

Supplemental Data Figures

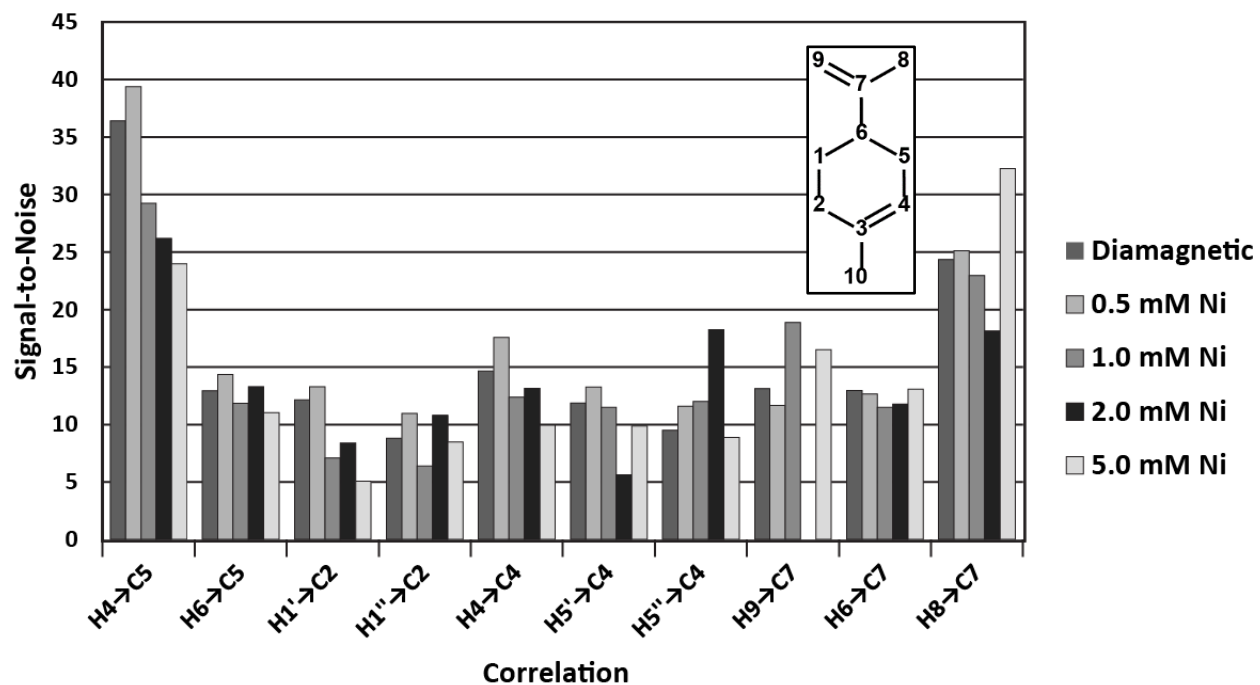


Figure S1: Signal-to-noise ratios of 1,1-ADEQUATE NMR of limonene in nickel acetylacetonate concentration screen. Up to 5 mM of NiAcAc demonstrated minimal increases in S/N for all measured peaks, and in several cases induced a significant decrease in S/N. Diastereotopic geminal protons are arbitrarily assigned and differentiated by ‘ and ‘‘.

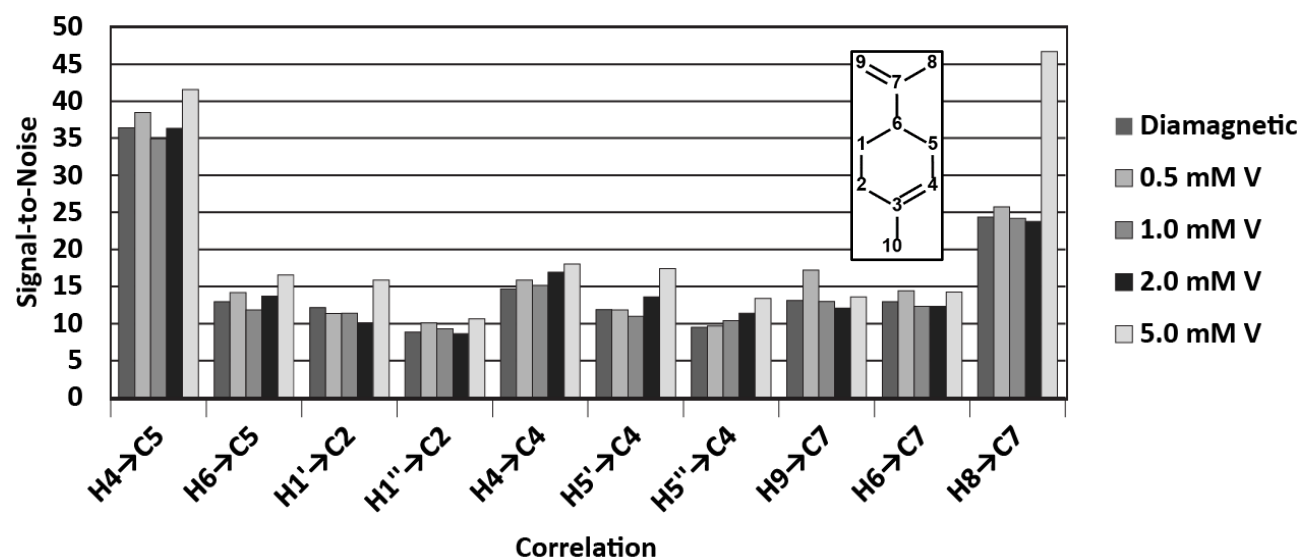


Figure S2: Signal-to-noise ratios of 1,1-ADEQUATE NMR of limonene in vanadyl acetylacetonate concentration screen. Relative to diamagnetic conditions, V treated samples demonstrated marginal increases in S/N up to 5 mM. Diastereotopic geminal protons are arbitrarily assigned and differentiated by ' and ''.

