

Supporting information

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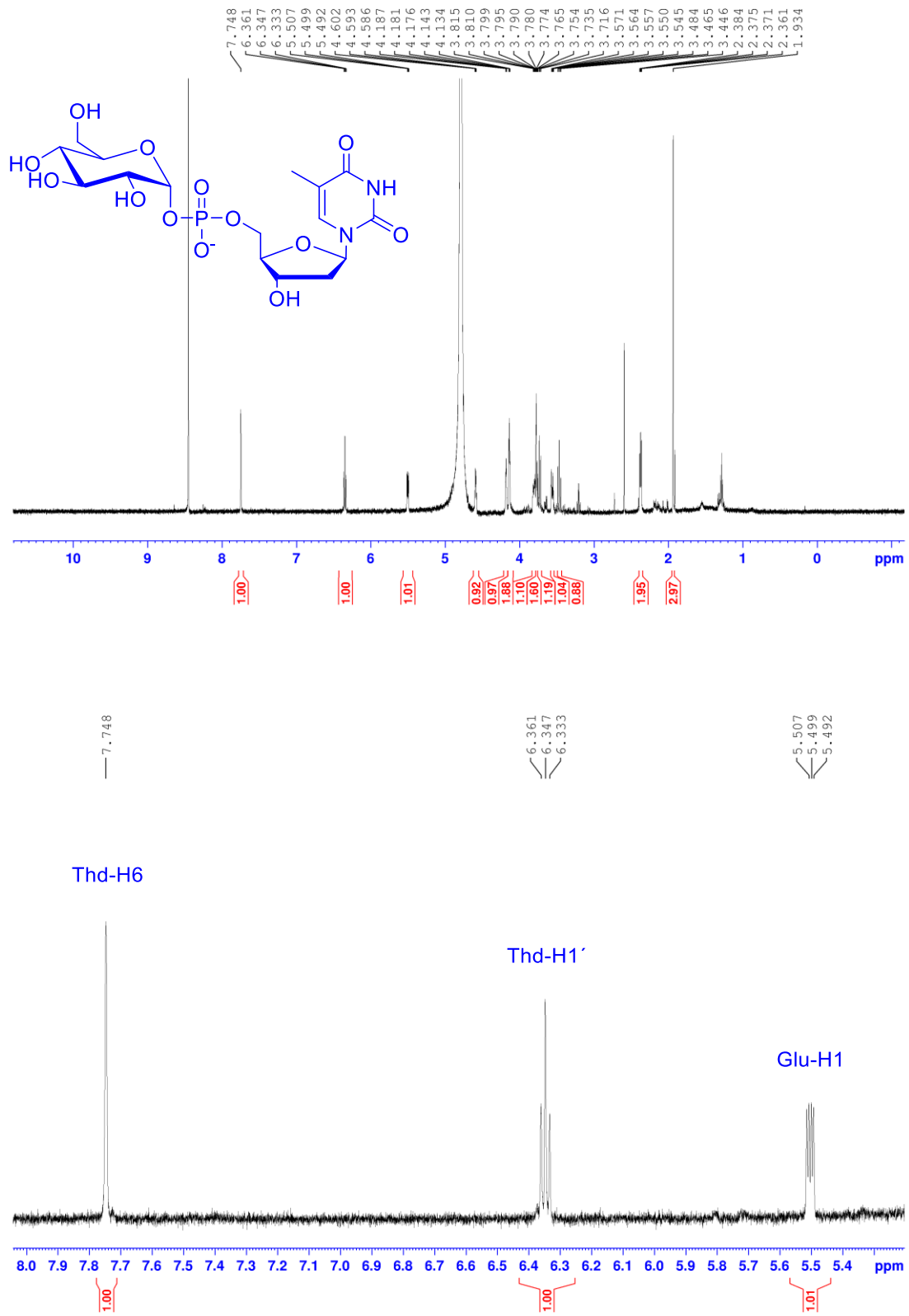


Figure S1. ^1H NMR spectrum (500 MHz, D_2O) of compound 6α .

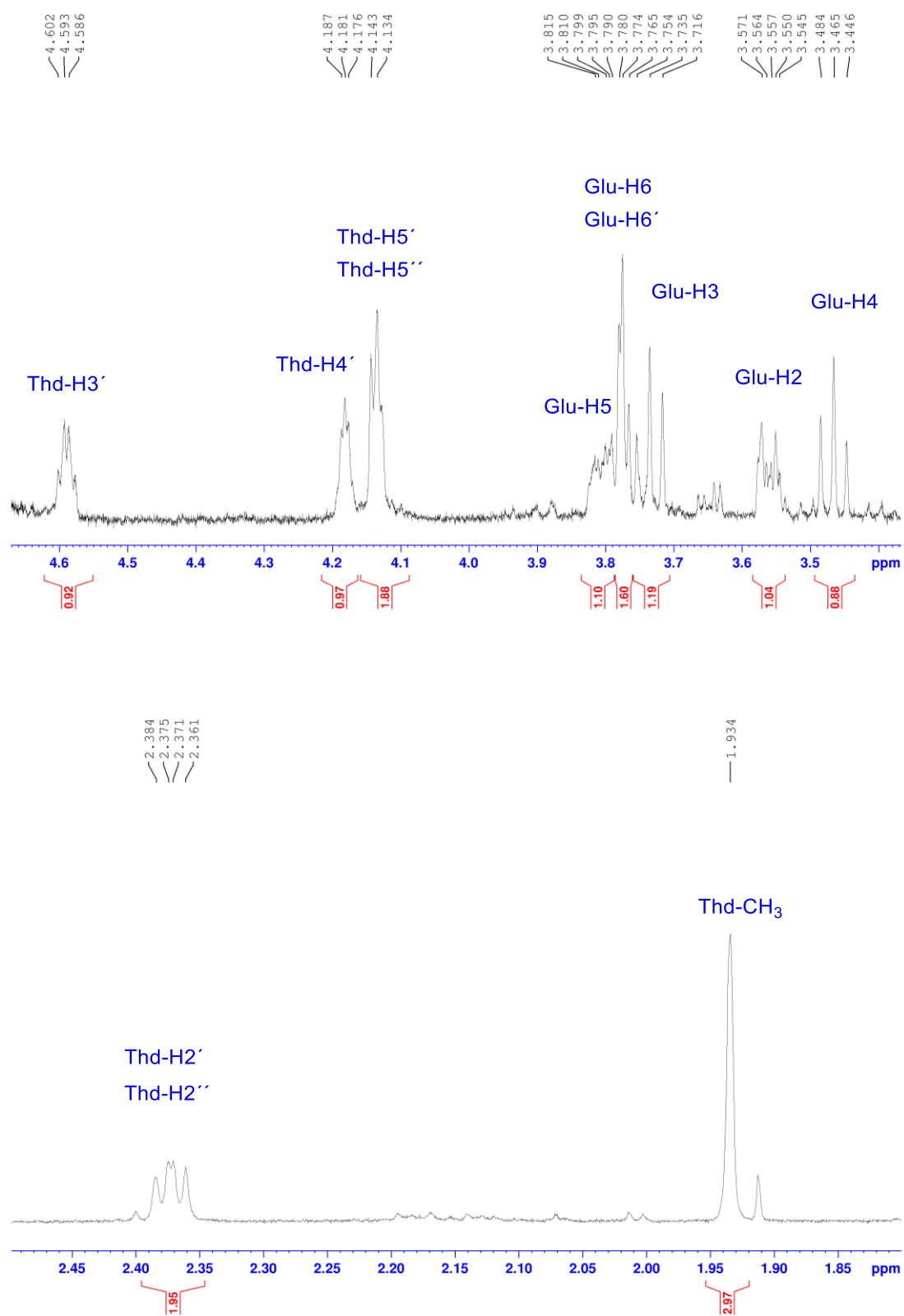


Figure S1 (continued). ¹H NMR spectrum (500 MHz, D₂O) of compound 6 α .

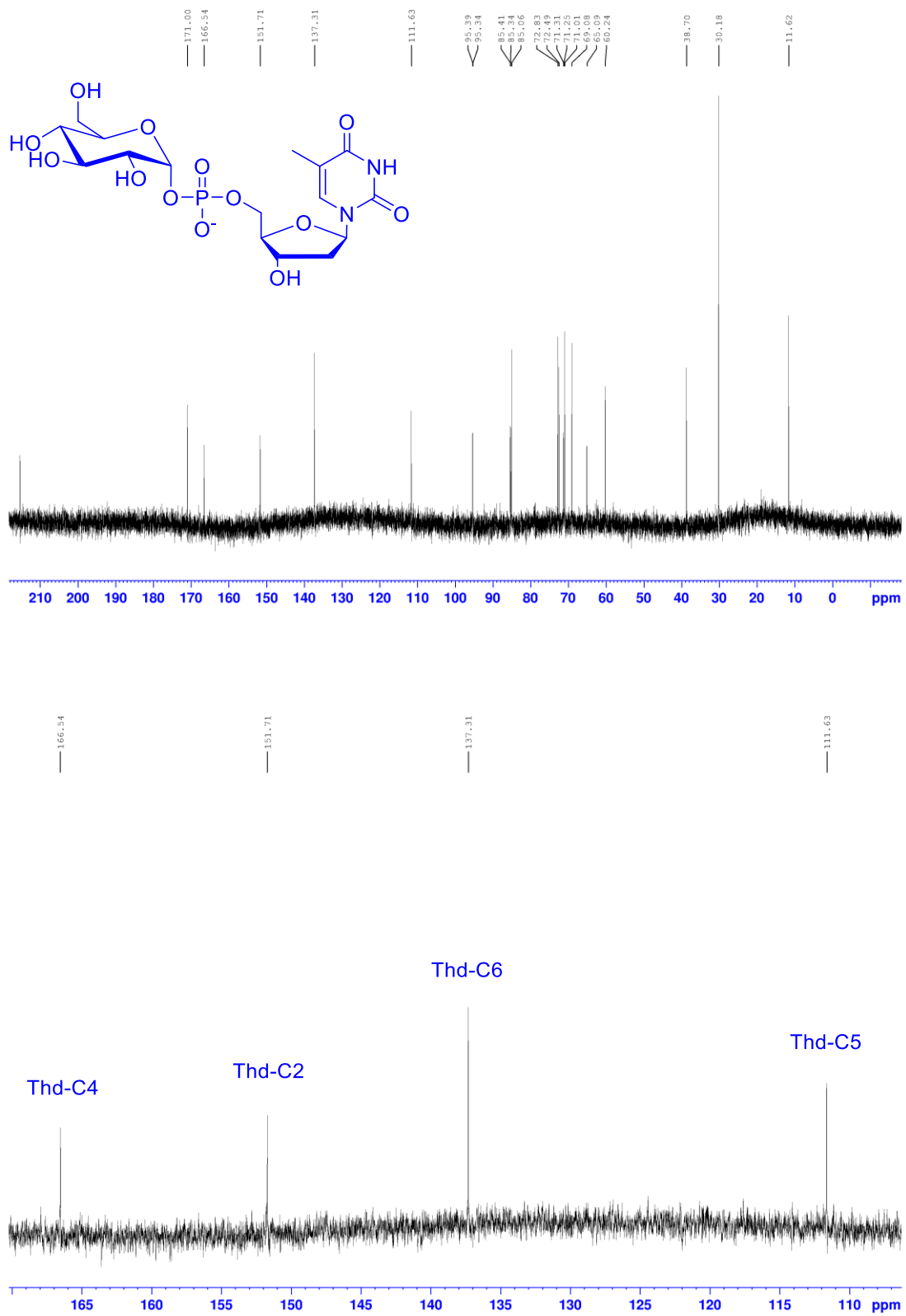


Figure S2. ^{13}C NMR spectrum (126 MHz, D_2O) of compound 6α .

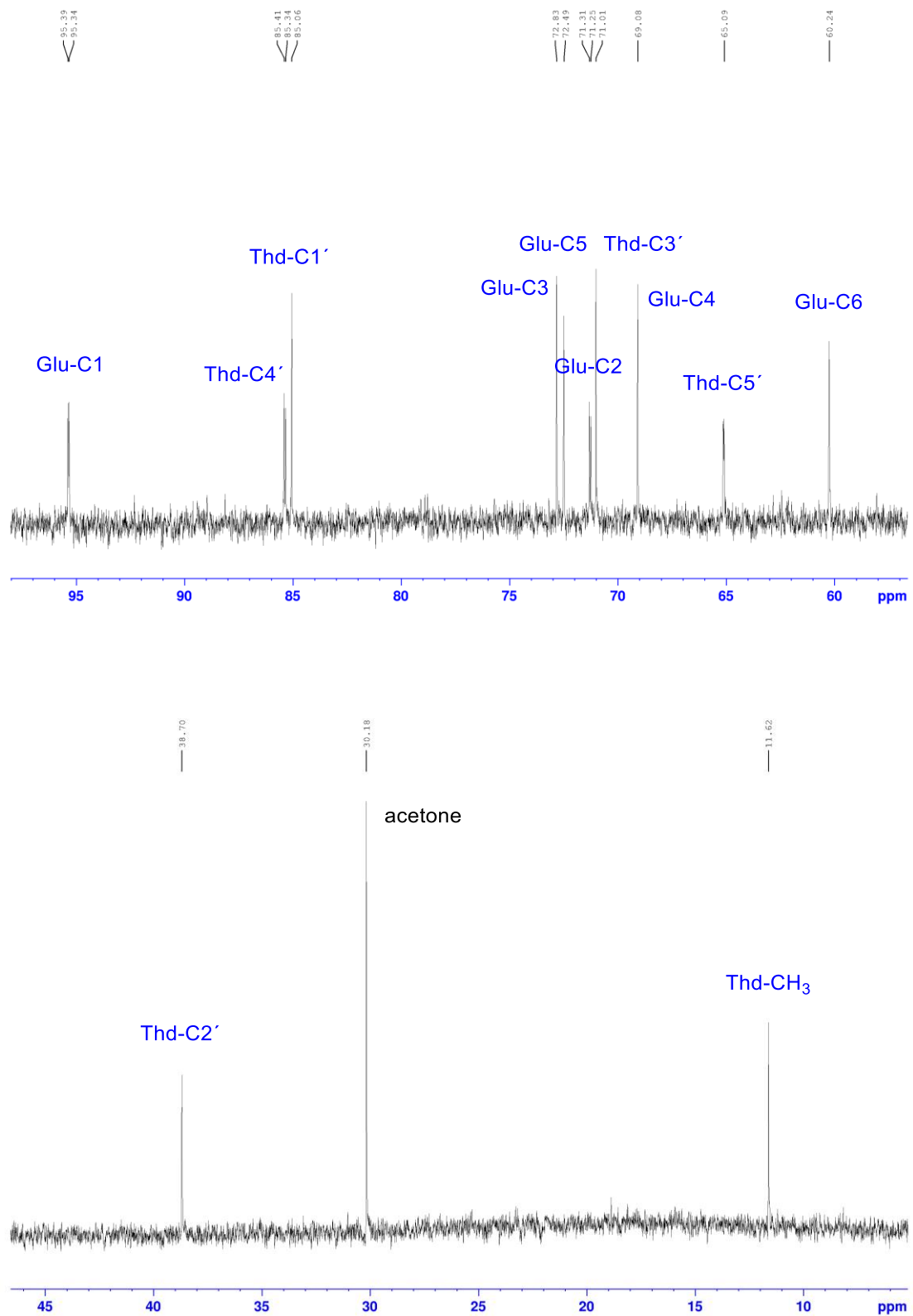


Figure S2 (continued). ^{13}C NMR spectrum (126 MHz, D_2O) of compound 6α .

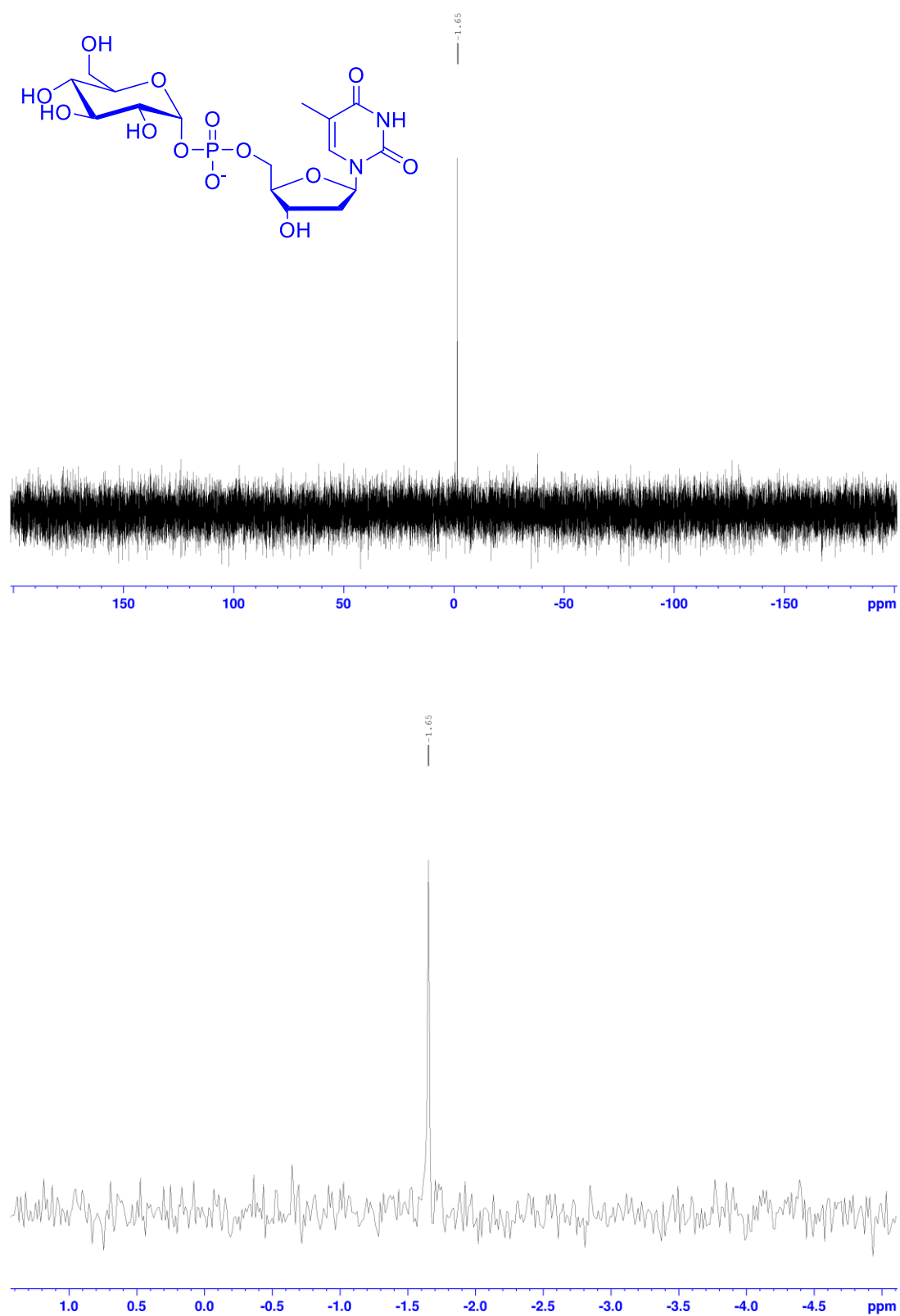


Figure S3. ^{31}P NMR spectrum (202 MHz, D_2O) of compound **6α**.

