Chemistry of Heterocyclic Compounds **2020**, *56*(8), 1015–1020

Formation of 1,2,4-triazole derivatives by oxidation of 4-phenyl-1-pivaloylsemicarbazide

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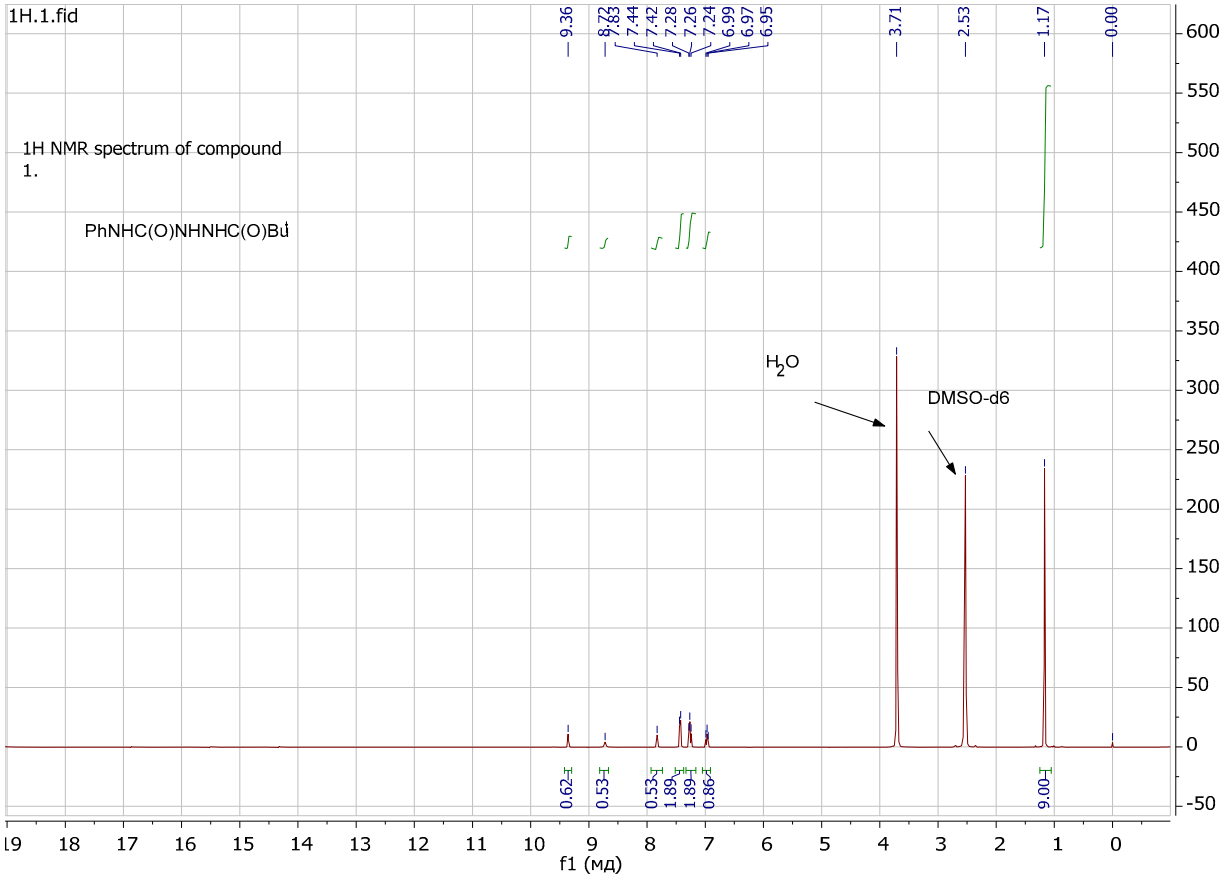
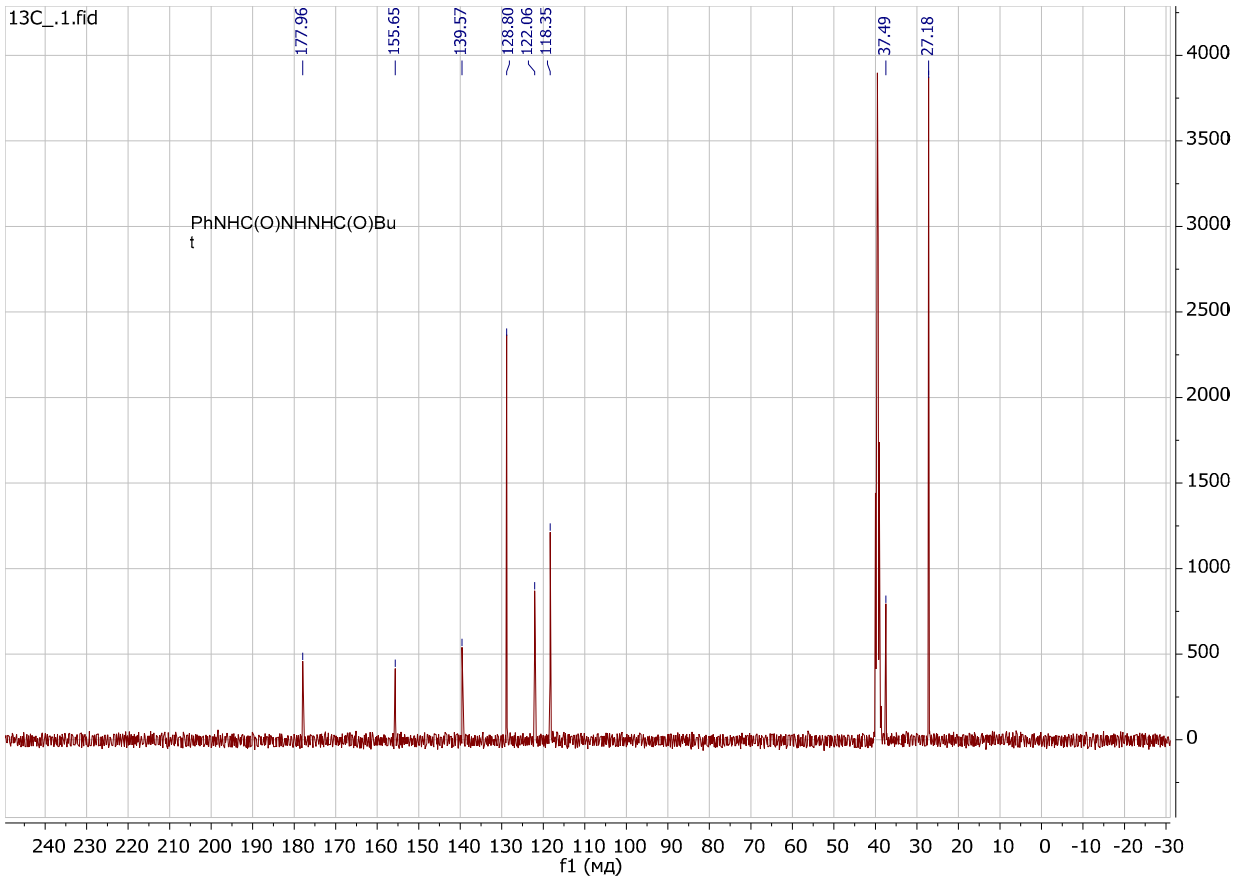
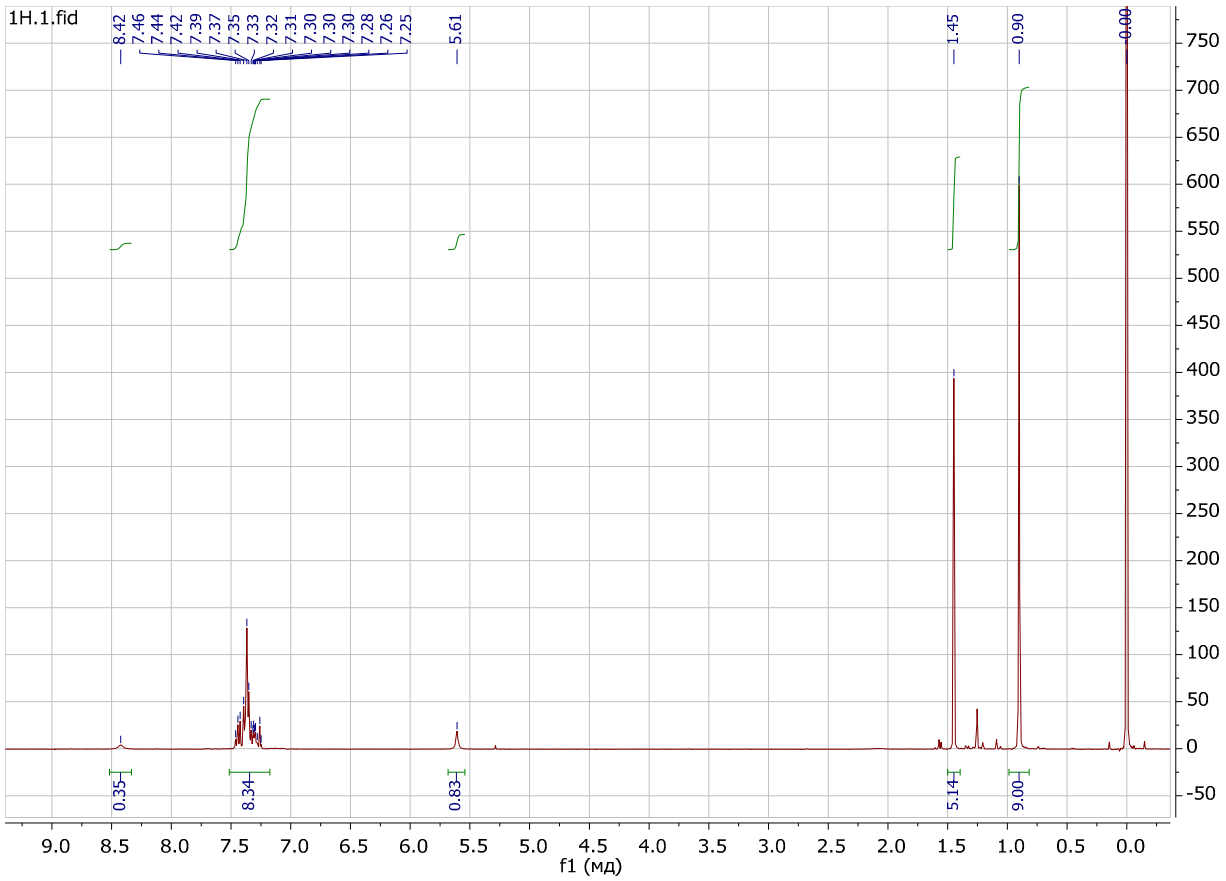
SUPPLEMENTARY INFORMATION



