Supporting Information for

^{15}N NMR Studies of Acid-Base Properties of Pyridoxal-5'-phosphate Aldimines in Aqueous Solution

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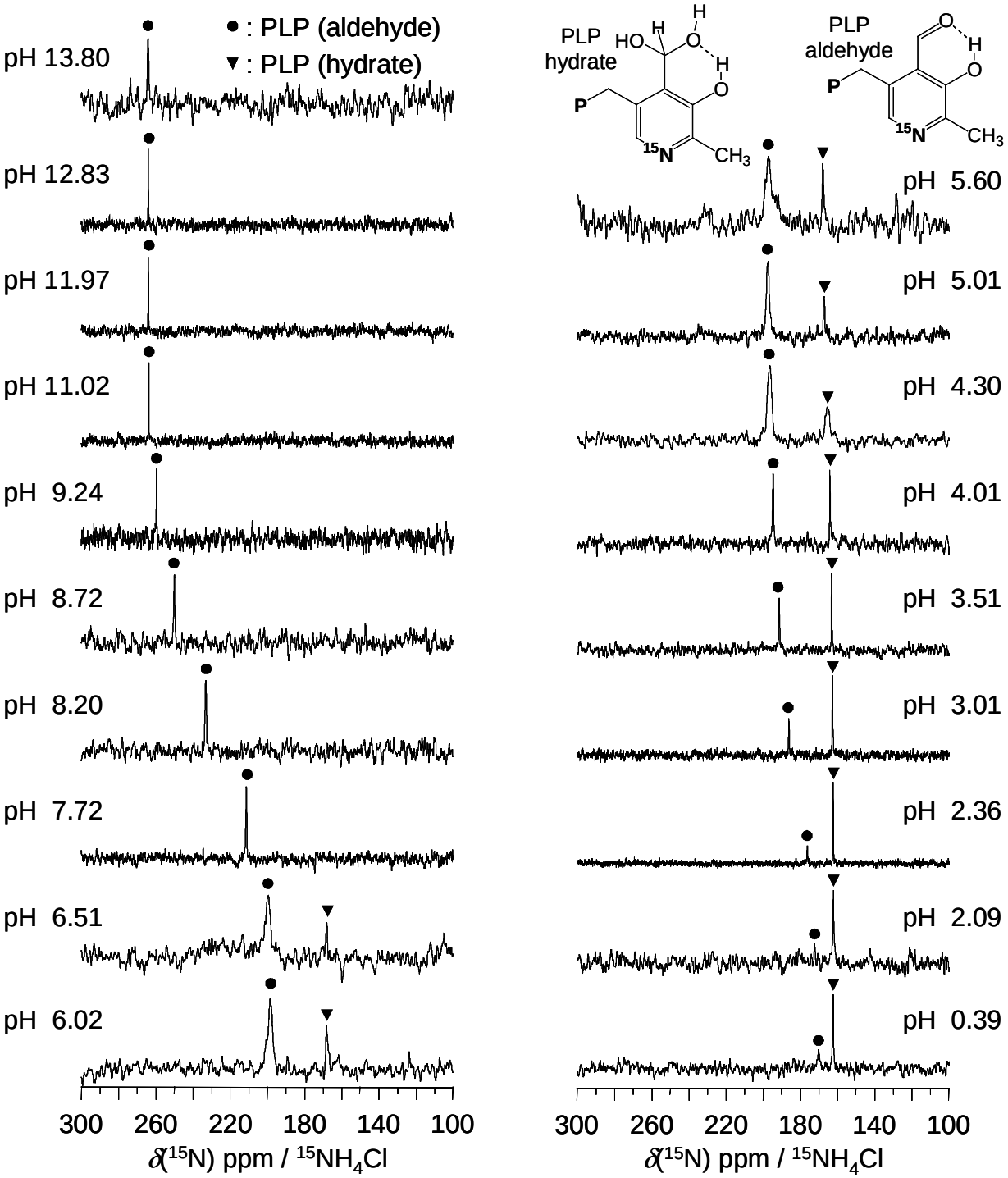

FIGURE S1: $^{15}N\{^{1}H\}$ NMR of the ^{15}N-labeled cofactor pyridoxal-5'-phosphate (PLP) in aqueous solution by locking to a D_2O capillary at room temperature. ●: the aldehyde form (**1a**), ▼: the hydrate form (**1b**).

