

Electronic Supplementary Information (ESI)

Increasing the limits of energy and safety in tetrazoles: Dioximes as unusual precursors to very thermostable and insensitive energetic materials

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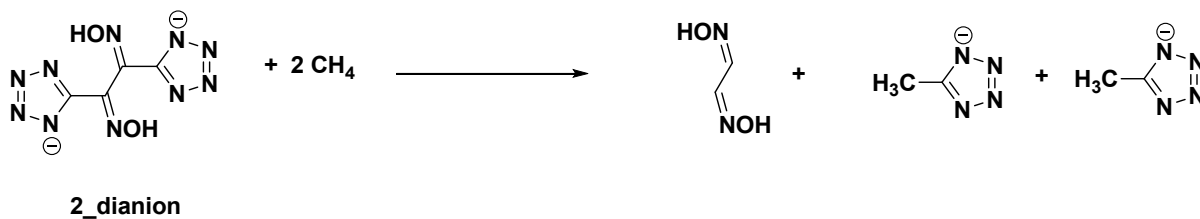
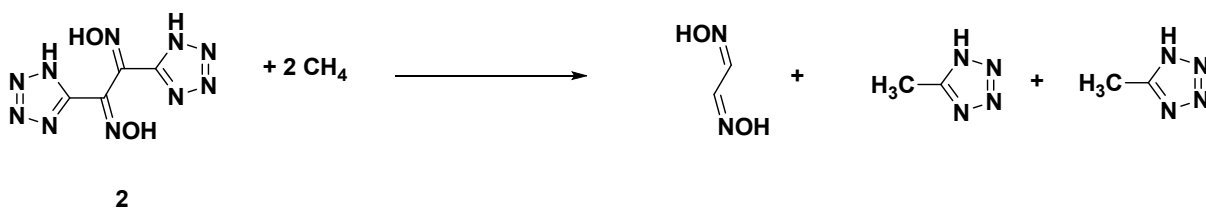
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Isodesmic reactions



Compound	ZPE	Hcorr	scaled ZPE	ΔHT	Mp-6-311++g**	Corrected	ΔHr	ΔHr (kJ/mol)	ΔHf (kJ/mol)
2	0.126563	0.140766	0.12150	0.014203	-850.6497469	-850.51404	0.01638286	43.0131948	666.1280569
2 dianion	0.099705	0.113359	0.09572	0.013654	-849.5294912	-849.42012	-0.03814988	-100.1625003	524.2947199

Scheme S1: Isodesmic reactions for compound **2** and its corresponding dianion.

Experimental section

Caution!

All compounds should be synthesized in milligram amounts. The compounds are energetic materials which show increased sensitivities toward various stimuli (e.g., higher temperatures, impact, and friction). Proper safety precautions such as leather gloves, face shield, and eye protection must be observed at all times when synthesizing and handling these materials.

General methods

All reagents (analytical grade) were purchased from AK Scientific or VWR and were used as supplied. 1H , ^{13}C NMR spectra were recorded using a 300 MHz (Bruker) NMR spectrometer operating at 300.17, and 75.47 MHz, respectively. ^{15}N NMR were recorded using a 500 MHz (Bruker Advance) NMR spectrometer operating at 50.69 MHz. Chemical shifts in the 1H and ^{13}C NMR spectra are reported relative to Me_4Si and ^{15}N NMR spectra to $MeNO_2$ as an external standard. Abbreviations for multiplicities and descriptors are: s = singlet, br = broad signal, m

= multiplet (denotes complex pattern), and q = quartet. The decomposition temperatures (onset) were obtained on a differential scanning calorimeter (TA Instruments Company, Q2000) at a scan rate of 5 °C min⁻¹. Infra-red spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The room temperature densities were measured at 25 °C by employing a gas pycnometer (Micromeritics AccuPyc II 1340). The impact and friction sensitivities were determined by using a standard BAM drop hammer and BAM friction tester. Elemental analyses were carried out on a Vario Micro cube Elementar Analyser.

Single crystals of **3**, **5** and **6** suitable for single-crystal X-ray analysis were obtained by cooling their saturated solutions in methanol/H₂O. Colorless block-shaped crystals of **3**, **5** and **6** with dimensions 0.33 × 0.03 × 0.02 mm³, 0.08 × 0.06 × 0.01 mm³ and 0.14 × 0.12 × 0.01 mm³, respectively, were selected and mounted on a nylon loop with Paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystals were kept at a steady $T = 100$ K during data collection. The structures were solved with the ShelXT¹ solution program using dual methods and by using Olex2.² The model was refined with ShelXL³ using full matrix least squares minimization on F^2 .

Theoretical study

The HOFs (heats of formation) of compound **2** and its dianion were calculated by using isodesmic reactions. The single crystal structures were used for the geometric optimization and frequency analyses using the B3LYP functional with the 6-31+G** basis set. The single-point energies were obtained at the MP2/6-311++G** level.⁴ The atomization energies for cations were calculated by using the *G²ab initio* method.⁵ All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. In case of the energetic salts, the solid-phase heats of formation were obtained based on a Born–Haber energy cycle.⁶ All calculated gas-phase enthalpies for covalent

materials are converted to solid phase values by subtracting the empirical heat of sublimation obtained based on Trouton's rule.⁷

Compounds **6** and **8** characterization data matches with the literature data.^{8,9} Compound **7** was prepared following a literature procedure.¹⁰

Synthesis of compound **2**

Compound **1** can be prepared in three steps from glyoxal (40% in water).¹¹ To a 200 mL round-bottomed flask was added **1** (1.00 g, 7.24 mmol), sodium azide (1.04 g, 15.93 mmol), zinc bromide (0.82 g, 3.62 mmol), and water (50 mL). The reaction mixture was stirred at reflux for 24 h. After cooling, HCl (2M, 20 mL) was added to the reaction mixture with vigorous stirring. The reaction mixture was heated at 50 °C, cooled and the resulting precipitate was filtered and washed with distilled water (3 x 30 mL) to obtain **2** as a white solid. (**2**): Physical description: Amorphous white solid. Yield: (1.50 g, 93%); T_d (onset) = 281 °C; ^1H NMR (300 MHz, ppm, d_6 -DMSO): 13.48 (br, NH), ^{13}C NMR (75 MHz, ppm, d_6 -DMSO): 146.3, 139.7; IR (ν , cm^{-1}): 3076, 3004, 2880, 2804, 1620, 1517, 1430, 1388, 1339, 1243, 1121, 1067, 1012, 867, 799, 758, 743, 715; Elemental analysis: Calcd (%) for $\text{C}_4\text{H}_4\text{N}_{10}\text{O}_2$ (224.14): C, 21.43; H, 1.80; N, 62.49; Found: C, 21.12; H, 2.10; N, 61.70.

