

Supporting Information:

Unearthing a Well-Defined Highly Active Bimetallic W/ Ti Precatalyst Anchored on a Single Silica Surface for Metathesis of Propane

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Experimental procedure

Reaction of propane metathesis in a continuous flow reactor.

The Tungsten and/or Titanium-based catalysts, kept refrigerated inside a glove box, were introduced into a glass cylinder reactor which remains isolated from atmosphere from the glove box to the setup for the study of the reaction under dynamic conditions. After connection to the gas lines and purgation of the tubes, a flow of propane controlled by mass flow-meter was sent onto the catalyst bed which was heated at 150°C. Reaction products were analyzed on line by gas chromatography (GC) measurements with a Varian 450-GC.

Hydrocarbons were separated and quantified using a gas chromatography column with a split injector coupled with a flame ionization detector (FID). A HP-PLOT Al₂O₃-KCl 30 m, 0.53 mm; 20.00 mm capillary column coated with a stationary phase of aluminum oxide deactivated with KCl was used with argon as the carrier gas at 30 kPa. Each analysis was carried out with the same conditions, Flow rate: 1 mL min⁻¹, split ratio: 50/1; inlet temperature: 250°C, detector temperature: 250°C; temperature program: 30°C (3 min), 30–250°C (12 °C min⁻¹), 250°C (3 min). GC response factors were calculated as an average of three independent runs with a calibration mixture of available C₁–C₄ n-alkane, iso-alkanes and olefins. The response factors were extrapolated for pentanes. Hydrogen was separated in a different channel using a set of different columns Hayesep Q/Molsieve 13X and quantified using thermal conductivity detector (TCD). GC response factor for hydrogen was calculated from H₂/Ar mixtures with hydrogen percentage in the range 0.05-4 %.

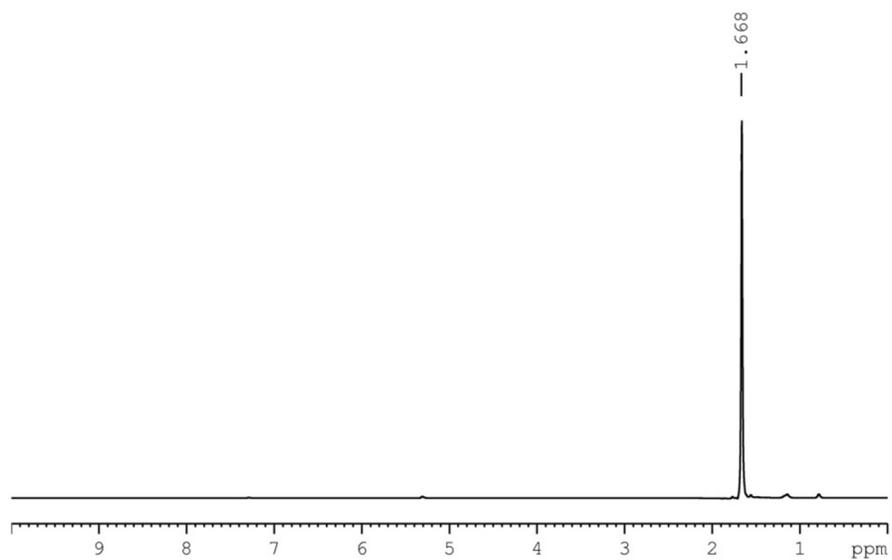


Figure S1: ^1H NMR spectrum of WMe_6 in CD_2Cl_2 recorded at 253 K.

