Supporting Information

Conformational Effects in Sugar Ions: Spectroscopic Investigations in the Gas Phase and in Solution

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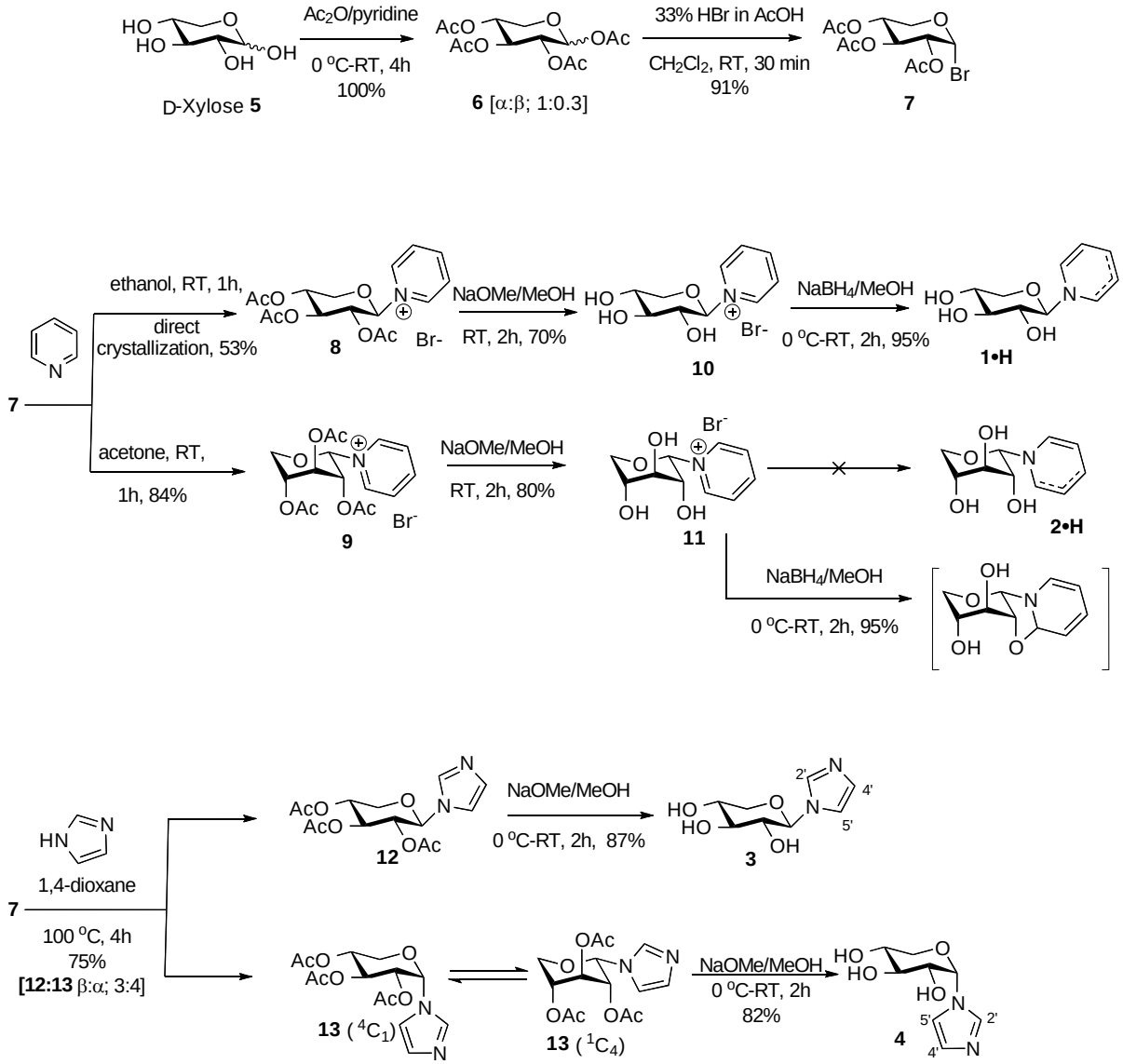
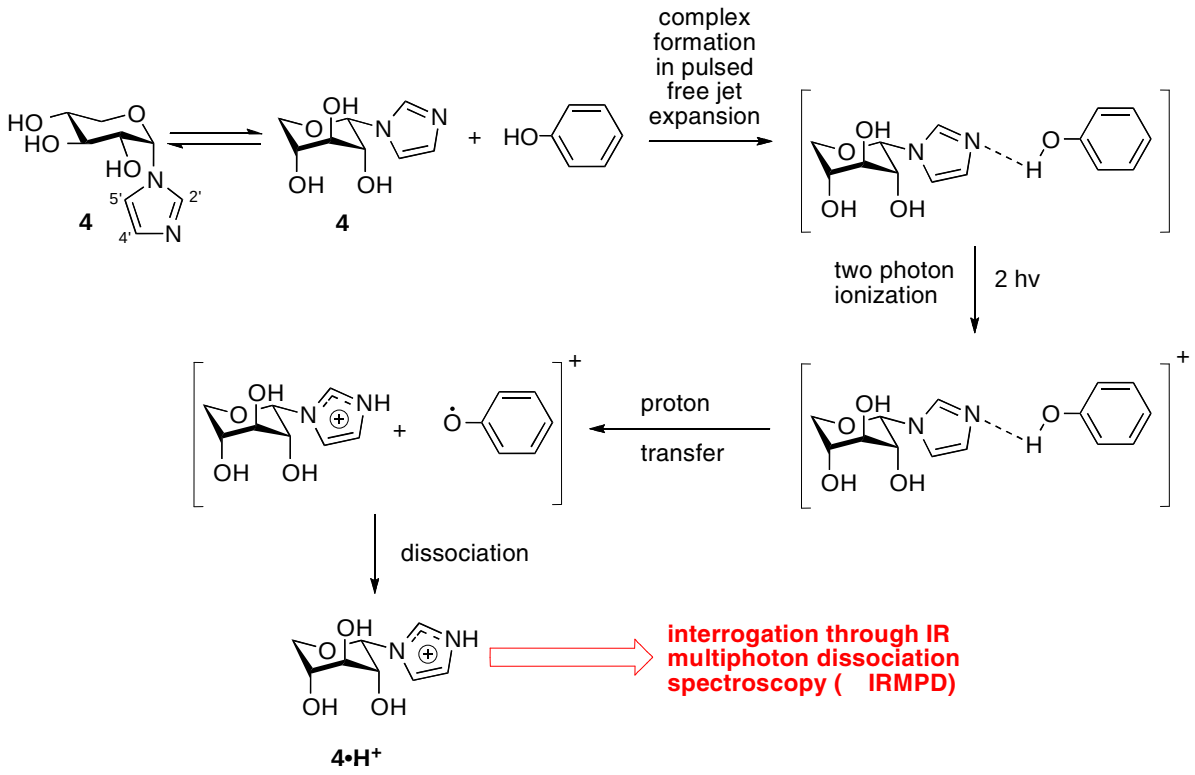


Scheme S1. Syntheses of Precursors



Scheme S2. Photoactivated Proton Transfer to Generate 4•H$^+$

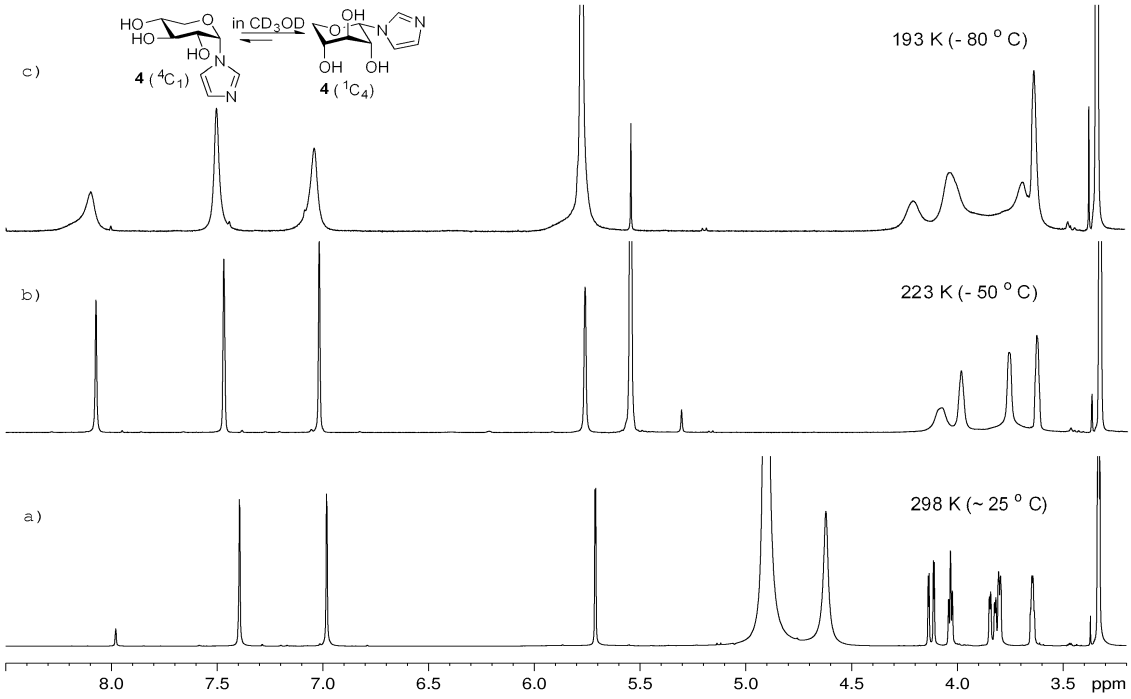
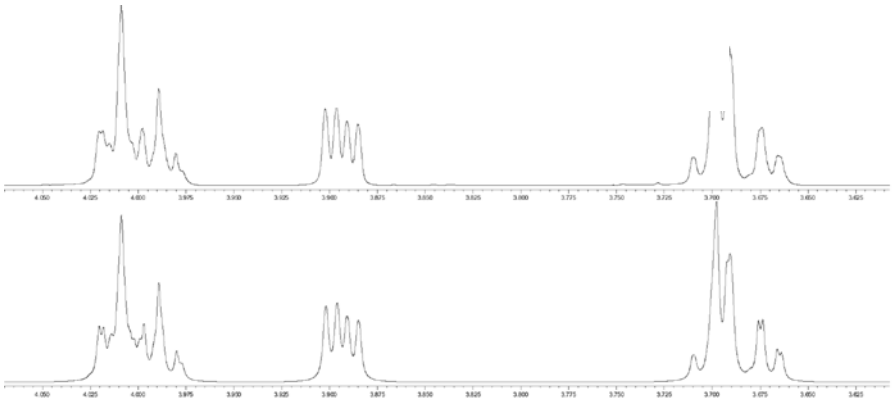


Figure S4. VT-NMR spectra of 4 in CD_3OD: a) NMR spectrum at 298 K (~ 25° C); b) at 223 K and c) at 193 K showing that lowering temperature results in peak broadening instead of separation of conformer's peaks. The 223 K spectrum clearly demonstrates significant differential broadening of certain sugar protons (3.5-4.2 ppm) whereas the imidazole resonances remain sharp. Possible viscosity effects can be rejected by examination of the solvent peak at 3.3 ppm, which shows no such broadening as would be anticipated for a highly viscous solution. The solution NMR data at room temperature are completely consistent with conformational averaging and as shown here lead to slower conformational averaging at lower temperatures, as would be expected.

a)

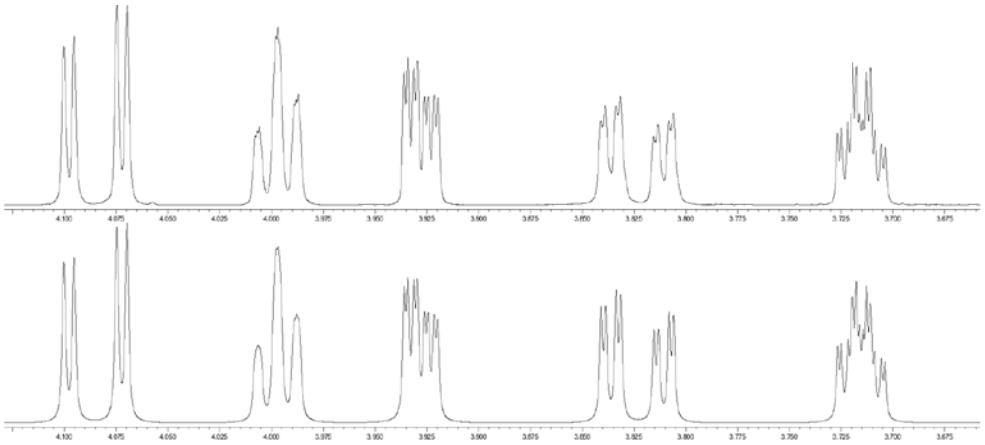
b)



	Protons		δ	J_s , 1	2	3	4	5ax
1	1H	1	5.770					
2	1H	1	3.894	2.98				
3	1H	1	4.008	0.00	5.60			
4	1H	1	3.696	0.00	0.69	5.08		
5ax	1H	1	3.998	0.00	0.00	0.00	2.85	
5eq	1H	1	3.684	0.00	0.00	1.11	4.95	-12.61

c)

d)



	Protons		δ	J_s , 1	2	3	4	5ax
1	1H	1	5.904					
2	1H	1	3.928	2.34				
3	1H	1	3.997	0.56	4.93			
4	1H	1	3.716	0.00	0.88	4.44		
5ax	1H	1	4.084	0.30	0.00	0.32	2.50	
5eq	1H	1	3.824	0.00	0.25	1.13	3.66	-12.77

Figure S5. Simulated and experimental spectra of 4 and 4•H$^+$ in D_2O: a) spectra of **4**; b) simulated spectra of **4** with calculated data; c) spectra of **4•H$^+$**; d) simulated spectra of **4•H$^+$** with calculated data.

1. General Experimental - Material and Methods:

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AV400 (400 MHz) and AVII 500 (500 MHz) spectrometer. Proton decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded on a Bruker AV400 (100 MHz) and AVII 500 (125.6 MHz) with sample temperatures regulated at 298K, unless otherwise stated. Spectra were assigned using COSY, DEPT-135, HMQC, HSQC, and HMBC if required. All chemical shifts are quoted on the δ scale in ppm using TMS as an internal standard. In case of acid titration experiments for compounds **3** and **4** in D_2O, traces amount of acetone was added and chemical shift was referenced with residual peak of acetone at δ 2.15 ppm. In case of **3•H**$^{+}$ and **4•H**$^{+}$ the spectra was also referenced with the same residual peak at δ 2.12 ppm. The chemical shift (δ) and coupling constant (*J*) given for compounds **3**, **4**, **3•H**$^{+}$ and **4•H**$^{+}$ are obtained from simulation calculated spectra.

NMR spin system simulation was performed with the gNMR program (v 5.06; http://home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html). Simulation of the ^{1}H spectrum of **4•H**$^{+}$ initially utilised chemical shift and coupling constant data derived directly from the ^{1}H NMR spectrum, followed by iterative lineshape fitting to the experimental spectrum. Simulation of the ^{1}H spectrum of **4** used the calculated parameters of **4•H**$^{+}$ as initial input data, followed by manual optimisation of parameters with final optimisations performed through iterative lineshape fitting.

Low resolution mass spectra were recorded on a Micromass Platform 1 spectrometer using electrospray ionization (ES), or on a Bruker Daltronic MicroTOF spectrometer. High resolution mass spectra were recorded on a Bruker Daltronic MicroTOF spectrometer. m/z values are reported in Daltons. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 589nm (Na D-line) with a path length of 1.0 dm and are reported in units of deg $dm^{-1}cm^{3}g^{-1}$. Concentrations are given in g/100 mL.

Thin Layer Chromatography (TLC) was carried out using Merck aluminium backed sheets coated with Kieselgel $60F_{254}$ silica gel. Visualization of the sheets was achieved using a UV lamp (λ_{max} = 254 or 365 nm) and/or ammonium molybdate (5% in 2M H_2SO_4), or sulfuric acid (0.2M in 1 MeOH : 1 H_2O). Compounds were purified using silica gel flash chromatography.

Anhydrous 1,4-dioxane, DCM, and diethyl ether were dried under pressure through a column of alumina. Other anhydrous solvents were purchased from Fluka, and stored under Argon over molecular sieves. All other solvents were used as supplied (analytical or HPLC grade). “Petrol” refers to the fraction of light petroleum ether boiling in the range 40-60°C. “Brine” refers to a saturated aqueous solution of sodium chloride.

2. Experimental procedures for preparation of compounds and spectral data:

Bromide Precursor – Description of Synthesis: D-xylose **5** was acetylated using acetic anhydride in pyridine to produce 1,2,3,4-tetra-*O*-acetyl-D-xylose **6** (α:β, 1:0.3) as a colourless oil in quantitative yield after 4h. [Note: in earlier reports (Org. Lett., 2007, 9, 3897 and Carbohydr. Res. 1982, 106, 43-57) using this method the reaction time was 22 h and the product was pale yellow]. Treatment of **6** with 33% HBr in acetic acid for 30 mins. at room temperature, using dichloromethane as solvent, gave the α-bromo derivative **7** exclusively. After work-up and recrystallization (ether:hexane) 2,3,4-tri-*O*-acetyl-α-D-xylopyranosylbromide **7** was obtained as a white crystalline solid in 91% yield.[1,2]

N-Glycosyl Dihydropyridines – Description of Synthesis:

The pyridinium salts were initially prepared using sodium borohydride reduction followed by deacetylation in methanol. Although the reduction produced a mixture of 1,4 and 1,2 DHP's (2:1 ratio based on beta compound) it was anticipated these should not differ when ionized to investigate the RAE. This procedure worked well for the beta compound but for the alpha compound a complex mixture of products was observed. The products formed using the alpha compound proved very difficult to handle and characterise. On standing in air the immediate formation of a yellow gum was observed. Despite these difficulties the synthesis was repeated several times in order to investigate if a fresh sample would give a suitable IR spectrum on ablation.

The attempted synthesis of the alpha compound was carried out according to the procedure outlined below (see experimental section). In only one case was any IR signal observed, this procedure is outlined in the experimental section below. An IR signal was observed only when the sample was lyophilized overnight and directly loaded on the ablation stage in a glove box. IR experiments were run immediately and gave a spectrum with vibrations corresponding to the 3 and 4-OH but not the 2-OH of a xylose derived compound. It was proposed that the 2-OH may have undergone an intramolecular cyclisation reaction (Scheme S1). The remaining starting material decomposed on contact with air and could not be characterised. Attempts to use solid supported reductants as reagents for synthesis resulted in products heavily contaminated with sodium bromide that did not give any signal in IR experiments or recovery of starting material. Attempts to remove the sodium bromide failed since the compound immediately decomposed. Direct NMR analysis of freshly prepared compound showed a complex mixture of products.

N-Glycosyl Imidazoles – Description of Synthesis

The bromide **7** was subjected to glycosidation under reflux conditions in 1,4-dioxane for 4h, using imidazole (5.0 equiv) as an acceptor, which furnished the glycosylated anomers, **12** and **13** in 3:4 ratio and in 75% combined yield.[3,4] They were subsequently purified by flash chromatography and the pure glycosides, **12** and **13**, were obtained in 33% and 42% yields, respectively. Their unprotected analogues, **3** and **4**, were obtained by stirring with NaOMe in methanol for 2h. Compound **3** was precipitated as white solid after diluting the reaction mixture with EtOAc; then filtered and washed with acetone to obtain N-(β-D-xylopyranosyl)imidazole **3** as a white crystalline solid in 87% yield. In the case of compound **4**, however, no precipitation was observed following dilution with EtOAc, and the reaction mixture was neutralised by adding Dowex-H^+ followed by filtration to yield **4** as a white solid in 82% yield.[3]

The *N*-(2,3,4-tri-*O*-acetyl-*β*-D-xylopyranosyl)imidazole **12** was observed mainly in $^4C_1$ conformation in $CDCl_3$ consistent with literature reports: there was a large coupling constant of anomeric proton with diaxial H-2 ($J_{1,2}$ = 9.2 Hz) and H-5ax with H-4 ($J_{4,5ax}$ = 14.4 Hz). Its alpha anomer *N*-(2,3,4-tri-*O*-acetyl-*α*-D-xylopyranosyl)imidazole **13** was observed as a dynamic equilibrium between $^4C_1$ and $^1C_4$ conformers in $CDCl_3$ at room temperature and the equilibrium shifted completely to $^1C_4$ upon protonation of the aglycon; this was also consistent with prior observations that the ratio of both conformers of this compound **13** depends on the solvent in unprotonated form.[5]

2.1. Synthesis of 1,2,3,4-tetra-*O*-acetyl-D-xylose 6. To a solution of D-xylose **5** (20 g, 133 mmol) in pyridine (75 mL) at 0 ^oC acetic anhydride (75 mL, 798 mmol, 1.5 equiv/OH) was added slowly within 20 min and resulting reaction mixture was stirred at 0 ^oC for 4 h. After 4 h the reaction mixture was poured into cold water and ethyl acetate was added. This reaction mixture was transferred to a separatory funnel and the organic layer was separated. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and followed by evaporation *in vacuo* to afford crude product. The crude product was dissolved in minimum amount of ether and diluted with petroleum to obtained white precipitate. The resulting precipitate was kept in refrigerator for 30 min and then organic layer was decanted to get white sticky precipitate. The resulting precipitate was dried *in vacuo* to obtained desired 1,2,3,4-tetra-*O*-acetyl-D-xylose **6** (42 g, 100%) as colourless oil. The ^1H NMR spectrum

showed it was anomeric mixture (α:β; 1:0.3) and all the data were consistent with those reported in the literature.

1,2,3,4-Tetra-*O*-acetyl-D-xylose 6. In a mixture form of alpha and beta anomer (1:0.3). ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.00, 2.02, 2.03, 2.04, 2.08, 2.15 (s, OAc of α and β anomer), 3.50 (dd, *J* = 11.6 Hz and *J* = 8.4 Hz, 1H, H-5' α), 3.69 (brt, *J* = 11.2 Hz 1H, H-5' β), 3.91 (dd, *J* = 11.2 Hz and *J* = 5.6 Hz, 1H, H-5 β), 4.12 (dd, *J* = 12.0 Hz and *J* = 5.2 Hz, 1H, H-5 α), 5.03–4.97 (m, 2H, H-2 and H-4), 5.18 (t, *J* = 8.0 Hz, 1H, H-3 β), 5.44 (t, *J* = 10.0 Hz, 1H, H-3 α), 5.69 (d, *J* = 6.8 Hz, 1H, H-1β), 6.22 (d, *J* = 4.0 Hz, 1H, H-1α); ^{13} C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.5, 20.6, 20.7, 20.8, 20.9 (CO*C*H$_3$), 60.5 (C-5 α), 62.7 (C-5 β), 68.2, 68.6, 69.2, 69.4, 70.9, 89.1 (C-1 α), 91.9 (C-1 β), 168.9, 169.0, 169.2, 169.6, 169.7, 169.8, 170.1 (*C*OCH$_3$); ESI-LRMS *m/z* calculated for $C_{13}H_{18}O_9$ $[M+ Na]^+$: 341.08; Found 341.10.

2.2. Synthesis of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide 7. 1,2,3,4-tetra-*O*-acetyl-D-xylose **6** (11 g, 34.6 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL). To this hydrogen bromide (33% in acetic acid, 20 mL) was added and the mixture was stirred under argon at room temperature. After a 30 min period, TLC indicated the formation of a product with complete consumption of the starting material. The reaction mixture was taken in separating funnel and partitioned between CH_2Cl_2 (50 mL) and chilled water (50 mL), and the aqueous layer re-extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with chilled sodium hydrogen carbonate and brine (50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Recrystallisation from ether/hexane afforded 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide **7** (10.6 g, 91%) as a white crystalline solid which was taken straight on next step due to the instability of the compound.

2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl bromide 7. ^{1}HNMR (400 MHz, $CDCl_3$) δ 1.99 (s, 6 H, $COCH_3$), 2.03 (s, 3 H, $COCH_3$), 3.81 (t, $J_{5ax,5eq=4}$ = 11.4 Hz, 1 H, H-5b), 3.98 (dd, $J_{5eq,5ax}$ = 11.6 Hz and $J_{5eq,4}$ = 6.4 Hz, 1 H, H-5a), 4.70 (dd, $J_{2,3}$ = 10 Hz and $J_{2,1}$ = 4.0 Hz, 1 H, H-2), 4.97 (ddd, $J_{4,5ax}$ = 10.8 Hz, $J_{4,3}$ = 9.6 and $J_{4,5eq}$ = 6.0 Hz, 1 H, H-4), 5.49 (t, $J_{3,4=2}$ = 9.6 Hz, 1 H, H-3), 6.51 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1); ^{13} C NMR (100 MHz, $CDCl_3$) δ 20.6, 20.7, 20.9 (CO*C*H$_3$), 62.4 (C-5), 68.1, 69.8, 70.8, 87.5 (C-1), 169.7, 169.8 (*C*OCH$_3$).

2.3. Synthesis of pyridinium 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide 8. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide **7** (4.0 g, 11.8 mmol) was dissolved in a mixture of anhydrous pyridine (25 mL) and dry ethanol (50 mL) and left to stirring at room temperature. After 1h it was noticed that reaction completed but left it for overnight stirring. After 18 hours the ethanol was evaporated in vacuo and product was precipitated by adding acetone to obtained anomeric mixture (**8**:**9**; β:α, 7:3) of glycosilated products in 80% of combined yield. The precipitate was first crystallised using EtOH: EtOAc (8:2) then re-crystallised using hot acetone afford the pyridinium 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside salt **8** (2.1 g, 53%) as a white crystalline solid.

Pyridinium 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide 8. $[\alpha]_D$ -19.0 (c, 0.95 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89, 1.96, 2.00 (3 x s, 9H, 3 x OAc), 4.11 (t, *J* = 11.2 Hz, 1H, H-5), 4.33 (dd, *J* = 12.0 Hz, *J* = 6.4 Hz, 1H, H-5a), 5.12 (t, *J* = 9.2 Hz, 1H, H-2), 5.17 (ddd, *J* = 9.6 Hz, *J* =10.9 Hz, *J* =5.9 Hz, 1H, H-4), 5.57 (t, *J* = 9.6 Hz, 1H, H-3), 7.38 (d, *J* = 8.8 Hz, 1H, H-1), 8.24 (t, *J* = 6.8 Hz, 2H, ArH), 8.71 (t, *J* = 8.0 Hz, 1H, ArH), 9.50 (d, *J* = 5.6 Hz, 2H, ArH); ^{13} C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.5, 20.6, (3 × $COCH_3$), 65.7 (C-5), 68.2, 71.3, 72.1, 91.4 (C-1), 128.5, 142.9, 148.5 (ArC), 169.2, 169.7, 169.8 (3 × $COCH_3$); ESI-LRMS *m/z* calculated for $C_{16}H_{20}NO_7$ $[M]^+$: 338.1; Found 338.1.

2.4. Pyridinium 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide 9. 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (4.0 g, 11.8 mmol) was dissolved in a dry acetone (50 mL) followed by the addition of anhydrous pyridine (25 mL) and leave the reaction mixture for stirring at room temperature. After 1h of stirring reaction was finished and product was precipitated as white solid but as per literature report reaction mixture left to stir overnight. After 18 hours the reaction was filtered to afford pyridinium 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside **7** (4.1 g, 84%) as a white crystalline solid as a single anomer.

Pyridinium 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide 9. $[\alpha]_D$ -44.0 (c, 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85, 2.11, 2.37 (3 x s, 9H, 3 x OAc), 4.31 (brd, *J* = 13.6 Hz, 1H, H-5), 4.46 (dd, *J* = 14.0 Hz, *J* = 2.0 Hz, 1H, H-5a), 4.79 (brs, 1H, H-2), 5.17 (brs, 1H, H-4), 5.35 (brs, 1H, H-3), 7.42 (brs, 1H, H-1), 8.16 (t, *J* = 6.8 Hz, 2H, ArH), 8.64 (t, *J* = 7.6 Hz, 1H, ArH), 9.72 (d, *J* = 6.0 Hz, 2H, ArH); ^{13} C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.9, 21.8 (3 × $COCH_3$), 65.4 (C-5), 65.8, 66.4, 67.6, 88.5 (C-1), 127.9, 142.4, 147.8 (ArC), 168.3, 169.3, 169.5 (3 × $COCH_3$); ESI-LRMS *m/z* calculated for $C_{16}H_{20}NO_7$ $[M]^+$: 338.1; Found 338.1.

2.5. Synthesis of β-D-pyridinium-xylopyranosyl bromide 10. To a stirred solution of Pyridinium 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide (460 mg, 1.1 mmol) in methanol (5 mL), sodium methoxide (6 mg, 0.11 mmol) was added at room temperature. After 2 h the reaction was diluted with ethyl acetate which caused pyridinium β-D-xylopyranosyl bromide **10** to precipitated (225 mg, 70%) as a white solid.

β-D-pyridinium-xylopyranosyl bromide 10. $[\alpha]_D$ -21.4 (c, 1.0 in H_2O); ^{1}H NMR (400 MHz, CD_3OD) δ 3.49 (t, *J* = 8.8 Hz, 1H, H-2), 3.59 (t, *J* = 9.2 Hz, 1H, H-3), 3.63 (t, *J* = 10.8 Hz, 1H, H-5b), 3.77-3.83 (m, 1H, H-4), 4.25 (dd, *J* = 10.8 Hz, *J* = 5.2 Hz, 1H, H-5a), 5.72 (d, *J* = 8.4 Hz, 1H, H-1), 8.22 (t, *J* = 6.8 Hz, 2H, ArH), 8.74 (t, *J* = 7.6 Hz, 1H, ArH), 9.15 (d, *J* = 6.0 Hz, 2H, ArH); ^{13} C NMR (100 MHz, CD_3OD) δ 69.1 (C-5), 69.3, 74.9, 76.9, 96.7 (C-1), 128.1, 142.7, 148.1 (ArC); ESI-HRMS *m/z* calculated for $C_{10}H_{14}NO_4$ $[M]^+$: 212.0917; Found 212.0915.

2.6. Synthesis of α-D-pyridinium-xylopyranosyl bromide 11. To a stirred solution of Pyridinium 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (1.0 g, 2.39 mmol) in methanol (10 mL), sodium methoxide (13 mg, 0.239 mmol) was added at room temperature. After 2 h the reaction was diluted with ethyl acetate which caused pyridinium α-D-xylopyranosyl bromide **11** to crystallise (556 mg, 80%) as a white solid.

α-D-pyridinium-xylopyranosyl bromide 11. $[\alpha]_D$ -62.0 (c, 1.0 in H_2O); ^{1}H NMR (400 MHz, CD_3OD) δ 3.75 (brs, 1H, H-2), 3.90 (brs, 1H, H-3), 4.16 (m, 1H, H-4), 4.24 (brd, *J* = 12.4 Hz, 1H, H-

5), 4.40 (dd, *J* = 12.4 Hz, *J* = 1.2 Hz, 1H, H-5a), 6.28 (brs, 1H, H-1), 8.18 (t, *J* = 6.8 Hz, 2H, ArH), 8.69 (t, *J* = 7.6 Hz, 1H, ArH), 9.15 (d, *J* = 5.6 Hz, 2H, ArH); ^{13} C NMR (100 MHz, CD_3OD) δ 68.1, 68.6, 69.7 (C-5), 71.2, 92.3 (C-1), 127.6, 142.6, 147.3 (ArC); ESI-HRMS *m/z* calculated for $C_{10}H_{14}NO_4$ $[M]^+$: 212.0917; Found 212.0921.

