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New heterocyclic furazano[3,4-*d*][1,2,3]triazine system as a platform for energetic compound engineering

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CONTENTS

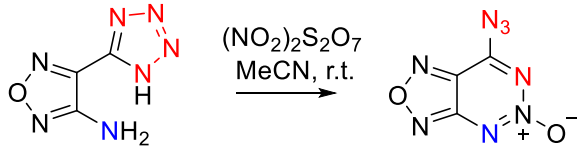
Experimental

IR spectra were recorded on a BrukerALPHA instrument in KBr pellets. ^{13}C, and ^{14}N spectra were acquired on a Bruker AM-300 instrument (75.47 and 21.69 MHz, respectively) in $CDCl_3$ or DMSO-d_6 at 299 K. The chemical shifts of ^{13}C nucleus were reported relative to TMS, for ^{14}N – relative to $MeNO_2$, high-filed chemical shifts are given with a minus sign. High-resolution mass spectra with electrospray ionization were recorded on a Bruker MicroOTOF II instrument. Elemental analysis was performed on a PerkinElmer 2400 Series II instrument. The reaction progress and purity of the obtained compounds were controlled by TLC on Merck Silicagel 60 F_{254} plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm).

Materials Most of the reagents and starting materials were purchased from commercial sources and used without additional purification. The starting 3-amino-4-(tetrazol-5-yl)furazan (**2**)[S1,S2], 3-amino-4-(2-hydroxytetrazol-5-yl)furazan (**3**)[S3,S4] and nitronium salts[S5-S7] were obtained published procedures.

Caution! Although we have encountered no difficulties during preparation and handling of these compounds, they are dangerous high explosives. Manipulations must be carried out by using appropriate standard safety precautions.

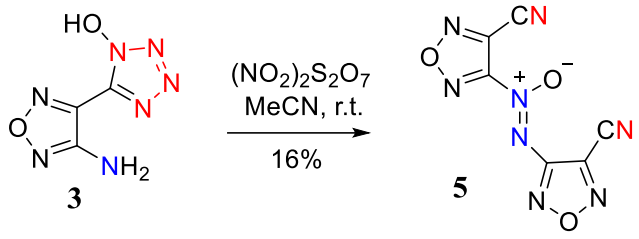
7-Azidofurazano[3,4-*d*][1,2,3]triazine 5-oxide (**1**)



2 **1**

Tetrazole derivative **2** (1.46 g, 9.5 mmol) was added in small portions to a suspension of $(NO_2)_2S_2O_7$ (7.5 g, 28 mmol) in MeCN (60 ml) at 20 °C with stirring under dried conditions. The mixture was stirred at room temperature for 4 h, then diluted with CH_2Cl_2 (60 ml), filtered and evaporated. The residue was purified by column chromatography (eluting with 3:1 $CHCl_3$/EtOAc) to give product **1** (1.17 g, 68%) as colorless crystals. R_f = 0.25 ($CHCl_3$: EtOAc, 3:1). ^{13}C NMR ($CDCl_3$) δ 131.47, 158.06, 159.47. ^{14}N NMR ($CDCl_3$) δ –47 ($\Delta\nu_{1/2}$ = 150 Hz, N→O), –135 ($\Delta\nu_{1/2}$ = 35 Hz, N_3). IR (KBr): 2246, 2199, 2170, 1617, 1537, 1496, 1461,1414, 1384, 1365, 1227, 1169, 1055, 1040, 962, 873, 844, 766, 751, 705, 600, 551, 535, 443 cm^{-1}. MS, *m/z*: 180 $[M]^+$. HRMS (ESI), *m/z* calcd for $C_3N_8O_2$ 181.0220 $[M + H]^+$, found, 181.0217 $[M + H]^+$. Anal. Calcd for $C_3N_8O_2$ (180.09): C, 20.01; N, 62.22. Found: C, 20.08; N, 62.19.

