Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Conformational behaviour of 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one: a sudden story of three desmotrops

Vanya B. Kurteva,*[a] Boris L. Shivachev,[b] Rositsa P. Nikolova,[b] Svetlana D. Simova,[a] Liudmil M. Antonov,[a] Lubomir A. Lubenov,[a] and Maria A. Petrova[c]

[a]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria; [b]Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 107, 1113 Sofia, Bulgaria; [c]University of Chemical Technology and Metallurgy, Department of General and Inorganic Chemistry, 8 Kliment Ohridski blvd., 1756 Sofia, Bulgaria

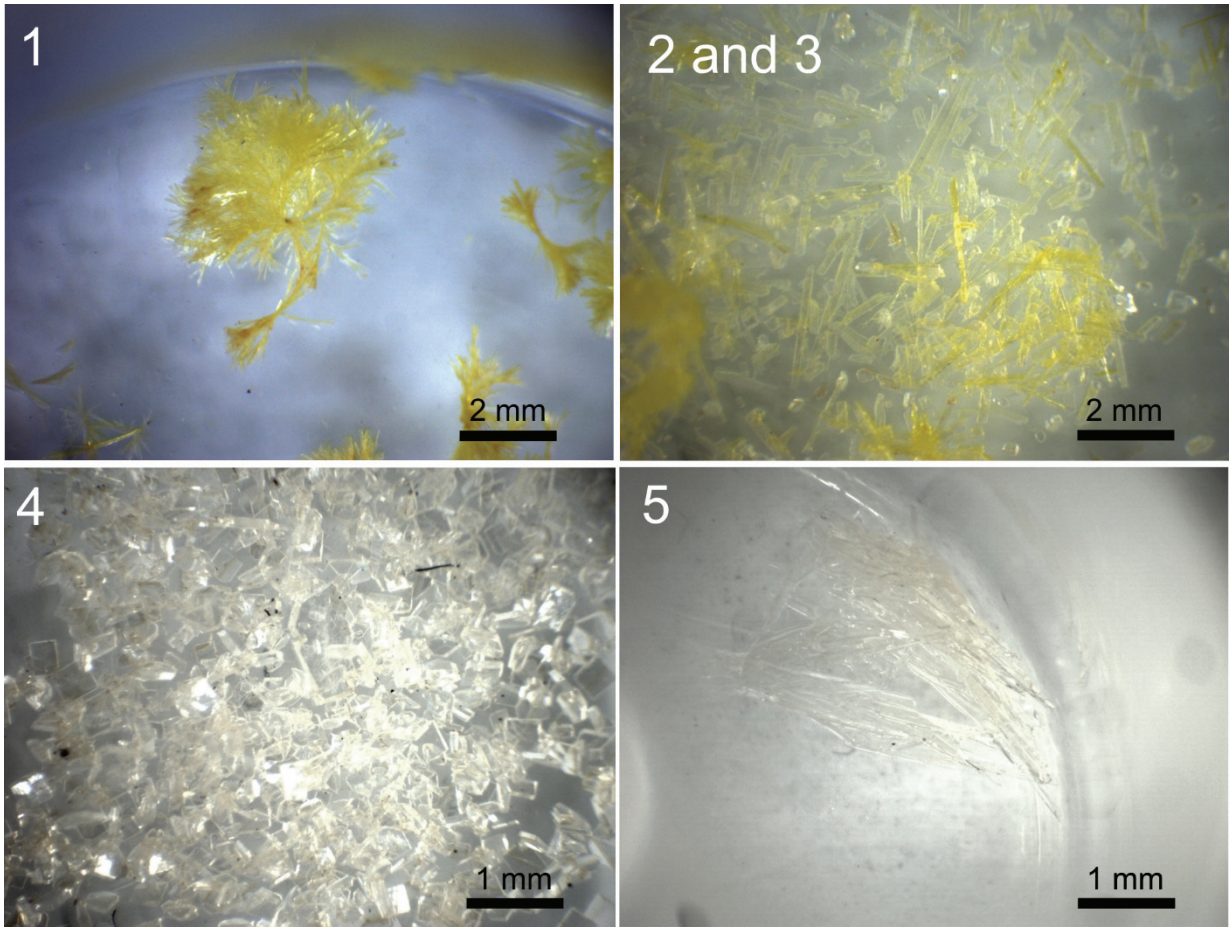


Figure S1. Images (optical microscopy) of the five types of crystal phases **1-5**; **2** (thick pale yellow needles) and **3** (yellow needles) were grown as a mixture; observed yellowish coloration on **4** and **5** is due to the employed light source.

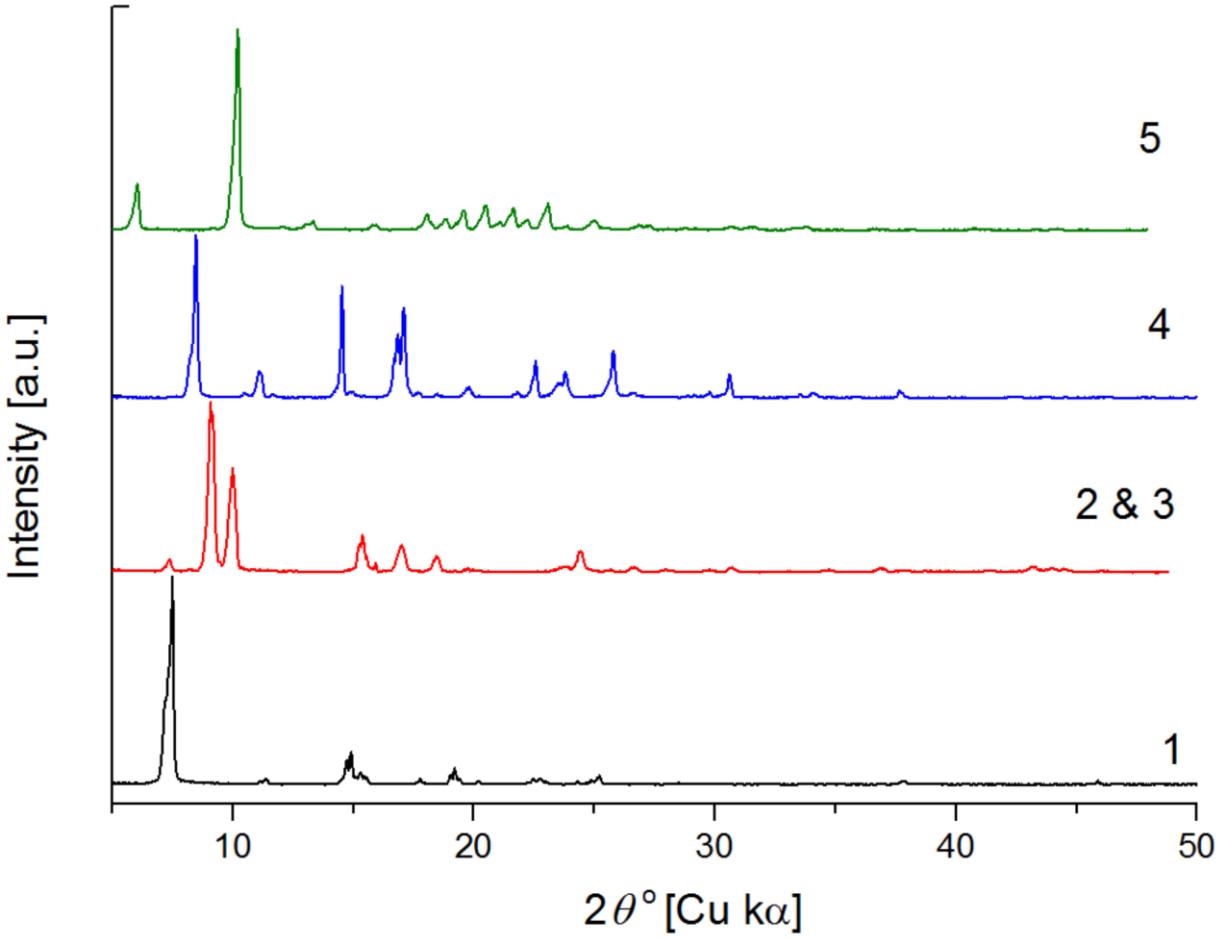


Figure S2. Powder XRD patterns of **1-5**. Crystal phases **2** and **3** grow as a mixture.