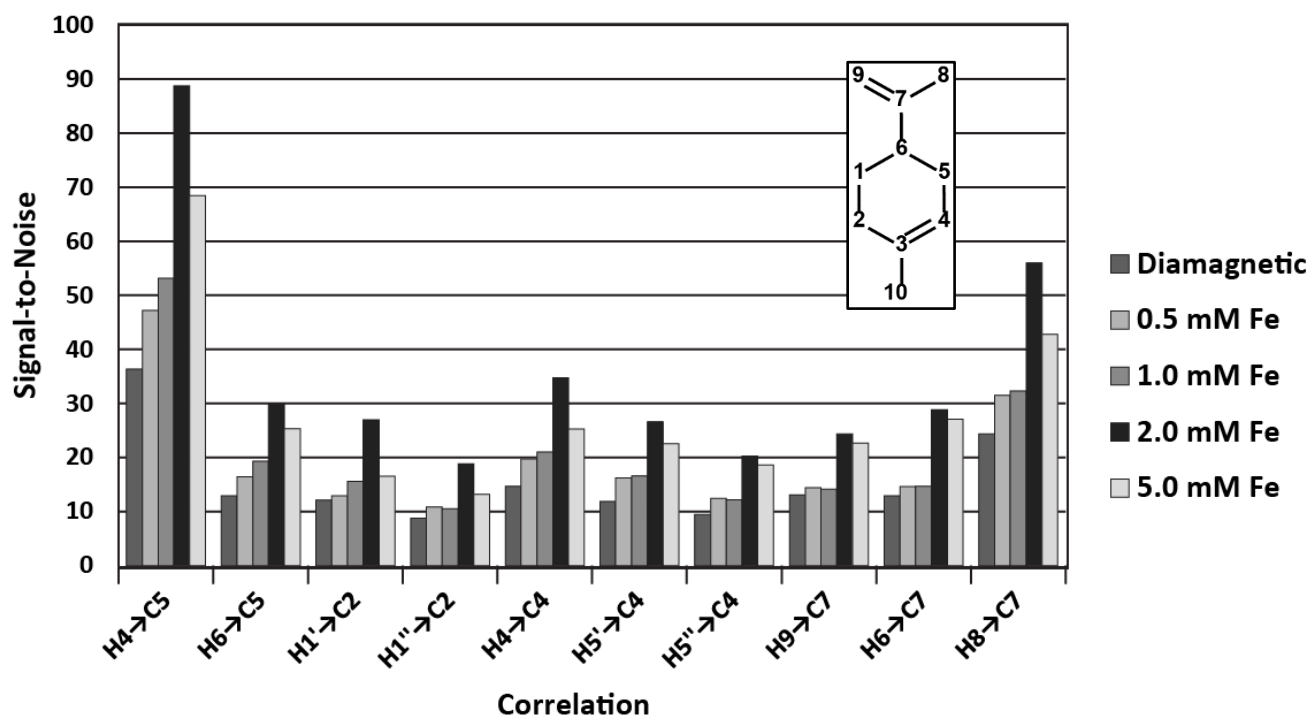


Figure S3: Signal-to-noise ratios of 1,1-ADEQUATE NMR of limonene in iron acetylacetonate concentration screen. Iron induced a significant increase in S/N at all concentrations, with a maximum achieved at 2.0 mM. Decreases in S/N above 2.0 mM were attributed to concomitant decrease in T_2 , which caused line broadening and reduced cross peak intensity. Diastereotopic geminal protons are arbitrarily assigned and differentiated by ' and ''.

