Supplemental information

Can cage-like cations function as antagonistic ions towards pentazolate anions?

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Supplemental Experimental Procedures

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1. Crystallographic Data

Table S1 Bond length parameters of *cyclo*-N$_5^-$ in compound **1**·H$_2$O crystals.

No.	Bond length (Å)	No.	Bond length (Å)
N1−N2	1.308(5)	N4−N5	1.298(4)
N2−N3	1.297(5)	N5−N1	1.308(4)
N3−N4	1.301(4)		

Table S2 Bond angle Parameters of *cyclo*-N$_5^-$ in compound **1**·H$_2$O crystal.

No.	Bond angle (°)	No.	Bond angle (°)
N1−N2−N3	107.2(4)	N4−N5−N1	107.8(3)
N2−N3−N4	109.0(3)	N5−N1−N2	108.2(4)
N3−N4−N5	107.8(3)		

Table S3 Torsion angles of *cyclo*-N$_5^-$ for compound **1**·H$_2$O crystal.

No.	Torsion angle (°)	No.	Torsion angle (°)
N1−N2−N3−N4	-0.5(5)	N4−N5−N1−N2	-0.1(5)
N2−N3−N4−N5	0.4(5)	N5−N1−N2−N3	0.4(5)
N3−N4−N5−N1	-0.2(5)		

Table S4 Bond length parameters of hydrogen bond in compound **1**·H$_2$O crystals.

No.	Lengths D−H (Å)	Lengths H···A (Å)	Lengths D···A (Å)
N1···H−O	0.850	2.077	2.913(5)
N3···H−N6	0.890	2.048	2.937(5)
N4···H−O	0.932	2.034	2.935(5)
N5···H−N6	0.891	2.102	2.990(4)
N6−H···O	0.890	1.937	2.826(4)

Table S5 Bond angle parameters of hydrogen bond in compound **1**·H$_2$O crystal.

No.	Bond angle (°)	No.	Bond angle (°)
N1···H−O	167.6	N5···H−N6	174.4
N3···H−N6	177.0	N6−H···O	176.4
N4···H−O	162.1		

Table S6 Bond length parameters of *cyclo*-N$_5^-$ in compound **2**·H$_2$O crystal.

No.	Bond length (Å)	No.	Bond length (Å)
N1−N2	1.307(3)	N3−N5	1.306(3)
N2−N4	1.309(3)	N5−N1	1.303(3)
N4−N3	1.299(3)		

Table S7 Bond angle Parameters of *cyclo*-N$_5^-$ in compound **2**·H$_2$O crystal.

No.	Bond angle (°)	No.	Bond angle (°)
N1−N2−N4	108.02(17)	N3−N5−N1	108.10(19)
N2−N4−N3	107.88(18)	N5−N1−N2	107.81(17)
N4−N3−N5	108.18(18)		

Table S8 Torsion angles of *cyclo*-N$_5^-$ for compound **2**·H$_2$O crystals.

No.	Torsion angle (°)	No.	Torsion angle (°)
N1−N2−N4−N3	0.0(2)	N3−N5−N1−N2	-0.2(2)
N2−N4−N3−N5	-0.2(2)	N5−N1−N2−N4	0.1(2)
N4−N3−N5−N1	0.2(2)		

Table S9 Bond length parameters of hydrogen bond in compound **2**·H$_2$O crystal.

No.	Lengths D−H (Å)	Lengths H···A (Å)	Lengths D···A (Å)
N1···H−N6	0.980	2.648	3.266
N1···H−N7	0.980	2.494	3.143
N2···H−O	0.87	2.01(3)	2.868
N6−H···O	0.980	2.046	2.820
N7−H···O	0.980	2.198	2.890

Table S10 Bond angle parameters of hydrogen bond in compound **2**·H$_2$O crystal.

