Supplementary Figures

**Supplementary Figure 1: ethyl-acetate, no field cycle.** Single scan $^{13}\text{C}$-NMR spectrum of parahydrogenated ethyl acetate (80 mM) before application of field cycle: 60 ppm and 15 ppm correspond to the CH$_2$ and CH$_3$ carbon signals.

**Supplementary Figure 2: ethyl acetate, field Cycle.** Single scan $^{13}\text{C}$-NMR spectrum of parahydrogenated ethyl acetate (80 mM) after magnetic field cycle: high polarization is achieved on the $^{13}\text{C}$ carbonyl signal at 170 ppm.
Supplementary Figure 3: deuterated propargyl-alcohol. $^{13}$C NMR spectrum of parahydrogenated 1-d$_2$-2-propynyl-2-oxopropanoate after the application of field cycling procedure. Small polarization is observed only on the olefinic carbon signals.

Supplementary Figure 4: characterization of the hydrogenation product: $^{13}$C spectrum. $^{13}$C-NMR spectrum (thermal equilibrium) of 2-oxo-propionic acid allyl ester obtained from parahydrogenation of 2-propynyl-2-oxopropanoate in Chloroform/methanol (10/1) mixture.
Supplementary Figure 5: characterization of the hydrogenation product: $^1$H spectrum. $^1$H-NMR spectrum (thermal equilibrium) of 2-oxo-propionic acid allyl ester obtained from parahydrogenation of 2-propynyl-2-oxopropanoate in Chloroform/methanol (10/1) mixture.
Supplementary Figure 6: spin states population. Singlet state percentage on each spin state as a function of the magnetic field after the non-adiabatic passage from earth to low field. A and b: states states $\psi_4$ (blue), $\psi_5$ (magenta) and $\psi_6$ (turquoise) derived from mixing of $S'_0 T'_0 \beta$ and $T_0 \alpha$; a) ethyl acetate J couplings ($J_{\alpha\beta}=3.2$ Hz, $J_{\alpha\gamma}=1.7$Hz, $J_{\alpha\delta}=7.5$ Hz); b) hydroxyl ethyl propiolate J couplings ($J_{\alpha\beta}=7.2$ Hz, $J_{\alpha\gamma}=-5.6$Hz, $J_{\alpha\delta}=7.5$ Hz). C and d: states $\psi_1$ (blue), $\psi_2$ (magenta) and $\psi_3$ (turquoise) derived from mixing of $S'_0 \alpha, T'_0 \alpha$ and $T_0 \beta$; c) ethyl acetate; d) hydroxyl ethyl propiolate. Notice the inversion between populations of the states $\psi_1$ and $\psi_3$ while there is no inversion between populations of the states with spin $\frac{1}{2}$. 
Supplementary Methods

Transition probability calculations

The spin states of an AA’X spin system (where A and A’ are the two parahydrogen protons and X is the heteroatom), are calculated using the basis spin states $\varphi_1$ to $\varphi_8$

$\varphi_1 = |\alpha\alpha\alpha\rangle$,

$\varphi_2 = |\alpha\alpha\beta\rangle$, $\varphi_3 = \frac{1}{\sqrt{2}}(|\alpha\beta + \beta\alpha\rangle\alpha\rangle$, $\varphi_4 = \frac{1}{\sqrt{2}}(|\alpha\beta + \beta\alpha\rangle\beta\rangle$,

$\varphi_5 = \frac{1}{\sqrt{2}}(|\alpha\beta - \beta\alpha\rangle\alpha\rangle$, $\varphi_6 = \frac{1}{\sqrt{2}}(|\alpha\beta - \beta\alpha\rangle\beta\rangle$, $\varphi_7 = |\beta\beta\alpha\rangle$,

$\varphi_8 = |\beta\beta\beta\rangle$.

and we calculate the eigenstates of the Hamiltonian

$$ H = -v_H (I_x^A + I_x^A) - v_x I_z^X + J_{AA'}I_A I_A' + J_{AX}I_z^A I_z^X + J_{A'X}I_z^{A'} I_z^X $$

(1)

