Electronic Supplementary Information (ESI)

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Synthesis and crystal structure of dimeric 1-hydroxyhexane-2,3-dione and spectral characteristics of a model acireductone

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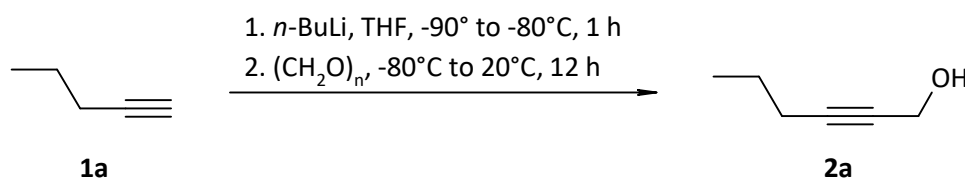[d] *European Synchrotron Radiation Facility, Avenue des Martyrs 71, Grenoble, France.*

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1. Detailed synthetic procedures for obtaining the compounds 2a and 4a

1.1 Hex-2-yn-1-ol (2a)[Ref. S1] $C_6H_{10}O$, M = 98.14

1. n-BuLi, THF, -90° to -80°C, 1 h
2. $(CH_2O)_n$, -80°C to 20°C, 12 h

1a   **2a**

Although hex-2-yn-1-ol **2a** is commercially available, we decided to obtain it from cheaper pent-1-yne. A modification of the method by *Peng, Yu, and Zhang*[Ref. S1] allowed us to get **2a** in a scale of up to about thirty grams. To a solution of **1a** (25 g, 36.2 cm³, 0.367 mol) in anhydrous [Note S1] THF (200 cm³) [Note S2] n-BuLi (2.5 M solution in hexanes) [Note S3] (161 cm³, 0.404 mol, 1.1 equiv.) was added dropwise [Note S4] with a syringe by a septum at between –90°C to –80°C [Note S5] under Ar, with intense mixing on a magnetic stirrer. Upon the addition of n-BuLi the mixture become more and more thick because white alkyne lithium salt started to precipitate. The reaction mixture was stirred at the same temperature for 15 min before the addition of $(CH_2O)_n$ (1.2 equiv.) [Note S6]. The resulting mixture was allowed to warm to room temperature gradually [Note S7] and stirred for around 12 h [Note S8] before quenched with NH_4Cl saturated aqueous solution. The mixture was extracted twice with Et_2O. The combined organic phases were dried over anhydrous $MgSO_4$ for 15 min and filtered. The filtrate was concentrated on a rotary evaporator [Note S9], and the light yellow residue was distilled under reduced pressure [Note S10] to give clean [Note S11] **2a** as colourless liquid.

[Ref. S1]	Y. Peng, M. Yu and L. Zhang, *Org. Lett.*, 2008, **10**, 5187.
[Note S1]	Boiling commercially available THF over CaH_2 in Ar atmosphere for 4 h and distilling it prior to the use was sufficient.
[Note S2]	Increasing the concentration of pent-1-yne **1a** to 1.55 M reduced the amount of anhydrous THF needed for the reaction. We do not exclude the possibility that the concentration of the alkyne could be even greater.
[Note S3]	We found that n-BuLi in concentration as high as 2.5 M can be used with no harm to the reaction, which reduced the amount of the solution. Although handling n-BuLi solutions can be dangerous, small amounts of 2.5 M n-BuLi solution in hexanes practically never auto-ignite in air – more concentrated solutions may require more care.
[Note S4]	A volume of 161 cm³ is a quite large amount – adding with a syringe takes a time of about an hour.
[Note S5]	A Dewar bath filled with acetone frozen by mixing it with an excess of liquid nitrogen was used. Such mixture let reach and maintain temperature as low as even –100°C by continuous adding the nitrogen. It is advisable not to rise the temperature of the reaction above –75°C by adjusting the rate of adding the n-BuLi solution. Higher temperatures lower the yield of **2a**.
[Note S6]	Reagent grade paraformaldehyde was used as received.
[Note S7]	We strongly advise to leave the mixture in the Dewar bath and let it warm slowly. Removing the bath results in a rapid rise of temperature – the mixture can even start to boil. It did not seem, however, to have a great impact on the yield of **2a**.
[Note S8]	*Peng, Yu, and Zhang* left the mixture for 2 h only. Overnight mixing at ambient temperature allows, in our opinion, the reaction to complete. From the other hand, further extending this time makes the mixture yellow and then brownish and lowers the yield of **2a**.
[Note S9]	The compound **2a** has a pungent odor. Using a vapor trap is advisable.
[Note S10]	The distillation proceeds smoothly, giving **2a** in a narrow range of temperature. No heads were collected and the residue was very small.
[Note S11]	Purity of **2a** is very close to 100%, which can be easily determined by gas chromatography.

1.2 1-(Tetrahydro-2*H*-pyran-2-yloxy)hexane-2,3-dione (4a) [Ref. S2] $C_{11}H_{18}O_4$, M = 214.26

3a → **4a**

Reagents: NaIO$_4$, RuO$_2$·xH$_2$O (cat.), CCl$_4$, MeCN/H$_2$O, rt., 15 min
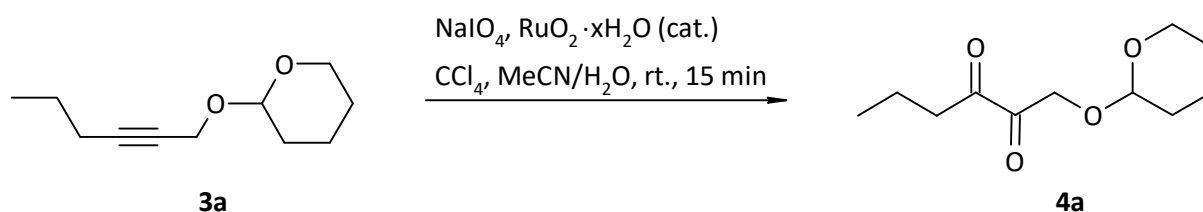
Oxidation of 2-(hex-2-yn-1-yloxy)tetrahydro-2*H*-pyran **3a** to 1-(tetrahydro-2*H*-pyran-2-yloxy)hexane-2,3-dione **4a** was performed by a slightly modified method by *Zibuck and Seebach*.[Ref. S2] It was found that the scale of the reaction can be enlarged by a factor of 10, to 30 mmol of the substrate, without a negative impact on the yield of the product. Thus, 2-(hex-1-yn-1-yloxy)tetrahydro-2*H*-pyran **3** (5.47 g, 30 mmol) was dissolved in a mixture of carbon tetrachloride (140 cm^3) and acetonitrile (140 cm^3). Separately a solution of NaIO$_4$ (19.25 g, 90 mmol) [Notes S12, S13] in water (210 cm^3) was prepared. The solutions were intensely mixed together in a 1000 cm^3 round-bottom flask with a big magnetic stirrer for 5 min. [Note S14] To the resulting emulsion a catalytic amount of RuO$_2$·xH$_2$O [Note S15] (0.118 g, 0.5 mmol) [Note S16] was added. CAUTION: The work-up of the reaction mixture should be performed as fast as possible and purification of the product should be carried out immediately. The mixture turned black immediately and then, within 1–2 minutes, the colour of it changed to grass-green and the temperature of the mixture rose to about 40°C. (If instead of NaIO$_4$ one uses KIO$_4$ the mixture can remain black and the rise of temperature is hardly observed). The mixture became gradually yellow-green and more and more white precipitate of NaIO$_3$ formed, and, after 15 min, the reaction was stopped by adding water (100 cm^3) [Note S17] and immediate separating the lower organic layer – which turns black – from the upper, which remains only slightly coloured. The aqueous layer was extracted with DCM (3 × 50 cm^3) – the extracts can be slightly coloured by small amounts of I$_2$ that can form during the reaction. If this happens, the iodine should be carefully separated during the column chromatography (CC). During the extraction the aqueous layer sometimes become black – the extracts were only slightly coloured. The combined dark coloured organic layers were quickly (10 min) dried over anhydrous MgSO$_4$ [Note S18], filtered through blotting paper (do not filter through Celite! [Note S19]) – the filtrate is clear and yellow-brown (sometimes green or even black) coloured – and concentrated on a rotary evaporator. CAUTION: Rising the temperature of the water bath over 60°C resulted in a considerable loss of the product by its thermal decomposition [Note S20], especially if it is contaminated by iodine. The remaining yellow-brown (sometimes dark green or black) oil was immediately chromatographed on silica gel (60 Å, 230–400 mesh ATSM) for CC. Mixture of CHCl$_3$ and MeOH (30:1 *v/v*) was used as eluent. 50 g of silica gel was used and the working length of the column was 45 cm. The process was conducted under small over-pressure, but not so fast as flash chromatography. All dark ruthenium compounds remained on the start and the canary-yellow coloured

4a went in the first fraction [Note S21]. Prolonged evaporation of the solution after the chromatography led to darkening and partial decomposition of the product.

[Ref. S2]   R. Zibuck and D. Seebach, *Helv. Chim. Acta*, 1988, **71**, 237.
[Note S12] The authors used 4.2 eqs of $NaIO_4$ but it was found that it was enough to use only 3 eqs (maybe even less would do).
[Note S13] KIO_4 can be used instead of $NaIO_4$. Even though KIO_4 is less soluble in water from $NaIO_4$, KIO_3 is *more* soluble than $NaIO_3$, so the overall amount of water (used to dissolve the periodate and added after the reaction) remained more or less the same.
[Note S14] On stopping the stirring two almost clear layers form within several minutes.
[Note S15] $RuO_2 \cdot xH_2O$ was provided by Sigma-Aldrich. They stated that the minimal concentration of Ru in the product was 44% so the value of x is equal to about 5.5.
[Note S16] Calculated for the formula $RuO_2 \cdot 5.5H_2O$.
[Note S17] Zibuck and Seebach used much more water; for the 30 mmol scale it would be 750 cm^3. However, 100 cm^3 of water was enough to dissolve all the precipitate of $NaIO_3$.
[Note S18] It was found that a prolonged contact with solid $MgSO_4$ (or a contact with the remains of $RuO_2 \cdot xH_2O$) caused gradual decomposition of the product.
[Note S19] Filtering the crude product solution through Celite in order to remove both insoluble and soluble ruthenium compounds resulted in a complete loss of the product!
[Note S20] Moreover the decomposition products were extremely difficult to be separated from **4a** during the CC.
[Note S21] In case of the contamination with I_2 it is advisable to collect only the main part of the first canary-yellow colored fraction containing **4a**. The tail of the fraction (dirty-yellow or dirty-greenish) contains iodine and other contaminants. It is sometimes difficult to distinguish between the fractions – control the process using thin layer chromatography.

FT-IR ATR spectrum of **4a**.

13C NMR spectrum of 4a in CDCl3 (99.8% D)   (T = 300 K; Bruker Avance III 600, 150 MHz)

199.82
195.63
98.96
77.21
77.00
76.79
68.40
62.33
38.18
30.10
25.19
19.05
16.31
13.59

