SUPPORTING INFORMATION

Molecular niobium(V) complexes with mononuclear {Nb_1} and dinuclear oxo species {Nb_2O} connected through aryl di- or tetra-carboxylate linker

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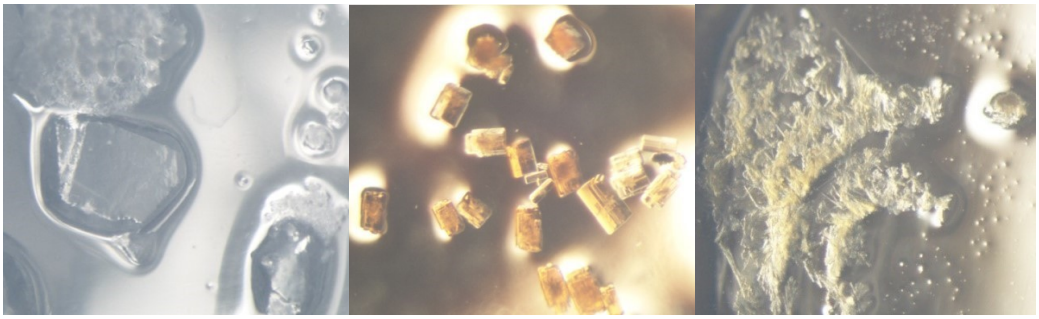

Figure S1. Optical microscope photographs of crystals of complex **1** (left), complex **2** (middle) and complex **3** (right).