No.	Bond angle (°)	No.	Bond angle (°)
N1···H−N6	123.5	N6−H···O	134.5
N1···H−N7	123.5	N7−H···O	126.4
N2···H−O	166		

Table S11 Bond length parameters of *cyclo*-N$_5^-$ in compound **3**·H$_2$O crystal.[1]

No.	Bond length (Å)	No.	Bond length (Å)
N2−N3	1.296(3)	N5−N6	1.307(3)
N3−N4	1.336(3)	N6−N2	1.320(3)
N4−N5	1.307(3)		

Table S12 Bond angle parameters of hydrogen bond in compound **3**·H$_2$O crystal.[1]

No.	Bond angle (°)	No.	Bond angle (°)
N2−N3−N4	108.3(2)	N5−N6−N2	106.8(2)
N3−N4−N5	106.2(2)	N6−N2−N3	108.7(2)
N4−N5−N6	109.9(2)		

Table S13 Torsion angles of *cyclo*-N$_5^-$ for compound **3**·H$_2$O crystals.[1]

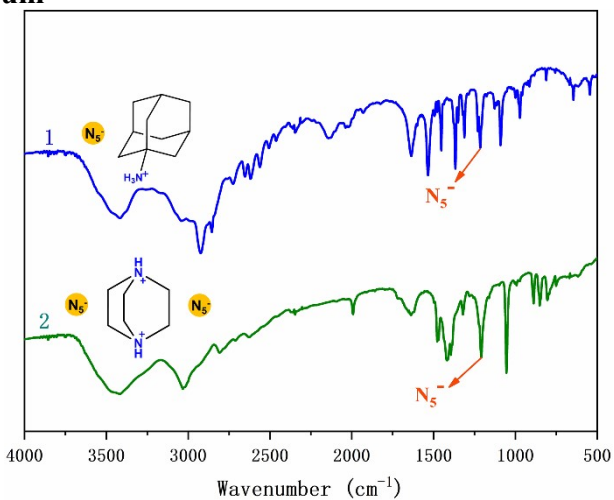| No.	Torsion angle (°)	No.	Torsion angle (°)
N2−N3−N4−N5	0.1(3)	N5−N6−N2−N3	0.9(3)
N3−N4−N5−N6	0.5(3)	N6−N2−N3−N4	-0.6(3)
N4−N5−N6−N2	-0.9(3)		

2. Infrared spectrum

Fig. S1 Infrared spectrum of compound **1** and compound **2**.

