
Supporting information (SI)

Combining 1,2,4-triazole and Pyrazole Frameworks for New Insensitive Energetic Materials

Changhao Dai,[a] Jieyi Chen,[a] Jie Tang,[a] Guangbin Cheng,[a] Hongwei Yang*,[a]

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

Email: hyang@mail.njust.edu.cn

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1 Experimental section

General methods

^{1}H and ^{13}C NMR spectra were recorded on 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 500 and 125 MHz, respectively, by using either DMSO-d_6 or acetone-d_6 as the solvent and locking solvent unless otherwise stated. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported relative to DMSO. DSC was performed at a heating rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 30 mL min^{-1} on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at 25 °C. Impact sensitivity, friction sensitivity and electrostatic discharge sensitivity of samples are measured by using the standard BAM methods.

X-ray crystallography

The data were collected with a Bruker three-circle platform D8 VENTURE with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). A Kryo-Flex low-temperature device was used to keep the crystals at a constant 170.0 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 (v8.40A) 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 F^2 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 SHELXT and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

2 The crystallographic data

The crystal of **$6 \bullet 3H_2O$** was performed on D8 VENTURE with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å), respectively. Integration and scaling of intensity data were accomplished using the SAINT program. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full- matrix least-squares technique using SHELXT2018. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS Relevant crystal data and refinement results are summarized in Table S1.

Table S1. Crystal data and structure refinement for **$6 \bullet 3H_2O$.**

Crystal	**$6 \bullet 3H_2O$.**
CCDC number	2053151
Empirical formula	$C_7H_{16}C_{l2}N_{10}O_{11}$
Formula weight	487.20
Temperature	170.0(2)K
Crystal system	triclinic
Space group	*P-1*
a [Å]	4.9672(3) Å
b [Å]	12.7852(10) Å
c [Å]	14.3081(13) Å
α [°]	88.990(3)°
β [°]	81.510(2)°
γ [°]	86.431(2)°
Volume	896.93(12) $Å^3$
Z	2
ρ(g cm^{-3})	1.804
F(000)	500.0

Crystal size (mm^3)	0.12 × 0.08 × 0.04
Theta range for data collection	4.316 to 52.772°
Index ranges	-
Independent reflections	3359[R_{int} = 0, R_{sigma} = 0.1158]
Goodness-of-fit on F^2	1.085
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0694, wR_2 = 0.1968
R indices (all data)	R_1 = 0.1048, wR_2 = 0.1758

3 Theoretical study

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 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. Atomization energies were calculated by the CBS-4M.[3] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.[4]

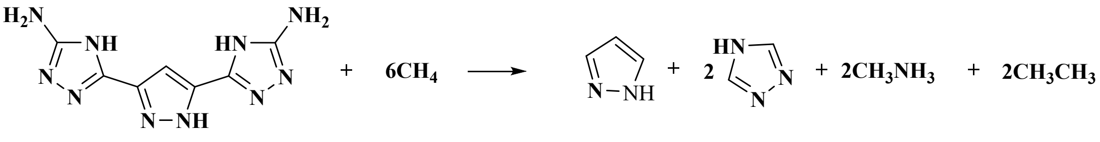
The predictions of heat of formation (*HOF*) adopt the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. 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

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

Where $\sum\Delta_f H_P$ and $\sum\Delta_f H_R$ 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 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 $\Delta(nRT)$ for the reactions of ideal gas. For the isodesmic reaction, $\Delta n = 0$, 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 is available from the experiments·



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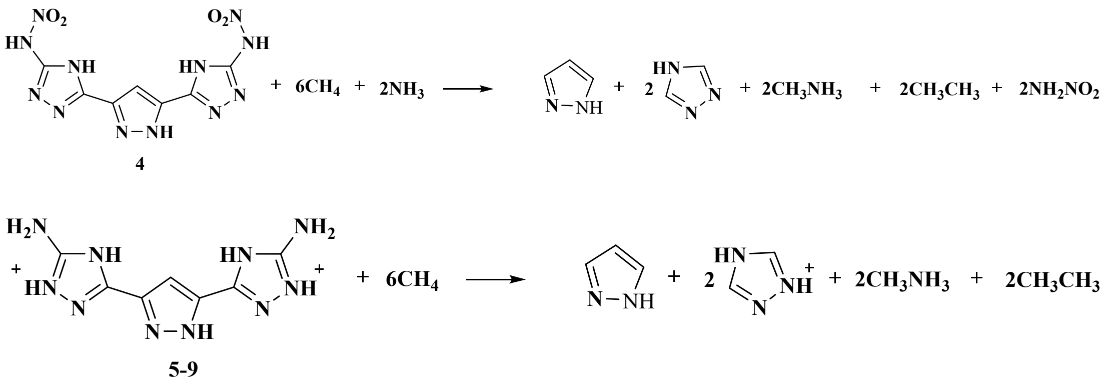
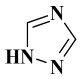
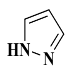


Scheme S1. Isodesmic reactions of target compounds.

Table S2. Ab initio 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
NH_2NO_2	-261.1248168	98.79	12.39	-3.9
CH_3NH_2	-95.8938402	160.78	11.64	-22.5
CH_3CH_3	-79.8565413	187.31	11.79	-84
	-242.3203873	150.39	12.06	192.7
	-226.2603313	179.2	12.57	177.4
3	-819.23	445.53	37.45	683.54
4	-1228.30	476.34	52.88	795.94

[a]Total energy calculated by B3LYP/6-311+G**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 Reference

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D. 01, Gaussian. Inc. Wallingford CT, 2009.

[2] P. C. Hariharan, J. A. Pople, Theor. Chim. Acta. 1973, 28, 213-222.

[3] J. W. Ochterski, G. A. Petersson, J. A. Montgomery, J. Chem. Phys. 1996, 104, 2598-2619.

[4] H. D. B. Jenkins, D. Tudeal, L. Glasser, Inorg. Chem. 2002, 41, 2364-2367.