4a

225   200   175   150   125   100   75   50   25   0
ppm (t1)
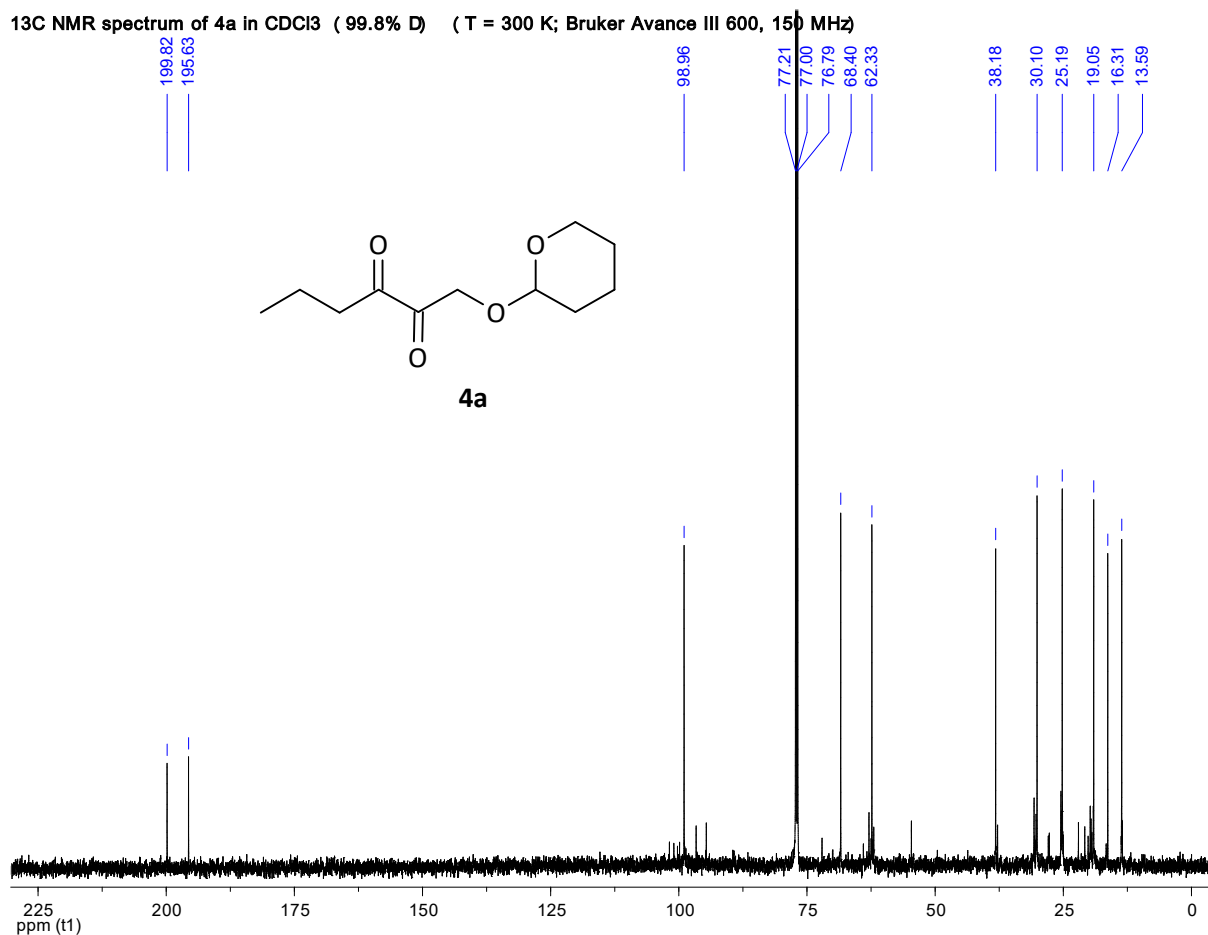
^{13}C NMR spectrum of **4a** in CDCl₃.
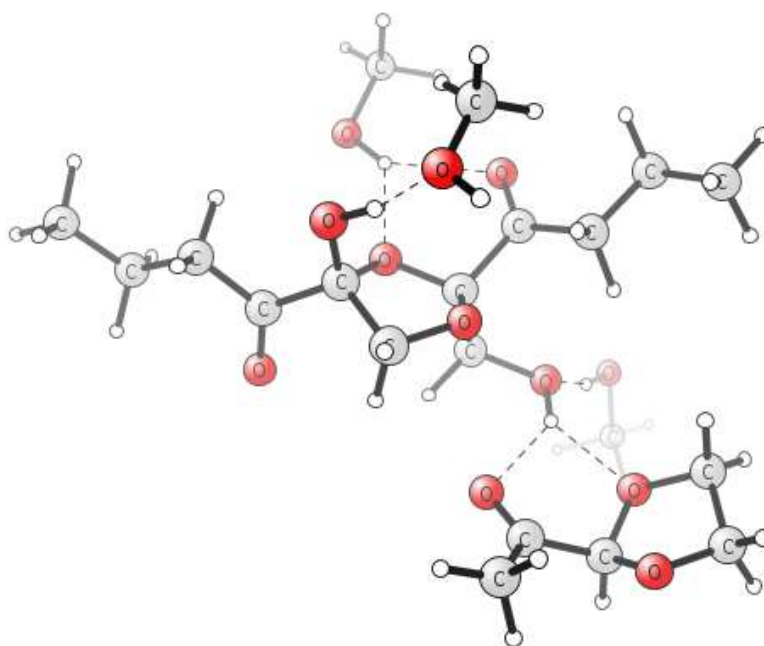
Fig. S1   The model accounting for hydrogen bonding contacts in the crystal of **6a** used to calculate the corrections to NMR isotropic shielding due to these interactions. Hydrogen bonds are marked with dashed lines.
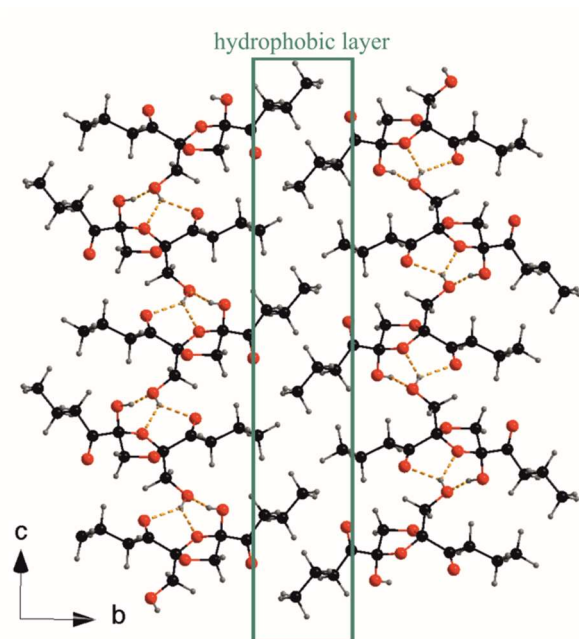
Fig. S2   Packing of molecules illustrating the presence of hydrophobic layers in the crystal structure of **6a**.
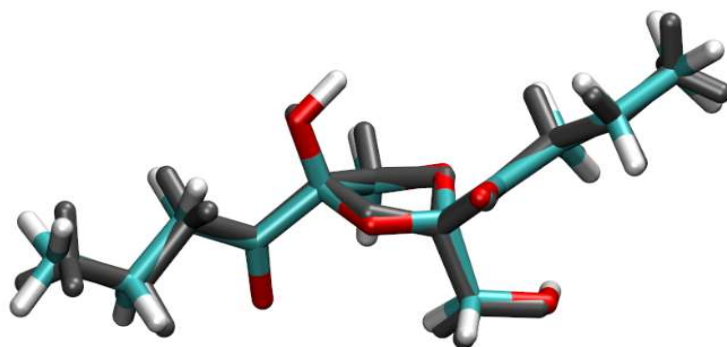
Fig. S3   Superimposed structures of the dimer **6a** molecules from the X-ray model (in gray) and from the solid state DFT optimization.
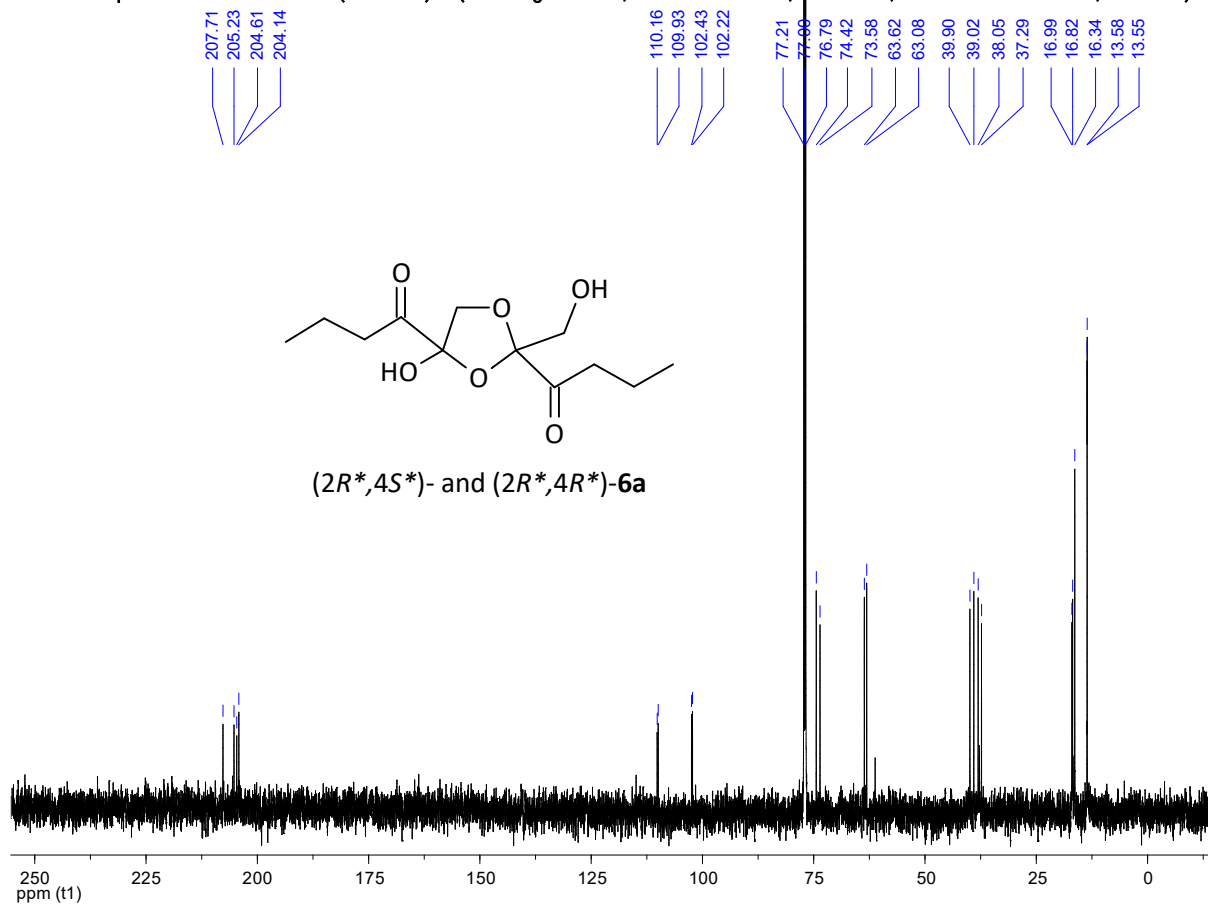
Fig S4 ^{13}C NMR spectrum of the dimer **6a** in CDCl3.

Fig. S5a ^{1}H NMR spectrum of the dimer **6a** measured 15 min after dissolving in D$_2$O. The sample contains mostly **5a hydrate**, but residual signals from **6a** between 4.40–3.80 ppm are visible. A singlet at 3.75 ppm comes from the C*H$_2$*OH group in the molecules of the major form of **5a hydrate**; the two minor form (probably **free, non-hydrated 5a** in various molecular geometries) are responsible for the singlets at 4.76 and 4.67 ppm. The alkyl signals from **5a hydrate** and **free 5a** are partially resolved; the residual signals from **6a** alkyl groups make the signals ragged. On the basis of the calculations, two low-energy forms of **free 5a**, differing in a position of a hydrogen bond, could be proposed, which give singlets from their C*H$_2$*OH groups. Their formulae are shown in the spectrum.