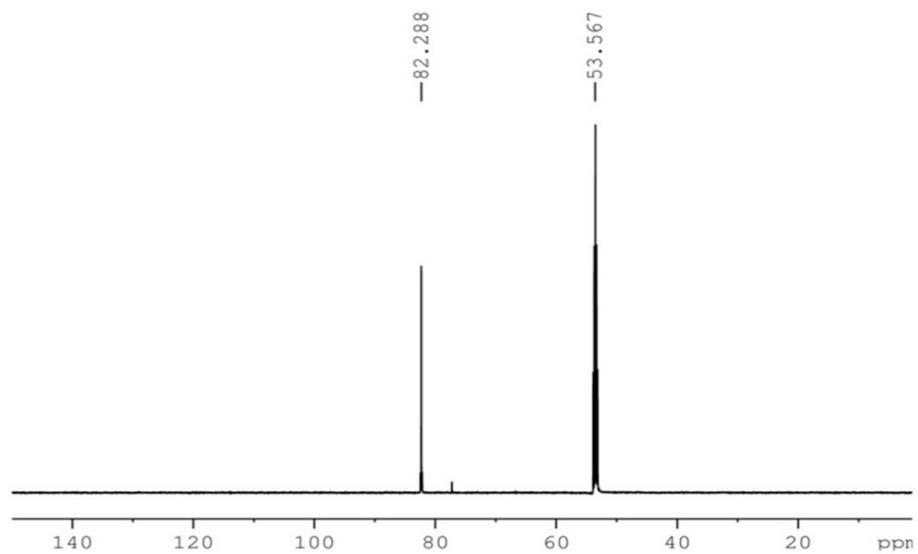


Figure S2: ^{13}C NMR spectrum of WMe_6 in CD_2Cl_2 recorded at 253 K.

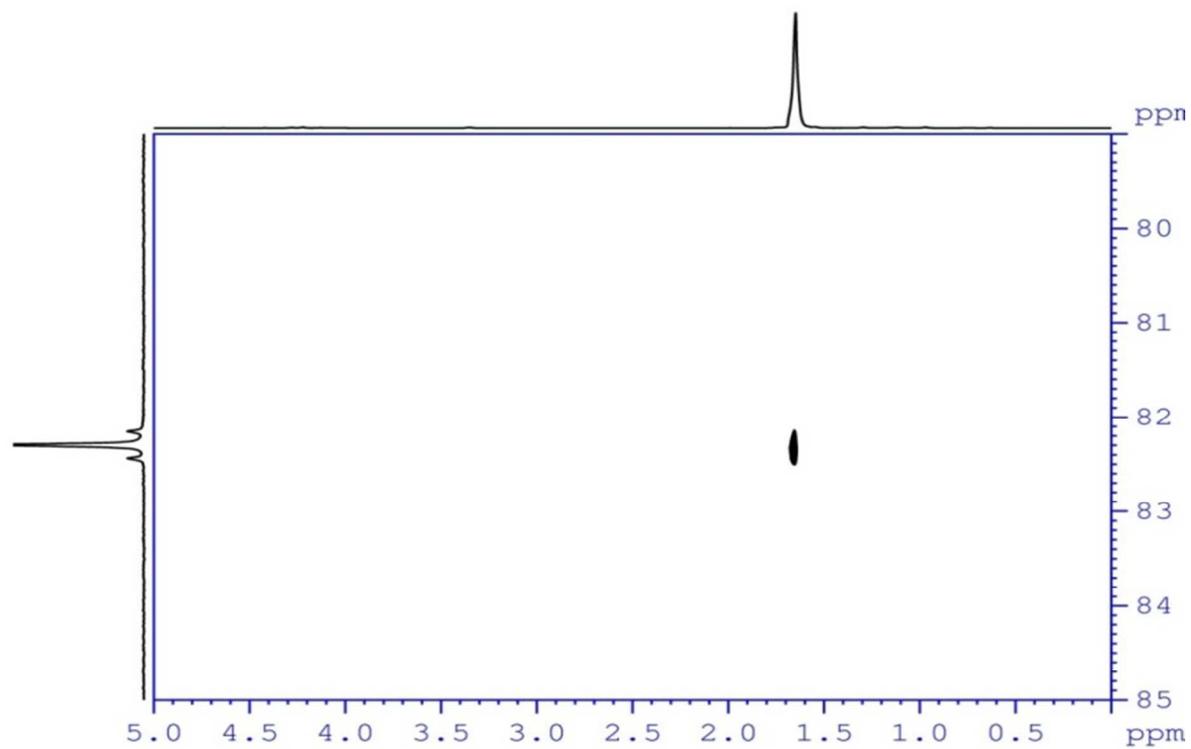


Figure S3: 2D solution ^1H - ^{13}C Heteronuclear Single Quantum Correlation (HSQC) NMR Spectra of WMe_6 in CD_2Cl_2 recorded at 253 K.

