Supporting Information

for

Synthesis and Acid-Base Properties of an Imidazole-Containing Nucleotide Analogue, 1-(2'-Deoxy-β-D-ribofuranosyl)imidazole 5'-Monophosphate ($dImMP^{2-}$)

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Table S1. *Chemical shifts (in ppm) of the protons for the protonated, that is, deuterated, and the free forms of dImMP^{2-} based on the macro acidity constants* [a]).

H	$\delta_{(D\cdot dImMP\cdot D)^{\pm}}$	$\delta_{(D\cdot dImMP)^{-}}$	$\delta_{dImMP^{2-}}$	$\Delta\delta_2$	$\Delta\delta_1$
H2	8.938 ± 0.030	8.614 ± 0.039	7.887 ± 0.020	0.324 ± 0.049	0.727 ± 0.044
H4	7.486 ± 0.011	7.294 ± 0.015	7.037 ± 0.008	0.192 ± 0.019	0.257 ± 0.017
H5	7.678 ± 0.008	7.602 ± 0.011	7.425 ± 0.006	0.076 ± 0.014	0.177 ± 0.013

[a] The macro acidity constants are $pK^{D}_{D_2(dImMP)} = 6.39 \pm 0.03$ and $pK^{D}_{D(dImMP)} = 7.43 \pm 0.04$ as calculated with equation 4 and the constants given on the horizontal arrow in Figure 4. For further details see footnotes a) and b) of Table 2.

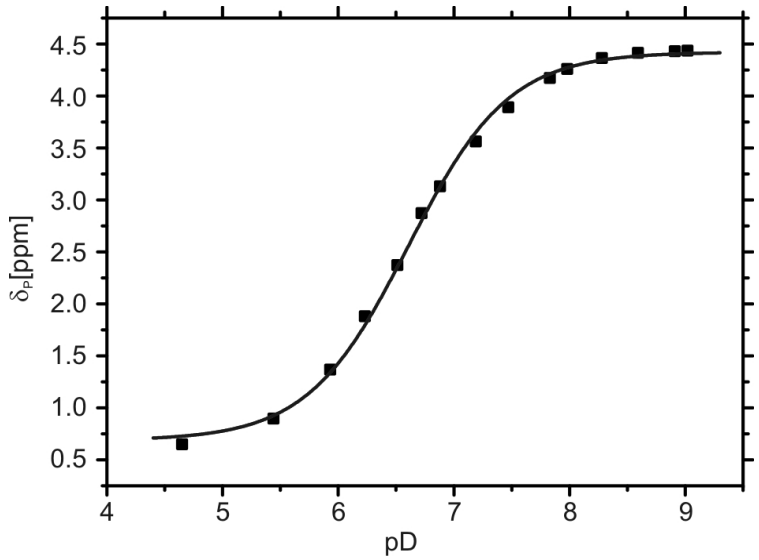

Figure S1. *Variation of the chemical shift δ_P for ^{31}P of the phosphate group of $dImMP^{2-}$ (1.8 mM) in dependence on pD (25 °C; I = 0.12 M, $NaClO_4$; see also Experimental Part) as mentioned in section 4. The solid curve is the calculated best fit of the experimental data using the micro acidity constants* $pk^{D\cdot dImMP}_{D\cdot dImMP\cdot D}$ *= 6.51 ± 0.05 and* $pk^{dImMP}_{D\cdot dImMP}$ *= 7.31 ± 0.07 (obtained from the upper pathway in Figure 4 with equation 4). The resulting chemical shifts are* $\delta_{P/(D\cdot dImMP\cdot D)^{\pm}}$ *= 0.687 ± 0.113 (3*σ*),* $\delta_{P/(D\cdot dImMP)^{-}}$ *= 3.687 ± 0.183 and* $\delta_{P/dImMP^{2-}}$ *= 4.422 ± 0.084. The corresponding shift differences are* $\Delta\delta_2$ *= –3.000 ± 0.215 and* $\Delta\delta_1$ *= – 0.735 ± 0.201 (see also footnotes a) and b) of Table 2).*

