Supplementary information (ESI) for *Dalton Trans*.


# Supplementary Information

## Mixed Amido/Imido/Guanidinato Complexes of Niobium: Potential Precursors for MOCVD of Niobium Nitride Thin Films

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### Synthesis, Purity (Microanalyses) and reversible cdi insertion

Spectroscopic pure (NMR) complexes were used for the microanalyses. For the compounds **3, 4** and **5** colourless crystals were obtained, which gave satisfactory microanalyses. For compound **5** however, we could not get satisfactory C analysis. The best set of values was: **5**, Anal. Calc. for $C_{36}H_{71}N_8Nb$: C 60.99, H 10.10, N 15.80. Found: C 59.63, H 9.93, N 15.97 %. For **3** and **4** however, there was not any trace of free carbodiimide detected by NMR (see the $^{1}H$- and $^{15}N$-HMBC-NMR of **3**). Since **5** and **6** are not useful for MOCVD we have not optimized the synthesis and purification. The reversibility of the cdi insertion has to be taken into account (see ref. 10 of the main text). This could possibly explain the somewhat lower experimental C-values of some samples depending on the thermal conditions of the purification process (sublimation/crystallisation). However, we have no indications for that process taking place under our conditions.

### NMR Spectra

Compound **3** was selected as representative example of the series **3**-**6** and some more detailed NMR studies were done as summarized below in Figures S1-S4.

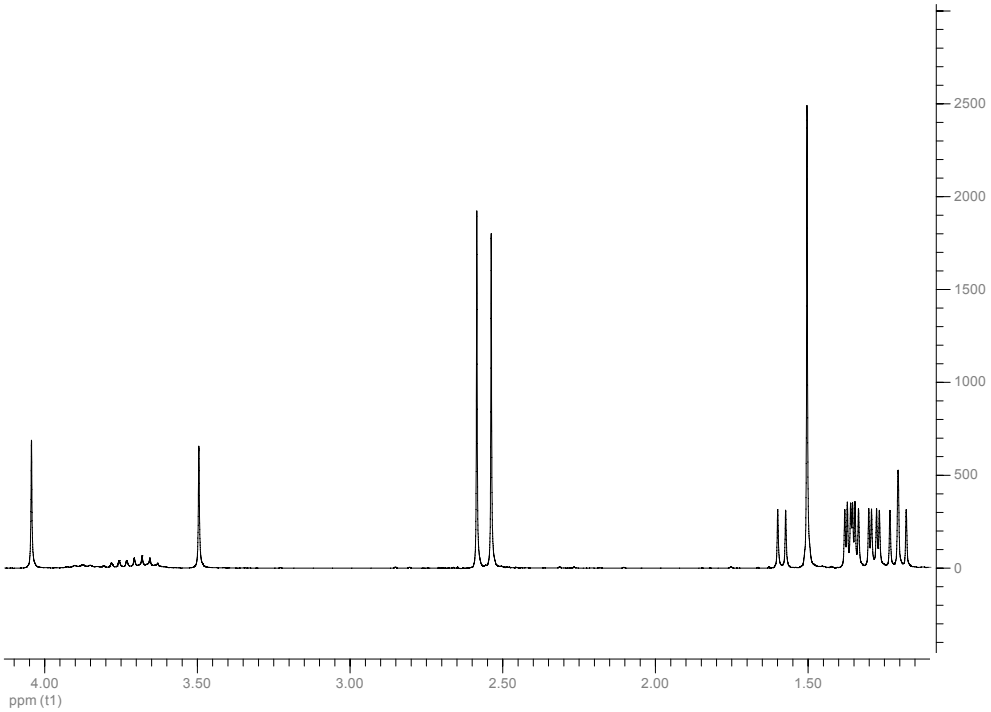



**Figure S1.** $^{1}$H-NMR (250 MHz, $C_6D_6$) of [Nb(NMe$_2$){$\eta^2$-(*i*-Pr-N)$_2$C(NMe$_2$)}$_2$(N-*t*-Bu)] (**3**).