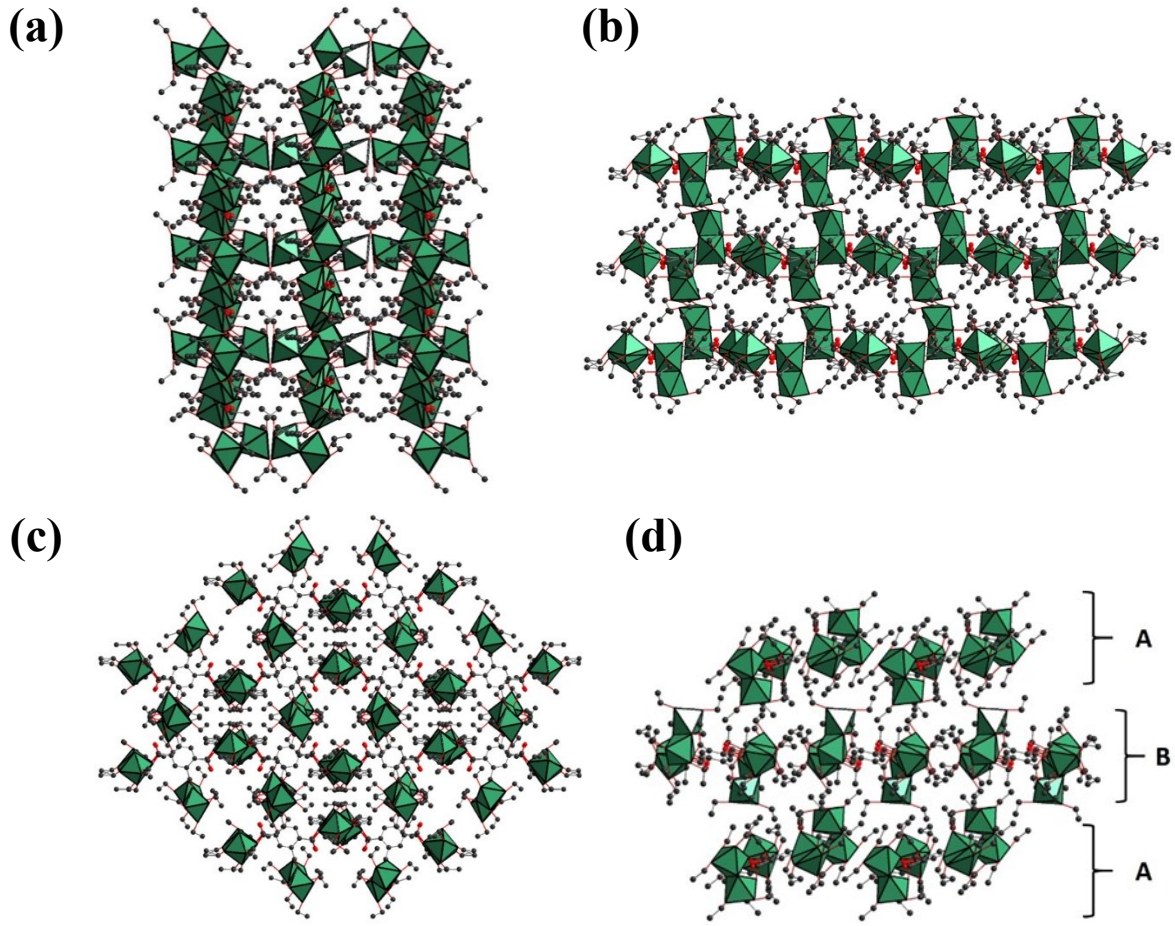

Figure S2a. Representation of the packing in the lattice of compound **1**. (a): view along the *a* axis; (b): view along the *b* axis; (c): view along the *c* axis and (d): view of the packing showing the A-B-A-B arrangement along the 110 direction.

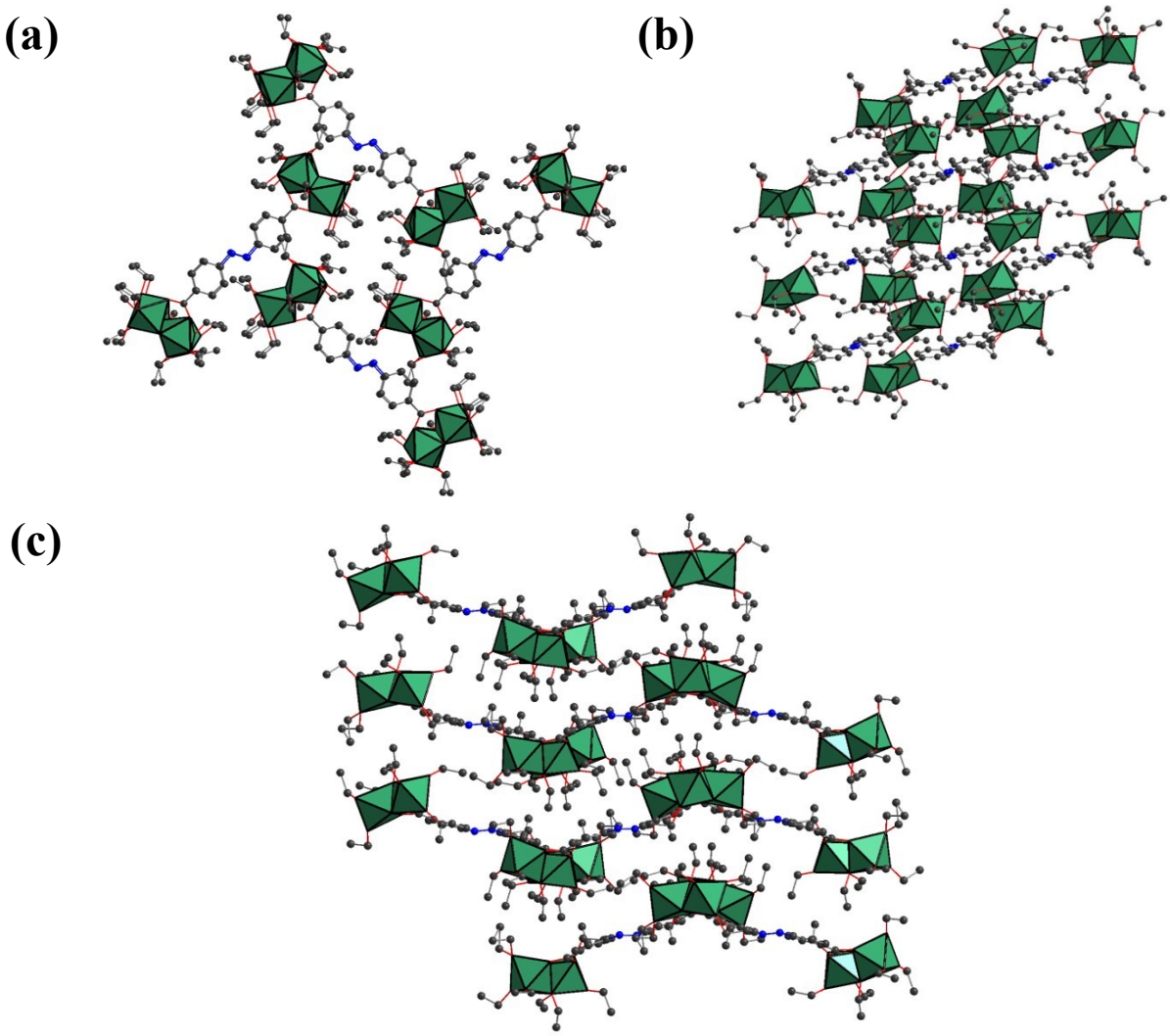

Figure S2b. Representation of the packing in the lattice of compound **2**. (a): view along the *a* axis; (b): view along the *b* axis; (c): view along the *c* axis.