Table S1. Selected bond distances for **1 - 5** (Å).

Bond	**Selected bond lengths, Å**				
	1	**2**	**3**	**4**	**5**
N1 – N2	1.3981(19)	1.395(3)	1.420(6)	1.3768(19)	1.374(2)
N2 – C3	1.313(2)	1.310(3)	1.294(6)	1.321(2)	1.326(2)
C3 – C4	1.499(2)	1.427(3)	1.425(7)	1.387(2)	1.393(2)
C4 – C41	1.434(2)	1.431(3)	1.424(7)	1.476(3)	1.469(3)
C4 – C5	1.410(2)	1.389(3)	1.391(8)	1.431(3)	1.428(3)
C5 – N1	1.346(2)	1.345(3)	1.318(7)	1.390(2)	1.385(2)
C5 – O5	1.303(2)	1.311(3)	1.301(6)	1.2502(19)	1.254(2)
C41 – O41	1.272(2)	1.268(3)	1.289(7)	1.219(2)	1.226(2)

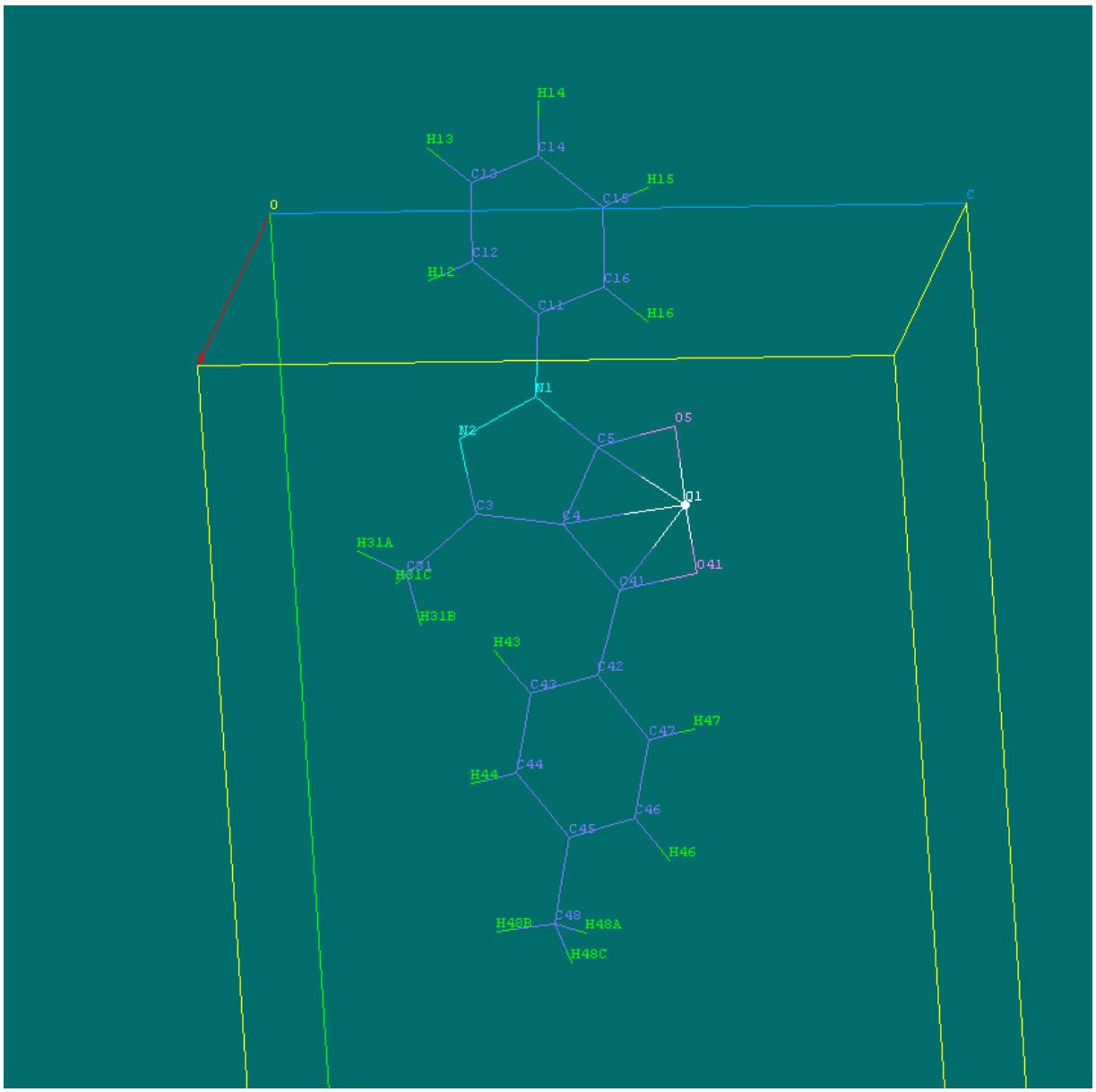


Figure S3. Difference Fourier map (*Fo* – *Fc*) and observed residual electron density (Q1) nearby O41 and O5 in **3**.

Table S2. Hydrogen bonding interactions and geometry in **1**-**5** (Å, ^{o}).

1	D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
	C16-H16	0.930	2.255	124.42	2.885	O5
	O5-H5	0.820	1.849	141.67	2.543	O41
2	D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
	C16-H16	0.930	2.252	124.03	2.877	O5
	O5-H5	0.820	1.874	140.49	2.560	O41
3	D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
	C16-H16	0.930	2.465	113.36	2.959	O5
	O5-H5	0.820	1.79	141.5	2.482	O41
	O41-H41	0.820	1.70	157.5	2.482	O5
4	D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
	C12-H12	0.930	2.584	142.97	3.374	O5 [x, -y+1/2, z-1/2]
	C16-H16	0.930	2.425	116.19	2.956	O5
	N2-H2	0.860	1.873	159.65	2.696	O5 [x, -y+1/2, z-1/2]
5	D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
	N2-H2	0.945	1.719	170.94	2.656	O5 [x, -y, z-1/2]