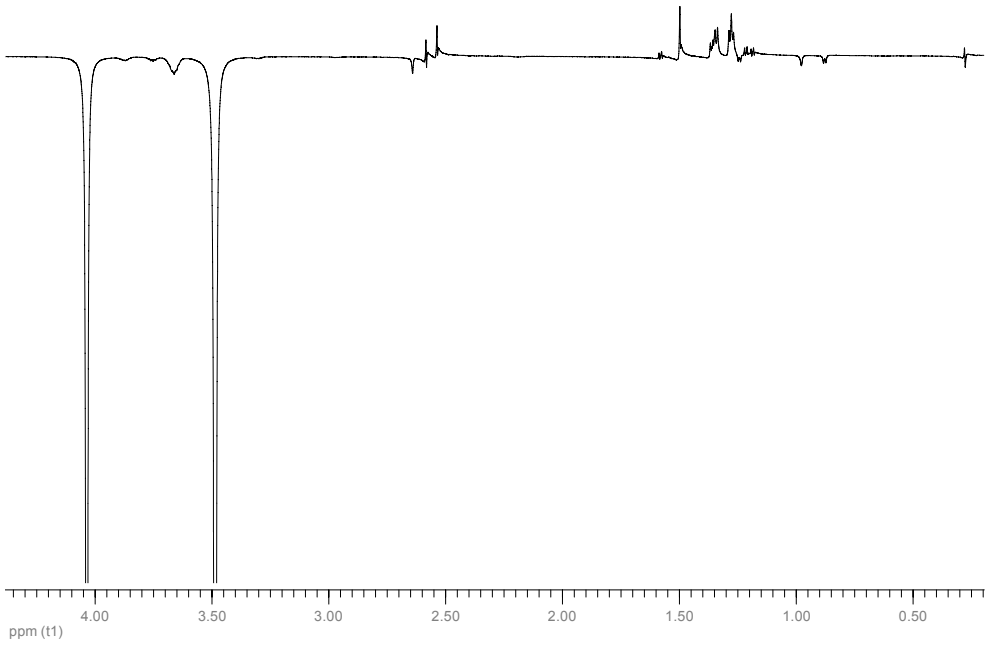



**Figure S2**. $^{1}$H-NMR NOESY (600 MHz instrument as above) of [Nb(NMe$_2$){$\eta^2$-(*i*-Pr-N)$_2$C(NMe$_2$)}$_2$(N-*t*-Bu)] (**3**) for the saturation of the Nb-NMe$_2$ protons is shown. It can easily be seen that the second singulet of the metal amide group shows the same negative intensity like the saturated one. This response typically indicates a methyl group exchange.