4,4'-Dicyanoazoxyfurazan (**5**)



Under dried conditions compound **3** (1.56 g, 9.2 mmol) was added in small portions with stirring to a suspension of $(NO_2)_2S_2O_7$ (6.2 g, 23 mmol) in MeCN (70 ml) at 5°C (in an ice-bath) upon which the mixture thickened and gas release was observed. After the addition was complete, the reaction was stirred for 2 h at 15-20 °C and then diluted with CH_2Cl_2 (70 ml), filtered and evaporated. The residue was purified by column chromatography (eluting with 3:1 $CHCl_3$/EtOAc, R_f = 0.33). Product containing fractions were combined and solvent removed *in vacuo* to give crude product **5** as a bluish solid, which crystallized from $CHCl_3$/EtOAc as colorless needles; yield: 176 mg (16%); mp 169–169.5 °C. ^{13}C NMR ($CDCl_3$) δ 106.1, 107.0, 130.6, 131.8, 154. 8, 159.9; ^{14}N NMR ($CDCl_3$) δ –69 ($\Delta\nu_{1/2}$ = 250 Hz, N→O). IR (KBr): 2272, 1563, 1517, 1472, 1448,1403, 1330, 1226, 1155, 1127, 1034, 937, 891, 775, 612, 582, 550, 422 cm^{-1}. MS, *m/z*: 232 $[M]^+$. HRMS (ESI), *m/z* calcd for $C_6N_8O_3$ 254.9980 $[M + Na]^+$, found: 254.9986 $[M + Na]^+$. Anal. Calcd for $C_6N_8O_3$ (232.12): C, 31.05; N, 48.28. Found: C, 31.13; N, 48.24.

Enthalpy of formation

The enthalpy of formation in the gas phase for compound **1** was calculated by using the program package Gaussian 03 (G3B3)[S8] and converted to the enthalpy of formation in the condensed phase ($\Delta_fH_{(s)} = \Delta_fH_{(g)} - \Delta H_{subl}$) taking into account the enthalpy of sublimation calculated in accordance with the Trouton rule: $\Delta H_{subl} = (188 \cdot T_m(K)/1000)/4.184$.[S9]

Crystal structure refinement and packing analysis for compound **1**

It is interesting to compare crystal packing of the present compound **1** with its nitropyrazole analog.[S11] We analyzed crystal packing of 452 and X compounds using the Crystal Explorer code.[S12] The difference of sensitivity values for compound **1** and **NAPTO** apperas to be in line with the analysis of Hirshfeld surfaces[S13] and distributions of types of close contacts penetrating these surfaces (see Figures S1 and S2). Indeed, the puck-like shape of Hirshfeld surface observed for **NAPTO** is known to indicate an anisotropic crystal packing (in particular, of layer type) and low sensitivity values for high-energetic solids.[S14] At the same time, although the distribution of contacts for compound **1** is characterized by larger positive kurtosis (5.63 *vs*. 3.72 for **NAPTO**), its standard deviation is also larger than that for **NAPTO** (15.77% *vs*. 8.48%). Moreover, nearly 50% of close contacts in compound **1** correspond to the N…N type (N…pi interactions) and are distributed rather uniformly over the Hirshfeld surface (Figure S3). In the other words, the distribution of contact types for compound **1** is smoother than that for **NAPTO** both statistically and geometrically. This can be interpreted as the manifestation of more isotropic molecular environment in compound **1** which may prevent from some of vibrational relaxation processes occurred upon detonation.

To some extent, the difference in the crystal packing anisotropy of compound **1** and **NAPTO** also follows from the analysis of the pair interaction energies calculated at the CE-B3LYP/6-31G(d,p) level and corresponding energy frameworks.[S15] The layer-type packing can be traced for **NAPTO** (Figure S4), although the interactions between layers in turn out to be even slightly stronger than those within them (–10.8 kcal mol^{-1} *vs*. –10.0 kcal mol^{-1}). For compound **1**, a sound chain-type packing motif with the parquet-type arrangement of molecules is clearly observed (Figure S5). This, especially taking into account weaker interaction within these chains (–8.6 kcal mol^{-1}) in comparison to the mentioned interactions in **NAPTO**, once again indicates a more isotropic crystal packing of compound **1**. The difference in crystal lattice energies estimated as a one half of all pair interaction energies (the condition of a molecule to form contacts shorter than 10Å produced 96 and 80 molecules for compound **1** and **NAPTO**, respectively) also agrees well with the larger sensitivity of compound **1** (–25.6 *vs*. –28.9 kcal mol^{-1}).