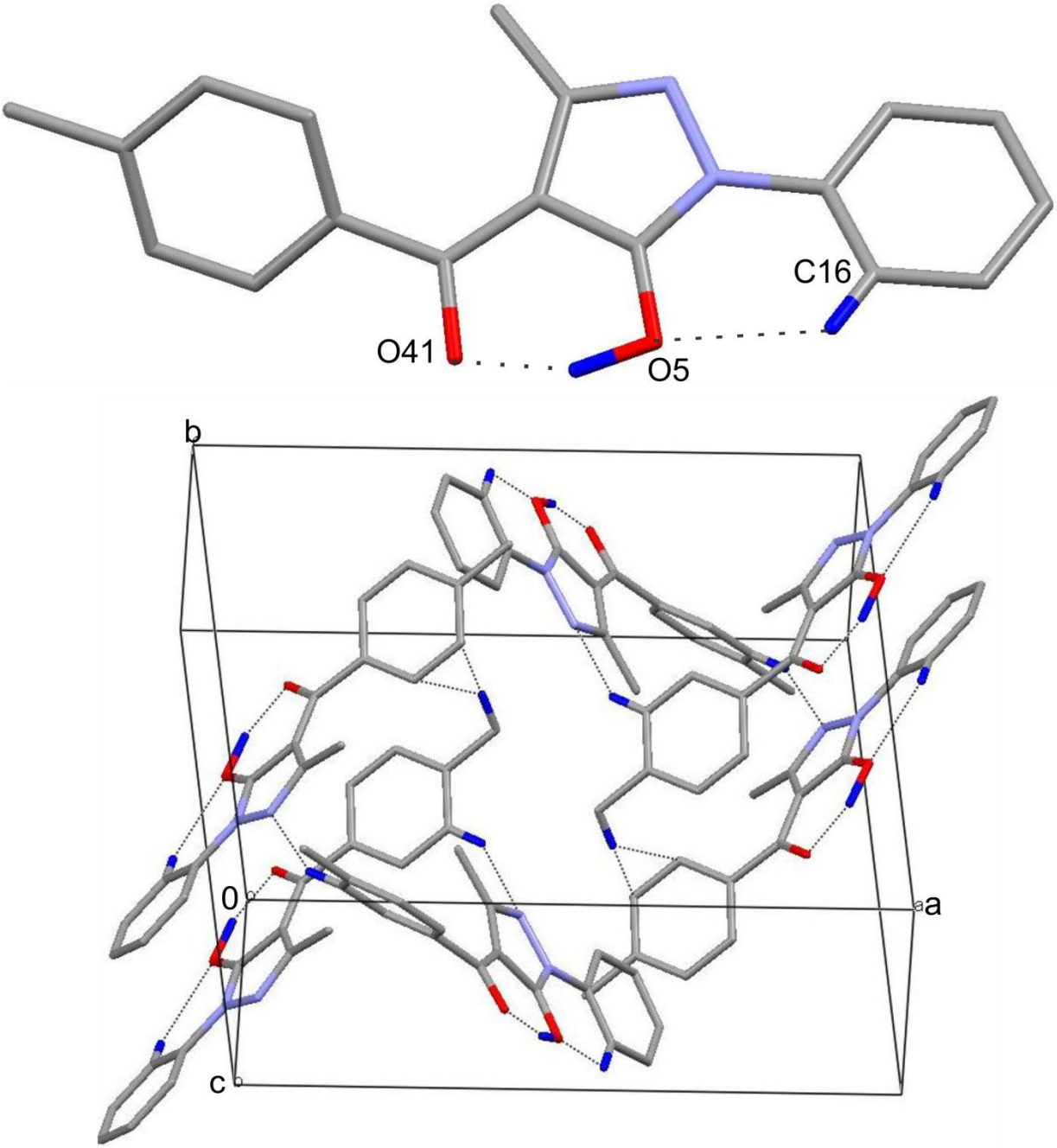


Figure S4. Intramolecular hydrogen bonding interactions (top) and crystal packing (bottom) of the molecules in **1**.

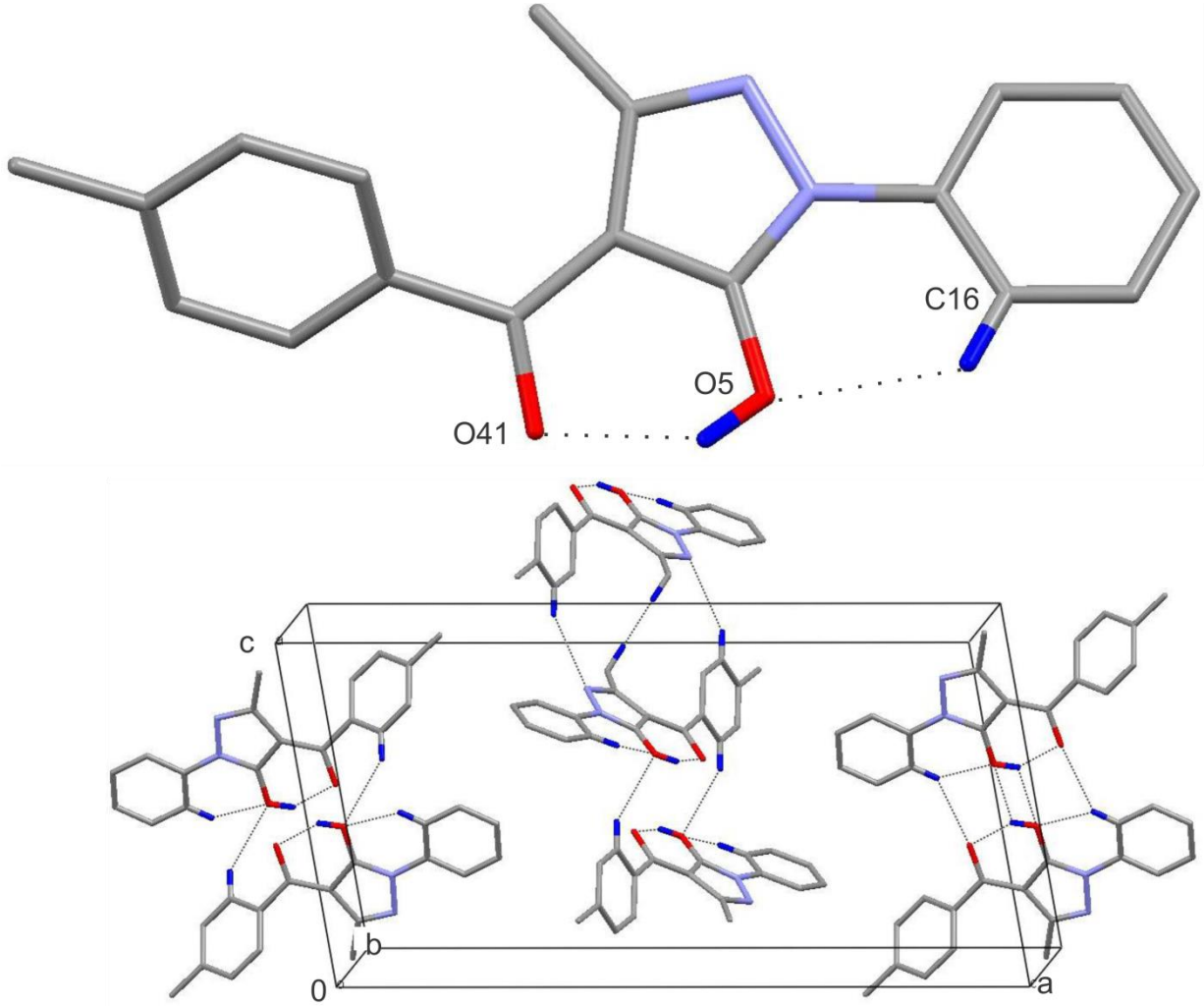


Figure S5. Intramolecular hydrogen bonding interactions (top) and crystal packing (bottom) of the molecules in **2**.