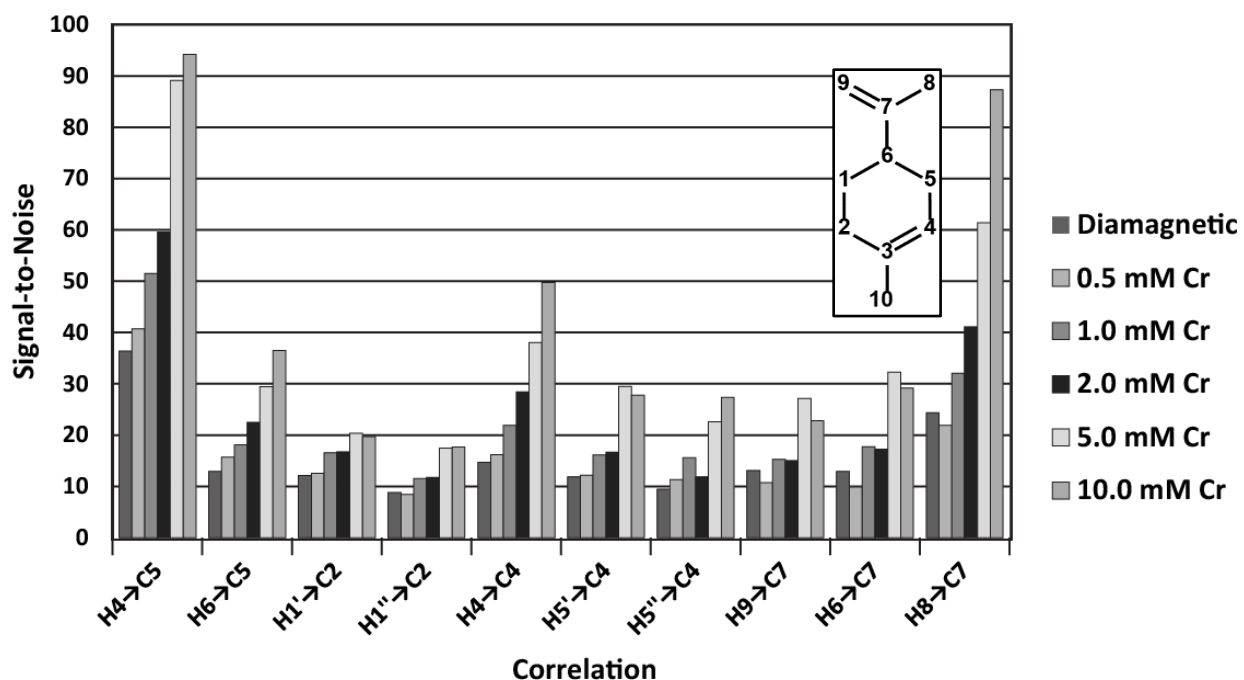


Figure S4: Signal-to-noise ratios of 1,1-ADEQUATE NMR of limonene in chromium acetylacetonate concentration screen. Chromium induced a significant increase in S/N at all concentrations, with a maximum achieved at 10 mM. This concentration was selected as the maximum, as several peaks demonstrated slight reductions in S/N moving from 5.0 mM to 10 mM. Diastereotopic geminal protons are arbitrarily assigned and differentiated by ' and ''.

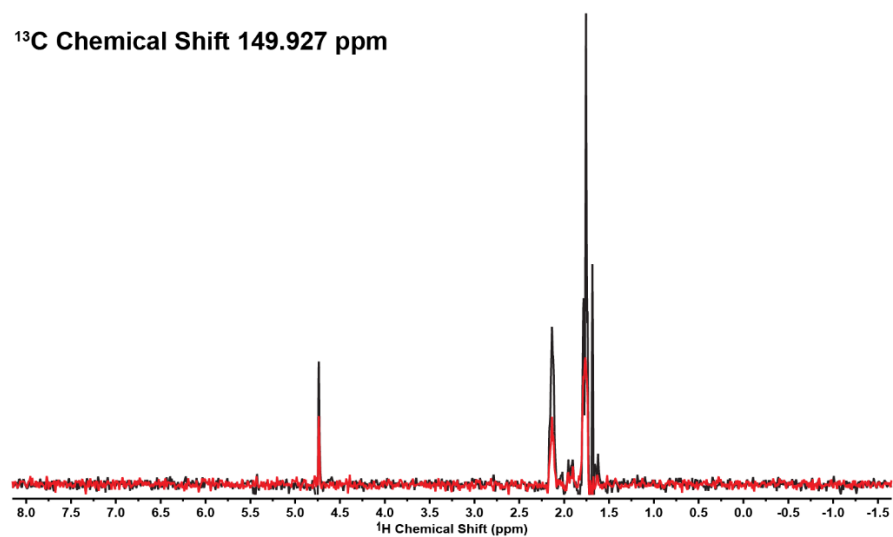
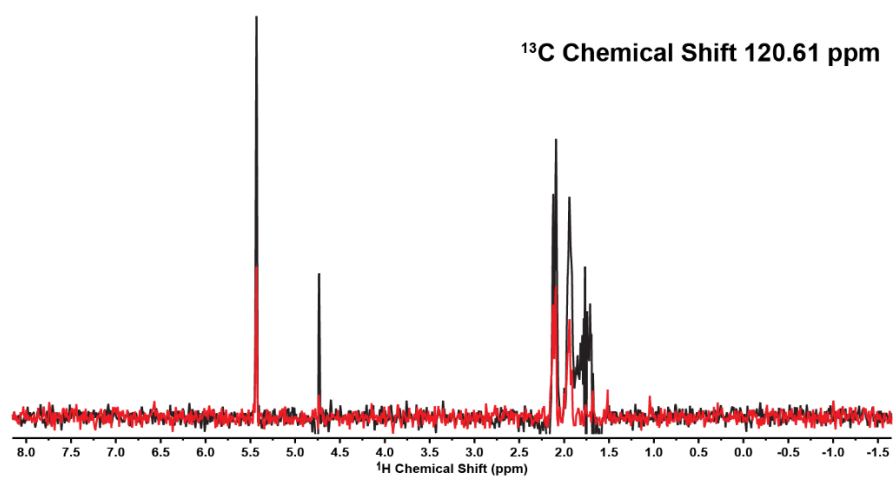
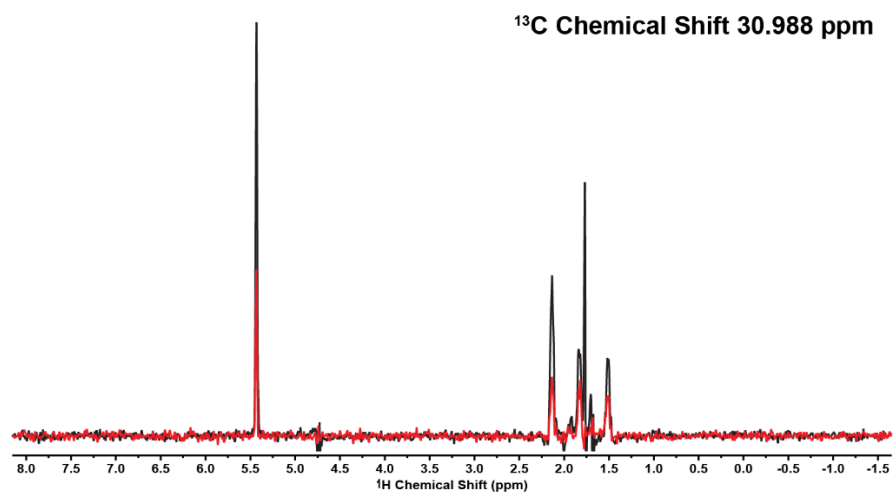


