Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Exploration of Low-melting Energetic Compounds: Influence of Substituents on Melting Points

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Computational details

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs[S1]. The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP functional with the 6–311+G** basis set. The geometrical were optimized with no constraints imposed under default convergence criteria. Total energy (E_0) and zero-point energy (ZPE) were calculated with vibrational frequency analysis. The heats of formation were obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

Based on a Born-Haber energy cycle (Scheme S1), the heat of formation of a salt can be simplified by the formula given in Equation (1):

H_f (salt, 298 K) = H_f (cation, 298K) + H_f (anion, 298K) –H_L (1)

where "H_L" is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins [S2]et al. [Eq. (2)]

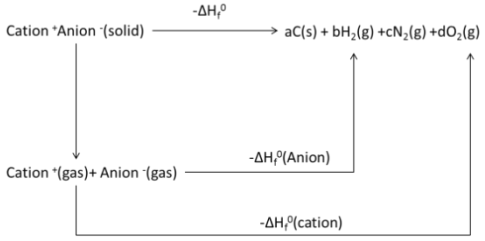
$H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)

Where n_M and n_X depend on the nature of the ions, M_q^+ and X_p^-, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

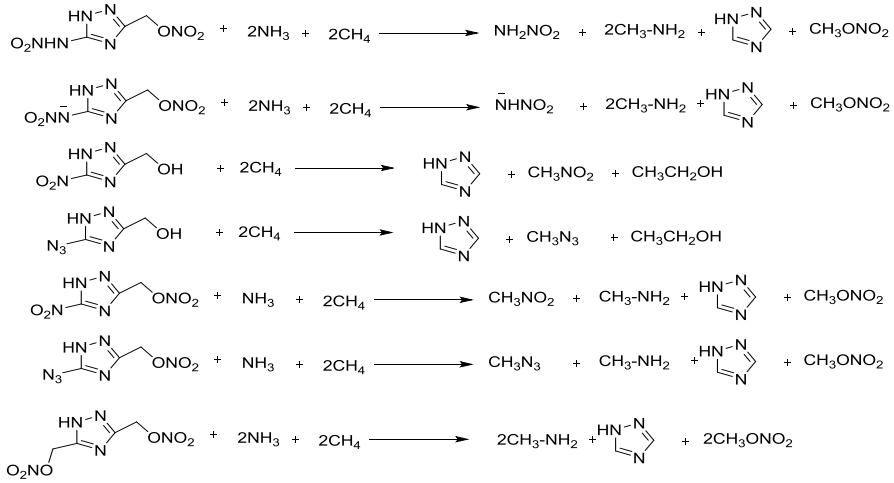
The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

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

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



Scheme S1. Born-Haber Cycle for the Formation of energetic salts



Scheme S2. Isodesmic reactions for calculating heats of formation for Triazole nitrate compounds.

Crystallographic data

Table S1 Crystallographic data for compound **2**·CH_3OH, **3**, **4** and **6**.

	2·CH_3OH	**3**	**4**	**6**
Formula	$C_3H_4N_6O_5$ CH_3OH	$C_3H_4N_4O_3$	$C_3H_3N_5O_5$	$C_3H_3N_7O_3$
F_W (g mol^{-1})	236.16	144.10	189.10	185.12
Temperature (K)	150	150	152	150
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	P 21/n	P 21/n	P 21 21 21	P -1
Z	4	4	4	2
a(Å)	8.598(2)	8.6101(8)	6.4603(8)	5.1255(5)
b(Å)	7.585(2)	6.4020(7)	10.1472(9)	7.7153(7)
c(Å)	14.530(4)	10.0437(9)	10.7225(12)	9.3101(9)
α(°)	90	90	90	99.722(5)
β(°)	95.064(8)	93.826(4)	90	96.581(5)
γ(°)	90	90	90	103.924(5)
V($Å^3$)	943.9(4)	552.39(9)	702.90(13)	347.55(6)
D_c (g cm^{-3})	1.662	1.733	1.787	1.769
μ(mm^{-1})	0.154	0.154	0.169	0.156
F(000)	488	296	384	188
Crystal size (mm^3)	0.2×0.15×0.1	0.2×0.15×0.1	0.2×0.15×0.1	0.25×0.2×0.1
Index ranges	-10＜h＜10 -9＜k＜9 -17＜l＜17	-10＜h＜11 -8＜k＜8 -12＜l＜13	-8＜h＜8 -12＜k＜10 -13＜l＜13	-6＜h＜6 --9＜k＜9 -11＜l＜11
θ(°)	2.654-25.343	3.018-27.866	2.764-26.384	2.249-26.421
Refl. Coll.	10151	6154	8659	8147
Independ. refl. [Rint]	1691	1312	1437	1435
R_1, wR_2 [I ＞2σ(I)]	0.0639, 0.1162	0.0370, 0.0898	0.0371, 0.0827	0.0374, 0.0827
R_1, wR_2 (all)	0.1059, 0.1358	0.0529, 0.0986	0.0467, 0.0871	0.0575,0.0911
CCDC	1983597	1983595	1983593	1978183

Crystal datas of the compounds **2**, **3**, **4** and **6**.

Table S2 - Bond Distances of crystal **2**

O1	-N1	1.207(4)	N4	-C3	1.342(5)
O2	-N1	1.202(4)	N5	-C3	1.358(5)
O3	-N1	1.412(4)	N5	-N6	1.337(4)
O3	-C1	1.450(4)	N2	-H2	0.8800
O4	-N6	1.242(4)	N4	-H4	0.8800
O5	-N6	1.258(4)	C1	-C2	1.487(5)
O6	-C4	1.421(5)	C1	-H1B	0.9900
O6	-H6	0.8400	C1	-H1A	0.9900
N2	-C3	1.348(4)	C4	-H4A	0.9800
N2	-C2	1.369(5)	C4	-H4B	0.9800
N3	-N4	1.384(4)	C4	-H4C	0.9800
N3	-C2	1.306(5)			

Table S3 - Bond Angles of crystal **2**

N1	-O3	-C1	112.1(2)	N2	-C2	-C1	123.4(3)
C4	-O6	-H6	109.00	N3	-C2	-C1	125.5(3)
O1	-N1	-O2	129.5(3)	N2	-C2	-N3	111.2(3)
O2	-N1	-O3	118.3(3)	N2	-C3	-N5	118.2(3)
O1	-N1	-O3	112.3(3)	N4	-C3	-N5	135.6(3)
C2	-N2	-C3	107.3(3)	N2	-C3	-N4	106.2(3)

N4	-N3	-C2	104.6(3)	O3	-C1	-H1A	111.00
N3	-N4	-C3	110.7(3)	O3	-C1	-H1B	111.00
N6	-N5	-C3	117.1(3)	C2	-C1	-H1B	111.00
O4	-N6	-O5	122.7(3)	H1A	-C1	-H1B	109.00
O5	-N6	-N5	114.3(3)	C2	-C1	-H1A	111.00
O4	-N6	-N5	122.9(3)	O6	-C4	-H4A	109.00
C2	-N2	-H2	126.00	O6	-C4	-H4B	109.00
C3	-N2	-H2	126.00	O6	-C4	-H4C	110.00
C3	-N4	-H4	125.00	H4A	-C4	-H4B	109.00
N3	-N4	-H4	125.00	H4A	-C4	-H4C	109.00
O3	-C1	-C2	105.3(3)	H4B	-C4	-H4C	109.00

Table S4 - Torsion Angles of crystal **2**

C1	-O3	-N1	-O1	175.4(3)
C1	-O3	-N1	-O2	-5.5(4)
N1	-O3	-C1	-C2	-163.3(3)
C3	-N2	-C2	-N3	0.2(4)
C3	-N2	-C2	-C1	179.4(3)
C2	-N2	-C3	-N4	-0.7(4)
C2	-N2	-C3	-N5	177.8(3)
C2	-N3	-N4	-C3	-0.8(4)
N4	-N3	-C2	-N2	0.4(4)
N4	-N3	-C2	-C1	-178.8(3)
N3	-N4	-C3	-N2	1.0(4)
N3	-N4	-C3	-N5	-177.2(4)
C3	-N5	-N6	-O4	-1.0(5)
C3	-N5	-N6	-O5	179.4(3)
N6	-N5	-C3	-N2	168.1(3)
N6	-N5	-C3	-N4	-13.9(6)
O3	-C1	-C2	-N2	76.5(4)
O3	-C1	-C2	-N3	-104.4(4)

Table S5 - Hydrogen Bonds of crystal **2**

	D--H	H ⋯A	D—H..A	Angles(°)
N2--H2..O5	0.8800	2.5300	3.285(4)	144.00
N2--H2..N5	0.8800	1.9900	2.829(4)	160.00
N4--H4..O4	0.8800	2.2500	2.685(4)	110.00
N4--H4..O6	0.8800	1.8400	2.686(4)	161.00
O6--H6..O4	0.8400	2.5600	2.832(3)	101.00
O6--H6..O5	0.8400	1.9300	2.769(4)	174.00
C1--H1A..O4	0.9900	2.5600	3.068(4)	112.00

Table S6 - Bond Distances of crystal **3**

O001	-C00A	1.4214(17)	N005	-C009	1.3132(19)
O002	-N006	1.2244(17)	N006	-C009	1.4533(18)
O003	-N006	1.2238(17)	N007	-C008	1.3366(18)
O001	-H001	0.8400	N007	-H007	0.8800
N004	-C009	1.3460(18)	C008	-C00A	1.495(2)
N004	-C008	1.3352(18)	C00A	-H00A	0.9900
N005	-N007	1.3510(17)	C00A	-H00B	0.9900

Table S7 - Bond Angles of crystal **3**

C00A	-O001	-H001	109.00	N004	-C008	-C00A	126.86(13)
C008	-N004	-C009	101.48(12)	N004	-C009	-N005	117.35(13)
N007	-N005	-C009	100.44(12)	N004	-C009	-N006	122.34(12)
O002	-N006	-O003	125.39(12)	N005	-C009	-N006	120.29(12)
O003	-N006	-C009	117.57(12)	O001	-C00A	-C008	110.53(11)
O002	-N006	-C009	117.04(12)	O001	-C00A	-H00A	110.00
N005	-N007	-C008	111.35(12)	O001	-C00A	-H00B	110.00
N005	-N007	-H007	124.00	C008	-C00A	-H00A	110.00
C008	-N007	-H007	124.00	C008	-C00A	-H00B	110.00
N007	-C008	-C00A	123.70(13)	H00A	-C00A	-H00B	108.00
N004	-C008	-N007	109.38(12)				

Table S8 - Torsion Angles of crystal **3**

C009	-N004	-C008	-N007	-0.61(15)
C009	-N004	-C008	-C00A	176.76(13)
C008	-N004	-C009	-N005	0.36(16)
C008	-N004	-C009	-N006	178.76(12)
C009	-N005	-N007	-C008	-0.44(15)
N007	-N005	-C009	-N004	0.03(16)
N007	-N005	-C009	-N006	-178.40(12)
O002	-N006	-C009	-N004	-7.72(19)
O002	-N006	-C009	-N005	170.63(13)
O003	-N006	-C009	-N004	172.18(13)
O003	-N006	-C009	-N005	-9.47(19)
N005	-N007	-C008	-N004	0.70(16)
N005	-N007	-C008	-C00A	-176.77(12)
N004	-C008	-C00A	-O001	-91.19(17)
N007	-C008	-C00A	-O001	85.83(16)

Table S9 - Hydrogen Bonds of crystal **3**

	D--H	H…A	D—H…A	Angles(°)
O001-- H001.. N004	0.8400	1.9700	2.8018(16)	172.00
N007-- H007.. O001	0.8800	1.8400	2.7104(16)	170.00

Table S10 - Bond Distances of crystal **4**

O001	-N00A	1.404(4)	N004	-N005	1.347(3)
O001	-C00D	1.437(4)	N004	-C00C	1.344(3)
O002	-N006	1.220(3)	N005	-C00B	1.306(3)
O007	-N006	1.217(3)	N006	-C00B	1.443(3)
O008	-N00A	1.201(4)	N004	-H004	0.88(3)
O009	-N00A	1.204(4)	C00C	-C00D	1.490(4)
N003	-C00B	1.345(3)	C00D	-H00A	0.9900
N003	-C00C	1.326(3)	C00D	-H00B	0.9900

Table S11 - Bond Angles of crystal **4**

N00A	-O001	-C00D	113.1(2)	N005	-C00B	-N006	120.7(2)
C00B	-N003	-C00C	101.11(18)	N003	-C00B	-N005	117.7(2)
N005	-N004	-C00C	110.62(19)	N003	-C00B	-N006	121.56(19)
N004	-N005	-C00B	100.71(19)	N003	-C00C	-N004	109.8(2)
O002	-N006	-O007	124.8(2)	N003	-C00C	-C00D	125.5(2)
O002	-N006	-C00B	117.5(2)	N004	-C00C	-C00D	124.6(2)
O007	-N006	-C00B	117.7(2)	O001	-C00D	-C00C	111.0(2)
O001	-N00A	-O008	112.3(3)	O001	-C00D	-H00A	109.00
O001	-N00A	-O009	117.9(3)	O001	-C00D	-H00B	109.00
O008	-N00A	-O009	129.8(3)	C00C	-C00D	-H00A	109.00
N005	-N004	-H004	117(2)	C00C	-C00D	-H00B	109.00
C00C	-N004	-H004	132(2)	H00A	-C00D	-H00B	108.00