General procedure for the synthesis of energetic salts

Base (2.0 mmol) was added to a suspension of **2** (1.0 mmol) in CH_3CN (30 mL). The reaction mixture was stirred for 3h. The resulting precipitate was collected by filtration to give the product, which was purified further by washing with CH_3CN (3 x 10 mL).

(**3**): Physical description: Amorphous white solid. Isolated yield: 95%; T_{dec} (onset) = 281 °C; ^1H NMR (300 MHz, ppm, d_6 -DMSO): 7.35 (br, 6H); ^{13}C NMR (75 MHz, ppm, d_6 -DMSO): 153.5, 143.1; IR (ν , cm^{-1}): 2712, 1640, 1533, 1435, 1361, 1239, 1261, 1167, 121, 1110, 1056, 1028, 997, 891; Elemental analysis: Calcd (%) for $\text{C}_4\text{H}_{10}\text{N}_{12}\text{O}_4$ (290.20): C, 16.56; H, 3.47; N, 57.92; Found: C 16.61, H 3.75, N 57.32.

(4): Physical description: Amorphous white solid. Isolated yield: 91%; $T_{\text{dec. (onset)}} = 290\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, d_6 -DMSO): 6.31 (br, 8H),; ^{13}C NMR (75 MHz, d_6 -DMSO): 155.7, 143.4; IR (ν , cm^{-1}): 2685, 1660, 1520, 1461, 1420, 1356, 1212, 1193, 1108, 1080; Elemental analysis: Calcd (%) for $\text{C}_4\text{H}_{10}\text{N}_{12}\text{O}_2$ (258.20): C, 18.61; H, 3.90; N, 65.10; Found: C 18.82, H 3.60, N 64.63.

(5): Isolated yield: 90%; $T_{\text{dec. (onset)}} = 238\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, d_6 -DMSO): 11.6 (bs, 4H), 7.29 (bs, 6H), 6.94 (s, 2H), 5.71 (s, 4H); ^{13}C NMR (75 MHz, d_6 -DMSO): 159.7, 152.2, 148.0, 142.1; IR (ν , cm^{-1}): 3332, 3219, 3096, 2678, 1675, 1624, 1606, 1441, 1355, 1201, 1165, 1124, 1106, 1014, 982, 922; Elemental analysis: Calcd (%) for $\text{C}_{10}\text{H}_{16}\text{N}_{26}\text{O}_2$ (532.41): C, 22.56; H, 3.03; N, 68.40; Found: C 22.68, H 3.05, N 67.43.

Synthesis of compound 9

The mixture of compound **2** (0.50 g, 2.2 mmol) and NaOH (0.35 g, 8.8 mmol) in water (30mL) was heated in a sealed stainless-steel tube at $140\text{ }^{\circ}\text{C}$ using an oil-bath for 12 h. The resulting clear solution was poured into ice (50 mL) and acidified with 2N HCl to pH 1. The resulting white crystalline (monohydrate) solid was filtered and washed with water (3 x 20 mL). **(9)**: Physical description: Crystalline white solid. Yield: (0.40 g, 80%); $T_{\text{d (onset)}} = 242\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, ppm, d_6 -DMSO): 9.28 (br, 2H); ^{13}C NMR (75 MHz, ppm, d_6 -DMSO): 147.6, 144.1; IR (ν , cm^{-1}): 3008, 2860, 1618, 1571, 1521, 1445, 1386, 1349, 1226, 1123, 1110, 1096, 1010, 955, 910; Elemental analysis: Calcd (%) for $\text{C}_4\text{H}_2\text{N}_{10}\text{O}_3\cdot\text{H}_2\text{O}$ (222.14): C, 21.43; H, 1.80; N, 62.49; Found: C, 21.37; H, 1.84; N, 62.55.

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Crystal Structure Data

Table S1: Crystal data and structure refinement for compounds **3**, **5**, and **6**.

Compound	3	5	6
CCDC #	2216920	2216921	2216922
Formula	C ₂ H ₅ N ₆ O ₂	C ₅ H ₈ N ₁₃ O	C ₄ H ₂ N ₁₀ O ₂
$d_{calc.}/\text{g cm}^{-3}$	1.838	1.748	1.803
μ/mm^{-1}	1.395	1.189	1.319
Formula Weight	145.12	266.24	222.16
Color	colorless	colorless	yellow
Shape	needle-shaped	hexagonal-shaped	plate-shaped
Size/mm ³	0.33×0.03×0.02	0.08×0.06×0.01	0.14×0.12×0.01
T/K	100.00(10)	100.00(10)	100.00(10)
Crystal System	monoclinic	monoclinic	orthorhombic
Flack Parameter	-	-	-0.1(4)
Hooft Parameter	-	-	-0.0(2)
Space Group	$P2_1/n$	$C2/c$	$P2_12_12_1$
$a/\text{Å}$	3.6274(2)	12.3231(3)	5.9741(3)
$b/\text{Å}$	13.3429(6)	7.9468(2)	9.6391(4)
$c/\text{Å}$	10.8736(7)	20.7961(6)	14.2140(7)
α°	90	90	90
β°	94.721(5)	96.465(2)	90
γ°	90	90	90
$V/\text{Å}^3$	524.49(5)	2023.60(9)	818.51(7)
Z	4	8	4
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K $_{\alpha}$	Cu K $_{\alpha}$	Cu K $_{\alpha}$
Q_{min}°	5.258	4.279	5.545
Q_{max}°	79.488	79.879	79.724
Measured Refl's.	3418	6800	5184
Indep't Refl's	1100	2097	1677
Refl's $I \geq 2 \sigma(I)$	988	1880	1560
R_{int}	0.0462	0.0210	0.0603
Parameters	111	204	153
Restraints	0	0	0
Largest Peak	0.333	0.405	0.534
Deepest Hole	-0.348	-0.236	-0.266
Goof	1.095	1.124	1.093
wR_2 (all data)	0.1336	0.1063	0.1446
wR_2	0.1292	0.1021	0.1414
R_1 (all data)	0.0508	0.0489	0.0578
R_1	0.0462	0.0416	0.0544

