

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 ν_1 and ν_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

$$\hat{\mathcal{H}}_0 = h \begin{bmatrix} -\frac{\nu_1 + \nu_2}{2} + \frac{J}{4} & 0 & 0 & 0 \\ 0 & \frac{J}{4} & 0 & \frac{\Delta\nu}{2} \\ 0 & 0 & \frac{\nu_1 + \nu_2}{2} + \frac{J}{4} & 0 \\ 0 & \frac{\Delta\nu}{2} & 0 & -\frac{3J}{4} \end{bmatrix}, \quad (\text{S1})$$

where the eigenstates are (from left to right) the three triplet states, $|T_-\rangle$, $|T_0\rangle$, and $|T_+\rangle$, and one singlet state, $|S_0\rangle$.

These can be represented as symmetric and antisymmetric combinations of the product states:

$$\begin{aligned}
|T_{-}\rangle &= |\uparrow\uparrow\rangle \\
|T_{0}\rangle &= \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \\
|T_{+}\rangle &= |\downarrow\downarrow\rangle \\
|S_{0}\rangle &= \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}.
\end{aligned} \tag{S2}$$

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

$$\hat{\mathcal{H}}_0 = h \begin{bmatrix} \frac{J}{4} & 0 & 0 & 0 \\ 0 & \frac{J}{4} & 0 & \frac{\Delta\nu}{2} \\ 0 & 0 & \frac{J}{4} & 0 \\ 0 & \frac{\Delta\nu}{2} & 0 & -\frac{3J}{4} \end{bmatrix}. \tag{S3}$$

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

$$\hat{\mathcal{H}}_{SL} = h \begin{bmatrix} \frac{J}{4} & \frac{\nu_n}{\sqrt{2}} & 0 & 0 \\ \frac{\nu_n}{\sqrt{2}} & \frac{J}{4} & \frac{\nu_n}{\sqrt{2}} & \frac{\Delta\nu}{2} \\ 0 & \frac{\nu_n}{\sqrt{2}} & \frac{J}{4} & 0 \\ 0 & \frac{\Delta\nu}{2} & 0 & -\frac{3J}{4} \end{bmatrix}. \tag{S4}$$

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

$$\hat{\mathcal{H}}_{SL,\text{dressed}} = h \begin{bmatrix} \frac{J}{4} - \nu_n & 0 & 0 & \frac{\Delta\nu}{2\sqrt{2}} \\ 0 & \frac{J}{4} & 0 & 0 \\ 0 & 0 & \frac{J}{4} + \nu_n & -\frac{\Delta\nu}{2\sqrt{2}} \\ \frac{\Delta\nu}{2\sqrt{2}} & 0 & -\frac{\Delta\nu}{2\sqrt{2}} & -\frac{3J}{4} \end{bmatrix}, \tag{S5}$$

and the resulting dressed states are

$$\begin{aligned}
|\phi_-\rangle &= \frac{1}{2}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle - |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\
&= \frac{1}{2}(|T_-\rangle + |T_+\rangle) - \frac{1}{\sqrt{2}}|T_0\rangle \\
|\phi_0\rangle &= \frac{1}{\sqrt{2}}(|\downarrow\downarrow\rangle - |\uparrow\uparrow\rangle) = \frac{1}{\sqrt{2}}(|T_+\rangle - |T_-\rangle) \\
|\phi_+\rangle &= \frac{1}{2}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle + |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\
&= \frac{1}{2}(|T_-\rangle + |T_+\rangle) + \frac{1}{\sqrt{2}}|T_0\rangle \\
|\phi_S\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = |S_0\rangle.
\end{aligned} \tag{S6}$$

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 ν_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

$$|T\rangle_i = \alpha_i|\phi_+\rangle_i + \beta_i|\phi_0\rangle_i + \gamma_i|\phi_-\rangle_i, \tag{S7}$$

and α_i , β_i , and γ_i are real amplitudes for spin pair i . To preserve normalization we require

$$\alpha_i^2 + \beta_i^2 + \gamma_i^2 = 1. \tag{S8}$$

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 :

$$\hat{\mathcal{H}} = h \begin{bmatrix} E_1 & C \\ C & E_2 \end{bmatrix}. \tag{S9}$$