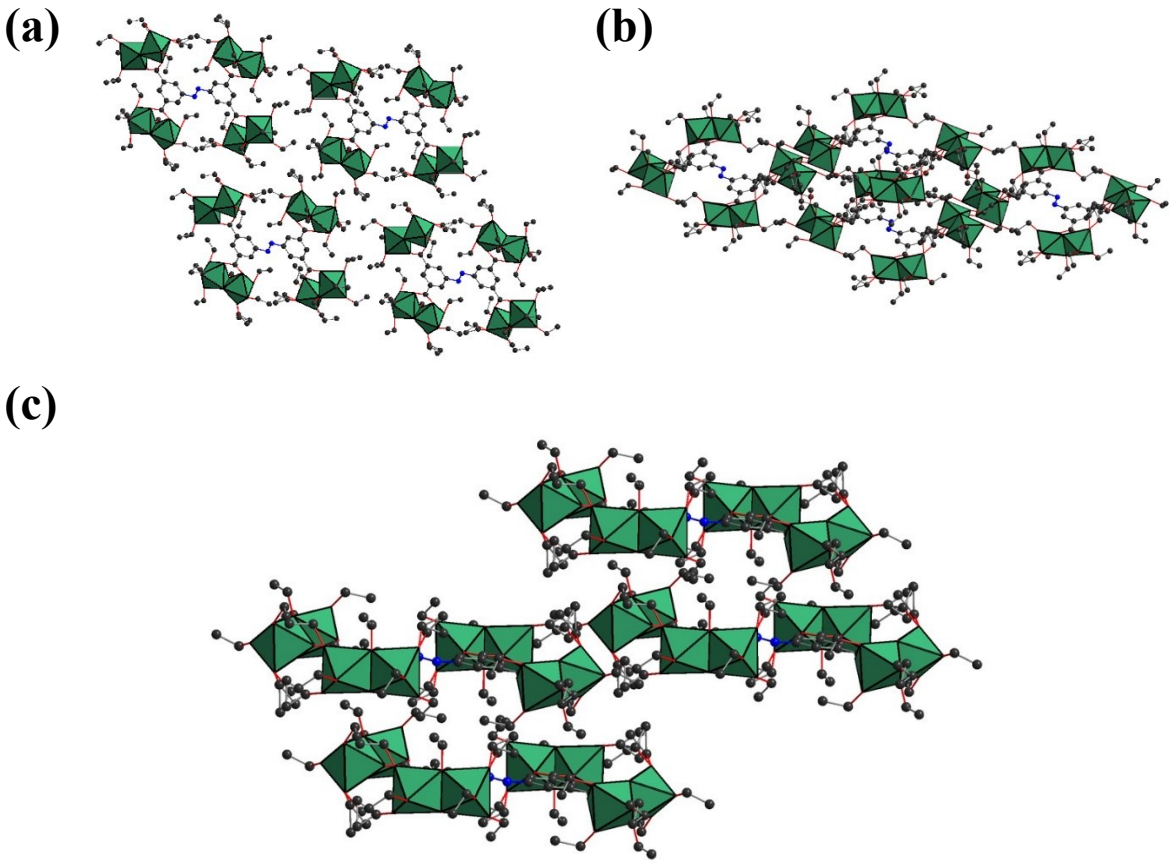

Figure S2c. Representation of the packing in the lattice of compound **2**. (a): view along the *a* axis; (b): view along the *b* axis; (c): view along the *c* axis.

