Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Extended Para-Hydrogenation Monitored by NMR Spectroscopy

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Supporting Information Provided:

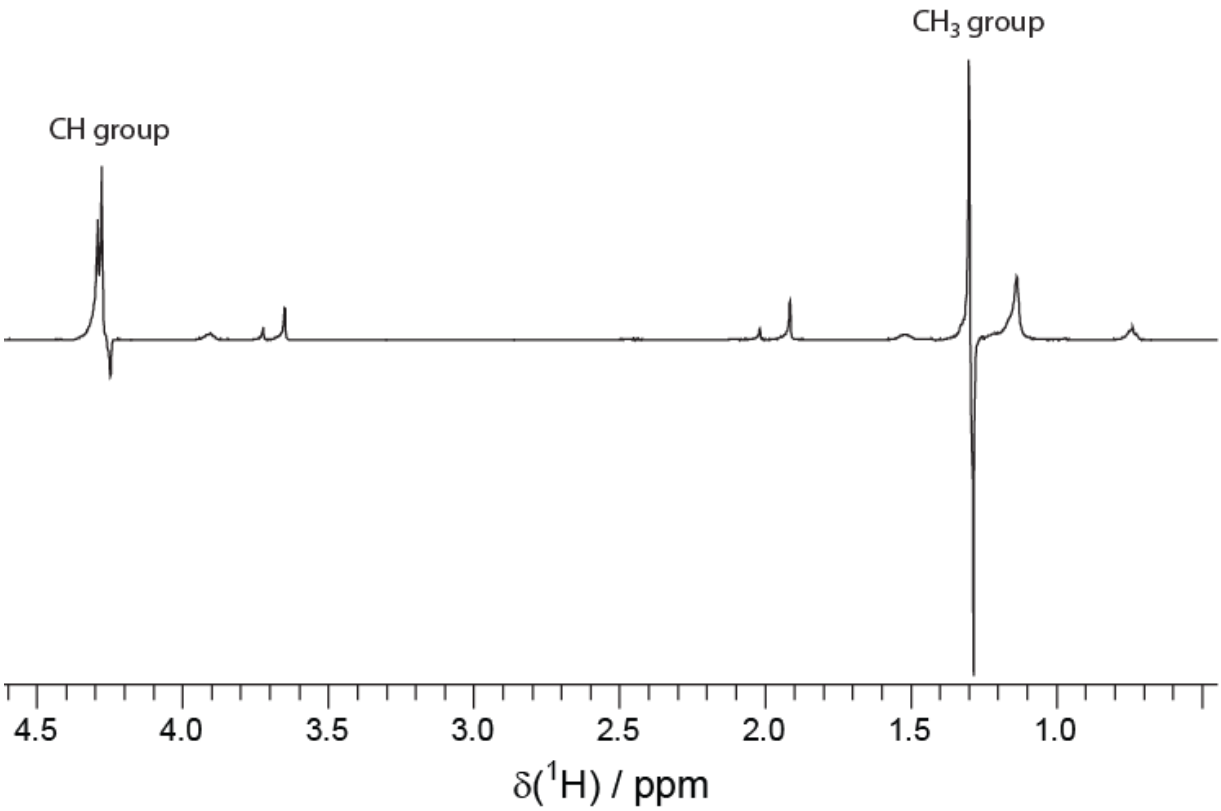

Figure S1: Single pulse experiments in the hydrogenation of methyl 2-acetamidoacrylate to methyl 2-acetamidopropanoate directly after hydrogenation with p-H_2.

