PNNL-37066

Expanding Scientific Horizons Through High Field Dynamic Nuclear Polarization with Advanced Organic BiRadicals

November 2024

Nancy Washton
Phillip Koech
David Bazak

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
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Abstract

This project aimed to advance the capabilities of high-field Dynamic Nuclear Polarization (DNP) Nuclear Magnetic Resonance (NMR) spectroscopy at 800 MHz through the synthesis and evaluation of novel biradicals. While the targeted HyTEK biradical synthesis faced significant challenges, alternative efforts focused on synthesizing intermediate compounds and exploring alternative biradicals. A portion of the BDPA precursor was successfully converted into BDPA-TEMPO, though further DNP testing could not be completed within the project timeline. Benchmarking experiments with existing biradicals, including TEKPol and M-TinyPol, were conducted to evaluate their performance under high-field conditions. These efforts provided valuable insights into DNP enhancements, refined operational protocols for high-field experiments, and established benchmarks for future polarizing agent development.

Summary

This project achieved several notable accomplishments in advancing high-field Dynamic Nuclear Polarization (DNP) Nuclear Magnetic Resonance (NMR) capabilities at 800 MHz. Significant progress was made in synthesizing intermediate compounds for the novel biradical HyTEK, though the final synthesis was not completed due to challenges with critical reaction steps. To address these hurdles, alternative approaches were pursued, including the successful conversion of the BDPA precursor to BDPA-TEMPO, laying the groundwork for future testing. In parallel, the project conducted extensive benchmarking of commercially available biradicals, including AsymPolTEK, TEKPol, and M-TinyPol, to evaluate their performance under high-field conditions. These efforts refined operational protocols, optimized field sweeps, and established best practices for utilizing the new DNP magnet and sweep coil. The findings provide critical insights into DNP enhancements and establish a robust framework for future studies, including the development of new polarizing agents and their applications in materials science and energy research.

Acknowledgments

This research was supported by the Physical and Computational Science Division Seed Investment, under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

BDPA - 1,3-Bisdiphenylene-2-phenylallyl: A stable radical precursor used in the synthesis of biradicals for DNP applications.

CE - Cross Effect: A polarization transfer mechanism in DNP involving electron-nuclear interactions.

CP-MAS - Cross Polarization Magic Angle Spinning: A specific NMR experiment combining cross-polarization and MAS techniques for enhanced signal detection.

DBU - 1,8-Diazabicyclo[5.4.0]undec-7-ene: A strong, non-nucleophilic base used in organic synthesis.

DCC - N,N'-Dicyclohexylcarbodiimide: A coupling reagent commonly used in peptide synthesis and other organic reactions.DMAP - 4-Dimethylaminopyridine: A catalyst often used in esterification reactions and other organic transformations.

DNP - Dynamic Nuclear Polarization: A technique used to enhance the sensitivity of Nuclear Magnetic Resonance (NMR) spectroscopy by transferring polarization from electrons to nuclei.

DOE - Department of Energy: The U.S. federal department funding the project.

EPR - Electron Paramagnetic Resonance: A spectroscopic method used to study materials with unpaired electrons.

FY - Fiscal Year: Denotes the year in which the activities were conducted (e.g., FY21, FY23).

GDH - Glycerol-D2O-H2O: A cryo-protectant matrix used for preparing aqueous-based samples for DNP.

LDRD - Laboratory Directed Research and Development: A program for funding innovative research at DOE laboratories.

MAS - Magic Angle Spinning: A technique used in solid-state NMR to average out anisotropic interactions.

M-TinyPol - A newer biradical designed for aqueous-based cryo-protectant matrices, used for high-field DNP.

NMR - Nuclear Magnetic Resonance: A spectroscopic method used to determine the structure, dynamics, and interactions of molecules.

PNNL - Pacific Northwest National Laboratory: A multi-program national laboratory under the U.S. Department of Energy.

TCE - Tetrachloroethane: A solvent used in the preparation of certain DNP biradical matrices.

TEKPol - A commercially available biradical optimized for DNP applications, especially at lower magnetic fields.

TEMPO - 2,2,6,6-Tetramethylpiperidine-1-oxyl: A nitroxide radical commonly used in DNP

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1.0 Introduction

Dynamic Nuclear Polarization (DNP) Nuclear Magnetic Resonance (NMR) spectroscopy has transformed the ability to investigate materials and biological systems with unparalleled sensitivity enhancements. At high magnetic fields, such as 800 MHz, DNP facilitates the study of systems with low analyte concentrations and challenging acquisition times. However, polarization transfer mechanisms, such as the cross effect (CE), exhibit reduced efficiency at these higher fields, necessitating the development of tailored biradicals optimized for such conditions.

This project was designed to address this challenge by synthesizing HyTEK, a novel biradical specifically engineered for high-field DNP. While key steps in HyTEK's synthesis proved difficult to execute, alternative efforts included the partial synthesis of BDPA-TEMPO, an established biradical. Benchmarking experiments were carried out with commercially available CE biradicals, including TEKPol and M-TinyPol, to evaluate their suitability for high-field DNP applications. These studies provided critical data on the performance of these agents and refined experimental methods for optimizing field sweeps and gyrotron operation at 800 MHz.

2.0 Synthetic Methods and Results

Synthesis of DNP Biradicals HyTEK and BDPA-TEMPOSynthesis of HyTEK DNP BiradicalThe synthesis of HyTEK shown in Scheme 1 started with condensation of fluorene 1 and 4-carboxybenzaldehyde 2 in ethanol to afford compound 3. Purification of 3 was achieved by liquid-liquid extraction followed by evaporation of the solvent to afford a dark yellow solid, which was washed with hot toluene yielding a bright yellow solid. Compound 3 was used in the next step without further purification, because bromination of acid 3 gives compound 4, which has lower solubility and allows isolation of the pure solid by simple filtration. Compound 3 was converted to Dibromide 4 using bromine in glacial acetic acid and then this Dibromide 4 was refluxed in ethanol with sodium hydroxide to eliminate hydrogen bromide producing the conjugate acceptor monobromide 5. This reaction is concentration sensitive at higher concentrations, bromine (Br2) instead of hydrogen bromide was eliminated. Reaction of 5 with the fluorene anion generated by deprotonation with sodium tert-butoxide in dimethylacetamide (DMA), at room temperature yields a deep blue solution of the stabilized carbanion. This intermediate was quenched with 2 M HCl and purified via column chromatography to give 1,3-bisdiphenylene-2-phenylallyl (BDPA) 6 as an off-white air-stable powder. All products had 1H and 13C NMR consistent literature reports.

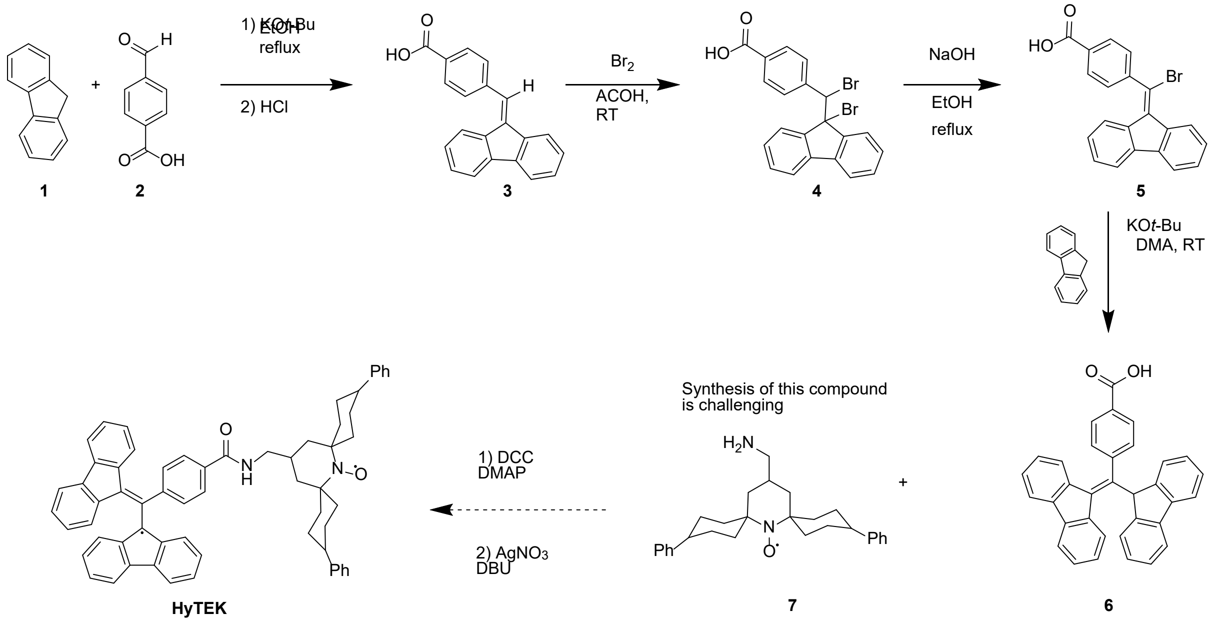

Figure 1. Synthetic scheme for HyTEK.

