Hyperpolarized Fumarate via Parahydrogen – Supporting Information

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1. Thermal equilibrium 1H spectra

Figure S1 shows thermal 1H reference spectra after trans-hydrogenation for a sample composed of 100 mM acetylenedicarboxylic acid disodium salt and 6 mM [RuCp*(MeCN)3]PF6 in D2O, 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 1H NMR spectrum).

Figure S1: Thermal 1H NMR spectra after trans-hydrogenation. (a) Reaction solution: 250mM acetylenedicarboxylic acid disodium salt, 6mM [RuCp*(MeCN)3]PF6 in D2O. (b) Reaction solution: as in (a) but with 100mM ammonium sulphite.
2. Relaxation data

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

![Figure S2: [1-13C]fumarate.](image)

The \textsuperscript{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 $T_1$ data (bottom).](image)

The \textsuperscript{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 $T_1$ data (bottom).](image)

The \textsuperscript{1}H $T_1$ 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 \textsuperscript{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 \textsuperscript{13}C channel to convert proton singlet order into \textsuperscript{13}C magnetization for detection.

For the M2S and S2hM sequences, the values $\tau = 15.8$ ms and $n = 7$ were used.
The $T_{\text{OFF}}$ filter parameters are given in the table below.

<table>
<thead>
<tr>
<th>PFG</th>
<th>Shape</th>
<th>Strength / Gcm$^{-1}$</th>
<th>Duration / ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_1$</td>
<td>SINE.100</td>
<td>10</td>
<td>8.8</td>
</tr>
<tr>
<td>$G_2$</td>
<td>SINE.100</td>
<td>-10</td>
<td>4.8</td>
</tr>
<tr>
<td>$G_3$</td>
<td>SINE.100</td>
<td>-15</td>
<td>4.0</td>
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