

Supporting Information

**Scalable two step synthesis of  $^{29}\text{Si}$  labelled tetraalkoxysilanes.**

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NMR spectra

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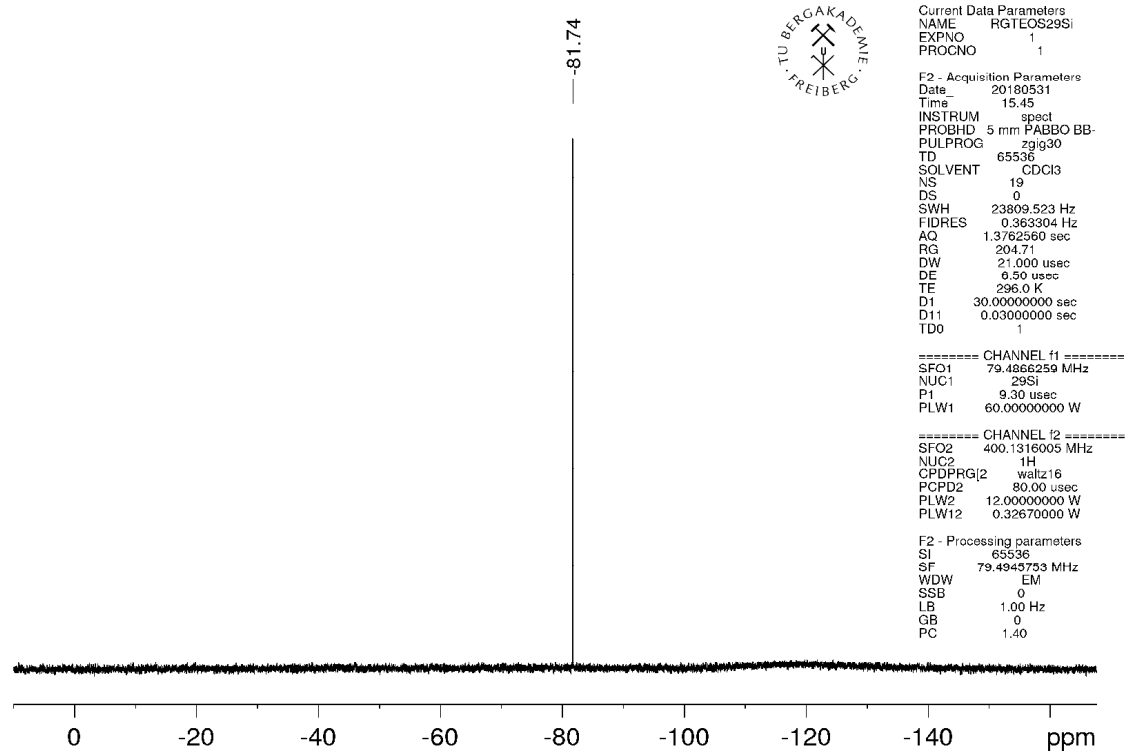


Fig. S1:  $^{29}\text{Si}$   $\{^1\text{H}\}$  gated NMR spectrum of  $^{29}\text{Si}$  enriched TEOS, NS = 19, 10  $\mu\text{l}$  dissolved in 500  $\mu\text{l}$   $\text{CDCl}_3$ . Note the high intensity of the TEOS signal compared to the glass signal of the probe head. The solvent contained TMS in a concentration suitable for  $^1\text{H}$  referencing, which is therefore too low to be visible beside the  $^{29}\text{Si}$  enriched TEOS.

Table S1: NMR data of  $^{29}\text{Si}$  enriched TEOS

group	$\delta_{\text{Si}}$ ppm	$\delta_{\text{H}}$ ppm	$\delta_{\text{C}}$ ppm	J(Si,H) Hz	J(Si,C) Hz	J(H,H) Hz
Si	-81.74					
OCH <sub>2</sub>		3.784	59.17	2.8	0.95	7.0
CH <sub>3</sub>		1.172	18.12	0.44	2.4	7.0

