On the use of solid-state ^{45}Sc NMR for structural investigations on molecular and silica-supported scandium amide catalysts.

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Supporting Information

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General considerations

Experiments were carried out under an argon atmosphere in an M-Braun glovebox or by using Schlenk techniques. Solvents and reactants were dried by using conventional reagents and stored in the glovebox over 3A molecular sieves. Aerosil 380 silica (Degussa, specific area 380 $m^2 g^{-1}$, prior to heat treatment) was subjected to heating under secondary vacuum (10^{-6} mbar) for 15 h at 500 °C, followed by 4 h at 700 °C, and stored in a glovebox for limited time. Liquid-state NMR spectroscopic analyses were run at 7 T (300 MHz for ^{1}H) using a Bruker Avance-II spectrometer. The 1D-^{45}Sc solution NMR experiments were recorded at 97.3 MHz and 300 K on a Bruker AVANCE II 400 spectrometer equipped with a 5 mm broad-band probe using the following parameters: a 8.8 µs pulse calibrated on a 0.18 M $Sc(NO_3)_3$ solution in D_2O, a 0.5 s recycling delay, a 6 ms acquisition time, a 60 kHz spectral width and 2048 scans. Solid-state MAS NMR spectra were recorded either (i) at 9.4 T (400 MHz for ^{1}H, 161.9 MHz for ^{31}P) using a Bruker AVANCE-II console equipped with a 4 mm probe spinning at 10 kHz or (ii) at 18.8 T (800 MHz) using a Bruker AVANCE-III console equipped with a 3.2 mm probe spinning at 20 kHz or used under static conditions. Chemical shifts for ^{1}H, ^{45}Sc, ^{31}P are given with respect to adamantane, $Sc(NO_3)_3.3H_2O$ and H_3PO_4 respectively as external references. For the ^{31}P CP MAS experiment, the spinning frequency was 10 kHz, the recycle delay was 5 s, and 11264 scans were collected with a pulse lasting 5 µs. 1D ^{45}Sc static spectra were recorded using a Hahn echo experiment with a QCPMG detection[1] (Quadrupolar Carr-Purcell Meiboom-Gill) using a train of refocusing pulses of echoes. The Hahn echo experiment used rf pulses lasting 0.80 µs and 1.60 µs for the 90° and the 180° pulses respectively and a rf amplitude of 78 kHz and the delay between the two pulses is 5 ms. A total of 22 echoes was recorded in the CPMG experiment. A 4 ms hyperbolic secant[2] (HS) inversion pulse was used initially in order to enhance the polarization of ^{45}Sc central transition. The optimal HS enhancement was obtained with an rf field of 12 kHz and an offset frequency of 180 kHz. A SPINAL-64 (small phase Incremental alternation with 64-steps[3]) proton decoupling of 78 kHz was used during the acquisition. The recycle delay was 1 s, the number of scans was 1024 and the experiments lasted for 17 minutes for samples **1** and **2**. The recycle delay was 0.5 s, the number of scans was 614400 and the experiments lasted for 3 days and 12 hours for samples **1-SiO$_{2\text{-}700}$** and **2-SiO$_{2\text{-}700}$**. 1D ^{45}Sc MAS spectrum of **2** was recorded using Hahn echo experiment with rf pulses lasting 1.4 µs and 2.80 µs for the 90° and the 180° pulses respectively and a rf amplitude of 45 kHz. The delay between the two pulses is rotor synchronized to 0.5 ms (one rotor period). The recycle delay was 1 s, the number of scans was 1024 and the experiment lasted for 17 minutes. The chemical shift parameters are defined according to the Haeberlen notation[4]: $\delta_{iso} = {}^1/_3(\delta_{XX} + \delta_{YY} + \delta_{ZZ})$ and $\Delta_{CSA} = \delta_{ZZ} - \delta_{iso}$. Where δ_{iso} denotes the isotropic chemical shift; δ_{XX}, δ_{YY}, and δ_{ZZ} are the principal components of the Chemical Shift Anisotropy (CSA) tensor ordered as $|\delta_{YY} - \delta_{iso}| \leq |\delta_{XX} - \delta_{iso}| \leq |\delta_{ZZ} - \delta_{iso}|$; and Δ_{CSA} is the anisotropic chemical shift. Simulation of the spectra were performed using TOPSPIN Bruker® software. Diffuse reflectance infrared spectra were collected with a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. Typically, 64 scans were accumulated for each spectrum (resolution of 4 cm^{-1}). Elemental analyses were conducted at London Metropolitan University (CHN) and at LASIR, University of Lille (Ln). For alkyne dimerization, reaction mixtures were analysed using a Shimadzu GC2010 chromatograph fitted with a CP-Sil 5CB column (25m× 0.25mm× 0.2 µm), argon as carrier gas, and both injector and detector temperature at 250 °C. Heating program: starting at 50 °C then a ramp of 10 °C/min up to 250°C, hold for 10 min.