Powder XRD patterns

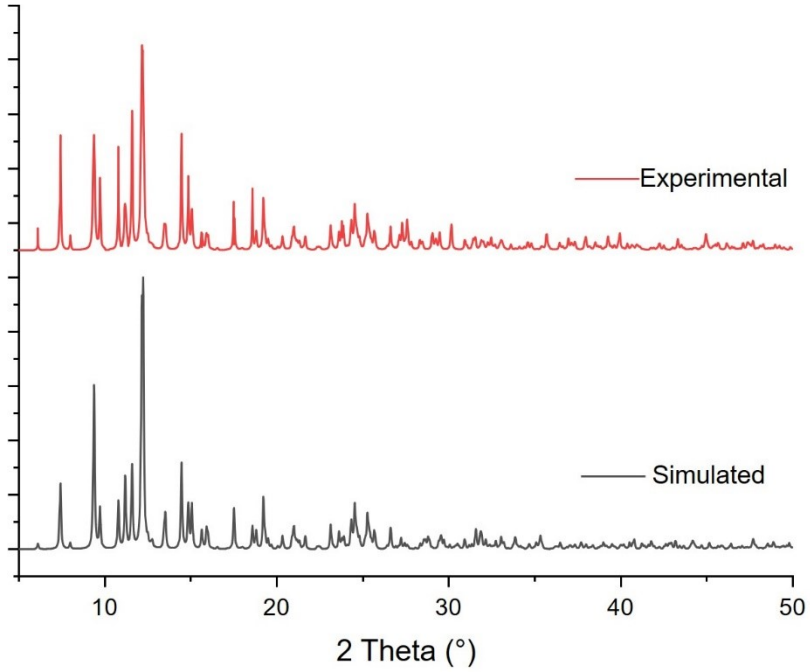

Figure S3a. Comparison of the experimental powder XRD pattern (red line) of complex **1** with the calculated one (black line). X-ray source; Copper $K\alpha$ radiation.

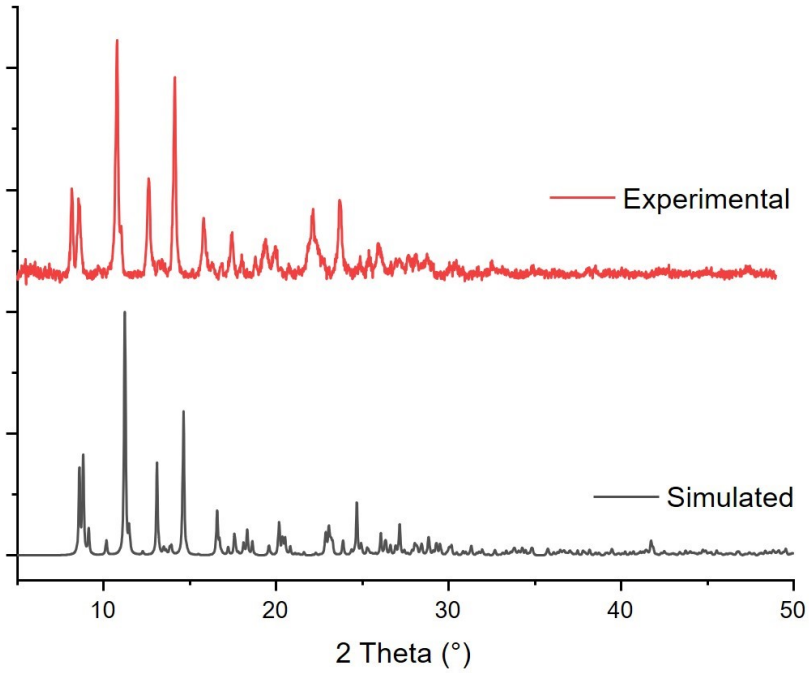

Figure S3b. Comparison of the experimental powder XRD pattern (red line) of complex **2** with the calculated one (black line). X-ray source; Copper $K\alpha$ radiation.

