

Supporting Information

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69451 Weinheim, Germany

**Scavenging Free Radicals To Preserve Enhancement and Extend  
Relaxation Times in NMR using Dynamic Nuclear Polarization\*\***

*Pascal Miéville, Puneet Ahuja, Riddhiman Sarkar, Sami Jannin,\* Paul R. Vasos, Sandrine Gerber-Lemaire, Mor Mishkovsky, Arnaud Comment, Rolf Gruetter, Olivier Ouari, Paul Tordo, and Geoffrey Bodenhausen*

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## Sample Preparation

Samples were prepared by dissolving 40 mM L-Ala-Gly and Acrylic Acid (Sigma-Aldrich) and 2.5 mM TEMPOL (Sigma-Aldrich) in D<sub>2</sub>O (Cambridge Isotope) with and without addition of 30 mM sodium ascorbate. NMR tubes were filled with 500  $\mu$ L and immediately sealed under argon atmosphere. The 1 M acrylic acid (Sigma-Aldrich) sample for DNP contained 30 mM TEMPOL in 40/60 v/v glycerol-*d*<sub>8</sub>/D<sub>2</sub>O (Cambridge Isotope) which has good glass-forming properties. 15 beads of 10  $\mu$ L each were rapidly frozen in liquid nitrogen and immediately inserted in the polarizer together with an equal number of beads containing only 3 M sodium ascorbate (Sigma-Aldrich) in D<sub>2</sub>O.

## Dissolution Dynamic Nuclear Polarization

The <sup>1</sup>H nuclear spins were polarized for 20 minutes by CW microwave irradiation (93.89 GHz, 30 mW) in a polarizer at 3.35 T and 1.2 K. The polarization build-up curve was measured by conventional solid-state <sup>1</sup>H NMR with  $\sim$ 1° pulses at 142.67 MHz. A build up time of 160 s was observed, yielding an absolute <sup>1</sup>H polarization of 40%. The sample was dissolved within 700 ms with 5 mL D<sub>2</sub>O vapor at  $\sim$ 130 °C and 1 MPa, and pushed with helium gas (6 MPa) through a PTFE capillary (2 mm inner diameter, 4 m length) within 4 s. 500  $\mu$ L of the hyperpolarized solution was then injected into an NMR tube in the NMR spectrometer (Bruker, 300 MHz) within 300 ms with a remotely controlled piston. Enhancements of 4000 are observed at 7.05 T after dissolution, transfer and injection, i.e., after an overall delay of 5 s. Such an enhancement corresponds to a residual absolute <sup>1</sup>H polarization of 9.6 %.

## NMR spectroscopy in presence of TEMPOL and Vitamin C

The presence of ascorbate or TEMPOL does not lead to a crowded <sup>1</sup>H NMR spectrum. Figure S1 below shows the <sup>1</sup>H NMR spectrum of acrylic acid (without DNP enhancement) mixed with ascorbic acid and TEMPOL (reduced into 2,2,6,6-tetramethylpiperidine-1,4-diol). Let us recall that ascorbate is never hyperpolarized (since TEMPOL is not present in the frozen ascorbate beads). On the other hand, TEMPOL is not visible in the NMR spectrum since it is paramagnetic.

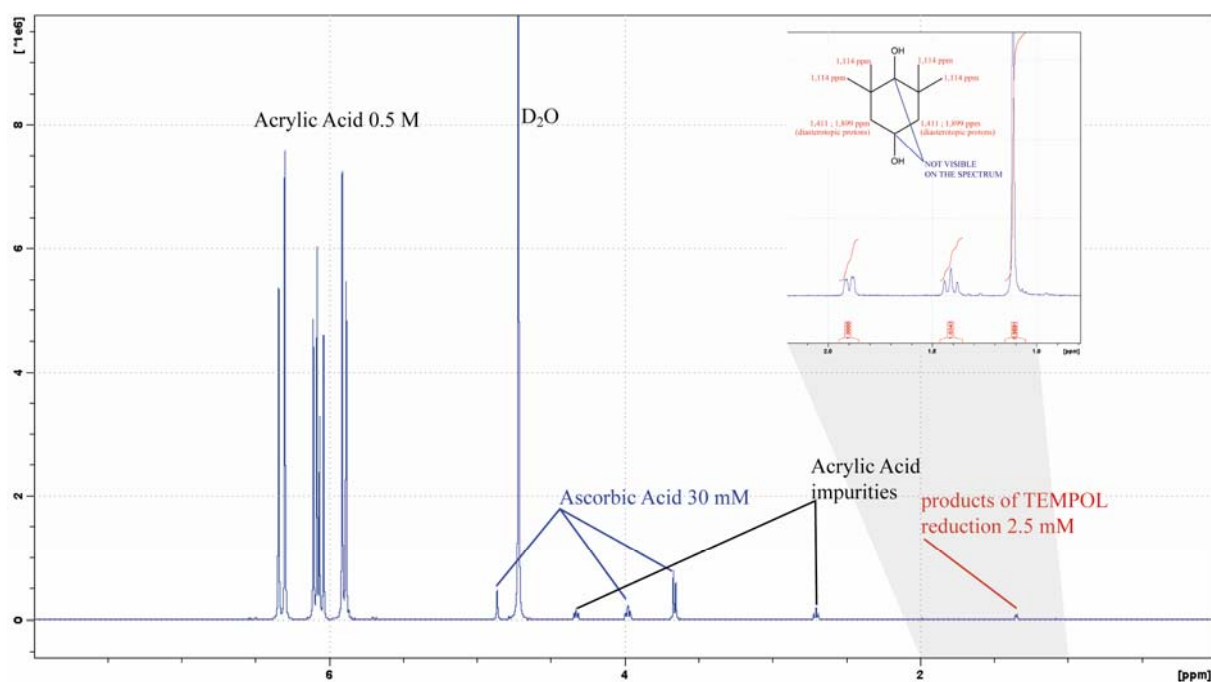


Figure S1. <sup>1</sup>H NMR of a mixture of acrylic acid (0.5 M), ascorbic acid (30 mM) and TEMPOL (2.5 M, reduced by ascorbic acid)