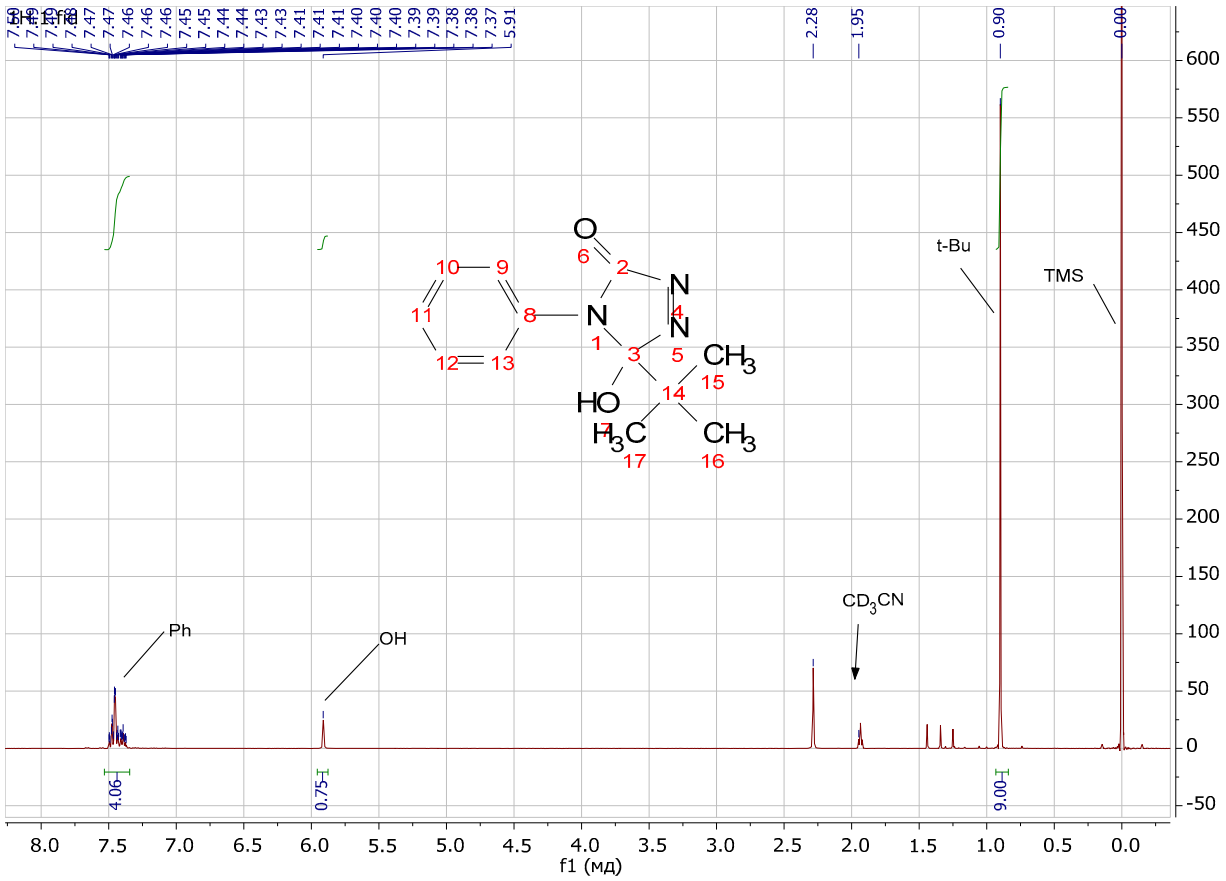
^{1}H NMR spectrum of compound **1**.