3. 2D fingerprint plots
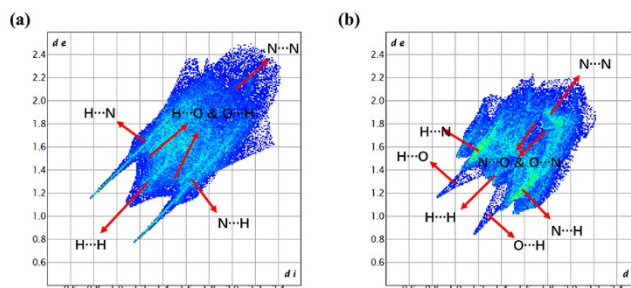
Fig. S2 (a) 2D fingerprint plot of compound **1**·H$_2$O; (b) 2D fingerprint plot of compound **2**·H$_2$O.
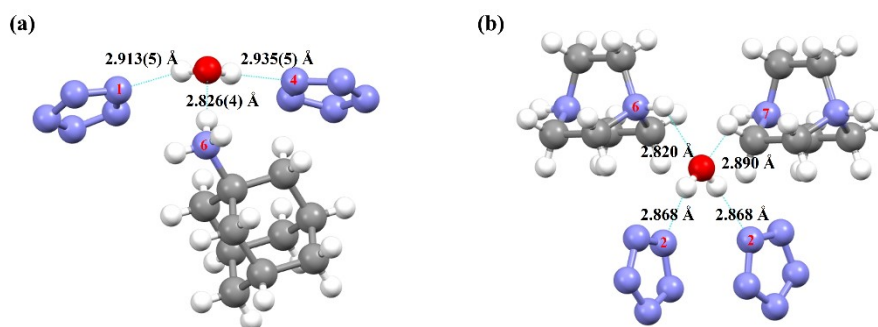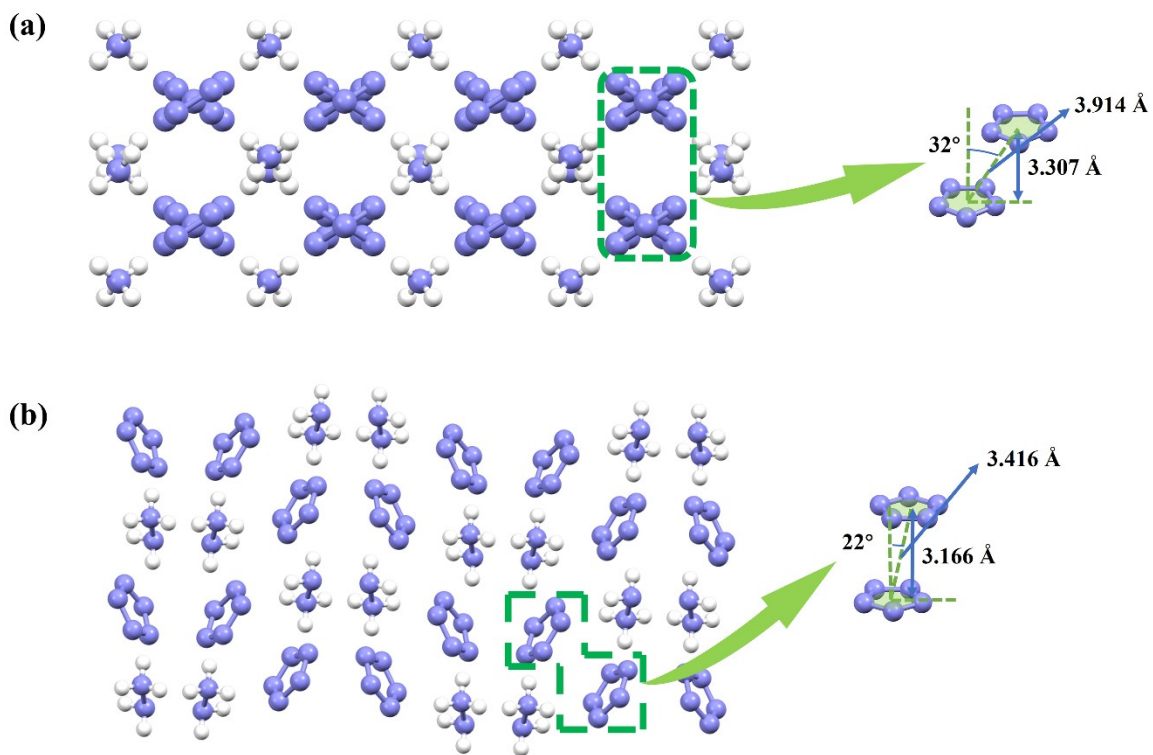
4. The plots of hydrogen bonds around crystalline water

Fig. S3 (a) Hydrogen bonds around crystalline water in compound **1**·H$_2$O; (b) hydrogen bonds around crystalline water in compound **2**·H$_2$O.

5. Comparison of crystal stacking of three types of non-metallic pentazolate salts

(a)

3.914 Å

32°

3.307 Å

(b)

3.416 Å

22°

3.166 Å

Fig. S4 Crystal stacking of chain-like cationic pentazolate salts (a: $(NH_4)^+N_5^-$; b: $(N_2H_5)^+N_5^-)^2$.

