Experimental Methods

General

All solvents were purchased from common vendors and were used as received. In particular, HPLC grade acetone (270725), 2-hydroxyethyl 1-^{13}C-acrylate-$d_{2,3,3}$ (HEA, 676071) and deuterium oxide (99.8%, 756822) were purchased from Sigma-Aldrich-Isotec, Miamisburg, OH. Bis(norbornadiene)rhodium(I) tetrafluoroborate ($[Rh(I)(NBD)_2]BF_4$, 45-0230) and tris(hydroxymethyl)phosphine (THP, 15-7901) were purchased from Strem Chemicals Inc., Newburyport, MA. Ultra-high purity nitrogen (PGNUHP-234) was purchased from A-L Gases, Nashville, TN. All NMR spectra were collected on Bruker 11.7 T high-resolution NMR spectrometer equipped with X-H dual channel RF probe.

THP titration experiments

THP (1.0 mmol, 0.124 g) containing 40% of the oxide form was dissolved in 99.8% D_2O, (20 mL) resulting in solution containing 0.050 mmol (1 eq.) in 1 mL. $[Rh(I)(NBD)_2]BF_4$ (0.25 mmol, 94 mg) was dissolved in HPLC grade acetone (1 mL) resulting in solution containing 0.050 mmol (1 eq.) in 0.2 mL. NaCl (0.40 g, 6.8 mmol) was dissolved in D_2O (5 mL) resulting in solution containing 1.4 mmol (27 eq.) in 1 mL. THP solution was divided between five vials as follows: 2, 3, 4, 5, and 6 mL respectively followed by addition of 0.2 mL (1 eq.) of $[Rh(I)(NBD)_2]BF_4$ solution to each vial producing solutions of corresponding to Rh(I):non-oxidized THP ratios 1:1.2, 1:1.8, 1:2.4, 1:3.0, and 1:3.6 respectively. 0.5 mL aliquot was taken from each vial for ^{31}P NMR spectroscopy analysis. After that 1.0 mL of NaCl solution (27 eq.) was added to each vial to prepare samples with excess NaCl, Fig. 2, main text.

PHIP catalyst solution preparation

The preparation of PASADENA precursor molecule was similar to that previously described.[1] Solution of NaCl (0.10 g, 1.7 mmol) and of THP (3 q., 0.402 mmol, 0.05 g) containing 40% of the oxide form in 50 mL D_2O was placed in Buchi 1 L evaporation flask. This ambient solution was then degassed with rotary evaporation (model Buchi R-215 equipped with V-710 pump and connected to a nitrogen line at 6 psi above atmospheric pressure, Buchi, New Castle, DE) by decrementing the onboard pressure slowly to avoid boiling, from 70 mbar to 25 mbar over approximately 5 minutes. The system was brought to the atmospheric pressure with ultra-high pure nitrogen gas. 0.5 mL aliquot was taken for ^{31}P NMR spectroscopy analysis corresponding to NMR spectrum in Fig. 4, bottom spectrum. $[Rh(I)(NBD)_2]BF_4$ (0.134 mmol, 0.05 g) was dissolved in 3 mL acetone and to avoid precipitation was added drop-wise to the phosphine ligand solution. The degassing procedure was repeated to minimize Rh(I) poisoning with atmospheric oxygen and the system was brought to the atmospheric pressure with ultra-high pure nitrogen gas. 2-hydroxyethyl acrylate-1-^{13}C,2,3,3-d_3 (HEA, 2 eq., 0.268 mmol, 0.032 g) was added to the catalyst solution and the resulting solution was transferred into 100 mL square bottle (431430, Corning Life Sciences, NY, USA). 0.5 mL aliquot was taken for ^{31}P NMR spectroscopy analysis corresponding to NMR spectrum in Fig. 4, middle spectrum, main text.

PHIP hyperpolarization experiments

The catalyst solution containing unsaturated precursor HEA prepared in the section above in 100 mL square plastic bottle was connected to a previously described, automated PHIP polarizer,[1] equipped with a dual-tuned $^{1}H/^{13}C$ coil optimized for ^{13}C detection.[2] All PHIP experiments were performed with this polarizer allowing keeping the solution under atmosphere on ultra-high purity nitrogen gas.

60 mL polysulfone reactor chamber residing in 0.0475 T field of temperature (35 °C) stabilized Halbach array magnet (Magritek, Wellington, New Zealand) was filled with 7 atm of 97% parahydrogen gas over the course of 8 seconds. The catalyst PHIP solution was equilibrated at 60 °C in a 1/8" OD 1/16" ID PTFE tubing prior to spraying into parahydrogen filled reactor. The solution was injected and sprayed into parahydrogen atmosphere using pressurized 17 atm ultra-high purity nitrogen gas. The reaction chamber was under condition of proton decoupling (B_1 = 5.0 kHz at 2.02 MHz ^{1}H resonant frequency at 10 Watts) during entire reaction time including catalyst solution spraying and foaming. The total reaction time was varied to elucidate PHIP hydrogenation kinetics. When proton decoupling was finished the RF pulse sequence progressed to polarization transfer from nascent parahydrogen singlet state to 1-13C carbon of 2-hydroxyethyl 1-^{13}C-propionate-$d_{2,3,3}$ (HEP). When PHIP and low field NMR detection of hyperpolarized ^{13}C were completed, the resulting solution was ejected to 100 mL square plastic bottle. 0.5 mL aliquot was taken for ^{31}P NMR spectroscopy analysis corresponding to NMR spectrum in Fig. 4, top spectrum, main text.

References

(1) Waddell, K. W.; Coffey, A. M.; Chekmenev, E. Y. In situ Detection of PHIP at 48 mT: Demonstration using a Centrally Controlled Polarizer. *J. Am. Chem. Soc.* **2011**, *133*, 97-101.

(2) Coffey, A. M.; Shchepin, R. V.; Wilkens, K.; Waddell, K. W.; Chekmenev, E. Y. A Large Volume Double Channel 1H-X RF Probe for Hyperpolarized Magnetic Resonance at 0.0475 Tesla. *J. Magn. Reson.* **2012**, *220*, 94–101.