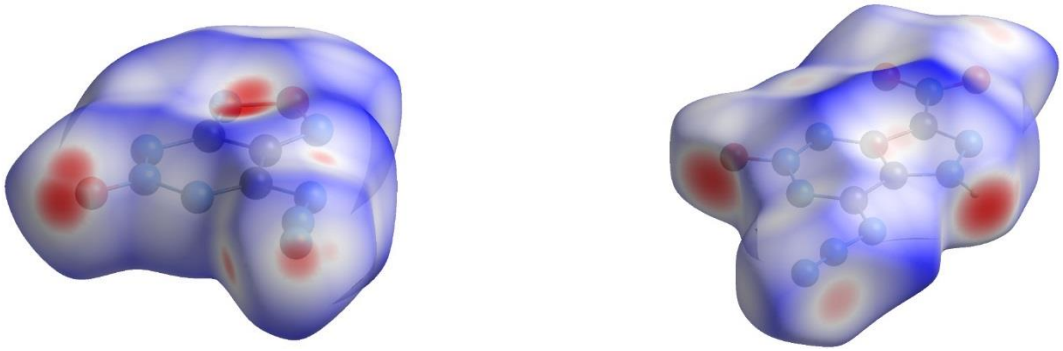


Figure S1 The Hirshfeld surfaces colored by the d_{norm} value for compound **1** (left) and **NAPTO** (right).

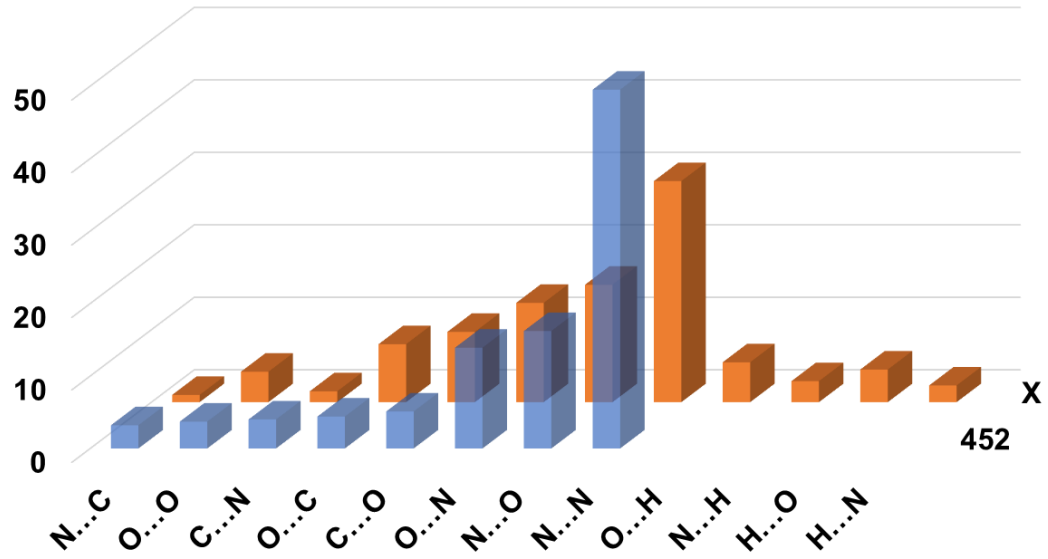


Figure S2 The distributions of types of close contacts (%) penetrating Hirshfeld surfaces of compound **1** and **NAPTO**.

