Supplementary Information.

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A molecular roundabout: triple cycle-arranged hydrogen bonds in light of experiment and theory

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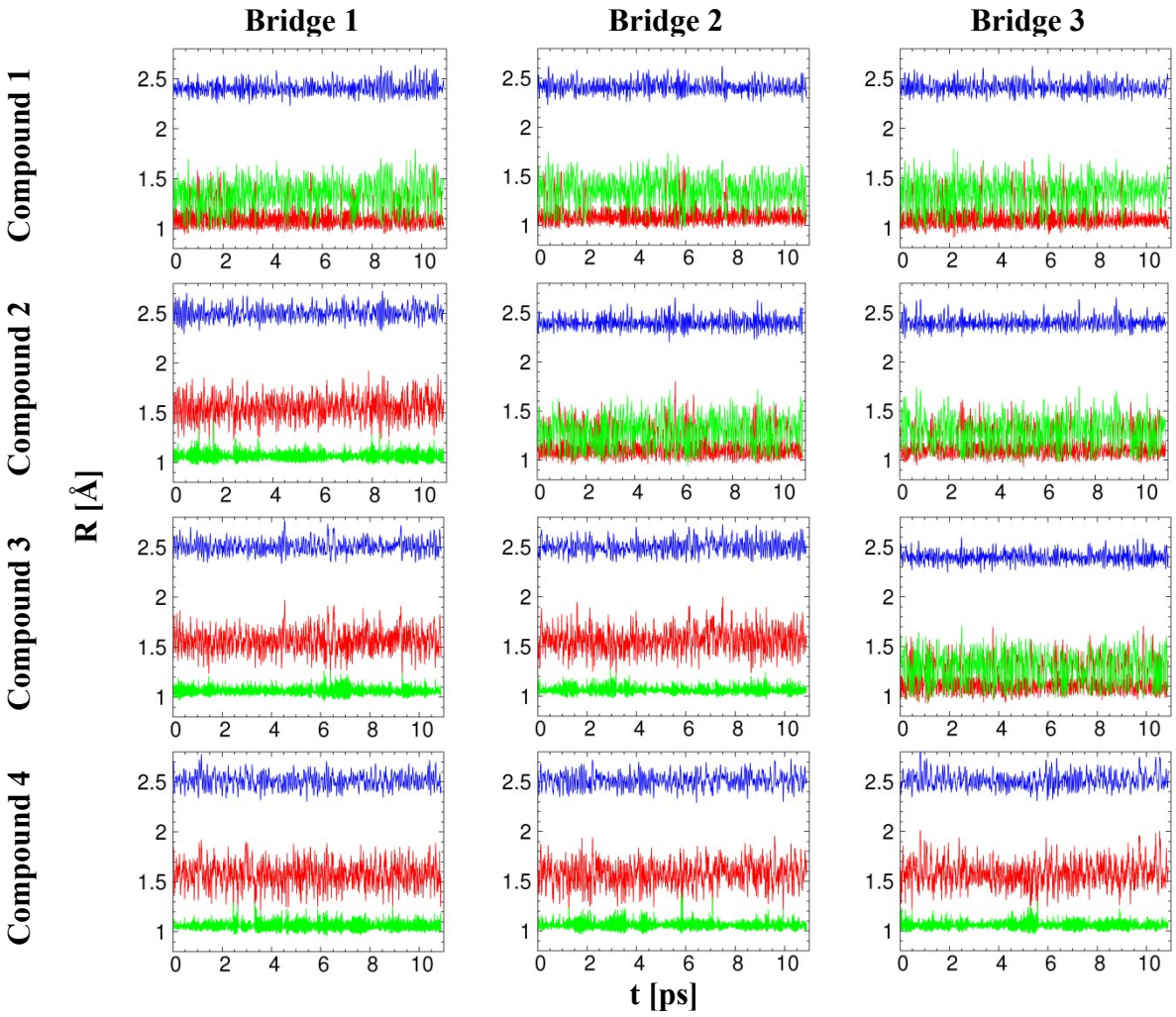


Fig. S1 Time evolution of the O···N, O-H and H-N interatomic distances in the three hydrogen bridges of the investigated compounds **1** – **4**obtained by gas-phase CPMD calculation. Red: hydroxyl oxygen – bridged hydrogen distance, green: acetyl oxygen or imine nitrogen – bridged hydrogen distance, blue: donor – acceptor distance.

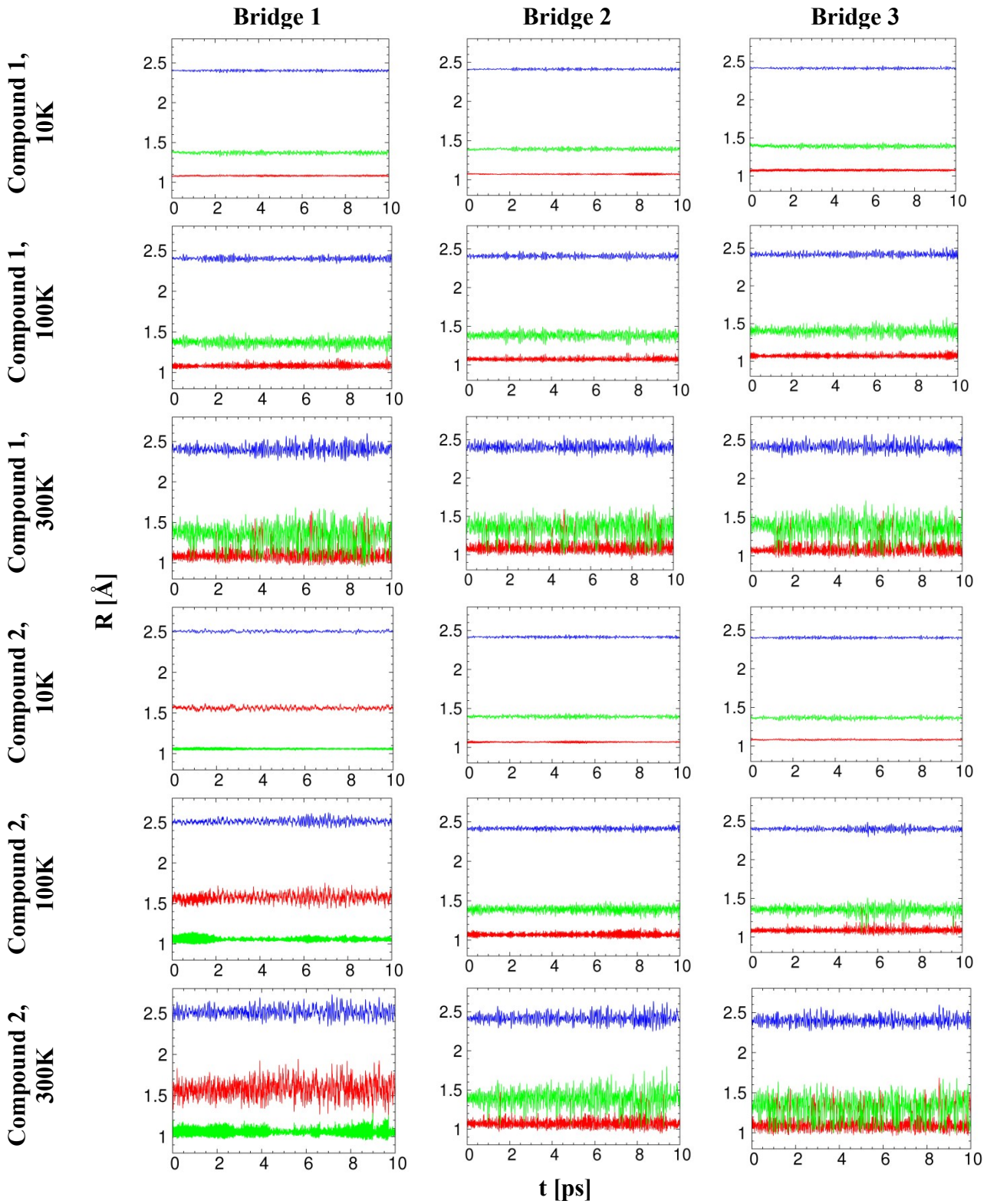
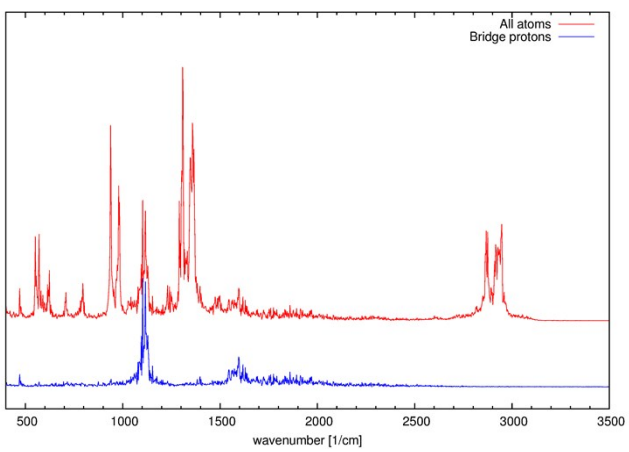
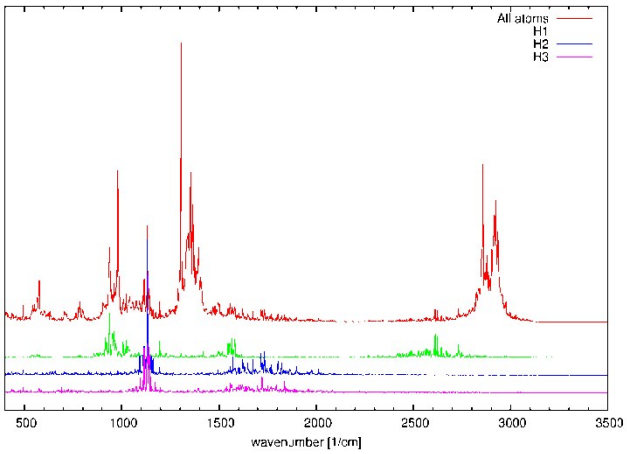


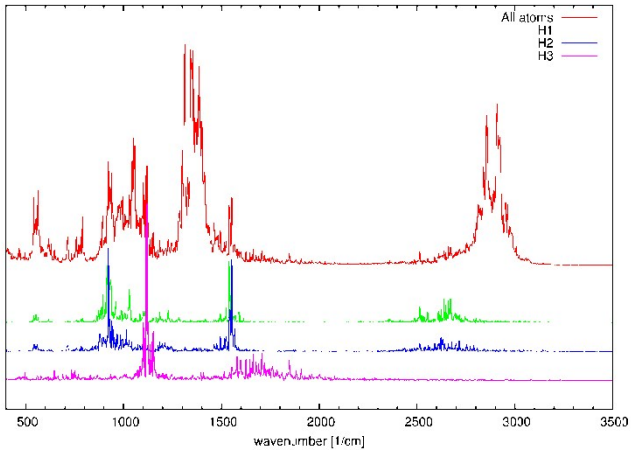
Fig. S2 Time evolution of interatomic distances in the three hydrogen bridges of the investigated compounds **1** and **2** for 10, 100 and 300 K (for which the X-ray structure was determined). Red: hydroxyl oxygen – proton distance, green: carbonyl oxygen or imine nitrogen – proton distance, blue: donor – acceptor distance. Results of the solid-state CPMD simulation.



