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Supporting Information

Tin Silsesquioxanes as Models for the "Open" Site in Tin-Containing Zeolite Beta

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Supplementary Material

1. Experimental Methods

All glassware was dried at 433 K prior to all syntheses, and purged with argon while cooling. All syntheses, purification procedures, and reaction tests were carried out under argon using standard air- and water-free techniques. Benzene (99.8%, anhydrous, Sigma-Aldrich), hexane (95%, anhydrous, Sigma-Aldrich), dimethyl sulfoxide (DMSO, ≥99.9%, anhydrous, Sigma-Aldrich), toluene (99.8%, anhydrous, Sigma-Aldrich) and acetonitrile (99.8%, anhydrous, Sigma-Aldrich) were used as received. Triethylamine (99.5%, Sigma-Aldrich) was distilled from 3 Å molecular sieves. Tin bis(acetylacetonate) dichloride (98%, Sigma-Aldrich) and chlorotrimethylsilane (≥99%, Sigma-Aldrich) were both used without further purification.

The incompletely condensed cyclohexyl-ligated trisilanol silsesquioxane, **1**, was obtained from Hybrid Plastics. **1** was purified by recrystallization by slow diffusion of acetonitrile into a concentrated solution of THF. Purity of **1** was then confirmed using ^{1}H, ^{13}C, and ^{29}Si.

1.1. Synthesis of 1a and 1b

The methods of synthesis for **1a** and **1b** were adapted from Duchateau et al[1] who alternatively used heptacyclopentyl trisilanol silsesquioxane as a starting material for their complexes.

1a was synthesized by the addition of tin bis(acetylacetonate) dichloride ($Sn(acac)_2Cl_2$) and heptacyclohexyl trisilanol silsesquioxane, **1**, to a dried round bottom flask in stoichiometric quantities, and subsequently dissolved in toluene. A slight excess of triethylamine was then introduced as a scavenger base. The flask was placed in an oil bath at 353 K and allowed to react over night. Triethylamine hydrochloride slowly precipated from solution, and after allowing the reaction to cool, was removed by filtration. The toluene was removed *in vacuo*. Hexane was then added, the solids were allowed to dissolve, and then the solvent was removed *in vacuo* yielding a white powder as a product in quantitative yields.

1b was synthesized by first reacting a stoichiometric quantity of chlorotrimethylsilane with **1** to produce a monosilylated intermediate compound, **1b-i**, as described by Feher et al.[2] The

crude silylated product was purified by fractional recrystallization to remove any undesired di- or tri-silylated species. **1b-i** was then reacted with $Sn(acac)_2Cl_2$ using the method described for **1a** to yield **1b** in quantitative yields.

To ensure that all triethylamine (used as a scavenger base, and reported to be a highly selective catalyst in the conversion of glucose to fructose)[3] and triethylamine hydrochloride were removed from both products, the purified solids were additionally heated to 70 °C and held under vacuum for 12 hours to sublimate any residual triethylamine hydrochloride salt. Characterization of the material demonstrated that neither the $Sn(acac)_2Cl_2$ nor triethylamine hydrochloride salt remained post-reaction.

1.2. Material Characterization

Nuclear magnetic resonance (NMR) spectra of **1a** and **1b** were collected either on a Varian Inova 500 (^{1}H, 499.7; ^{13}C, 125.7 MHz) equipped with a broadband probe or on a Varian Inova 400 (^{29}Si, 79.4; ^{119}Sn, 149.1 MHz). ^{29}Si and ^{119}Sn NMR were referenced to $SiMe_4$ and $SnMe_4$, respectively. Chromium(III) acetylacetonate ($Cr(acac)_3$) was added to samples for ^{29}Si and ^{119}Sn NMR characterization as a shiftless relaxation agent.