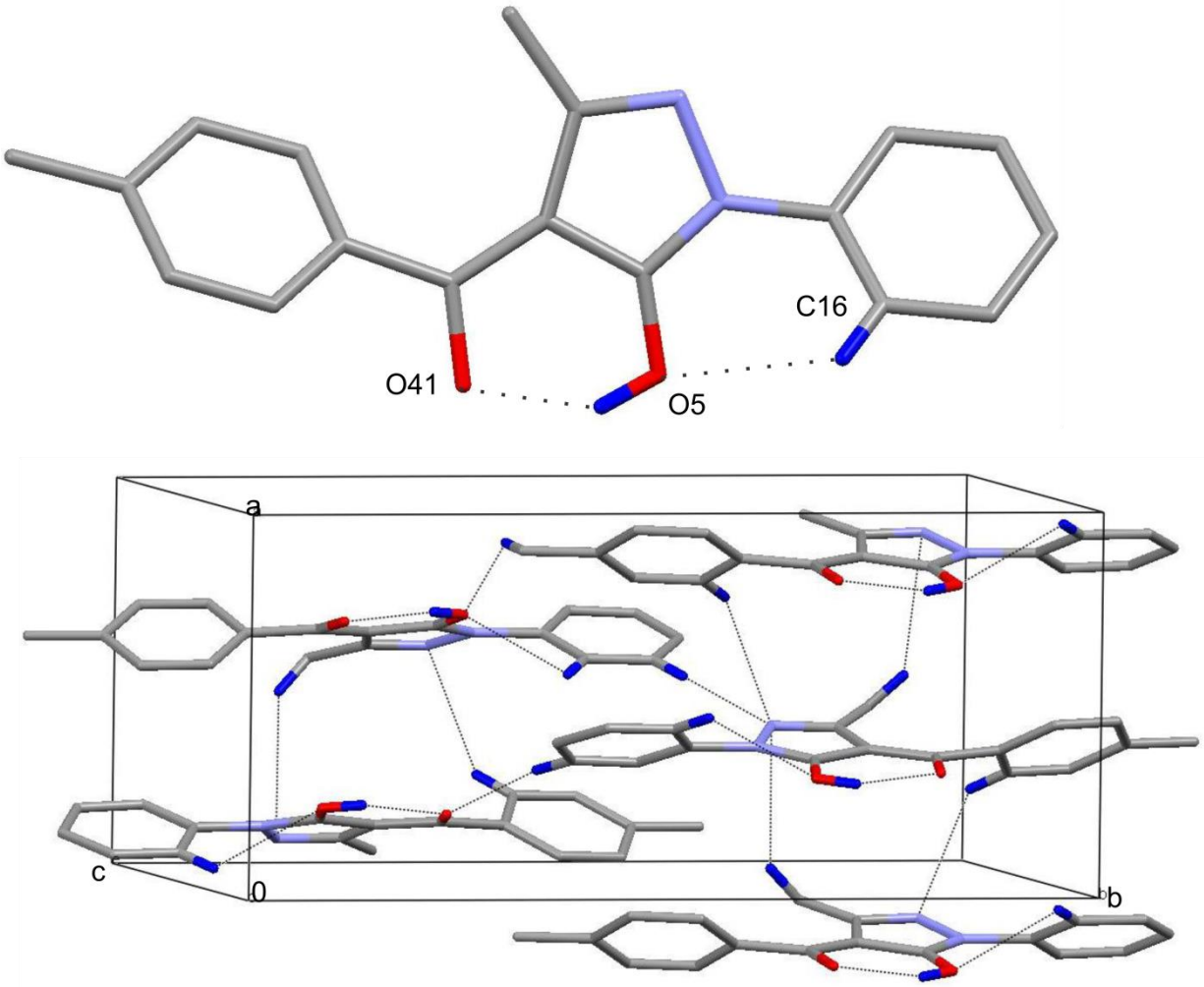


Figure S6. Intramolecular hydrogen bonding interactions (top) and crystal packing (bottom) of the molecules in **3**.

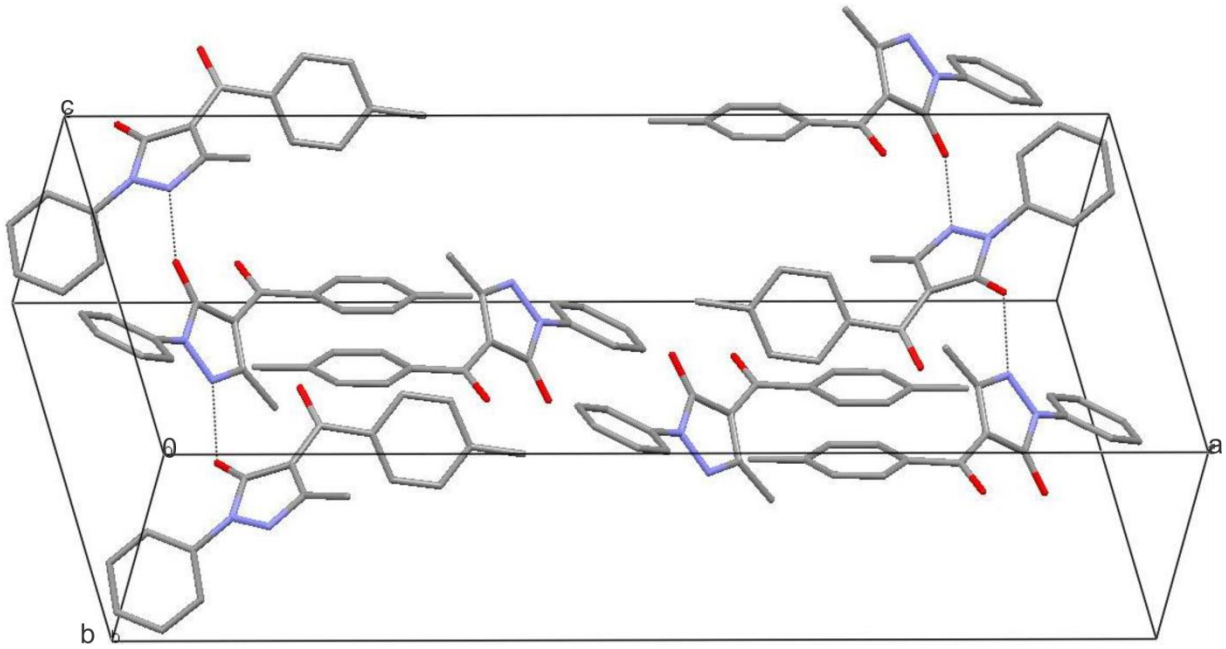


Figure S7. Crystal packing of the molecules in **4**.