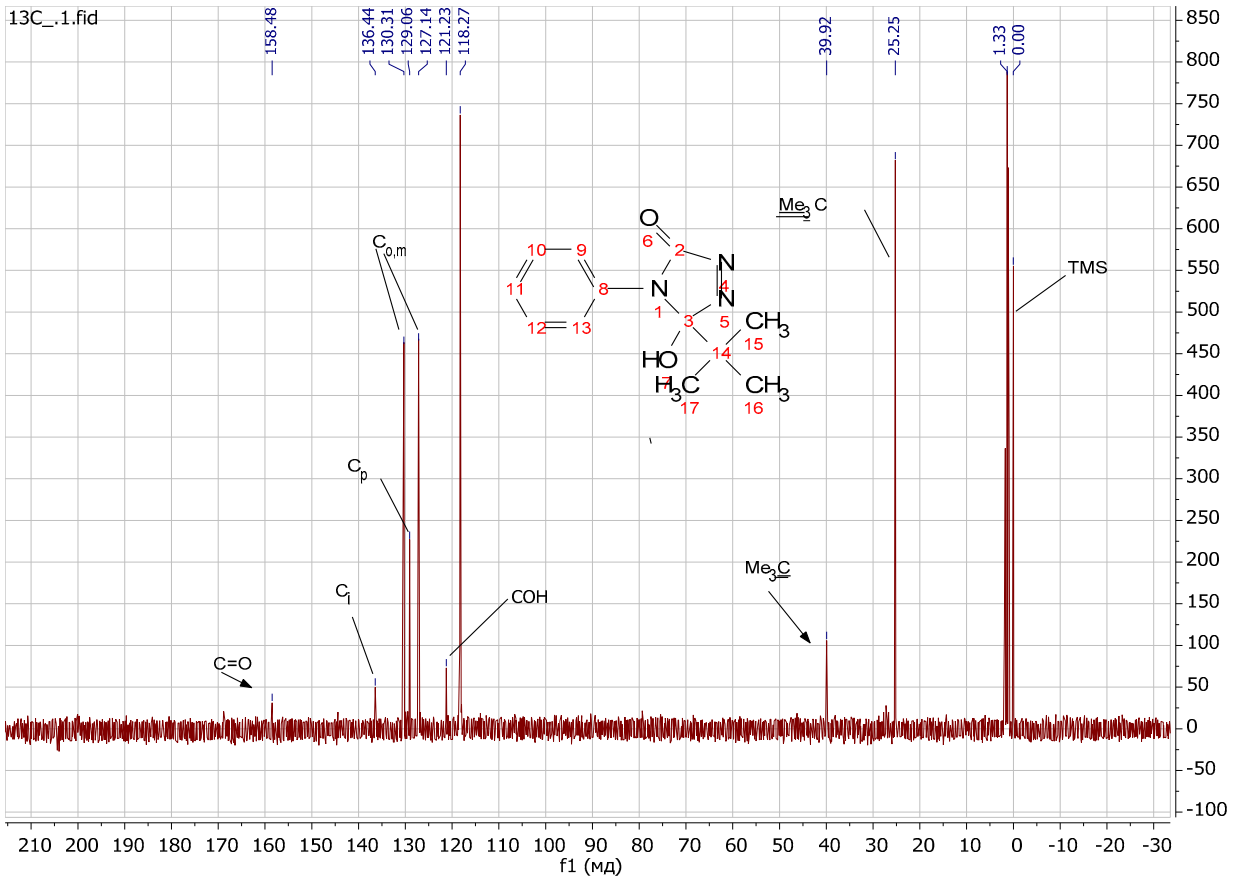
^{13}C NMR spectrum of compound **1**.



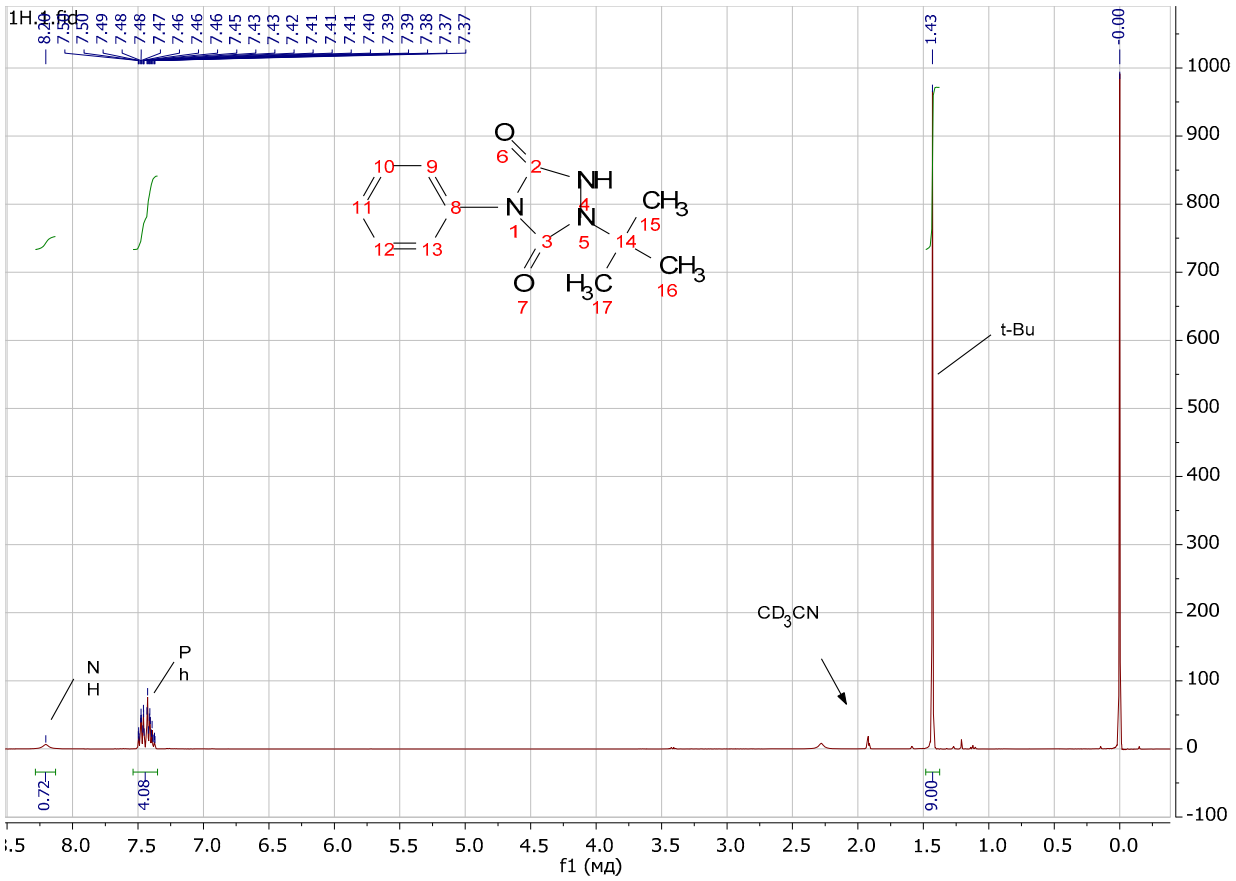
^{1}H NMR spectrum of reaction mixture at oxidation of compound **1**.