Fig. S5b   ^{1}H NMR spectrum of the dimer **6a** measured 30 min after dissolving in D_2O. The sample contains mostly **5a hydrate**, but residual signals from **6a** between 4.40–3.80 ppm are visible. A singlet at 3.75 ppm comes from the CH_2OH group in the molecules of the major form of **5a hydrate**; the two minor form (probably **free, non-hydrated 5a** in various molecular geometries) are responsible for the singlets at 4.76 and 4.67 ppm. The alkyl signals from **5a hydrate** and **free 5a** are partially resolved; the residual signals from **6a** alkyl groups make the signals ragged. On the basis of the calculations, two low-energy forms of **free 5a**, differing in a position of a hydrogen bond, could be proposed, which give singlets from their CH_2OH groups. Their formulae are shown in the spectrum.
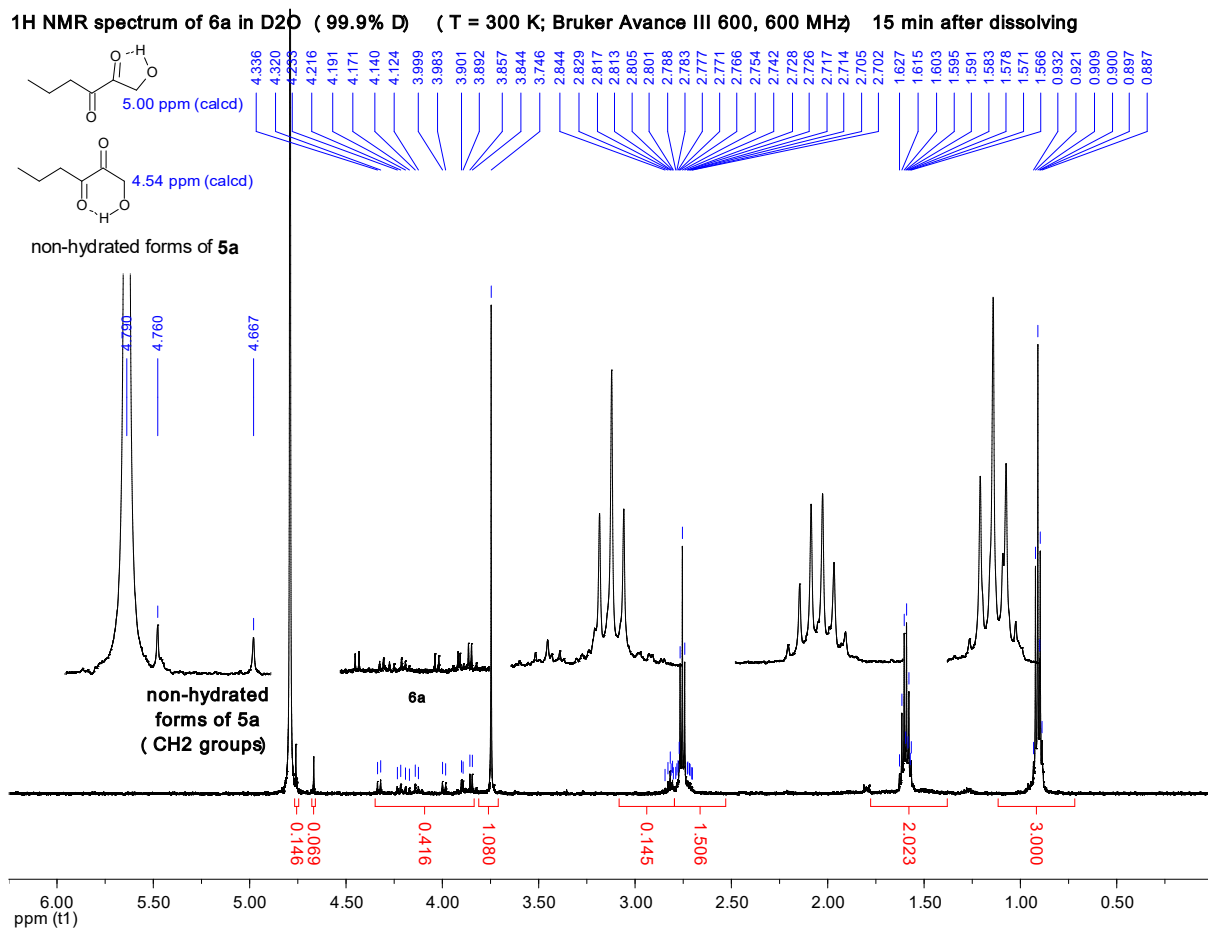
Fig. S5c ^{1}H NMR spectrum of the dimer **6a** measured 60 min after dissolving in D$_2$O. The sample contains mostly **5a hydrate**; residual signals from **6a** between 4.40–3.80 ppm can practically be neglected. A singlet at 3.75 ppm comes from the C*H*$_2$OH group in the molecules of the major form of **5a hydrate**; the two minor form (probably **free, non-hydrated 5a** in various molecular geometries) are responsible for the singlets at 4.76 and 4.67 ppm. Alkyl signals from **5a hydrate** and **free 5a** are partially resolved and smooth. On the basis of the calculations, two low-energy forms of **free 5a**, differing in a position of a hydrogen bond, could be proposed, which give singlets from their C*H*$_2$OH groups. Their formulae are shown in the spectrum.
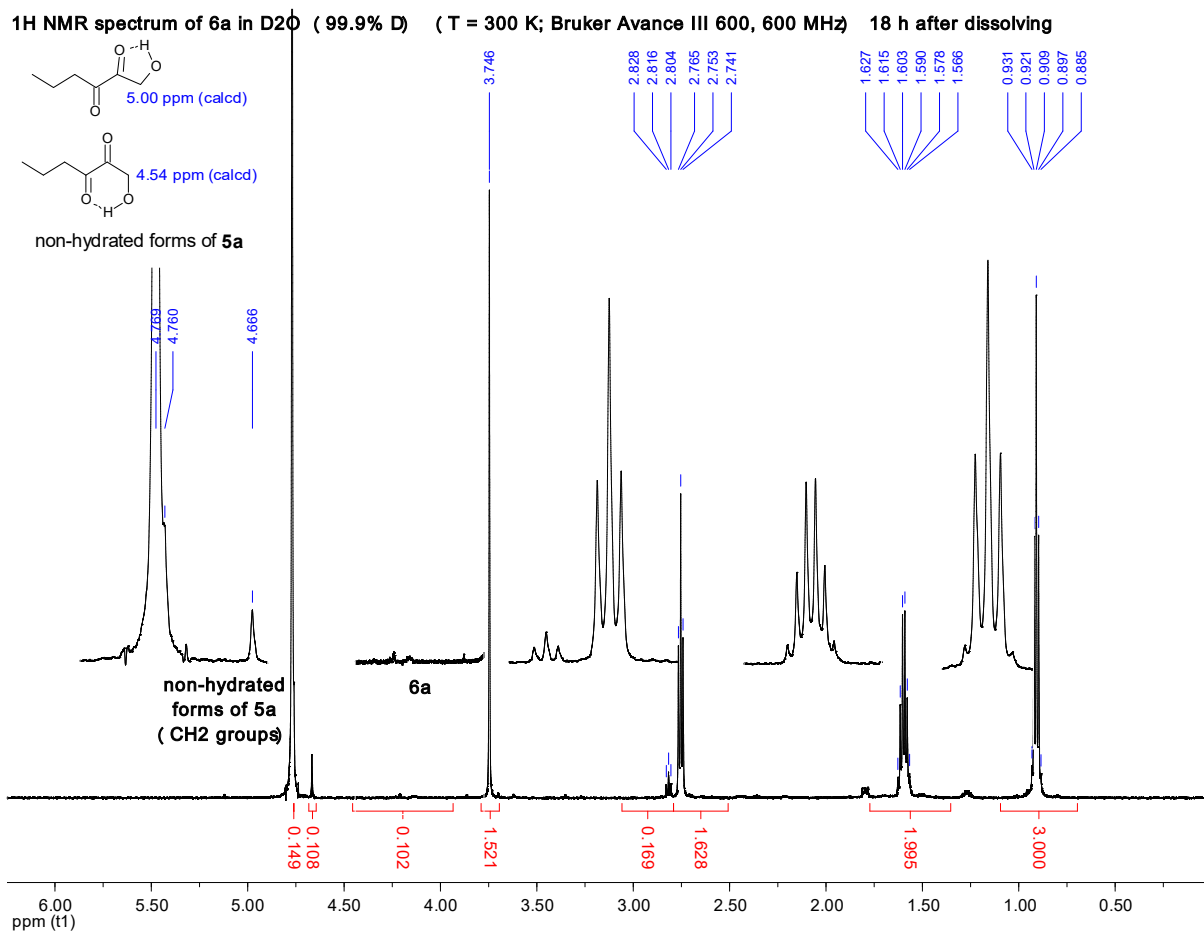
Fig. S5d ^{1}H NMR spectrum of the dimer **6a** measured 18 h after dissolving in D$_2$O (the signal of which was locked at 4.77 ppm instead of the proper value of 4.79 ppm). The sample contains mostly **5a hydrate**; residual signals from **6a** between 4.40–3.80 ppm are practically invisible. A singlet at 3.75 ppm comes from the C*H*$_2$OH group in the molecules of the major form of **5a hydrate**; the two minor form (probably **free, non-hydrated 5a** in various molecular geometries) are responsible for the singlets at 4.76 and 4.67 ppm. Alkyl signals from **5a hydrate** and **free 5a** are partially resolved and smooth. On the basis of the calculations, two low-energy forms of **free 5a**, differing in a position of a hydrogen bond, could be proposed, which give singlets from their C*H*$_2$OH groups. Their formulae are shown in the spectrum.
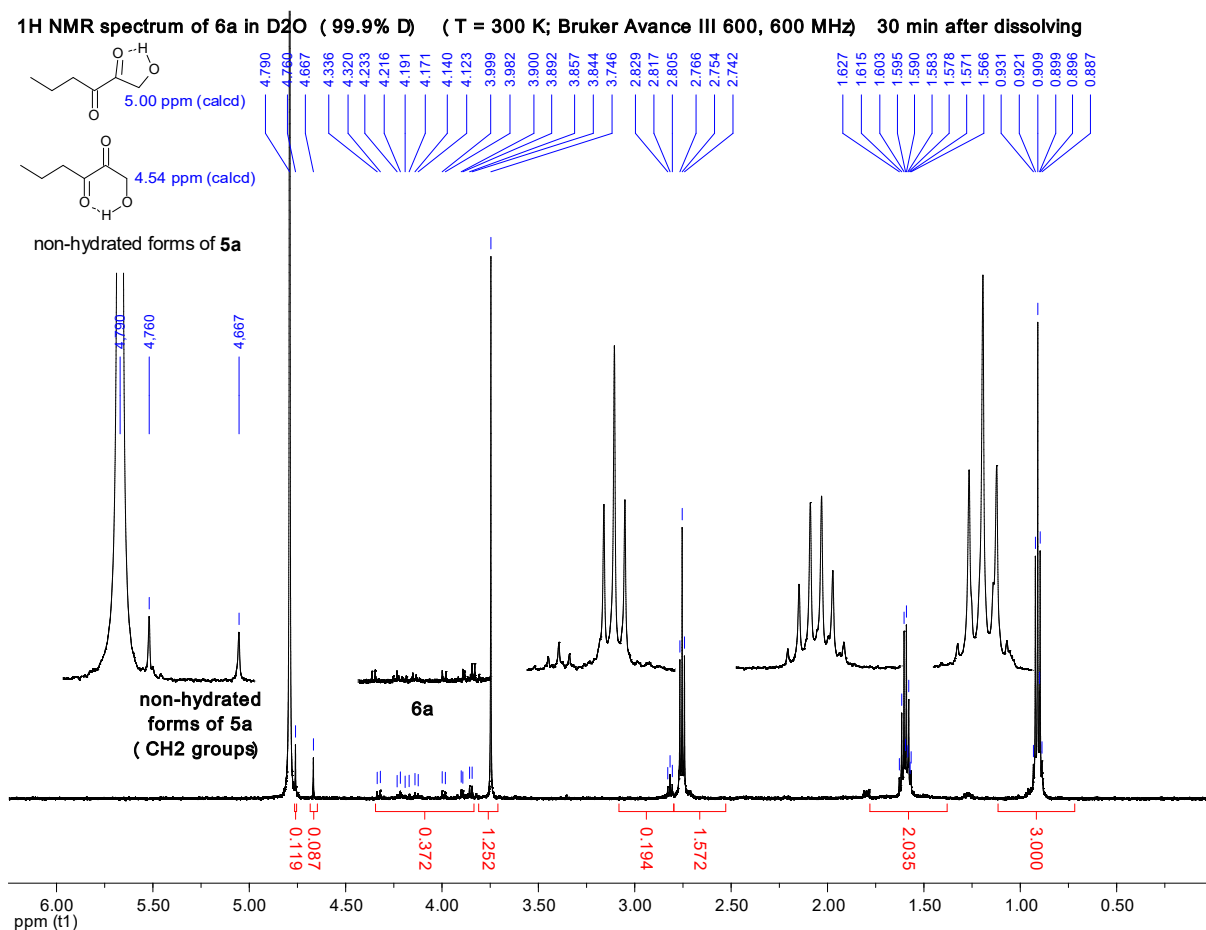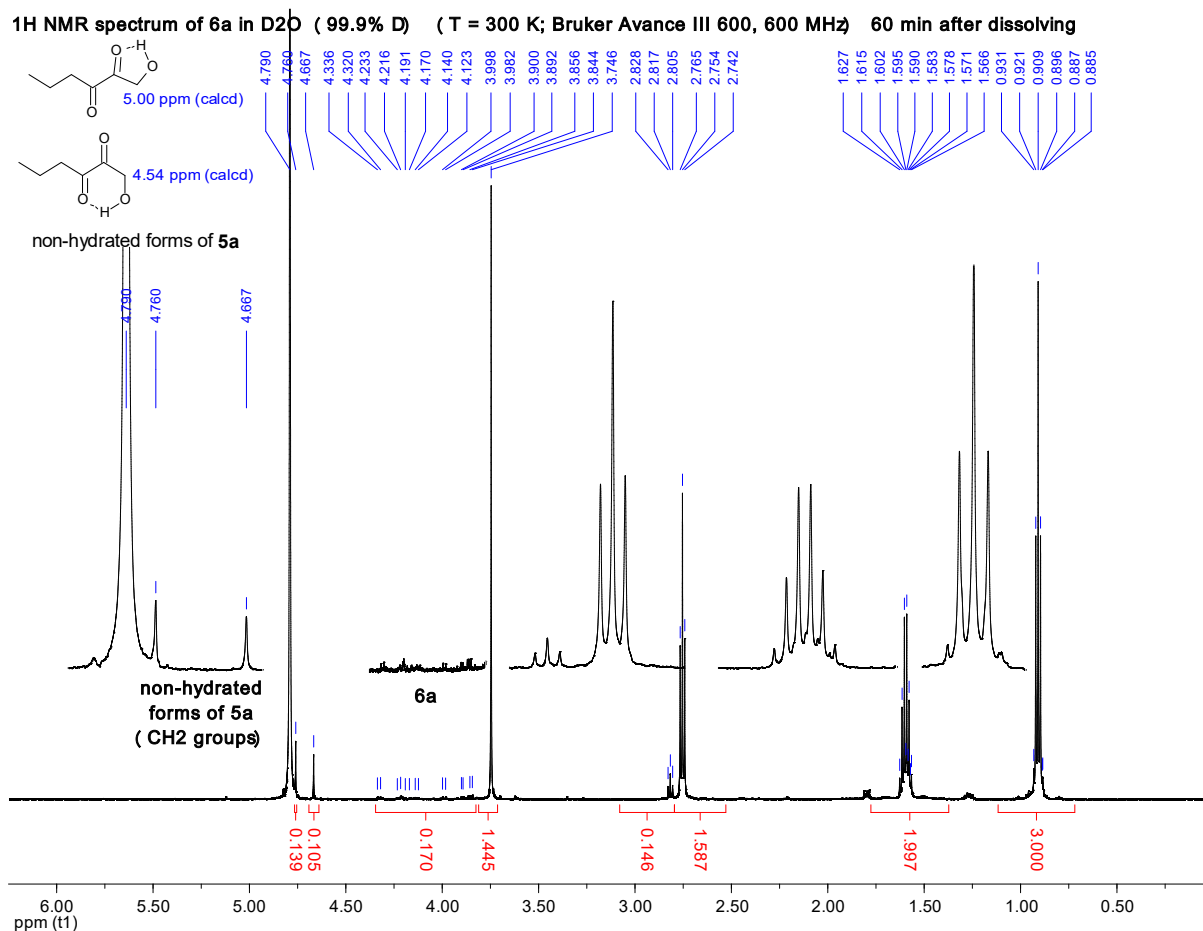
13C NMR spectrum of 6a in D2O (99.9% D)   (10,4 mg/0,8 cm3; T = 300 K; Bruker Avance III 600, 150 MHz)

213.14

17.27
17.02
16.65

14.28

13.79
13.72

96.85

65.71
65.18
65.06

41.12

39.39
38.88

17.27
17.02
16.65
14.28
13.79
13.72

41.12

39.39
38.88

65.71

65.18
65.06

ppm (t1)   200   150   100   50   0

Fig. S6 ^{13}C NMR spectrum of the dimer **6a** (*i.e.* **5a hydrate**) in D$_2$O. All the alkyl regions contain small signals coming from **non-hydrated** *minor* forms of **5a**.

13C NMR spectrum of 5a in CDCl3 (99.8% D)   (300 K; Bruker Avance III 600, 600 MHz)

209.46 207.13 205.59 204.72 204.19 198.33 197.23

110.24 109.93 102.57 102.28 98.41 98.15 97.78 97.34 77.21 77.00 76.79 74.32 73.51 65.18 65.00 63.56 62.86 61.22 54.91 50.68 50.03 49.72 39.88 38.96 38.84 38.27 38.15 37.93 37.75 37.38 16.91 16.72 16.67 16.38 16.30 16.25 13.60 13.57 13.51

Fig. S7 ^{13}C NMR spectrum of **5a** in CDCl$_3$. Signals from **5a hydrate**, from the **free** forms of **5a**, and from both diastereomers of **6a** are visible in the spectrum.

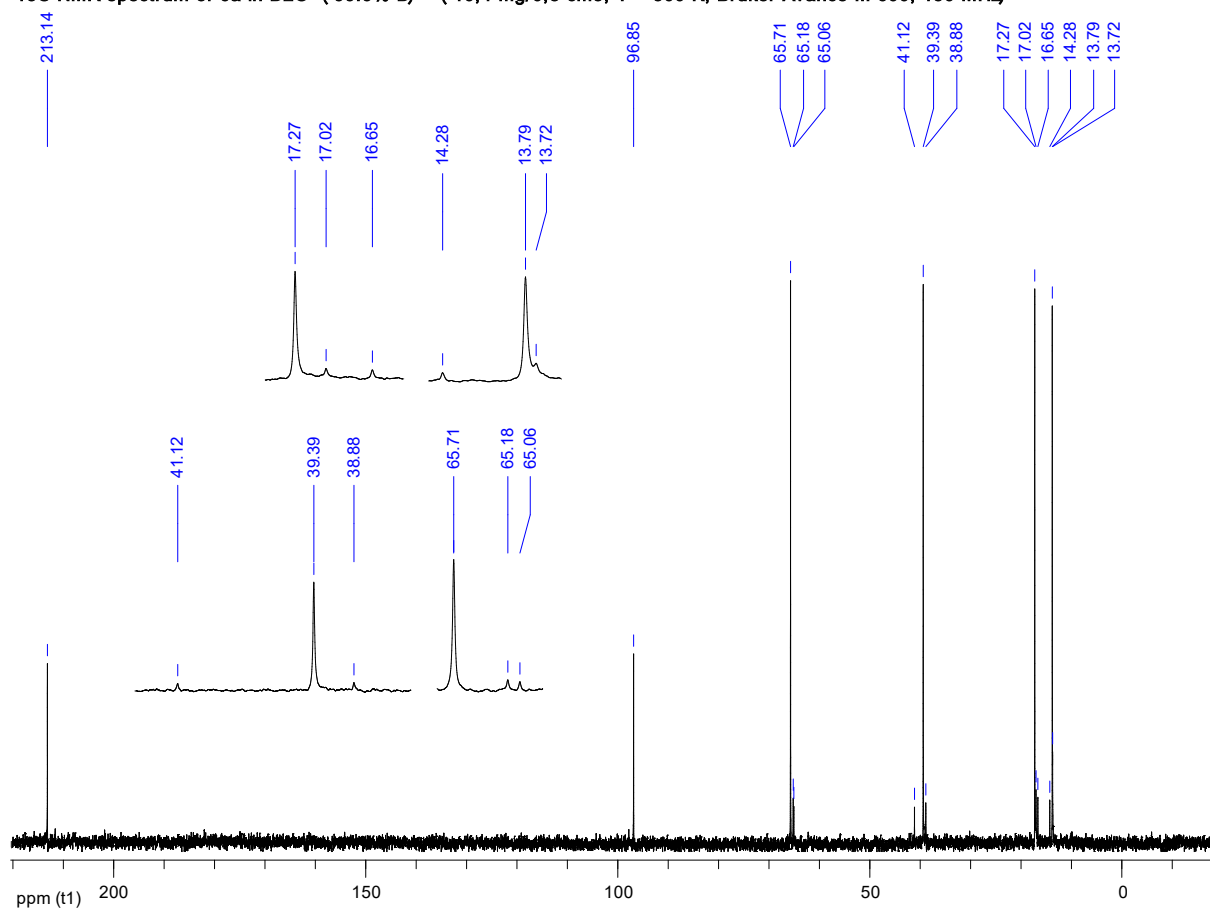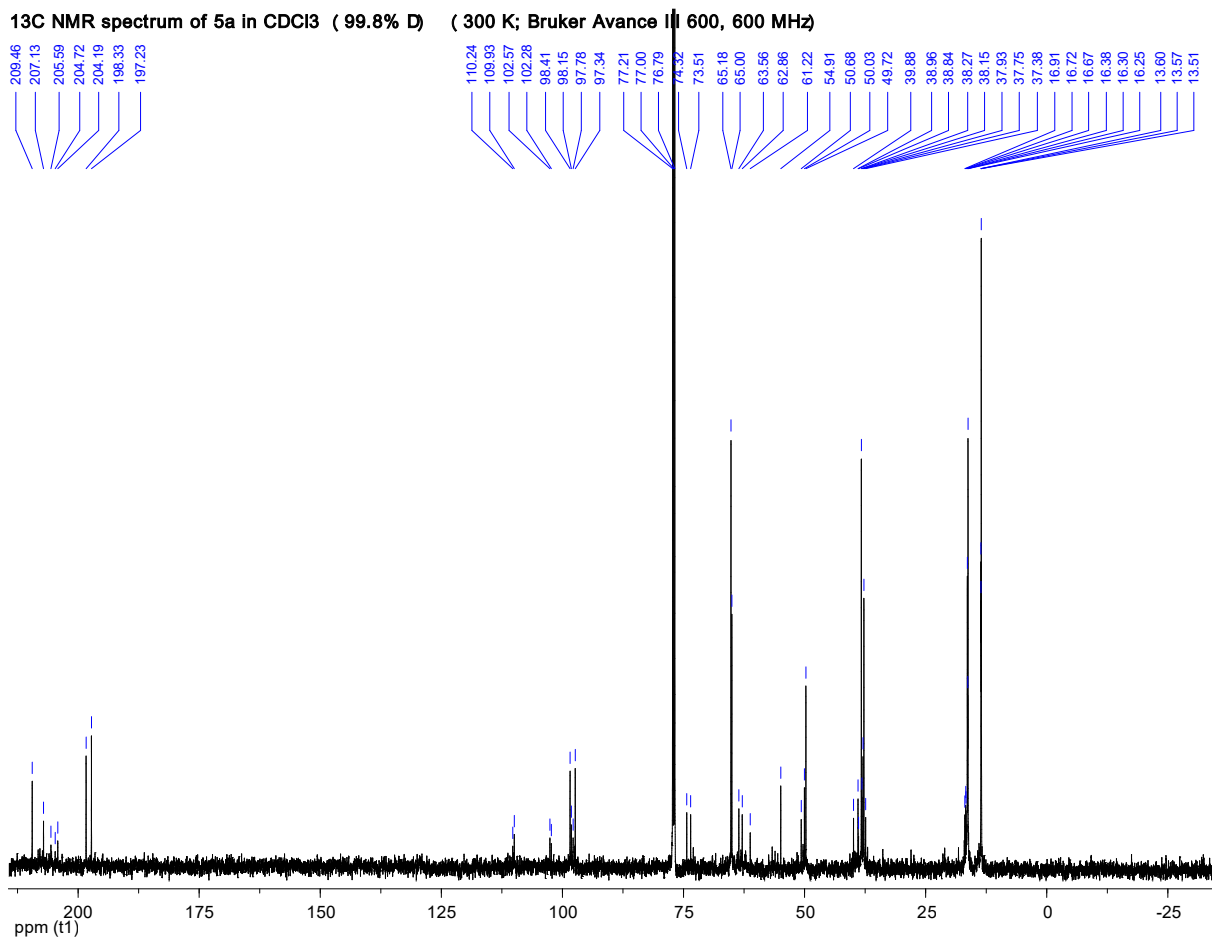Table S1   Harmonic frequencies, infrared intensities, Raman scattering activities and intensities, and Potential Energy Distributions (PEDs) of normal modes for **6a** calculated at the B3LYP/cc-pVTZ level. Frequencies are scaled by the factor of 0.965, PEDs of vibrations (in %) are given in brackets (only PEDs > 5% are included)