Table S2: Hydrogen bond information for compound **3**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	N4 ¹	0.84(3)	2.04(3)	2.776(2)	146(3)
O1	H1	O2 ²	0.84(3)	2.41(3)	3.008 (2)	129(2)
O2	H2	N5 ¹	0.95(4)	1.64(4)	2.582(2)	174(3)
N6	H6A	N3 ³	0.92(3)	1.99(3)	2.825(2)	150(2)
N6	H6B	O1	0.88(3)	2.12(3)	2.841(2)	140(2)
N6	H6B	N2 ⁴	0.88(3)	2.38(3)	2.862(2)	115(2)
N6	H6C	O2 ⁴	0.91(3)	1.92(3)	2.828(2)	174(2)

^1H and ^{13}C -NMR spectra of compounds 3-9

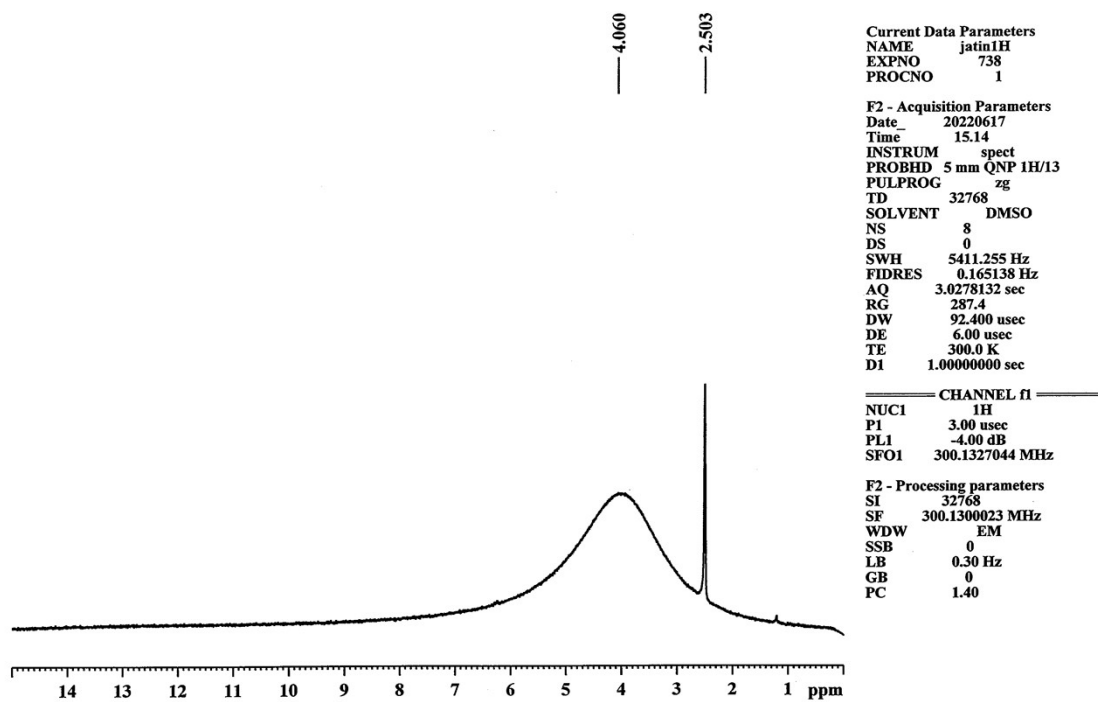


Figure S1: ^1H NMR spectra of compound 1.

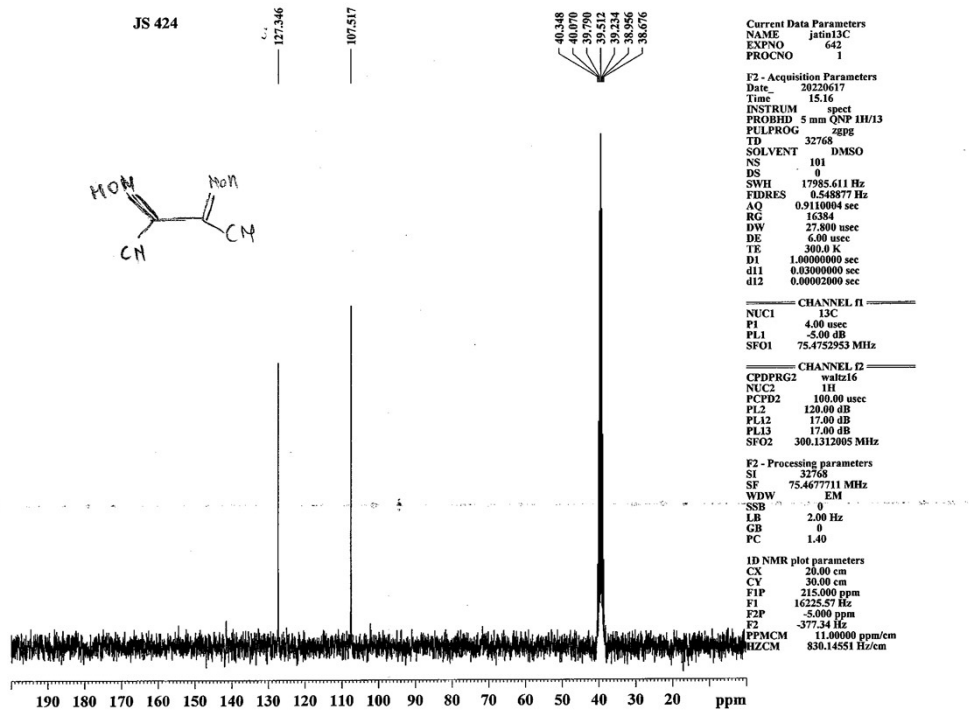


Figure S2: ¹³C NMR spectra of compound 1.