To complete the synthesis of HyTEK, spirocyclic amine 7 is required, Figure 2 shows the synthetic scheme for making spirocyclic amine 7 starting with the reaction of 2,2,6,6-tetramethylpiperidinone 8 and methyl iodide to give 1,2,2,6,6-Pentamethylpiperidin-4-one 9, followed by reaction with 4-phenylcyclohexanone in the presence of ammonium chloride to afford spirocyclic piperidone 10. This is a very low yielding reaction and thus it limits production of enough material for multistep synthesis. Compound 10 was oxidized using catalytic sodium tungstate dihydrate (Na2WO4.2 H2O) in ethanol and excess hydrogen peroxide (H2O2) yielding the spirocyclic piperidone N-oxide 11 as an orange solid. Next spirocyclic piperidone N-oxide 11 was converted to the corresponding sporocyclic cyano Compound 12 using 1-(isocyanomethylsulfonyl)-4-methylbenzene (TsCH2CN) in 1,2-dimethoxyethane and potassium tbutoxide. Finally compound 7 can be achieved by lithium Aluminum hydride reduction of the cyano group. At the time of writing this report the last step was in progress.

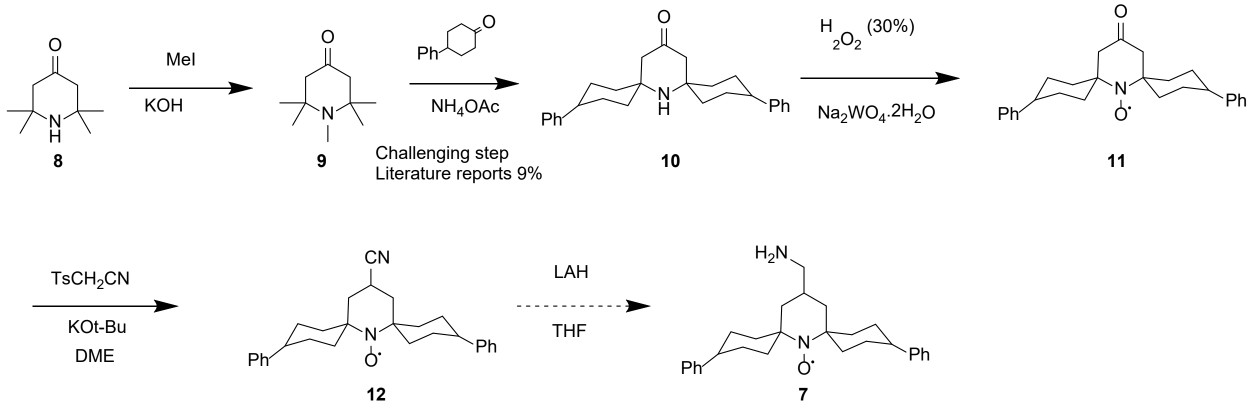

Figure 2. Synthesis of spirocylic amine 7Synthesis of BDPA-TEMPO Biradical

Due to challenges experienced in the synthesis of HyTEK a portion of BDPA 6 was converted to a TEMPO biradical for DNP testing. Synthesis of BDPA-TEMPO monoradical 13 was achieved by N,N'-Dicyclohexylcarbodiimide (DCC) coupling of BDPA 6 with 4-amino TEMPO catalyzed by N,N-dimethylaminopyridine (DMAP) as shown in Figure 3. The resulting BDPA-TEMPO monoradical 13 was purified via column chromatography and characterized by electrospray ionization mass spectroscopy (ESI-MS) indicating [M+H]+ 616.9 for C43H39N2O2 compared to calculated [M] 615.3 Figure 4. BDPA-TEMPO monoradical 13 is stable when stored as a solid at room temperature, the desired BDPA-TEMPO biradical 14 can be generated by deprotonating 13 using DBU, followed by silver nitrate one-electron oxidation.