1a: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 5.57, 5.56 (s, 2 x C*H*, acac, 2H), 4.76 (s, SiO*H*, 1H), 2.18, 2.12, 2.04, 2.01 (s, 4 x CH_3, acac, 12 H), 1.82 – 1.60 (vbr m, CH_2, cyclohexyl, 35 H), 1.35 – 1.05 (vbr m, CH_2, cyclohexyl, 35 H), 0.80 – 0.64 (vbr m, C*H*, cyclohexyl, 6 H), 0.58 (m, C*H*, cyclohexyl, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 196.94, 196.10, 195.26, 194.76 (4 x *C*=O, acac), 102.39, 102.16 (2 x *C*H, acac), 28.30 – 26.50 (*C*H_2, cyclohexyl), 25.21, 25.18, 24.17, 24.03, 23.83, 23.56, 23.42 (*C*H, cyclohexyl, 1:1:1:1:1:1:1 ratio). ^{29}Si NMR (79.4 MHz, $CDCl_3$, 298 K, 0.02 M $Cr(acac)_3$) δ = -58.37 (*Si*OH), -64.31, -65.83, -67.47, -68.30, -69.14, -70.67 (O_3*Si*C_6H_{11}, 1:1:1:1:1:1:1 ratio). ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 298 K, 0.02 M $Cr(acac)_3$) δ = -729.96.

1b: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 5.55, 5.53 (s, 2 x C*H*, acac, 2H), 2.15, 2.12, 2.01, 2.00 (s, 4 x CH_3, acac, 12 H), 1.85 – 1.59 (vbr m, CH_2, cyclohexyl, 35 H), 1.32-1.10 (vbr m, CH_2, cyclohexyl, 35 H), 0.76 – 0.65 (vbr m, C*H*, cyclohexyl, 5 H), 0.60 (m, C*H*, cyclohexyl, 1 H), 0.45 (m, C*H*, cyclohexyl, 1 H), 0.13 (s, OSi(CH_3)$_3$, 9 H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 298 K) δ = 196.52, 195.37, 194.87, 194.83 (4 x *C*=O, acac), 102.28, 102.10 (2 x *C*H, acac), 28.50 –

26.50 (CH$_2$, cyclohexyl), 25.67, 25.58, 25.43, 25.27, 24.49, 23.59, 23.45 (CH, cyclohexyl, 1:1:1:1:1:1:1 ratio), 2.13 (OSi(CH$_3$)$_3$). ^{29}Si NMR (79.4 MHz, CDCl$_3$, 298 K, 0.02 M Cr(acac)$_3$) δ = 8.84 (s, OSi(CH_3)$_3$, -65.69, -67.33, -67.60, -67.83, -68.31, -70.33, -71.87 (O$_3$$SiC_6H_{11}$, 1:1:1:1:1:1:1 ratio). ^{119}Sn NMR (149.1 MHz, CDCl$_3$, 298 K, 0.02 M Cr(acac)$_3$) δ = -738.01.

2. Glucose Reaction Procedures

Reactions with D-glucose (Sigma-Aldrich, anhydrous, ≥99.5%) were conducted in 10 mL thick-walled glass reactors (VWR) that were heated in a temperature-controlled oil bath placed on top of a digital stirring hot plate (Fisher Scientific). Glucose, **1a**, and **1b** were separately dried under vacuum (<50 mTorr) for at least 12 hours prior to the addition of the anhydrous DMSO and benzene solvents, respectively. Additionally, the glass reactors and stir bars were dried at 433 K for at least 3 hours in an oven, capped with a Teflon septum, and allowed to cool under an argon purge. In a typical reaction, the dried reactors were charged with equivalent volumetric quantities of glucose and catalyst stock solutions to obtain a 6 mL reactor volume. The resultant mixture yielded a 2% (w/w) initial glucose solution, with a Sn/glucose molar ratio of 1:75. Reactors were placed in the oil bath at 353 K, and approximately 125 mg aliquots were extracted every 15 minutes. These reaction aliquots were mixed with 125 mg of a 2% (w/w) aqueous D-mannitol (Sigma-Aldrich, ≥98%) solution, which was used as an internal standard for quantification. To ensure thorough catalyst removal from the aliquot solution prior to quantification, 0.3 mL of H_2O was added, and the solution was filtered using a 0.2 μm PTFE syringe filter.

Reaction aliquots were analyzed by high performance liquid chromatography (HPLC) using an Agilent 1200 system (Agilent) equipped with refractive index (RI) and evaporative light scattering (ELS) detectors. The glucose, fructose, mannose, and mannitol fractions were separated with a Hi-Plex Ca column (6.5 x 300 mm, 8 μm particle size, Agilent) held at 353 K. Ultrapure water was used as the mobile phase at a flow rate of 0.6 mL min^{-1}.