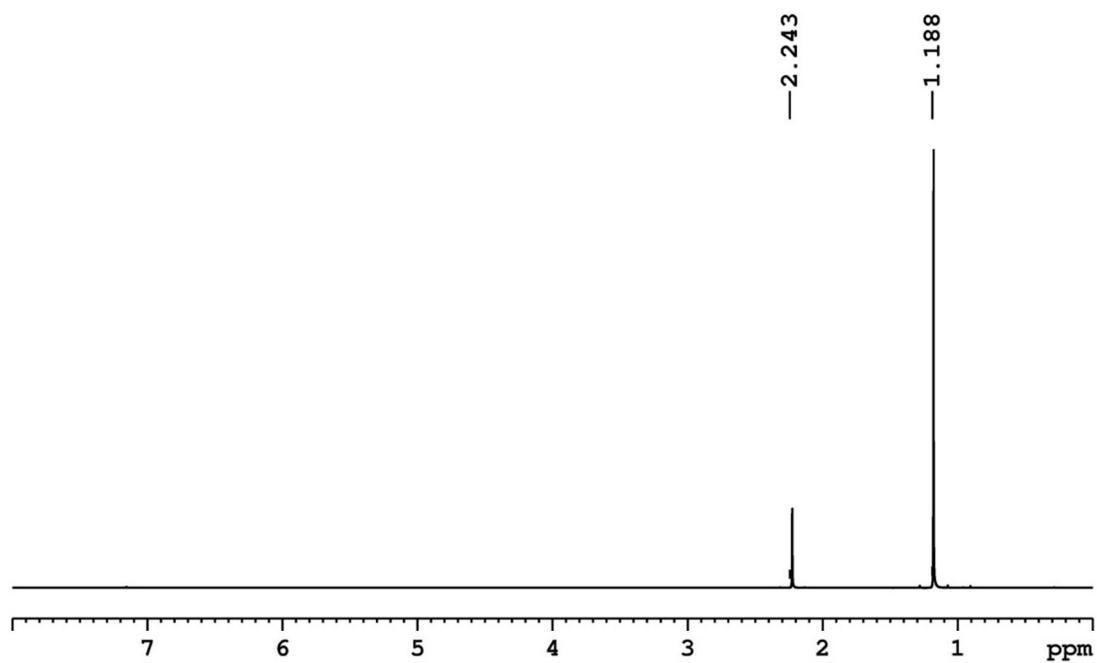


Figure S4: ^1H NMR spectrum of TiNp_4 in C_6D_6 recorded at 298 K.