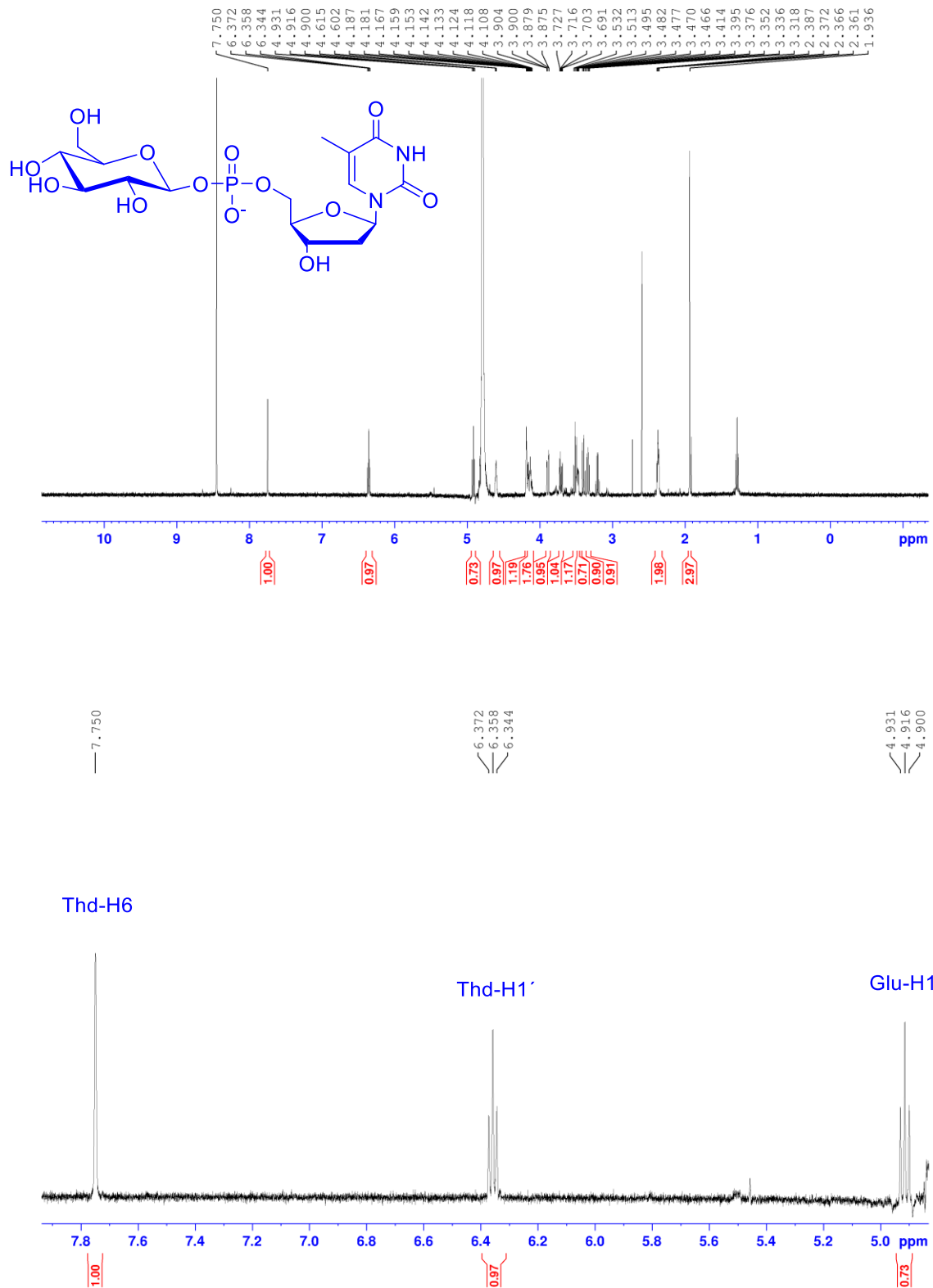


Figure S4. ^1H NMR spectrum (500 MHz, D_2O) of compound **6β**.

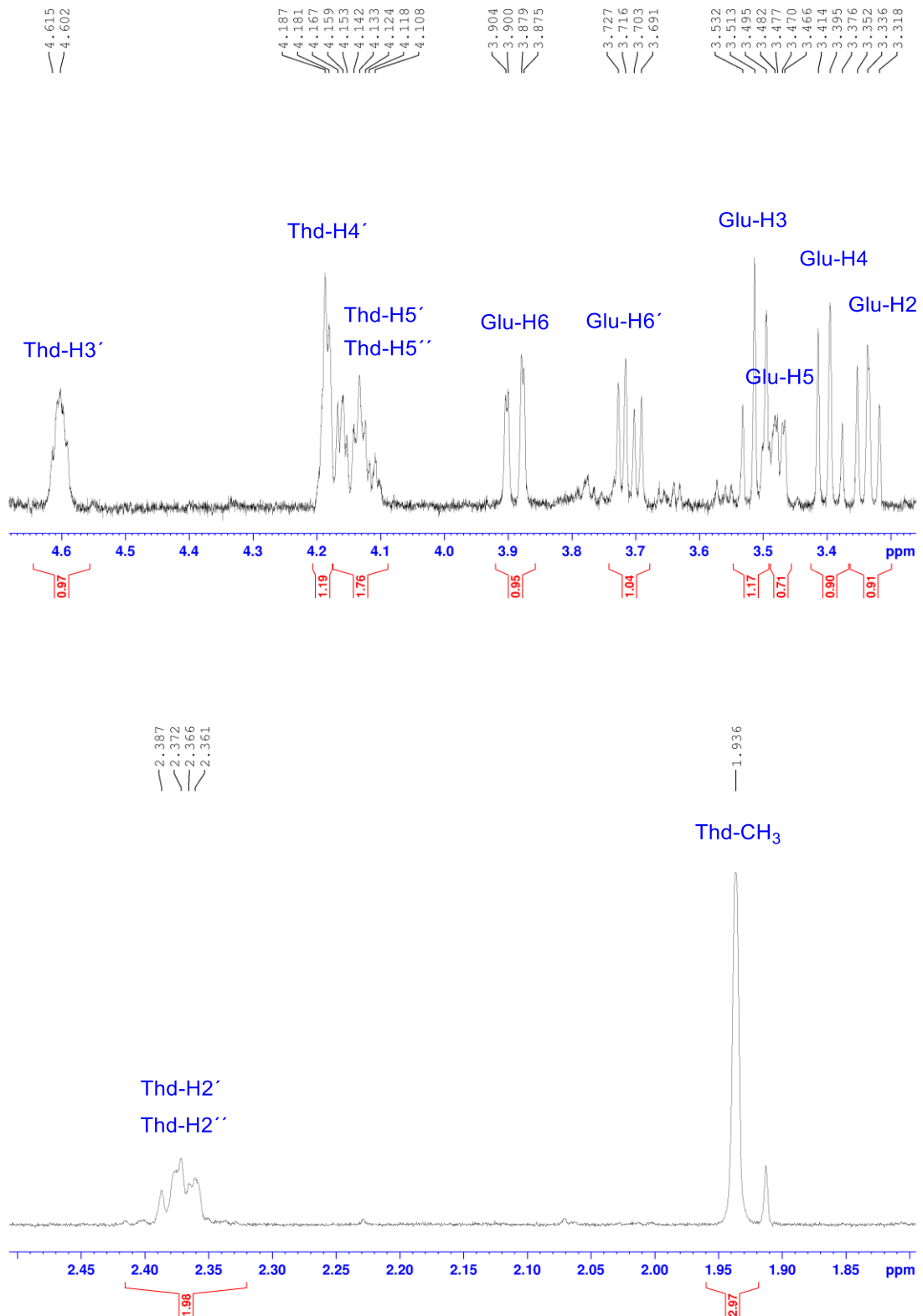


Figure S4 (continued). ¹H NMR spectrum (500 MHz, D₂O) of compound 6β.

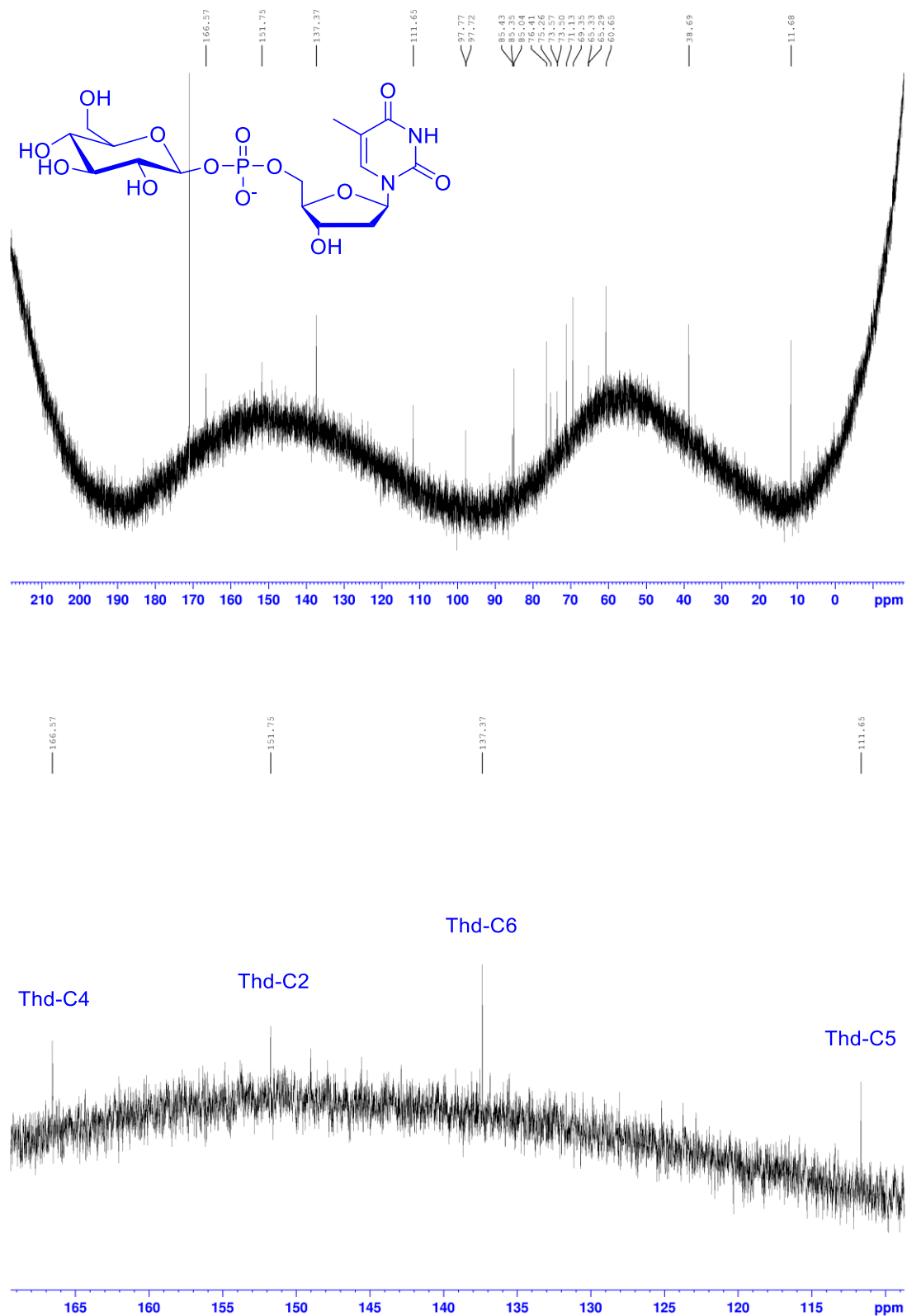


Figure S5. ^{13}C NMR spectrum (126 MHz, D_2O) of compound 6β .

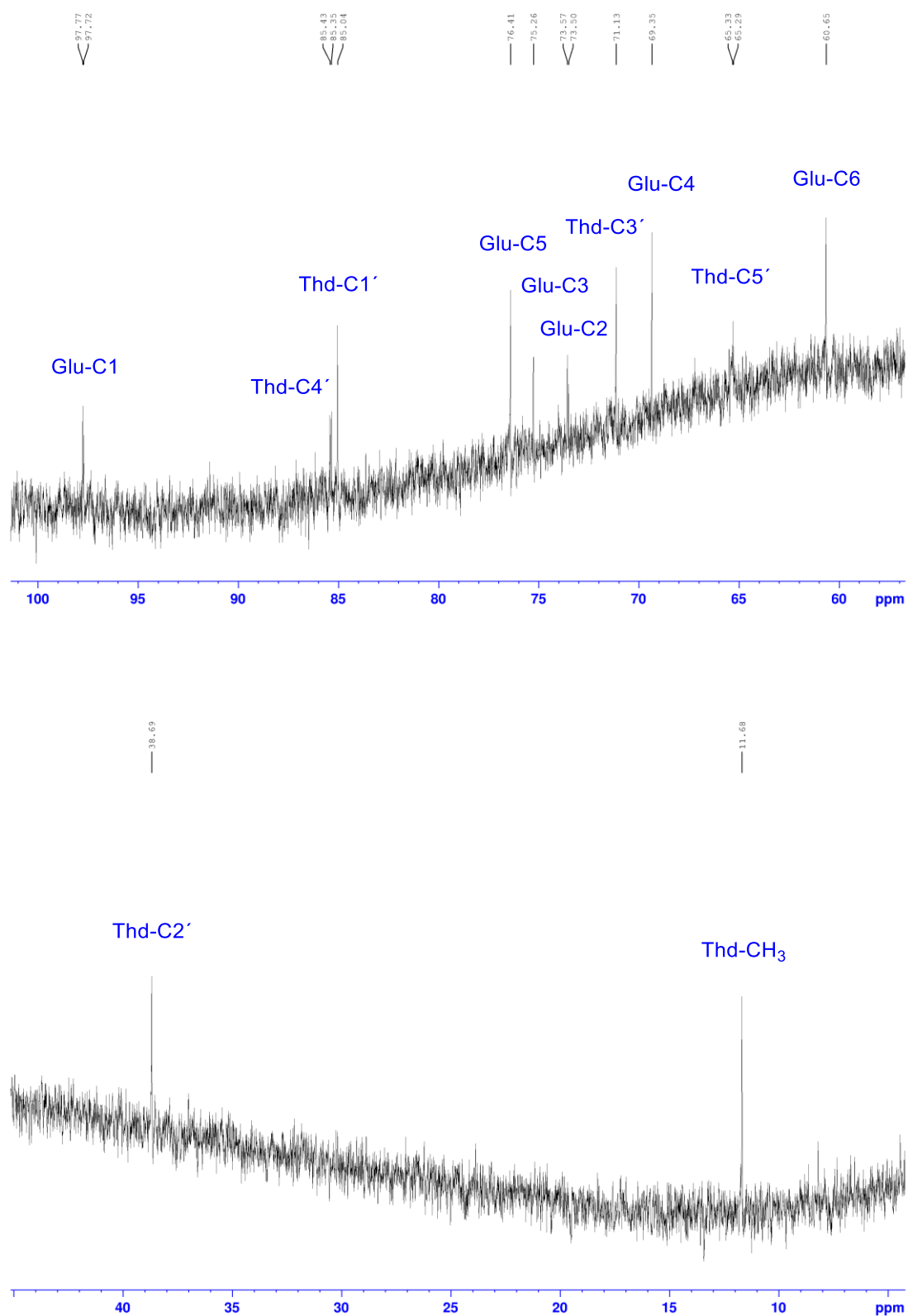


Figure S5 (continued). ¹³C NMR spectrum (126 MHz, D₂O) of compound **6β**.

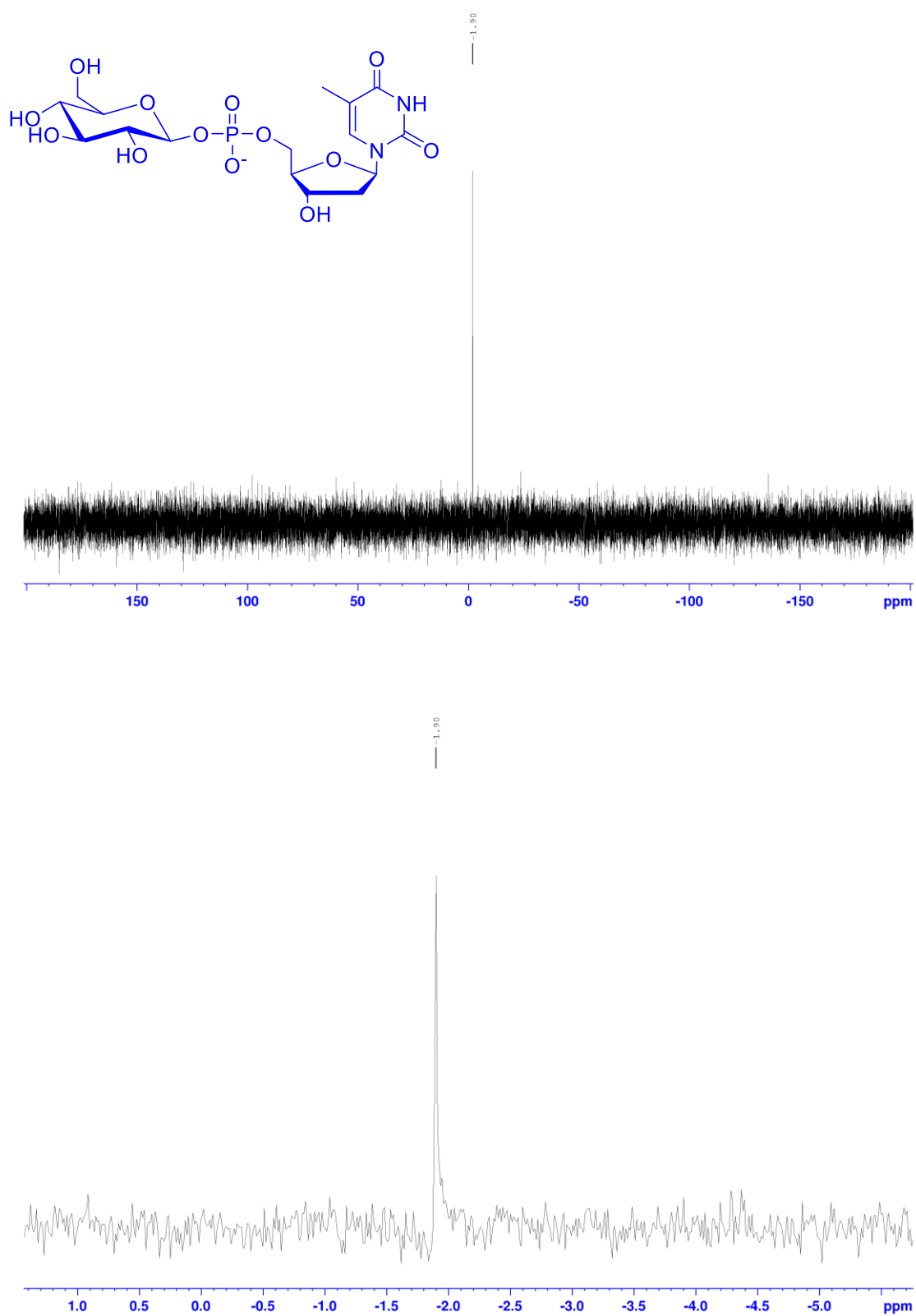


Figure S6. ³¹P NMR spectrum (202 MHz, D₂O) of compound **6β**.

