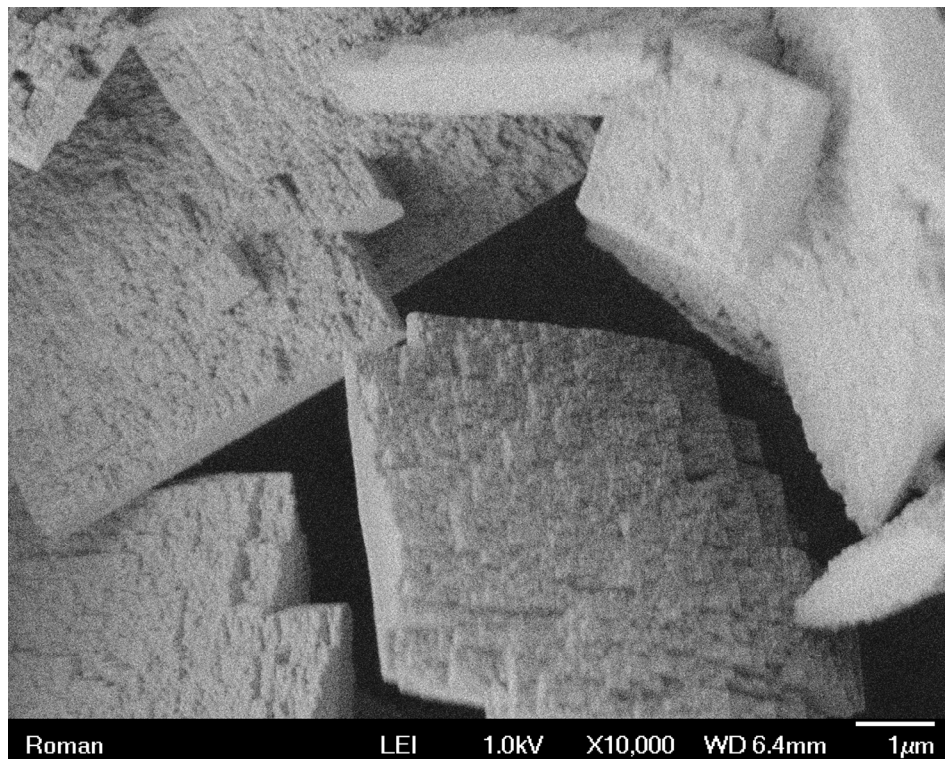


Dynamic nuclear polarization NMR enables the analysis of Sn-Beta zeolite prepared with natural abundance ^{119}Sn precursors

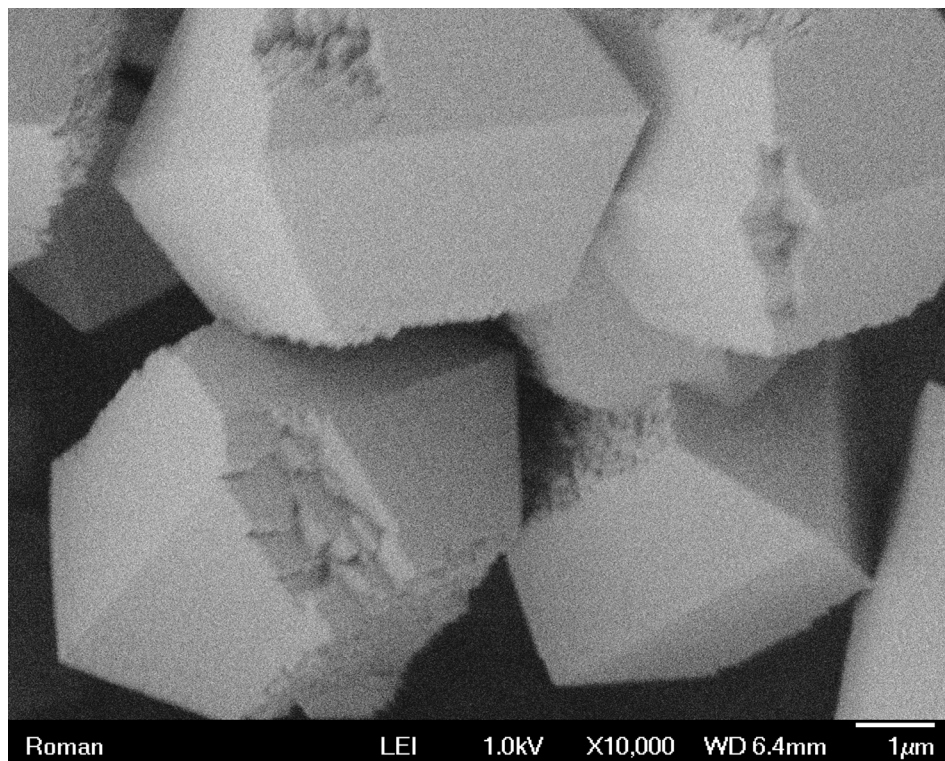
William R. Gunther,^{†,#} Vladimir K. Michaelis,^{‡,#} Marc A. Caporini,[§] Robert G. Griffin,[‡] and Yuriy Román-Leshkov^{†,*}

