Supplementary Information

Singlet lifetime measurements in an all-proton chemically equivalent spin system by hyperpolarization and weak spin lock transfers

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General Information

Para-hydrogen was generated by flowing H_2 gas through activated charcoal at 77 K.[1] The catalyst [1,4-bis(diphenylphosphino)butane](1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (1.2 μmol) and 1 (3.3 μmol) were dissolved in CD_3OD (600μL) in an NMR tube. Water and methanol were degassed separately by the freeze-pump-thaw (FPT) method in FPT samples. Samples were placed in Schlenck tubes, frozen in liquid nitrogen, and thawed to release dissolved gasses. The cycle was repeated for both methanol and water at least for four cycles. In non-FPT samples, only water was purged by nitrogen gas for half an hour prior to injection; methanol solutions were not degassed by bubbling in these samples, but were used as received (sealed vials). Degassed water was taken up into a gas-tight syringe via a long tubing (Tefzel (EFTE), o.d. 0.16 cm, i.d. 0.05 cm, length 1.5 m.). The tubing containing water was inserted into the NMR tube for further dilution. *Para*-hydrogen was bubbled through the reaction solution in the NMR tube for 15 s at a rate of 1 mL/s at earth field. Then it was lowered into high field (11.76T) quickly with a string. Once the sample was locked, the first spoiler pulse was applied. The period between the beginning of bubbling para-hydrogen and the initiation of NMR pulses lasted 30s.

All PHIP NMR experiments were performed at 11.76 T using a Bruker Avance Spectrometer. T_1 measurements were carried out by inversion recovery. For the SLIC experiment, the resonance frequency was set on the vinylene protons of DMM in the final stable solution. The nutation frequency was found to be optimal at 11.6 Hz, which should equal the *J* coupling between the vinylene protons.[2] The duration of the conversion pulse was optimized to be 1.77s.

Supplementary figures

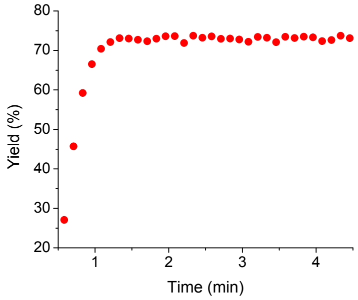

Fig. 1 Yield (%) of the hydrogenation reaction in MeOD. The reaction completes after bubbling hydrogen gas in the NMR tube for 30 s. Subsequent small flip-angle pulses were used to monitor the reaction. Product **2** reached its maximum within one minute.

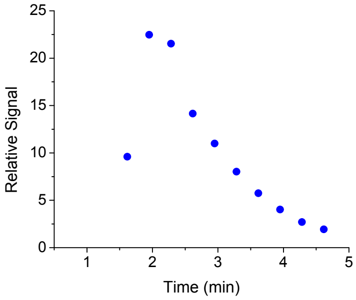

Fig. 2 Multi-conversion SLIC-monitored signal integral as a function of time after water addition. One can deduce that solvent mixing is complete within approximately 40 s.

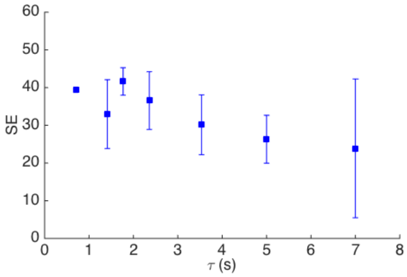

Fig. 3 Optimization of the SLIC pulse duration. Signal enhancement, SE, changes with spin-lock duration, τ . The optimized duration is 1.77s.