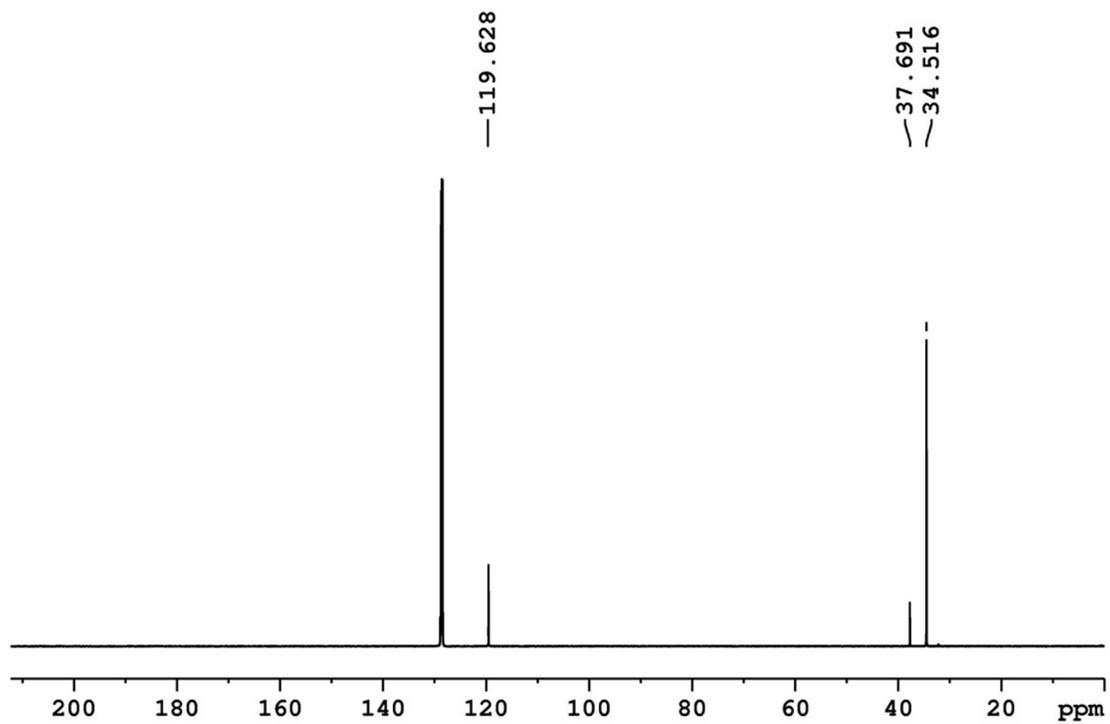


Figure S5 : ^{13}C NMR spectrum of TiNp_4 in C_6D_6 recorded at 298 K.

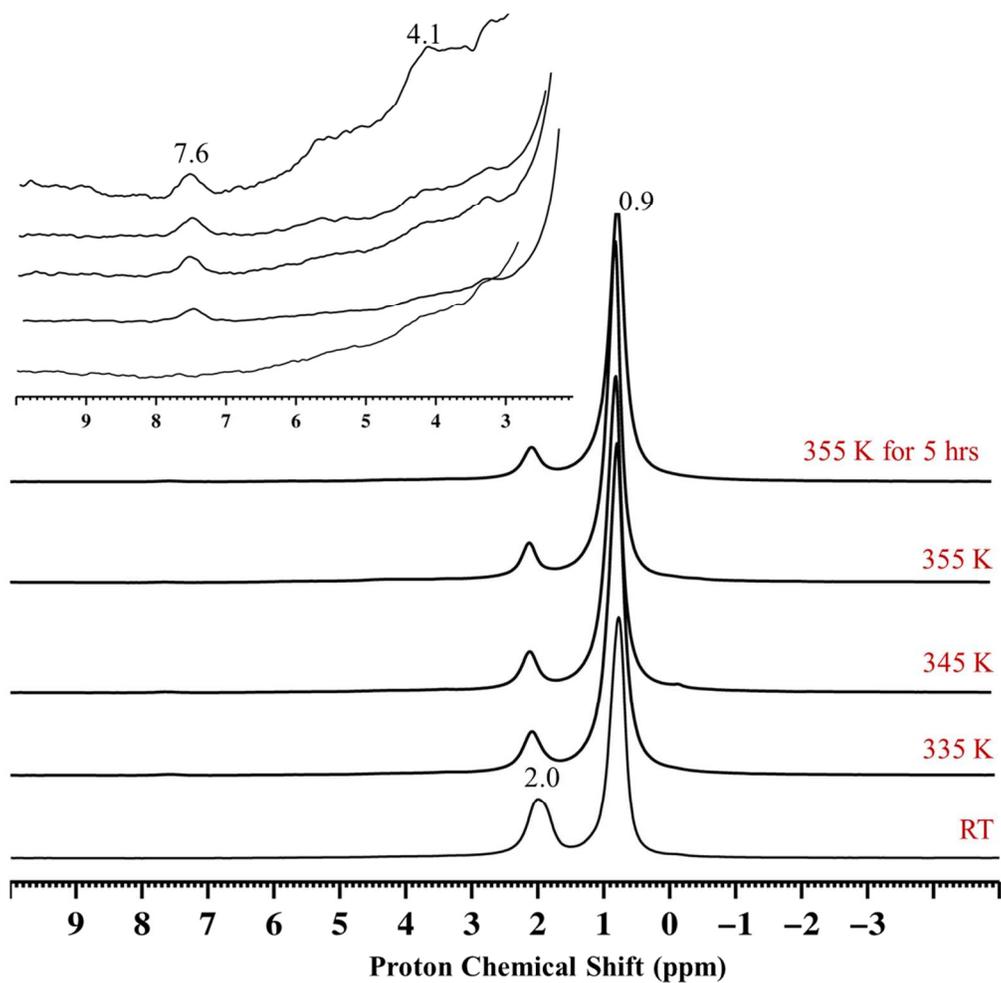


Figure S6: Variable temperature: ¹H spin echo MAS solid-state NMR spectra of the thermal transformation of species **4** (acquired at 600 MHz NMR spectrometer under 20 KHz MAS spinning frequency, number of scans = 8, repetition delay = 5 s) the true sample temperatures were calibrated by separately measuring the ⁷⁹Br isotropic chemical shift and longitudinal relaxation times of KBr