Figure S5: Extracted 1D slices of limonene 1,1-ADEQUATE NMR under paramagnetic and diamagnetic conditions. Direct dimension spectra were extracted from two-dimensional 1,1-ADEQUATE NMR at the ¹³C chemical shift indicated in each panel. Increases in signal-to-noise under paramagnetic conditions (10 mM Cr(acac)₃, black) can be clearly observed relative to diamagnetic conditions (red).

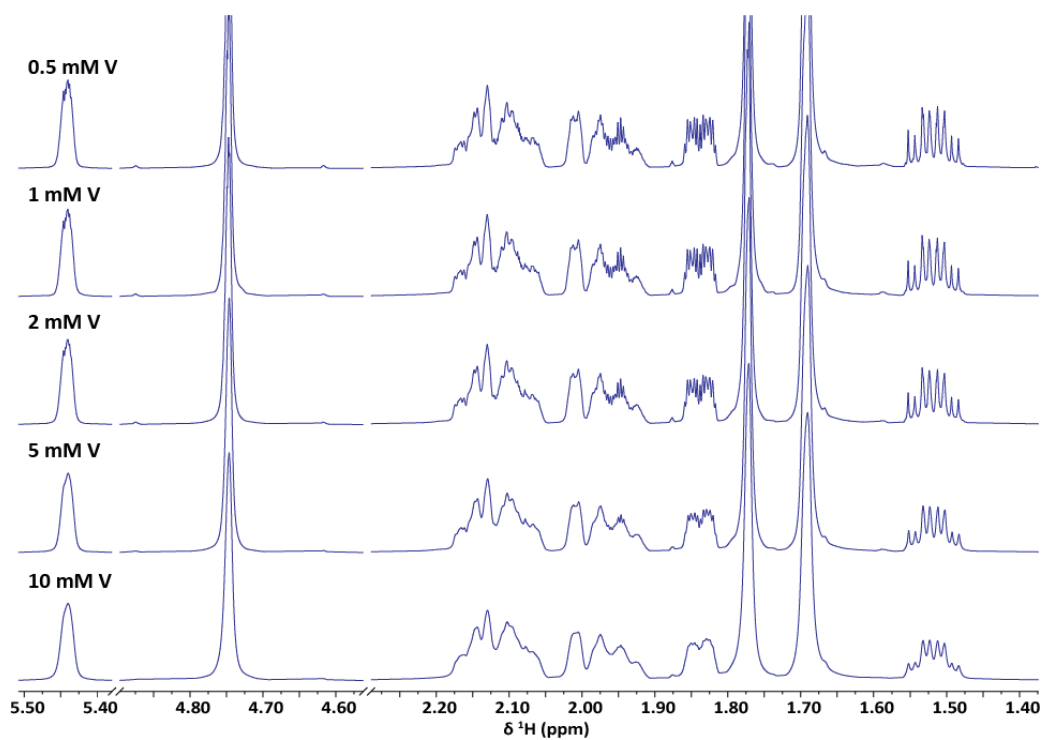


Figure S6: Comparative 1D ¹H NMR of Limonene in the Presence of Vanadium. Based on 1D analysis, T_2 -dependent linewidth impacts of vanadium were relatively minor up to 2 mM, with significant impact on linewidth at and above 5 mM.