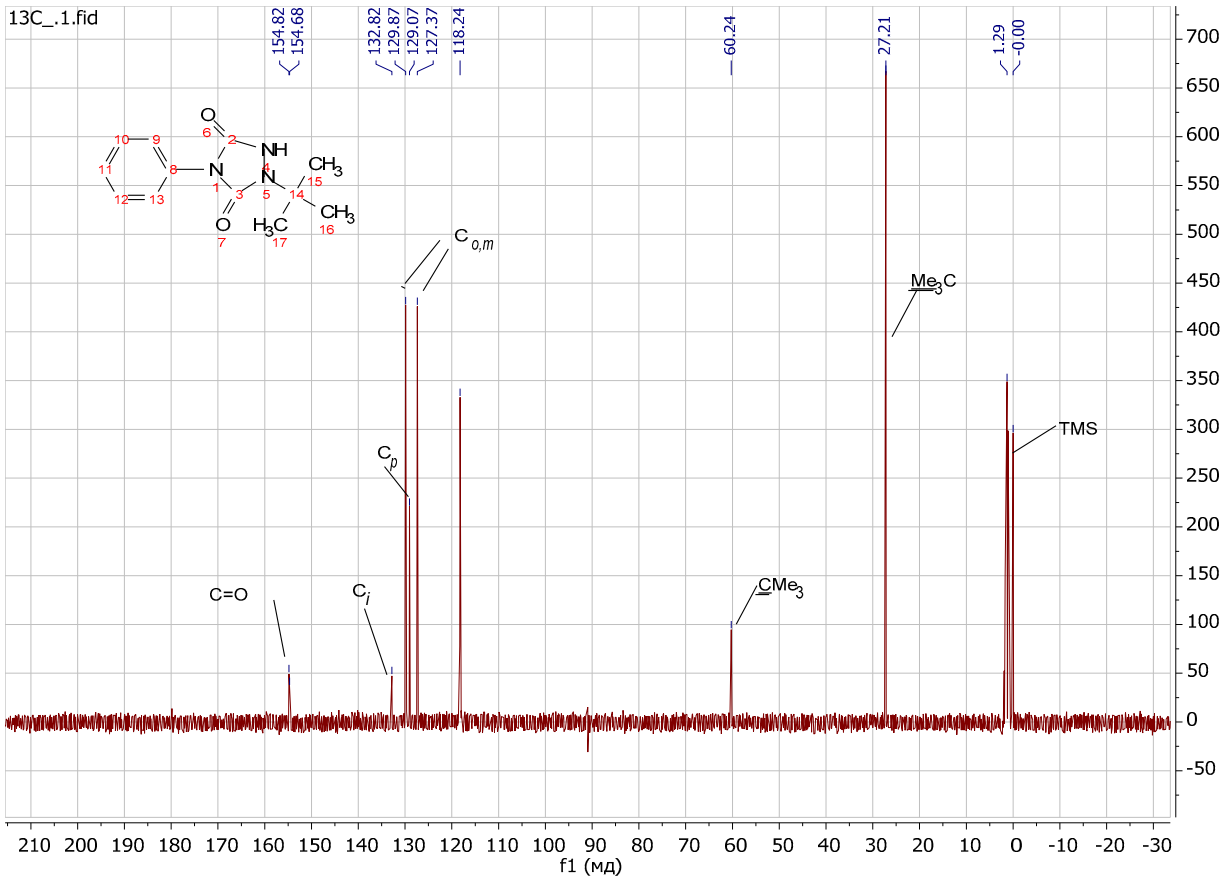
^{1}H NMR spectrum of compound **4**.



^{13}C NMR spectrum of compound **4**.



^{1}H NMR spectrum of compound **5**.



^{13}C NMR spectrum of compound **5**.

Table 1. Crystal data, details of intensity measurements, and structure refinement

for compound **1**

Empirical formula	$C_{12}H_{17}N_3O_2$
Formula weight / g·mol^{-1}	235.28
Crystal system	tetragonal
Space group	P 4_3
a / Å	9.1233(17)
b / Å	9.1233(17)
c / Å	16.108(3)
α, β, γ / °	90
Volume / Å^3	1340.7(5)
Z	4
Density (calculated) / g·cm^{-3}	1.166
Absorptions coefficient / mm^{-1}	0.1378
Radiation (λ / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	4.4 – 52.0
Crystal size / mm	0.08 × 0.08 × 0.5
Crystal habit	colorless prism
F(000)	504
Index ranges	$-10 \leq h \leq 11$, $-11 \leq k \leq 11$, $-19 \leq l \leq 19$
Reflections collected	11208
Independent reflections	2504
Number of ref. parameters	161
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0504 / 0.0876
R_1 / wR_2 (all data)	0.1309 / 0.1075
Goodness-of-fit on F^2	0.96
Largest diff. peak and hole / e·Å^{-3}	0.13 / -0.16
Weight scheme	$w = 1/[\sigma^2(F_o^2) + (0.0399\ P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 2. Selected bond lengths, bond and torsion angles in compound **1.**