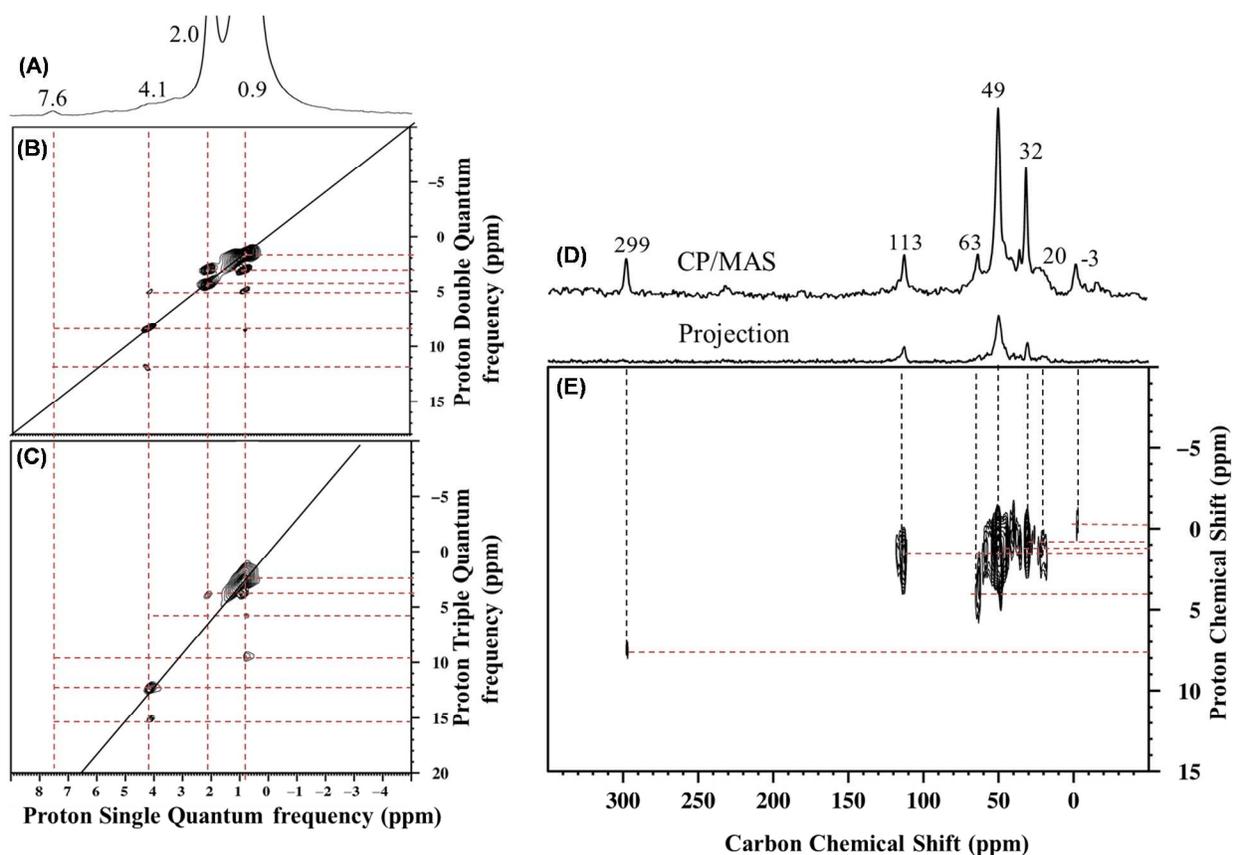


Figure S7. (A) 1D ^1H spin-echo MAS solid-state NMR spectrum of thermally treated sample **4** (70 % ^{13}C labelled of W- CH_3) after maintaining the temperature at 355 K for 6 hours (acquired on a 600 MHz NMR spectrometer under a 20 kHz MAS spinning frequency, number of scans = 8, repetition delay = 5 s). (B) 2D ^1H - ^1H DQ and (C) ^1H - ^1H TQ (acquired on a 600 MHz NMR spectrometer under 22 kHz MAS spinning frequency with a back-to-back recoupling sequence, number of scans = 128, repetition delay = 5 s, number of t1 increments = 128) (D) ^{13}C CP/MAS NMR spectrum (10 kHz MAS at the same field as above, number of scans = 20000, repetition delay = 4 