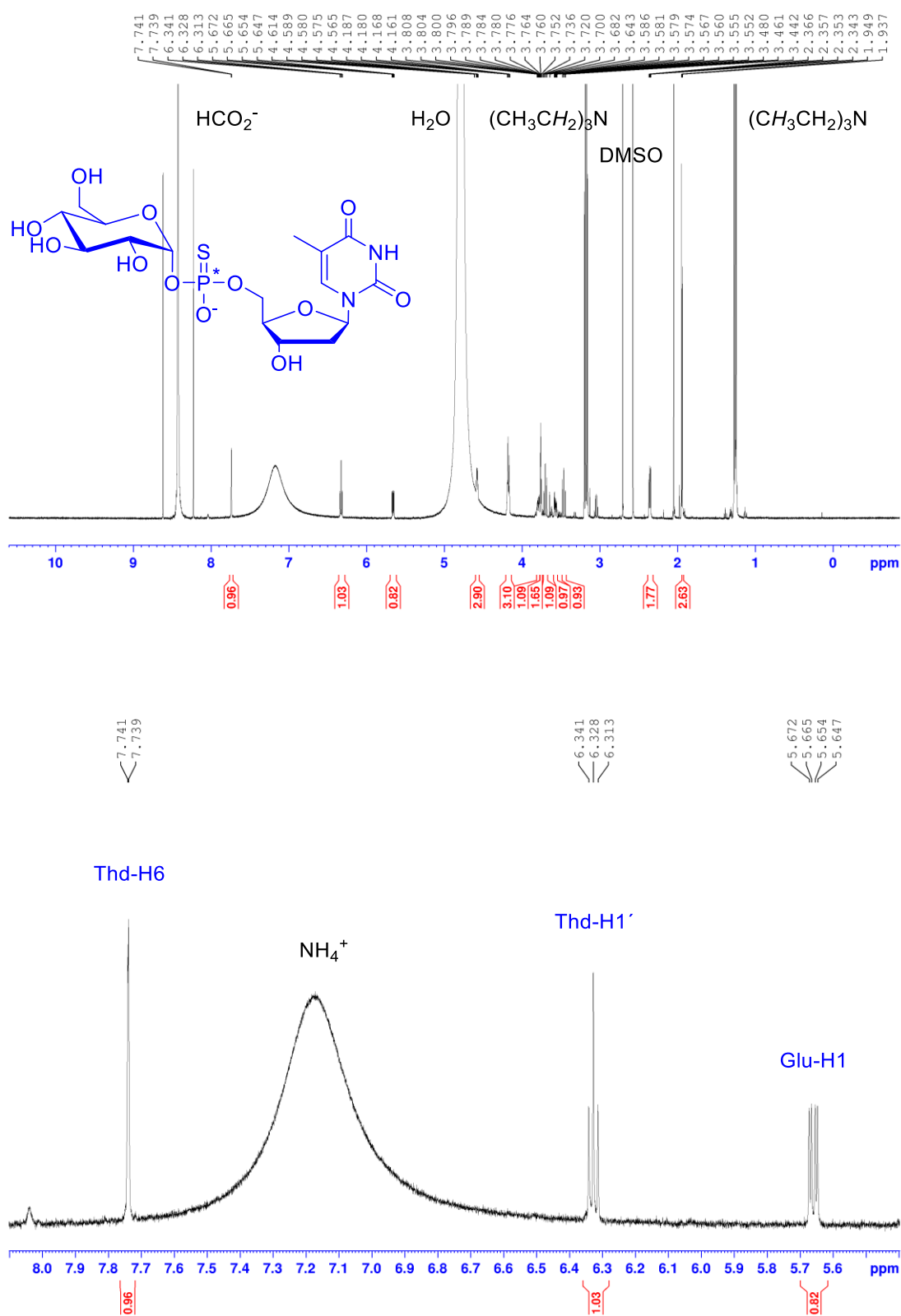


Figure S7. ^1H NMR spectrum (500 MHz, D_2O) of compound **7 α 1**.

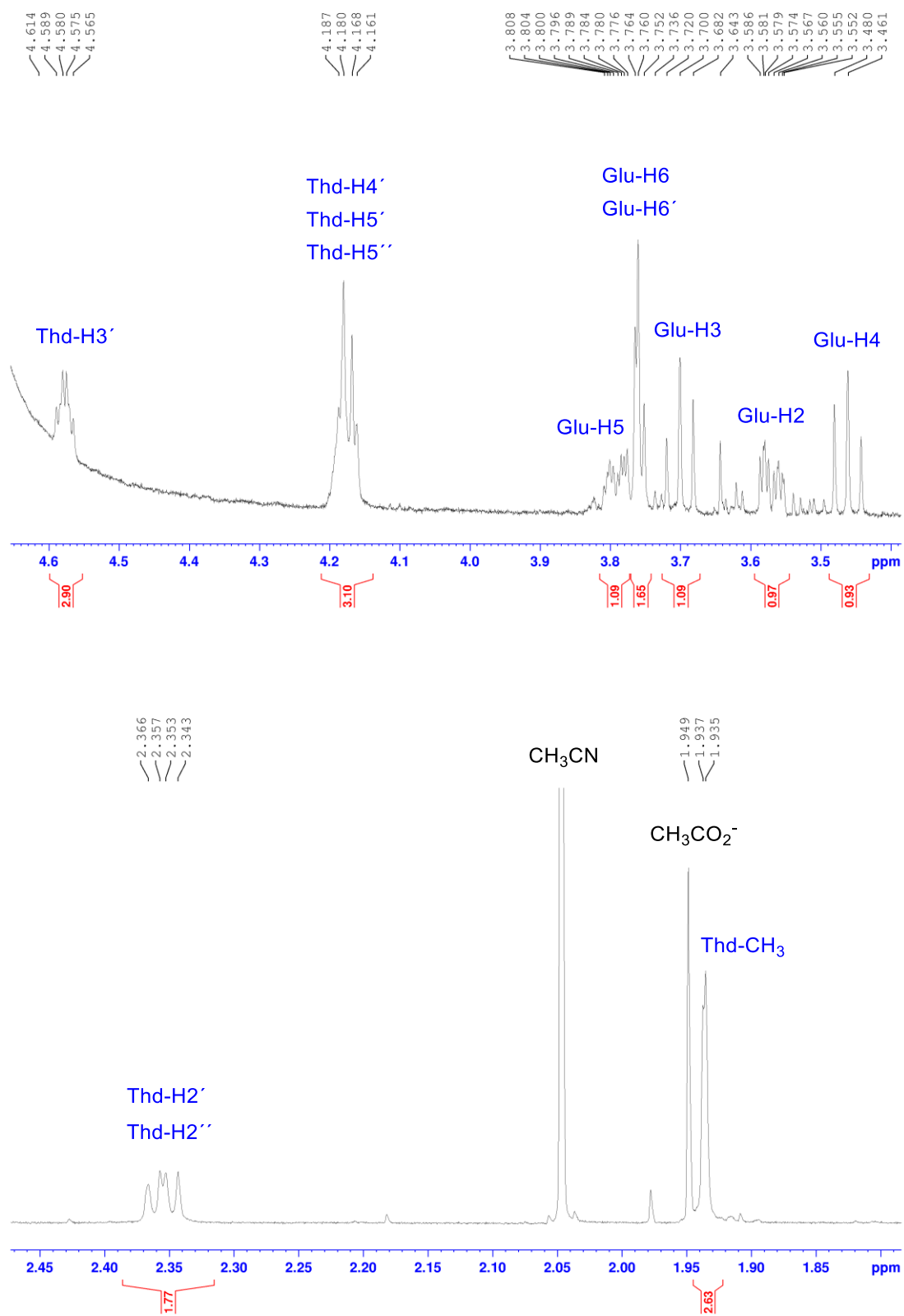


Figure S7 (continued). ¹H NMR spectrum (500 MHz, D₂O) of compound **7α1**.

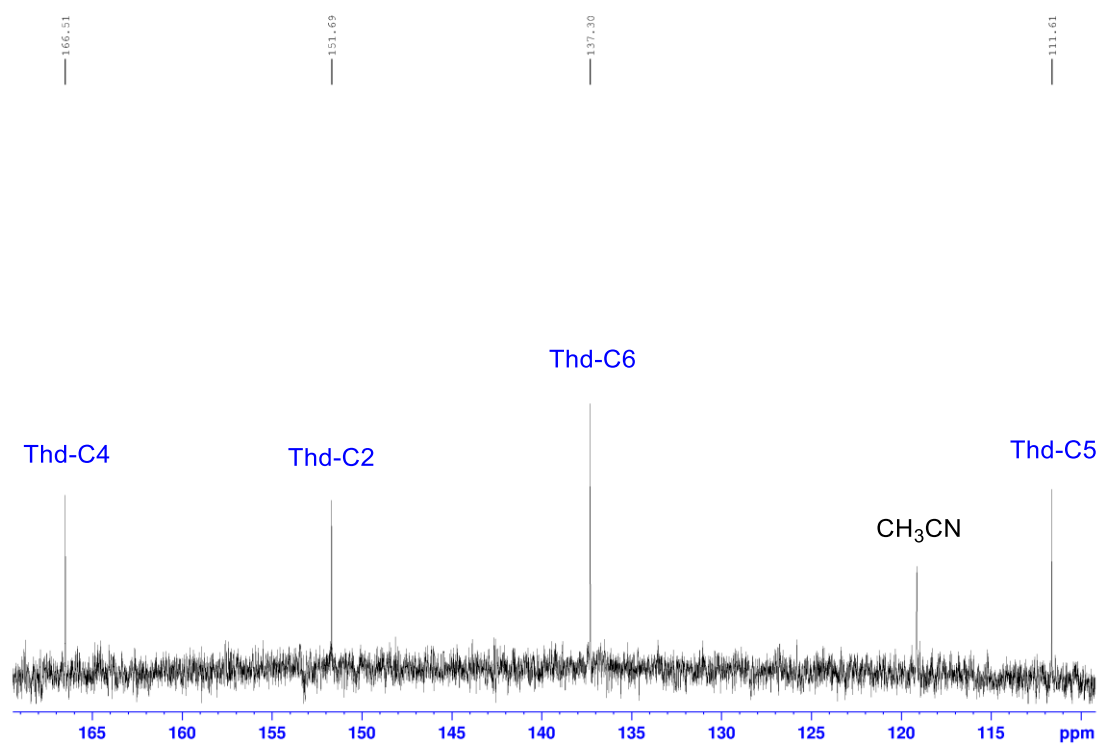
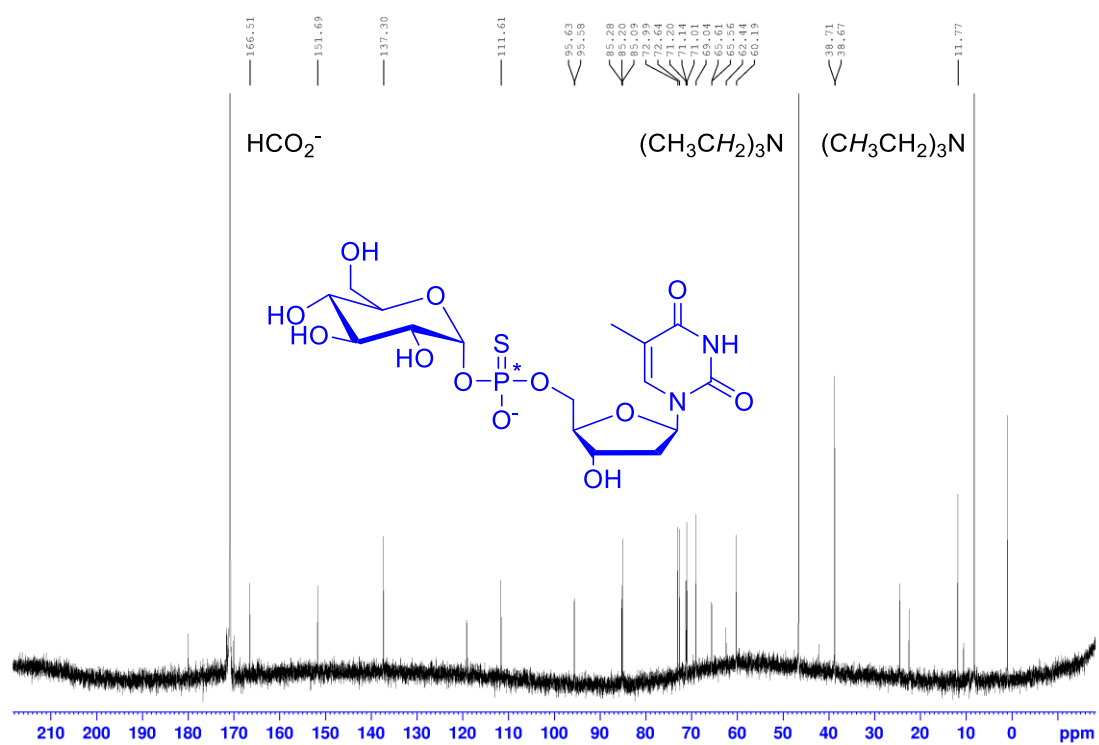


Figure S8. ^{13}C NMR spectrum (126 MHz, D_2O) of compound **7 α 1**.

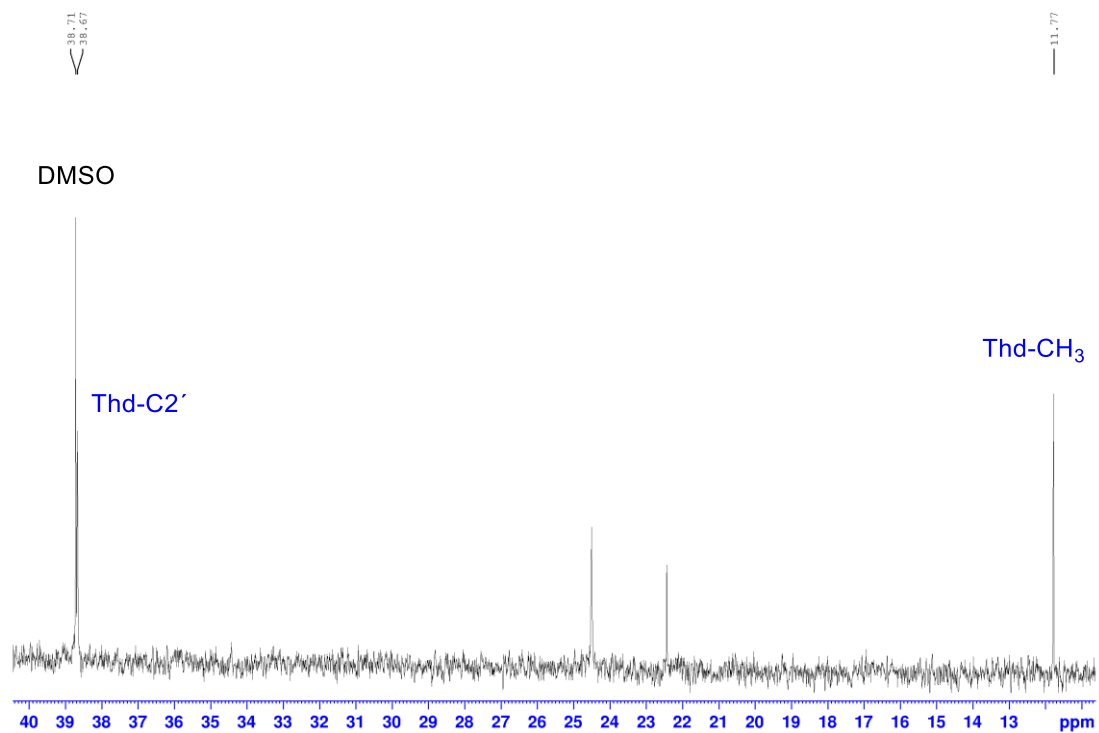
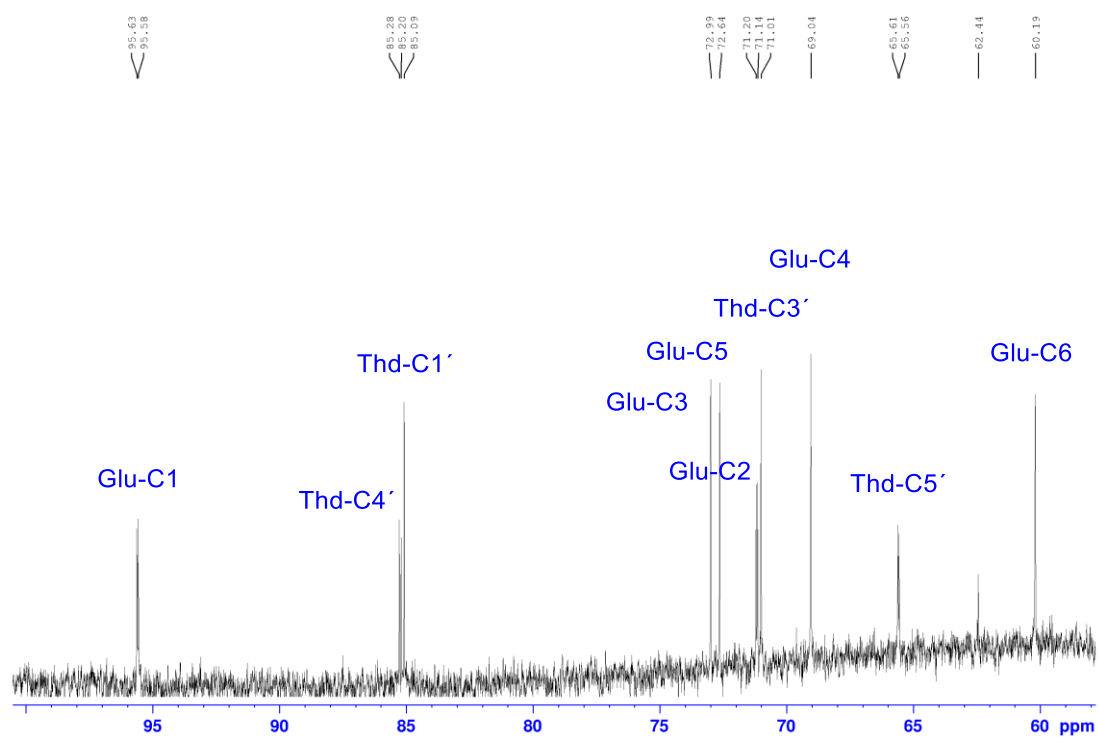


Figure S8 (continued). ¹³C NMR spectrum (126 MHz, D₂O) of compound 7α1.