The Hamiltonian sub-matrix corresponding to mixing of the states S$\alpha$-T$_0$$\alpha$ is

$$
\begin{pmatrix}
\frac{-v_x}{2} + \frac{I_{AA'}}{4} & \frac{I_{AX} - J_{AX}}{4} \\
\frac{I_{AX} - J_{AX}}{4} & \frac{-v_x}{2} - \frac{3I_{AA'}}{4}
\end{pmatrix}
$$

(2)

And that corresponding to mixing of the states S$\beta$-T$_0$$\beta$ is

$$
\begin{pmatrix}
\frac{v_x}{2} + \frac{I_{AA'}}{4} & \frac{-I_{AX} + J_{AX}}{4} \\
\frac{-I_{AX} + J_{AX}}{4} & \frac{v_x}{2} + \frac{3I_{AA'}}{4}
\end{pmatrix}
$$

(3)

Eigenstates are numerically calculated using Matlab 7.0 and the J coupling values $J_{HX}$=7.2, $J_{H'X}$=-5.6Hz, $J_{HH'}$=7.5 Hz for hydroxyl ethyl propiolate and $J_{HX}$=3.2 Hz, $J_{H'X}$=1.7 Hz, $J_{HH'}$=7.5 Hz for ethyl acetate:

$T_0'\alpha = c_{11}(\alpha\beta + \beta\alpha)\alpha + c_{12}(\alpha\beta - \beta\alpha)\alpha$ (4a)

$S'\alpha = c_{21}(\alpha\beta + \beta\alpha)\alpha + c_{22}(\alpha\beta - \beta\alpha)\alpha$ (4b)

Ethyl acetate: c$_{11}$=-0.99, c$_{12}$=-0.09, c$_{21}$=0.09, c$_{22}$=-0.99

Hydroxy ethyl propiolate: c$_{11}$=-0.8676, c$_{12}$=-0.4972, c$_{21}$=0.4972, c$_{22}$=-0.8676

$T_0'\beta = d_{11}(\alpha\beta + \beta\alpha)\beta + d_{12}(\alpha\beta - \beta\alpha)\beta$ (4c)

$S'\beta = d_{21}(\alpha\beta + \beta\alpha)\beta + d_{22}(\alpha\beta - \beta\alpha)\beta$ (4d)
Ethyl acetate: $d_{11} = -0.99$, $d_{12} = -0.09$, $d_{21} = -0.09$, $d_{22} = 0.99$

Hydroxy ethyl propiolate: $d_{11} = -0.8676$, $d_{12} = -0.4972$, $d_{21} = -0.4972$, $d_{22} = 0.8676$

Transition probability is $|\langle S'\alpha | I_x^X | T_0^\alpha \beta \rangle|^2 = (c_{21}^* d_{11})^2 + (c_{22}^* d_{12})^2 = 0.37$ (HEP); 0.02 (ethyl acetate)
And $|\langle S'\beta | I_x^X | T_0^\alpha \alpha \rangle|^2 = (c_{11}^* d_{21})^2 + (c_{12}^* d_{22})^2 = 0.37$ (HEP); 0.02 (ethyl acetate)

### Magnetic field cycle

The spin states $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, at earth field are calculated as reported above and the coefficients of singlet-triplet linear combination are obtained. The non-adiabatic passage to low field can be considered as a sudden transformation of these states, therefore the spin states at low magnetic field are calculated using the states $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, (total spin $\frac{1}{2}$) and the low field Hamiltonian (5)

$$ H = -\nu_H (I_z^X + I_z^{X'}) - \nu_x I_x^X + J_{AA} I_A I_A + J_{AAX} I_A X + J_{AAX} X A I^X $$

The Hamiltonian sub-matrix associated with the states having total spin $\frac{1}{2}$ is

$$
\begin{pmatrix}
H_{11} & H_{12} & H_{13} \\
H_{21} & H_{22} & H_{23} \\
H_{31} & H_{32} & H_{33}
\end{pmatrix}
\begin{pmatrix}
c_{11} & c_{12} & 0 \\
c_{21} & c_{22} & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

While that related to the states $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$, is

$$
\begin{pmatrix}
H_{11} & H_{12} & H_{13} \\
H_{21} & H_{22} & H_{23} \\
H_{31} & H_{32} & H_{33}
\end{pmatrix}
\begin{pmatrix}
d_{11} & d_{12} & 0 \\
d_{21} & d_{22} & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

The eigenstates are calculated numerically using the following functions written with Matlab 7.7.0 (functions LowField and LowFieldB).