Glucose conversion and product yields were calculated by

$$X_{Gluc}(t) = \frac{n_{Gluc}(t\ =\ 0) - n_{Gluc}(t)}{n_{Gluc}(t\ =\ 0)}\ x\ 100\ [\%]$$

$$Y_i(t) = \frac{n_i(t)}{n_{Gluc}(t\ =\ 0)}\ x\ 100\ [\%]$$

where $X_{gluc}(t)$ is the glucose conversion at time t; $Y_i(t)$ is the yield of product i at time t; $n_{gluc}(t = 0)$ is the initial moles of glucose in the reactor; and $n_i(t)$ is the moles of product i at time t.

Reactions performed using labeled ^{13}C glucose at the C_1 position (Cambridge Isotope Laboratories, 1-^{13}C D-glucose, 98-99%), glucose enriched with deuterium at the C_2 position of glucose (Omicron Biochemicals, D-[2-D]-glucose, 98% D), and doubly labeled glucose with deuterium at the C_2 position and labeled ^{13}C glucose at the C_1 position (Omicron Biochemicals, D-[1-^{13}C;2-D]-glucose, 99% 13C, 98% D) were performed utilizing the same procedures outlined for D-glucose. Generally, 10 % (w/w) initial glucose solutions were used for isotopic labeling experiments. All other conditions remain equivalent as described for D-glucose. However, these reactions were quenched in cold water after a set duration. To separate the catalyst from the reaction solution, approximately 6 mL of ultrapure water was added and the resultant biphasic solution was filtered. The solvent of the catalyst-free fraction was then removed *in vacuo*. The recovered solids were then dissolved in deuterium oxide and analyzed using ^1H (64 scans) and ^{13}C (2048 scans) NMR. These NMR spectra were referenced to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS).

3. Examination of the structural integrity of 1a and 1b

Variable-temperature (VT) NMR experiments were used to determine how the structures of the catalysts were affected under reaction conditions. In a typical experiment, a 2% (w/w) glucose solution (1:1 volumetric ratio of benzene and DMSO) was mixed with each catalyst (maintaining a 25:1 glucose to Sn molar ratio) in an NMR tube. Due to a number of overlapping peaks in the ^1H and ^{13}C NMR spectra amongst the catalysts, glucose, and reaction products, only ^{29}Si and ^{119}Sn spectra were collected to evaluate the structure of the catalyst. In conducting the VT NMR experiments, the system was allowed to equilibrate at a given temperature in the NMR for 10 minutes, and then a spectrum was obtained (256 scans for each nuclei). Due to line broadening effects, ^{29}Si spectra were only obtained at 278 and 353 K. Figures S1 – S3 depict the results of these experiments performed with **1b**.