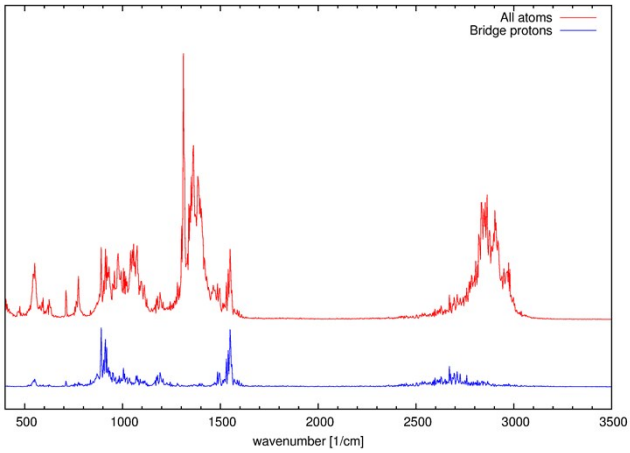
Compound **1**



Compound **2**



Compound **3**



Compound **4**

Fig. S3 Power spectra of atomic velocities – results of the CPMD runs for the studied compounds. Intensities (the *y* axis) are arbitrary and are not related to the IR absorption intensities. The spectra presented only for the bridged protons vibrational modes.

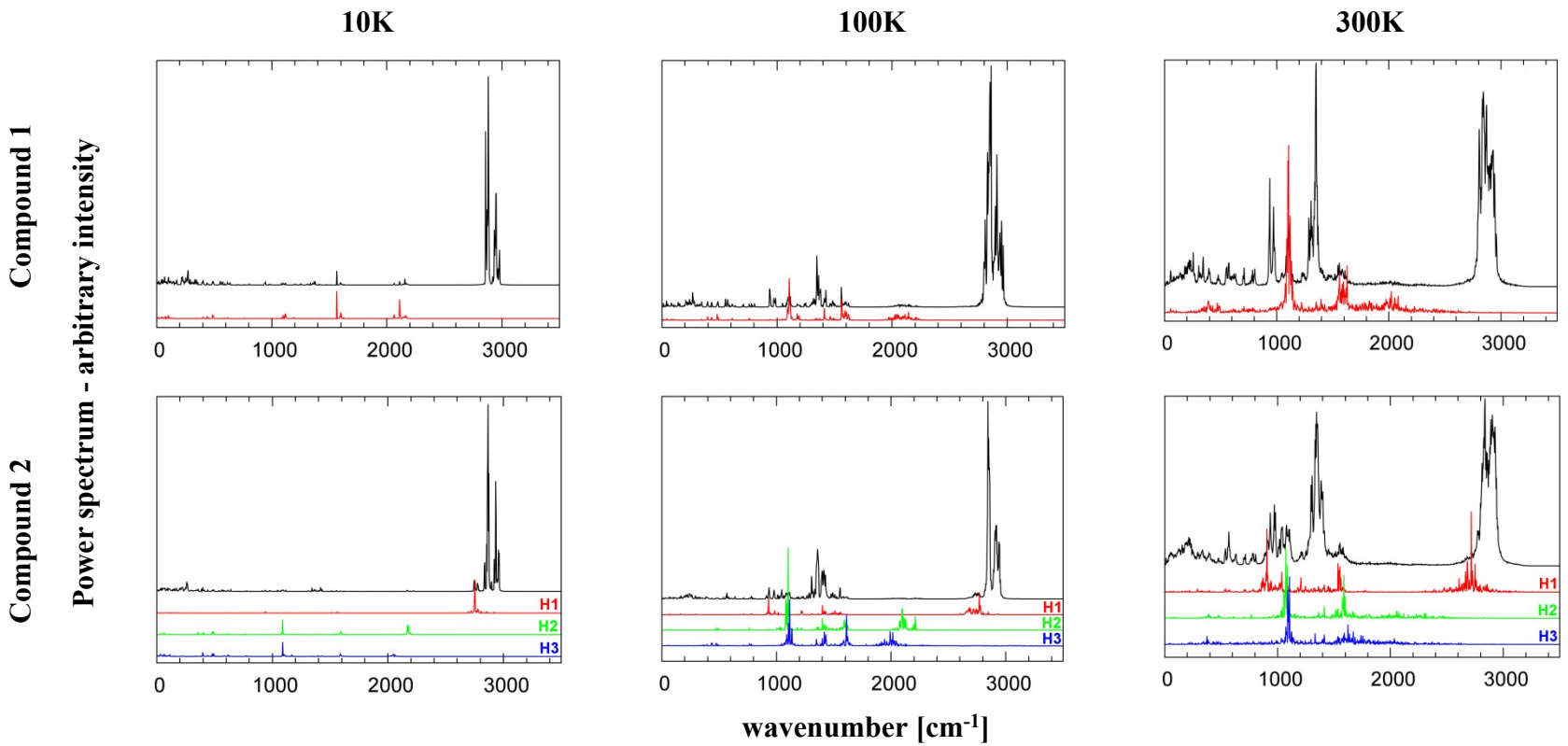


Fig. S4 Power spectra of the atomic velocity for the investigated compounds **1** and **2** - results of the solid-state CPMD simulation. For **1**, total power spectrum (black) and joint contribution of the bridge protons (red) are given. For **2**, total power spectrum (black) and individual contributions of the bridge protons are given.

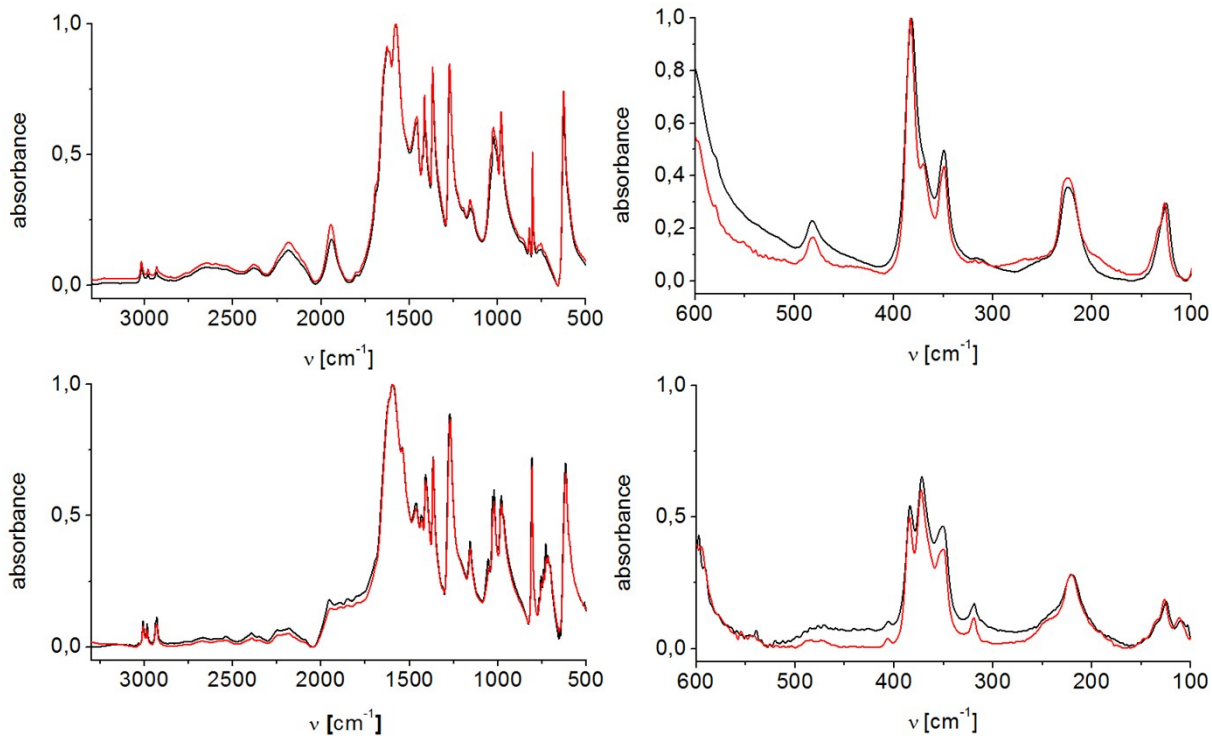


Fig. S5 Infrared spectra of 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**1**, upper spectra) and its deuteroderivative (**1D**, lower spectra) in 3300 - 500 cm^{-1} (left side) and 600 - 100 cm^{-1} (right side) regions measured as function of temperature - T = 300 K (black line) and 10 K (red line).

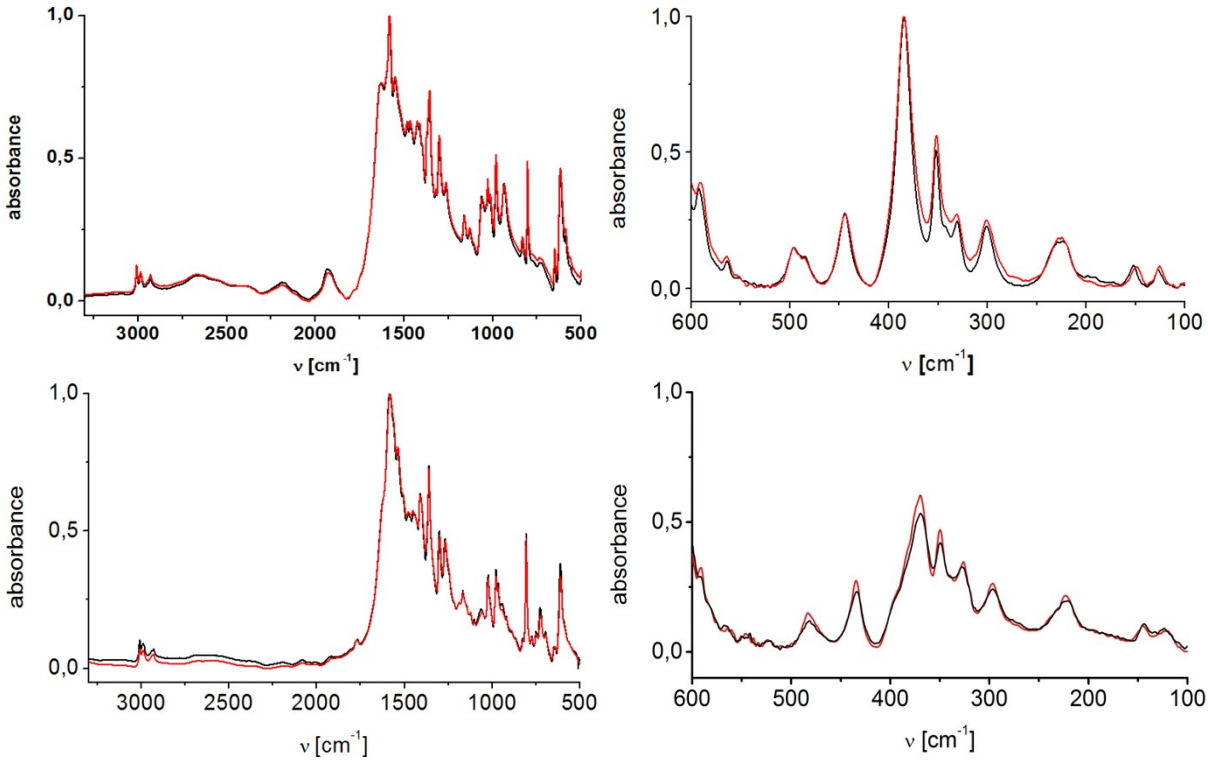


Fig. S6 Infrared spectra of (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-N-methylethaniminium (**2**, upper spectra) and its deuteroderivative (**2**, lower spectra) in 3300 - 500 cm^{-1} (left side) and 600 - 100 cm^{-1} (right side) regions measured as function of temperature - T = 300 K (black line) and 10 K (red line).