Synthesis of $Sc[N(SiMe_3)_2]_3$ (1)[5]

In a Schlenk tube a solution of $ScCl_3$ (120 mg, 0.8 mmol) in THF (20 mL) was stirred for 2 days then LiHMDS (412 mg, 2.4 mmol) in solution in THF (10 mL) was slowly added. The mixture was stirred further for 3 days then the solvent is removed under vacuum for 3h at 100°C. The solid extracted with pentane and the washing fractions were filtered over celite. Volatiles were evacuated. Sublimation under high vacuum (10^{-5}bar) afforded white crystals in 54 % yield (210 mg). Analytical data are identical to literature values.

Synthesis of $Sc[N(SiMe_3)_2]_3(OPPh_3)$ (2)[6]

In glovebox, a Schlenk tube was filled with **1** (75 mg, 0.143 mmol) and freshly sublimed triphenylphosphine (44 mg, 0.157 mmol), dissolved in 5 mL of toluene. After 3 h of stirring at room temperature, the solution was filtered over Celite and washed 3 times with pentane. Crystallization from pentane afforded **2** as white solid (109 mg, 95% yield). ^1H NMR (300 MHz, C_6D_6): δ 7.7 (m, 6H, PPh_3), 7.0 (m, 9H, PPh_3), 0.52 (s, 54H, $N(Si(CH_3)_3)$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ 39.8 (s, $OPPh_3$). δ(^{45}Sc) 360 ppm (C_6D_6, 300 K, FWHM: 4500 Hz).

General procedure for grafting (1) or (2) onto $SiO_{2\text{-}700}$ to form (1-$SiO_{2\text{-}700}$) or (2-$SiO_{2\text{-}700}$)

In a glovebox, a double-Schlenk vessel was loaded with the tri or tetra-coordinated scandium precursor (0.3 mmol) dissolved in 20 ml of pentane in one compartment and with $SiO_{2\text{-}700}$ (1 g) suspended in 20 mL of pentane in the other compartment. The colourless complex solution was added at room temperature to the support by filtering through the sintered glass separating the two Schlenk tubes, and the reaction mixture was stirred for 15 h. The supernatant liquid was then separated by filtration into the other compartment, from which the solvent was gas-phase transferred by trap-to-trap distillation back into the compartment containing the modified support in order to wash away the residual molecular precursor. This operation was repeated thrice. The resulting material (**1-$SiO_{2\text{-}700}$**) or (**2-$SiO_{2\text{-}700}$**) was then dried under secondary vacuum (10^{-6} mbar) at 80°C for 5 h. Elemental analysis (w%): **1**: Sc 1.04, C 3.35, H 0.77, N 0.69, **2**: Sc: 0.67, C 6.29, H 0.50, N 0.58.

Alkyne dimerization procedure

In the glove box, a glass reactor is filled with the catalyst (0.05 mmol), 3 ml of toluene and terminal alkyne (5 mmol, 100 mol eq. per Sc). The reaction mixture is heated at 100 °C. After the desired time, the reaction is quenched by exposure to air. The supernatant is analysed by GC using *n*-decane (10 mg) as a standard (added after quenching).

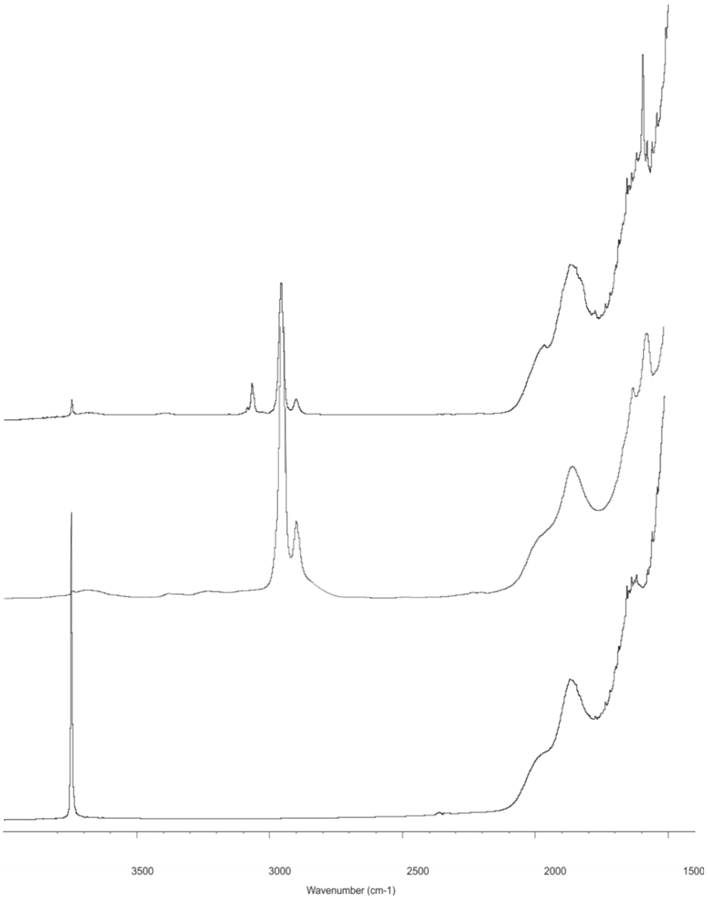

Figure S1. DRIFT of a) $SiO_{2\text{-}700}$, b) **1-$SiO_{2\text{-}700}$**, and c) **2-$SiO_{2\text{-}700}$**

