Supporting info for:

Self-organization of 1,6-dialkyl-3a,6a-diphenylglycolurils in the crystalline state

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1. X-ray diffraction data

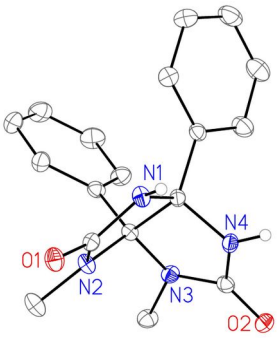
Table TS1 Crystal data and structure refinement for **1a** solid forms.

	1a	**1a**·2CH_3COOH	**1a**·$C_6H_{10}O$	**1a**·1.5$C_4H_8O_2$	**1a**·CHOOH	**1a**·$C_4H_8O_3$	**1a**·CH_3OH
CCDC	2072843	2072840	2072846	2072849	2072844	2072841	2072842
Empirical formula	$C_{18}H_{18}N_4O_2$	$C_{22}H_{26}N_4O_6$	$C_{24}H_{28}N_4O_3$	$C_{24}H_{30}N_4O_5$	$C_{19}H_{20}N_4O_4$	$C_{22}H_{26}N_4O_5$	$C_{19}H_{22}N_4O_3$
Formula weight	322.36	442.47	420.50	454.52	368.39	426.47	354.40
T, K	120	120	120	120	100	120	120
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/c$	P-1	P-1	$P2_12_12_1$	P-1
Z / Z'	4 / 1	4 / 2	4 / 1	4 / 2	2 / 1	4 / 1	2 / 1
a, Å	15.1775(15)	8.340(2)	10.5144(6)	10.8013(8)	9.2955(10)	10.8660(5)	9.4667(10)
b, Å	11.3912(11)	25.809(7)	13.2689(7)	14.8820(11)	9.6189(10)	12.6977(6)	9.5371(10)
c, Å	9.0508(9)	10.622(3)	15.6124(8)	16.5499(12)	11.1769(12)	15.5356(7)	10.9139(11)
α, °				100.2147(16)	68.975(2)		71.045(2)
β, °	99.279(2)	94.689(7)	91.5967(12)	108.5370(16)	70.514(2)		72.014(2)
γ, °				109.0343(17)	82.886(2)		82.789(2)
V, $Å^3$	1544.3(3)	2278.7(11)	2177.3(2)	2264.1(3)	879.38(16)	2143.50(17)	886.04(16)
d_{calc}, g cm^{-3}	1.386	1.290	1.283	1.333	1.391	1.322	1.328
μ, cm^{-1}	0.94	0.95	0.86	0.95	1.00	0.95	0.92
Reflns collected	20184	40191	28543	50823	11709	27874	19210
Independent reflns [Rint]	4509 [0.0572]	13265 [0.1111]	6342 [0.0558]	13207 [0.0663]	5116 [0.0225]	6254 [0.0253]	5177 [0.0298]
Observed refls [I>2σ(I)]	3354	7289	4582	8478	4354	5690	4058
Parameters	227	602	290	652	258	296	250
R1	0.0478	0.0765	0.0473	0.0500	0.0410	0.0353	0.0414
wR2	0.1224	0.1784	0.1177	0.1256	0.1090	0.0989	0.1085
GOF	1.019	1.022	1.009	1.020	1.037	1.014	1.025
Residual density, e $Å^{-3}$ (d_{min}/d_{max})	0.440/ -0.238	0.362/ -0.388	0.399/ -0.239	0.381/ -0.243	0.400/ -0.257	0.309/ -0.177	0.375/ -0.224

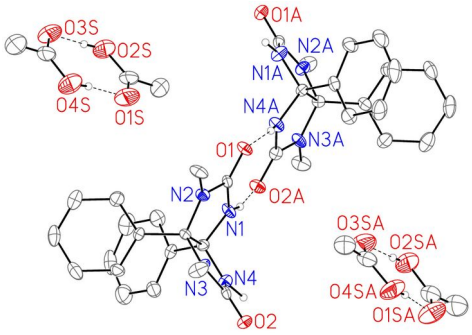
Table TS2 Crystal data and structure refinement for **1b** solid forms.

	1b	**1b**·CH_3COOH	**1b**·$C_4H_8O_2$	**1b**·C_2H_5OH	**1b**·CHOOH	**1b**·$(CH_3)_2CO$	**1b**·CH_3CN	**1b**·CH_3OH	**1b**·C_5H_5N
CCDC	2072845	2072855	2072853	2072848	2072847	2072850	2072854	2072852	2072851
Empirical formula	$C_{20}H_{22}N_4O_2$	$C_{22}H_{26}N_4O_4$	$C_{24}H_{30}N_4O_4$	$C_{22}H_{28}N_4O_3$	$C_{21}H_{24}N_4O_4$	$C_{23}H_{28}N_4O_3$	$C_{22}H_{25}N_5O_2$	$C_{21}H_{26}N_4O_3$	$C_{25}H_{27}N_5O_2$
Formula weight	350.41	410.47	438.52	396.48	396.44	408.49	391.47	382.46	429.51
T, K	120	120	120	120	120	120	120	120	120
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	P-1	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$	P-1
Z / Z'	8 / 2	8 / 2	2 / 1	4 / 2	4 / 1	2 / 1	4 / 1	4 / 1	4 / 2
a, Å	12.3392(12)	14.6755(14)	8.2337(9)	12.5231(9)	8.9850(4)	8.0523(10)	12.6677(14)	12.7245(7)	13.2527(11)
b, Å	8.4864(8)	17.8903(16)	10.7773(12)	12.9844(10)	23.1322(11)	10.7345(13)	9.9394(11)	9.4309(5)	13.5955(11)
c, Å	34.065(3)	16.1564(15)	12.9970(14)	13.4742(10)	9.9624(5)	13.0559(16)	16.7019(18)	17.0038(9)	14.5032(12)
α, °			98.025(3)	103.8760(16)		97.828(3)			112.4997(17)
β, °	99.814(2)	91.586(2)	97.959(3)	96.9424(17)	109.7820(10)	97.868(3)	101.334(2)	100.2190(10)	98.1336(17)
γ, °			91.457(3)	97.1860(17)		91.711(3)			104.9098(18)
V, $Å^3$	3515.0(6)	4240.2(7)	1129.8(2)	2084.3(3)	1948.42(16)	1106.1(2)	2061.9(4)	2008.15(19)	2247.1(3)
d_{calc}, g cm^{-3}	1.324	1.286	1.289	1.264	1.351	1.226	1.261	1.265	1.270
μ, cm^{-1}	0.88	0.90	0.89	0.86	0.95	0.83	0.84	0.86	0.83
Refls collected	45663	56043	15161	37248	16615	14838	44091	26222	30094
Independent refls [Rint]	10234 [0.0917]	12373 [0.0940]	6587 [0.0452]	12149 [0.0558]	5602 [0.0353]	6439 [0.0600]	6006 [0.0630]	5856 [0.0565]	13077 [0.0376]
Observed refls [I>2σ(I)]	6428	7075	4495	8319	4269	3845	4303	4144	8879
Parameters	489	571	299	578	276	302	273	268	597
R1	0.0586	0.0553	0.0532	0.0572	0.0483	0.0584	0.0474	0.0459	0.0530
wR2	0.1412	0.1302	0.1283	0.1510	0.1153	0.1403	0.1266	0.1213	0.1466
GOF	1.009	1.010	1.030	1.014	1.028	1.009	1.016	1.014	1.025
Residual density, e $Å^{-3}$ (d_{min}/d_{max})	0.344/ -0.270	0.255/ -0.327	0.422/ -0.262	0.681/ -0.294	0.411/ -0.241	0.331/ -0.253	0.366/ -0.233	0.357/ -0.222	0.375/ -0.234

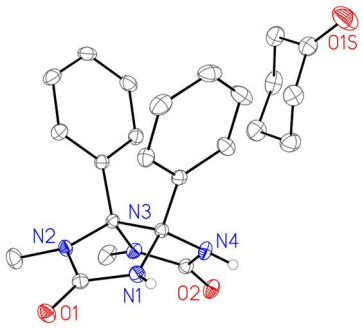
2. Asymmetric unit and crystal packing images



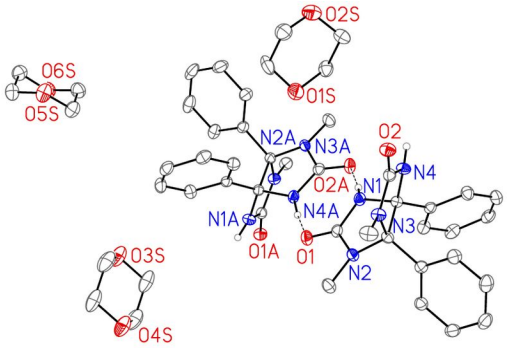
1a



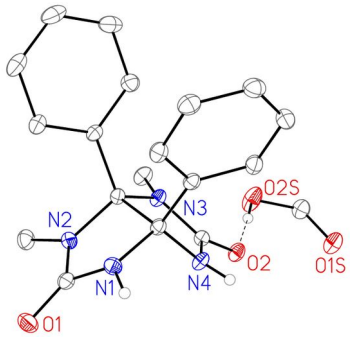
1a·2(CH_3COOH)



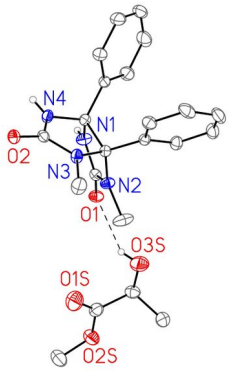
1a·$C_6H_{10}O$



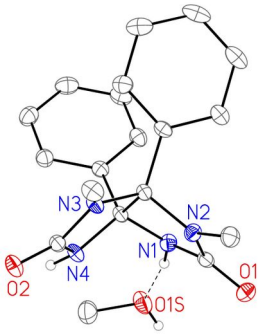
1a·1.5($C_4H_8O_2$)