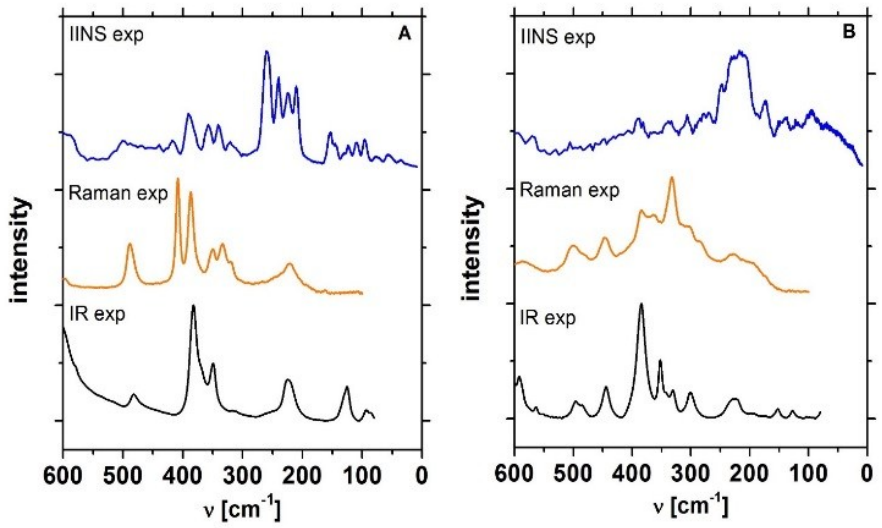


Fig. S7 Experimental IR (black colour), Raman (red colour) and INS (blue colour) spectra of 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**1**) (**A**) and (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-N-methylethaniminium (**2**) (**B**).

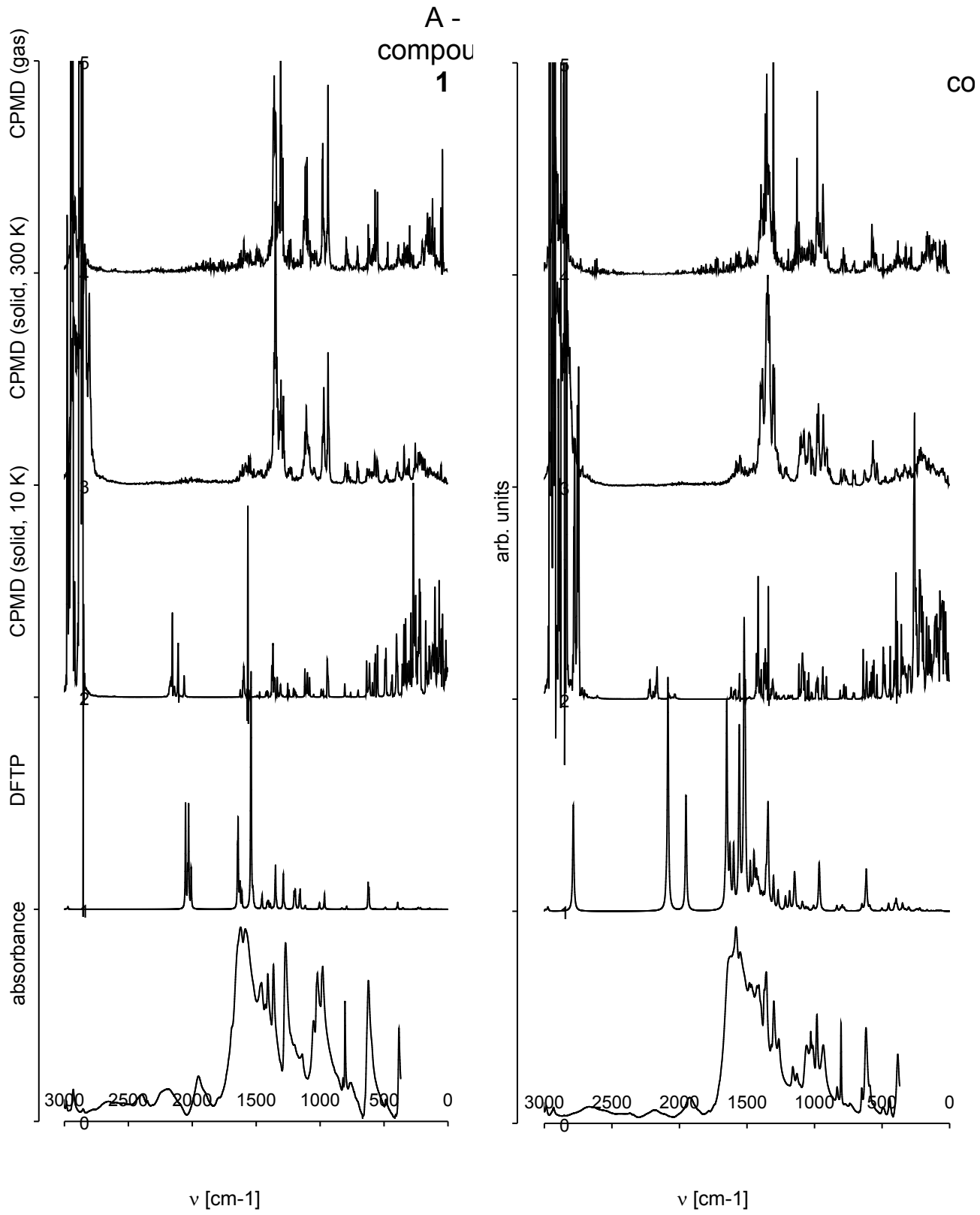
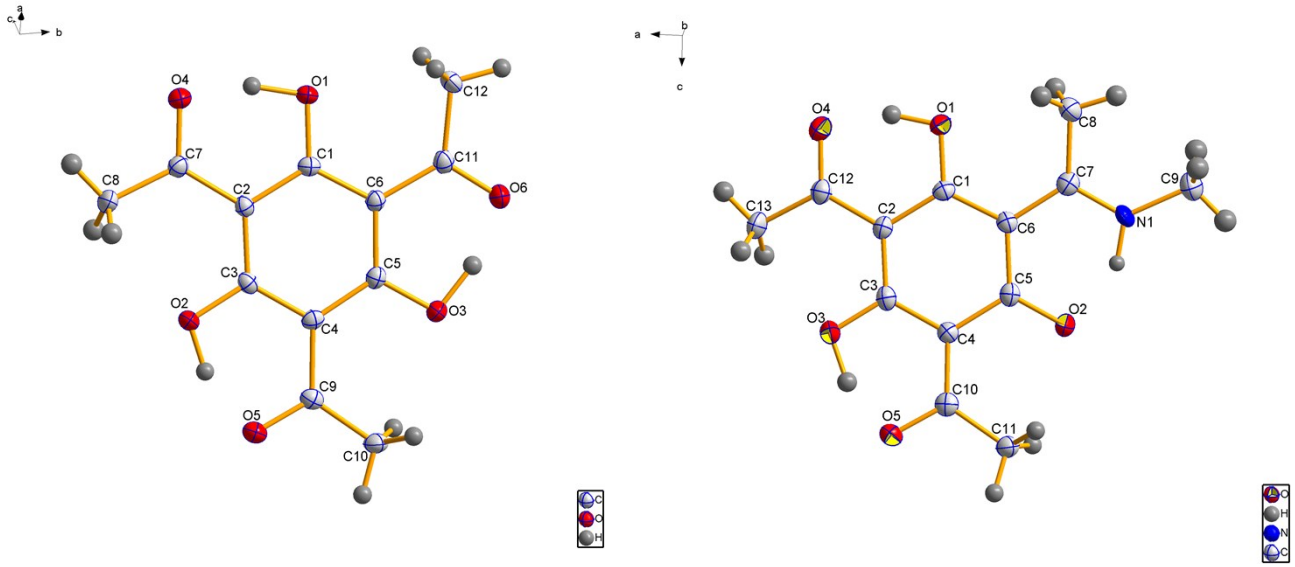


Fig. S8 Experimental and calculated DFTP IR spectra, as well as CPMD and CPMD-solid hydrogens vibrational spectra (300 K and 10 K) of 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**1**, panel **A**) and (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-N-methylethaniminium (**2**, panel **B**).



1 **2**

Fig. S9 The molecular structure and atom labelling scheme of 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**1**) and (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-N-methylethaniminium (**2**). Crystal structures were visualized using the DIAMOND program.[61]

Table S1. Definitions of internal coordinates used in potential energy distribution (PED) analysis for the assignment of the vibrational spectra of compounds **1** and **2**.

ν(CH) – stretching of the C-H bond
ν(OH) – stretching of the O-H bond
ν(OD) – stretching of the O-D bond
ν(NH) – stretching of the N-H bond
ν(ND) – stretching of the N-D bond
ν(C=O) – stretching of the C=O bond
ν(CO) – stretching of the C-O bond
ν($C_{alk}C_{alk}$) – stretching of the C_{alk}-C_{alk} bond
ν($C_{ar}C_{alk}$) – stretching of the C_{ar}-C_{alk} bond
ν(C=N) – stretching of the C=N bond
ν(CC) - ring stretching
ν(NC) - stretching of the N-C_{alk} bond
α(CC) - in plane bending of the C=C=C chain in the aromatic ring
δ($CC_{im}N$) - in plane bending of the C-C_{im}=N chain
δ(CCH_3) – in plane bending of the C-CH_3 unit
δ(NCH_3) – in plane bending of the N-CH_3 unit
δ(CCC_{im}) - in plane bending of the C=C-C_{im} chain
δ(CCC_{alk}) – in plane bending of the C-C-C_{alk} chain
δ(CC=O) – in plane bending of the C-C=O chain
δ(CCO) – in plane bending of the C-C-O chain
δ(COH) - in plane bending of the C-O-H chain
δ(COD) - in plane bending of the C-O-D chain
δ(CNH) - in plane bending of the C=N-H chain
δ(CND) - in plane bending of the C-O-D chain
γ(C=O) – out of plane bending of the C=O bond (the change in angle between the C=O and C-C bonds)
γ(C=N) – out of plane bending of the C=N bond (the change in angle between the C=N and C-C bonds)
γ(COH) – out of plane bending of the O-H bond (the change in angle between the O-H and C-O bonds)
γ(COD) – out of plane bending of the O-D bond (the change in angle between the O-D and C-O bonds)
γ(CNH) – out of plane bending of the N-H bond (the change in angle between the O-H and C-O bonds)
γ(CND) – out of plane bending of the N-D bond (the change in angle between the O-D and C-O bonds)
γ(CO) – out of plane bending of the C-O bond (the change in angle between the C-O and C=C bonds)
γ(CC_{alk}) – out of plane bending of the C-C_{alk} (the change in angle between the C-C_{alk} bond and plane defined by three carbon atoms in the ring)
τ(CC) – torsion angle in the ring (the change in the dihedral angle between two C=C=C planes in the ring)
τ(CC_{alk}) – torsion angle in the ring (the change in the dihedral angle between C=C=C and C=C-C_{alk} planes)
τ(C=N) – torsion around the C=N bond (the change in the dihedral angle between C-C=N and C=C-C planes)
τ(CH_3) – torsion around the C_{alk}-C_{alk} bond (the change in the dihedral angle between C-C-H and C-C-C planes)
τ(NC) – torsion around the N-C_{alk} bond (the change in the dihedral angle between C=N-C and C=C-C planes)

Table S2. Experimental (IR, Raman and IINS) and calculated (B3LYP/6-31+G(d,p)) vibrational frequencies (ν, cm^{-1}) with the assignments (PED, %) for 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**1**) and its OD derivative. Only internal coordinates contributing more than 5% to the normal coordinates are reported.

