Electronic supporting information (ESI)

Field-cycling NMR experiments in ultra-wide magnetic field range: relaxation and coherent polarization transfer

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NMR parameter determination

We used high resolution ¹³C NMR spectra (176 MHz, 16.4 T) for the determination of chemical shifts and scalar spin-spin couplings in four isotopomers of methyl propiolate (MP) (${}^{13}C_1$ -methyl propiolate, ${}^{13}C_2$ -methyl propiolate, ${}^{13}C_3$ -methyl propiolate, ${}^{13}C_4$ -methyl propiolate).

The spectrometer was shimmed well to resolve splittings \leq 0.1 Hz of carbon nuclei. The NMR spectrum contained 2048k points in the FID with a total acquisition time of 32.3 s. Simulation and fitting of the NMR spectra (**Figures S1-S4**) was done with a help of software published in Ref. 1. Every carbon in all four isotopomers was treated as a coupled 5-spin system (¹³C, ¹H, 3x¹H). Coupling between protons was set to zero. The resulting coupling constants are summarized in **Table T1**.

 Table T1. NMR parameters of four isotopomers of methyl propiolate measured at a magnetic field of 16.4 T.

Molecule	¹³ C Chemical shift, ppm	J(C -C H), Hz	J(C -C H ₃), Hz
¹³ C ₁ -methyl propiolate (C1-MP)	75.840	¹ Ј _{С-Н} =258.51	⁵ J _{C-H} =0.14
¹³ C ₂ -methyl propiolate (C2-MP)	74.313	² J _{C-H} =50.38	⁴ Ј _{С-Н} =0.56
¹³ C ₃ -methyl propiolate (C3-MP)	152.906	³ Ј _{С-Н} =4.93	³ Ј _{С-Н} =4.24
¹³ C ₄ -methyl propiolate (C4-MP)	52.403	⁵ J _{C-H} =0.10	¹ J _{C-H} =148.35



Figure S1. Experimental (black, positive) and simulated (blue, negative) ¹³C NMR spectra of ${}^{13}C_1$ -methyl propiolate (natural abundance) in acetone-d₆ at room temperature. Simulation performed with parameters shown in **Table T1**.



Figure S2. Experimental (black, positive) and simulated (blue, negative) ¹³C NMR spectra of ${}^{13}C_2$ -methyl propiolate (natural abundance) in acetone-d₆ at room temperature. Simulation performed with parameters shown in **Table T1**.

¹³C₃-Methylpropiolate



Figure S3. Experimental (black, positive) and simulated (blue, negative) ¹³C NMR spectra of ${}^{13}C_3$ -methyl propiolate (natural abundance) in acetone-d₆ at room temperature. Simulation performed with parameters shown in **Table T1**.



Figure S4. Experimental (black, positive) and simulated (blue, negative) ¹³C NMR spectra of ${}^{13}C_4$ -methyl propiolate (natural abundance) in acetone-d₆ at room temperature. Simulation performed with parameters shown in **Table T1**.

Kinetics fitting at ultralow field

To determine frequency and damping of the oscillations of the C1 components we measured the polarization transfer kinetics curve using polarization transfer protocol. To shorten the time of our experiment we used a special delay list. It contains several expanded parts with fine dwell time of 1 ms every 3 s. Mainly the C1 β component shows strong oscillatory behavior. Since C1-H1 is in good approximation a two-spin system ½ it is possible to fit the decaying oscillation using a damped sine function with a single frequency.

The fitting function was:

$$y = y0 + A_{short} \cdot \exp\left(-\frac{\tau}{T_1^{short}}\right) + A_{long} \cdot \exp\left(-\frac{\tau}{T_1^{long}}\right) + B \cdot \exp\left(-\frac{\tau}{T_2}\right) \cdot \sin\left(2\pi\nu\tau + 2\pi\varphi/360\right),$$

Where:

 y_0 – offset

 A_{short}, A_{long}, B – amplitudes of individual exponents

- T_1^{short} fast decay time, triplet relaxation time
- T_1^{long} long decay time, relaxation of long lived states
- T_2 damping time of oscillation, T₂-relaxation time
- u oscillation frequency
- φ phase in degrees

Table T2. Fitting parameters for the data in Figure S5.

Fitting parameter	Value	Error
y_0	0.0178	0.007
A _{short}	0.533	0.004
A_{long}	-0.261	0.006
В	0.853	0.002
T_1^{short}	5.6	0.1
T_1^{long}	66.8	4.3
<i>T</i> ₂	14.64	0.04
ν	258.5372	0.0001
φ	-65.01	0.08



Figure S5. Fitting of C1 β oscillations at 53 nT by a bi-exponential function plus a damping time of the oscillation. Experimental points (black circles) and fitting curve (red line) are shown on top; residuals between experimental data and fitting curve are shown at the bottom subplot. Inserts show data on expanded scale. Fitting parameters are shown in **Table T2**.