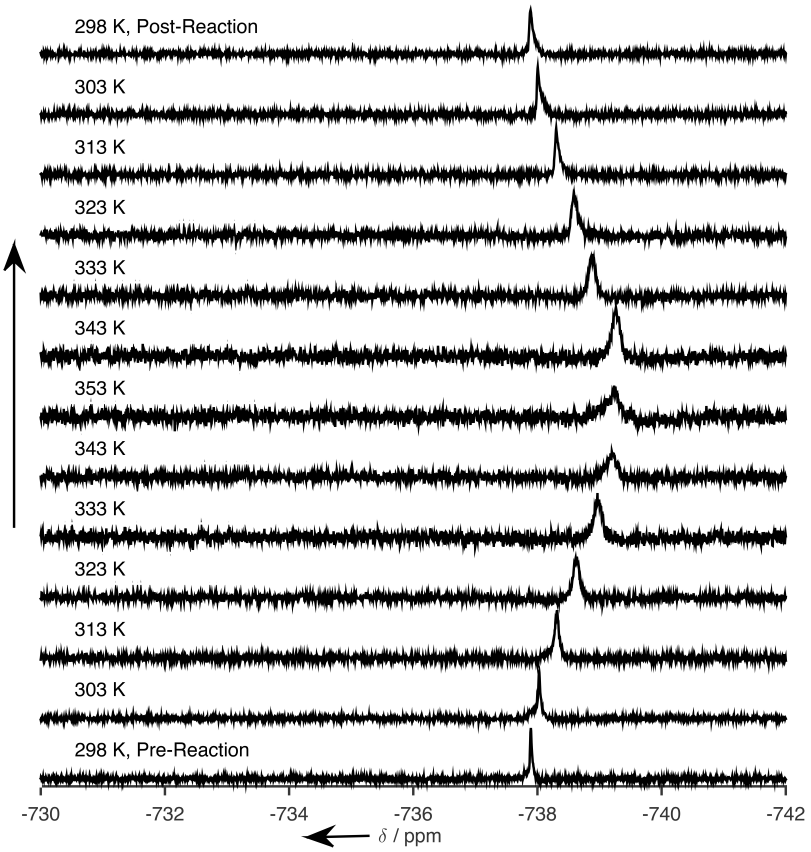

Figure S1: Variable-temperature ^{119}Sn NMR spectra for **1b** collected between 298 K and 353 K in 10 K increments.

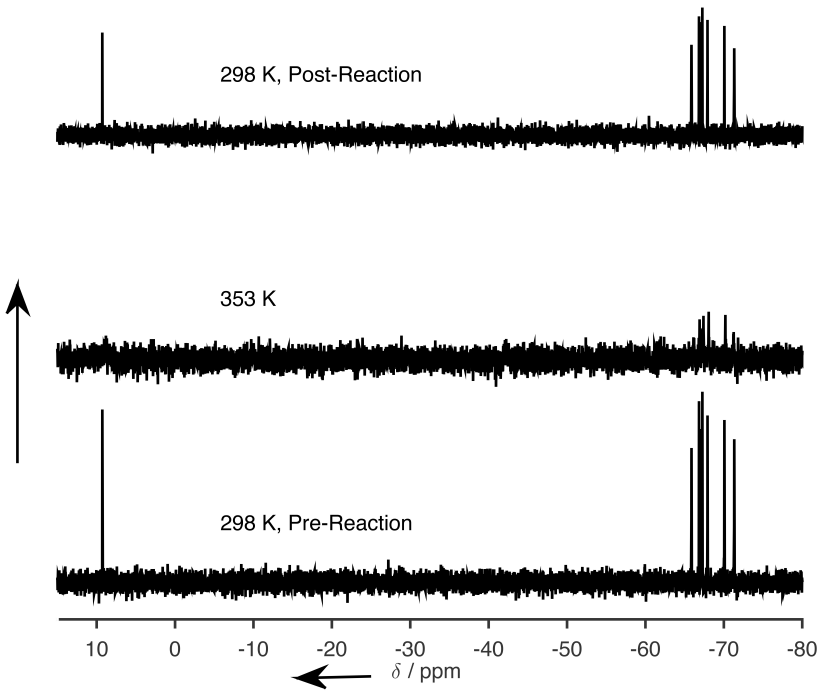

Figure S2: Variable-temperature ^{29}Si NMR spectra for **1b** collected at 298 K prior to heating, at 353 K, then again at 298 K after cooling the sample.

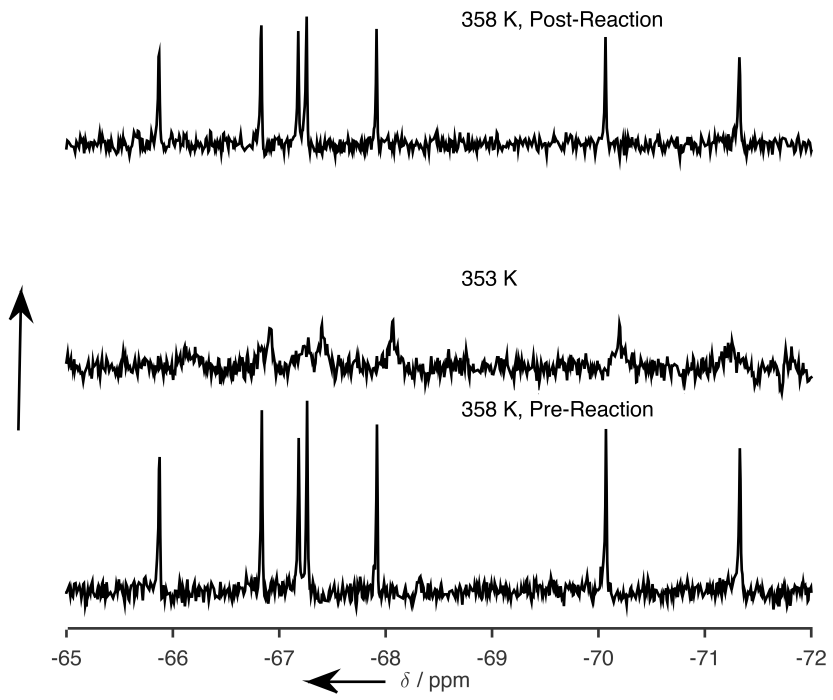

Figure S3: Enhanced view of the variable-temperature ^{29}Si NMR spectra for **1b** collected at 298 K prior to heating, at 353 K, then again at 298 K after cooling the sample.