[†]Department of Chemical Engineering, [‡]Department of Chemistry and [‡]Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

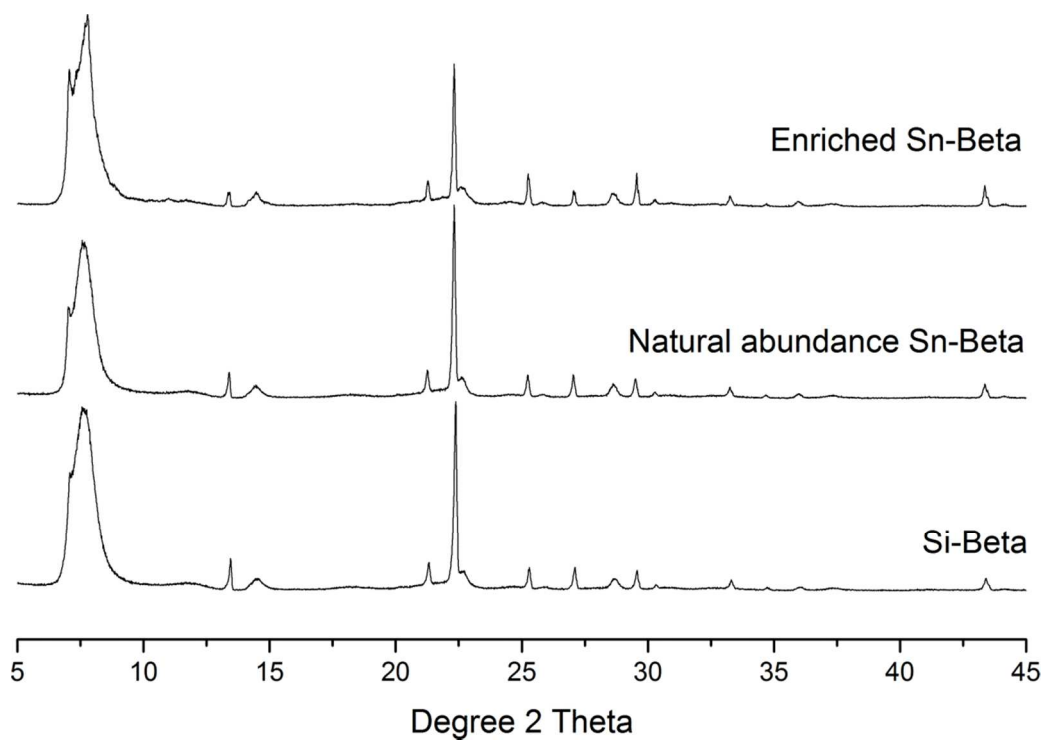
[§]Bruker BioSpin Corporation, Billerica, Massachusetts 01821, United States



Supplementary Figure S1. Scanning Electron Microscopy image of enriched Sn-Beta illustrating crystal dimensions over which polarization must diffuse. Note the crystal size may be much smaller than the aggregates.