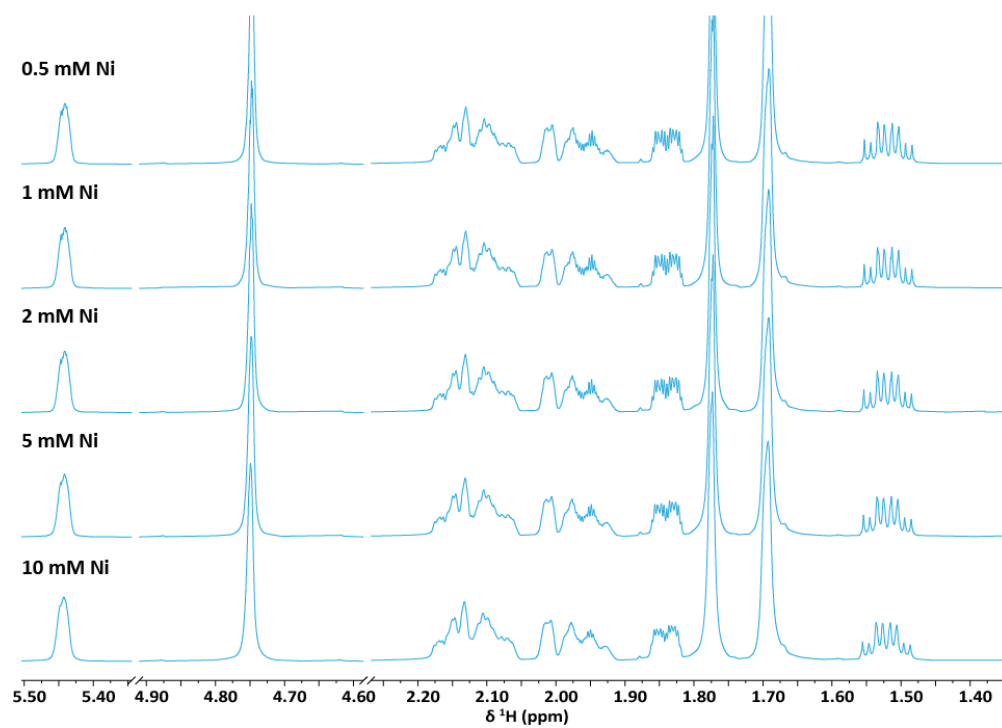


Figure S7: Comparative 1D ^1H NMR of Limonene in the Presence of Nickel. Based on 1D analysis, T_2 -dependent linewidth impacts of nickel were minor up to 10 mM, suggesting a limited impact on nuclear relaxation of limonene.

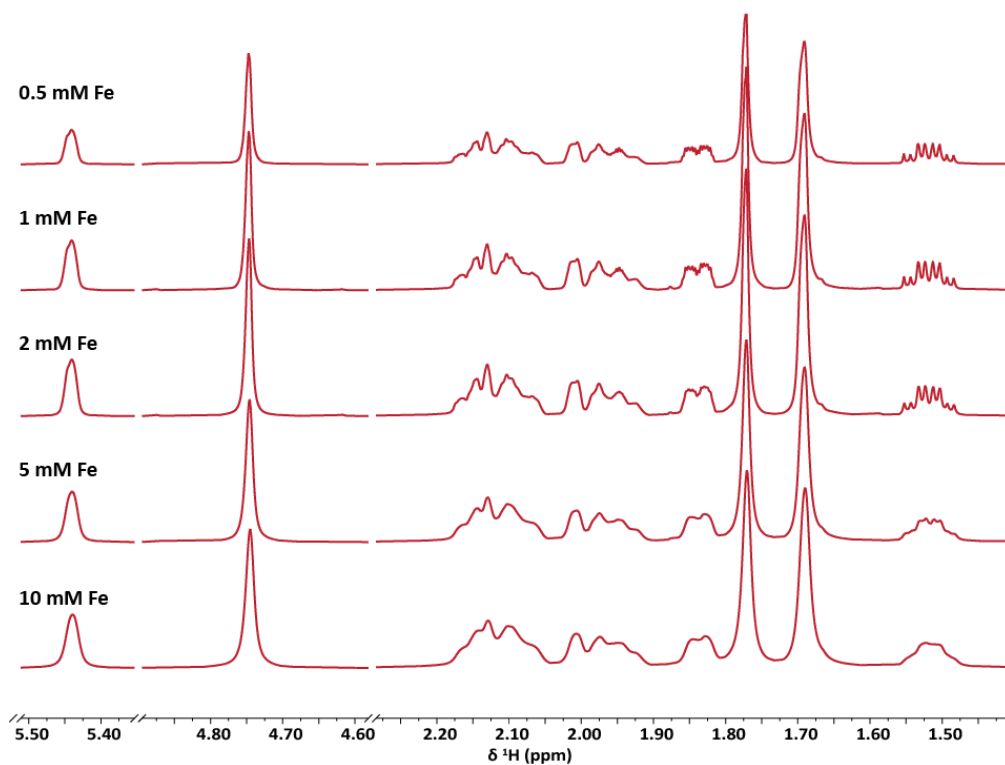


Figure S8: Comparative 1D ¹H NMR of Limonene in the Presence of Iron. Based on 1D analysis, T_2 -dependent linewidth impacts of iron were relatively minor up to 2 mM, with significant impact on linewidth at and above 5 mM. These results are consistent with S/N experiments, as significant line broadening above 2.0 mM was concomitant with a decrease in signal intensity.