Table S12 - Torsion Angles of crystal **4**

C00D	-O001	-N00A	-O008	-179.7(3)
C00D	-O001	-N00A	-O009	-0.4(4)
N00A	-O001	-C00D	-C00C	67.1(3)
C00C	-N003	-C00B	-N005	-1.2(3)
C00C	-N003	-C00B	-N006	178.3(2)
C00B	-N003	-C00C	-N004	1.0(3)
C00B	-N003	-C00C	-C00D	-176.9(3)
C00C	-N004	-N005	-C00B	-0.2(3)
N005	-N004	-C00C	-N003	-0.6(3)
N005	-N004	-C00C	-C00D	177.3(2)
N004	-N005	-C00B	-N003	0.9(3)
N004	-N005	-C00B	-N006	-178.6(2)
O002	-N006	-C00B	-N003	4.7(4)
O002	-N006	-C00B	-N005	-175.8(3)
O007	-N006	-C00B	-N003	-174.8(2)
O007	-N006	-C00B	-N005	4.7(4)
N003	-C00C	-C00D	-O001	33.7(4)
N004	-C00C	-C00D	-O001	-143.9(2)

Table S13 - Hydrogen Bonds of crystal **4**

	D--H	H…A	D--H..A	Angles(°)
N004 -- H004 .. N003	0.88(3)	2.14(3)	2.983(3)	161(2)
C00D -- H00A .. O002	0.9900	2.2900	3.041(4)	132.00
C00D-- H00B.. O008	0.9900	2.5000	3.283(4)	136.00

Table S14 - Bond Distances of crystal **6**

O001	-N007	1.3932(19)	N006	-C00C	1.317(2)
O001	-C00D	1.455(2)	N008	-N009	1.257(2)
O002	-N007	1.206(2)	N008	-C00B	1.392(2)
O003	-N007	1.205(2)	N009	-N00A	1.116(2)
N004	-C00B	1.323(2)	N005	-H005	0.8800
N004	-C00C	1.373(2)	C00C	-C00D	1.487(2)
N005	-N006	1.360(2)	C00D	-H00A	0.9900
N005	-C00B	1.333(2)	C00D	-H00B	0.9900

Table S15 - Bond Angles of crystal **6**

N007	-O001	-C00D	112.66(12)	N004	-C00B	-N005	111.19(15)
C00B	-N004	-C00C	101.86(14)	N004	-C00B	-N008	129.31(15)
N006	-N005	-C00B	109.54(15)	N004	-C00C	-N006	114.82(15)
N005	-N006	-C00C	102.59(14)	N004	-C00C	-C00D	123.72(14)
O001	-N007	-O002	118.85(15)	N006	-C00C	-C00D	121.41(15)
O001	-N007	-O003	112.54(14)	O001	-C00D	-C00C	105.68(12)
O002	-N007	-O003	128.61(16)	O001	-C00D	-H00A	111.00
N009	-N008	-C00B	113.65(15)	O001	-C00D	-H00B	111.00
N008	-N009	-N00A	171.28(18)	C00C	-C00D	-H00A	111.00
N006	-N005	-H005	125.00	C00C	-C00D	-H00B	111.00
C00B	-N005	-H005	125.00	H00A	-C00D	-H00B	109.00
N005	-C00B	-N008	119.46(15)				

Table S16 - Torsion Angles of crystal **6**

C00D	-O001	-N007	-O002	-6.6(2)
C00D	-O001	-N007	-O003	173.99(14)
N007	-O001	-C00D	-C00C	-164.00(12)
C00C	-N004	-C00B	-N005	0.14(18)
C00C	-N004	-C00B	-N008	-177.34(16)
C00B	-N004	-C00C	-N006	-0.08(19)
C00B	-N004	-C00C	-C00D	177.28(15)
C00B	-N005	-N006	-C00C	0.09(18)
N006	-N005	-C00B	-N004	-0.16(19)
N006	-N005	-C00B	-N008	177.61(14)
N005	-N006	-C00C	-N004	0.00(19)
N005	-N006	-C00C	-C00D	-177.44(14)

N009	-N008	-C00B	-N004	4.2(3)
N009	-N008	-C00B	-N005	-173.08(15)
N004	-C00C	-C00D	-O001	79.57(18)
N006	-C00C	-C00D	-O001	-103.24(17)

Table S17 - Hydrogen Bonds of crystal **6**

	D--H	H..A	D--H..A	Angles(°)
N005-- H005.. N004	0.8800	2.1500	2.945(2)	149.00
C00D-- H00B.. N004	0.9900	2.6200	3.557(2)	158.00