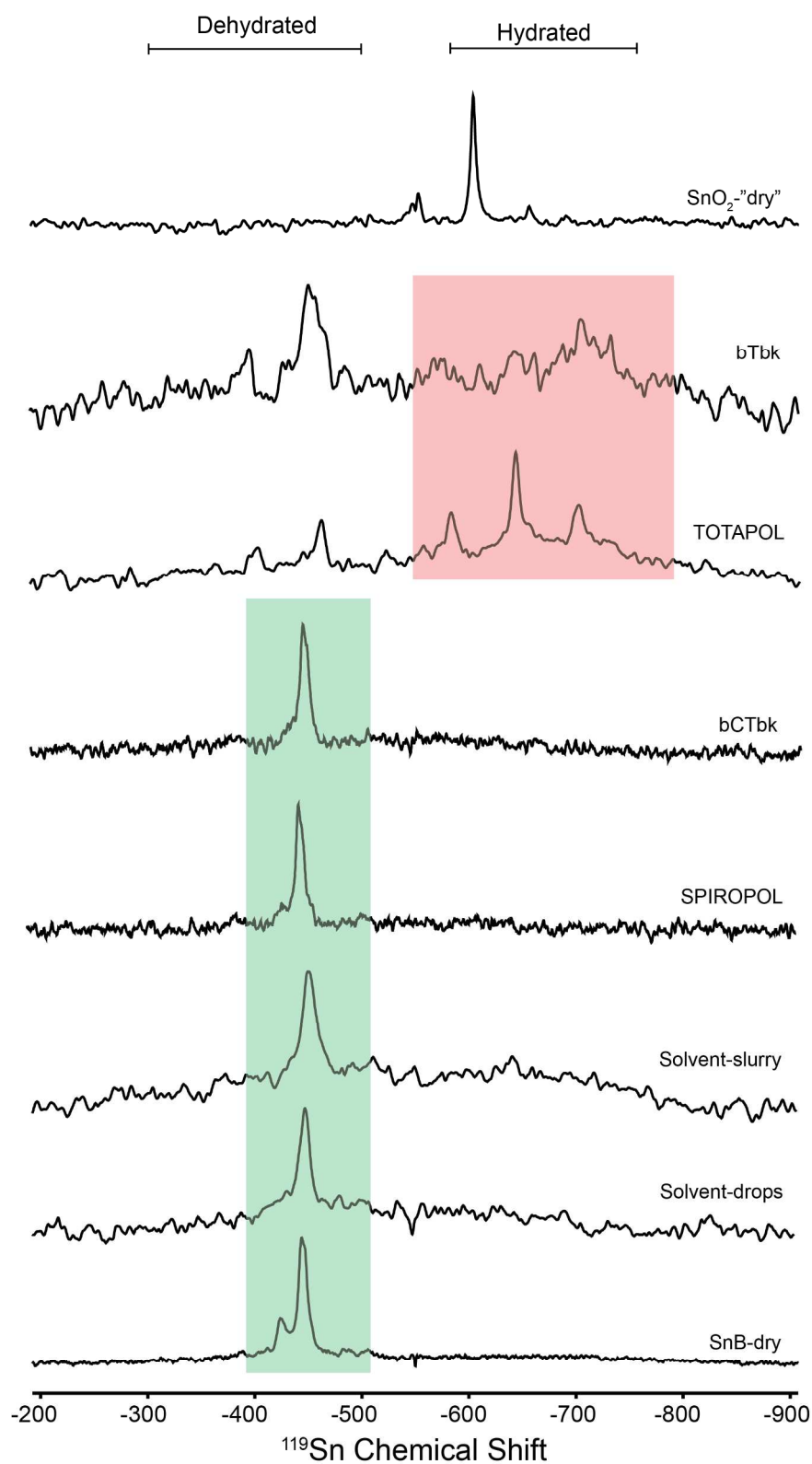
Supplementary Figure S2. Scanning Electron Microscopy (SEM) images of natural abundance Sn-Beta showing zeolite crystal dimensions.