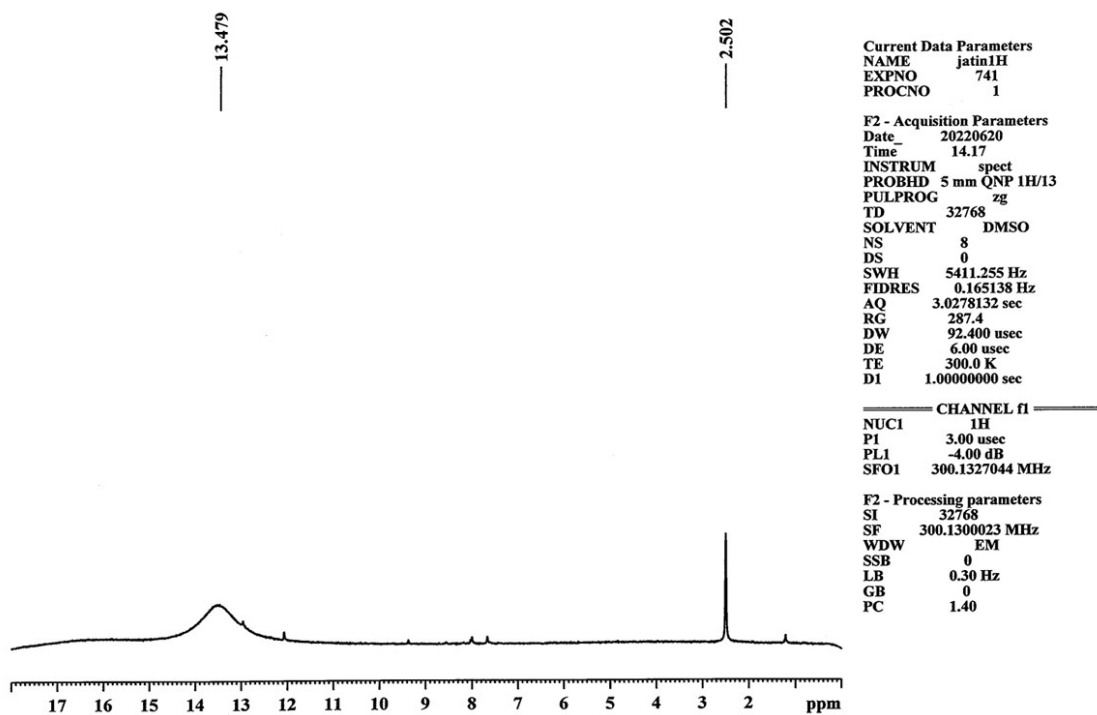


Figure S3: ¹H NMR spectra of compound 2.

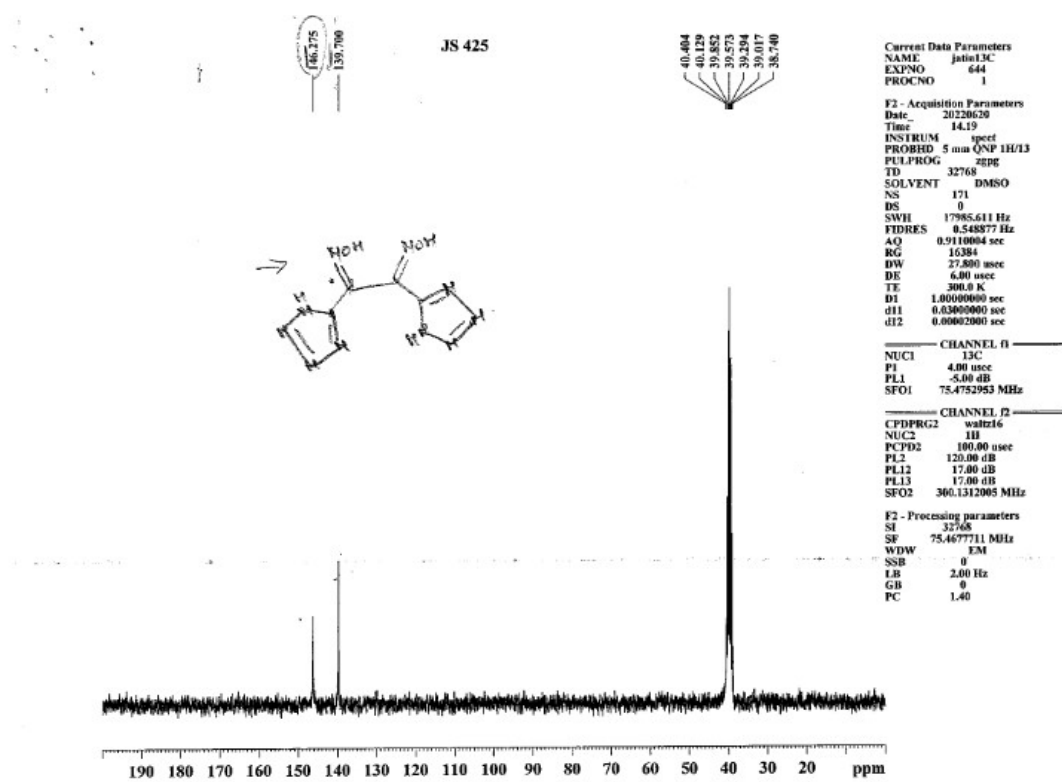


Figure S4: ¹³C NMR spectra of compound 2.

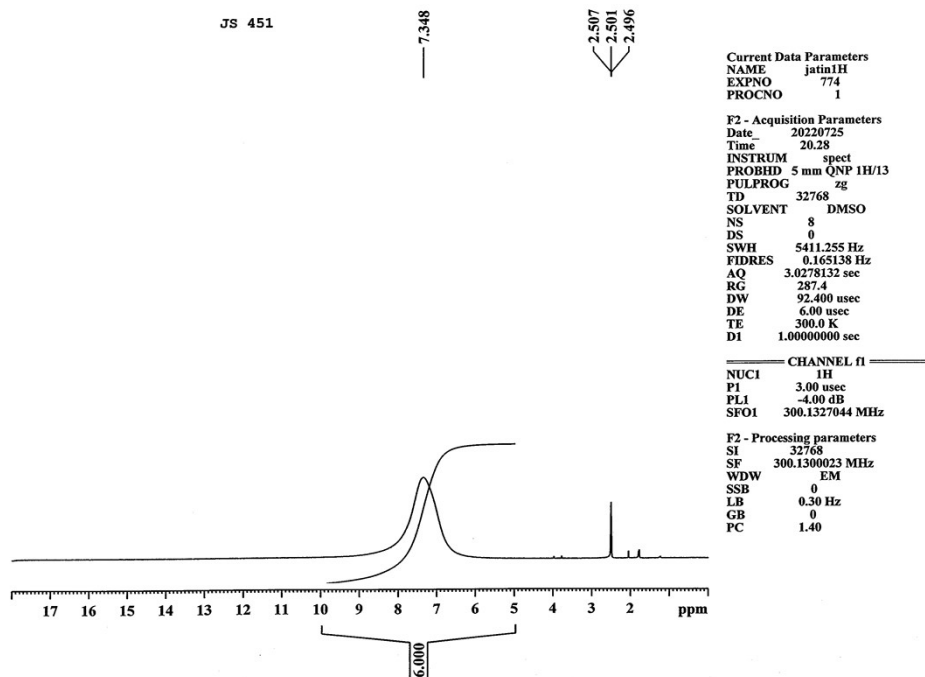


Figure S5: ¹H NMR spectra of compound 3.