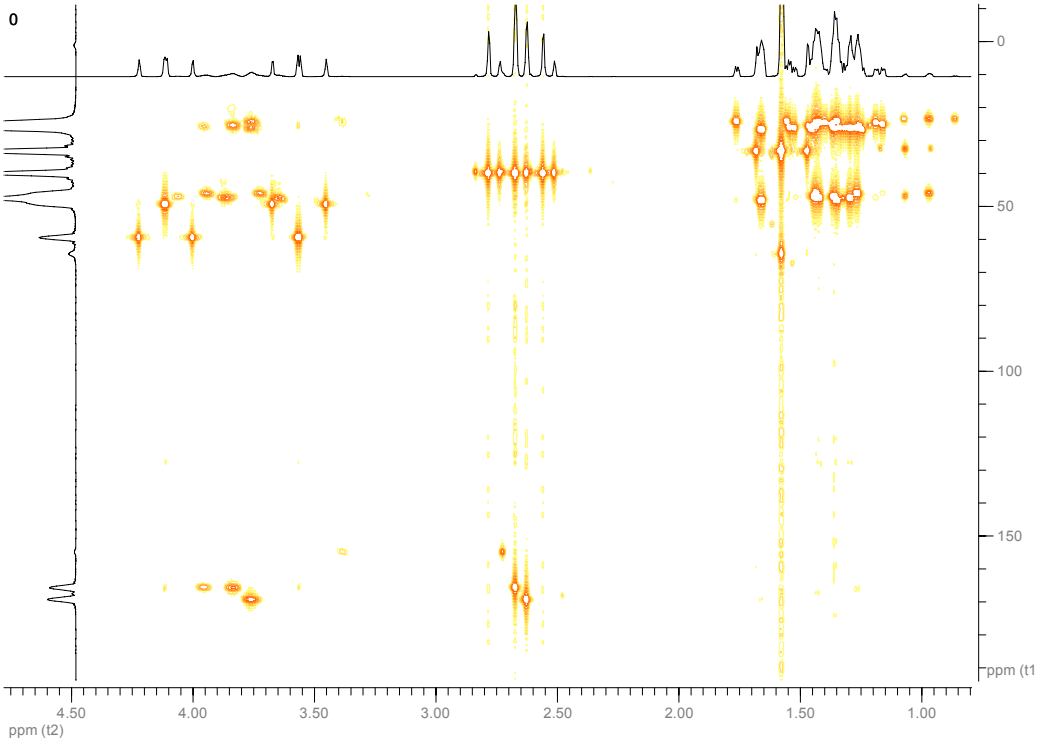



**Figure S3**. $^{13}C$-$^{1}H$-HMBC (600 MHz, $C_6D_6$). The single brown dots mark the $^{3}J$ couplings between carbon atoms and protons in the two dimensional HMBC spectrum. As no low pass filter is active for this NMR experiment, the $^{1}J$ couplings are also visible in this spectrum. They appear as doublets. The vertical spectrum shows the $^{13}C$-NMR spectrum of [Nb(NMe$_2$){$\eta^2$-(*i*-Pr-N)$_2$C(NMe$_2$)}$_2$(N-*t*-Bu)] (**3**), the horizontal spectrum represents the $^{1}H$-NMR without low pass filter.