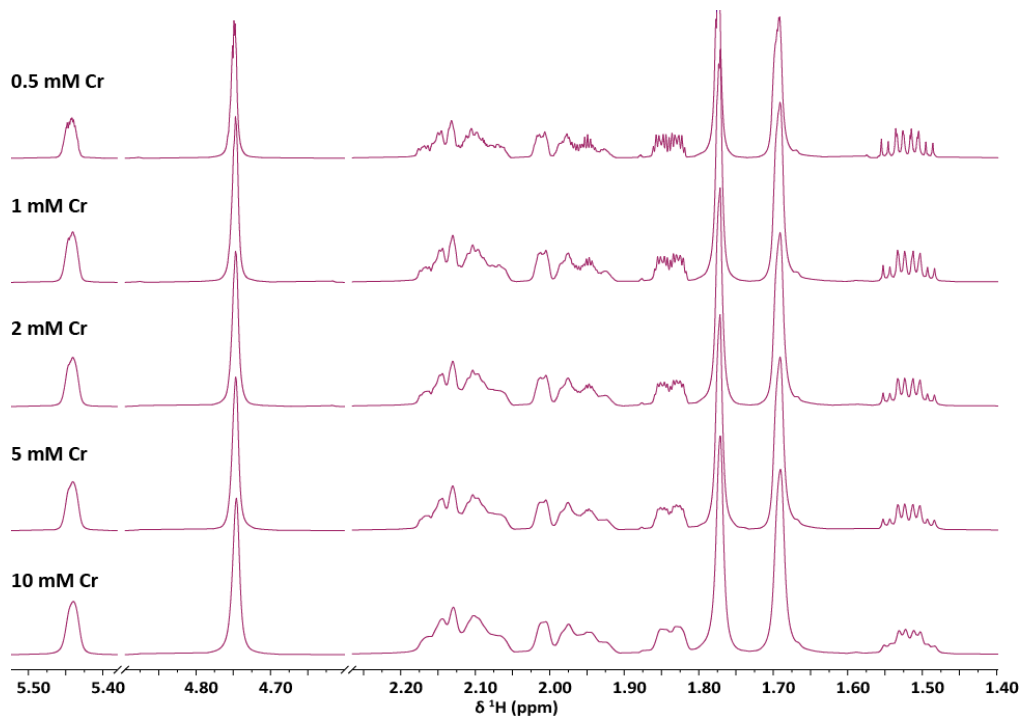


Figure S9: Comparative 1D ¹H NMR of Limonene in the Presence of Chromium. Based on 1D analysis, T_2 -dependent linewidth impacts of chromium were relatively minor up to 10 mM. In comparison to iron, line-broadening was much less severe, demonstrating a more selective impact on T_1 over T_2 with chromium.

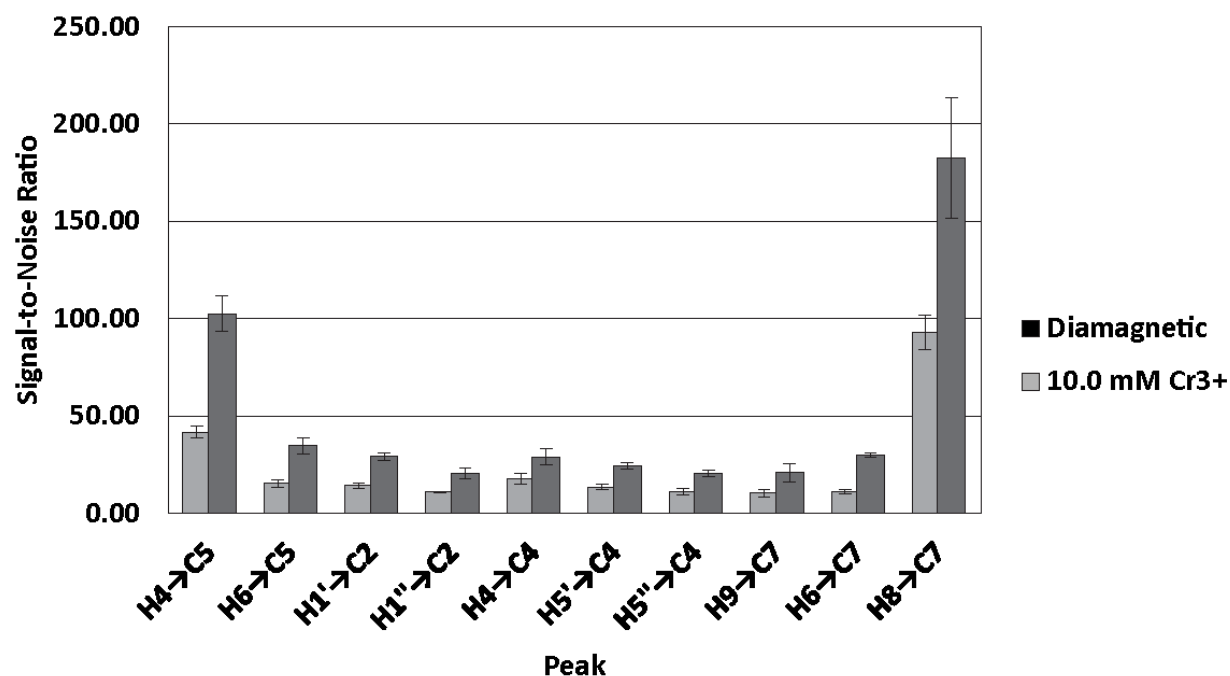


Figure S10: Observed deviations in Signal-to-Noise measurements. Diamagnetic and paramagnetic samples were run in triplicate and signal-to-noise ratios of selected peaks were measured. Error bars represent the standard deviation of the signal-to-noise measurements and demonstrate significant S/N improvement in limonene correlations under paramagnetic conditions. Larger deviations in S/N ratios under paramagnetic conditions were attributed to the increased T_1 noise observed for paramagnetic samples. The H₄-C₄ HSQC artifact correlation was included in this data, as with Figure 2.

