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Supporting Information

Crown ether adducts of light alkali metal triphenylsilyls: synthesis, structure and hydrosilylation catalysis.

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^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$ and $^{7}Li\{^{1}H\}$ NMR spectra of $[Li(12\text{-crown-}4)SiPh_3]\cdot(thf)_{0.5}$

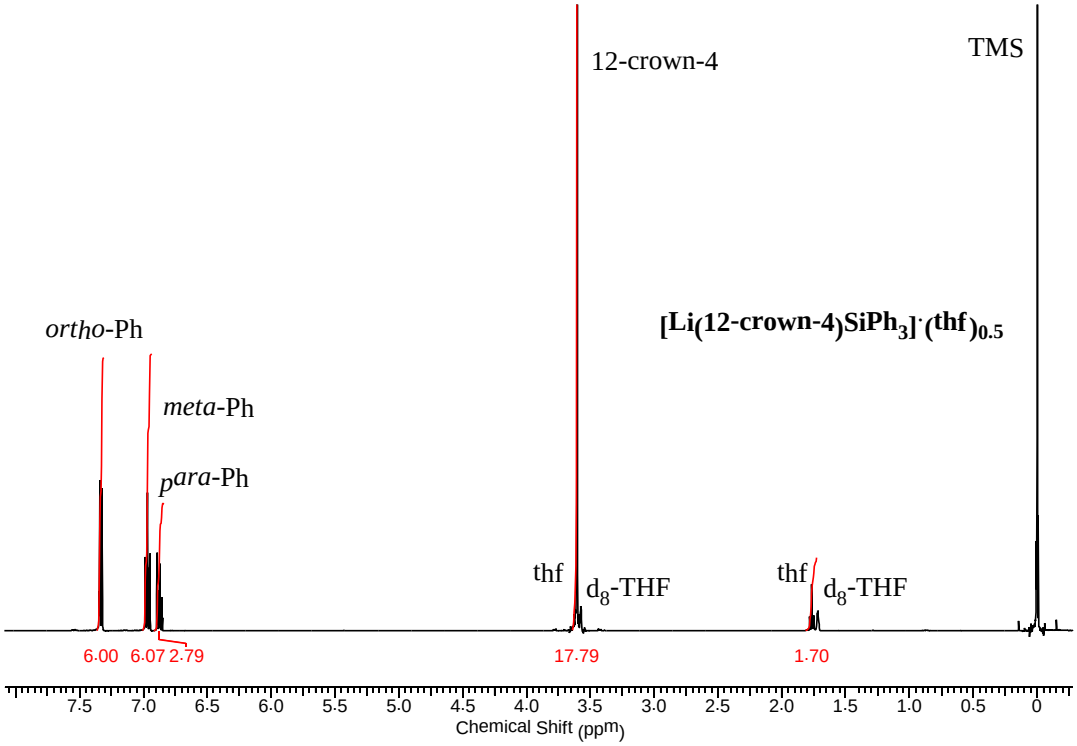

Figure S1 ^{1}H NMR spectrum of **2β** in d_8-THF at 25 °C.

