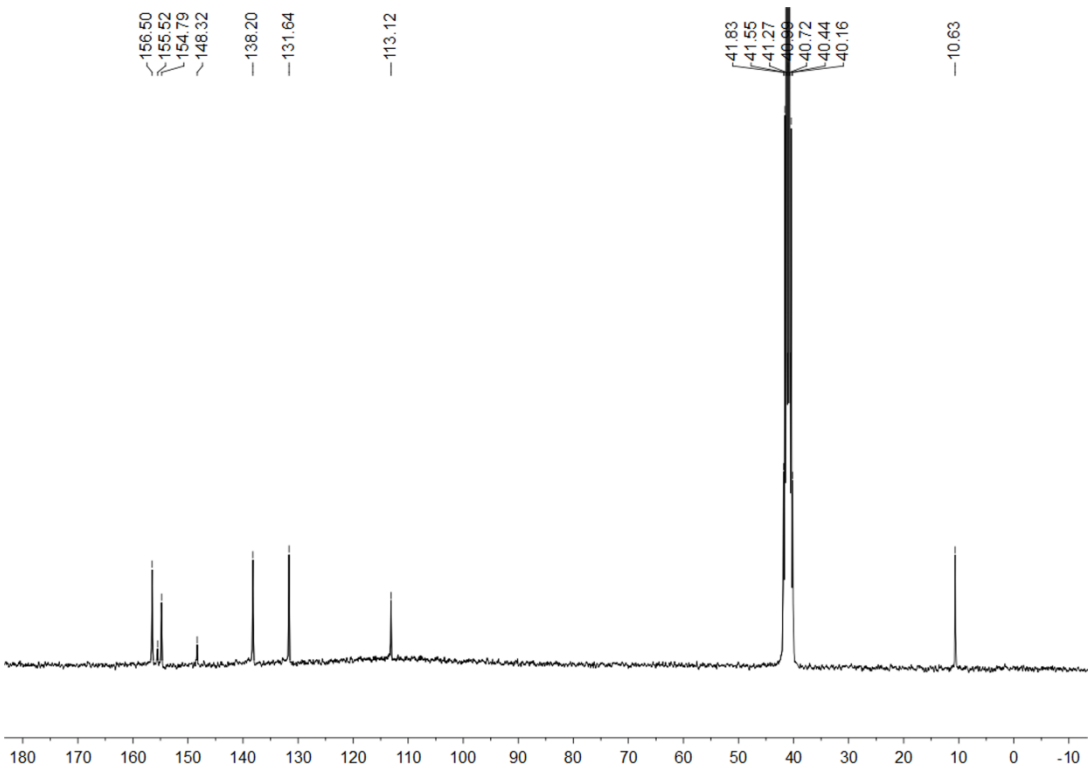


Figure S20 ^{13}C NMR specta (75 MHz) of **8** in [D_6]DMSO at 25 ^{o}C

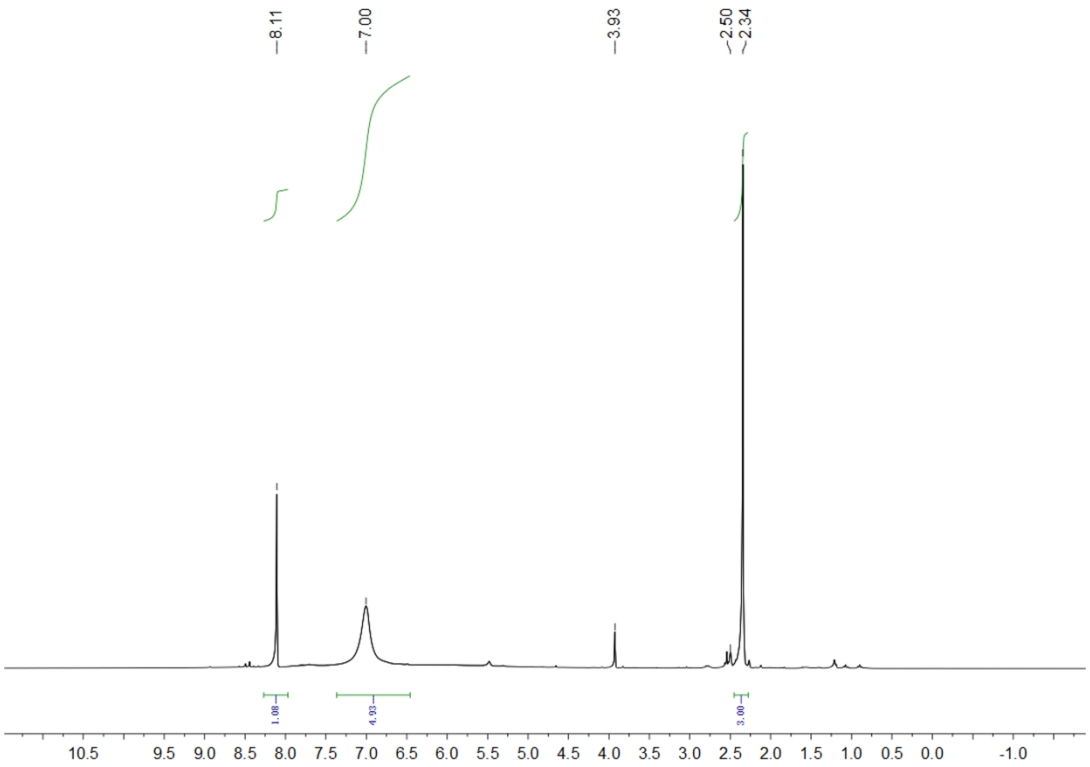