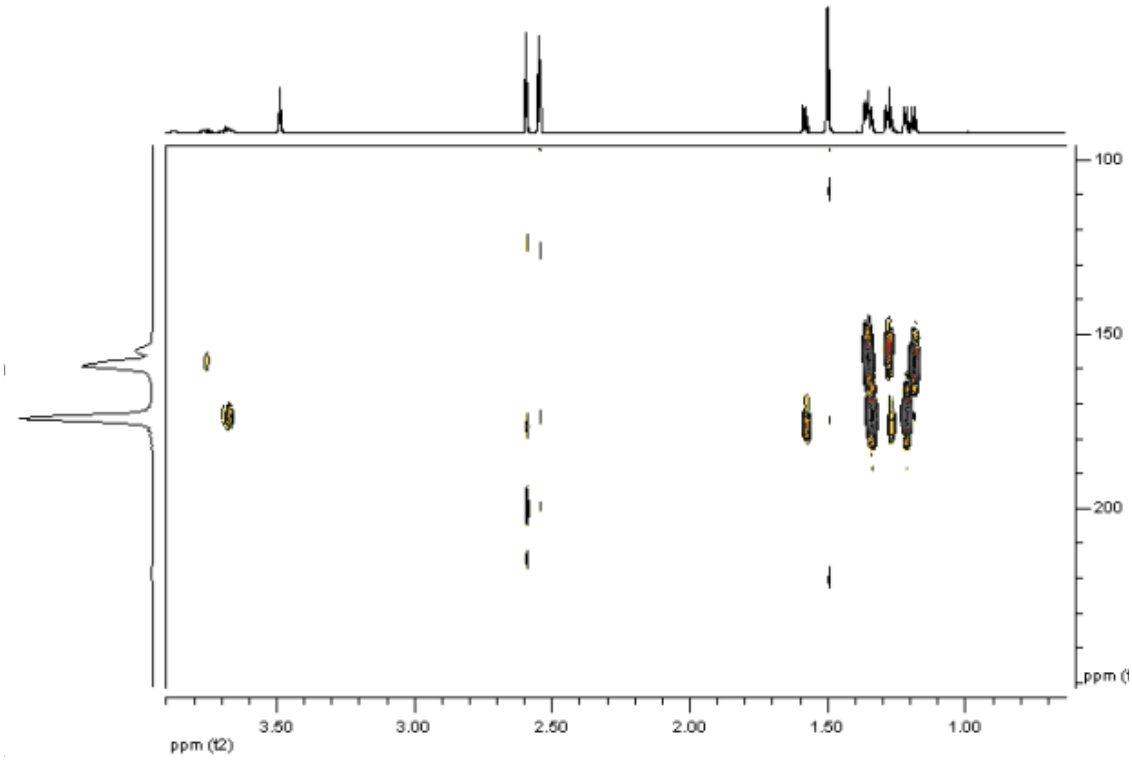



**Figure S4.** $^{15}$N-$^{1}$H-HMBC (600 MHz, $C_6D_6$). The 1D-$^{15}$N-NMR (again a 600 MHz NMR spectrometer was used) is plotted vertically; the 1D-$^{1}$H-NMR is plotted horizontally. The pulse program was chosen in order to intensify the sensitivity for the measurement of the $^{3}$J coupling. In principle it is also possible to detect the weaker $^{2}$J and $^{4}$J signals. Surprisingly, the imido nitrogen could not be seen.

**MOCVD Studies**

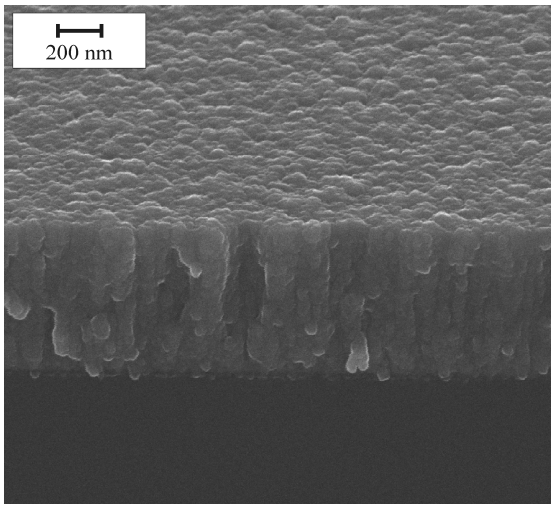



**Figure S5**. SEM cross section of a film deposited at 600 °C substrate temperature using $[Nb(NMe_2)_3(N\text{-}t\text{-}Bu)]$ (**1**) as single source precursor in the absence of ammonia. The growth of the crystallites is columnar. The diameter of the crystalline grains varies between 3 nm and 40 nm.

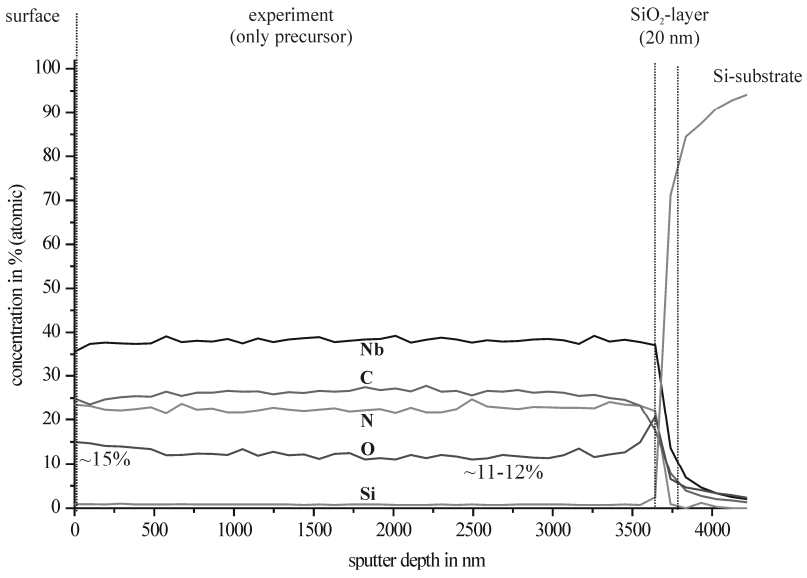



**Figure S6.** SNMS-analysis of a film deposited at 700 °C substrate temperature using $[Nb(NMe_2)_3(N\text{-}t\text{-}Bu)]$ (**1**) as precursor. Atomic concentration (av.) for Nb: 38.3 %; N: 22.7 %; C: 26.3 %; O: 11.4 %. The oxygen contamination is likely to be due to both, leakage during the low pressure MOCVD experiment and post-deposition oxidation of the film prior to the ex-situ SNMS measurement.