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

$$\begin{aligned}
\hat{\mathcal{H}}_{J,ij} &= J_{ij} \left(\hat{I}_{iz}\hat{I}_{jz} + \hat{I}_{ix}\hat{I}_{jx} + \hat{I}_{iy}\hat{I}_{jy} \right) \\
&= J_{ij} \left(\hat{I}_{iz}\hat{I}_{jz} + \frac{\hat{I}_i^+ \hat{I}_j^- + \hat{I}_i^- \hat{I}_j^+}{2} \right).
\end{aligned} \tag{S10}$$

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

$$\hat{\mathcal{H}}_J = \hat{\mathcal{H}}_{J,1a2a} + \hat{\mathcal{H}}_{J,1b2b} + \hat{\mathcal{H}}_{J,1a2b} + \hat{\mathcal{H}}_{J,1b2a}, \tag{S11}$$

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

$$\begin{aligned} \langle TS_0|\hat{\mathcal{H}}_J|S_0T\rangle &= (\alpha_1\langle\phi_+\phi_S| + \beta_1\langle\phi_0\phi_S| + \gamma_1\langle\phi_-\phi_S|) \left(\hat{\mathcal{H}}_{J,1a2a} + \hat{\mathcal{H}}_{J,1b2b} + \hat{\mathcal{H}}_{J,1a2b} + \hat{\mathcal{H}}_{J,1b2a} \right) \\ &\times (\alpha_2|\phi_S\phi_+\rangle + \beta_2|\phi_S\phi_0\rangle + \gamma_2|\phi_S\phi_-\rangle). \end{aligned} \quad (\text{S12})$$

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 $\alpha_1\alpha_2\langle\phi_+\phi_S|\hat{\mathcal{H}}_{J,1a2a}|\phi_S\phi_+\rangle$ can be calculated by expanding the definitions of $|\phi_S\rangle$, $|\phi_+\rangle$, and $\hat{\mathcal{H}}_{J,1a2a}$ to give

$$\begin{aligned} \alpha_1\alpha_2\langle\phi_+\phi_S|\hat{\mathcal{H}}_{J,1a2a}|\phi_S\phi_+\rangle &= \alpha_1\alpha_2\frac{J_{1a2a}}{8}(\langle\uparrow\downarrow|_1 + \langle\downarrow\uparrow|_1 + \langle\uparrow\uparrow|_1 + \langle\downarrow\downarrow|_1)(\langle\uparrow\downarrow|_2 - \langle\downarrow\uparrow|_2) \\ &\times \left(\hat{I}_{1az}\hat{I}_{2az} + \frac{\hat{I}_{1a}^+\hat{I}_{2a}^- + \hat{I}_{1a}^-\hat{I}_{2a}^+}{2} \right) (|\uparrow\downarrow\rangle_1 - |\downarrow\uparrow\rangle_1)(|\uparrow\downarrow\rangle_2 + |\downarrow\uparrow\rangle_2 + |\uparrow\uparrow\rangle_2 + |\downarrow\downarrow\rangle_2) \\ &= \alpha_1\alpha_2\frac{J_{1a2a}}{8}(\langle\uparrow\downarrow|_1 + \langle\downarrow\uparrow|_1 + \langle\uparrow\uparrow|_1 + \langle\downarrow\downarrow|_1)(\langle\uparrow\downarrow|_2 - \langle\downarrow\uparrow|_2) \\ &\times \left[\frac{(|\uparrow\downarrow\rangle_1 + |\downarrow\uparrow\rangle_1)(|\uparrow\downarrow\rangle_2 - |\downarrow\uparrow\rangle_2 + |\uparrow\uparrow\rangle_2 - |\downarrow\downarrow\rangle_2)}{4} \right. \\ &\left. + \frac{(|\downarrow\downarrow\rangle_1)(|\uparrow\uparrow\rangle_2 + |\uparrow\downarrow\rangle_2)}{2} - \frac{(|\uparrow\uparrow\rangle_1)(|\downarrow\downarrow\rangle_2 + |\downarrow\uparrow\rangle_2)}{2} \right] \\ &= \alpha_1\alpha_2\frac{J_{1a2a}}{4}. \end{aligned} \quad (\text{S13})$$