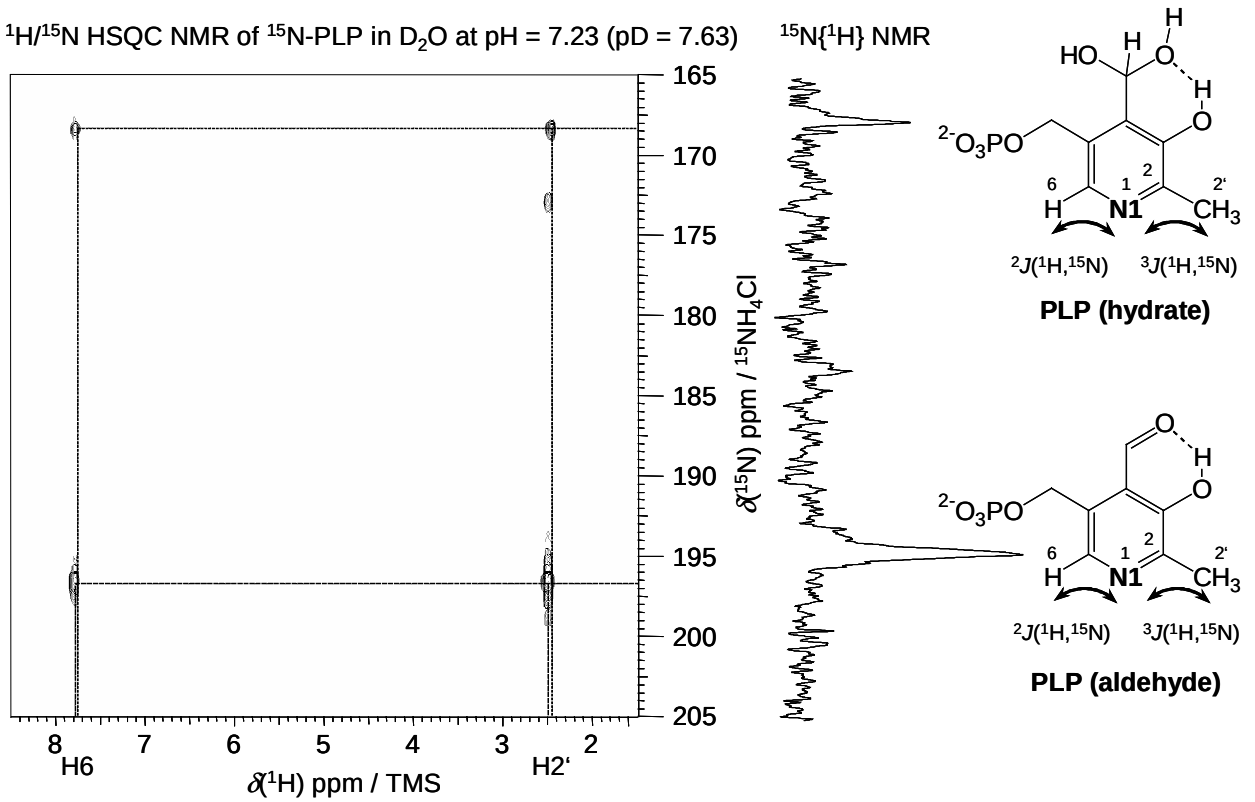

FIGURE S2: ^{1}H / ^{15}N HSQC NMR with water suppression of the ^{15}N-labeled cofactor pyridoxal-5'-phosphate (PLP) in D_2O with a pH = 7.23. The pD = 7.63 value is calculated from the measured pH value with the relation pD = pH + 0.40. On the right-hand side the ^{15}N {^{1}H} NMR spectrum is presented.