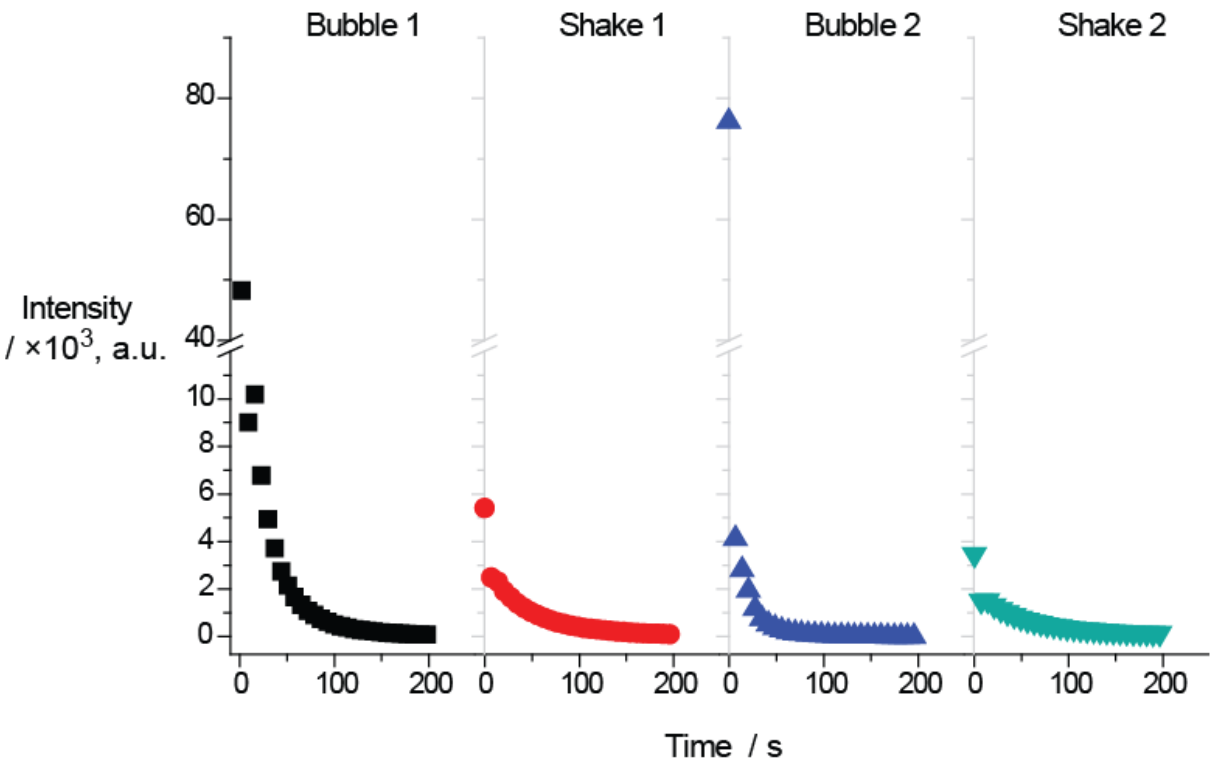

Figure S2: Decay of the hyperpolarized signal of the methylene group in Et-acrylate produced from the hydrogenation of Et-propiolate. Intensities were measured from the signals of consecutive OPSY experiments.