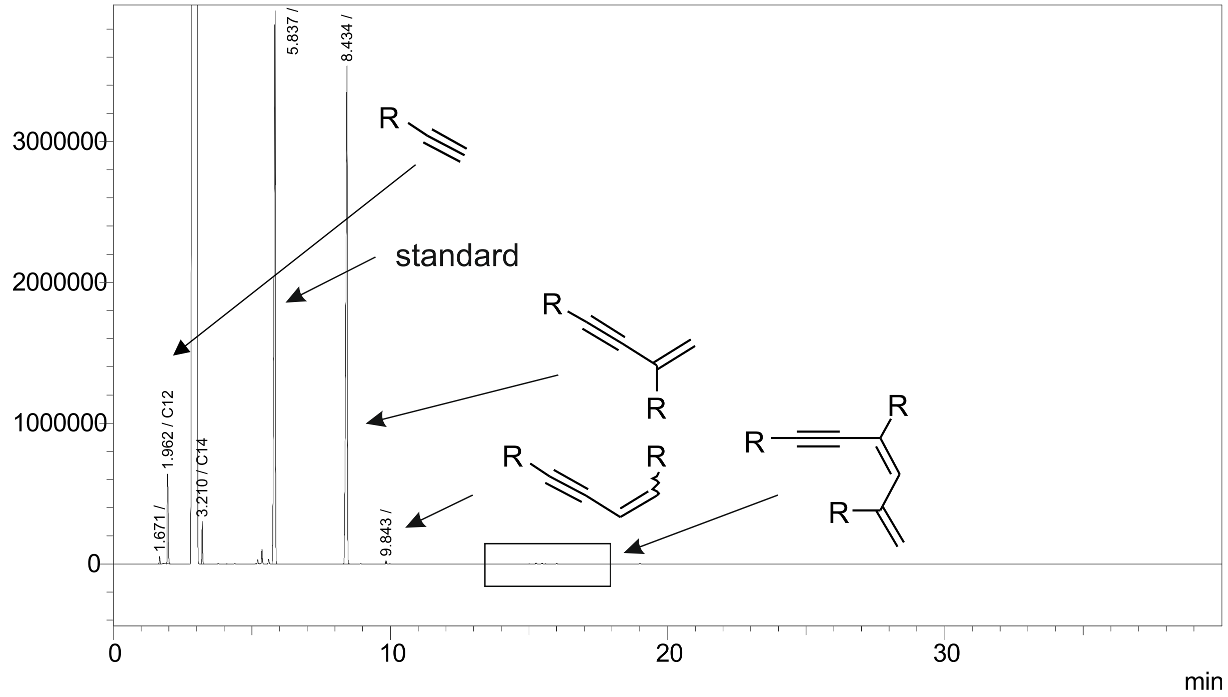

Figure S2. GC trace from dimerization of 1-hexyne with **1**

Table S1. Scandium-catalysed 1-hexyne dimerization

Entry	Catalyst	Conv. (%)	Selec. 3a/3b	Selec. 3a,3b/4
1	**1**	91	99	>99
2	**2**	-	-	-
3	**1-SiO$_{2-700}$**	47	99	94/6
4	**2-SiO$_{2-700}$**	-	-	-

