Methacrylonitrile is believed to be an astrochemically relevant molecule due to the detection of acrylonitrile (C\textsubscript{3}H\textsubscript{3}N) in Saturn’s moon, Titan, and in the interstellar medium. We synthesized methacrylonitrile via the hydrocyanation and subsequent dehydration of acetone and obtained its rotational spectrum in the 130 – 360 GHz frequency region. The main isotopologue ground state has been least-squares fit to a sextic Hamiltonian accounting for internal rotation splitting from the 3-fold symmetric methyl rotor, and resulting spectroscopic constants compare well with those previously reported. The improved determination of centrifugal distortion constants improve the spectral prediction over a broad frequency range and thus the radioastronomical search for this molecule. Additionally, a study of pyrimidine, using 16 isotopologues, demonstrated that it is possible to determine very accurate semi-experimental equilibrium structures (\(r_e^{SE}\)) using multiple isotopic substitution combined with coupled-cluster calculations treating the vibration-rotation interaction and the electron mass correction. With the goal of such a structure determination for methacrylonitrile, we have analyzed the spectra of all singly-substituted heavy-atom isotopologues (\(^{13}\)C and \(^{15}\)N), which were detectable at natural abundance, and least-squares fit them to sextic Hamiltonians. To obtain deuterated isotopologues, the synthesis of methacrylonitrile was modified by using partially deuterated or fully deuterated acetone to yield samples of varying deuterium incorporation. We have currently assigned the rotational spectra of 22 isotopologues, with additional isotopologues yet to be analyzed. The current \(r_e^{SE}\) will be presented and compared to theoretical \(r_e\) structures.