Population of each spin states derives from the singlet state contribution to that state. Figure 1S (c and d) reports spin states population after non-adiabatic transport of the parahydrogenated molecules from earth field to low field for the states with total spin $\frac{1}{2}$ (states $\psi_1$, $\psi_2$ and $\psi_3$ derived from mixing of $T_0^\alpha$, $T_0^\beta$, $T_0^\alpha$, $T_0^\beta$).

$$\psi_1 = c'_{11} T_0^\alpha + c'_{12} T_0^\beta + c'_{13} T_0^\alpha$$
\[
\psi_2 = c'_2T_0\alpha' + c'_2S'\alpha + c'_2T_4\beta
\]
\[
\psi_3 = c'_3T_0\alpha' + c'_3S'\alpha + c'_3T_4\beta
\]

In the upper part of the figure (a and b) are reported the spin states \(\psi_4\), \(\psi_5\) and \(\psi_6\) derived from mixing of \(T_0\beta, S'\beta, T_-\alpha\).

\[
\psi_4 = d'_1T_0\beta + d'_2S'\beta + d'_3T_4\alpha
\]
\[
\psi_5 = d'_1T_0\beta + d'_2S'\beta + d'_3T_4\alpha
\]
\[
\psi_6 = d'_1T_0\beta + d'_2S'\beta + d'_3T_4\alpha
\]

Note that there in an inversion between the spin state population of the most stable state (state \(\alpha\alpha\beta\) at high field) and the state \(S'\alpha\) (high field state) therefore the most stable state becomes the most populated one. Conversely, there is no inversion between population of the three spin states with total spin \(-\frac{1}{2}\) (states \(T_0\beta, S'\beta, T_-\alpha\)) at low magnetic field.

It can be derived from figure 1S that for hydroxyethyl-propilate, before the fast transport to low field, population of para-hydrogen is shared between \(S'\alpha\) (red) and \(T_0\alpha\) (green) states, population of \(S'\alpha\) state is 0.9 and that of the \(T_0\alpha\) is 0.1. At low magnetic field, after the non adiabatic passage, population of the intermediate state (state \(S'\alpha\) at earth field) is about 0.1 while that of the most stable state (state \(\alpha\alpha\beta\) at earth field) is 0.7. Population of the spin states is maintained after the adiabatic transport to earth field, therefore intensity of the hyperpolarized transitions is uniquely due to the difference between spin states population and is 0.6.

Conversely, if ethyl acetate is considered, at earth field, before field cycling, all the singlet state population is on the state \(S'\alpha\) (0.99) while the \(T_0\alpha\) state is almost coincident with the triplet state \(T_0\). After the nonadiabatic passage to low field (zero field) all the singlet state population is transferred to the most stable state (state \(\alpha\alpha\beta\) at earth field) and the intensity of the hyperpolarized transitions is close to unit, therefore is 1.68 times than that of HEP.

%paraHydrogen addition at earth field: calculation of the spin states population

function C=LowField(JHH,JHC,JH1C)

nH=100; nC=nH*0.2514345;

I11=0.5*(-nC+0.5*JHH); I12=0.25*(JHC-JH1C); I22=0.5*(-nC-1.5*JHH);

M=[I11, I12; I12, I22]; %Hamiltonian matrix with basis functions (ab+ba)a, (ab-ba)a

[V,T]=eig(M)

c11=V(1,1); c12=V(2,1); c21=V(1,2); c22=V(2,2); % c12, c22: singlet state coefficients
I12=0.25*(JHC-JH1C);
I13=1/(2*sqrt(2))*(JHC+JH1C); 
I23=1/(2*sqrt(2))*(JH1C-JHC);