Figure S21 ^{1}H NMR spectra (300 MHz) of **9** in [D_6]DMSO at 25 ^{o}C

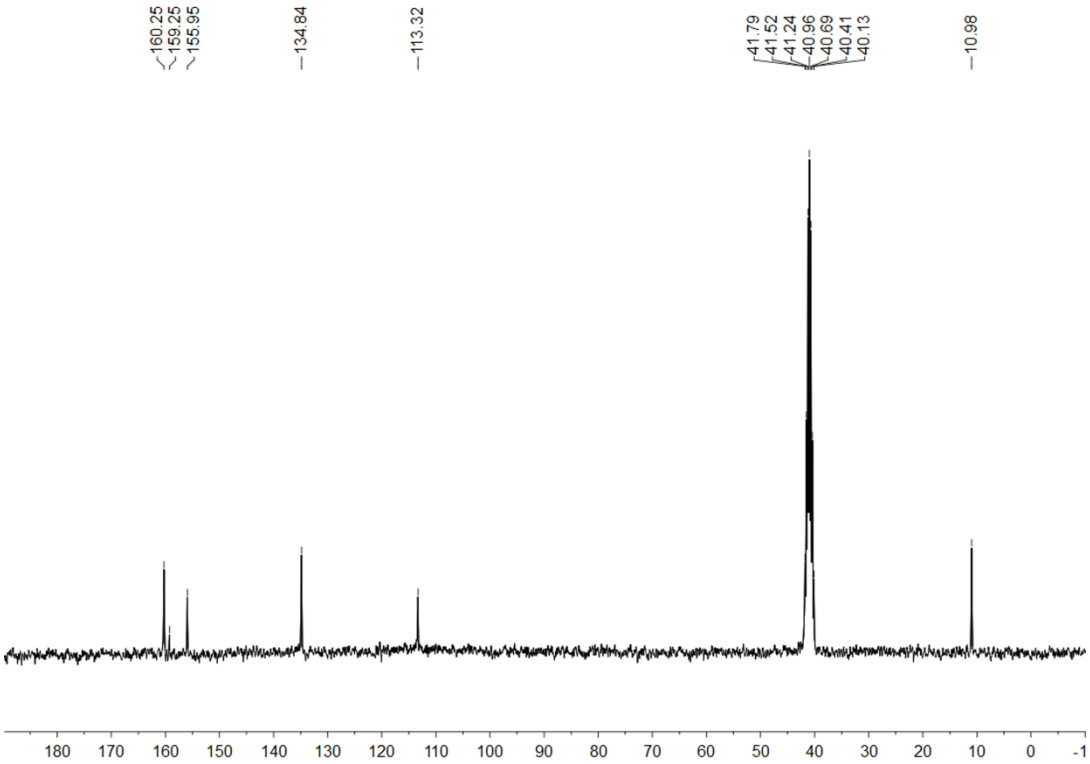


Figure S22^{13}C NMR specta (75 MHz) of **9** in [D_6]DMSO at 25 ^{o}C

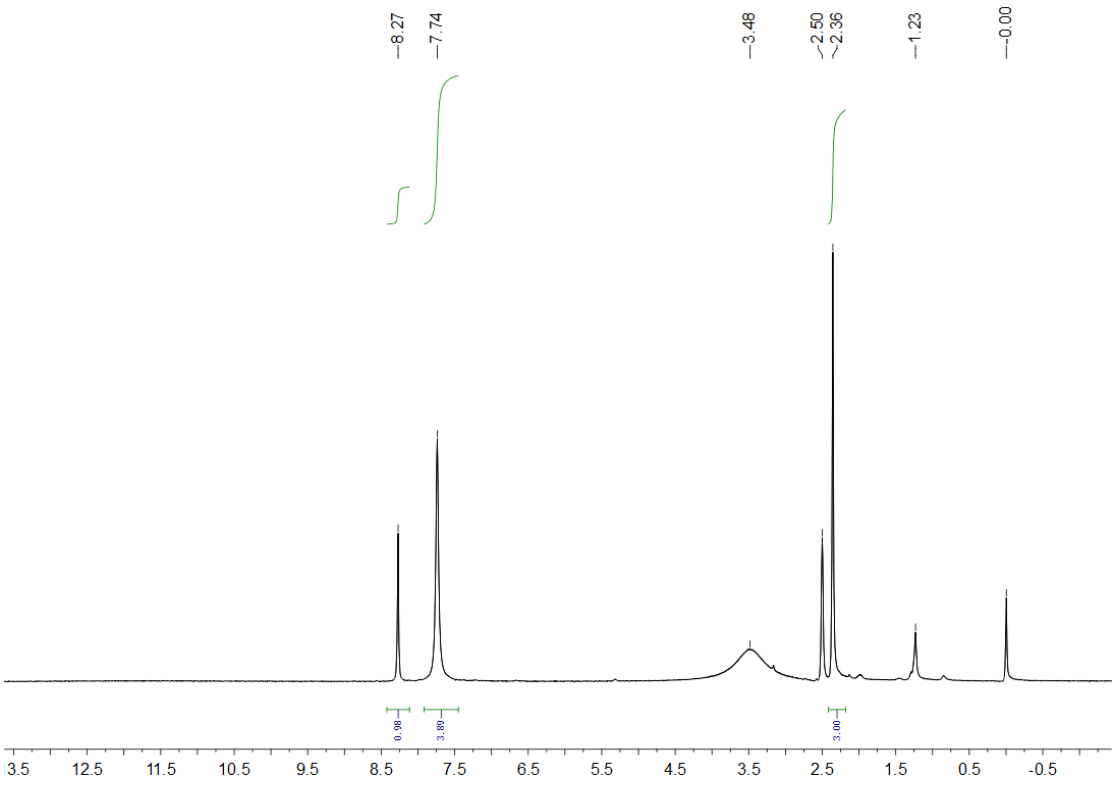


Figure S23 ^{1}H NMR spectra (300 MHz) of **10** in [D_6]DMSO at 25 ^{o}C