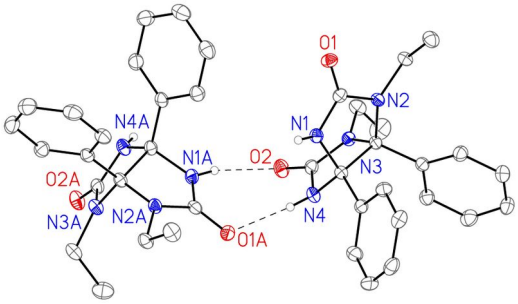
1a·CHOOH



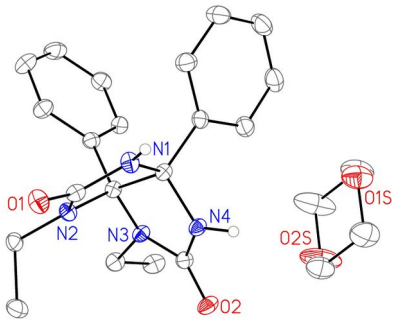
1a·$C_4H_8O_3$



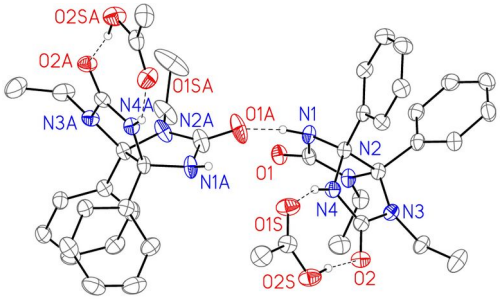
1a·CH_3OH



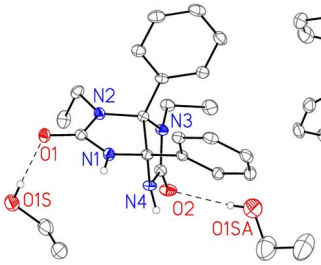
1b



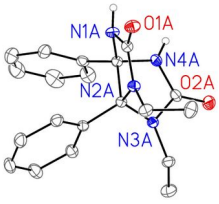
1b·$C_4H_8O_2$

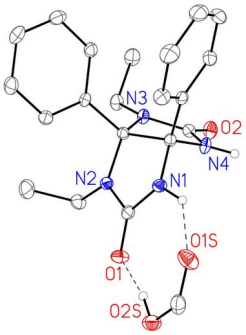


1b·CH_3COOH

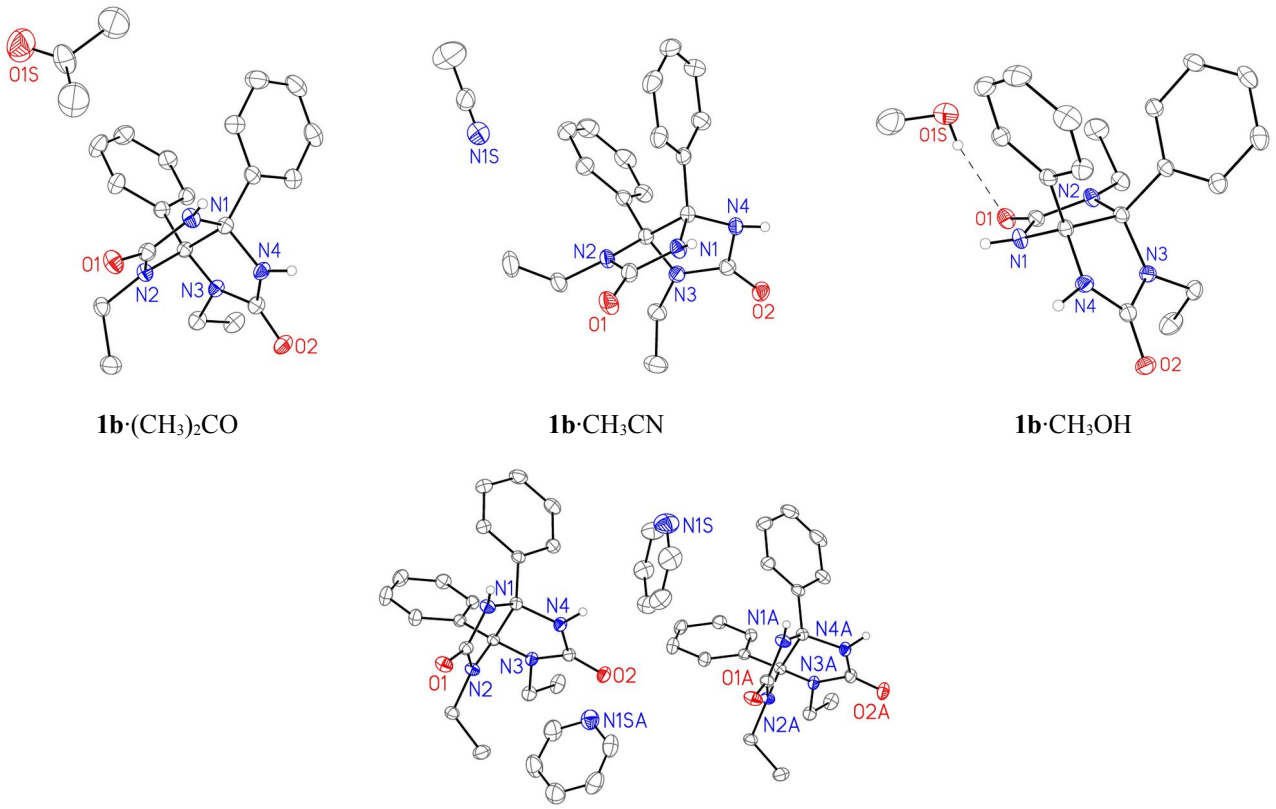


1b·C_2H_5OH





1b·CHOOH



1b·$(CH_3)_2CO$ **1b**·CH_3CN **1b**·CH_3OH

1b·C_5H_5N

Fig. S1 Asymmetric units of the structures studied in representation of atoms with thermal ellipsoids (p=50%). The minor components of the disordered structures **1a**·$C_4H_8O_2$, **1b**·$(CH_3)_2CO$ and **1b**·C_2H_5OH and hydrogen atoms connected to carbon atoms are omitted for clarity.

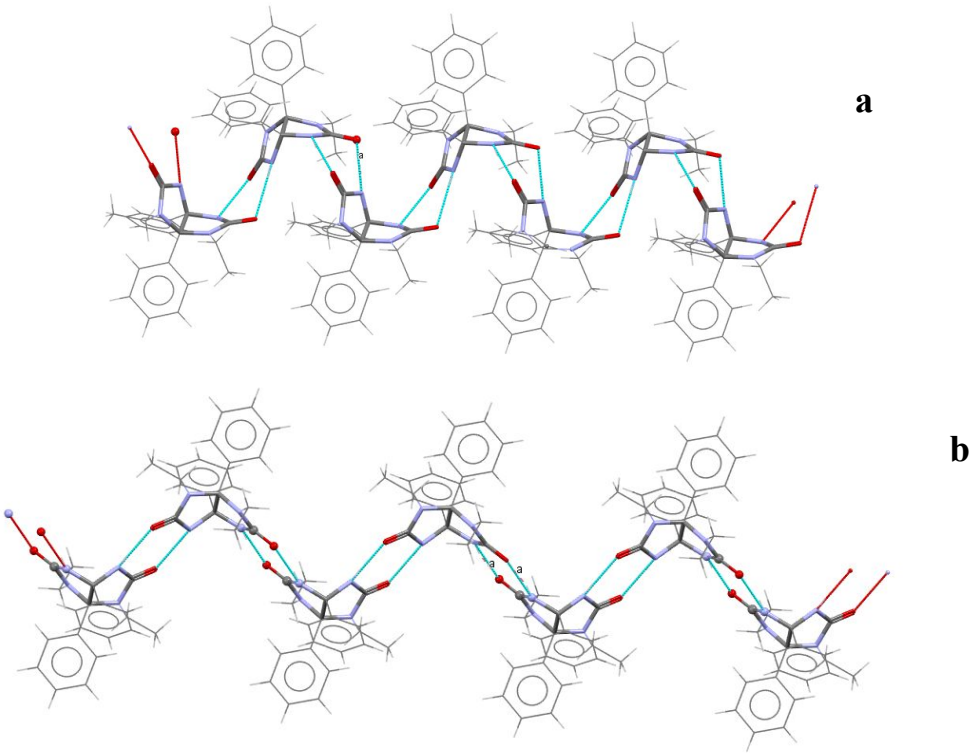


Fig. S2 "Waved" and "zigzag" conformations of H-bonded chains in structures **1b** (a) and **1b**·$C_4H_8O_2$ (b). H-bonds are dotted blue.

3. CE-B3LYP calculations

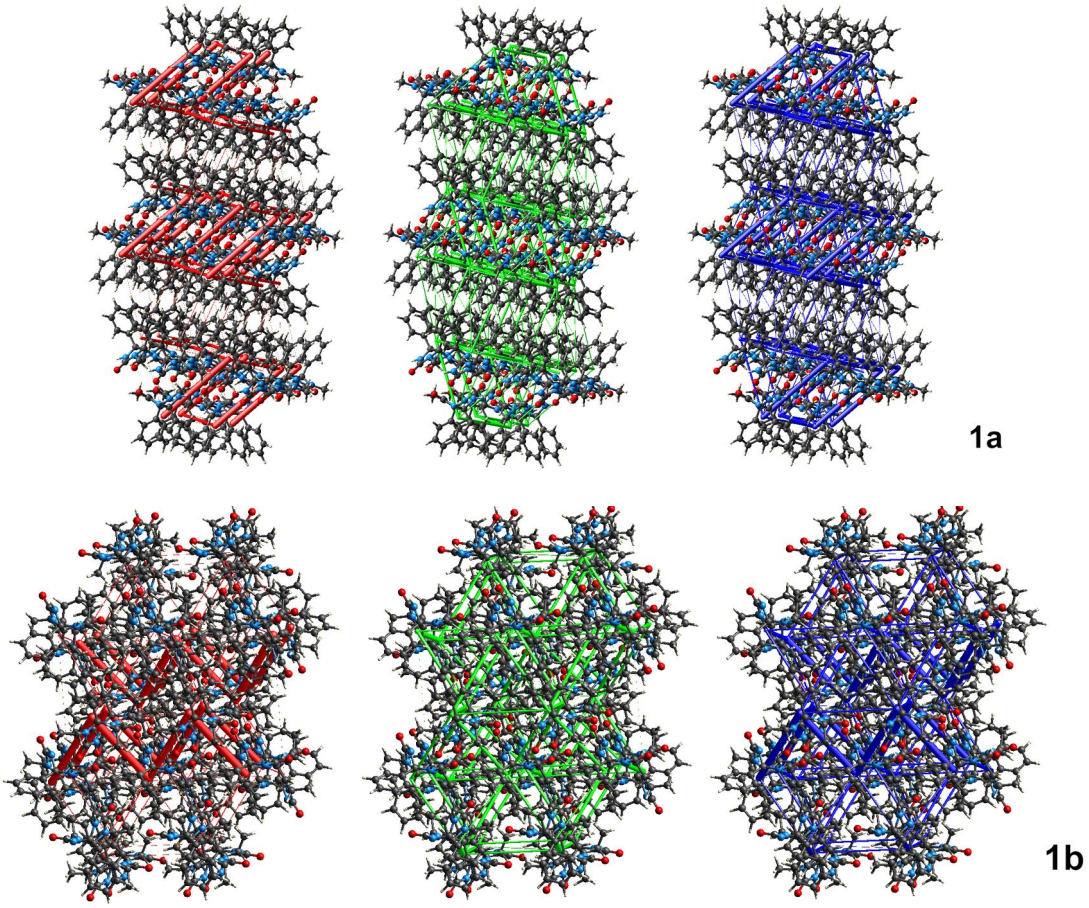


Fig. S3 Coulomb (red), dispersion (green) and total (blue) energy frameworks for **1a** and **1b**.