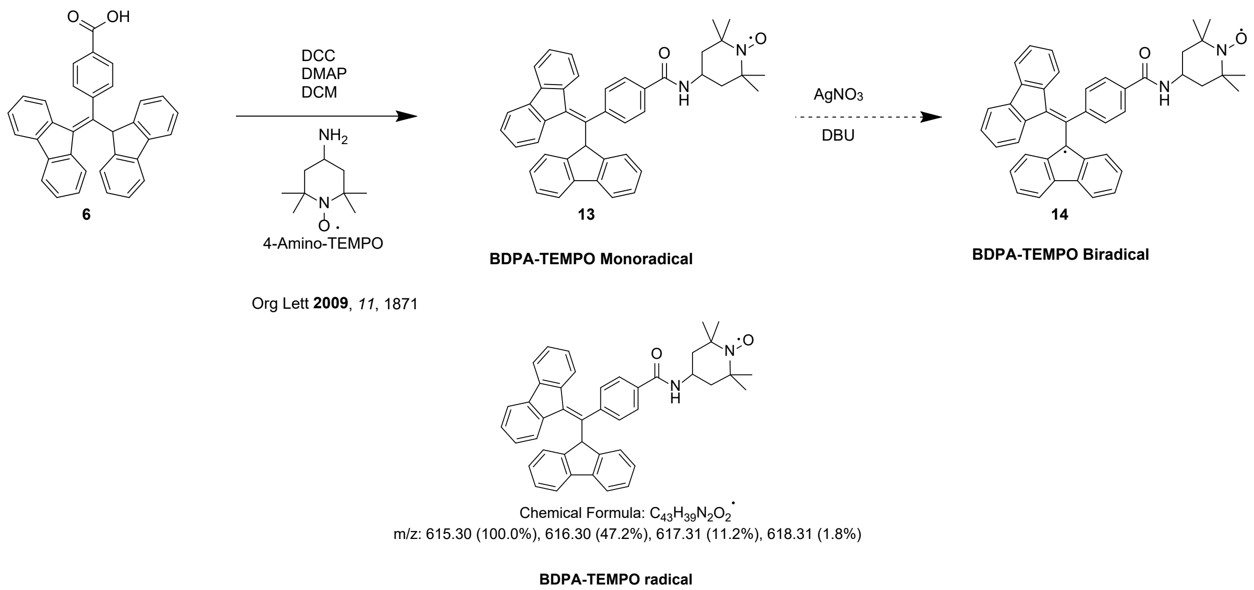

Figure 3. Synthetic scheme for BDPA-TEPO biradical

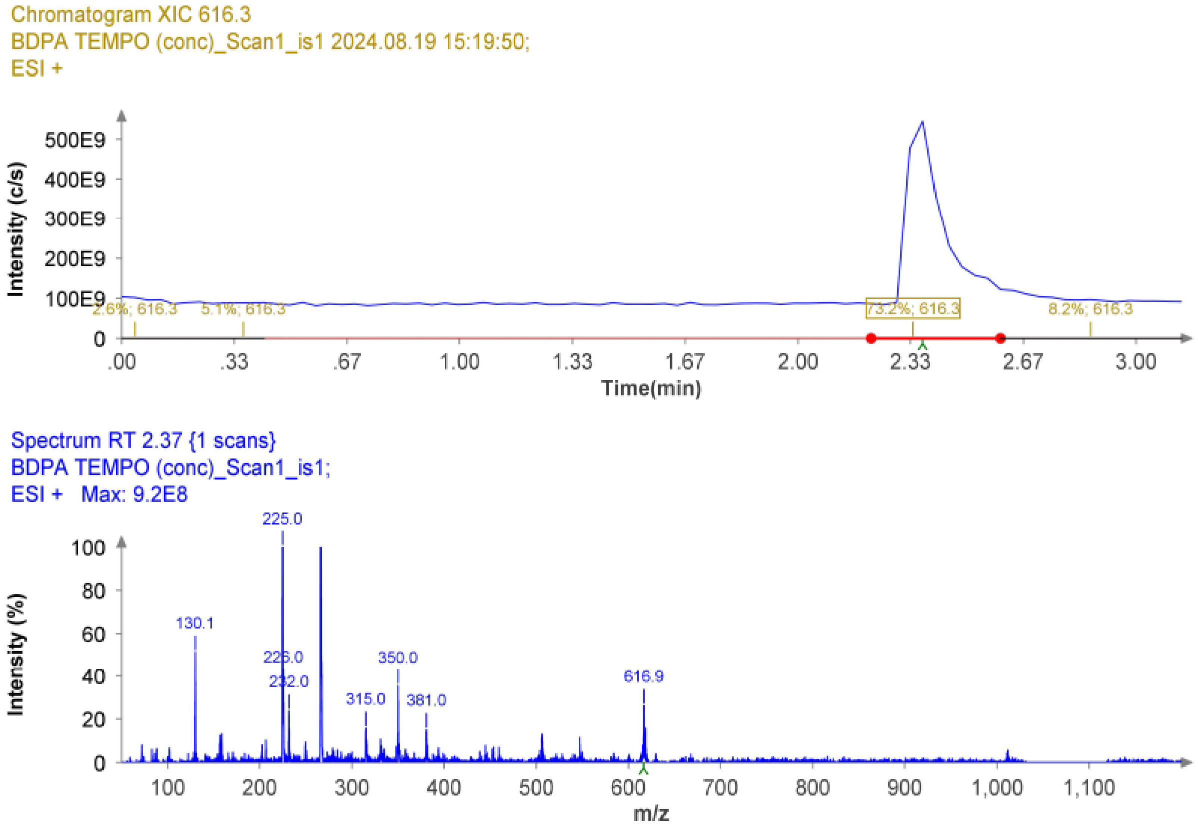

Figure 4. ESI mass spectrum for BDPA-TEMPO monoradical

3.0 Results: DNP Enhancement Testing with Sweep Coil

3.1 Background

High-field DNP offers unparalleled sensitivity for studying complex materials, enabling the analysis of structural, compositional, and dynamic properties that are otherwise inaccessible. However, its full potential hinges on the availability of tailored polarizing agents that can overcome the intrinsic challenges of high-field polarization transfer. By systematically evaluating the performance of different radicals, researchers can determine their suitability for specific materials and refine experimental protocols to optimize DNP performance. This effort directly supports the broader goal of advancing materials science, catalysis, and energy research by unlocking the capabilities of the 800 MHz DNP system

The recently completed DNP magnet replacement enables the use of a more streamlined approach to optimization of DNP signal enhancement, which is more standardized between samples/radical matrices and leads to more stable gyrotron output. This is key to benchmarking the performance of new biradicals for the commonly used cross-effect (CE) DNP mechanism, as well as other sources of endogenous hyperpolarization such as doped paramagnetic centers, defects, and permeation with solvated transition metal ions. As opposed to operating at fixed field and optimizing gyrotron parameters (which was the case for the FY21 and FY23 DNP investigations), the gyrotron is engaged with parameters that lead to stable, consistent microwave output, and the field position of the primary magnet is swept to locate the optimum enhancement. Combined with the fact that this prevents spontaneous ‘drop-outs’ in microwave power when operating near the edge of the stable gyrotron parameters – which was necessary for some CE biradicals with the fixed-field approach – it also enables a considerable reduction in complexity of setup for a given radical, as an experienced operator can ‘park’ the primary magnetic field at the radical’s optimum. With the gyrotron configuration fixed, this then reduces the optimization of a CE DNP experiment to that of a conventional solid-state NMR cross-polarization experiment, which will lower the barrier to entry for new users of the system. Unconventional radicals/hyperpolarization sources (e.g. metal-ion DNP with Fe^{3+}/Mn^{2+} dopants in a crystal lattice) will still require sweeping of the primary magnet. It is also noteworthy that, while sweeping of a DNP magnet is quite common at lower fields (e.g. 9.4 T), it is unclear that this mapping process has ever previously been conducted for a ‘materials science’ (i.e. non-bio, ^{1}H-^{13}C-^{15}N) sample, such as the mesoporous (MP) γ-Al_2O_3 utilized as a model material for this study.

Few organic radicals are designed to perform efficiently at high magnetic fields (600 MHz or greater) in Dynamic Nuclear Polarization (DNP) Nuclear Magnetic Resonance (NMR). The polarization transfer mechanisms underlying DNP, such as the cross effect, and the organic radicals that facilitate polarization transfer, are highly field-dependent. At high fields, many conventional radicals perform sub optimally or are entirely ineffective. As such, testing and benchmarking available radicals under high-field DNP conditions is critical to identifying radicals capable of maximizing signal enhancements.

High-field DNP offers unparalleled sensitivity for studying complex materials, enabling the analysis of structural, compositional, and dynamic properties that are otherwise inaccessible. However, its full potential hinges on the availability of tailored polarizing agents that can overcome the intrinsic challenges of high-field polarization transfer. By systematically evaluating the performance of different radicals, researchers can determine their suitability for specific materials and refine experimental protocols to optimize DNP performance. This effort directly supports the broader goal of advancing materials science, catalysis, and energy research by unlocking the capabilities of the 800 MHz DNP system.

3.2 Approach

Three common CE biradicals were selected for the sweep benchmarking, two of which were comparatively recently developed: AsymPolTEK and M-TinyPol. The third, TEKPol, is widely used at the lower 9.4 T field, but is known to under-perform at 18.8 T. The 'TEK' biradicals are designed for use in a non-aqueous matrix with tetrachloroethane (TCE), while M-TinyPol is used with an aqueous-based cryo-protectant formulation, consisting of 60% d8-glycerol, 30% D_2O, and 10% H_2O (v/v/v), denoted 'GDH.' The actual proton density is comparable between these TCE-based and GDH-based matrices, which are wetted onto the (ideally, porous) powder sample using incipient wetness impregnation. The biradical concentrations were based on previously established (FY21 and FY23) optimal values. Once the sample is spinning in the DNP magnet at the operating temperature of 100 K, the cross-polarization (CP) parameters, which transfer the magnetization from the ^{1}H bath of the radical matrix to the target nucleus (in this case, ^{27}Al) are optimized for each sample preparation, and the hyperpolarization build-up time is measured. This is the 'indirect DNP' mode of signal enhancement, where the 1H nuclei in the radical matrix vector the radical magnetization onto the surface of the sample particles. Conversely, 'direct DNP' involves the acquisition of a conventional, single-pulse NMR experiment while the microwaves are turned on to factor out the influence of differential efficiency in CP mechanisms between sites on the sample. Both modes ultimately yield surface-enhanced DNP spectra, however, as the hyperpolarization source is exogenous to the sample parameters. In both cases, once optimized, these experimental parameters are then fixed as the magnet is incrementally swept to trace out the signal enhancement and find the optimum field for the given radical preparation.

3.3 Sweep Curve Benchmarking Results on Conventional CE Biradicals

Initial testing was performed with AsymPolTEK, a new non-aqueous radical which has improved build-up times relative to TEKPol. As part of the testing, the sweep coil was fully exercised over the useful enhancement range, and a small field sweep increment was used to carefully examine the enhancement variation and avoid hysteresis issues with the field sweep (to be discussed subsequently). The raw ^{1}H enhancement, ^{27}Al direct DNP, and ^{1}H-^{27}Al indirect DNP enhancements were measured, as laid out in the spectral overlays of **Figures 5-7**, compared against the equivalent 'microwaves-off' non-DNP experiments. The key points of interest were the field values where maximum overall enhancement was achieved, the crossover point to 'negative enhancement' (an inversion of the enhanced magnetization as modulated by the electron resonance), the lowest 'negative enhancement' point, and the edges of the sweep curve where enhancement is attenuated to the point that it is equivalent to the non-DNP experiment (an 'enhancement factor,' ϵ, of unity), along with how these differ between the direct and indirect modes and raw ^{1}H bath enhancement. In all cases, the dashed lines on the figures represent this equivalence point.