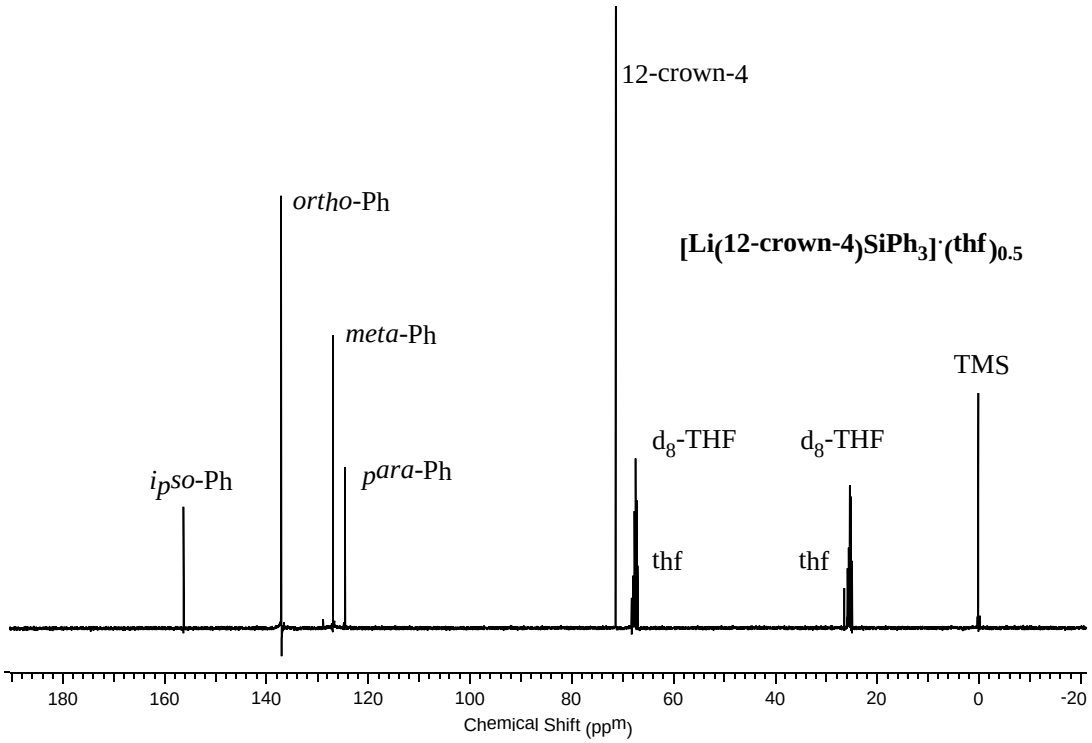

Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum of **2β** in d_8-THF at 25 °C.

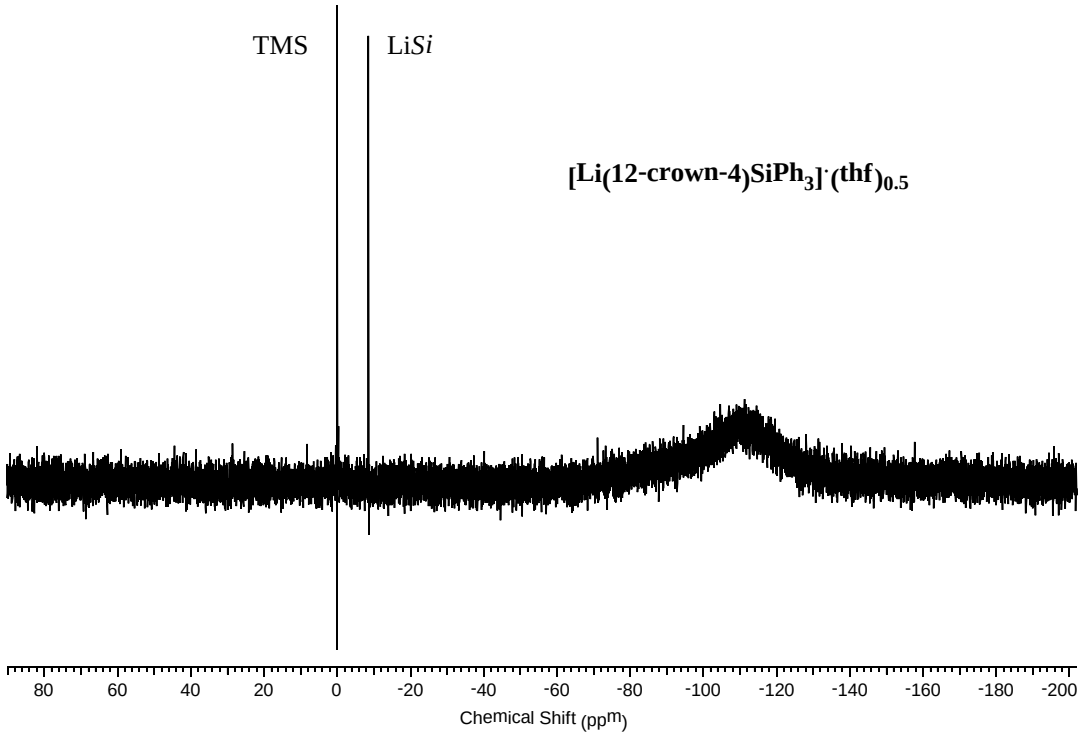

Figure S3 $^{29}Si\{^{1}H\}$ NMR spectrum of **2β** in d_8-THF at 25 °C.

