Supporting Information (SI)

The Introduction of Acylamino Group to Bridge Bis-(Nitroamino-1,2,4-Triazole): A Strategy toward insensitive Energetic Materials

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Table of contents

1. Experimental Section

X-ray crystallography

The data was collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 173 K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

2. Crystallographic Data for Compounds 3.

Table S1 Crystal data and structure refinement details for $3 \cdot 3H_2O$.

molecule	$3 \cdot 3H_2O$
CCDC number	2027401
Empirical formula	$C_5H_6N_{10}O_3 \cdot 3H_2O$
Formula weight	208.23
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.9197(14)
b/Å	7.1740(7)
c/Å	16.673(2)
$\alpha/°$	90
$\beta/°$	106.745(4)
$\gamma/°$	90
Volume/Å^3	1136.2(2)
Z	4
ϱ (calc) mg/mm^3	1.697
Absorptioncoefficient m/mm^{-1}	0.149
F(000)	600
Crystal size/mm^3	0.02×0.11× 0.23

2Θ range for data collection	3.1 to 25.6
Index ranges	-17≤h≤13,
	-7≤k≤7,
	-26≤l≤21
Reflections collected	6638
Independent reflections	2119 [R_{int} = 0.0960, R_{sigma} = 0.0863]
Data/restraints/parameters	2119/0/224
Goodness-of-fit on F2	1.040
Final R indexes [I>=2σ (I)]	0.0522，0.1276
Final R indexes [all data]	-0.25，0.35

3. Computational Methodology

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 6-311G** 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 title compounds 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

$$\Delta H_{298} = \Sigma \Delta_f H_p - \Sigma \Delta_f H_R \qquad (1)$$

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:

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

where E_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, $\circledcirc$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[6].
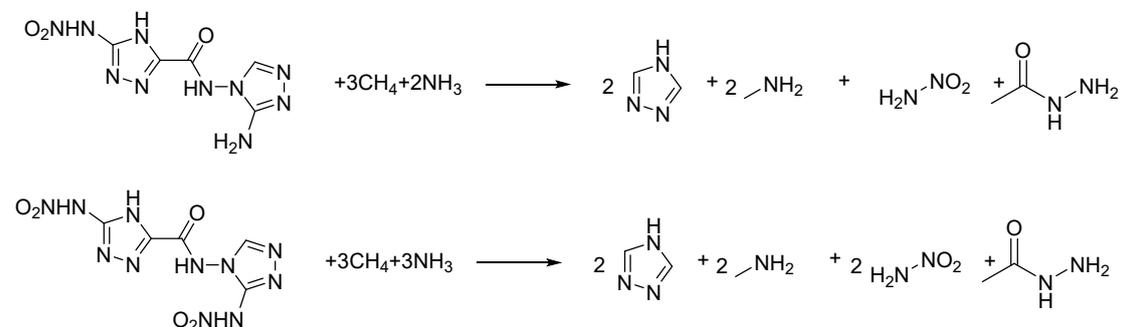
Scheme S1 Isodesmic and tautomeric reactions for **3** and **4** to calculate the HOF.

Table S2 Abinitio computational values of small molecules used in isodesmic and tautomeric reactions.

compound	E_0 [a]	ZPE [b]	H_T [c]	HOF [d]
CH_4	-40.5339263	112.26	10.04	-74.6
NH_3	-56.5826356	86.27	10.05	-45.9
CH_3NH_2	-95.8718463	160.78	11.64	-22.5
NH_2NO_2	-261.125	98.79	12.39	-3.9
$CH_3C(O)NHNH_2$	-264.537	238.35	14.49	362.5896
1,2,4-triazole	-242.2683231	150.39	12.06	192.7

[a] Total energy calculated by B3LYP/6-31G** method (*a.u.*); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}).