Thermal behaviour

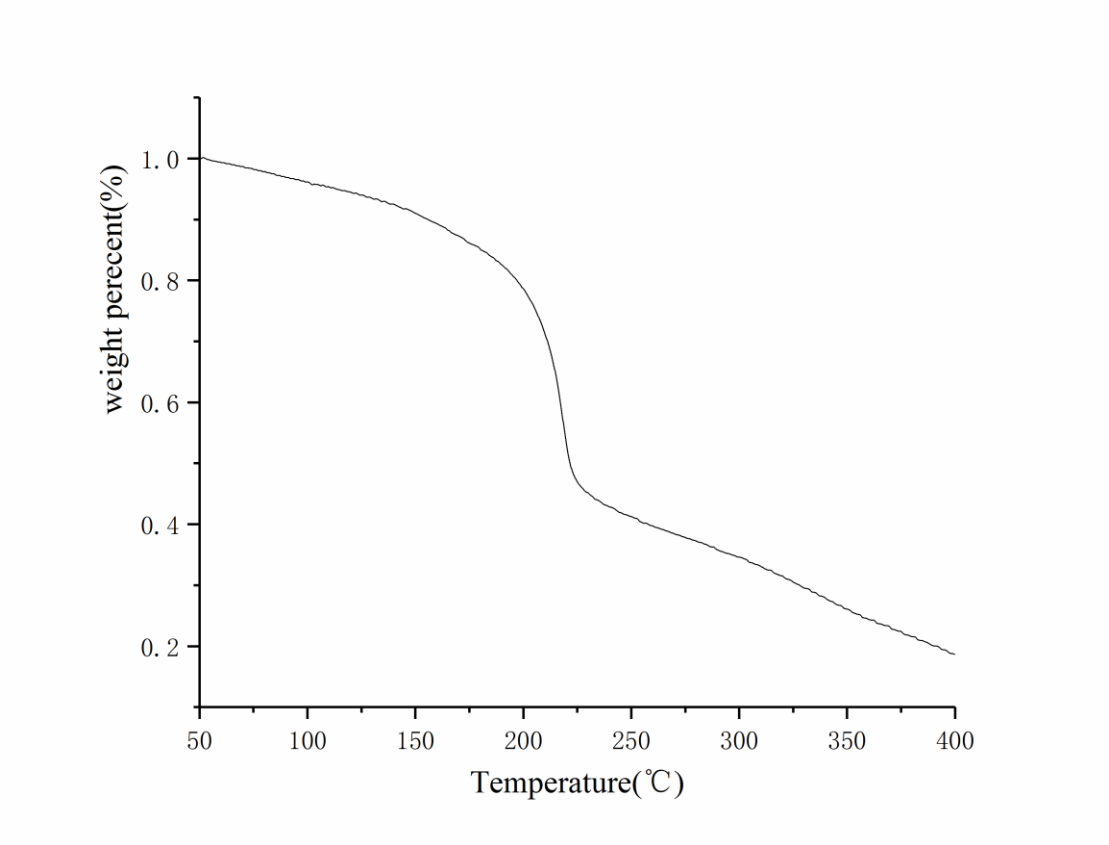


Figure S1 TG plot of compound **2**

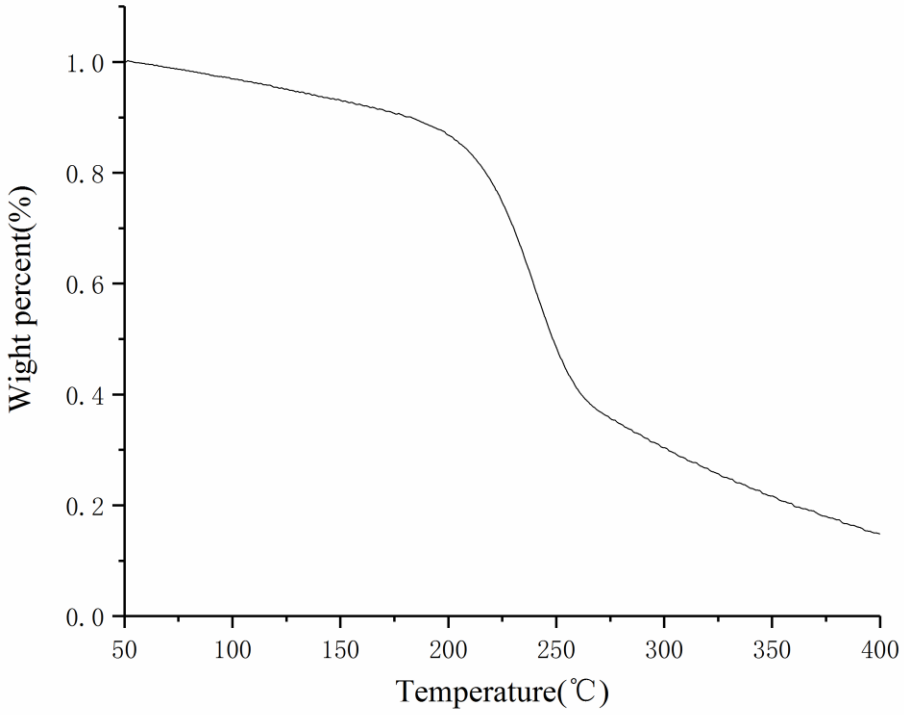


Figure S2 TG plot of compound **3**

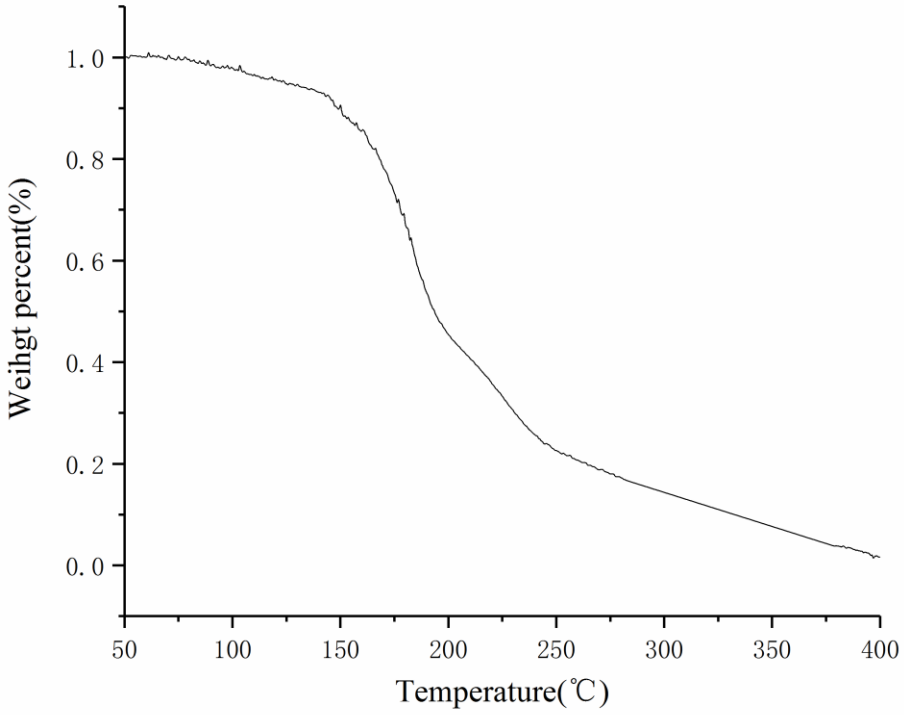


Figure S3 TG plot of compound **4**

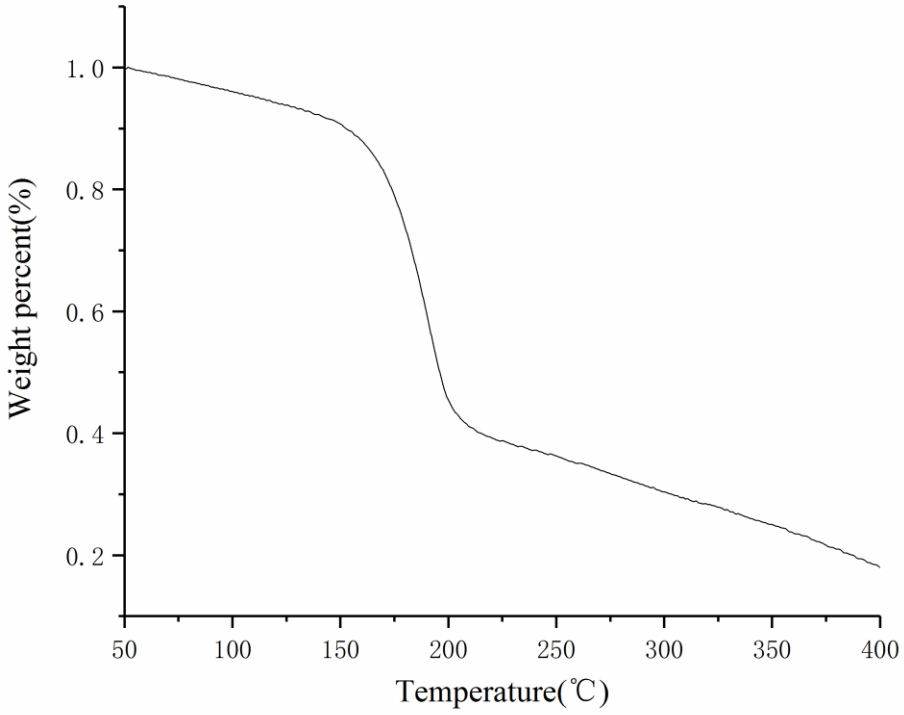


Figure S4 TG plot of compound **5**

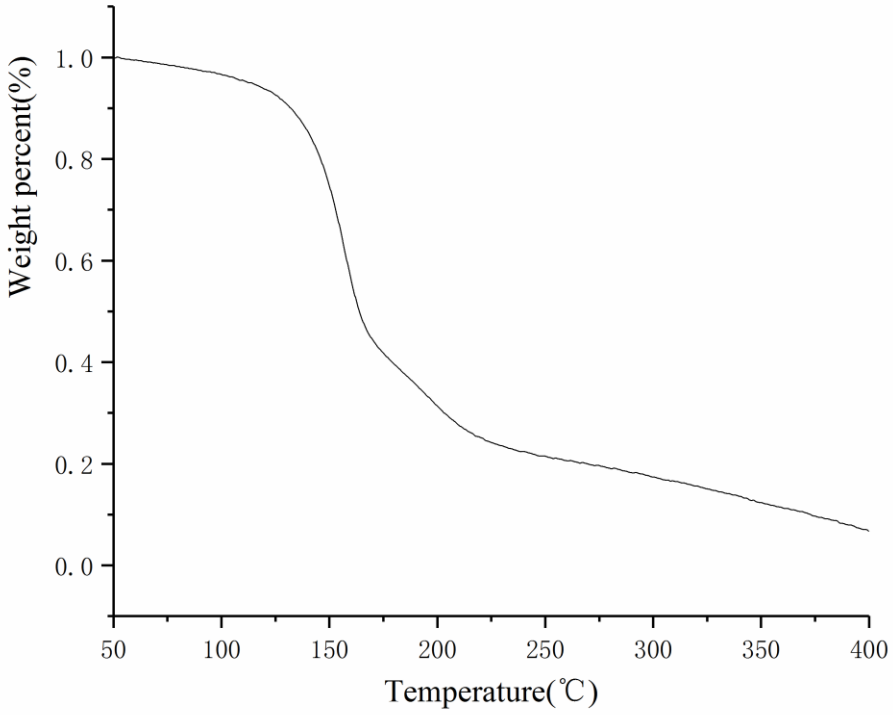


Figure S5 TG plot of compound **6**

Spectral data of all compounds

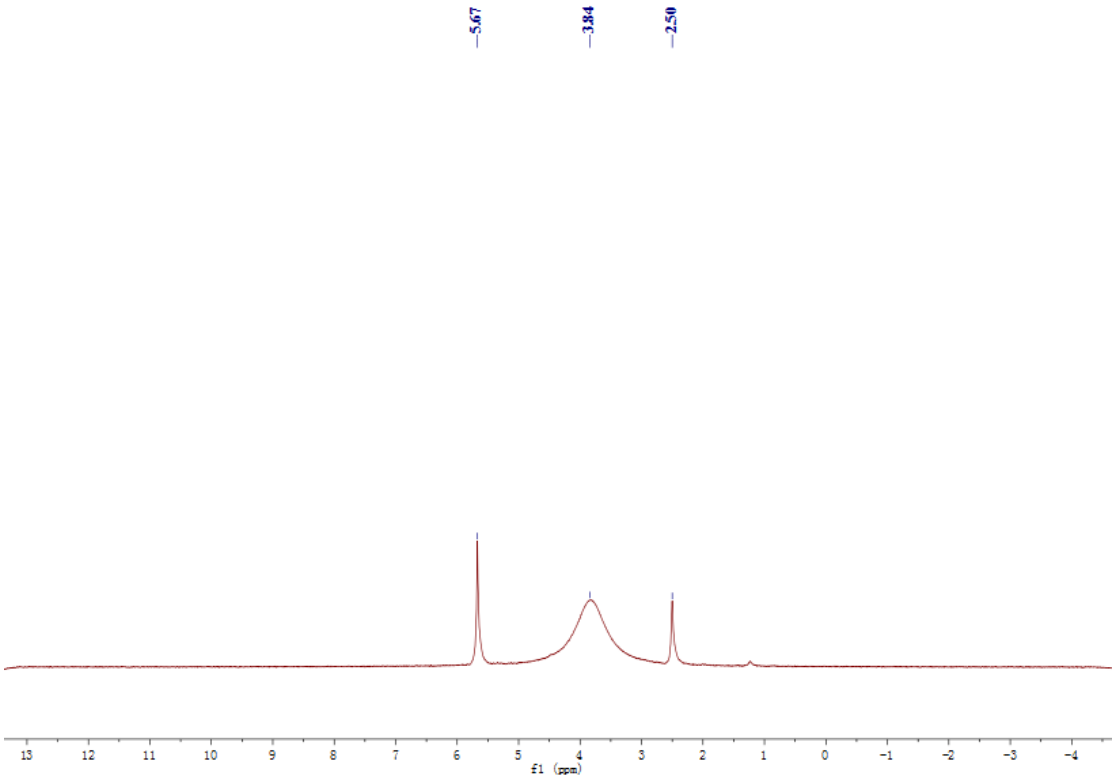


Figure S6 ^{1}H NMR for compound **2**

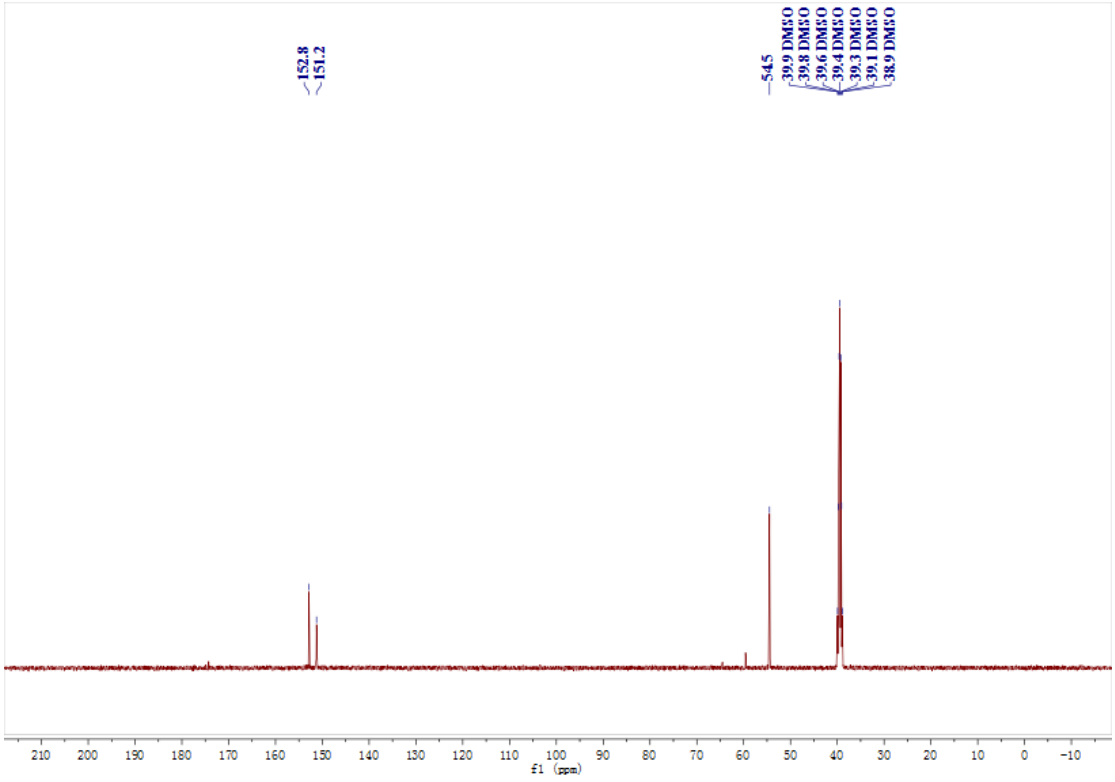