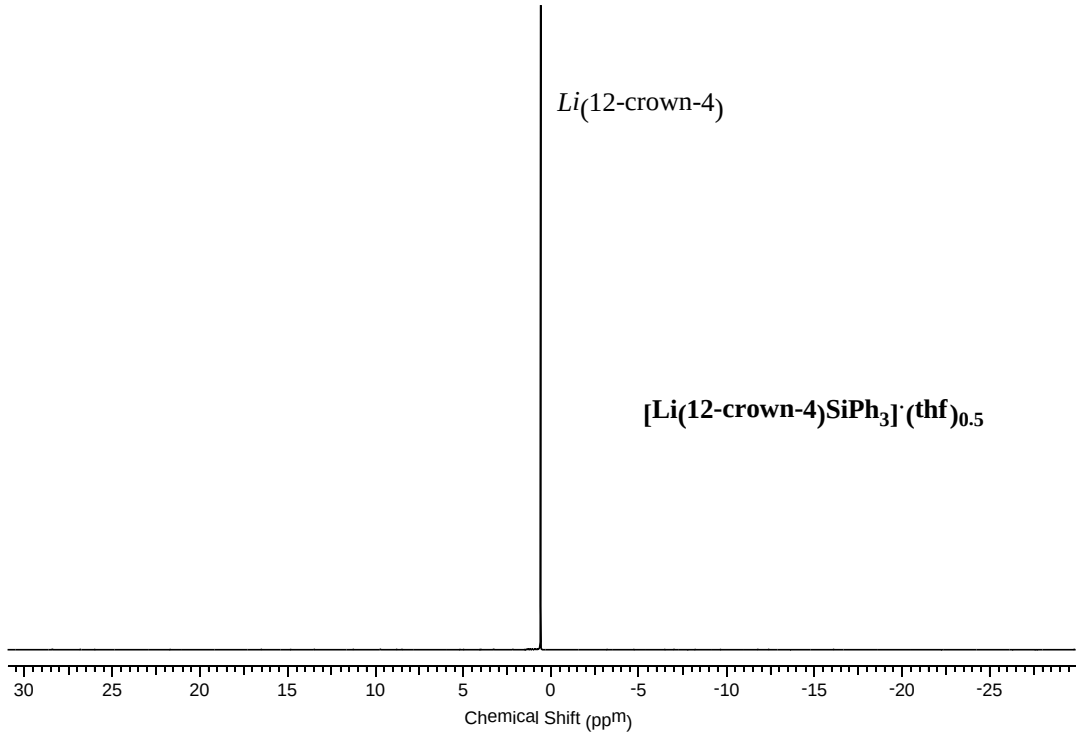

Figure S4 $^{7}Li\{^{1}H\}$ NMR spectrum of **2β** in d_8-THF at 25 °C.

^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$ NMR spectra of $[Na(15\text{-crown-}5)SiPh_3]\cdot(thf)_{0.5}$

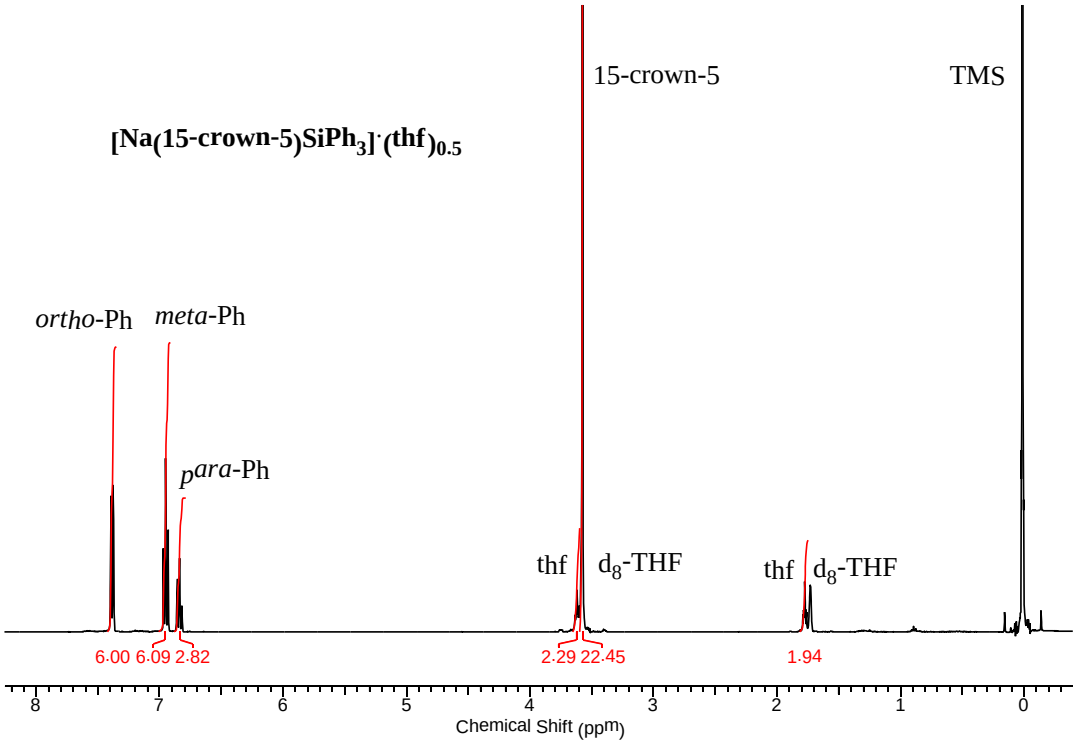

Figure S5 ^{1}H NMR spectrum of **3β** in d_8-THF at 25 °C.