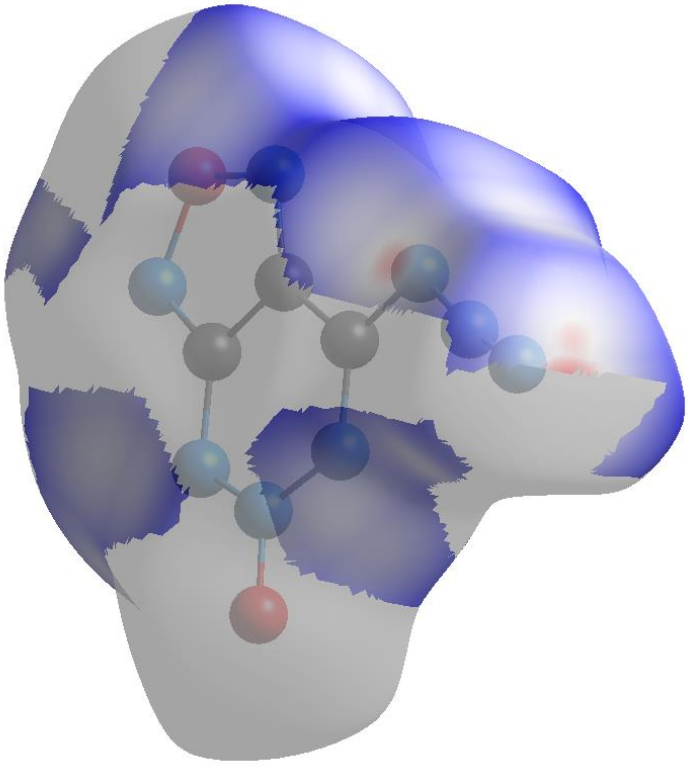


Figure S3 The Hirshfeld surface for compound **1** colored by the d_{norm} value for contacts of N…N type.

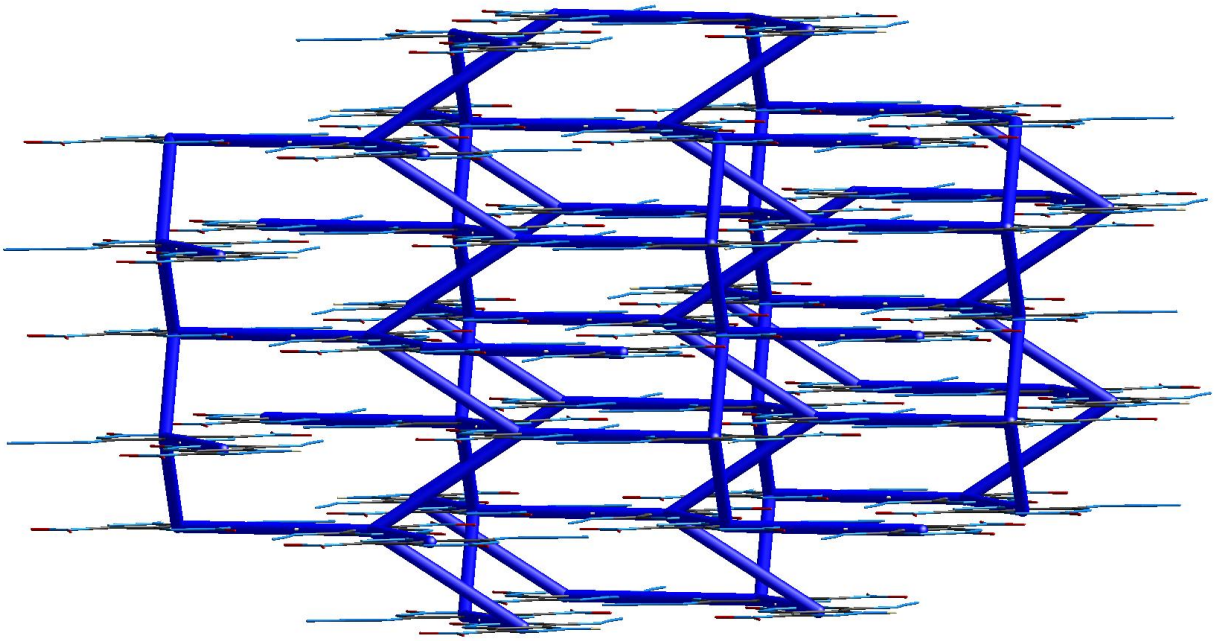


Figure S4 A fragment of crystal packing of **NAPTO** demonstrating the energy framework calculated at the CE-B3LYP/6-31G(d,p) level (20 kJ mol^{-1} as a cut-off).

