Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Detection of low-populated reaction intermediates with hyperpolarized NMR

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Experimental Details: Acetate formulation for hyperpolarization

Acetate was hyperpolarized in a preparation yielding a signal enhancement of 31,000 relative to the thermal polarization at 310 K in 9.4 T magnetic field (400 MHz Varian Inova spectrometer). To this end, a 1:1 Tris salt of 1-^{13}C acetic acid was prepared as follows: 474 mg or 7.77 mmol of [1-^{13}C]acetic acid were dissolved in 50 ml water. To this solution, Tris was added (946 mg, 7.80 mmol). After dissolution, the preparation is diluted in water to 200 ml and subsequently freeze-dried. To ensure that acetate was converted into a 1:1 Tris salt, some sample can be transferred to an NMR tube and the ratio of Tris (3.6 ppm) to acetate (1.8 ppm) was determined from the integrals in a 1H spectrum.

A DNP preparation was established using Tris [1-^{13}C]-acetate salt (44.03 mg, 0.24 mmol 13C, 93 % purity, 7% excess of Tris), the trityl radical OX063 (4.63 mg of 139 µmol/g solution), a trimeric Gd-DOTA complex[1] (1 mg of 14.6 µmol/g solution) and 6 µl water. Addition of the Gd complex enhances the solid state polarization.[2] This mixture is sonicated and gently heated to aid dissolution. The solution is viscous and requires heating prior to transfer to a sample cup. The sample has a total volume of approximately 50 µl, and contains ^{13}C concentration 4.8 M, OX063 at 12.8 mM and Gd-DOTA complex at 0.4 mM concentration.

The sample is polarized for one hour and dissolved in 6 ml of 20 mM Tris buffer of pH 7.6, which additionally contains EDTA.

1. WO2007/064226 US Patent.
2. Johannesson H, Macholl S, Ardenkjaer-Larsen JH. Dynamic Nuclear Polarization of [1-^{13}C]pyruvic acid at 4.6 tesla. J Magn Reson 2008.