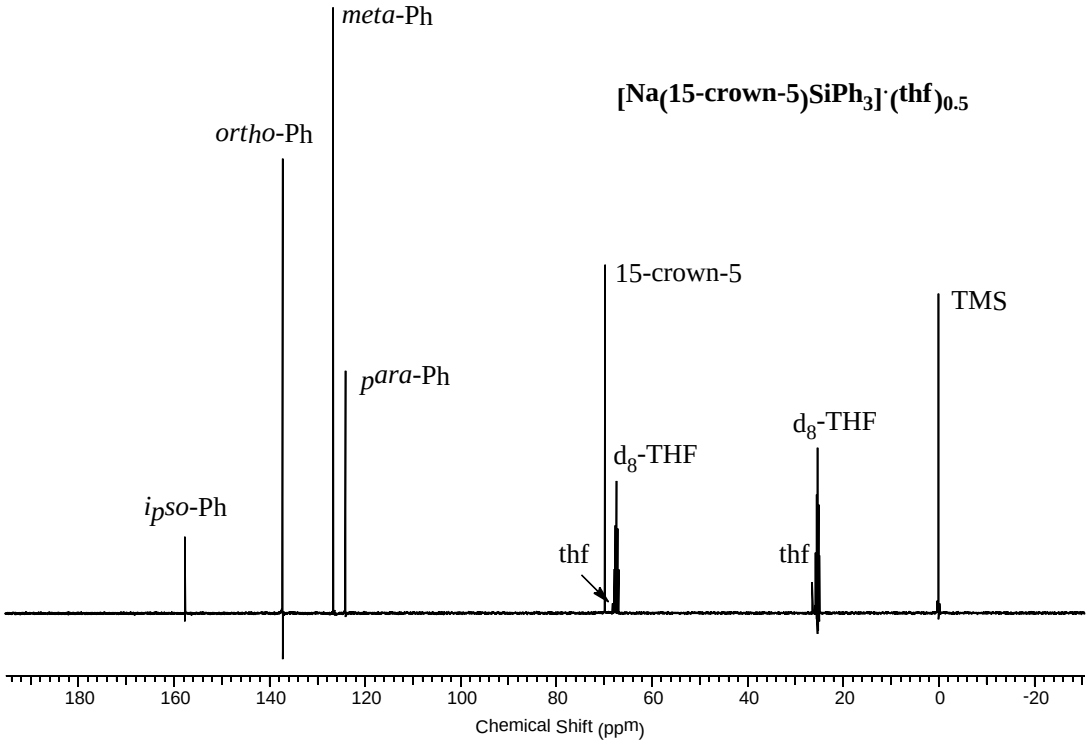

Figure S6 $^{13}C\{^{1}H\}$ NMR spectrum of **3β** in d_8-THF at 25 °C.

