Low RF-field strength cross polarization combined with photo-induced non-persistent radicals for clinically applicable dDNP

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Low RF-field strength cross polarization combined with photo-induced non-persistent radicals for clinically applicable dDNP

Work in progress

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Cross Polarisation for SPINlab-like polarisers using non-persistent radicals is demonstrated.

The efficiency of the transfer from transfer to carbon is modest at the currently achievable low B1 fields of 4-5 kHz still yielding 13C polarisation levels up to 15%. Based on the presented results, we foresee polarisation levels superior to direct 13C DNP in our next generation of double-tuned probes incorporating local tune and match.

Abstract
We demonstrate the possibility of 1H Dynamic Nuclear Polarization followed by cross polarization to carbon (DNP-CP) using a modified low cost benchtop console (Kea2) equipped with an external amplifier (Tomco) and a SPINlab-like dissolution DNP polarizer i.e. using the same fluid path and allowing for hyperpolarisation of a full human dose. Cross polarization (CP) using Laboratory Frame De- and Remagnetisation (LAFDR) was found superior to alternative sequences at the limited B1 fields employed. Faster build-up rates compared to 13C DNP are demonstrated using TEMPOL (4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) and DNP-CP 13C polarisations up to 15% are achieved using non-persistent UV-induced radicals.

Introduction
Dissolution Dynamic Nuclear Polarization (dDNP) is used to enhance the MR signals in imaging by factors of 10,000 2 paving the road for metabolic MRI studies. However, the polarisation build-up on 13C typically takes tens of minutes to hours, significantly lowering the versatility and throughput. Recently, studies have shown the possibility of speeding up the process by polarizing 1H, which has a faster build-up, followed by polarization transfer to e.g. 13C.3 However, strong B1 fields and small sample volumes are used, which makes the technique incompatible with clinical dDNP-MRI. Moreover, for clinical use, and in general to eliminate the relaxation effect, the radical essential for DNP needs to be removed during dissolution. Use of pyruvnic acid (PA) non-persistent photo-induced radicals for dDNP has been demonstrated to solve this issue4 and recently polarization build-up on protons with 1H→13C has been presented5.

Methods
Overview

DNP
CP
DNP-CP

Results
The efficiency of DNP-CP depends on the build-up rate and final polarization achieved on protons as well as the transfer efficiency of the CP sequence.
1. For B1=5 kHz LAFDR (fig. B) was found to outperform other CP sequences (data not shown).
2. On the TEMPOL, containing sample, DNP-CP using optimised LAFDR outperforms 13C DNP for build-up times < 1 hour, and 20% 13C polarization was achieved in only 20 min (fig. C).
3. Using 13CJCPA as the substrate for non-persistent radicals gives a too narrow EPR-line for efficient 13C DNP resulting in poor DNP-CP performance (fig. D).
4. Introduction of hyperfine coupling to the unpaired electron by 13C labelling in position 2 increases the EPR linewidth yielding 1H DNP build-up, but a polarization of only 18%, and therefore still inefficient DNP-CP (fig. E).
5. Deuterating the methyl group of PA increases the 1H DNP polarization to 62% and maintains the efficiency of CP. This yields a final 13C polarization of 15% after CP (fig. F).

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Conclusion and Outlook
We have demonstrated DNP-CP on a clinical-compatible SPINlab-like polarising using a low-cost benchtop console equipped with an external amplifier. Moreover, the technique has been combined with non-persistent UV induced radicals. At the current state, with B1≤5 kHz, direct 13C DNP still outperforms the DNP-CP. However, the goal is to implement local tuning of the probe to achieve sufficient B1 fields to improve the transfer efficiency. We expect that sufficiently strong B1 fields are achievable for this setup to outperform direct 13C DNP both with respect to build up rates and polarization levels.

References