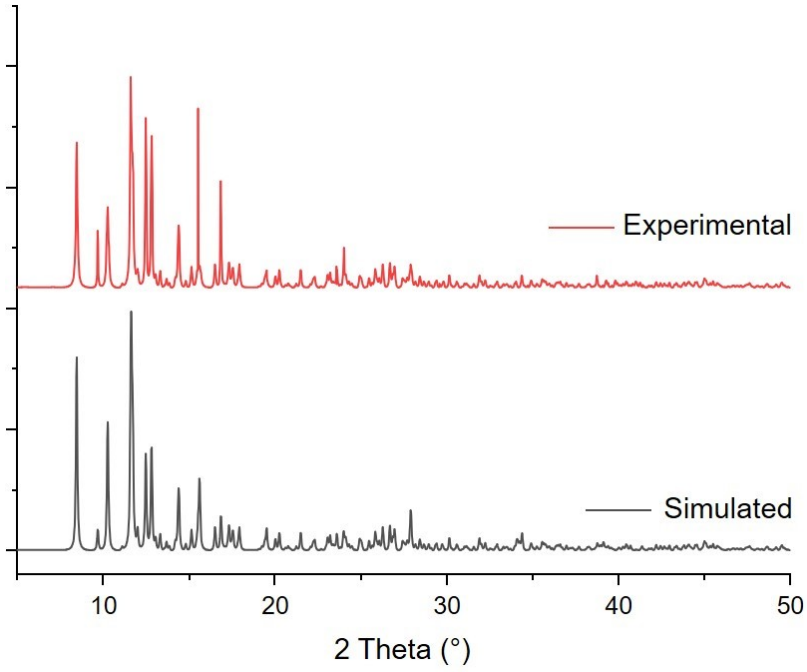

Figure S3c. Comparison of the experimental powder XRD pattern (red line) of complex **3** with the calculated one (black line). X-ray source; Copper $K\alpha$ radiation.