Conditions: Sc (0.05 mmol), 100 eq 1-hexyne, 3 ml toluene, 4h, 100°C

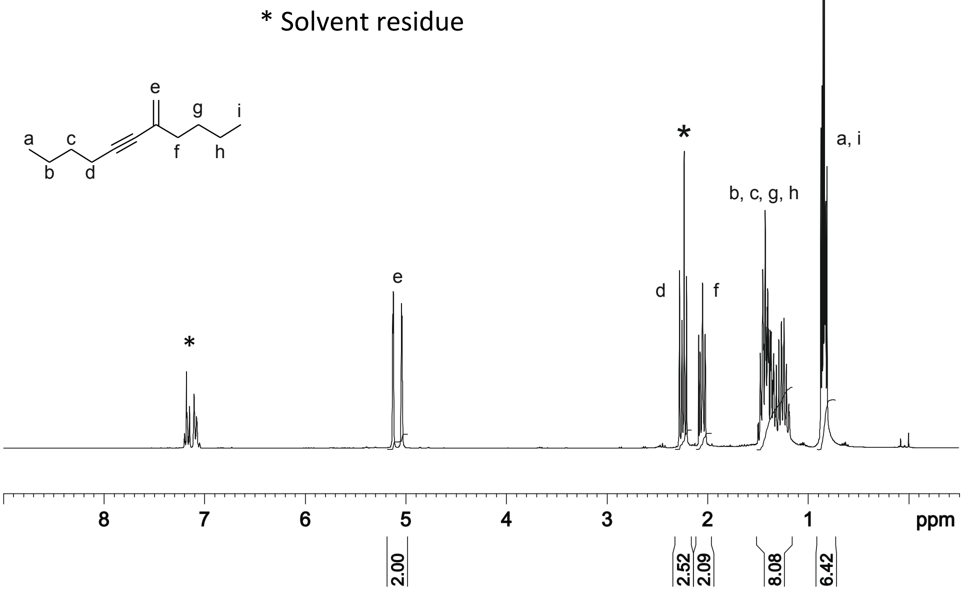

Figure S3. ^{1}H NMR spectrum (300 MHz) of 7-methyleneundec-5-yne (C_7D_8)

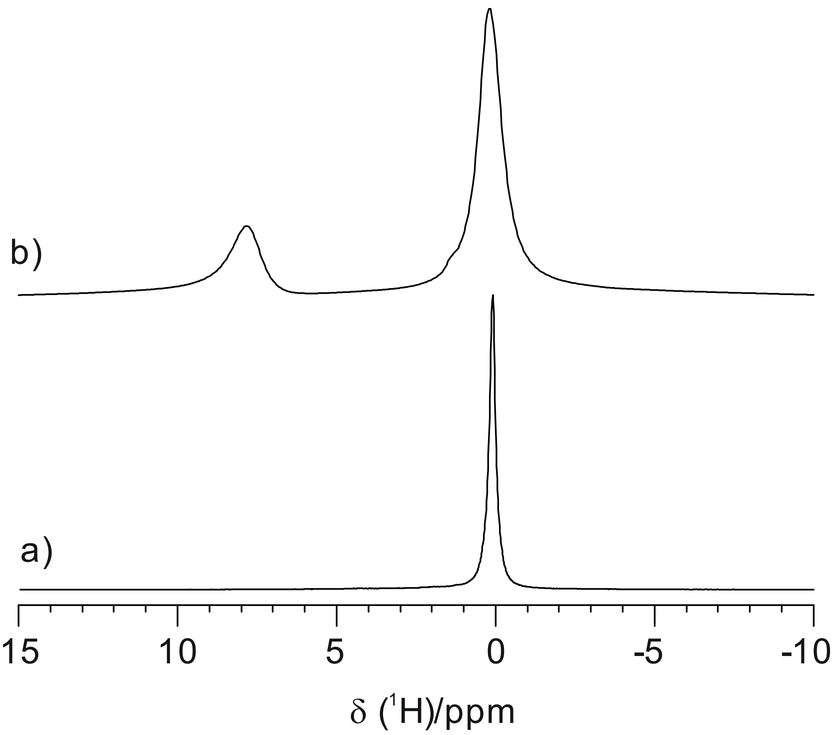

Figure S4. ^{1}H MAS NMR spectra (400 MHz) of a) **1-SiO$_{2\text{-}700}$**, b) **2-SiO$_{2\text{-}700}$**

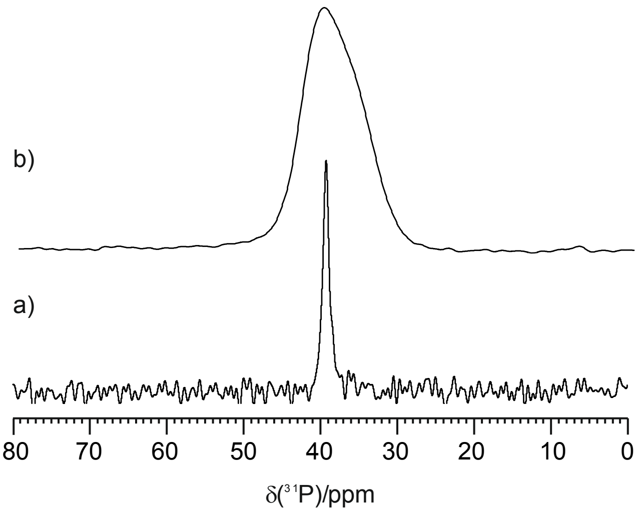

Figure S5. ^{31}P NMR spectrum (161.9 MHz) of a) **2** (C_6D_6, 300 K), b) **2-SiO$_{2\text{-}700}$** (CPMAS)