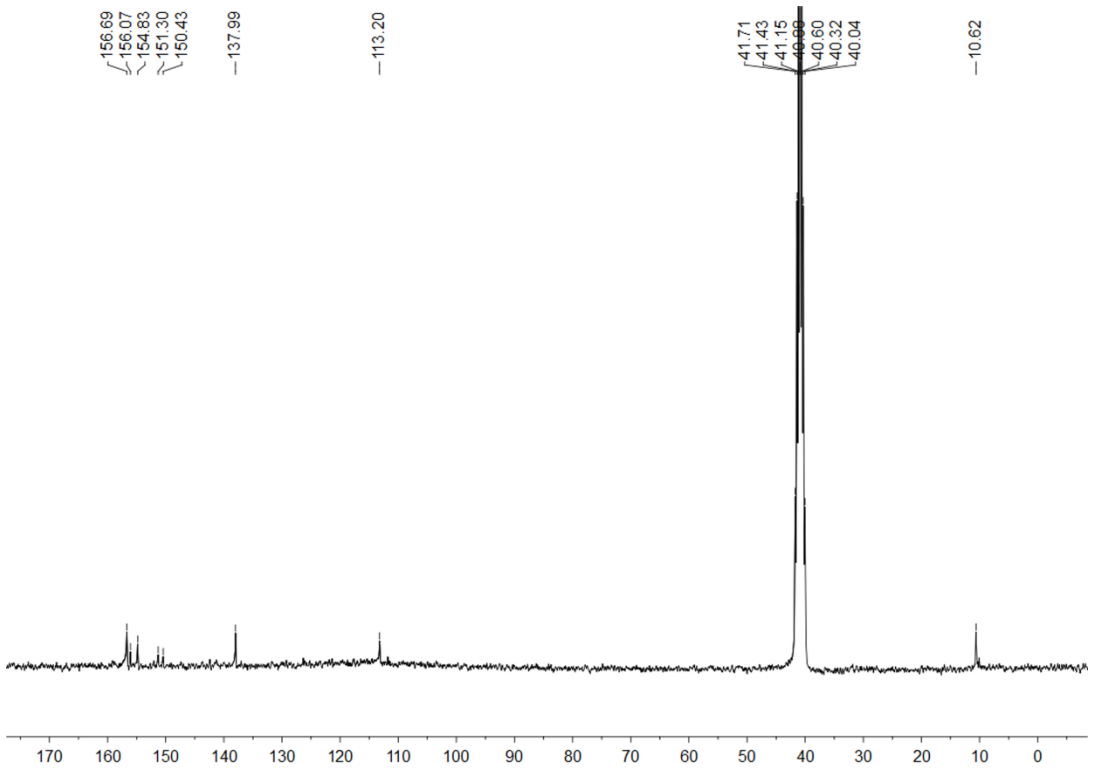


Figure S24 ^{13}C NMR specta (75 MHz) of **10** in [D_6]DMSO at 25 ^{o}C

5. DSC curves of compounds 3-10

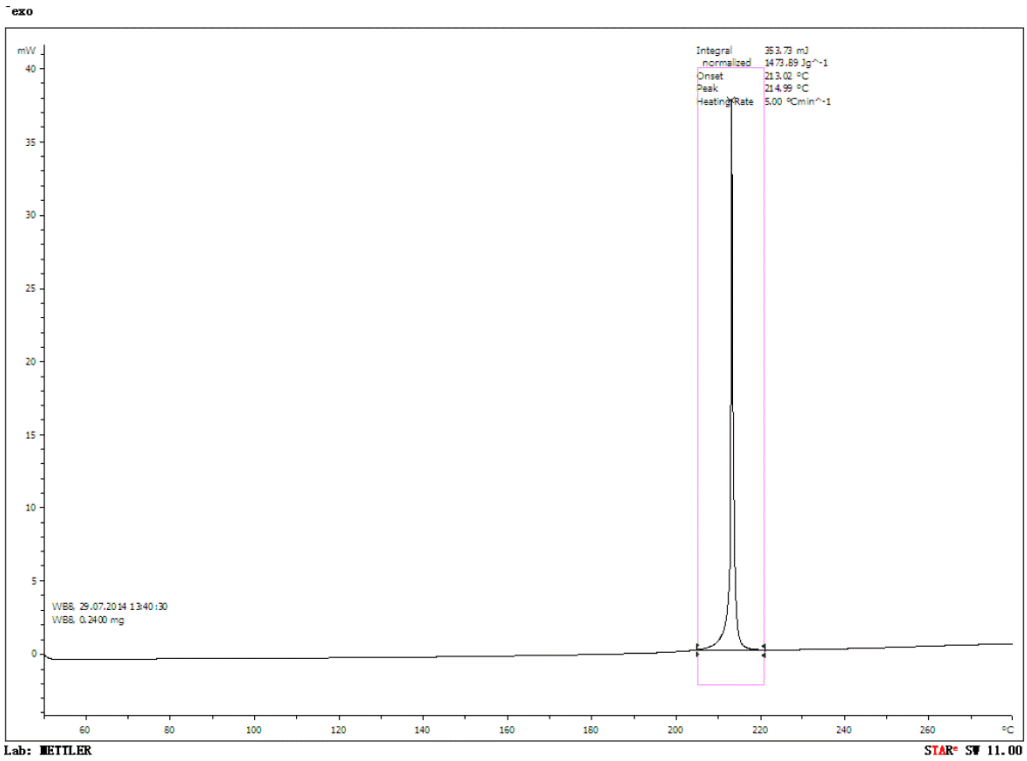