5 ^{1}H and ^{13}C NMR spectra of compounds

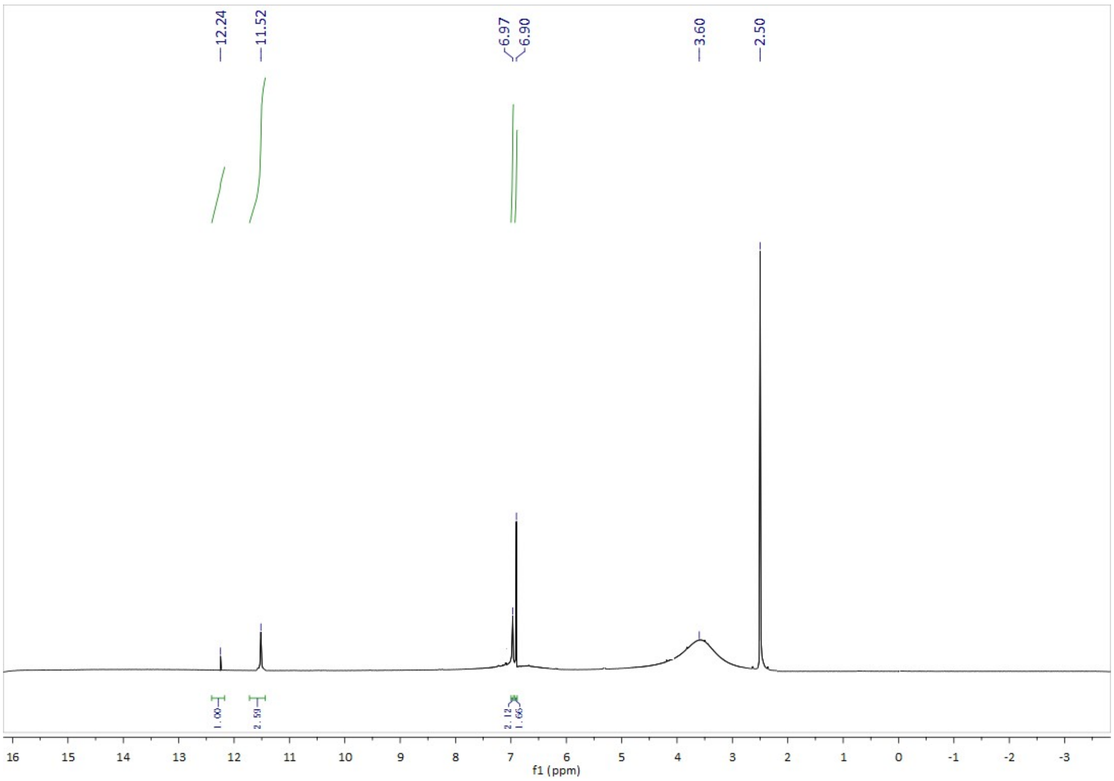


Figure S1 ^{1}H NMR spectra (500 MHz) of **3** in [D$_6$] DMSO at 25 ^{o}C.

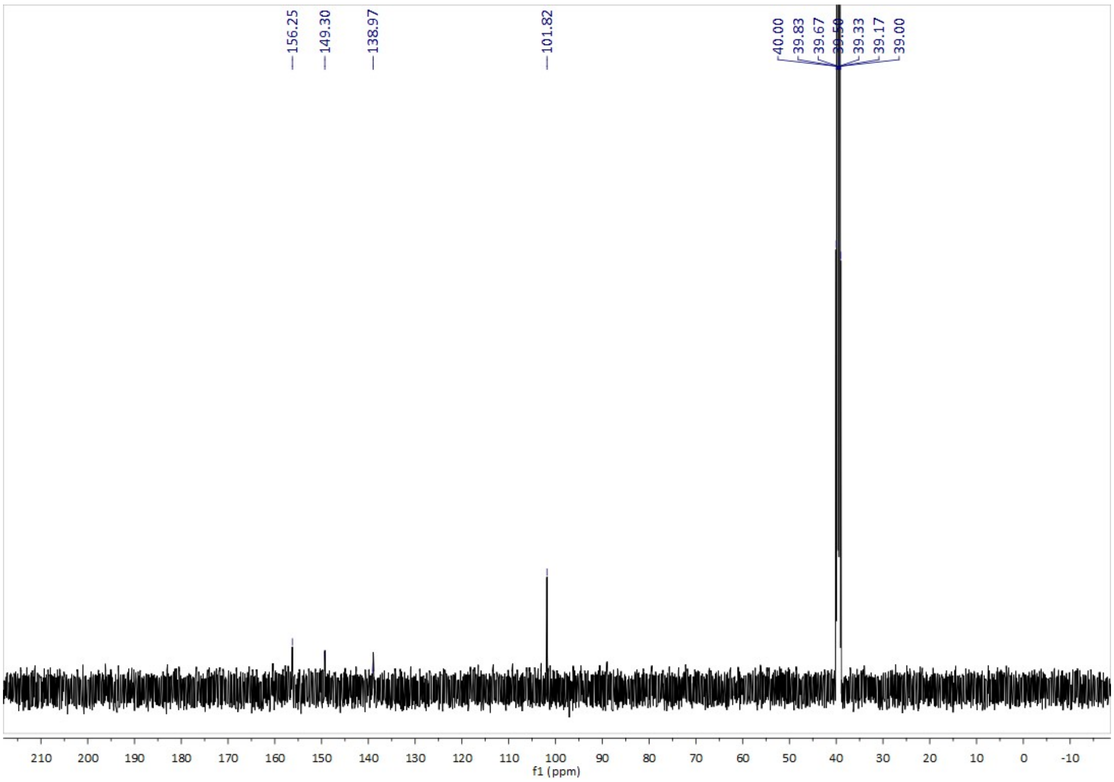


Figure S2 ^{13}C NMR spectra (125 MHz) of **3** in [D$_6$] DMSO at 25 ^{o}C.