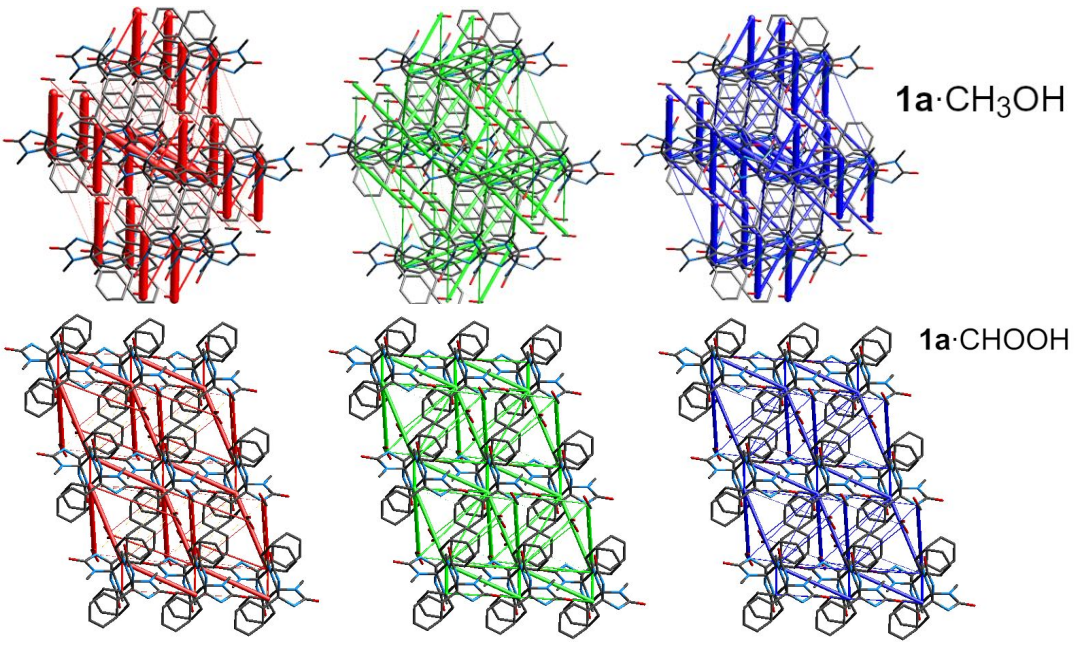


Fig. S4 Coulomb (red), dispersion (green) and total (blue) energy frameworks for **1a** and **1b**.

Table TS3 CE-B3LYP interaction energies (kJ mol^{-1}) for **1a**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	-x, y+1/2, -z+1/2	8.70	B3LYP/6-31G(d,p)	0.6	-4.9	-15.4	9.4	-10.6
2	x, -y+1/2, z+1/2	7.29	B3LYP/6-31G(d,p)	-37.9	-12.3	-36.7	46.3	-52.6
1	-x, -y, -z	7.71	B3LYP/6-31G(d,p)	-2	-7.3	-43.8	32.7	-25.4
1	-x, -y, -z	8.24	B3LYP/6-31G(d,p)	-76.8	-18.4	-18.6	67.7	-69.2
2	x, -y+1/2, z+1/2	7.26	B3LYP/6-31G(d,p)	-3	-2.8	-37.8	21.7	-24.8
1	-x, -y, -z	8.58	B3LYP/6-31G(d,p)	-6.1	-1.1	-33.7	22.7	-22.6
2	-x, y+1/2, -z+1/2	10.58	B3LYP/6-31G(d,p)	-1.4	-0.4	-12	8	-7.3

Table TS4 CE-B3LYP interaction energies (kJ mol^{-1}) for **1a**·CH_3OH

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
			1a					
1	-	4.96	B3LYP/6-31G(d,p)	-36.1	-9.1	-14.2	42.6	-31
1	-x, -y, -z	6.66	B3LYP/6-31G(d,p)	-6.9	-4.8	-39	17.5	-34
1	-x, -y, -z	8.00	B3LYP/6-31G(d,p)	-19.6	-7.5	-43	37.1	-40.7
1	-	6.54	B3LYP/6-31G(d,p)	-47.5	-11.7	-7.1	53.5	-32.1
1	-x, -y, -z	8.22	B3LYP/6-31G(d,p)	-88.5	-22	-21	85.7	-75.2
1	-	7.2	B3LYP/6-31G(d,p)	-2.1	-2.3	-5.3	4.7	-5.6
2	x, y, z	9.47	B3LYP/6-31G(d,p)	-3.2	-1.6	-13	4.8	-12.9
1	-x, -y, -z	9.64	B3LYP/6-31G(d,p)	0.7	-0.4	-20.7	12.5	-9.9
1	-x, -y, -z	6.61	B3LYP/6-31G(d,p)	-8.4	-2.5	-48.8	28.4	-35.6
1	-	8.05	B3LYP/6-31G(d,p)	-1.4	-0.4	-4.9	2.6	-4.4
1	-x, -y, -z	7.92	B3LYP/6-31G(d,p)	-4.4	-0.8	-31.9	15	-23.8
1	-	7.27	B3LYP/6-31G(d,p)	-5.8	-1.8	-5.7	9.6	-6.6
1	-	6.25	B3LYP/6-31G(d,p)	-3.1	-0.7	-12.4	8	-9.6
1	-x, -y, -z	10.46	B3LYP/6-31G(d,p)	-6.8	-0.5	-1.8	0	-9.1
1	-	8.8	B3LYP/6-31G(d,p)	0.7	0	-0.5	0	0.3
			CH_3OH					
1	-	6.54	B3LYP/6-31G(d,p)	0.8	-0.1	-1.2	0	-0.3
1	-	6.25	B3LYP/6-31G(d,p)	-8.4	-2.5	-48.8	28.4	-35.6
1	-x, -y, -z	4.85	B3LYP/6-31G(d,p)	-0.8	-0.1	-0.3	0	-1.2
1	-x, -y, -z	5.03	B3LYP/6-31G(d,p)	-0.2	0	-0.1	0	-0.3
1	-	8.05	B3LYP/6-31G(d,p)	-1.1	-0.3	-1.3	0	-2.6
1	-	7.27	B3LYP/6-31G(d,p)	-0.3	-0.1	-0.3	0	-0.6
1	-	7.5	B3LYP/6-31G(d,p)	-0.8	-0.1	-0.3	0	-1.2
1	-	4.96	B3LYP/6-31G(d,p)	-88.5	-22	-21	85.8	-75.2

Table TS5 CE-B3LYP interaction energies (kJ mol^{-1}) for **1a**·CHOOH

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
			1a					
1	-x, -y, -z	8.24	B3LYP/6-31G(d,p)	-79.7	-19.8	-19.3	66.3	-74.9
2	x, y, z	9.62	B3LYP/6-31G(d,p)	-1.2	-1.9	-11.1	3.9	-9.9
1	-x, -y, -z	7.95	B3LYP/6-31G(d,p)	-20.9	-7.9	-40.9	40.6	-38.6
1	-	7.91	B3LYP/6-31G(d,p)	0.4	-0.1	-1.3	0	-0.7
1	-x, -y, -z	6.50	B3LYP/6-31G(d,p)	-11.8	-5.4	-46.4	31.1	-37.7
1	-x, -y, -z	6.63	B3LYP/6-31G(d,p)	-11.2	-3.3	-45.8	27.7	-37.1
1	-x, -y, -z	9.69	B3LYP/6-31G(d,p)	0.6	-0.4	-20.6	12.7	-9.8
2	x, y, z	9.3	B3LYP/6-31G(d,p)	-0.9	-0.7	-16.7	9	-10.4
1	-x, -y, -z	7.84	B3LYP/6-31G(d,p)	-5.3	-1	-33.9	16.8	-25.5
1	-	7.8	B3LYP/6-31G(d,p)	0.6	-0.4	-20.6	12.7	-9.8
1	-	5.98	B3LYP/6-31G(d,p)	-1.2	-1.9	-11.1	3.9	-9.9
1	-	8.08	B3LYP/6-31G(d,p)	-0.9	-0.7	-16.7	9	-10.4
1	-	7.68	B3LYP/6-31G(d,p)	-11.8	-5.4	-46.4	31.1	-37.7
1	-	7.24	B3LYP/6-31G(d,p)	-4	-0.2	-1.1	0	-5.4
			HCOOH					
1	-	7.68	B3LYP/6-31G(d,p)	-11.8	-5.4	-46.4	31.1	-37.7
1	-	7.24	B3LYP/6-31G(d,p)	-4	-0.2	-1.1	0	-5.4
1	-	8.08	B3LYP/6-31G(d,p)	-0.9	-0.7	-16.7	9	-10.4
1	-	7.8	B3LYP/6-31G(d,p)	0.6	-0.4	-20.6	12.7	-9.8
1	-	7.91	B3LYP/6-31G(d,p)	0.4	-0.1	-1.3	0	-0.7
1	-x, -y, -z	3.92	B3LYP/6-31G(d,p)	-0.3	0	-0.2	0	-0.5
1	-	6.35	B3LYP/6-31G(d,p)	-79.7	-19.8	-19.3	66.3	-74.9
1	-	5.98	B3LYP/6-31G(d,p)	-1.2	-1.9	-11.1	3.9	-9.9

