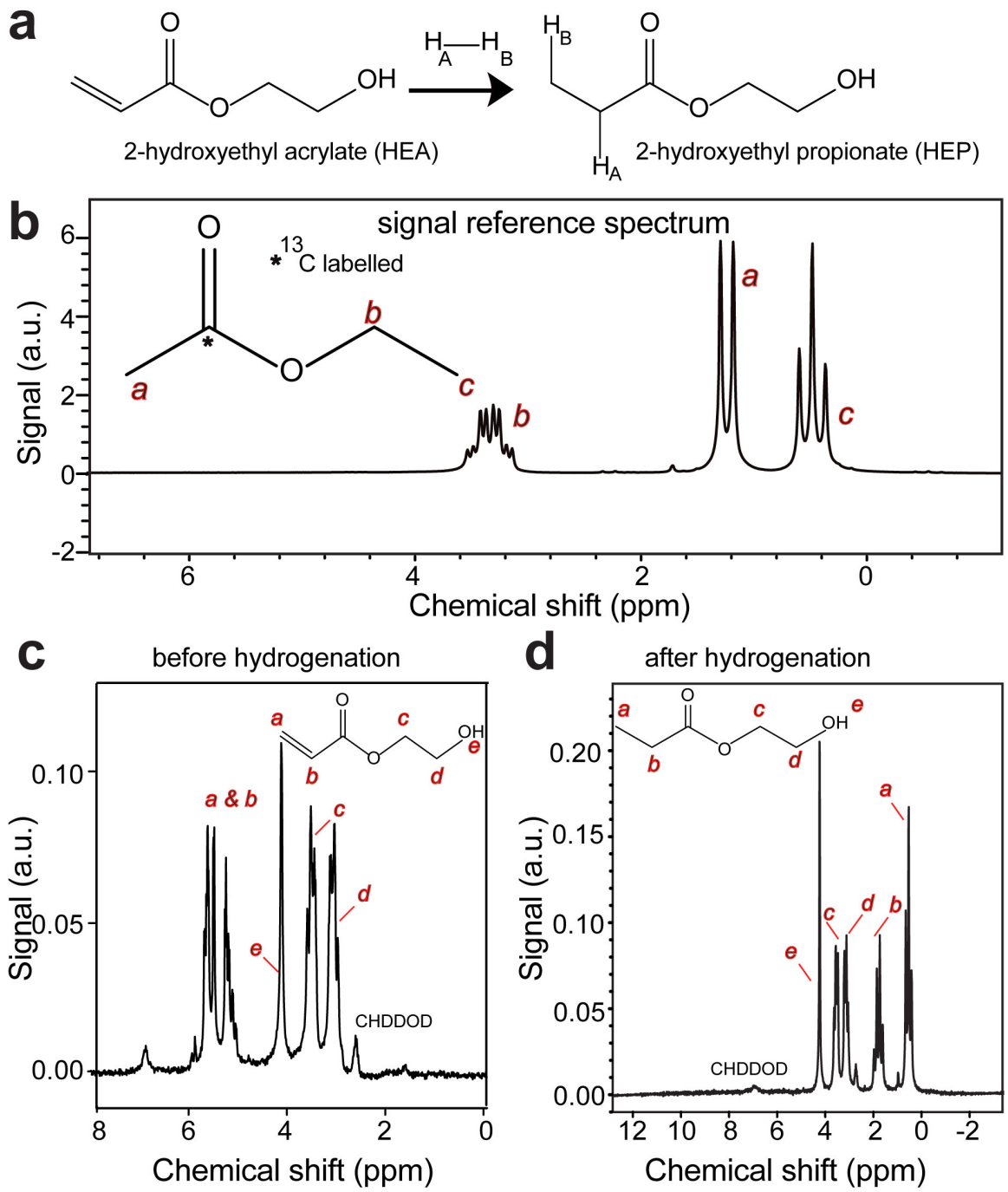

Figure S1. ^{1}H NMR spectroscopy of thermally polarized samples using 1.4 T bench-top NMR spectrometer. All spectra were collected using 90° excitation RF pulses, a single average and otherwise identical parameters. Spectral assignments of the different proton environments are labeled in red. a) Reaction scheme of parahydrogen pairwise addition to HEA resulting in production of HP HEP. b) Fourier spectrum of the thermally polarized signal reference sample of 10 M (neat) ethyl acetate-1-^{13}C employed for determination of concentration and chemical conversion. c,d) Fourier spectra of thermally polarized solutions recorded before and after the reaction of HEA with parahydrogen, respectively, indicating complete conversion to HEP.