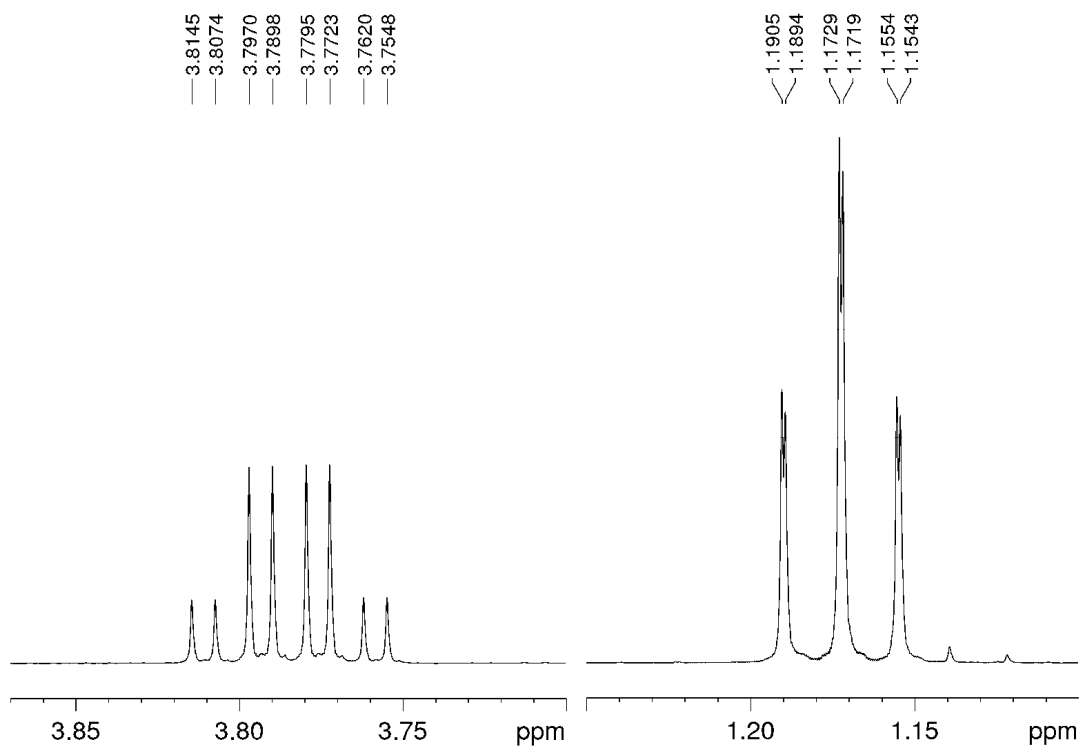


Fig. S2: Sections of the  $^1\text{H}$  NMR spectrum of  $^{29}\text{Si}$  enriched TEOS (10  $\mu\text{l}$  dissolved in 500  $\mu\text{l}$   $\text{CDCl}_3$ ) showing the  $^3J(\text{Si},\text{H})$  and  $^4J(\text{Si},\text{H})$  couplings.

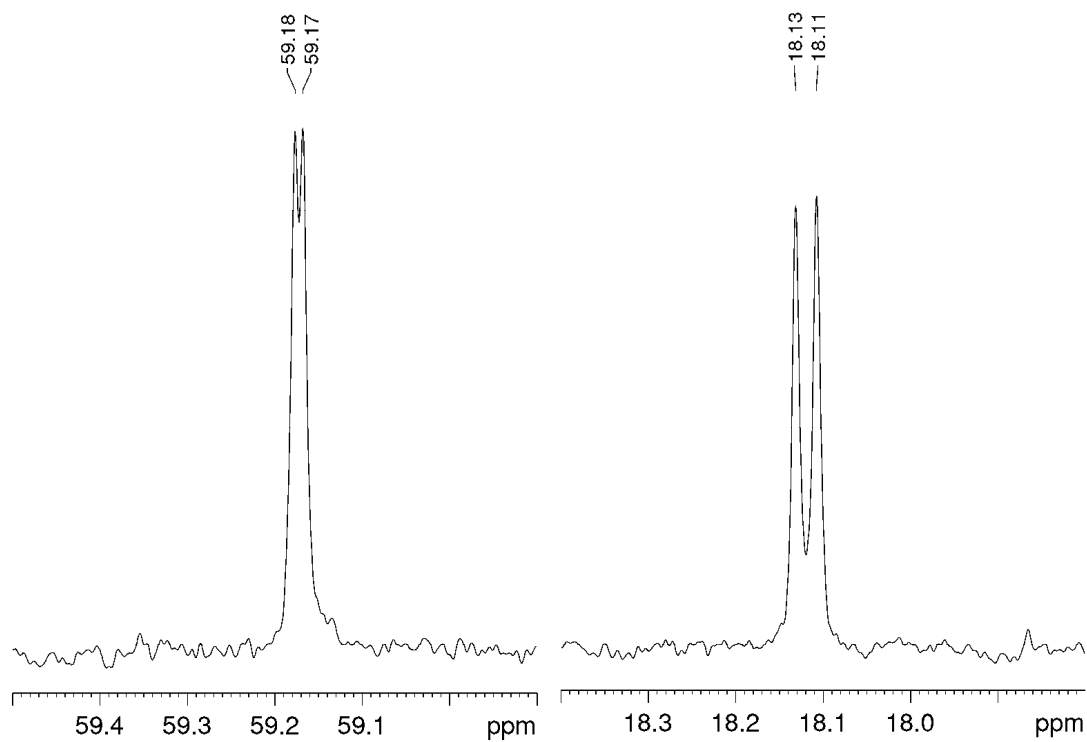


Fig. S3: Sections of the  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum of  $^{29}\text{Si}$  enriched TEOS (10  $\mu\text{l}$  dissolved in 500  $\mu\text{l}$   $\text{CDCl}_3$ ) showing the  $^2J(\text{Si},\text{C})$  and  $^3J(\text{Si},\text{C})$  couplings.