Table TS6 CE-B3LYP interaction energies (kJ mol^{-1}) for **1b**

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
			1st molecule					
1	-	7.39	B3LYP/6-31G(d,p)	-76.1	-19.9	-33.3	78.4	-75.8
1	-	8.4	B3LYP/6-31G(d,p)	-4.8	-1.1	-38.1	22.9	-25
1	-	12.05	B3LYP/6-31G(d,p)	0.1	-0.3	-6.2	2.9	-3.7
2	x, y, z	8.49	B3LYP/6-31G(d,p)	-2.9	-4.9	-22.2	11.2	-19.1
1	-	7.21	B3LYP/6-31G(d,p)	-87.8	-22.1	-46.2	110.1	-81.4
1	-	14.18	B3LYP/6-31G(d,p)	-0.3	-0.1	-0.3	0	-0.6
1	x, y, z	14.98	B3LYP/6-31G(d,p)	0	0	-0.2	0	-0.2
1	-x, -y, -z	14.36	B3LYP/6-31G(d,p)	0.7	-0.1	-0.3	0	0.4
1	x, y, z	12.34	B3LYP/6-31G(d,p)	-1.3	-0.2	-1.3	0	-2.6
1	-x, y+1/2, -z+1/2	12.99	B3LYP/6-31G(d,p)	-0.2	0	-0.5	0	-0.7
1	-	10.15	B3LYP/6-31G(d,p)	-8.1	-2.9	-18.1	12.2	-18.9
1	-	8.2	B3LYP/6-31G(d,p)	-8.2	-1.2	-38	27.2	-25.7
1	-	8.05	B3LYP/6-31G(d,p)	-10	-1.6	-44.3	34.6	-29
			2nd molecule					
1	-	7.39	B3LYP/6-31G(d,p)	-76.1	-19.9	-33.3	78.4	-75.8
1	-	8.4	B3LYP/6-31G(d,p)	-4.8	-1.1	-38.1	22.9	-25
2	x, y, z	8.49	B3LYP/6-31G(d,p)	-2.9	-4.9	-22.2	11.2	-19.1
1	-	7.21	B3LYP/6-31G(d,p)	-87.8	-22.1	-46.2	110.1	-81.4
1	-	10.15	B3LYP/6-31G(d,p)	-8.1	-2.9	-18.1	12.2	-18.9
1	-	8.2	B3LYP/6-31G(d,p)	-8.2	-1.2	-38	27.2	-25.7
1	-	8.05	B3LYP/6-31G(d,p)	-10	-1.6	-44.3	34.6	-29
1	-x, -y, -z	7.13	B3LYP/6-31G(d,p)	-10.6	-1.7	-68.4	42.6	-45.7

Table TS7 CE-B3LYP interaction energies (kJ mol^{-1}) for **1b**·CH_3CN

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
			1b					
1	-	8.55	B3LYP/6-31G(d,p)	-3.1	-1.5	-3.7	3.3	-5.5
2	-x, y+1/2, -z+1/2	8.09	B3LYP/6-31G(d,p)	-84	-20.7	-21.9	83.2	-71.8
1	-x, -y, -z	9.68	B3LYP/6-31G(d,p)	-6.6	-3.7	-18.3	9	-20.1
1	-	5.68	B3LYP/6-31G(d,p)	-18.8	-5.3	-15.3	20.1	-24.7
1	-x, -y, -z	9.51	B3LYP/6-31G(d,p)	-17.9	-8.8	-24.7	24.2	-32
1	-	5.85	B3LYP/6-31G(d,p)	-3.2	-2.8	-21	13.7	-15.2
2	-x, y+1/2, -z+1/2	8.25	B3LYP/6-31G(d,p)	-6.4	-0.8	-37	21.9	-26.1
2	x, -y+1/2, z+1/2	8.35	B3LYP/6-31G(d,p)	-4	-1.4	-36.7	20.6	-24.5
1	-	5.94	B3LYP/6-31G(d,p)	-4.3	-1.9	-13.2	9.1	-11.8
1	-	7.52	B3LYP/6-31G(d,p)	-2.3	-1.3	-5.8	7.3	-4
1	-x, -y, -z	11.88	B3LYP/6-31G(d,p)	0.4	-0.2	-3.3	0.2	-2.4
1	x, -y+1/2, z+1/2	13.74	B3LYP/6-31G(d,p)	-0.9	-0.1	-0.7	0	-1.6
			MeCN					
1	-	8.55	B3LYP/6-31G(d,p)	-3.1	-1.5	-3.7	3.3	-5.5
2	-x, y+1/2, -z+1/2	8.09	B3LYP/6-31G(d,p)	-84	-20.7	-21.9	83.2	-71.8
1	-x, -y, -z	9.68	B3LYP/6-31G(d,p)	-6.6	-3.7	-18.3	9	-20.1
1	-	5.68	B3LYP/6-31G(d,p)	-18.8	-5.3	-15.3	20.1	-24.7
1	-x, -y, -z	9.51	B3LYP/6-31G(d,p)	-17.9	-8.8	-24.7	24.2	-32
1	-	5.85	B3LYP/6-31G(d,p)	-3.2	-2.8	-21	13.7	-15.2
2	-x, y+1/2, -z+1/2	8.25	B3LYP/6-31G(d,p)	-6.4	-0.8	-37	21.9	-26.1
2	x, -y+1/2, z+1/2	8.35	B3LYP/6-31G(d,p)	-4	-1.4	-36.7	20.6	-24.5
1	-	5.94	B3LYP/6-31G(d,p)	-4.3	-1.9	-13.2	9.1	-11.8
1	-	7.52	B3LYP/6-31G(d,p)	-2.3	-1.3	-5.8	7.3	-4
1	-x, -y, -z	11.88	B3LYP/6-31G(d,p)	0.4	-0.2	-3.3	0.2	-2.4
1	x, -y+1/2, z+1/2	13.74	B3LYP/6-31G(d,p)	-0.9	-0.1	-0.7	0	-1.6

Table TS8 CE-B3LYP interaction energies (kJ mol^{-1}) for **1a**·CH_3OH

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
			1b					
1	-	5.55	B3LYP/6-31G(d,p)	-0.3	-1.4	-15.8	10.4	-8.7
2	-x, y+1/2, -z+1/2	8.05	B3LYP/6-31G(d,p)	-85.3	-21.6	-22.8	84.5	-73.9
1	-x, -y, -z	9.53	B3LYP/6-31G(d,p)	-9	-4.7	-23.6	18.5	-22
1	-	5.31	B3LYP/6-31G(d,p)	-33.3	-7.5	-15	35.4	-32
1	-x, -y, -z	9.86	B3LYP/6-31G(d,p)	-12.7	-7	-18.5	13.6	-26.4
2	-x, y+1/2, -z+1/2	8.05	B3LYP/6-31G(d,p)	-8.8	-1	-42.8	29.3	-29.2
2	x, -y+1/2, z+1/2	8.51	B3LYP/6-31G(d,p)	-4.4	-1.5	-36.7	20.8	-24.8
1	-	5.09	B3LYP/6-31G(d,p)	-8.2	-1.8	-14.2	10.2	-16.1
1	-	7.23	B3LYP/6-31G(d,p)	-6.4	-2.2	-6.7	6.3	-10.4
1	-	7.67	B3LYP/6-31G(d,p)	-0.9	-0.2	-5.6	3.1	-4
1	x, y, z	12.72	B3LYP/6-31G(d,p)	-1	-0.1	-0.9	0	-1.9
			MeOH					
1	-	5.55	B3LYP/6-31G(d,p)	-0.3	-1.4	-15.8	10.4	-8.7
2	-x, y+1/2, -z+1/2	8.05	B3LYP/6-31G(d,p)	-85.3	-21.6	-22.8	84.5	-73.9
1	-x, -y, -z	9.53	B3LYP/6-31G(d,p)	-9	-4.7	-23.6	18.5	-22
1	-	5.31	B3LYP/6-31G(d,p)	-33.3	-7.5	-15	35.4	-32
1	-x, -y, -z	9.86	B3LYP/6-31G(d,p)	-12.7	-7	-18.5	13.6	-26.4
2	-x, y+1/2, -z+1/2	8.05	B3LYP/6-31G(d,p)	-8.8	-1	-42.8	29.3	-29.2
2	x, -y+1/2, z+1/2	8.51	B3LYP/6-31G(d,p)	-4.4	-1.5	-36.7	20.8	-24.8
1	-	5.09	B3LYP/6-31G(d,p)	-8.2	-1.8	-14.2	10.2	-16.1
1	-	7.23	B3LYP/6-31G(d,p)	-6.4	-2.2	-6.7	6.3	-10.4
1	-	7.67	B3LYP/6-31G(d,p)	-0.9	-0.2	-5.6	3.1	-4
1	x, y, z	12.72	B3LYP/6-31G(d,p)	-1	-0.1	-0.9	0	-1.9
1	-x, -y, -z	12.04	B3LYP/6-31G(d,p)	1	-0.3	-6.3	2	-3.4

4. Crystal morphology

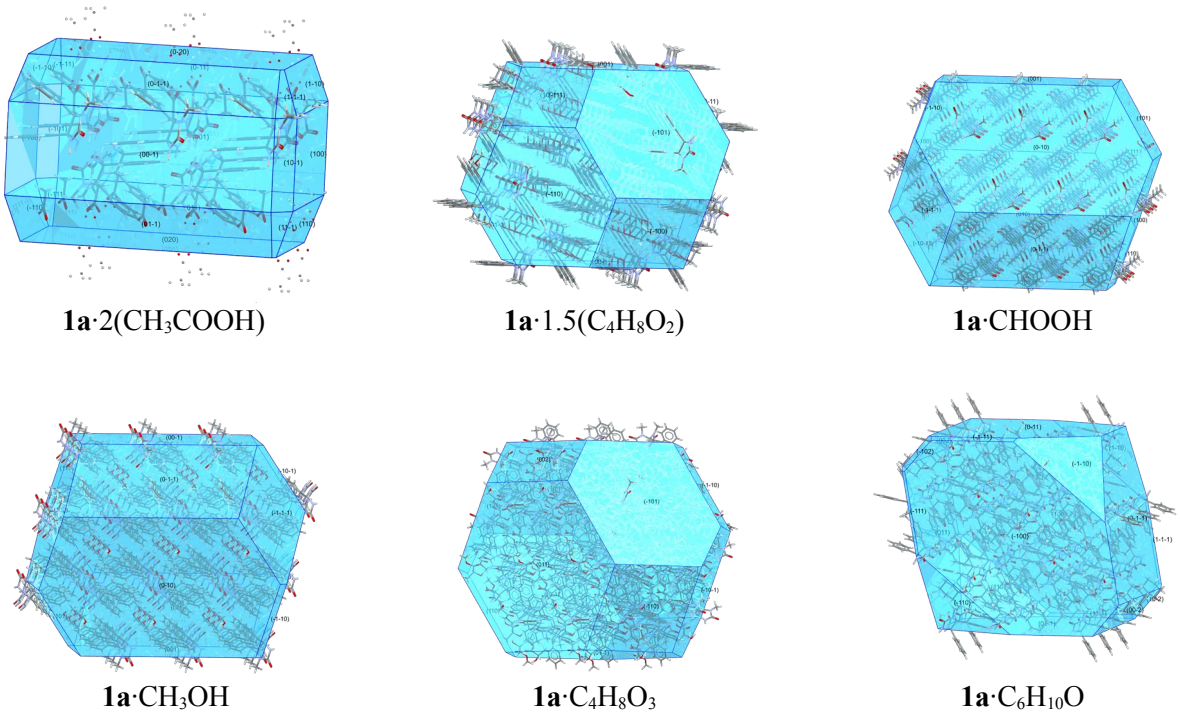


Fig. S5 BFDH predicted morphology (blue, prismatic) and groups forming the main crystal faces for **1a**·2(CH_3COOH) (amide and carboxylate), **1a**·1.5($C_4H_8O_2$) (a mixture of alkyl/aryl groups and amide residues/oxygen atoms of solvent molecules), **1a**·CHOOH a mixture of alkyl/aryl groups and amide residues/oxygen atoms of solvent molecules), **1a**·CH_3OH (amide groups of glycouril molecules), **1a**·$C_4H_8O_3$, **1a**·$C_6H_{10}O$.