Observation of oscillations starting from different initial conditions

In order to prove that oscillation at 53 nT are determined only by -couplings we performed the polarization transfer experiment with different starting conditions. **Figure S6** shows experimental results of coherent polarization transfer starting from thermal carbon polarization (black) and zero carbon polarization (red). In both cases the NMR intensity was scaled to the thermally relaxed NMR spectrum at 9.4 T. Both experiments demonstrate oscillatory behavior. The frequencies of the beatings (**Figure S6** right) for the same carbon nuclei coincide very well. Differences in the amplitudes can be explained by different starting polarization.



Figure S6. Comparison of carbon kinetic curves measured at 53 nT with different starting conditions: black lines – protons and carbons are thermally polarized; red lines – protons are thermally polarized, carbon polarization was destroyed by a 90 degree pulse at high field prior to field switch. Time domain is shown on the left side, Fourier transformation on the right side. Experiments are done using the polarization transfer protocol with fast field switch (See main text, **Figure 3B**).

Dipolar cross-relaxation in a two-spin system

Let us briefly present the description of cross-relaxation in a system of two-spins $\frac{1}{2}$, S and I.² The differential equation for the vector of spin magnetizations, **M**, is of the form:

$$\frac{d\mathbf{M}}{dt} = \hat{R}(\mathbf{M} - \mathbf{M}_{eq})$$

with the initial condition $\mathbf{M}(t = 0) = \mathbf{M}_0$. Here, we introduce

$$\mathbf{M} = \begin{pmatrix} S_z \\ I_z \end{pmatrix}, \qquad \mathbf{M}_{eq} = \begin{pmatrix} S_{eq} \\ I_{eq} \end{pmatrix}, \qquad \mathbf{M}_0 = \begin{pmatrix} S_0 \\ I_0 \end{pmatrix}$$

For each of the spins we introduce its magnetization, $S_z(t)$ and $I_z(t)$, equilibrium magnetization, S_{eq} and I_{eq} , and starting magnetization at t = 0, S_0 and I_0 .

For pure dipolar relaxation the relaxation matrix takes the form:

$$\widehat{R} = \begin{pmatrix} -R_1 & -\sigma \\ -\sigma & -R_1 \end{pmatrix}$$

Here R_1 and σ stand for the rates of T₁-relaxation and cross-relaxation.

For a system of two hetero-nuclei we take the following ratio of equilibrium polarization at the NMR field and the relaxation field:

$$\frac{S_0}{I_0} = \frac{S_{eq}}{I_{eq}} = \frac{\gamma_S}{\gamma_I}$$

We also assume that $\frac{S_0}{S_{eq}} = \alpha$, here the α value is the ratio of the detection field and the relaxation field. Assuming dipolar relaxation in the fast motional regime we write $R_1 = 2\sigma$. In this case, the relaxation rates in the system, which are eigen-values of \hat{R} , are equal to $\lambda_1 = 3\sigma$ and $\lambda_2 = \sigma$. The ratio $\frac{\lambda_1}{\lambda_2} = 3$ is consistent with our experimental findings. The solution of the equation for $\mathbf{M}(t)$ is then written as follows:

$$S_{z}(t) = \frac{\gamma_{S}}{\gamma_{I}} + \frac{\alpha - 1}{2} \cdot \frac{\gamma_{S}}{\gamma_{I}} (e^{-\sigma t} + e^{-3\sigma t}) + \frac{\alpha - 1}{2} (e^{-3\sigma t} - e^{-\sigma t})$$
$$I_{z}(t) = 1 + \frac{\alpha - 1}{2} (e^{-\sigma t} + e^{-3\sigma t}) + \frac{\alpha - 1}{2} \cdot \frac{\gamma_{S}}{\gamma_{I}} (e^{-3\sigma t} - e^{-\sigma t})$$

Typical time traces of spin magnetizations are presented in the **Figure S7**. In the calculation, we use the following parameters: $\frac{\gamma_S}{\gamma_I} = 4$ (corresponding to $S = {}^{1}$ H and $I = {}^{13}$ C) and $\alpha = 2$ (corresponding to the situation where the relaxation field is half of the NMR spectrometer field). Both time traces, $S_z(t)$ and $I_z(t)$, decay from $S_0 = 2S_{eq}$ and $I_0 = 2I_{eq}$ to S_{eq} and I_{eq} , respectively. For the *I*-spin $I_z(t)$ clearly approaches the stationary magnetization from below, which is consistent with our experimental observations (**Figure 5A**, main text).



Figure S7. Time evolution of magnetization of S-spin and I-spin. Here $\gamma_S/\gamma_I = 4$, $\alpha = 2$, $R_1 = 1$ s⁻¹. Magnetization is plotted in units of S_0 .

References.

- 1. D. A. Cheshkov, D. O. Sinitsyn, K. F. Sheberstov and V. A. Chertkov, *Journal of Magnetic Resonance*, 2016, **272**, 10-19.
- 2. I. Solomon, *Physical Review*, 1955, **99**, 559-565.