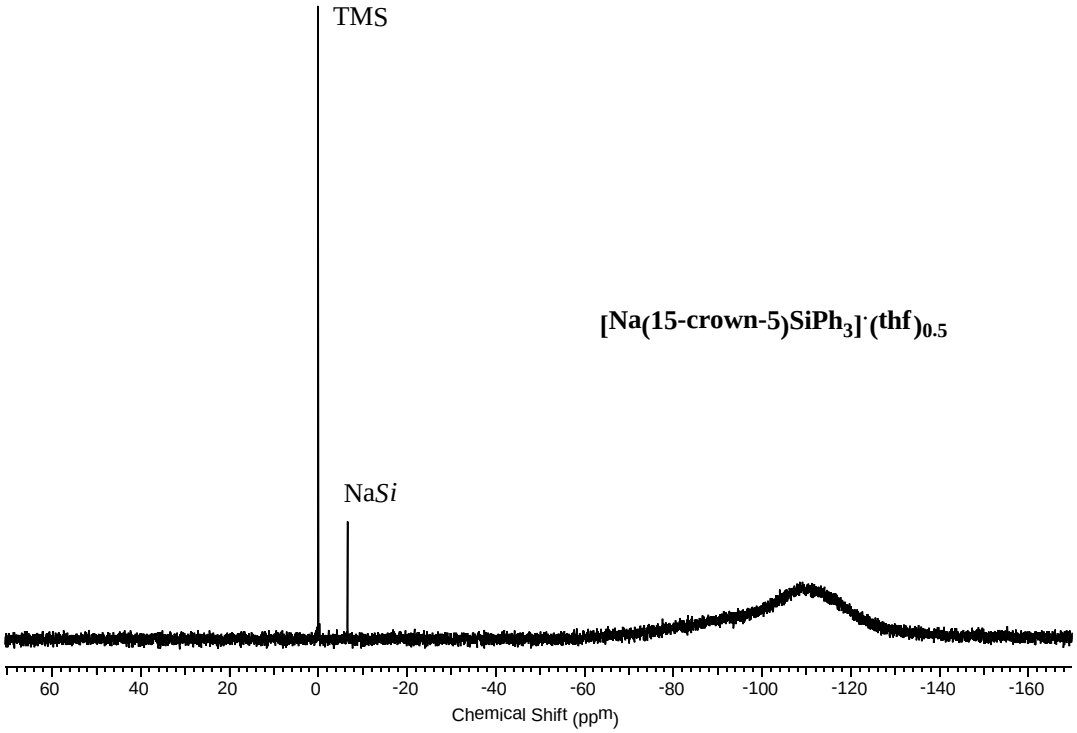

Figure S7 $^{29}Si\{^{1}H\}$ NMR spectrum of **3β** in d_8-THF at 25 °C.

^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$ NMR spectra of [K(18-crown-6)SiPh$_3$(thf)]

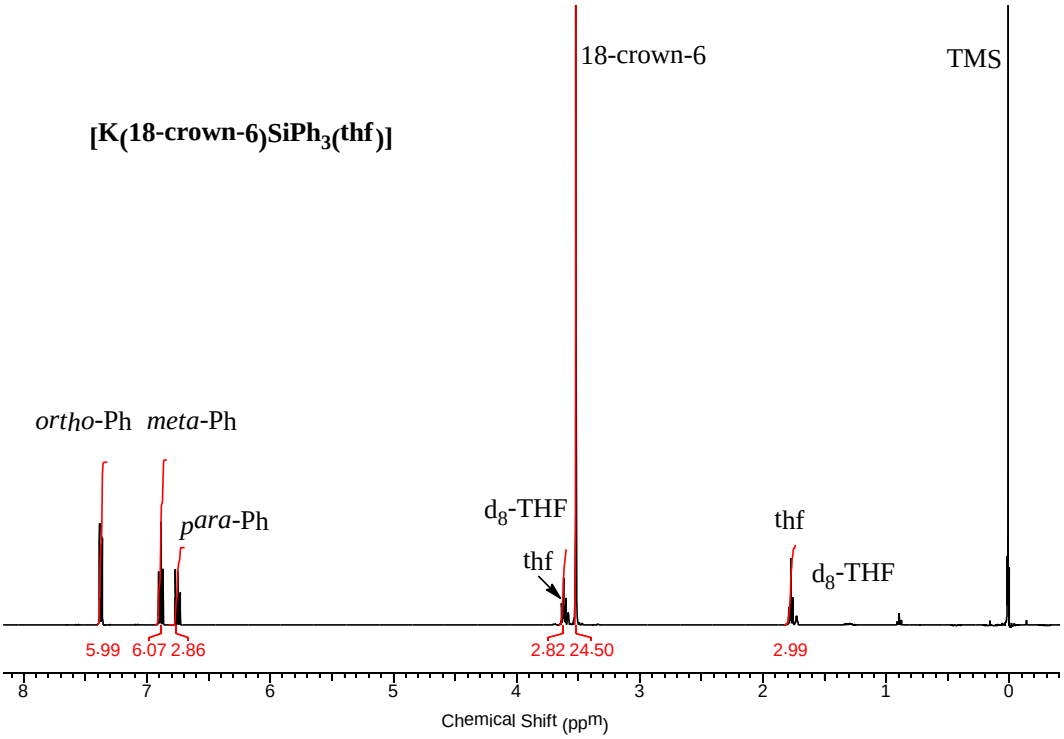

Figure S8 ^{1}H NMR spectrum of **4** in d_8-THF at 25 °C.