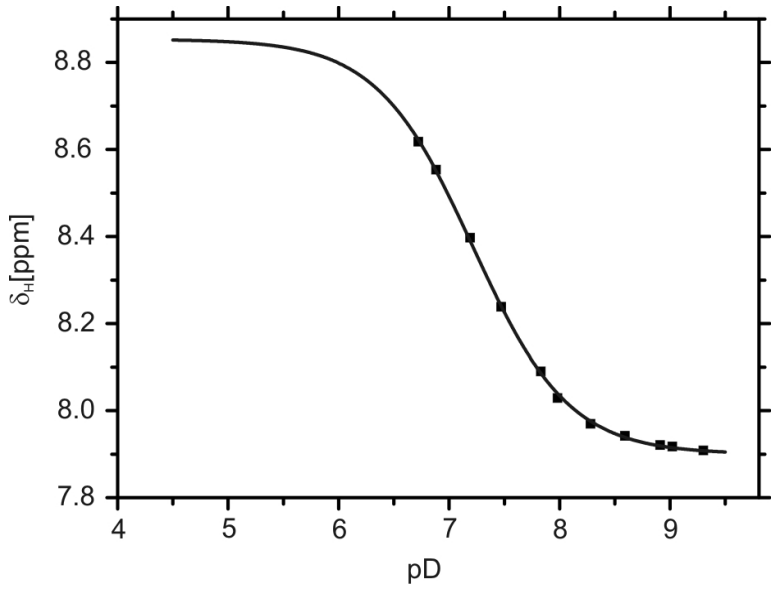

Figure S2. *Variation of the chemical shift δ_H for the H2 proton of the imidazole residue in dImMP^{2-} (1.8 mM) in dependence on pD (25 °C; I = 0.12 M, $NaClO_4$; see also Experimental Part). The solid curve represents the calculated best fit of the experimental data in the pD range of 6.72 to 9.30 giving the micro acidity constant* $pk^{\mathrm{dImMP}}_{\mathrm{D\cdot dImMP}} = 7.22 \pm 0.05$ *(3σ). The corresponding chemical shifts are $\delta_{(D\cdot dImMP)^-} = 8.853 \pm 0.037$ and $\delta_{dImMP^{2-}} = 7.900 \pm 0.009$, which lead to the shift difference $\Delta\delta_I = 0.953 \pm 0.038$ (see also footnotes a) and b) of Table 2).*

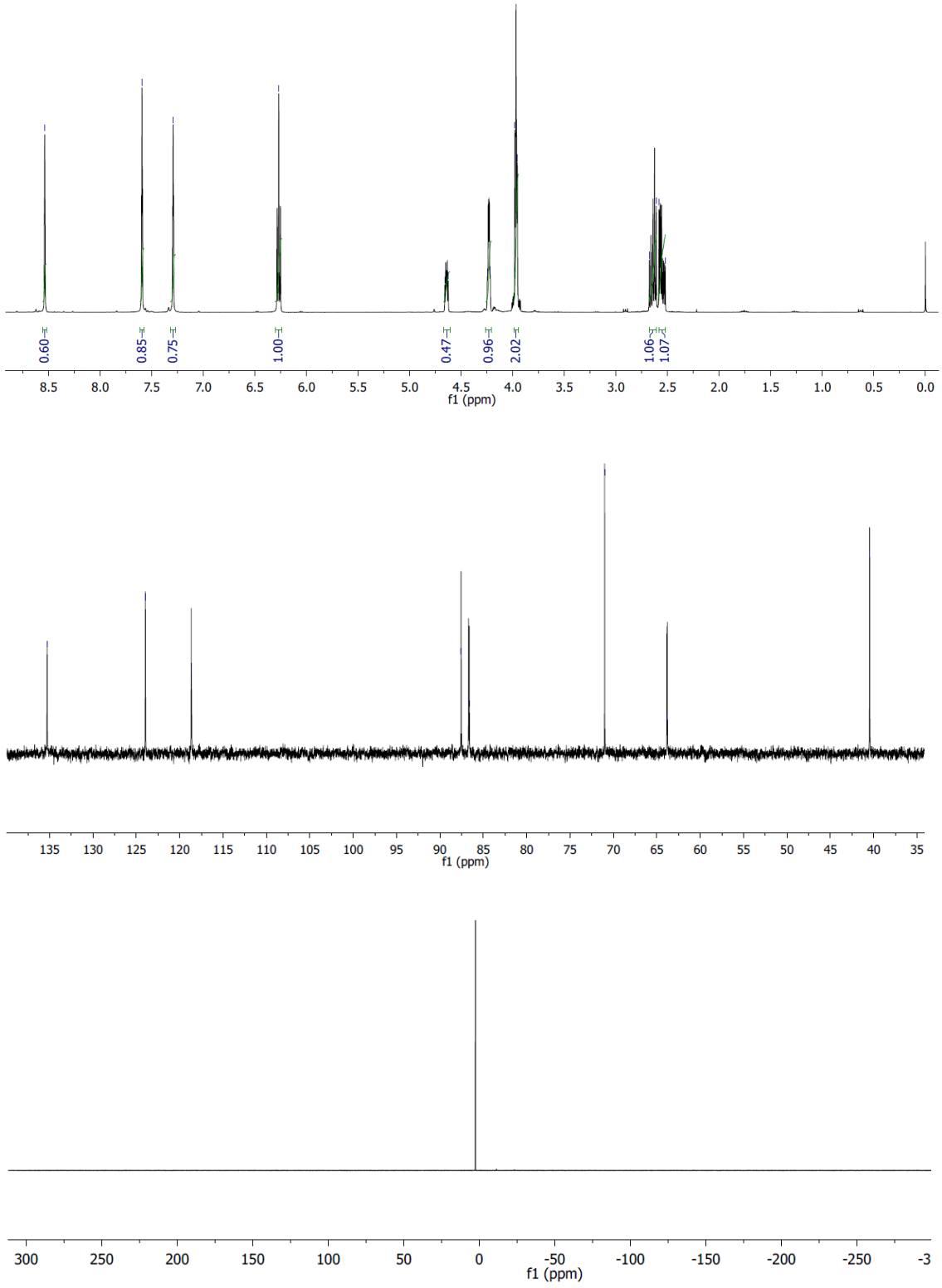

Figure S3. *^{1}H NMR (top), ^{13}C NMR (middle), and ^{31}P NMR spectra of dImMP^{2-} in D_2O.*