

Table of Contents

1. Catalyst preparation.....	S-1
2. Sample preparation and aqueous phase heterogeneous hydrogenation of ¹³ C-labeled vinyl acetate.....	S-2
3. Additional ¹³ C NMR spectra and XPS studies of the catalyst.....	S-3
4. References Used In Supporting Information.....	S-8

1. Catalyst preparation

For the preparation of Rh/TiO₂ catalyst with 23.2 wt% metal loading, the 5.68 mL of acidic solution of Rh(NO₃)₃ (c_{Rh} = 88 mg/mL) was evaporated to dryness and then was diluted with water to a total volume of 2 mL. Next, approximately 5 drops of 25 wt% tetramethylammonium hydroxide aqueous solution (Acros, CAS:75-59-2) was added. The 2 g of TiO₂ was impregnated with obtained rhodium solution for 2.5 h at room temperature. Then the solvent excess was evaporated and the obtained catalyst was dried in air at 120 °C for 4 h. The subsequent calcination of the sample at 400 °C in air for 3 h and reduction in H₂ flow at 330 °C for 3 h resulted in the formation of 23.2 wt% Rh/TiO₂.

2. Sample preparation and aqueous phase heterogeneous hydrogenation of ^{13}C -labeled vinyl acetate

For the aqueous phase heterogeneous hydrogenation of vinyl acetate, 10 mL of D_2O , was premixed with 68.8 mg of vinyl acetate. The resulting 80 mM solution (0.5 mL) was placed in a medium wall 5 mm NMR tube with 30 mg of 23.2 wt% Rh/ TiO_2 catalyst placed at the bottom. The NMR tube was heated to $\sim 90^\circ\text{C}$. The hydrogenation was performed at ~ 7.1 atm of *para*- H_2 pressure at 150 standard cubic centimeters per minute (scm) flow rate controlled by the mass flow controller (MFC). For the polarization transfer experiments, the field cycling approach with magnetic shield was used. The full experimental setup is shown in Figure S1. The detailed information about the setup, polarization transfer procedure and magnetic field strength are given in references [1] and [2].

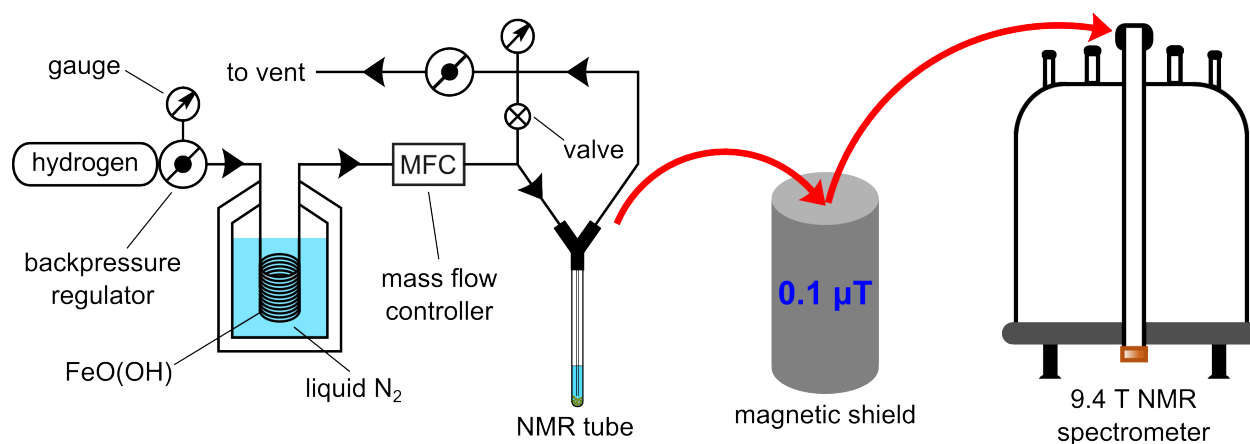


Figure S1. Experimental setup for aqueous phase heterogeneous hydrogenation with polarization transfer to ^{13}C nuclei using magnetic field cycling. MFC = mass flow controller.