2.7. Attempted syntheses of α-N-xylopyranosyl dihydropyridine 2•H.

Method a) Pyridinium 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide **9** (300 mg, 0.72 mmol) was dissolved in water to which sodium borohydride (54 mg, 1.44 mmol) was added. After a period of 15 min, the reaction was partitioned with diethyl ether (20 mL) and the phases were separated. The organic phase was washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was resuspended in methanol (5 mL) and sodium methoxide (3 mg, 0.048 mmol) was added and the reaction was left at RT. After 2h, the reaction was quenched by the addition of dry ice and concentrated *in vacuo*. The resulting residue was resuspended in water and immediately lyophilised (12 h). The lyophilised compound was transferred under argon to a glove box into which had previously been placed a clean dry ablation stage. The compound was transferred onto the stage in preparation for ablation. The stage was removed from the glove box and transferred under argon to the IR instrument. The compound was immediately ablated and an IR spectrum displaying two peaks that may have been due to OH vibration was observed. Attempts to characterise the remaining starting material failed but it is proposed that some form of decomposition occurred either before or during the ablation procedure.

Method b) To a stirred solution of **11** (58 mg, 0.20 mmol) in methanol (2 mL) at room temperature $NaBH_4$ (3.8 mg, 0.10 mmol) was added and resulting mixture was stirred for 15min at room temperature. After 2h it gave complex mixture of products in NMR and the resulting complex mixture turned yellow at room temperature indicating the compounds is highly unstable. From above experiment it appeared that the reduced products **2•H** were not stable at room temperature and they either rearranged or degraded in to various products. Lowering the temperature of this reaction (-20 ^oC) resulted in to recovery of only starting material without any notable reduction.

At this stage it was decided to explore the solid support mediated reduction of α-D-pyridinium xylopyranoside **11** to obtain the desired products **2•H**. Two solid supported reagents (basic Al_2O_3 supported with $NaBH_4$ and Polymer supported borohydride (BER)) were explored using MeOH and

H_2O solvent and longer reaction time. But none of the tried condition gave desired product **2•H**. The milder reaction condition using Et_3SiH was also not successful. The details are summarised in Chart S1.

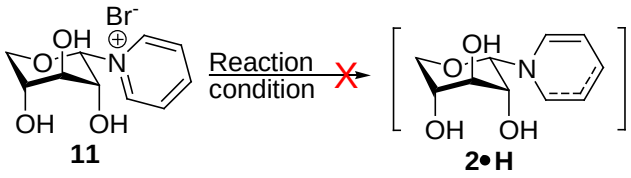


Chart S1. Attempted reduction of pyridinium salt **11** using a range of reducing agents.

S. No.	Reaction condition	Results
1	BER/MeOH/ 0 ^{o}C-RT, 4h	NR
2[a]	BER/MeOH/ 0 ^{o}C-RT, 24h	NR
3[a]	Et_3SiH/ MeOH/RT, 24h	NR
4[a]	$NaBH_4$-Al_2O_3/MeOH, RT, 1h	NR
5	$NaBH_4$-Al_2O_3/H_2O, RT, 1h	NR

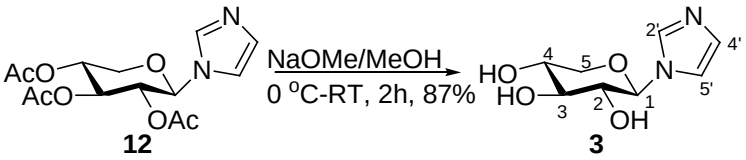
NR= No reaction; [a]These reactions were also tried with substrate **10** and obtained similar results.

2.8. Synthesis of β-N-xylopyranosyl-dihydroxypyridine 1•H. Pyridinium 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide (300 mg, 0.72 mmol) **8** was dissolved in water to which sodium borohydride (54 mg, 1.44 mmol) was added. After a period of 2h, the reaction was partitioned with diethyl ether (20 mL) and the phases were separated. The organic phase was washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was resuspended in methanol (5 mL) and sodium methoxide (3 mg, 0.048 mmol) was added and the reaction was left at RT. After 2h, the reaction was quenched by the addition of dry ice and concentrated *in vacuo*. The resulting residue was resuspended in water and lypholised to afford 1,4-dihydropyridyl-β-D-xylopyranoside (150 mg, 97% over 2 steps) as a white amorphous foam; $[\alpha]_D^{20}$ -6.9 (c, 1.05 in $CHCl_3$); υ_{max} (KBr) 1749 (s, C=O) cm^{-1}; δ_H (500 MHz, CD_3OD) 2.89-2.91 (2H, m, CH_2), 3.20 (1H, at, *J* 11.2 Hz, H-5), 3.29-3.48 (3H, H-2, H-3, H-4), 3.82 (1H, dd, $J_{4,5'}$ 4.5 Hz, $J_{5,5'}$ 11.3 Hz, H-5'), 3.95 (1H, d, $J_{1,2}$ 9.0 Hz, H-1), 4.42-4.44 (2H, m, C=C<u>H</u>CH_2), 5.95 (1H, d, *J* 8.1 Hz, NC<u>H</u>=CH_2); δ_C (125 MHz, CD_3OD) 23.8 (t, CH_2), 68.8 (t, C-5), 71.1, 71.5, 79.2 (3 x d, C-2, C-3, C-4), 93.6 (d, C-1), 100.0, 130.0 (2 x d, 4 x ArC).

2.9. Synthesis of *N*-(2,3,4-tri-*O*-acetyl-α-and *β*-D-xylopyranosyl)imidazoles 12 and 13. A mixture of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide **7** (2.5 g, 7.3 mmol) and imidazole (2.5 g, 36.7 mmol) in 1,4-dioxane (15 mL) was heated at reflux temperature for 4 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure; the residue was dissolved in CH_2Cl_2, and the solution was washed sequentially with sat. $NaHCO_3$ and water, dried, filtered, and the solvent was removed under reduced pressure to obtained crude product mixture. The column chromatography purification of the crude product mixture (8:2 EtOAc:petroleum to 95:5 EtOAc:MeOH) furnished the pure compounds **12** (0.8 g, 33%) and **13** (1.0 g, 42%) respectively.

***N*-(2,3,4-tri-*O*-acetyl-*β*-D-xylopyranosyl)imidazole 12.** $[\alpha]_D$ -49.5 (1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 3 H, OAc), 1.98 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 3.44 (brt, $J_{5ax,5eq=4}$ = 11.6, 1 H, H-5a), 4.21 (dd, $J_{5eq,5ax}$ = 11.2 Hz, $J_{5eq,4}$ = 6.0 Hz, 1 H, H-5b), 5.08 (td, $J_{4,3=5ax}$ = 14.4 Hz and $J_{4,eq}$ = 5.2 Hz, 1H, H-4), 5.15 (d, $J_{1,2}$ = 8.8 Hz, 1H, H-1), 5.21 (t, $J_{3,4=2}$ = 9.2 Hz, 1H, H-3), 5.28 (t, $J_{2,1}$ = 9.2 Hz, 1 H, H-2), 6.99 (s, 1H, ArH), 7.01 (s, 1H, ArH), 7.54 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 20.5, 20.6 (OAc), 65.5 (C-5), 68.4, 70.8, 72.4 (C-2,3,4), 84.3 (C-1), 116.6, 130.4, 136.6 (ArC), 168.8, 169.7, 170.0 (OAc); ESI-LRMS *m/z* calculated for $C_{14}H_{18}N_2O_7$ $[M+H]^+$: 327.1; Found 327.1.

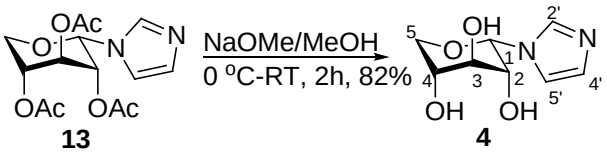
***N*-(2,3,4-tri-*O*-acetyl-*α*-D-xylopyranosyl)imidazole 13.** $[\alpha]_D$ -6.2 (1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 2.15 (s, 3 H, OAc), 3.79 (dd, $J_{5a,5b}$ = 12.9, $J_{5a,4}$ = 4.9 Hz, 1 H, H-5a), 4.02 (dd, $J_{5b,5a}$ = 12.9 and $J_{5b,4}$ = 3.4 Hz, 1 H, H-5b), 4.88–4.90 (m, 1 H, H-4), 5.10 (dd, $J_{2,3}$ = 6.5 and $J_{2,1}$ = 3.3 Hz, 1 H, H-2), 5.41 (t, $J_{3,2}$ = 6.5 Hz, 1 H, H-3), 5.80 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1), 7.10 (s, 1 H, ArH), 7.14 (s, 1 H, ArH), 7.78 (s, 1 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 20.7, 20.8 (OAc), 64.1 (C-5), 66.7, 67.7, 68.3 (C-2,3,4), 81.01 (C-1), 117.8, 129.5, 136.4 (ArC), 168.8, 169.1, 169.6 (OAc); ESI-LRMS *m/z* calculated for $C_{14}H_{18}N_2O_7$ $[M+H]^+$: 327.1; Found 327.1.



12 3

2.10. Synthesis of *N*-(α-and *β*-D-xylopyranosyl)imidazoles 3 and 4. To a solution of *N*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)imidazole **12** (375 mg, 1.15 mmol) in MeOH (4 mL) was added sodium methoxide (6.2 mg, 0.115 mmol). The solution was stirred for 2 h under nitrogen atmosphere. The reaction mixture was diluted with EtOAc which resulted precipitation of **3** as white crystalline solid which after filtration and washing with EtOAc furnished pure compound *N*-(*β*-D-xylopyranosyl)imidazoles **3** (200 mg, 87%) as white solid. Similar reaction protocol was adapted for the synthesis of *N*-(*α*-D-xylopyranosyl)imidazoles **4** from **13**. But compound **4** was not precipitated after dilution with EtOAc so reaction mixture was neutralised with Dowex-H^+ followed by filtration. Filtrate was concentrated to afford *N*-(*α*-D-xylopyranosyl)imidazoles **4** as white solid in 82% yield.

***N*-(*β*-D-xylopyranosyl)imidazole 3.** $[\alpha]_D$ -21.5 (1.0, MeOH:H_2O, (9:1)); ^{1}H NMR (500 MHz, D_2O): δ 3.44 (brt, $J_{5ax,5eq=4}$ = 11.4, 1 H, H-5ax), 3.52 (t, $J_{3,2=4}$ = 9.2 Hz, 1H, H-3), 3.72 (ddd, $J_{4,5ax}$ = 10.6 Hz, $J_{4,3}$ = 9.2 Hz, $J_{4,5eq}$ = 5.5 Hz, 1H, H-4), 3.73 (brt, $J_{2,3}$ = 9.2 Hz, 1H, H-2), 4.01 (dd, $J_{5eq,5ax}$ = 11.4 Hz, and $J_{5eq,4}$ = 5.5 Hz, 1 H, H-5eq), 5.21 (d, $J_{1,2}$ = 9.2 Hz, 1H, H-1), 7.02 (s, 1H, H-4′), 7.28 (brs, 1H, H-5′), 7.83 (s, 1H, H-2′); ^{13}C NMR (125 MHz, D_2O): δ 68.1 (C-5), 69.1 (C-4), 72.7 (C-2), 76.5 (C-4), 86.2(C-1), 118.1 (C-5′), 129.1 (C-4′), 138.0 (C-2′); ESI-HRMS *m/z* calculated for $C_8H_{12}O_4N_2$ [M+ H]$^+$: 201.875; Found 201.874.



***N*-(*α*-D-xylopyranosyl)imidazole 4.** $[\alpha]_D$ -16.0 (1.0, MeOH); NMR data from simulation calculated spectra ^{1}H NMR (500 MHz, D_2O): δ 3.68 (dd, $J_{5eq,5ax}$ = 12.6 Hz and $J_{5eq,4}$= 4.9 Hz, 1H, H-5eq), 3.69 (ddd, $J_{4,3}$ = 5.1 Hz, $J_{4,5eq}$= 4.9 Hz and $J_{4,5ax}$ = 2.8 Hz, 1H, H-4), 3.89 (dd, $J_{2,3}$ = 5.6 Hz and $J_{2,1}$= 3.0 Hz, 1H, H-2), 3.99 (dd, $J_{5ax,5eq}$ = 12.6 Hz and $J_{5ax,4}$= 2.8 Hz, 1H, H-5ax), 4.00 (dd, $J_{3,2}$ = 5.6 Hz and $J_{3,4}$= 5.1 Hz, 1H, H-3), 5.77 (d, $J_{1,2}$ = 3.0 Hz, 1H, H-1), 6.98 (s, 1 H, H-5′), 7.33 (s, 1 H, H-4′), 7.90 (s, 1 H, H-2′); ^{13}C NMR (125 MHz, D_2O): δ 66.7 (C-5), 67.8 (C-4), 70.0 (C-2), 70.3 (C-3), 82.4 (C-1), 119.4 (C-5′), 127.5 (C-4′), 137.7 (C-2′); ESI-HRMS *m/z* calculated for $C_8H_{12}O_4N_2$ [M+ H]$^+$: 201.875; Found 201.875.

2.11. NMR acid titration on *N*-(α-and *β*-D-xylopyranosyl)imidazoles 3 and 4 using TFA in D_2O. The 6 mg of compound **3** was dissolved in 0.5 mL of D_2O in NMR tube, to this 2 µL of 1.0% acetone solution in D_2O (v/v) was added (in order to observe any chemical shift after protonation with reference to acetone and also used δ 2.15 as references) and NMR spectra were taken of thus prepared solution. Trifluoroacetic acid (TFA, 5 µL) was added in the same NMR tube and shaken well and spectra were recorded again. The protonation on **3** confirmed by chemical shift of imidazole proton

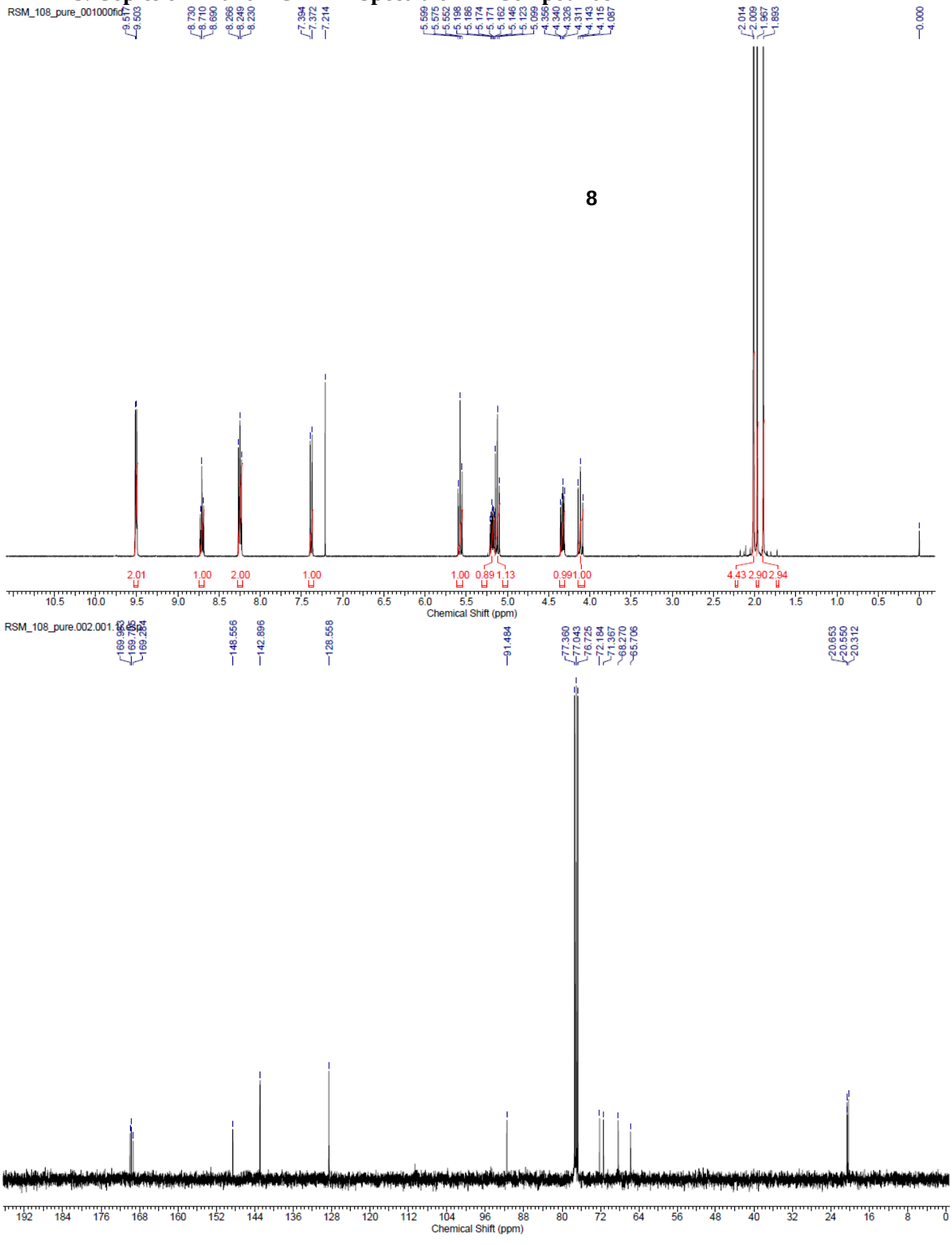
(H-2') which was shifted almost 1 ppm downfield from 7.83 ppm to 8.95 ppm which did not change further on continued addition of TFA, confirming protonation to be complete. The compound **3** in its protonated form **3•H**$^+$ exist almost in same conformer ($^4C_1$) as evidented by NMR of sugar region. Similar titration was carried out on compounds **4** and found that, in its protonated form **4•H**$^+$ the equilibrium shifted towards $^1C_4$ conformation.

***N*-(*β*-D-xylopyranosyl)imidazolium 3•H$^+$.** ^{1}H NMR (500 MHz, D_2O): δ 3.46 (brt, $J_{5ax,5eq=4}$ = 11.4, 1 H, H-5ax), 3.53 (t, $J_{3,2=4}$ = 9.2 Hz, 1H, H-3), 3.62 (brt, $J_{2,3}$ = 9.2 Hz, 1H, H-2), 3.72 (ddd, $J_{4,5ax}$ = 10.6 Hz, $J_{4,3}$ = 9.2 Hz, $J_{4,5eq}$ = 5.5 Hz, 1H, H-4), 4.07 (dd, $J_{5eq,5ax}$ = 11.4 Hz, and $J_{5eq,4}$ = 5.5 Hz, 1 H, H-5eq), 5.38 (d, J = 9.2 Hz, 1H, H-1), 7.49 (t, J =2.0 Hz, 1H, H-4′), 7.66 (t, J =2.0 Hz, 1H, H-5′), 8.95 (t, J =2.0 Hz, 1H, H-2′); ^{13}C NMR (125 MHz, D_2O): δ 68.4 (C-5), 68.9 (C-4), 73.1 (C-2), 76.0 (C-4), 87.8 (C-1), 119.9 (C-5′), 120.6 (C-4′), 134.8 (C-2′).

***N*-(*α*-D-xylopyranosyl)imidazolium 4•H$^+$.** ^{1}H NMR (500 MHz, D_2O): δ 3.72 (ddt, $J_{4,3}$ = 4.4 Hz, $J_{4,5ax}$ =2.5 Hz, $J_{4,5eq}$ = 3.6 Hz and $J_{4,2}$ = 0.9 Hz, 1H, H-4), 3.82 (ddd, $J_{5eq,5ax}$ = 12.7 Hz, $J_{5eq,4}$ = 3.6 Hz and $J_{5eq,3}$ = 1.1 Hz, 1H, H-5 eq), 3.93 (ddd, $J_{2,3}$ = 4.9 Hz, $J_{2,1}$ = 2.3 Hz and $J_{2,4}$ = 0.9 Hz, 1 H, H-2), 4.00 (dt, $J_{3,2=4}$ = 4.4 Hz and $J_{3,5eq}$= 1.1 Hz, 1H, H-3), 4.08 (dd, $J_{5ax,5eq}$ = 12.7 Hz and $J_{5ax,4}$ = 2.5 Hz, 1H, H-5ax), 5.90 (d, $J_{1,2}$ = 2.3 Hz, 1 H, H-1), 7.43 (t, J =2.0 Hz, 1H, H-4′), 7.62 (t, J =2.0 Hz, 1H, H-5′), 8.91 (t, J =2.0 Hz, 1H, H-2′); ^{13}C NMR (125 MHz, D_2O): δ 67.6 (C-5), 68.1 (C-4), 69.5 (C-2), 69.6 (C-3), 84.7 (C-1), 119.7 (C-5′), 120.7 (C-4′), 134.8 (C-2′).

3. Copies of ^{1}H and ^{13}C NMR Spectra of All Compounds

8



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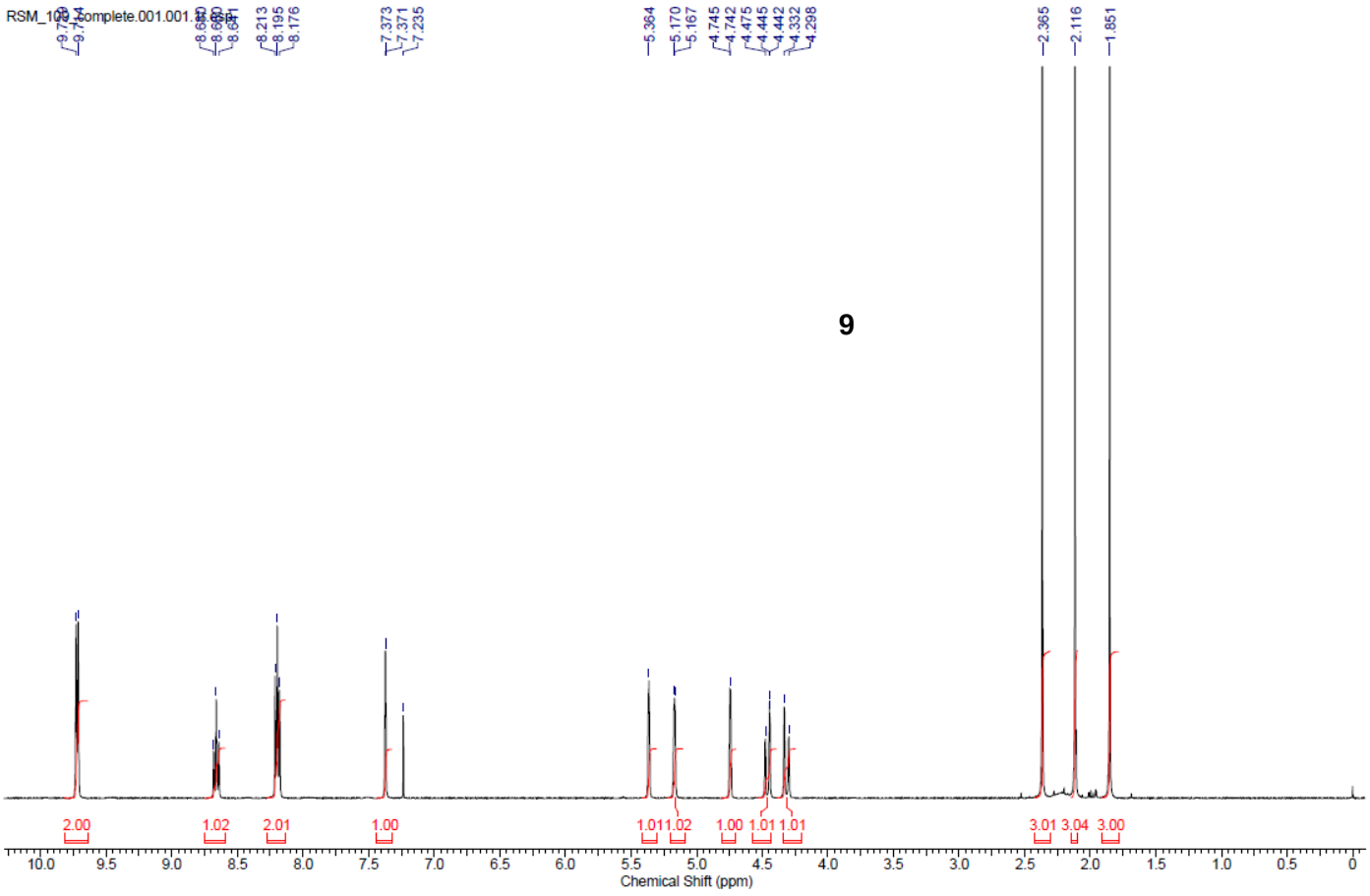
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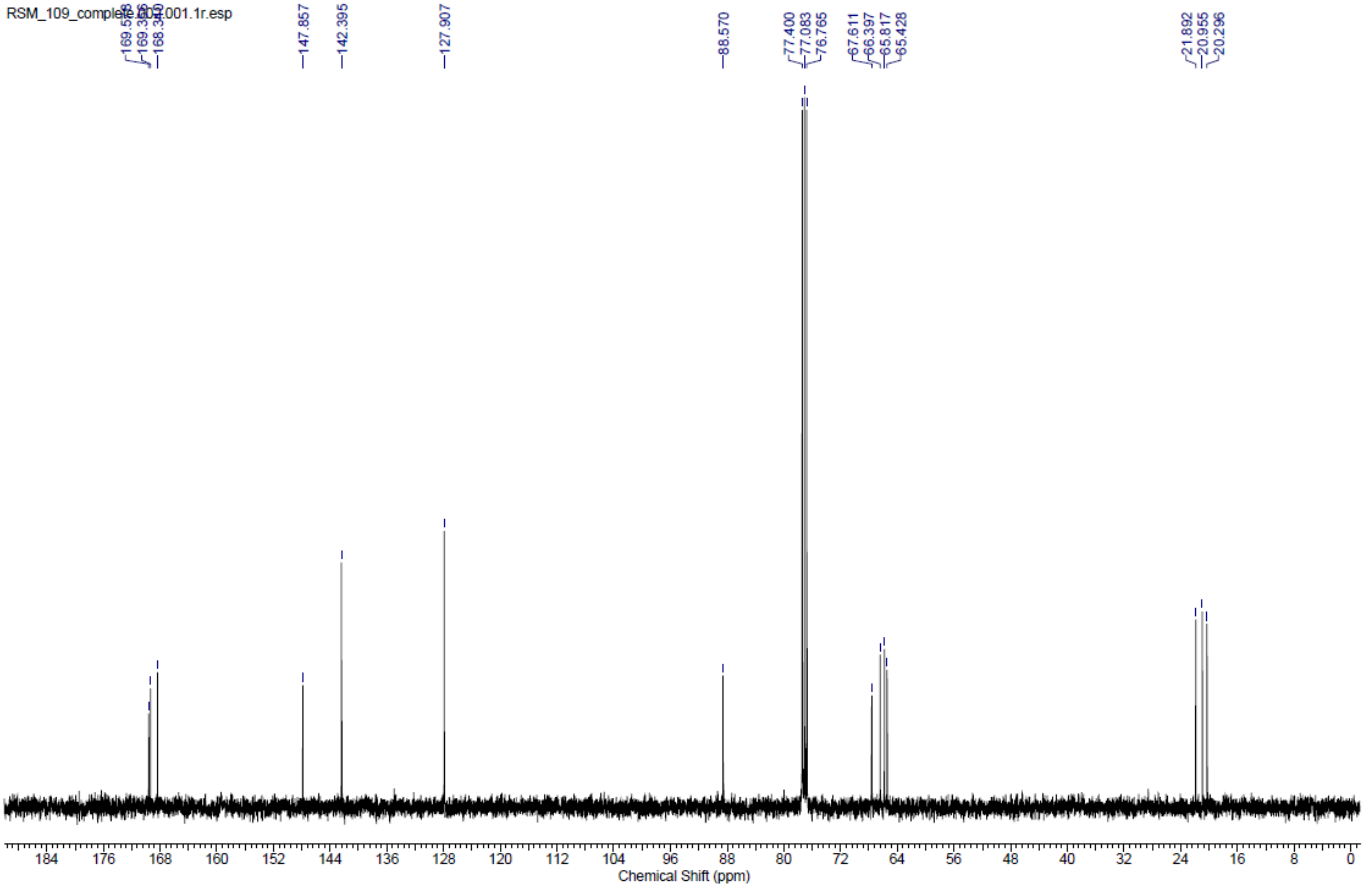
Chemical Shift (ppm)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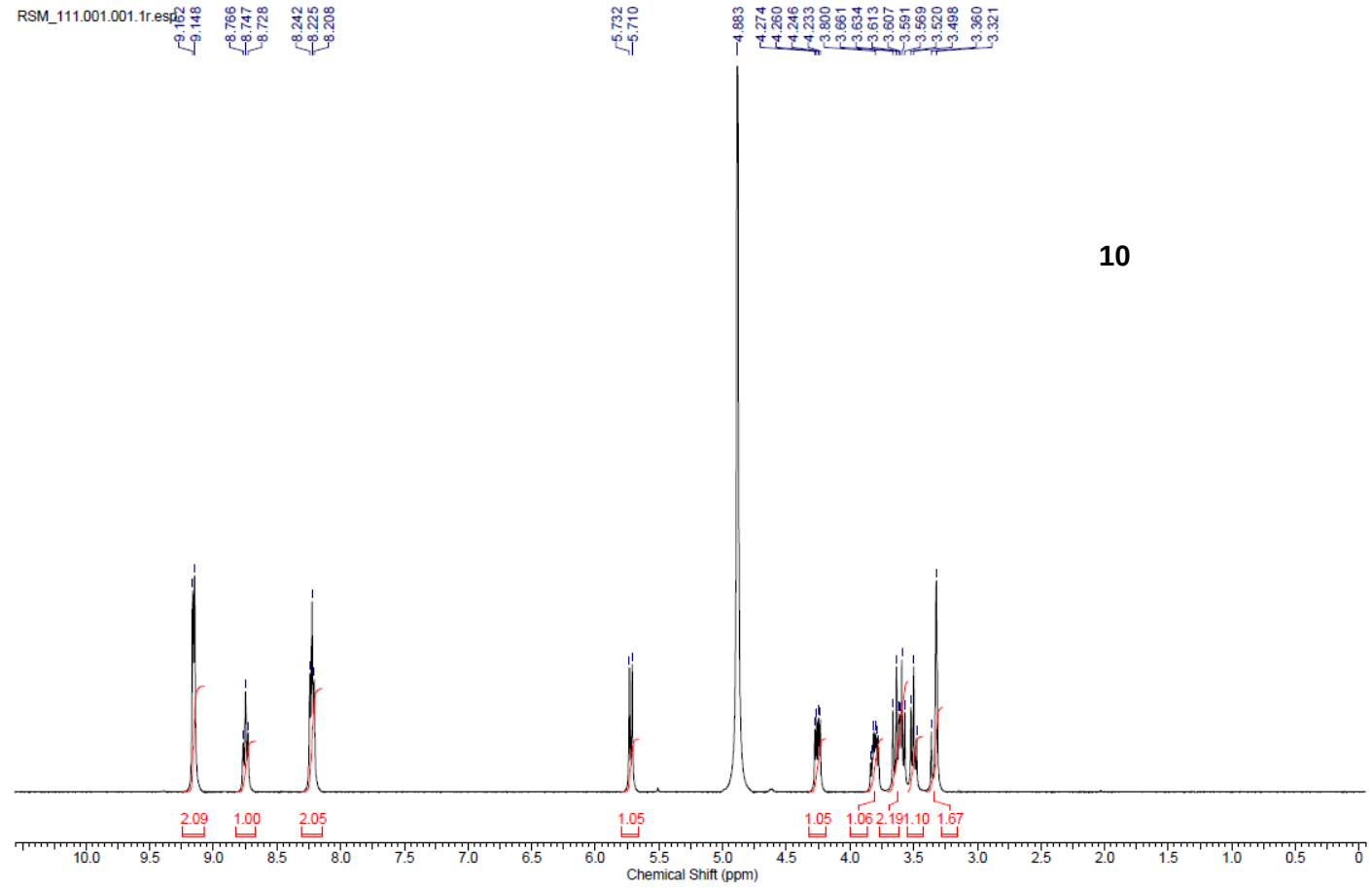
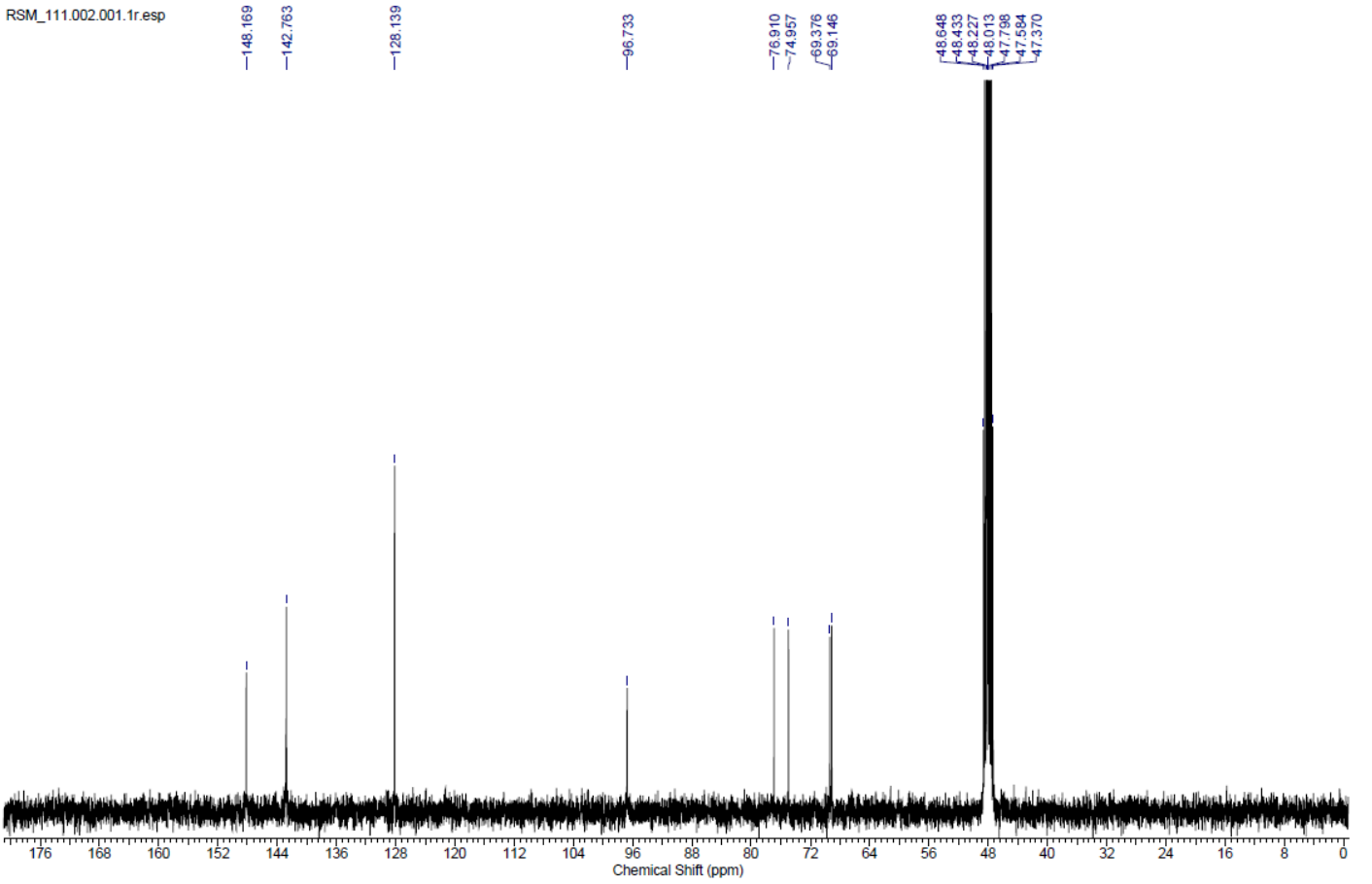
Chemical Shift (ppm)