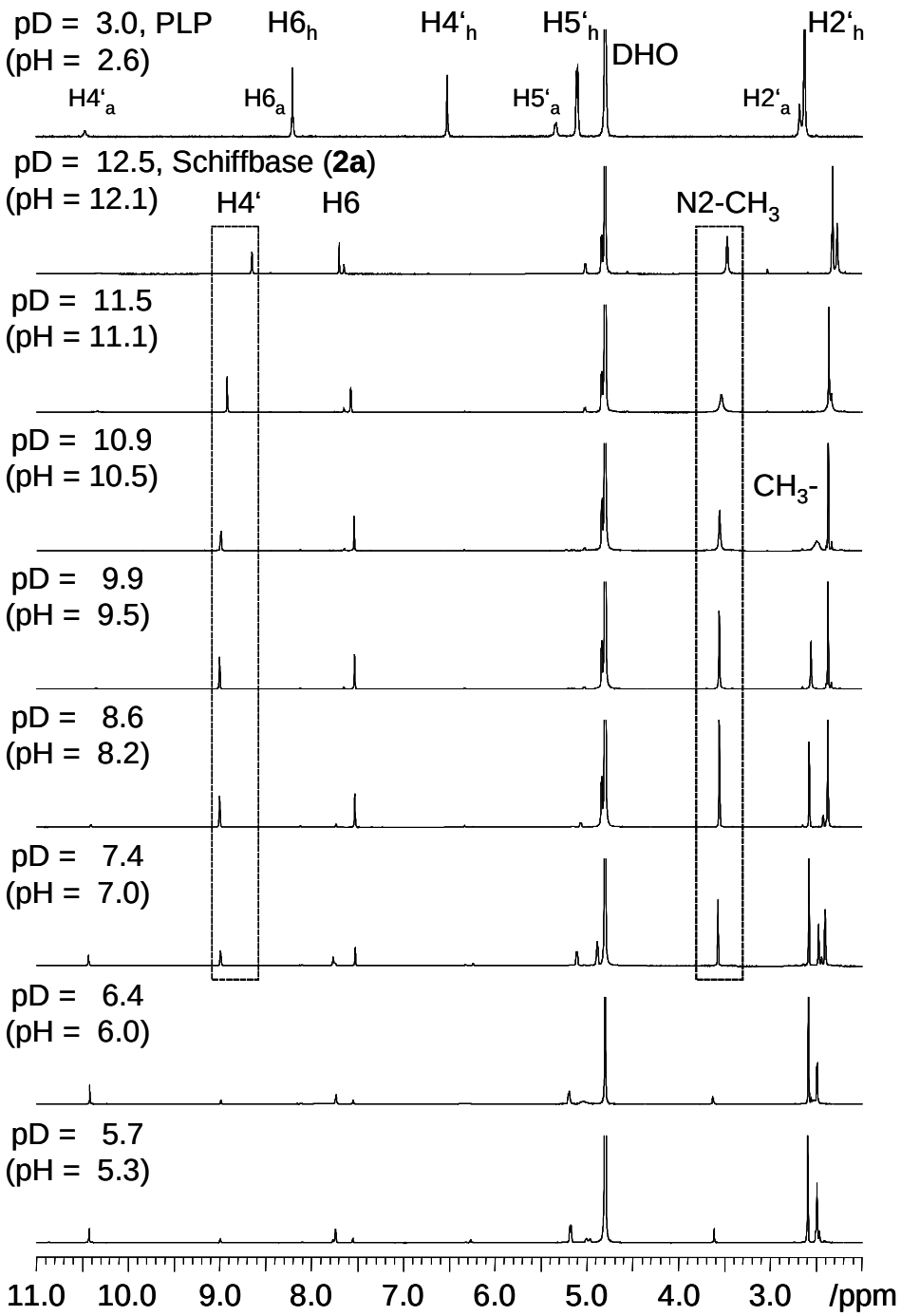

FIGURE S3: ^{1}H NMR spectra of the formed *in vitro* Schiff base (**2a**) from PLP and ^{15}N-enriched methylamine in D_2O. The pD values given are calculated from the measured pH values (in brackets) with the relation pD= pH + 0.40. Signals are marked with letter a for the aldehyde form (**1a**) and with letter h for hydrated form (**1b**). The most characteristic signals of the Schiff bases are highlighted with boxes.