Bond	l, Å	Angle	φ, ˚	Torsion angle	θ, ˚
O1-C3	1.230(5)	C3 -N1 -N2	119.9(4)	N1 -N2 -C4 -O2	-22.0(6)
O2-C4	1.228(5)	C4-N2-N1	118.2(4)	N1 -N2 -C4 -N3	161.1(4)
N1-N2	1.394(5)	C4-N3-C5	128.8(4)	N2 -N1 -C3 -O1	4.4(7)
N1-C3	1.323(5)	C1-C2-C3	106.4(4)	N2 -N1 -C3 -C2	-173.7(4)
N2-C4	1.375(6)	C1-C2-C9	108.0(5)	N3 -C5 -C6 -C7	179.1(5)
N3-C4	1.356(5)	C3-C2-C9	107.3(4)	N3-C5 -C11-C10	-178.7(5)
N3-C5	1.412(6)	C12-C2-C1	111.8(5)	C1 -C2 -C3 -O1	-63.1(6)
C1-C2	1.512(7)	C12-C2-C3	114.3(4)	C1 -C2 -C3 -N1	115.1(5)
C2-C3	1.524(6)	C12-C2-C9	108.8(5)	C3 -N1 -N2 -C4	-98.1(5)
C2-C9	1.546(8)	O1-C3-N1	121.1(4)	C4 -N3 -C5 -C6	-3.5(7)
C2-C12	1.509(7)	O1-C3-C2	119.5(4)	C4 -N3 -C5 -C11	176.4(5)
C5-C6	1.386(6)	N1-C3-C2	119.3(4)	C5 -N3 -C4 -O2	3.5(7)
C5-C11	1.382(6)	O2-C4-N2	122.9(4)	C5 -N3 -C4 -N2	-179.6(4)
C6-C7	1.375(7)	O2-C4-N3	124.7(4)	C5 -C6 -C7 -C8	-0.2(8)
C7-C8	1.364(8)	N3-C4-N2	112.4(4)	C6 -C5 -C11-C10	1.2(8)
C8-C10	1.357(7)	C6-C5-N3	124.6(4)	C6 -C7 -C8 -C10	0.6(8)
C10-C11	1.376(7)	C11-C5-N3	116.4(4)	C7-C8-C10 -C11	-0.2(9)
		C11-C5-C6	119.0(4)	C8-C10 -C11-C5	-0.8(10)
		C7-C6-C5	119.1(5)	C9 -C2 -C3 -O1	52.3(6)
		C8-C7-C6	121.7(5)	C9 -C2 -C3 -N1	-129.5(5)
		C10-C8-C7	119.3(5)	C11 -C5 -C6 -C7	-0.7(7)
		C8-C10-C11	120.5(5)	C12 -C2 -C3 -O1	173.0(5)
		C10-C11-C5	120.4(5)	C12 -C2 -C3 -N1	-8.8(7)

Table 3. Crystal data, details of intensity measurements, and structure refinement for compound **4**.

Empirical formula	$C_{12}H_{15}N_3O_2$
Formula weight / g·mol^{-1}	235.28
Crystal system	monoclinic
Space group	P 2_1/n
a / Å	12.218(7)
b / Å	6.081(4)
c / Å	16.966(10)
α, β, γ / °	90, 106.223(17), 90
Volume / Å^3	1210.4(13)
Z	4
Density (calculated) / g·cm^{-3}	1.280
Absorptions coefficient / mm^{-1}	0.1011
Radiation (λ / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	4.8 – 52.0
Crystal size / mm	0.38 × 0.29 × 0.27
Crystal habit	clear, prism
F(000)	496
Index ranges	$-15 \le h \le 13$, $-7 \le k \le 7$, $-20 \le l \le 20$
Reflections collected	25205
Independent reflections	2380
Number of ref. parameters	160
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0403 / 0.0954
R_1 / wR_2 (all data)	0.0620 / 0.1044
Goodness-of-fit on F^2	1.09
Largest diff. peak and hole / e·Å^{-3}	0.16 / -0.15
Weight scheme	$w = 1/[\sigma^2(F_o^2) + (0.0423\ P)^2 + 0.3429P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 4. Selected bond lengths, bond and torsion angles in compound **4.**

Bond	*l*, Å	Angle	φ, ˚	Torsion angle	θ, ˚
O1-C3	1.382(2)	C4 -N1-C3	127.53(12)	N1-C4-C5-C6	-179.90(15)
O2-C10	1.2120(19)	C10-N1-C3	110.28(12)	N1-C1-C11-C12	-179.81(15)
N1-C3	1.466(2)	C10-N1-C4	122.18(13)	N2-N3 -C3 -O1	-120.26(15)
N1-C4	1.442(2)	N3-N2-C10	109.57(13)	N2-N3 -C3-N1	-1.05(16)
N1-C10	1.341(2)	N2-N3-C3	112.14(13)	N2-N3-C3-C2	120.88(15)
N2-N3	1.241(2)	C1-C2-C3	110.11(14)	N3-N2-C10-O2	176.55(14)
N2-C10	1.476(2)	C1-C2-C8	109.30(14)	N3-N2-C10-N1	-1.31(17)
N3-C3	1.510(2)	C1-C2-C9	110.04(15)	C1-C2-C3-O1	178.59(13)
C1-C2	1.527(3)	C3-C2-C8	108.24(14)	C1-C2-C3-N1	50.39(18)
C2-C3	1.546(2)	C3-C2-C9	110.47(14)	C1-C2-C3-N3	-62.01(16)
C2-C8	1.540(2)	C9-C2-C8	108.62(16)	C3-N1-C4-C5	-120.18(17)
C2-C9	1.529(3)	O1-C3-N1	112.89(12)	C3-N1-C4-C11	61.2(2)
C4-C5	1.381(2)	O1-C3-N3	109.65(12)	C3-N1-C10-O2	-177.04(15)
C4-C11	1.382(2)	O1-C3-C2	108.79(13)	C3-N1-C10-N2	0.59(16)
C5-C6	1.383(2)	N1-C3-N3	100.73(13)	C4-N1-C3-O1	-63.43(19)
C6-C7	1.375(3)	N1-C3-C2	115.59(12)	C4-N1-C3-N3	179.74(13)
C7-C12	1.373(3)	N3-C3-C2	108.80(13)	C4-N1-C3-C2	62.71(19)
C11-C12	1.388(3)	C5-C4-N1	118.78(14)	C4-N1-C10-O2	3.4(2)
		C5-C4-C11	120.95(15)	C4-N1-C10-N2	-179.00(12)
		C11-C4-N1	120.26(14)	C4-C5-C6-C7	-0.1(3)
		C4-C5-C6	119.44(17)	C4-C11-C12-C7	-0.5(3)
		C7-C6-C5	120.15(18)	C5-C4-C11-C12	1.6(2)
		C12-C7-C6	120.08(17)	C5-C6-C7-C12	1.3(3)
		O2-C10-N1	130.20(15)	C6-C7-C12-C11	-0.9(3)
		O2-C10-N2	122.49(14)	C8-C2-C3-O1	-61.98(17)
		N1-C10-N2	107.27(14)	C8-C2-C3-N1	169.82(14)
		C4-C11-C12	118.62(17)	C8-C2-C3-N3	57.42(18)
		C7-C12-C11	120.74(18)	C9-C2-C3-O1	56.84(16)

Table 5. Crystal data, details of intensity measurements, and structure refinement for compound **5**.