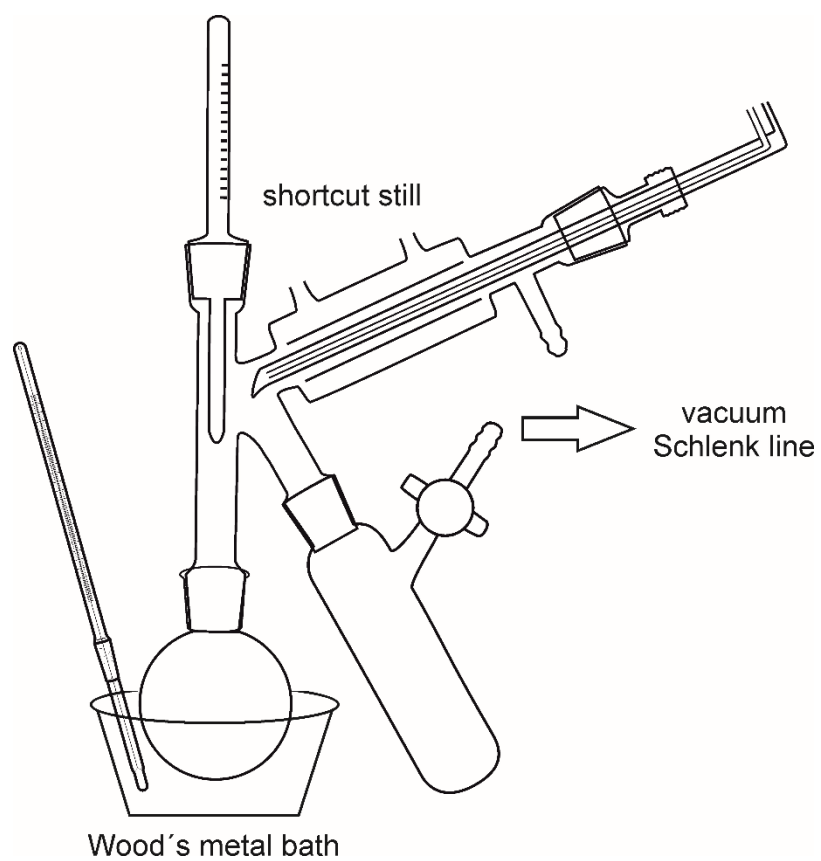
### Synthesis of calcium ethanolate $\text{Ca}(\text{OEt})_2$

Ethyl alcohol was dried over magnesium and stored over molecular sieve 3 Å.<sup>1</sup> Granules of elemental calcium (5.22 g, 130 mmol) were transferred into a Schlenk flask under Ar atmosphere. For removal of the oxide layer, the calcium was then stirred with ethanol (12.6 g, 274 mmol) until the evolution of gas bubbles commenced. If necessary (long delay of gas evolution), the reaction mixture was gently heated. The Ca was then washed with ethanol (3×5 mL). The process was repeated up to three times to obtain bright and shining Ca granules. Subsequent, a new portion of ethanol (12.56 g, 273 mmol) was added to the freshly purified calcium, and the mixture was slowly heated up to reflux. At 40 °C the reaction commenced with vigorous gas evolution. After refluxing for 1.5 h, n-hexadecane (120 mL) was added in portions of 20 mL after every 1 h, whilst the oil bath temperature was maintained at 130 °C. Thereafter, further ethanol (6.2 g, 135 mmol) was added to the mixture, and heating under reflux was continued for another 2.5 days (oil bath, 130-140 °C) until all metallic calcium had finally vanished. Thereafter, the hot mixture (a suspension of calcium ethanolate) was filtered and, upon attaining room temperature, washed with diethyl ether (35 mL). Thereafter, the frit was attached to a new Schlenk flask (charged with diethyl ether, 50 mL) and to a reflux condenser, and an extraction of the product (still on the frit) was performed. Finally, the white fine powder was dried *in vacuo* for 3 days and stored under argon atmosphere.

### Synthesis of sodium hexafluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) starting from silicon

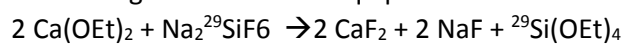
In an HF resistant beaker 500 mg silicon powder were dissolved in 13.8 mL acidic etching solution (volume ratio HF:HNO<sub>3</sub>:H<sub>2</sub>O = 2:1:1) containing 5.52 mL (0.128 mmol, 20% excess) of 48% HF solution. The silicon powder was added under stirring in very small portions to the acid solution. A portion should be completely dissolved before adding the next. After completed addition of the silicon further 1 mL HF and 1 mL HNO<sub>3</sub> were added. The clear, colourless solution obtained was filtered, the filter washed two times with 3 mL of H<sub>2</sub>O. 2.31 g NaCl were added, the solution was stirred for 2-3 h and left to crystallize overnight. For further treatment see synthesis starting from SiO<sub>2</sub>. Yield  $\eta$  = 85%.

1 Team of Authors, Organikum, VEB Deutscher Verlag der Wissenschaften, Berlin, 16<sup>th</sup> edition, 1986, 647.



Scheme S1:

Schematic drawing of the reaction equipment used for the reaction of



and the distillation of the tetraalkoxysilane.