### I. HYPERPOLARIZATION SETUP

Fig. S1 shows the overall hyperpolarization setup, containing the lasers employed for DNP, along with thermal management systems and a Helmholtz coil for application of the polarization field. The setup consists of a three-sided panel design, each with total edge length 18in. and constructed in a compact manner for positioning under a 7T magnet. The laser diodes were mounted on the interior panels, and driver modules on the exterior panels as shown in Fig. S1(a)-(b). This allows the use of short 0.5m fibers while preventing tight bends.

The panels were designed in a manner that allows the laser diodes and drivers to be easily accessible. Each exterior panel holds up to 12 driver modules (Lasertack PD-01289), and each interior panel holds the corresponding Lasertack 520nm laser diodes. The structure can mount laser diodes and modules on up to four sides (allowing a total of 32 lasers). These panels are fastened onto 8020 aluminum frames and can easily screw on or off without having to remove any other parts of the structure. The laser diodes are electrically connected to the driver modules by snap-on connectors. For our experiments we mounted a total of 30 lasers (≈0.8W each) onto three panels.

An Arduino Leonardo microcontroller mounted on each panel, controls the laser diodes. Each microcontroller connects to a central computer via USB serial communication. This permits the ability to turn on or off any combination of lasers with individually set times and duty cycles that can be dynamically reprogrammed.

A large 12in. Helmholtz coil surrounds the dome at the center of the setup. The dome and coil require precise vertical positioning relative to the 7T magnet that is difficult to calibrate ex-situ. To ease in-situ calibration we constructed a multilevel mount connected to a plexiglass plate cover by bolts that can be adjusted to change the vertical positions of the coil and dome simultaneously. This structure is designed such that all of the components could be fabricated in-house using an entry level laser-cutter or 3D printer.

We took a multi-tiered approach to thermal management. There is a need to cool both the sample and the laser diodes themselves to ensure optimal performance. We focus our discussion here to the laser diode cooling, while details of the sample cooling (heat exchanger) are presented in Sec. III. A Peltier cooler (TE Inc. TE-63-1.0-1.3) is attached to the base of each diode to maintain a temperature at or below 25°C (i.e., diamond that transmits the injected heat to the surrounding water, to eject heat from the water. Overall, this creates an efficient and hyperpolarization compatible heatsink around the diamond. Importantly, the sample test tube itself has no liquids flowing into it, and hence it can be mechanically shuttled for NMR measurements [67].

The sample cooling column (Fig. S2-Fig. S3) consists of two concentric slotted cylindrical shells. Cooled nitrogen (at -20°C) is fed into ports from the top of the cylindrical column at 48 cfm to chill the water surrounding the diamond. Similar to the operation of a Dyson bladeless fan, the slots in the cylindrical shells create vortex currents which increase the characteristic length of heat transfer. Additionally, this design increases turbulence within the chamber, which better dissipated heat within the gaseous medium. The top of the column has an orifice for warmer gases to escape;
Fig. S1. **Construction of the laser excitation setup.** (a) Photograph of the laser excitation setup consisting of 30 individual lasers placed on three faces (walls) of a cubical (12in) box, built out of 1/4in sheet aluminum. Fibers here are shown removed for clarity. The laser heads (see (d)) occupy the inner faces, while the drivers are placed on the outer faces. (b) Picture of an outer face showing 12 mounted laser drivers. They are interfaced to power by means of a custom centrally located PCB. (c) Photograph of supporting structure laser-cut out of plexiglass which supports the laser dome and the Helmholtz coil. It also ensures central alignment of the entire structure and permits rapid insertion and extraction of the sample from it. (d) Single laser diode (Lasertack). It consists of a fiber coupling attachment where a multimode fiber is screwed on. Its lower surface consists of a Peltier cooler for temperature regulation. We employ 30 such lasers, each with an output power (after the fiber) of $\approx 0.8\text{W}$. (e) Photograph of the fully assembled apparatus with fibers connected, and the laser dome mounted. The fibers (each 0.5m long) are coiled in a symmetric fashion to ensure tight laser packing. All structural support is provided by the plexiglass structure in (c). The 3D printed sample cooling column at the neck of the dome (see Fig. 5 of the main paper) is visible in the top portion of the picture along with the plexiglass supports.