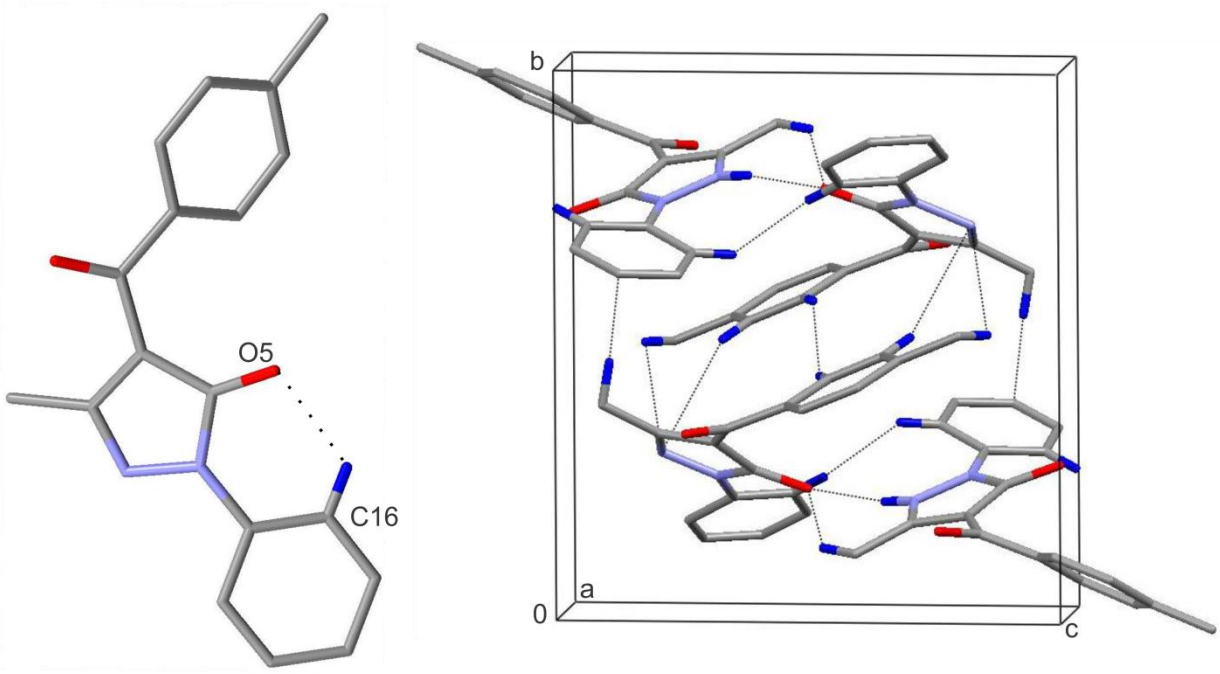


Figure S8. Intramolecular hydrogen bonding interactions (left) and crystal packing (right) of the molecules in **5**.

Table S3. Comparison of room temperature and low temperature crystal data for **1-5**.

sample	**1**		**2**		**3**		**4**		**5**	
TT	101.1-101.2°C		103.9-104.0°C		105.8-105.9°C		126.2-126.4°C		135.4-135.6°C	
	RT	LT	RT	LT	RT	LT	RT	LT	RT	LT
a	15.3847(5)	15.3484(4)	11.8744(7)	11.7774(7)	7.6533(5)	7.4723(5)	10.966(5)	10.9709(4)	29.4373(11)	29.4321(19)
b	5.2035(2)	5.12120(10)	5.3140(5)	5.3159(16)	17.3165(8)	17.3131(8)	12.084(5)	11.8263(3)	9.0493(4)	8.8489(4)
c	18.2280(7)	18.0639(5)	23.4934(14)	23.349(3)	11.3945(5)	11.3273(5)	11.968(5)	11.9472(4)	11.4932(4)	11.4832(6)
beta	90.913(3)	90.970(2)	97.072(5)	97.592(7)	90	90	110.14(4)	110.334(4)	97.476(4)	97.478(5)
V	1459.04(9)	1419.66(6)	1471.2(1)	1449.0(5)	1510.09(14)	1465.4(1)	1488.9(12)	1453.49(9)	3035.6(2)	2965.3(3)
ρ	1.331	1.368	1.320	1.34	1.286	1.325	1.304	1.336	1.279	1.31

Table S4. Chemical shifts in the NMR spectra of 3-methyl-4-(4-methylphenyl)-1-phenyl-pyrazol-5-one signals in solid state.

	$CDCl_3$	**1**	**2**[a]	**3**[b]	**4**	**5**
CH_3-3	16.02	16.27	15.86	18.16	11.11	12.45
CH_3, Ar	21.68	22.72	22.09	21.09	21.74	21.01
CH-Ar, Ph	120.73 126.62 128.17 129.08 129.13	117.79[c] 125.61 128.12 129.54[c] 130.54 131.53	118.02[c] 125.92 128.46 129.90 130.09	120.79[c] 125.01 128.96[c] 131.04	116.83 119.98 125.54 127.37 130.00[c] 131.76	122.30 124.55 126.11 129.24[c] 130.67 132.76
C_q-3	147.91	145.22	145.52	146.46	151.09	146.84
C_q-4	103.53	102.88	103.33	101.57	105.02	103.16
C_q-5	161.81	163.13	162.35	163.28	158.86	160.12
C_q-O, aroyl	191.63	188.70	190.86	189.91	187.12	190.22
C_q-1, Ar	134.64	134.36	135.03	131.20	135.64[c]	135.62[c]
C_q-1, Ph	137.27	138.27	137.92	137.34		
C_q-4, Ar	142.69	141.59	141.89	143.79	144.04	143.49
N-1		191.74	191.60	191.33	174.25	176.72
N-2		277.62	279.55	284.72	162.66	167.41

[a] Assigned as difference between the spectra of **1**+**2** mixture and pure **1**. [b] Mixture containing >90 % **3** according to powder XRD. [c] Signals with increased intensity (more than one carbon).