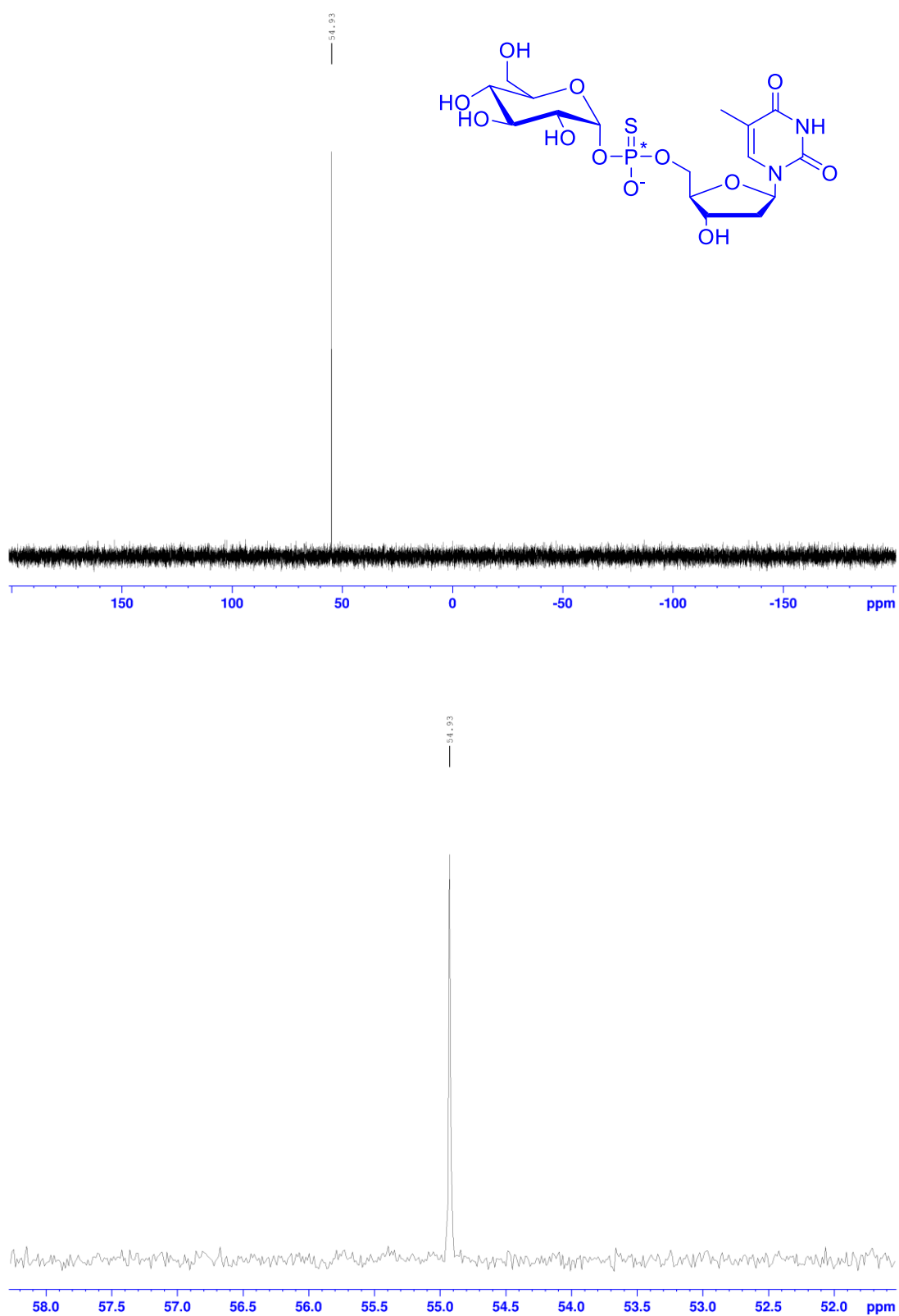


Figure S9. ^{31}P NMR spectrum (202 MHz, D_2O) of compound **7 α 1**.

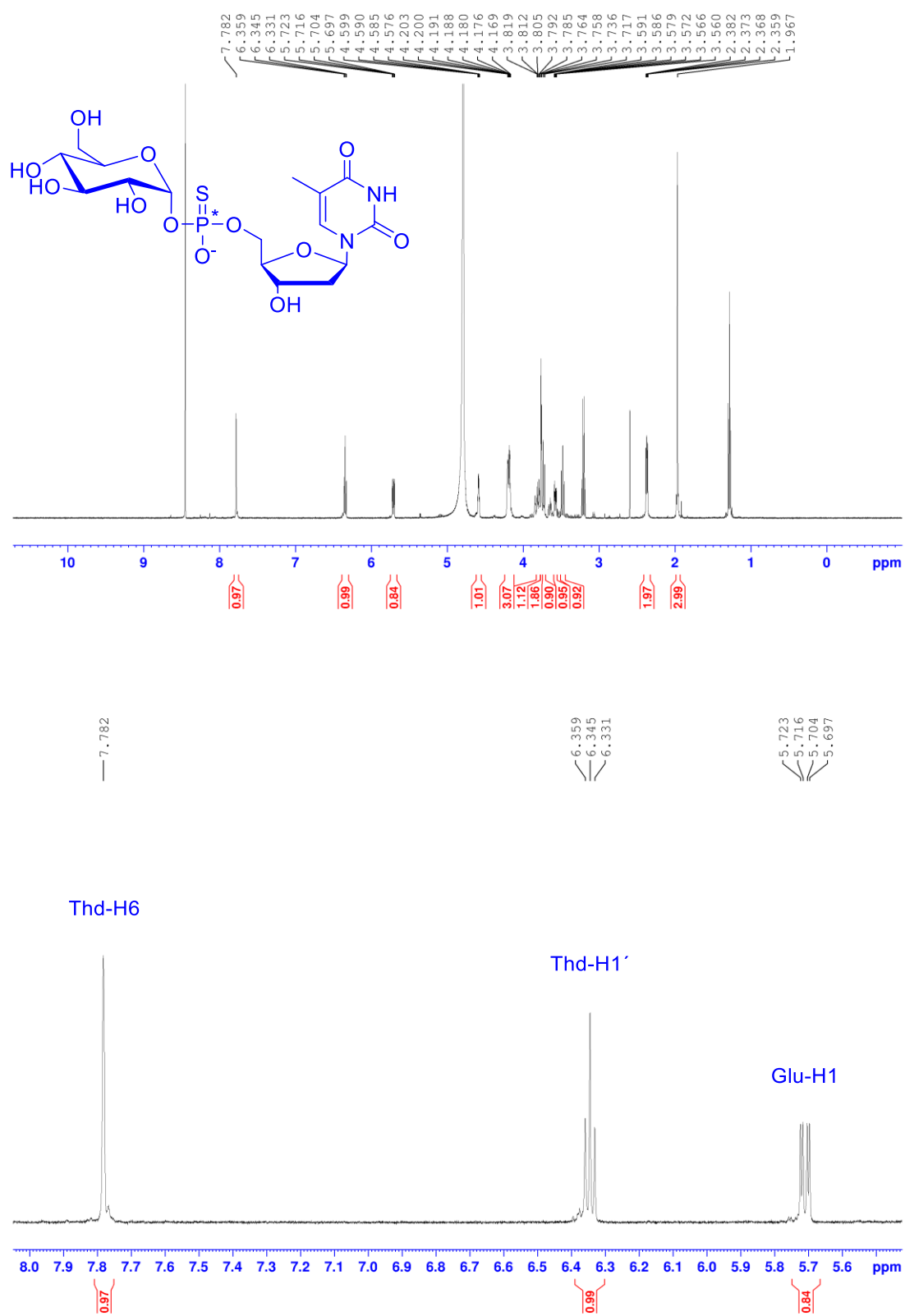


Figure S10. ^1H NMR spectrum (500 MHz, D_2O) of compound **7a2**.

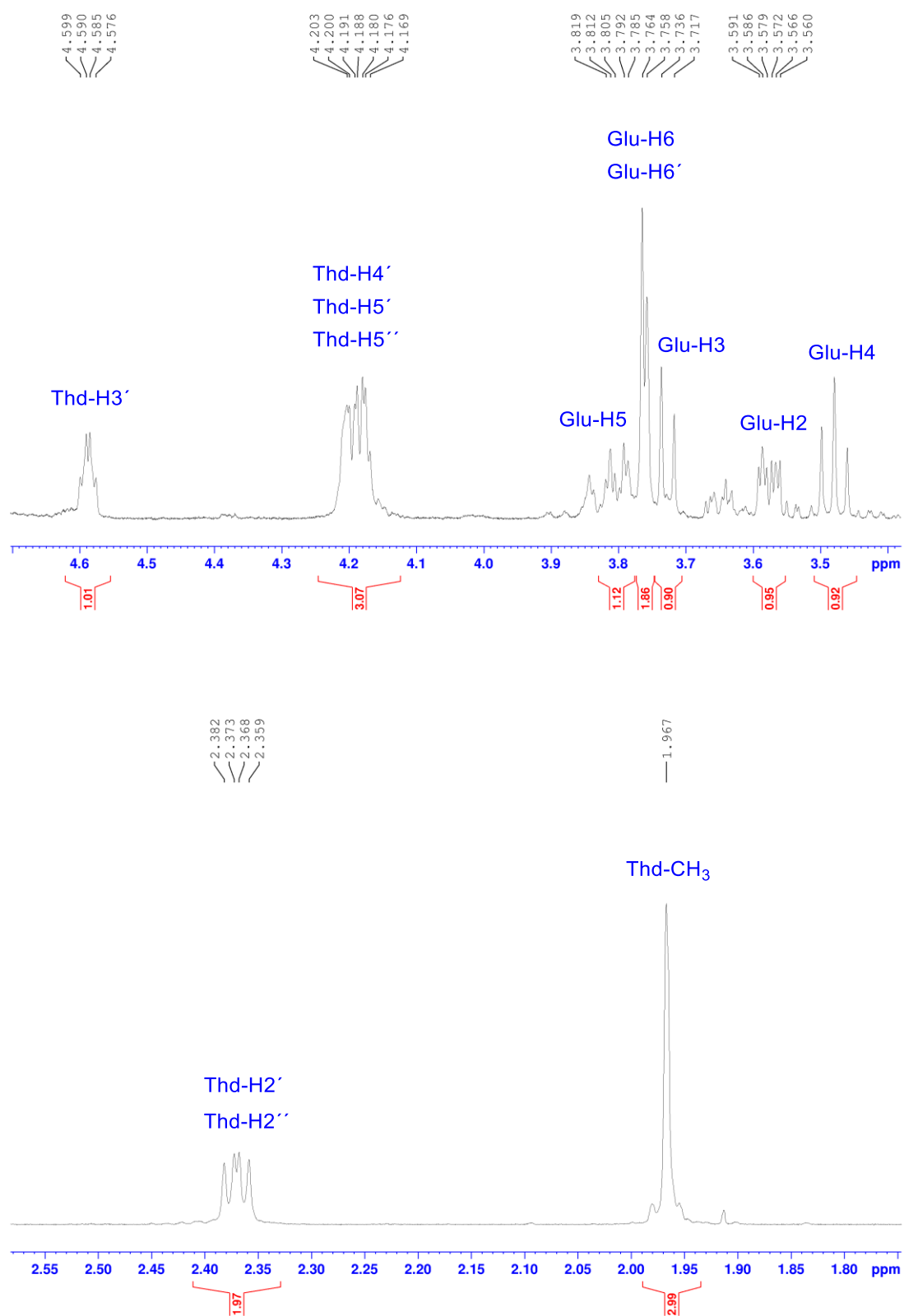


Figure S10 (continued). ¹H NMR spectrum (500 MHz, D₂O) of compound **7α2**.

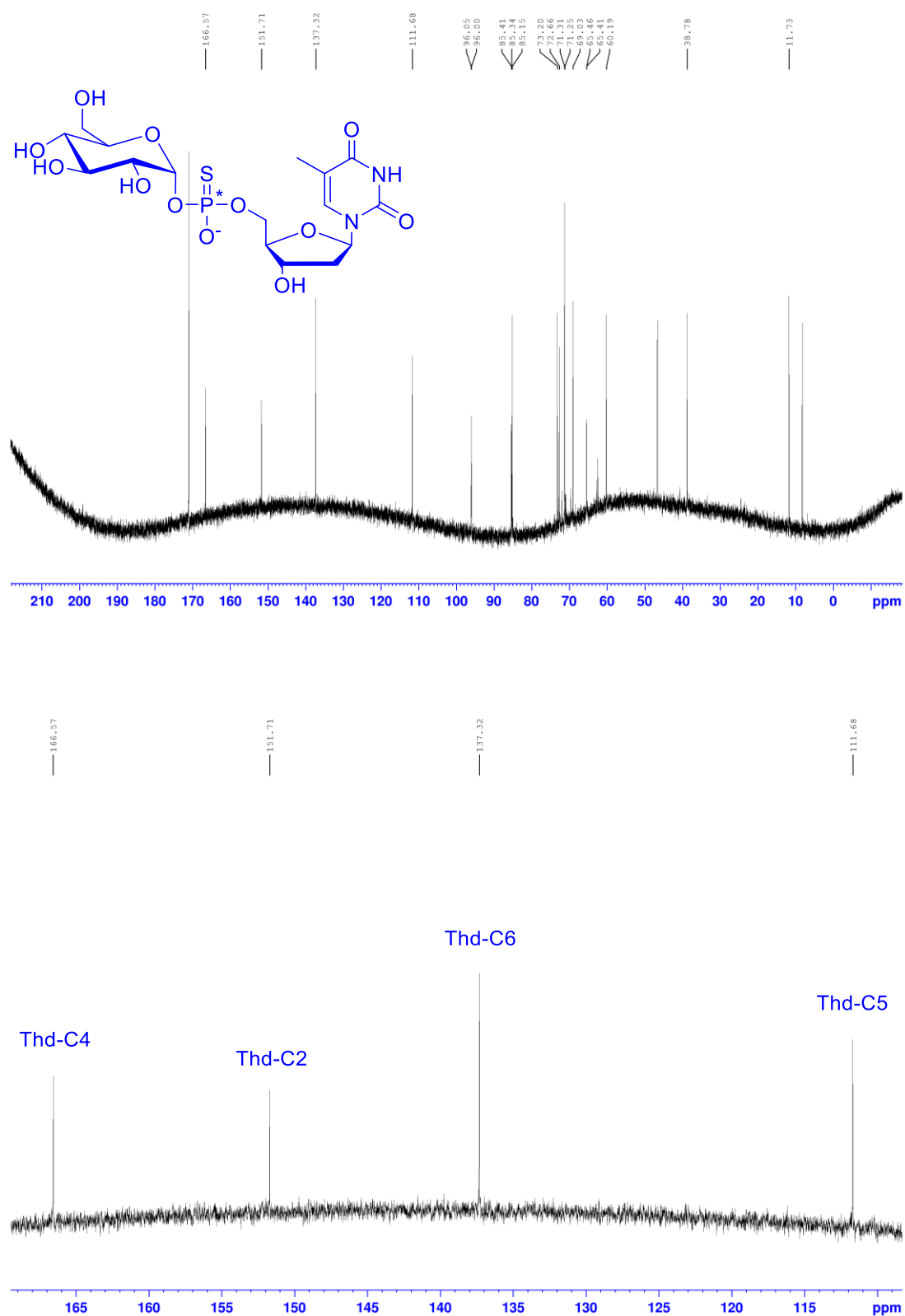


Figure S11. ^{13}C NMR spectrum (126 MHz, D_2O) of compound **7 α 2**.

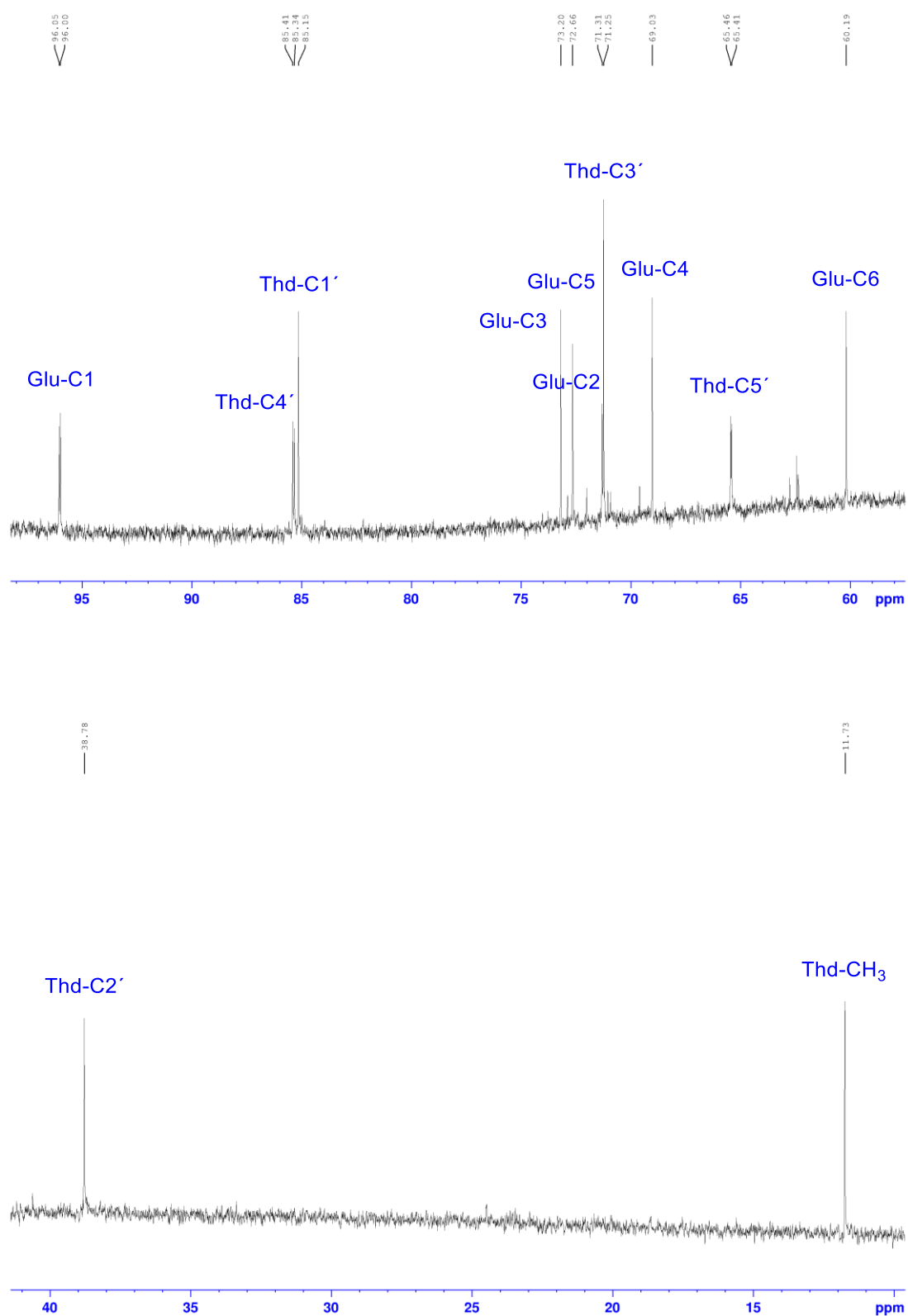


Figure S11 (continued). ^{13}C NMR spectrum (126 MHz, D_2O) of compound **7 α 2**.