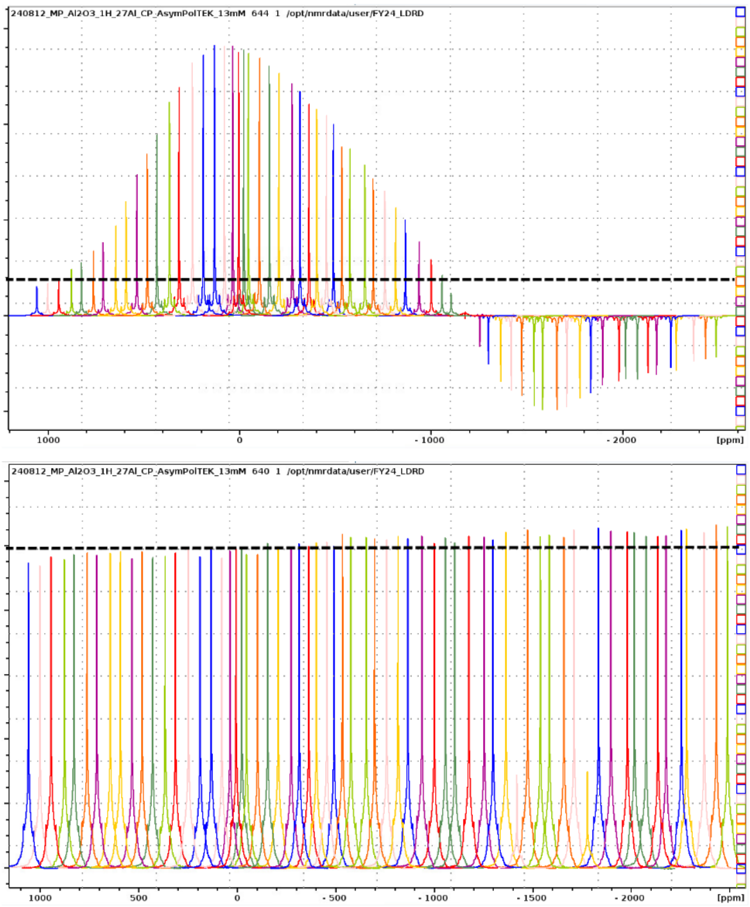

Figure 5. DNP sweep sweep enhancement spectral composite for raw ^{1}H enhancement of MP γ-Al_2O_3 with 13 mM AsymPolTEK/TCE, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

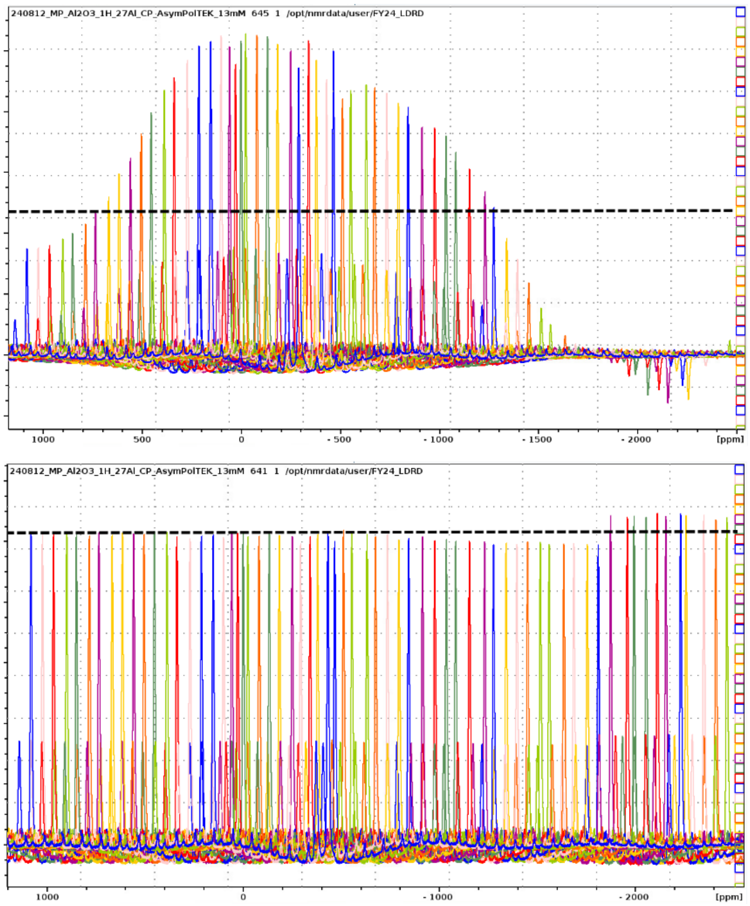

Figure 6. DNP sweep enhancement spectral composite for direct ^{27}Al enhancement of MP γ-Al_2O_3 with 13 mM AsymPolTEK/TCE, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

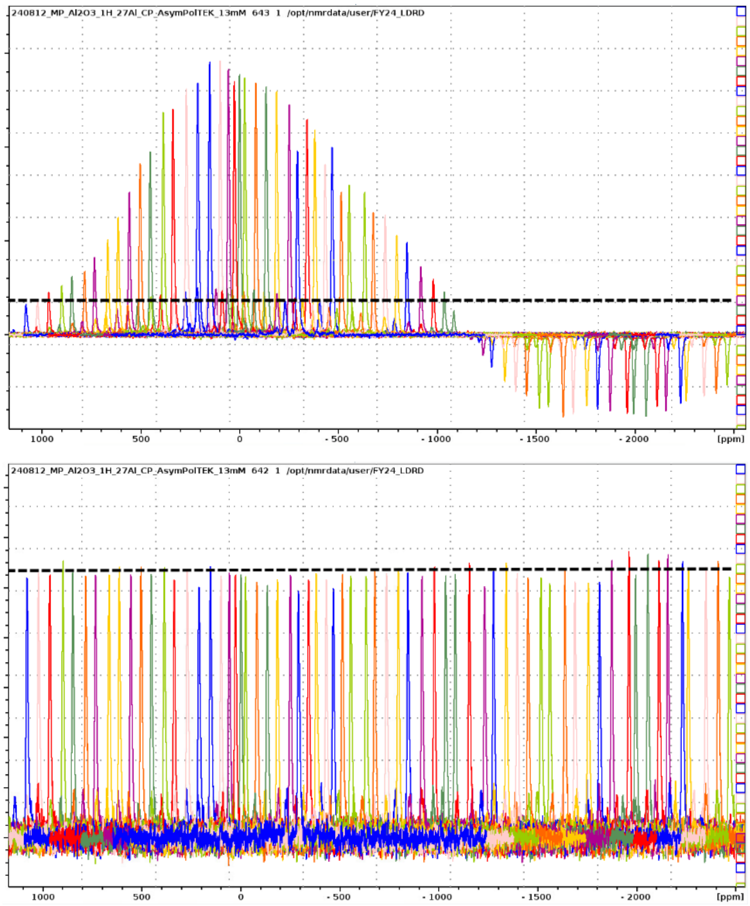

Figure 7. DNP sweep enhancement spectral composite for indirect ^{1}H-^{27}Al enhancement of MP γ-Al_2O_3 with 13 mM AsymPolTEK/TCE, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

AsymPolTEK delivers modest 1H and indirect 1H-27Al enhancement, with much smaller relative enhancement for the direct 27Al mode. The latter is, by default, less efficient for cases where there is strong cross-polarization between the particle surface and the solvent bath, as is the case for MP Al2O3. Interestingly, while the raw 1H and indirect 1H-27Al enhancements (unsurprisingly) strongly correlate, the crossover point to negative enhancment for direct 27Al DNP is at considerably lower frequency (negative ppm). This point is also reached at a field where, surprisingly, the non-DNP (microwaves-off) 27Al signal suddenly experiences a ~20% boost; as the positions correlate and there is no radical hyperpolarization without the microwaves on, it suggests that there is potentially some sort of cross-relaxation effect occurring involving long-range interaction of the radical electrons with the surface 27Al sites, but this remains to be further investigated and it is unclear if this type of effect has previously been observed in conjunction with the direct-DNP crossover point.