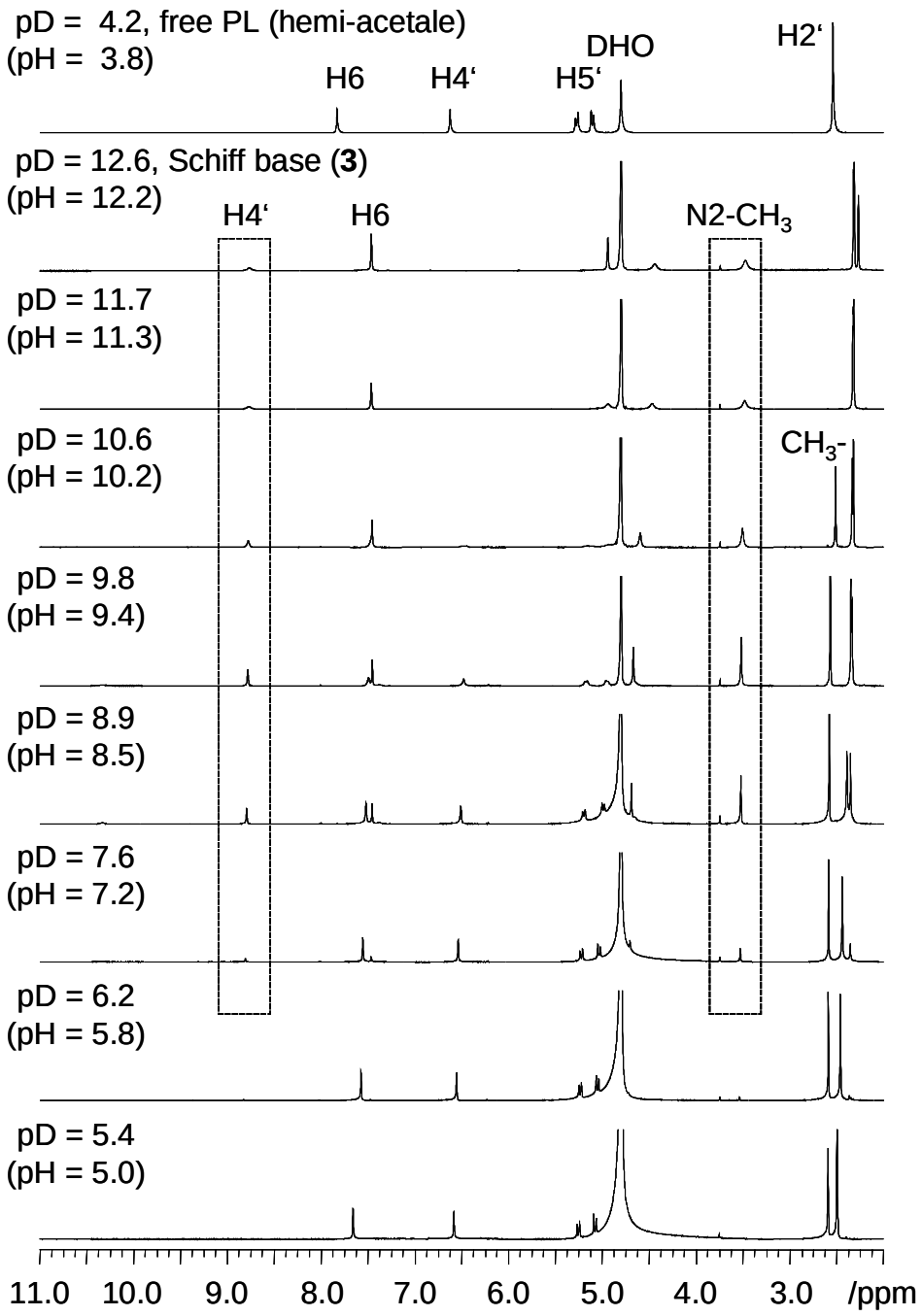

FIGURE S4: ^{1}H NMR spectra of the Schiff base (**3**) in D_2O. The pD values given are calculated from the measured pH values (in brackets) with the relation pD= pH + 0.40. Free PL is in the cyclic hemi-acetal form. The most characteristic signals of the Schiff bases are highlighted with boxes.