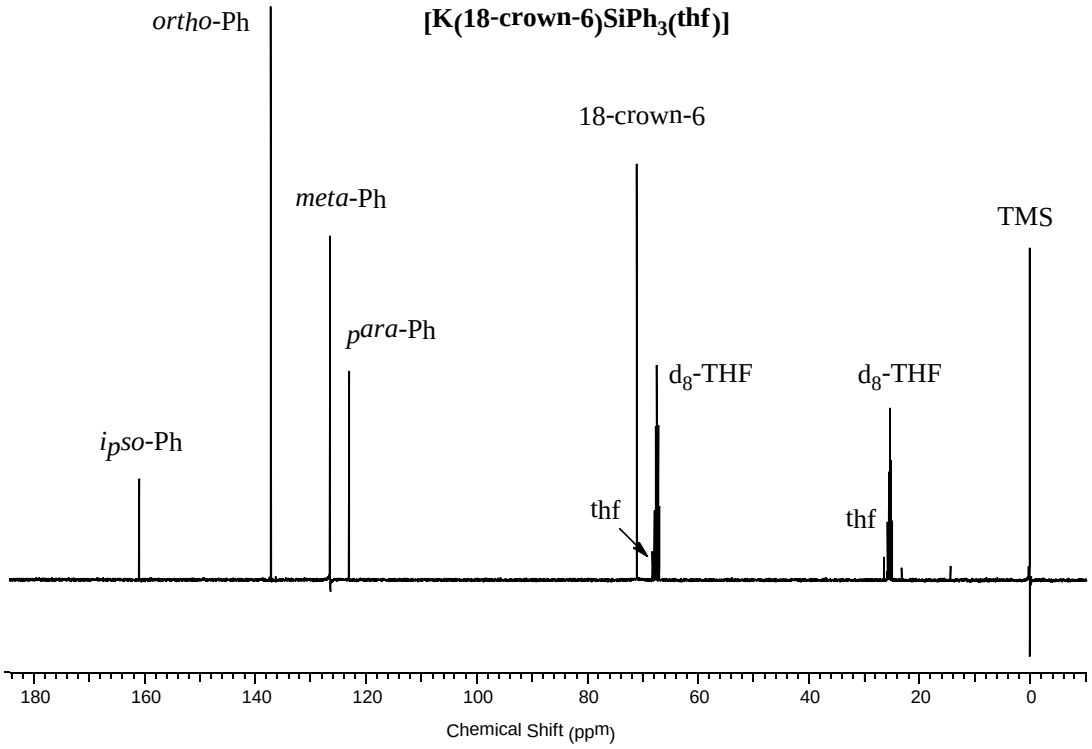

Figure S9 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in d_8-THF at 25 °C.

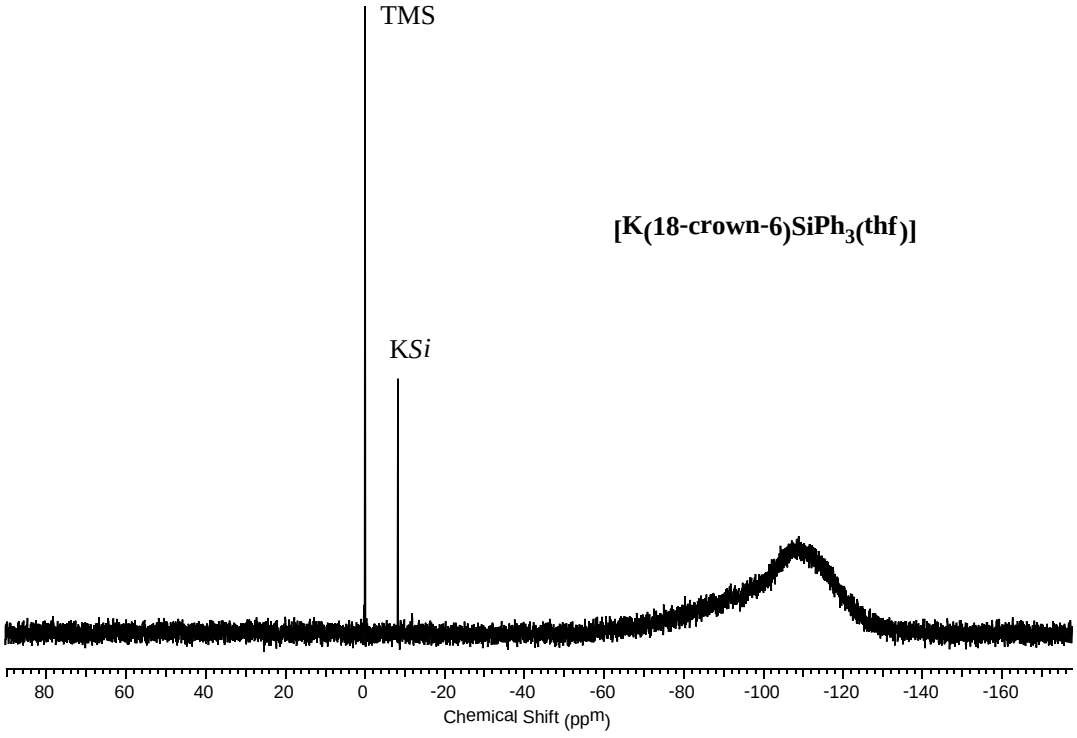

Figure S10 $^{29}Si\{^{1}H\}$ NMR spectrum of **4** in d_8-THF at 25 °C.