(a)

(b)
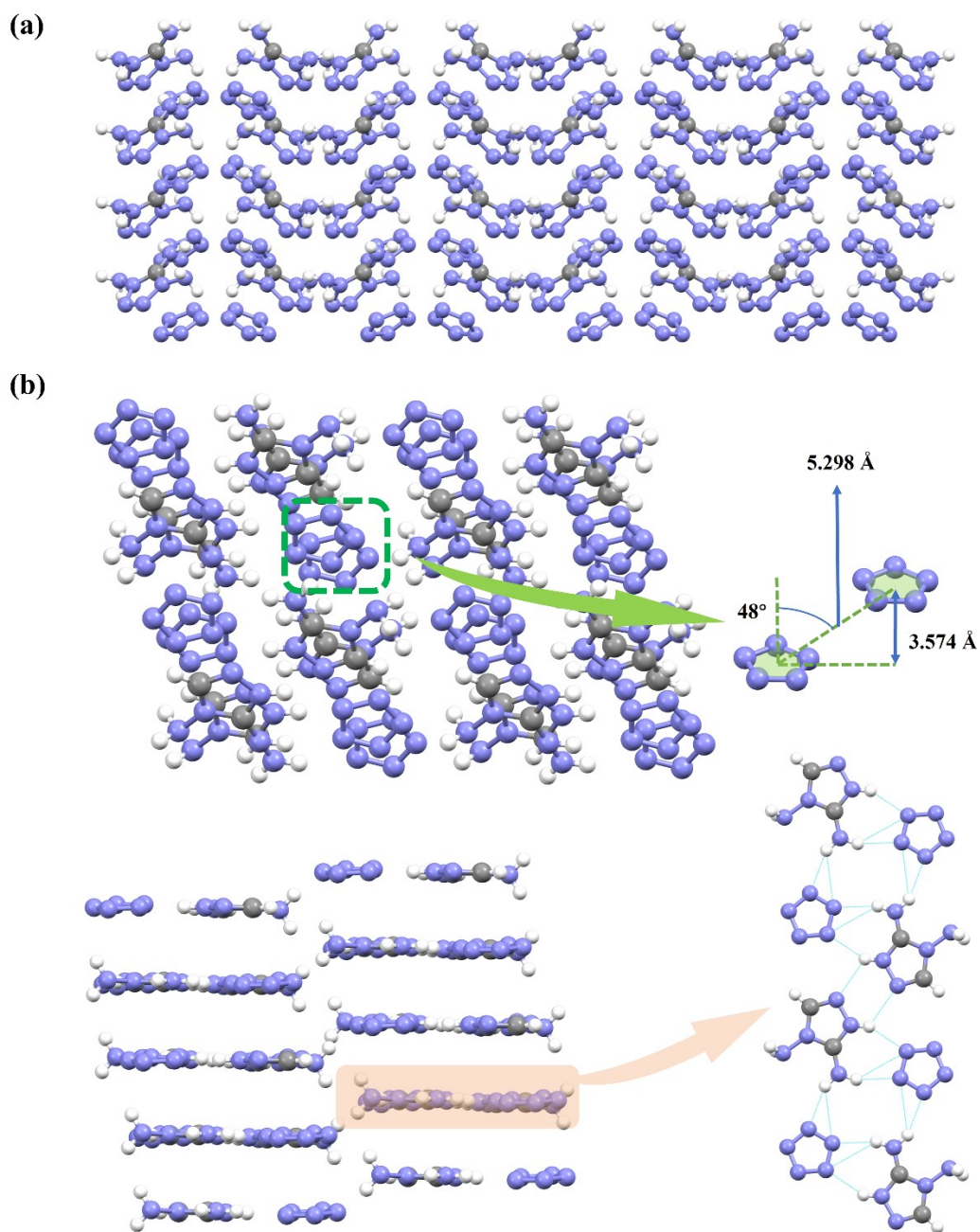
Fig. S5 Crystal stacking of cyclic-like cationic pentazolate salts (a: TATe$^+$N$_5^-$; b: C$_2$H$_6$N$_5$$^+N_5^-$)[3,4].
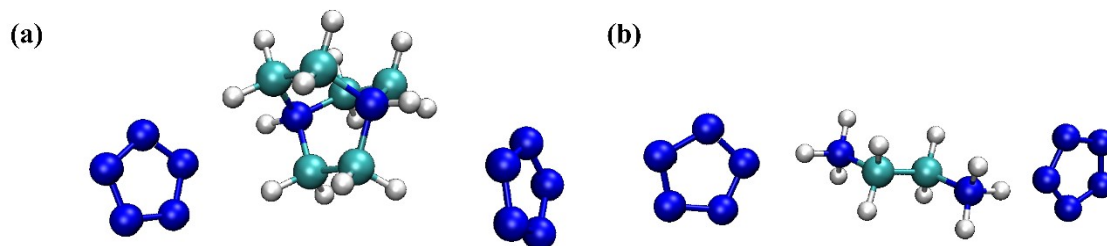
6. Structural similarity

Fig. S6 Structural similarity of compound **2** (a) and compound **3**[1] (b).