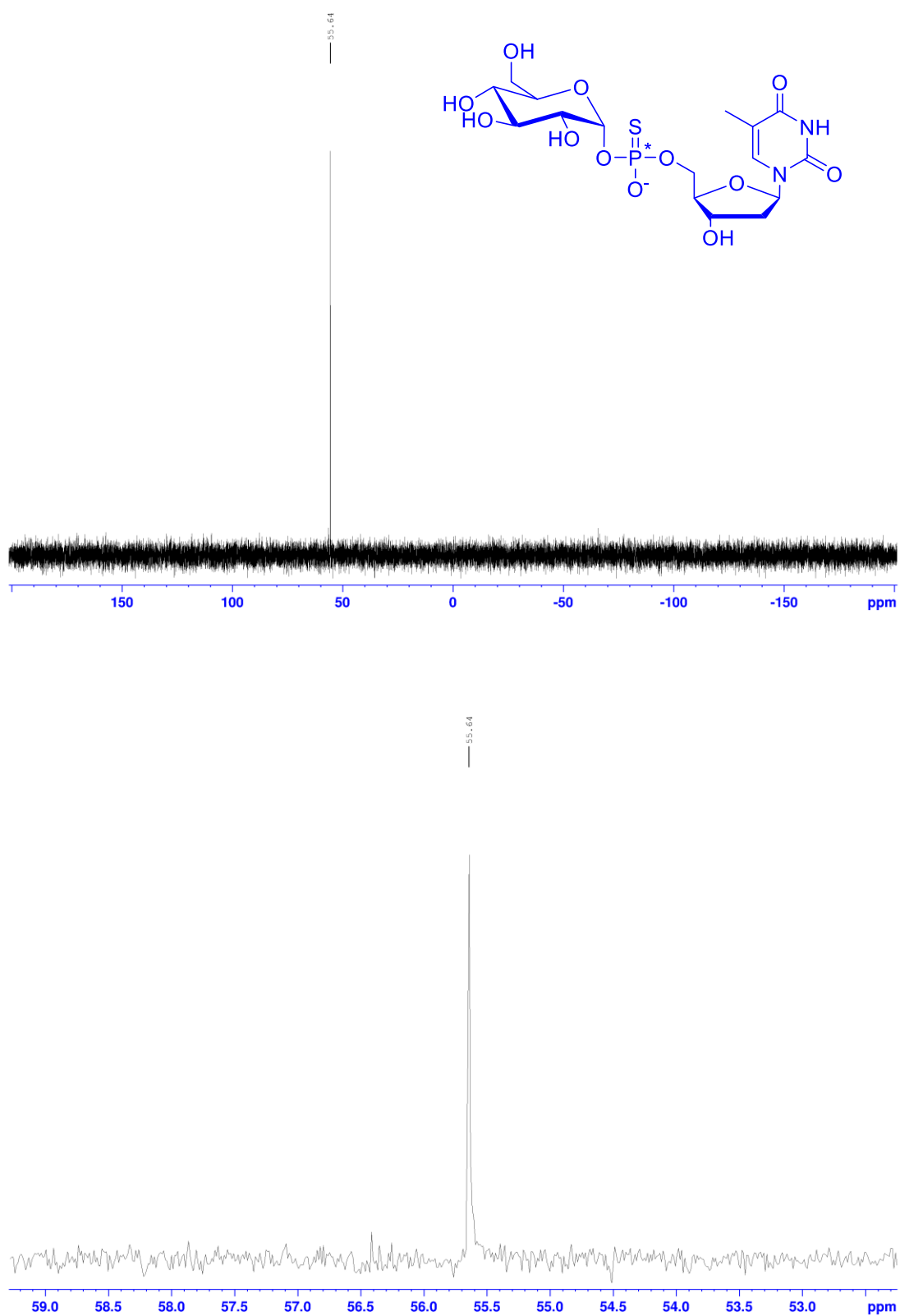


Figure S12. ^{31}P NMR spectrum (202 MHz, D_2O) of compound **7 α 2**.

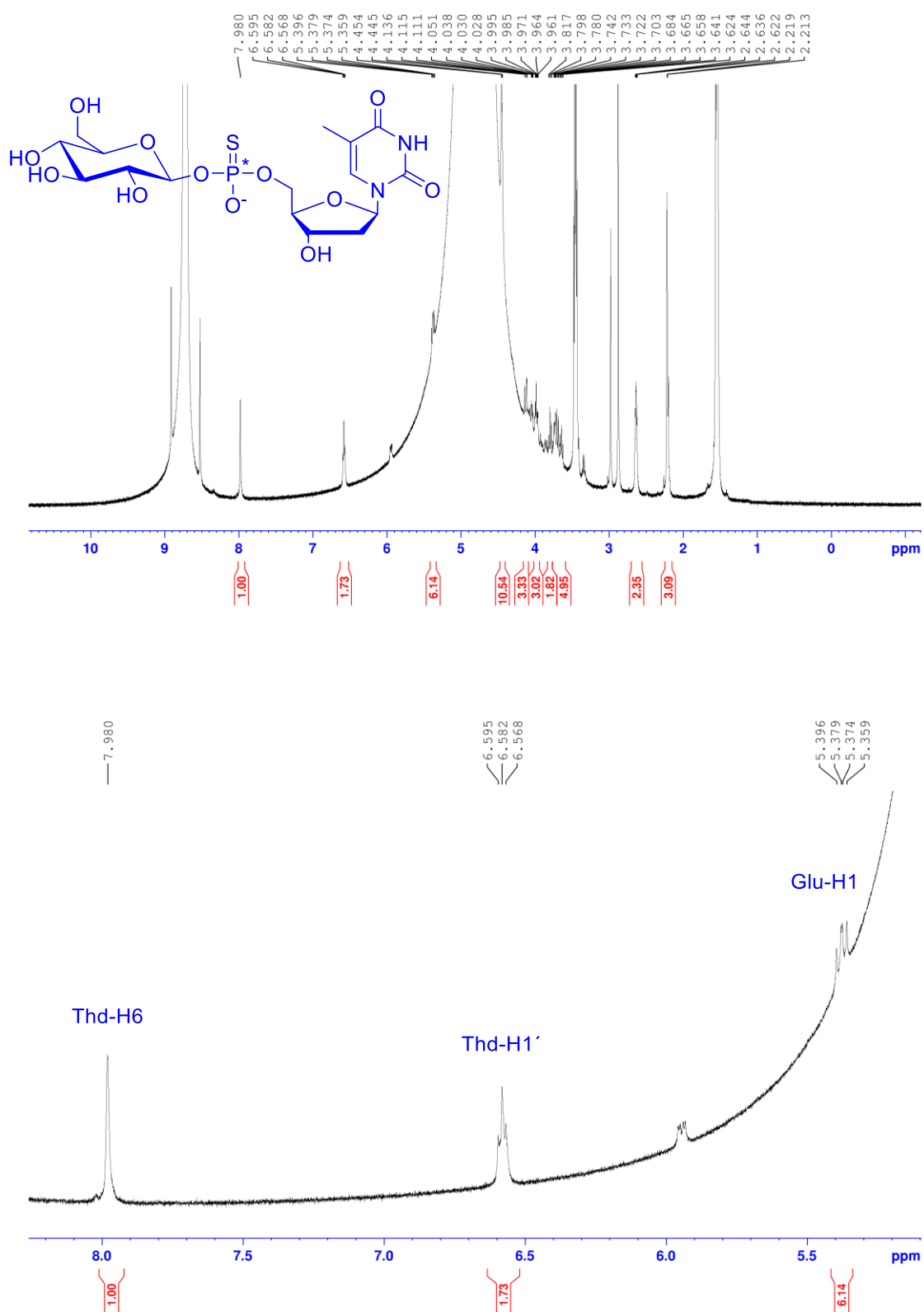


Figure S13. ^1H NMR spectrum (500 MHz, D_2O) of compound **7 β 1**.

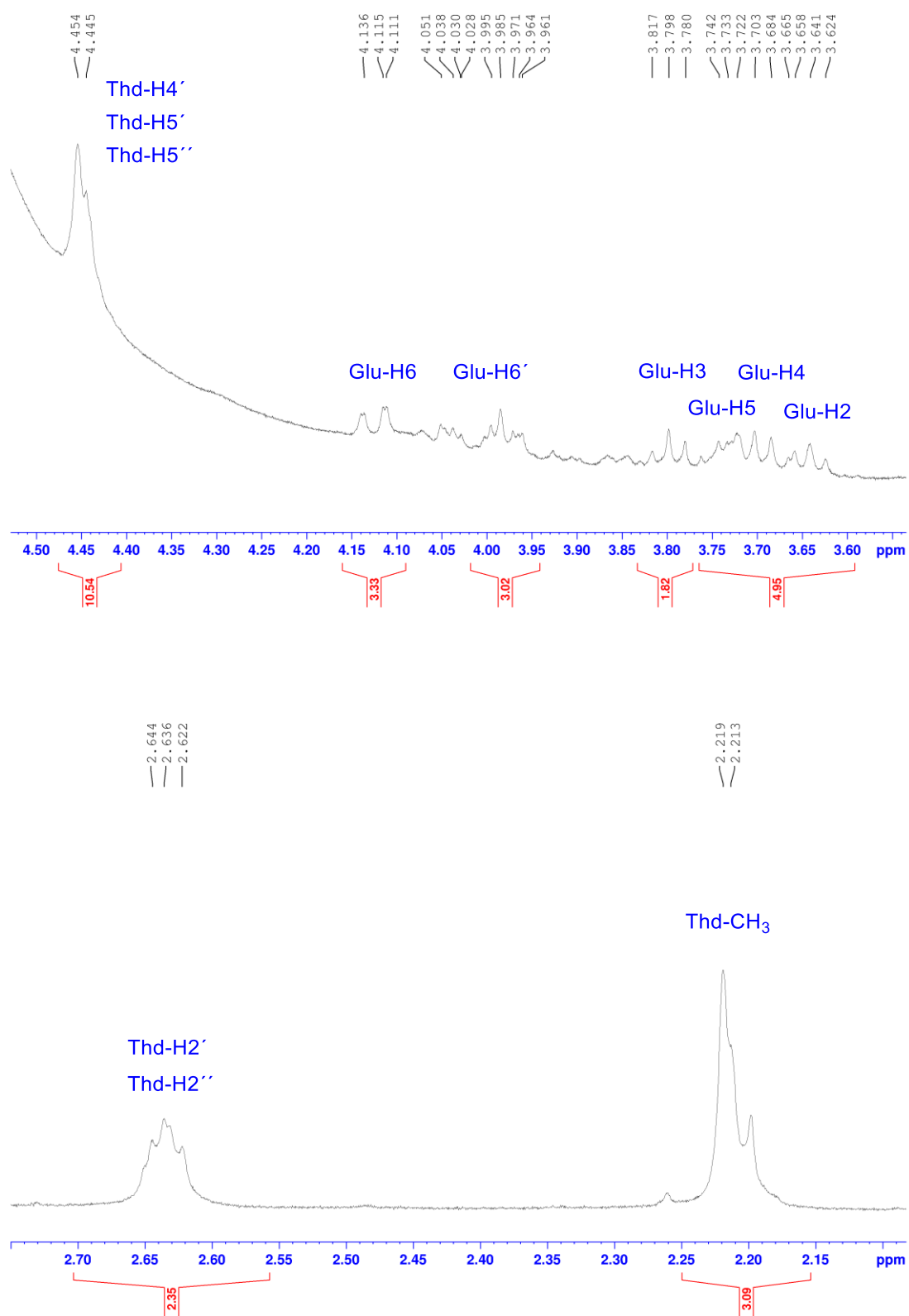


Figure S13 (continued). ¹H NMR spectrum (500 MHz, D₂O) of compound **7β1**.

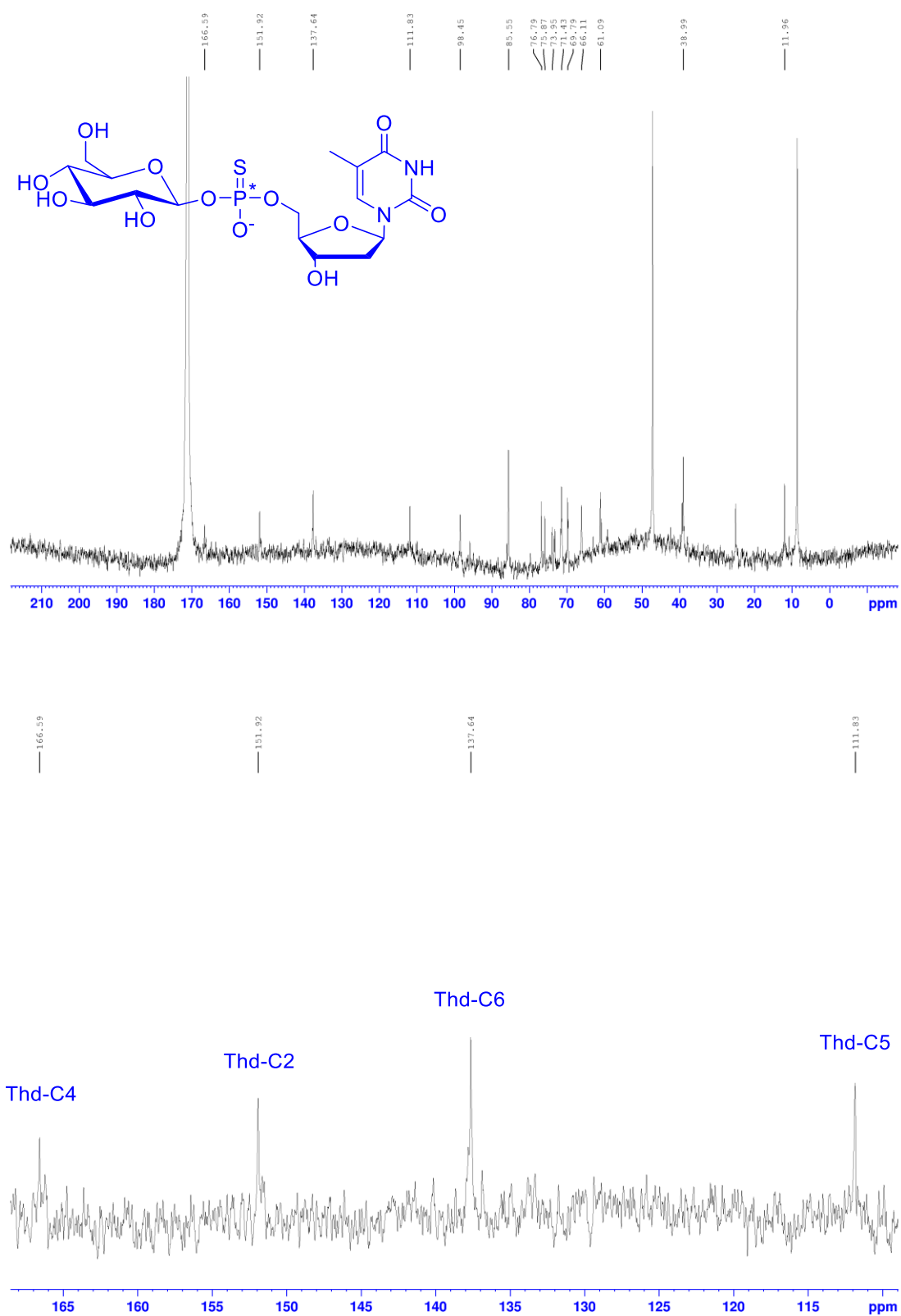


Figure S14. ^{13}C NMR spectrum (126 MHz, D_2O) of compound **7 β 1**.

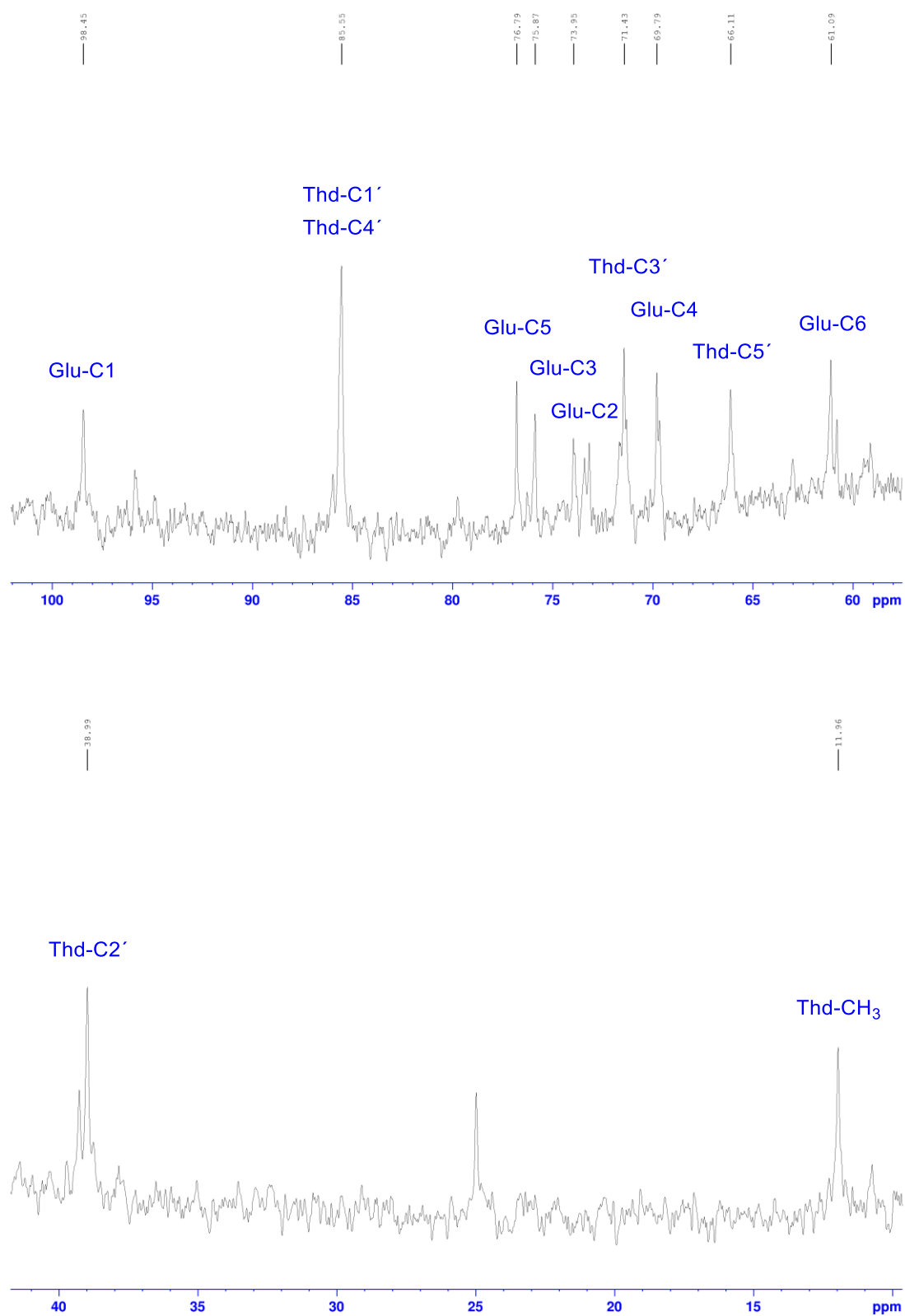


Figure S14 (continued). ¹³C NMR spectrum (126 MHz, D₂O) of compound **7β1**.