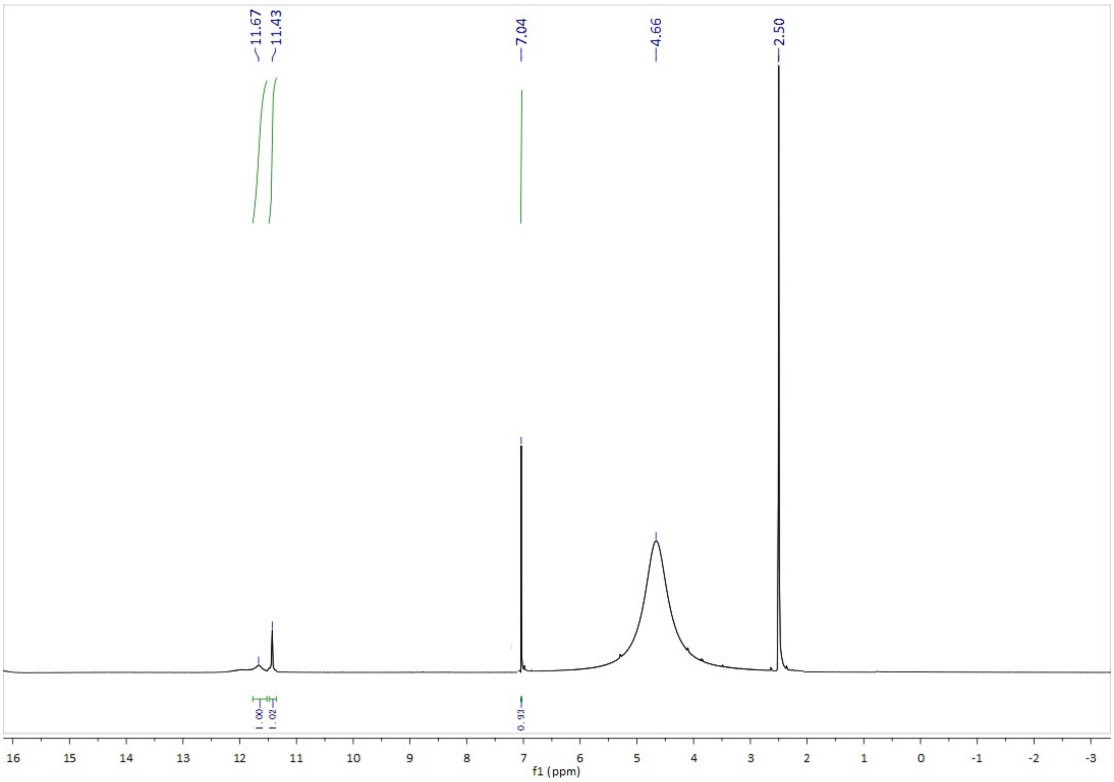


Figure S3 ^{1}H NMR spectra (500 MHz) of **4** in [D$_6$] DMSO at 25 ^{o}C

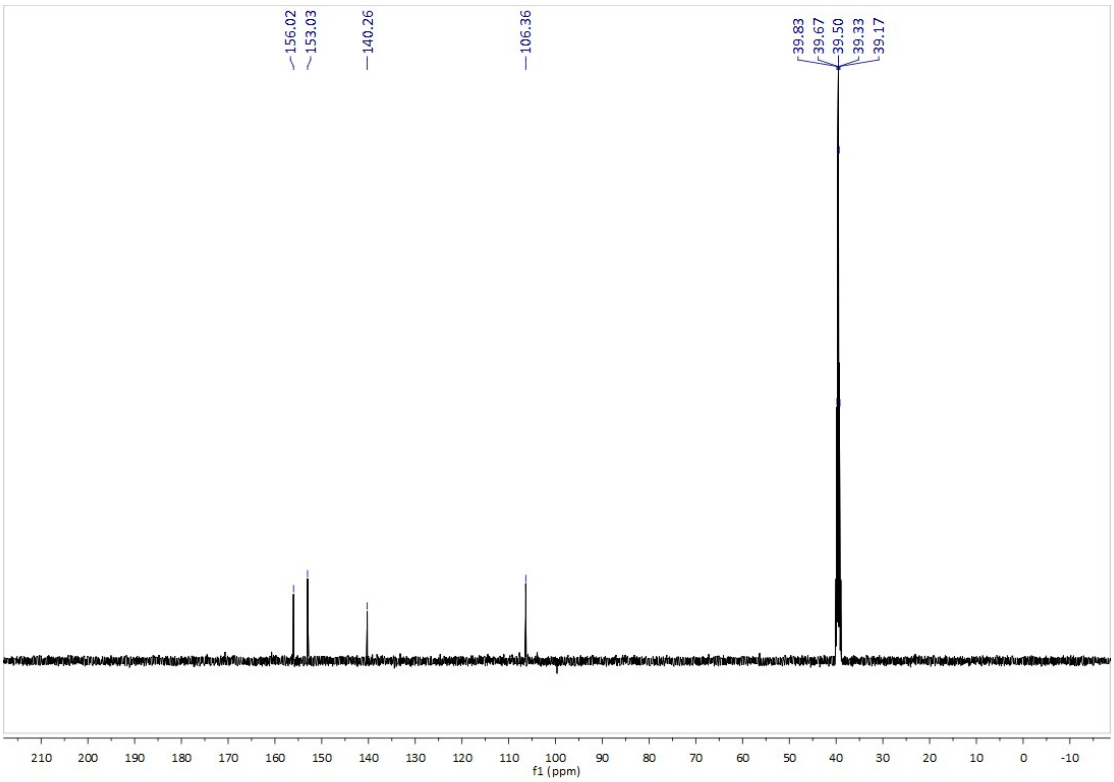


Figure S4 ^{13}C NMR spectra (125 MHz) of **4** in [D$_6$] DMSO at 25 ^{o}C