No.	Freq. /cm^{-1}	Freq_ Scal /cm^{-1}	IR intensity /km·mol^{-1}	Raman activity /Å^{4}a.u.$^{-1}$	Raman intensity /a.u.	PED (*contributions > 5%*)
1	20.7	20.0	0.46	0.44	170.66	$\tau C_{10}C_{11}[34]$, $\tau C_{10}C_9[12]$, $\tau C_2C_3[7]$, $\delta C_{11}C_{10}O_5[5]$, $\omega_{out}C_{10}C_{11}[5]$
2	27.3	26.4	1.79	0.65	190.25	$\tau C_{10}C_{11}[29]$, $\tau C_3C_4[17]$, $\tau C_{10}C_9[14]$, $\tau C_5C_4[9]$, $\tau C_{11}O_5[8]$, $\delta C_{11}C_{10}O_5[6]$, $\omega_{out}C_{10}C_{11}[5]$
3	42.6	41.1	0.60	0.27	50.11	$\tau C_5C_4[26]$, $\tau C_{11}O_5[24]$, $\tau C_2C_3[16]$
4	56.0	54.0	0.53	0.44	61.48	$\tau C_{10}C_9[20]$, $\tau C_3C_4[20]$, $\tau C_{10}C_{11}[12]$, $\omega_{out}C_{10}C_{11}[8]$, $\tau C_5C_4[5]$
5	72.3	69.8	0.78	0.10	10.31	$\tau C_3C_4[20]$, $\tau C_2C_3[19]$, $\tau_{2/R5}[18]$, $\tau C_5C_4[5]$
6	83.4	80.5	2.19	0.16	14.71	$\rho C_4C_3[17]$, $\delta_2C_3H_6H_7[13]$, $\tau C_{11}O_5[8]$, $\tau C_6C_5[8]$, $\tau_{1/R5}[7]$
7	98.4	95.0	1.95	0.17	13.20	$\tau C_6C_5[59]$, $\delta_2C_6H_8H_9[10]$, $\tau C_6O_1[9]$
8	106.7	103.0	0.61	0.21	14.99	$\tau_{1/R5}[14]$, $\delta C_5C_6C_4[10]$, $\tau C_{10}C_9[9]$, $\delta_2C_3H_6H_7[9]$
9	121.9	117.6	1.54	0.38	23.94	$\tau C_{10}C_9[67]$, $\tau C_8C_9[12]$, $\tau C_{10}C_{11}[7]$
10	131.0	126.4	1.16	0.05	3.09	$\tau C_3C_4[64]$, $\rho C_3H_6H_7[14]$, $\tau C_5C_4[6]$
11	151.1	145.8	1.88	0.23	11.61	$\delta_2C_9H_{17}H_{16}[20]$, $\delta_2C_8H_{14}H_{15}[12]$, $\tau_{2/R5}[11]$, $\tau_{1/R5}[10]$, $\beta C_9C_{10}O_6[9]$, $\rho C_{10}C_{11}[6]$, $\tau C_{11}O_5[6]$

Table S1 (continued)

No.	Freq. /cm^{-1}	Freq_Scal /cm^{-1}	IR intensity /km·mol^{-1}	Raman activity /Å^{4}a.u.$^{-1}$	Raman intensity /a.u.	PED (contributions > 5%)
12	182.7	176.3	3.55	1.07	44.01	$\tau_{1/R5}$[18], $\rho C_{11}C_{10}O_5$[10], $\delta_2 C_9H_{17}H_{16}$[8], τC_8C_9[7], $\tau C_{11}C_{10}O_5$[7], $\tau C_5C_6C_4$[5], $\delta_2 C_2H_5H_4$[5], $\delta C_{11}C_{10}O_5$[5]
13	210.2	202.8	0.76	0.06	2.28	τC_8C_9[56], $\tau C_{10}C_9$[16], $\rho C_9H_{17}H_{16}$[8]
14	244.7	236.1	0.94	0.19	5.71	τC_1C_2[68], $\rho C_3H_6H_7$[9], τC_3C_4[8]
15	254.1	245.2	0.06	0.02	0.49	$\tau C_5C_6C_4$[24], $\delta C_5C_6C_4$[17], $\delta_2 C_6H_8H_9$[15], $\tau_{2/R5}$[6]
16	259.0	249.9	0.13	0.02	0.62	$\omega C_5C_6C_4$[27], $\delta C_5C_6C_4$[26], $\omega_{out}C_4C_3$[10], $\tau_{1/R5}$[6], τC_6O_1[5]
17	272.8	263.2	13.73	0.45	12.00	$\tau C_5C_6C_4$[19], $\delta_2 C_3H_6H_7$[14], $\delta C_5C_6C_4$[13], $\delta C_{11}C_{10}O_5$[7], $\beta C_5C_4O_3$[6], $\tau_{2/R5}$[6], $\delta_2 C_2H_5H_4$[5]
18	289.2	279.1	1.49	0.46	11.51	$\delta C_{11}C_{10}O_5$[19], $\tau C_{11}C_{10}O_5$[13], $\delta_2 C_8H_{14}H_{15}$[10], $\rho C_{11}C_{10}O_5$[8], $\delta_2 C_9H_{17}H_{16}$[8], $\rho C_{10}C_{11}$[7], $\rho C_5C_6C_4$[5]
19	301.6	291.1	2.77	1.83	43.32	$\delta_2 C_9H_{17}H_{16}$[19], $\tau C_{11}C_{10}O_5$[12], $\rho C_{10}C_{11}$[10], $\nu C_{10}C_9$[9], $\nu C_{10}C_{11}$[8], νC_8C_9[6]
20	320.1	308.9	11.38	4.47	98.78	$\tau_{1/R5}$[17], $\omega C_{11}C_{10}O_5$[9], νC_5C_4[8], $\rho C_5C_6C_4$[6], τC_6O_1[5], $\delta_2 C_3H_6H_7$[5], $\delta_2 C_6H_8H_9$[5]
21	363.4	350.7	3.68	1.55	29.62	τC_6O_1[38], $\delta_2 C_2H_5H_4$[9]
22	379.3	366.0	3.07	1.17	21.28	$\delta_2 C_8H_{14}H_{15}$[18], $\beta C_9C_{10}O_6$[16], $\rho C_{11}C_{10}O_5$[11], $\delta_2 C_2H_5H_4$[8]
23	385.8	372.3	2.29	0.58	10.27	τC_6O_1[34], $\delta_2 C_8H_{14}H_{15}$[16], $\rho C_5C_6C_4$[10], $\beta C_9C_{10}O_6$[6]
24	414.2	399.7	33.91	1.32	21.59	$\delta_2 C_2H_5H_4$[18], $\beta C_5C_4O_3$[17], $\delta_2 C_6H_8H_9$[12], ρC_4C_3[11], $\rho C_5C_6C_4$[9], $\tau_{1/R5}$[7]
25	425.4	410.5	110.34	1.96	31.20	ρC_4C_3[10], $\delta_2 C_2H_5H_4$[9], $\delta C_5C_6C_4$[7], $\rho C_{11}C_{10}O_5$[6], νC_6C_5[5], $\delta_2 C_6H_8H_9$[5]
26	451.8	436.0	6.34	0.95	14.12	$\tau C_{11}C_{10}O_5$[19], $\tau_{1/R5}$[11], $\rho C_{10}C_{11}$[11], $\nu C_{10}C_{11}$[9], $\rho C_5C_6C_4$[9], $\tau C_5C_6C_4$[7], $\tau C_{11}O_5$[5]
27	470.9	454.4	1.26	2.89	40.74	$\omega C_{11}C_{10}O_5$[14], $\delta C_{11}C_{10}O_5$[13], $\rho C_{11}C_{10}O_5$[11], $\nu C_{12}C_{11}$[10], $\beta_{1/R5}$[6]
28	558.2	538.6	1.01	0.46	5.30	$\rho C_3H_6H_7$[30], $\omega_{out}C_4C_3$[20], $\rho C_9H_{17}H_{16}$[7], $\tau C_5C_6C_4$[6], $\omega_{out}C_{10}C_{11}$[6]
29	588.1	567.5	5.42	2.05	21.95	$\rho C_9H_{17}H_{16}$[23], $\omega_{out}C_{10}C_{11}$[14], $\tau C_{11}O_5$[13], $\rho C_3H_6H_7$[7], $\rho C_{11}C_{10}O_5$[6]
30	608.5	587.2	28.36	1.27	13.01	$\tau C_{11}O_5$[51], $\rho C_{11}C_{10}O_5$[11], $\rho C_{10}C_{11}$[6], $\nu C_{10}C_{11}$[6]
31	643.0	620.5	35.59	2.99	28.63	$\tau C_{11}O_5$[16], $\rho C_5C_6C_4$[12], $\tau_{1/R5}$[9], $\rho C_{11}C_{10}O_5$[9], $\omega C_{11}C_{10}O_5$[8], $\nu C_{11}O_5$[7], $\beta_{1/R5}$[7]
32	655.9	633.0	60.38	1.38	12.84	$\rho C_5C_6C_4$[21], $\delta_2 C_6H_8H_9$[16], $\beta C_5C_4O_3$[10], $\tau_{1/R5}$[8], νC_5C_4[7], νC_6C_5[5]
33	721.9	696.7	22.83	1.32	10.83	$\beta_{1/R5}$[21], $\rho C_8H_{14}H_{15}$[8], $\beta C_9C_{10}O_6$[8], $\beta_{2/R5}$[8], $\rho C_2H_5H_4$[6]
34	732.6	707.0	12.08	1.96	15.86	$\beta_{2/R5}$[28], $\rho C_8H_{14}H_{15}$[8], $\beta C_9C_{10}O_6$[7], ρC_4C_3[6], $\delta_2 C_6H_8H_9$[5]
35	761.0	734.4	8.20	0.22	1.68	$\rho C_2H_5H_4$[47], $\rho_1 C_1H_1H_2H_3$[11], $\omega_{out}C_4C_3$[8], $\tau C_3H_6H_7$[6]
36	763.4	736.7	4.89	0.19	1.43	$\rho C_8H_{14}H_{15}$[41], $\rho_1 C_7H_{11}H_{12}H_{13}$[12], $\omega_{out}C_{10}C_{11}$[6], $\tau C_9H_{17}H_{16}$[5]
37	800.2	772.2	2.47	9.14	65.56	νC_3C_4[12], $\beta_{2/R5}$[12], νC_5O_4[10], $\nu C_{12}C_{11}$[9], νO_2C_{11}[9], νC_5C_4[8], ρC_4C_3[8], $\delta_2 C_3H_6H_7$[7]