Compound 1												
IR		**Raman**		**IINS**		**OH B3LYP/6-31+G(d,p), PED (%)**				**OD B3LYP/6-31+G(d,p), PED (%)**		
OH	**OD**	**OH**	**OD**	**OH**	**OD**	**ν**	**IR**	**R**	**PED (%)**	**ν**	**IR**	**PED (%)**
						3166.5	11.0	83.0	ν(CH) 99	3166.5	11.55	ν(CH) 100
						3166.0	9.4	94.3	ν(CH) 99	3165.9	8.47	ν(CH) 100
3033		3030	3033			3165.9	20.4	95.8	ν(CH) 100	3165.9	20.04	ν(CH) 100
						3135.4	2.1	31.2	ν(CH) 100	3135.4	2.13	ν(CH) 100
		3008	3010			3135.0	2.1	37.9	ν(CH) 100	3135.0	2.09	ν(CH) 100
3007	3007	3000	3000			3134.5	2.1	64.7	ν(CH) 100	3134.5	2.07	ν(CH) 100
2983	2984	2985	2985			3066.8	1.4	134.6	ν(CH) 99	3066.8	1.51	ν(CH) 99
2932	2932					3066.5	1.4	61.1	ν(CH) 99`	3066.5	1.47	ν(CH) 99
2857	2859	2930	2929			3066.3	1.3	395.3	ν(CH) 99	3066.3	1.39	ν(CH) 99
2900-1000*						2588.5	1355.7	27.4	ν(OH) 94			
						2587.3	1354.9	27.3	ν(OH) 97			
						2572.0	4.3	158.5	ν(OH) 97			
	2700-900*									1915.5	842.43	ν(OD) 85
										1914.7	834.63	ν(OD) 88
										1911.9	29.15	ν(OD) 84
1692sh						1683.2	594.6	40.3	δ(COH) 44, ν(C=O) 8, ν(CC) 7			
						1682.0	609.3	40.5	δ(COH) 41, ν(C=O) 7, ν(CC) 7, δ(CCO) 5			
		1611 b	1611			1664.3	2.7	93.3	ν(C=O) 44, δ(COH) 29			
1620						1633.9	837.4	8.5	ν(C=O) 26, ν(CC) 17, $\delta(CCC_{alk})$ 16	1636.4	994.64	ν(C=O) 30, $\gamma(CC_{alk})$ 21, ν(CC) 11, $\delta(CCH_3)$ 5
1582			1572			1633.6	818.7	8.5	ν(C=O) 28, ν(CC) 11, $\delta(CCC_{alk})$ 10	1635.7	998.41	ν(C=O) 29, δ(CC=O) 13, ν(CC) 7, $\gamma(CC_{alk})$ 6, $\delta(CCH_3)$ 5
	1596wb									1610.3	0.58	ν(C=O) 48
	1537		1539			1561.6	0.0	21.4	δ(COH) 46, α(CC) 9, ν(CO) 24	1563.6	300.10	ν(CC) 45, γ(CO) 11, $\delta(CCH_3)$ 8, ν(C=O) 6
										1563.3	299.68	ν(CC) 40, γ(CO) 9, $\delta(CCH_3)$ 8, γ(C=O) 7, ν(C=O) 7
						1505.1	185.3	32.4	ν(CC) 25, ν(CO) 19, δ(COH) 7, $\delta(CCC_{alk})$ 6			
						1504.7	185.1	32.3	ν(CC) 24, ν(CO) 19, δ(COH) 7, $\delta(CCC_{alk})$ 7			
										1478.1	0.00	$\delta(CH_3)$ 20, ν(CO) 31
						1475.5	13.8	7.0	$\delta(CCH_3)$ 99	1475.5	13.40	$\delta(CH_3)$ 99
						1475.3	11.1	10.9	$\delta(CCH_3)$ 99	1475.3	10.93	α(CC) 93, τ(CC) 6

1461	1464	1460			1474.1	11.7	10.5	$\delta(CCH_3)$ 100	1474.1	11.52	$\delta(CH_3)$ 100
									1462.7	23.19	$\delta(CH_3)$ 32, α(CC) 31
					1457.9	0.5	1.4	$\delta(CCH_3)$ 36, δ(CC) 8	1461.8	23.93	$\delta(CH_3)$ 47, α(CC) 10
					1451.0	55.2	14.9	$\delta(CCH_3)$ 64	1451.4	0.15	$\delta(CH_3)$ 53, α(CC) 24
					1450.2	52.3	14.8	$\delta(CCH_3)$ 60	1415.1	189.78	ν(CO) 18, α(CC) 10, τ(CC) 9, ν(CC) 13, ν(C=O) 12
1426	1426	1427	1427		1438.1	0.0	38.9	α(CC) 7, ν(C=O) 15			
1408	1408	1413	1411		1409.5	82.0	13.2	$\delta(CCH_3)$ 73, $\nu(C_{alk}C_{alk})$ 8	1414.1	186.30	ν(CO) 17, ν(CC) 13, $\delta(CH_3)$ 8, ν(C=O) 8
									1406.4	0.19	α(CC) 62, $\nu(C_{alk}C_{alk})$ 8
					1407.8	81.7	13.2	$\delta(CCH_3)$ 73, $\nu(C_{alk}C_{alk})$ 5	1405.0	1.78	τ(CC) 57, $\nu(C_{alk}C_{alk})$ 8, $\delta(CH_3)$ 6
			1386		1403.8	6.8	1.1	$\delta(CCH_3)$ 75	1403.9	4.60	$\delta(CH_3)$ 65, $\nu(C_{alk}C_{alk})$ 9
1365	1365	1370	1370		1346.7	0.4	1.4	ν(CC) 50, $\nu(C_{ar}C_{alk})$ 18	1356.7	0.01	ν(CC) 75
					1343.0	197.0	91.1	$\nu(C_{ar}C_{alk})$ 24, ν(CC) 18, ν(C=O) 5, δ(COH) 5			
		1327			1342.3	196.7	91.1	$\nu(C_{ar}C_{alk})$ 20, ν(CC) 11, ν(C=O) 6	1325.4	0.02	$\nu(C_{ar}C_{alk})$ 33, ν(CC) 16, ν(CO) 15
1309sh		1304	1307		1307.3	0.2	59.5	ν(CC) 36	1304.8	278.14	$\nu(C_{ar}C_{alk})$ 31, δ(COD) 9, δ(CC=O) 9, $\nu(C_{alk}C_{alk})$ 7
1270	1273	1271	1271		1286.6	177.3	8.0	ν(CO) 23, ν(CC) 16, δ(CC=O) 8, $\nu(C_{alk}C_{alk})$ 6, $\nu(C_{ar}C_{alk})$ 5	1304.5	278.09	$\nu(C_{ar}C_{alk})$ 29, δ(CC=O) 12, $\nu(C_{alk}C_{alk})$ 7
1228sh					1286.2	175.6	8.1	ν(CO) 26, ν(CC) 10, δ(CC=O) 7, $\nu(C_{alk}C_{alk})$ 7, $\nu(C_{ar}C_{alk})$ 6			
1201											
	1213	1184							1196.6	31.32	ν(CO) 26, γ(COD) 10, ν(CC) 9, δ(CC=O) 7, $\gamma(CCC_{alk})$ 6
	1157								1196.1	30.94	γ(COD) 30, ν(CO) 25, $\gamma(CCC_{alk})$ 9, ν(CC) 14
			1160						1181.7	0.01	γ(COD) 48, $\delta(CH_3)$ 7
					1161.2	3.5	5.8	ν(CC) 15, ν(CO) 11, $\delta(CCC_{alk})$ 15, δ(CCO) 6, $\nu(C_{alk}C_{alk})$ 5			
1141					1160.6	3.4	5.8	ν(CC) 10, ν(CO) 16, $\delta(CCC_{alk})$ 10, δ(CCO) 7, δ(CC=O) 5			
		1120			1103.3	0.0	18.1	ν(CC) 21, $\delta(CH_3)$ 20, δ(CC) 15, $\nu(C_{alk}C_{alk})$ 10	1091.9	0.07	$\delta(CH_3)$ 25, τ(CC) 8, ν(CC) 19
		1087			1100.5	203.0	0.0	γ(COH) 98	1080.4	53.29	γ(COD) 43, $\delta(CH_3)$ 6, ν(CC) 5
1052	-		1072		1096.8	4.9	0.4	γ(COH) 98	1079.6	52.96	γ(COD) 46, ν(CC) 6, $\delta(CH_3)$ 6
950	-			925 -	1093.7	16.8	0.4	γ(COH) 94	1050.0	6.46	τ(CC) 62, δ(COD) 18
	1058sh				1049.3	6.6	0.2	$\delta(CCH_3)$ 69, γ(C=O) 19	1049.3	2.63	$\delta(CH_3)$ 62, γ(C=O) 18
1020	1028	1033	1034		1048.7	10.8	0.2	$\delta(CCH_3)$ 69, γ(C=O) 19	1048.4	2.06	$\delta(CH_3)$ 70, γ(C=O) 19
			1015		1047.7	16.4	0.0	$\delta(CCH_3)$ 64, γ(C=O) 19			
					1000.2	5.0	24.8	$\delta(CCH_3)$ 32, $\nu(C_{alk}C_{alk})$ 12, δ(CC=O) 5			
978	981	984	984		998.4	44.9	7.1	$\delta(CCH_3)$ 47, $\nu(C_{alk}C_{alk})$ 12, $\nu(C_{ar}C_{alk})$ 5	992.9	53.66	$\delta(CH_3)$ 32, $\nu(C_{alk}C_{alk})$ 29, τ(CC) 10
864sh	967	867	977		997.3	45.3	7.1	$\delta(CCH_3)$ 48, $\nu(C_{alk}C_{alk})$ 13, $\nu(C_{ar}C_{alk})$ 6	991.9	51.70	τ(CC) 21, $\delta(CH_3)$ 20, $\nu(C_{alk}C_{alk})$ 16