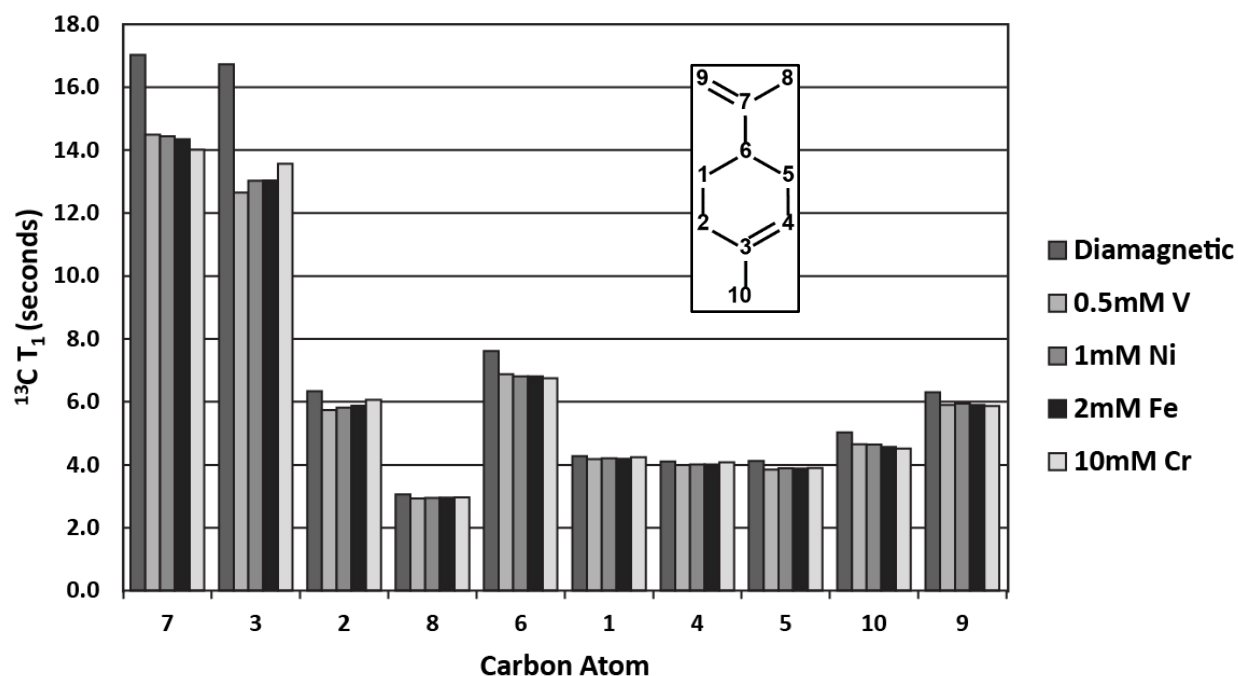


Figure S11: ^{13}C Inversion Recovery of Limonene. Spin-lattice relaxation times were calculated for all carbon atoms in limonene at select paramagnetic nuclei concentrations. Relative to diamagnetic conditions, paramagnetic-dependent T_1 reduction of ^{13}C were relatively minimal, suggesting S/N impacts of PRE were due largely to ^1H T_1 effects.