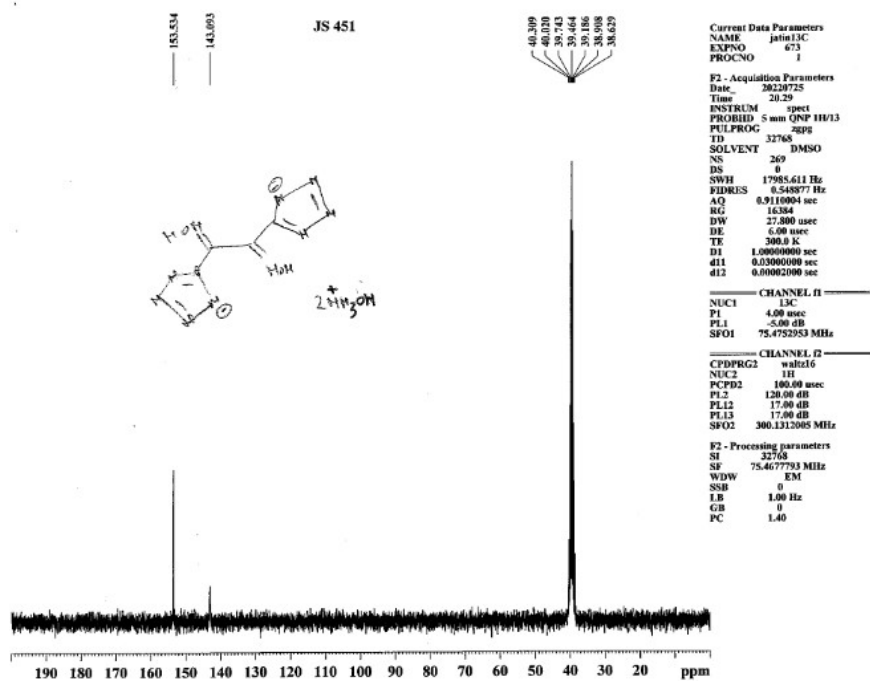


Figure S6: ^{13}C NMR spectra of compound 3.

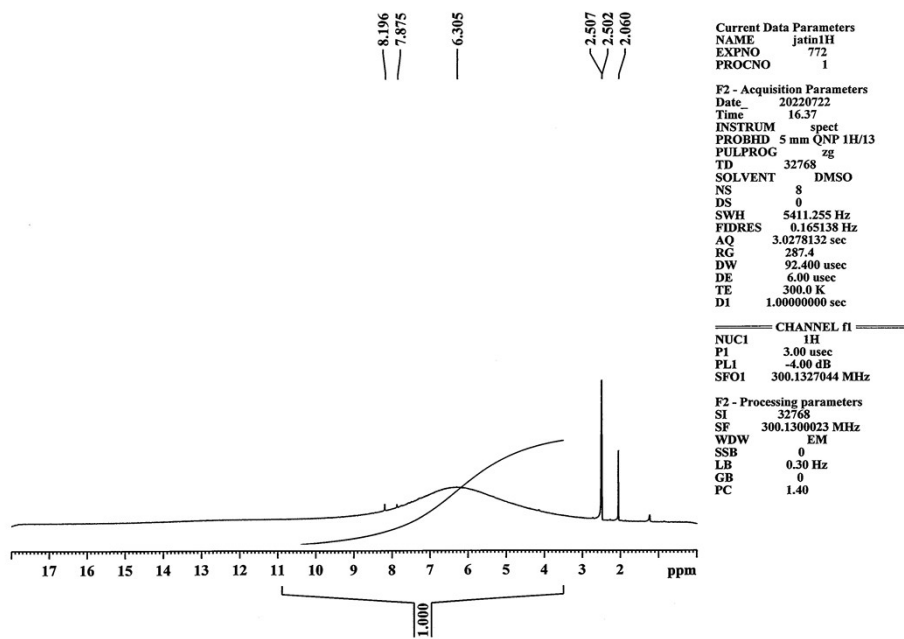


Figure S7: ^1H NMR spectra of compound 4.

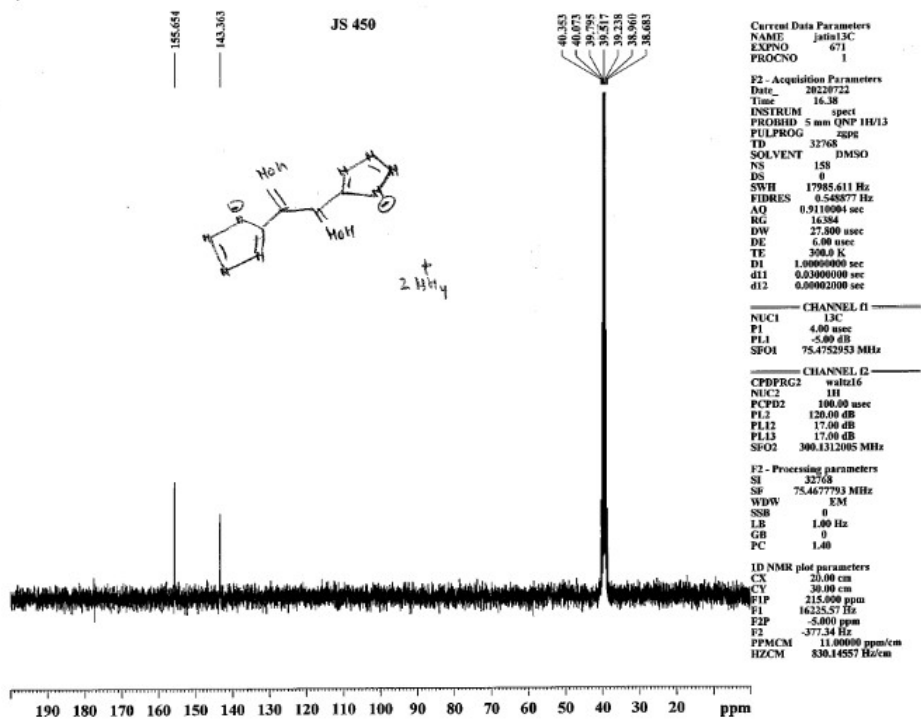


Figure S8: ¹³C NMR spectra of compound 4.