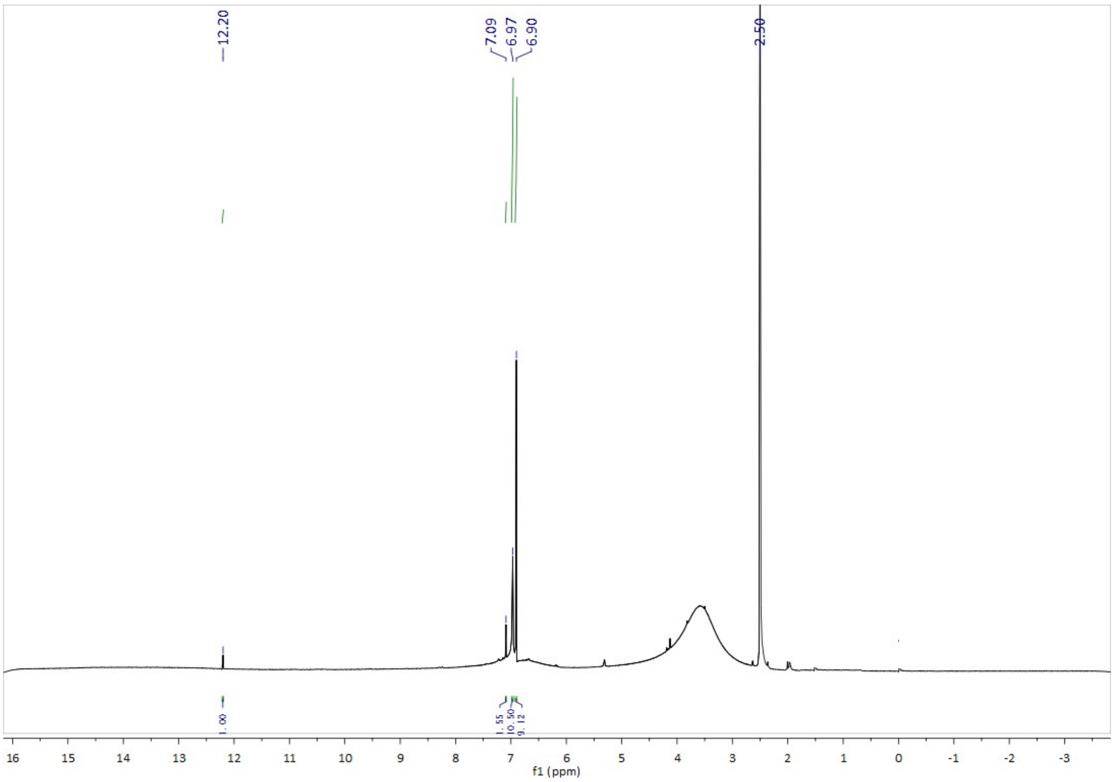


Figure S5 ^{1}H NMR spectra (500 MHz) of **5** in [D$_6$] DMSO at 25 ^{o}C

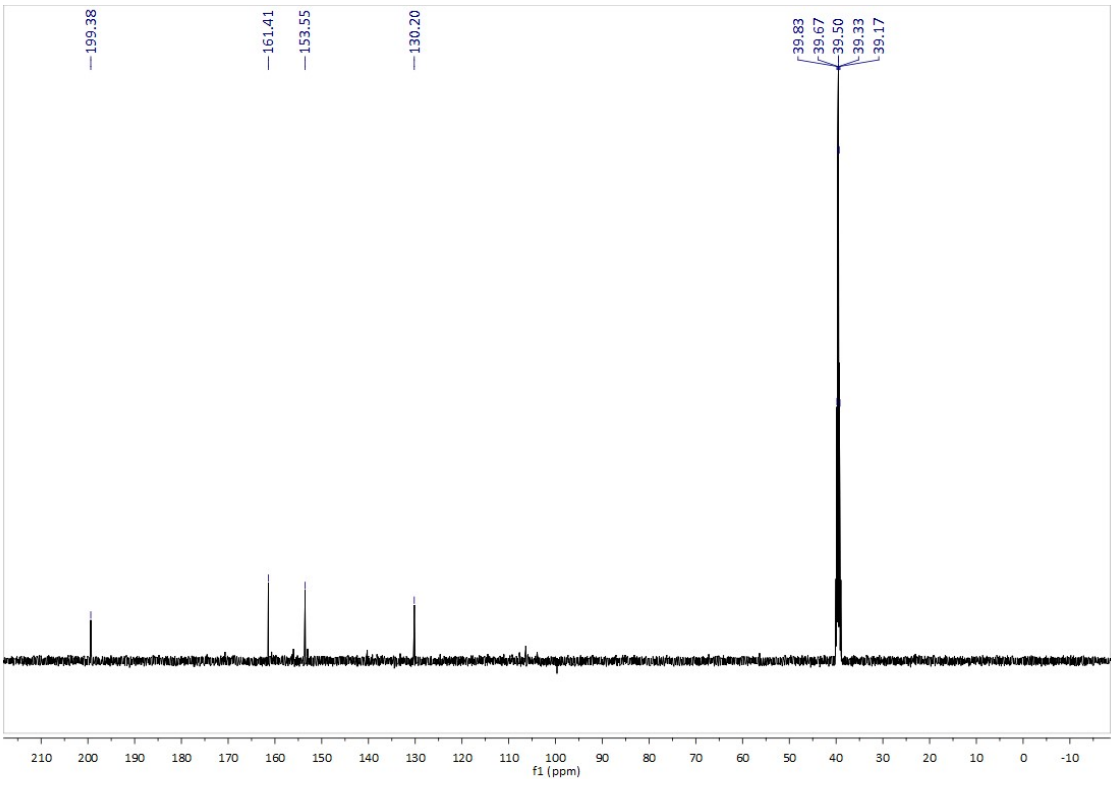


Figure S6 ^{13}C NMR spectra (125 MHz) of **5** in [D$_6$] DMSO at 25 ^{o}C