Details to crystallographic data

Crystals of [Li(12-crown-4)$SiPh_3$]·$(thf)_{0.5}$ (**2**) and [Na(15-crown-5)$SiPh_3$]·$(thf)_{0.5}$ (**3**) showed a reversible phase transition below 220 K associated with a symmetry decrease resulting in an increase of reflections at low temperature.

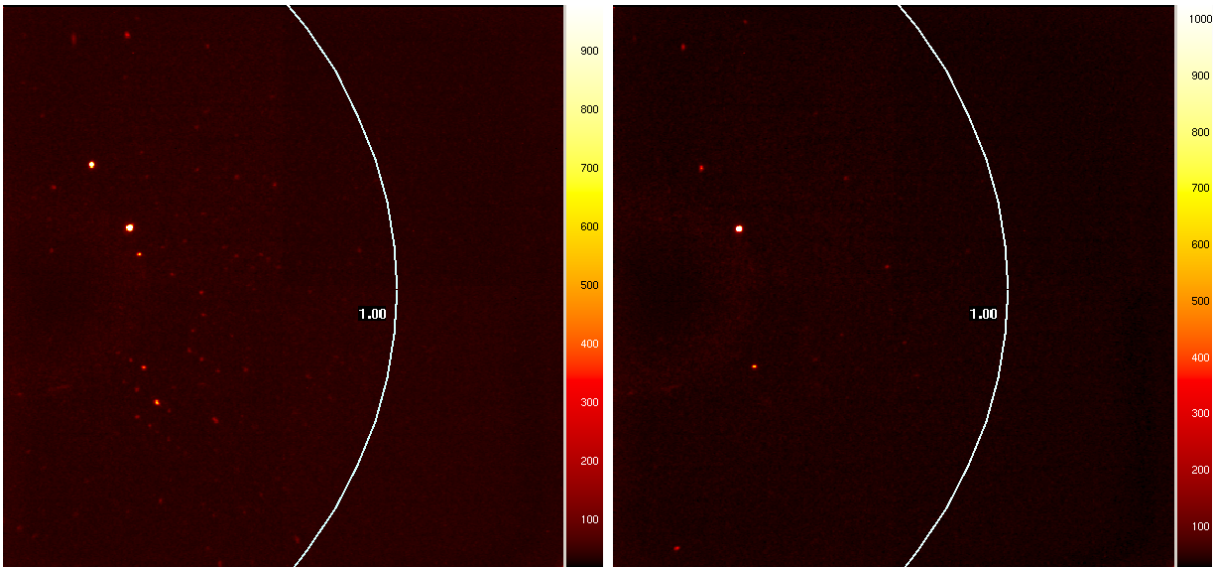

Figure S11 Diffraction pattern of **2** at 100 K (left) and 220 (K) right at the same angles.

Indexing of **2α** showed the symmetry decrease in form of translational symmetry. Using a unit cell 4 times the size of **2β** was not sufficient to assign all harvested reflections with only one domain. This is not surprising, as phase transitions with symmetry reduction – corresponding to the symmetry principle[1] – often reflect the lost symmetry in the transformation matrices between different twin domains. However, data reduction showed that the assignment of different twin domains is not reliable and even other unit cell setups may be considered.

The phase transition in [Na(15-crown-5)$SiPh_3$]$(thf)_{0.5}$ (**3α**) can be tracked in a more reliable way: The low temperature phase crystallizes in triclinic space group $P\bar{1}$ in a nearly trigonal unit cell with doubled *a* and *b* axis. Several independent domains can be found but the low diffraction power only allowed data reduction with a single domain. The structure was solved analogue to the experimental in the main article but with isotropic displacement ellipsoids for non metal atoms. Overall only a rudimentary structure model could be applied and agreement factors stayed high. This may also be accounted to strong correlations within the structure due to pseudo translation symmetry along $\frac{1}{2}00$ and untreated twinning. However, the refinement is

[1] U. Müller, *Symmetriebeziehungen zwischen verwandten Kristallstrukturen*, Vieweg + Teubner, **2011**

stable and overall the same connectivity as in **3β** is found. A total of 4 independent molecules occupy the asymmetric unit and are closely packed. The average Si-Na distance is the same as in the high temperature phase. Formally the two phases are related by a *translationsgleiche* symmetry reduction of index 3, followed by a *klassengleiche* transition of index 4. The *cif*-file can be obtained on request directly from the authors.