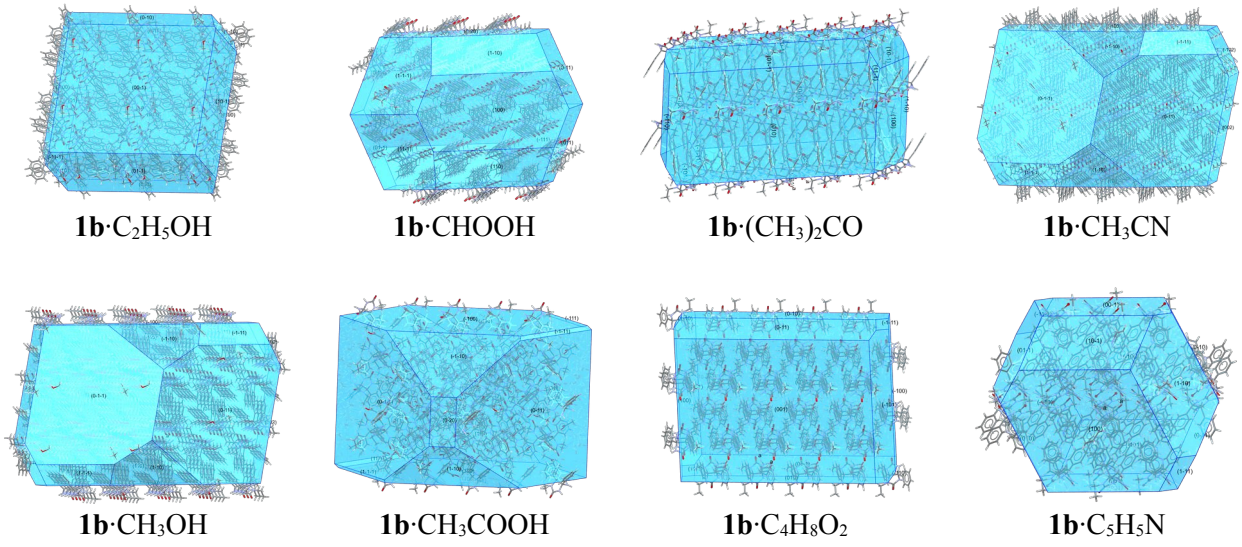


Fig. S6. BFDH predicted morphology (blue, prismatic) and groups forming the main crystal faces for **1b**·C_2H_5OH, **1b**·CHOOH, **1b**·$(CH_3)_2CO$, **1b**·CH_3CN, **1b**·CH_3OH, **1b**·CH_3COOH, **1b**·$C_4H_8O_2$, **1b**·C_5H_5N.

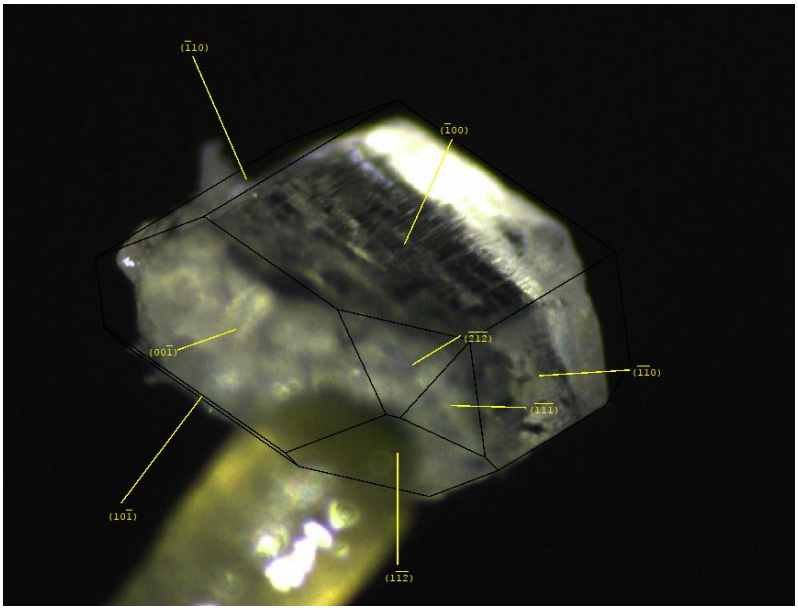


Fig. S7 Experimentally assigned crystal faces of **1a**.

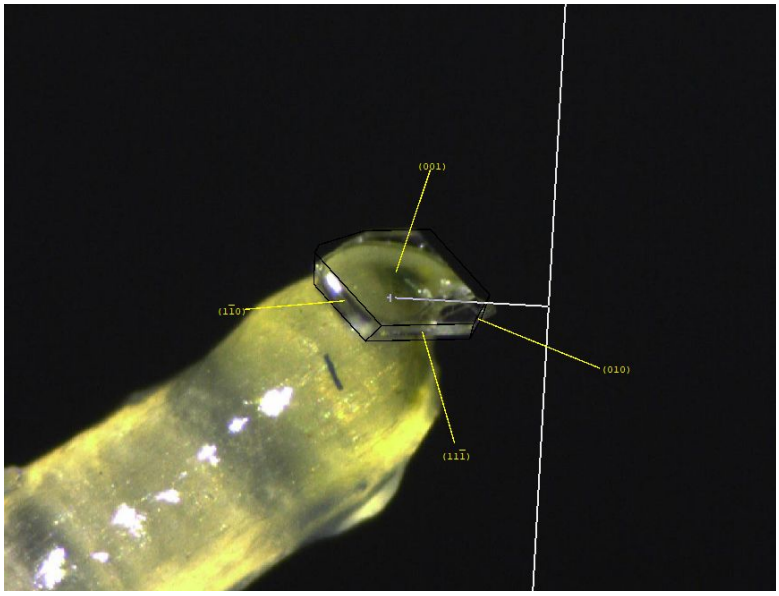


Fig. S8 Experimentally assigned crystal faces of **1a**.

5. Powder diffraction

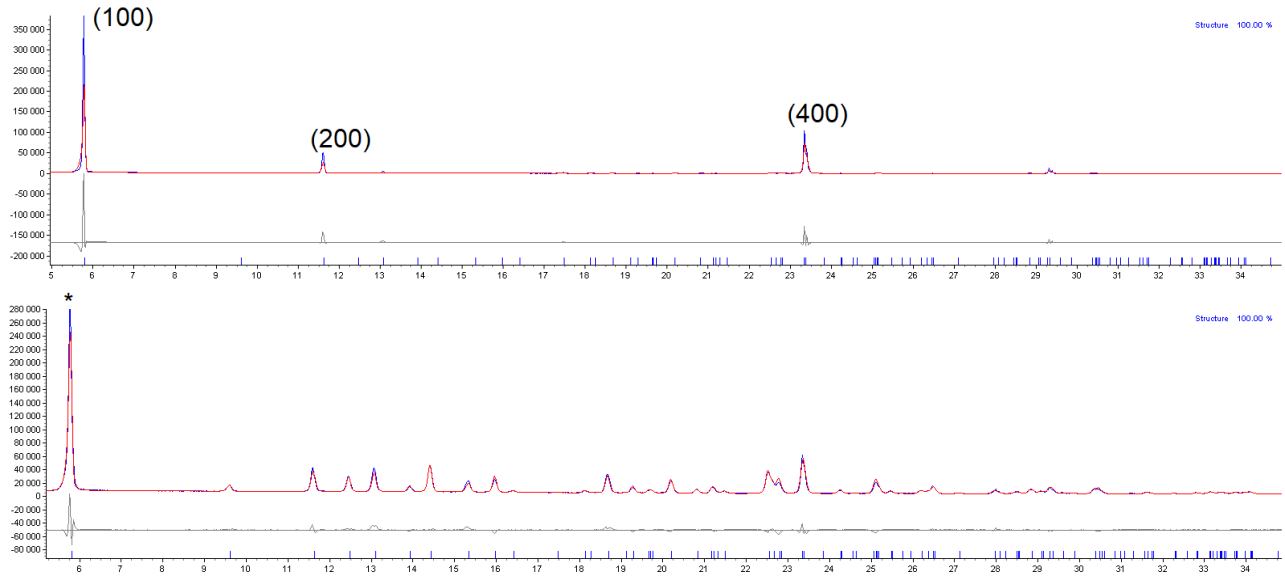


Fig. S9 The experimental (blue), calculated (red) and their difference (grey) curves for powder XRD patterns for as crystallized solid (top) **1a** and (bottom) powdered **1a**. For the former and latter patterns Rwp/Rbragg = 33.57/17.91 and 8.53/5.82. Crystallite size for powder pattern is 900 nm.

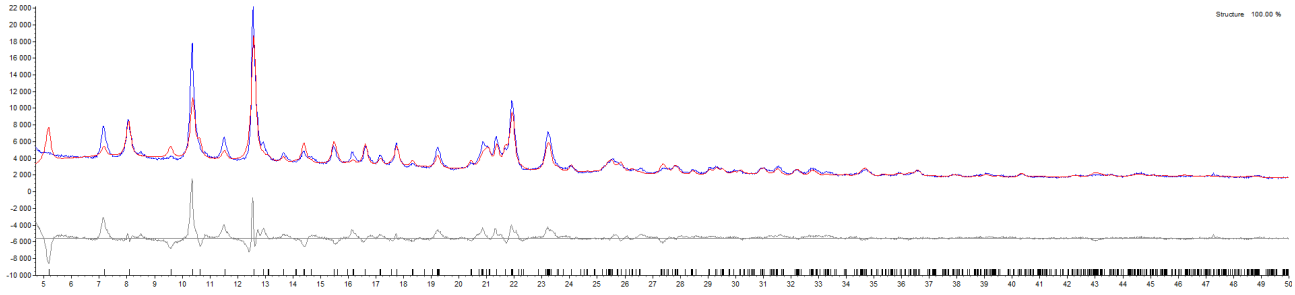


Fig. S10 The experimental (blue) and calculated (red) powder XRD pattern for **1b** and their difference (grey) curves are depicted. Rwp/Rbragg= 10.3/8.7 % indicates purity of the sample.

6. Measurements of hydrophobic properties

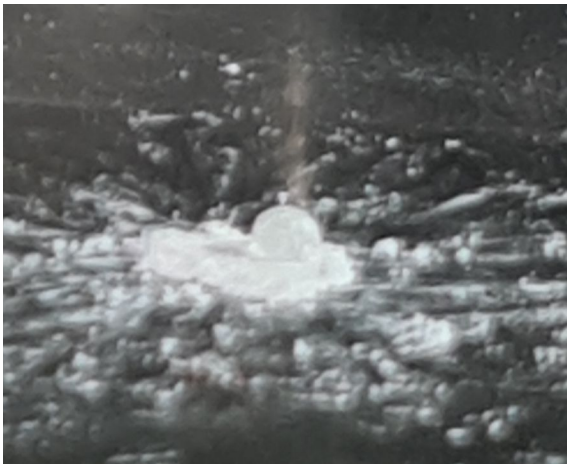


Fig. S11 Drops of water on powder of **1a**.