4. ^{1}H and ^{13}C NMR spectra of the compounds 1-13
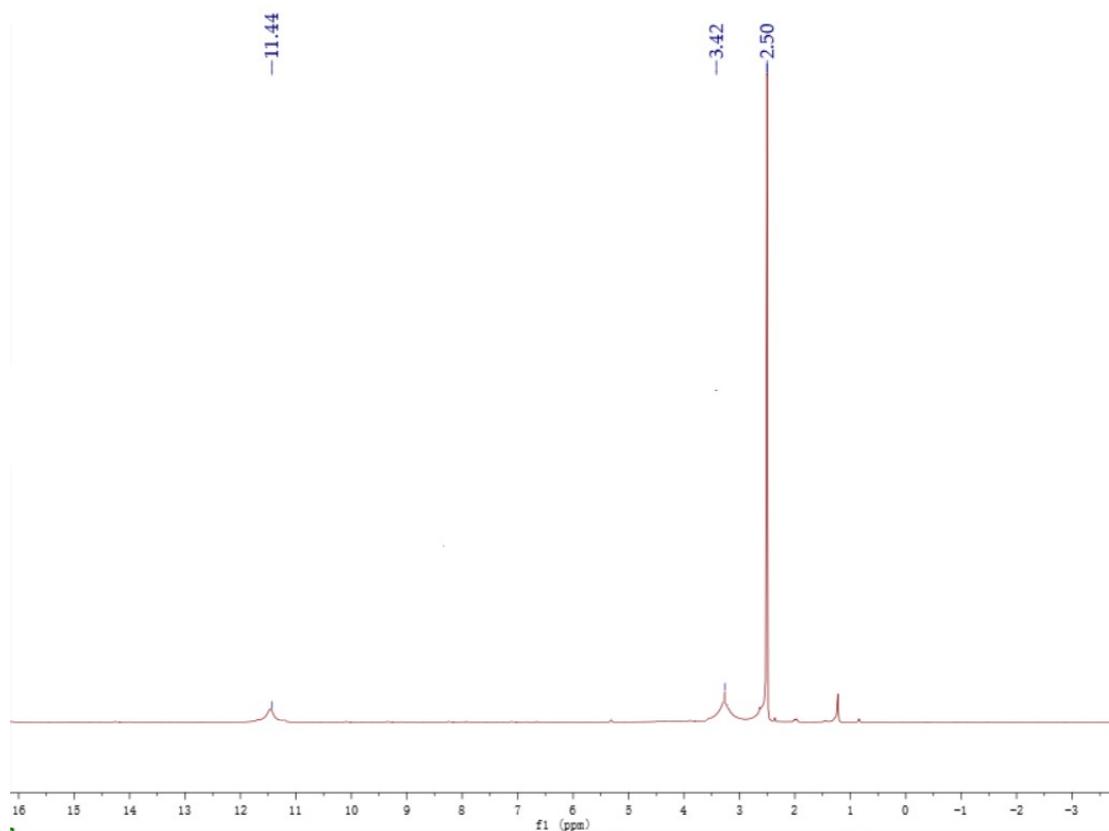
Figure S1 ^{1}H NMR spectra (500 MHz) of **1** in DMSO-d_6 at 25 °C