These data demonstrate that there is no perturbation of the bulk geometry or local electronic structure at the Sn site, strongly suggesting that under the reaction conditions used the Sn-OSi bonds are not hydrolyzed to irreversibly form a free tin species and **1**.

The hydrogen bonding capacity of the silanol moiety on **1a** complicates the analysis demonstrated with **1b**, but generally leads to the same conclusion. The ^{119}Sn spectrum at 353 K is shown in Figure S4. Compared to **1a** in $CDCl_3$, there is a noticeable shift upfield in the ^{119}Sn spectra (no such shift is observed with **1b**). This indicates that the Sn center has become more shielded, perhaps due to a small interaction between the electron rich silanol group and the Sn. This peak does not correspond to a free tin species. The ^{29}Si spectrum collected after cooling the sample is additionally shown in Figure S4. This confirms that a shift in the geometry of the catalyst occurs, however, none of the peaks corresponding to the starting material are present. This strongly suggests that hydrolysis of the material has not occurred.[2] The implied geometry of this complex is not in agreement with typical dimer formation due to the interaction between two silanol groups. Rather, the 3:1:1:2 relative peak ratio is suggestive of a complex of higher

symmetry that may perhaps be induced by an interaction between the silanol group and Sn. The results obtained from the VT NMR experiments performed with **1b** indicate that the Sn-OSi bond are not broken under reaction conditions. Generally, the substitution of the TMS moiety with a hydroxyl group to form **1a** would not be expected to destabilize these bonds, further indicating that **1a** simply rearranges under reaction conditions.

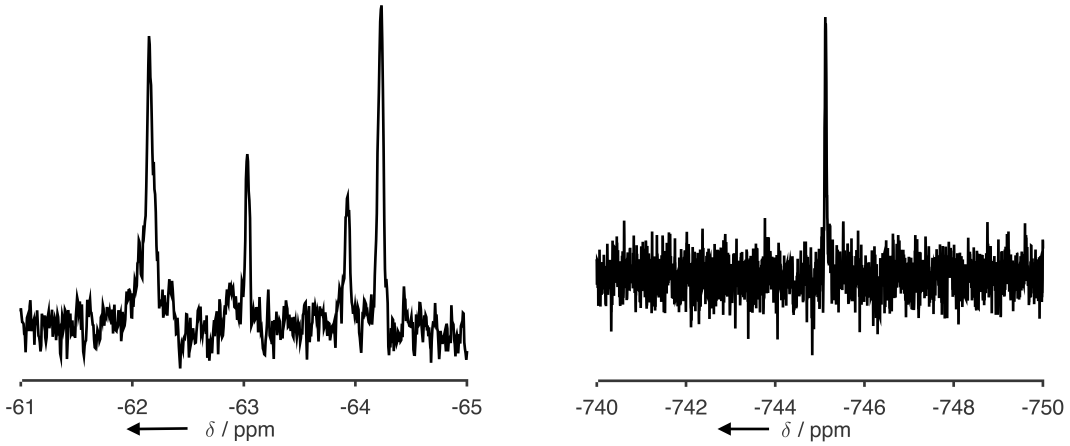

Figure S4: ^{29}Si NMR spectrum obtained at 298 K post-reaction (left) and ^{119}Sn (right) at 353 K of **1a** under reaction conditions.

In general, for both **1a** and **1b,** the Sn-OSi bonds appear to remain intact throughout the reaction conditions used throughout this study. Interestingly, the silanol moiety on **1a** appears to induce a geometric change in the catalyst structure upon heating the reaction solution, most likely through an interaction with the Sn site.