10





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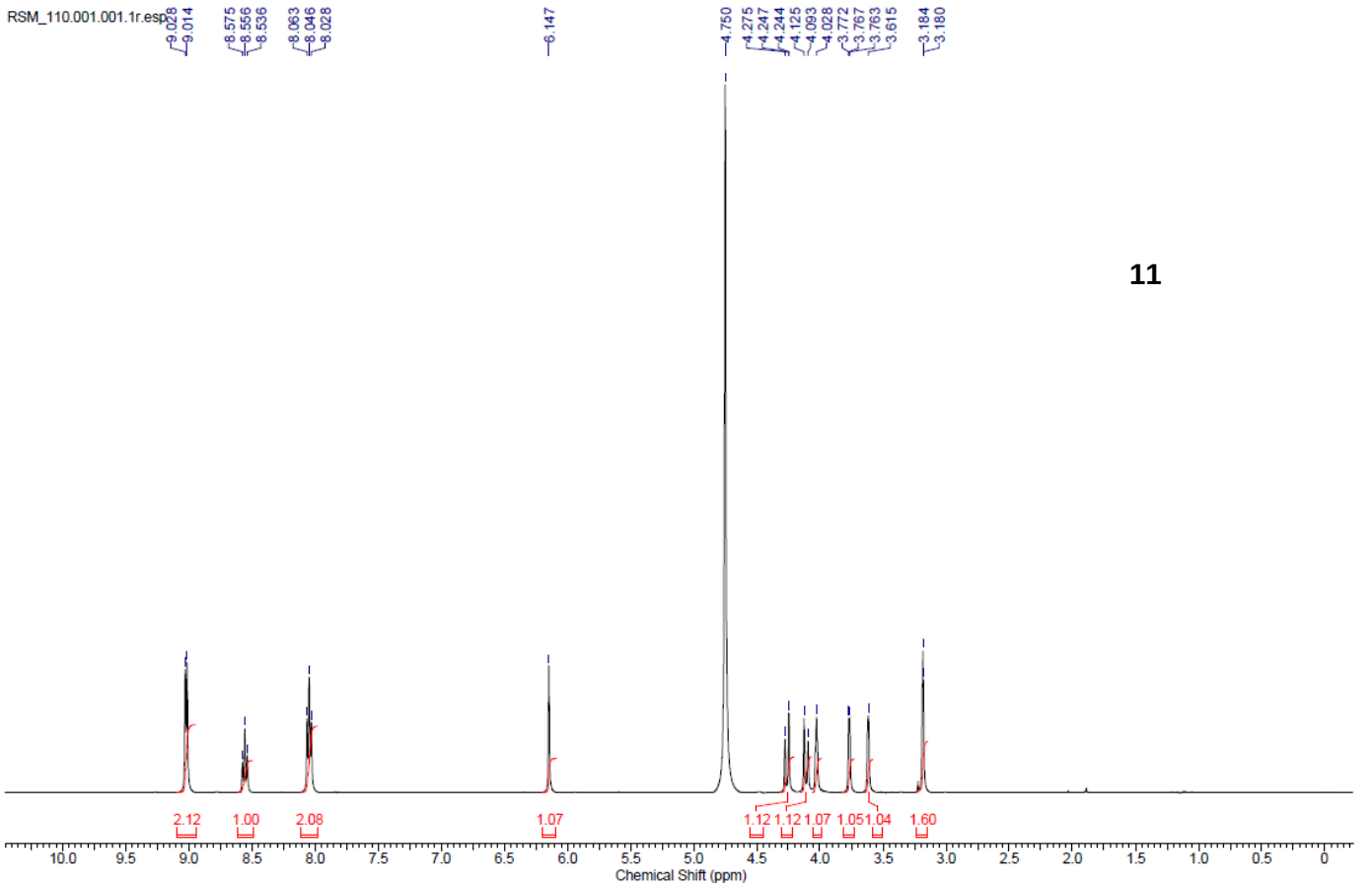

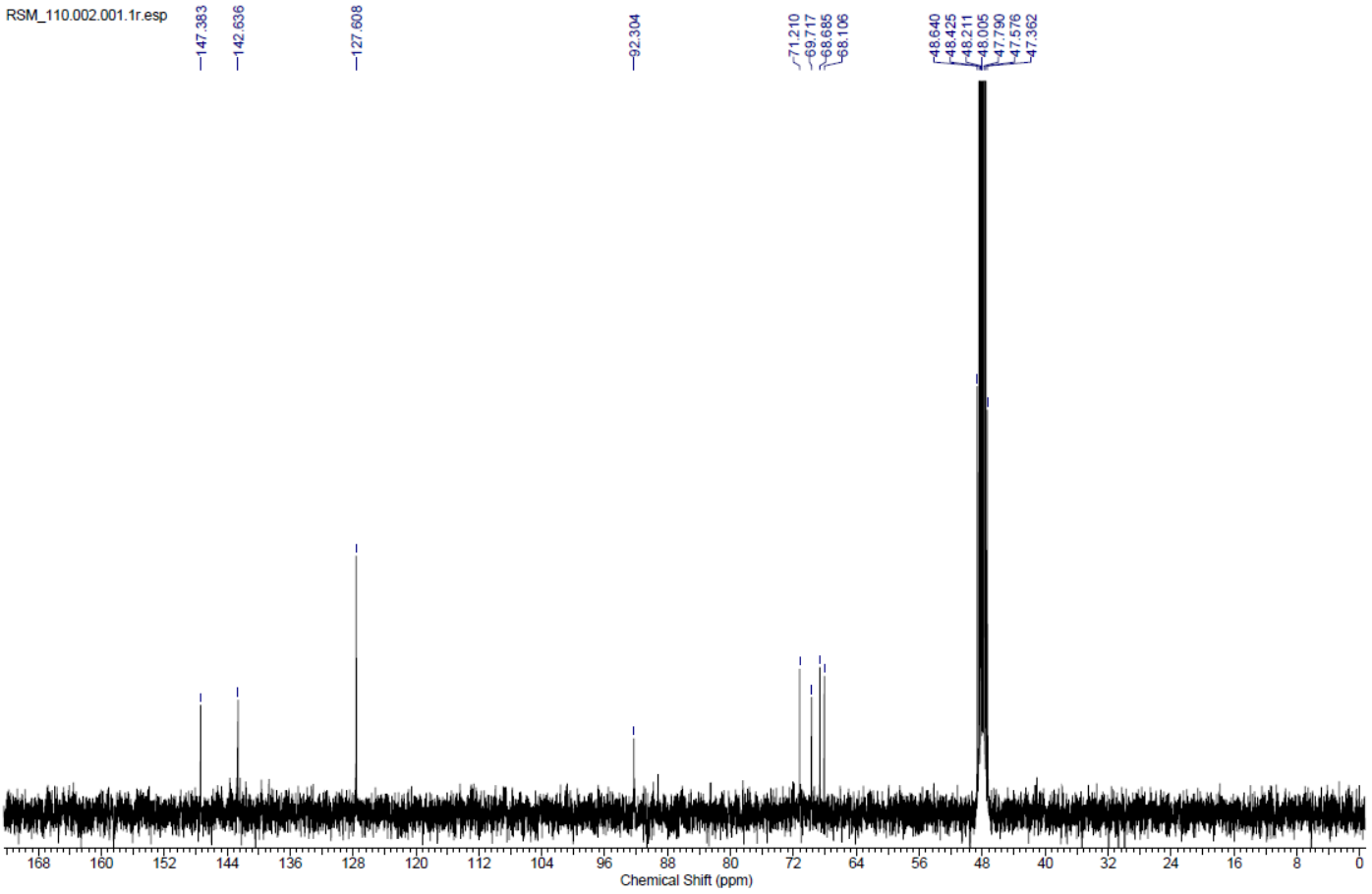

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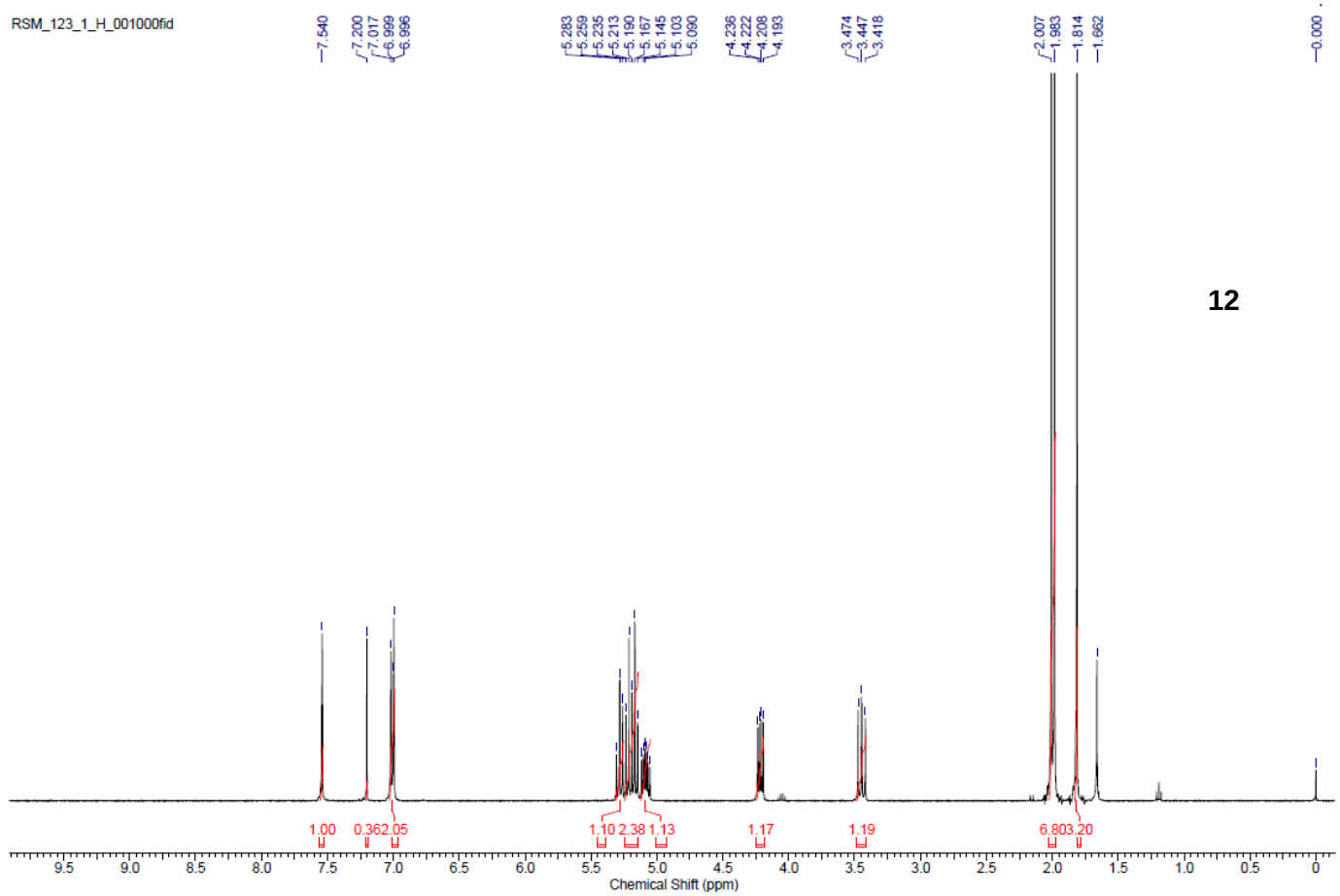
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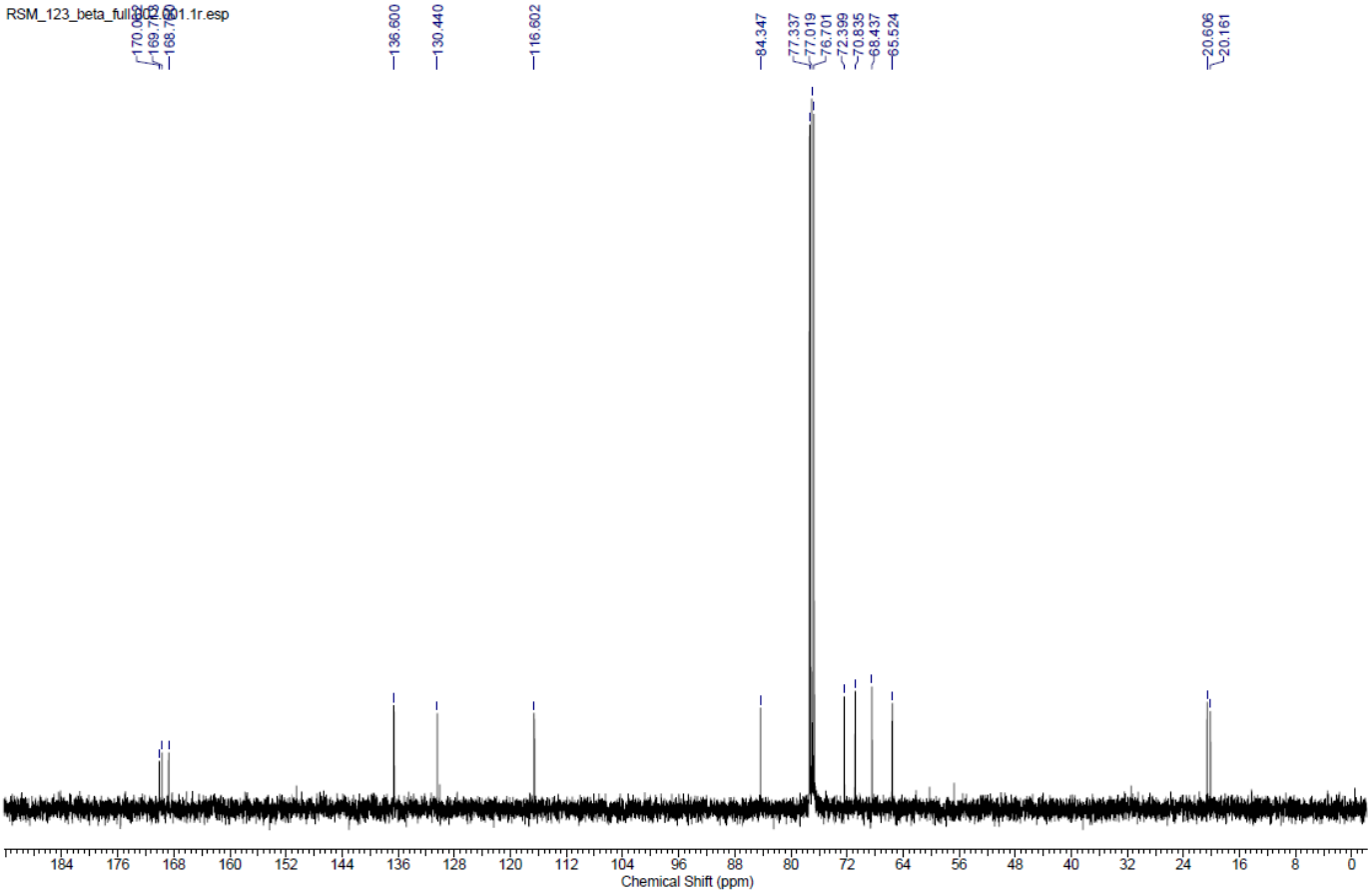
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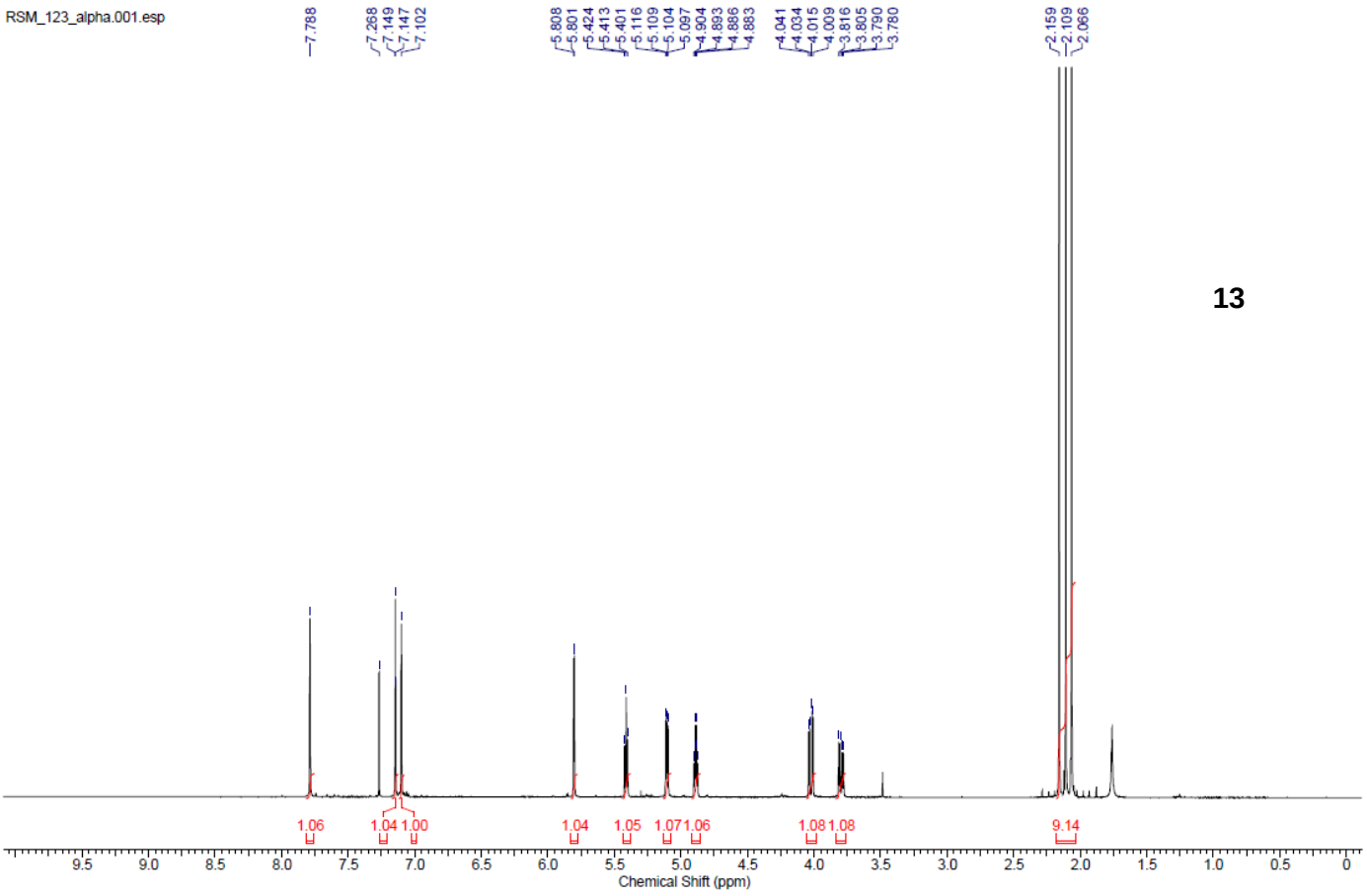
Chemical Shift (ppm)

13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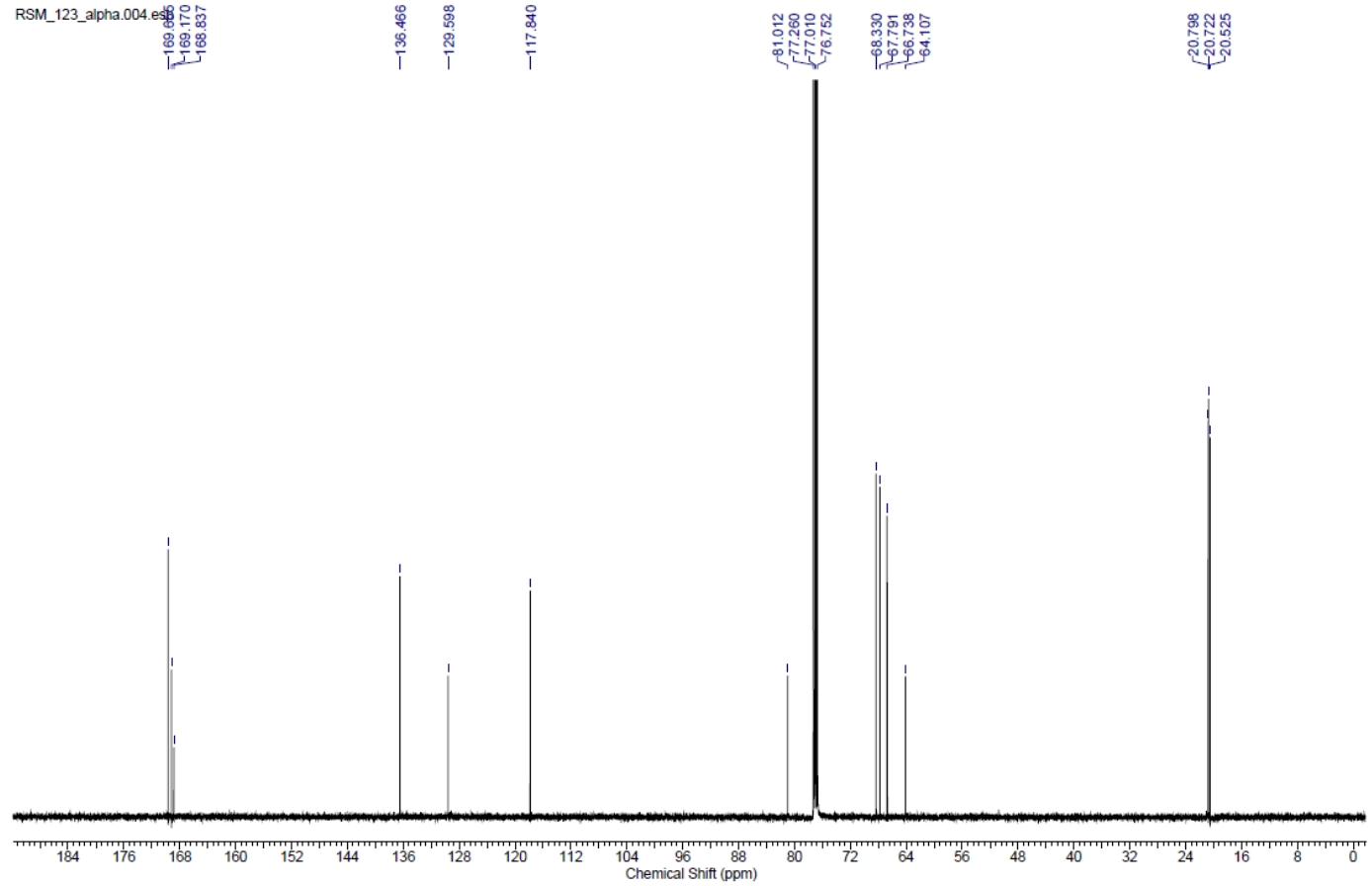
Chemical Shift (ppm)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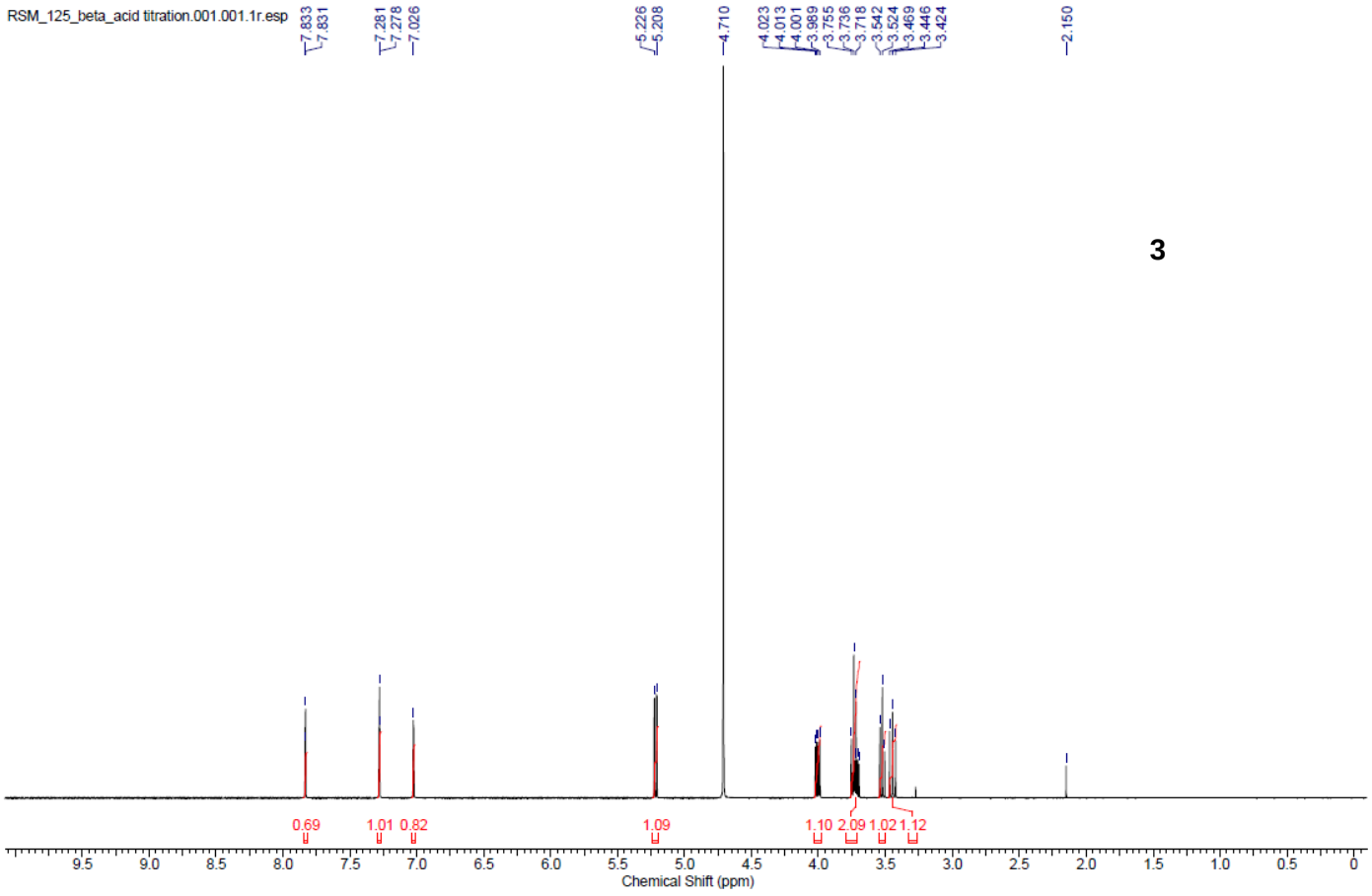
Chemical Shift (ppm)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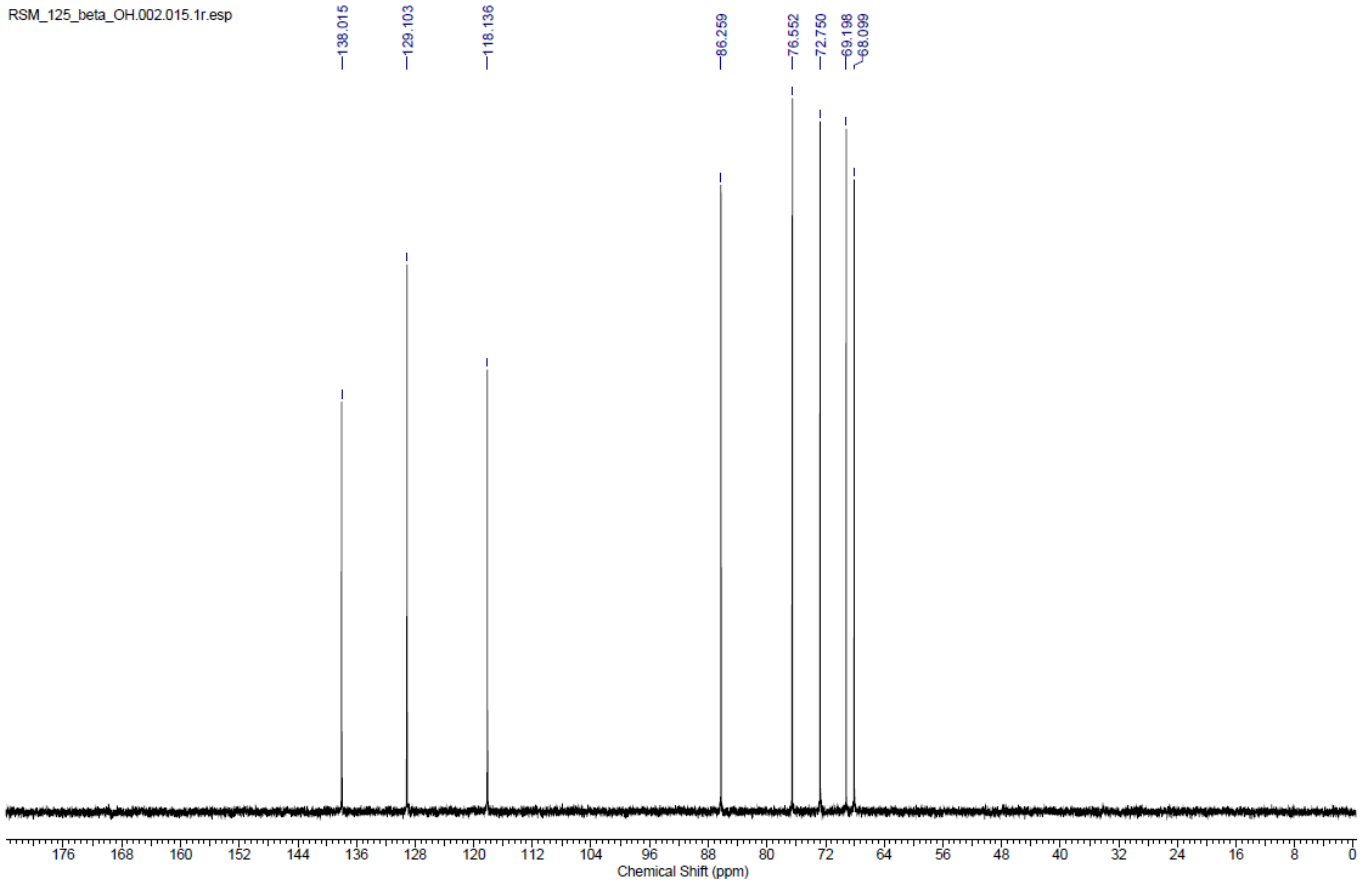
Chemical Shift (ppm)