7. Analytical data for 2a and 2b

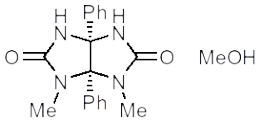
1,4-Dimethyl-3a,6a-diphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 2a.

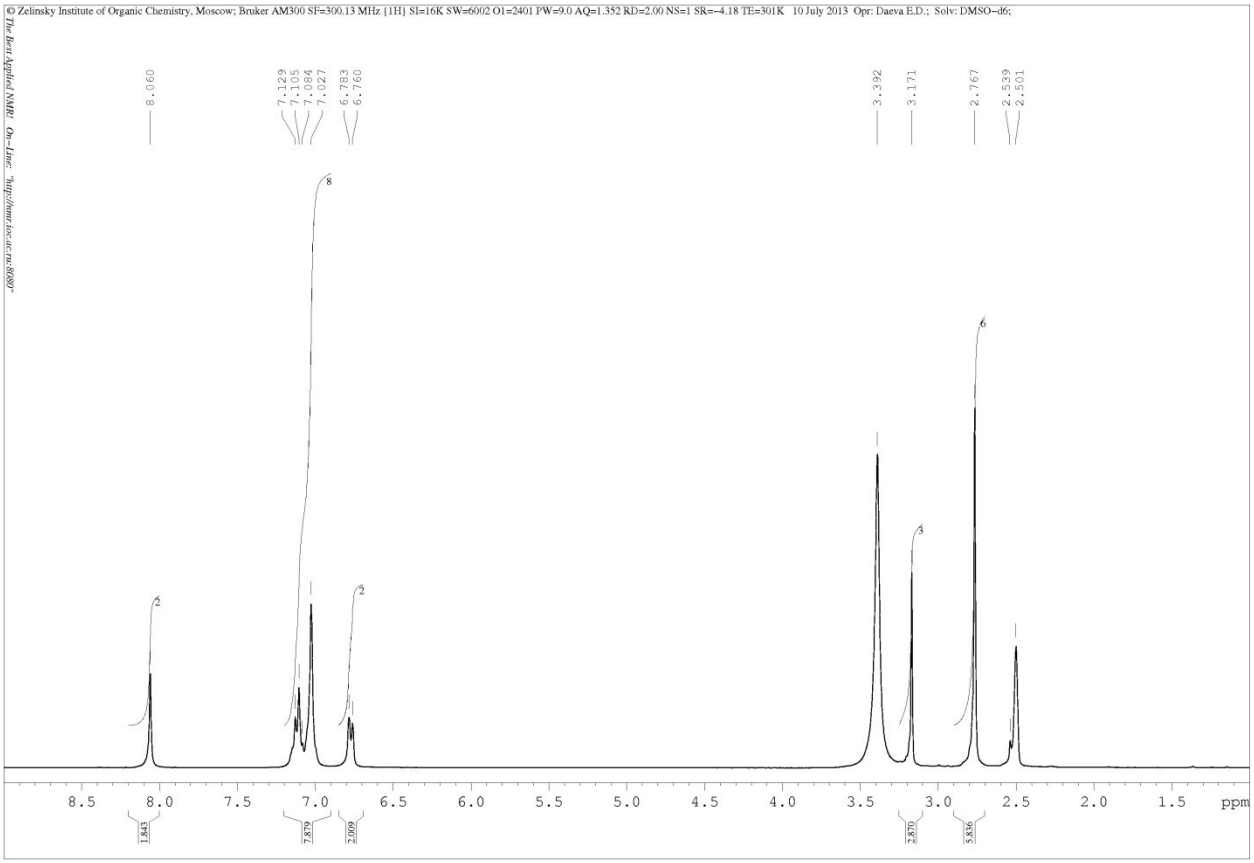
White powder, yield 0.77 g (24%), mp 340 – 343 °C (HCOOH). ^{1}H NMR, δ, ppm.; *J*/Hz (300 MHz, DMSO-d_6): 2.51 (s, 6 H, Me), 6.92 – 7.01 (m, 4 H, Ph), 7.03 – 7.17 (m, 6 H, Ph), 8.41 (s, 2 H, NH). ^{13}C **1a** NMR, δ, ppm.; (75 MHz, DMSO-d_6): 25.63 (Me), 83.41 (C-C), 127.37, 128.04, 128.36 (CH(Ph)), 135.11 (C(Ph)), 159.32 (C=O). HRMS, m/z, found: 323.1511 $[M+H]^+$ (calcd for $C_{18}H_{18}N_4O_2$+H 323.1508).

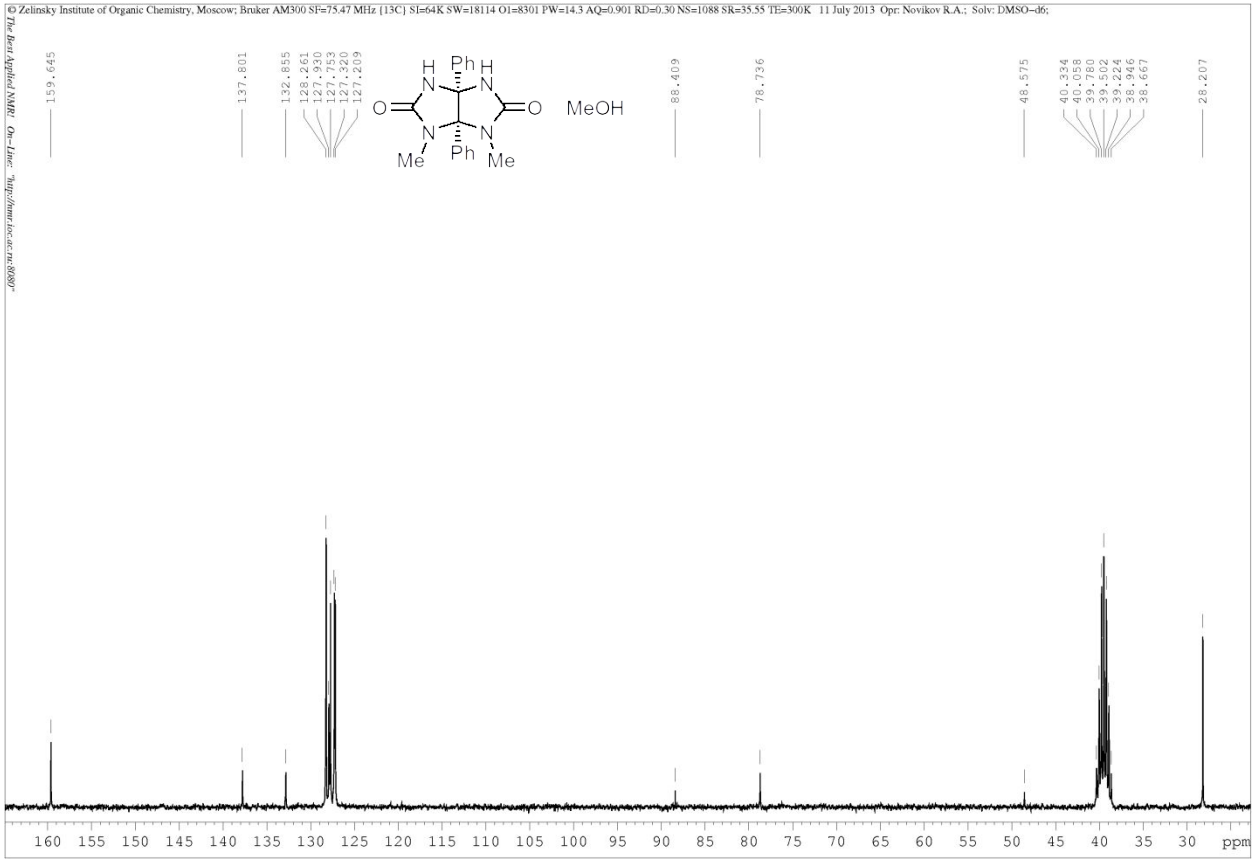
1,4-Diethyl-3a,6a-diphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione 2b.

White powder, yield 0.70 g (20%), mp > 335 °C (HCOOH). ^{1}H NMR, δ, ppm.; *J*/Hz (300 MHz, DMSO-d_6): 0.99 (t, 6 H, Me, J = 7.0 Hz), 2.70 – 2.88 (m, 2 H, CH_2), 3.12 – 3.30 (m, 2 H, CH_2), 6.92 – 7.01 (m, 4 H, Ph), 7.03 – 7.17 (m, 6 H, Ph), 8.26 (s, 2 H, NH). ^{13}C NMR, δ, ppm.; (75 MHz, DMSO-d_6): 14.61 (Me), 35.02 (CH_2), 83.76 (C-C), 127.33, 127.61, 128.11 (CH(Ph)), 136.08 (C(Ph)), 159.02 (C=O). HRMS, m/z, found: 351.1817 $[M+H]^+$ (calcd for $C_{20}H_{22}N_4O_2$+H 351.1821).