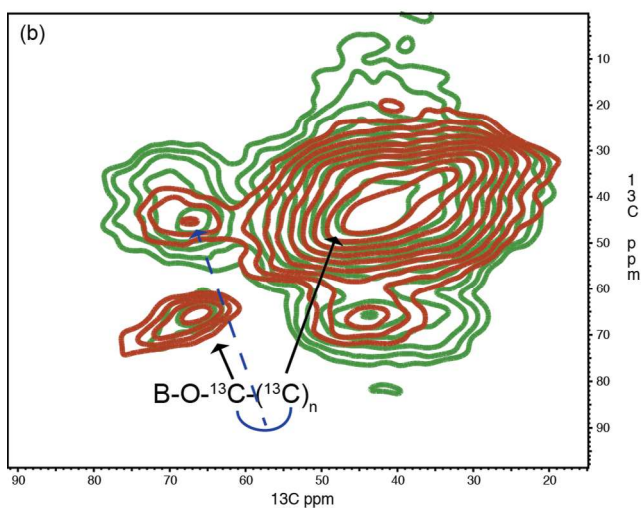
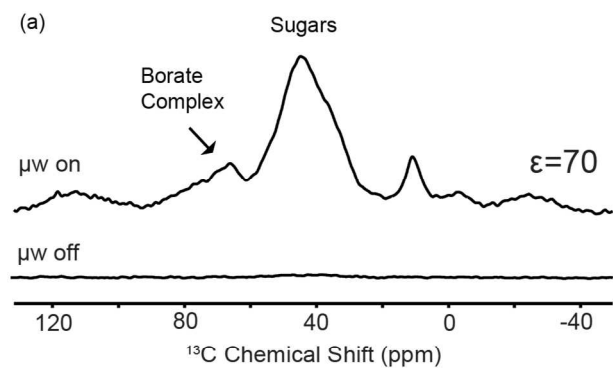
Supplementary Figure S3. Powder X-ray diffraction patterns of Sn-Beta zeolites.

Supplementary Table S1. Metal content calculated from ICP measurements and pore volumes of Sn-Beta samples.

Material	Si/Sn	Total pore volume [cm ³ /g]	Micropore volume [cm ³ /g]
Enriched Sn-Beta	102	0.663	0.208
Natural abundance Sn-Beta	89	0.393	0.212



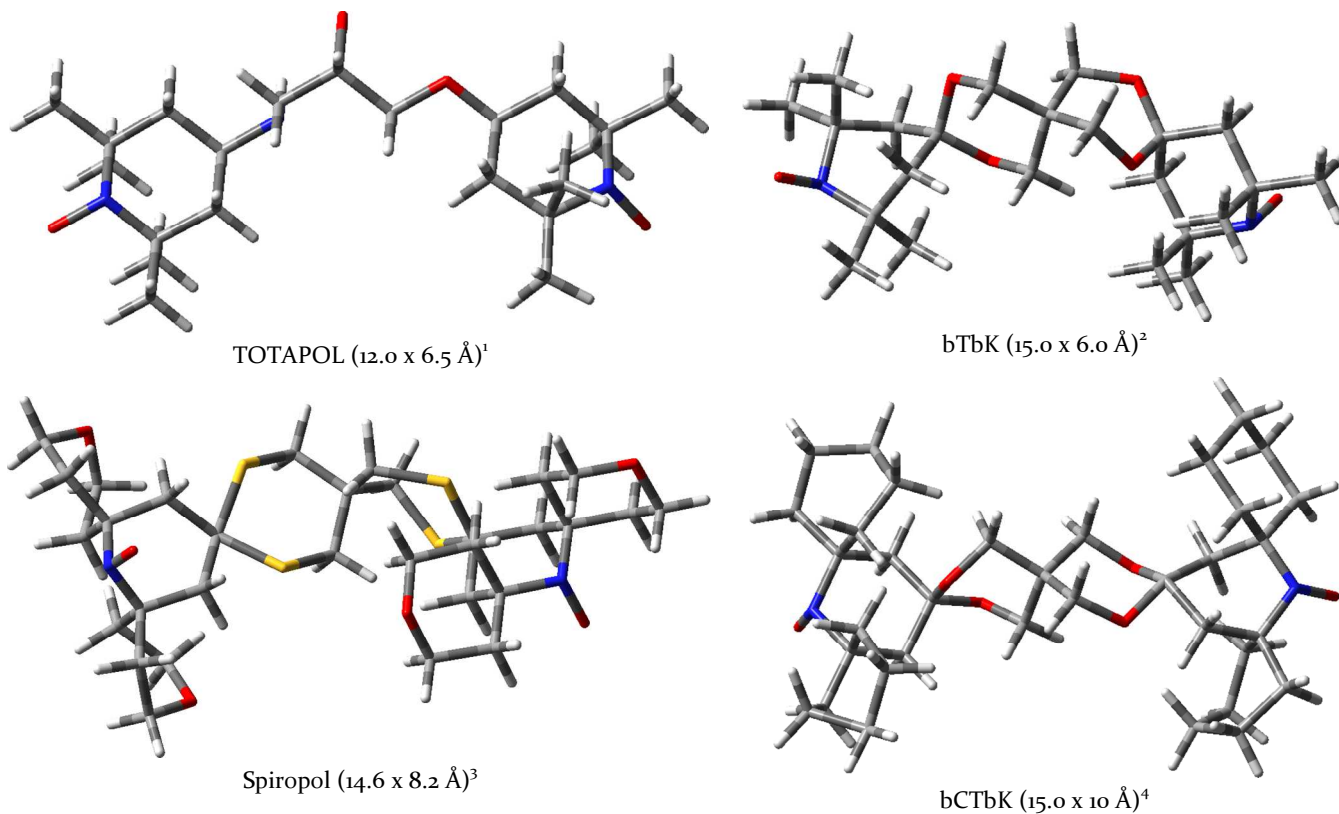
Supplementary Figure S4. ¹¹⁹Sn MAS NMR spectra (8.4 T) of ¹¹⁹Sn-enriched Sn-Beta obtained without DNP (i.e., no microwaves and a sample temperature of 300 K) showing the zeolite remains dehydrated and the solvent/radical combination does not interfere with the Sn site (green) or it does interfere with the Sn site (red). All spectra shown were acquired using a 4 mm ZrO₂ rotor (80 ul fill volume); experimental times varied between 48 and 96 hours.