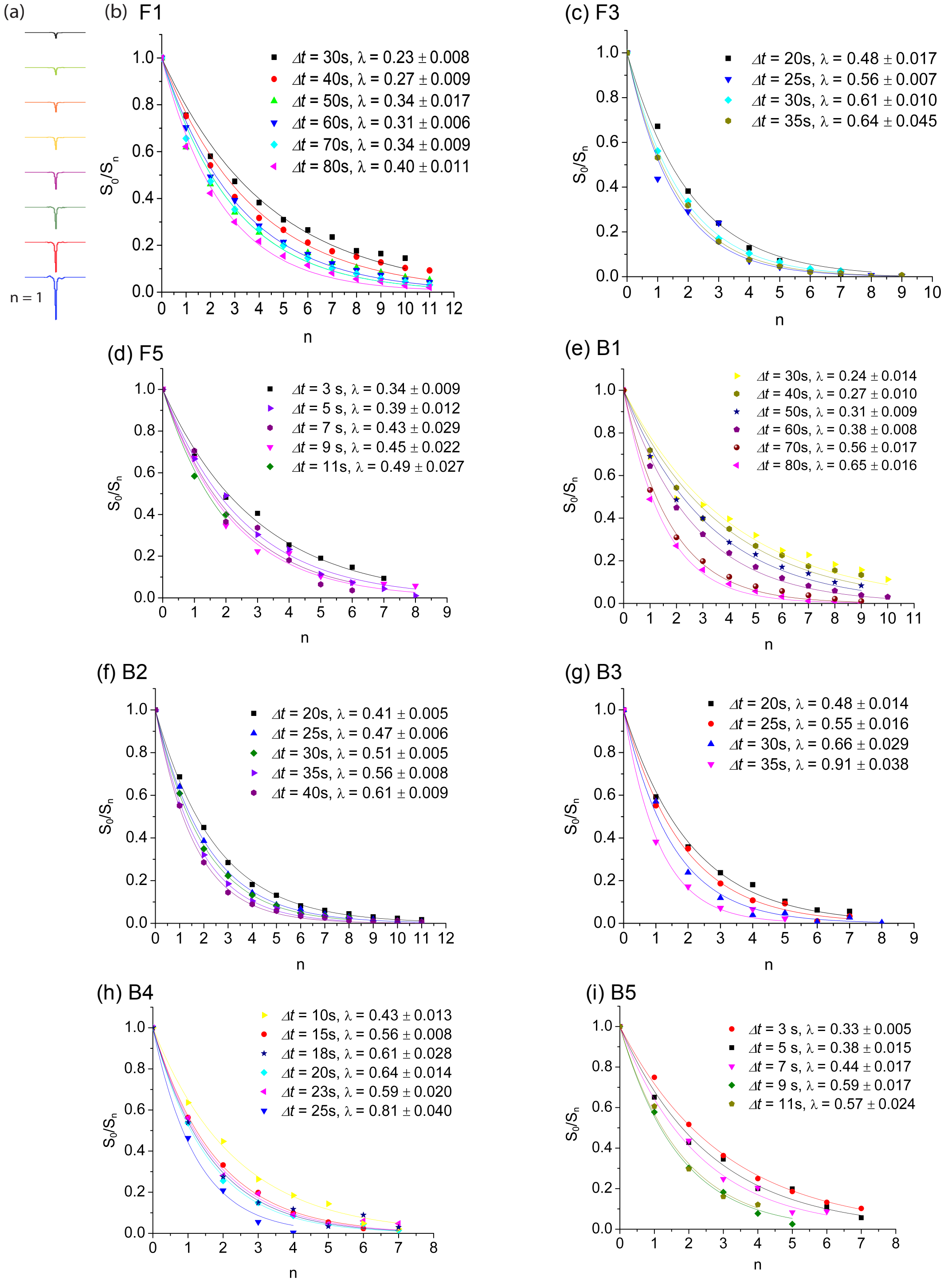

Fig. 4 (a) Typical spectra of obtained signal with a multi-conversion SLIC sequence with Δ*t* = 60s. (b)~(i) Processed data of sample F1, F3, F5, B1, B2, B3, B4 and B5. Relative integral of vinylene signal as a function of additional numbers of conversion blocks, *n*. The decay constant, λ, depends on Δ*t*.[2]

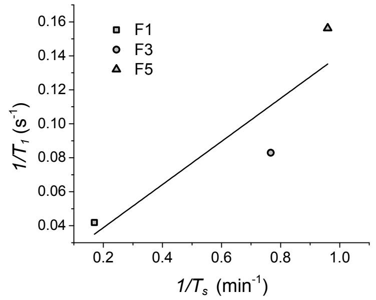

Fig. 5 The correlation between T_1 and T_s relaxation rates (s^{-1}) for freeze-pump-thaw samples F1, F3 and F5.

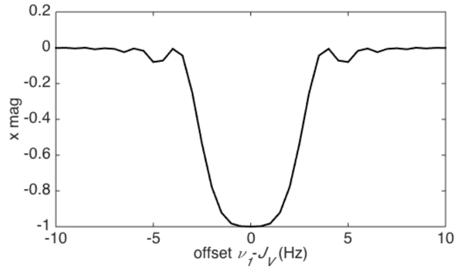

Fig. 6 Simulation of offset effects during SLIC conversion for the DMM molecule. The singlet state of the vinylene protons is converted to observable x magnetization by SLIC. The observed transverse magnetization changes with offsets. The offset corresponds to $\nu_1 - J_V$ according to Eq. (5).

References

1 J. A. Tang, F. Gruppi, R. Fleysher, D. K. Sodickson, J. W. Canary and A. Jerschow, *Chem. Commun.,* 2011, **47**, 958-960.

2 M. B. Franzoni, H. W. Spiess, K. Münnemann et al , *Phys. Chem. Chem. Phys.,* 2013, **15,** 17233-17239.