3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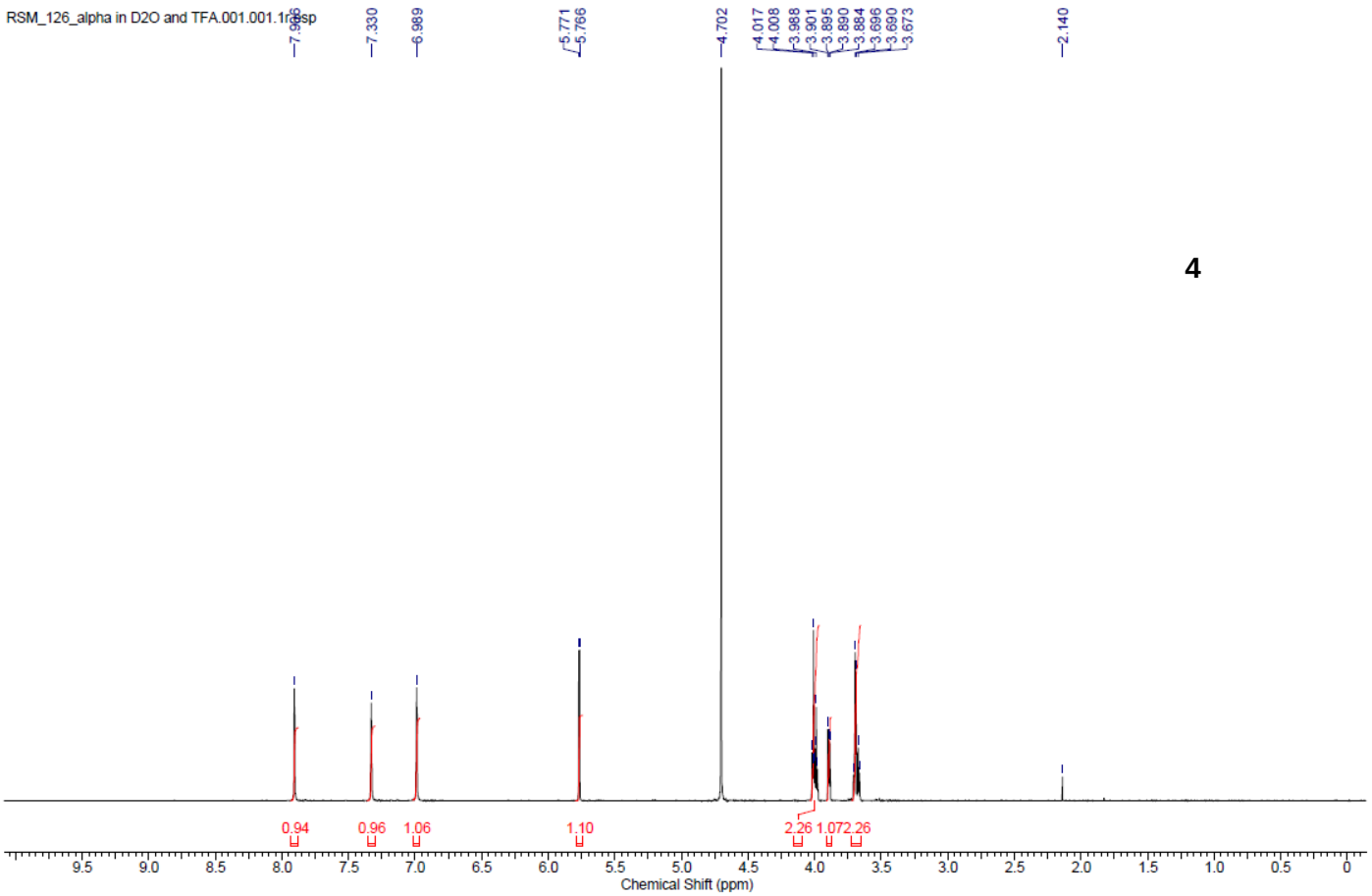
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3.696
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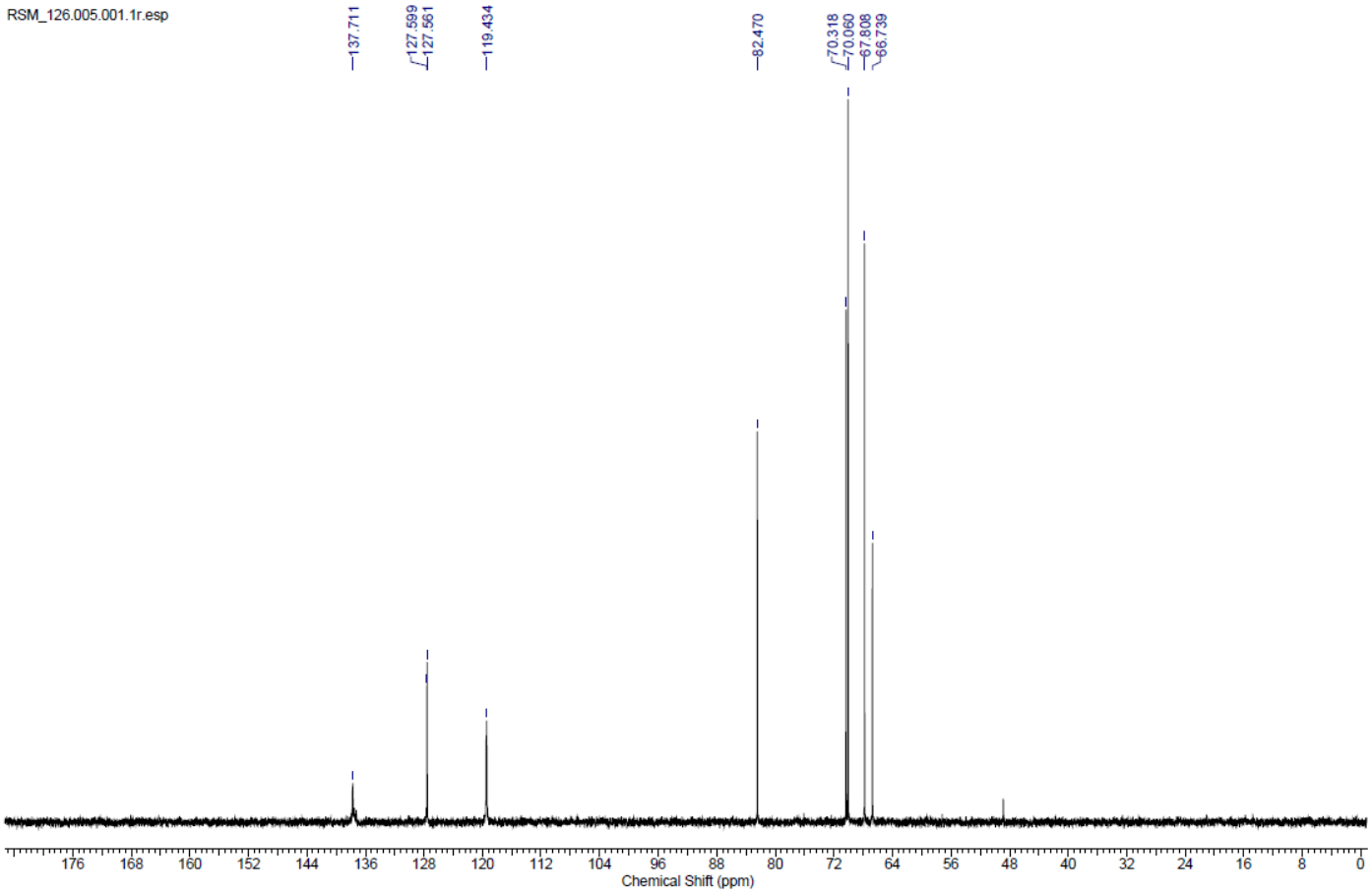
2.26
Chemical Shift (ppm)

4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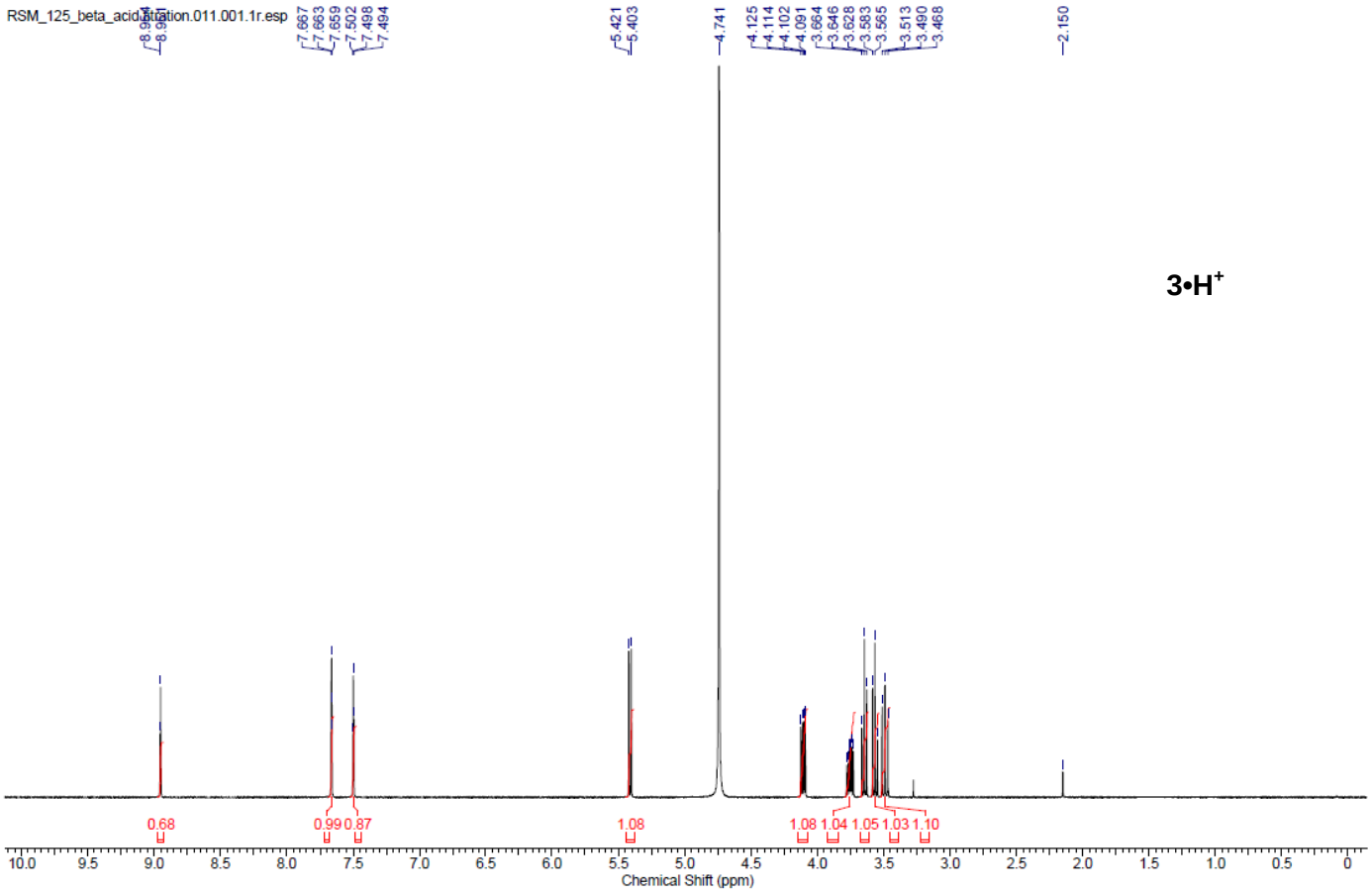
Chemical Shift (ppm)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3.628
3.583
3.565
3.513
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0.87
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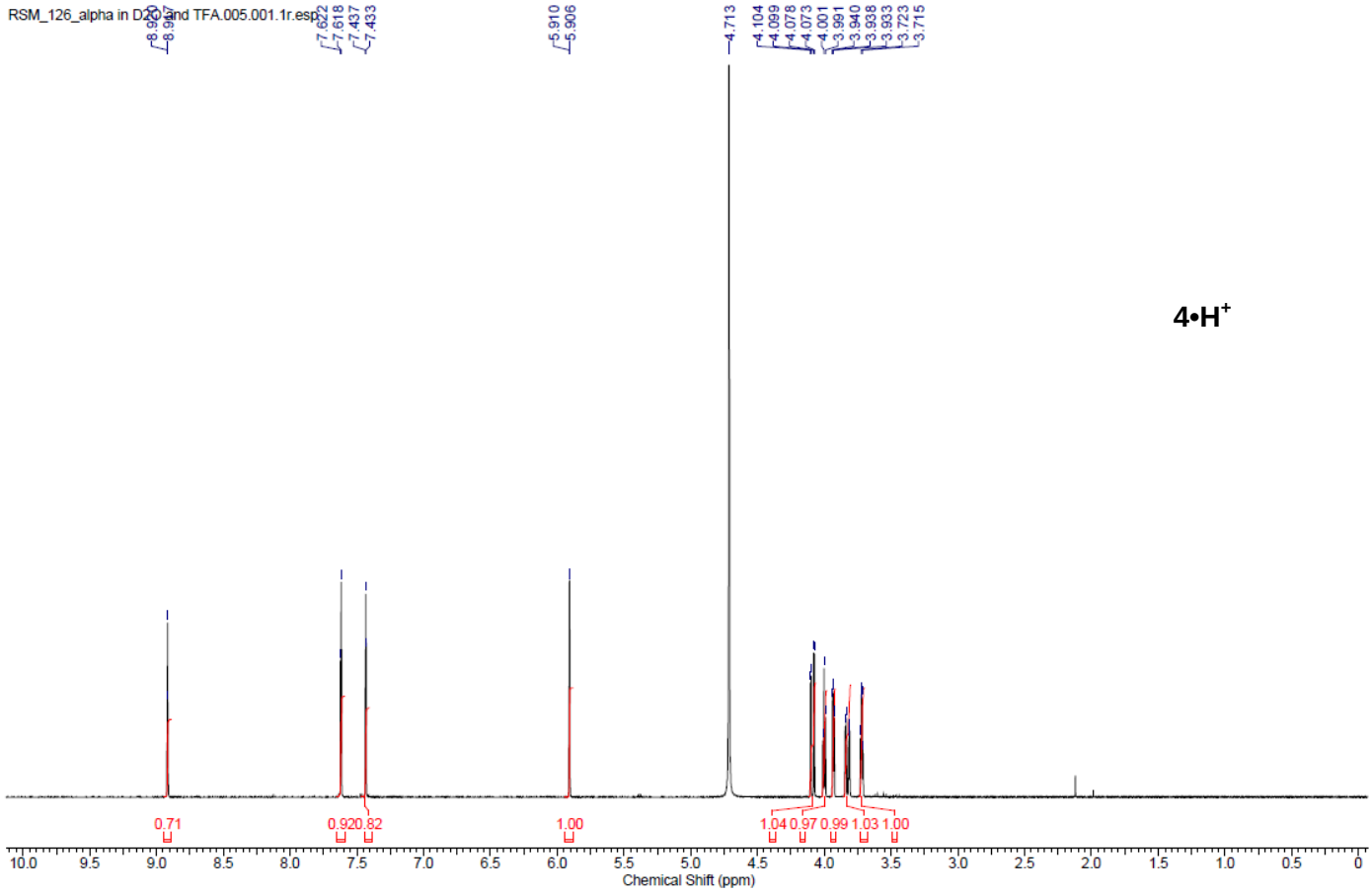
1.08
1.04
1.05
1.03
1.10
Chemical Shift (ppm)

3•H$^+$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8.000
7.997
7.622
7.618
7.437
7.433
5.910
5.906
4.713
4.104
4.099
4.078
4.073
4.001
3.991
3.940
3.938
3.933
3.723
3.715
0.71
0.92
0.82
1.00
1.04
0.97
0.99
1.03
1.00
Chemical Shift (ppm)

4•H$^+$

4. Further analyses of solution phase (NMR) conformational studies

Table S1. Tabulated ^{1}H NMR Data for Compound 4 in Differing Solvents

Compound **4** in DMSO-d6

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.60					
2	1H	1	3.60	2.37				
3	1H	1	3.83	-	4.87			
4	1H	1	3.50	-	-	4.75		
5ax	1H	1	3.91	-	-	-	2.46	
5eq	1H	1	3.62	-	-	-	3.94	12.23

Compound **4.H+** in DMSO-d6

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.86					
2	1H	1	3.72	1.80				
3	1H	1	3.86	-	4.50			
4	1H	1	3.55	-	1.4	4.36		
5ax	1H	1	4.02	-	-	-	2.28	
5eq	1H	1	3.79	-	-	0.95	2.90	12.49

Compound **4** in CD_3OD

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.71					
2	1H	1	3.79	1.94				
3	1H	1	4.03	-	4.72			
4	1H	1	3.64	-	1.27	4.47		
5ax	1H	1	4.12	-	-	-	2.23	
5eq	1H	1	3.83	-	-	1.32	3.35	12.30

Compound **4.H+** in CD_3OD

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.96					
2	1H	1	3.85	1.79				
3	1H	1	4.08	-	4.16			
4	1H	1	3.70	-	-	3.92		
5ax	1H	1	4.25	-	-	-	1.84	

5eq	1H	1	4.01	-	-	1.28	2.32	12.32

Compound **4** in $CDCl_3$:CD_3OD (9:1)

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.57					
2	1H	1	3.76	1.79				
3	1H	1	4.03	-	4.39			
4	1H	1	3.61	-	-	4.07		
5ax	1H	1	4.11	-	-	-	1.95	
5eq	1H	1	3.89	-	-	1.31	2.69	12.40

Compound **4.H+** in $CDCl_3$:CD_3OD (9:1)

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.79					
2	1H	1	3.83	1.63				
3	1H	1	4.07	-	4.12			
4	1H	1	3.67	-	-	3.92		
5ax	1H	1	4.18	-	-	-	1.76	
5eq	1H	1	3.99	-	-	1.28	1.93	12.47

Compound **4** as its peracetylated variant **13** in $CDCl_3$

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	5.86					
2	1H	1	5.16	3.38				
3	1H	1	5.46	-	6.60			
4	1H	1	4.94	-	-	5.92		
5ax	1H	1	4.07	-	-	-	3.62	
5eq	1H	1	3.85	-	-	-	5.34	12.89

Compound **4•H+** as its peracetylated variant **13•H+** in $CDCl_3$

Protons			**δ**	**J_s , 1**	**2**	**3**	**4**	**5ax**
1	1H	1	6.06					
2	1H	1	5.23	2.07				
3	1H	1	5.37	-	3.37			
4	1H	1	4.93	-	-	3.33		
5ax	1H	1	4.35	-	-	-	1.82	
5eq	1H	1	4.29	-	-	1.40	2.24	13.54

Table S2. Tabulated ^{1}H NMR Data for Related Compounds Taken from the Literature. Coupling constant (J/Hz) of different conformers in varied solvents.

Compound	Solvent	Coupling constant (J value Hz)	Predicted conformer	References
	$CDCl_3$	$J_{1,2}$ = 8.8, $J_{2,3}$ =9.2, $J_{3,2}$ = 9.6 $J_{4,3}$ = 9.4, $J_{4,5eq}$ = 5.9, $J_{4,5ax}$ = 10.9, $J_{4,3}$ = 9.6, $J_{5ax,5eq=4}$ = 11.2, $J_{5eq,5ax}$ = 12.0 $J_{5eq,4}$=6.4	$^4C_1$	Observed
	$CDCl_3$	$J_{1,2}$ = 1.5 $J_{4,5eq}$ = 1.2 $J_{4,5ax}$ = 1.9 $J_{5ax,5eq}$ = 13.4	$^1C_4$	Observed
	CD_3NO_2	$J_{1,2}$ = 1.4, $J_{2,4}$ = 1.2, $J_{3,5eq}$ = 1.2 $J_{2,3}$ = 2.7 $J_{3,4}$ = 2.5 $J_{4,5eq}$ = 1.5 $J_{4,5ax}$ = 1.8 $J_{5ax,5eq}$ = 13.4	$^1C_4$	*Chem. Ber.* **1974**, *107*, 1590
	D_2O	$J_{1,2}$ = 1.4, $J_{2,4}$ = 1.2, $J_{3,5eq}$ = 1.2 $J_{2,3}$ = 2.7 $J_{3,4}$ = 2.5 $J_{4,5eq}$ = 1.5 $J_{4,5ax}$ = 1.8 $J_{5ax,5eq}$ = 13.4	$^1C_4$	*J. Chem. Soc. Perkin T II*, **1984**, 1121
	D_2O	$J_{1,2}$ = 2.8 $J_{2,3}$ = 3.1 $J_{3,4}$ = 3.2 $J_{4,5}$ = 5.7	$B_{2,5}$ in crystal	*J. Chem. Soc. Perkin T II*, **1984**, 1121
	$CDCl_3$	$J_{1,2}$ = 2.4, $J_{2,3}$ = 2.9 $J_{3,4}$ = 2.9 $J_{4,5}$ = 2.9 $J_{5,6}$ = 5.9 $J_{6a,6b}$ = 12.7	$^1C_4$ and $^4C_1$	*J. Carbohydr. Chem.* **1998**, *17*, 49
	D_2O	$J_{1,2}$ = 3.9 $J_{2,3}$ = 7.1 $J_{3,4}$ = 5.6	$^1S_3$ but other conformer can't be rule out	*J. Chem. Soc. Perkin T II*, **1984**, 1121
	$CDCl_3$	$J_{1,2}$ = 1.6 $J_{2,3}$ = 3.0 $J_{3,4}$ = 2.8	$^1C_4$ >95%	*Chem. Ber.* **1974**, *107*, 1590

	$(CD_3)_2CO$	$J_{1,2}$ = 2.4, $J_{2,4}$ = 0.9, $J_{3,5eq}$ = 1.3 $J_{2,3}$ = 4.3 $J_{3,4}$ = 4.3 $J_{4,5eq}$ = 2.8 $J_{4,5ax}$ = 3.0 $J_{5ax,5eq}$ = 12.8	$^1C_4$ >85%	*Chem. Ber.* **1974**, *107*, 1590
	$CDCl_3$	$J_{1,2}$ = 3.3 $J_{2,3}$ = 6.5 $J_{3,4}$ = 4.3 $J_{4,5eq}$ = 3.4 $J_{4,5ax}$ = 4.9 $J_{5ax,5eq}$ = 12.9	$^1C_4$ and $^4C_1$ 65 and 35%	Observed
	$CDCl_3$	$J_{1,2}$ = 3.8 $J_{2,3}$ = 6.4 $J_{3,4}$ = 5.8 $J_{5ax,5eq}$ = 12.8	$^1C_4$ and $^4C_1$ No comments about ratio	*J. Org. Chem.* **1996**, *61*, 4514
		Calculated: used for conformer population $J_{1,2}$ = 1.3 $J_{2,3}$ = 3.0 $J_{3,4}$ = 2.8 $J_{4,5}$ = 1.8	$^1C_4$	*Carbohydr. Res.* **1976**, *49*, 275
	D_2O	*Found* $J_{1,2}$ = 4.73 $J_{2,3}$ = 8.19 $J_{3,4}$ = 3.71 $J_{4,5}$ = 5.32	Calc 4C1 $J_{1,2}$ = 2.2 $J_{2,3}$ = 2.7 $J_{3,4}$ = 3.4 $J_{4,5}$ = 1.4	Calc 1C4 $J_{1,2}$ = 8.0 $J_{2,3}$ = 10.2 $J_{3,4}$ = 2.4 $J_{4,5}$ = 1.4	Calc 0S2 $J_{1,2}$ = 4.0 $J_{2,3}$ = 10.2 $J_{3,4}$ = 4.5 $J_{4,5}$ = 6.4	Ave $J_{1,2}$ = 4.9 $J_{2,3}$ = 8.3 $J_{3,4}$ = 3.5 $J_{4,5}$ = 5.5	ratio $^4C_1$/ $^1C_4$/ $^oS_2$ 26: 34: 40, (1:1: 1)	*Chem.Eur. J.* **1999**, *5*, 3185
	$CDCl_3$	$J_{1,2}$ = 9.5 $J_{2,3}$ = 3.2 $J_{3,4}$ = 3.8 $J_{4,5}$ = 1.8	$^{*1}C_4$	*Carbohydr. Res.* **1976**, *49*, 275
	D_2O	$J_{1,2}$ = 8.2 $J_{2,3}$ = 3.1 $J_{3,4}$ = 1.5 $J_{4,5}$ = 1.5	$^{*1}C_4$	*Carbohydr. Res.* **1976**, *49*, 275

*Based on individual coupling constant percentage of $^1C_4$ conformer calculated which then averaged and reported the ratio of these conformations.

5. Relative energies, Cartesian coordinates and vibrational frequencies

Ideally, the structures of the neutral carbohydrate anomers would have been determined in the gas phase using infrared "ion-dip" (IRID) vibrational spectroscopy, a double resonance IR-UV technique that depletes the ground state population of the target molecule whenever the IR radiation is 'in tune' with one of its fundamental vibrational modes. Unfortunately, UV excitation of the imidazole ring, results in rapid dissociation, which compromises the operation of the resonant two photon ionisation scheme.[6] However, past experience in comparing the experimental IRID and theoretically computed vibrational spectra of a wide range of carbohydrates in the gas phase, has confirmed the high accuracy of DFT and *ab initio* theory in predicting their conformational preferences and structures.[7]

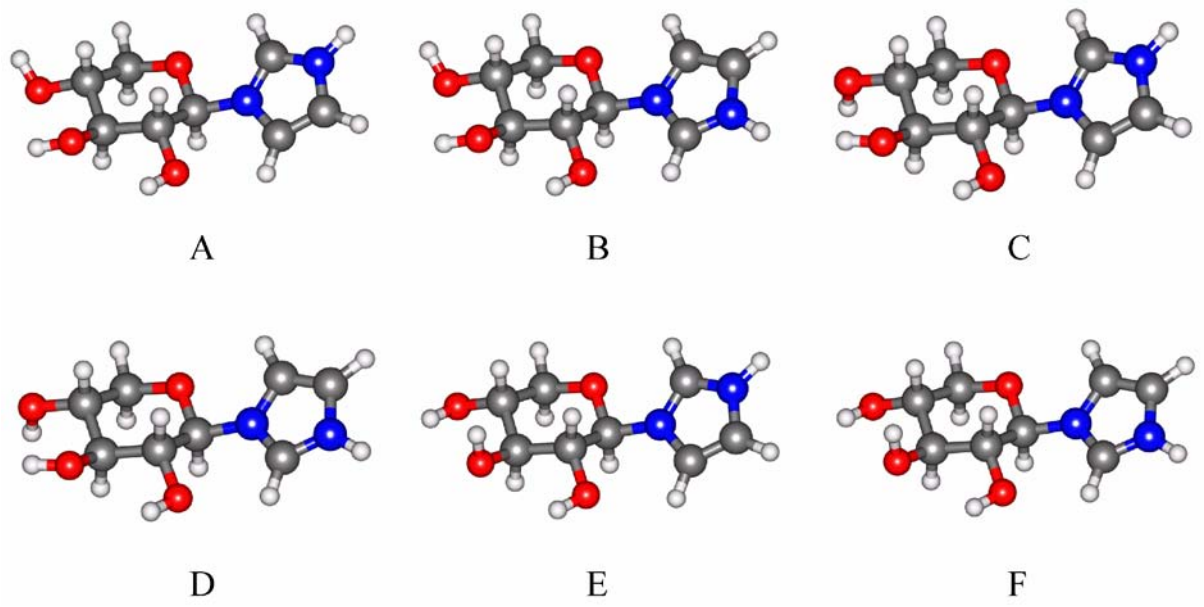
The relative energies, Cartesian coordinates of optimized geometries, and the vibrational frequencies of molecules of interest and their various lowest energy conformers, obtained using the Gaussian 03 package of programs,[8] and derived at the B3LYP/6-311++G(d,p) level of theory are given below. They enable complete and precise reproduction of the calculated structures. In tables with coordinates of optimized geometries, the first column represents atomic number, followed by columns with *x*, *y* and *z* coordinates respectively. The origin of the coordinate system is the centre-of-mass of the molecular system. The geometrical coordinates are taken from the 'Standard orientation' table of the output file for each calculation.

For initial conformational selection prior to calculation we employed a molecular mechanics conformational search using the mixed Monte Carlo multiple minimization and large-scale low-mode method (see the "Computation" section of the main manuscript for more details). Distorted (e.g. skew $^{2}S_{0}$ or half chair) conformers were derived in the case of all the compounds of interest. Notably, all of these more distorted conformers were significantly higher in energy (25-50 kJ/mol) in comparison with the lowest energy structures (found experimentally in the gas phase).

Table S3. **3•H**$^{+}$ protonated on N3';

(a) Relative energies, with respect to those of the lowest energy conformer at 0 K, calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Corresponding optimized structures are provided as well.

Conformer	B3LYP/6-311++G(d,p) energy / kJ mol^{-1}	MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) energy / kJ mol^{-1}
A	0.00	0.00
B	0.65	0.68
C	8.96	9.32
D	9.93	10.29
E	12.87	13.47
F	13.91	14.51



(b) Cartesian coordinates of optimized geometries (in Å) of lowest energy conformers.