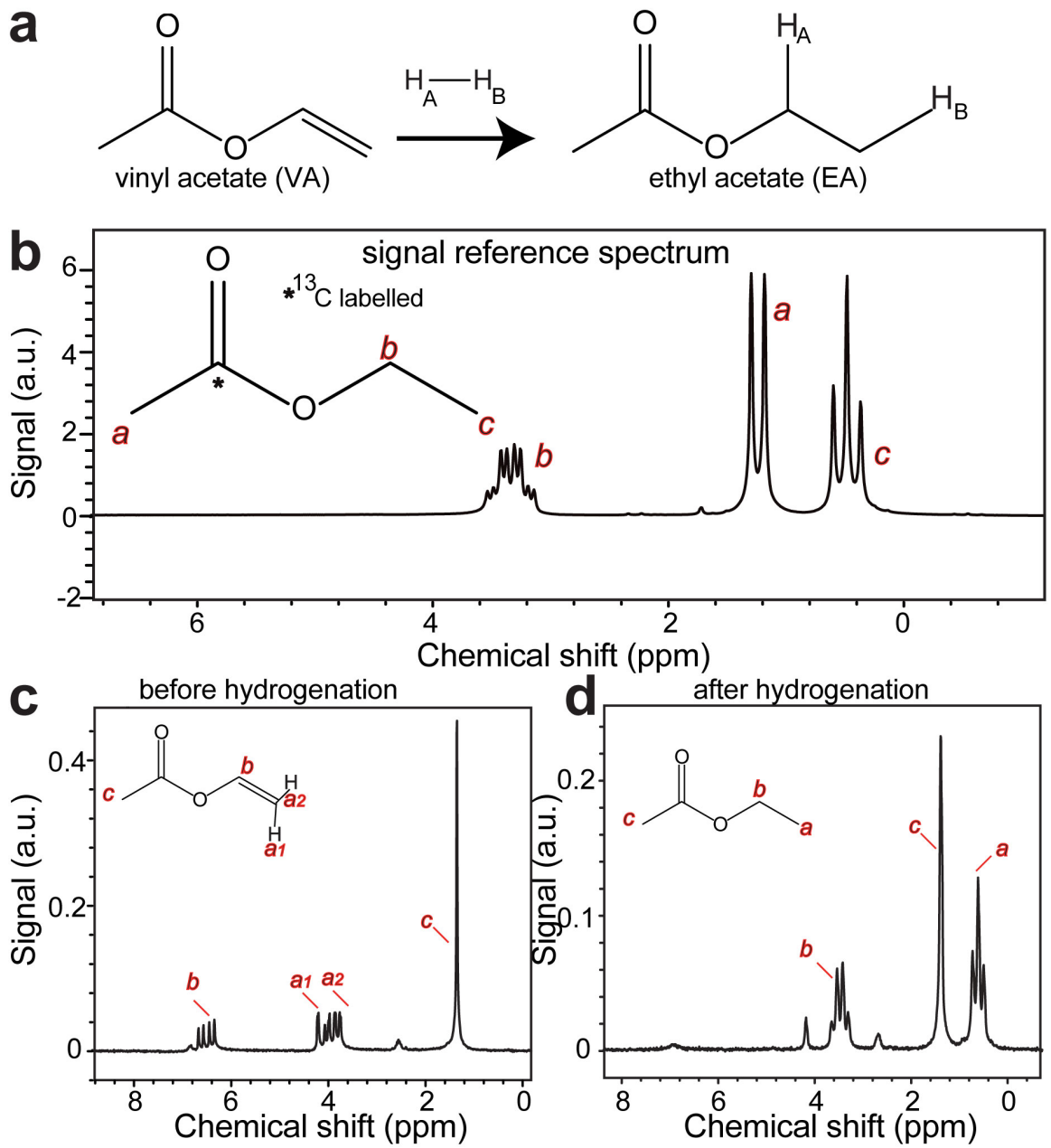

Figure S2. ^{1}H NMR spectroscopy of thermally polarized samples using 1.4 T bench-top NMR spectrometer. All spectra were collected using 90° excitation RF pulses, a single average and otherwise identical parameters. Spectral assignments of the different proton environments are labeled in red. a) Reaction scheme of parahydrogen pairwise addition to VA resulting in production of HP EA. b) Fourier spectrum of the thermally polarized reference sample of 10 M (neat) ethyl acetate-1-^{13}C employed for determination of concentration and chemical conversion. c,d) Fourier spectra