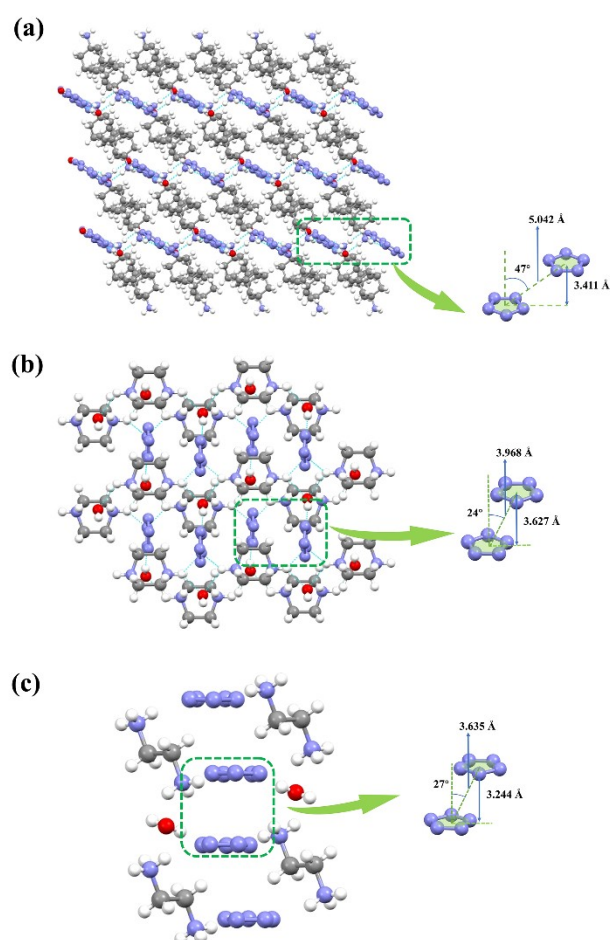## 7. Structural parameters of adjacent pentazolate anions in crystals

Fig. S7 Structural parameters of adjacent pentazolate anions in crystals (a: compound **1**·H_2O; b: compound **2**·H_2O; c: compound **3**·H_2O[1]).

8. Computational details

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 (Revision D.01) suite of programs.[5] For ESP, the geometric optimization of the structures is based on the B3LYP functional with the 6-31G** basis set, and the optimization also considers dispersion correction (D3(BJ)). To approach the conditions in the crystal as closely as possible, the coordinates for structural optimization are selected from the crystal structure, with fixed heavy atom coordinates (C and N) and only optimized hydrogen atom coordinates. IRI analyses was used B3LYP functional with the 6-31G* basis set. The gas state heat of formation was calculated by G4(MP2)_6x method. G4(MP2)_6x is a composite procedure with a lower cost but performance approaching that of G4.[6] For all the compounds, 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:

$$\Delta H_f^0(salt, 298K) = \Delta H_f^0(cation, 298K) + \Delta H_f^0(anion, 298K) - \Delta H_L \quad (Equation\ 1)$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al.[7] (Equation 2)

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

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} (Equation 3) has the form:

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

where ρ_m (g·cm^{-3}) is the density of the salt, M_m is the formula mass of the ionic compound, and values for γ (kJ·mol^{-1}·cm) and δ (kJ·mol^{-1}) are assigned literature values.[8]
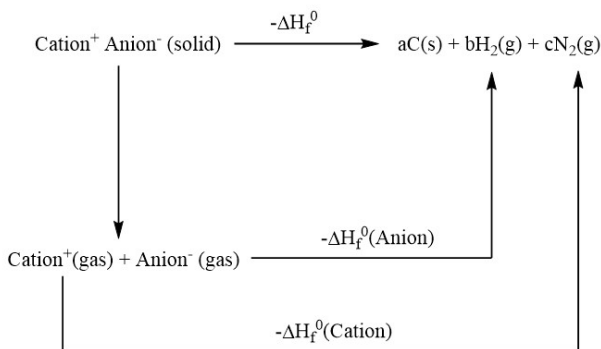
Scheme S1. Born-Haber cycle for the formation of energetic salts.