820		820		893						988.6	2.05	$\delta(CH_3)$ 23, $\nu(C_{alk}C_{alk})$ 27, τ(CC) 8
										827.3	7.45	$\nu(C_{ar}C_{alk})$ 25, $\nu(C_{alk}C_{alk})$ 23, $\delta(CH_3)$ 8, γ(CO) 7, $\gamma(CC_{alk})$ 6
										826.7	7.42	$\nu(C_{ar}C_{alk})$ 26, $\nu(C_{alk}C_{alk})$ 25, $\delta(CH_3)$ 8, $\gamma(CC_{alk})$ 7, γ(C=O) 7
				873	873	834.4	5.8	1.8	$\nu(C_{alk}C_{alk})$ 25, $\nu(C_{ar}C_{alk})$ 21, α(CC) 8, δ(CCO) 7, $\delta(CCC_{alk})$ 6	803.8	0.86	$\tau(CC_{alk})$ 46, $\tau(CH_3)$ 28, $\delta(CCC_{alk})$ 8
804	807	805	808	826	844	833.8	5.7	1.8	$\nu(C_{alk}C_{alk})$ 27, $\nu(C_{ar}C_{alk})$ 26, δ(CC) 8, δ(CCO) 7, $\delta(CCC_{alk})$ 6	802.6	20.57	$\tau(CH_3)$ 34, γ(CO) 21, $\tau(CC_{alk})$ 19, $\delta(CCC_{alk})$ 7
765		756		765		789.0	0.0	8.1	δ(CCO) 48, $\delta(CCC_{alk})$ 36	799.3	128.29	γ(CO) 51, $\tau(CH_3)$ 12, $\delta(CH_3)$ 9, $\tau(CC_{alk})$ 9, $\delta(CCC_{alk})$ 9
	754				741					649.6	0.02	δ(COD) 18, δ(CC=O) 35
	725				741					622.1	103.16	δ(COD) 41, δ(CC=O) 24, $\delta(CH_3)$ 8
										594.1	0.00	δ(COD) 32, γ(C=O) 14, $\delta(CCC_{alk})$ 12, τ(CC) 11, δ(CCO) 7
						745.2	10.6	0.0	τ(CC) 50, γ(CO) 31, $\gamma(CC_{alk})$ 18	756.2	0.00	γ(C=O) 14, γ(CO) 28, $\gamma(CC_{alk})$ 26, δ(CC=O) 13
		730	729			733.2	0.0	0.1	γ(CO) 47, τ(CC) 29, $\gamma(CC_{alk})$ 15	741.1	0.21	$\delta(CH_3)$ 50, $\delta(CCC_{alk})$ 20, $\delta(CCC_{alk})$ 10, δ(CCO) 12, δ(CC=O) 6
708sh	702sh		714	696	-	733.2	0.0	0.1	γ(CO) 46, τ(CC) 29, $\gamma(CC_{alk})$ 16	724.7	0.01	$\delta(CCC_{alk})$ 45, $\delta(CH_3)$ 30, δ(CCO) 10, δ(CC=O) 5
		649	647	661	669	649.7	0.0	16.3	δ(CC=O) 52	724.4	0.01	$\delta(CCC_{alk})$ 45, $\delta(CH_3)$ 30, δ(CCO) 10, δ(CC=O) 6
622	615	612		635	629	625.7	107.2	1.0	δ(CC=O) 64, α(CC) 8	621.7	103.74	δ(CC=O) 65, $\delta(CH_3)$ 8
						625.3	107.8	1.0	δ(CC=O) 68, α(CC) 8	616.7	0.09	$\delta(CCH_3)$ 41, ν(CC) 21, ν(CC) 21
597sh			607	605	610	622.5	0.2	14.4	α(CC) 39, ν(CC) 28, ν(CO) 14			
				593		596.2	0.0	0.3	γ(C=O) 46, γ(CO) 15, $\delta(CCH_3)$ 11, $\gamma(CC_{alk})$ 12	593.3	0.00	γ(C=O) 47, $\delta(CCC_{alk})$ 18, $\delta(CH_3)$ 15, δ(CC=O) 8
				555		595.4	0.0	0.3	γ(C=O) 47, γ(CO) 18, $\delta(CCH_3)$ 16, $\gamma(CC_{alk})$ 8	576.5	0.01	γ(C=O) 32, $\delta(CH_3)$ 26, δ(COD) 14, $\delta(CCC_{alk})$ 17
					525	577.4	0.1	0.0	γ(C=O) 47, γ(CO) 17, τ(CC) 17, $\delta(CCH_3)$ 11	474.6	4.38	γ(CO) 28, δ(COD) 14, δ(CC=O) 13, $\delta(CH_3)$ 5
482		487		501		488.6	4.6	5.5	δ(CCO) 38, δ(CC=O) 18			
	467		472		480					473.6	4.71	δ(CC=O) 28, γ(C=O) 19, γ(CO) 6, $\delta(CH_3)$ 5
				443		487.8	4.9	5.5	δ(CCO) 48, δ(CC=O) 19	412.7	0.00	δ(CC=O) 22, δ(COD) 11, γ(CO) 18, γ(C=O) 9
				436	428	422.4	0.0	3.5	$\delta(CCC_{alk})$ 27, δ(CCO) 26, δ(CC=O) 22	392.1	13.97	$\delta(CH_3)$ 20, γ(CO) 14, δ(CC=O) 14, γ(C=O) 9, ν(OD) 6
		408	402	418		403.5	10.3	2.7	δ(CC=O) 25, α(CC) 19, δ(CCO) 15	391.7	12.02	$\delta(CH_3)$ 17, δ(COD) 17, γ(CO) 11, γ(C=O) 8, δ(CC=O) 8, ν(OD) 6
						403.1	10.3	2.8	δ(CC=O) 32, α(CC) 18, δ(CCO) 17	390.2	2.43	ν(OD) 13, $\nu(C_{ar}C_{alk})$ 11, $\gamma(CC_{alk})$ 9, γ(CO) 8

382		387		391	384	399.7	0.3	5.0	$\nu(C_{ar}C_{alk})$ 26, δ(CC=O) 18, α(CC) 6, ν(OH) 6	349.7	8.89	$\delta(CH_3)$ 22, γ(CO) 6, δ(CC=O) 26, $\gamma(CC_{alk})$ 6
	373		373							349.5	8.69	$\delta(CH_3)$ 22, δ(COD) 20, δ(CC=O) 8, γ(CO) 6, $\nu(C_{ar}C_{alk})$ 6, $\gamma(CC_{alk})$ 6
349	350	350	349	357	358	351.3	8.8	4.0	α(CC) 23, δ(CC=O) 20, δ(CCO) 6, $\delta(CCC_{alk})$ 6, $\nu(C_{ar}C_{alk})$ 5			
		333		341	348	351.0	8.6	4.0	α(CC) 23, δ(CC=O) 28, $\nu(C_{ar}C_{alk})$ 6, $\delta(CCC_{alk})$ 6	323.7	0.00	δ(CC=O) 34, δ(COD) 16
			333			324.2	0.0	9.6	$\delta(C_{alk}C{=}O)$ 50	309.4	0.00	δ(CCO) 31, δ(CC=O) 23, $\delta(CH_3)$ 28, $\tau(CC_{alk})$ 6
	323	320	320	323	328	310.2	0.0	0.2	$\gamma(CC_{alk})$ 54, τ(CC) 28, γ(COH) 6	309.2	0.00	δ(CCO) 42, $\delta(CH_3)$ 28, δ(CC=O) 13, γ(CO) 6
				311		310.0	0.0	0.2	$\gamma(CC_{alk})$ 55, τ(CC) 28, γ(COH) 7	239.3	0.94	$\delta(CH_3)$ 32, $\tau(CC_{alk})$ 19, $\gamma(CC_{alk})$ 12, δ(CC=O) 6, δ(CCO) 5
				259	264	240.2	1.1	0.0	τ(CC) 33, $\tau(CH_3)$ 28, $\gamma(CC_{alk})$ 18	226.6	0.01	$\tau(CC_{alk})$ 39, $\gamma(CC_{alk})$ 38, $\delta(CH_3)$ 6, τ(CC) 6
				240	243	226.7	0.0	0.7	$\tau(CH_3)$ 76, $\delta(CCH_3)$ 11	219.8	0.02	$\tau(CC_{alk})$ 56, $\gamma(CC_{alk})$ 14, $\delta(CH_3)$ 7
				225	227	220.0	0.0	0.7	$\tau(CH_3)$ 70, $\delta(CCH_3)$ 7	218.1	12.24	$\gamma(CC_{alk})$ 71
				210	213	198.4	0.3	0.0	τ(CC) 35, $\tau(CH_3)$ 27, $\gamma(CC_{alk})$ 21	217.1	12.34	δ(CC=O) 46, $\gamma(CC_{alk})$ 27, γ(CO) 5
223	223	221	221	154	153	218.3	12.4	1.9	$\delta(CCC_{alk})$ 71	197.5	0.36	$\delta(CH_3)$ 35, $\tau(CC_{alk})$ 19, δ(CC=O) 8, δ(CCO) 14, $\gamma(CC_{alk})$ 7
				145	148	217.3	12.5	1.9	$\delta(CCC_{alk})$ 71			
126	126			127	129	126.0	0.0	0.0	γ(COH) 38, $\tau(CC_{alk})$ 33, τ(CC) 11	125.9	0.01	δ(CCO) 26, γ(CO) 12, $\delta(CH_3)$ 11, $\tau(CH_3)$ 33
				124	123	124.6	0.0	0.0	γ(COH) 38, $\tau(CC_{alk})$ 36, τ(CC) 11	124.6	0.00	$\tau(CC_{alk})$ 24, $\tau(CH_3)$ 37, γ(CO) 14, $\delta(CH_3)$ 11
				111	111	110.9	4.0	0.0	γ(COH) 40, $\tau(CC_{alk})$ 32, $\gamma(CC_{alk})$ 21	110.7	3.89	$\tau(CC_{alk})$ 14, γ(CO) 14, $\tau(CH_3)$ 33, δ(CCO) 24, δ(CCO) 8
				95	94							
				79	77	58.2	3.6	0.0	$\tau(CC_{alk})$ 49, τ(CC) 29, $\tau(CH_3)$ 5	57.9	3.55	$\delta(CH_3)$ 30, δ(CCO) 23, $\tau(CH_3)$ 26, $\gamma(CC_{alk})$ 5
				61	57	48.4	0.1	0.2	τ(CC) 49, $\tau(CC_{alk})$ 30	47.9	0.12	$\delta(CH_3)$ 48, $\tau(CH_3)$ 17, δ(CCO) 4
				40	38	47.0	0.1	0.2	$\tau(CC_{alk})$ 37, τ(CC) 46, $\tau(CH_3)$ 6	46.5	0.06	$\tau(CH_3)$ 37, $\delta(CH_3)$ 47, $\tau(C_{ar}C_{alk})$ 6

* Sub-picks of stretching vibration mode ν(OH) observed in IR spectra: 2650, 2395, 2190, 1795 cm^{-1} and ν(OD): 2700, 2531, 2390 - 2340, 2250 – 2180 and 2000 - 1700 cm^{-1}. The ν(OH) bands are sensitive on deuteroreplacement in hydrogen bond.

Table S3. Experimental and calculated (B3LYP/6-31+G(d,p)) vibrational frequencies (cm^{-1}) with the assignments (PED, %) for (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-N-methylethaniminium (**2**) and its OD/ND derivative. Only internal coordinates contributing more than 5% to the normal coordinates are reported.