of thermally polarized solutions recorded before and after the reaction of VA with parahydrogen, respectively, indicating complete conversion to EA.

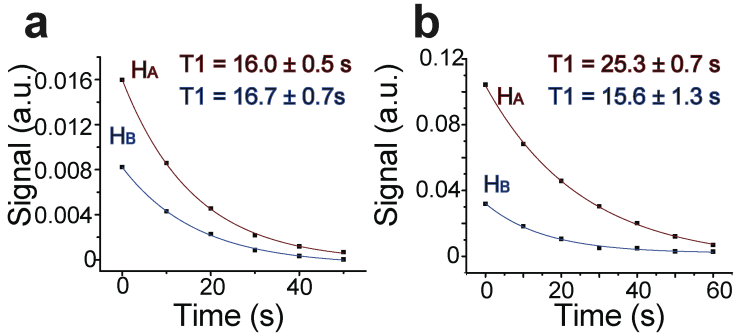

Figure S3. T_1 relaxation values of hyperpolarized H_A and H_B protons in HP 2-hydrpxyethyl propionate (HEP) (display a) and HP ethyl acetate (EA) (display b) after homogeneous pairwise p-H_2 addition in CD_3OD measured at 1.4 T.

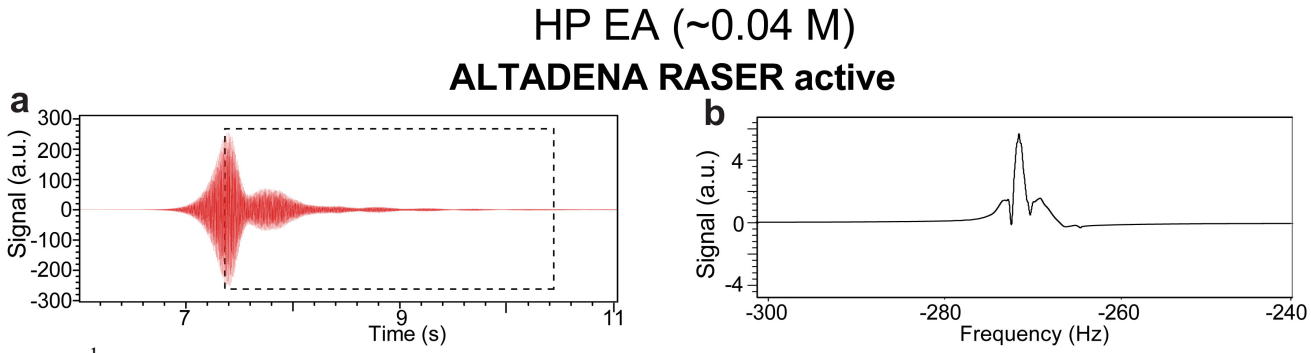

Figure S4. ^{1}H NMR spectroscopy of solution-phase PHIP of 40 mM HP ethyl acetate (EA) probed at 1.4 T. a) ALTADENA RASER active signal. b) Fourier spectrum.