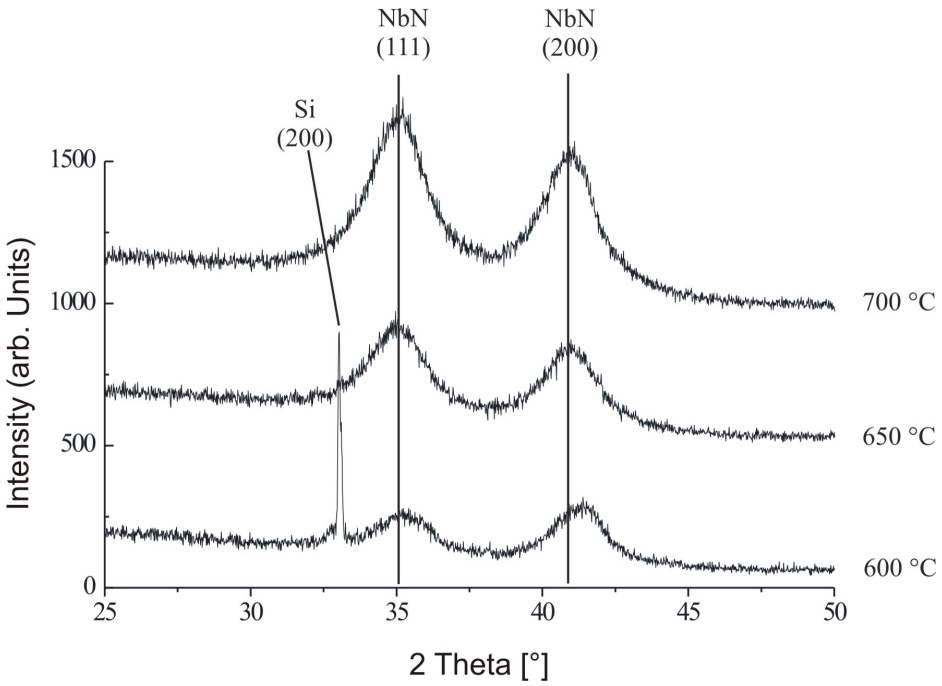
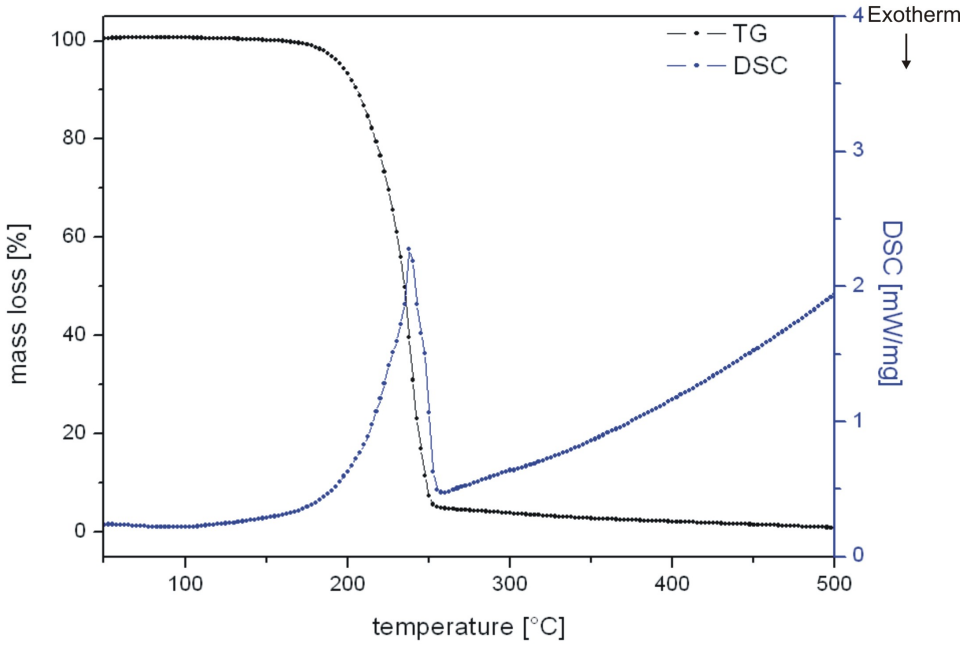