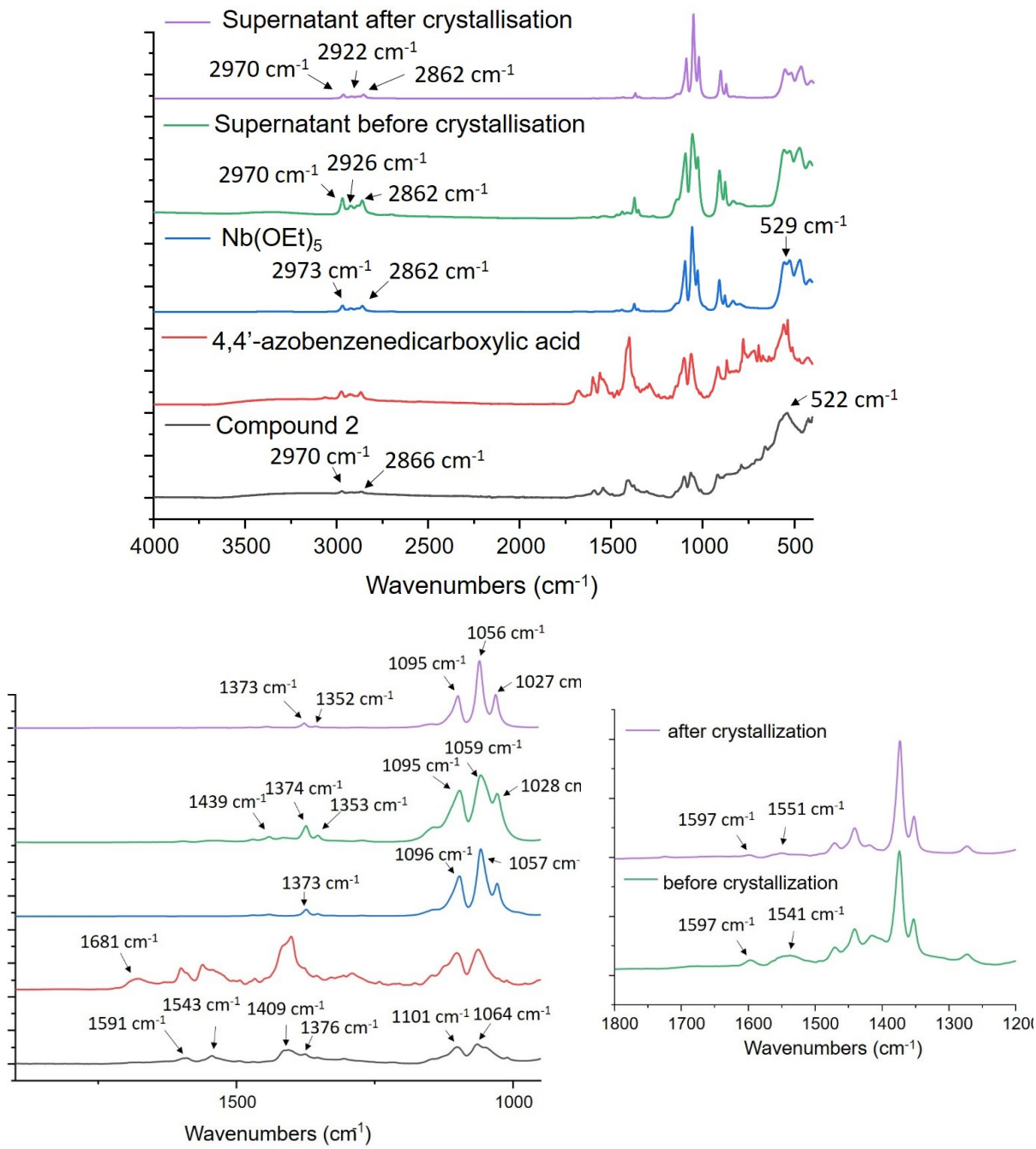

Figure S4a. Infrared spectroscopy analysis for the niobium(V) / 4,4'-azobenzenedicarboxylic acid system **2**. $Nb(OEt)_5$ (blue line), 4,4'-azobenzenedicarboxylic acid (red line), supernatant solution after 1h mixing at room temperature (green), supernatant after crystallization for 1 week at room temperature (purple) and compound **2** (black line). Top: full spectrum in the 4000-400 cm^{-1} range; bottom left: detailed region in the 1900-950 cm^{-1} range; bottom right: highlight on the 1800-1200 cm^{-1} region before and after crystallization.