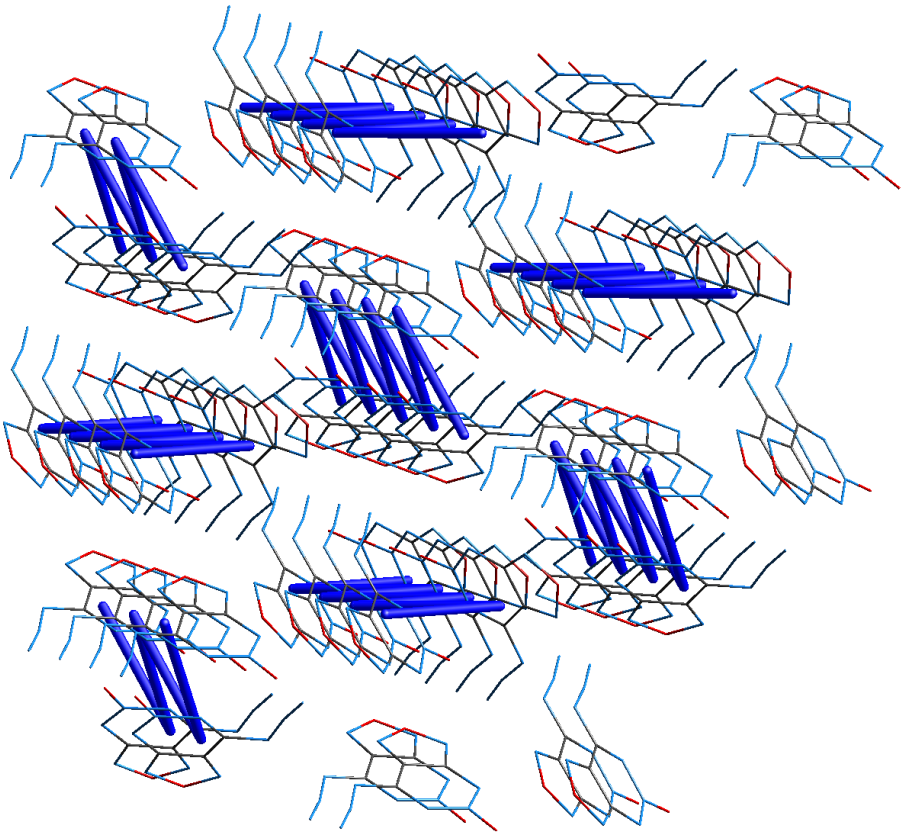


Figure S5 A fragment of crystal packing of compound **1** demonstrating the energy framework calculated at the CE-B3LYP/6-31G(d,p) level (20 kJ mol^{-1} as a cut-off).