Figure S25 DSC curve of compound **3**

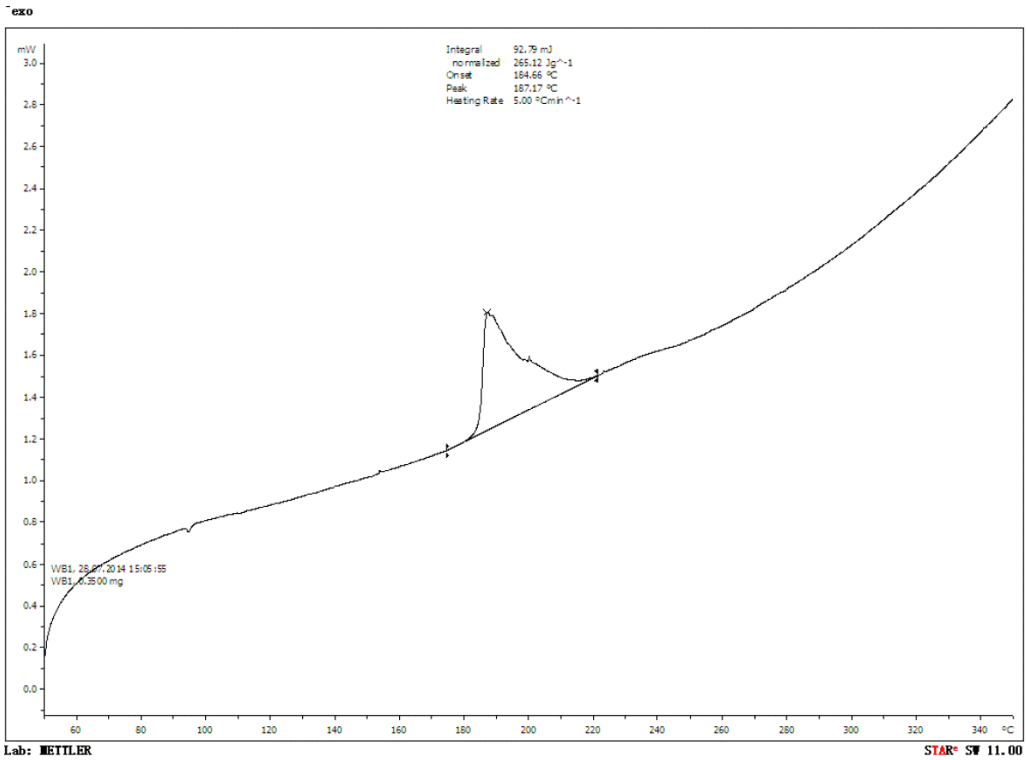


Figure S26 DSC curve of compound **4**