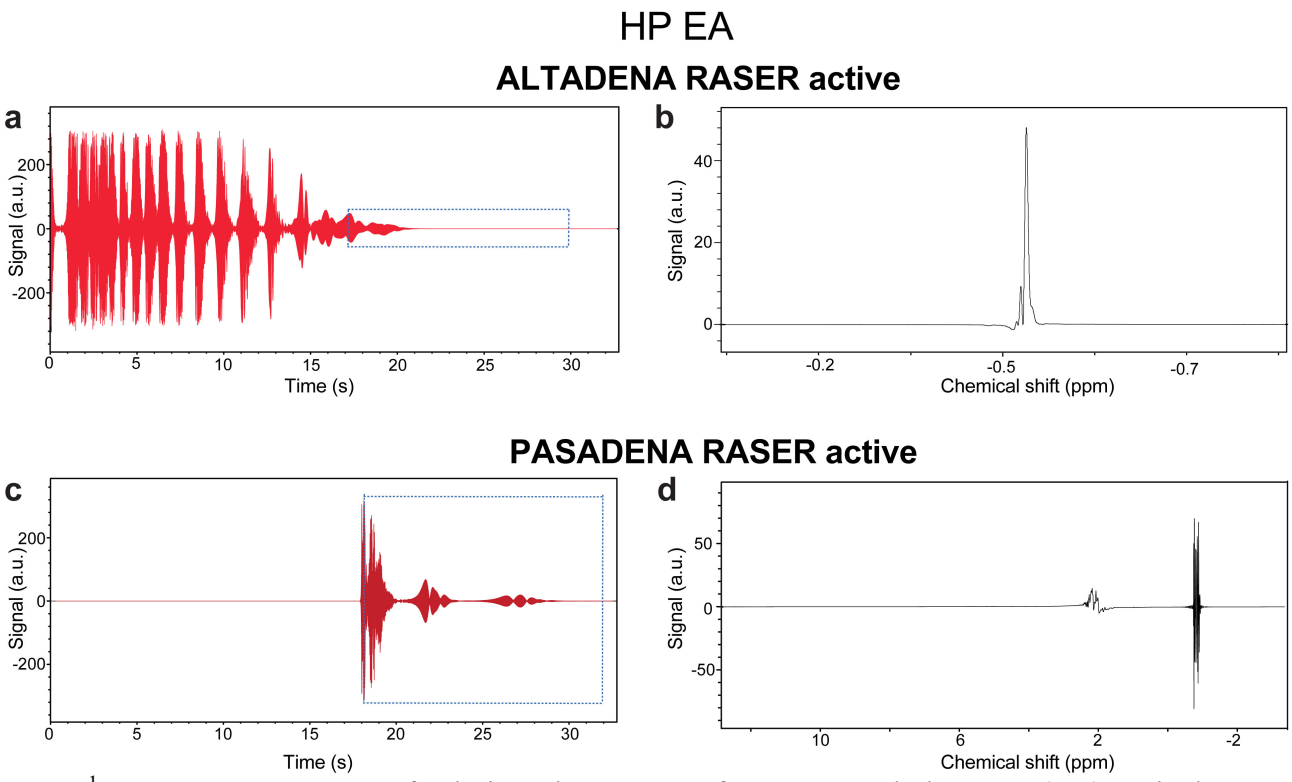

Figure S4. ^{1}H NMR spectroscopy of solution-phase PHIP of 0.4 M HP ethyl acetate (EA) probed at 1.4 T. The catheter used for bubbling *p*-H_2 was left inside the NMR tube resulting in shorter T_2* during signal acquisition. a) ALTADENA RASER active signal. b) Fourier spectrum of the region outline by the blue box in display a). c) PASADENA RASER active signal. d) Fourier spectrum of the region outline by the blue box in display c).