Compound 2												
IR		**Raman**		**IINS**		**DFT**						
H	**D**	**H**	**D**	**H**	**D**	**ν**	**IR**	**R**	**OD B3LYP/6-31+G(d,p), PED (%)**	**ν**	**IR**	**OD B3LYP/6-31+G(d,p), PED (%)**
						3175.5	21.2	76.7	ν(CH) 98	3175.5	22.3	ν(CH) 98
						3163.6	16.7	96.1	ν(CH) 100	3163.6	16.4	ν(CH) 100
						3159.0	19.0	91.9	ν(CH) 100	3159.0	19.2	ν(CH) 100
						3147.8	0.6	89.3	ν(CH) 100	3147.8	0.6	ν(CH) 100
3015	3015					3147.7	9.9	41.3	ν(CH) 98	3147.6	10.2	ν(CH) 98
		3010	3010			3135.9	2.7	49.3	ν(CH) 100	3135.9	2.7	ν(CH) 100
2990	2986	2989	2989			3133.4	3.5	42.5	ν(CH) 100	3133.4	3.5	ν(CH) 100
2935	2937		2937			3105.7	16.4	129.7	ν(CH) 100	3105.6	16.2	ν(CH) 100
		2932	2932			3085.7	6.3	167.9	ν(CH) 99	3085.7	6.3	ν(CH) 99
						3066.8	3.1	230.7	ν(CH) 99	3066.8	3.2	ν(CH) 99
						3064.1	6.4	217.8	ν(CH) 99	3064.1	6.6	ν(CH) 99
						3043.7	46.3	426.9	ν(CH) 99	3043.0	62.0	ν(CH) 99
2900-1000*						2926.4	491.0	21.4	ν(NH) 97			
						2439.8	915.4	48.0	ν(OH) 93			
						2397.8	918.8	61.5	ν(OH) 93			
	2850-1000*									2165.2	280.5	ν(ND) (93)
										1824.9	545.5	ν(OD) 89, ν(C=O) 13
										1801.9	678.1	ν(OD) 89, ν(C=O) 16
1635						1692.4	607.0	20.0	δ(COH) 50, δ(CCO) 6	1626.0	866.4	ν(C=N) 31, ν(CO) 16, δ(CC_{alk}) 9, δ($CC_{alk}C_{alk}$) 8, ν(CC_{alk}) 7
	1625sh					1672.9	134.3	58.3	δ(COH) 21, δ(CNH) 19, ν(C=N) 11, ν(C=O) 10	1619.3	779.6	ν(C=O) 22, δ(CC_{alk}) 22, ν(CC) 16, δ(CC) 6
						1662.5	522.6	39.2	δ(CNH) 22, δ(COH) 28, ν(C=O) 9, ν(C=N) 8	1596.2	552.4	ν(C=O) 24, δ(CC_{alk}) 10, ν(CO) 9
		1614sh	1615sh			1628.0	1092.6	73.3	ν(CO) 17, δ(CCC_{alk}) 10, ν(C=N) 9, ν(C=O) 13, α(CC) 6	1570.8	278.67	ν(CO) 16, ν(CC) 16, ν(C=N) 12, ν(C=O) 5
		1586sh	1589			1611.7	408.9	37.0	ν(CO) 20, ν(C=O) 19, δ(CCC_{alk}) 7, ν(CC) 6			
1580	1580	1562	1562			1593.9	669.3	27.2	ν(C=O)17, ν(CO)8, δ(COH)8, ν(CC)6, δ(CCC_{alk})6, δ(CCC_{im})5	1540.6	134.87	ν(CC) 25, ν(CO) 13, δ(CO) 11, ν(C=O) 8, δ(OD) 5
1550	1536	1502	1534			1514.9	26.2	18.4	δ(NCH_3) 75	1512.5	76.65	δ(CH_3) 71, δ(NCH_3) 7
			1506			1509.2	3.1	11.9	δ(NCH_3) 83, δ(CH_3) 12	1509.2	3.21	δ(CH_3) 88, δ(NCH_3) 7
						1507.5	122.7	41.8	δ(CH_3) 29, ν(CC) 10, ν(CO) 8	1495.0	550.33	ν(CC) 15, δ(CH_3) 13
1485						1500.6	311.8	22.9	ν(CC) 19, ν(CO) 10, δ(CH_3) 15			
1472	1475	1471	1475			1483.7	6.0	8.6	δ(CH_3) 23, ν(CC) 8, δ(NCH_3) 6, ν(CO) 5, α(CC) 5	1485.0	3.47	δ(CH_3) 69
						1478.2	16.0	14.6	δ(CH_3) 81, δ(NCH_3) 13	1478.2	15.37	δ(CH_3) 94

					1474.0	11.4	9.9	$\delta(CH_3)$ 93	1474.0	11.22	$\delta(CH_3)$ 100
					1468.5	10.5	8.9	$\delta(CH_3)$ 93	1468.5	10.45	$\delta(CH_3)$ 100
			1463		1467.0	168.2	57.8	$\delta(CH_3)$ 28, ν(CC) 15, ν(CO) 10	1463.3	122.74	$\delta(CH_3)$ 22, $\nu(CC_{alk})$ 14
	1452	1457							1455.7	2.62	$\delta(CH_3)$ 55
					1449.0	68.0	25.2	$\delta(CH_3)$ 61	1449.3	349.42	$\delta(CH_3)$ 57, ν(N-C) 6
					1445.2	16.2	14.4	$\delta(CH_3)$ 59			
1424					1436.4	48.1	76.8	$\delta(CH_3)$ 39, ν(C=N) 11	1436.4	25.61	$\delta(CH_3)$ 28, $\delta(CC_{alk})$ 5, ν(C=O) 6
1413		1418sh	1415		1415.4	33.1	6.1	$\delta(CH_3)$ 80	1415.2	12.03	$\delta(CH_3)$ 70
									1406.5	72.58	$\delta(CH_3)$ 77, $\nu(C_{alk}C_{alk})$ 11
1397sh	1407	1401			1408.0	72.1	12.1	$\delta(CH_3)$ 73, $\nu(C_{alk}C_{alk})$ 10	1404.4	27.62	$\delta(CH_3)$ 68
					1406.4	26.7	7.3	$\delta(CH_3)$ 65, $\nu(C_{alk}C_{alk})$ 9			
									1392.5	36.39	ν(CC) 23, ν(CO) 21, ν(C=O) 15, δ(OD) 9
1371		1372	1372								
1358	1362				1354.2	101.0	35.5	$\nu(C_{ar}C_{alk})$ 21, ν(CO) 12, $\delta(CH_3)$ 6, δ(CC=O) 6, ν(CC) 5	1368.8	24.54	ν(CC) 17, ν(CO) 13, $\nu(CC_{alk})$ 12, $\delta(NCC_{alk})$ 10, δ(OD) 9, $\nu(C_{alk}C_{alk})$ 6
		1336	1336		1348.8	138.6	42.1	$\nu(C_{ar}C_{alk})$ 20, ν(CC) 26	1342.0	39.17	$\nu(CC_{alk})$ 30, ν(CC) 16, ν(CC) 7
1319		1319	1317		1323.0	136.2	102.9	ν(CC) 29, δ(CC=O) 6, ν(C=O) 6, $\delta(CCC_{alk})$ 5, $\nu(C_{ar}C_{alk})$ 5	1330.2	160.93	ν(CC) 25, $\nu(CC_{alk})$ 14, δ(C=O) 10, ν(CC) 9
1301	1301	1301	1301		1312.3	131.9	61.6	ν(CC) 30, $\nu(C_{ar}C_{alk})$ 16, δ(CC=O) 6	1293.2	129.43	ν(CC) 21, δ(C=O) 15, $\nu(CC_{alk})$ 8, $\delta(CC_{alk})$ 7, $\nu(C_{alk}C_{alk})$ 6
1263	1267	1280	1280		1283.0	10.2	12.1	ν(CO) 22, $\nu(C_{ar}C_{alk})$ 12, ν(CC) 13			
		1228			1266.0	29.3	41.6	ν(CC) 27, ν(CO) 13, $\nu(C_{alk}C_{alk})$ 6, δ(CC=O) 6	1233.2	4.90	ν(N-C) 14, δ(ND) 13, ν(CO) 9, $\nu(CC_{alk})$ 8, $\delta(CC_{alk})$ 7, $\delta(CC_{alk}C_{alk})$ 7,
									1199.5	50.65	ν(CO) 20, δ(OD) 10, $\delta(CC_{alk})$ 9, ν(CC) 8, δ(C=O) 5
1162			1188		1187.1	30.7	0.7	$\delta(NCH_3)$ 40, ν(NC) 8, δ(CNH) 7, ν(CO) 5, $\delta(CC_{im}N)$ 5	1181.7	39.23	δ(OD) 20, ν(CC) 15, δ(CO) 6, ν(CO) 6, $\delta(CC_{alk})$ 5
			1166		1163.4	3.1	28.9	$\delta(CCC_{im})$13, ν(CC)20, δ(CCO) 7, $\delta(CCC_{alk})$ 7, $\nu(C_{alk}C_{alk})$ 6	1165.5	6.93	$\delta(NCH_3)$ 63
1128	1147sh	1139	1142		1151.8	4.3	2.9	$\delta(NCH_3)$ 15, $\delta(CCC_{alk})$ 10, ν(CO) 9, ν(CC) 8			
					1134.0	11.7	0.4	$\delta(NCH_3)$ 82, γ(COH) 6	1131.9	0.21	$\delta(NCH_3)$ 89, $\delta(CH_3)$ 5
1104sh					1130.6	142.3	0.3	γ(COH) 93, $\delta(NCH_3)$ 6			
1013				958	1128.1	0.5	0.5	γ(COH) 98			
	1168							δ(OD)	1105.4	25.94	$\delta(CH_3)$ 19, δ(OD) 17, ν(N-C) 11, ν(CC) 8
	1099				1097.0	3.3	3.6	$\delta(CH_3)$ 12, α(CC) 11, $\nu(C_{alk}C_{alk})$ 11, ν(CC) 14, $\delta(CC_{im}N)$ 6	1086.7	13.99	$\delta(CH_3)$ 20, δ(OD) 14, δ(CC) 8, ν(CC) 9, $\nu(C_{alk}C_{alk})$ 5
1061	1076				1079.1	18.0	23.6	ν(NC) 37, $\delta(CH_3)$ 11, $\nu(C_{alk}C_{alk})$ 7, ν(CC) 7	1074.9	26.76	δ(OD) 38, ν(OD) 6
	1056	1050	1055		1057.9	0.5	0.2	$\delta(CH_3)$ 71, γ(C=N) 9, τ(C=N) 7	1050.7	3.22	$\delta(CH_3)$ 78, γ(C=N) 13
1029	1029	1034	1033		1049.1	8.9	0.2	$\delta(CH_3)$ 73, γ(C=O) 18	1049.5	3.97	$\delta(CH_3)$ 63, γ(C=O) 18
	1020				1048.1	3.4	0.3	$\delta(CH_3)$ 73, γ(C=O) 19	1048.2	2.15	$\delta(CH_3)$ 63, γ(C=O) 19
					1003.9	48.8	11.8	$\delta(CH_3)$ 48, $\nu(C_{alk}C_{alk})$ 10			
					1003.2	63.5	0.4	γ(CNH) 46, τ(C=N) 27, $\delta(CH_3)$ 11,			