s, contact time = 2 ms, line broadening = 80 Hz) (E) 2D ^1H - ^{13}C CP/MAS dipolar HETCOR NMR spectrum acquired with short contact times of 0.2 ms under 10 kHz MAS, number of scans per increment = 3000, repetition delay = 4 s, number of t1 increments = 32, line broadening = 80 Hz).

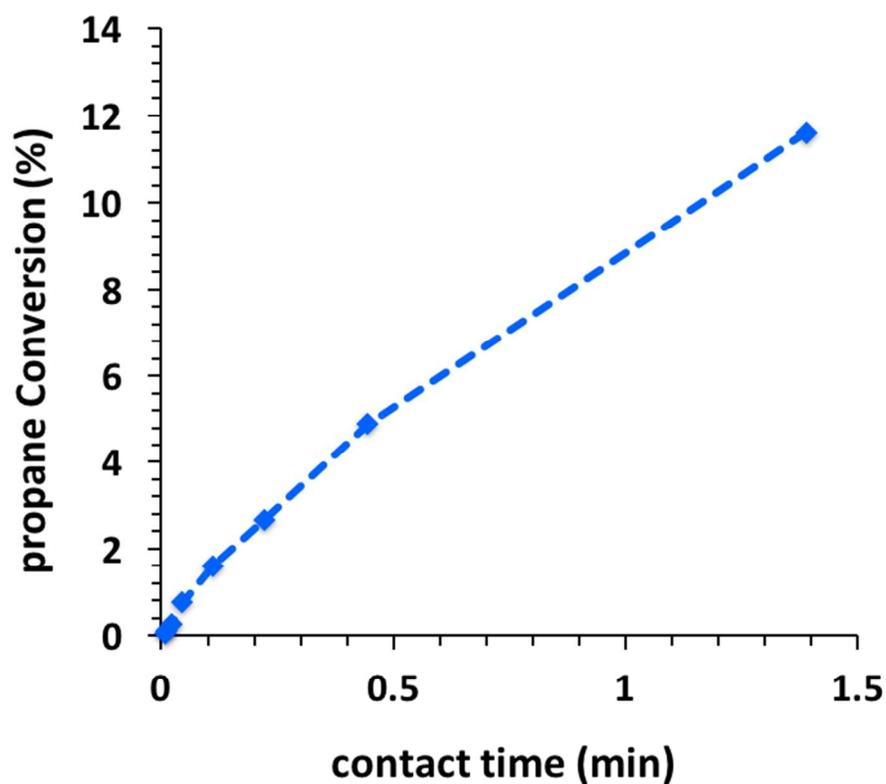


Figure S8. Effect of contact time on the conversion of propane during the metathesis catalyzed by pre-catalyst $[(\equiv\text{Si-O})\text{W}(\text{Me})_5 (\equiv\text{Si-O})\text{Ti}(\text{Np})_3]$ **4** (0.34 %_{wt} W and 1.02 %_{wt} Ti) 100mg, in a continuous flow reactor at 150 °C with the flow of propane 0.1-15 ml/min propane, VHSV= 43-8100 h⁻¹, contact time= 0.007-1.389 min.