Figure S7 ^{13}C NMR for compound **2**

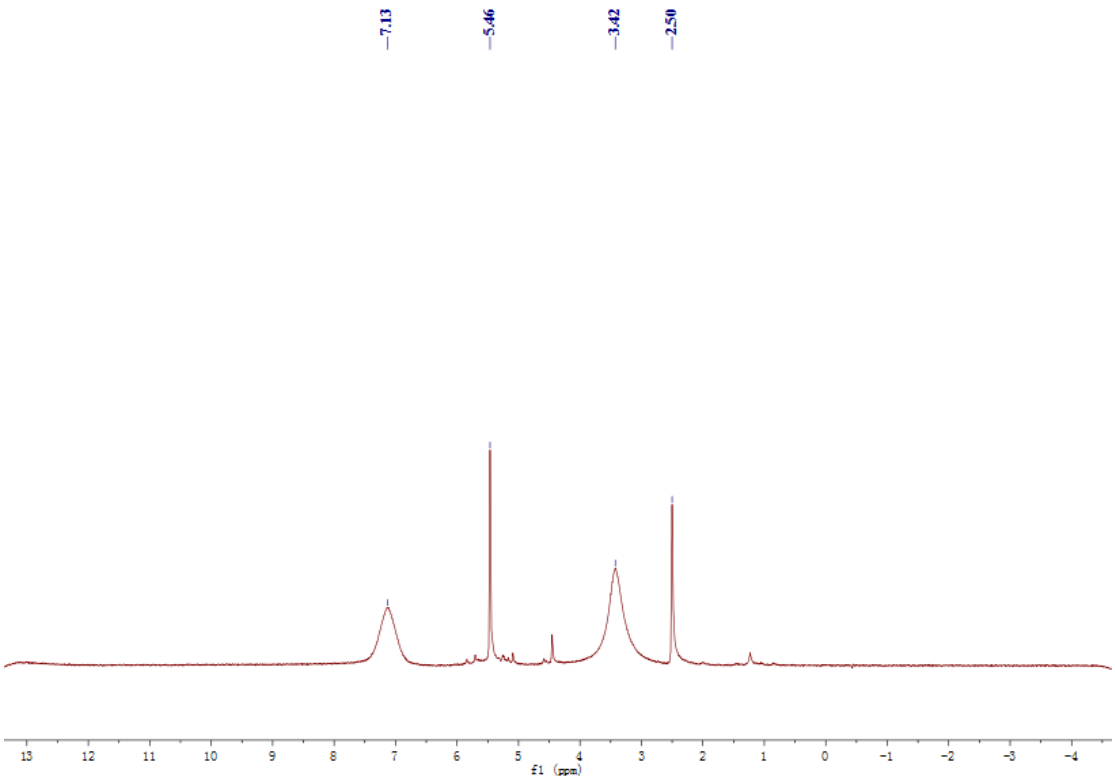


Figure S8 ^{1}H NMR for compound **2a**

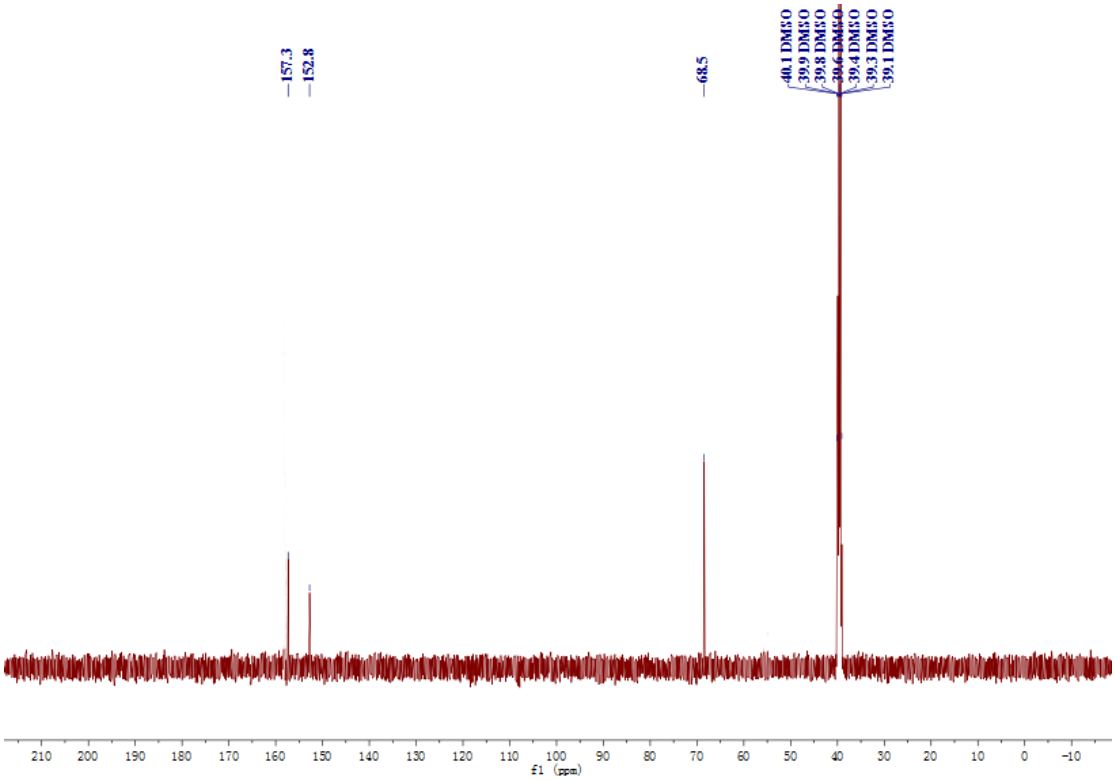


Figure S9 ^{13}C NMR for compound **2a**

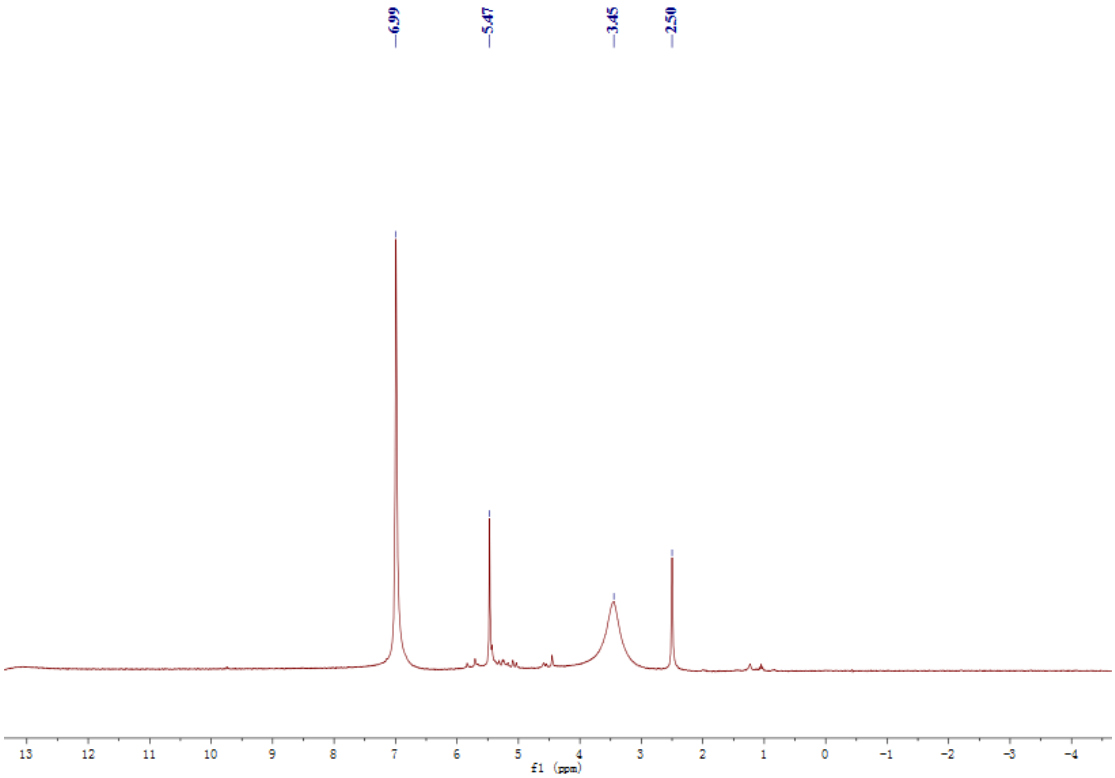


Figure S10 ^{1}H NMR for compound **2b**

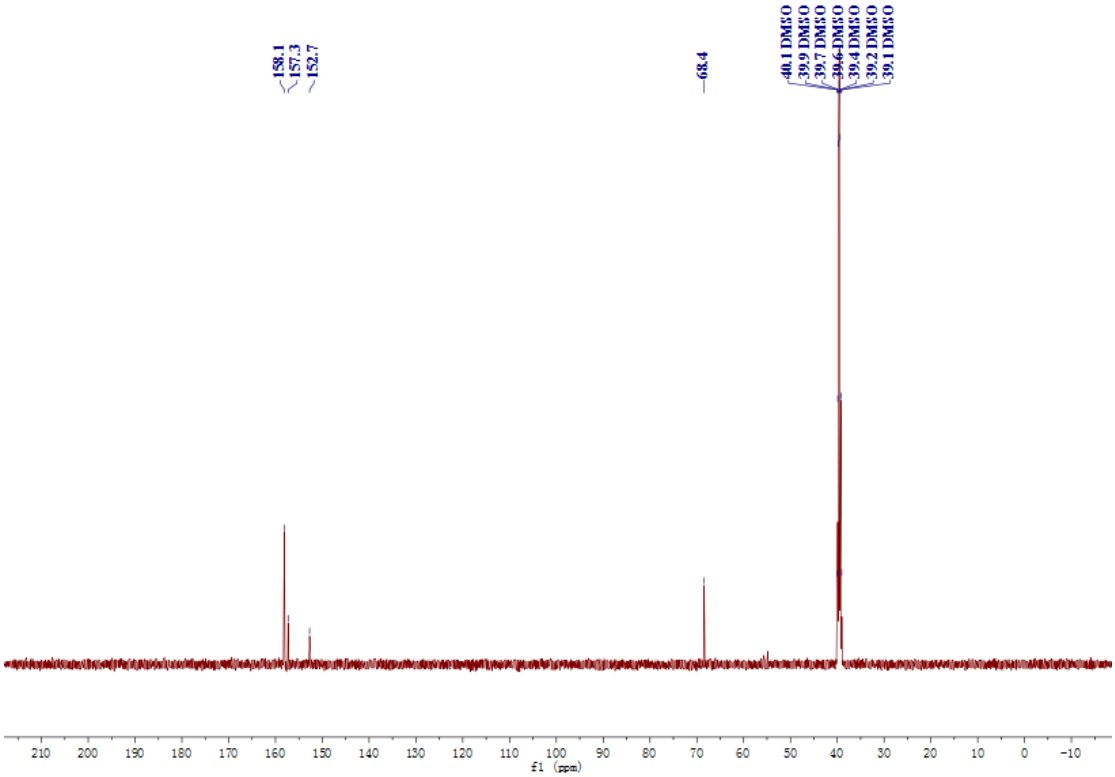


Figure S11 ^{13}C NMR for compound **2b**

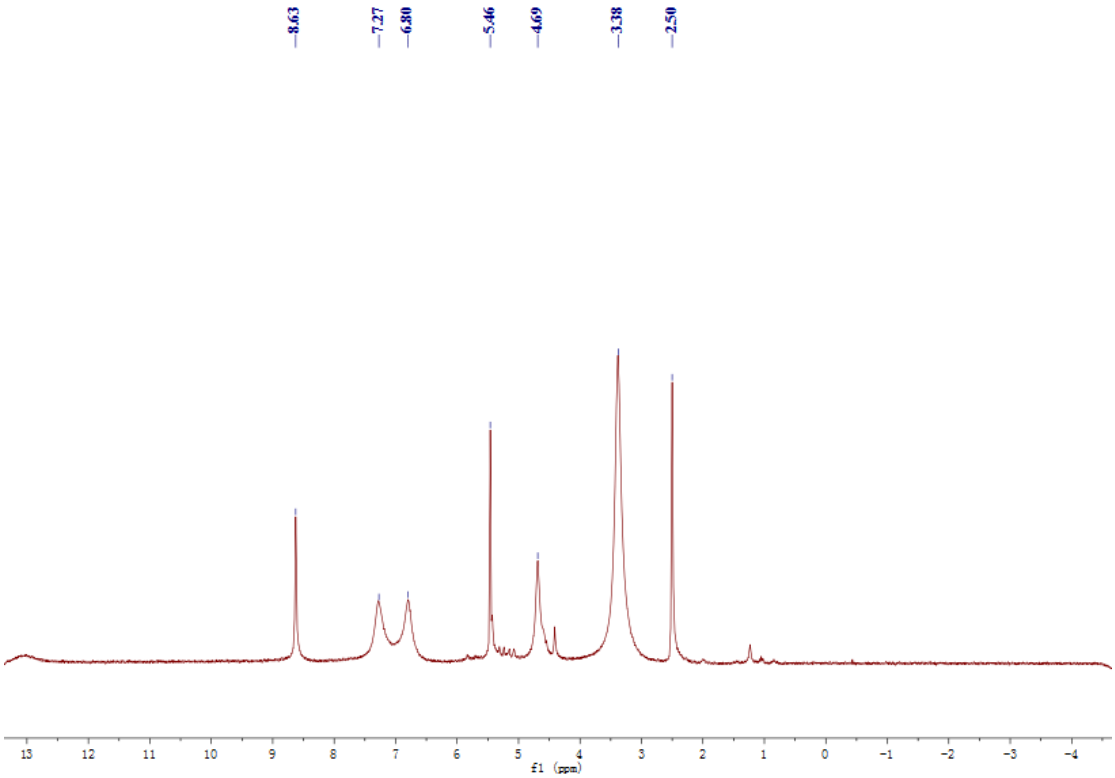


Figure S12 ^{1}H NMR for compound **2c**

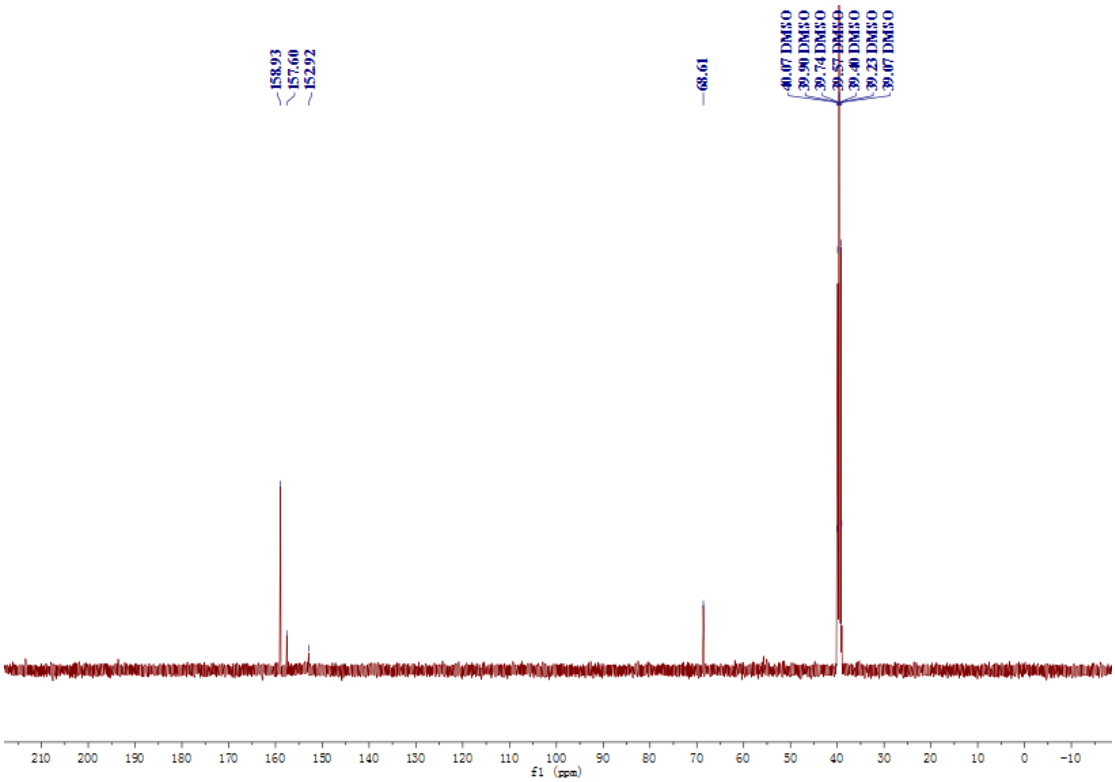


Figure S13 ^{13}C NMR for compound **2c**