A			
6	0.306591	-0.205278	0.514582
6	-0.483777	0.901361	-0.194065
6	-1.973621	0.690380	0.080790
6	-2.407625	-0.723417	-0.305063
6	-1.502873	-1.738155	0.406734
8	-0.113115	-1.474910	0.109157
8	-0.028021	2.144521	0.303342
8	-2.640490	1.698377	-0.654262
8	-3.755187	-0.861329	0.121962
1	-0.643841	2.828444	0.006889
1	-3.583261	1.661098	-0.451533
1	-0.308592	0.824126	-1.275885
1	-2.157302	0.820404	1.157861
1	-2.323101	-0.839344	-1.391828
1	-1.668634	-1.695809	1.489267
1	-1.683028	-2.755906	0.064215
1	-4.219246	-1.506099	-0.422001
6	2.433558	-1.137783	-0.400478
7	1.751020	-0.148052	0.179140
6	2.612129	0.908860	0.442718
6	3.842059	0.535585	0.001161
1	2.022016	-2.084085	-0.703499
1	2.259447	1.821548	0.889246
1	4.782889	1.058167	0.009573
7	3.703674	-0.738032	-0.517833
1	4.443576	-1.295451	-0.923888
1	0.232086	-0.077114	1.602563

B			
6	0.301471	-0.233375	0.496913
6	-0.482942	0.891986	-0.185762
6	-1.970955	0.688724	0.098342
6	-2.417668	-0.712460	-0.318365
6	-1.512522	-1.749897	0.360650
8	-0.124972	-1.487067	0.057789
8	-0.013974	2.127932	0.327511
8	-2.635319	1.721407	-0.604296
8	-3.762990	-0.849128	0.115828
1	-0.640359	2.815947	0.063370
1	-3.578337	1.679402	-0.403212
1	-0.316213	0.833084	-1.269607
1	-2.144194	0.793031	1.179965
1	-2.342400	-0.802514	-1.408221
1	-1.670440	-1.733910	1.445347
1	-1.701432	-2.757408	-0.006435
1	-4.233226	-1.485600	-0.432682
6	2.543634	0.888656	0.333205
7	1.751576	-0.174495	0.162687
6	2.505094	-1.229603	-0.331430
6	3.780493	-0.778265	-0.464732
1	2.220400	1.852642	0.688401
1	2.061913	-2.186344	-0.537923
1	4.670372	-1.271491	-0.815498
7	3.776283	0.537884	-0.044546
1	4.576506	1.156587	-0.026110
1	0.220803	-0.136894	1.588028

C			
6	0.304524	-0.202859	0.523157
6	-0.482204	0.907184	-0.184978
6	-1.975126	0.699992	0.081652
6	-2.406052	-0.717511	-0.306799
6	-1.507795	-1.739300	0.397957
8	-0.117353	-1.472314	0.117258
8	-0.020206	2.146988	0.315857
8	-2.633618	1.705850	-0.661414
8	-3.780097	-0.936659	-0.036003
1	-0.613166	2.840939	-0.002462
1	-3.588096	1.568771	-0.611943
1	-0.307137	0.830236	-1.266532
1	-2.156769	0.843979	1.160454
1	-2.307987	-0.832992	-1.389288
1	-1.668609	-1.722392	1.484950
1	-1.693974	-2.747488	0.033841
1	-3.938880	-0.949197	0.916390
6	2.421381	-1.132685	-0.417503
7	1.747976	-0.149977	0.185027
6	2.616715	0.897186	0.462482
6	3.841706	0.525179	0.006479
1	2.002918	-2.070828	-0.736198
1	2.272784	1.803893	0.927502
1	4.785573	1.042216	0.018637
7	3.692753	-0.737747	-0.535156
1	4.426945	-1.291728	-0.956236
1	0.232584	-0.075380	1.611533

D			
6	0.299264	-0.230376	0.504623
6	-0.481628	0.897859	-0.178046
6	-1.972183	0.698094	0.100160
6	-2.416292	-0.706633	-0.320212
6	-1.517217	-1.751279	0.350179
8	-0.128885	-1.484080	0.065072
8	-0.006217	2.130951	0.337073
8	-2.630579	1.728797	-0.608308
8	-3.789688	-0.920573	-0.042591
1	-0.612110	2.828749	0.052292
1	-3.585248	1.591839	-0.559969
1	-0.315813	0.838308	-1.261704
1	-2.141467	0.815121	1.184180
1	-2.328157	-0.795176	-1.406037
1	-1.670692	-1.762237	1.438669
1	-1.711448	-2.748358	-0.039381
1	-3.937619	-0.974524	0.910070
6	2.547367	0.880535	0.351204
7	1.748637	-0.175833	0.168508
6	2.493818	-1.226797	-0.347440
6	3.770624	-0.779724	-0.480847
1	2.231844	1.840902	0.722489
1	2.044936	-2.177898	-0.567304
1	4.655773	-1.271840	-0.844968
7	3.775763	0.529402	-0.039361
1	4.579387	1.143621	-0.016115
1	0.220232	-0.134320	1.596061

E			
6	-0.304006	-0.207537	-0.489456
6	0.488282	0.909164	0.203796
6	1.981933	0.687896	-0.078655
6	2.423524	-0.730525	0.295335
6	1.492046	-1.747752	-0.369570
8	0.112768	-1.465256	-0.051340
8	0.035739	2.149293	-0.303013
8	2.757747	1.700552	0.551164
8	3.720030	-1.025448	-0.173799
1	0.706548	2.820785	-0.118027
1	2.733256	1.588692	1.510795
1	0.301761	0.838523	1.286231
1	2.159948	0.833105	-1.149303
1	2.363350	-0.851592	1.389022
1	1.637975	-1.731855	-1.455357
1	1.681833	-2.754080	-0.003634
1	4.334988	-0.342936	0.120708
6	-2.444903	-1.131612	0.399212
7	-1.752083	-0.143247	-0.171262
6	-2.608222	0.913954	-0.450714
6	-3.845237	0.542401	-0.028024
1	-2.039029	-2.078051	0.709886
1	-2.248838	1.824876	-0.895616
1	-4.785506	1.065543	-0.053023
7	-3.716122	-0.730261	0.495694
1	-4.463077	-1.286500	0.890604
1	-0.216555	-0.101023	-1.578951

F			
6	-0.298072	-0.235792	-0.469973
6	0.485980	0.899555	0.198378
6	1.978742	0.689871	-0.092878
6	2.436956	-0.717775	0.303877
6	1.503400	-1.757288	-0.324325
8	0.126802	-1.476060	0.001570
8	0.017008	2.131452	-0.323347
8	2.746928	1.723985	0.511407
8	3.728240	-1.012092	-0.180193
1	0.688761	2.808476	-0.162178
1	2.742359	1.622105	1.472461
1	0.307786	0.845447	1.282605
1	2.146769	0.816187	-1.167482
1	2.394772	-0.815798	1.400553
1	1.638694	-1.768328	-1.411833
1	1.704220	-2.752400	0.065447
1	4.348094	-0.332371	0.110002
6	-2.543933	0.887037	-0.355815
7	-1.752213	-0.171224	-0.154795
6	-2.511275	-1.220196	0.344381
6	-3.789672	-0.769784	0.449381
1	-2.218615	1.845715	-0.723276
1	-2.069223	-2.172599	0.572869
1	-4.684182	-1.259518	0.793338
7	-3.781630	0.539330	0.007757
1	-4.583340	1.155035	-0.035083
1	-0.203775	-0.160748	-1.561812

(c) Vibrational frequencies.

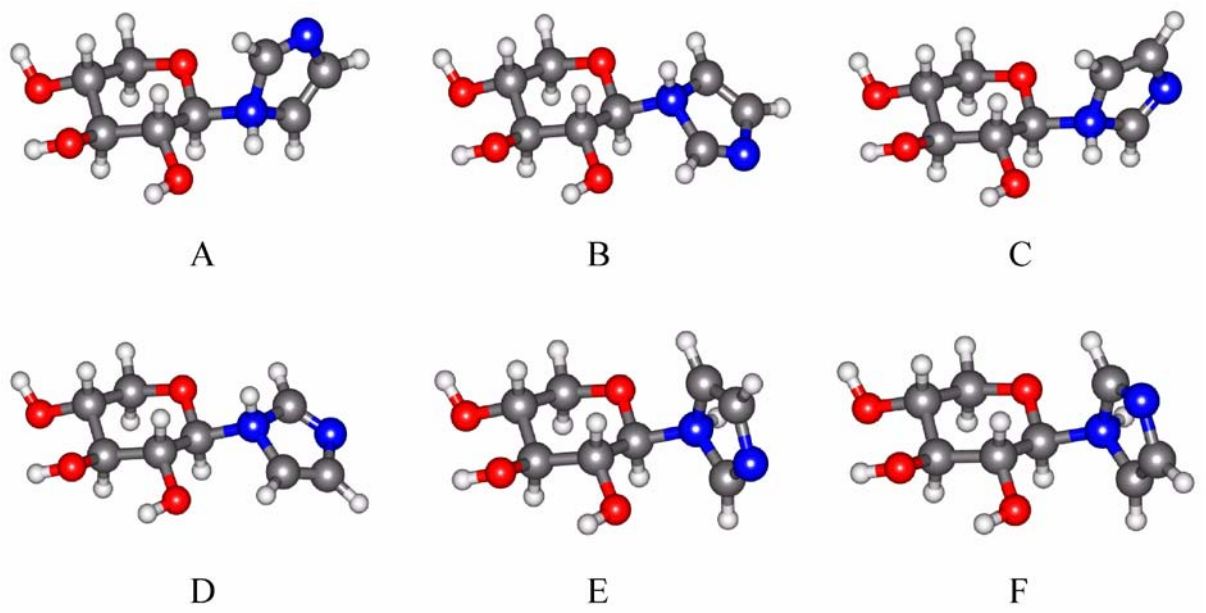
	A		B		C	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	44.9816	1.0327	31.6356	0.6821	44.2296	2.0008
v2	60.2898	2.5623	61.7451	3.3060	59.6958	3.2938
v3	108.6237	0.6631	110.2431	0.5389	106.4622	4.3447
v4	123.2974	4.4389	131.6573	8.2313	121.6679	3.0243
v5	184.4996	6.2685	182.1136	3.1634	185.8642	1.4030
v6	234.7349	44.5132	235.4942	39.0644	227.8744	16.4446
v7	255.3777	19.5661	259.7285	18.6825	256.5211	7.8481
v8	274.0199	2.6713	275.9659	61.3265	270.9308	2.4656
v9	274.5557	60.0534	278.1367	7.2494	299.3778	1.7338
v10	301.8506	5.8684	302.7219	6.1981	305.5713	13.6777
v11	308.1624	4.8738	308.0674	4.2966	319.7491	54.9055
v12	336.4183	5.4488	336.5163	2.6137	337.0554	16.1153
v13	398.3230	77.7272	401.8758	90.5697	395.4482	133.2945
v14	412.0888	35.6799	415.9319	6.9879	406.1772	72.4139
v15	428.2494	104.9117	437.2478	103.2623	418.2836	69.4307
v16	454.9663	16.5948	454.7916	33.6391	454.1041	8.0374
v17	514.3842	2.5106	514.7502	4.1991	515.2551	2.0112
v18	528.5823	12.4261	530.4251	10.8498	529.8257	18.7432
v19	573.6330	28.1394	575.0481	30.2392	574.0841	3.8540
v20	596.7292	7.3163	594.5244	8.3375	595.6912	9.2028
v21	619.1215	39.3989	621.1560	27.3644	619.6105	37.5820
v22	650.1667	65.1154	647.4698	69.1153	650.4281	62.8629
v23	680.7508	49.7214	690.4722	55.8166	681.7539	50.9548
v24	761.3794	50.5595	761.3878	48.8078	760.2963	51.3020
v25	817.3519	1.2613	813.9608	3.0417	817.1179	4.0637
v26	861.5367	15.2172	870.5709	16.1814	861.7497	14.5667
v27	891.1145	2.5142	891.9873	2.4637	889.5090	1.8182
v28	897.3279	5.7987	897.5548	6.4196	895.7033	14.1659
v29	934.3373	4.6242	935.7829	0.4733	934.2243	4.1538
v30	989.7429	61.7358	989.6755	41.6800	990.1792	66.9334
v31	1013.9542	63.1828	1017.2637	94.5107	1011.4177	63.7831
v32	1019.6765	25.9613	1019.4525	11.8920	1015.7839	9.0914
v33	1053.9111	22.7727	1047.1688	21.8162	1045.2057	14.9647
v34	1070.3129	40.0416	1069.7969	35.6726	1054.2336	23.2374
v35	1079.0885	7.5749	1079.9625	8.9800	1086.9788	212.7657
v36	1087.5693	155.8842	1087.4696	186.6497	1096.1419	27.9430
v37	1097.4363	118.4870	1092.2543	68.5453	1109.2598	86.9753
v38	1119.6141	110.6463	1114.2637	104.6891	1124.0170	53.6962
v39	1124.9533	31.1366	1122.3153	25.7496	1133.5155	78.4587
v40	1135.0382	12.0268	1133.1443	29.2088	1138.0502	21.4716
v41	1145.1084	42.8249	1144.6092	97.5954	1155.3146	24.5749
v42	1159.6779	23.8085	1170.4631	10.6624	1160.4649	28.7968
v43	1209.9381	13.0276	1209.8564	12.5911	1209.7949	22.9012
v44	1235.1102	58.9803	1234.5681	68.7432	1237.4933	14.7277
v45	1253.4862	31.1918	1252.3773	31.8351	1254.4933	29.0063
v46	1260.1594	12.7009	1260.6449	10.8995	1266.1821	7.0596
v47	1268.8296	14.9835	1284.7830	13.7825	1273.7201	34.8672
v48	1313.0876	20.4611	1311.1233	17.8458	1312.8649	41.1696
v49	1337.3648	27.0408	1337.4052	26.4530	1326.7790	41.3552
v50	1339.8481	7.1075	1341.0932	19.7683	1339.7011	11.9010
v51	1349.8156	22.1501	1349.8936	10.1690	1346.7972	12.7830
v52	1355.0069	55.2020	1356.9616	29.0563	1357.5323	37.9555
v53	1370.0539	7.2732	1371.2355	2.6419	1380.9250	4.2717
v54	1375.6338	4.6628	1373.9920	9.5974	1397.3330	22.6103
v55	1410.2160	1.4051	1408.6833	24.0301	1410.7550	2.1271
v56	1429.5169	8.9450	1430.8351	7.4433	1423.8553	6.8901
v57	1433.1418	5.9898	1434.5815	8.9150	1428.4731	14.3652
v58	1440.7497	2.8852	1441.6527	3.6150	1433.1286	11.6973
v59	1470.3121	10.9181	1470.1688	10.1958	1470.4375	11.0211
v60	1504.3401	10.1093	1504.0739	10.4744	1502.9619	9.2566
v61	1561.3202	47.0922	1560.4466	32.8937	1561.4019	46.7318
v62	1614.1401	23.9122	1605.4058	27.5873	1614.0489	24.2087
v63	2986.4503	9.3154	2986.0529	9.9466	2948.8237	24.9537
v64	3005.7423	3.7855	3006.3481	0.4750	3002.8707	28.8560
v65	3022.3490	14.7794	3021.1406	18.0436	3007.7093	1.2599
v66	3029.5821	6.4983	3028.6379	4.1334	3022.5341	28.1147
v67	3041.8550	47.3270	3041.0537	49.4279	3076.8159	14.0956
v68	3133.5215	7.9711	3133.8315	7.6729	3143.0273	3.2561
v69	3285.8496	28.6989	3287.5021	47.8790	3285.9032	28.3980
v70	3303.4216	56.5365	3290.2509	39.7851	3303.3875	59.9878
v71	3308.4179	11.3869	3315.5275	20.0687	3308.0305	8.2030
v72	3622.1230	211.5541	3620.3261	205.5805	3621.1826	213.5917
v73	3786.6311	111.5690	3781.8014	118.1322	3790.5644	107.6637
v74	3814.0925	94.8968	3813.0598	95.6020	3792.2430	49.5974
v75	3841.2319	90.7958	3840.5873	91.0347	3803.8917	90.4206

	D		E		F	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	30.8357	0.6807	46.0936	1.0564	32.7108	0.3779
v2	61.5611	3.4047	60.5534	1.7623	61.6084	2.1750
v3	108.9257	3.7300	107.7889	2.3958	108.7494	2.3371
v4	130.5566	5.6772	123.5230	2.2958	130.7130	5.9311
v5	183.2720	1.0979	181.4645	14.8652	178.6808	10.1807
v6	227.8388	15.1412	231.2606	27.0218	229.9906	30.5902
v7	260.2653	8.2065	256.4602	4.6414	261.7176	4.7061
v8	273.9826	2.0124	274.4125	4.6594	276.2198	5.3022
v9	299.2748	2.0729	293.7549	3.3435	292.9042	4.4134
v10	305.5083	11.6474	305.8253	23.2438	304.5374	22.4216
v11	322.1648	54.7691	323.1636	28.4802	322.1703	34.7862
v12	337.0057	11.6317	336.5749	0.1560	336.9522	1.1738
v13	399.6899	152.5748	380.4272	114.7410	380.6235	110.1432
v14	410.5273	20.9923	414.0828	8.4866	414.6445	5.0513
v15	426.9724	98.6800	450.9688	25.7795	450.1126	15.3321
v16	452.8821	13.3299	467.7979	151.1010	470.1291	156.1673
v17	516.3076	4.2468	521.6840	5.5120	521.4553	9.4346
v18	531.1769	16.7818	527.5692	8.7831	530.0674	6.1339
v19	575.3668	4.8907	585.1887	22.8384	585.7085	21.7414
v20	593.3290	9.8069	595.6727	1.3220	593.7102	2.1911
v21	621.2679	26.3975	619.9418	34.7861	621.4789	25.7964
v22	647.6423	67.4186	650.3340	40.6118	647.8553	0.6999
v23	691.2772	56.2548	682.5455	55.3164	691.2464	0.3388
v24	761.5279	48.5931	762.4589	50.0332	762.7077	0.4162
v25	813.4773	5.4731	818.0114	2.8763	814.4712	4.7404
v26	868.5800	16.1702	863.1707	18.5456	869.8752	19.1811
v27	892.2334	1.4680	891.9476	3.6116	893.6874	3.5352
v28	895.4440	15.4607	896.9326	15.1752	896.3252	16.0265
v29	935.6619	1.0240	934.2430	4.8082	935.7094	0.8023
v30	990.1142	46.0305	988.1155	87.4913	987.1596	63.0847
v31	1010.6194	59.9331	1009.8506	87.8532	1015.3422	129.0193
v32	1019.5999	28.1587	1028.4279	41.3894	1030.9510	27.2074
v33	1044.2393	11.8772	1039.4712	33.8594	1033.6790	26.1200
v34	1047.7472	22.6506	1056.3037	10.2361	1049.0491	15.6488
v35	1085.8953	219.6774	1074.0799	76.7502	1074.8832	82.1318
v36	1093.9549	27.7689	1096.1687	18.0199	1092.1214	28.1827
v37	1104.3488	82.7620	1111.0825	185.8241	1108.9268	125.3480
v38	1120.7573	4.4059	1120.5762	52.7855	1119.6345	14.4260
v39	1133.0396	140.0221	1128.1056	7.8802	1122.0859	90.9976
v40	1137.3112	22.9804	1133.9275	51.7641	1131.3743	38.0279
v41	1152.4233	64.6221	1157.9144	6.1589	1157.6810	93.8798
v42	1172.2771	2.5381	1163.7465	52.0498	1173.5133	0.0453
v43	1210.3764	23.6441	1221.5358	13.8829	1221.5933	13.1561
v44	1236.0214	13.4326	1228.9504	52.4169	1227.6115	56.5119
v45	1255.8987	23.0964	1255.7682	33.4676	1253.7534	26.1239
v46	1266.7848	56.2605	1266.4377	14.2575	1275.2783	32.0639
v47	1287.9827	13.4735	1281.5695	28.8519	1283.0519	34.5092
v48	1311.3672	16.2957	1291.8563	19.0889	1299.1625	9.6194
v49	1327.9715	47.2024	1313.6654	16.2070	1311.0402	18.7999
v50	1338.5298	9.6560	1332.2029	6.4648	1330.9649	15.5982
v51	1348.3108	15.1544	1350.9173	79.8059	1353.7055	21.8509
v52	1358.9606	5.4964	1365.6573	3.4554	1364.5009	6.1561
v53	1379.4864	16.4491	1380.0745	7.9034	1380.6062	15.1239
v54	1397.2855	33.2490	1397.0229	20.0233	1395.8725	15.1050
v55	1409.3881	3.4853	1407.7695	5.0337	1408.6153	33.6475
v56	1425.7537	10.5050	1418.5685	1.9813	1418.5770	1.5341
v57	1429.0421	19.7699	1429.2033	5.5859	1429.9732	4.9705
v58	1434.7575	12.2859	1436.8373	27.1944	1436.8076	28.8523
v59	1470.2522	10.0560	1470.3947	10.9781	1469.8277	9.4767
v60	1501.7952	9.5882	1506.6994	10.6221	1505.4048	10.9669
v61	1560.5444	33.0567	1560.8669	46.3609	1560.6134	32.9945
v62	1605.5808	27.8061	1613.7764	24.0207	1605.3449	27.7503
v63	2948.8914	24.6619	2960.1333	22.7820	2962.5374	23.8796
v64	2998.5667	29.2116	2981.3762	24.6955	2987.6682	16.5505
v65	3006.0831	3.7039	3017.5954	12.1337	3012.0880	16.9441
v66	3023.6117	27.2630	3040.9759	15.4141	3037.6803	16.6870
v67	3077.7428	13.3763	3058.2685	17.9708	3058.6399	17.5483
v68	3143.2074	2.9914	3150.6970	3.1564	3151.2102	2.9643
v69	3287.5845	41.7570	3285.5199	29.0391	3287.1860	44.1995
v70	3291.0162	45.0801	3302.6068	61.5375	3290.2399	42.8851
v71	3315.6216	20.4699	3307.2469	7.6468	3314.5708	20.6724
v72	3619.6757	206.9343	3620.6651	213.7250	3619.1380	206.5311
v73	3785.7475	117.2245	3778.7160	114.5866	3774.9322	116.4459
v74	3792.6924	47.7647	3782.7892	28.3366	3782.1980	33.0817
v75	3802.3608	90.1381	3813.4058	76.5521	3815.5471	75.6186

Table S4. **3•H**$^{+}$ protonated on N1';

(a) Relative energies, with respect to those of the lowest energy conformer at 0 K, calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Corresponding optimized structures are provided as well.

Conformer	B3LYP/6-311++G(d,p) energy / kJ mol^{-1}	MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) energy / kJ mol^{-1}
A	0.00	0.00
B	0.37	2.01
C	0.58	0.55
D	1.53	3.05
E	6.16	4.10
F	9.40	7.75



(b) Cartesian coordinates of optimized geometries (in Å) of lowest energy conformers.

A			
6	-0.346724	0.024503	-0.498372
6	0.622084	1.022083	0.124688
6	2.038420	0.538335	-0.174426
6	2.203591	-0.904334	0.326620
6	1.090715	-1.802090	-0.243929
8	-0.222801	-1.244212	0.029901
8	0.288601	2.276402	-0.440465
8	2.902028	1.451459	0.467211
8	3.474390	-1.338295	-0.129074
1	0.959973	2.930464	-0.203485
1	3.815865	1.231344	0.247465
1	0.494950	1.042381	1.215636
1	2.203604	0.548072	-1.262027
1	2.156393	-0.899868	1.421885
1	1.221642	-1.921785	-1.325334
1	1.084524	-2.785858	0.221205
1	3.839643	-2.005703	0.461495
6	-2.312652	0.232664	1.150770
6	-2.831451	-0.086924	-1.070567
6	-3.759736	-0.576296	-0.248809
7	-3.422135	-0.362682	1.117050
1	-1.748929	0.562188	2.010954
1	-2.741142	-0.047765	-2.143498
1	-4.678575	-1.080586	-0.505022
1	-0.246091	0.044816	-1.591730
7	-1.779191	0.505556	-0.229797
1	-1.715801	1.531704	-0.374752

B			
6	-0.377895	-0.225782	-0.124471
6	0.534517	0.920974	0.313277
6	1.938240	0.644071	-0.235356
6	2.438866	-0.730035	0.212861
6	1.403090	-1.794303	-0.175166
8	0.093934	-1.445989	0.346794
8	0.009907	2.140509	-0.164791
8	2.733840	1.712430	0.235029
8	3.664223	-0.949507	-0.466652
1	0.708943	2.808495	-0.113269
1	3.614735	1.646796	-0.154329
1	0.592380	0.924932	1.413017
1	1.898754	0.652342	-1.334933
1	2.582711	-0.720098	1.299386
1	1.352950	-1.893299	-1.265088
1	1.631053	-2.766546	0.257659
1	4.237288	-1.533069	0.041805
6	-2.623967	1.053674	0.013215
6	-2.660908	-1.253769	0.231653
6	-3.773806	-0.762433	-0.313918
7	-3.730213	0.653796	-0.436986
1	-2.208226	2.048170	0.078186
1	-2.324947	-2.245760	0.477622
1	-4.645248	-1.305203	-0.646659
1	-0.549068	-0.217859	-1.208284
7	-1.775822	-0.105326	0.507758
1	-1.633133	-0.012117	1.523868

C			
6	-0.344963	0.020163	-0.482600
6	0.626120	1.024921	0.123963
6	2.041469	0.536865	-0.173723
6	2.206669	-0.900244	0.342243
6	1.094843	-1.803081	-0.221878
8	-0.219854	-1.245365	0.047889
8	0.291324	2.270015	-0.460299
8	2.907900	1.456351	0.454808
8	3.477897	-1.338861	-0.107885
1	0.965673	2.926699	-0.239920
1	3.820824	1.231519	0.235883
1	0.500184	1.059979	1.214252
1	2.203828	0.534095	-1.261853
1	2.157877	-0.885495	1.437299
1	1.089463	-2.783381	0.250481
1	1.226826	-1.930795	-1.302249
1	3.843413	-1.999102	0.490508
6	-2.827990	-0.166718	-1.053781
6	-2.321492	0.317106	1.139236
6	-3.475806	-0.336324	1.006705
7	-3.768697	-0.628560	-0.355207
1	-2.699591	-0.193907	-2.127478
1	-1.791710	0.702168	1.993242
1	-4.161245	-0.640357	1.782578
1	-0.249890	0.037068	-1.577678
7	-1.778145	0.504673	-0.216817
1	-1.729000	1.515473	-0.448006

D			
6	-0.382644	-0.195610	-0.137754
6	0.544726	0.939005	0.302686
6	1.948817	0.639919	-0.235550
6	2.427488	-0.739523	0.218351
6	1.382407	-1.789820	-0.180744
8	0.072633	-1.425516	0.329252
8	0.044642	2.165780	-0.180078
8	2.755989	1.697682	0.239396
8	3.656425	-0.976042	-0.448845
1	0.754779	2.820993	-0.118401
1	3.638543	1.619255	-0.143775
1	0.595487	0.942745	1.402973
1	1.917625	0.647178	-1.335390
1	2.560435	-0.731266	1.306266
1	1.340937	-1.886600	-1.271124
1	1.593502	-2.765600	0.252669
1	4.217322	-1.565434	0.066423
6	-2.673822	-1.248352	0.205022
6	-2.614259	1.061468	0.047035
6	-3.752713	0.535087	-0.405957
7	-3.768755	-0.884063	-0.300055
1	-2.311149	-2.238531	0.435501
1	-2.220700	2.061124	0.112443
1	-4.603923	1.054013	-0.819011
1	-0.558208	-0.178241	-1.220444
7	-1.776208	-0.067785	0.502149
1	-1.627424	-0.024976	1.520876

E			
6	-0.272925	-0.514954	-0.634219
6	0.221462	0.752427	0.050266
6	1.741807	0.820578	-0.119592
6	2.402865	-0.466198	0.382872
6	1.769041	-1.674936	-0.320490
8	0.326755	-1.669076	-0.147461
8	-0.448361	1.832455	-0.563377
8	2.145575	1.969531	0.594945
8	3.778850	-0.363889	0.053715
1	-0.046324	2.659486	-0.263989
1	3.087965	2.117678	0.447747
1	-0.003213	0.706046	1.124258
1	1.977774	0.930563	-1.188764
1	2.258570	-0.540788	1.467008
1	2.013764	-1.660950	-1.388373
1	2.101284	-2.619691	0.105502
1	4.316889	-0.865952	0.674876
6	-2.736213	0.274987	-0.922450
6	-2.223874	-0.898886	1.003518
6	-3.280252	-0.095911	1.144360
7	-3.582460	0.609550	-0.052369
1	-2.635848	0.606987	-1.945504
1	-1.719202	-1.590848	1.655687
1	-3.887774	0.052187	2.024059
1	-0.178852	-0.417139	-1.724519
7	-1.771413	-0.761238	-0.392862
1	-1.961931	-1.650584	-0.879544

F			
6	-0.286215	-0.482786	-0.663382
6	0.224462	0.775416	0.032291
6	1.749713	0.810921	-0.120767
6	2.386858	-0.485292	0.384431
6	1.742560	-1.677801	-0.335070
8	0.299419	-1.647042	-0.177094
8	-0.400246	1.883237	-0.575303
8	2.165754	1.953851	0.596695
8	3.767825	-0.401350	0.071209
1	0.060498	2.684627	-0.290087
1	3.111893	2.086028	0.458677
1	-0.009767	0.727870	1.105452
1	1.996709	0.917647	-1.187905
1	2.229019	-0.563988	1.466384
1	2.053302	-2.631699	0.086759
1	1.998626	-1.659444	-1.400131
1	4.291828	-0.912328	0.697058
6	-2.213905	-0.862148	1.020111
6	-2.759149	0.233983	-0.939840
6	-3.578440	0.534969	0.067713
7	-3.224795	-0.149557	1.263745
1	-1.668464	-1.533709	1.666713
1	-2.697245	0.560999	-1.963767
1	-4.421172	1.208362	0.060191
1	-0.190483	-0.380253	-1.752306
7	-1.784436	-0.740911	-0.419849
1	-1.947450	-1.663971	-0.851285

(c) Vibrational frequencies.