3. Additional ^{13}C NMR spectra and XPS studies of the catalyst

XPS studies

XPS experiments were performed on a SPECS photoelectron spectrometer equipped with PHOIBOS-150-MCD-9 hemispherical energy analyzer and X-Ray source with a double Al/Mg anode. Non-monochromatic Al $K\alpha$ irradiation ($h\nu = 1486.6$ eV, 200 W) was used as the primary excitation. The samples were supported onto double-sided conducting copper Scotch tape. Binding energy (BE) scale was preliminarily calibrated by position of Au $4f_{7/2}$ (BE = 84.0 eV) and Cu $2p_{3/2}$ (BE = 932.67 eV) core levels peaks. Binding energy of samples peaks was calibrated by position of the C 1s peak (BE = 284.8 eV) corresponding to the surface hydrocarbon-like deposits (C-C and C-H bonds). Pass energy of analyzer was 50 eV for the survey and 20 eV for the narrow spectral regions. Rh foil and Rh $_2\text{O}_3$ powder were used as reference materials. For quantitative analysis, the integral intensities of photoelectron spectra were corrected by the corresponding atomic sensitivity factors [3]. Spectral analysis and data processing were performed with XPS Peak 4.1 program [4].

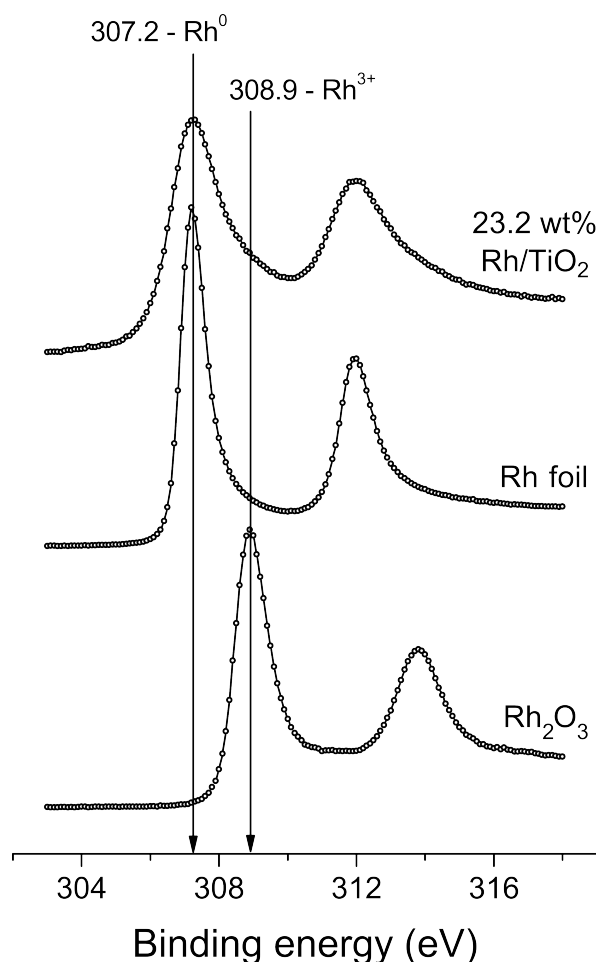


Figure S2. The Rh 3d_{5/2} core-level spectra obtained for 23.2% Rh/TiO₂ catalyst and for the rhodium foil and Rh₂O₃ used as reference samples. The Rh 3d_{5/2} peak at 307.2 eV can be attributed to metallic Rh (Rh⁰), and the peak at 308.9 eV can be attributed to Rh³⁺ (Rh₂O₃) [5].