TEKPol in TCE was next examined, with the sweep spectral profiles presented in **Figures 8-9**. As has been previously established in the literature, TEKPol performance at high field is inadequate for useful enhancement, where in a signal enhancement of approximately one order of magnitude is minimally desirable. (For context, since the signal-to-noise gain scales as the square of the signal enhancement factor, one would have to perform a non-DNP experiment with signal-averaging for ϵ^2-times the DNP experiment to achieve the equivalent signal-to-noise ratio.

With low-signal samples, this translates to a scaling from a duration of days to a duration of hours; for higher-signal samples, this enables feasible acquisition of multi-dimensional experiments which would otherwise be overly consuming of instrument time to be practical.)

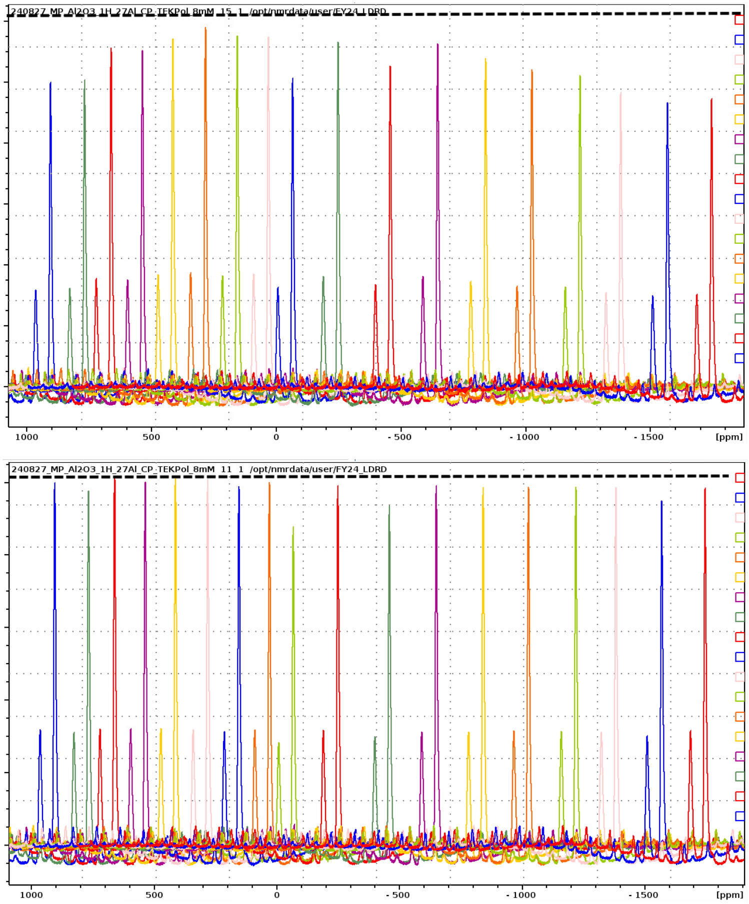

Figure 8. DNP sweep enhancement spectral composite for direct ^{27}Al enhancement of MP γ-Al_2O_3 with 8 mM TEKPol/TCE, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

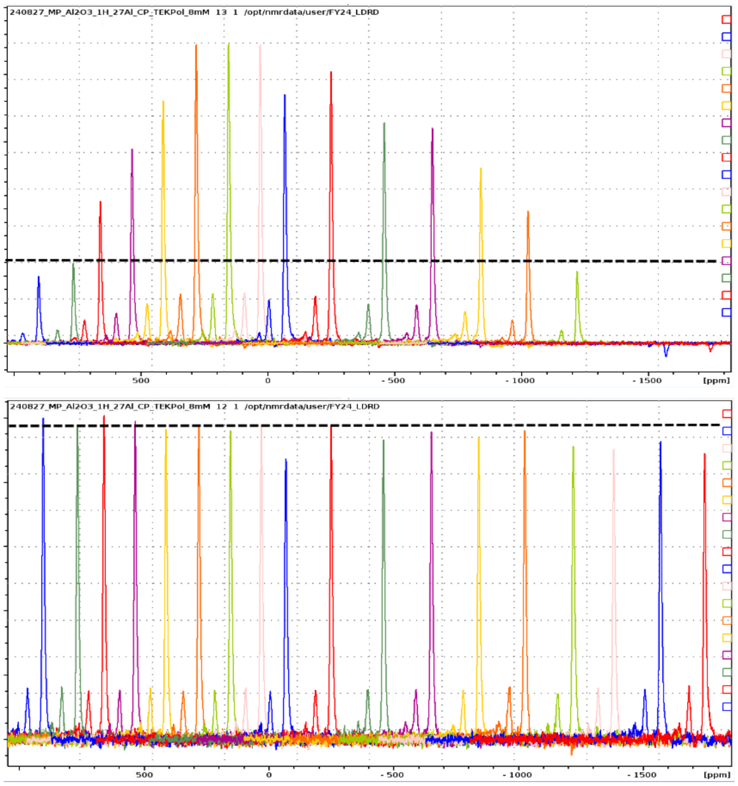

Figure 9. DNP sweep enhancement spectral composite for indirect ^{1}H-^{27}Al enhancement of MP γ-Al_2O_3 with 8 mM TEKPol/TCE, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

The direct DNP mode for TEKPol yields de-enhancement relative to the non-DNP ^{27}Al single-pulse experiment – the signal reduction from microwave heating does not offset the lack of signal gain from poor hyperpolarization transfer – while the raw ^{1}H enhancement and corresponding ^{1}H-^{27}Al indirect DNP enhancement are approximately half that of AsymPolTEK, confirming that it is insufficient for practical application at high-field, which underscores the need for new non-aqueous CE biradicals that can perform well in this regime.

The sweep profiles for the aqueous M-TinyPol/GDH biradical were then measured, as presented in **Figures 10-12**. Previous FY results on M-TinyPol at high field had already demonstrated its considerable strength in this regime – for which it was developed, it should be noted – so this series of measurements was simply to evaluate its performance across the span of the sweep coil and determine the locations of the key points of interest. While it yields maximum enhancement factors that translate to almost three orders of magnitude gain in signal-to-noise acquisition rate, note all samples (especially in the energy storage and catalysis contexts) are amenable to aqueous-based polarization matrices. Nevertheless, when feasible, it is clearly the CE biradical of choice at present for high-field, indirect-DNP measurements.

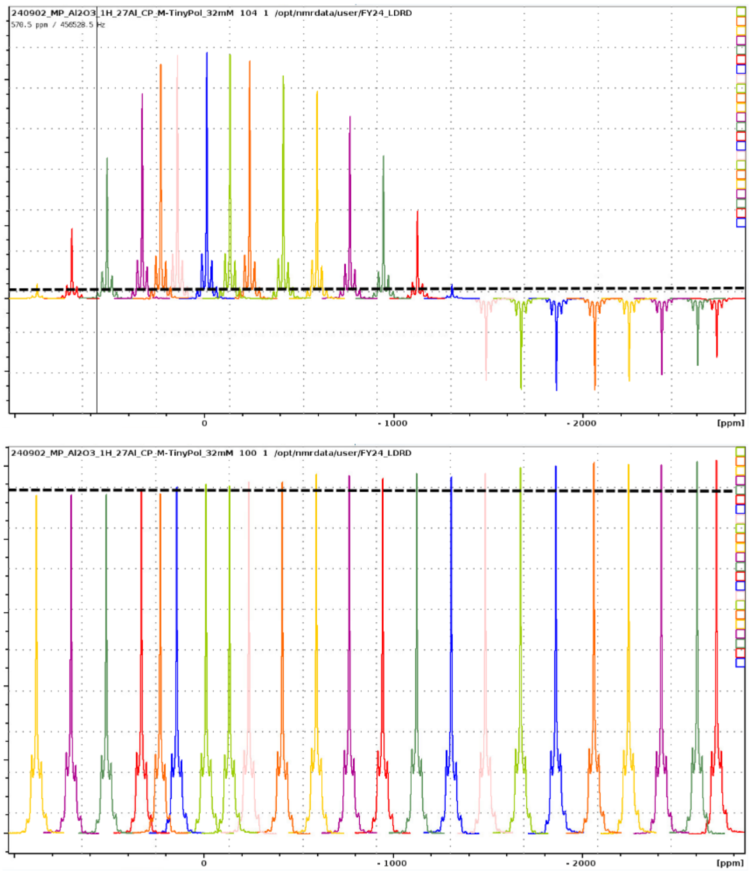

Figure 10. DNP sweep enhancement spectral composite for indirect ^{1}H enhancement of MP γ-Al_2O_3 with 8 mM TEKPol/TCE, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