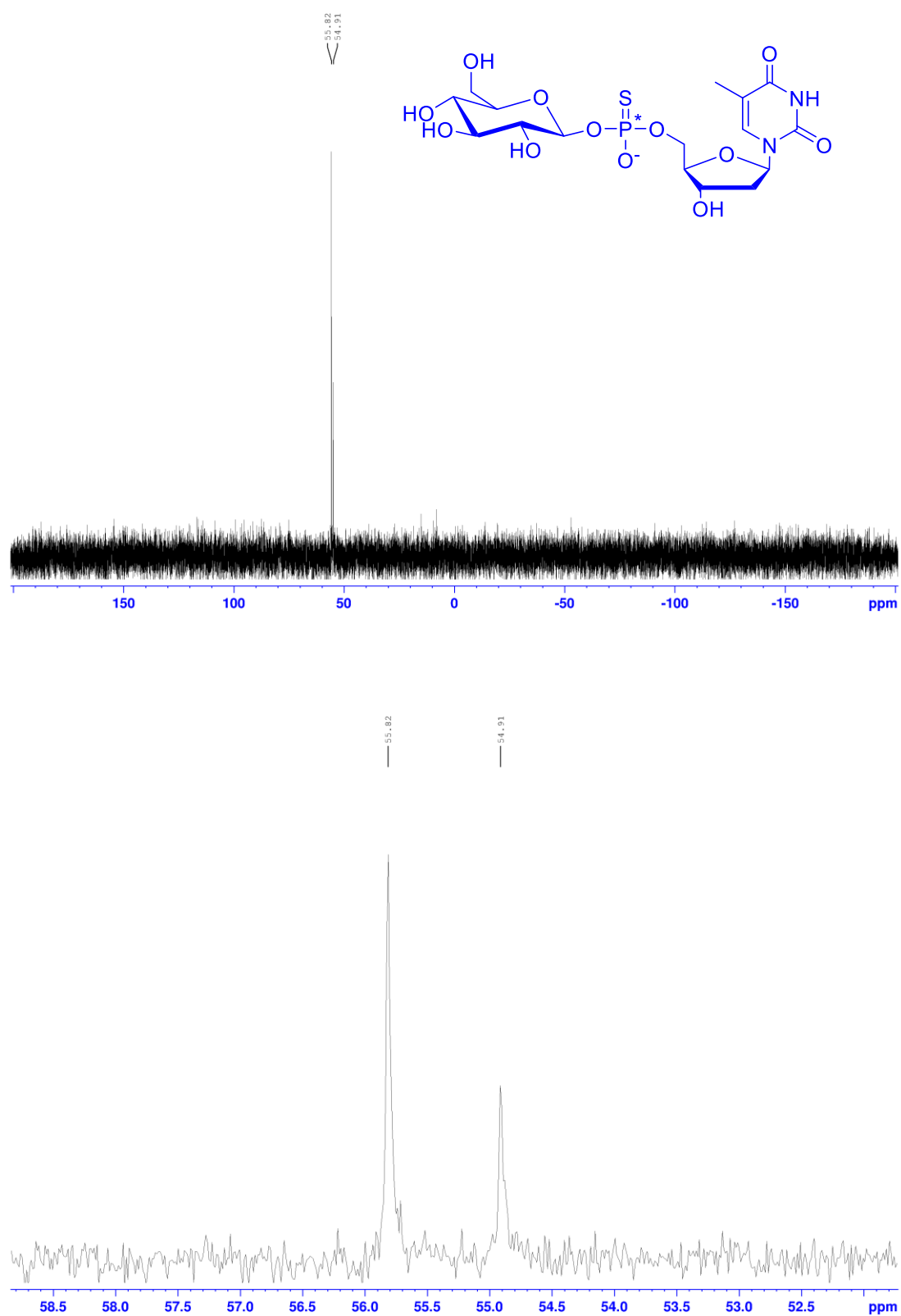


Figure S15. ^{31}P NMR spectrum (202 MHz, D_2O) of compound **7 β 1**.

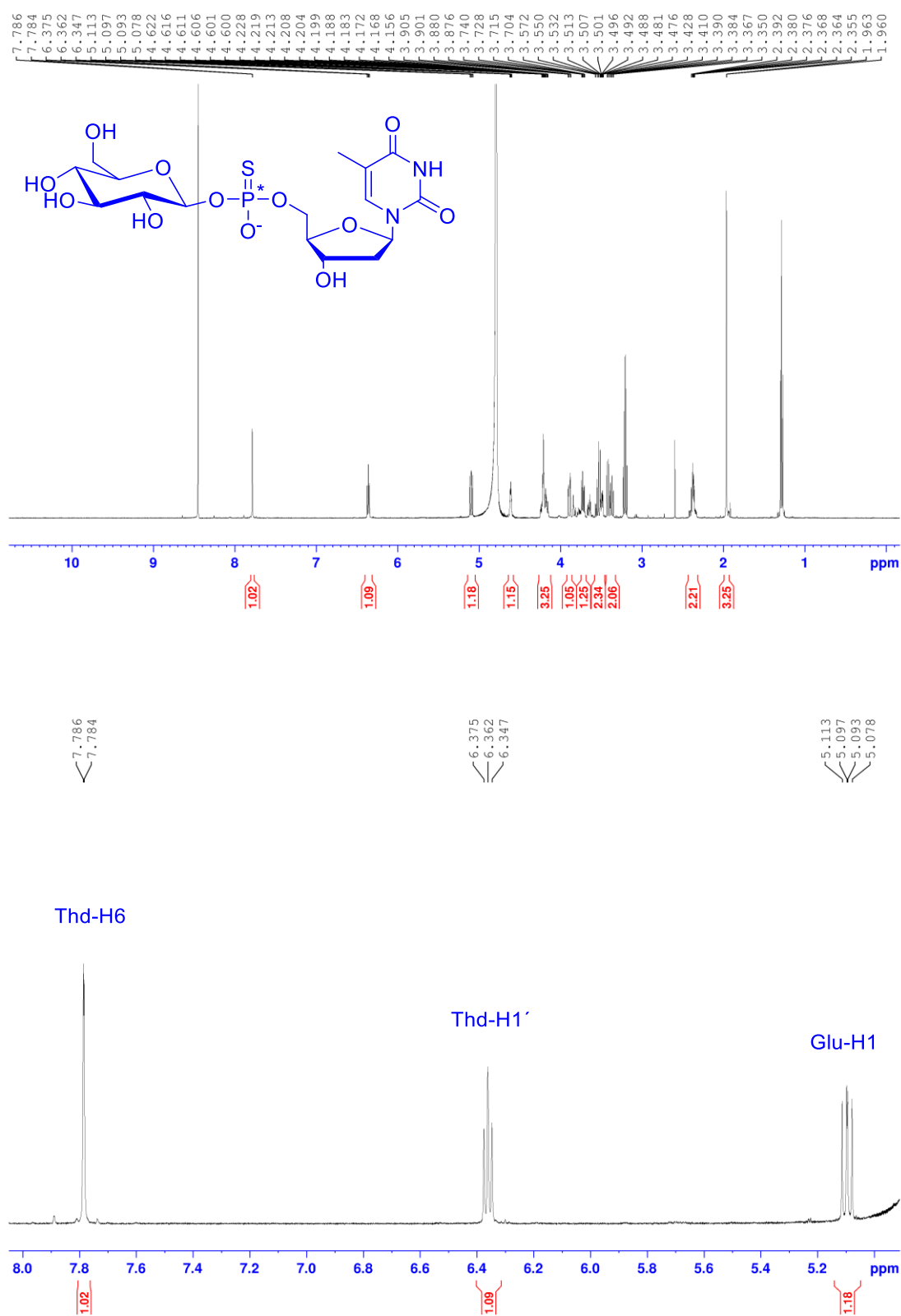


Figure S16. ¹H NMR spectrum (500 MHz, D₂O) of compound **7β2**.

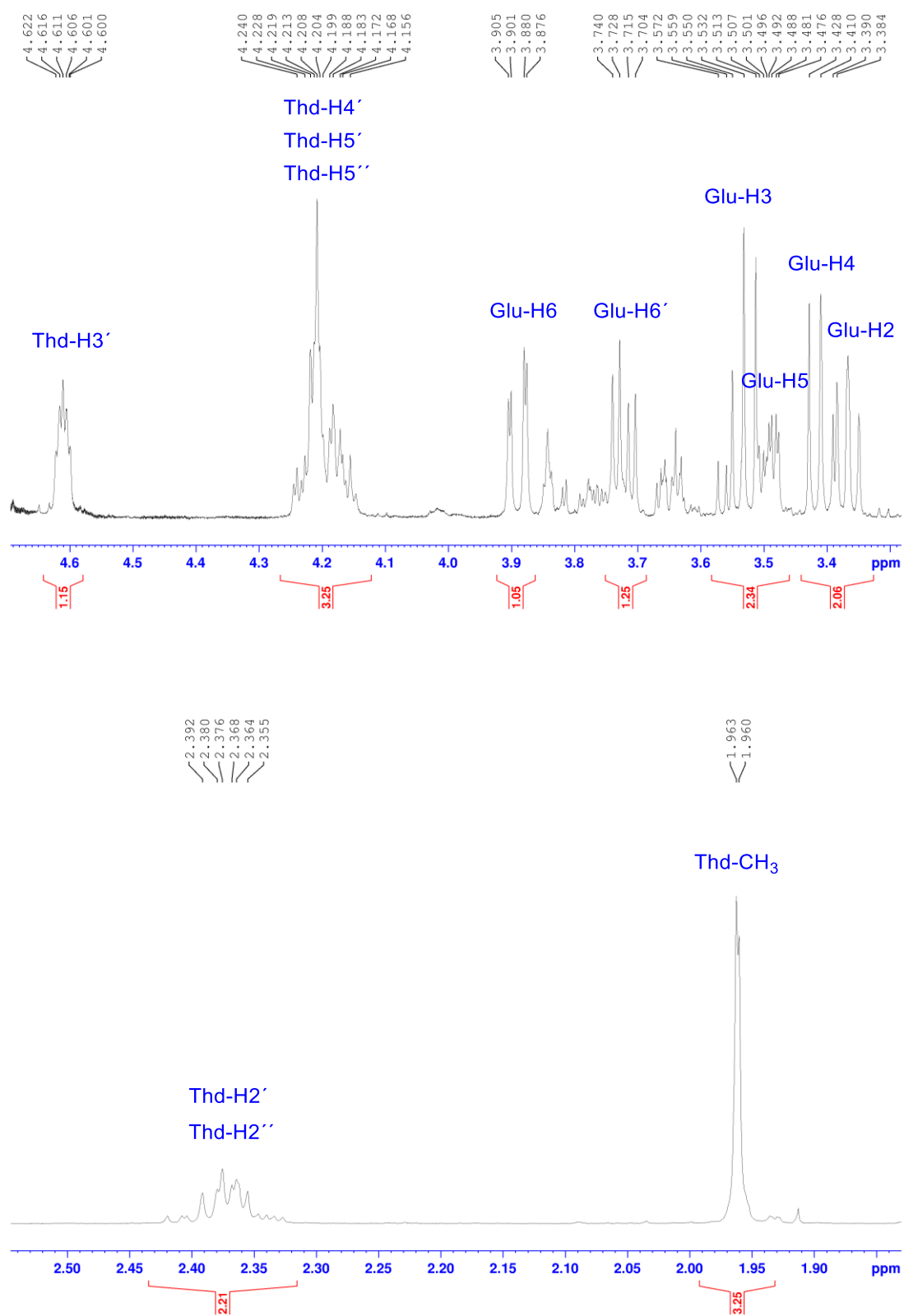


Figure S16 (continued). ¹H NMR spectrum (500 MHz, D₂O) of compound **7β2**.

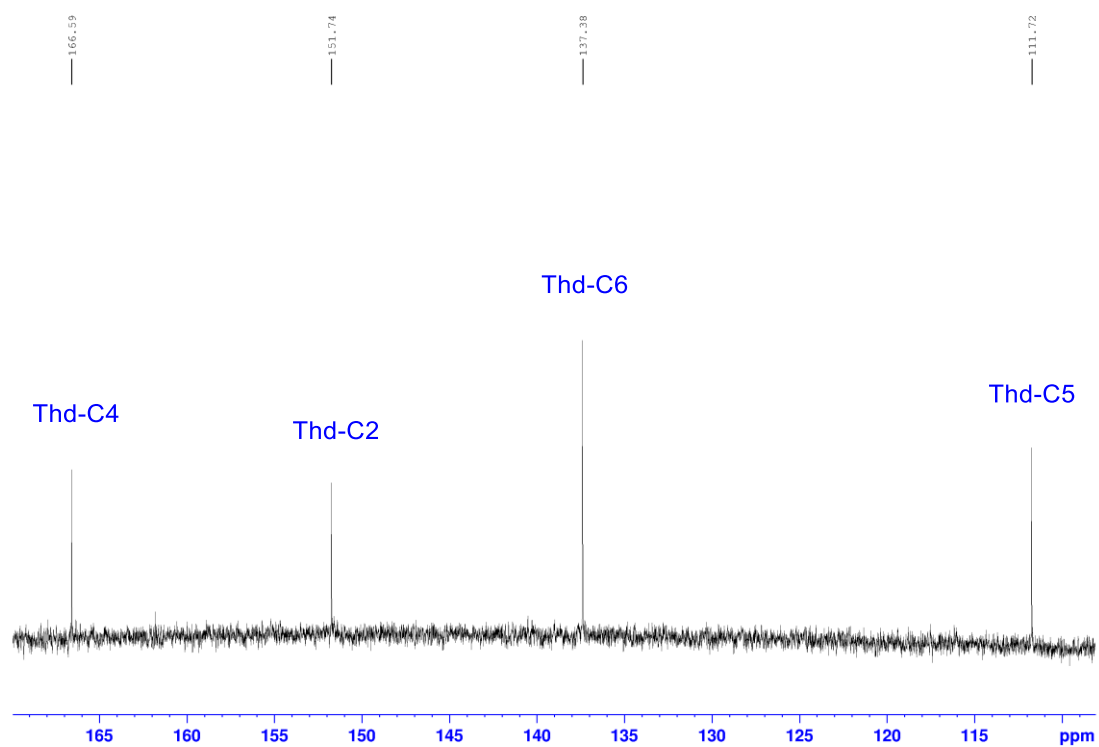
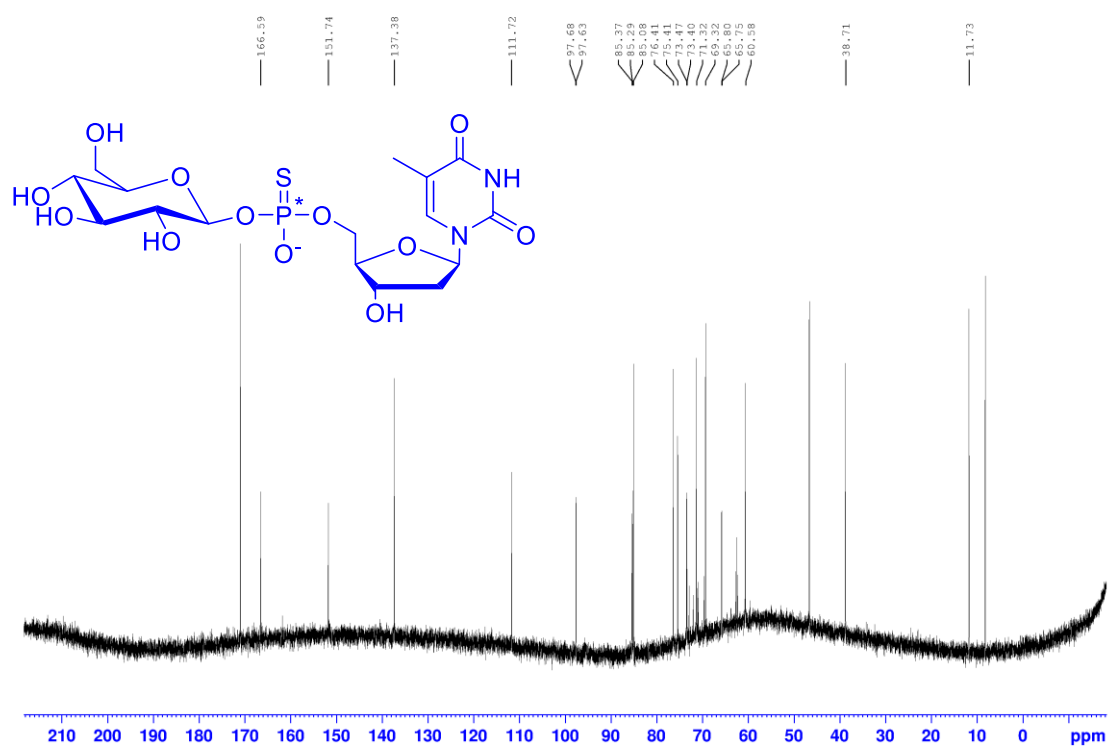


Figure S17. ¹³C NMR spectrum (126 MHz, D₂O) of compound 7β2.