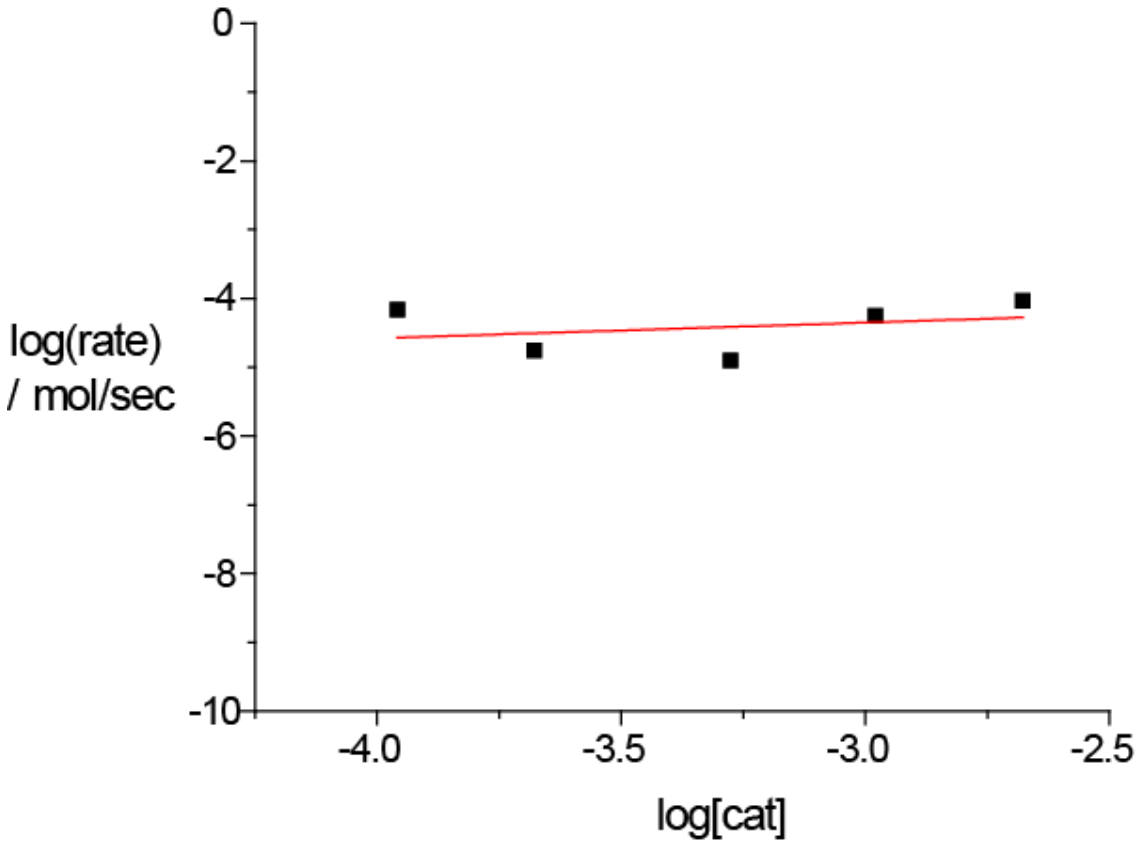

Figure S3: A double-log plot of reaction rate vs. catalyst concentration for the reaction of methyl 2-acetamidoacrylate (MAA) to methyl 2-acetamidopropanoate (MAP), where the rate was derived by dividing the number of mols of product by the hydrogenating time in seconds. The plot shows zero order kinetics of a sample in 100% D_2O.

Experimental Details

Reagents: All solid and liquid compounds were purchased from Sigma-Aldrich except for (-)-2,2-dimethyl-4,5-bis(diphenylphosphino)methyl-1,3-dioxolane ((-)DIOP) which was purchased from Alfa Aesar. All compounds were used without further purification.

Catalyst Preparation: 0.62 mg (1.25×10^{-6} mol) of (-)-2,2-dimethyl-4,5-bis(diphenylphosphino)methyl-1,3-dioxolane ((-)DIOP) was added to a solution of 0.42 mg (1.04×10^{-6} mol) of bis(1,5-cyclooctadiene)rhodium(I)tetrafluoroborate in 0. 5 mL of pre-degassed H_2O and 1.00 mg (3.7×10^{-6} mol) of SDS. The solution was stirred under Argon for 30 minutes at room temperature.

Hydrogenation in NMR Tube: 3.00 mg (2.09×10^{-5} mol) of methyl 2-acetamidoacrylate and 2.00 mg (7.40×10^{-6} mol) of SDS were dissolved in 0.5 mL of pre-degassed D_2O in a septum screw capped NMR tube. 0.5 mL of the catalyst solution previously prepared was added using a syringe and the solution was bubbled with *p*-H_2 gas.

NMR Spectroscopy: All experiments were conducted on an 11.74T ($\nu_0(^1H)$ = 499.859 MHz) Bruker Avance NMR spectrometer equipped with a multinuclear broadband inverse (BBI) liquids probe. *p*-H_2 enhanced ^1H NMR spectra acquired using a single-pulse experiment employed a $\pi/4$ pulse width of 4.1 μs. One transient was collected for each spectrum. For the Only Parahydrogen SpectroscopY (OPSY) sequence, $\pi/2$ pulse width of 8.2 μs and gradient strengths for the first and second gradients were 6.25 and 12.5 G/cm, both for a duration of 1.2 ms, were employed. A single transient was collected for each spectrum.

The conversion of hydrogen gas to *p*-H_2 was done using an in-house custom-built portable parahydrogen apparatus. For the conversion from ortho- to parahydrogen, a copper tube

containing activated charcoal catalyst was submerged in liquid nitrogen for approximately 15 min. The initial H_2 gas within the apparatus is purged before introducing *p*-H_2 to the sample at a low magnetic field, approximately 3 m away from the NMR magnet, and at ambient temperature and pressure. The gas was inserted into the solution in one of two ways: (i) the *p*-H_2 gas was bubbled through the septum of the NMR tube for 15 seconds (to relieve pressure in the tube, the cap was loosely screwed onto the NMR tube) and (ii) the NMR tube (equipped with a Young valve) was pressurized by adding 5 mL of *p*-H_2 gas to the headspace of the tube. The tube was then agitated (by shaking and/or inverting) for 20 seconds.

The sample was then placed at the top of the magnet and transported to the probe using the pneumatic air lift of the Bruker NMR system. The typical time required for the sample to go down the bore of the probe was measured as 11 s. Once a signal lock was established, the experiment was initiated. Sequential spectra were acquired in a 2-dimensional manner with a 7 second delay between each experiment.

After the hyperpolarized signal completely decayed, the sample was removed and "shaken"; the tube was inverted two times and vigorously shaken twice. The sample was placed back at the top of the magnet bore and brought back down to the probe. A new experiment was executed as soon as the signal lock was achieved. The total time from the start of adding *p*-H_2 to the solution to the establishment of the lock was approximately 40 s This time includes bubbling/shaking (15/25sec), walking over to the spectrometer and placing at the top of the bore (~10s), bringing it down with the airlift (11s) and getting a lock (3s).