There are many circumstances in modern microwave spectroscopy where the observed spectra contain contributions from many distinct sub-populations, creating a complicated spectrum with interleaved transitions due to its components making spectral assignment challenging. A new method, exploiting multi resonance effects with broadband CP-FTMW was developed and implemented to differentiate the structural isomers: (E)- and (Z)-phenylvinylnitrile. This method will output an exclusive set of isomer-specific transitions reducing the spectral assignment time. Details of the method implementation and structural analysis of the two-isomer mixture will be discussed. The application of the method to other circumstances where selective modulation of the transitions due to a single set of connected transitions is vital for complex spectral assignment, will also be considered.