NMR spectroscopy is a prime tool to investigate molecular structure and dynamics at atomic resolution under non-perturbative conditions. Unfortunately, the low sensitivity of NMR imposes severe limitations to the number of detectable nuclear spins, and hampers the applicability of NMR to many important problems of biological significance. To address this limitation, we developed a novel NMR technology combining laser or LED irradiation inside cryogenic probes and radiofrequency pulses generating heteronuclear spin coherence to perform photochemically induced dynamic nuclear polarization (photo-CIDNP) at high applied magnetic fields. In addition, we discovered novel additives (including photosensitizers, heavy-metal-containing and oxygen-scavenging agents) that can be added in minute amounts (low micromolar or sub-micromolar) to the samples and synergistically combined to generate an even higher-sensitivity version of NMR spectroscopy in liquids at high field. With this methodology, hypersensitive data collection on biological samples at sub-micromolar concentration can be achieved within only a few seconds, with thousand-fold time savings relative to regular NMR experiments. Finally, we also take advantage of pump-probe transient absorption spectroscopy to assess the dependence of the photoexcited triplet lifetime of photo-sensitizer dyes on the extent of nuclear hyperpolarization. Applications of the above technologies to the 1D and nD NMR analysis of very dilute amino acids, peptides and proteins in solution for the study of protein folding and dynamics will be presented.