(c)

Radical	Solvent	ϵ
bTbk	neat-TCE	3
TOTAPOL	neat-TCE	2
TOTAPOL	DMSO/D ₂ O/H ₂ O	70
TOTAPOL	<i>d</i> ₈ -glycerol/D ₂ O/H ₂ O	100

Supplementary Figure S5. ^{13}C DNP NMR data acquired at 212 MHz / 140 GHz on a glucose Sn-Beta zeolite with borate salt using 8 W of microwave power at 85 K. (a) $^{13}\text{C}\{^1\text{H}\}$ microwave on and off spectrum using 10 mM TOTAPOL and DMSO/D₂O/H₂O glassing/cryoprotecting agent, (b) ^{13}C - ^{13}C Proton-Driven Spin Diffusion (PDS) correlation experiment acquired using 5 (rust) and 40 (green) ms of mixing and (c) enhancement results using 10 mM of bTbk or TOTAPOL in various glassing agents.



Supplementary Figure S6. 3-D structural representations and dimensions of the biradicals used in this study. The atoms are colored in the following manner: blue for nitrogen, red for oxygen, yellow for sulfur, grey for carbon, and white for hydrogen.

Catalyst Synthesis

Sn-Beta was synthesized as follows: 26.735 g of aqueous tetraethylammonium hydroxide (Sigma-Aldrich, 35% (w/w)) and 24.069 g of tetraethylorthosilicate (Sigma-Aldrich, 99% (w/w)) were added to a Teflon® (Polytetrafluoroethylene, [PTFE]) dish, which was magnetically stirred at room temperature for 90 min and then cooled in an ice bath. Then, 0.261 g of tin (II) chloride dihydrate (Sigma-Aldrich, 98% (w/w)) dissolved in 15 g of cold deionized water (DI H₂O) was added dropwise. Sn(II) which oxidizes to Sn(IV) in water was used in place of SnCl₄·5H₂O and has resulted in Sn-Beta consistently free of extraframework SnO₂.⁵ The solution was left uncovered on a stir plate for 10 h to reach a total mass of 35 g. Next, 2.600 g of aqueous hydrofluoric acid (Sigma-Aldrich, 48% (w/w)) was added dropwise and the mixture was homogenized using a PTFE spatula, resulting in a thick gel. Then, 0.358 g of previously-made Sn-Beta was seeded into the mixture, which was allowed to evaporate to 33.776 g, which corresponds to a final molar composition of SiO₂/0.01 SnCl₂/0.55 TEAOH/0.54 HF/7.52 H₂O. The thick paste was transferred to a 45 ml PTFE-lined stainless steel autoclave and heated to 413 K for 40 days under static conditions. The solids were recovered by filtration, washed with DI H₂O, dried at 373 K and calcined at 853 K for 10 h with a 1 K min⁻¹ ramp and 1 h stops at 423 and 623 K, leading to an overall inorganic oxide yield of 80–90%. Enriched samples were prepared with 82% ¹¹⁹SnCl₂. We note that the resulting samples have been used in isomerization/epimerization reactivity studies and show identical results to those obtained with a zeolite prepared under identical conditions but using a Sn(IV) salt.⁶ This confirms that the Sn(II) atoms oxidize to Sn(IV) during synthesis and are tetrahedrally incorporated into the zeolite framework.

Zeolite Characterization

Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 diffractometer with Cu K α radiation. Ultraviolet-visible (UV-vis) measurements were recorded using a Varian Cary 5000 UV-vis-NIR spectrometer with a diffuse reflectance cell after calcination without subsequent drying. The ultraviolet-visible diffuse reflectance spectrum of the calcined sample shows the presence of a unique band at 200 nm, which has been associated with Sn tetrahedrally coordinated into the zeolite framework. Sn content was measured using a Horiba Jobin Yvon ACTIVA-S ICP-AES. Catalyst samples were dissolved in a few drops of 48% HF and diluted in 2% nitric acid after evaporation of the HF. SEM spectra were recorded on a JEOL 6700F at an electron high tension of 1 kV. Nitrogen adsorption/desorption experiments were performed on a Quantachrome Autosorb iQ apparatus. Micropore volume was measured using a P/Po of 0.01. X-band EPR was performed at 90 K on SPIROPOL and bCTbk over 24 hours; no evidence of Sn-radical reactivity was observed.

DNP Sample Preparation

In a typical preparation, 100 mg of zeolite was dried under vacuum at 473K and transferred into a glovebox. The zeolite powder was prepacked into 3.2 mm sapphire rotors. Small aliquots of 10 mM biradical (i.e. bTbk, TOTAPOL, SPIROPOL and bCTbk) in 1,1,2,2-tetrachloroethane (TCE) were added to the rotor of either dry (packed under N₂ atmosphere) or wet (in-air) Sn-Beta zeolites using a glass Hamilton syringe. The TCE solution was prepared outside the glovebox and without special anhydrous treatment. The hydrophobic zeolite readily adsorbs TCE as seen by the slight contraction of the sample volume. Note that although incipient wetness impregnation methods are typically used to analyze porous materials, the highest enhancements observed in this study involved a slurry. Thus, in the present study, there does not appear to be a tradeoff between sample volume and radical solution. When treating the sample, we ensured that the whole sample contained in the rotor was exposed to solvent. Full solvation was easily observed by watching the solvent penetrate down the transparent sapphire rotor. Zeolites readily adsorb liquid and we note that the final state of the sample was paste-like. To ensure full wetting of the zeolite with this methodology, we performed three different control experiments to capture potential irregularities in radical distribution throughout the sample: 1) we allowed the solvent to penetrate the sample contained in the rotor by dripping the solvent/radical mixture with a pipette without further disruption (this is the standard method used for all experiments in this work); 2) we thoroughly mixed the zeolite and the solvent/radical mixture in a mortar and pestle and then packed the rotor; and 3) we introduced the solvent/radical mixture directly into the rotor and stirred the sample with a small spatula to enhance the wetting/mixing process. Analyzing these three samples, we noticed virtually identical behavior in terms of relaxation and enhancements for all samples. Samples were sealed inside the rotors using silicone plugs and hydrated samples were exposed to ambient conditions prior to adding the radical solution. Centrifugation provided a means to speed up the process. Identical protocols were carried out for TOTAPOL, bTbk, Spiropol and bCTbk. For the ¹³C experiments samples were ground in an agate mortar and pestle.

