Rotation of the difluoromethyl group in 2,3,3-trifluoropropene results in three minima: a higher energy, achiral rotamer that contains a plane of symmetry and two equivalent, chiral lower-energy rotamers that form an enantiomeric pair. As revealed through the analysis of the microwave spectra of the gas-phase heterodimers formed between each rotamer and acetylene, the acetylene adopts a different bonding motif in each case. Furthermore, both modes of bonding are distinct from that observed in 1,2-difluoroethylene-acetylene where the acetylene interacts with an ethylenic fluorine-hydrogen pair located cis to each other, despite the existence of a similar pair in 2,3,3-trifluoropropene.