No.	Freq. /cm^{-1}	Freq_ Scal /cm^{-1}	IR intensity /km·mol^{-1}	Raman activity /Å^{4}a.u.$^{-1}$	Raman intensity /a.u.	PED *(contributions > 5%)*
38	815.1	786.6	19.85	1.20	8.40	$\nu C_{10}C_9[14]$, $\nu O_2C_{11}[11]$, $\nu C_{10}C_{11}[9]$, $\beta_{1/R5}[7]$, $\beta C_9C_{10}O_6[7]$, $\nu C_3C_4[7]$, $\delta_2 C_9H_{17}H_{16}[6]$
39	870.6	840.1	18.34	7.36	47.03	$\rho C_3H_6H_7[18]$, $\rho_1 C_1H_1H_2H_3[17]$, $\tau C_2H_5H_4[15]$, $\rho_2 C_1H_1H_2H_3[8]$, $\omega_{out}C_4C_3[7]$, $\rho C_6H_8H_9[6]$
40	885.5	854.5	1.79	1.49	9.30	$\rho_1 C_7H_{11}H_{12}H_{13}[26]$, $\rho C_9H_{17}H_{16}[22]$, $\tau C_8H_{14}H_{15}[18]$, $\omega_{out}C_{10}C_{11}[7]$
41	889.4	858.3	4.84	0.27	1.65	$\nu C_5O_4[14]$, $\rho C_6H_8H_9[12]$, $\nu C_{10}C_9[7]$, $\nu O_2C_{11}[6]$, $\rho_1 C_1H_1H_2H_3[6]$, $\rho C_{12}H_{19}H_{18}[5]$, $\rho_2 C_7H_{11}H_{12}H_{13}[5]$
42	894.4	863.1	13.38	6.94	42.67	$\rho C_6H_8H_9[13]$, $\nu C_5O_4[11]$, $\rho_2 C_7H_{11}H_{12}H_{13}[8]$, $\nu C_2C_3[7]$, $\nu C_8C_9[6]$, $\rho_2 C_1H_1H_2H_3[5]$
43	912.5	880.6	36.33	2.44	14.61	$\rho_2 C_1H_1H_2H_3[19]$, $\nu C_2C_3[17]$, $\nu C_1C_2[9]$, $\rho_2 C_7H_{11}H_{12}H_{13}[8]$, $\rho_1 C_1H_1H_2H_3[7]$, $\nu C_8C_9[7]$
44	929.6	897.1	13.83	2.82	16.41	$\rho C_{12}H_{19}H_{18}[12]$, $\nu O_2C_{11}[10]$, $\rho_2 C_7H_{11}H_{12}H_{13}[9]$, $\nu C_8C_9[9]$, $\nu C_7C_8[8]$, $\tau C_{12}H_{19}H_{18}[5]$
45	985.7	951.2	98.67	2.58	13.79	$\nu O_2C_{11}[35]$, $\beta_{1/R5}[15]$, $\nu C_{11}O_5[10]$, $\omega C_{11}C_{10}O_5[9]$, $\nu C_{12}C_{11}[7]$
46	1027.4	991.4	22.22	3.02	15.21	$\rho C_{12}H_{19}H_{18}[21]$, $\nu C_{10}C_9[14]$, $\nu C_{12}O_4[8]$, $\nu C_5O_4[8]$, $\omega C_9H_{17}H_{16}[6]$, $\nu C_{12}C_{11}[6]$
47	1032.2	996.1	155.37	0.18	0.88	$\nu C_3C_4[28]$, $\nu C_5O_2[13]$, $\omega C_3H_6H_7[11]$, $\beta C_5C_4O_3[9]$, $\rho C_6H_8H_9[7]$
48	1049.9	1013.2	4.27	3.56	17.37	$\beta C_6O_1H_{10}[12]$, $\nu C_5O_4[9]$, $\rho C_6H_8H_9[9]$, $\nu C_{12}O_4[9]$, $\nu C_6O_1[8]$, $\omega C_5C_6C_4[6]$
49	1050.7	1013.9	5.05	6.17	30.08	$\nu C_7C_8[52]$, $\nu C_8C_9[13]$, $\nu C_1C_2[9]$
50	1052.1	1015.3	36.03	1.76	8.55	$\nu C_1C_2[50]$, $\nu C_2C_3[15]$, $\nu C_7C_8[5]$
51	1056.6	1019.6	35.09	3.38	16.36	$\nu C_{12}O_4[44]$, $\nu C_5O_4[13]$
52	1081.8	1043.9	182.09	2.25	10.48	$\nu C_6O_1[39]$, $\tau C_3H_6H_7[9]$, $\beta C_6O_1H_{10}[7]$, $\rho C_2H_5H_4[6]$, $\rho_1 C_1H_1H_2H_3[5]$
53	1114.6	1075.5	0.16	1.12	4.98	$\tau C_9H_{17}H_{16}[19]$, $\rho C_8H_{14}H_{15}[11]$, $\rho C_9H_{17}H_{16}[11]$, $\tau C_8H_{14}H15[7]$, $\nu C_6O_1[7]$, $\rho_1 C_7H_{11}H_{12}H_{13}[6]$, $\rho_2 C_7H_{11}H_{12}H_{13}[5]$
54	1117.3	1078.2	15.71	0.49	2.17	$\nu C_6O_1[22]$, $\tau C_3H_6H_7[7]$, $\rho_1 C_1H_1H_2H_3[6]$
55	1126.6	1087.2	23.72	3.15	13.85	$\nu C_2C_3[14]$, $\rho_2 C_1H_1H_2H_3[10]$, $\nu C_8C_9[7]$, $\rho C_5C_6C_4[5]$
56	1140.3	1100.4	44.76	0.72	3.12	$\nu C_8C_9[17]$, $\rho_2 C_7H_{11}H_{12}H_{13}[9]$, $\nu C_2C_3[8]$, $\rho_1 C_7H_{11}H_{12}H_{13}[7]$, $\nu C_5O_2[6]$, $\rho_2 C_1H_1H_2H_3[6]$
57	1165.6	1124.8	20.76	6.90	28.75	$\tau C_6H_8H_9[11]$, $\nu C_5C_4[8]$, $\nu C_6O_1[6]$, $\nu C_2C_3[5]$, $\nu C_{10}C_{11}[5]$
58	1178.8	1137.6	73.28	1.96	8.04	$\nu C_{11}O_5[18]$, $\beta C_{11}O_5H_{20}[10]$, $\rho C_{12}H_{19}H_{18}[9]$, $\rho C_{11}C_{10}O_5[7]$, $\nu C_5O_2[6]$, $\nu C_{10}C_{11}[6]$
59	1198.7	1156.8	17.52	0.82	3.29	$\nu C_{12}C_{11}[13]$, $\tau C_{12}H_{19}H_{18}[11]$, $\nu C_5O_2[11]$, $\nu C_{11}O_5[9]$, $\omega C_{11}C_{10}O_5[7]$, $\nu C_6C_5[6]$
60	1243.5	1199.9	25.81	2.83	10.65	$\tau C_{12}H_{19}H_{18}[43]$, $\nu C_{11}O_5[11]$, $\beta C_{11}O_5H_{20}[7]$
61	1251.1	1207.3	44.68	4.92	18.36	$\tau C_3H_6H_7[26]$, $\rho_1 C_1H_1H_2H_3[10]$, $\tau C_9H_{17}H_{16}[10]$, $\rho C_2H_5H_4[10]$, $\tau C_2H_5H_4[7]$
62	1255.8	1211.9	0.42	0.42	1.56	$\tau C_9H_{17}H_{16}[29]$, $\rho_1 C_7H_{11}H_{12}H_{13}[10]$, $\rho C_8H_{14}H_{15}[10]$, $\tau C_8H_{14}H_{15}[8]$, $\tau C_{12}H_{19}H_{18}[7]$, $\tau C_3H_6H_7[6]$, $\nu C_{11}O_5[5]$
63	1258.0	1214.0	26.86	3.30	12.18	$\tau C_6H_8H_9[20]$, $\rho C_5C_6C_4[18]$, $\nu C_6C_5[15]$, $\beta C_6O_1H_{10}[12]$, $\nu C_5C_4[9]$, $\rho C_6H_8H_9[6]$

No.	Freq. /cm^{-1}	Freq_ Scal /cm^{-1}	IR intensity /km·mol^{-1}	Raman activity /Å^{4}a.u.$^{-1}$	Raman intensity /a.u.	PED (*contributions > 5%*)
64	1268.0	1223.6	12.93	1.02	3.72	$\beta_{2/R5}$[15], νC_6C_5[10], νC_5O_4[10], $\delta C_5C_6C_4$[7], $\nu C_{11}O_5$[6], $\omega C_6H_8H_9$[6]
65	1327.6	1281.1	11.74	4.27	14.48	$\tau C_8H_{14}H_{15}$[56], $\tau C_9H_{17}H_{16}$[17], $\omega C_8H_{14}H_{15}$[7], $\omega C_9H_{17}H_{16}$[6]
66	1331.9	1285.3	2.16	6.49	21.88	$\tau C_2H_5H_4$[65], $\tau C_3H_6H_7$[24]
67	1335.8	1289.0	17.93	4.70	15.78	$\omega C_8H_{14}H_{15}$[39], $\omega C_9H_{17}H_{16}$[21], $\tau C_8H_{14}H_{15}$[8], $\nu C_{10}C_9$[7]
68	1338.2	1291.4	4.16	0.94	3.15	$\omega C_2H_5H_4$[44], $\omega C_3H_6H_7$[19], νC_3C_4[8]
69	1375.5	1327.4	3.93	2.03	6.48	$\omega C_{12}H_{19}H_{18}$[69], $\nu C_{12}C_{11}$[9], $\omega C_6H_8H_9$[7]
70	1388.3	1339.7	40.69	1.59	5.01	$\tau C_6H_8H_9$[30], $\beta C_6O_1H_{10}$[27], $\omega C_6H_8H_9$[16]
71	1405.2	1356.0	48.76	1.45	4.48	$\omega C_9H_{17}H_{16}$[31], $\omega C_8H_{14}H_{15}$[29], νC_8C_9[11], $\nu C_{10}C_9$[8], $\beta C_{11}O_5H_{20}$[5]
72	1411.2	1361.8	10.43	1.39	4.26	$\omega C_3H_6H_7$[30], $\omega C_2H_5H_4$[19], νC_3C_4[10], $\delta_I C_3H_6H_7$[9], νC_2C_3[8], $\omega C_6H_8H_9$[6]
73	1419.6	1369.9	1.86	0.42	1.28	$\beta_s C_7H_{11}H_{12}H_{13}$ [85], νC_7C_8[10]
74	1422.8	1373.0	5.22	0.29	0.86	$\omega C_6H_8H_9$[32], $\omega C_3H_6H_7$[8], $\beta_s C_1H_1H_2H_3$[8], $\beta C_6O_1H_{10}$[8], $\delta_I C_3H_6H_7$[7], $\omega C_2H_5H_4$[7], νC_6C_5[5]
75	1425.8	1375.9	19.42	1.97	5.94	$\beta_s C_1H_1H_2H_3$[80], $\omega C_6H_8H_9$[7], νC_1C_2[7]
76	1432.5	1382.4	28.89	5.27	15.74	$\delta_I C_3H_6H_7$[73], $\omega C_6H_8H_9$[11]
77	1450.3	1399.6	14.58	4.66	13.63	$\beta C_{11}O_5H_{20}$[46], $\nu C_{10}C_{11}$[15], $\rho C_{11}C_{10}O_5$[6]
78	1452.9	1402.0	78.87	3.90	11.36	$\delta_I C_9H_{17}H_{16}$[85]
79	1495.0	1442.6	2.28	11.63	32.29	$\delta_I C_2H_5H_4$[71], $\beta_{a1}C_1H_1H_2H_3$[24]
80	1495.2	1442.9	1.79	12.03	33.40	$\delta_I C_8H_{14}H_{15}$[69], $\beta_{a2}C_7H_{11}H_{12}H_{13}$ [20], $\beta_{a1}C_7H_{11}H_{12}H_{13}$[7]
81	1501.6	1449.0	5.14	4.83	13.31	$\delta_I C_6H_8H_9$[93]
82	1503.4	1450.8	6.49	8.52	23.43	$\beta_{a1}C_7H_{11}H_{12}H_{13}$[68], $\beta_{a2}C_7H_{11}H_{12}H_{13}$[23], $\rho_1 C_7H_{11}H_{12}H_{13}$[6]
83	1504.9	1452.2	6.79	9.10	24.99	$\beta_{a2}C_1H_1H_2H_3$[57], $\delta C_{12}H_{19}H_{18}$[36]
84	1510.1	1457.3	6.64	0.84	2.30	$\delta C_{12}H_{19}H_{18}$[60], $\beta_{a2}C_1H_1H_2H_3$[33]
85	1510.3	1457.4	6.17	0.79	2.16	$\beta_{a1}C_1H_1H_2H_3$[62], $\delta_I C_2H_5H_4$[27], $\rho_2 C_1H_1H_2H_3$[5]
86	1511.8	1458.9	8.63	7.52	20.47	$\beta_{a2}C_7H_{11}H_{12}H_{13}$[45], $\delta_I C_8H_{14}H_{15}$[29], $\beta_{a1}C_7H_{11}H_{12}H_{13}$[15]
87	1756.9	1695.4	114.32	6.40	13.29	νC_4O_3[84]
88	1797.8	1734.9	123.07	6.15	12.22	νO_6C_{10}[86]
89	3019.0	2913.3	32.28	138.80	84.27	νC_7H_{13}[38], νC_7H_{12}[37], νC_7H_{11}[23]
90	3021.3	2915.5	30.89	146.04	88.48	νC_1H_3[38], νH_1C_1[37], νC_1H_2[22]
91	3023.0	2917.2	27.79	104.01	62.91	νC_6H_8[85], νC_6H_9[14]
92	3027.3	2921.4	2.49	172.16	103.72	$\nu H_{17}C_9$[48], νC_9H_{16}[42], νC_8H_{15}[5]
93	3029.1	2923.1	7.01	171.58	103.20	νH_6C_3[69], νC_3H_7[21]
94	3038.5	2932.2	17.67	36.63	21.84	νC_8H_{15}[60], νC_8H_{14}[28], $\nu H_{17}C_9$[8]
95	3041.5	2935.1	15.25	43.34	25.77	νC_2H_5[49], νC_2H_4[42], νH_6C_3[6]
96	3046.4	2939.8	1.36	92.92	55.00	$\nu C_{12}H_{19}$[89], $\nu C_{12}H_{18}$[11]
97	3048.9	2942.2	1.57	83.14	49.10	νC_9H_{16}[45], $\nu H_{17}C_9$[33], νC_8H_{14}[16]
98	3051.1	2944.3	28.55	94.42	55.65	νC_3H_7[64], νH_6C_3[16], νC_2H_4[12], νC_2H_5[6]

No.	Freq. /cm^{-1}	Freq_ Scal /cm^{-1}	IR intensity /km·mol^{-1}	Raman activity /Å^{4}a.u.$^{-1}$	Raman intensity /a.u.	PED (*contributions > 5%*)
99	3062.9	2955.7	0.49	30.42	17.73	vC$_8$H$_{14}$[24], vC$_7$H$_{13}$[24], vC$_7$H$_{12}$[22], vC$_8$H$_{15}$[13], vC$_9$H$_{16}$[8], vH$_{17}$C$_9$[8]
100	3064.9	2957.6	0.29	29.87	17.38	vH$_1$C$_1$[22], vC$_1$H$_3$[22], vC$_2$H$_5$[21], vC$_2$H$_4$[19], vC$_3$H$_7$[10]
101	3086.2	2978.2	54.83	11.62	6.63	vC$_7$H$_{12}$[28], vC$_8$H$_{14}$[26], vC$_7$H$_{13}$[24], vC$_8$H$_{15}$[18]
102	3087.6	2979.6	42.80	114.14	65.03	vH$_1$C$_1$[24], vC$_1$H$_3$[23], vC$_2$H$_5$[19], vC$_2$H$_4$[18], vC$_6$H$_9$[12]
103	3088.0	2979.9	42.54	7.93	4.52	vC$_7$H$_{11}$[74], vC$_7$H$_{13}$[12], vC$_7$H$_{12}$[12]
104	3090.5	2982.3	29.38	51.36	29.19	vC$_6$H$_9$[73], vC$_6$H$_8$[12]
105	3091.2	2983.0	33.99	121.81	69.17	vC$_1$H$_2$[75], vC$_1$H$_3$[12], vH$_1$C$_1$[12]
106	3141.4	3031.4	1.38	64.15	34.78	vC$_{12}$H$_{18}$[89], vC$_{12}$H$_{19}$[11]
107	3613.4	3486.9	298.90	114.15	39.98	vO$_5$H$_{20}$[100]
108	3795.9	3663.0	38.70	41.03	12.12	vO$_1$H$_{10}$[100]

Table S2   Definitions of internal coordinates used in the normal analysis of **6a** in GAR2PED program

Vibration	Definition	
vC$_6$O$_1$	vC$_6$O$_1$	the stretching vibrations
vC$_6$H$_8$	vC$_6$H$_8$	the stretching vibrations
vC$_6$H$_9$	vC$_6$H$_9$	the stretching vibrations
vC$_6$C$_5$	vC$_6$C$_5$	the stretching vibrations
vO$_1$H$_{10}$	vO$_1$H$_{10}$	the stretching vibrations
vO$_6$C$_{10}$	vO$_6$C$_{10}$	the stretching vibrations
vC$_7$C$_8$	vC$_7$C$_8$	the stretching vibrations
vC$_7$H$_{13}$	vC$_7$H$_{13}$	the stretching vibrations
vC$_7$H$_{11}$	vC$_7$H$_{11}$	the stretching vibrations
vC$_7$H$_{12}$	vC$_7$H$_{12}$	the stretching vibrations
vC$_8$H$_{14}$	vC$_8$H$_{14}$	the stretching vibrations
vC$_8$H$_{15}$	vC$_8$H$_{15}$	the stretching vibrations
vC$_8$C$_9$	vC$_8$C$_9$	the stretching vibrations
vC$_{10}$C$_9$	vC$_{10}$C$_9$	the stretching vibrations
vC$_{10}$C$_{11}$	vC$_{10}$C$_{11}$	the stretching vibrations
vH$_{17}$C$_9$	vH$_{17}$C$_9$	the stretching vibrations
vC$_5$O$_4$	vC$_5$O$_4$	the stretching vibrations
vC$_5$C$_4$	vC$_5$C$_4$	the stretching vibrations
vC$_5$O$_2$	vC$_5$O$_2$	the stretching vibrations
vC$_{12}$O$_4$	vC$_{12}$O$_4$	the stretching vibrations
vC$_{12}$H$_{19}$	vC$_{12}$H$_{19}$	the stretching vibrations
vC$_{12}$H$_{18}$	vC$_{12}$H$_{18}$	the stretching vibrations
vC$_{12}$C$_{11}$	vC$_{12}$C$_{11}$	the stretching vibrations
vH$_1$C$_1$	vH$_1$C$_1$	the stretching vibrations
vH$_6$C$_3$	vH$_6$C$_3$	the stretching vibrations
vC$_1$C$_2$	vC$_1$C$_2$	the stretching vibrations