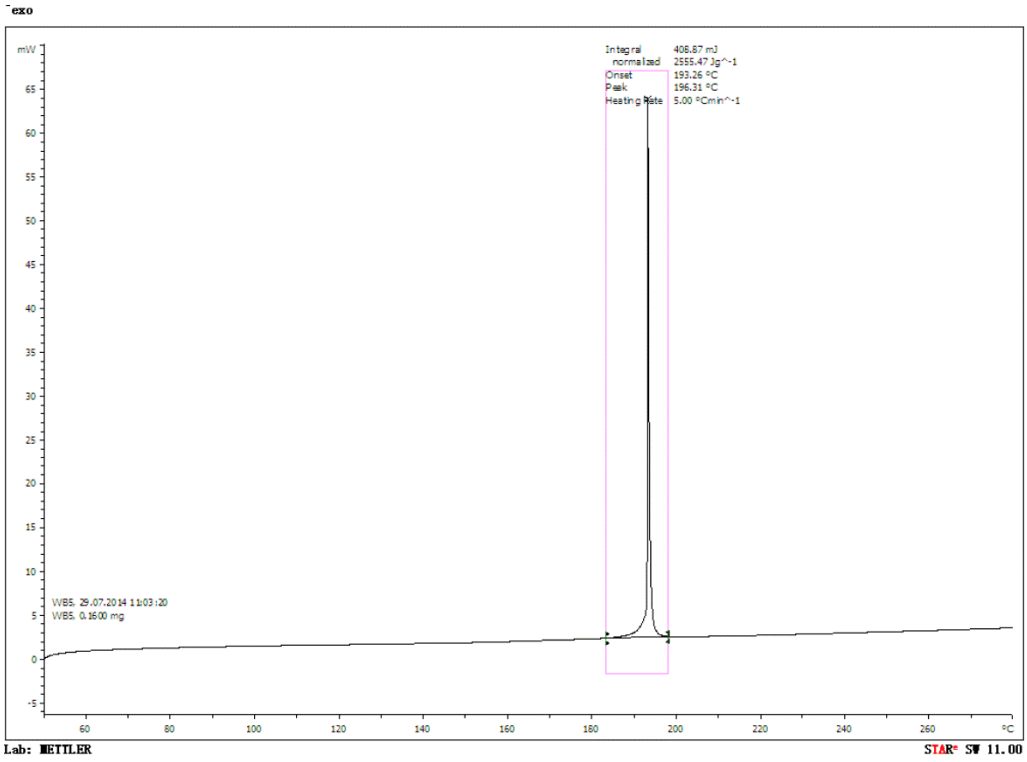


Figure S27 DSC curve of compound **5**

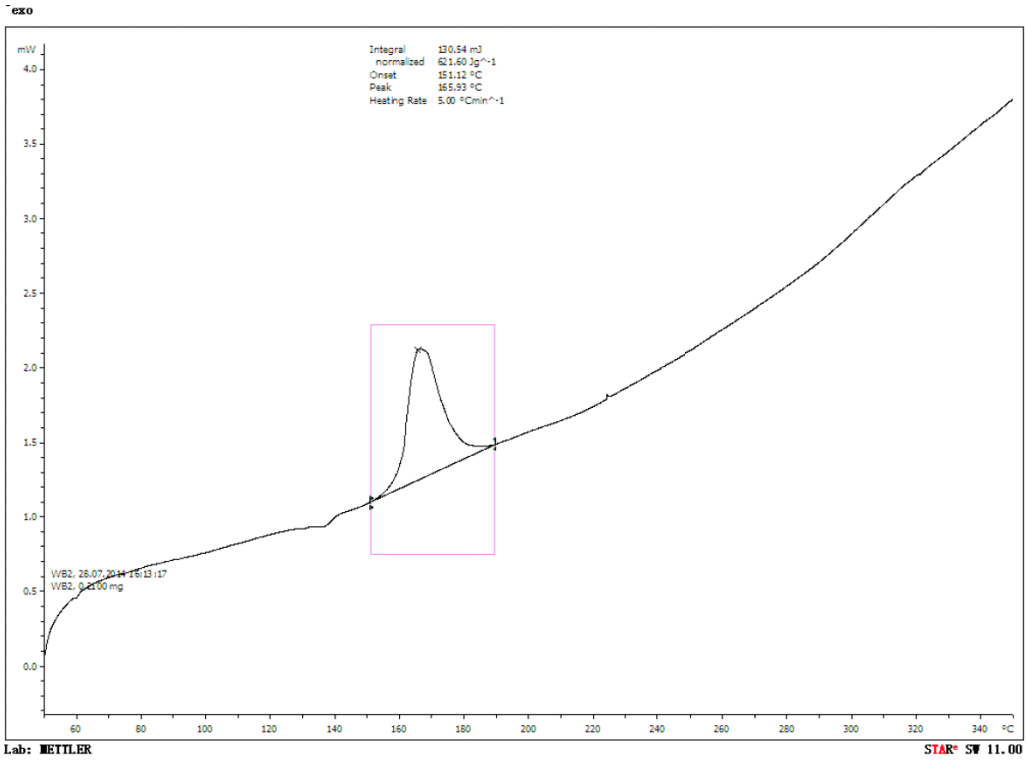


Figure S28 DSC curve of compound **6**

