Supplementary Information: Probing Scalar Coupling Differences via Long-Lived Singlet States

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S1. Expanded Theory

A number of works have explored the manipulation of singlet states via spin-locking and have presented various aspects of the theoretical background [1–7]. Here, we provide a more in-depth derivation of our key results, equations 4-8 in the main text.

In the four-spin systems studied here, geminal spin-spin coupling dominates, so the spin states of each methylene group should be considered first. Each proton pair consists of two coupled spin-1/2 nuclei with resonance frequencies \(\nu_1\) and \(\nu_2\) (in units of Hz), with \(\Delta \nu = \nu_1 - \nu_2\). The two spins experience a scalar coupling \(J\), and dipolar couplings are eliminated due to fast reorientation of the molecule in the liquid state. The Hamiltonian for this system written in the singlet/triplet basis is described by

\[
\hat{H}_0 = h \begin{bmatrix}
-\frac{\nu_1 + \nu_2}{2} + \frac{J}{4} & 0 & 0 & 0 \\
0 & \frac{J}{4} & 0 & \frac{\Delta \nu}{2} \\
0 & 0 & \frac{\nu_1 + \nu_2}{2} + \frac{J}{4} & 0 \\
0 & \frac{\Delta \nu}{2} & 0 & -\frac{3J}{4}
\end{bmatrix},
\]

(S1)

where the eigenstates are (from left to right) the three triplet states, \(|T_\downarrow\rangle\), \(|T_0\rangle\), and \(|T_\uparrow\rangle\), and one singlet state, \(|S_0\rangle\).
These can be represented as symmetric and antisymmetric combinations of the product states:

\[
|T_\pm\rangle = \frac{|\uparrow\uparrow\rangle \pm |\downarrow\downarrow\rangle}{\sqrt{2}}
\]

\[
|T_0\rangle = \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}
\]

\[
|S_0\rangle = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}.
\]  

(S2)

It is convenient to work in the rotating frame at the average resonance frequency of the nuclei, so that \((\nu_1 + \nu_2)/2 = 0\). Then

\[
\hat{H}_0 = h \begin{bmatrix}
\frac{J}{4} & 0 & 0 & 0 \\
0 & \frac{J}{4} & 0 & \frac{\Delta \nu}{2} \\
0 & 0 & \frac{J}{4} & 0 \\
0 & \frac{\Delta \nu}{2} & 0 & -\frac{3J}{4}
\end{bmatrix}.
\]  

(S3)

Spin-locking with a nutation frequency \(\nu_n\) applied on resonance with the triplet transitions produces off-diagonal elements that drive transitions between triplet states:

\[
\hat{H}_{SL} = h \begin{bmatrix}
\frac{J}{4} & \frac{\nu_n}{\sqrt{2}} & 0 & 0 \\
\frac{\nu_n}{\sqrt{2}} & \frac{J}{4} & \frac{\nu_n}{\sqrt{2}} & \frac{\Delta \nu}{2} \\
0 & \frac{\nu_n}{\sqrt{2}} & \frac{J}{4} & 0 \\
0 & \frac{\Delta \nu}{2} & 0 & -\frac{3J}{4}
\end{bmatrix}.
\]  

(S4)

Since the spin-locking is on for a long time relative to a precession period, the triplet states can be rediagonalized to find the true eigenstates in the presence of spin-locking. The new dressed-state Hamiltonian is

\[
\hat{H}_{SL,\text{dressed}} = h \begin{bmatrix}
\frac{J}{4} - \nu_n & 0 & 0 & \frac{\Delta \nu}{2\sqrt{2}} \\
0 & \frac{J}{4} & 0 & 0 \\
0 & 0 & \frac{J}{4} + \nu_n & -\frac{\Delta \nu}{2\sqrt{2}} \\
\frac{\Delta \nu}{2\sqrt{2}} & 0 & -\frac{\Delta \nu}{2\sqrt{2}} & -\frac{3J}{4}
\end{bmatrix}.
\]  

(S5)
and the resulting dressed states are

\[ |\phi_-\rangle = \frac{1}{2} (|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle - |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \]

\[ = \frac{1}{2} ((T_- + |T_+\rangle) - \frac{1}{\sqrt{2}} |T_0\rangle) \]

\[ |\phi_0\rangle = \frac{1}{\sqrt{2}} (|\downarrow\downarrow\rangle - |\uparrow\uparrow\rangle) = \frac{1}{\sqrt{2}} ((T_+ - |T_-\rangle) \]

\[ |\phi_+\rangle = \frac{1}{2} (|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle + |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \]

\[ = \frac{1}{2} ((T_- + |T_+\rangle) + \frac{1}{\sqrt{2}} |T_0\rangle) \]

\[ |\phi_S\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = |S_0\rangle. \] (S6)