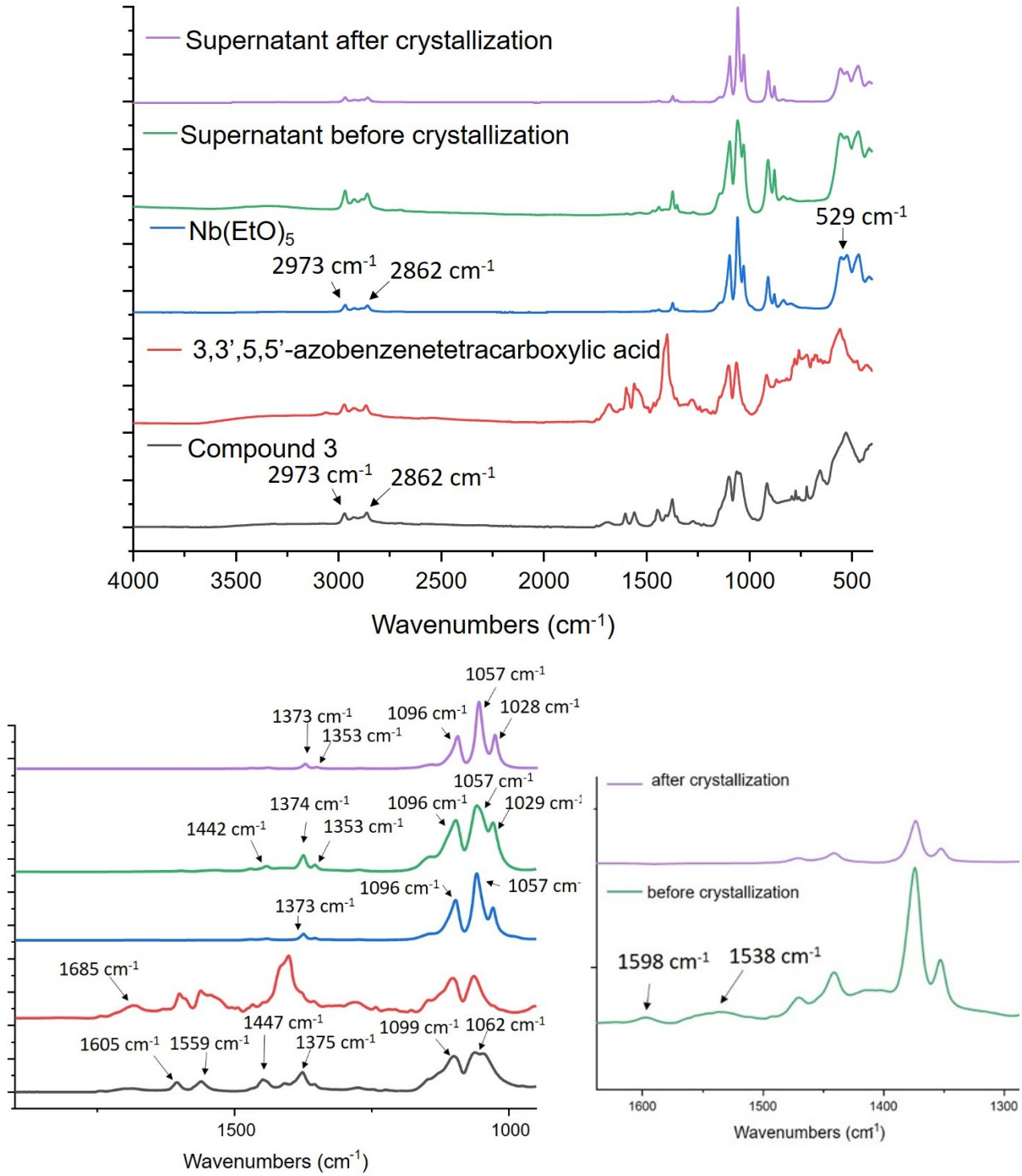

Figure S4b. Infrared spectroscopy analysis for the niobium(V) / 4,4'-azobenzenedicarboxylic acid system **3**. $Nb(OEt)_5$ (blue line), 3,3',5,5'-azobenzenetetracarboxylic acid (red line), supernatant solution after 1h mixing at room temperature (green), supernatant after crystallization for 1 month at room temperature (purple) and compound **3** (black line). Top: full spectrum in the 4000-400 cm^{-1} range; bottom left: detailed region in the 1900-950 cm^{-1} range; bottom right: highlight on the 1600-1300 cm^{-1} region before and after crystallization.