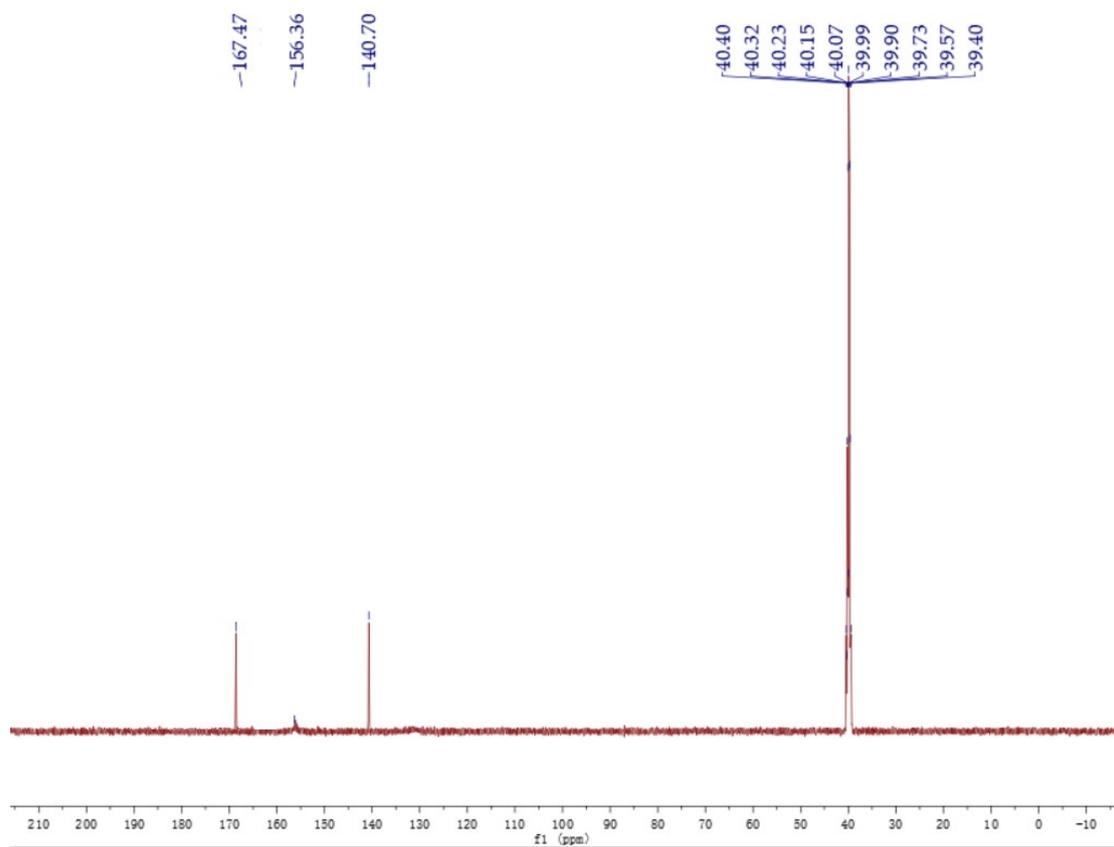
Figure S2 ^{13}C NMR spectra (125 MHz) of **1** in DMSO-d_6 at 25 °C
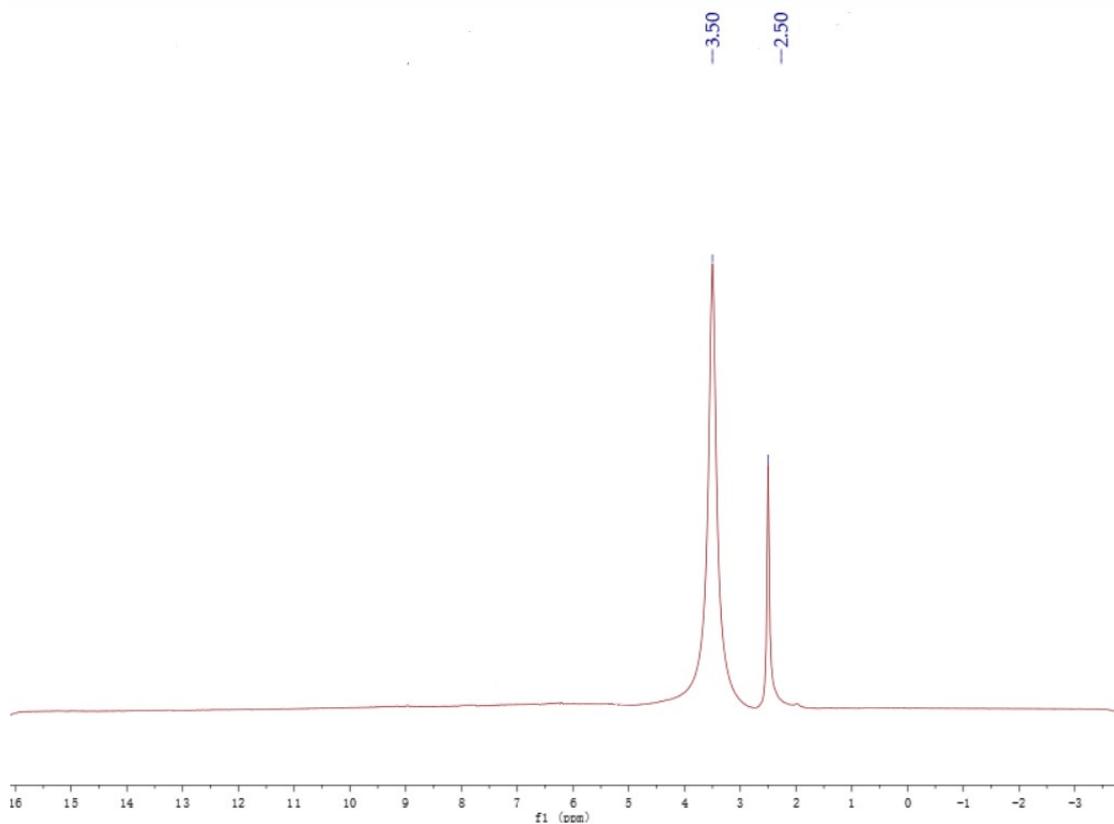