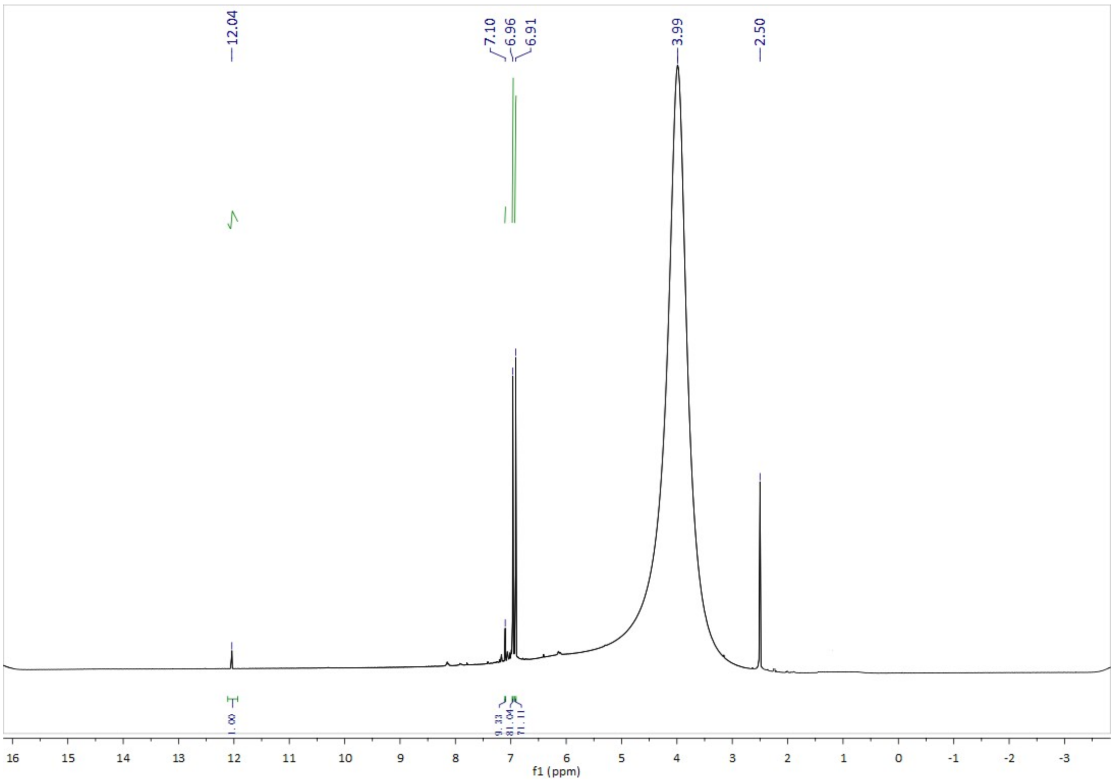


Figure S7 ^{1}H NMR spectra (500 MHz) of **6** in [D$_6$] DMSO at 25 ^{o}C.

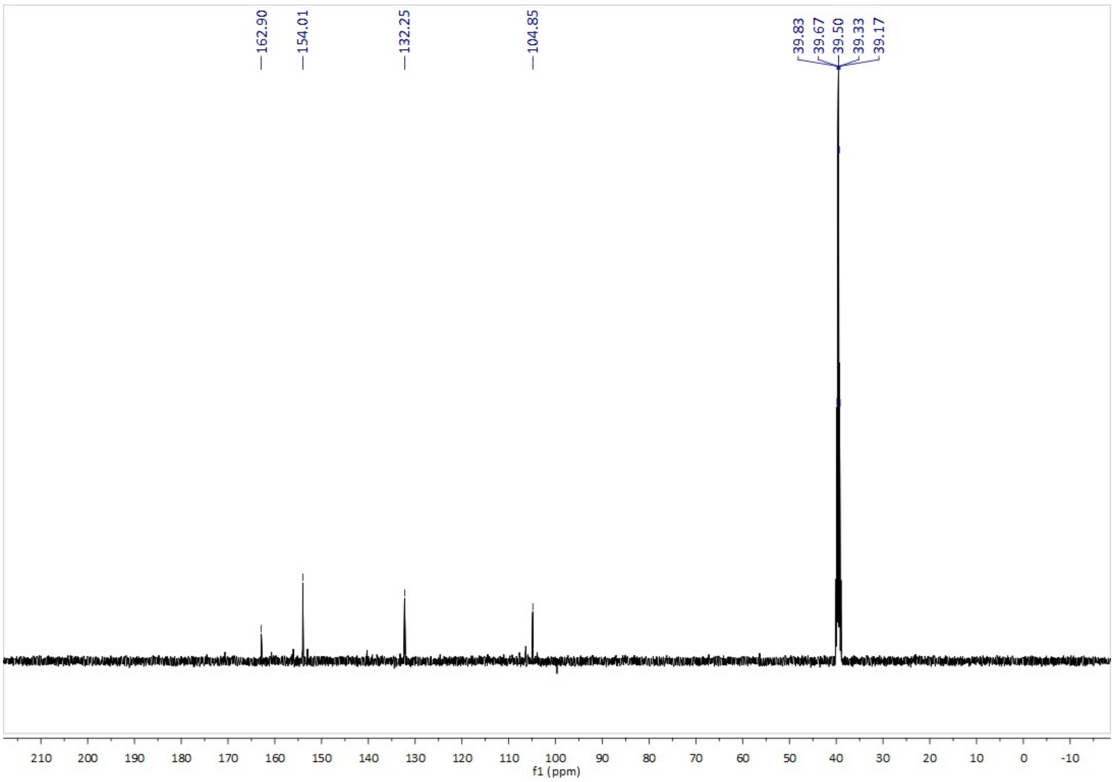


Figure S8 ^{13}C NMR spectra (125 MHz) of **6** in [D$_6$] DMSO at 25 ^{o}C.