Empirical formula	$C_{12}H_{15}N_3O_2$
Formula weight / g·mol^{-1}	233.27
Crystal system	monoclinic
Space group	P 2_1/c
a / Å	5.929(5)
b / Å	18.208(19)
c / Å	11.574(10)
α, β, γ / °	90, 100.97(3), 90
Volume / Å^3	1227(2)
Z	4
Density (calculated) / g·cm^{-3}	1.263
Absorptions coefficient / mm^{-1}	0.1059
Radiation (λ / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	4.4 – 53.6
Crystal size / mm	0.22 × 0.13 × 0.09
Crystal habit	clear, prism
F(000)	496
Index ranges	$-7 \leq h \leq 7$, $-23 \leq k \leq 22$, $-23 \leq l \leq 22$
Reflections collected	21120
Independent reflections	2617
Number of ref. parameters	161
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0472 / 0.1035
R_1 / wR_2 (all data)	0.0876 / 0.1201
Goodness-of-fit on F^2	1.08
Largest diff. peak and hole / e·Å^{-3}	0.13 / -0.27
Weight scheme	$w = 1/[\sigma^2(F_o^2) + (0.0524\ P)^2 + 0.1935P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 6. Selected bond lengths, bond and torsion angles in compound **5.**

Bond	*l*, Å	Angle	φ, ˚	Torsion angle	θ, ˚
O1-C10	1.226(2)	C5-N1-C4	124.83(13)	N1-C4-C12-C11	179.54(16)
O2-C5	1.210(2)	C10-N1-C4	124.75(14)	N2-N3-C10-O1	-170.27(17)
N1-C4	1.429(2)	C10-N1-C5	110.28(15)	N2-N3-C10-N1	9.06(18)
N1-C5	1.398(2)	N3-N2-C6	115.56(12)	N3-N2-C5-O2	-169.40(17)
N1-C10	1.383(2)	C5-N2-N3	106.22(13)	N3-N2-C5-N1	9.80(17)
N2-N3	1.418(2)	C5-N2-C6	120.69(14)	N3-N2-C6-C7	77.01(18)
N2-C5	1.380(2)	C10-N3-N2	110.01(13)	N3-N2-C6-C8	-161.97(14)
N2-C6	1.501(2)	C11-C1-C2	119.76(19)	N3-N2-C6-C9	-44.00(19)
N3-C10	1.346(2)	C1-C2-C3	120.53(18)	C1-C2-C3-C4	0.2(3)
C1-C11	1.372(3)	C4-C3-C2	118.86(18)	C1-C11-C12-C4	-0.1(3)
C2-C3	1.371(3)	C3-C4-N1	119.27(16)	C2-C1-C11-C12	0.9(3)
C3-C4	1.380(3)	C12-C4-N1	119.62(15)	C2-C3-C4-N1	-179.58(15)
C4-C12	1.374(2)	C12-C4-C3	121.11(17)	C2-C3-C4-C12	0.6(3)
C6-C7	1.371(3)	O2-C5-N1	125.49(16)	C3-C4-C12-C11	-0.7(3)
C6-C8	1.514(3)	O2-C5-N2	128.28(16)	C4-N1-C5-O2	-1.3(3)
C6-C9	1.518(3)	N2-C5-N1	106.23(14)	C4-N1-C5-N2	179.42(14)
C11-C12	1.516(3)	N2-C6-C7	109.86(14)	C4-N1-C10-O1	-7.5(3)
C11-C12	1.375(3)	N2-C6-C8	107.54(14)	C4-N1-C10-N3	173.17(14)
		N2-C6-C9	108.12(15)	C5-N1-C4-C3	-57.6(2)
		C7-C6-C8	111.09(16)	C5-N1-C4-C12	122.14(19)
		C7-C6-C9	110.79(16)	C5-N1-C10-O1	176.59(17)
		C9-C6-C8	109.35(15)	C5-N1-C10-N3	-2.75(18)
		O1-C10-N1	126.47(16)	C5-N2-N3-C10	-12.07(18)
		O1-C10-N3	127.58(15)	C5-N2-C6-C7	-53.1(2)
		N3-C10-N1	105.94(15)	C5-N2-C6-C8	67.95(14)
		C1-C11-C12	120.4(2)	C5-N2-C6-C9	-174.08(15)
		C4-C12-C11	119.29(17)	C6-N2-N3-C10	-148.82(14)

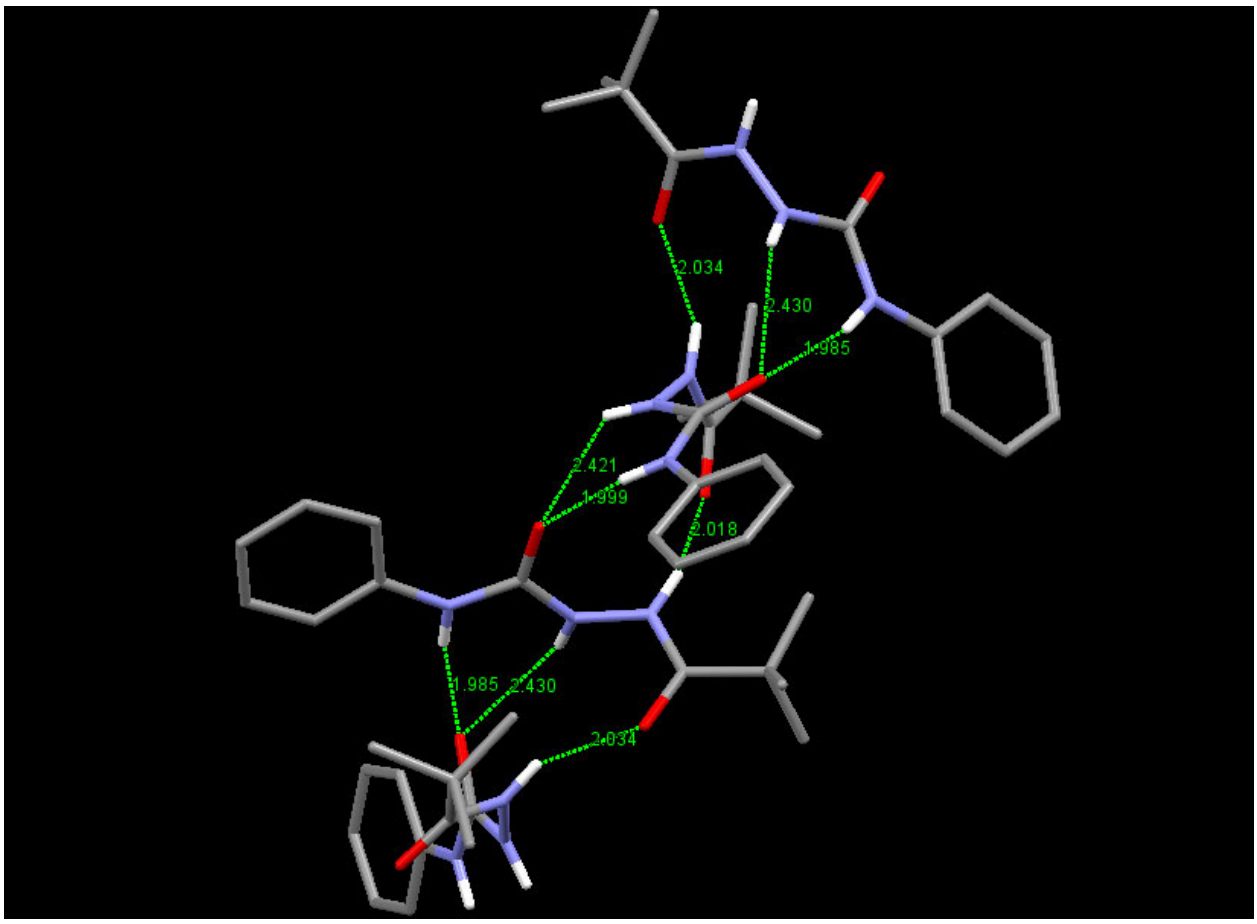
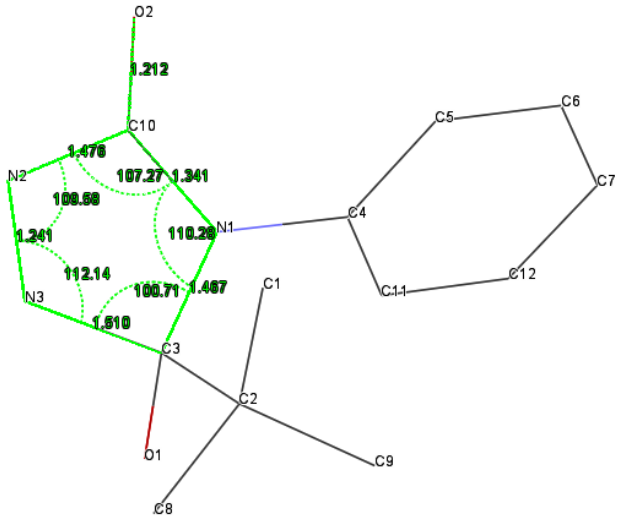
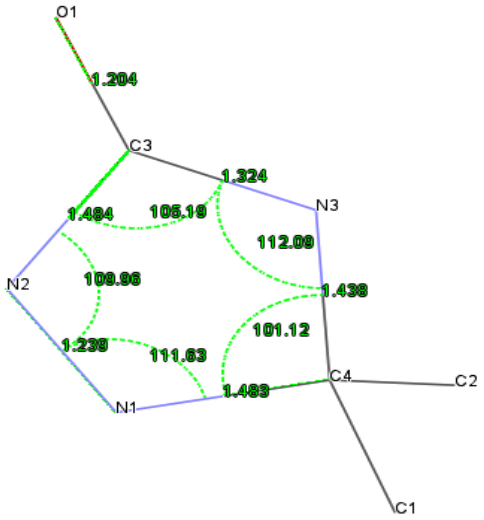