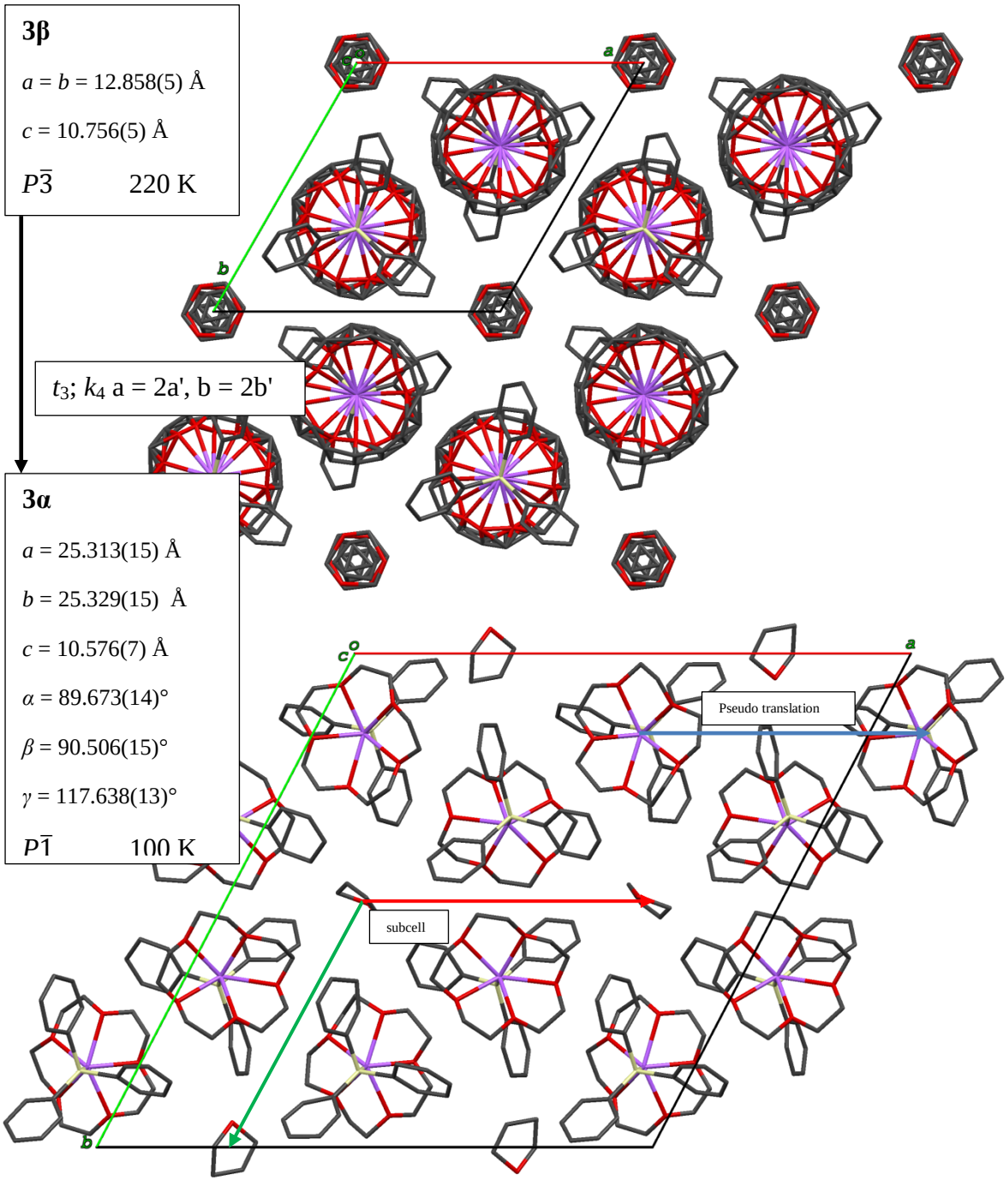

Figure S12 Comparison of the packing and unit cells of **3β** (top) and **3α** (bottom). The high temperature cell can be found as subcell in **3α** and the main molecules are related by pseudo translation.