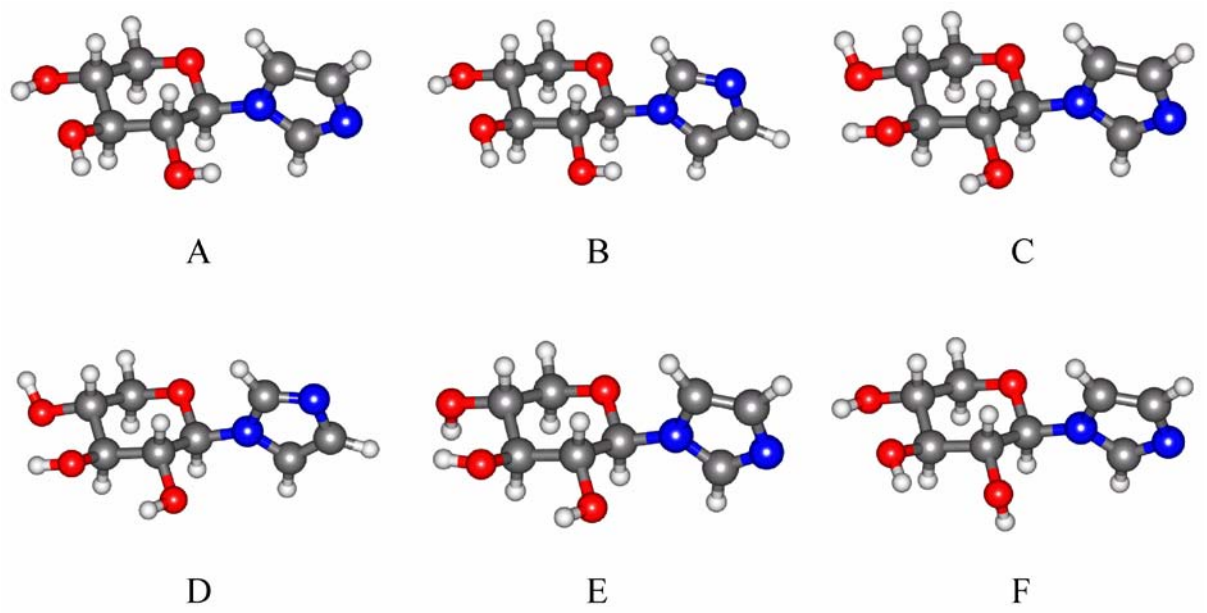
	A		B		C	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	59.2480	2.2107	47.0663	1.2115	54.4829	2.2799
v2	71.4675	3.16	64.5244	0.2787	74.9263	2.0689
v3	88.2455	0.4393	112.7147	0.2734	87.6562	1.3925
v4	114.2582	167.3437	140.7840	3.4086	114.1507	0.3933
v5	167.3437	215.2427	153.8068	0.9258	170.9677	13.6599
v6	215.2427	0.6334	223.8209	53.8385	211.8489	1.5968
v7	237.1007	58.4937	249.3506	26.6309	235.9240	61.0619
v8	253.5007	28.5582	267.4921	18.8922	252.1876	26.7959
v9	275.7835	34.5256	272.1689	44.9794	272.3406	28.0186
v10	284.1189	28.9001	291.9675	6.5675	282.6458	34.0626
v11	306.6324	2.2875	307.4239	3.6742	308.9982	2.6208
v12	324.7704	6.4739	312.3995	6.9048	320.9517	4.3422
v13	388.1310	60.1743	395.1850	93.3390	386.7557	48.9218
v14	400.2246	66.4558	411.3694	1.3161	398.9267	94.9104
v15	417.5466	95.6793	440.0097	1.8620	415.0276	83.0907
v16	456.7845	10.3969	458.0810	146.5050	455.6167	5.5865
v17	476.3185	1.2274	493.6116	2.8207	476.8827	1.3143
v18	524.2380	21.1570	518.6655	13.3766	526.2359	15.2404
v19	571.2338	22.2993	555.5656	1.2302	567.7546	24.9823
v20	577.3115	3.6500	572.3036	17.5823	579.3061	4.8180
v21	607.0492	39.0377	595.0380	28.6001	607.4585	32.3414
v22	693.0147	39.2356	642.2608	20.8282	694.1417	37.8496
v23	745.9113	18.1335	758.0404	49.9434	750.3375	7.0441
v24	755.2481	2.2754	789.4371	24.8436	788.1164	34.6063
v25	834.5901	13.5343	825.4932	62.8042	816.2568	7.1697
v26	863.4801	17.4954	865.3626	87.9418	865.9054	18.9762
v27	879.6742	84.5016	882.1697	65.6886	889.0220	7.3752
v28	888.5220	6.2632	894.8754	15.2900	890.2368	102.5562
v29	952.2148	1.9169	953.2321	4.4548	938.4139	30.5645
v30	966.6399	23.4476	965.2337	1.9226	952.6066	2.0428
v31	988.5729	61.0245	971.6454	14.7933	992.3804	30.2968
v32	1006.7627	23.8146	1011.2034	63.3395	1007.2148	23.7956
v33	1030.4395	99.4364	1023.5550	73.9863	1033.4302	53.5458
v34	1044.8946	17.5390	1041.7998	25.3769	1045.2076	56.5463
v35	1050.5020	35.7306	1054.0415	110.6159	1049.9506	36.2862
v36	1066.0336	38.6385	1073.3112	6.5765	1066.4959	36.0563
v37	1078.2331	108.9748	1081.6714	36.3280	1079.8674	132.0113
v38	1094.8501	88.0904	1087.7631	182.5915	1092.7798	84.0485
v39	1126.9133	104.9955	1124.0746	107.2740	1126.0662	98.6458
v40	1135.5374	22.1656	1134.5685	15.5479	1136.3068	18.1017
v41	1138.9026	93.1829	1139.7126	4.6066	1140.2534	109.5306
v42	1151.1339	17.4466	1148.2880	13.9998	1152.7966	12.1430
v43	1209.8604	12.5620	1199.9133	39.7965	1207.9691	5.9717
v44	1225.9428	63.6598	1205.9017	17.4165	1225.3580	84.5103
v45	1232.9297	46.5432	1234.8286	55.6320	1237.5658	29.7196
v46	1249.3317	18.7205	1250.2699	4.3580	1246.2610	37.2680
v47	1256.9618	23.1988	1258.3920	41.4521	1254.6875	28.5303
v48	1291.8607	33.8241	1275.4429	7.8574	1282.3305	51.0713
v49	1305.8392	57.8585	1303.6639	35.5885	1303.9259	36.7867
v50	1330.4853	18.1591	1328.2547	4.2267	1334.2250	17.9636
v51	1340.9842	12.5093	1335.0155	2.7808	1340.8477	15.3579
v52	1347.0366	28.6779	1341.2733	25.8838	1346.8329	31.6650
v53	1358.5972	23.9400	1352.6431	2.0112	1356.9838	21.2606
v54	1365.4523	5.9396	1370.1089	8.6630	1365.8693	5.7004
v55	1378.7807	24.2192	1374.8971	34.9314	1378.2714	19.8390
v56	1410.2682	5.7901	1394.4927	47.4576	1417.1358	4.4220
v57	1433.9894	25.1908	1431.2109	9.1923	1434.4737	21.6491
v58	1435.1361	1.4780	1435.2992	9.0682	1436.2785	7.1868
v59	1445.2701	0.2882	1441.9029	3.2098	1445.6552	0.4815
v60	1501.3143	12.5748	1500.7114	10.6551	1501.8991	12.3827
v61	1616.2678	3.7111	1613.5608	3.7361	1614.3826	4.6249
v62	1679.0477	48.2636	1676.8642	51.2192	1680.2923	39.1602
v63	2990.4939	8.4494	2975.3168	11.1087	2989.9888	8.4736
v64	3005.1801	4.2896	2991.5029	16.1004	3001.9748	1.9379
v65	3022.2277	13.8688	3032.3495	2.3210	3017.8363	18.8550
v66	3029.8173	8.9187	3036.4321	9.6621	3030.0997	7.1479
v67	3042.7317	38.5710	3045.4901	36.0449	3042.7668	39.7065
v68	3143.1298	4.0136	3140.8332	4.7200	3143.1782	4.1224
v69	3254.2638	175.7936	3257.0831	16.3523	3238.5755	14.8245
v70	3256.1539	16.5888	3262.8599	43.9573	3258.2745	97.9686
v71	3257.6381	17.0538	3300.2432	17.6682	3260.5246	87.1586
v72	3282.2949	10.6402	3363.8550	67.4355	3292.8612	11.8602
v73	3794.2167	136.4459	3766.7315	132.1931	3795.3353	136.7442
v74	3810.9525	104.0084	3811.5360	105.5614	3810.3467	103.5756
v75	3837.1814	99.3493	3838.3932	101.9228	3837.1752	99.0739

	D		E		F	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	49.4979	2.1263	44.2258	0.3465	36.1717	0.6988
v2	62.3114	0.4819	78.2180	0.9734	75.0444	1.5710
v3	111.5799	0.2530	104.8208	1.0702	104.3097	1.9656
v4	137.4817	6.0802	110.3975	0.8685	107.0528	0.6982
v5	153.9744	1.2594	177.7224	4.1101	173.3828	0.6691
v6	222.1098	53.4335	224.5246	41.8407	223.2128	47.3175
v7	246.6368	25.9989	240.4521	2.3146	243.4496	3.2504
v8	267.1546	10.9812	244.5465	33.2751	244.5514	29.8263
v9	271.5119	49.2822	273.5369	52.5958	272.7907	55.8452
v10	298.7309	7.2728	286.9834	7.9881	290.7402	3.5423
v11	306.9359	7.3044	309.9716	4.9922	311.6121	7.8547
v12	308.1646	3.1207	316.7935	15.2747	314.1202	8.8048
v13	393.8821	94.5601	390.1618	50.6396	392.9988	68.4375
v14	410.5632	0.7322	402.4267	78.2445	405.7901	29.3906
v15	439.4215	1.1661	419.9604	86.5025	423.9953	121.1645
v16	456.6724	140.0036	446.0373	8.1727	445.8999	4.7973
v17	500.3388	5.6343	488.9364	7.0477	493.3601	11.6993
v18	520.9349	12.0238	527.2826	13.3936	525.9094	12.4456
v19	545.8942	4.6818	543.9639	34.7811	541.6415	28.7067
v20	574.3363	30.2988	574.0516	33.7299	577.5251	1.1879
v21	594.8603	10.2682	604.4203	9.8073	602.6163	39.0595
v22	643.0835	18.6826	685.3639	20.4603	678.3447	28.8185
v23	766.0336	41.4789	758.4952	28.3090	738.1118	39.1821
v24	786.9373	25.5538	780.8951	42.2070	756.2768	2.5518
v25	826.1670	57.4319	810.1884	14.9667	835.0677	10.9523
v26	870.2825	80.8974	861.2141	12.3145	871.0780	23.5607
v27	883.7271	66.3577	875.3948	134.9430	877.4037	102.3062
v28	894.3767	9.8862	895.0263	5.7892	895.6845	5.9883
v29	948.6184	15.3668	931.1965	16.7142	951.0713	1.3093
v30	958.7768	7.8041	964.2124	0.8927	954.5556	14.3602
v31	982.7043	49.1303	980.1671	18.9781	972.0495	70.5218
v32	1011.9595	24.9627	1010.4835	29.0523	1016.5944	58.0289
v33	1021.3840	111.2953	1032.9429	35.8699	1038.1525	15.3747
v34	1043.2051	14.9930	1046.0830	19.0211	1042.3447	11.1015
v35	1052.8911	104.5382	1056.8117	207.0517	1053.4096	205.2426
v36	1072.1361	11.2963	1074.2841	17.8363	1074.6916	27.0020
v37	1082.2501	24.9828	1083.9673	121.5454	1082.1512	20.7691
v38	1088.1314	191.6740	1090.5017	75.9223	1089.1369	155.1496
v39	1123.6003	104.7154	1125.3598	104.5817	1124.4756	103.5520
v40	1137.0264	5.9374	1133.9391	2.2958	1136.2895	7.8024
v41	1139.7441	31.0533	1138.7991	24.8763	1144.8822	17.3068
v42	1152.3822	3.3063	1152.9010	8.0347	1153.7718	13.7062
v43	1196.9008	5.7760	1201.7485	10.8912	1197.3230	36.5319
v44	1210.2400	41.0203	1210.1595	37.6092	1210.1941	16.7003
v45	1235.1812	58.6615	1231.9804	46.3237	1230.8066	25.5946
v46	1250.9889	2.6773	1248.9452	29.1539	1253.2944	27.4251
v47	1257.7483	41.7012	1256.5210	6.5503	1259.2746	5.1152
v48	1274.4311	18.9516	1277.6348	11.7753	1276.1919	11.3908
v49	1301.6713	16.4072	1296.0051	58.1270	1294.9900	80.8285
v50	1327.4917	11.1834	1331.6771	7.8193	1326.7235	4.0368
v51	1334.0646	1.7296	1339.4763	35.2526	1339.1902	40.1560
v52	1341.2153	27.8596	1346.9672	14.8038	1344.0517	11.6721
v53	1352.7388	2.2239	1357.1107	12.3759	1356.6660	11.6757
v54	1369.7510	13.8555	1362.0073	9.3900	1363.8326	5.7936
v55	1374.4876	44.1172	1376.2144	4.9078	1377.2994	5.9135
v56	1391.5702	38.9097	1398.6120	14.7049	1392.1935	8.5821
v57	1430.9427	6.0072	1432.2774	2.3588	1431.5229	1.9342
v58	1435.9559	11.4737	1439.6930	3.6132	1440.3657	2.9217
v59	1441.8546	3.2947	1458.6730	8.1737	1455.8770	10.9929
v60	1500.9841	10.8604	1504.0505	11.9537	1504.6369	11.5193
v61	1612.7403	5.6141	1608.9886	3.1505	1609.8579	6.6549
v62	1676.9424	42.1330	1676.4626	46.7993	1673.0872	37.9746
v63	2973.1195	12.6295	2987.1399	9.8903	2984.6495	9.4831
v64	2991.2298	16.2295	3007.9932	1.5550	2999.3835	9.8393
v65	3032.8007	3.4126	3021.1765	13.9445	3025.3916	10.0772
v66	3040.0288	8.0432	3031.0219	9.9177	3031.2048	10.1777
v67	3046.2684	35.4557	3044.3966	38.0369	3045.3264	35.2627
v68	3140.9624	4.6169	3141.6767	4.6368	3141.9234	4.5498
v69	3258.6385	20.2187	3255.7212	11.7091	3258.4608	19.0982
v70	3267.9800	26.0368	3257.4486	21.7112	3260.6296	17.7684
v71	3295.0347	33.0319	3292.9068	16.1831	3290.8847	14.2398
v72	3362.4457	68.4527	3350.2986	92.2381	3345.2532	93.1050
v73	3767.2847	128.0372	3786.7610	118.5675	3779.9852	111.9271
v74	3811.3933	105.5515	3812.3849	101.2412	3812.4672	102.0983
v75	3838.2477	101.8833	3839.1394	98.8932	3839.5143	99.5011

Table S5. Compound **3**;

(a) Relative energies, with respect to those of the lowest energy conformer at 0 K, calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Corresponding optimized structures are provided as well.

Conformer	B3LYP/6-311++G(d,p) energy / kJ mol^{-1}	MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) energy / kJ mol^{-1}
A	0.00	0.00
B	2.36	2.56
C	8.18	9.80
D	10.25	11.89
E	12.70	14.58
F	13.21	15.15



(b) Cartesian coordinates of optimized geometries (in Å) of lowest energy conformers.

A			
6	-0.359650	-0.312880	-0.435406
6	0.435126	0.880426	0.134967
6	1.918356	0.694520	-0.169743
6	2.401351	-0.664960	0.325594
6	1.502510	-1.765827	-0.236403
8	0.132962	-1.528633	0.098676
8	0.043132	2.110769	-0.462080
8	2.719044	1.688394	0.459336
8	3.727362	-0.935634	-0.099587
1	-0.834096	2.354649	-0.146049
1	2.418212	2.552179	0.154035
1	0.294841	0.914249	1.222043
1	2.057665	0.739668	-1.260009
1	2.340716	-0.675130	1.422557
1	1.628258	-1.825416	-1.326157
1	1.760835	-2.731846	0.194463
1	4.278937	-0.193110	0.173857
6	-2.791113	-0.104543	-1.036789
7	-1.767310	-0.220975	-0.129368
6	-2.354709	-0.210648	1.126065
6	-3.698909	-0.083583	0.898664
7	-3.959853	-0.013154	-0.452358
1	-2.607577	-0.083130	-2.100792
1	-1.780720	-0.334760	2.028220
1	-4.493162	-0.048301	1.627968
1	-0.271545	-0.304343	-1.530502

B			
6	-0.360127	-0.299733	-0.449813
6	0.438774	0.884503	0.133263
6	1.922097	0.693163	-0.168006
6	2.396024	-0.672952	0.318096
6	1.492738	-1.764674	-0.254754
8	0.123137	-1.522311	0.076989
8	0.055489	2.121663	-0.455767
8	2.726034	1.677665	0.471062
8	3.721480	-0.947737	-0.106086
1	-0.823559	2.365390	-0.144624
1	2.429400	2.545654	0.173581
1	0.294767	0.910840	1.220161
1	2.064800	0.745910	-1.257563
1	2.332647	-0.691185	1.414763
1	1.621750	-1.817133	-1.344494
1	1.744003	-2.735118	0.170253
1	4.277340	-0.212481	0.178167
6	-2.354190	-0.229584	1.098887
7	-1.770422	-0.203661	-0.144713
6	-2.803774	-0.075407	-1.058332
6	-3.950422	-0.018508	-0.313559
7	-3.658940	-0.118545	1.029084
1	-1.778451	-0.360639	2.001695
1	-2.620806	-0.033534	-2.119063
1	-4.965282	0.085789	-0.663977
1	-0.266919	-0.283135	-1.543774

C			
6	-0.382072	-0.268177	-0.454270
6	0.437078	0.901718	0.118246
6	1.924306	0.683445	-0.156978
6	2.377688	-0.687298	0.327325
6	1.469056	-1.754815	-0.291189
8	0.107597	-1.507164	0.047983
8	-0.027201	2.089301	-0.495542
8	2.620627	1.746864	0.483415
8	3.738913	-0.836738	-0.084776
1	0.543525	2.810053	-0.203600
1	3.561300	1.635577	0.303186
1	0.285237	0.940318	1.205183
1	2.089141	0.733383	-1.243621
1	2.301588	-0.723552	1.420714
1	1.606269	-1.767100	-1.381860
1	1.700521	-2.748795	0.094857
1	4.162386	-1.523529	0.439413
6	-2.816126	-0.082989	-1.018786
7	-1.780120	-0.185761	-0.125476
6	-2.351110	-0.201417	1.135573
6	-3.700067	-0.107369	0.926534
7	-3.979745	-0.030369	-0.421009
1	-2.644765	-0.037090	-2.083885
1	-1.763115	-0.304899	2.030990
1	-4.485377	-0.095280	1.666212
1	-0.309654	-0.242858	-1.549556

D			
6	-0.382909	-0.257727	-0.466555
6	0.440964	0.906540	0.110269
6	1.927594	0.679549	-0.161661
6	2.371418	-0.693748	0.324440
6	1.458219	-1.756243	-0.296091
8	0.096976	-1.499831	0.038160
8	-0.014368	2.098172	-0.502502
8	2.628674	1.738994	0.479711
8	3.732859	-0.851747	-0.083930
1	0.558160	2.815217	-0.204953
1	3.569279	1.620854	0.303541
1	0.287225	0.944494	1.196968
1	2.094909	0.728013	-1.248040
1	2.292178	-0.729014	1.417589
1	1.598862	-1.770281	-1.386307
1	1.682105	-2.751226	0.091728
1	4.152019	-1.537340	0.445254
6	-2.348287	-0.184863	1.110354
7	-1.783445	-0.167737	-0.140291
6	-2.831049	-0.086839	-1.040921
6	-3.968533	-0.052354	-0.282534
7	-3.656213	-0.118021	1.058319
1	-1.756908	-0.270749	2.008213
1	-2.663008	-0.045502	-2.103963
1	-4.990377	0.018455	-0.620752
1	-0.304465	-0.233211	-1.560791

E			
6	-0.377811	-0.270823	-0.445545
6	0.436068	0.906031	0.119676
6	1.923871	0.688382	-0.155052
6	2.385017	-0.681508	0.336703
6	1.472424	-1.762515	-0.247310
8	0.110771	-1.503473	0.074385
8	-0.034392	2.087160	-0.502787
8	2.622381	1.755382	0.473817
8	3.762602	-0.901447	0.030358
1	0.510585	2.819992	-0.193018
1	3.567237	1.565816	0.428213
1	0.285665	0.950166	1.206234
1	2.076350	0.739483	-1.246794
1	2.329702	-0.709286	1.427632
1	1.602887	-1.816458	-1.341516
1	1.708839	-2.739732	0.172775
1	3.861505	-1.015350	-0.922774
6	-2.807979	-0.088466	-1.026829
7	-1.777451	-0.188636	-0.126472
6	-2.356280	-0.197771	1.131279
6	-3.703710	-0.103316	0.913190
7	-3.974909	-0.031865	-0.436434
1	-2.630041	-0.046893	-2.091018
1	-1.774134	-0.299522	2.030715
1	-4.493520	-0.087615	1.647939
1	-0.299049	-0.258165	-1.540910

F			
6	-0.374014	-0.287571	-0.404247
6	0.455887	0.906689	0.109861
6	1.938123	0.666667	-0.192866
6	2.397521	-0.684325	0.345888
6	1.466286	-1.778262	-0.171953
8	0.108788	-1.492019	0.169794
8	0.030378	2.158667	-0.417278
8	2.760248	1.668300	0.390557
8	3.713591	-1.001192	-0.079816
1	-0.066167	2.094291	-1.375087
1	2.393665	2.530880	0.160939
1	0.323533	0.990883	1.190836
1	2.079807	0.661462	-1.286952
1	2.344447	-0.654549	1.442585
1	1.578869	-1.877780	-1.260676
1	1.702498	-2.736799	0.287408
1	4.291383	-0.275960	0.185218
6	-2.800006	-0.263961	-1.022082
7	-1.777083	-0.173816	-0.109585
6	-2.373827	-0.001050	1.127664
6	-3.720273	0.011002	0.886039
7	-3.975434	-0.150018	-0.459119
1	-2.610593	-0.411788	-2.075343
1	-1.803423	0.075585	2.036973
1	-4.520014	0.124025	1.601119
1	-0.288606	-0.338585	-1.501978

(c) Vibrational frequencies.

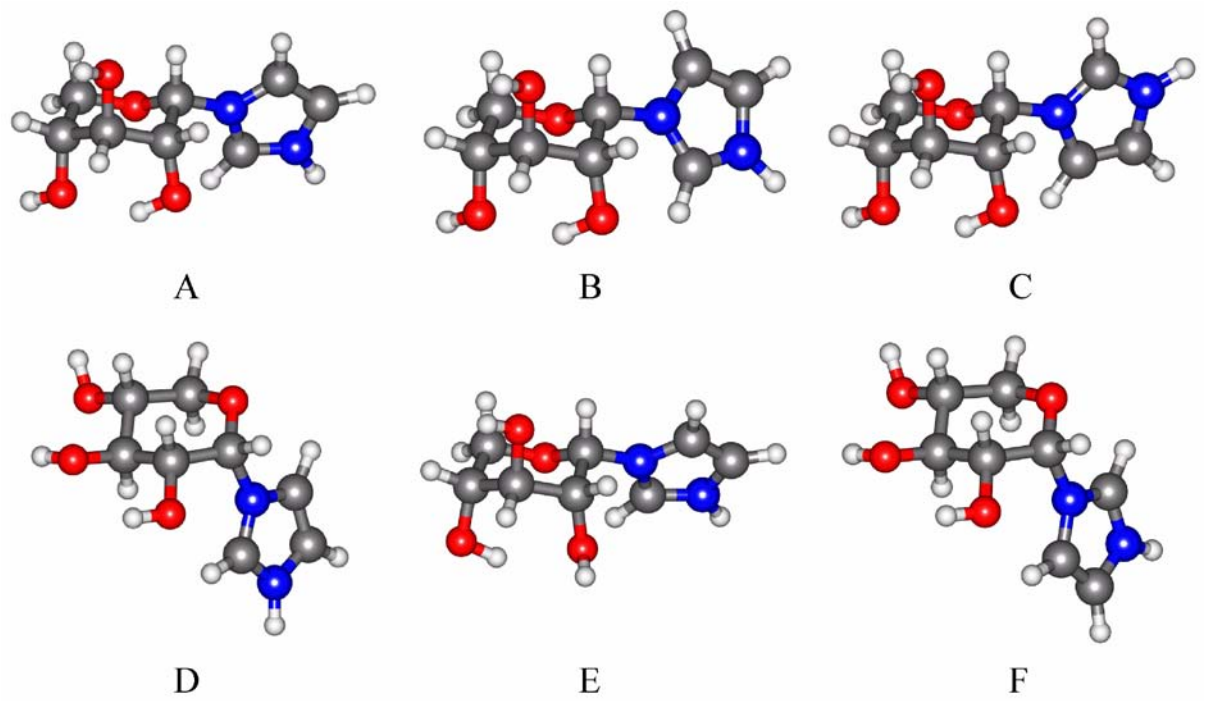
	A		B		C	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	39.9559	1.7304	31.5645	0.4170	35.2844	1.0062
v2	62.3629	2.4561	62.9252	1.8816	61.1031	0.6048
v3	77.0574	0.6205	75.8833	2.2185	79.3858	0.1640
v4	110.4270	1.6810	110.2895	1.8332	108.5356	0.6534
v5	180.9069	3.8637	180.0453	2.4862	185.4350	5.1905
v6	237.2478	6.5887	236.2873	5.6231	234.8160	6.6255
v7	245.9672	8.8750	246.1961	9.3423	246.2269	24.4182
v8	279.2604	1.5698	278.7106	1.0070	260.7363	82.1558
v9	300.5177	23.6984	299.3355	24.2246	280.7056	19.0835
v10	305.3464	1.4333	305.4550	1.1015	301.4605	14.2113
v11	325.9037	29.6077	327.3244	35.5119	310.2745	1.4630
v12	349.5048	84.4864	348.8000	84.0621	331.8963	7.0609
v13	386.2978	82.2383	387.8258	80.0821	372.3840	64.8364
v14	394.4776	130.9117	394.4449	134.4724	392.2425	135.5891
v15	410.5405	10.1304	410.8383	10.2116	410.5489	4.2584
v16	470.7530	9.2524	470.0378	9.5419	473.4857	4.6619
v17	502.6266	7.8393	503.5796	8.7892	499.8540	4.8391
v18	528.4200	24.6791	528.0564	23.1155	528.9891	14.1887
v19	586.4775	16.5589	586.9980	16.3378	584.5294	28.2634
v20	605.6053	13.2729	605.0303	11.3833	603.8399	28.4510
v21	649.1631	4.5218	642.1778	2.3592	647.4438	16.6335
v22	670.6334	16.7320	675.1018	21.0319	668.9312	19.5818
v23	733.7245	32.0169	732.8923	31.2651	727.5927	25.0443
v24	815.1723	27.1258	817.9538	27.7000	812.8327	24.6258
v25	828.9053	18.8935	825.2793	20.0670	828.4605	11.8701
v26	874.6036	1.8246	869.1430	1.9557	869.7277	2.0900
v27	899.1974	5.2160	899.2766	5.0839	902.9992	8.4667
v28	916.1229	9.7709	915.6803	8.3573	916.1533	7.7500
v29	994.1920	29.2160	994.9623	31.9600	979.9569	80.2025
v30	1016.5936	24.5872	1015.8662	25.5931	1013.0040	69.9495
v31	1029.0685	89.7281	1030.9813	106.4146	1031.7212	18.7648
v32	1039.1783	105.3541	1039.7430	92.0949	1052.5548	60.9137
v33	1062.2617	88.5406	1063.7584	84.8135	1072.0913	12.0522
v34	1079.8093	25.4918	1083.4809	24.3007	1072.6190	19.0628
v35	1093.1447	32.1507	1094.7672	40.2203	1084.3046	236.5903
v36	1103.7584	132.7089	1102.8360	136.3452	1096.9299	63.2569
v37	1108.2534	123.6540	1109.2452	90.8673	1110.9158	92.6933
v38	1117.6573	48.1448	1117.8283	46.0856	1117.8035	23.5957
v39	1130.1487	9.1564	1130.1134	8.4120	1127.5603	39.3470
v40	1138.5230	17.0463	1138.3932	22.6211	1138.0949	11.1111
v41	1212.7761	11.9906	1212.7016	14.7716	1201.6361	16.1281
v42	1237.9165	58.9051	1238.7070	52.7971	1233.8130	58.8965
v43	1243.7355	3.6078	1240.3953	18.8876	1248.0481	8.7774
v44	1248.9017	32.6552	1248.8775	30.3753	1250.0939	14.1005
v45	1263.0990	44.5854	1255.9689	41.9610	1257.6874	46.7801
v46	1290.2774	7.9109	1288.3215	27.1178	1306.0663	36.3589
v47	1304.2852	33.7540	1297.7084	4.6828	1312.0244	32.6799
v48	1323.5756	18.1376	1330.3981	35.6482	1330.8837	6.6560
v49	1348.9265	52.0662	1348.9928	53.1481	1342.8702	38.0662
v50	1359.0755	2.1383	1360.6355	2.4099	1345.6042	7.2060
v51	1365.5212	2.5303	1366.0035	7.5302	1363.5195	6.7110
v52	1380.1491	16.6007	1380.5504	14.8095	1376.2023	11.3250
v53	1398.5808	9.8779	1392.7323	7.4657	1401.3889	19.7825
v54	1412.9869	5.1833	1412.8911	5.1387	1415.7839	11.2890
v55	1431.0207	19.6908	1431.0632	20.1408	1425.6395	3.4016
v56	1436.5158	2.8038	1436.7939	1.3301	1436.7529	2.6638
v57	1442.1085	53.7948	1443.9910	32.4829	1454.8504	43.0851
v58	1503.7625	5.9528	1503.7510	6.7456	1502.2772	6.8309
v59	1508.1870	84.3504	1509.6819	77.5216	1512.6741	100.2705
v60	1542.6375	15.6620	1540.3098	16.0318	1545.3684	15.3442
v61	2984.2938	4.5351	2983.7178	5.4038	2983.4154	5.0725
v62	2994.9932	1.9589	2995.2499	1.8812	2994.2452	31.7584
v63	3003.3206	5.7170	3007.8172	2.2667	3003.9094	1.0457
v64	3009.4815	65.6583	3009.6681	64.1822	3018.2869	17.7319
v65	3032.7341	52.6244	3032.3127	55.0800	3029.7466	74.9201
v66	3127.4207	13.8650	3127.7669	13.5845	3098.7890	25.2718
v67	3238.4619	1.8022	3241.7227	3.8302	3238.6600	4.1638
v68	3242.0364	3.9186	3251.5876	1.2009	3241.2506	2.5988
v69	3277.9461	0.4679	3270.1930	0.8221	3278.8032	0.5496
v70	3812.7028	57.3163	3812.7726	57.2786	3814.0561	64.1860
v71	3818.9258	56.4993	3818.6480	56.6197	3819.4143	64.1528
v72	3823.9577	49.4837	3823.6200	49.8186	3844.0201	55.3522

	D		E		F	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	21.2808	0.9623	35.6270	1.6025	36.7554	2.5927
v2	61.2277	1.6743	60.2845	0.7236	58.6819	2.3416
v3	77.4958	0.2506	79.1533	0.3511	80.0663	0.1483
v4	108.1594	0.8118	106.1531	3.8577	107.0516	6.6034
v5	184.3267	1.6860	183.0515	2.3292	182.3287	1.8647
v6	234.0831	7.3462	230.5545	6.9499	235.7304	5.5755
v7	246.6415	26.6850	243.2735	11.4205	245.4029	3.7523
v8	261.5086	79.9427	276.7956	5.3738	273.6250	62.2546
v9	280.9807	20.8271	296.3455	10.4936	278.1457	8.7414
v10	300.4502	12.9284	305.5934	13.7061	299.0902	36.9579
v11	310.7261	2.2526	318.6195	59.8511	313.9598	4.6656
v12	333.2829	6.5505	333.3012	19.5209	329.3748	3.3785
v13	373.4716	61.7362	366.1055	70.5108	383.6317	116.0361
v14	391.8168	136.3907	404.6853	68.5714	407.4693	6.7673
v15	410.7858	4.9837	411.1359	103.9026	418.4890	166.1473
v16	473.0531	6.1156	470.2792	1.2905	472.6120	1.7437
v17	500.7361	6.2378	501.9343	2.8865	501.7087	3.1208
v18	528.8419	13.6595	531.6807	21.8082	526.2181	10.5491
v19	585.4084	24.8940	585.1212	5.9170	589.3922	11.8727
v20	603.2217	28.4635	603.2468	25.5872	611.1612	26.5625
v21	640.5937	9.6145	647.4315	16.0259	647.5644	7.7398
v22	673.7183	26.2684	668.6856	19.4171	669.7243	17.8070
v23	726.8132	34.1652	728.2678	25.3882	727.0907	24.7128
v24	814.8743	22.0035	811.7733	24.9188	803.8605	28.2128
v25	825.2091	12.8274	828.5346	18.3713	831.5217	21.5365
v26	865.0096	2.1402	870.4401	2.0692	872.2924	2.1100
v27	902.9490	8.7081	899.8211	23.1989	901.8427	0.5310
v28	915.7586	8.8220	915.9906	9.6684	915.1388	10.3440
v29	980.4570	76.4448	977.9017	71.0607	987.9826	9.8509
v30	1012.3299	68.1361	1006.4981	85.4864	1004.3268	114.2118
v31	1033.8334	16.6839	1031.6737	16.3807	1029.8182	30.1642
v32	1053.8340	59.3294	1045.4967	10.6557	1033.9404	179.2573
v33	1072.3666	16.9695	1053.6654	45.6893	1058.3585	14.9739
v34	1072.7163	47.7399	1081.3822	177.4568	1085.1946	77.2257
v35	1084.5894	223.4181	1095.7726	21.6980	1095.2797	85.2285
v36	1100.0804	47.6259	1101.3275	141.6096	1102.0881	116.9919
v37	1112.3339	91.1530	1111.9065	74.3892	1119.8116	15.9593
v38	1117.8857	14.9093	1128.4757	49.9776	1126.5921	40.8095
v39	1128.2941	25.6299	1138.0953	9.6858	1130.2136	31.0106
v40	1136.7013	18.1418	1145.5397	12.3692	1138.3562	15.6000
v41	1200.3669	18.5412	1201.6536	19.2031	1211.2464	34.9279
v42	1233.6794	62.3897	1232.9060	17.2357	1222.0663	14.1453
v43	1246.0359	7.8272	1246.9873	12.9769	1244.6120	20.3675
v44	1248.7178	47.7203	1253.3909	8.9344	1256.0574	37.3277
v45	1261.3177	29.6834	1267.2779	70.3459	1262.5184	37.1346
v46	1283.6226	9.9084	1305.9930	39.4115	1294.4489	19.2267
v47	1322.4609	56.3926	1310.3039	53.8341	1305.7320	41.2700
v48	1333.5967	9.7776	1328.7484	6.1057	1323.7002	14.1438
v49	1343.3871	38.7963	1329.8186	13.6954	1350.4482	25.2543
v50	1345.9019	14.3670	1343.9795	12.8243	1354.9900	11.2794
v51	1363.7360	3.3280	1377.2413	17.8967	1376.2324	20.0550
v52	1376.6164	6.4680	1392.9565	20.7760	1387.9179	6.0311
v53	1396.7994	12.1810	1402.6032	19.7407	1405.2816	26.8243
v54	1415.3767	13.4125	1415.4583	9.6634	1413.8601	19.6923
v55	1425.9248	2.5490	1419.5460	19.3254	1422.9914	15.9382
v56	1437.0267	2.5543	1425.1190	6.9331	1435.2586	14.9163
v57	1456.8787	26.4052	1453.8355	43.2508	1442.1895	47.6373
v58	1502.1018	7.0417	1497.6147	6.3355	1502.8998	6.3394
v59	1514.1287	90.5603	1512.3814	99.2142	1510.8010	96.1129
v60	1542.9650	17.3408	1545.6221	15.4196	1546.2028	15.6186
v61	2982.9321	5.5577	2940.5739	5.6562	2946.1046	12.7778
v62	2994.2110	32.7421	2951.3613	79.0897	2961.9081	40.6179
v63	3005.3261	2.3871	3004.2768	2.3085	2993.3522	10.2293
v64	3022.0119	10.6511	3019.9665	45.5751	3009.6510	68.1430
v65	3030.7305	77.2967	3078.0311	17.3361	3085.7278	13.2460
v66	3099.3347	24.8494	3116.5098	14.8773	3127.2057	13.2254
v67	3240.7923	4.8171	3238.7238	3.4968	3231.8815	1.9242
v68	3251.6228	1.0352	3241.6382	3.1522	3242.2806	4.3640
v69	3270.9617	1.2506	3278.9963	0.4920	3279.7119	0.3790
v70	3813.9647	64.4411	3797.0116	31.0165	3801.6100	36.3998
v71	3819.4187	64.5496	3808.0246	56.3083	3806.2730	45.0891
v72	3844.2986	55.8492	3818.0516	68.1558	3815.9281	60.6515

Table S6. **4•H**$^+$ protonated on N3';

(a) Relative energies, with respect to those of the lowest energy conformer at 0 K, calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Corresponding optimized structures are provided as well.