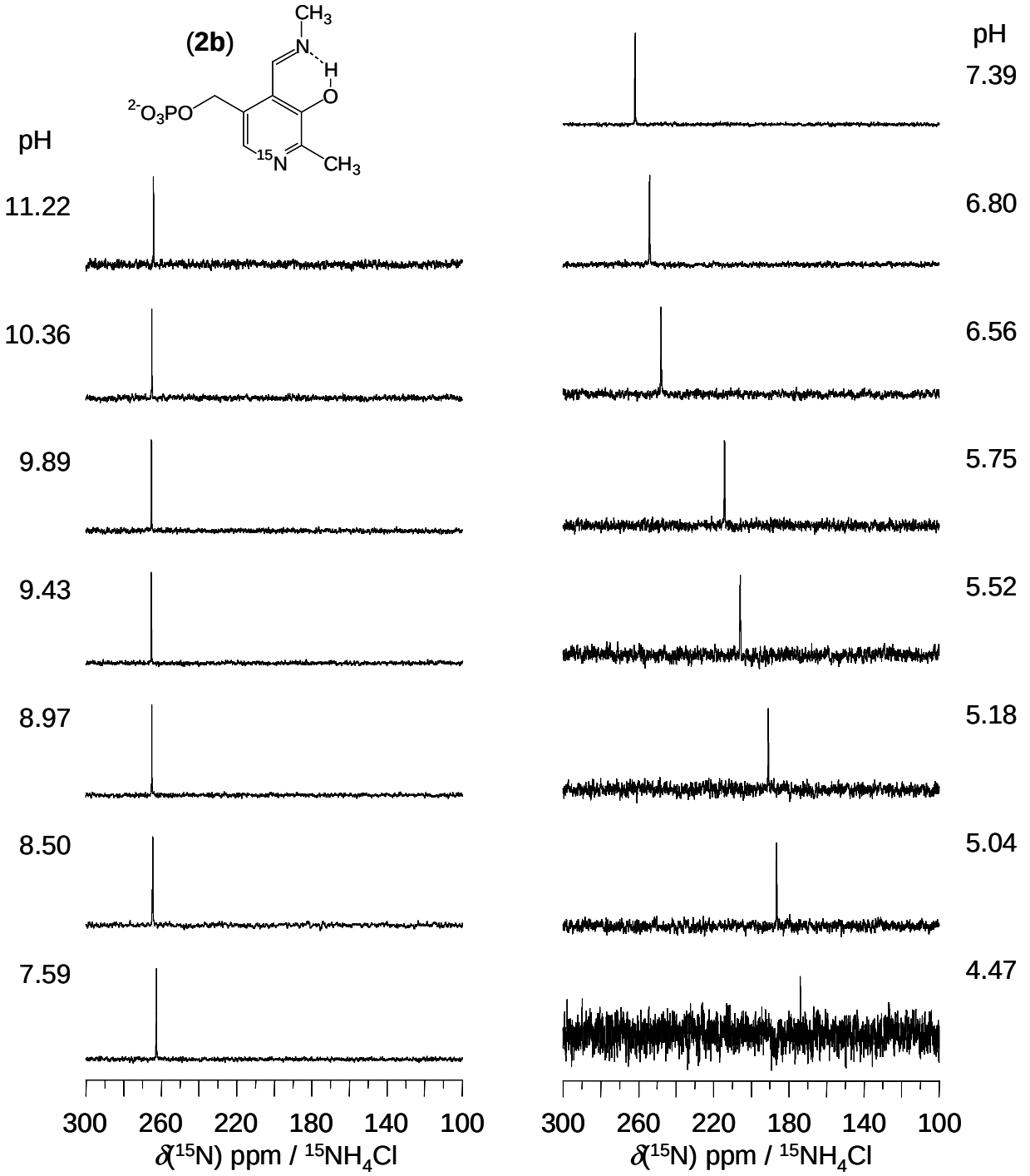

FIGURE S5: $^{15}N\ \{^{1}H\}$ NMR spectra of the ^{15}N labeled Schiff base¸ N-(pyridoxyl-5'-phosphate-^{15}N-idine)-methylamine (**2b**), formed *in vitro*, in aqueous solution by locking to a D_2O capillary at room temperature.