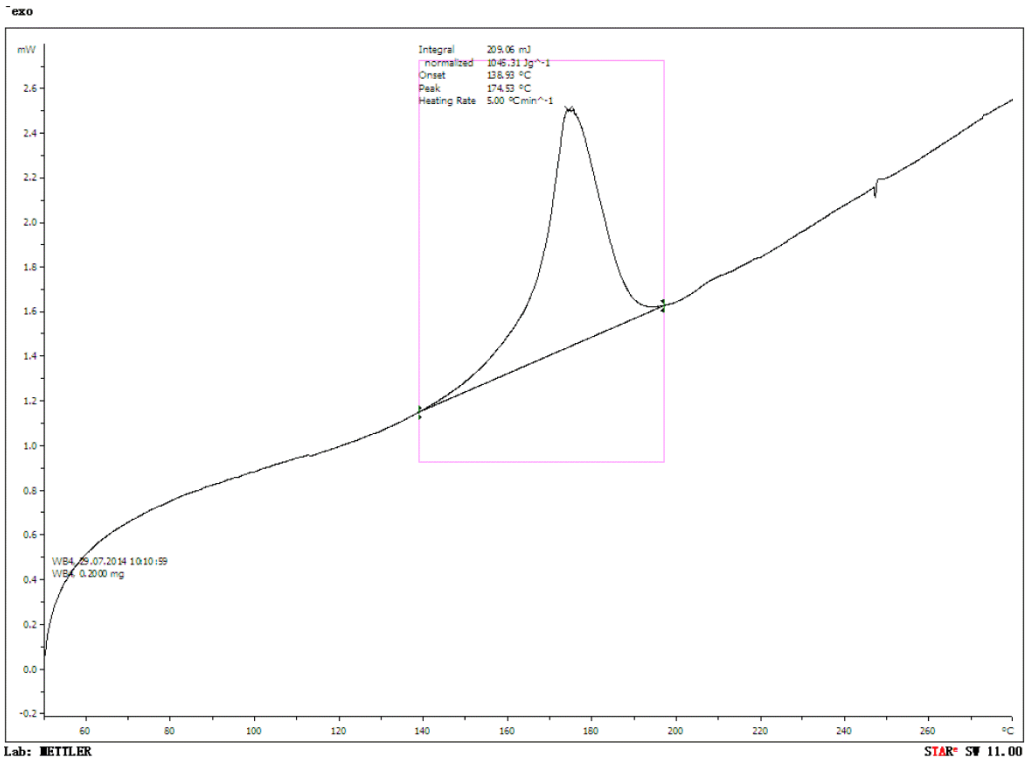


Figure S29 DSC curve of compound **7**

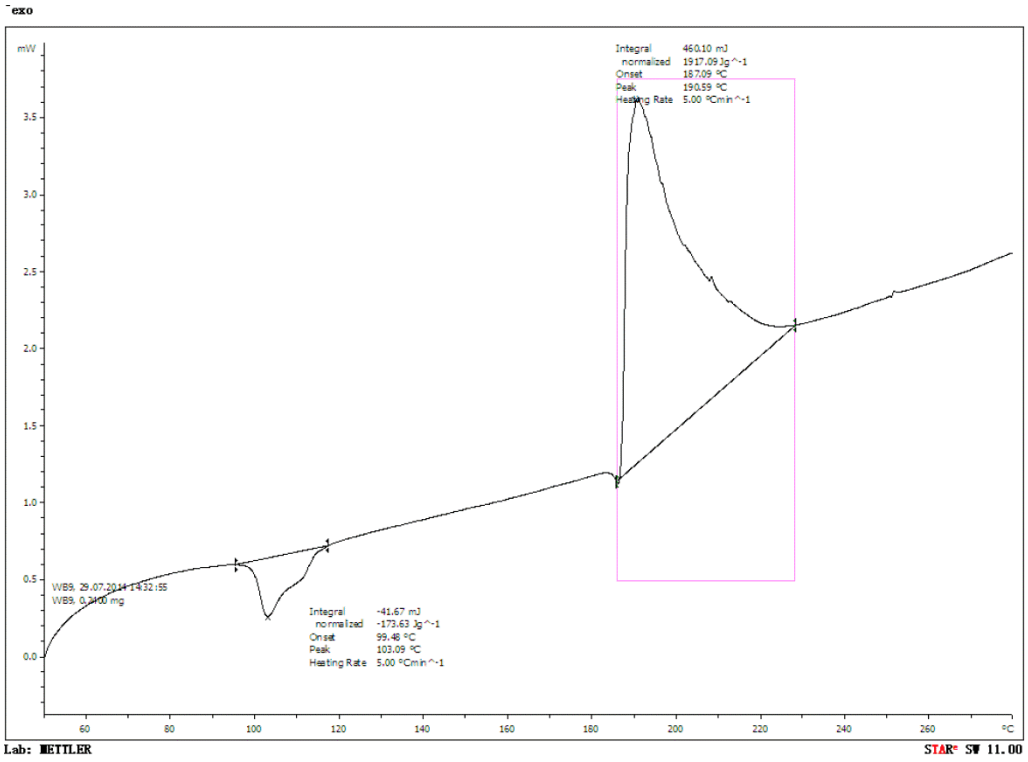


Figure S30 DSC curve of compound **8**