4. Isotopic Labeling Experiments

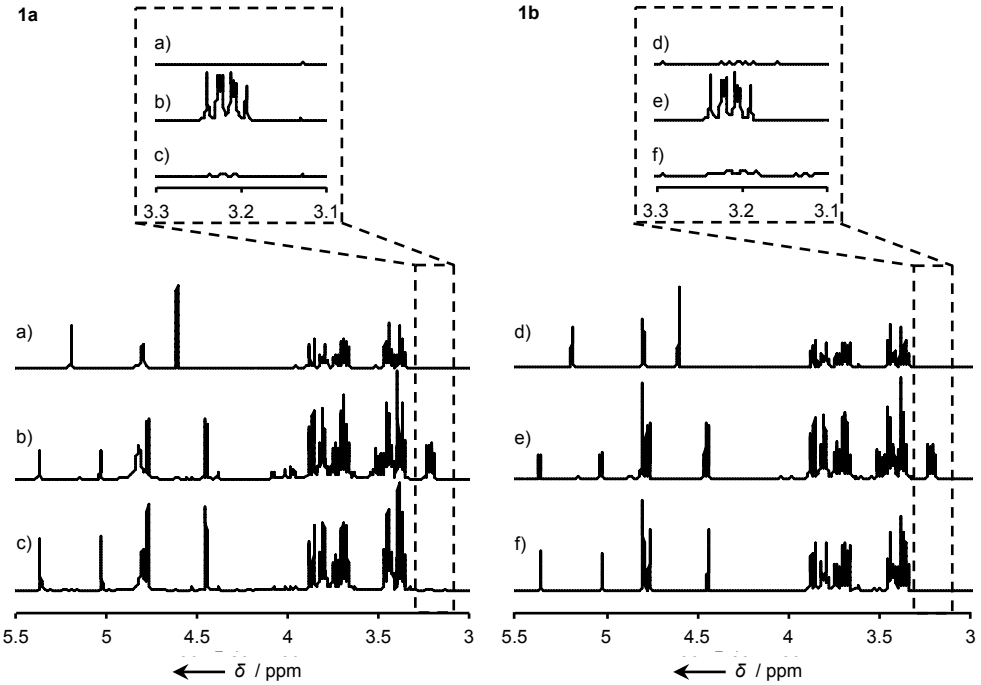

Figure S5: ^{1}H NMR spectra of the reactant and product solutions in D_2O obtained after reacting a) 2-^{2}H glucose, b) 1-^{13}C glucose, and c) 2-^{2}H; 1-^{13}C glucose with **1a**; d) 2-^{2}H glucose, e) 1-^{13}C glucose, and f) 2-^{2}H; 1-^{13}C glucose with **1b**.

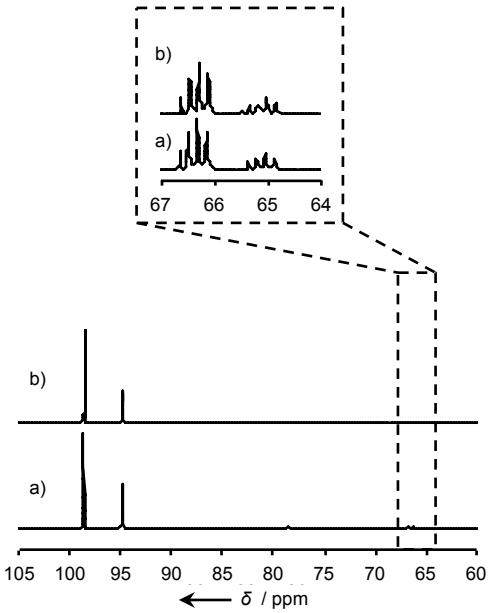

Figure S6: ^{13}C NMR spectra of the reactant and product solutions in D_2O obtained after reaction with a 10% (w/w) 2-^{2}H;1-^{13}C glucose with Sn-Beta in a) H_2O and b) D_2O after 1 hour and 353 K.

5. References

[1] R. Duchateau, T. W. Dijkstra, J. R. Severn, R. A. van Santen, I. V. Korobkov, *Dalton Trans.* **2004**, 2677–82.

[2] F. J. Feher, D. A. Newman, J. F. Walzer, *J. Am. Chem. Soc.* **1989**, *111*, 1741–1748.

[3] C. Liu, J. M. Carraher, J. L. Swedberg, C. R. Herndon, C. N. Fleitman, J.-P. Tessonnier, *ACS Catal.* **2014**, *4*, 4295–4298.