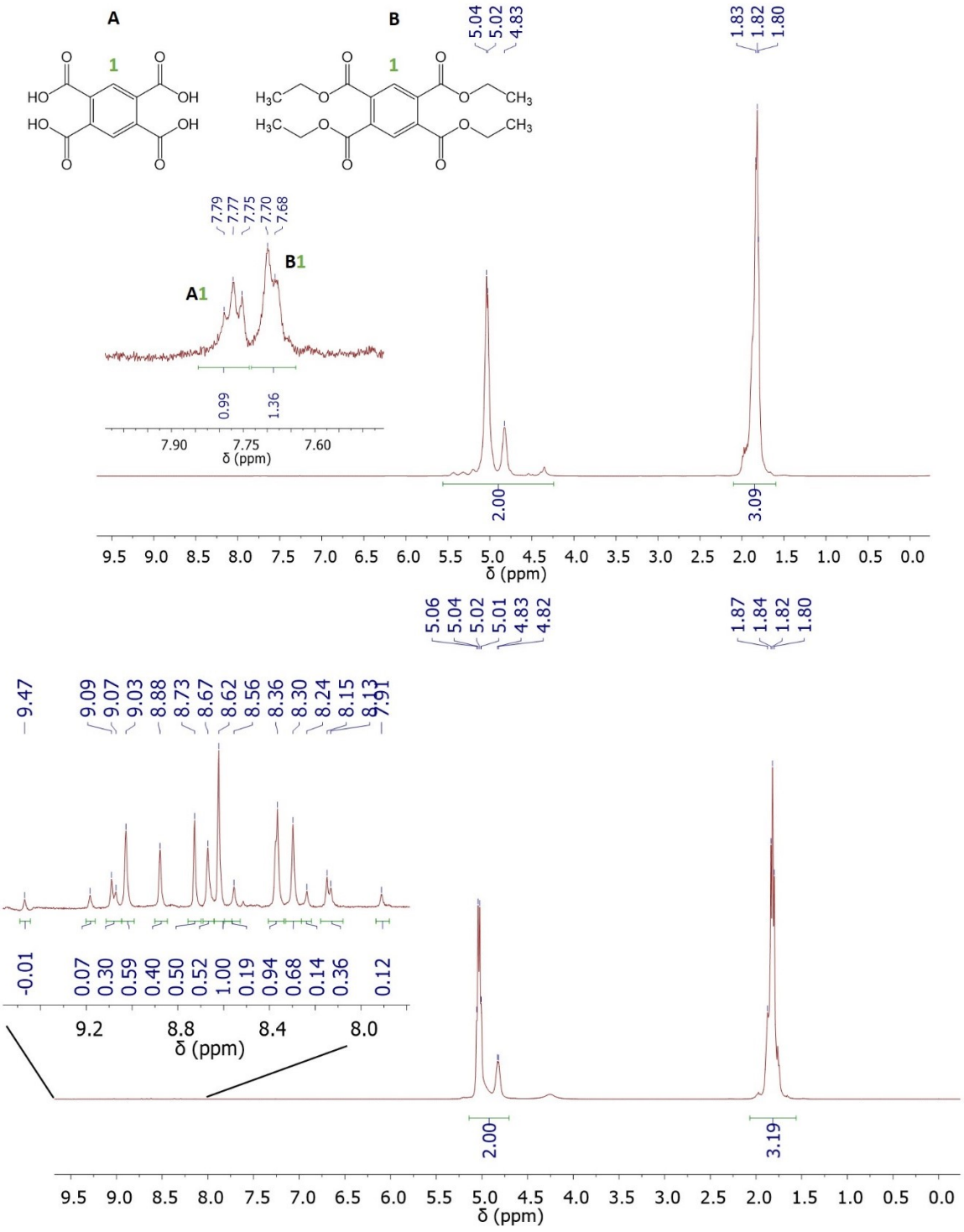

Figure S5a. ^{1}H NMR spectra for the supernatant in the synthesis of complex **1** before (top) and after the crystallization (bottom) with a focus in the aromatic region.

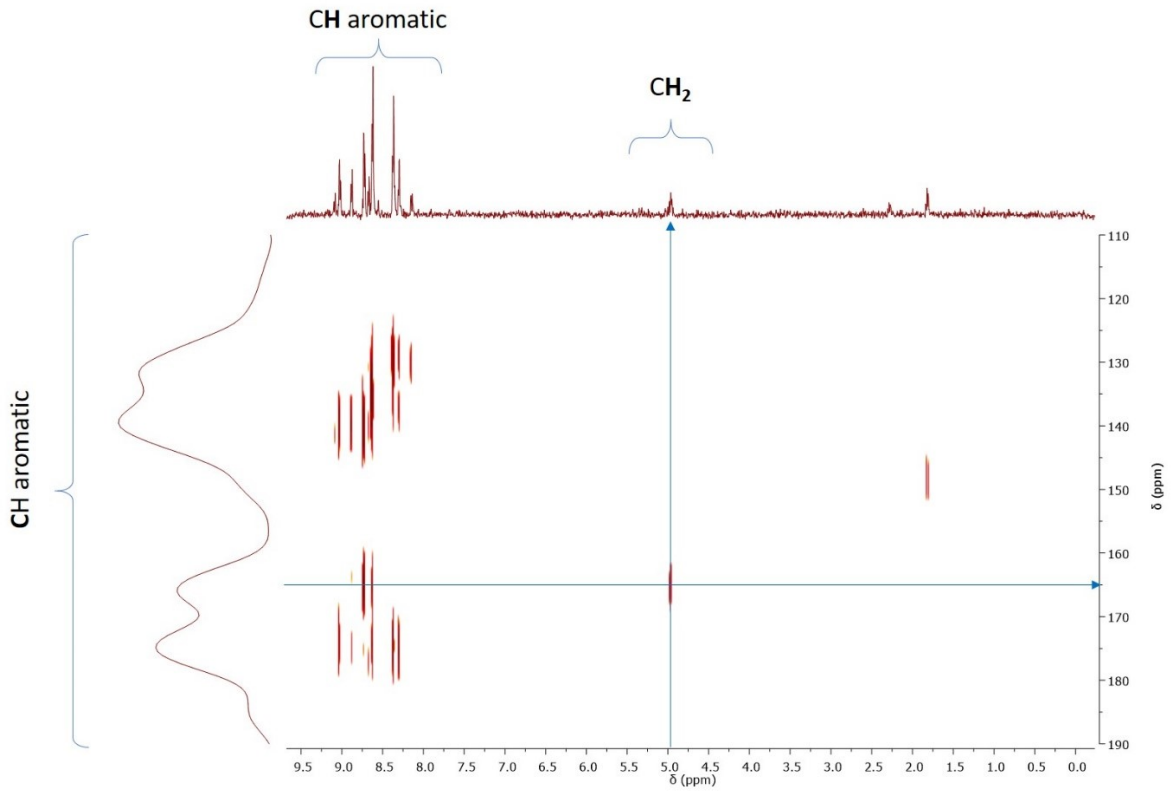

Figure S5b: ^{13}C-HMBC spectrum for the supernatant solution of compound **1** after crystallization.