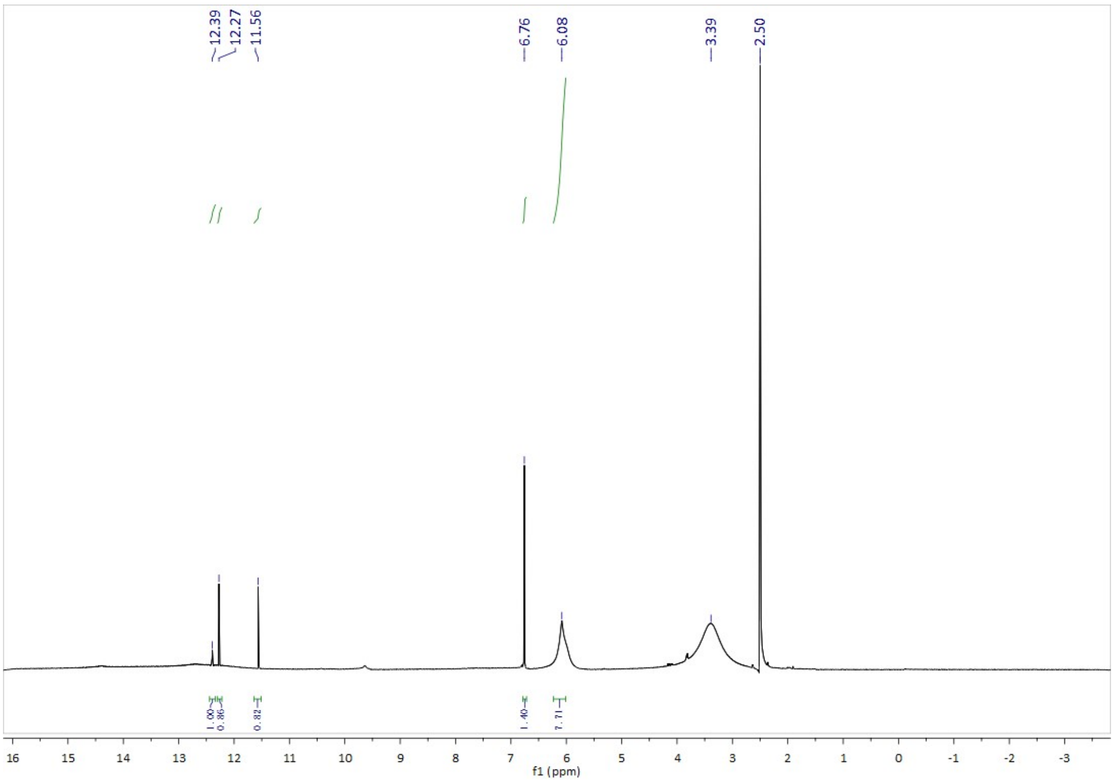


Figure S9 ^{1}H NMR spectra (500 MHz) of **7** in [D$_6$] DMSO at 25 ^{o}C.

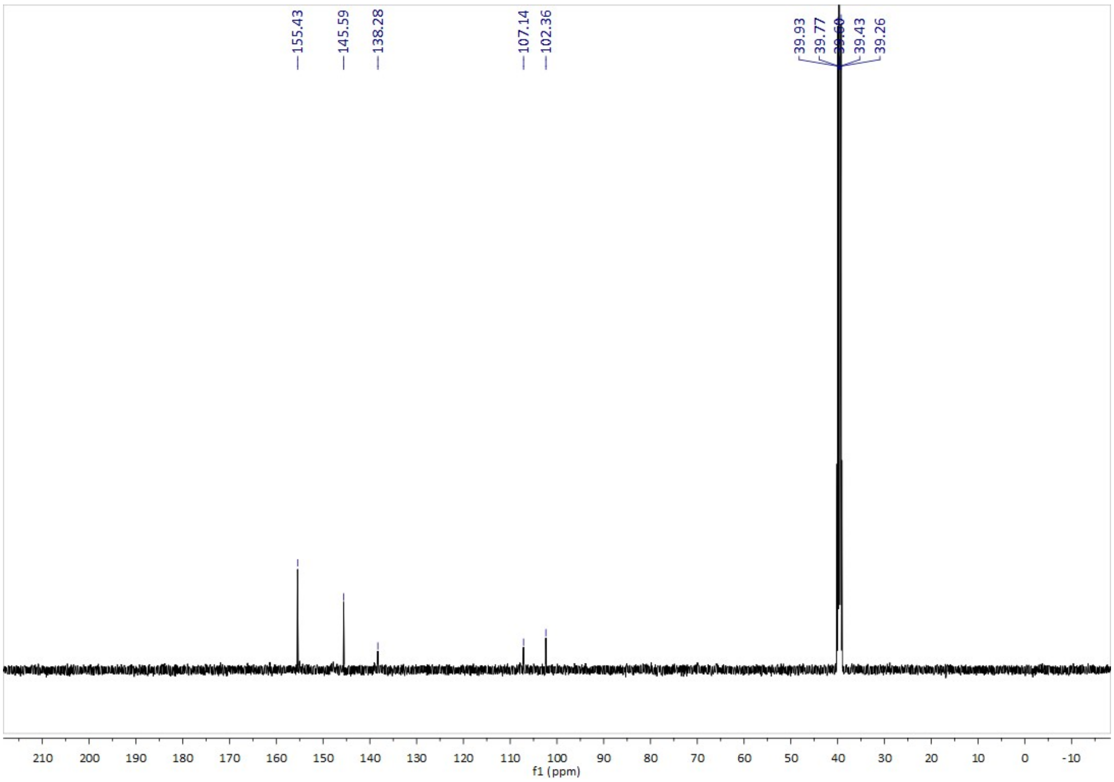


Figure S10 ^{13}C NMR spectra (125 MHz) of **7** in [D$_6$] DMSO at 25 ^{o}C.