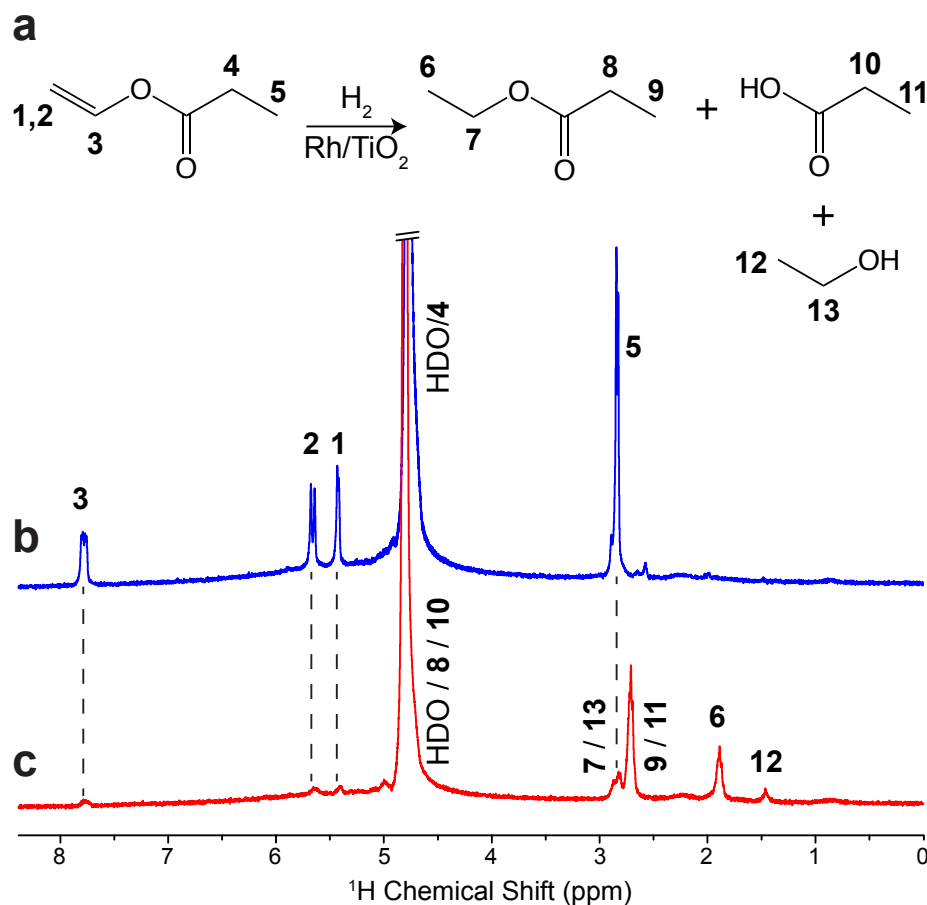


Figure S3. a) Molecular diagram of vinyl acetate (VA) hydrogenation in D₂O using Rh/TiO₂ catalyst. ¹H NMR spectra of reaction mixture (80 mM of vinyl acetate (VA) dissolved in D₂O) before (b) and after (c) heterogeneous hydrogenation over Rh/TiO₂ catalyst. Based on the signal intensities of the corresponding NMR peaks from these two spectra (e.g. resonances corresponding to acetic acid, VA and ethanol, the total conversion of VA is estimated at ~90.4% with conversion to ethyl acetate being ~85.9%, and conversion to ethanol (and acetate) being ~4.5%. Final reaction mixture composition is therefore the following: ~8 mM reagent (VA), ~68 mM HP ethyl acetate, and ~4 mM ethanol and acetic acid.