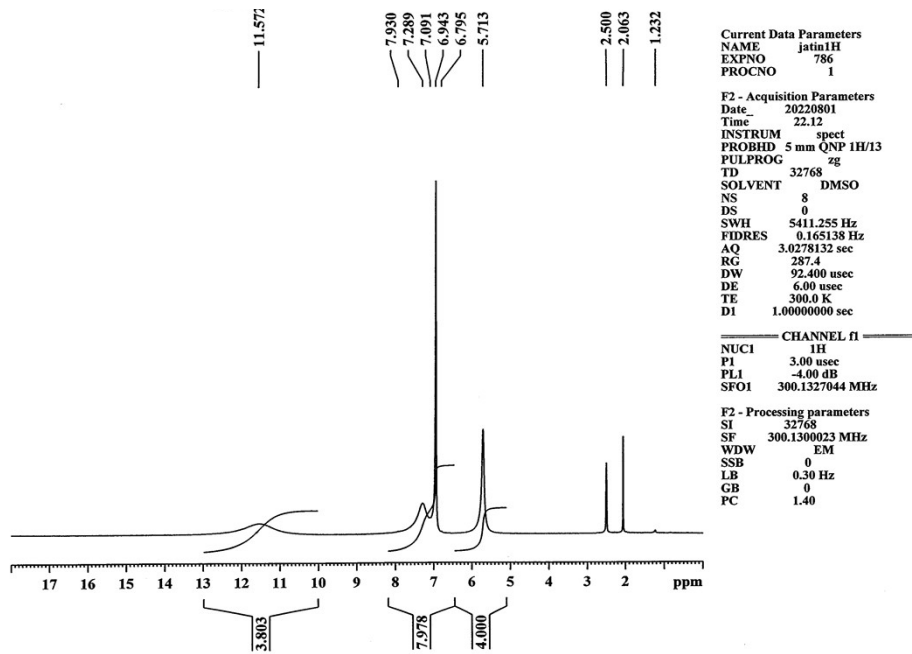


Figure S9: ¹H NMR spectra of compound 5.

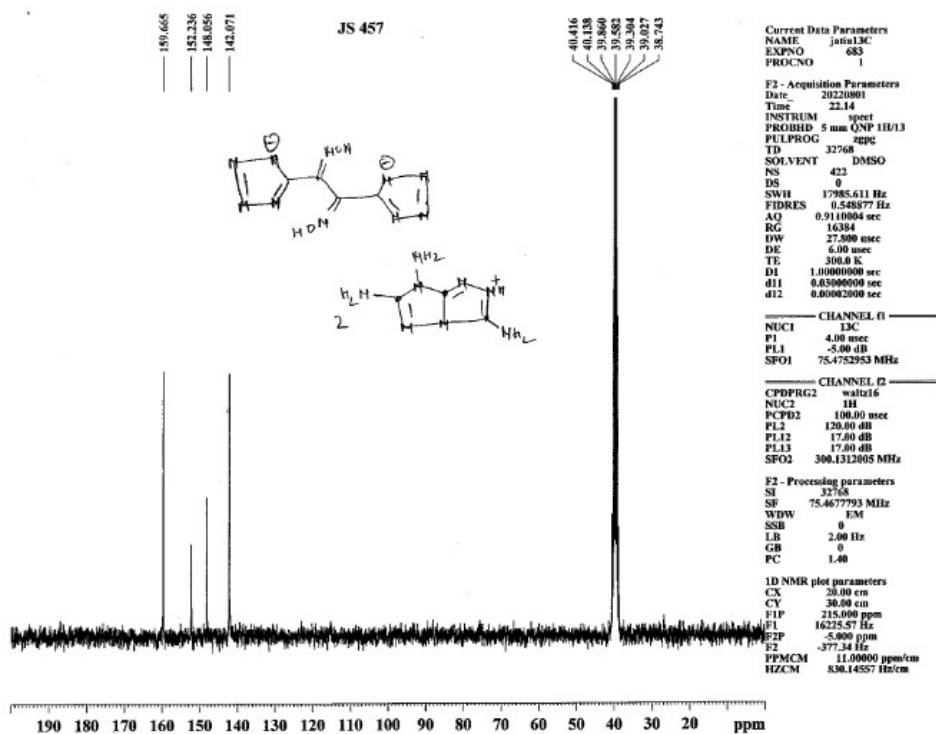


Figure S10: ¹³C NMR spectra of compound 5.

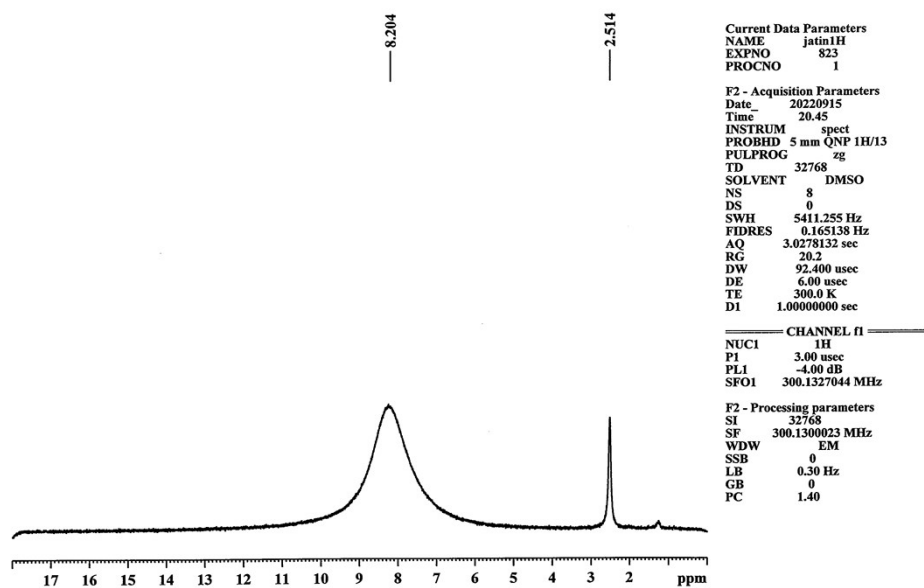


Figure S11: ^1H NMR spectra of compound **6**.