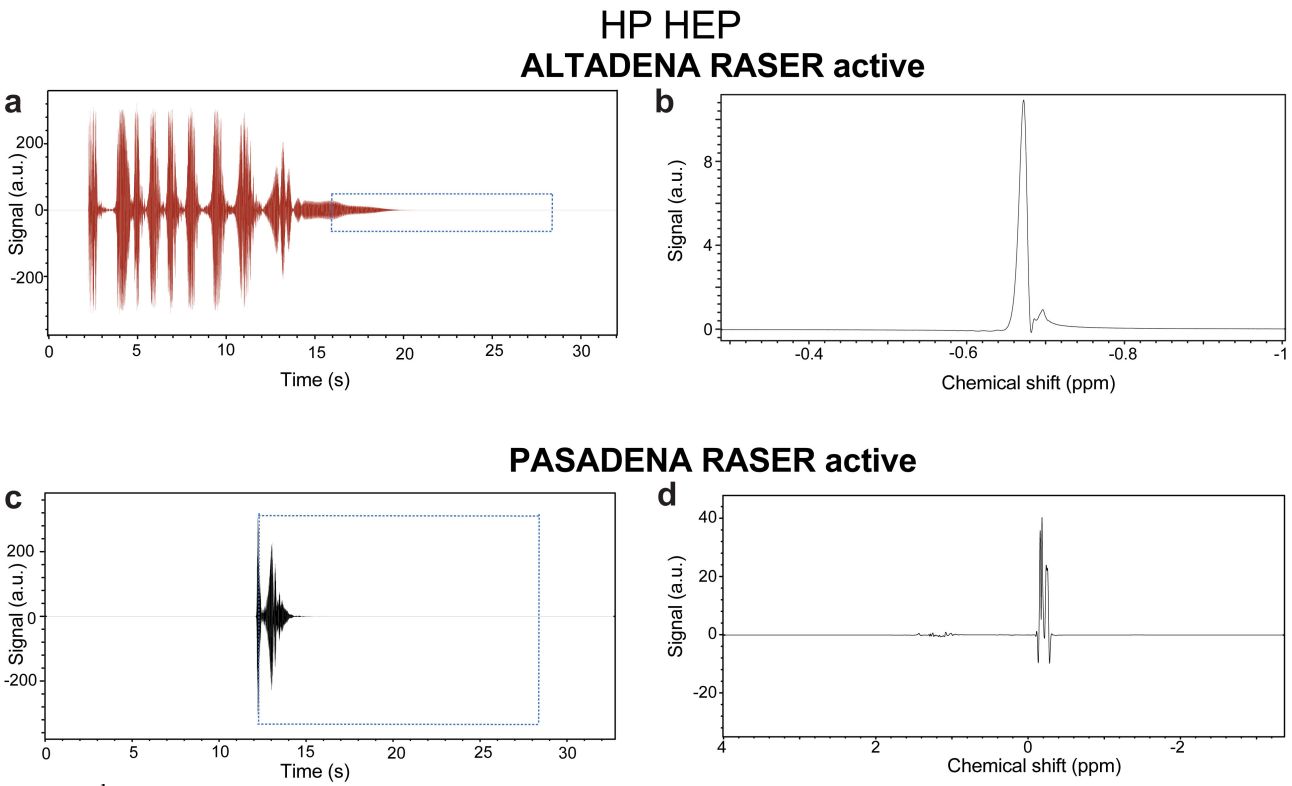

Figure S5. ^{1}H NMR spectroscopy of solution-phase PHIP of 0.4 M HP 2-hydroxyethyl propionate (HEP) probed at 1.4 T. The catheter used for bubbling *p*-H_2 was left inside the NMR tube resulting in shorter T_2* during signal acquisition. a) ALTADENA RASER active signal. b) Fourier spectrum of the region outline by the blue box in display a). c) PASADENA RASER active signal. d) Fourier spectrum of the region outline by the blue box in display c).