Figure S3 ^{1}H NMR spectra (300 MHz) of **2** in DMSO-d_6 at 25 °C
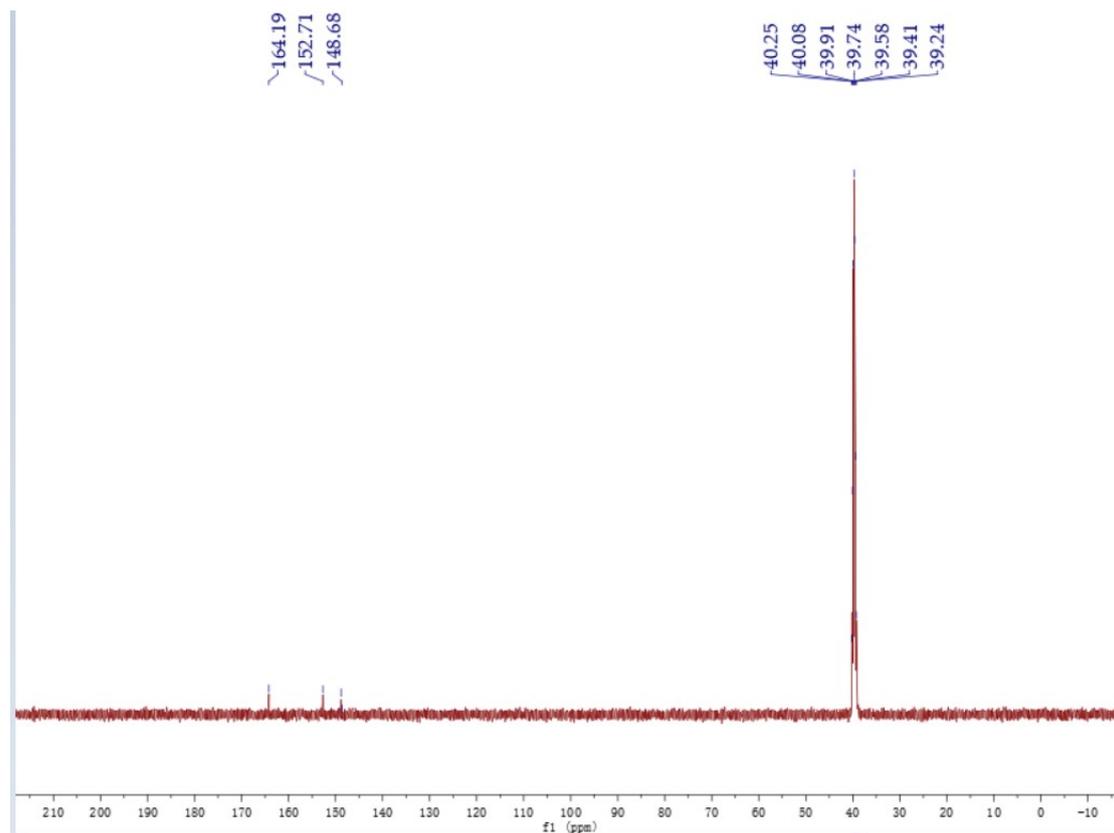
Figure S4 ^{13}C NMR spectra (125 MHz) of **2** in DMSO-d_6 at 25 °C
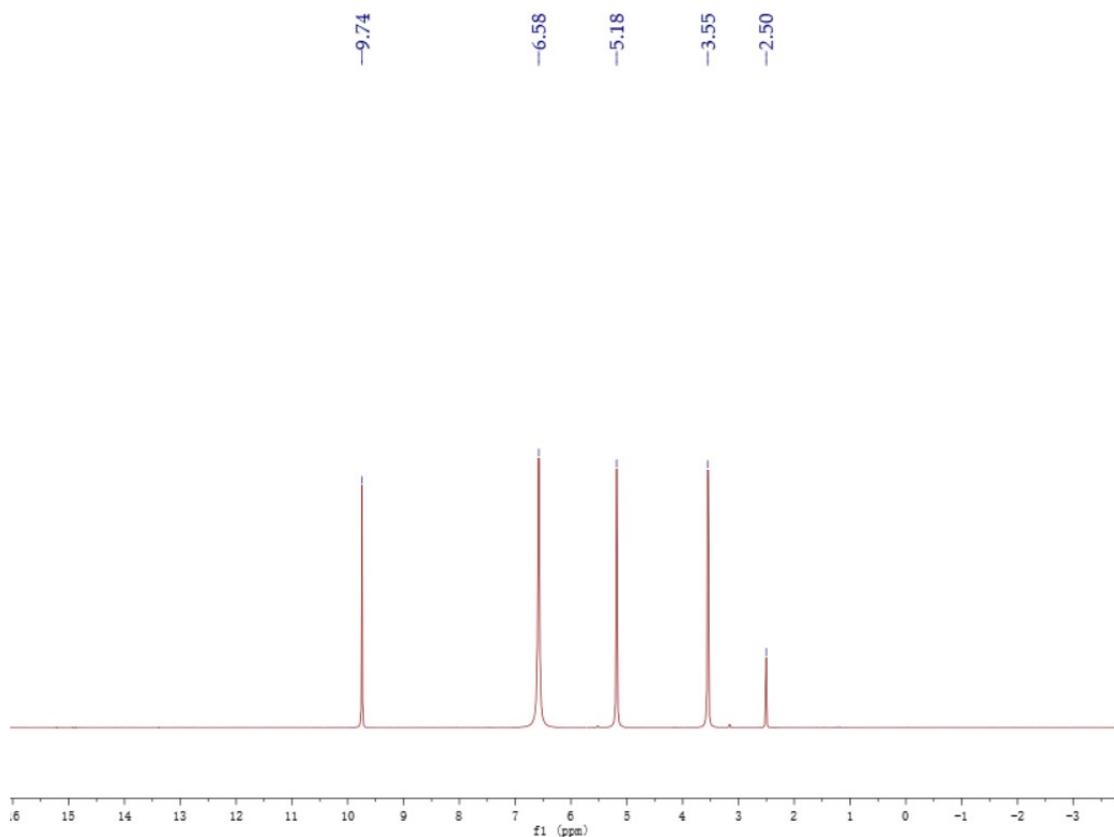
Figure S5 ^1H NMR spectra (300 MHz) of **3** in DMSO-d_6 at 25 °C