Conformer	B3LYP/6-311++G(d,p) energy / kJ mol^{-1}	MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) energy / kJ mol^{-1}
A	0.00	0.00
B	0.82	2.24
C	7.37	6.56
D	9.77	12.19
E	14.68	14.52
F	15.39	17.41



(b) Cartesian coordinates of optimized geometries (in Å) of lowest energy conformers.

A			
6	-0.172535	0.495219	0.436659
6	0.538085	0.497271	-0.939486
6	2.043454	0.710396	-0.681459
6	2.574705	-0.357212	0.297974
6	1.717489	-0.382878	1.563812
8	0.316232	-0.528834	1.263265
8	0.250417	-0.688670	-1.645268
8	2.168612	2.006703	-0.106903
8	2.529798	-1.593939	-0.422238
1	0.924785	-1.352561	-1.424482
1	3.009760	2.403167	-0.355204
1	0.164720	1.338847	-1.528575
1	2.576316	0.628600	-1.632488
1	3.605681	-0.108416	0.575112
1	1.964507	-1.234899	2.197286
1	1.878757	0.538582	2.133716
1	2.983299	-2.293628	0.060443
6	-2.123176	-0.987619	0.043115
7	-1.608093	0.220438	0.272993
6	-2.622972	1.163907	0.225825
6	-3.777754	0.497213	-0.034146
1	-1.569073	-1.908069	0.018351
1	-2.438692	2.212236	0.386100
1	-4.788995	0.849036	-0.141928
7	-3.438825	-0.839398	-0.138825
1	-4.080461	-1.599174	-0.322758
1	-0.086423	1.479123	0.910635

B			
6	0.186362	-0.552119	-0.102330
6	-0.621156	0.386431	-1.021480
6	-2.098000	-0.055207	-0.930989
6	-2.565821	-0.061748	0.540734
6	-1.610360	-0.896477	1.394149
8	-0.243656	-0.474525	1.234770
8	-0.442819	1.748999	-0.681448
8	-2.162868	-1.371055	-1.469127
8	-2.596573	1.314015	0.936621
1	-1.077087	1.976851	0.020719
1	-3.005288	-1.510130	-1.913239
1	-0.283744	0.253462	-2.052294
1	-2.703656	0.653558	-1.501543
1	-3.568104	-0.502286	0.595793
1	-1.823183	-0.785765	2.457712
1	-1.709281	-1.953829	1.123412
1	-2.956662	1.410738	1.825210
6	2.197343	0.963174	-0.114635
7	1.630153	-0.248041	-0.079655
6	2.621759	-1.203459	0.094320
6	3.809944	-0.549372	0.146312
1	1.656306	1.887364	-0.237110
1	2.394481	-2.253060	0.165063
1	4.815942	-0.913888	0.261131
7	3.515368	0.795796	0.013008
1	4.188752	1.550753	0.006253
1	0.099781	-1.574855	-0.487590

C			
6	-0.184398	0.518937	0.269687
6	0.581338	0.256572	-1.047501
6	2.066215	0.578336	-0.778346
6	2.581067	-0.240001	0.425536
6	1.666012	-0.035625	1.633454
8	0.284757	-0.288993	1.315877
8	0.374882	-1.057293	-1.512530
8	2.129032	1.971207	-0.488157
8	2.608873	-1.599237	-0.021343
1	1.047535	-1.635291	-1.114898
1	2.977651	2.331912	-0.764274
1	0.211259	0.945224	-1.811748
1	2.644407	0.317780	-1.668810
1	3.589760	0.101555	0.686558
1	1.906108	-0.729768	2.439084
1	1.778160	0.988516	2.006807
1	3.020560	-2.171864	0.635198
6	-2.599356	1.114734	0.222803
7	-1.620194	0.211225	0.141101
6	-2.176816	-1.041904	-0.065606
6	-3.524816	-0.874568	-0.116259
1	-2.474603	2.171023	0.393032
1	-1.564960	-1.917811	-0.169524
1	-4.320092	-1.584468	-0.263608
7	-3.760969	0.476287	0.061884
1	-4.669012	0.921664	0.077735
1	-0.114466	1.584578	0.520167

D			
6	-0.313723	0.018755	1.218792
6	0.773396	1.025455	0.812465
6	1.602510	0.545305	-0.376594
6	2.138649	-0.856189	-0.098562
6	0.964130	-1.778596	0.238843
8	0.185005	-1.267605	1.348835
8	0.182466	2.294081	0.583544
8	2.623556	1.510661	-0.536875
8	2.791308	-1.285419	-1.285919
1	0.894465	2.916481	0.382385
1	3.184763	1.254078	-1.278914
1	1.440004	1.076698	1.682442
1	0.978824	0.499035	-1.282039
1	2.839296	-0.810032	0.742734
1	0.332604	-1.905545	-0.647794
1	1.301523	-2.760410	0.567521
1	3.480768	-1.925443	-1.079920
6	-2.020347	0.968574	-0.470251
7	-1.514114	-0.014686	0.280604
6	-2.362049	-1.112574	0.209420
6	-3.386235	-0.780627	-0.618795
1	-1.586634	1.947993	-0.577645
1	-2.154810	-2.018830	0.750594
1	-4.243557	-1.343982	-0.944639
7	-3.149494	0.517755	-1.026912
1	-3.734545	1.059407	-1.649862
1	-0.724103	0.294704	2.190696

E			
6	0.162116	0.392190	-0.509145
6	-0.557329	0.694635	0.818388
6	-2.068571	0.804743	0.523342
6	-2.579087	-0.443859	-0.235713
6	-1.705520	-0.708742	-1.460610
8	-0.304281	-0.786244	-1.095766
8	-0.252116	-0.379298	1.702379
8	-2.195710	1.987575	-0.259912
8	-2.677983	-1.567632	0.618689
1	-0.512985	-0.146147	2.600743
1	-3.112330	2.283567	-0.271099
1	-0.201366	1.652257	1.213662
1	-2.609508	0.887730	1.472539
1	-3.596409	-0.244434	-0.585528
1	-1.941750	-1.676919	-1.896956
1	-1.834290	0.076939	-2.212174
1	-1.811514	-1.738295	1.009102
6	2.162104	-1.011915	-0.055217
7	1.606931	0.175245	-0.295097
6	2.585267	1.155299	-0.244477
6	3.761346	0.531506	0.029321
1	1.638256	-1.951315	-0.037948
1	2.366626	2.195260	-0.417061
1	4.758759	0.920134	0.140942
7	3.469713	-0.815180	0.140189
1	4.137705	-1.551177	0.328383
1	0.061054	1.253612	-1.178692

F			
6	-0.313669	0.062718	1.212136
6	0.785190	1.047679	0.786817
6	1.598820	0.537062	-0.399944
6	2.138230	-0.854741	-0.081032
6	0.968850	-1.770680	0.291470
8	0.169823	-1.228350	1.374878
8	0.216144	2.320843	0.554000
8	2.620916	1.494296	-0.596355
8	2.781441	-1.330084	-1.255917
1	0.933239	2.921536	0.309519
1	3.160067	1.229729	-1.351627
1	1.458081	1.091527	1.653530
1	0.964033	0.467667	-1.295930
1	2.844798	-0.779350	0.752906
1	0.349841	-1.937919	-0.597433
1	1.312803	-2.735498	0.661240
1	3.493815	-1.936975	-1.029049
6	-2.273538	-1.077692	0.166772
7	-1.513815	0.016299	0.272547
6	-2.103795	1.041233	-0.458468
6	-3.229674	0.531252	-1.026129
1	-2.079254	-2.021645	0.646336
1	-1.664757	2.021421	-0.495274
1	-3.963017	0.986129	-1.669585
7	-3.311597	-0.786632	-0.621811
1	-4.039608	-1.441064	-0.877396
1	-0.721224	0.372152	2.175031

(c) Vibrational frequencies.

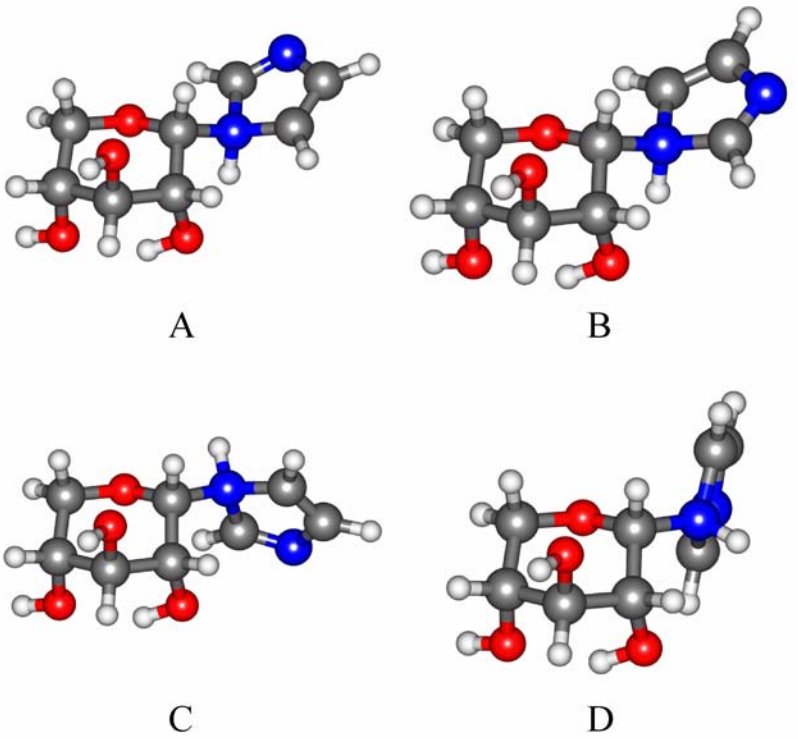
	A		B		C	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	26.4986	1.4914	33.7401	0.6926	24.5513	3.0200
v2	77.0721	5.3736	76.8886	5.6885	77.2907	4.3864
v3	92.8747	8.5286	121.7067	6.4884	105.0089	5.3188
v4	161.1039	16.8490	162.8408	51.5505	165.0595	15.5592
v5	176.2199	10.6959	172.9928	42.0508	176.3362	4.4836
v6	194.0030	100.6857	179.1834	36.3813	199.5655	103.9868
v7	238.7645	11.6727	236.7357	3.3846	238.5205	6.5678
v8	256.4060	7.6999	265.1056	32.6581	258.3861	6.9358
v9	266.7763	111.2642	274.4488	60.3078	273.7047	30.0616
v10	278.7929	17.2446	278.8942	39.8854	286.8005	103.3671
v11	301.4446	1.4402	302.1374	3.2728	296.4263	1.9766
v12	376.8823	1.2967	375.2469	1.1663	376.0643	1.3414
v13	389.2250	6.9228	379.1926	0.6233	388.1057	0.0546
v14	397.8011	2.0409	398.0289	8.7867	392.8801	7.2311
v15	444.3867	0.5049	438.9808	1.0488	441.3052	1.1146
v16	530.1079	9.7878	532.1529	8.6286	530.9698	8.6554
v17	570.2501	29.6322	570.9372	7.3399	568.8753	13.0277
v18	574.2519	79.4610	592.7854	97.1585	574.3130	98.6741
v19	615.3471	27.4696	624.8948	31.0236	617.9947	34.3507
v20	648.8849	39.1356	661.7558	64.0826	658.5373	60.4404
v21	680.3767	21.3785	681.8267	3.9663	682.0126	10.8235
v22	685.8697	16.3606	696.2349	39.7344	683.3357	32.7447
v23	746.9450	61.8421	755.1862	52.9153	749.1979	37.2890
v24	804.0325	9.7289	802.7720	9.9960	800.0423	11.7187
v25	817.4054	36.6855	819.3162	20.6984	817.0948	30.9775
v26	839.9391	0.8940	855.8354	2.4553	834.0443	6.7265
v27	858.3822	3.2780	879.5104	2.5881	857.6520	3.8203
v28	877.2008	0.1134	887.2451	33.8391	881.5025	1.1748
v29	883.7800	35.4782	907.1615	21.4783	884.2728	34.7862
v30	919.4795	20.3680	922.6882	15.6864	918.8986	16.3364
v31	933.9980	1.4623	932.3182	3.9264	935.8633	10.6144
v32	981.7241	5.0403	981.7654	5.0991	982.0805	5.1305
v33	1033.1881	51.6548	1033.3429	43.8545	1028.4515	18.6300
v34	1056.1868	65.8509	1055.3246	18.3850	1050.7585	90.3224
v35	1068.6407	96.0099	1065.8040	155.2749	1068.0393	102.9288
v36	1082.1905	60.2398	1077.6378	108.0413	1083.4038	54.9387
v37	1092.4869	23.8345	1089.1679	57.6014	1088.2451	63.3146
v38	1100.3689	57.3637	1094.9679	101.7966	1094.6080	38.0874
v39	1104.1944	106.0331	1103.2400	68.6609	1106.3199	96.1514
v40	1119.5775	40.8453	1115.2049	28.4066	1116.5833	79.4247
v41	1125.5672	8.8712	1125.5441	4.7182	1123.6326	6.3779
v42	1164.2288	17.6228	1151.3187	19.1260	1169.5782	19.4060
v43	1205.0114	35.5753	1202.8779	35.4004	1205.1447	35.8867
v44	1221.9435	22.9012	1220.6910	18.8211	1221.7121	18.1276
v45	1259.9288	7.1514	1246.4925	10.3753	1264.0508	1.6406
v46	1273.0505	20.3656	1280.1551	18.6296	1272.7850	50.4730
v47	1291.3683	30.0509	1286.7489	23.4541	1298.6646	16.5911
v48	1311.9872	9.2099	1315.4938	18.2236	1315.4572	25.2830
v49	1321.6274	14.3499	1320.4777	32.1011	1316.4452	10.7843
v50	1345.4322	4.3783	1344.8067	38.2157	1342.9545	3.6348
v51	1353.5798	31.5719	1356.4015	6.2537	1350.1567	13.4613
v52	1372.4348	15.1148	1373.9345	17.8381	1372.1024	2.3684
v53	1377.1320	10.7306	1379.1309	9.7494	1377.9221	10.6468
v54	1393.8695	3.0229	1393.9030	4.3138	1393.4970	1.3465
v55	1408.1906	12.5831	1407.1401	6.7341	1406.9845	17.0160
v56	1431.5870	5.0682	1432.1594	8.7815	1432.2357	4.9917
v57	1438.7738	4.8789	1439.3086	0.1798	1448.5286	17.2049
v58	1461.6525	65.4019	1465.2564	72.6068	1462.6574	72.2252
v59	1476.2748	17.4309	1472.5017	15.6467	1468.1807	7.7819
v60	1490.1254	10.7351	1489.5138	10.2004	1490.9978	10.5408
v61	1561.9362	58.7318	1552.8231	44.0799	1566.9594	57.4298
v62	1614.4294	21.2344	1614.3977	24.5592	1610.6713	28.0166
v63	3029.7749	9.4300	3027.5395	4.6464	3025.2661	8.5636
v64	3044.3211	36.2879	3038.2487	8.3330	3030.7148	8.9145
v65	3048.2270	5.0656	3039.4139	40.6355	3039.5771	40.4918
v66	3066.1196	14.9925	3068.6548	12.2941	3064.9754	15.8503
v67	3073.2517	14.4014	3077.9608	13.5365	3071.0756	13.5800
v68	3119.9399	8.5625	3116.5221	8.8781	3117.8157	8.8608
v69	3280.0209	17.6746	3274.3942	97.6409	3283.2285	35.7236
v70	3297.5969	23.6834	3281.3753	19.3456	3288.8397	17.6046
v71	3317.0100	26.6792	3298.9171	10.5702	3326.5319	22.3653
v72	3623.7269	206.7757	3619.8807	205.2236	3621.4761	221.4796
v73	3672.5234	255.3623	3646.3108	266.9376	3669.4886	248.2006
v74	3830.8196	72.0372	3828.2862	69.7007	3830.0245	69.9814
v75	3846.4796	98.6806	3847.0705	99.4845	3844.7630	95.4332

	D		E		F	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	40.9031	1.2214	32.4572	2.0876	46.3451	0.2682
v2	59.8340	3.0103	69.9098	4.1062	59.3727	5.0546
v3	95.9119	1.4303	95.3136	2.0475	97.3866	0.5037
v4	157.9884	1.7634	140.3031	9.4362	160.8870	1.3195
v5	201.2714	4.7872	174.9187	5.7706	196.3090	2.6481
v6	235.0018	22.3805	212.5334	8.6818	232.3071	44.5657
v7	245.4234	46.2453	235.3075	6.9509	246.6318	44.0463
v8	258.1242	26.7511	253.1909	13.7582	259.4793	21.6115
v9	271.6313	7.2644	273.4377	224.0951	268.4935	8.3441
v10	284.6158	39.9352	281.9758	18.2221	281.9649	28.2427
v11	335.4295	1.1428	297.7330	10.6232	333.4557	1.5116
v12	369.9214	2.0482	373.9314	5.9679	368.3348	0.7460
v13	398.9418	115.2856	376.7677	4.2377	392.1375	112.1026
v14	414.8188	19.0086	405.2445	6.1416	413.7451	28.0163
v15	429.5038	84.3120	447.7512	1.7550	425.5620	78.5444
v16	481.5115	14.4335	491.2683	63.6997	477.4774	14.2929
v17	505.3648	7.3115	522.8470	19.6852	504.9105	7.8339
v18	526.7253	25.2926	568.2659	5.4571	525.7328	23.8847
v19	596.5461	8.0559	616.8487	35.1437	593.2777	10.1459
v20	614.4663	54.7578	647.1717	27.3113	620.3978	68.6548
v21	622.3584	34.7679	672.4105	26.1419	624.4529	12.9848
v22	657.7441	38.3938	685.5292	35.2710	654.5425	39.9813
v23	689.4239	63.8289	750.9445	58.3845	692.8675	64.2596
v24	768.0995	50.4646	797.0273	13.9128	773.8702	42.2110
v25	802.8991	15.3022	813.4728	55.7911	798.0648	22.0477
v26	892.5412	12.9507	853.6321	5.9026	868.1580	15.3253
v27	896.9782	3.6208	870.5840	2.4299	900.4496	5.0046
v28	903.1444	6.5626	878.9116	0.0719	914.7353	4.3476
v29	925.7038	42.6987	885.1550	13.6409	921.5223	49.8370
v30	933.5318	7.7529	925.1111	19.4642	932.1967	3.6357
v31	946.5708	14.0950	934.3975	1.3904	948.1467	17.5269
v32	1011.1486	8.5891	985.2779	22.7280	1009.9580	6.3538
v33	1053.9418	128.7165	1022.2035	76.1928	1055.2559	151.7488
v34	1072.0794	205.0621	1048.3312	13.1432	1074.8618	151.7696
v35	1079.4264	9.4368	1072.2595	71.2393	1078.8223	32.7557
v36	1090.7135	80.6692	1081.0475	51.8532	1091.8635	77.8857
v37	1106.7873	28.4822	1095.3106	69.4725	1105.9421	36.3481
v38	1114.9162	60.8124	1103.3909	106.7500	1119.7826	31.3579
v39	1126.1190	63.1077	1110.3695	57.3587	1127.5802	124.4162
v40	1129.7369	73.4781	1124.6130	2.9198	1138.5100	7.1212
v41	1138.1590	14.1640	1127.6606	59.4362	1145.4110	33.1260
v42	1170.9401	16.1532	1160.4851	15.3219	1161.3306	24.1539
v43	1214.3015	15.3088	1206.1482	0.7374	1213.4361	24.0788
v44	1232.6416	38.9147	1231.9944	73.7244	1226.9702	29.9583
v45	1244.5660	24.5831	1251.8144	48.3348	1239.6635	29.5618
v46	1262.4805	30.1942	1263.0798	2.9988	1263.9223	15.1732
v47	1264.7917	8.4705	1279.2669	12.7377	1271.2005	29.0625
v48	1298.4448	22.1661	1303.0460	29.1426	1299.0874	7.9835
v49	1336.0102	8.8951	1321.1585	4.6427	1334.9226	8.5756
v50	1349.2355	34.9725	1339.8450	3.8346	1348.1602	18.8660
v51	1352.2684	5.6993	1356.7442	2.2677	1353.7939	4.9434
v52	1369.9622	8.1548	1362.8569	38.3006	1369.1483	20.2168
v53	1372.8493	12.5729	1380.1688	18.3309	1375.6900	6.5464
v54	1386.9561	1.4476	1398.0551	11.9791	1382.4464	9.4292
v55	1399.2857	7.1950	1400.5102	2.8611	1400.3887	19.0753
v56	1435.3255	34.0071	1428.2695	4.0276	1435.7447	19.6603
v57	1439.3360	5.1915	1434.1691	31.8812	1438.8928	7.8554
v58	1443.5290	1.7643	1438.8562	15.4647	1444.9811	3.6435
v59	1469.9986	3.4649	1473.9555	15.9826	1469.0285	5.8950
v60	1506.4011	1.4548	1488.8347	12.1536	1504.6495	5.6755
v61	1546.1644	27.1462	1562.4436	55.1134	1555.5856	30.5198
v62	1606.9220	30.5161	1614.8952	21.5422	1603.9530	28.7032
v63	2982.4061	24.9010	3032.7082	19.0471	2985.3110	19.8926
v64	3024.4908	7.7562	3040.9384	10.6106	3014.3836	13.4996
v65	3030.0502	3.3101	3044.3251	14.1955	3027.2492	7.3091
v66	3044.4372	43.0643	3049.8220	15.6644	3044.7586	39.7957
v67	3104.9276	2.8287	3063.1855	25.1967	3105.5154	2.5795
v68	3131.5537	7.7048	3146.8402	3.0940	3130.3518	8.0270
v69	3282.9694	27.5665	3278.0463	18.2101	3284.7257	32.1644
v70	3288.3835	81.4309	3295.5503	29.9797	3292.5417	40.7750
v71	3301.9114	9.6218	3307.0402	28.9607	3308.8362	37.3050
v72	3617.9747	192.2868	3620.9438	207.6990	3618.4723	201.4295
v73	3789.6326	114.1310	3788.8009	79.8226	3789.0190	111.6216
v74	3813.0015	90.8984	3825.9501	87.3608	3814.8198	89.7339
v75	3838.1745	93.6278	3834.0313	87.6647	3839.4993	95.1712

Table S7. **4•H**$^{+}$ protonated on N1';

(a) Relative energies, with respect to those of the lowest energy conformer at 0 K, calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Corresponding optimized structures are provided as well.

Conformer	B3LYP/6-311++G(d,p) energy / kJ mol^{-1}	MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) energy / kJ mol^{-1}
A	0.00	0.00
B	1.97	1.75
C	18.12	16.17
D	20.05	19.30



(b) Cartesian coordinates of optimized geometries (in Å) of lowest energy conformers.

A			
6	-0.267570	-0.048870	-0.423698
6	0.619405	-1.050296	0.347785
6	2.057315	-0.953642	-0.197293
6	2.554350	0.504517	-0.137426
6	1.567217	1.414440	-0.864339
8	0.225163	1.253905	-0.349141
8	0.498028	-0.770099	1.732609
8	1.982644	-1.394841	-1.545627
8	2.661079	0.809205	1.256261
1	1.198269	-0.143002	1.990273
1	2.798641	-1.835557	-1.804413
1	0.262664	-2.068207	0.177279
1	2.705017	-1.587749	0.413608
1	3.530596	0.573867	-0.629914
1	1.799445	2.467928	-0.712654
1	1.579361	1.196057	-1.936385
1	3.142703	1.630522	1.404639
6	-2.469701	1.183803	-0.024155
6	-2.506522	-1.105485	0.196770
6	-3.682677	-0.605994	-0.189140
7	-3.638689	0.807991	-0.322375
1	-2.051965	2.178442	-0.018648
1	-2.175138	-2.103087	0.429531
1	-4.598664	-1.140165	-0.389459
1	-0.493965	-0.367294	-1.445771
7	-1.591405	0.032671	0.348553
1	-1.252532	0.097418	1.334823

B			
6	-0.265570	-0.017601	-0.426340
6	0.606468	-1.038406	0.337492
6	2.047131	-0.955860	-0.202973
6	2.561474	0.495356	-0.131531
6	1.587393	1.421594	-0.855840
8	0.243671	1.276456	-0.341342
8	0.484125	-0.773614	1.725422
8	1.970243	-1.387203	-1.554284
8	2.665375	0.788603	1.264840
1	1.189168	-0.155371	1.991486
1	2.780908	-1.837159	-1.813979
1	0.239690	-2.050979	0.154937
1	2.684775	-1.602305	0.405579
1	3.540618	0.556365	-0.619331
1	1.597970	1.207668	-1.928872
1	1.833379	2.471264	-0.699332
1	3.153468	1.604600	1.421213
6	-2.510478	-1.092969	0.183656
6	-2.465947	1.197435	-0.012669
6	-3.659558	0.677773	-0.307980
7	-3.667022	-0.738111	-0.178325
1	-2.152624	-2.088058	0.405383
1	-2.071883	2.198015	-0.002526
1	-4.555609	1.196225	-0.611782
1	-0.491874	-0.323684	-1.452731
7	-1.590952	0.074562	0.343677
1	-1.254961	0.110383	1.332525

C			
6	-0.132009	0.501943	0.663409
6	0.305339	0.524700	-0.809009
6	1.838224	0.725439	-0.810822
6	2.522942	-0.366155	0.040661
6	1.923193	-0.389789	1.446409
8	0.481040	-0.510245	1.402538
8	-0.116447	-0.641544	-1.475435
8	2.070123	2.007694	-0.241148
8	2.309557	-1.591629	-0.664241
1	0.569772	-1.324936	-1.383221
1	2.838645	2.423729	-0.645050
1	-0.154463	1.381375	-1.308026
1	2.192302	0.658178	-1.842446
1	3.592335	-0.140298	0.118734
1	2.260980	-1.254501	2.016125
1	2.197095	0.523510	1.983812
1	2.879284	-2.294557	-0.333242
6	-2.126967	-1.121676	0.207571
6	-2.591025	1.141702	0.288206
6	-3.481468	0.447161	-0.424646
7	-3.193820	-0.941745	-0.439516
1	-1.600999	-2.034551	0.437764
1	-2.500672	2.185080	0.540931
1	-4.347263	0.824476	-0.947194
1	0.003441	1.488548	1.123254
7	-1.618761	0.171006	0.814062
1	-1.745950	0.064975	1.832368

D			
6	-0.197778	0.686872	-0.071721
6	0.817053	0.303477	-1.163062
6	2.220212	0.453167	-0.533149
6	2.315400	-0.388597	0.758308
6	1.180566	-0.018294	1.713847
8	-0.107749	-0.106589	1.064010
8	0.561298	-0.983629	-1.679074
8	2.374848	1.834169	-0.233470
8	2.248098	-1.749904	0.326011
1	1.052497	-1.634907	-1.148387
1	3.295712	2.099534	-0.326042
1	0.740834	1.018058	-1.989322
1	2.960785	0.098761	-1.254642
1	3.272096	-0.181699	1.251403
1	1.118528	-0.706896	2.555767
1	1.332082	0.997132	2.094074
1	2.454980	-2.359221	1.043353
6	-2.157222	-0.952751	-0.526648
6	-2.671858	1.176960	0.216020
6	-3.561377	0.262996	0.600706
7	-3.231014	-1.036041	0.123250
1	-1.589296	-1.701423	-1.056241
1	-2.592439	2.239831	0.372933
1	-4.450968	0.409171	1.193716
1	-0.113426	1.756422	0.156165
7	-1.639740	0.477041	-0.569818
1	-1.668044	0.782872	-1.552431

(c) Vibrational frequencies.