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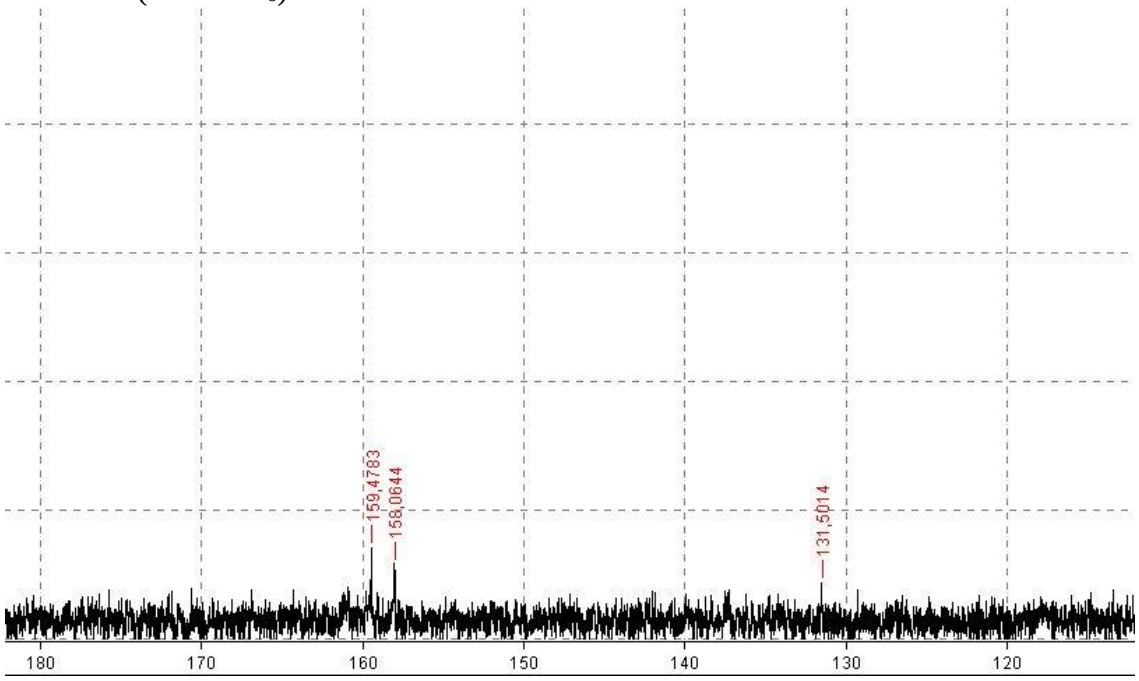
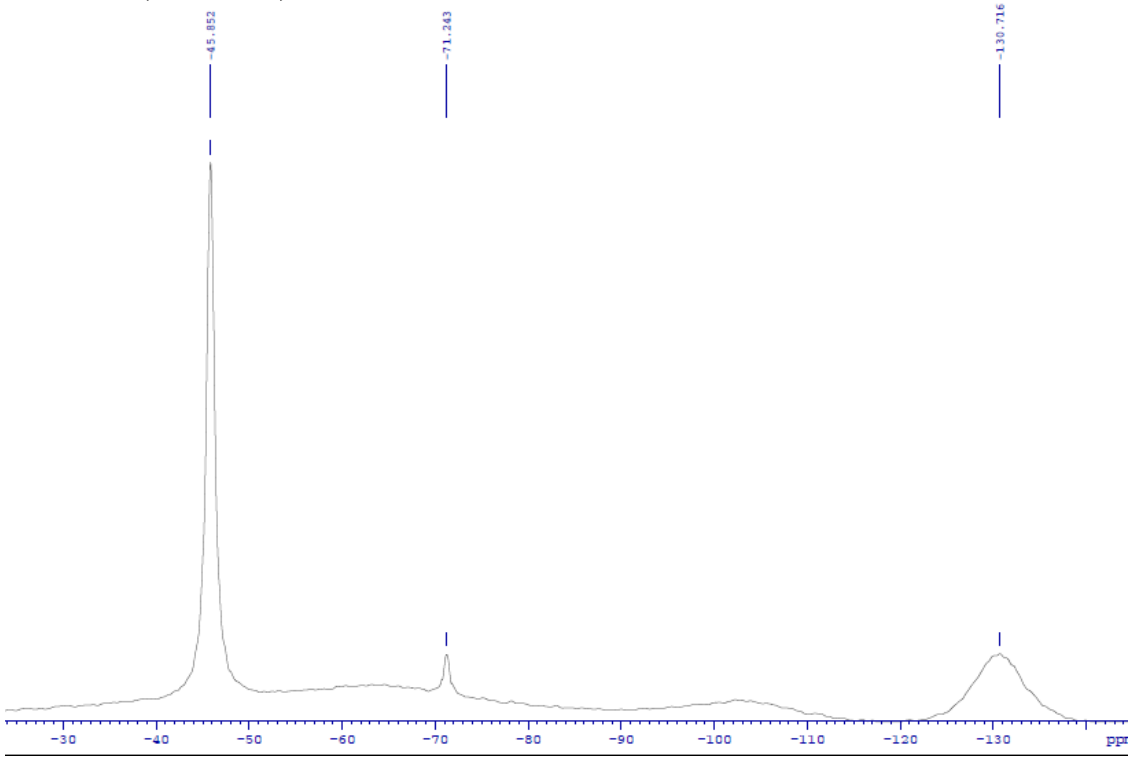
Spectra of compound **1**