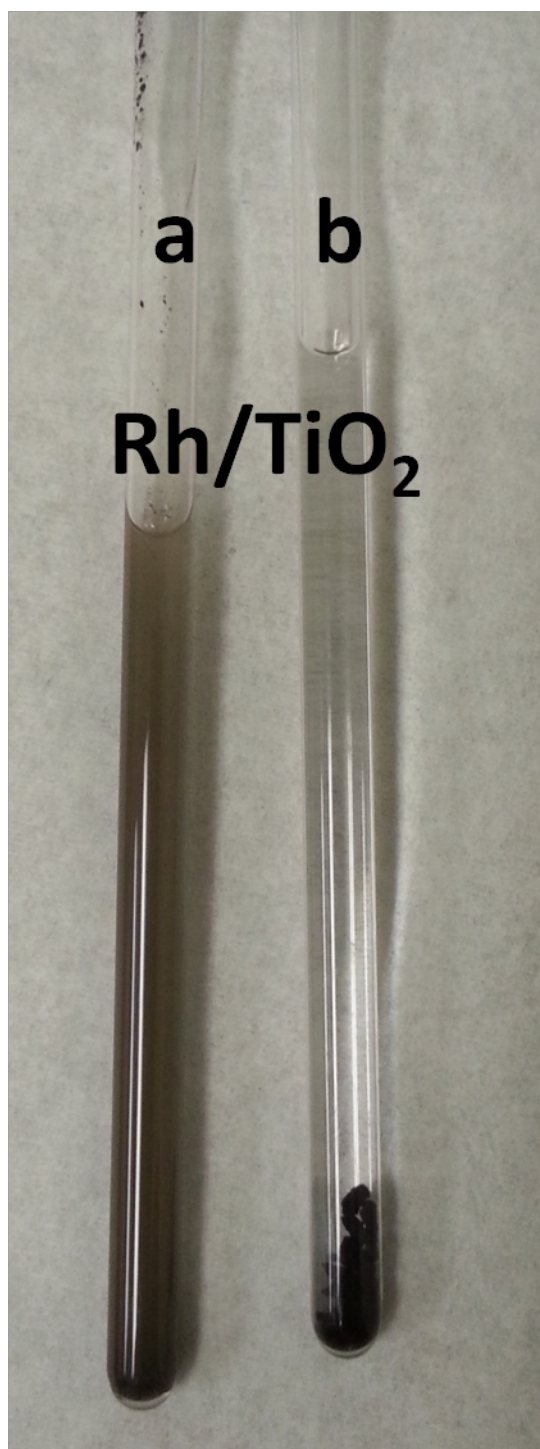


Figure S4. The photos of NMR tubes filled with the solution of ethyl acetate in D₂O with 0.1 mm size (a) and 2-3 mm size (b) Rh/TiO₂ beads obtained after hydrogenation reaction.