**Figure S7.** XRD-data of the Nb(N,C)-film of figure S5 and S6 derived from **1**.



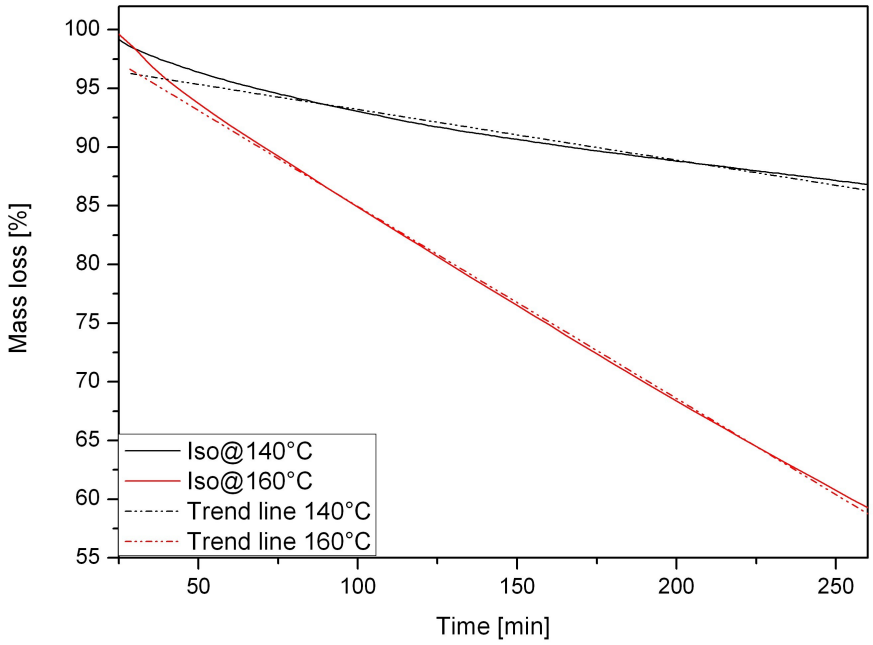



**Figure S8.** *Above*, TGA/DTA analysis of compound **3**. Note, the broad endothermic peak at 200-250 °C, whith overlapping melting at 211 °C and decomposition at somewhat higher temperature. *Below,* isothermal studies of compound **3**.

