Direct evidence for an enzyme generated LPP intermediate in (+)-limonene synthase using a fluorinated GPP substrate analog

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Fig. S1. Expanded view of proton NMR data for DFM from Fig. 5B.
Fig. S2. Active-site electron density ($2Fo - Fc$ at 1 σ cutoff) shown in wall-eyed stereoview for ligand and metal ions following a 30 min soak of (+)-LS with DFGPP and MnCl$_2$. Electron density modeled with 3 Mn$^{2+}$ ions and DFGPP.
Fig. S3. Active-site electron density shown in wall-eyed stereoview for ligand and metal ions. The figure shows electron density for two superimposed Polder maps calculated individually for 3 Mn$^{2+}$ ions (at 13 $\sigma$ cutoff colored in red) and for the DFLPP ligand (at 4 $\sigma$ cutoff colored in cyan) modeled with two conformations of DFLPP in which carbons C1/C2 and C10 have very different positions. The figure also shows a bifurcated H-bond from the hydroxyl hydrogen of T446 (donor) to the two fluorine atoms of the DFLPP ligand (acceptors). Coordinating solvent molecules have not been modeled into the electron density surrounding the metal ions.