The crystal stacking coefficient (PC) of compounds 2 and 3 were calculated using Multiwfn.[9] Molecular volume is estimated by basin integration on electron density according to the AIM theory developed by R. Bader.[10] One advantage of estimating the molecular volume by AIM is that the atomic volume can be obtained. So, the molecular density can be split into parts of fragmentation contributions and even atomic contributions. Based on this method, we calculated the cationic density in compound 2 and 3, and the results are shown in **Table S14**.

Table S14 Calculation table for cationic density of compounds **2** and **3**.

Formula	Molecular weight (g mol^{-1})	Volume (Å^3)	Density (g cm^{-3})
$C_6H_{14}N_2$	114.11	148.02	1.280
$C_2H_{10}N_2$	62.08	90.64	1.137

9. NMR Spectra
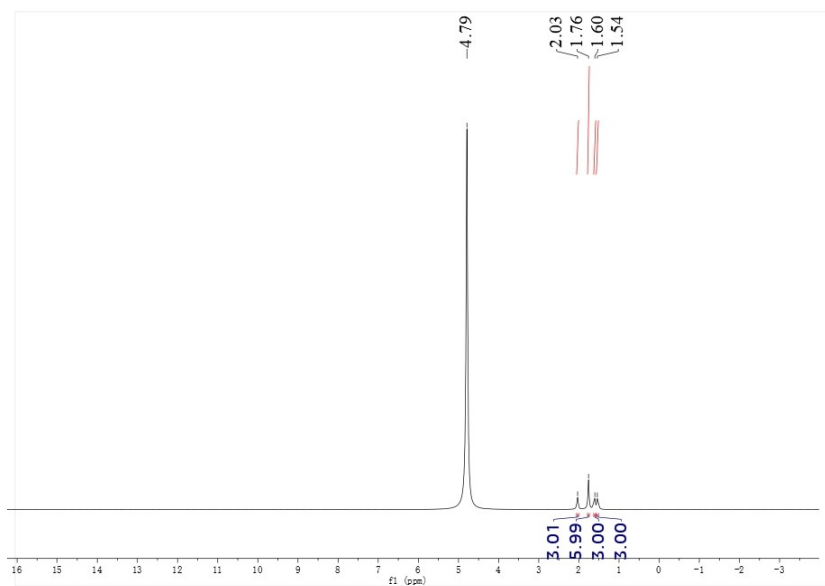
Fig. S8 ^{1}H NMR spectrum of compound **1**.

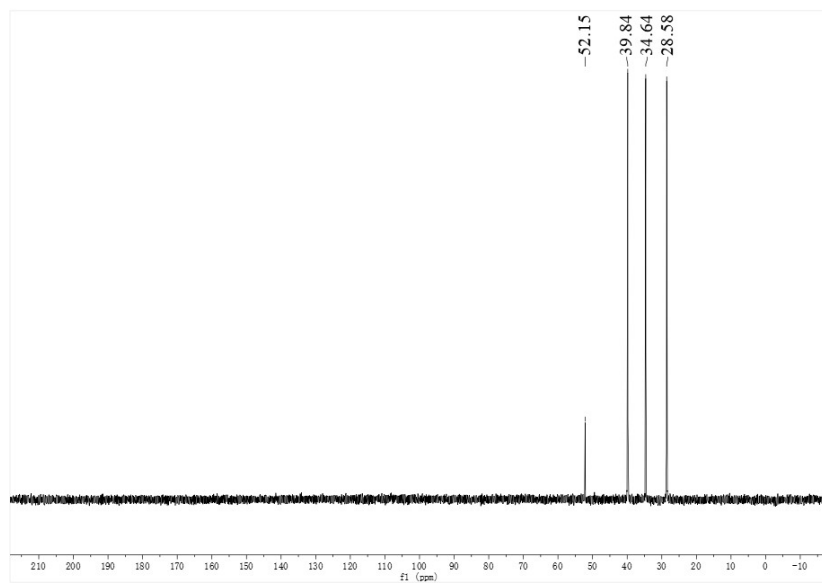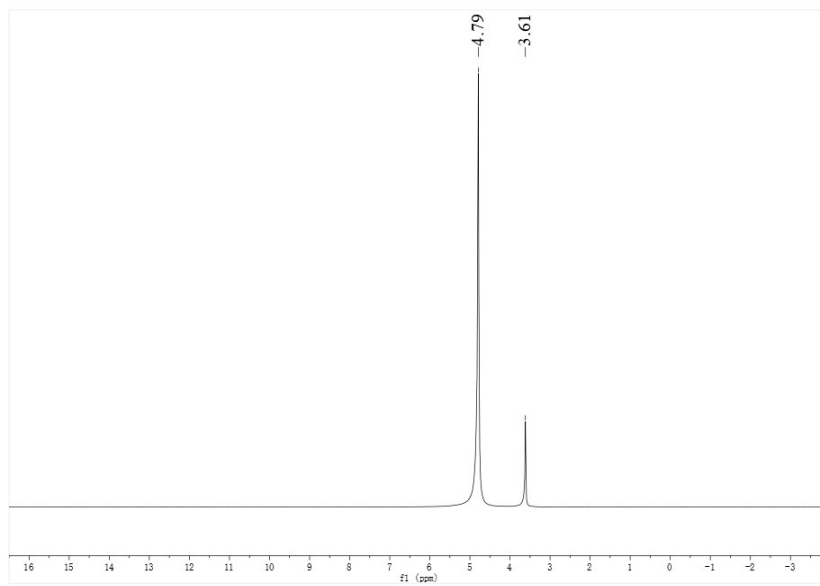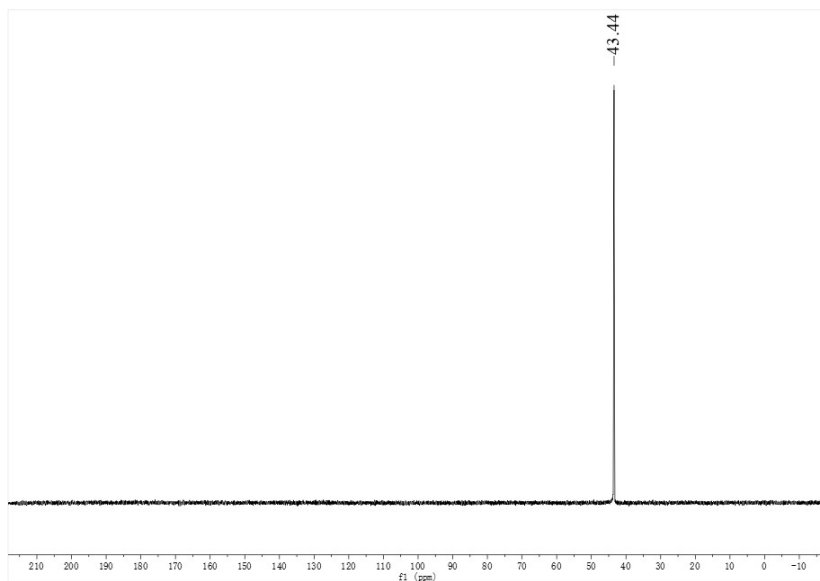**Fig. S9** ^{13}C NMR spectrum of compound **1**.

Fig. S10 ^{1}H NMR spectrum of compound **2**.

Fig. S11 ^{13}C NMR spectrum of compound **2**.

10. Reference

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