DNP MAS NMR

¹¹⁹Sn{¹H} DNP MAS NMR experiments were performed on a 9.4 T Bruker Avance III DNP NMR spectrometer equipped with a 263 GHz gyrotron delivering high power microwaves to the sample.⁷ Experimental data were recorded using a 3.2 mm triple resonance (HXY) MAS probe doubly tuned to ¹H ($\nu_L = 400$ MHz) and ¹¹⁹Sn ($\nu_L = 150$ MHz). The ¹H field position was set to the maximum field position for bTbk, bCTbk and TOTAPOL and shifted by ~ 50 kHz for SPIROPOL. All DNP NMR data were acquired under MAS, $\omega_{r/2\pi}$ of 10,000 (3) Hz, a sample temperature of T = 100 K, a recycle delay of $1.3 \times T_B^3$ and between 512 and 20,480 co-added transients. ¹¹⁹Sn{¹H} cross-polarization MAS experiments were acquired using a mixing time of 2 or 6 ms for the hydrated and dehydrated samples, respectively. Data were acquired using high power ¹H ($\omega_1/2\pi = 71$ kHz) decoupling using SPINAL-64, the Hartmann-Hahn match condition was optimized with $\omega_1/2\pi = 70$ kHz for ¹¹⁹Sn and placing a ramp on ¹H's. Spectra were referenced with respect to tin oxide (SnO₂, -604.3 ppm) at room temperature (T = 298 K) and cross-polarization was

initially setup on triphenyl tin chloride in TCE/bCTbk at 100 K ($\epsilon = 20$). Contact times were optimized for the respective Sn-Beta samples.

$^{13}\text{C}\{^1\text{H}\}$ DNP MAS NMR experiments were performed on a home-built spectrometer (courtesy of Dr. David Ruben, FBML, MIT), consisting of a 212 MHz (^1H , 5 T) NMR magnet and a 140.6 GHz gyrotron generating high-power microwaves up to 14 W.⁴ Spectra were recorded on a home-built cryogenic 4 mm quadrupole resonance (^1H , ^{13}C , ^{15}N & e^-) DNP NMR probe equipped with a Kel-F stator (*Revolution NMR*, Fort Collins, CO). Microwaves are guided to the sample via a circular overmoded waveguide whose inner surface has been corrugated to reduce mode conversion and ohmic losses. Sample temperatures were maintained at 85 (± 1) K, with a spinning frequency, $\omega_r/2\pi = 4,500$ (2) Hz. $^{13}\text{C}\{^1\text{H}\}$ Cross Polarization (CP) and Proton-Driven Spin Diffusion (PDS) experiments were acquired using a 1.5 ms contact time. A series of PDS mixing times were collected ranging from 5 to 40 ms with 64 increments. High-power TPPM proton decoupling (^1H $\omega_r/2\pi = 100$ kHz) was used during acquisition. Buildup times (T_B) were determined using a saturation recovery experiment, recycle delay was chosen as $T_B \times 1.3$, yielding optimum sensitivity per unit of time. Microwave power was kept constant at 8 W using a PID control interfaced within Labview. ^1H cross-effect conditions were optimized for bTbk and TOTAPOL by sweeping the main NMR field using a ± 750 Gauss sweep coil. Samples were contained in 4 mm sapphire rotors equipped with a Vespel drive tip and Kel-F spacer using either neat-TCE, 60/30/10 v/v d_8 -glycerol/ $\text{D}_2\text{O}/\text{H}_2\text{O}$ or 60/30/10 DMSO/ $\text{D}_2\text{O}/\text{H}_2\text{O}$.