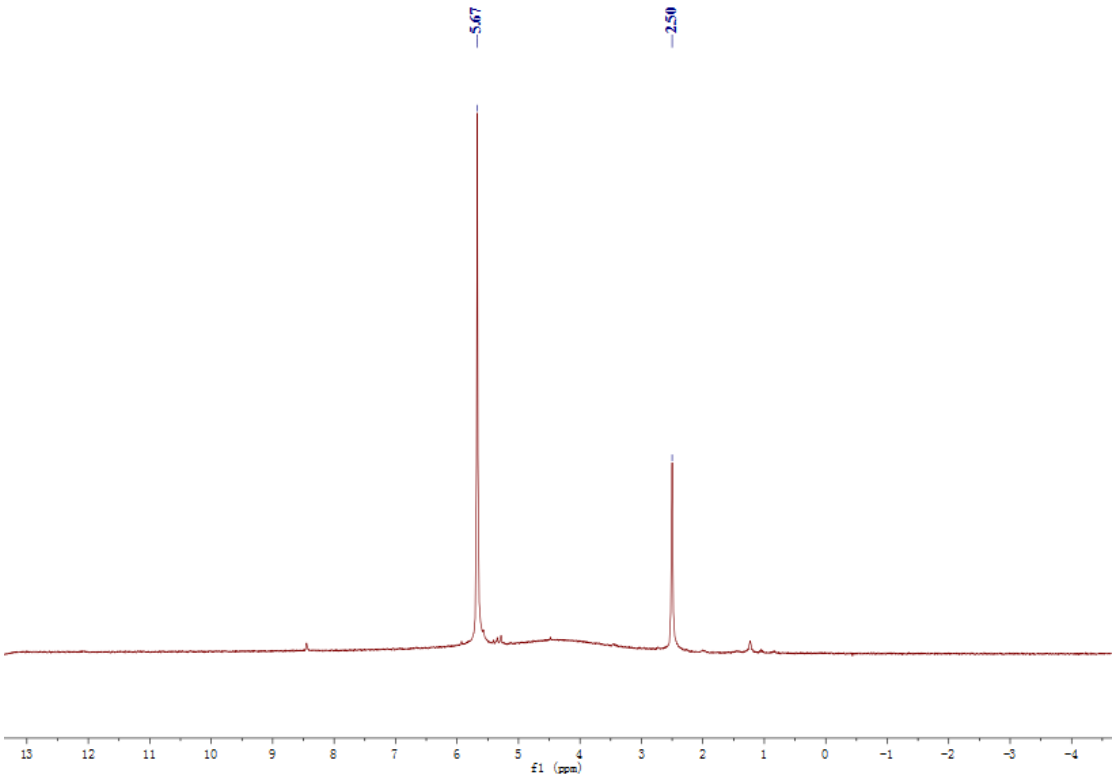


Figure S14 ^{1}H NMR for compound **2d**

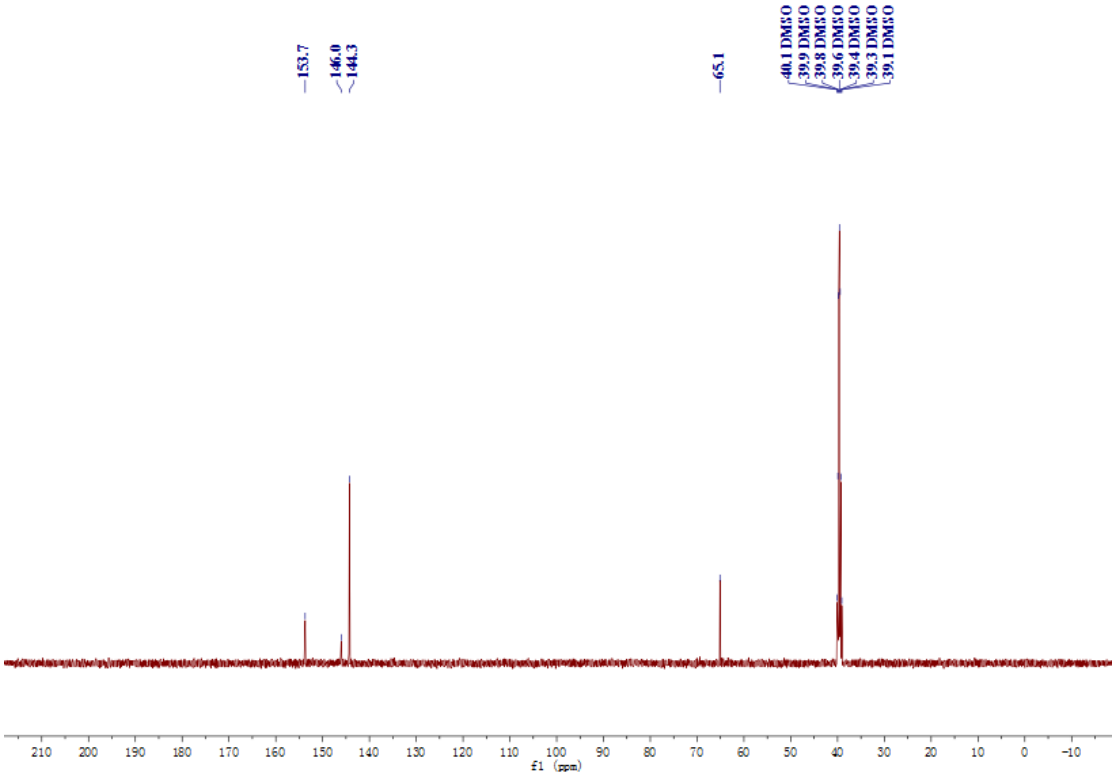


Figure S15 ^{13}C NMR for compound **2d**

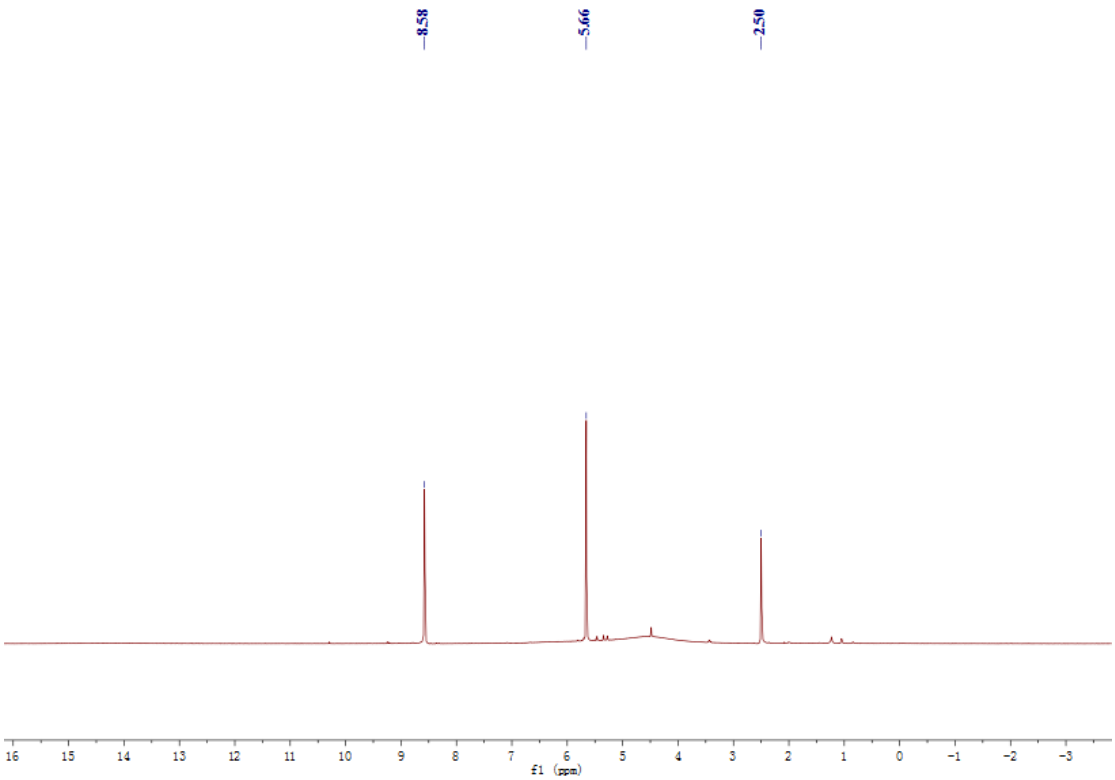


Figure S16 ^{1}H NMR for compound **2e**

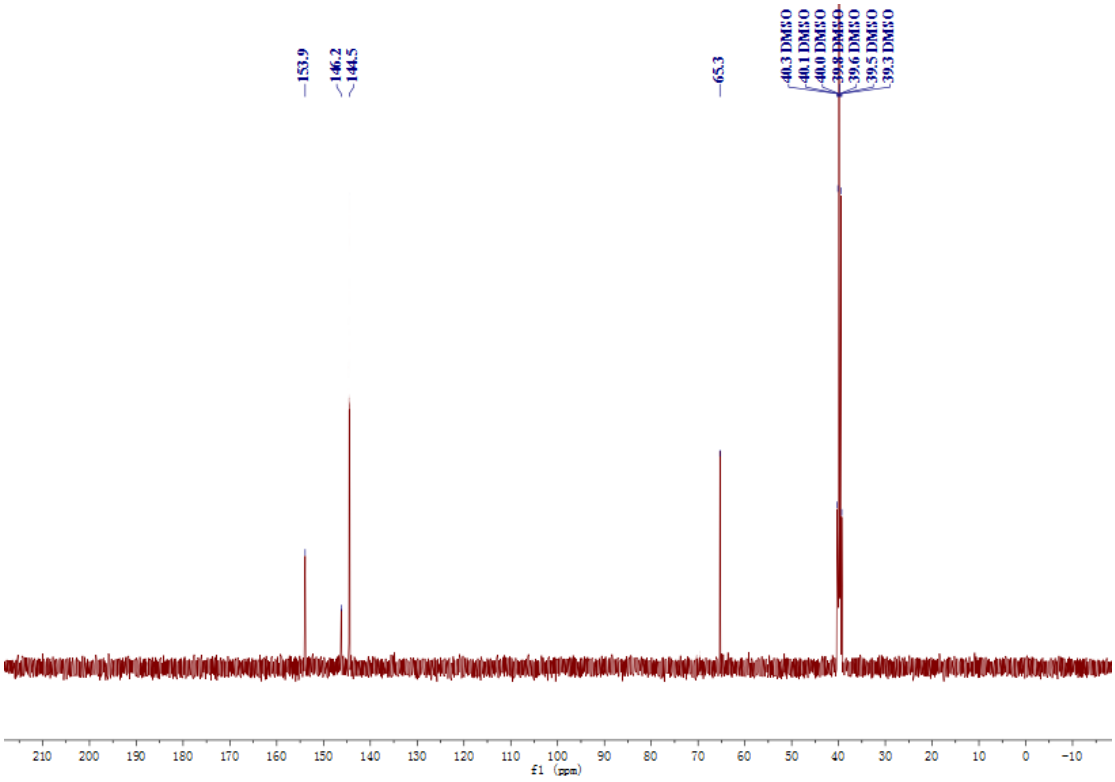


Figure S17 ^{13}C NMR for compound **2e**

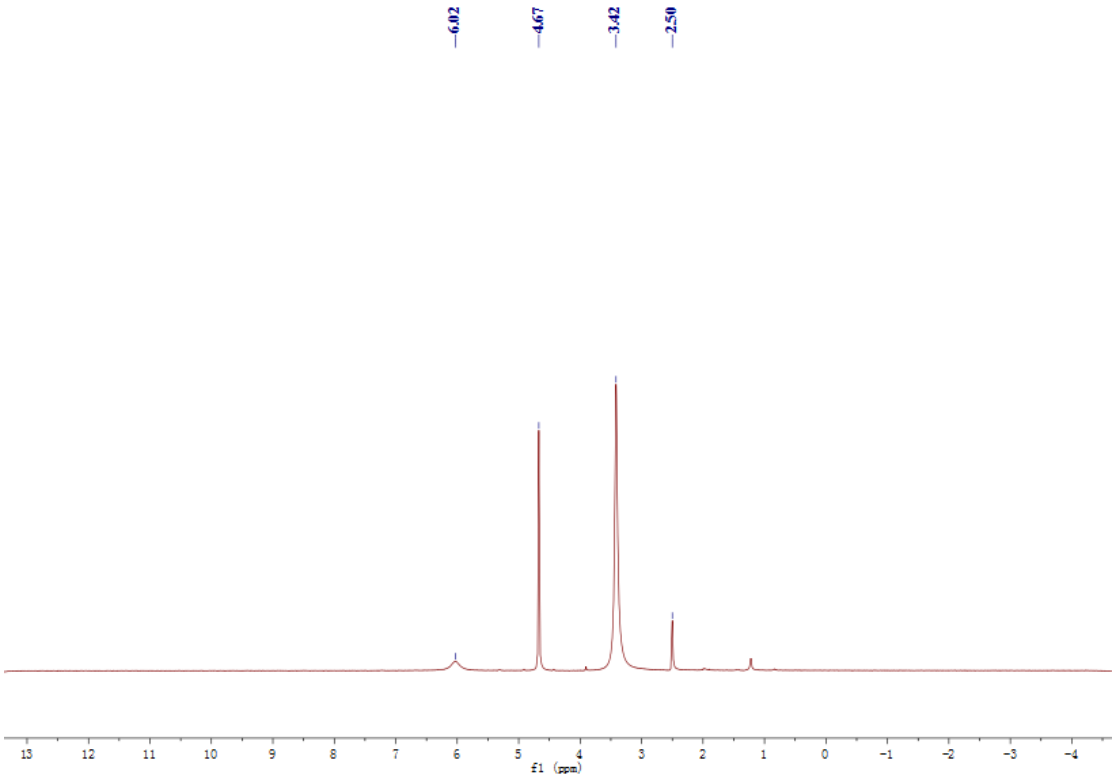


Figure S18 ^{1}H NMR for compound **3**

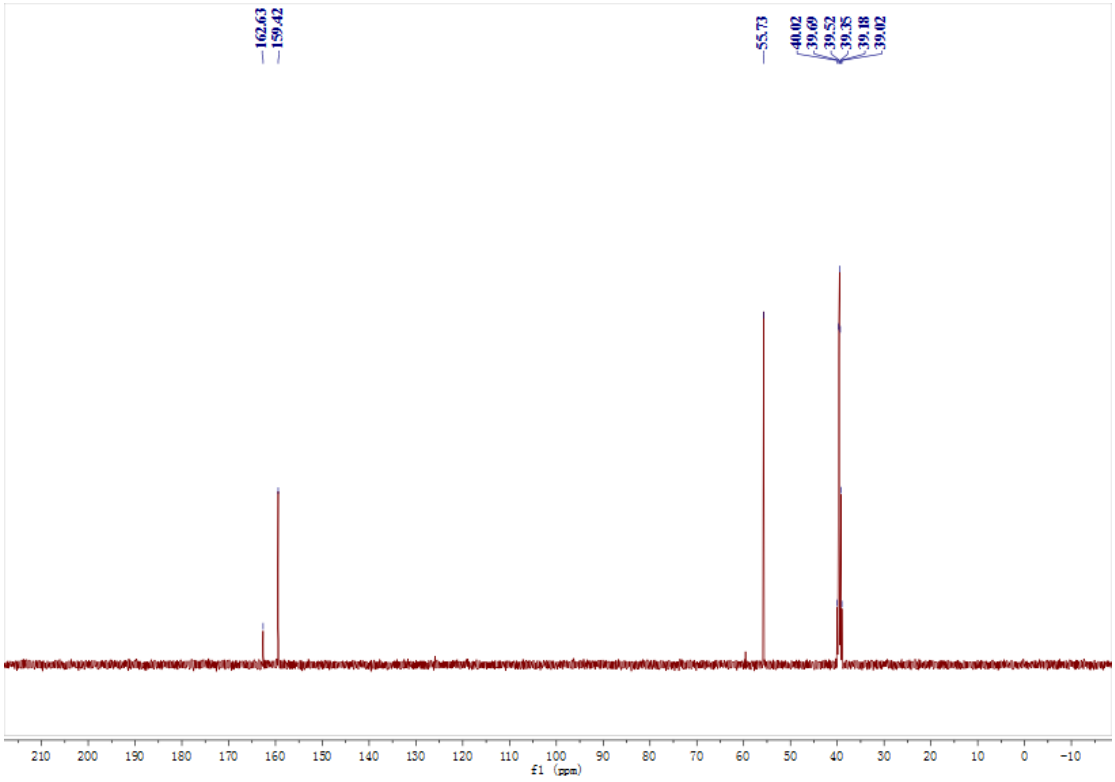


Figure S19 ^{13}C NMR for compound **3**

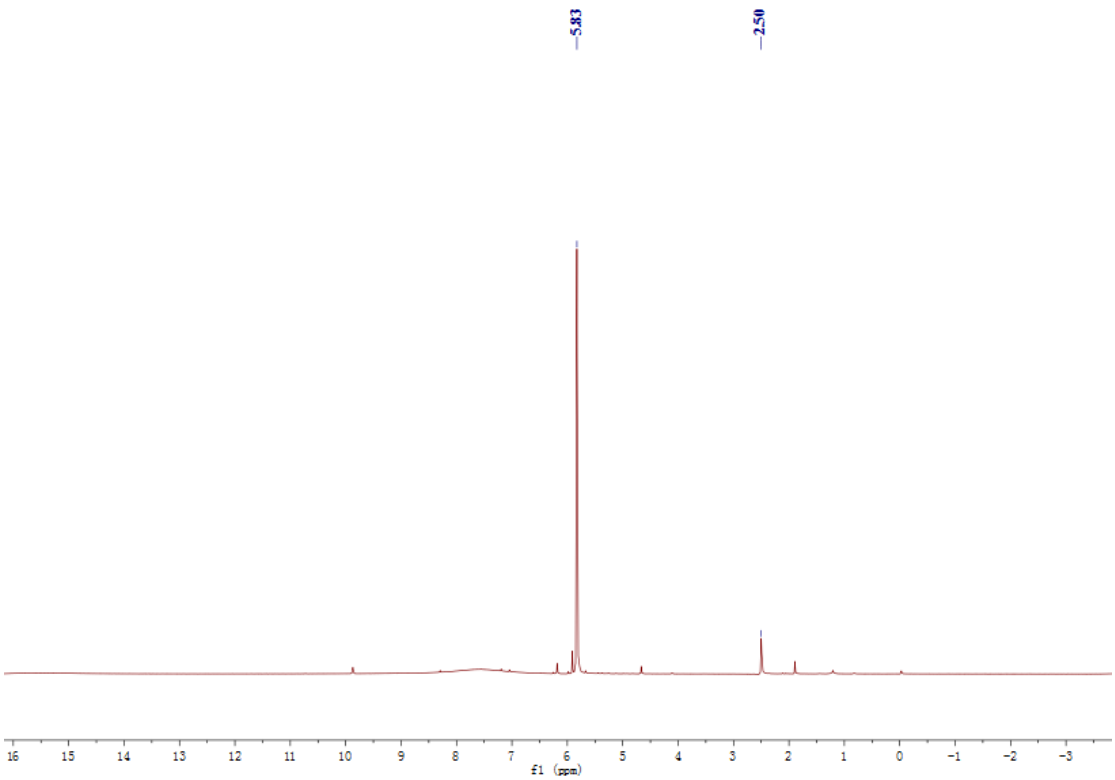