Vibration	Definition	
νC_1H_3	νC_1H_3	the stretching vibrations
νC_1H_2	νC_1H_2	the stretching vibrations
νC_2C_3	νC_2C_3	the stretching vibrations
νC_2H_5	νC_2H_5	the stretching vibrations
νC_2H_4	νC_2H_4	the stretching vibrations
νC_3C_4	νC_3C_4	the stretching vibrations
νC_3H_7	νC_3H_7	the stretching vibrations
νC_4O_3	νC_4O_3	the stretching vibrations
νO_2C_{11}	νO_2C_{11}	the stretching vibrations
νC_9H_{16}	νC_9H_{16}	the stretching vibrations
$\nu C_{11}O_5$	$\nu C_{11}O_5$	the stretching vibrations
νO_5H_{20}	νO_5H_{20}	the stretching vibrations
$\beta C_{11}O_4C_{12} -0.809\beta C_{12}C_5O_4 -0.809\beta O_2C_{12}C_{11} +0.309\beta O_4O_2C_5 +0.309\beta C_5C_{11}O_2$	$\beta_{1/R5}$	the five–membered ring deformations
$-1.118\beta C_{12}C_5O_4 +1.118\beta O_2C_{12}C_{11} +1.809\beta O_4O_2C_5 -1.809\beta C_5C_{11}O_2$	$\beta_{2/R5}$	
$0.309\tau C_{11}C_{12}O_4C_5 +0.309\tau O_2C_{11}C_{12}O_4 -0.809\tau C_{12}O_4C_5O_2 -0.809\tau C_5O_2C_{11}C_{12} +\tau O_4C_5O_2C_{11}$	$\tau_{1/R5}$	
$-1.118\tau C_5O_2C_{11}C_{12} +1.118\tau C_{12}O_4C_5O_2 +1.809\tau O_2C_{11}C_{12}O_4 -1.809\tau C_{11}C_{12}O_4C_5$	$\tau_{2/R5}$	
$\beta C_6H_{10}O_1$	$\beta C_6O_1H_{10}$	the O–H bending
$\beta C_{11}H_{20}O_5$	$\beta C_{11}O_5H_{20}$	
$\beta H_{19}H_{18}C_{12}$	$\delta C_{12}H_{19}H_{18}$	the CH_2 in the ring deformations
$\beta O_4H_{19}C_{12} -\beta O_4H_{18}C_{12} +\beta C_{11}H_{19}C_{12} -\beta C_{11}H_{18}C_{12}$	$\rho C_{12}H_{19}H_{18}$	
$\beta O_4H_{19}C_{12} +\beta O_4H_{18}C_{12} -\beta C_{11}H_{19}C_{12} -\beta C_{11}H_{18}C_{12}$	$\omega C_{12}H_{19}H_{18}$	
$\beta O_4H_{19}C_{12} -\beta O_4H_{18}C_{12} -\beta C_{11}H_{19}C_{12} +\beta C_{11}H_{18}C_{12}$	$\tau C_{12}H_{19}H_{18}$	
$\beta C_6C_4C_5$	$\delta C_5C_6C_4$	the CH_2 in the ring deformations
$\beta O_4C_6C_5 -\beta O_4C_4C_5 +\beta O_2C_6C_5 -\beta O_2C_4C_5$	$\rho C_5C_6C_4$	
$\beta O_4C_6C_5 +\beta O_4C_4C_5 -\beta O_2C_6C_5 -\beta O_2C_4C_5$	$\omega C_5C_6C_4$	
$\beta O_4C_6C_5 -\beta O_4C_4C_5 -\beta O_2C_6C_5 +\beta O_2C_4C_5$	$\tau C_5C_6C_4$	
$\beta C_{10}O_5C_{11}$	$\delta C_{11}C_{10}O_5$	the CH_2 in the ring deformations
$\beta C_{12}C_{10}C_{11} -\beta C_{12}O_5C_{11} +\beta O_2C_{10}C_{11} -\beta O_2O_5C_{11}$	$\rho C_{11}C_{10}O_5$	
$\beta C_{12}C_{10}C_{11} +\beta C_{12}O_5C_{11} -\beta O_2C_{10}C_{11} -\beta O_2O_5C_{11}$	$\omega C_{11}C_{10}O_5$	
$\beta C_{12}C_{10}C_{11} -\beta C_{12}O_5C_{11} -\beta O_2C_{10}C_{11} +\beta O_2O_5C_{11}$	$\tau C_{11}C_{10}O_5$	
$2\beta O_3C_5C_4 -\beta O_3C_3C_4 -\beta C_5C_3C_4$	$\beta C_5C_4O_3$	the C=O group deformations
$\beta O_3C_3C_4 -\beta C_5C_3C_4$	ρC_4C_3	
$\gamma C_3O_3C_5C_4$	$\omega_{out}C_4C_3$	
$2\beta O_6C_9C_{10} -\beta O_6C_{11}C_{10} -\beta C_9C_{11}C_{10}$	$\beta C_9C_{10}O_6$	the C=O group deformations
$\beta O_6C_{11}C_{10} -\beta C_9C_{11}C_{10}$	$\rho C_{10}C_{11}$	
$\gamma C_{11}O_6C_9C_{10}$	$\omega_{out}C_{10}C_{11}$	
$5\beta H_8H_9C_6 +\beta O_1C_5C_6$	$\delta_1C_6H_8H_9$	the aliphatic CH_2 deformations
$\beta H_8H_9C_6 +5\beta O_1C_5C_6$	$\delta_2C_6H_8H_9$	

Vibration	Definition	
$\beta O_1H_8C_6 - \beta O_1H_9C_6 + \beta C_5H_8C_6 - \beta C_5H_9C_6$	$\rho C_6H_8H_9$	
$\beta O_1H_8C_6 + \beta O_1H_9C_6 - \beta C_5H_8C_6 - \beta C_5H_9C_6$	$\omega C_6H_8H_9$	
$\beta O_1H_8C_6 - \beta O_1H_9C_6 - \beta C_5H_8C_6 + \beta C_5H_9C_6$	$\tau C_6H_8H_9$	
$5\beta H_6H_7C_3 + \beta C_4C_2C_3$	$\delta_1 C_3H_6H_7$	the aliphatic CH_2 deformations
$\beta H_6H_7C_3 + 5\beta C_4C_2C_3$	$\delta_2 C_3H_6H_7$	
$\beta C_4H_6C_3 - \beta C_4H_7C_3 + \beta C_2H_6C_3 - \beta C_2H_7C_3$	$\rho C_3H_6H_7$	
$\beta C_4H_6C_3 + \beta C_4H_7C_3 - \beta C_2H_6C_3 - \beta C_2H_7C_3$	$\omega C_3H_6H_7$	
$\beta C_4H_6C_3 - \beta C_4H_7C_3 - \beta C_2H_6C_3 + \beta C_2H_7C_3$	$\tau C_3H_6H_7$	
$5\beta H_5H_4C_2 + \beta C_3C_1C_2$	$\delta_1 C_2H_5H_4$	the aliphatic CH_2 deformations
$\beta H_5H_4C_2 + 5\beta C_3C_1C_2$	$\delta_2 C_2H_5H_4$	
$\beta C_3H_5C_2 - \beta C_3H_4C_2 + \beta C_1H_5C_2 - \beta C_1H_4C_2$	$\rho C_2H_5H_4$	
$\beta C_3H_5C_2 + \beta C_3H_4C_2 - \beta C_1H_5C_2 - \beta C_1H_4C_2$	$\omega C_2H_5H_4$	
$\beta C_3H_5C_2 - \beta C_3H_4C_2 - \beta C_1H_5C_2 + \beta C_1H_4C_2$	$\tau C_2H_5H_4$	
$5\beta H_{17}H_{16}C_9 + \beta C_8C_{10}C_9$	$\delta_1 C_9H_{17}H_{16}$	the aliphatic CH_2 deformations
$\beta H_{17}H_{16}C_9 + 5\beta C_8C_{10}C_9$	$\delta_2 C_9H_{17}H_{16}$	
$\beta C_8H_{17}C_9 - \beta C_8H_{16}C_9 + \beta C_{10}H_{17}C_9 - \beta C_{10}H_{16}C_9$	$\rho C_9H_{17}H_{16}$	
$\beta C_8H_{17}C_9 + \beta C_8H_{16}C_9 - \beta C_{10}H_{17}C_9 - \beta C_{10}H_{16}C_9$	$\omega C_9H_{17}H_{16}$	
$\beta C_8H_{17}C_9 - \beta C_8H_{16}C_9 - \beta C_{10}H_{17}C_9 + \beta C_{10}H_{16}C_9$	$\tau C_9H_{17}H_{16}$	
$5\beta H_{14}H_{15}C_8 + \beta C_7C_9C_8$	$\delta_1 C_8H_{14}H_{15}$	the aliphatic CH_2 deformations
$\beta H_{14}H_{15}C_8 + 5\beta C_7C_9C_8$	$\delta_2 C_8H_{14}H_{15}$	
$\beta C_7H_{14}C_8 - \beta C_7H_{15}C_8 + \beta C_9H_{14}C_8 - \beta C_9H_{15}C_8$	$\rho C_8H_{14}H_{15}$	
$\beta C_7H_{14}C_8 + \beta C_7H_{15}C_8 - \beta C_9H_{14}C_8 - \beta C_9H_{15}C_8$	$\omega C_8H_{14}H_{15}$	
$\beta C_7H_{14}C_8 - \beta C_7H_{15}C_8 - \beta C_9H_{14}C_8 + \beta C_9H_{15}C_8$	$\tau C_8H_{14}H_{15}$	
$\beta H_{13}H_{11}C_7 + \beta H_{13}H_{12}C_7 + \beta H_{11}H_{12}C_7 - \beta H_{13}C_8C_7 - \beta H_{11}C_8C_7 - \beta H_{12}C_8C_7$	$\beta_s C_7H_{11}H_{12}H_{13}$	the methyl group deformations $C_7H_{11}H_{12}H_{13}$
$2\beta H_{13}H_{11}C_7 - \beta H_{13}H_{12}C_7 - \beta H_{11}H_{12}C_7$	$\beta_{a1} C_7H_{11}H_{12}H_{13}$	
$\beta H_{13}H_{12}C_7 - \beta H_{11}H_{12}C_7$	$\beta_{a2} C_7H_{11}H_{12}H_{13}$	
$2\beta H_{13}C_8C_7 - \beta H_{11}C_8C_7 - \beta H_{12}C_8C_7$	$\rho_1 C_7H_{11}H_{12}H_{13}$	
$\beta H_{11}C_8C_7 - \beta H_{12}C_8C_7$	$\rho_2 C_7H_{11}H_{12}H_{13}$	
$\beta H_1H_3C_1 + \beta H_1H_2C_1 + \beta H_3H_2C_1 - \beta H_1C_2C_1 - \beta H_3C_2C_1 - \beta H_2C_2C_1$	$\beta_s C_1H_1H_2H_3$	the methyl group deformations $C_1H_1H_2H_3$
$2\beta H_1H_3C_1 - \beta H_1H_2C_1 - \beta H_3H_2C_1$	$\beta_{a1} C_1H_1H_2H_3$	
$\beta H_1H_2C_1 - \beta H_3H_2C_1$	$\beta_{a2} C_1H_1H_2H_3$	
$2\beta H_1C_2C_1 - \beta H_3C_2C_1 - \beta H_2C_2C_1$	$\rho_1 C_1H_1H_2H_3$	
$\beta H_3C_2C_1 - \beta H_2C_2C_1$	$\rho_2 C_1H_1H_2H_3$	
$\tau C_{10}C_{11}O_5H_{20} + \tau C_{12}C_{11}O_5H_{20} + \tau O_2C_{11}O_5H_{20}$	$\tau C_{11}O_5$	torsions
$\tau O_1C_6C_5O_4 + \tau H_8C_6C_5O_4 + \tau H_9C_6C_5O_4 + \tau O_1C_6C_5C_4 + \tau H_8C_6C_5C_4 + \tau H_9C_6C_5C_4 + \tau O_1C_6C_5O_2 + \tau H_8C_6C_5O_2 + \tau H_9C_6C_5O_2$	τC_6C_5	torsions
$\tau H_8C_6O_1H_{10} + \tau H_9C_6O_1H_{10} + \tau C_5C_6O_1H_{10}$	τC_6O_1	torsions
$\tau C_6C_5C_4C_3 + \tau O_4C_5C_4C_3 + \tau O_2C_5C_4C_3 + \tau C_6C_5C_4O_3 + \tau O_4C_5C_4O_3 + \tau O_2C_5C_4O_3$	τC_5C_4	torsions
$\tau H_6C_3C_4C_5 + \tau C_2C_3C_4C_5 + \tau H_7C_3C_4C_5 + \tau H_6C_3C_4O_3 + \tau C_2C_3C_4O_3 + \tau H_7C_3C_4O_3$	τC_3C_4	torsions
$\tau C_1C_2C_3H_6 + \tau H_5C_2C_3H_6 + \tau H_4C_2C_3H_6 + \tau C_1C_2C_3C_4 + \tau H_5C_2C_3C_4 + \tau H_4C_2C_3C_4 + \tau C_1C_2C_3H_7 + \tau H_5C_2C_3H_7 + \tau H_4C_2C_3H_7$	τC_2C_3	torsions

Table S2 *(continued)*

Vibration	Definition	
$\tau H_1C_1C_2C_3$ $+\tau H_3C_1C_2C_3$ $+\tau H_2C_1C_2C_3$ $+\tau H_1C_1C_2H_5$ $+\tau H_3C_1C_2H_5$ $+\tau H_2C_1C_2H_5$ $+\tau H_1C_1C_2H_4$ $+\tau H_3C_1C_2H_4$ $+\tau H_2C_1C_2H_4$	τC_1C_2	torsions
$\tau O_6C_{10}C_{11}C_{12}$ $+\tau C_9C_{10}C_{11}C_{12}$ $+\tau O_6C_{10}C_{11}O_2$ $+\tau C_9C_{10}C_{11}O_2$ $+\tau O_6C_{10}C_{11}O_5$ $+\tau C_9C_{10}C_{11}O_5$	$\tau C_{10}C_{11}$	torsions
$\tau O_6C_{10}C_9C_8$ $+\tau C_{11}C_{10}C_9C_8$ $+\tau O_6C_{10}C_9H_{17}$ $+\tau C_{11}C_{10}C_9H_{17}$ $+\tau O_6C_{10}C_9H_{16}$ $+\tau C_{11}C_{10}C_9H_{16}$	$\tau C_{10}C_9$	torsions
$\tau C_7C_8C_9C_{10}$ $+\tau H_{14}C_8C_9C_{10}$ $+\tau H_{15}C_8C_9C_{10}$ $+\tau C_7C_8C_9H_{17}$ $+\tau H_{14}C_8C_9H_{17}$ $+\tau H_{15}C_8C_9H_{17}$ $+\tau C_7C_8C_9H_{16}$ $+\tau H_{14}C_8C_9H_{16}$ $+\tau H_{15}C_8C_9H_{16}$	τC_8C_9	torsions
$\tau H_{13}C_7C_8H_{14}$ $+\tau H_{11}C_7C_8H_{14}$ $+\tau H_{12}C_7C_8H_{14}$ $+\tau H_{13}C_7C_8H_{15}$ $+\tau H_{11}C_7C_8H_{15}$ $+\tau H_{12}C_7C_8H_{15}$ $+\tau H_{13}C_7C_8C_9$ $+\tau H_{11}C_7C_8C_9$ $+\tau H_{12}C_7C_8C_9$	τC_7C_8	torsions