									γ(C=N) 8			
981	975	982	976			997.4	29.9	12.9	$\delta(CH_3)$51, $\nu(C_{alk}C_{alk})$15, $\nu(C_{ar}C_{alk})$6, δ(CC=O) 5, ν(C=O) 5	997.2	55.13	$\delta(CH_3)$ 45, $\nu(C_{alk}C_{alk})$ 13, δ(OD) 5
										992.3	25.36	$\delta(CH_3)$ 44, $\nu(C_{alk}C_{alk})$ 16, $\nu(CC_{alk})$ 5
	969sh	953	967			965.7	2.3	13.2	$\delta(CH_3)$ 21, ν(NC) 12, $\nu(C_{alk}C_{alk})$ 14, ν(C=N) 6, $\nu(C_{ar}C_{alk})$ 6	963.9	0.27	δ(ND) 14, $\delta(CH_3)$ 14, $\nu(C_{alk}C_{alk})$ 20, $\nu(CC_{alk})$ 9, ν(C=N) 7
										956.6	3.31	ν(N-C) 33, δ(ND) 28, ν(ND) 8, $\delta(CH_3)$ 7
932									γ(COH)			
831	945	945	951	873	838	842.6	17.4	2.5	$\nu(C_{alk}C_{alk})$ 25, $\nu(C_{ar}C_{alk})$ 24, α(CC) 8, $\delta(CCC_{im})$ 7	839.8	22.08	$\nu(C_{alk}C_{alk})$ 43, $\delta(CC_{alk})$ 9, δ(CC) 8, δ(CO) 7
802	831	920	923	825		820.5	15.8	2.2	$\nu(C_{alk}C_{alk})$23, δ(CCO)14, $\delta(CCC_{alk})$11, $\nu(C_{ar}C_{alk})$9, α(CC)5			
	805		885	751		798.0	2.4	5.6	δ(CCO) 48, $\delta(CCC_{alk})$ 26, $\delta(CCC_{im})$ 8	813.0	11.91	$\nu(C_{alk}C_{alk})$ 26, $\nu(CC_{alk})$ 16, δ(CO) 11, δ(CC) 6, $\delta(CC_{alk})$ 10
										790.4	26.34	γ(C-O) 28, $\gamma(C_{alk}C)$ 14
										773.7	4.21	δ(CO) 45, $\delta(CC_{alk})$ 36
770	775		750			779.4	8.0	0.1	τ(CC) 45, γ(CO) 31, $\gamma(CC_{alk})$ 13	752.1	8.96	τ(CC) 37, γ(C-O) 31, $\gamma(C_{alk}C)$ 17, γ(ND) 5
	747									825.4	2.68	γ(COD) 79, γ(C-O) 7
										824.1	90.43	γ(COD) 77, γ(C-O) 8, τ(CC) 5
	724					736.0	0.1	0.2	τ(CC) 28, γ(CO) 49, $\gamma(CC_{alk})$ 11			
736		731				744.7	1.9	0.2	γ(CO) 47, $\gamma(CC_{alk})$ 18, τ(CC) 27	731.8	1.98	γ(C-O) 44, τ(CC) 25, $\gamma(C_{alk}C)$ 15
	695									724.6	4.63	γ(C-O) 50, τ(CC) 24, $\gamma(C_{alk}C)$ 5, γ(ND) 5
652		654	650		662	659.2	19.1	11.3	δ(CC=O) 32, $\delta(CC_{im}N)$ 16, α(CC) 8, δ(CNH) 7	655.8	22.13	δ(C=O) 35, $\delta(NC_{alk})$ 9, δ(CC) 7, δ(ND) 7
622	647	618	613			628.3	98.8	4.2	δ(CC=O) 59, α(CC) 6	624.7	83.65	δ(C=O) 54, δ(CC) 14
591	612			600	600	624.5	15.8	14.9	α(CC) 30, δ(CC=O) 11, ν(CC) 26, ν(CO) 7	620.2	27.23	δ(CC) 25, δ(C=O) 24, ν(CC) 19, ν(CO) 7,
						604.1	14.4	1.6	$\delta(CC_{im}N)$ 34, δ(CNH) 13, δ(CC=O) 11, α(CC) 8			
	590sh	583	583			599.7	0.1	0.4	γ(C=O) 47, $\gamma(CC_{alk})$ 10, γ(CO) 10, $\delta(CH_3)$ 8	597.8	0.12	γ(C=O) 49, $\delta(CH_3)$ 16, δ(ND) 15, $\gamma(C_{alk}C)$ 15, γ(C-O) 10
										596.6	11.59	$\delta(NC_{alk})$ 27, $\delta(C_{alk}C_{alk})$ 7, δ(CC) 7, δ(C=O) 5
566	547			572	-	593.0	0.4	0.5	γ(C=O) 32, γ(C=N) 18, γ(CO) 17, $\delta(CH_3)$ 7, $\gamma(CC_{alk})$ 5	588.6	0.32	γ(C=O) 43, γ(C-O) 17, $\delta(CH_3)$ 14, γ(C=N) 7
						576.3	0.2	0.1	γ(C=N) 34, γ(C=O) 24, $\delta(CH_3)$ 8, τ(CC) 7, γ(CO) 6	568.1	2.03	γ(C=N) 46, $\delta(CH_3)$ 12, γ(C=O) 8, γ(C-O) 6
497	485	502			499	503.5	8.4	10.3	δ(CCO) 35, δ(CC=O) 16, $\delta(CCC_{alk})$ 6	490.8	11.73	δ(CO) 29, δ(C=O) 25, $\delta(CC_{alk})$ 7
			483			487.9	4.0	2.0	δ(CCO) 42, ν(CC) 13	479.1	5.71	δ(CO) 40, $\delta(C_{alk}C_{alk})$ 12, ν(CC) 12, ν(OD) 5
442	432	443	436			449.3	23.8	4.2	$\delta(CCC_{alk})$ 32, δ(CC=O) 21, $\delta(CCC_{im})$ 8, δ(CCO) 14	442.9	17.68	δ(C=O) 31, $\delta(CC_{alk})$ 22, δ(CO) 12, δ(CC) 5
						411.2	11.2	7.6	α(CC) 16, δ(CC=O) 23, $\nu(C_{ar}C_{alk})$ 8,			

								ν(OH) 7, δ(CCC_{im}) 7				
						403.6	13.9	2.3	α(CC) 18, δ(CC=O) 38, δ(CCO) 17, ν(OH) 6	403.5	13.96	δ(C=O) 24, δ(CC) 12, δ(ND) 9, ν(CC_{alk}) 9, ν(OD) 9, δ(CC_{alk}) 6
		383	372			390.4	2.1	6.9	δ($CC_{im}N$) 47, δ(CCO) 19, δ(CNH) 6, α(CC) 5	392.1	13.25	δ(C=O) 31, δ(CO) 23, ν(OD) 10, δ(CC_{alk}) 9, δ(CC) 8
385	384sh			389	386				ν_σ(OO) and ν_σ(ON)			
	373					349.9	17.4	2.7	α(CC) 26, δ(CC=O) 16, δ(CNH) 6, δ(CCC_{im}) 6, ν(CC) 6, ν($C_{ar}C_{alk}$) 6	384.6	8.35	δ($CC_{alk}C_{alk}$) 38, δ(CO) 22, δ(CC) 11, ν(OD) 6
		363		339	347	360.9	7.4	4.2	α(CC) 24, ν($C_{ar}C_{alk}$) 12, ν(CC) 7, δ(CC=O) 17, δ(CCO) 6	359.6	7.25	δ(CC) 24, ν(CC_{alk}) 13, ν(CC) 7, δ(C=O) 6
351	350	332	331			332.5	0.0	0.2	γ(CC_{alk}) 40, τ(CC) 21, τ(CN) 11, γ(COH) 8, γ(CNH) 7	347.8	15.92	δ(CC) 25, δ(C=O) 17, δ(ND) 8, δ(CC_{alk}) 7, ν(CC_{alk}) 6, ν(CC) 5
331	329			305	302	327.5	2.4	20.6	δ(CC=O) 26, ν($C_{ar}C_{alk}$) 12, δ(CCC_{im}) 7, ν(CC) 6	330.8	0.02	γ(C_{alk}C) 42, τ(CC) 21, τ(C=N) 12, τ(COD) 8, γ(ND) 6
										326.0	2.05	δ(C=O) 25, ν(CC_{alk}) 7, ν(CC) 6, δ(ND) 6, δ(CC_{alk}) 6
302	297	303	298			303.7	0.0	0.3	γ(CC_{alk}) 58, τ(CC) 22, γ(COH) 8	303.2	0.05	γ(C_{alk}C) 58, τ(CC) 22, τ(COD) 8
		283		278	275	296.7	14.5	4.0	δ($CC_{im}N$) 35, δ(CCC_{alk}) 26, δ(CCC_{im}) 13, δ(CNH) 9, δ(CC=O) 7	293.7	14.59	δ(CC_{alk}) 27, δ(NC_{alk}) 22, δ($C_{alk}C_{alk}$) 13, δ(ND) 9, δ(C=O) 6
				248	252	243.3	0.8	0.3	τ(CH_3) 43, τ(CC) 24, γ(CC_{alk}) 9	242.9	0.75	τ($C_{alk}C_{alk}$) 45, τ(CC) 23, γ(C_{alk}C) 9
227	222	229	223	217		225.5	0.9	0.9	τ(CC) 22, τ(CH_3) 34, γ(CC_{alk}) 19	224.8	0.80	τ($C_{alk}C_{alk}$) 37, τ(CC) 21, γ(C_{alk}C) 18
						218.8	12.7	4.1	δ(CCC_{alk}) 72, δ(CCO) 5	218.6	12.67	δ(CC_{alk}) 78
						213.9	0.0	0.8	τ(CH_3) 72, δ(CH_3) 5	213.8	0.01	τ($C_{alk}C_{alk}$) 75, δ(CH_3) 6
				173		197.2	0.0	0.1	τ(CC) 21, τ(CH_3) 26, γ(CC_{alk}) 26, τ(C=N) 6	196.3	0.00	τ($C_{alk}C_{alk}$) 24, γ(C_{alk}C) 26, τ(CC) 22, τ(C=N) 7
150	144					181.3	0.9	0.9	γ(CNH) 30, τ(CH_3) 23, τ(NC) 17, τ(CC) 7	179.9	0.77	γ(ND) 29, τ(N-C) 20, τ(C=N) 18, τ($C_{alk}C_{alk}$) 6, τ(CC) 6
						167.0	0.4	0.3	τ(NC) 32, γ(CNH) 26, γ(COH) 10, τ(C=N) 9, τ(CC) 12	166.7	0.44	τ(N-C) 29, γ(ND) 28, τ(CC) 12, τ(C=N) 10, τ(COD) 10
						166.5	1.2	1.6	δ(CCC_{im}) 34, δ(CCC_{alk}) 14, δ($CC_{im}N$) 11, δ(CCO) 6 δ(CNH) 6	165.3	1.17	δ(CC_{alk}) 46, δ(NC_{alk}) 11, δ(ND) 9, δ(CO) 6
				136		127.4	0.3	0.0	γ(COH) 36, τ(CH_3) 25, τ(CC_{alk}) 13, τ(CC) 12	127.4	0.28	τ(C=O) 37, τ(COD) 36, τ(CC) 12
124	125			122		123.0	2.6	0.0	γ(COH) 39, τ(CC_{alk}) 31, τ(CC) 5	123.0	2.63	τ(COD) 39, τ(C=O) 31, τ(CC) 5
				93		73.8	0.4	0.0	τ(CC_{alk}) 37, τ(C=N) 22, τ(CH_3) 11, τ(CC) 7	73.6	0.46	τ(C=N) 47, τ(C=O) 11, τ($C_{alk}C_{alk}$) 11, τ(CC) 5
						55.5	3.6	0.0	τ(CC) 28, τ(CC_{alk}) 42, τ(CH_3) 12	55.2	3.50	τ(C=O) 43, τ(CC) 28, τ($C_{alk}C_{alk}$) 12
						42.6	0.7	0.1	τ(CC) 55, τ(CC_{alk}) 28	42.3	0.63	τ(CC) 55, τ(C=O) 28
						31.6	1.0	0.1	τ(CC_{alk}) 33, τ(CC) 44, τ(CH_3) 15	31.4	1.02	τ(CC) 43, τ(C=N) 33, τ($C_{alk}C_{alk}$) 12

* Sub-picks of stretching vibration mode ν(OH): 1924, 1744 and ν(OD): 2078, 1803. These bands are sensitive on deuteronsubstitution in hydrogen bonding. **Assignments made on base of experimental deuteronsubstitution spectrum.