% calculation of the spin states while decreasing the magnetic field strength
for t=1:1000;
    nH=nH-0.1; nC=nH*0.2514345; % gradually decreasing magnetic field strength
    I11=0.5*(-nC+0.5*JHH);
    I22=0.5*(-nC-1.5*JHH); % old: I22=0.5*(nC-1.5*JHH);
    I33=-nH+(nC/2)+0.25*(JH-HC-JH1C);
    H11=(c11^2)*I11+c11*c12*I12*2+(c12^2)*I22;
    H12=c11*c21*I11+c11*c22*I12+c12*c21*I12+c12*c22*I22;
    H13=c11*I13+c12*I23;
    H22=c21^2*I11+c22^2*2*I22+c22*c21*I12*2;
    H23=c21*I13+c22*I23;
    H33=I33;

    A=[H11,H12,H13;H12,H22,H23;H13,H23,H33]; % Hamiltonian sub-matrix corresponding to mixing of the states S'-T'-aa?

[V,T]=eig(A);

% singlet state contribution to the most stable state
F(t)=((V(1,1))*(c12))^2+(((V(2,1)))*(c22))^2;

% singlet state contribution to the intermediate state
D(t)=((V(1,2))*(c12))^2+((V(2,2))*(c22))^2;

% singlet state contribution to the most instable state
E(t)=((V(1,3))*(c12))^2+((V(2,3))*(c22))^2;

    x(t)=nH/42.54;
end

C=[V,T];
y=F; y2=D; y3=E;

plot(x,y,x,y2,x,y3);

-------------------------------
%paraHydrogen addition at earth field: calculation of the spin states population %states T0b, Sb, bba

function C=LowFieldB(JHH,JHC,JH1C)
nH=100; nC=nH*0.2514345;
I11=0.5*(nC+0.5*JHH); I12=0.25*(-JHC+JH1C); I22=0.5*(nC-1.5*JHH);
M=[I11,I12;I12,I22]; %Hamiltonian matrix with basis functions (ab+ba)a, (ab-ba)a
[V,T]=eig(M)
c11=V(1,1); c12=V(2,1);c21=V(1,2); c22=V(2,2); % c12, c22: singlet state coefficients

I12=0.25*(-JHC+JH1C);
I13=1/(2*sqrt(2))*(JHC+JH1C); %
I23=1/(2*sqrt(2))*(JH1C-JHC); %

% calculation of the spin states while decreasing the magnetic field strength
for t=1:1000;
    nH=nH-0.1; nC=nH*0.2514345; % gradually decreasing magnetic field strength
    %I11=((-nC+0.5*JHH);
    I11=0.5*(nC+0.5*JHH);
    I22=0.5*(nC-1.5*JHH);
    %I13=(1/2*sqrt(2))*(JHC+JH1C);
    %I23=(1/2*sqrt(2))*(JH1C-JHC);
    I33=nH- (nC/2)+0.25*(JHH-JHC-JH1C);
    H11=(c11^2)*I11+c11*c12*I12*2+(c12^2)*I22;
    H12=c11*c12*I11+c11*c22*I12+c12*c11*I12+c12*c22*I22;
    H13=c11*I13+c12*I23;
    H22=c21^2*I11+c22^2*I22+c22*c21*I12+c21*I12*2;
    H23=c21*I13+c22*I23;
    H33=I33;
    A=[H11,H12,H13;H12,H22,H23;H13,H23,H33]; % Hamiltonian sub-matrix corresponding to mixing of the states S’-T’-aa?
    [V,T]=eig(A);
    % singlet state contribution to the most stable state
    F(t)=((V(1,1))*(c12))^2+(((V(2,1)))*(c22))^2;
    % singlet state contribution to the intermediate state
    D(t)=(V(1,2)*((c12)))^2+((V(2,2))*((c22)))^2;
    % singlet state contribution to the most instable state
    E(t)=(V(1,3)*((c12)))^2+((V(2,3))*((c22)))^2;
    x(t)=nH/42.54;
end
C = [V, T];
y = F; y2 = D; y3 = E;
plot(x, y, x, y2, x, y3);
%plot(x, y, x, y2);
%plot(x, y)