8. NMR spectra for samples 1a·MeOH, 1b, 2a,2b






© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz [13C] SI=64K SW=18114 O1=8301 PW=14.3 AQ=0.901 RD=0.30 NS=1088 SR=55.55 TE=300K 11 July 2013 Opr: Novikov R.A.; Solv: DMSO–d6;
The Best Applied NMR! On–Line: "http://nmr.ioc.ac.ru:8080/"
159.645
137.801
132.855
128.261
127.930
127.753
127.320
127.209
MeOH
88.409
78.736
48.575
40.334
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39.224
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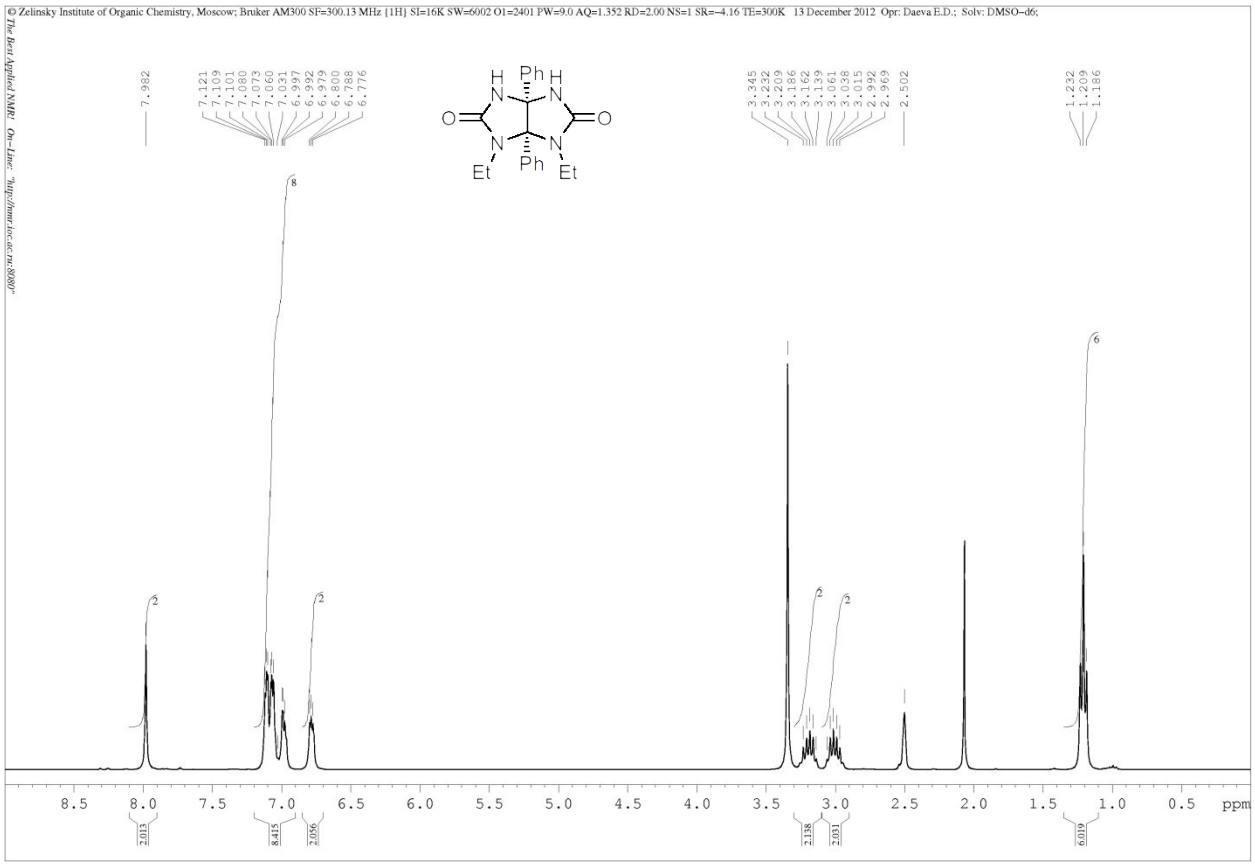
38.667
28.207
ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz [1H] SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.16 TE=300K 13 December 2012 Opr: Daeva E.D.; Solv: DMSO–d6;
The Best Applied NMR! On–Line: "http://nmr.ioc.ac.ru:8080/"
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7.121
7.109
7.101
7.080
7.073
7.060
7.031
6.997
6.992
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6.800
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6.776
3.345
3.232
3.209
3.186
3.162
3.139
3.061
3.038
3.015
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2.096
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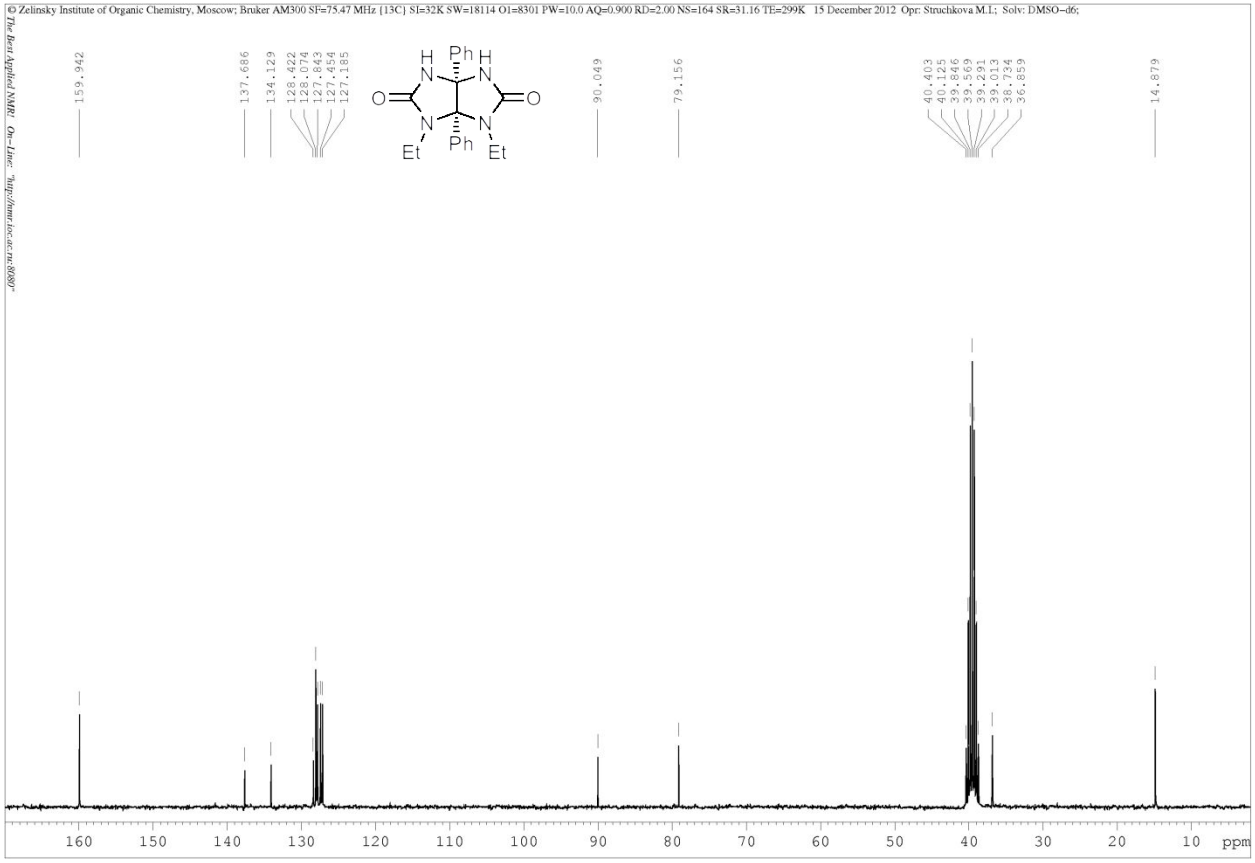
6.019
ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz [13C] SI=32K SW=18114 O1=8301 PW=10.0 AQ=0.900 RD=2.00 NS=164 SR=31.16 TE=299K 15 December 2012 Opr: Struchkova M.I.; Solv: DMSO-d6;