The states $|\phi_0\rangle$ and $|\phi_S\rangle$ are split by energy $J$ and are unaffected by the strength of spin-locking, whereas the energies of states $|\phi_-\rangle$ and $|\phi_+\rangle$ have a linear dependence on $\nu_n$. This energy level dependence on spin-lock power enables triplet-singlet polarization transfer when the system is held at the spin-lock induced crossing (SLIC) condition, $\nu_n = J$.

The spin state for two pairs of strongly-coupled spins can be written as a product state with the form $|\phi_1\phi_2\rangle$. We are interested in the two particular states $|TS_0\rangle$ and $|S_0T\rangle$, where $|S_0\rangle = |\phi_S\rangle$ and $|T\rangle$ is a generalized triplet state given by

\[ |T\rangle_i = \alpha_i|\phi_+\rangle_i + \beta_i|\phi_0\rangle_i + \gamma_i|\phi_-\rangle_i, \] (S7)

and $\alpha_i$, $\beta_i$, and $\gamma_i$ are real amplitudes for spin pair $i$. To preserve normalization we require

\[ \alpha_i^2 + \beta_i^2 + \gamma_i^2 = 1. \] (S8)

Writing $|T\rangle$ this way allows us to compact the six eigenstates into two. The Hamiltonian matrix describing this two-level system consists of energy terms $E_1$ and $E_2$ and a coupling term $C$:

\[ \hat{H} = \hbar \begin{bmatrix} E_1 & C \\ C & E_2 \end{bmatrix}. \] (S9)

To determine the coupling term $C$, the contributions from all interpair scalar couplings must be considered. The scalar coupling Hamiltonian for any two spins $i$ and $j$ is

\[ \hat{H}_{J,ij} = J_{ij} \left( I_{iz} I_{jz} + I_{ix} I_{jx} + I_{iy} I_{jy} \right) \]

\[ = J_{ij} \left( I_{iz} I_{jz} + \frac{I^+_i I^-_j + I^-_i I^+_j}{2} \right). \] (S10)

Since each of the four spins interacts with the other, the scalar coupling Hamiltonian can be consolidated as

\[ \hat{H}_J = \hat{H}_{J,1a2a} + \hat{H}_{J,1b2b} + \hat{H}_{J,1a2b} + \hat{H}_{J,1b2a}, \] (S11)
where the number indicates spin pair and the letter identifies each spin within the pair. The coupling between \(|TS_0\rangle\) and \(|S_0T\rangle\) is then given by

\[
\langle TS_0|\hat{H}_J|S_0T\rangle = (\alpha_1\langle \phi_+\phi_S | + \beta_1 \langle \phi_0 \phi_S | + \gamma_1 \langle \phi_- \phi_S | ) \left( \hat{H}_{J,1a2a} + \hat{H}_{J,1b2b} + \hat{H}_{J,1a2b} + \hat{H}_{J,1b2a} \right) \\
\times (\alpha_2|\phi_S \phi_+ \rangle + \beta_2 |\phi_S \phi_0 \rangle + \gamma_2 |\phi_S \phi_- \rangle).
\]

(S12)

There are a total of 36 interactions that need to be calculated, which can be divided into 12 with homogeneous coefficients such as \(\alpha_1\alpha_2\), and 24 with heterogeneous coefficients such as \(\alpha_1\beta_2\). As an example, the term \(\alpha_1\alpha_2\langle \phi_+\phi_S|\hat{H}_{J,1a2a}|\phi_S\phi_+\rangle\) can be calculated by expanding the definitions of \(|\phi_S\rangle\), \(|\phi_+\rangle\), and \(\hat{H}_{J,1a2a}\) to give

\[
\alpha_1\alpha_2\langle \phi_+\phi_S|\hat{H}_{J,1a2a}|\phi_S\phi_+\rangle = \alpha_1\alpha_2 \frac{J_{1a2a}}{8} \left( \langle \uparrow \downarrow | + \langle \downarrow \uparrow | + \langle \uparrow \uparrow | + \langle \downarrow \downarrow | \right) \left( \langle \uparrow \downarrow | - \langle \downarrow \uparrow | \right)
\]