Figure S20 ^{1}H NMR for compound **4**

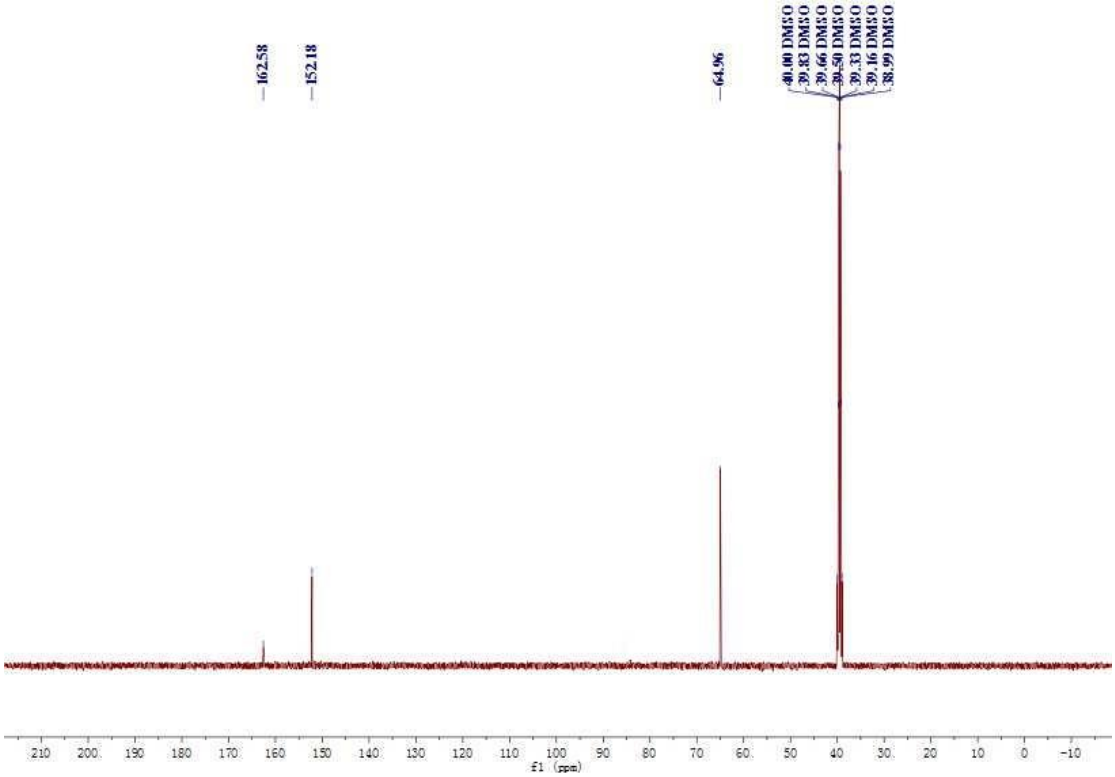


Figure S21 ^{13}C NMR for compound **4**

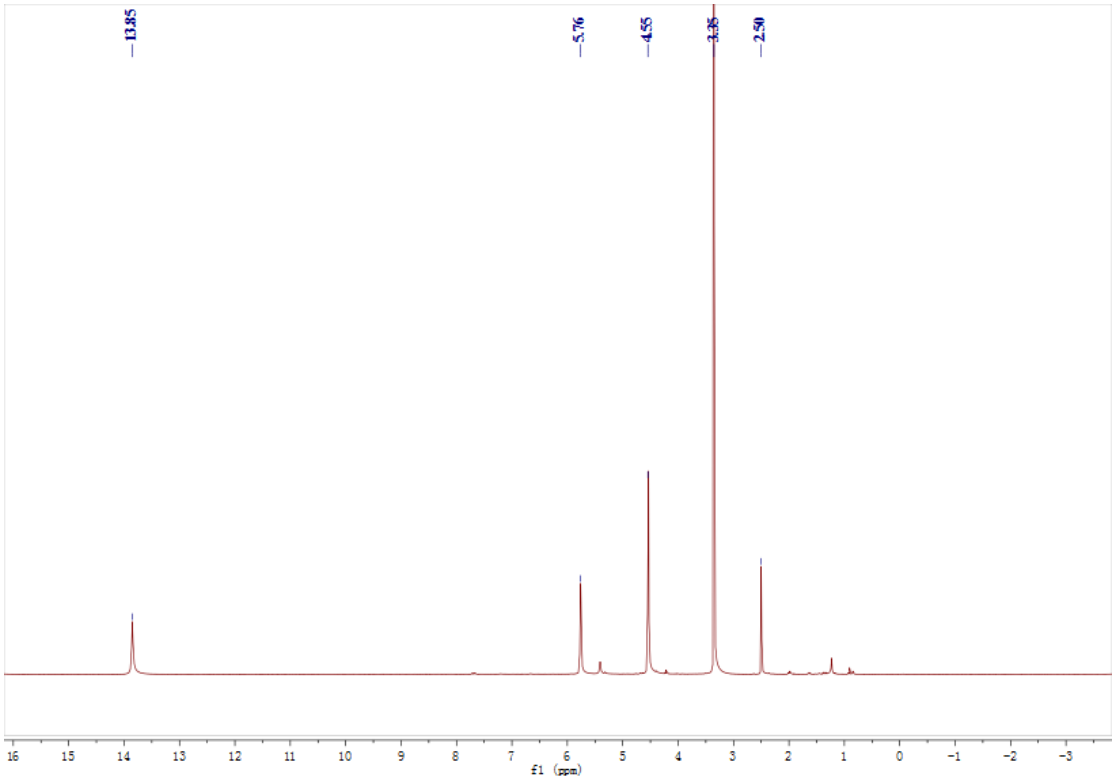


Figure S22 ^{1}H NMR for compound **5**

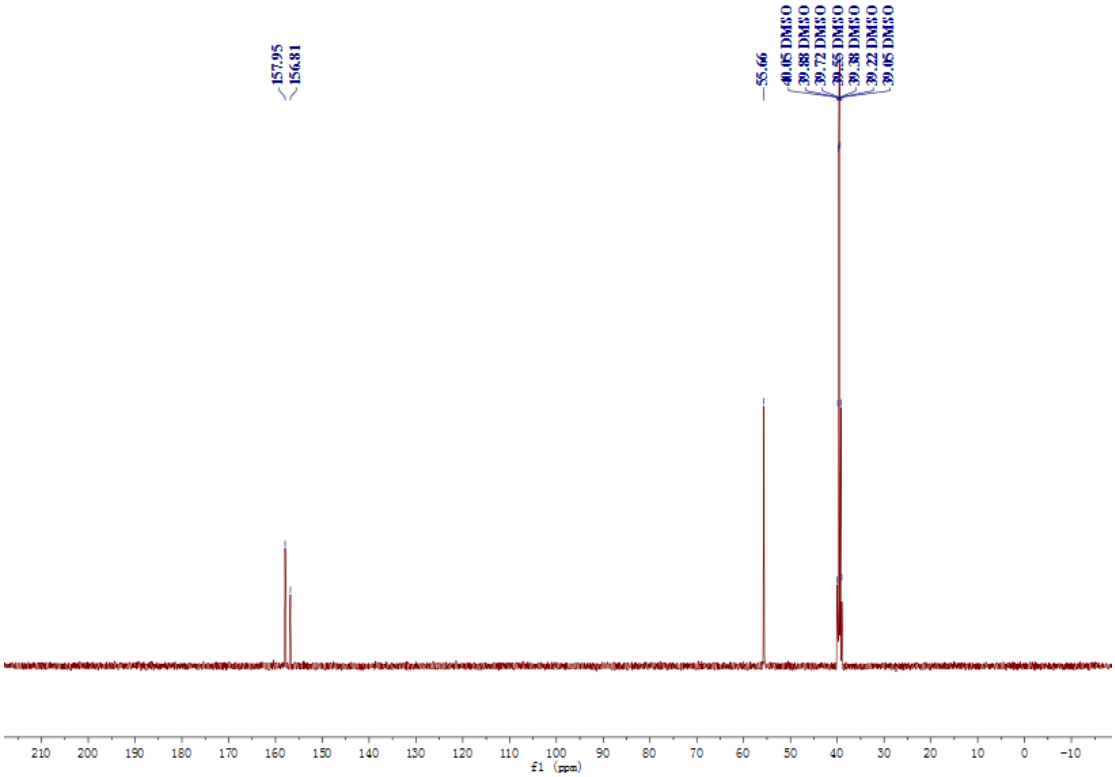


Figure S23 ^{13}C NMR for compound **5**

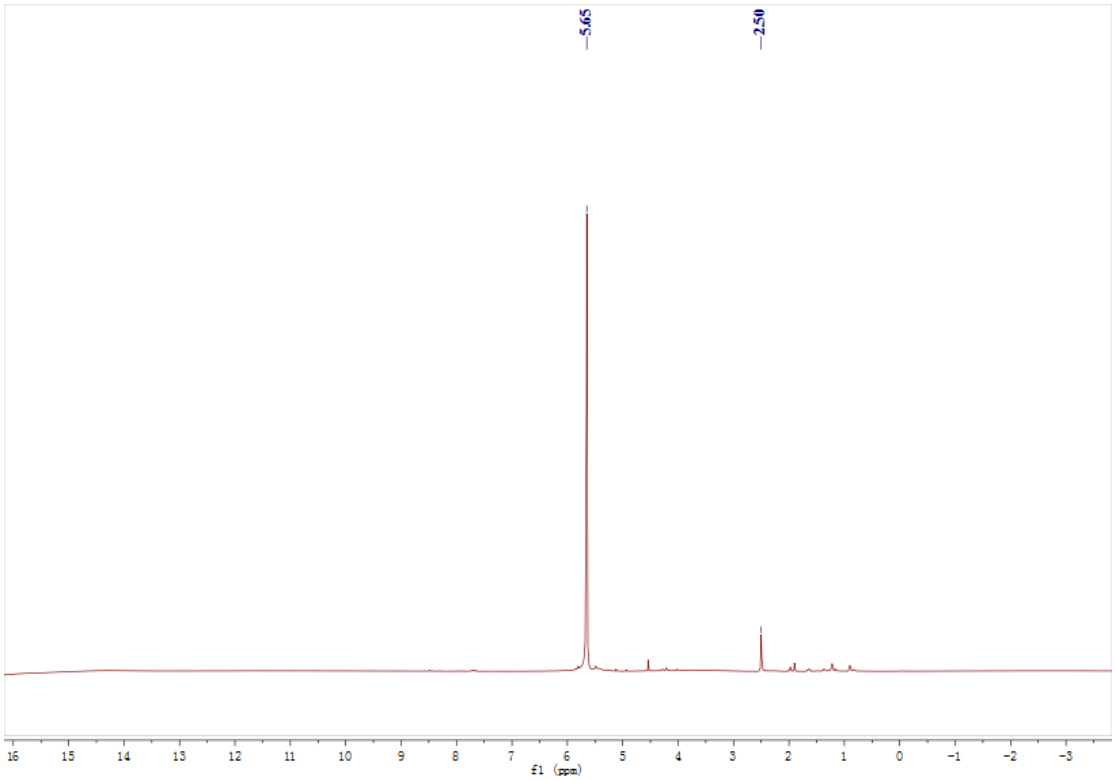


Figure S24 ^{1}H NMR for compound **6**

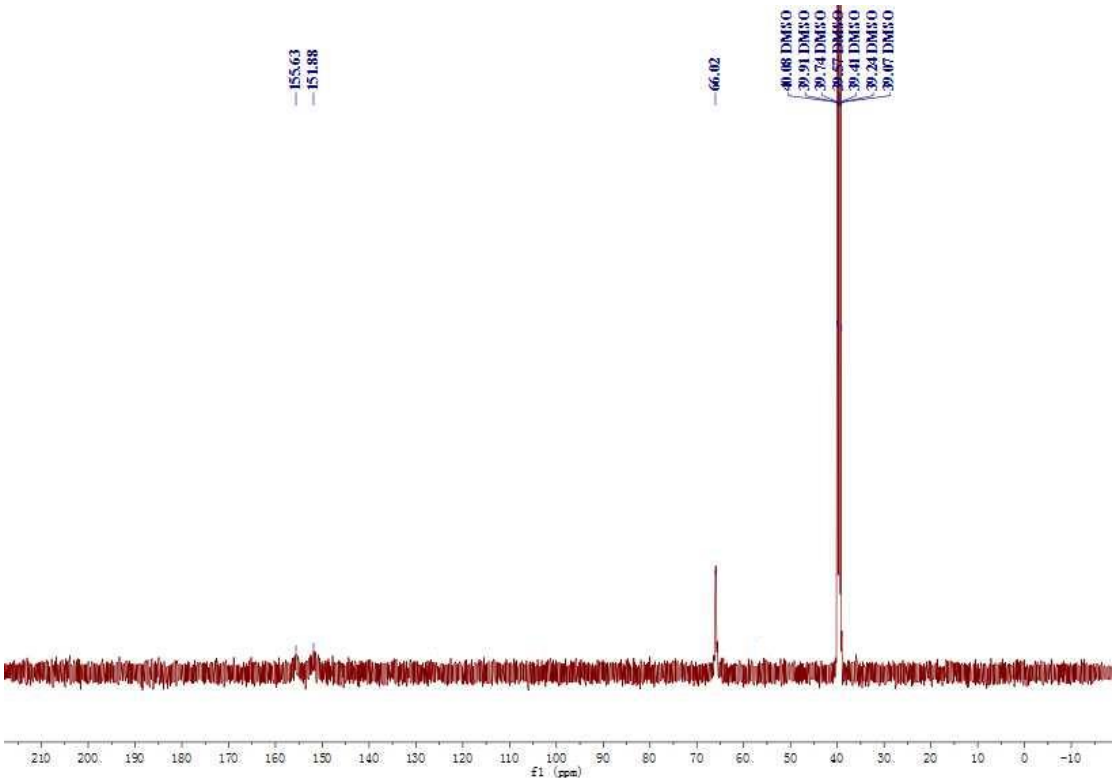


Figure S25 ^{13}C NMR for compound **6**

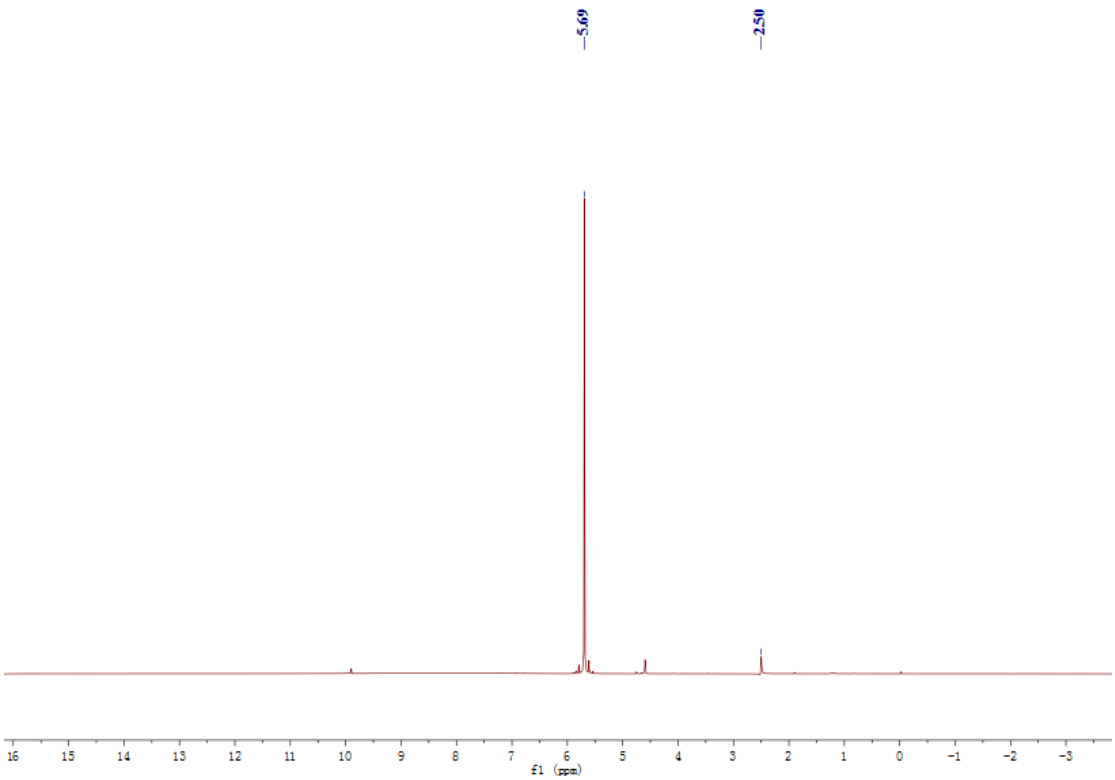


Figure S26 ^{1}H NMR for compound **9**

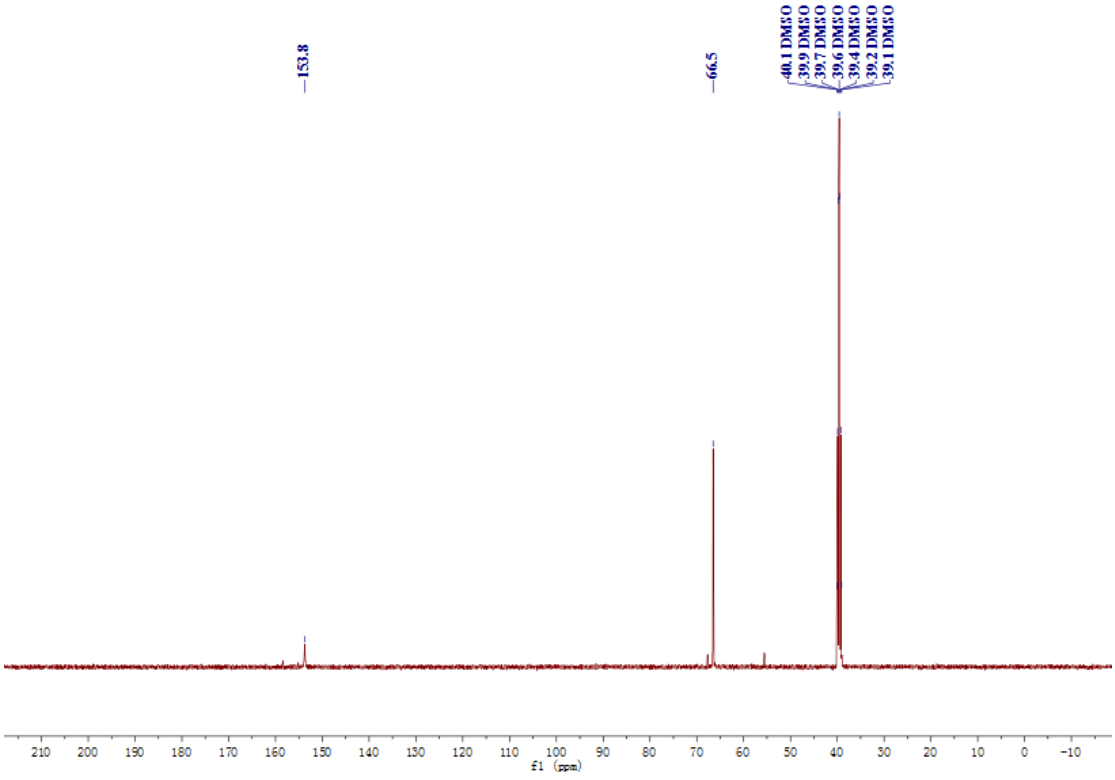