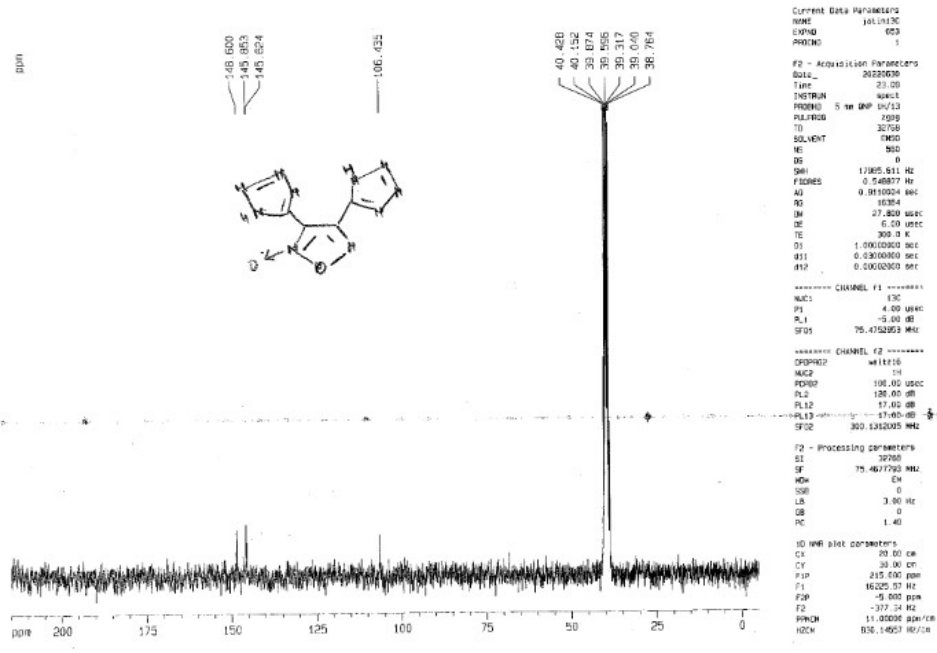


Figure S12: ¹³C NMR spectra of compound 6.

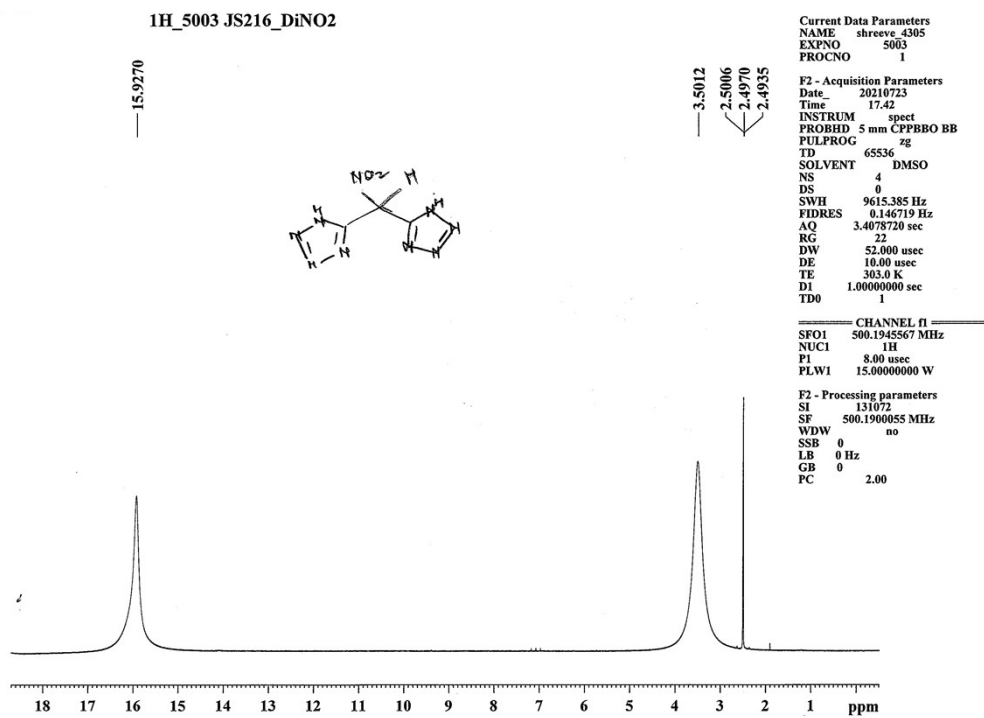


Figure S13: ¹H NMR spectra of compound 8.