^{119}Sn MAS NMR

Magic-angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed on a custom designed spectrometer (courtesy of D. J. Ruben, Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology) operating at 360 MHz (^1H , 8.4 T). The spectrometer was equipped with either a double resonance homebuilt (FBML-MIT) or a triple resonance Varian-Chemagnetics probe (Palo Alto, CA) which were singly and doubly tuned to ^{119}Sn and $^{119}\text{Sn}/^1\text{H}$, respectively. Powdered samples were packed into 4 mm (80 μl , fill volume) outer diameter ZrO_2 rotors equipped with Vespel drive- and top-caps. Top-caps were equipped with rubber O-ring seals, inhibiting water contamination within the sample (*Revolution NMR*, Fort Collins, CO) and solvent evaporation over the experiment. Dehydrated enriched ^{119}Sn , Sn-Beta samples were prepared by heating to 473 K under a 0.1 mbar vacuum and packing the NMR rotor in an Ar-filled glovebox. ^{119}Sn MAS NMR spectra were acquired using either a Hahn-echo (^{119}Sn , $\omega_r/2\pi = 50$ kHz) or CP experiments with recycle delays between 4 and 30 seconds. All spectra were acquired with a spinning frequency, $\omega_r/2\pi = 8,000$ (5) Hz and between 32,384 and 172,800 scans. CP experiments were acquired with contact times between 0.4 and 4 ms and high-power ^1H decoupling (TPPM, $\omega_r/2\pi = 83$ kHz). ^{119}Sn spectra were referenced with powdered SnO_2 (-604.3 ppm) as an external standard relative to trimethyltin (0 ppm). Sample temperatures were maintained between 294 and 300 K.

References

- (1) (a) Pourpoint, F.; Thankamony, A. S. L.; Volkringer, C.; Loiseau, T.; Trebosc, J.; Aussenac, F.; Carnevale, D.; Bodenhausen, G.; Vezin, H.; Lafon, O.; Amoureux, J.-P. *Chem. Commun. (Cambridge, U. K.)* **2014**, 50, 933; (b) Song, C.; Hu, K.-N.; Joo, C.-G.; Swager, T. M.; Griffin, R. G. *J. Am. Chem. Soc.* **2006**, 128, 11385.
- (2) (a) Matsuki, Y.; Maly, T.; Ouari, O.; Karoui, H.; Le Moigne, F.; Rizzato, E.; Lyubenova, S.; Herzfeld, J.; Prisner, T.; Tordo, P.; Griffin, R. G. *Angew. Chem., Int. Ed.* **2009**, 48, 4996; (b) Rossini, A. J.; Zagdoun, A.; Lelli, M.; Canivet, J.; Aguado, S.; Ouari, O.; Tordo, P.; Rosay, M.; Maas, W. E.; Coperet, C.; Farrusseng, D.; Emsley, L.; Lesage, A. *Angew. Chem., Int. Ed.* **2012**, 51, 123.
- (3) Kiesewetter, M. K.; Corzilius, B.; Smith, A. A.; Griffin, R. G.; Swager, T. M. *J. Am. Chem. Soc.* **2012**, 134, 4537.
- (4) (a) Blanc, F.; Chong, S. Y.; McDonald, T. O.; Adams, D. J.; Pawsey, S.; Caporini, M. A.; Cooper, A. I. *J. Am. Chem. Soc.* **2013**, 135, 15290; (b) Zagdoun, A.; Casano, G.; Ouari, O.; Lapadula, G.; Rossini, A. J.; Lelli, M.; Baffert, M.; Gajan, D.; Veyre, L.; Maas, W. E.; Rosay, M.; Weber, R. T.; Thieuleux, C.; Coperet, C.; Lesage, A.; Tordo, P.; Emsley, L. *J. Am. Chem. Soc.* **2012**, 134, 2284.
- (5) Bui, L.; Luo, H.; Gunther, W. R.; Roman-Leshkov, Y. *Angew. Chem., Int. Ed.* **2013**, 52, 8022.
- (6) Gunther, W. R.; Duong, Q.; Roman-Leshkov, Y. *J. Mol. Catal. A: Chem.* **2013**, 379, 294.
- (7) Rosay, M.; Tometich, L.; Pawsey, S.; Bader, R.; Schauwecker, R.; Blank, M.; Borchard, P. M.; Cauffman, S. R.; Felch, K. L.; Weber, R. T.; Temkin, R. J.; Griffin, R. G.; Maas, W. E. *Phys. Chem. Chem. Phys.* **2010**, 12, 5850.