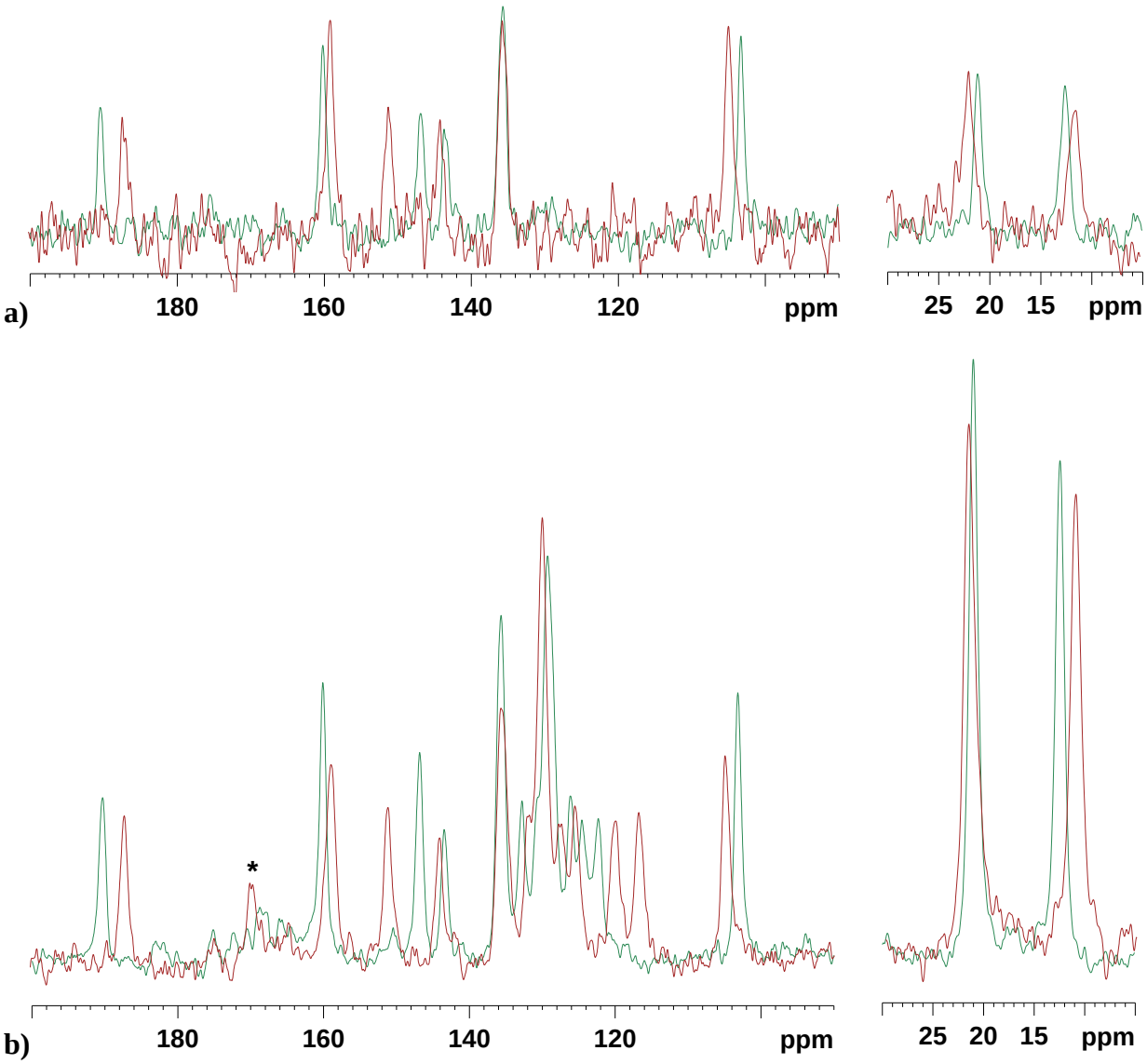


Figure S9 ^{13}C spectra of **4** (brown) and **5** (green): a) CPTOSS-NQS; b) CPTOSS. Residual spinning sideband is marked with asterisk.

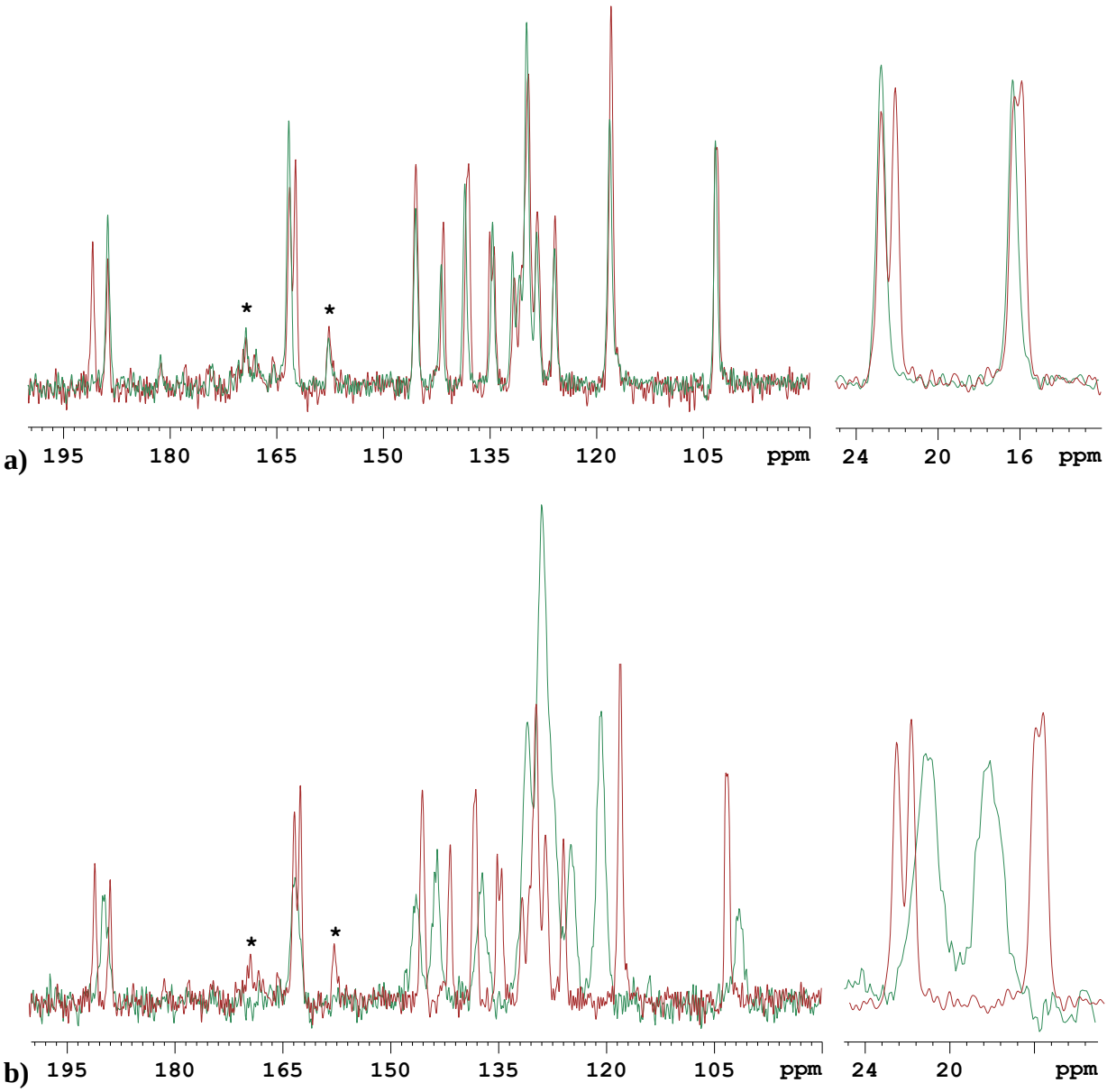


Figure S10 ^{13}C CPTOSS spectra of **1** + **2** mixture (brown) and: a) **1** (green); b) **3** (green). Residual spinning sidebands are marked with asterisks.