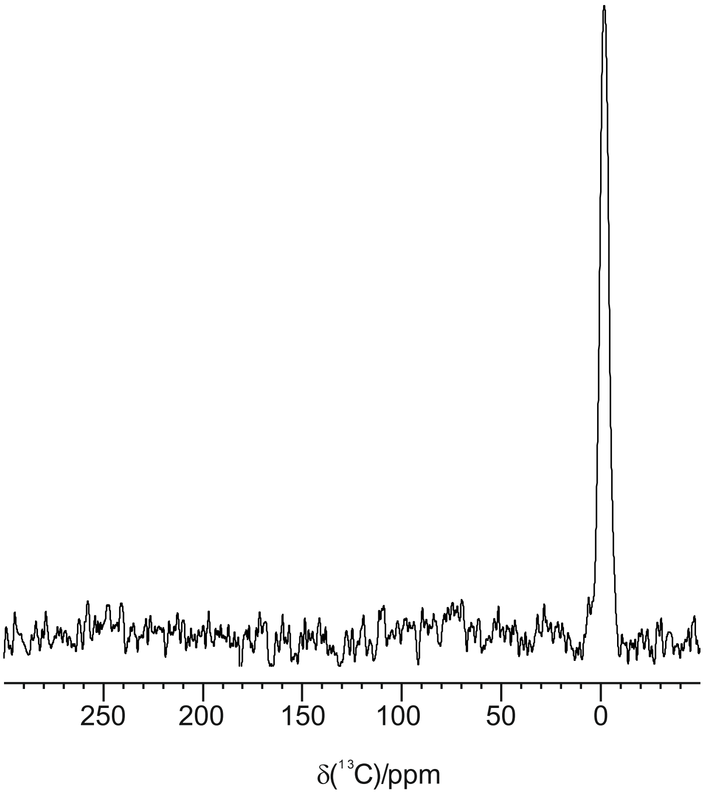

Figure S6. ^{13}C CPMAS NMR spectrum of (100.6 MHz) of **1-SiO$_{2\text{-}700}$**