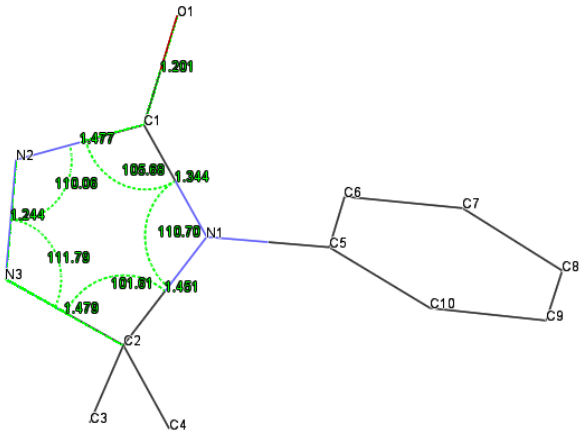
Fig. 1S. Four molecules of compound **1** in asymmetric unit cell .



Heterocycle of compound **4**, this work



J.G.Schantl, H.Gstach, N.Lanznaster, A.Gieren, V.Lamm, *J.Heterocycl.Chem.* (1987), **24**, 1401



A.R.Katritzky, H.M.Faid-Allah, H.Aghabozorg, G.J.Palenik, *Chem.Scr.* (1984), **23**, 134

Fig. 2S. Geometrical parameters for derivatives 5-dihydro-3H-1,2,4-triazol-3-one.

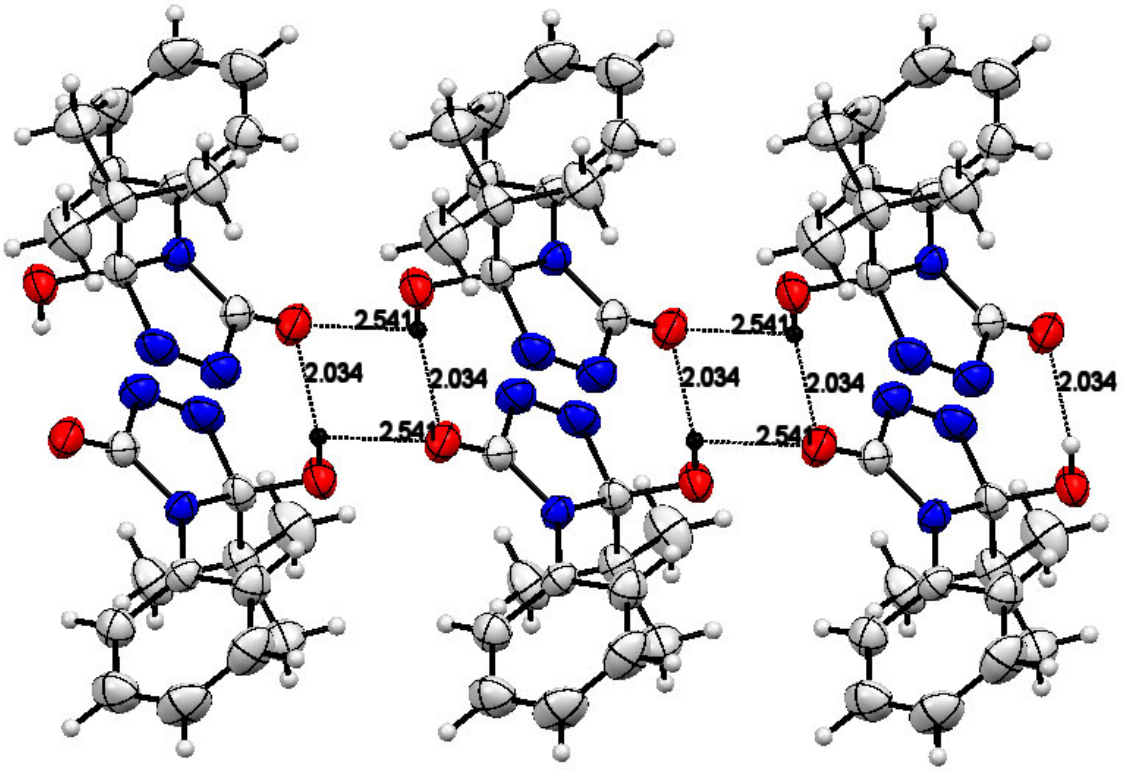


Fig 3S. H-bonding of molecules of compound **4**.