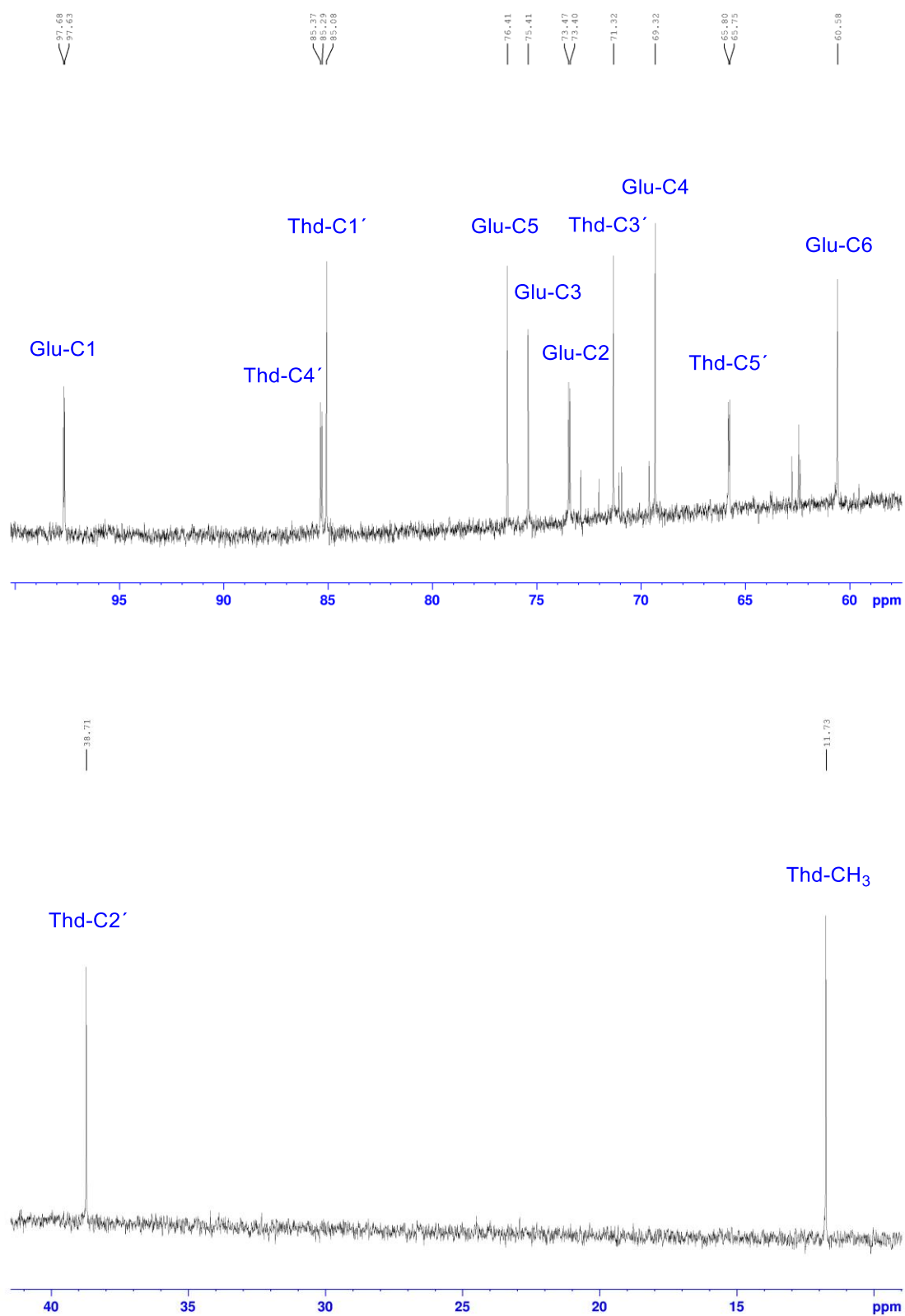


Figure S17 (continued). ^{13}C NMR spectrum (126 MHz, D_2O) of compound **7 β 2**.

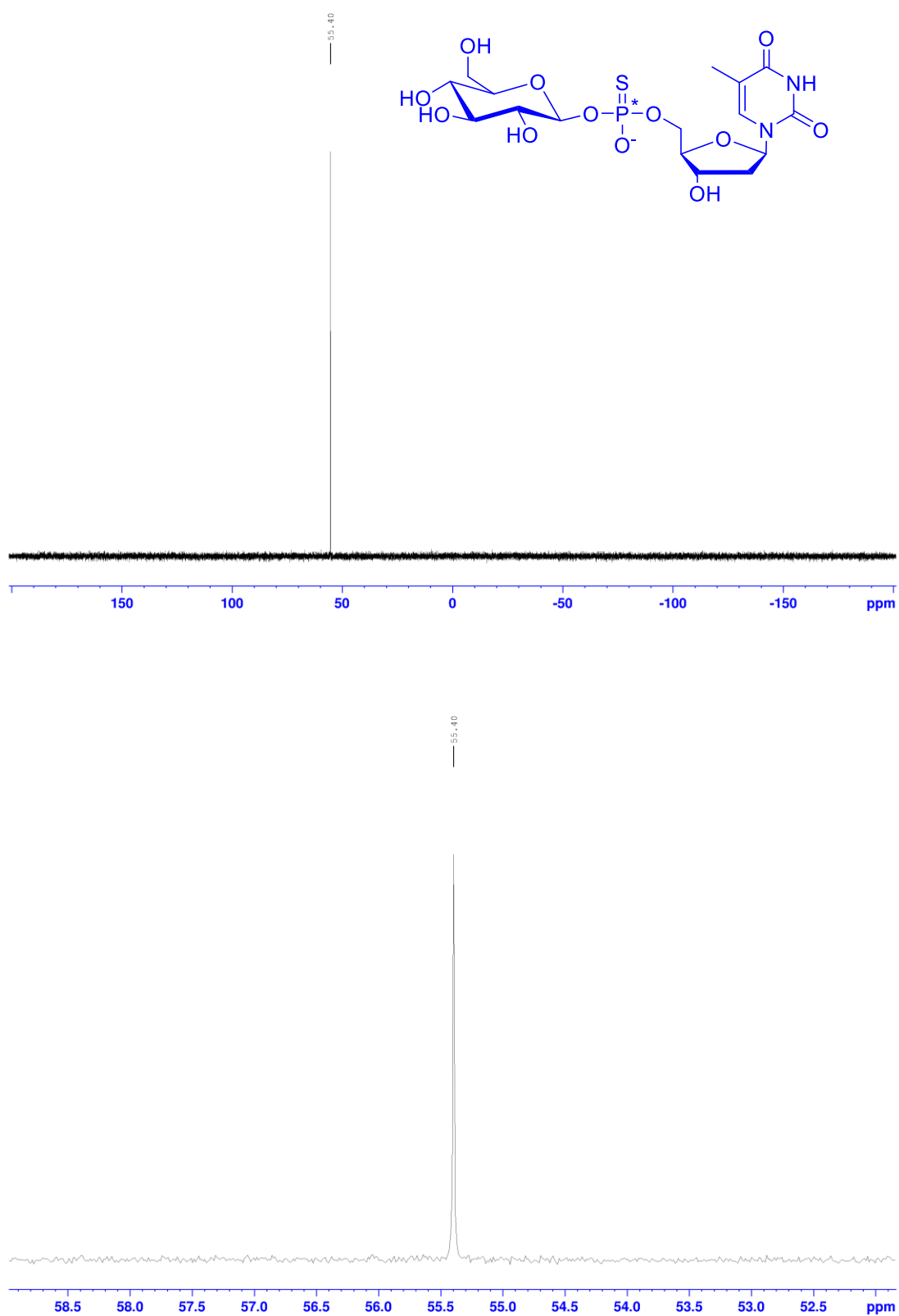


Figure S18. ^{31}P NMR spectrum (202 MHz, D_2O) of compound **7β2**.

Conditions of capillary electrophoresis and HPLC analysis

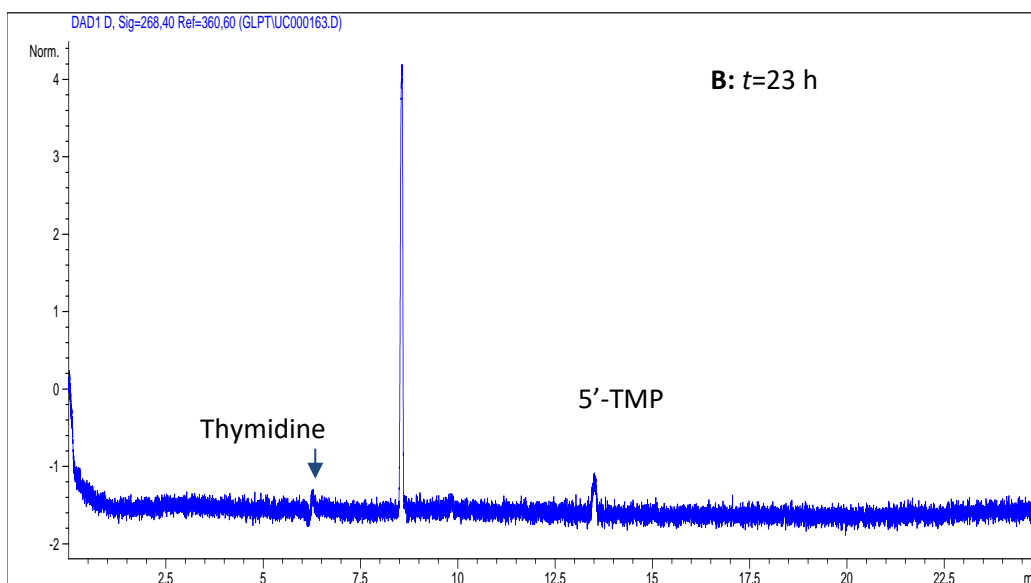
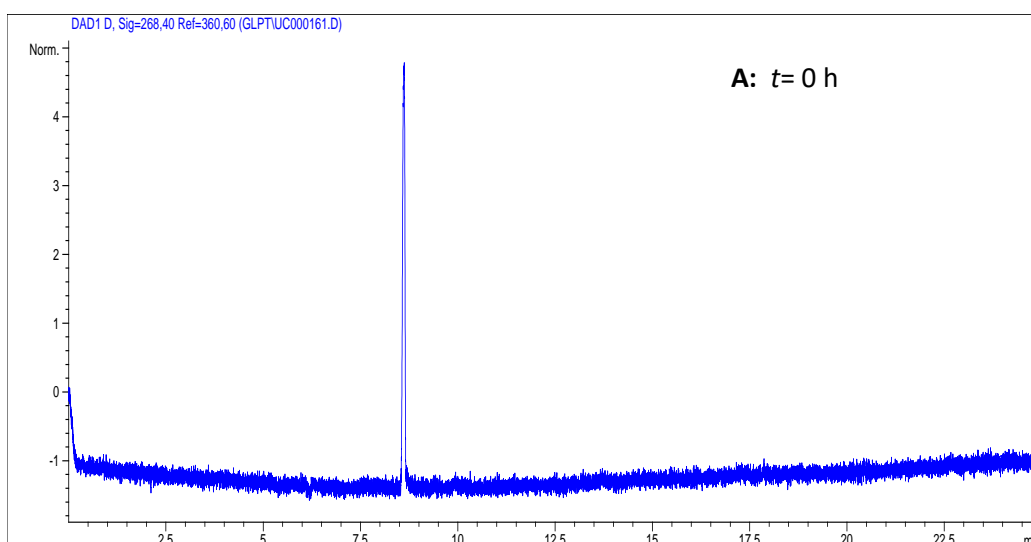
Electropherograms and chromatograms have been obtained under the following experimental conditions, unless otherwise stated.

Electropherograms: fused silica capillary (77 cm effective length, *i.d.* 75 μm). Background electrolyte MOPSO buffer (0.1 M, pH 6.7), Voltage of 30 kV, 25 $^{\circ}\text{C}$.

HPLC chromatograms: Aquasil C18 column (150x4 mm, particle size 5 μm), isocratic elution with 1.1 % acetonitrile in acetate buffer (50 mM, pH, 4.3, 0.1 M NH_4Cl).

Reaction components were detected by UV-detection at 268 nm in both methods.

Figures S19A-C: Electropherograms of samples from reaction of α -phosphate **6a** at pH 6.7 at 90 $^{\circ}\text{C}$



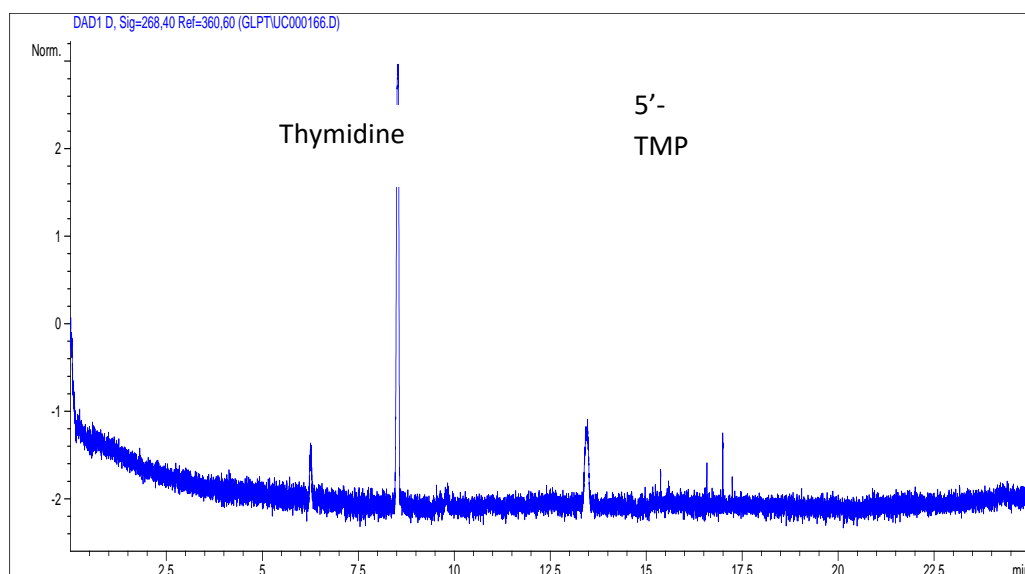


Figure S20: An electropherogram of a sample from the reaction of α -phosphate **6a** at pH 3.0 at 90 °C

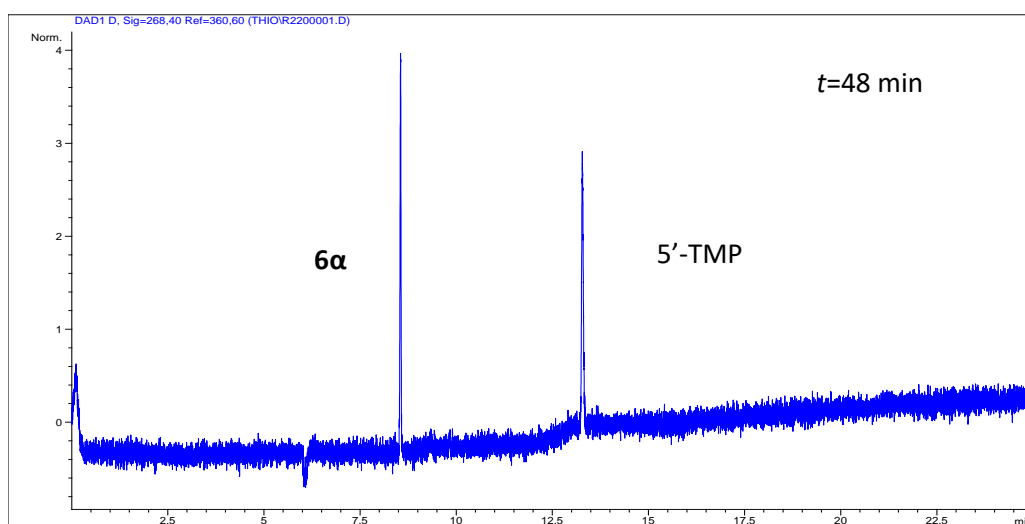
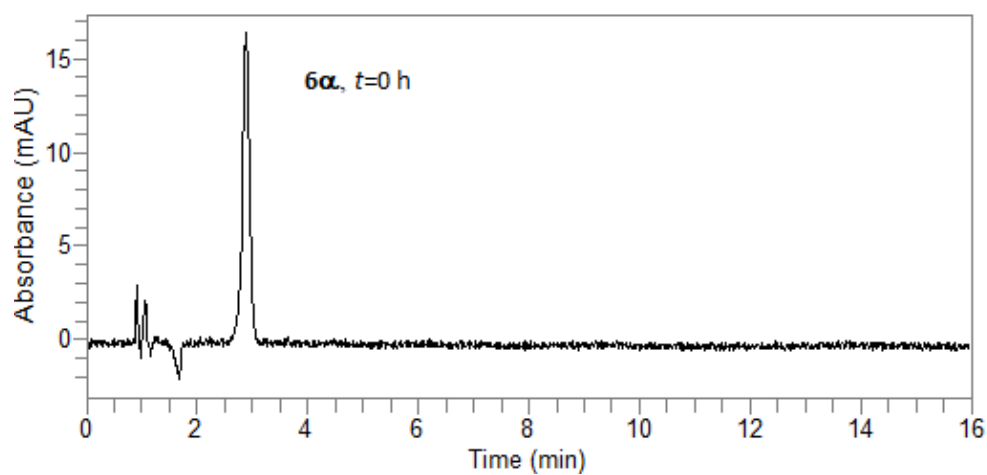


Figure S21A,B: HPLC-chromatograms of the reaction of **6a** with 10 mM CuBiPy at pH 6.7, 90 °C .



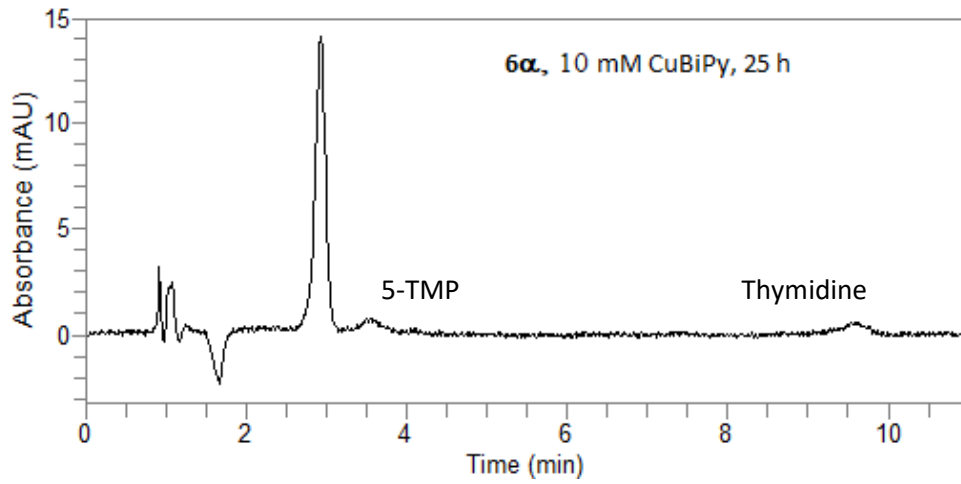


Figure S22: An HPLC-chromatogram of the reaction of α -phosphate 6α with 10 mM CuTerPy at pH 6.7, 90 °C .