163.13
159.20
154.61
151.12
144.35

40.21
40.05
39.88
39.71
39.55

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
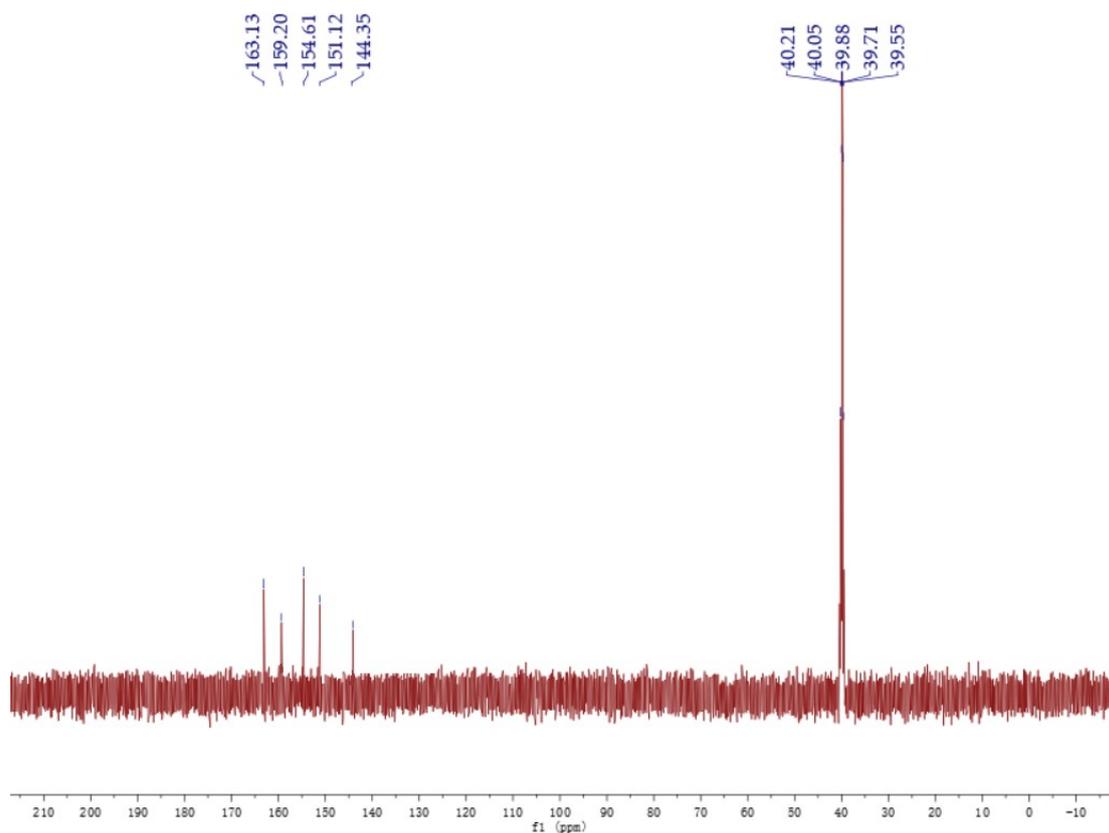
Figure S6 ^{13}C NMR spectra (125 MHz) of **3** in DMSO-d_6 at 25 °C