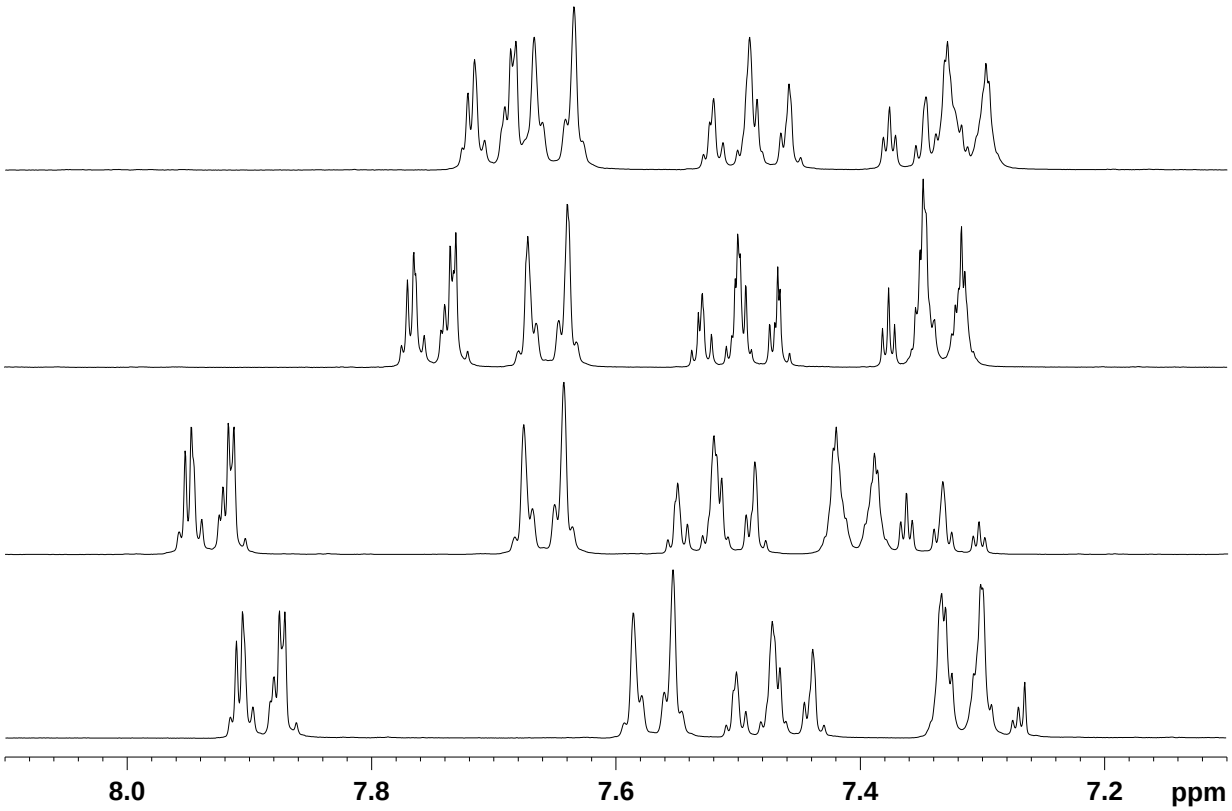


Figure S11. The aromatic area in ^{1}H NMR spectra of 3-methyl-4-(4-methylphenyl)-1-phenyl-pyrazol-5-one in different solvents. From bottom to top: $CDCl_3$, CD_3COCD_3, CD_3OD:CD_3COCD_3 5:1, CD_3OD.

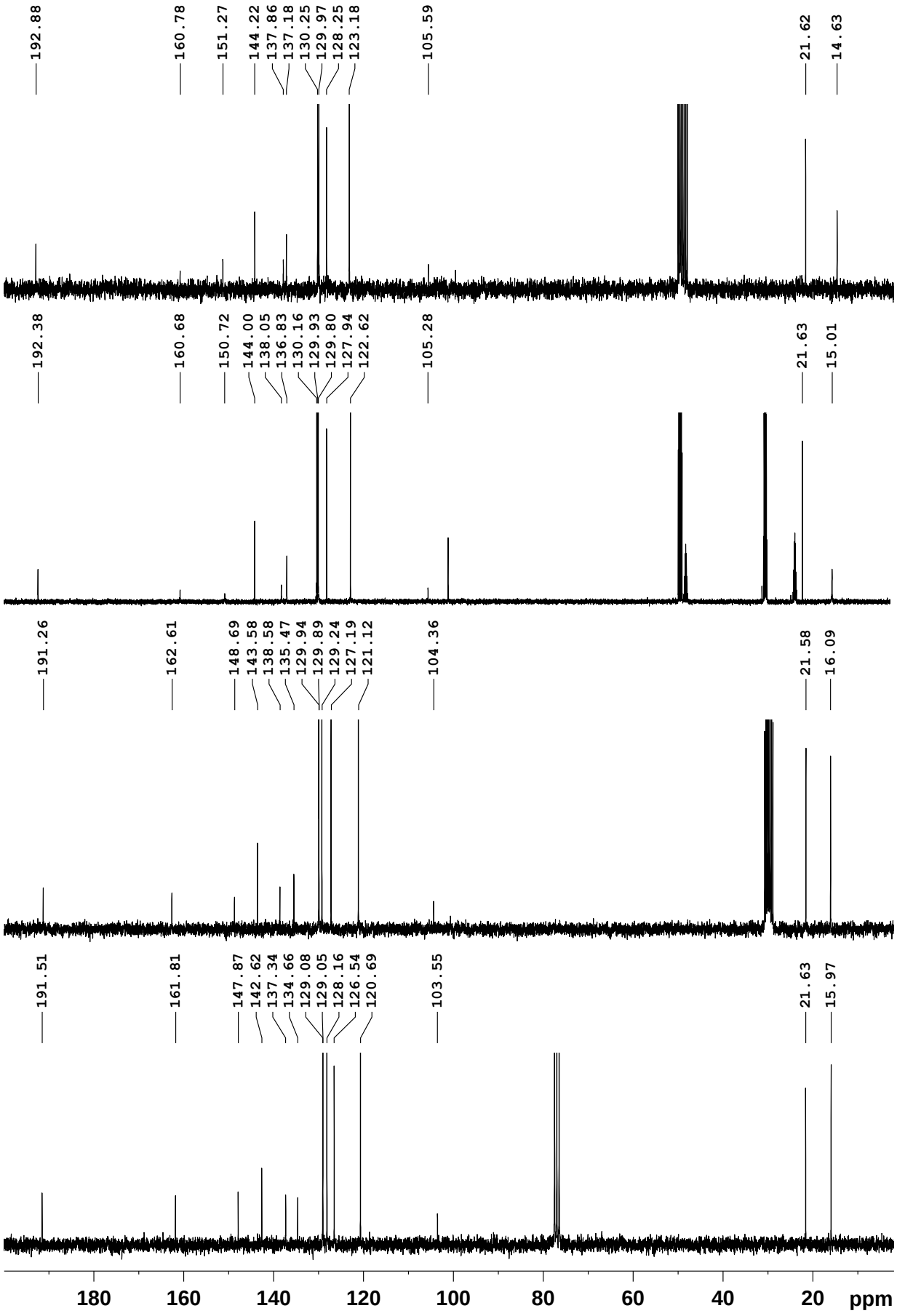
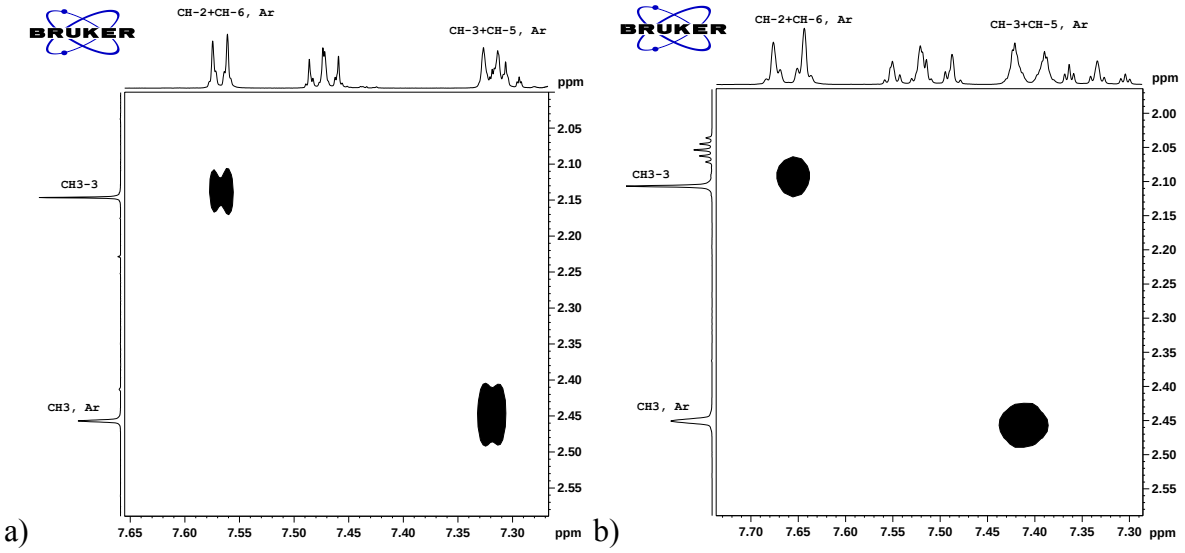