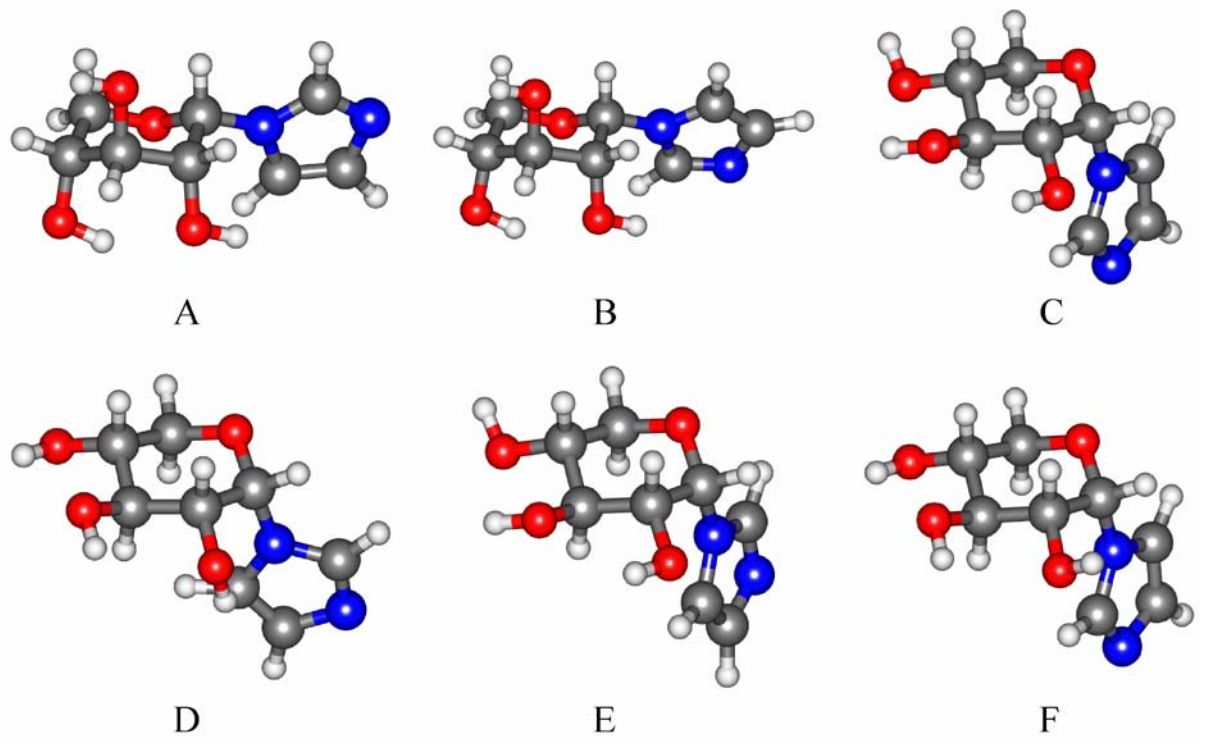
	A		B		C	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	53.6520	1.4608	57.7359	2.2773	49.7829	0.8305
v2	77.6186	3.6190	74.1179	1.9660	92.4012	2.9715
v3	124.9331	2.8422	128.0876	0.9879	112.8293	1.3128
v4	155.3108	11.8864	155.6376	11.2094	163.1931	17.1709
v5	165.3391	15.3689	162.6310	17.0833	179.8700	6.3225
v6	193.7739	107.5157	192.5672	107.6561	192.6962	100.0200
v7	221.7313	8.7073	221.6942	8.7754	215.2266	8.9368
v8	256.9124	8.3679	259.0003	4.7536	239.5833	140.2552
v9	260.3588	125.3747	261.6805	132.2224	257.9525	5.2024
v10	272.4213	15.2140	273.7162	12.9255	269.4887	4.8371
v11	287.1445	9.9018	289.8398	11.4212	276.1078	8.6621
v12	372.9365	5.9256	361.4065	6.0305	358.9792	8.5460
v13	376.5917	4.8030	377.0192	4.5294	376.1673	1.9120
v14	396.2706	11.3276	399.0815	12.4100	382.5179	8.5887
v15	438.2840	2.7996	438.8586	1.8501	437.4931	1.2339
v16	528.4968	7.4578	528.4820	7.7342	525.0640	9.5677
v17	559.0342	15.9233	561.4996	15.9620	562.0451	12.0954
v18	588.3113	7.3582	587.7218	15.7721	581.1740	5.1556
v19	603.9794	10.7210	604.5344	5.1438	585.2220	97.1723
v20	623.1354	74.6483	624.4564	76.9441	634.3487	6.3171
v21	692.2637	8.0902	692.8355	8.2663	702.7528	13.0824
v22	745.7152	44.6975	762.2844	49.5979	730.3276	43.0037
v23	801.7387	36.8495	803.0814	45.7508	747.0989	21.1315
v24	803.8296	24.0701	806.6330	1.3427	805.8300	10.3481
v25	824.6196	0.5229	826.4785	39.9284	815.5207	19.8397
v26	840.0351	9.4817	839.5603	11.2195	837.1283	7.5911
v27	875.9429	43.2324	870.0465	45.4656	868.3208	22.6770
v28	887.9505	49.6124	885.2814	67.7505	876.3540	59.8995
v29	908.3616	2.0848	900.8283	48.6846	898.7889	29.8201
v30	913.5416	68.4807	921.6192	18.1751	908.6062	4.6485
v31	956.3446	4.4830	953.9364	4.9482	962.8346	13.8867
v32	971.1836	33.6576	962.6433	20.3461	973.0692	14.6977
v33	1003.6526	24.3202	1004.7942	20.0311	1001.7631	7.5334
v34	1033.3075	89.0258	1027.9575	29.3687	1026.5092	54.2198
v35	1047.8880	35.0437	1046.4809	37.9575	1053.3079	55.6240
v36	1062.0007	183.0238	1060.2129	149.0713	1062.0420	190.3071
v37	1071.3015	31.6011	1069.3614	78.5898	1075.2920	58.8356
v38	1083.8036	50.3969	1083.7654	58.4985	1086.2513	36.3325
v39	1098.2438	17.4550	1098.5968	19.4197	1096.0965	16.3896
v40	1107.3287	49.5913	1111.6847	56.4716	1117.1262	100.4962
v41	1122.4710	46.7310	1121.6240	52.9958	1124.0713	27.1731
v42	1152.0051	9.1357	1149.4875	5.4253	1151.5237	12.0227
v43	1205.3782	33.2645	1205.7162	31.6555	1203.7509	44.8348
v44	1214.5368	83.7204	1218.7697	27.0732	1205.5209	13.4970
v45	1225.1848	74.0565	1236.0602	59.9294	1216.8206	25.9704
v46	1253.8481	13.1529	1263.3773	20.3314	1247.3415	2.7729
v47	1274.8948	15.0464	1277.0787	22.0149	1272.5399	2.4262
v48	1287.0179	38.8567	1289.3593	35.8340	1287.2436	40.4113
v49	1314.4672	18.4792	1312.8849	13.3847	1293.0441	43.7670
v50	1329.1887	32.2291	1322.8263	48.0277	1320.1178	22.3004
v51	1336.8443	3.7002	1337.0177	4.2440	1332.9853	10.7400
v52	1355.6866	13.3753	1356.2630	18.7303	1361.1850	12.4836
v53	1358.7833	48.1282	1357.4909	57.9880	1373.1646	8.8541
v54	1374.2474	19.8192	1374.6255	17.9002	1375.0668	14.1288
v55	1384.5127	65.4371	1384.8402	67.6149	1394.9862	15.3774
v56	1399.2185	1.3532	1399.7271	2.2172	1413.1693	0.4730
v57	1412.6515	1.2355	1413.0064	0.6837	1416.5970	3.8837
v58	1434.1684	18.6240	1434.5399	21.3754	1435.9567	16.8686
v59	1452.7477	69.2308	1452.2975	68.0921	1452.7877	69.2323
v60	1491.0726	10.5955	1491.2944	10.3742	1491.3818	11.6659
v61	1607.1485	5.9977	1605.2451	6.1349	1606.2250	8.7794
v62	1668.0043	46.7722	1669.9906	40.2300	1668.4279	71.1877
v63	3039.3350	10.5130	3039.3839	10.2565	3036.0907	6.9813
v64	3057.4464	23.5265	3056.8775	24.0987	3037.5077	9.2628
v65	3068.6666	0.8277	3063.6280	4.7194	3054.2215	27.0375
v66	3070.9403	15.1594	3069.8763	12.8465	3072.0676	11.8410
v67	3083.9565	13.6952	3080.7363	12.8931	3077.8719	6.8486
v68	3130.4592	4.1851	3130.1249	4.2410	3131.7718	5.1487
v69	3149.2614	289.2458	3147.4467	292.9992	3253.8381	12.1807
v70	3257.1926	11.2753	3252.2038	13.1482	3276.2947	24.0363
v71	3273.6237	23.0445	3260.2530	12.8841	3281.9778	2.8841
v72	3289.8268	8.0934	3304.7752	18.0752	3346.8548	87.5932
v73	3629.7941	289.9224	3629.4047	287.5089	3655.5874	280.9249
v74	3831.4660	89.4206	3831.5486	89.3943	3832.5226	86.1406
v75	3843.4119	112.1990	3843.2109	112.7170	3844.2049	108.8318

	D	
	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	46.5201	3.2753
v2	75.6368	1.3488
v3	102.1952	1.0004
v4	162.7359	18.6533
v5	177.8319	10.8796
v6	194.6060	95.4581
v7	231.2870	9.6277
v8	251.7636	8.6783
v9	262.6135	69.1617
v10	267.0256	58.2530
v11	275.5991	24.8815
v12	323.6388	0.7809
v13	375.4049	1.3793
v14	390.2519	5.3123
v15	433.4575	0.6678
v16	528.1730	18.0147
v17	564.6158	41.0300
v18	567.4452	47.3256
v19	576.2068	33.6713
v20	638.9626	4.8298
v21	714.4442	39.1218
v22	726.1521	23.1229
v23	756.8602	9.9449
v24	809.6514	3.6528
v25	829.1396	20.9364
v26	853.5230	2.4554
v27	865.4135	32.5680
v28	870.8423	59.2199
v29	883.5330	24.4124
v30	927.3672	15.2049
v31	954.0638	39.0495
v32	958.6986	5.3055
v33	1000.5120	16.9886
v34	1014.6491	12.7736
v35	1042.4114	18.5026
v36	1054.0804	140.3194
v37	1070.9068	85.6147
v38	1086.6398	69.1460
v39	1094.5841	4.1672
v40	1106.8188	63.7538
v41	1122.1536	93.1772
v42	1149.6824	0.0656
v43	1186.3188	70.0781
v44	1205.6031	26.9298
v45	1220.0427	19.3878
v46	1250.6860	63.5448
v47	1256.0277	6.7681
v48	1286.4691	17.1667
v49	1311.3173	58.7962
v50	1318.5258	9.8406
v51	1324.7207	4.0423
v52	1360.5681	3.7412
v53	1367.4371	12.1803
v54	1375.7631	10.8432
v55	1387.2247	8.3145
v56	1401.6068	3.3677
v57	1417.5338	6.7746
v58	1438.4355	3.9659
v59	1456.1192	73.7071
v60	1490.5756	11.1376
v61	1620.3171	4.1665
v62	1682.1782	56.1117
v63	3033.8833	5.3383
v64	3034.2247	7.1947
v65	3050.0306	26.6208
v66	3051.2402	22.7553
v67	3071.9487	6.9170
v68	3129.6601	5.0275
v69	3256.0355	13.2109
v70	3276.5887	37.7214
v71	3282.8856	1.6316
v72	3376.2019	75.6709
v73	3649.7732	251.4148
v74	3830.0659	81.8651
v75	3843.4323	109.7951

Table S8. Compound **4**;

(a) Relative energies, with respect to those of the lowest energy conformer at 0 K, calculated at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Corresponding optimized structures are provided as well.

Conformer	B3LYP/6-311++G(d,p) energy / kJ mol^{-1}	MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) energy / kJ mol^{-1}
A	0.00	0.00
B	0.91	0.95
C	3.03	2.38
D	4.03	5.55
E	4.71	3.85
F	4.74	4.65



(b) Cartesian coordinates of optimized geometries (in Å) of lowest energy conformers.

A			
6	0.223188	0.415457	-0.475685
6	-0.506908	0.557928	0.881069
6	-2.013852	0.729315	0.641208
6	-2.551373	-0.386567	-0.281856
6	-1.689124	-0.485599	-1.541901
8	-0.299614	-0.652760	-1.232055
8	-0.354508	-0.597463	1.700480
8	-2.165548	2.020006	0.045613
8	-2.657152	-1.621071	0.407427
1	0.585954	-0.769569	1.837563
1	-3.096980	2.261376	0.050181
1	-0.125211	1.450351	1.390108
1	-2.525862	0.674030	1.607381
1	-3.569972	-0.125875	-0.591035
1	-1.823098	0.412138	-2.159426
1	-1.970684	-1.365877	-2.118518
1	-1.831021	-1.764059	0.891265
6	2.634330	1.105793	-0.270076
7	1.641348	0.162212	-0.301846
6	2.241744	-1.051888	-0.004735
6	3.569436	-0.762496	0.183982
7	3.802670	0.582797	0.020324
1	2.437896	2.149810	-0.464914
1	1.690256	-1.975734	-0.032874
1	4.369786	-1.449443	0.411272
1	0.120746	1.366447	-1.014102

B			
6	0.219641	0.357581	-0.534491
6	-0.508781	0.691490	0.788813
6	-2.018264	0.811059	0.533187
6	-2.546738	-0.430204	-0.220333
6	-1.681734	-0.705916	-1.451789
8	-0.292700	-0.816875	-1.117481
8	-0.342276	-0.334794	1.761656
8	-2.185623	2.003068	-0.237951
8	-2.645584	-1.552892	0.639459
1	0.599243	-0.483520	1.914150
1	-3.120546	2.228463	-0.269836
1	-0.135613	1.651168	1.164346
1	-2.527580	0.886895	1.499321
1	-3.566526	-0.223228	-0.564218
1	-1.956407	-1.663198	-1.892902
1	-1.818130	0.090523	-2.195040
1	-1.815257	-1.625556	1.131648
6	2.268300	-1.047966	-0.028470
7	1.641112	0.138868	-0.320798
6	2.612421	1.122235	-0.267164
6	3.775796	0.472777	0.054468
7	3.551929	-0.875855	0.197950
1	1.739236	-1.986871	-0.039711
1	2.389268	2.157481	-0.466189
1	4.758879	0.899039	0.180321
1	0.107755	1.213316	-1.212748

C			
6	-0.395661	0.095044	1.219440
6	0.764330	1.029021	0.833389
6	1.554658	0.495374	-0.362540
6	1.996264	-0.938721	-0.097093
6	0.776920	-1.779693	0.292432
8	0.118831	-1.210211	1.431512
8	0.293624	2.348070	0.621808
8	2.660017	1.379587	-0.531634
8	2.609312	-1.407513	-1.300455
1	1.053218	2.878714	0.350651
1	3.166279	1.080030	-1.295306
1	1.437558	1.011195	1.701067
1	0.929495	0.504464	-1.263900
1	2.722732	-0.934205	0.724688
1	1.069554	-2.785476	0.597771
1	0.090669	-1.859483	-0.557904
1	3.148618	-2.181093	-1.108911
6	-1.847013	0.874979	-0.778770
7	-1.514670	0.049306	0.272156
6	-2.544299	-0.875030	0.377061
6	-3.422435	-0.568634	-0.625199
7	-2.980196	0.523077	-1.338244
1	-1.243843	1.723193	-1.050417
1	-2.531897	-1.649119	1.125100
1	-4.344917	-1.069703	-0.874725
1	-0.784255	0.401289	2.192344

D			
6	0.415850	0.067644	-1.128586
6	-0.624666	1.116331	-0.664516
6	-1.613348	0.573950	0.372260
6	-2.189556	-0.762230	-0.083667
6	-1.055406	-1.720885	-0.436456
8	-0.202789	-1.160431	-1.442639
8	-0.030288	2.335032	-0.238068
8	-2.703577	1.472124	0.552272
8	-2.967130	-1.375391	0.933815
1	0.662417	2.139508	0.406520
1	-2.345186	2.345807	0.749952
1	-1.206237	1.378935	-1.552139
1	-1.109655	0.422784	1.336627
1	-2.800464	-0.583951	-0.979091
1	-1.454025	-2.638720	-0.866132
1	-0.484934	-1.986774	0.460185
1	-3.651552	-0.749384	1.197676
6	2.870074	-0.014043	-0.662728
7	1.566262	-0.063680	-0.231405
6	1.632638	-0.295702	1.139929
6	2.966863	-0.363544	1.440493
7	3.729524	-0.184375	0.309807
1	3.113879	0.157085	-1.700853
1	0.761823	-0.409815	1.759829
1	3.418215	-0.533578	2.405732
1	0.840790	0.414698	-2.070537

E			
6	-0.390132	0.109121	1.221749
6	0.773420	1.036644	0.829074
6	1.543937	0.497494	-0.376125
6	1.993447	-0.932538	-0.102304
6	0.781726	-1.775294	0.307331
8	0.120998	-1.195181	1.440843
8	0.316136	2.362191	0.627373
8	2.644915	1.381648	-0.572210
8	2.594610	-1.411452	-1.307641
1	1.078581	2.881265	0.342042
1	3.144074	1.069667	-1.335589
1	1.453797	1.009242	1.691021
1	0.901181	0.497934	-1.265274
1	2.729431	-0.917133	0.710836
1	1.082388	-2.773987	0.627577
1	0.094941	-1.873437	-0.540373
1	3.137536	-2.182205	-1.114808
6	-2.484176	-0.914615	0.311271
7	-1.508154	0.054115	0.270206
6	-1.888199	0.942842	-0.726529
6	-3.056167	0.443436	-1.237061
7	-3.418077	-0.715149	-0.586920
1	-2.435929	-1.737911	1.006365
1	-1.325946	1.833571	-0.935348
1	-3.656917	0.854704	-2.033428
1	-0.775936	0.425339	2.192616

F			
6	-0.391503	0.081208	1.213199
6	0.770923	1.025027	0.826423
6	1.564664	0.490182	-0.366794
6	2.001128	-0.948166	-0.103768
6	0.792538	-1.790865	0.292907
8	0.126536	-1.216929	1.428527
8	0.374599	2.359841	0.514470
8	2.746277	1.255779	-0.582182
8	2.579093	-1.540319	-1.255790
1	0.210566	2.852480	1.324670
1	2.484969	2.166020	-0.762650
1	1.441709	1.028299	1.693205
1	0.939688	0.506325	-1.268140
1	2.723227	-0.938907	0.724487
1	0.104983	-1.886828	-0.554063
1	1.103606	-2.786953	0.603798
1	3.295057	-0.966567	-1.552798
6	-1.836217	0.860271	-0.792776
7	-1.512763	0.042190	0.267715
6	-2.557081	-0.863296	0.387928
6	-3.436058	-0.552908	-0.612317
7	-2.979121	0.522726	-1.340413
1	-1.218843	1.690746	-1.086715
1	-2.550863	-1.632271	1.141423
1	-4.367495	-1.041763	-0.852271
1	-0.785829	0.379302	2.188925

(c) Vibrational frequencies.

	A		B		C	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	53.6055	3.4908	45.4874	0.3264	43.3390	1.4534
v2	72.2062	1.1413	69.5325	0.8832	62.8820	1.5267
v3	85.3644	1.1899	87.5701	0.9032	98.4487	0.5385
v4	149.2907	7.0341	145.6908	6.7379	142.0666	1.2390
v5	176.5814	2.0284	178.6245	2.8194	190.3787	1.4135
v6	224.6451	35.9310	220.7897	6.7306	228.9188	7.4050
v7	232.7672	64.1704	237.3112	55.0631	247.4760	33.9470
v8	241.2653	9.8797	243.3767	42.4026	258.6447	84.4119
v9	275.2545	7.1923	278.2034	6.1873	272.2713	1.5756
v10	289.6436	3.1627	282.2523	10.5457	276.7500	12.5922
v11	365.8958	36.7169	350.6736	65.6818	338.9477	5.7392
v12	381.3821	30.4666	378.6149	6.2307	373.9372	3.9091
v13	388.5101	19.5566	387.5893	15.9938	378.6851	103.7936
v14	396.2801	5.5016	405.9241	3.0847	408.4329	98.1320
v15	441.2201	3.1010	446.8286	3.2638	418.0199	11.2203
v16	501.5712	143.6252	503.7072	117.4287	484.3735	8.4679
v17	524.8688	33.8604	525.0314	45.1344	506.6529	8.5550
v18	572.0845	9.7392	573.1137	9.4752	529.4500	26.0638
v19	640.3928	2.9194	635.8311	3.0829	595.2342	2.6082
v20	672.0689	22.7492	674.1301	9.7007	616.2053	22.7077
v21	687.7968	12.5140	687.4707	15.5547	662.8178	49.0805
v22	752.7954	16.5611	726.4831	40.5748	670.2991	13.6697
v23	807.9426	13.3209	808.3086	9.7843	744.7122	33.2318
v24	808.5059	57.5660	809.2125	34.4292	817.5567	7.9228
v25	815.0695	1.4702	832.5112	17.6823	838.6449	26.1320
v26	853.0998	2.5581	852.5458	2.0444	876.3746	0.1579
v27	873.2097	4.1147	871.0544	2.7266	905.3514	9.5423
v28	887.6816	16.0633	886.6750	20.2388	916.1287	7.5226
v29	918.4048	8.3855	918.3100	10.8711	934.4606	46.7531
v30	927.0965	11.5265	929.2622	5.1945	955.3822	5.9883
v31	988.4643	2.7018	989.4548	5.9237	1029.9417	90.1646
v32	1038.5138	76.7591	1037.6559	54.6537	1051.5369	71.6005
v33	1043.1872	14.8683	1048.2583	37.8251	1069.0980	166.1802
v34	1066.5986	141.1617	1066.5940	128.0152	1075.3916	59.6781
v35	1078.0216	11.5967	1079.8754	22.9455	1089.5235	16.4796
v36	1087.7649	64.6433	1091.9951	56.6755	1093.3938	39.5268
v37	1095.2583	31.7228	1100.3499	20.9379	1109.6853	97.7406
v38	1111.4447	83.3459	1113.5874	91.2089	1119.5123	25.9063
v39	1130.4305	80.4820	1131.5171	69.8739	1131.3956	26.7858
v40	1141.0717	26.9972	1138.6595	25.9977	1139.0157	5.5410
v41	1215.1410	74.2430	1211.8417	73.8446	1206.5410	38.8353
v42	1227.0167	38.4731	1229.2752	31.5151	1230.9245	31.9653
v43	1249.6428	10.5911	1251.3122	44.0086	1238.0425	88.9001
v44	1267.0027	43.9730	1260.1078	19.5059	1261.4253	7.7328
v45	1295.6902	16.2611	1278.7110	20.6909	1268.9803	20.4663
v46	1301.7722	18.2279	1301.8548	15.7061	1280.7889	3.3103
v47	1311.9412	34.5337	1320.2011	51.4899	1314.9546	54.7139
v48	1322.7082	0.4164	1326.7449	8.1242	1340.7074	10.0806
v49	1344.3757	12.5805	1346.1830	18.6806	1347.5233	16.4552
v50	1369.2204	10.8845	1368.9232	4.4491	1365.6729	8.2540
v51	1370.0950	5.8753	1371.9572	9.2139	1371.0330	12.8786
v52	1386.5119	6.4073	1381.6325	5.2384	1382.9128	4.6286
v53	1398.4913	38.7526	1398.7294	16.4430	1387.1467	6.1594
v54	1399.4201	0.5308	1399.3069	16.7522	1397.3787	18.2342
v55	1430.2408	16.4879	1427.2847	8.0260	1431.6085	29.0858
v56	1440.9460	13.7591	1439.0956	10.6183	1438.3564	8.6729
v57	1446.9309	59.4993	1447.9245	56.7086	1443.3248	6.1371
v58	1483.1782	9.6490	1487.1399	9.7735	1501.9144	7.4199
v59	1505.6362	62.3689	1507.6481	74.9774	1507.7951	43.7071
v60	1535.8258	21.7285	1532.9513	7.9528	1543.3838	9.0138
v61	3006.8935	25.9424	3007.9521	25.2029	3000.6974	12.3919
v62	3017.3756	5.7651	3013.6766	8.6372	3015.2498	2.2732
v63	3031.9551	35.0513	3031.5308	34.2856	3028.1433	19.6501
v64	3033.1778	60.6587	3033.8581	60.9693	3038.7006	56.7553
v65	3044.6665	28.6580	3044.8466	28.0667	3082.8957	19.7610
v66	3122.5109	13.5459	3123.9850	13.0889	3103.4346	24.3703
v67	3235.5255	1.4667	3238.3930	4.0060	3238.4185	5.8310
v68	3241.4206	4.7574	3263.4201	0.4731	3276.4465	1.0903
v69	3280.9454	1.8644	3268.3641	2.7168	3288.0361	3.8622
v70	3745.3482	154.6220	3744.9588	139.3633	3800.9639	70.1935
v71	3780.8845	60.0678	3795.7634	49.0196	3823.9656	65.0741
v72	3843.2434	52.8048	3843.1402	52.3111	3842.2266	53.6069

	D		E		F	
	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}	Frequency / cm^{-1}	Intensity / km mol^{-1}
v1	52.7888	1.6979	43.8863	0.5182	42.6247	1.5858
v2	66.7908	0.4347	61.3235	0.8627	63.8492	0.7227
v3	96.0626	0.7129	98.7559	1.5181	97.9257	1.4966
v4	117.4080	2.9222	144.7436	1.9254	139.5736	1.9749
v5	192.8667	1.6876	192.6738	2.4019	187.0440	1.2371
v6	234.1685	13.6128	229.3314	7.6957	233.1539	10.0091
v7	248.8736	2.0206	247.6466	34.9406	249.4195	27.2530
v8	257.7788	10.2703	258.9707	80.8169	262.3184	67.4117
v9	281.2550	7.0528	272.9884	11.5413	268.9925	6.0386
v10	333.4173	5.5354	275.9675	2.9683	281.5206	34.0980
v11	351.5611	44.2519	337.4022	5.4233	333.8707	11.1068
v12	370.5310	37.4746	375.4347	3.7047	372.0624	12.0287
v13	384.9865	79.0757	378.4788	108.7524	381.5189	67.4000
v14	415.2374	23.3770	408.7373	94.3214	400.0353	136.4686
v15	429.2473	143.4969	417.7571	9.5054	419.9872	9.9202
v16	482.9485	1.3770	487.2393	8.2358	482.1540	7.3919
v17	506.8815	11.5145	505.9009	8.7664	506.3768	9.7624
v18	532.5703	5.2510	529.0327	26.0333	528.5922	26.1152
v19	576.5689	8.2376	596.0622	3.2290	596.6807	0.9642
v20	633.3399	20.9202	615.1850	16.1558	617.2566	22.2854
v21	668.5632	15.6306	652.9875	45.7798	666.9572	32.7954
v22	685.4058	40.7227	676.6519	22.3842	670.8986	18.9295
v23	729.7557	45.5613	761.9029	33.5893	746.3213	33.6468
v24	807.9952	10.6487	812.4670	13.6456	817.5972	9.9676
v25	823.4582	23.2651	829.9509	22.5821	836.8998	27.1187
v26	874.2062	1.8023	875.3752	0.0673	877.9919	0.4154
v27	904.7220	0.0561	904.3143	8.9581	901.4765	3.7301
v28	911.9931	5.7565	917.2241	8.8089	915.8370	7.9117
v29	942.9672	31.8655	935.4939	38.6968	939.5573	37.4378
v30	954.8665	48.8745	954.5215	4.3065	967.8932	6.5467
v31	1026.6931	43.9704	1028.0975	73.7121	1032.3857	15.2699
v32	1032.7103	115.6796	1052.9116	99.3292	1036.7138	125.7034
v33	1058.8101	58.2809	1066.5441	180.8192	1056.0286	121.8748
v34	1086.5330	164.3489	1075.1840	36.8582	1075.1709	133.1861
v35	1093.5857	36.6638	1090.0504	22.8185	1096.1019	10.7490
v36	1110.0757	83.8479	1096.5674	56.6947	1099.1198	15.0219
v37	1121.4551	48.5834	1115.6397	98.2565	1108.6503	110.9552
v38	1127.8502	14.9117	1119.6462	5.5053	1118.2063	21.7020
v39	1142.0834	16.2324	1132.7656	23.2701	1127.0220	31.1165
v40	1152.4108	26.5391	1138.2556	13.9740	1137.9897	10.6608
v41	1212.3784	40.0829	1206.5553	39.6199	1217.1239	31.1296
v42	1236.0167	33.3609	1231.5891	34.5070	1231.7075	30.8648
v43	1241.7540	47.1819	1232.4100	76.2516	1248.4051	43.8725
v44	1247.1908	75.3426	1262.5233	6.3515	1254.2872	99.2882
v45	1271.6234	21.3720	1264.6940	10.9661	1258.8763	7.6545
v46	1292.6866	14.5633	1298.4158	33.0389	1294.1024	17.3406
v47	1299.8069	29.2991	1306.5687	19.1329	1300.1350	21.6268
v48	1327.9798	32.6371	1341.4630	10.4395	1343.1640	25.2695
v49	1344.3344	12.3149	1347.6491	14.2824	1355.0051	13.8898
v50	1362.1289	9.9700	1366.1174	6.8238	1363.0244	10.9753
v51	1377.1198	9.0941	1371.6135	20.5440	1373.1829	5.0386
v52	1383.1349	12.1534	1382.0440	3.9887	1383.4048	0.6657
v53	1394.5574	10.5702	1382.5523	20.8444	1387.1114	17.8066
v54	1425.0112	34.3153	1394.2649	18.5046	1392.7286	36.9276
v55	1428.4891	12.3220	1432.7908	26.6224	1424.1088	17.4067
v56	1437.8787	1.7379	1439.0208	10.1666	1436.0203	1.5206
v57	1452.5946	20.5638	1444.1064	7.0426	1444.9965	1.2556
v58	1500.1089	34.5846	1501.3792	3.5414	1504.5675	23.3070
v59	1514.4292	6.5213	1508.0921	34.7562	1508.3199	28.3905
v60	1544.9220	24.7385	1541.6110	14.6376	1543.4020	8.7096
v61	2996.0183	4.8924	2999.4040	13.2436	2995.3856	16.2072
v62	3008.0469	42.3861	3014.6384	1.9774	3019.5467	4.9824
v63	3039.2861	36.3219	3027.9240	23.4329	3034.2685	20.8913
v64	3069.5755	17.5941	3039.5302	52.3417	3043.9264	39.3921
v65	3103.0496	10.2649	3082.1575	19.6295	3052.7716	41.7199
v66	3125.7597	14.3644	3104.4589	24.0128	3129.2402	14.1331
v67	3237.4280	1.7744	3240.1405	6.2815	3239.7574	5.4073
v68	3240.8830	3.0044	3253.9673	0.6818	3276.1044	1.1968
v69	3288.2682	0.5282	3306.9678	8.3635	3286.0950	2.7425
v70	3779.3208	54.4402	3800.2680	70.9869	3816.3749	53.5378
v71	3808.7949	53.4279	3823.7790	64.5884	3821.3138	56.7150
v72	3816.9933	61.1226	3841.9360	54.1065	3843.2425	61.0572

6. Infrared Spectroscopy in the Gas Phase.

The carbohydrate samples **3** and **4** were mixed with a small amount of graphite powder and deposited as a thin homogeneous layer on a graphite rod positioned close to the nozzle (0.8 mm diameter) of a pulsed valve (General Valve). The carbohydrate was desorbed from the graphite surface, using the fundamental (1064 nm) output of a focused Nd:YAG laser, providing energies ~0.4 mJ/pulse at 10 Hz repetition rate, and entrained into a supersonic jet expansion of argon (stagnation pressure, 4 bars), seeded with phenol. The jet subsequently passed through a 2 mm skimmer to form a collimated molecular beam which was intersected by UV and IR laser beams in the ionization region of a Wiley-McClaren time-of-flight mass spectrometer. The complexes between phenol and the carbohydrate, generated within the molecular beam, were ionized using a lightly focused, frequency doubled dye laser (Lambda Physik) pumped by the third harmonic of the Nd:YAG laser; UV laser energies were ~1 mJ/pulse. The protonated ions, produced at temperatures estimated to be ~300 - 350 K, were generated through rapid, exothermic proton transfer from the phenol cation to the carbohydrate, followed by loss of the phenoxy radical.[9] Their OH, NH and CH vibrational action spectra were recorded through mass-selected infrared multiphoton dissociation (IRMPD) spectroscopy, monitoring the depletion of the parent ions. The IR radiation was provided by a KTP/KTA OPO/OPA laser system (LaserVision), tuned over the range 2800 – 3800 cm^{-1} and operating at energies ~10-20 mJ/pulse with a bandwidth of ~2 cm^{-1}. Its tightly focused beam intersected the ion beam ~110 ns after the UV laser.

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