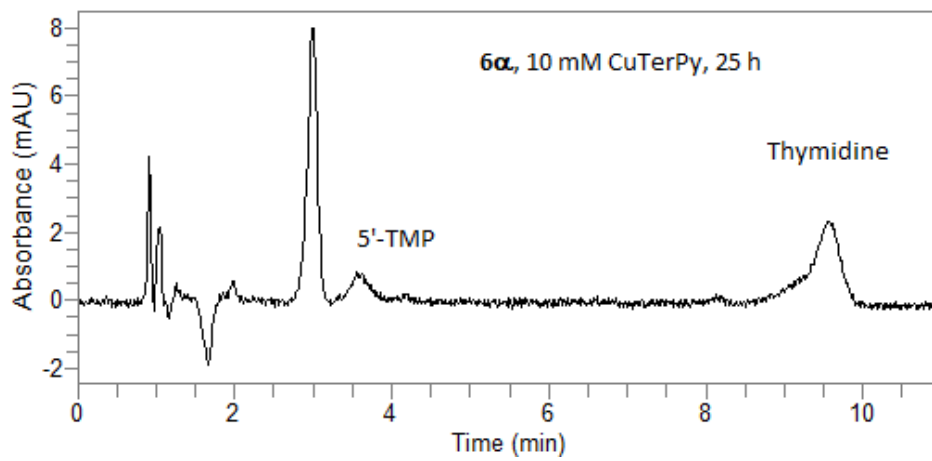


Figure S23: HPLC-chromatogram of TMP with 10 mM CuTerPy at pH 6.7, 20 h

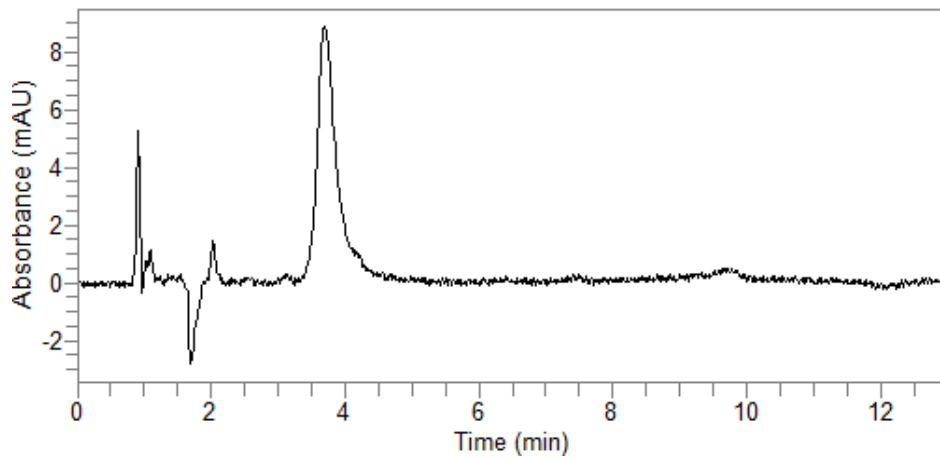


Figure S24: An electropherogram of a sample from a reaction of **7 β 2** at pH 3.0 to identify thio-TMP

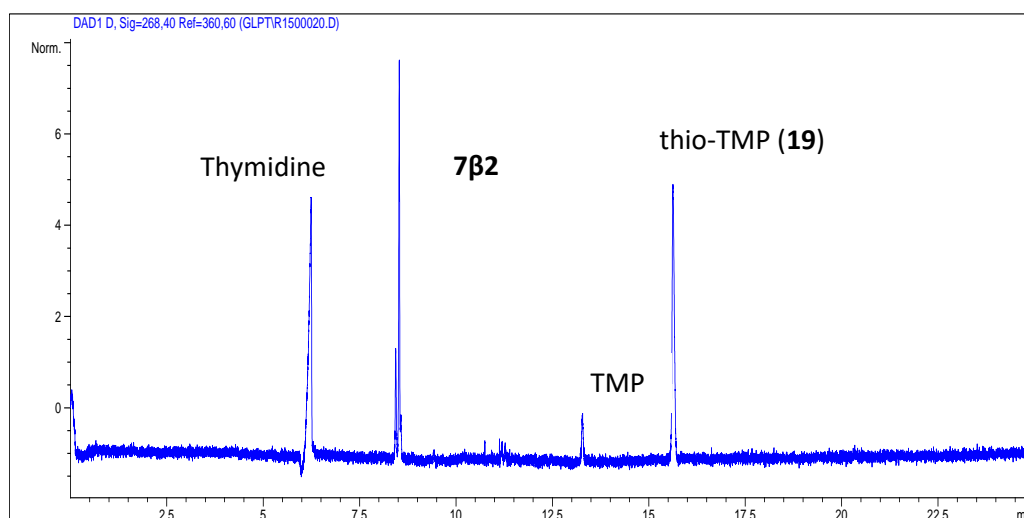


Figure S25: An electropherogram of a sample from a reaction of **7 α 2** at pH 6.7, 90 °C showing an extra peak close to the starting material

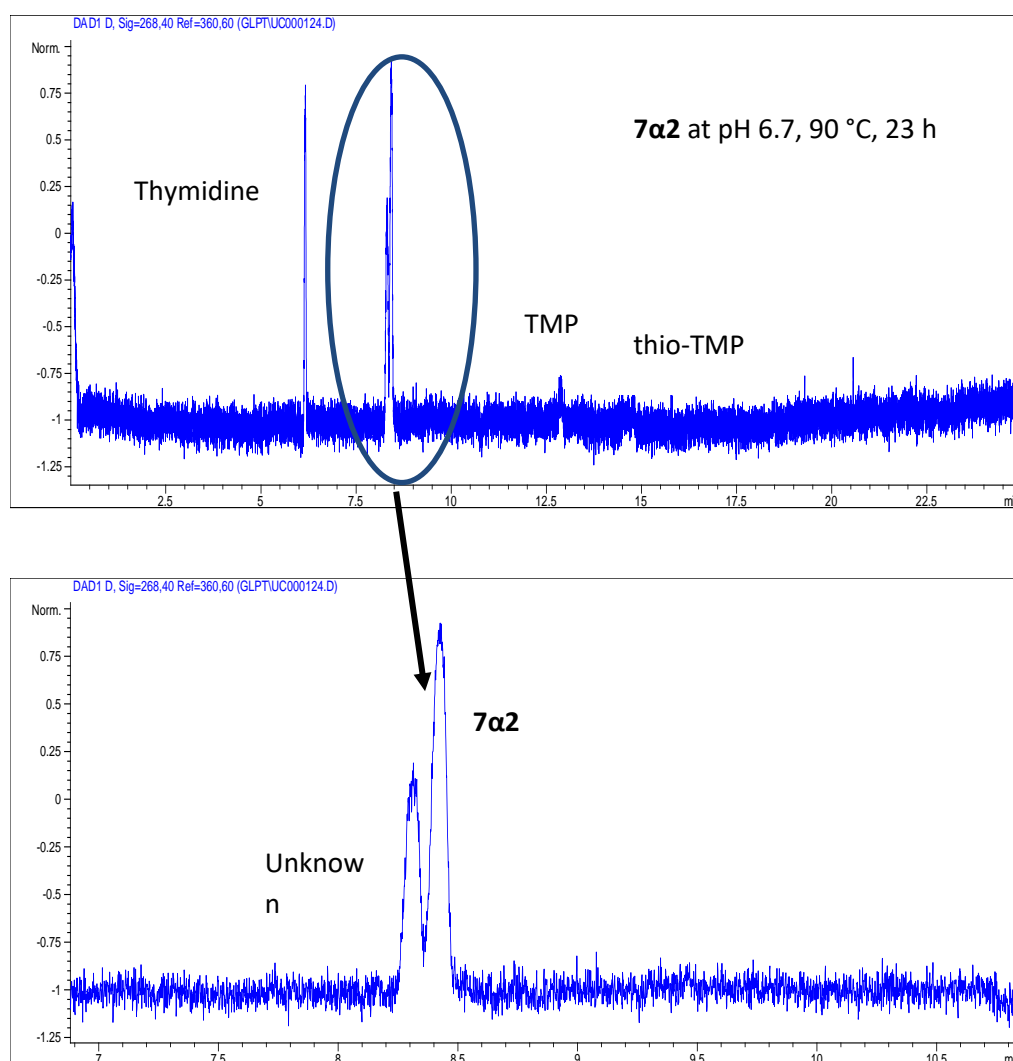


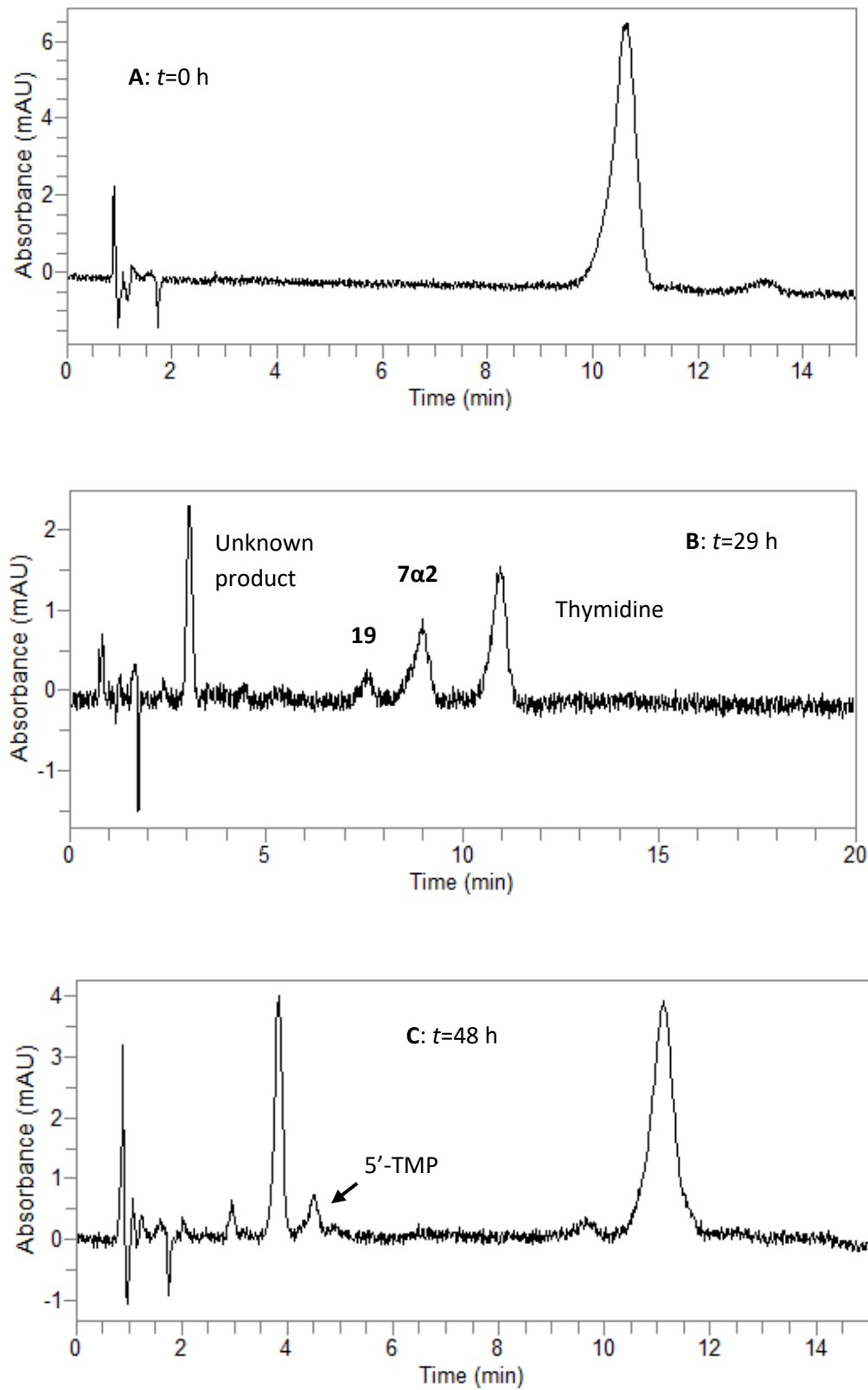
Figure S26A-C: HPLC-chromatograms of samples from reaction of **7 α 2** at pH 6.7 and 90 °C

Figure S27A,B. HPLC-chromatograms of sample from reaction of **7 α 2** at pH 6.7 (29 h). A gradient elution is applied. In **B** α -phosphate is added in the sample to show that the unknown peak is not the corresponding phosphate.

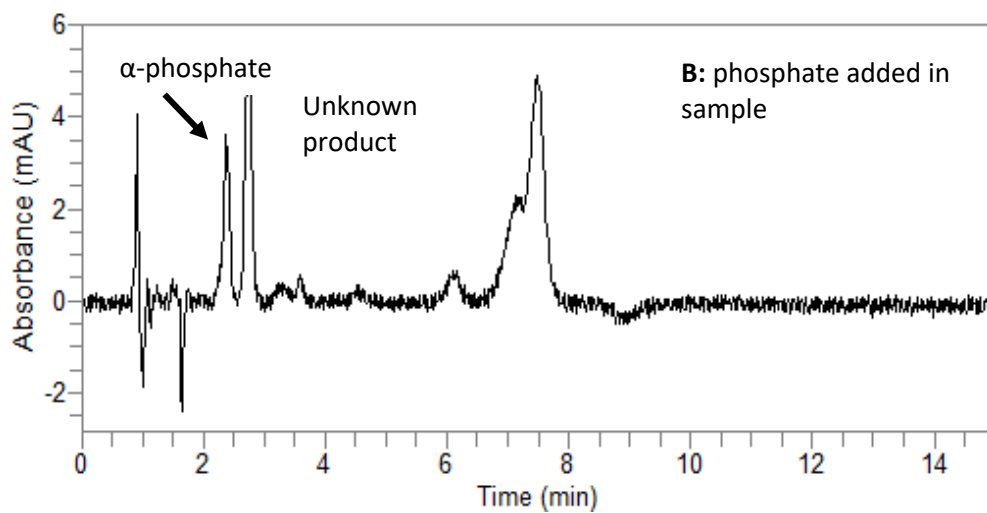
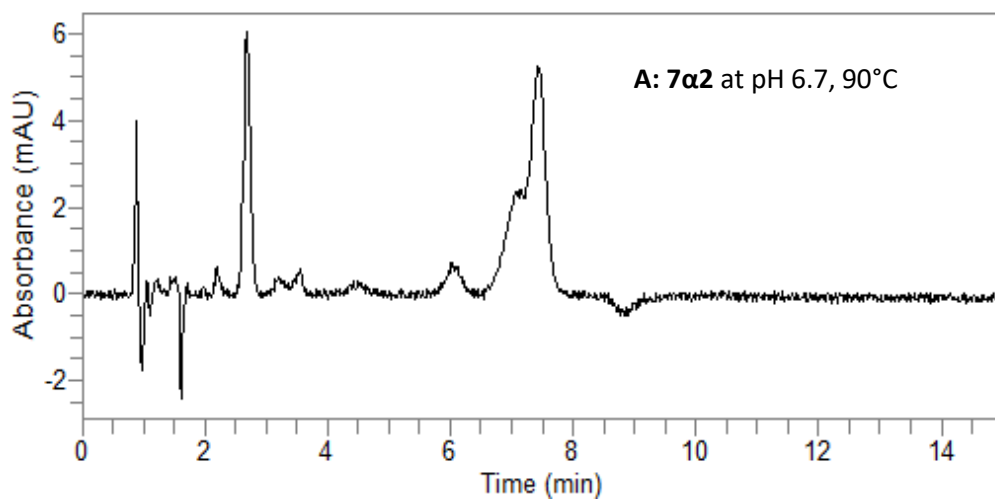


Figure 28A,B: HPLC-chromatograms of samples from the reaction of **7 α 2** with CuBiPy at pH 6.7 and 90 °C

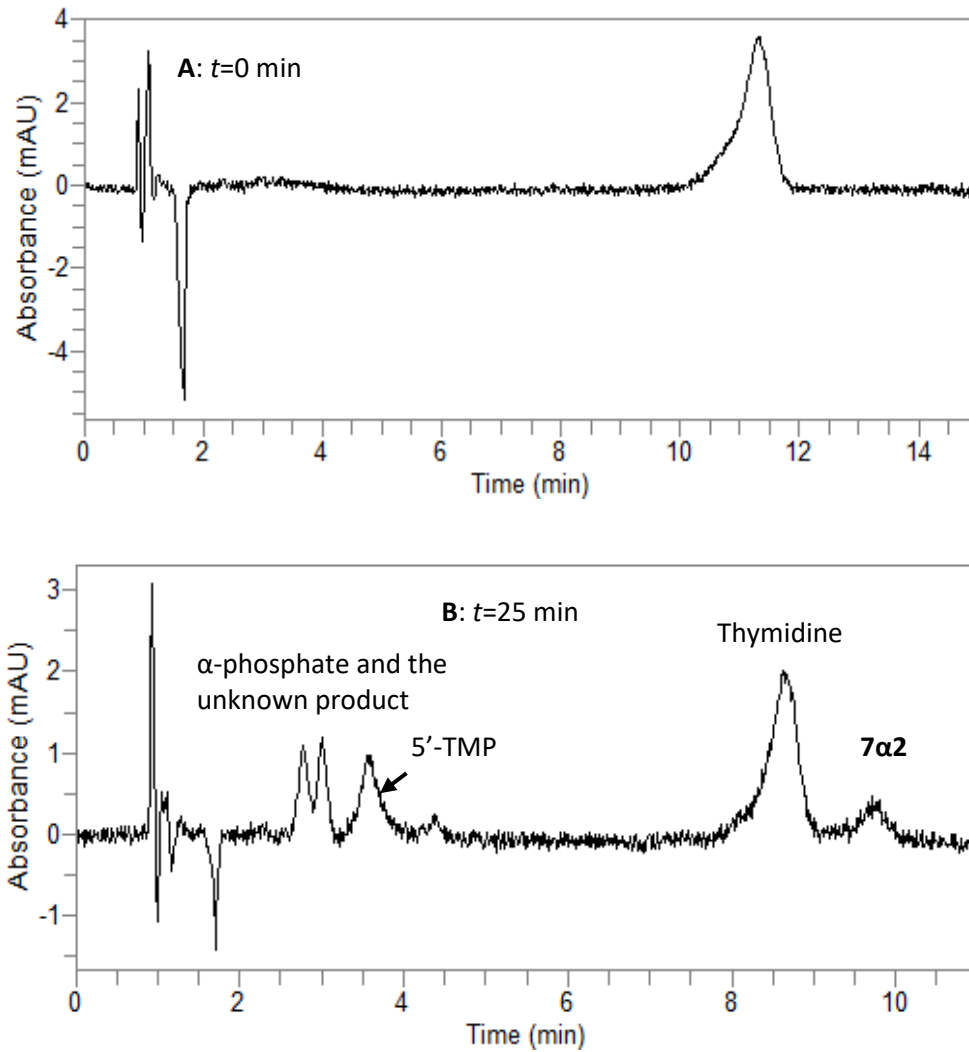


Figure 29A,B: HPLC-chromatograms of samples from the reaction of **7 α 2** with CuTerPy at pH 6.7 and 90 °C