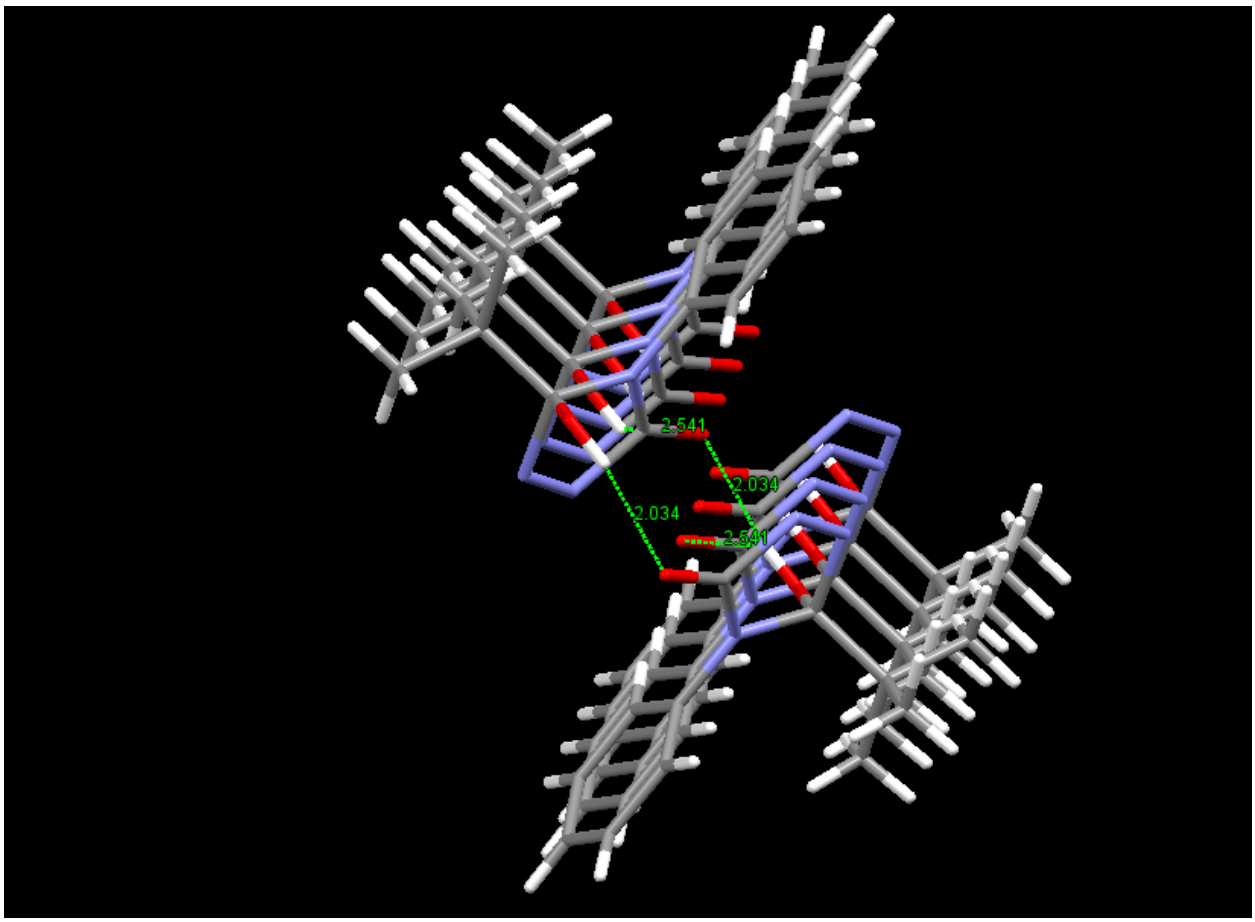


Fig. 4S. The polymeric hydrogen bonded assembly consisting of compound **4.**

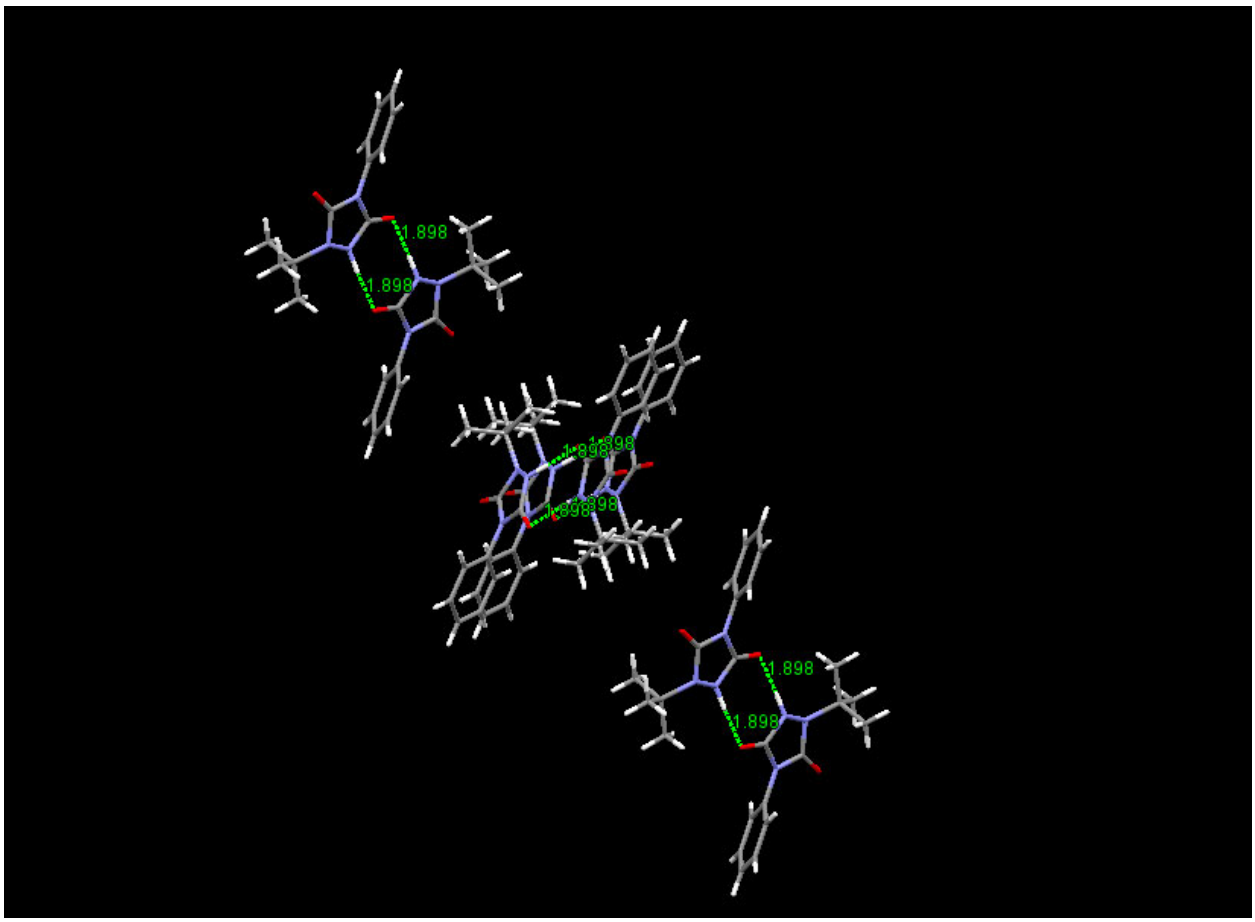


Fig. 5S. The dimers of compound **5.**