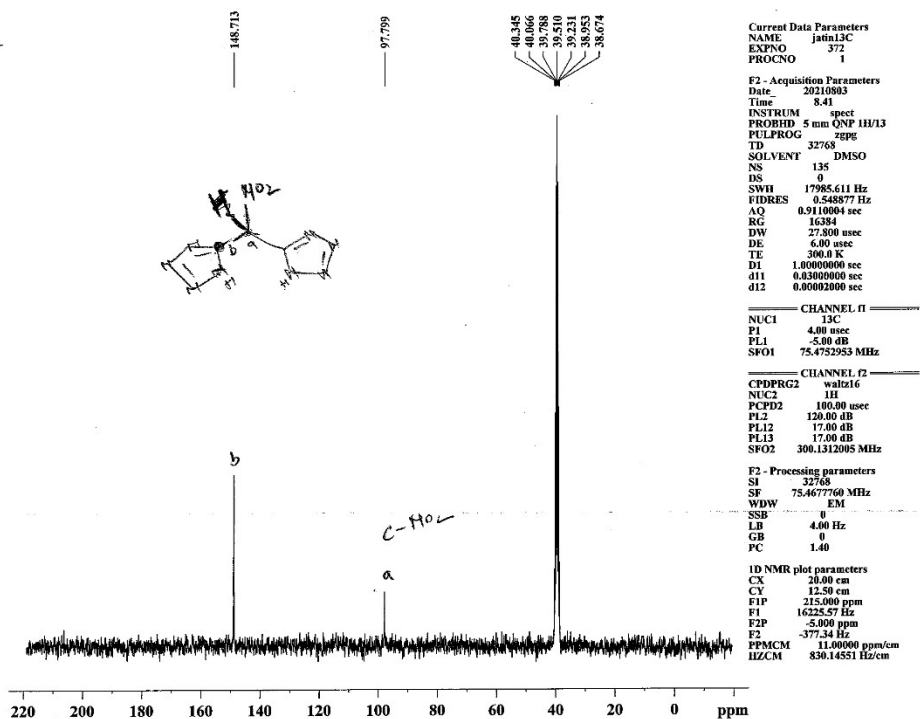


Figure S14: ¹³C NMR spectra of compound 8.

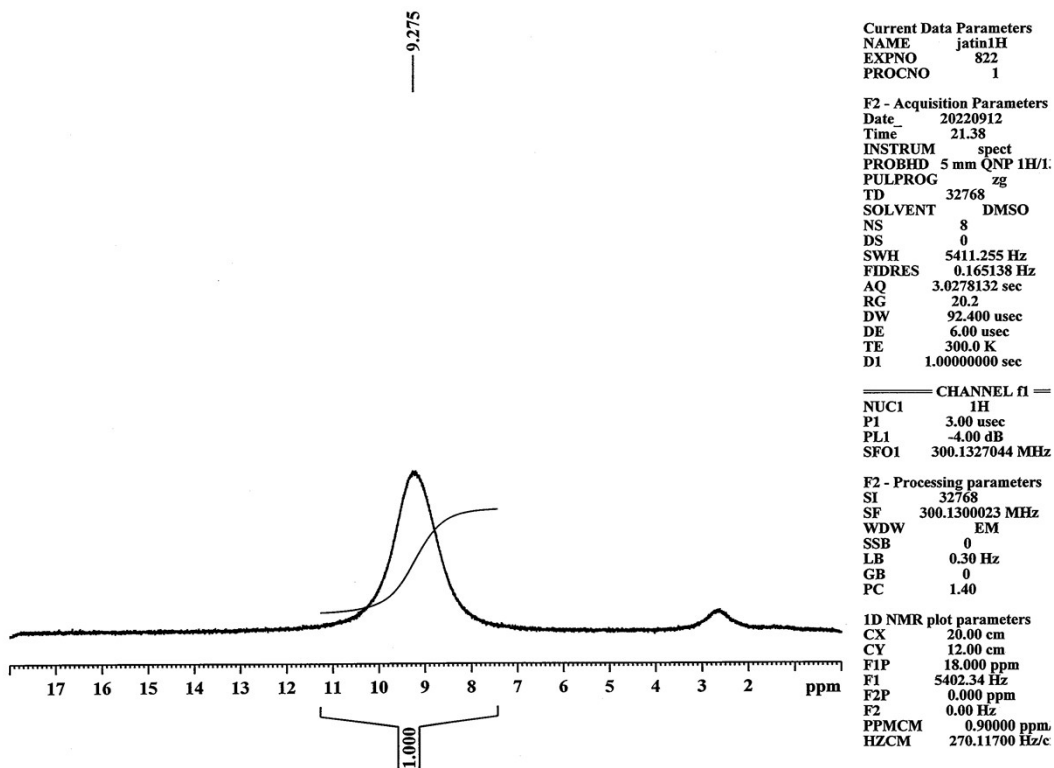


Figure S15: ¹H NMR spectra of compound 9.

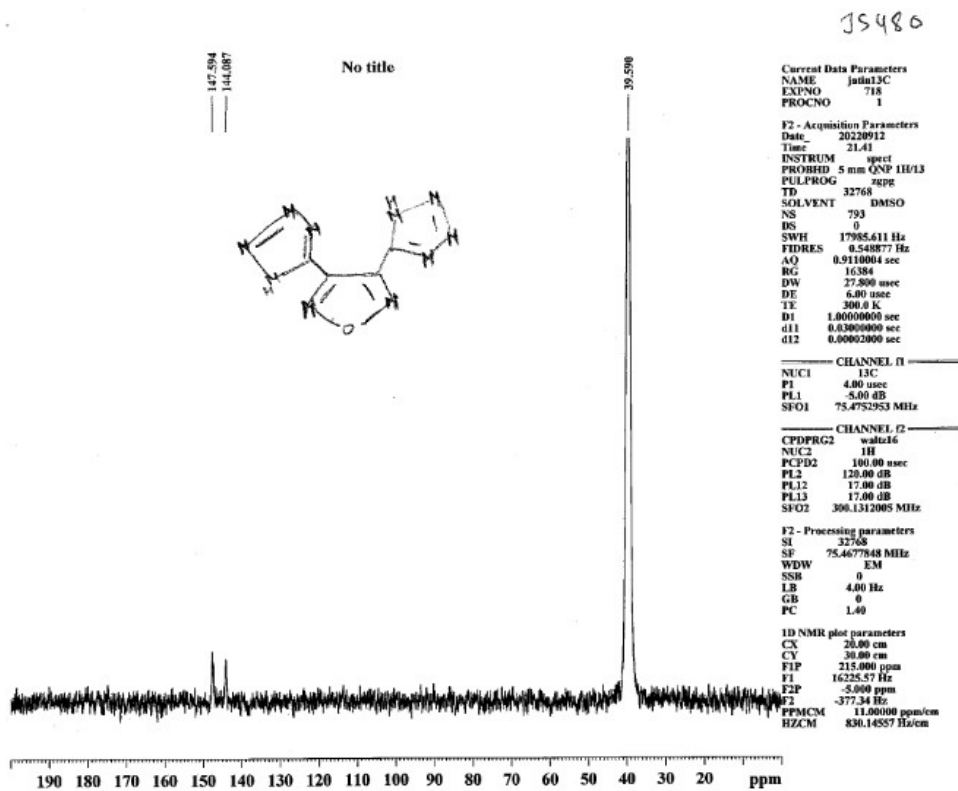


Figure S16: ^{13}C NMR spectra of compound 9.