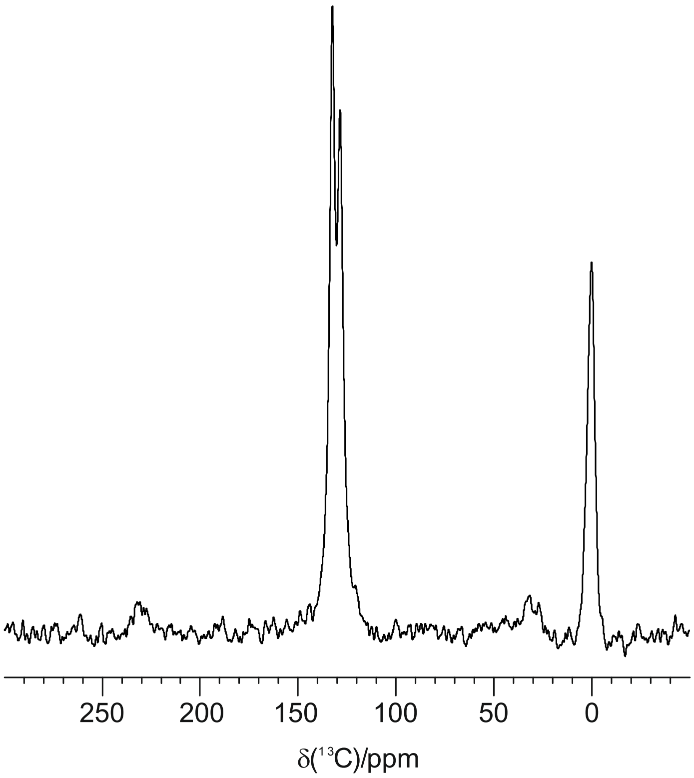

Figure S7. ^{13}C CPMAS NMR spectrum (100.6 MHz) of **2-SiO$_{2\text{-}700}$**

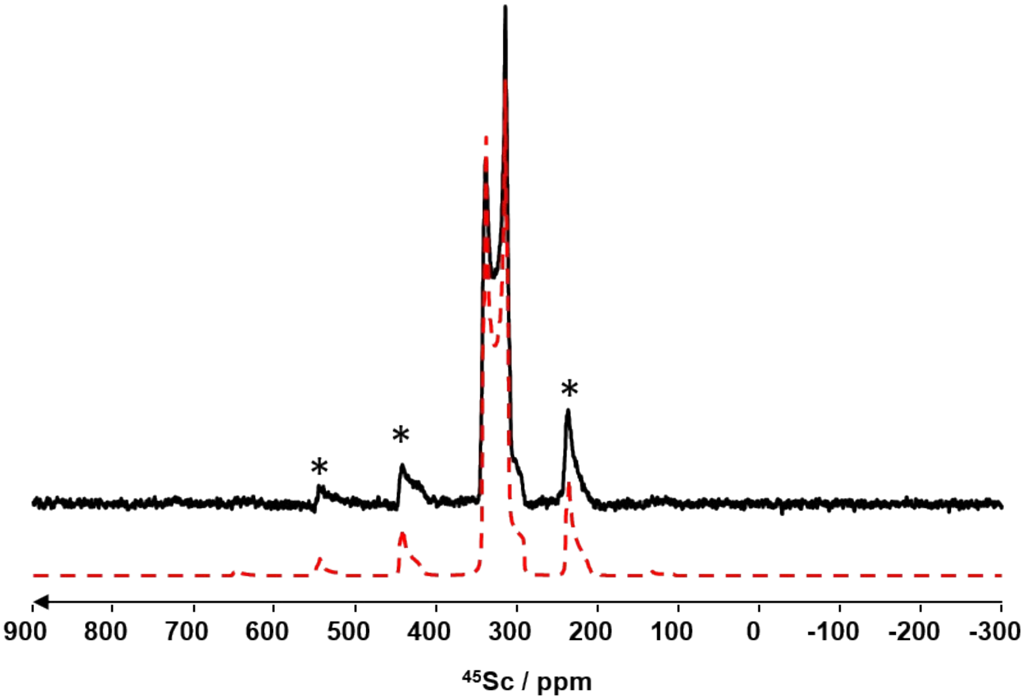

Figure S8.^{45}Sc NMR spectrum of **2** recorded using a Hahn echo experiment at 18.8 T and a spinning speed of 20 kHz. The simulations (red dashed line spectrum) lead to the NMR parameters given in Table 1.

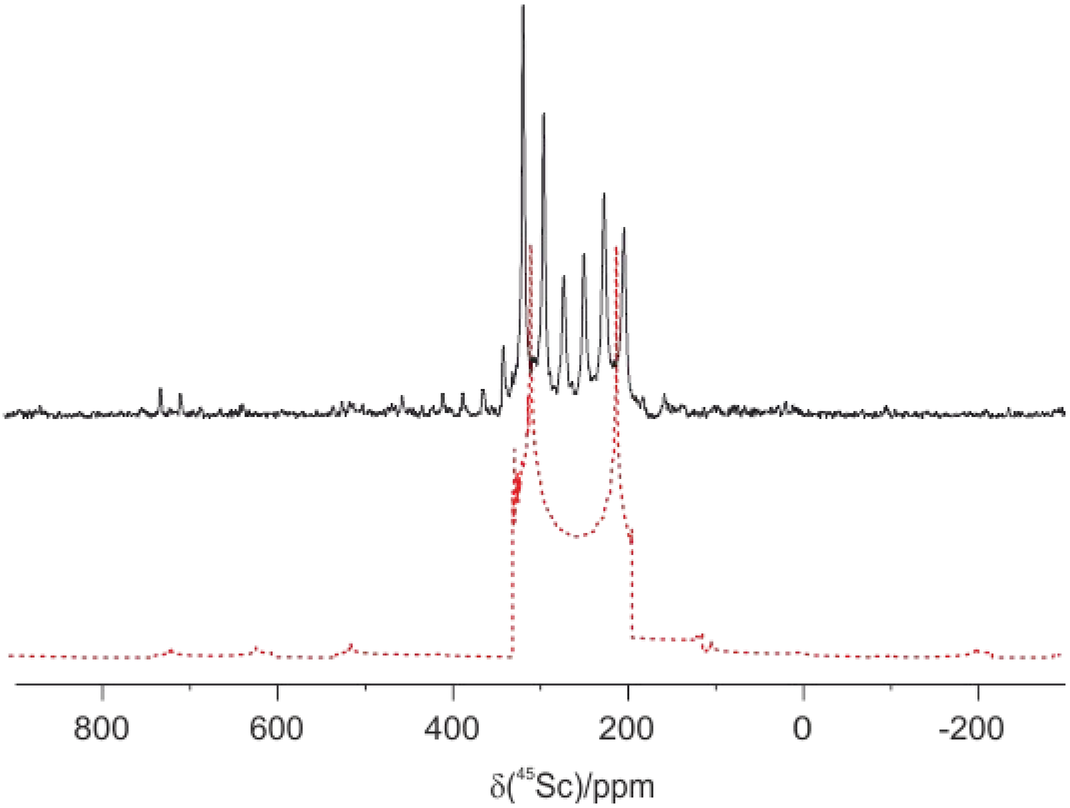

Figure S9.^{45}Sc NMR spectrum of **2** recorded using a QCPMG experiment at 9.4T and a spinning speed of 20 kHz. The simulation (red dashed line spectrum) was done with the NMR parameters given in Table 1.