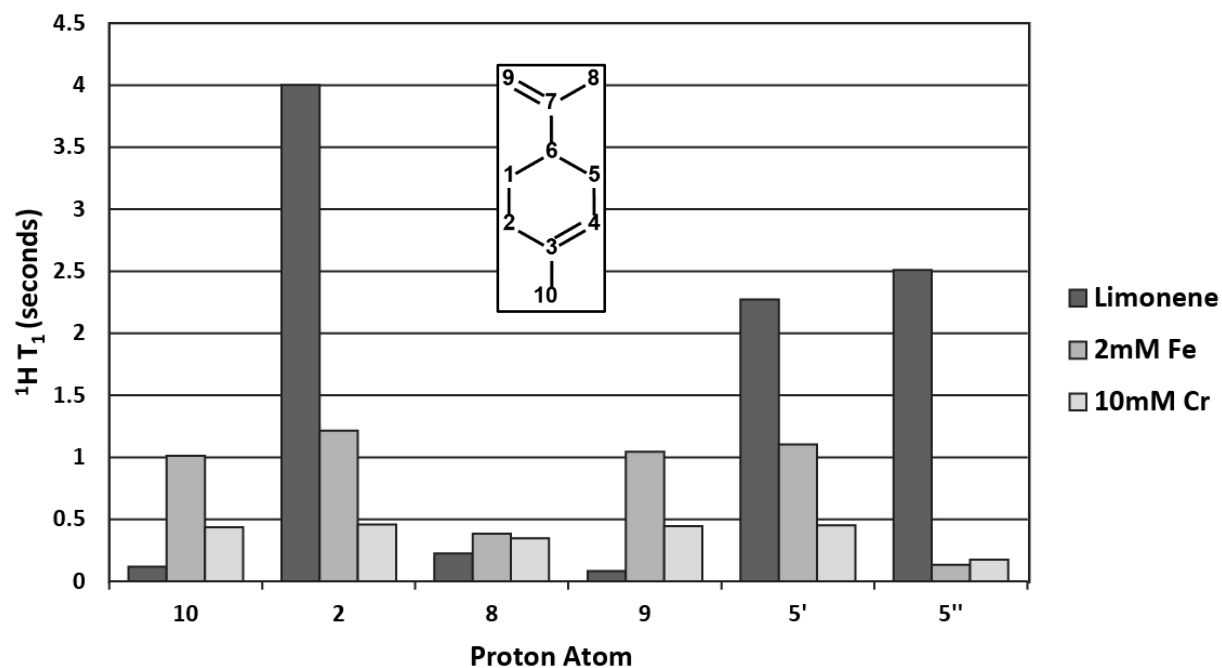


Figure S12: ^1H Inversion Recovery of Limonene. Spin-lattice relaxation times were calculated for select hydrogen atoms in limonene with 2mM Fe or 10 mM Cr. Protons that were excluded from analysis demonstrated significant spectral overlap. Relative to diamagnetic conditions, paramagnetic-dependent T_1 reductions were significant for several functional groups. Increases in T_1 were observed for several groups corresponding to the rotatable groups of limonene, suggesting positive impact of PRE is limited to higher rigidity analytes/moieties. Diastereotopic geminal protons are arbitrarily assigned and differentiated by ' and ''.

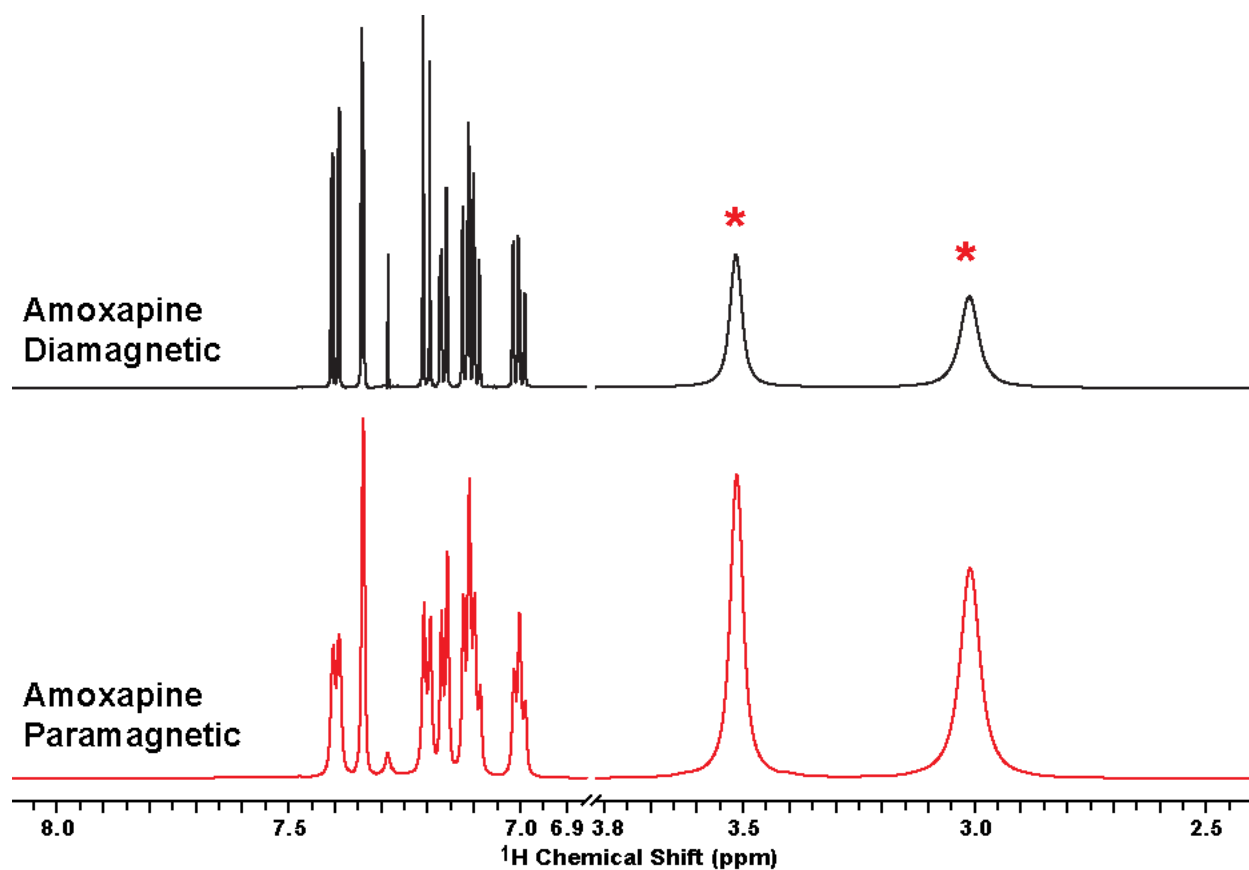


Figure S13: ^1H NMR of Amoxapine Under Diamagnetic and Paramagnetic Conditions. Piperazine methylenes (red asterisks) exhibited significant line broadening, presumably due to chemical and/or conformational exchange.