Table S4. Selected normal modes of compound **1** calculated by DFPT method (frequencies in cm^{-1}).

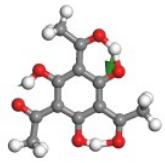
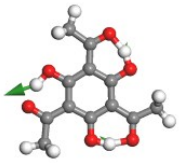
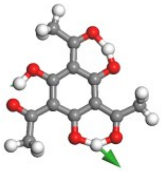
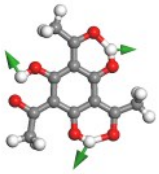
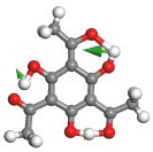
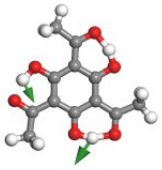
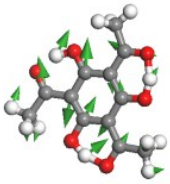
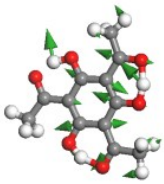
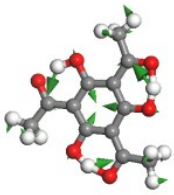
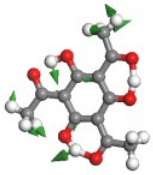
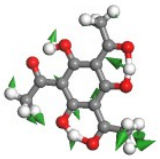
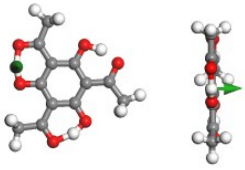
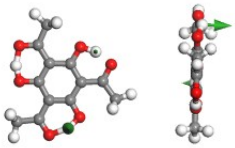
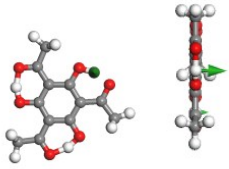
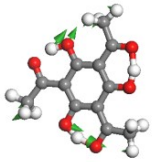
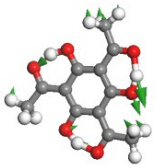
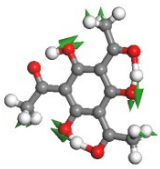
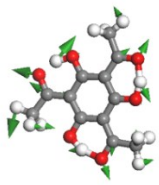
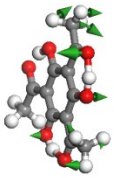
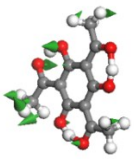
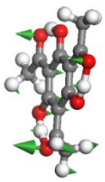
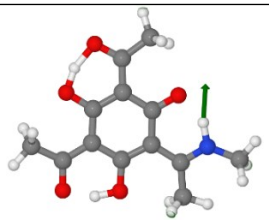
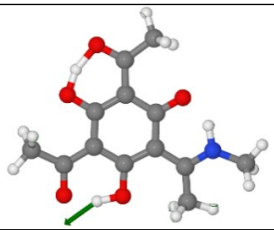
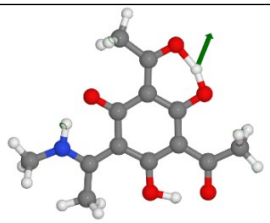
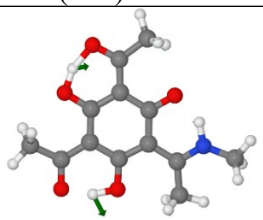
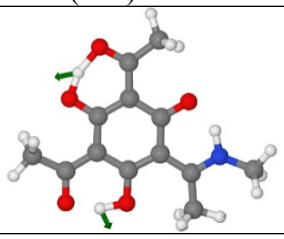
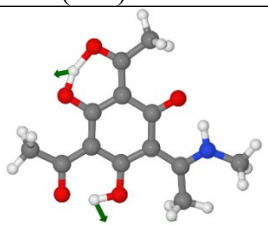
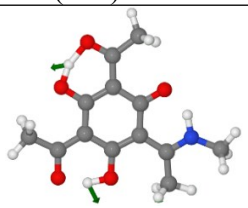
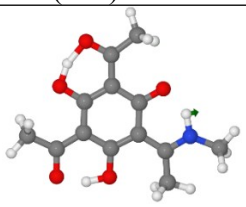
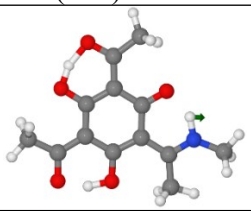
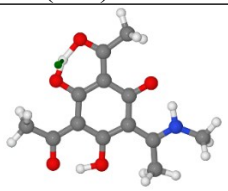
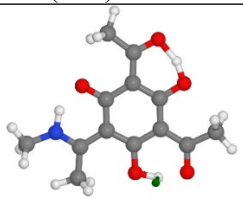
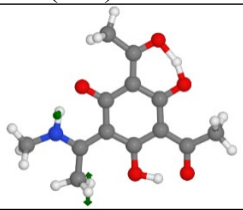
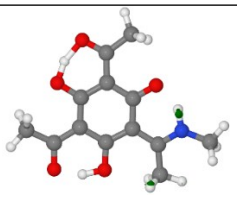
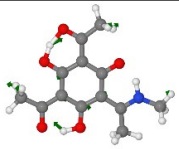
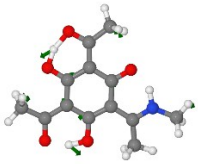
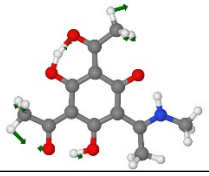
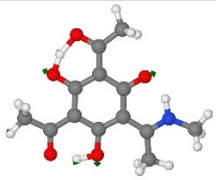
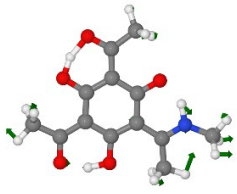
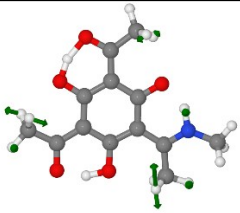
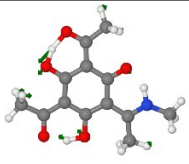
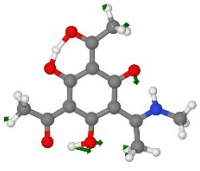
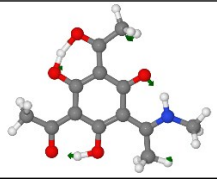
			
ν(OH) = 2082	ν(OH) = 2074	ν(OH) = 2063	
			
δ(OH) = 1639	δ(OH) =1664	δ(OH) =1665	
			
δ(OH) = 1568	δ(OH) = 1566	δ(OH) = 1536	
			
δ(OH) = 1477	δ(OH) = 1467		
			
γ(OH) = 1170	γ(OH) = 1156	γ(OH) = 1153	
			
ν_σ = 492	ν_σ = 491	ν_σ = 425	ν_σ = 403
			
ν_β = 146	ν_β = 135	ν_β = 118	

Table S5. Selected normal modes of compound **2** calculated by DFTP method (frequencies in cm^{-1}).

			
ν(NH) = 2798	ν(OH) = 2133	ν(OH) = 1958	
			
δ(OH) =1656	δ(OH) =1632	δ(OH) =1630	
			
δ(OH) =1617	δ(NH) = 1562	δ(NH) = 1263	
			
γ(OH) = 1181	γ(OH) = 1132	γ(NH) = 1021	γ(NH) = 979
			
780	779	617, 616, 615, 614	
			
610, 609	591 - 590	554	
			
ν_σ=500, 499, 498, 497	ν_σ=485	ν_σ=483-482	ν_σ=454, 450

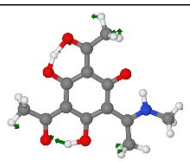
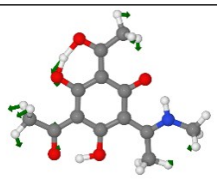
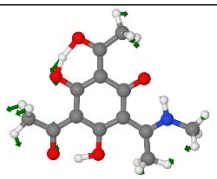
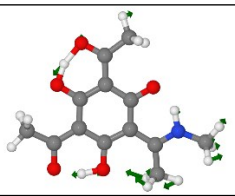
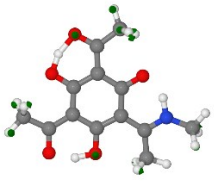
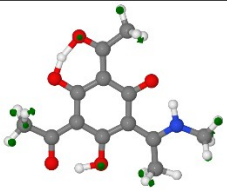
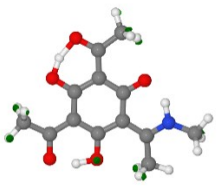
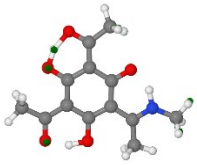
			
ν_{σ}=406 - 405	ν_{σ}=399	ν_{σ}=395	ν_{σ}=384-381
			
ν_{β} = 142	ν_{β} = 140	ν_{β} = 139	ν_{β} = 122

Table S6. Crystal data and structure refinement for 1,1′,1″-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**1**) and (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-N-methylethaniminium (**2**).

Identification code	**1**	**2**
Empirical formula	$C_{12}H_{12}O_6$	$C_{13}H_{15}NO_5$
Formula weight	252.22	265.26
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, Pbca
Unit cell dimensions	a = 9.298(3) Å b = 16.631(4) Å β = 106.90(4) ° c = 7.232(3) Å	a = 17.6428(7) Å b = 7.0164(3) Å c = 19.1027(9) Å
Volume	1070.0(6) A^3	2364.70(18) $Å^3$
Z, Calculated density	4, 1.566 mg/m^3	8, 1.490 mg/m^3
Absorption coefficient	0.127 mm^{-1}	0.115 mm^{-1}
F(000)	528	1120
Crystal size	0.15 x 0.13 x 0.11 mm	0.25 x 0.10 x 0.08 mm
Theta range for data collection	3.19 to 26.07 °	3.14 to 28.67 °
Limiting indices	-11<=h<=11, -20<=k<=19, -8<=l<=8	-22<=h<=19, -9<=k<=9, -21<=l<=25
Reflections collected / unique	11575/2111 [R(int) = 0.0371]	11591/2870 [R(int) = 0.0620]
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.911 and 0.798	0.678 and 0.567
Completeness to theta = 25.00	99.8 %	99.6%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2111/0/166	2870/0/176
Goodness-of-fit on F^2	0.94	0.90
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0886	R1 = 0.0492, wR2 = 0.0983
R indices (all data)	R1 = 0.0517, wR2 = 0.0941	R1 = 0.1082, wR2 = 0.1089
Largest diff. peak and hole	0.339 and -0.266 $e.A^{-3}$	0.320 and -0.246 e. $Å^{-3}$