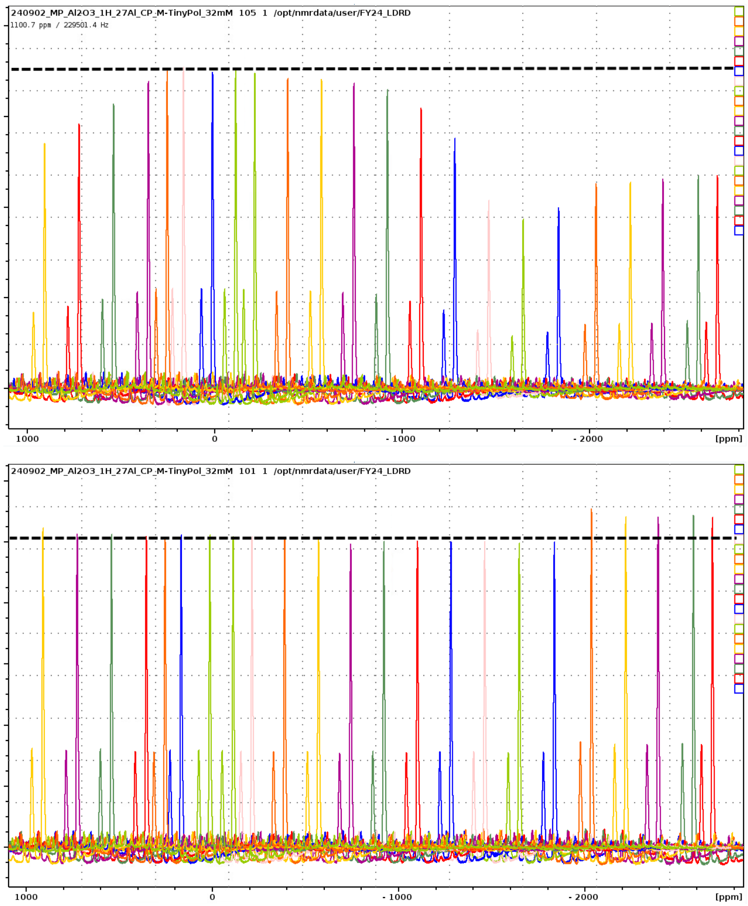

Figure 11. DNP sweep enhancement spectral composite for direct direct ^{27}Al enhancement of MP γ-Al_2O_3 with 32 mM M-TinyPol/GDH, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

Despite the strong raw ^{1}H enhancement and correspondingly powerful ^{1}H-^{27}Al indirect DNP enhancement, M-TinyPol surprisingly lead to de-enhancement in the ^{27}Al direct DNP mode across all field values. It is not a priori clear why this otherwise much more efficient biradical fails to directly enhance the particle surface compared with the less powerful, non-aqueous AsymPolTEK, but it may simply be a case of saturation of the hyperpolarization in the exterior solvent bath without using CP to force it to transfer to the surface aluminum sites. If this is the case, then further experiments with the relative deuteration level in the radical matrix should impact the direct DNP efficiency, which can be carried out when a case occurs with a sample where the relative importance of the direct and indirect pathways is scientifically relevant.

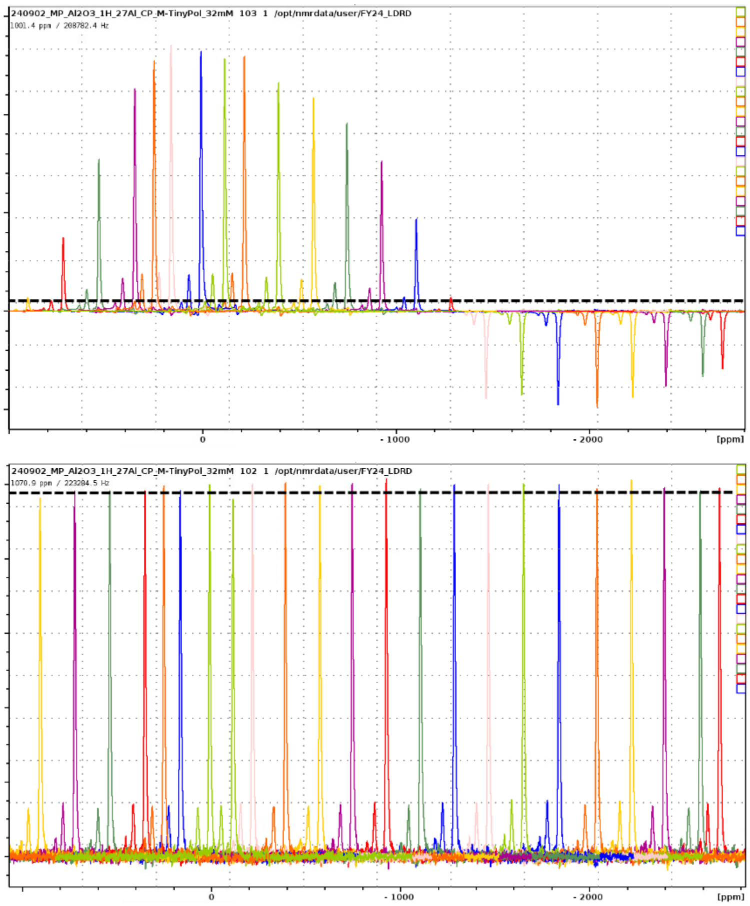

Figure 12. DNP seep enhancement spectral composite for indirect indirect ^{1}H-^{27}Al enhancement of MP γ-Al_2O_3 with 32 mM M-TinyPol/GDH, top panel, compared with the non-DNP equivalent. The dashed line represents unity enhancement factor.

The quantitative signal enhancements for the non-aqueous biradicals and aqueous M-TinyPol are presented in **Figure 13** and **Figure 14**, respectively. These field sweep maps define the ‘parking positions’ of the magnet for standard CE DNP operation with these radicals for routine surface-enhanced DNP experiments, with fixed gyrotron output, from which the sample-specific spectroscopic parameter optimization would be performed. The overall maximum enhancements offered for this model material with each radical are summarized in Figure 15.

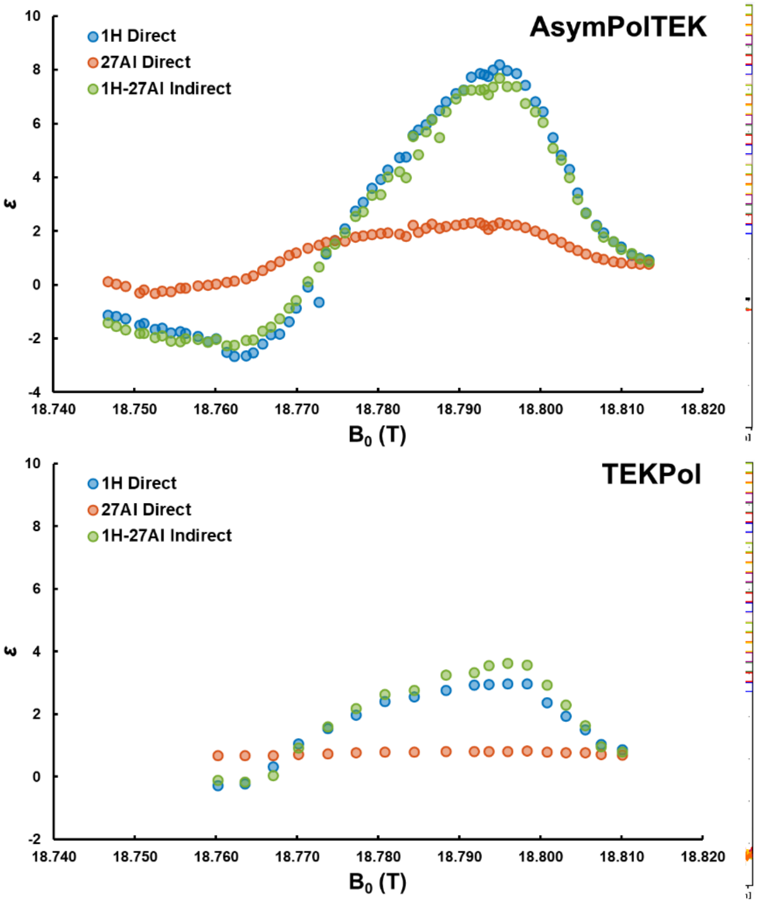

Figure 13. Quantitative DNP sweep enhancement curves for the non-aqueous AsymPolTEK/TCE and TEKPol/TCE radical formulations with MP Al_2O_3, illustrating the locations of the key points of interest (particularly, the maxima) of the field sweep for each DNP mode.