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

$$C = \langle TS_0|\hat{\mathcal{H}}_J|S_0T\rangle = \frac{J_{1a2a} + J_{1b2b} - J_{1a2b} - J_{1b2a}}{4}(\alpha_1\alpha_2 + \beta_1\beta_2 + \gamma_1\gamma_2). \quad (\text{S14})$$

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

$$\begin{aligned} \langle\phi_0\phi_+|\hat{\mathcal{H}}_J|\phi_+\phi_S\rangle &= \frac{J_{1a2a} - J_{1b2b} - J_{1a2b} + J_{1b2a}}{4} \\ \langle\phi_+\phi_0|\hat{\mathcal{H}}_J|\phi_+\phi_S\rangle &= \frac{-J_{1a2a} + J_{1b2b} + J_{1a2b} - J_{1b2a}}{4} \\ \langle\phi_0\phi_-|\hat{\mathcal{H}}_J|\phi_-\phi_S\rangle &= \frac{-J_{1a2a} + J_{1b2b} + J_{1a2b} - J_{1b2a}}{4} \\ \langle\phi_-\phi_0|\hat{\mathcal{H}}_J|\phi_-\phi_S\rangle &= \frac{J_{1a2a} - J_{1b2b} - J_{1a2b} + J_{1b2a}}{4} \\ \langle\phi_+\phi_-|\hat{\mathcal{H}}_J|\phi_0\phi_S\rangle &= \frac{J_{1a2a} - J_{1b2b} - J_{1a2b} + J_{1b2a}}{4} \\ \langle\phi_-\phi_+|\hat{\mathcal{H}}_J|\phi_0\phi_S\rangle &= \frac{-J_{1a2a} + J_{1b2b} + J_{1a2b} - J_{1b2a}}{4} \end{aligned} \quad (\text{S15})$$

For our experiments, these terms should be significantly smaller than C because the differences within *syn* and *anti* J coupling combinations, $J_{1a2a} - J_{1b2b}$ and $J_{1a2b} - J_{1b2a}$, are generally much smaller than the differences between *syn* and *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

$$\begin{aligned}\hat{\mathcal{H}}_E = & \nu_{1a}\hat{I}_{1az} + \nu_{1b}\hat{I}_{1bz} + \nu_{2a}\hat{I}_{2az} + \nu_{2b}\hat{I}_{2bz} + J_{1a1b}\hat{I}_{1a} \cdot \hat{I}_{1b} + J_{2a2b}\hat{I}_{2a} \cdot \hat{I}_{2b} \\ & + \frac{\nu_{n,1}}{2}\hat{I}_{1ax} + \frac{\nu_{n,1}}{2}\hat{I}_{1bx} + \frac{\nu_{n,2}}{2}\hat{I}_{2ax} + \frac{\nu_{n,2}}{2}\hat{I}_{2bx}.\end{aligned}\quad (\text{S16})$$

The analysis is simplified by starting with eigenstates $|\phi\rangle$, since their energy levels have no ν_i (B_0) dependence and a linear dependence on ν_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

$$\begin{aligned}E_1 &= \langle TS_0 | \hat{\mathcal{H}}_E | TS_0 \rangle \\ &= \frac{J_{1a1b}}{4} - \frac{3J_{2a2b}}{4} + (\alpha_1^2 - \gamma_1^2)\nu_{n,1} \\ E_2 &= \langle S_0T | \hat{\mathcal{H}}_E | S_0T \rangle \\ &= \frac{J_{2a2b}}{4} - \frac{3J_{1a1b}}{4} + (\alpha_2^2 - \gamma_2^2)\nu_{n,2}.\end{aligned}\quad (\text{S17})$$

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 γ_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

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

where ν_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

$$\Delta\nu_n = \sqrt{\nu_n^2 + \Delta\nu^2} - \nu_n. \quad (\text{S19})$$

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

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

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

$$J_{1a1b} - J_{2a2b} = \nu_{n,2} - \nu_{n,1}, \quad (\text{S21})$$

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

$$J_{1a1b} - J_{2a2b} = \nu_{n,1} - \nu_{n,2}. \quad (\text{S22})$$

The Rabi oscillation frequency is $\nu_{Rabi} = 2C$, and the period is $\tau_{Rabi} = 1/2C$. 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):

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{\mathcal{H}}|\psi(t)\rangle. \quad (\text{S23})$$

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

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

which has solution

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

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