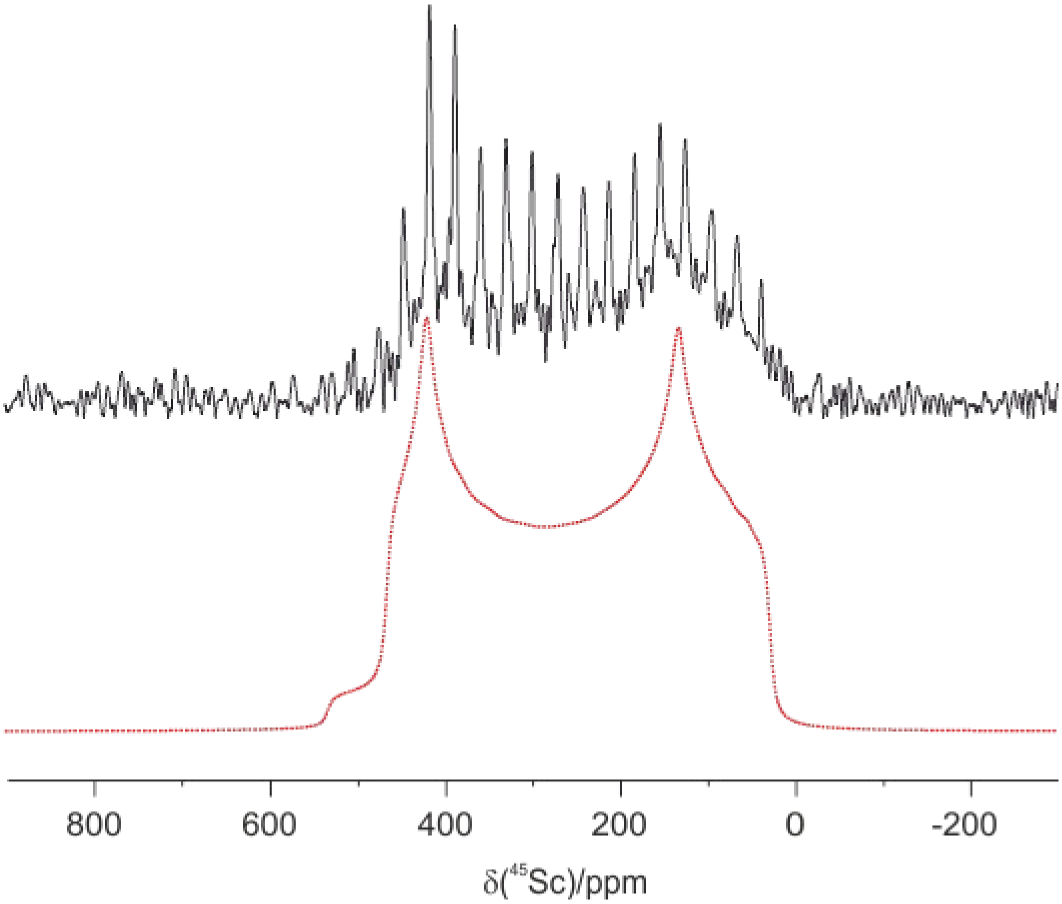

Figure S10. ^{45}Sc NMR spectrum of **2** recorded using a QCPMG experiment at 9.4T under static conditions. The simulation (red dashed line spectrum) was done with the NMR parameters given in Table 1.