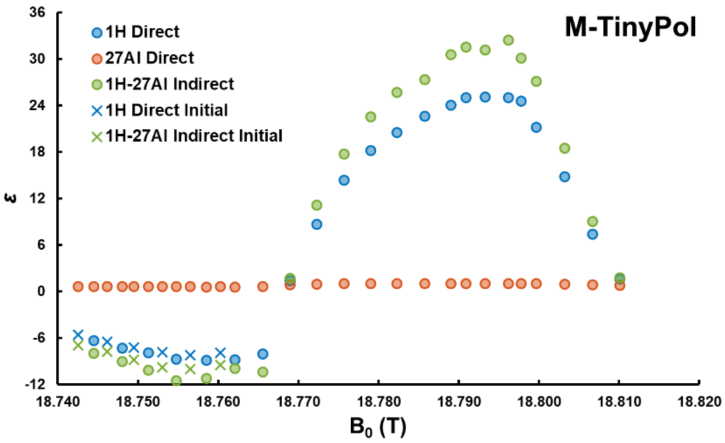

Figure 14. Quantitative DNP sweep enhancement curves for the aqueous M-TinyPol/GDH radical formulation with MP Al_2O_3, illustrating the locations of the key points of interest (particularly, the maxima) of the field sweep for each DNP mode. The 'X' markers correspond to the initial start of the sweep, moving from 18.760 T down to lower field, prior to a de-gassing cycle (to be elaborated below).

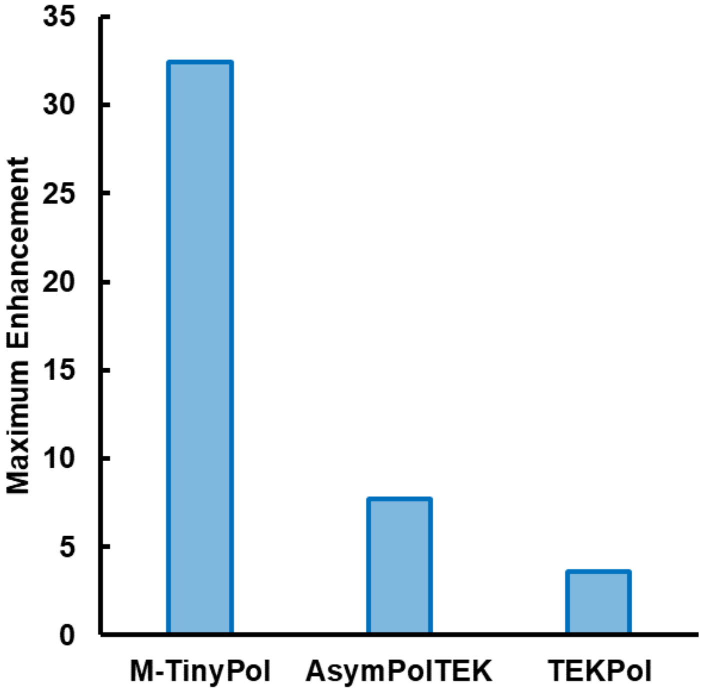

Figure 15. Quantitative comparison of the maximum enhancements of the MP Al_2O_3 model material offered by the CE biradicals for ^{1}H-^{27}Al indirect DNP studied for benchmarking at the optimum sweep position.

3.4 Considerations for Sample Preparation and Instrumental Effects

As described in **Figure 14** for the M-TinyPol sweep enhancement curve, a discrepancy in the smoothness of the enhancement curve was discovered when sweeping back from the endpoint. The rotor spinning had been somewhat unstable, so the rotor was spun down and ejected from the probe, and then re-spun on the test spinner platform to evaluate whether the sample needed to be re-packed. This re-warming process not only fixed the spinning issue (likely due to non-uniform freezing of the radical matrix on the initial spin-up), it also revealed that the enhancement factors were improved on re-commencing the sweep measurements. While it is known in the literature that freeze-thaw de-gassing cycles are beneficial to remove molecular oxygen for maximizing enhancement (in the context of demonstrating the largest possible efficacy of a newly developed radical), it was clear that this process could have a significant effect even for routine samples. Correspondingly, a TEKPol/MP Al_2O_3 sample was prepared in a rotor and placed in the benchtop X-band EPR, where a series of four freeze-thaw cycles was undertaken while monitoring the EPR signal (**Figure 16**).

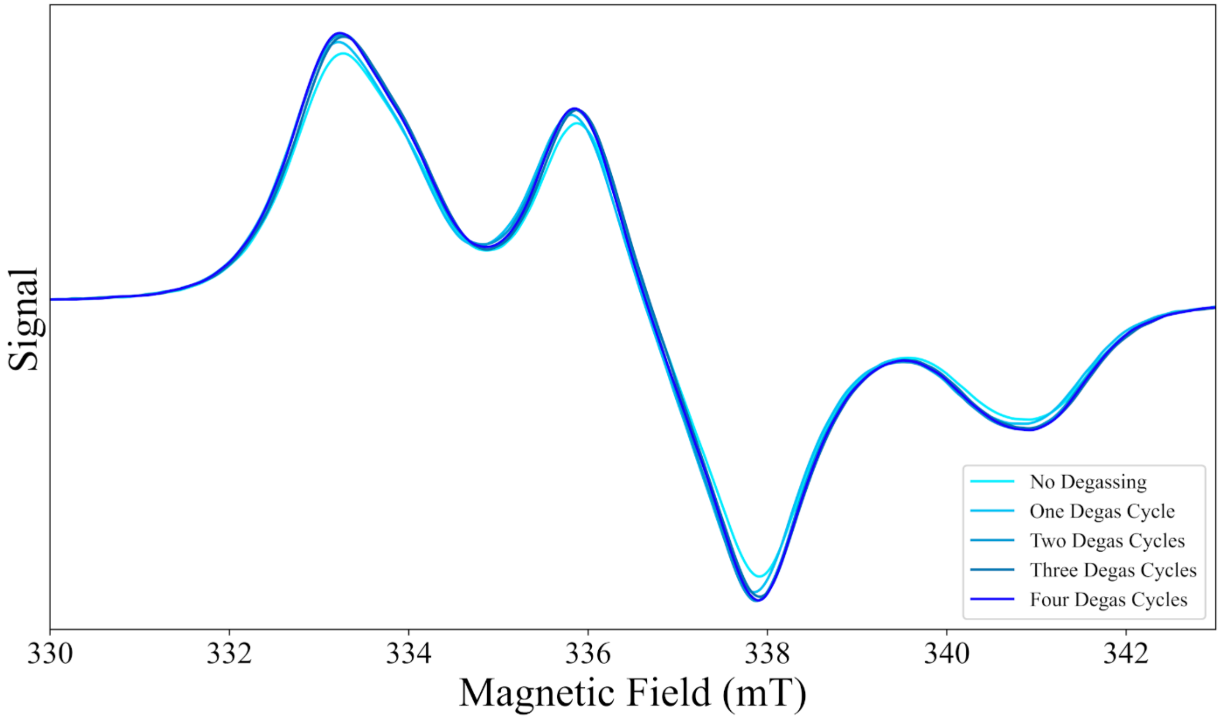

Figure 16. X-band EPR of an 8 mM TEKPol/TCE wetted MP Al_2O_3 sample in situ in a rotor while a series of four freeze-thaw de-gassing cycles (293 K to 100 K, and reverse) were carried out. The effect on the EPR lineshape is comparatively minute, but even this small change signals a potentially quite large impact for hyperpolarization relay to the particle surface.