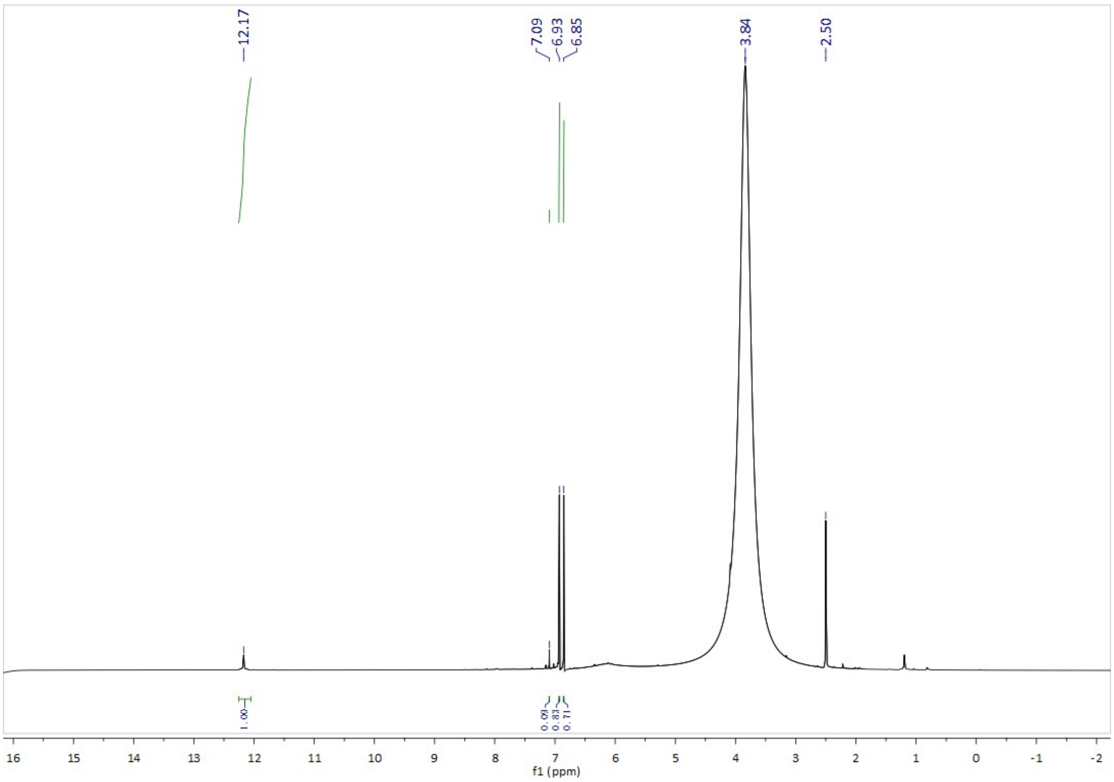


Figure S11 ^{1}H NMR spectra (500 MHz) of **8** in [D$_6$] DMSO at 25 ^{o}C.

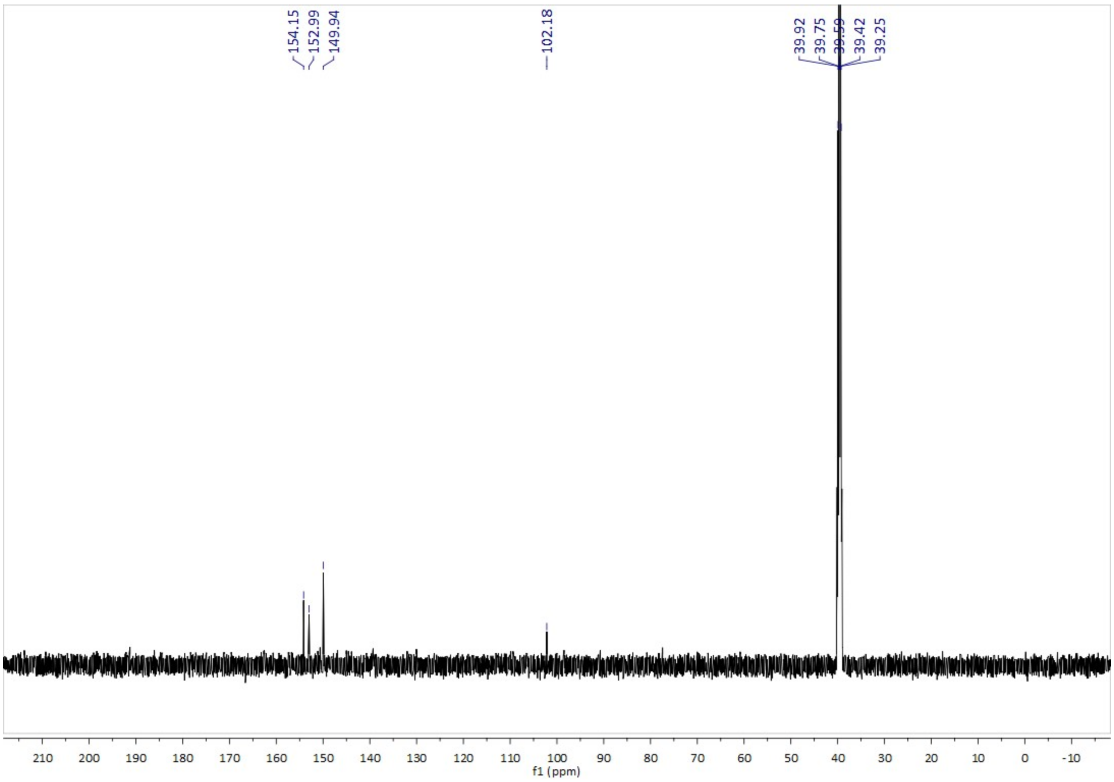


Figure S12 ^{13}C NMR spectra (125 MHz) of **8** in [D$_6$] DMSO at 25 ^{o}C.