Figure S27 ^{13}C NMR for compound **9**

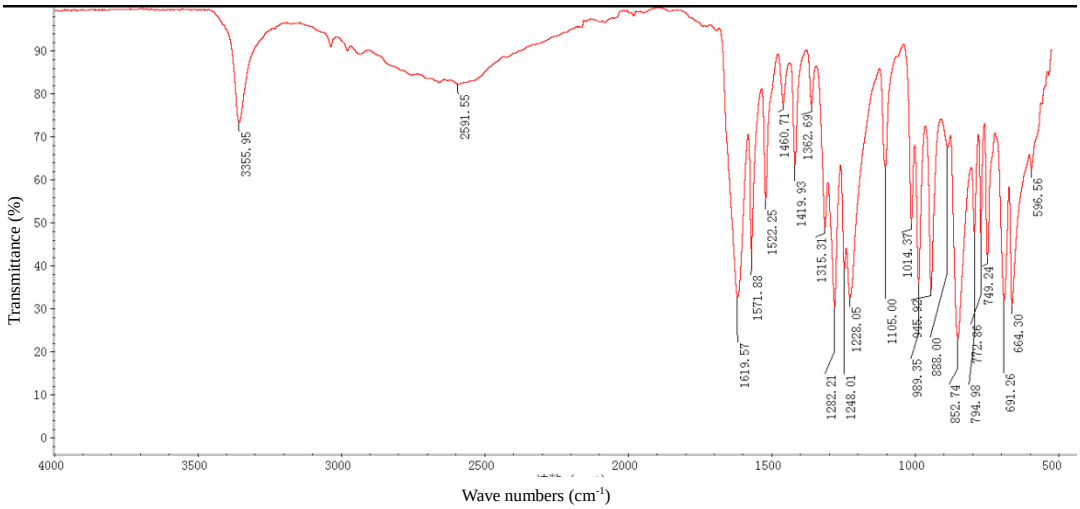


Figure.S28 IR for compound **2**

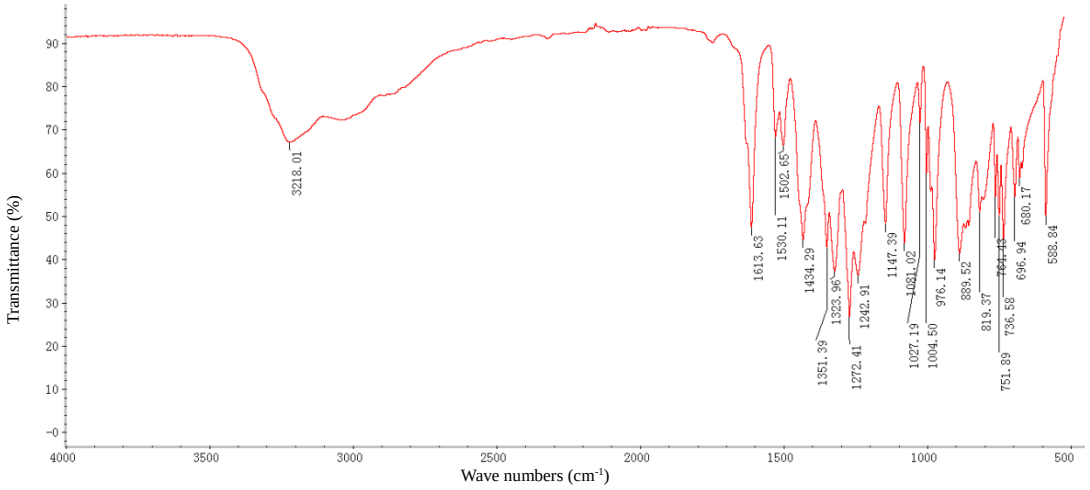


Figure.S29 IR for compound **2a**

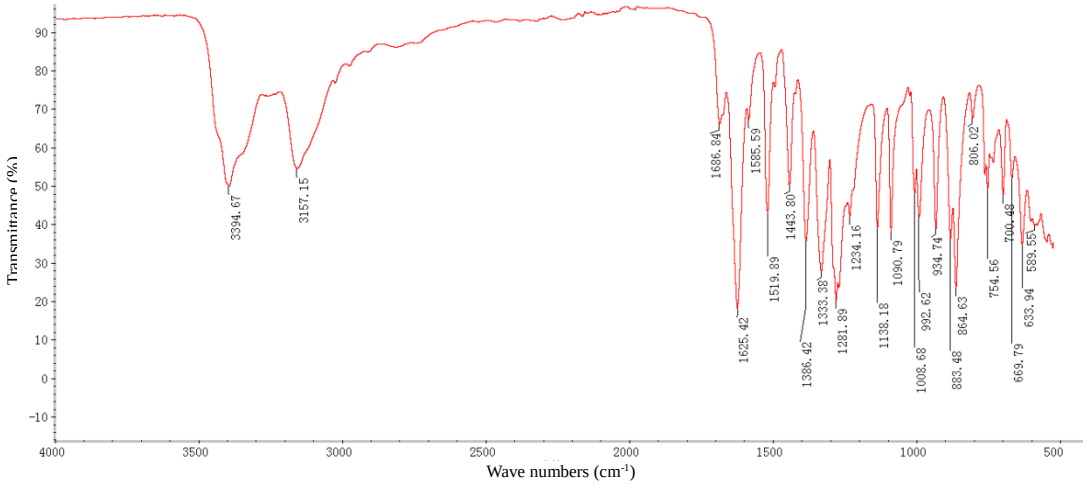


Figure.S30 IR for compound **2b**

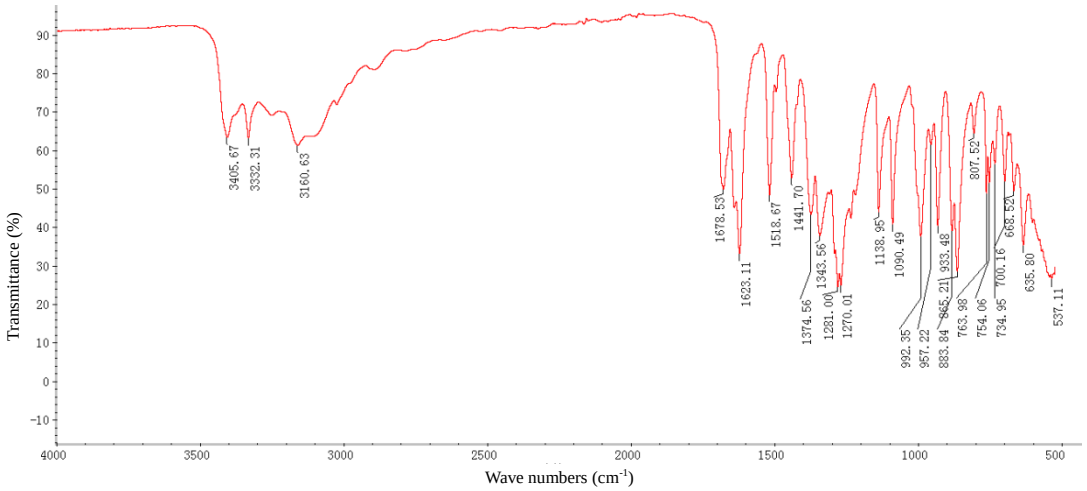


Figure.S31 IR for compound **2c**

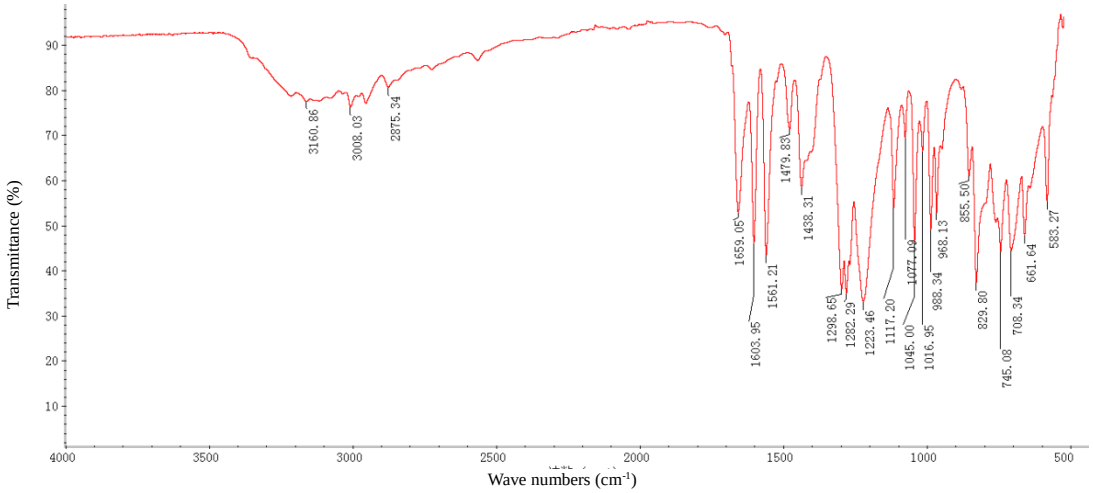


Figure.S32 IR for compound **2d**

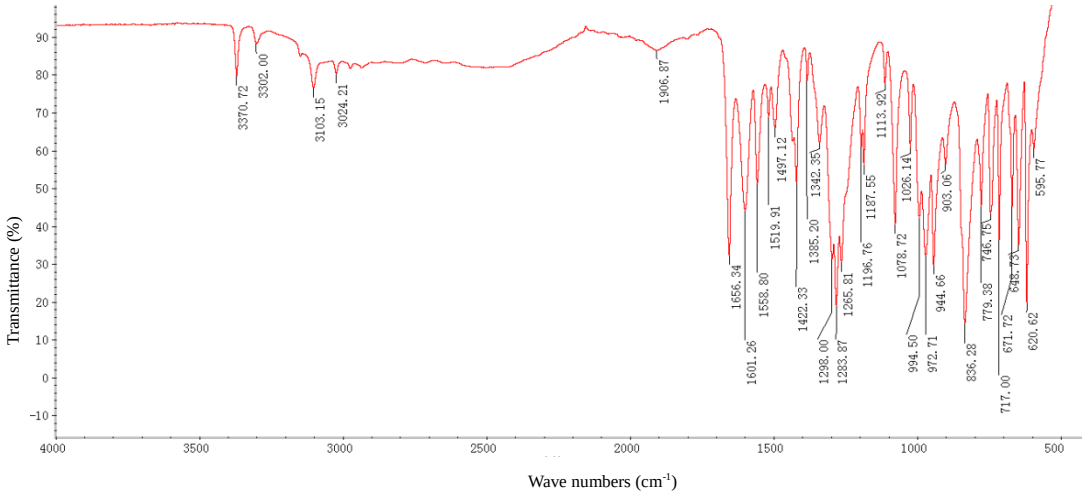


Figure.S33 IR for compound **2e**

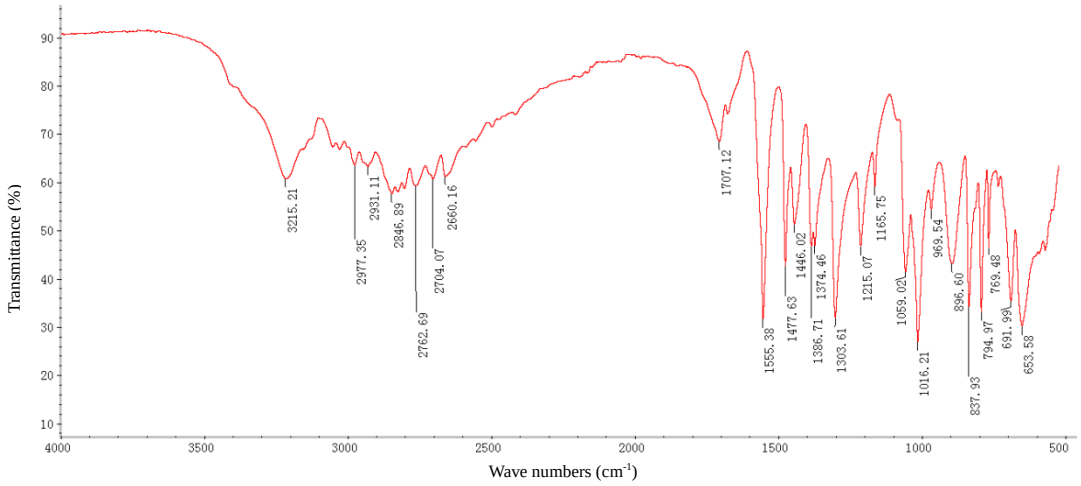