Table S3   Titration of pre-heated aqueous solutions of **5a hydrate** with KOH (Fig. 7). Details of preparing the solutions

Sample	$\%_{KOH}$	$c_{KOH}/10^{-5}\ mol\cdot dm^{-3}$
II[a]	0	0
II[a] + x KOH	2.50	3.08
II[a] + 2x KOH	5.00	6.16
II[a] + 3x KOH	7.50	9.23
II[a] + 4x KOH	10.00	12.31
II[a] + 4.5x KOH	11.25	13.85

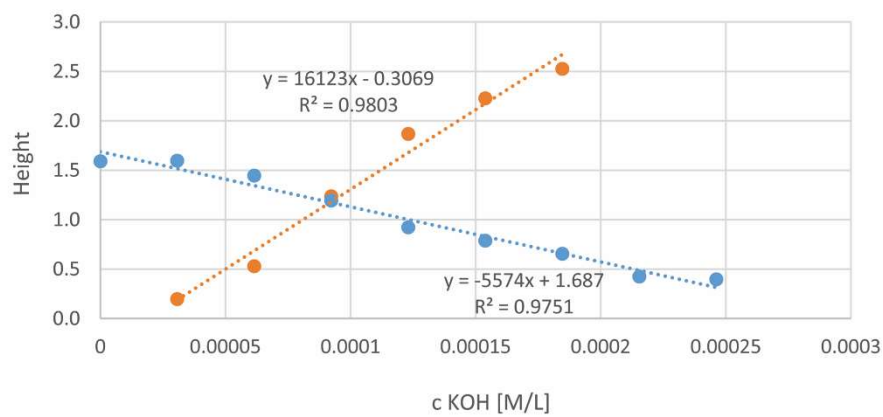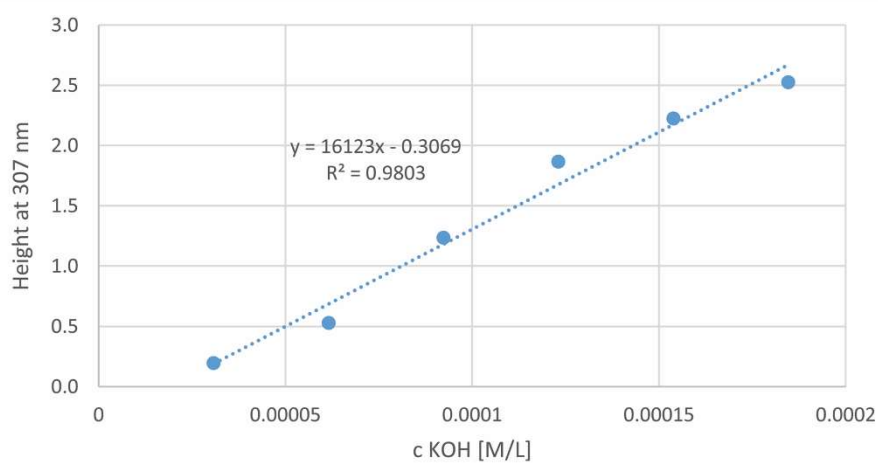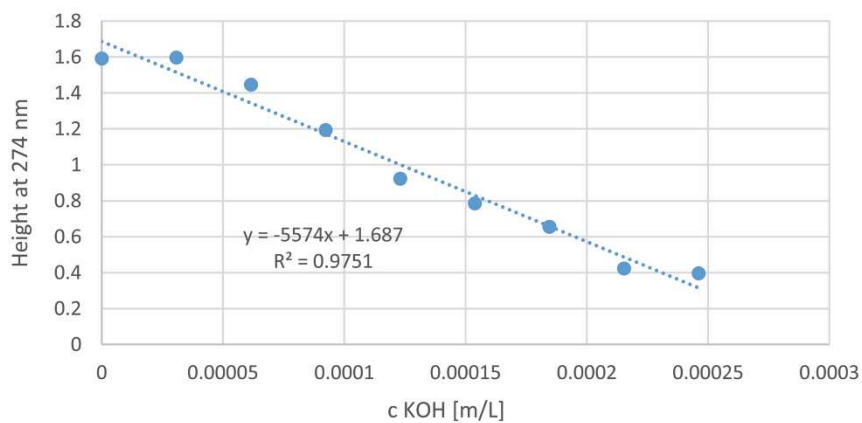[a] after heating up to 96°C for 30 min

Fig. S8a (I)   Regression curves for the acidic and the basic forms (**II** and **II**⁻) (Series I).
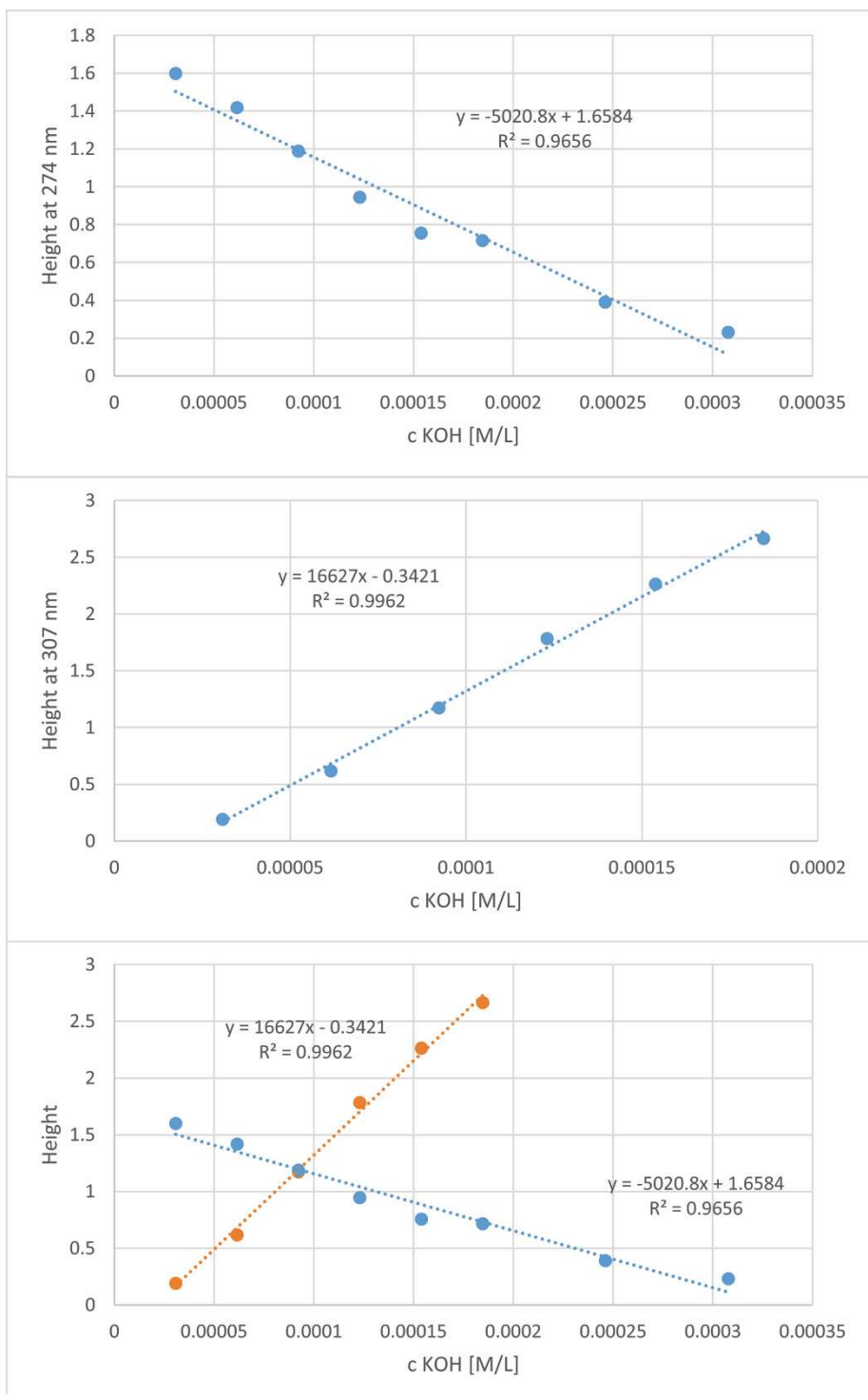
Fig. S8a (II)   Regression curves for the acidic and the basic forms (**II** and **II⁻**) (Series II).
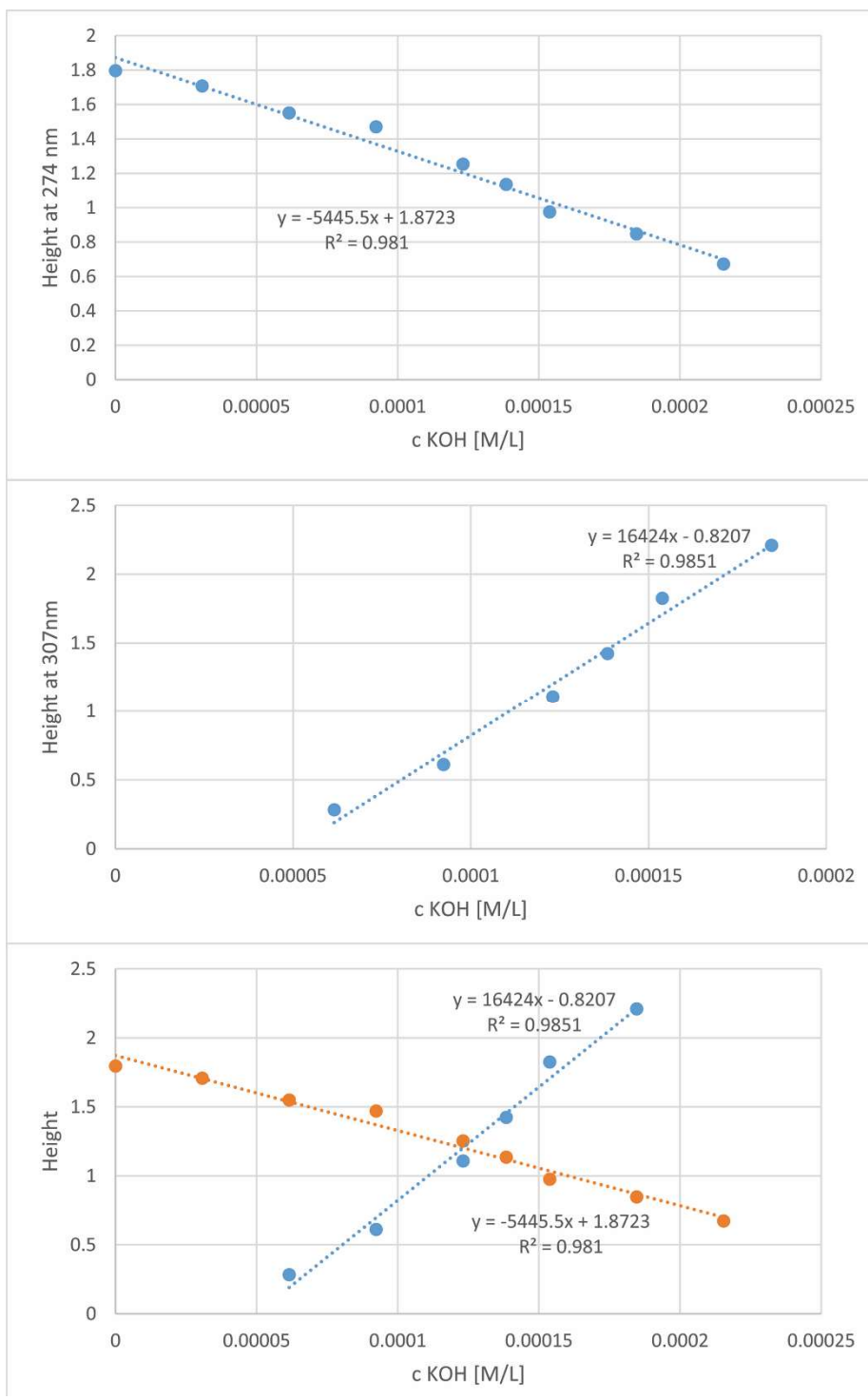
Fig. S8a (III)   Regression curves for the acidic and the basic forms (**II** and **II**⁻) (Series III).
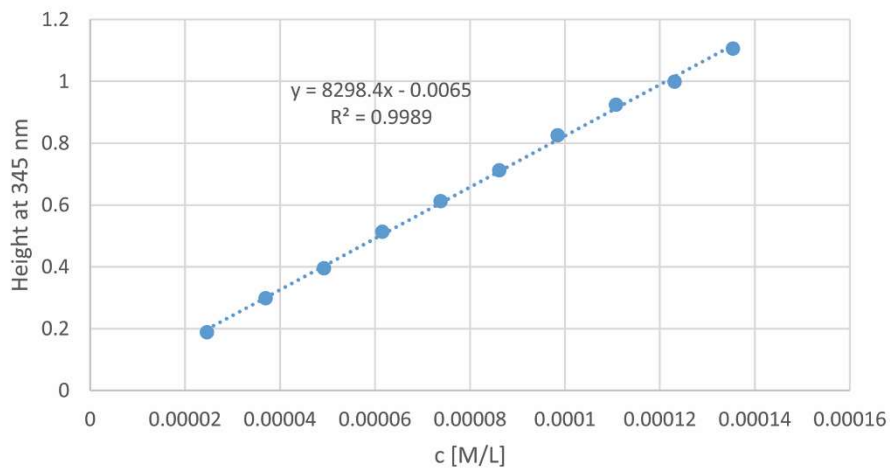
Fig. S8b (III)   Regression curves for the dianionic form **II⁻** (Series III).
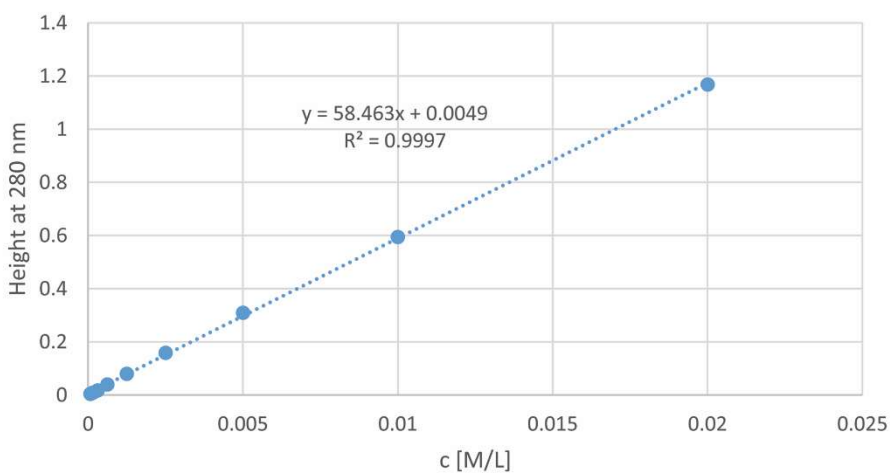

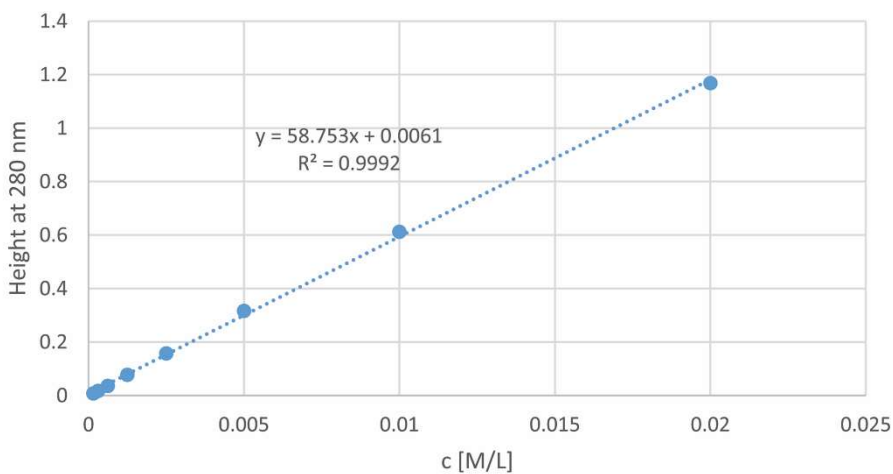Fig. S8c (I)   Regression curves for **5a hydrate** (Series I).