A measurable difference in the EPR signal of the TEKPol was detectable over the course of this process; while the effect in the EPR is slight, it should be noted that there is likely to be relatively minimal penetration of the molecular oxygen into the solvation shell of the radical itself, affecting the EPR line. Where this *can* have a significant impact is in the hyperpolarization relay to the particle surface, transmitted over the tens-of-nanometer length scale from the bleaching zone in the radical vicinity to the particle surface, which would then adversely impact DNP enhancement (by both the direct and indirect modes). This de-gassed rotor was then placed in the DNP and a comparison was made between the nearest field position of the previous TEKPol sweep curve and this rotor at the contemporary field position, demonstrated in **Figure 17**. Note that the sweep power supply was experiencing an interlock issue requiring a warranty repair at this point, so a full sweep curve, to interrogate the effect at the optimum enhancement position, could not be undertaken. Nevertheless, even at this non-optimal field position, a 50% increase in enhancement efficacy was demonstrated. De-gassing and monitoring in the EPR prior to performing DNP will therefore be a standard procedure in all future experiments.

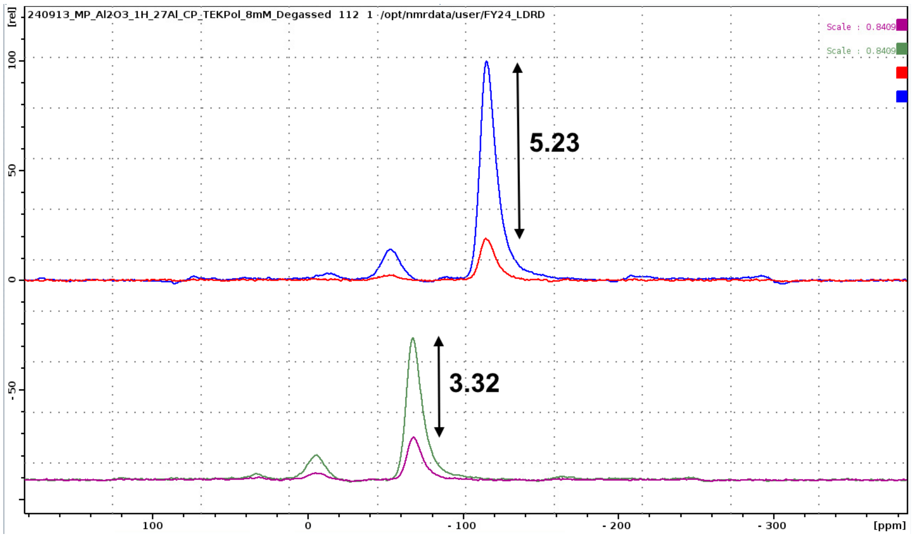

Figure 17. Comparison of indirect DNP enhancement for a de-gassed MP Al_2O_3/8 mM TEKPol/TCE sample with the nearest field position from the original TEKPol sweep curve (**Figure 9**), demonstrating a 50% improvement in enhancement. If this same approximate gain holds for AsymPolTEK (which is in the same solvent medium), then at optimum field position, it will achieve the key order-of-magnitude enhancement benchmark, which will be tested as soon as possible.

A final important aspect of this sweep-coil benchmarking exercise regards the development of best-practices for the operation of the sweep coil itself. The absolute current applied to the sweep coil does not correlate with the resultant field position; there is a degree of hysteresis that results from both the location of the sweep coil within its range and from opening the switch heater to effect a movement of the field. This is demonstrated in **Figure 18**, for a sweep loop which was conducted moving from zero current to positive current, then stepping back through zero to negative current, and starting a return to zero. On reversing directions and interpolating between the original steps of the field moves, a linear return to the intervening field positions does not occur.

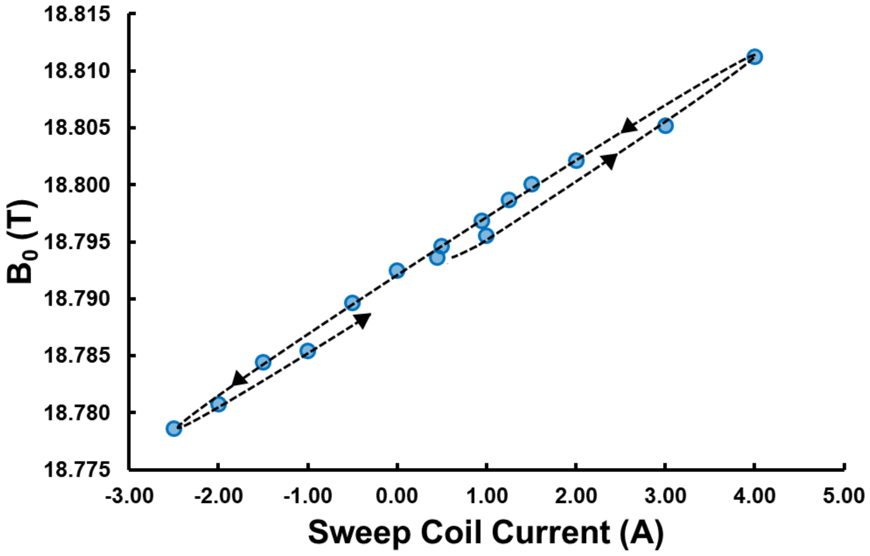

Figure 18. A polot of the applied sweep coil current versus the resultant field (back-calculated from the transmitter offset) on traversing the loop indicated by the arrowed dashed line. The apparently small gaps in field position translate to multiple tens of ppm offset in ^{1}H spectrum position.

Accordingly, the following principles of operation for sweeping have been developed to guide future enhancement curve development:

- Given that the maximum current applied to the sweep coil per 24-hour period is limited, for large sweeps, the most useful approach is to move to the necessary end point with double the desired mesh increment, and then reverse course from the end point with an offset of one mesh point. Otherwise, an entire day of idling at one field position is necessary to move back from the endpoint to zero (or beyond to the other current direction).
- When moving the field back towards zero after venturing to the endpoint, the mesh steps will likely need to be shrunken by ~25%, as the coil typically moves more per ampere when restoring to the natural B_0 of the main coil than when moving in either direction away from it.
- Limiting steps to 0.5 A (corresponding to ~130 ppm ^{1}H) will limit post-sweep field drift, enabling immediate resumption of DNP experiments following the sweep.
- Opening the switch to perform a sweep after running up the current in the leads produces typically ~10 ppm of drift before the sweep engages; the direction of this drift *does not* appear to correlate with either the existing current in the sweep coil, or the prior direction of movement; effectively, this means that the smallest possible move is 0.1 A, which will result in 10-30 ppm of field correction depending on whether the switch opening drift aligns with, or against, the intended direction of field movement.
- The largest impact to the magnet's cryogen bath temperatures (and consequently, flow rate of the needle valve which maintains its internal temperature at safe levels) comes from opening the switch itself, rather than the current change in the sweep coil, even for multi-ampere sweeps. Correspondingly, it is not advisable to repeatedly open the switch

to perform small corrections in the field, and care should be taken to accurately gauge the necessary amount of current (per the ‘rules of thumb’ above) to achieve the target field position.

4.0 Conclusions Regarding Sweep Coil Testing

This LDRD project enabled the successful testing of the DNP sweep coil on a series of standard CE biradicals, thereby verifying this functionality in the newly replaced and now fully functional magnet and mapping out the key points of interest – and optimal field positions – for these radicals. Coupled with the operation of the gyrotron at fixed parameters, this will greatly reduce the complexity of starting up DNP investigations of new sample classes and considerably lower the barrier to entry for operation by new users. Along with the thorough characterization of the radical performance on a non-biological material at high-field, which has not been previously undertaken as yet to the best of the authors' knowledge, this process yielded new operational guidelines which will greatly improve performance for experiments under direct-sponsored projects where extensive benchmarking of this nature is infeasible.

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