9.43
8.53
8.36
7.36

2.50

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)
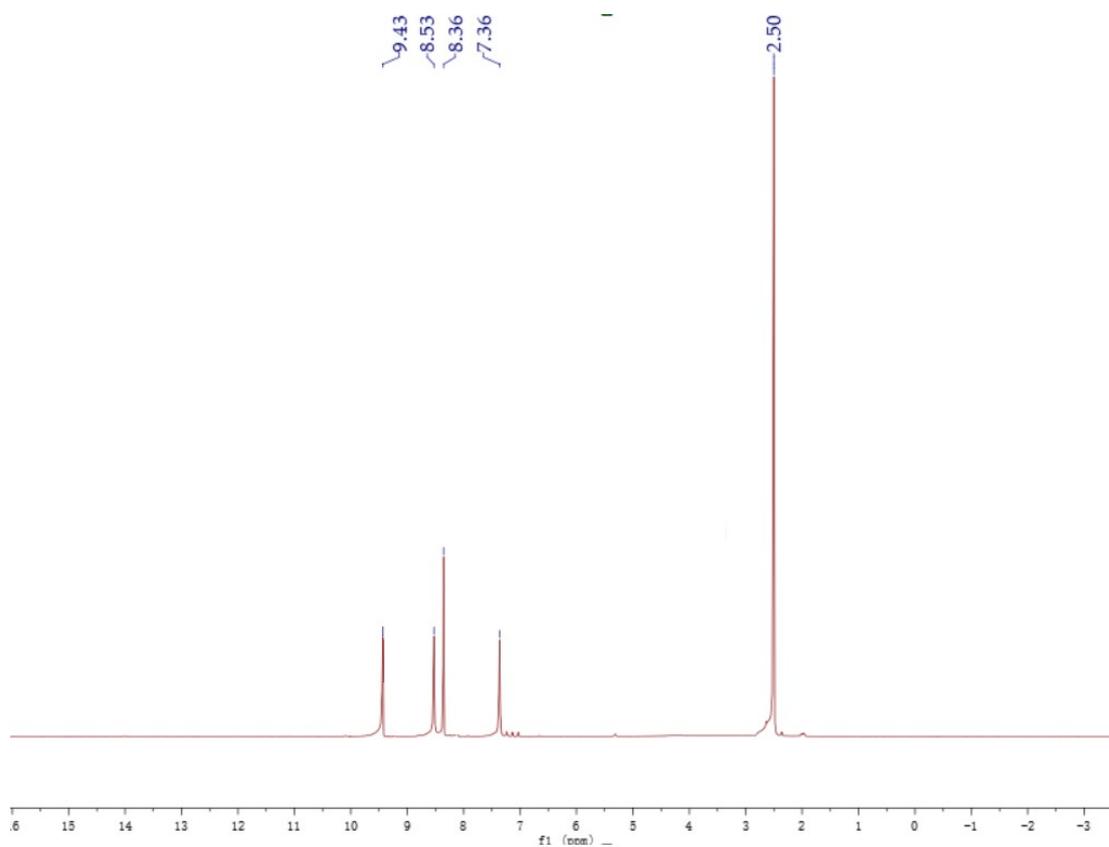
Figure S7 ^{1}H NMR spectra (300 MHz) of **4** in DMSO-d_6 at 25 °C
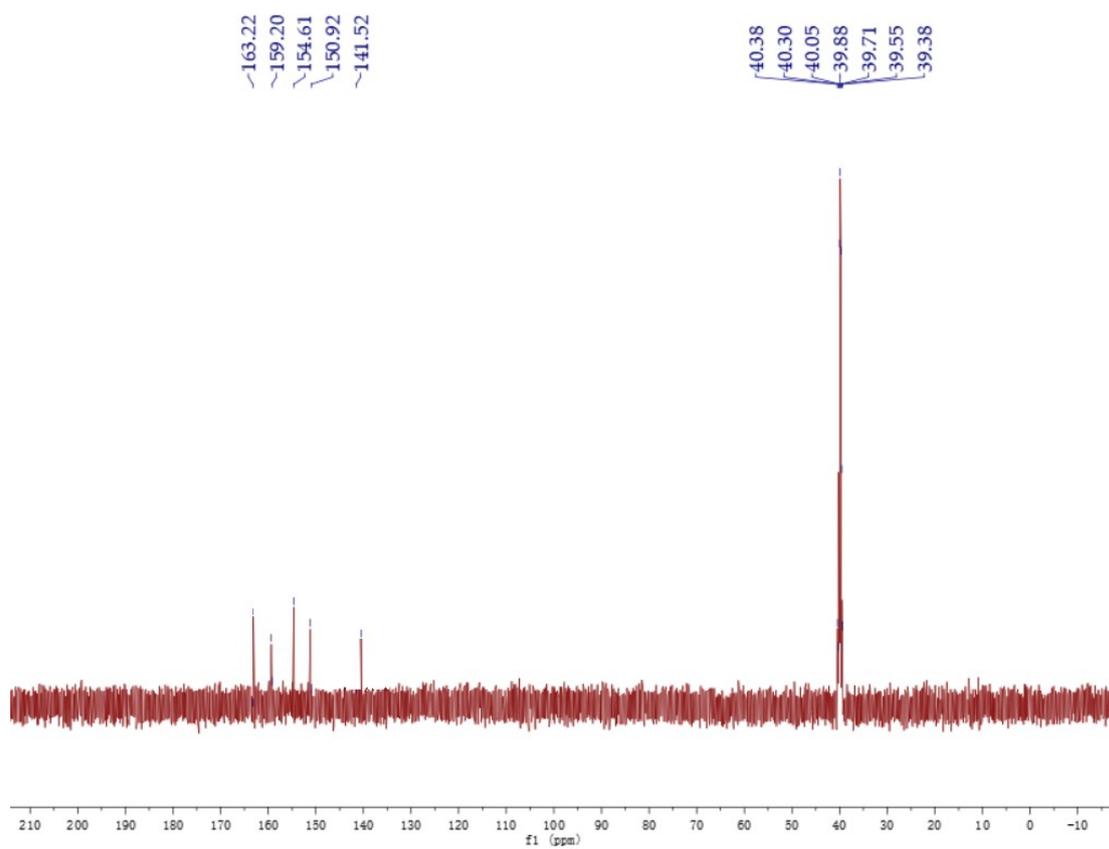
Figure S8 ^{13}C NMR spectra (125 MHz) of **4** in DMSO-d_6 at 25 °C

5. References

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