Figure S12. ^{13}C NMR spectra of 3-methyl-4-(4-methylphenyl)-1-phenyl-pyrazol-5-one in different solvents. From bottom to top: $CDCl_3$, CD_3COCD_3, CD_3OD:CD_3COCD_3 5:1, CD_3OD.

Table S5. Chemical shifts in the NMR spectra of 3-methyl-4-(4-methylphenyl)-1-phenyl-pyrazol-5-one signals in different solvents.

	$CDCl_3$		**CD_3COCD_3**		**CD_3OD: CD_3COCD_3 5:1**		**CD_3OD**	
	δ_H	**δ_C**	**δ_H**	**δ_C**	**δ_H**	**δ_C**	**δ_H**	**δ_C**
CH_3-3	2.146	16.02	2.107	16.09	2.201	15.10	2.234	14.63
CH_3, Ar	2.457	21.68	2.451	21.58	2.431	21.63	2.426	21.62
CH-2,6, Ar	7.568	128.17	7.661	129.24	7.652	129.80	7.652	130.26
CH-3,5, Ar	7.320	129.08	7.405	129.89	7.340	129.93	7.314	129.97
CH-2,6, Ph	7.880	120.73	7.932	121.12	7.771	122.62	7.700	123.18
CH-3,5, Ph	7.473	129.13	7.519	129.94	7.500	130.16	7.492	129.97
CH-4, Ph	7.306	126.62	7.334	127.19	7.349	127.94	7.351	128.25
C_q-3		147.91		148.69		150.72		151.27
C_q-4		103.53		104.36		105.28		105.59
C_q-5		161.81		162.61		160.68		160.78
C=O		191.63		191.26		192.38		192.88
C_q-1, Ar		134.64		135.47		136.47		137.18
C_q-4, Ar		142.69		143.58		144.00		144.22
C_q-1, Ph		137.27		138.58		138.05		137.86



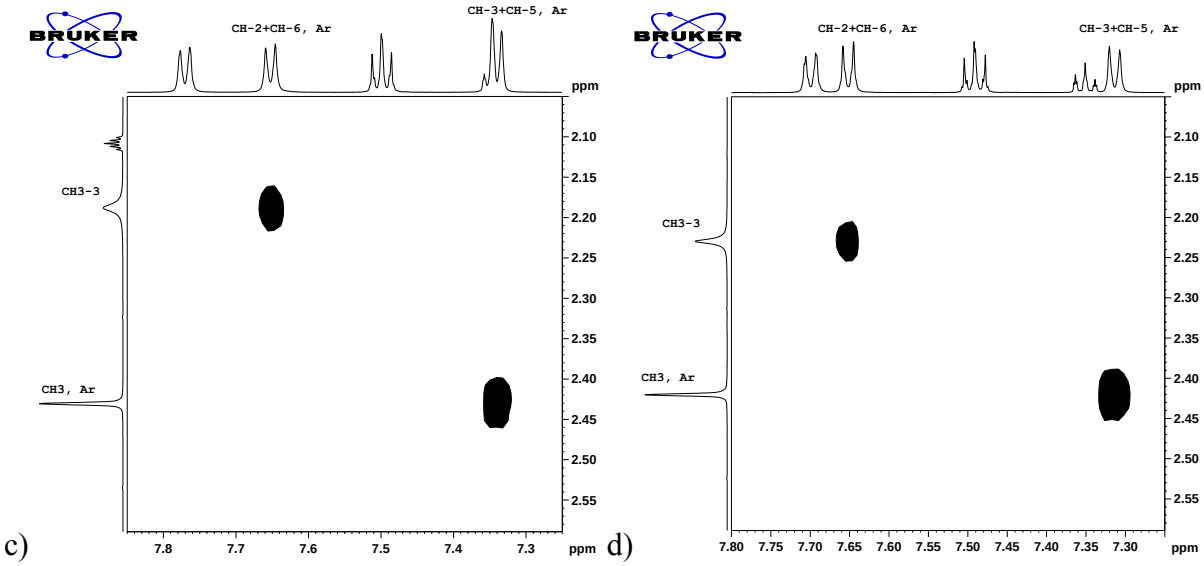


Figure S13. Partial ^{1}H-^{1}H NOESY spectra of 3-methyl-4-(4-methylphenyl)-1-phenyl-pyrazol-5-one in: a) $CDCl_3$; b) CD_3COCD_3; c) CD_3OD:CD_3COCD_3 5:1; d) CD_3OD.

Table S6. Relative stability and major structural parameters of tautomers and isomers (M06-2X/TZVP) in methanol (PCM model).

Structure	ΔE [kcal/mol]	ΔE+ZPE [kcal/mol]	ΔG [kcal/mol]	angle C4-C41-C42-C47	angle C3-C4-C41-O41	angle C16-C11-N1-C5
A1	0.00	0.00	0.00	-43.1	164.8	-34.9
A2	0.22	0.16	0.03	44.1	-167.1	-34.7
B1	1.50	1.16	1.06	-45.4	169.6	-26.2
B2	1.50	1.16	1.06	45.4	-169.6	26.1
A3	3.62	3.36	3.20	41.9	17.6	-40.3
A4	3.75	3.40	3.00	-42.9	-18.2	-40.6
D1	4.20	3.78	2.87	30.3	23.8	-50.1
D2	4.73	4.16	3.49	-32.6	-22.6	-48.6
D3	5.25	4.85	4.26	32.3	-143.7	-46.7
D4	6.02	5.53	5.93	-34.5	142.4	-49.7
C1	7.06	6.17	6.23	-5.1	17.4	29.5
C2	7.80	6.89	5.78	-3.3	-115.1	-32.7
C3	7.82	7.10	6.08	-0.3	86.3	27.2
B4	9.72	9.41	9.05	40.2	10.2	28.6
B3	9.72	9.41	9.05	-40.2	-10.2	-28.6