This presentation explores the development of solid-state NMR and computational modeling methods designed to provide crystal structures for materials that are not suitable for conventional diffraction methods. The initial focus is on accurately predicting structure of the molecule forming the repeating unit (i.e. the crystallographic asymmetric unit). This approach involves a combination of experimental and computed NMR data and establishes conformation, relative stereochemistry and (rarely) some lattice connections. Two paths are described for expanding this structure into a crystal structure. One route provides a complete crystal structure without any type of diffraction data while the second uses certain information from x-ray powder diffraction. In each case, the crystal structure obtained has small inaccuracies and a final lattice-including refinement is needed to obtain coordinates that agree with data from NMR, diffraction and force calculations. These final structures are still incomplete in that they lack errors for individual atomic positions. Accordingly, a final aim is to demonstrate that errors in individual atomic positions can now be obtained using a Monte Carlo sampling scheme together with computational methods. The final errors in atom positions are predicted the be nearly an order of magnitude smaller that those obtained from “thermal ellipsoids” from x-ray diffractions and nearly half the volume of ellipsoids derived from single crystal neutron diffraction.