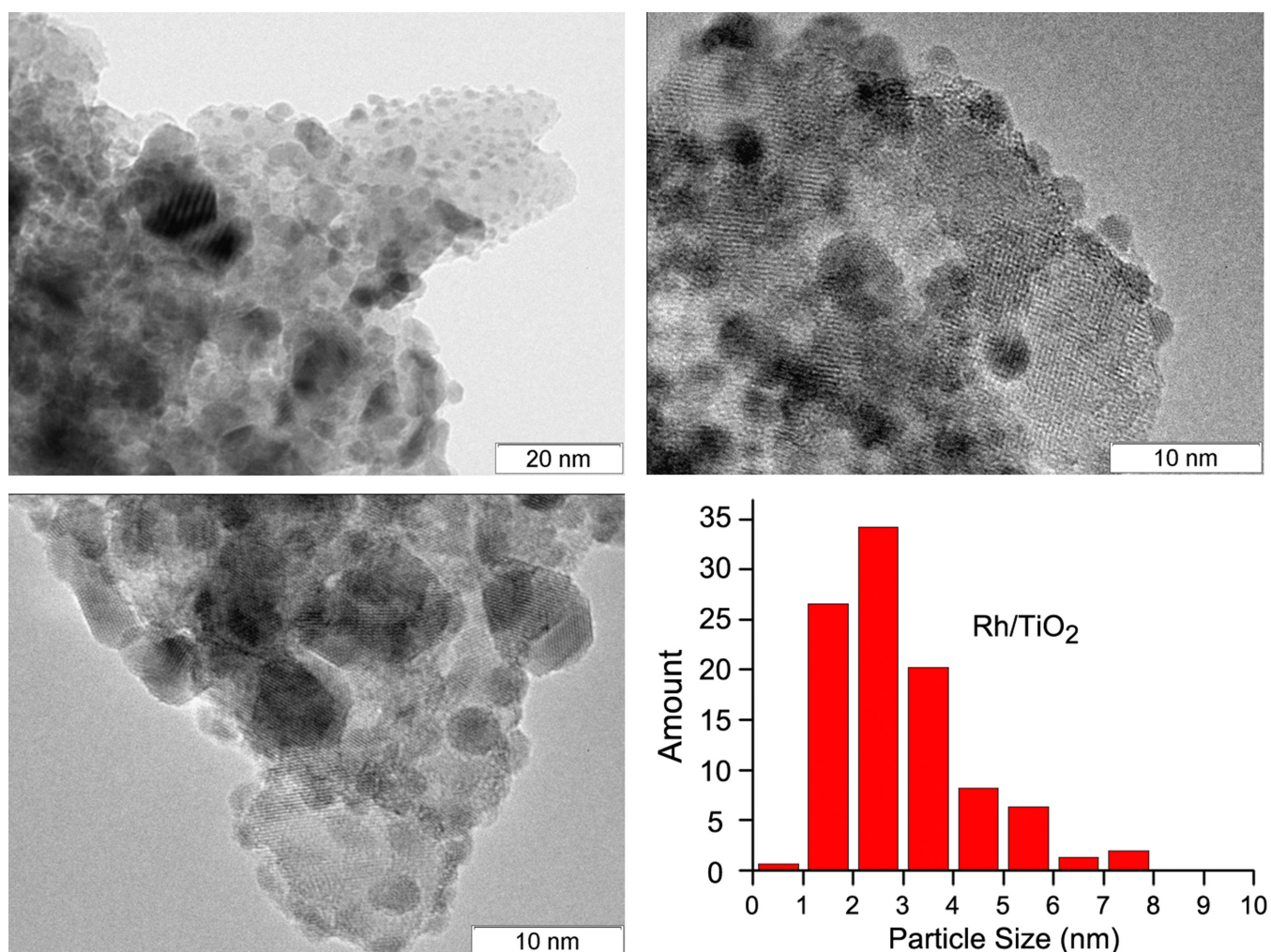


Figure S5. Color enlarged version of Figure 1 (main text): TEM images and metal particles size distribution for 23.2 wt% Rh/TiO₂ catalyst obtained via wet precipitation from aqueous rhodium nitrate solution. The average size of metal particles is *ca.* 3 nm.

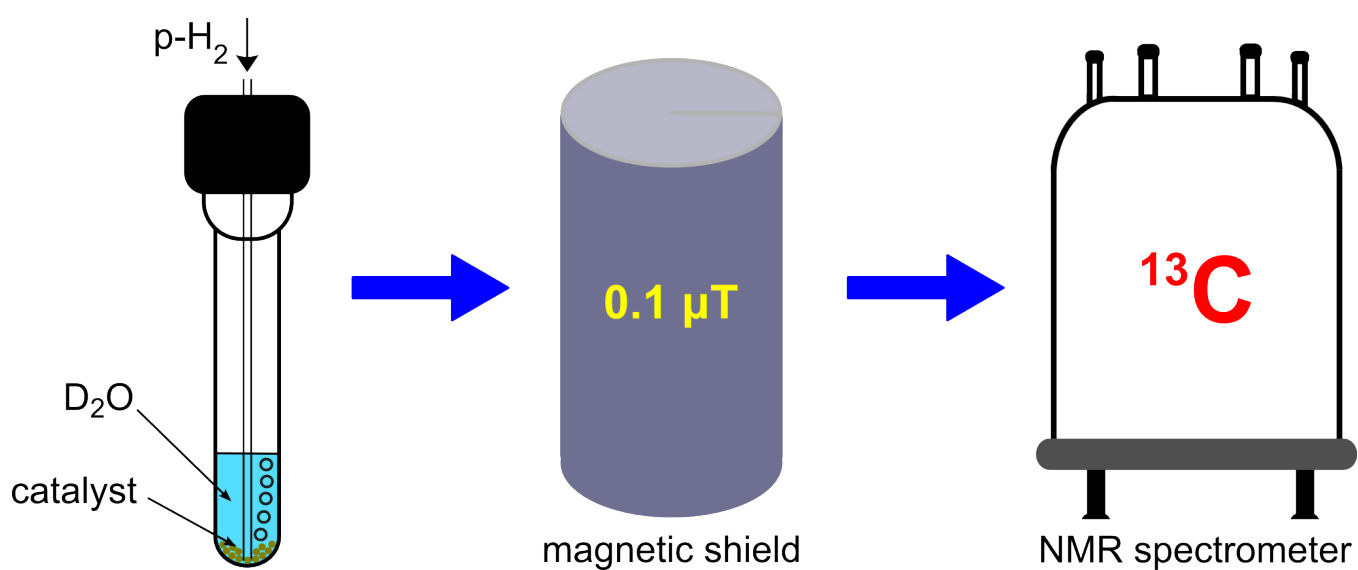


Figure S6. Color enlarged version of Figure 2 (main text): Experimental procedure for ¹³C hyperpolarization and NMR spectra detection via Phip-SAH and magnetic field cycling.

