Hyperpolarized Fumarate via Parahydrogen – Supporting Information

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1. Thermal equilibrium ^{1}H spectra

Figure S1 shows thermal ^{1}H reference spectra after *trans*-hydrogenation for a sample composed of 100 mM acetylenedicarboxylic acid disodium salt and 6 mM $[RuCp^*(MeCN)_3]PF_6$ in D_2O, both with and without 100 mM sodium sulphite present in solution. To react the sample, a high-pressure NMR tube containing the sample solution was pressurised with 5 bar of hydrogen gas and heated to 55°C. The sample tube was shaken vigorously by hand for 300 s. It can be observed that without sodium sulphite (Fig. S5a), the ratio of fumarate:maleate:succinate is 1:0.25:0.18. With 100 mM sodium sulphite in the sample solution (Fig. S5b), the ratio is 1:0:0.09 (i.e. there is no detectable maleate in the 32 transient ^{1}H NMR spectrum).

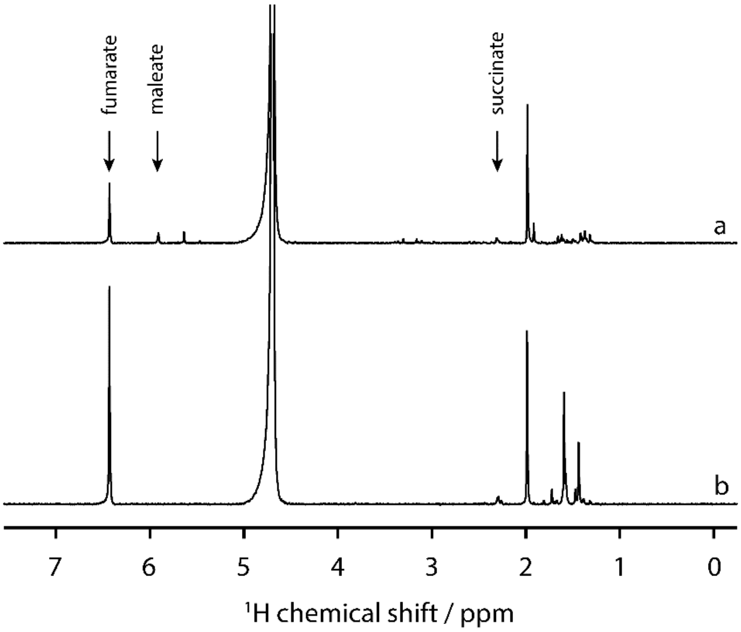

Figure S1: Thermal ^{1}H NMR spectra after trans-hydrogenation. (a) Reaction solution: 250mM acetylenedicarboxylic acid disodium salt, 6mM $[RuCp^*(MeCN)_3]PF_6$ in D_2O. (b) Reaction solution: as in (a) but with 100mM ammonium sulphite.

2. Relaxation data

Proton and carbon relaxation times were measured on [1-^{13}C]fumarate. The molecule is shown in Figure S2.

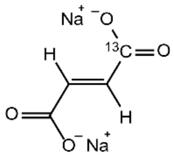

Figure S2: [1-13C]fumarate.

The ^{1}H T_1 was measured by inversion recovery, and the data is shown in Figure S3 along with the pulse sequence.

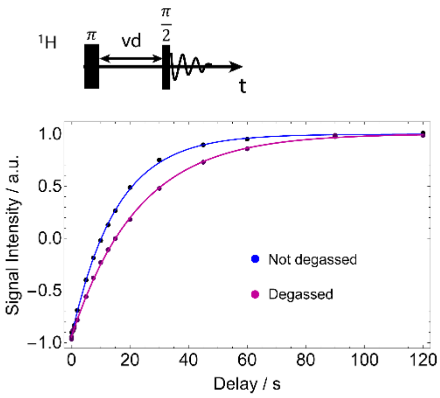

Figure S3: Inversion recovery pulse sequence (top) and the ^{1}H T_1 data (bottom).

The ^{13}C T_1 was measured by saturation recovery, and the data is shown in Figure S4 along with the pulse sequence.

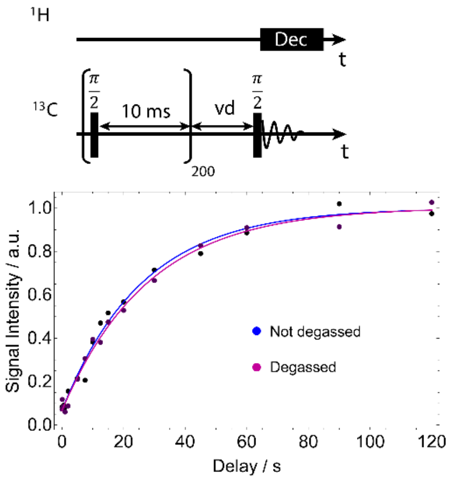

Figure S4: Saturation recovery pulse sequence (top) and the ^{13}C T_1 data (bottom).

The ^{1}H T_s was measured by the pulse sequence shown in Figure S5. Firstly, proton magnetization is converted into singlet order through the differential *J*-coupling to the ^{13}C spin, using the M2S pulse sequence. Then, a variable delay allows the singlet order to relax. This is followed by a T_{00} filter [1], which removes spin operators higher than rank-0. Finally, the S2hM sequence is applied to the ^{13}C channel to convert proton singlet order into ^{13}C magnetization for detection.

For the M2S and S2hM sequences, the values $\tau = 15.8$ ms and $n = 7$ were used.

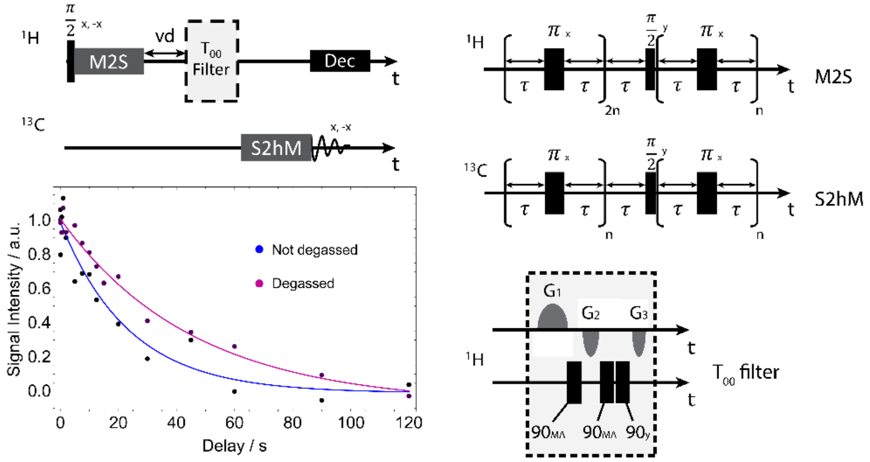

Figure S5: Pulse sequence used to measure the ^{1}H T_s (top left) and the data (bottom left). The individual components of the pulse sequence are shown to the right. Pulse and receiver phases are included, and MA stands for magic angle.

The T_{00} filter parameters are given in the table below.

PFG	Shape	Strength / Gcm^{-1}	Duration / ms
G_1	SINE.100	10	8.8
G_2	SINE.100	-10	4.8
G_3	SINE.100	-15	4.0

[1] Tayler M. C. D.; Levitt M. H. *J. Am. Chem. Soc.* 2013, **135**, 2120-2123