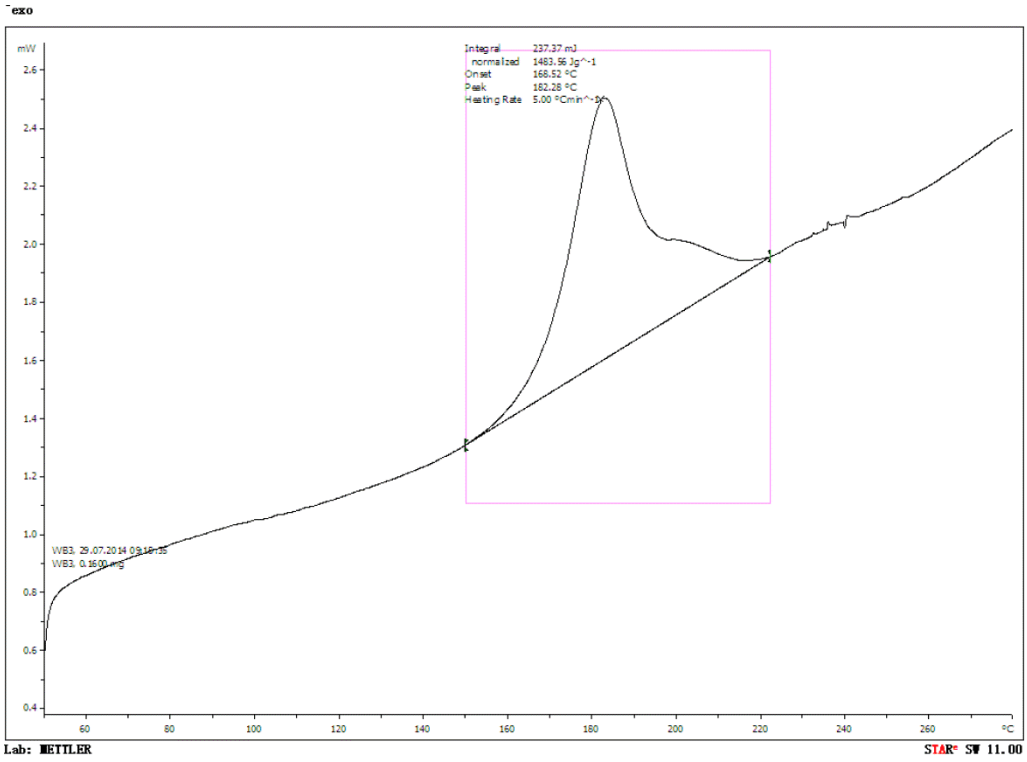


Figure S31 DSC curve of compound **9**

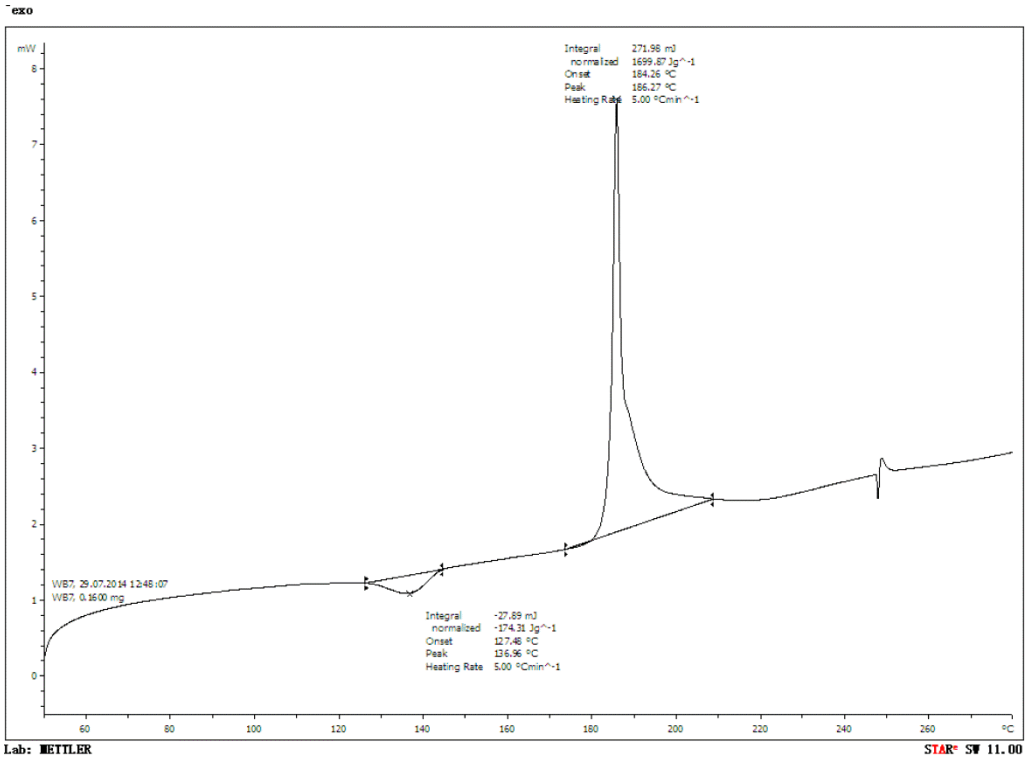


Figure S32 DSC curve of compound **10**