The Best Applied NMR On-Line: http://nmr.ioc.ac.ru:8080/
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39.569
39.291
39.013
38.734
36.859
14.879
H
Ph
H
N
N
O
O
N
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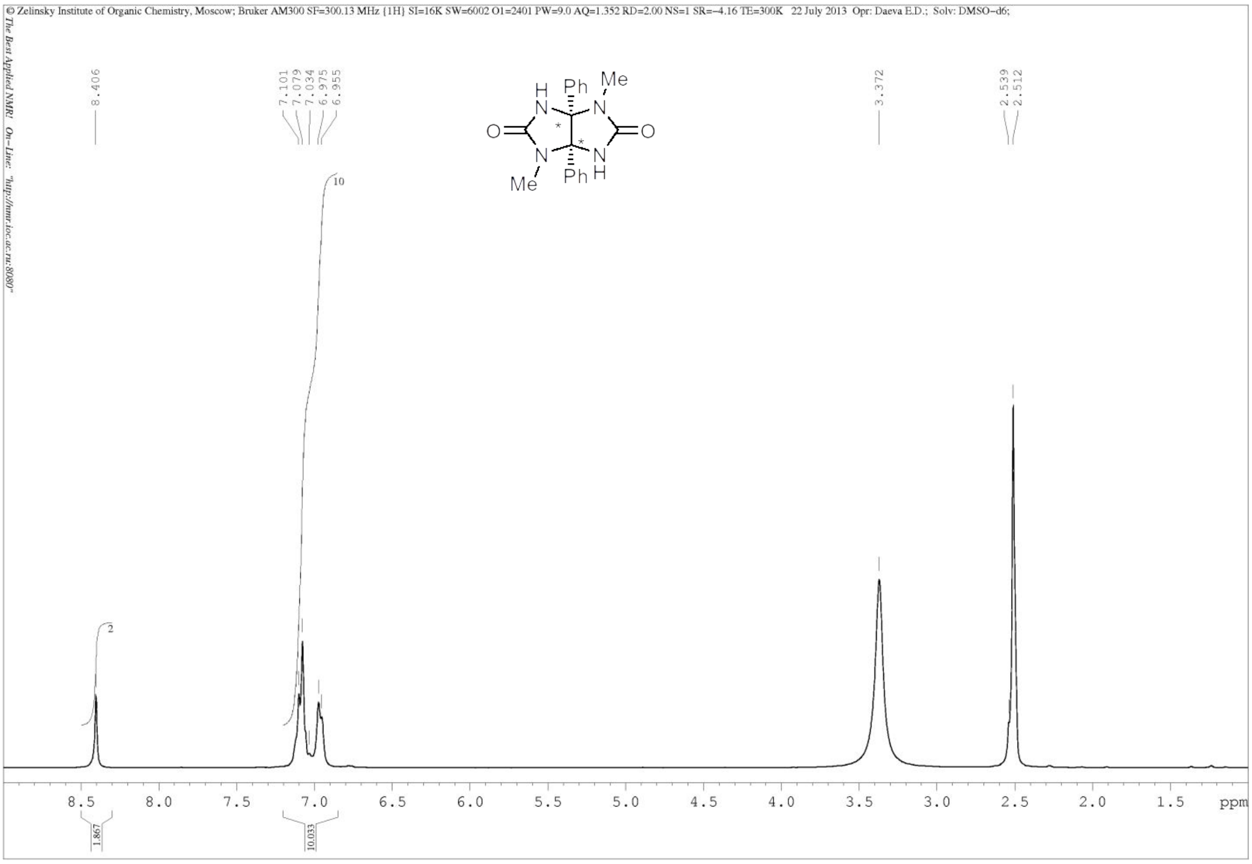
10
ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.16 TE=300K 22 July 2013 Opr: Daeva E.D.; Solv: DMSO-d6;
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Ph
Me
Ph
Me
ppm
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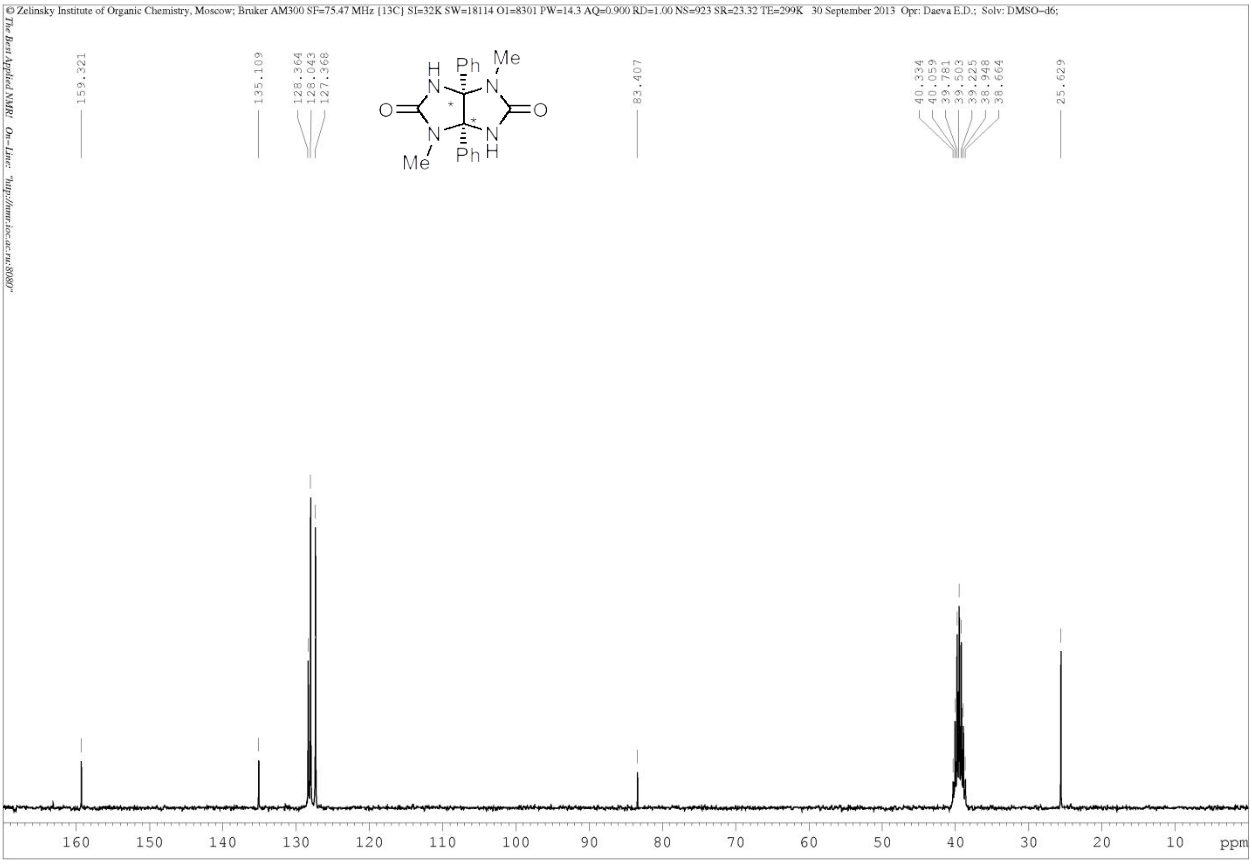
10.033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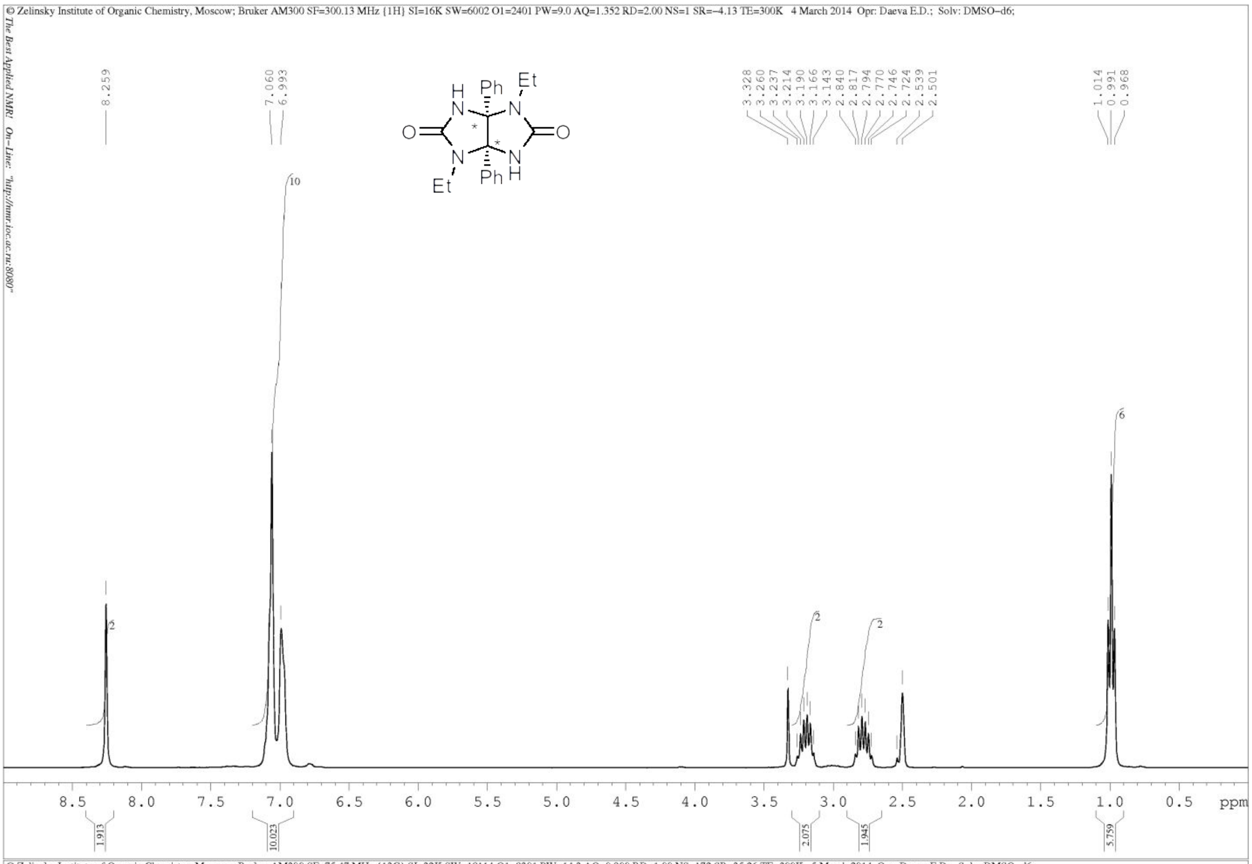
Ph
Me
Ph
Me
ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6002 O1=2401 PW=9.0 AQ=1.352 RD=2.00 NS=1 SR=-4.13 TE=300K 4 March 2014 Opr: Daeva E.D.; Solv: DMSO-d6;
The Best Applied NMR! On-Line: "http://nmr.ioc.ac.ru:8080"
8.259
7.060
6.993
3.328
3.260
3.237
3.214
3.190
3.166
3.143
2.840
2.817
2.794
2.770
2.746
2.724
2.539
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1.014
0.991
0.968
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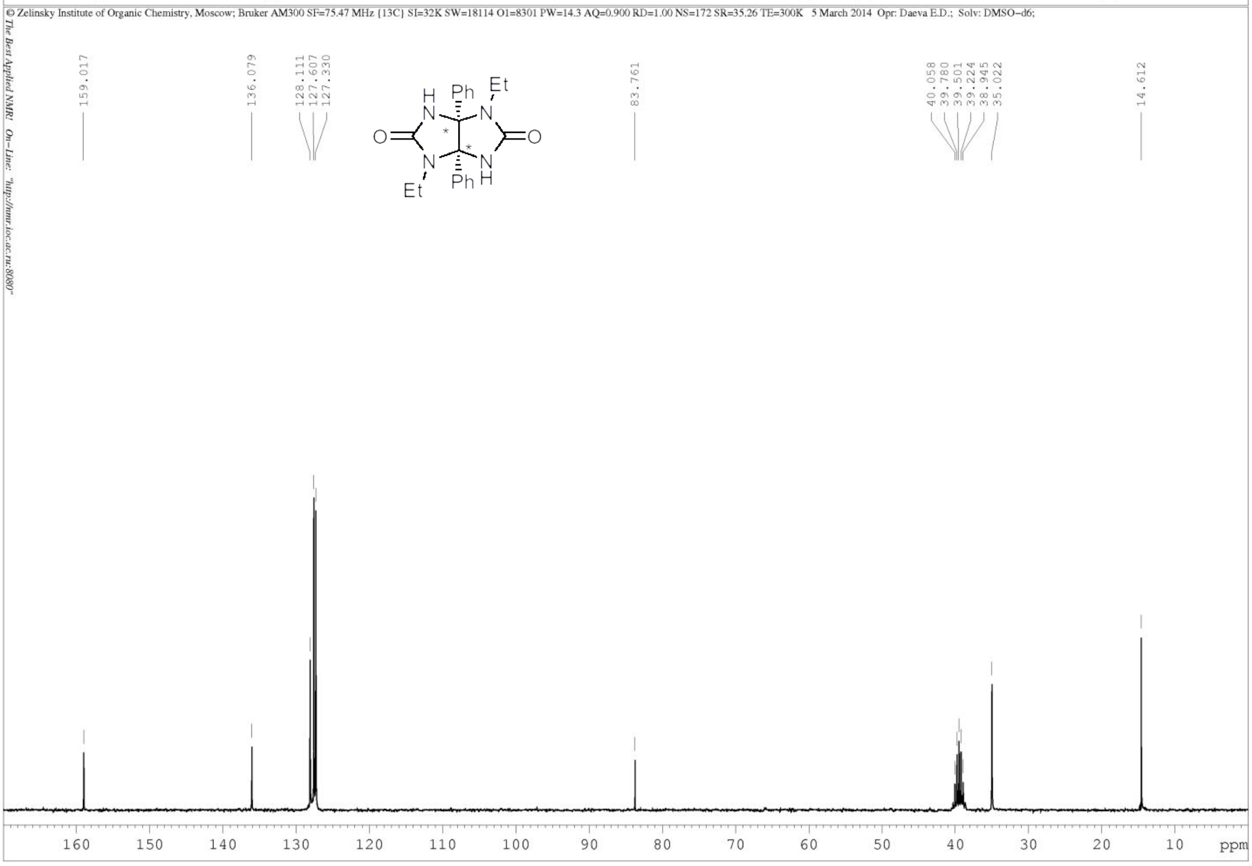
2.075
1.945
5.759


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=14.3 AQ=0.900 RD=1.00 NS=172 SR=35.26 TE=300K 5 March 2014 Opr: Daeva E.D.; Solv: DMSO-d6;
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159.017
136.079
128.111
127.607
127.330
83.761
40.058
39.780
39.501
39.224
38.945
35.022
14.612
ppm