Fluorine substitution in molecules is a common practice in bio-organic chemistry in order to modulate physicochemical properties and biological activity of molecules and an increasing number of drugs on the market contain fluorine, the presence of which is often of major importance to modify pharmacokinetics properties and molecular activity. The rationale for such a strategy is that fluorine is generally a stronger electron acceptor than the other halogen atoms and its size is intermediate between that of hydrogen and oxygen. We have studied two fluorinated analogs of 2-phenylethylamine (PEA), the prototype molecule for adrenergic neurotransmitters, namely: 4-Fluoro (4FPEA) and 2-Fluoro-2-phenylethylamine (2FPEA) by Molecular Beam Fourier Transform Microwave Spectroscopy in the frequency range 6-18 GHz and \textit{ab initio} calculations at the MP2/6311++G** level. The aim is to obtain information on the spatial arrangement of the ethylamine side chain and the effects of fluorination on the energy landscape. The conformational space is dominated by low energy gauche conformations stabilized by weak interactions between the aminic hydrogens and the electron cloud of the benzene ring and anti conformations higher in energy. In 2FPEA the presence of the fluorine atom almost duplicate the number of possible conformation with respect to 4FPEA. We observed two conformers of 4FPEA and five conformers of 2FPEA which have been classified with the guide provided by accurate \textit{ab initio} calculations. The identification of the conformational species was helped by the analysis of the quadrupole hyperfine pattern which is greatly influenced by the orientation of the amino group and acts as a fingerprint for each conformation. The orientation of the dipole moment within the principal axis frame and the order of stability of the different conformations are other independent pieces of evidence for the unambiguous assignment and identification of the conformers. The order of stability was found to be altered in both molecules with respect to the prototype PEA molecule, especially in the case of 2FPEA where we observe a stabilization of some of the anti forms and great destabilization of some of the gauche forms. These observations are in agreement with the results of the theoretical calculation and can be rationalized in terms of the effect of the fluorine atom on the electron density of the molecule and in particular on the electron cloud on the benzene ring.