This is also from where the sample test tube is shuttled for $^{13}\text{C}$ NMR [67].

Our experimental observations of the heat exchanger performance are presented in Fig. 6 of the main paper. In experiments, a K-type thermocouple is used to record system temperature under 120s of continuous illumination with an increasing number of lasers. We visually observe small yet complicated microbubbling at the boundary of the diamond. Fortunately, the bubbling has a negligible effect on heat exchange. Overall, we are able to keep the system steady state temperature under 30°C even under the sustained high-power illumination.

**IV. OPTICAL SIMULATION**

Our experiments are carried out on a 4x4x1mm diamond sample. Using the exact position of the fibers, we employed COMSOL to carry out a simple optical simulation based on laser ray tracing from the laser fiber tip positions in the dome, passing through air (refractive index $n=1$), glass ($n=1.6$), water ($n=1.33$) and ultimately the diamond ($n=2.54$) (Fig. 5(e) of the main paper). We included effects of refraction, and the intrinsic 6° laser beam divergence. Attenuation was not included; attenuation in air, glass (absorption coefficient $k=0.34 \text{m}^{-1}$), and water ($k=0.045 \text{m}^{-1}$) is negligible. The optical simulation (Fig. 5(e) of the main paper) shows an overlapping pattern of ray traces indicating a concentration of light at the center of the diamond. Diamond has a high absorption coefficient of 12.7 mm$^{-1}$ and penetration depth of 0.0787 mm; this regime overcomes some of the potential attenuation losses due to the overlapping rays produced by the lasers.
V. CHARACTERIZATION OF LASER HOMOGENEITY

In this section, we describe experiments to characterize and optimize the homogeneity of the laser excitation on the diamond sample. Our goals are to maximize the uniformity of the optical illumination in order to ensure that every part of the sample sees approximately the same laser excitation intensity (here ≈0.8W per laser). These measurements will be employed in order to normalize the effective laser intensities in the experiments performed in Fig. 2 of the main paper. Optical inhomogeneity itself can arise from factors including:

i. Misplacement of the laser. From the vantage point of a few lasers excitation slots, the MW coil casts a shadow on the sample. Lasers mounted on these positions therefore strike the sample with their intensity greatly suppressed. The exact positions depends on the exact MW coil employed in the experiment. We find that for a typical split coil design, 30 lasers can easily be accommodated with minimal loss.

ii. Off-center MW coil. The 3D printed slots in the laser dome ensure that fibers placed into them are naturally aligned to the exact geometric center of the dome structure. This assumes, however, that the MW coil itself is centrally located in the dome cavity in order to minimize overlap with the laser beams.

iii. Total internal reflection. Depending on the size, shape and orientation of the sample, some of the lasers are more effective because optical beams from them undergo total internal reflection within the diamond.

Hyperpolarization levels obtained from each laser applied individually to the sample provide the best means to characterize the homogeneity of the optical excitation. We carry out such DNP experiments with each laser illuminated for 20s, and measure the $^{13}$C hyperpolarized NMR signal under pulsed spin lock for 20s. The resulting integrated signals are then correlated with position on the dome. Any inhomogeneities due to coil or laser misplacement can then be easily identified. It is evident from Fig. 5(e) of the main paper that hyperpolarization can be arranged to be homogenous to a good degree even for the 28 applied lasers. Two lasers in Fig. S4 had degraded in performance and were at reduced intensity. The experiments also reveal that the maximum hyperpolarization intensity arises, somewhat counterintuitively, for lasers striking the sample at the diagonal top positions.