\[
\times \left( \frac{\hat{I}_{1a2a} + \hat{I}_{2a2a}}{2} \right) \left( \langle \uparrow \downarrow | - \langle \downarrow \uparrow | \right) \left( \langle \uparrow \downarrow | + \langle \downarrow \uparrow | \right)
\]

\[
= \alpha_1\alpha_2 \frac{J_{1a2a}}{8} \left( \langle \uparrow \downarrow | + \langle \downarrow \uparrow | + \langle \uparrow \uparrow | + \langle \downarrow \downarrow | \right) \left( \langle \uparrow \downarrow | - \langle \downarrow \uparrow | \right)
\]

\[
\times \left[ \frac{(\langle \uparrow \downarrow | + \langle \downarrow \uparrow |)(\langle \uparrow \downarrow | - \langle \downarrow \uparrow |)}{4} + \frac{(\langle \uparrow \downarrow | + \langle \downarrow \uparrow |)(\langle \uparrow \downarrow | + \langle \downarrow \uparrow |)}{2} \right]
\]

\[
= \alpha_1\alpha_2 \frac{J_{1a2a}}{4}.
\]

(S13)

Solving all other components of equation S12 in the same way gives

\[
C = \langle TS_0|\hat{H}_J|S_0T\rangle = \frac{J_{1a2a} + J_{1b2b} - J_{1a2b} - J_{1b2a}}{4}(\alpha_1\alpha_2 + \beta_1\beta_2 + \gamma_1\gamma_2).
\]

(S14)

Note that another set of antisymmetric interactions is also present that can drive polarization between singlet and triplet states:

\[
\langle \phi_0\phi_+|\hat{H}_J|\phi_+\phi_S\rangle = \frac{J_{1a2a} - J_{1b2b} - J_{1a2b} + J_{1b2a}}{4}
\]

\[
\langle \phi_+\phi_0|\hat{H}_J|\phi_+\phi_S\rangle = -\frac{J_{1a2a} + J_{1b2b} + J_{1a2b} - J_{1b2a}}{4}
\]

\[
\langle \phi_0\phi_-|\hat{H}_J|\phi_-\phi_S\rangle = -\frac{J_{1a2a} + J_{1b2b} + J_{1a2b} - J_{1b2a}}{4}
\]

\[
\langle \phi_-\phi_0|\hat{H}_J|\phi_-\phi_S\rangle = \frac{J_{1a2a} - J_{1b2b} - J_{1a2b} + J_{1b2a}}{4}
\]

\[
\langle \phi_+\phi_-|\hat{H}_J|\phi_0\phi_S\rangle = \frac{J_{1a2a} - J_{1b2b} - J_{1a2b} + J_{1b2a}}{4}
\]

\[
\langle \phi_-\phi_+|\hat{H}_J|\phi_0\phi_S\rangle = -\frac{J_{1a2a} + J_{1b2b} + J_{1a2b} - J_{1b2a}}{4}
\]

(S15)

For our experiments, these terms should be significantly smaller than \(C\) because the differences within \textit{syn} and \textit{anti} \(J\) coupling combinations, \(J_{1a2a} - J_{1b2b}\) and \(J_{1a2b} - J_{1b2a}\), are generally much smaller than the differences between \textit{syn} and \textit{anti} \(J\) couplings. Moreover, the resonance condition needed to enable these transitions is different from the resonance condition for singlet transfer. Nevertheless, these interactions could be an interesting focus for a future study.
The energies $E_1$ and $E_2$ for $|TS_0\rangle$ and $|S_0T\rangle$, respectively, are determined by the intrapair $J$ couplings $J_{1a1b}$ and $J_{2a2b}$, and by the effective nutation frequencies $\nu_{n,1}$ and $\nu_{n,2}$. The energy operator is

$$\hat{H}_E = \nu_{1a} \hat{I}_{1ax} + \nu_{1b} \hat{I}_{1bx} + \nu_{2a} \hat{I}_{2ax} + \nu_{2b} \hat{I}_{2bx} + J_{1a1b} \hat{I}_{1a} \cdot \hat{I}_{1b} + J_{2a2b} \hat{I}_{2a} \cdot \hat{I}_{2b}$$

$$+ \frac{\nu_{n,1}}{2} \hat{I}_{1ax} + \frac{\nu_{n,1}}{2} \hat{I}_{1bx} + \frac{\nu_{n,2}}{2} \hat{I}_{2ax} + \frac{\nu_{n,2}}{2} \hat{I}_{2bx}. \tag{S16}$$