^{13}C NMR (DMSO-d_6)

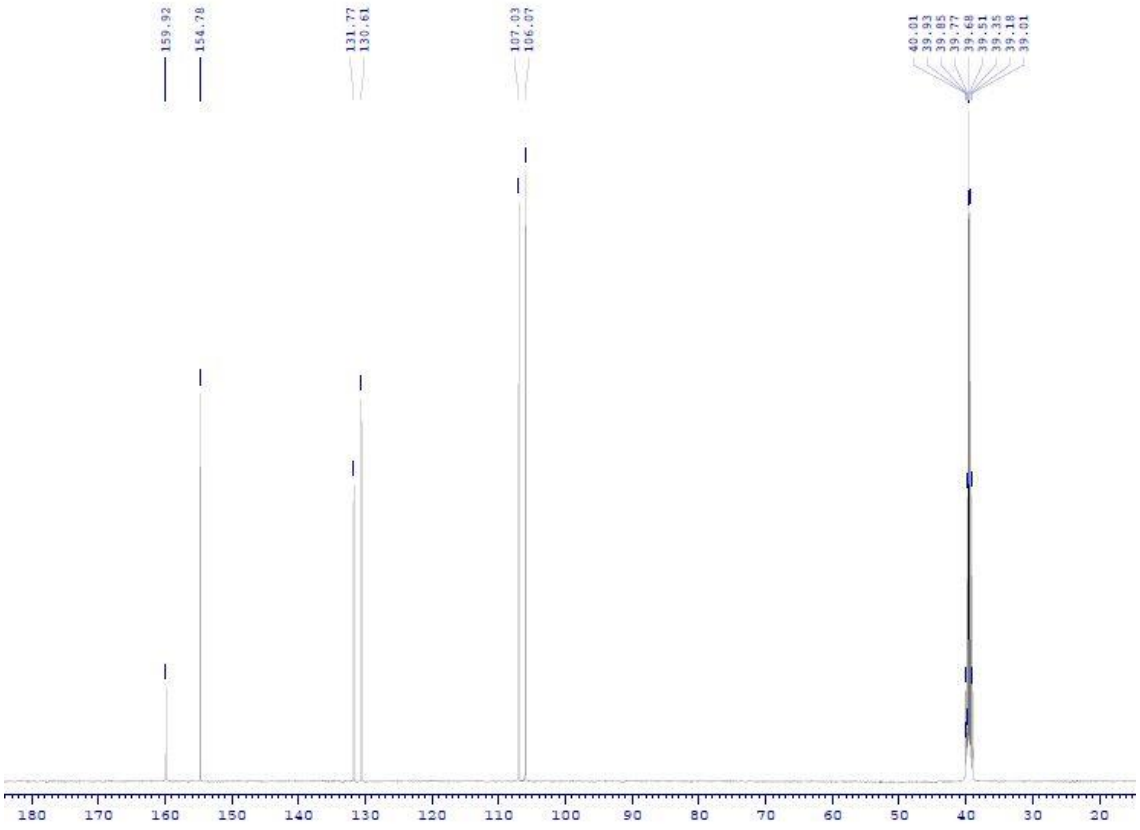


^{14}N NMR (DMSO-d_6)



Spectra of compound **5**

^{13}C NMR (DMSO-d_6)



^{14}N NMR (DMSO-d_6)