Figure.S34 IR for compound **3**

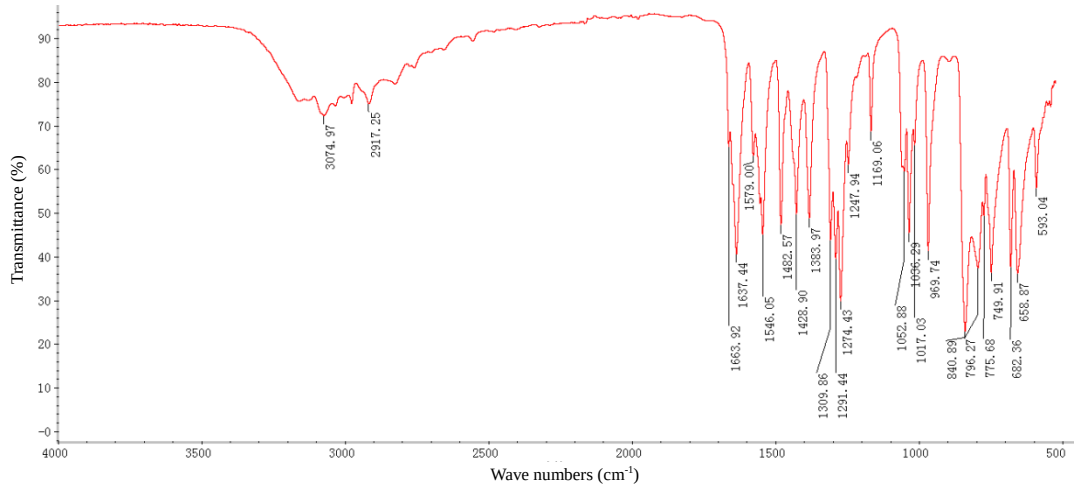


Figure.S35 IR for compound **4**

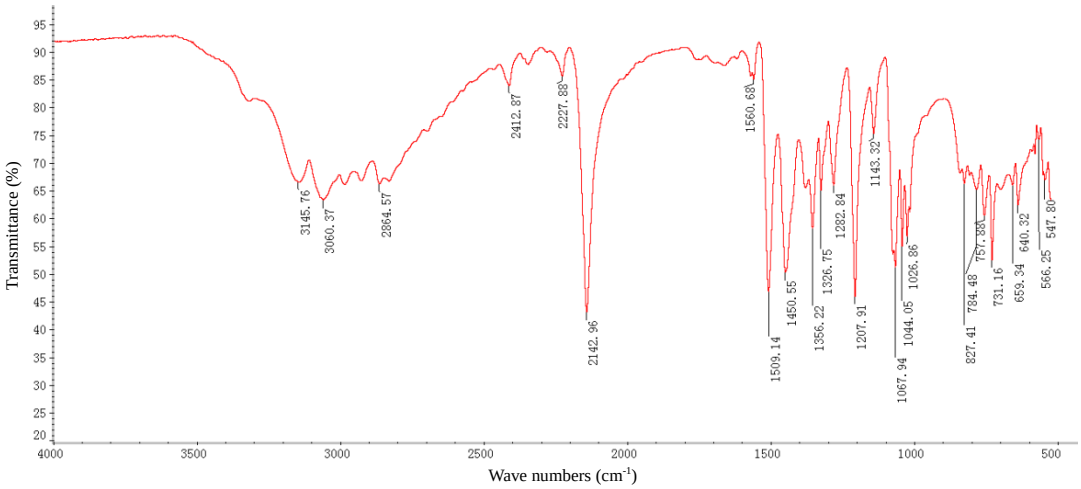


Figure.S36 IR for compound **5**

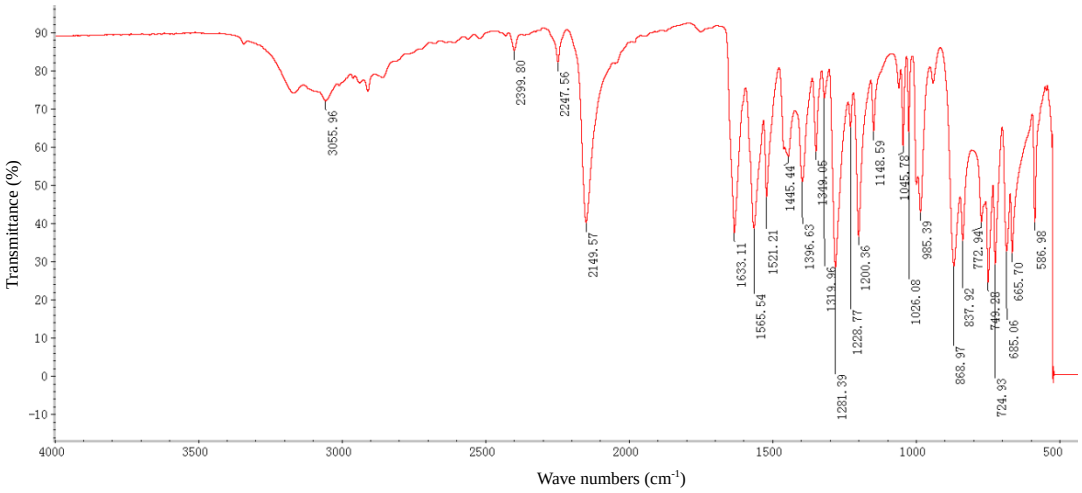


Figure.S37 IR for compound **6**

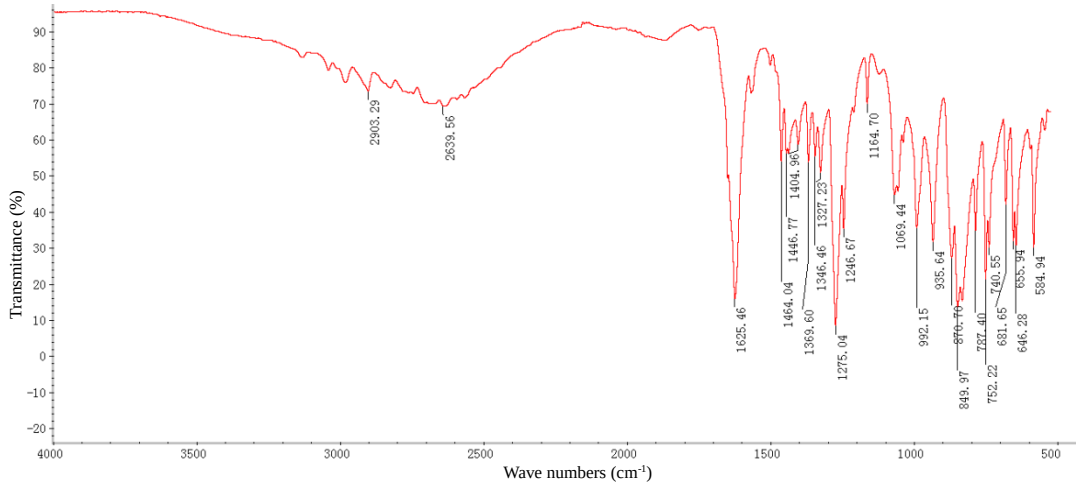


Figure.S38 IR for compound **9**

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[S2] H. D. B. Jenkins, D. Tudela, L. Glasser, Lattice potential energy estimation for complex ionic salts from density measurements, *Inorg. Chem.* 2002, 41, 2364-2367.