The analysis is simplified by starting with eigenstates $|\phi\rangle$, since their energy levels have no $\nu_i (B_0)$ dependence and a linear dependence on $\nu_n$. Note, however, that the $\nu \hat{I}_z$ operators can mix triplet eigenstates when the spectrometer resonance frequency does not match the spin resonance frequency, as discussed in the main text. Since the energy of a product state is the sum of its components’ energies, we can add the appropriate energy terms from Eq. S5 to find

$$E_1 = \langle TS_0 | \hat{H}_E | TS_0 \rangle$$

$$= \frac{J_{1a1b}}{4} - \frac{3J_{2a2b}}{4} + (\alpha_1^2 - \gamma_1^2)\nu_{n,1}$$

$$E_2 = \langle S_0T | \hat{H}_E | S_0T \rangle$$

$$= \frac{J_{2a2b}}{4} - \frac{3J_{1a1b}}{4} + (\alpha_2^2 - \gamma_2^2)\nu_{n,2}. \tag{S17}$$

The spin-lock nutation frequencies, $\nu_{n,1}$ and $\nu_{n,2}$, depend on RF amplitude and transmitter frequency. For a continuous application of RF power on resonance with a spin, the nutation frequency is directly proportional to $B_1$, the transverse magnetic field in the rotating frame: $\nu_n = -\gamma_n B_1/2\pi$, where $\gamma_n$ is the gyromagnetic ratio of the nucleus. However, for off-resonance spins, the effective nutation frequency changes with the detuning, $\Delta \nu$, and is given by

$$\nu_{n,\text{effective}} = \sqrt{\nu_n^2 + \Delta \nu^2}, \tag{S18}$$

where $\nu_n$ is the nutation frequency for a spin on resonance [8]. For two spin pairs, one on resonance and one detuned by $\Delta \nu$, the difference in spin-lock nutation frequencies, $\Delta \nu_n$, is

$$\Delta \nu_n = \sqrt{\nu_n^2 + \Delta \nu^2} - \nu_n. \tag{S19}$$

Just as the original SLIC method used spin-lock nutation frequency $|\nu_n| = |J|$ to match the energies of singlet and triplet states, setting $|\Delta \nu_n| = |\nu_{n,1} - \nu_{n,2}| = |J_{1a1b} - J_{2a2b}|$ matches the energy levels of $|TS_0\rangle$ and $|S_0T\rangle$ such that $C$ induces Rabi oscillations between the two states. For example, at resonance the energy difference is

$$E_1 - E_2 = J_{1a1b} - J_{2a2b} + (\alpha_1^2 - \gamma_1^2)\nu_{n,1} - (\alpha_2^2 - \gamma_2^2)\nu_{n,2} = 0. \tag{S20}$$

Then for the $|\phi_+\rangle$ component ($\alpha_1 = \alpha_2 = 1$) the resonance condition is

$$J_{1a1b} - J_{2a2b} = \nu_{n,2} - \nu_{n,1}, \tag{S21}$$

and for the $|\phi_-\rangle$ component ($\gamma_1 = \gamma_2 = 1$) the resonance condition is

$$J_{1a1b} - J_{2a2b} = \nu_{n,1} - \nu_{n,2}. \tag{S22}$$
The Rabi oscillation frequency is $\nu_{\text{Rabi}} = 2C$, and the period is $\tau_{\text{Rabi}} = 1/2C$. This results from solving the time-dependent Schrödinger equation, letting $E_1 = E_2 = 0$ (i.e., working in the rotating frame of the two-level system):

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\psi(t)\rangle.$$  \hspace{1cm} (S23)

If $c_1(t)$ and $c_2(t)$ are the coefficients for $|TS_0\rangle$ and $|S_0T\rangle$, respectively, then

$$\begin{bmatrix} \dot{c}_1(t) \\ \dot{c}_2(t) \end{bmatrix} = -i \begin{bmatrix} 0 & C \\ C & 0 \end{bmatrix} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix},$$ \hspace{1cm} (S24)

which has solution

$$\begin{bmatrix} |c_1(t)|^2 \\ |c_2(t)|^2 \end{bmatrix} = \begin{bmatrix} \cos^2(2\pi Ct) \\ \sin^2(2\pi Ct) \end{bmatrix}.$$ \hspace{1cm} (S25)