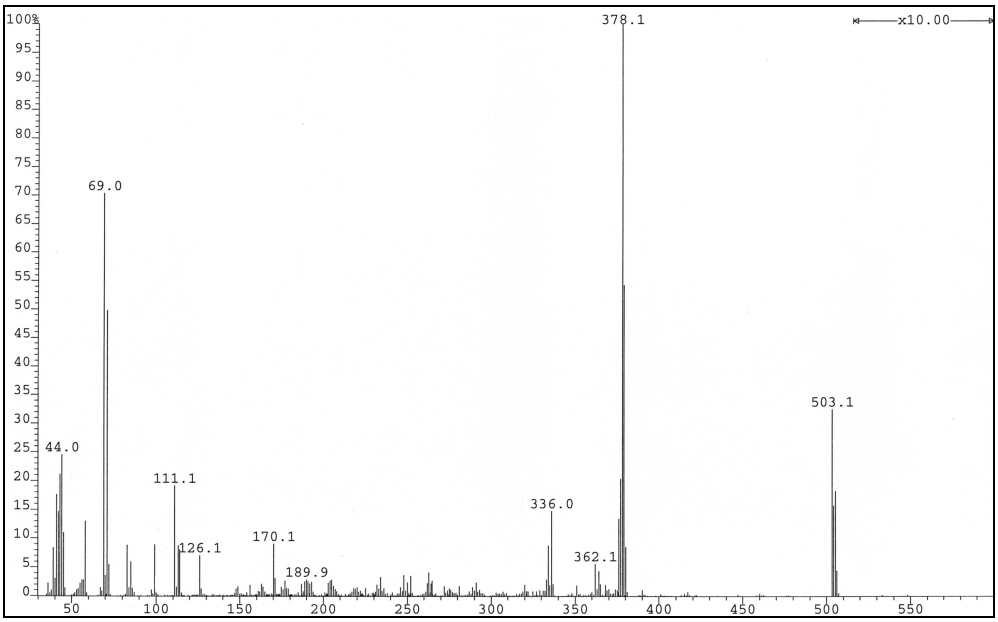



**Figure S9.** EI-MS of compound **3**. The base peak at m/z = 378.1 refers to a fragmentation such as $[M^+ - (N\text{-}i\text{-}Pr)_2C(NMe_2)]$.

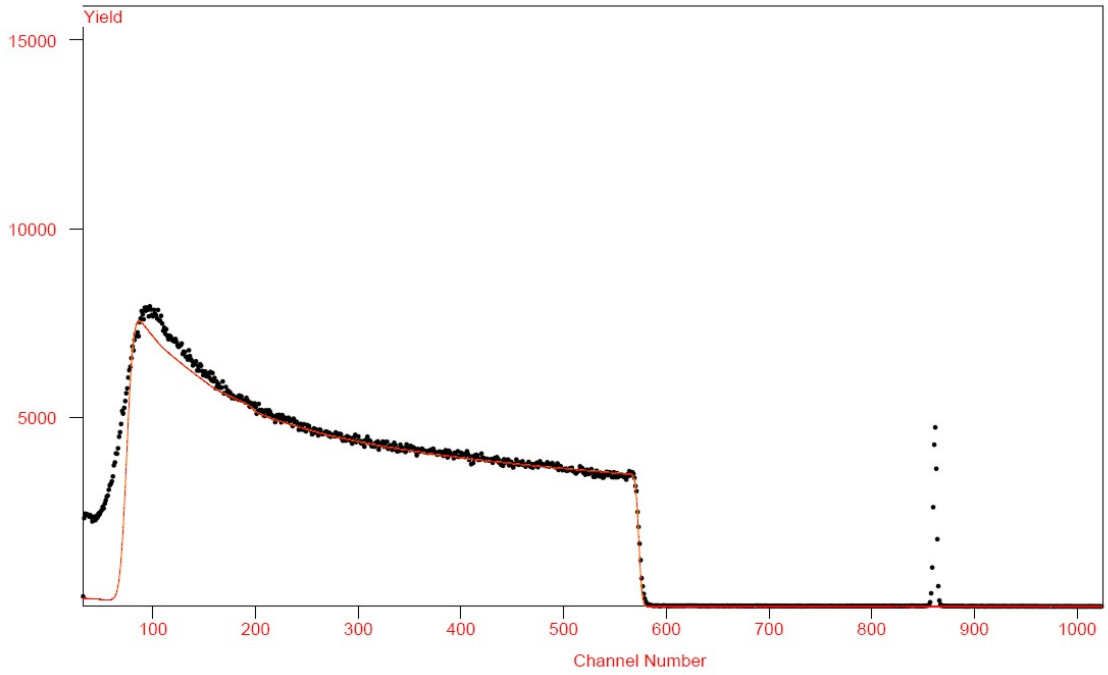



**Figure S10.** RBS-analysis of a NbN thin film deposited at 600°C substrate temperature using [Nb(NMeMe){η$^2$-(*i*-Pr-N)$_2$C(NMe$_2$)}$_2$(N-*t*-Bu)] (**3**) as precursor. The black dots represent the experimentally determined values. The red graph displays a calculated fit to the experimental values. The calculated fit afforded an elemental ratio of Nb:N:O = 1 : 1 : 0.1. The broad signal of Niobium is due to the fact that the analyzed film was about ~1µm thick.