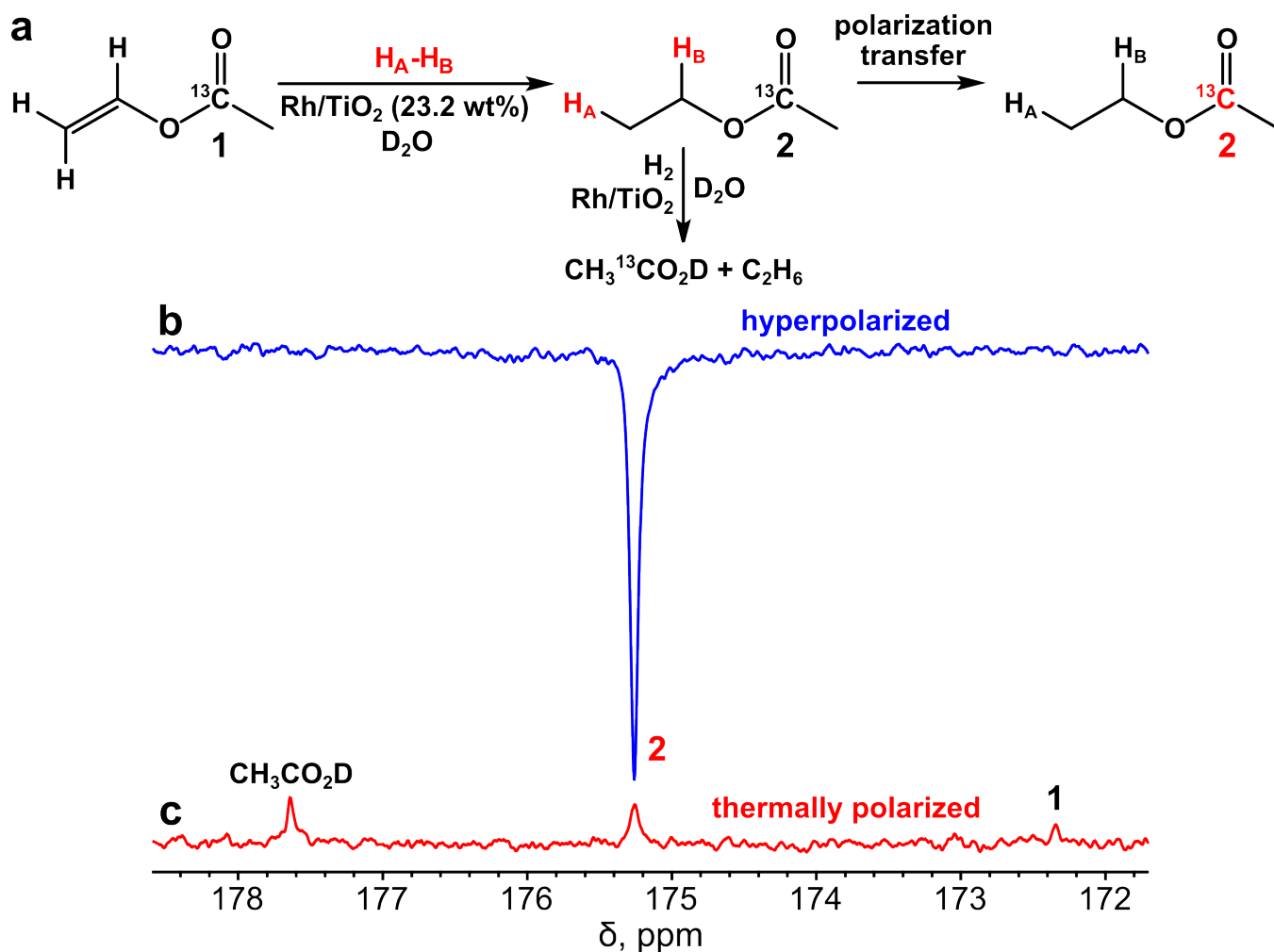


Figure S7. Color enlarged version of Figure 3 (main text): (a) Reaction scheme of vinyl acetate-1- ^{13}C heterogeneous hydrogenation with parahydrogen (p-H₂) over 23.2 wt% Rh/TiO₂ catalyst in D₂O solution with subsequent polarization transfer from protons to ^{13}C nuclei, (b) ^{13}C NMR spectrum of HP ethyl acetate-1- ^{13}C , and (c) corresponding ^{13}C spectrum of thermally polarized sample after waiting for a time period longer than $5 \cdot T_1$. All spectra were acquired with 1 signal scan. NMR tube with the hydrogenation products was placed in a magnetic shield after termination of hydrogen bubbling. The ^{13}C signal enhancement ($\epsilon_{^{13}\text{C}}$) is ~ 14 , $\%P_{^{13}\text{C}} \sim 0.011\%$.

4. References Used In Supporting Information

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