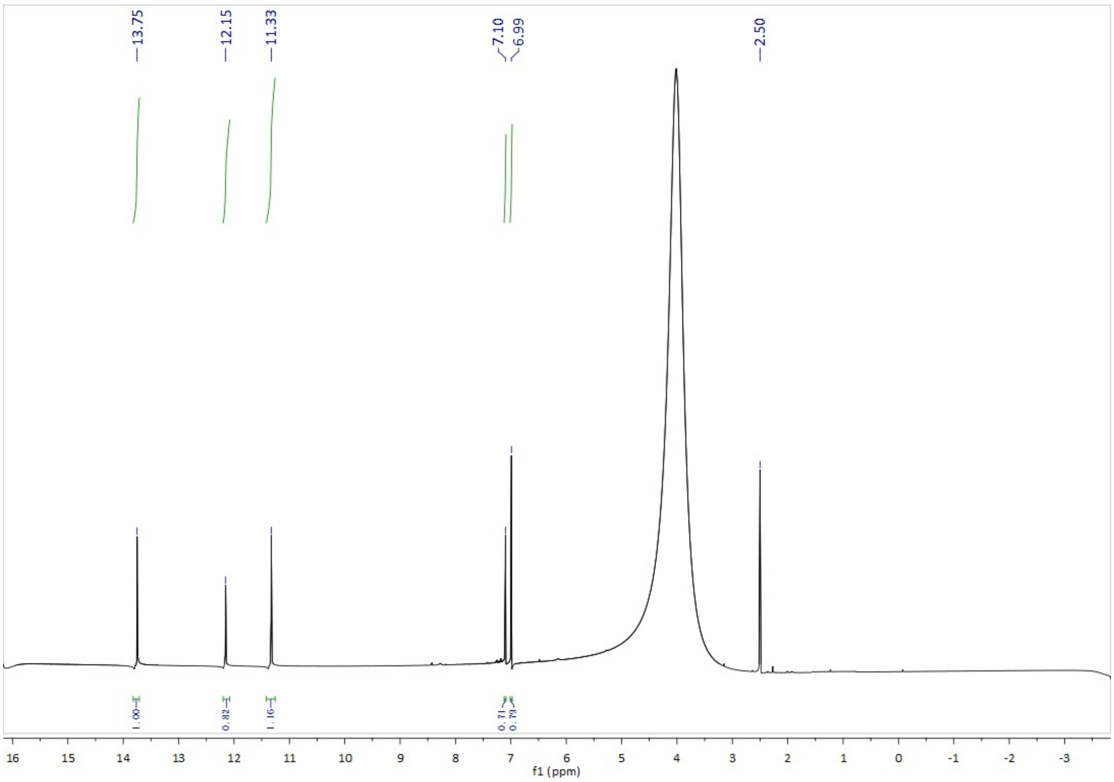


Figure S13 ^{1}H NMR spectra (500 MHz) of **9** in [D$_6$] DMSO at 25 ^{o}C.

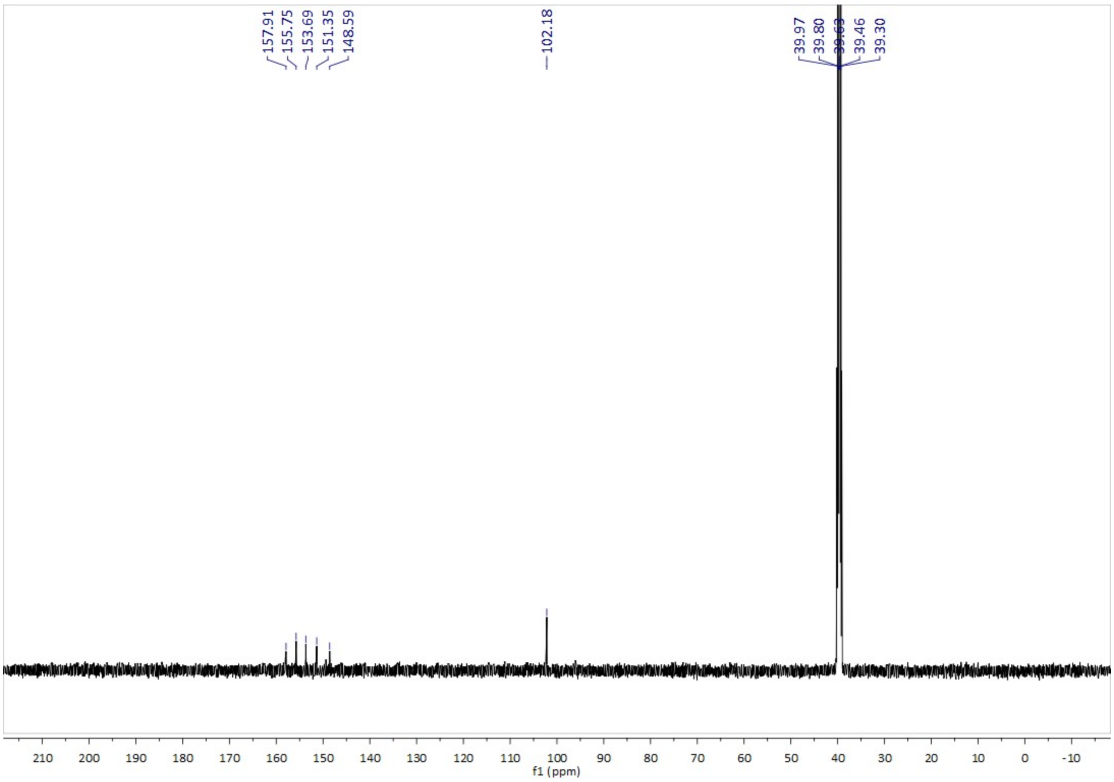


Figure S14 ^{13}C NMR spectra (125 MHz) of **9** in [D$_6$] DMSO at 25 ^{o}C.