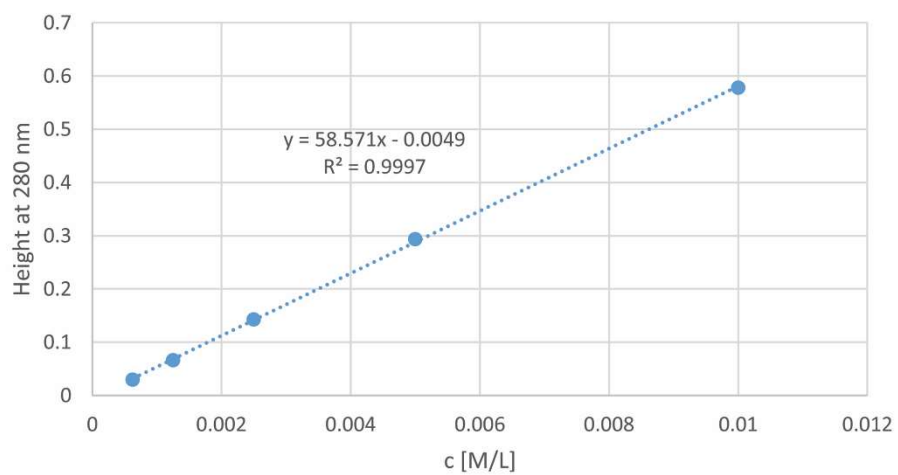Fig. S8c (II)   Regression curves for **5a hydrate** (Series II).

Fig. S8c (III) Regression curves for **5a hydrate** (Series III).

$y = 58.571x - 0.0049$
$R^2 = 0.9997$

5a hydrate

40

41

II
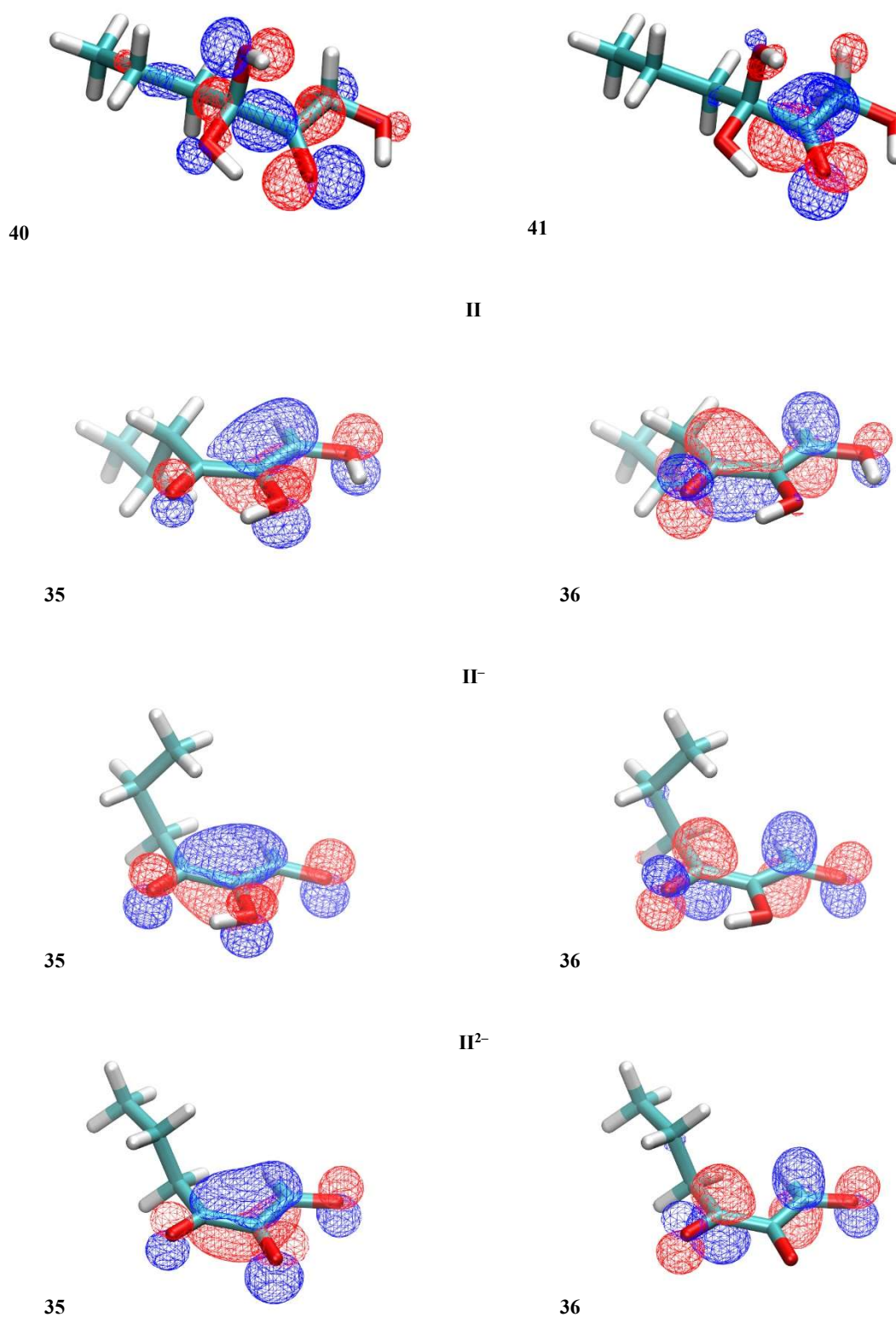

35

36

II⁻

35

36

II²⁻

35

36

Fig. S9   Contours of key molecular KS orbitals (plotted at 0.05 a.u.) for intense low-energy electronic transitions of various forms of the compound **II** (**5a hydrate**, **II**, **II⁻**, and **II²⁻**).

13C NMR spectrum of 6a in 50 mM Kpi (50 mM; T = 300 K; Bruker Avance III 600, 150 MHz)   at pH > 7, after 3 h in air
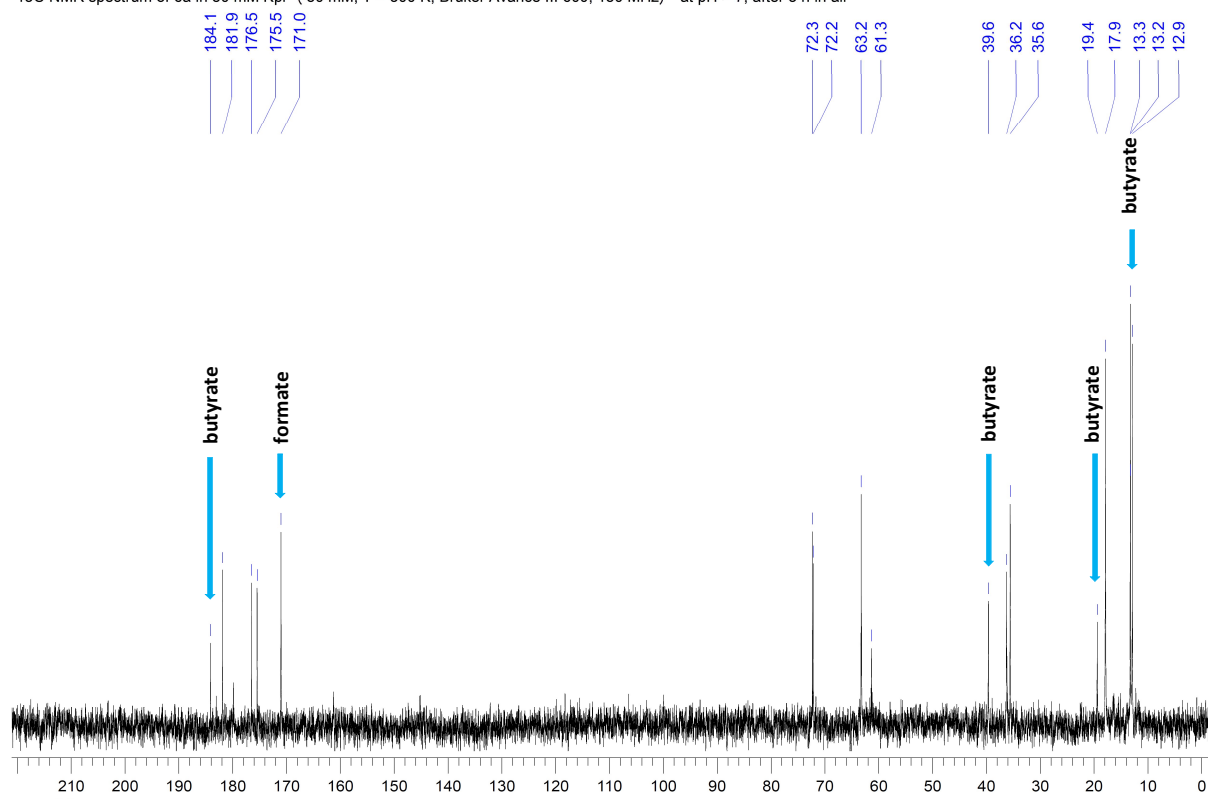
Fig. S10 ^{13}C NMR spectrum of **6a** (c = 50 mmol·dm^{-3}) in Kp$_i$ (c = 50 mmol·dm^{-3}), at pH > 7, after 3 h at 20°C in air. 10% v/v D$_2$O was added prior to the measurement. Apart from these from formate, also signals probably from butyrate are visible, but *not* from 2-oxopentanoate.

13C NMR spectrum of 6a in 50 mM Kpi (70 mM; T = 300 K; Bruker Avance III 600, 150 MHz) after 3 h in air
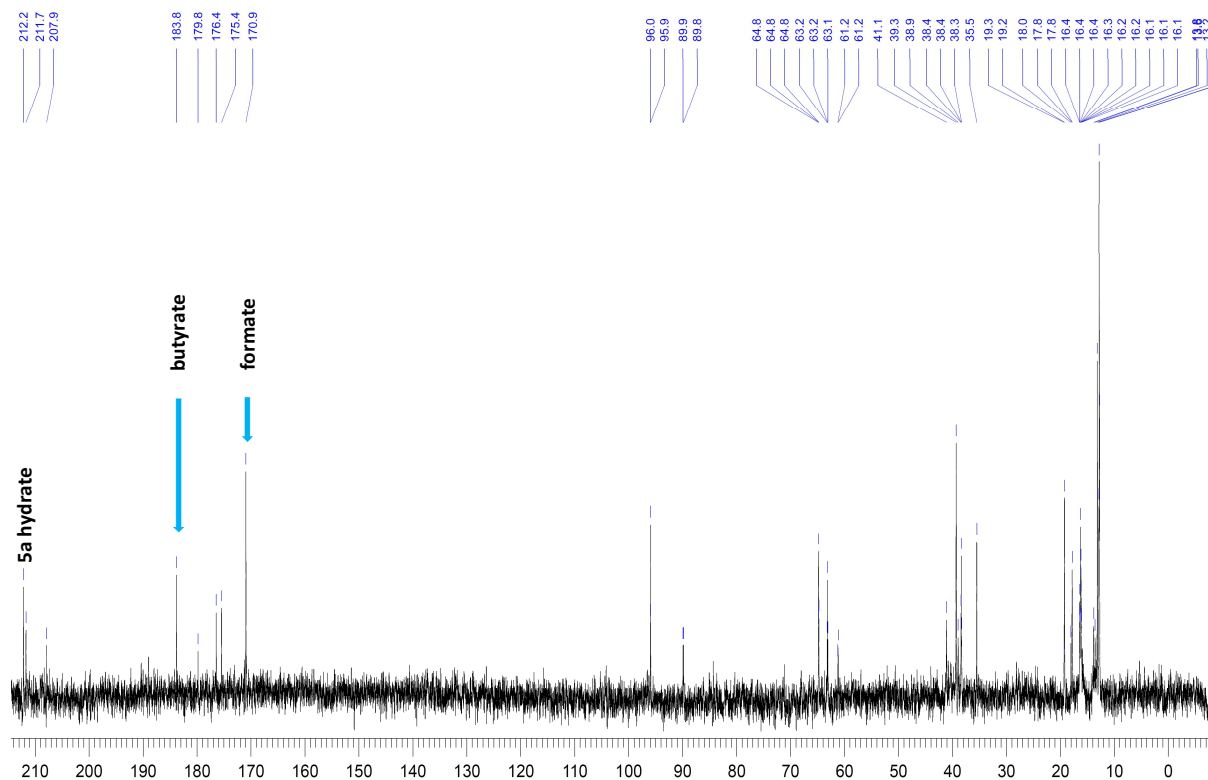
Fig. S11 ^{13}C NMR spectrum of **6a** (c = 70 mmol·dm^{-3}) in Kp$_i$ (c = 50 mmol·dm^{-3}), after 3 h at 20°C in air. 10% v/v D$_2$O was added prior to the measurement. Under such conditions the reaction could not be completed, however, apart from these from the substrate and formate, also a signal probably from butyrate is visible, but *not* from 2-oxopentanoate.

1H NMR spectrum of II- in Kpi (c = 1 M) , after 90 min at 20°C (c = 0.01 M) , T = 300 K; Bruker Avance III 600, 600 MHz)
10% v/v D2O added

8.101
8.096
8.055

0.828
0.816
0.804

0.592
0.583
0.570
0.558
0.555
0.543
0.537
0.532
0.524
0.520
0.512
0.507
0.500
0.485

0.315
0.106
0.001

3.000

0.422

3.000

ppm (t1)

Fig. S12 ^{1}H NMR spectrum of **6a** (c = 10 mmol·dm^{-3}) in Kp$_i$ (c = 1000 mmol·dm^{-3}), after 90 min at 20°C. 10% *v/v* D$_2$O was added prior to the measurement. The signals coming from water was removed during the measurement.