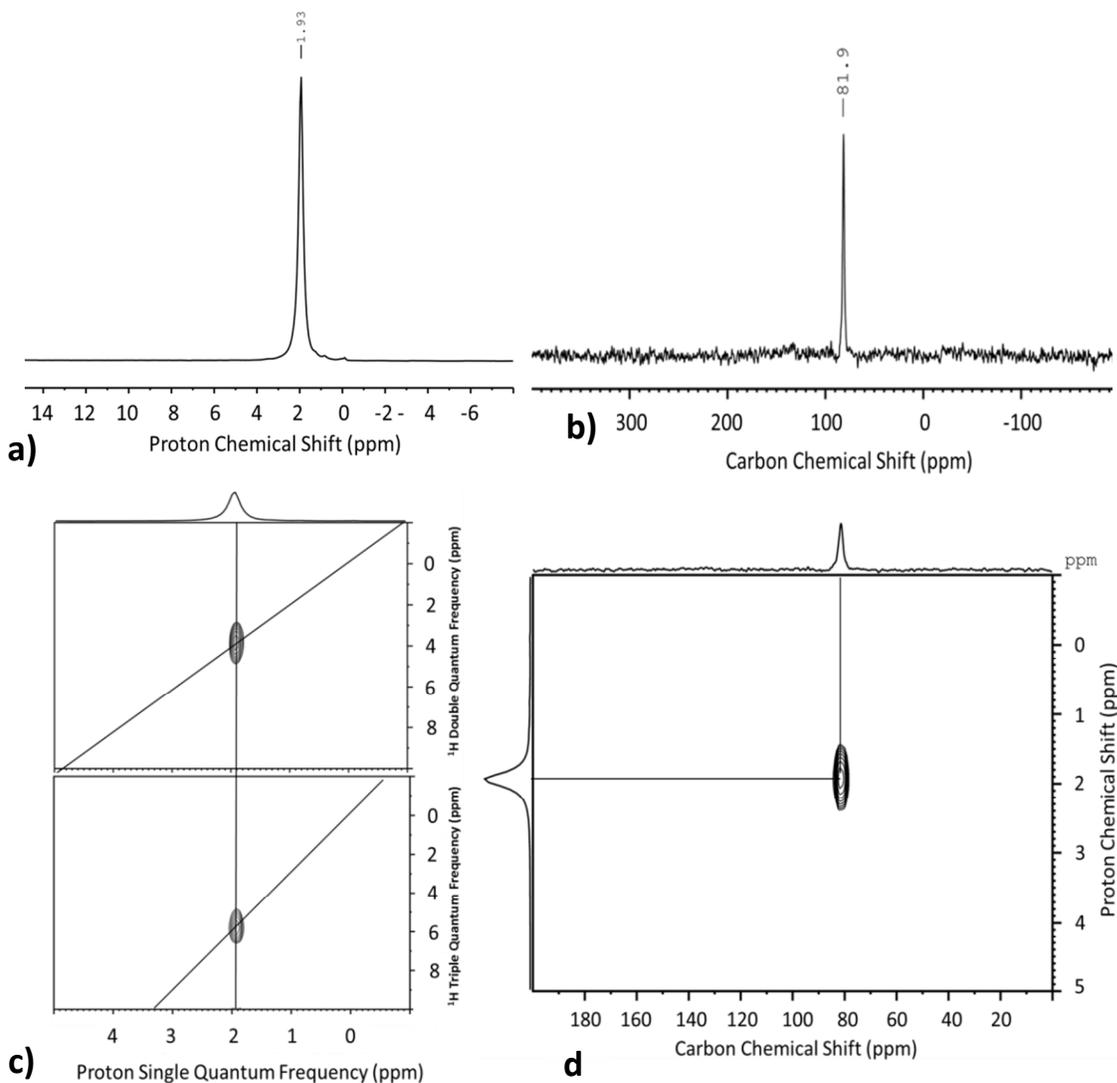


Figure S9: Solid state NMR of complex **3** [(≡Si-O-)W(Me)₅]: a) One-dimensional (1D) ¹H MAS solid-state NMR spectrum. b) ¹³C CP/MAS NMR spectrum of **3** acquired at 9.4 T ($\nu_0(^1\text{H}) = 400$ MHz) with a 10 kHz MAS frequency, 1000 scans, 4 s repetition delay, and a 2 ms contact time. An exponential line broadening of 80 Hz was applied prior to Fourier transformation. c) Two-dimensional (2D) ¹H-¹H double-quantum (DQ)/single-quantum (SQ) and ¹H-¹H triple-quantum (TQ)/SQ NMR spectra of **3** (acquired with 32 scans per t₁ increment, 5 s repetition delay, 32 individual t₁ increments). d) ²D ¹H-¹³C CP/MAS dipolar HETCOR spectrum of **3** (acquired at 9.4 T with an 8.5 kHz MAS frequency, 2000 scans per t₁ increment, 4 s repetition delay, 64 individual t₁ increments, and a 0.2 ms contact time).