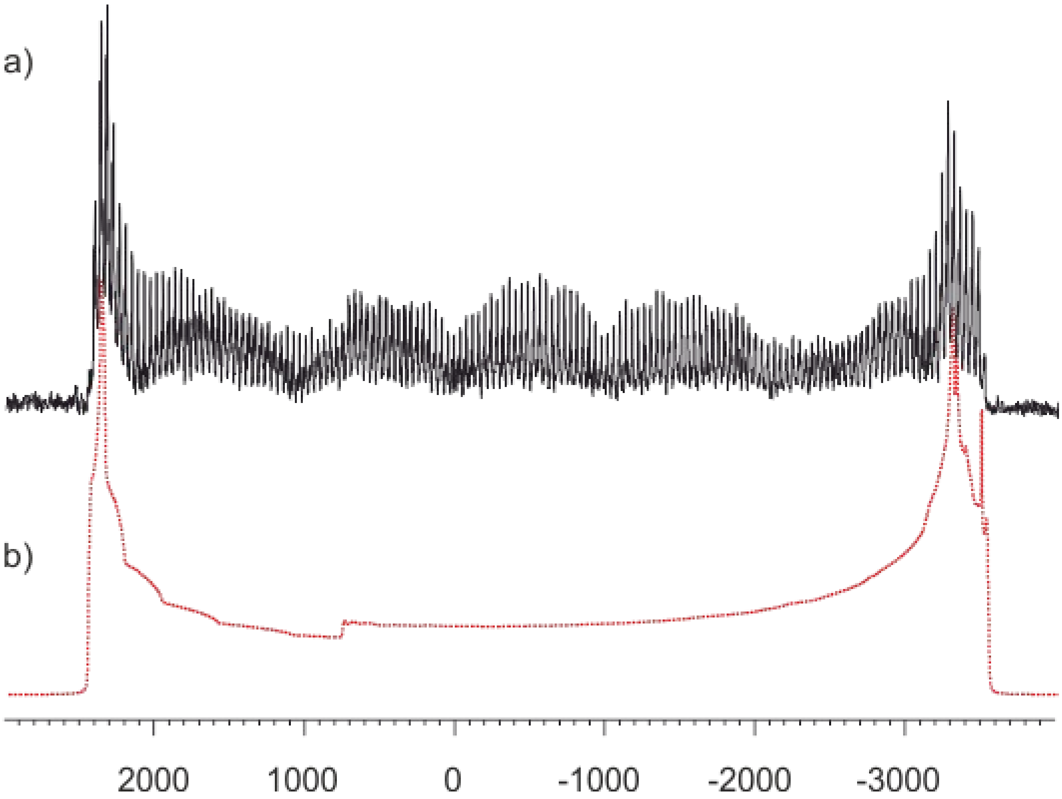

Figure S11.^{45}Sc NMR spectrum of **1** recorded using a QCPMG experiment at 9.4T under static conditions (a). The simulation (red dashed line spectrum) was done with the NMR parameters given in Table 1 (b).

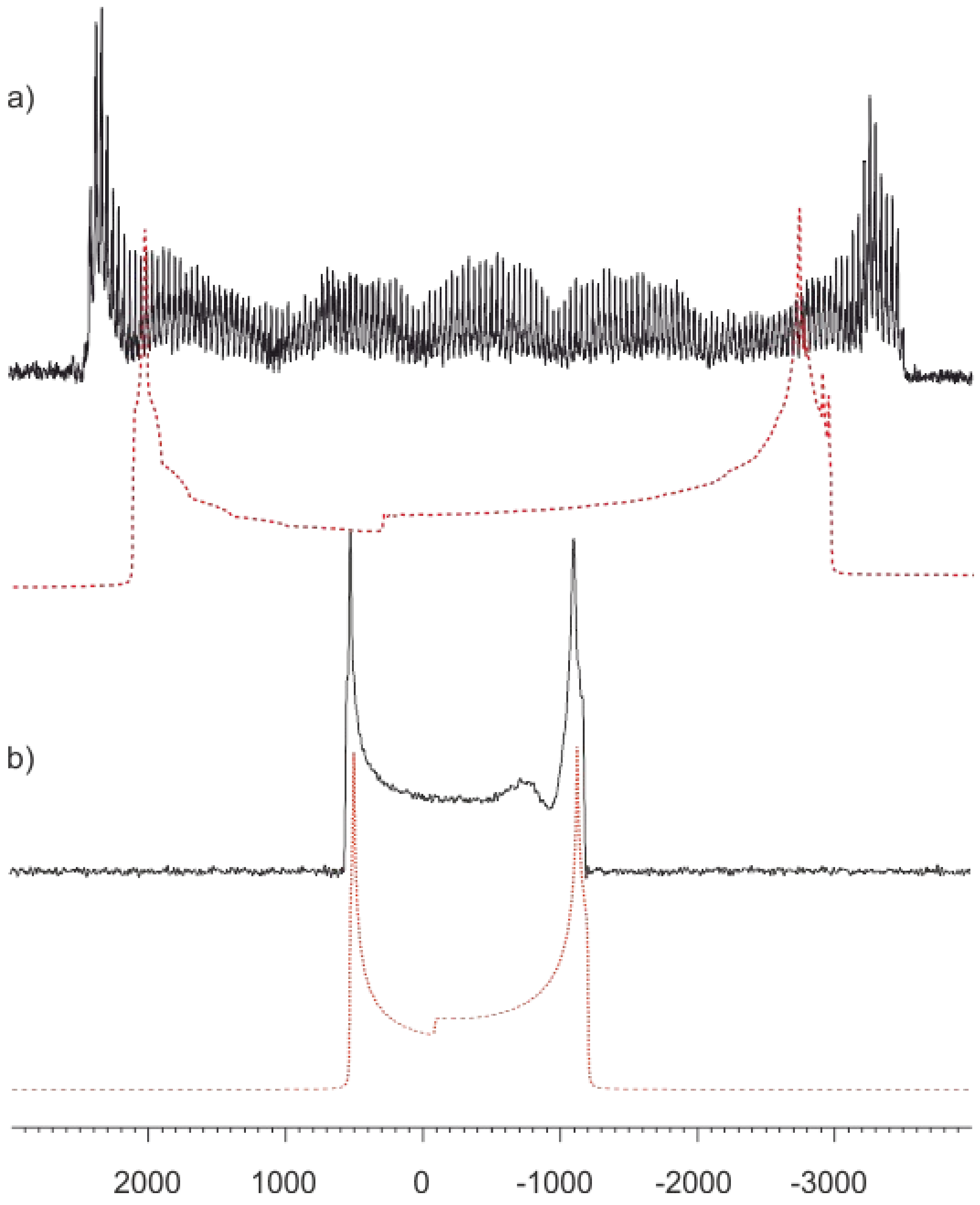

Figure S12.^{45}Sc NMR spectrum of **1** recorded using a QCPMG experiment at 9.4 (a) and at 18.8 T (b) under static conditions. The simulations (red dashed line spectra) use the NMR parameters obtained by best-fit simulation of the spectrum at 18.8 T, considering no CSA contribution.

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